Supporting Information

Aerobic Acyloxylation of Allylic C–H Bonds Initiated by a Pd^0 Precatalyst with 4,5-Diazafluoren-9-one as an Ancillary Ligand

Caitlin V. Kozack, Jennifer A. Sowin, Jonathan N. Jaworski, Andrei V. Iosub, and Shannon S. Stahl*

Table of Contents

1. General Considerations

All reagents were used as received without further purification. $Pd_2(dba)_3$ was obtained from Sigma-Aldrich and Combi-Blocks. It was stored at room temperature and looked like a dark purple/black powder. Fe(Pc) was purchased from Strem, Me_2BQ was obtained from Sigma-Aldrich and TCI, and methyl-4-cyclopentenecarboxylate which was purchased from TCI. All other chemicals were from Sigma-Aldrich except for *tert*-butyl *N*-but-3-enyl carbamate,[1] *N*-pheny-3-butenamide,[2] and **6**[3] which were prepared according to the literature. ^1H and ^{13}C NMR spectra were obtained using a Bruker Avance-400 MHz NMR or Bruker Avance-500 MHz spectrometer with residual solvent peaks or tetramethylsilane as the internal reference. Multiplicities are described using the following abbreviations: s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet. High-resolution mass spectra were obtained using a Thermo Q Exactive™ Plus via (ESI-MS) by the mass spectrometry facility at the University of Wisconsin-Madison (funded by NIH grant: 1S10OD020022-1). Flash chromatography was performed using a Biotage Isolera One automated column and a Biotage SNAP Ultra 25 g column.

Note – caution should be used when conducting reactions in organic solvents using oxygen gas. Efforts should be made to stay below the limiting oxygen concentration (LOC) of the solvent and/or reagents used in the reaction.[4]

2. Optimization of Reaction Conditions

General procedure for preliminary optimization of reaction conditions (Table S1-S3): A parallel reactor composed of an aluminum block mounted on a Large Capacity Mixer (Glas-Col) that enabled up to 48 reactions to be performed simultaneously under a constant pressure of (approx.) 1 atm O_2 with orbital agitation and a cold water condenser. The parallel reactor was pre-heated to the desired temperature. The desired amounts of additive (base, quinone, ETM) and BzOH were added to a 13-mm heavy wall culture tube. A stock solution composed of DAF ligand and Pd complex was made at the appropriate concentration in the solvent being tested. A stock solution of allylbenzene was prepared at the desired concentration being tested. The heavy wall test tubes containing the catalyst solution were placed in the reactor which was purged with O_2 for 5-10 min, and then sealed. The substrate stock solution was injected to initiate the reaction. After 24 hours, the reactor was turned off and allowed to cool to room temperature before the reactions were removed. NMR yields were obtained as follows: An external standard stock solution of 1,3,5-trimethoxybenzene (TMB) was prepared in $CDCl_3$. The standard solution (1 mL) was injected into the reaction tube. The reaction solution was filtered through a Celite plug with $CDCl_3$. ^1H NMR spectra were obtained with the Bruker Avance-400 MHz spectrometer with a relaxation delay of 25 s and yields were calculated relative to the standard.

Reaction conditions were developed by considering the previous conditions developed by White and co-workers[5] for acyloxylation with low acid loading and our previous aerobic allylic acetoxylation conditions.[6] DAF was used as an ancillary ligand and reactions were carried out under O_2 while different Pd sources and additives were screened. Using the Pd(II) source $Pd(CH_3CN)_4(BF_4)_2$, the best conditions were achieved with the solvent DCE and the base Na_2HPO_4 (Table S1, entry 13). Lowering the temperature from 70 °C to 60 °C provided a slight boost in yield (Table S1, Entry 15). Upon changing the Pd source to $Pd_2(dba)_3$, Na_2HPO_4 was no longer necessary to obtain a good yield. (Table S1, entry 17). Preliminary screening of additives while using $Pd(CH_3CN)_4(BF_4)_2$ demonstrated that Me_2BQ and Fe(Pc) increased the yield. Another common ETM, Co(Salophen), decreased the yield (Table S2, entry 5). Increasing the concentration of allylbenzene and adding Me_2BQ and Fe(Pc) with $Pd_2(dba)_3$ improved the yield (Table S3, entry 6).

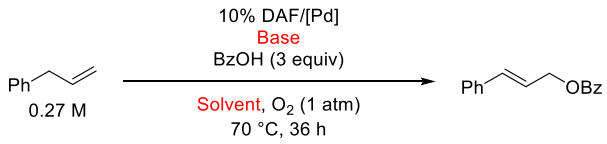


Table S1: Preliminary Optimization of Solvents and Base Additives

Entry	Pd Source	Base	Equiv	Solvent	%Yield[a]
1	$[Pd(CH_3CN)_4](BF_4)_2$	Lutidine	0.7	Dioxane	0
2	$[Pd(CH_3CN)_4](BF_4)_2$	Acridine	0.7	Dioxane	0
3	$[Pd(CH_3CN)_4](BF_4)_2$	DIPEA	0.7	Dioxane	7
4	$[Pd(CH_3CN)_4](BF_4)_2$	DBU	0.7	Dioxane	8
5	$[Pd(CH_3CN)_4](BF_4)_2$	K_3PO_4	0.7	Dioxane	4
6	$[Pd(CH_3CN)_4](BF_4)_2$	Na_2HPO_4	1.5	Dioxane	6
7	$[Pd(CH_3CN)_4](BF_4)_2$	Na_2CO_3	1.5	Dioxane	13
8	$[Pd(CH_3CN)_4](BF_4)_2$	Lutidine	0.7	DCE	<1
9	$[Pd(CH_3CN)_4](BF_4)_2$	Acridine	0.7	DCE	<1
10	$[Pd(CH_3CN)_4](BF_4)_2$	DIPEA	0.7	DCE	21
11	$[Pd(CH_3CN)_4](BF_4)_2$	DBU	0.7	DCE	15
12	$[Pd(CH_3CN)_4](BF_4)_2$	K_3PO_4	0.7	DCE	6
13	$[Pd(CH_3CN)_4](BF_4)_2$	**Na_2HPO_4**	**1.5**	**DCE**	**23**
14	$[Pd(CH_3CN)_4](BF_4)_2$	Na_2CO_3	1.5	DCE	12
15[b]	$[Pd(CH_3CN)_4](BF_4)_2$	Na_2HPO_4	1.5	DCE	**29**
16[c]	$Pd_2(dba)_3$	Na_2HPO_4	1.5	DCE	41
17[c]	$Pd_2(dba)_3$	-------	-------	DCE	**39**

[a] NMR yield relative to TMB

[b] 5 mol% $[Pd(CH_3CN)_4](BF_4)_2$, 5 mol% DAF, 60 °C, 24 h

[c] 2.5 mol% $Pd_2(dba)_3$ ($[Pd]_{Total}$ is 5 mol%), 5 mol% DAF, 60 °C, 24 h

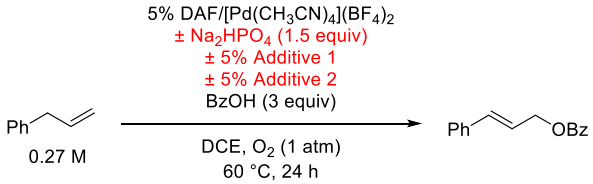


Table S2: Preliminary Optimization of Additives

Entry	Na_2HPO_4 (equiv)	Additive 1	Additive 2	%Yield[a]
1	0	------	------	0
2	1.5	Me_2BQ	------	29
3	1.5	Me_2BQ	------	46
4	**1.5**	**Me_2BQ**	**Fe(Pc)**	**41**
5	**1.5**	**Me_2BQ**	**Co(Salophen)**	**18**
6	1.5	dba	------	33
7	**1.5**	**Maleimide**	**------**	**46**
8	1.5	Me_2-Fumurate	------	43

[a] NMR yield relative to TMB

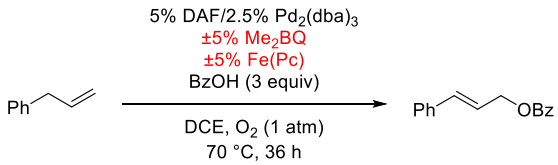


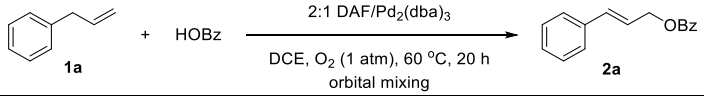
Table S3: Preliminary Optimization of [allylbenzene] [Me_2BQ] and [Fe(Pc)]

Entry	[allylbenzene] M	%Me_2BQ	%Fe(Pc)	%Yield[a]
1	0.27	------	------	18
2	0.27	5	------	22
3	0.27	5	5	22
4	0.54	------	------	23
5	0.54	5	------	43
6	0.54	5	5	52

[a] NMR yield relative to TMB

General procedure for final optimization of reaction conditions and temperature screening (Table 1, Table S4-S5): A parallel reactor composed of an aluminum block mounted on a Large Capacity Mixer (Glas-Col) that enabled up to 48 reactions to be performed simultaneously under a constant pressure of (approx.) 1 atm O_2 with orbital agitation and a cold water condenser. The parallel reactor was pre-heated to the desired temperature. The desired amount of Fe(Pc), Me_2BQ, DAF, $Pd_2(dba)_3$, and benzoic acid were added to a 13-mm heavy wall culture tube. 1,2-dichloroethane (DCE) (0.8 mL was added). A stock solution of allylbenzene was prepared in a volumetric flask at the desired concentration being tested. The heavy wall test tubes containing the catalyst solution were placed in the reactor which was then purged with O_2 for 5 min then sealed. The substrate stock solution (0.2 mL) was injected to initiate the reaction. After 20 hours, the reactor was turned off and allowed to cool to room temperature before the reactions were removed. NMR yields were obtained as follows: An external standard stock solution of 1,3,5-trimethoxybenzene (TMB) (0.108 M) was prepared in $CDCl_3$. The standard solution (1 mL) was injected into the reaction tube. The reaction solution was filtered through a Celite plug with $CDCl_3$. ^1H NMR spectra were obtained with the Bruker Avance-400 MHz spectrometer with a relaxation delay of 25 s and yields were calculated relative to the standard.

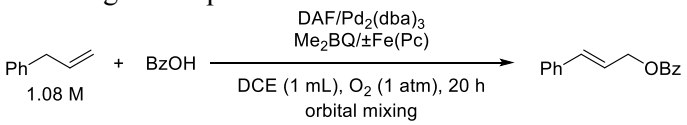
Table S4. Optimization of Reaction Conditions



Entry	%[DAF/Pd][a]	**1a** (M)	BzOH (eq)	%Me_2BQ	%Fe(Pc)	%Yield[b]
1	5	0.27	3	----	----	75
2	10	0.27	3	----	----	75
3	5	0.54	3	----	----	35
4	2.5	1.08	3	----	----	24
5	2.5	1.08	3	5	----	56
6	2.5	1.08	3	5	2.5	72
7	2.5	1.08	3	5	0.5	78
8	2.5	1.08	3	1.25	0.5	51
9	5	1.08	2	10	0.5	98
10	**5**	**1.08**	**1.2**	**10**	**0.5**	**93**
11	5	1.08	1	10	0.5	91
12[c]	5	1.08	1.2	10	0.5	4

[a]. [DAF/Pd] = 2:1 DAF:$Pd_2(dba)_3$ Reported mol% DAF and mol% total Pd [b] NMR yield relative to 1,3,5-trimethoxybenzene [c] No DAF

Table S5. Temperature Screening with Optimized Conditions



	Yield[b] at varied temperatures				
	40 °C	50 °C	60 °C[c]	70 °C	80 °C
2.5% DAF/Pd[a] 5% Me_2BQ 3 eq BzOH	17%	36%	56%	53%	43%
2.5% DAF/Pd[a] 5% Me_2BQ 0.5% Fe(Pc) 3 eq BzOH	44%	66%	78%	78%	79%
5% DAF/Pd[a] 10% Me_2BQ 0.5% Fe(Pc) 1.2 eq BzOH	57%	82%	**93%**	83%	80%

[a] DAF/Pd = 2:1 DAF:$Pd_2(dba)_3$ Reported mol% DAF and mol% total Pd [b] NMR yield relative to 1,3,5-trimethoxybenzene, average of two reactions [c] Reported data from entries 5, 7, and 10 in Table S4

3. Time Course of Acyloxylation using Different Pd Sources

The reactions were carried out in the parallel reactor as described above. The reaction was run on a 6 mL scale. Stock solution **A** was prepared in a volumetric flask with DAF (1.08 mmol, 196.8 mg), Me_2BQ (2.16 mmol, 294.1 mg), and Fe(Pc) (0.108 mmol, 61.4 mg) in 10 mL DCE. Stock solution **B** was prepared with 1,2,3-trimethoxybenzene (TMB) (1.25 mmol, 210.2 mg) in 10 mL DCE. Stock solution **C** was prepared with allylbenzene (32.4 mmol, 3.831 g) in 5 mL DCE. Benzoic acid (7.78 mmol, 949.6 mg) and either $Pd_2(dba)_3$ (0.162 mmol, 148.4 mg), $Pd(OBz)_2$ (0.324 mmol, 113.0 mg), or $Pd(OAc)_2$ (0.324 mmol, 72.7 mg) were weighed into the reaction vessel. Stock solution **A** (3 mL), stock solution **B** (0.5 mL), and DCE (1.5 mL) were added to the reaction vessels. They were placed on in the reactor and purged with O_2 for 5 min. The reactor was sealed and stock solution **C** (1 mL) was injected to initiate the reaction. At each time point, an aliquot (~100 μL) was removed, and the reaction was quenched by filtration through a silica plug with ethyl acetate containing 10% pyridine. The solvent was removed in vacuo using a ThermoFisher Scientific Savant™ SPD131DDA Speedvac™ Concentrator. The residue was dissolved in $CDCl_3$ and ^1H NMR spectra were obtained on a Bruker Avance-500 MHz spectrometer with a relaxation delay = 25 s. The yield at each timepoint was determined by comparative integration of the starting material and product relative to the internal standard.

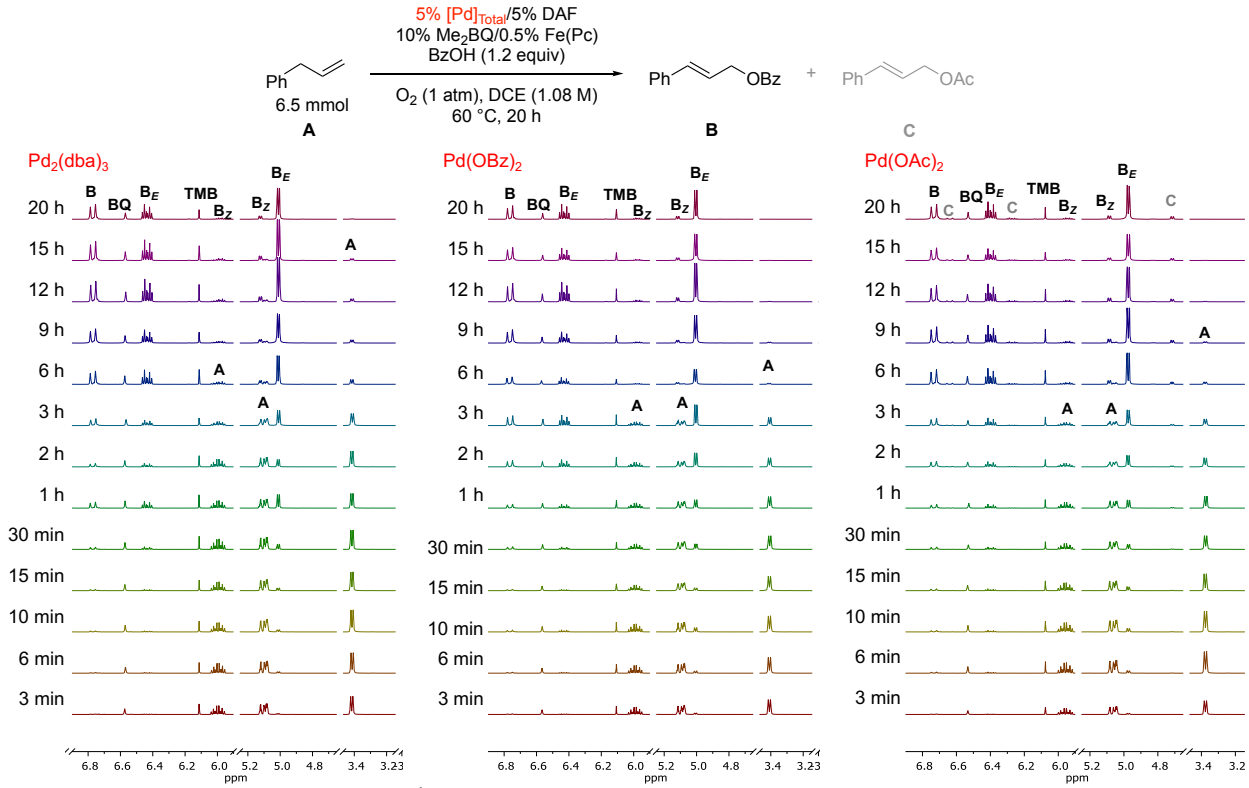


Figure S1: Diagnostic peaks in the ^1H NMR spectra of the acyloxylation reactions catalyzed by $Pd_2(dba)_3$, $Pd(OBz)_2$, or $Pd(OAc)_2$ that were used to obtain the data for the plot in Figure 3. TMB = trimethoxybenzene internal standard.

4. General Procedures for Acyloxylation of Alkenes (Figures 4, 5, and 6-conditions B)

General Procedure for reactions carried out in parallel reactors: The parallel reactor described above was pre-heated to 60 °C. Fe(Pc) (0.0054 mmol, 3.1 mg), DAF (0.054 mmol, 9.8 mg), Me_2BQ (0.108 mmol, 14.7 mg), $Pd_2(dba)_3$ (0.027 mmol, 24.7 mg), and carboxylic acid (1.296 mmol) were weighed into a 13-mm heavy wall test tube. DCE (0.8 mL) was added. A solution of the alkene (5.4 M in DCE) was prepared in a volumetric flask. The heavy wall test tubes containing the catalyst solution were placed in the reactor which was purged with O_2 for 5 min and then sealed. The alkene stock solution (0.2 mL) was injected to initiate the reaction. After 20 hours, the reactor was turned off and allowed to cool to room temperature before the reactions were removed.

For NMR yields: An external standard stock solution of 1,3,5-trimethoxybenzene (TMB) (0.108 M) was prepared in $CDCl_3$. The standard solution (1 mL) was injected into the reaction tube. The reaction solution was filtered through a Celite plug with $CDCl_3$. ^1H NMR spectra were obtained with the Bruker Avance-400 MHz spectrometer with a relaxation delay of 25 s and yields were calculated relative to the standard.

For isolated yields: The entire reaction volume was injected onto a Biotage SNAP Ultra 25 g column and isolated using a Biotage Isolera One automated column with a pentane/ethyl acetate gradient of 0% to 20% ethyl acetate over 20 column volumes.

General Procedure for reactions carried out in round bottom flasks:
1 g scale synthesis of 2b: To a 100-mL round bottom flask was added *trans*-cinnamic acid (10.15 mmol, 1.50 g), $Pd_2(dba)_3$ (0.211 mmol, 193.7 mg), Me_2BQ (0.846 mmol, 115.2 mg), DAF(0.423 mmol, 77.1 mg), and Fe(Pc) (0.0423 mmol, 24.0 mg), followed by 6.4 mL DCE. A stock solution of allylbenzene (12.1 mmol, 1.428 g in 2 mL DCE) was prepared. The round bottom flask was purged with O_2 for 5 min. The O_2 inlet and purge needles were removed and replaced with a balloon to maintain the O_2 atmosphere. The allylbenzene stock solution (1.4 mL, 1 g, 8.46 mmol allylbenzene) was injected and the reaction was stirred at 60 °C for 20 h. The reaction mixture was allowed to cool to room temperature and then was condensed onto silica and purified via column chromatography with the Biotage Isolera One automated column with a pentane/ethyl acetate gradient of 0% to 20% ethyl acetate over 20 column volumes. A clear oil was obtained with 85% yield (1.89 g, *E*:*Z* 7:1).

1 g scale synthesis of 3a: To a 100-mL round bottom flask was added benzoic acid (9.07 mmol, 1.11 g), $Pd_2(dba)_3$ (0.181 mmol, 173.2 mg), Me_2BQ (0.756 mmol, 103.0 mg), DAF (0.378 mmol, 68.9 mg), and Fe(Pc) (0.0378 mmol, 21.5 mg), followed by 5.6 mL DCE. A stock solution of allyltoluene (7.56 mmol, 1.428 g in 2 mL DCE) was prepared. The round bottom flask was purged with O_2 for 5 min. The O_2 inlet and purge needles were removed and replaced with a balloon to maintain the O_2 atmosphere. The allylbenzene stock solution (1.4 mL, 1 g, 7.56 mmol allyltoluene) was injected and the reaction was stirred at 60 °C for 20 h. The reaction mixture was allowed to cool to room temperature, and then was condensed onto silica and purified via column chromatography with the Biotage Isolera One automated column with a pentane/ethyl acetate gradient of 0% to 20% ethyl acetate over 20 column volumes. A white solid was obtained with 80% yield (1.53 g, *E*:*Z* 10:1).

5. Diastereoselectivity Dependence on Acid

Diastereoselectivity Dependence on Acid: Under different preliminary conditions, the diastereoselectivity was found to change based on the identity of the acid and the conditions used (Figure S2). When $Pd(OAc)_2$ and solvent AcOH are used without DAF, the *trans*-5-OAc forms in quantities greater than 20:1. However, once DAF is added, the selectivity drops to 1.4:1, although reactivity remains the same, indicating that DAF contributes to the selectivity determining step. When $Pd_2(dba)_3$ and benzoic acid were used in DCE, the reactivity dropped in the absence of DAF, and *trans*-5-OBz is favored, although not nearly as dramatically as under the acetic acid conditions at 5:1. With the addition of DAF, the reactivity increased, and the selectivity switched to favor the formation of *cis*-5-OBz (1:2).

Procedure for 5-OAc formation (Conditions A): $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Me_2BQ (5.5 mg, 0.04 mmol), and DAF(1.8 mg 0.1 mmol, when applicable) were added to a 13-mm heavy walled culture tube. AcOH (0.8 mL) was added. A stock solution of **4** (252 mg in 2 mL AcOH, 25.2 mg, 0.2 mmol per reaction) was prepared. The stock solution (0.2 mL) was injected into the culture tube. It was placed on the parallel reactor described above at 60 °C under O_2 (1 atm) with orbital mixing for 20 h. NMR yields were obtained by injecting each tube with an internal standard stock solution of 1,1,2,2-tetrachloroethane (25 mg in 10 mL $CDCl_3$, 1 mL per reaction). Each reaction was filtered through Celite with $CDCl_3$. ^1H NMR spectra were obtained with the Bruker Avance-400 MHz spectrometer with a relaxation delay of 25 s and yields were calculated relative to the standard.

Procedure for 5-OBz formation in Figure S2: $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), Me_2BQ (5.5 mg, 0.04 mmol), BzOH (73.3 mg, 0.6 mmol) and DAF(1.8 mg 0.1 mmol, when applicable) were added to a 13-mm heavy walled culture tube. DCE (0.8 mL) was added. A stock solution of **4** (252 mg in 2 mL DCE, 25.2 mg, 0.2 mmol per reaction) was prepared. The stock solution (0.2 mL) was injected into the culture tube. It was placed on the parallel reactor described above at 60 °C under O_2 (1 atm) with orbital mixing for 20 h. Each reaction was filtered through silica with EtOAc and the solvent was removed in vacuo using a ThermoFisher Scientific Savant™ SPD131DDA Speedvac™ Concentrator. NMR yields were obtained by injecting each tube with an internal standard stock solution of dimethoxymethane (25 mg in 10 mL $CDCl_3$, 1 mL per reaction). ^1H NMR spectra were obtained with the Bruker Avance-400 MHz spectrometer with a relaxation delay of 25 s and yields were calculated relative to the standard.

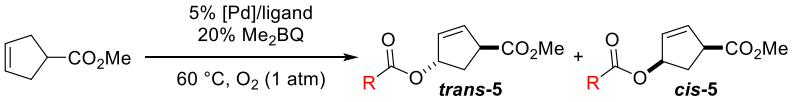


Figure S2: Changing the identity of the acid from acetic acid to benzoic acid changes the diastereoselectivity to favor formation of the *cis* isomer.

Differentiating Diastereomers by NMR: The diastereomers had distinct multiple distinct peaks in a ^1H NMR spectrum in $CDCl_3$. Using selective 1D NOESY ^1H NMR experiments, the NOE between various protons was observed, and the correlations enabled stereochemical assignments to be made. In the *trans* product, there is a NOE present between the allylic enolate proton at 5.77 ppm and the methoxy group, consistent with the acetate and methyl ester being *trans* to each other (Figure S3). In the *cis* product, that correlation is no longer present (Figure S4).

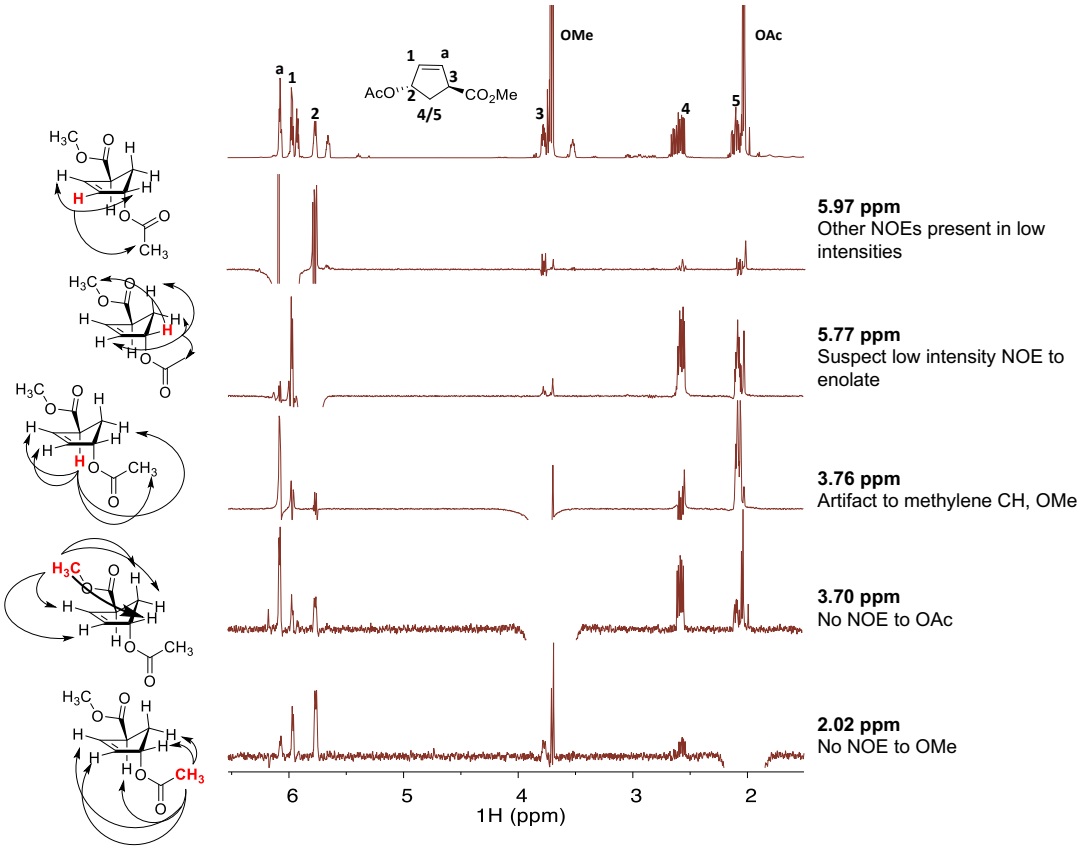


Figure S3: 1D NOESY NMR spectra showing the NOE correlations for ***trans*-5-OAc** product. Irradiated proton is red, and NOE correlations are depicted using arrows.

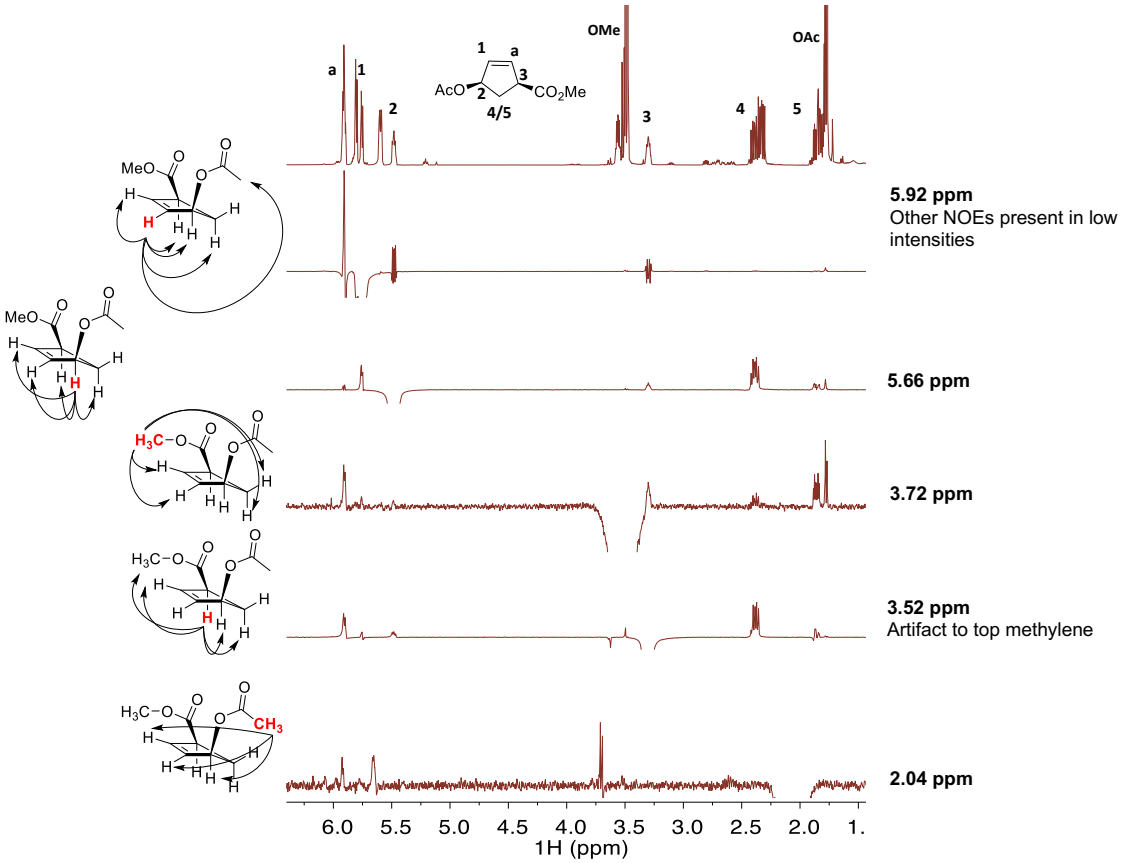


Figure S4: 1D NOESY NMR spectra showing the NOE correlations for ***cis*-5-OAc**. Irradiated proton is red, and NOE correlations are depicted using arrows.

6. Structural Determination of Compound 7

Allylic acyloxylation of substrate **6** had the possibility of forming two different regioisomers based on the π-allyl intermediate that forms as the result of C–H activation (Figure S5). The regioisomer that formed was determined through the use of selective 1D COSY ^{1}H NMR spectroscopy. In regioisomer **7**, the allylic enolate CH **a** would couple directly with the methylene protons **b** and **c** as seen by the NMR spectrum in Figure S5 in which peak **a** was irradiated. In the other regioisomer, **9**, the methylene protons **b** and **c** would not couple directly to **a**, and **a** would couple strongly with the bridgehead proton **f**. The 1D COSY ^{1}H NMR spectrum with allyl enolate proton **a** irradiated revealed direct coupling to **b**, **c**, and **f**, which is consistent with the allyl enolate proton **a** having a vicinal location to the methylene group and the alkene (Figure S5). A 2D COSY ^{1}H^{1}H NMR further confirmed the assignment of regioisomer **7** by showing that the bridgehead protons **f** and **g** do not couple to **a** as they would if regioisomer **9** formed (Figure S6).

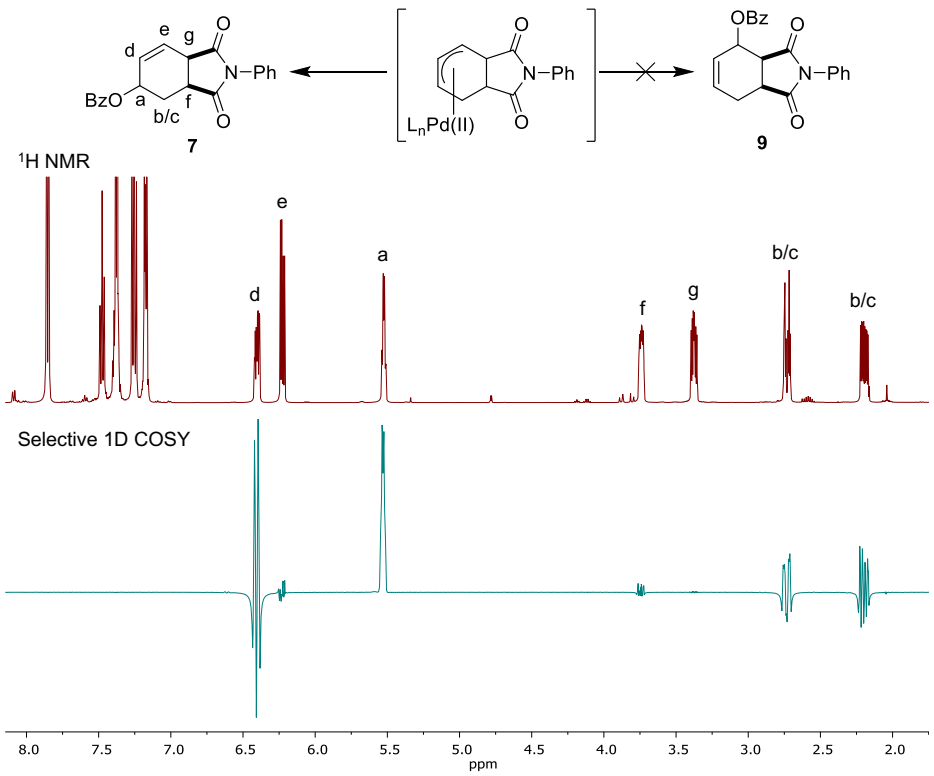


Figure S5: ^{1}H NMR (top) and selective 1D COSY (bottom) NMR spectra of **7**. Allylic enolate proton signal **a** at 5.53 ppm was irradiated.

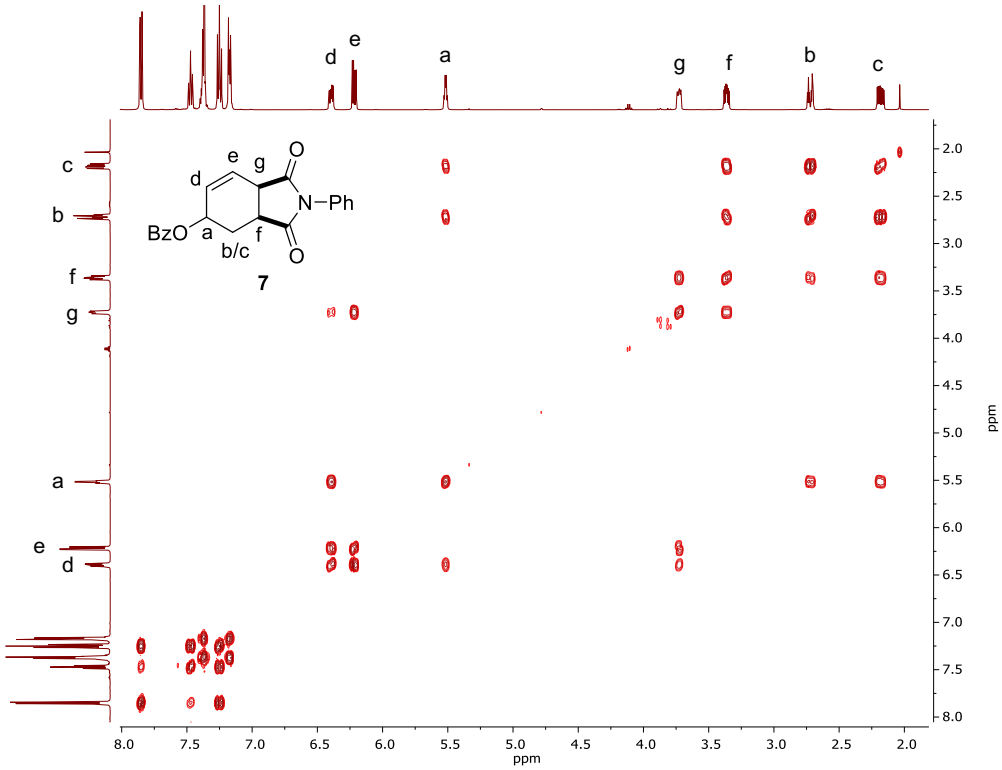


Figure S6: 2D COSY ^{1}H^{1}H NMR (500 MHz, $CDCl_3$) spectrum showing the direct coupling correlations between protons within **7**.

Determination of the major diastereomer was done through observing NOE correlations. The geometrically optimized structures of *trans*-**7** and *cis*-**7** were determined through an optimization and vibrational frequency calculation using WebMO (Theory: B3LYP, Basis Set: STO-3G) (Figure S7).[7] Selective gradient ^{1}H NOESY spectroscopy revealed that the allylic enolate proton **a** had NOE correlations with both bridgehead protons, which would not likely be observed with *trans*-7 (Figure S7). There is also a NOE correlation with the *ortho* benzoate protons **h**, which is consistent with their spacial proximity (Figure S8).

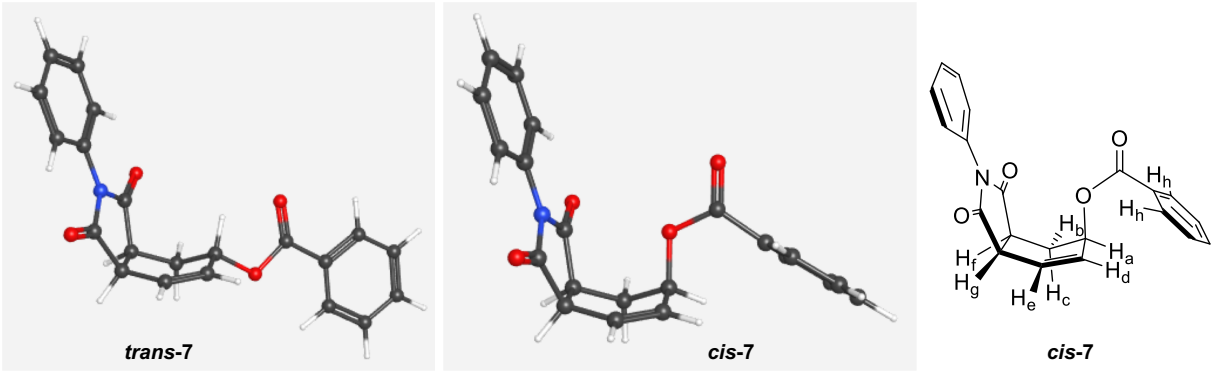


Figure S7: Calculated optimized geometric structures for *trans*-**7** and *cis*-**7**.

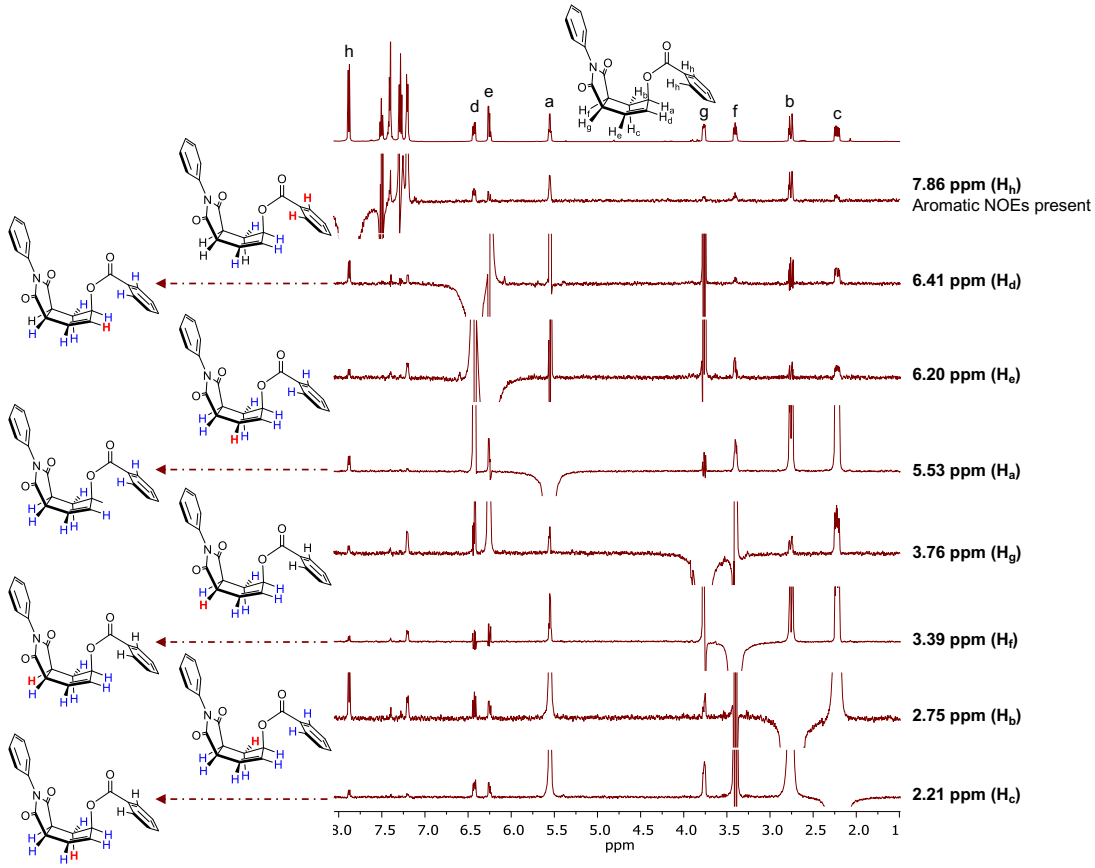
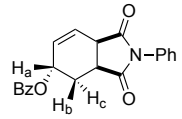
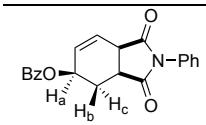


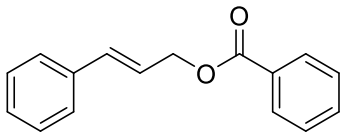
Figure S8: 1D NOESY NMR spectra showing the NOE correlations for the acetoxylation product **7**. The irradiated proton is red, and protons with NOE correlations are blue.

Additional support for the *cis* diastereomer can be obtained from the geometrically optimized structures. The dihedral angles between H_a and H_b or H_c could be measured and applied to the Bothner-By equation ($J = 7 - \cos\Theta + 5\cos(2\Theta)$) to obtain a rough estimate of the $^3J_{HH}$ coupling constant between the two protons (Table S6). This provides only a very rough estimate because ring strain and substituents may cause deviation from the predicted values. Comparison of the calculated values to the measured values from the NMR spectrum (H_a–C–C–H_b = 3.8 Hz; H_a–C–C–H_c = 3.5 Hz) is consistent with the *cis*-**7** diastereomer. If the product were the *trans*-**7** diastereomer, a large difference in coupling constants between H_a and each methylene proton would be expected because H_a and H_c are pseudo-axial trans to each other, whereas in the *cis*-**7** diastereomer, the dihedral angles are much more similar.

Table S6: Bothner-By equation estimations of ^3J for the *trans* and *cis* isomers of **7**.

Compound	Dihedral Angle	Angle Measurement	Bothner-By Estimation (Hz)
 ***trans-7***	H_a–C–C–H_b	45.290º	6.2
	H_a–C–C–H_c	163.707º	12.2
 ***cis-7***	H_a–C–C–H_b	65.504º	3.3
	H_a–C–C–H_c	52.781º	5.0

7. Product Characterization Data



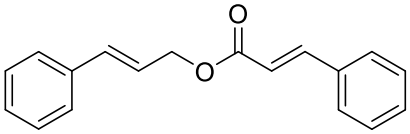
Cinnamyl benzoate (2a)

Prepared according to the general procedure using allylbenzene and benzoic acid. Clear oil obtained in 92% isolated yield (*E*:*Z* 10:1). ^{1}H NMR data agree with previously reported values.[8]

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 8.13 – 8.03 (m, 1H), 7.60 – 7.54 (m, 1H), 7.48 – 7.25 (m, 8H), 6.75 (bd, *J* = 15.9 Hz, 1H), 6.42 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.99 (dd, *J* = 6.4, 1.4 Hz, 2H) ppm. ***Z* isomer:** δ 8.13 – 8.03 (m, 1H), 7.60 – 7.54 (m, 1H), 7.48 – 7.25 (m, 8H), 6.74 (bd, *J* = 11.8 Hz, 1H), 5.96 (dt, *J* = 11.7, 6.7 Hz, 1H), 5.10 (dd, *J* = 6.6, 1.7 Hz, 2H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 166.38, 136.21, 134.25, 132.98, 130.19, 129.65, 128.61, 128.37, 128.08, 126.63, 123.24, 65.53 ppm. ***Z* isomer:** δ 166.38, 136.05, 134.25, 133.18, 130.19, 129.64, 128.74, 128.42, 127.55, 125.81, 123.24, 61.94 ppm.

HRMS (ESI) calculated m/z for $C_{16}H_{14}O_2$ ($[M+Na]^+$): 261.0886, measured: 261.0887.



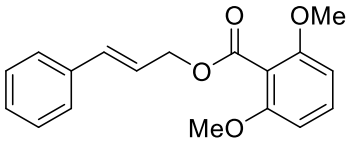
Cinnamyl (*E*)-cinnamate (2b)

Prepared according to the general procedure with allylbenzene and *trans*-cinnamic acid. White solid obtained in 91% isolated yield (*E*:*Z* 12:1). ^{1}H NMR data agree with previously reported values.[9]

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 7.74 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.45 – 7.24 (m, 8H), 6.72 (dt, *J* = 15.9, 1.3 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.37 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.88 (dd, *J* = 6.4, 1.4 Hz, 2H) ppm. ***Z* isomer:** δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.45 – 7.24 (m, 8H), 6.72 (dt, *J* = 11.8, 1.7 Hz, 1H), 6.48 (d, *J* = 16.0 Hz), 5.90 (dt, *J* = 11.7, 6.6 Hz, 1H), 4.99 (dd, *J* = 6.6, 1.7 Hz, 2H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 166.71, 145.09, 136.21, 134.36, 134.23, 130.33, 128.89, 128.60, 128.10, 128.06, 126.62, 123.26, 117.88, 65.15 ppm. ***Z* isomer:** δ166.71, 145.06, 136.21, 134.36, 133.09, 130.33, 128.74, 128.40, 128.10, 127.53, 125.86, 123.26, 117.84, 61.54 ppm.

HRMS (ESI) calculated m/z for $C_{18}H_{16}O_2$ ($[M+Na]^+$): 287.1043, measured: 287.1041.



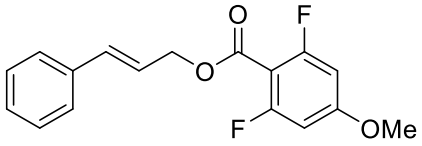
Cinnamyl 2,6-dimethoxybenzoate (2c)

Prepared according to the general procedure with allylbenzene and 2,6-dimethoxybenzoic acid. Tan solid obtained in 32% isolated yield (*E*:*Z* 14:1).

^{1}H NMR (500 MHz, Chloroform-*d*) ***E*** **isomer:** δ 7.41 (m, 2H), 7.35-7.22 (m, 4H), 6.75 (bd, *J* = 16.1 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.39 (dt, *J* = 15.9, 6.2 Hz, 1H), 5.00 (dd, *J* = 6.2, 1.5 Hz, 2H), 3.83 (s, 6H) ppm. ***Z*** **isomer:** δ 7.37 (m, 2H), 7.35-7.22 (m, 4H), 6.71 (bd, *J* = 11.9 Hz, 1H), 6.56 (d, *J* = 8.5 Hz, 2H), 5.95 (dt, *J* = 11.7, 6.8 Hz, 1H), 5.08 (dd, *J* = 6.8, 1.6 Hz, 2H), 3.82 (s, 6H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E*** **isomer:** δ 166.3, 157.4, 136.5, 133.7, 131.1, 128.5, 127.9, 126.6, 123.3, 113.0, 103.9, 65.7, 56.0 ppm. ***Z*** **isomer:** δ 166.3, 157.4, 136.5, 133.2, 131.1, 128.8, 128.3, 127.5, 123.3, 113.0, 103.9, 62.4, 56.0 ppm.

HRMS (ESI) calculated m/z for $C_{18}H_{18}O_4$ ($[M+H]^+$): 299.1278, measured: 299.1272.



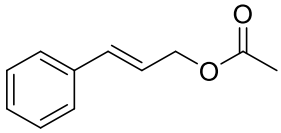
Cinnamyl 2,6-difluoro-4-methoxybenzoate (2d)

Prepared according to the general procedure with allylbenzene and 2,6-difluoro-4-methoxybenzoic acid. Yellow oil obtained in 51% isolated yield (*E*:*Z* 13:1).

^{1}H NMR (500 MHz, Chloroform-*d*) ***E*** **isomer:** δ 7.41 (m, 2H), 7.33 (m, 2H), 7.27 (m, 1H), 6.75 (dt, *J*= 15.8, 1.5 Hz, 1H), 6.49 (m, 2H), 6.38 (dt, *J* = 15.8, 6.3 Hz, 1H), 4.98 (dd, *J* = 6.3, 1.4 Hz, 2H), 3.83 (s, 3H) ppm. ***Z*** **isomer:** δ 7.41 (m, 2H), 7.33 (m, 2H), 7.27 (m, 1H), 6.75 (m, 1H), 6.49 (m, 2H), 5.94 (dt, *J* = 11.7, 6.7 Hz, 1H), 5.08 (dd, *J* = 6.7, 1.6 Hz, 2H), 3.83 (s, 3H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E*** **isomer:** δ 163.4 (t, *J* = 14.5 Hz), 162.5 (dd, *J* = 256, 9 Hz), 161.4 (t, *J* = 2.6 Hz), 136.2, 134.4, 128.6, 128.1, 126.7, 122.7, 103.1 (t, *J* = 17 Hz), 98.6 (m), 65.9, 56.0 ppm. ***Z*** **isomer:** δ 163.4 (t, *J* = 14.5 Hz), 162.5 (dd, *J* = 256, 9 Hz), 161.4 (t, *J* = 2.6 Hz), 136.0, 134.0, 128.8, 128.4, 127.6, 125.3, 103.1 (t, *J* = 17 Hz), 98.6 (m), 62.4, 56.0 ppm.

HRMS (ESI) calculated m/z for $C_{17}H_{14}F_2O_3$ ($[M+Na]^+$): 327.0803, measured: 327.0779.



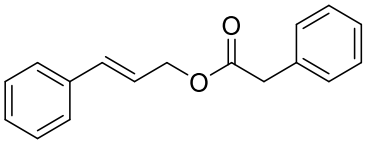
Cinnamyl Acetate (2e)

Prepared according to the general procedure with allylbenzene and acetic acid. Clear oil obtained in 68% isolated yield (*E*:*Z* 14:1). ^{1}H NMR data agree with previously reported values.[9]

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 7.42-7.24 (m, 5H), 6.66 (bd, *J* = 15.7 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.73 (dd, *J* = 6.5, 1.4 Hz, 2H), 2.10 (s, 3H) ppm. ***Z* isomer:** δ 7.42-7.20 (m, 5H), 6.67 (bd, *J* = 11.4 Hz, 1H), 5.82 (dt, *J* = 11.7, 6.6 Hz, 1H), 4.85 (dd, *J* = 6.7, 1.7 Hz, 2H), 2.09 (s, 3H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 170.8, 136.2, 134.2, 128.6, 128.1, 126.6, 123.1, 65.1, 21.0 ppm. ***Z* isomer:** δ 170.9, 136.0, 133.0, 128.7, 128.4, 127.5, 125.8, 61.5, 21.0 ppm.

HRMS (ESI) calculated m/z for $C_{11}H_{12}O_2$ ($[M+Na]^+$): 199.0730, measured: 199.0730.



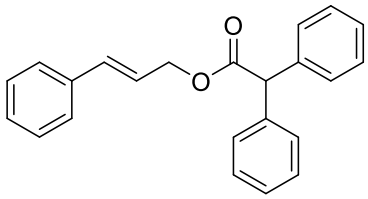
Cinnamyl phenylacetate (2f)

Prepared according to the general procedure with allylbenzene and phenyl acetic acid. Clear oil obtained in 77% isolated yield (*E*:*Z* 13:1). ^{1}H NMR data agree with previously reported values.[10]

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 7.39 – 7.23 (m, 10H), 6.60 (bd, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.76 (dd, *J* = 6.4, 1.4 Hz, 2H), 3.68 (s, 2H) ppm. ***Z* isomer:** δ 7.39 – 7.23 (m, 10H), 6.67 (bd, *J* = 11.7 Hz, 1H), 5.80 (dt, *J* = 11.7, 6.7 Hz, 1H), 4.86 (dd, *J* = 6.6, 1.6 Hz), 3.66 (s, 2H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 171.33, 136.16, 134.10, 133.93, 129.30, 128.59, 128.58, 128.05, 127.13, 126.59, 123.00, 65.38, 41.39 ppm. ***Z* isomer:** 171.33, 136.16, 134.10, 133.23, 129.25, 128.69, 128.36, 127.52, 127.11, 125.57, 123.00, 61.84, 41.36 ppm.

HRMS (ESI) calculated m/z for $C_{17}H_{16}O_2$ ($[M+NH_4]^+$): 270.1489, measured: 270.1489.



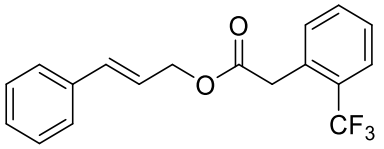
Cinnamyl diphenylacetate (2g)

Prepared according to the general procedure with allylbenzene and diphenyl acetic acid. White solid obtained in 75% isolated yield (*E*:*Z* 12:1). ^{1}H NMR data agree with previously reported values.[11]

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 7.38 – 7.20 (m, 15H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.26 (dt, *J* = 15.9, 6.3 Hz), 1H), 5.08 (s, 1H), 4.81 (dd, *J* = 6.4, 1.4 Hz, 2H) ppm. ***Z* isomer:** δ 7.38 – 7.20 (m, 15H), 6.66 (d, *J* = 11.8 Hz, 1H), 5.80 (dt, *J* = 11.7, 6.7 Hz), 5.06 (s, 1H), 4.90 (dd, *J* = 6.7, 1.6 Hz, 2H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 172.21, 138.57, 136.14, 134.20, 128.61, 128.60, 128.56, 128.04, 127.28, 126.58, 122.82, 65.62, 57.10 ppm. ***Z* isomer:** δ 172.27, 138.54, 135.89, 133.46, 128.68, 128.60, 128.34, 128.04, 127.52, 125.36, 122.82, 62.13, 57.03 ppm.

HRMS (ESI) calculated m/z for $C_{23}H_{20}O_2$([M+NH_4]$^+$): 346.1802, measured: 346.1799.



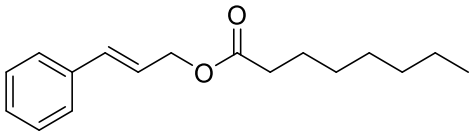
Cinnamyl 2-(trifluoromethyl)phenyl acetate (2h)

Prepared according to the general procedure with allylbenzene and 2-(trifluoromethyl)phenyl acetic acid. White oil obtained in 71% isolated yield (*E*:*Z* 13:1).

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 7.67 (bd, *J* = 8.0 Hz, 1H), 7.53 (bt, *J* = 7.7 Hz, 1H), 7.39 (m, 4H), 7.32 (m, 2H), 7.26 (m, 1H), 6.61 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.26 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.77 (dd, *J* = 6.4, 1.4 Hz, 2H), 3.88 (s, 2H) ppm. ***Z* isomer:** δ 7.67 (bd, *J* = 8.0 Hz, 1H), 7.53 (bt, *J* = 7.7 Hz, 1H), 7.39 (m, 4H), 7.32 (m, 2H), 7.26 (m, 1H), 6.67 (d, *J* = 11.8 Hz, 1H), 5.79 (dt, *J* = 11.7, 6.7 Hz, 1H), 4.87 (dd, *J* = 6.7, 1.6 Hz, 2H), 3.88 (s, 2H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 170.5, 136.2, 134.2, 132.6, 132.3 (q, *J* = 2 Hz), 131.9 (q, *J* = 1 Hz), 129.0 (q, *J* = 30 Hz), 128.6, 128.1, 127.4, 126.6, 126.1 (q, *J* = 5.5 Hz), 124.3 (q, *J* = 274 Hz), 122.8, 65.6, 38.2 (q, *J* = 2 Hz) ppm. ***Z* isomer:** δ 170.5, 135.9, 133.3, 132.5, 132.3 (q, *J* = 2 Hz), 131.9 (q, *J* = 1 Hz), 129.0 (q, *J* = 30 Hz), 128.7, 128.4, 127.5, 126.6, 126.1 (q, *J* = 5.5 Hz), 124.3 (q, *J* = 274 Hz), 122.8, 62.1, 38.2 (q, *J* = 2 Hz) ppm.

HRMS (ESI) calculated m/z for $C_{14}H_{12}O_2S$ ([M+Na]$^+$): 343.0916, measured: 343.0915.



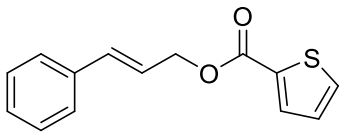
Compound 2i

Prepared according to the general procedure with allylbenzene and octanoic acid. Clear oil obtained in 42% isolated yield (*E*:*Z* 12:1).

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 7.39 (m, 2H), 7.33 (m, 2H), 7.26 (m, 1H), 6.65 (bd, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.74 (dd, *J* = 6.4, 1.4 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.29 (m, 8H), 0.88 (m, 3H) ppm. ***Z* isomer:** δ 7.39 (m, 2H), 7.33 (m, 2H), 7.26 (m, 1H), 6.67 (bd, *J* = 11.9 Hz, 1H), 5.82 (dt, *J* = 11.8, 6.7 Hz, 1H), 4.85 (dd, *J* = 6.6, 1.7 Hz, 2H) 2.35 (t, *J* = 7.6 Hz, 2H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.29 (m, 8H), 0.88 (m, 3H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 173.6, 136.2, 134.0, 128.6, 128.0, 126.6, 123.4, 64.8, 34.3, 31.7, 29.1, 28.9, 25.0, 22.6, 14.0 ppm. ***Z* isomer:** δ 173.7, 136.0, 132.9, 128.7, 128.4, 127.5, 126.0, 61.3, 34.3, 31.7, 29.1, 28.9, 25.0, 22.6, 14.0 ppm.

HRMS (ESI) calculated m/z for $C_{17}H_{24}O_2$ ([M+Na]$^+$): 283.1669, measured: 327.0779.



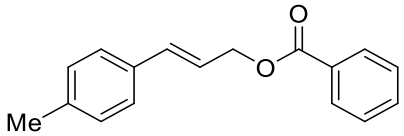
Compound 2j

Prepared according to the general procedure with allylbenzene and 2-thiophenecarboxylic acid. Clear oil obtained in 64% isolated yield (*E*:*Z* 12:1).

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 7.84 (dd, *J* – 3.8, 1.3 Hz, 1H), 7.57 (dd, *J* – 5.0, 1.3 Hz, 1H), 7.42 (m, 2 H), 7.34 (m, 2 H), 7.27 (m, 1H), 7.11 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.74 (dt, *J*- 16.0, 1.4 Hz, 1H), 6.39 (dt, *J* – 15.9, 6.4 Hz, 1H), 4.96 (dd, *J* = 6.4, 1.4 Hz, 2H) ppm. ***Z* isomer:** δ 7.84 (dd, *J* – 3.8, 1.3 Hz, 1H), 7.57 (dd, *J* – 5.0, 1.3 Hz, 1H), 7.42 (m, 2 H), 7.34 (m, 2 H), 7.27 (m, 1H), 7.11 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.74 (m, 1H), 5.93 (dt, *J* = 11.8, 6.7 Hz), 5.07 (dd, *J* = 6.6, 1.6 Hz) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 162.0, 136.2, 134.5, 133.7, 133.6, 132.5, 128.6, 128.1, 127.8, 126.7, 123.0, 65.7 ppm. ***Z* isomer:** δ 162.0, 135.9, 134.0, 133.3, 132.9, 132.5, 128.7, 128.4, 127.6, 125.6, 123.0, 62.1 ppm.

HRMS (ESI) calculated m/z for $C_{14}H_{12}O_2S$ ([M+Na]$^+$): 267.0450, measured: 267.0448.



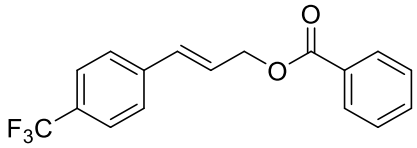
4-methylcinnamyl benzoate (3a)

Prepared according to the general procedure with allyltoluene and benzoic acid. White solid obtained in 82% isolated yield (*E*:*Z* 11:1). ^{1}H NMR data agree with previously reported values.[8]

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 8.09 (m, 2H), 7.57 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.36 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.98 (dd, *J* = 6.5, 1.3 Hz, 2H), 2.34 (s, 3H) ppm. ***Z* isomer:** δ 8.09 (m, 2H), 7.57 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.70 (d, *J* = 11.7 Hz, 1H), 5.91 (dt, *J* = 11.7, 6.6 Hz, 1H), 5.10 (dd, *J* = 6.6, 1.7 Hz, 2H), 2.36 (s, 3H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 166.4, 138.0, 134.3, 133.4, 132.9, 130.2, 129.6, 129.3, 128.4, 126.6, 122.2, 65.7, 21.2 ppm. ***Z* isomer:** δ 166.4, 138.0, 134.3, 133.4, 132.9, 130.2, 129.6, 129.1, 128.4, 126.6, 122.2, 65.7, 21.2 ppm.

HRMS (ESI) calculated m/z for $C_{17}H_{16}O_2$ ([M+Na]$^+$): 275.1043, measured: 275.1042.



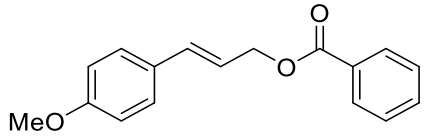
4-(trifluoromethyl)cinnamyl benzoate (3b)

Prepared according to the general procedure with 4-(trifluoromethyl)allylbenzene and benzoic acid. White solid obtained in 91% isolated yield (*E*:*Z* 11:1).

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 8.09 (m, 2H), 7.59 (m, 3H), 7.51 (d, *J* = 8.16 Hz, 2H), 7.47 (m, 2H), 6.77 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.50 (dt, *J* = 15.9, 6.1 Hz, 1H), 5.02 (dd, *J* = 6.2, 1.5 Hz, 2H) ppm. ***Z* isomer:** δ 8.05 (m, 2H), 7.59 (m, 3H), 7.51 (d, *J* = 8.16 Hz, 2H), 7.47 (m, 2H), 6.75 (m, 1H), 6.07 (dt, *J* = 11.8, 6.6 Hz, 1H), 5.07 (dd, *J* = 6.7, 1.8 Hz, 2H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 166.3, 139.7 (m), 133.1, 132.4, 130.0, 129.8 (q, *J* = 32 Hz), 129.7, 128.4, 126.8, 126.1, 125.6 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272 Hz), 65.0 ppm.
***Z* isomer:** δ 166.3, 139.7 (m), 133.1, 131.8, 130.0, 129.8 (q, *J* = 32 Hz), 129.6, 128.4, 126.7, 126.1, 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272 Hz), 61.5 ppm.

HRMS (ESI) calculated m/z for $C_{17}H_{13}F_3O_2$ ($[M+NH_4]^+$): 324.1206, measured: 324.1204.



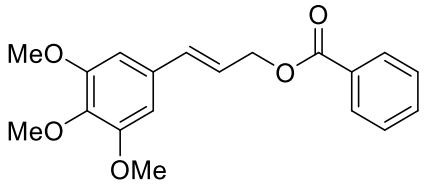
4-Methoxycinnamyl benzoate (3c)

Prepared according to the general procedure with allylanisole and benzoic acid. yellow solid obtained in 80% isolated yield (*E*:*Z* 13:1). ^{1}H NMR data are in agreement with previously reported values.[12]

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 8.08 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.56 (tt, *J* = 7.3, 1.6 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.36 (m, 2H), 6.87 (m, 2H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.96 (dd, *J* = 6.5, 1.3 Hz, 2H), 3.82 (s, 3H) ppm. ***Z* isomer:** δ 8.08 (m, 2H), 7.56 (tt, *J* = 7.3, 1.6 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J*= 8.7 Hz, 2H), 6.91 (m, 1H), 6.67 (d, *J* = 11.9 Hz, 1H), 5.86 (dt, *J* = 11.6, 6.6 Hz, 1H), 5.09 (dd, *J* = 6.6, 1.6 Hz, 2H), 3.83 (s, 3H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 166.4, 159.6, 134.1, 132.9, 130.3, 129.6, 129.0, 128.3, 127.9, 120.9, 114.0, 65.8, 55.3 ppm. ***Z* isomer:** δ 166.4, 159.6, 134.1, 132.8, 130.3, 130.1, 129.6, 128.3, 127.9, 120.9, 113.8, 62.1, 55.3 ppm.

HRMS (ESI) calculated m/z for $C_{17}H_{16}O_3$ ($[M+Na]^+$): 291.0992, measured: 291.0986.



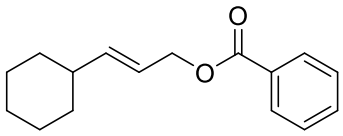
3,4,5-trimethoxycinnamyl benzoate (3d)

Prepared according to the general procedure with 4-(trifluoromethyl)allylbenzene and benzoic acid. Yellow oil obtained in 83% isolated yield (*E*:*Z* 12:1).

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 8.09 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.56 (m, 1H), 7.46 (m, 2H), 6.67 (bd, *J* = 15.9 Hz, 1H), 6.64 (s, 2H), 6.33 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.98 (dd, *J* = 6.4, 1.4 Hz, 2H), 3.88 (s, 6H), 3.85 (s, 3H) ppm. ***Z* isomer:** δ 8.06 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.56 (m, 1H), 7.46 (m, 2H), 6.68 (bd, *J* = 11.4 Hz, 1H), 6.53 (s, 2H), 5.93 (dt, *J* = 11.6, 6.9 Hz, 1H), 5.09 (dd, *J* = 6.9, 1.5 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 6H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 166.4, 153.3, 138.2, 134.3, 133.0, 131.9, 130.2, 129.7, 128.4, 122.8, 103.7, 65.5, 60.9, 56.1 ppm. ***Z* isomer:** δ 166.4, 153.2, 137.6, 133.8, 133.1, 131.7, 130.1, 129.6, 128.4, 125.3, 105.9, 61.8, 60.9, 56.1 ppm.

HRMS (ESI) calculated m/z for $C_{19}H_{20}O_5$ ($[M+NH_4]^+$): 346.1649, measured: 346.1644.



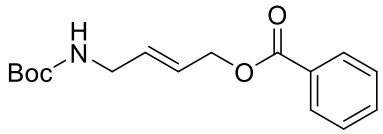
(*E*)-3-benzoyl-1-cyclohexyl-1-propene (3e)

Prepared according to the general procedure with allylcyclohexane and benzoic acid. Clear oil obtained in 75% isolated yield (*E* isomer only). NMR data agree with previously reported spectrum.[13]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.06 (m, 2H), 7.55 (m, 1H), 7.44 (t, *J* = 7.78 Hz, 2H), 5.80 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.63 (dtd, *J* = 15.5, 6.4, 1.3 Hz, 1H), 4.76 (d, *J* = 6.54 Hz, 2H), 2.01 (m, 1H), 1.74 (m, 4H), 1.66 (m, 1 H), 1.26 (m, 2H), 1.13 (m, 3H) ppm.

^{13}C NMR (500 MHz, Chloroform-*d*): δ 166.4, 142.1, 132.8, 130.4, 129.6, 128.3, 121.3, 66.0, 40.4, 32.6, 26.1, 26.0 ppm.

HRMS (ESI) calculated m/z for $C_{16}H_{20}O_2$ ($[M+Na]^+$): 267.1356, measured: 267.1351.



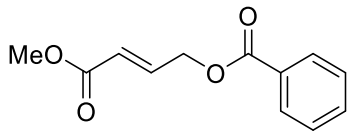
Compound 3f

Prepared according to the general procedure with *tert*-butyl-3-enyl carbamate and benzoic acid. White solid obtained in 61% isolated yield (*E*:*Z* >20:1).

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 8.05 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.56 (m, 1H), 7.44 (m, 2H), 5.85 (m, 2H), 4.81 (dt, *J* = 4.5, 1.1 Hz, 2H), 4.61 (bs, 1H), 3.80 (m, 2H), 1.45 (s, 9H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 166.3, 155.7, 122.0, 131.5, 130.1, 129.6, 128.4, 125.5, 79.5, 64.6, 41.9, 28.4 ppm.

HRMS (ESI) calculated m/z for $C_{16}H_{21}NO_4$ ($[M+NH_4]^+$): 309.1809, measured: 309.1806.



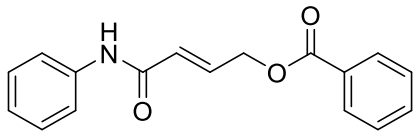
Compound 3g

Prepared according to the general procedure with methyl-3 butenoate, benzoic acid, and *tert*-butylbenzoquinone (17.3 mg, 108 mM) instead of 2,6-dimethylbenzoquinone. White solid obtained in 88% isolated yield (*E:Z* 19:1 from NMR yield). NMR data agree with previously reported spectrum.[14]

^{1}H NMR (500 MHz, Chloroform-*d*) ***E* isomer:** δ 8.08 (m, 2H), 7.59 (m, 1H), 7.47 (m, 2H), 7.07 (dt, *J* = 15.8, 4.5 Hz, 1H), 6.14 (dt, *J* = 15.8, 2.0 Hz, 1H), 5.00, (dd, *J* = 4.5, 2.0 Hz, 2H), 3.77 (s, 3H) ppm. ***Z* isomer:** δ 8.07 (m, 2H), 7.58 (m, 1H), 7.46 (m, 2H), 6.40 (dt, *J* = 11.6, 5.1 Hz, 1H), 5.94 (dt, *J* = 11.6, 2.4 Hz, 1H), 5.44 (dd, *J* = 11.6, 2.4 Hz, 2H), 3.77 (s, 3H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*) ***E* isomer:** δ 166.2, 165.8, 141.5, 133.4, 129.7, 129.5, 128.5, 121.8, 62.9, 51.8 ppm. ***Z* isomer:** δ 166.3, 166.2, 145.0, 133.1, 129.9, 129.7, 128.4, 120.9, 63.1, 51.2 ppm.

HRMS (ESI) calculated m/z for $C_{12}H_{12}O_4$ ($[M+Na]^+$): 238.1074, measured: 238.1072.



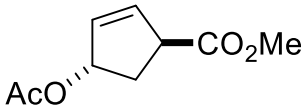
Compound 3h

Prepared according to the general procedure with *N*-phenyl-3-butenamide and benzoic acid. Tan solid obtained in 30% isolated yield (*E* isomer only).

^{1}H NMR (500 MHz, Chloroform-*d*)**:** δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.61 (m, 1H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.34 (m, 2H), 7.22 (bs, 1H), 7.11 (dt, *J* = 15.2, 4.4 Hz, 1H), 6.22 (bd, *J* = 15.2, 1H), 5.05 (dd, *J* = 4.6, 2.0, 2H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*): δ 165.9, 162.7, 138.8, 137.6, 133.4, 129.7, 129.6, 129.1, 128.5, 124.7, 124.6, 119.9, 63.2 ppm.

HRMS (ESI) calculated m/z for $C_{17}H_{15}NO_3$ ($[M+H]^+$): 282.1125, measured: 282.1122.



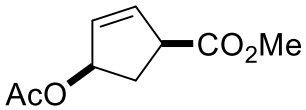
Compound *trans*-5-OAc

Prepared according to the procedure in section 5 without DAF. Obtained in 75% NMR yield.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.10 (ddd, *J* = 5.5, 2.3, 1.0 Hz, 1H), 5.99 (dt, *J* = 5.6, 2.4 Hz, 1H), 5.78 (m, 1H), 3.80 (m, 1H), 3.71 (s, 3H), 2.59 (ddd, *J* = 14.4, 7.5, 5.2 Hz, 1H), 2.11 (m, 1H), 2.04 (s, 3H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*): δ 173.6, 170.7, 135.1, 132.1, 79.4, 52.1, 49.4, 33.4, 21.1 ppm.

HRMS (ESI) calculated m/z for $C_{17}H_{15}NO_3$ ($[M+NH_4]^+$): 202.1074, measured: 202.1073.



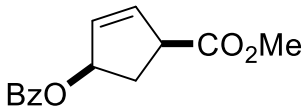
Compound *cis*-5-OAc

Prepared according to the procedure in section 5 using DAF. Obtained in 77% NMR yield (1.4:1 *trans*:*cis*). Characterization NMR and HRMS was done on a sample that was 1:8 *trans*:*cis*.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.07 (m, 1H), 5.92 (dt, *J* = 5.6, 2.3 Hz, 1H), 5.66 (ddt, *J* = 7.8, 4.4, 1.7 Hz, 1H), 3.72 (s, 3H), 3.52 (m, 1H), 2.63 (ddd, *J* = 14.2, 8.8, 7.8 Hz, 1H), 2.12 (m, *J* = 14.5, 5.5, 4.5 Hz, 1H), 2.04 (s, 3H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*): δ 173.4, 170.9, 134.0, 132.0, 178.7, 52.1, 48.9, 32.8, 21.2 ppm.

HRMS (ESI) calculated m/z for $C_{17}H_{15}NO_3$ ($[M+Na]^+$): 207.0628, measured: 207.0623.



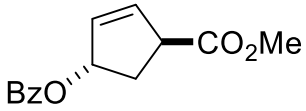
Compound *cis*-5-OBz

Prepared according to the general procedure with methyl 3-cyclopentenecarboxylate and benzoic acid. The substrate stock solution was prepared in 2 mL DCE at 2.71 M, and 0.4 mL was injected into the reaction test tube before it was placed on the reactor. Clear oil obtained in 50% NMR yield.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.04 (m, 2H), 7.54 (m, 1H), 7.43 (m, 2H), 6.14 (ddd, *J* = 5.6, 2.4, 1.2 Hz, 1H), 6.06 (dt, *J* = 5.6, 2.3 Hz, 1H), 5.92 (m, 1H), 3.73 (s, 3H), 3.60 (m, 1H), 2.74 (ddd, *J* = 14.4, 8.7, 7.7 Hz, 1H), 2.30 (ddd, *J* – 14.4, 5.5, 4.4 Hz, 1H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*): δ 173.4, 166.3, 134.2, 132.9, 132.1, 130.2, 129.7, 128.3, 79.3, 52.1, 49.0, 33.0 ppm.

HRMS (ESI) calculated m/z for $C_{14}H_{14}O_4$ ($[M+Na]^+$): 269.0784, measured: 269.0782.



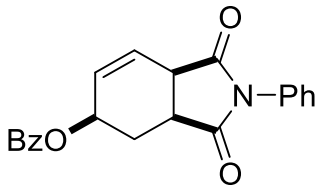
Compound *trans*-5-OBz

Prepared according to the general procedure with methyl 3-cyclopentenecarboxylate and benzoic acid. The substrate stock solution was prepared in 2 mL DCE at 2.71 M. 0.4 mL was injected into the reaction test tube before it was placed on the reactor. Clear oil obtained in 31% NMR yield.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.02 (m, 2H), 7.55 (m, 1H), 7.43 (m, 2H), 6.15 (ddd, *J* = 5.7, 2.2, 0.8 Hz, 1H), 6.11 (dt, *J* = 5.5, 2.3 Hz, 1H), 6.04 (m, 1H), 3.86 (m, 1H), 3.73 (s, 3H), 2.71 (ddd, *J* = 14.6, 7.4, 5.1 Hz, 1H), 2.26 (ddd, *J* = 14.6, 8.4, 3.0 Hz) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*): δ 173.8, 166.3, 135.3, 133.0, 132.2, 130.3, 129.6, 128.3, 80.1, 52.2, 49.6, 33.7 ppm.

HRMS (ESI) calculated m/z for $C_{14}H_{14}O_4$ ($[M+NH_4]^+$): 264.1230, measured: 264.1228.



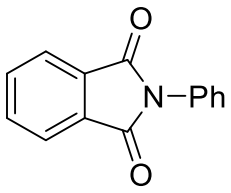
Compound 7

Prepared according to the general procedure with **6** and benzoic acid. The substrate stock solution was prepared in 1 mL DCE at 1.35 M. 0.8 mL was injected into the reaction test tube before it was placed on the reactor. White solid obtained in 73% NMR yield.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.86 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.48 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.39 (m, 3H), 7.27 (m, 2H), 7.18 (m, 2H), 6.41 (ddd, *J* = 9.9, 5.3, 2.1 Hz, 1H), 6.20 (dd, *J* = 9.9, 4.6 Hz, 1H), 5.53 (bq, *J* = 4.4 Hz, 1H), 3.76 (m, 1H), 3.39 (ddd, *J* = 8.7, 7.1, 3.7 Hz, 1H), 2.75 (dt, *J* = 14.5, 3.8 Hz, 1H), 2.21 (ddd, *J* = 14.2, 6.9, 3.5 Hz, 1H) ppm.

^{13}C NMR (125 MHz, Chloroform-*d*): δ 177.4, 175.2, 165.9, 133.0, 131.8, 129.8, 129.6, 129.07, 129.06, 128.6, 128.3, 126.8, 126.6, 65.2, 40.9, 36.2, 26.3 ppm.

HRMS (ESI) calculated m/z for $C_{21}H_{17}NO_4$ ($[M+NH_4]^+$): 365.1496, measured: 365.1495.



Compound 8

Obtained as a side product when following the general procedure with **6** and benzoic acid. The substrate stock solution was prepared in 1 mL DCE at 1.35 M. 0.8 mL was injected into the reaction test tube before it was placed on the reactor. White solid obtained in 15% NMR yield. NMR data are in agreement with previously reported values.[15]

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.97 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.53 (m, 2H), 7.43 (m, 3H) ppm.

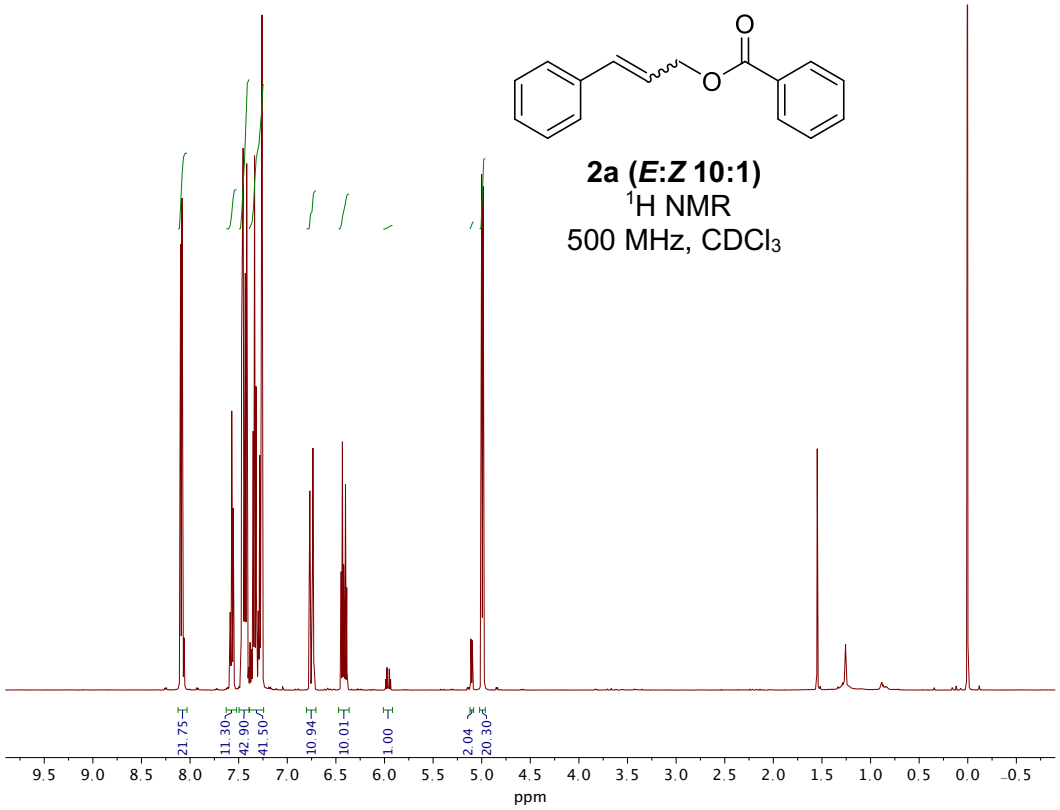
^{13}C NMR (125 MHz, Chloroform-*d*): δ 167.3, 134.4, 131.8, 131.7, 129.1, 128.1, 126.6, 123.8 ppm.

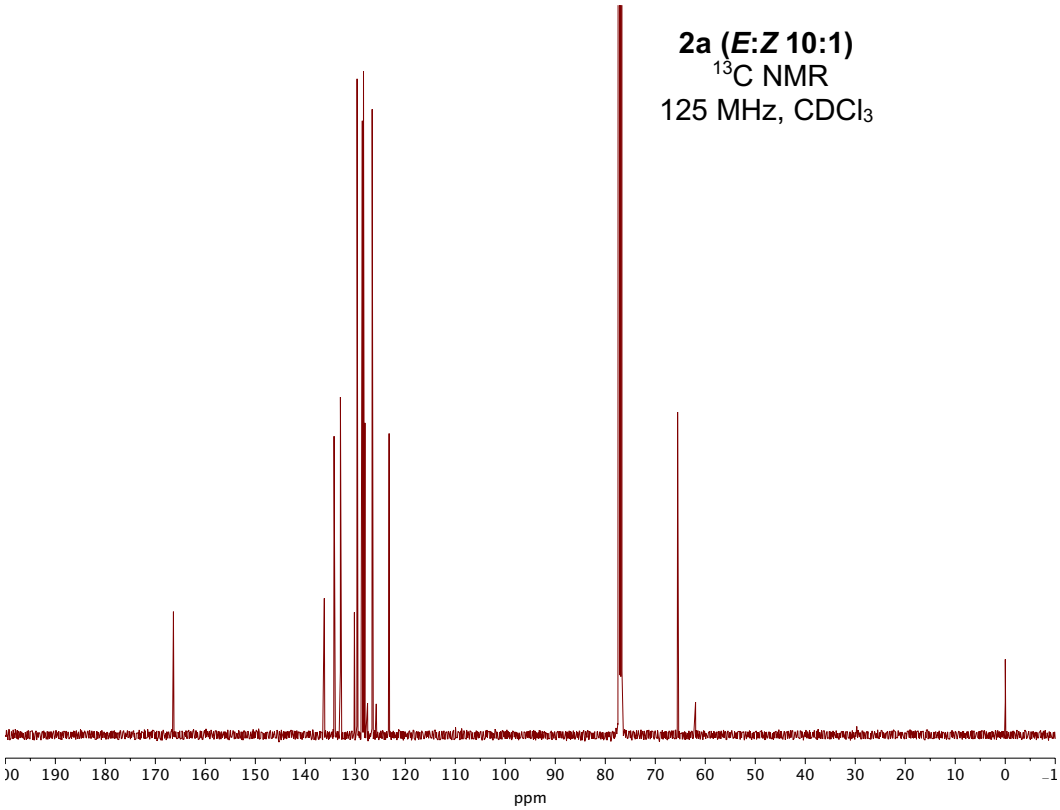
HRMS (ESI) calculated m/z for $C_{21}H_{17}NO_4$ ($[M+Na]^+$): 246.0526, measured: 246.0525.

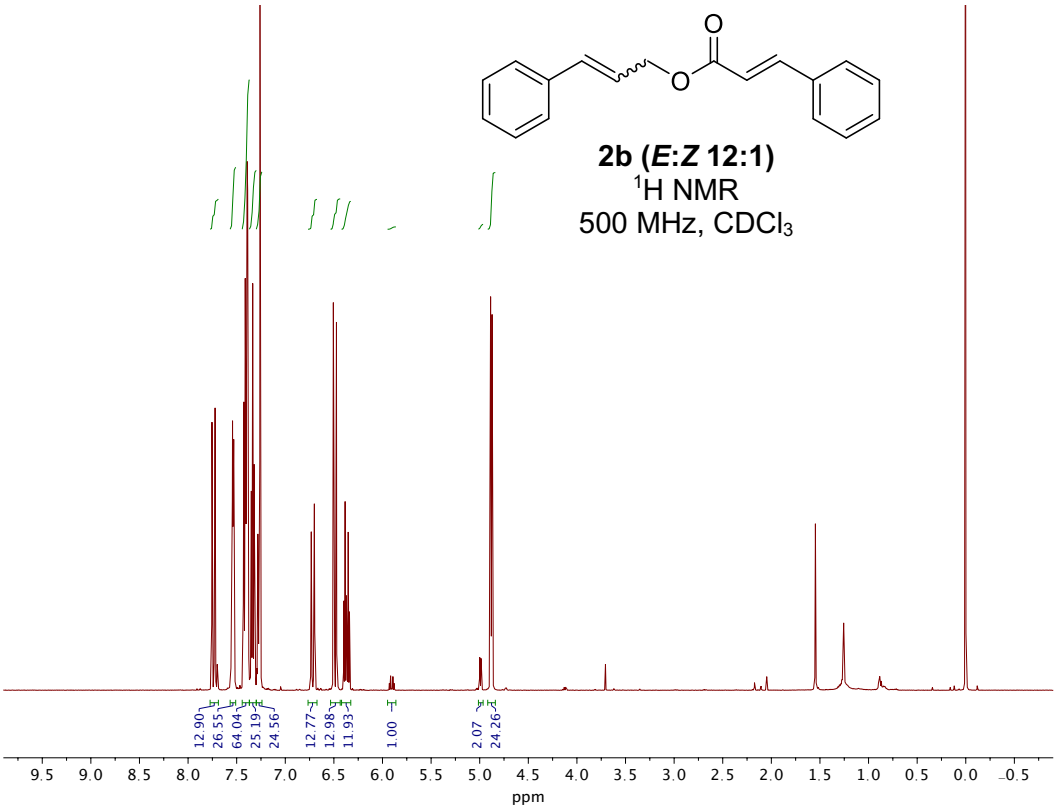
8. References

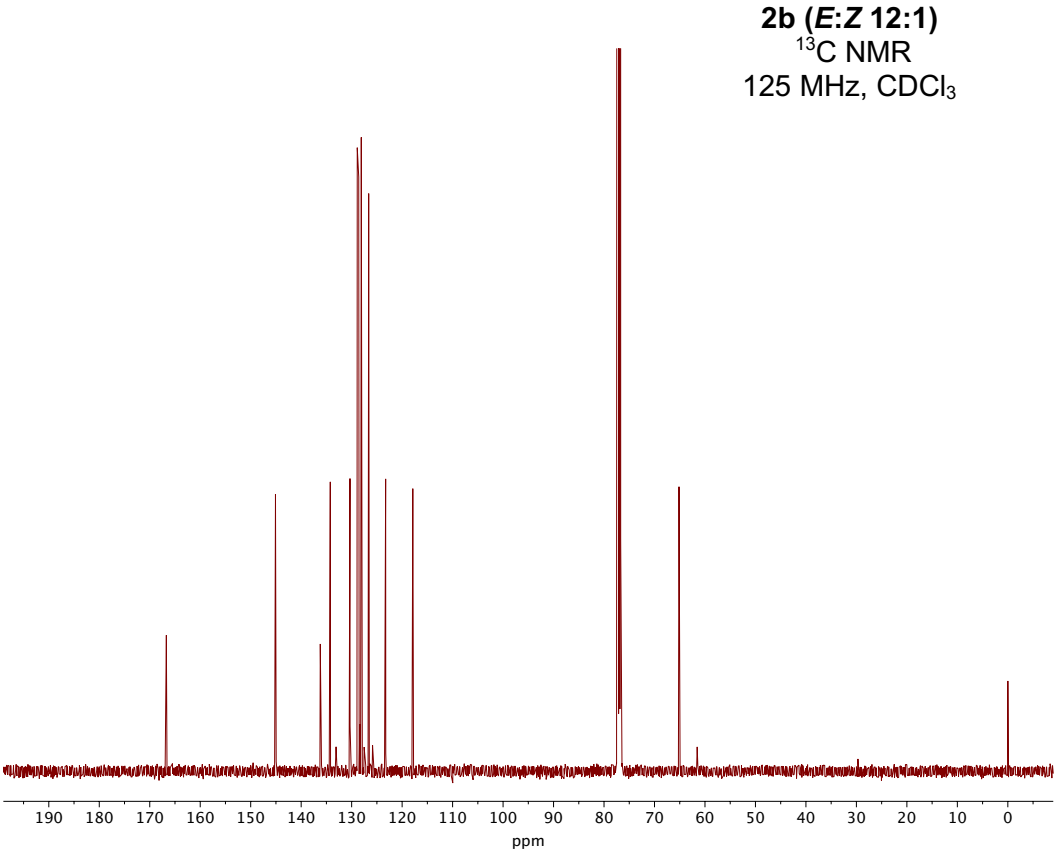
[1] O.Pavlyuk, H. , Teller, M. C. Mcmills, *Tet. Lett.* **2009**, *50*, 2716-2718.
[2] B. Gaspar, E. M. Carreira, *Angew. Chem. Int. Ed.* **2008**, *47*, 57550-57560.
[3] A. Tan, B. Koc, E. Sahin, N. H. Kishali, Y. Kara, *Synthesis* **2011**, *7*, 1079-1084.
[4] P. M. Osterberg, J. K. Niemeier, C. J. Welch, J. M. Hawkins, J. R. Martinelli, T. E. Johnson, T. W. Root, S. S. Stahl, *Org. Process Res. Dev.* **2015**, *19*, 1537–1543.
[5] N. A. Vermeulen, J. H. Delcamp, M. C. White, *J. Am. Chem. Soc.* **2010**, *132*, 11323-11328.
[6] A. N. Campbell, P. B. White, S. S. Stahl, *J. Am. Chem. Soc.* **2010**, *132*, 15116-15119.
[7] J. R. Schmidt, W. F. Polik, *WebMO Enterprise*, version 18.1.002; WebMO LLC: Holland, MI, USA, 2018; *http://webmo.net* (accessed March 2019).
[8] T. Niwa, M. Nakada, *J. Am. Chem. Soc.* **2012**, *134*, 13538-13541.
[9] X. Huang, B. Fulton, K. White, A. Bugarin. *Org. Lett*. **2015**, *17*, 2594-2597.
[10] Z. Zhang, Y. Liu, L. Ling, Y. Li, Y. Dong, M. Gong, X. Zhao, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 4330-4341.
[11] N. T. Patil, NK. Pahadi, Y. Yamamoto, *Can. J. Chem*. **2005**, *83*, 569-573.
[12] S. Lim, M. Ji, X. Wang, C. Lee, H.-Y. Jang, *Eur. J. Org. Chem.* **2015**, 591-595.
[13] R. Correia, P. DeShong, *J. Org. Chem.* **2001**, *66*, 7159-7165.
[14] L. T. Pilarski, N. Selander, D. Böse, K. J. Szabó, *Org. Lett.* **2009**, *11*, 5518-5521.
[15] A. V. Iosub, S. S. Stahl, *J. Am. Chem. Soc.* **2015**, *137*, 3454-3457.

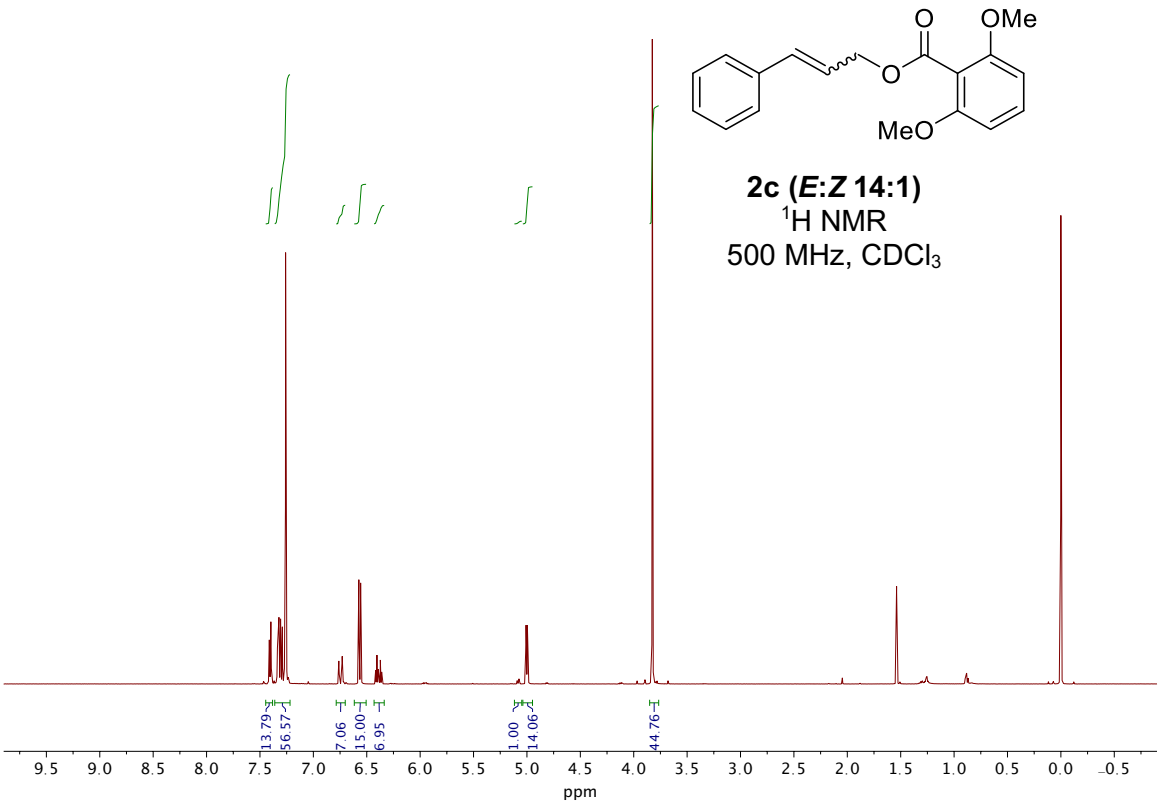
9. NMR Spectra

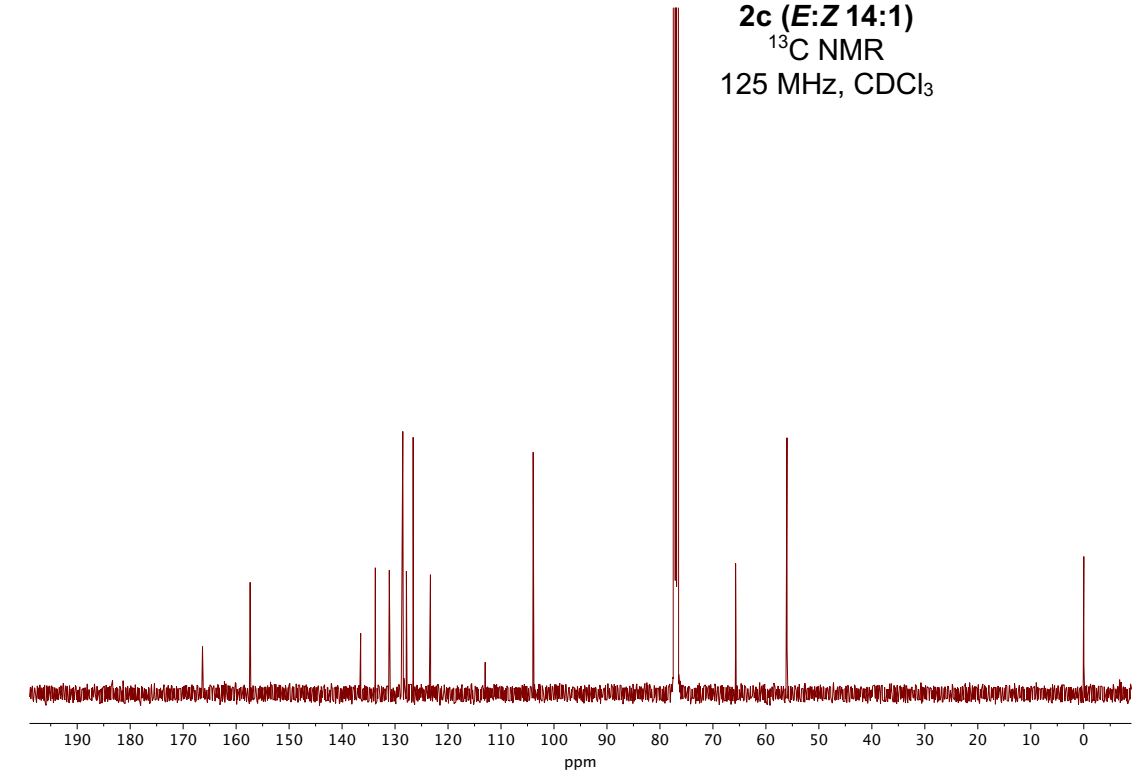


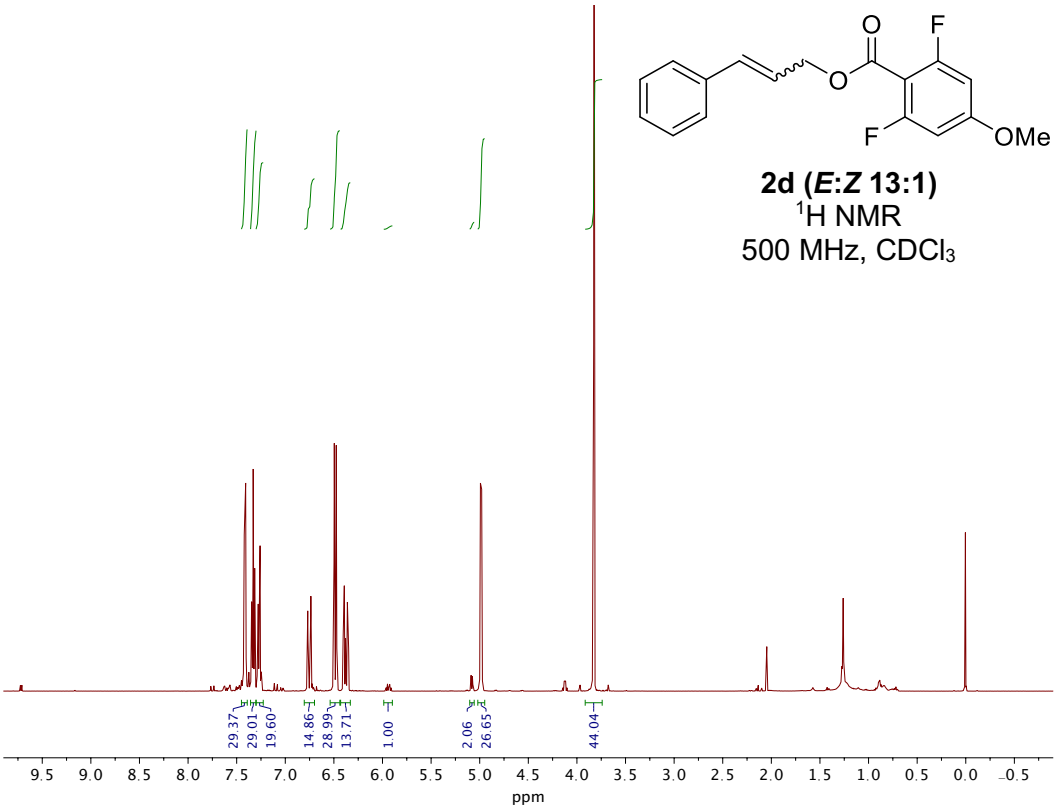


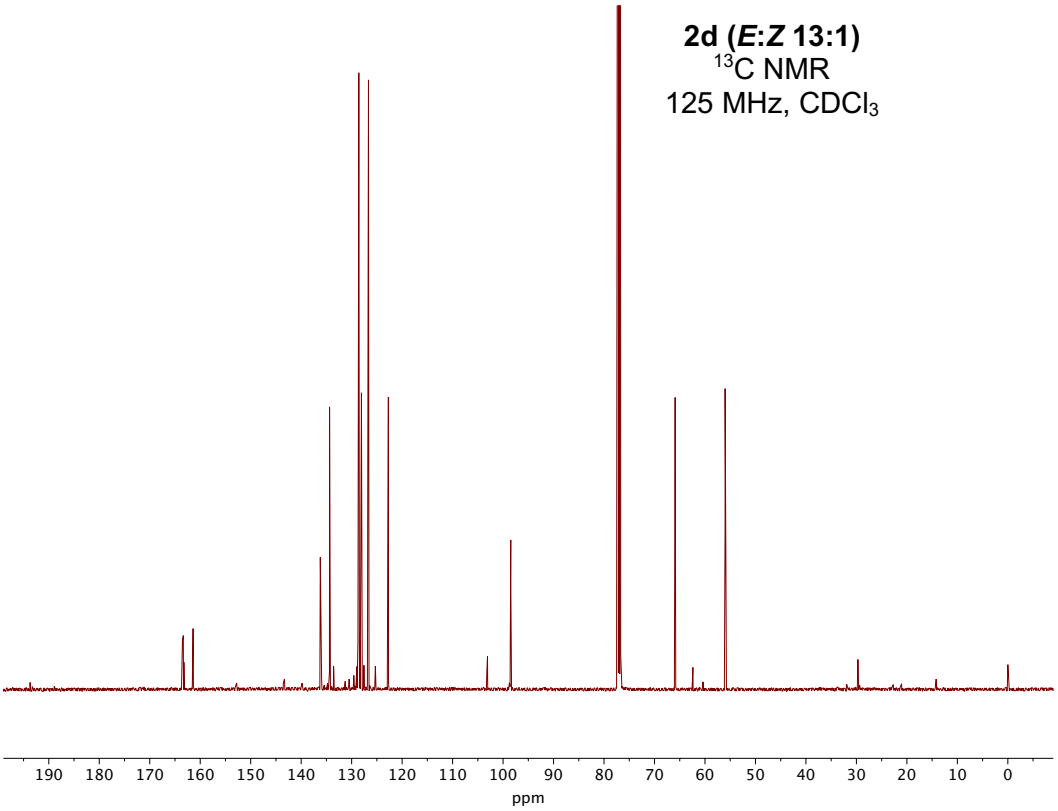

O
O
2b (E:Z 12:1)
1H NMR
500 MHz, CDCl3
12.90
26.55
64.04
25.19
24.56
12.77
12.98
11.93
1.00
2.07
24.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

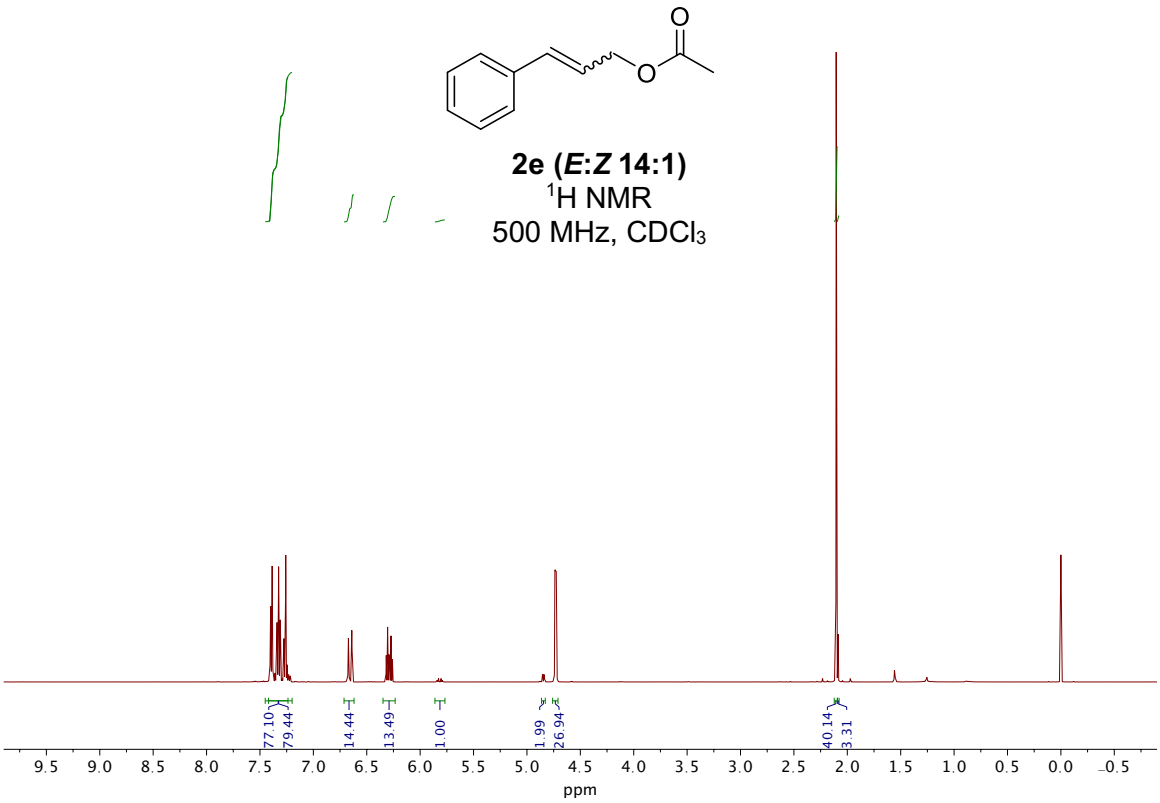

2b (E:Z 12:1)
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

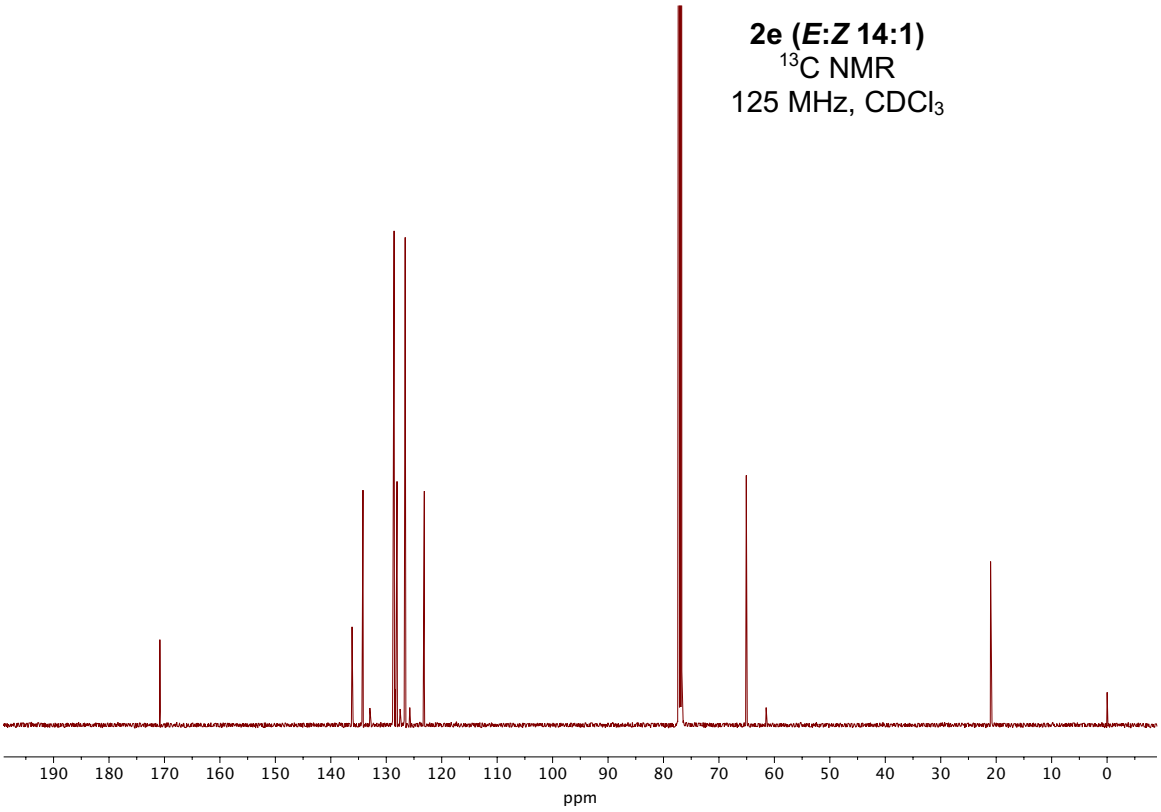

O
OMe
O
MeO
2c (E:Z 14:1)
1H NMR
500 MHz, CDCl3
13.79
56.57
7.06
15.00
6.95
1.00
14.06
44.76
ppm

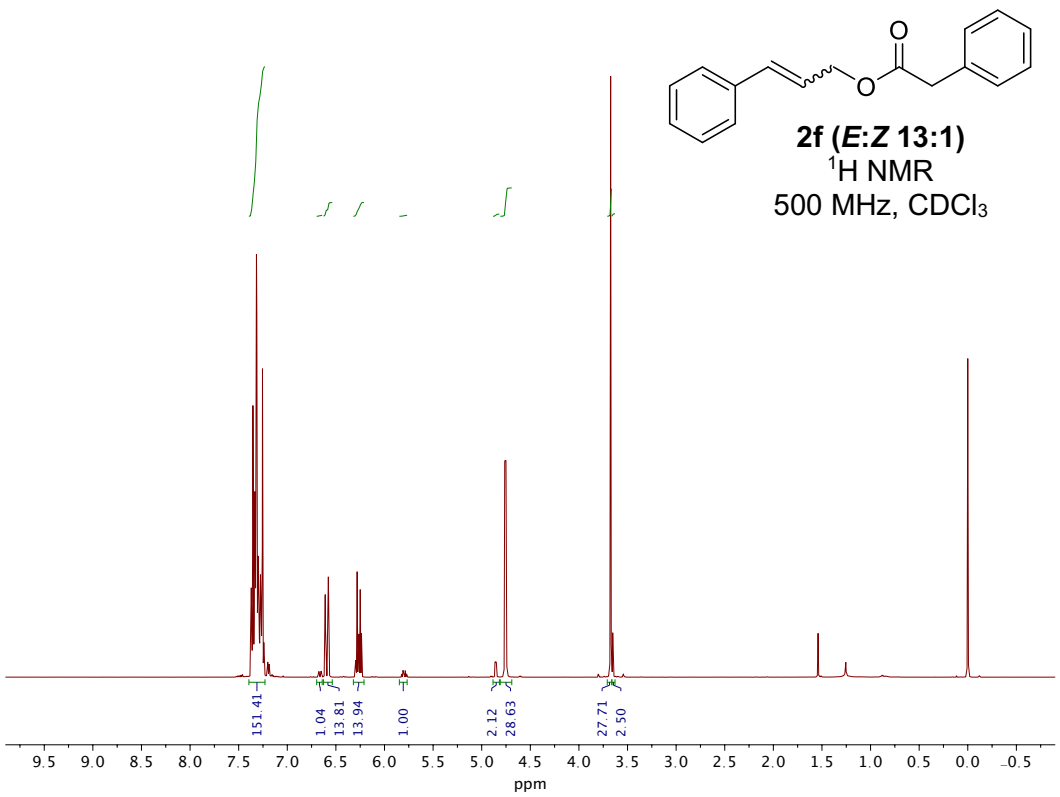

2c (E:Z 14:1)
13C NMR
125 MHz, CDCl3
ppm

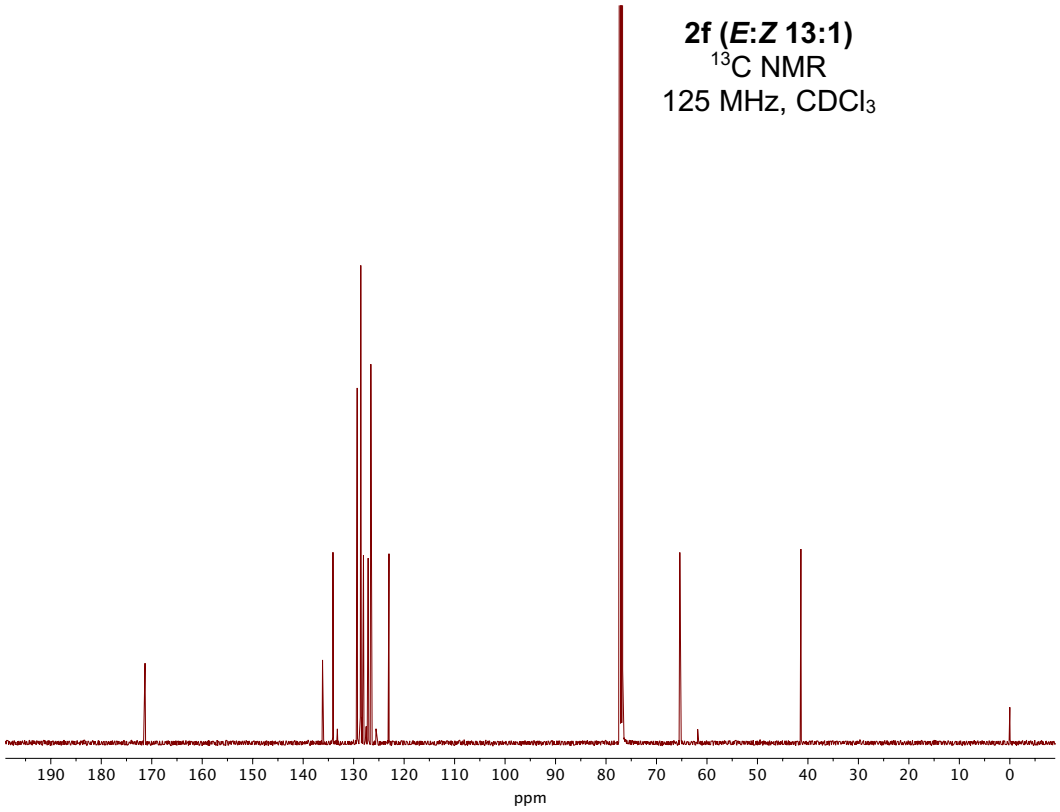

O
F
O
F
OMe
2d (E:Z 13:1)
1H NMR
500 MHz, CDCl3
29.37
29.01
19.60
14.86
28.99
13.71
1.00
2.06
26.65
44.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

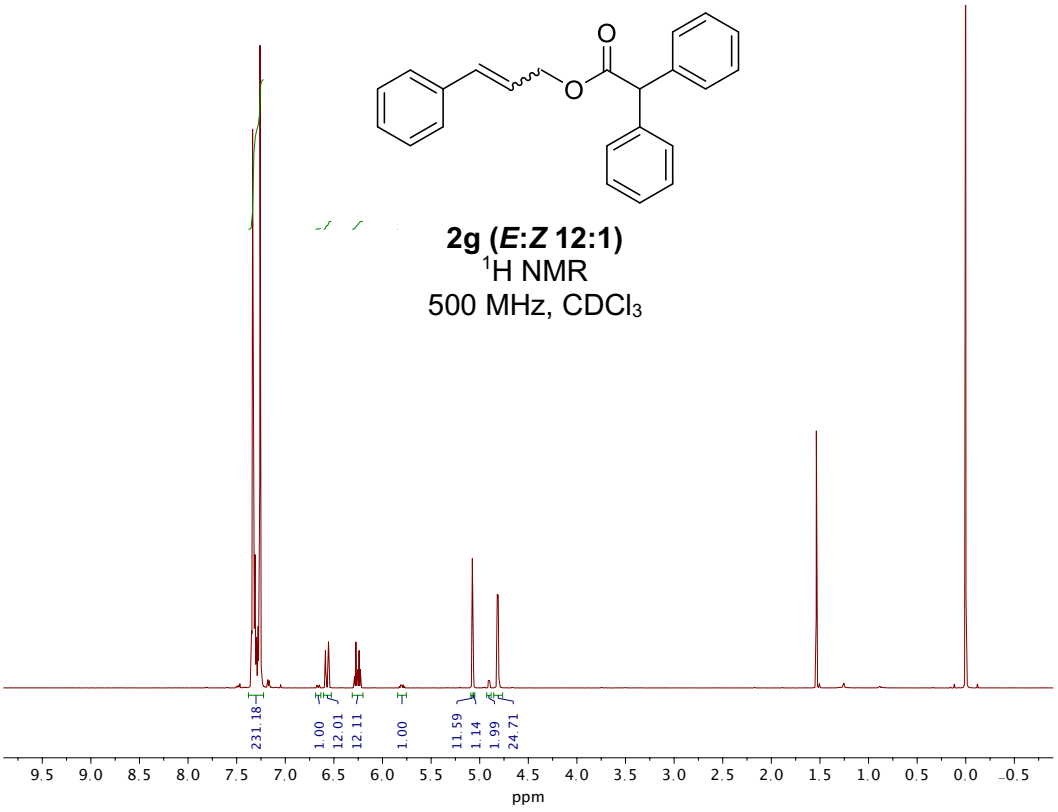

2d (E:Z 13:1)
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
O
2e (E:Z 14:1)
1H NMR
500 MHz, CDCl3
77.10
79.44
14.44
13.49
1.00
1.99
26.94
40.14
3.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

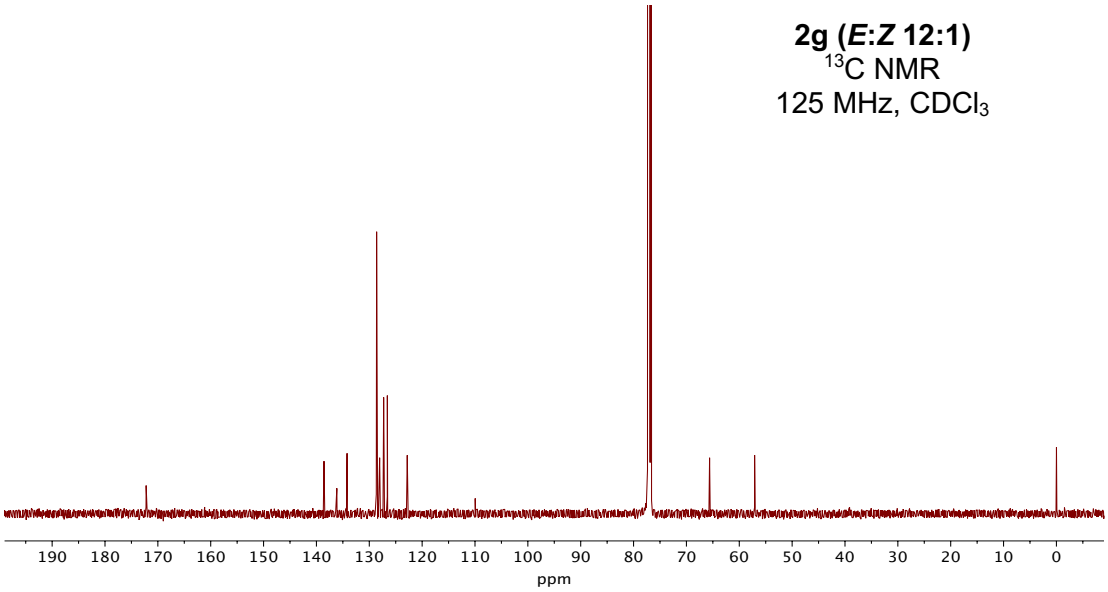

2e (E:Z 14:1)
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
O
2f (E:Z 13:1)
1H NMR
500 MHz, CDCl3
151.41
1.04
13.81
13.94
1.00
2.12
28.63
27.71
2.50
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

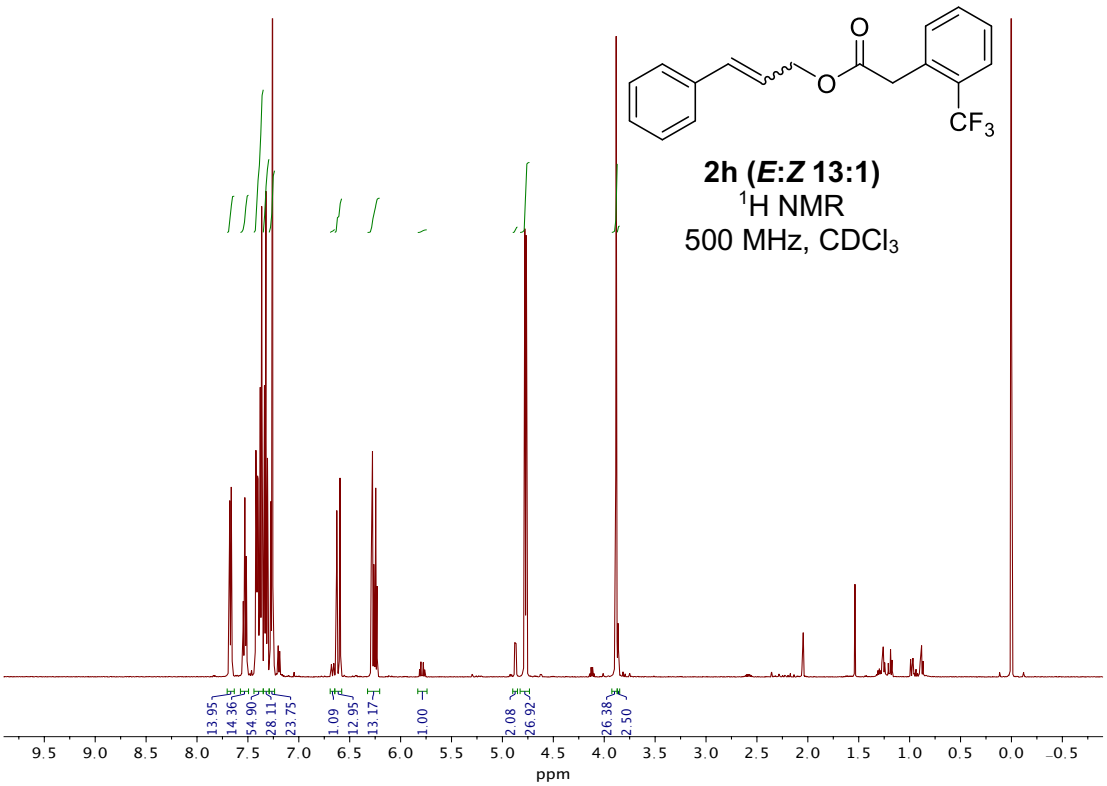

2f (E:Z 13:1)
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

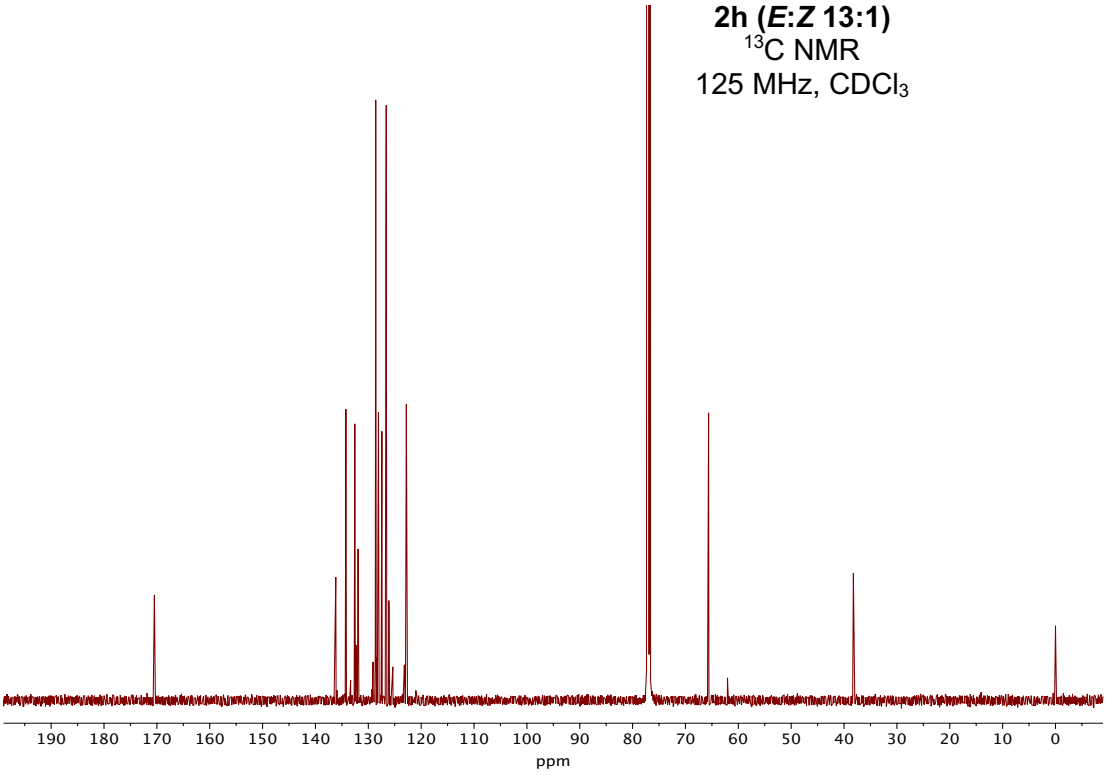


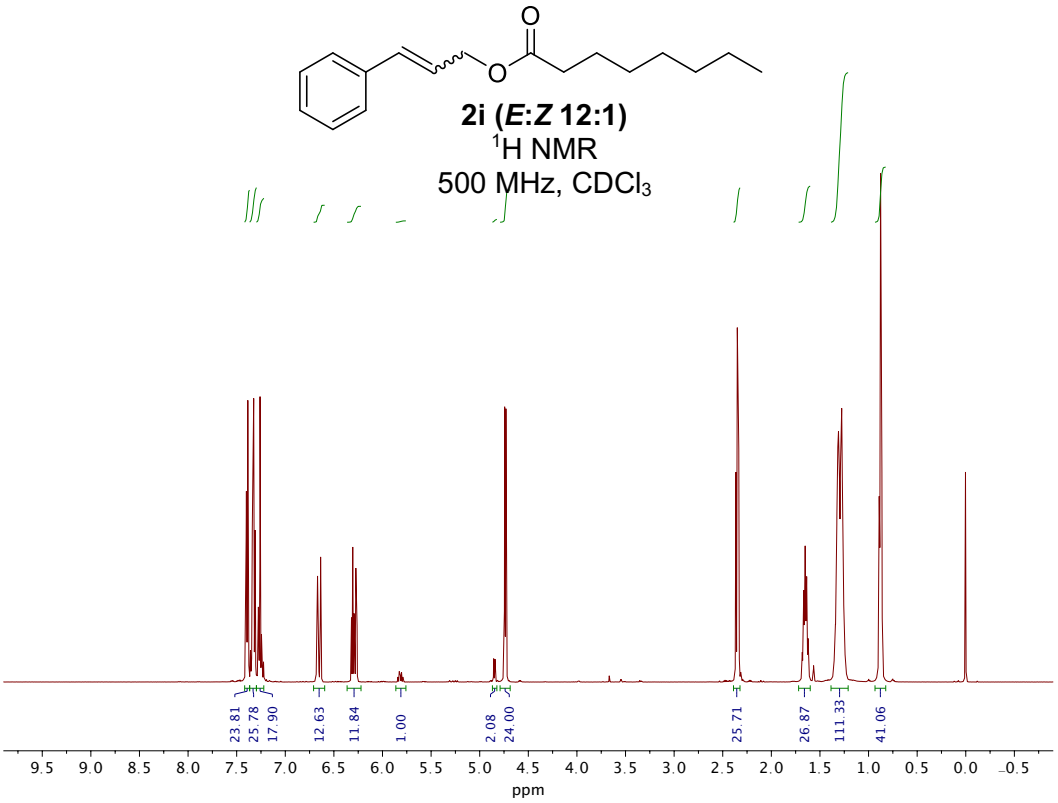
2g (*E*:*Z* 12:1)
^{1}H NMR
500 MHz, $CDCl_3$

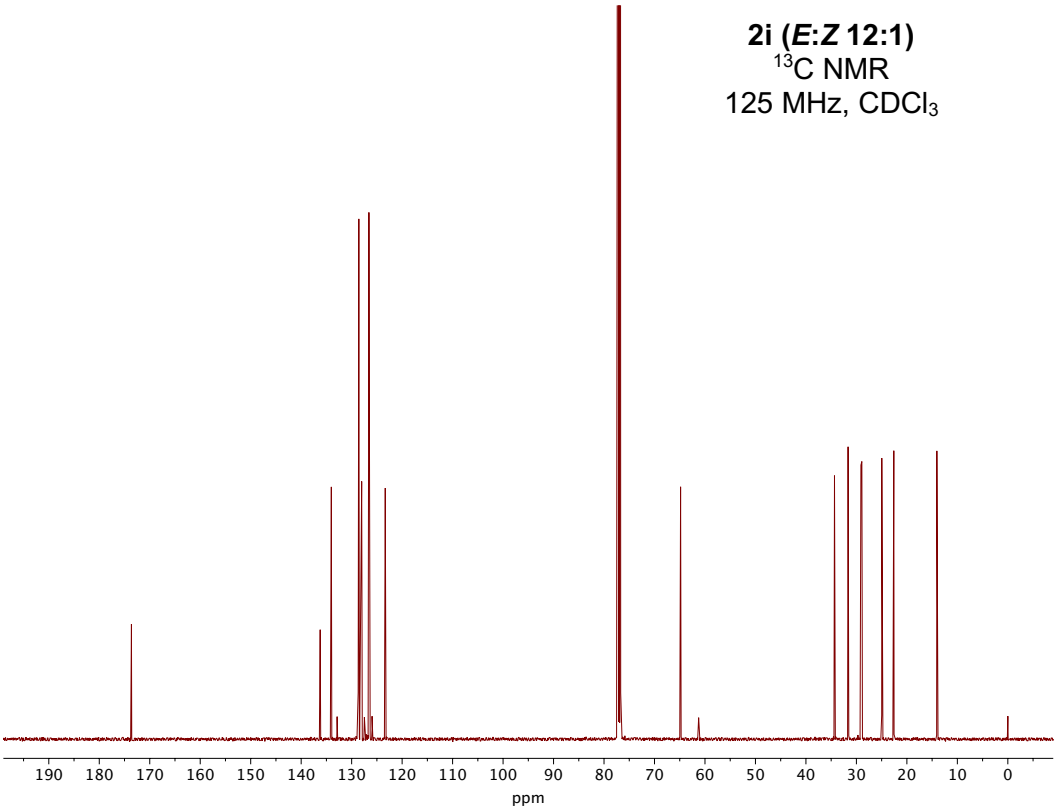


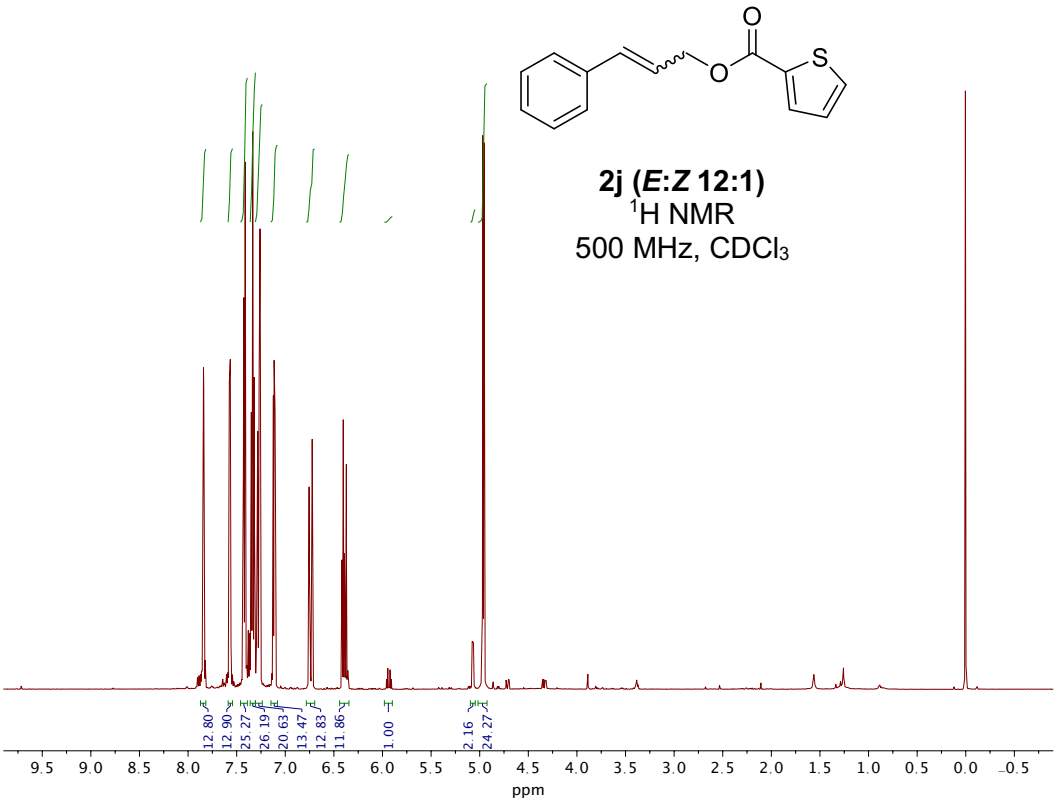
2g (*E*:*Z* 12:1)
^{13}C NMR
125 MHz, $CDCl_3$

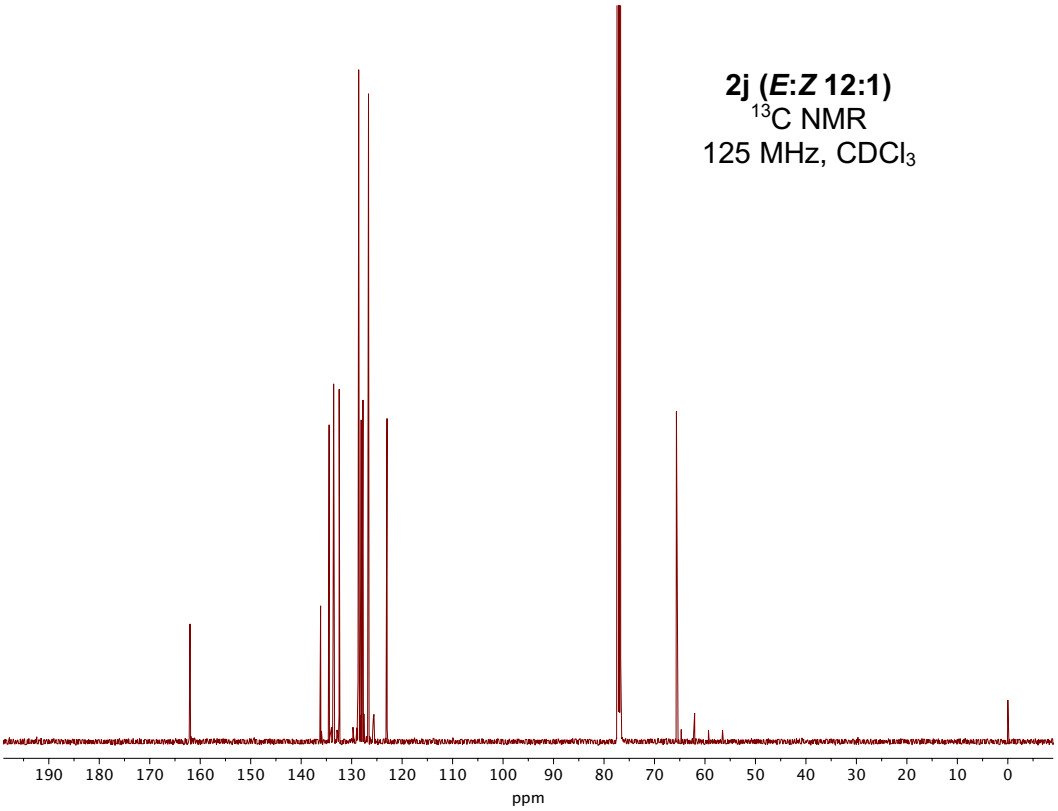

O
O
CF3
2h (E:Z 13:1)
1H NMR
500 MHz, CDCl3
13.95
14.36
54.90
28.11
23.75
1.09
12.95
13.17
1.00
2.08
26.92
26.38
2.50
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


2h (E:Z 13:1)
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

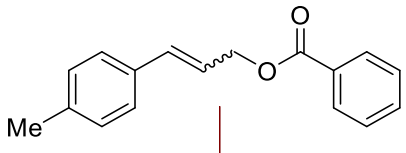

O
O
2i (E:Z 12:1)
1H NMR
500 MHz, CDCl3
23.81
25.78
17.90
12.63
11.84
1.00
2.08
24.00
25.71
26.87
111.33
41.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

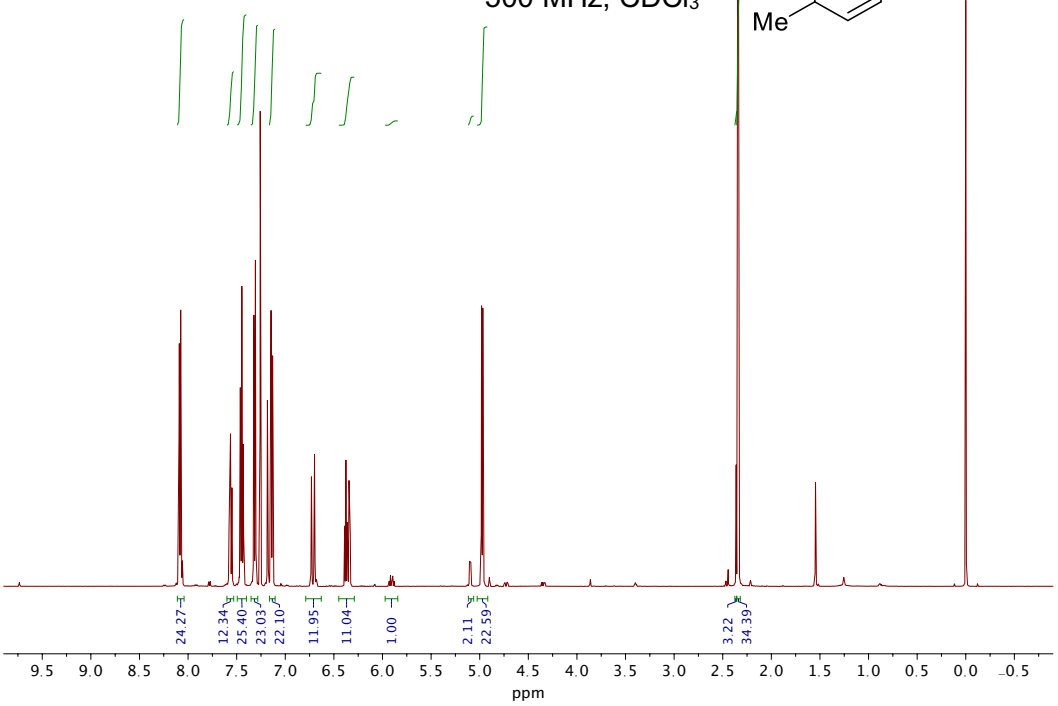

2i (E:Z 12:1)
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
O
S
2j (E:Z 12:1)
1H NMR
500 MHz, CDCl3
12.80
12.90
25.27
26.19
20.63
13.47
12.83
11.86
1.00
2.16
24.27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

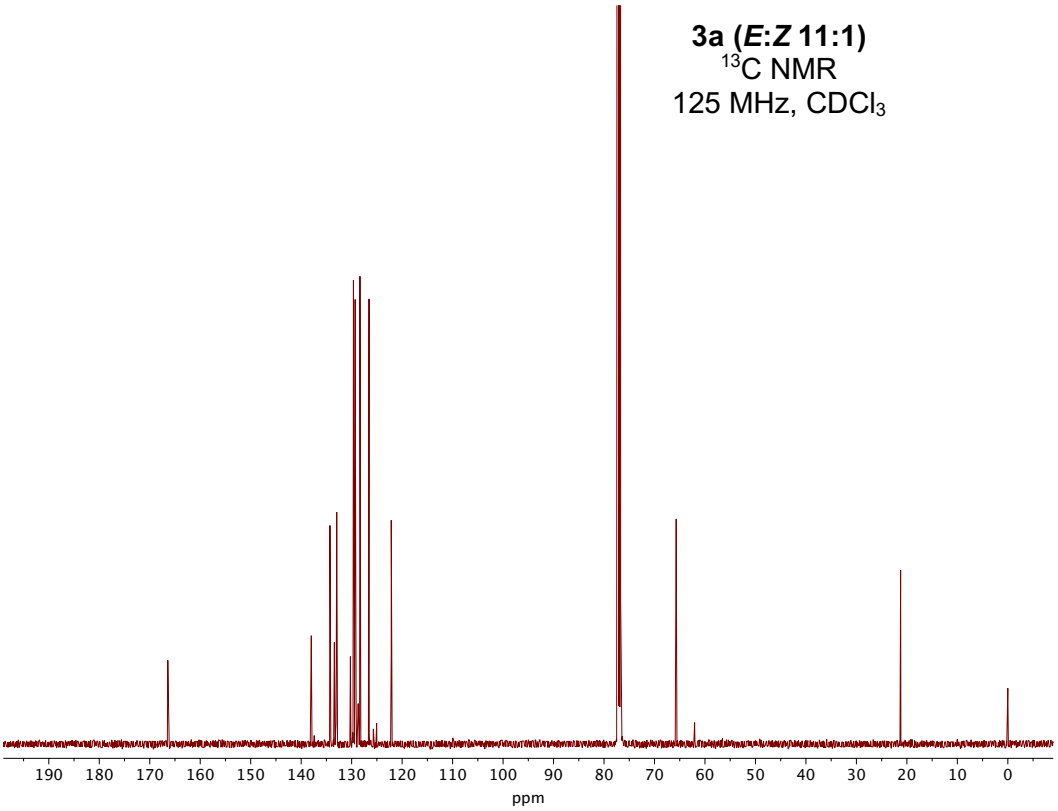

2j (E:Z 12:1)
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

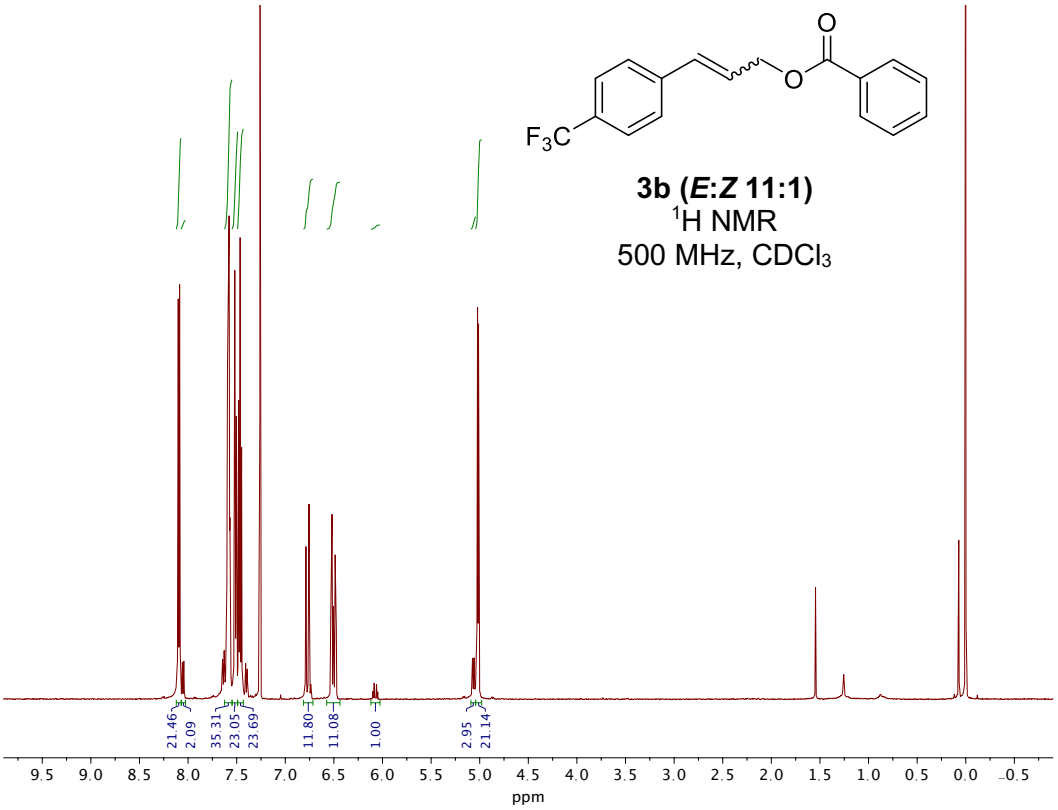
3a (*E*:*Z* 11:1)
^{1}H NMR
500 MHz, $CDCl_3$

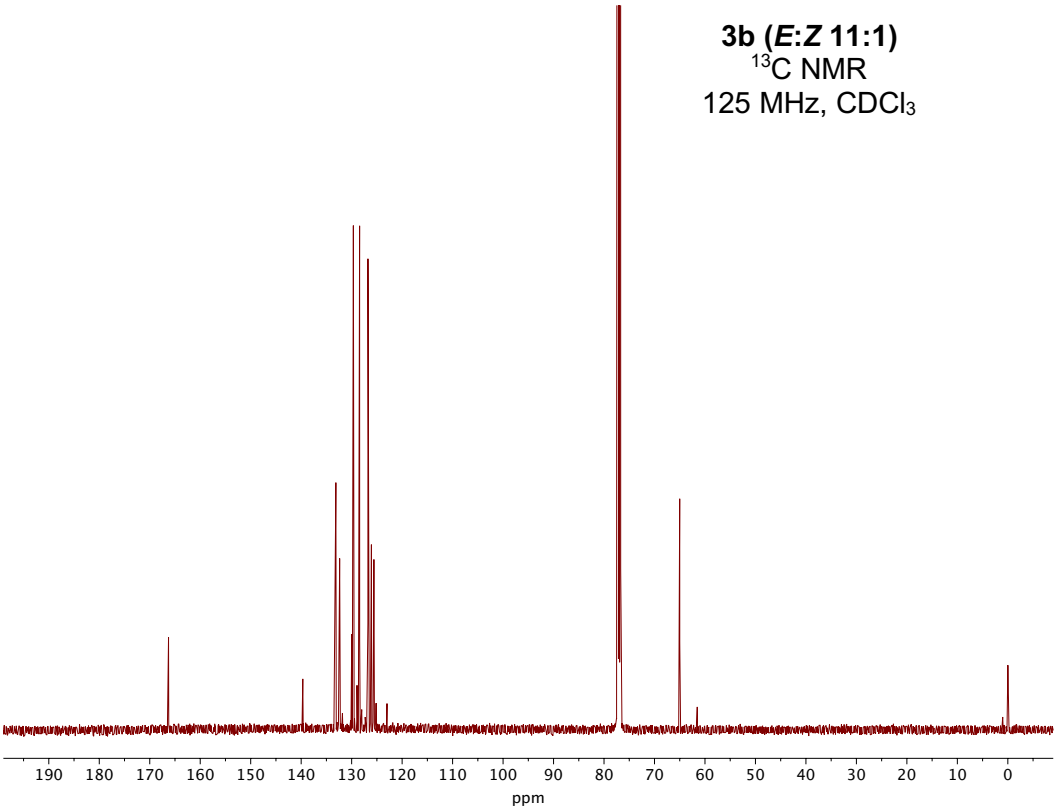


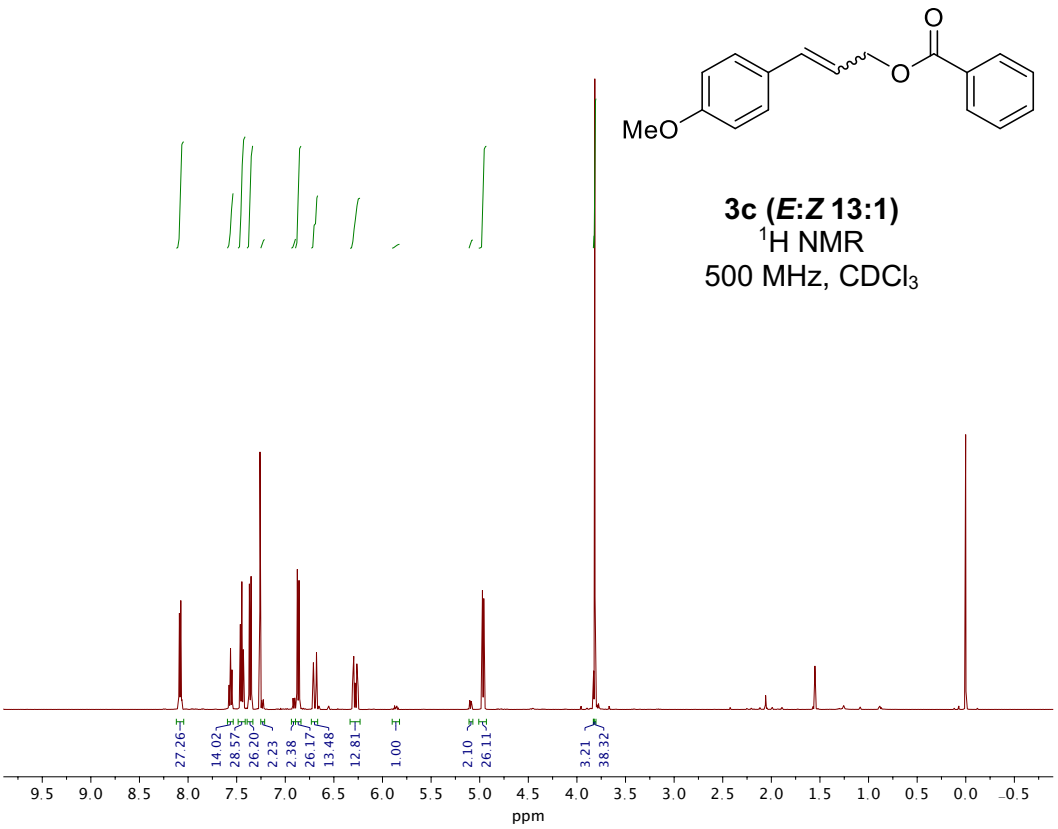


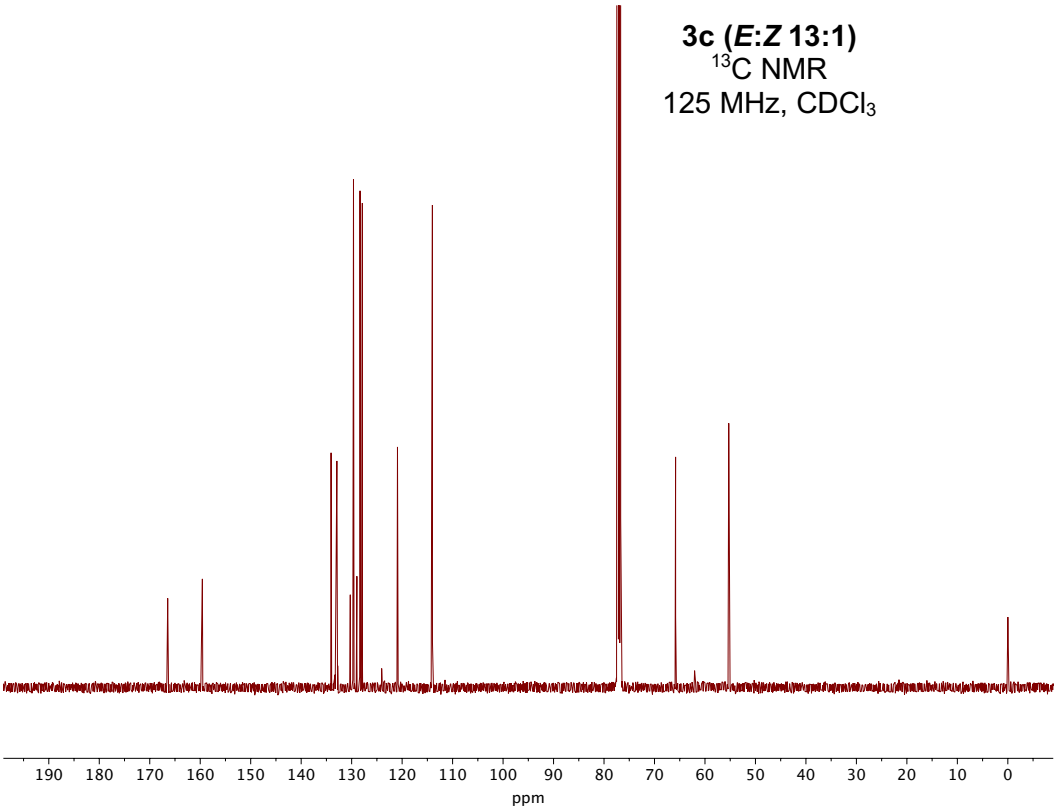
3a (*E*:*Z* 11:1)
^{13}C NMR
125 MHz, $CDCl_3$

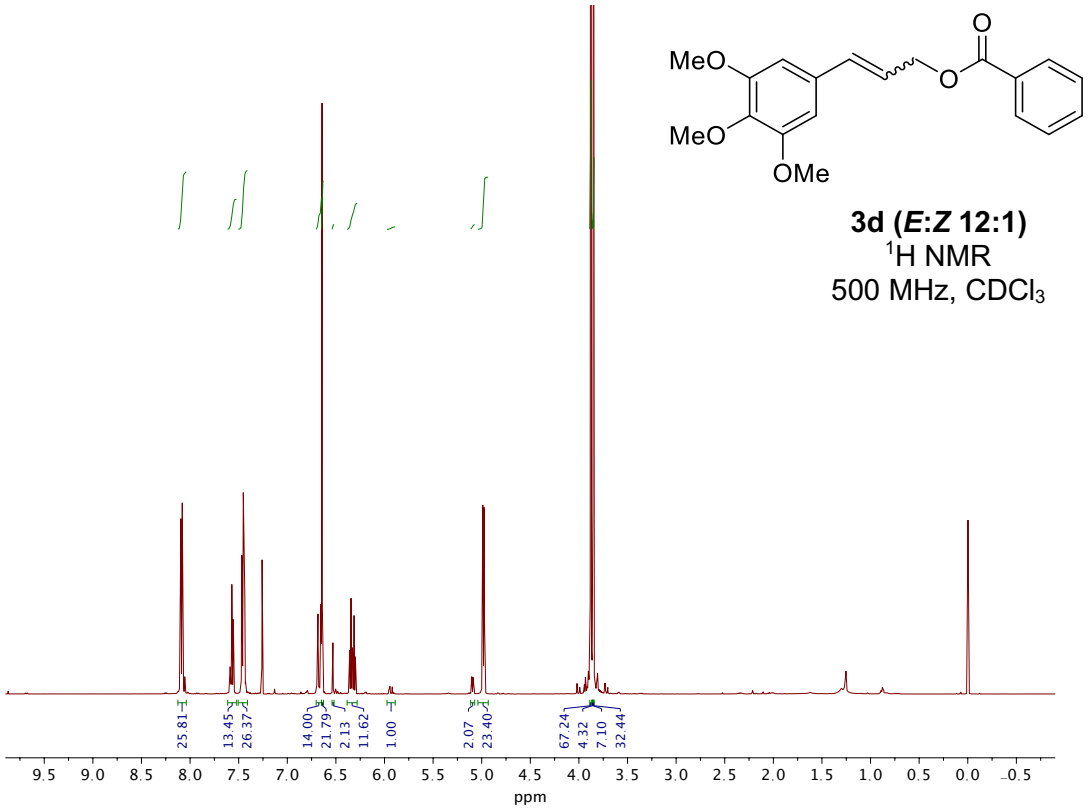


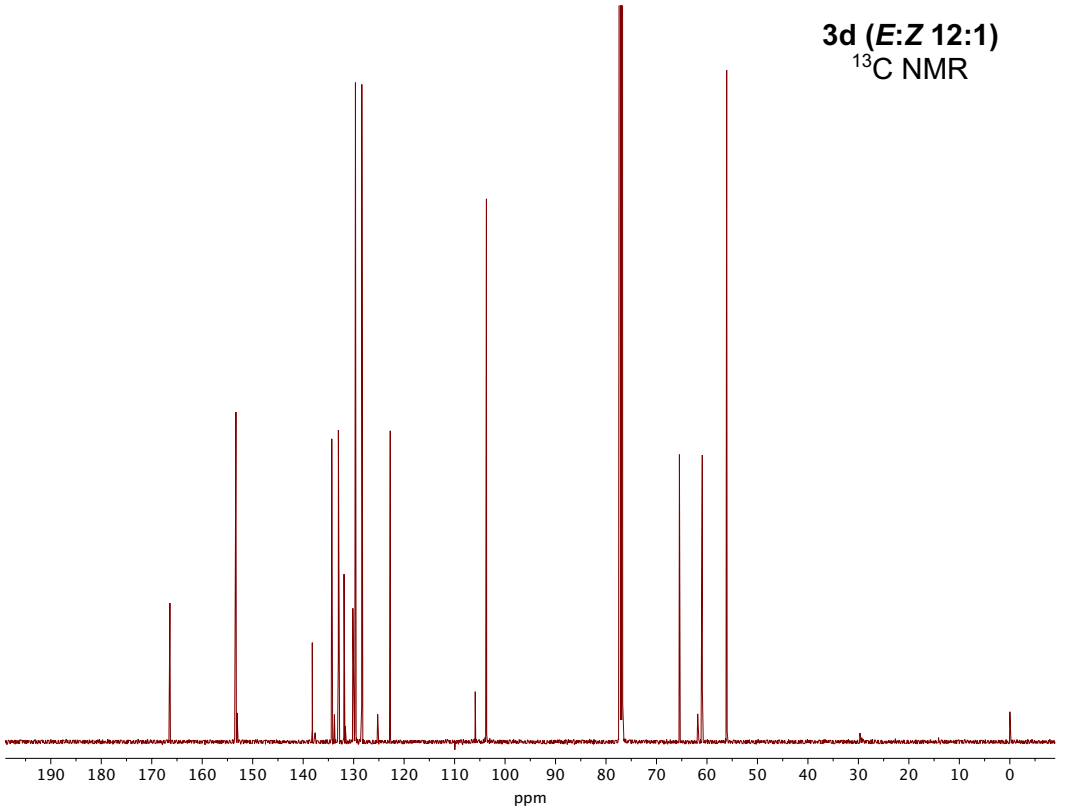

O
O
F3C
3b (E:Z 11:1)
1H NMR
500 MHz, CDCl3
21.46
2.09
35.31
23.05
23.69
11.80
11.08
1.00
2.95
21.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

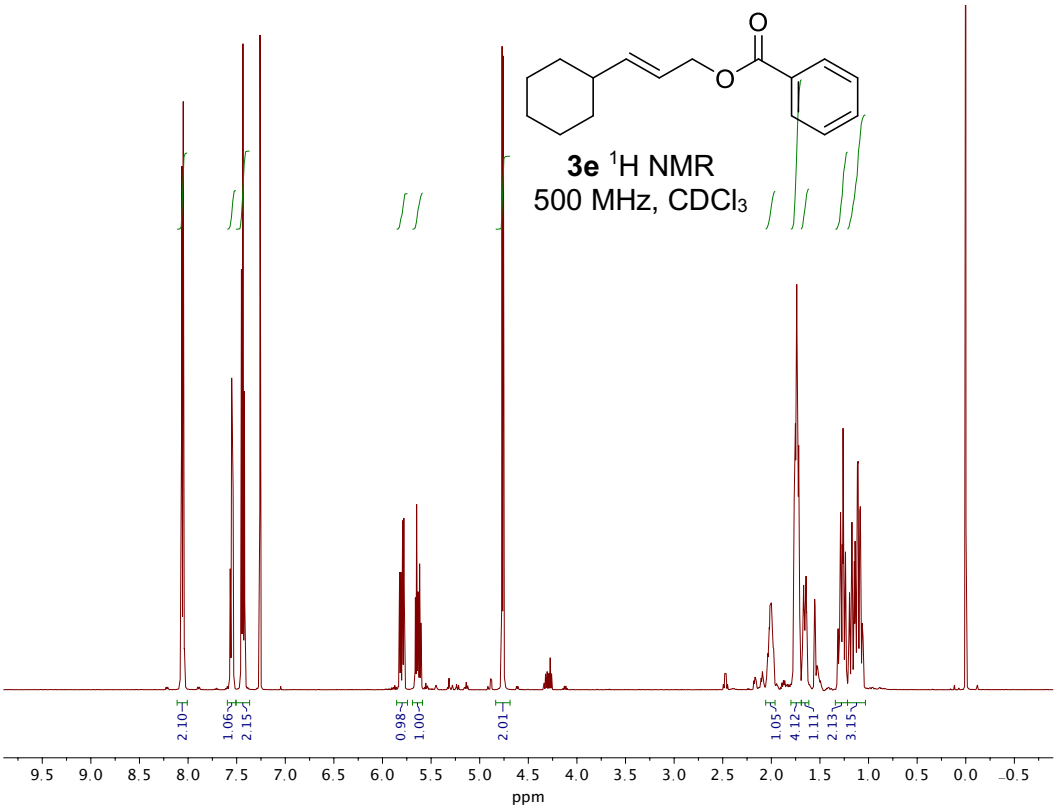

3b (E:Z 11:1)
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

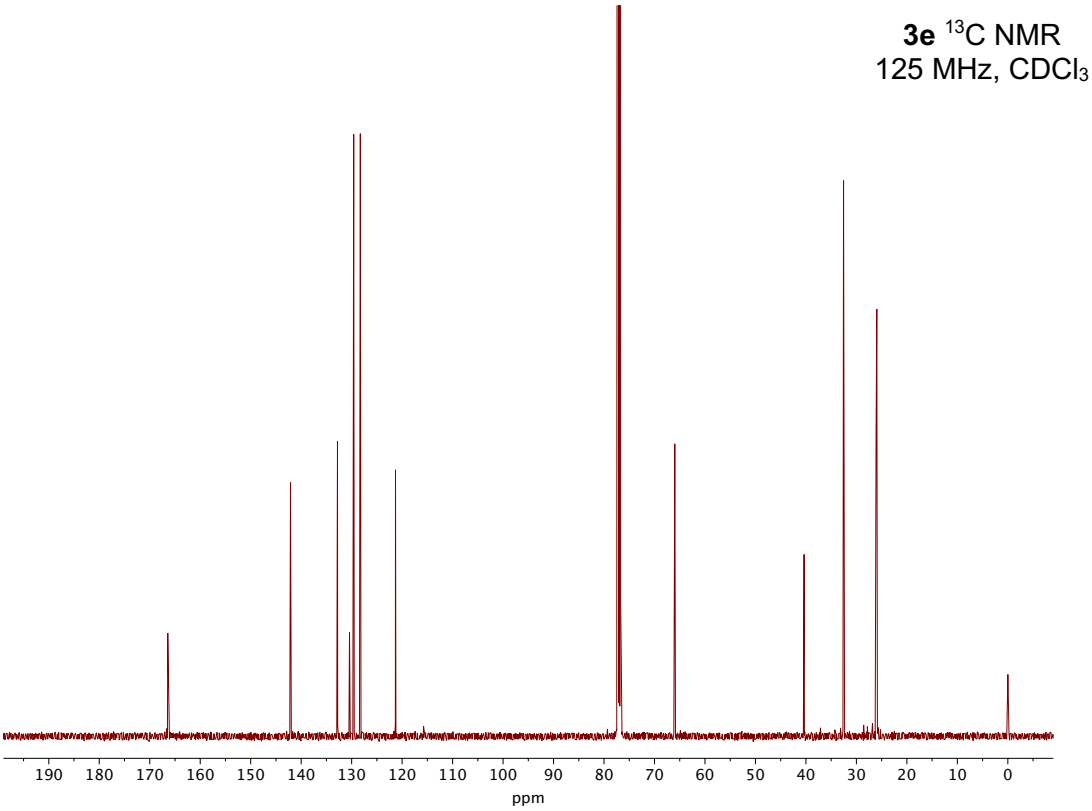

MeO
O
O
3c (E:Z 13:1)
1H NMR
500 MHz, CDCl3
27.26
14.02
28.57
26.20
2.23
2.38
26.17
13.48
12.81
1.00
2.10
26.11
3.21
38.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

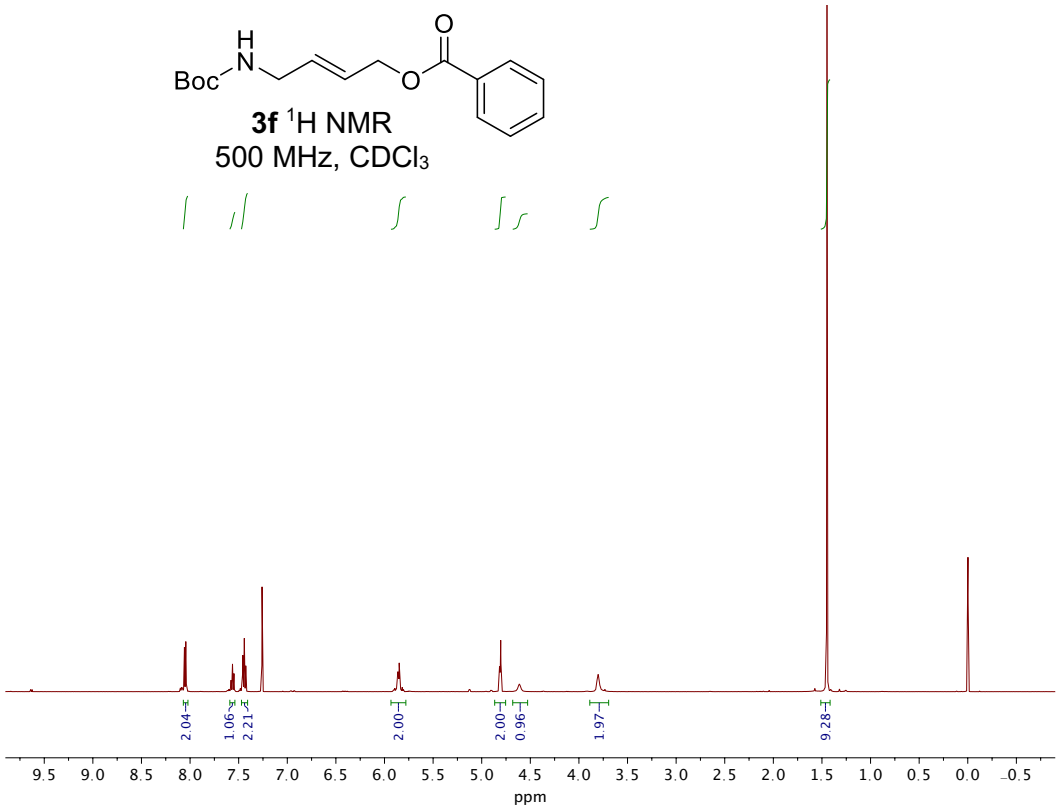

3c (E:Z 13:1)
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

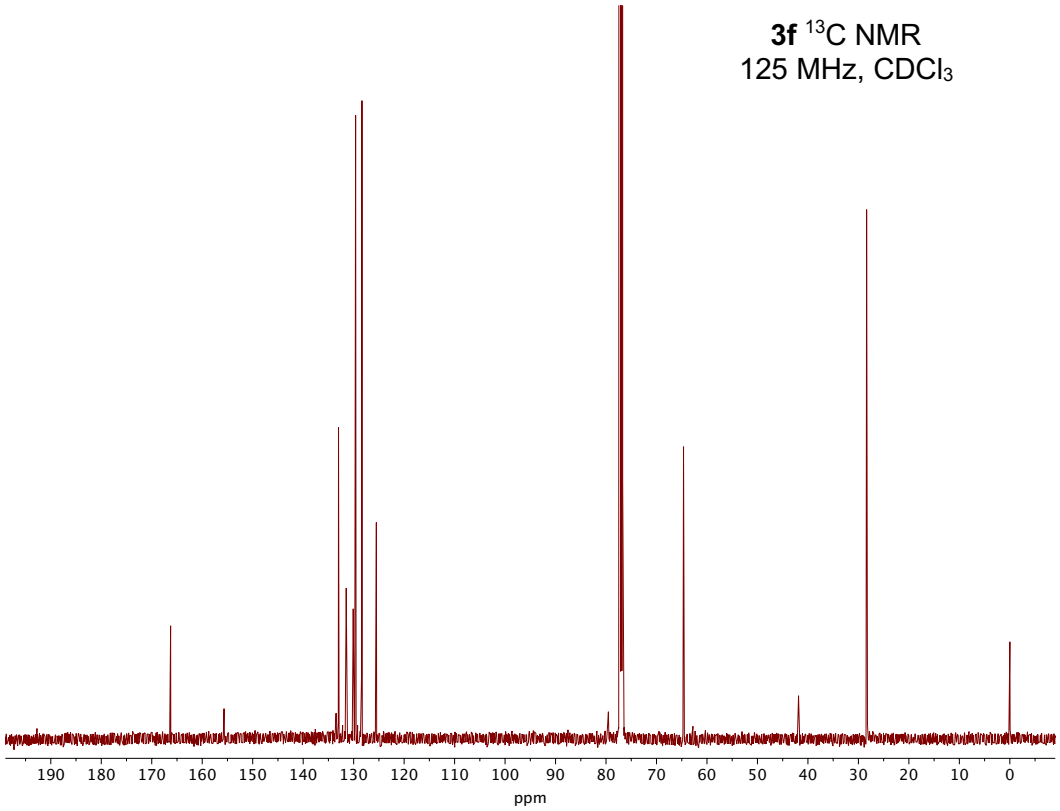

MeO
MeO
OMe
O
O
3d (E:Z 12:1)
1H NMR
500 MHz, CDCl3
25.81
13.45
26.37
14.00
21.79
2.13
11.62
1.00
2.07
23.40
67.24
4.32
7.10
32.44
ppm

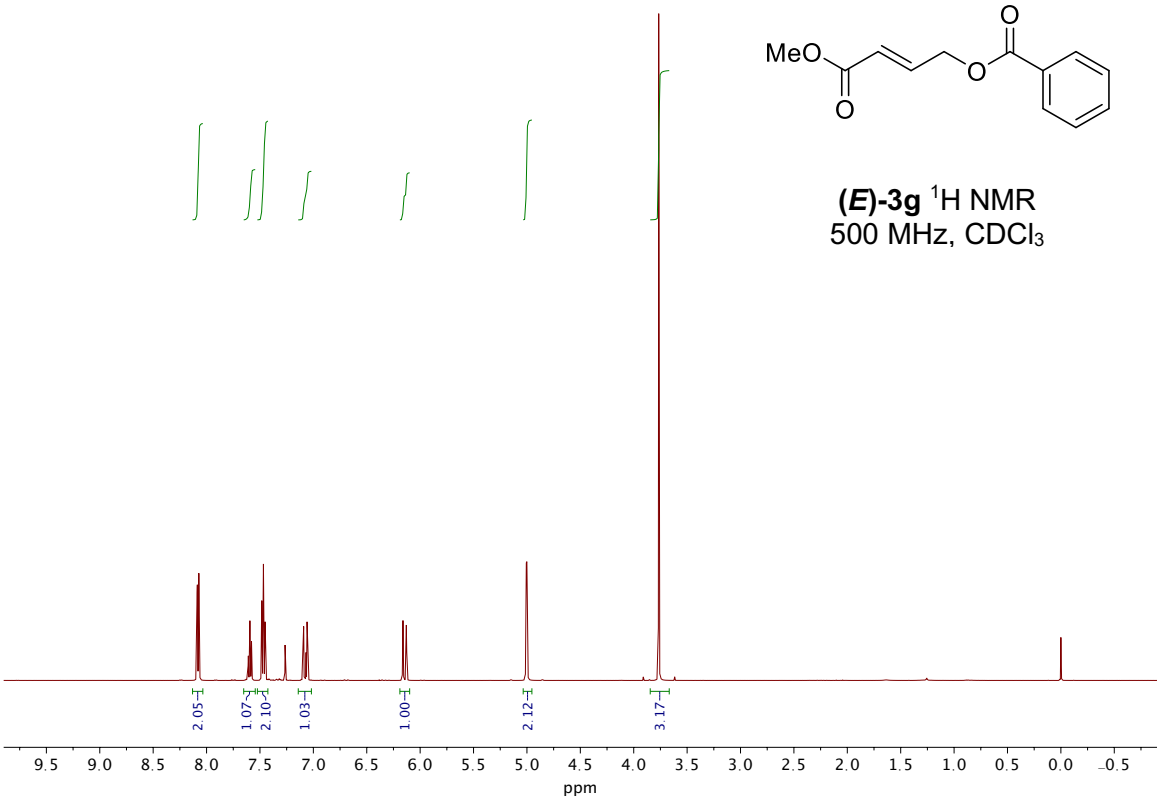

3d (E:Z 12:1)
13C NMR
ppm


O
O
3e 1H NMR
500 MHz, CDCl3
2.10
1.06
2.15
0.98
1.00
2.01
1.05
4.12
1.11
2.13
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

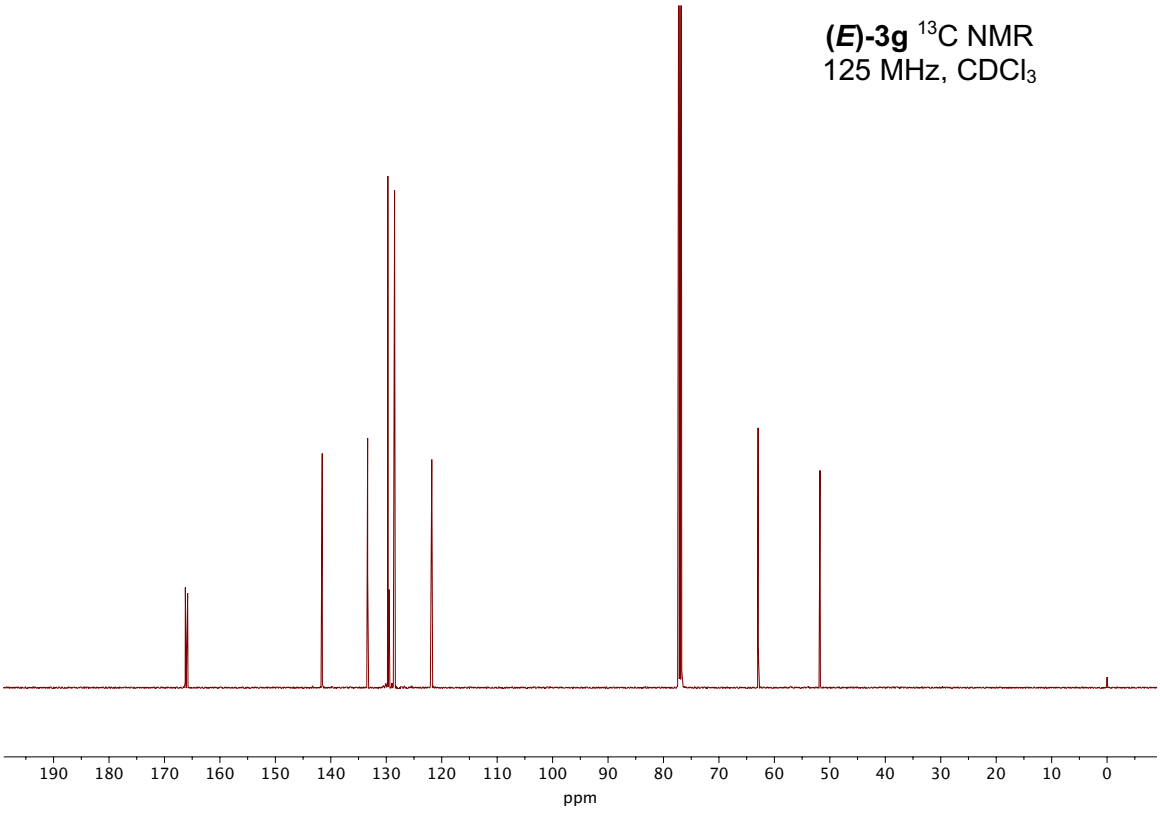

3e 13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


Boc
H
N
O
O
3f 1H NMR
500 MHz, CDCl3
2.04
1.06
2.21
2.00
2.00
0.96
1.97
9.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

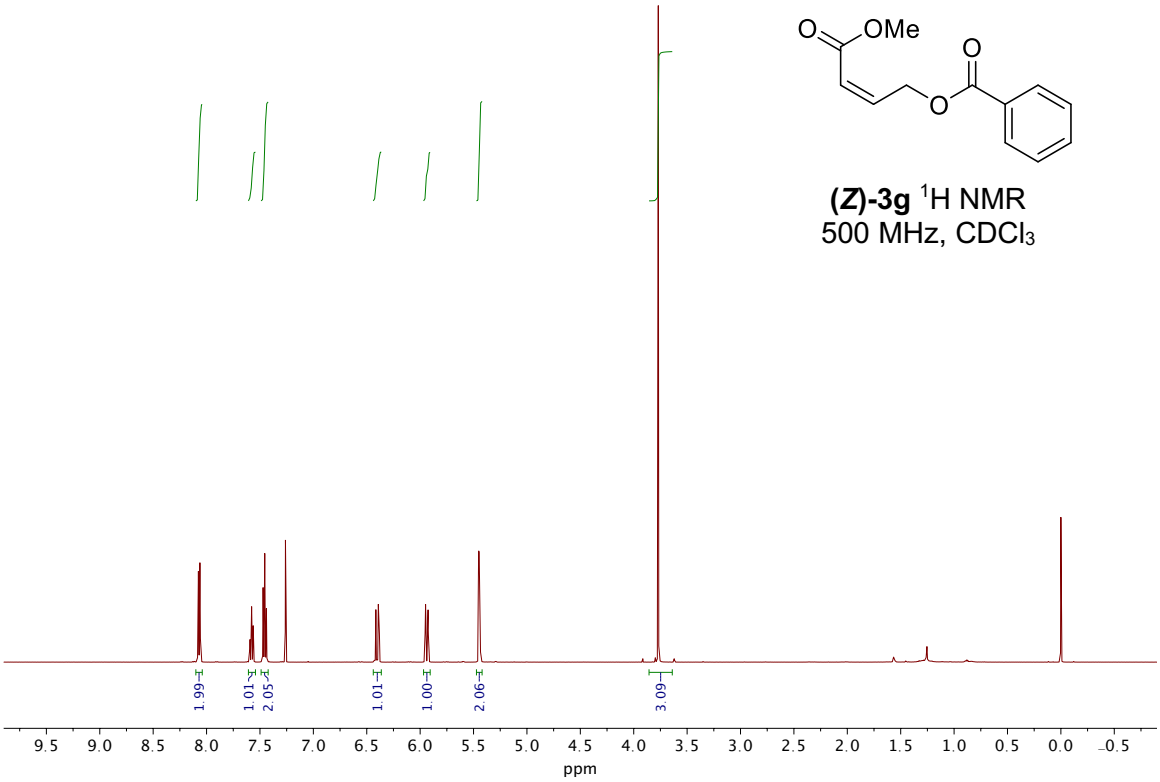

3f 13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



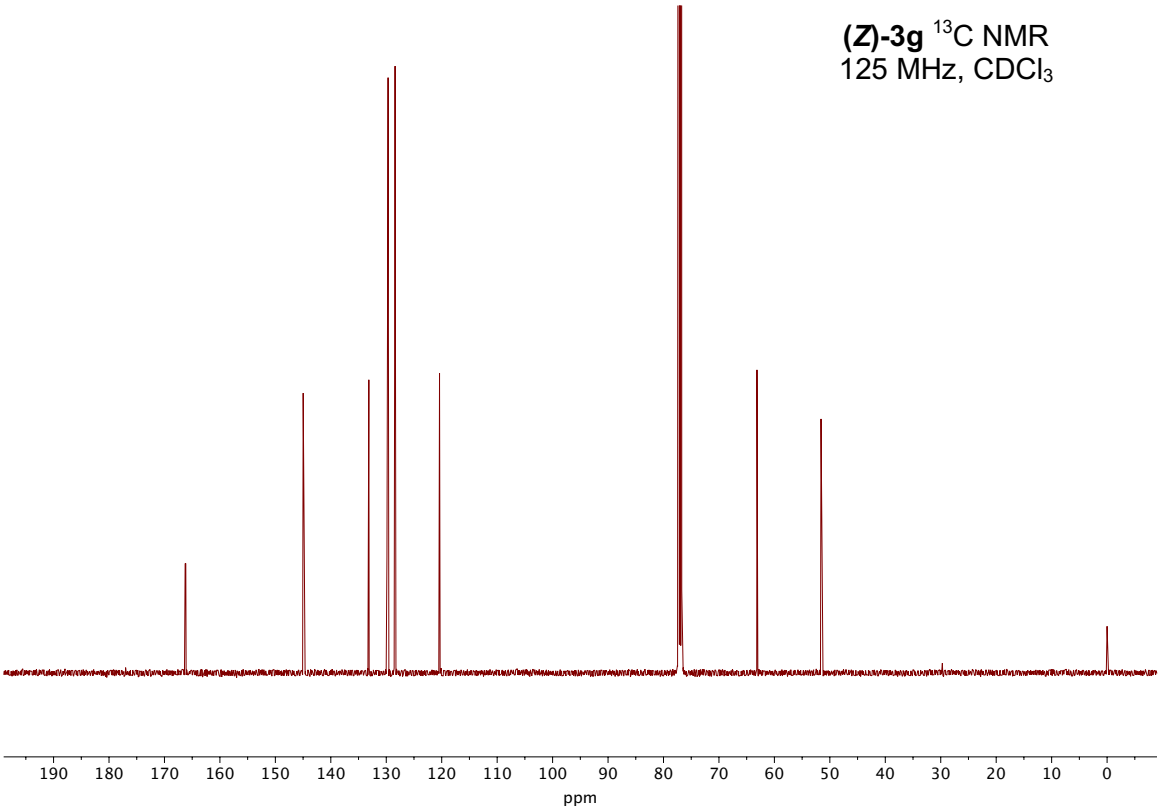
(*E*)-3g ^{1}H NMR
500 MHz, $CDCl_3$



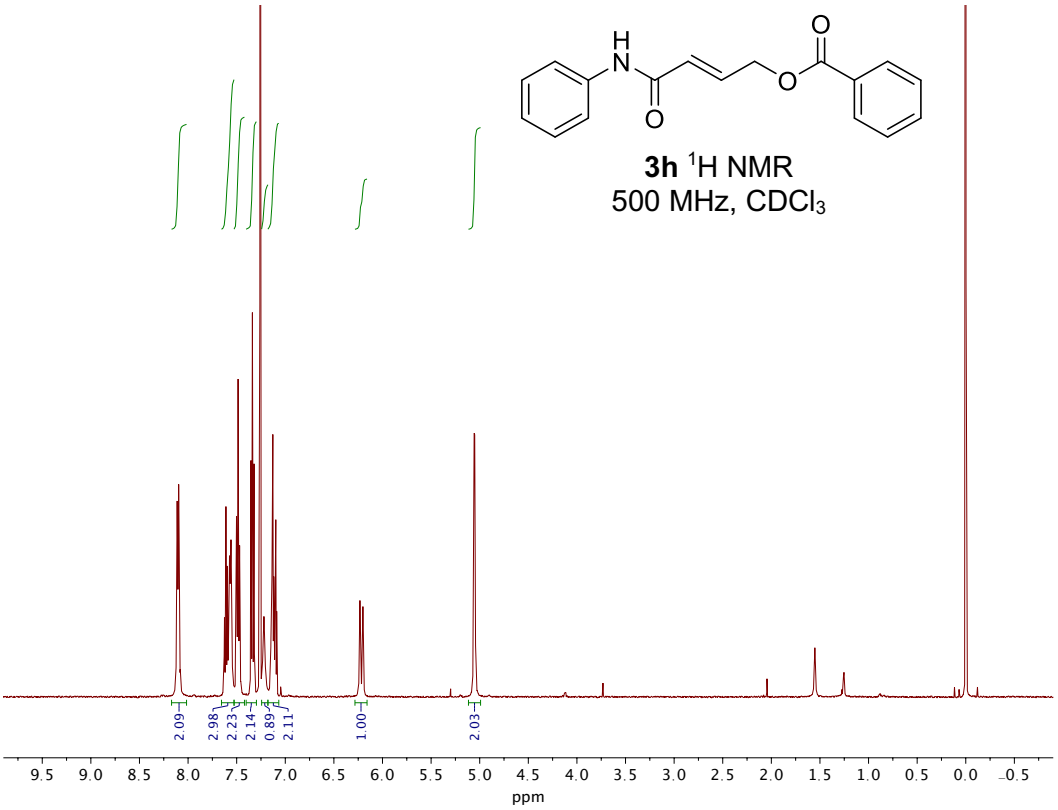
(*E*)-3g ^{13}C NMR
125 MHz, $CDCl_3$

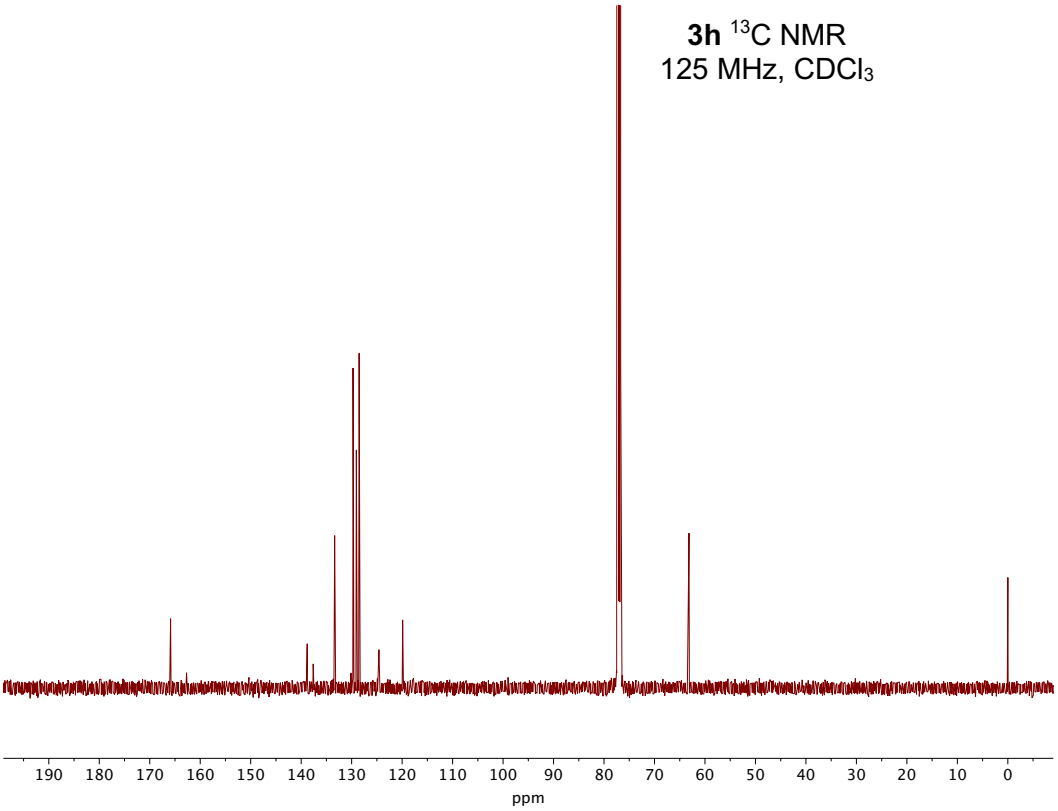


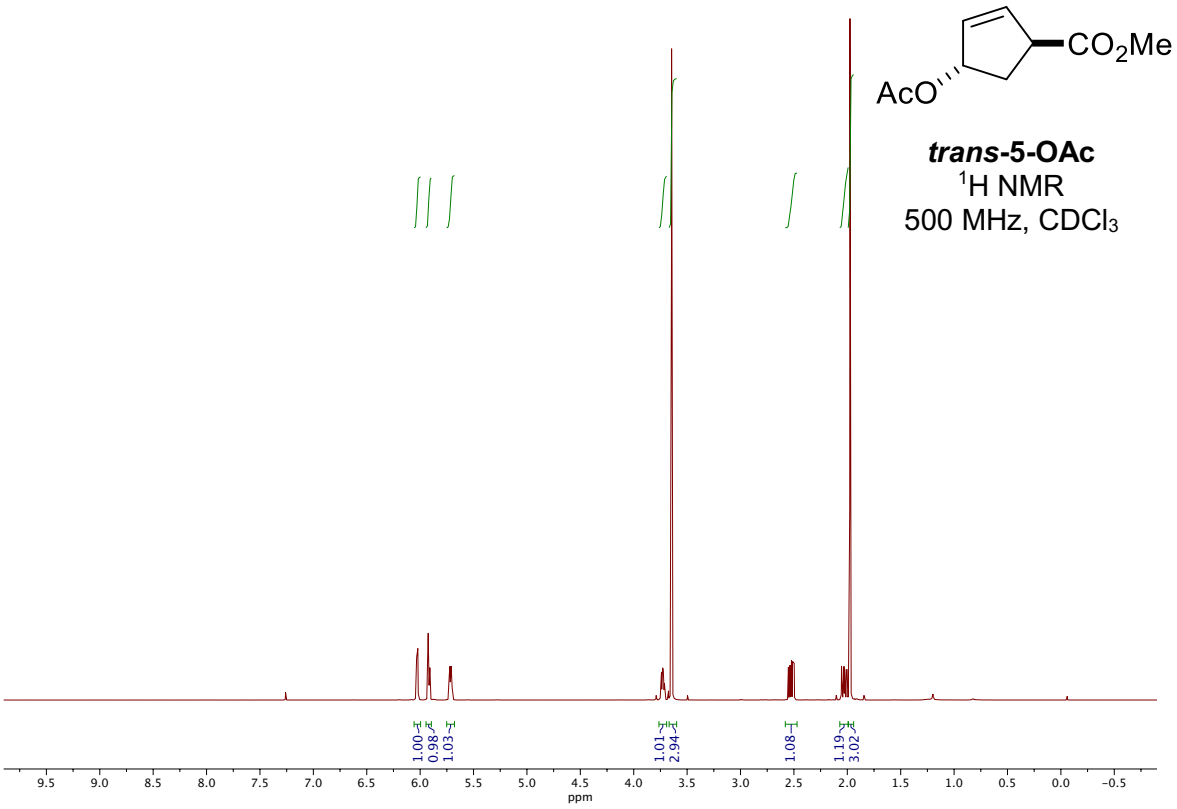
(*Z*)-3g ^{1}H NMR
500 MHz, $CDCl_3$

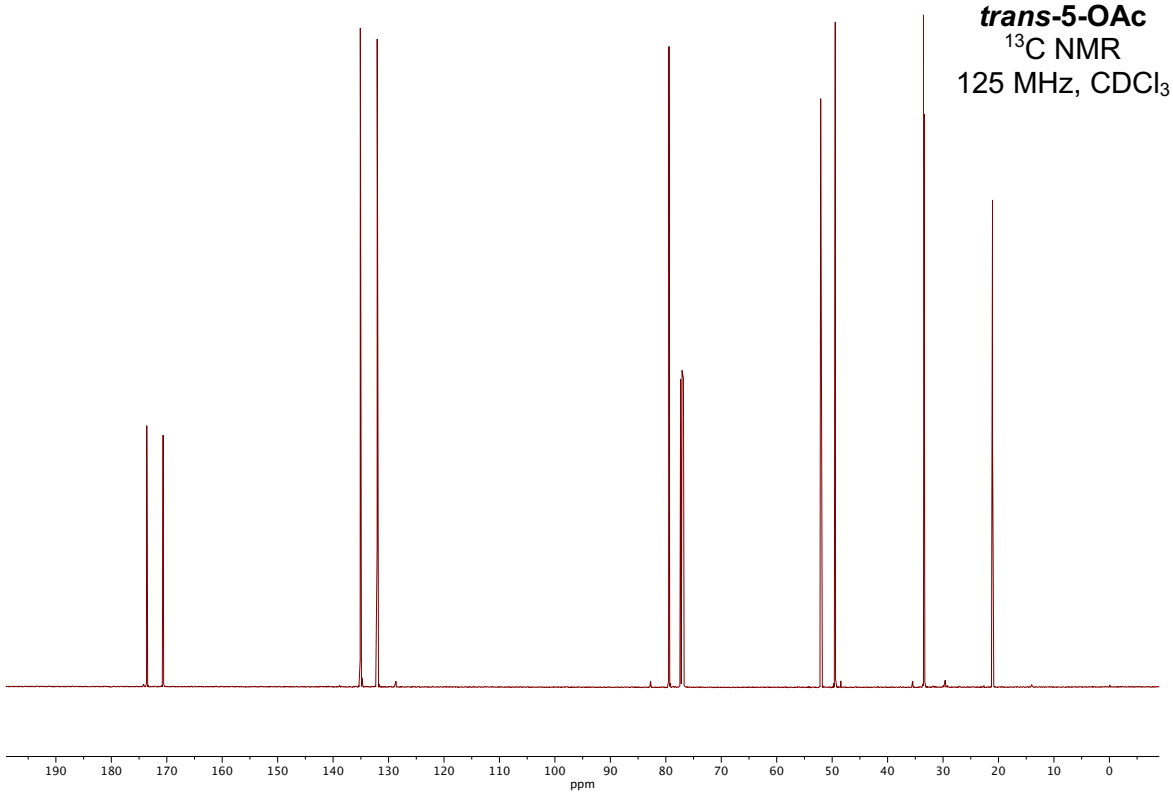


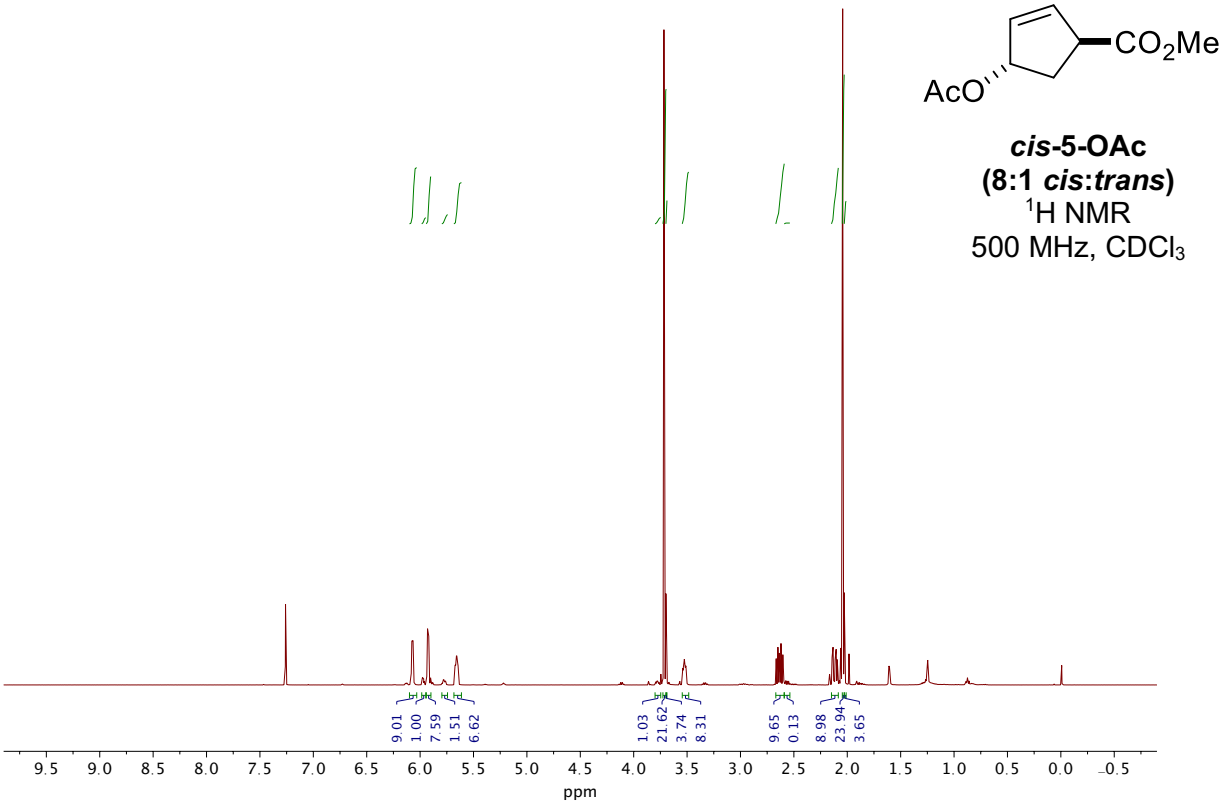
(*Z*)-3g ^{13}C NMR
125 MHz, $CDCl_3$


H
N
O
O
O
3h 1H NMR
500 MHz, CDCl3
2.09
2.98
2.23
2.14
0.89
2.11
1.00
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

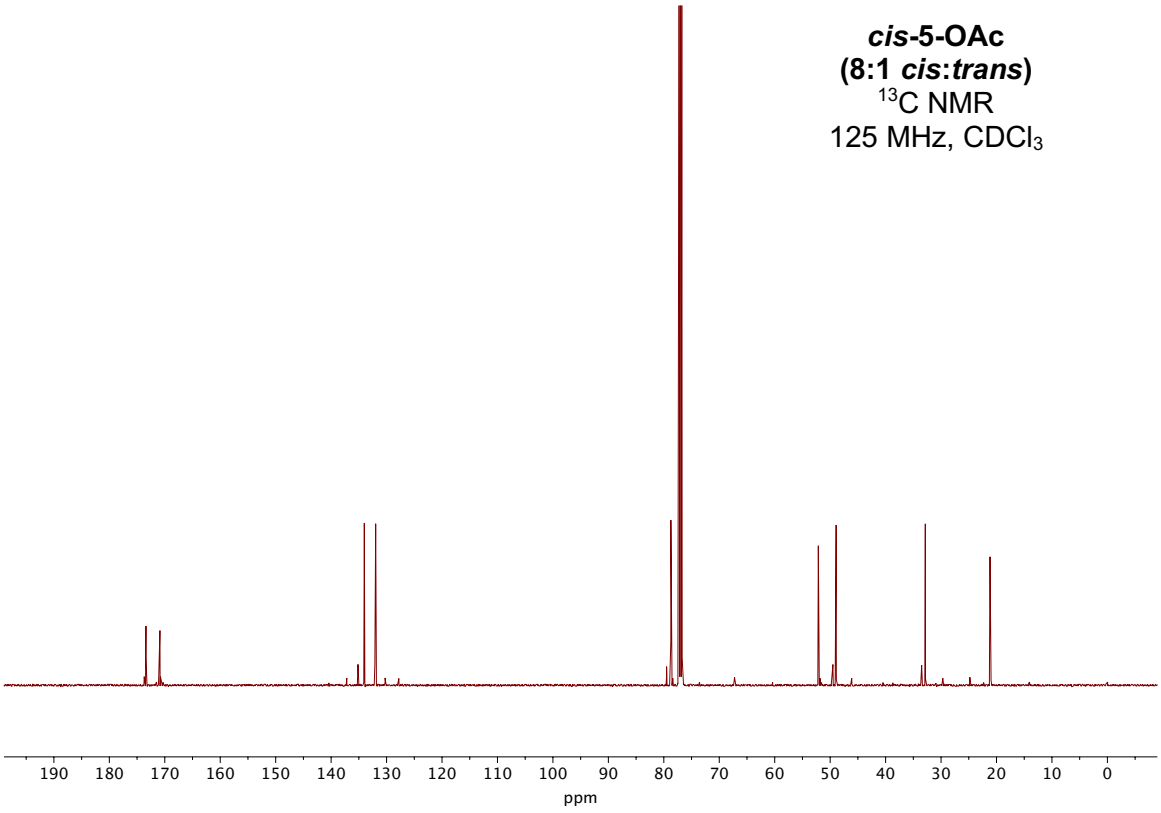

3h 13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


CO2Me
AcO
trans-5-OAc
1H NMR
500 MHz, CDCl3
1.00
0.98
1.03
1.01
2.94
1.08
1.19
3.02
ppm

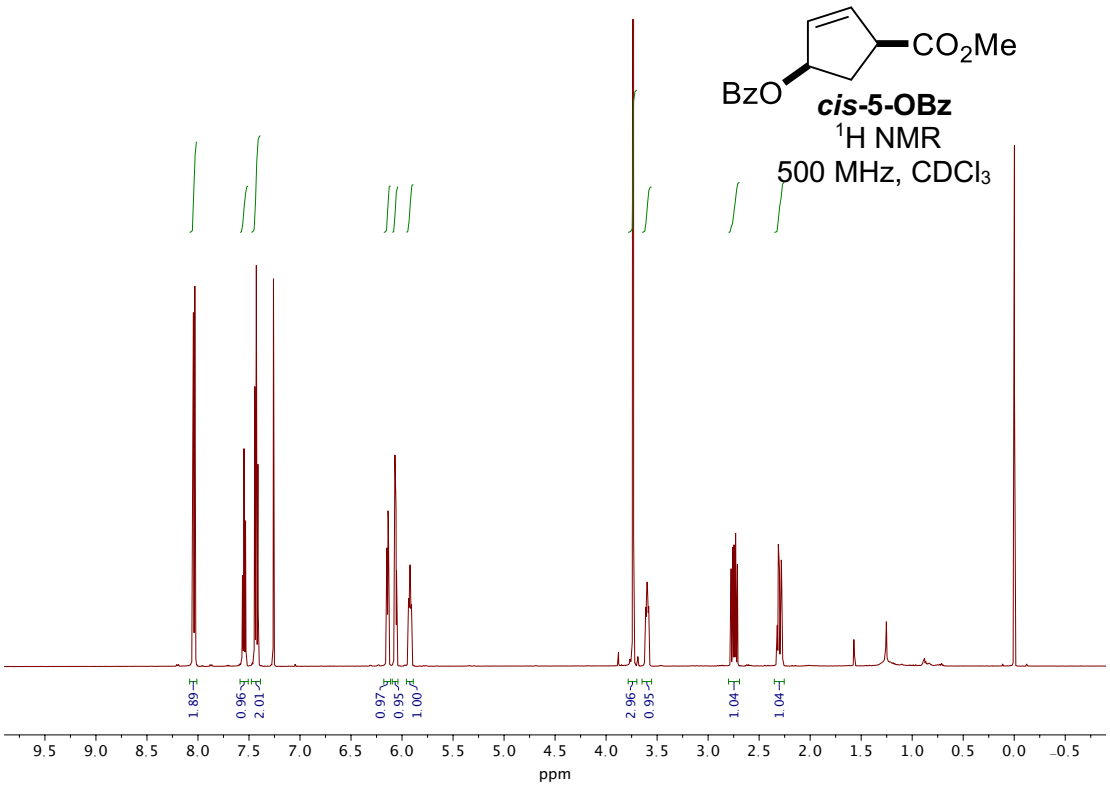

trans-5-OAc
13C NMR
125 MHz, CDCl3
ppm

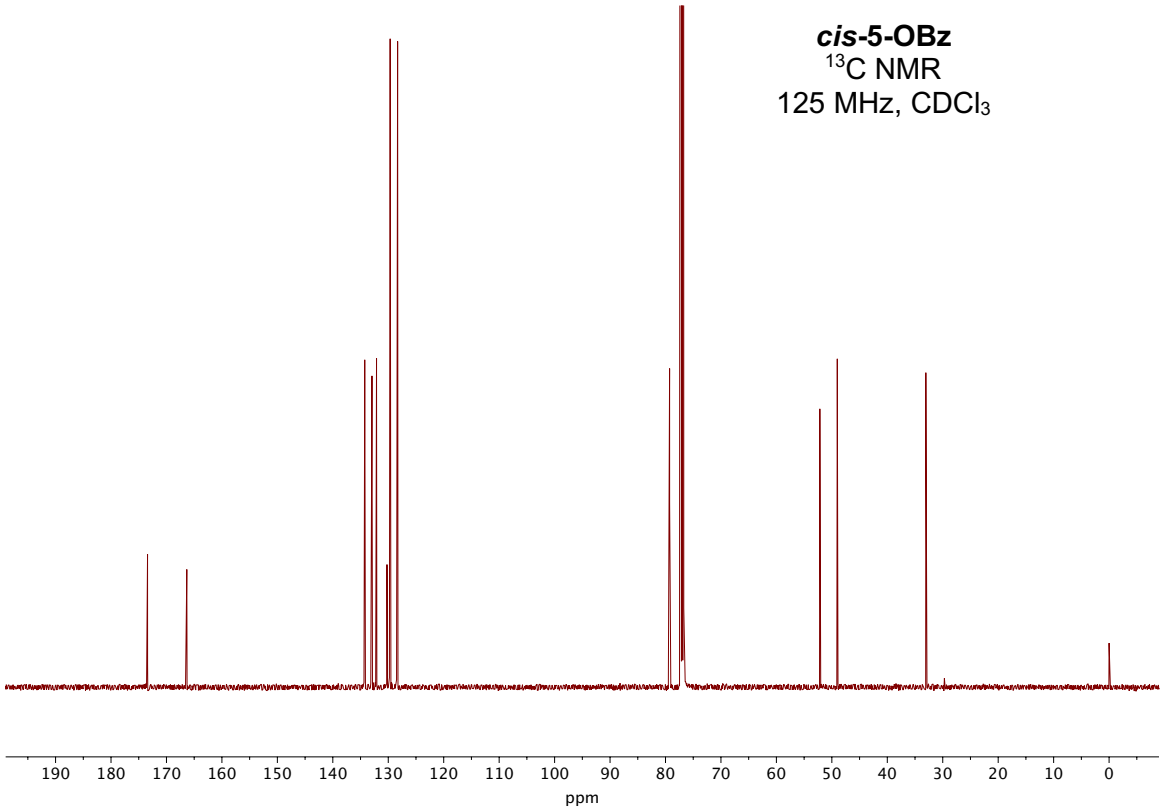


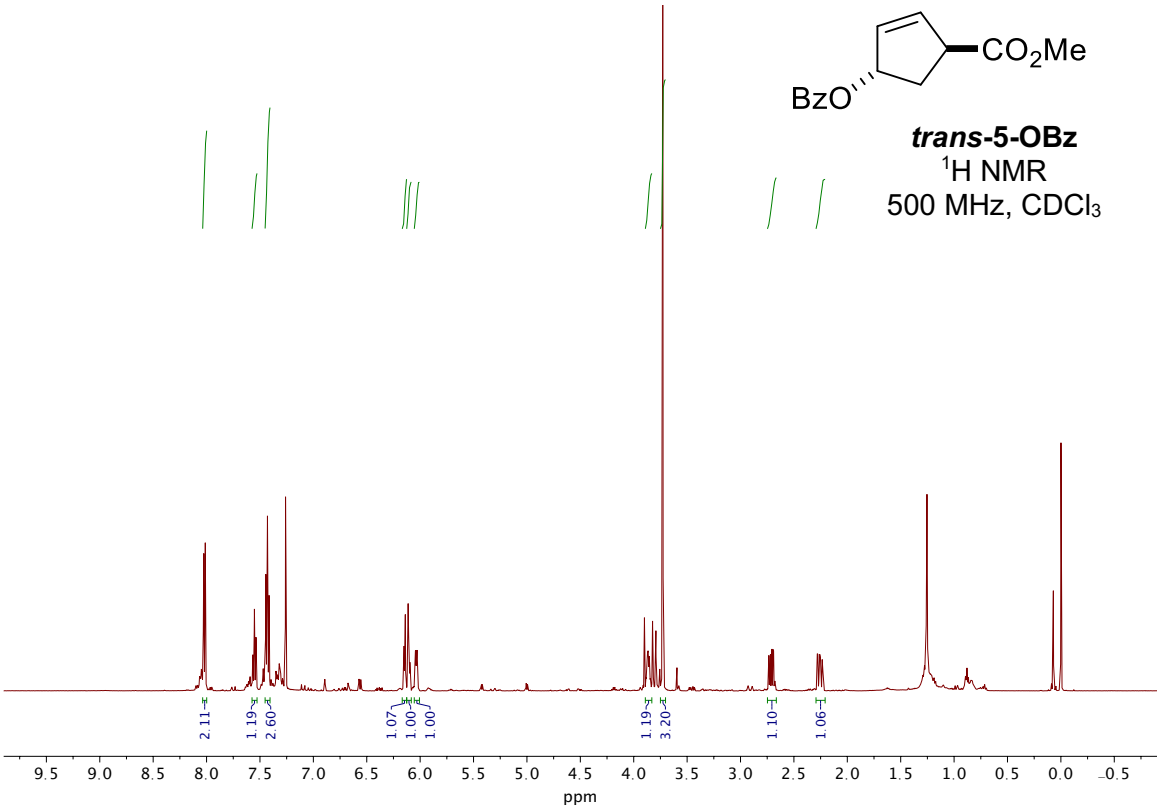
***cis*-5-OAc**
(8:1 *cis*:*trans*)
^{1}H NMR
500 MHz, $CDCl_3$



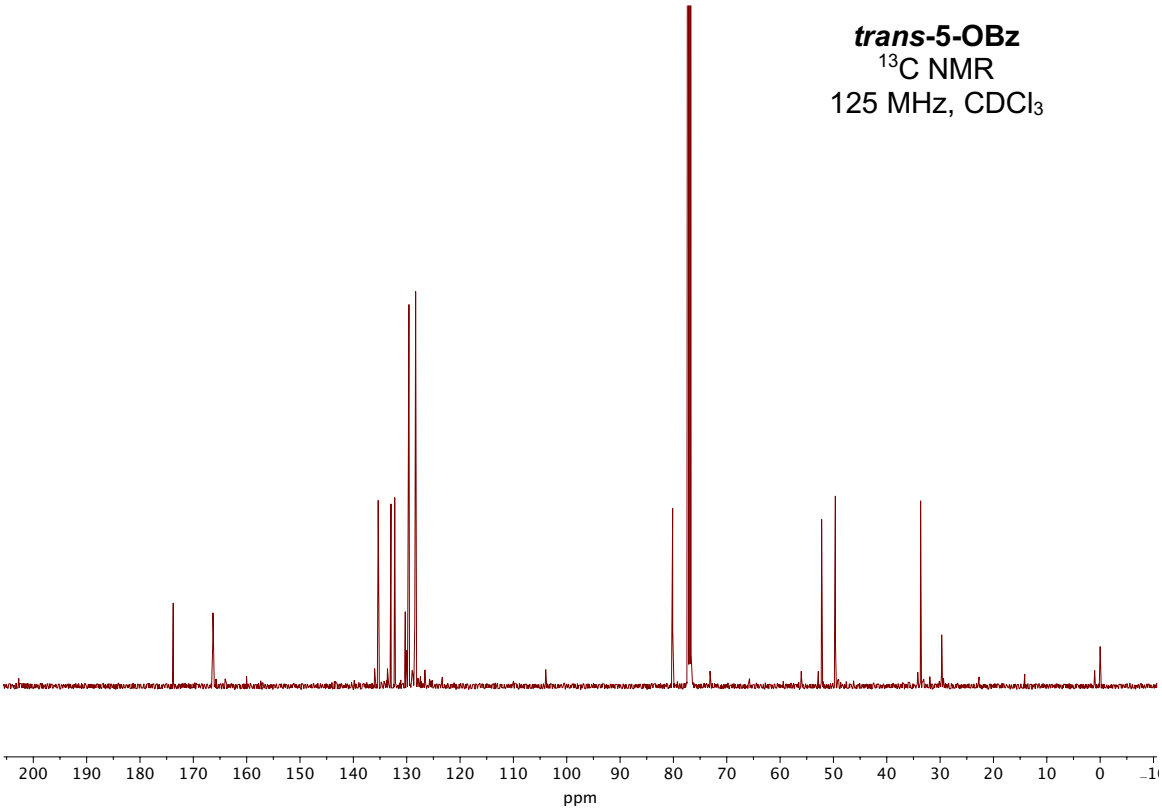
***cis*-5-OAc**
(8:1 *cis*:*trans*)
^{13}C NMR
125 MHz, $CDCl_3$


CO2Me
BzO
cis-5-OBz
1H NMR
500 MHz, CDCl3
1.89
0.96
2.01
0.97
0.95
1.00
2.96
0.95
1.04
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

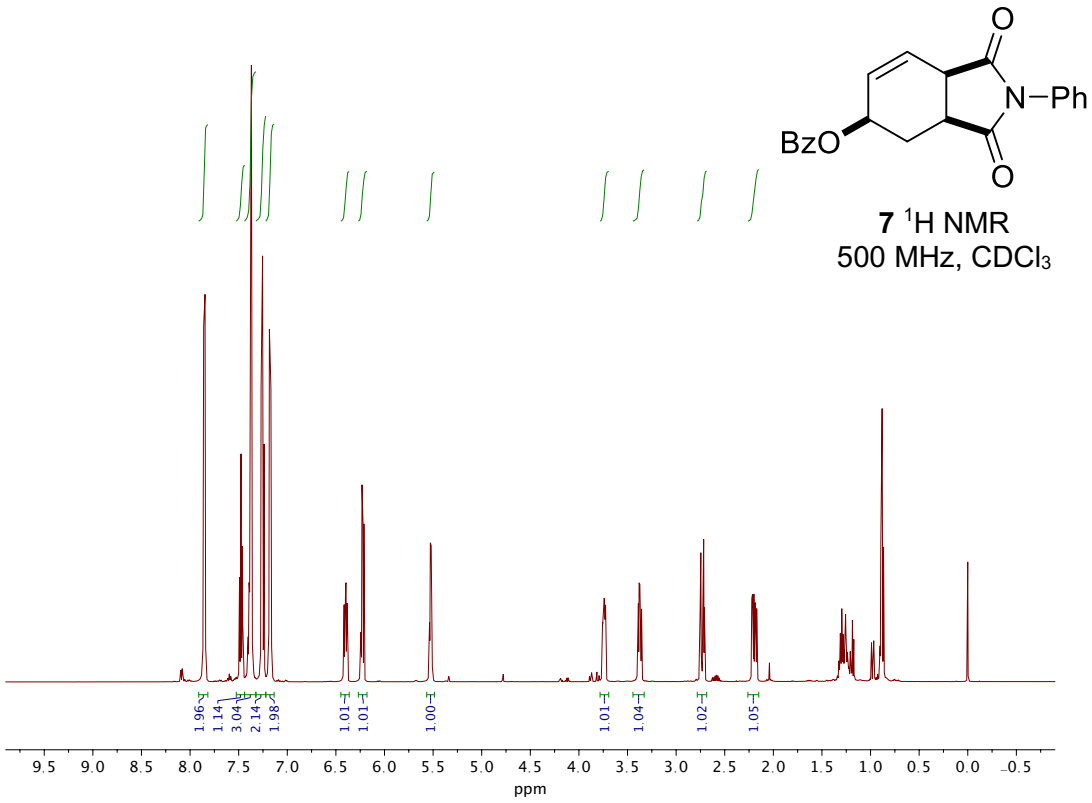

cis-5-OBz
13C NMR
125 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

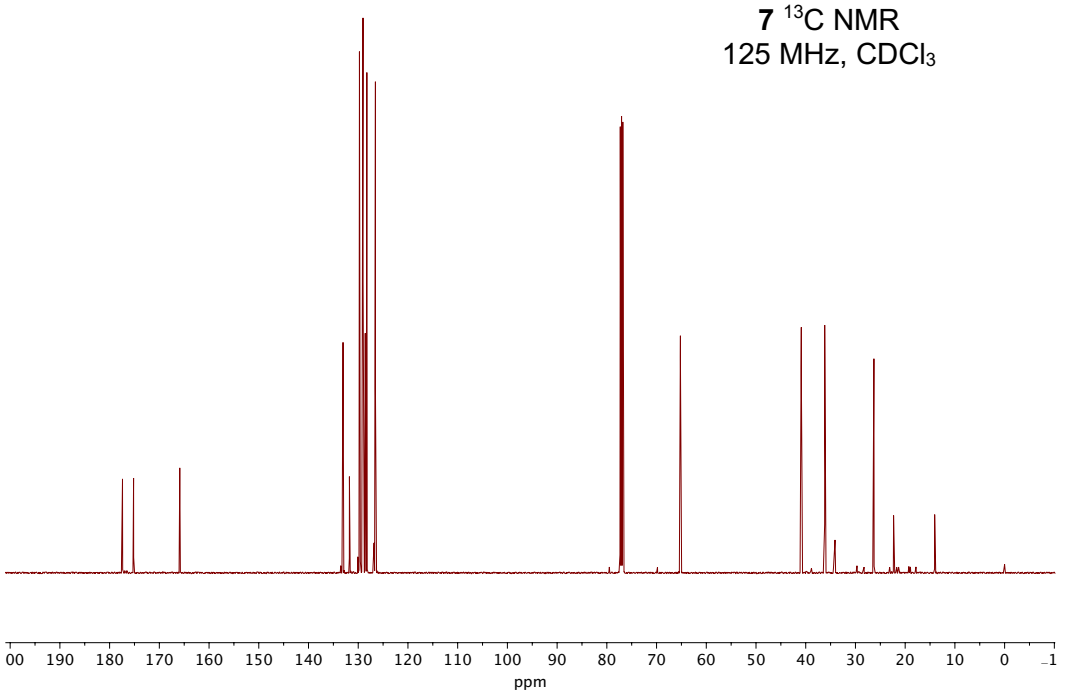


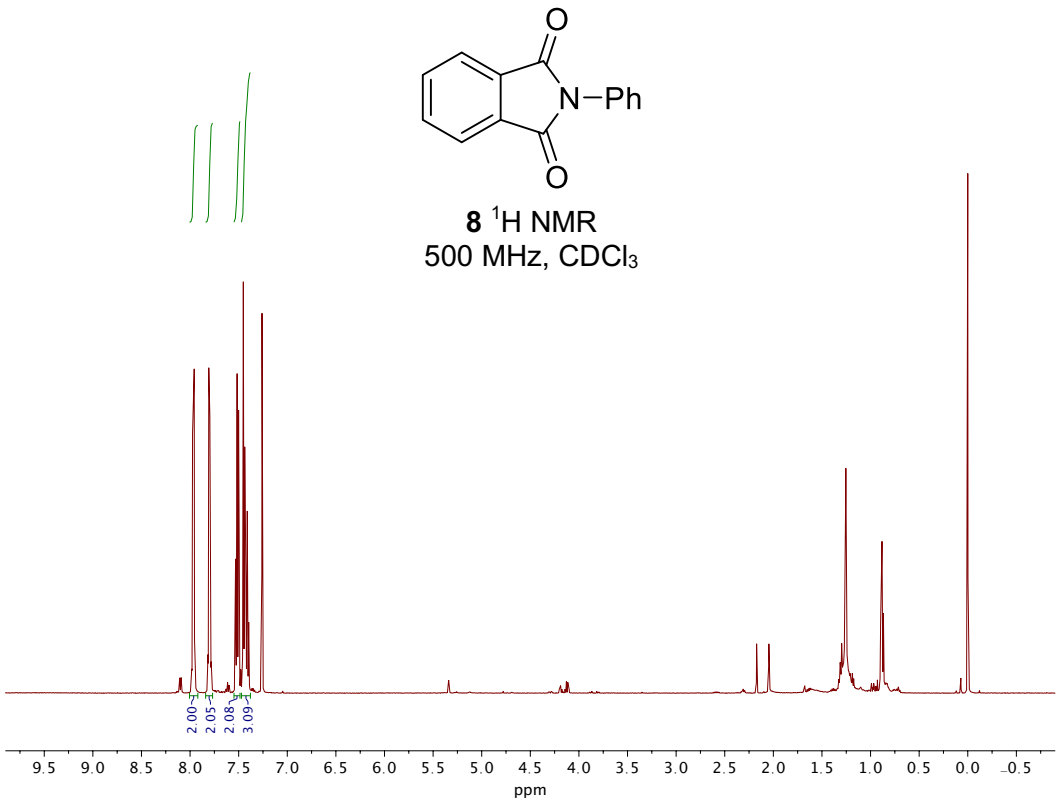
***trans*-5-OBz**
^{1}H NMR
500 MHz, $CDCl_3$



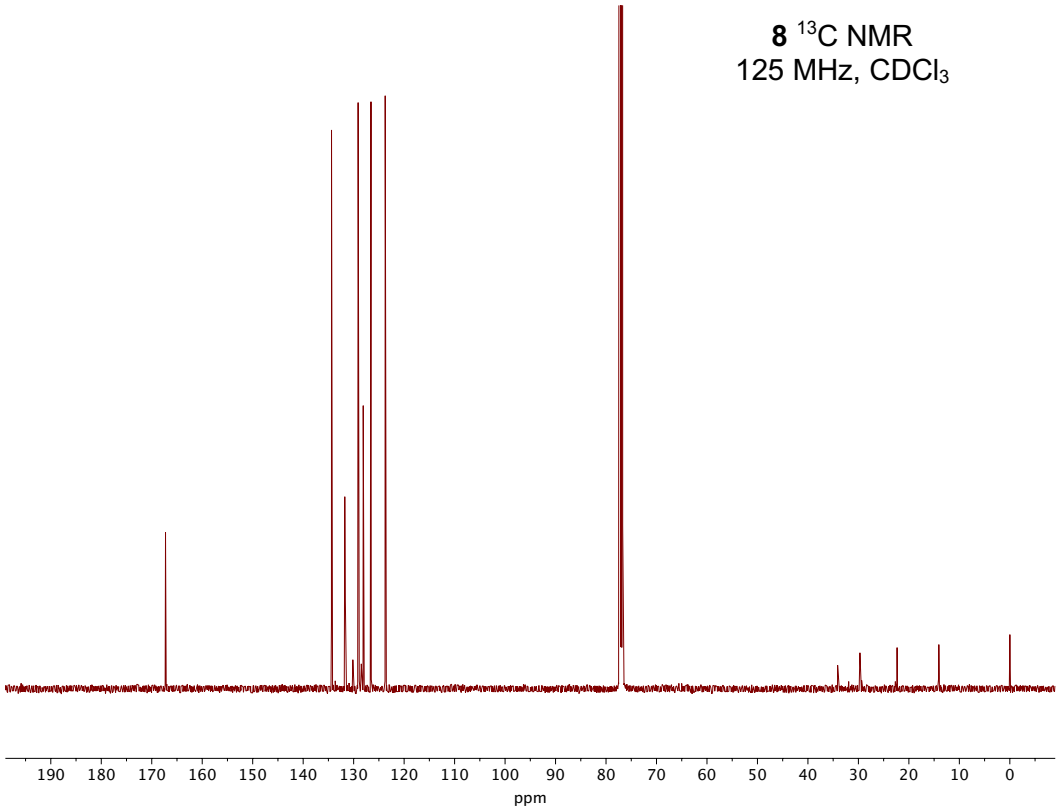
***trans*-5-OBz**
^{13}C NMR
125 MHz, $CDCl_3$


O
N−Ph
BzO
O
7 1H NMR
500 MHz, CDCl3
1.96
1.14
3.04
2.14
1.98
1.01
1.01
1.00
1.01
1.04
1.02
1.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
ppm


7 13C NMR
125 MHz, CDCl3
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
ppm



8 ^{1}H NMR
500 MHz, $CDCl_3$



8 ^{13}C NMR
125 MHz, $CDCl_3$