

**CATALYTIC REDUCTIVE CARBENE AND VINYLIDENE TRANSFER
REACTIONS**

by

Conner M Farley

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THE PURDUE UNIVERSITY GRADUATE SCHOOL
STATEMENT OF COMMITTEE APPROVAL

Prof. Christopher Uyeda, Chair

Department of Chemistry

Prof. Mingji Dai

Department of Chemistry

Prof. Suzanne Bart

Department of Chemistry

Prof. Abram Axelrod

Department of Chemistry

Approved by:

Dr. Christine Hrycyna

To my family

Mom, Dad, Grandpa, Grandma, Jackson, Brianna, James

The love of my life, Hailey

The cabin in the mountains

The river that forks south

“Many men go fishing all of their lives without knowing that it is not the fish they are after”

-Henry David Thoreau

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ABSTRACT

Carbenes are reactive organic intermediates comprised of a neutral, divalent carbon atom. The reactivity of carbenes is often orthogonal to polar functional groups (nucleophiles and electrophiles), making them valuable intermediates for organic synthesis. For example, carbenes can engage in cheletropic reactions with olefins to form cyclopropane rings or undergo insertions into weak element-hydrogen bonds. The most established strategy for accessing carbene intermediates is through a redox-neutral decomposition of diazoalkanes to form a transient $M=CR_2$ species. Over the course of nearly a half-century of development, many instrumental synthetic methods have emerged that operate on this basis. Despite the combined utility of these methods, the scope of catalytic carbene transfer reactions remains largely constrained by the inherent instability of the starting materials. Diazoalkanes often require electron-withdrawing groups to provide stability through resonance effects.

Contrary to redox-neutral methods, reductive carbene transfer reactions utilize non-stabilized 1,1-dihaloalkanes as carbene precursors. The Simmons-Smith cyclopropanation reaction represents the most documented example of this class, and remains today as the most practical method for parent methylene ($:CH_2$) transfer. Nevertheless, reductive carbene transfer processes have proven to be remarkably resistant to catalysis. Our group is interested in developing first-row transition metal catalysts which can initiate an oxidative addition into 1,1-dihaloalkanes, followed by a two-electron reduction with an outer-sphere reductant to provide access to a $M=CR_2$ intermediate for carbene transfer.

The application of this mechanistic hypothesis toward reductive methylene transfer using CH_2Cl_2 as the carbene source and a Ni catalyst is outlined in chapter one. The discovery of an unexpected cyclooligomerization of methylene carbenes is discussed. Mechanistic studies are presented, which are consistent with a pathway in which carbenes are iteratively inserted into an expanding metallacycle. In chapter two, the corresponding activation of 1,1-dichloroalkenes for vinylidene transfer in [5+1]-cycloadditions with vinylcyclopropanes is outlined. Finally, in the third and final chapter, organic reactions catalyzed by complexes which feature metal-metal bonds are reviewed.

CHAPTER 1. CATALYTIC CYCLOOLIGOMERIZATION OF ENONES WITH THREE METHYLENE EQUIVALENTS

Reproduced with permission from Farley, C. F.; Zhou, Y.-Y.; Banka, N.; Uyeda, C. J. *Am. Chem. Soc.* **2018**, 140, 40, 12710-12714. DOI: 10.1021/jacs.8b08296. Copyright 2018 American Chemical Society.

1.1 Abstract

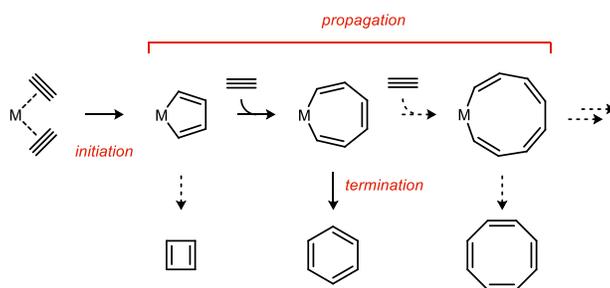
Cyclic structures are highly represented in organic molecules, motivating a wealth of catalytic methods targeting their synthesis. Among the various ring-forming processes, cyclooligomerization reactions possess several attractive features but require addressing a unique challenge associated with controlling ring-size selectivity. Here we describe the catalytic reductive cocyclooligomerization of an enone and three carbene equivalents to generate a cyclopentane, a process that constitutes a formal [2 + 1 + 1 + 1]-cycloaddition. The reaction is promoted by a (quinox)Ni catalyst and uses $\text{CH}_2\text{Cl}_2/\text{Zn}$ as the C_1 component. Mechanistic studies are consistent with a metallacycle-based pathway, featuring sequential migratory insertions of multiple carbene equivalents to yield cycloalkanes larger than cyclopropanes.

1.2 Introduction

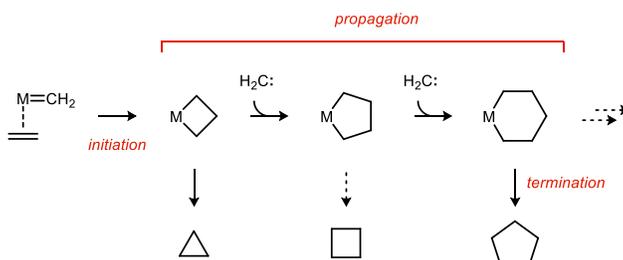
Cyclooligomerization reactions are a mechanistically interesting subclass of cycloadditions that currently have limited utility in organic synthesis. The potential value of these reactions derives from their ability to directly assemble cyclic molecules from the repeated coupling of a simple building block. However, this same feature introduces a significant challenge associated with controlling ring-size selectivity. The most prominent class of cyclooligomerization reactions involves the use of alkynes as substrates. Cyclotrimers are favored under most transition-metal-catalyzed conditions because of the high thermodynamic stability of benzenes relative to cyclobutadienes, cyclooctatetraenes, and higher-order annulenes. Cyclooligomerization reactions using other π -components, such as 1,3-dienes and allenes, have also been studied but generally exhibit poor selectivity and narrow substrate scopes. Catalytic alkyne cyclotrimerizations are commonly initiated by an oxidative coupling reaction at a low-

valent metal center to form a metallacyclopentadiene (Figure 1.1a). This intermediate then undergoes ring expansion through additional alkyne insertion events until the cyclic product is eliminated from the catalyst. In principle, a related mechanism may be accessible using a C_1 component as the monomer unit (Figure 1.1b). For example, a [2 + 2]-cycloaddition between a $M=CR_2$ species and an alkene would likewise generate a metallacycle, in this case a saturated metallacyclobutane. The reaction would then propagate by iterative insertions of carbene equivalents and terminate by C–C reductive elimination. Because the cycloalkane would be constructed one carbon at a time, any ring size is potentially accessible by this pathway. Here, we describe a catalytic reductive cocyclooligomerization of an enone and three methylene equivalents to generate a cyclopentane (Figure 1.1c). The reaction constitutes a formal [2 + 1 + 1 + 1]-cycloaddition and uses CH_2Cl_2 as the C_1 partner in combination with Zn metal as a stoichiometric reductant.

A Cyclooligomerization Reactions of Alkynes



B A Proposed Cyclooligomerization Using a C_1 Component



C [2 + 1 + 1 + 1]-Cycloaddition of Enones and Methylene

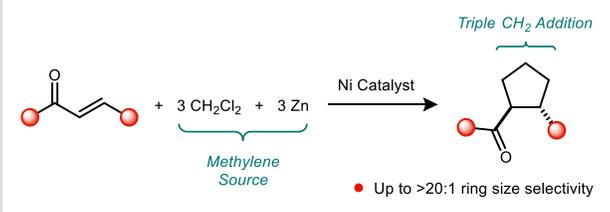
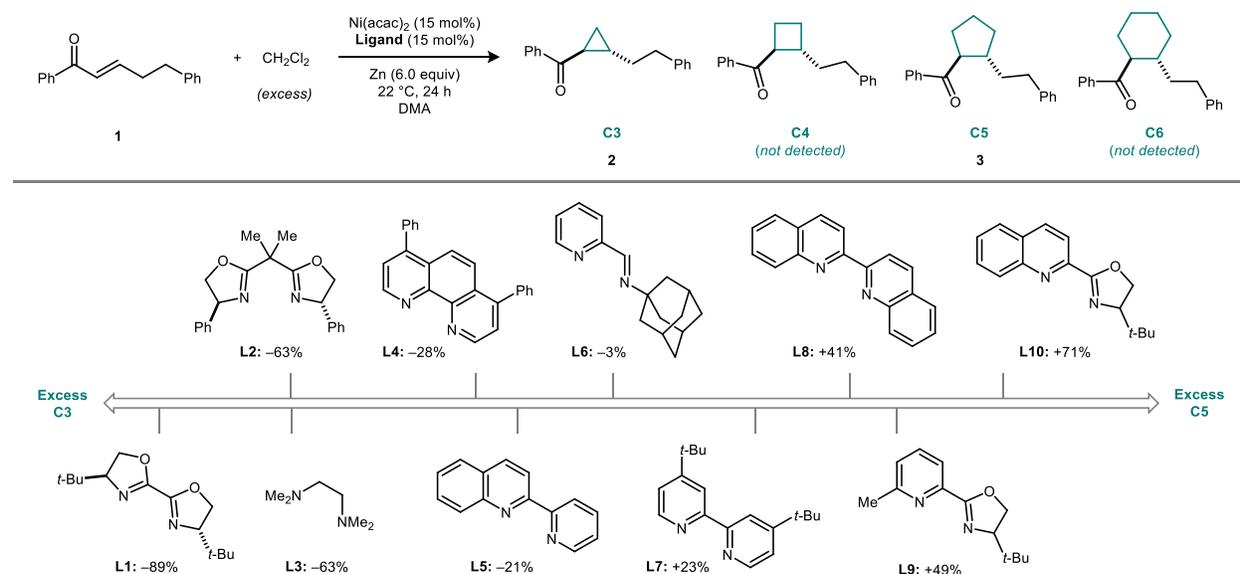


Figure 1.1. Cyclooligomerization strategies for the synthesis of cyclic molecules. (a) Transition-metal-catalyzed cyclotrimerization reactions of alkynes proceeding through metallacyclic intermediates. (b) A proposed cyclooligomerization reaction using a carbene as the propagating monomer. (c) A catalytic reductive [2 + 1 + 1 + 1]-cycloaddition of enones with CH_2Cl_2/Zn to generate cyclopentanes.

1.3 Catalyst Comparison and Optimization Studies

Table 1.1. Conversions of **1**, yields of **2** (C3), and yields of **3** (C5) were determined from crude reaction mixtures by GC analysis against mesitylene as an internal standard. Reaction conditions: **1** (0.07 mmol, 1.0 equiv), Zn (6.0 equiv), metal source (0.15 equiv), ligand (0.15 equiv), 1.25:1 CH₂Cl₂/ DMA (0.3 mL). Selectivities for cyclopropane vs cyclopentane formation are expressed as excess values, defined as $[(C5 - C3)/(C5 + C3)] \times 100\%$.



Entry	Metal source	Ligand	Conversion	Yield C3	Yield C5
1	Ni(acac) ₂	L1	38%	36%	2%
2	Ni(acac) ₂	L2	40%	26%	6%
3	Ni(acac) ₂	L3	38%	27%	6%
4	Ni(acac) ₂	L4	85%	16%	9%
5	Ni(acac) ₂	L5	93%	26%	17%
6	Ni(acac) ₂	L6	92%	32%	30%
7	Ni(acac) ₂	L7	92%	18%	29%
8	Ni(acac) ₂	L8	85%	25%	60%
9	Ni(acac) ₂	L9	89%	21%	62%
10	Ni(acac) ₂	L10	95%	12%	70%
11	Ni(dme)Br ₂	L1	85%	21%	42%
12	Co(acac) ₂	L1	0%	0%	0%
13	Fe(acac) ₂	L1	46%	0%	0%
14	Ni(acac) ₂	None	10%	0%	0%

We discovered the reductive cyclooligomerization unexpectedly while studying transition-metal-catalyzed variants of the Simmons–Smith reaction. The key intermediates of the

classical Simmons–Smith reaction are Zn carbenoids ($XZnCH_2Y$ species), which are electrophilic in character and known to react preferentially with electron-rich alkenes. Kanai et al. observed that electron-deficient alkenes, such as enones, are also amenable to cyclopropanation under CH_2X_2/Zn conditions by the addition of NiX_2 salts in catalytic loadings. The active carbenoid species could not be unambiguously identified but was hypothesized to be a nucleophilic $Ni=CH_2$ complex that undergoes cyclopropanation by a stepwise $[2 + 2]$ -cycloaddition/ $C-C$ reductive elimination pathway. Studies by Grubbs, Miyashita, and Hillhouse probing the stoichiometric reactivity of $Ni=CR_2$ species and their associated nickelcyclobutanes lend credence to this proposal. Our initial interest was in examining ligand effects in the nickel-catalyzed Simmons–Smith reaction. Accordingly, catalysts generated from $Ni(acac)_2$ and nitrogen-based bidentate ligands (**L1**–**L10**) were tested in the cyclopropanation of model enone **1** (Table 1.1). The relatively inert CH_2Cl_2 reagent was selected as the methylene source because of the absence of any background cyclopropanation using Zn as a stoichiometric reductant. Across the range of ligand types examined, the yield of cyclopropane **2** was found to vary significantly but never exceed 36%. GC-MS analyses of the crude reaction mixtures indicated the formation of a single major byproduct with a mass corresponding to the enone (**1**) bearing three additional CH_2 equivalents. Subsequent isolation and spectroscopic characterization of this species revealed its structure to be a *trans*-disubstituted cyclopentane, derived from a formal reductive $[2 + 1 + 1 + 1]$ -cycloaddition process. To the extent that other cyclooligomers, such as cyclobutanes or cyclohexanes, are formed, they fall below the limits of GC-MS detection; masses corresponding to these other cyclooligomers are found in trace quantities using other enones. The ratio of cyclopropane to cyclopentane is strongly dependent on the identity of the supporting ligand. For example, *t*-Bu-Biox **L1** forms cyclopropane nearly exclusively (**2:3** = 18:1), whereas *t*-Bu-quinox **L10** is selective for cyclopentane formation (**2:3** = 1:5.8).

1.4 Substrate Scope for the Catalytic Cyclooligomerization

Summarized in Figure 1.2 is the substrate scope of the nickel-catalyzed reductive cyclooligomerization reaction under conditions that were optimized for cyclopentane formation. Yields are of the isolated cyclopentane following separation from the cyclopropane byproduct. Common functional groups are tolerated, including nitriles, ethers, protected alcohols, protected

amines, electron-rich heterocycles, and esters. Thioethers are susceptible to ylide formation in the Simmons–Smith reaction but are left untouched under the catalytic cyclooligomerization conditions.

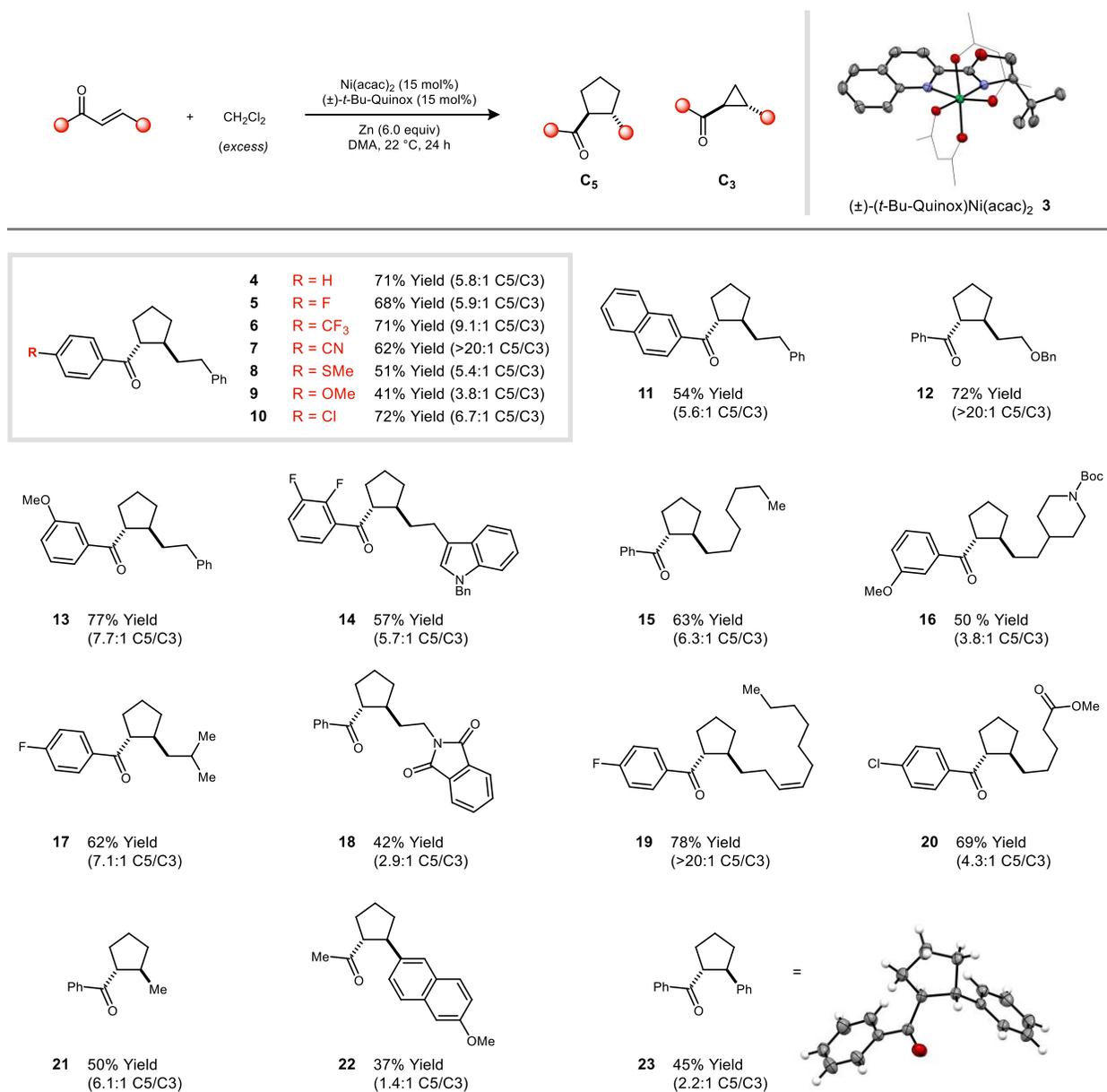


Figure 1.2. Substrate scope studies. Yields are of the isolated cyclopentane following purification. C5/C3 ratios were determined from the crude reaction mixtures by ¹H NMR integration. Reaction conditions: enone (1.0 equiv, 0.21 mmol); Zn (6.0 equiv); Ni(acac)₂ (0.15 equiv); (\pm)-**L10** (0.15 equiv); CH₂Cl₂ (0.5 mL); DMA (0.4 mL); 22 °C, 16 h.

Likewise, aryl chlorides, which participate in nickel-catalyzed reductive cross-coupling reactions, are not competitively activated. A substrate possessing two alkenes, one conjugated with a ketone and the other substituted only with alkyl groups, reacts exclusively at the electron-deficient alkene (**19**). The highest selectivities for cyclopentane formation were observed using substrates containing an aryl ketone and an alkyl substituent at the β -position of the alkene. For example, methyl ketone **22** and chalcone **23**, which do not fulfill these criteria, were viable substrates for the reaction but afforded only modest selectivities for cyclopentane formation ($\leq 2.2:1$). The product of this latter reaction (**23**) proved to be a crystalline solid, whose structure was assigned by X-ray diffraction analysis.

The aryl ketones present in the cyclopentane products may be converted to other useful functional groups by the Baeyer–Villiger oxidation (Figure 1.3). For example, **9** bearing an electron-rich 4-methoxyphenyl group is oxidized to ester **24** with high regioselectivity (rr = 14:1). The alternative regioisomeric ester is also accessible by employing the electron-deficient 4-trifluoromethyl group (**25**), which possesses a low migratory aptitude (rr = >20:1). Upon ester hydrolysis, the former product would provide a cyclopentane carboxylic acid and the latter a cyclopentanol.

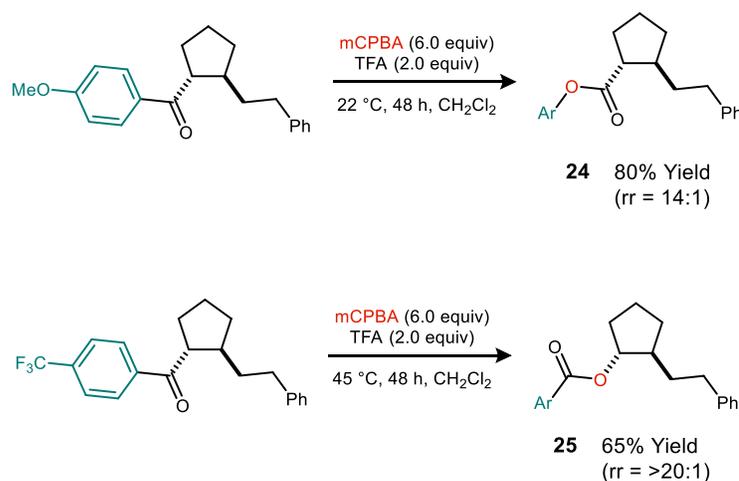


Figure 1.3. Baeyer–Villiger oxidations of aryl cyclopentyl ketone products.

1.5 Mechanistic Studies Toward the Catalytic Cyclooligomerization

Given the unusual nature of this transformation, our first mechanistic experiment sought to confirm the origin of the $-(\text{CH}_2)_3-$ fragment in product **3** (Figure 1.4). When the catalytic cyclopentane of **1** was conducted using CD_2Cl_2 in the place of CH_2Cl_2 , the expected CD_2 -incorporation was observed to form **3-d₆** (60% isolated yield). Second, a tandem cyclopropanation–ring-opening mechanism was ruled out by subjecting the separately synthesized cyclopropane **2** to the standard catalytic condition (Figure 1.4b). In this experiment, the cyclopropane was recovered in >98% yield, and no conversion to cyclopentane **3** was observed. Third, we examined a potential mechanism involving the oxidative coupling of enone **1** with ethylene, which could be generated from the reductive coupling of two CH_2Cl_2 equivalents (Figure 1.4c). Miyashita previously observed the formation of ethylene from the dimerization of a proposed transient $\text{Ni}=\text{CH}_2$ species. Furthermore, ethylene is known to undergo nickel-mediated oxidative coupling reactions with electron-deficient π -systems.

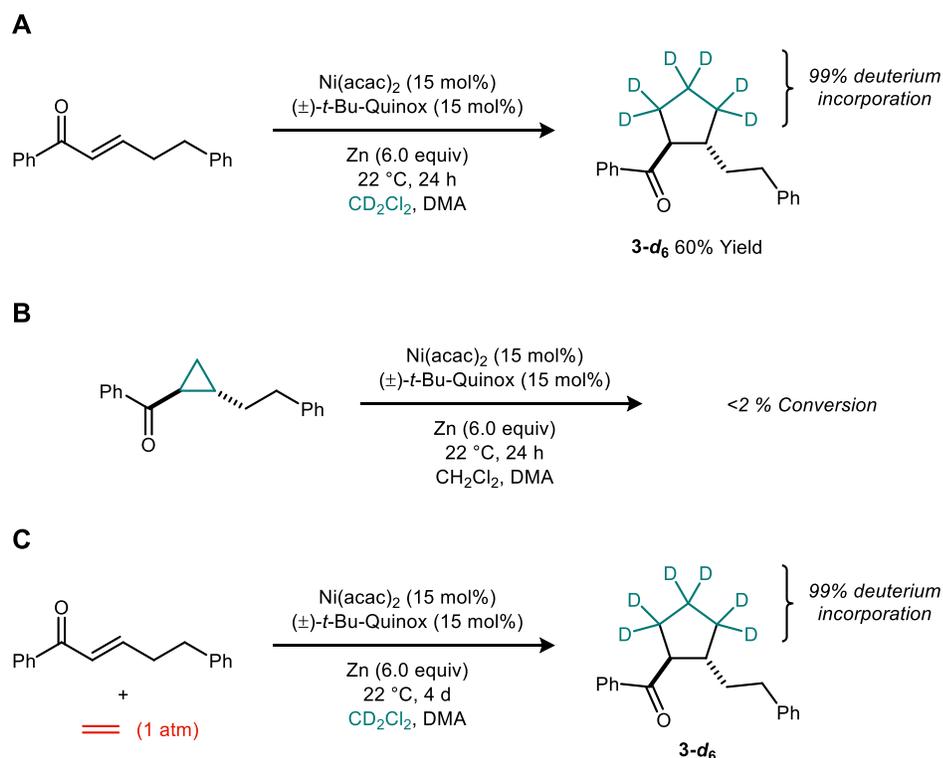


Figure 1.4. Mechanistic experiments. (a) Experiment identifying the origin of the $-(\text{CH}_2)_3-$ fragment in product **3**. (b) Excluding a mechanism involving cyclopropane ring-opening. (c) Excluding a mechanism involving a coupling of enone **1** and ethylene.

The catalytic cyclopentananation of enone **1** was carried out using labeled CD_2Cl_2 under an atmosphere of nondeuterated ethylene gas. The presence of ethylene was found to inhibit the rate of cyclopentananation, but product **3-d₆** was nonetheless obtained in fully deuterium-labeled form. This result suggests that either ethylene is not an intermediate in the reaction or that it is generated but remains tightly bound to Ni and thus cannot exchange with free ethylene.

Finally, during our substrate scope studies, we noted a pronounced dependence of the selectivity for cyclopropane versus cyclopentane formation on the electronic properties of the aryl ketone (Figure 1.5). For a series of 4-substituted aryl enones (**3**, **5–10**), there is a linear relation between the selectivity values (C5/C3) and the substituent σ parameters ($\rho = 0.45$). Electron-withdrawing substituents result in the highest selectivities for cyclopentane formation.

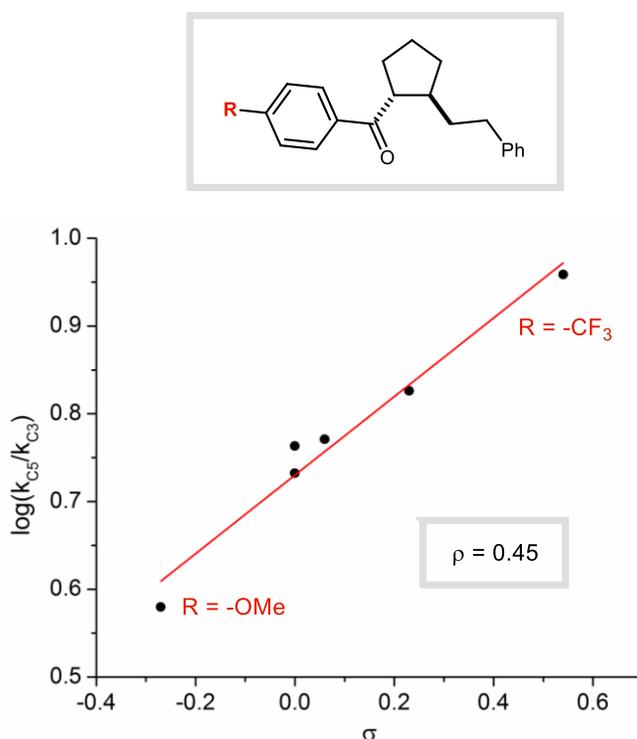


Figure 1.5. Hammett plot of the C5/C3 selectivity vs the substituent σ parameters.

One possible interpretation of this trend is in the context of the metallacyclobased mechanism proposed by Kanai. In this pathway, the selectivity for cyclopropanation versus cyclooligomerization would be governed by the relative rates of reductive elimination

(termination) and carbene insertion (propagation) (Figure 1.6). Carbon–carbon reductive elimination reactions are known to be accelerated by the presence of an electron-donating group conjugated to one of the carbons undergoing bond formation; electron-donating groups generally destabilize M–C bonds to a greater extent than the product C–C bond. On the other hand, the carbene insertion step would likely be insensitive to the electronic properties of the aryl group. Previous kinetics studies have shown that CO migratory insertion reactions occur preferentially at more electron-rich M–C bonds. The analogous process in the reductive cyclooligomerization would therefore favor carbene insertion into the Ni–alkyl over the Ni–enolate bond such that the aryl group would exert only an indirect effect on the rate of this step.

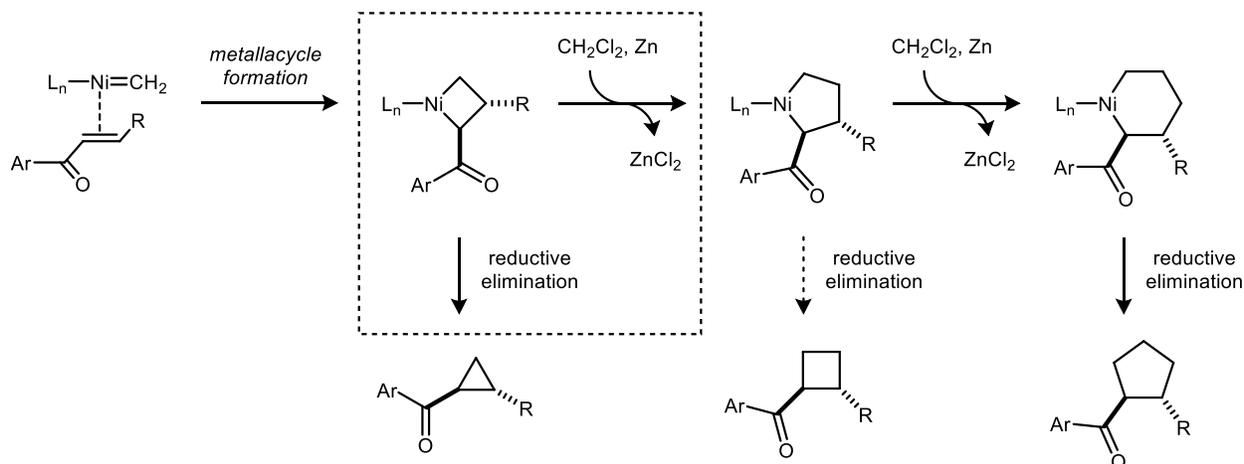


Figure 1.6. A proposed cyclooligomerization mechanism involving metallacycle ring expansion. The branch point for cyclopentane vs cyclopropane formation is highlighted.

1.6 Conclusions

In summary, zinc carbenoid additions to alkenes have been extensively studied since the seminal work of Emschwiller, Simmons, and Smith. However, in no cases have these reactions been observed to access pathways that lead to multiple CH_2 addition, presumably because of the concerted nature of the carbene-transfer mechanism. In this context, transition metal-bound carbenes are attractive as alternative CH_2 transfer agents because of their potential to react through stepwise organometallic pathways. By intercepting transient metallacyclic intermediates prior to C–C reductive elimination, it is possible to develop new transformations that form ring systems other than cyclopropanes. This strategy is demonstrated here in the context of a nickel-

catalyzed [2 + 1 + 1 + 1]-cycloaddition of enones using three methylene equivalents derived from CH₂Cl₂ and six reducing equivalents supplied by Zn metal. Together, these results point to opportunities for the development of other multicomponent cycloaddition reactions using reductively generated CH₂ as a C₁ partner.

1.7 Acknowledgements

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CHAPTER 2. CATALYTIC [5+1]-CYCLOADDITIONS OF VINYL CYCLOPROPANES AND VINYLIDENES

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2.1 Abstract

Polysubstituted cyclohexenes bearing 1,3 (meta) substitution patterns are challenging to access using the Diels–Alder reaction (the *ortho–para* rule). Here we report a cobalt-catalyzed reductive [5 + 1]-cycloaddition between a vinylcyclopropane and a vinylidene to provide methylenecyclohexenes bearing all-meta relationships. Vinylidene equivalents are generated from 1,1-dichloroalkenes in combination with Zn as a stoichiometric reductant. Experimental observations are consistent with the intermediacy of a cobaltacyclobutane formed from a [2 + 2]-cycloaddition between a cobalt vinylidene and a vinylcyclopropane.

2.2 Introduction

The Diels–Alder reaction provides one of the most direct routes to polysubstituted cyclohexenes and has been used extensively in the synthesis of complex biologically active molecules.¹ Diels–Alder reactions between unsymmetrical dienes and dienophiles generally proceed with high regioselectivity to form cycloadducts bearing 1,2 and 1,4 substitution patterns (Figure 1). This selectivity principle applies to both normal and inverse electron-demand Diels–Alder reactions and is commonly referred to as the *ortho–para* rule.² Frontier molecular orbital interactions provide a rationale for this preference,³ and it is challenging to overcome in order to access 1,3-substituted (*meta*) cycloadducts.

An alternative cycloaddition that yields six-membered carbocycles is the [5 + 1]-cycloaddition between a vinylcyclopropane and a carbene equivalent.⁴ Sarel,⁵ Aumann,⁶ and Taber⁷ have reported carbonylation reactions of vinylcyclopropanes using stoichiometric Fe(CO)₅. Catalytic variants have also been developed using Co or Rh catalysts and CO gas.⁸ In

these reactions, 1,3-substituted products can be generated provided that the metal complex is capable of selectively cleaving the less-hindered C–C bond of an unsymmetrically substituted vinylcyclopropane. It would be attractive to employ this approach more broadly in [5 + 1]-cycloadditions with C₁ partners other than CO.

Recently, we reported that dinickel catalysts promote reductive [2 + 1]- and [4 + 1]-cycloaddition reactions using 1,1-dichloroalkenes as vinylidene precursors.⁹ In the course of these studies, we found that additions of 1,1-dichloroalkene **2** to vinylcyclopropane (**1**) yielded a mixture of the [2 + 1]- and [5 + 1]-cycloaddition products. Despite this promising initial finding, efforts to improve the selectivity for [5 + 1]-cycloaddition using a dinickel catalyst proved to be unfruitful. Furthermore, we were unable to adequately control the *E/Z* geometry of the exocyclic alkene. Here, we report that (quinox)Co catalysts promote high-yielding [5 + 1]-cycloadditions of vinylidenes and vinylcyclopropanes. This method provides access to di- and trisubstituted methylenecyclohexenes bearing all-*meta* relationships.

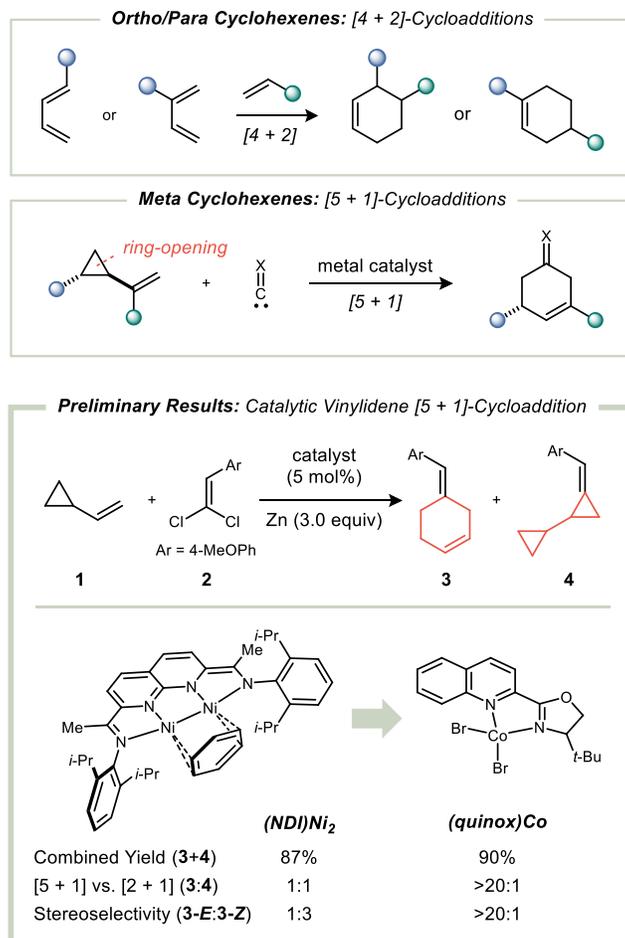
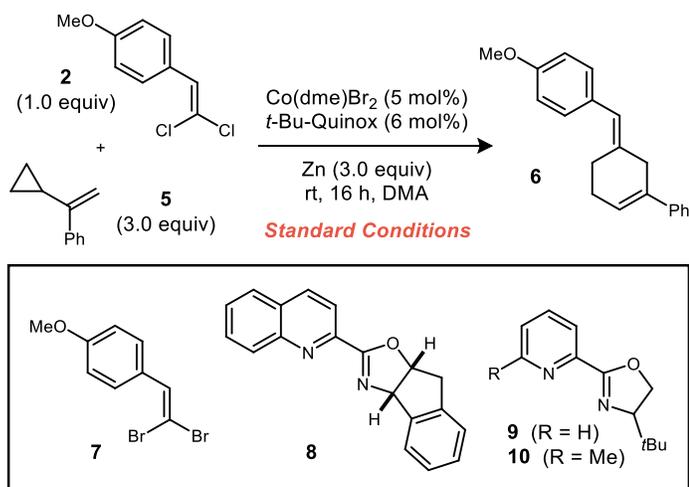


Figure 2.1. Catalytic reductive [5 + 1]-cycloadditions of vinylcyclopropanes and 1,1-dichloroalkenes.

2.3 Catalyst Comparison and Optimization Studies

Optimized conditions for the reductive [5 + 1]-cycloaddition of dichloroalkene **2** and vinylcyclopropane **5** are shown in Table 2.1. A catalyst derived from $\text{Co}(\text{dme})\text{Br}_2$ (5 mol%) and (\pm) -*t*-Bu-Quinox (6 mol%) provides cycloadduct **6** in 97% yield with nearly exclusive *E* stereochemistry (>20:1 *E:Z*) at the exocyclic double bond (entry 1). The reaction benefits from excess vinylcyclopropane. However, the additional 2.0 equiv remains unreacted and can be quantitatively reisolated from the crude reaction mixture during chromatographic purification. With a smaller excess of **5** (1.5 equiv), yields up to 73% could be obtained at a slightly elevated reaction temperature of 60 °C (entry 4). When dichloroalkene **2** was substituted with its dibromo counterpart **7**, low yields of **6** were obtained (entry 5).

Table 2.1. Catalytic reductive [5 + 1]-cycloadditions: effect of reaction parameters.^a



entry	changes from standard conditions ^b	yield (3)	<i>E</i> : <i>Z</i> (3)
1	none	97%	>20:1
2	no Zn	<1%	–
3	1.5 equiv of 2	42%	>20:1
4	1.5 equiv of 2 at 60 °C instead of rt	73%	>20:1
5	7 instead of 2	15%	>20:1
6	Mn instead of Zn	93%	>20:1
7	TDAE instead of Zn	<1%	–
8	Cp ₂ Co instead of Zn	<1%	–
9	Cp ₂ Co and ZnBr ₂ instead of Zn	63%	>20:1
10	Ni(dme)Br ₂ instead of Co(dme)Br ₂	<1%	–
11	Fe(dme)Br ₂ instead of Co(dme)Br ₂	<1%	–
12	no (±)- <i>t</i> -Bu-Quinox	<1%	–
13	8 instead of (±)- <i>t</i> -Bu-Quinox	83%	>20:1
14	9 instead of (±)- <i>t</i> -Bu-Quinox	15%	>20:1
15	10 instead of (±)- <i>t</i> -Bu-Quinox	<1%	–

^aYields and *E*:*Z* ratios of **6** were determined by ¹H NMR analysis of crude reaction mixtures containing 1,3,5-trimethoxybenzene as an internal standard. ^bReaction conditions: **2** (0.1 mmol, 1.0 equiv), **5** (3.0 equiv), Zn (3.0 equiv), Co(dme)Br₂ (0.05 equiv), (±)-*t*-Bu-Quinox (0.06 equiv), DMA (0.75 mL), rt, 16 h.

Zn proved to be the optimal reductant, but Mn provided comparable yields (entry 6). Interestingly, Cp₂Co, a soluble outersphere reductant, also promoted formation of **6** but only in the presence of added ZnBr₂ (entries 8 and 9). This result suggests that ZnX₂, a reaction

byproduct formed under the standard conditions, may play a critical role in the catalytic mechanism.

When Co(dme)Br₂ was replaced with Fe(dme)Br₂ or Ni(dme)Br₂, no conversion of dichloroalkene **2** was observed (entries 10 and 11). The reaction is highly sensitive to the structure of the ancillary ligand. The oxazoline portion can be varied to some extent with only moderate changes in yield (entry 13). However, ligands containing pyridine in the place of quinoline led to little or no yield of **6** (entries 14 and 15). Other nitrogen-based chelating ligands, including those commonly used in catalytic reductive cross-coupling reactions,¹⁰ were also investigated but found to be ineffective at promoting the [5 + 1]-cycloaddition (see Supporting Information).

2.4 Substrate Scope Studies

1,1-Dichloroalkenes bearing alkyl, aryl, or heteroaryl substituents undergo [5 + 1]-cycloaddition in high yield with model vinylcyclopropane **5** (Figure 2.2). Ketone-derived 1,1-dichloroalkenes are viable substrates and afford products containing hindered tetrasubstituted alkenes (products **16** and **17**). A variety of common functional groups are tolerated, including free alcohols, ethers, thioethers, esters, carbamates, sulfonamides, and boronate esters. Vinylcyclopropanes containing terminal alkenes (either monosubstituted or 1,1-disubstituted) generally react efficiently. Vinylcyclopropanes containing internal alkenes are a limitation of the method. For all products, *E* stereochemistry is favored at the *exo* methylene. The diastereomeric ratio is dependent on the nature of the substituent on the 1,1-dichloroalkene: aryl and heteroaryl groups provide the *E* diastereomer almost exclusively, whereas alkyl substituents lead to lower selectivities in the range of 5:1 to 12:1. The products generated in the [5 + 1]-cycloaddition possess a skipped diene, and no isomerization was observed during the reaction or during product isolation.

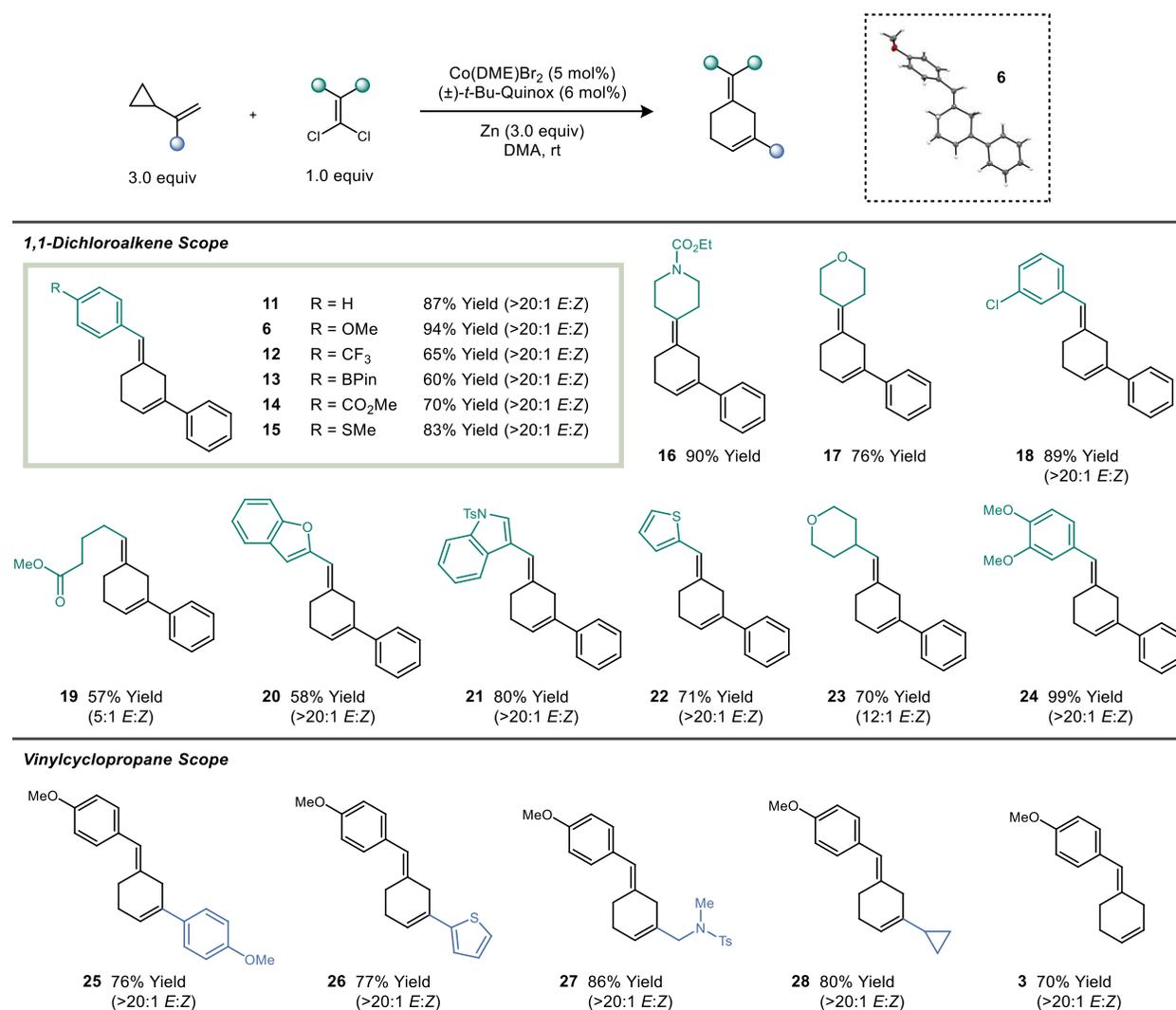


Figure 2.2. Catalytic reductive [5 + 1]-cycloadditions of vinylcyclopropanes and vinylidenes. Reactions were conducted using the standard conditions shown in Table 2.1.

The [5 + 1]-cycloaddition provides access to all-*meta* trisubstituted methylenecyclohexenes using vinylcyclopropanes of the general structure shown in Figure 2.3. Vinylcyclopropane **29** was prepared in highly enantioenriched form and was converted into methylenecyclohexene **30** without any loss in enantiomeric excess.^{7a} For all substrates that were examined, the catalyst only targeted the less hindered C–C bond of the cyclopropane. The alternative 1,2,4-regioisomer, which would be formed by cleavage of the more hindered C–C bond, was not detected. Organometallic mechanisms for cyclopropane ring-opening (either oxidative addition or σ -bond metathesis) are generally sensitive to steric effects.^{4,11} However, a

recent nitrene cycloaddition produced the alternative 1,2,4-regioisomers due to a proposed radical based ring-opening mechanism.¹²

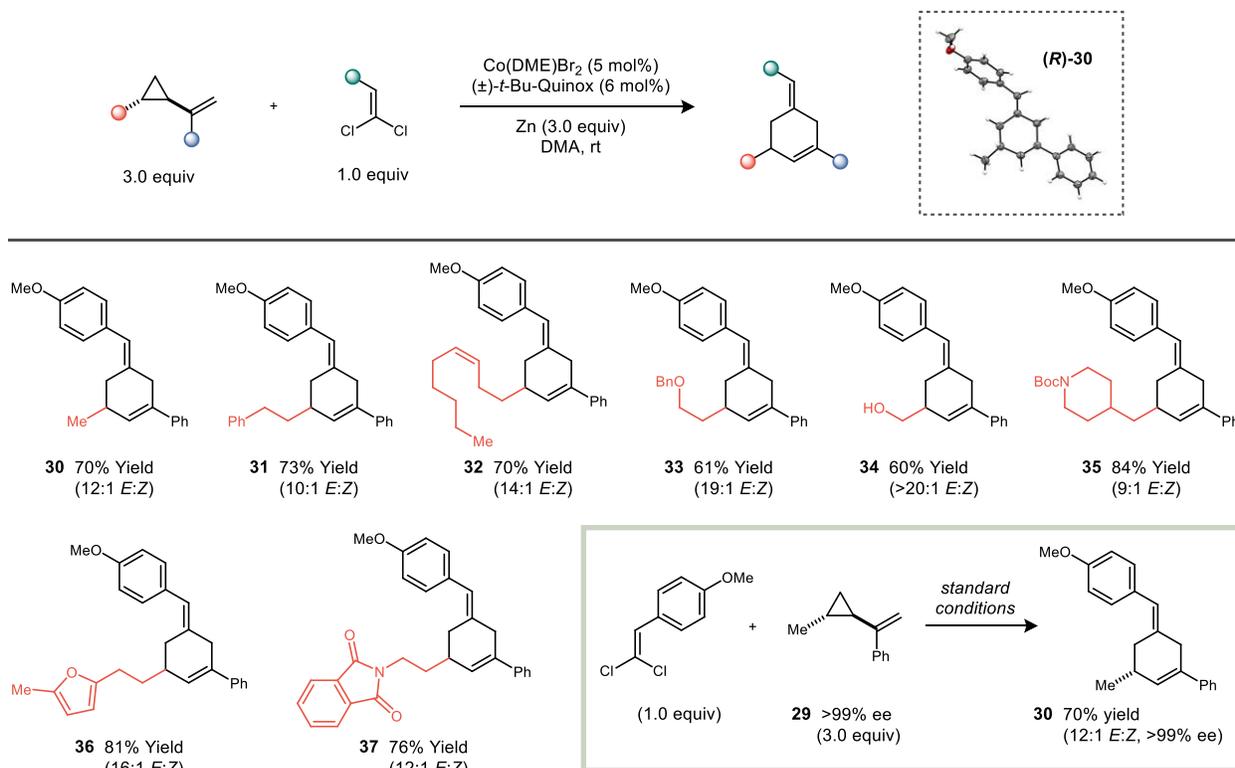


Figure 2.3. Synthesis of all-*meta* trisubstituted methylenecyclohexenes via [5 + 1]-cycloadditions. Reactions were conducted using the standard conditions shown in Table 2.1.

2.5 Product Derivatization Studies

The [5 + 1]-cycloadducts can be oxidized to form 1,3,5-trisubstituted aromatic products. Arenes of this type, possessing all-*meta* substitution patterns, would be challenging to synthesize through conventional aromatic substitution or cross-coupling approaches. Dehydrogenation reactions were accomplished using Pd/C as a catalyst without the need for an H₂ acceptor (products **38–42**).¹³ Dehydrogenation of the methylenecyclohexenes could also be carried out with SeO₂ but led to concomitant oxidation of the benzhydryl group to a benzophenone (products **44** and **45**). Finally, the skipped diene in the cycloaddition products can be isomerized into conjugation using KO*t*-Bu (products **43**).

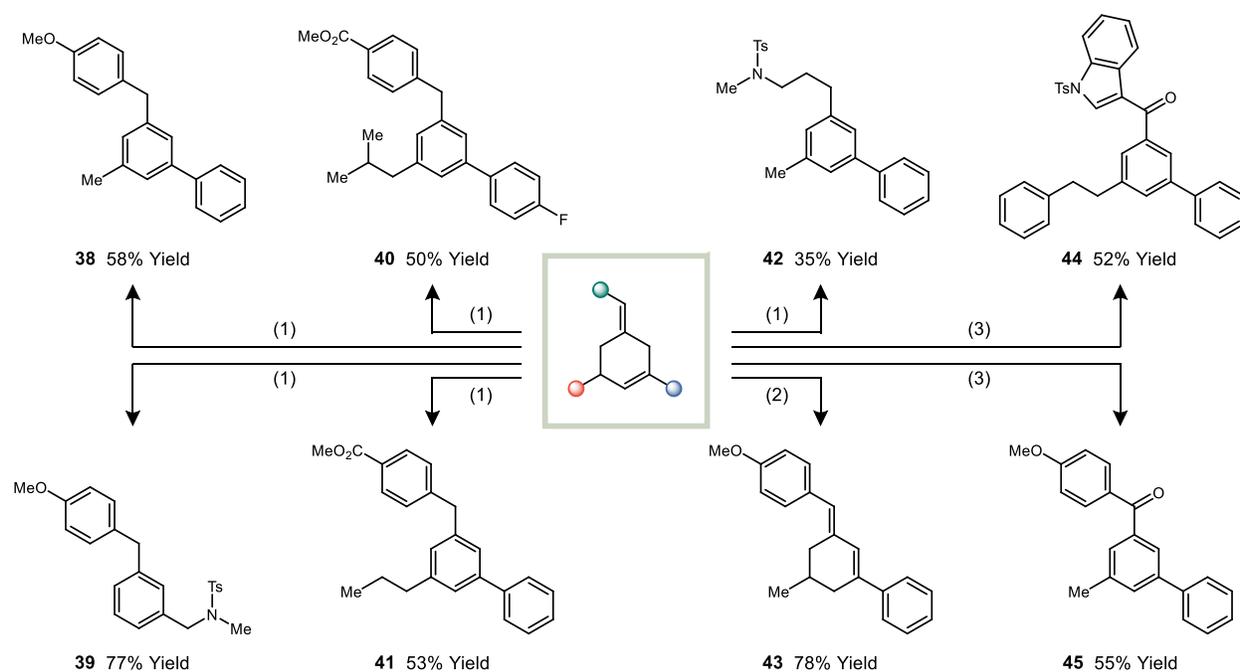


Figure 2.4. Oxidation and isomerization reactions of cycloadducts. Reaction conditions: (1) Pd/C (10 wt%), ethylene glycol, 200 °C; (2) KO^tBu, DMF, 0 °C; (3) SeO₂, 1,4-dioxane, 100 °C.

2.6 Reaction Mechanism Studies

Results pertaining to the mechanism of the reaction are summarized in Figure 3.5. Our first experiment was aimed at determining whether the (quinox)Co catalyst promotes the ring-opening of vinylcyclopropanes¹⁴ in the absence of the 1,1-dichloroalkene. When subjected to the standard [5 + 1]-cycloaddition conditions, vinylcyclopropane **5** was recovered unreacted (Figure 2.5a). This result is consistent with a mechanism in which vinylidene formation precedes ring-opening of the vinylcyclopropane. We next considered a mechanism involving an initial [2 + 1]-cycloaddition followed by rearrangement to form a six-membered ring.¹⁵ This mechanism was ruled out by subjecting dicyclopropane **4**, the putative intermediate in this sequential mechanism, to the standard [5 + 1]-cycloaddition conditions. No conversion of **4** was observed after 48 h at room temperature (Figure 2.5b).

When allyl benzene (**46**), a monosubstituted alkene lacking the cyclopropane, was subjected to the standard [5 + 1]-cycloaddition conditions, a methylenecyclopropane product (**47**) was obtained (Figure 2.5c). Interestingly, the reaction is highly selective for the *Z* diastereomer.

This finding is in striking contrast to Ni₂ catalyzed methylenecyclopropanations,^{9a} which generally produce near 1:1 *E/Z* mixtures for this class of alkenes. Taken together, these results suggest that the [2 + 1]- and [5 + 1]-cycloadditions may be mechanistically related and that a common step is responsible for determining the *E/Z* selectivity. Finally, unlike the [5 + 1]-cycloaddition, more hindered 1,1-disubstituted alkenes, such as α -methylstyrene, are unreactive, presumably due to the increased steric hindrance in the ring-closure step.

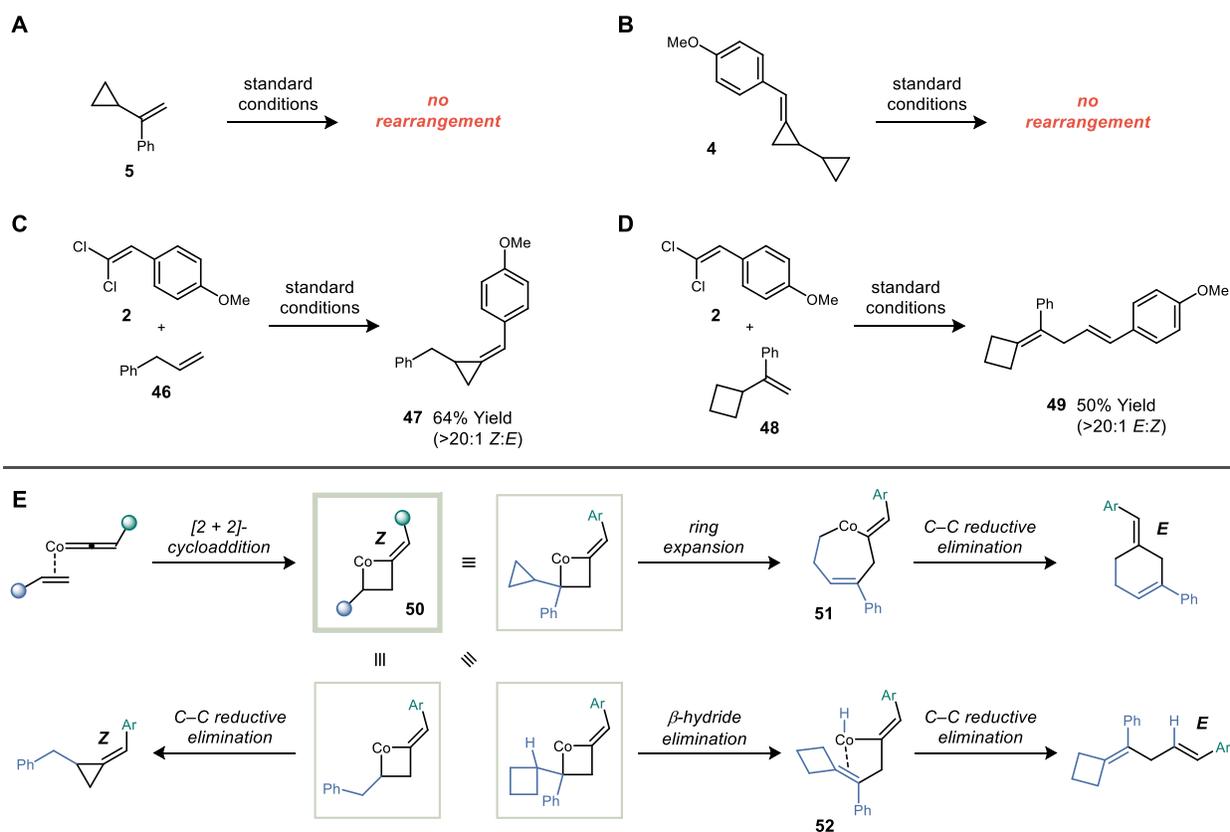


Figure 2.5. Experiments probing potential (a) vinylcyclopropane ring-opening and (b) dicyclopropane rearrangement mechanisms. (c) Catalytic reductive methylenecyclopropanation of a terminal alkene. (d) Catalytic reductive addition/isomerization of vinylidenes to a vinylcyclobutane. Reactions were conducted using the standard conditions shown in Table 1. (e) Unified vinylidene [2 + 2]-cycloaddition mechanism for the formation of [2 + 1]-cycloaddition, [5 + 1]-cycloaddition, and coupling products.

Cyclobutanes are moderately less strained than cyclopropanes¹⁶ and generally less reactive toward transition metal catalyzed ring-opening processes.¹⁷ Accordingly, vinylcyclobutane **48** did not yield the corresponding [6 + 1]-cycloaddition product, but instead

generated diene **49**, containing the intact cyclobutane ring (Figure 2.5d). The formation of this product can be rationalized by invoking a β -hydride elimination that outcompetes other ring-opening or ring-closing steps.

The three different products obtained from simple alkenes, vinylcyclopropanes, and vinylcyclobutanes can be rationalized according to a single general mechanism as shown in Figure 2.5e. Oxidative addition of the 1,1-dichloroalkene followed by Zn reduction would generate a Co(vinylidene) intermediate. [2 + 2]-cycloaddition of the Co(vinylidene) and the alkene forms a metallacyclobutane (**50**). The *E/Z* selectivity for all three product classes is established in this step of the mechanism and requires the alkene to approach the Co(vinylidene) from the less hindered face. From here, methylenecyclopropanes are generated by C–C reductive elimination. In the case of the vinylcyclopropane substrate, ring-expansion of metallacyclobutane **50** forms metallacycloheptene **51**, which then undergoes reductive elimination to yield the [5 + 1]-cycloadduct. Finally, because cyclobutanes are less strained than cyclopropanes, intermediate **50** may undergo β -hydride elimination instead of ring expansion. C–H reductive elimination from **52** would yield the linear skipped diene product.

2.7 Conclusions

In summary, cobalt-catalyzed vinylidene [5 + 1]-cycloadditions are a useful complement to the Diels–Alder reaction in that they provide access to six-membered rings containing *meta* substitution patterns. The stereoselectivity of the reaction and the products generated from additions to simple alkenes and vinylcyclobutanes have led us to propose a cobaltacyclobutane intermediate, which may arise from a [2 + 2]-cycloaddition between a cobalt vinylidene species and an alkene. We are currently exploring other avenues to generate or intercept this intermediate as a platform to develop new reductive vinylidene transfer reactions.

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CHAPTER 3. ORGANIC REACTIONS ENABLED BY CATALYTICALLY ACTIVE METAL-METAL BONDS

3.1 Abstract

Molecular transition metal catalysts are predominantly Werner-type coordination complexes, wherein a single metal ion surrounded by ligands functions as the sole locus of reactivity. A major focus of organometallic chemistry has been to understand how supporting ligands can be rationally modified in order to access more active and selective catalysts. Since the 1960's, however, it has been recognized that metals can also form direct metal-to-metal bonds, giving rise to an extraordinary diversity of multinuclear assemblies. If metal-metal bonding could be harnessed productively in catalysis, it would provide access to a large parameter space that is not available through ligand modification. This review highlights recent examples of organic transformations that were discovered using catalysts containing metal-metal bonds.

3.2 Introduction

Transition metal catalysis provides access to valuable organic transformations that would otherwise suffer from prohibitively high activation barriers or poor selectivity. Developing a catalyst for a reaction of interest is typically a lengthy process that begins with identifying an initial hit then carrying out systematic modifications in order to achieve the desired level of efficiency. One of the most powerful tools available to synthetic chemists for optimizing the performance of a catalyst is the identity of the supporting ligands. Supporting ligands exert an influence on the d-orbital structure of metal ions and thus control the types of organic substrates that can bind to a catalyst as well as the organometallic processes that are feasible (Figure 3.1a). Additionally, the steric environment of supporting ligands can be precisely engineered in order to achieve high levels of regio- or stereoselectivity.

Beyond coordinating ligands, transition metals are also capable of engaging in direct metal-to-metal interactions. Since the seminal work of Cotton in the 1960's, there have been considerable advances in our understanding of the electronic factors that underlie metal-metal

bonding.^{1,2} There are now over 40,000 structurally characterized metal–metal bonds compiled in the Cambridge Structural Database between elements spanning much of the d-block.³ The scope of metal–metal bonding interactions between two transition metals is particularly rich due to the availability of d-orbitals.⁴ Examples range from strong metal–metal quintuple bonds to weak metallophilic interactions that are similar in strength to non-covalent hydrogen bonds.

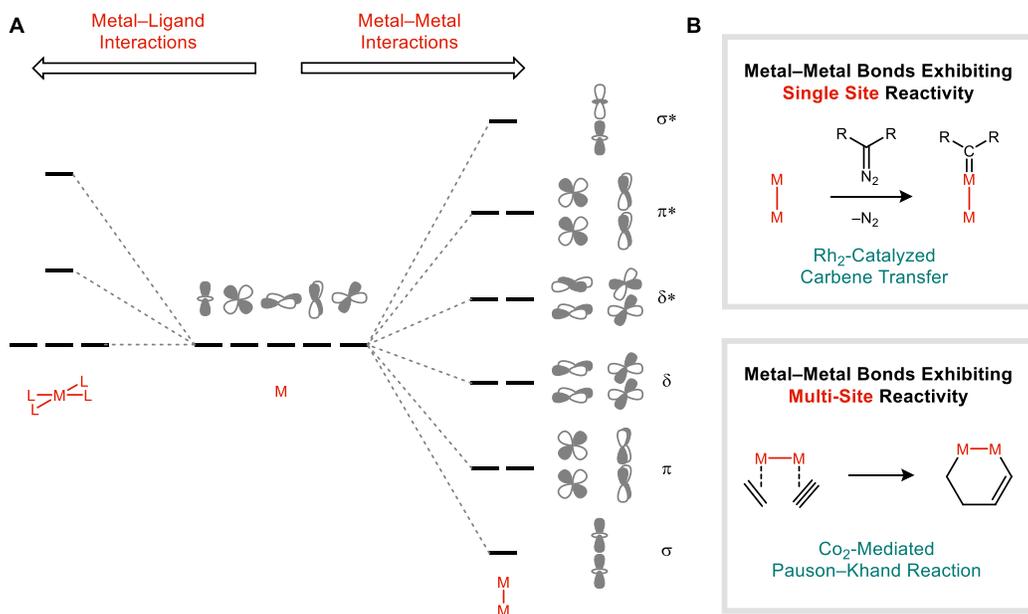


Figure 3.1. (A) Metal–ligand and metal–metal interactions provide complementary tools to control the electronic structure of transition metal catalysts. (B) Metal–metal bonds can serve as single site or multi-site catalysts.

Understanding how metal–metal bonding might play a role in catalysis, either beneficial or deleterious, is a research area that is still very much in its infancy.⁵⁻⁸ Nevertheless, there is significant evidence to suggest that metal–metal bonds can give rise to unique catalytic properties that are challenging to access with just a single transition metal. Examples of catalysts featuring metal–metal bonds can be broadly divided into two categories (Figure 3.1b). In the first, only one of the two metals acts as the site of reactivity (single site reactivity), but the second metal nonetheless plays an important supporting electronic role. For example, Rh₂-based catalysts generate unusually electrophilic carbene complexes due to three-centered bonding interactions in the Rh–Rh–CR₂ fragment.⁹ In the second category, both metals directly bind substrates and mediate organometallic transformations (multi-site reactivity). One of the most

prominent examples in organic chemistry is the $\text{Co}_2(\text{CO})_8$ -mediated Pauson–Khand reaction^{10,11}, which is initiated by a dinuclear oxidative coupling of an alkene and an alkyne to yield a dicobaltacyclic intermediate. In this Review, we highlight select cases in which metal–metal bonded catalysts carry out organic transformations that are not viable using their closest mononuclear counterparts. A focus of our discussion is on connecting the fundamental electronic properties of metal–metal bonds with observed catalytic phenomena.

3.3 Pd(I)–Pd(I) bonds in cross-coupling reactions: from off-cycle resting states to catalytic intermediates

One potential consequence of metal–metal bonding in a catalytic process is to create off-cycle dimers that decrease the fraction of active catalyst and result in lower-than-expected turnover frequencies (Figure 3.2a). For example, the canonical mechanism of the Suzuki–Miyaura cross-coupling reaction invokes only the even oxidation states of Pd, specifically Pd(0) and Pd(II). However, recent studies from Hazari indicate that Pd(I)–Pd(I) species may also assemble under standard catalytic conditions and that the extent of catalyst dimerization may be a key determinant of reaction efficiency.¹² Prior to this work, Nolan had noted a striking enhancement in cross-coupling rates using a second-generation (IPr)Pd(cinnamyl)Cl precatalyst (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in the place of their previously reported (IPr)Pd(allyl)Cl precatalyst.^{13,14} Given that the allyl ligand is not retained during catalytic turnover, this enhancement was attributed to a faster rate of precatalyst activation. Hazari later recognized that the reduction of (IPr)Pd(allyl)Cl precatalysts using boronic acid and base leads to the formation of dimeric (IPr)₂Pd₂(μ -allyl)(μ -Cl) species **1**, which is in equilibrium with monomeric Pd(0).¹² By carrying out equilibrium constant measurements, it was shown that the cinnamyl group serves to sterically disfavor dimerization, leading to a higher fraction of active mononuclear catalyst.

Related phenomena have since been documented in other Pd-catalyzed reactions. Barnard reported the Pd-catalyzed aminocarbonylation of aryl chlorides using CO and NH_4Cl .^{20,21} In subsequent mechanistic studies, Hartwig observed that (dcpp)Pd₂(CO)(H) dimer **2** (dcpp = dicyclohexylphosphinopropane) is generated under catalytic conditions and that it accumulates as the reaction progresses.¹⁵ The dimer was determined to be an inactive catalyst state that forms

when the mononuclear (dcp)Pd(CO)₂ complex, which is the dominant on-cycle resting state, undergoes protonation by NH₄Cl. This finding suggests that longer-lived catalysts for Pd-catalyzed carbonylation reactions might be identified by designing sufficiently hindered supporting ligands to disfavor dimerization. In a similar vein, Ni-catalyzed reactions are also susceptible to the deleterious formation of Ni(I) dimers.

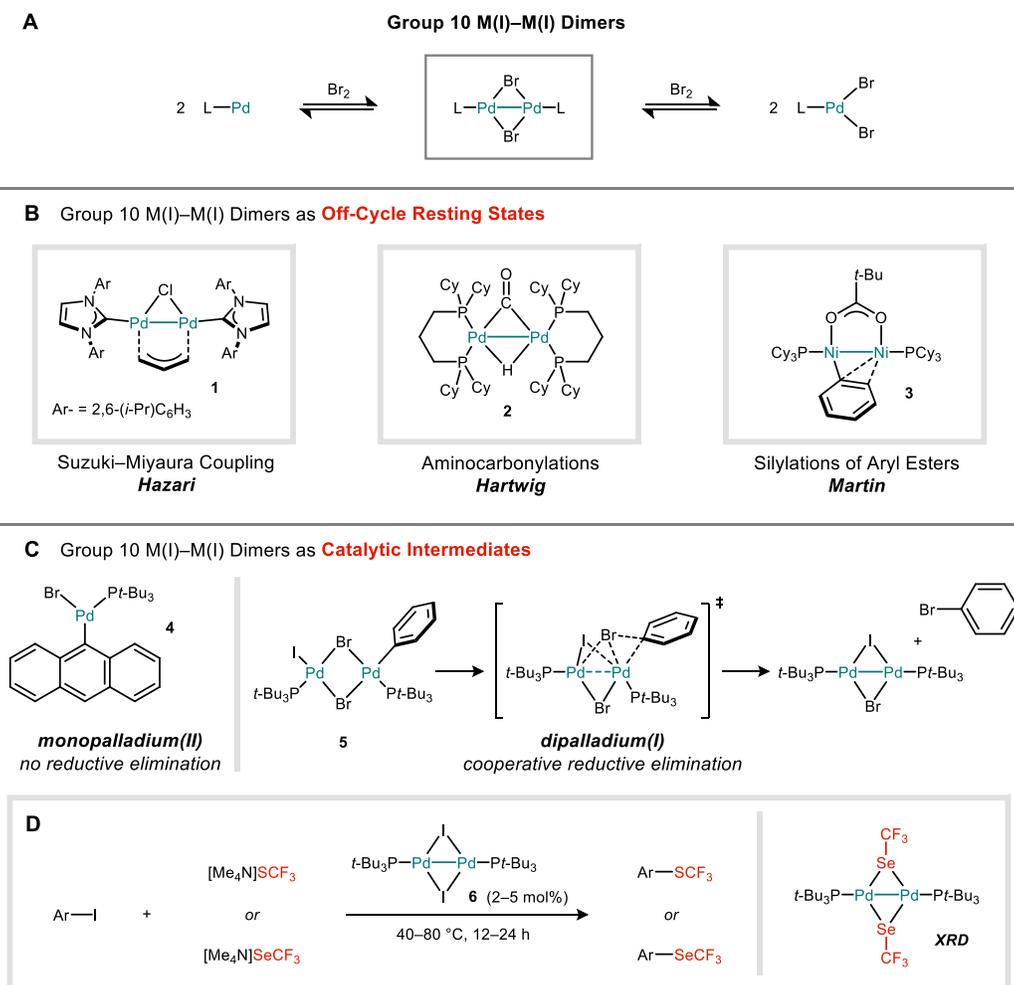


Figure 3.2. (A) Pd exhibits a propensity to form metal–metal bonded dimers in the +1 oxidation state. (B) Pd(I) dimers as off-cycle resting states or catalyst decomposition products in cross-coupling reactions.^{12,15,16} (C) Pd(I) dimers as catalytic intermediates in transhalogenation reactions.¹⁷ (D) Development of catalytic aryl halide trifluoromethylthiolation¹⁸, and trifluoromethylselenolation reactions¹⁹

Martin carried out mechanistic studies of a Ni-catalyzed C–Si cross-coupling reaction and discovered a series of dinuclear (Cy₃P)Ni₂(Ar)(OPiv) complexes (**3**) that are produced when

the Ar–OPiv substrate undergoes C–O oxidative addition at Ni(0).^{16,22} Presumably, this dimer is formed because a transient Ni(II) species is rapidly captured by Ni(0). Unlike the Pd-catalyzed aminocarbonylation reaction, however, these dimers are in rapid equilibrium with on-cycle mononuclear Ni(II) due to a relatively facile disproportionation process. Consequently, the ability of the Ni catalyst to dimerize has the net effect of slowing down turnover but does not lead to catalyst deactivation.

A less common role of metal–metal bonded dimers in a cross-coupling process is to facilitate catalysis by lowering the activation barrier of the rate-determining step. For example, reductive eliminations become increasingly challenging as the reacting fragments become more electron deficient. This step represents one of the principal impediments to the development of Pd-catalyzed cross-coupling reactions that involve weakly nucleophilic partners, such as fluoride or related polyfluorinated nucleophiles.^{23,24} Nevertheless, the installation of fluorine has attracted significant interest in medicinal chemistry due to the ability of fluorine to block drug metabolism. Additionally, ¹⁹F-labelled compounds have applications as PET imaging agents. One solution that has been employed is to oxidize Pd to the +4 oxidation state, thereby triggering a facile reductive elimination to Pd(II).^{25,26} One drawback, however, is the need for a strong oxidant in order to access this unusually high-valent state of Pd.

An alternative approach is to couple a challenging C–X reductive elimination to the formation of a stabilizing Pd–Pd bond (Figure 3.2c). The net consequence of a dinuclear reductive elimination would be to delocalize the overall two-electron process over two redox-active Pd atoms, allowing each to contribute only a single electron. In this context, Schoenebeck described a catalytic halide exchange reaction that converts an aryl iodide into an aryl bromide using *n*-Bu₄NBr.¹⁷ The catalyst is the [(*t*-Bu₃P)PdI]₂ dimer **6**. Mechanistic studies revealed that the isolable mononuclear (*t*-Bu₃P)Pd(Ar)(Br) species **4** is incapable of undergoing C–Br reductive elimination. However, reductive elimination becomes facile using the dimeric analogue **5**, and kinetics studies indicate that the dimer remains intact during this process rather than undergoing a pre-equilibrium dissociation. Computational models of the reductive elimination transition state show partial Pd–Pd bonding (Pd–Pd = 2.79 Å), which is indicative of direct electronic communication between the two Pd centers. By exploiting this dinuclear mechanism,

Schoenebeck was able to discover the first catalytic C–SeCF₃ cross-coupling reaction of aryl iodides¹⁹, along with a related C–SCF₃ cross-coupling (Figure 3.2d).¹⁸

3.4 Circumventing one-electron pathways to enable catalytic C–H borylations with Fe

As exemplified in the cross-coupling reactions described above, two-electron redox processes, such as oxidative addition and reductive elimination, underlie the mechanisms of many catalytic transformations. For this reason, noble transition metals feature prominently in homogeneous catalysis relative to their more abundant and less expensive first-row congeners. Base metal-catalyzed reactions often suffer from lower efficiencies due to competing one-electron processes, which can lead to side-product formation or catalyst degradation.²⁷ Cooperativity between two base metals has recently emerged as a strategy to combat this limitation. In these cases, two first-row transition metals that would individually undergo facile single-electron chemistry instead act in concert to achieve a net two-electron redox process.

One such example was recently described by Mankad in the context of a photochemical arene C–H borylation using heterobimetallic (IPr)Cu–Fp catalyst **12** (Fp = Fe(Cp)(CO)₂).²⁸ C–H borylation reactions are of significant value in organic synthesis because they transform ubiquitous C–H bonds into valuable C–B linkages, which can then be parlayed into a range of other functional groups. The most general C–H borylation reactions currently rely on Ir-based catalysts that generate Ir(III)-boryl species (**7**) as key intermediates (Figure 3.3a).^{29–31} However, prior to the development of Ir-catalyzed C–H borylations, Hartwig found that the very simple Fp–Bcat complex **8**, derived from the Fp anion and Cl–Bcat, was capable of borylating the C–H bond of benzene when activated with light (Figure 3.3b).³² The metal-containing byproduct of this reaction is Fp–H **9**, which dimerizes and eliminates H₂ to form Fp₂ **10**. The Fp₂ dimer is sufficiently stable that it does not activate R₂B–H reagents, a requisite step for catalytic turnover.

Mankad hypothesized that Fp₂ dimer formation could be circumvented by intercepting the transient Fp–H **9** with a reactive Cu–H species (**11**) to yield a Fe–Cu heterobimetallic complex (**12**).²⁸ Then, a bimetallic oxidative addition of H–Bpin would regenerate the Cu–H **11** and form the Fp–Bpin species required to activate the arene substrate. In support of this proposed

pathway, it was found that Fp–H, generated *in situ* from K₂Fp and HCl, reacts with [(IPr)CuH]₂ **11** to provide the heterobimetallic (IPr)Cu–Fp complex **12**. This species was shown to undergo an endothermic oxidative addition³³ of H–Bpin to form [(IPr)CuH]₂ and Fp–Bpin, the species shown by Hartwig to undergo C–H borylation.

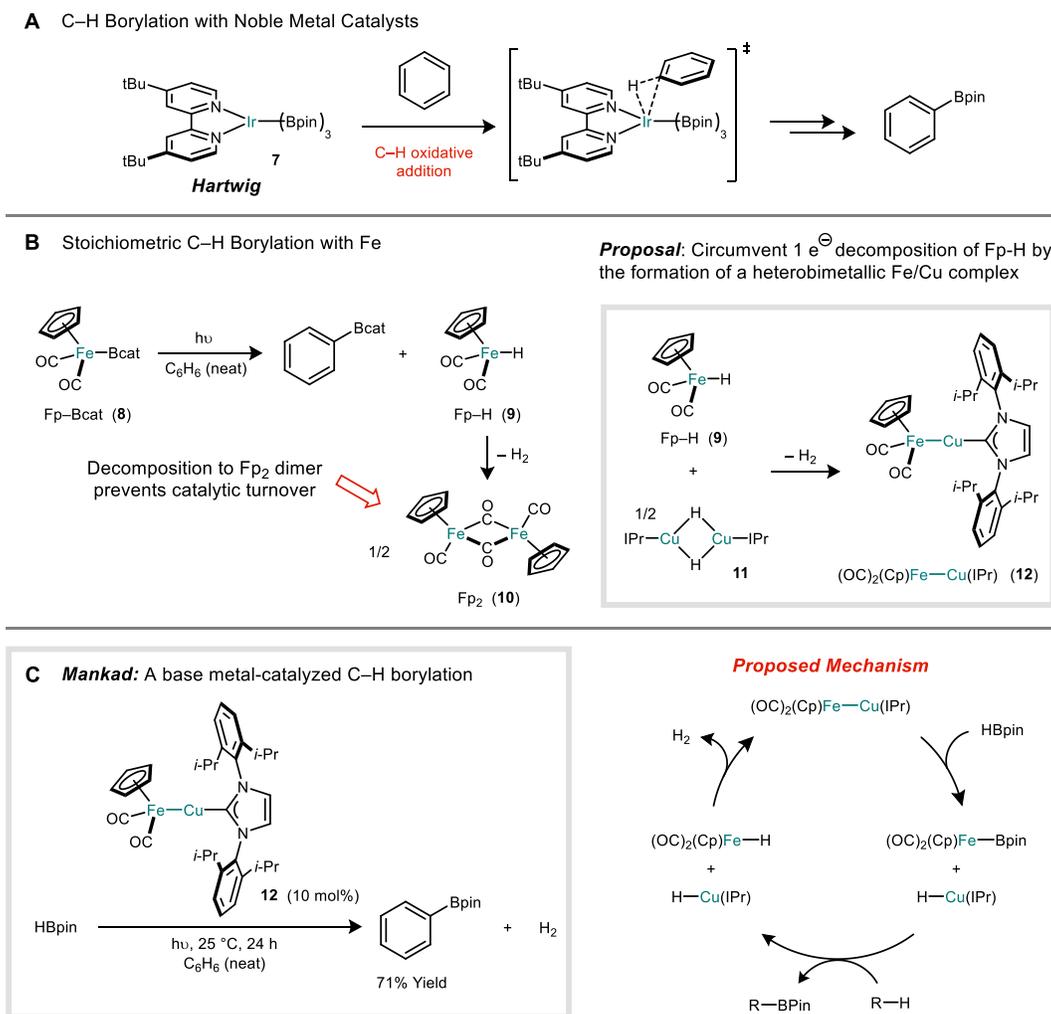


Figure 3.3. (A) Arene C–H borylations using Ir catalysts.³⁰ (B) From stoichiometric to catalytic C–H borylations using base metal catalysts.³² (C) Photoinduced catalytic C–H borylations using heterobimetallic Fe/Cu catalysts.²⁸

This sequence of stoichiometric reactions was combined to enable a catalytic protocol for arene C–H borylation using complex **12** as a catalyst (10 mol% loading) and a Hg lamp as the light source (Figure 3.3c).²⁸ Lending credence to the critical role of metal–metal cooperativity in this reaction, it was found that neither of the individual mononuclear components, Fp–Bpin or

(IPr)Cu–Cl, were effective catalysts on their own. Together, these studies illustrate that the two-electron processes characteristic of noble metals can be emulated by exploiting bimetallic pathways that involve two base metals.

3.5 Ni₂ catalysts suppress 1,2-rearrangements of vinylidenes and promote transfer reactions to olefins

Group 10 elements such as Pd and Ni form metal–metal bonds in the odd-electron oxidation states but prefer to remain mononuclear in the M(0) and M(II) oxidation states. Consequently, when M(I)–M(I) dimers undergo redox reactions, such as oxidative addition or reductive elimination, the metal–metal bond is invariably cleaved.³⁴ Our group is interested in designing metal–metal bonds that are capable of remaining intact during a catalytic process rather than undergoing reversible dissociation and reassociation. In order to accomplish this goal, we employed a naphthyridine–diimine (NDI) pincer ligand, which possesses a highly conjugated π -system that is redox active and capable of being reduced at mildly anodic potentials.³⁵ The redox-active nature of the NDI ligand proved to be valuable in preparing stable dinuclear complexes of low-valent Ni. Free NDI reacts with Ni(COD)₂ (2.0 equiv) in C₆H₆ to afford the [NDI]Ni₂(C₆H₆) complex **13**. An analysis of the electronic structure of **13** reveals that Ni(0) has undergone an oxidation to Ni(I), which allows for the assembly of a stable metal–metal covalent single bond. Correspondingly, the ligand is reduced by two electrons to its 2– charge state. Common organic electrophiles react at the Ni–Ni bond to generate oxidative addition products in which the ligand has been returned to its neutral charge state. For example, complex **13** reacts with β -bromostyrene to yield Ni₂(vinyl)Br complex **14** (Figure 4.4b). An unusual structural feature of **14** relative to mononuclear Ni(vinyl) complexes is the presence of a secondary η^2 - π interaction, which is enabled by the proximity of the two Ni atoms.

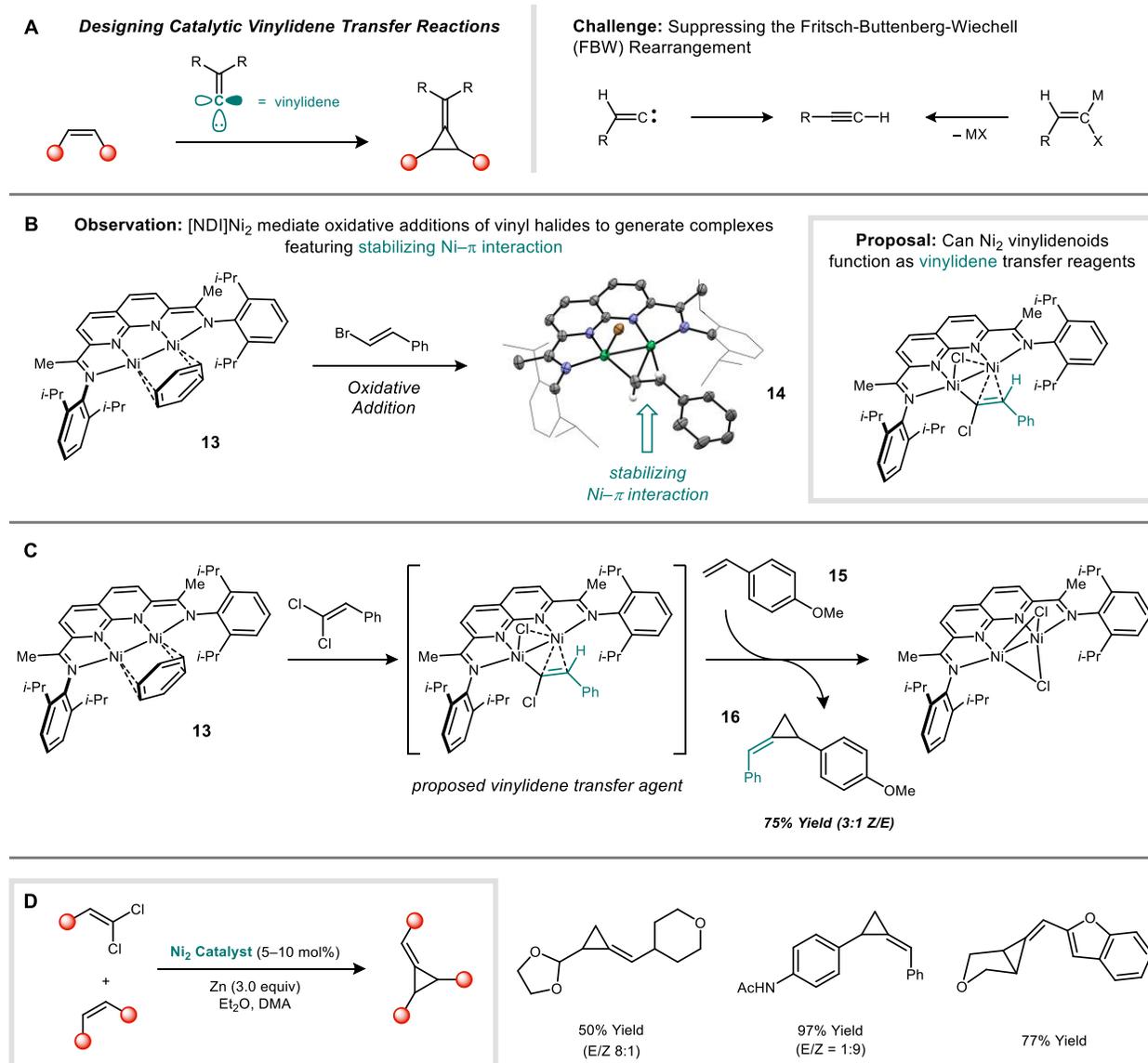


Figure 3.4. (A) Designing catalytic vinylidene transfer reactions by suppressing the competing Fritsch–Buttenberg–Wiechell (FBW) rearrangement. (B) Dinuclear stabilization of vinyl ligands and a proposed Ni₂-bound vinylidenoid. (C) Stoichiometric methylenecyclopropanation using a 1,1-dichloroalkene. (D) Catalytic reductive methylenecyclopropanations of alkenes.³⁶

The stability afforded to vinyl ligands by the dinuclear active site of **13** may be leveraged to carry out catalytic transfer reactions of vinylidenes (Figure 3.4a).³⁶ Vinylidenes exhibit similar reactivity patterns to carbenes but suffer from a competing rearrangement known as the Fritsch–Buttenberg–Wiechell (FBW) rearrangement, which generates the corresponding isomeric alkyne.^{37–39} This rearrangement is the mechanistic basis for common alkylation methods such as the Corey–Fuchs⁴⁰ and Seyferth–Gilbert homologation reactions.^{41,42} According to

computational models, vinylidene rearrangements are exothermic by approximately 45 kcal/mol and, when the migrating group is a hydrogen atom, possess activation barriers as low as 1.5 kcal/mol.⁴³ Consequently, cyclopropanation reactions using free vinylidenes are only viable in specialized cases where the rearrangement can be sufficiently disfavored to allow the vinylidene to react productively with the olefin substrate.

In our early experiments, we noted that Ni₂ complex **13** reacts stoichiometrically with 1,1-dichloroalkenes to generate reactive vinylidene equivalents (Figure 3.4c).³⁶ These species were not sufficiently stable to be isolated but could be trapped in situ with an alkene to afford the corresponding methylenecyclopropane product in high yield. Notably, the reaction proceeds without any competing formation of a terminal alkyne byproduct, indicating that the metal complex is effectively serving to suppress the FBW rearrangement. This stoichiometric process was rendered catalytic by employing a suitable reductant that is capable of returning the oxidized Ni₂Cl₂ catalyst to its initial reduced state. Accordingly, catalytic methylenecyclopropanation reactions of terminal alkenes and unhindered internal alkenes were accomplished using 1,1-dichloroalkenes in combination with Zn (Figure 3.4d).

3.6 Rh–Rh bonds form highly electrophilic carbene complexes that react with unactivated C–H bonds

Beyond the vinylidene transfer reaction described above, dinuclear catalysts have also enabled remarkable transformations of simple carbenes. A long-standing goal in organic synthesis is to develop selective catalytic processes that are capable of functionalizing a single C–H bond within a complex substrate.^{44,45} In this context, carbene transfer reactions have garnered significant interest, because free carbenes possess sufficiently high reactivity to undergo insertions into aliphatic C–H bonds, even in cases where there are no activating substituents present. The challenges for catalyst design are to avoid overly tempering the reactivity of the metal-bound carbene while maintaining an appropriate catalyst environment to control C–H bond selectivity.

Dirhodium tetracarboxylates were introduced as carbene insertion catalysts by Teyssié in the 1970's and have since emerged as being among the most synthetically useful catalysts for C–H

functionalization reactions.^{46,47} While many other catalysts are also capable of decomposing diazoacetate reagents to form reactive carbene equivalents, Rh₂ catalysts are distinguished by their unusually high reactivity. The basic mechanistic framework for these reactions involves an initial binding event of the diazoalkane reagent to the metal catalyst, inducing N₂ elimination to form a metal-bound carbene (Figure 3.5a). This M=CR₂ species is then poised to undergo bond insertion through a concerted three-centered transition state.⁴⁸⁻⁵⁰

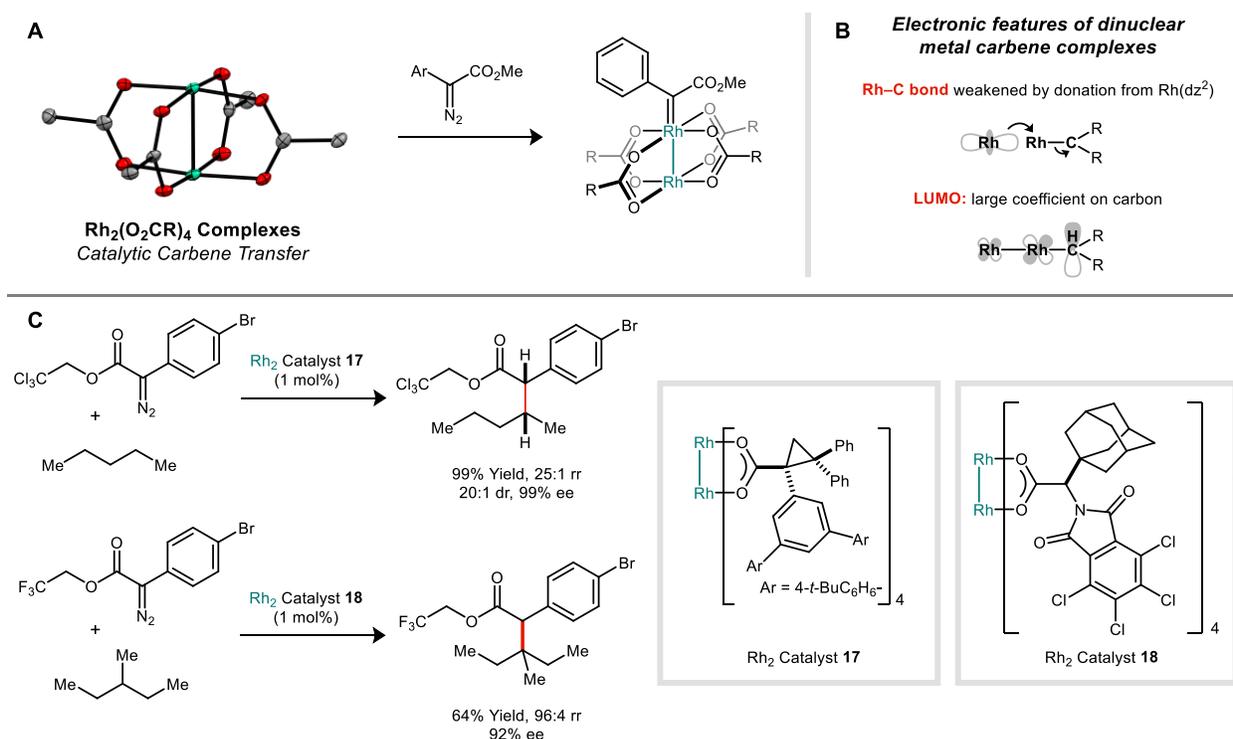


Figure 3.5. (A) Formation of Rh₂ carbene complexes using Rh₂ tetracarboxylate catalysts. (B) Rh₂ carbenes are highly reactive due to three-centered σ - and π -bonding interactions.^{9,51} (C) Regio- and stereoselective C–H insertion reactions using chiral Rh₂ catalysts.^{52,53}

At the time of its initial discovery, there was little understanding of how the dinuclear nature of the Rh₂(O₂CR)₄ catalysts contributed to their remarkable reactivity. However, this question has recently been addressed using modern experimental and computational techniques. In 2013, Davies and Berry obtained direct spectroscopic data on an authentic donor–acceptor carbene bound to Rh₂.⁵⁴ This work was quickly followed by the first crystallographic structure of a Rh₂ donor–acceptor carbene complex reported by Fürstner.⁵⁵ These data, combined with DFT modeling studies, have suggested two electronic factors that contribute to the high reactivity of

Rh₂ carbenes (Figure 3.5b).^{9,51} First, σ -bonding in the linear Rh–Rh–CR₂ fragment is a net three-centered/four-electron interaction, which has the effect of substantially weakening the Rh–CR₂ bond. This phenomenon can be viewed as a type of *trans* influence, where the high-energy dz² orbital of the second Rh donates into the Rh–CR₂ σ^* . Second, the LUMO of the Rh–Rh–CR₂ is a three-centered π^* orbital that is highly polarized toward carbon. This polarization causes the carbon to be electrophilic in character, facilitating its interaction with C–H σ -bonds. While it may be feasible to access similarly electrophilic M=CR₂ species using mononuclear catalysts, the weakening of the Rh–C σ -bond and the high LUMO coefficient on C are electronic features that are specifically conferred by the dinuclear nature of Rh₂ catalysts.

The high reactivity of Rh₂ carbenes provides a powerful platform for the development of selective C–H bond insertion reactions (Figure 3.5c). For example, Davies described the use of a hindered chiral catalyst to carry out regioselective insertions of carbenes into the more accessible secondary carbon of n-pentane.⁵² The reaction proceeds with high diastereo- and enantioselectivity due to the highly engineered binding pocket of the catalyst. By decreasing the steric profile of the catalyst, more electrophilic tertiary carbons could be selectively targeted, again with high levels of stereocontrol.⁵³

3.7 Facile ligand exchange in Ru₂-catalyzed propargylic substitution reactions

Hidai and Nishibayashi have also observed a beneficial effect of a dinuclear catalyst in a series of propargylic substitution reactions that proceed through allenylidene intermediates.^{56,57} Metal-mediated propargylic substitutions have been extensively documented since the seminal work of Nicholas using Co₂(CO)₈ and a Lewis acid to activate propargylic ethers.⁵⁸ However, rendering these processes catalytic has proven to be difficult due to the requirement for an oxidative demetallation step to release the product from the dicobalt complex. In 2000, Hidai and Nishibayashi demonstrated a catalytic substitution reaction of propargyl alcohols using simple alcohols as nucleophiles (Figure 3.6a).⁵⁶ The catalyst was the dinuclear Ru₂ complex **19**, which was shown to react stoichiometrically with terminal alkynes to generate allenylidene species **20**.^{59,60} The proposed mechanism involves a sequence of vinylidene formation, via a 1,2-hydrogen atom shift, followed by dehydration. Notably, when monoruthenium complexes were

examined as catalysts, none were found to be active, despite their similar ability to convert alkynes into metal allenylidenes.

Hidai's studies suggest that whereas a single Ru site may be capable of mediating the stoichiometric steps of a propargylic substitution, the intermediates of this process do not fall at appropriate relative energies to promote facile catalytic turnover. To provide insight into the role of the metal–metal interaction in achieving efficient catalysis, Nakamura reported a computational study on the mechanism of substitution (Figure 3.6b).⁶¹ The calculated pathway was shown to be akin to the mechanism of Rh₂ carbene transfer reactions in the sense that one metal center bears the carbene, while the second metal acts as a supporting metallaligand. In the case of Ru₂-catalyzed substitution reactions, the Ru–Ru bond was proposed to stabilize the coordinatively unsaturated intermediate that forms when the product alkyne dissociates. Additionally, calculations suggested that the supporting Ru withdraws electron density from the active Ru, decreasing its back-bonding ability and accelerating the rearrangement of the alkyne to a metal vinylidene.

Many other catalysts have since been demonstrated to promote propargylic substitution reactions. However, the Ru₂-catalyzed process remains unusual in the breadth of its nucleophile scope.⁵⁷ A variety of simple heteroatom nucleophiles, such as alcohols, anilines, amides, and thiols are viable. In addition, carbon nucleophiles, such as simple ketones, undergo substitution even in the absence of an added base. π -Nucleophiles such as electron-rich arenes and simple alkenes also provide substitution products in high yield. Intramolecular variants of these processes provide access to polycyclic structures. Finally, highly enantioselective propargylic substitutions were carried out using Ru₂ catalysts bearing chiral thiolate ligands (Figure 3.6c). Enantioselectivities in the >90% ee range were demonstrated in both inter- and intramolecular reactions.⁶²⁻⁶⁴

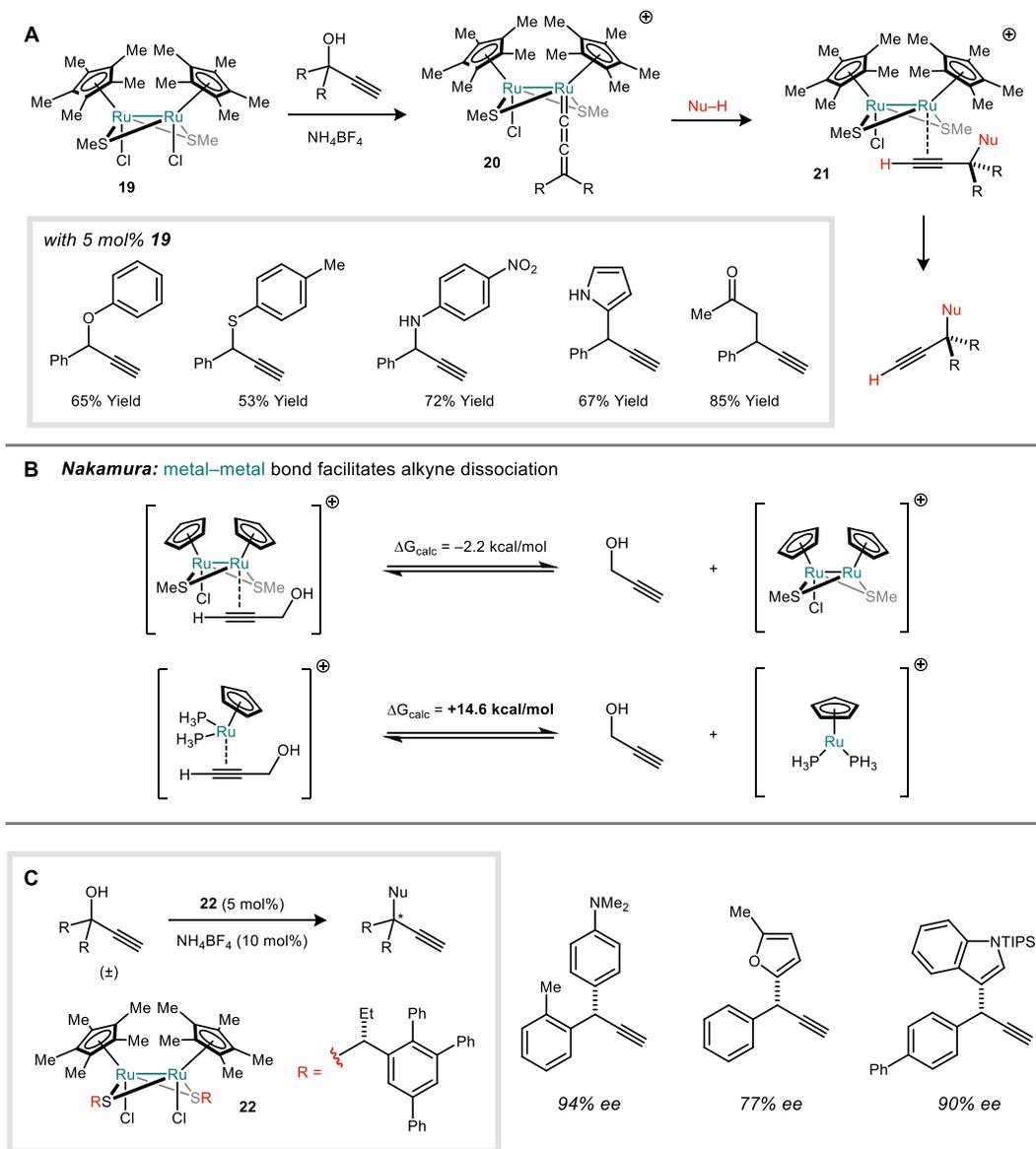


Figure 3.6. (A) Ru_2 catalysts for the substitution reactions of propargylic alcohols.⁵⁶ (B) Ru – Ru interaction facilitates ligand substitution by stabilizing the low-coordinate state.⁶¹ (C) Catalytic asymmetric propargylic substitutions using chiral Ru_2 catalysts.⁶²

3.8 Concluding remarks

There are now several documented examples of catalytic processes in which the formation of a metal–metal bonded dimer either inhibits turnover or leads to irreversible catalyst deactivation.^{12,15,22} In these cases, designing new sterically hindered ligands that impede dimerization may present future avenues to rationally improve catalytic efficiency. More

tantalizing are the few cases in which metal–metal bonding confers a uniquely beneficial effect that is challenging, or perhaps impossible, to replicate using a single transition metal.

Early examples of catalytically active metal–metal bonds were discovered serendipitously, without regard for how the metal–metal interaction might impact catalysis. Such is the case with Rh₂ tetracarboxylates, which were identified nearly half a century ago as being superior to other classes of mononuclear carbene transfer catalysts in certain C–H functionalization reactions.⁴⁶ It was not until many decades later that modern experimental data and theoretical models have shed light on these empirical observations.^{9,51,54,55} In parallel with these advances, metal–metal bonded species are increasingly being identified from reactions, whose accepted mechanisms only involve mononuclear complexes. These cases appear to be particularly common in the Ni triad, where a catalyst can be diverted from a M(II)/M(0) cycle by a comproportionation process that forms a M(I)–M(I) dimer.¹⁷ A future goal in this field will be to take the mechanistic insights gleaned from these case studies to rationally design multinuclear catalysts that can capitalize on the delocalized electronic structure of metal–metal bonds.

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APPENDIX A. SUPPORTING INFORMATION FOR CHAPTER 2

1. General Information

General considerations. Solvents were degassed and stored over activated 3 Å molecular sieves prior to use. Commercially available anhydrous *N,N*-dimethylacetamide (DMA) subjected to additional drying over activated 3 Å molecular sieves prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, and stored over activated 3 Å molecular sieves. All other reagents and starting materials were purchased from commercial vendors and used without further purification unless otherwise noted. Liquid reagents were degassed and stored over activated 3 Å molecular sieves prior to use. Zn powder (325 mesh, 99.9%) was purchased from Strem Chemicals, stored under inert atmosphere, and used without further purification. The [ⁱPrNDI]Ni₂(C₆H₆) complex was prepared according to previously reported procedures.¹ The Ni(Ph,Me-acac)₂² and Ni(Ph₂-acac)₂³ complexes were prepared according to previously reported procedures.

Physical methods. ¹H, ¹⁹F and ¹³C{¹H} NMR spectra were collected at room temperature on a Varian INOVA 300 MHz or a Bruker AV-III-800 NMR spectrometer. ¹H and ¹³C{¹H} NMR spectra are reported in parts per million relative to tetramethylsilane, using the residual solvent resonances as an internal standard. High-resolution mass data were obtained using a Thermo Scientific LTQ Orbitrap XL mass spectrometer or a Thermo Electron Corporation MAT 95XP-Trap mass spectrometer. ATR-IR data were collected on a Thermo Scientific Nicolet Nexus spectrometer containing a MCT* detector and KBr beam splitter with a range of 350–7400 cm⁻¹.

X-Ray Crystallography. Single crystals of **4** were coated with Fomblin oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon100 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073$ Å) at 150 K. Single crystals of **23** were also coated with Fomblin oil and quickly transferred to the goniometer

head of a Bruker Quest diffractometer with kappa geometry, an I- μ -S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon2 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at 150 K.

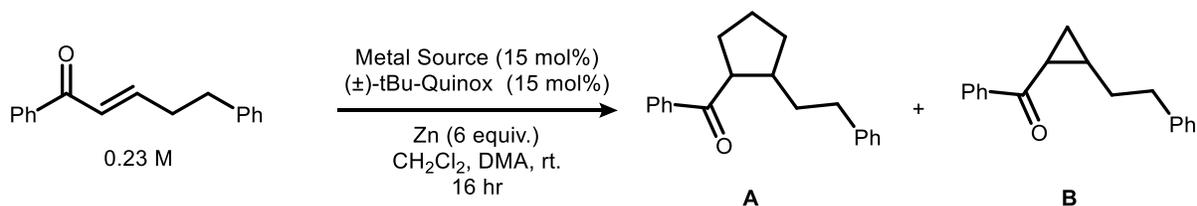
For both, data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3.⁴ The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs and refined by full matrix least squares against F² with all reflections using Shelxl2018 using the graphical interface Shelxle.⁵⁻⁹ If not specified otherwise H atoms attached to carbon and nitrogen atoms and hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 \AA for and aromatic C-H, 1.00, 0.99 and 0.98 \AA for aliphatic C-H, CH₂ and CH₃ moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{\text{iso}}(\text{H})$ values were set to a multiple of $U_{\text{eq}}(\text{C})$ with 1.5 for CH₃, and 1.2 for C-H units, respectively. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1854302–1854303 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In the structure of **4**, a toluene molecule was refined as three fold disordered. The benzene rings were constrained to resemble ideal hexagons with C-C bond distances of 1.39 \AA . The three disordered moieties were restrained to have similar geometries. U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 \AA were restrained to be similar. Subject to these conditions the occupancy rates refined to 0.485(3), 0.342(3) and 0.173(3).

2. Reaction Optimization Studies

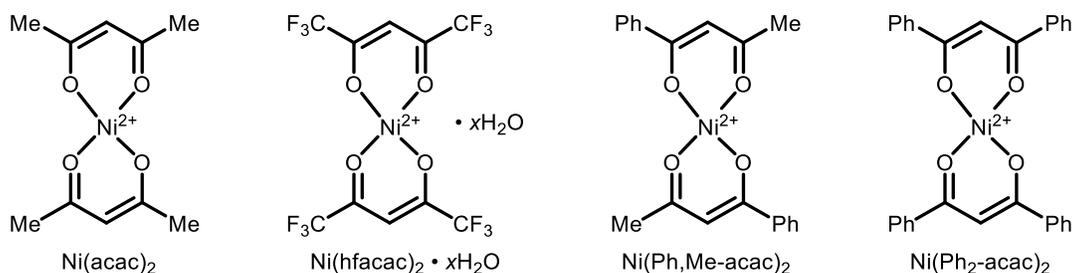
General Procedure for metal source comparison study. In an N₂-filled glovebox, a 5-mL vial was charged with the metal source, (0.01 mmol, 0.15 equiv), (\pm)-*t*-Bu-Quinox **L10** (2.62 mg, 0.01 mmol, 0.15 equiv), Zn Powder (27 mg, 0.41 mmol, 6 equiv), and a magnetic stir bar. A solution of (*E*)-1,5-diphenylpent-2-en-1-one (**1**) (0.3 mL of a 0.23 M stock solution in 1.25:1 CH₂Cl₂:DMA containing 0.24 M mesitylene, 0.07 mmol, 1.0 equiv) was added. The reaction was

stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and diluted with CH₂Cl₂. An aliquot was analyzed by GC.

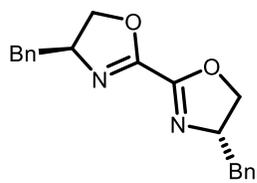


Entry	Metal Source	Conversion	Yield A	Yield B
1	Ni(acac) ₂	95%	70%	12%
2	Ni(DME)Br ₂	85%	42%	21%
3	Ni(DME)Cl ₂	93%	31%	13%
4	Ni(hfacac) ₂ · xH ₂ O	24%	0%	18%
5	Ni(Ph,Me-acac) ₂	95%	66%	10%
6	Ni(Ph ₂ -acac) ₂	95%	70%	12%
7	Ni(COD) ₂	77%	23%	36%
8	Ni(PPh ₃) ₂ Cl ₂	85%	24%	41%
9	Co(DME)Br ₂	51%	0%	12%
10	Fe(acac) ₂	46%	0%	0%
11	Cu(acac) ₂	< 1%	0%	0%
12	NiI ₂	83%	9%	19%
13 ^a	NiI ₂	92%	< 1%	17%
14 ^a	[ⁱ Pr ⁺ NDI]Ni ₂ (C ₆ H ₆)	86%	8%	39%

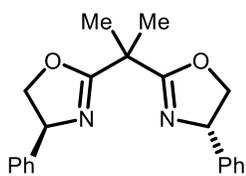
^aNo **L10** was added to the reaction



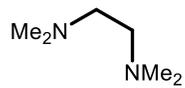
General Procedure for ligand comparison study. In an N₂-filled glovebox, a 5-mL vial was charged with Ni(acac)₂ (2.65 mg, 0.01 mmol, 0.15 equiv), ligand (0.01 mmol, 0.15 equiv), Zn powder (27 mg, 0.41 mmol, 6.0 equiv), and a magnetic stir bar. A solution of (*E*)-1,5-



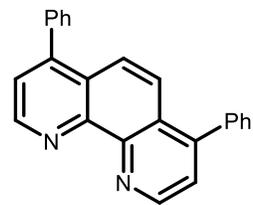
L1



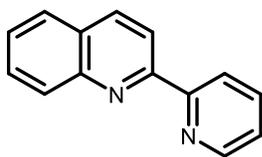
L2



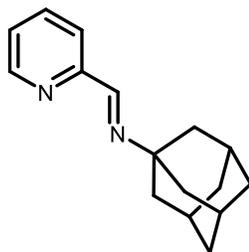
L3



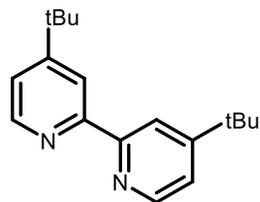
L4



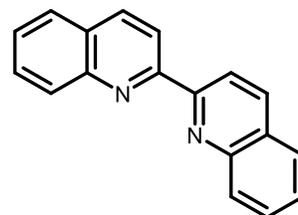
L5



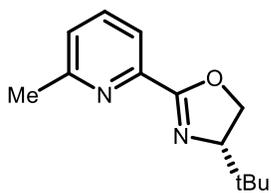
L6



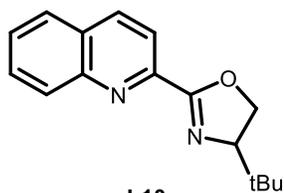
L7



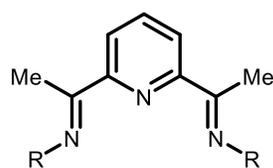
L8



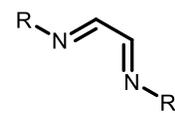
L9



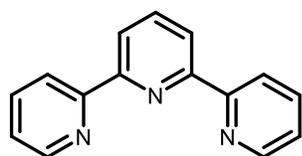
L10



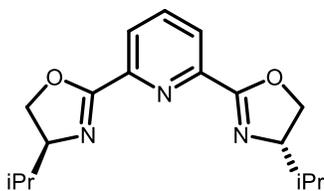
L11



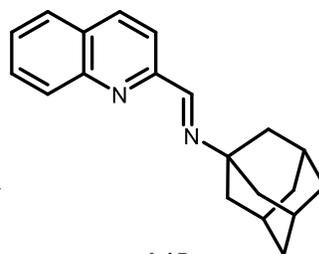
L12 R = 2,6-iPr₂-Ph



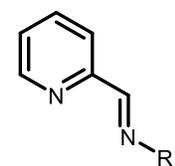
L13



L14

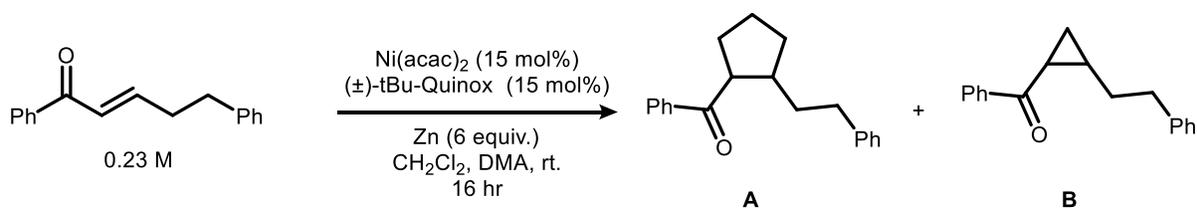


L15



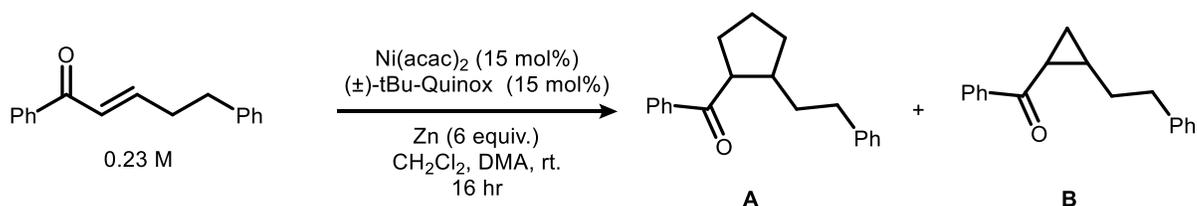
L16 R = 2,6-iPr₂-Ph

General Procedure for control experiments. In an N₂-filled glovebox, a 5-mL vial was charged with Ni(acac)₂ (2.65 mg, 0.01 mmol, 0.15 equiv), (±)-*t*-Bu-Quinox **L10** (2.62 mg, 0.01 mmol, 0.15 equiv), Zn Powder (27 mg, 0.41 mmol, 6 equiv), and a magnetic stir bar. A solution of (*E*)-1,5-diphenylpent-2-en-1-one (**1**) (0.3 mL of a 0.23 M stock solution in 1.25:1 CH₂Cl₂:DMA containing 0.24 M mesitylene, 0.07 mmol, 1.0 equiv) was added. The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, exposed to ambient atmosphere, and diluted with CH₂Cl₂. An aliquot was used for GC analysis.



Entry	Deviation from Standard Conditions	Conversion	Yield A	Yield B
1	None	95%	70%	12%
2	No Ni(acac) ₂ was added	0%	0%	0%
3	No (±)- <i>t</i> Bu-Quinox was added	10%	0%	0%
4	No Zn was added	0%	0%	0%
5	No DMA was added	11%	0%	0%

General Procedure for CH₂Cl₂ equivalence study. In an N₂-filled glovebox, a 5-mL vial was charged with Ni(acac)₂ (3.98 mg, 0.015 mmol, 0.15 equiv), (±)-*t*-Bu-Quinox **L10** (3.94 mg, 0.015 mmol, 0.15 equiv), Zn Powder (40.5 mg, 0.60 mmol, 6 equiv), and a magnetic stir bar. A solution of (*E*)-1,5-diphenylpent-2-en-1-one (**1**) (24.4 mg, 0.10 mmol, 1.0 equiv.) and mesitylene (12.5 μL) in DCM (X μL) was added. The reaction mixture was diluted up to 0.45 mL with DMA (Y μL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, exposed to ambient atmosphere, and diluted with CH₂Cl₂. An aliquot was used for GC analysis.



Entry	X	Y	Conversion	Yield A	Yield B
1	19.7 μL (3.0 equiv.)	430.2 μL	77%	33%	9%
2	62.5 μL (9.5 equiv.)	387.5 μL	70%	34%	13%
3	125 μL (19 equiv.)	325 μL	72%	38%	14%
4	250 μL (38 equiv.)	200 μL	96%	70%	14%

Under suboptimal reaction conditions, masses corresponding to the enone bearing 1, 2, 3, and 4 additional CH₂ equivalents were detected by GC/MS analysis using (*E*)-chalcone as a substrate.

Procedure for characterization of the crude product mixture profile. In an N₂-filled glovebox, a 5-mL vial was charged with Ni(DME)Br₂ (3.18 mg, 0.01 mmol, 0.05 equiv), (±)-*t*-Bu-Quinox **L10** (3.14 mg, 0.012 mmol, 0.06 equiv), Zn Powder (67.5 mg, 1.0 mmol, 5.0 equiv), and a magnetic stir bar. A solution of (*E*)-chalcone (43.0 mg, 0.21 mmol, 1.0 equiv.) in DCM (0.5 mL) and DMA (50 μL) was added. The reaction was stirred at room temperature. After 16 h,

the crude reaction mixture was removed from the glovebox, exposed to ambient atmosphere, and diluted with CH₂Cl₂. An aliquot was used for GC/MS analysis.

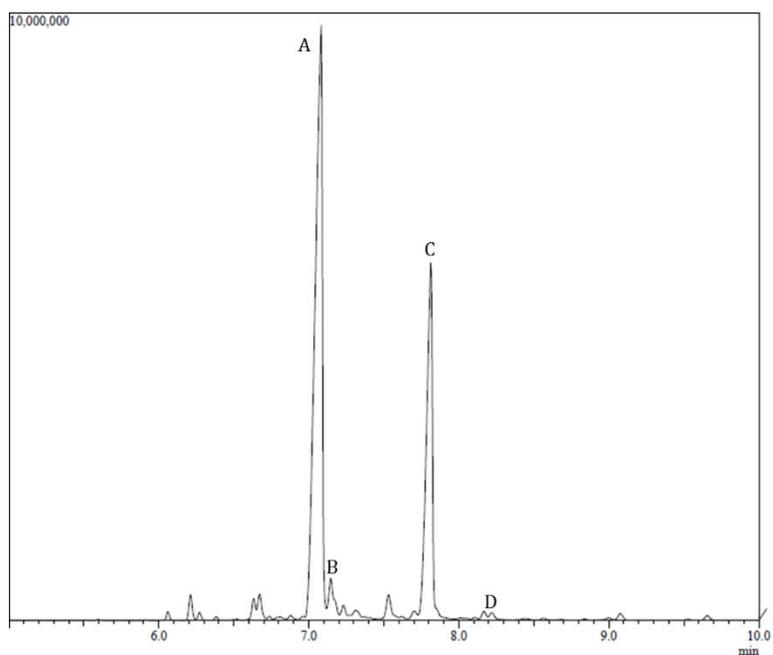
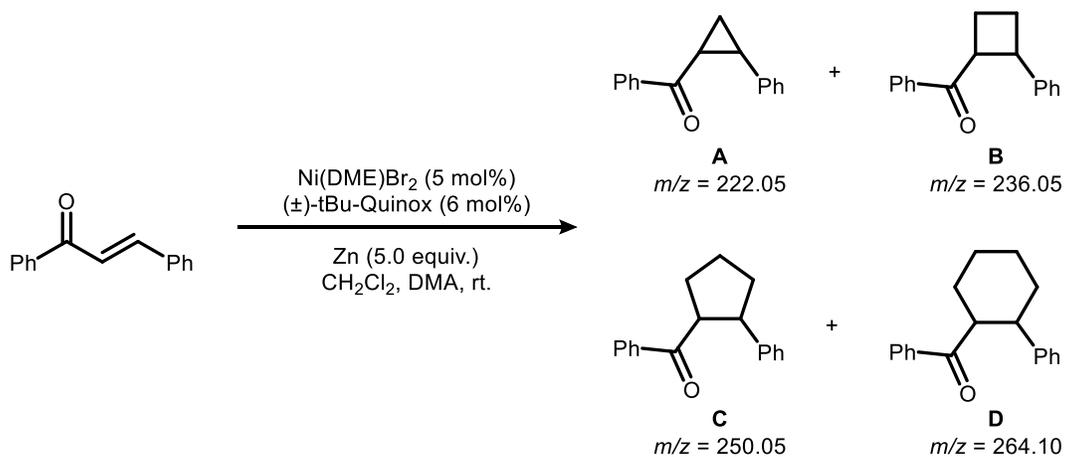
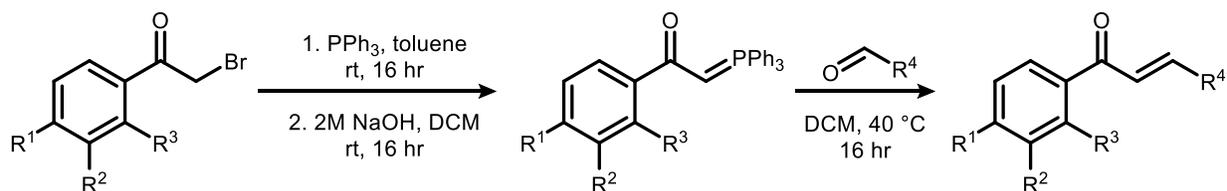


Figure S1. GC/MS spectrum of the crude reaction mixture using (*E*)-chalcone.

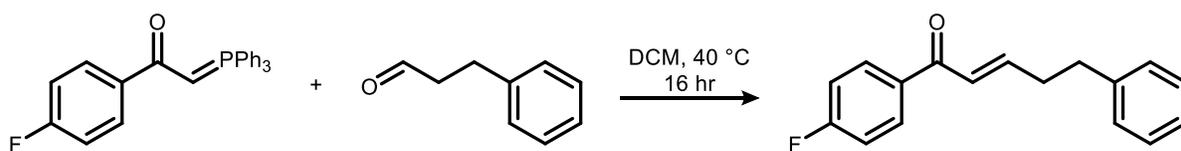
Peak	Ret. Time	<i>m/z</i>
A	7.033 min	222.05
B	7.233 min	236.05
C	7.792 min	250.05
D	8.167 min	264.10

3. Synthesis and Characterization of Enone Substrates



General procedure for the synthesis of Wittig reagents. A round-bottom flask was charged with a magnetic stir bar, the appropriate bromoketone (1 equiv) and toluene (1 M). A solution of PPh_3 (1 equiv) in toluene (0.5 M) was added dropwise. After 16 h, the precipitated triphenylphosphonium bromide salt was isolated by filtration, washed with Et_2O , and dried under vacuum. The crude triphenylphosphonium bromide salt was dissolved in CH_2Cl_2 (1 M), and 2 M aqueous NaOH (1 equiv) was added. After stirring for 16 h, the phases were separated, and the aqueous phase was extracted 3x with CH_2Cl_2 . The combined organic phases were dried over MgSO_4 and filtered. The filtrate was evaporated to dryness under reduced pressure to provide the ylide as a solid, which was carried forward without purification.

General procedure for the synthesis of enone substrates. A round-bottom flask was charged with a stir bar, the Wittig reagent (2 equiv), the aldehyde (1 equiv), and CH_2Cl_2 (0.5 M). The mixture was heated at reflux. After 16 h, the crude reaction mixture was concentrated under reduced pressure. The residue was loaded directly onto a SiO_2 column for purification.



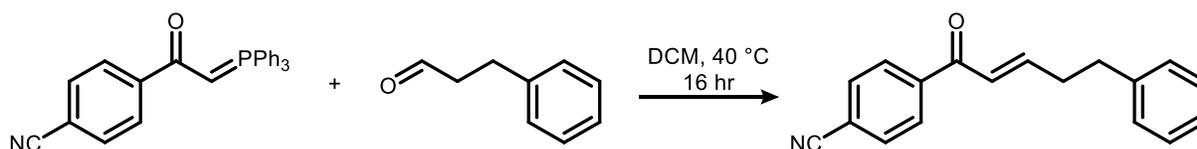
(E)-1-(4-fluorophenyl)-5-phenylpent-2-en-1-one (S1). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (500 mg, 3.72 mmol, 1.0 equiv) and 4-fluorophenacyltriphenylphosphorane (2.96 g, 7.44 mmol, 2.0 equiv). Purification by column chromatography (SiO_2 , 10% EtOAc in hexanes) provided (E)-1-(4-fluorophenyl)-5-phenylpent-2-en-1-one as a colorless oil (662 mg, 70% yield).

^1H NMR (300 MHz, CDCl_3) δ 8.00 – 7.85 (m, 2H), 7.37 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 7.17 – 7.10 (m, 2H), 7.10 – 7.02 (m, 1H), 6.83 (dq, $J = 15.4, 1.3$ Hz, 1H), 2.86 (t, $J = 7.6$ Hz, 2H), 2.74 – 2.57 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 189.14, 165.53 (d, $^1J_{\text{CF}} = 254.3$ Hz), 148.57, 140.73, 134.18 (d, $^4J_{\text{CF}} = 3.0$ Hz), 131.12 (d, $^3J_{\text{CF}} = 9.2$ Hz), 128.53, 128.42, 126.23, 126.18, 115.61 (d, $^2J_{\text{CF}} = 21.7$ Hz), 34.50, 34.48.

^{19}F NMR (282 MHz, CDCl_3) δ -107.36.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{15}\text{FO}$: 255.1178; found: 255.1177

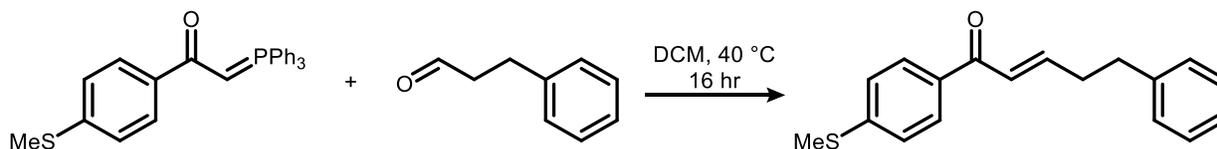


(E)-4-(5-phenylpent-2-enyl)benzonitrile (S2). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (473 mg, 3.52 mmol, 1.0 equiv) and 4-cyanophenacyltriphenylphosphorane (2.85 g, 7.04 mmol, 2.0 equiv). Purification by column chromatography (SiO_2 , 10% EtOAc in hexanes) provided (E)-4-(5-phenylpent-2-enyl)benzonitrile as a white solid (561 mg, 61 % yield).

^1H NMR (300 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.32 (dd, $J = 7.9, 6.4$ Hz, 2H), 7.24 – 7.16 (m, 3H), 7.15 – 7.03 (m, 1H), 6.79 (dt, $J = 15.5, 1.5$ Hz, 1H), 2.86 (t, $J = 7.5$ Hz, 2H), 2.67 (td, $J = 8.3, 7.9, 6.2$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 189.51, 150.57, 141.10, 140.48, 132.41, 128.93, 128.60, 128.42, 126.35, 126.04, 118.09, 115.84, 34.62, 34.34.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{16}\text{NO}$: 262.1226; found: 262.1229



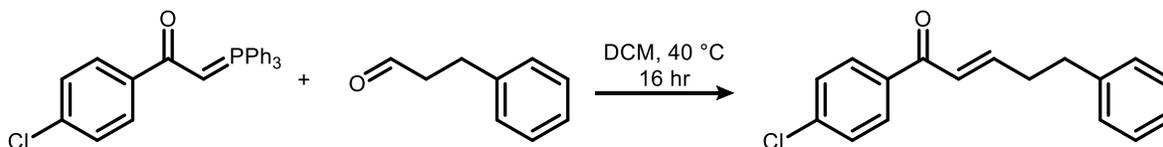
(E)-1-(4-(methylthio)phenyl)-5-phenylpent-2-en-1-one (S3). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (539

mg, 4.02 mmol, 1.0 equiv) and 4-(methylthio)phenacyltriphenylphosphorane (3.43 g, 8.04 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 10% EtOAc in hexanes) provided (*E*)-1-(4-(methylthio)phenyl)-5-phenylpent-2-en-1-one (3) as a yellow solid (851 mg, 81% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.85 – 7.76 (m, 2H), 7.35 – 7.27 (m, 3H), 7.25 – 7.18 (m, 4H), 7.08 (dt, *J* = 15.3, 6.7 Hz, 1H), 6.90 – 6.79 (m, 1H), 2.85 (t, *J* = 7.7 Hz, 2H), 2.64 (q, *J* = 7.8, 7.3, 7.3 Hz, 2H), 2.53 (s, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 189.51, 147.96, 145.43, 140.84, 134.11, 128.98, 128.51, 128.42, 126.19, 125.03, 34.54, 34.53, 14.84.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₁₈OS: 283.1151; found: 283.1155

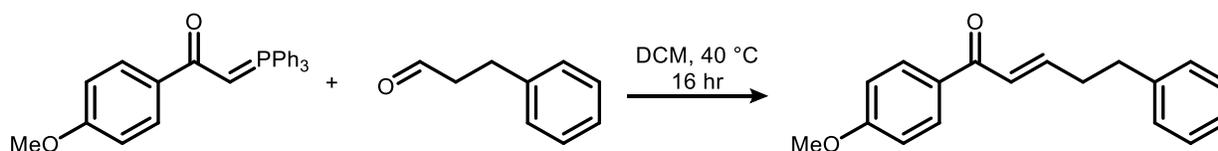


(*E*)-1-(4-chlorophenyl)-5-phenylpent-2-en-1-one (S4). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (300 mg, 2.23 mmol, 1.0 equiv) and 4-chlorophenacyltriphenylphosphorane (1.87 g, 4.47 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 8% EtOAc in hexanes) provided (*E*)-1-(4-chlorophenyl)-5-phenylpent-2-en-1-one as a yellow oil (278 mg, 46% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.86 – 7.78 (m, 2H), 7.47 – 7.39 (m, 2H), 7.36 – 7.29 (m, 2H), 7.25 – 7.18 (m, 3H), 7.15 – 7.02 (m, 1H), 6.82 (dtd, *J* = 15.4, 1.5, 0.7 Hz, 1H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.72 – 2.55 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 189.49, 148.94, 140.69, 139.08, 136.16, 129.96, 128.82, 128.54, 128.41, 126.25, 126.15, 34.52, 34.46.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₇H₁₅ClO: 271.0084; found: 271.0086

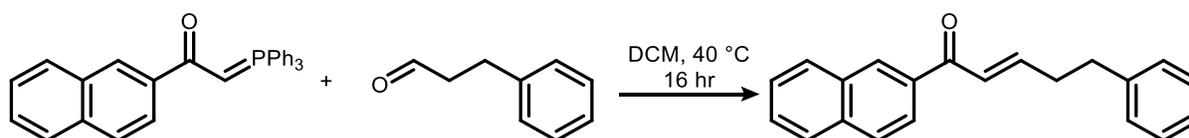


(E)-1-(4-methoxyphenyl)-5-phenylpent-2-en-1-one (S5). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (435 mg, 3.25 mmol, 1.0 equiv) and 4-methoxyphenacyltriphenylphosphorane (2.67 g, 6.50 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 10% EtOAc in hexanes) provided (E)-1-(4-methoxyphenyl)-5-phenylpent-2-en-1-one as a yellow oil (761 mg, 88% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.81 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.17 (m, 3H), 7.07 (dt, *J* = 15.3, 6.8 Hz, 1H), 6.98 – 6.82 (m, 3H), 3.88 (s, 3H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.73 – 2.54 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 189.05, 163.31, 147.32, 140.93, 130.84, 130.76, 128.50, 128.42, 126.21, 126.16, 113.73, 55.47, 34.59, 34.51.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₁₈O₂: 267.1380; found: 267.1382

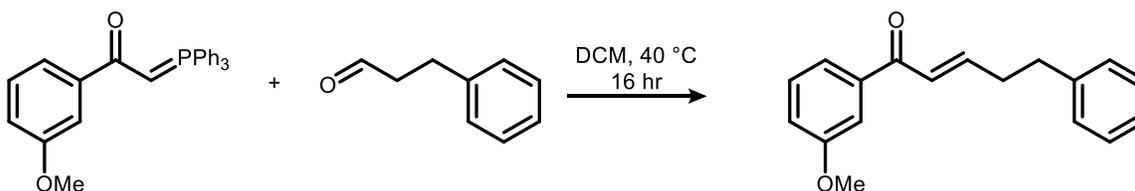


(E)-1-(naphthalen-2-yl)-5-phenylpent-2-en-1-one (S6). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (500 mg, 3.72 mmol, 1.0 equiv) and [(*p*-naphthylbenzyl)methylene]triphenylphosphorane (2.13 g, 7.44 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 10% EtOAc in hexanes) provided (E)-1-(naphthalen-2-yl)-5-phenylpent-2-en-1-one as a yellow solid (887 mg, 83% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.37 (s, 1H), 8.05 – 7.85 (m, 4H), 7.65 – 7.52 (m, 2H), 7.37 – 7.29 (m, 2H), 7.24 (dd, *J* = 5.9, 2.4 Hz, 3H), 7.19 – 7.09 (m, 1H), 7.02 (dt, *J* = 15.4, 1.2 Hz, 1H), 2.90 (dd, *J* = 8.6, 6.6 Hz, 2H), 2.77 – 2.61 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 190.62, 148.27, 140.86, 135.43, 135.20, 132.51, 130.03, 129.47, 128.54, 128.46, 128.45, 128.31, 127.80, 126.71, 126.62, 126.22, 124.52, 34.57.

HRMS(ESI) (*m/z*): [M + Na]⁺ Calcd for C₂₁H₁₈O: 309.1250; found: 309.1252

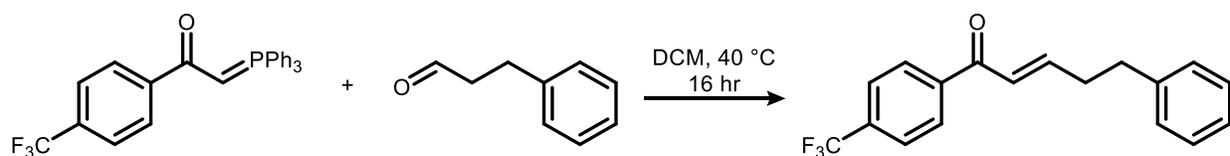


(E)-1-(3-methoxyphenyl)-5-phenylpent-2-en-1-one (S7). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (435 mg, 3.25 mmol, 1.0 equiv) and 3-methoxyphenacyltriphenylphosphorane (2.67 g, 6.50 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 5% Et₂O in hexanes) provided (E)-1-(3-methoxyphenyl)-5-phenylpent-2-en-1-one as a yellow oil (383 mg, 44 % yield).

¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.40 (m, 2H), 7.40 – 7.27 (m, 3H), 7.25 – 7.17 (m, 3H), 7.15 – 7.02 (m, 2H), 6.85 (dt, *J* = 15.3, 1.4 Hz, 1H), 3.86 (s, 3H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.65 (td, *J* = 7.8, 6.2 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 190.54, 159.80, 148.46, 140.81, 139.27, 129.45, 128.52, 126.56, 126.20, 121.14, 119.23, 112.82, 55.46, 34.52, 34.50.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₁₈O₂: 267.1380; found: 267.1385



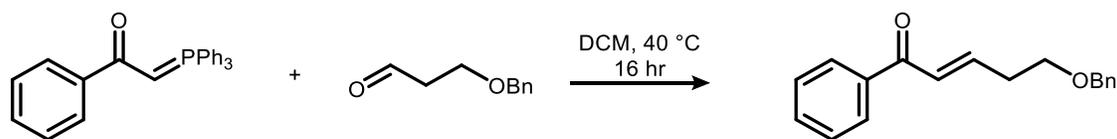
(E)-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-2-en-1-one (S8). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (500 mg, 3.72 mmol, 1.0 equiv) and 4-trifluoromethylphenacyltriphenylphosphorane (3.34 g, 7.44 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 5% Et₂O in hexanes) provided (E)-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-2-en-1-one as a white solid (691 mg, 61% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.24 – 7.19 (m, 3H), 7.10 (dt, *J* = 15.5, 6.8 Hz, 1H), 6.82 (dt, *J* = 15.5, 1.4 Hz, 1H), 2.87 (dd, *J* = 8.4, 6.7 Hz, 2H), 2.67 (dtt, *J* = 8.0, 6.8, 1.2 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 190.00, 150.00, 140.68, 140.60, 133.91 (q, ²*J*_{CF} = 32.6 Hz), 128.84, 128.59, 128.44, 126.33, 125.57 (q, ³*J*_{CF} = 3.8 Hz), 123.66 (q, ¹*J*_{CF} = 272.7 Hz), 34.61, 34.39.

¹⁹F NMR (282 MHz, CDCl₃) δ -64.57.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₁₅F₃O: 305.1148; found: 305.1145

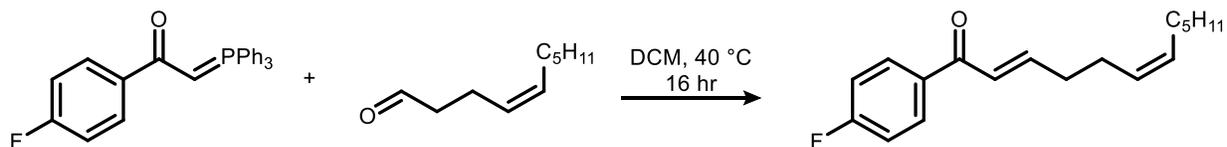


(E)-5-(benzyloxy)-1-phenylpent-2-en-1-one (S9). The reaction was conducted according to the general procedure without modification using 3-(benzyloxy)propanal¹⁰ (500 mg, 3.0 mmol, 1 equiv) and phenacyltriphenylphosphorane (2.31 g, 6.0 mmol, 2 equiv). Purification by column chromatography (SiO₂, 10% Et₂O in hexanes) provided (E)-5-(benzyloxy)-1-phenylpent-2-en-1-one as a colorless oil (720 mg, 89% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.84 (m, 2H), 7.60 – 7.51 (m, 1H), 7.51 – 7.42 (m, 2H), 7.37 – 7.26 (m, 5H), 7.14 – 7.00 (m, 1H), 7.00 – 6.90 (m, 1H), 4.55 (s, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.64 (qd, *J* = 6.4, 1.1 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 190.73, 146.06, 138.10, 137.85, 132.66, 128.59, 128.51, 128.45, 127.73, 127.72, 127.47, 73.14, 68.39, 33.25.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₁₈O₂: 267.1380; found: 267.1376



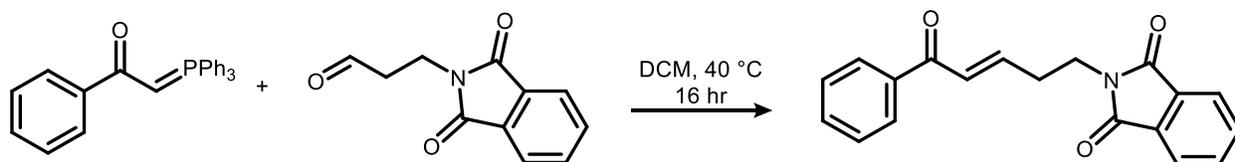
(2E,6Z)-1-(4-fluorophenyl)dodeca-2,6-dien-1-one (S10). The reaction was conducted according to the general procedure without modification using *cis*-4-decenal (573 mg, 3.72 mmol, 1.0 equiv) and 4-fluorophenyltriphenylphosphorane (2.96 g, 7.44 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 5% Et₂O in hexanes) provided (2E,6Z)-1-(4-fluorophenyl)dodeca-2,6-dien-1-one as a colorless oil (602 mg, 59 % yield).

¹H NMR (300 MHz, CDCl₃) δ 8.37 (s, 1H), 8.05 – 7.85 (m, 4H), 7.65 – 7.52 (m, 2H), 7.37 – 7.29 (m, 2H), 7.24 (dd, *J* = 5.9, 2.4 Hz, 3H), 7.19 – 7.09 (m, 1H), 7.02 (dt, *J* = 15.4, 1.2 Hz, 1H), 2.90 (dd, *J* = 8.6, 6.6 Hz, 2H), 2.77 – 2.61 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 189.17, 165.50 (d, $^1J_{\text{CF}} = 254.1$ Hz), 149.42, 134.29 (d, $^4J_{\text{CF}} = 3.0$ Hz), 131.46, 131.10 (d, $^3J_{\text{CF}} = 9.2$ Hz), 127.73, 125.78, 115.60 (d, $^2J_{\text{CF}} = 21.7$ Hz), 32.94, 31.51, 29.30, 27.28, 25.88, 22.56, 14.06.

^{19}F NMR (282 MHz, CDCl_3) δ -107.50.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{FO}$: 275.1806; found: 275.1812

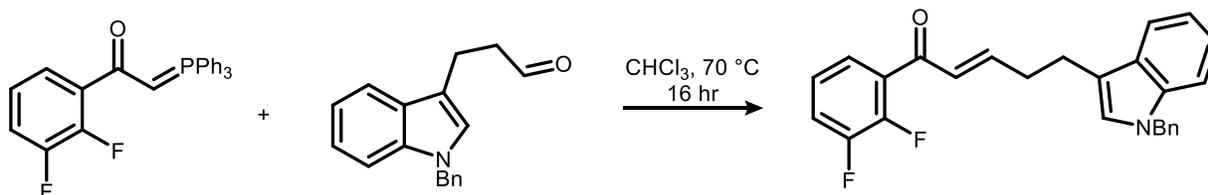


(E)-2-(5-oxo-5-phenylpent-3-en-1-yl)isoindoline-1,3-dione (S11). The reaction was conducted according to the general procedure without modification using 3-(1,3-dioxoisoindolin-2-yl)propanal (200 mg, 0.98 mmol, 1.0 equiv) and phenacyltriphenylphosphorane (897 mg, 1.96 mmol, 2.0 equiv). Purification by column chromatography (SiO_2 , 20% EtOAc in hexanes) provided (E)-2-(5-oxo-5-phenylpent-3-en-1-yl)isoindoline-1,3-dione as a white solid (252 mg, 84 % yield).

^1H NMR (300 MHz, CDCl_3) δ 7.95 – 7.81 (m, 4H), 7.73 (dt, $J = 5.2, 2.1$ Hz, 2H), 7.61 – 7.50 (m, 1H), 7.45 (tt, $J = 7.8, 1.2$ Hz, 2H), 7.07 – 6.85 (m, 2H), 3.92 (t, $J = 7.1$ Hz, 2H), 2.74 (q, $J = 6.9$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 190.40, 168.13, 144.34, 137.54, 134.08, 132.75, 131.96, 128.60, 128.53, 128.12, 123.35, 36.43, 31.68.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_3$: 306.1125; found: 306.1129



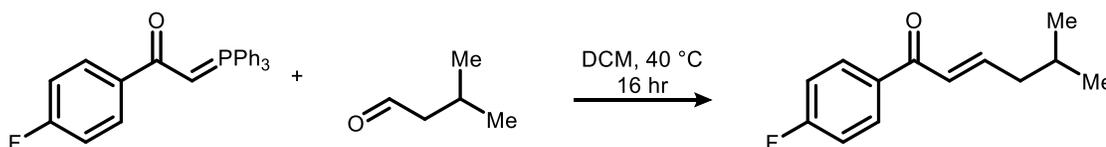
(E)-5-(1-benzyl-1H-indol-3-yl)-1-(2,3-difluorophenyl)pent-2-en-1-one (S12). The reaction was conducted according to the general procedure with the following modification:

CHCl₃ was used instead of CH₂Cl₂, and the reaction was heated at 70 °C for 16 h using 3-(1-benzyl-1H-indol-3-yl)propanal¹¹ (254 mg, 0.97 mmol, 1.0 equiv) and 2,3-difluorophenacyltriphenylphosphorane (1.21 g, 2.90 mmol, 3.0 equiv). Purification by column chromatography (SiO₂, 15% EtOAc in hexanes) provided (*E*)-5-(1-benzyl-1H-indol-3-yl)-1-(2,3-difluorophenyl)pent-2-en-1-one as a viscous dark-yellow oil (356 mg, 92% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.76 – 7.49 (m, 3H), 7.32 – 7.21 (m, 3H), 7.21 – 7.03 (m, 6H), 6.94 (s, 1H), 6.85 – 6.71 (m, 1H), 5.28 (s, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.75 (q, *J* = 7.1 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 153.31 (dd, *J* = 256.3, 12.9 Hz), 150.34 (dd, *J* = 250.6, 13.0 Hz), 150.33, 137.63, 136.74, 134.88, 128.75, 127.87, 127.59, 126.73, 125.75, 125.46, 121.93, 119.12, 118.97, 117.86 (dd, *J* = 17.6, 1.1 Hz), 117.44, 117.35, 114.19, 109.84, 49.88, 33.53, 23.92.

HRMS(ESI) (*m/z*): [M + H]⁺ C₂₆H₂₁F₂NO: 402.1664; found: 402.1661



(*E*)-1-(4-fluorophenyl)-5-methylhex-2-en-1-one (S13). The reaction was conducted according to the general procedure without modification using isovaleraldehyde (400 mg, 4.68 mmol, 1.0 equiv) and 4-fluorophenacyltriphenylphosphorane (3.7 g, 9.2 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 10% Et₂O in hexanes) provided (*E*)-1-(4-fluorophenyl)-5-methylhex-2-en-1-one as a light yellow oil (878 mg, 91 % yield).

¹H NMR (300 MHz, CDCl₃) δ 8.03 – 7.92 (m, 2H), 7.19 – 7.09 (m, 2H), 7.11 – 6.97 (m, 2H), 6.92 – 6.76 (m, 1H), 2.28 – 2.13 (m, 2H), 1.83 (dp, *J* = 13.3, 6.7 Hz, 1H), 0.96 (dd, *J* = 6.7, 0.5 Hz, 7H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 189.10, 165.49 (d, ¹*J*_{CF} = 254.0 Hz), 149.11, 134.33 (d, ⁴*J*_{CF} = 3.0 Hz), 131.08 (d, ³*J*_{CF} = 9.2 Hz), 126.50, 115.60 (d, ²*J*_{CF} = 21.8 Hz), 42.13, 28.00, 22.47.

¹⁹F NMR (282 MHz, CDCl₃) δ -107.55.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₃H₁₅FO: 207.1180; found: 207.1179

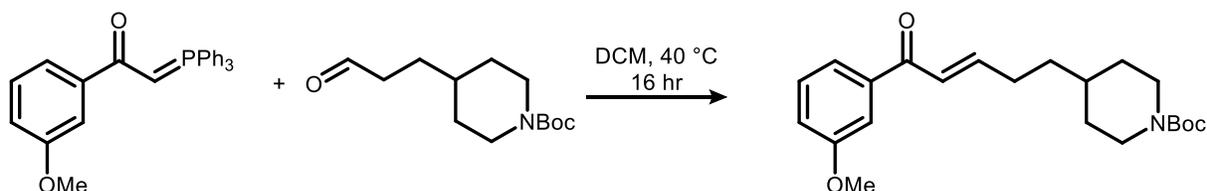


methyl (*E*)-8-(4-chlorophenyl)-8-oxooct-6-enoate (S14). The reaction was conducted according to the general procedure without modification using methyl-6-oxohexanoate (250 mg, 1.73 mmol, 1.0 equiv) and 4-chlorophenacyltriphenylphosphorane (1.44 g, 3.47 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 20% EtOAc in hexanes) provided methyl (*E*)-8-(4-chlorophenyl)-8-oxooct-6-enoate as a yellow oil (152 mg, 31% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.93 – 7.80 (m, 2H), 7.49 – 7.38 (m, 2H), 7.05 (dt, J = 15.3, 6.8 Hz, 1H), 6.85 (dt, J = 15.3, 1.4 Hz, 1H), 3.68 (s, 3H), 2.34 (qd, J = 6.8, 1.7 Hz, 4H), 1.78 – 1.64 (m, 2H), 1.57 (dq, J = 9.6, 6.8 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 189.41, 173.82, 149.64, 139.08, 136.20, 129.95, 128.85, 125.71, 51.58, 33.75, 32.46, 27.57, 24.48.

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C₁₅H₁₈ClO₃: 281.0939; found: 281.0937



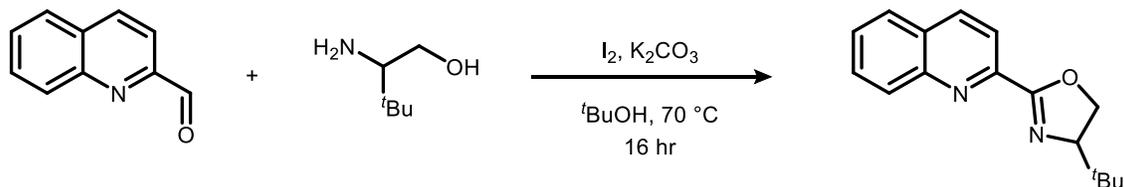
tert-butyl (*E*)-4-(5-(3-methoxyphenyl)-5-oxopent-3-en-1-yl)piperidine-1-carboxylate (S15). The reaction was conducted according to the general procedure without modification using tert-butyl 4-(3-oxopropyl)piperidine-1-carboxylate (250 mg, 1.03 mmol, 1.0 equiv) and 3-methoxyphenacyltriphenylphosphorane (850 mg, 2.07 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 20% EtOAc in hexanes) provided methyl (tert-butyl (*E*)-4-(5-(3-methoxyphenyl)-5-oxopent-3-en-1-yl)piperidine-1-carboxylate as a light yellow oil (339 mg, 88% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.52 – 7.44 (m, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.09 – 7.00 (m, 1H), 6.87 (dt, J = 15.3, 1.4 Hz, 1H), 4.11 (bs, 2H), 3.87 (s, 3H), 2.66 (q, J = 10.9, 8.9 Hz, 2H), 2.35 (q, J = 6.9 Hz, 2H), 1.68 (d, J = 12.8 Hz, 2H), 1.49 (s, 12H), 1.22 – 1.03 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 190.46, 159.82, 154.86, 149.56, 139.30, 129.48, 125.99, 121.08, 119.15, 112.91, 79.28, 77.22, 55.47, 35.54, 34.88, 29.91, 28.48.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{13}\text{NO}_4$: 374.2310; found: 374.2318

4. Synthesis of the (\pm)-*t*-Bu-Quinox ligand



(\pm)-*t*-Bu-Quinox (L10). To a 500 mL round bottom flask were added quinoline-2-carboxaldehyde (3.4 g, 21.7 mmol, 1 equiv.), *t*-BuOH (100 mL), (\pm)-*t*-leucinol (2.8 g, 23.9 mmol, 1.1 equiv) and a magnetic stir bar. The mixture was stirred at 30 °C for 2 h under an N_2 atmosphere. K_2CO_3 (9.01 g, 65.2 mmol, 3.0 equiv) and I_2 (11.0 g, 43.5 mmol, 2.0 equiv) were added, and the mixture was heated at 70 °C for 16 h. After cooling to ambient temperature, the reaction mixture was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (~50 mL), which resulted in the solution turning from dark red to light yellow. Water was added (100 mL), and the solution was extracted with CH_2Cl_2 (5 x 100 mL). The combined organic phases were washed with brine (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude material was loaded directly onto a SiO_2 column for purification (15% EtOAc in hexanes), providing (\pm)-*t*-Bu-Quinox (3.92 g, 71% yield) as a white crystalline solid. The spectral data match those previously reported.¹²

1H NMR (300 MHz, $CDCl_3$) δ 8.32 – 8.19 (m, 3H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.76 (dd, $J = 8.3, 7.1$ Hz, 1H), 7.61 (dd, $J = 8.0, 6.9$ Hz, 1H), 4.55 (ddd, $J = 10.1, 8.7, 0.9$ Hz, 1H), 4.48 – 4.35 (m, 1H), 4.26 – 4.10 (m, 1H), 1.02 (s, 9H).

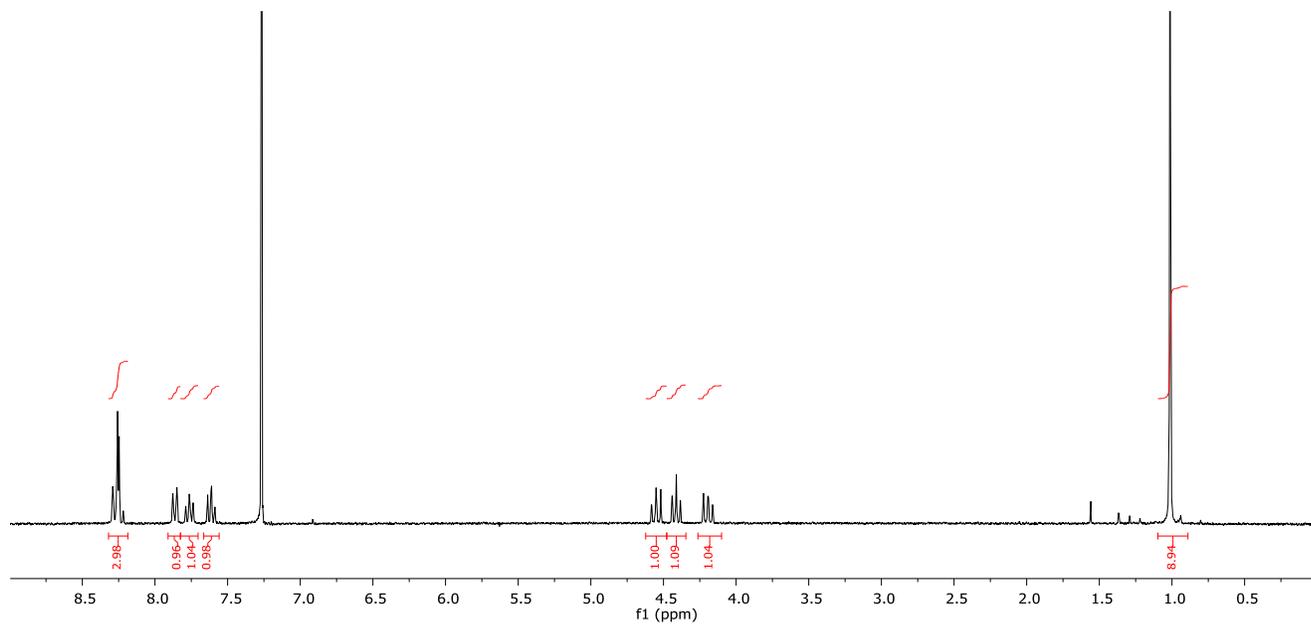
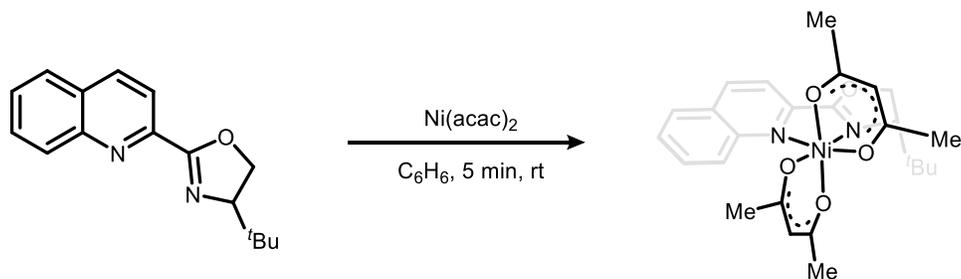


Figure S2. ^1H NMR of **L10** (CDCl_3 , 273K)

5. Synthesis of the (\pm)-(*t*-Bu-Quinox)Ni(acac)₂ Complex



(\pm)-(*t*-Bu-Quinox)Ni(acac)₂ (**4**). In an N₂-filled glovebox, a 5-mL vial was charged with (\pm)-*t*-Bu-Quinox (**L10**) (10.0 mg, 0.039 mmol, 1.0 equiv.), Ni(acac)₂ (10.1 mg, 0.039 mmol, 1.0 equiv.), C₆H₆ (1 mL) and a magnetic stir bar. An immediate color change to dark green was observed. After stirring for 5 min, the mixture was lyophilized to yield (\pm)-(*t*-Bu-Quinox)Ni(acac)₂ as a green solid (19.5 mg, 98% yield). Single crystals of **4** suitable for x-ray diffraction analysis were obtained by slow evaporation of a concentrated solution in toluene at room temperature. Complex **4** is NMR silent.

$$\mu_{\text{eff}} = 3.3 \mu_{\text{B}} \text{ (Evans method, 293 K, C}_6\text{D}_6\text{)}$$

Anal. Cald. for (C₃₆H₃₂N₂NiO₅): C 61.03, H 6.31, N 5.48; found: C 60.86, H 6.42, N 5.24.

UV-Vis-NIR (THF, nm {M⁻¹cm⁻¹}): 235 {60391}, 294 {41422}, 389 {sh}

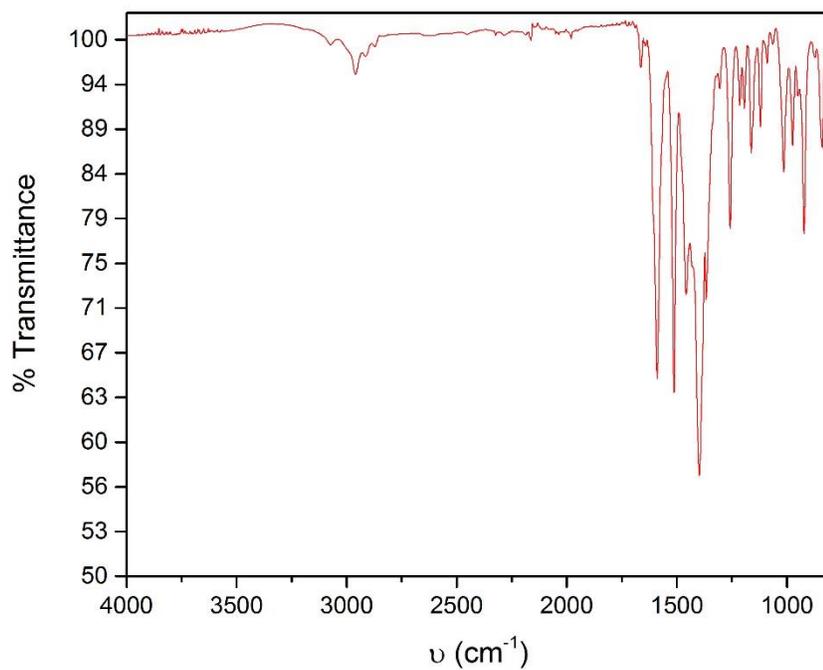


Figure S3. FT-IR of **4**.

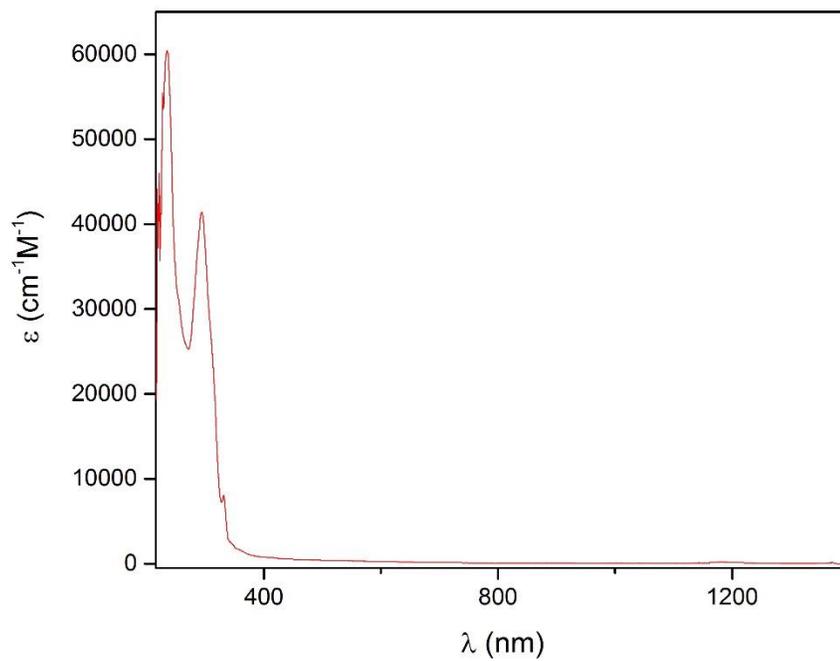
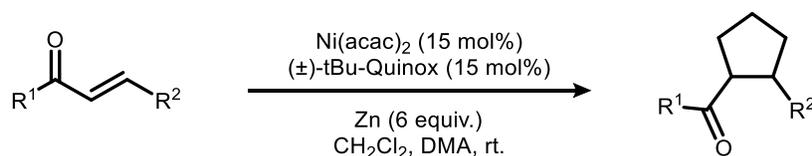


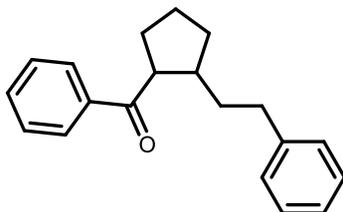
Figure S4. UV-Vis-NIR spectrum of **4** in THF (0.0078 mM).

6. Substrate Scope Studies and Cyclopentane Characterization



General Procedure for the synthesis of cyclopentanes from enones. In an N₂-filled glovebox, a 5-mL vial was charged with Ni(acac)₂ (7.9 mg, 0.031 mmol, 0.15 equiv), (±)-*t*-Bu-Quinox (**L10**) (7.9 mg, 0.031 mmol, 0.15 equiv), Zn powder (81 mg, 1.23 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of the substrate (0.21 mmol, 1.0 equiv) dissolved in CH₂Cl₂ (0.5 mL) and DMA (0.4 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and loaded directly onto a SiO₂ column for purification.

The ratios of C₅:C₃ were determined by ¹H NMR integration from aliquots of the crude reaction mixtures. Reported yields are of the purified cyclopentane product. In all cases, the products were isolated exclusively with the *trans* relative stereochemistry.



(2-phenethylcyclopentyl)(phenyl)methanone (3). The reaction was conducted according to the general procedure without modification using (*E*)-1,5-diphenylpent-2-en-1-one (**1**)¹³ (48.8 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 20% CH₂Cl₂ in hexanes).

Ratio of C₅ : C₃ = 5.8 : 1

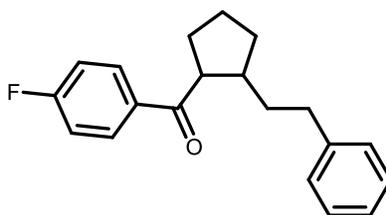
Run 1: 40.1 mg isolated (70% yield), yellow oil

Run 2: 40.7 mg isolated (71% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 8.08 – 7.83 (m, 2H), 7.61 – 7.50 (m, 1H), 7.49 – 7.38 (m, 2H), 7.26 – 7.19 (m, 2H), 7.14 (td, $J = 7.1, 6.5, 1.5$ Hz, 3H), 3.41 (ddd, $J = 11.0, 7.9, 6.0$ Hz, 1H), 2.77 – 2.39 (m, 3H), 2.07 (dddd, $J = 13.8, 12.1, 7.1, 3.2$ Hz, 2H), 1.87 – 1.49 (m, 5H), 1.46 – 1.30 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 203.12, 142.53, 137.35, 132.82, 128.57, 128.38, 128.28, 128.24, 125.66, 52.95, 42.86, 37.48, 35.03, 32.71, 31.78, 25.14.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: 279.1743; found: 279.1746



(4-fluorophenyl)(2-phenethylcyclopentyl)methanone (5). The reaction was conducted according to the general procedure without modification using (*E*)-1-(4-fluorophenyl)-5-phenylpent-2-en-1-one (**S1**) (52.5 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 0.5% Et_2O in hexanes).

Ratio of $\text{C}_5 : \text{C}_3 = 5.9 : 1$

Run 1: 43.3 mg isolated (71% yield), yellow oil

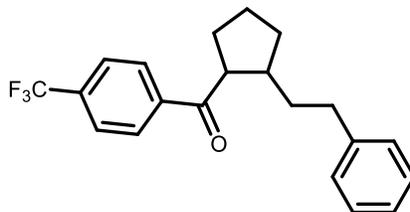
Run 2: 39.1 mg isolated (64% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 8.02 – 7.91 (m, 2H), 7.25 – 7.19 (m, 2H), 7.18 – 7.05 (m, 5H), 3.34 (q, $J = 8.0$ Hz, 1H), 2.58 (dddd, $J = 39.0, 14.7, 9.8, 5.6$ Hz, 3H), 2.15 – 1.95 (m, 2H), 1.71 (d, $J = 5.5$ Hz, 4H), 1.67 – 1.56 (m, 1H), 1.38 (dd, $J = 12.1, 8.1$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 201.45, 165.61 (d, $^1J_{\text{CF}} = 254.3$ Hz), 142.43, 133.69 (d, $^4J_{\text{CF}} = 3.0$ Hz), 130.96 (d, $^3J_{\text{CF}} = 9.3$ Hz), 128.29, 128.22, 125.70, 115.62 (d, $^2J_{\text{CF}} = 21.7$ Hz), 52.89, 42.84, 37.44, 35.00, 32.66, 31.73, 25.10.

^{19}F NMR (282 MHz, CDCl_3) δ -107.37.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{21}\text{FO}$: 297.1649; found: 297.1651



(2-phenethylcyclopentyl)(4-(trifluoromethyl)phenyl)methanone (6). The reaction was conducted according to the general procedure without modification using (*E*)-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-2-en-1-one (**S8**) (62.6 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 0.5% Et₂O in hexanes).

Ratio of C₅ : C₃ = 9.1 : 1

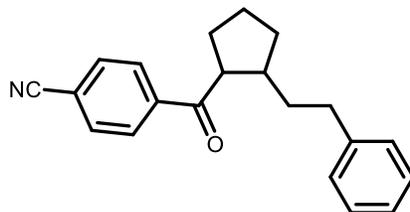
Run 1: 51.4 mg isolated (72% yield), yellow oil

Run 2: 49.9 mg isolated (70% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, *J* = 9.4 Hz, 2H), 7.73 (d, *J* = 9.4 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.18 – 7.05 (m, 3H), 3.37 (dd, *J* = 23.9, 7.5 Hz, 1H), 2.70 – 2.58 (m, 1H), 2.52 (ddd, *J* = 13.1, 10.3, 5.9 Hz, 2H), 2.20 – 1.90 (m, 2H), 1.86 – 1.56 (m, 5H), 1.46 – 1.33 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 202.03, 142.27, 139.97, 134.12 (q, ²*J*_{CF} = 32.6 Hz), 128.66, 128.31, 128.20, 125.74, 125.63 (q, ³*J*_{CF} = 3.7 Hz), 123.64 (q, ¹*J*_{CF} = 271.9 Hz), 53.27, 42.70, 37.36, 34.95, 32.62, 31.51, 25.11.

¹⁹F NMR (300 MHz, CDCl₃) δ -64.6



4-(2-phenethylcyclopentane-1-carbonyl)benzonitrile (7). The reaction was conducted according to the general procedure without modification using (*E*)-4-(5-phenylpent-2-enoyl)benzonitrile (**S2**) (54.0 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 0.5% Et₂O in hexanes).

Ratio of C₅ : C₃ = >20 : 1

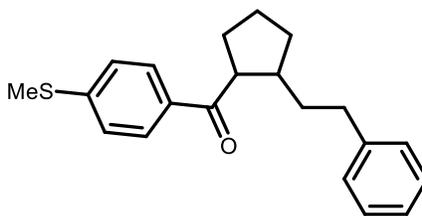
Run 1: 39.4 mg isolated (63% yield), yellow oil

Run 2: 38.2 mg isolated (61% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 7.99 (d, $J = 9.9$ Hz, 2H), 7.75 (d, $J = 9.9$ Hz, 2H), 7.25 – 7.20 (m, 2H), 7.18 – 7.08 (m, 3H), 3.34 (td, $J = 9.3, 8.5, 6.6$ Hz, 1H), 2.65 (ddd, $J = 15.4, 10.3, 5.6$ Hz, 1H), 2.58 – 2.42 (m, 2H), 2.20 – 1.92 (m, 2H), 1.86 – 1.50 (m, 5H), 1.46 – 1.32 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 201.62, 142.17, 140.26, 132.46, 128.74, 128.33, 128.20, 125.79, 118.01, 116.08, 53.28, 42.69, 37.32, 34.93, 32.59, 31.45, 25.09.

HRMS(ESI) (m/z): $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{21}\text{NO}$: 326.1515; found: 326.1514



(4-(methylthio)phenyl)(2-phenethylcyclopentyl)methanone (8). The reaction was conducted according to the general procedure without modification using (*E*)-1-(4-methylthio)-5-phenylpent-2-en-1-one (**S3**) (58.3 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 0.5% Et_2O in hexanes).

Ratio of $\text{C}_5 : \text{C}_3 = 5.4 : 1$

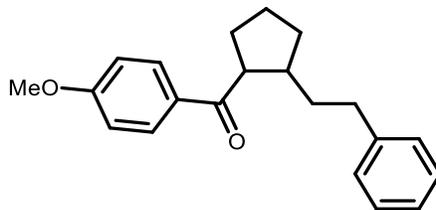
Run 1: 35.3 mg isolated (53% yield), yellow oil

Run 2: 32.7 mg isolated (49% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 7.94 – 7.81 (m, 2H), 7.28 – 7.19 (m, 4H), 7.14 (td, $J = 7.4, 6.8, 1.7$ Hz, 3H), 3.35 (q, $J = 8.0$ Hz, 1H), 2.72 – 2.42 (m, 6H), 2.18 – 1.96 (m, 2H), 1.86 – 1.50 (m, 5H), 1.43 – 1.30 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 202.09, 145.49, 142.53, 133.64, 128.82, 128.27, 128.23, 125.66, 125.05, 52.71, 42.93, 37.49, 35.03, 32.71, 31.81, 25.12, 14.83.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{OS}$: 325.1621; found: 325.1623



(4-methoxyphenyl)(2-phenethylcyclopentyl)methanone (9). The reaction was conducted according to the general procedure without modification using (*E*)-1-(4-methoxyphenyl)-5-phenylpent-2-en-1-one (**S5**) (54.9 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 40% CH₂Cl₂ in hexanes).

Ratio of C₅ : C₃ = 3.8 : 1

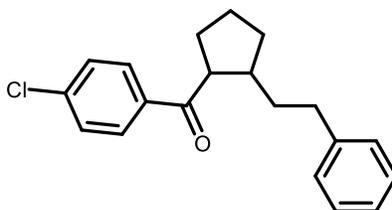
Run 1: 26.3 mg isolated (41% yield), yellow oil

Run 2: 28.2 mg isolated (44% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 7.99 – 7.90 (m, 2H), 7.27 – 7.20 (m, 2H), 7.20 – 7.09 (m, 3H), 6.97 – 6.90 (m, 2H), 3.87 (s, 3H), 3.36 (td, *J* = 8.9, 7.1 Hz, 1H), 2.72 – 2.40 (m, 3H), 2.19 – 1.95 (m, 2H), 1.86 – 1.68 (m, 4H), 1.67 – 1.51 (m, 1H), 1.46 – 1.30 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 201.70, 163.31, 142.62, 130.63, 130.40, 128.26, 128.24, 125.63, 113.71, 55.47, 52.59, 43.00, 37.52, 35.06, 32.73, 31.91, 25.13.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₂₄O₂: 309.1849; found: 309.1851



(4-chlorophenyl)(2-phenethylcyclopentyl)methanone (10). The reaction was conducted according to the general procedure without modification using (*E*)-1-(4-chlorophenyl)-5-phenylpent-2-en-1-one (**S4**) (55.8 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 30% CH₂Cl₂ in hexanes).

Ratio of C₅ : C₃ = 6.7 : 1

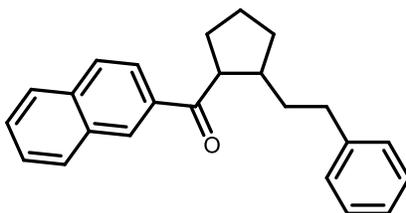
Run 1: 43.1 mg isolated (67% yield), clear oil

Run 2: 47.2 mg isolated (74% Yield), clear oil

^1H NMR (300 MHz, CDCl_3) δ 7.93 – 7.84 (m, 2H), 7.47 – 7.39 (m, 2H), 7.29 – 7.21 (m, 2H), 7.20 – 7.09 (m, 3H), 3.34 (dt, $J = 9.2, 7.1$ Hz, 1H), 2.65 (ddd, $J = 13.6, 10.7, 5.5$ Hz, 1H), 2.58 – 2.43 (m, 2H), 2.20 – 1.96 (m, 2H), 1.86 – 1.68 (m, 4H), 1.68 – 1.55 (m, 1H), 1.48 – 1.30 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 201.81, 142.39, 139.25, 135.60, 129.79, 128.87, 128.30, 128.22, 125.71, 52.94, 42.81, 37.42, 35.00, 32.66, 31.67, 25.11.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{21}\text{ClO}$: 313.1354; found: 313.1352



naphthalen-2-yl(2-phenethylcyclopentyl)methanone (11). The reaction was conducted according to the general procedure without modification using (*E*)-1-(naphthalen-2-yl)-5-phenylpent-2-en-1-one (**S6**) (59.1 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 0.5% Et_2O in hexanes).

Ratio of $\text{C}_5 : \text{C}_3 = 5.6 : 1$

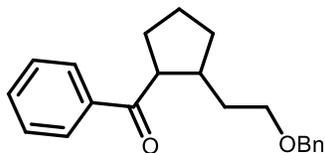
Run 1: 34.3 mg isolated (51% yield), yellow oil

Run 2: 37.9 mg isolated (56% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 8.47 (d, $J = 1.7$ Hz, 1H), 8.06 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.98 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.96 – 7.84 (m, 2H), 7.67 – 7.50 (m, 2H), 7.34 – 7.18 (m, 2H), 7.18 – 7.09 (m, 3H), 3.59 (dt, $J = 9.5, 7.4$ Hz, 1H), 2.82 – 2.43 (m, 3H), 2.14 (dddd, $J = 19.8, 12.3, 9.4, 5.0$ Hz, 2H), 1.94 – 1.56 (m, 5H), 1.50 – 1.38 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 203.08, 142.51, 135.52, 134.71, 132.60, 129.88, 129.60, 128.46, 128.41, 128.34, 128.27, 128.24, 127.76, 126.73, 126.70, 125.66, 124.35, 53.00, 42.99, 37.49, 35.05, 32.77, 31.99, 25.19.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{25}\text{O}$: 329.1900; found: 329.1899



(2-(2-(benzyloxy)ethyl)cyclopentyl)(phenyl)methanone (12). The reaction was conducted according to the general procedure without modification using (*E*)-5-(benzyloxy)-1-phenylpent-2-en-1-one (**S9**) (55.0 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 6% Et₂O in hexanes).

Ratio of C₅ : C₃ = >20 : 1

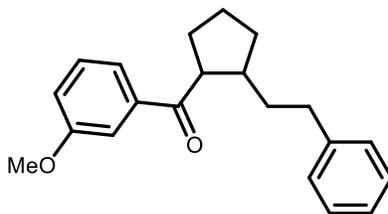
Run 1: 44.5 mg isolated (70% yield), yellow oil

Run 2: 46.9 mg isolated (74% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.90 (m, 2H), 7.54 (ddt, *J* = 8.2, 6.6, 1.4 Hz, 1H), 7.44 (ddt, *J* = 8.5, 7.6, 0.8 Hz, 2H), 7.35 – 7.16 (m, 5H), 4.36 (d, *J* = 2.9 Hz, 2H), 3.56 – 3.30 (m, 3H), 2.55 (h, *J* = 7.8 Hz, 1H), 2.15 – 1.89 (m, 2H), 1.83 – 1.59 (m, 5H), 1.41 – 1.28 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 202.91, 138.45, 137.31, 132.71, 128.51, 128.40, 128.26, 127.63, 127.39, 72.85, 69.71, 52.73, 40.14, 35.20, 33.09, 31.69, 25.06.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₂₄O₂: 309.1849; found: 309.1847



(3-methoxyphenyl)(2-phenethyl)cyclopentylmethanone (13). The reaction was conducted according to the general procedure without modification using (*E*)-1-(3-methoxyphenyl)-5-phenylpent-2-en-1-one (**S7**) (55.0 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 1% Et₂O in hexanes).

Ratio of C₅ : C₃ = 7.7 : 1

Run 1: 47.7 mg isolated (75% yield), yellow oil

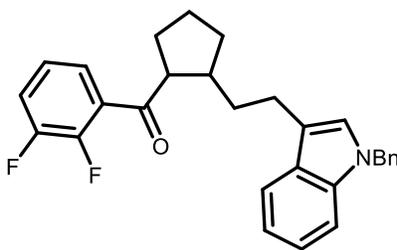
Run 2: 49.8 mg isolated (78% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 7.60 – 7.46 (m, 2H), 7.43 – 7.33 (m, 1H), 7.31 – 7.20 (m, 2H), 7.20 – 7.00 (m, 4H), 3.86 (s, 3H), 3.39 (ddd, $J = 10.3, 7.9, 6.1$ Hz, 1H), 2.72 – 2.42 (m, 3H), 2.24 – 1.92 (m, 2H), 1.85 – 1.50 (m, 5H), 1.46 – 1.31 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 202.94, 159.85, 142.52, 138.76, 129.52, 128.27, 128.24, 125.66, 120.99, 119.27, 112.72, 55.44, 53.07, 42.92, 37.45, 35.02, 32.70, 31.85, 25.13.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2$: 309.1849; found: 309.1852

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{21}\text{F}_3\text{O}$: 347.1617; found: 347.1622



(2-(2-(1-benzyl-1H-indol-3-yl)ethyl)cyclopentyl)(2,3-difluorophenyl)methanonene

(14). The reaction was conducted according to the general procedure without modification using (*E*)-5-(1-benzyl-1H-indol-3-yl)-1-(2,3-difluorophenyl)pent-2-en-1-one (**S12**) (82.9 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 20% CH_2Cl_2 in hexanes).

Ratio of $\text{C}_5 : \text{C}_3 = 5.7 : 1$

Run 1: 51.6 mg isolated (57% yield), yellow oil

Run 2: 52.1 mg isolated (57% Yield), yellow oil

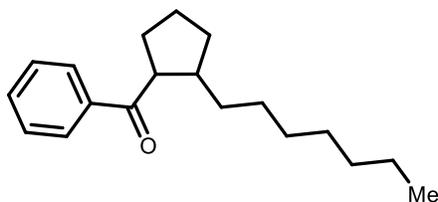
^1H NMR (300 MHz, CDCl_3) δ 7.75 (ddd, $J = 11.1, 7.7, 2.2$ Hz, 1H), 7.65 (ddd, $J = 7.8, 4.0, 2.2$ Hz, 1H), 7.53 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.27 (d, $J = 5.8$ Hz, 2H), 7.24 – 7.14 (m, 3H), 7.08 (dddd, $J = 8.1, 6.8, 2.9, 1.2$ Hz, 4H), 6.84 (s, 1H), 5.21 (s, 2H), 3.31 (q, $J = 7.6$ Hz, 1H), 2.80 (ddd, $J = 15.2, 9.9, 5.6$ Hz, 1H), 2.67 (td, $J = 9.2, 8.5, 4.9$ Hz, 1H), 2.56 (q, $J = 7.4$ Hz, 1H), 2.16 – 1.96 (m, 2H), 1.92 – 1.63 (m, 5H), 1.50 – 1.38 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 200.51, 153.37 (dd, $^1J_{\text{CF}} = 256.2, ^2J_{\text{CF}} = 13.0$ Hz), 150.38 (dd, $^1J_{\text{CF}} = 250.8, ^2J_{\text{CF}} = 13.0$ Hz), 137.76, 136.68, 134.36 (ap t, $^4J_{\text{CF}} = 3.5$ Hz), 128.69,

128.01, 127.49, 126.75, 125.25, 125.21 (dd, $^3J_{\text{CF}} = 7.3$, $^4J_{\text{CF}} = 3.4$ Hz), 121.65, 117.62 (d, $^2J_{\text{CF}} = 17.9$ Hz), 117.31 (d, $^2J_{\text{CF}} = 17.7$ Hz), 115.69, 109.59, 52.82, 49.78, 42.95, 35.98, 32.68, 31.56, 25.14, 24.18.

^{19}F NMR (282 MHz, CDCl_3) δ -132.07, -137.83.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{27}\text{F}_2\text{NO}$: 444.2133; found: 444.2136



(2-hexylcyclopentyl)(phenyl)methanone (15). The reaction was conducted according to the general procedure without modification using (*E*)-1-phenyldec-2-en-1-one¹⁶ (47.6 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 10% CH_2Cl_2 in hexanes).

Ratio of $\text{C}_5 : \text{C}_3 = 6.3 : 1$

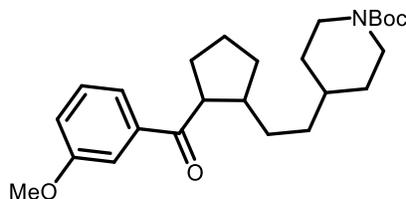
Run 1: 34.6 mg isolated (65% yield), yellow oil

Run 2: 32.5 mg isolated (61% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 8.00 – 7.93 (m, 2H), 7.60 – 7.50 (m, 1H), 7.51 – 7.41 (m, 2H), 3.35 (q, $J = 8.2, 7.4$ Hz, 1H), 2.52 – 2.26 (m, 1H), 2.15 – 1.87 (m, 2H), 1.85 – 1.61 (m, 3H), 1.52 – 1.06 (m, 13H), 0.90 – 0.80 (m, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 203.42, 137.48, 132.70, 128.51, 128.37, 52.91, 43.09, 35.53, 32.71, 31.82, 31.70, 29.76, 29.24, 28.56, 25.14, 22.64, 14.09.

HRMS(ESI) (m/z): HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{28}\text{O}$: 273.2213; found: 273.2215



***tert*-butyl-4-(2-(2-(3-methoxybenzoyl)cyclopentyl)ethyl)piperidine-1-carboxylate (16).**

The reaction was conducted according to the general procedure without modification using *tert*-butyl-(*E*)-4-(5-(3-methoxyphenyl)-5-oxopent-3-en-1-yl)piperidine-1-carboxylate (**S15**) (77.0 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 15% Et₂O in hexanes).

Ratio of C₅ : C₃ = 3.8 : 1

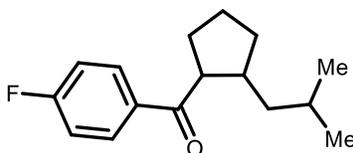
Run 1: 42.3 mg isolated (50% yield), yellow oil

Run 2: 44.9 mg isolated (52% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 7.56 – 7.47 (m, 2H), 7.37 (ddd, *J* = 8.1, 7.6, 0.4 Hz, 1H), 7.10 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 4.03 (br s, 2H), 3.86 (s, 3H), 3.29 (m, 1 H), 2.62 (t, *J* = 12.5 Hz, 2H), 2.39 (dq, *J* = 15.7, 8.0 Hz, 1H), 2.12 – 1.91 (m, 2H), 1.82 – 1.66 (m, 3H), 1.57 (d, *J* = 13.1 Hz, 2H), 1.44 (d, *J* = 2.8 Hz, 12H), 1.34 – 1.10 (m, 4H), 1.01 (tq, *J* = 10.8, 5.7, 5.0 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 203.03, 159.83, 154.88, 138.78, 129.53, 120.94, 119.17, 112.76, 79.11, 55.43, 53.08, 42.93, 36.01, 35.28, 32.68, 32.32, 31.84, 30.32, 28.48, 28.47, 25.07.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₅H₃₇NO₄: 416.2795; found: 416.2792



(4-fluorophenyl)(2-isobutylcyclopentyl)methanone (17). The reaction was conducted according to the general procedure without modification using (*E*)-1-(4-fluorophenyl)-5-methylhex-2-en-1-one (**S13**) (42.6 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 15% CH₂Cl₂ in hexanes).

Ratio of C₅ : C₃ = 7.1 : 1

Run 1: 32.8 mg isolated (64% yield), colorless oil

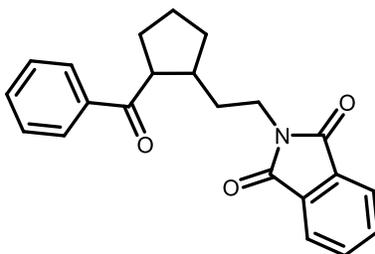
Run 2: 31.8 mg isolated (62% Yield), colorless oil

^1H NMR (300 MHz, CDCl_3) δ 8.02 – 7.94 (m, 2H), 7.17 – 7.08 (m, 2H), 3.28 (dt, $J = 9.1$, 7.0 Hz, 1H), 2.58 – 2.41 (m, 1H), 2.12 – 1.89 (m, 2H), 1.82 – 1.61 (m, 3H), 1.53 – 1.41 (m, 1H), 1.33 – 1.13 (m, 3H), 0.84 (d, $J = 6.6$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 201.70, 165.57 (d, $J = 254.3$ Hz), 133.83 (d, $J = 3.0$ Hz), 130.94 (d, $J = 9.3$ Hz), 115.57 (d, $J = 22.0$ Hz), 53.21, 45.15, 40.90, 32.78, 31.66, 26.93, 25.12, 23.39, 22.16.

^{19}F NMR (282 MHz, CDCl_3) δ -107.60.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{21}\text{FO}$: 249.1649; found: 249.1646



2-(2-(2-benzoylcyclopentyl)ethyl)isoindoline-1,3-dione (18). The reaction was conducted according to the general procedure without modification using (*E*)-2-(5-oxo-5-phenylpent-3-en-1-yl)isoindoline-1,3-dione (**S11**) (63.0 mg, 0.21 mmol, 1 equiv). Isolated yields were determined following column chromatography (SiO_2 , CH_2Cl_2).

Ratio of $\text{C}_5 : \text{C}_3 = 2.9 : 1$

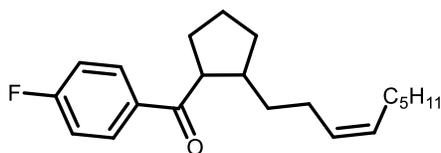
Run 1: 27.2 mg isolated (38% yield), yellow oil

Run 2: 32.1 mg isolated (45% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 8.01 – 7.88 (m, 2H), 7.80 (dd, $J = 5.5$, 3.1 Hz, 2H), 7.68 (dd, $J = 5.4$, 3.1 Hz, 2H), 7.59 – 7.49 (m, 1H), 7.44 (dd, $J = 8.2$, 6.6 Hz, 2H), 3.73 – 3.54 (m, 2H), 3.47 – 3.34 (m, 1H), 2.63 – 2.36 (m, 1H), 2.19 – 1.95 (m, 2H), 1.93 – 1.58 (m, 5H), 1.50 – 1.33 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 202.51, 168.27, 137.06, 133.81, 132.86, 132.15, 128.56, 128.40, 123.15, 52.74, 40.02, 37.16, 34.06, 32.50, 31.75, 25.15.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{21}\text{O}_3$: 348.1594; found: 348.1596



(Z)-(4-fluorophenyl)(2-(non-3-en-1-yl)cyclopentyl)methanone (19). The reaction was conducted according to the general procedure without modification using (2*E*,6*Z*)-1-(4-fluorophenyl)dodeca-2,6-dien-1-one (**S10**) (56.7 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 0.2% Et₂O in hexanes).

Ratio of C₅ : C₃ = >20 : 1

Run 1: 50.7 mg isolated (78% yield), yellow oil

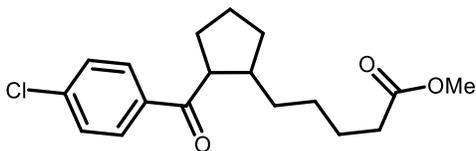
Run 2: 50.8 mg isolated (78% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 8.05 – 7.93 (m, 2H), 7.21 – 7.05 (m, 2H), 5.43 – 5.15 (m, 2H), 3.32 (q, *J* = 7.8, 7.4 Hz, 1H), 2.43 (dq, *J* = 15.3, 8.2 Hz, 1H), 2.16 – 1.85 (m, 5H), 1.83 – 1.62 (m, 3H), 1.53 – 1.15 (m, 10H), 0.91 – 0.82 (m, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 201.60, 165.59 (d, ¹*J*_{CF} = 254.1 Hz), 133.77 (d, ⁴*J*_{CF} = 3.0 Hz), 130.95 (d, ³*J*_{CF} = 9.1 Hz), 130.16, 129.31, 115.59 (d, ²*J*_{CF} = 21.4 Hz), 52.79, 42.92, 35.62, 31.69, 31.50, 29.37, 27.15, 26.31, 25.11, 22.70, 14.06.

¹⁹F NMR (282 MHz, CDCl₃) δ -107.53.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₂₉FO: 317.2275; found: 317.2281



methyl 5-(2-(4-chlorobenzoyl)cyclopentyl)pentanoate (20). The reaction was conducted according to the general procedure without modification using (*E*)-8-(4-chlorophenyl)-8-oxooct-6-enoate (**S14**) (57.9 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 60% CH₂Cl₂ in hexanes).

Ratio of C₅ : C₃ = 4.3 : 1

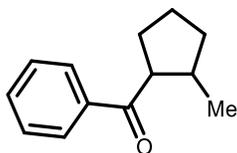
Run 1: 46.1 mg isolated (69% yield), yellow oil

Run 2: 42.6 mg isolated (64% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 7.93 – 7.86 (m, 2H), 7.47 – 7.41 (m, 2H), 3.63 (s, 3H), 3.34 – 3.21 (m, 1H), 2.41 (q, $J = 7.5$ Hz, 1H), 2.30 – 2.21 (m, 2H), 2.15 – 1.88 (m, 2H), 1.78 – 1.65 (m, 2H), 1.65 – 1.50 (m, 2H), 1.49 – 1.11 (m, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 201.92, 174.12, 139.24, 135.62, 129.80, 128.86, 52.89, 51.44, 42.72, 35.02, 33.97, 32.61, 31.66, 28.06, 25.08, 25.05.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{ClO}_3$: 323.1409; found: 323.1412



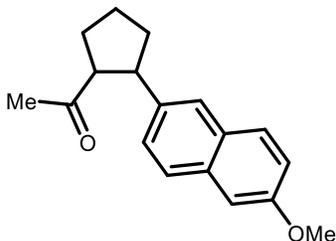
(2-methylcyclopentyl)(phenyl)methanone (21) [100611-76-5]. The reaction was conducted according to the general procedure without modification using (*Z*)-1-phenylbut-2-en-1-one¹⁴ (30.2 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 10% CH_2Cl_2 in hexanes). The spectral data matched those previously reported.¹⁵

Ratio of $\text{C}_5 : \text{C}_3 = 6.1 : 1$

Run 1: 19.0 mg isolated (49% yield), yellow oil

Run 2: 19.4 mg isolated (50% Yield), yellow oil

^1H NMR (300 MHz, CDCl_3) δ 8.01 – 7.91 (m, 2H), 7.61 – 7.51 (m, 1H), 7.51 – 7.41 (m, 2H), 3.29 (q, $J = 8.1$ Hz, 1H), 2.41 (tt, $J = 14.3, 6.8$ Hz, 1H), 2.14 – 2.00 (m, 1H), 2.00 – 1.88 (m, 1H), 1.88 – 1.66 (m, 3H), 1.37 – 1.29 (m, 1H), 1.03 (dd, $J = 6.7, 0.6$ Hz, 3H).



1-(2-(6-methoxynaphthalen-2-yl)cyclopentyl)ethan-1-one (22). The reaction was conducted according to the general procedure without modification using (*E*)-4-(6-methoxynaphthalen-2-yl)but-3-en-2-one (46.7 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 7% Et₂O in hexanes).

Ratio of C₅ : C₃ = 1.4 : 1

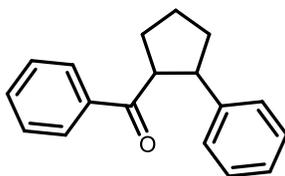
Run 1: 21.3 mg isolated (39% yield), yellow oil

Run 2: 18.6 mg isolated (34% Yield), yellow oil

¹H NMR (800 MHz, CDCl₃) δ 7.71 (dd, *J* = 13.8, 8.7 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.37 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 3.93 (s, 3H), 3.42 (q, *J* = 9.1, 8.7 Hz, 1H), 3.14 (q, *J* = 8.8 Hz, 1H), 2.27 – 2.20 (m, 1H), 2.17 – 2.09 (m, 1H), 2.02 (s, 3H), 1.99 (ddd, *J* = 15.6, 8.0, 4.0 Hz, 1H), 1.97 – 1.91 (m, 1H), 1.91 – 1.81 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 210.73, 157.37, 139.56, 133.32, 129.06, 128.98, 127.17, 126.14, 125.48, 118.84, 105.62, 60.27, 55.31, 48.99, 35.87, 30.08, 29.87, 25.43.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₂₀O₂: 269.1536; found: 269.1539



phenyl(2-phenylcyclopentyl)methanone (23) . The reaction was conducted according to the general procedure without modification using (*E*)-chalcone (43.0 mg, 0.21 mmol, 1 equiv). Isolated yields were determined following column chromatography (SiO₂, 50% CH₂Cl₂ in hexanes). Single crystals of **23** suitable for X-ray diffraction analysis were obtained by cooling a saturated Et₂O solution to -5 °C.

Ratio of C₅ : C₃ = 2.2 : 1

Run 1: 23.7 mg isolated (45% yield), white solid

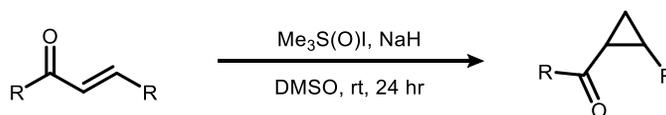
Run 2: 22.0 mg isolated (42% Yield), white solid

¹H NMR (300 MHz, CDCl₃) δ 7.86 – 7.77 (m, 2H), 7.56 – 7.42 (m, 1H), 7.44 – 7.32 (m, 2H), 7.26 – 7.24 (m, 4H), 7.20 – 7.11 (m, 1H), 3.90 – 3.75 (m, 1H), 3.66 (q, *J* = 8.4 Hz, 1H), 2.25 (td, *J* = 6.8, 6.3, 3.1 Hz, 2H), 2.03 – 1.76 (m, 4H).

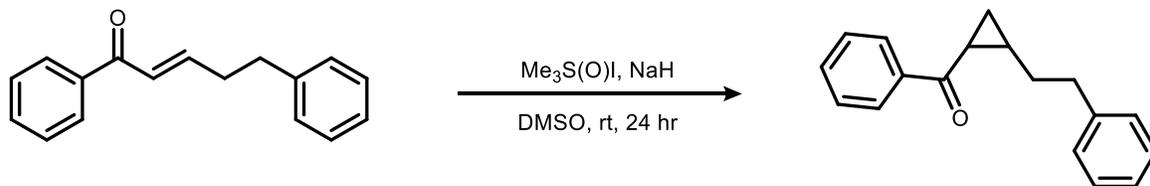
¹³C{¹H} NMR (201 MHz, CDCl₃) δ 202.19, 144.72, 136.95, 132.79, 128.46, 128.42, 127.36, 126.16, 109.32, 54.72, 48.32, 35.30, 32.01, 25.84.

HRMS(APCI) (m/z): [M + H]⁺ Calcd for C₁₈H₁₈O: 251.1430; found: 251.1433

7. Synthesis and Characterization of Representative Cyclopropanes



General procedure for the synthesis of cyclopropanes from enones. A flame-dried 100 mL flask was charged with solid NaH (60% in mineral oil, 1.2 equiv), trimethylsulfoxonium iodide (1.2 equiv), and a magnetic stir bar. The flask was placed under N₂ atmosphere, and DMSO (0.35 M) was added dropwise with stirring. After hydrogen evolution ceased, the reaction mixture was stirred for an additional 15 min, during which time the solution became clear. The enone (1.0 equiv) was added by syringe. The reaction was allowed to stir at room temperature. After 24 h, the reaction was quenched with water, and the mixture was extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was loaded onto a SiO₂ column for purification.

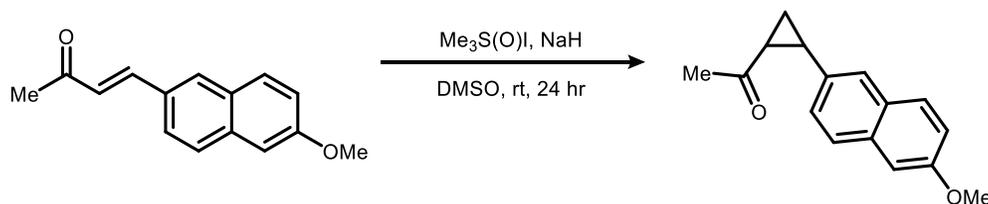


(2-phenethylcyclopropyl)(phenyl)methanone (2). The reaction was conducted according to the general procedure without modification using (*E*)-1,5-diphenylpent-2-en-1-one (**1**) (250 mg, 1.05 mmol, 1.0 equiv). (2-phenethylcyclopropyl)(phenyl)methanone (**2**) was isolated by column chromatography (SiO₂, 10% Et₂O in hexanes) as a light yellow oil (78.8 mg, 30% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.00 – 7.83 (m, 2H), 7.61 – 7.51 (m, 1H), 7.45 (ddt, *J* = 8.3, 6.6, 1.2 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.20 – 7.12 (m, 3H), 2.77 (ddd, *J* = 10.8, 9.2, 5.4 Hz, 2H), 2.40 (dt, *J* = 8.1, 4.2 Hz, 1H), 1.88 – 1.70 (m, 2H), 1.68 – 1.59 (m, 1H), 1.53 – 1.39 (m, 1H), 0.91 (ddd, *J* = 7.8, 6.1, 3.5 Hz, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 199.95, 141.66, 138.00, 132.61, 128.44, 128.41, 128.38, 127.97, 125.88, 35.60, 35.38, 26.58, 25.26, 18.75.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₁₉O: 251.1430; found: 251.1431

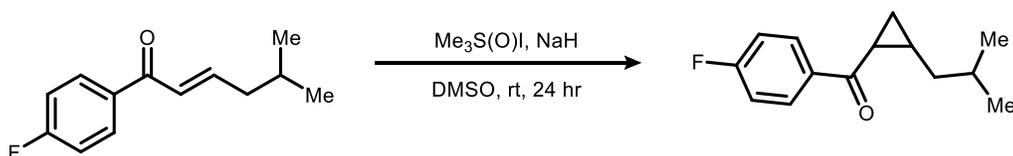


(2-(6-methoxynaphthalen-2-yl)cyclopropyl)ethan-1-one (S16). The reaction was conducted according to the general procedure without modification using (*E*)-4-(6-methoxynaphthalen-2-yl)but-3-en-2-one (100 mg, 0.44 mmol, 1.0 equiv). 1-(2-(6-methoxynaphthalen-2-yl)cyclopropyl)ethan-1-one (**S16**) was isolated by column chromatography (SiO₂, 20% Et₂O in hexanes) as a white solid (23.8 mg, 23% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.14 (ddd, *J* = 15.9, 7.6, 2.2 Hz, 3H), 3.91 (s, 3H), 2.66 (ddd, *J* = 9.1, 6.6, 4.0 Hz, 1H), 2.33 (s, 3H), 2.29 (ddd, *J* = 8.1, 5.2, 4.0 Hz, 1H), 1.73 (ddd, *J* = 9.2, 5.2, 4.2 Hz, 1H), 1.49 (ddd, *J* = 8.1, 6.6, 4.2 Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 206.88, 157.45, 135.34, 133.38, 128.89, 128.84, 127.05, 124.98, 124.50, 119.16, 105.65, 55.31, 32.87, 30.89, 29.29, 18.99.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$: 241.1223; found: 241.1225



(4-fluorophenyl)(2-isobutylcyclopropyl)methanone (S17). The reaction was conducted according to the general procedure without modification using (*E*)-1-(4-fluorophenyl)-5-methylhex-2-en-1-one (**S13**) (255 mg, 1.24 mmol, 1.0 equiv). (4-fluorophenyl)(2-isobutylcyclopropyl)methanone (**S17**) was isolated by column chromatography (SiO_2 , 10% Et_2O in hexanes) as a light yellow oil (95.0 mg, 35% yield).

^1H NMR (300 MHz, CDCl_3) δ 8.09 – 7.92 (m, 2H), 7.20 – 7.09 (m, 2H), 2.37 (dt, $J = 8.1, 4.3$ Hz, 1H), 1.74 (dq, $J = 13.4, 6.8$ Hz, 1H), 1.66 – 1.54 (m, 1H), 1.54 – 1.45 (m, 1H), 1.45 – 1.19 (m, 3H), 0.93 (dd, $J = 6.6, 1.4$ Hz, 6H).

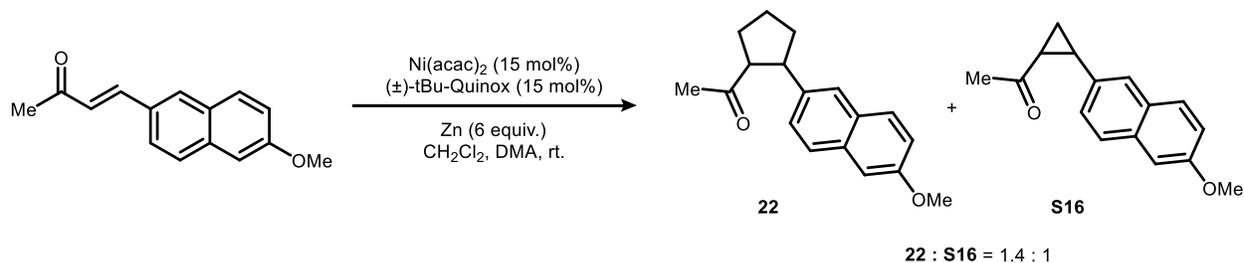
$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 198.54, 165.53 (d, $^1J_{\text{CF}} = 254.0$ Hz), 134.48 (d, $^4J_{\text{CF}} = 3.0$ Hz), 130.50 (d, $^3J_{\text{CF}} = 9.2$ Hz), 115.53 (d, $^2J_{\text{CF}} = 21.7$ Hz), 42.74, 28.59, 25.73, 25.15, 22.61, 22.50, 19.26.

^{19}F NMR (282 MHz, CDCl_3) δ -107.85.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{17}\text{FO}$: 221.1336; found: 221.1338

8. Assignment of Ratios Between the Cyclopentane and Cyclopropane Products

The assignment of the ratios between the cyclopentane and cyclopropane products were made using a combination of ^1H NMR analysis and GC analysis of the crude reaction mixtures. Two product classes are discussed below. The remainder of the substrate classes were assigned by analogy.



Top spectrum (3): Isolated **22**

Middle spectrum (2): Crude reaction mixture with ratio of **22** : **S16** indicated

Bottom Spectrum (1): Isolated **S16**

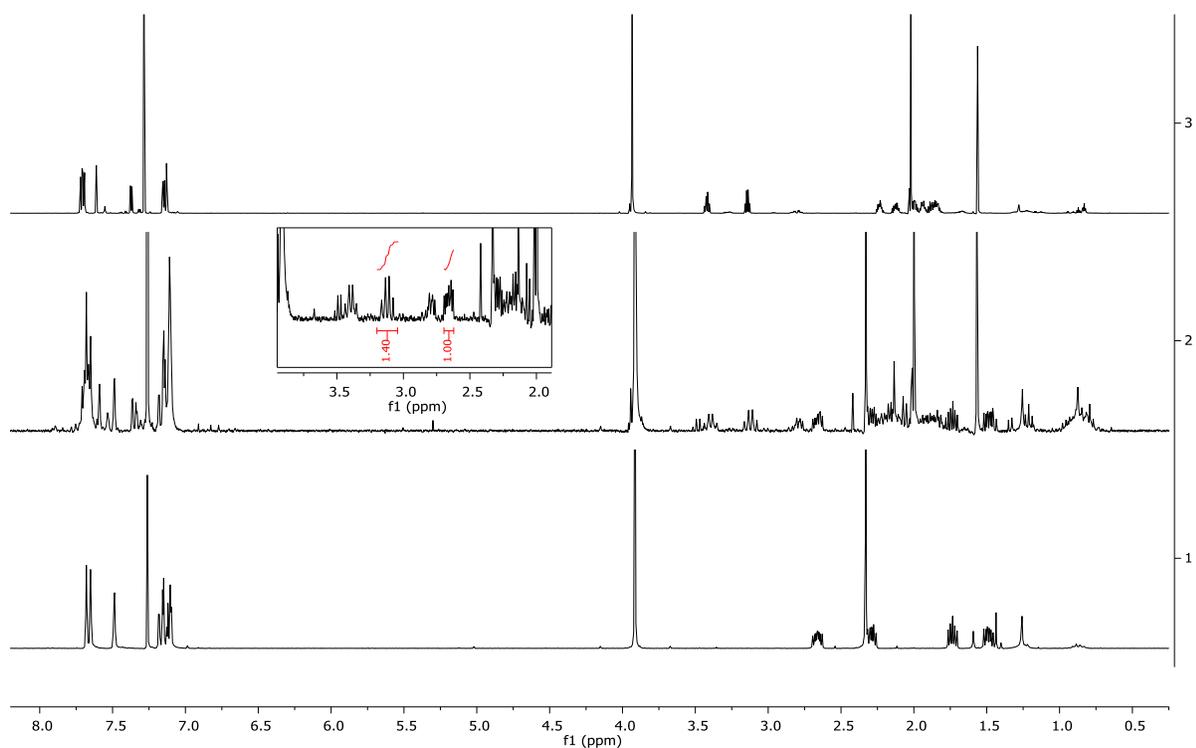
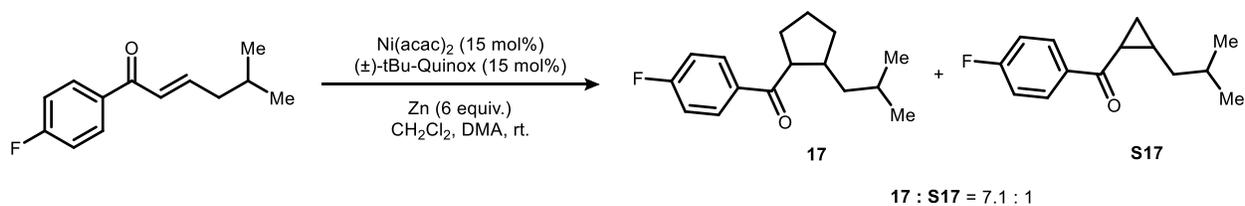


Figure S5. ^1H NMR of isolated **22** (Top spectrum), crude reaction mixture (Middle spectrum), and isolated **S16** (Bottom Spectrum). (CDCl_3 , 273 K).



Top spectrum (3): Isolated **17**

Middle spectrum (2): Crude reaction mixture with ratio of **17** : **S17** indicated

Bottom Spectrum (1): Isolated **S17**

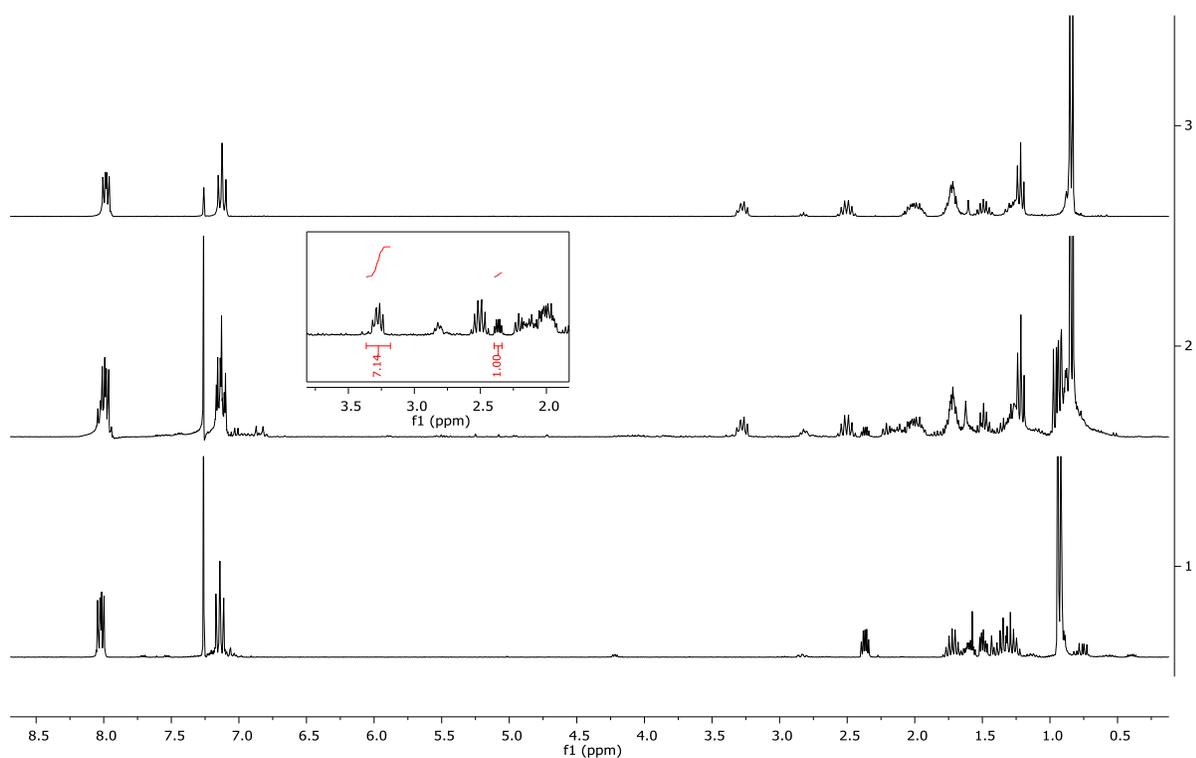
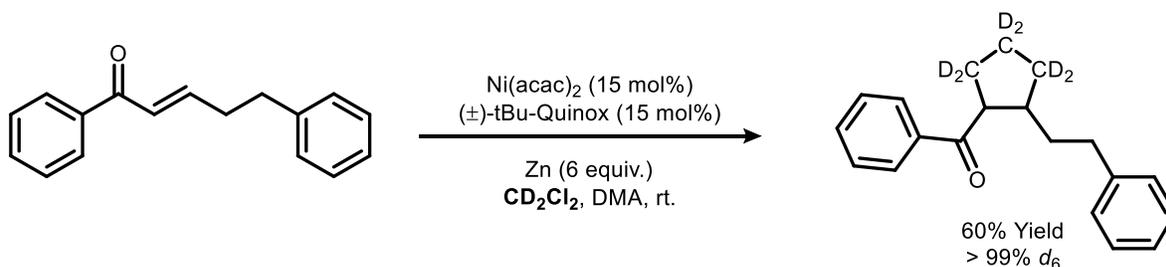


Figure S6. ^1H NMR of isolated **17** (Top spectrum), crude reaction mixture (Middle spectrum), and isolated **S17** (Bottom Spectrum). (CDCl_3 , 273 K).

9. Mechanistic Studies

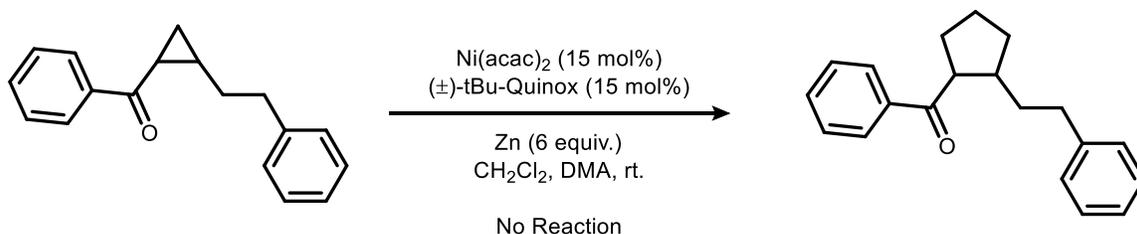


(2-phenethylcyclopentyl-3,3,4,4,5,5- d_6)(phenyl)methanone (3- d_6). In an N_2 -filled glovebox, a 5-mL vial was charged with $\text{Ni}(\text{acac})_2$ (7.9 mg, 0.031 mmol, 0.15 equiv), $(\pm)\text{-}t\text{-Bu-Quinox}$ (**L10**) (7.9 mg, 0.031 mmol, 0.15 equiv), Zn powder (81 mg, 1.23 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of (*E*)-1,5-diphenylpent-2-en-1-one (**1**) (48.8 mg, 0.21 mmol, 1 equiv) in CD_2Cl_2 (0.5 mL) and DMA (0.4 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and loaded directly onto a SiO_2 column for purification (SiO_2 , 20% CH_2Cl_2 in hexanes) to provide (2-phenethylcyclopentyl-3,3,4,4,5,5- d_6)(phenyl)methanone as a colorless oil (34.9 mg, 60% yield, > 99% deuterium incorporation).

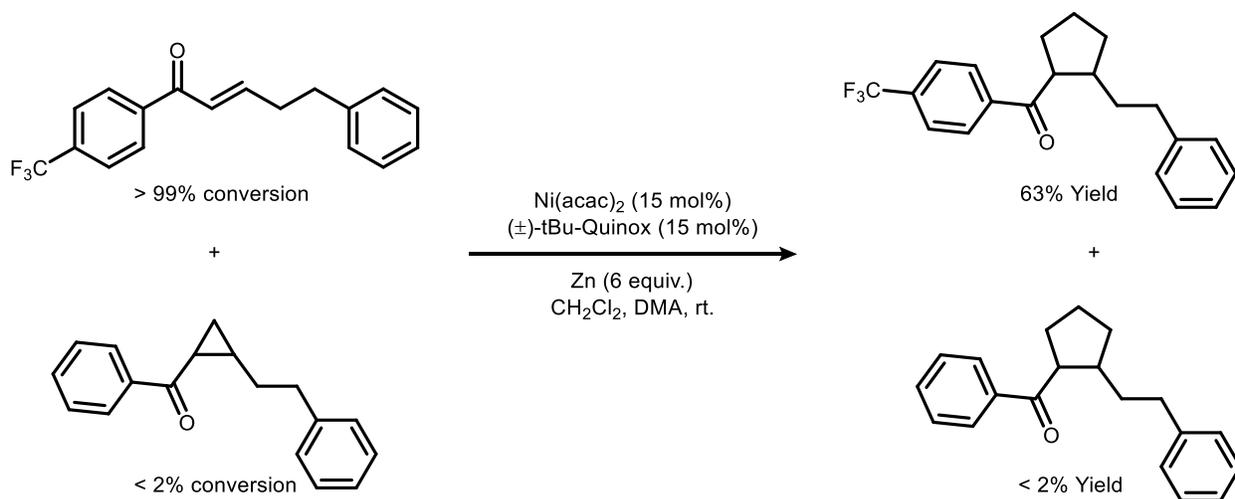
^1H NMR (300 MHz, CDCl_3) δ 8.01 – 7.89 (m, 2H), 7.61 – 7.51 (m, 1H), 7.51 – 7.39 (m, 2H), 7.26 – 7.18 (m, 2H), 7.18 – 7.08 (m, 3H), 3.39 (d, $J = 7.9$ Hz, 1H), 2.72 – 2.44 (m, 3H), 1.77 (ddt, $J = 13.1, 11.1, 5.8$ Hz, 1H), 1.68 – 1.56 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 203.17, 142.53, 137.35, 132.80, 128.55, 128.37, 128.27, 128.22, 125.65, 52.81, 42.72, 37.42, 35.02.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{16}\text{D}_6\text{O}$: 285.2120; found: 285.2122

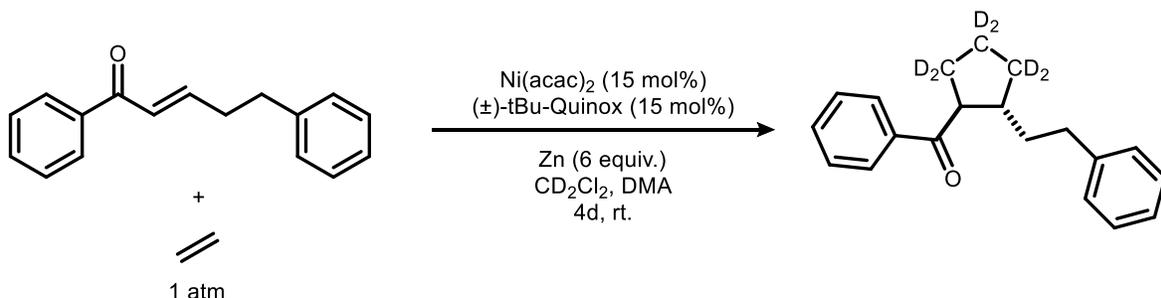


In an N_2 -filled glovebox, a 5-mL vial was charged with $\text{Ni}(\text{acac})_2$ (2.65 mg, 0.01 mmol, 0.15 equiv), $(\pm)\text{-}t\text{Bu-Quinox}$ (**L10**) (2.7 mg, 0.01 mmol, 0.15 equiv), Zn Powder (27 mg, 0.41 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of (2-phenethylcyclopropyl)(phenyl)methanone (**2**) (17.2 mg, 0.07 mmol, 1.0 equiv) in CH_2Cl_2 (0.17 mL) and DMA (0.13 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, and an aliquot was used for GC analysis. The conversion of **2** was determined by integration against mesitylene (< 2% conversion). Compound **3** was not detected in the mixture.



In an N_2 -filled glovebox, a 5-mL vial was charged with $\text{Ni}(\text{acac})_2$ (2.65 mg, 0.01 mmol, 0.15 equiv), $(\pm)\text{-}t\text{Bu-Quinox}$ (2.65 mg, 0.01 mmol, 0.15 equiv), Zn Powder (27 mg, 0.41 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of (2-phenethylcyclopropyl)(phenyl)methanone (**2**) (17.2 mg, 0.07 mmol, 1.0 equiv) and (*E*)-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-2-en-1-one (**S8**) (20.9 mg, 0.07 mmol, 1.0 equiv) in CH_2Cl_2

(0.17 mL) and DMA (0.13 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, and an aliquot was used for GC analysis. The conversions and yields were determined by integration against mesitylene.



In an N₂-filled glovebox, a 10 mL Schenk tube was charged with Ni(acac)₂ (7.9 mg, 0.031 mmol, 0.15 equiv), (±)-*t*-Bu-Quinox (**L10**) (7.9 mg, 0.031 mmol, 0.15 equiv), Zn powder (81 mg, 1.23 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of (*E*)-1,5-diphenylpent-2-en-1-one (**1**) (48.8 mg, 0.21 mmol, 1.0 equiv) in CD₂Cl₂ (0.5 mL) and DMA (0.4 mL). The reaction mixture was removed the glovebox and immediately placed in liquid N₂. The Schlenk tube was connected to a Schlenk line, the N₂ atmosphere was evacuated, and the reaction vessel was back-filled with ethylene (1 atm). The reaction was stirred at room temperature. After 4 days, an aliquot of the crude reaction mixture was filtered through silica gel and used for NMR analysis (CDCl₃). Spectra of the pure **3-d₆** and **3** are shown for comparison to indicate complete *d*₆-incorporation.

Top spectrum (3): Crude ethylene experiment mixture

Middle spectrum (2): Isolated **3-d₆**

Bottom Spectrum (1): Isolated **3**

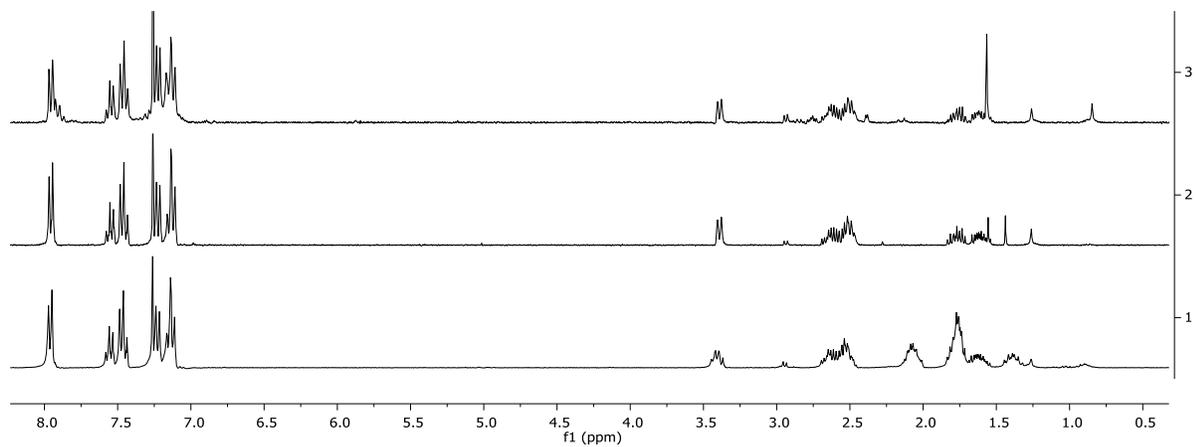
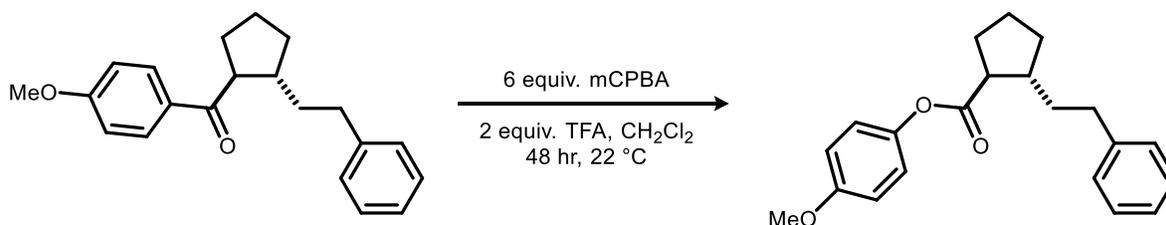


Figure S7. ¹H NMR of crude ethylene experiment mixture (Top spectrum), isolated **3-d₆**, (Middle spectrum), and isolated **3** (Bottom Spectrum). (CDCl₃, 273 K)

10. Cyclopentane Product Derivatization

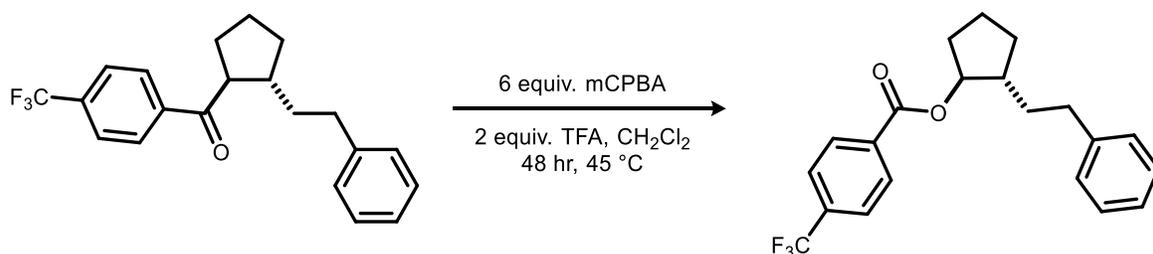


4-methoxyphenyl 2-phenethylcyclopentane-1-carboxylate (24). A flame-dried microwave vial was charged with *m*CPBA (>77%, 95 mg, 0.55 mmol, 6.0 equiv), a solution of (4-methoxyphenyl)(2-phenethylcyclopentyl)methanone (**9**) (28.2 mg, 0.09 mmol, 1.0 equiv) dissolved in CH₂Cl₂ (2 mL), and a magnetic stir bar. The vial was sealed, evacuated and backfilled three times with N₂, and cooled to 0 °C in an ice bath. Trifluoroacetic acid (14 μL, 0.18 mmol, 2.0 equiv) was added by syringe, and the vial was then wrapped in aluminum foil. The reaction was stirred at room temperature. After 48 h, the crude reaction mixture was loaded directly onto a SiO₂ column for purification (40% CH₂Cl₂ in hexanes) to provide 4-methoxyphenyl 2-phenethylcyclopentane-1-carboxylate as a colorless oil (23.6 mg, 81% yield, 14:1 selectivity).

¹H NMR (300 MHz, CDCl₃) δ 7.33 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 7.00 – 6.92 (m, 2H), 6.91 – 6.84 (m, 2H), 3.80 (s, 3H), 2.80 – 2.52 (m, 3H), 2.29 (pd, *J* = 8.4, 5.6 Hz, 1H), 2.16 – 1.90 (m, 4H), 1.84 – 1.62 (m, 3H), 1.43 – 1.24 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 175.43, 157.13, 144.36, 142.32, 128.36, 128.33, 125.77, 122.28, 114.40, 55.61, 50.38, 44.29, 37.32, 34.63, 32.68, 30.39, 24.91.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₂₄O₃: 325.1798; found: 325.1802



2-phenethylcyclopentyl 4-(trifluoromethyl)benzoate (25). A flame-dried microwave vial was charged with *m*CPBA (>77%, 124 mg, 0.72 mmol, 6.0 equiv), a solution of (2-phenethylcyclopentyl)(4-(trifluoromethyl)phenyl)methanone (**6**) (41.4 mg, 0.12 mmol, 1.0 equiv) in CH₂Cl₂ (2 mL), and a magnetic stir bar. The vial was sealed, evacuated and backfilled three times with N₂, and cooled to 0 °C with an ice bath. Trifluoroacetic acid (18 μL, 0.24 mmol, 2.0 equiv) was added by syringe, and the vial was then wrapped in aluminum foil. The reaction was stirred at 45 °C. After 48 h, the crude reaction mixture was loaded directly onto a SiO₂ column for purification (20% CH₂Cl₂ in hexanes) to provide 2-phenethylcyclopentyl 4-(trifluoromethyl)benzoate as a colorless oil (27.9 mg, 65% Yield, >20:1 selectivity).

¹H NMR (300 MHz, CDCl₃) δ 8.13 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.70 (dd, *J* = 8.1, 0.7 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.23 – 7.10 (m, 3H), 5.12 (dt, *J* = 6.5, 3.8 Hz, 1H), 2.68 (ddq, *J* = 13.9, 9.4, 7.0, 6.6 Hz, 2H), 2.21 – 1.96 (m, 3H), 1.96 – 1.70 (m, 4H), 1.69 – 1.57 (m, 1H), 1.47 – 1.29 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 165.18, 142.14, 134.28 (q, ²*J*_{CF} = 32.7 Hz), 133.96, 129.92, 128.33, 125.79, 125.33 (q, ³*J*_{CF} = 3.8 Hz), 123.67 (q, ¹*J*_{CF} = 275.1 Hz), 82.63, 45.12, 35.44, 34.31, 32.01, 30.31, 22.82.

¹⁹F NMR (282 MHz, CDCl₃) δ -64.61.

HRMS(ESI) (*m/z*): [M + Na]⁺ Calcd for C₂₁H₂₁F₃O₂: 385.1386; found: 385.1391

11. NMR Data for Enone Substrates

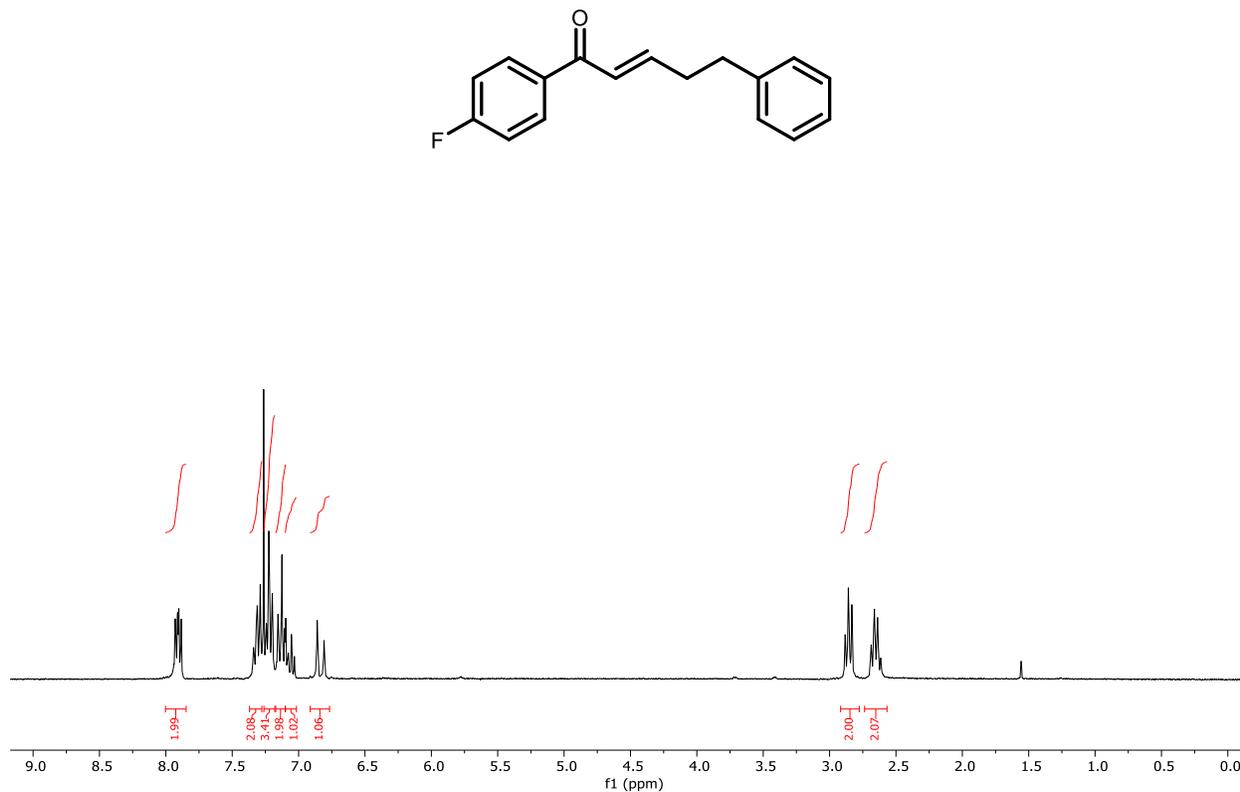


Figure S8. ¹H NMR of S1 (CDCl₃, 295 K).

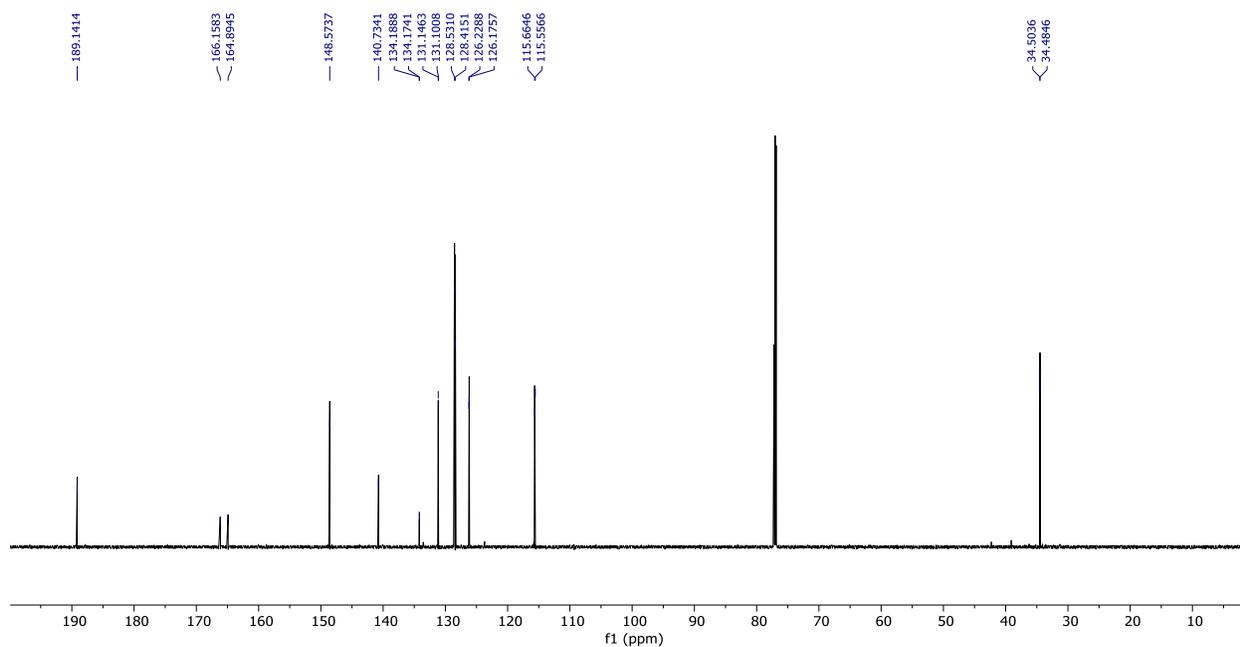


Figure S9. ¹³C{¹H} NMR of S1 (CDCl₃, 295 K).

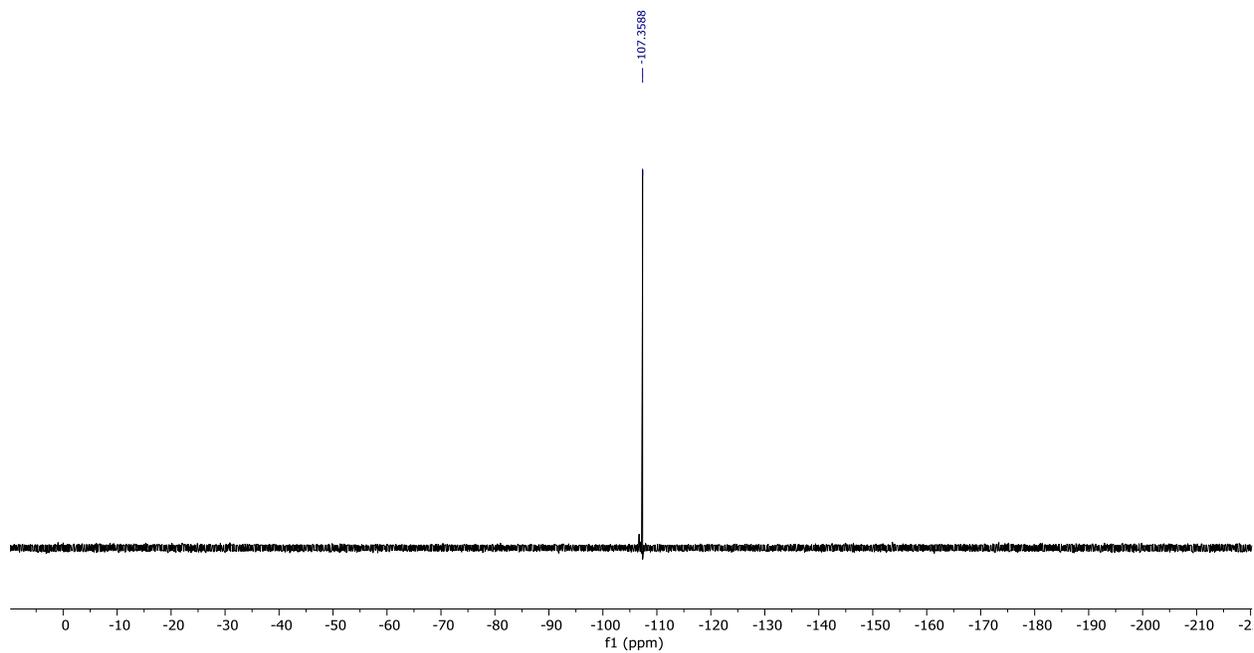


Figure S10. ^{19}F NMR of **S1** (CDCl_3 , 295 K).

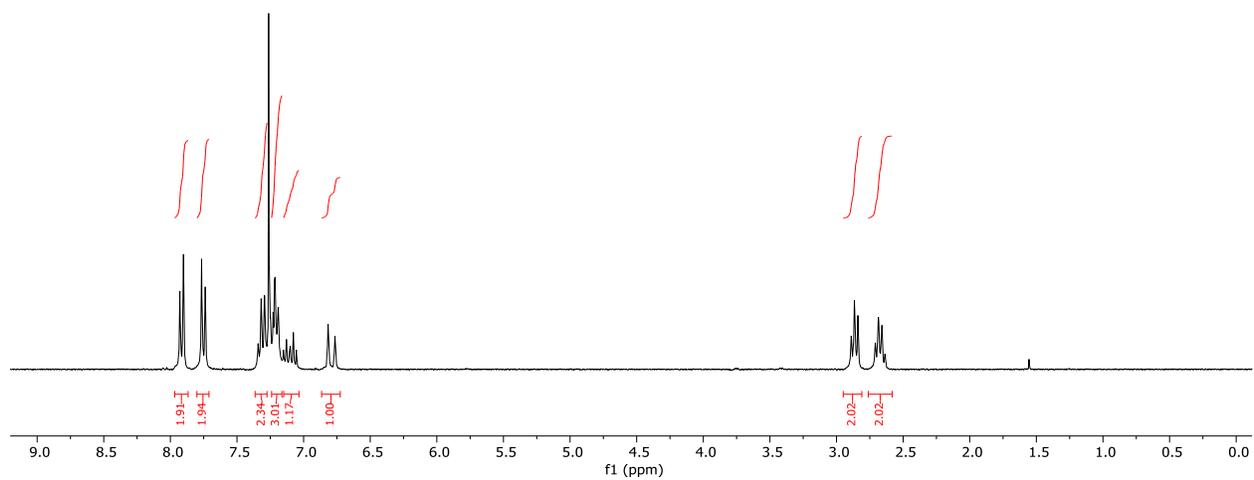
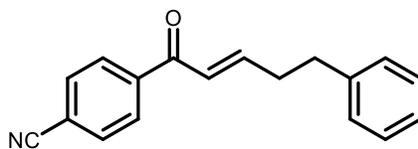


Figure S11. ^1H NMR of **S2** (CDCl_3 , 295 K).

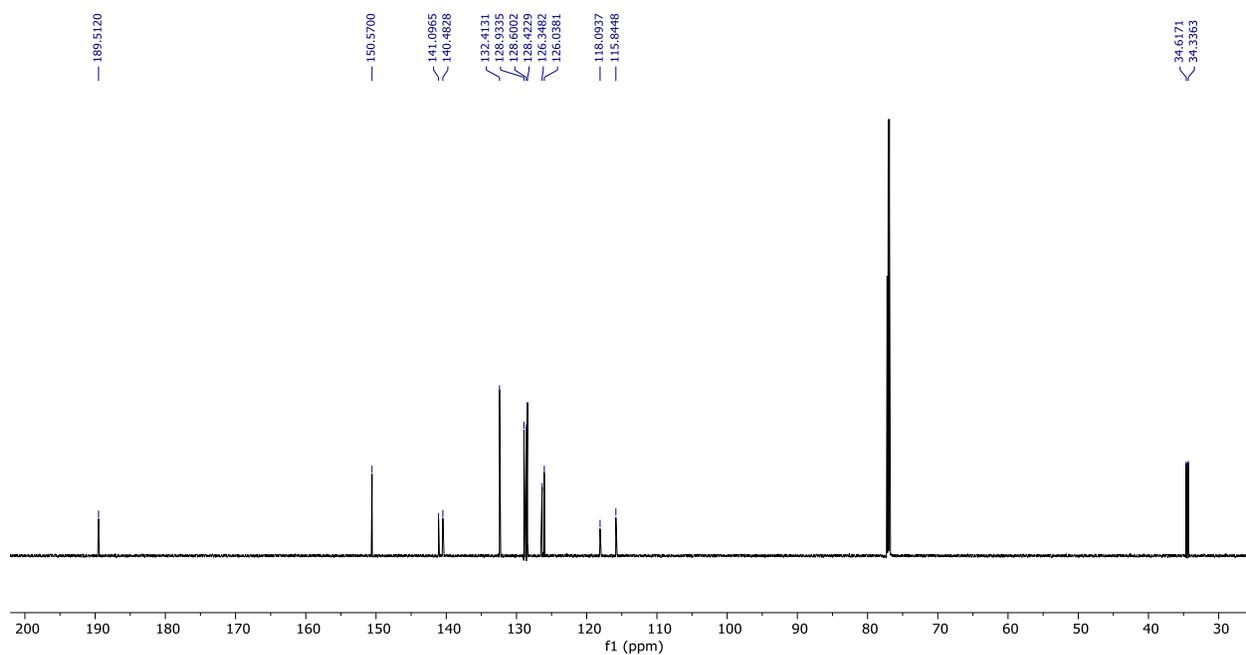


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR of **S2** (CDCl_3 , 295 K).

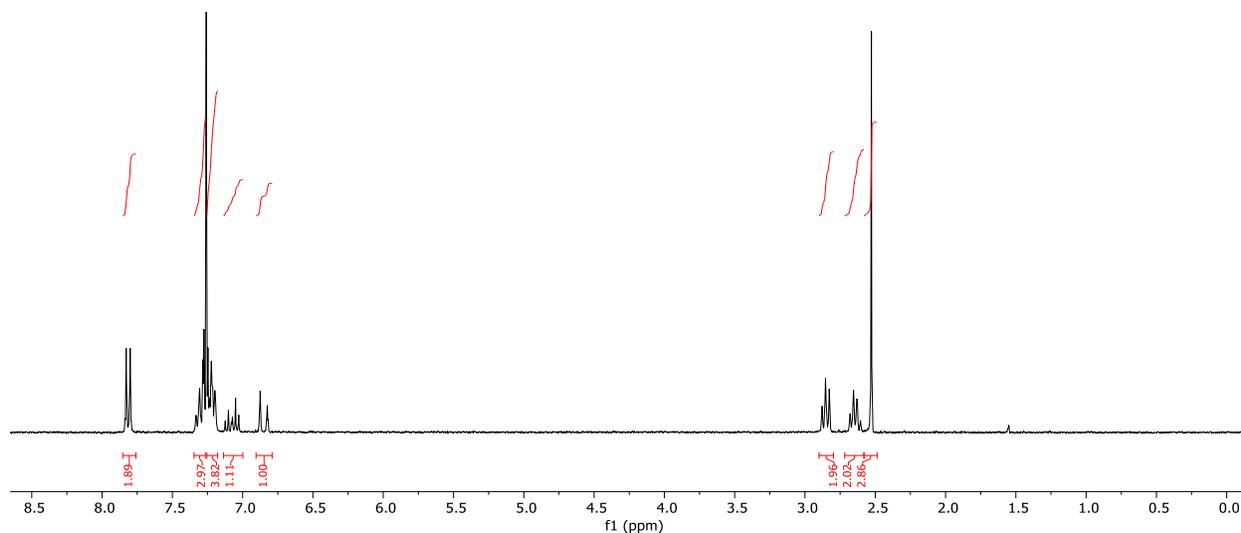
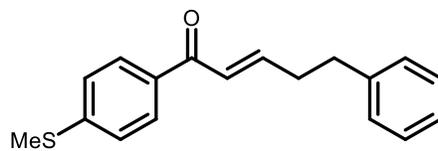


Figure S13. ^1H NMR of S3 (CDCl₃, 295 K).

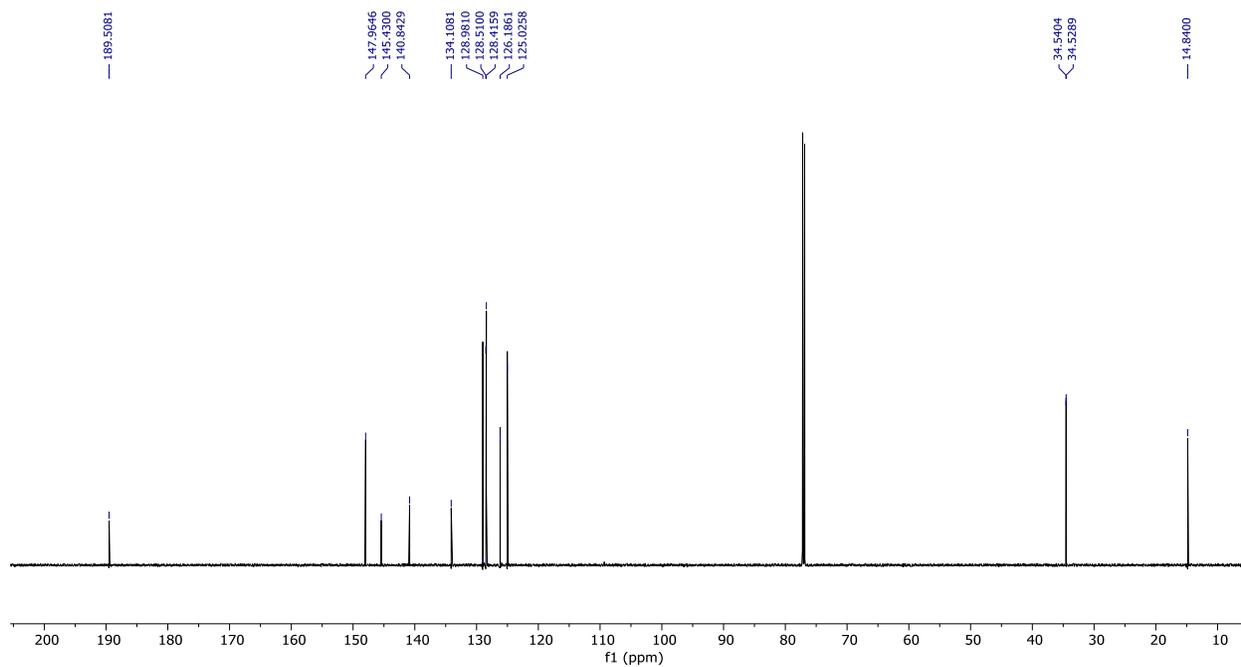


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR of S3 (CDCl₃, 295 K).

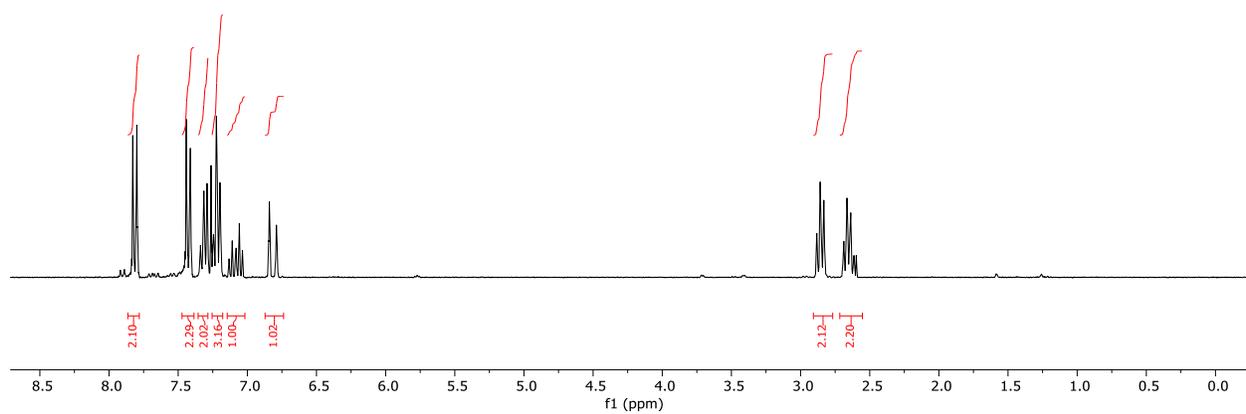
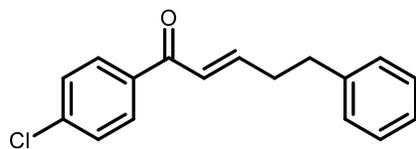


Figure S15. ^1H NMR of S4 (CDCl_3 , 295 K).

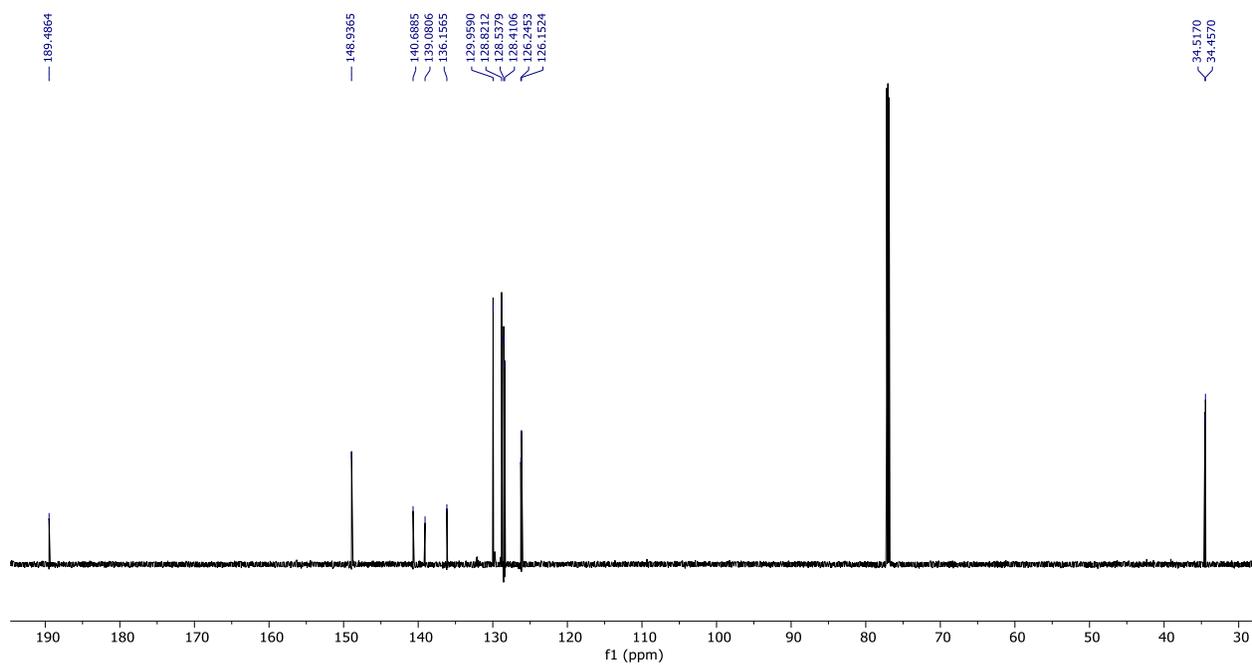


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR of S4 (CDCl_3 , 295 K).

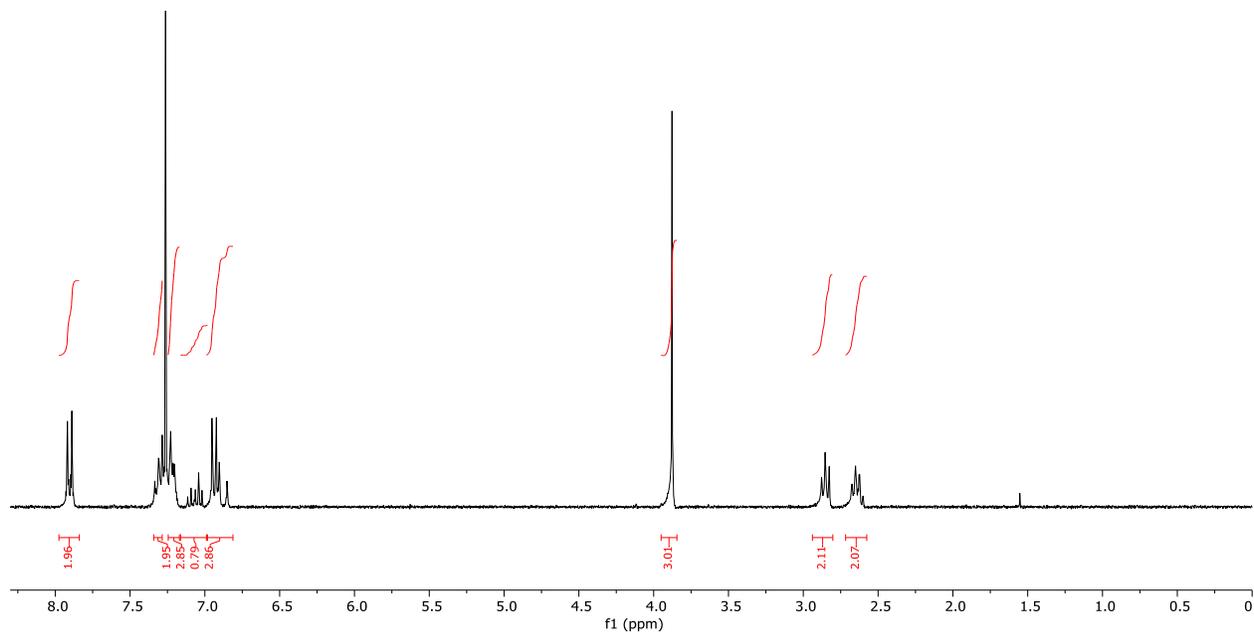
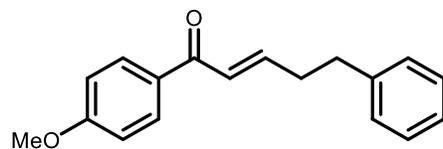


Figure S17. ^1H NMR of **S5** (CDCl_3 , 295 K).

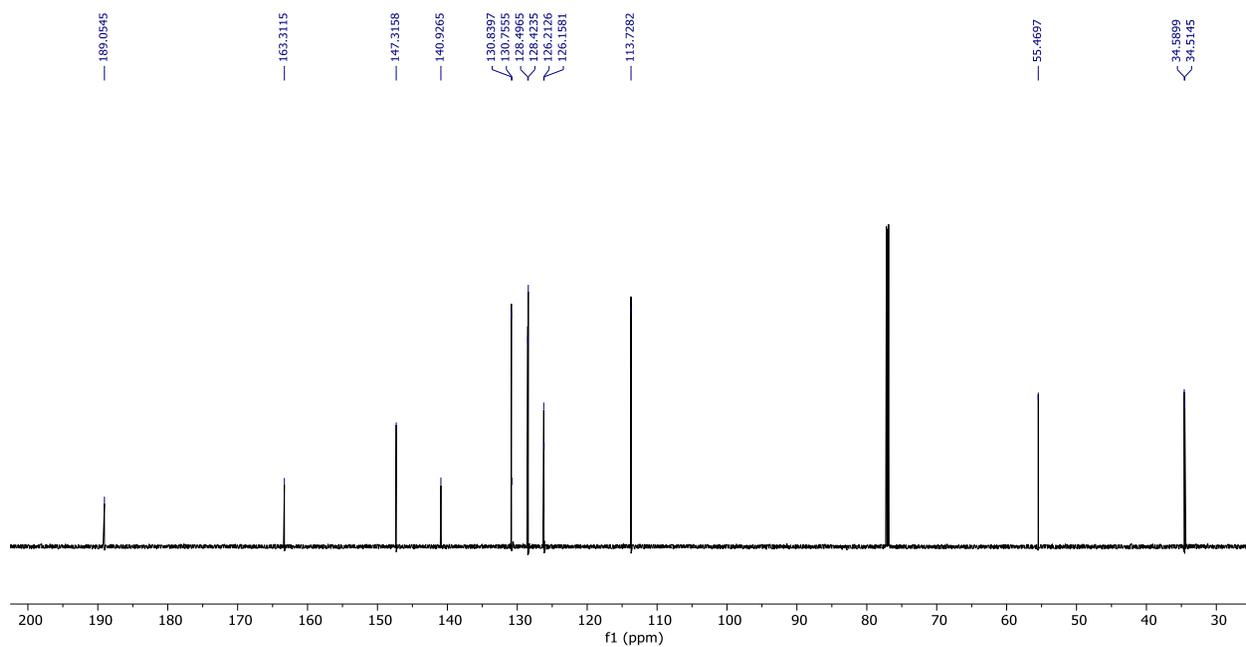


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR of **S5** (CDCl_3 , 295 K).

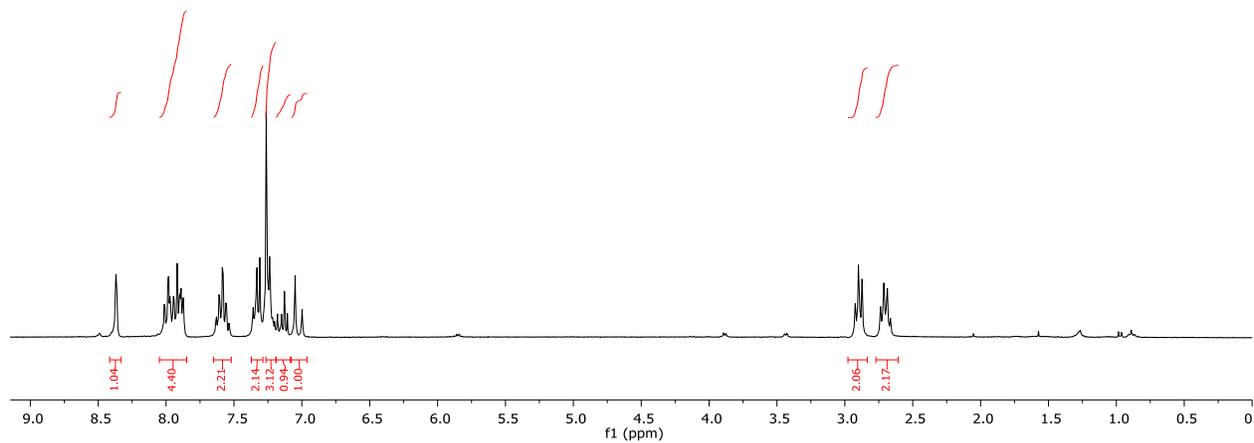
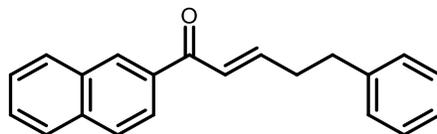


Figure S19. ^1H NMR of **S6** (CDCl_3 , 295 K).

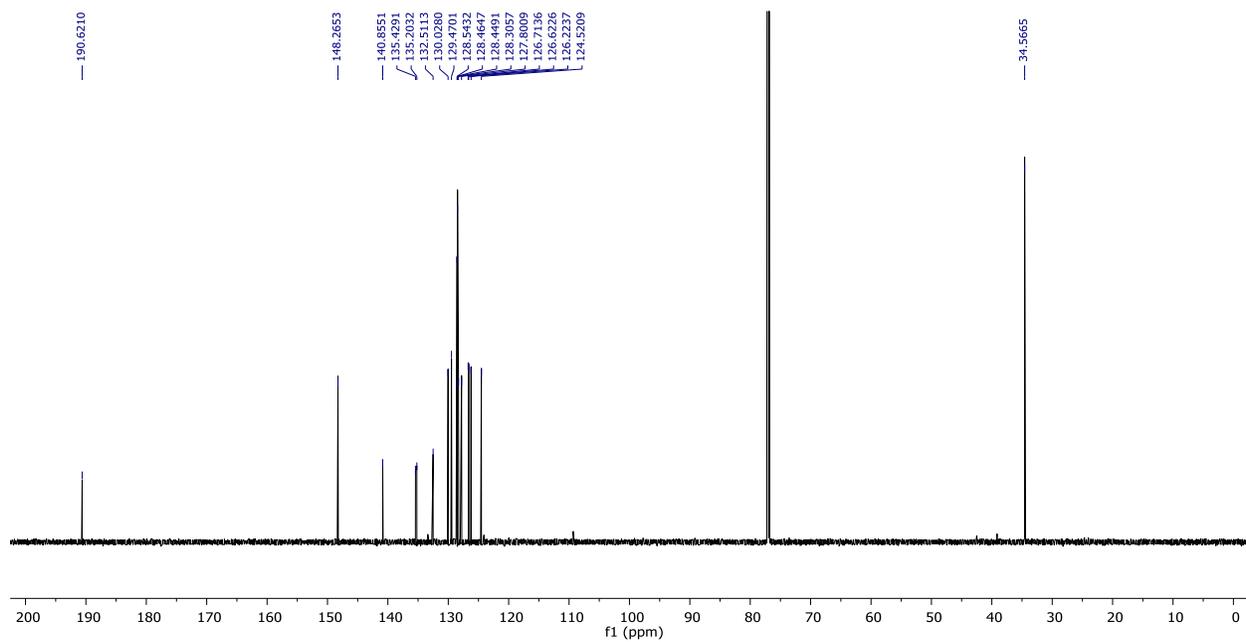


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR of **S6** (CDCl_3 , 295 K).

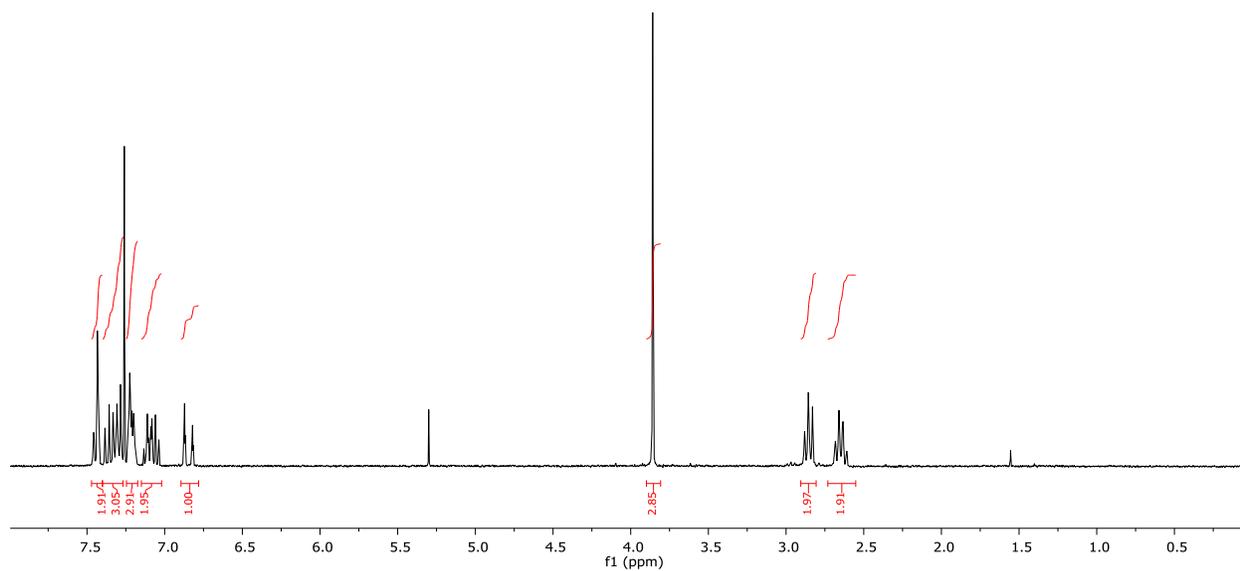
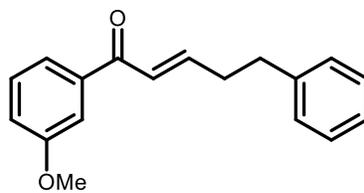


Figure S21. ^1H NMR of **S7** (CDCl_3 , 295 K).

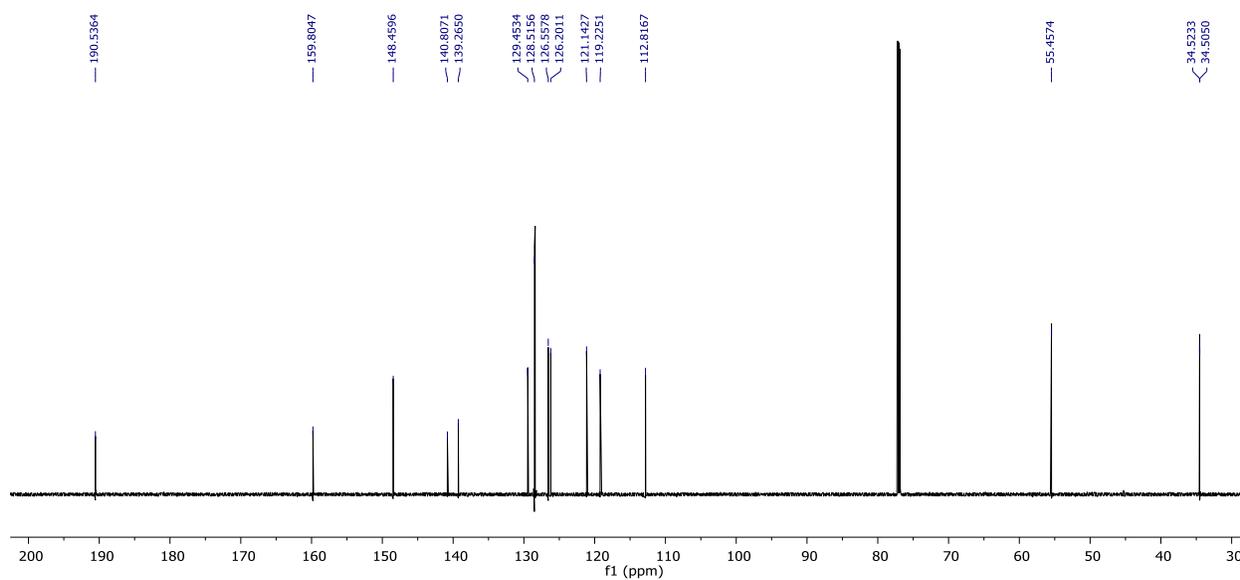


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR of **S7** (CDCl_3 , 295 K).

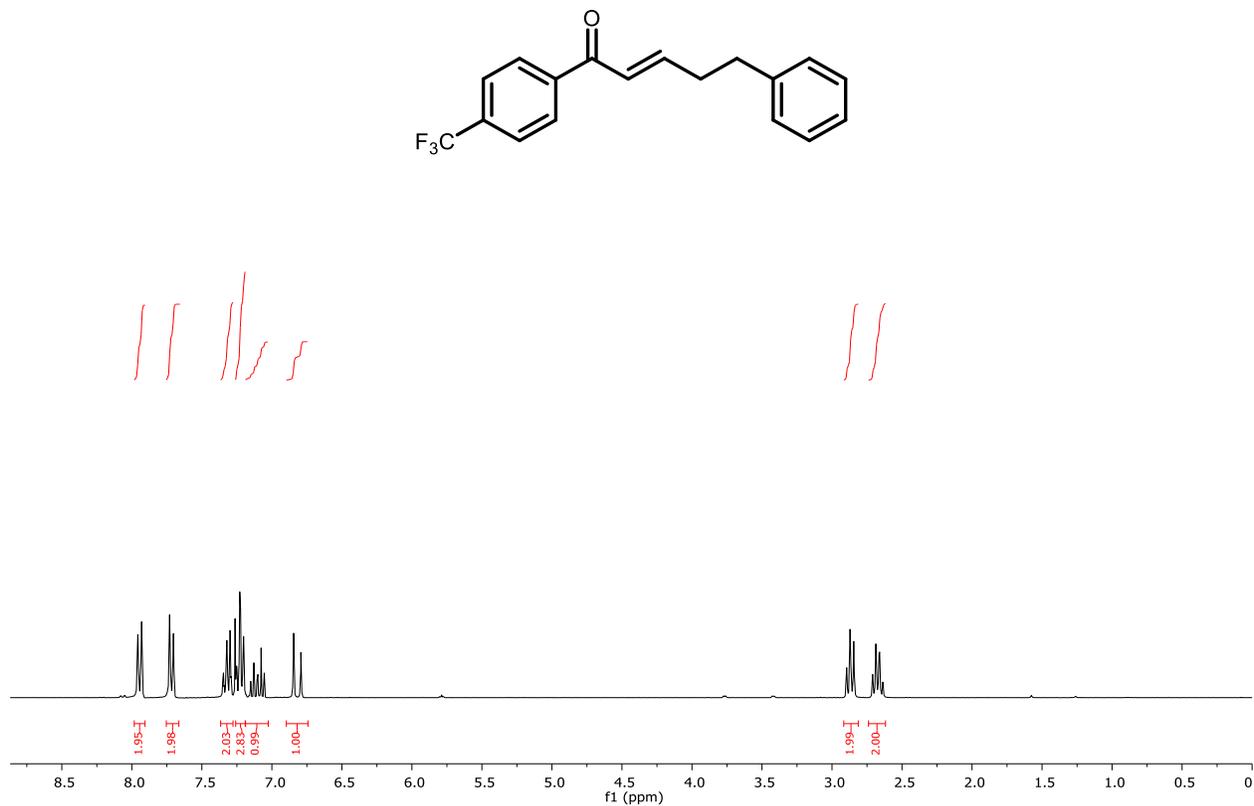


Figure S23. ^1H NMR of **S8** (CDCl_3 , 295 K).

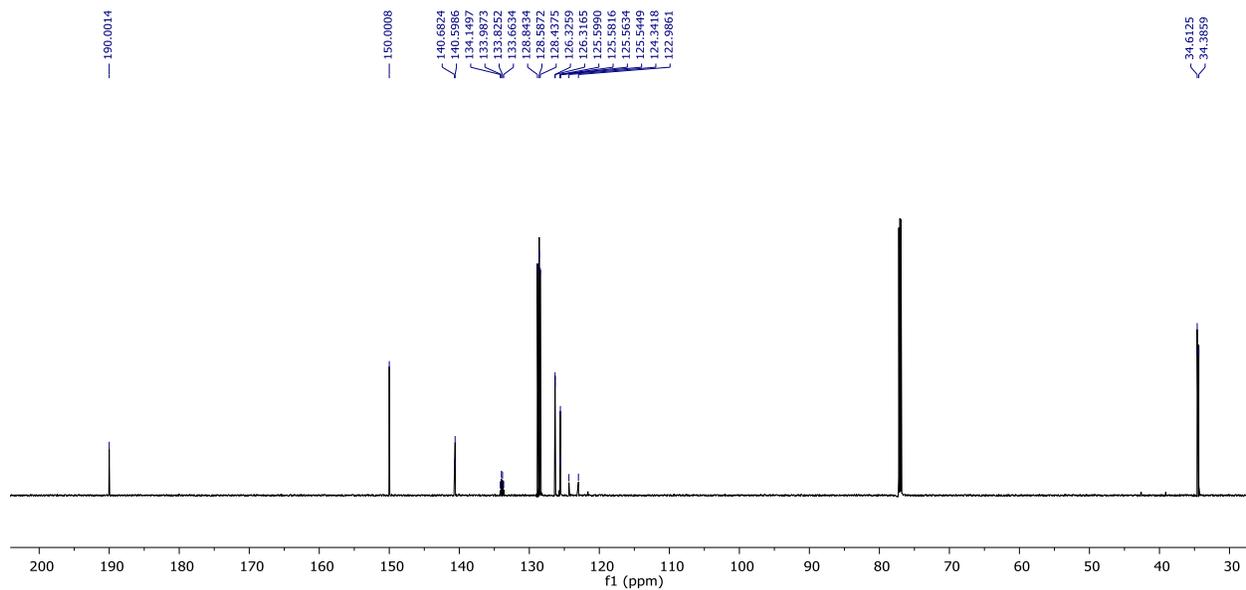


Figure S24. $^{13}\text{C}\{^1\text{H}\}$ NMR of **S8** (CDCl_3 , 295 K).

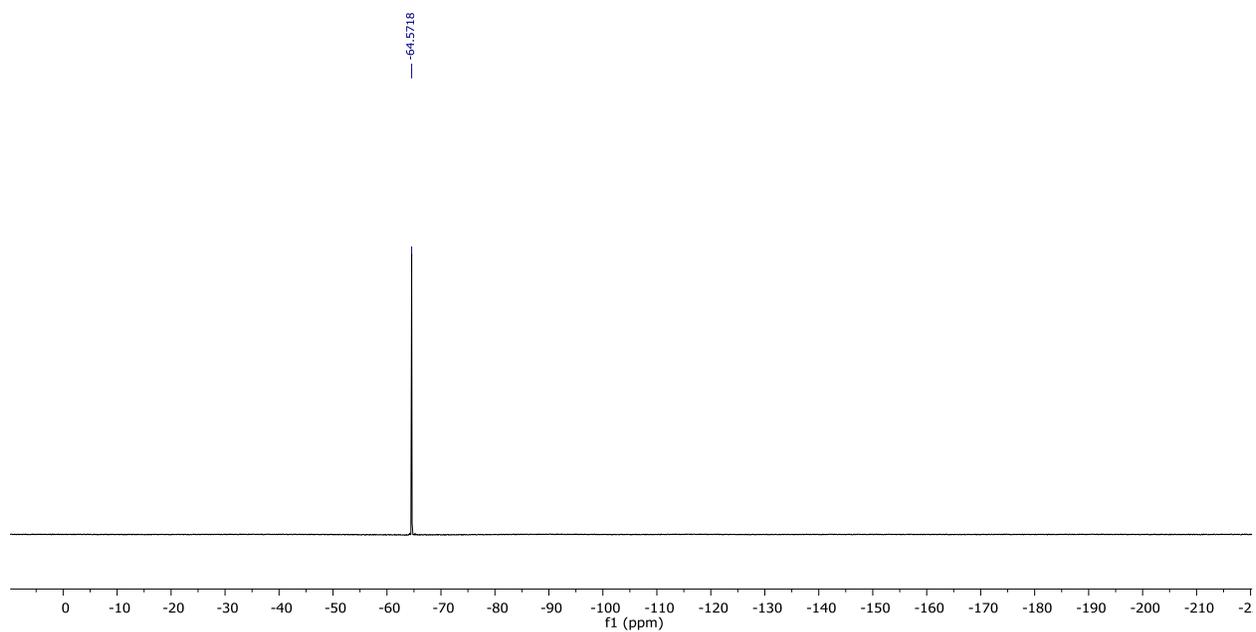


Figure S25. ^{19}F NMR of **S8** (CDCl_3 , 295 K).

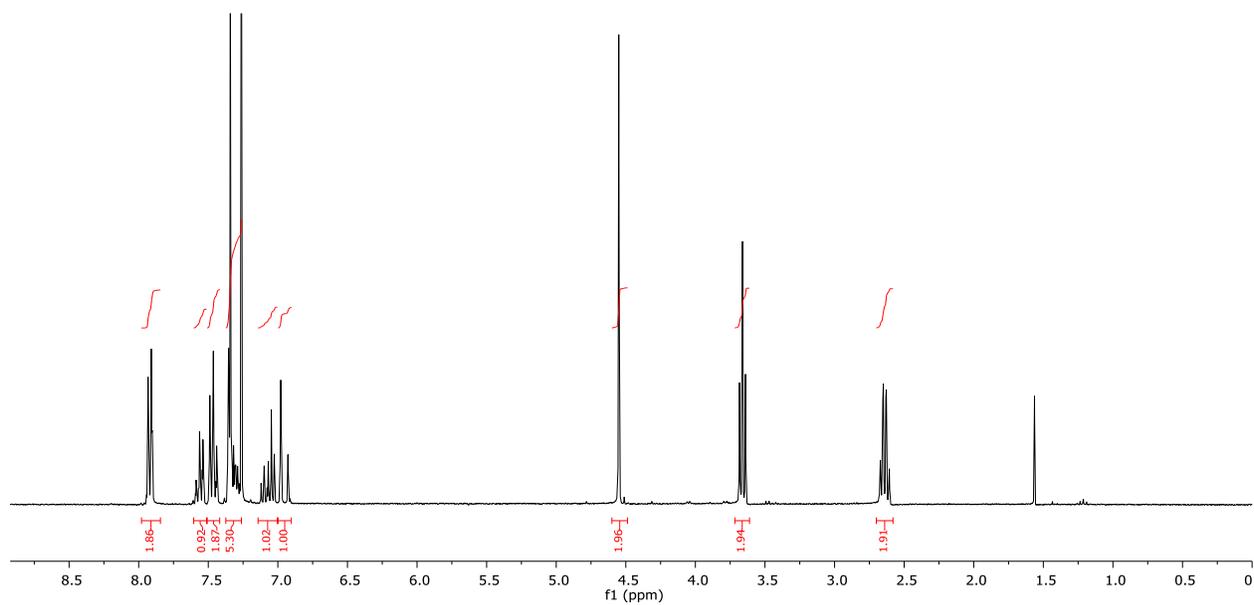
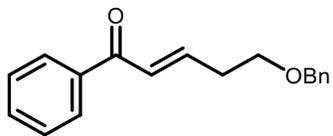


Figure S26. ^1H NMR of **S9** (CDCl_3 , 295 K).

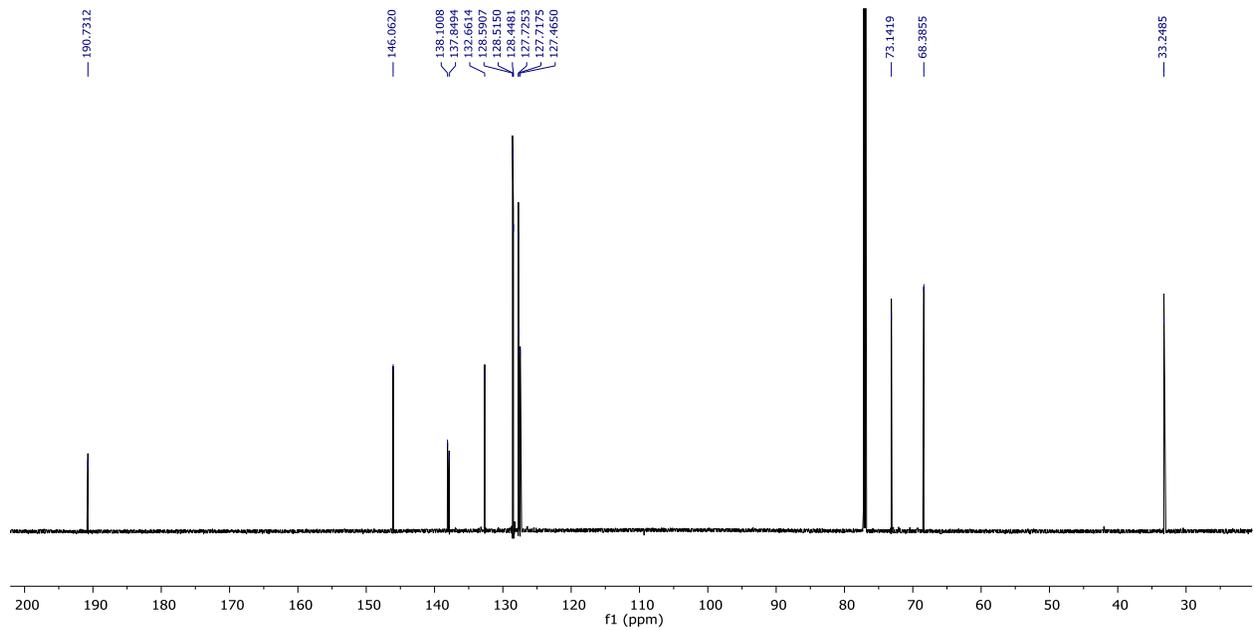


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR of **S9** (CDCl_3 , 295 K).

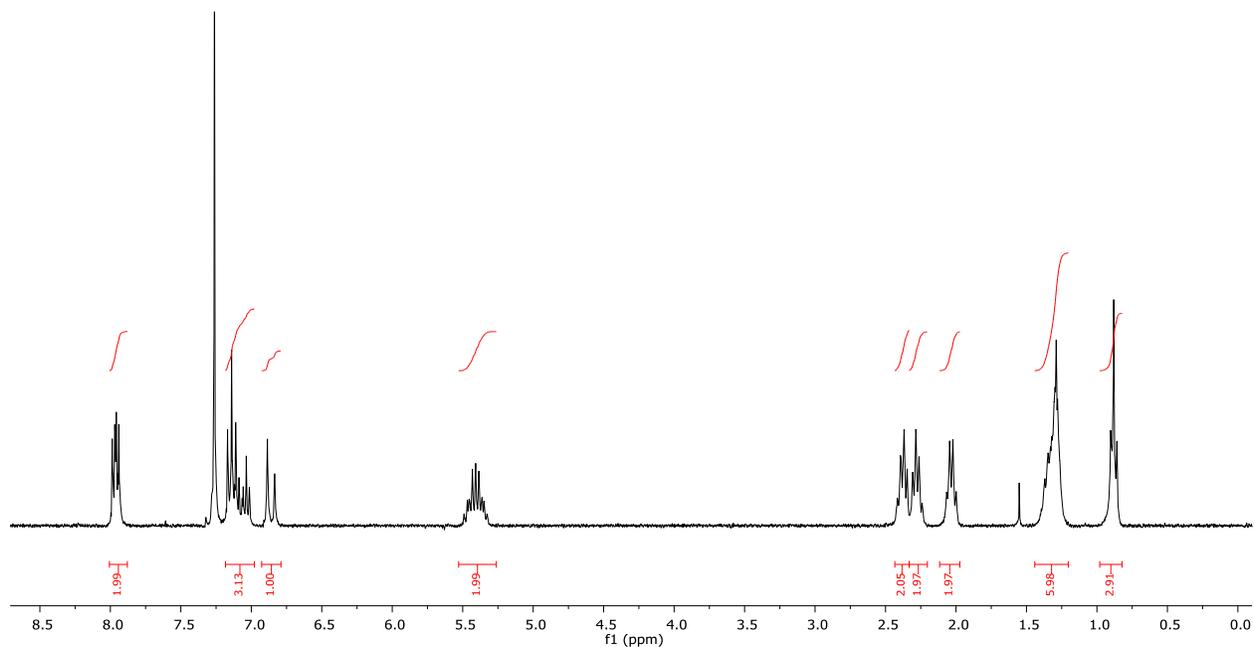
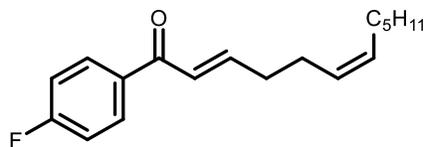


Figure S28. ¹H NMR of S10 (CDCl₃, 295 K).

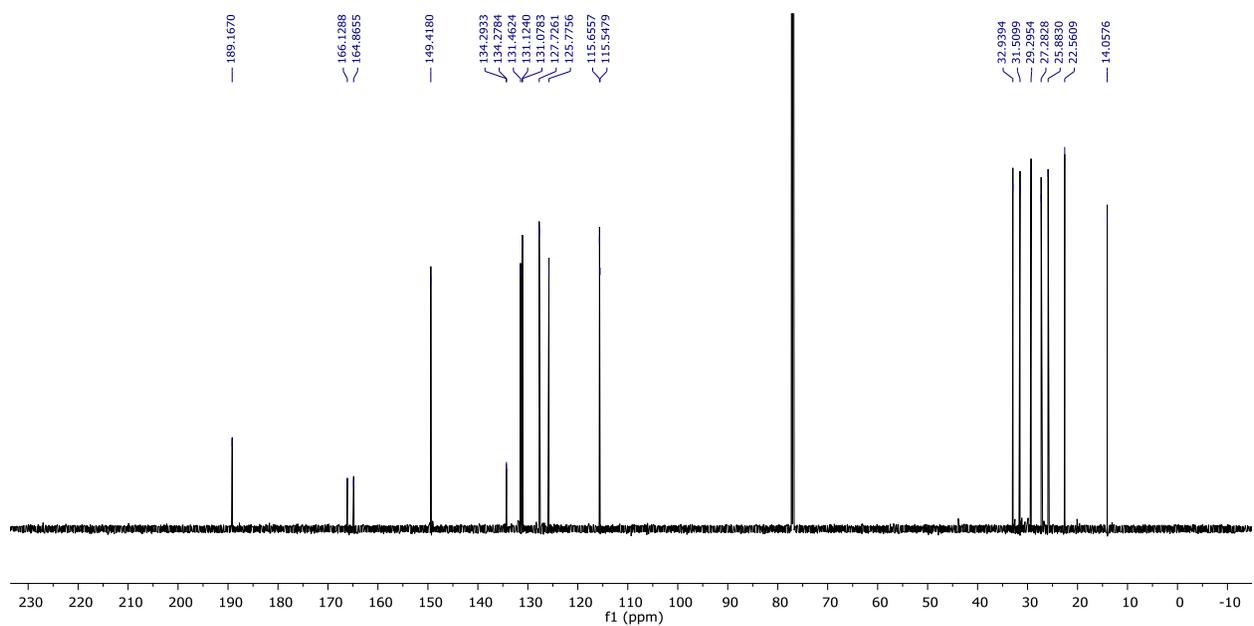


Figure S29. ¹³C{¹H} NMR of S10 (CDCl₃, 295 K).

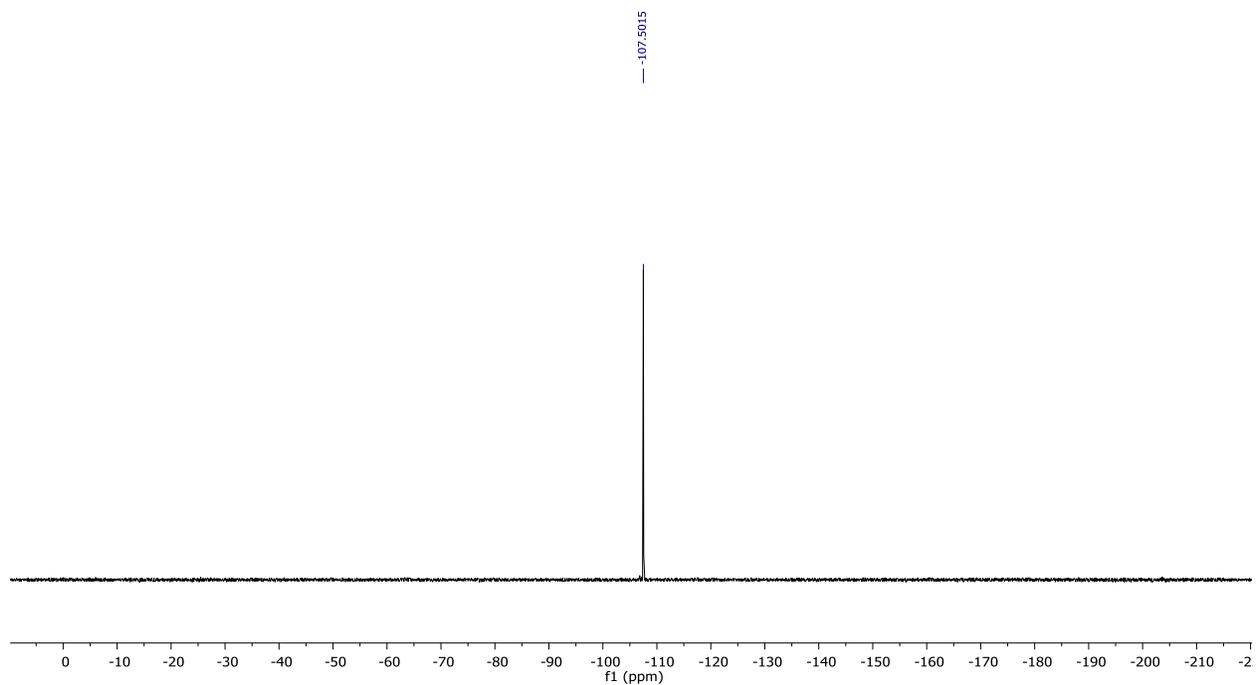


Figure S30. ^{19}F NMR of **S10** (CDCl_3 , 295 K).

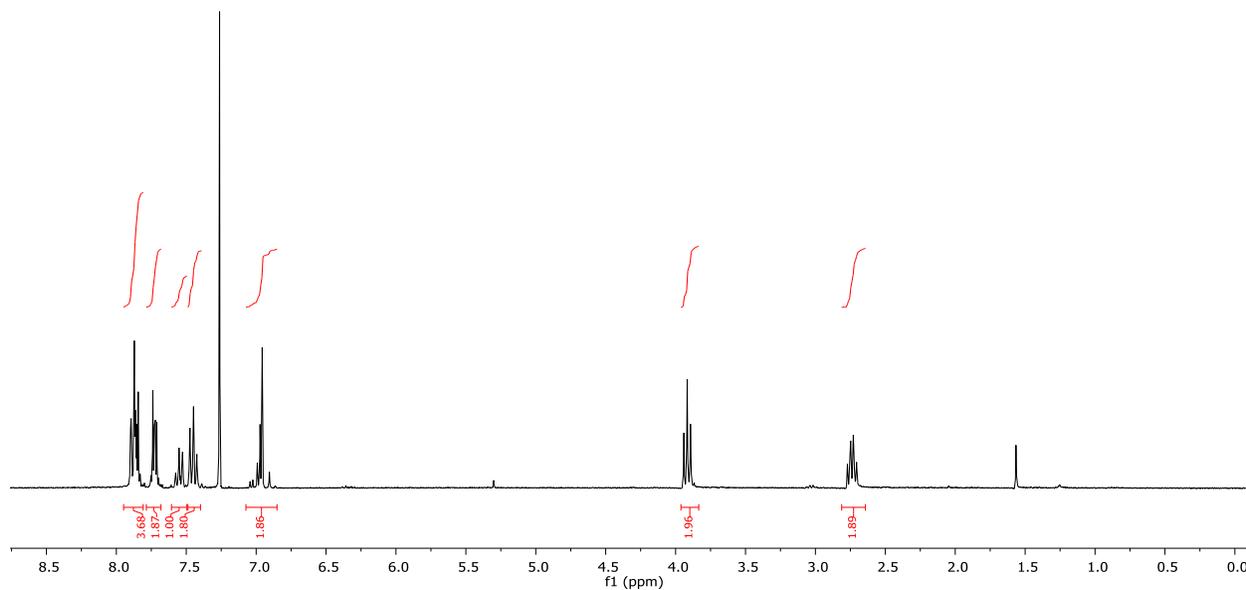
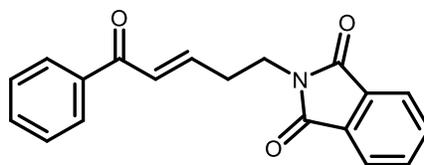


Figure S31. ^1H NMR of **S11** (CDCl_3 , 295 K).

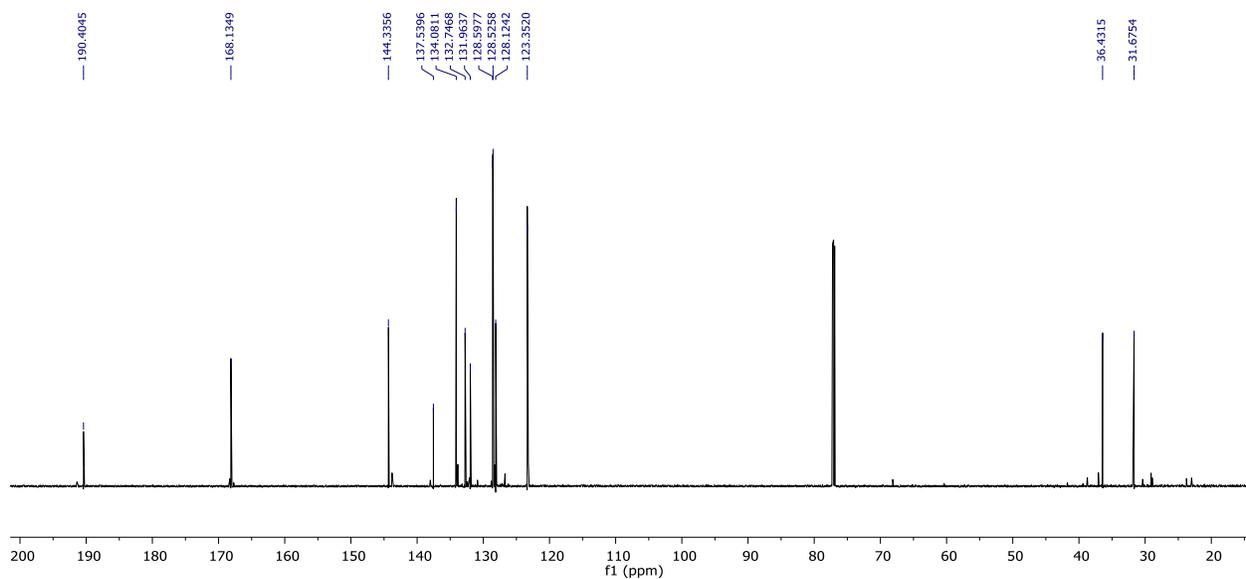


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR of **S11** (CDCl_3 , 295 K).

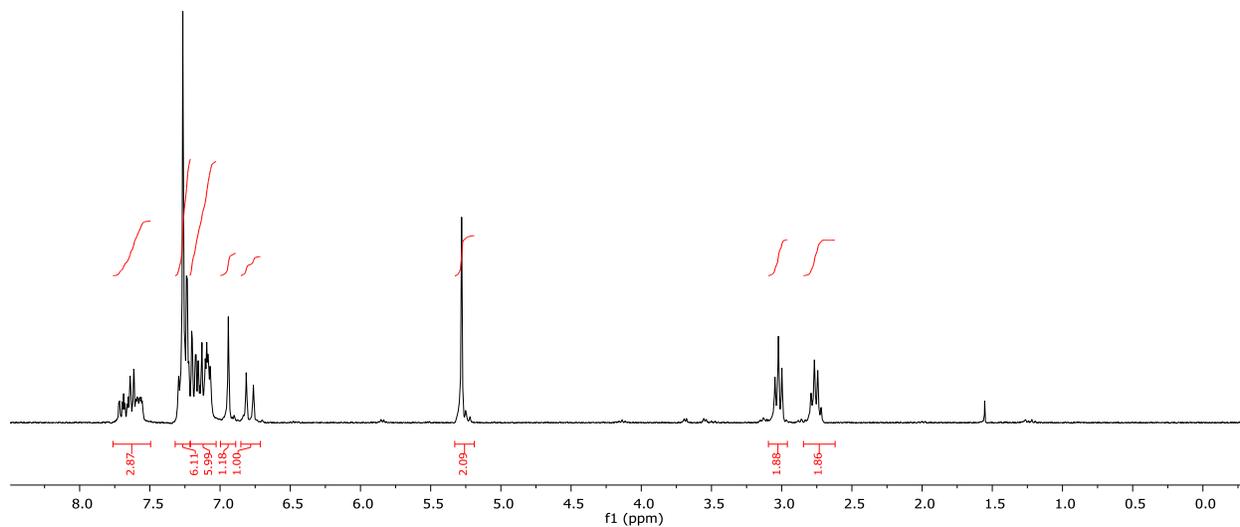
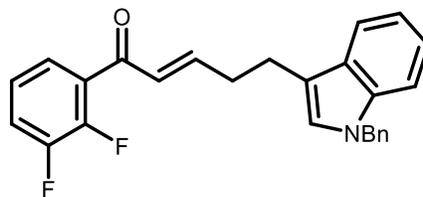


Figure S33. ^1H NMR of **S12** (CDCl_3 , 295 K).

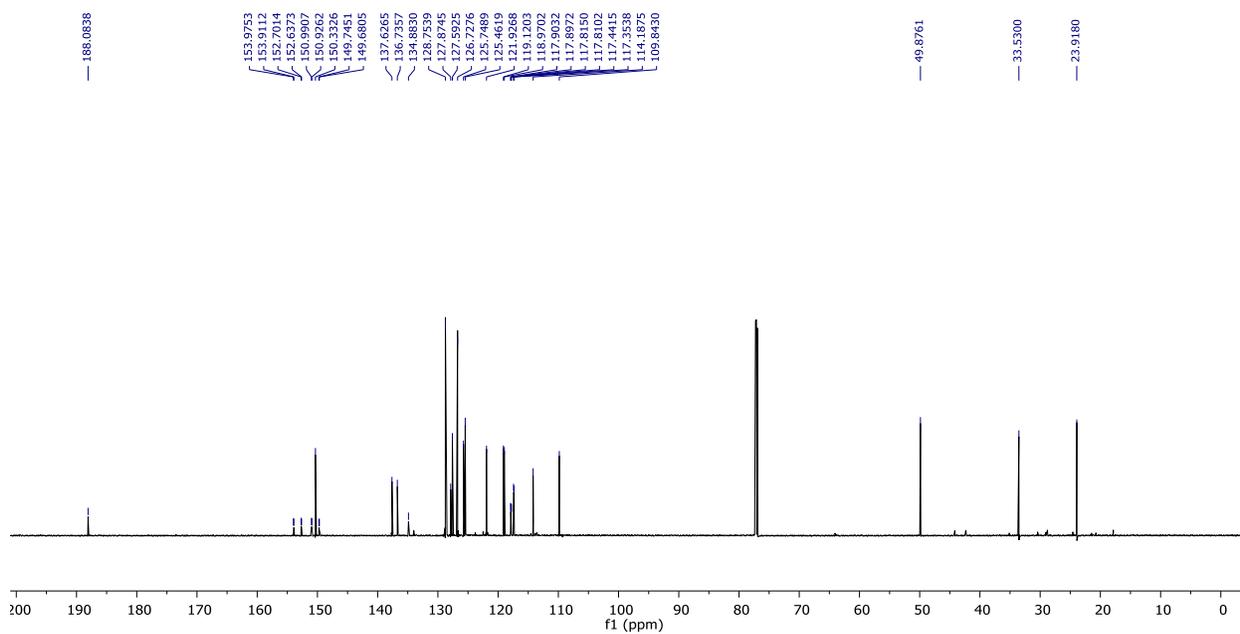


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR of **S12** (CDCl_3 , 295 K).

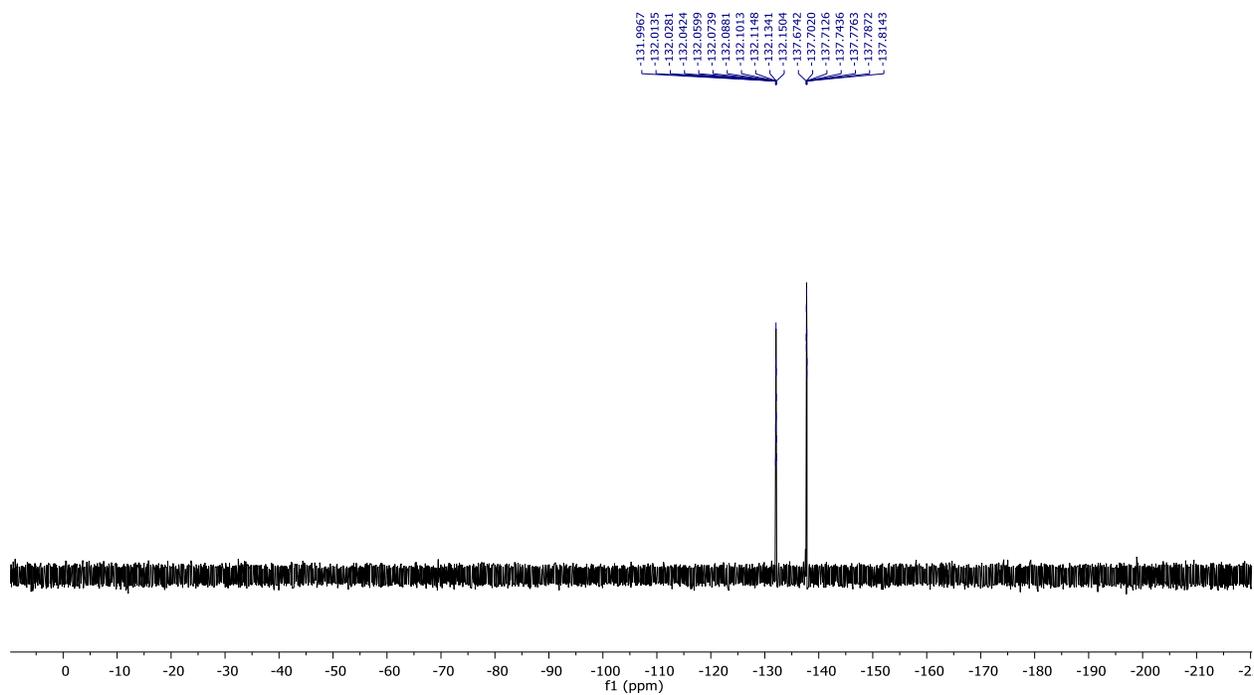


Figure S35. ^{19}F NMR of **S12** (CDCl_3 , 295 K).

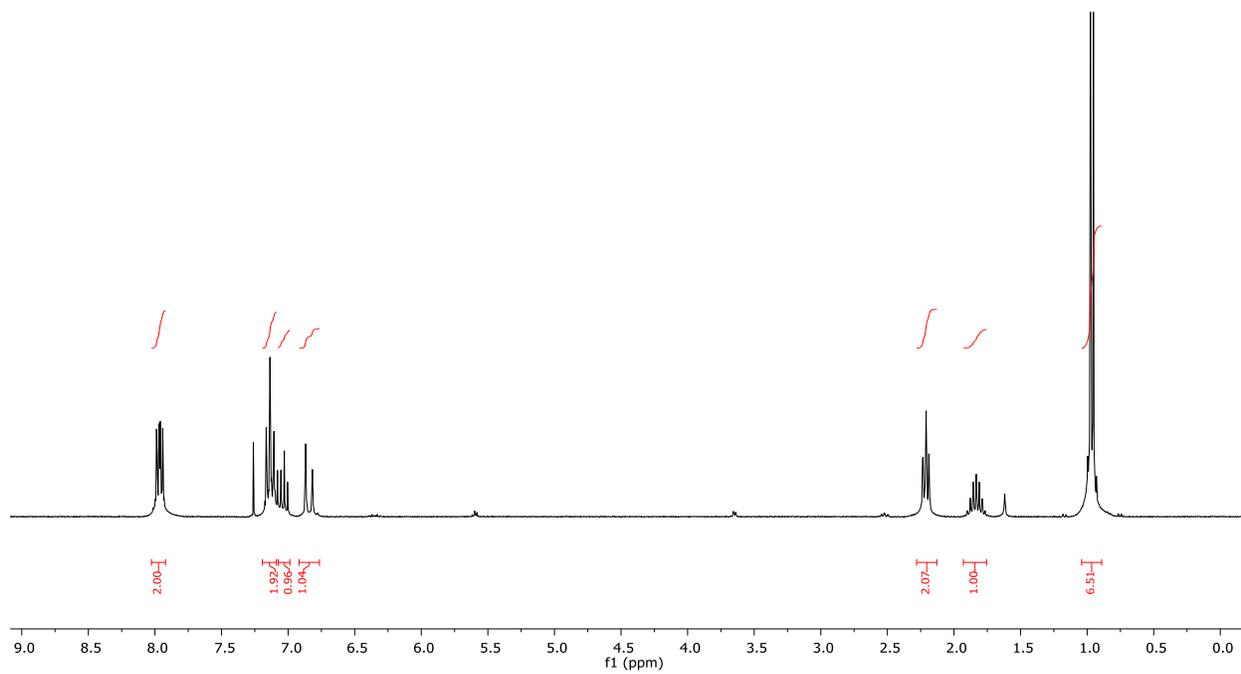
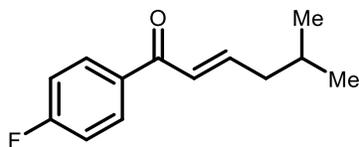


Figure S36. ^1H NMR of S13 (CDCl_3 , 295 K).

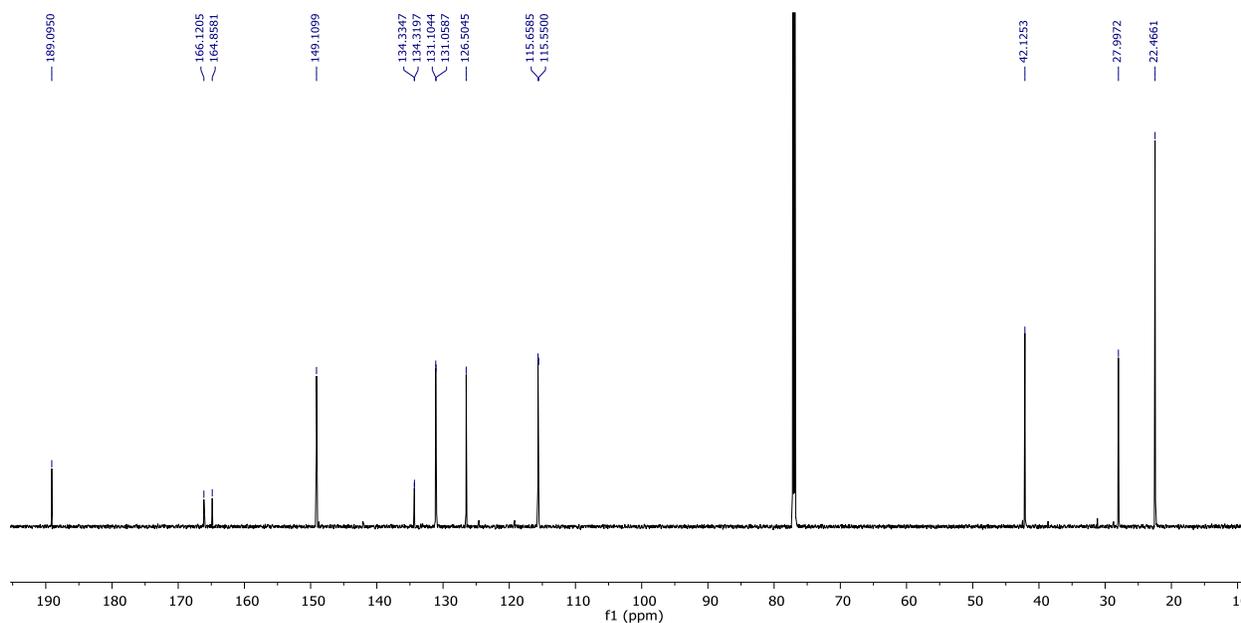


Figure S37. $^{13}\text{C}\{^1\text{H}\}$ NMR of S13 (CDCl_3 , 295 K).

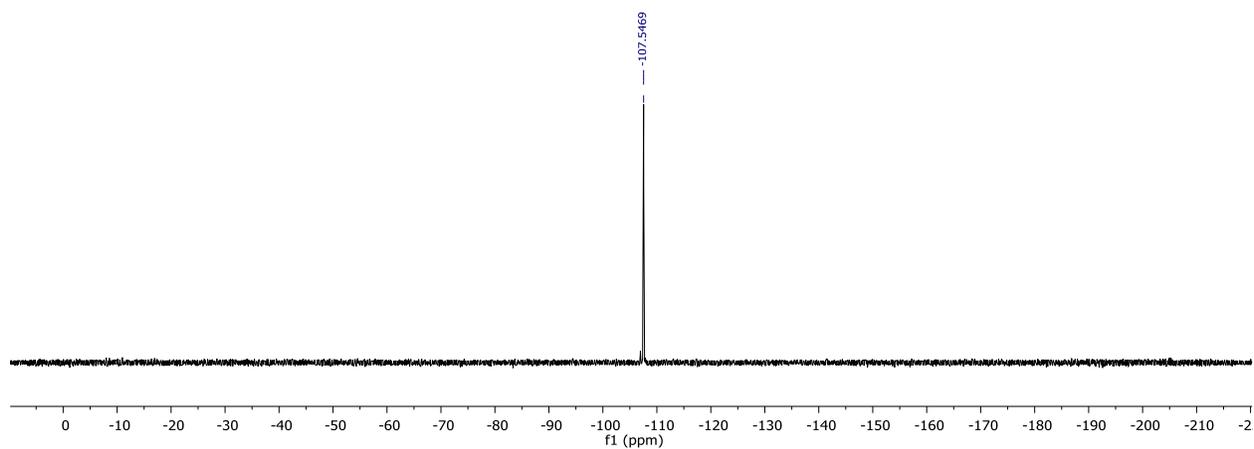
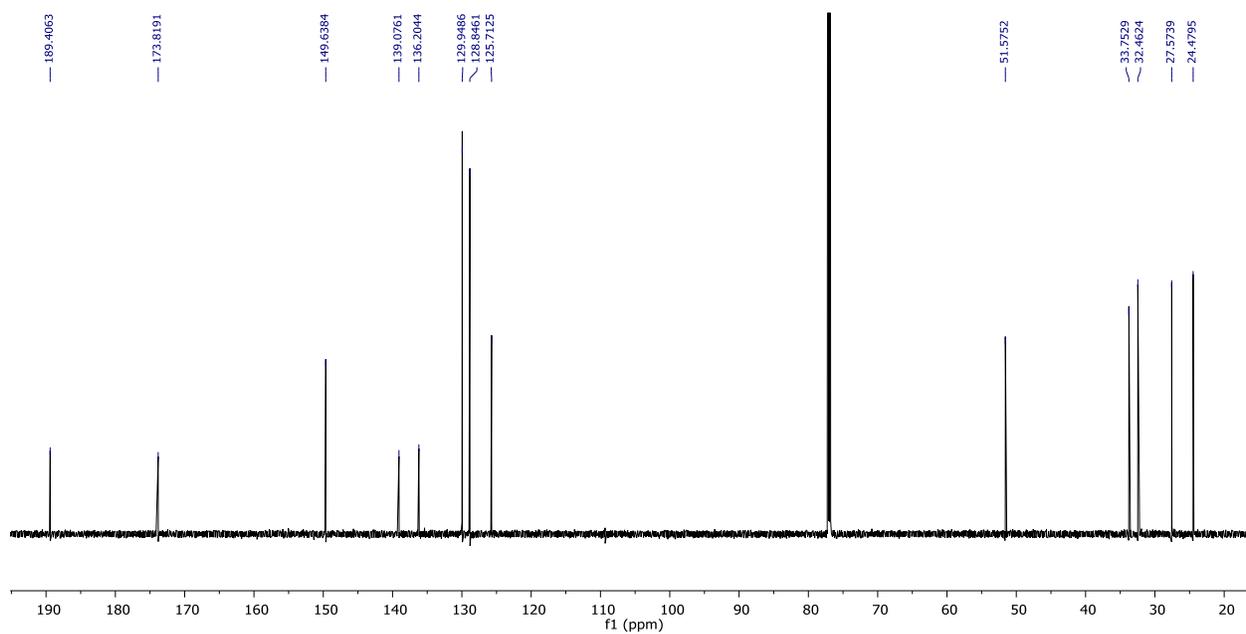
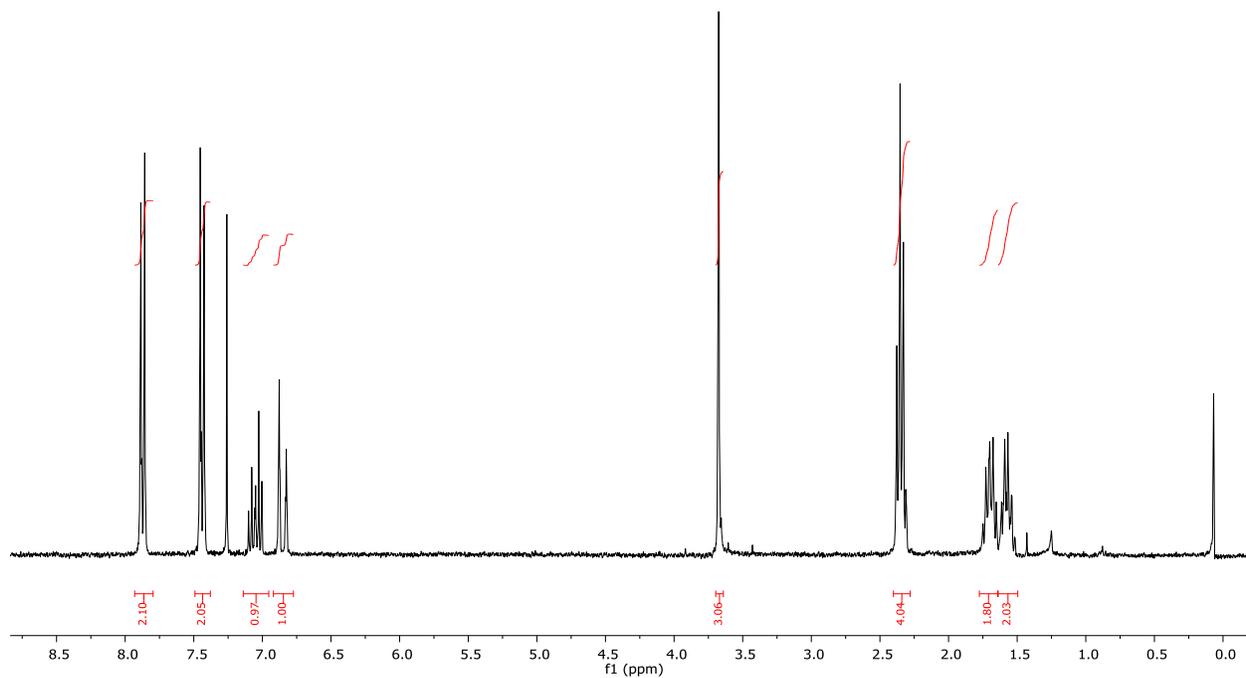
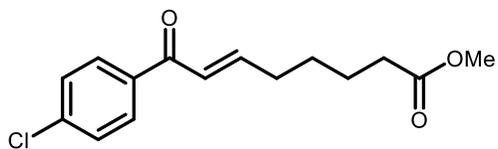


Figure S38. ^{19}F NMR of **S13** (CDCl_3 , 295 K).



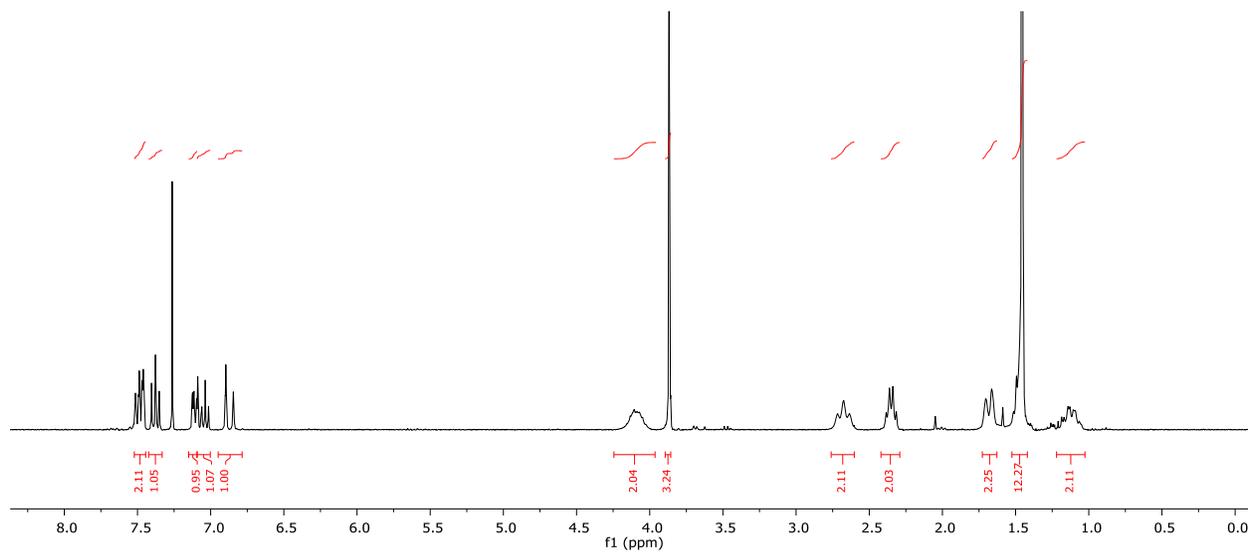
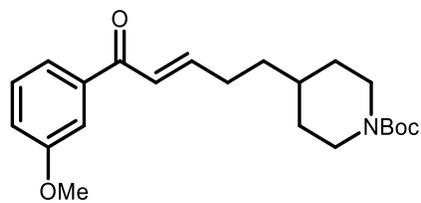


Figure S41. ^1H NMR of S15 (CDCl₃, 295 K).

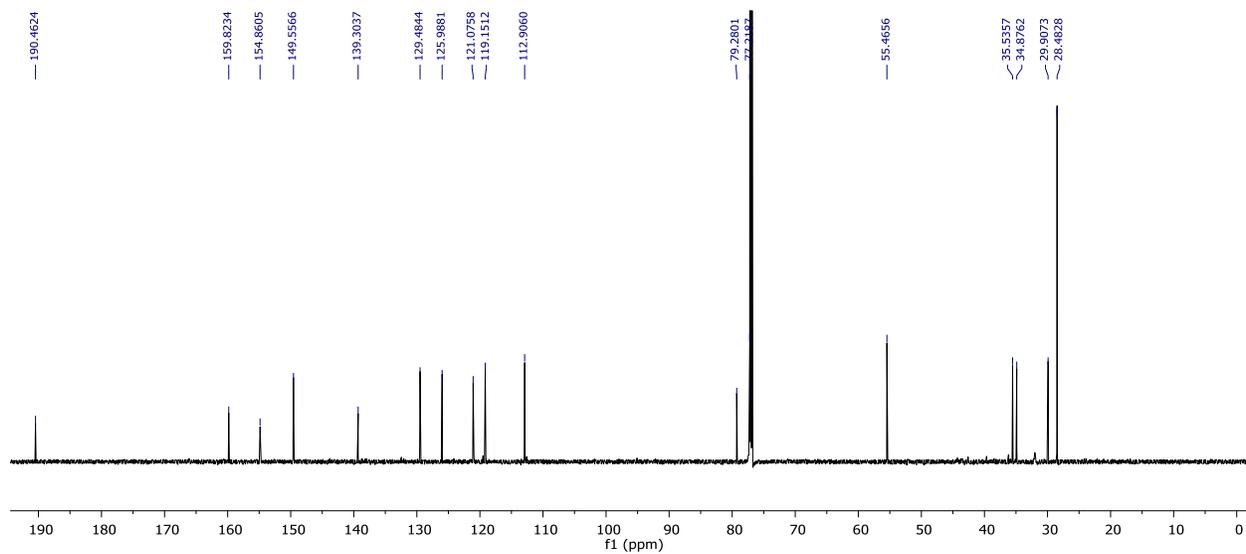


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ NMR of S15 (CDCl₃, 295 K).

12. NMR Data for Cyclopentanes

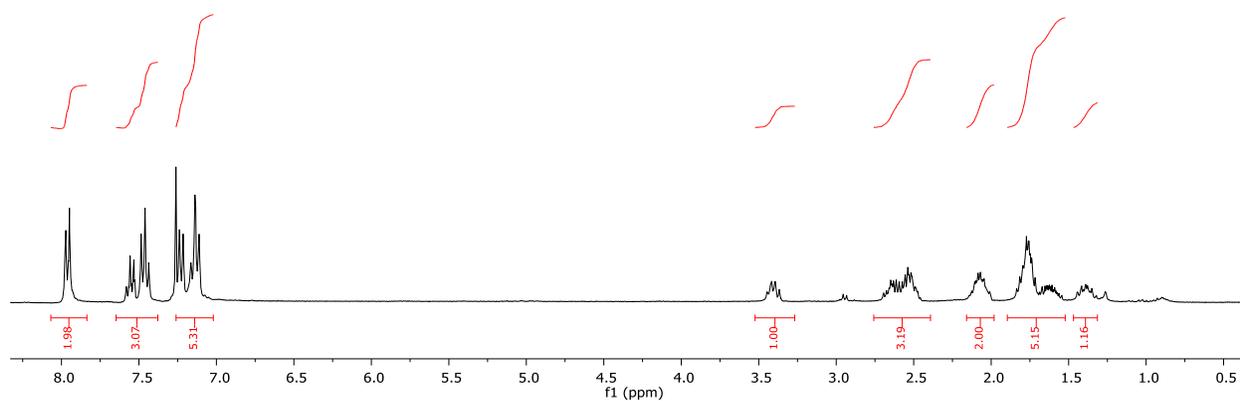
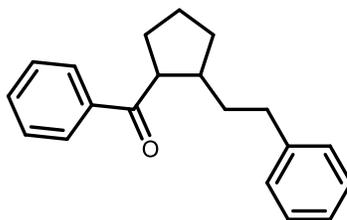


Figure S43. ^1H NMR of **3** (CDCl_3 , 295 K).

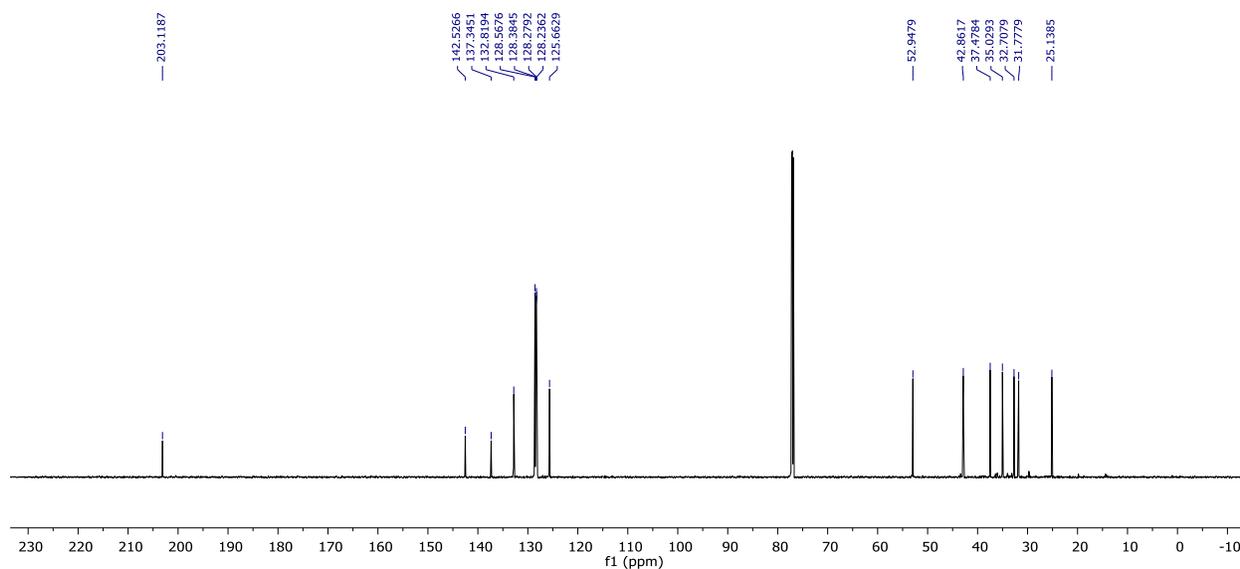


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR of **3** (CDCl_3 , 295 K).

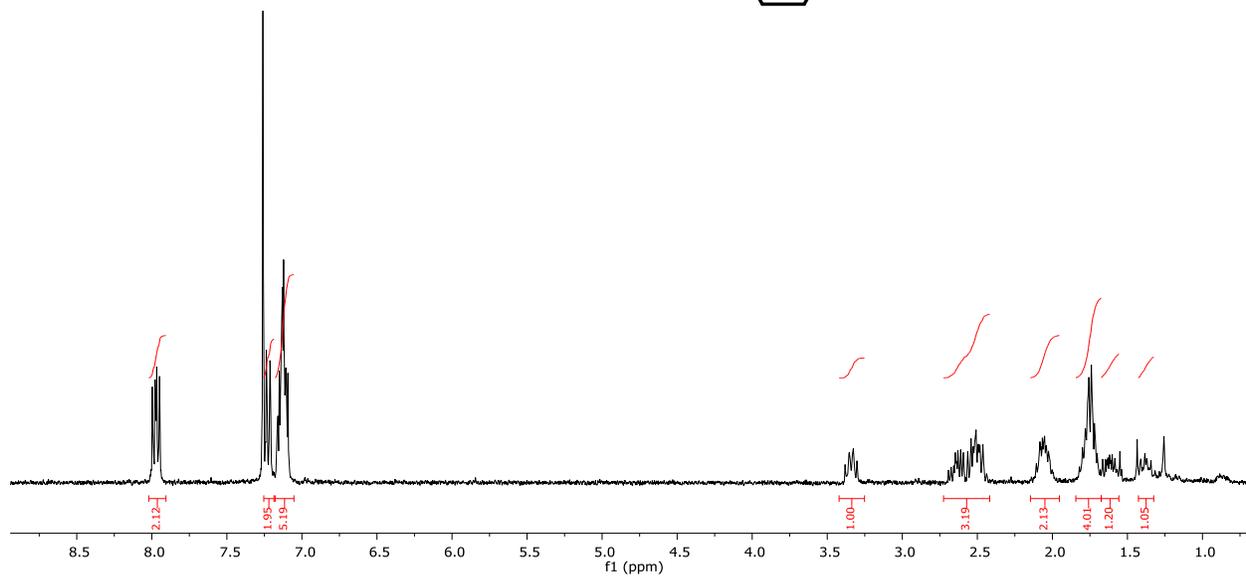
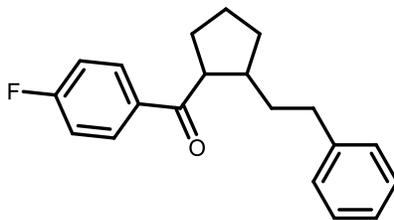


Figure S45. ^1H NMR of **5** (CDCl_3 , 295 K).

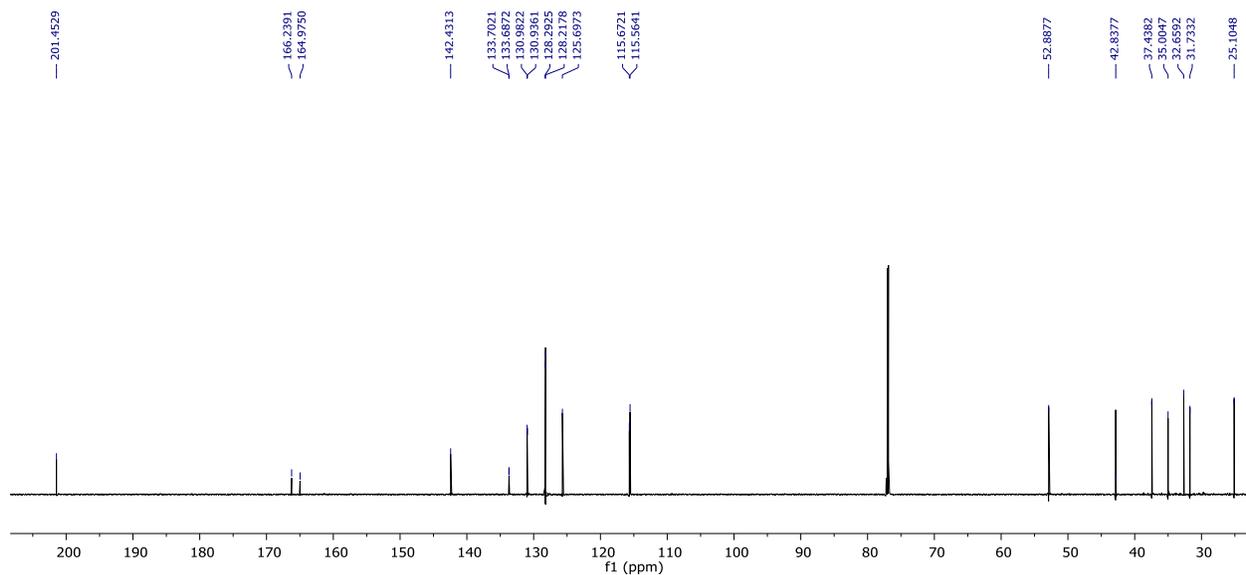


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR of **5** (CDCl_3 , 295 K).

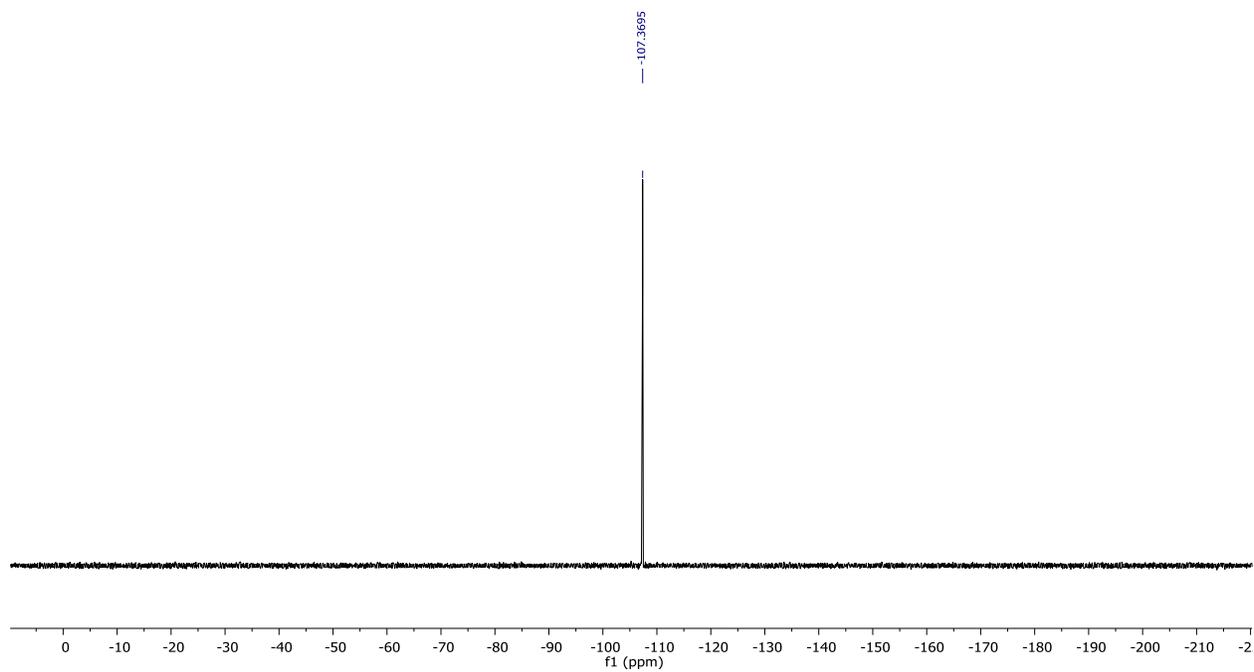


Figure S47. ^{19}F NMR of **5** (CDCl_3 , 295 K).

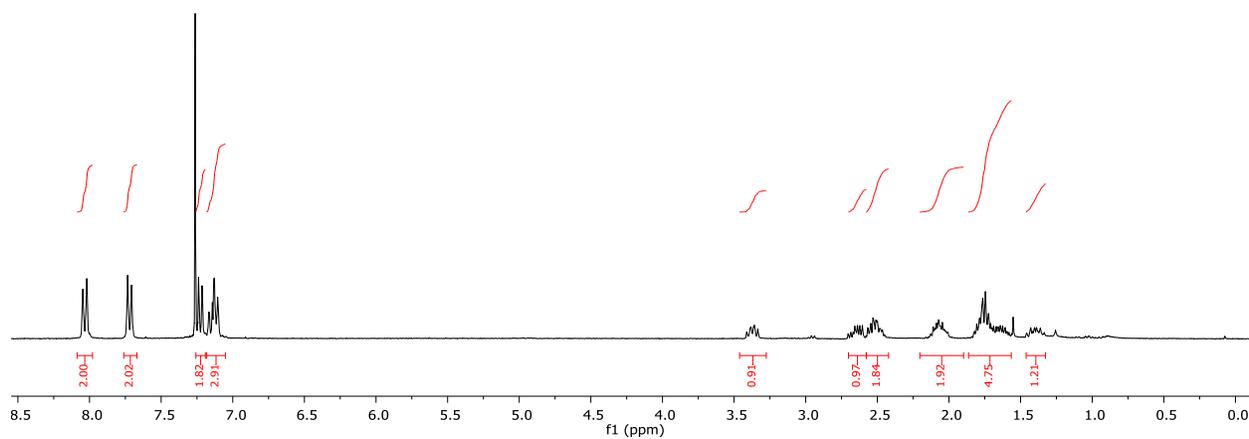
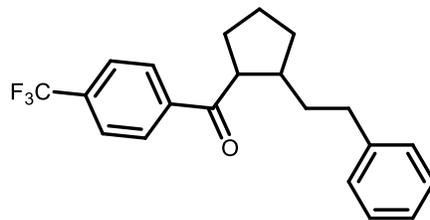


Figure S48. ^1H NMR of **6** (CDCl_3 , 295 K).

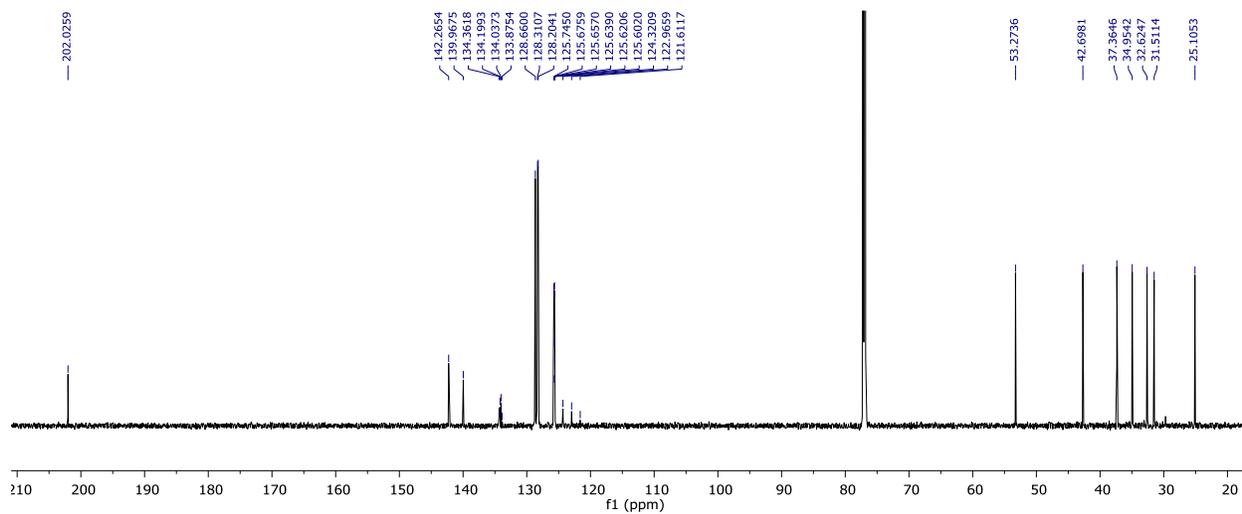


Figure S49. $^{13}\text{C}\{^1\text{H}\}$ NMR of **6** (CDCl_3 , 295 K).

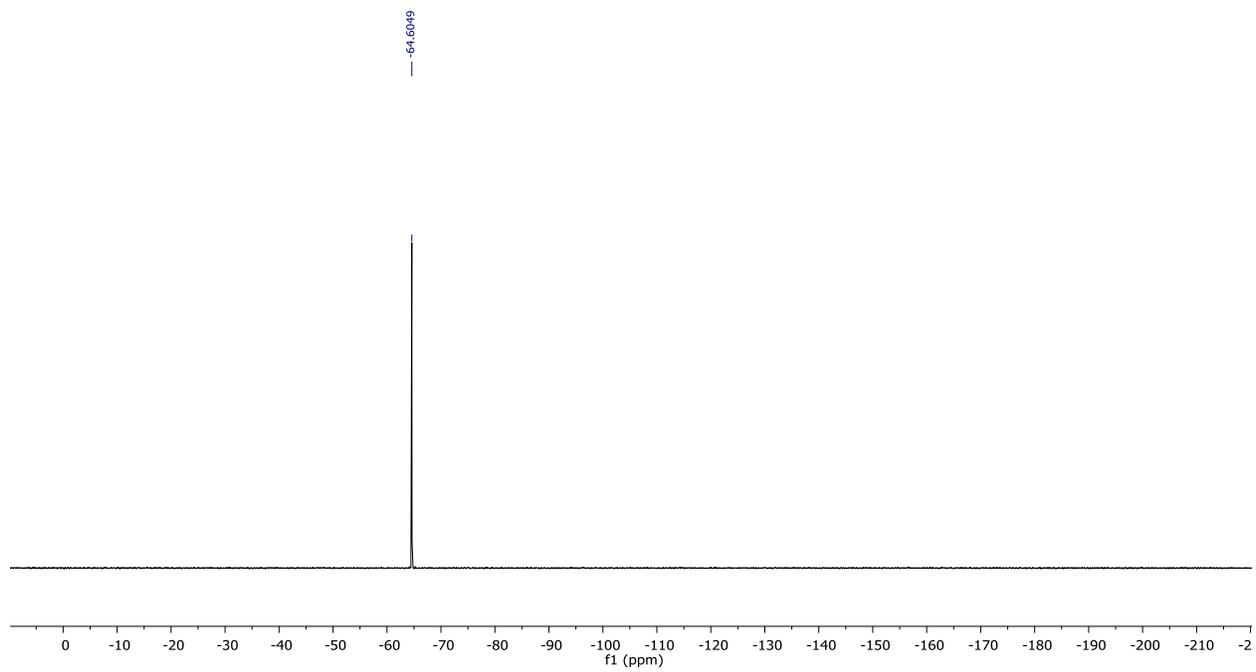


Figure S50. ^{19}F NMR of **6** (CDCl_3 , 295 K).

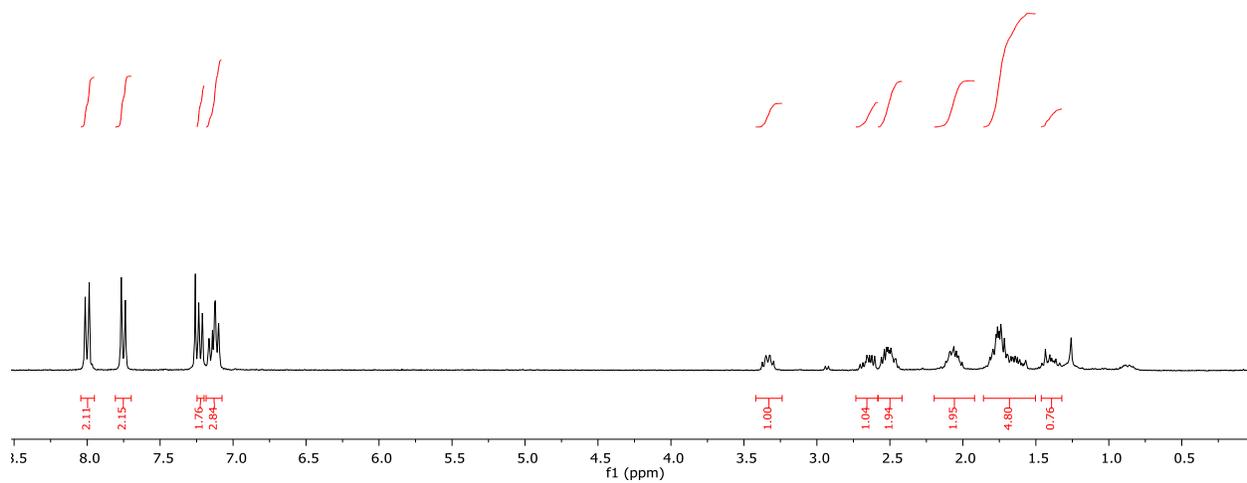
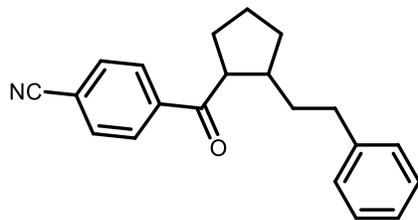


Figure S51. ^1H NMR of **7** (CDCl_3 , 295 K).

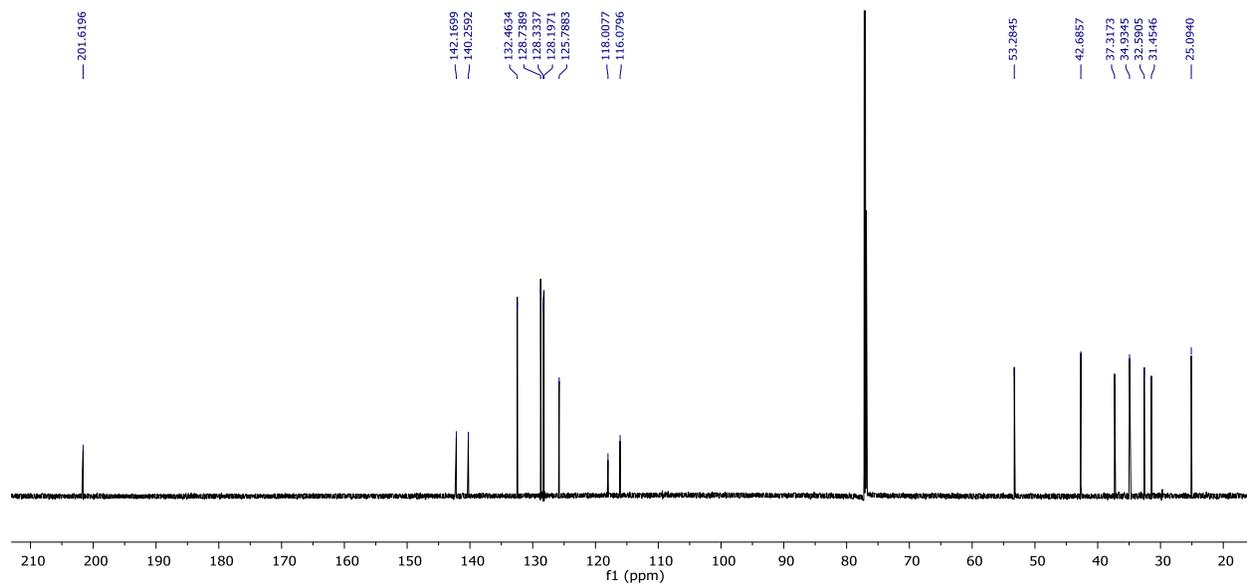


Figure S52. $^{13}\text{C}\{^1\text{H}\}$ NMR of **7** (CDCl_3 , 295 K).

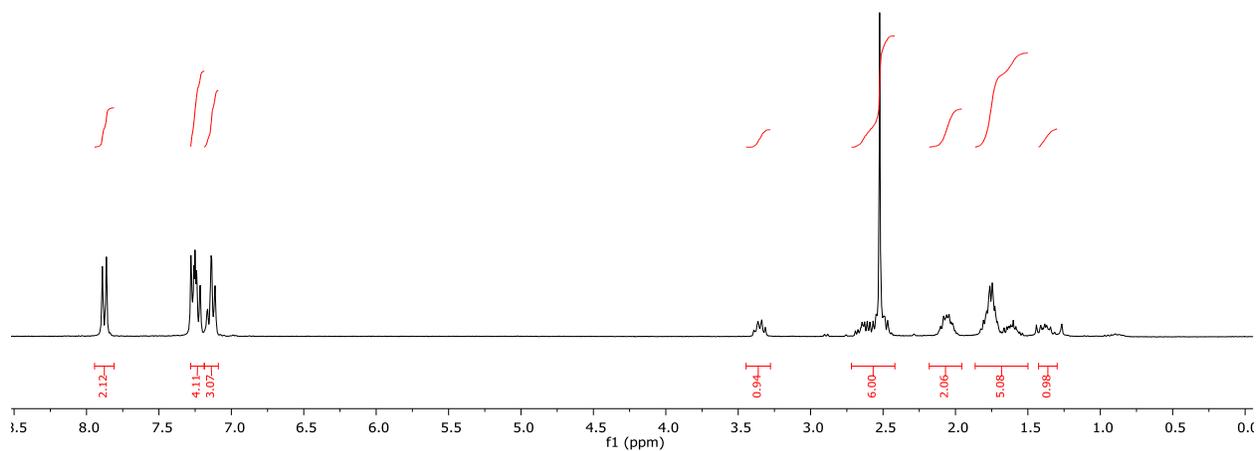
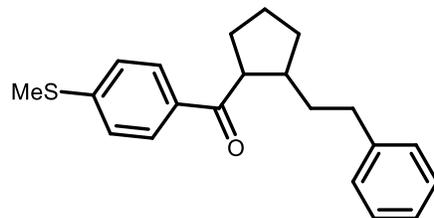


Figure S53. ^1H NMR of **8** (CDCl_3 , 295 K).

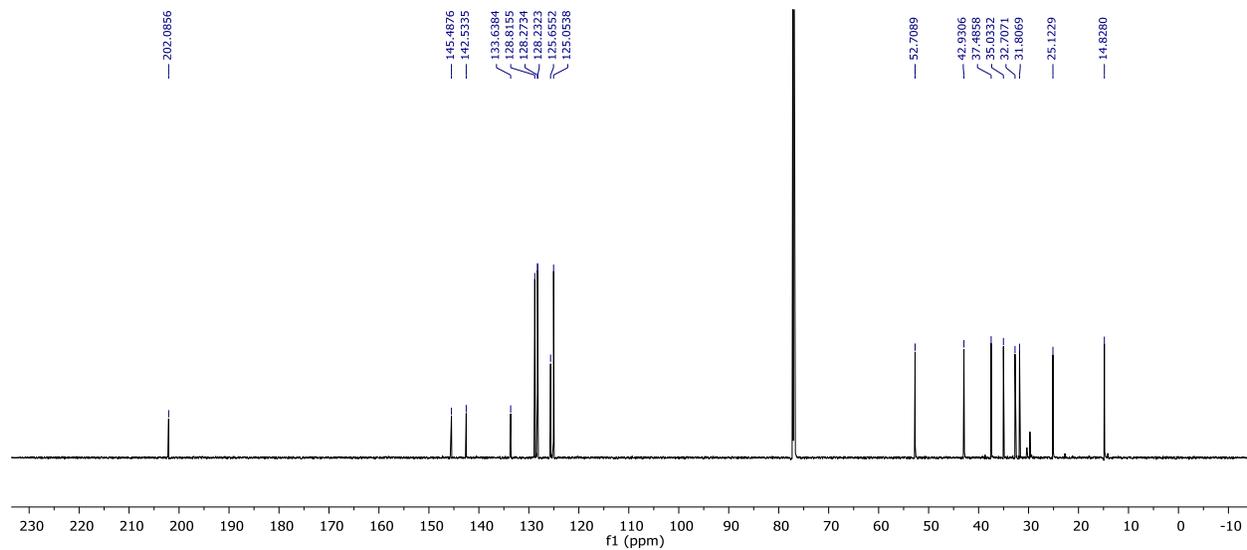


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR of **8** (CDCl_3 , 295 K).

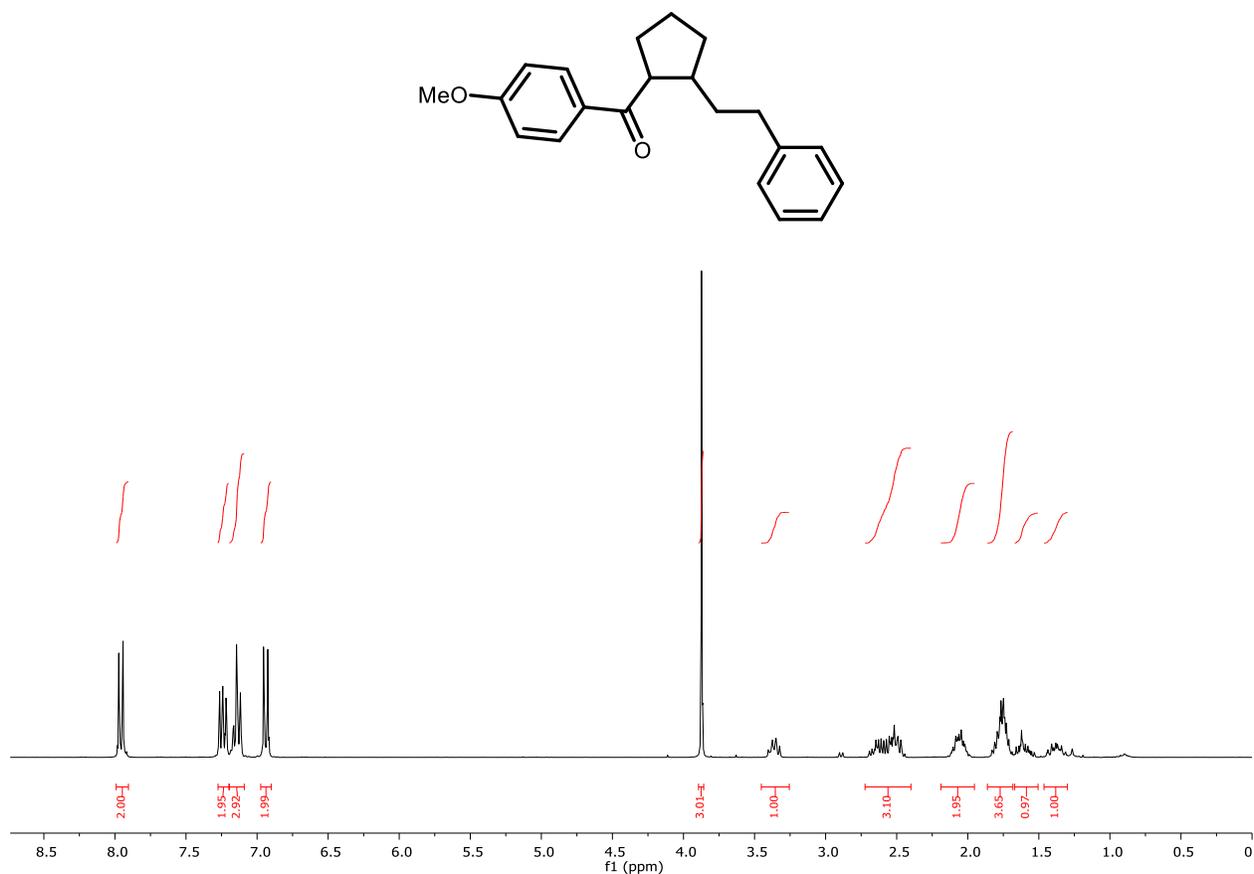


Figure S55. ¹H NMR of **9** (CDCl₃, 295 K).

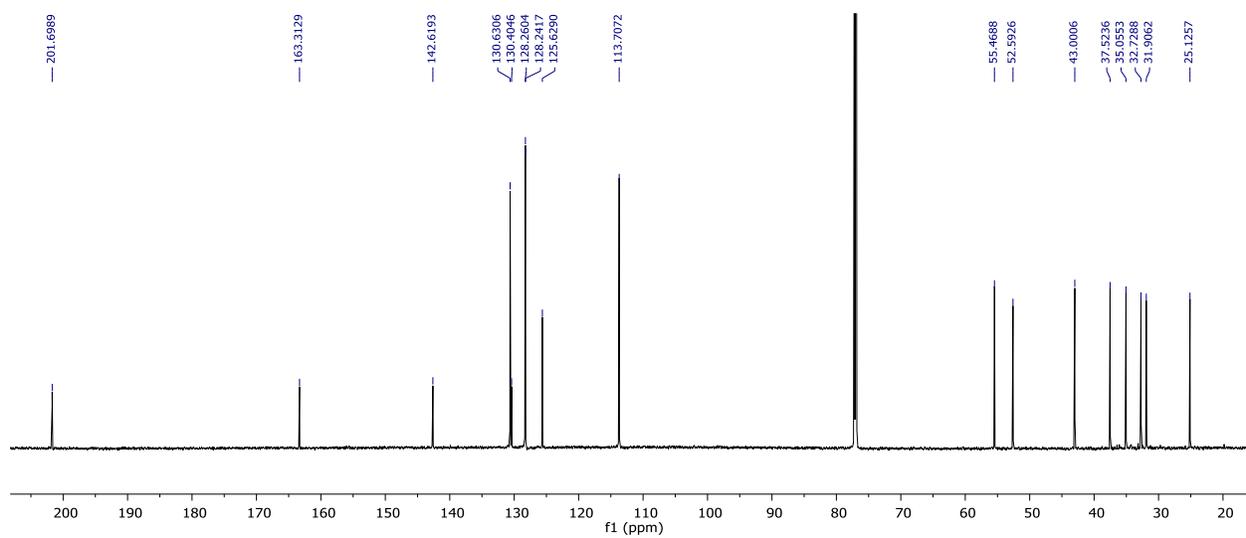


Figure S56. ¹³C{¹H} NMR of **9** (CDCl₃, 295 K).

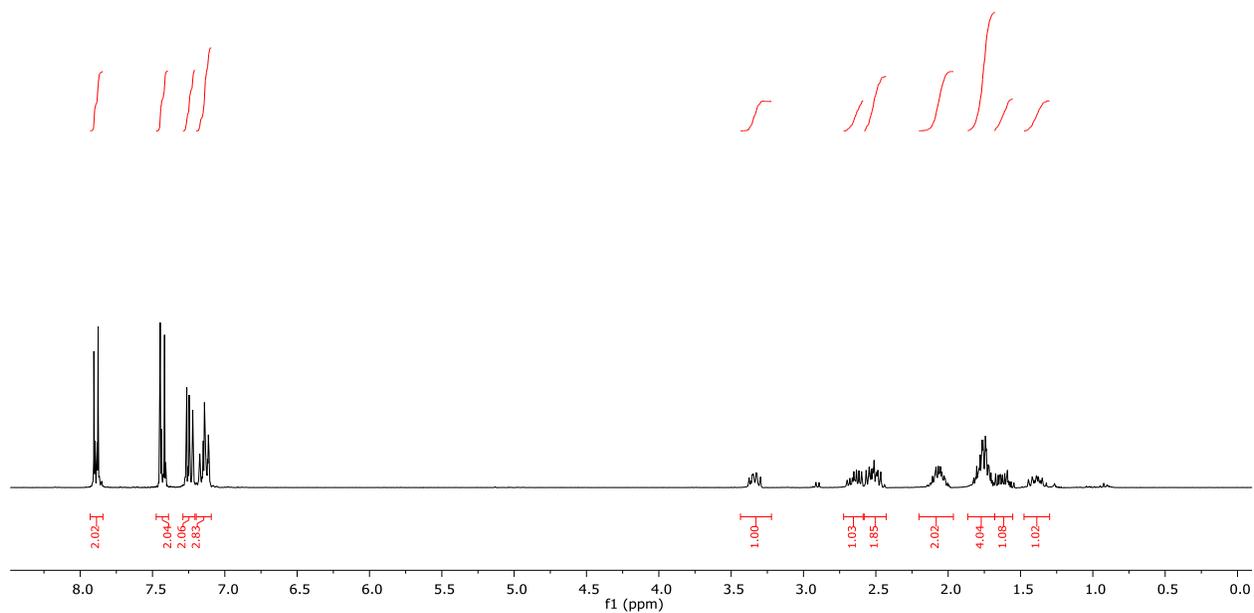
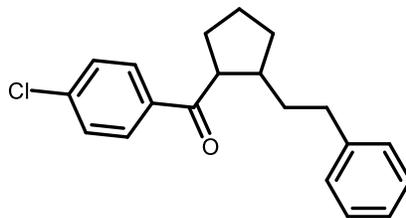


Figure S57. ^1H NMR of **10** (CDCl_3 , 295 K).

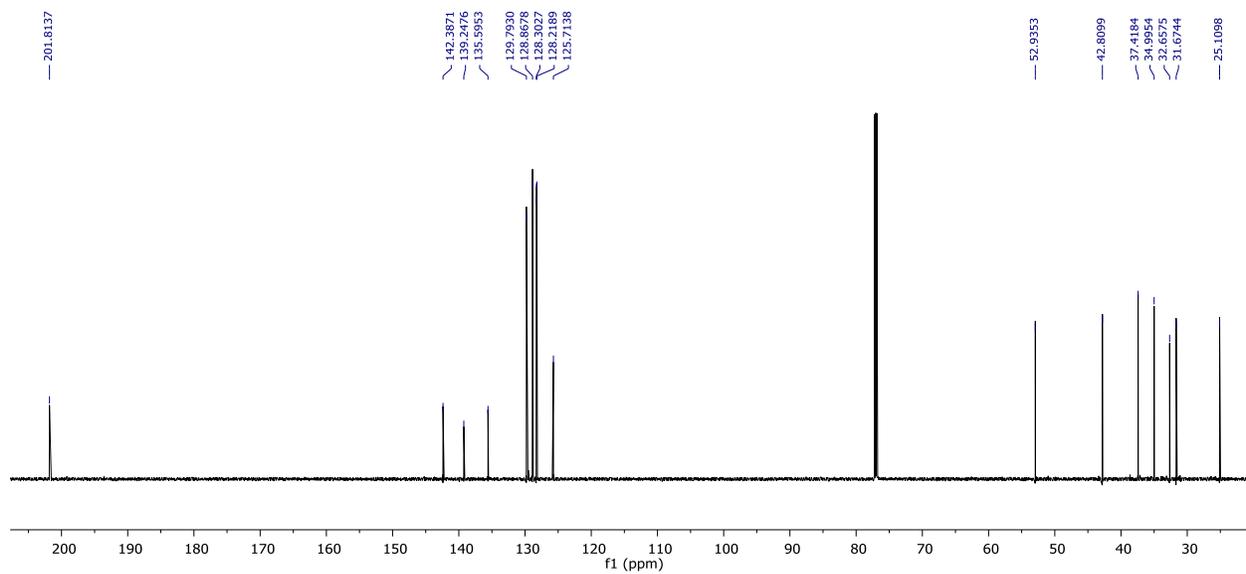


Figure S58. $^{13}\text{C}\{^1\text{H}\}$ NMR of **10** (CDCl_3 , 295 K).

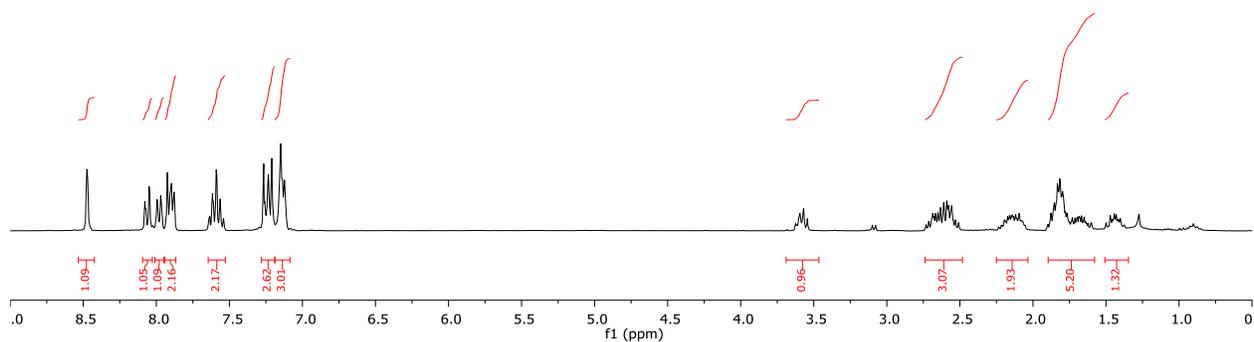
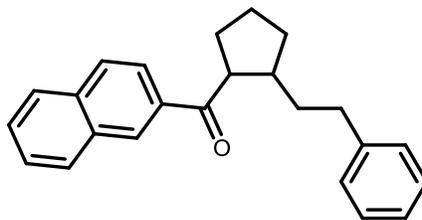


Figure S59. ^1H NMR of **11** (CDCl₃, 295 K).

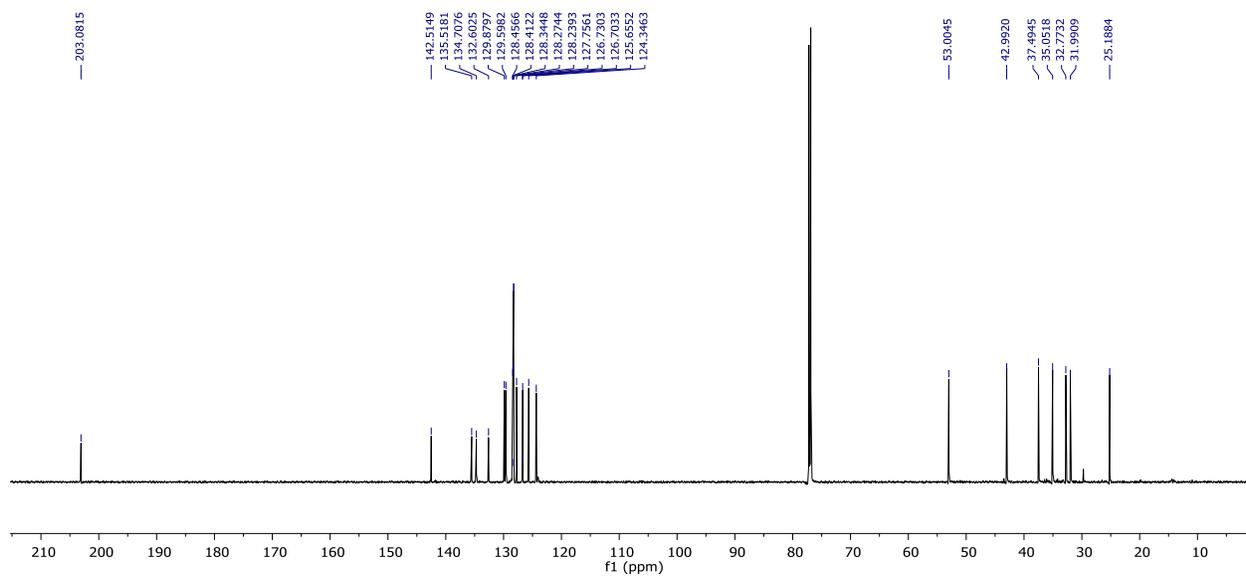


Figure S60. $^{13}\text{C}\{^1\text{H}\}$ NMR of **11** (CDCl₃, 295 K).

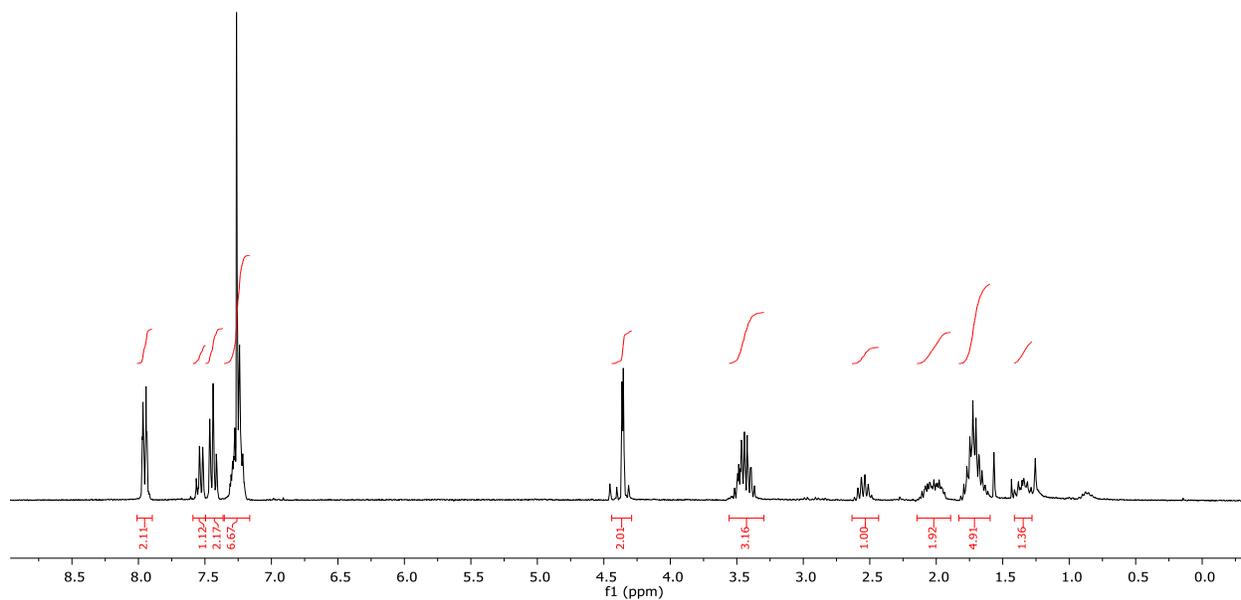
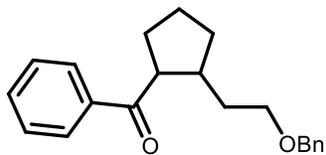


Figure S61. ^1H NMR of **12** (CDCl_3 , 295 K).

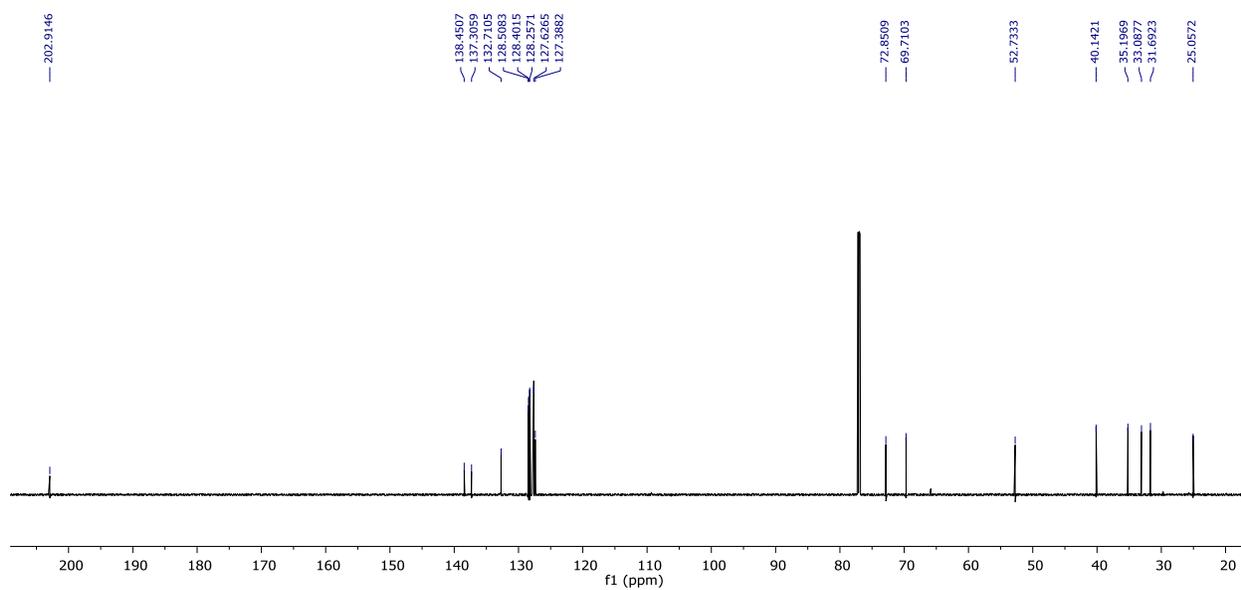


Figure S62. $^{13}\text{C}\{^1\text{H}\}$ NMR of **12** (CDCl_3 , 295 K).

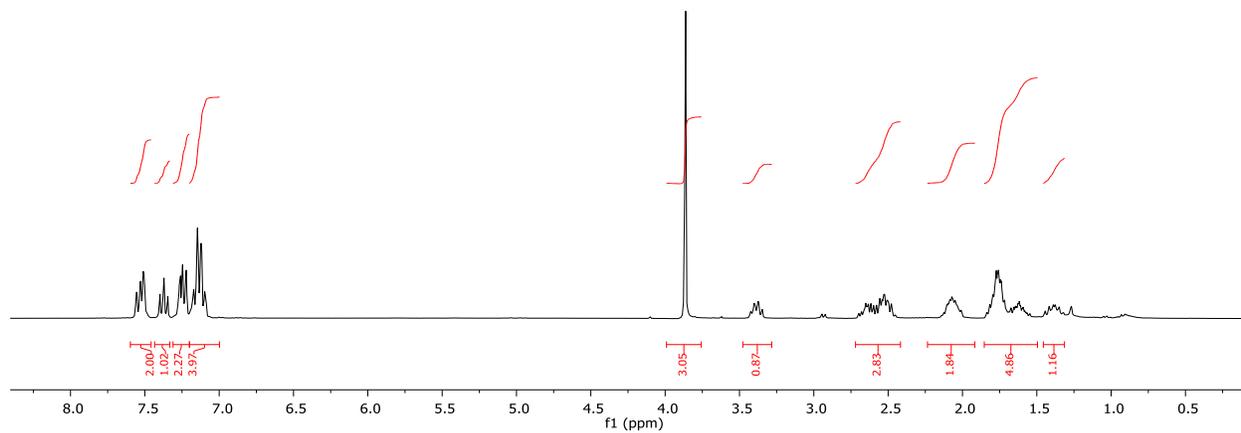
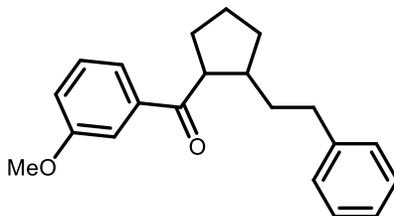


Figure S63. ^1H NMR of **13** (CDCl_3 , 295 K).

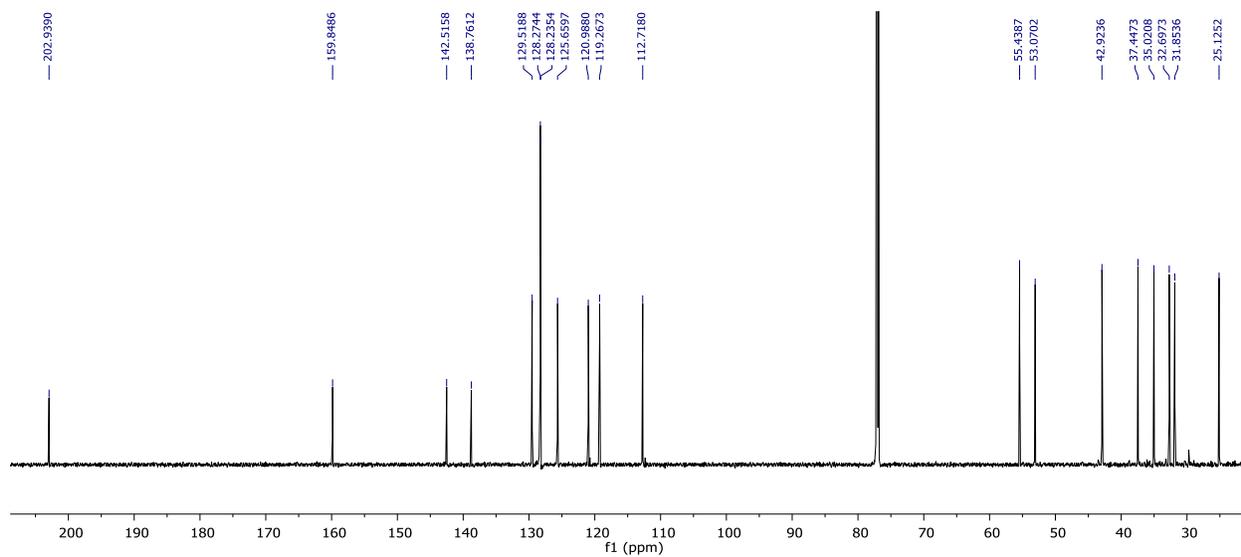


Figure S64. $^{13}\text{C}\{^1\text{H}\}$ NMR of **13** (CDCl_3 , 295 K).

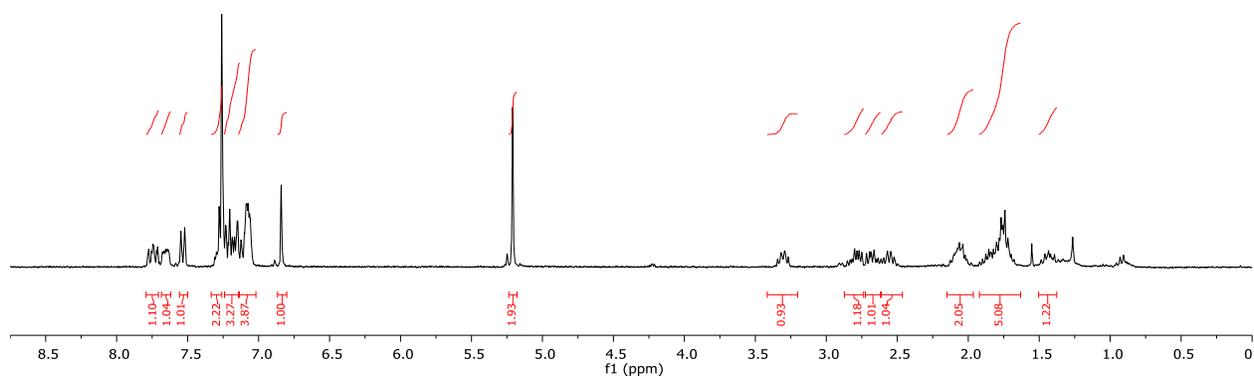
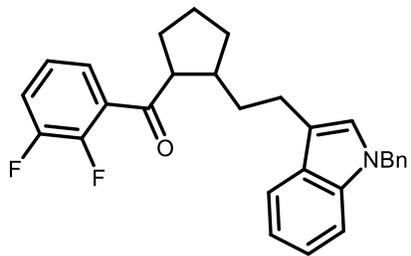


Figure S65. ^1H NMR of **14** (CDCl_3 , 295 K).

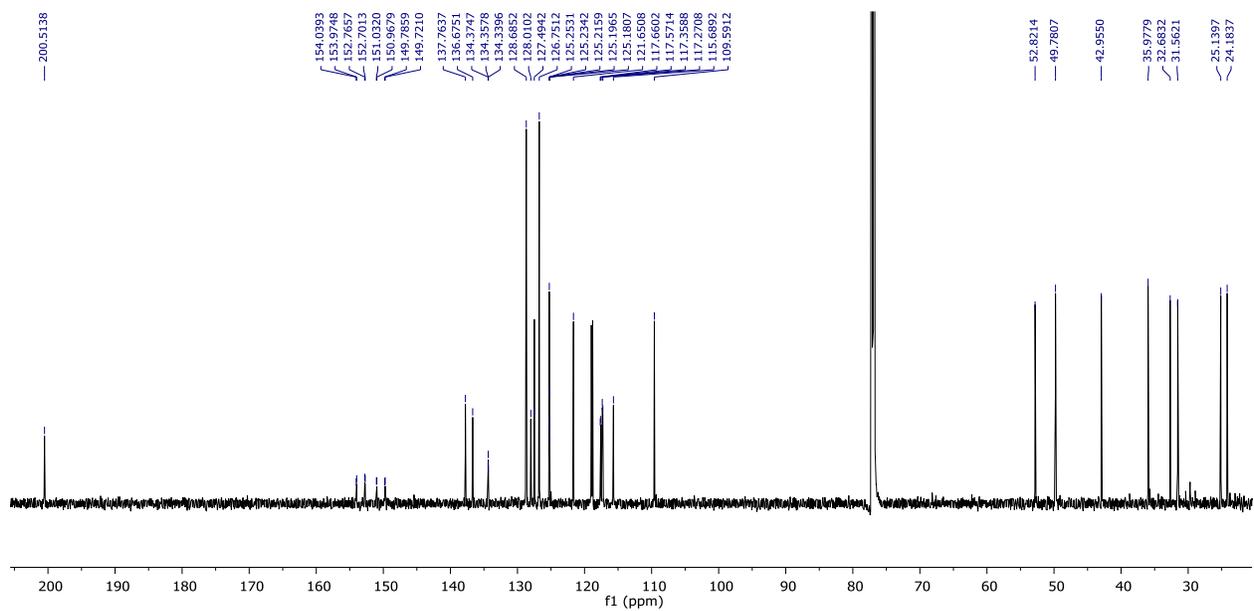


Figure S66. $^{13}\text{C}\{^1\text{H}\}$ NMR of **14** (CDCl_3 , 295 K).

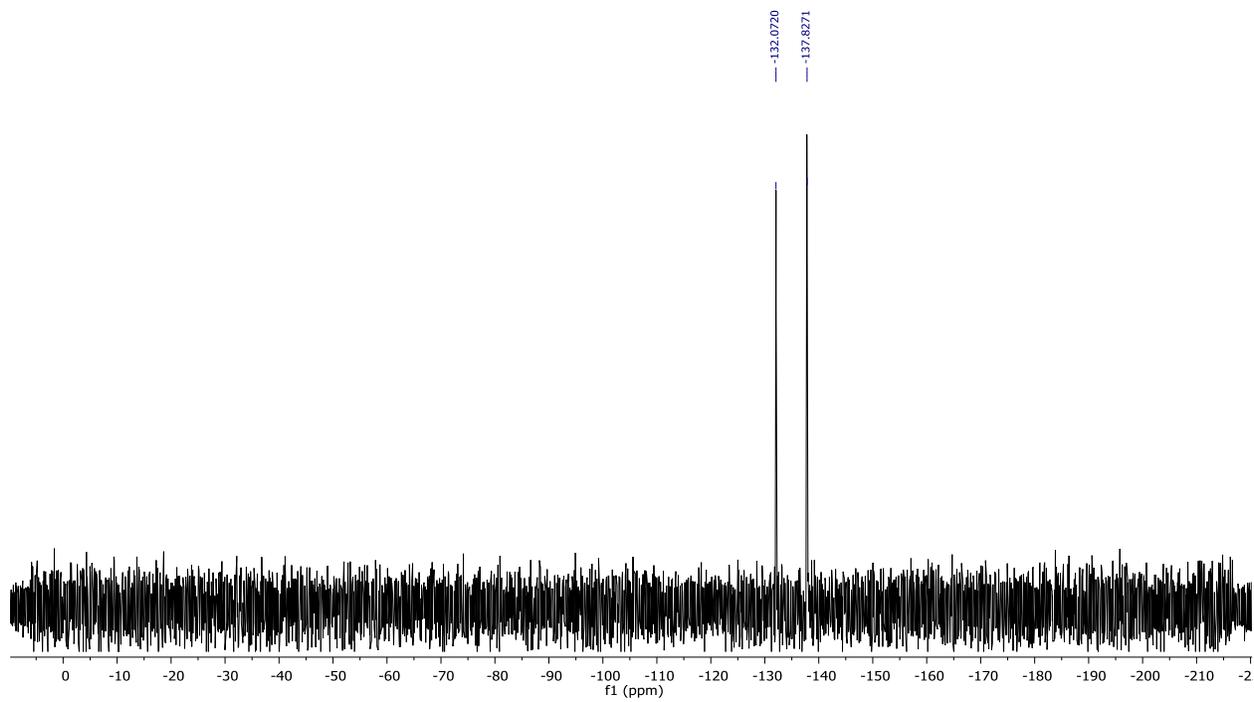


Figure S67. ^{19}F NMR of **14** (CDCl_3 , 295 K).

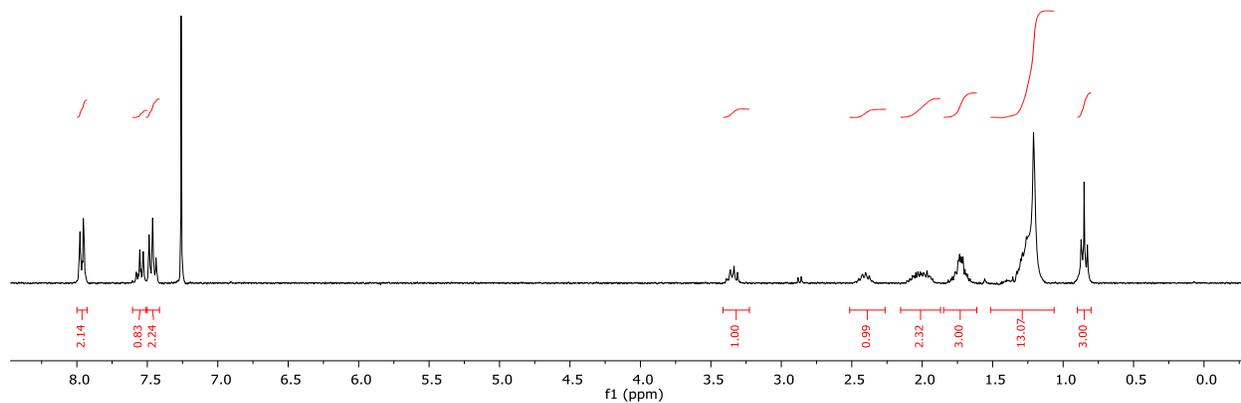
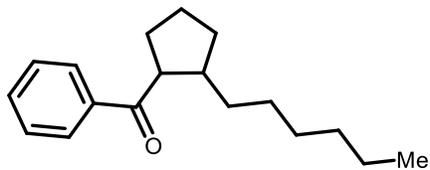


Figure S68. ^1H NMR of **15** (CDCl_3 , 295 K).

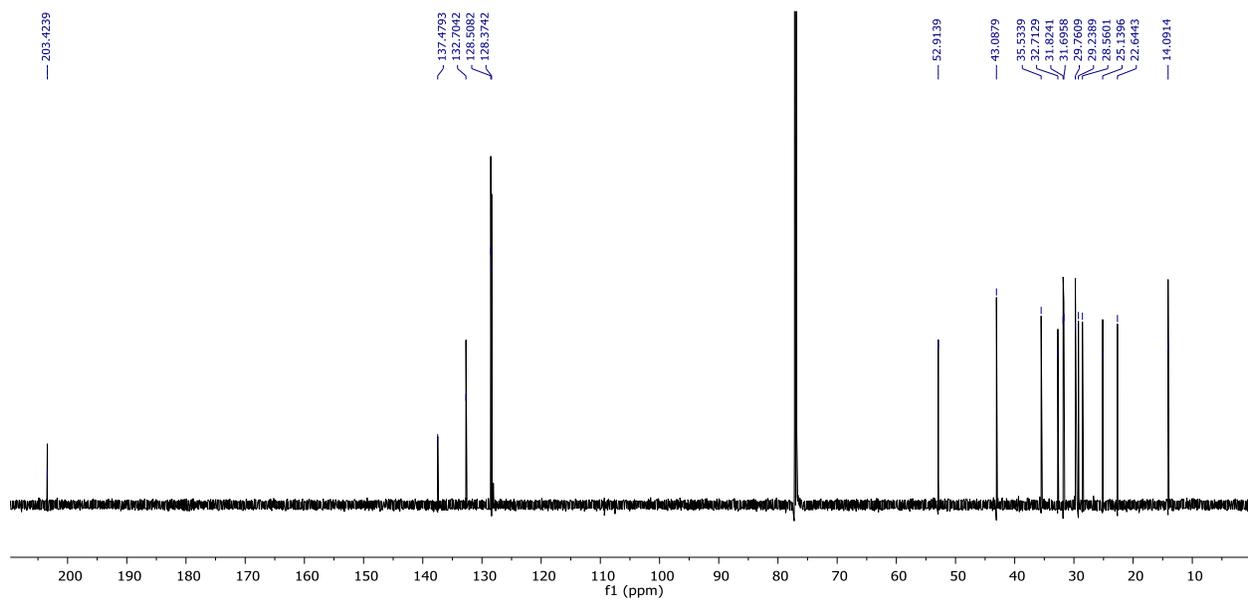


Figure S69. $^{13}\text{C}\{^1\text{H}\}$ NMR of **15** (CDCl_3 , 295 K).

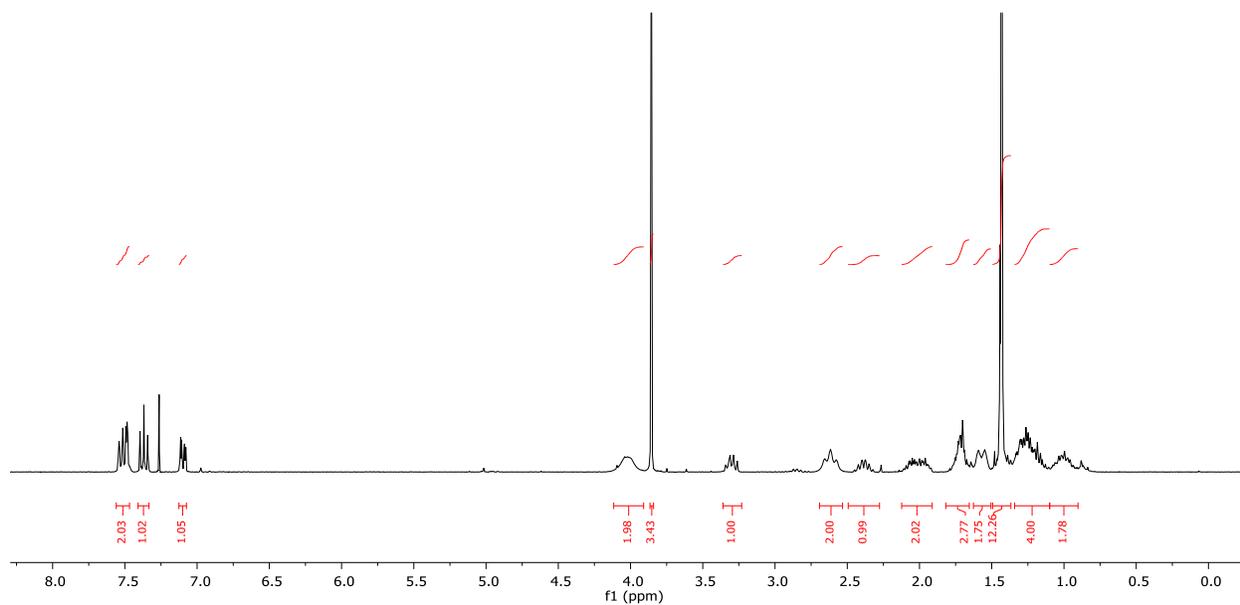
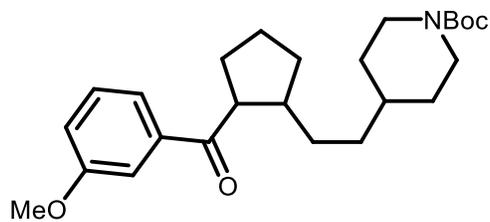


Figure S70. ^1H NMR of **16** (CDCl_3 , 295 K).

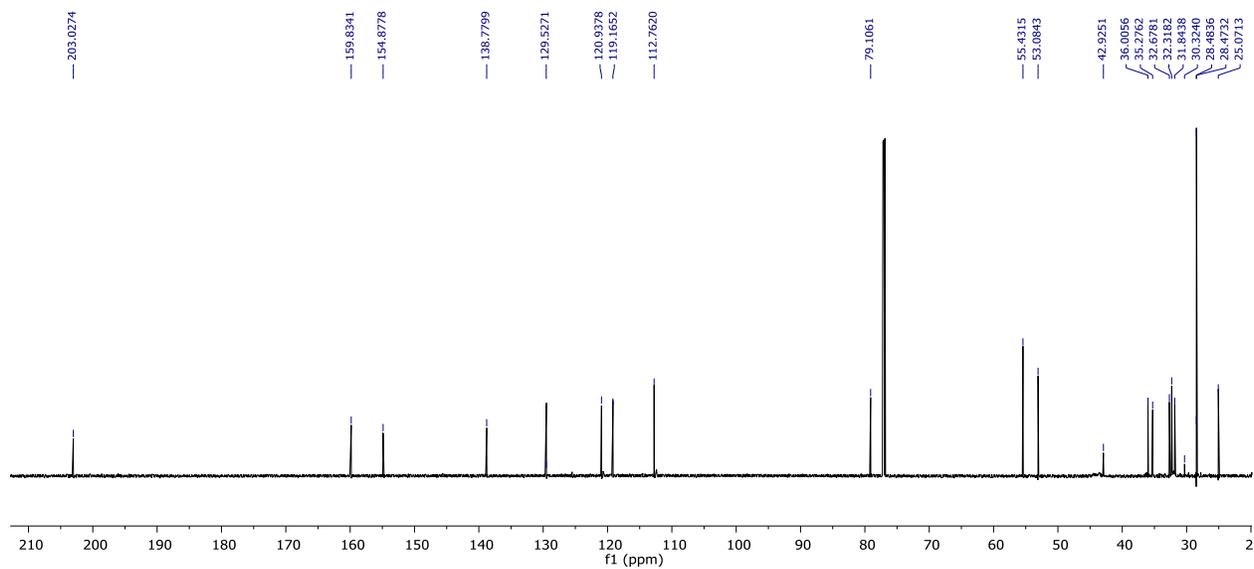


Figure S71. $^{13}\text{C}\{^1\text{H}\}$ NMR of **16** (CDCl_3 , 295 K).

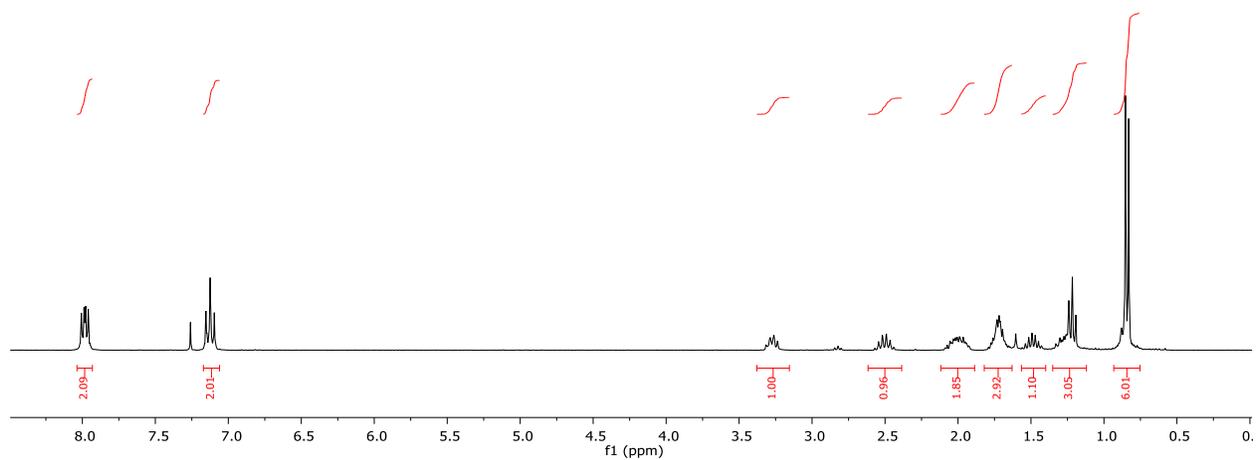
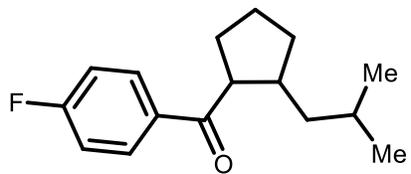


Figure S72. ^1H NMR of **17** (CDCl_3 , 295 K).

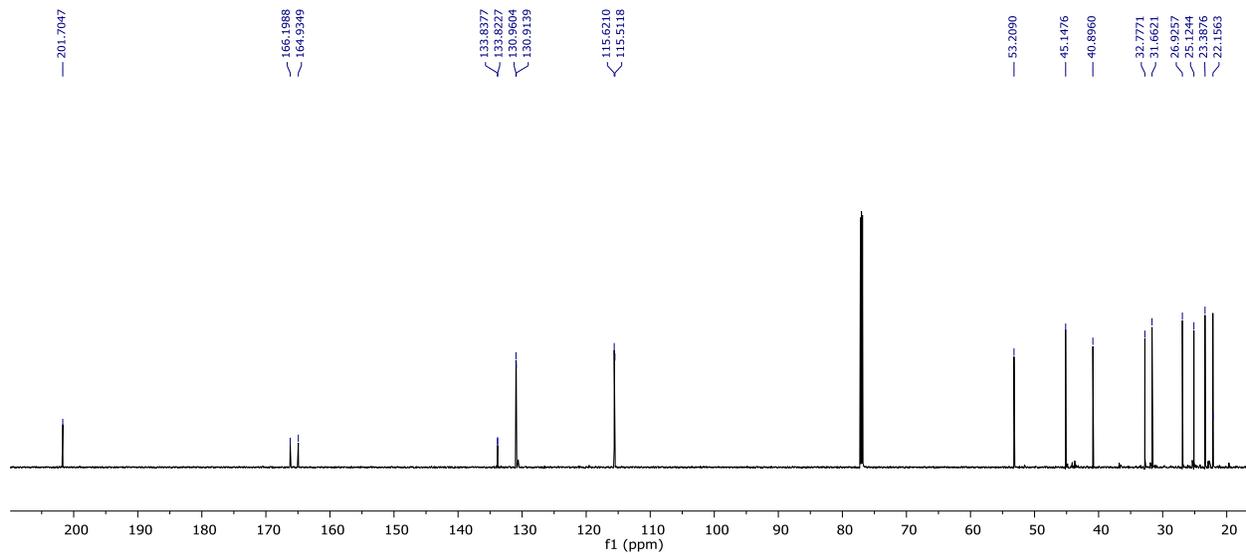


Figure S73. $^{13}\text{C}\{^1\text{H}\}$ NMR of **17** (CDCl_3 , 295 K).

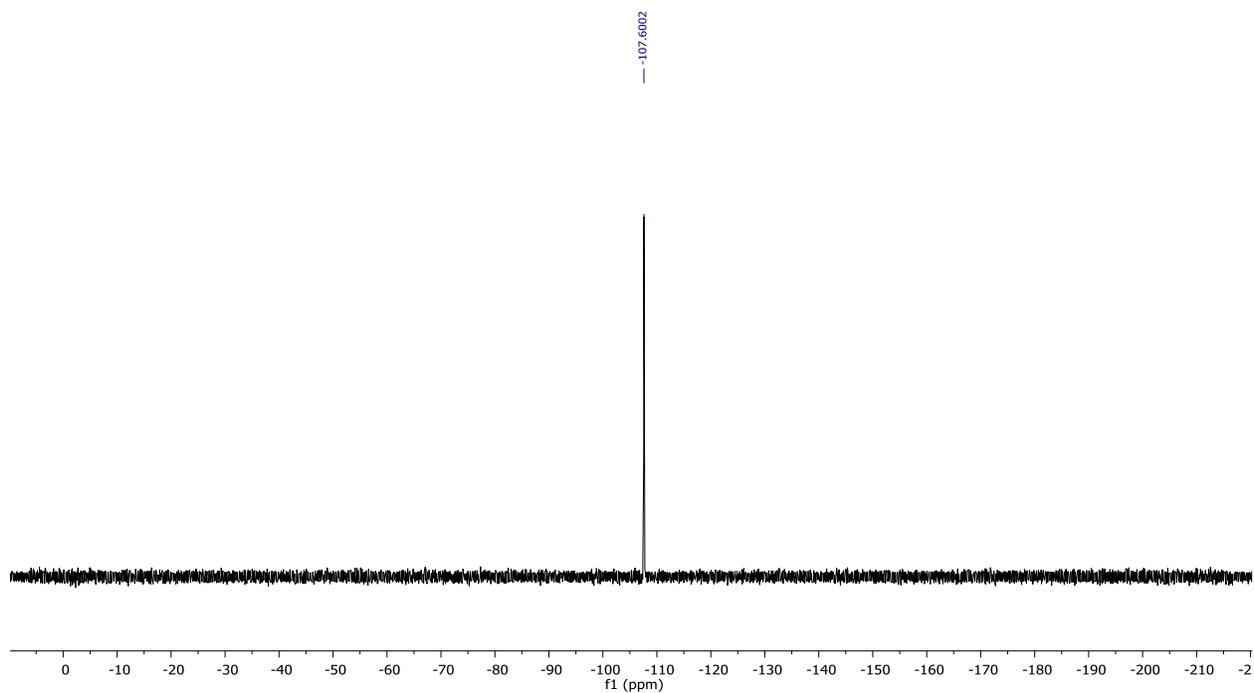


Figure S74. ^{19}F NMR of **17** (CDCl_3 , 295 K).

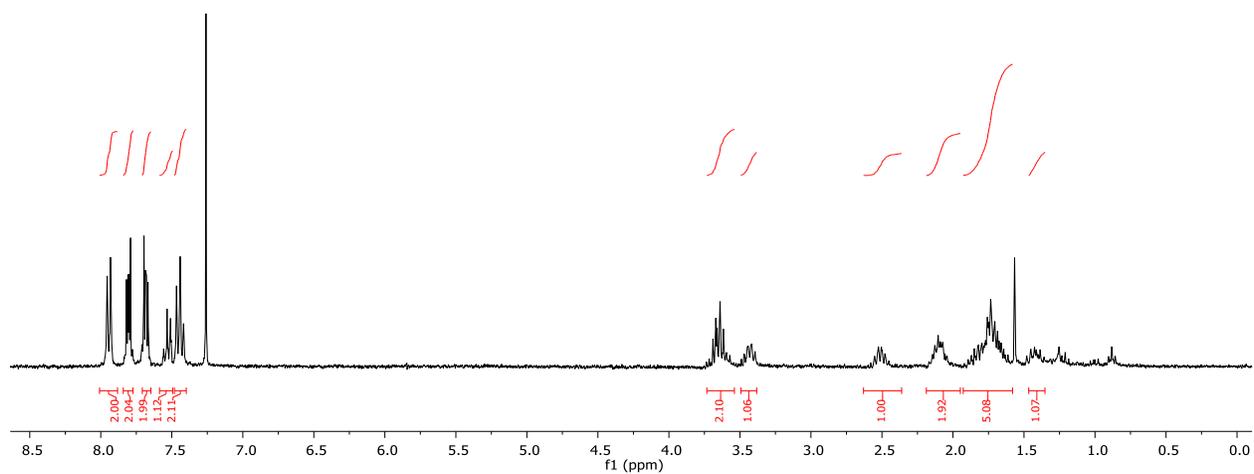
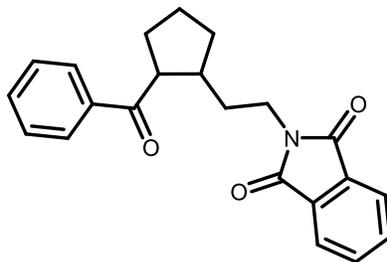


Figure S75. ^1H NMR of **18** (CDCl_3 , 295 K).

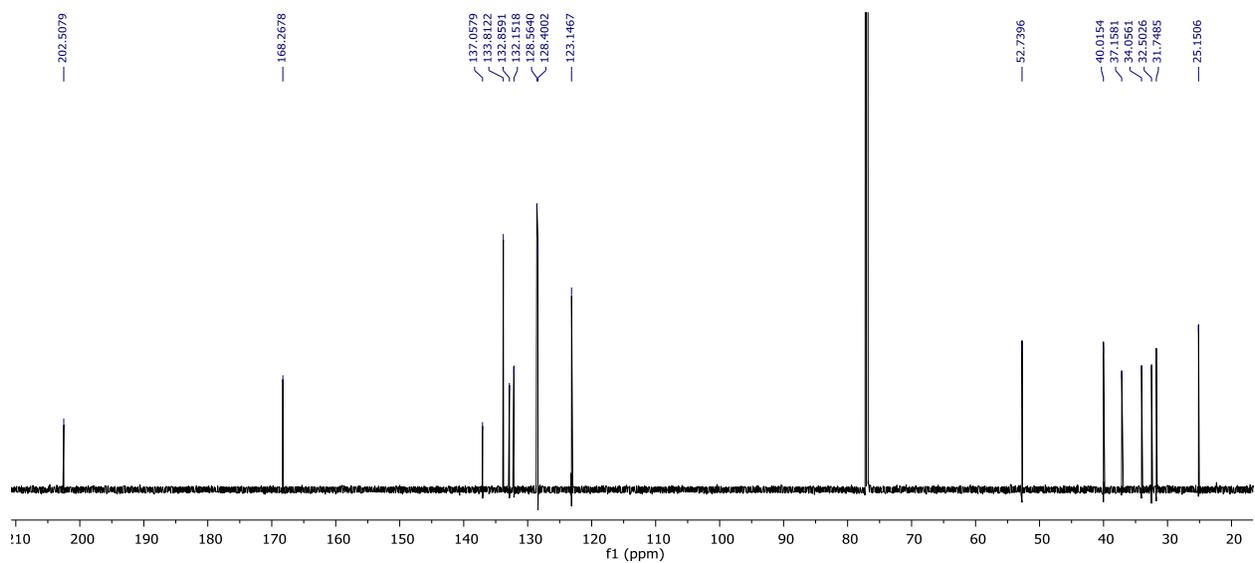


Figure S76. $^{13}\text{C}\{^1\text{H}\}$ NMR of **18** (CDCl_3 , 295 K).

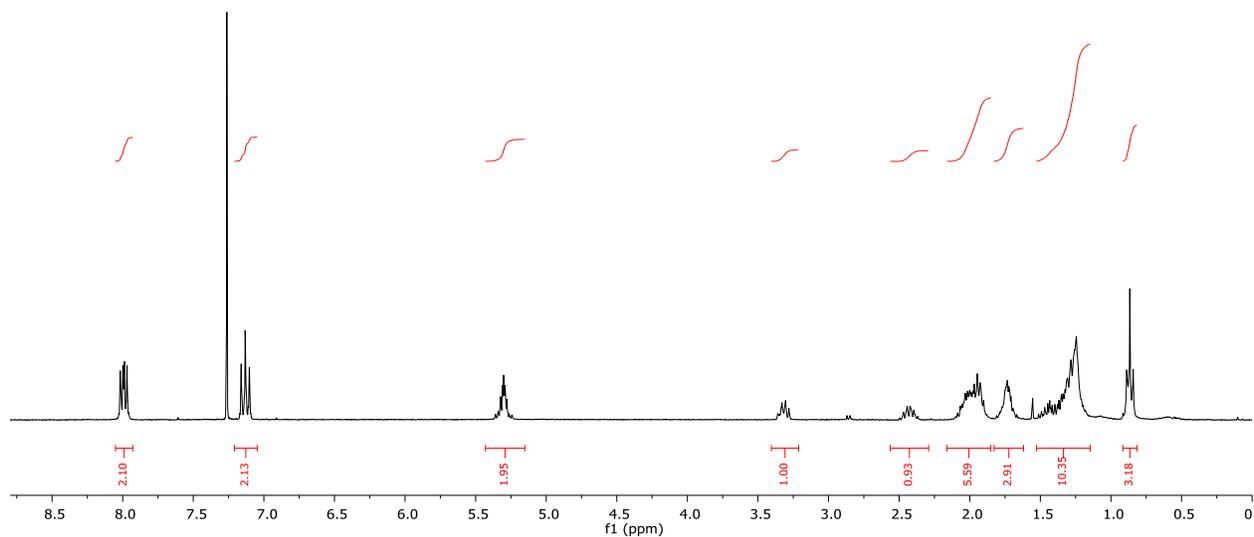
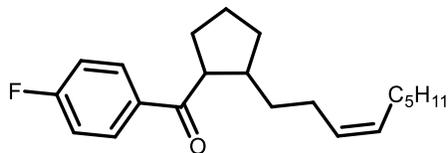


Figure S77. ^1H NMR of **19** (CDCl_3 , 295 K).

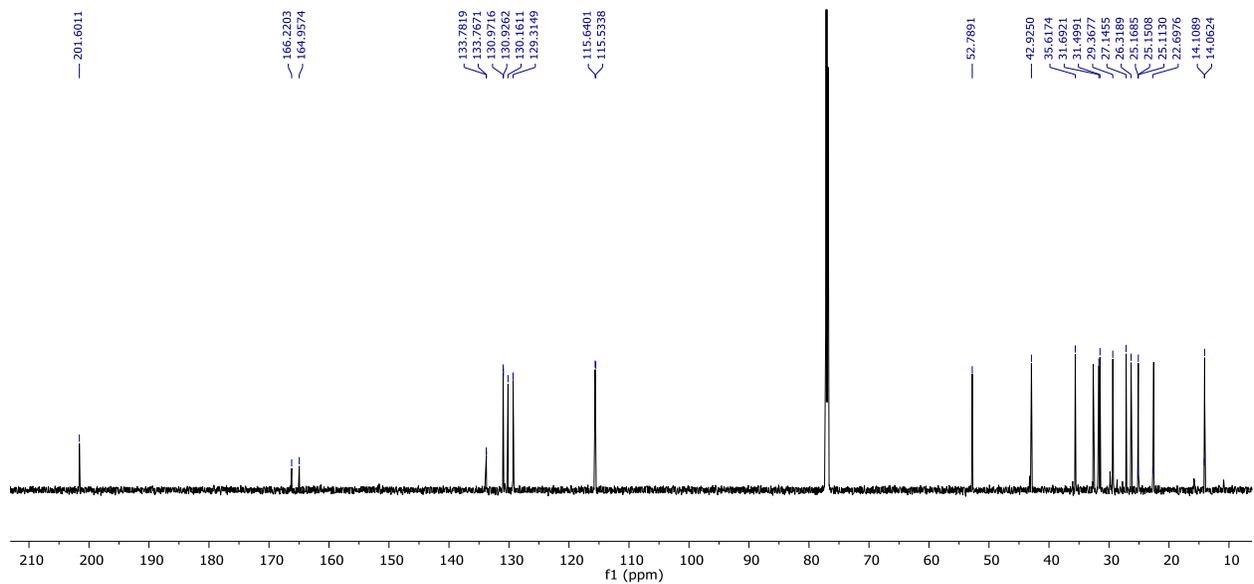


Figure S78. $^{13}\text{C}\{^1\text{H}\}$ NMR of **19** (CDCl_3 , 295 K).

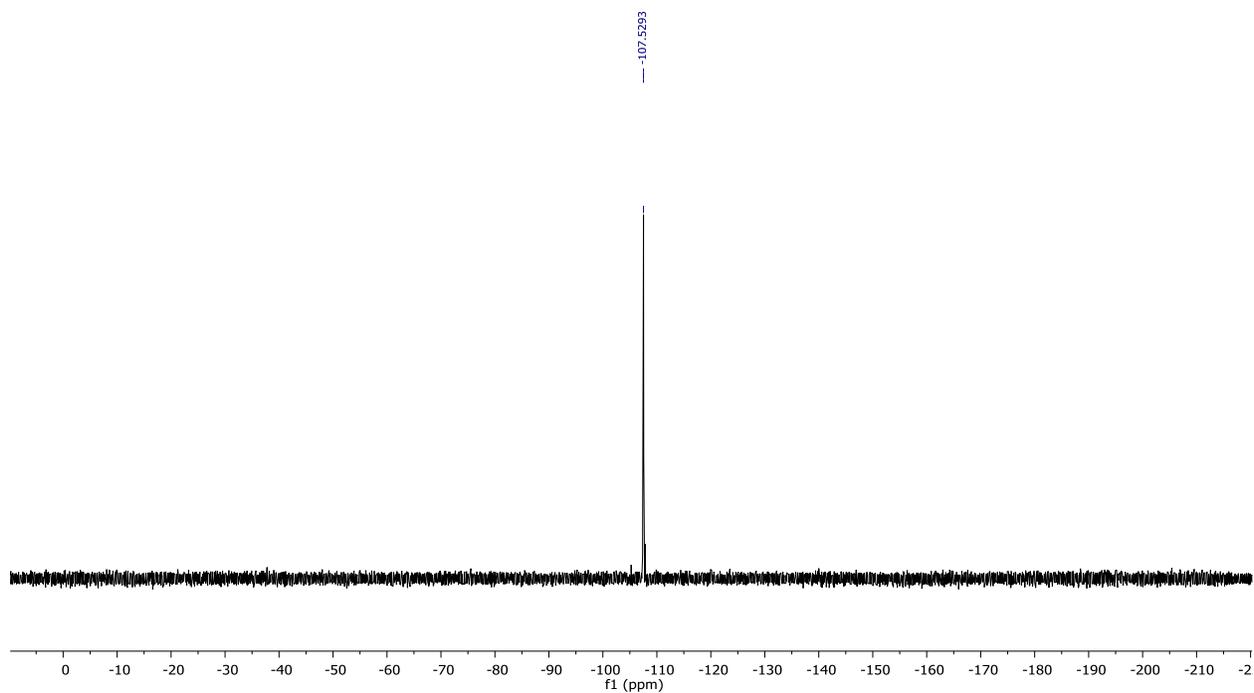


Figure S79. ^{19}F NMR of **19** (CDCl_3 , 295 K).

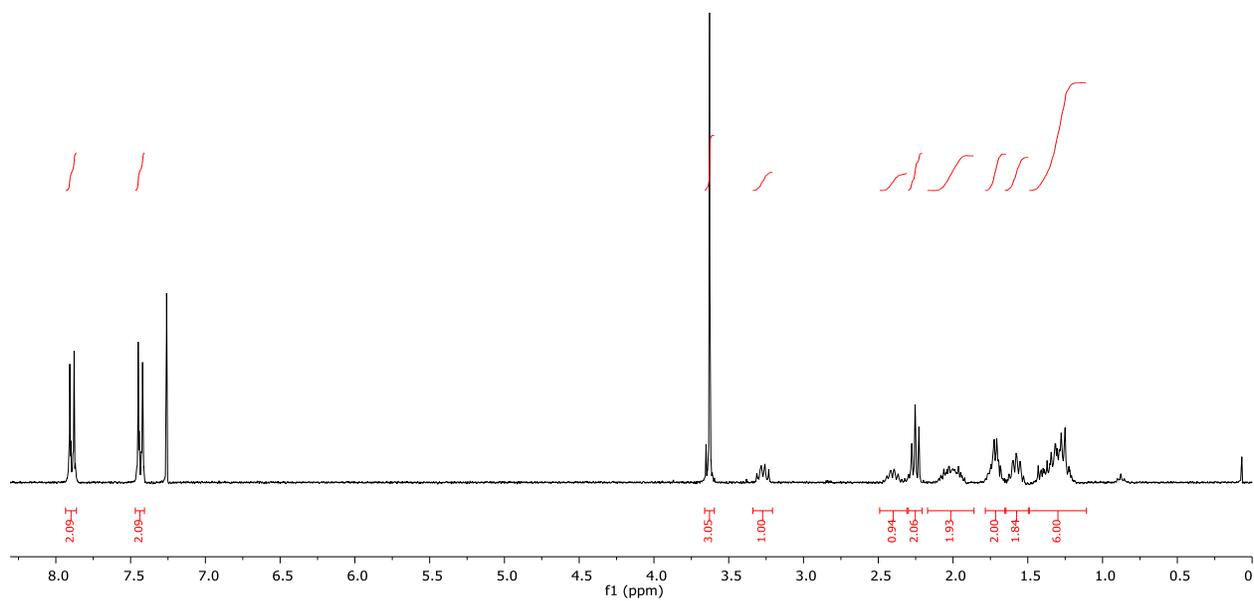
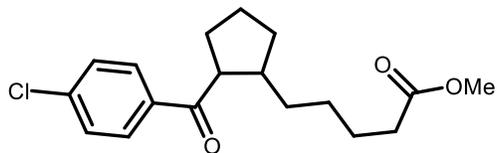


Figure S80. ^1H NMR of **20** (CDCl_3 , 295 K).

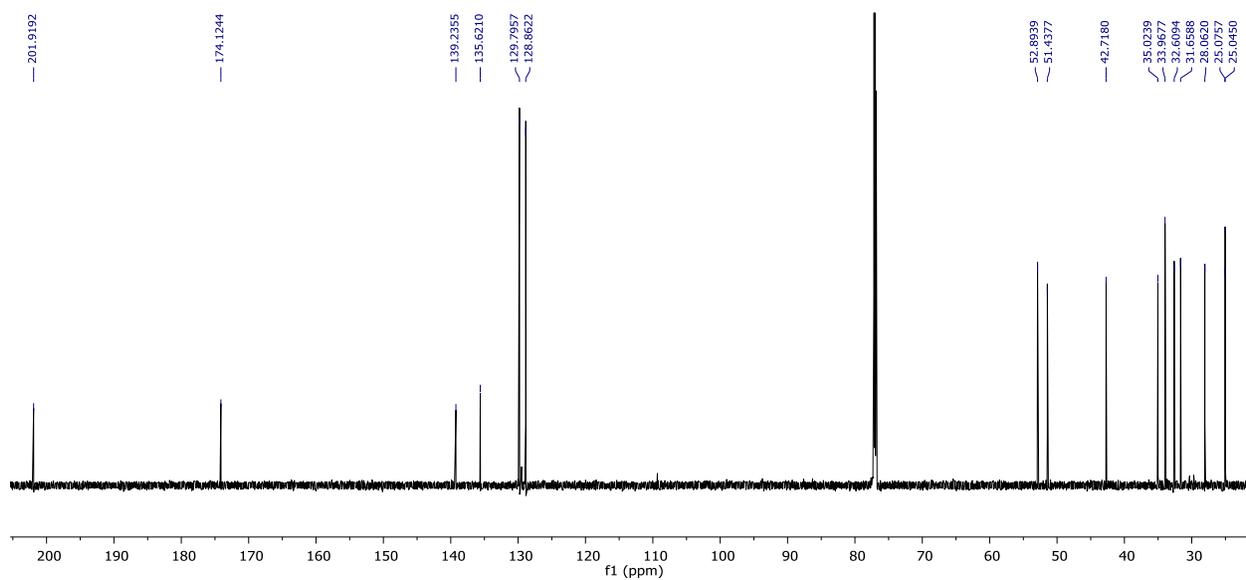


Figure S81. $^{13}\text{C}\{^1\text{H}\}$ NMR of **20** (CDCl_3 , 295 K).

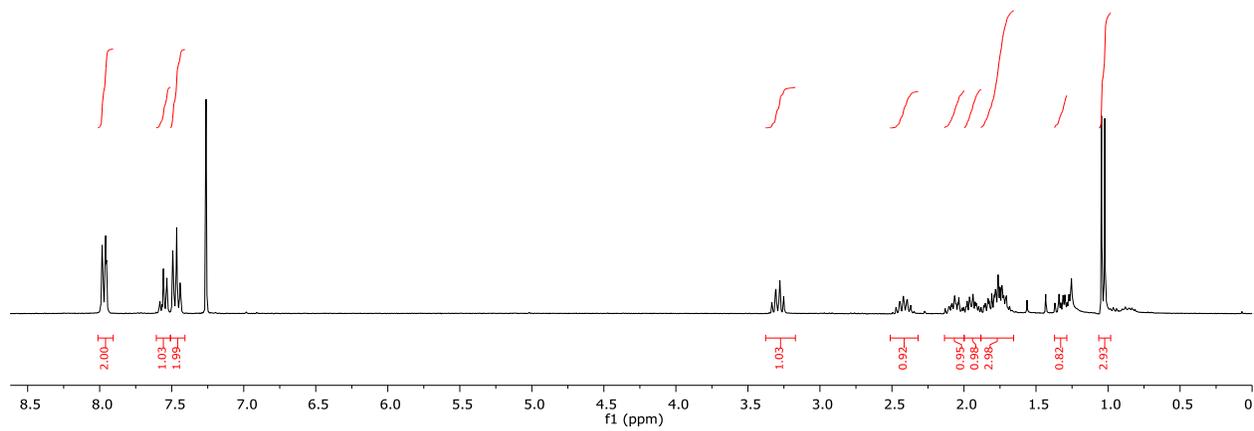
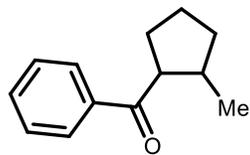


Figure S82. ¹H NMR of **21** (CDCl₃, 295 K).

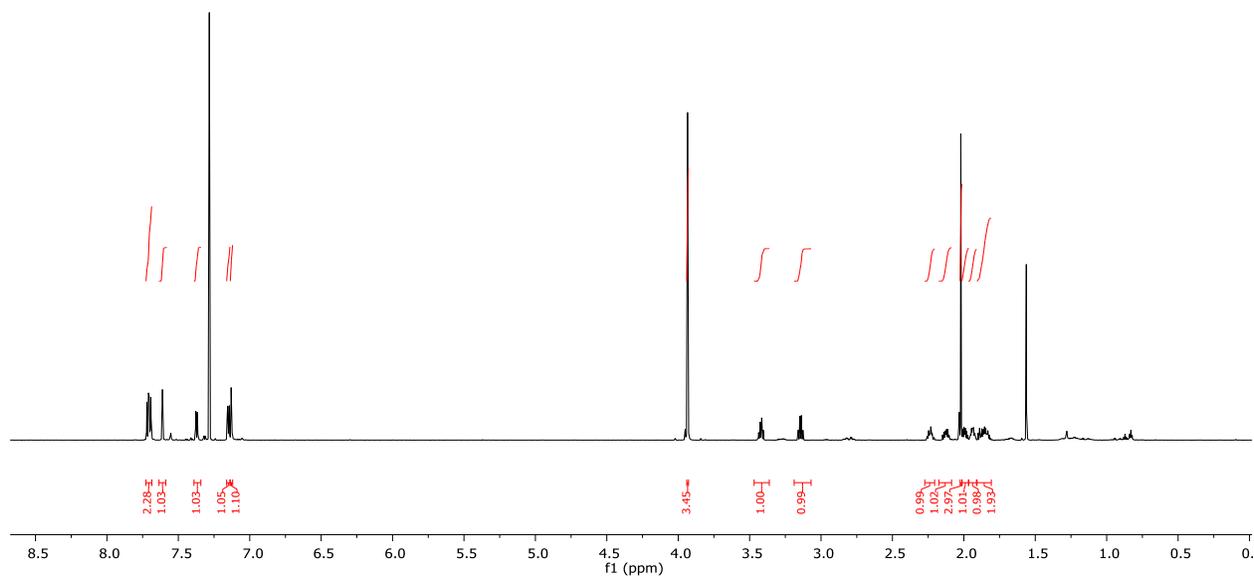
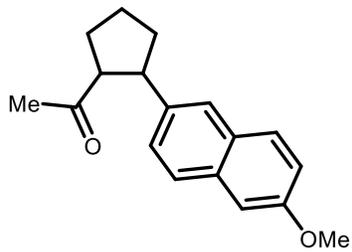


Figure S83. ^1H NMR of **22** (CDCl_3 , 295 K).

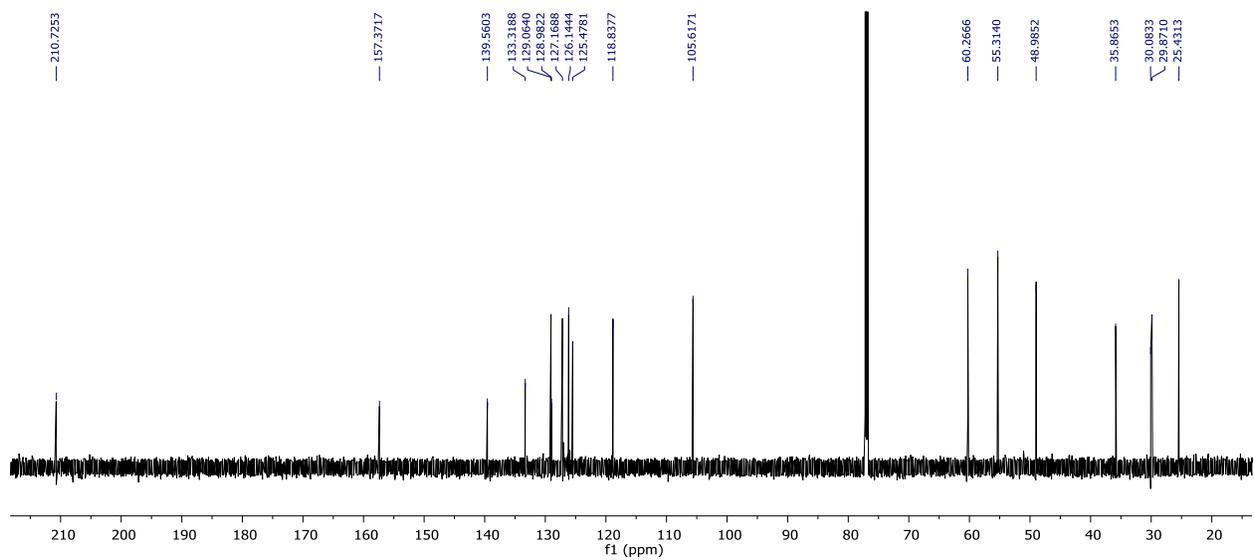


Figure S84. $^{13}\text{C}\{^1\text{H}\}$ NMR of **22** (CDCl_3 , 295 K).

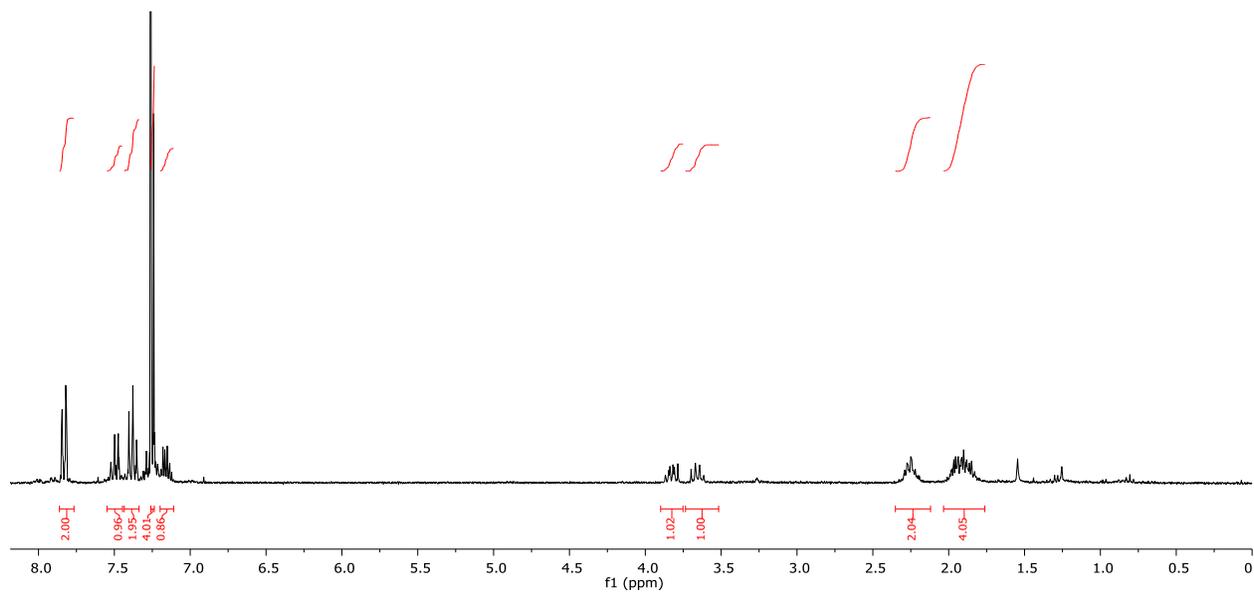
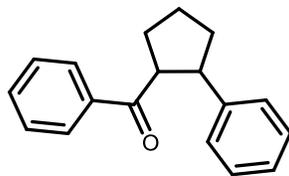


Figure S85. ^1H NMR of **23** (CDCl₃, 295 K).

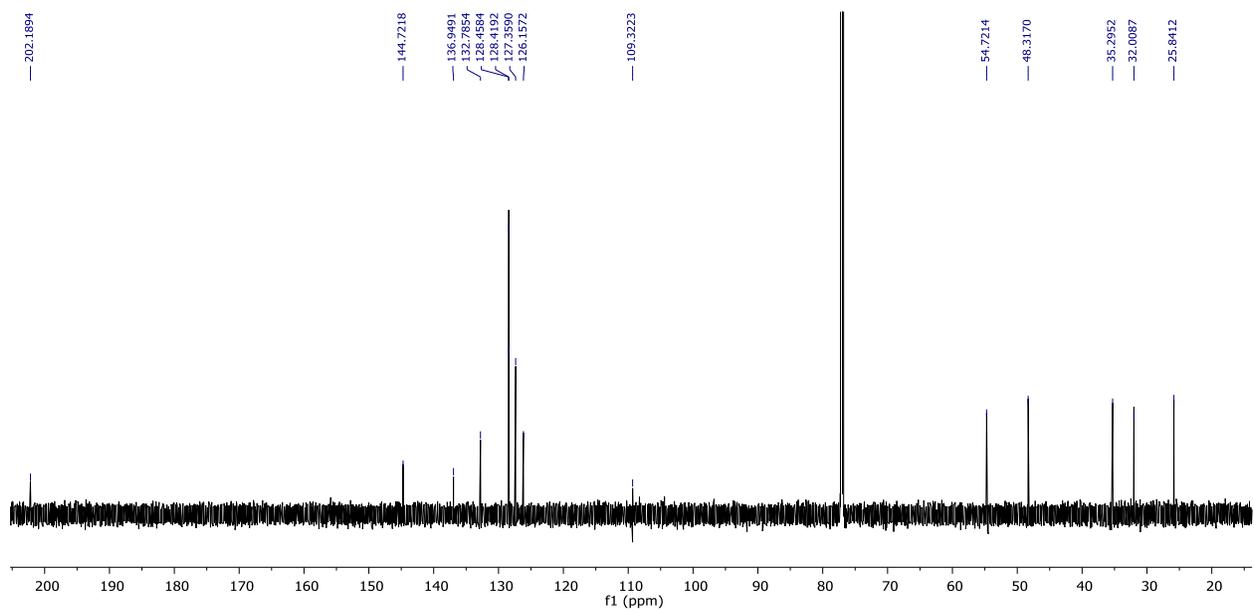


Figure S86. $^{13}\text{C}\{^1\text{H}\}$ NMR of **23** (CDCl₃, 295 K).

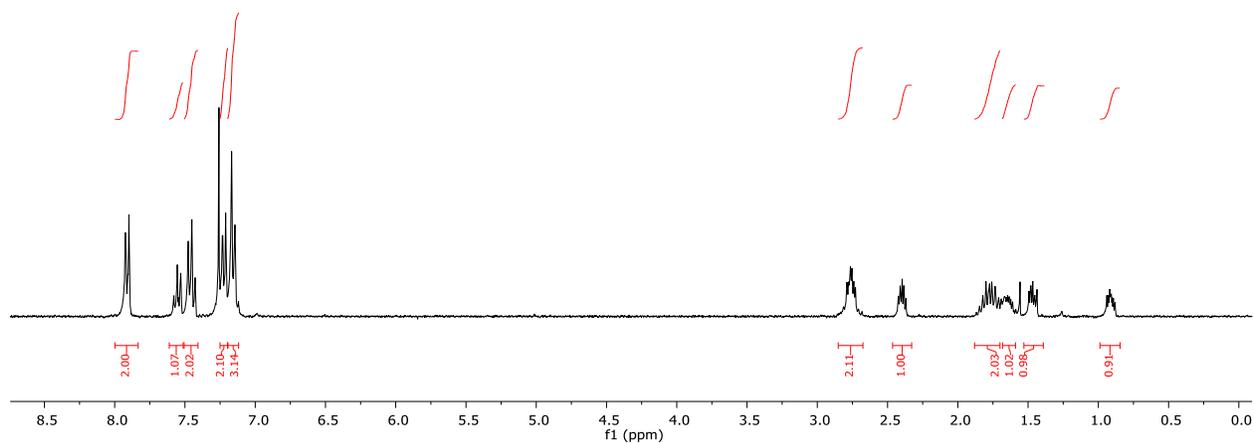
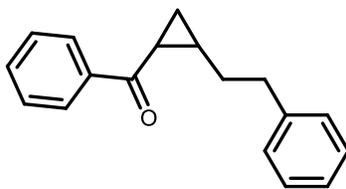


Figure S87. ^1H NMR of **2** (CDCl_3 , 295 K).

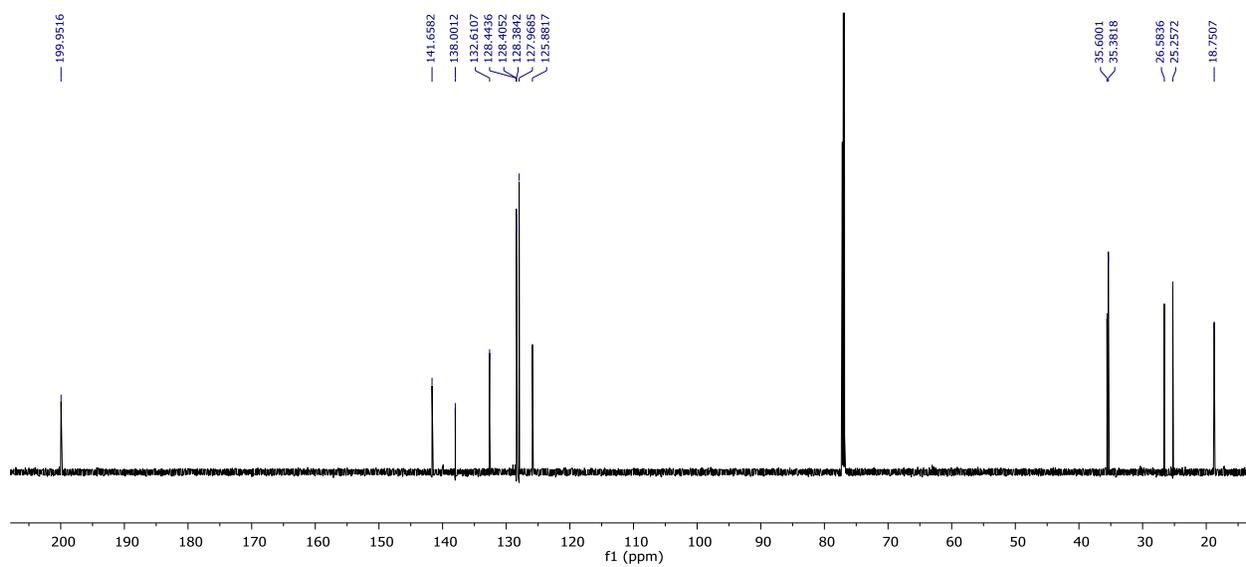


Figure S88. $^{13}\text{C}\{^1\text{H}\}$ NMR of **2** (CDCl_3 , 295 K).

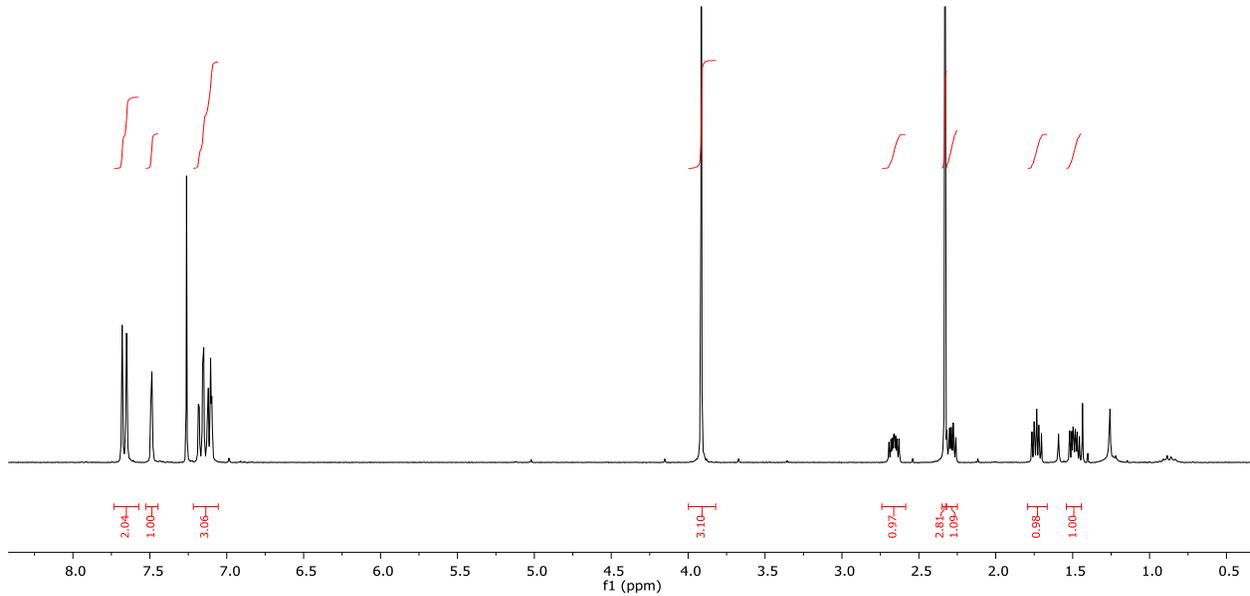
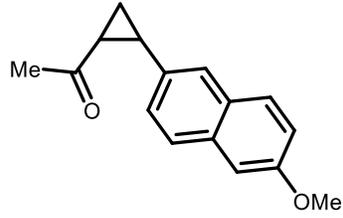


Figure S89. ^1H NMR of S16 (CDCl_3 , 295 K).

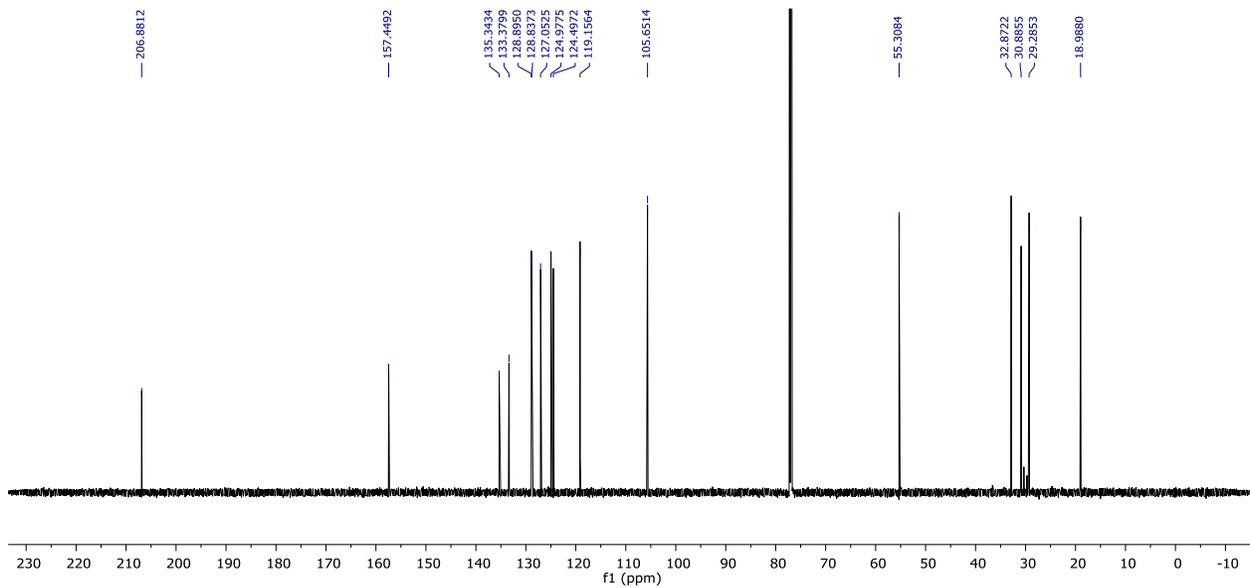


Figure S90. $^{13}\text{C}\{^1\text{H}\}$ NMR of S16 (CDCl_3 , 295 K).

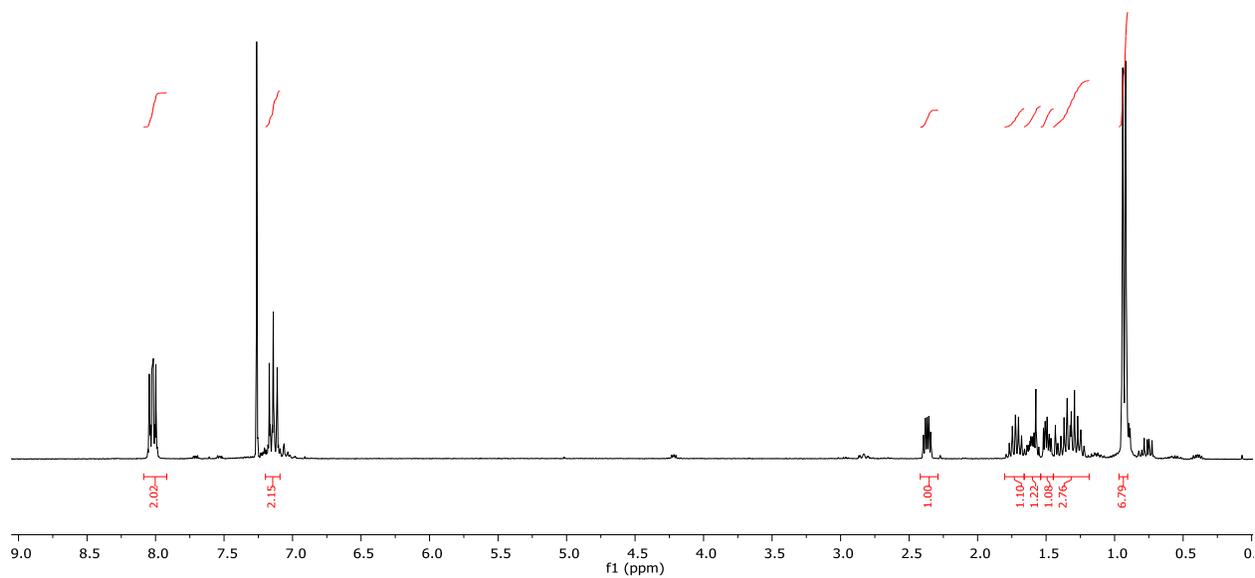
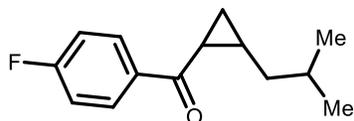


Figure S91. ^1H NMR of **S17** (CDCl_3 , 295 K).

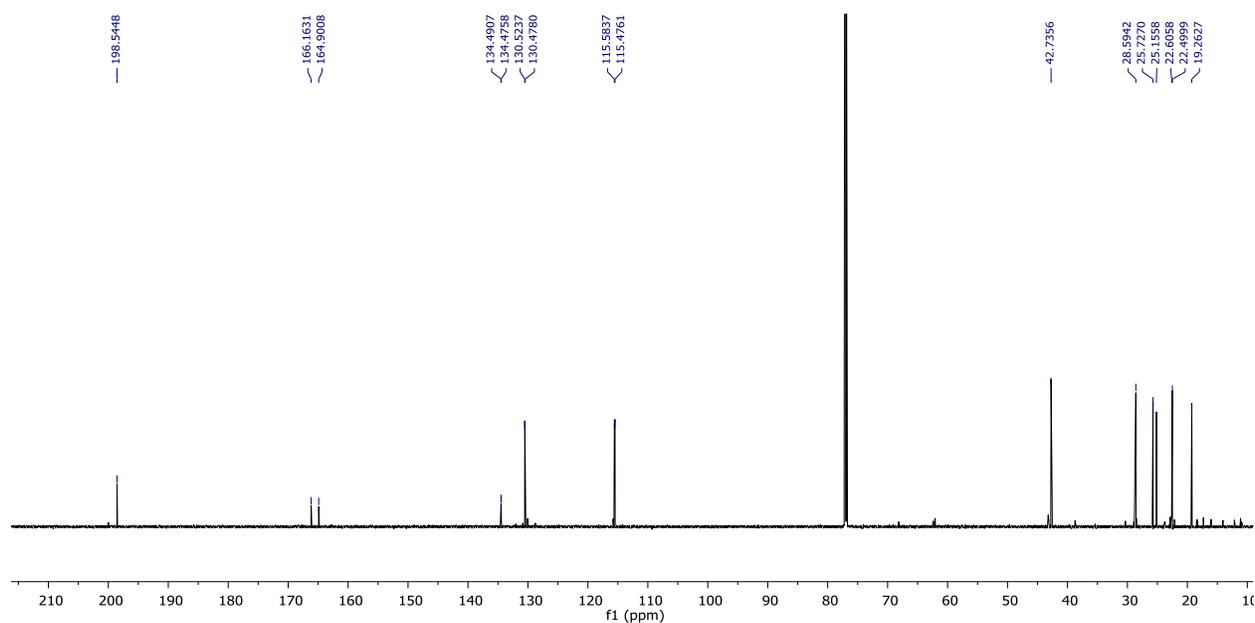


Figure S92. $^{13}\text{C}\{^1\text{H}\}$ NMR of **S17** (CDCl_3 , 295 K).

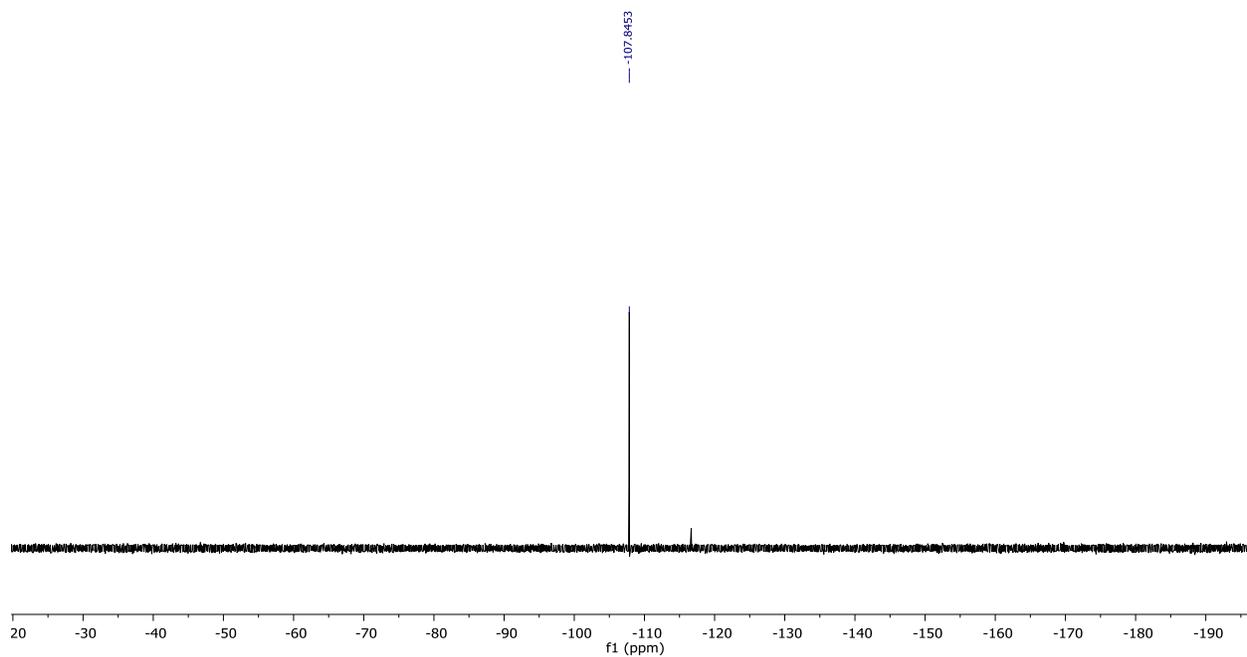


Figure S93. ^{19}F NMR of **S17** (CDCl_3 , 295 K).

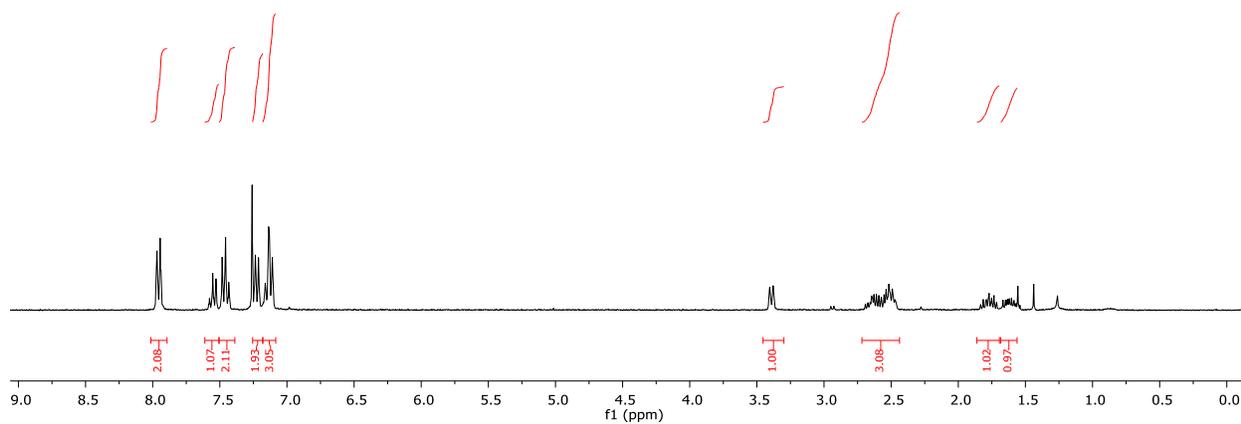
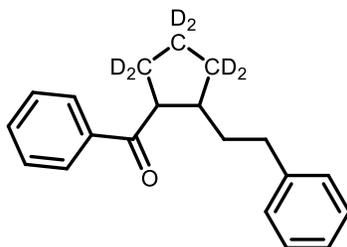


Figure S94. ¹H NMR of 3-d₆ (CDCl₃, 295 K).

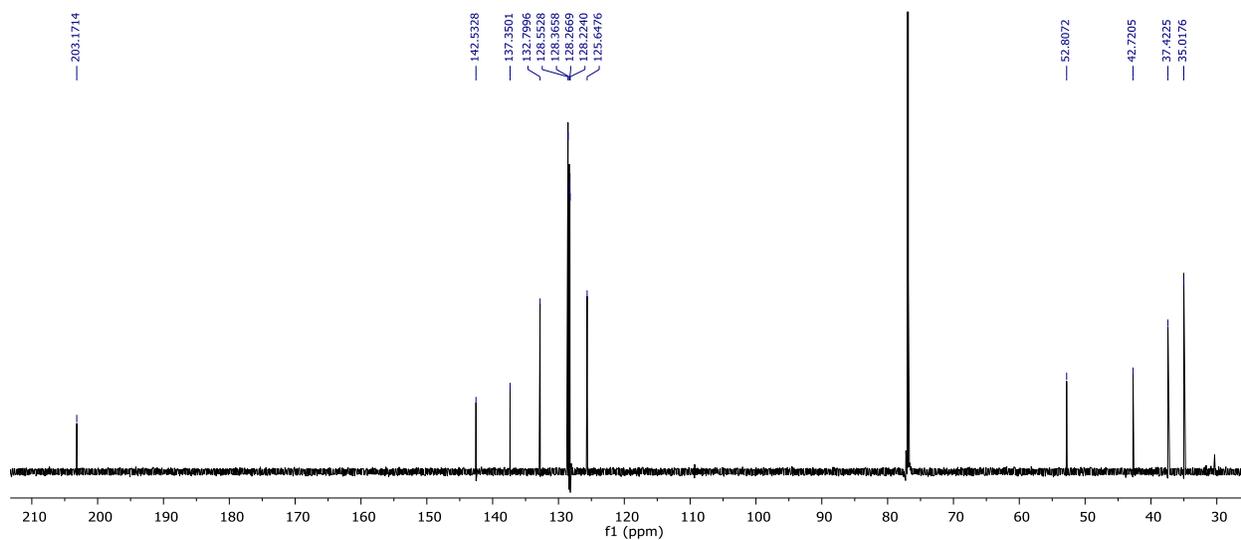
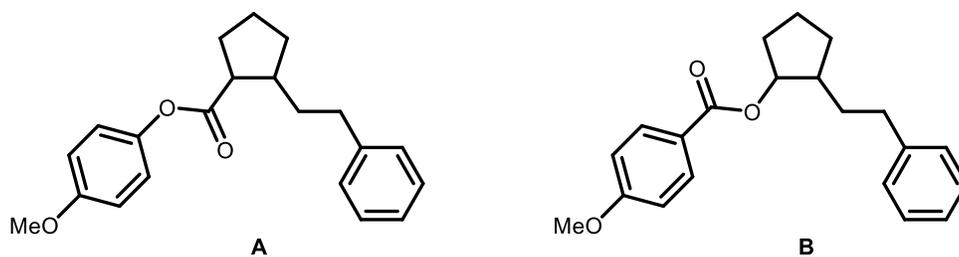


Figure S95. ¹³C{¹H} NMR of 3-d₆ (CDCl₃, 295 K).



A : B = 14 : 1

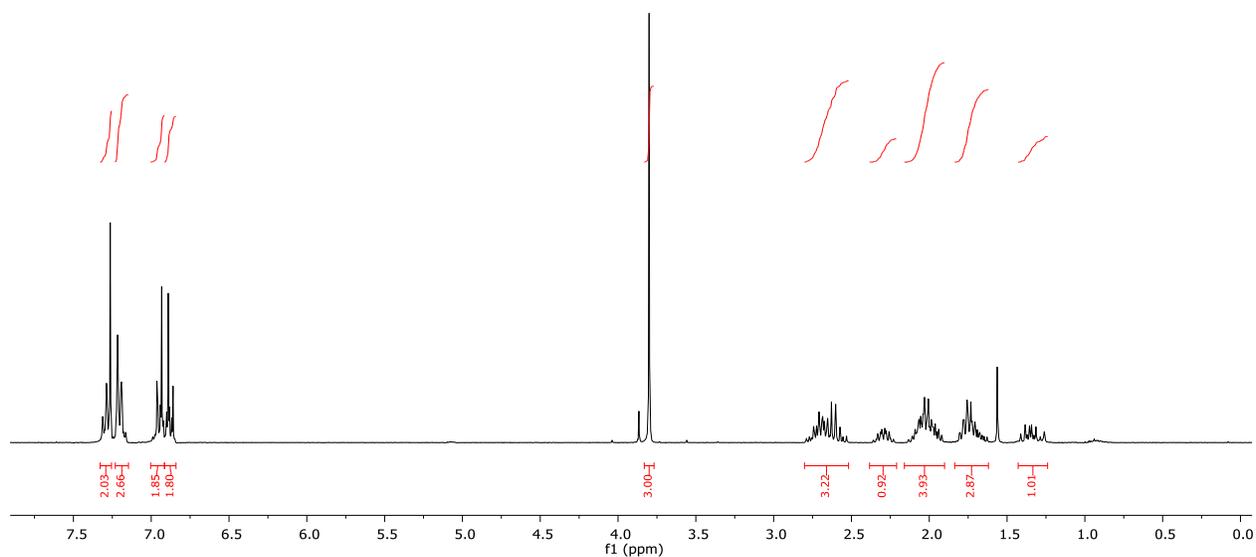


Figure S96. ^1H NMR of **24** (CDCl_3 , 295 K).

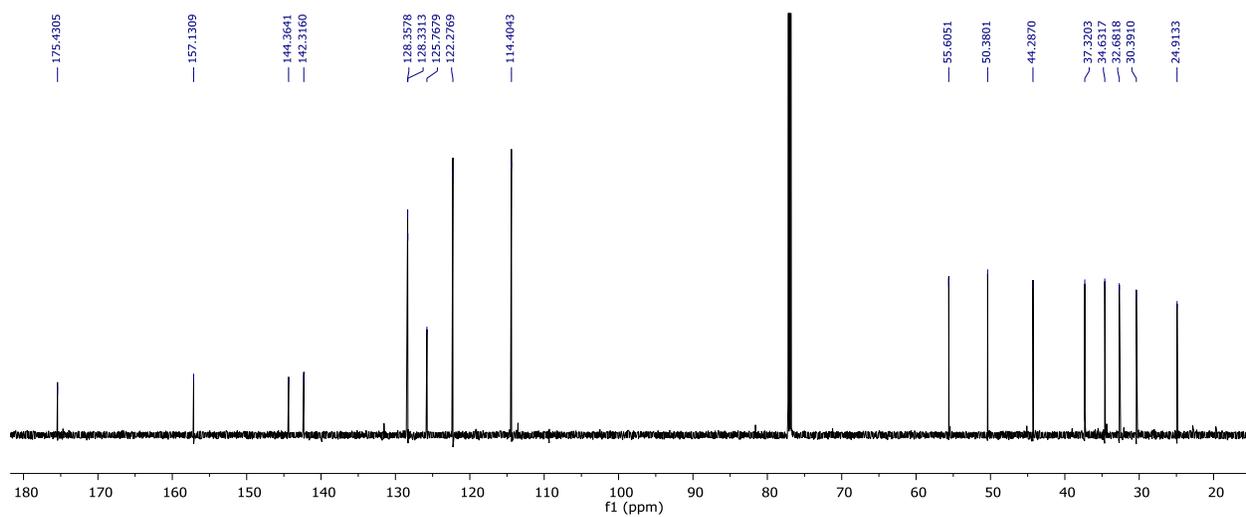


Figure S97. $^{13}\text{C}\{^1\text{H}\}$ NMR of **24** (CDCl_3 , 295 K).

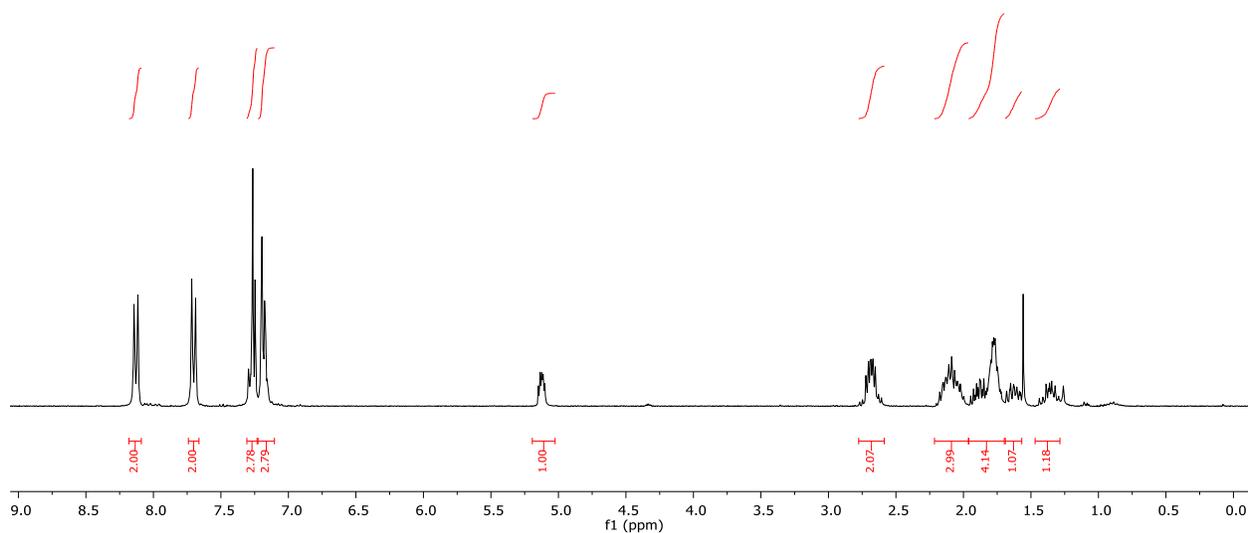
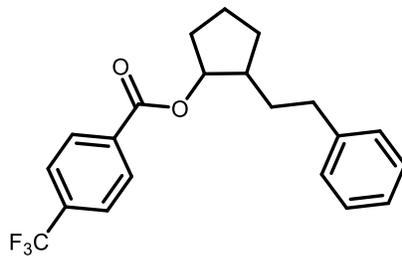


Figure S98. ^1H NMR of **25** (CDCl_3 , 295 K).

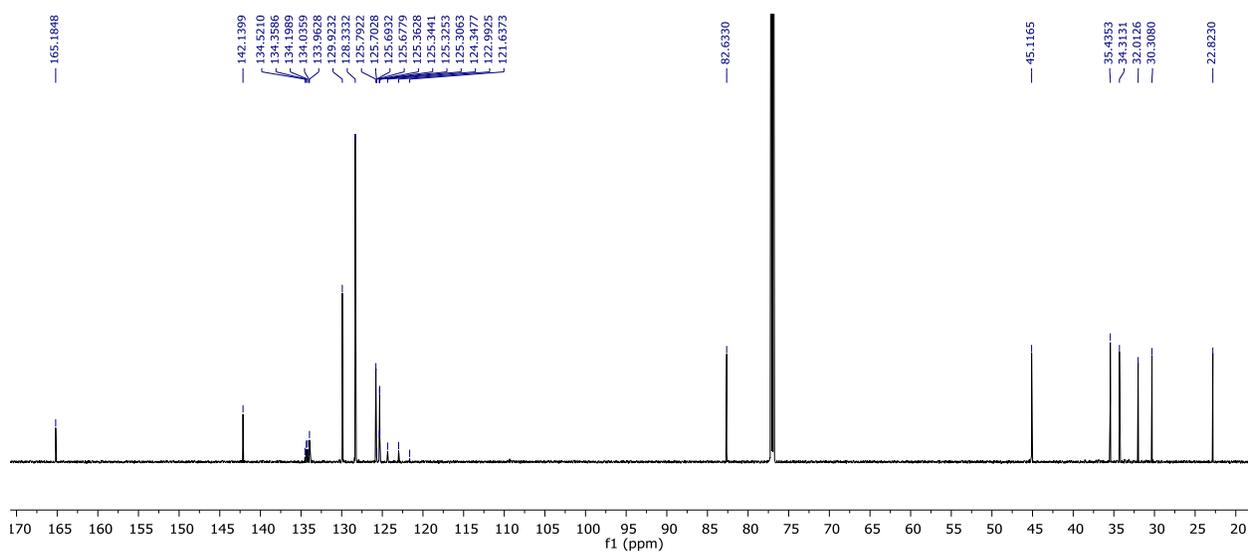


Figure S99. $^{13}\text{C}\{^1\text{H}\}$ NMR of **25** (CDCl_3 , 295 K).

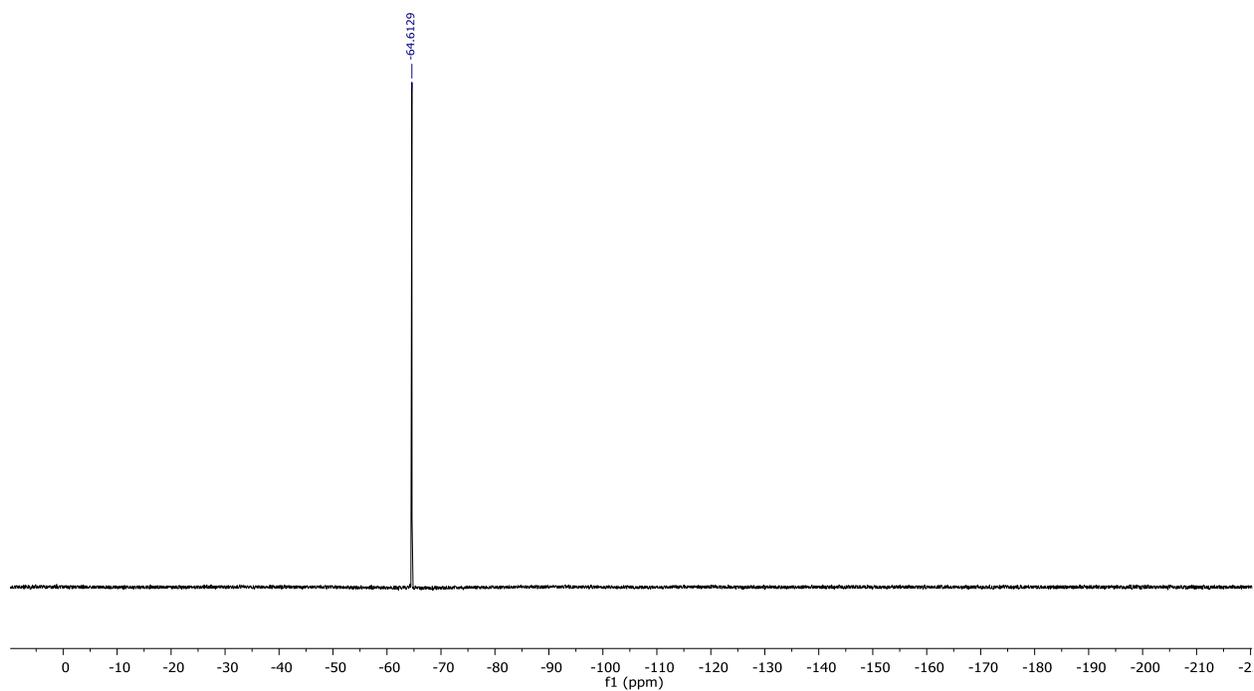


Figure S100. ^{19}F NMR of **25** (CDCl_3 , 295 K).

13. IR Data for Enones and Cyclopentanes

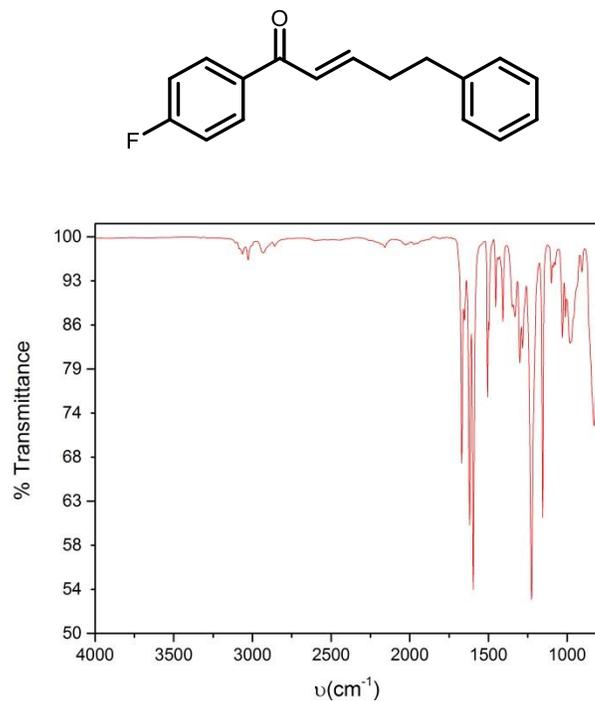


Figure S101. FT-IR of S1.

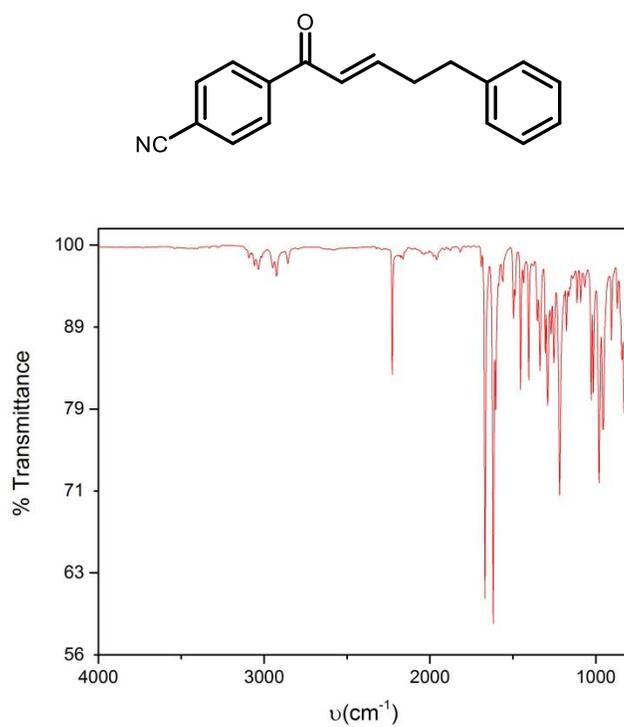


Figure S102. FT-IR of S2.

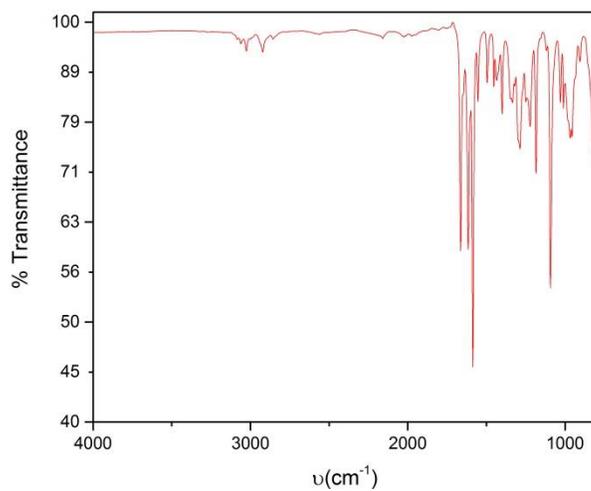
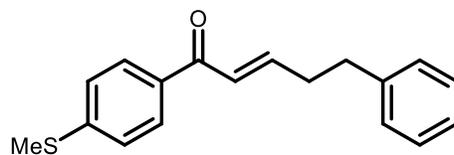


Figure S103. FT-IR of S3.

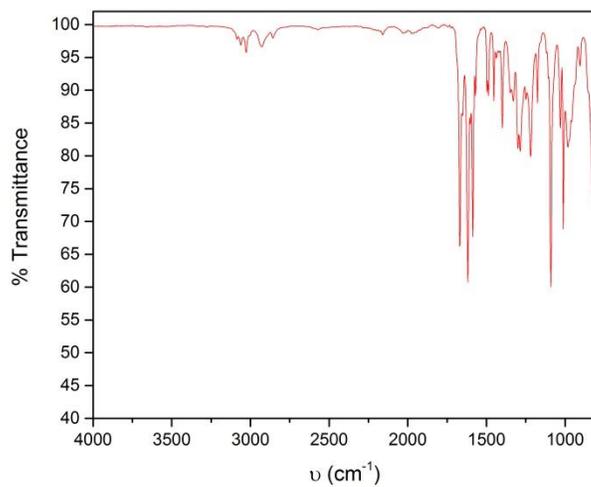
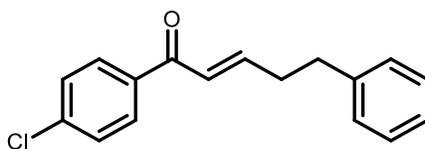


Figure S104. FT-IR of S4.

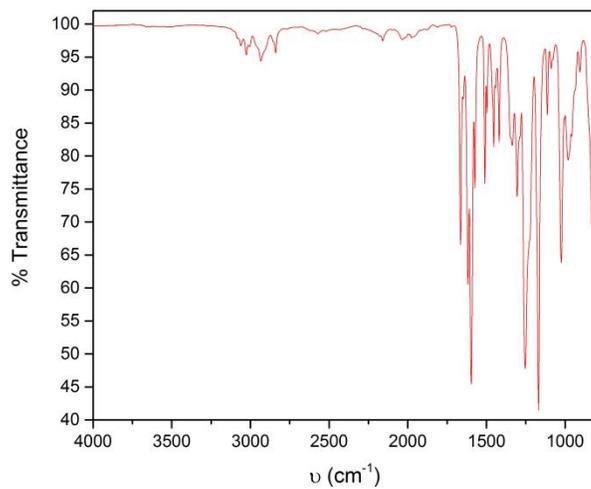
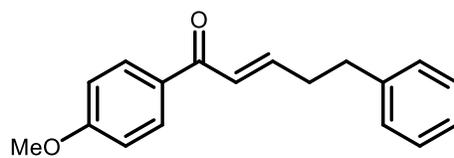


Figure S105. FT-IR of S5.

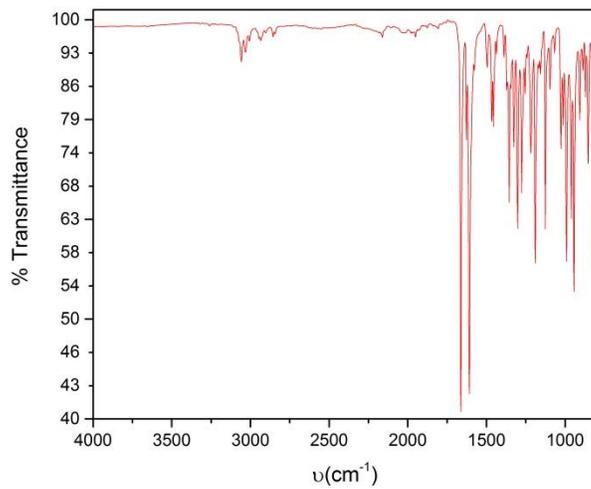
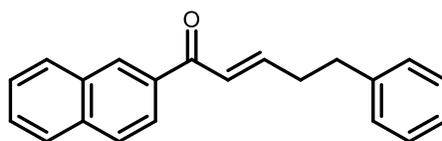


Figure S106. FT-IR of S6.

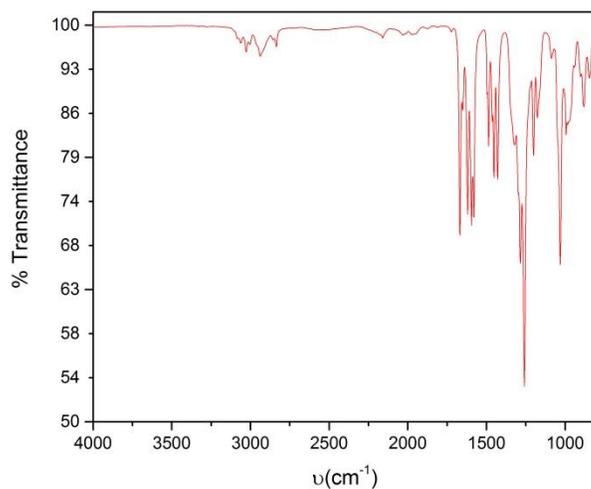
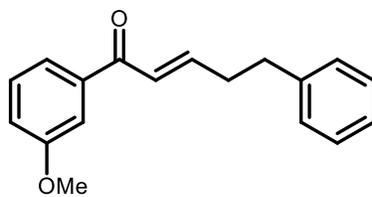


Figure S107. FT-IR of **S7**.

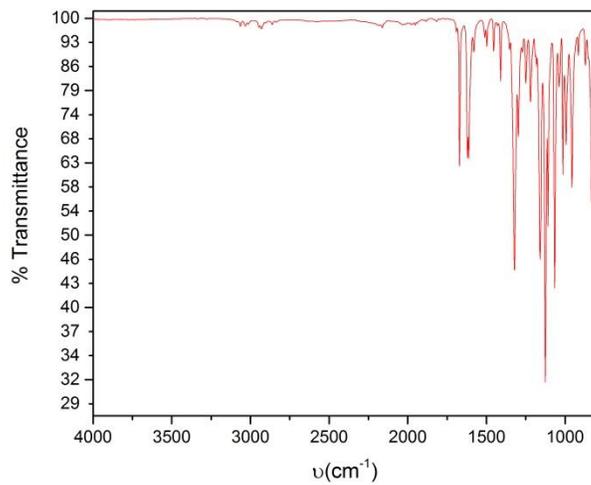
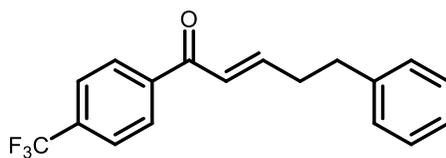


Figure S108. FT-IR of **S8**.

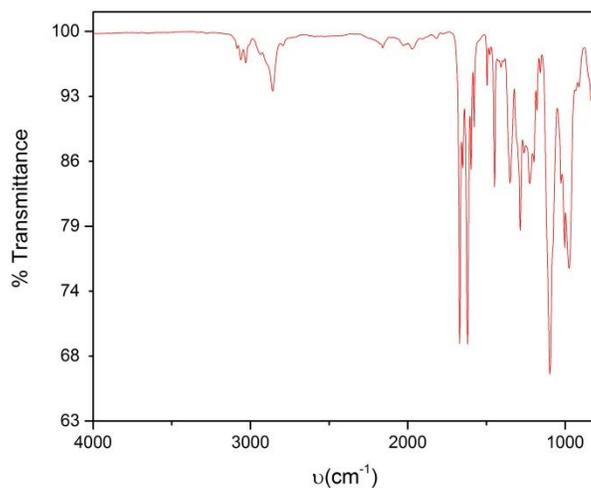
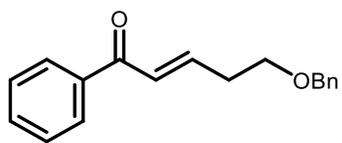


Figure S109. FT-IR of S9.

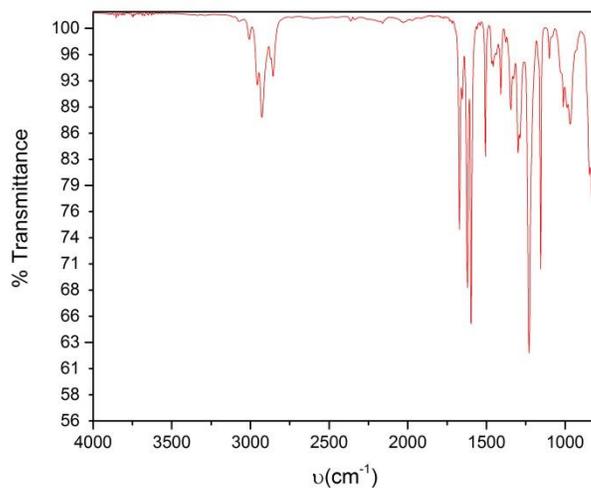
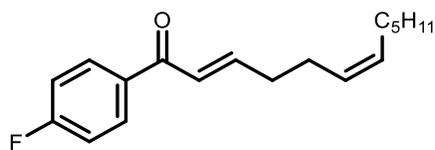


Figure S110. FT-IR of S10.

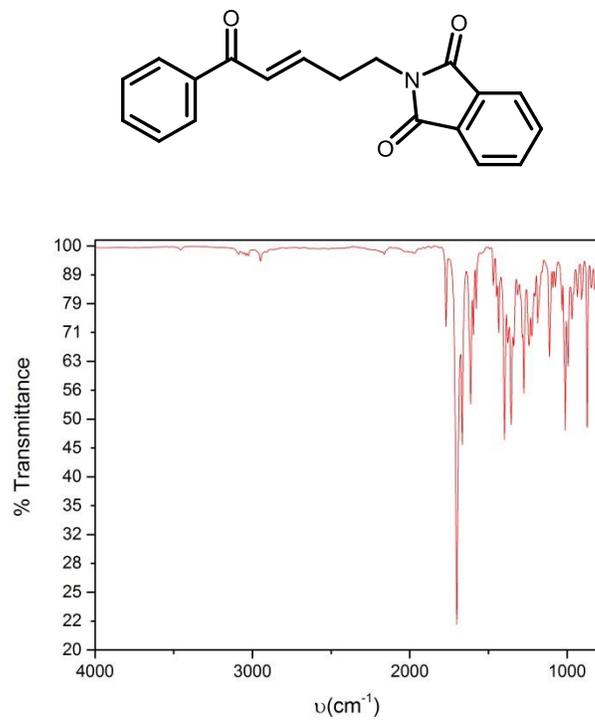


Figure S111. FT-IR of S11.

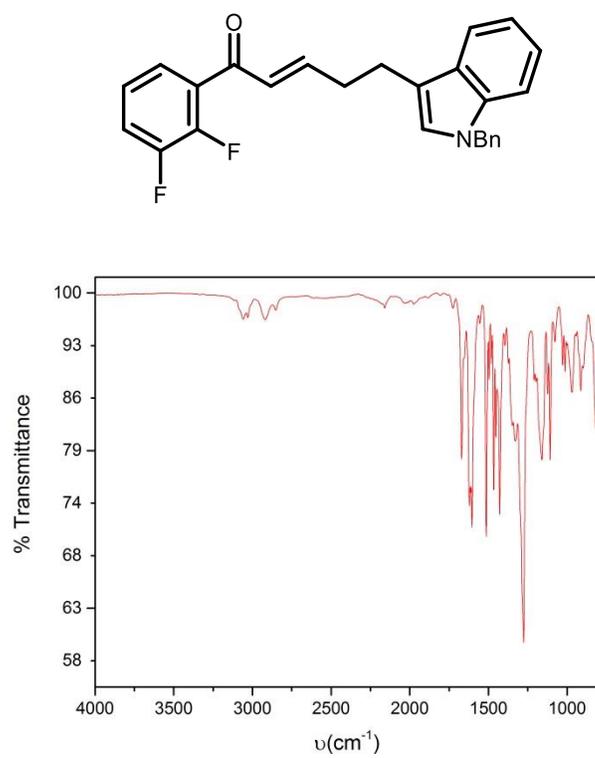


Figure S112. FT-IR of S12.

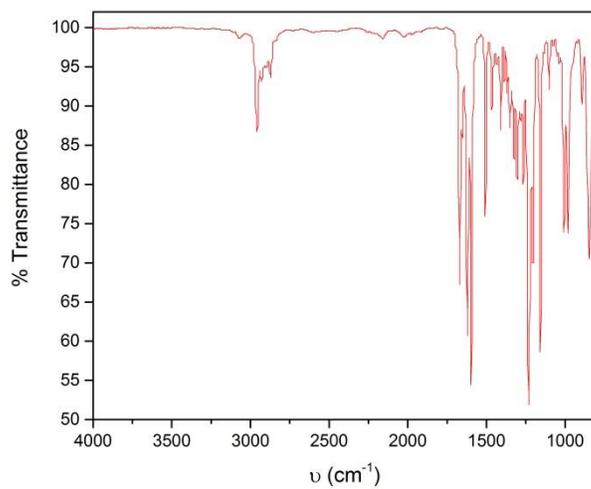
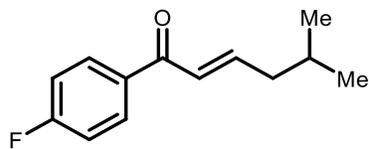


Figure S113. FT-IR of S13.

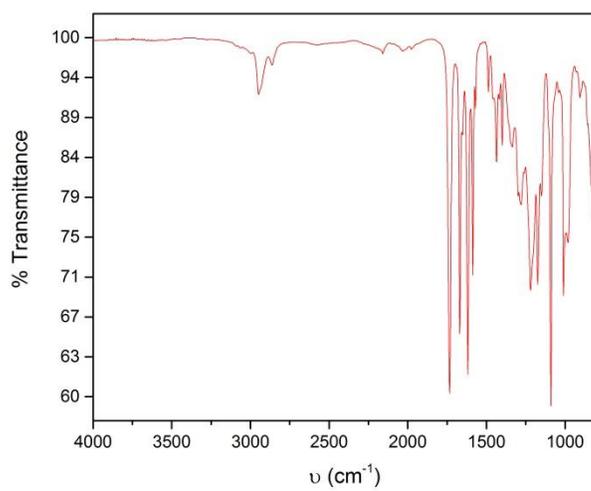
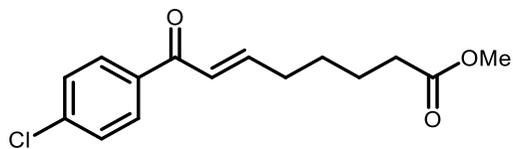


Figure S114. FT-IR of S14.

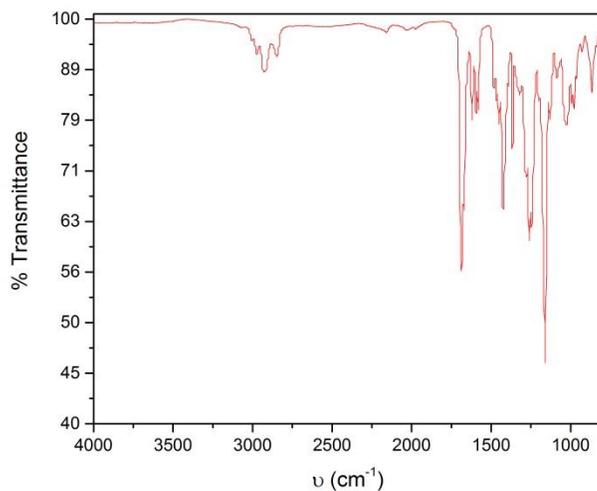
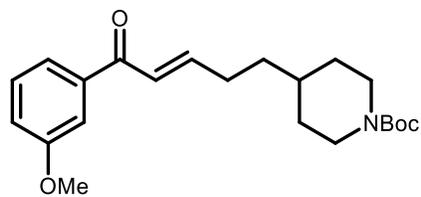


Figure S115. FT-IR of S15.

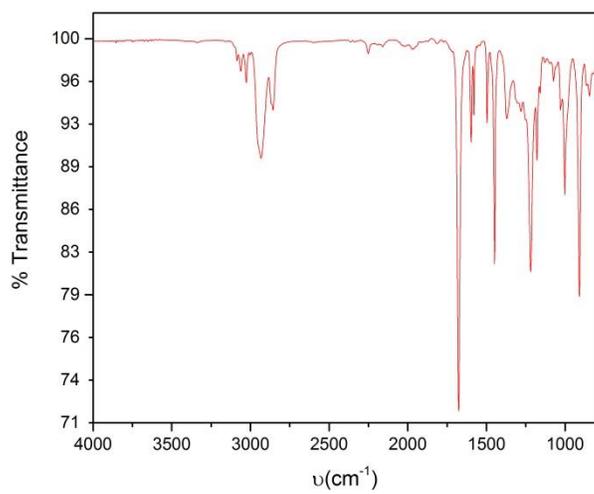
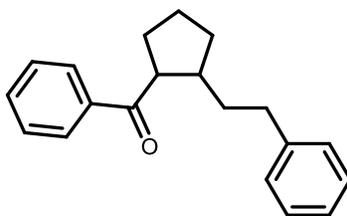


Figure S116. FT-IR of 3.

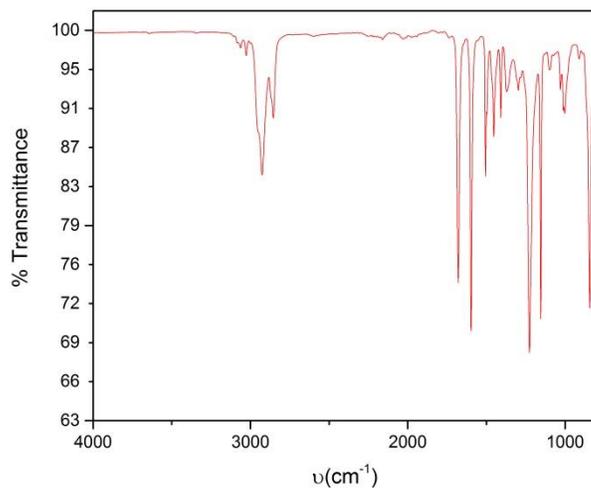
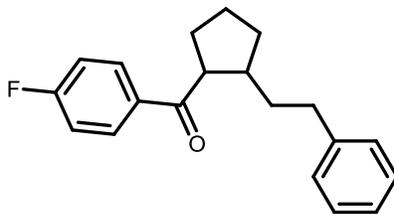


Figure S117. FT-IR of **5**.

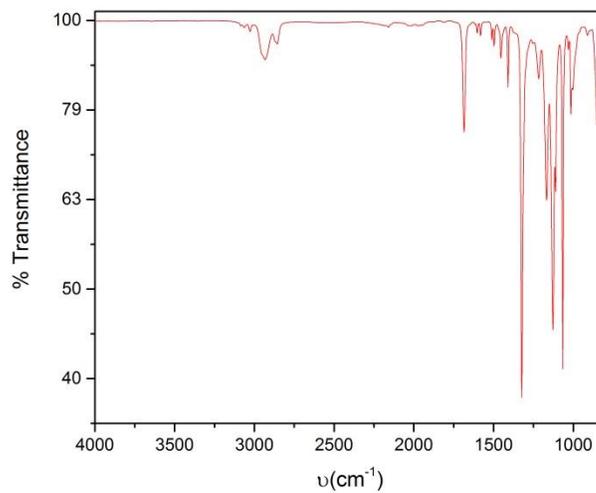
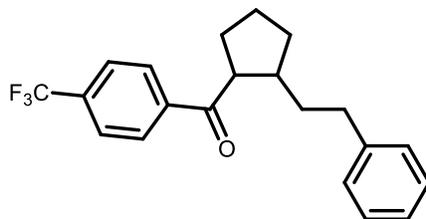


Figure S118. FT-IR of **6**.

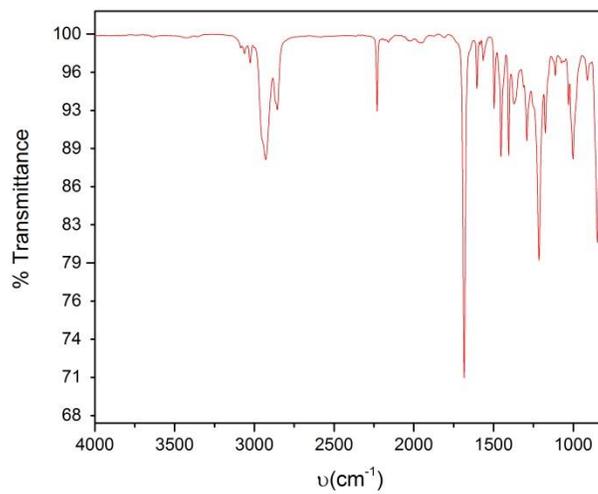
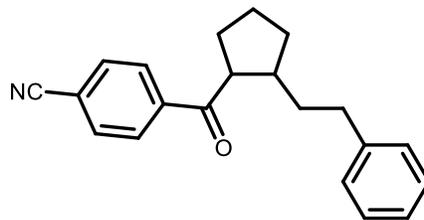


Figure S119. FT-IR of **7**.

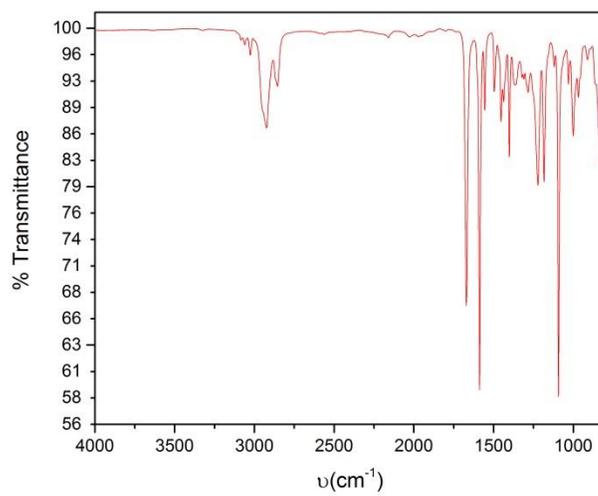
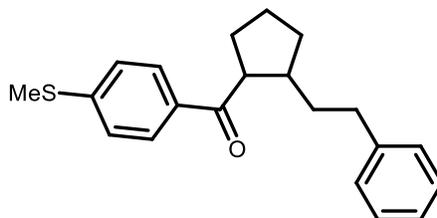


Figure S120. FT-IR of **8**.

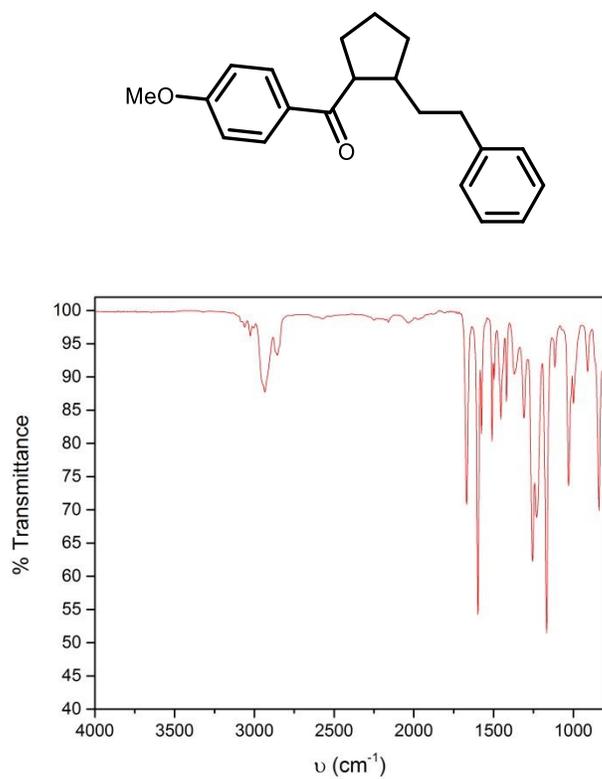


Figure S121. FT-IR of **9**.

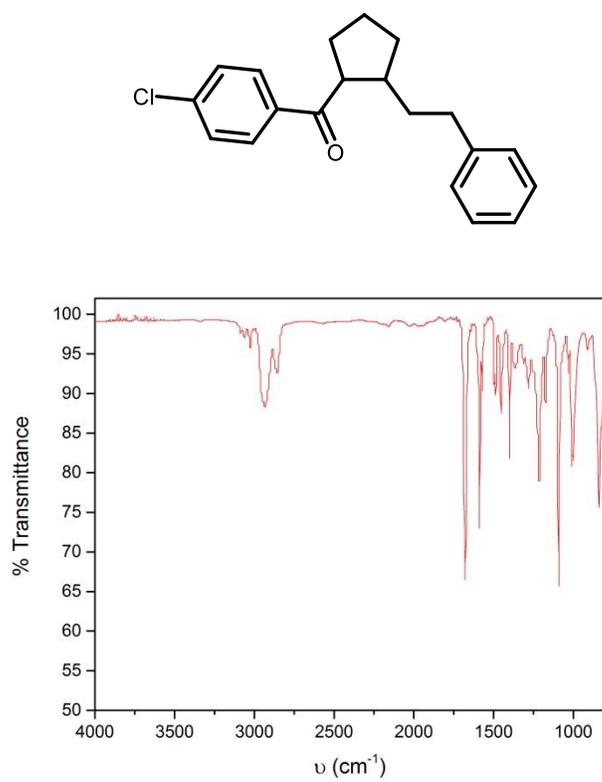


Figure S122. FT-IR of **10**.

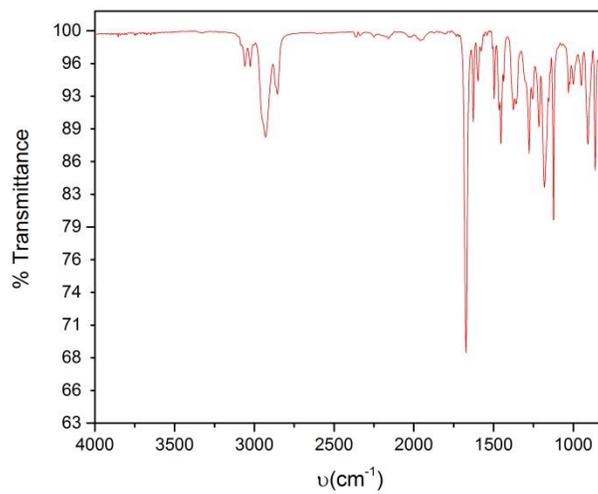
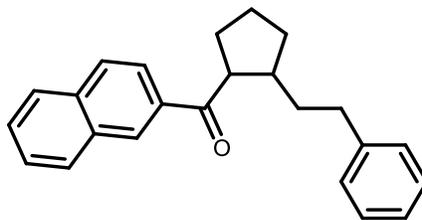


Figure S123. FT-IR of **11**.

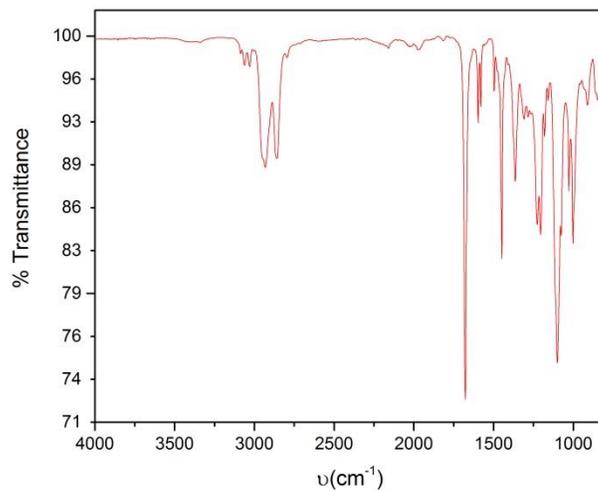
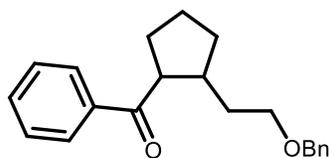


Figure S124. FT-IR of **12**.

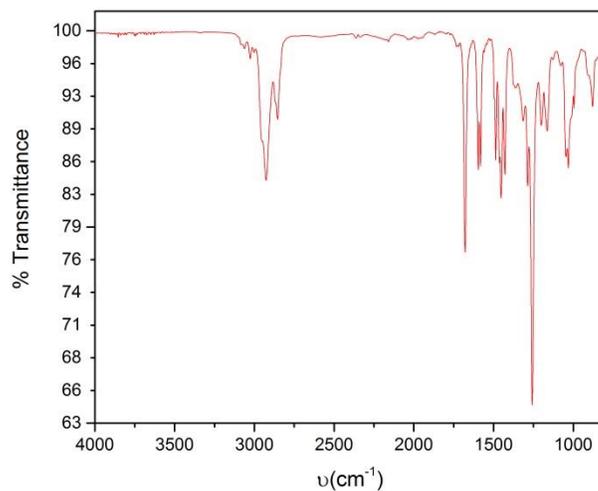
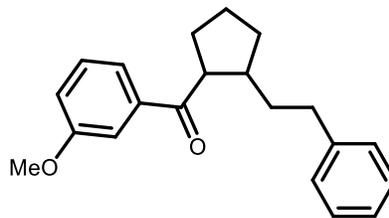


Figure S125. FT-IR of **13**.

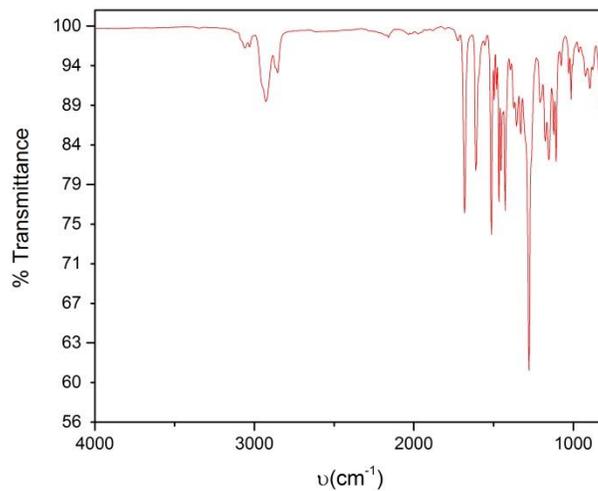
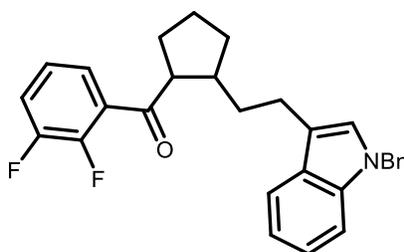


Figure S126. FT-IR of **14**.

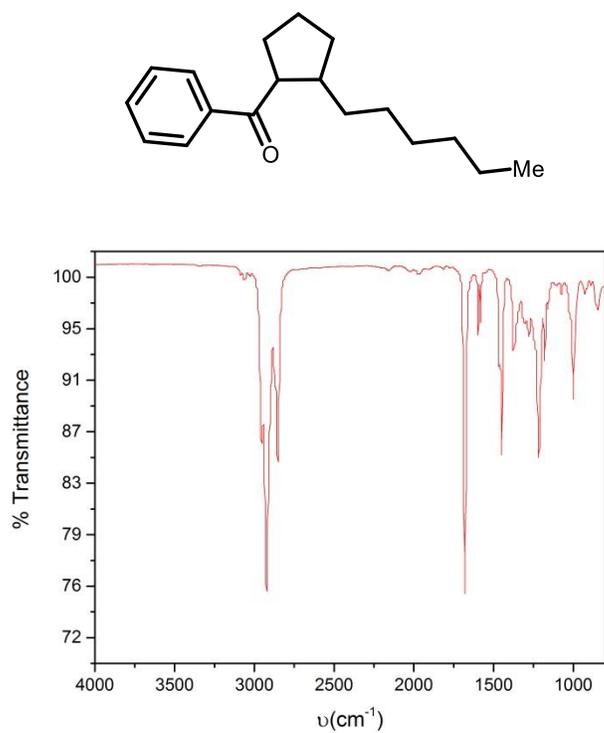


Figure S127. FT-IR of 15.

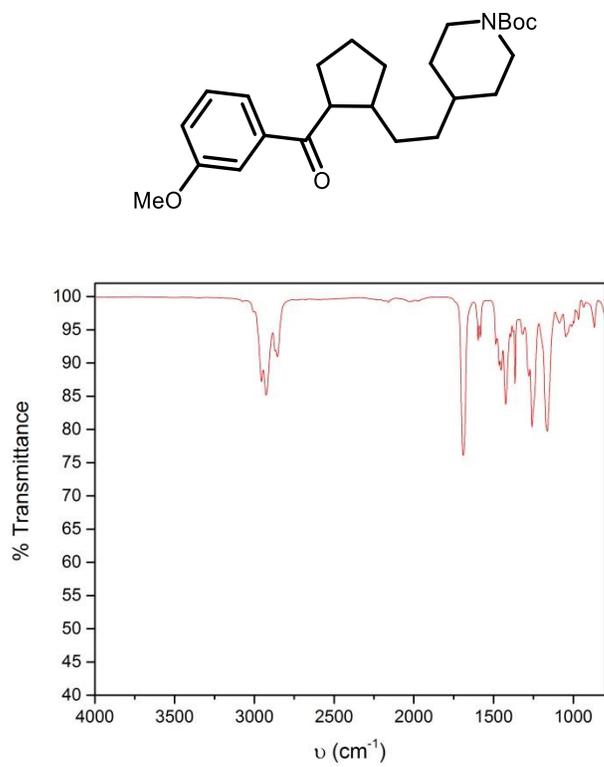


Figure S128. FT-IR of 16.

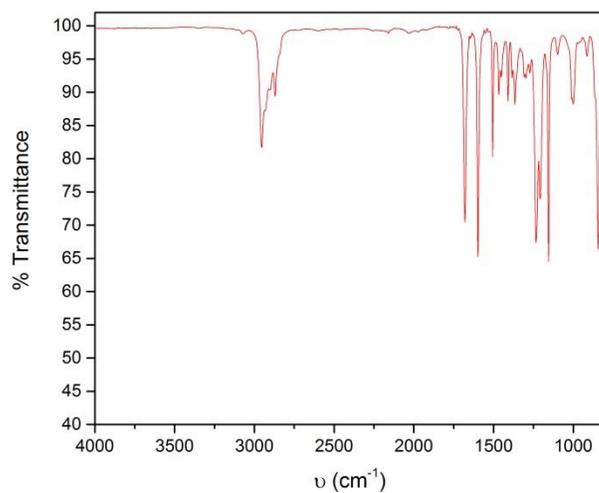
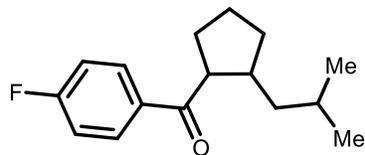


Figure S129. FT-IR of **17**.

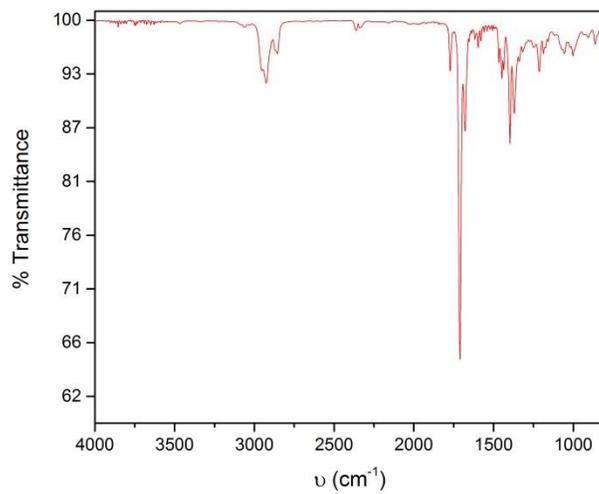
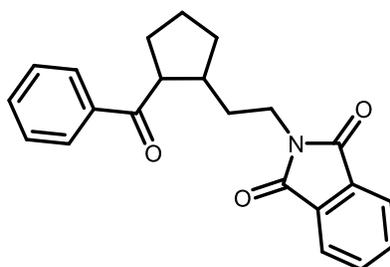


Figure S130. FT-IR of **18**.

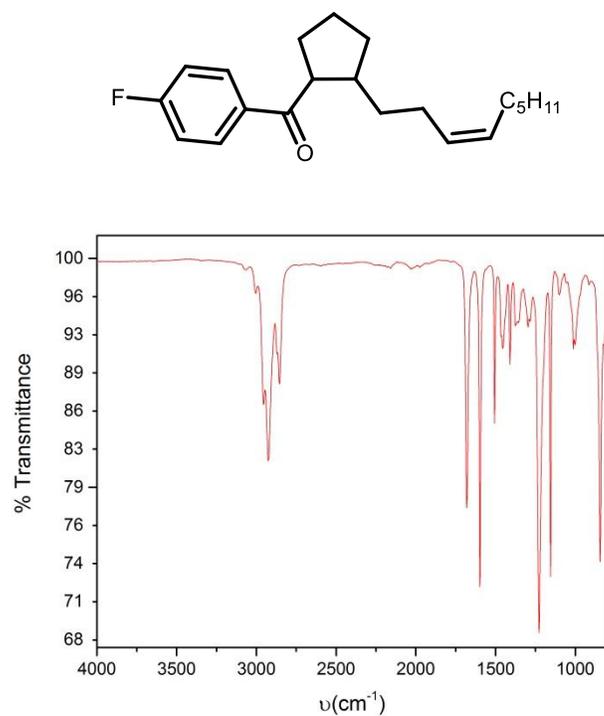


Figure S131. FT-IR of **19**.

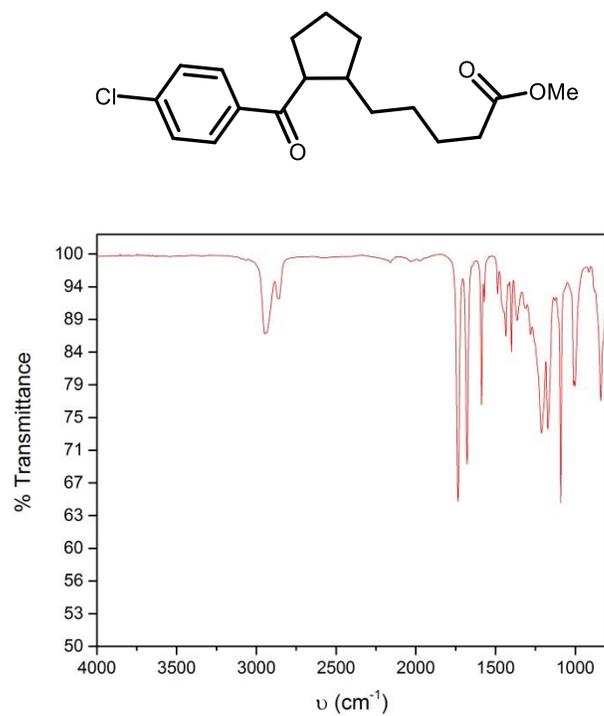


Figure S132. FT-IR of **20**.

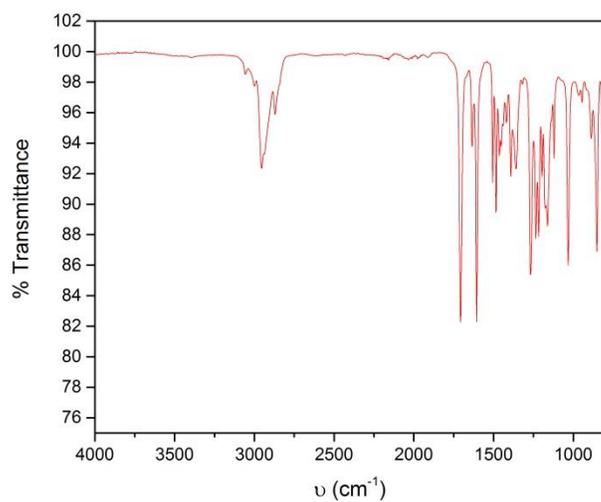
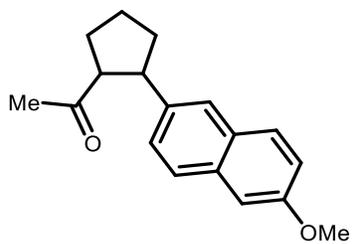


Figure S133. FT-IR of **22**.

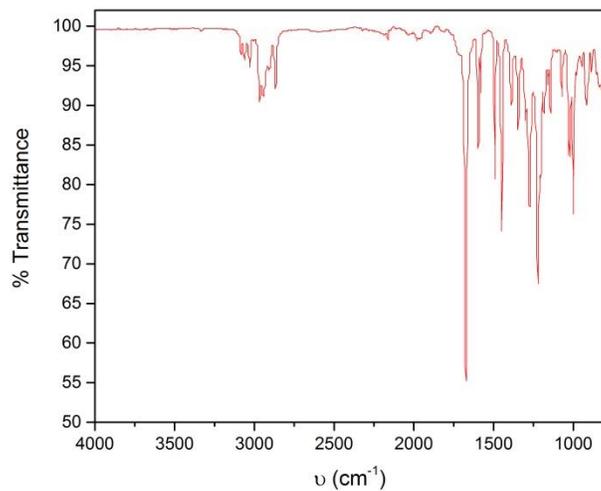
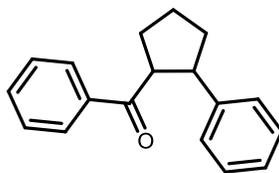


Figure S134. FT-IR of **23**.

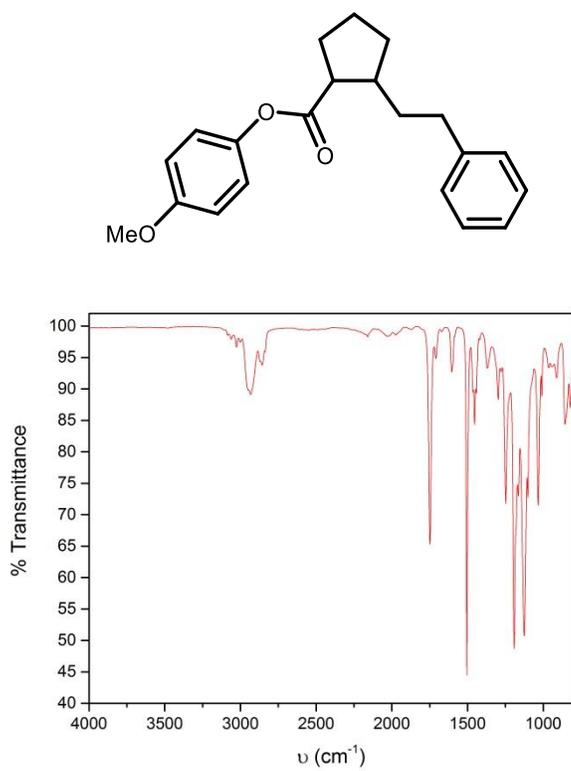


Figure S135. FT-IR of 24.

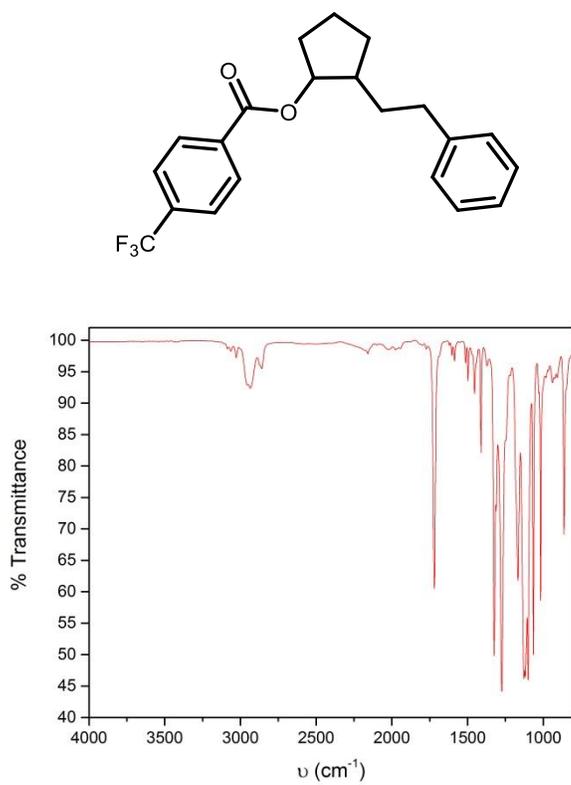


Figure S136. FT-IR of 25.

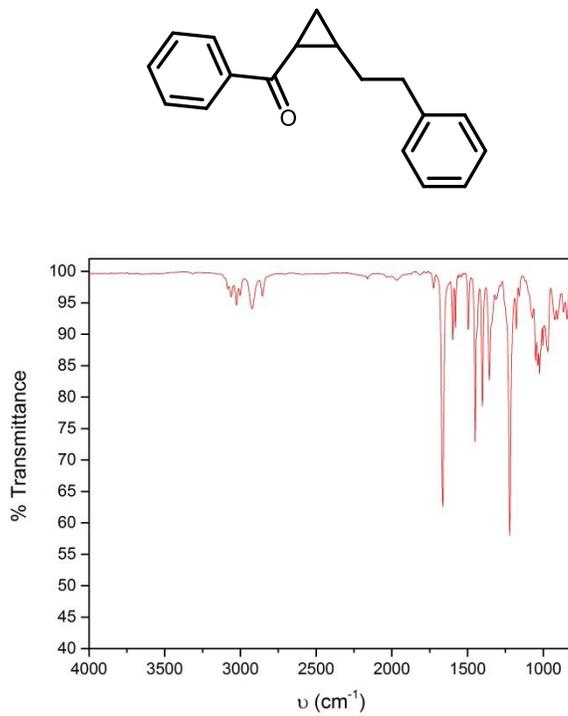


Figure S137. FT-IR of 2.

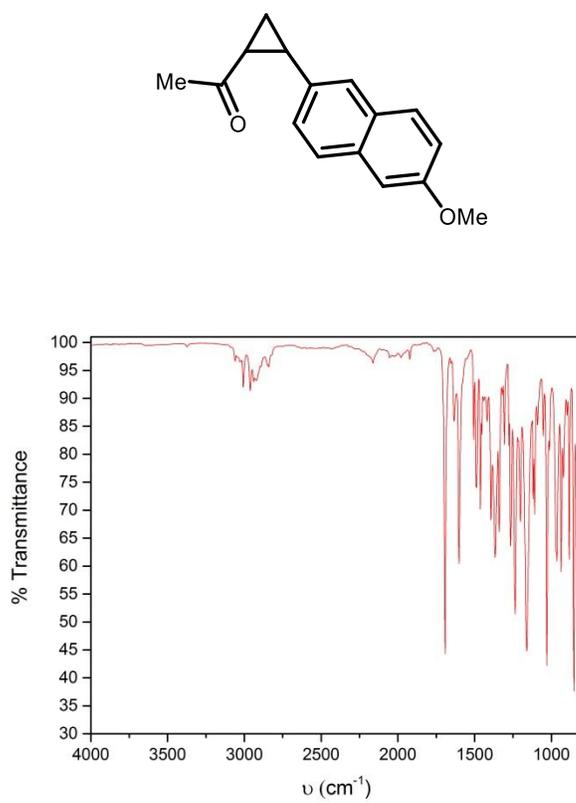


Figure S138. FT-IR of S16.

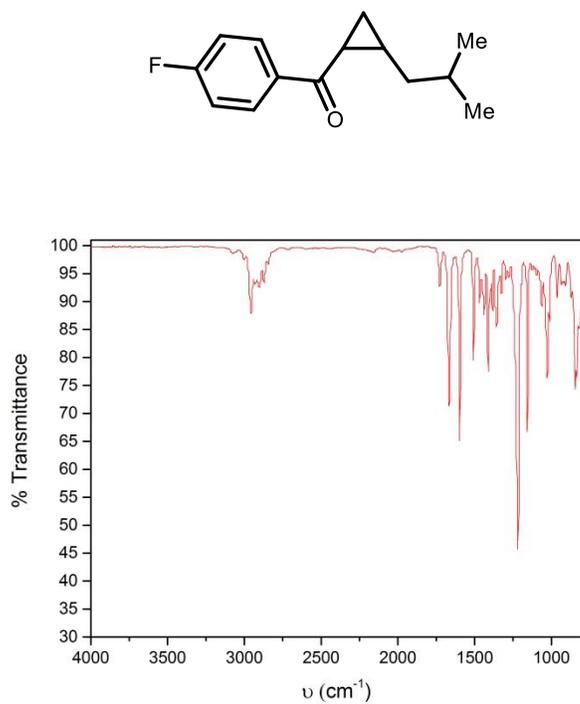


Figure S139. FT-IR of S17.

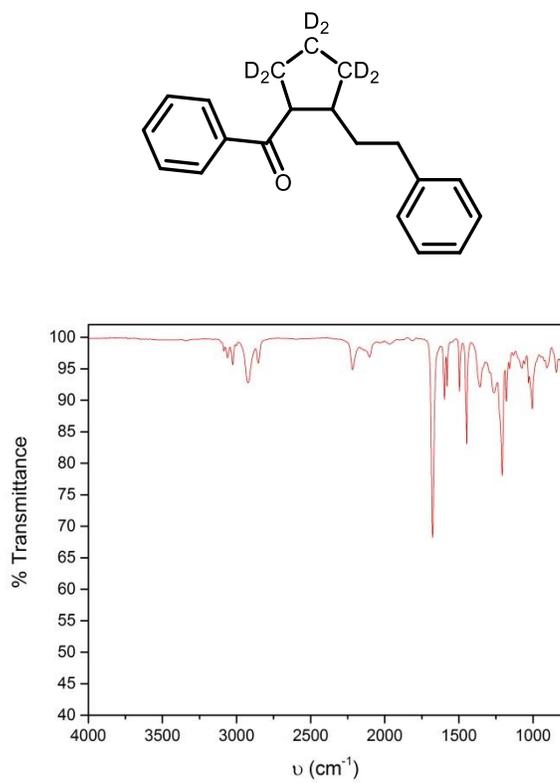
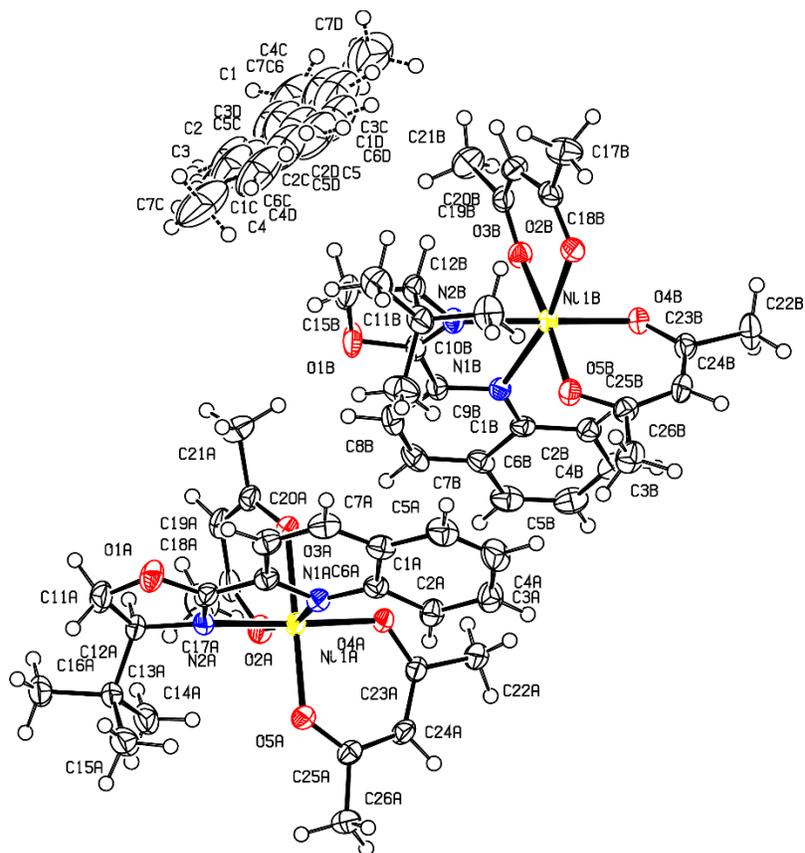


Figure S140. FT-IR of 3-d₆.

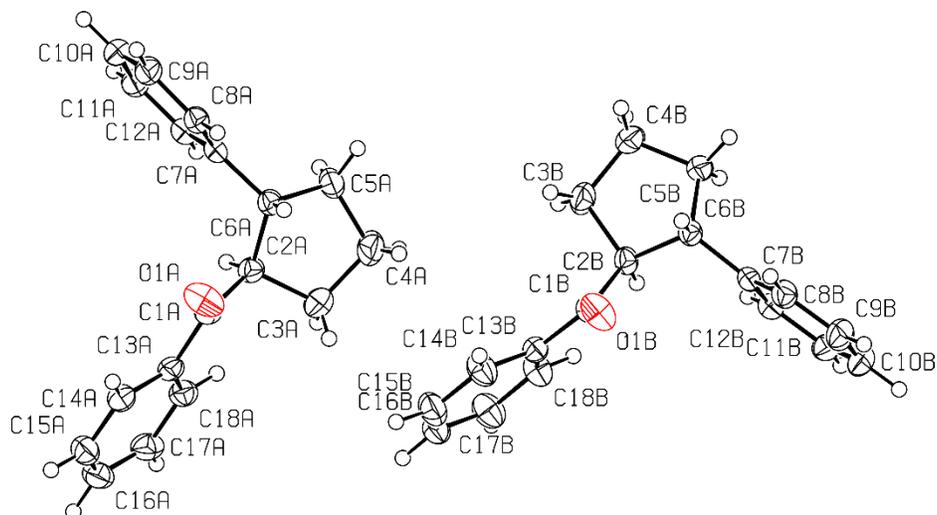
14. X-Ray Diffraction Data



Compound 4

Crystal data	
Chemical formula	C ₅₉ H ₇₂ N ₄ Ni ₂ O ₁₀
<i>M</i> _r	1114.62
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.8726 (5), 10.2560 (5), 32.4162 (17)
α , β , γ (°)	83.7260 (17), 82.6157 (18), 75.5173 (16)
<i>V</i> (Å ³)	2823.2 (3)
<i>Z</i>	2
<i>F</i> (000)	1180
<i>D</i> _x (Mg m ⁻³)	1.311
Radiation type	Mo <i>K</i> α
No. of reflections for cell measurement	9434
θ range (°) for cell	2.9–28.3

measurement	
μ (mm ⁻¹)	0.73
Crystal shape	Plate
Colour	Green
Crystal size (mm)	0.19 × 0.18 × 0.05
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Radiation source	sealed tube X-ray source
Monochromator	Triumph curved graphite crystal
Scan method	ω and phi scans
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{\min}, T_{\max}	0.656, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37118, 13147, 10377
R_{int}	0.039
θ values (°)	$\theta_{\max} = 28.3, \theta_{\min} = 2.9$
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.668
Range of h, k, l	$h = -11 \div 10, k = -13 \div 12, l = -43 \div 43$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.089, 1.04
No. of reflections	13147
No. of parameters	787
No. of restraints	568
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 2.0196P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.002
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.34, -0.41
Extinction method	SHELXL2018/3 (Sheldrick 2018), $F_c^* = kFc[1 + 0.001xFc^2/\sin(2\theta)]^{-1/4}$
Extinction coefficient	0.0042 (3)



Compound 23

Crystal data	
Chemical formula	C ₁₈ H ₁₈ O
<i>M_r</i>	250.32
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.6796 (6), 13.8004 (18), 17.618 (2)
α , β , γ (°)	98.691 (8), 91.838 (9), 93.043 (7)
<i>V</i> (Å ³)	1362.0 (3)
<i>Z</i>	4
<i>F</i> (000)	536
<i>D_x</i> (Mg m ⁻³)	1.221
Radiation type	Cu <i>K</i> α
No. of reflections for cell measurement	9724
θ range (°) for cell measurement	2.5–80.3
μ (mm ⁻¹)	0.57
Crystal shape	Fragment
Colour	Colourless
Crystal size (mm)	0.40 × 0.23 × 0.21
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Radiation source	I-mu-S microsource X-ray tube
Monochromator	Laterally graded multilayer (Goebel) mirror
Scan method	ω and ϕ scans
Absorption correction	Multi-scan

	SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{\min}, T_{\max}	0.474, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27448, 5832, 5311
R_{int}	0.083
θ values ($^{\circ}$)	$\theta_{\max} = 80.8, \theta_{\min} = 2.5$
$(\sin \theta/\lambda)_{\max}$ (\AA^{-1})	0.640
Range of h, k, l	$h = -7 \rightarrow 7, k = -16 \rightarrow 17, l = -22 \rightarrow 22$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.051, 0.144, 1.06
No. of reflections	5832
No. of parameters	343
No. of restraints	0
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 0.2621P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	< 0.001
$\Delta\rho_{\max}, \Delta\rho_{\min}$ ($e \text{\AA}^{-3}$)	0.35, -0.26

15. References

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APPENDIX B. SUPPORTING INFORMATION FOR CHAPTER 3

1. General Information

General considerations. Solvents were degassed and stored over activated 3 Å molecular sieves prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, and stored over activated 3 Å molecular sieves. Liquid reagents were degassed and stored over activated 3 Å molecular sieves prior to use. Zn powder (325 mesh, 99.9%) was purchased from Strem Chemicals, stored under inert atmosphere, and used without further purification. The [ⁱPrNDI]Ni₂(C₆H₆) complex was prepared according to a previously reported procedure.¹ The (±)-*t*-Bu-Quinox ligand was prepared according to a previously reported procedure.² Unless otherwise noted, all 1,1-dichloroalkenes were prepared according to previously reported procedures.^{3,4} All other reagents and starting materials were purchased from commercial vendors and used without further purification unless otherwise noted.

Physical methods. ¹H, ¹⁹F and ¹³C{¹H} NMR spectra were collected at room temperature on a Varian INOVA 300 MHz or a Bruker AV-III-800 NMR spectrometer. ¹H and ¹³C{¹H} NMR spectra are reported in parts per million relative to tetramethylsilane, using the residual solvent resonances as an internal standard. High-resolution mass data were obtained using a Thermo Scientific LTQ Orbitrap XL mass spectrometer or a Thermo Electron Corporation MAT 95XP-Trap mass spectrometer. ATR-IR data were collected on a Thermo Scientific Nicolet Nexus spectrometer containing a MCT* detector and KBr beam splitter with a range of 350–7400 cm⁻¹. Optical rotation data for **29** and **30** were obtained at room temperature using a Rudolph Autopol III S2 Polarimeter.

X-Ray Crystallography. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3.⁵ The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs^{6,7} and refined by full matrix least squares against F² with all reflections using Shelxl2018⁸ using the graphical interface Shelxle.⁹ If not specified otherwise H atoms attached to carbon, boron and nitrogen atoms as well as hydroxyl hydrogens were positioned geometrically

and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H and CH₂ and alkyne C-H moieties, and to 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH₂ and CH₃ moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. U_{iso}(H) values were set to a multiple of U_{eq}(C) with 1.5 for CH₃, NH₃⁺ and OH, and 1.2 for C-H, CH₂, B-H, N-H and NH₂ units, respectively. Additional data collection and refinement details, including description of disorder (where present) can be found in the Supporting Information. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1973505–1973507 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

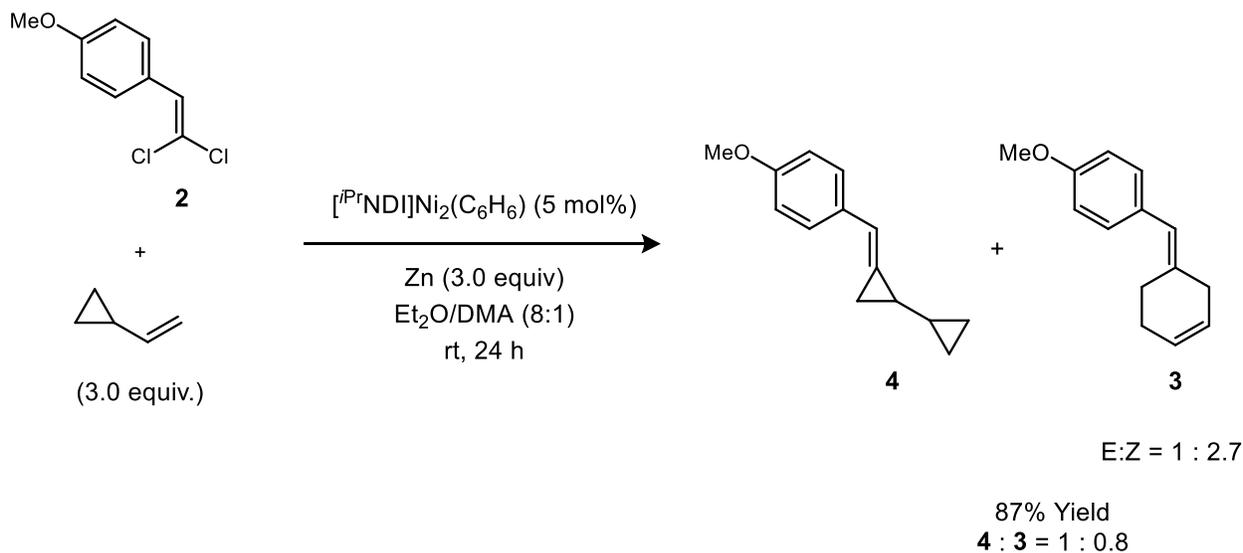
Bruker Quest with Mo radiation:

Single crystals of **6** and **49** were coated with Fomblin oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon100 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073$ Å) at 150 K.

Bruker Quest with Cu radiation:

Single crystals of **30** were coated with Fomblin oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, an I- μ -S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon-II CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu K α radiation ($\lambda = 1.54178$ Å) at 150 K.

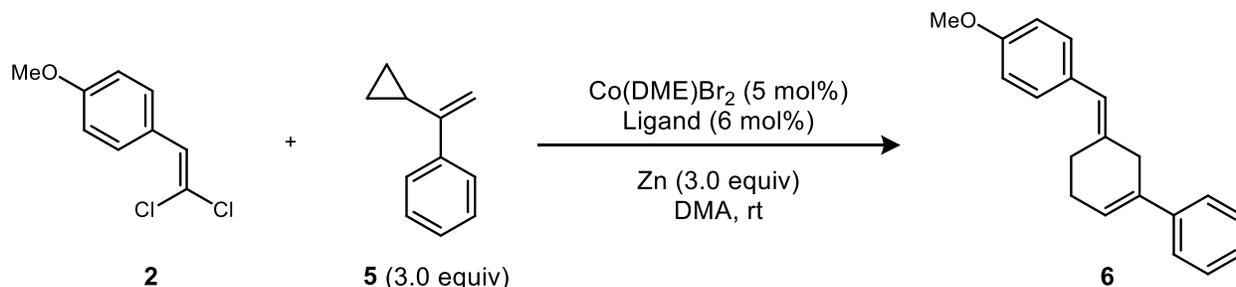
2. Reaction Optimization Studies



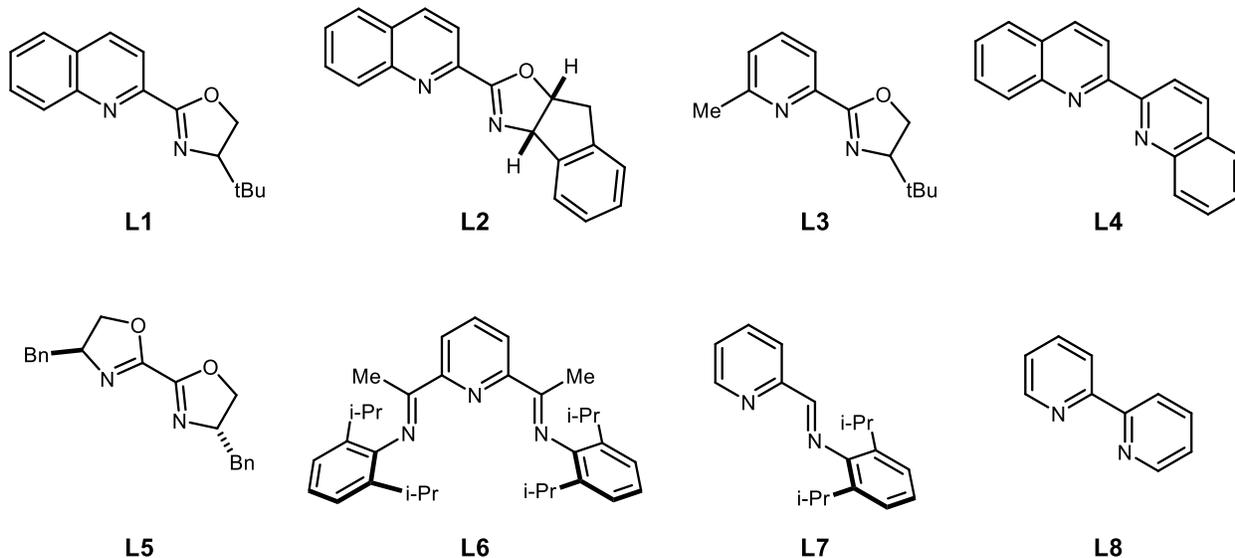
Initial detection of the [5 + 1]-product. In an N_2 -filled glovebox, a 5-mL vial was charged with $[\text{iPrNDI}]\text{Ni}_2(\text{C}_6\text{H}_6)$ (3.6 mg, 0.005 mmol, 0.05 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv), vinylcyclopropane (20.4 mg, 0.3 mmol, 3.0 equiv), and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) dissolved in Et_2O (0.8 mL) and DMA (0.1 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and diluted with Et_2O . An aliquot was filtered through a glass fiber pad, concentrated, and analyzed by ^1H NMR.

General Procedure for ligand comparison study. In an N_2 -filled glovebox, a 5-mL vial was charged with $\text{Co}(\text{DME})\text{Br}_2$ (1.5 mg, 0.005 mmol, 0.05 equiv), the ligand (0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv), (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv), and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) dissolved in DMA (0.75 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere,

and diluted with Et₂O. An aliquot was filtered through a glass fiber pad, concentrated, and analyzed by ¹H NMR.

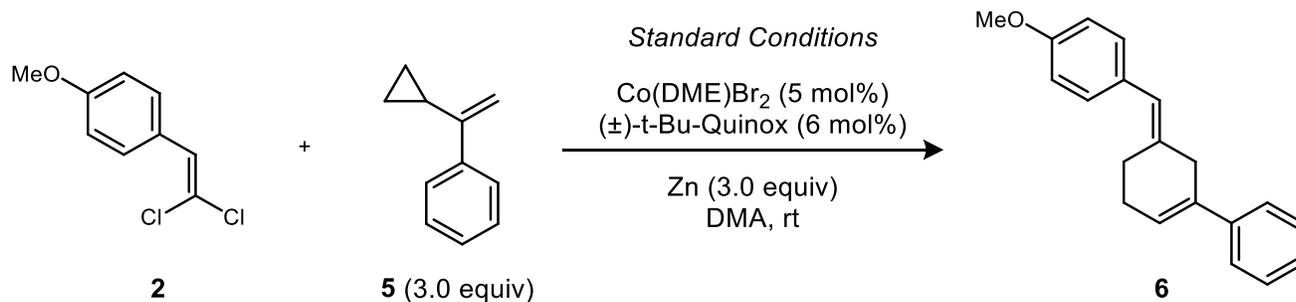


Entry	Ligand	Conversion of 2	Yield 6	E/Z Ratio of 6
1	L1	> 99%	94%	> 20 : 1
2	L2	> 99%	83%	> 20 : 1
3	L3	> 99%	15%	> 20 : 1
4	L4	11%	0%	N/A
5	L5	10%	0%	N/A
6	L6	22%	0%	N/A
7	L7	55%	0%	N/A
8	L8	29%	7%	> 20 : 1

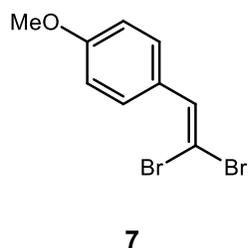


General Procedure for standard condition comparison study. In an N₂-filled glovebox, a 5-mL vial was charged with the metal source (0.005 mmol, 0.05 equiv), (±)-*t*-Bu-Quinox (1.52 mg, 0.006 mmol, 0.06 equiv), the reductant (0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of the 1,1-dihaloalkene (0.1 mmol, 1.0 equiv), the vinylcyclopropane, and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) dissolved in DMA (0.75

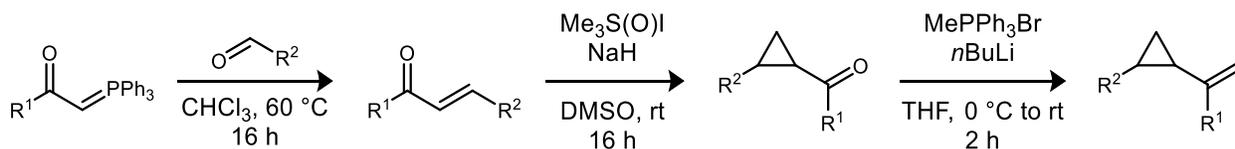
mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and diluted with Et₂O. An aliquot was filtered through a glass fiber pad, concentrated, and analyzed by ¹H NMR.



Entry	Deviation from Standard Conditions	Yield 6	E/Z of 6
1	none	97%	>20:1
2	3.0 equiv Mn instead of Zn	93%	>20:1
3	3.0 equiv TDAE instead of Zn	< 1%	NA
4	7 instead of 2	15%	>20:1
5	Ni(DME)Br ₂ or Fe(DME)Br ₂ instead of Co(DME)Br ₂	< 1%	NA
6	1.5 equiv of 5	42%	>20:1
7	1.5 equiv of 6 at 60 °C instead of rt	73%	>20:1
8	No (±)-t-Bu-Quinox	< 1%	NA
9	No Zn	< 1%	NA
10	3.0 equiv Cp ₂ Co instead of Zn	< 1%	NA
11	3.0 equiv Cp ₂ Co and 5.0 equiv ZnCl ₂ instead of Zn	63%	>20:1



3. Synthesis and Characterization of Vinylcyclopropane Substrates

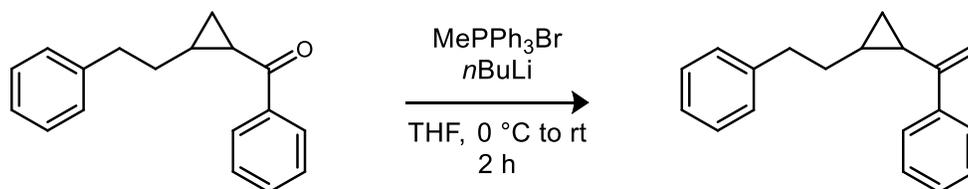


General procedure A: synthesis of α,β -unsaturated ketones from aldehydes. A round-bottom flask was charged with a stir bar, the Wittig reagent (1.5 equiv), the aldehyde (1.0 equiv), and CHCl_3 (0.5 M). The mixture was heated at reflux. After 16 h, the crude reaction mixture was concentrated under reduced pressure. The residue was loaded directly onto a SiO_2 column for purification.

General procedure B: synthesis of *trans*-cyclopropylketones from α,β -unsaturated ketones. A flame-dried round bottom flask was charged with solid NaH (60% in mineral oil, 1.2 equiv), trimethylsulfoxonium iodide (1.2 equiv), and a magnetic stir bar. The flask was placed under N_2 atmosphere, and DMSO (0.35 M) was added dropwise with stirring. After hydrogen evolution ceased, the reaction mixture was stirred for an additional 15 min, during which time the solution became clear. The α,β -unsaturated ketone (1.0 equiv) was added by syringe. The reaction was allowed to stir at room temperature. After 16 h, the reaction was quenched with water, and the mixture was extracted 3x with Et_2O . The combined organic layers were dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was loaded directly onto a SiO_2 column for purification.

General procedure C: synthesis of *trans*-vinylcyclopropanes from *trans*-cyclopropylketones. A flame-dried round-bottom flask was charged with a stir bar, MePPh_3Br (1.5 equiv), and THF (~ 0.2 M). The mixture was cooled to 0°C under N_2 atmosphere, followed by dropwise addition of $n\text{BuLi}$ (2.5 M in hexanes, 1.5 equiv). The mixture was stirred at 0°C for 30 min. A solution of the *trans*-cyclopropylketone in THF (1 mL) was added dropwise, and the reaction was then warmed to room temperature and stirred. After 2 h, the reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted 3x with Et_2O . The combined organic

layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was loaded directly onto a SiO₂ column for purification.



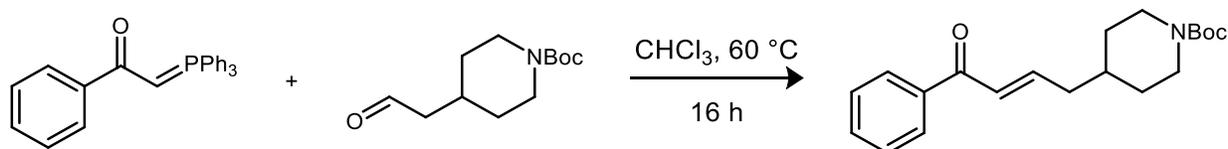
(1-(2-phenethylcyclopropyl)vinyl)benzene (S1). The reaction was conducted according to the general procedure C without modification using (2-phenethylcyclopropyl)(phenyl)methanone² (1.06 g, 4.2 mmol, 1.0 equiv), MePPh₃Br (2.25 g, 6.3 mmol, 1.5 equiv), and *n*BuLi (2.5 M in hexanes, 2.52 mL, 6.3 mmol, 1.5 equiv) in THF (25 mL). The product was purified by column chromatography (100% hexanes) to provide (1-(2-phenethylcyclopropyl)vinyl)benzene (949 mg, 91% yield) as a clear, colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, *J* = 6.8 Hz, 2H), 7.43 – 7.28 (m, 4H), 7.24 – 7.12 (m, 3H), 5.23 (s, 1H), 4.88 (s, 1H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.01 – 1.74 (m, 1H), 1.68 – 1.55 (m, 1H), 1.50 – 1.39 (m, 1H), 1.08 – 0.91 (m, 1H), 0.88 – 0.76 (m, 1H), 0.73 – 0.59 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 149.3, 142.3, 141.9, 128.5, 128.3, 128.2, 127.4, 126.2, 125.7, 108.9, 36.3, 35.8, 23.4, 21.1, 14.0.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₉H₂₀: 249.1638; found: 249.1643

TLC: R_f = 0.72 (100% hexanes)



***tert*-butyl (E)-4-(4-oxo-4-phenylbut-2-en-1-yl)piperidine-1-carboxylate (S2).** The reaction was conducted according to the general procedure A without modification using *tert*-butyl 4-(2-oxoethyl)piperidine-1-carboxylate (1.0 g, 4.4 mmol, 1.0 equiv) and phenacyltriphenylphosphorane (2.34 g, 6.2 mmol, 1.5 equiv) in CHCl₃ (10 mL). The product was

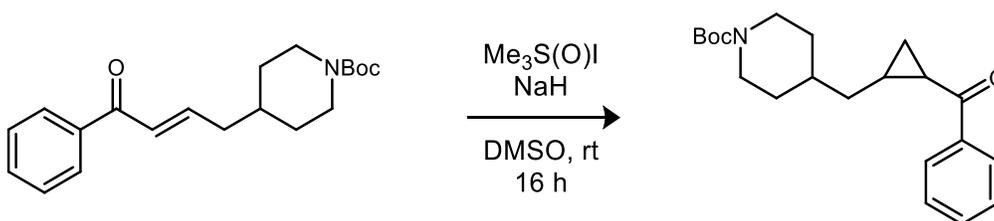
purified by column chromatography (20% Et₂O in hexanes) to provide *tert*-butyl (*E*)-4-(4-oxo-4-phenylbut-2-en-1-yl)piperidine-1-carboxylate (1.35 g, 93% yield) as an orange solid.

¹H NMR (300 MHz, CDCl₃) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.64 – 7.51 (m, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.03 (dt, *J* = 14.7, 7.2 Hz, 1H), 6.90 (d, *J* = 15.4 Hz, 1H), 4.10 (br s, 2H), 2.69 (t, *J* = 12.7 Hz, 2H), 2.28 (t, *J* = 6.8 Hz, 2H), 1.70 (d, *J* = 12.9 Hz, 3H), 1.45 (s, 9H), 1.33 – 0.98 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 190.5, 154.8, 147.3, 137.8, 132.7, 128.6, 128.5, 127.4, 79.4, 41.0, 39.8, 35.8, 32.0, 28.5.

HRMS(ESI) (*m/z*): [M + Na]⁺ Calcd for C₂₀H₂₇NO₃: 352.1883; found: 352.1887

TLC: R_f = 0.21 (15% Et₂O in hexanes)



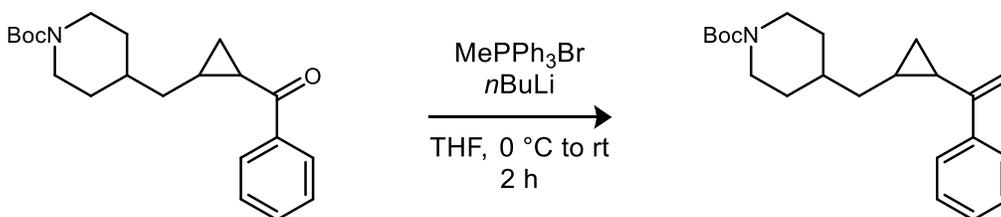
***tert*-butyl 4-((2-benzoylcyclopropyl)methyl)piperidine-1-carboxylate (S3).** The reaction was conducted according to the general procedure B without modification using **S2** (1.35 g, 4.4 mmol, 1.0 equiv), trimethylsulfoxonium iodide (1.08 g, 4.9 mmol, 1.2 equiv), NaH (60% in mineral oil, 196 mg, 1.2 equiv). The product was purified by column chromatography (20% Et₂O in hexanes) to provide *tert*-butyl 4-((2-benzoylcyclopropyl)methyl)piperidine-1-carboxylate (741 mg, 53% yield) as a yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 7.99 (d, *J* = 7.0 Hz, 2H), 7.63 – 7.53 (m, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 4.08 (br s, 2H), 2.66 (t, *J* = 12.9 Hz, 2H), 2.51 – 2.35 (m, 1H), 1.80 – 1.66 (m, 2H), 1.67 – 1.47 (m, 4H), 1.45 (s, 9H), 1.38 – 1.01 (m, 3H), 1.00 – 0.79 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 199.9, 154.8, 137.9, 132.7, 128.5, 128.0, 79.2, 40.4, 36.5, 32.1, 28.5, 25.6, 25.1, 24.5, 19.2.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₂₉NO₃: 344.2220; found: 344.2222

TLC: R_f = 0.27 (15% Et₂O in hexanes)



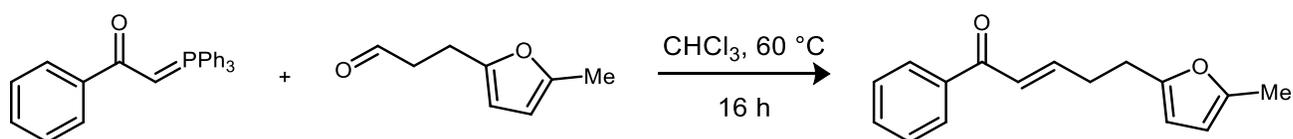
***tert*-butyl 4-((2-benzoylcyclopropyl)methyl)piperidine-1-carboxylate (S4).** The reaction was conducted according to the general procedure C without modification using **S3** (741 mg, 2.16 mmol, 1.0 equiv), MePPh₃Br (1.14 g, 3.2 mmol, 1.5 equiv), and *n*BuLi (2.5 M in hexanes, 1.3 mL, 3.2 mmol, 1.5 equiv) in THF (10 mL). The product was purified by column chromatography (10% Et₂O in hexanes) to provide *tert*-butyl 4-((2-benzoylcyclopropyl)methyl)piperidine-1-carboxylate (448 mg, 61% yield) as a clear, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.30 – 7.26 (m, 1H), 5.21 (s, 1H), 4.87 (s, 1H), 4.07 (s, 2H), 2.67 (s, 2H), 1.71 (d, *J* = 13.1 Hz, 2H), 1.62 – 1.49 (m, 2H), 1.45 (s, 9H), 1.41 – 1.34 (m, 1H), 1.25 – 1.18 (m, 1H), 1.18 – 1.05 (m, 2H), 0.98 – 0.92 (m, 1H), 0.84 – 0.76 (m, 1H), 0.69 – 0.56 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 154.9, 149.4, 141.8, 128.2, 127.4, 126.1, 108.8, 79.2, 41.2, 36.7, 32.2, 28.5, 23.3, 18.9, 14.3.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₂H₃₁NO₂: 342.2428; found: 342.2426

TLC: R_f = 0.16 (5% Et₂O in hexanes)



(*E*)-5-(5-methylfuran-2-yl)-1-phenylpent-2-en-1-one (S5). The reaction was conducted according to the general procedure A without modification using 3-(5-methylfuran-2-yl)propanal (1.4 g, 10.1 mmol, 1.0 equiv) and phenacyltriphenylphosphorane (5.7 g, 15.2 mmol, 1.5 equiv) in CHCl₃ (20 mL). The product was purified by column chromatography (20% Et₂O in hexanes) to provide (*E*)-5-(5-methylfuran-2-yl)-1-phenylpent-2-en-1-one (2.06 g, 84% yield) as an orange oil.

^1H NMR (300 MHz, CDCl_3) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.61 – 7.52 (m, 1H), 7.47 (t, $J = 7.3$ Hz, 2H), 7.07 (dt, $J = 15.4, 6.6$ Hz, 1H), 6.90 (d, $J = 15.5$ Hz, 1H), 5.88 (d, $J = 13.6$ Hz, 2H), 2.82 (t, $J = 7.4$ Hz, 2H), 2.73 – 2.56 (m, 2H), 2.26 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 190.9, 152.6, 150.6, 148.2, 137.9, 132.7, 128.6, 128.5, 126.6, 106.1, 106.0, 31.4, 26.8, 13.5.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$: 241.1223; found: 241.1220

TLC: $R_f = 0.29$ (15% Et_2O in hexanes)



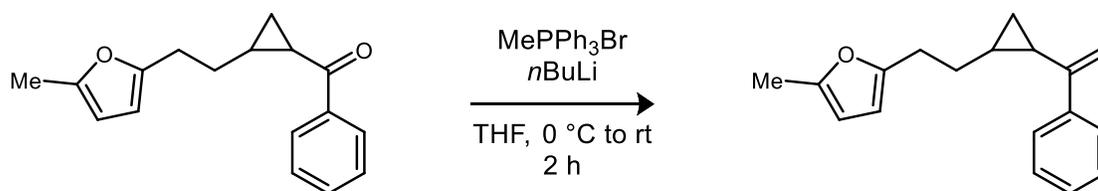
(2-(2-(5-methylfuran-2-yl)ethyl)cyclopropyl)(phenyl)methanone (S6). The reaction was conducted according to the general procedure B without modification using **S5** (2.06 g, 8.1 mmol, 1.0 equiv), trimethylsulfoxonium iodide (2.14 g, 9.71 mmol, 1.2 equiv), NaH (60% in mineral oil, 389 mg, 1.2 equiv). The product was purified by column chromatography (15% Et_2O in hexanes) to provide (2-(2-(5-methylfuran-2-yl)ethyl)cyclopropyl)(phenyl)methanone (1.02 g, 50% yield) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 7.96 (d, $J = 7.0$ Hz, 2H), 7.62 – 7.49 (m, 1H), 7.46 (t, $J = 7.3$ Hz, 2H), 5.81 (d, $J = 9.3$ Hz, 2H), 2.71 (t, $J = 7.3$ Hz, 2H), 2.48 – 2.40 (m, 1H), 2.20 (s, 3H), 1.90 – 1.70 (m, 2H), 1.68 – 1.58 (m, 1H), 1.53 – 1.40 (m, 1H), 1.02 – 0.85 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 199.9, 153.4, 150.3, 138.0, 132.6, 128.4, 128.0, 105.9, 105.8, 32.2, 27.8, 26.4, 25.0, 18.7, 13.5.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$: 255.1380; found: 255.1382

TLC: $R_f = 0.33$ (15% Et_2O in hexanes)



2-methyl-5-(2-(2-(1-phenylvinyl)cyclopropyl)ethyl)furan (S7). The reaction was conducted according to the general procedure C without modification using **S6** (1.02 g, 4.01 mmol, 1.0 equiv), MePPh₃Br (2.15 g, 6.01 mmol, 1.5 equiv), and *n*BuLi (2.5 M in hexanes, 2.4 mL, 6.01 mmol, 1.5 equiv) in THF (20 mL). The product was purified by column chromatography (100% hexanes) to provide 2-methyl-5-(2-(2-(1-phenylvinyl)cyclopropyl)ethyl)furan (403 mg, 42% yield) as a clear, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 6.8 Hz, 2H), 7.38 – 7.27 (m, 3H), 5.92 – 5.80 (m, 2H), 5.23 (s, 1H), 4.89 (s, 1H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.25 (s, 3H), 1.98 – 1.77 (m, 1H), 1.72 – 1.50 (m, 1H), 1.50 – 1.34 (m, 1H), 1.08 – 0.90 (m, 1H), 0.88 – 0.73 (m, 1H), 0.71 – 0.58 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 154.2, 150.2, 149.3, 141.8, 128.2, 127.4, 126.2, 109.0, 105.8, 105.4, 33.1, 28.0, 23.4, 21.0, 13.8, 13.5.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₂₀O: 253.1587; found: 253.1585

TLC: R_f = 0.47 (100% hexanes)



2-(2-(2-benzoylcyclopropyl)ethyl)isoindoline-1,3-dione (S8). The reaction was conducted according to the general procedure B without modification using (*E*)-2-(5-oxo-5-phenylpent-3-en-1-yl)isoindoline-1,3-dione² (1.16 g, 3.8 mmol, 1.0 equiv), trimethylsulfoxonium iodide (1.0 g, 4.5 mmol, 1.2 equiv), NaH (60% in mineral oil, 182 mg, 1.2 equiv). The product was purified by

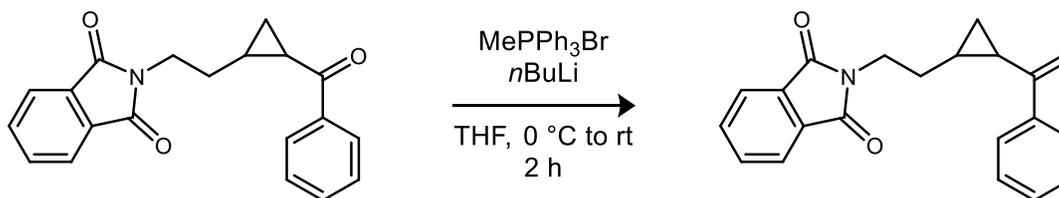
column chromatography (30% EtOAc in hexanes) to provide 2-(2-(2-benzoylcyclopropyl)ethyl)isoindoline-1,3-dione (424 mg, 35% yield) as a white solid.

^1H NMR (300 MHz, CDCl_3) δ 7.91 (d, $J = 6.9$ Hz, 2H), 7.79 – 7.71 (m, 2H), 7.69 – 7.61 (m, 2H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.39 (t, $J = 7.7$ Hz, 2H), 3.81 (t, $J = 7.3$ Hz, 2H), 2.56 – 2.37 (m, 1H), 1.95 – 1.72 (m, 2H), 1.69 – 1.57 (m, 1H), 1.53 – 1.34 (m, 1H), 1.02 – 0.84 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 199.3, 168.2, 137.8, 133.9, 132.6, 132.0, 128.4, 127.9, 123.2, 37.5, 32.0, 24.5, 23.7, 18.2.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{NO}_3$: 320.1281; found: 320.1284

TLC: $R_f = 0.21$ (30% EtOAc in hexanes)



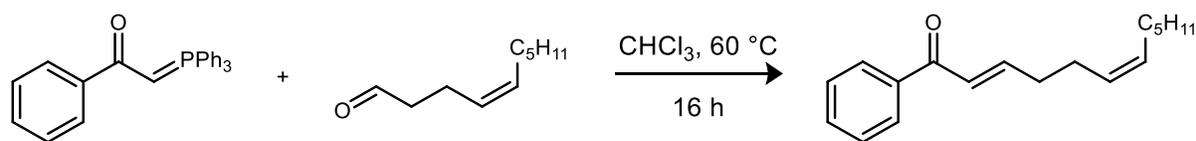
2-(2-(2-(1-phenylvinyl)cyclopropyl)ethyl)isoindoline-1,3-dione (S9). The reaction was conducted according to the general procedure C without modification using **S8** (587 mg, 1.84 mmol, 1.0 equiv), MePPh₃Br (986 mg, 2.76 mmol, 1.5 equiv), and *n*BuLi (2.5 M in hexanes, 1.1 mL, 2.76 mmol, 1.5 equiv) in THF (20 mL). The product was purified by column chromatography (15% EtOAc in hexanes) to provide 2-(2-(2-(1-phenylvinyl)cyclopropyl)ethyl)isoindoline-1,3-dione (84 mg, 14% yield) as a yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 7.89 – 7.76 (m, 2H), 7.76 – 7.62 (m, 2H), 7.46 (d, $J = 7.9$ Hz, 2H), 7.33 – 7.26 (m, 3H), 5.19 (s, 1H), 4.85 (s, 1H), 3.83 (t, $J = 7.2$ Hz, 2H), 2.08 – 1.87 (m, 1H), 1.65 – 1.56 (m, 1H), 1.51 – 1.35 (m, 1H), 1.09 – 0.87 (m, 1H), 0.83 – 0.72 (m, 1H), 0.72 – 0.59 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 168.4, 148.7, 141.5, 133.9, 132.2, 128.1, 127.4, 126.1, 123.2, 109.3, 37.8, 32.8, 23.0, 18.3, 13.5.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$: 318.1489; found: 318.1487

TLC: $R_f = 0.25$ (15% Et₂O in hexanes)



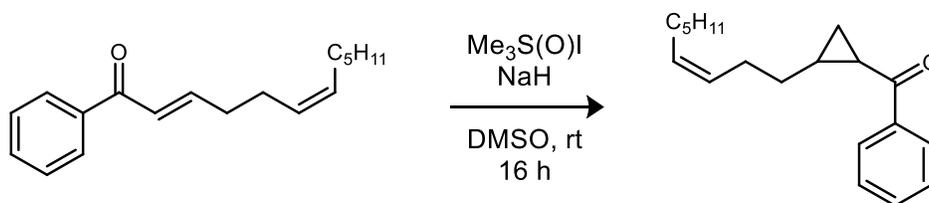
(2E,6Z)-1-phenyldodeca-2,6-dien-1-one (S10). The reaction was conducted according to the general procedure A without modification using *cis*-4-decenal (1.0 g, 6.48 mmol, 1.0 equiv) and phenyltriphenylphosphorane (3.7 g, 9.72 mmol, 1.5 equiv) in CHCl₃ (20 mL). The product was purified by column chromatography (5% Et₂O in hexanes) to provide (2E,6Z)-1-phenyldodeca-2,6-dien-1-one (1.50 g, 90% yield) as yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.06 (dt, *J* = 15.5, 6.5 Hz, 1H), 6.88 (d, *J* = 15.4 Hz, 1H), 5.54 – 5.26 (m, 2H), 2.47 – 2.32 (m, 2H), 2.32 – 2.19 (m, 2H), 2.03 (q, *J* = 6.8 Hz, 2H), 1.42 – 1.19 (m, 6H), 0.95 – 0.80 (m, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 190.9, 149.2, 138.0, 132.6, 131.4, 128.5, 128.5, 127.8, 126.2, 32.9, 31.5, 29.3, 27.3, 25.9, 22.6, 14.1.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₂₄O: 256.1807; found: 256.1814

TLC: R_f = 0.39 (5% Et₂O in hexanes)



(Z)-(2-(non-3-en-1-yl)cyclopropyl)(phenyl)methanone (S11). The reaction was conducted according to the general procedure B without modification using S10 (1.5 g, 5.85 mmol, 1.0 equiv), trimethylsulfoxonium iodide (1.55 g, 7.0 mmol, 1.2 equiv), NaH (60% in mineral oil, 182 mg, 1.2 equiv). The product was purified by column chromatography (5% Et₂O in hexanes) to

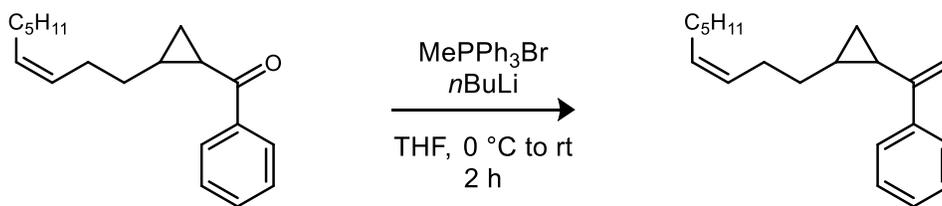
provide (Z)-(2-(non-3-en-1-yl)cyclopropyl)(phenyl)methanone (778 mg, 49% yield) as a yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 8.01 (d, $J = 7.0$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.47 (t, $J = 7.3$ Hz, 2H), 5.45 – 5.31 (m, 2H), 2.53 – 2.38 (m, 1H), 2.24 – 2.08 (m, 2H), 2.05 – 1.89 (m, 2H), 1.70 – 1.55 (m, 1H), 1.55 – 1.38 (m, 3H), 1.35 – 1.17 (m, 6H), 0.99 – 0.90 (m, 1H), 0.90 – 0.81 (m, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 200.0, 138.1, 132.6, 130.8, 128.6, 128.5, 128.0, 33.8, 31.5, 29.4, 27.2, 26.9, 26.9, 25.2, 22.6, 18.9, 14.1.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{26}\text{O}$: 271.2056; found: 271.2063

TLC: $R_f = 0.43$ (5% Et_2O in hexanes)



(Z)-(1-(2-(non-3-en-1-yl)cyclopropyl)vinyl)benzene (S12). The reaction was conducted according to the general procedure C without modification using **S11** (778 mg, 2.87 mmol, 1.0 equiv), MePPh_3Br (1.54 g, 4.30 mmol, 1.5 equiv), and $n\text{BuLi}$ (2.5 M in hexanes, 1.7 mL, 4.30 mmol, 1.5 equiv) in THF (30 mL). The product was purified by column chromatography (100% hexanes) to provide (Z)-(1-(2-(non-3-en-1-yl)cyclopropyl)vinyl)benzene (473 mg, 61% yield) as a clear, colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 7.57 (d, $J = 6.8$ Hz, 2H), 7.39 – 7.27 (m, 3H), 5.49 – 5.33 (m, 2H), 5.24 (s, 1H), 4.89 (s, 1H), 2.32 – 2.12 (m, 2H), 2.12 – 1.95 (m, 2H), 1.74 – 1.53 (m, 1H), 1.50 – 1.24 (m, 9H), 1.03 – 0.88 (m, 3H), 0.86 – 0.76 (m, 1H), 0.74 – 0.57 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 149.5, 141.9, 130.3, 129.3, 128.1, 127.4, 126.1, 108.7, 34.5, 31.6, 29.5, 27.2, 27.1, 23.4, 22.6, 21.3, 14.1, 13.9.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{28}$: 269.2264; found: 269.2262

TLC: $R_f = 0.84$ (100% hexanes)



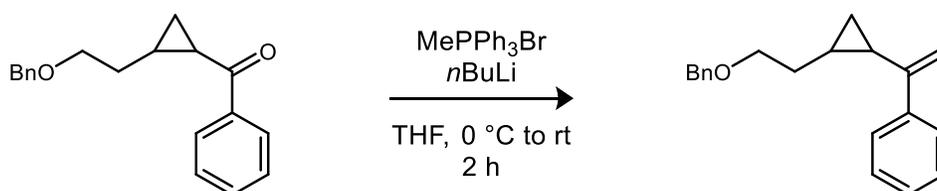
(2-(2-(benzyloxy)ethyl)cyclopropyl)(phenyl)methanone (S13). The reaction was conducted according to the general procedure B without modification using (*E*)-5-(benzyloxy)-1-phenylpent-2-en-1-one² (613 mg, 2.30 mmol, 1.0 equiv), trimethylsulfoxonium iodide (608 g, 2.76 mmol, 1.2 equiv), NaH (60% in mineral oil, 110 mg, 1.2 equiv). The product was purified by column chromatography (20% Et₂O in hexanes) to provide (2-(2-(benzyloxy)ethyl)cyclopropyl)(phenyl)methanone (323 mg, 50% yield) as a yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 7.99 (d, *J* = 6.9 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.37 (m, 2H), 7.38 – 7.28 (m, 5H), 4.50 (s, 2H), 3.58 (t, *J* = 6.2 Hz, 2H), 2.64 – 2.43 (m, 1H), 1.96 – 1.77 (m, 1H), 1.77 – 1.60 (m, 2H), 1.56 – 1.43 (m, 1H), 1.04 – 0.85 (m, 1H).

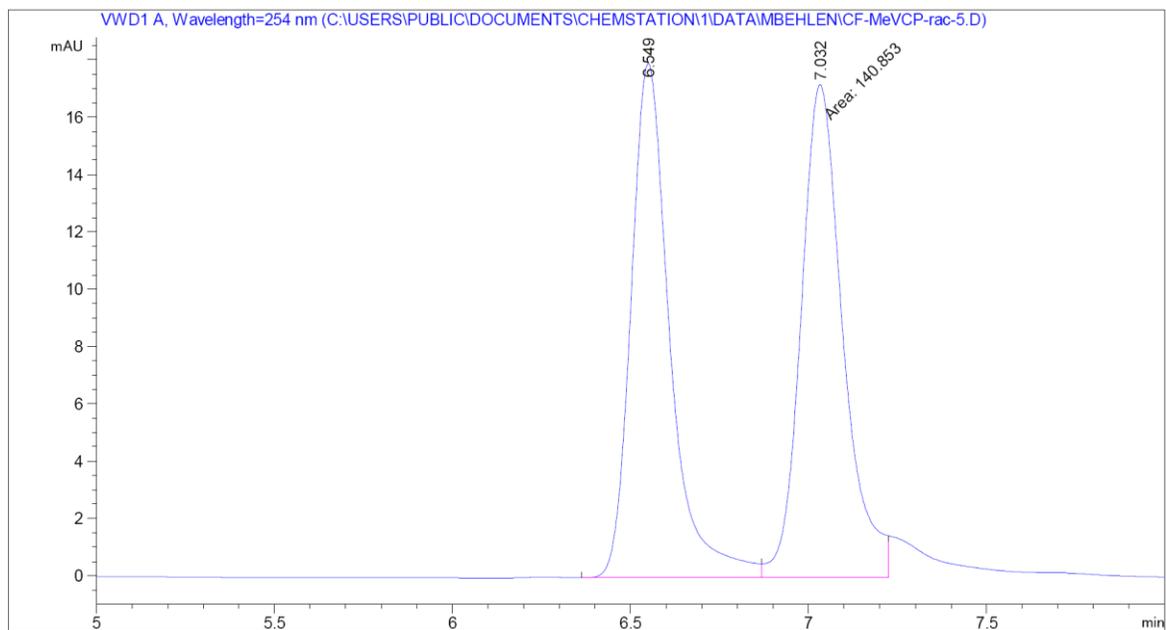
¹³C{¹H} NMR (201 MHz, CDCl₃) δ 200.0, 138.4, 138.0, 132.6, 128.5, 128.4, 128.0, 127.6, 127.5, 73.1, 69.8, 33.7, 25.0, 24.2, 18.2.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₁₉H₂₀O₂: 281.1536; found: 281.1538

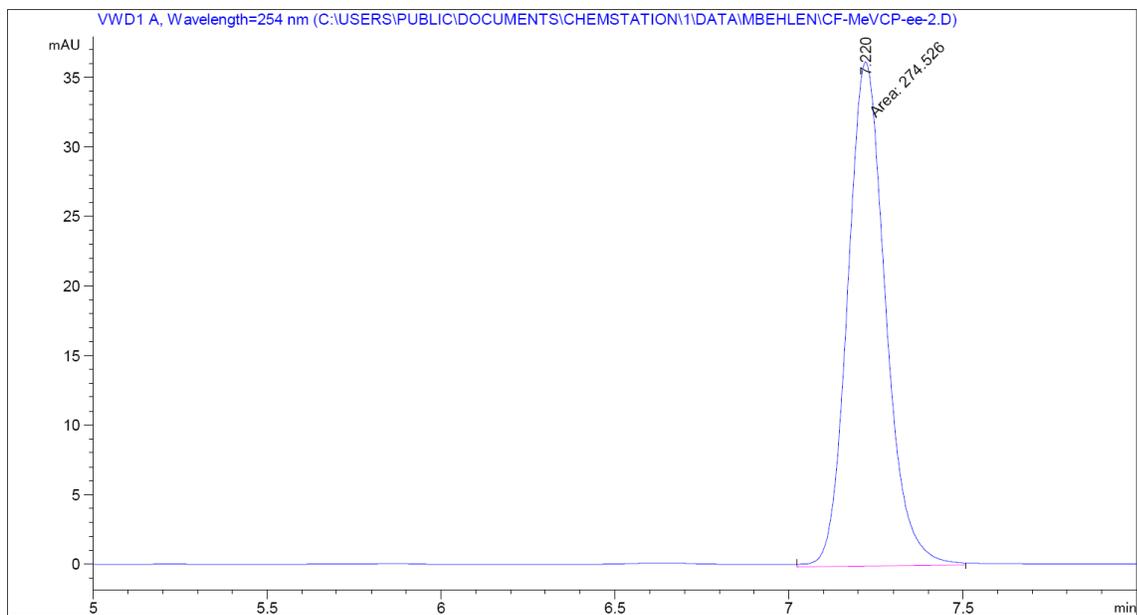
TLC: R_f = 0.22 (20% Et₂O in hexanes)



(1-(2-(2-(benzyloxy)ethyl)cyclopropyl)vinyl)benzene (S14). The reaction was conducted according to the general procedure C without modification using **S13** (322 mg, 1.15 mmol, 1.0 equiv), MePPh₃Br (616 mg, 1.73 mmol, 1.5 equiv), and *n*BuLi (2.5 M in hexanes, 0.7 mL, 1.73 mmol, 1.5 equiv) in THF (10 mL). The product was purified by column chromatography (5% Et₂O in hexanes) to provide (1-(2-(2-(benzyloxy)ethyl)cyclopropyl)vinyl)benzene (209 mg, 65% yield) as a clear, colorless oil.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.549	BV	0.1146	136.38600	17.95396	49.1945
2	7.032	MF	0.1364	140.85257	17.21415	50.8055

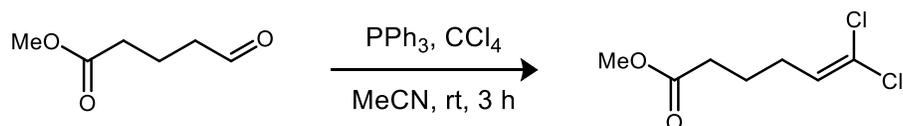


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.220	MM	0.1262	274.52582	36.26334	100.0000

Figure S1. HPLC data for **29**. (racemate, top; **29**, bottom).

4. Synthesis and Characterization of Vinylidene Substrates

General procedure for the synthesis of 1,1-dichlorolakenes from aldehydes. Under an N₂ atmosphere, a round bottom flask equipped with a magnetic stir bar was charged with Ph₃P (4.0 equiv) and MeCN (5 mL/mmol). With stirring, a solution of the aldehyde (1.0 equiv) and CCl₄ (2.0 equiv) in MeCN (2 mL/mmol) was added dropwise over 1 h. Following addition, the reaction mixture was stirred at room temperature for 2 h. The reaction was then quenched by addition of H₂O (100 mL). The crude reaction mixture was extracted with Et₂O (3 x 50 mL). The combined organic phases were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was loaded directly onto a SiO₂ column for purification.



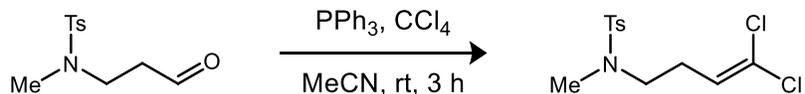
methyl 6,6-dichlorohex-5-enoate (S15). The reaction was conducted according to the general procedure without modification using methyl 5-oxopentanoate (1.8 g, 13.8 mmol, 1.0 equiv), triphenylphosphine (14.5 g, 55.3 mmol, 4.0 equiv), and CCl₄ (4.26 g, 2.69 mL, 27.6 mmol, 2.0 equiv). The product was purified by column chromatography (10% Et₂O in hexanes) to provide methyl 6,6-dichlorohex-5-enoate (1.19 g, 44% yield) as a clear, colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 5.84 (t, *J* = 7.5 Hz, 1H), 3.68 (s, 3H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.22 (q, *J* = 7.5 Hz, 2H), 1.85 – 1.65 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 173.4, 128.6, 120.9, 51.6, 33.1, 28.8, 23.3.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₇H₁₀Cl₂O₂: 197.0131; found: 197.0129

TLC: R_f = 0.29 (10% Et₂O in hexanes)



N-(4,4-dichlorobut-3-en-1-yl)-N,4-dimethylbenzenesulfonamide (S16). The reaction was conducted according to the general procedure without modification using N,4-dimethyl-N-(3-

oxopropyl)benzenesulfonamide¹² (1.89 g, 7.83 mmol, 1.0 equiv), triphenylphosphine (8.22 g, 31.3 mmol, 4.0 equiv), and CCl₄ (2.41 g, 0.89 mL, 15.7 mmol, 2.0 equiv). The product was purified by column chromatography (30% EtOAc in hexanes) to provide N-(4,4-dichlorobut-3-en-1-yl)-N,4-dimethylbenzenesulfonamide (869 mg, 36% yield) as a yellow oil.

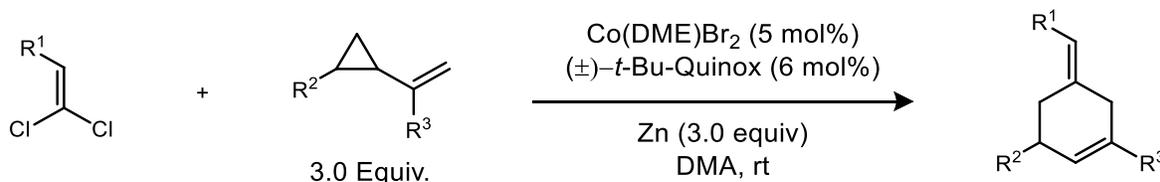
¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.89 (t, *J* = 7.2 Hz, 1H), 3.08 (t, *J* = 7.1 Hz, 2H), 2.74 (s, 3H), 2.49 – 2.34 (m, 5H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 143.4, 134.4, 129.7, 127.3, 125.8, 122.2, 48.2, 34.7, 28.2, 21.4.

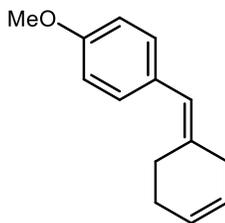
HRMS(APCI) (*m/z*): [*M* + *H*]⁺ Calcd for C₁₂H₁₅Cl₂NO₂S: 308.0273; found: 308.0271

TLC: *R*_f = 0.15 (10% Et₂O in hexanes)

5. Substrate Scope Studies and Product Characterization



General Procedure for the [5 + 1]-Cycloaddition Reaction. In an N₂-filled glovebox, a 5-mL vial was charged with Co(DME)Br₂ (1.54 mg, 0.005 mmol, 0.05 equiv), (±)-*t*-Bu-Quinox (1.52 mg, 0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of the 1,1-dichloroalkene (0.1 mmol, 1.0 equiv) and the vinylcyclopropane (0.3 mmol, 3.0 equiv) dissolved in DMA (0.75 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and loaded directly onto a SiO₂ column for purification.



(E)-1-(cyclohex-3-en-1-ylidenemethyl)-4-methoxybenzene (3). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and vinylcyclopropane (20.4 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 15% CH₂Cl₂ in hexanes).

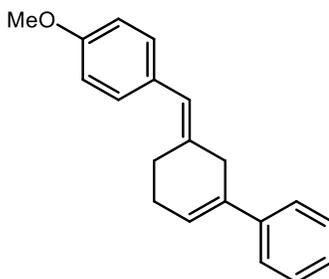
14.1 mg isolated (70% yield), colorless oil, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.16 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.33 (s, 1H), 5.81 – 5.65 (m, 2H), 3.81 (s, 3H), 2.89 (s, 2H), 2.55 (t, *J* = 6.4 Hz, 2H), 2.25 – 2.10 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 157.7, 137.9, 130.5, 129.8, 126.8, 126.6, 122.1, 113.4, 55.1, 35.6, 27.1, 25.8.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₁₄H₁₆O: 201.1274; found: 201.1272

TLC: R_f = 0.51 (5% Et₂O in hexanes)



(E)-3-(4-methoxybenzylidene)-2,3,4,5-tetrahydro-1,1'-biphenyl (6). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 15% CH₂Cl₂ in hexanes). Single crystals of **6** suitable for X-ray diffraction analysis were obtained by evaporation of a saturated Et₂O solution at room temperature.

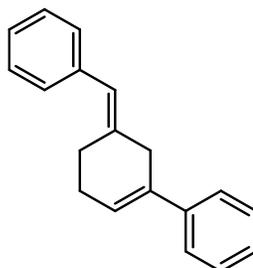
25.9 mg isolated (94% yield), white solid, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.43 (s, 1H), 6.26 – 6.11 (m, 1H), 3.82 (s, 3H), 3.29 (s, 2H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.43 – 2.30 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 157.9, 141.5, 137.8, 136.4, 130.6, 129.9, 128.3, 126.9, 125.1, 124.2, 122.8, 113.6, 55.3, 37.9, 27.5, 25.5.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{O}$: 277.1587; found: 277.1589

TLC: R_f = 0.46 (5% Et_2O in hexanes)



(E)-3-benzylidene-2,3,4,5-tetrahydro-1,1'-biphenyl (11). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)benzene (17.3 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 15% CH_2Cl_2 in hexanes).

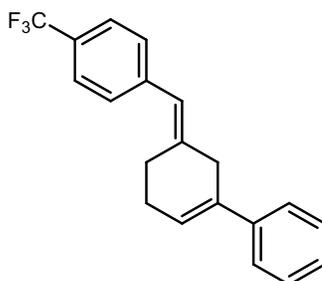
21.5 mg isolated (87% yield), white solid, $E/Z = >20 : 1$

^1H NMR (300 MHz, CDCl_3) δ 7.44 (d, $J = 8.0$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 4H), 7.29 – 7.27 (m, 1H), 7.26 – 7.17 (m, 3H), 6.50 (s, 1H), 6.27 – 6.10 (m, 1H), 3.39 – 3.25 (m, 2H), 2.62 (t, $J = 6.4$ Hz, 2H), 2.47 – 2.27 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 141.5, 139.0, 138.0, 136.3, 128.9, 128.3, 128.1, 126.9, 126.1, 125.1, 124.2, 123.4, 38.0, 27.5, 25.5.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{18}$: 245.1325; found: 245.1327

TLC: R_f = 0.61 (5% Et_2O in hexanes)



(E)-3-(4-(trifluoromethyl)benzylidene)-2,3,4,5-tetrahydro-1,1'-biphenyl (12). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-(trifluoromethyl)benzene (24.1 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% Et₂O in hexanes).

20.5 mg isolated (65% yield), white solid, *E/Z* = >20 : 1

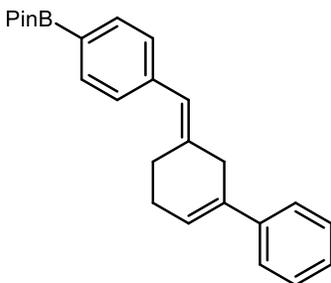
¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 6.51 (s, 1H), 6.27 – 6.14 (m, 1H), 3.34 (s, 2H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.47 – 2.32 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 141.7, 141.3, 141.3, 136.1, 129.1, 128.4, 128.1(q, ²*J*_{CF} = 32.5 Hz), 127.0, 125.1(q, ³*J*_{CF} = 3.6 Hz), 125.1, 124.1(q, ¹*J*_{CF} = 272.8 Hz), 124.0, 122.3, 38.0, 27.4, 25.6.

¹⁹F NMR (282 MHz, CDCl₃) δ -63.86.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₂₀H₁₇F₃: 315.1355; found: 315.1348

TLC: R_f = 0.51 (5% Et₂O in hexanes)



(E)-2-(4-((4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13). The reaction was conducted according to the general procedure without modification using 2-(4-(2,2-dichlorovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29.9 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% Et₂O in hexanes).

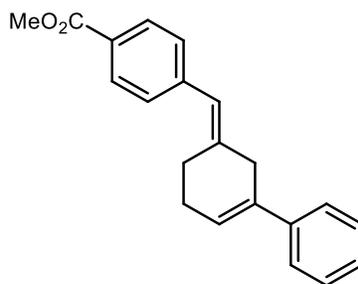
22.3 mg isolated (60% yield), white solid, *E/Z* = >20 : 1

^1H NMR (300 MHz, CDCl_3) δ 7.78 (d, $J = 7.8$ Hz, 2H), 7.43 (d, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.29 – 7.26 (m, 3H), 6.50 (s, 1H), 6.19 (s, 1H), 3.31 (s, 2H), 2.62 (t, $J = 6.4$ Hz, 2H), 2.43 – 2.29 (m, 2H), 1.35 (s, 12H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 141.4, 141.0, 139.9, 136.2, 134.6, 128.3, 128.2, 126.9, 125.1, 124.2, 123.5, 83.7, 38.1, 27.5, 25.6, 24.9.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{29}\text{BO}_2$: 372.2370; found: 372.2370

TLC: $R_f = 0.46$ (5% Et_2O in hexanes)



methyl (*E*)-4-((4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)benzoate (14). The reaction was conducted according to the general procedure without modification using methyl 4-(2,2-dichlorovinyl)benzoate (23.1 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 15% Et_2O in hexanes).

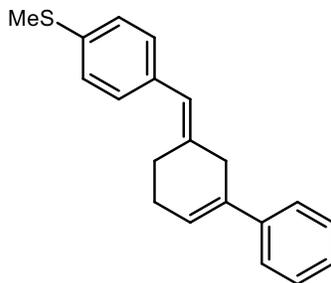
21.2 mg isolated (70% yield), white solid, $E/Z = >20 : 1$

^1H NMR (300 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 7.0$ Hz, 2H), 7.39 – 7.27 (m, 5H), 6.51 (s, 1H), 6.27 – 6.12 (m, 1H), 3.92 (s, 3H), 3.33 (s, 2H), 2.63 (t, $J = 6.4$ Hz, 2H), 2.49 – 2.30 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 167.0, 142.9, 141.3, 136.1, 129.5, 128.8, 128.4, 127.8, 127.0, 125.1, 124.0, 122.8, 52.0, 38.1, 27.4, 25.7.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_2$: 305.1536; found: 305.1538

TLC: $R_f = 0.31$ (5% Et_2O in hexanes)



(E)-4-((4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)phenyl(methyl)sulfane (15). The reaction was conducted according to the general procedure without modification using (4-(2,2-dichlorovinyl)phenyl)(methyl)sulfane (21.9 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 15% CH₂Cl₂ in hexanes).

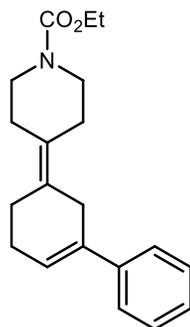
24.2 mg isolated (83% yield), white solid, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.25 (s, 1H), 7.24 – 7.13 (m, 4H), 6.44 (s, 1H), 6.26 – 6.11 (m, 1H), 3.30 (s, 2H), 2.61 (t, *J* = 6.5 Hz, 2H), 2.50 (s, 3H), 2.42 – 2.28 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 141.4, 139.1, 136.3, 135.9, 135.0, 129.3, 128.3, 126.9, 126.6, 125.1, 124.1, 122.8, 38.0, 27.4, 25.6, 16.1.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₀H₂₀S: 293.1359; found: 293.1355

TLC: R_f = 0.45 (5% Et₂O in hexanes)



ethyl 4-((4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)piperidine-1-carboxylate (16). The reaction was conducted according to the general procedure without modification using ethyl 4-(dichloromethylene)piperidine-1-carboxylate (23.8 mg, 0.1 mmol, 1.0 equiv) and (1-

cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 20% Et₂O in hexanes).

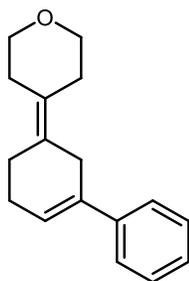
28.0 mg isolated (90% yield), white solid

¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.27 (m, 2H), 7.28 – 7.18 (m, 1H), 6.25 – 6.08 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.47 (s, 4H), 3.20 (s, 2H), 2.47 – 2.22 (m, 8H), 1.27 (t, *J* = 7.1 Hz, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 155.7, 142.0, 136.3, 128.3, 128.0, 126.8, 126.0, 125.1, 124.7, 61.2, 44.8, 44.4, 31.6, 29.3, 28.9, 27.3, 26.0, 14.8.

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C₂₀H₂₅NO₂: 312.1985; found: 312.1956

TLC: R_f = 0.33 (15% Et₂O in hexanes)



4-(4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)tetrahydro-2H-pyran (17). The reaction was conducted according to the general procedure without modification using 4-(dichloromethylene)tetrahydro-2H-pyran (16.7 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 10% Et₂O in hexanes).

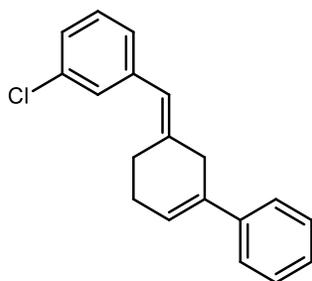
18.2 mg isolated (76% yield), white solid

¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 6.30 – 6.06 (m, 1H), 3.69 (q, *J* = 5.4 Hz, 4H), 3.20 (s, 2H), 2.46 – 2.34 (m, 6H), 2.34 – 2.21 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 141.9, 136.3, 128.2, 126.9, 126.7, 125.7, 125.0, 124.6, 69.1, 68.8, 31.3, 30.8, 30.5, 27.3, 25.6.

HRMS(APCI) (m/z): [M + H]⁺ Calcd for C₁₇H₂₀O: 241.1587; found: 241.1590

TLC: R_f = 0.74 (15% Et₂O in hexanes)



(E)-3-(3-chlorobenzylidene)-2,3,4,5-tetrahydro-1,1'-biphenyl (18). The reaction was conducted according to the general procedure without modification using 1-chloro-3-(2,2-dichlorovinyl)benzene (20.7 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% Et₂O in hexanes).

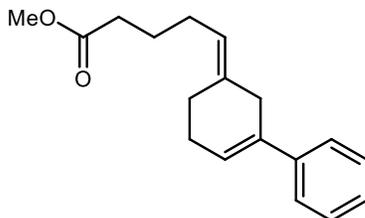
25.1 mg isolated (89% yield), yellow oil, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.17 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.43 (s, 1H), 6.27 – 6.11 (m, 1H), 3.31 (s, 2H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.47 – 2.31 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 141.3, 140.5, 139.8, 136.1, 134.0, 129.4, 128.8, 128.4, 127.0, 127.0, 126.2, 125.1, 124.1, 122.2, 37.9, 27.4, 25.6.

HRMS(APCI) (*m/z*): [M - H]⁺ Calcd for C₁₉H₁₇Cl: 279.0935; found: 279.0931

TLC: R_f = 0.69 (5% Et₂O in hexanes)



methyl (E)-5-(4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)pentanoate (19). The reaction was conducted according to the general procedure without modification using methyl 6,6-dichlorohex-5-enoate (19.7 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg,

0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% Et₂O in hexanes).

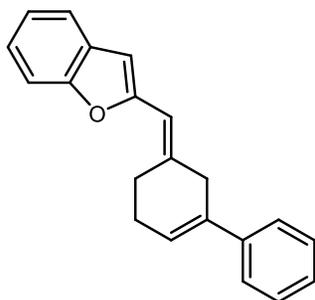
15.5 mg isolated (57% yield), colorless oil, *E/Z* = 5 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 3H), 7.24 (d, *J* = 7.1 Hz, 2H), 6.25 – 6.04 (m, 1H), 5.32 (t, *J* = 7.3 Hz, 1H), 3.66 (s, 3H), 3.13 (s, 2H), 2.44 – 2.23 (m, 6H), 2.13 (q, *J* = 7.3 Hz, 2H), 1.73 (q, *J* = 7.3 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 174.1, 141.5, 136.5, 136.4, 128.2, 126.7, 124.9, 124.0, 121.5, 51.4, 37.4, 33.4, 27.3, 26.4, 25.2, 24.7.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₈H₂₂O₂: 271.1693; found: 271.1691

TLC: R_f = 0.41 (10% Et₂O in hexanes)



(*E*)-2-((4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)thiophene (20). The reaction was conducted according to the general procedure without modification using 2-(2,2-dichlorovinyl)benzofuran (21.3 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% Et₂O in hexanes).

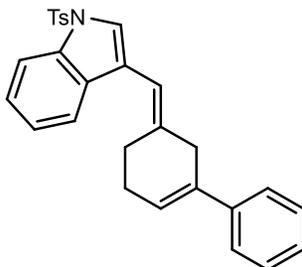
16.7 mg isolated (58% yield), white solid, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 3H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.26 – 7.16 (m, 2H), 6.57 (s, 1H), 6.34 (s, 1H), 6.27 – 6.20 (m, 1H), 3.36 (s, 2H), 3.01 (t, *J* = 6.5 Hz, 2H), 2.53 – 2.42 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 155.2, 154.3, 142.8, 141.2, 136.0, 128.9, 128.4, 127.0, 125.1, 124.4, 123.8, 122.7, 120.4, 112.4, 110.9, 104.6, 38.3, 27.3, 26.8.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₁₈O: 287.1430; found: 287.1433

TLC: $R_f = 0.49$ (5% Et₂O in hexanes)



(E)-3-((4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)-1-tosyl-1H-indole (21). The reaction was conducted according to the general procedure without modification using 3-(2,2-dichlorovinyl)-1-tosyl-1H-indole (36.6 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 30% CH₂Cl₂ in hexanes).

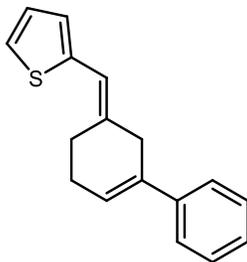
35.2 mg isolated (80% yield), white solid, $E/Z = >20 : 1$

¹H NMR (300 MHz, CDCl₃) δ 7.99 (d, $J = 8.2$ Hz, 1H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.55 – 7.46 (m, 2H), 7.47 – 7.40 (m, 2H), 7.35 (t, $J = 7.5$ Hz, 3H), 7.31 – 7.27 (m, 1H), 7.25 – 7.18 (m, 3H), 6.36 (s, 1H), 6.25 – 6.18 (m, 1H), 3.38 (s, 2H), 2.62 (t, $J = 6.5$ Hz, 2H), 2.45 – 2.36 (m, 2H), 2.34 (s, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 144.8, 141.6, 141.3, 136.2, 135.3, 134.8, 131.2, 129.8, 128.4, 127.0, 126.8, 125.1, 124.8, 124.2, 123.2, 123.1, 119.8, 119.5, 113.6, 112.1, 37.8, 27.2, 26.6, 21.6.

HRMS(APCI) (m/z): [M + H]⁺ Calcd for C₂₈H₂₅NO₂S: 440.1674; found: 440.1675

TLC: $R_f = 0.30$ (15% Et₂O in hexanes)



(E)-2-((4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)thiophene (22). The reaction was conducted according to the general procedure without modification using methyl 2-(2,2-dichlorovinyl)thiophene (17.9 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% CH₂Cl₂ in hexanes).

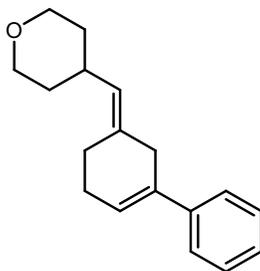
18.0 mg isolated (71% yield), yellow oil, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 1.5 Hz, 1H), 7.21 (d, *J* = 5.1 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.94 (d, *J* = 3.4 Hz, 1H), 6.55 (s, 1H), 6.25 – 6.14 (m, 1H), 3.30 (s, 2H), 2.78 (t, *J* = 6.5 Hz, 2H), 2.50 – 2.36 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 141.3, 140.5, 138.7, 136.4, 128.3, 126.9, 126.7, 126.5, 125.1, 124.2, 123.9, 116.3, 38.1, 27.0, 26.5.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₁₇H₁₆S: 253.1046; found: 253.1048

TLC: R_f = 0.41 (5% Et₂O in hexanes)



4-((4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)tetrahydro-2H-pyran (23). The reaction was conducted according to the general procedure without modification using 4-(2,2-dichlorovinyl)tetrahydro-2H-pyran (18.1 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 10% Et₂O in hexanes).

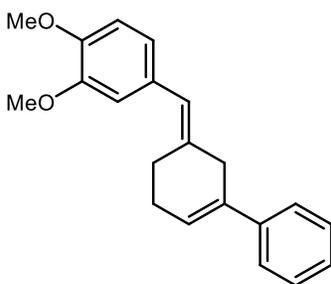
19.6 mg isolated (77% yield), white solid, *E/Z* = 12.5 : 1

^1H NMR (300 MHz, CDCl_3) δ 7.39 (d, $J = 6.8$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.22 (d, $J = 7.1$ Hz, 1H), 6.14 (s, 1H), 5.19 (d, $J = 8.8$ Hz, 1H), 3.96 (d, $J = 11.5$ Hz, 2H), 3.46 (t, $J = 9.7$ Hz, 2H), 3.11 (s, 2H), 2.65 – 2.43 (m, 1H), 2.41 – 2.26 (m, 4H), 1.57 – 1.38 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 141.5, 136.7, 133.2, 128.3, 127.5, 126.8, 125.0, 124.0, 67.8, 67.3, 37.5, 33.4, 31.2, 27.7, 25.3.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{22}\text{O}$: 255.1743; found: 255.1740

TLC: $R_f = 0.68$ (15% Et_2O in hexanes)



(E)-3-(3,4-dimethoxybenzylidene)-2,3,4,5-tetrahydro-1,1'-biphenyl (24). The reaction was conducted according to the general procedure without modification using 4-(2,2-dichlorovinyl)-1,2-dimethoxybenzene (23.3 mg, 0.1 mmol, 1.0 equiv) and (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 5% Et_2O in hexanes).

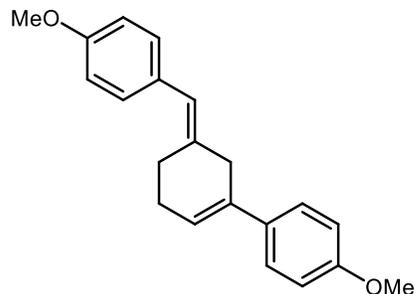
30.5 mg isolated (99% yield), white solid, $E/Z = >20 : 1$

^1H NMR (300 MHz, CDCl_3) δ 7.43 (d, $J = 7.0$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 2H), 7.28 (t, $J = 1.4$ Hz, 1H), 6.88 – 6.80 (m, 2H), 6.79 (s, 1H), 6.44 (s, 1H), 6.25 – 6.12 (m, 1H), 3.89 (s, 6H), 3.30 (s, 2H), 2.63 (t, $J = 6.4$ Hz, 2H), 2.44 – 2.31 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 148.6, 147.5, 141.5, 138.1, 136.4, 130.9, 128.3, 126.9, 125.1, 124.1, 123.1, 121.1, 112.2, 111.0, 55.9, 55.8, 37.9, 27.5, 25.6.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2$: 307.1693; found: 307.1691

TLC: $R_f = 0.28$ (5% Et_2O in hexanes)



(E)-4'-methoxy-3-(4-methoxybenzylidene)-2,3,4,5-tetrahydro-1,1'-biphenyl (25). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and 1-(1-cyclopropylvinyl)-4-methoxybenzene (52.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% Et₂O in hexanes).

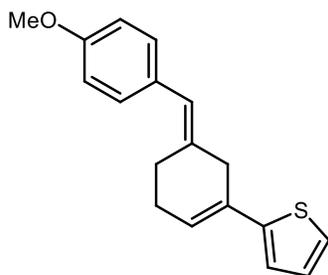
23.2 mg isolated (76% yield), white solid, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 4H), 6.43 (s, 1H), 6.19 – 5.96 (m, 1H), 3.82 (s, 6H), 3.26 (s, 2H), 2.59 (t, *J* = 6.3 Hz, 2H), 2.41 – 2.30 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 158.7, 157.9, 137.9, 135.7, 134.2, 130.6, 129.9, 126.1, 122.7, 122.5, 113.7, 113.6, 55.3, 55.3, 38.0, 27.4, 25.5.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₂₂O₂: 307.1693; found: 307.1701

TLC: R_f = 0.32 (5% Et₂O in hexanes)



(E)-2-(5-(4-methoxybenzylidene)cyclohex-1-en-1-yl)thiophene (26). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and 2-(1-cyclopropylvinyl)thiophene (45.1

mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 15% CH₂Cl₂ in hexanes).

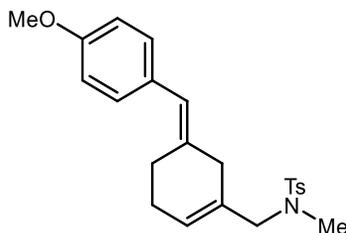
24.3 mg isolated (86% yield), white solid, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.21 – 7.15 (m, 2H), 7.13 (dd, *J* = 4.3, 1.9 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.44 (s, 1H), 6.31 – 6.16 (m, 1H), 3.82 (s, 3H), 3.29 (s, 2H), 2.59 (t, *J* = 6.4 Hz, 2H), 2.41 – 2.28 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 158.0, 145.9, 137.0, 131.0, 130.4, 129.9, 127.2, 123.4, 123.2, 123.0, 121.4, 113.6, 55.3, 37.9, 27.2, 25.5.

HRMS(APCI) (m/z): [M + H]⁺ Calcd for C₁₈H₁₈OS: 283.1151; found: 283.1154

TLC: R_f = 0.46 (5% Et₂O in hexanes)



(*E*)-N-((5-(4-methoxybenzylidene)cyclohex-1-en-1-yl)methyl)-N,4-

dimethylbenzenesulfonamide (27). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and N-(2-cyclopropylallyl)-N,4-dimethylbenzenesulfonamide (79.6 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 15% CH₂Cl₂ in hexanes).

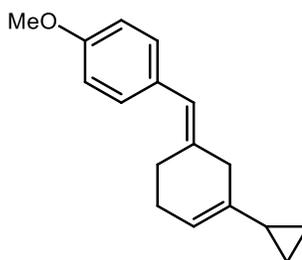
30.0 mg isolated (75% yield), yellow oil, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.35 (s, 1H), 5.63 (s, 1H), 3.81 (s, 3H), 3.50 (s, 2H), 2.87 (s, 2H), 2.61 (s, 3H), 2.50 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 2.25 – 2.08 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 157.9, 143.3, 136.9, 134.3, 132.5, 130.5, 129.9, 129.7, 127.5, 126.3, 122.9, 113.6, 56.3, 55.3, 36.3, 33.9, 26.8, 25.5, 21.5.

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C₂₃H₂₇NO₃S: 398.1784; found: 398.1787

TLC: R_f = 0.12 (5% Et₂O in hexanes)



(E)-1-((3-cyclopropylcyclohex-3-en-1-ylidene)methyl)-4-methoxybenzene (28). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and ethene-1,1-diyldicyclopropane (32.5 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% Et₂O in hexanes).

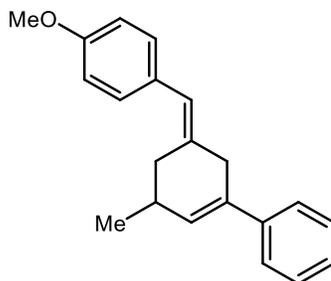
16.8 mg isolated (70% yield), colorless oil, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.32 (s, 1H), 5.55 – 5.44 (m, 1H), 3.81 (s, 3H), 2.74 (s, 2H), 2.49 (t, *J* = 6.5 Hz, 2H), 2.18 – 2.08 (m, 2H), 1.43 – 1.27 (m, 1H), 0.70 – 0.53 (m, 2H), 0.53 – 0.42 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 157.8, 138.2, 130.7, 129.9, 127.1, 122.1, 119.2, 113.5, 55.3, 37.4, 26.9, 26.0, 16.9, 4.3.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₁₇H₂₀O: 241.1587; found: 241.1585

TLC: R_f = 0.44 (5% Et₂O in hexanes)



(E)-3-(4-methoxybenzylidene)-5-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (30). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and (1-(2-methylcyclopropyl)vinyl)benzene (47.5 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% Et₂O in hexanes).

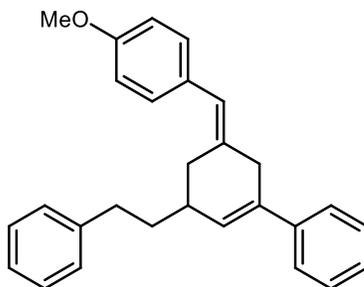
20.3 mg isolated (70% yield), white solid, $E/Z = 12.4 : 1$

^1H NMR (300 MHz, CDCl_3) δ 7.44 (d, $J = 8.2$ Hz, 2H), 7.35 (t, $J = 7.1$ Hz, 2H), 7.20 (d, $J = 8.2$ Hz, 3H), 6.89 (d, $J = 8.7$ Hz, 2H), 6.45 (s, 1H), 6.03 (s, 1H), 3.82 (s, 3H), 3.37 (d, $J = 19.2$ Hz, 1H), 3.17 (d, $J = 18.7$ Hz, 1H), 2.88 (dd, $J = 12.8, 5.5$ Hz, 1H), 2.50 (s, 1H), 2.05 (dd, $J = 13.0, 8.7$ Hz, 1H), 1.09 (d, $J = 7.0$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 157.8, 141.3, 137.0, 135.3, 133.6, 130.4, 129.9, 128.2, 126.9, 125.1, 123.2, 113.5, 55.2, 37.7, 33.8, 32.8, 21.7.

HRMS(APCI) (m/z): $[\text{M} - \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{O}$: 291.1743; found: 291.1740

TLC: $R_f = 0.43$ (5% Et_2O in hexanes)



(*E*)-3-(4-methoxybenzylidene)-5-phenethyl-2,3,4,5-tetrahydro-1,1'-biphenyl (31). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and (1-(2-phenethylcyclopropyl)vinyl)benzene (74.5 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 5% Et_2O in hexanes).

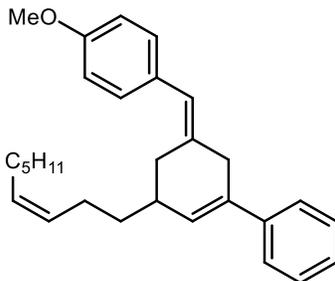
27.8 mg isolated (70% yield), colorless oil, $E/Z = 10.0 : 1$

^1H NMR (300 MHz, CDCl_3) δ 7.45 (d, $J = 7.0$ Hz, 2H), 7.36 (t, $J = 7.4$ Hz, 2H), 7.32 – 7.25 (m, 1H), 7.25 (d, $J = 4.0$ Hz, 2H), 7.19 (d, $J = 8.6$ Hz, 3H), 7.12 (d, $J = 6.7$ Hz, 2H), 6.91 (d, $J = 8.7$ Hz, 2H), 6.48 (s, 1H), 6.17 – 6.05 (m, 1H), 3.84 (s, 3H), 3.37 (d, $J = 18.4$ Hz, 1H), 3.23 (d, $J = 18.5$ Hz, 1H), 2.88 (dd, $J = 12.7, 5.4$ Hz, 1H), 2.64 (t, $J = 8.0$ Hz, 2H), 2.53 – 2.36 (m, 1H), 2.27 (dd, $J = 13.4, 8.6$ Hz, 1H), 1.87 – 1.57 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 157.9, 142.3, 141.3, 136.7, 136.0, 133.7, 133.6, 130.5, 129.9, 128.3, 128.2, 126.9, 125.6, 125.1, 123.6, 113.6, 55.2, 38.0, 37.7, 37.2, 33.2, 31.2.

HRMS(APCI) (m/z): $[\text{M} - \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{28}\text{O}$: 381.2213; found: 381.2210

TLC: $R_f = 0.39$ (5% Et₂O in hexanes)



3-((*E*)-4-methoxybenzylidene)-5-((*Z*)-non-3-en-1-yl)-2,3,4,5-tetrahydro-1,1'-biphenyl (32).

The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and (*Z*)-(1-(2-(non-3-en-1-yl)cyclopropyl)vinyl)benzene (80.5 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 15% CH₂Cl₂ in hexanes).

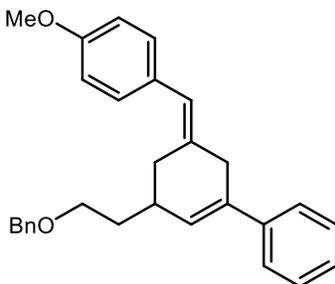
27.9 mg isolated (70% yield), colorless oil, *E/Z* = 14.6 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 1.4 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.45 (s, 1H), 6.15 – 6.04 (m, 1H), 5.44 – 5.22 (m, 2H), 3.82 (s, 3H), 3.36 (d, *J* = 18.4 Hz, 1H), 3.20 (d, *J* = 18.4 Hz, 1H), 2.84 (dd, *J* = 12.8, 5.5 Hz, 1H), 2.42 (s, 1H), 2.17 (dd, *J* = 12.6, 7.7 Hz, 1H), 2.07 (q, *J* = 7.3 Hz, 2H), 1.96 (q, *J* = 6.7 Hz, 2H), 1.53 – 1.16 (m, 8H), 0.92 – 0.84 (m, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 157.9, 141.5, 136.9, 135.8, 130.6, 130.4, 129.9, 129.3, 129.0, 128.3, 126.9, 125.2, 123.5, 113.6, 55.2, 38.1, 37.3, 36.1, 31.5, 31.5, 29.4, 27.2, 24.6, 22.6, 14.1.

HRMS(APCI) (*m/z*): [M - H]⁺ Calcd for C₂₉H₃₆O: 399.2682; found: 399.2686

TLC: $R_f = 0.44$ (5% Et₂O in hexanes)



(E)-5-(2-(benzyloxy)ethyl)-3-(4-methoxybenzylidene)-2,3,4,5-tetrahydro-1,1'-biphenyl (33).

The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and (1-(2-(2-(benzyloxy)ethyl)cyclopropyl)vinyl)benzene (83.5 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 20% Et₂O in hexanes).

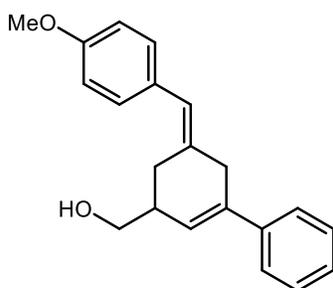
25.1 mg isolated (61% yield), colorless oil, *E/Z* = 19.2 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, *J* = 8.1 Hz, 3H), 7.39 – 7.27 (m, 7H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.46 (s, 1H), 6.13 – 6.03 (m, 1H), 4.48 (s, 2H), 3.80 (s, 3H), 3.62 – 3.45 (m, 2H), 3.35 (d, *J* = 18.3 Hz, 1H), 3.21 (d, *J* = 17.5 Hz, 1H), 2.86 (dd, *J* = 12.8, 5.5 Hz, 1H), 2.65 (s, 1H), 2.20 (dd, *J* = 12.8, 7.8 Hz, 1H), 1.89 – 1.72 (m, 1H), 1.72 – 1.58 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 161.5, 157.9, 141.3, 138.6, 136.7, 136.0, 130.5, 129.9, 128.7, 128.3, 127.6, 127.0, 125.2, 123.6, 113.6, 92.9, 73.0, 68.1, 55.3, 38.0, 35.9, 34.8, 31.5.

HRMS(ESI) (*m/z*): [M + Na]⁺ Calcd for C₂₉H₃₀O₂: 433.2138; found: 433.2142

TLC: R_f = 0.37 (5% Et₂O in hexanes)



(E)-5-(4-methoxybenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)methanol (34). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and (2-(1-

phenylvinyl)cyclopropyl)methanol¹³ (52.3 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 40% Et₂O in hexanes).

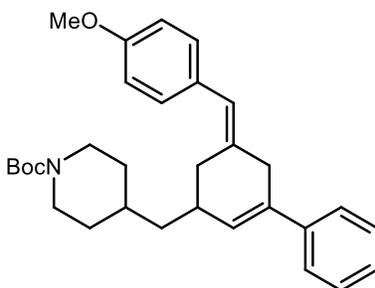
21.7 mg isolated (68% yield), light yellow solid, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.45 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 (s, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.49 (s, 1H), 6.09 (s, 1H), 3.82 (s, 3H), 3.61 (t, *J* = 5.5 Hz, 2H), 3.37 (d, *J* = 19.0 Hz, 1H), 3.25 (d, *J* = 18.7 Hz, 1H), 2.79 (dd, *J* = 12.8, 5.6 Hz, 1H), 2.63 (s, 1H), 2.43 (dd, *J* = 12.9, 7.4 Hz, 1H), 1.29 – 1.22 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 158.0, 141.0, 138.5, 135.9, 130.2, 129.9, 128.4, 127.3, 125.2, 124.5, 124.2, 113.7, 66.5, 55.3, 40.7, 38.1, 28.1.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₂₂O₂: 307.1693; found: 307.1690

TLC: R_f = 0.21 (30% Et₂O in hexanes)



tert-butyl-4-((5-(4-methoxybenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)methyl)piperidine-1-carboxylate (35). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and tert-butyl 4-((2-(1-phenylvinyl)cyclopropyl)methyl)piperidine-1-carboxylate (102.5 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 20% Et₂O in hexanes).

39.6 mg isolated (84% yield), yellow solid, *E/Z* = 8.6 : 1

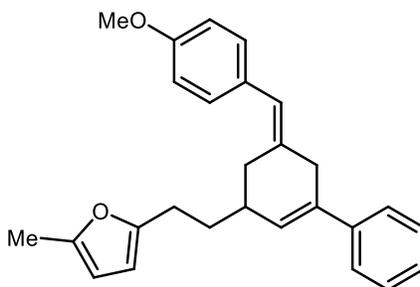
¹H NMR (300 MHz, CDCl₃) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 3H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.48 (s, 1H), 6.05 (s, 1H), 4.05 (s, 2H), 3.82 (s, 3H), 3.33 (d, *J* = 17.7 Hz, 1H), 3.23 (d, *J* = 18.7 Hz, 1H), 2.73 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.56 (s, 3H),

2.22 (dd, $J = 12.7, 7.3$ Hz, 1H), 1.73 – 1.47 (m, 2H), 1.45 (s, 10H), 1.40 – 1.16 (m, 4H), 1.03 (q, $J = 11.6, 9.7$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 158.0, 154.9, 141.3, 136.7, 136.0, 130.5, 129.9, 128.8, 128.3, 127.0, 125.2, 123.8, 113.6, 79.2, 55.3, 42.7, 38.1, 36.5, 34.4, 33.2, 31.5, 29.7, 28.5.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{40}\text{NO}_3$: 474.3003; found: 474.2988

TLC: $R_f = 0.13$ (15% Et_2O in hexanes)



(E)-2-(2-(5-(4-methoxybenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethyl)-5-methylfuran (36). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and 2-methyl-5-(2-(2-(1-phenylvinyl)cyclopropyl)ethyl)furan (75.7 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO_2 , 15% CH_2Cl_2 in hexanes).

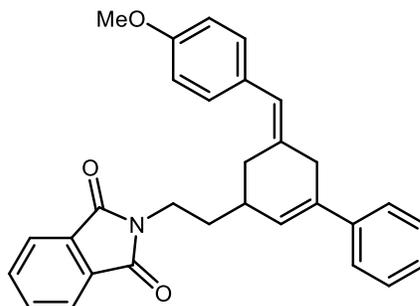
31.0 mg isolated (81% yield), colorless oil, $E/Z = 16.2 : 1$

^1H NMR (300 MHz, CDCl_3) δ 7.44 (d, $J = 8.1$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 2H), 7.28 (t, $J = 1.4$ Hz, 1H), 7.18 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 6.46 (s, 1H), 6.14 – 6.02 (m, 1H), 5.82 (d, $J = 3.9$ Hz, 2H), 3.83 (s, 3H), 3.37 (d, $J = 18.5$ Hz, 1H), 3.20 (d, $J = 18.7$ Hz, 1H), 2.88 (dd, $J = 12.8, 5.5$ Hz, 1H), 2.61 (t, $J = 7.8$ Hz, 2H), 2.44 (s, 1H), 2.25 (s, 3H), 2.16 (dd, $J = 12.8, 8.2$ Hz, 1H), 1.88 – 1.74 (m, 1H), 1.74 – 1.59 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 158.0, 154.1, 150.2, 141.4, 136.8, 136.2, 130.5, 129.9, 128.6, 128.3, 127.0, 125.2, 123.6, 113.6, 105.8, 105.5, 55.3, 38.0, 37.1, 34.4, 31.4, 25.5, 13.5.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{28}\text{O}$: 385.2162; found: 385.2166

TLC: $R_f = 0.33$ (5% Et_2O in hexanes)



(E)-2-(2-(5-(4-methoxybenzylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethyl)isoindoline-1,3-dione (37). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and 2-(2-(2-(1-phenylvinyl)cyclopropyl)ethyl)isoindoline-1,3-dione (95.2 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 10% Et₂O in hexanes).

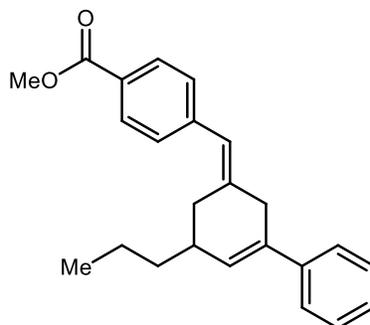
34.2 mg isolated (76% yield), yellow oil, *E/Z* = 12.1 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.24 (m, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.47 (s, 1H), 6.16 (s, 1H), 3.82 (s, 3H), 3.78 – 3.64 (m, 2H), 3.37 (d, *J* = 19.9 Hz, 1H), 3.20 (d, *J* = 18.6 Hz, 1H), 2.87 (dd, *J* = 12.8, 5.4 Hz, 1H), 2.45 (s, 1H), 2.31 (dd, *J* = 12.9, 8.0 Hz, 1H), 1.79 (q, *J* = 7.1 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 168.4, 158.0, 141.1, 136.7, 136.1, 133.9, 132.1, 130.3, 130.0, 128.3, 127.4, 127.1, 125.2, 124.1, 123.2, 113.7, 55.3, 37.9, 35.8, 35.3, 34.5, 31.2.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₃₀H₂₇NO₃: 450.2063; found: 450.2067

TLC: R_f = 0.13 (15% Et₂O in hexanes)



methyl (*E*)-4-((5-propyl-4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)benzoate (S17).

The reaction was conducted according to the general procedure without modification using methyl 4-(2,2-dichlorovinyl)benzoate (23.1 mg, 0.1 mmol, 1.0 equiv) and (1-(2-propylcyclopropyl)vinyl)benzene¹³ (55.9 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 10% Et₂O in hexanes).

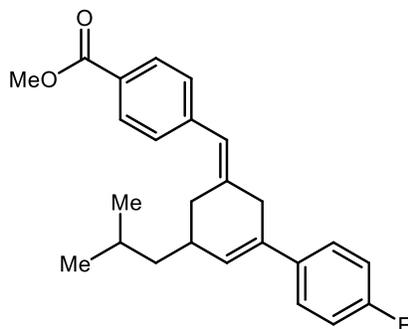
25.2 mg isolated (73% yield), colorless oil, *E/Z* = 8.2 : 1

¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.25 – 7.19 (m, 1H), 6.53 (s, 1H), 6.10 (s, 1H), 3.93 (s, 3H), 3.40 (d, *J* = 18.8 Hz, 1H), 3.23 (d, *J* = 18.5 Hz, 1H), 2.84 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.42 (s, 1H), 2.16 (dd, *J* = 13.2, 8.2 Hz, 1H), 1.50 – 1.22 (m, 4H), 1.01 – 0.77 (m, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 167.0, 142.9, 141.2, 140.7, 135.2, 129.4, 129.2, 128.7, 128.3, 127.0, 125.1, 123.2, 52.0, 38.3, 38.2, 37.6, 31.8, 20.0, 14.1.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₄H₂₆O₂: 347.2006; found: 347.2005

TLC: R_f = 0.40 (10% Et₂O in hexanes)



methyl (E)-4-((4'-fluoro-5-isobutyl-4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)benzoate (S18). The reaction was conducted according to the general procedure without modification using methyl 4-(2,2-dichlorovinyl)benzoate (23.1 mg, 0.1 mmol, 1.0 equiv) and 1-fluoro-4-(1-(2-isobutylcyclopropyl)vinyl)benzene² (65.5 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 10% Et₂O in hexanes).

24.2 mg isolated (64% yield), colorless oil, *E/Z* = 8.1 : 1

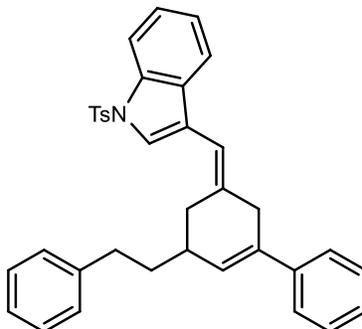
¹H NMR (300 MHz, CDCl₃) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.34 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 8.8 Hz, 2H), 6.53 (s, 1H), 6.08 – 5.95 (m, 1H), 3.93 (s, 3H), 3.34 (d, *J* = 20.3 Hz, 1H), 3.20 (d, *J* = 17.3 Hz, 1H), 2.79 (dd, *J* = 12.9, 5.5 Hz, 1H), 2.48 (s, 1H), 2.22 – 2.10 (m, 1H), 1.67 – 1.52 (m, 1H), 1.33 – 1.13 (m, 2H), 0.86 (dd, *J* = 6.6, 4.2 Hz, 6H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 167.0, 162.0 (d, ¹*J*_{CF} = 245.7 Hz), 142.8, 140.2, 137.3 (d, ⁴*J*_{CF} = 3.1 Hz), 134.3, 129.4, 129.1, 128.7, 127.7, 126.6 (d, ³*J*_{CF} = 8.0 Hz), 123.4, 115.0 (d, ²*J*_{CF} = 21.3 Hz), 52.0, 45.4, 38.3, 35.3, 31.8, 25.1, 22.8, 22.4.

¹⁹F NMR (282 MHz, CDCl₃) δ -117.34.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₅H₂₇FO₂: 379.2068; found: 379.2070

TLC: *R_f* = 0.30 (10% Et₂O in hexanes)



(E)-3-((5-phenethyl-4,5-dihydro-[1,1'-biphenyl]-3(2H)-ylidene)methyl)-1-tosyl-1H-indole

(S19). The reaction was conducted according to the general procedure without modification using 3-(2,2-dichlorovinyl)-1-tosyl-1H-indole (36.6 mg, 0.1 mmol, 1.0 equiv) and (1-(2-phenethylcyclopropyl)vinyl)benzene (74.5 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 30% Et₂O in hexanes).

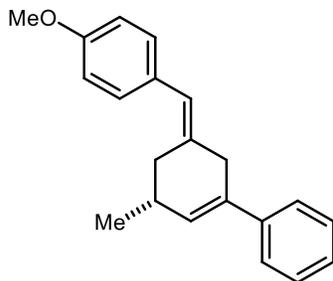
39.4 mg isolated (72% yield), light yellow solid, *E/Z* = 3.9 : 1

¹H NMR (300 MHz, CDCl₃) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 3H), 7.32 – 7.27 (m, 2H), 7.18 – 7.07 (m, 5H), 6.92 (d, *J* = 5.8 Hz, 2H), 6.41 (s, 1H), 6.18 – 6.08 (m, 1H), 3.48 – 3.27 (m, 2H), 2.85 – 2.73 (m, 1H), 2.56 – 2.36 (m, 4H), 2.24 (s, 3H), 1.80 – 1.57 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 144.8, 142.0, 141.1, 140.5, 135.7, 135.1, 134.8, 131.2, 129.8, 128.6, 128.3, 128.2, 128.2, 127.0, 126.6, 125.6, 125.1, 124.8, 123.2, 123.0, 119.8, 119.5, 113.6, 113.1, 37.9, 37.7, 37.2, 33.6, 32.1, 21.4.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₃₆H₃₃NO₂S: 544.2305; found: 544.2302

TLC: R_f = 0.28 (15% Et₂O in hexanes)

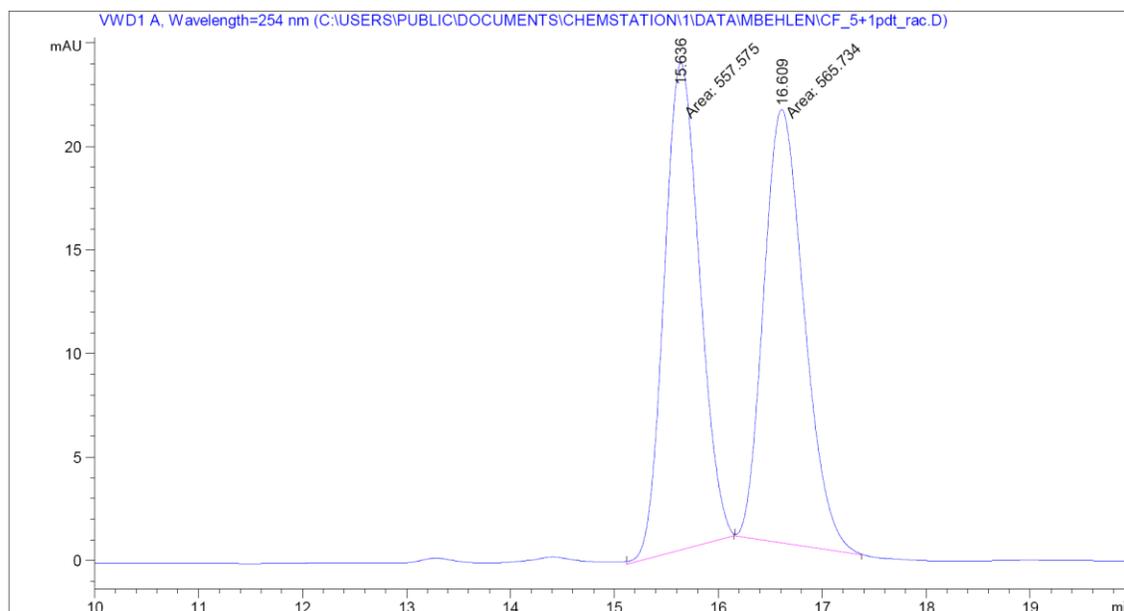


(*R,E*)-3-(4-methoxybenzylidene)-5-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (30). The reaction was conducted according to the general procedure without modification using 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and (1-((1*R*,2*R*)-2-methylcyclopropyl)vinyl)benzene (47.5 mg, 0.3 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 5% Et₂O in hexanes). Spectroscopic and mass spectrometry data were identical to those of the racemic product. Single crystals of **30** suitable for X-ray diffraction analysis were obtained by cooling a saturated Et₂O solution to -20 °C.

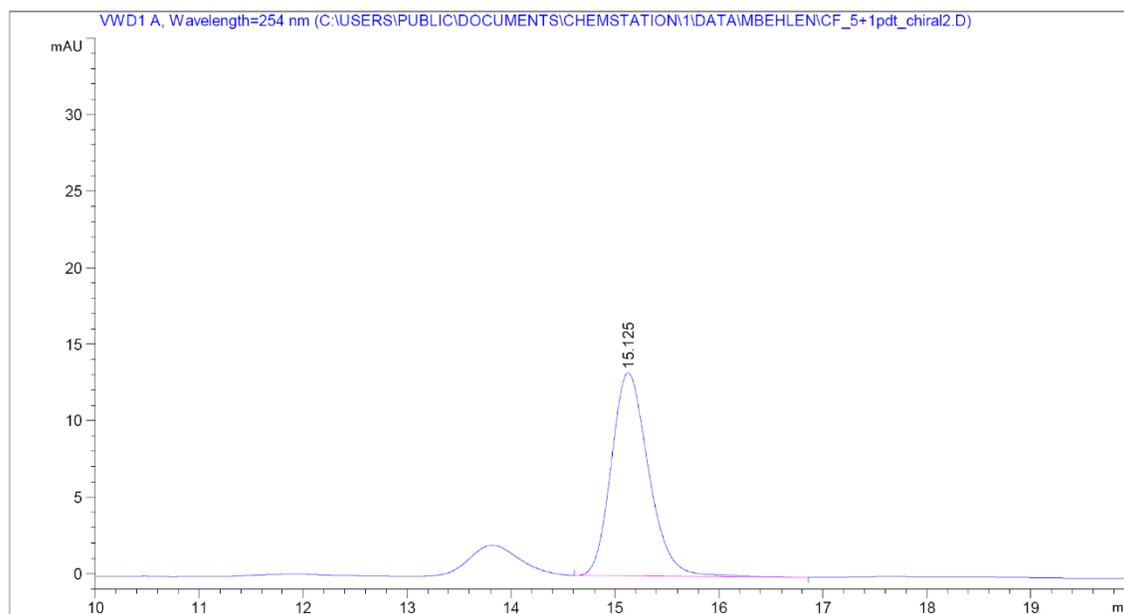
20.2 mg isolated (70% yield), white solid, *E/Z* = 12.3 : 1

$[\alpha]_D^{23} = -181^\circ$ (c 0.184, CHCl₃).

HPLC: Chiralpak® OJ-H column (hexane/IPA = 98:2, 1.0 mL/min, $\lambda = 254$ nm) *tr* = 15.64 min (major), 16.61 min (minor): >99:1 er.



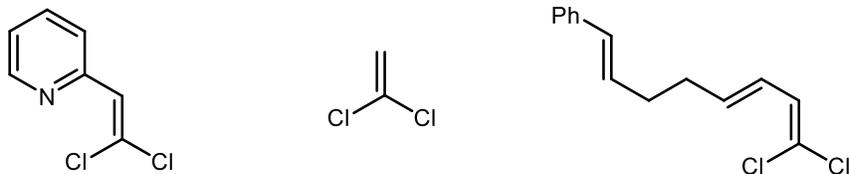
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.636	MM T	0.4793	557.57458	23.52308	49.6368
2	16.609	MM T	0.4504	565.73358	20.93578	50.3632



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.125	BB	0.3840	331.16827	13.27600	100.0000

Figure S2. HPLC data for **30**. (racemate, top; *(R)*-**30**, bottom).

1,1-Dichloroalkenes:



Vinylcyclopropanes:

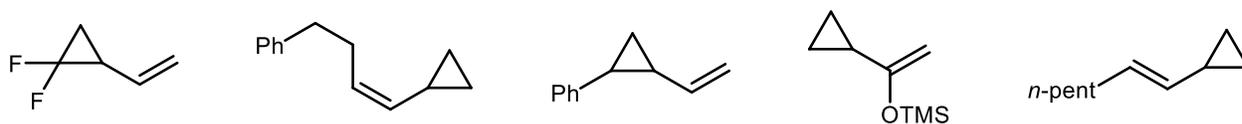
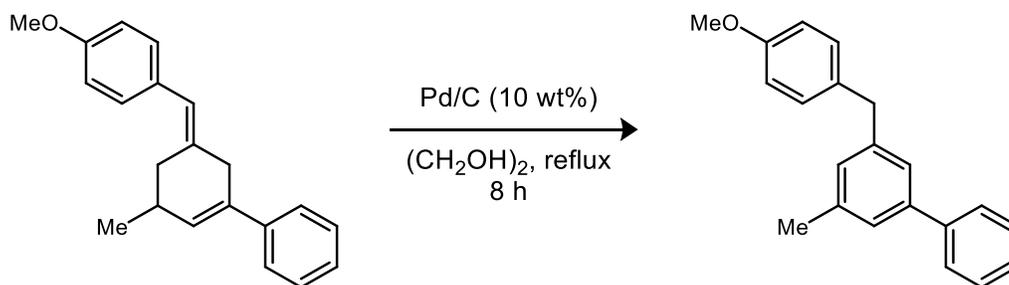


Figure S3. Substrates that were found to be ineffective in the [5 + 1]-cycloaddition (no detectable product using the general procedure).

6. [5 + 1]-Product Derivatization

General procedure for the dehydrogenation reaction. A flame-dried round bottom flask was charged with the [5 + 1]-product (1.0 equiv), Pd/C (10 wt% on activated carbon, 10 wt% relative to the [5+1]-product), 1.0 mL ethylene glycol, and a magnetic stir bar. The reaction was refluxed at 200 °C and stirred. After 8 hr, the reaction was cooled to ambient temperature and extracted with CH₂Cl₂ (3 x 5 mL). The combined organic phases were dried over MgSO₄, concentrated under reduced pressure, and loaded directly onto a SiO₂ column for purification.¹⁴



3-(4-methoxybenzyl)-5-methyl-1,1'-biphenyl (38). The reaction was conducted according to the general procedure without modification using **30** (19.7 mg, 0.068 mmol, 1.0 equiv) and Pd/C (10 wt%, 1.9 mg). Isolated yields were determined following column chromatography (5% Et₂O in hexanes).

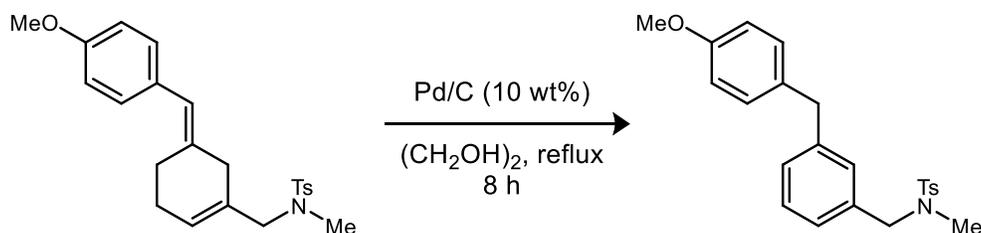
11.4 mg isolated (77% yield), colorless oil

¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.99 (s, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.95 (s, 2H), 3.79 (s, 3H), 2.38 (s, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 157.9, 141.9, 141.3, 141.3, 138.4, 133.2, 129.8, 128.6, 128.5, 127.1, 127.0, 125.7, 124.8, 113.8, 55.2, 41.0, 21.4.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₂₀O: 289.1587; found: 289.1583

TLC: R_f = 0.42 (5% Et₂O in hexanes)



N-(3-(4-methoxybenzyl)benzyl)-N,4-dimethylbenzenesulfonamide (39). The reaction was conducted according to the general procedure without modification using **27** (29.6 mg, 0.074 mmol, 1.0 equiv.) and Pd/C (10 wt%, 2.9 mg). Isolated yields were determined following column chromatography (20% Et₂O in hexanes).

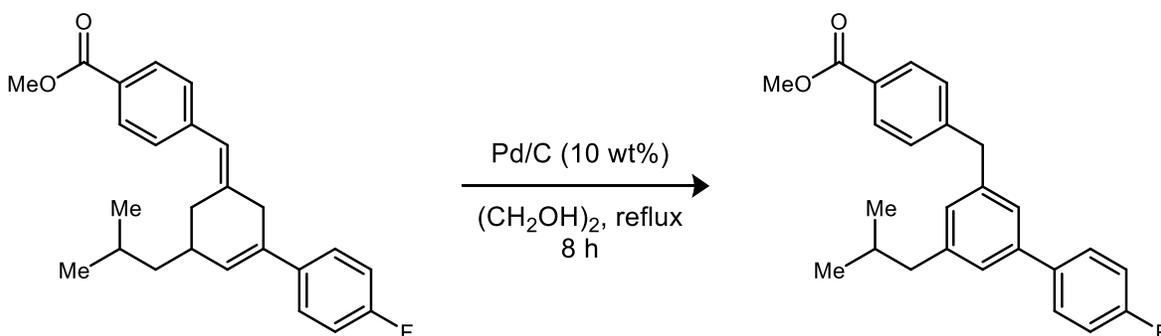
22.7 mg isolated (77% yield), yellow solid

¹H NMR (300 MHz, CDCl₃) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.00 (m, 5H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.08 (s, 2H), 3.89 (s, 2H), 3.78 (s, 3H), 2.56 (s, 3H), 2.45 (s, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 158.0, 143.4, 142.1, 135.8, 134.3, 133.0, 129.8, 129.7, 128.8, 128.8, 128.4, 127.6, 126.1, 113.9, 55.3, 54.1, 40.9, 34.4, 21.6.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₃H₂₅NO₃S: 396.1628; found: 396.1630

TLC: R_f = 0.15 (5% Et₂O in hexanes)



methyl 4-((4'-fluoro-5-isobutyl-[1,1'-biphenyl]-3-yl)methyl)benzoate (40). The reaction was conducted according to the general procedure without modification using **S18** (24.6 mg, 0.065 mmol, 1.0 equiv) and Pd/C (10 wt%, 2.5 mg). Isolated yields were determined following column chromatography (10% Et₂O in hexanes).

12.2 mg isolated (50% yield), colorless oil

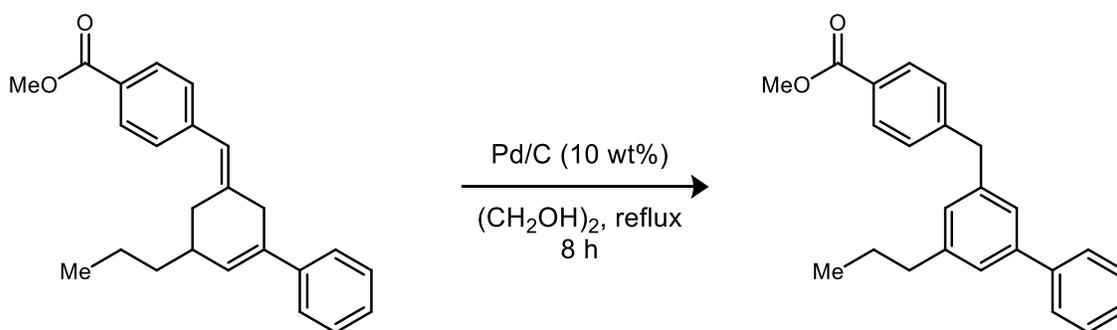
^1H NMR (300 MHz, CDCl_3) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.57 – 7.44 (m, 2H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.17 (d, $J = 5.7$ Hz, 2H), 7.09 (t, $J = 8.7$ Hz, 2H), 6.94 (s, 1H), 4.06 (s, 2H), 3.90 (s, 3H), 2.49 (d, $J = 7.1$ Hz, 2H), 1.96 – 1.79 (m, 1H), 0.91 (d, $J = 6.6$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 167.0, 162.3 (d, $^1J_{\text{CF}} = 246.6$ Hz), 146.4, 142.6, 140.3, 137.3 (d, $^4J_{\text{CF}} = 3.0$ Hz), 129.8, 128.8, 128.7, 128.6 (d, $^3J_{\text{CF}} = 8.3$ Hz), 128.0, 125.9, 125.0, 115.4 (d, $^2J_{\text{CF}} = 21.4$ Hz), 52.0, 45.3, 41.9, 30.2, 22.3.

^{19}F NMR (282 MHz, CDCl_3) δ -117.47.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{25}\text{FO}_2$: 377.1911; found: 377.1909

TLC: $R_f = 0.47$ (10% Et_2O in hexanes)



methyl 4-((5-propyl-1,1'-biphenyl-3-yl)methyl)benzoate (41). The reaction was conducted according to the general procedure without modification using **S17** (25.3 mg, 0.073 mmol, 1.0 equiv) and Pd/C (10 wt%, 2.5 mg). Isolated yields were determined following column chromatography (10% Et_2O in hexanes).

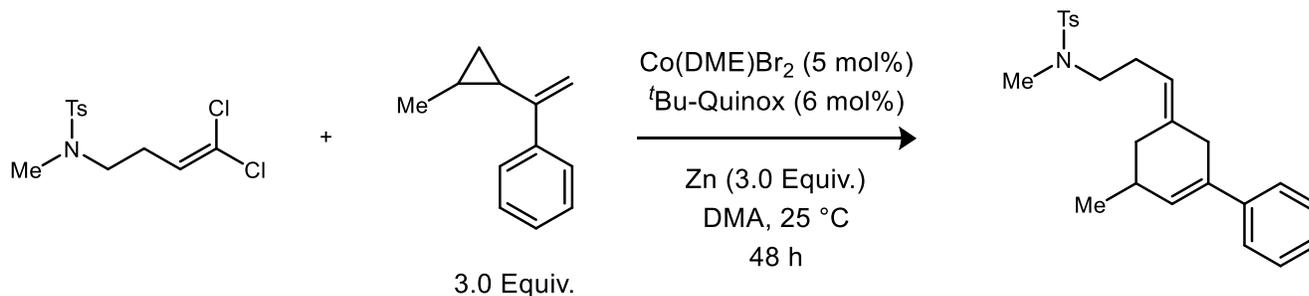
13.3 mg isolated (53% yield), colorless oil

^1H NMR (300 MHz, CDCl_3) δ 7.97 (d, $J = 8.3$ Hz, 2H), 7.55 (d, $J = 7.0$ Hz, 2H), 7.41 (t, $J = 7.3$ Hz, 2H), 7.36 – 7.27 (m, 4H), 7.21 (s, 1H), 6.98 (s, 1H), 4.07 (s, 2H), 3.90 (d, $J = 8.1$ Hz, 3H), 2.61 (t, $J = 8.1$ Hz, 2H), 1.73 – 1.57 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 167.0, 146.5, 143.5, 141.4, 141.2, 140.0, 129.8, 128.9, 128.6, 128.0, 127.1, 125.5, 125.2, 51.9, 41.9, 38.0, 24.5, 13.8.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_2$: 345.1849; found: 245.1847

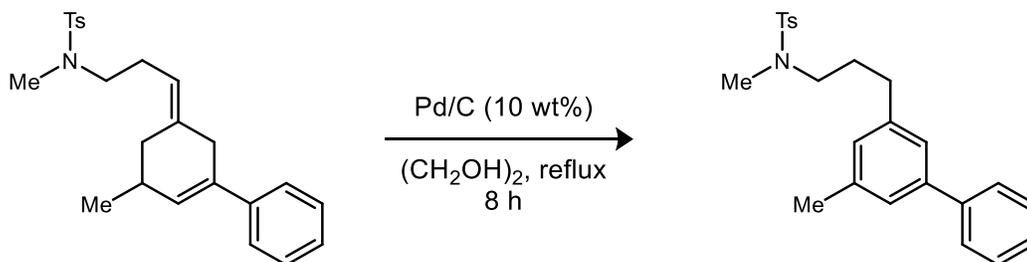
TLC: $R_f = 0.53$ (10% Et₂O in hexanes)



(E)-N,4-dimethyl-N-(3-(5-methyl-4,5-dihydro-[1,1'-biphenyl]-3(2H)-

ylidene)propyl)benzenesulfonamide (S20). In an N₂-filled glovebox, a 5-mL vial was charged with Co(DME)Br₂ (1.54 mg, 0.005 mmol, 0.05 equiv), (±)-*t*-Bu-Quinox (1.52 mg, 0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of **S16** (30.8 mg, 0.1 mmol, 1.0 equiv) and (1-(2-methylcyclopropyl)vinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv) in DMA (0.75 mL). The reaction was stirred at room temperature. After 48 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and loaded directly onto a SiO₂ column for purification (30% Et₂O in hexanes). Compound **S20** is highly unstable and was used immediately in the dehydrogenation reaction.

20.9 mg isolated (53% yield), yellow oil



N,4-dimethyl-N-(3-(5-methyl-[1,1'-biphenyl]-3-yl)propyl)benzenesulfonamide (42). The reaction was conducted according to the general procedure without modification using **S20** (20.9

mg, 0.053 mmol, 1.0 equiv.) and Pd/C (10 wt%, 2.1 mg). Isolated yields were determined following column chromatography (30% Et₂O in hexanes).

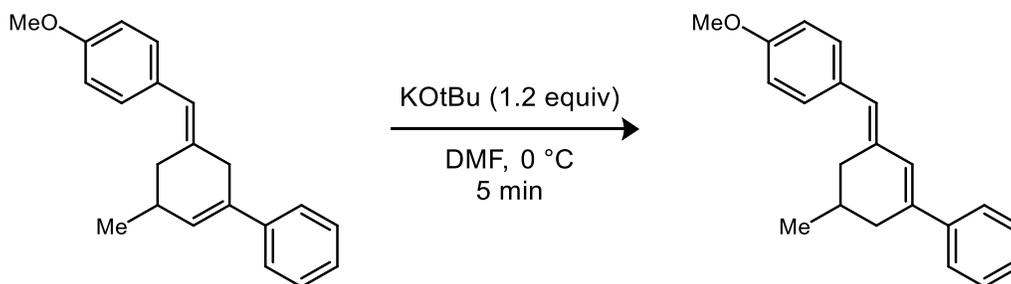
7.3 mg isolated (35% yield), colorless oil

¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 7.0 Hz, 2H), 7.49 – 7.37 (m, 2H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.22 (d, *J* = 13.5 Hz, 2H), 7.00 (s, 1H), 3.06 (t, *J* = 7.1 Hz, 2H), 2.73 (s, 3H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 1.98 – 1.78 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 143.2, 141.7, 141.3, 141.3, 138.4, 134.5, 129.6, 128.6, 128.1, 127.4, 127.1, 127.1, 125.7, 124.4, 49.7, 34.7, 32.7, 29.3, 21.4, 21.4.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₂₄H₂₇NO₂S: 394.1835; found: 394.1833

TLC: R_f = 0.21 (15% Et₂O in hexanes)



(*E*)-5-(4-methoxybenzylidene)-3-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (43). A solution of **30** (24.3 mg, 0.083 mmol, 1.0 equiv.) in DMF (1 mL) was cooled to 0 °C using an ice bath and stirred. To this solution was added KOtBu (10.8 mg, 0.097 mmol, 1.2 equiv) in one portion. The reaction was stirred at 0 °C. After 5 min, the reaction was quenched with H₂O (1 mL) and extracted with Et₂O (3x5 mL). The combined organic phases were dried over MgSO₄, concentrated under reduced pressure, and loaded directly onto a SiO₂ column for purification (5% Et₂O in hexanes).

18.8 mg isolated (78% yield), white solid

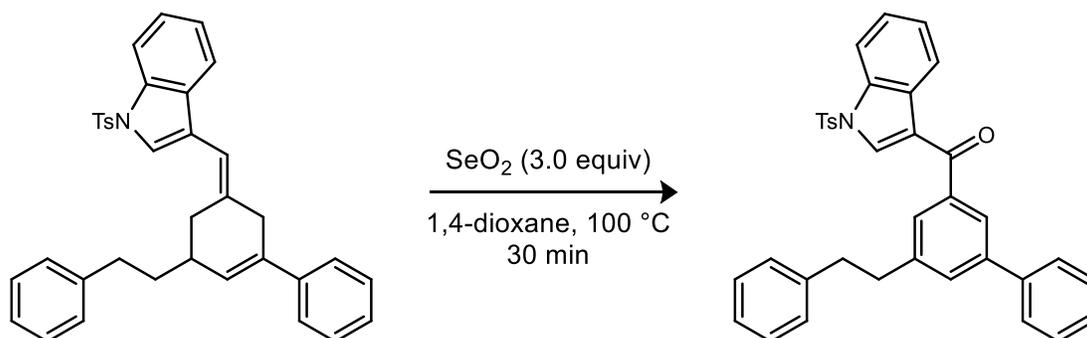
¹H NMR (300 MHz, CDCl₃) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 3H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 2.0 Hz, 1H), 6.41 (s, 1H), 3.83 (s, 3H), 2.89 (dd, *J* = 14.8, 3.5 Hz, 1H), 2.63 (dd, *J* = 16.8, 4.4 Hz, 1H), 2.36 – 2.10 (m, 2H), 1.93 (s, 1H), 1.11 (d, *J* = 6.5 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 158.1, 141.5, 137.4, 136.7, 130.7, 130.3, 128.7, 128.4, 127.3, 127.0, 125.0, 113.7, 55.3, 36.0, 34.9, 29.4, 21.8.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{O}$: 291.1743; found: 291.1741

TLC: $R_f = 0.45$ (5% Et_2O in hexanes)

General procedure for the Riley oxidation reaction. A flame-dried microwave vial was charged with the [5 + 1]-product (1.0 equiv), SeO_2 (3.0 equiv), 1.0 mL 1,4-dioxane, and a magnetic stir bar. The reaction was heated to 100 °C and stirred. After 30 min, the reaction was cooled to ambient temperature and loaded directly onto a SiO_2 column for purification.



(5-phenethyl-[1,1'-biphenyl]-3-yl)(1-tosyl-1H-indol-3-yl)methanone (44). The reaction was conducted according to the general procedure without modification using **S19** (39.4 mg, 0.072 mmol, 1.0 equiv) and SeO_2 (24.1 mg, 0.22 mmol, 3.0 equiv). Isolated yields were determined following column chromatography (30% Et_2O in hexanes).

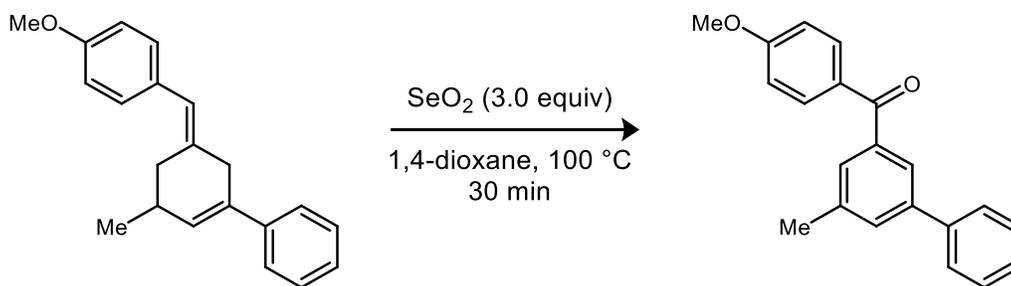
20.7 mg isolated (52% yield), yellow solid

^1H NMR (300 MHz, CDCl_3) δ 8.30 (d, $J = 8.1$ Hz, 1H), 8.13 – 7.95 (m, 2H), 7.87 (s, 1H), 7.80 (d, $J = 8.3$ Hz, 2H), 7.68 (s, 1H), 7.65 – 7.54 (m, 3H), 7.52 – 7.38 (m, 5H), 7.38 – 7.28 (m, 4H), 7.23 – 7.14 (m, 3H), 3.19 – 2.94 (m, 4H), 2.36 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 190.9, 145.8, 142.8, 141.6, 141.1, 140.2, 139.9, 135.0, 134.5, 133.5, 131.3, 130.2, 128.8, 128.4, 128.4, 127.8, 127.7, 127.2, 127.0, 126.1, 125.9, 125.6, 124.8, 122.8, 120.6, 113.17, 37.7, 30.3, 21.6.

HRMS(ESI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{29}\text{NO}_3\text{S}$: 556.1941; found: 556.1937

TLC: $R_f = 0.24$ (30% Et_2O in hexanes)



(4-methoxyphenyl)(5-methyl-[1,1'-biphenyl]-3-yl)methanone (45). The reaction was conducted according to the general procedure without modification using **30** (24.3 mg, 0.083 mmol, 1.0 equiv.) and SeO₂ (28.0 mg, 0.25 mmol, 3.0 equiv.). Isolated yields were determined following column chromatography (10% EtOAc in hexanes).

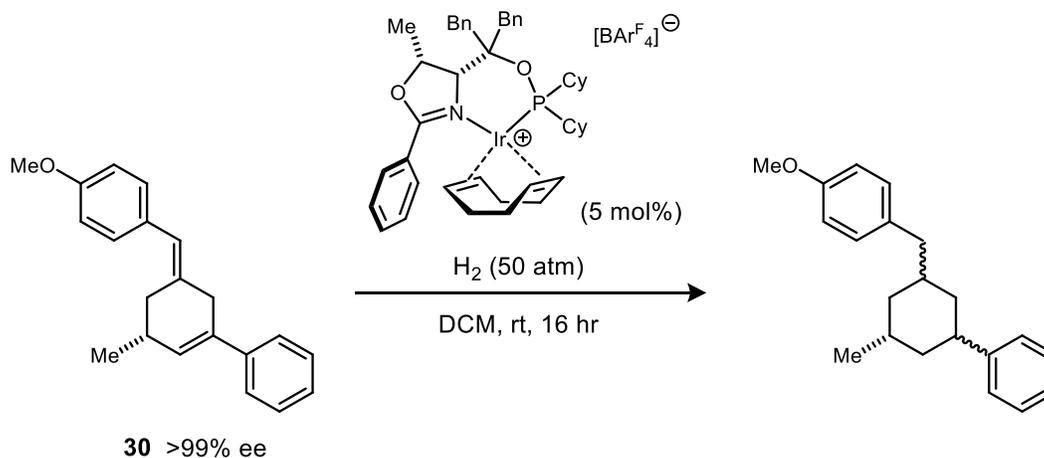
11.2 mg isolated (55% yield), colorless oil

¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.75 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 3H), 7.56 (s, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 5.8 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H), 2.49 (s, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 195.7, 163.3, 141.1, 140.4, 138.9, 138.6, 132.6, 131.4, 130.3, 129.1, 128.8, 127.6, 127.2, 125.7, 113.6, 55.5, 21.5.

HRMS(ESI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₁₈O₂: 303.1380; found: 303.1382

TLC: R_f = 0.22 (15% Et₂O in hexanes)



Attempted diastereoselective hydrogenation reaction. In an N₂-filled glovebox, a 2-dram vial was equipped with a magnetic stir bar, **30** (20.3 mg, 0.07 mmol, 1.0 equiv), (*R,R*)-[COD]Ir[Cy₂PThrePHOX] (6.0 mg, 0.0035 mmol, 0.05 equiv), and CH₂Cl₂ (1.0 mL). The vial

was capped and removed from the glovebox. A Parr bomb reactor vessel was placed under argon. The vial was uncapped and quickly placed into the Parr apparatus while under argon. The Parr apparatus was purged and backfilled with hydrogen (3x), then pressurized to 730 psi. After stirring for 16 h, the crude reaction mixture was filtered through a glass fiber pad. The filtrate was concentrated under reduced pressure, and the crude residue was analyzed using by ^1H NMR spectroscopy. The hydrogenated product was obtained as a mixture of all four possible diastereomers.

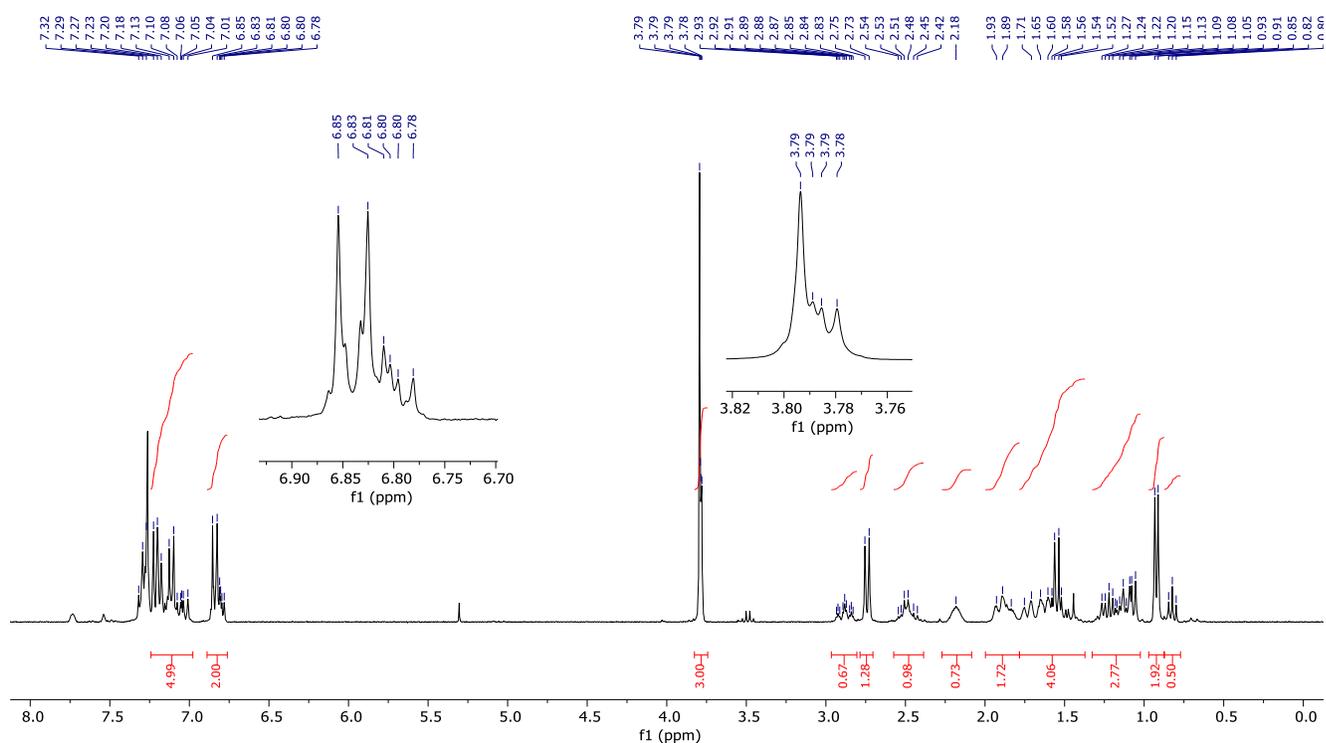
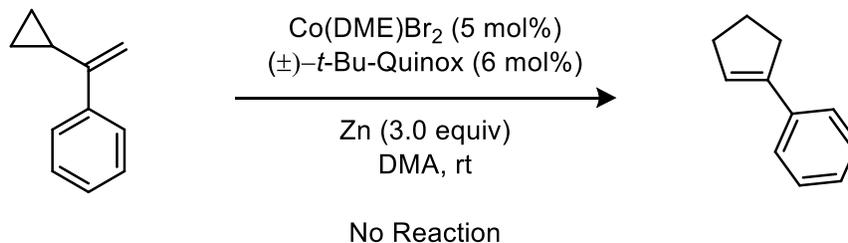
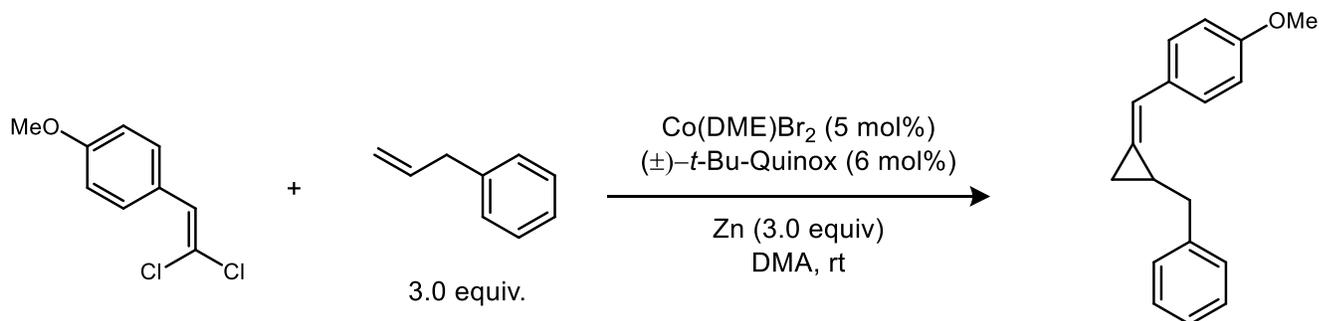


Figure S4. Crude ^1H NMR spectrum for the hydrogenation of **30** using a chiral Ir catalyst to provide a diastereomeric mixture of products (300 MHz, CDCl_3 , 295 K).

7. Mechanistic Studies



Vinylcyclopropane rearrangement experiment. In an N₂-filled glovebox, a 5-mL vial was charged with Co(DME)Br₂ (1.5 mg, 0.005 mmol, 0.05 equiv), (±)-*t*-Bu-Quinox (1.5 mg, 0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of (1-cyclopropylvinyl)benzene (43.3 mg, 0.3 mmol, 3.0 equiv) and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) in DMA (0.75 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and diluted with Et₂O. An aliquot was filtered through a glass fiber pad and analyzed by ¹H NMR. The conversion of (1-cyclopropylvinyl)benzene was determined by integration against 1,3,5-trimethoxybenzene (< 1% conversion). 1-phenylcyclopentene was not detected in the mixture.



(Z)-1-((2-benzylcyclopropylidene)methyl)-4-methoxybenzene (47). In an N₂-filled glovebox, a 5-mL vial was charged with Co(DME)Br₂ (1.5 mg, 0.005 mmol, 0.05 equiv), (±)-*t*-Bu-Quinox (1.5 mg, 0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4

mg, 0.1 mmol, 1.0 equiv) and allylbenzene (35.4 mg, 0.3 mmol, 3.0 equiv) in DMA (0.75 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and loaded directly onto a SiO₂ column for purification (5% Et₂O in hexanes).

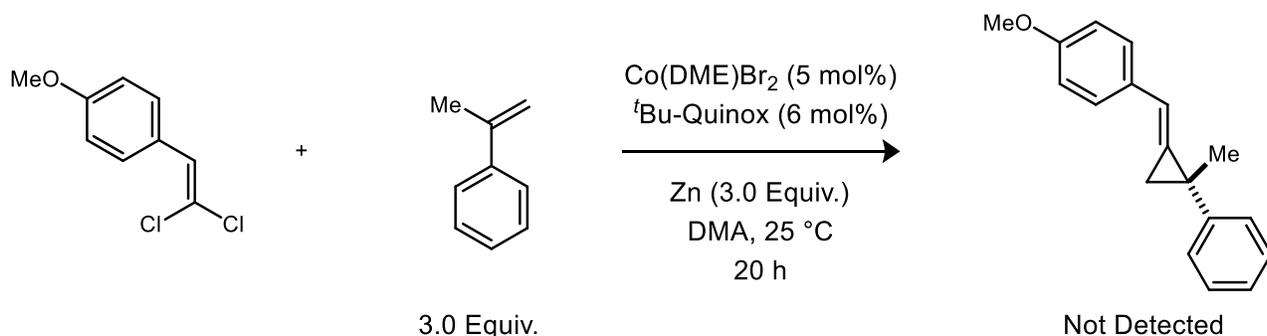
16.0 mg isolated (64% yield), colorless oil, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.27 – 7.19 (m, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.68 (s, 1H), 3.83 (s, 3H), 3.25 (dd, *J* = 14.6, 4.5 Hz, 1H), 2.45 (dd, *J* = 14.6, 8.9 Hz, 1H), 2.19 – 1.93 (m, 1H), 1.37 (t, *J* = 8.7 Hz, 1H), 1.05 – 0.86 (m, 1H).

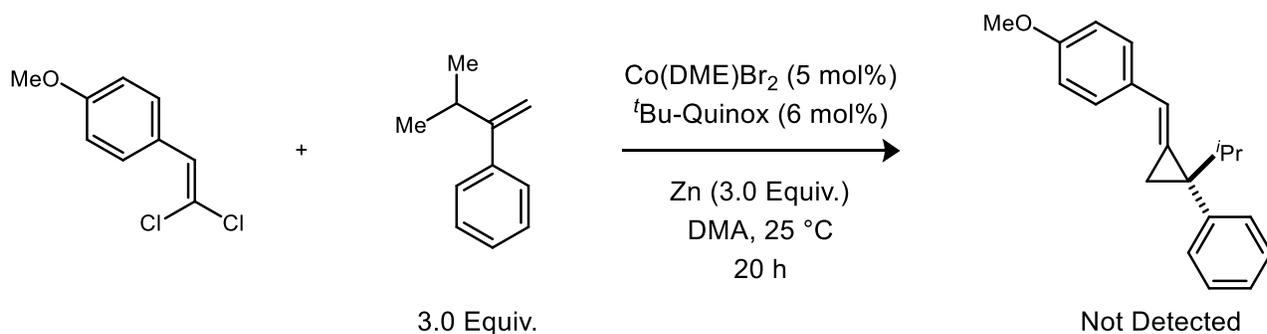
¹³C{¹H} NMR (201 MHz, CDCl₃) δ 158.5, 140.5, 130.7, 128.6, 128.2, 127.8, 126.4, 126.1, 118.8, 113.9, 55.2, 37.7, 17.6, 7.8.

HRMS(APCI) (*m/z*): [M - H]⁺ Calcd for C₁₈H₁₈O: 249.1247; found: 249.1127

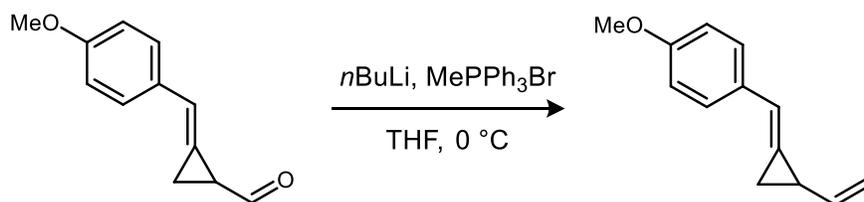
TLC: R_f = 0.47 (5% Et₂O in hexanes)



In an N₂-filled glovebox, a 5-mL vial was charged with Co(DME)Br₂ (1.5 mg, 0.005 mmol, 0.05 equiv), (\pm)-*t*-Bu-Quinox (1.5 mg, 0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv), α -methylstyrene (35.5 mg, 0.3 mmol, 3.0 equiv), and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) in DMA (0.75 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and diluted with Et₂O. An aliquot was filtered through a glass fiber pad and analyzed by ¹H NMR. The conversion of 1-(2,2-dichlorovinyl)-4-methoxybenzene was determined by integration against 1,3,5-trimethoxybenzene (>99% conversion). The product shown was not detected in the mixture.



In an N_2 -filled glovebox, a 5-mL vial was charged with Co(DME)Br_2 (1.5 mg, 0.005 mmol, 0.05 equiv), (\pm)-*t*-Bu-Quinox (1.5 mg, 0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv), (3-methylbut-1-en-2-yl)benzene (43.9 mg, 0.3 mmol, 3.0 equiv), and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) in DMA (0.75 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and diluted with Et_2O . An aliquot was filtered through a glass fiber pad and analyzed by $^1\text{H NMR}$. The conversion of 1-(2,2-dichlorovinyl)-4-methoxybenzene was determined by integration against 1,3,5-trimethoxybenzene (>99% conversion). The product shown was not detected in the mixture.



(*E*)-1-methoxy-4-((2-vinylcyclopropylidene)methyl)benzene (S21). A flame-dried round-bottom flask was charged with a stir bar, MePPh_3Br (3.82 g, 10.6 mmol, 1.5 equiv), and THF (30 mL). The mixture was cooled to 0 °C under N_2 atmosphere, followed by dropwise addition of $n\text{BuLi}$ (2.5 M in hexanes, 4.27 mL, 10.6 mmol, 1.5 equiv). The mixture was stirred at 0 °C for 30 min. A solution of (*E*)-2-(4-methoxybenzylidene)cyclopropane-1-carbaldehyde¹⁵ (1.33 g, 7.1 mmol, 1.0 equiv) in THF (5 mL) was added dropwise, and the reaction was then warmed to room

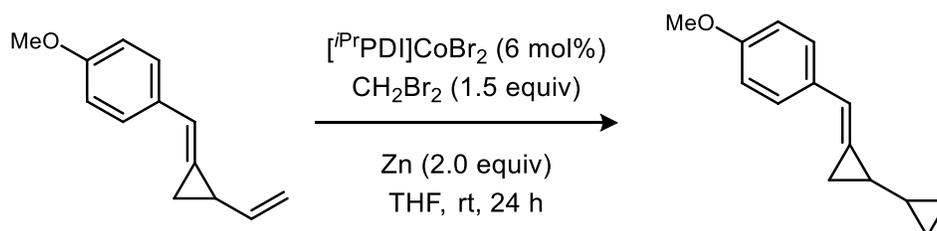
temperature and stirred. After 2 hr, the reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with Et_2O (3 x 20 mL). The combined organic layers were dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was loaded directly onto a SiO_2 column for purification (5% Et_2O in hexanes), providing (*E*)-1-methoxy-4-((2-vinylcyclopropylidene)methyl)benzene as a white solid (846 mg, 64% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, $J = 8.9$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 6.76 (s, 1H), 5.59 – 5.39 (m, 1H), 5.18 (d, $J = 17.0$ Hz, 1H), 4.96 (d, $J = 11.8$ Hz, 1H), 3.82 (s, 3H), 2.27 – 2.08 (m, 1H), 1.84 (t, $J = 8.8$ Hz, 1H), 1.40 – 1.28 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 158.7, 139.4, 130.5, 127.8, 125.4, 118.5, 113.8, 113.1, 55.2, 17.4, 12.8.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{14}\text{O}$: 187.1117; found: 187.1122

TLC: $R_f = 0.49$ (5% Et_2O in hexanes)



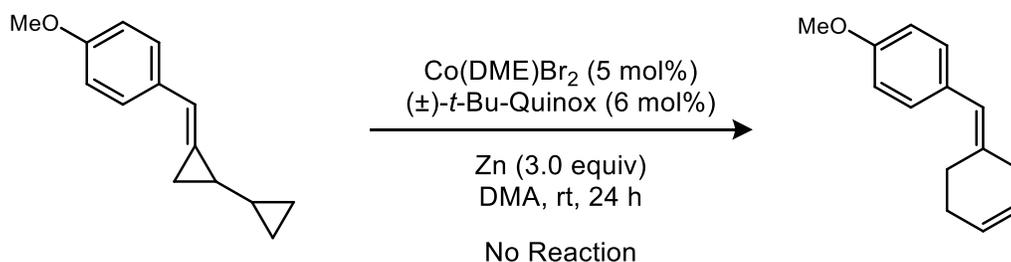
(*E*)-2-(4-methoxybenzylidene)-1,1'-bi(cyclopropane) (4). In an N_2 -filled glovebox, a 20 mL scintillation vial was charged with $[\text{iPrPDI}]\text{CoBr}_2$ (44.8 mg, 0.06 mmol, 0.06 equiv), Zn powder (140 mg, 2.14 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of **S21** (200 mg, 1.07 mmol, 1.0 equiv) and CH_2Br_2 (280 mg, 1.61 mmol, 1.5 equiv) in THF (8 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, concentrated under reduced pressure, and loaded directly onto a SiO_2 column for purification (5% Et_2O in hexanes), providing (*E*)-2-(4-methoxybenzylidene)-1,1'-bi(cyclopropane) as a yellow oil (190.5 mg, 89% yield).¹⁶

^1H NMR (300 MHz, CDCl_3) δ 7.46 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 6.62 (q, $J = 2.2$ Hz, 1H), 3.82 (s, 3H), 1.75 – 1.66 (m, 1H), 1.48 (td, $J = 8.7, 2.3$ Hz, 1H), 1.15 – 0.99 (m, 2H), 0.52 – 0.38 (m, 1H), 0.31 – 0.04 (m, 3H).

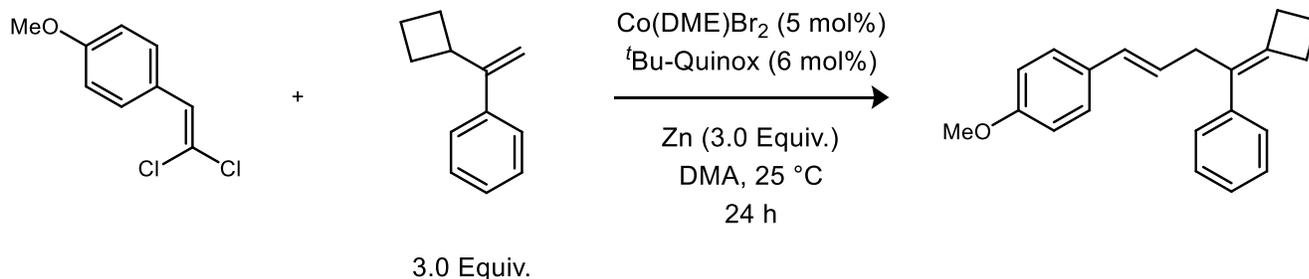
$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 158.5, 131.0, 127.6, 124.8, 117.5, 113.8, 55.2, 14.7, 11.6, 9.6, 3.9, 0.9.

HRMS(APCI) (m/z): $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: 201.1274; found: 201.1277

TLC: $R_f = 0.57$ (5% Et_2O in hexanes)



In an N_2 -filled glovebox, a 5-mL vial was charged with $\text{Co}(\text{DME})\text{Br}_2$ (1.5 mg, 0.005 mmol, 0.05 equiv), (\pm) -*t*-Bu-Quinox (1.5 mg, 0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of **4** (20.0 mg, 0.1 mmol, 1.0 equiv) and 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) in DMA (0.75 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and diluted with Et_2O . An aliquot was filtered through a glass fiber pad and analyzed by ^1H NMR. The conversion of **4** was determined by integration against 1,3,5-trimethoxybenzene (< 1% conversion). Compound **3** was not detected in the mixture.



(E)-1-(4-cyclobutylidene-4-phenylbut-1-en-1-yl)-4-methoxybenzene (49). In an N₂-filled glovebox, a 5-mL vial was charged with Co(DME)Br₂ (1.5 mg, 0.005 mmol, 0.05 equiv), (*±*)-*t*-Bu-Quinox (1.5 mg, 0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and (1-cyclobutylvinyl)benzene¹⁷ (47.5 mg, 0.3 mmol, 3.0 equiv) in DMA (0.75 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and loaded directly onto a SiO₂ column for purification (5% Et₂O in hexanes). Single crystals of **49** suitable for X-ray diffraction analysis were obtained by cooling the purified, neat material to -20 °C.

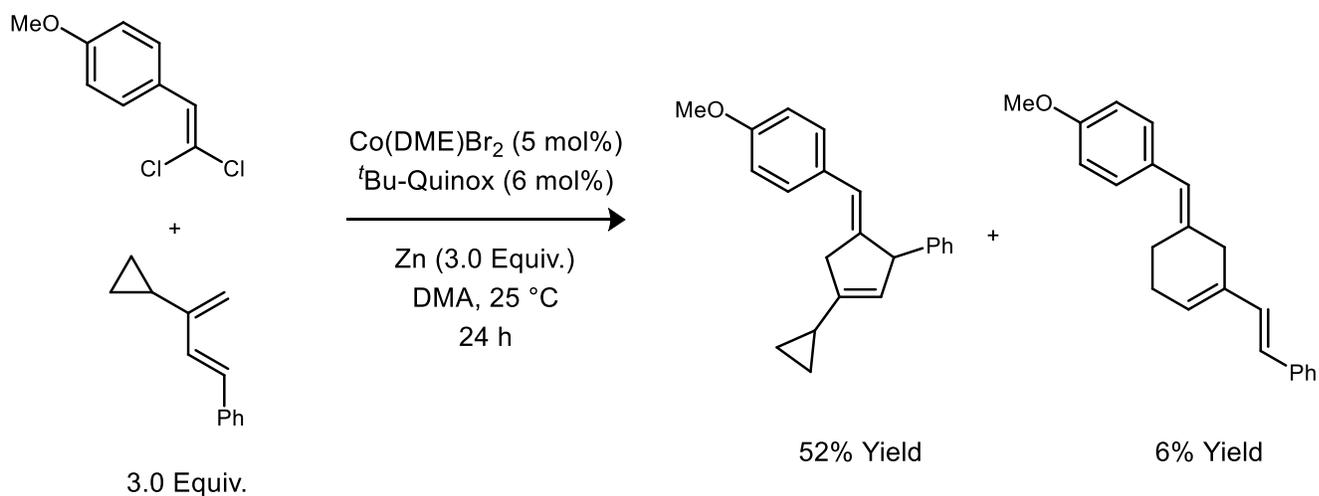
14.5 mg isolated (50% yield), colorless oil, *E/Z* = >20 : 1

¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.34 (m, 1H), 7.33 – 7.28 (m, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.22 – 7.12 (m, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.38 (d, *J* = 17.6 Hz, 1H), 6.17 – 6.02 (m, 1H), 3.80 (s, 3H), 3.24 (d, *J* = 5.6 Hz, 2H), 3.00 – 2.85 (m, 4H), 2.12 – 1.96 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 158.6, 140.0, 139.9, 130.6, 129.4, 128.1, 127.9, 127.0, 126.3, 125.8, 113.7, 55.2, 34.5, 32.2, 30.8, 17.0.

HRMS(APCI) (*m/z*): [M + H]⁺ Calcd for C₂₁H₂₂O: 291.1743; found: 291.1749

TLC: R_f = 0.54 (5% Et₂O in hexanes)



[4+1] cycloaddition competition experiment. In an N₂-filled glovebox, a 5-mL vial was charged with Co(DME)Br₂ (1.5 mg, 0.005 mmol, 0.05 equiv), (±)-*t*-Bu-Quinox (1.5 mg, 0.006 mmol, 0.06 equiv), Zn powder (19.6 mg, 0.3 mmol, 3.0 equiv), and a magnetic stir bar. To this mixture was added a solution of 1-(2,2-dichlorovinyl)-4-methoxybenzene (20.4 mg, 0.1 mmol, 1.0 equiv) and (*E*)-(3-cyclopropylbuta-1,3-dien-1-yl)benzene (51.1 mg, 0.3 mmol, 3.0 equiv) in DMA (0.75 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and loaded directly onto a SiO₂ column for purification (5% Et₂O in hexanes). The [4+1] and [5+1] products were inseparable.

17.5 mg isolated (58% yield), white solid

¹H NMR (300 MHz, CDCl₃) δ 7.23 (d, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.1, 3H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 5.53 (s, 1H), 4.64 (s, 1H), 3.73 (s, 3H), 3.39 (d, *J* = 20.3 Hz, 1H), 3.08 (d, *J* = 20.3 Hz, 1H), 1.54 – 1.46 (m, 1H), 0.70 – 0.62 (m, 2H), 0.57 – 0.48 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 157.83, 144.29, 142.85, 142.22, 130.03, 129.48, 128.52, 127.29, 127.11, 125.83, 124.11, 113.33, 77.09, 76.93, 76.78, 55.08, 53.81, 41.98, 11.87, 5.52, 5.29.

LRMS(ESI) (*m/z*): [M - H]⁺ Calcd for C₂₂H₂₂O: 302.4; found: 301.2

TLC: R_f = 0.53 (5% Et₂O in hexanes)

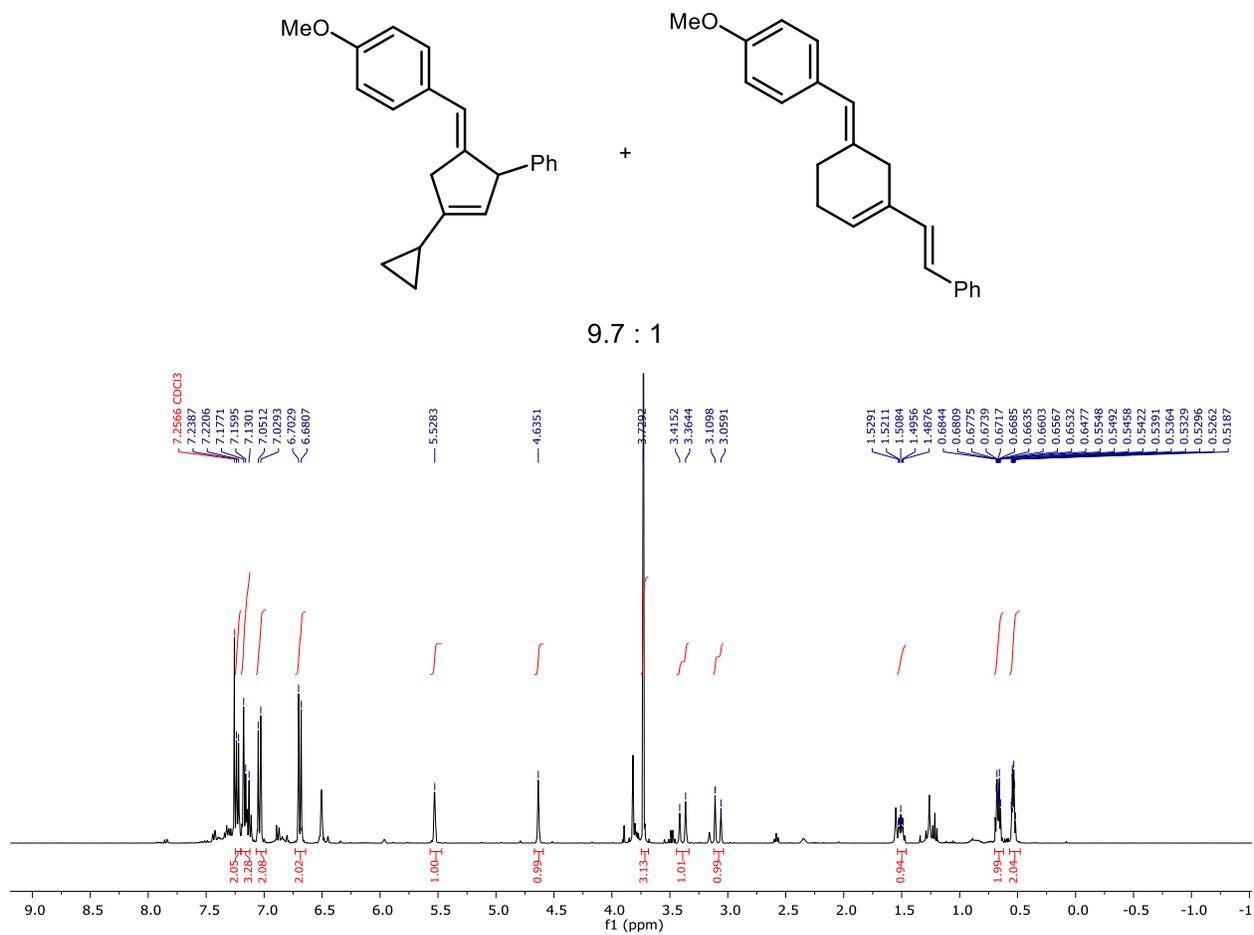


Figure S5. ^1H NMR of competition experiment (400 MHz, CDCl_3 , 295 K).

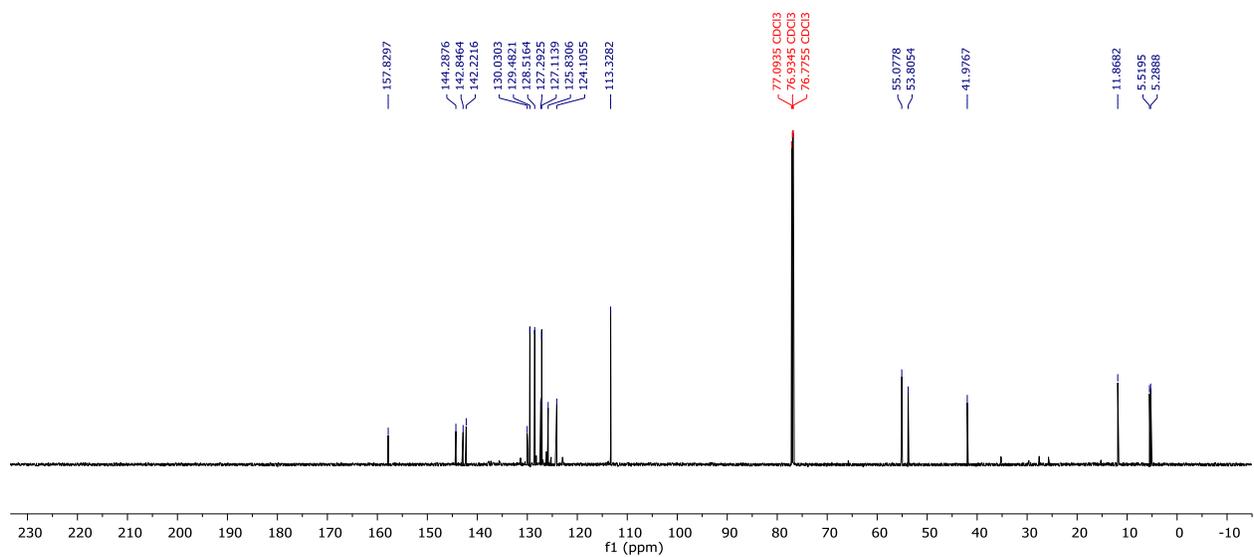


Figure S6. ^{13}C NMR of competition experiment (800 MHz, CDCl_3 , 295 K).

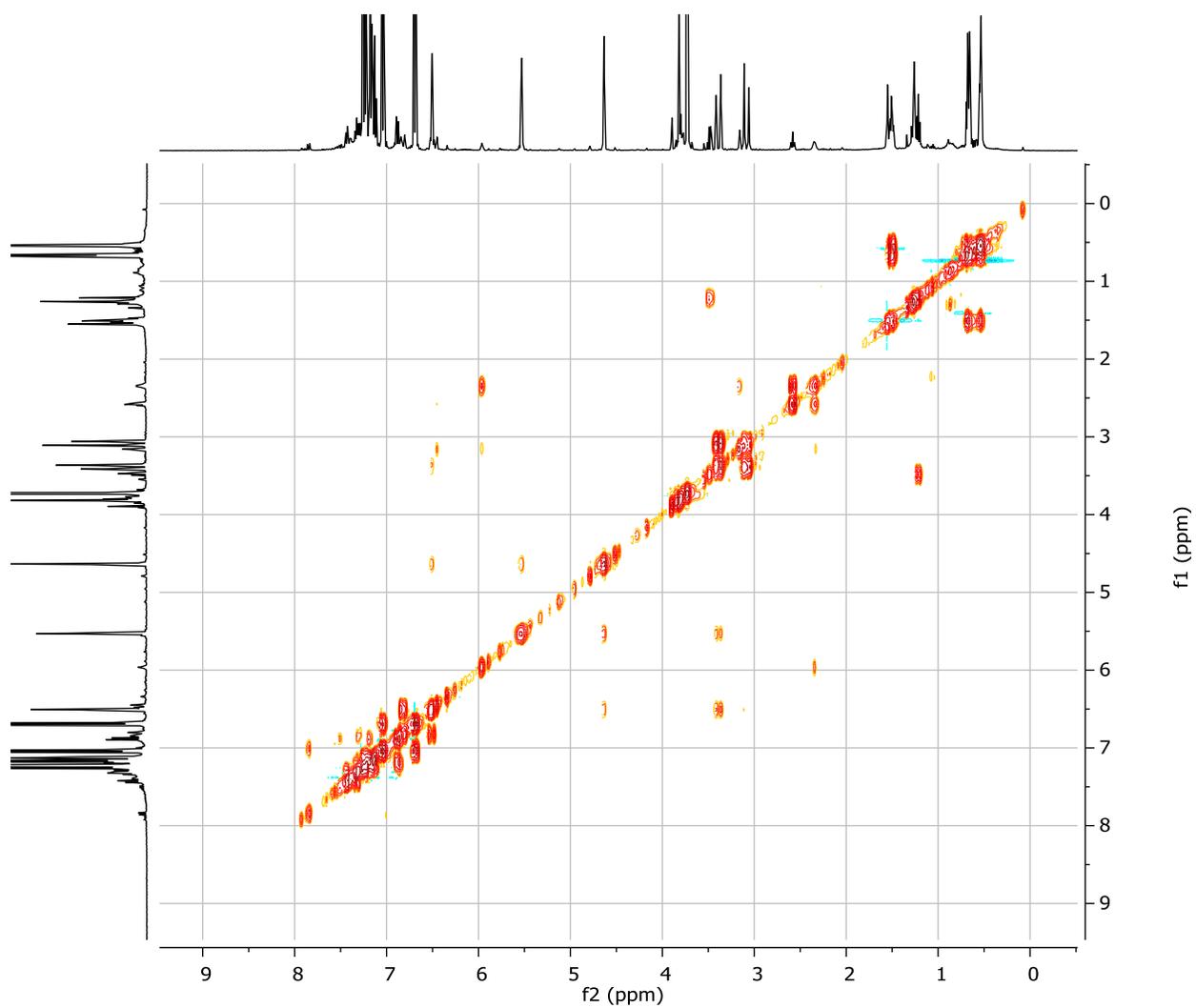


Figure S7. COSY of competition experiment (400 MHz, CDCl₃, 295 K).

8. NMR Data for Vinylcyclopanes and Vinylidenes

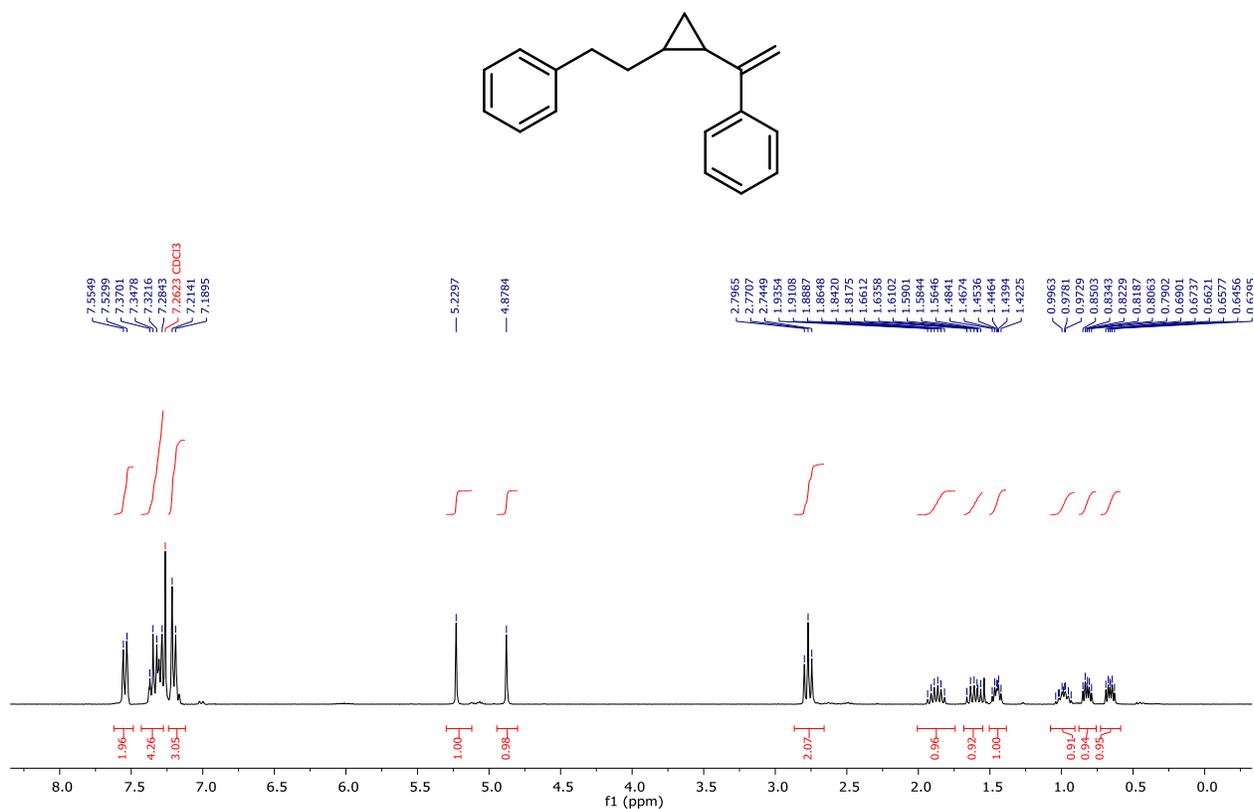


Figure S8. ¹H NMR of S1 (300 MHz, CDCl₃, 295 K).

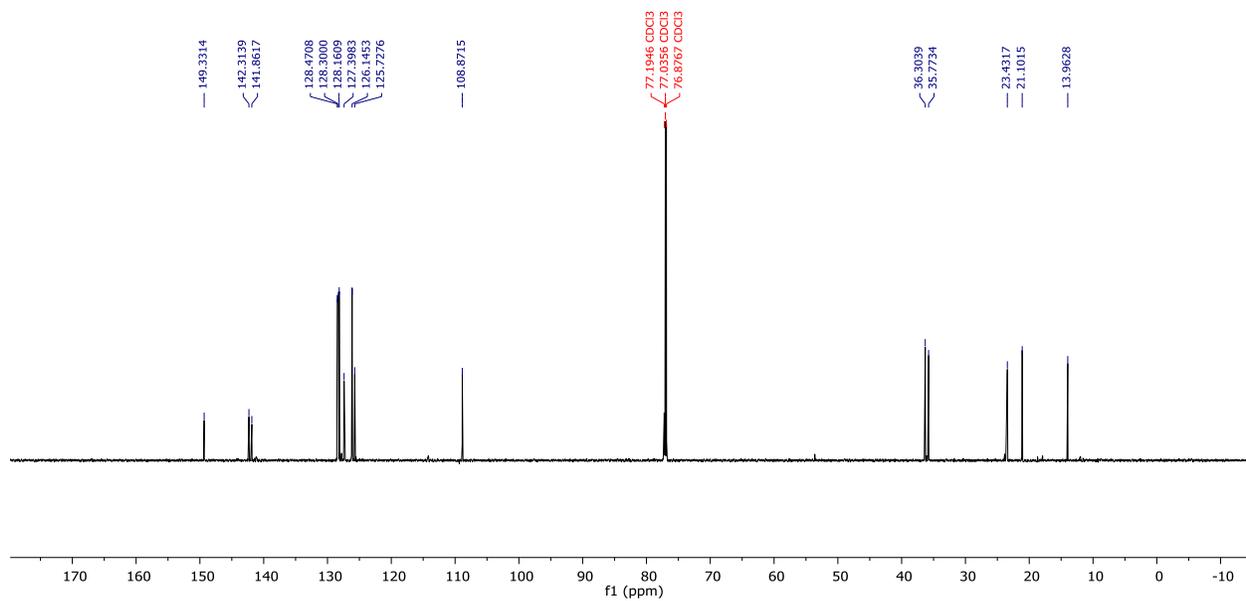


Figure S9. ¹³C NMR of S1 (800 MHz, CDCl₃, 295 K).

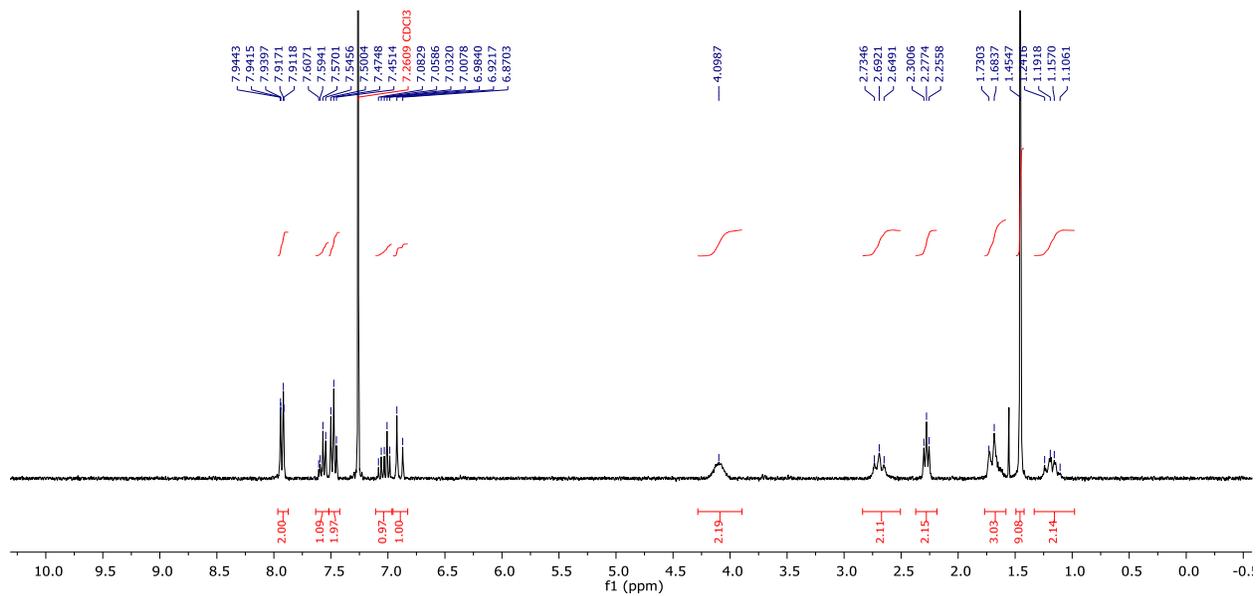
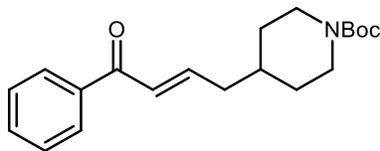


Figure S10. ¹H NMR of S2 (300 MHz, CDCl₃, 295 K).

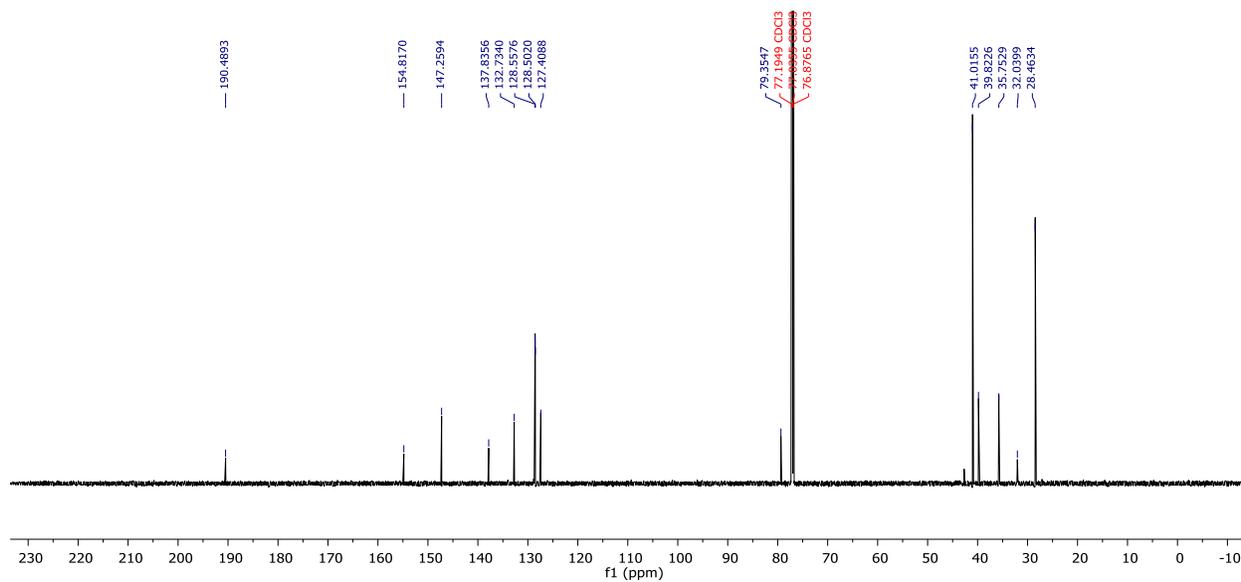


Figure S11. ¹³C NMR of S2 (800 MHz CDCl₃, 295 K).

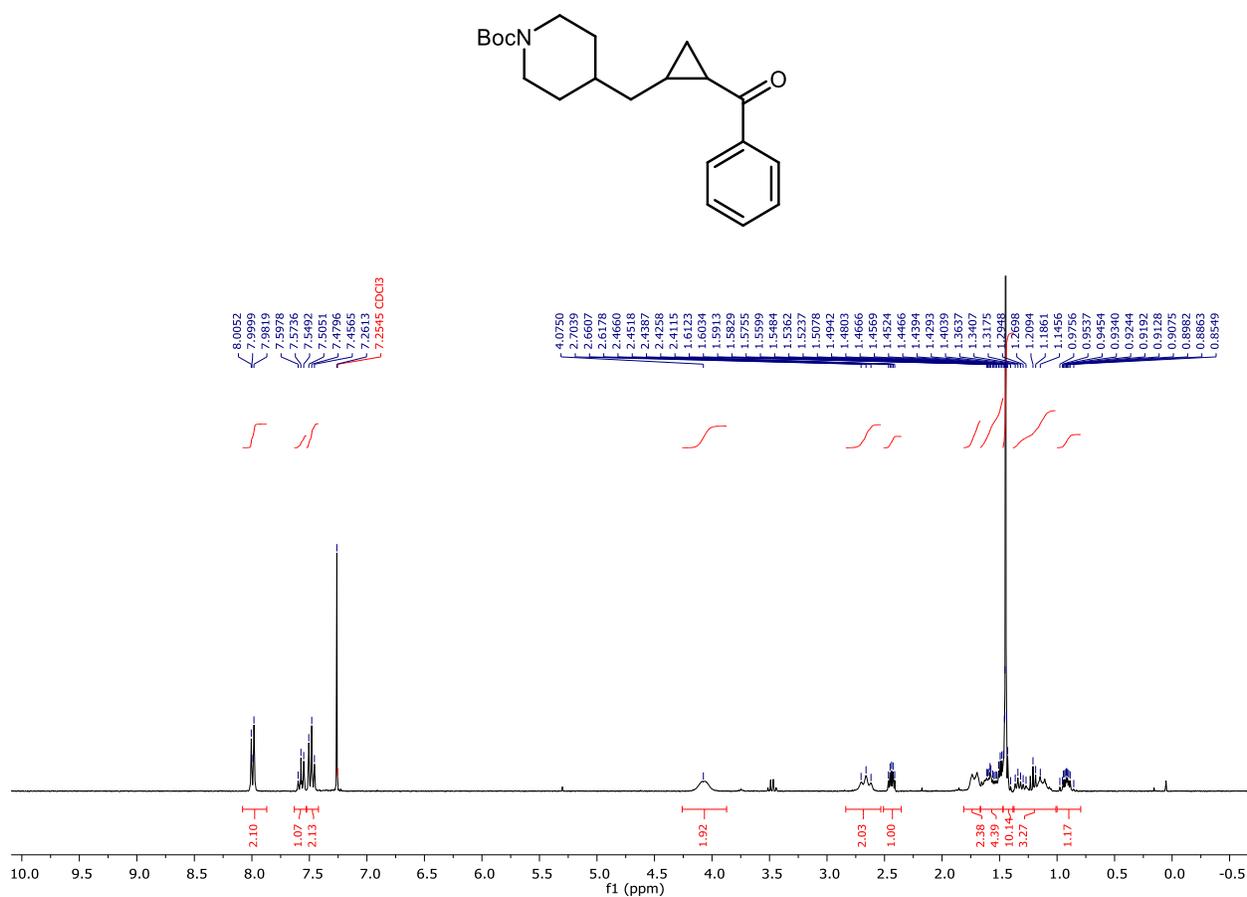


Figure S12. ¹H NMR of S3 (300 MHz, CDCl₃, 295 K).

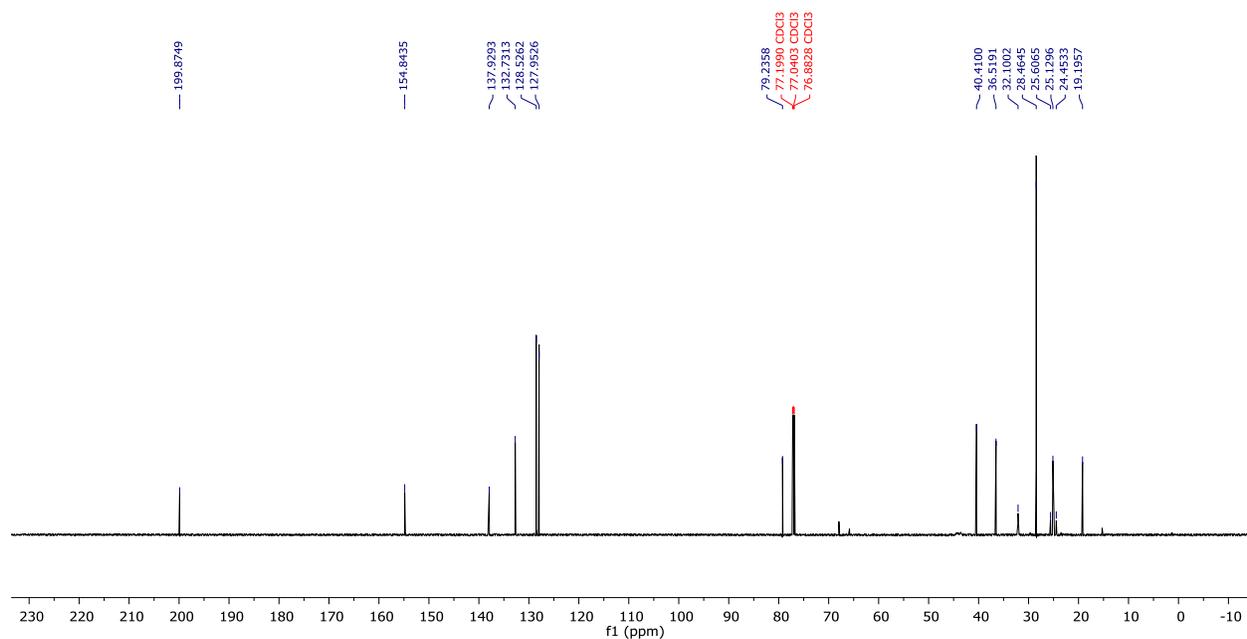


Figure S13. ¹³C NMR of S3 (800 MHz, CDCl₃, 295 K).

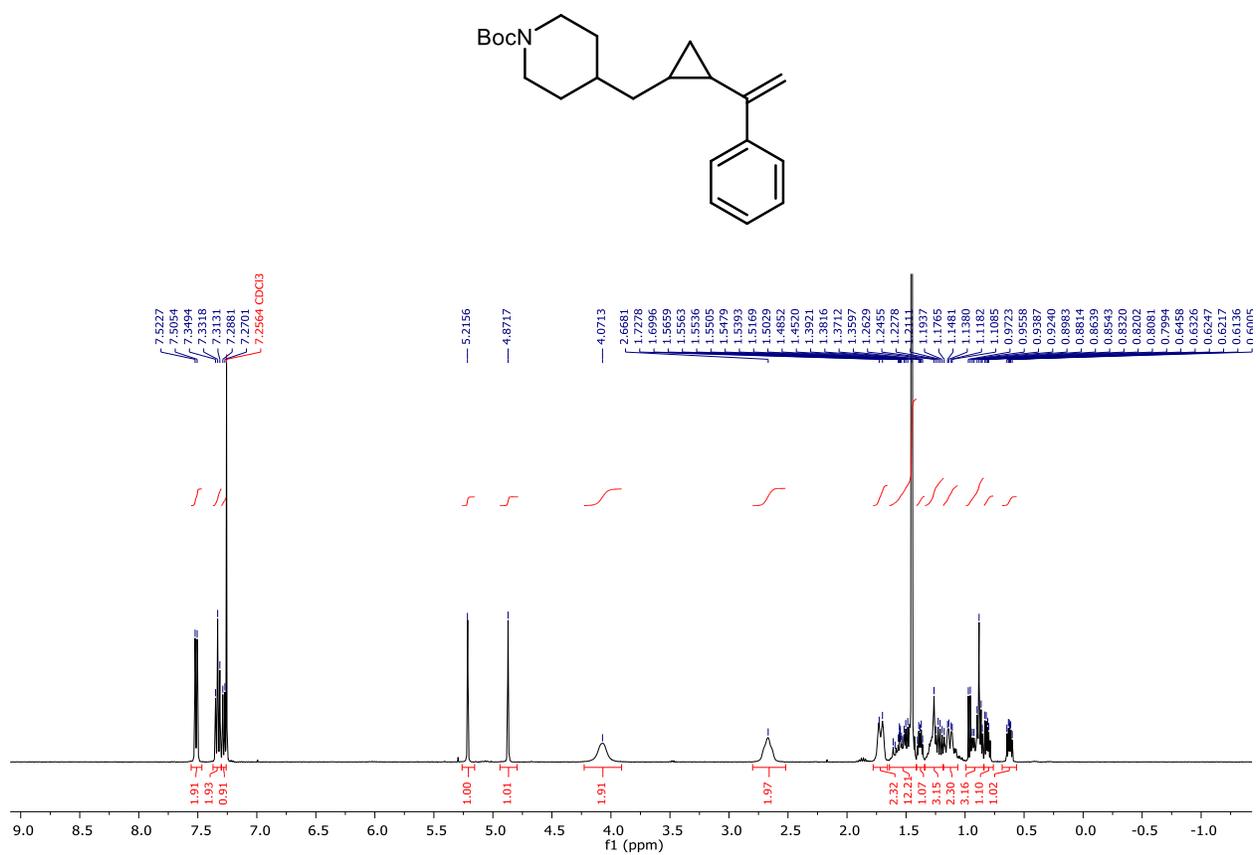


Figure S14. ¹H NMR of S4 (300 MHz, CDCl₃, 295 K).

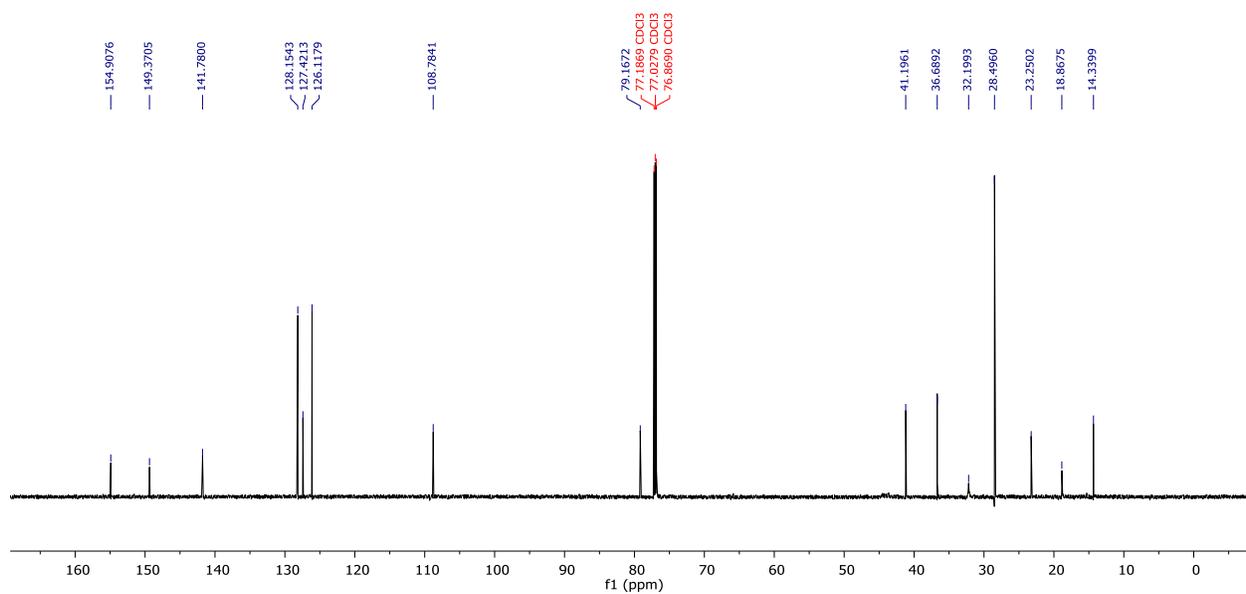


Figure S15. ¹³C NMR of S4 (800 MHz CDCl₃, 295 K).

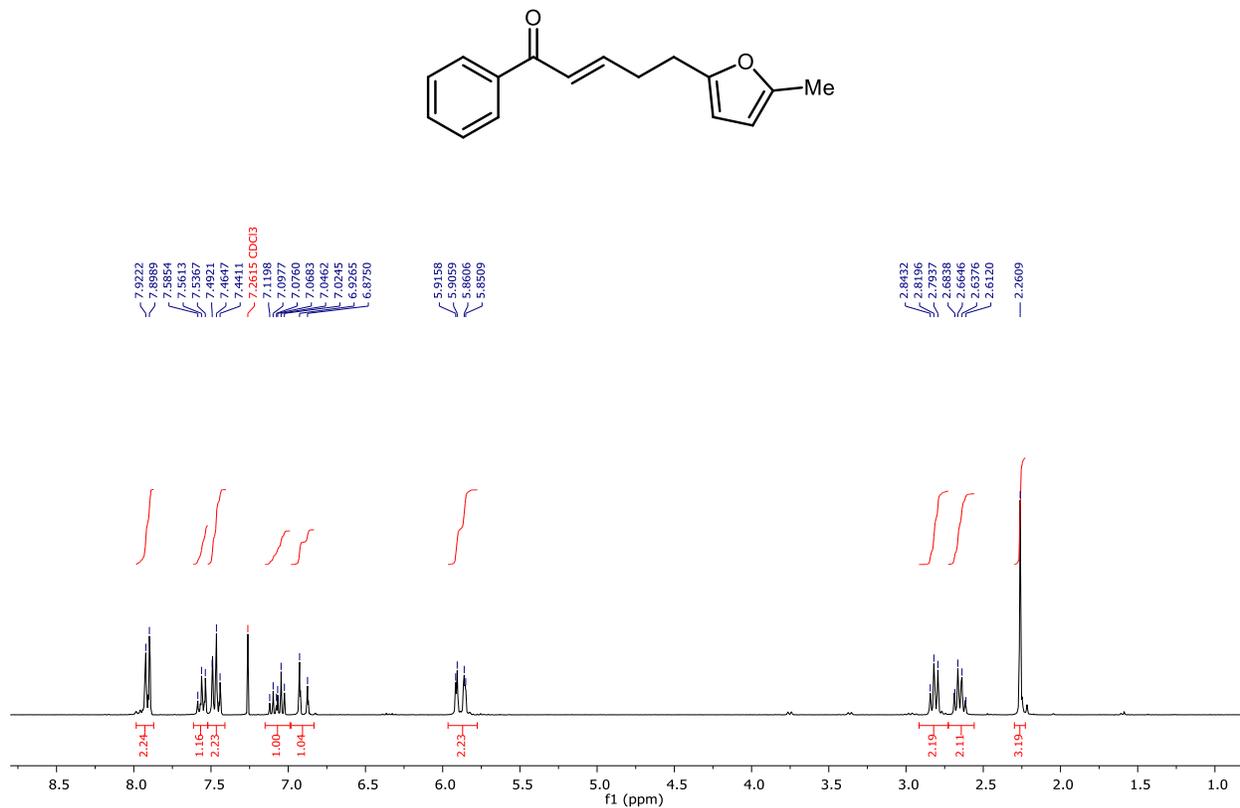


Figure S16. ¹H NMR of S5 (300 MHz, CDCl₃, 295 K).

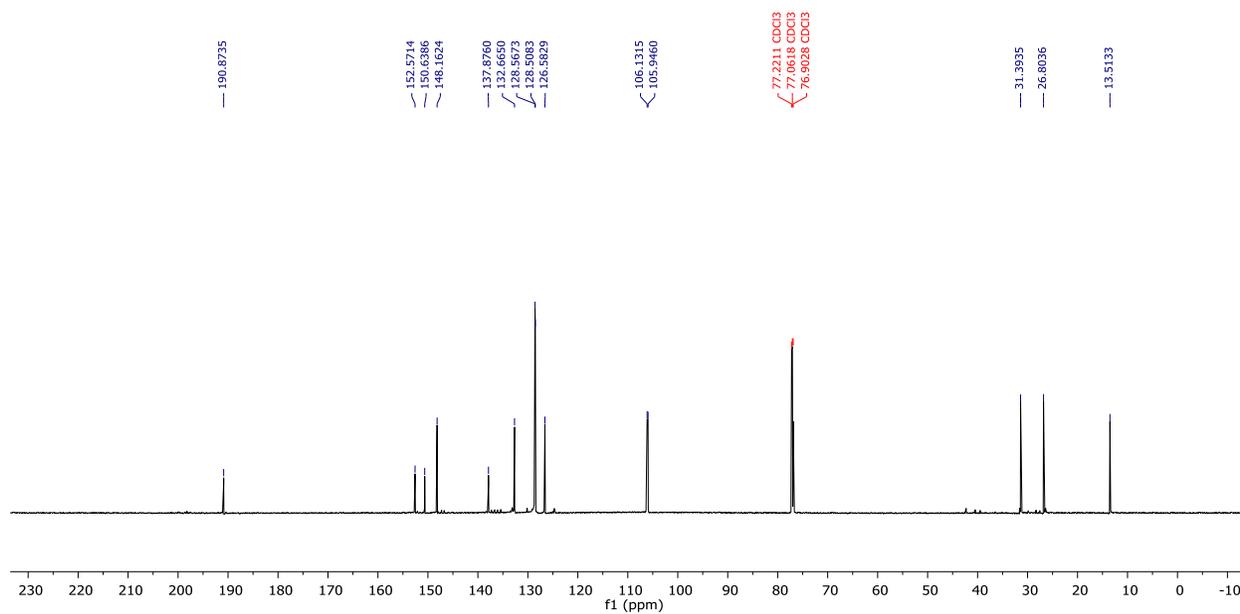


Figure S17. ¹³C NMR of S5 (800 MHz, CDCl₃, 295 K).

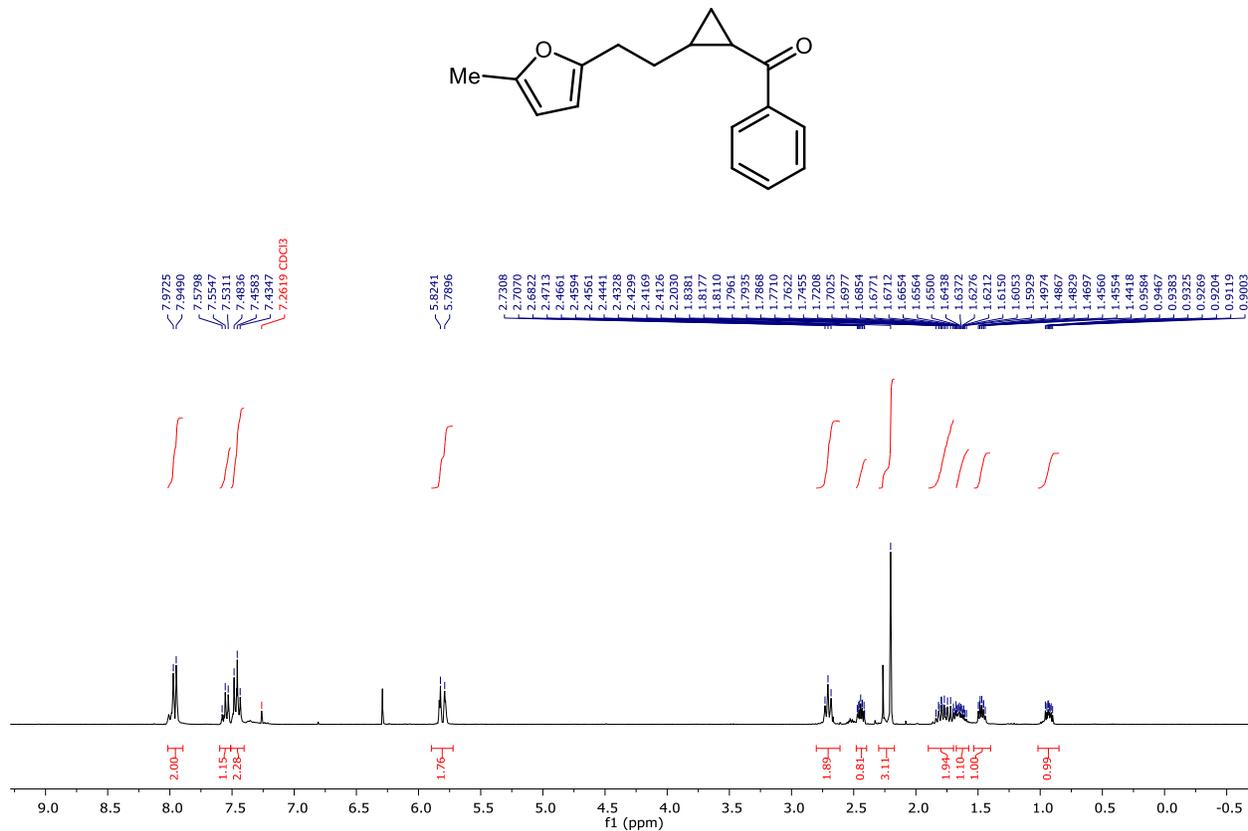


Figure S18. ¹H NMR of S6 (300 MHz, CDCl₃, 295 K).

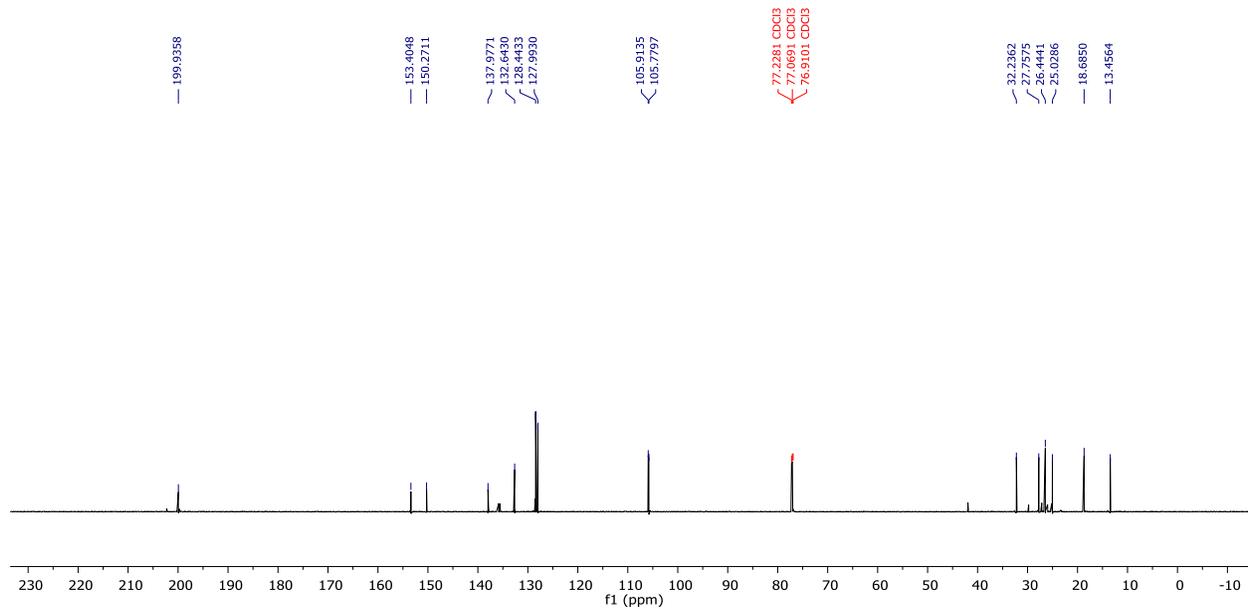


Figure S19. ¹³C NMR of S6 (800 MHz, CDCl₃, 295 K).

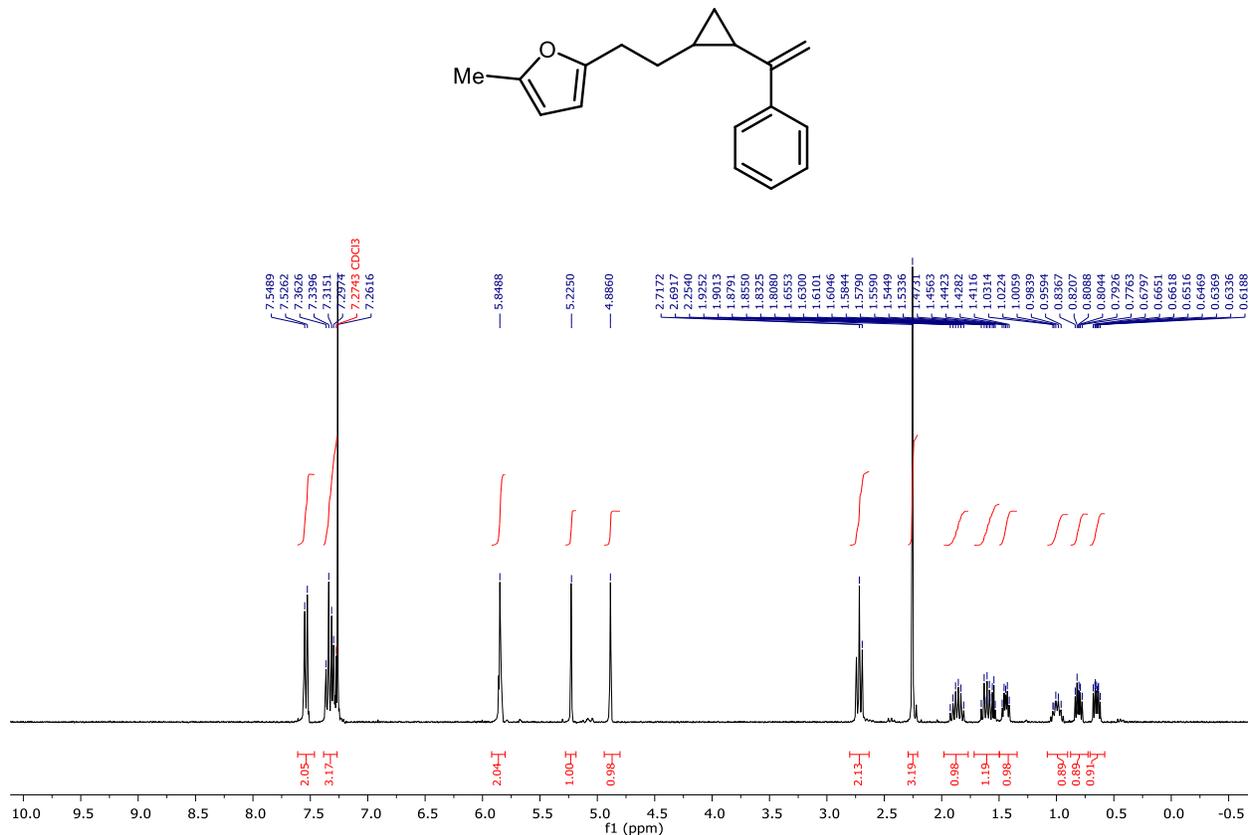


Figure S20. ¹H NMR of S7 (300 MHz, CDCl₃, 295 K).

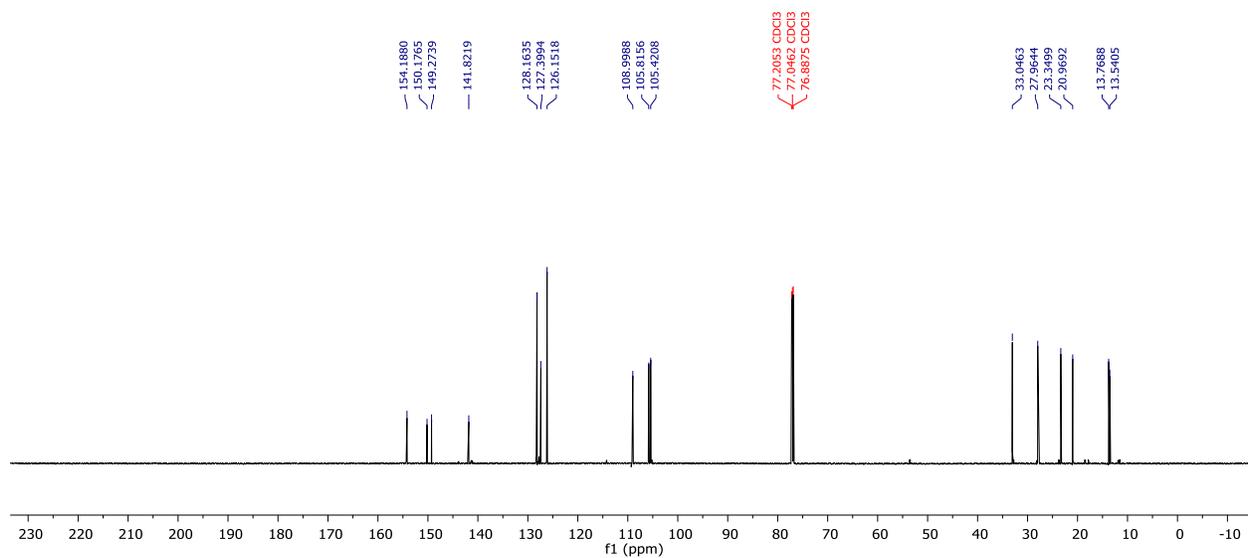


Figure S21. ¹³C NMR of S7 (800 MHz, CDCl₃, 295 K).

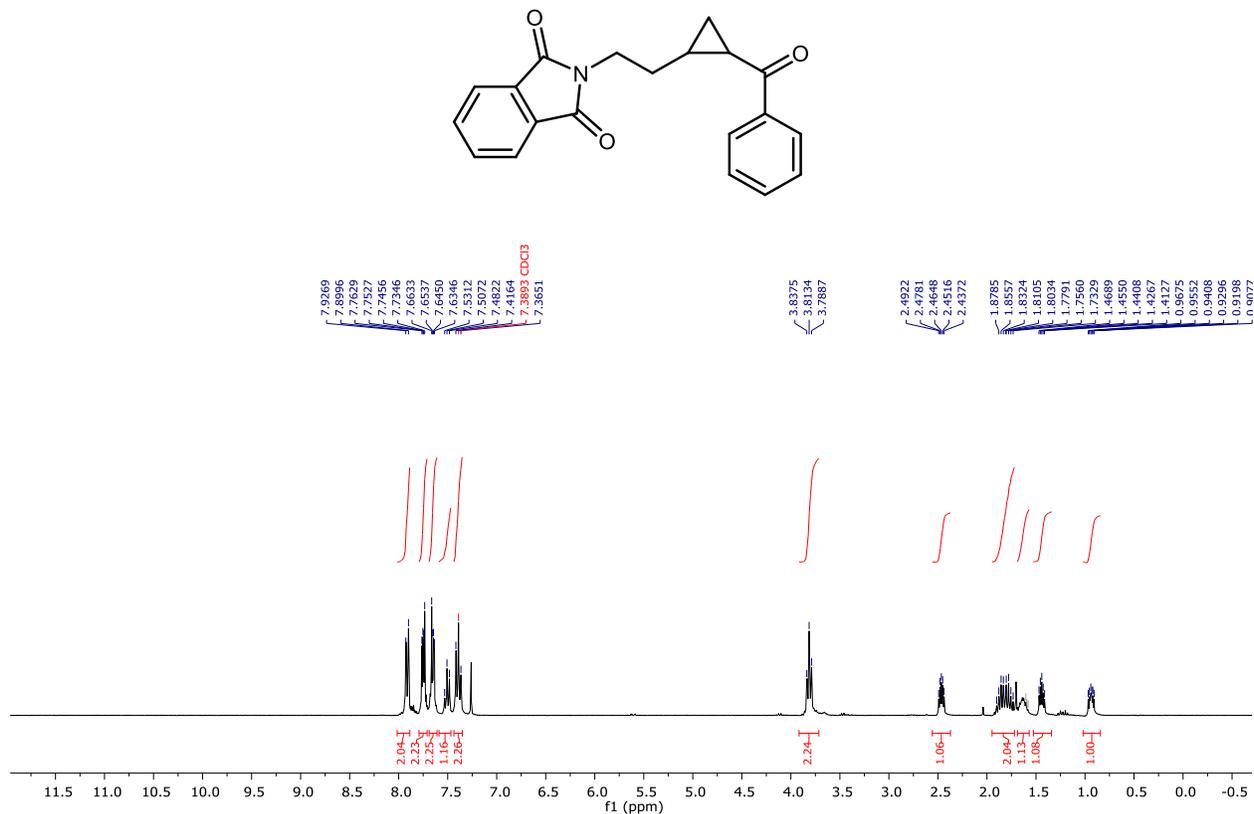


Figure S22. ¹H NMR of S8 (300 MHz, CDCl₃, 295 K).

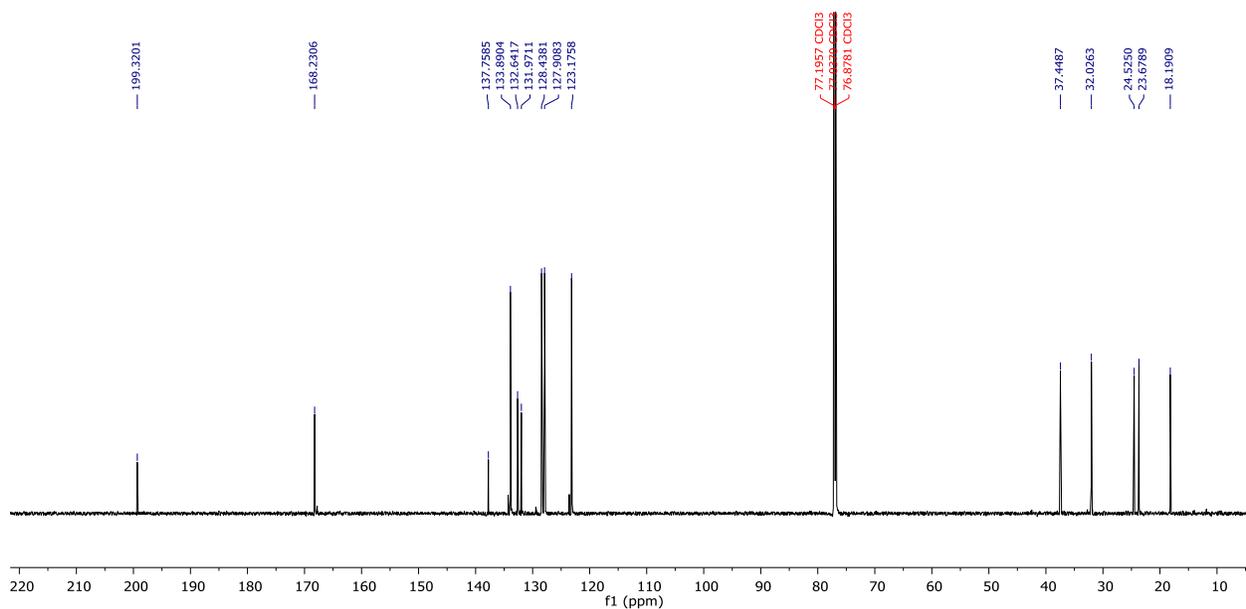


Figure S23. ¹³C NMR of S8 (800 MHz, CDCl₃, 295 K).

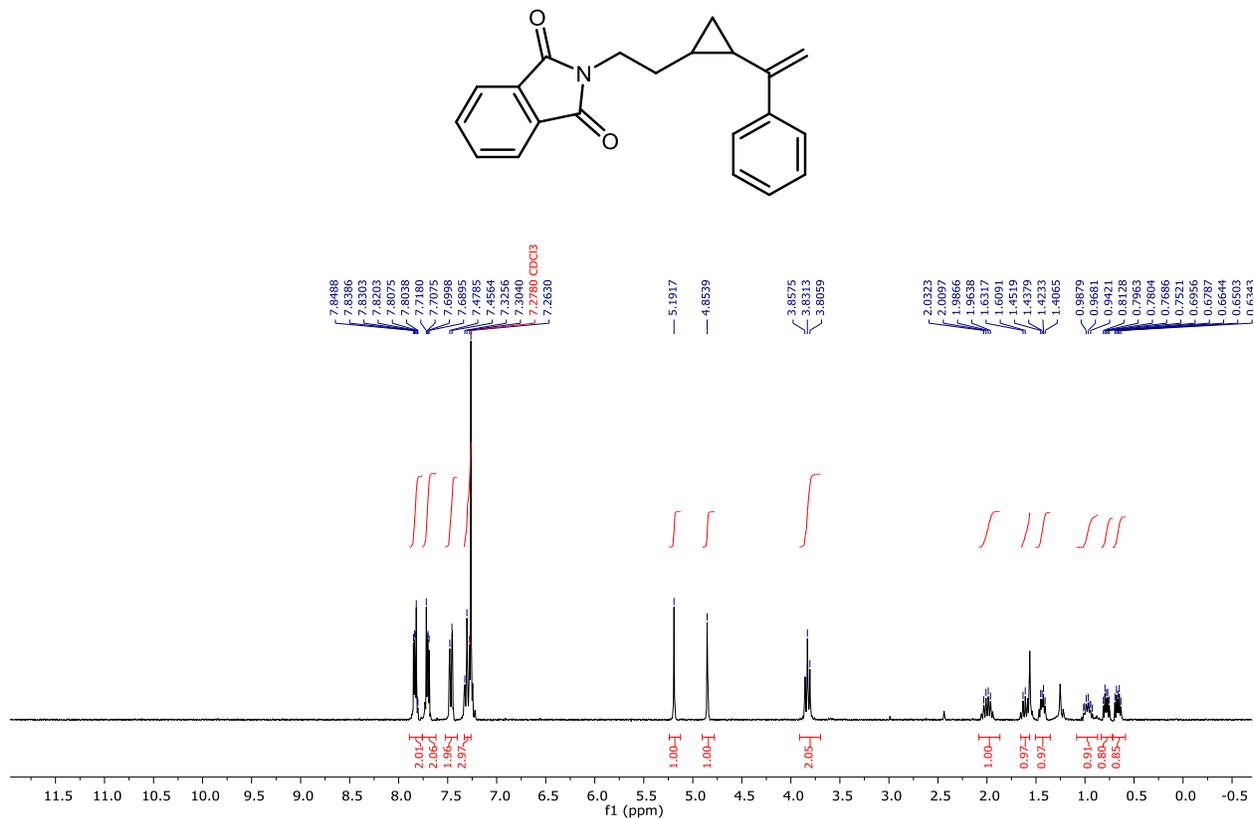


Figure S24. ¹H NMR of **S9** (300 MHz, CDCl₃, 295 K).

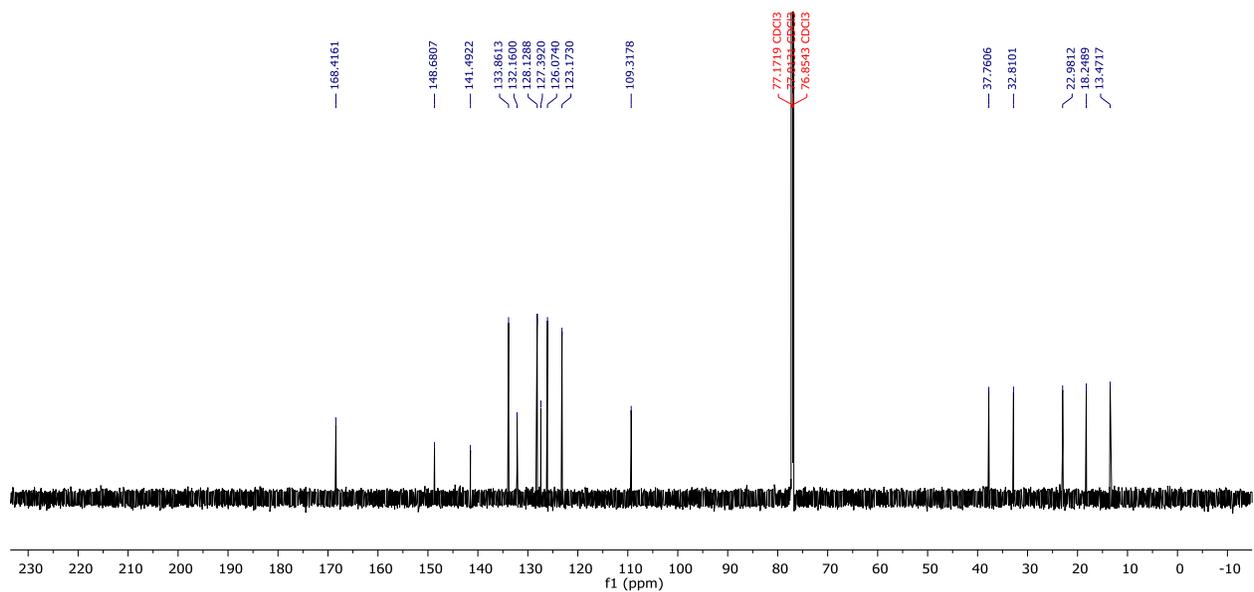


Figure S25. ¹³C NMR of **S9** (800 MHz, CDCl₃, 295 K).

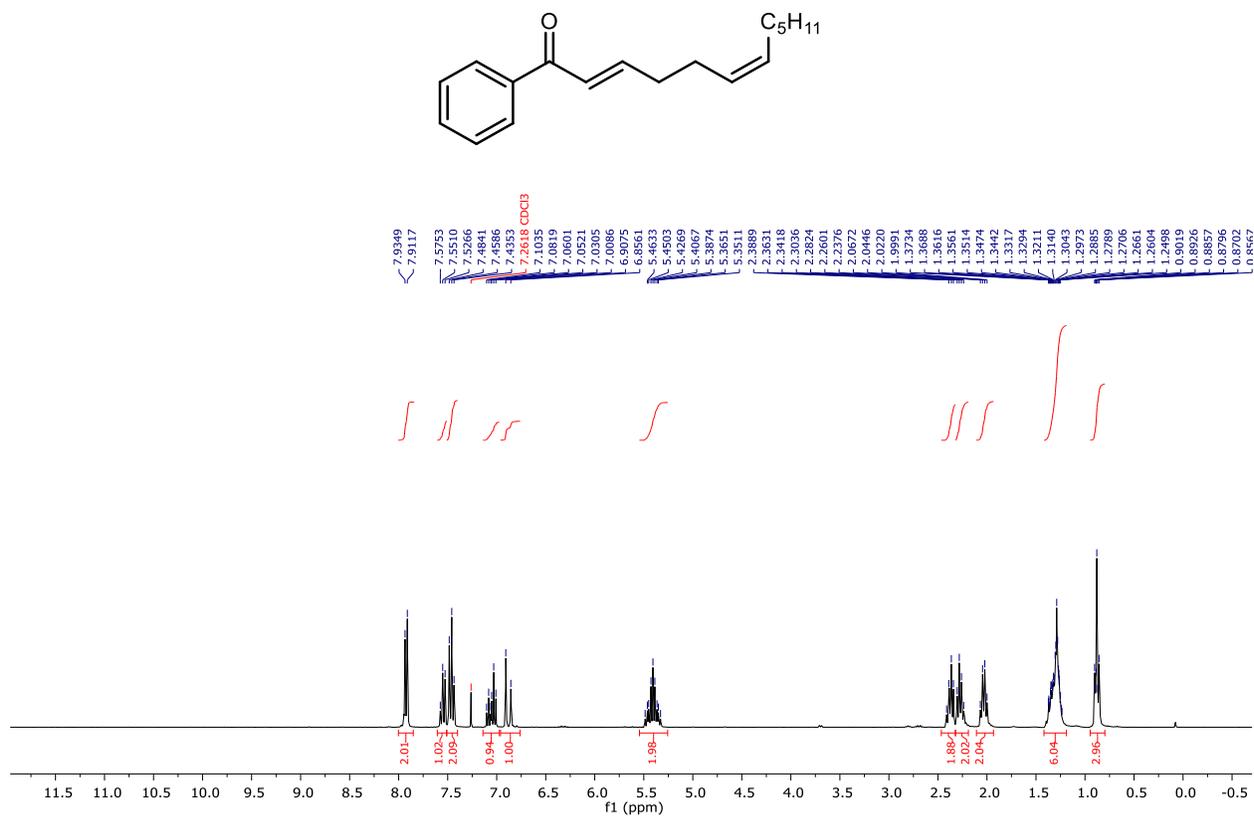


Figure S26. ¹H NMR of **S10** (300 MHz, CDCl₃, 295 K).

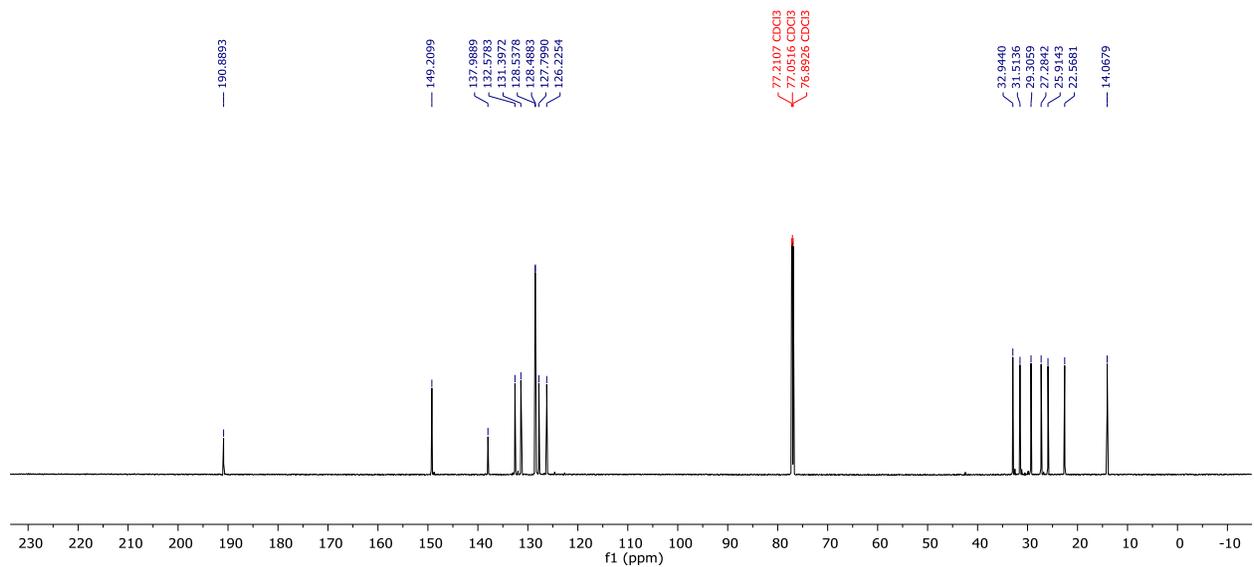


Figure S27. ¹³C NMR of **S10** (800 MHz, CDCl₃, 295 K).

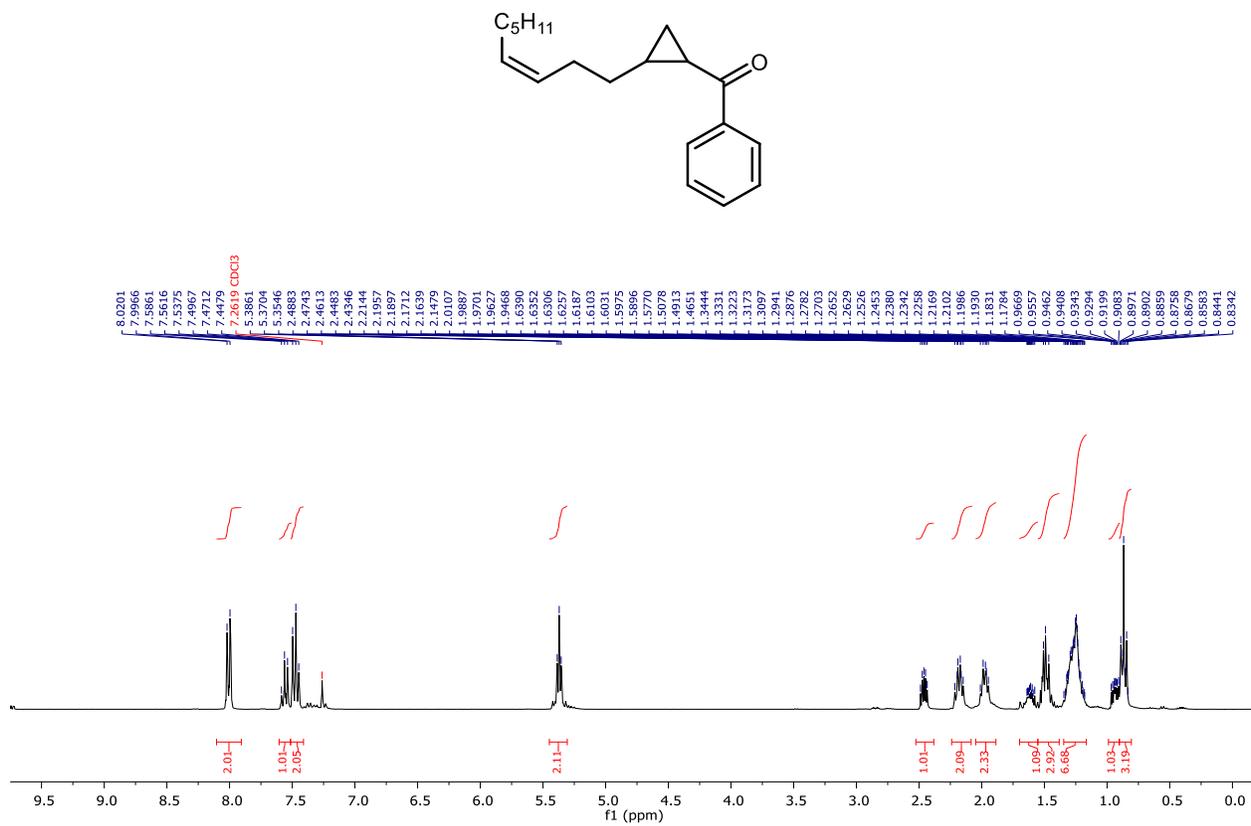


Figure S28. ¹H NMR of S11 (300 MHz, CDCl₃, 295 K).

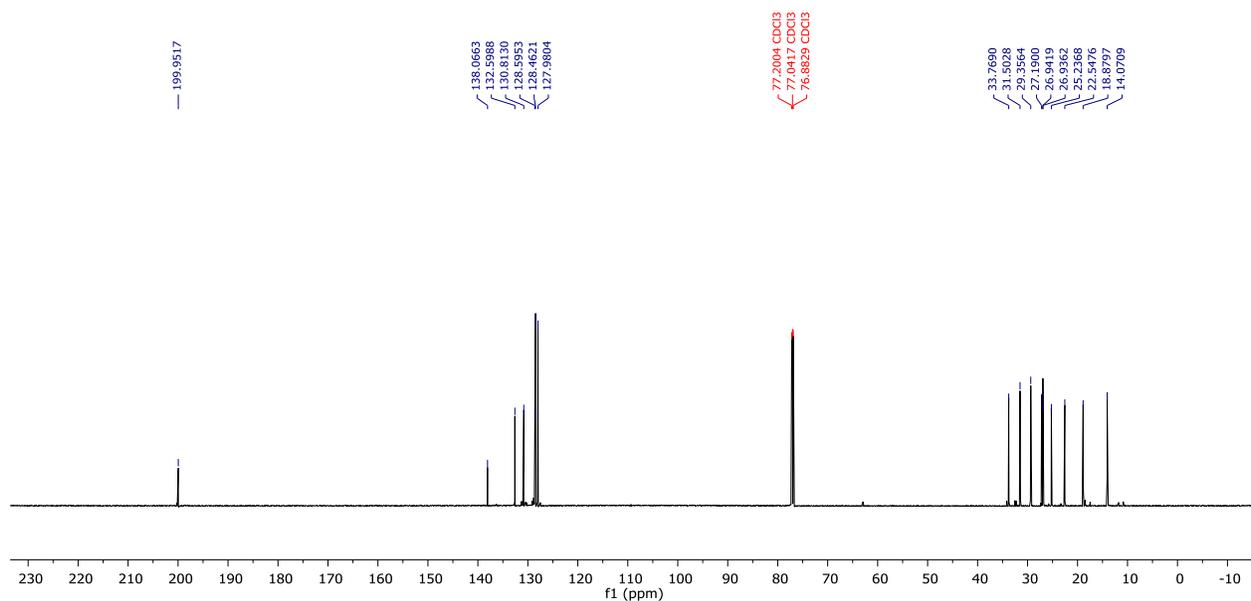


Figure S29. ¹³C NMR of S11 (800 MHz, CDCl₃, 295 K).

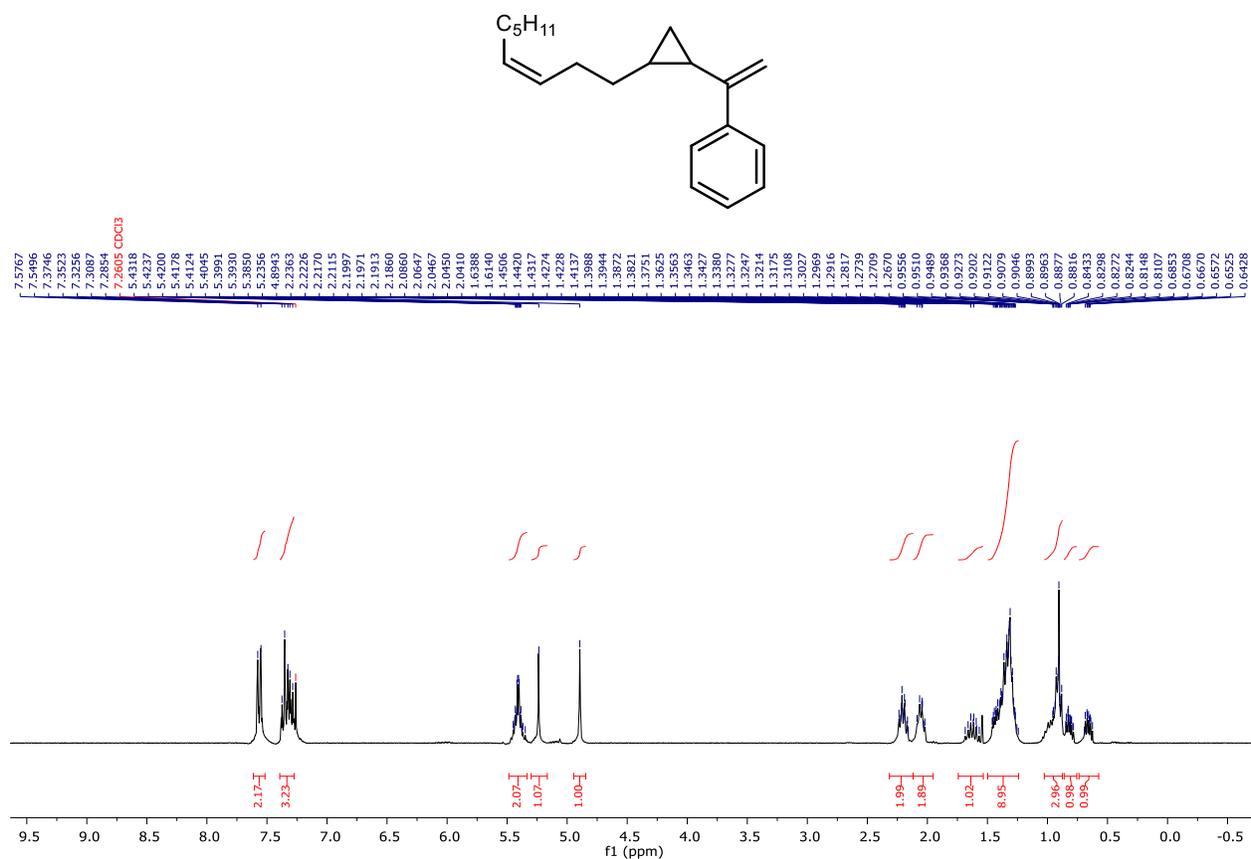


Figure S30. ^1H NMR of S12 (300 MHz, CDCl_3 , 295 K).

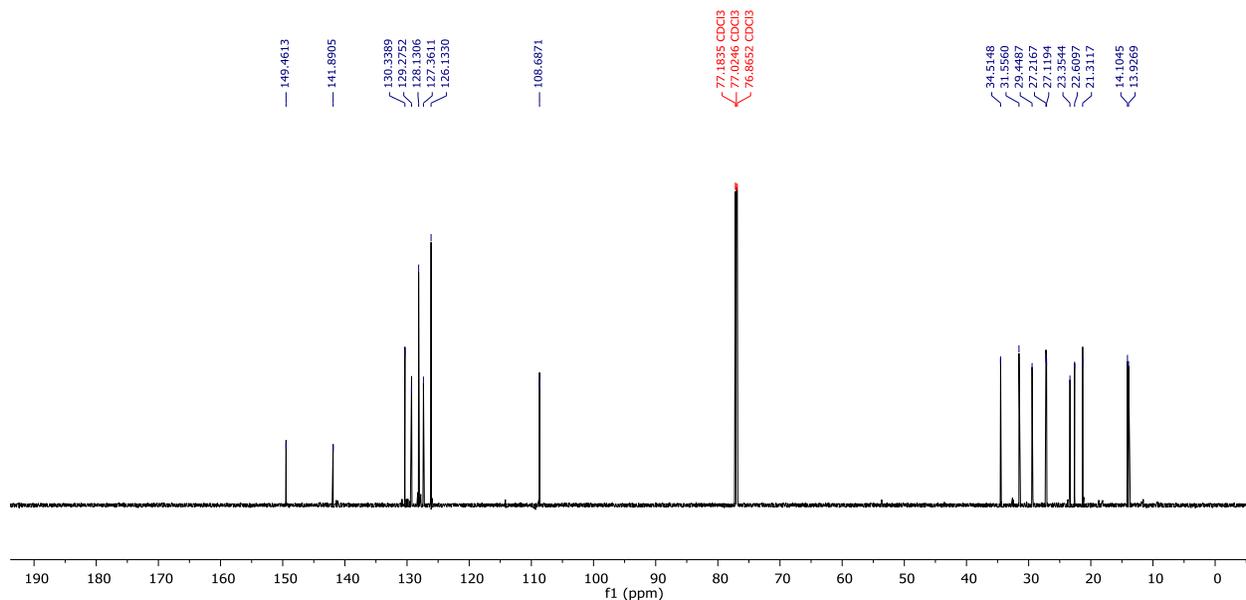


Figure S31. ^{13}C NMR of S12 (800 MHz, CDCl_3 , 295 K).

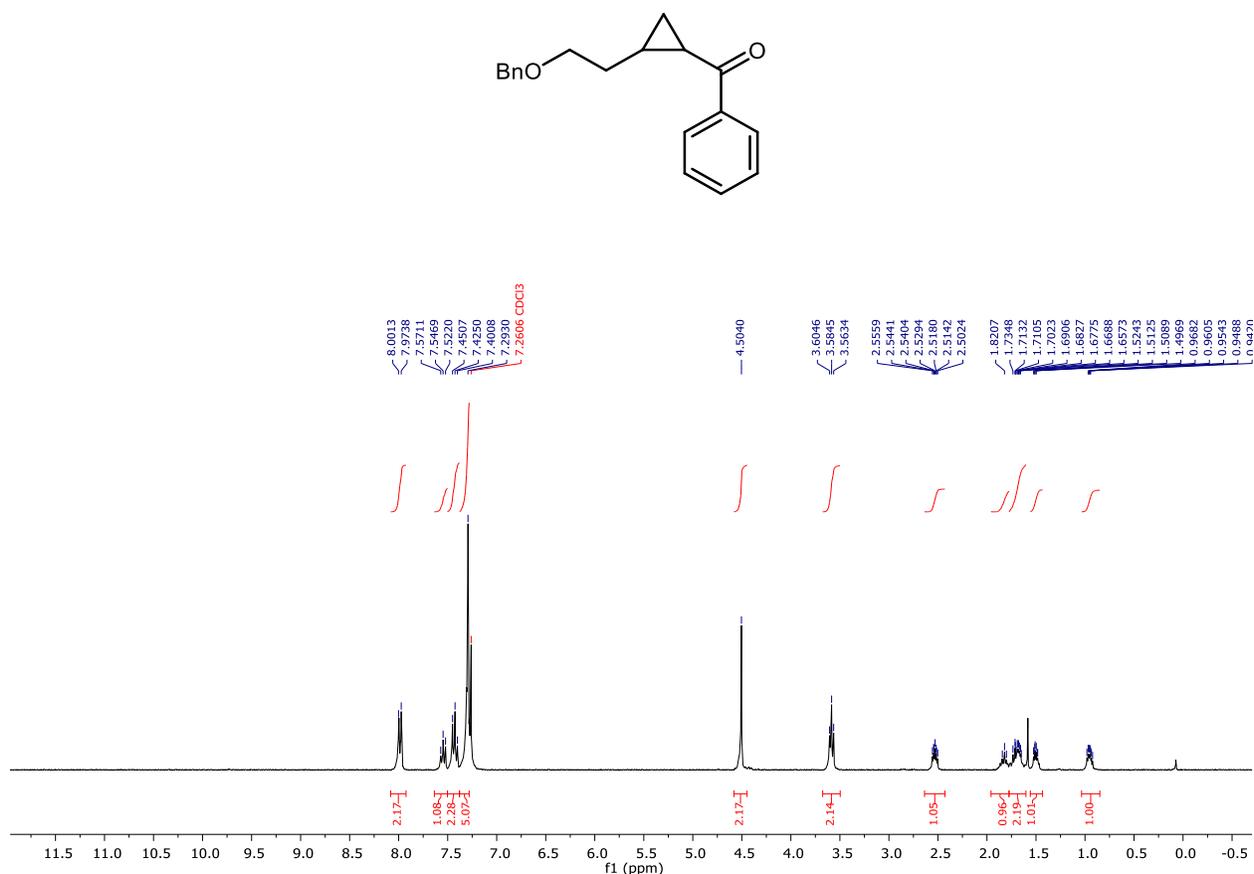


Figure S32. ¹H NMR of S13 (300 MHz, CDCl₃, 295 K).

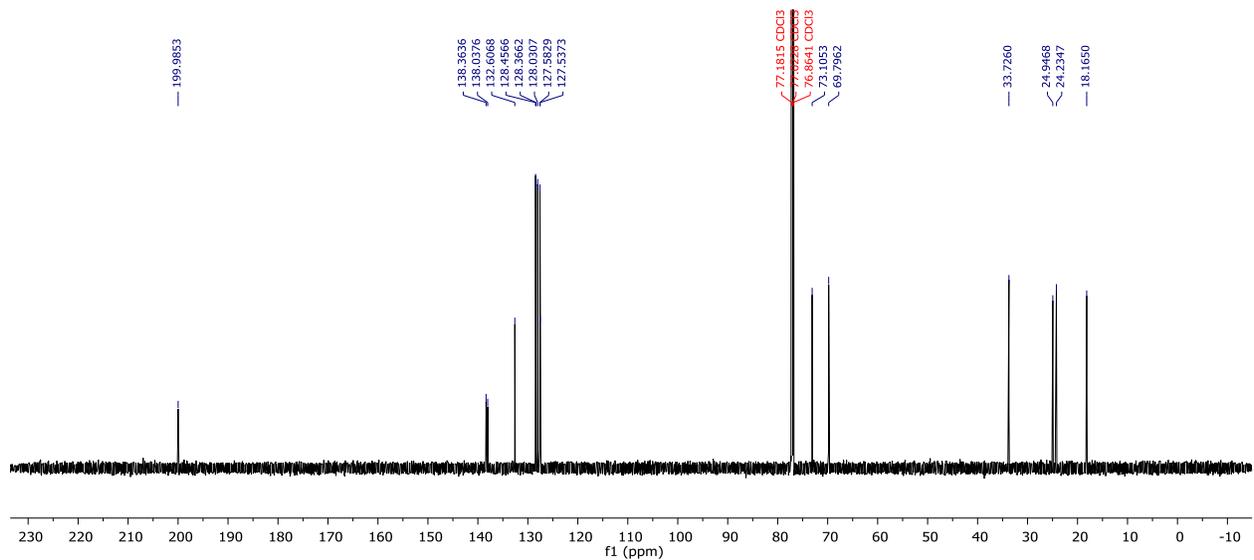


Figure S33. ¹³C NMR of S13 (800 MHz, CDCl₃, 295 K).

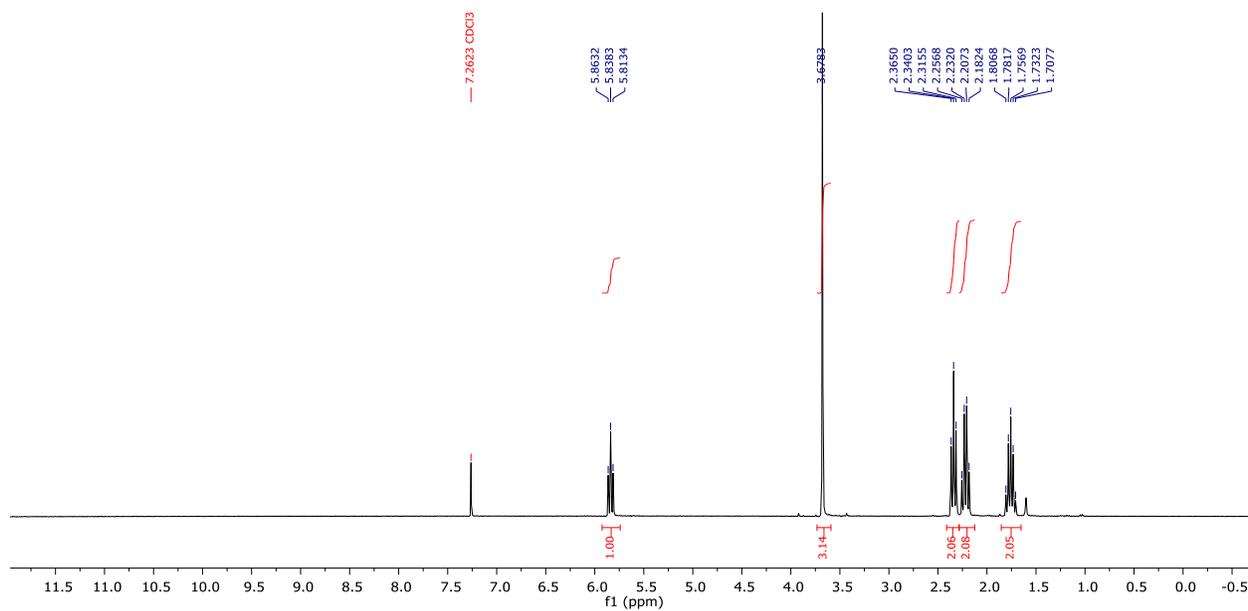
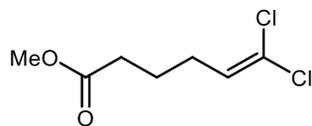


Figure S36. ¹H NMR of S15 (300 MHz, CDCl₃, 295 K).

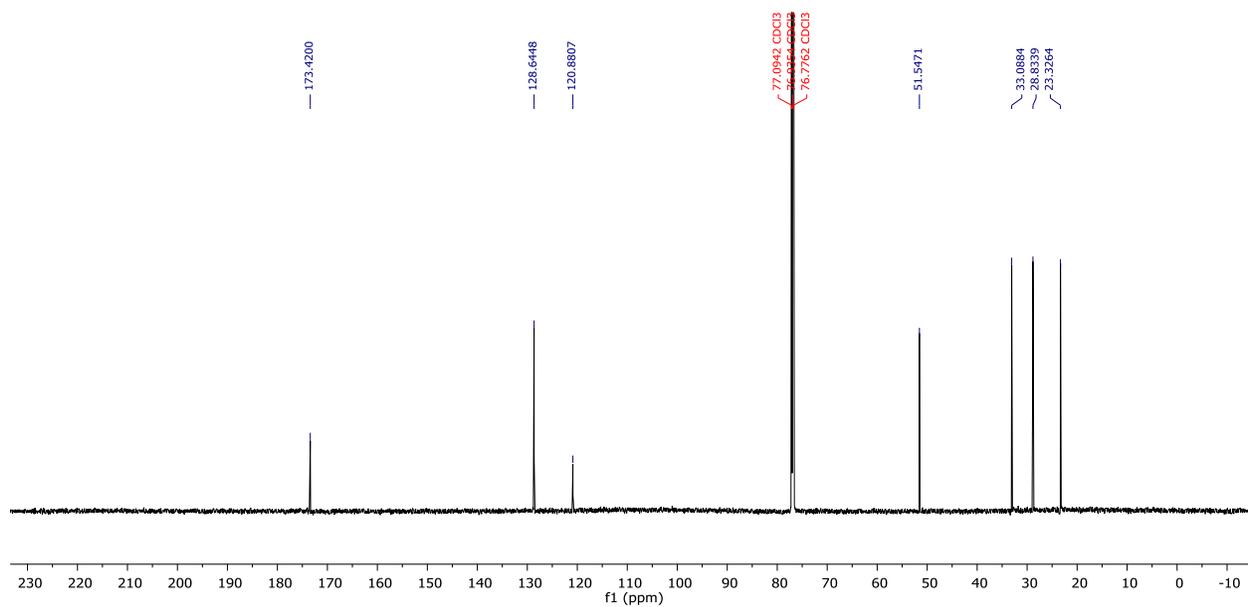


Figure S37. ¹³C NMR of S15 (800 MHz, CDCl₃, 295 K).

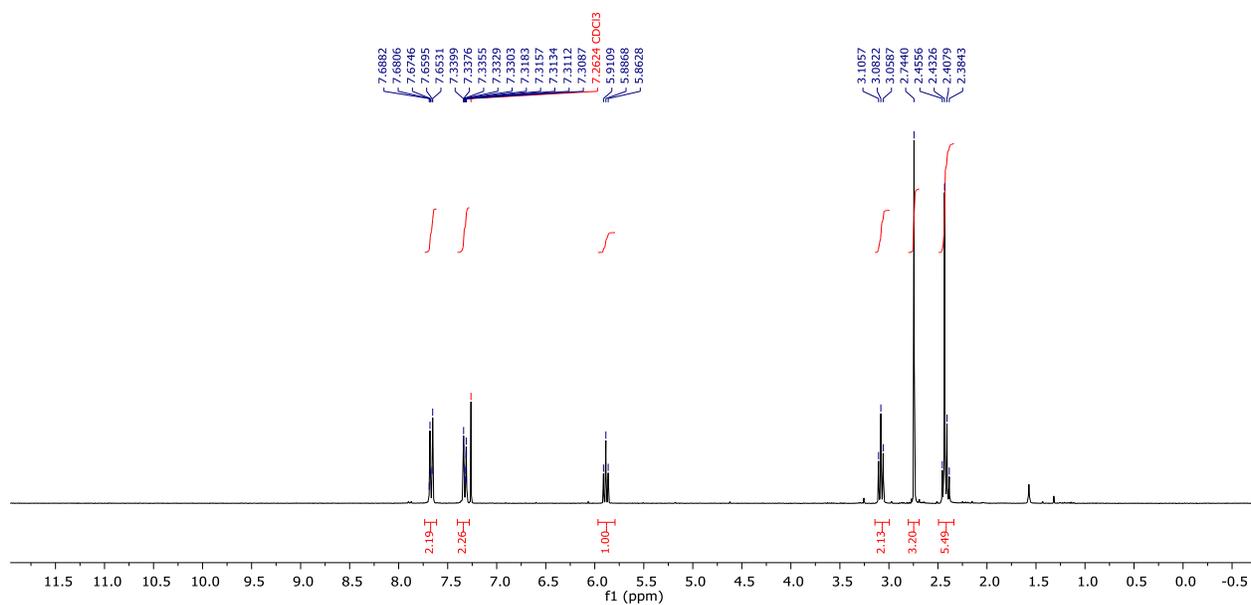
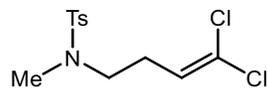


Figure S38. ¹H NMR of S16 (300 MHz, CDCl₃, 295 K).

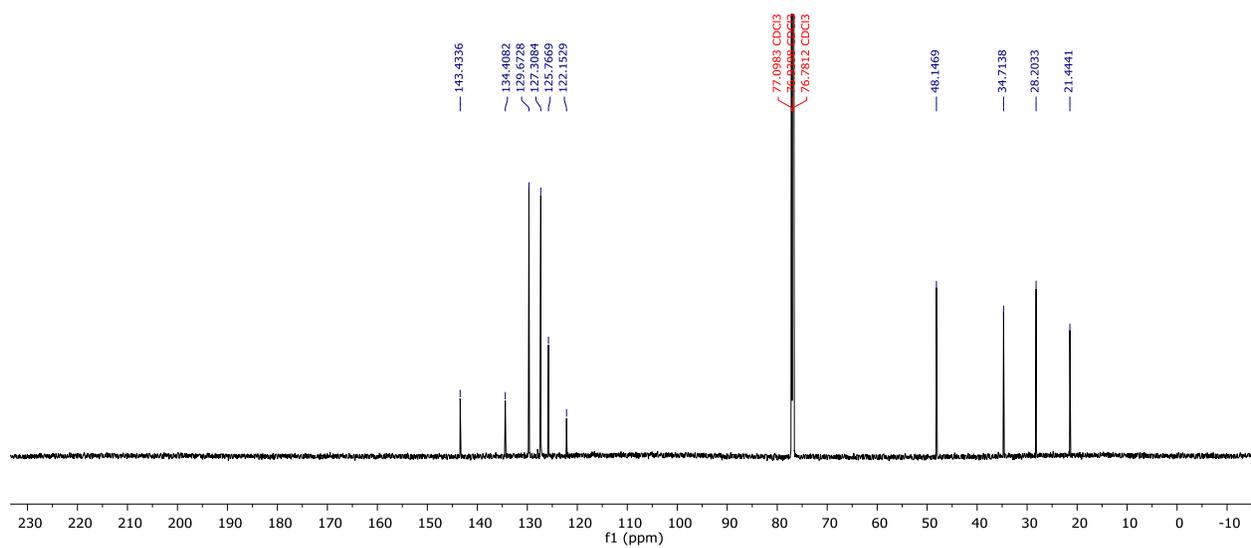


Figure S39. ¹³C NMR of S16 (800 MHz, CDCl₃, 295 K).

9. NMR Data for [5+1]-Products

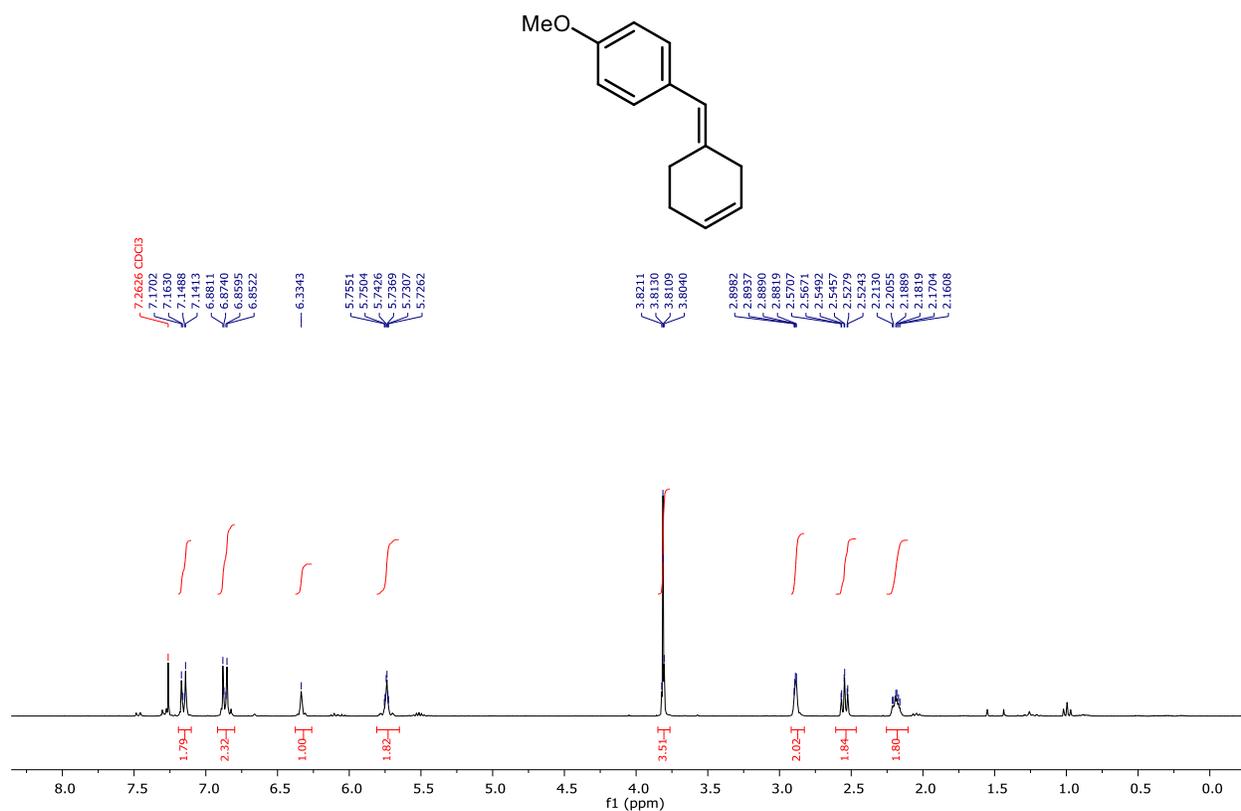


Figure S40. ¹H NMR of **3** (300 MHz, CDCl₃, 295 K).

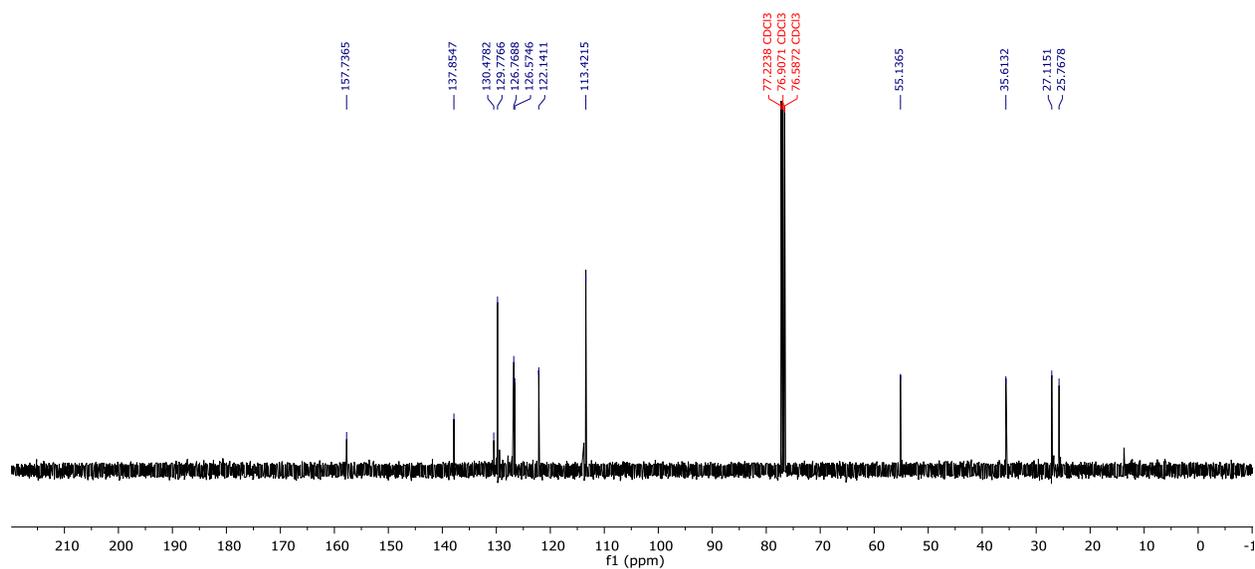


Figure S41. ¹³C NMR of **3** (800 MHz, CDCl₃, 295 K).

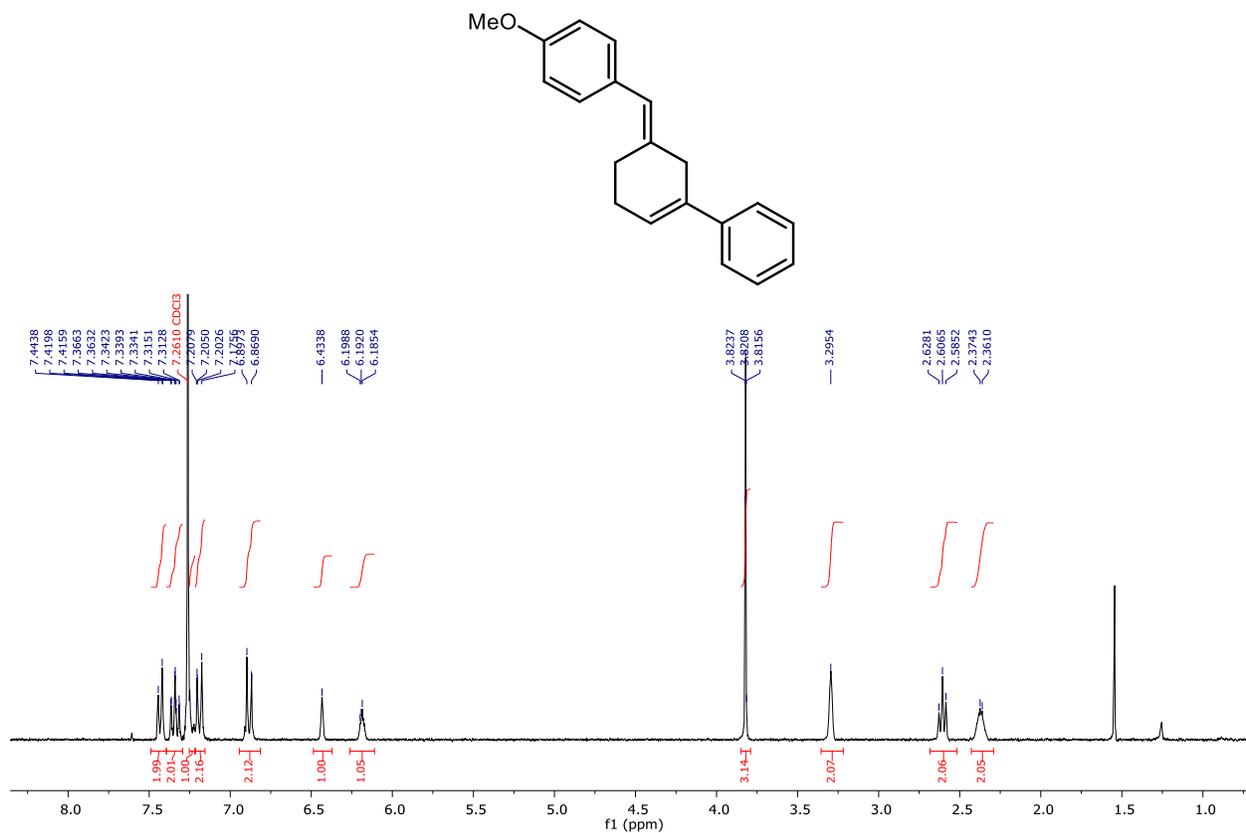


Figure S42. ¹H NMR of **6** (300 MHz, CDCl₃, 295 K).

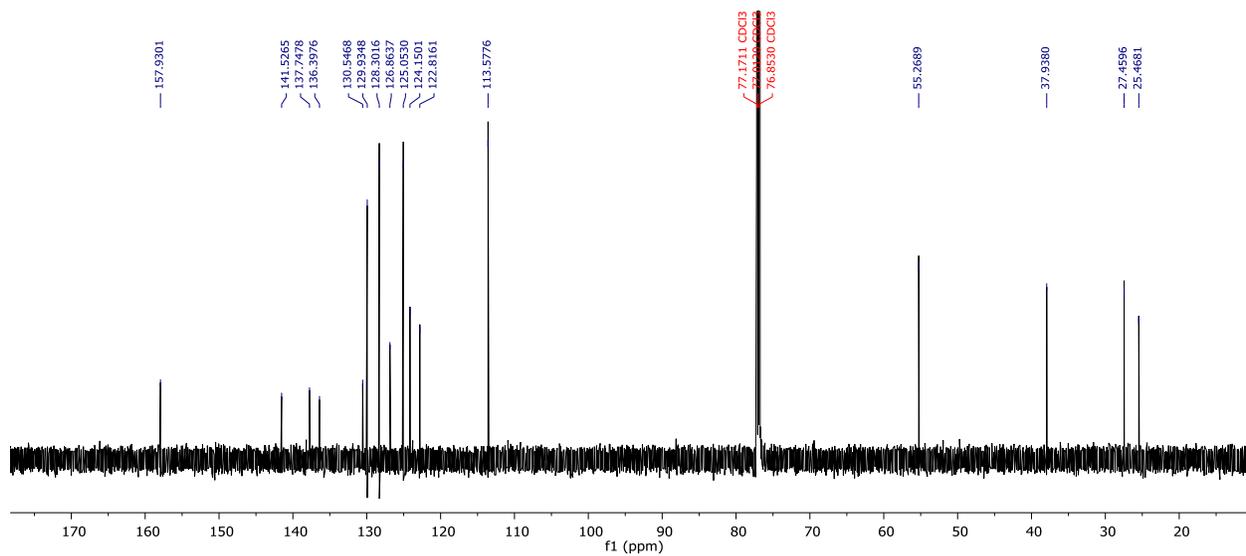


Figure S43. ¹³C NMR of **6** (800 MHz, CDCl₃, 295 K).

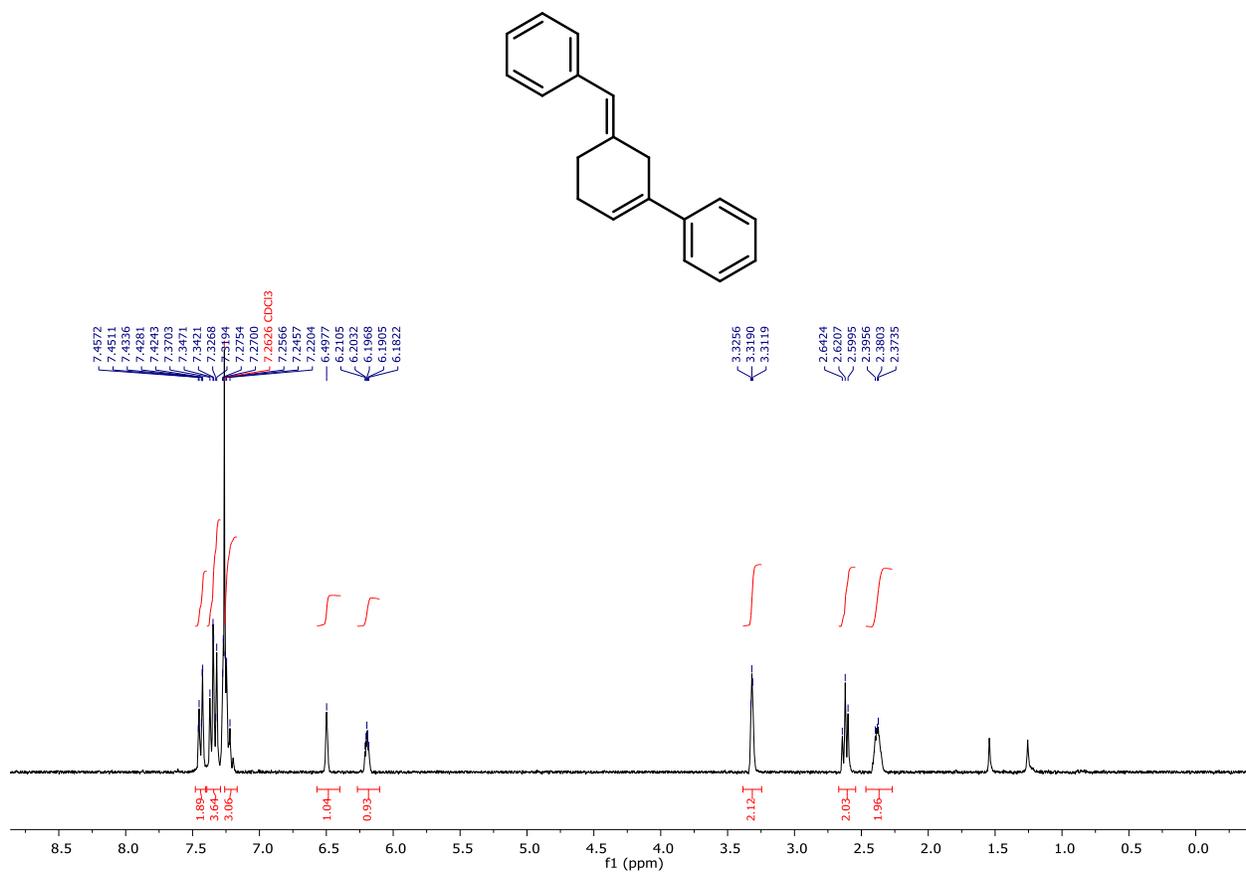


Figure S44. ¹H NMR of **11** (300 MHz, CDCl₃, 295 K).

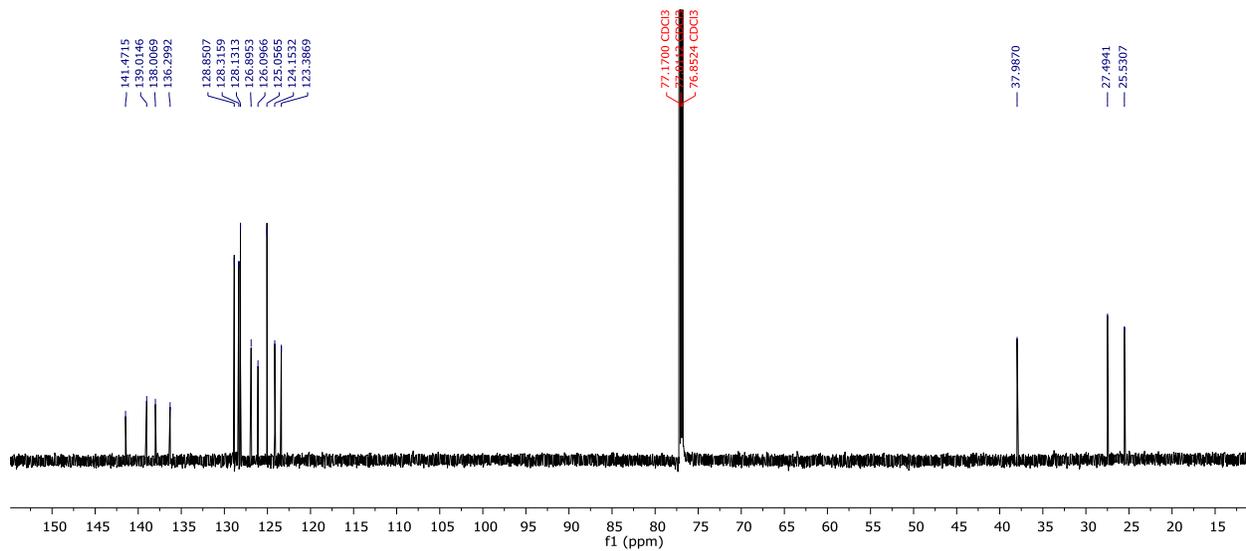


Figure S45. ¹³C NMR of **11** (800 MHz, CDCl₃, 295 K).

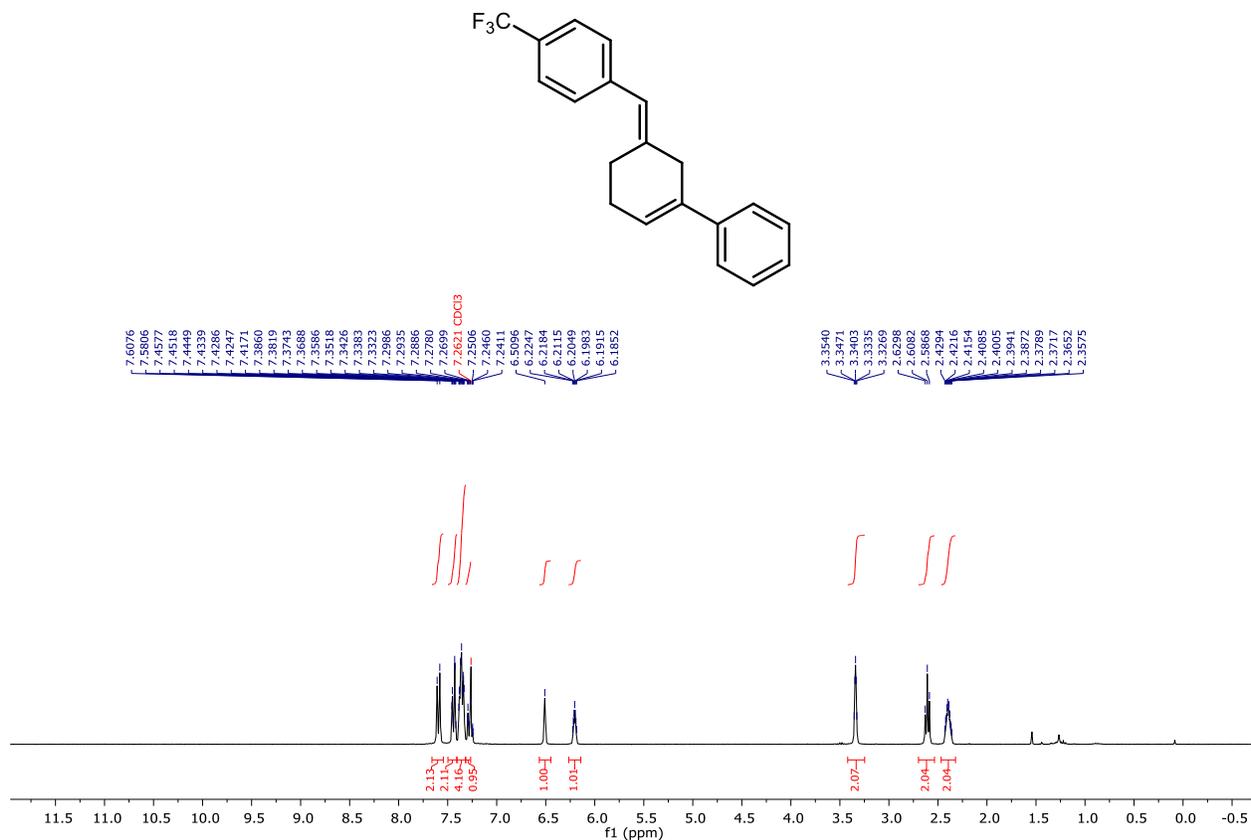


Figure S46. ¹H NMR of **12** (300 MHz, CDCl₃, 295 K).

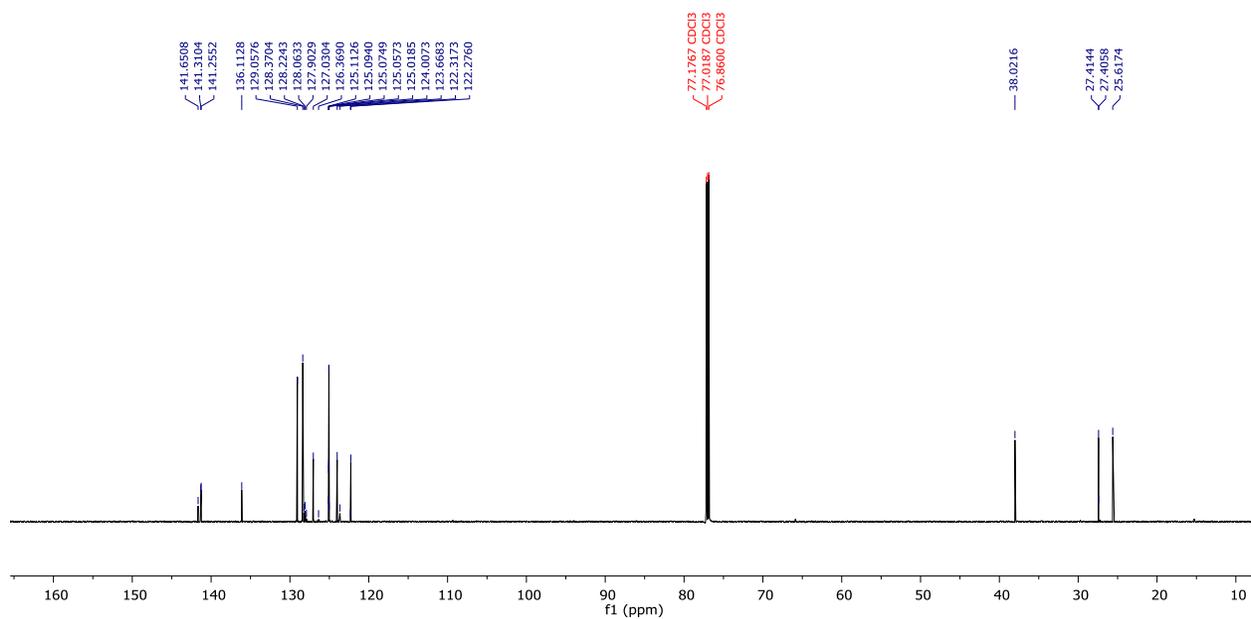


Figure S47. ¹³C NMR of **12** (800 MHz, CDCl₃, 295 K).

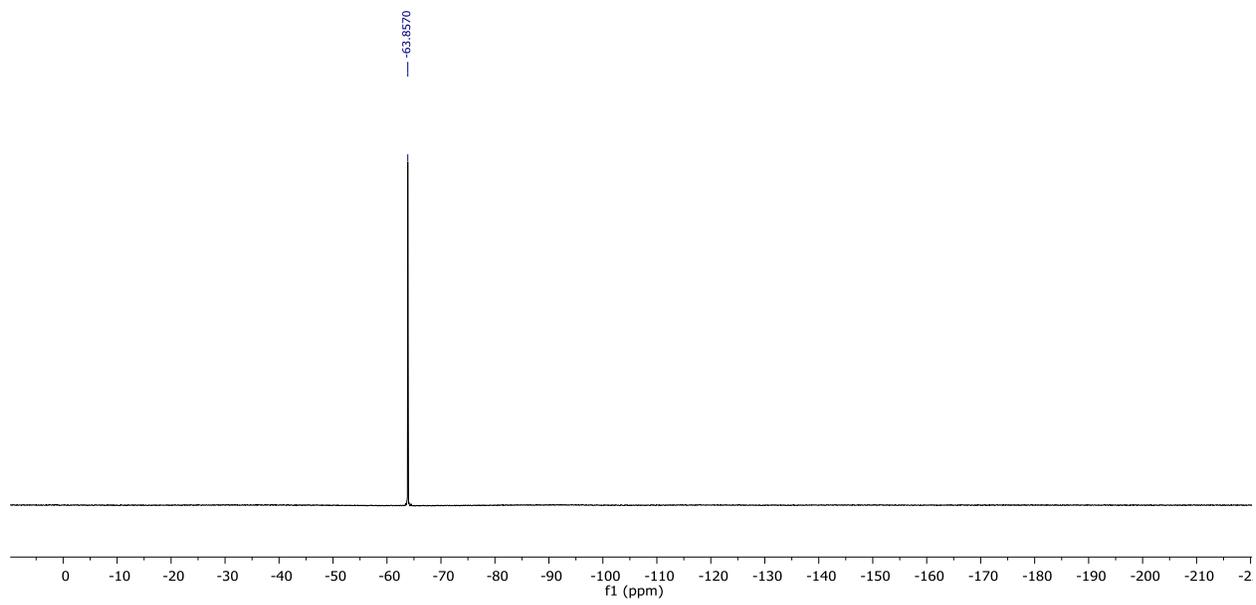


Figure S48. ^{19}F NMR of **12** (300 MHz, CDCl_3 , 295 K).

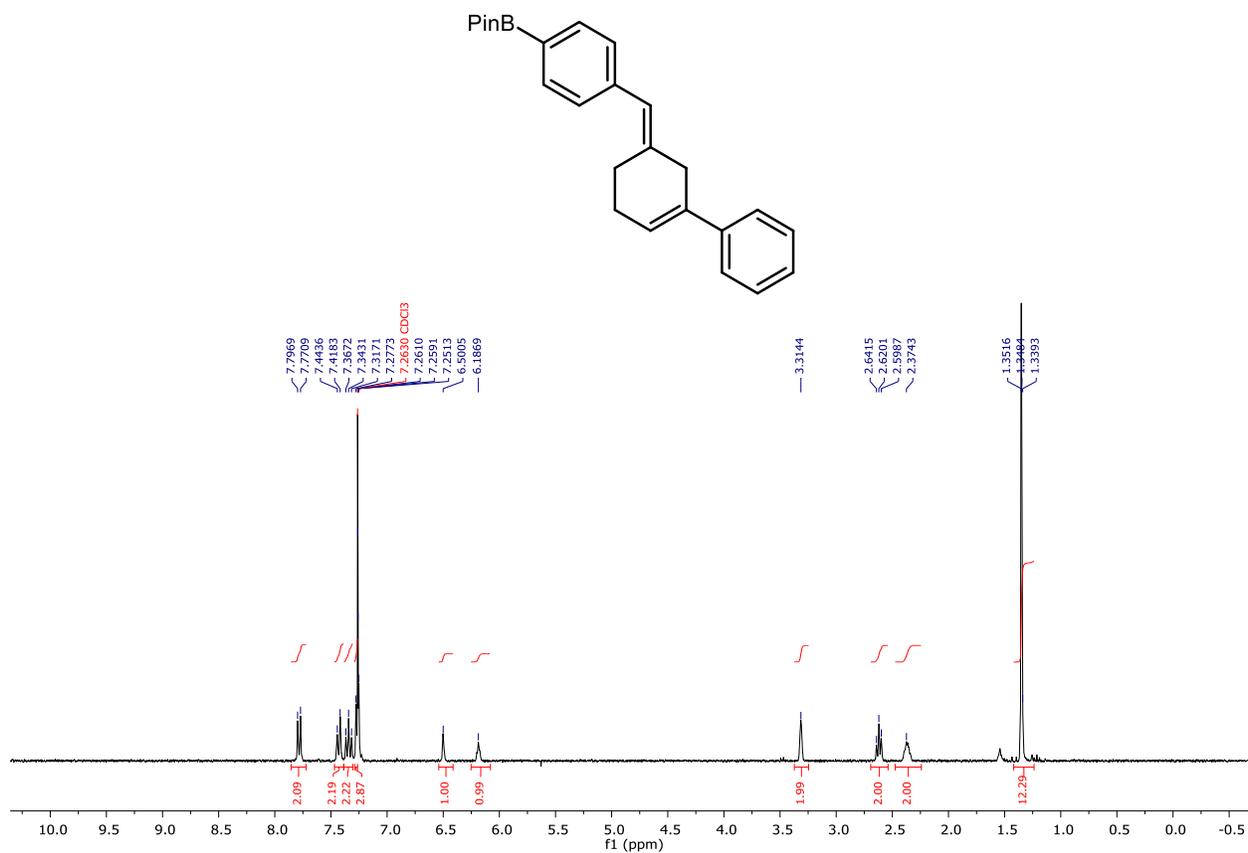


Figure S49. ¹H NMR of **13** (300 MHz, CDCl₃, 295 K).

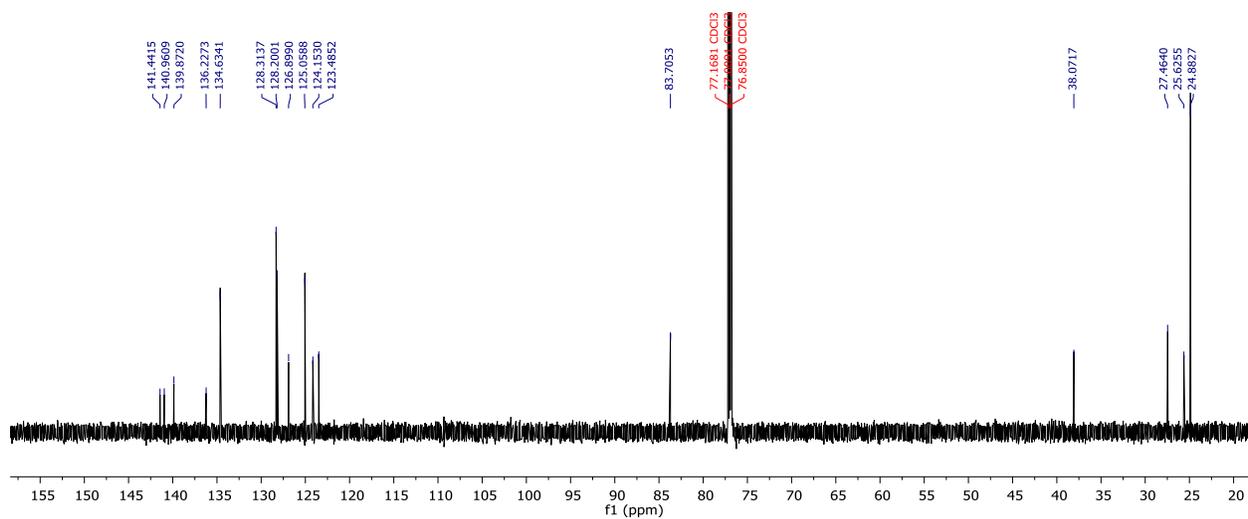


Figure S50. ¹³C NMR of **13** (800 MHz, CDCl₃, 295 K).

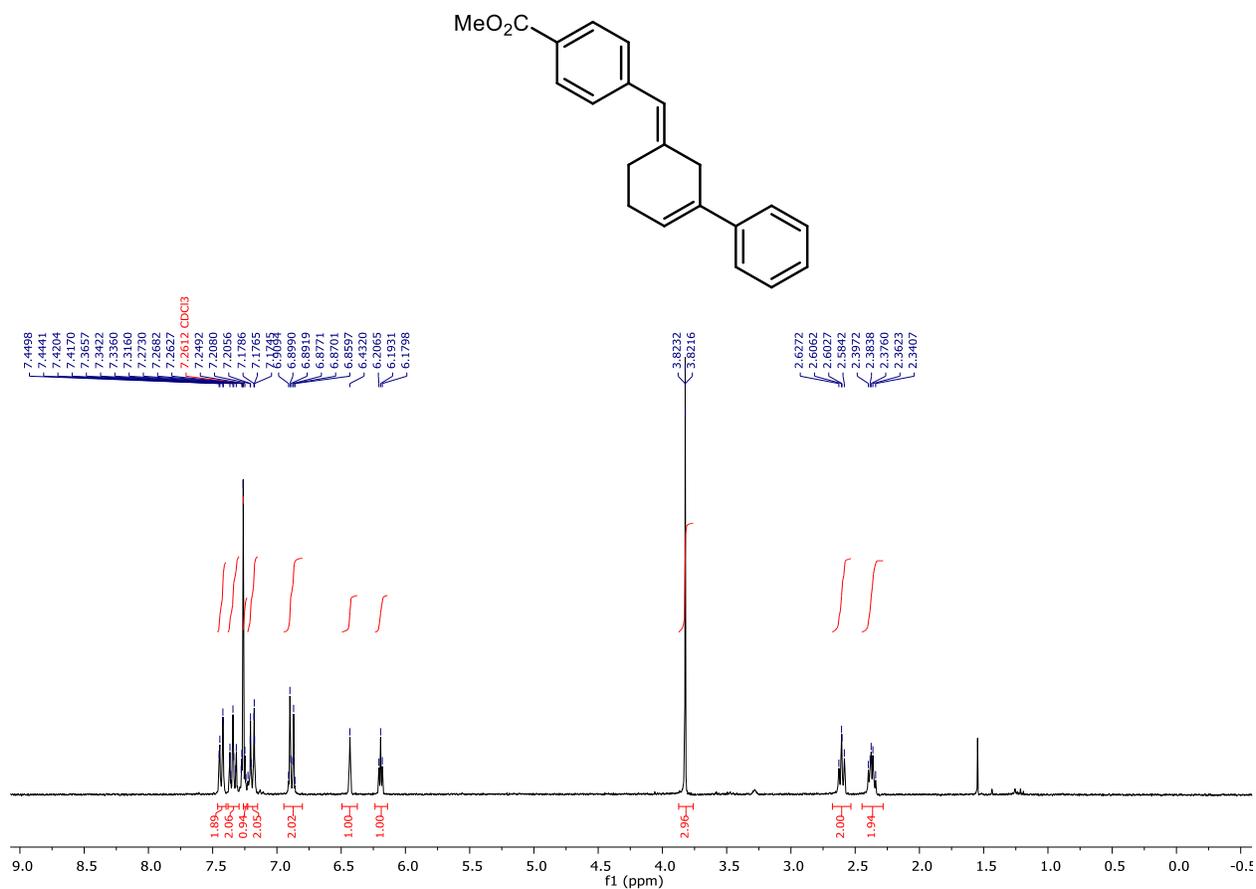


Figure S51. ¹H NMR of **14** (300 MHz, CDCl₃, 295 K).

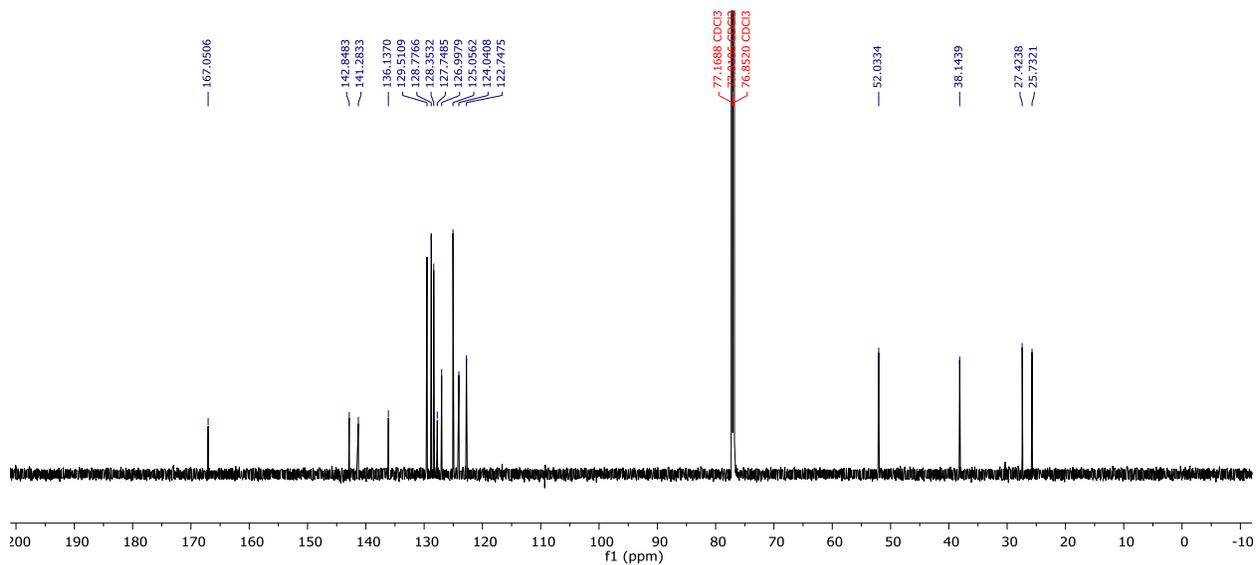


Figure S52. ¹³C NMR of **14** (800 MHz, CDCl₃, 295 K).

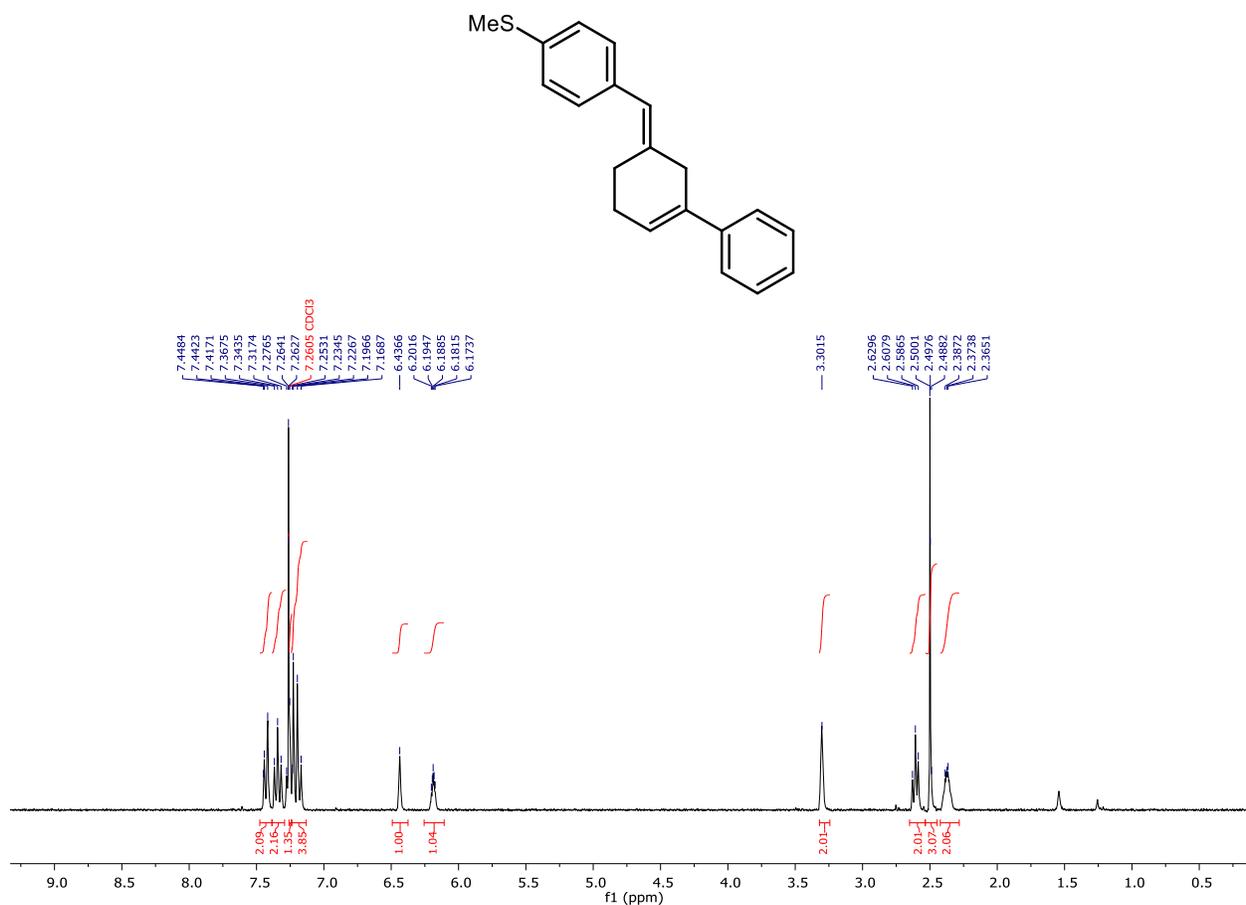


Figure S53. ¹H NMR of **15** (300 MHz, CDCl₃, 295 K).

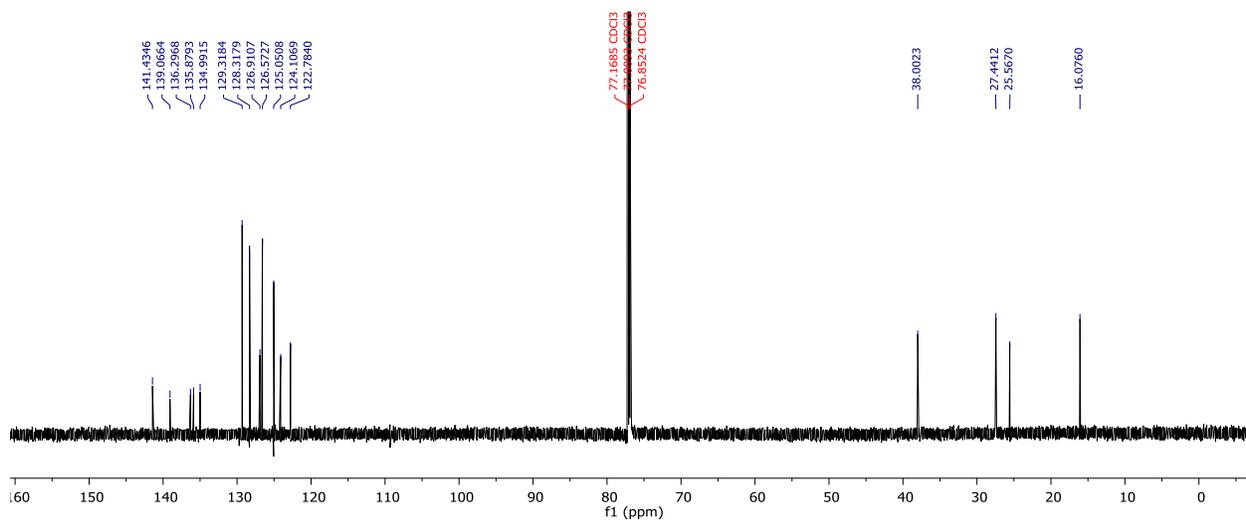


Figure S54. ¹³C NMR of **15** (800 MHz, CDCl₃, 295 K).

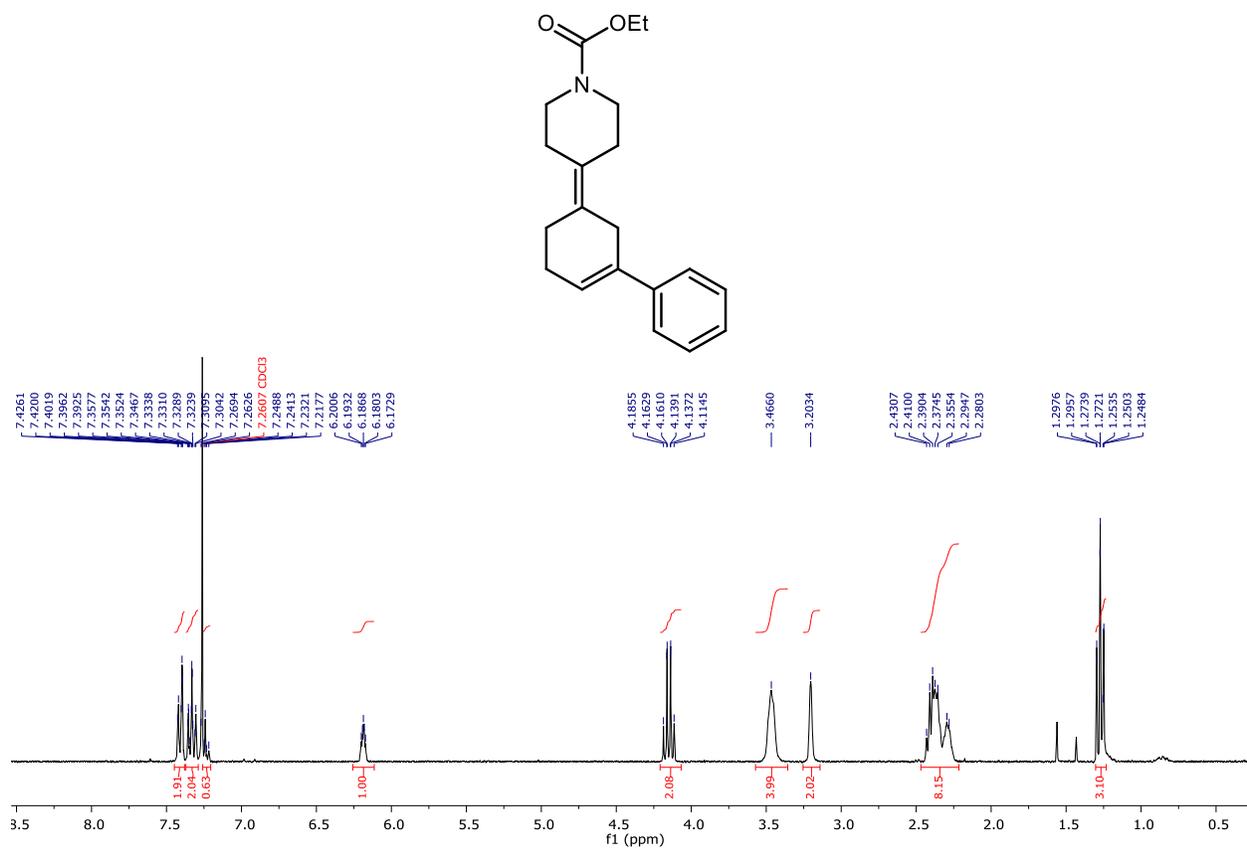


Figure S55. ¹H NMR of 16 (300 MHz, CDCl₃, 295 K).

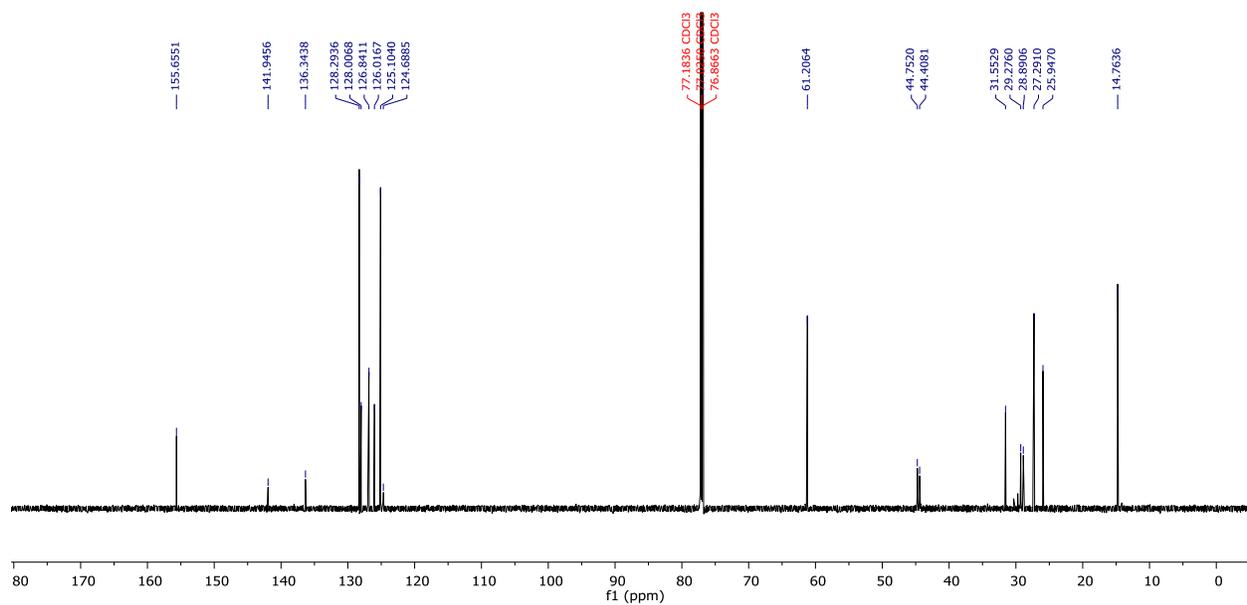


Figure S56. ¹³C NMR of 16 (800 MHz, CDCl₃, 295 K).

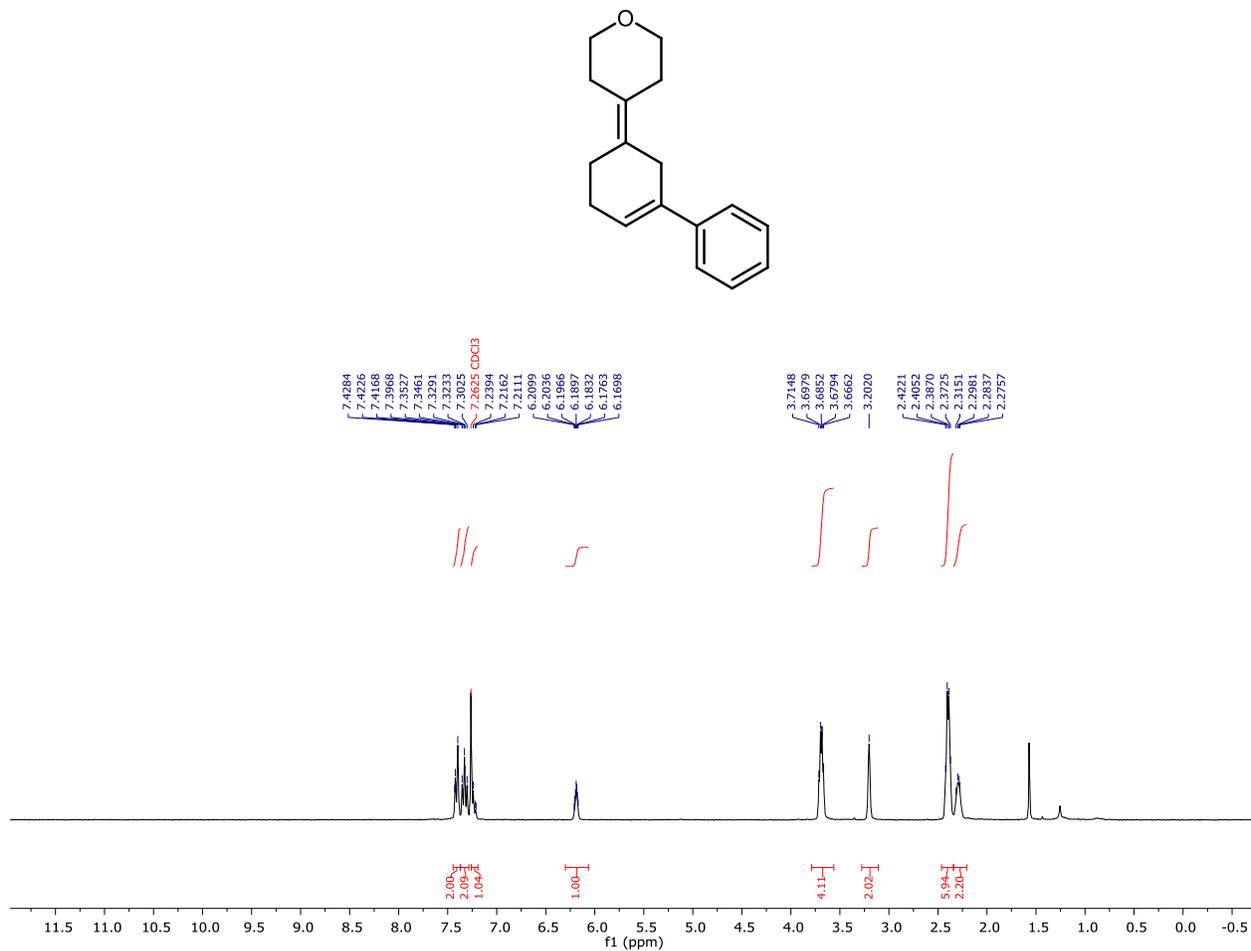


Figure S57. ¹H NMR of **17** (300 MHz, CDCl₃, 295 K).

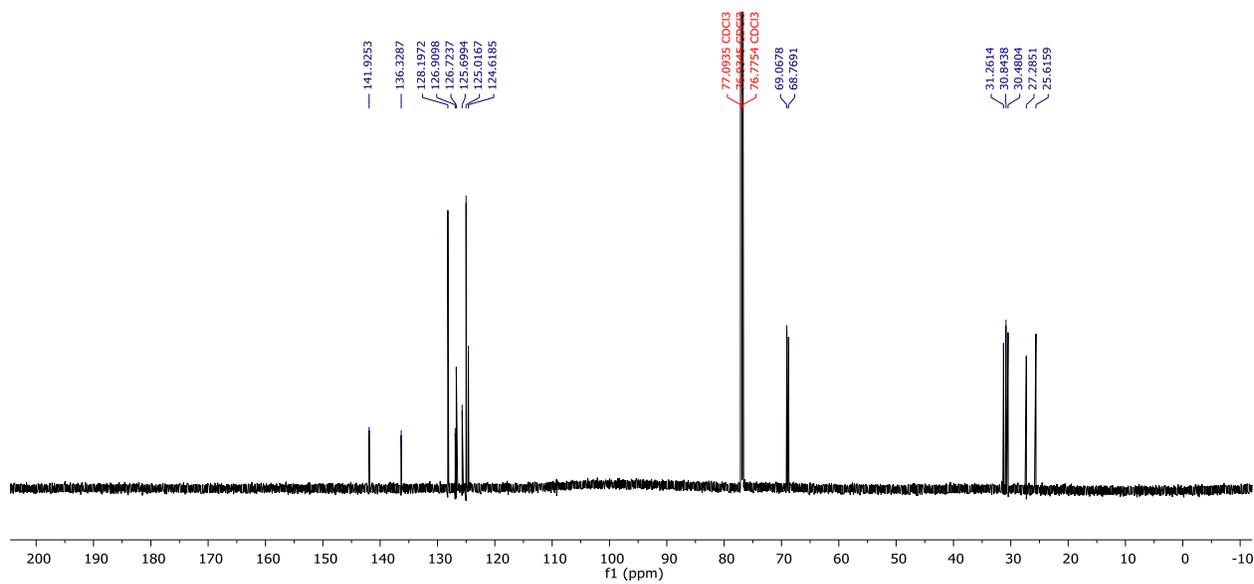


Figure S58. ¹³C NMR of **17** (800 MHz, CDCl₃, 295 K).

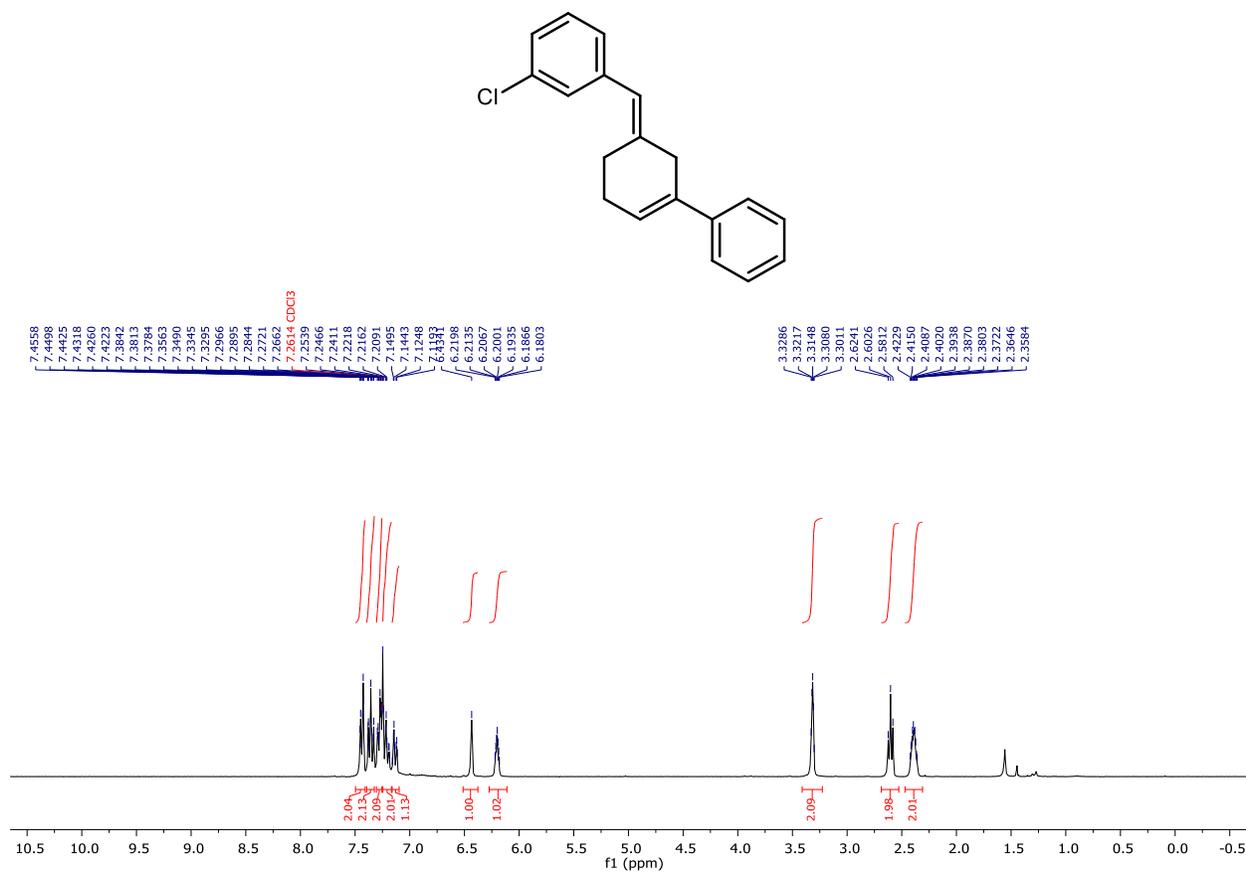


Figure S59. ¹H NMR of 18 (300 MHz, CDCl₃, 295 K).

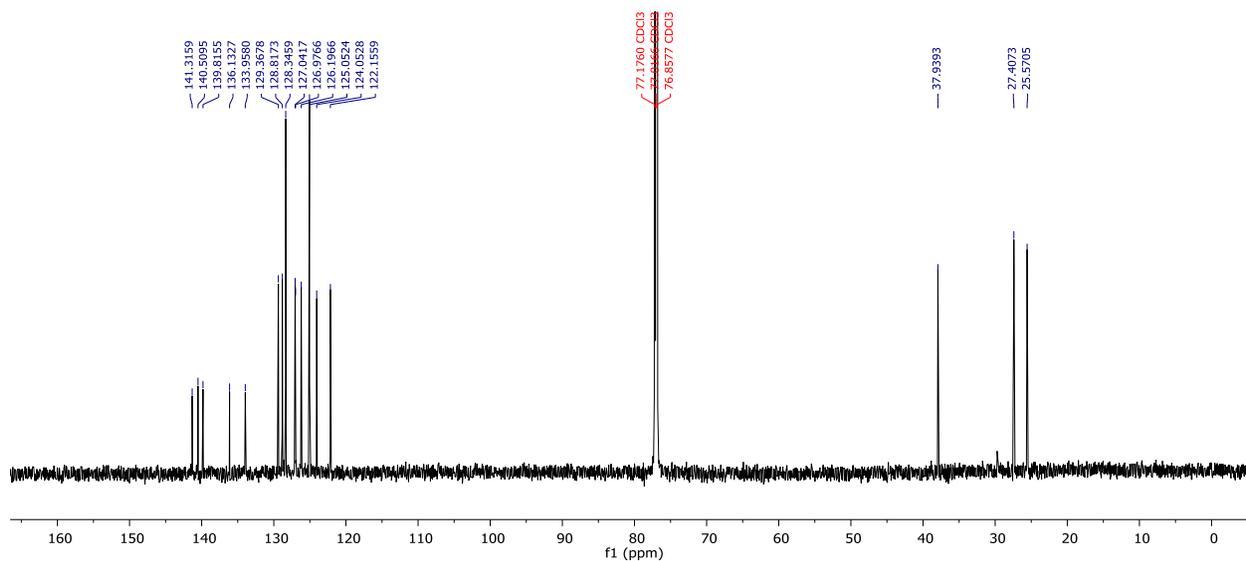


Figure S60. ¹³C NMR of 18 (800 MHz, CDCl₃, 295 K).

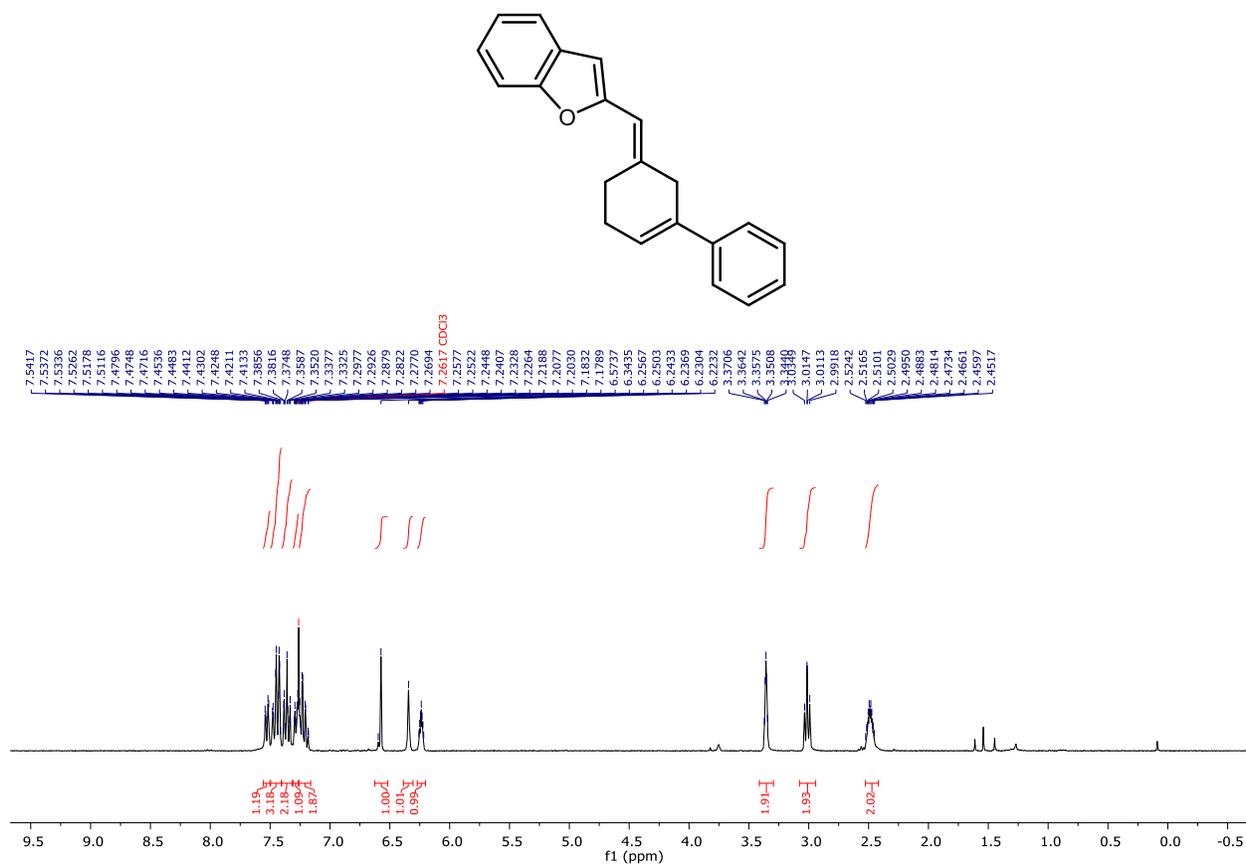


Figure S63. ¹H NMR of **20** (300 MHz, CDCl₃, 295 K).

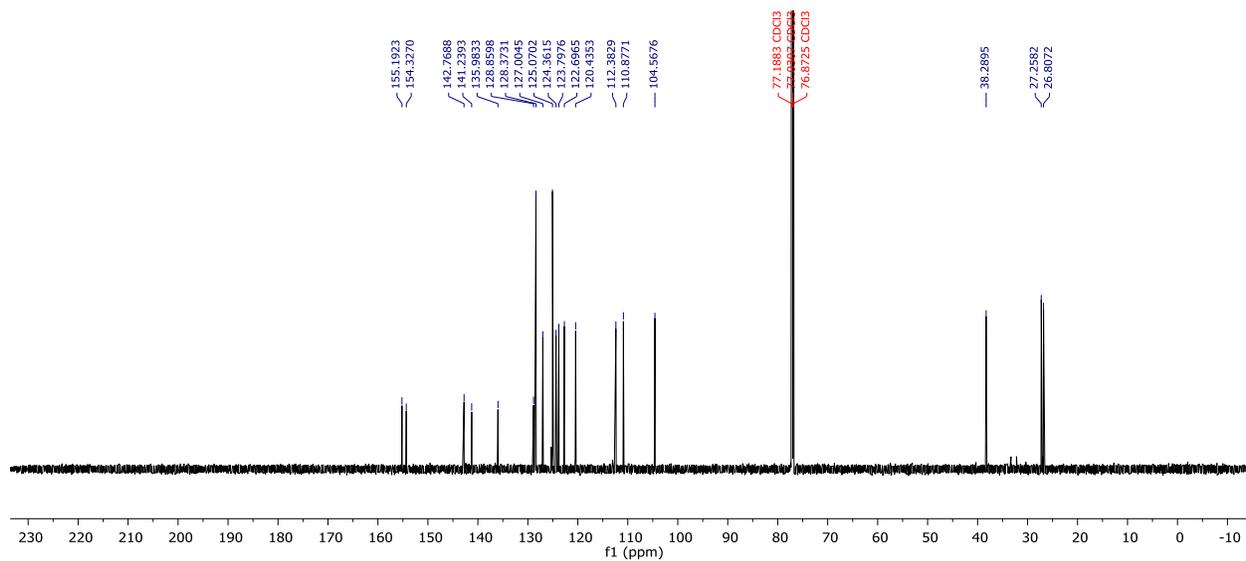


Figure S64. ¹³C NMR of **20** (800 MHz, CDCl₃, 295 K).

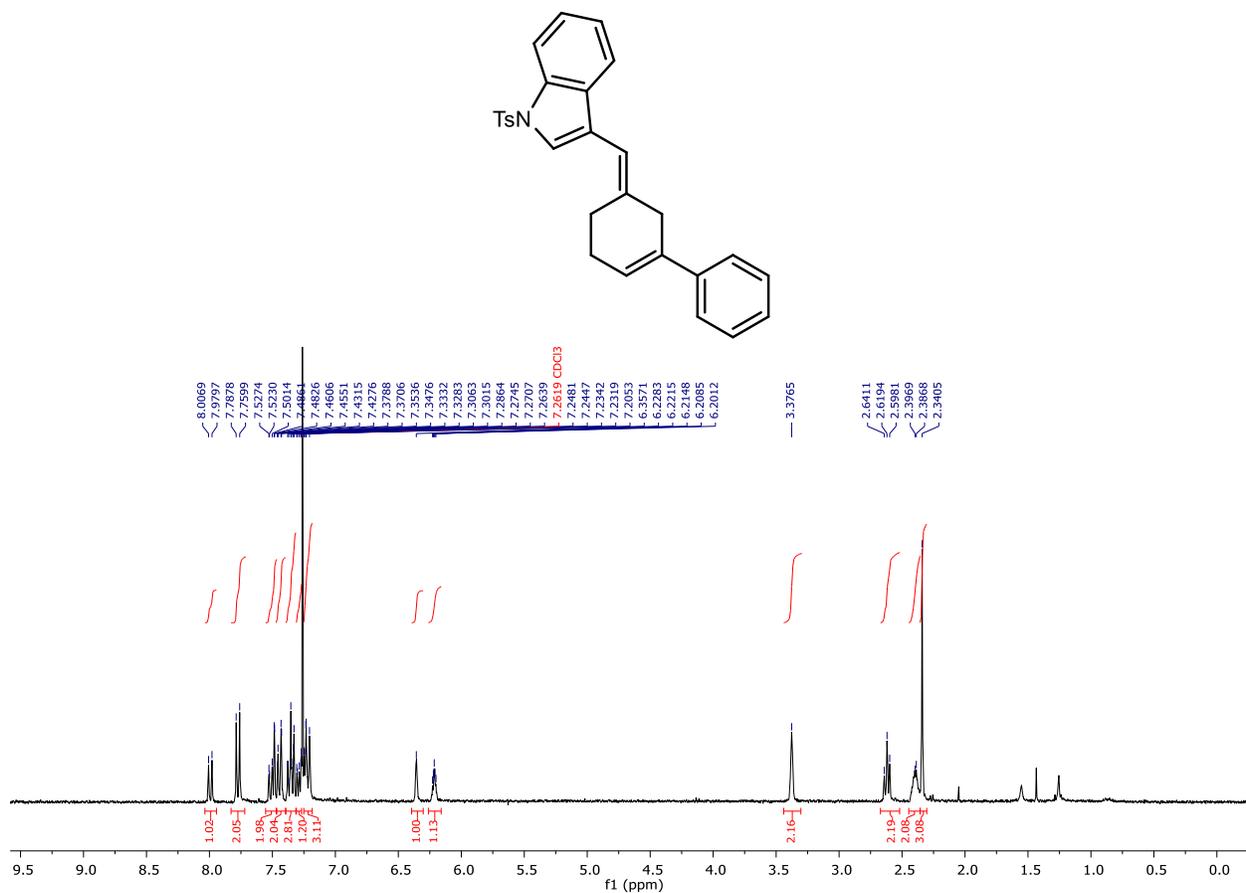


Figure S65. ¹H NMR of **21** (300 MHz, CDCl₃, 295 K).

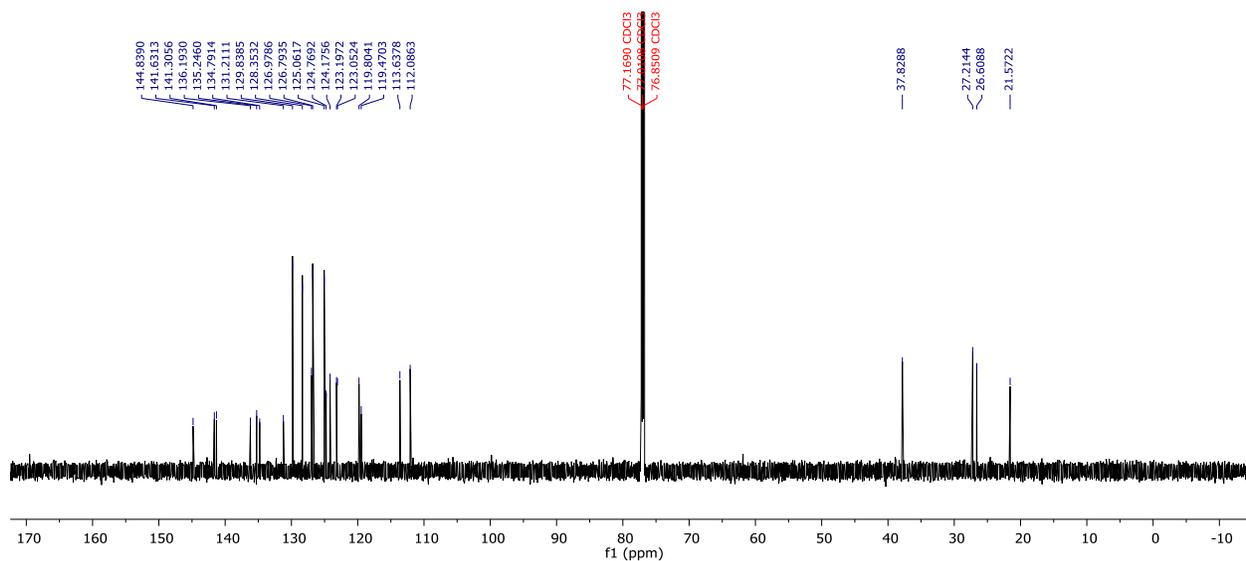


Figure S66. ¹³C NMR of **21** (800 MHz, CDCl₃, 295 K).

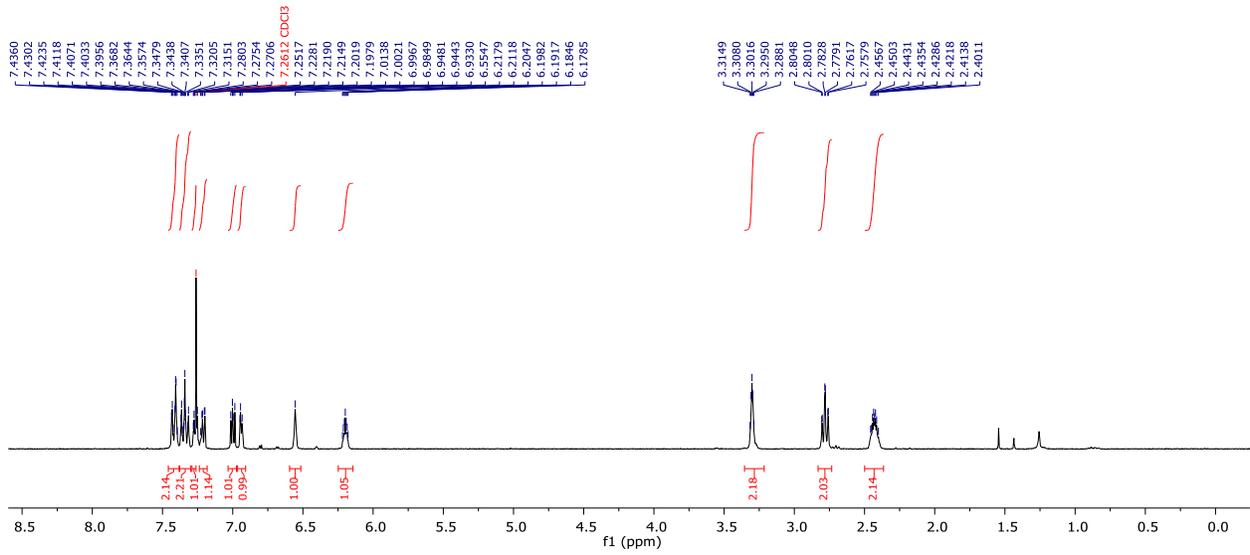
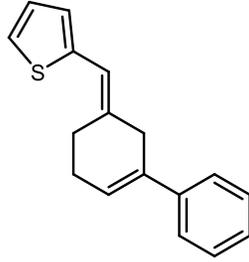


Figure S67. ¹H NMR of **22** (300 MHz, CDCl₃, 295 K).

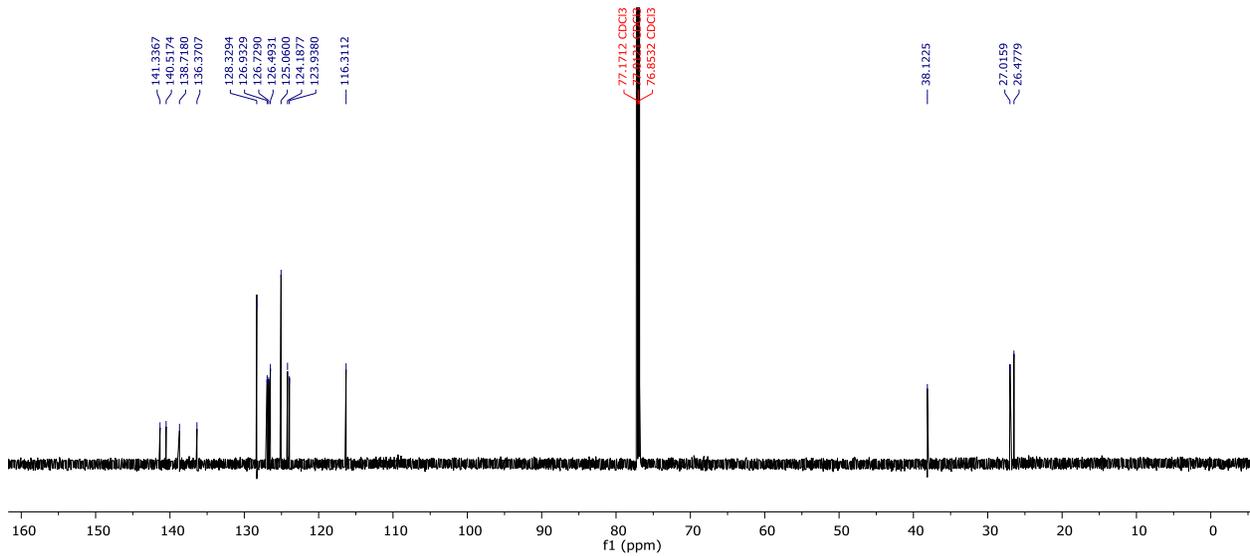


Figure S68. ¹³C NMR of **22** (800 MHz, CDCl₃, 295 K).

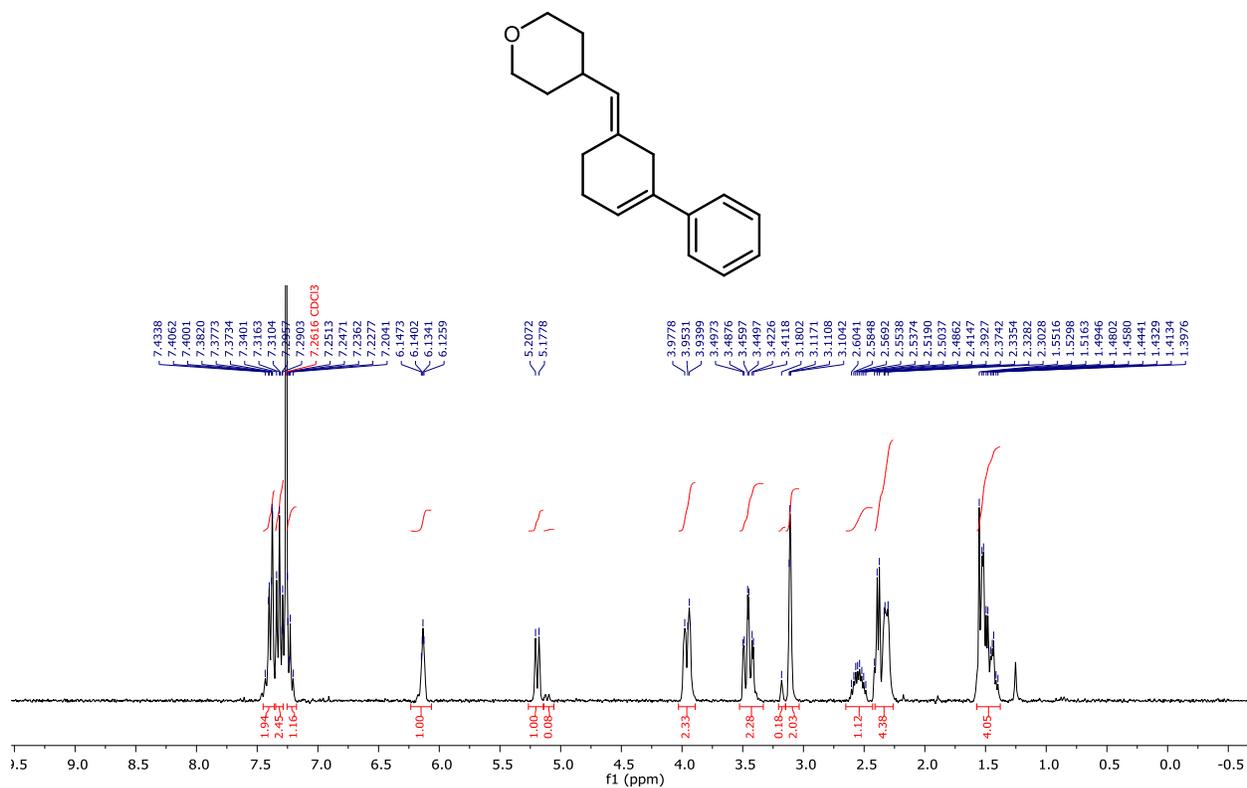


Figure S69. ¹H NMR of **23** (300 MHz, CDCl₃, 295 K).

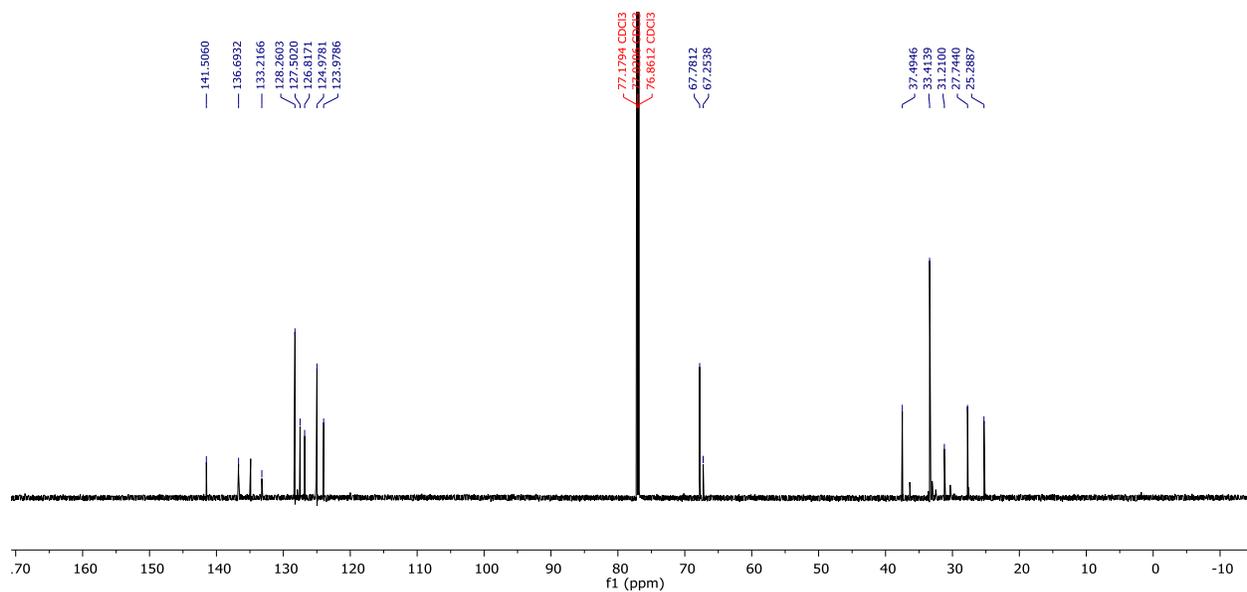


Figure S70. ¹³C NMR of **23** (800 MHz, CDCl₃, 295 K).

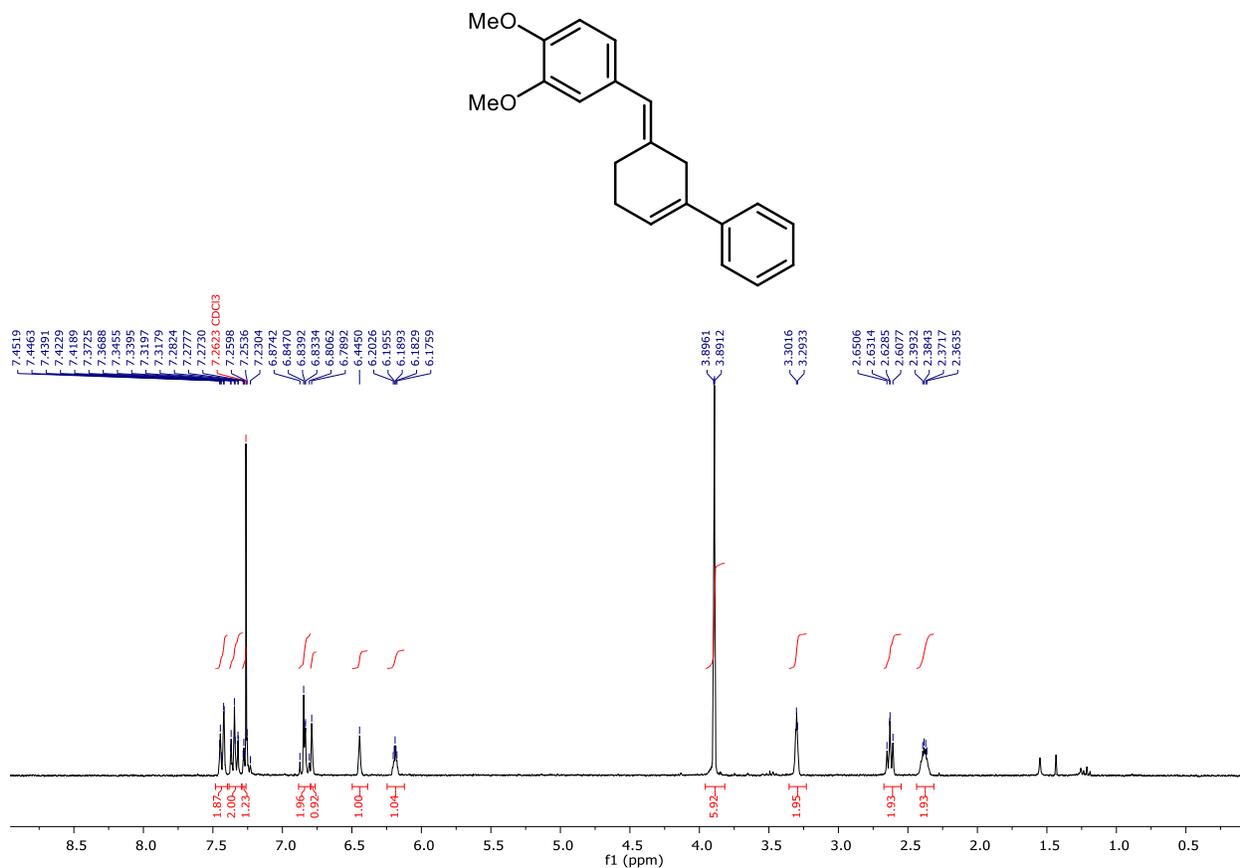


Figure S71. ¹H NMR of **24** (300 MHz, CDCl₃, 295 K).

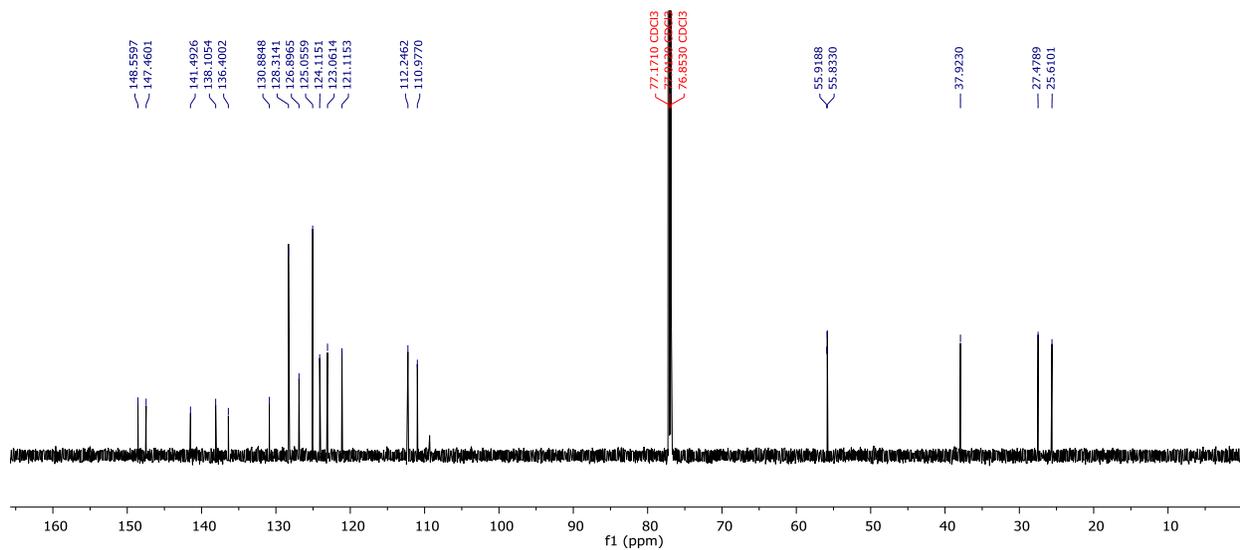


Figure S72. ¹³C NMR of **24** (800 MHz, CDCl₃, 295 K).

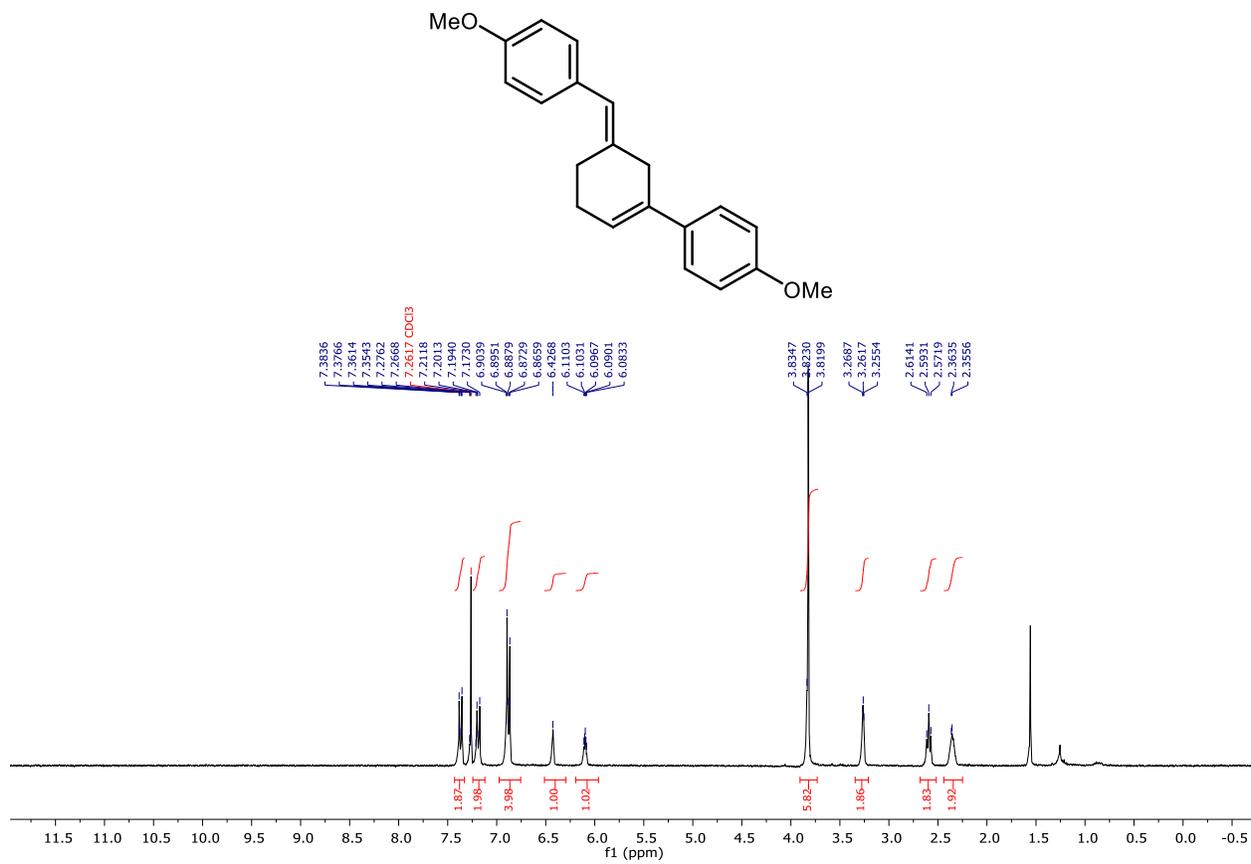


Figure S73. ¹H NMR of **25** (300 MHz, CDCl₃, 295 K).

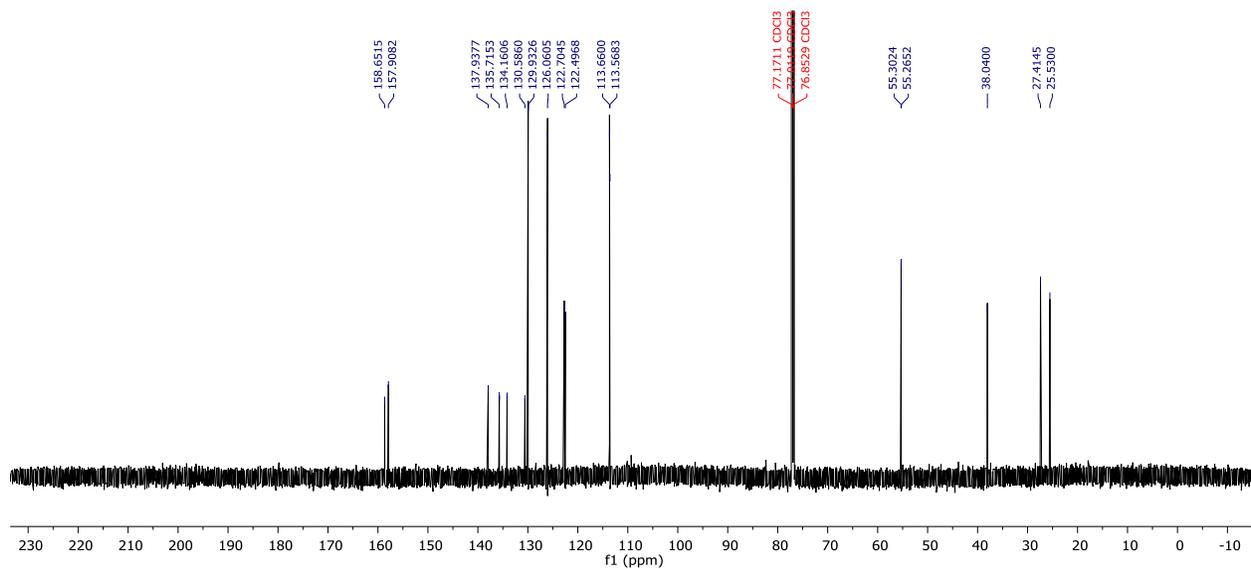


Figure S74. ¹³C NMR of **25** (800 MHz, CDCl₃, 295 K).

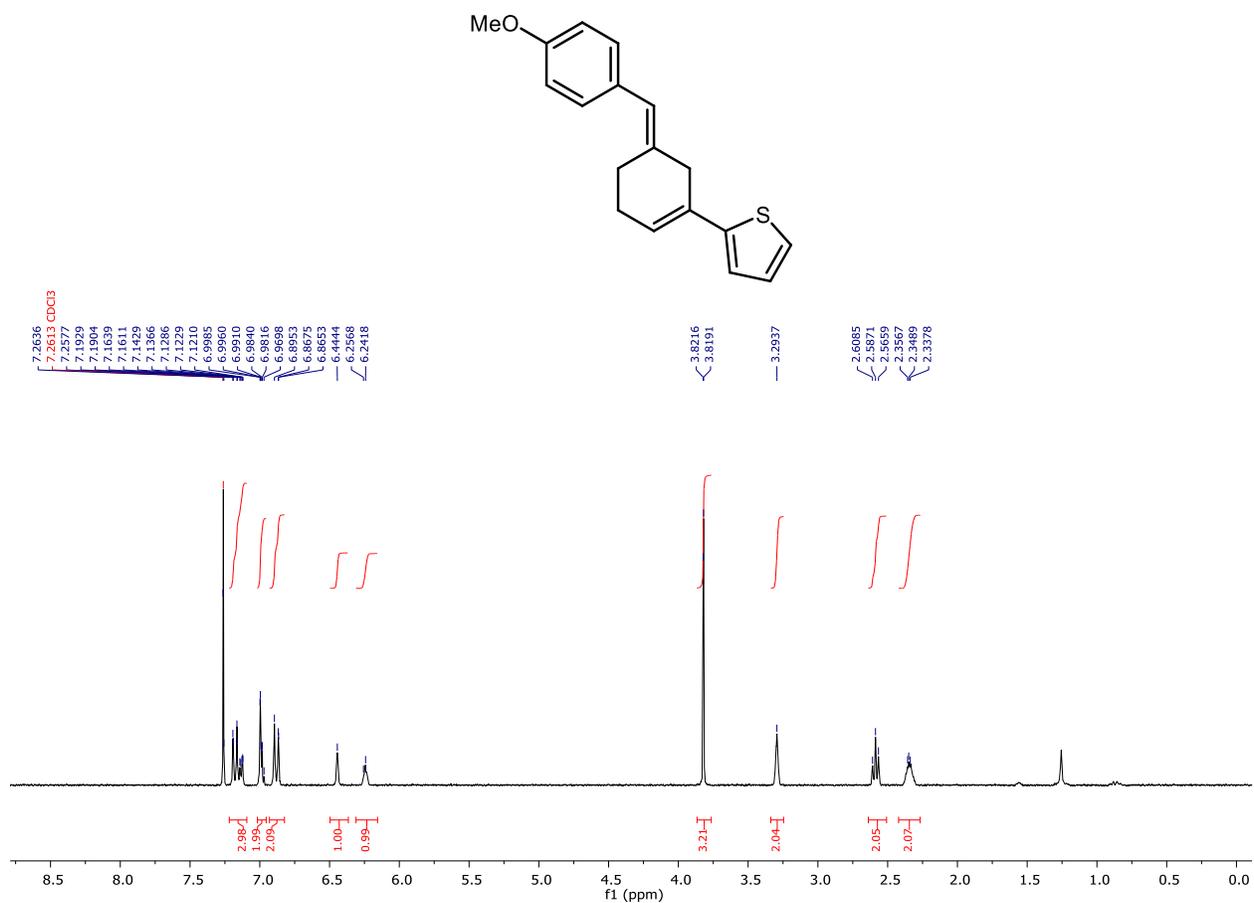


Figure S75. ¹H NMR of **26** (300 MHz, CDCl₃, 295 K).

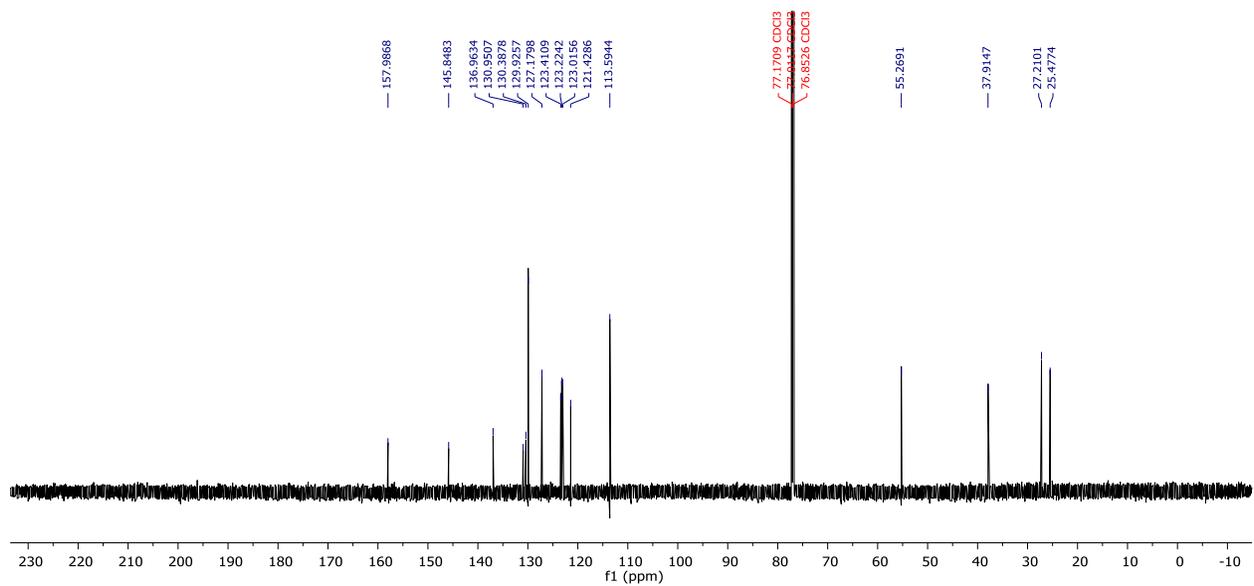


Figure S76. ¹³C NMR of **26** (800 MHz, CDCl₃, 295 K).

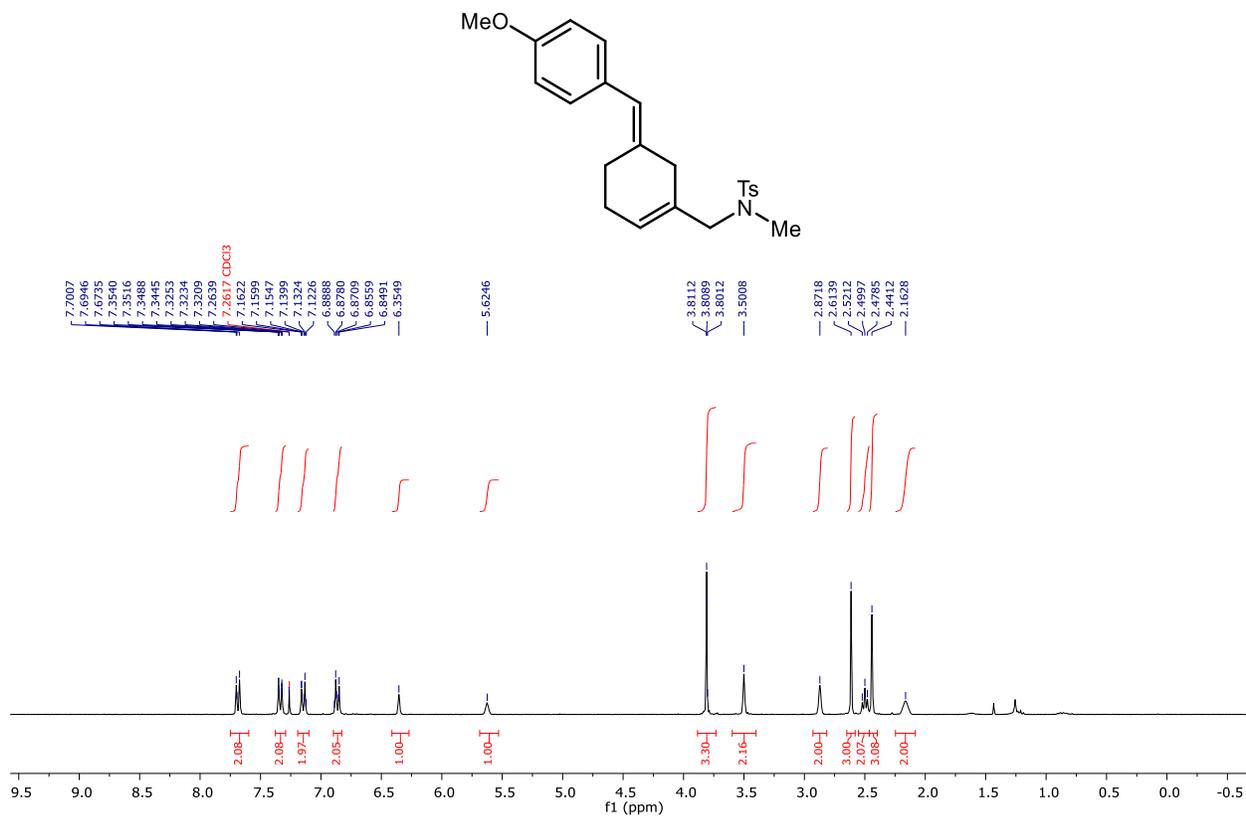


Figure S77. ¹H NMR of **27** (300 MHz, CDCl₃, 295 K).

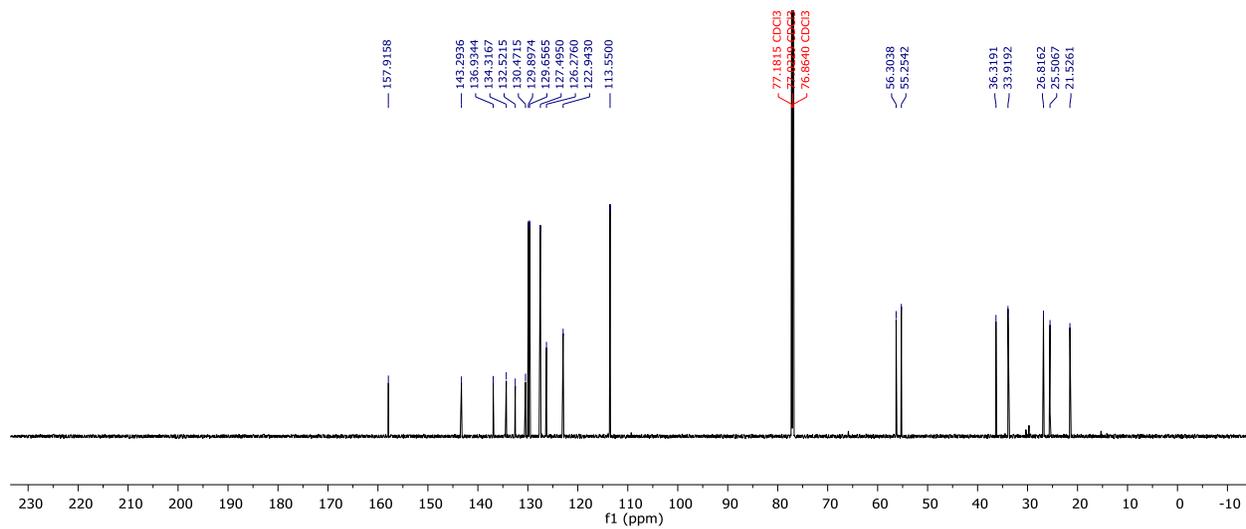


Figure S78. ¹³C NMR of **27** (800 MHz, CDCl₃, 295 K).

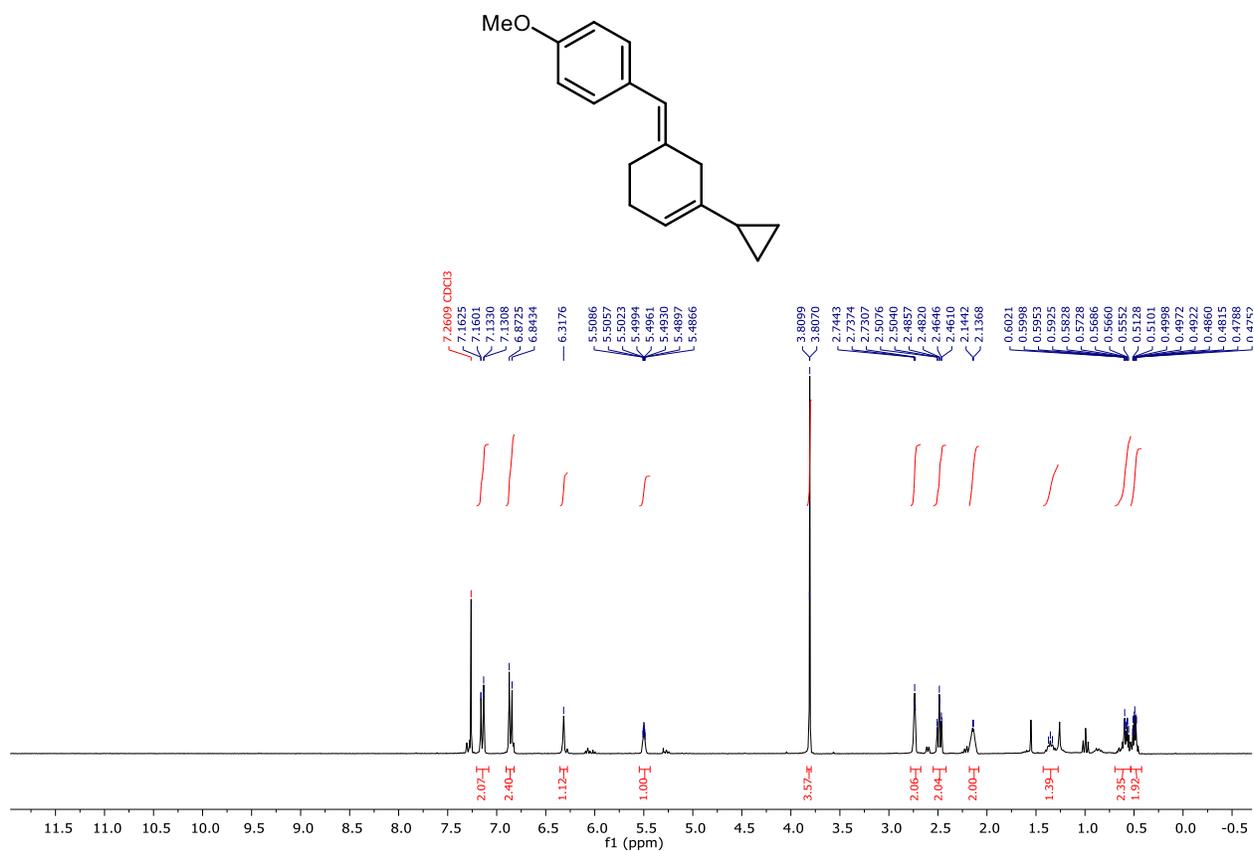


Figure S79. ^1H NMR of **28** (300 MHz, CDCl_3 , 295 K).

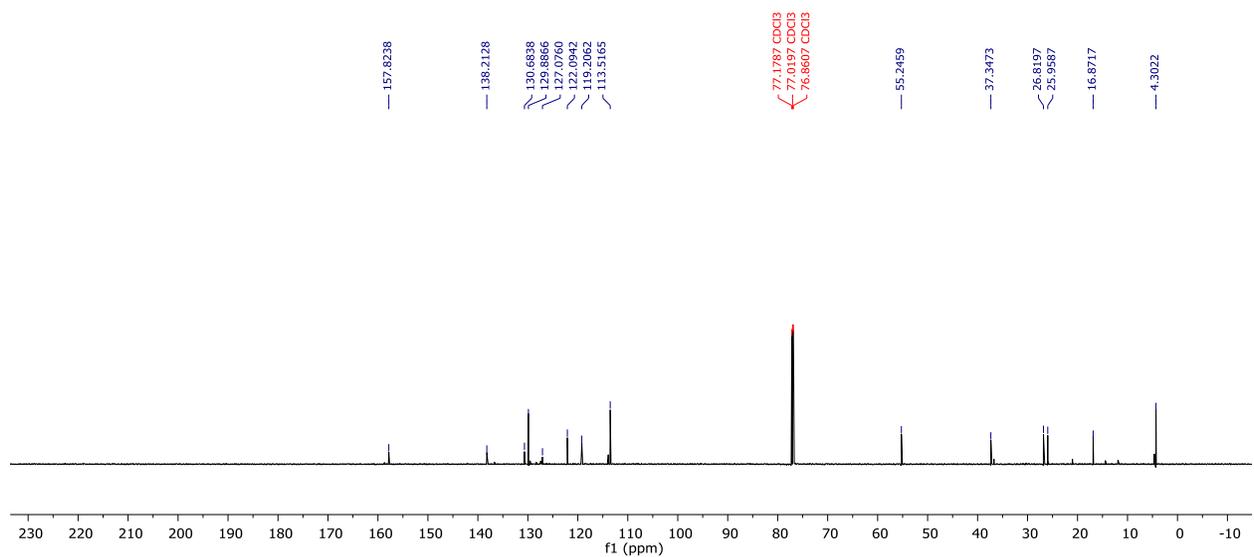


Figure S80. ^{13}C NMR of **28** (800 MHz, CDCl_3 , 295 K).

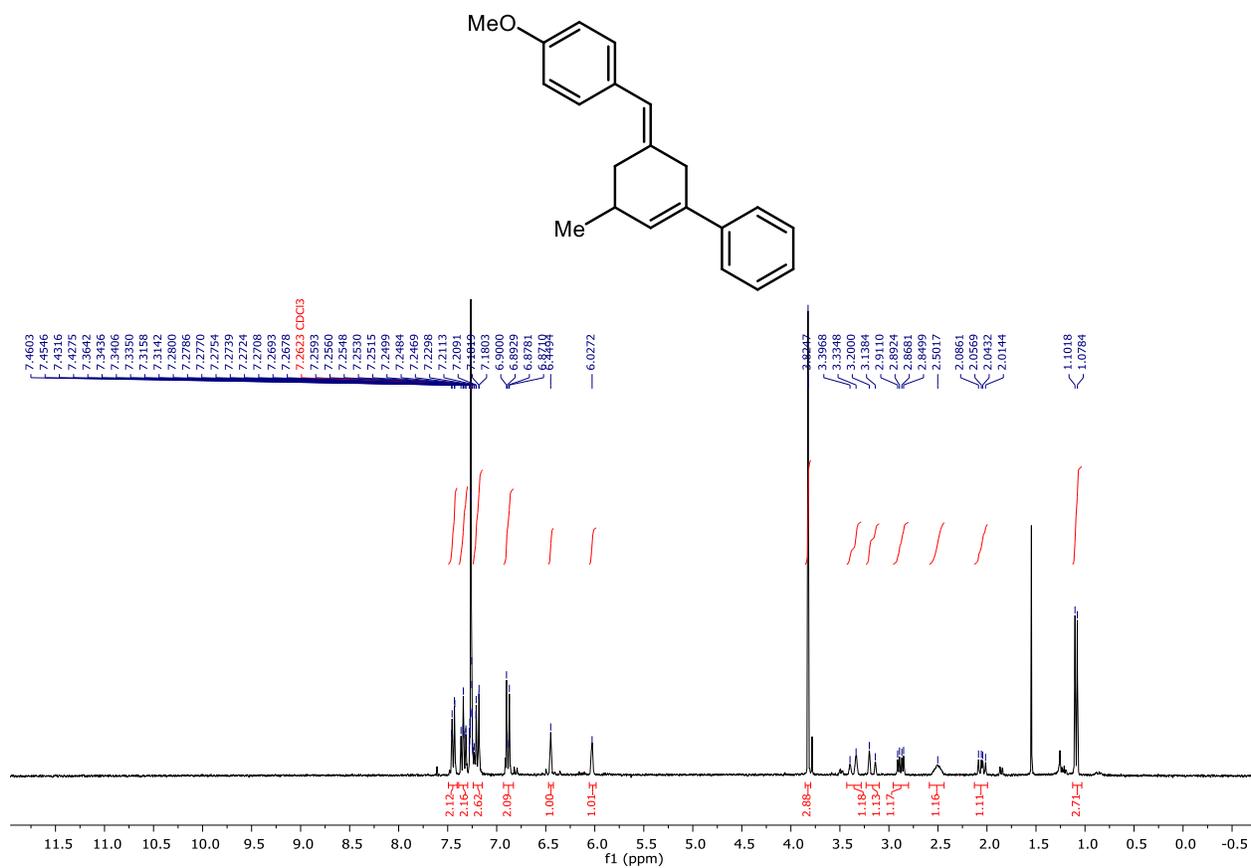


Figure S81. ¹H NMR of **30** (300 MHz, CDCl₃, 295 K).

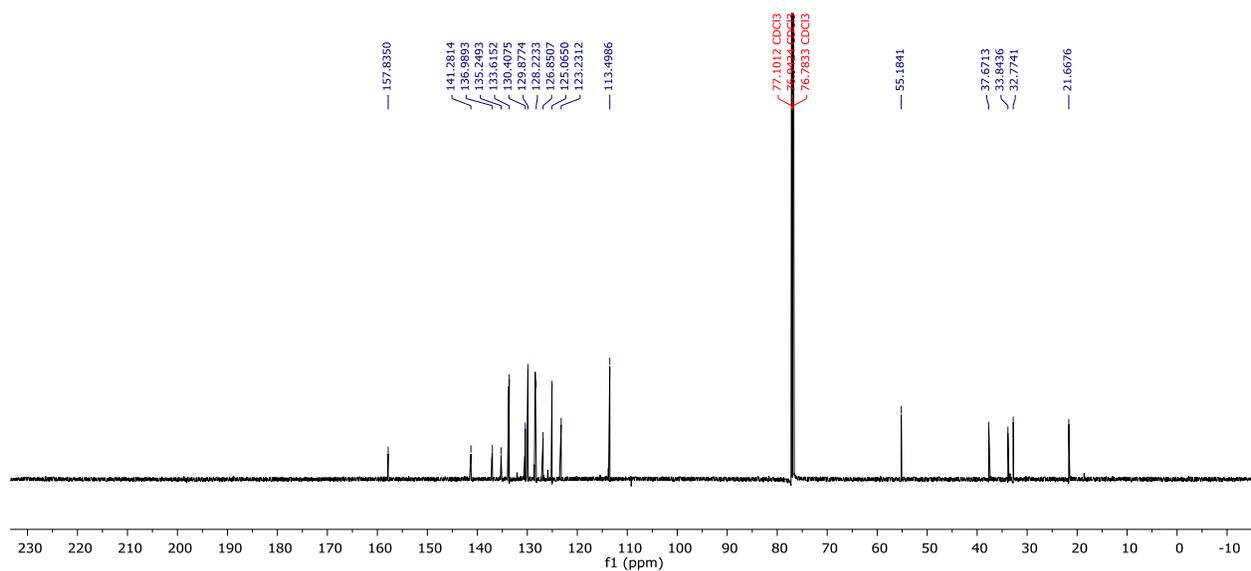


Figure S82. ¹³C NMR of **30** (800 MHz, CDCl₃, 295 K).

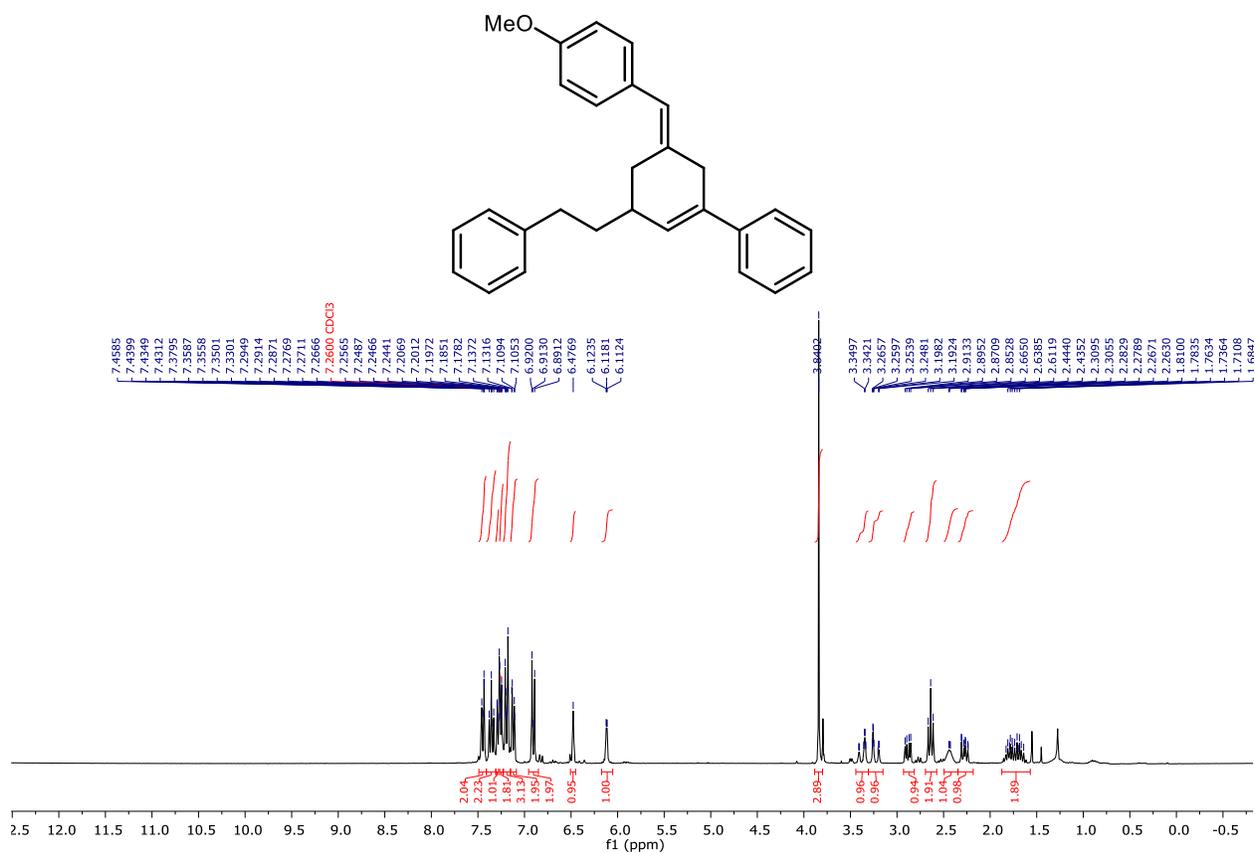


Figure S83. ¹H NMR of **31** (300 MHz, CDCl₃, 295 K).

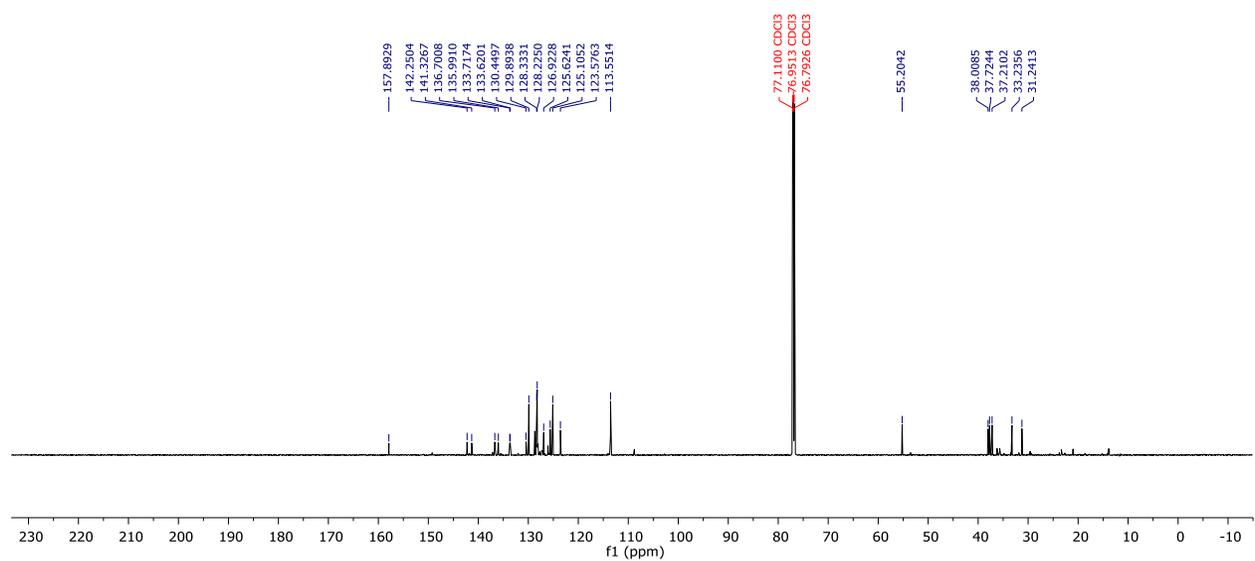


Figure S84. ¹³C NMR of **31** (800 MHz, CDCl₃, 295 K).

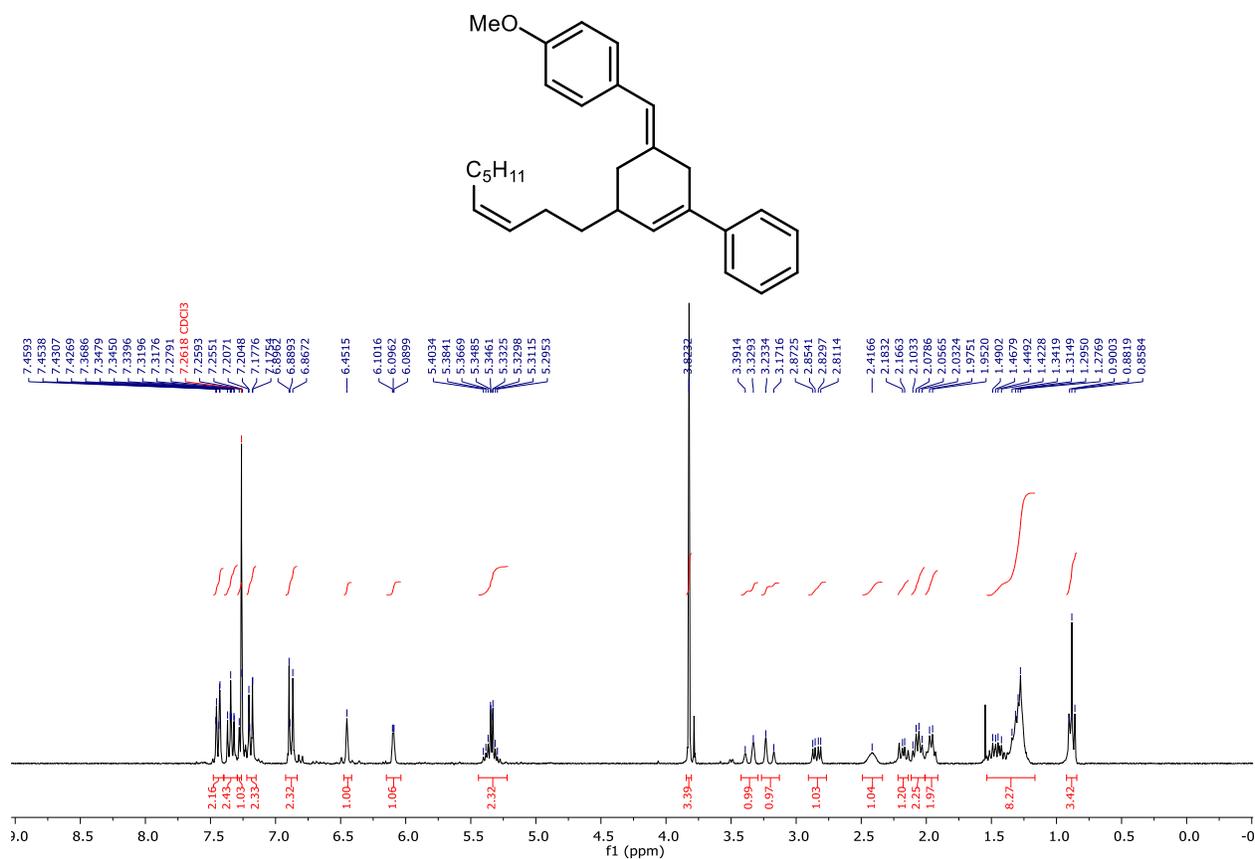


Figure S85. ¹H NMR of **32** (300 MHz, CDCl₃, 295 K).

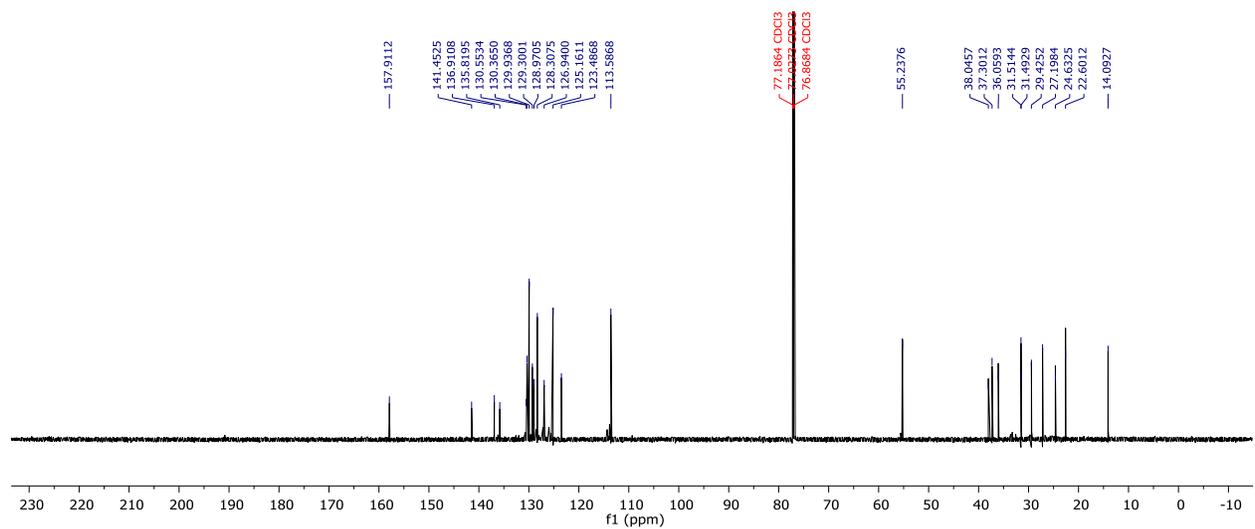


Figure S86. ¹³C NMR of **32** (800 MHz, CDCl₃, 295 K).

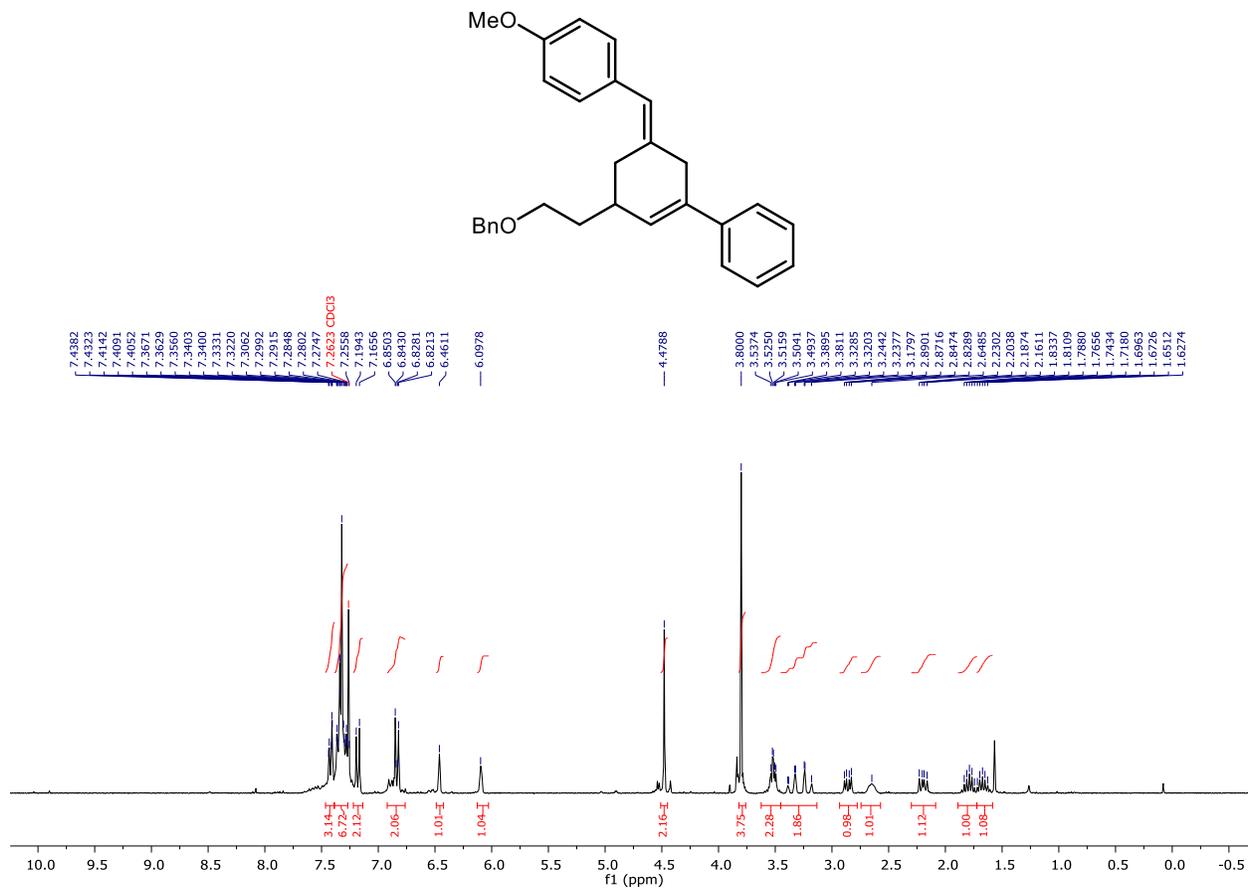


Figure S87. ^1H NMR of **33** (300 MHz, CDCl_3 , 295 K).

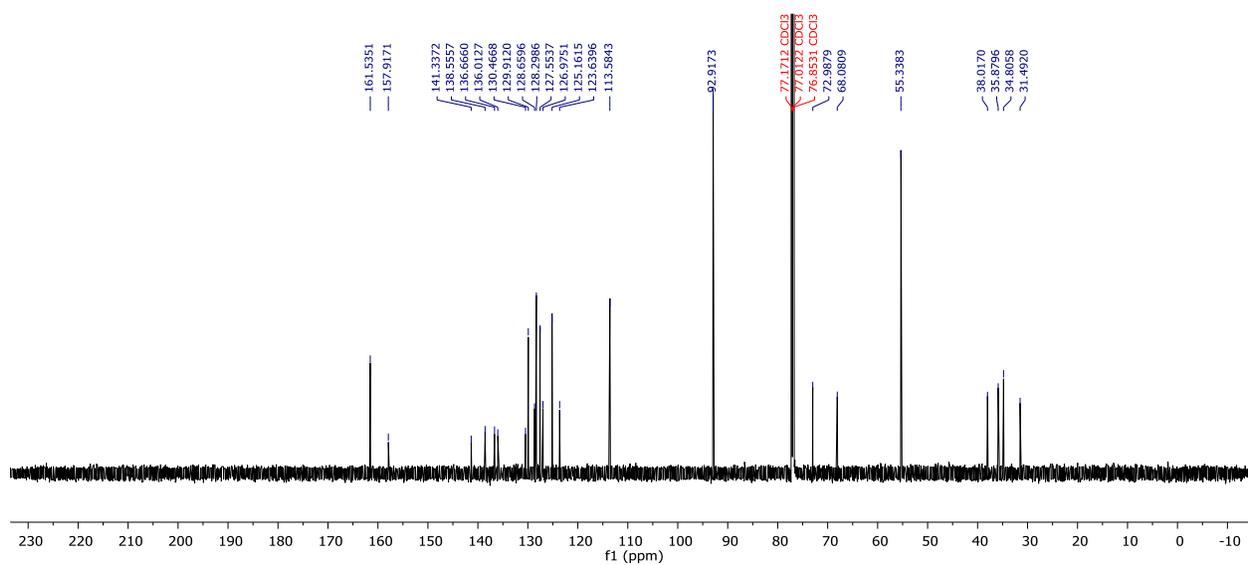


Figure S88. ^{13}C NMR of **33** (800 MHz, CDCl_3 , 295 K).

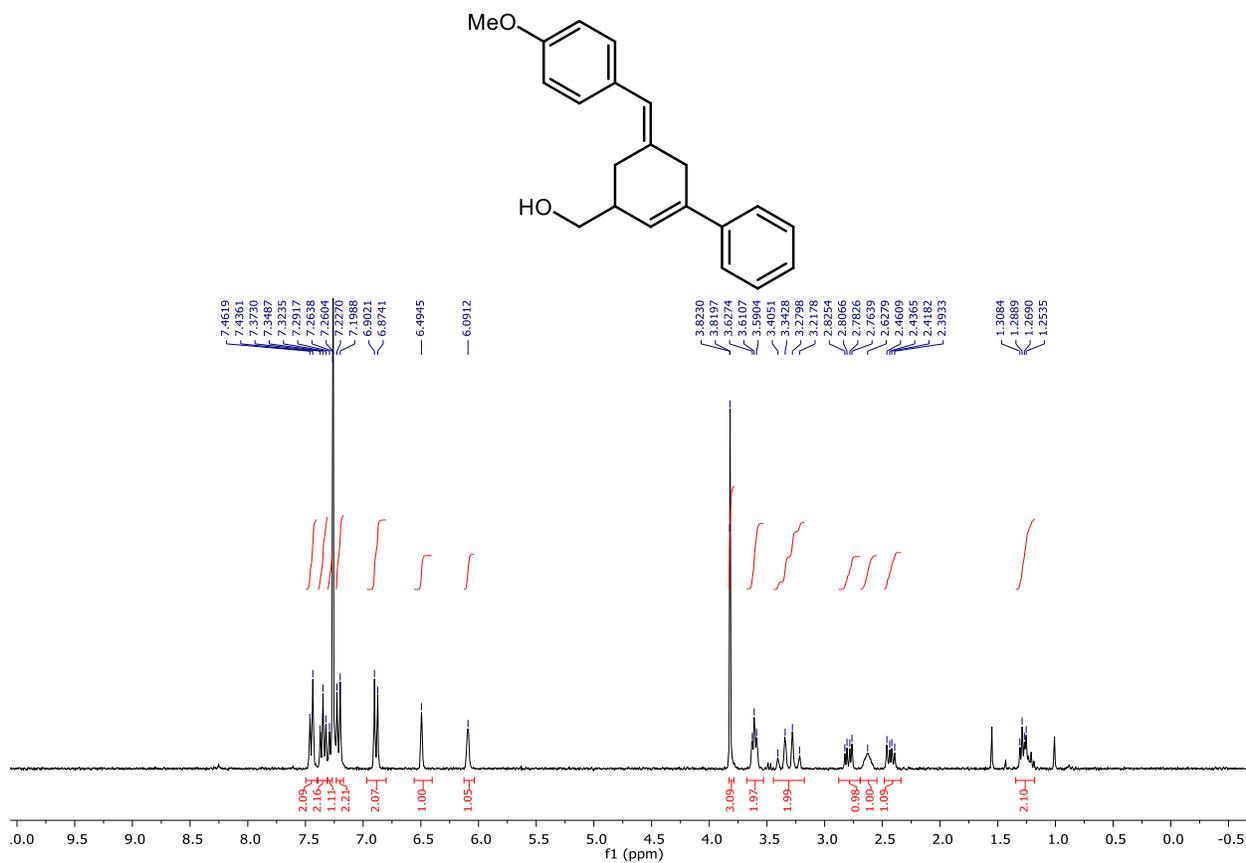


Figure S89. ¹H NMR of **34** (300 MHz, CDCl₃, 295 K).

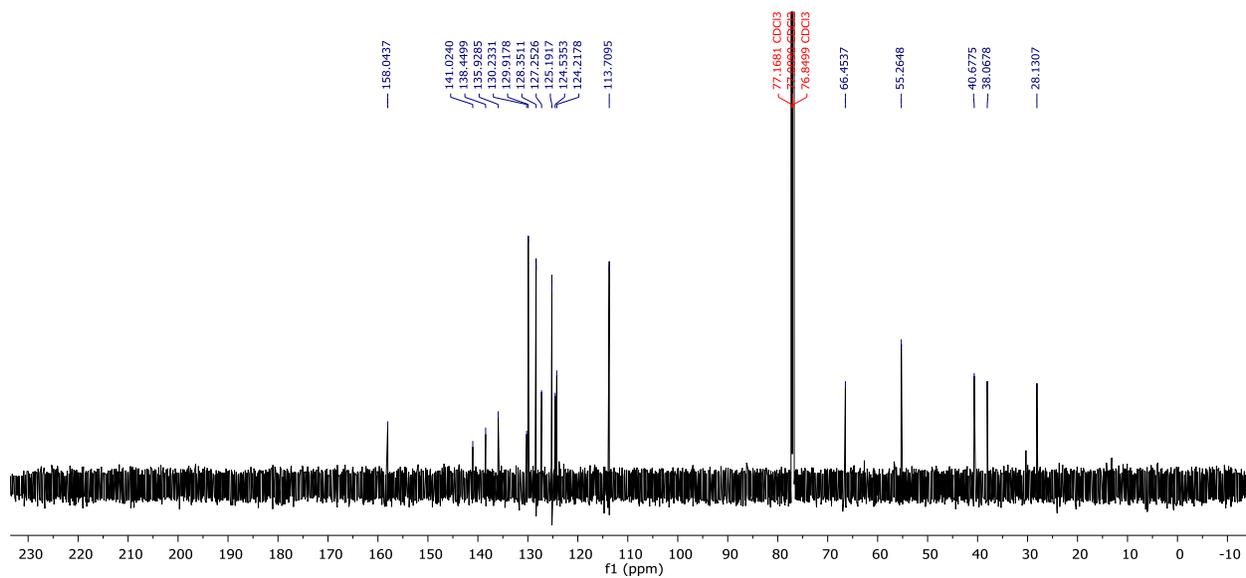


Figure S90. ¹³C NMR of **34** (800 MHz, CDCl₃, 295 K).

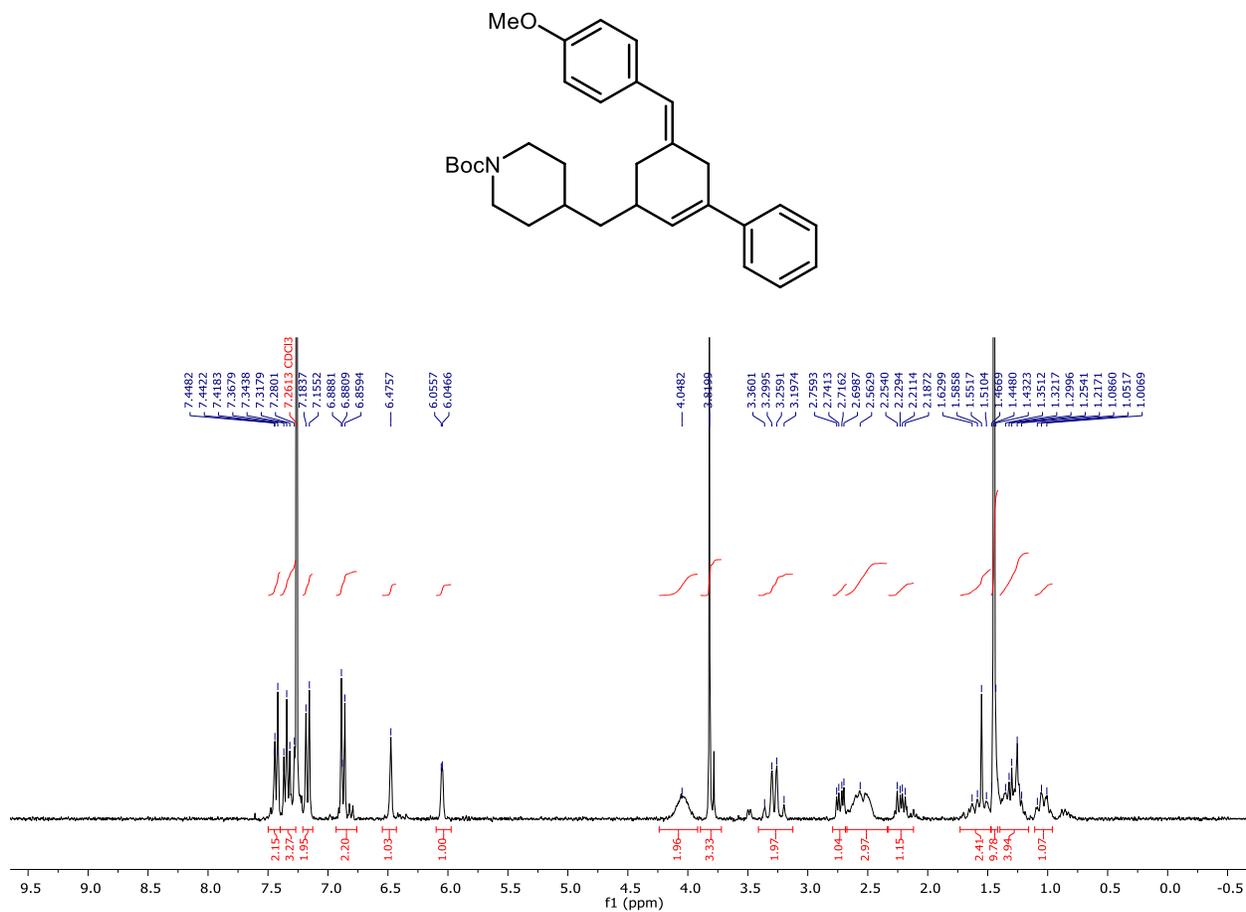


Figure S91. ^1H NMR of **35** (300 MHz, CDCl_3 , 295 K).

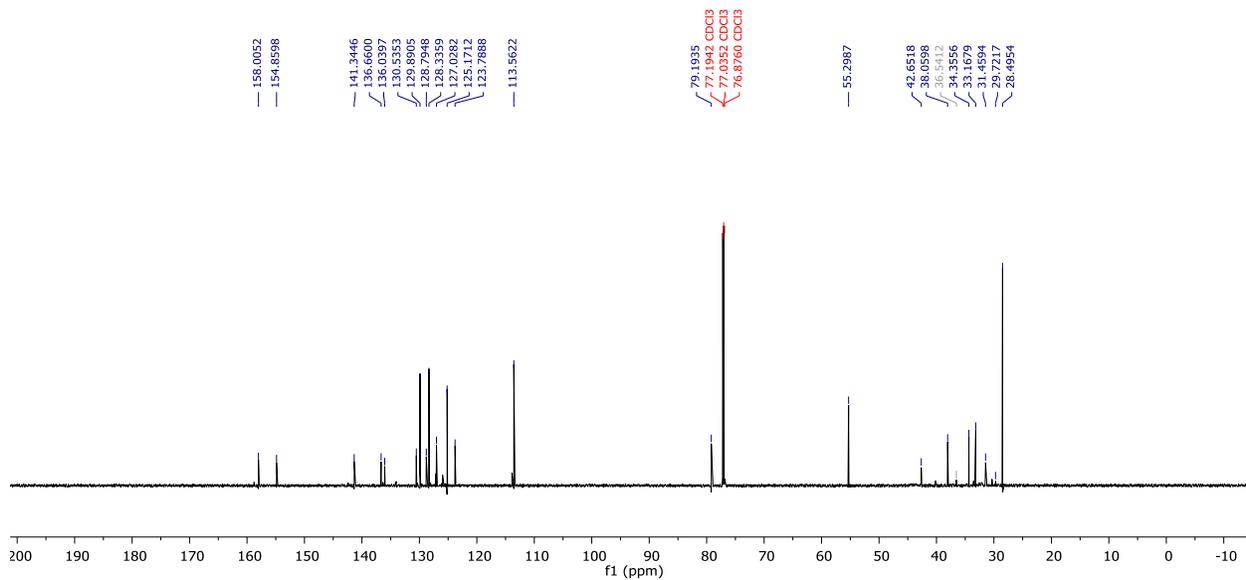


Figure S92. ^{13}C NMR of **35** (800 MHz, CDCl_3 , 295 K).

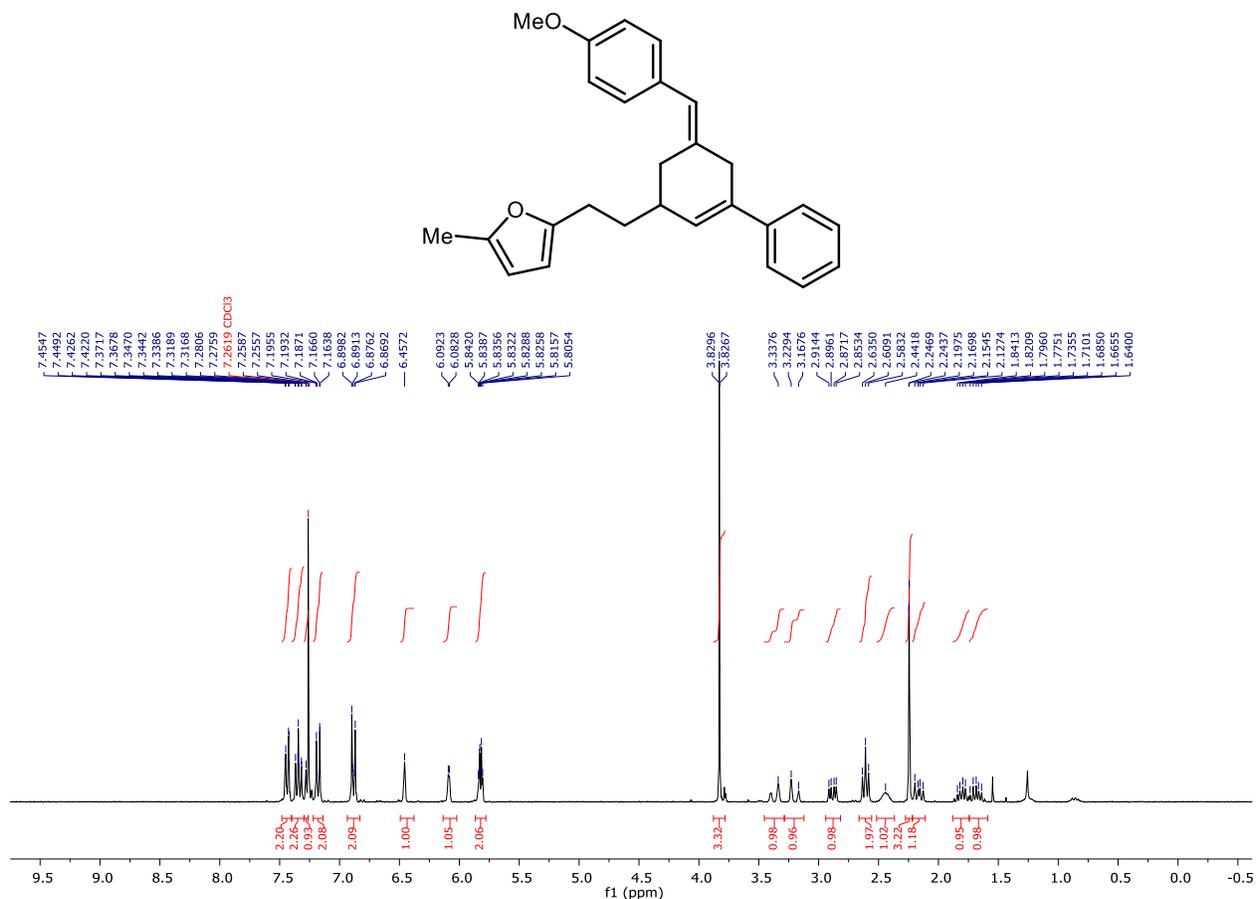


Figure S93. ^1H NMR of **36** (300 MHz, CDCl_3 , 295 K).

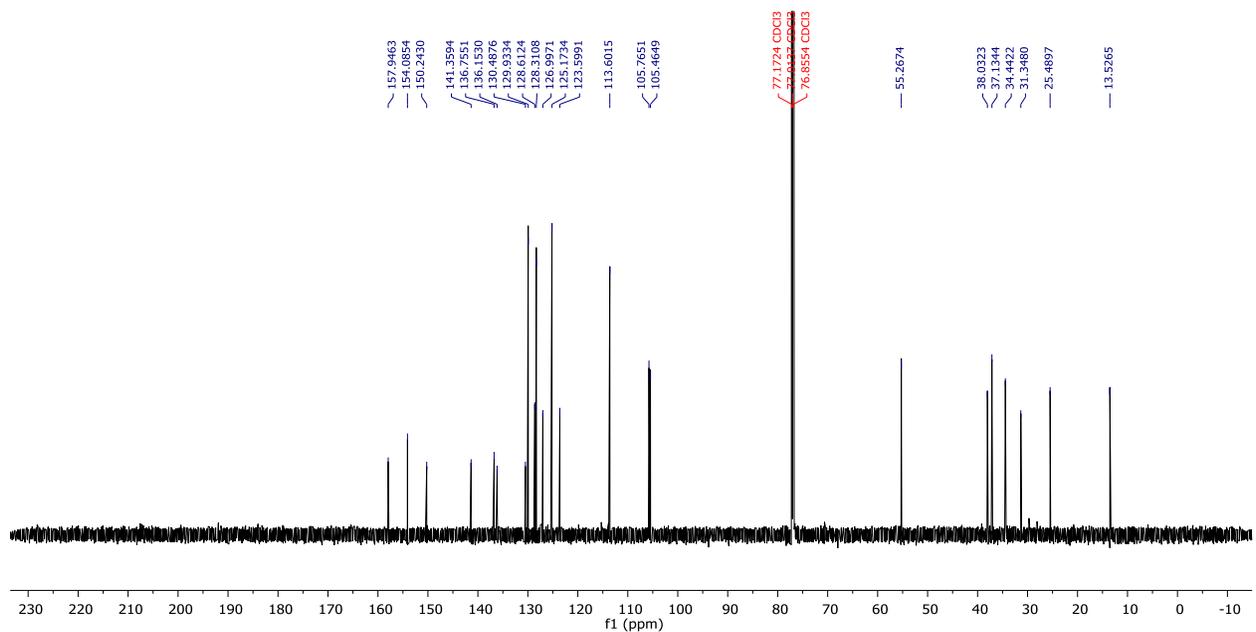


Figure S94. ^{13}C NMR of **36** (800 MHz, CDCl_3 , 295 K).

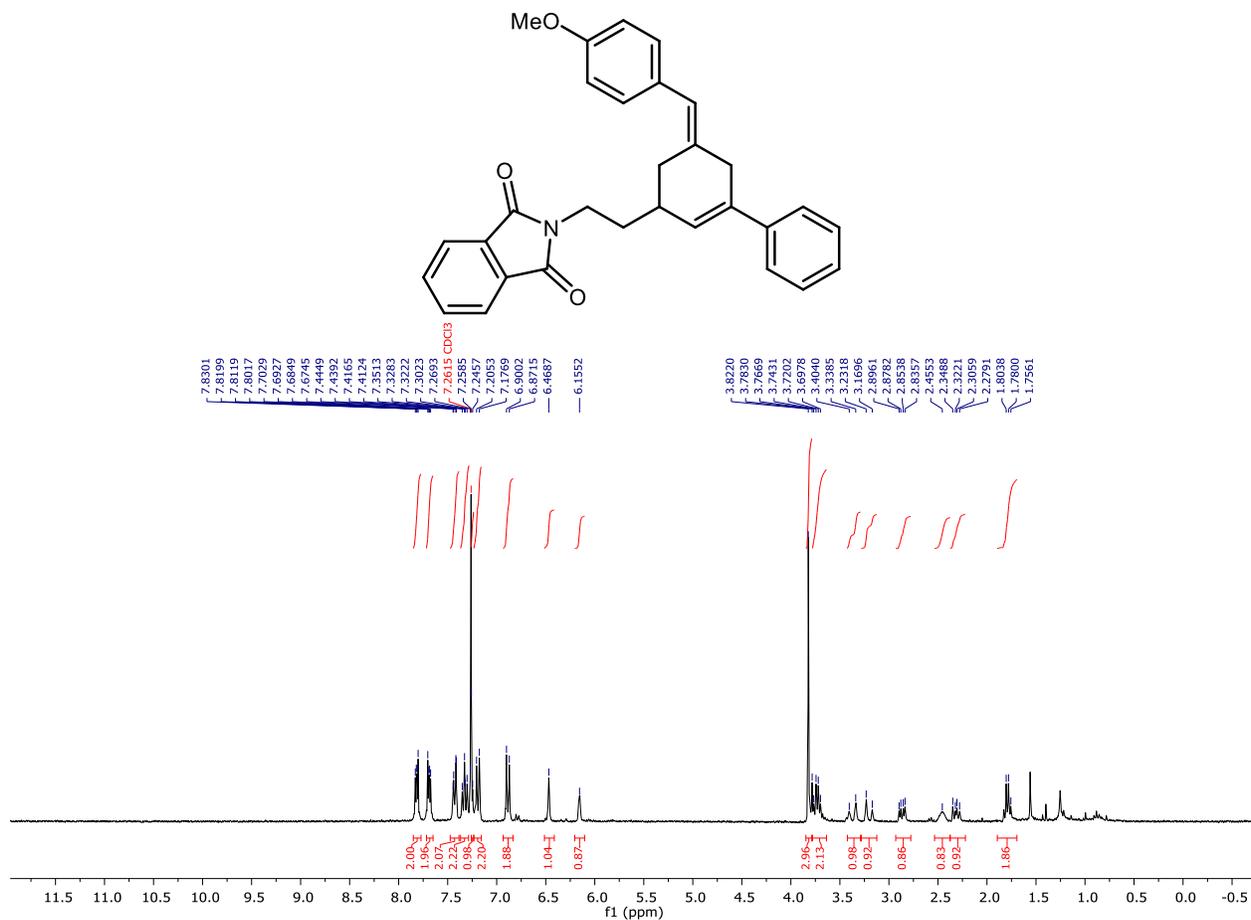


Figure S95. ¹H NMR of **37** (300 MHz, CDCl₃, 295 K).

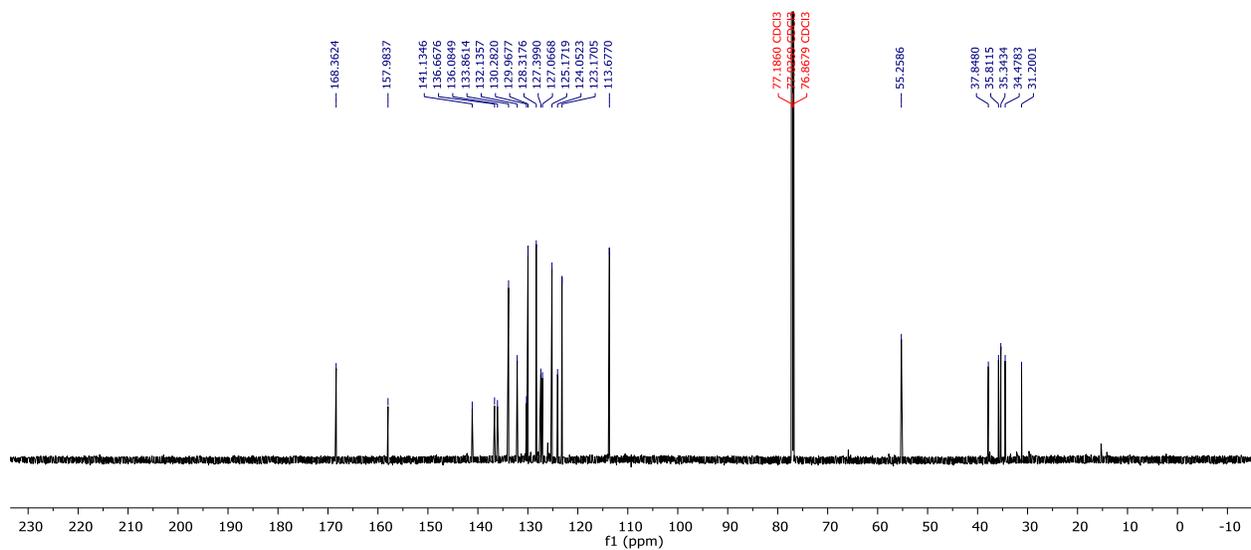


Figure S96. ¹³C NMR of **37** (800 MHz, CDCl₃, 295 K).

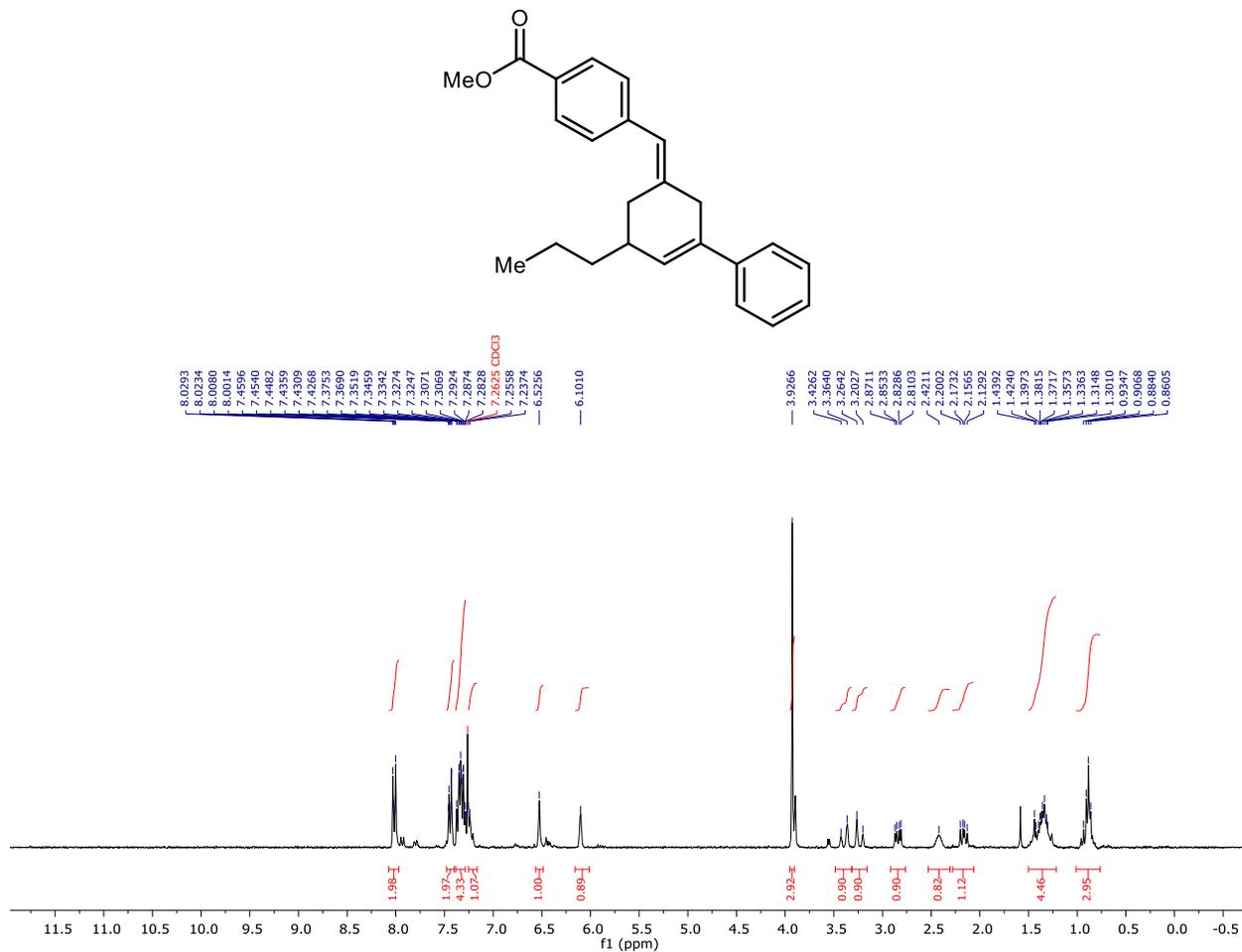


Figure S97. ¹H NMR of S17 (300 MHz, CDCl₃, 295 K).

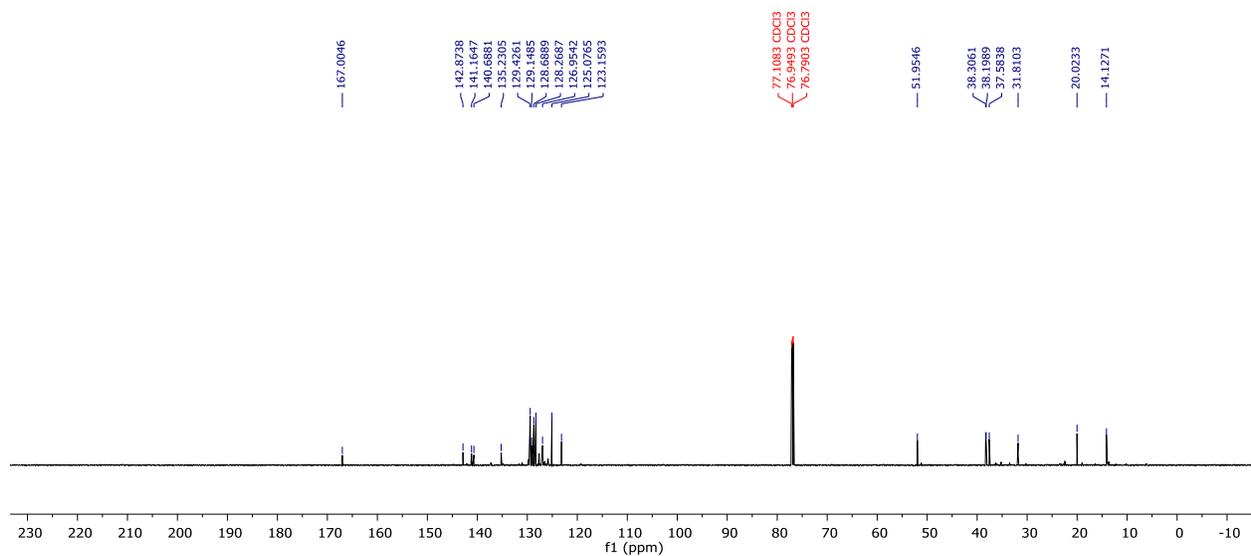


Figure S98. ¹³C NMR of S17 (800 MHz, CDCl₃, 295 K).

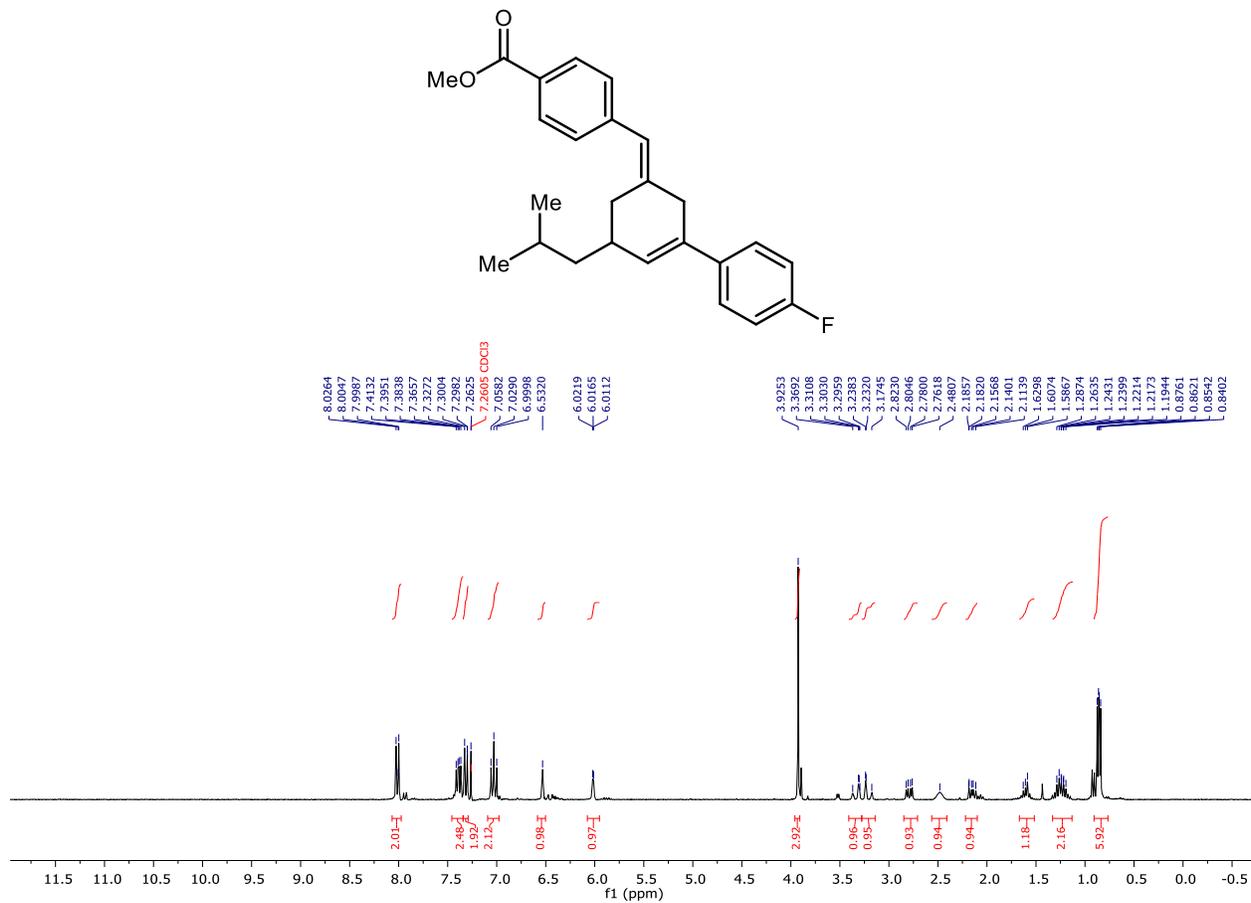


Figure S99. ¹H NMR of **S18** (300 MHz, CDCl₃, 295 K).

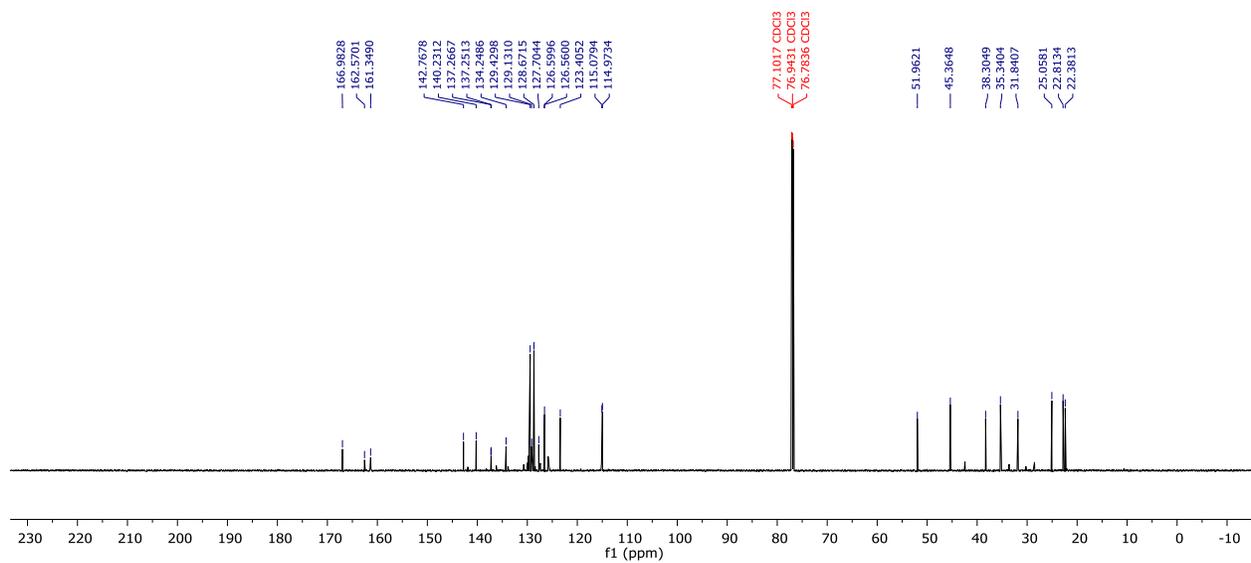


Figure S100. ¹³C NMR of **S18** (800 MHz, CDCl₃, 295 K).

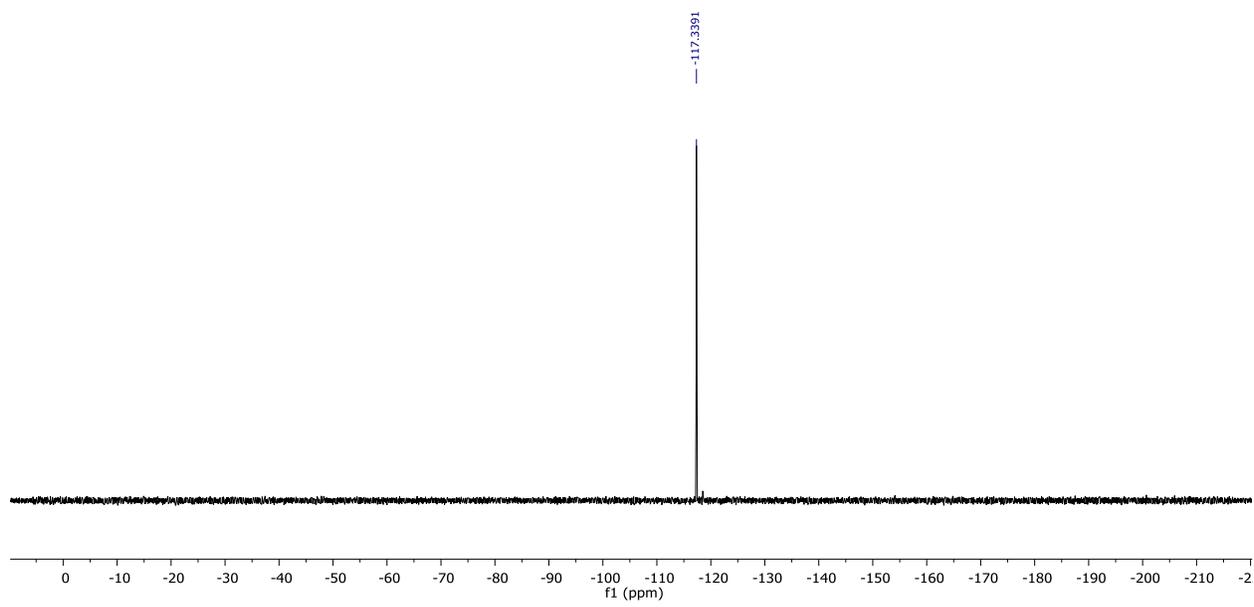


Figure S101. ^{19}F NMR of **S18** (300 MHz, CDCl_3 , 295 K).

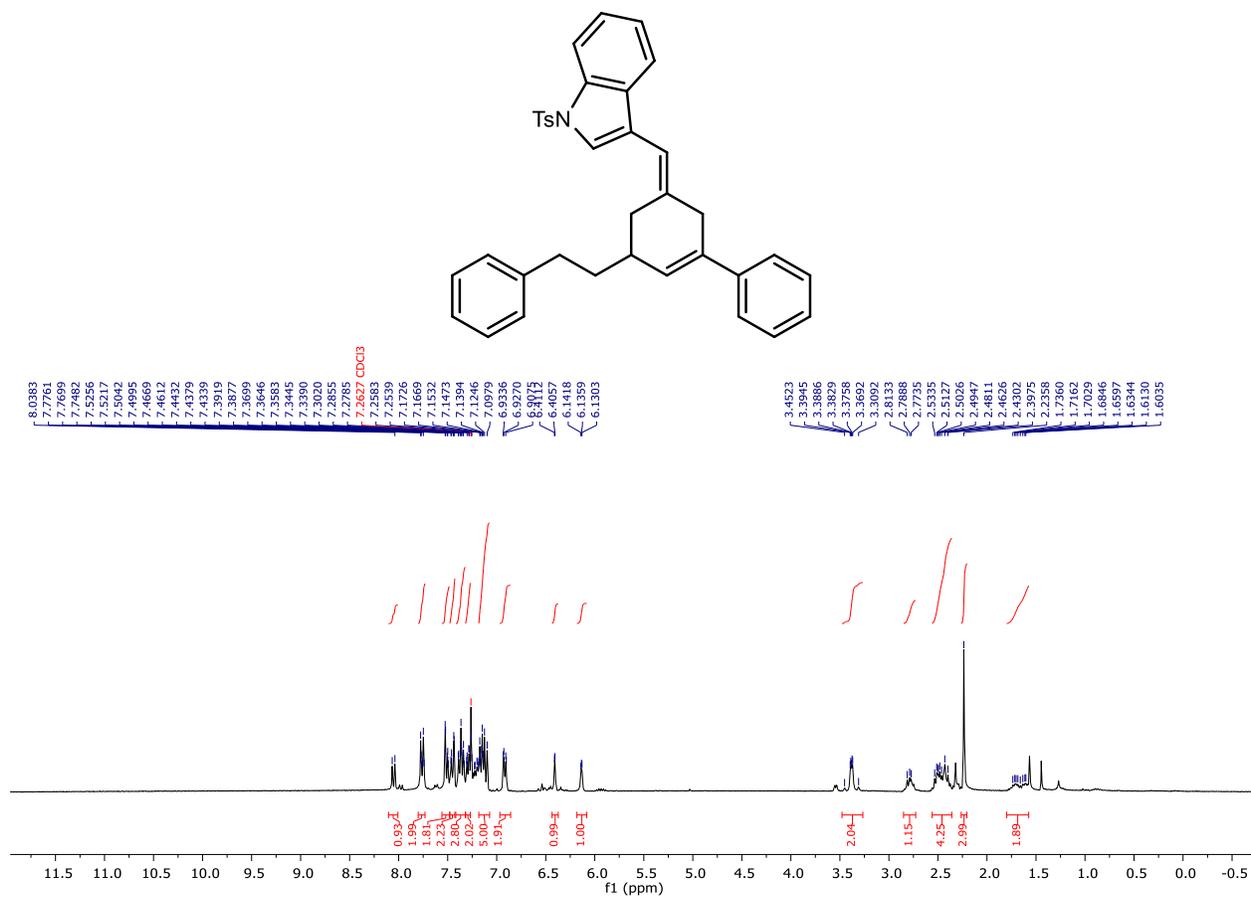


Figure S102. ¹H NMR of S19 (300 MHz, CDCl₃, 295 K).

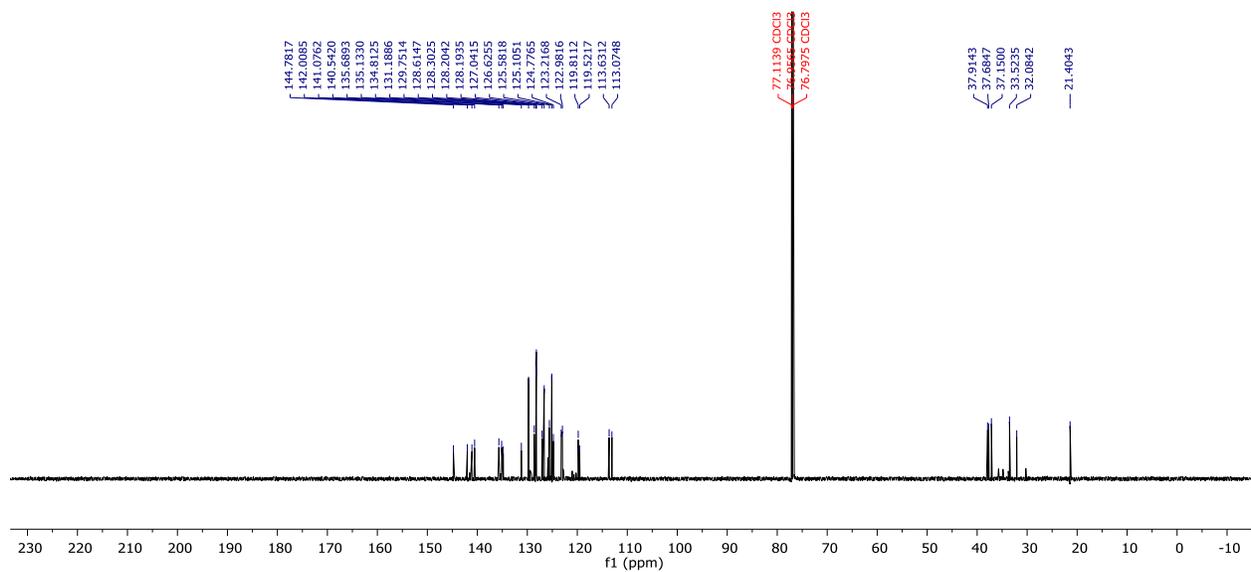


Figure S103. ¹³C NMR of S19 (800 MHz, CDCl₃, 295 K).

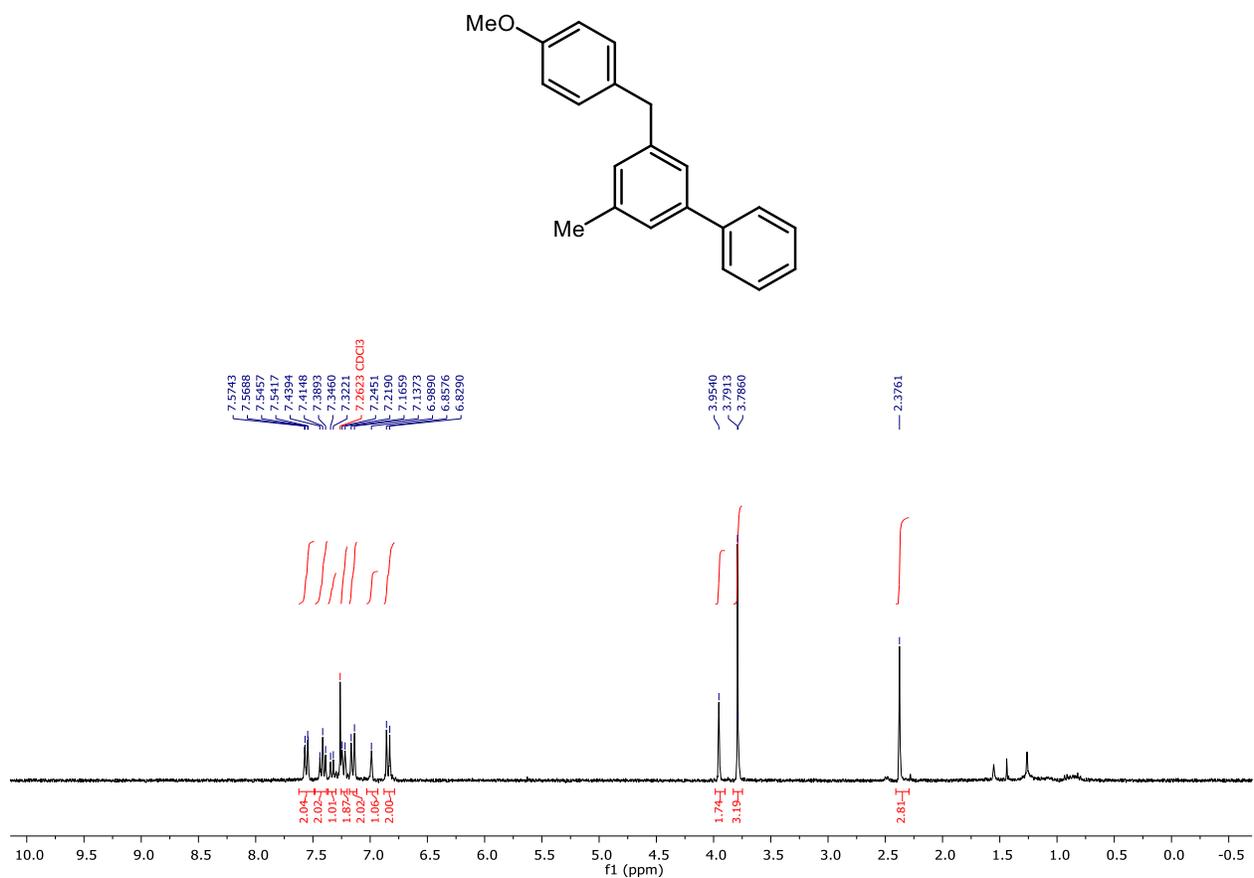


Figure S104. ¹H NMR of **38** (300 MHz, CDCl₃, 295 K).

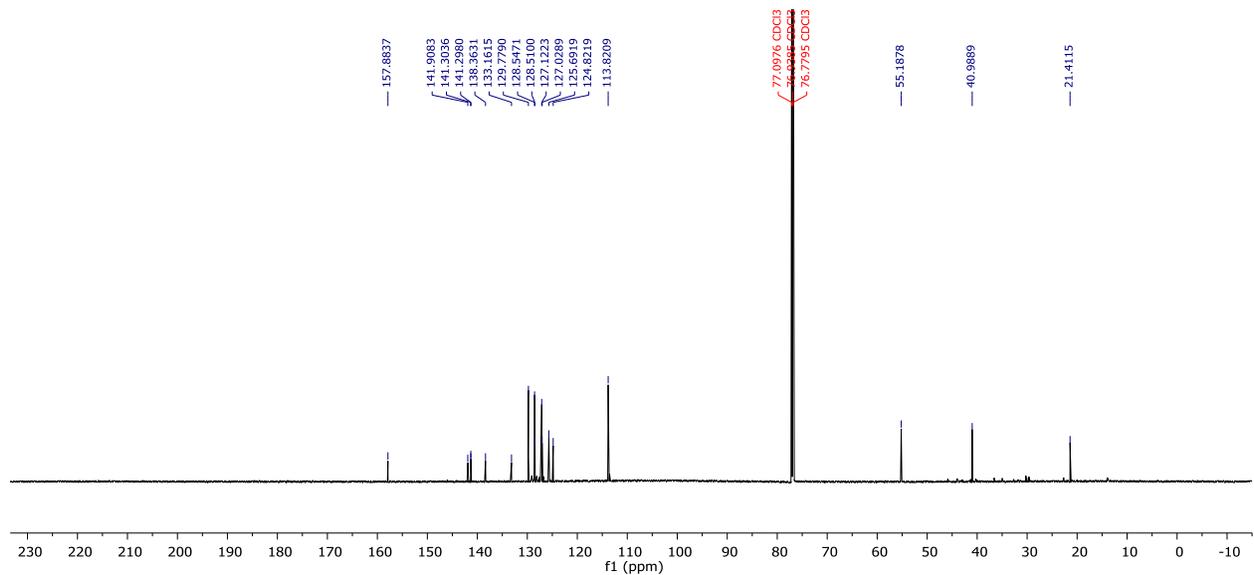
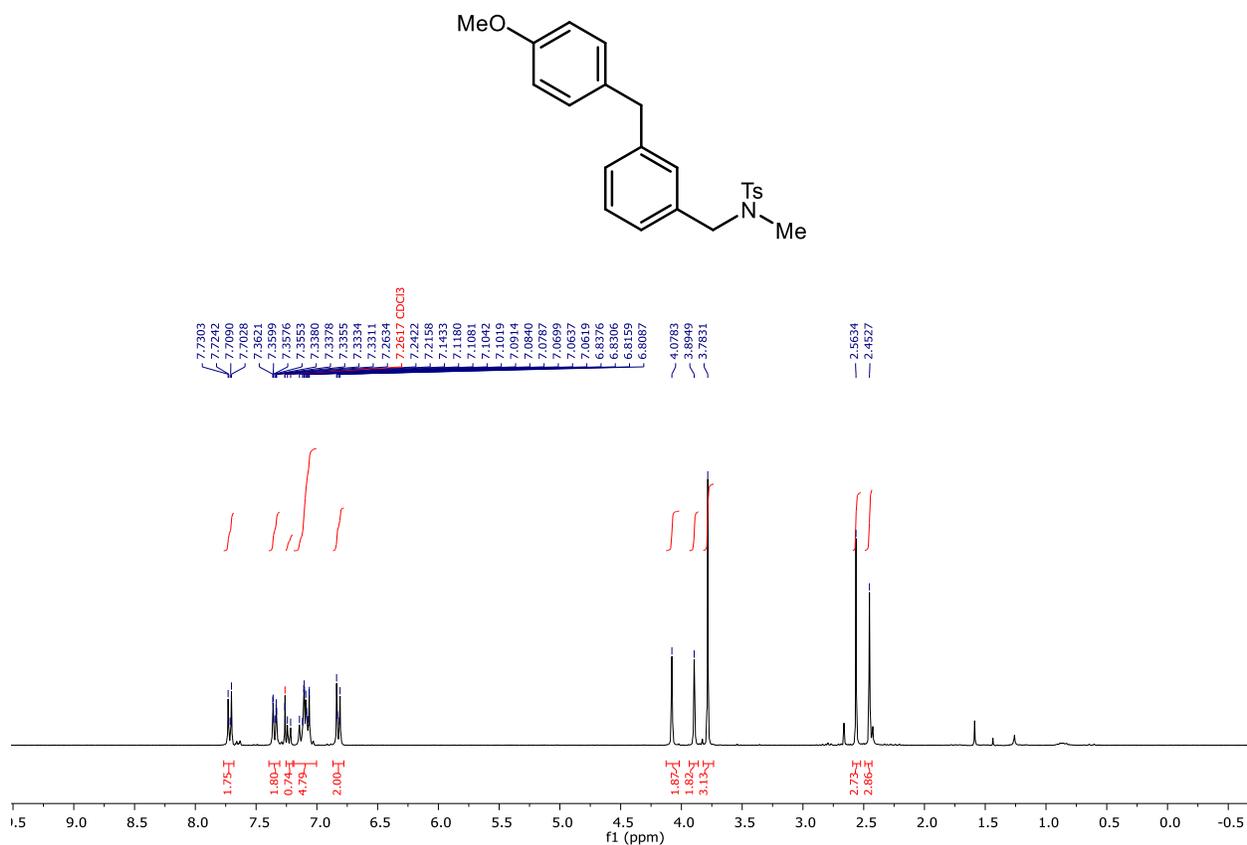


Figure S105. ¹³C NMR of **38** (800 MHz, CDCl₃, 295 K).



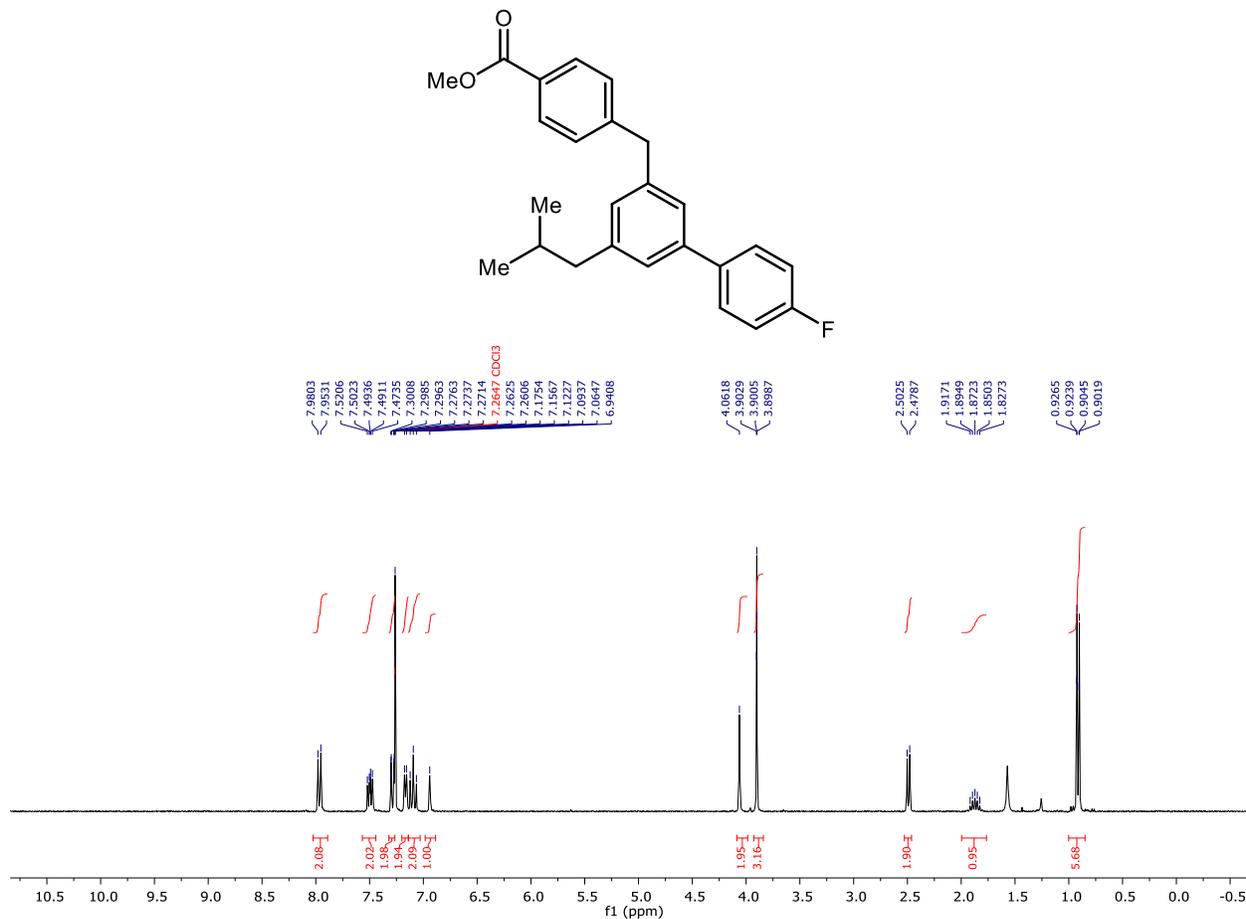


Figure S108. ^1H NMR of **40** (300 MHz, CDCl_3 , 295 K).

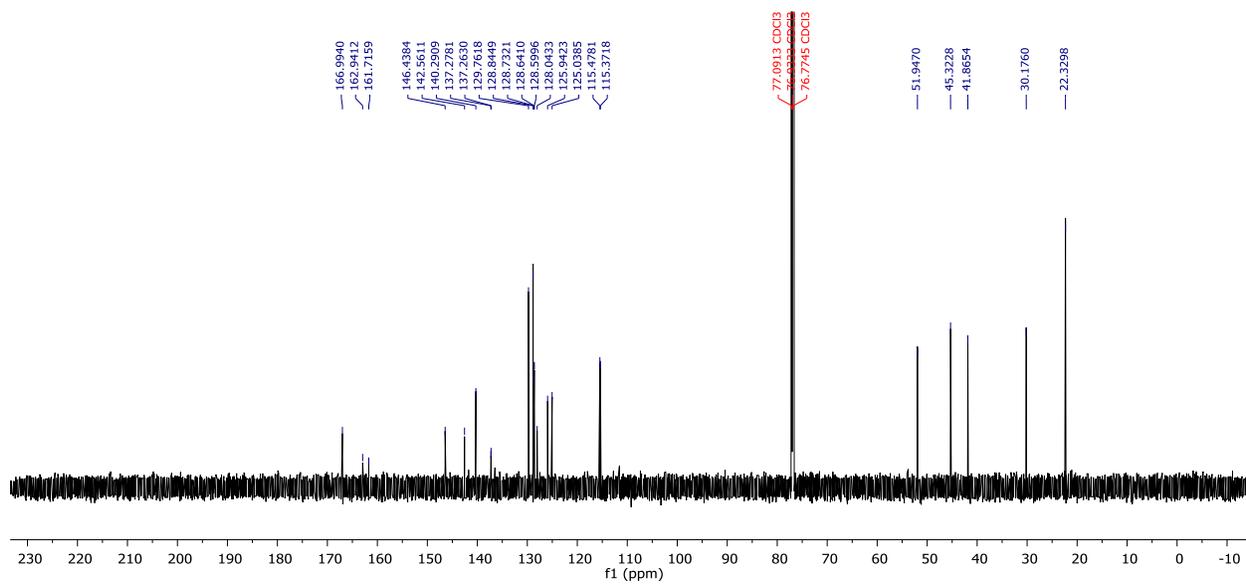


Figure S109. ^{13}C NMR of **40** (800 MHz, CDCl_3 , 295 K).

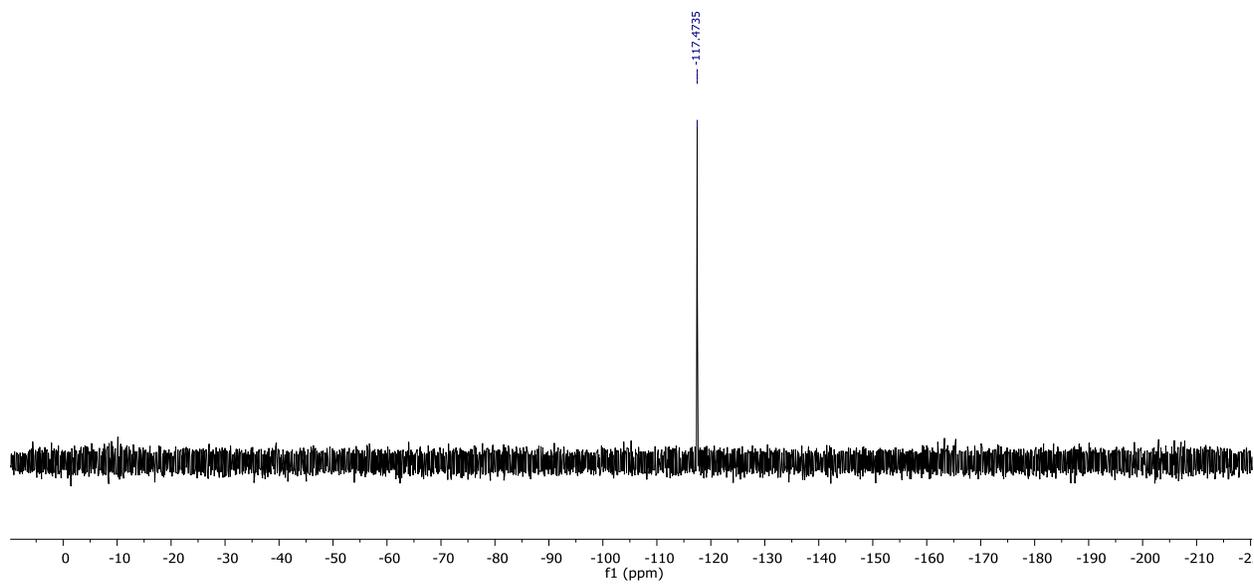


Figure S110. ^{19}F NMR of **39** (300 MHz, CDCl_3 , 295 K).

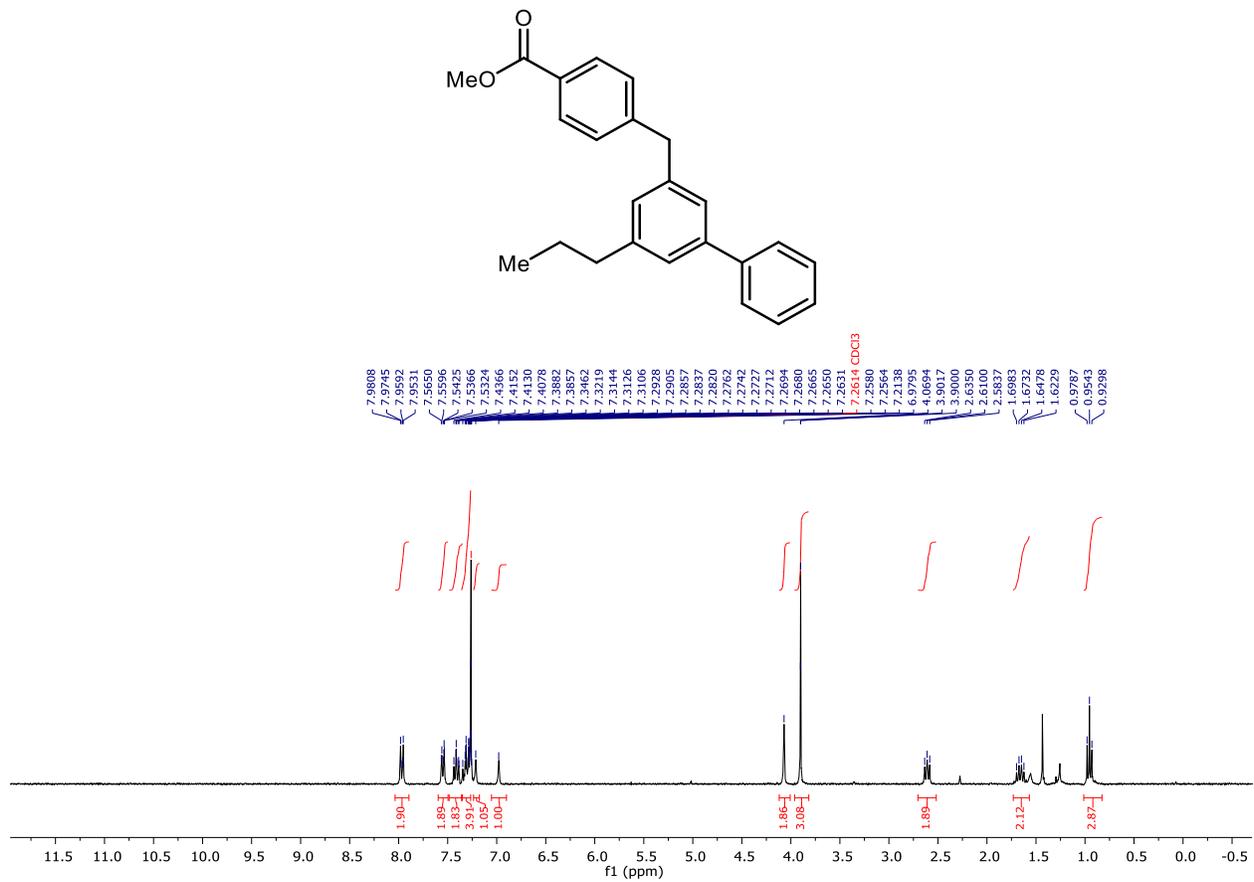


Figure S111. ¹H NMR of **41** (300 MHz, CDCl₃, 295 K).

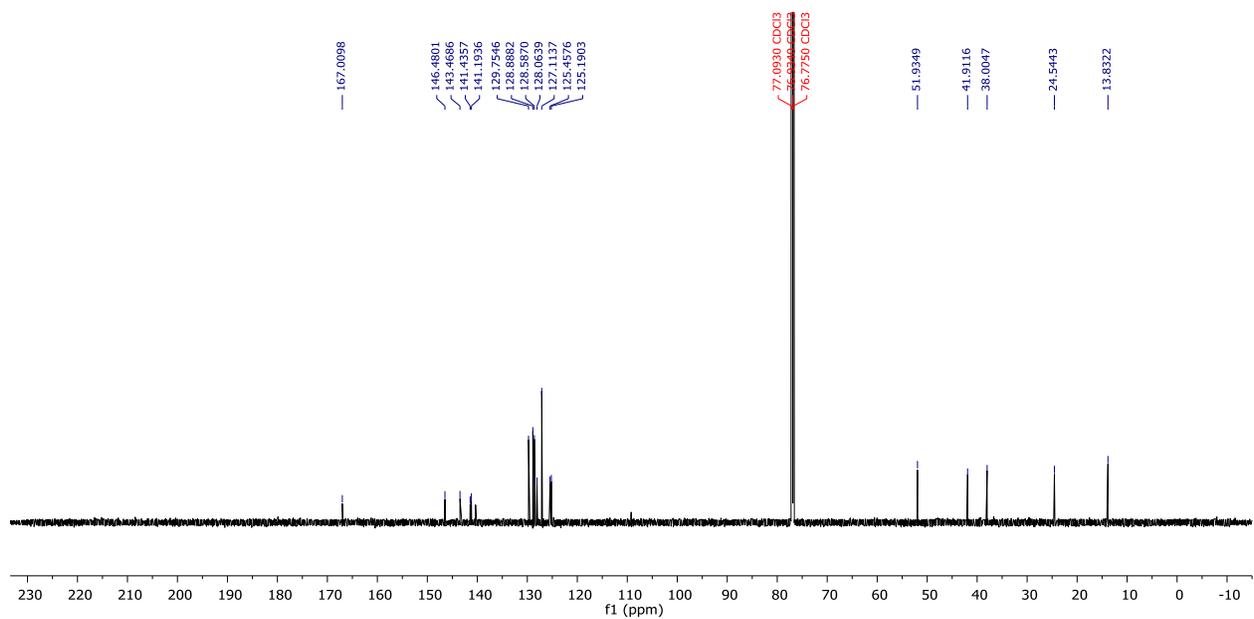


Figure S112. ¹³C NMR of **41** (800 MHz, CDCl₃, 295 K).

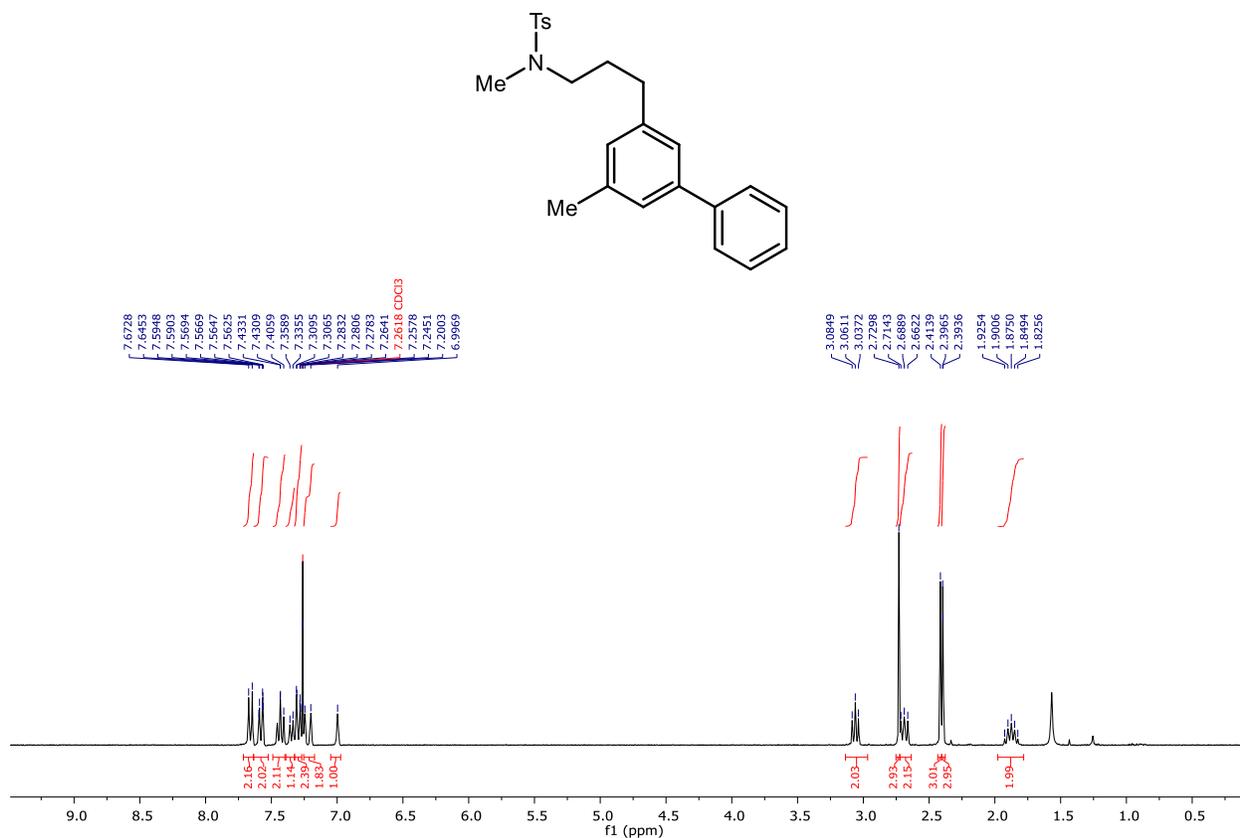


Figure S113. ¹H NMR of **42** (300 MHz, CDCl₃, 295 K).

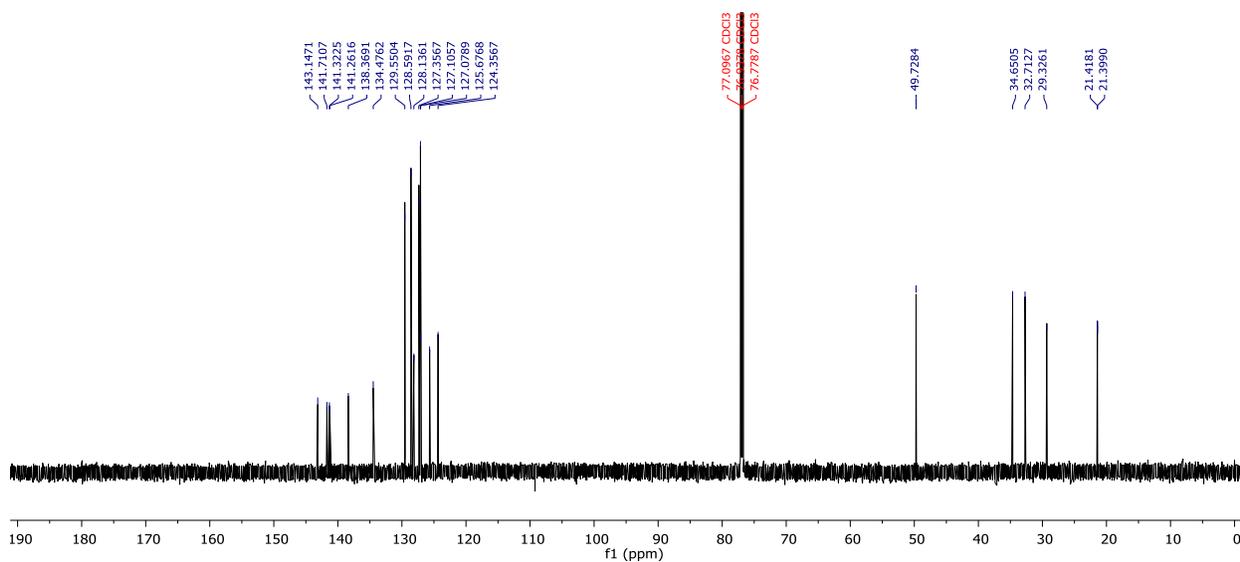


Figure S114. ¹³C NMR of **42** (800 MHz, CDCl₃, 295 K).

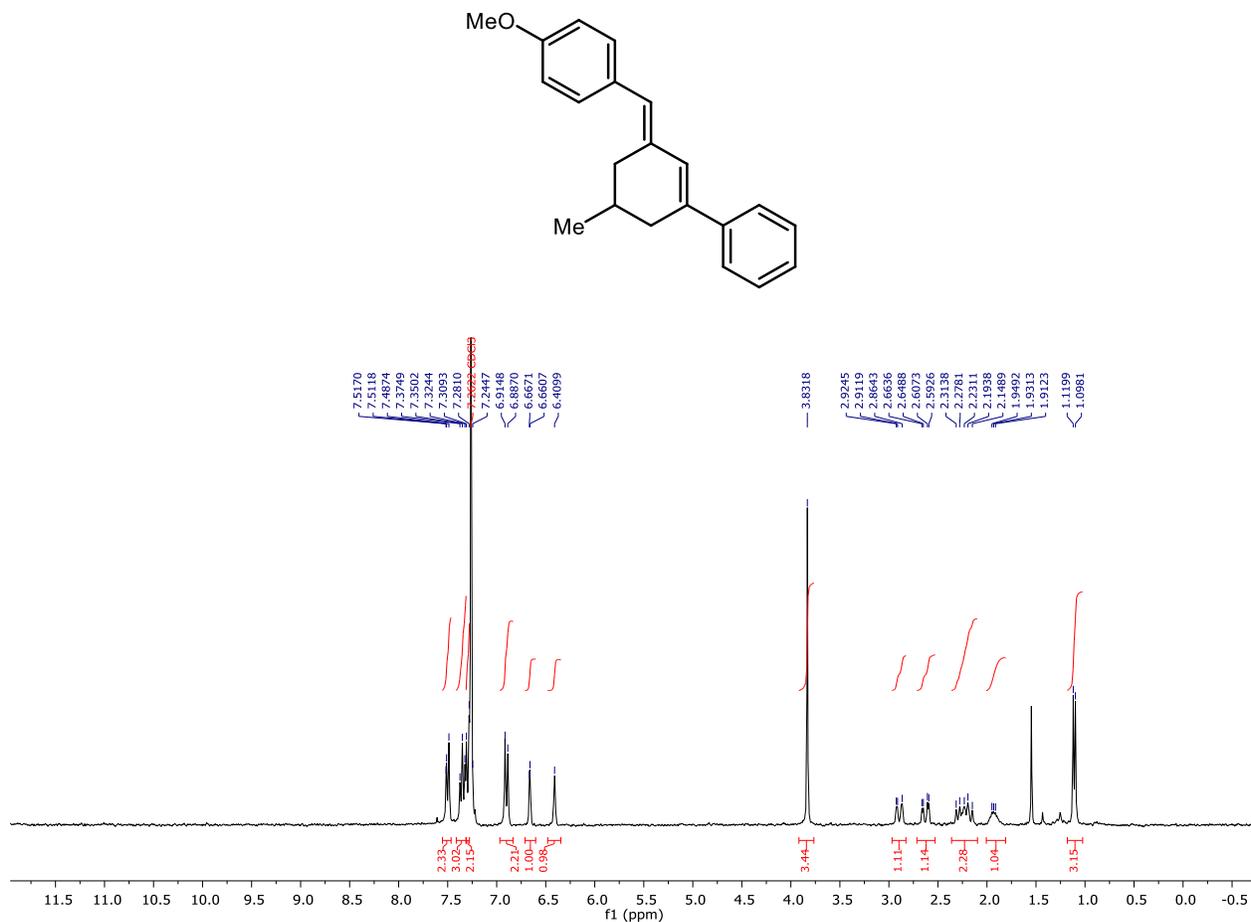


Figure S115. $^1\text{H NMR}$ of **43** (300 MHz, CDCl_3 , 295 K).

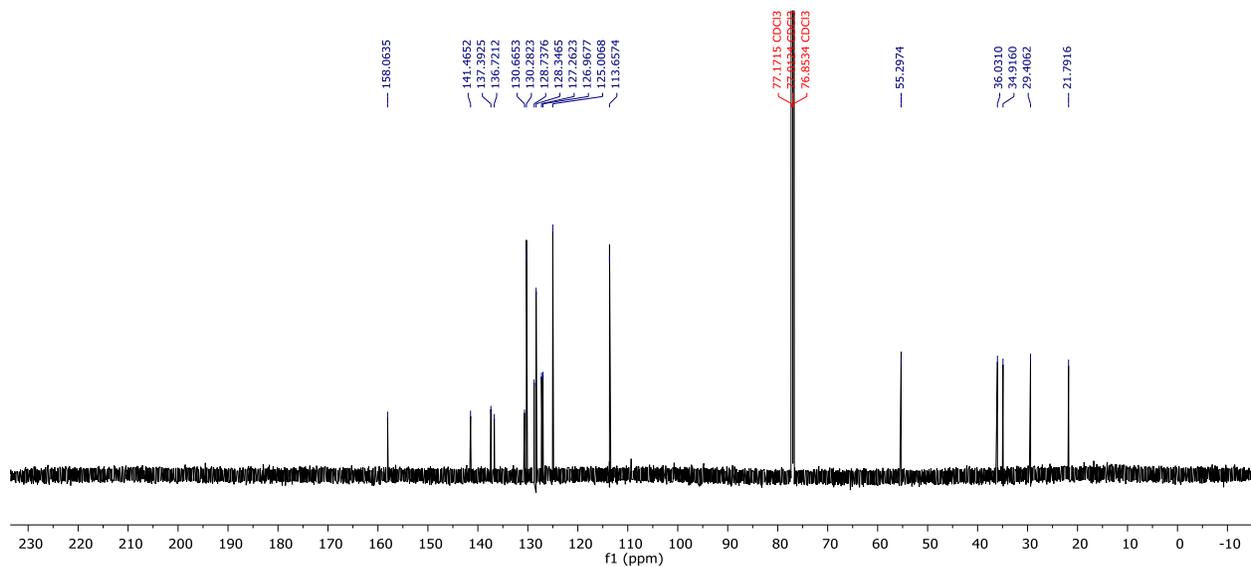


Figure S116. $^{13}\text{C NMR}$ of **43** (800 MHz, CDCl_3 , 295 K).

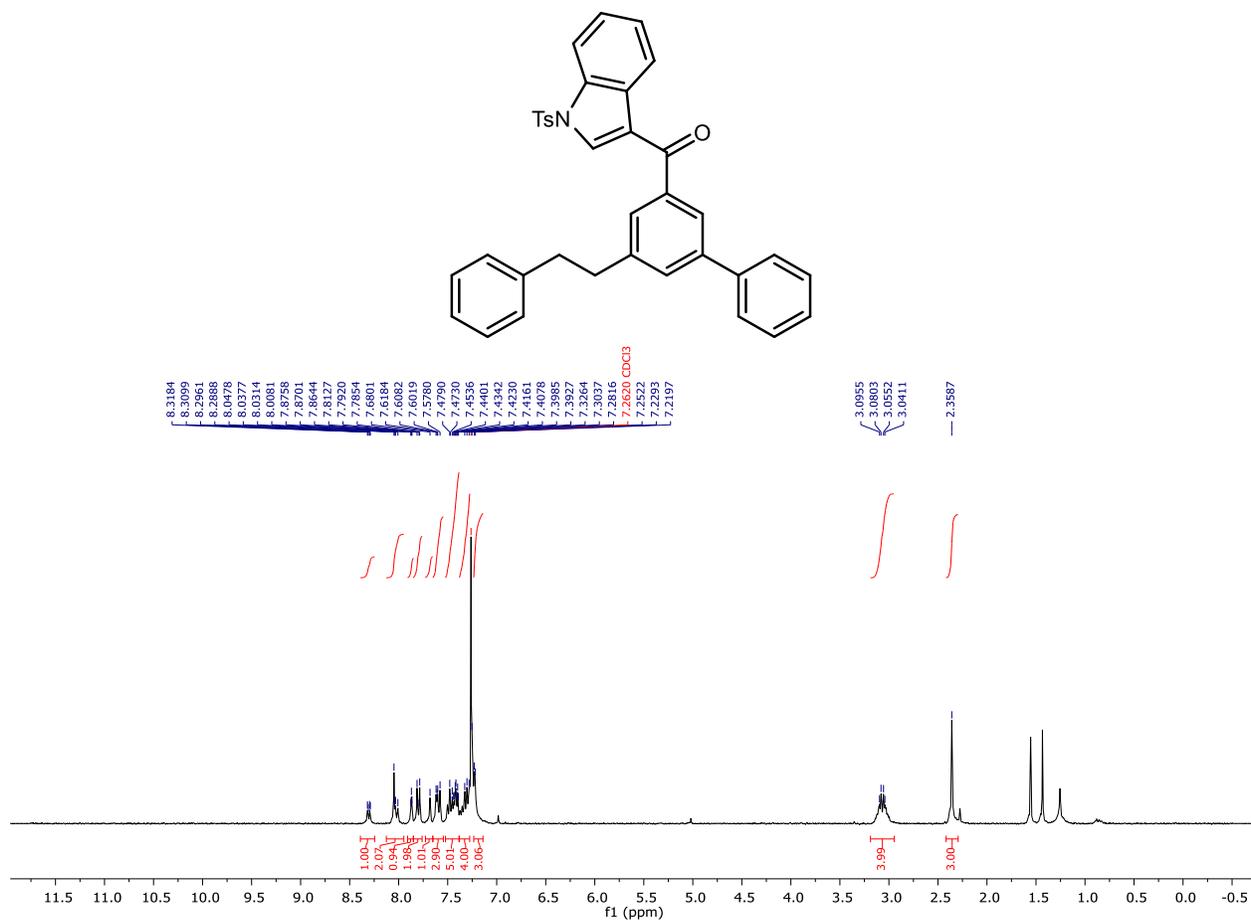


Figure S117. ¹H NMR of **44** (300 MHz, CDCl₃, 295 K).

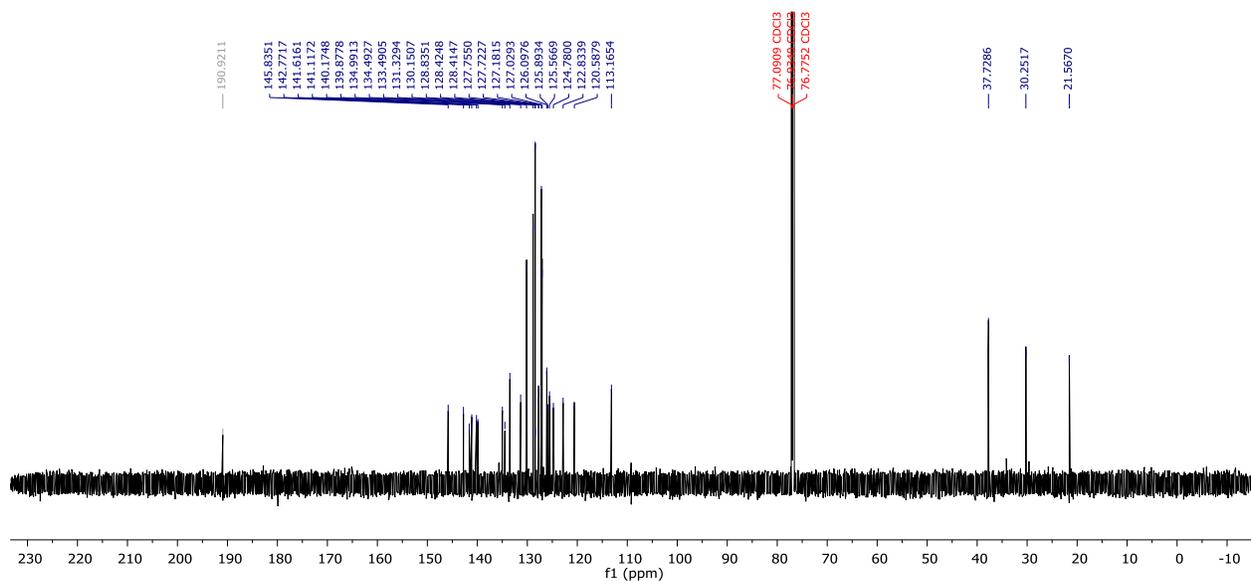


Figure S118. ¹³C NMR of **44** (800 MHz, CDCl₃, 295 K).

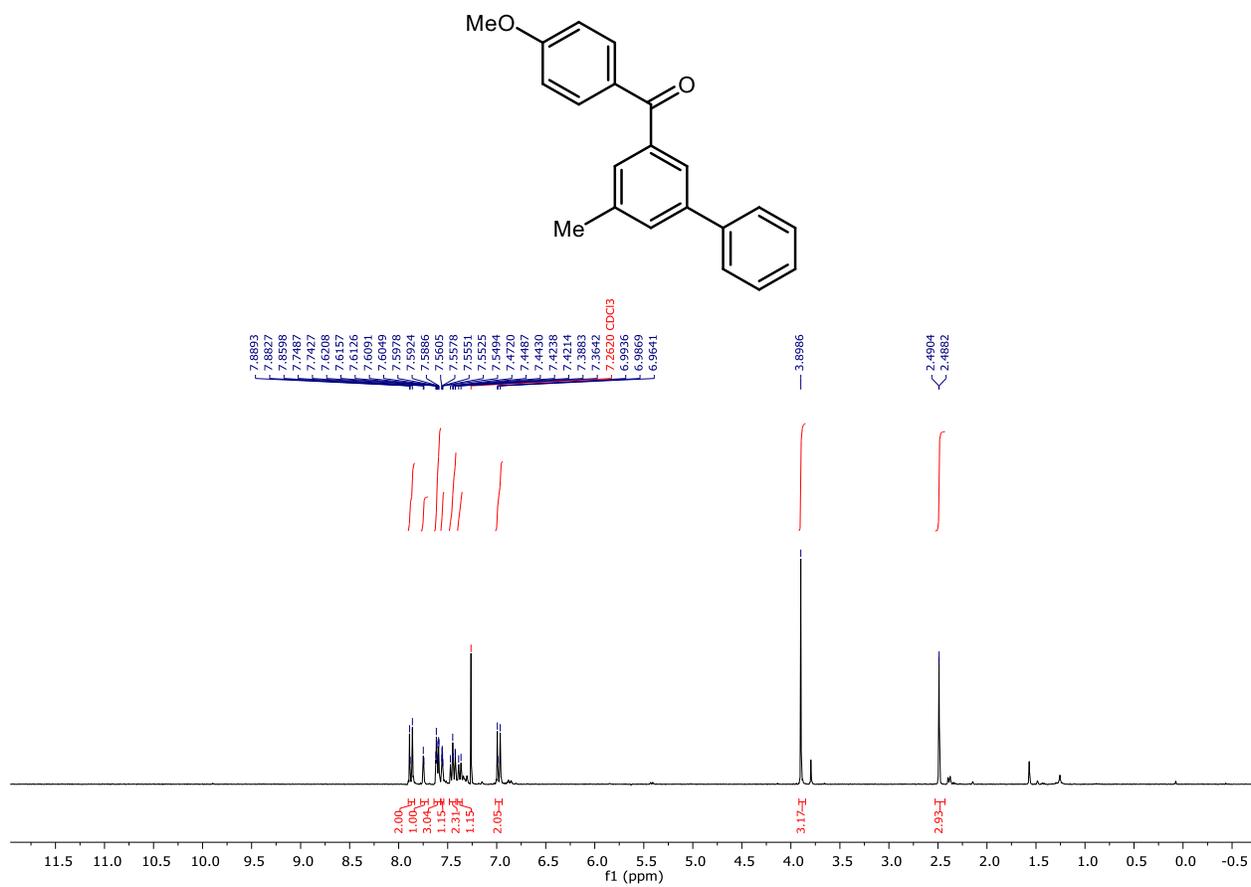


Figure S119. ¹H NMR of **45** (300 MHz, CDCl₃, 295 K).

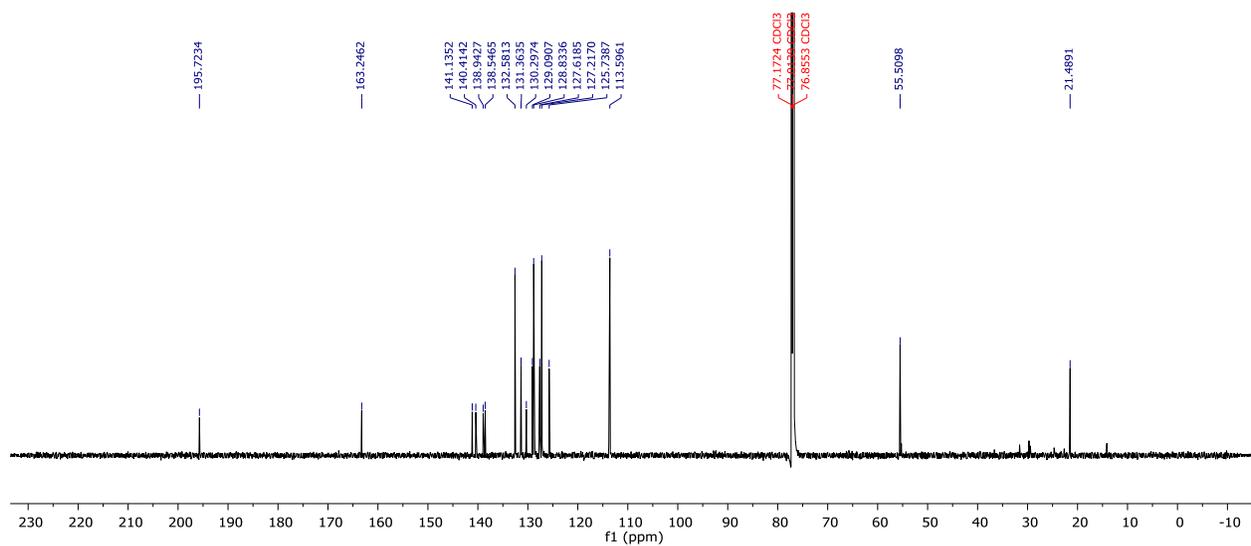


Figure S120. ¹³C NMR of **45** (800 MHz, CDCl₃, 295 K).

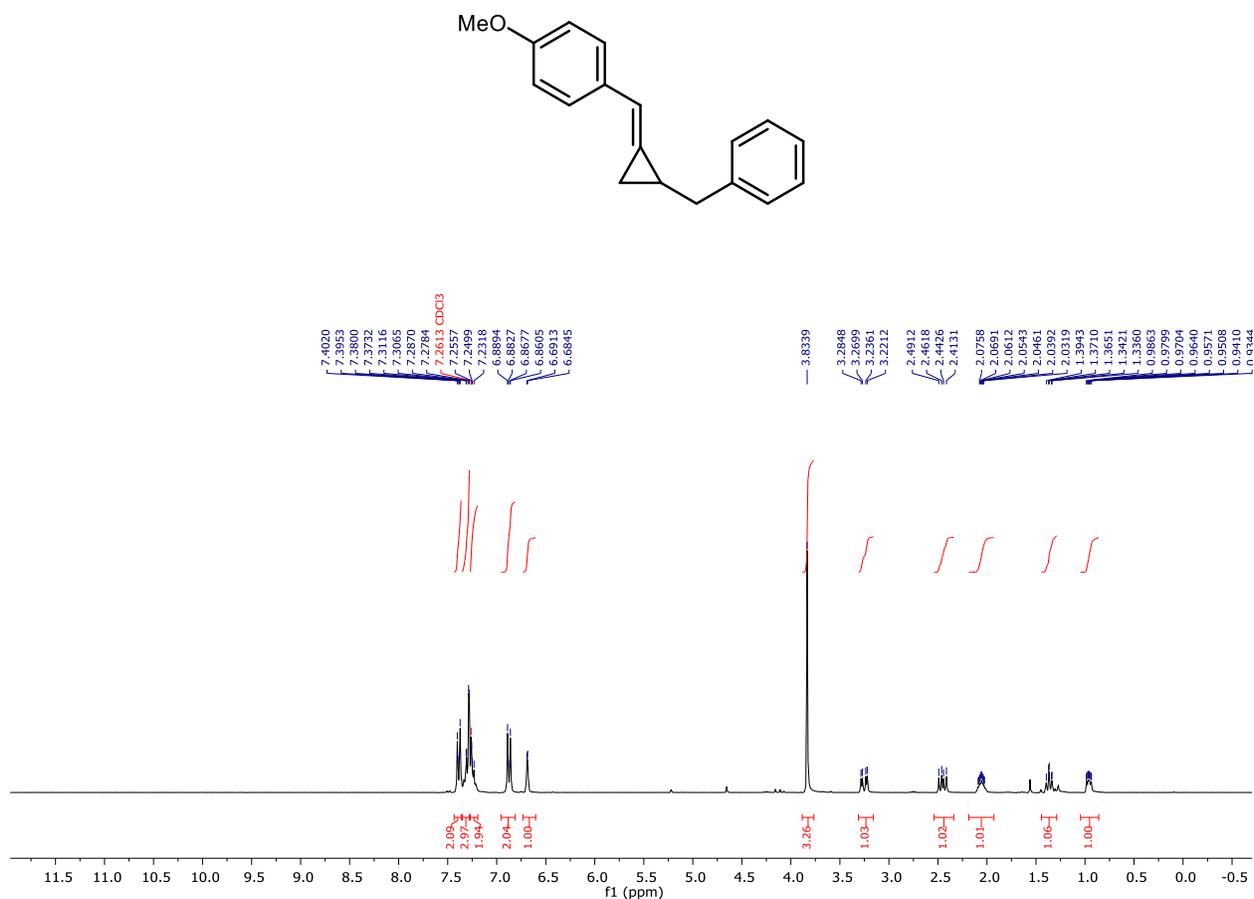


Figure S121. ¹H NMR of **47** (300 MHz, CDCl₃, 295 K).

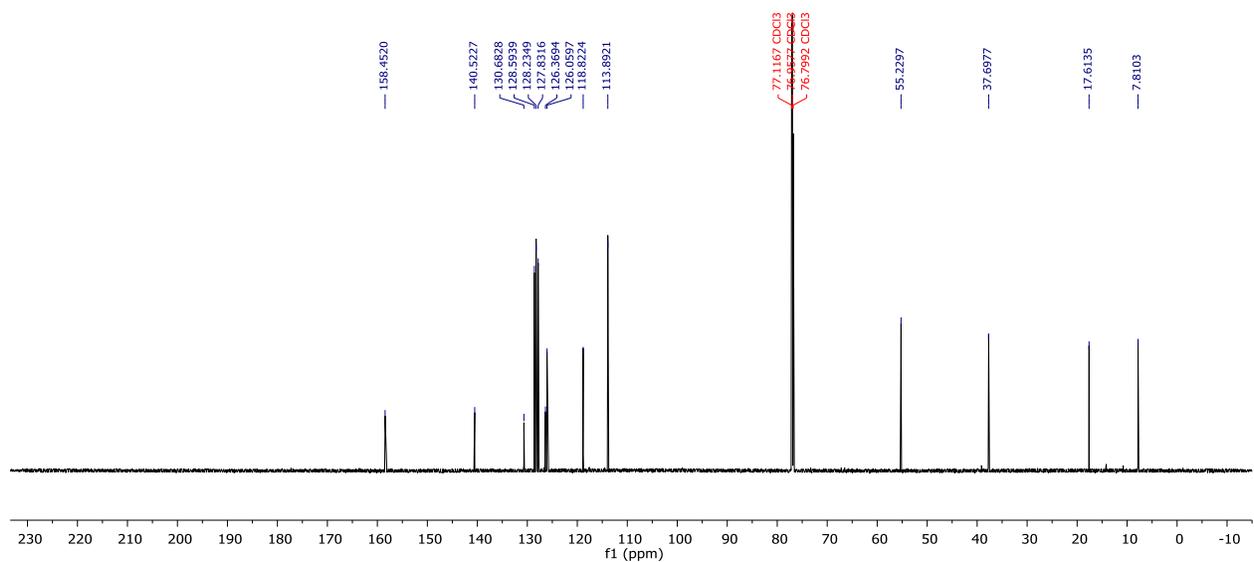


Figure S122. ¹³C NMR of **47** (800 MHz, CDCl₃, 295 K).

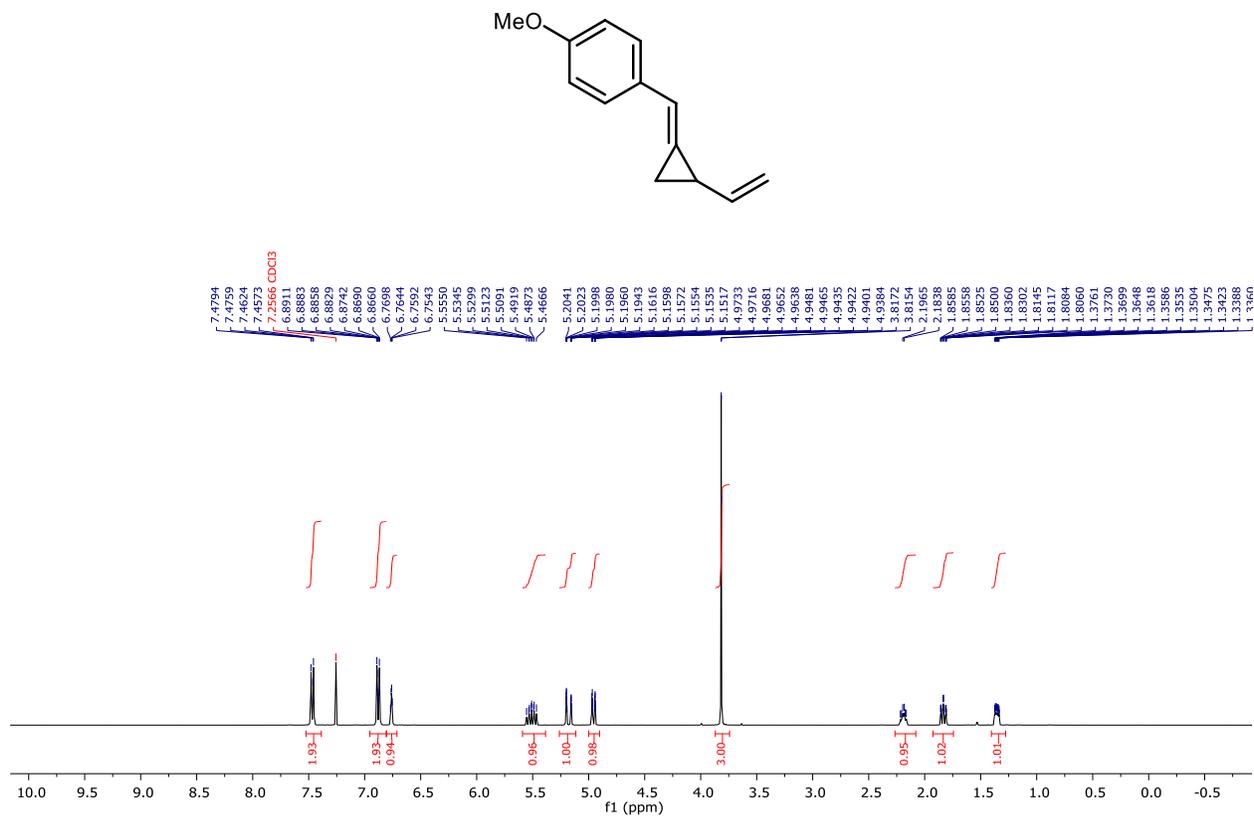


Figure S123. ¹H NMR of S21 (400 MHz, CDCl₃, 295 K).

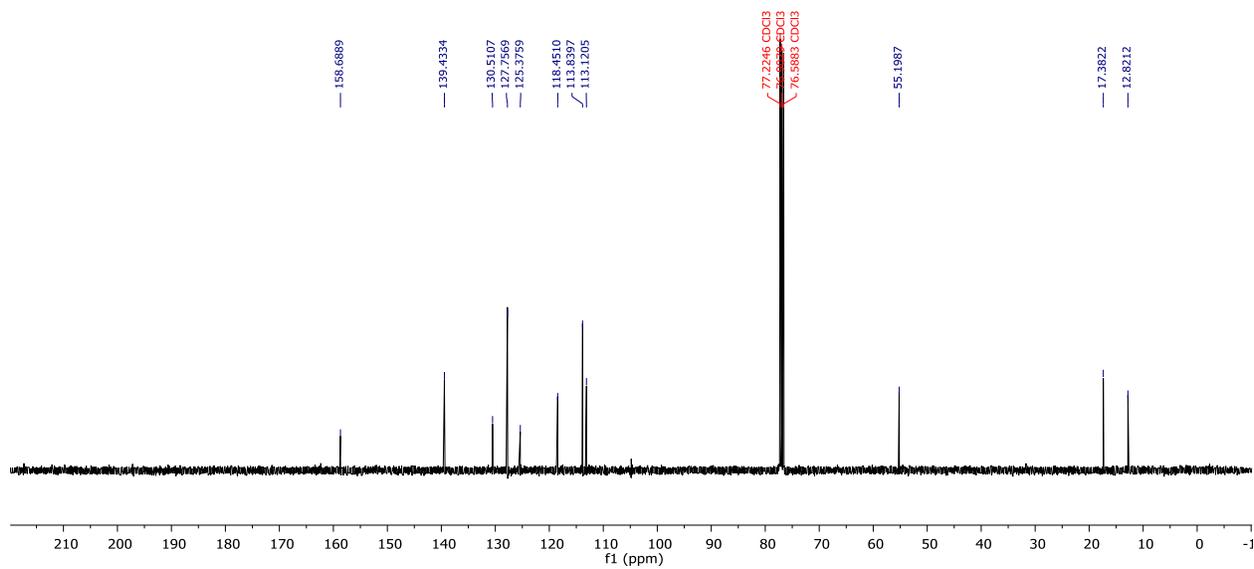


Figure S124. ¹³C NMR of S21 (400 MHz, CDCl₃, 295 K).

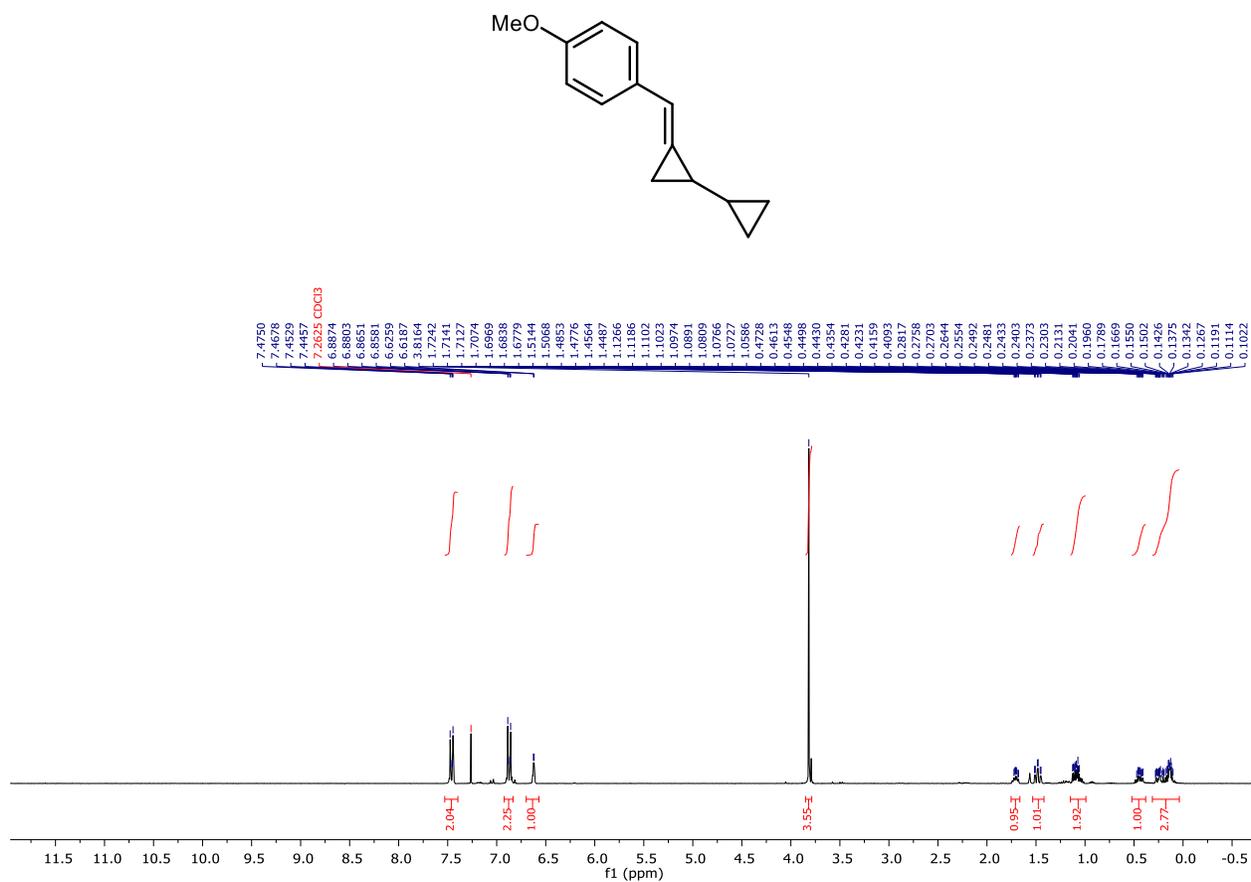


Figure S125. ¹H NMR of 4 (300 MHz, CDCl₃, 295 K).

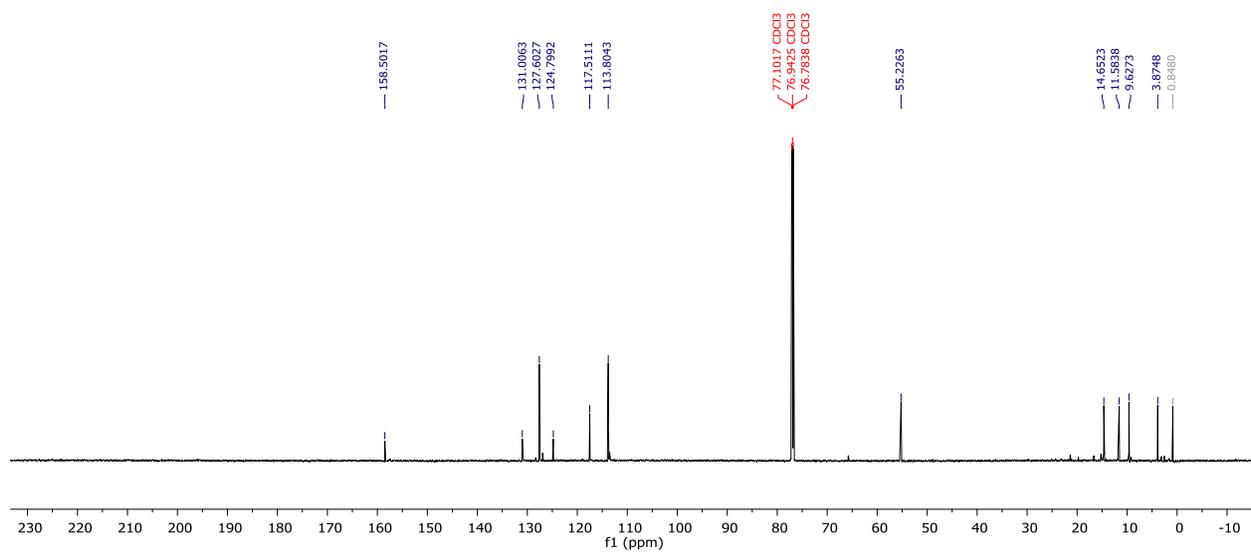


Figure S126. ¹³C NMR of 4 (800 MHz, CDCl₃, 295 K).

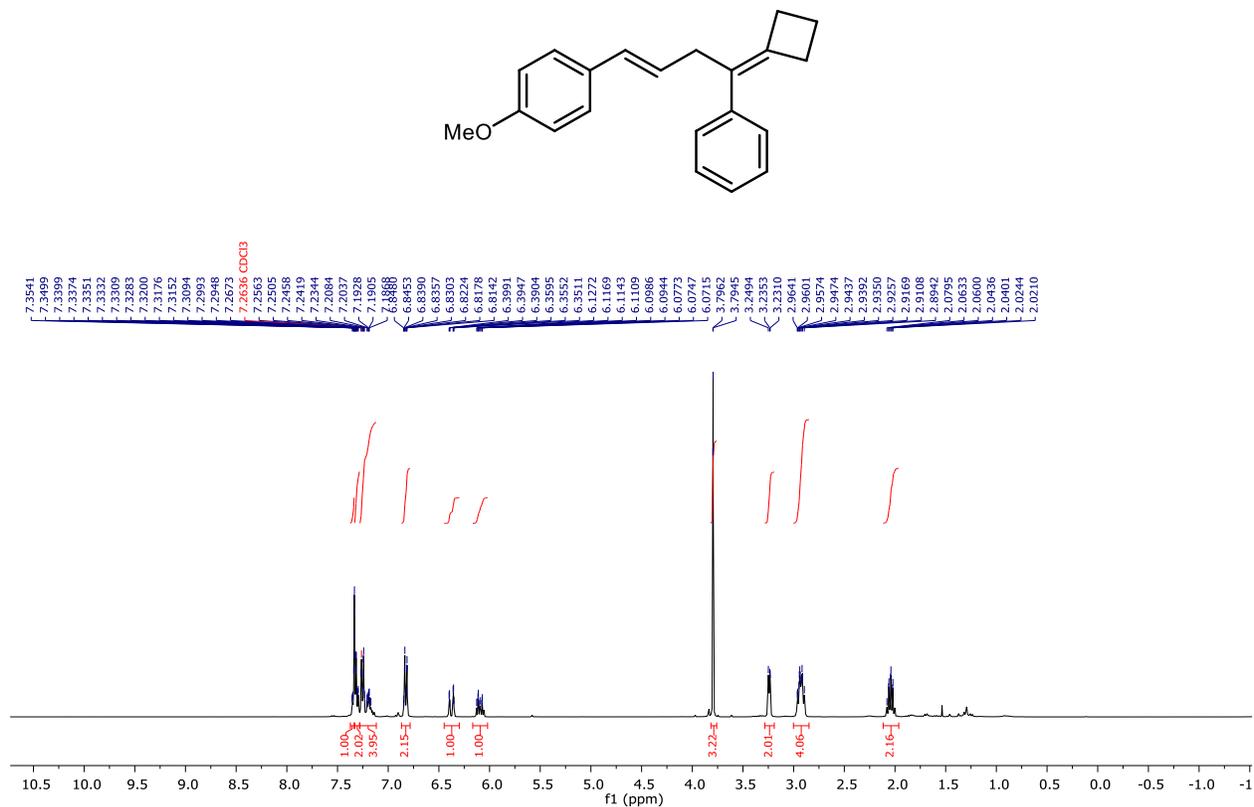


Figure S127. ¹H NMR of **49** (300 MHz, CDCl₃, 295 K).

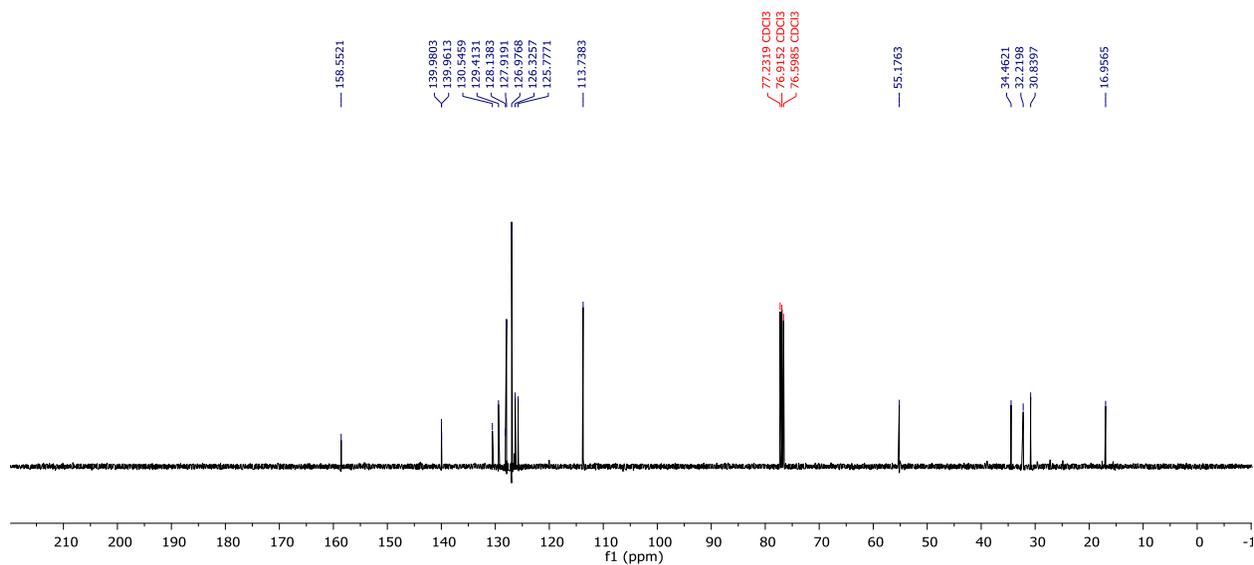


Figure S128. ¹³C NMR of **49** (800 MHz, CDCl₃, 295 K).

10. IR Data for Vinylcyclopropanes and [5+1]-Products

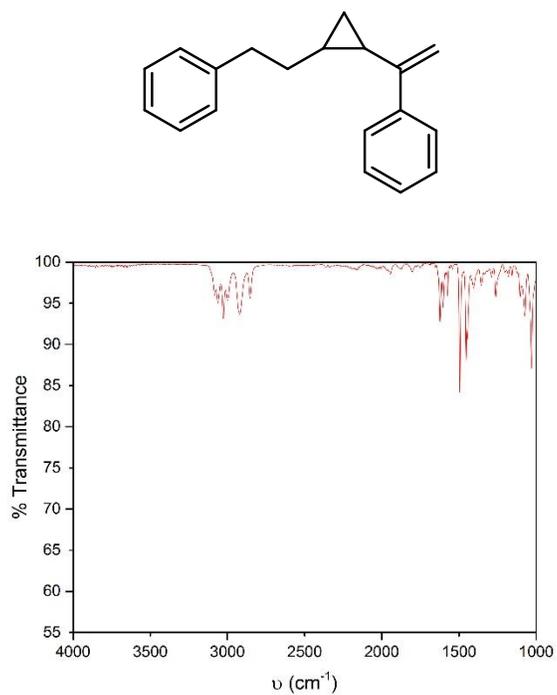


Figure S1. FT-IR of S1.

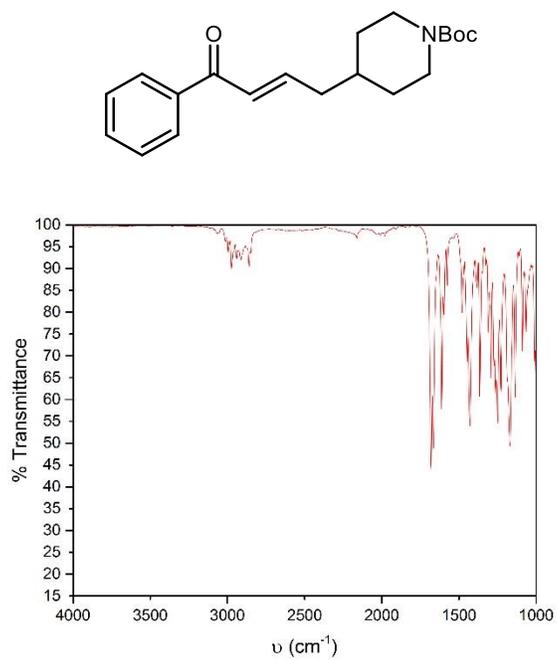


Figure S2. FT-IR of S2.

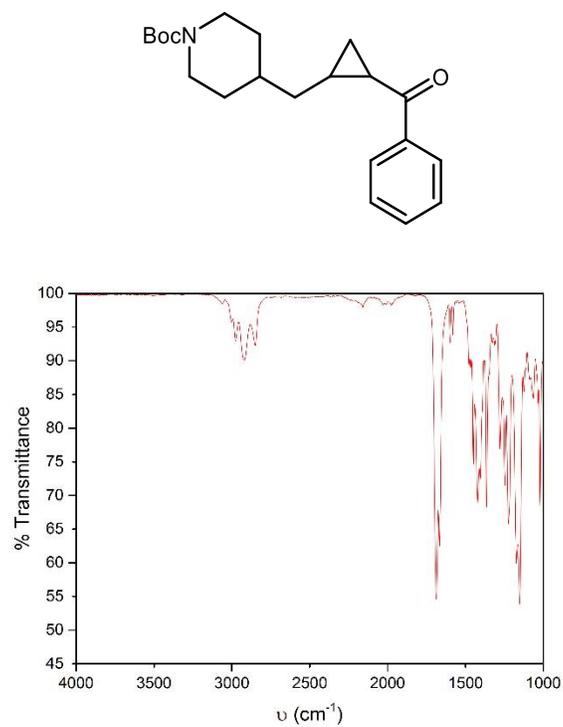


Figure S3. FT-IR of S3.

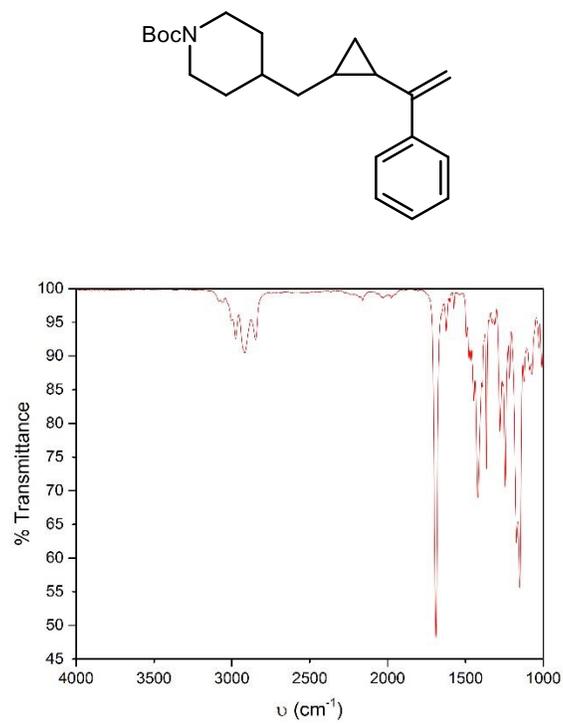


Figure S4. FT-IR of S4.

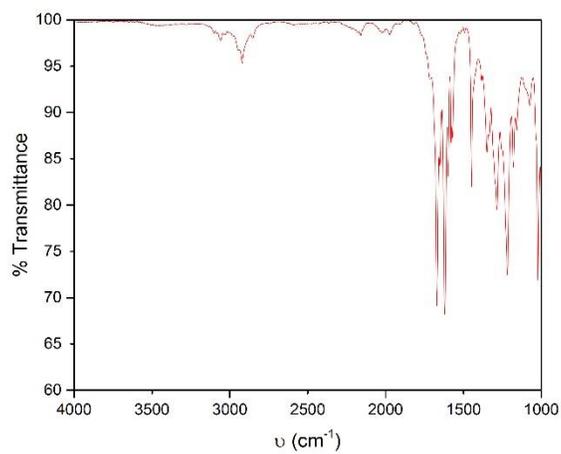
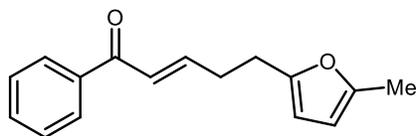


Figure S5. FT-IR of S5.

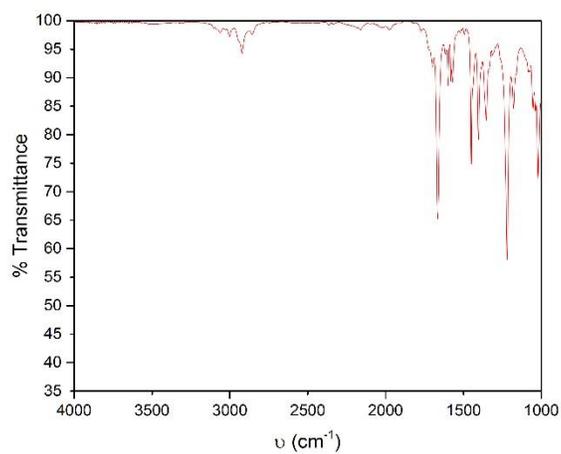
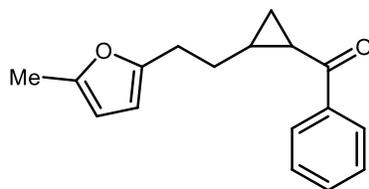


Figure S6. FT-IR of S6.

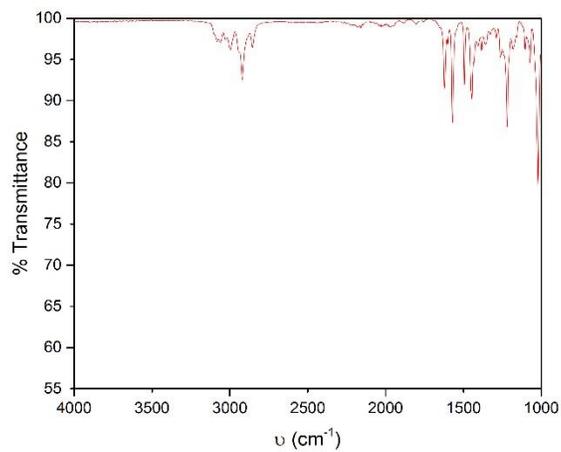
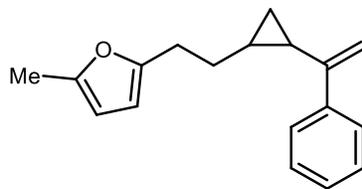


Figure S7. FT-IR of S7.

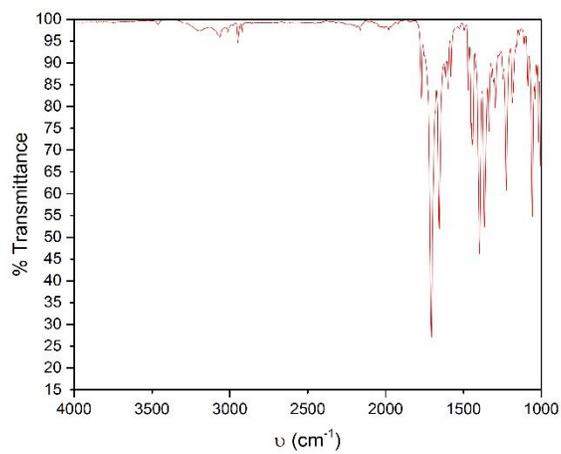
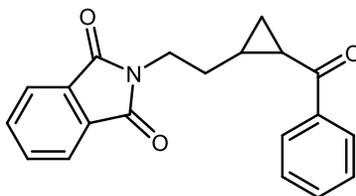


Figure S8. FT-IR of S8.

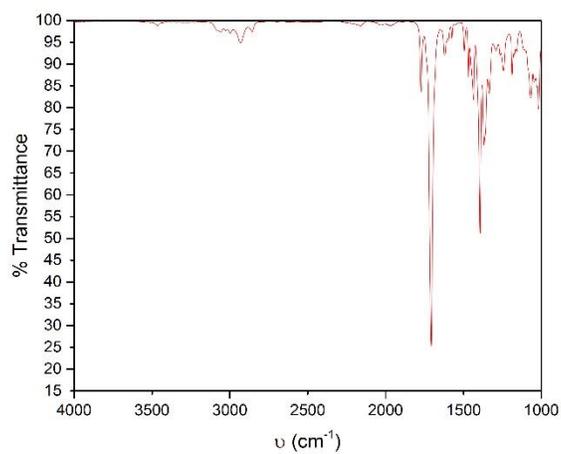
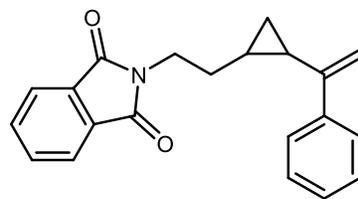


Figure S9. FT-IR of S9.

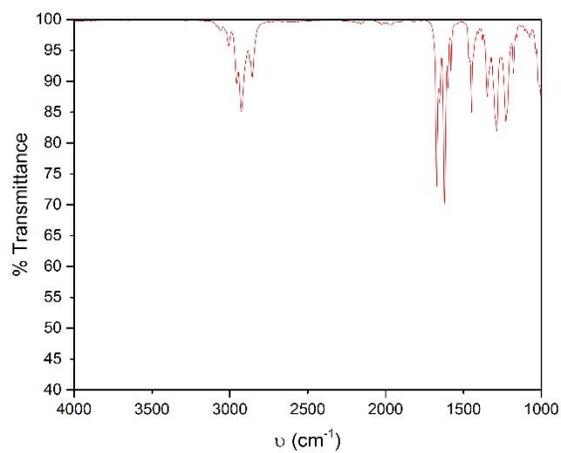
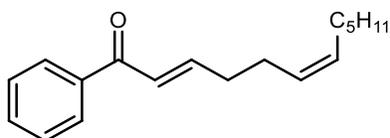


Figure S10. FT-IR of S10.

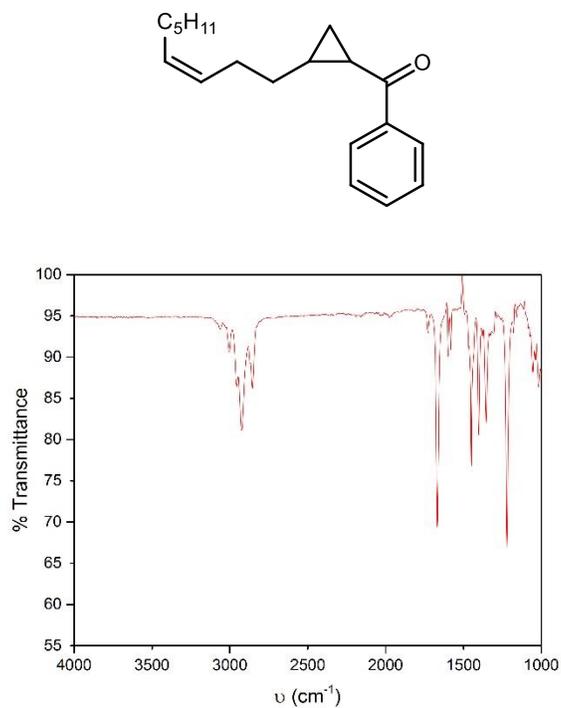


Figure S11. FT-IR of S11.

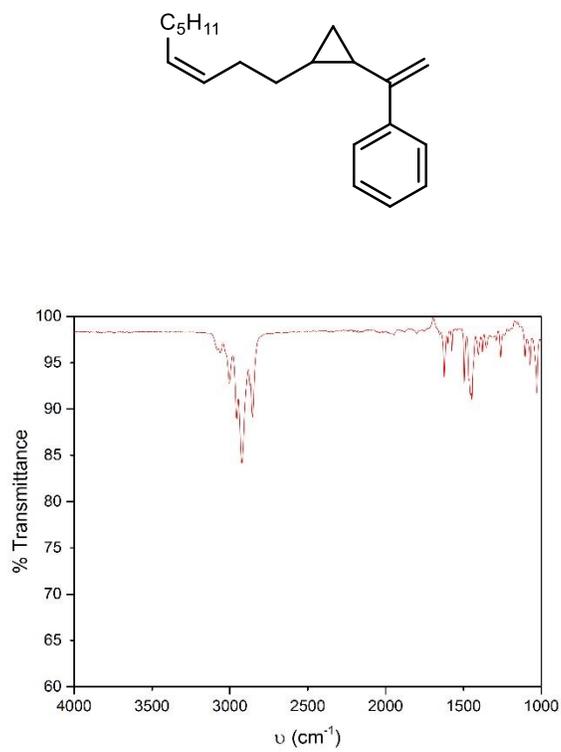


Figure S12. FT-IR of S12.

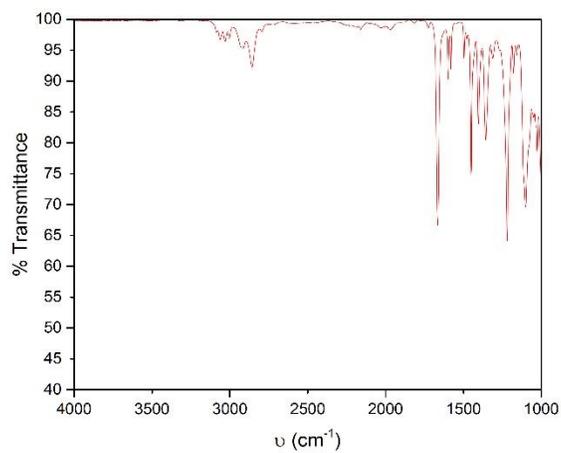
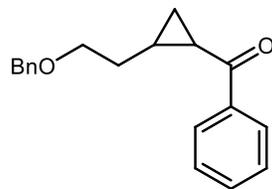


Figure S13. FT-IR of S13.

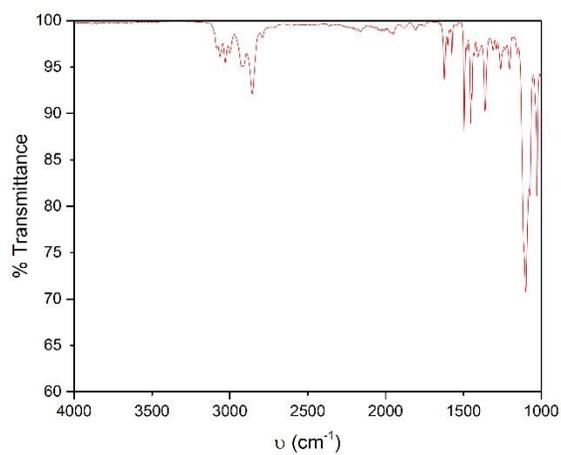
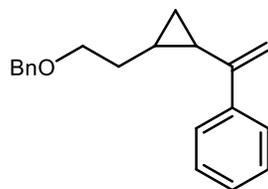


Figure S14. FT-IR of S14.

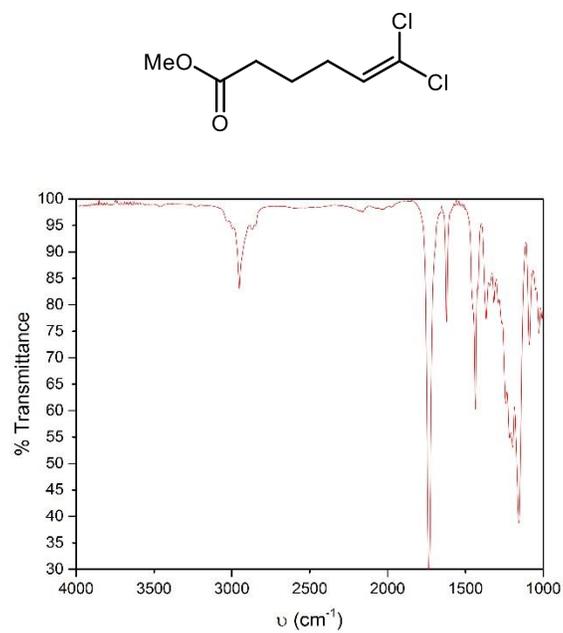


Figure S15. FT-IR of S15.

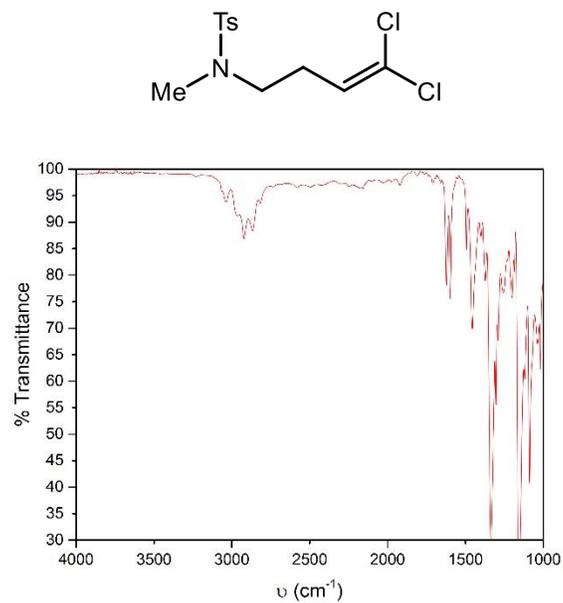


Figure S16. FT-IR of S16.

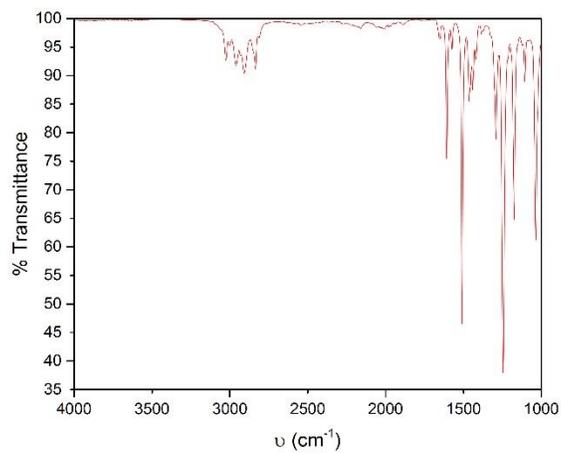
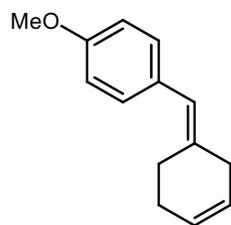


Figure S17. FT-IR of **3**.

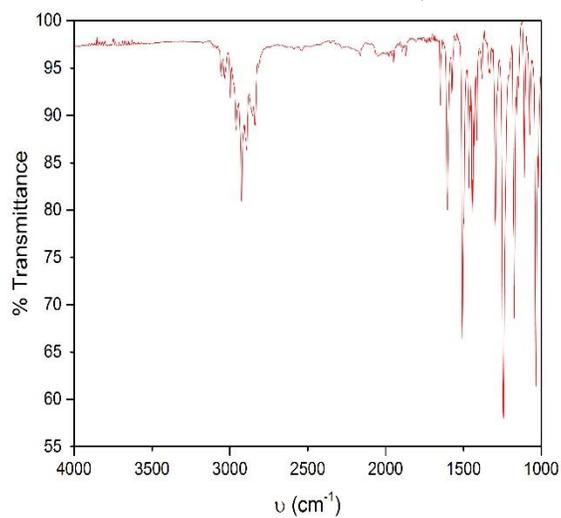
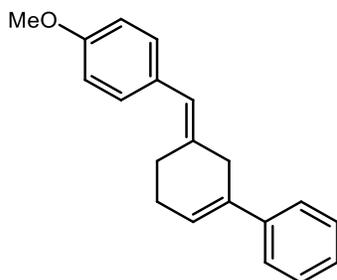


Figure S18. FT-IR of **6**.

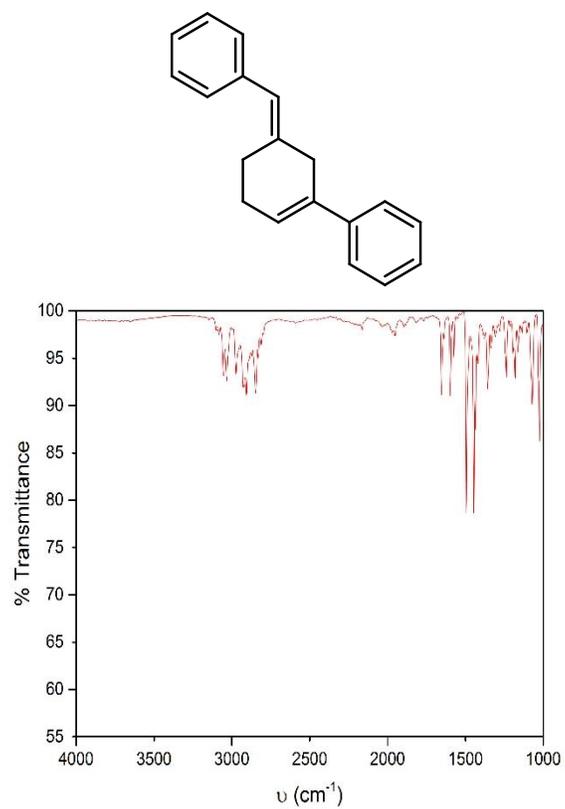


Figure S19. FT-IR of 11.

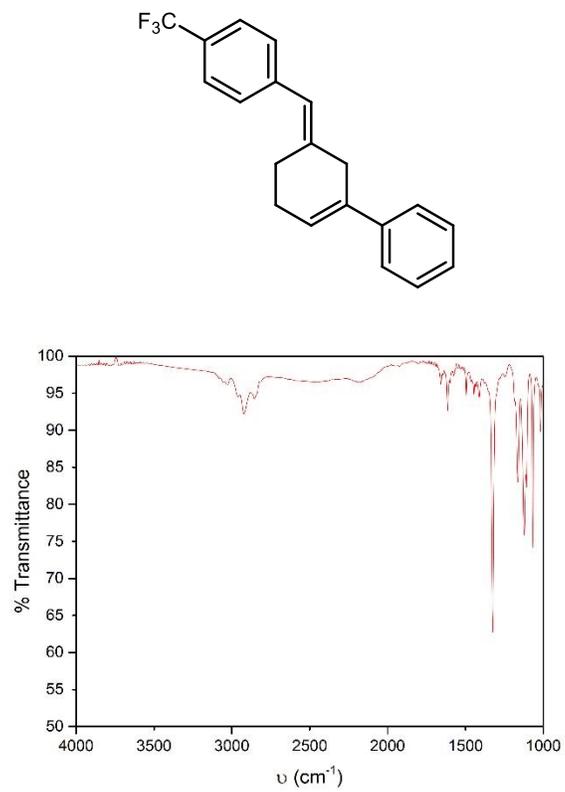


Figure S20. FT-IR of 12.

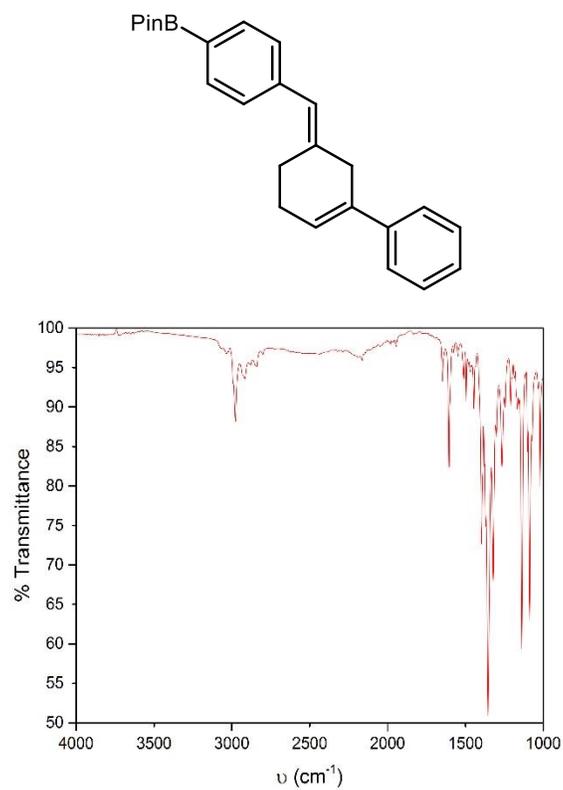


Figure S21. FT-IR of **13**.

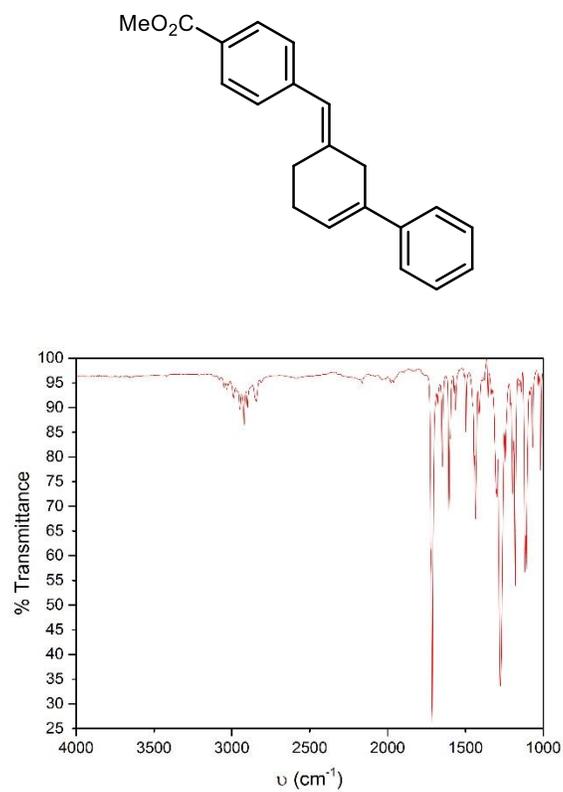


Figure S22. FT-IR of **14**.

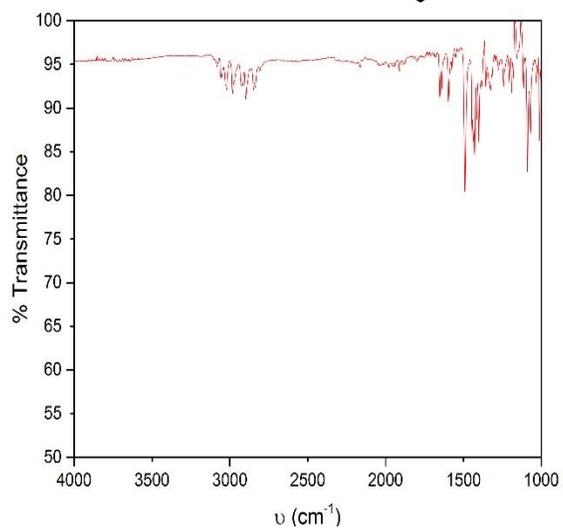
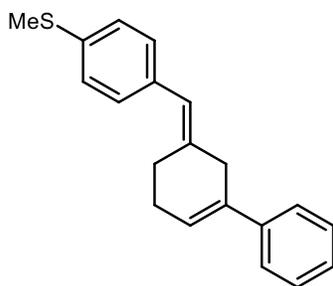


Figure S23. FT-IR of **15**.

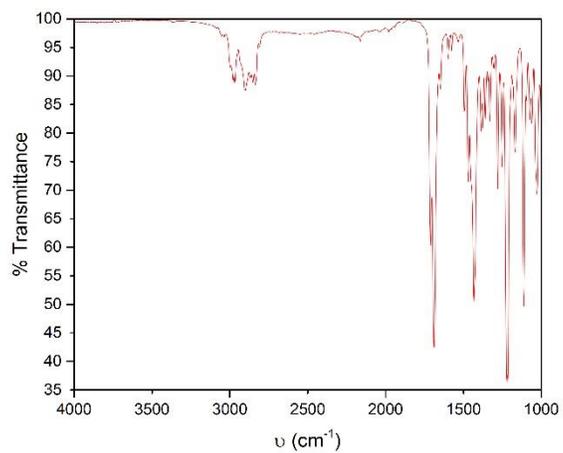
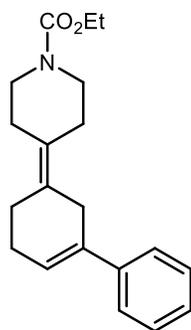


Figure S24. FT-IR of **16**.

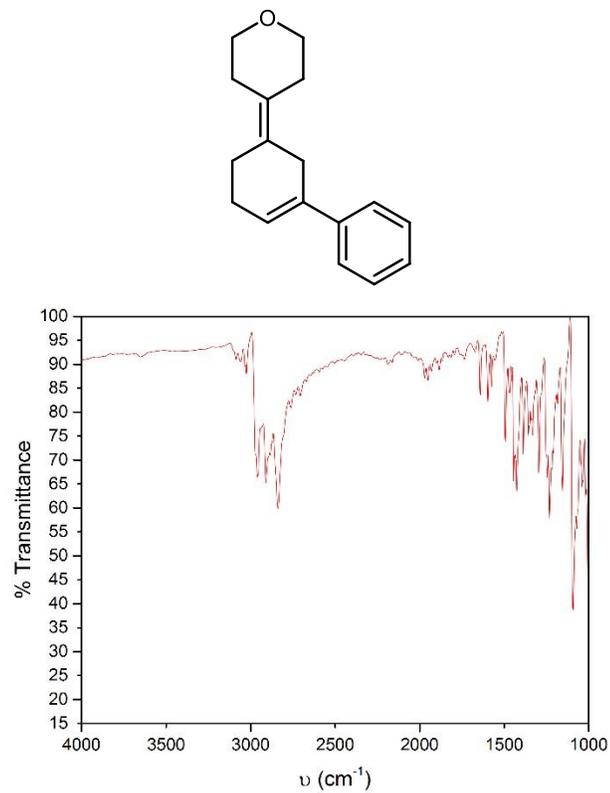


Figure S25. FT-IR of **17**.

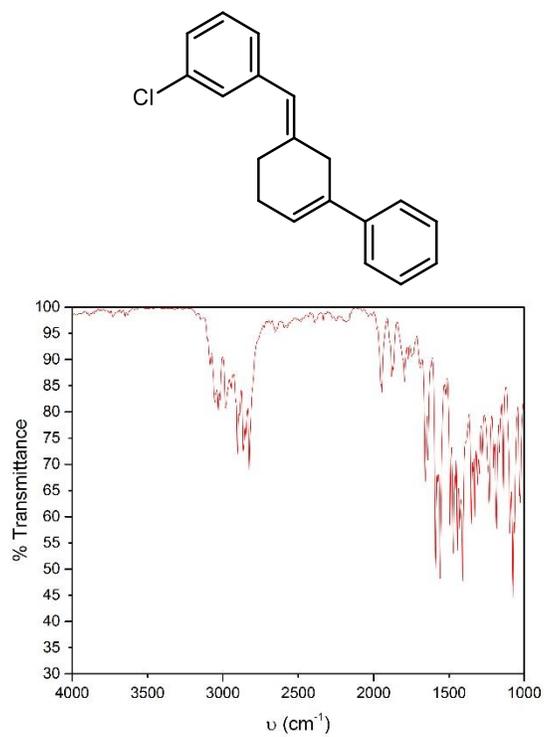


Figure S26. FT-IR of **18**.

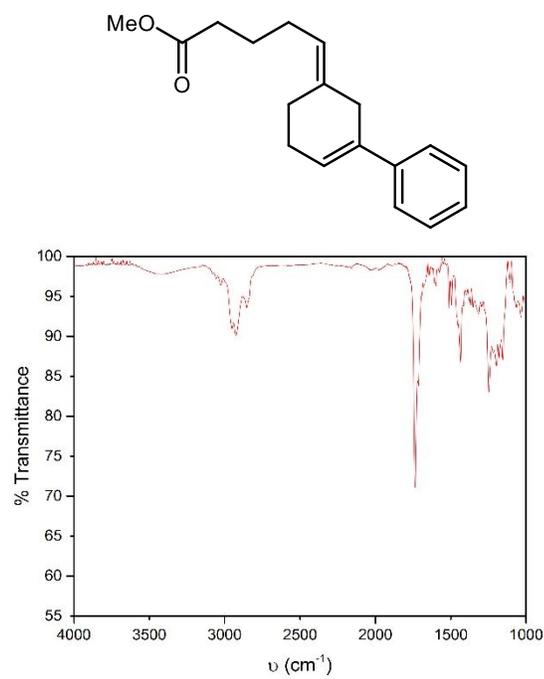


Figure S27. FT-IR of **19**.

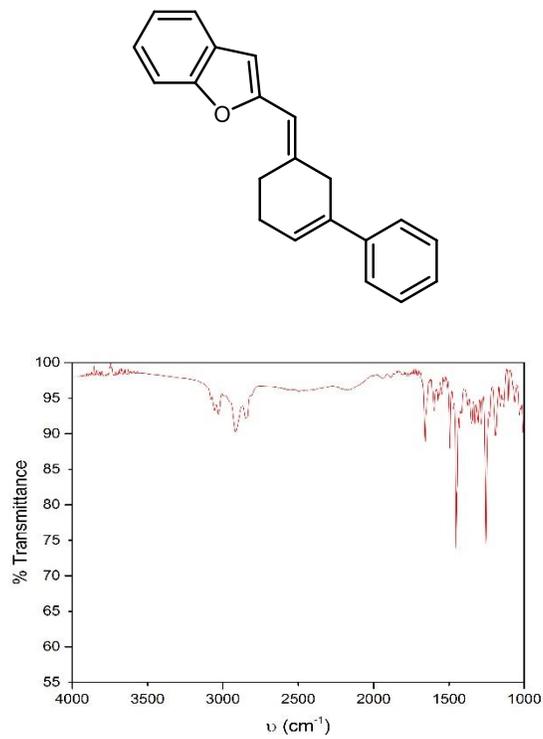


Figure S28. FT-IR of **20**.

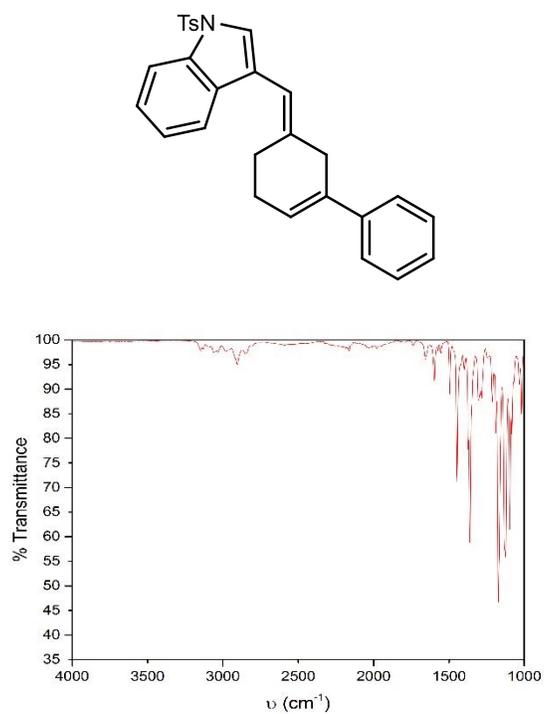


Figure S29. FT-IR of 21.

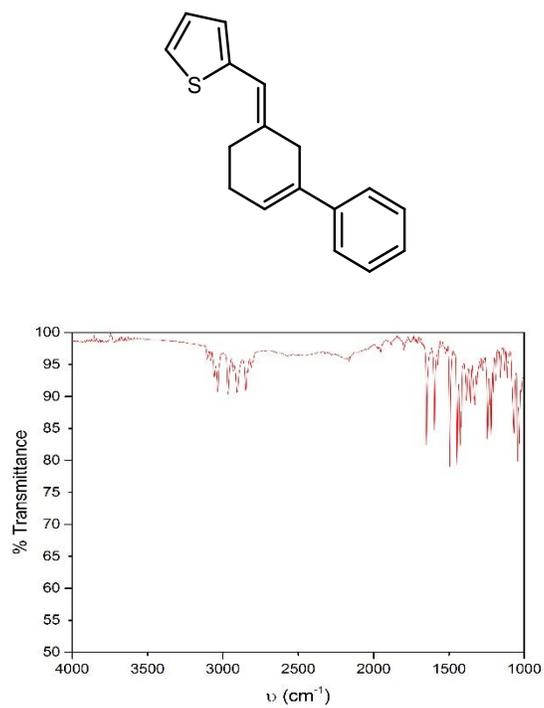


Figure S30. FT-IR of 22.

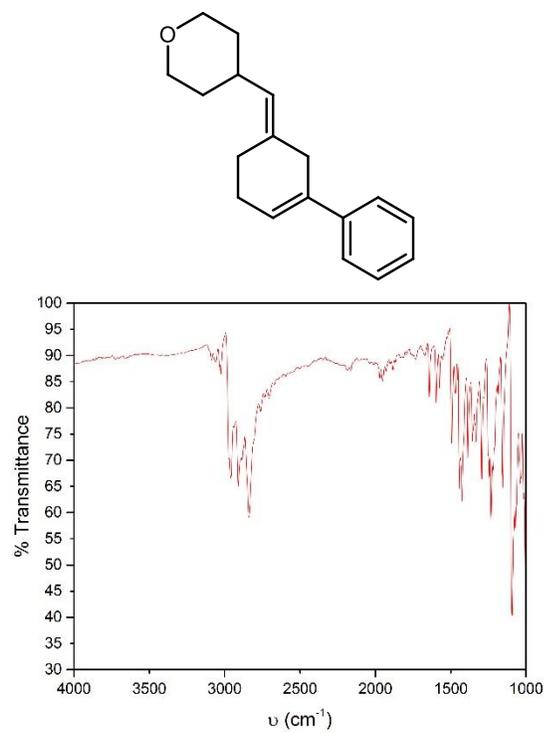


Figure S31. FT-IR of 23.

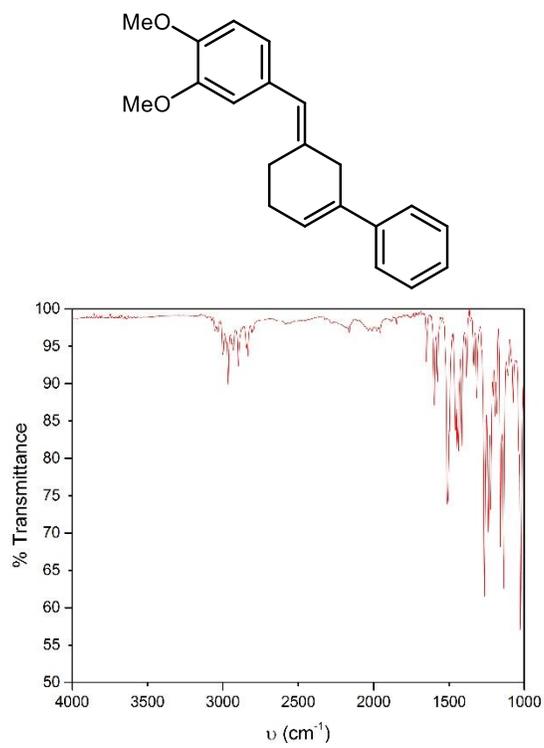


Figure S32. FT-IR of 24.

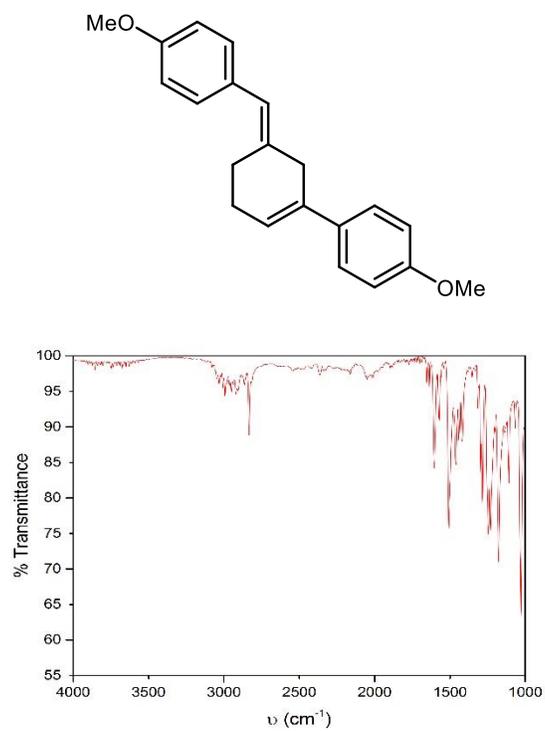


Figure S33. FT-IR of 25.

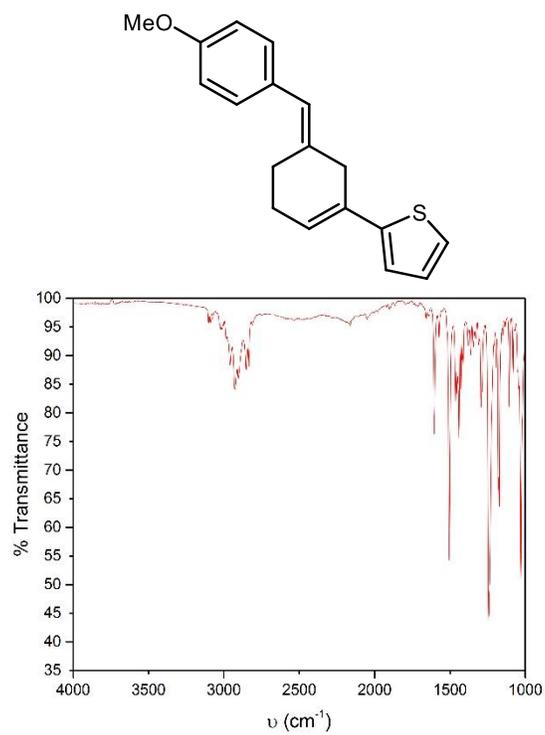


Figure S34. FT-IR of 26.

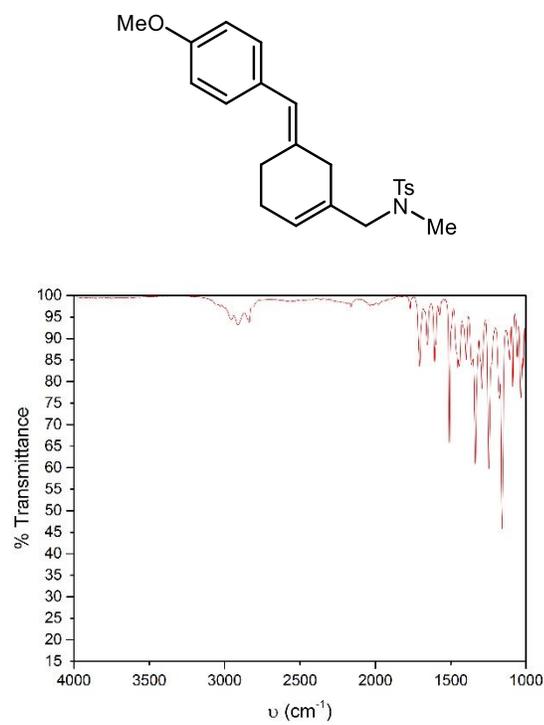


Figure S35. FT-IR of **27**.

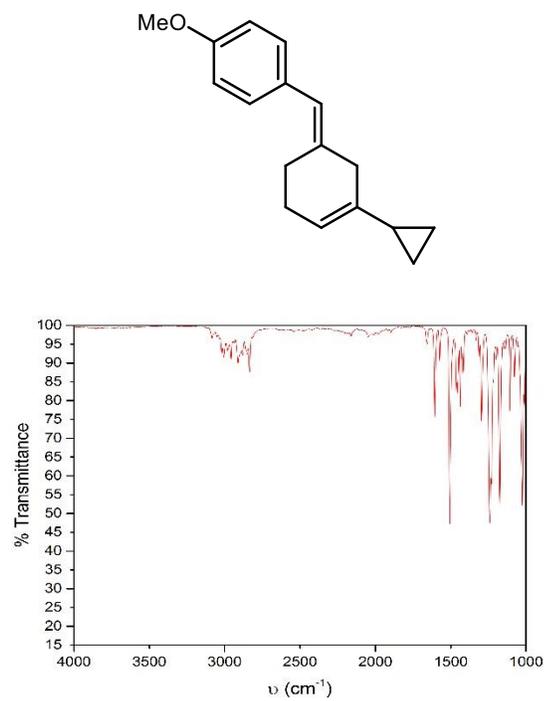


Figure S36. FT-IR of **28**.

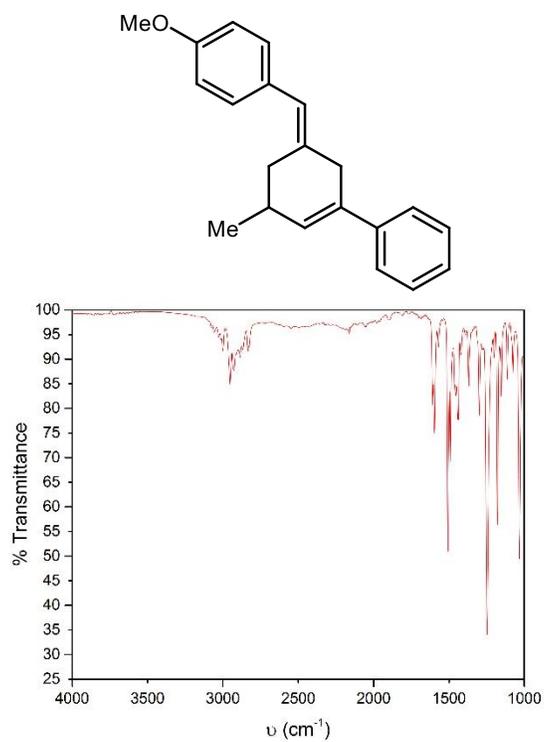


Figure S37. FT-IR of **30**.

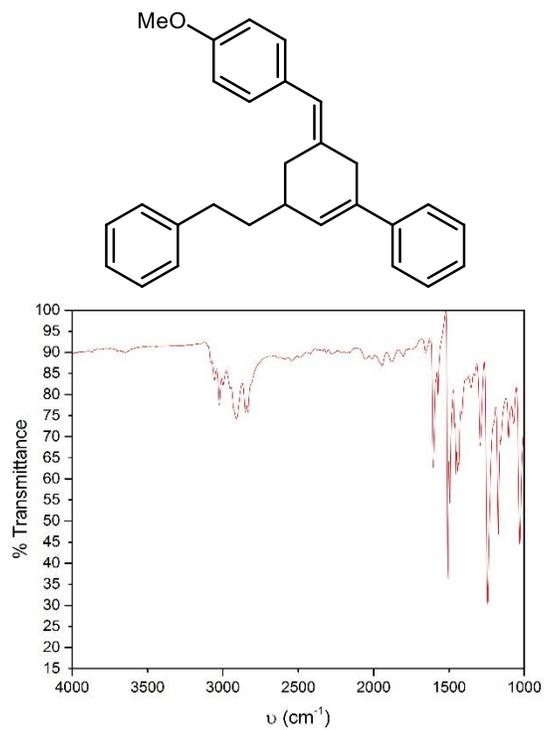


Figure S38. FT-IR of **31**.

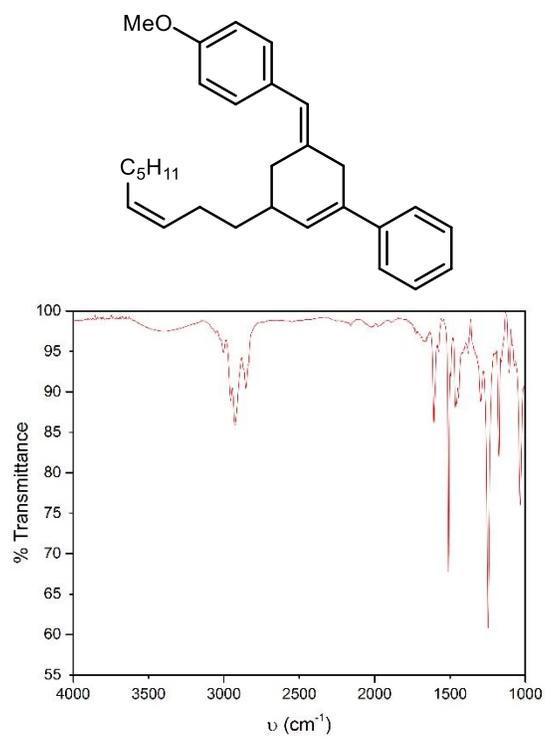


Figure S39. FT-IR of 32.

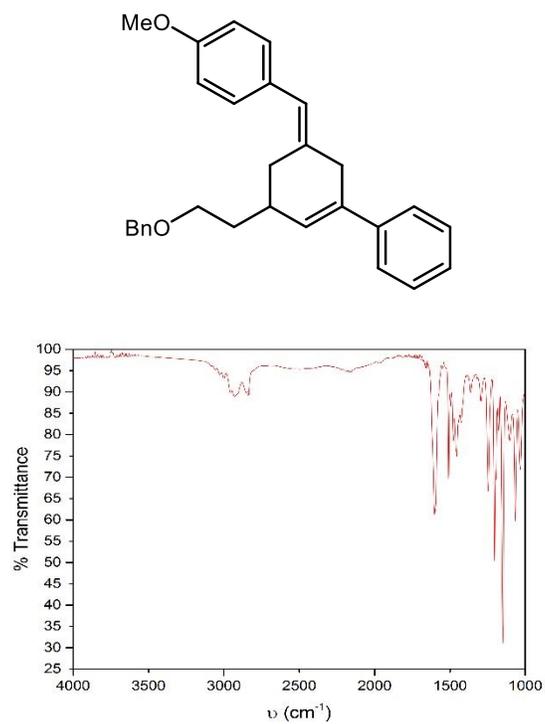


Figure S40. FT-IR of 33.

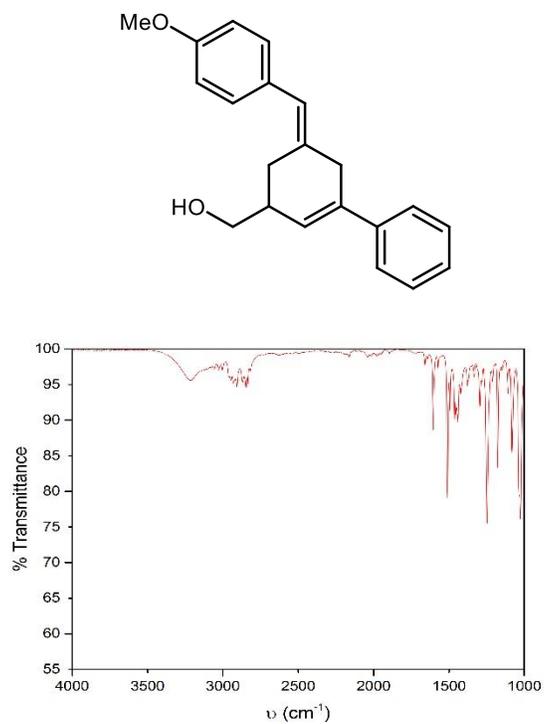


Figure S41. FT-IR of 34.

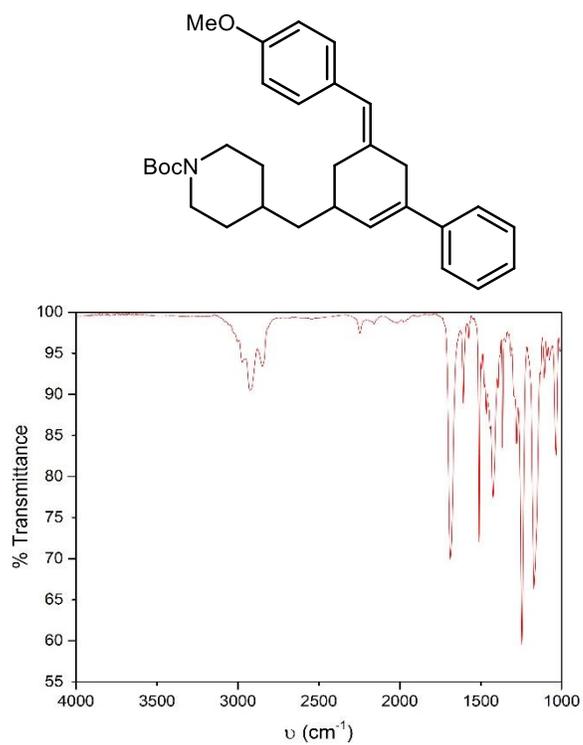


Figure S42. FT-IR of 35.

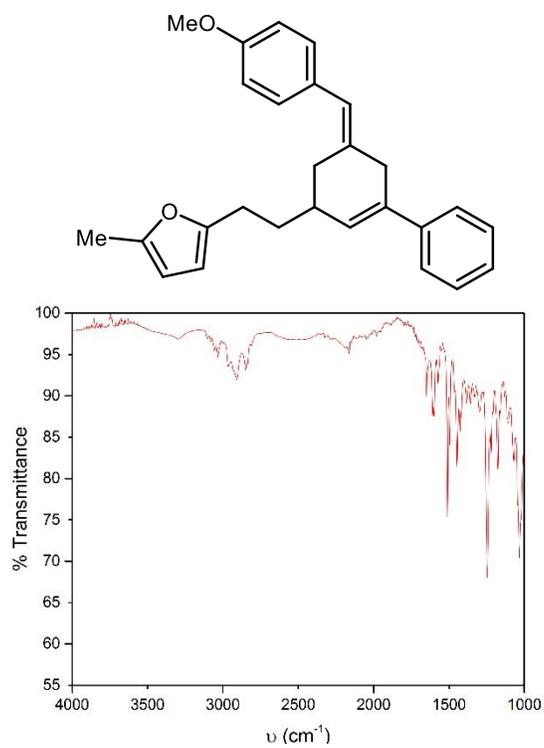


Figure S43. FT-IR of 36.

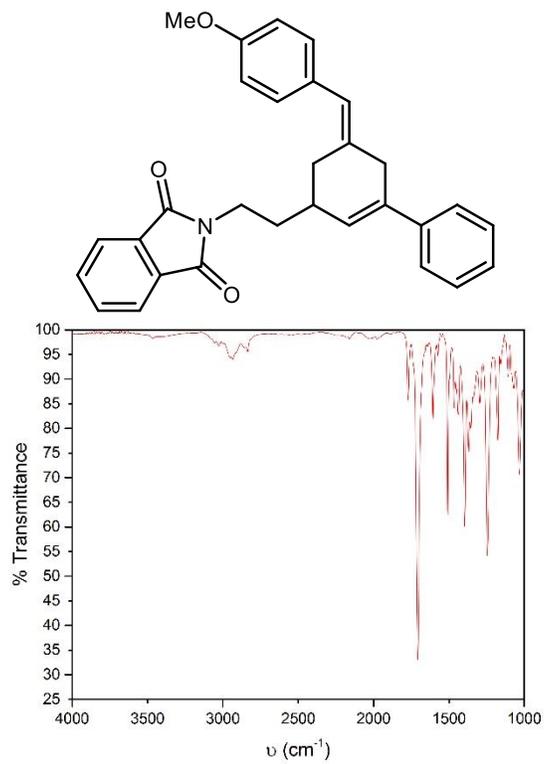


Figure S44. FT-IR of 37.

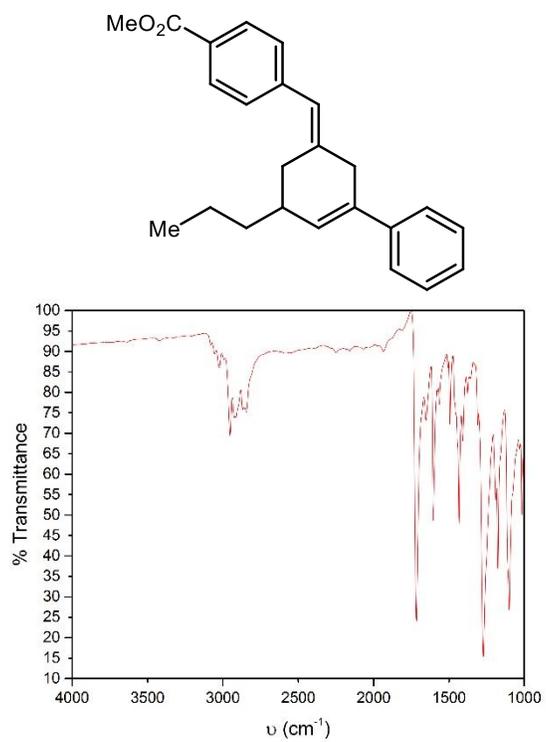


Figure S45. FT-IR of S18.

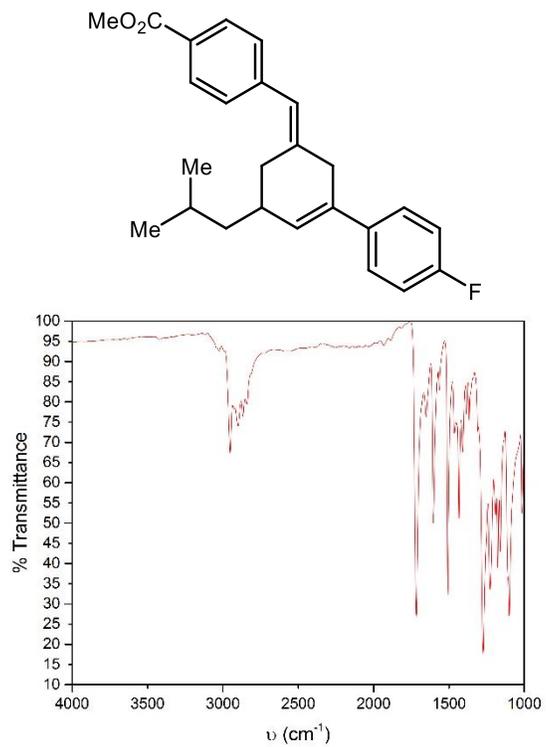


Figure S46. FT-IR of S19.

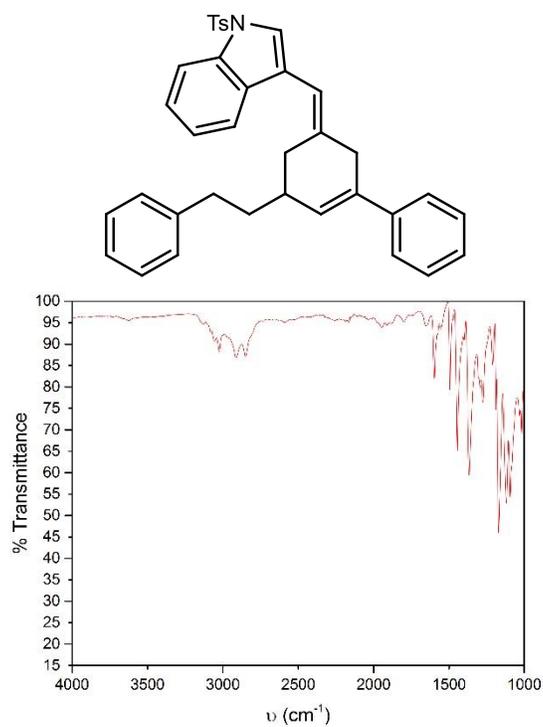


Figure S47. FT-IR of S20.

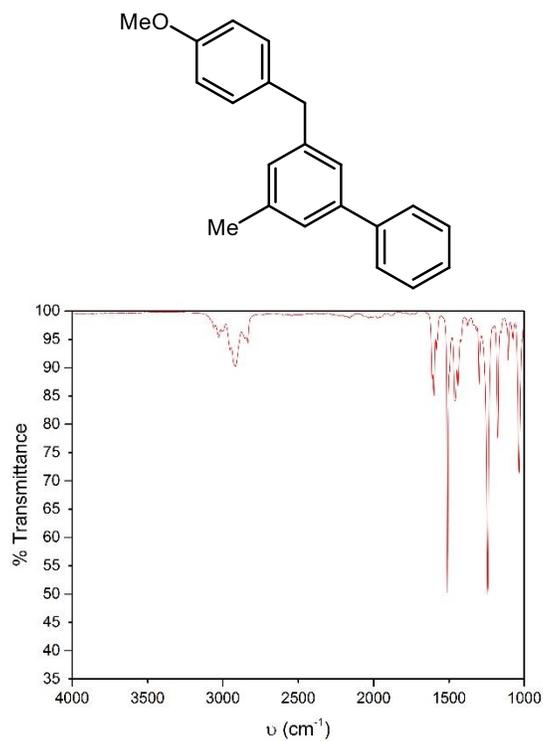


Figure S48. FT-IR of 38.

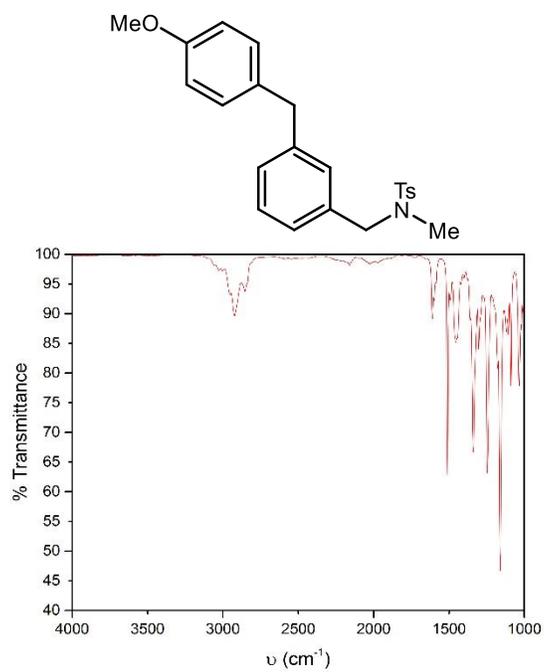


Figure S49. FT-IR of 39.

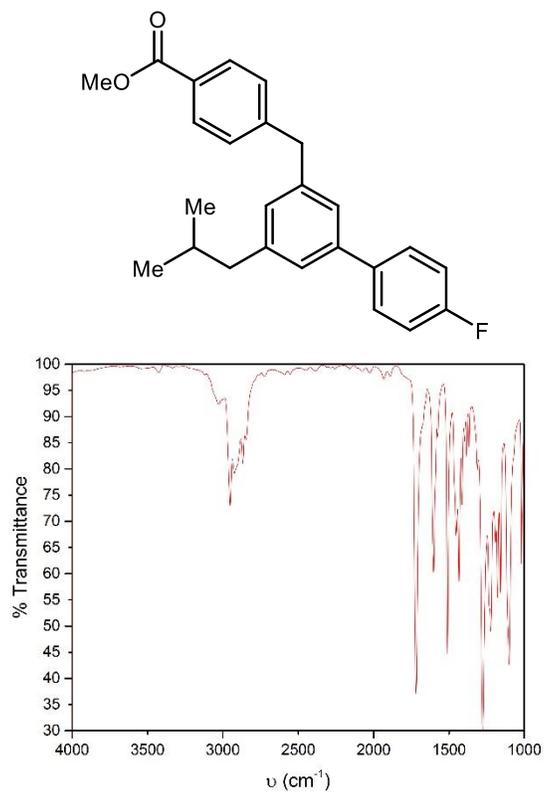


Figure S50. FT-IR of 40.

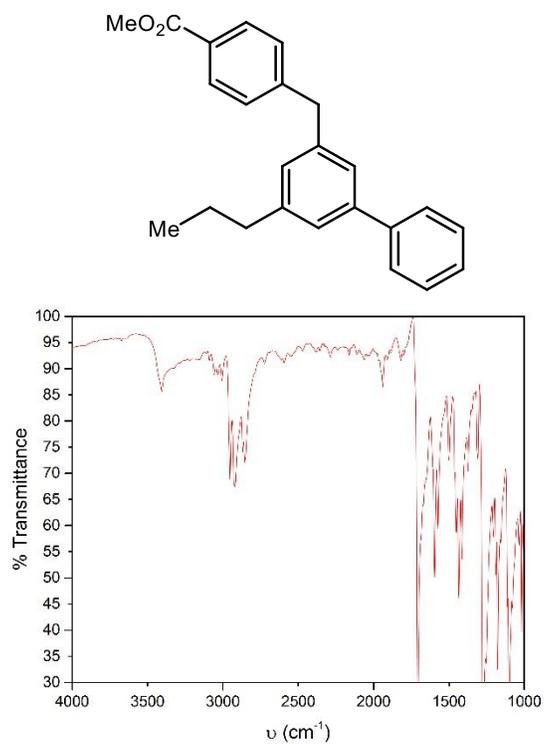


Figure S51. FT-IR of **41**.

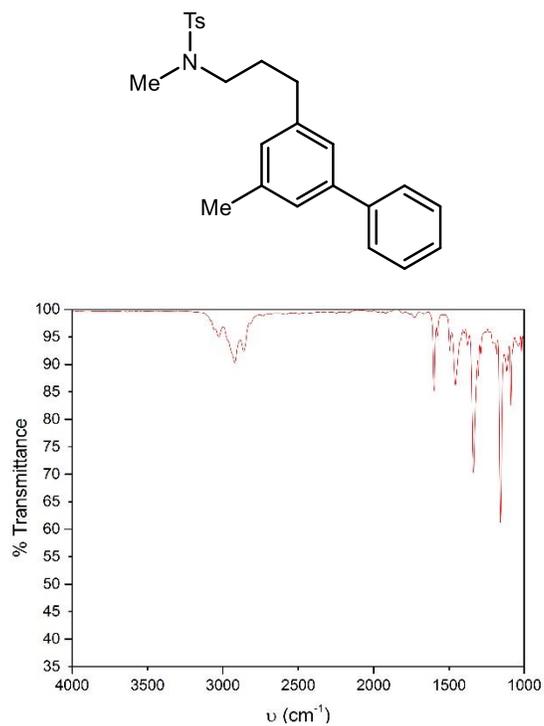


Figure S52. FT-IR of **42**.

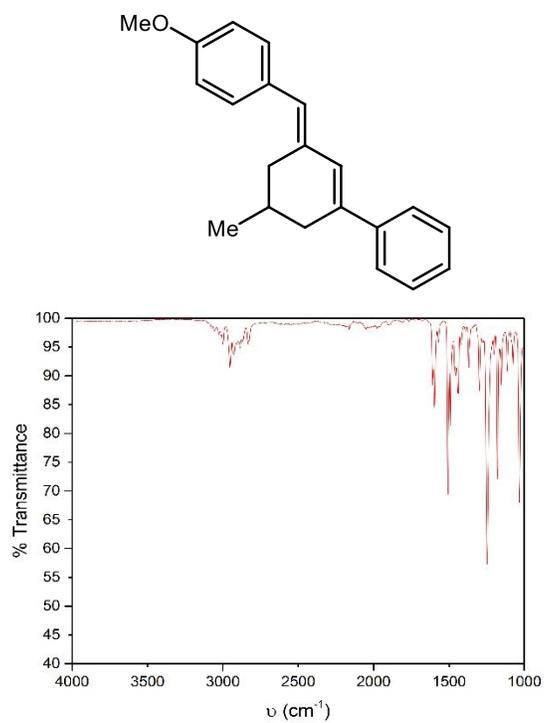


Figure S53. FT-IR of **43**.

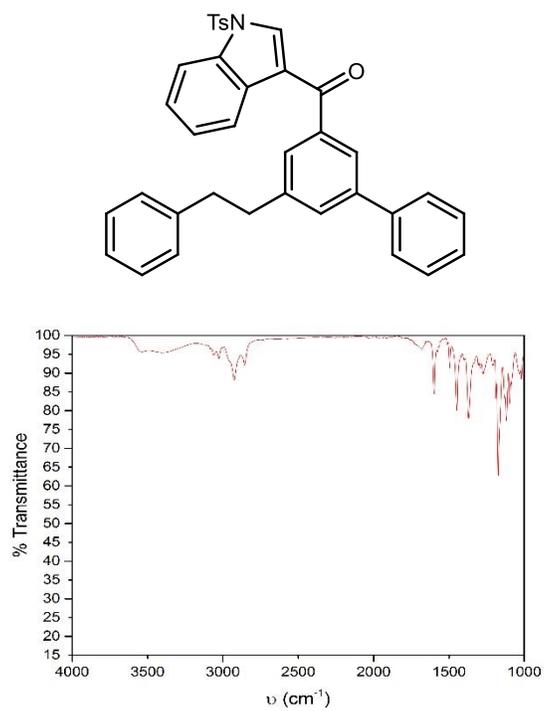


Figure S54. FT-IR of **44**.

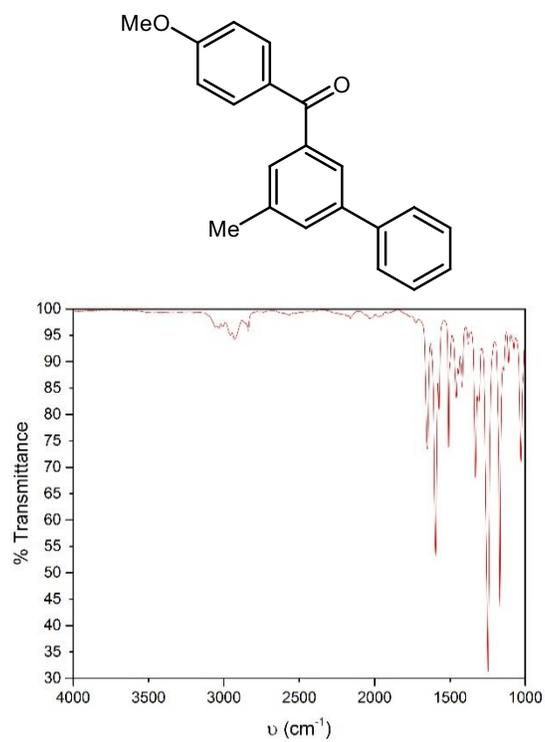


Figure S55. FT-IR of **45**.

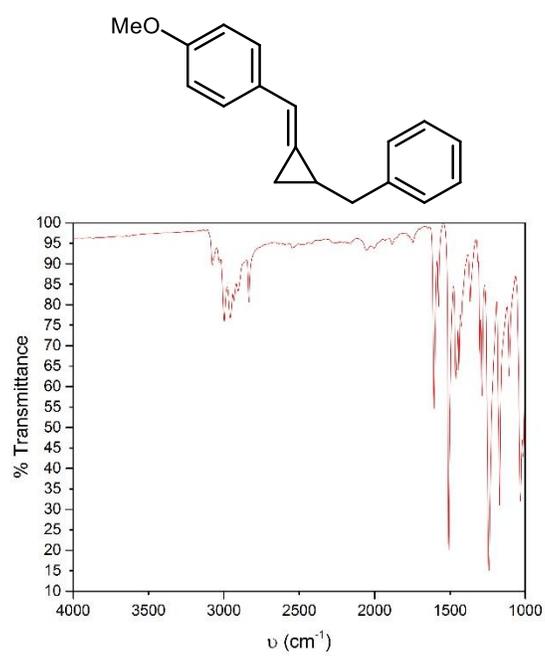


Figure S56. FT-IR of **47**.

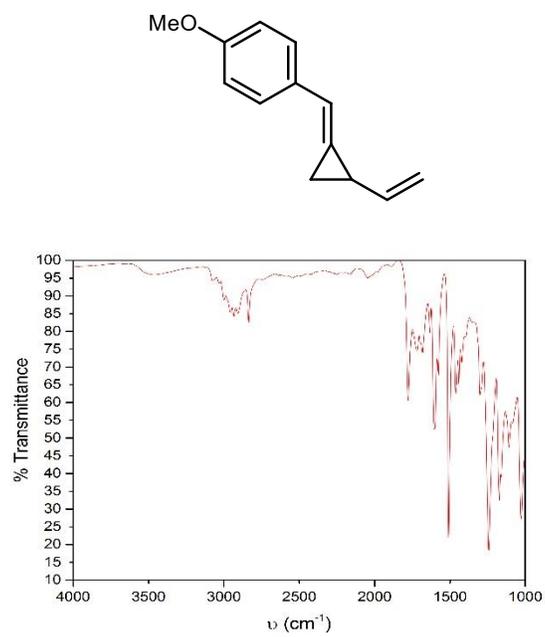


Figure S57. FT-IR of S21.

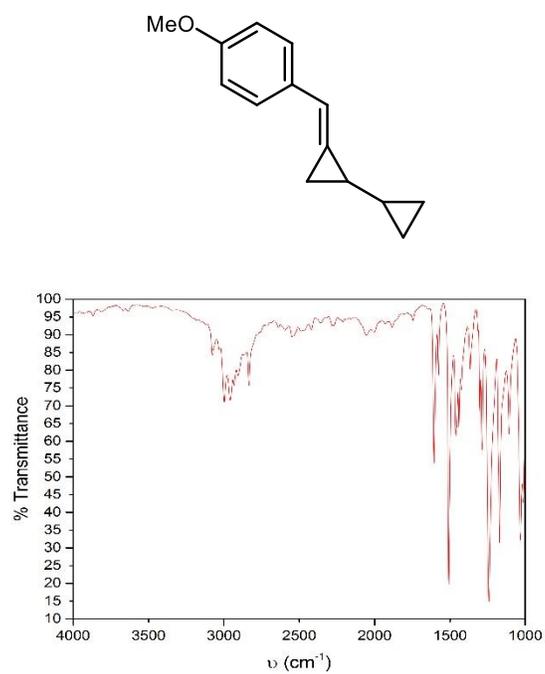


Figure S58. FT-IR of 4.

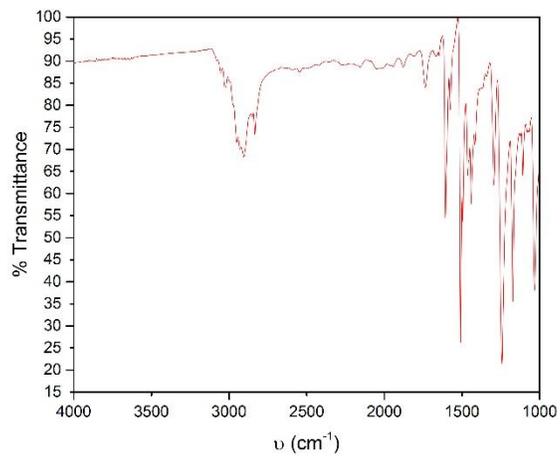
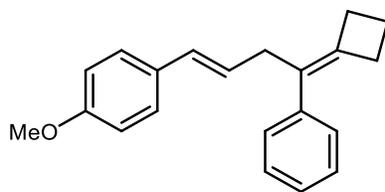
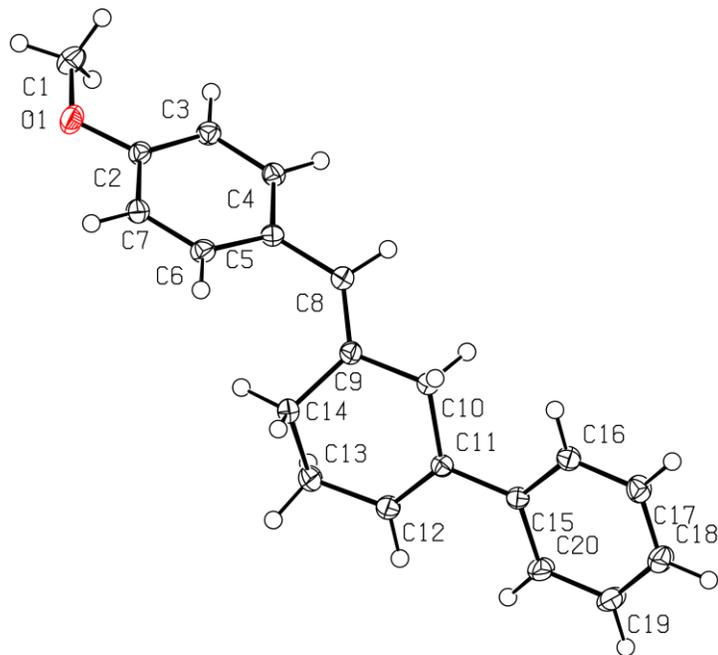


Figure S59. FT-IR of **49**.

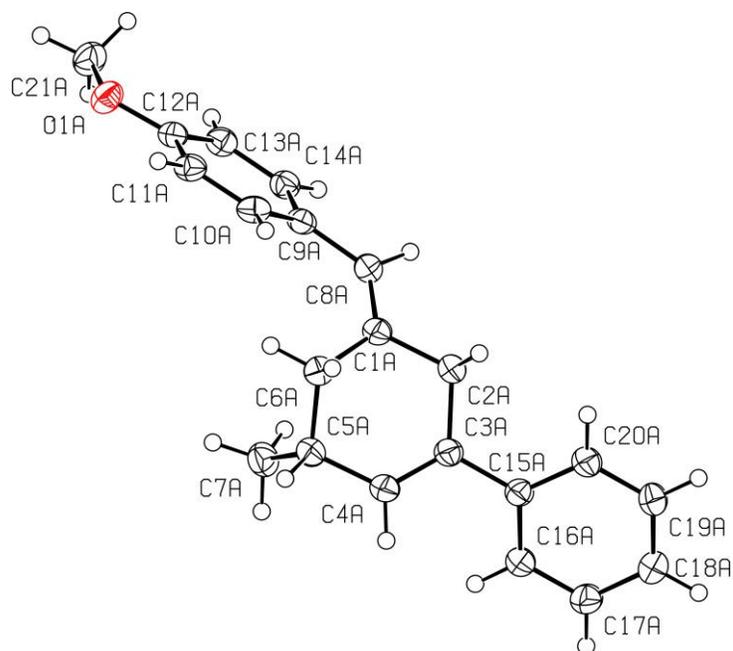
11. X-Ray Diffraction Data



Compound 6

Crystal data	
Chemical formula	C ₂₀ H ₂₀ O
<i>M_r</i>	276.36
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.6419 (16), 9.7478 (14), 9.9639 (15)
<i>a</i> , <i>b</i> , γ (°)	65.235 (5), 62.617 (4), 67.916 (4)
<i>V</i> (Å ³)	735.3 (2)
<i>Z</i>	2
<i>F</i> (000)	296
<i>D_x</i> (Mg m ⁻³)	1.248
Radiation type	Mo <i>K</i> α
No. of reflections for cell measurement	9917
θ range (°) for cell measurement	2.4–33.2
μ (mm ⁻¹)	0.08
Crystal shape	Block
Colour	Colorless
Crystal size (mm)	0.60 × 0.40 × 0.20

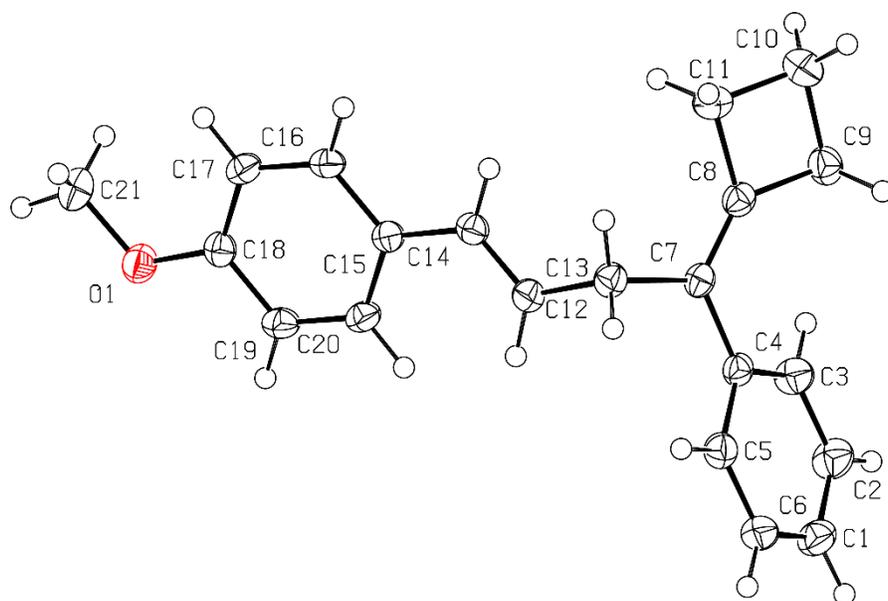
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Radiation source	sealed tube X-ray source
Monochromator	Triumph curved graphite crystal
Scan method	ω and phi scans
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., <i>J. Appl. Cryst.</i> 48 (2015) 3-10
T_{\min}, T_{\max}	0.721, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20324, 5621, 4479
R_{int}	0.027
θ values ($^{\circ}$)	$\theta_{\max} = 33.2, \theta_{\min} = 2.4$
$(\sin \theta/\lambda)_{\max}$ (\AA^{-1})	0.771
Range of h, k, l	$h = -14 \rightarrow 14, k = -15 \rightarrow 14, l = -15 \rightarrow 15$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.046, 0.138, 1.03
No. of reflections	5621
No. of parameters	191
No. of restraints	0
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.1416P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001
$\Delta\rho_{\max}, \Delta\rho_{\min}$ ($e \text{\AA}^{-3}$)	0.39, -0.23



Compound 30

Crystal data	
Chemical formula	C ₂₁ H ₂₂ O
<i>M_r</i>	290.38
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.0693 (2), 10.1210 (2), 18.5597 (4)
<i>a</i> , <i>b</i> , γ (°)	85.6232 (13), 85.2461 (14), 60.4624 (14)
<i>V</i> (Å ³)	1638.59 (6)
<i>Z</i>	4
<i>F</i> (000)	624
<i>D_x</i> (Mg m ⁻³)	1.177
Radiation type	Cu <i>K</i> α
No. of reflections for cell measurement	9828
θ range (°) for cell measurement	4.8–79.6
μ (mm ⁻¹)	0.54
Crystal shape	Block
Colour	Colourless
Crystal size (mm)	0.17 × 0.15 × 0.13
Data collection	

Diffractionmeter	Bruker AXS D8 Quest CMOS diffractometer
Radiation source	I-mu-S microsource X-ray tube
Monochromator	Laterally graded multilayer (Goebel) mirror
Scan method	ω and ϕ scans
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{\min}, T_{\max}	0.644, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25527, 12612, 11829
R_{int}	0.039
θ values ($^{\circ}$)	$\omega_{\max} = 80.6, \omega_{\min} = 2.4$
$(\sin \theta/\lambda)_{\max}$ (\AA^{-1})	0.640
Range of h, k, l	$h = -12 \dots 12, k = -12 \dots 12, l = -23 \dots 23$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.040, 0.104, 1.04
No. of reflections	12612
No. of parameters	802
No. of restraints	3
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\omega^2(F_o^2) + (0.0449P)^2 + 0.2845P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001
$\Delta\rho_{\max}, \Delta\rho_{\min}$ ($e \text{\AA}^{-3}$)	0.28, -0.20
Refinement on	SHELXL2018/3 (Sheldrick 2018), $F_c^* = kFc[1+0.001xFc^2\omega^3/\sin(2\omega)]^{-1/4}$
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0008 (3)
No. of reflections	Flack x determined using 4857 quotients $[(I+)-(I-)]/[(I+)+(I-)]$ (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
No. of parameters	-0.04 (11)



Compound 49

Crystal data	
Chemical formula	C ₂₁ H ₂₂ O
<i>M_r</i>	290.38
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.5996 (7), 9.8322 (7), 18.0348 (13)
<i>a</i> , <i>b</i> , γ (°)	87.595 (3), 77.541 (3), 75.984 (3)
<i>V</i> (Å ³)	1612.6 (2)
<i>Z</i>	4
<i>F</i> (000)	624
<i>D_x</i> (Mg m ⁻³)	1.196
Radiation type	Mo <i>K</i> α
No. of reflections for cell measurement	4620
θ range (°) for cell measurement	2.3–30.5
μ (mm ⁻¹)	0.07
Crystal shape	Plate
Colour	Colorless
Crystal size (mm)	0.5 × 0.5 × 0.5
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS

	diffractometer
Radiation source	sealed tube X-ray source
Monochromator	ω and phi scans
Scan method	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., <i>J. Appl. Cryst.</i> 48 (2015) 3-10
Absorption correction	0.642, 0.747
T_{\min}, T_{\max}	76183, 9831, 6241
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	0.076
R_{int}	$\sigma_{\text{max}} = 30.5, \sigma_{\text{min}} = 2.3$
θ values ($^{\circ}$)	0.714
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	$h = -13 \dots 13, k = -14 \dots 14, l = -25 \dots 25$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.055, 0.141, 1.01
No. of reflections	9831
No. of parameters	399
No. of restraints	0
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.412P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.001
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.35, -0.27

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VITA

Conner M. Farley was born in August 1993 in Boise, Idaho, where he grew up and attended Timberline High School. Following his high school graduation in 2011, he moved to Moscow, Idaho to study biochemistry at the University of Idaho. As an undergraduate student, he conducted three years of medicinal chemistry research in the laboratory of Prof. Jakob Magolan regarding the synthesis and antiausterity activity of functionalized coumarins. In 2015, he graduated with two bachelor's degrees in chemistry and biochemistry. He then attended Purdue University in West Lafayette, Indiana to pursue his doctorate in chemistry in the laboratory of Prof. Christopher Uyeda. In August 2020, Conner will begin a postdoctoral research appointment at the California Institute of Technology in Pasadena, California in the area of natural product total synthesis. He hopes to become a professor of chemistry one day.

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