Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Iron-Catalyzed Synthesis of Cyclopropanes by in situ Generation and Decomposition of Electronically Diversified Diazo Compounds

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1. General Information

All cyclopropanation reactions were run under an argon atmosphere with oven-dried glassware using standard techniques for manipulating air-sensitive compound.[1] CH_2Cl_2 was distilled over calcium hydride under argon prior to use. Flash column chromatography was performed on 230-400 μm mesh silica with the indicated eluent. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on either a 400 or 500 MHz spectrometers (Bruker Ultrashield 400 or Bruker Ultrashield 500 plus) at 293 K. The corresponding chemical shifts for ^{1}H NMR and ^{13}C NMR spectra are reported in parts per million relative to the chemical shift of tetramethylsilane and recorded in $(CD_3)_2SO$, using the residual $(CH_3)_2SO$ as reference (^{1}H: δ2.50 ppm, ^{13}C: δ39.52 ppm); or in $CDCl_3$, using the residual $CHCl_3$ as reference (^{1}H: δ7.26 ppm, ^{13}C: δ77.16 ppm). The corresponding chemical shifts of ^{19}F NMR spectra are reported in parts per million and recorded in DMSO-d_6 or $CDCl_3$, using α,α,α-trifluorotoluene (^{19}F: -63.72 ppm) as reference. The data is reported as follows: chemical shift (ppm), multiplicity (s = singlet, br = broad singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, dtd = doublet of triplet of doublets, t = triplet, app. t = apparent triplet, q = quadruplet, quin = quintet, sext = sextet and m = multiplet), coupling constant in Hz, integration. For new compounds, DEPT 135 experiments were conducted to assign the substitution pattern for each carbon (Cq, CH, CH_2, CH_3). Infrared spectra were recorded on a Bruker Vertex Series FTIR and are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra were performed by the Centre régional de spectroscopie de masse de l'Université de Montréal.

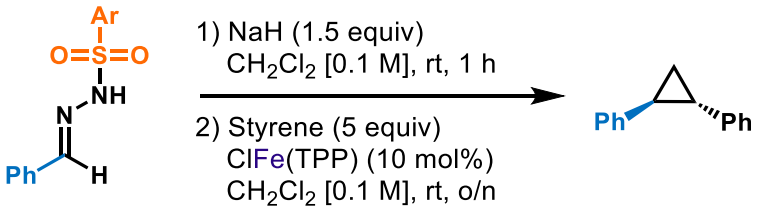
2. Reagents

Commercially available reagents were used as supplied or purified by standard techniques where necessary. Non-commercial starting materials were synthesized according to literature procedures.

[1] Shriver, D. F. & Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; 2nd Edition; Wiley: New York, 1986.

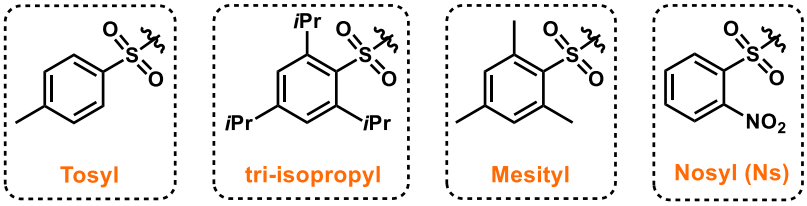
3. Optimization

Hydrazones screening

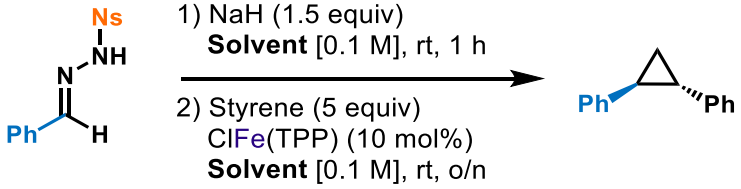


Entry	Ar	dr	Yield (%)[a,b]	Mass balance
1	Tolyl	-	27%	hydrazone recovered
2	Triisopropylphenyl	92:8	24%	dimerization
3	Mesityl	-	17%	dimerization
4	o-nitroaryl	92:8	65%	dimerization

[a] Determined by ^{1}H NMR (Ph_3CH used as internal standard).
[b] Combined ^{1}H NMR yields of both diastereomers.



Solvents screening

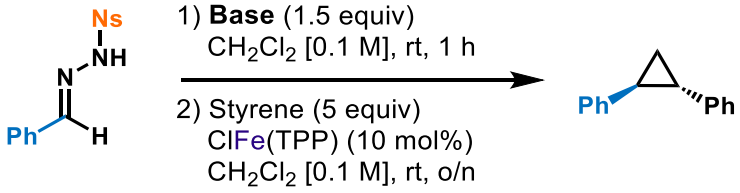


Entry	Solvent	dr	Yield (%)[a,b]	Mass balance
1	CH_2Cl_2	92:8	65%	dimerization
2	Et_2O	-	6%	hydrazone recovered
3	ACN	93:7	43%	dimerization
4	THF	94:6	56%	dimerization

5	dioxane	-	17%	hydrazone recovered
6	MeOH	-	12%	hydrazone recovered
7	toluene	-	0%	hydrazone recovered

[a] Determined by ^{1}H NMR (Ph_3CH used as internal standard).
[b] Combined ^{1}H NMR yields of both diastereomers.

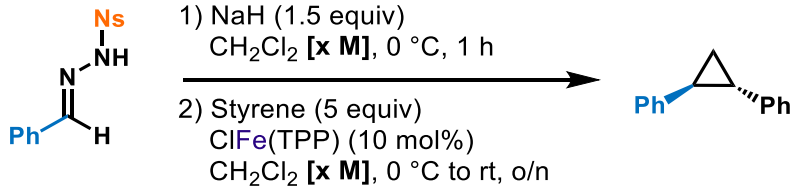
Bases screening



Entry	Solvent	dr	Yield (%)[a,b]	Mass balance
1	NaH	92:8	65%	dimerization
2	NaH (1.01 equiv)	91:9	40%	hydrazone recovered
3	LiO*t*-Bu	-	0%	hydrazone recovered
4	NaO*t*-Bu	90:10	26%	hydrazone recovered
5	KO*t*-Bu	92:8	14%	hydrazone recovered
6	Cs_2CO_3	-	12%	hydrazone recovered
7	K_2CO_3 (temperature of the reaction = 40 °C)	81:9	67%	dimerization
8	Cs_2CO_3 (temperature of the reaction = 40 °C)	90:10	73%	dimerization

[a] Determined by ^{1}H NMR (1,3,5-trimethoxybenzene used as internal standard).
[b] Combined ^{1}H NMR yields of both diastereomers.

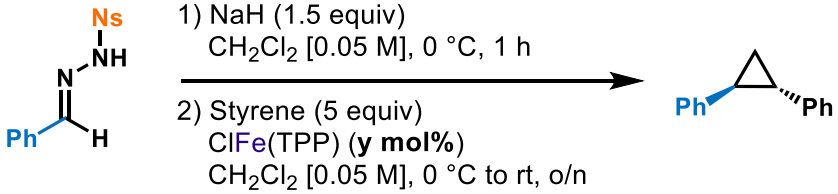
Concentrations screening



Entry	Concentration [x M]	dr	Yield (%)[a,b]	Mass balance
1	[0.1 M] (deprotonation at rt)	92:8	65%	dimerization
2	[0.1 M]	91:9	75%	dimerization
3	[0.2 M]	92:8	74%	dimerization
4	[0.05 M]	92:8	85%	quench of the diazo
5	[0.025 M]	91:9	74%	dimerization

[a] Determined by ^{1}H NMR (1,3,5-trimethoxybenzene used as internal standard).
[b] Combined ^{1}H NMR yields of both diastereomers.

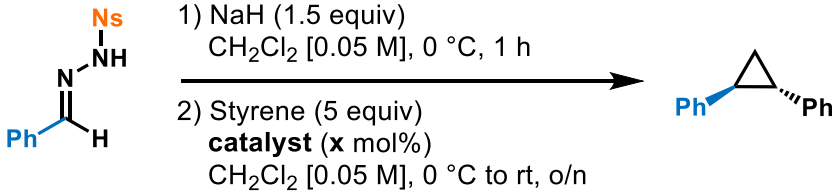
Catalyst loading



Entry	Loading (y mol%)	dr	Yield (%)[a,b]	Mass balance
1	10 mol%	92:8	85%	quench of the remaining diazo
2	5 mol%	91:9	53%	hydrazone recovered
3	2.5 mol%	91:9	64%	hydrazone recovered
4	2.5 mol% (2 days)	92:8	75%	dimerization

[a] Determined by ^{1}H NMR (1,3,5-trimethoxybenzene used as internal standard).
[b] Combined ^{1}H NMR yields of both diastereomers.

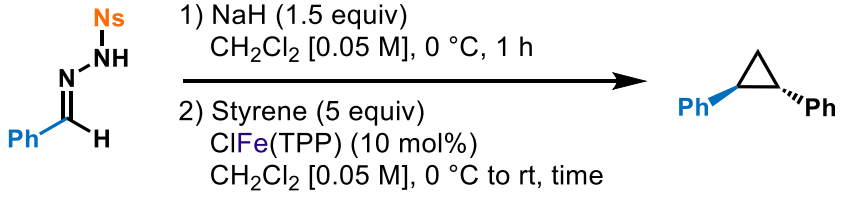
Attempts using others transition metal catalysts



Entry	Catalyst (x mol%)	dr	Yield (%)[a,b]	Mass balance
1	$AgBF_4$ (20 mol%) (in CH_2Cl_2 [0.1M])	22:78	54%	hydrazone recovered
2	$Rh_2(OPiv)_4$ (10 mol%)	17:83	72%	hydrazone recovered

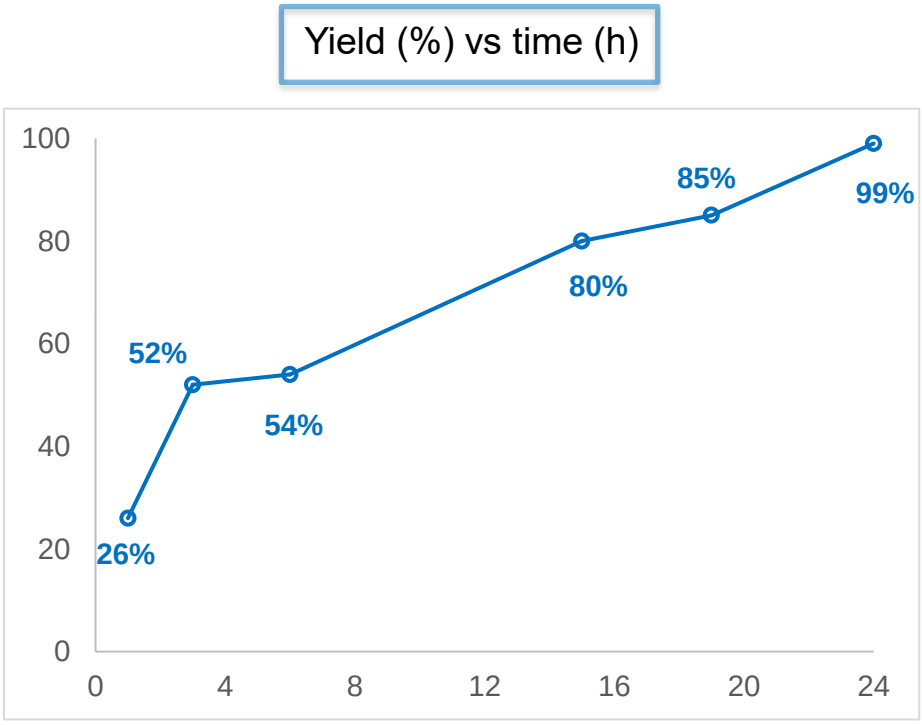
[a] Determined by ^1H NMR (triphenylmethane used as internal standard).
[b] Combined ^1H NMR yields of both diastereomers.

Timerange of the reaction



Entry	Time	dr	Yield (%)[a,b]	Mass balance
1	1 h	92:8	26%	hydrazone recovered
2	3 h	92:8	52%	hydrazone recovered
3	6 h	91:9	54%	hydrazone recovered
4	15 h	92:8	80%	hydrazone recovered
5	19 h	92:8	85%	quench of the remaining diazo
5	24 h	91:9	99%	-

[a] Determined by ^{1}H NMR (1,3,5-trimethoxybenzene used as internal standard).
[b] Combined ^{1}H NMR yields of both diastereomers



4. Synthetic procedures

o-nitrobenzenesulfonylhydrazide synthesis

N-nitrobenzenesulfonylhydrazide ($NsNHNH_2$) was prepared according to literature procedure.[2]

General procedure A - N-nosylhydrazones synthesis

According to a procedure previously used in our group.[3]

To a 20 mL glass vial containing a suspension of *o*-nitrobenzenesulfonylhydrazide (1.00 equiv) in EtOH [0.67M] were added the chosen aldehyde (1.01 or 1.05 equiv) in one portion and acetic acid (0.05 equiv). The heterogeneous mixture was vigorously stirred for 2 hours. The reaction mixture was then concentrated under vacuum until about 1/10$_{th}$ of the original volume remains, and excess hexanes was added, causing precipitation. The solid was recovered by filtration on a fritted glass filter then thoroughly washed with hexanes. The resulting solid was dried under reduced pressure overnight to give the pure desired N-nosylhydrazones.

General procedure B - Cyclopropanation reaction, room temperature

To an oven-dried 20 mL glass microwave vial equipped with a magnetic stirrer was weighted the chosen nosylhydrazone (0.50 mmol, 1.0 equiv). The flask was then capped with a septum and flushed with argon during few minutes, after which the freshly distilled CH_2Cl_2 (10 mL, [0.05M]) was added. The reaction mixture was then cooled down to 0 °C with a water/ice bath and the flask was briefly opened to add NaH 50 wt% (36.0 mg, 0.75 mmol, 1.5 equiv) and the reaction mixture was stirred at this temperature for 1 hour. The chosen styrene (2.6 mmol, 5.2 equiv) was then added via syringe and the ClFe(TPP) (35.2 mg, 0.05 mmol, 10 mol%) was added in one portion. The ice-bath was removed and the reaction mixture was allowed to warm up to room temperature and to stir under an argon atmosphere for 24 hours. The reaction mixture was the quenched with an aqueous solution of HCl 2M and diluted with CH_2Cl_2. The biphasic mixture was then filtered over celite to remove the iron residues, and the cake was washed several times with CH_2Cl_2. The layers were separated and the aqueous one was extracted three times with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude product was then purified by silica gel chromatography.

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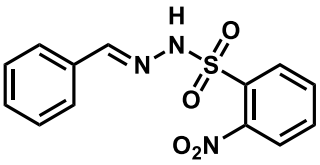
[2] Myers, A. G.; Zheng, B.; Movassaghi, M. *J. Org. Chem.* **1997**, *62*, 7507.
[3] Lévesque, E.; Laporte, S. T.; Charette, A. B. *Angew. Chem., Int. Ed*. **2017**, *56*, 837.

General procedure B' - Cyclopropanation reaction, 40 °C

To an oven-dried 20 mL glass microwave vial equipped with a magnetic stirrer was weighted the chosen nosylhydrazone (0.50 mmol, 1.0 equiv). The flask was then capped with a septum and flushed with argon during few minutes, after which the freshly distilled CH_2Cl_2 (10 mL, [0.05M]) was added. The reaction mixture was then cooled down to 0 °C with a water/ice bath and the flask was briefly opened to add NaH 50 wt% (36.0 mg, 0.75 mmol, 1.5 equiv) and the reaction mixture was stirred at this temperature for 1 hour. The chosen styrene (2.6 mmol, 5.2 equiv) was then added via syringe and the ClFe(TPP) (35.2 mg, 0.05 mmol, 10 mol%) was added in one portion. The ice-bath was removed and the reaction mixture was allowed to warm up to room temperature. The flask was then sealed with a pressure cap, put into a 40 °C oil-bath and stirred at this temperature for 24 hours. Then reaction mixture was then cooled down to room temperature, quenched with an aqueous solution of HCl 2M and diluted with CH_2Cl_2. The biphasic mixture was then filtered over celite to remove the iron residues, and the cake was washed several times with CH_2Cl_2. The layers were separated and the aqueous one was extracted three times with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude product was then purified by silica gel chromatography.

5. Characterization Data

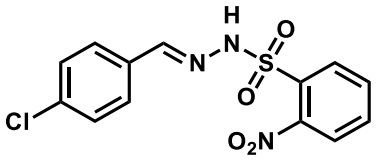
(a) Hydrazones



(E)-N'-benzylidene-2-nitrobenzenesulfonohydrazide (1a)

Synthesized from benzaldehyde (440 μL, 4.31 mmol, 1.01 equiv), acetic acid (13 μL, 0.213 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (927 mg, 4.27 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellow solid (1.28 g, 4.23 mmol, 99%). Product corresponds to literature characterization data.[4]

^{1}H NMR (400 MHz, DMSO) δ 12.12 (s, 1H), 8.07 – 8.05 (m, 2H), 8.02 – 8.00 (m, 1H), 7.91 – 7.86 (m, 2H), 7.58 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.42 – 7.38 (m, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 147.87 (Cq), 147.75 (CH), 134.79 (CH), 133.38 (Cq), 132.60 (CH), 130.90 (Cq), 130.50 (CH), 130.36 (CH), 128.83 (CH), 126.93 (CH), 124.52 (CH).

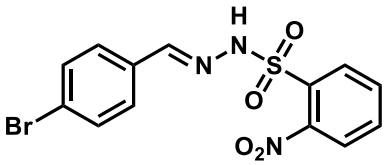


(E)-N'-(4-chlorobenzylidene)-2-nitrobenzenesulfonohydrazide (1b)

Synthesized from 4-chlorobenzaldehyde (630 μL, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a white solid (1.30 g, 3.82 mmol, 83%). Product corresponds to literature characterization data.[4]

^{1}H NMR (400 MHz, DMSO) δ 12.24 (s, 1H), 8.07 – 8.00 (m, 3H), 7.92 – 7.87 (m, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR (126 MHz, DMSO)** δ 147.85 (Cq), 146.45 (CH), 134.84 (CH), 132.63 (CH), 132.33 (Cq), 130.86 (Cq), 130.47 (CH), 128.93 (CH), 128.58 (CH), 124.56 (CH).

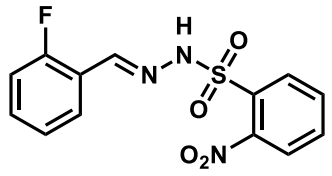
[4] (a) Liu, Z.; Li, Q.; Liao, P.; Bi, X. *Chem. – Eur. J.* **2017,** *23,* 4756. (b) Liu, Z.; Li, Q.; Yang, Y.; Bi, X. *Chem. Commun*. **2017**, *53*, 2503.



(E)-N'-(4-bromobenzylidene)-2-nitrobenzenesulfonohydrazide (1c)

Synthesized from 4-bromobenzaldehyde (860 mg, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellowish solid (1.62 g, 4.23 mmol, 92%). **mp**: 154 - 158 °C (degradation).

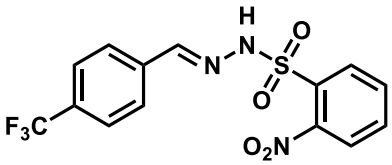
^{1}H NMR (400 MHz, DMSO) δ 12.24 (s, 1H), 8.06 – 8.00 (m, 3H), 7.91 – 7.86 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR (126 MHz, DMSO)** δ 147.84 (Cq), 146.53 (CH), 134.84 (CH), 132.67 (Cq), 132.64 (CH), 131.84 (CH), 130.87 (Cq), 130.46 (CH), 128.79 (CH), 124.57 (CH), 123.64 (Cq). **FTIR (cm^{-1}) (neat):** 3237, 1529, 1369, 1181, 936, 819, 583. **HRMS (ESI, Pos)** calculated for $C_{13}H_{10}BrN_3O_4S$ $[M+H]^+$: 383.9648 m/z, found 383.9652 m/z.



(E)-N'-(2-fluorobenzylidene)-2-nitrobenzenesulfonohydrazide (1d)

Synthesized from 2-fluorobenzaldehyde (490 μL, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellow solid (1.32 g, 4.09 mmol, 89%). **mp**: 168 - 170 °C.

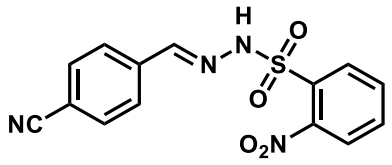
^{1}H NMR (400 MHz, DMSO) δ 12.29 (br, 1H), 8.26 (s, 1H), 8.07 – 8.01 (m, 2H), 7.94 – 7.84 (m, 2H), 7.70 (t, *J* = 6.1 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.28 – 7.21 (m, 2H). **^{13}C NMR (101 MHz, DMSO)** δ 160.55 (d, *J* = 250.5 Hz, Cq), 147.79, 140.46 (d, *J* = 4.6 Hz), 134.87, 132.66, 132.35 (d, *J* = 8.3 Hz), 130.80, 130.58, 126.16, 124.91, 124.58, 120.90 (d, *J* = 9.9 Hz), 116.03 (d, *J* = 20.8 Hz). **^{19}F NMR (376 MHz, DMSO)** δ 4.14 (dd, *J* = 10.2, 5.7 Hz). **FTIR (cm^{-1}) (neat):** 3236, 1529, 1175, 1038, 768, 585. **HRMS (ESI, Pos)** calculated for $C_{13}H_{10}FN_3O_4S$ $[M+H]^+$: 324.0449 m/z, found 324.0454 m/z.



(E)-2-nitro-N'-(4-(trifluoromethyl)benzylidene)benzenesulfonohydrazide (1e)

Synthesized from 4-(trifluoromethyl)benzaldehyde (633 μL, 4.64 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (997 mg, 4.59 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a white solid (1.45 g, 3.90 mmol, 85%). **mp**: 118 - 120 °C.

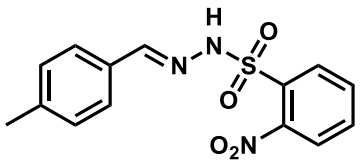
^{1}H NMR (400 MHz, DMSO) δ 12.44 (br, 1H), 8.15 (s, 1H), 8.09 – 8.07 (m, 1H), 8.03 – 8.01 (m, 1H), 7.92 – 7.87 (m, 2H), 7.78 (dd, *J* = 17.9, 8.1 Hz, 4H). **^{13}C NMR (101 MHz, DMSO)** δ 147.81, 145.90, 137.32, 134.89, 132.67, 130.84, 130.46, 130.09, 129.78, 127.53, 125.71 (dd, *J* = 7.5, 3.7 Hz, Cq), 124.59. **^{19}F NMR (376 MHz, DMSO)** δ -61.27. **FTIR (cm^{-1}) (neat):** 3206, 1537, 1310, 1066, 941, 833, 577. **HRMS (ESI, Pos)** calculated for $C_{14}H_{11}F_3N_3O_4S$ $[M+H]^+$: 374.0417 m/z, found 374.0427 m/z.



(E)-N'-(4-cyanobenzylidene)-2-nitrobenzenesulfonohydrazide (1f)

Synthesized from 4-cyanobenzaldehyde (609 mg, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (999 mg, 4.60 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellow solid (1.39 g, 4.19 mmol, 91%). Product corresponds to literature characterization data.[4]

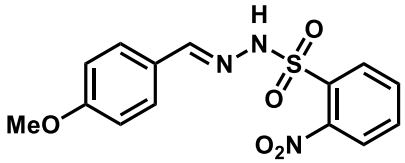
^{1}H NMR (400 MHz, DMSO) δ 12.51 (br, 1H), 8.12 (s, 1H), 8.10 – 8.05 (m, 1H), 8.05 – 7.99 (m, 1H), 7.90 – 7.85 (m, 4H), 7.77 – 7.76 (m, 2H). **^{13}C NMR (101 MHz, DMSO)** δ 147.78, 145.57, 137.76, 134.93, 132.72, 132.66, 130.75, 130.52, 127.46, 124.56, 118.51, 112.17.



(E)-N'-(4-methylbenzylidene)-2-nitrobenzenesulfonohydrazide (1g)

Synthesized from 4-methylbenzaldehyde (437 μL, 4.69 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.64 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellow solid (1.18 g, 3.71 mmol, 80%). **mp**: 133 - 140 °C.

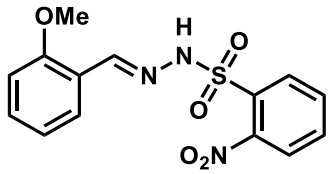
^{1}H NMR (400 MHz, DMSO) δ 12.02 (s, 1H), 8.13 – 7.94 (m, 3H), 7.94 – 7.79 (m, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 2.30 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 147.97 (CH), 147.93 (Cq), 140.31 (Cq), 134.77 (CH), 132.60 (CH), 130.99 (Cq), 130.73 (Cq), 130.53 (CH), 129.45 (CH), 126.96 (CH), 124.54 (CH), 21.03 (CH_3). **FTIR (cm^{-1}) (neat):** 3265, 1533, 1367, 1176, 740, 570. **HRMS (ESI, Pos)** calculated for $C_{14}H_{14}N_3O_4S$ $[M+H]^+$: 320.0700 m/z, found 320.0706 m/z.



(E)-N'-(4-methoxybenzylidene)-2-nitrobenzenesulfonohydrazide (1h)

Synthesized from 4-methoxybenzaldehyde (570 μL, 4.67 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.63 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as an orange solid (1.35 g, 4.03 mmol, 87%). **mp**: 94 - 100 °C.

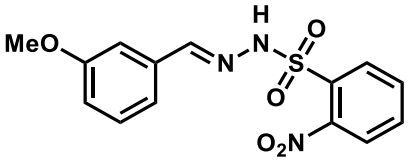
^{1}H NMR (400 MHz, DMSO) δ 11.91 (s, 1H), 8.06 – 8.04 (m, 1H), 8.01 – 7.99 (m, 2H), 7.89 – 7.87 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.99 (Cq), 147.92 (Cq), 147.81 (CH), 134.68 (CH), 132.52 (CH), 130.98 (Cq), 130.47 (CH), 128.59 (CH), 125.97 (Cq), 124.47 (CH), 114.30 (CH), 55.30 (CH_3). **FTIR (cm^{-1}) (neat):** 3252, 1545, 1464, 1174, 1126, 810, 735, 570. **HRMS (ESI, Pos)** calculated for $C_{14}H_{14}N_3O_5S$ $[M+H]^+$: 336.0649 m/z, found 336.0643 m/z.



((E)-N'-(2-methoxybenzylidene)-2-nitrobenzenesulfonohydrazide (1i)

Synthesized from 2-methoxybenzaldehyde (560 μL, 4.64 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellow solid (1.39 g, 4.14 mmol, 90%). **mp**: 159 - 162 °C.

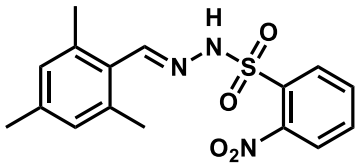
^{1}H NMR (400 MHz, DMSO) δ 12.03 (s, 1H), 8.39 (s, 1H), 8.02 (dd, *J* = 15.5, 3.5 Hz, 2H), 7.94 – 7.80 (m, *J* = 2.6 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.37 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.94 (t, *J* = 7.35 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 157.60 (Cq), 147.86 (Cq), 143.30 (CH), 134.75 (CH), 132.60 (CH), 131.95 (CH), 130.95 (Cq), 130.52 (CH), 125.27 (CH), 124.53 (CH), 121.33 (Cq), 120.70 (CH), 111.87 (CH), 55.71 (CH_3). **FTIR (cm^{-1}) (neat):** 3252, 1531, 1375, 1177, 766, 574. **HRMS (ESI, Pos)** calculated for $C_{14}H_{14}N_3O_5S$ $[M+H]^+$: 336.0649 m/z, found 336.0652 m/z.



(E)-N'-(3-methoxybenzylidene)-2-nitrobenzenesulfonohydrazide (1j)

Synthesized from 3-methoxybenzaldehyde (570 μL, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a white solid (1.31 g, 3.82 mmol, 83%). Product corresponds to literature characterization data.[4]

^{1}H NMR (400 MHz, DMSO) δ 12.13 (s, 1H), 8.10 – 8.04 (m, 1H), 8.04 – 7.97 (m, 2H), 7.95 – 7.84 (m, 2H), 7.31 (t, *J* = 8.1 Hz, 1H), 7.21 – 7.08 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 159.51 (Cq), 147.98 (Cq), 147.64 (CH), 134.91 (CH), 134.85 (Cq), 132.60 (CH), 130.81 (Cq), 130.60 (CH), 130.03 (CH), 124.50 (CH), 119.66 (CH), 116.37 (CH), 111.55 (CH), 55.20 (CH_3).

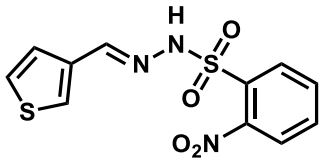


(E)-2-nitro-N'-(2,4,6-trimethylbenzylidene)benzenesulfonohydrazide (1k)

Synthesized from mesitaldehyde (690 μL, 4.69 mmol, 1.02 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv)

using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellowish solid (1.51 g, 4.37 mmol, 95%). **mp**: 128 - 130 °C.

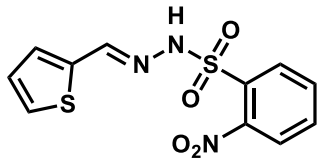
^{1}H NMR (400 MHz, DMSO) δ 11.89 (s, 1H), 8.36 (s, 1H), 8.06 – 8.03 (m, 1H), 8.02 – 7.99 (m, 1H), 7.92 – 7.86 (m, 2H), 6.85 (s, 2H), 2.20 (s, 3H), 2.16 (s, 6H). **^{13}C NMR (101 MHz, DMSO)** δ 148.04, 147.90, 138.58, 137.07, 134.72, 132.46, 130.88, 130.79, 129.34, 127.40, 124.50, 20.63 (CH_3), 20.60 (CH_3). **FTIR (cm^{-1}) (neat):** 3236, 1533, 1369, 1177, 782, 578. **HRMS (ESI, Pos)** calculated for $C_{16}H_{17}N_3O_4S$ $[M+H]^+$: 348.1013 m/z, found 348.1021 m/z.



(E)-2-nitro-N'-(thiophen-3-ylmethylene)benzenesulfonohydrazide (1l)

Synthesized from 3-thiophenecarboxaldehyde (410 μL, 4.69 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.65 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellow solid (1.19 g, 3.81 mmol, 82%). Product corresponds to literature characterization data.[4]

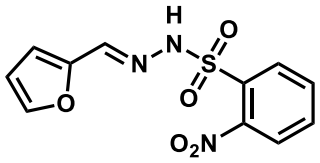
^{1}H NMR (400 MHz, DMSO) δ 11.95 (s, 1H), 8.08 (s, 1H), 8.05 – 8.03 (m, 1H), 8.01 – 7.98 (m, 1H), 7.88 – 7.87 (m, 3H), 7.57 – 7.55 (m, 1H), 7.29 (d, *J* = 5.0 Hz, 1H). **^{13}C NMR (126 MHz, DMSO)** δ 147.91 (Cq), 143.55 (CH), 136.55 (Cq), 134.76 (CH), 132.57 (CH), 130.90 (Cq), 130.56 (CH), 128.82 (CH), 127.80 (CH), 124.50 (CH), 124.35 (CH).



(E)-2-nitro-N'-(thiophen-2-ylmethylene)benzenesulfonohydrazide (1m)

Synthesized from 2-thiophenecarboxaldehyde (435 μL, 4.65 mmol, 1.01 equiv)acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.61 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellow solid (1.08 g, 3.46 mmol, 75%). **mp**: 122 - 128 °C.

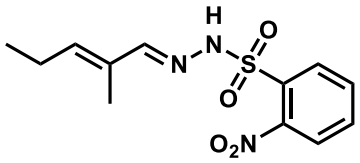
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (br, 1H), 8.29 – 8.26 (m, 1H), 8.14 (s, 1H), 7.85 – 7.83 (m, 1H), 7.79 – 7.75 (m, 2H), 7.37 (d, *J* = 4.72 Hz, 1H), 7.02 (t, *J* = 4.5 Hz, 1H), 1.68 (br, 1H). **^{13}C NMR (126 MHz, DMSO)** δ 147.82 (Cq), 142.95 (CH), 137.86 (Cq), 134.77 (CH), 132.57 (CH), 131.34 (CH), 130.91 (Cq), 130.44 (CH), 129.19 (CH), 127.88 (CH), 124.60 (CH). **FTIR (cm^{-1}) (neat):** 3245, 1529, 1349, 1173, 718, 570. **HRMS (ESI, Pos)** calculated for $C_{11}H_9N_3O_4S_2$ $[M+H]^+$: 312.0107 m/z, found 312.0111 m/z.



(E)-N'-(furan-2-ylmethylene)-2-nitrobenzenesulfonohydrazide (1n)

Synthesized from 2-furaldehyde (310 μL, 3.75 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (806 mg, 3.71 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a yellow solid (905 mg, 3.08 mmol, 83%). **mp**: 82 - 89 °C.

^{1}H NMR (300 MHz, DMSO) δ 12.10 (br, 1H), 8.04 – 7.99 (m, 2H), 7.95 (s, 1H), 7.95 – 7.86 (m, 2H), 7.77 (d, *J* = 1.2 Hz, 1H), 6.87 (d, *J* = 3.4 Hz, 1H), 6.58 (dd, *J* = 3.4, 1.8 Hz, 1H). **^{13}C NMR (75 MHz, DMSO)** δ 148.30 (Cq), 147.82 (Cq), 145.38 (CH), 137.60 (CH), 134.73 (CH), 132.74 (CH), 131.09 (Cq), 130.37 (CH), 124.73 (CH), 114.65 (CH), 112.12 (CH). **FTIR (cm^{-1}) (neat):** 3229, 1530, 1362, 1172, 736, 583, 519. **HRMS (ESI, Pos)** calculated for $C_{11}H_9N_3O_5S$ $[M+H]^+$: 296.0336 m/z, found 296.0338 m/z.

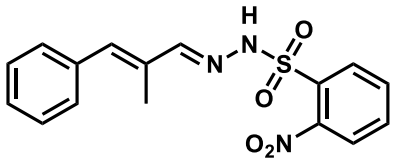


N'-((1E,2E)-2-methylpent-2-en-1-ylidene)-2-nitrobenzenesulfonohydrazide (1o)

Synthesized from 2-methyl-2-pentenal (530 μL, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the **general procedure A for N-nosylhydrazones synthesis**. Product obtained as a white solid (1.13 g, 3.77 mmol, 82%). **mp**: 108 - 110 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.23 (m, 1H), 8.09 (br, 1H), 7.84 – 7.81 (m, 1H), 7.78 – 7.74 (m, 2H), 7.52 (s, 1H), 5.80 (t, *J* = 7.1 Hz, 1H), 2.19 (quin, *J* = 7.5 Hz, 2H), 1.70 (s, 3H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.94 (CH), 148.41 (Cq),

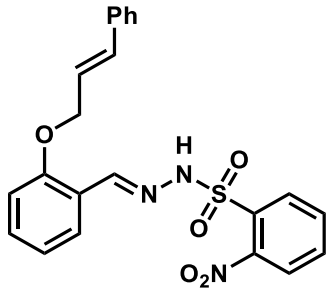
144.39 (CH), 134.28 (CH), 133.23 (CH), 132.64 (CH), 132.11 (Cq), 131.75 (Cq), 125.21 (CH), 21.91 (CH_2), 13.45 (CH_3), 11.14 (CH_3). **FTIR (cm^{-1}) (neat):** 3203, 1541, 1440, 1174, 604. **HRMS (ESI, Pos)** calculated for $C_{12}H_{16}N_3O_4S$ $[M+H]^+$: 298.08560 m/z, found 298.08546 m/z.



N'-((1E,2E)-2-methyl-3-phenylallylidene)-2-nitrobenzenesulfonohydrazide (1p)

Synthesized from α-methyl-*trans*-cinnamaldehyde (650 μL, 4.65 mmol, 1.01 equiv), acetic acid (13 μL, 0.23 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (1.00 g, 4.60 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a white solid (1.23 g, 3.54 mmol, 77%). **mp**: 148 - 150 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.28 (m, 1H), 8.26 (br, 1H), 7.87 – 7.83 (m, 1H), 7.79 – 7.75 (m, 2H), 7.70 (s, 1H), 7.38 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 6.72 (s, 1H), 2.01 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.63 (CH), 148.46 (Cq), 139.31 (CH), 136.10 (Cq), 134.41 (CH), 133.66 (Cq), 133.21 (CH), 132.74 (CH), 131.78 (Cq), 129.53 (CH), 128.57 (CH), 128.24 (CH), 125.31 (CH), 13.00 (CH_3). **FTIR (cm^{-1}) (neat):** 3200, 1542, 1365, 1171, 1021, 854, 579, 556. **HRMS (ESI, Pos)** calculated for $C_{16}H_{15}N_3O_4S$ $[M+H]^+$: 346.0856 m/z, found 346.0859 m/z.



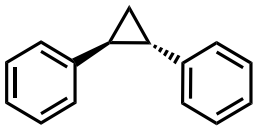
N'-((E)-2-(cinnamyloxy)benzylidene)-2-nitrobenzenesulfonohydrazide (1q)

Synthesized from 2-(cinnamyloxy)benzaldehyde (436 mg, 1.83 mmol, 1.02 equiv), acetic acid (5 μL, 0.90 mmol, 0.05 equiv) and o-nitrobenzenesulfonylhydrazide (390 mg, 1.80 mmol, 1.00 equiv) using the general procedure A for N-nosylhydrazones synthesis. Product obtained as a yellow solid (684 mg, 1.57 mmol, 87%). **mp**: 158 – 162 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.36 (br, 1H), 8.32 – 8.30 (m, 1H), 7.83 – 7.78 (m, 2H), 7.77 – 7.72 (m, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.27 (m, 4H), 6.94 – 6.91 (m, 2H), 6.70 (d, *J* = 16.1 Hz, 1H), 6.39 (dt, *J* = 16.1, 5.9 Hz, 1H), 4.72 (dd, *J* = 5.89, 1.14

Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.37 (Cq), 146.45 (CH), 136.20 (Cq), 134.33 (CH), 133.85 (CH), 133.14 (CH), 132.87 (CH), 132.36 (CH), 132.10 (Cq), 128.85 (CH), 128.35 (CH), 126.92 (CH), 126.78 (CH), 125.32 (CH), 123.76 (CH), 121.67 (Cq), 121.13 (CH), 112.53 (CH), 69.37 (CH_2). **FTIR (cm^{-1}) (neat):** 3276, 2868, 1528, 1379, 1254, 1179, 749, 596, 581. **HRMS (ESI, Pos)** calculated for $C_{22}H_{19}N_3O_5S$ $[M+K]^+$: 476.0677 m/z, found 476.0682 m/z.

(b) Cyclopropanes

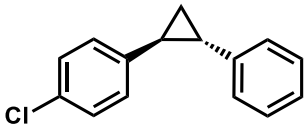


1,2-diphenylcyclopropane (2a)

Synthesized from **1a** (153 mg, 0.500 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. The product was observed in 99% yield (determined by ^{1}H NMR) and isolated by flash chromatography (100% petroleum ether) yielded a clear oil (89.5 mg, 0.460 mmol, 92%) (volatile compound) as a mixture of diastereomers *trans/cis*: 91/9. **Rf** (100% petroleum ether) = 0.39. The characterization data match the literature.[5]

Characterization data for the major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 4H), 7.22 – 7.15 (m, 6H), 2.21 – 2.17 (m, 2H), 1.47 (td, *J* = 7.4, 1.1 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.67 (Cq), 128.53 (CH), 125.91 (CH), 28.16 (CH), 18.35 (CH_2).



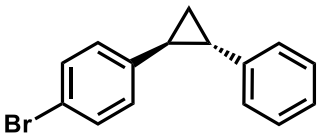
1-chloro-4-(2-phenylcyclopropyl)benzene (2b)

Synthesized from **1b** (170 mg, 0.500 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (99.7 mg, 0.435 mmol, 87%) as a mixture of diastereomers *trans/cis*: 89/11. **Rf** (100% petroleum ether) = 0.54.

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.18 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.08 – 7.05 (m, 2H), 2.16 – 2.11 (m, 2H), 1.48 – 1.44 (m, 1H), 1.43 – 1.39 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.25 (Cq), 141.17 (Cq), 131.50 (Cq), 128.60 (CH), 127.27 (CH), 126.05 (CH), 125.89 (CH), 28.26 (CH), 27.54 (CH), 18.35 (CH_2). **FTIR (cm^{-1}) (neat):** 3027, 2923, 2853, 1582, 1493, 1091, 1013, 816, 745, 695, 520. **HRMS (APPI, Pos)** calculated for $C_{15}H_{13}Cl$ $[M]^+$: 228.0706 m/z, found 228.0721 m/z.

[5] Aggarwal, V. K.; de Vicente, J.; Bonnert, R. V. *Org. Lett.* **2001***, 3,* 2785.

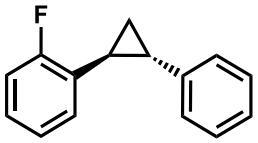


1-bromo-4-(2-phenylcyclopropyl)benzene (2c)

Synthesized from **1c** (192 mg, 0.499 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (115.2 mg, 0.424 mmol, 85%) as a mixture of diastereomers *trans/cis*: 91/9. **Rf** = 0.39 (100% petroleum ether).

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.32 – 7.29 (m, 2H), 7.22 – 7.19 (m, 1H), 7.15 – 7.13 (m, 2H), 7.03 – 7.01 (m, 2H), 2.16 – 2.11 (m, 2H), 1.50 – 1.45 (m, 1H), 1.44 – 1.40 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.20 (Cq), 141.72 (Cq), 131.53 (CH), 128.59 (CH), 127.66 (CH), 126.06 (CH), 125.88 (CH), 119.43 (Cq), 28.28 (CH), 27.60 (CH), 18.34 (CH_2). **FTIR (cm^{-1}) (neat):** 3025, 2923, 2852, 1603, 1488, 1073, 1008, 812, 742, 695, 516. **HRMS (APPI, Pos)** calculated for $C_{15}H_{13}Br$ $[M]^+$: 272.0201 m/z, found 272.0232 m/z.



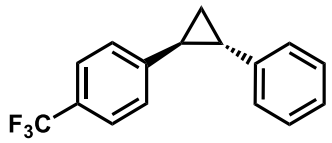
1-fluoro-2-(2-phenylcyclopropyl)benzene (2d)

Synthesized from **1d** (161 mg, 0.499 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (85.9 mg, 0.404 mmol, 81%) as a mixture of diastereomers *trans/cis*: 90/10. **Rf** = 0.51 (100% petroleum ether). The characterization data match the literature.[6]

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.22 – 7.19 (m, 3H), 7.17 – 7.14 (m, 1H), 7.11 – 7.08 (m, 1H), 7.05 – 7.01 (m, 2H), 2.40 – 2.36 (m, 1H), 2.24 – 2.20 (m, 1H), 1.48 – 1.45 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.84 (d, *J* = 245.3 Hz, Cq), 142.26 (Cq), 129.55 (d, *J* = 14.4 Hz, Cq), 128.55 (CH), 127.76 (CH), 127.15 (d, *J* = 8.1 Hz, CH), 126.34 (d, *J* = 4.2 Hz, CH), 126.20 (CH), 126.06 (CH), 124.14 (d, *J* = 3.5 Hz, CH), 115.26 (d, *J* = 22.1 Hz, CH), 26.69 (CH), 20.89 (d, *J* = 4.7 Hz, CH), 17.00 (CH_2).

[6] Wang, Y.; Wen, X.; Cui, X.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2017**, *139*, 1049.

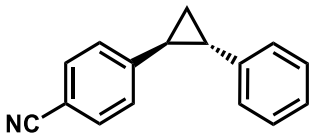


1-(2-phenylcyclopropyl)-4-(trifluoromethyl)benzene (2e)

Synthesized from **1e** (186 mg, 0.499 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (127 mg, 0.484 mmol, 97%) as a mixture of diastereomers *trans/cis*: 91/9. **Rf** = 0.64 (100% petroleum ether).

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.24 – 7.21 (m, 3H), 7.16 – 7.14 (m, 2H), 2.22 (t, 2H), 1.57 – 1.47 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.93 (Cq), 141.89 (Cq), 128.65 (CH), 126.22 (CH), 126.03 (CH), 125.94 (CH), 125.47 (q, *J* = 7.4, 3.7 Hz, Cq), 28.84 (CH), 27.91 (CH), 18.73 (CH_2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.24. **FTIR (cm^{-1}) (neat):** 3028, 2926, 2855, 1619, 1322, 1162, 1114, 1066, 1015, 823, 695, 517. **HRMS (APPI, Pos)** calculated for $C_{16}H_{13}F_3$ $[M]^+$: 262.0969 m/z, found 298.0989 m/z.

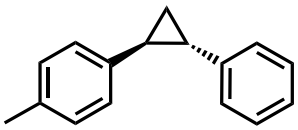


4-(2-phenylcyclopropyl)benzonitrile (2f)

Synthesized from **1f** (163 mg, 0.495 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (100% petroleum ether) yielded a clear oil (103 mg, 0.470 mmol, 95%) as a mixture of diastereomers *trans/cis*: 85/15. **Rf** = 0.42 (10% ethyl acetate in hexanes).

Characterization data for the major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.19 (m, 3H), 7.15 – 7.13 (m, 2H), 2.25 – 2.17 (m, 2H), 1.62 – 1.56 (m, 1H), 1.53 – 1.48 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.60 (Cq), 141.44 (Cq), 132.36 (CH), 128.68 (CH), 126.39 (CH), 125.93 (CH), 119.25 (Cq), 109.41 (Cq), 29.40 (CH), 28.23 (CH), 19.09 (CH_2). **FTIR (cm^{-1}) (neat):** 3027, 2924, 2224, 1604, 1497, 1179, 821, 750, 696, 549. **HRMS (APPI, Pos)** calculated for $C_{16}H_{13}N$ $[M]^+$: 220.1121 m/z, found 220.1149 m/z.



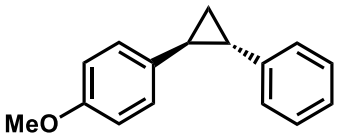
1-methyl-4-(2-phenylcyclopropyl)benzene (2g)

Synthesized from **1g** (159 mg, 0.499 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (100% hexanes) yielded a clear oil (23 mg, 0.110 mmol, 22%) as a mixture of diastereomers *trans/cis*: 92/8.

Synthesized from **1g** (160 mg, 0.502 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (100% petroleum ether) yielded a clear oil (95.3 mg, 0.457 mmol, 91%) as a mixture of diastereomers *trans/cis*: 90/10. **Rf** = 0.67 (100% petroleum ether).

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.7 Hz, 2H), 7.20 – 7.11 (m, 5H), 7.05 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 3H), 2.17 – 2.12 (m, 2H), 1.43 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.83 (Cq), 139.59 (Cq), 135.42 (Cq), 129.21 (CH), 128.51 (CH), 125.87 (CH), 125.84 (CH), 125.80 (CH), 27.98 (CH), 27.88 (CH), 21.12 (CH_3), 18.16 (CH_2). **FTIR (cm^{-1}) (neat):** 3025, 2922, 2854, 1603, 1498, 809, 750, 695, 512. **HRMS (APPI, Pos)** calculated for $C_{16}H_{16}$ $[M]^+$: 208.1252 m/z, found 208.1259 m/z.

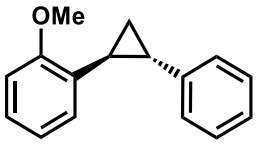


1-methoxy-4-(2-phenylcyclopropyl)benzene (2h)

Synthesized from **1h** (169 mg, 0.504 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a red oil (95.4 mg, 0.423 mmol, 84%) as a mixture of diastereomers *trans/cis*: 89/11. **Rf** = 0.52 (2% ethyl acetate in hexanes). The characterization data match the literature.[6]

Characterization data for the major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.22 – 7.13 (m, 3H), 7.11 – 7.07 (m, 2H), 6.87 – 6.83 (m, 2H), 3.80 (s, 3H), 2.17 – 2.07 (m, 2H), 1.42 – 1.38 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.00 (Cq), 142.88 (Cq), 134.66 (Cq), 128.51 (CH), 127.06 (CH), 125.84 (CH), 125.78 (CH), 114.00 (CH), 55.48 (CH_3), 27.65 (CH), 27.47 (CH), 17.95 (CH_2).



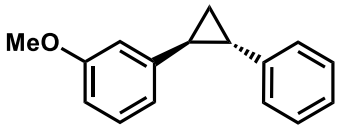
1-methoxy-2-(2-phenylcyclopropyl)benzene (2i)

Synthesized from **1i** (169 mg, 0.504 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded an orange oil (68.0 mg, 0.302 mmol, 60%) as a mixture of diastereomers *trans/cis*: 89/11.

Synthesized from **1i** (168 mg, 0.501 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a redish oil (108.0 mg, 0.481 mmol, 96%) as a mixture of diastereomers *trans/cis*: 86/14. **Rf** = 0.59 (2% ethyl acetate in hexanes). The characterization data match the literature.[6]

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.16 (m, 4H), 6.99 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 2.53 – 2.47 (m, 1H), 2.17 – 2.13 (m, 1H), 1.43 – 1.37 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.30 (Cq), 143.14 (Cq), 130.99 (Cq), 128.42 (CH), 126.77 (CH), 126.27 (CH), 125.72 (CH), 125.22 (CH), 120.64 (CH), 110.44 (CH), 55.65 (CH_3), 26.67 (CH), 21.77 (CH), 17.18 (CH_2).



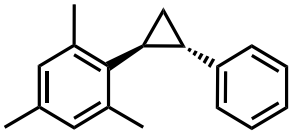
1-methoxy-3-(2-phenylcyclopropyl)benzene (2j)

Synthesized from **1j** (168 mg, 0.502 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a red oil (94.0 mg, 0.417 mmol, 83%) as a mixture of diastereomers *trans/cis*: 90/10. **Rf** = 0.43 (2% ethyl acetate in hexanes). The characterization data match the literature.[6]

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dt, *J* = 9.5, 1.7 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.16 – 7.14 (m, 2H), 6.76 – 6.73 (m, 2H), 6.71 – 6.70 (m, 1H), 3.81 (s, 3H), 2.21 – 2.13 (m, 2H), 1.46 (t, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.89 (Cq), 144.41 (Cq), 142.59 (Cq), 129.51

(CH), 128.53 (CH), 125.90 (CH), 118.30 (CH), 111.81 (CH), 111.16 (CH), 55.32 (CH_3), 28.22 (CH), 28.18 (CH), 18.34 (CH_2).

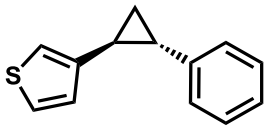


1,3,5-trimethyl-2-((1S,2S)-2-phenylcyclopropyl)benzene (2k)

Synthesized from **1k** (173 mg, 0.499 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (100% petroleum ether) yielded a clear oil (70.0 mg, 0.294 mmol, 59%) as a mixture of diastereomers *trans/cis*: 71/29. **Rf** = 0.28 (100% petroleum ether).

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 10.8, 4.4 Hz, 2H), 7.22 – 7.18 (m, 3H), 6.86 (s, 2H), 2.37 (s, *J* = 10.9 Hz, 6H), 2.27 (s, 3H), 2.05 – 1.98 (m, 2H), 1.47 – 1.43 (m, 1H), 1.28 – 1.24 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.40 (Cq), 138.79 (Cq), 136.01 (Cq), 135.46 (Cq), 128.89 (CH), 128.51 (CH), 125.69 (CH), 125.59 (CH), 26.03 (CH), 25.02 (CH), 20.98 (CH_3), 20.95 (CH_3), 19.67 (CH_2). **FTIR (cm^{-1}) (neat):** 3026, 2918, 2859, 1604, 1496, 1458, 1445, 1376, 1029, 849, 741, 695, 530. **HRMS (APCI, Pos)** calculated for $C_{18}H_{21}$ $[M+H]^+$: 237.16378 m/z, found 237.16459 m/z.



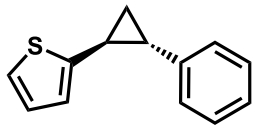
3-(2-phenylcyclopropyl)thiophene (2l)

Synthesized from **1l** (157 mg, 0.504 mmol, 1.0 equiv) and styrene (300 μL, 2.62 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a redish oil (41 mg, 0.207 mmol, 41%) as a mixture of diastereomers *trans/cis*: 92/8.

Synthesized from **1l** (156 mg, 0.500 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a redish oil (68.5 mg, 0.340 mmol, 68%) as a mixture of diastereomers *trans/cis*: 89/11. **Rf** = 0.72 (2% ethyl acetate in hexanes).

Characterization data for the major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 3H), 7.22 – 7.17 (tt, *J* = 7.3, 1.3, 1H), 7.14 (dd, *J* = 5.3, 3.4 Hz, 2H), 6.95 (ddd, *J* = 3.0, 1.3, 0.5 Hz, 1H), 6.92 (dd, *J* = 5.0, 1.3 Hz, 1H), 2.26 – 2.21 (ddd, *J* = 8.5, 6.1, 4.6 Hz, 1H), 2.17 – 2.13 (m, 1H), 1.45 – 1.37 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.83 (Cq), 142.52 (Cq), 128.53 (CH), 126.28 (CH), 125.88 (CH), 125.84 (CH), 125.70 (CH), 118.49 (CH), 27.38 (CH), 23.86 (CH), 18.25 (CH_2). **FTIR (cm^{-1}) (neat):** 3025, 2924, 2853, 1604, 1499, 775, 746, 695, 635, 506. **HRMS (APCI, Pos)** calculated for $C_{13}H_{13}S$ $[M+H]^+$: 201.0732 m/z, found 201.0735 m/z.

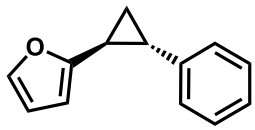


2-(2-phenylcyclopropyl)thiophene (2m)

Synthesized from **1m** (155 mg, 0.498 mmol, 1.0 equiv) and styrene (300 μL, 2.60 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (using a gradient from 100% hexanes to 99:1 hexanes/ethyl acetate) yielded a redish oil (57.4 mg, 0.289 mmol, 58%) as a mixture of diastereomers *trans/cis*: 89/11. **Rf** = 0.54 (4% ethyl acetate in hexanes).

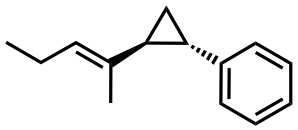
Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.19 (m, 1H), 7.16 – 7.14 (m, 2H), 7.09 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.84 (d, *J* = 3.5 Hz, 1H), 2.39 – 2.36 (m, 1H), 2.25 – 2.21 (m, 1H), 1.52 – 1.44 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.13 (Cq), 141.96 (Cq), 128.58 (CH), 127.00 (CH), 126.08 (CH), 125.94 (CH), 122.89 (CH), 122.40 (CH), 28.79 (CH), 23.27 (CH), 19.27 (CH_2). **FTIR (cm^{-1}) (neat):** 3026, 2924, 2852, 1604, 1499, 750, 510. **HRMS (APCI, Pos)** calculated for $C_{13}H_{13}S$ $[M+H]^+$: 201.0732 m/z, found 201.0728 m/z.



2-(2-phenylcyclopropyl)furan (2n)

Synthesized from **1n** (59.3 mg, 201 mmol, 1.0 equiv) and styrene (120 μL, 1.05 mmol, 5.22 equiv) using **general procedure B'**. The product was observed in 44% yield (determined by ^{1}H NMR). This compound is unstable on silica gel.



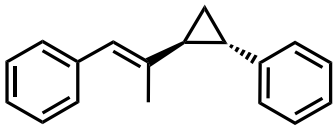
(2-((E)-pent-2-en-2-yl)cyclopropyl)benzene (2o)

Synthesized from **1o** (149 mg, 0.502 mmol, 1.0 equiv) and styrene (300 μL, 2.62 mmol, 5.22 equiv) using **general procedure B'.** Flash chromatography (100% petroleum ether) yielded a clear oil (28.3 mg, 0.151 mmol, 30%) as a mixture of diastereomers *trans/cis*: 94/6.

Synthesized from **1o** (149 mg, 0.502 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B' (with a reaction time of 48 hours)**. Flash chromatography (100% petroleum ether) yielded a clear oil (51.5 mg, 0.276 mmol, 55%) as a mixture of diastereomers *trans/cis*: 91/9. **Rf** = 0.86 (100% petroleum ether).

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.20 – 7.13 (m, 1H), 7.13 – 7.07 (m, 2H), 5.25 (td, *J* = 7.0, 1.1 Hz, 1H), 2.09 – 2.00 (m, 2H), 1.90 (dt, *J* = 8.7, 4.3 Hz, 1H), 1.67 – 1.62 (m, 1H), 1.60 (s, 3H), 1.22 – 1.17 (m, 1H), 1.02 (dtd, *J* = 6.4, 5.4, 1.4 Hz, 1H), 0.96 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.55 (Cq), 133.89 (Cq), 128.40 (CH), 126.02 (CH), 125.86 (CH), 125.49 (CH), 31.64, 29.86, 23.28, 21.32, 14.60, 14.47. **FTIR (cm^{-1}) (neat):** 3064, 2961, 2928, 1655, 1499, 1458, 750, 695, 515. **HRMS (APCI, Pos)** calculated for $C_{14}H_{19}$ $[M+H]^+$: 187.1481 m/z, found 187.1480 m/z.



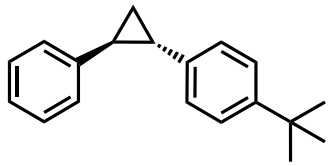
((E)-2-(-2-phenylcyclopropyl)prop-1-en-1-yl)benzene (2p)

Synthesized from **1p** (173 mg, 0.501 mmol, 1.0 equiv) and styrene (300 μL, 2.61 mmol, 5.22 equiv) using **general procedure B' (with a reaction time of 48 hours)**. Flash chromatography (100% petroleum ether) yielded a clear oil (86.0 mg, 0.366 mmol, 73%) as a mixture of diastereomers *trans/cis*: 86/14. **Rf** = 0.65 (100% petroleum ether).

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 3H), 7.32 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 7.18 (d, *J* = 7.88 Hz, 2H), 6.42 (s, 1H), 2.10 – 2.15 (m, 1H), 1.89 (s, 3H), 1.44 – 1.38 (m, 1H), 1.25 – 1.20 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.03 (Cq), 138.42 (Cq), 138.31 (Cq), 128.98 (CH), 128.50 (CH), 128.20 (CH), 126.05 (CH), 125.96 (CH), 125.74 (CH), 124.25 (CH), 32.62 (CH), 23.90 (CH), 16.07 (CH_3), 15.05 (CH_2). **FTIR (cm^{-1}) (neat):**

3023, 2924, 2854, 1600, 1494, 1441, 733, 694, 516. **HRMS (APCI, Pos)** calculated for $C_{18}H_{19}$ $[M+H]^+$: 235.14813 m/z, found 235.1472 m/z.

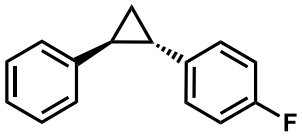


1-(tert-butyl)-4-(2-phenylcyclopropyl)benzene (3a)

Synthesized from **1a** (153 mg, 0.501 mmol, 1.0 equiv) and 4-tert-butylstyrene (480 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (124 mg, 0.496 mmol, 99%) as a mixture of diastereomers *trans/cis*: 92/8. **Rf** = 0.70 (100% petroleum ether).

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 2.19 – 2.13 (m, 2H), 1.44 (t, *J* = 7.3 Hz, 2H), 1.33 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.80 (Cq), 142.84 (Cq), 139.65 (Cq), 128.50 (CH), 125.89 (CH), 125.79 (CH), 125.59 (CH), 125.44 (CH), 34.52 (Cq), 31.54 (CH_3), 27.99 (CH), 27.80 (CH), 18.26 (CH_2). **FTIR (cm^{-1}) (neat):** 3027, 2959, 2925, 1604, 1499, 820, 746, 695, 552. **HRMS (APCI, Pos)** calculated for $C_{19}H_{23}$ $[M+H]^+$: 251.17943 m/z, found 251.18066 m/z.



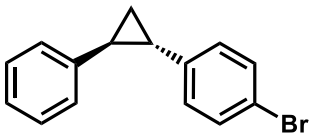
1-fluoro-4-(2-phenylcyclopropyl)benzene (3b)

Synthesized from **1a** (154 mg, 0.503 mmol, 1.0 equiv) and 4-fluorostyrene (310 μL, 2.62 mmol, 5.20 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (85.0 mg, 0.402 mmol, 80%) as a mixture of diastereomers *trans/cis*: 91/9. **Rf** = 0.17 (100% petroleum ether).

Characterization data for the major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.20 (tt, *J* = 7.34, 1.95 or 1.34 Hz, 1H), 7.16 – 7.09 (m, 4H), 7.02 – 6.96 (m, 2H), 2.19 – 2.10 (m, 2H), 1.47 – 1.38 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.38 (d, *J* = 243.6 Hz, Cq), 142.45 (Cq), 138.20 (d, *J* = 3.0 Hz, Cq), 128.57 (CH), 127.39 (d, *J* = 7.8 Hz, CH), 125.96 (CH), 125.86 (CH), 115.28 (d, *J* = 21.3 Hz, CH), 27.92 (CH), 27.36 (CH), 18.18 (CH_2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -

117.55 – -117.65 (m). **FTIR (cm^{-1}) (neat):** 3027, 1603, 1510, 1227, 1208, 1158, 820, 763, 751, 695, 518. **HRMS (APCI, Pos)** calculated for $C_{15}H_{13}F$ $[M]^+$: 212.1001 m/z, found 212.0993 m/z.

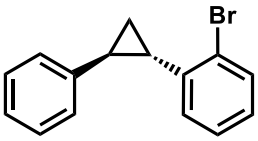


1-bromo-4-(2-phenylcyclopropyl)benzene (3c = 2c)

Synthesized from **1a** (153 mg, 0.501 mmol, 1.0 equiv) and 4-bromostyrene (340 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (119.4 mg, 0.436 mmol, 87%) as a mixture of diastereomers *trans/cis*: 91/9. **Rf** = 0.39 (100% petroleum ether).

Characterization data for the major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.14 (d, *J* = 7.58 Hz, 2H), 7.01 (d, *J* = 8.41 Hz, 2H), 2.16 – 2.10 (m, 2H), 1.51 – 1.39 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.20 (Cq), 141.71 (Cq), 131.52 (CH), 128.59 (CH), 127.65 (CH), 126.05 (CH), 125.88 (CH), 119.42 (Cq), 28.27 (CH), 27.59 (CH), 18.33 (CH_2). **FTIR (cm^{-1}) (neat):** 3025, 2923, 2852, 1603, 1488, 1073, 1008, 811, 742, 695, 516. **HRMS (APPI, Pos)** calculated for $C_{15}H_{13}Br$ $[M]^+$: 272.01951 m/z, found 272.01923 m/z.



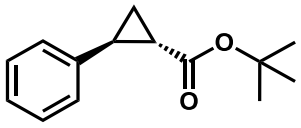
1-bromo-2-(2-phenylcyclopropyl)benzene (3d)

Synthesized from **1a** (154 mg, 0.505 mmol, 1.0 equiv) and 2-bromostyrene (320 μL, 2.56 mmol, 5.07 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (105 mg, 0.384 mmol, 76%) as a mixture of diastereomers *trans/cis*: 91/9. **Rf** (100% petroleum ether) = 0.29.

Characterization data for the major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 4H), 7.14 – 7.09 (m, 2H), 2.54 – 2.49 (m, 1H), 2.19 – 2.15 (m, 1H), 1.49 (t, *J* = 7.39 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.31 (Cq), 141.50 (Cq), 132.66 (CH), 128.49 (CH), 127.57 (CH), 127.50 (CH), 127.04 (CH), 126.25 (Cq), 126.21 (CH), 126.01 (CH), 28.06 (CH), 27.01 (CH), 17.25 (CH_2). **FTIR (cm^{-1}) (neat):** 3026, 2924, 1603, 1475, 1022,

740, 694. **HRMS (APCI, Pos)** calculated for $C_{15}H_{14}Br$ $[M+H]^+$: 273.0273 m/z, found 273.025 m/z.

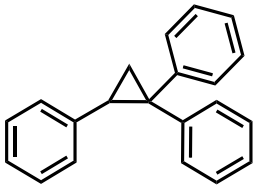


tert-butyl 2-phenylcyclopropane-1-carboxylate (3e)

Synthesized from **1a** (153 mg, 0.502 mmol, 1.0 equiv) and tert-butyl acrylate (370 μL, 2.55 mmol, 5.07 equiv) using **general procedure B**. Flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a red oil (52.3 mg, 0.241 mmol, 48%) as a mixture of diastereomers *trans/cis*: 72/28. **Rf** = 0.30 (2% ethyl acetate in hexanes).

Characterization data for the major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 2H), 7.22 (tt, *J* = 7.37, 2.07 or 1.29 Hz, 1H), 7.13 – 7.11 (m, 2H), 2.49 – 2.45 (m, 1H), 1.88 – 1.85 (m, 1H), 1.58 – 1.54 (m, 1H), 1.50 (s, 9H), 1.28 – 1.24 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.72 (Cq), 140.67 (Cq), 128.56 (CH), 126.46 (CH), 126.21 (CH), 80.70 (Cq), 28.31 (CH_3), 25.88 (CH), 25.43 (CH), 17.20 (CH_2). **FTIR (cm^{-1}) (neat):** 2977, 1716, 1146, 843, 695. **HRMS (ESI, Pos)** calculated for $C_{14}H_{18}O_2Na$ $[M+Na]^+$: 241.1199 m/z, found 241.1194 m/z.

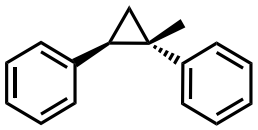


cyclopropane-1,1,2-triyltribenzene (3f)

Synthesized from **1a** (154 mg, 0.503 mmol, 1.0 equiv) and 1,1-diphenylethylene (460 μL, 2.61 mmol, 5.18 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (128.2 mg, 0.473 mmol, 94%). **Rf** = 0.23 (2% ethyl acetate in hexanes). The characterization data match the literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.20 – 7.16 (m, 1H), 7.15 – 7.03 (m, 8H), 6.89 – 6.87 (m, 2H), 2.87 (dd, *J* = 9.0, 6.6 Hz, 1H), 2.00 (dd, *J* = 6.6, 5.4 Hz, 1H), 1.82 (dd, *J* = 9.0, 5.4 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.14 (Cq), 140.33 (Cq), 138.83 (Cq), 131.32 (CH), 128.48 (CH), 128.06 (CH), 127.77 (CH), 127.55 (CH), 126.37 (CH), 126.04 (CH), 125.72 (CH), 39.46 (Cq), 32.53 (CH), 21.03 (CH_2).

[7] Nakano, T.; Endo, K.; Ukaji, Y. Synlett **2015,** *26*, 671.

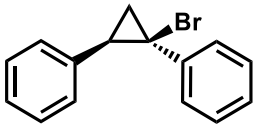


(1-methylcyclopropane-1,2-diyl)dibenzene (3g)

Synthesized from **1a** (152 mg, 0.498 mmol, 1.0 equiv) and α-methylstyrene (520 μL, 2.60 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (100% petroleum ether) yielded a clear oil (89.9 mg, 0.433 mmol, 87%) as a mixture of diastereomers *trans/cis*: 90/10. **Rf** (100% petroleum ether) = 0.35. The characterization data match the literature.[8]

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 8H), 7.26 – 7.20 (m, 2H), 2.44 – 2.41 (m, 1H), 1.47 (dd, *J* = 8.7, 5.1 Hz, 1H), 1.26 (t, *J* = 5.77 Hz, 1H), 1.13 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.98 (Cq), 139.24 (Cq), 129.30 (CH), 128.50 (CH), 128.22 (CH), 127.04 (CH), 126.14 (CH), 125.86 (CH), 31.53 (CH), 27.06 (Cq), 21.12 (CH_3), 18.78 (CH_2).



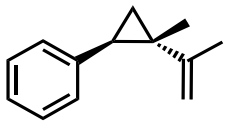
(1-methylcyclopropane-1,2-diyl)dibenzene (3h)

Synthesized from **1a** (154 mg, 0.503 mmol, 1.0 equiv) and α-bromostyrene (341 μL, 2.63 mmol, 5.22 equiv) using **general procedure B'**. Flash chromatography (using a gradient from 100% hexanes to 99.5:0.5 hexanes/ethyl acetate) yielded a yellowish oil (112 mg, 0.412 mmol, 82%) as a mixture of diastereomers *trans/cis*: 72/28. **Rf** = 0.51 (2% ethyl acetate in hexanes).

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.43 – 7.36 (m, 6H), 7.35 – 7.28 (m, 2H), 2.53 (dd, *J* = 9.8, 7.9 Hz, 1H), 1.96 – 1.87 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.47 (Cq), 138.00 (Cq), 129.44 (CH), 128.80 (CH), 128.68 (CH), 128.24 (CH), 128.15 (CH), 127.14 (CH), 41.88 (Cq), 31.16 (CH), 21.21 (CH_2). **FTIR (cm^{-1}) (neat):** 3059, 3027, 1601, 1496, 1446, 1029, 765, 692, 571, 550. Methods available to us did not allow correct product ionization.

[8] Müller, D. S.; Marek, I. *J. Am. Chem. Soc.* **2015**, *137*, 15414.

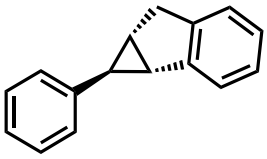


(2-methyl-2-(prop-1-en-2-yl)cyclopropyl)benzene (3i)

Synthesized from **1a** (153 mg, 0.502 mmol, 1.0 equiv) and 2,3-dimethyl-1,3-butadiene (300 μL, 2.66 mmol, 5.30 equiv) using **general procedure B'**. Flash chromatography (100% petroleum ether) yielded a clear oil (24.1 mg, 0.141 mmol, 28%) as a mixture of diastereomers *trans/cis*: 73/27. **Rf** = 0.68 (100% petroleum ether). The characterization data match the literature.[5]

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 3H), 4.86 – 4.85 (m, 1H), 4.79 – 4.78 (m, 1H), 2.17 (dd, *J* = 8.7, 6.4 Hz, 1H), 1.83 – 1.81 (m, 3H), 1.23 (dd, *J* = 8.8, 4.9 Hz, 1H), 0.95 (dd, *J* = 6.2, 5.1 Hz, 1H), 0.88 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.40 (Cq), 139.52 (Cq), 129.28 (CH), 128.11 (CH), 125.93 (CH), 109.43 (Cq), 29.32 (CH_3), 28.66 (Cq), 20.48 (CH), 18.63 (CH_3), 17.24 (CH_2).

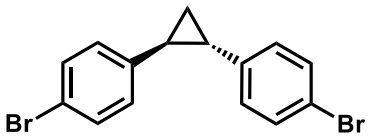


1-phenyl-1,1a,6,6a-tetrahydrocyclopropa[a]indene (3j)

Synthesized from **1a** (153 mg, 0.502 mmol, 1.0 equiv) and indene (300 μL, 2.58 mmol, 5.14 equiv) using **general procedure B'**. Flash chromatography (100% petroleum ether) yielded a yellow solid (with a very low melting point) (38.6 mg, 0.186 mmol, 37%) as a mixture of diastereomers *trans/cis*: 84/16. **Rf** (100% petroleum ether) = 0.21.

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$ δ 7.55 – 7.52 (m, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.16 – 7.13 (m, 2H), 7.08 – 7.05 (m, 2H), 3.36 (dd, *J* = 17.3, 6.6 Hz, 1H), 3.16 (d, *J* = 17.3 Hz, 1H), 2.71 – 2.68 (m, 1H), 2.23 – 2.19 (m, 1H), 1.52 (t, *J* = 3.1 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.56 (Cq), 142.47 (Cq), 137.47 (Cq), 128.83 (CH), 128.49 (CH), 127.77 (CH), 126.65 (CH), 125.43 (CH), 123.68 (CH), 36.44 (CH_2), 34.54 (CH), 27.87 (CH). **FTIR (cm^{-1}) (neat):** 3025, 2954, 2921, 2852, 1601, 1477, 961, 748, 694, 522, 429. **HRMS (APCI, Pos)** calculated for $C_{16}H_{15}$ $[M+H]^+$: 207.1168 m/z, found 207.1176 m/z.



1,2-bis(4-bromophenyl)cyclopropane (5)

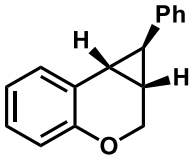
Synthesized from **1c** (192 mg, 0.501 mmol, 1.0 equiv) and 4-bromostyrene (340 μL, 2.61 mmol, 5.22 equiv) using **general procedure B**. Flash chromatography (100% petroleum ether) yielded a clear oil (153 mg, 0.436 mmol, 87%) as a mixture of diastereomers *trans/cis*: 92/8. **Rf** = 0.67 (100% petroleum ether). The characterization data match the literature.[9]

Characterization data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 4H), 7.01 – 6.98 (m, 4H), 2.08 (t, *J* = 7.49 or 7.28 Hz, 2H), 1.43 (t, *J* = 7.49 or 7.28 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.25 (Cq), 131.59 (CH), 127.64 (CH), 119.62 (Cq), 27.71 (CH), 18.30 (CH_2).

[9] Bender, J. A.; Hewawasam, P.; Kadow, J. F.; Lopez, O. D.; Meanwell, N. A.; Nguyen, V. N.; Romine, J. L.; Snyder, L. B.; St. Laurent, D. R.; Wang, G.; Xu N.; Belema, M. WO2010117635 A1, 2010.

6. Procedure for the intramolecular cyclopropanation reaction



1-phenyl-1,1a,2,7b-tetrahydrocyclopropa[c]chromene (4)

To an oven-dried 20 mL glass microwave vial equipped with a magnetic stirrer was weighted the N'-((E)-2-(cinnamyloxy)benzylidene)-2-nitrobenzenesulfonohydrazide (**1q**) (220 mg, 0.503 mmol, 1.0 equiv). The flask was then flushed with argon during few minutes and freshly distilled CH_2Cl_2 (10 mL, [0.05M]) was added. The reaction mixture was then cooled down to 0 °C with a water/ice bath and the flask was briefly opened to add NaH 50 wt% (36.0 mg, 0.75 mmol, 1.5 equiv) and the reaction mixture was stirred at this temperature for 1 hour. The ClFe(TPP) (35.2 mg, 0.05 mmol, 10 mol%) was added in one portion. The ice-bath was removed and the reaction mixture was allowed to warm up to room temperature. The flash was then screw-capped, put into a 40 °C oil-bath and stirred for 24 hours. The reaction mixture was then cooled down to room temperature, quenched with an aqueous solution of HCl 2M and diluted with CH_2Cl_2 and then filtered over celite with copious CH_2Cl_2 washing. The layers were separated and the aqueous one extracted three times with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude desired product was the purified by flash chromatography (using a gradient from 100% hexanes to 98:2 hexanes/ethyl acetate) yielded a brown oil (99.5 mg, 0.448 mmol, 89%) as a single diastereomer. **Rf** = 0.52 (2% ethyl acetate in hexanes). The characterization data match the literature.[10,11]

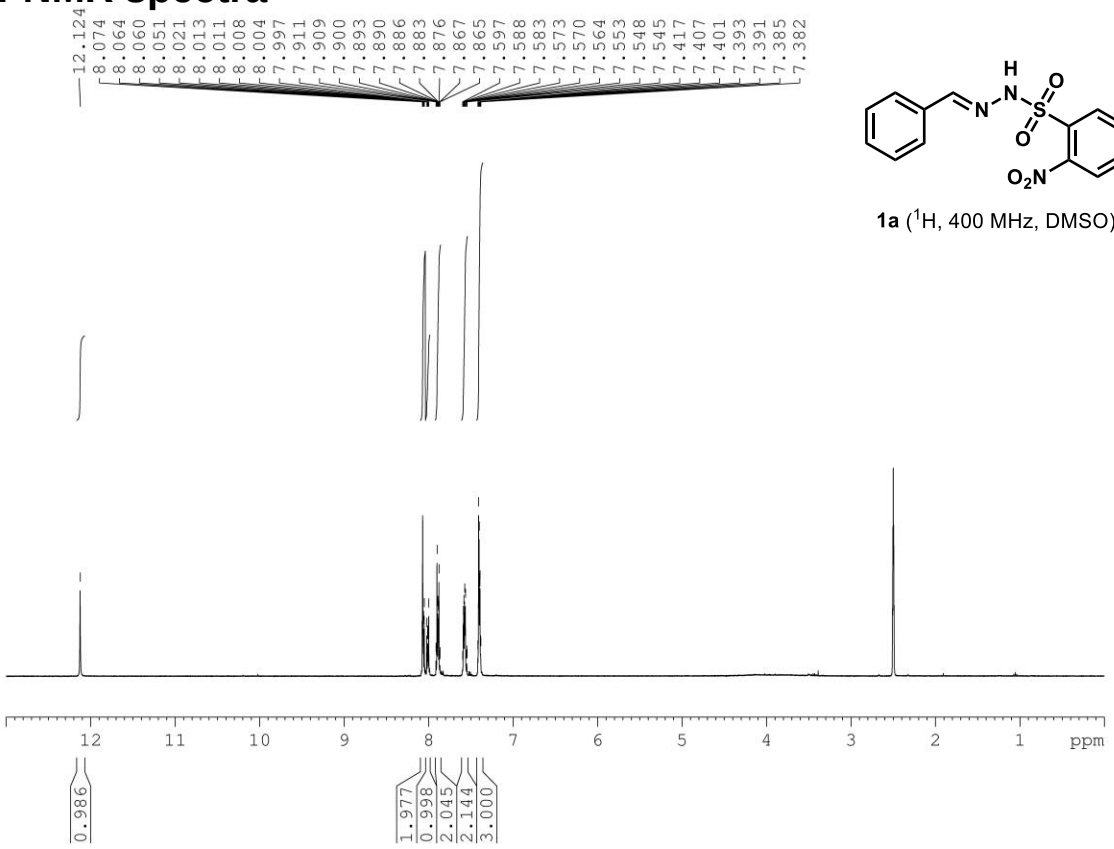
The diastereomeric ratio (96:4) was determined by ^{1}H NMR on the crude mixture.

Characterization data for the major diastereomer:

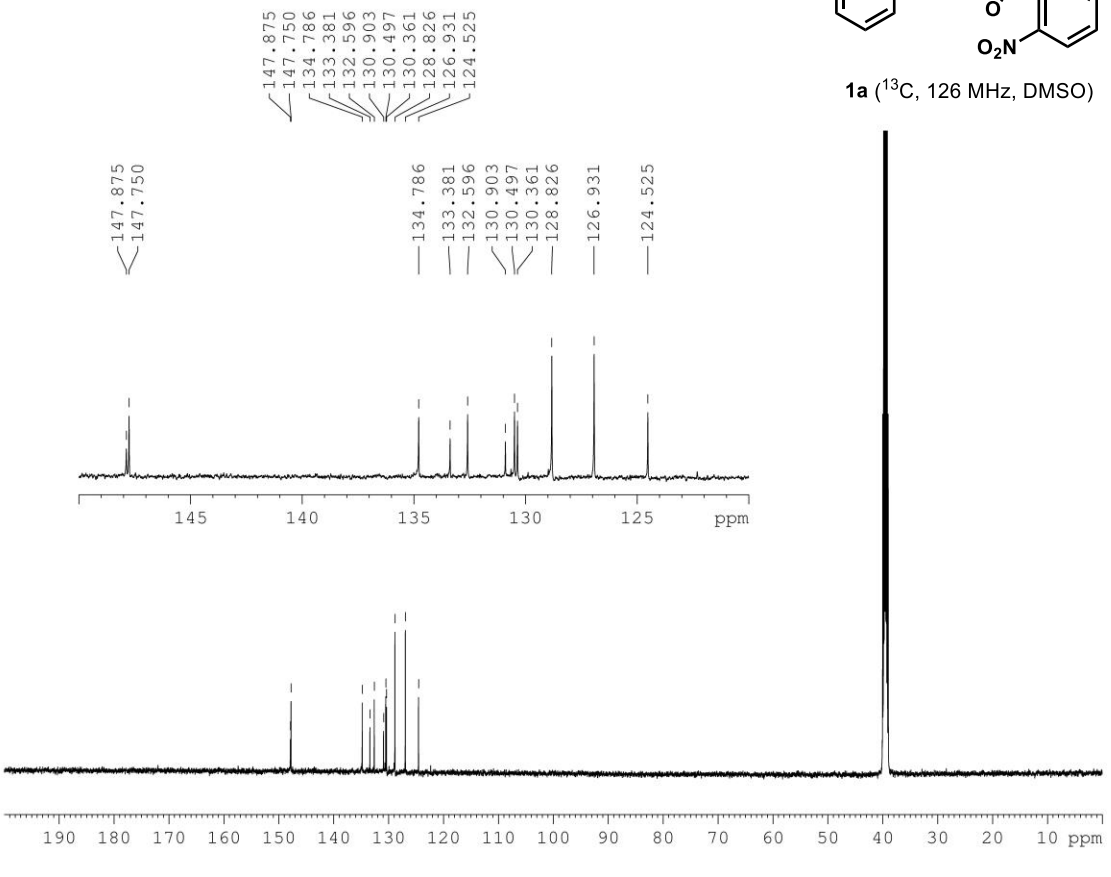
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.13 – 7.09 (m, 3H), 6.94 – 6.91 (m, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 4.47 (d, *J* = 10.6 Hz, 1H), 3.98 – 3.95 (m, 1H), 2.56 (t, *J* = 4.3 Hz, 1H), 2.28 (dd, *J* = 8.8, 3.8 Hz, 1H), 2.17 – 2.14 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.57 (Cq), 141.12 (Cq), 128.67 (CH), 128.54 (CH), 126.65 (CH), 126.38 (Cq), 126.08 (CH), 125.82 (CH), 121.81 (CH), 117.43 (CH), 62.30 (CH_2), 28.11 (CH), 27.41 (CH), 24.90 (CH).

[10] Sun, B.; Adachi, K.; Noguchi, M. *Synthesis* **1997**, *1*, 53.
[11] Liu ,Z. ;Zhang, X.; Zanoni, G.; Bi, X. *Org. Lett.* **2017**, *19*, 6646.

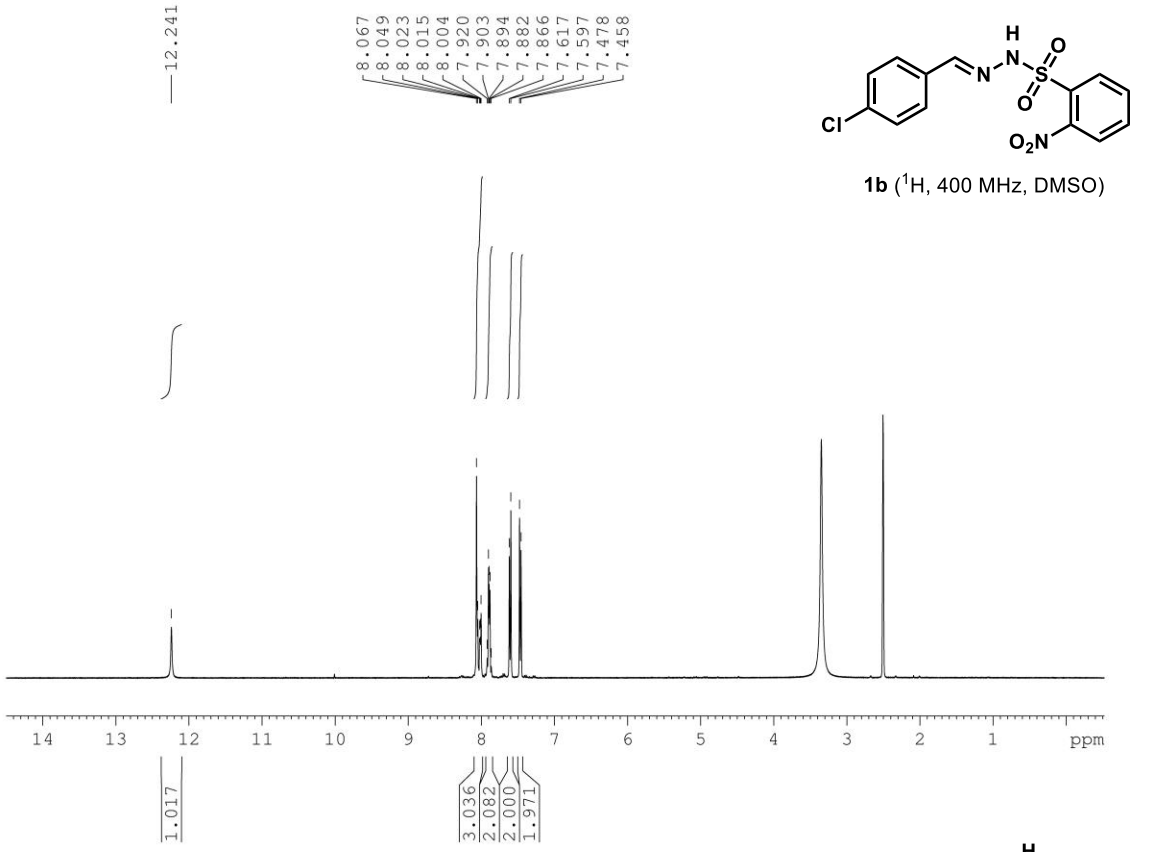
7. NMR spectra



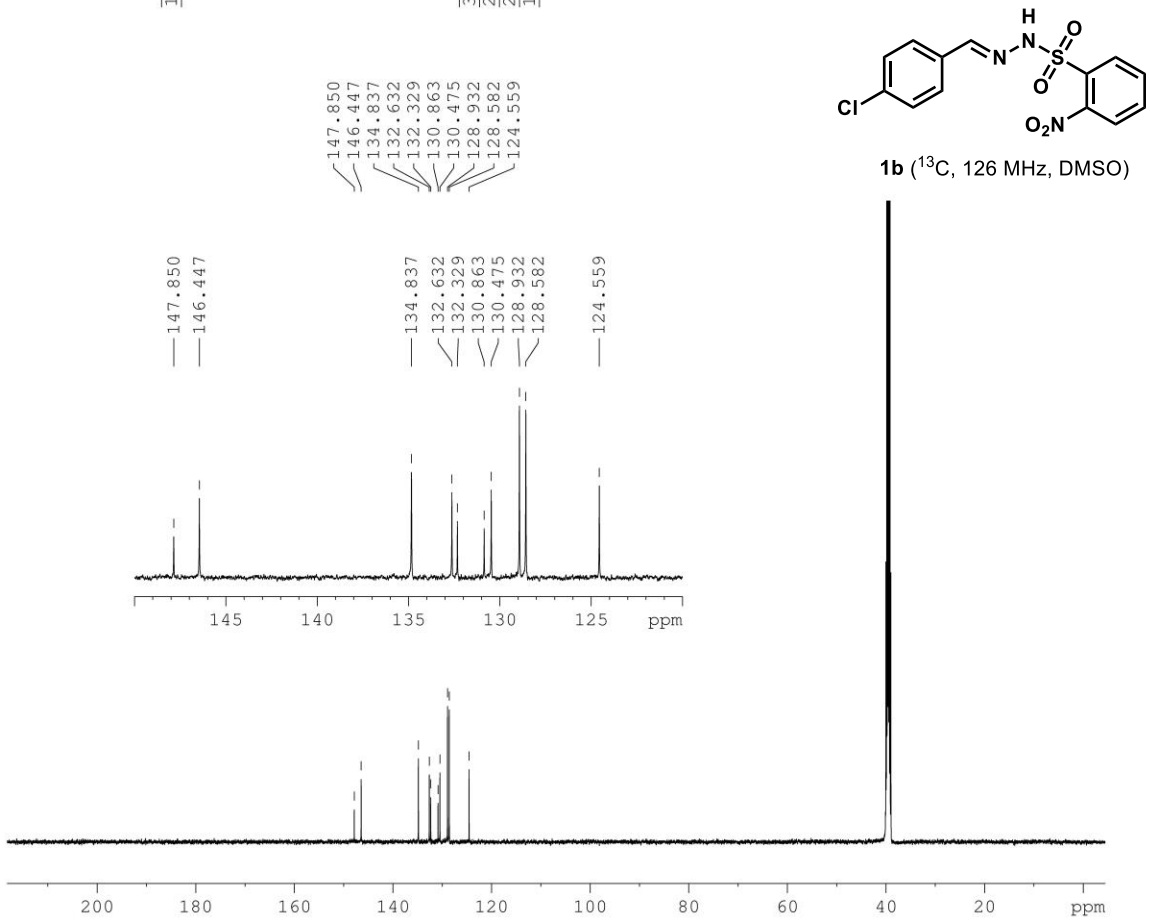
1a (^{1}H, 400 MHz, DMSO)



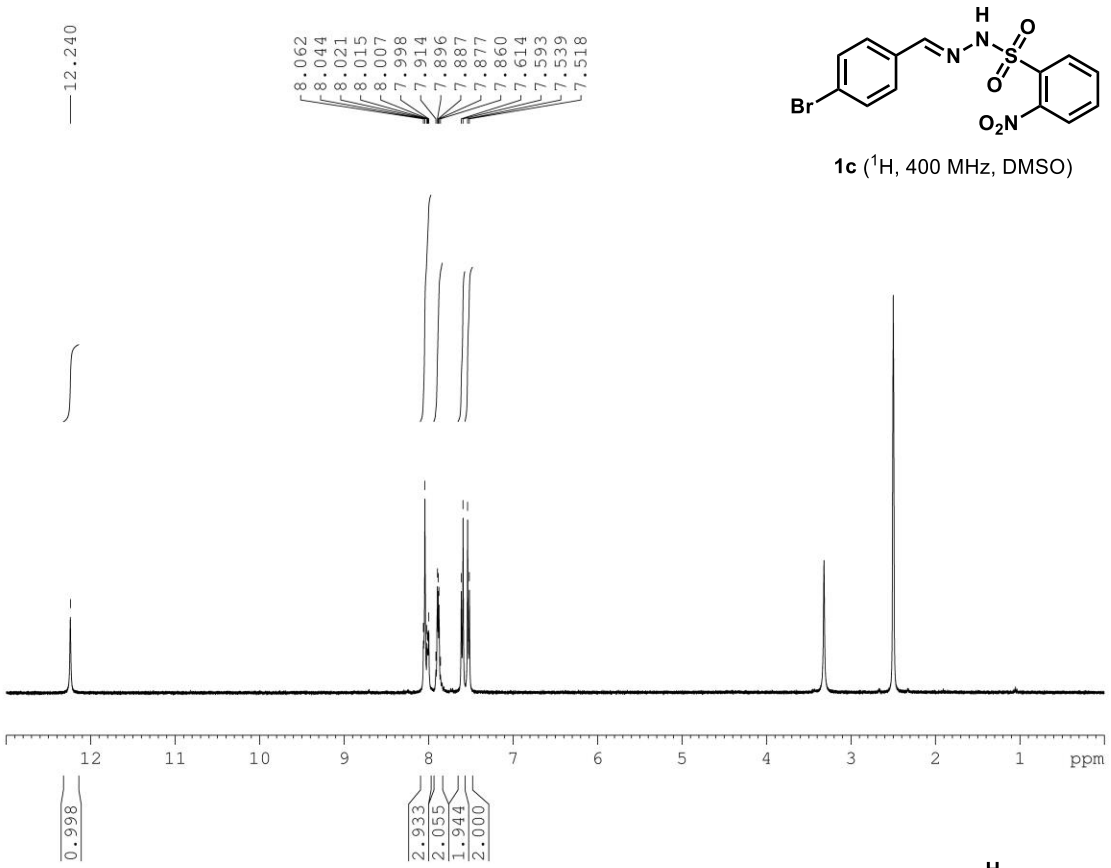
1a (^{13}C, 126 MHz, DMSO)



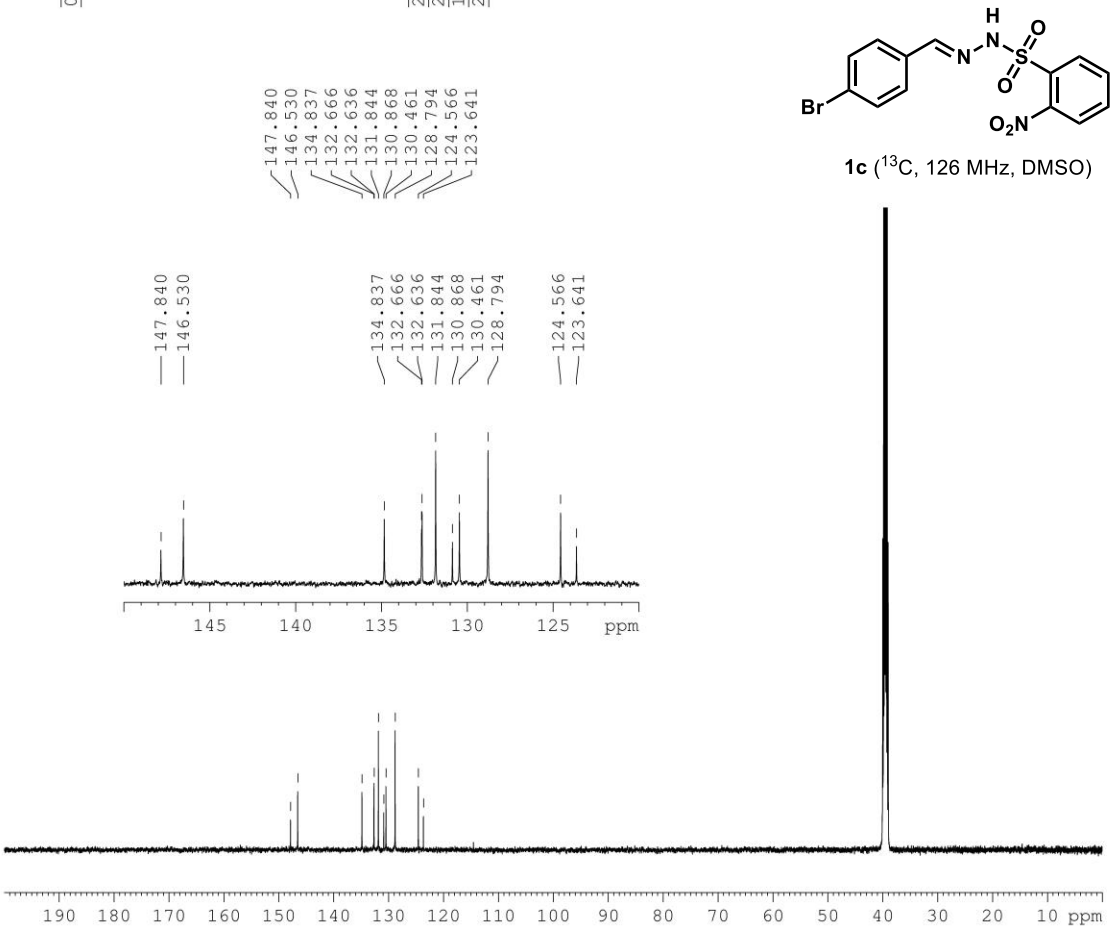
1b (^{1}H, 400 MHz, DMSO)



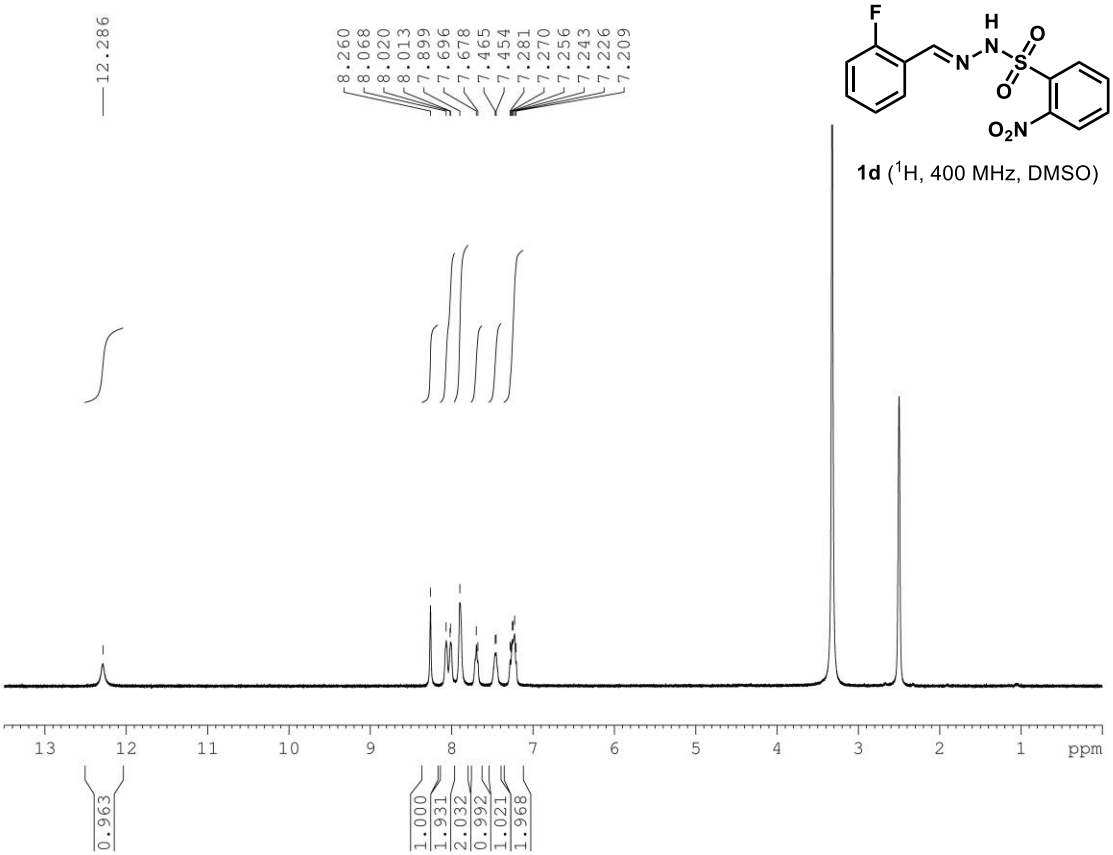
1b (^{13}C, 126 MHz, DMSO)

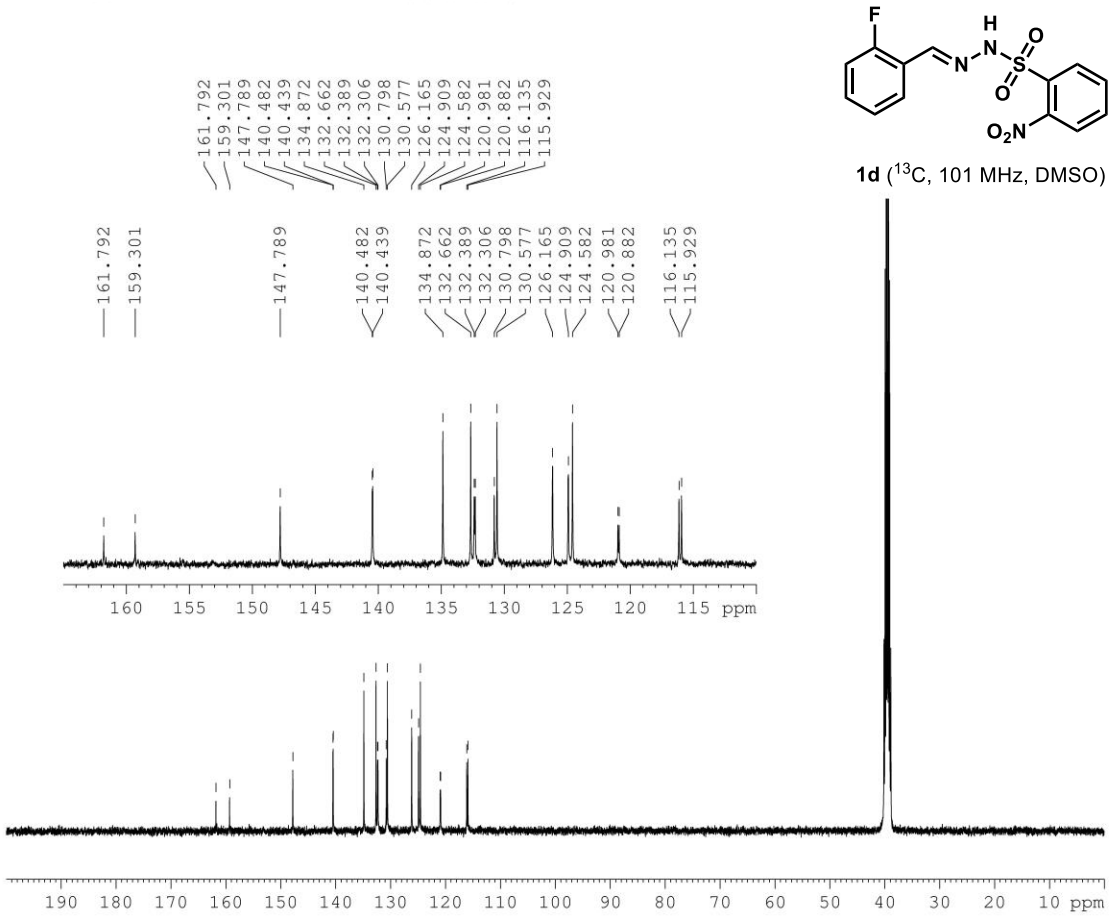


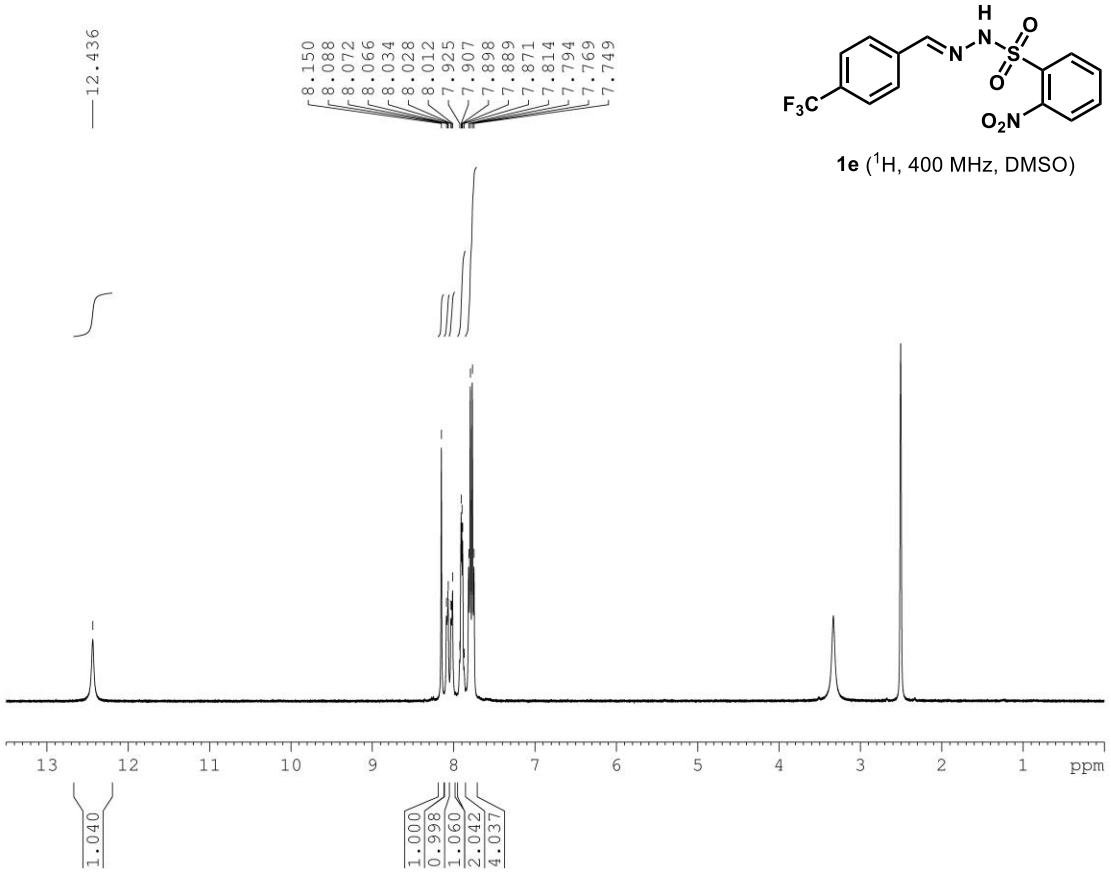
1c (^{1}H, 400 MHz, DMSO)



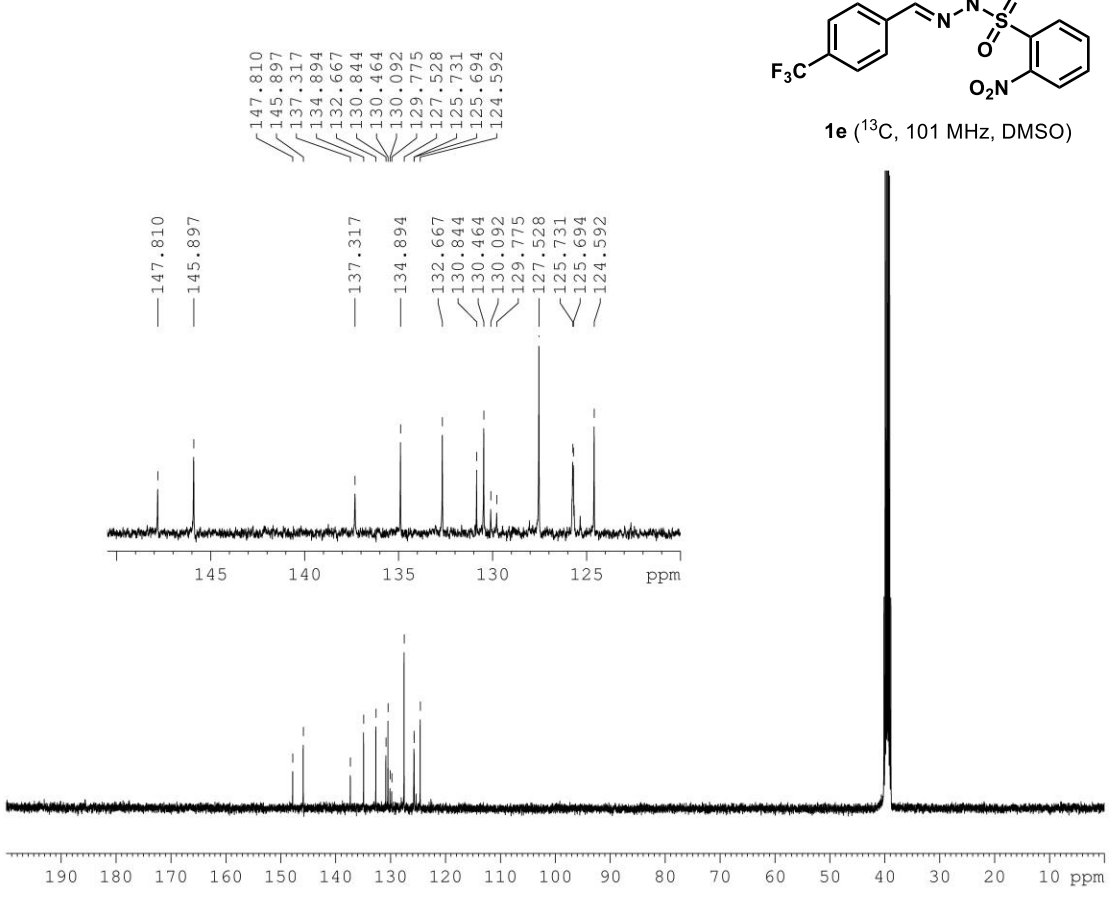
1c (^{13}C, 126 MHz, DMSO)


12.286
8.260
8.068
8.020
8.013
7.899
7.696
7.678
7.465
7.454
7.281
7.270
7.256
7.243
7.226
7.209
F
H
N
N
O
S
O
O2N
1d (1H, 400 MHz, DMSO)
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.963
1.000
1.931
2.032
0.992
1.021
1.968

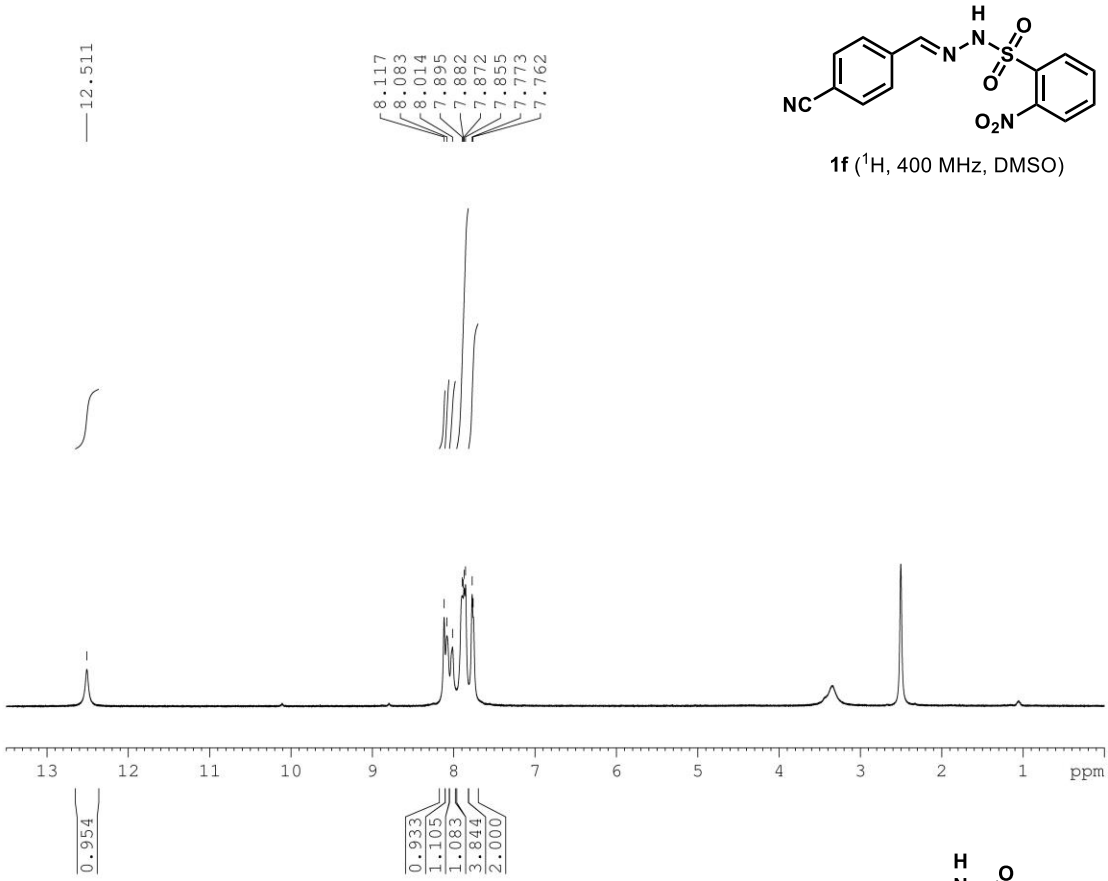

161.792
159.301
147.789
140.482
140.439
134.872
132.662
132.389
132.306
130.798
130.577
126.165
124.909
124.582
120.981
120.882
116.135
115.929
F
H
N
N
O
S
O
O2N
1d (13C, 101 MHz, DMSO)
160 155 150 145 140 135 130 125 120 115 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



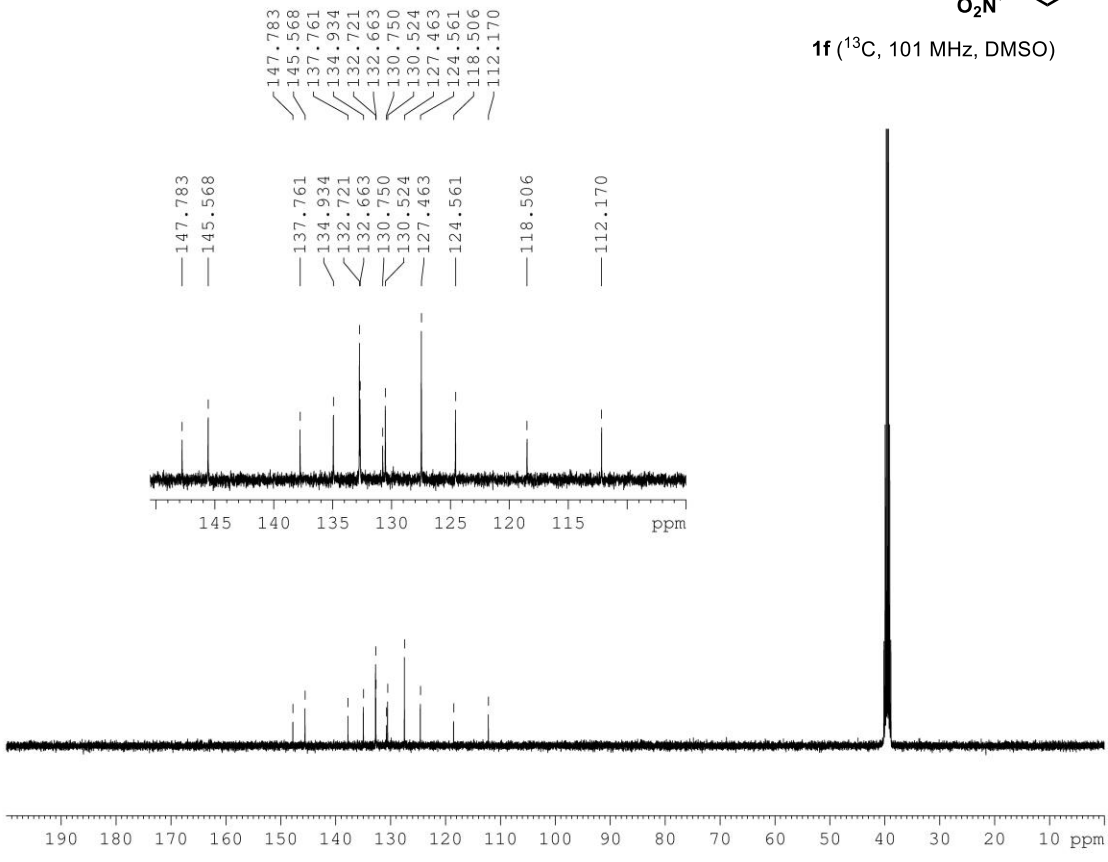
1e (^{1}H, 400 MHz, DMSO)

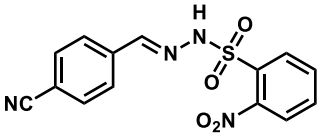


1e (^{13}C, 101 MHz, DMSO)

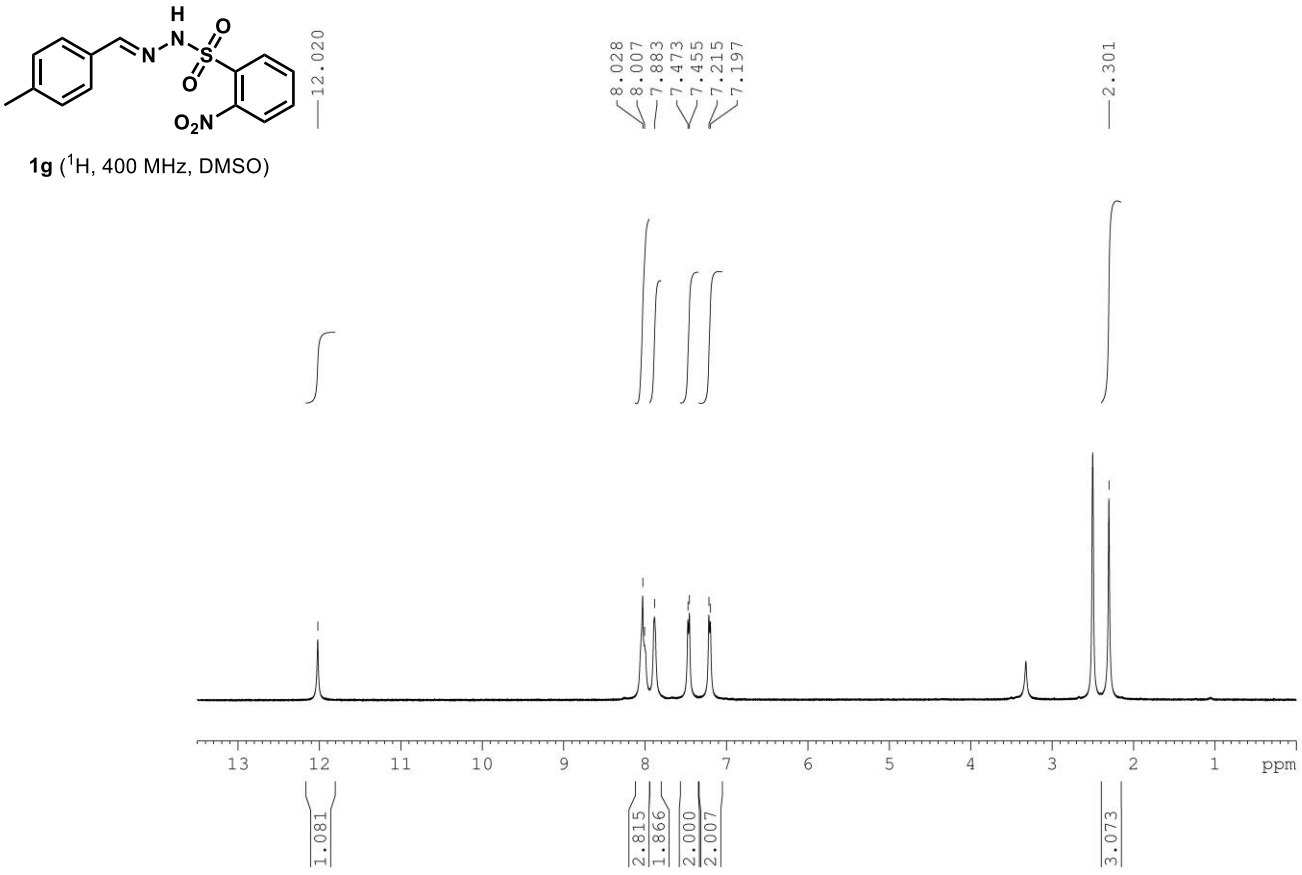


1f (^{1}H, 400 MHz, DMSO)

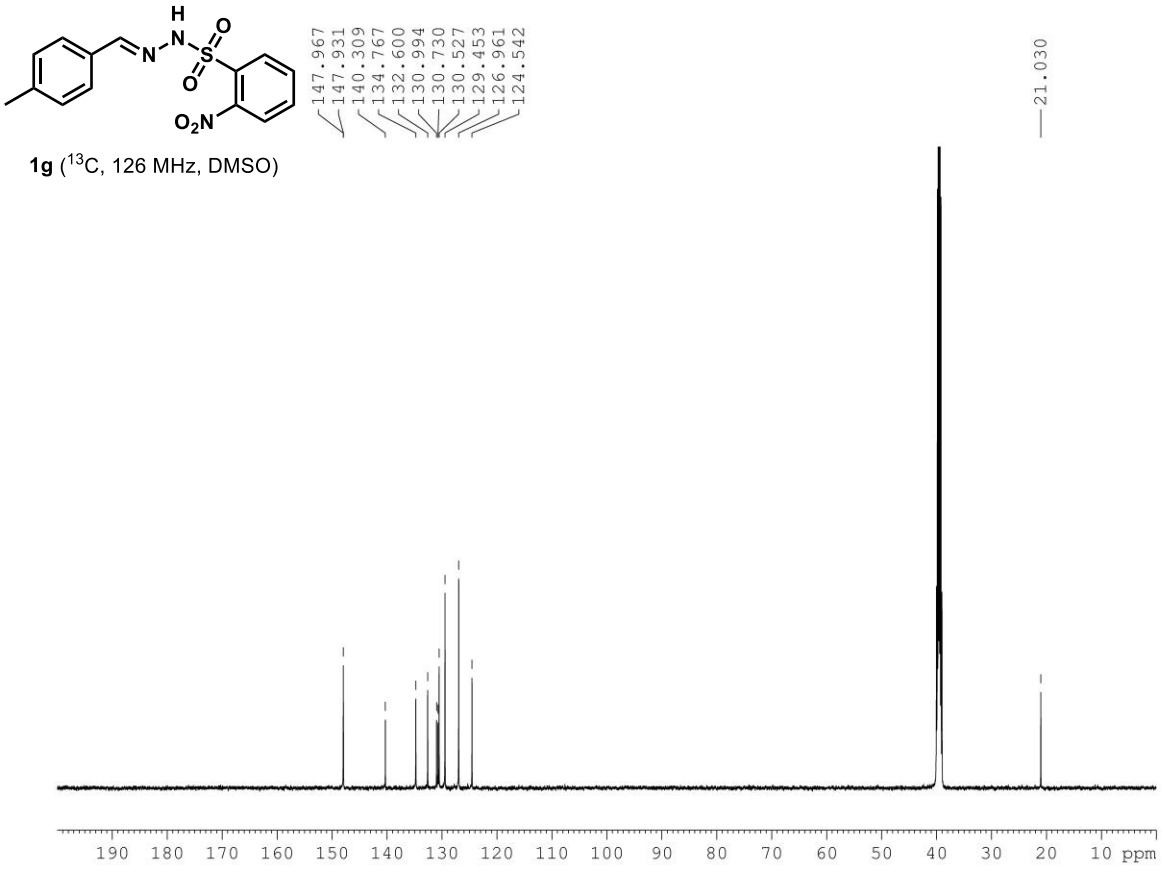




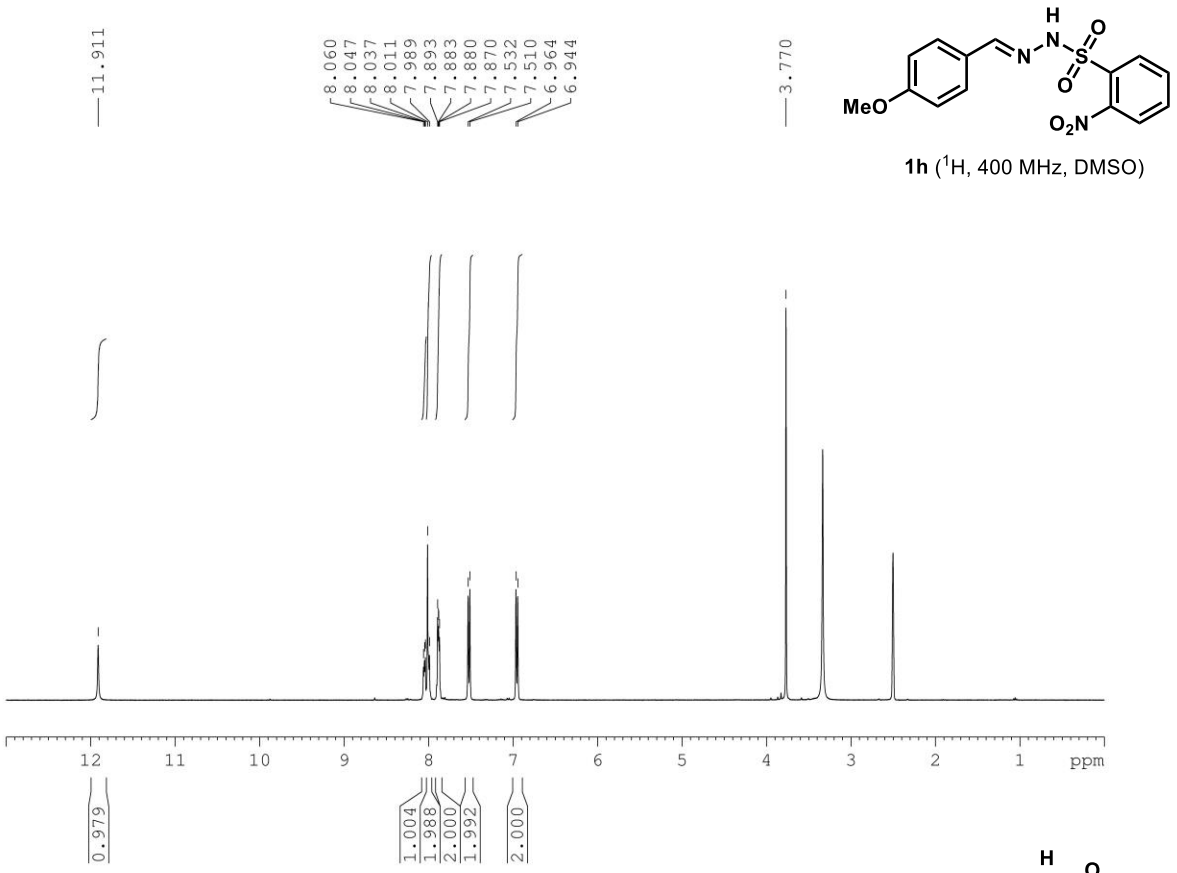
1f (^{13}C, 101 MHz, DMSO)



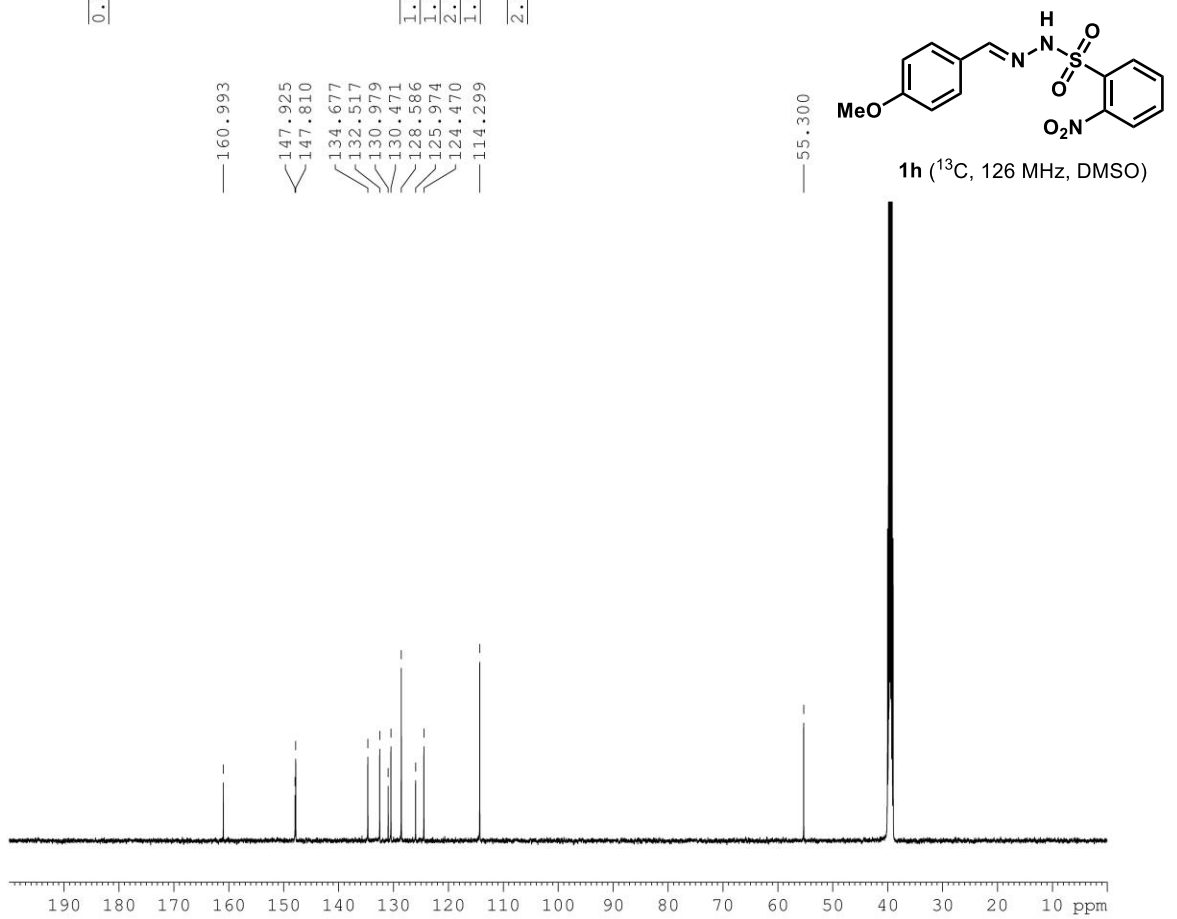
1g (^{1}H, 400 MHz, DMSO)



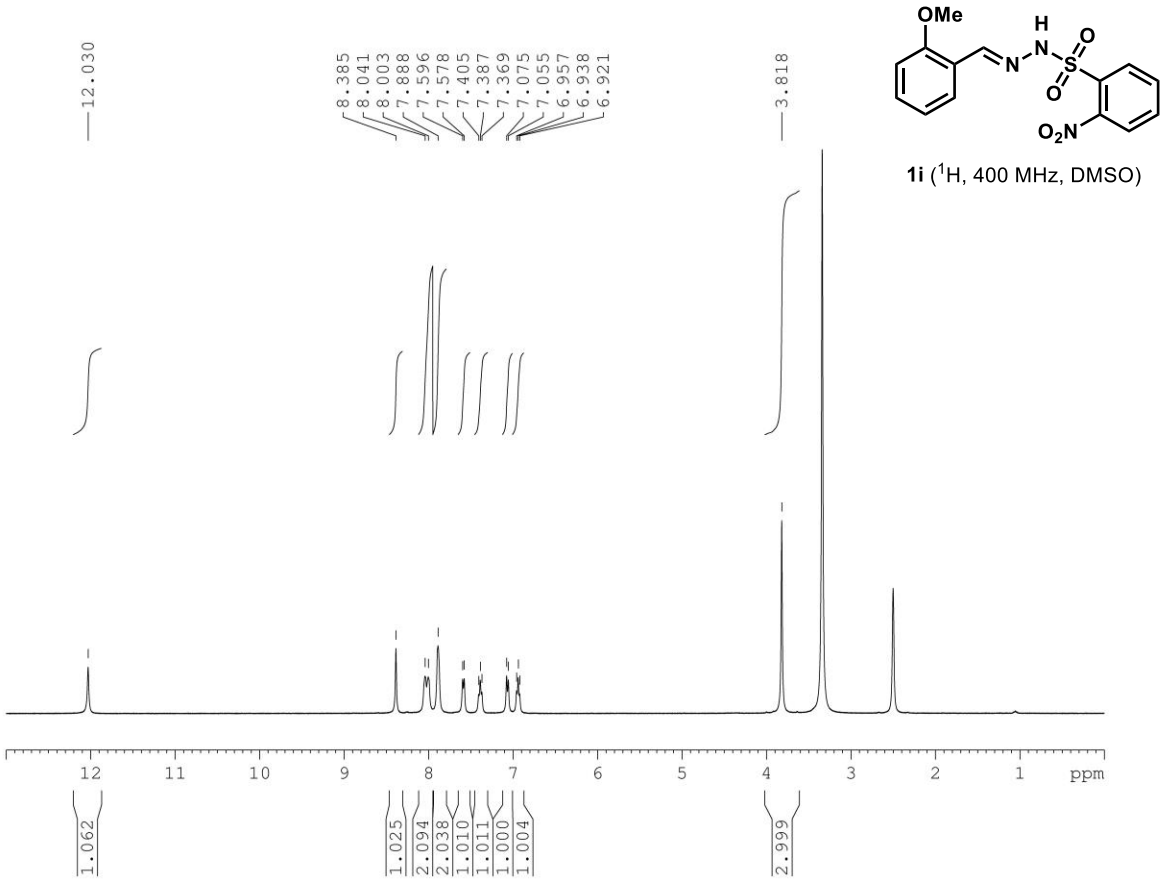
1g (^{13}C, 126 MHz, DMSO)



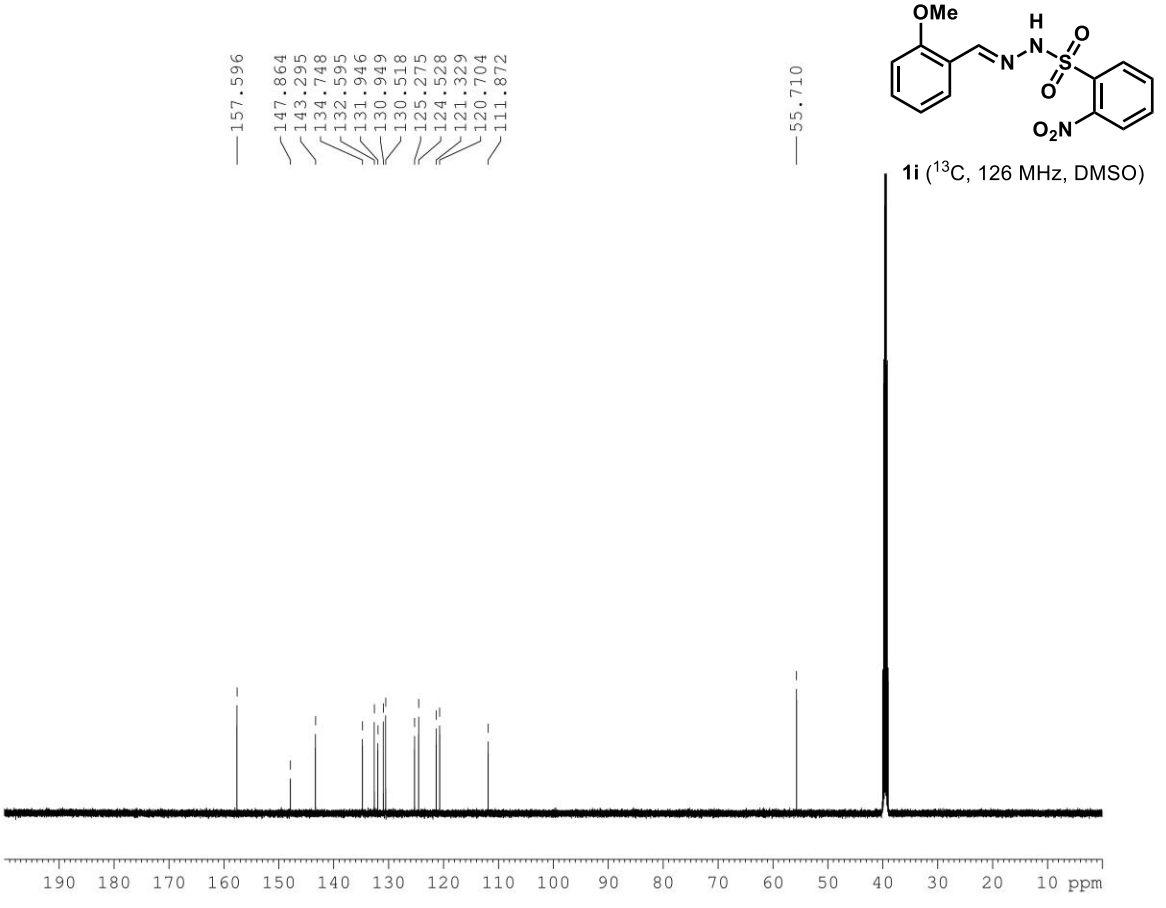
1h (^{1}H, 400 MHz, DMSO)



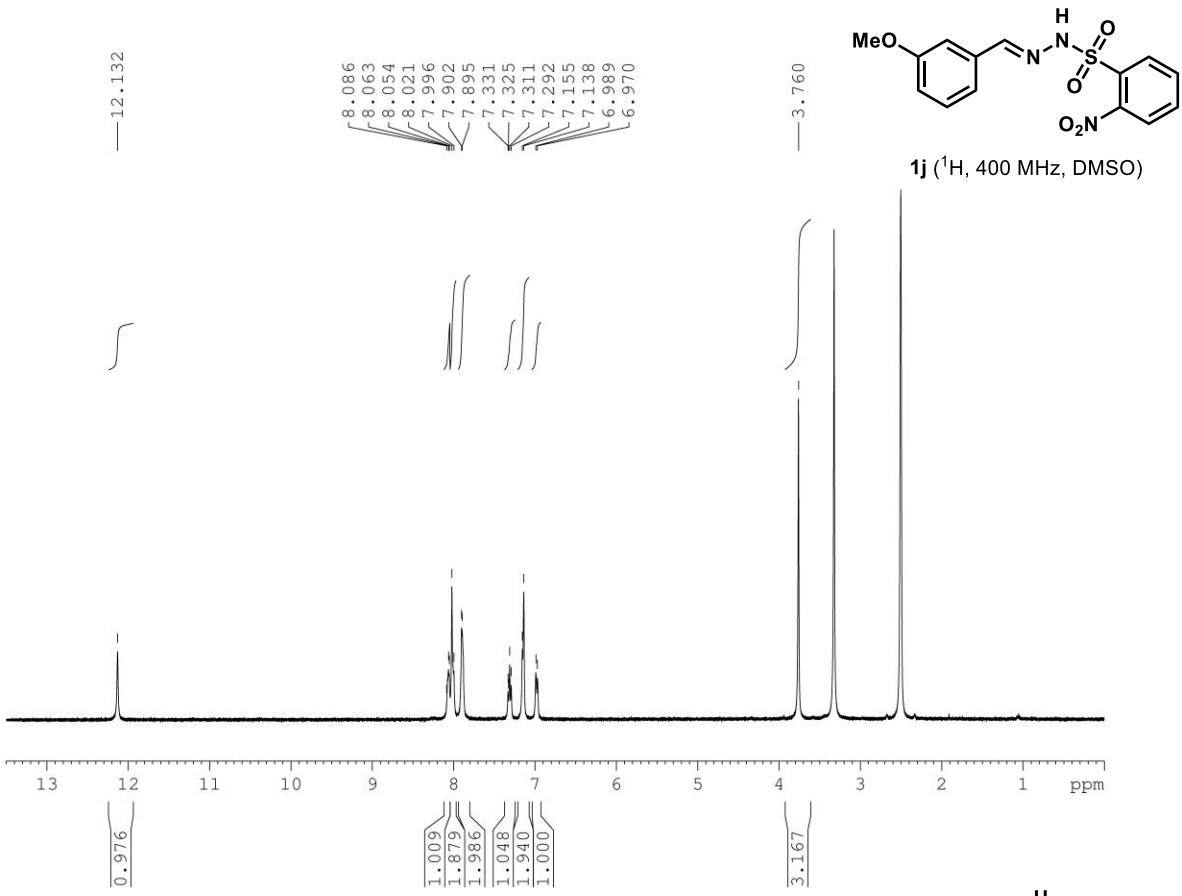
1h (^{13}C, 126 MHz, DMSO)



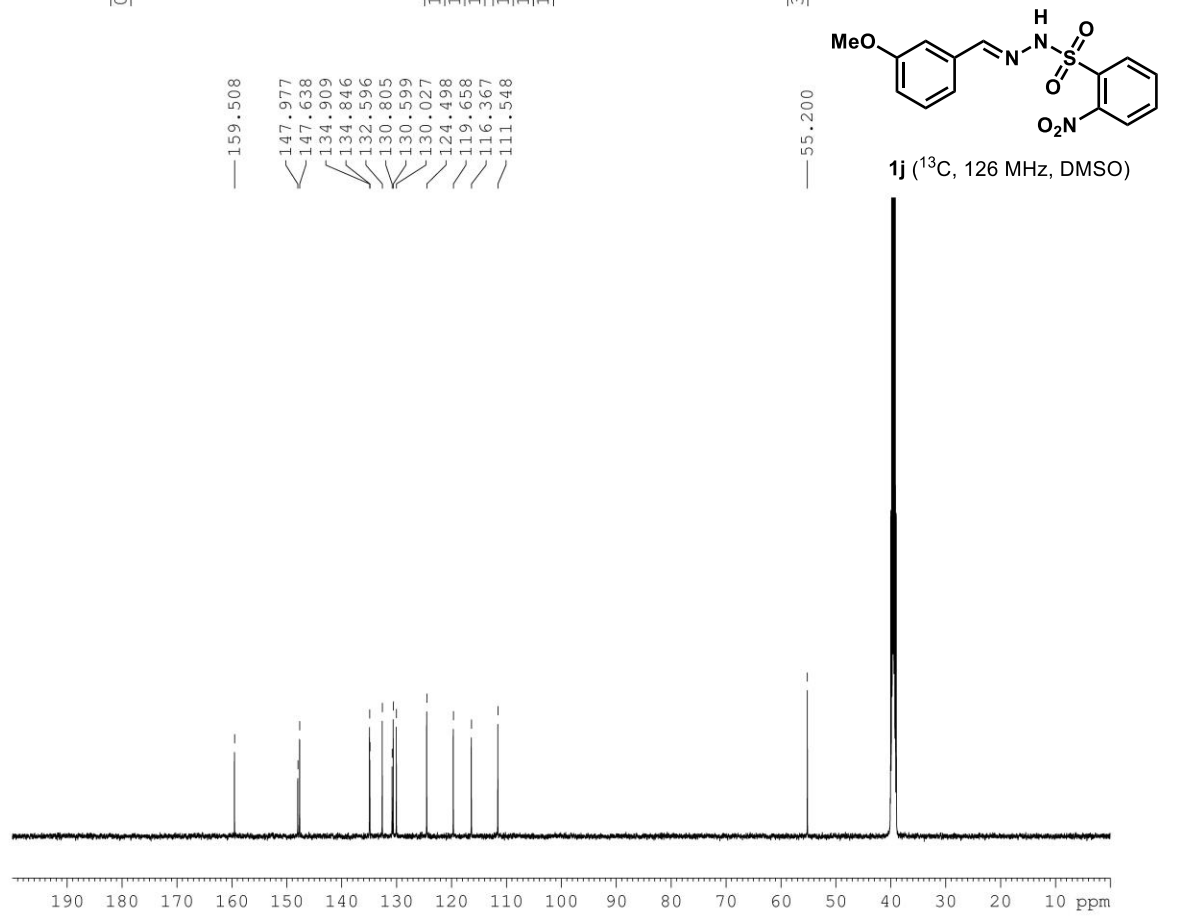
1i (^{1}H, 400 MHz, DMSO)



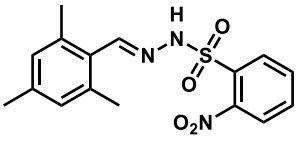
1i (^{13}C, 126 MHz, DMSO)



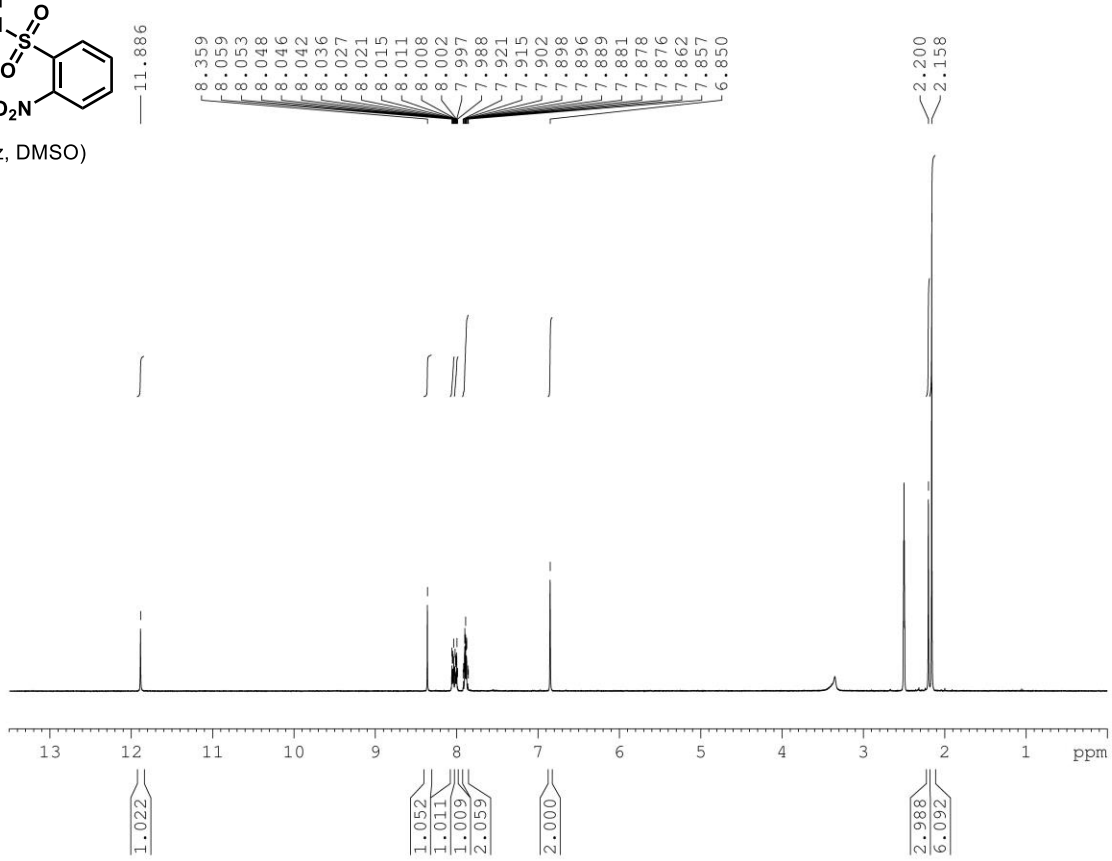
1j (^{1}H, 400 MHz, DMSO)

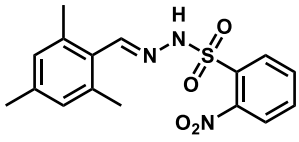


1j (^{13}C, 126 MHz, DMSO)

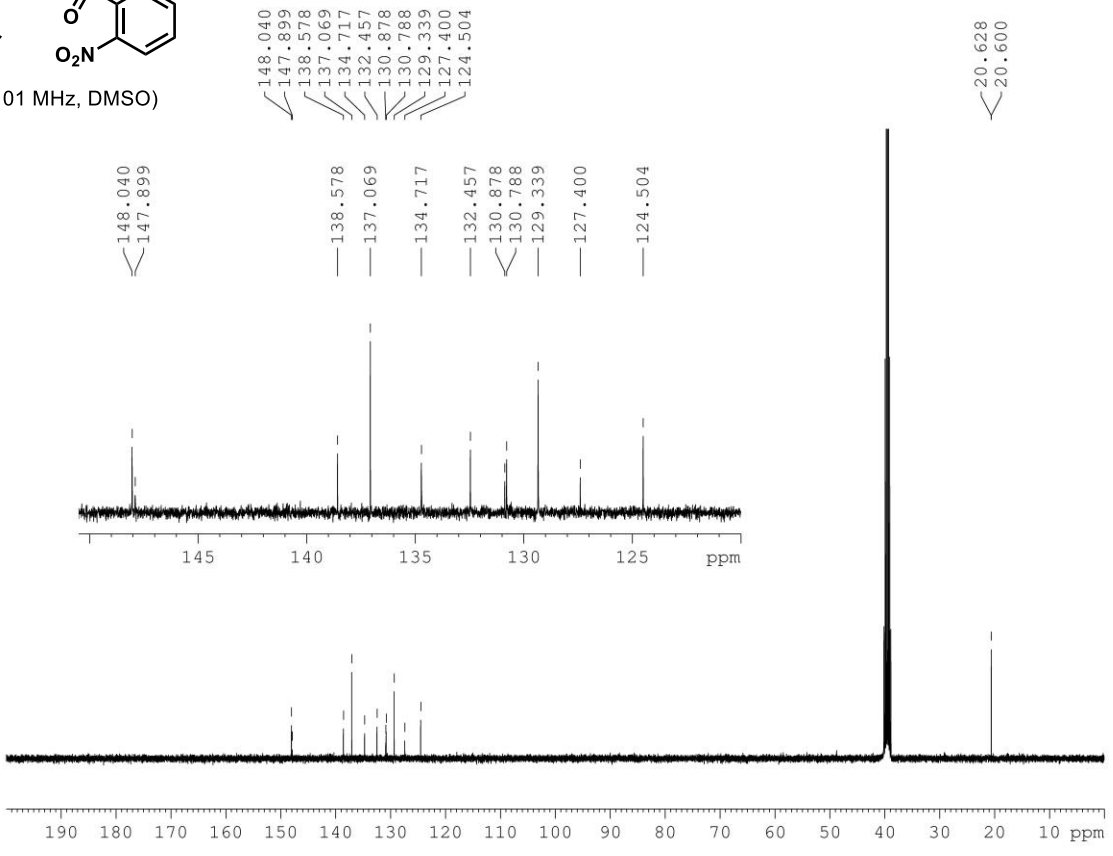


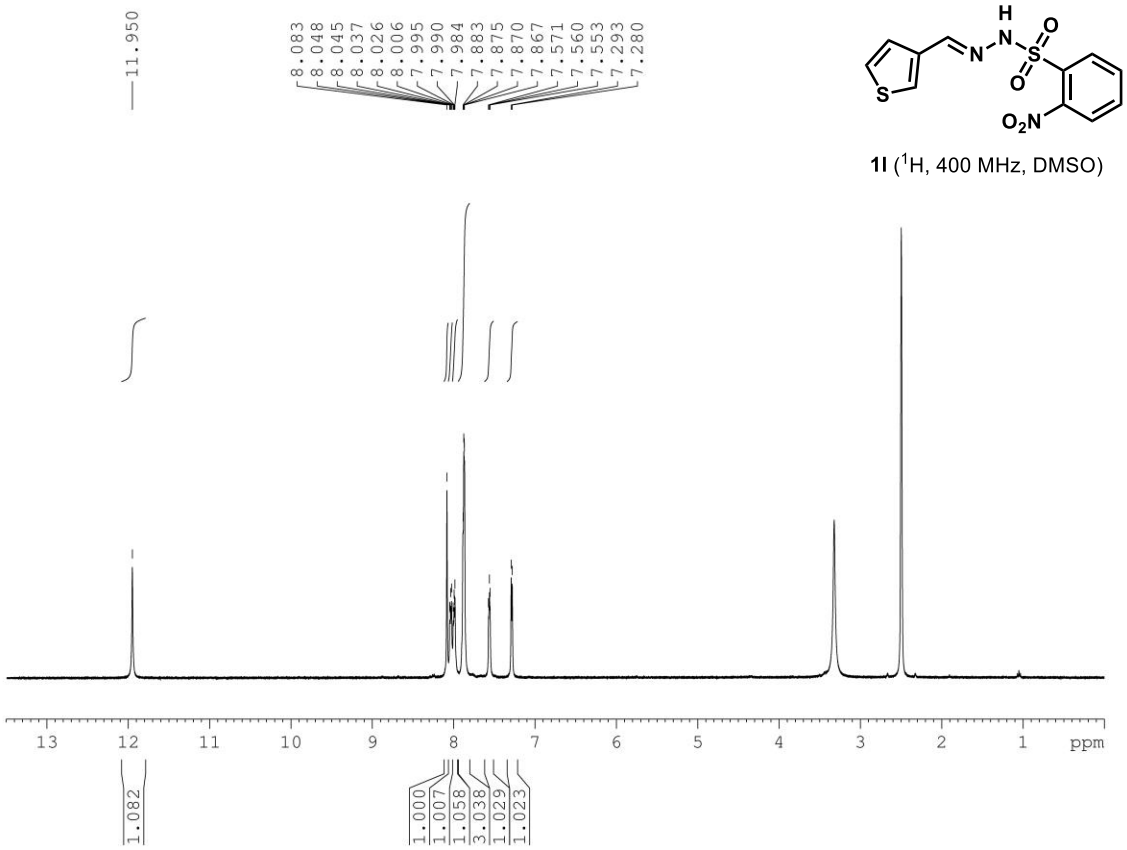
1k (^{1}H, 400 MHz, DMSO)



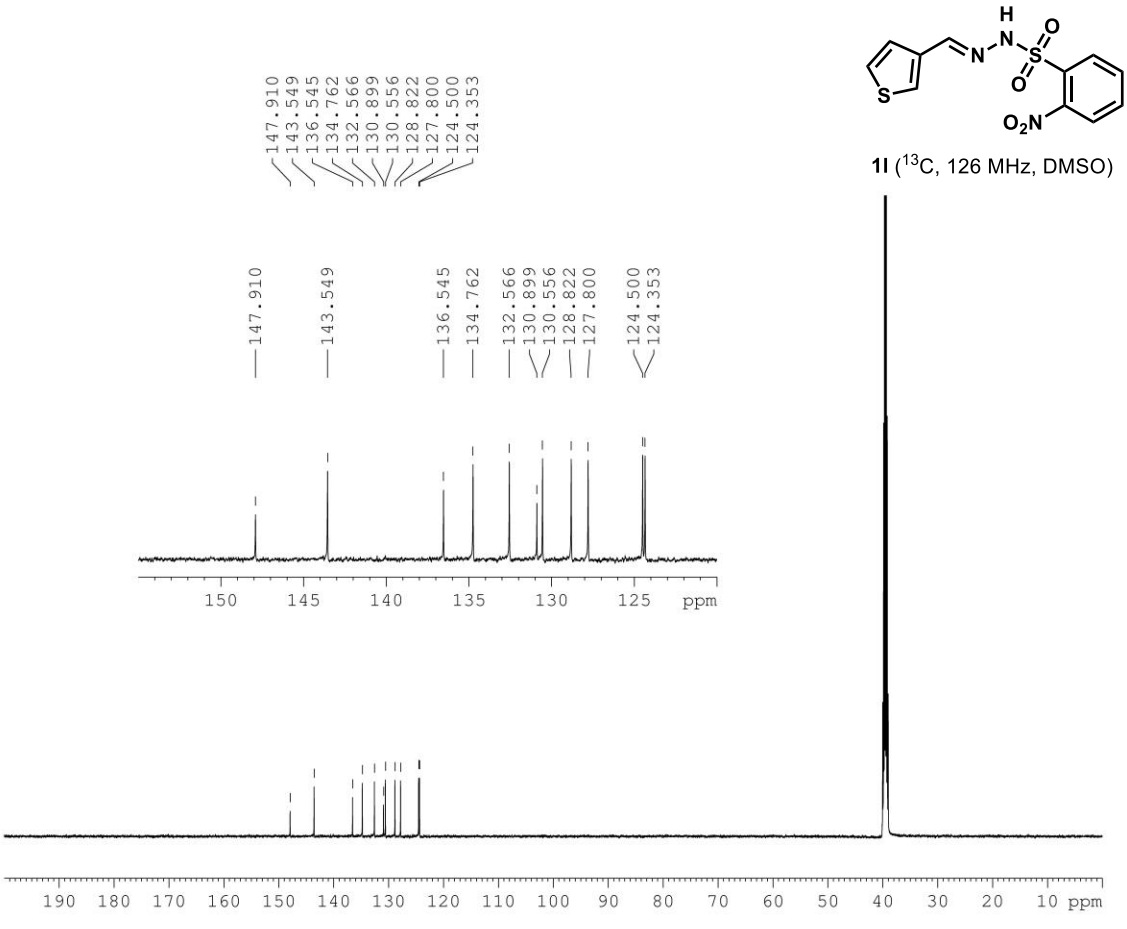


1k (^{13}C, 101 MHz, DMSO)

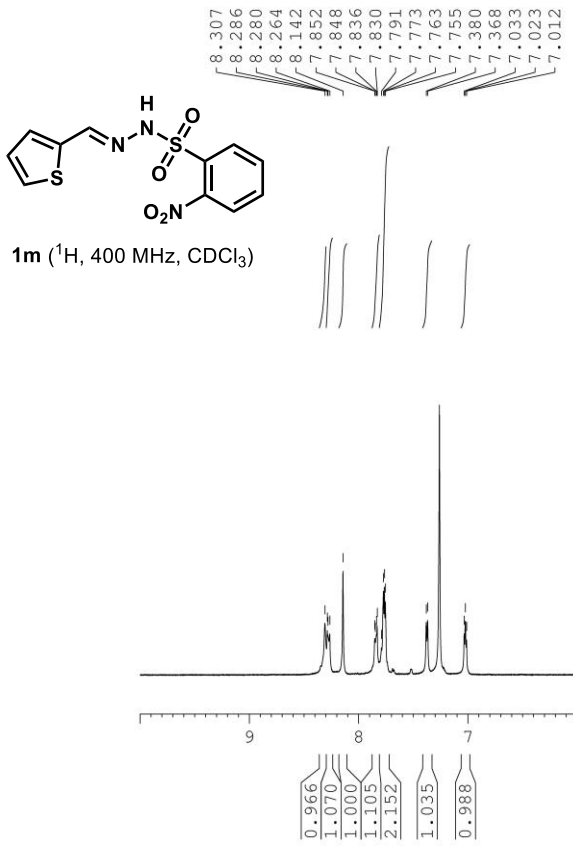




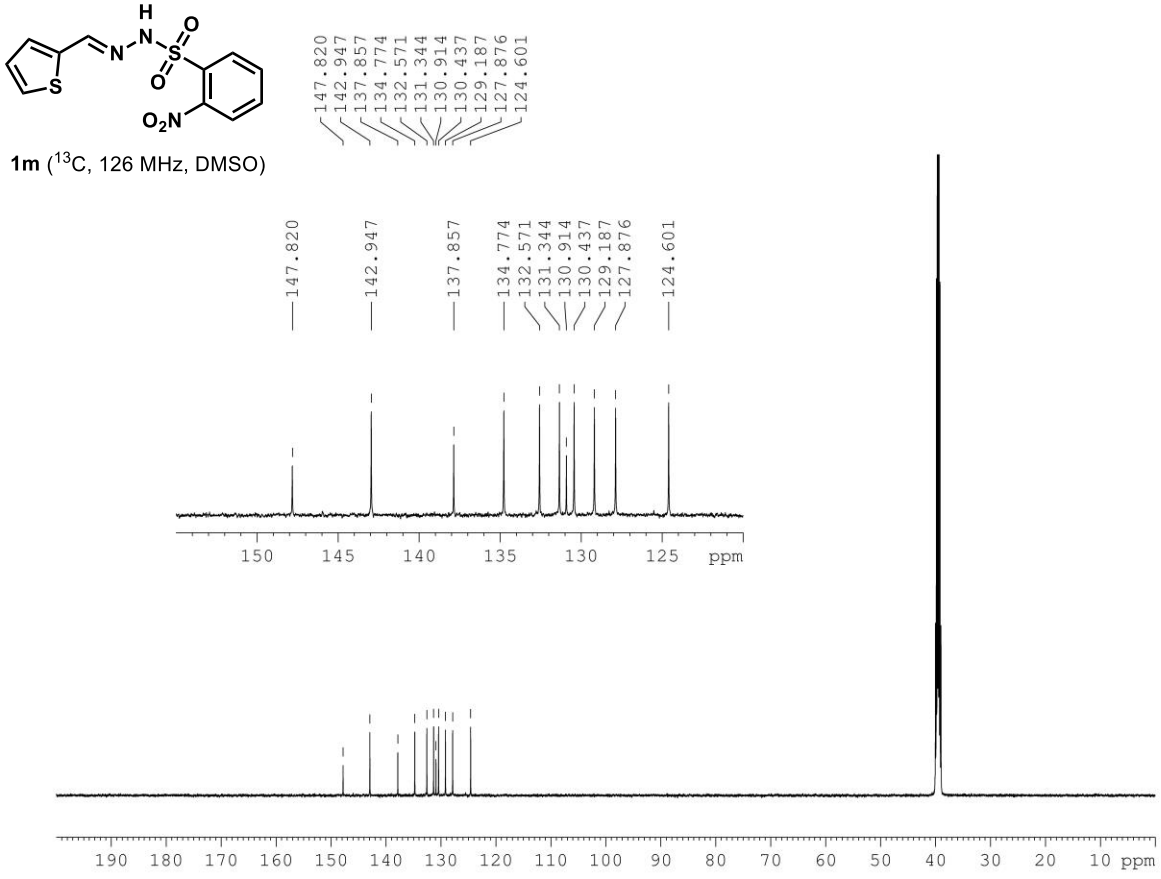
1l (^{1}H, 400 MHz, DMSO)



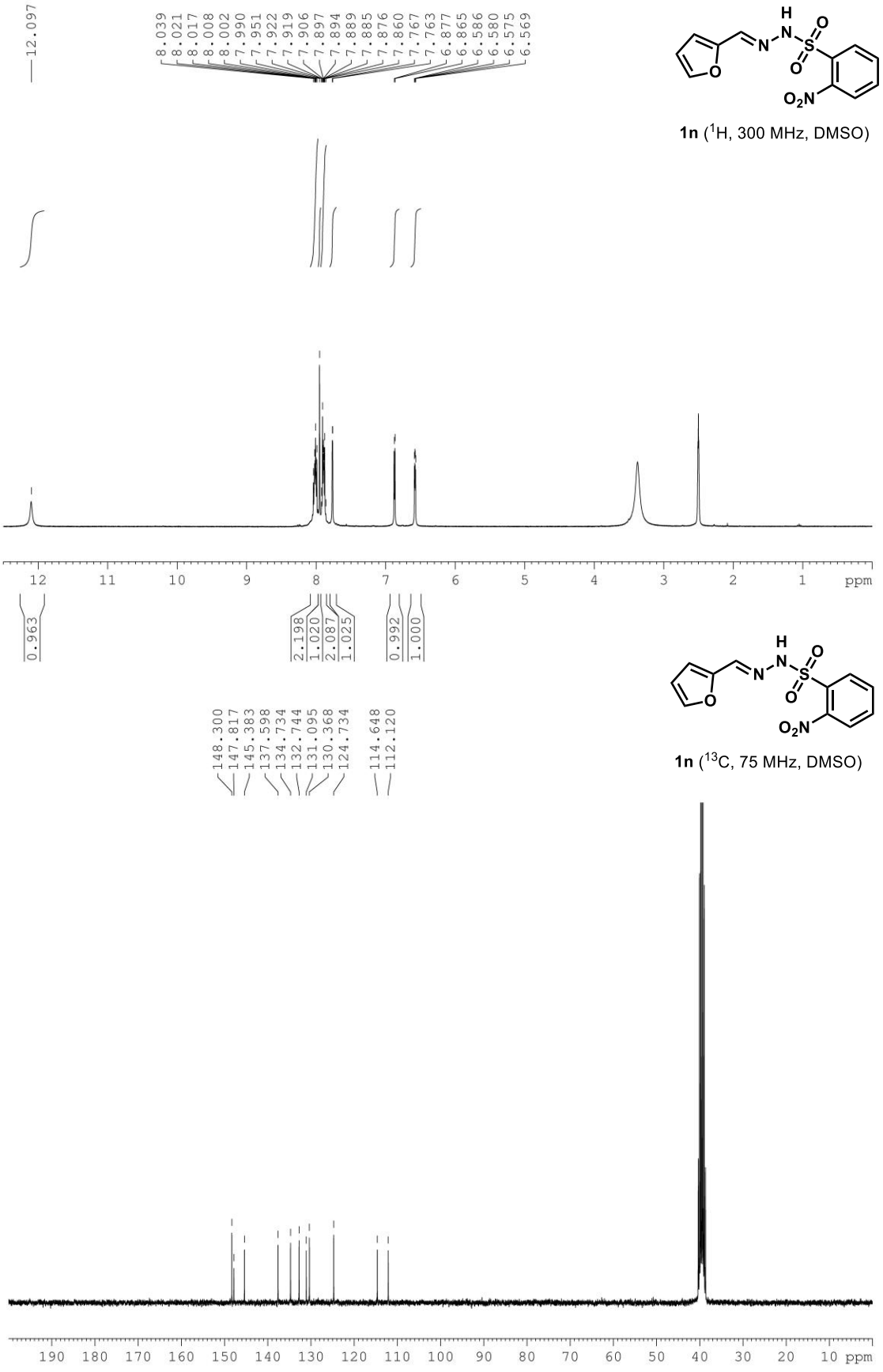
1l (^{13}C, 126 MHz, DMSO)



1m (^{1}H, 400 MHz, $CDCl_3$)

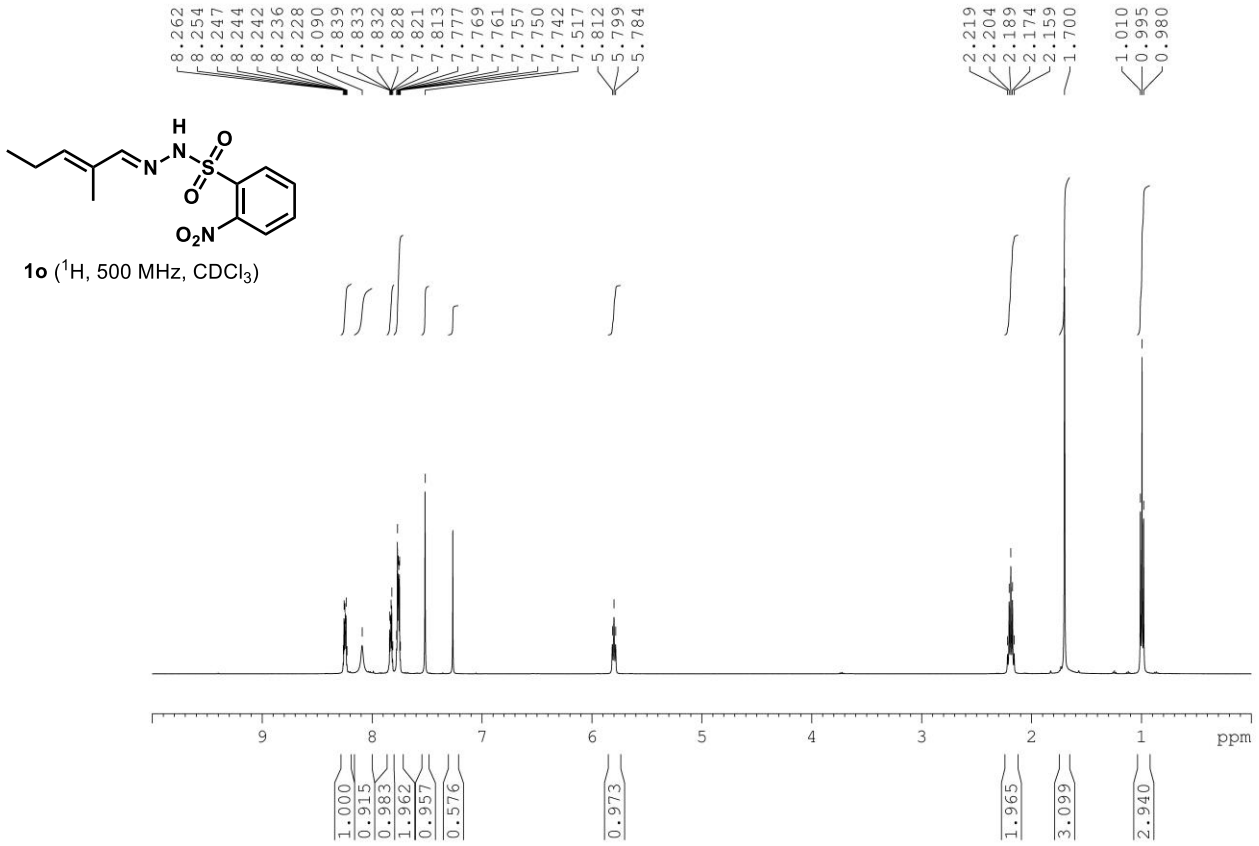


1m (^{13}C, 126 MHz, DMSO)

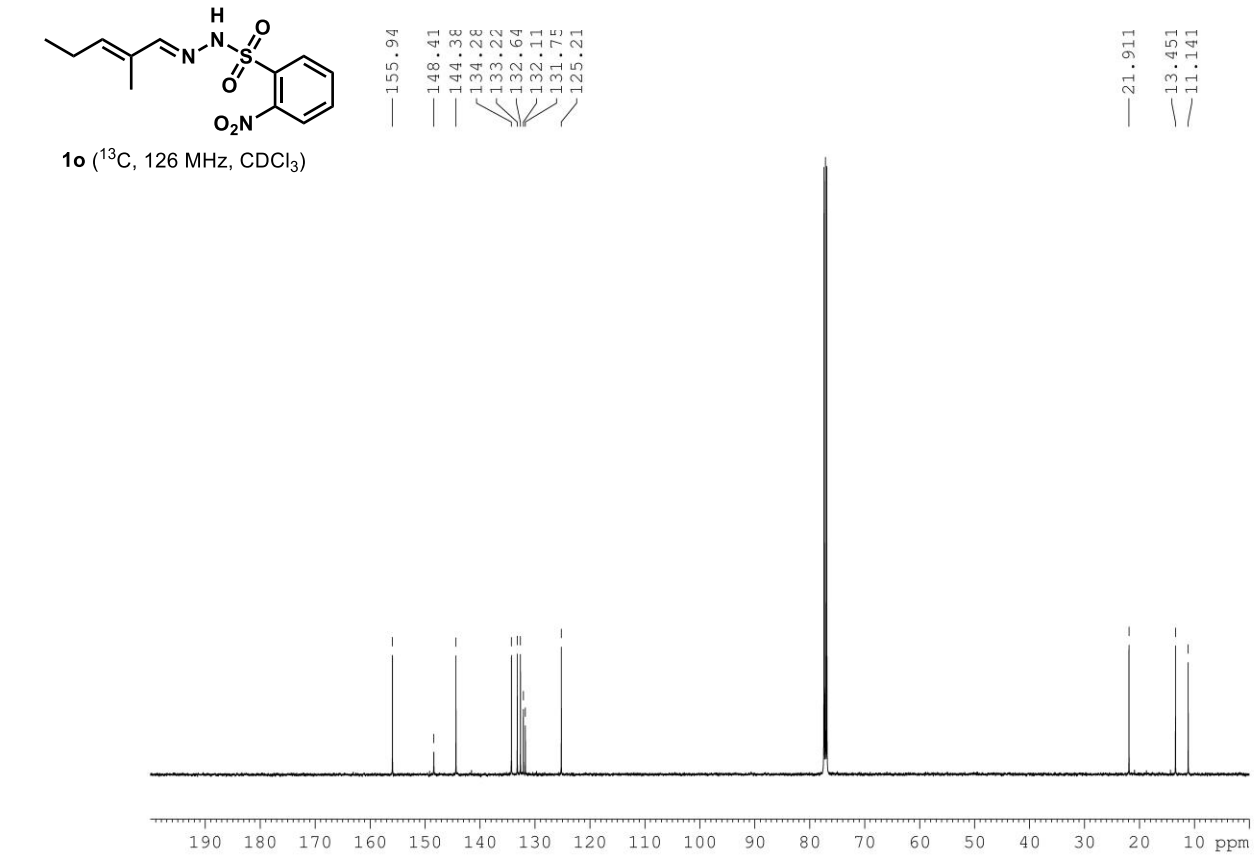


1n (^{1}H, 300 MHz, DMSO)

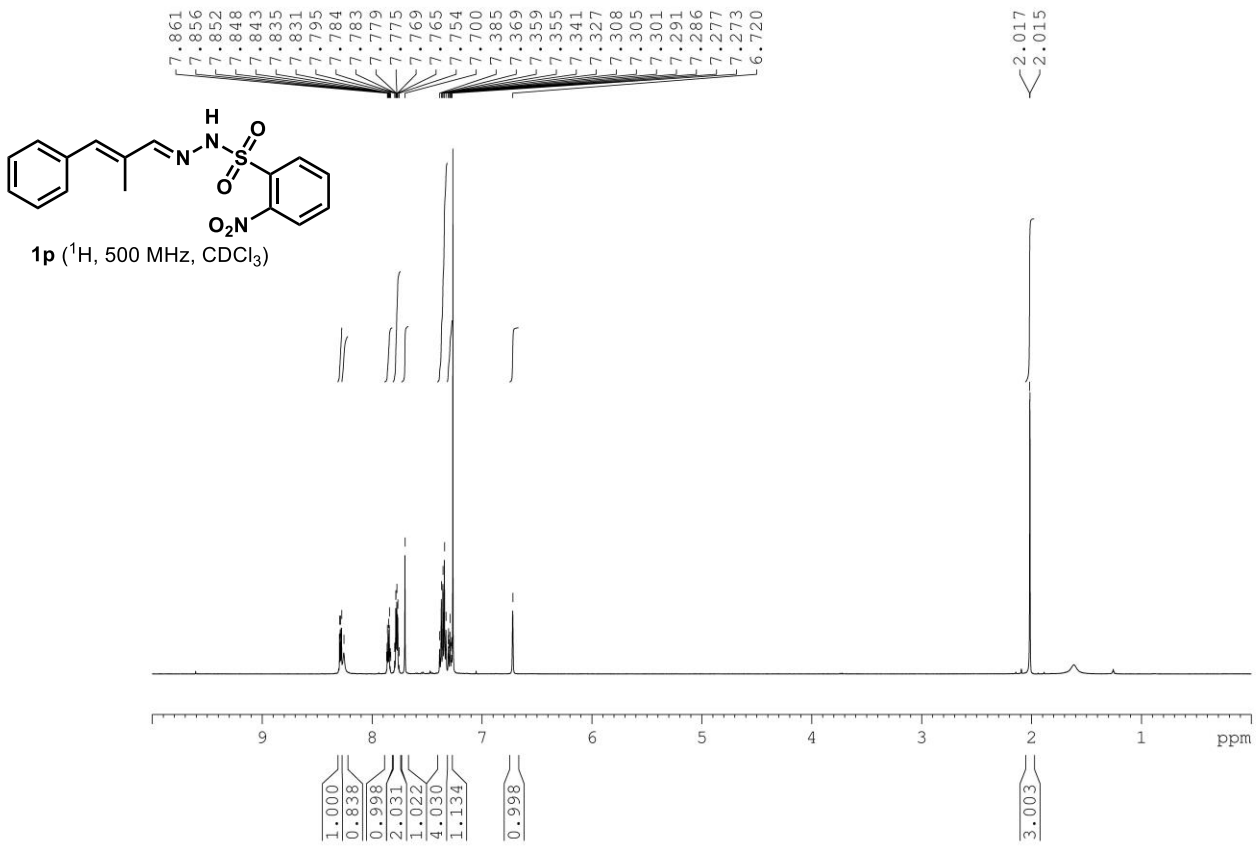
1n (^{13}C, 75 MHz, DMSO)



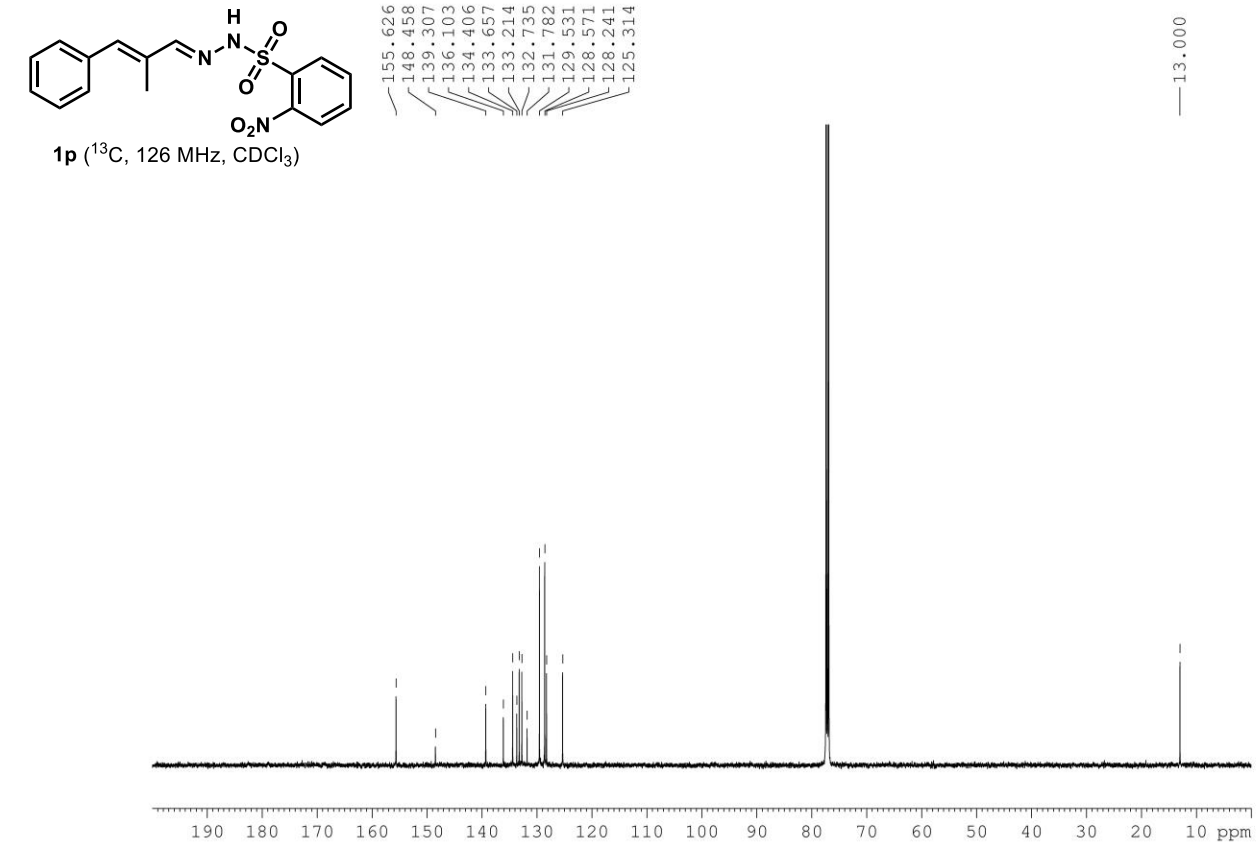
1o (^{1}H, 500 MHz, $CDCl_3$)



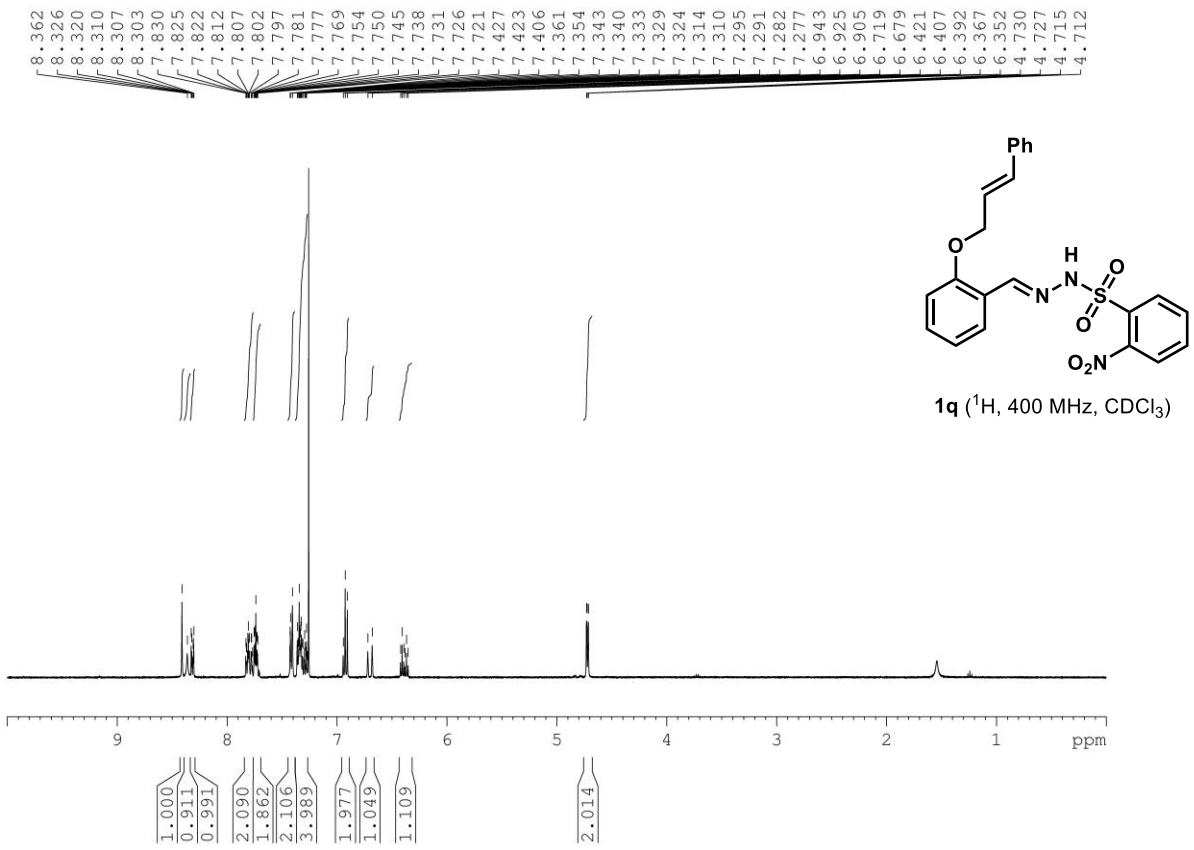
1o (^{13}C, 126 MHz, $CDCl_3$)



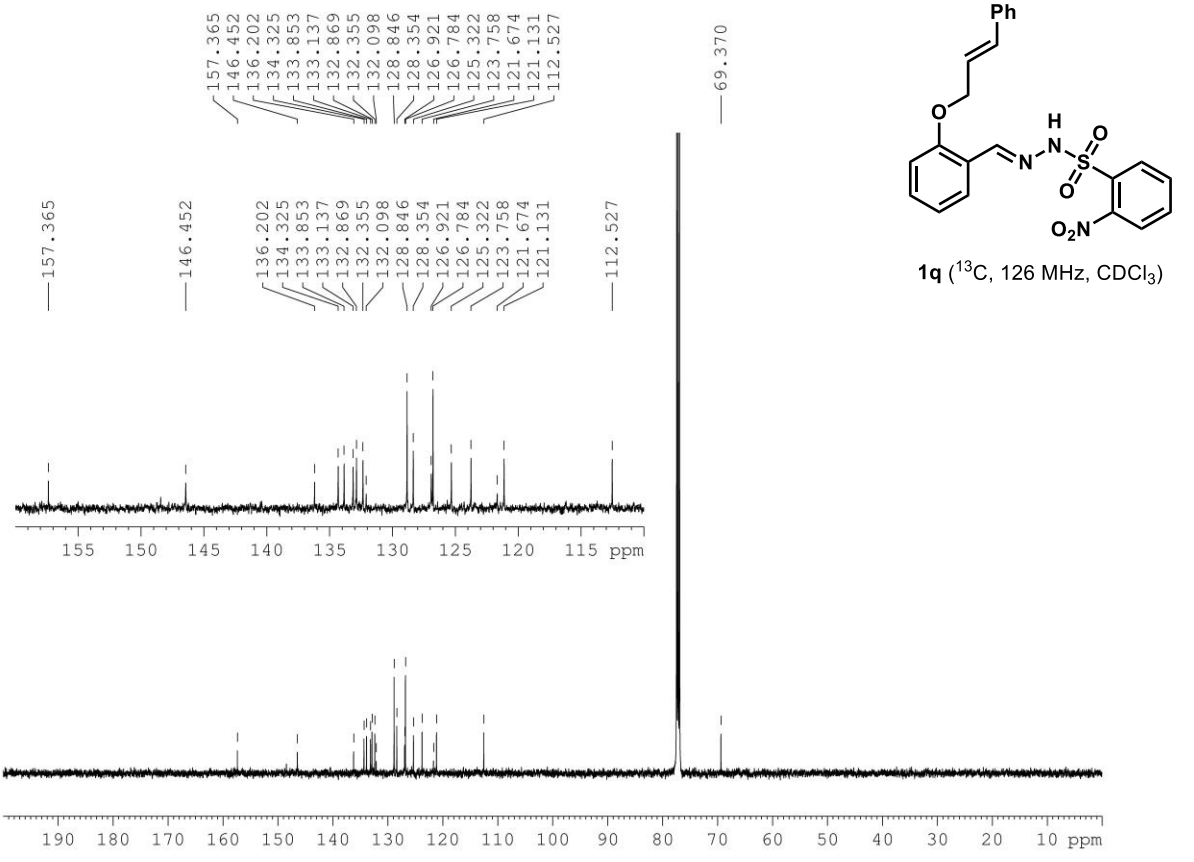
1p (^{1}H, 500 MHz, $CDCl_3$)



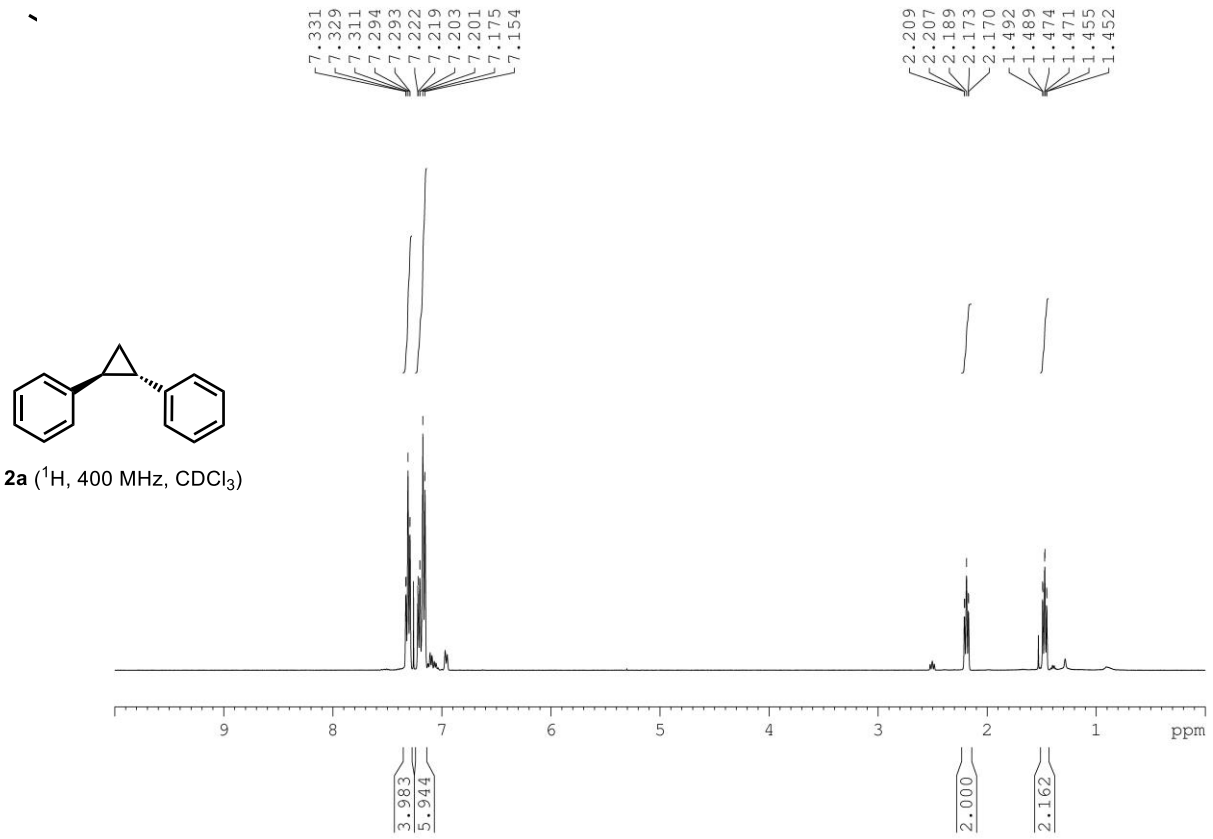
1p (^{13}C, 126 MHz, $CDCl_3$)



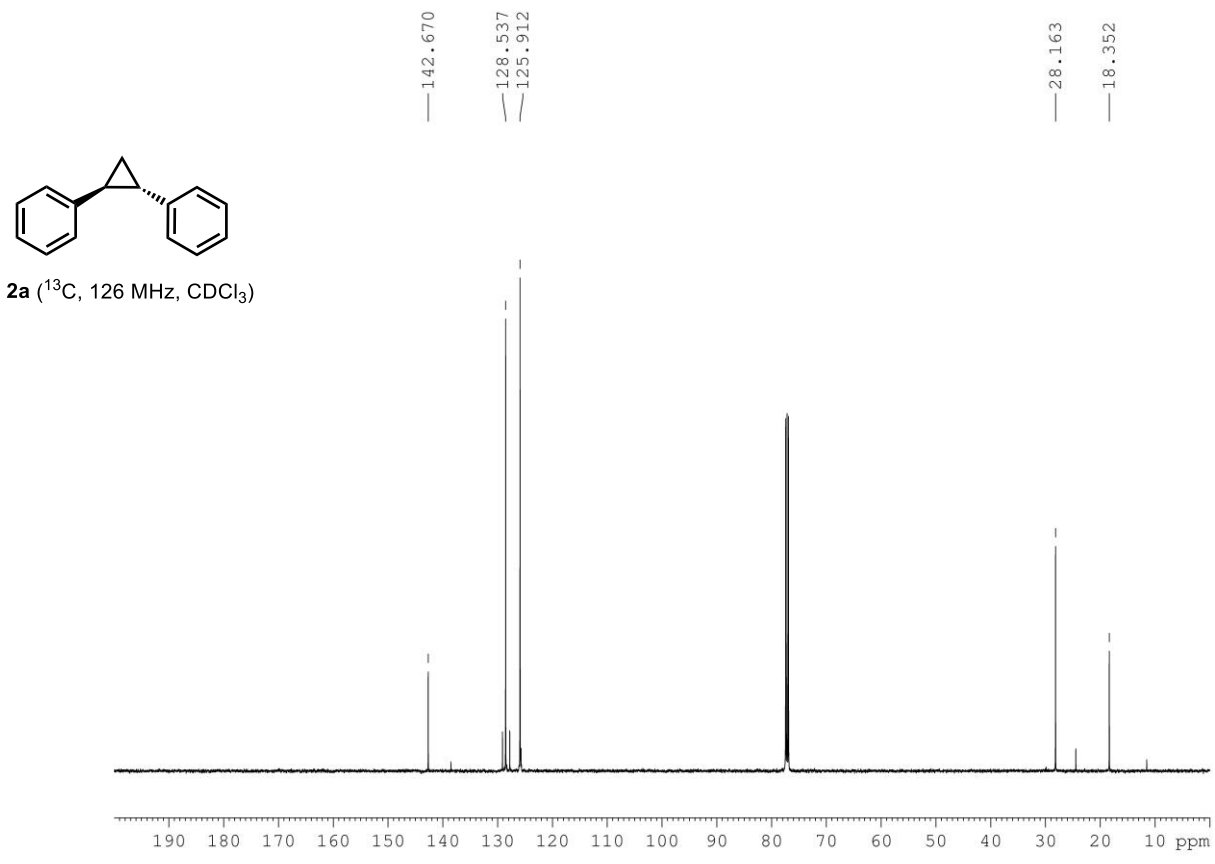
1q (^{1}H, 400 MHz, $CDCl_3$)



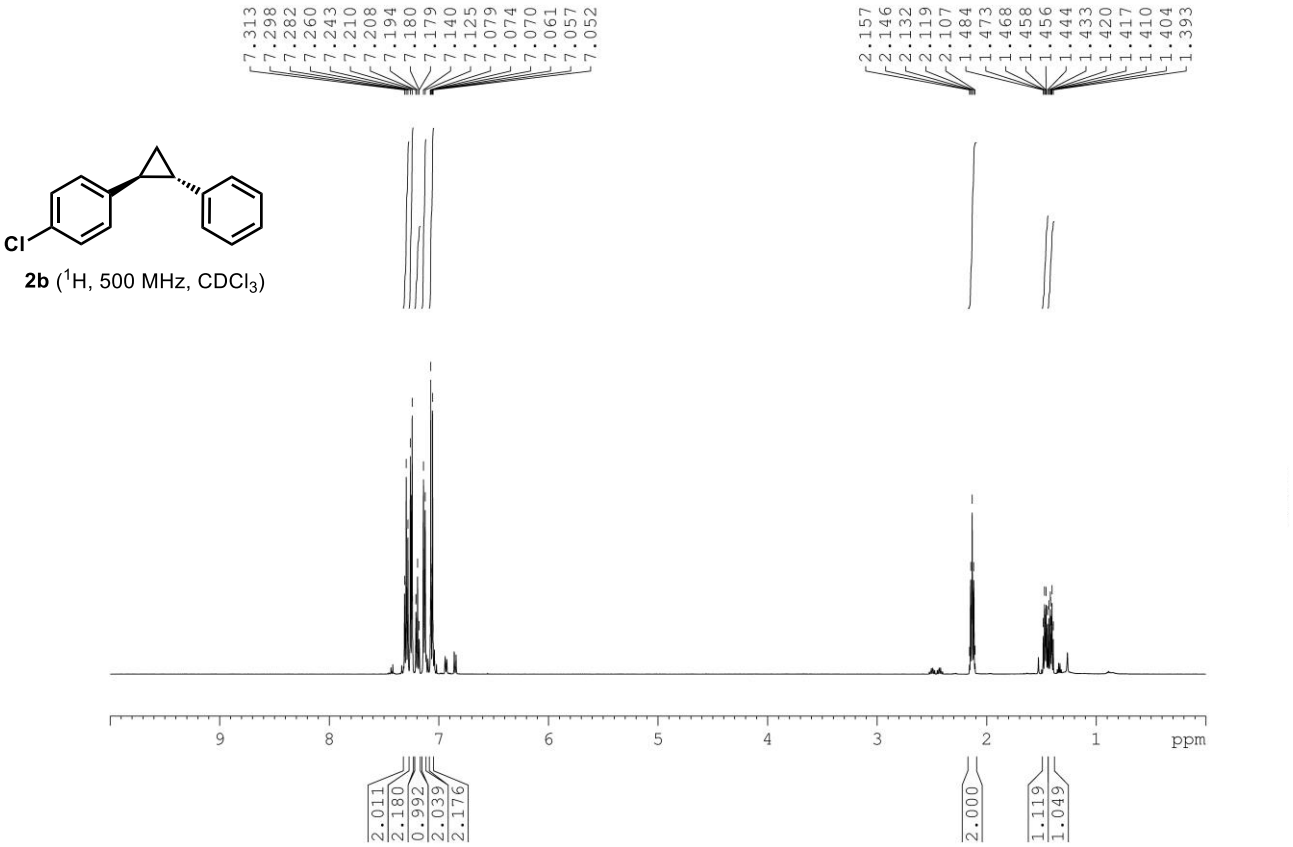
1q (^{13}C, 126 MHz, $CDCl_3$)



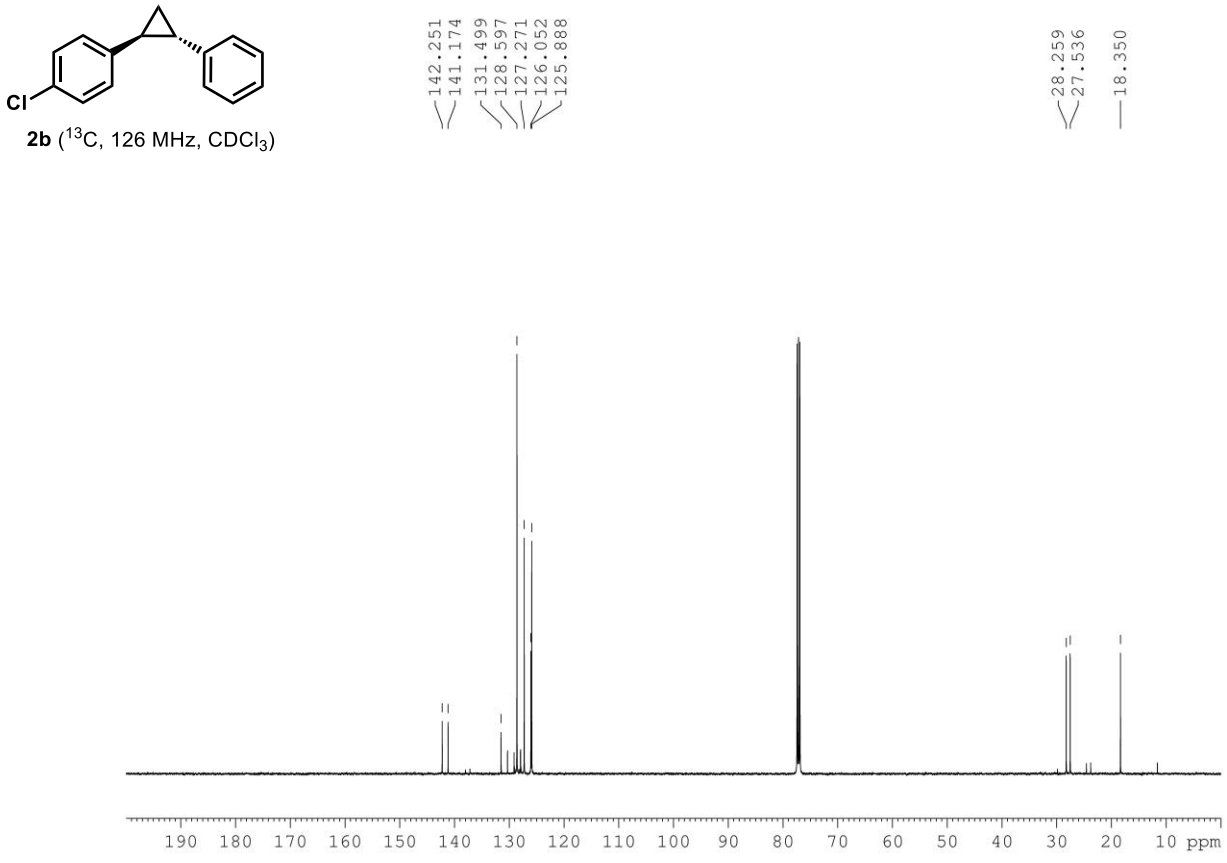
2a (^{1}H, 400 MHz, $CDCl_3$)



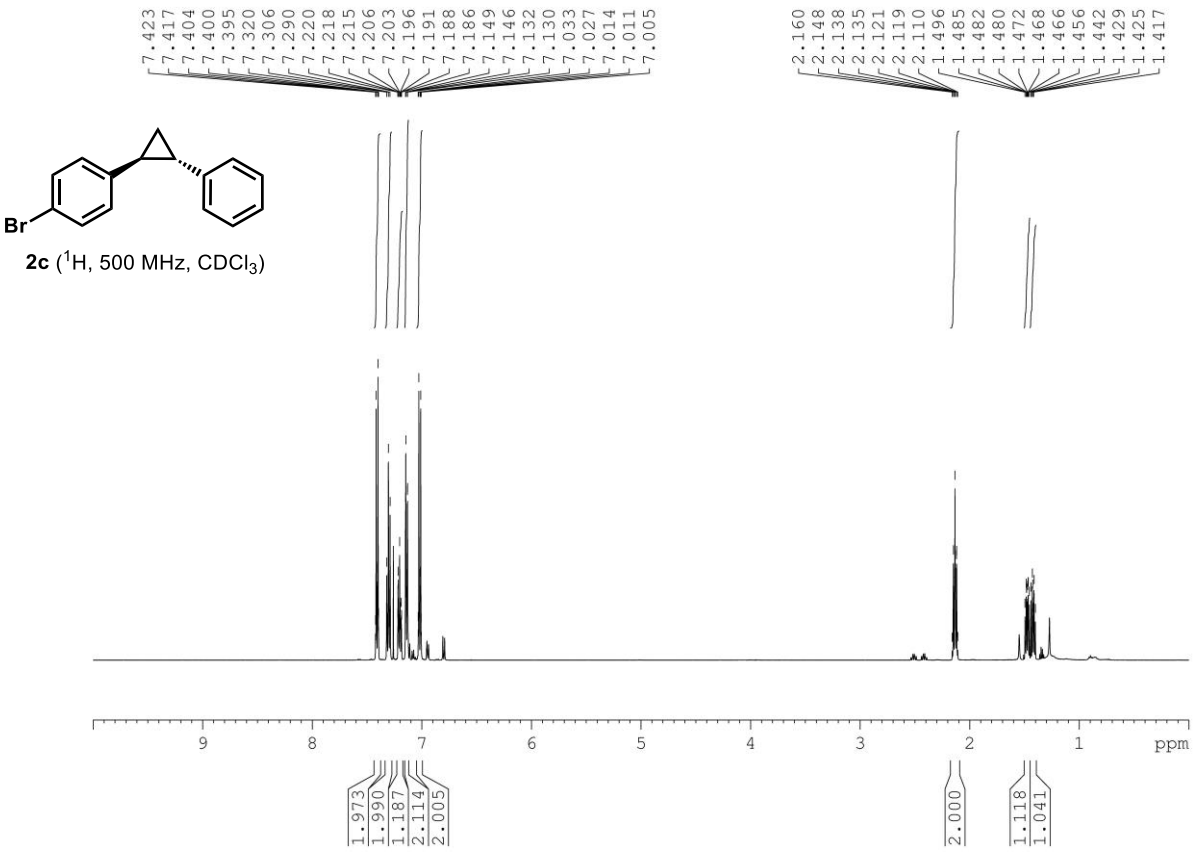
2a (^{13}C, 126 MHz, $CDCl_3$)



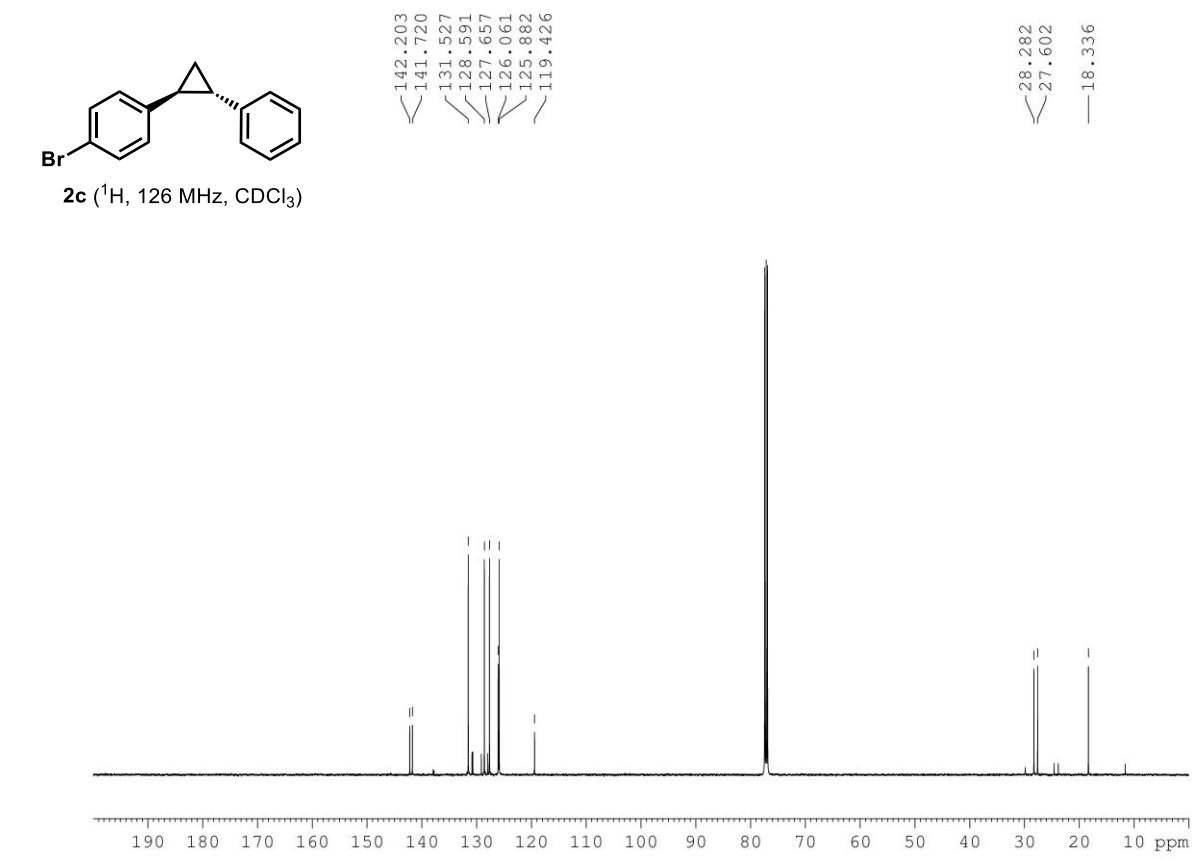
2b (^{1}H, 500 MHz, $CDCl_3$)



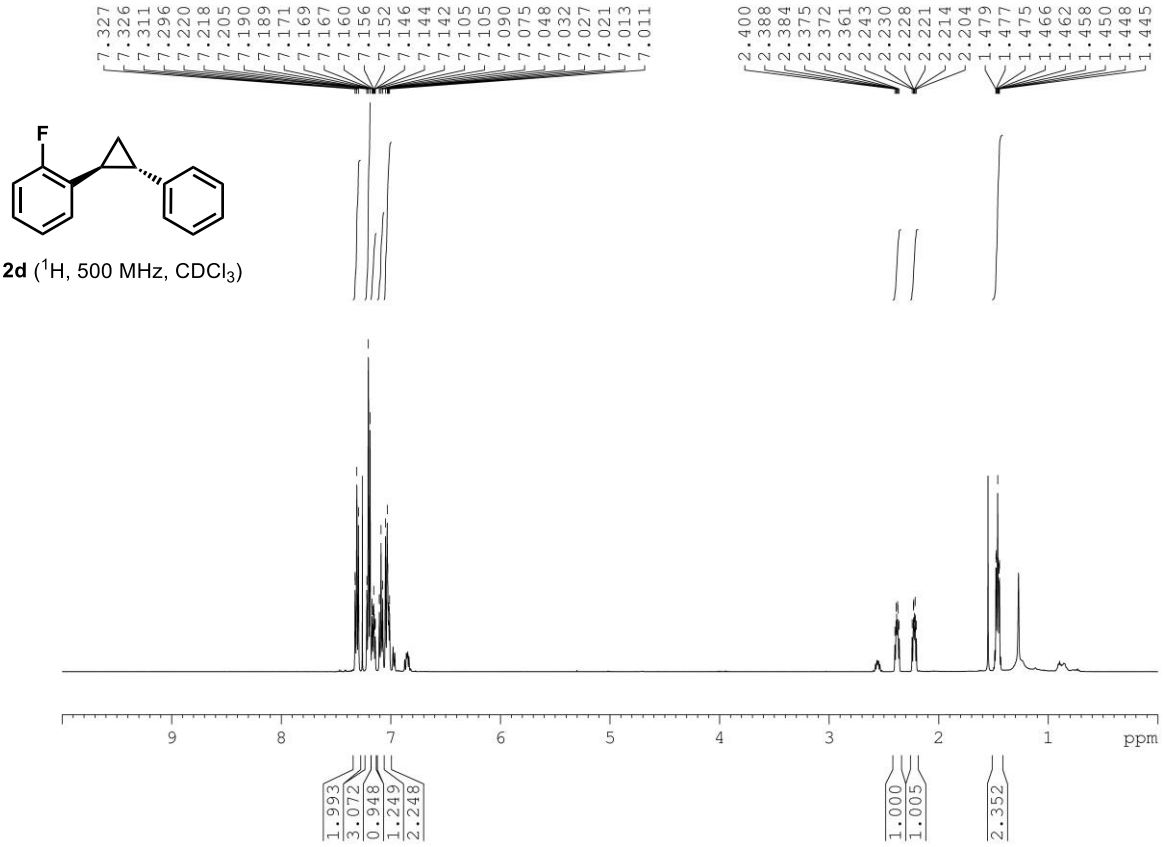
2b (^{13}C, 126 MHz, $CDCl_3$)



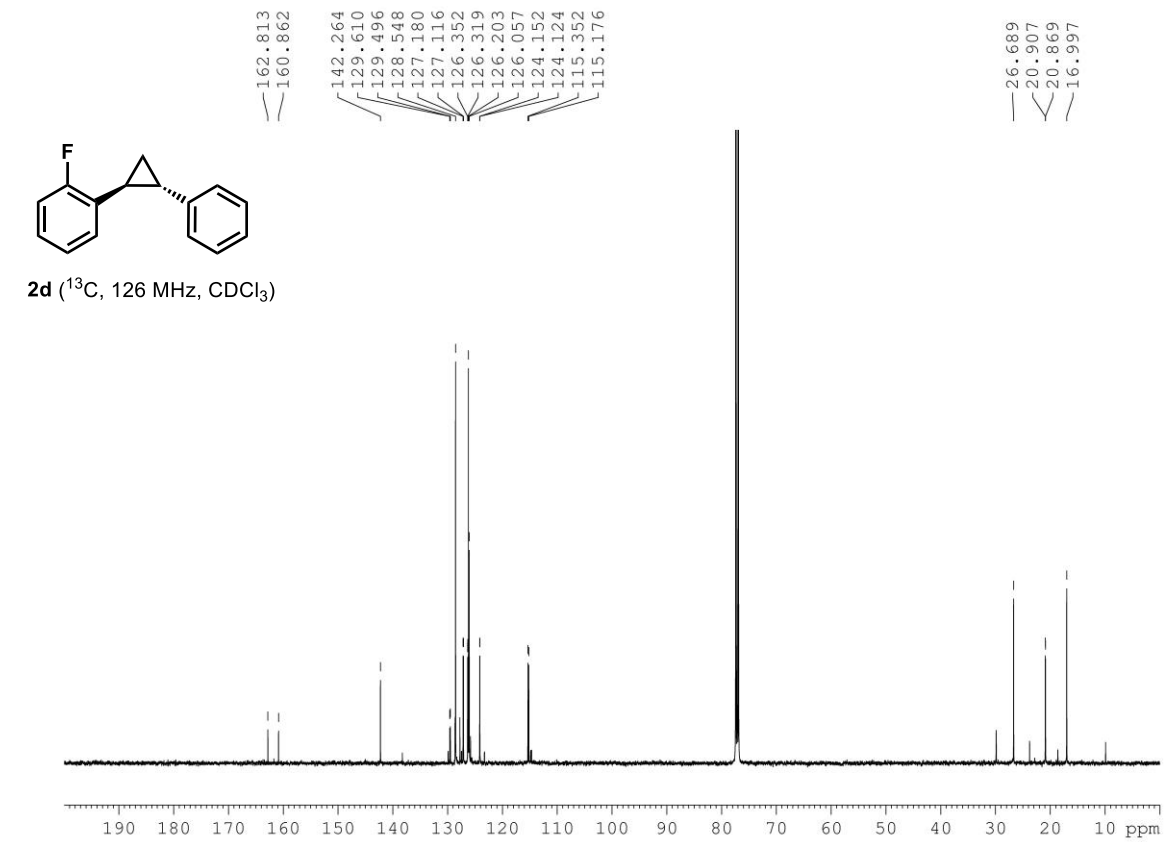
2c (^{1}H, 500 MHz, $CDCl_3$)



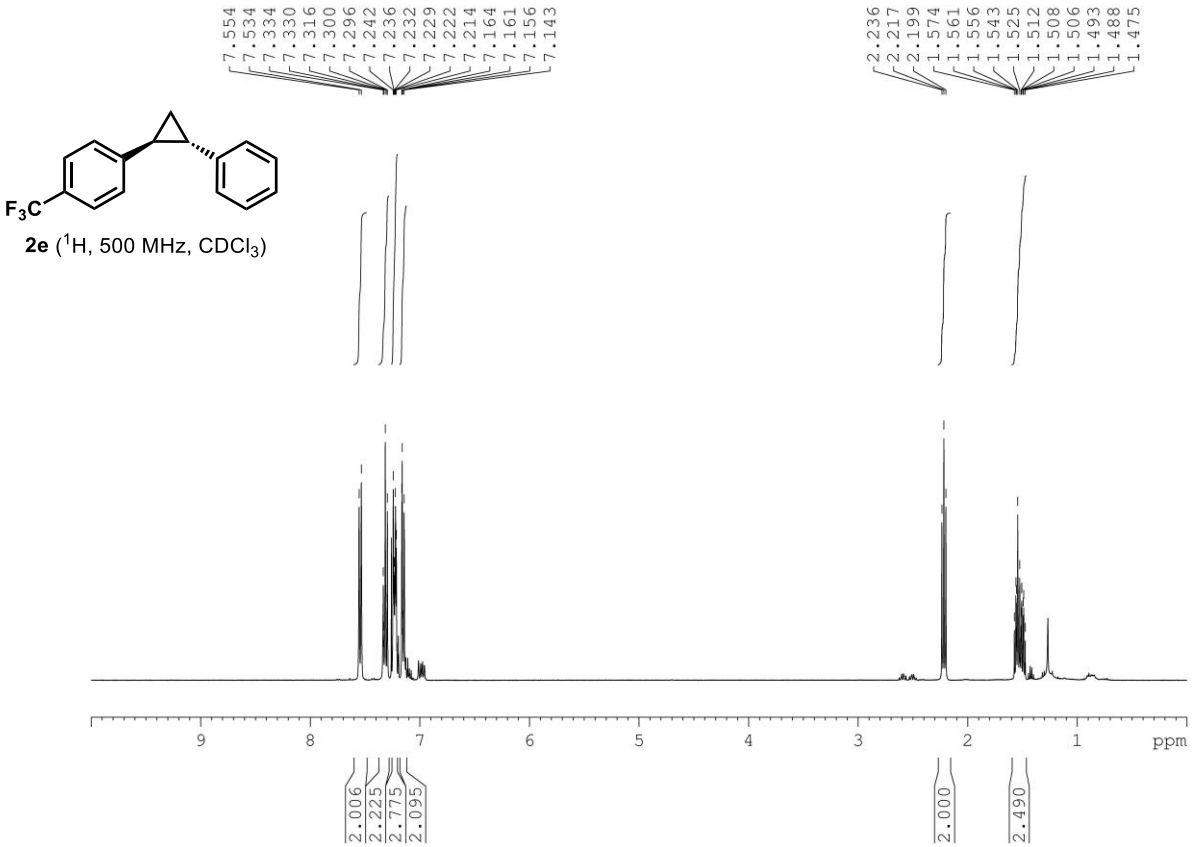
2c (^{1}H, 126 MHz, $CDCl_3$)



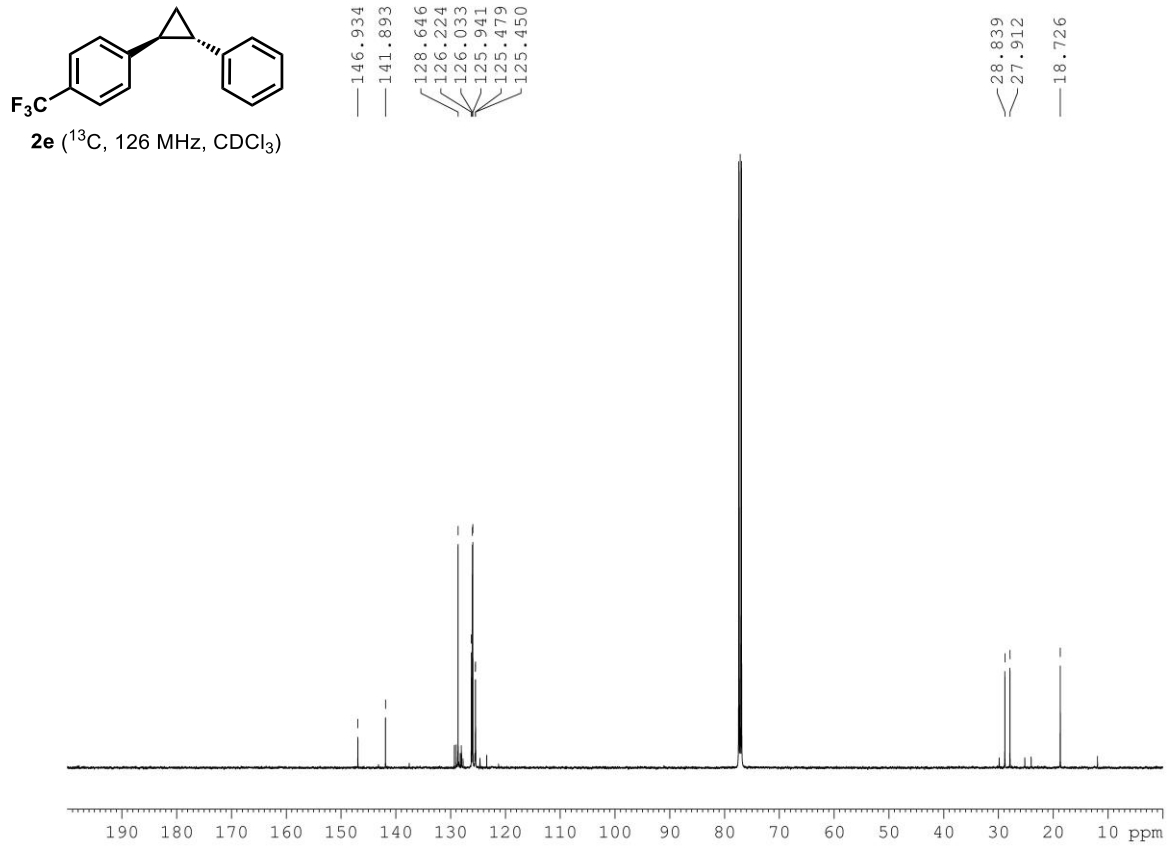
2d (^{1}H, 500 MHz, $CDCl_3$)



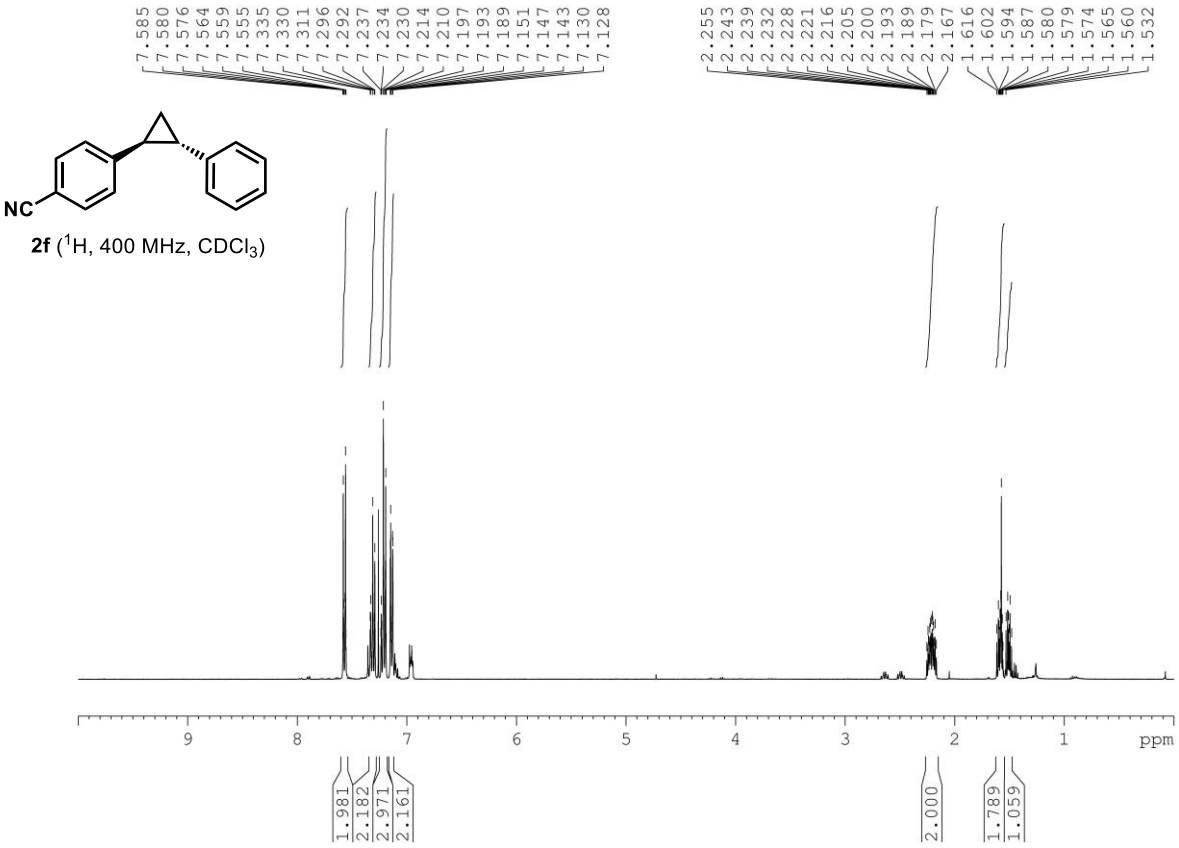
2d (^{13}C, 126 MHz, $CDCl_3$)



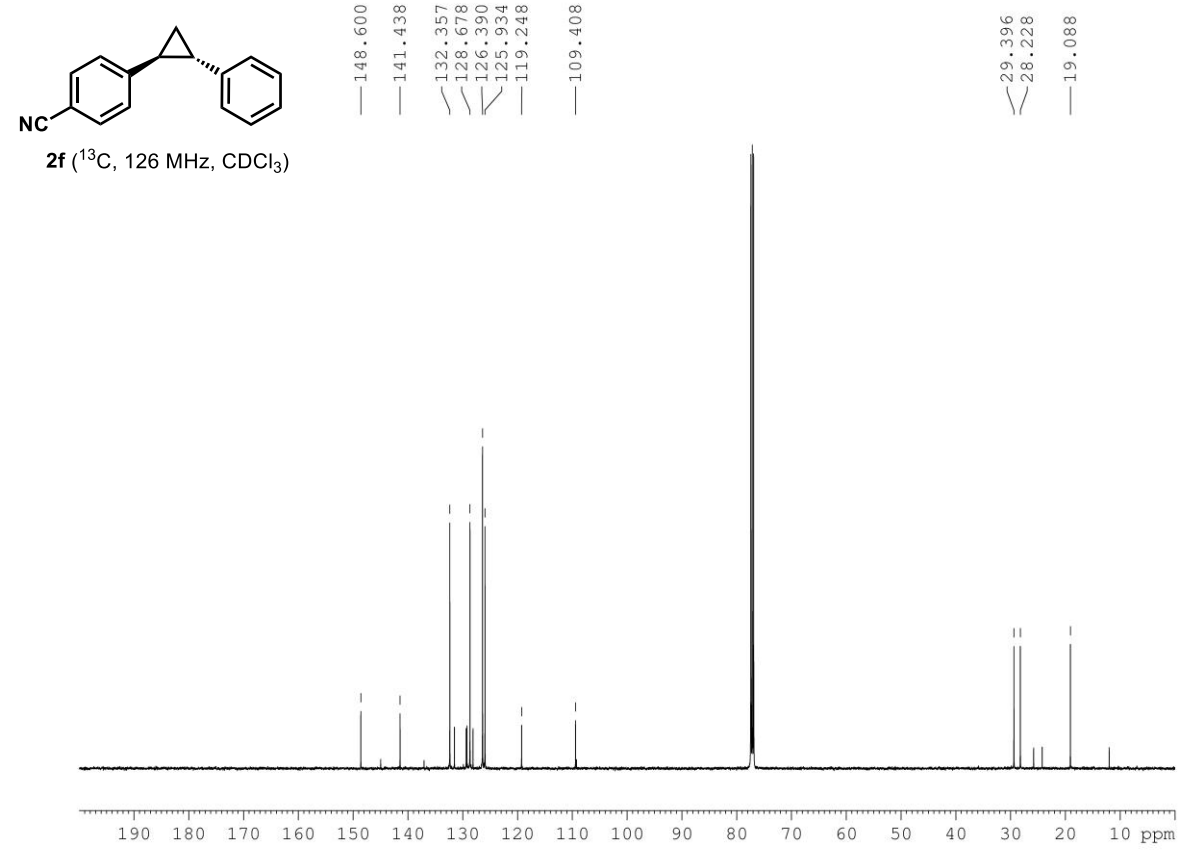
2e (^{1}H, 500 MHz, $CDCl_3$)



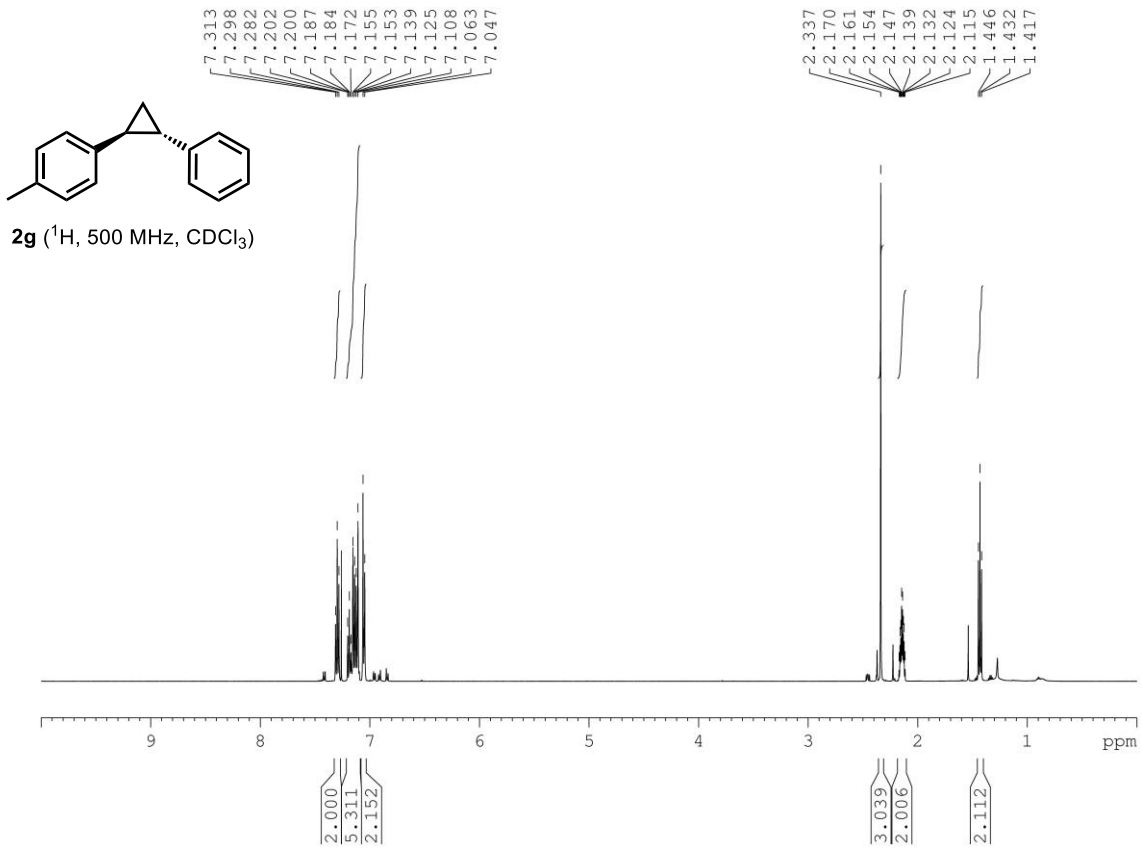
2e (^{13}C, 126 MHz, $CDCl_3$)



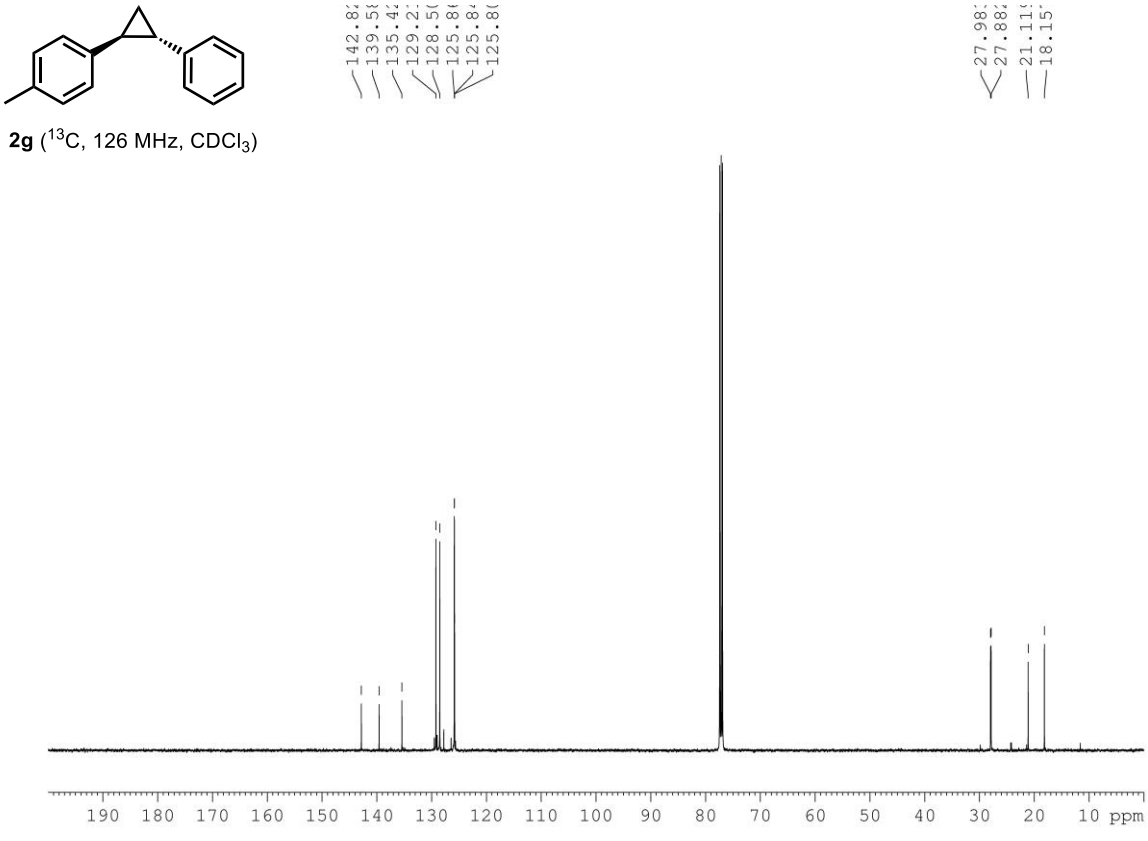
2f (^{1}H, 400 MHz, $CDCl_3$)



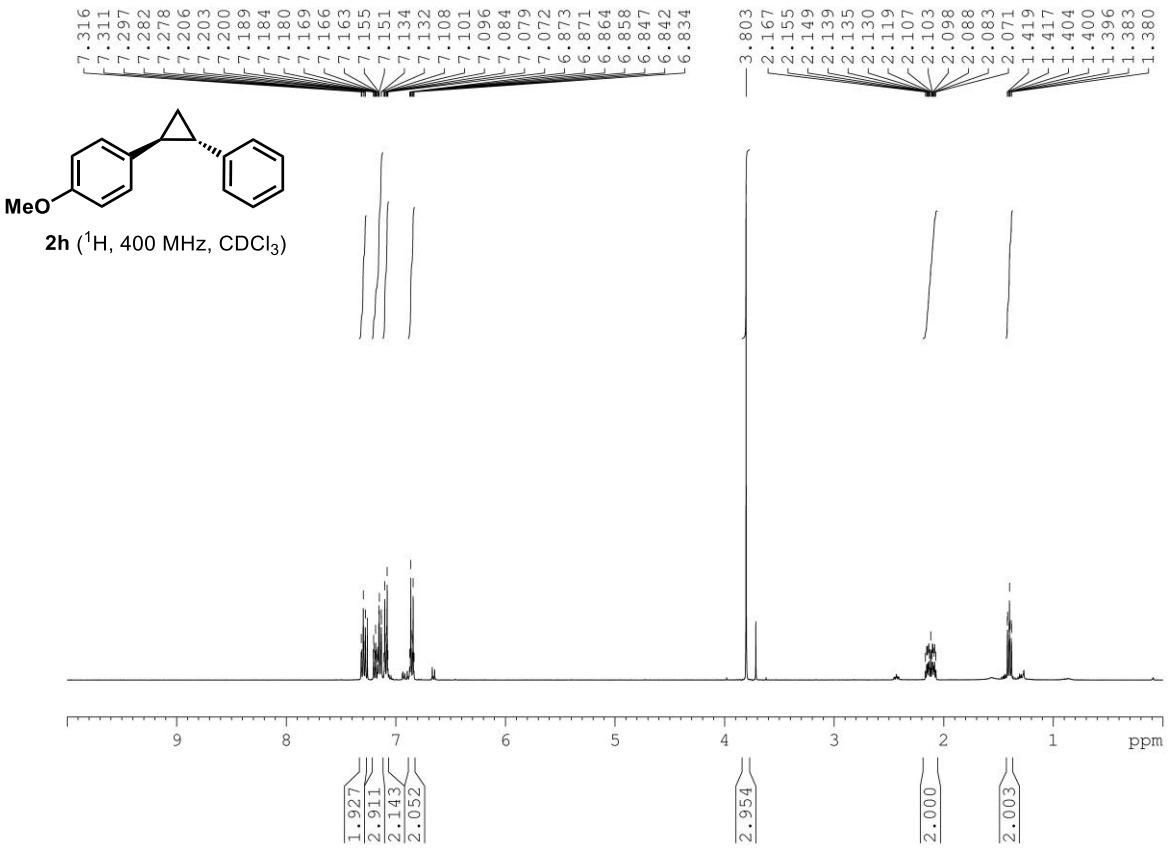
2f (^{13}C, 126 MHz, $CDCl_3$)

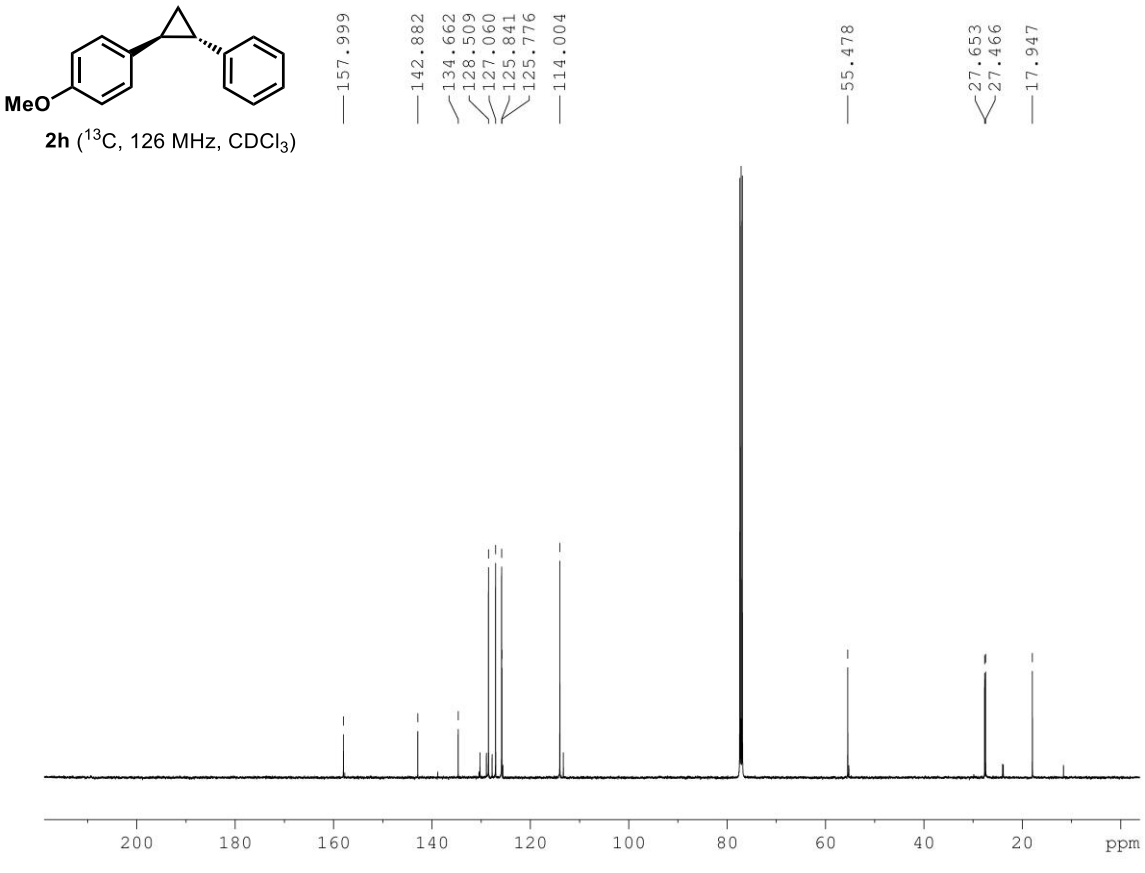


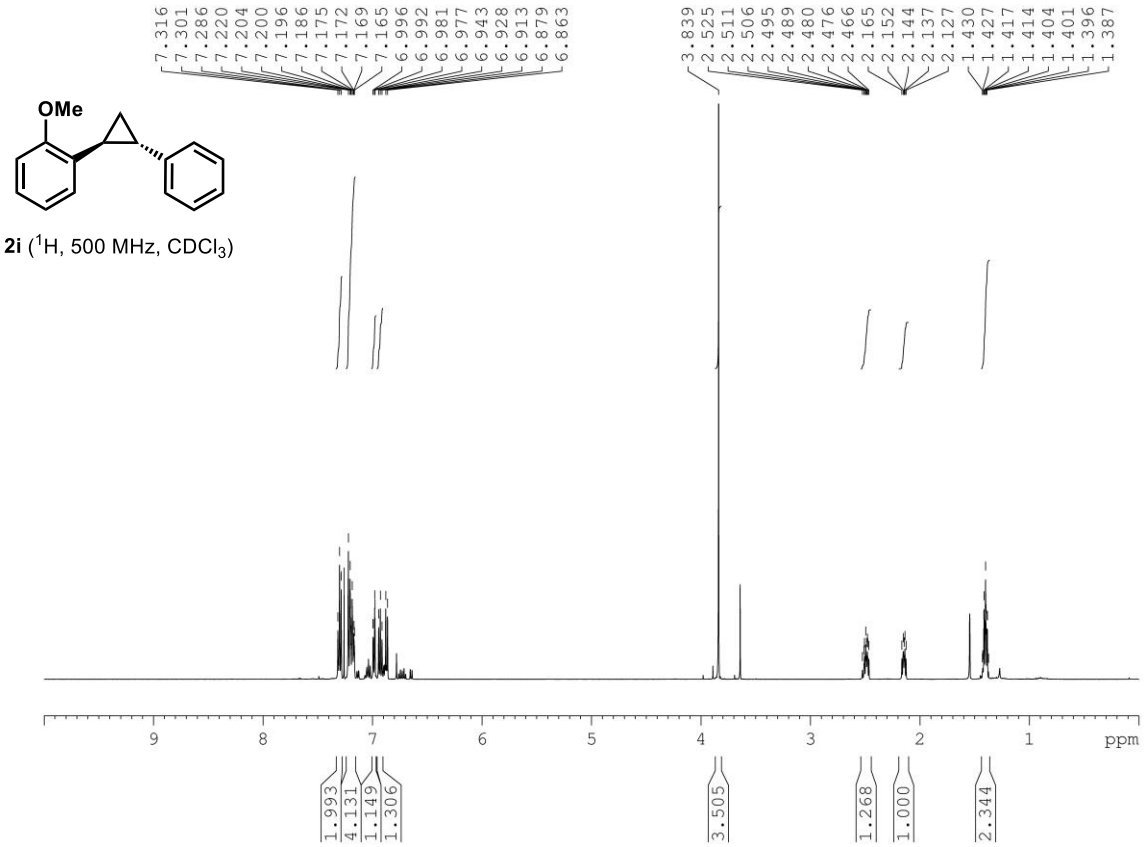
2g (^{1}H, 500 MHz, $CDCl_3$)



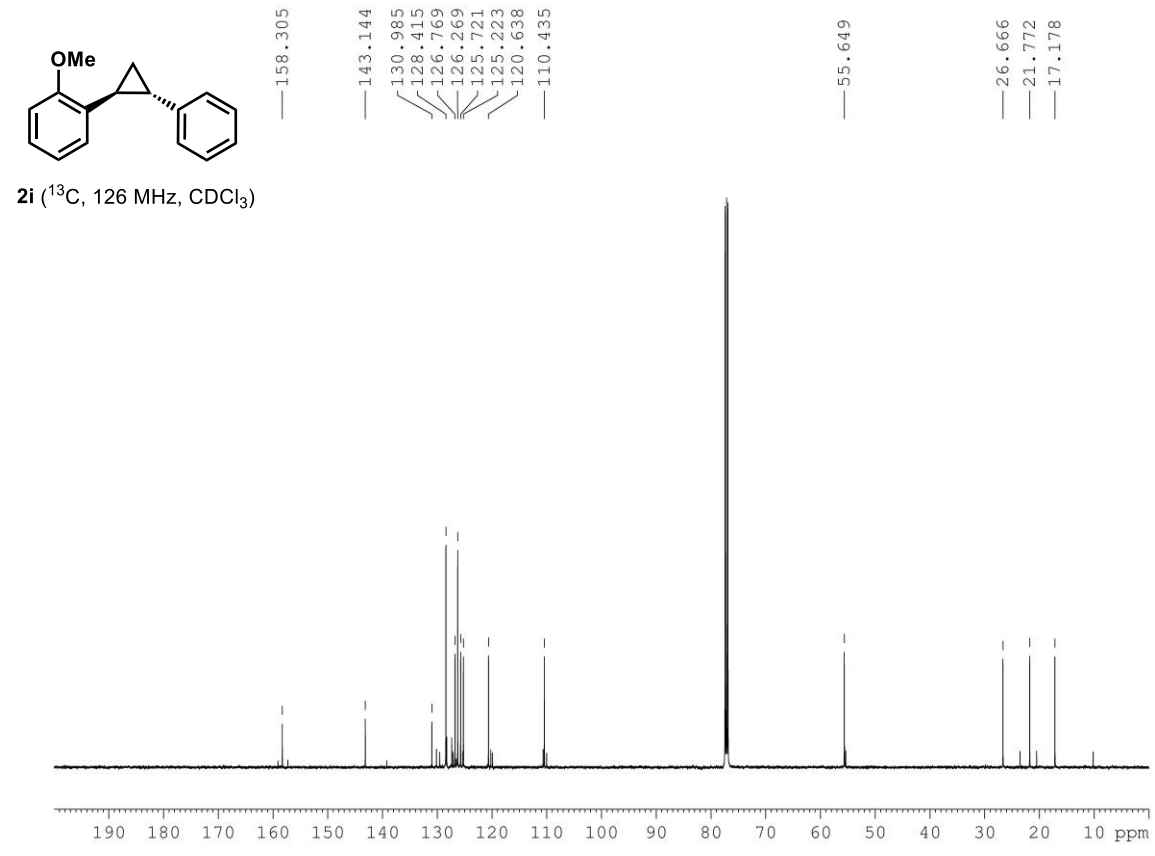
2g (^{13}C, 126 MHz, $CDCl_3$)


7.316
7.311
7.297
7.282
7.278
7.206
7.203
7.200
7.189
7.184
7.180
7.169
7.166
7.163
7.155
7.151
7.134
7.132
7.108
7.101
7.096
7.084
7.079
7.072
6.873
6.871
6.864
6.858
6.847
6.842
6.834
3.803
2.167
2.155
2.149
2.139
2.135
2.130
2.119
2.107
2.103
2.098
2.088
2.083
2.071
1.419
1.417
1.404
1.400
1.396
1.383
1.380
MeO
2h (1H, 400 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
ppm
1.927
2.911
2.143
2.052
2.954
2.000
2.003

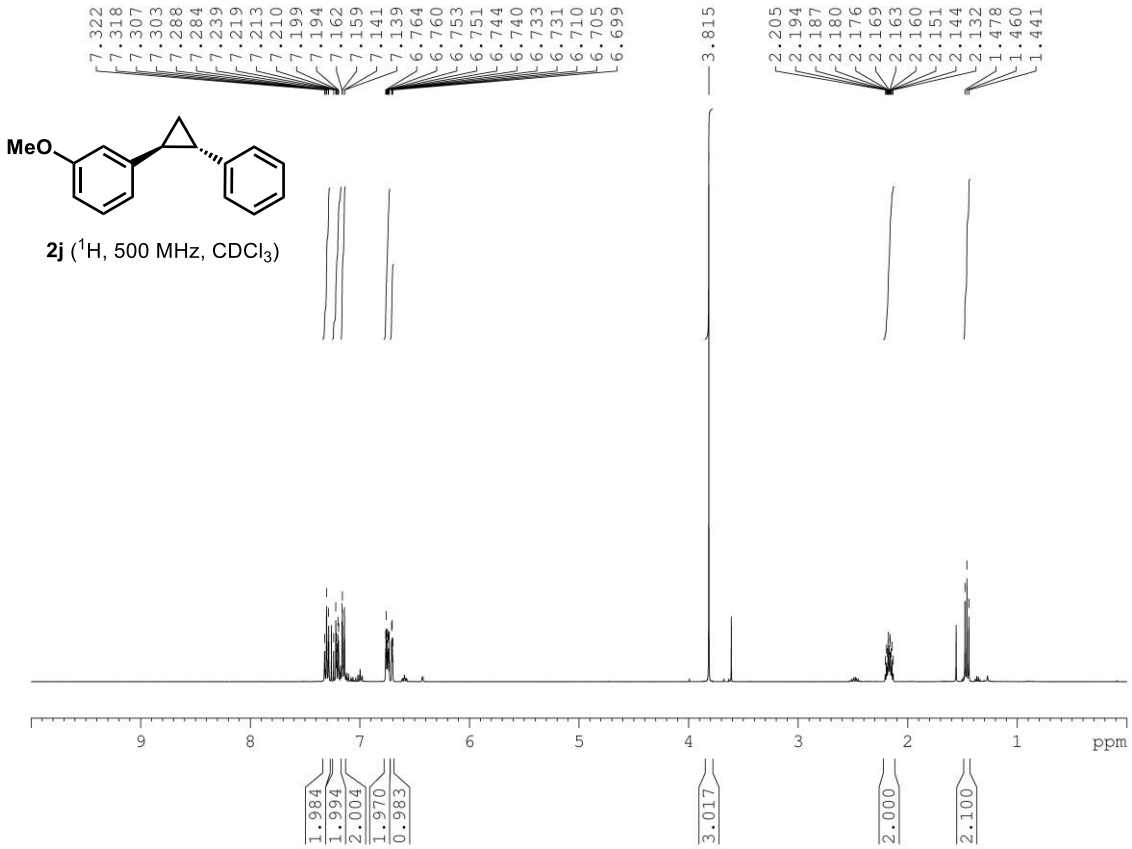

MeO
2h (13C, 126 MHz, CDCl3)
157.999
142.882
134.662
128.509
127.060
125.841
125.776
114.004
55.478
27.653
27.466
17.947
200
180
160
140
120
100
80
60
40
20
ppm



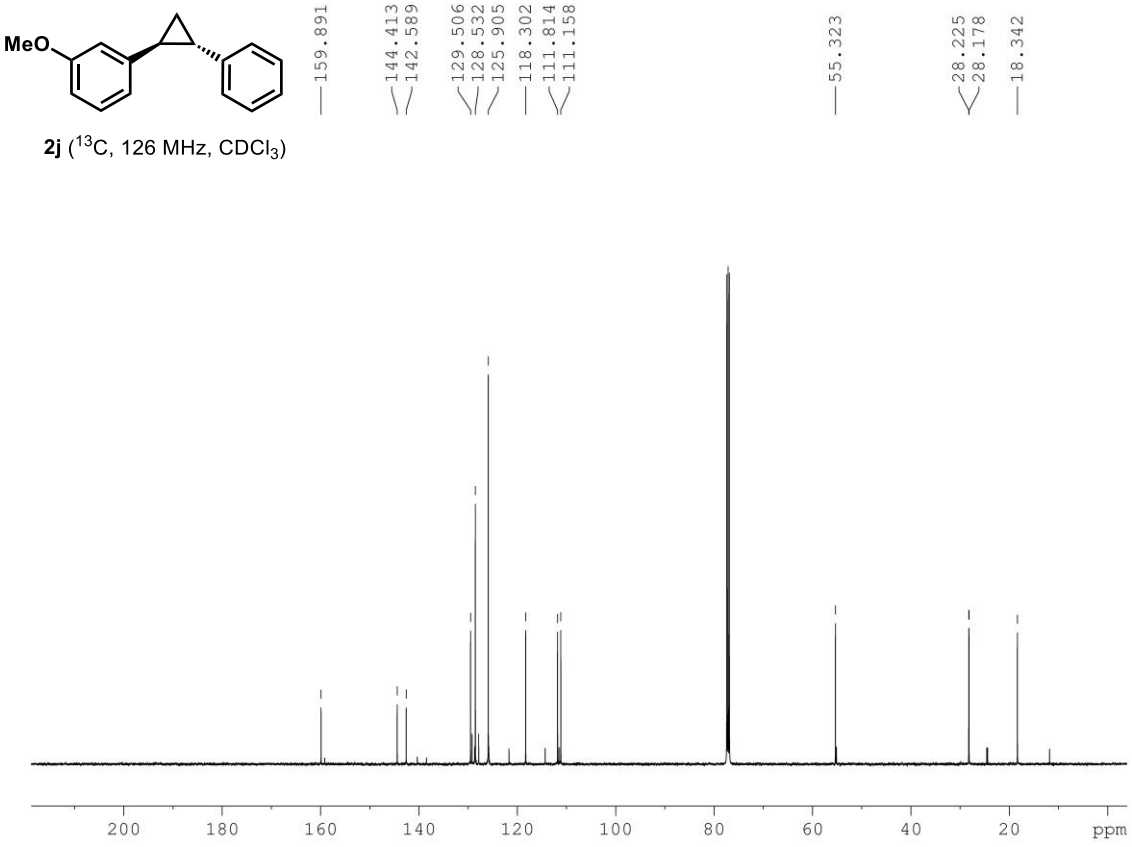
2i (^{1}H, 500 MHz, $CDCl_3$)



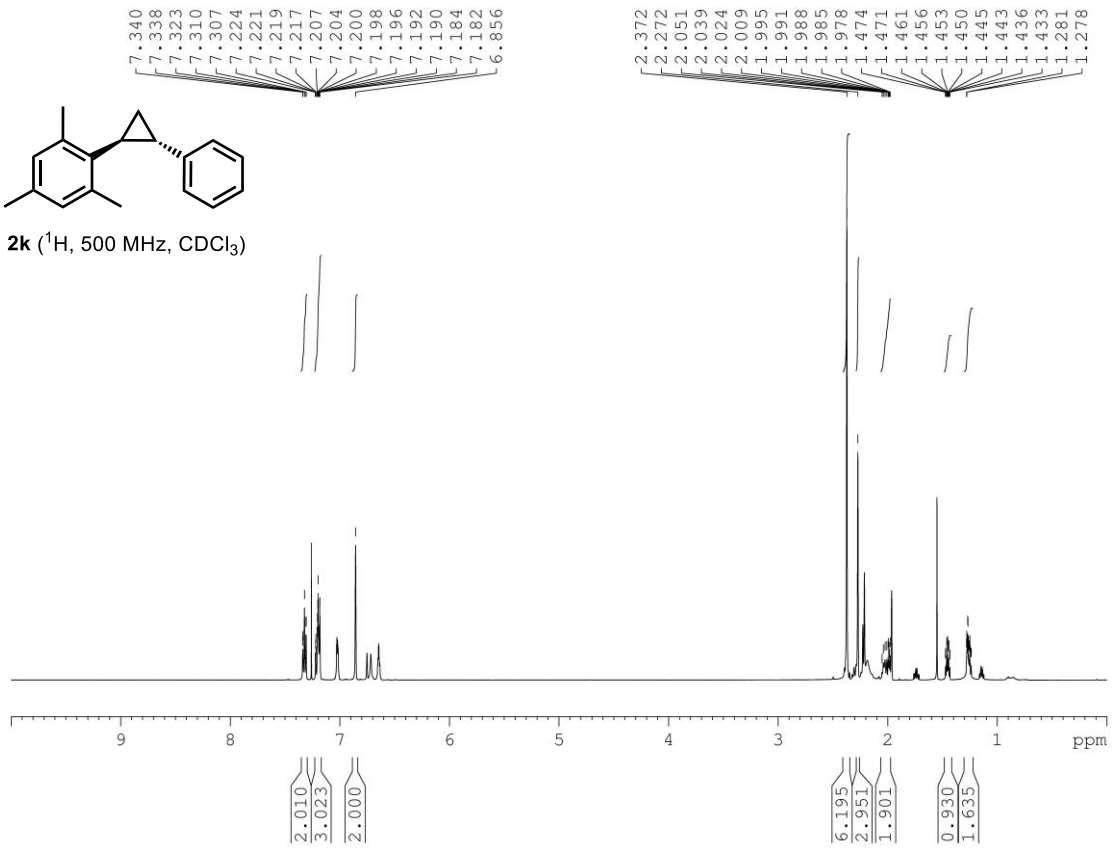
2i (^{13}C, 126 MHz, $CDCl_3$)



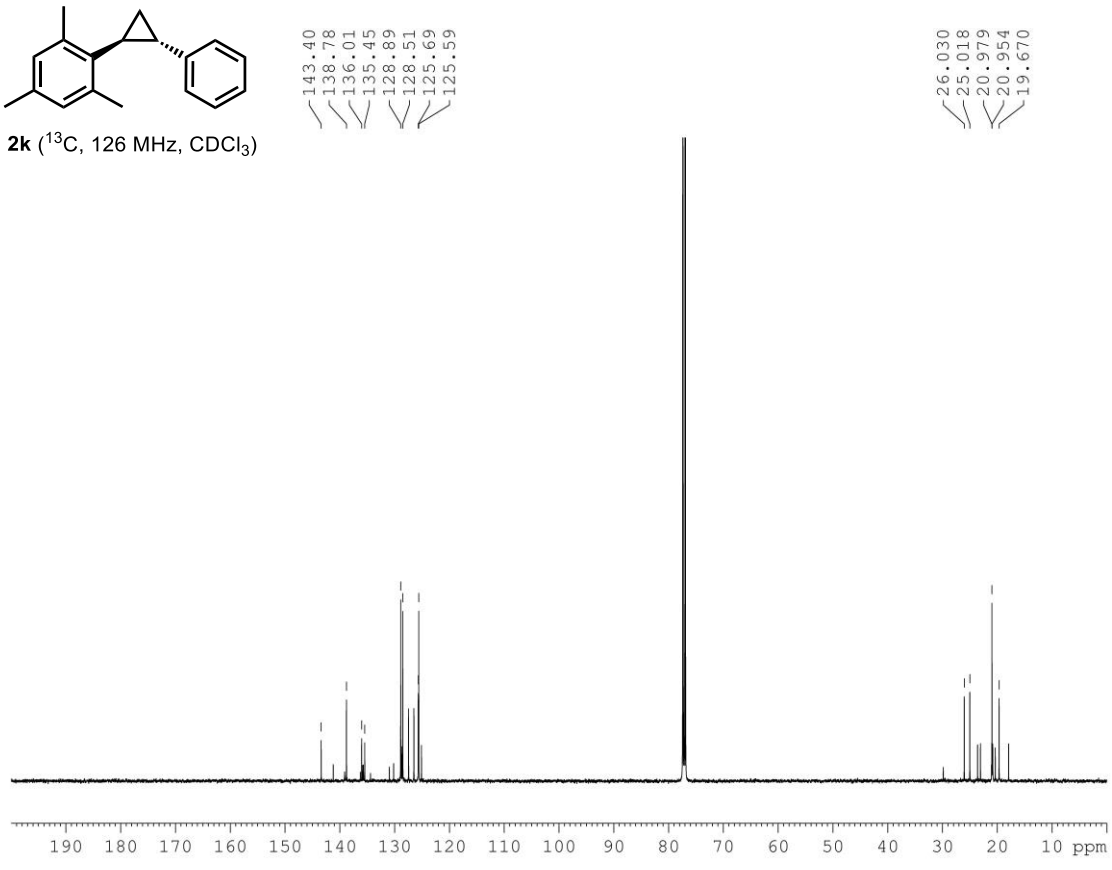
2j (^{1}H, 500 MHz, $CDCl_3$)



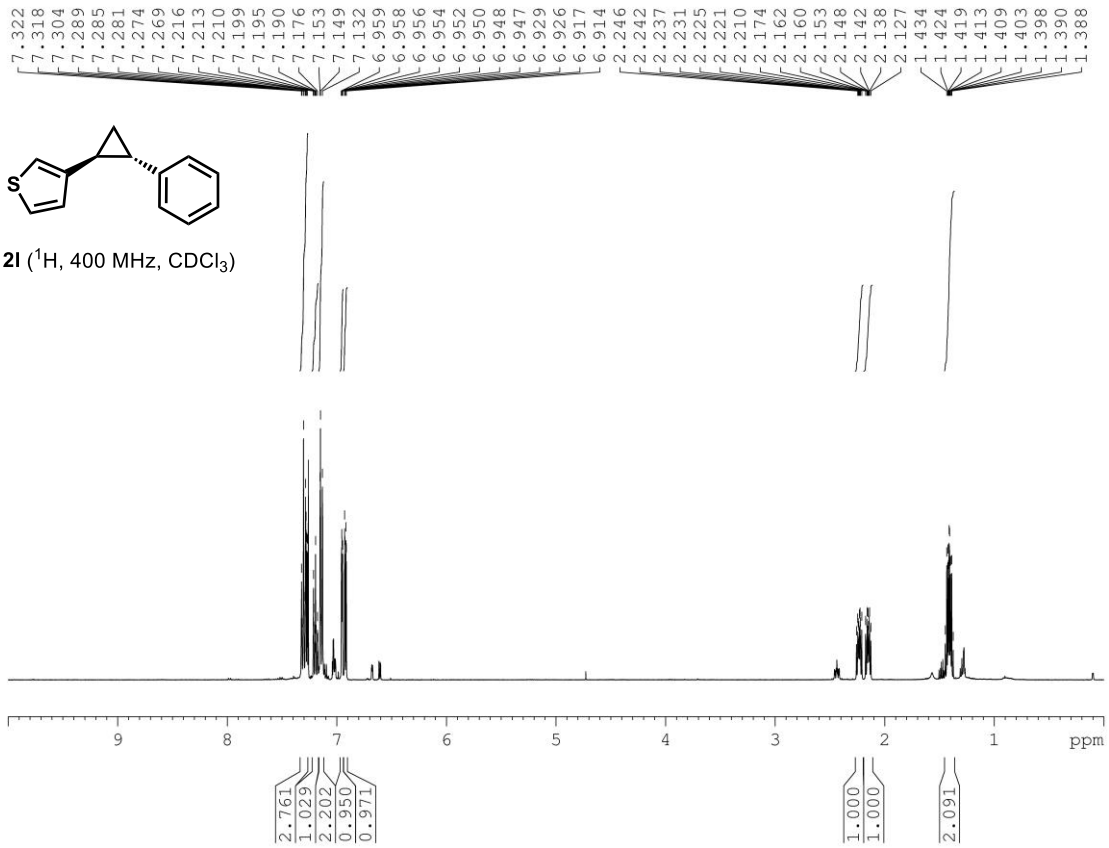
2j (^{13}C, 126 MHz, $CDCl_3$)



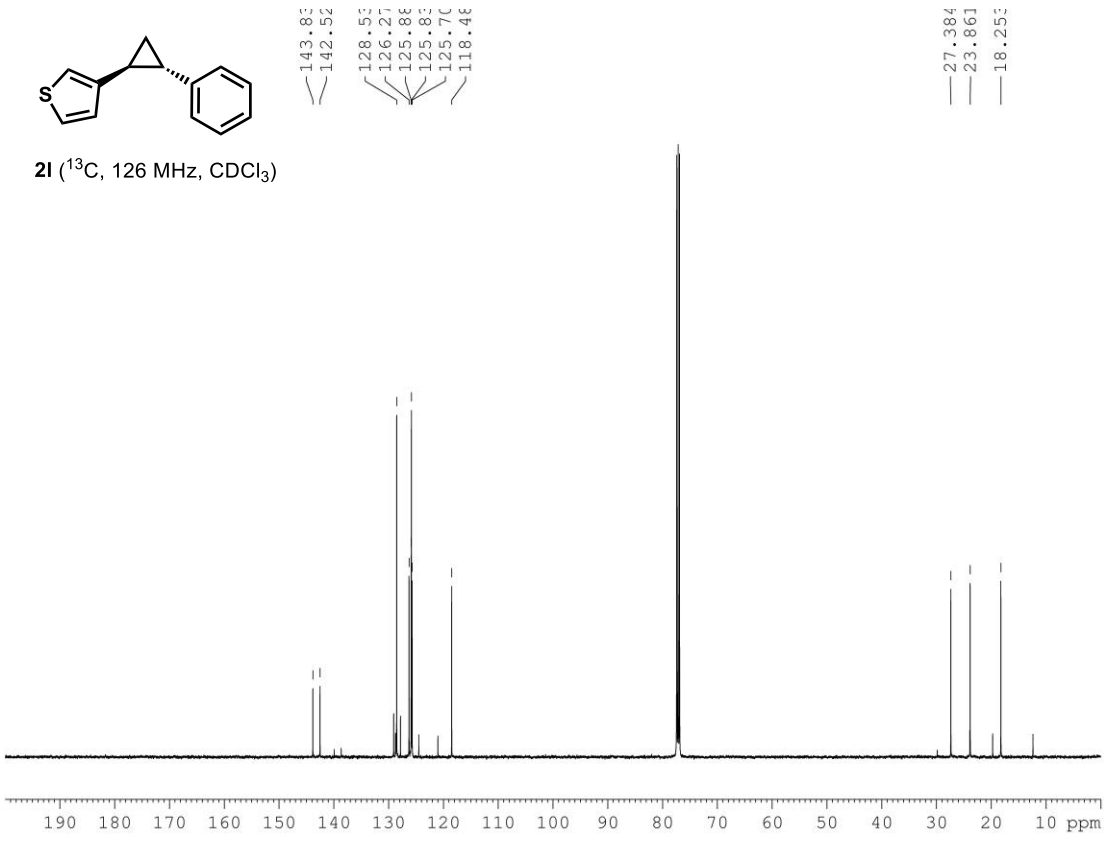
2k (^{1}H, 500 MHz, $CDCl_3$)



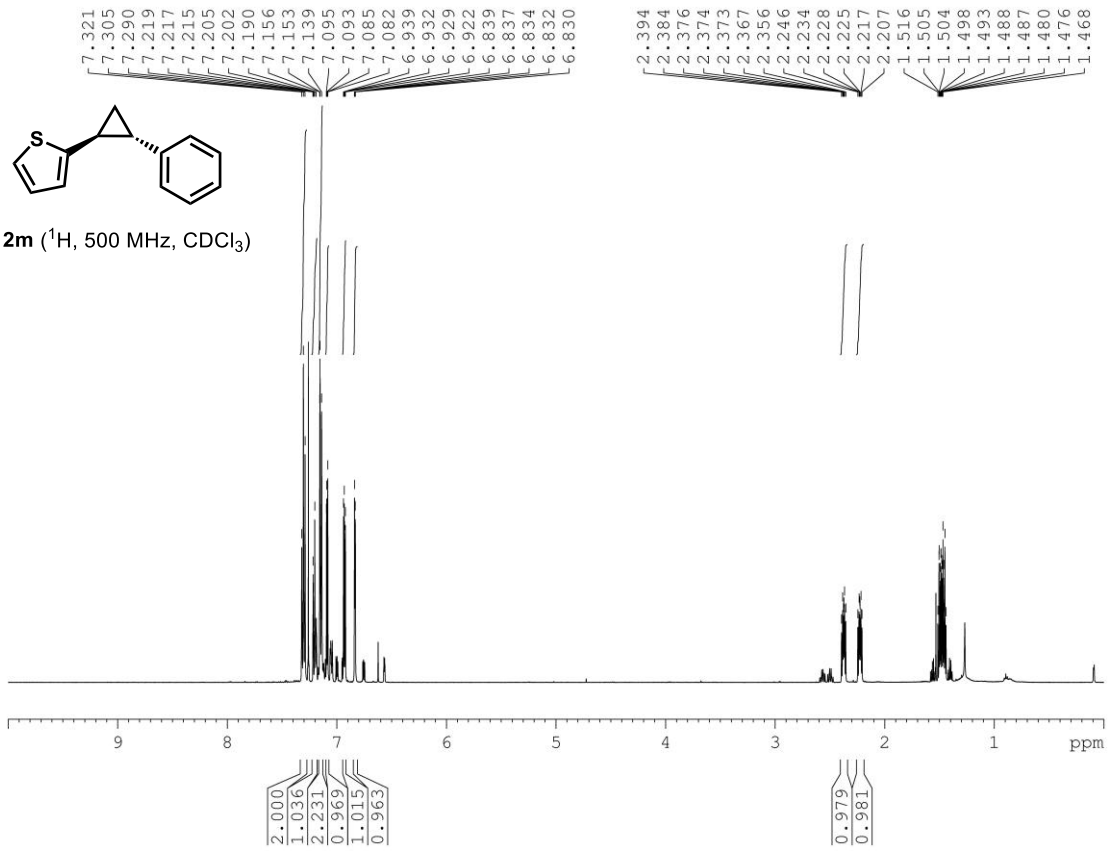
2k (^{13}C, 126 MHz, $CDCl_3$)

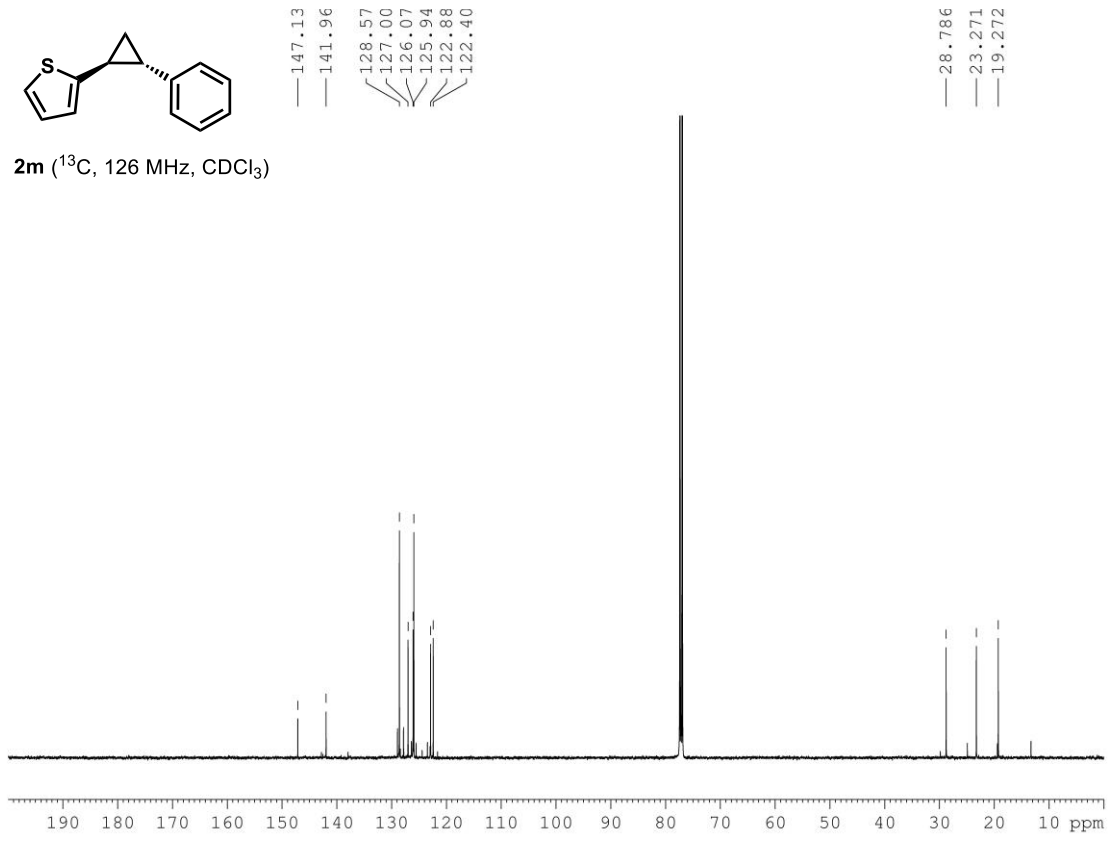


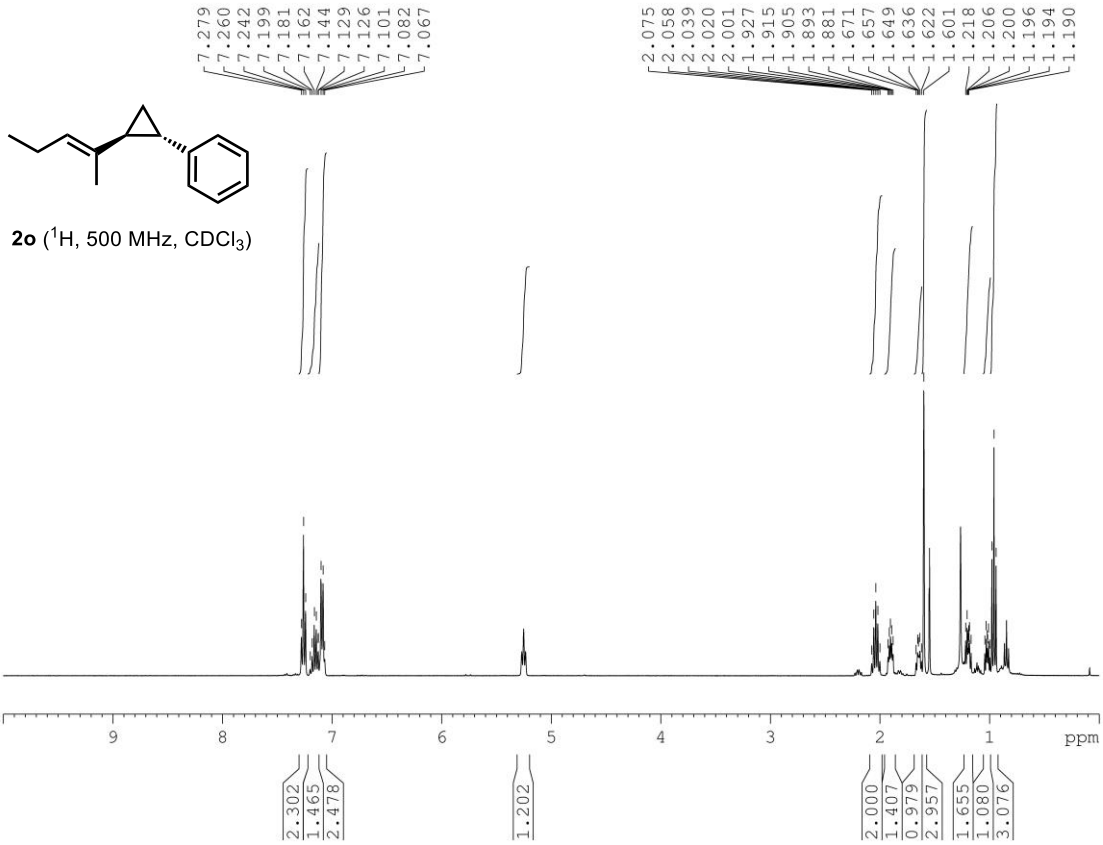
2l (^{1}H, 400 MHz, $CDCl_3$)



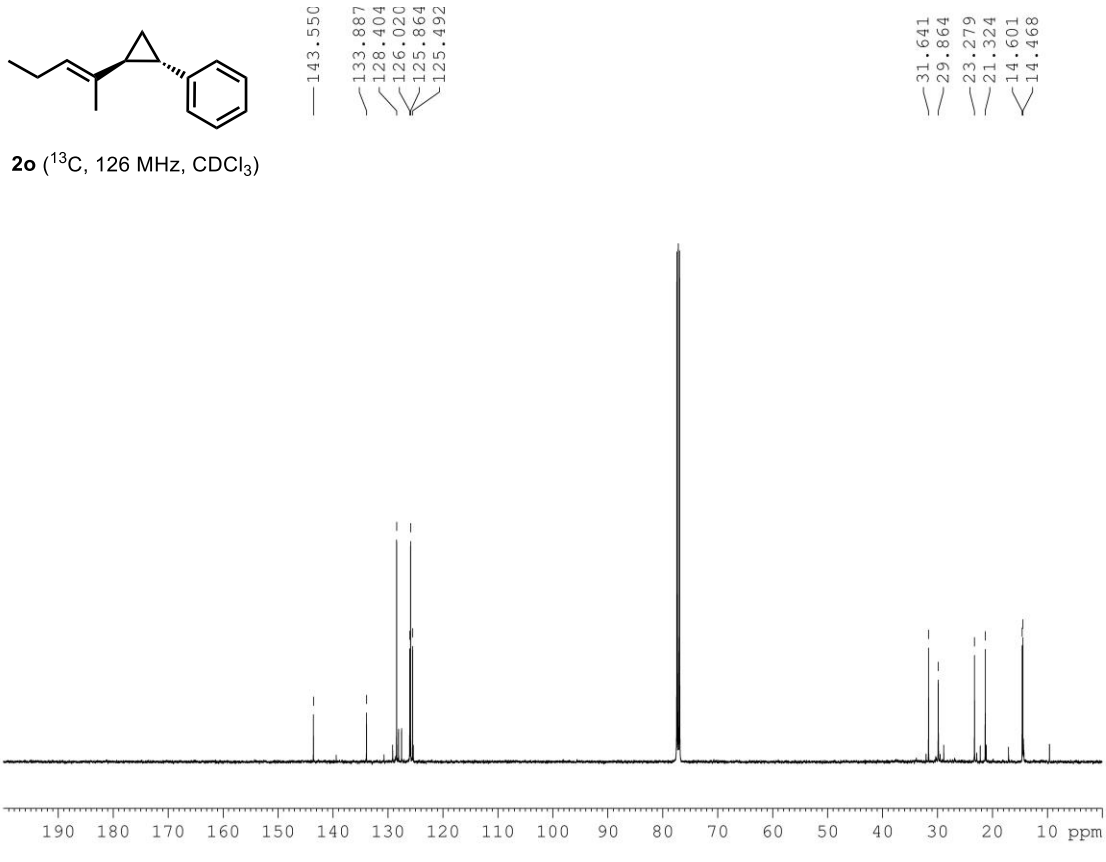
2l (^{13}C, 126 MHz, $CDCl_3$)


7.321
7.305
7.290
7.219
7.217
7.215
7.205
7.202
7.190
7.156
7.153
7.139
7.095
7.093
7.085
7.082
6.939
6.932
6.929
6.922
6.839
6.837
6.834
6.832
6.830
2.394
2.384
2.376
2.374
2.373
2.367
2.356
2.246
2.234
2.228
2.225
2.217
2.207
1.516
1.505
1.504
1.498
1.493
1.488
1.487
1.480
1.476
1.468
S
2m (1H, 500 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
ppm
2.000
1.036
2.231
0.969
1.015
0.963
0.979
0.981

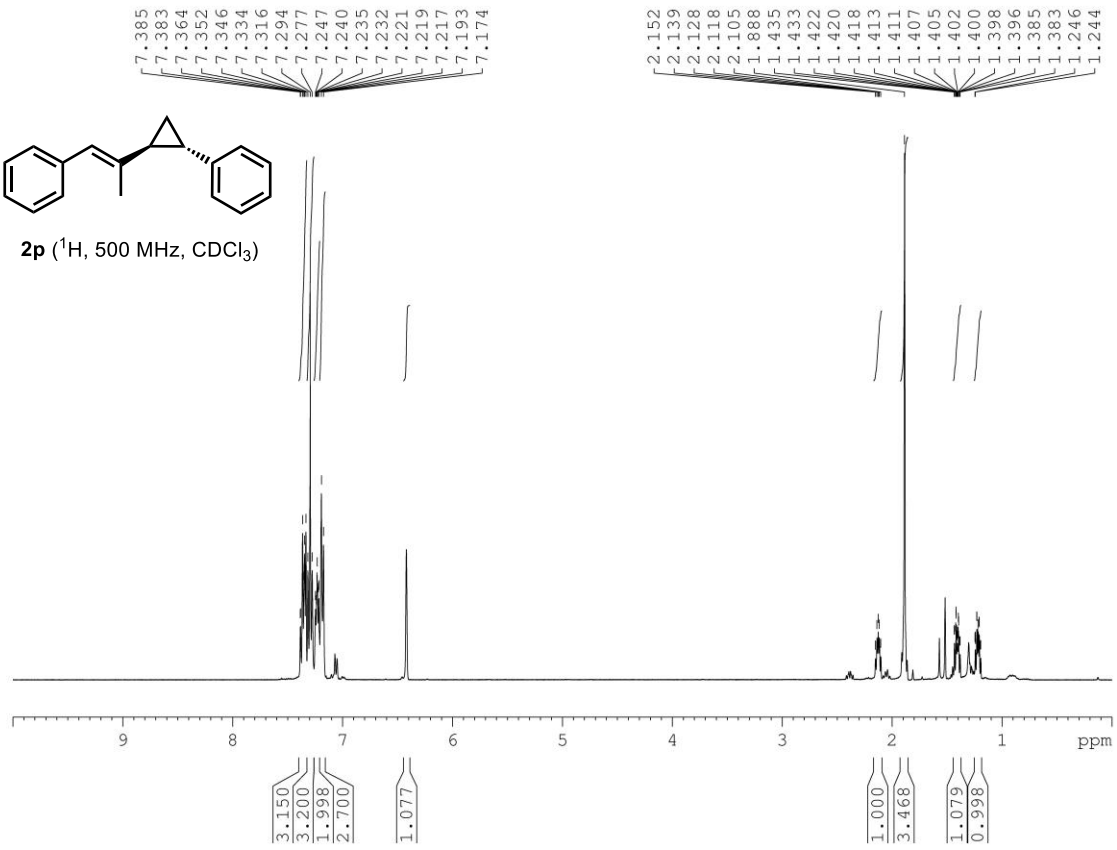

147.13
141.96
128.57
127.00
126.07
125.94
122.88
122.40
28.786
23.271
19.272
S
2m (13C, 126 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



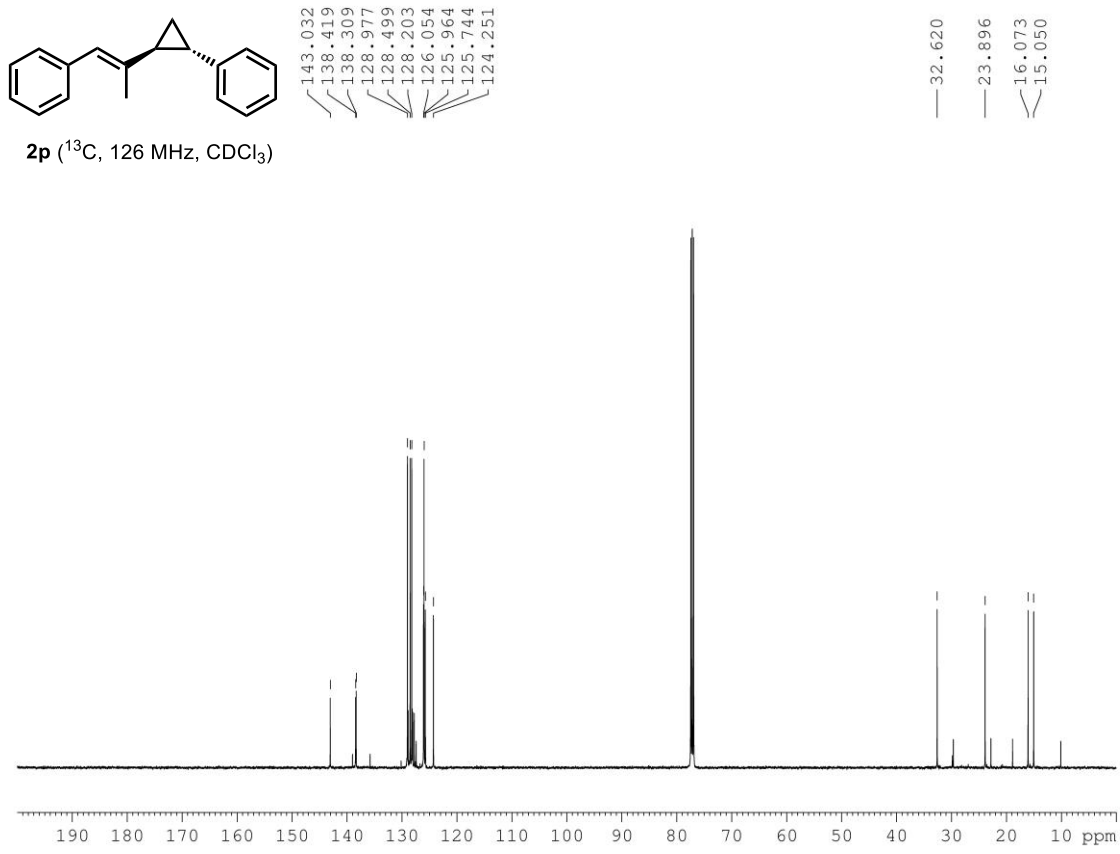
2o (^{1}H, 500 MHz, $CDCl_3$)



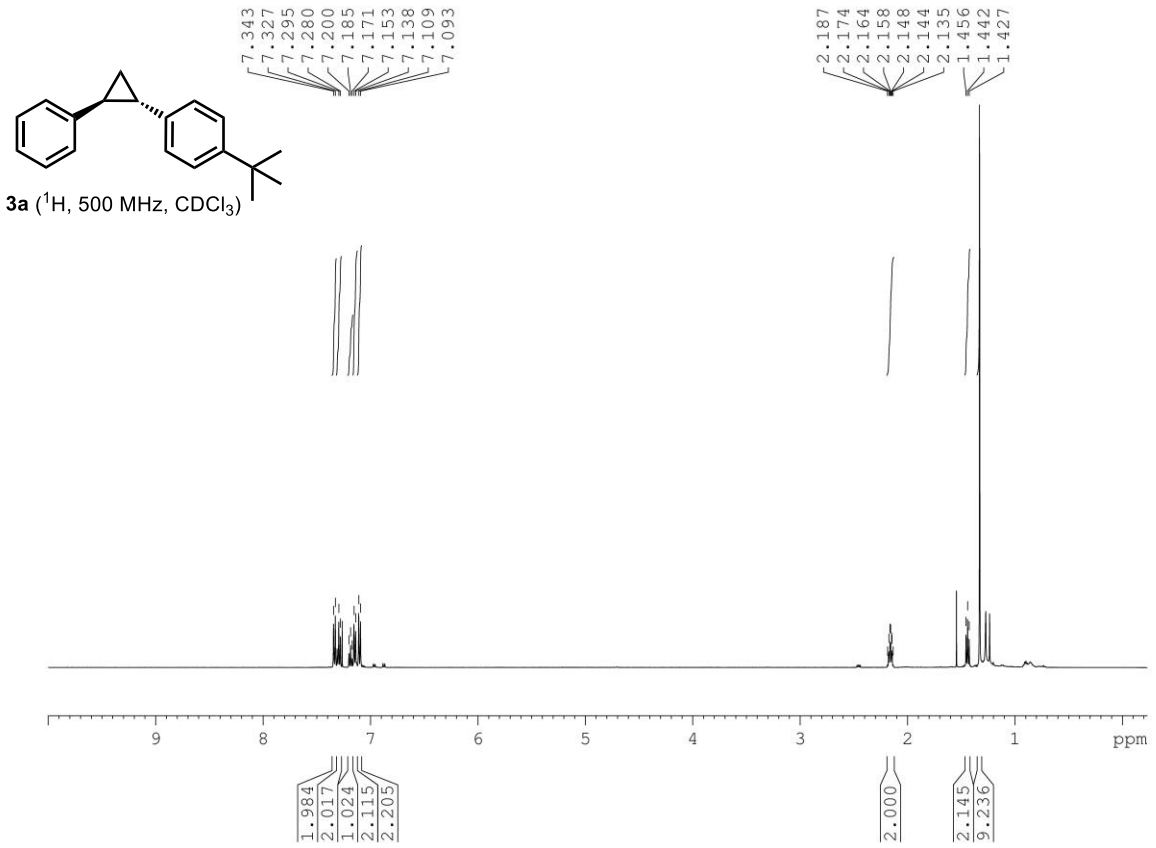
2o (^{13}C, 126 MHz, $CDCl_3$)



2p (^{1}H, 500 MHz, $CDCl_3$)

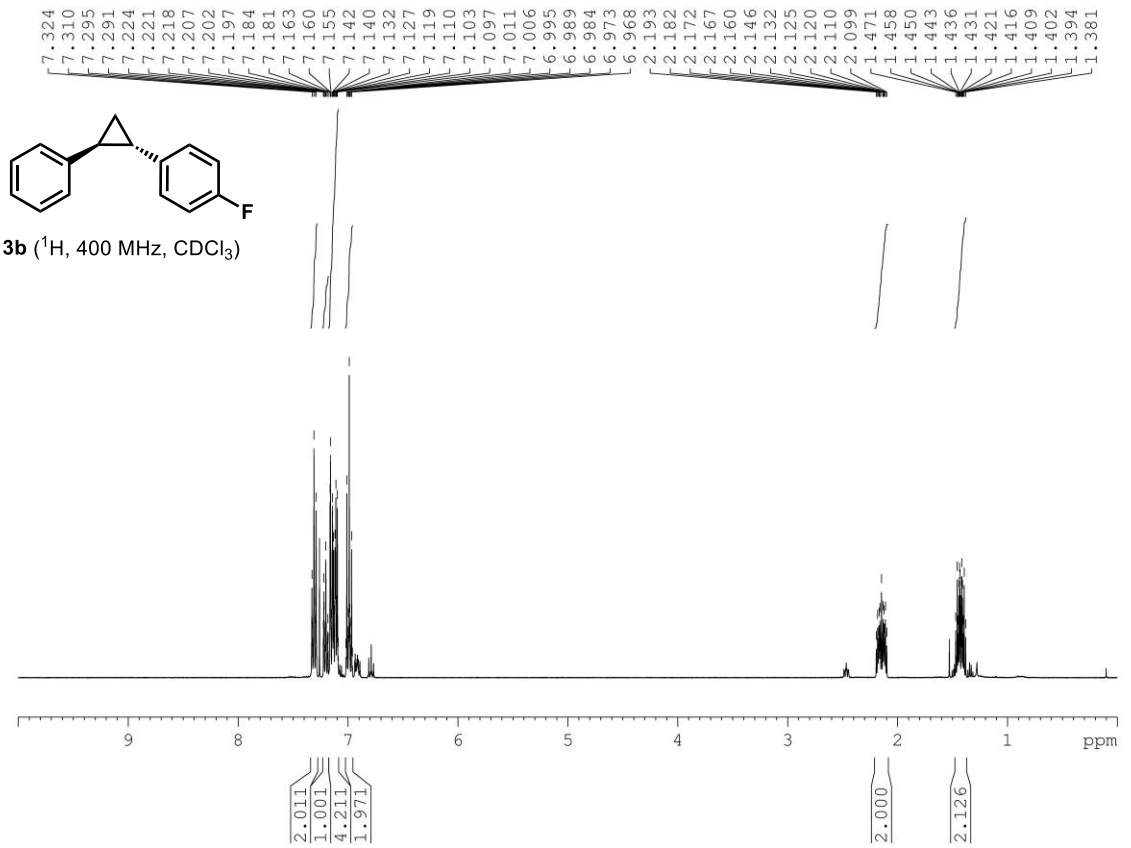


2p (^{13}C, 126 MHz, $CDCl_3$)

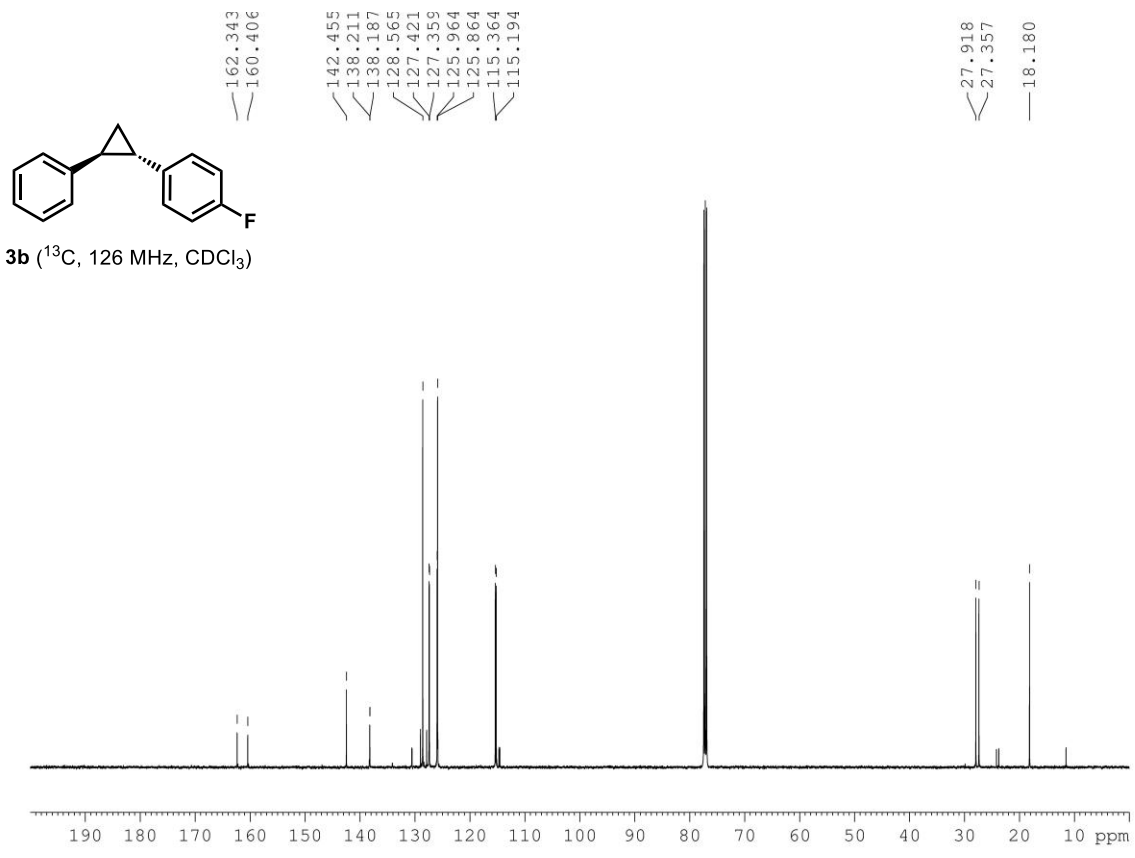


3a (^{1}H, 500 MHz, $CDCl_3$)

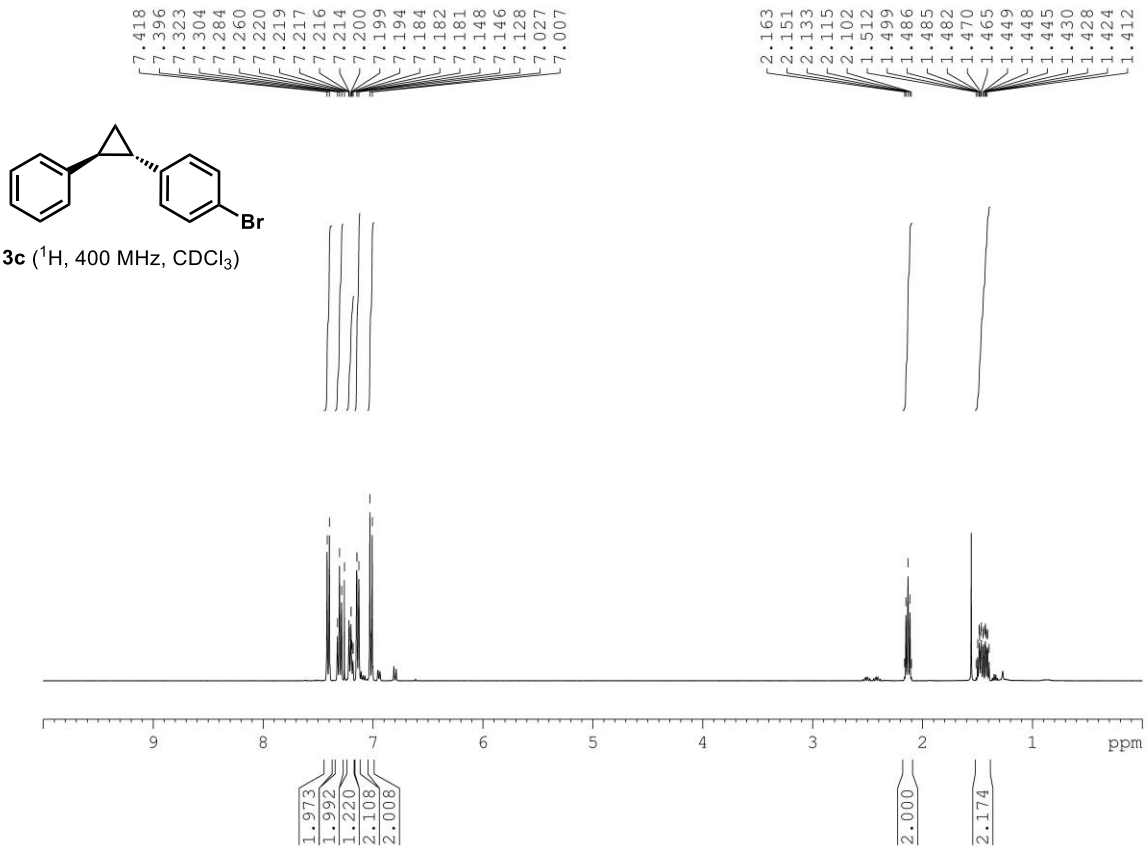
3a (^{13}C, 126 MHz, $CDCl_3$)



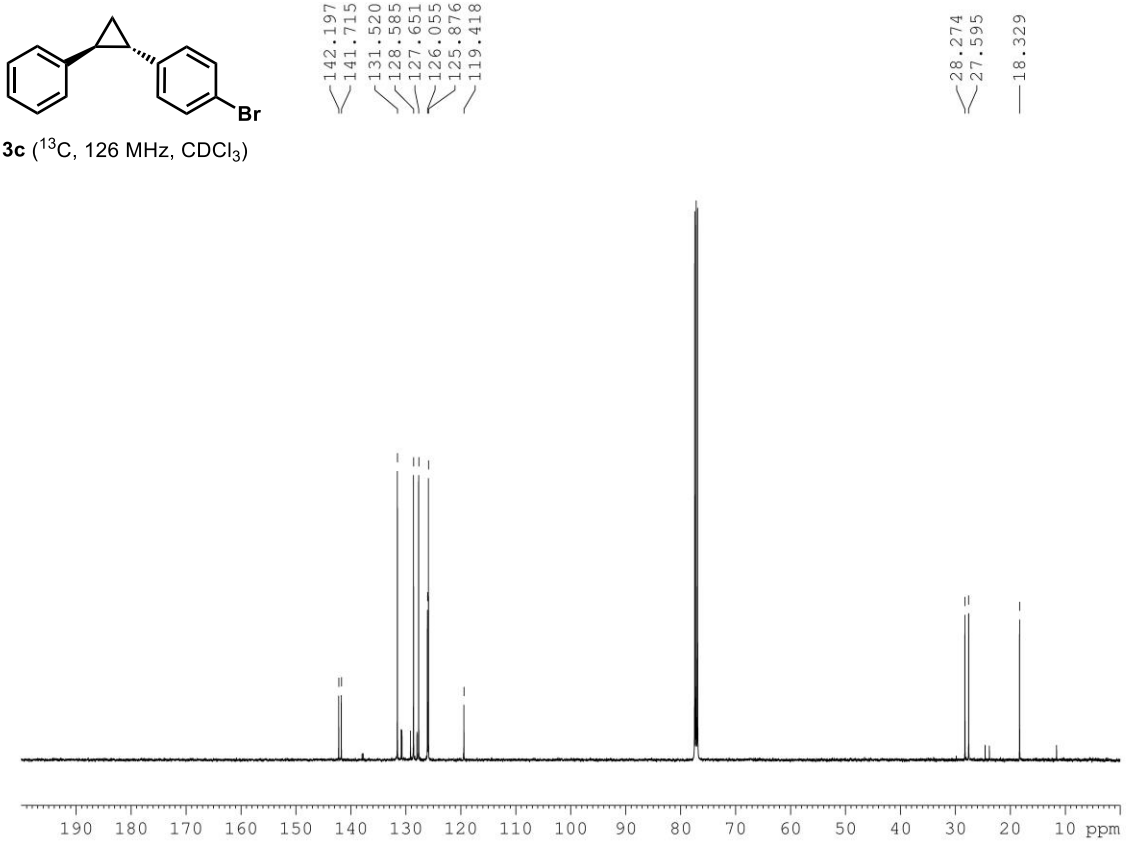
3b (^{1}H, 400 MHz, $CDCl_3$)



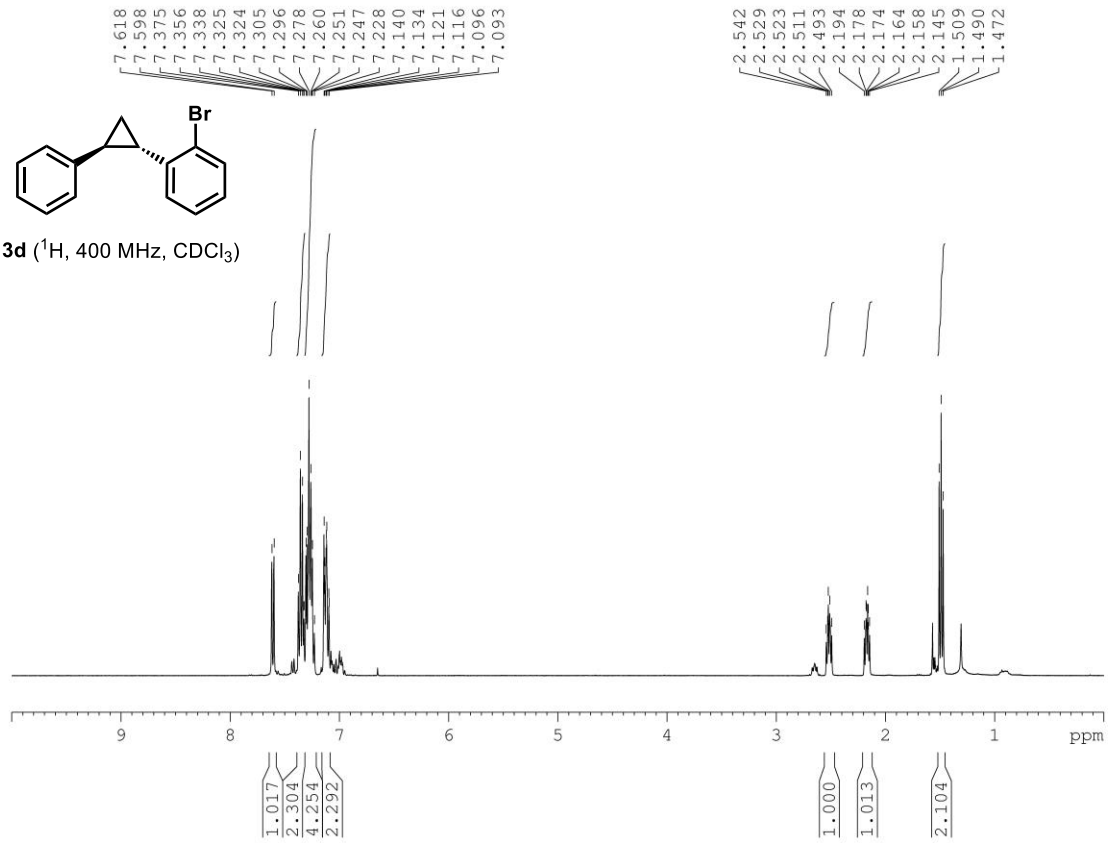
3b (^{13}C, 126 MHz, $CDCl_3$)



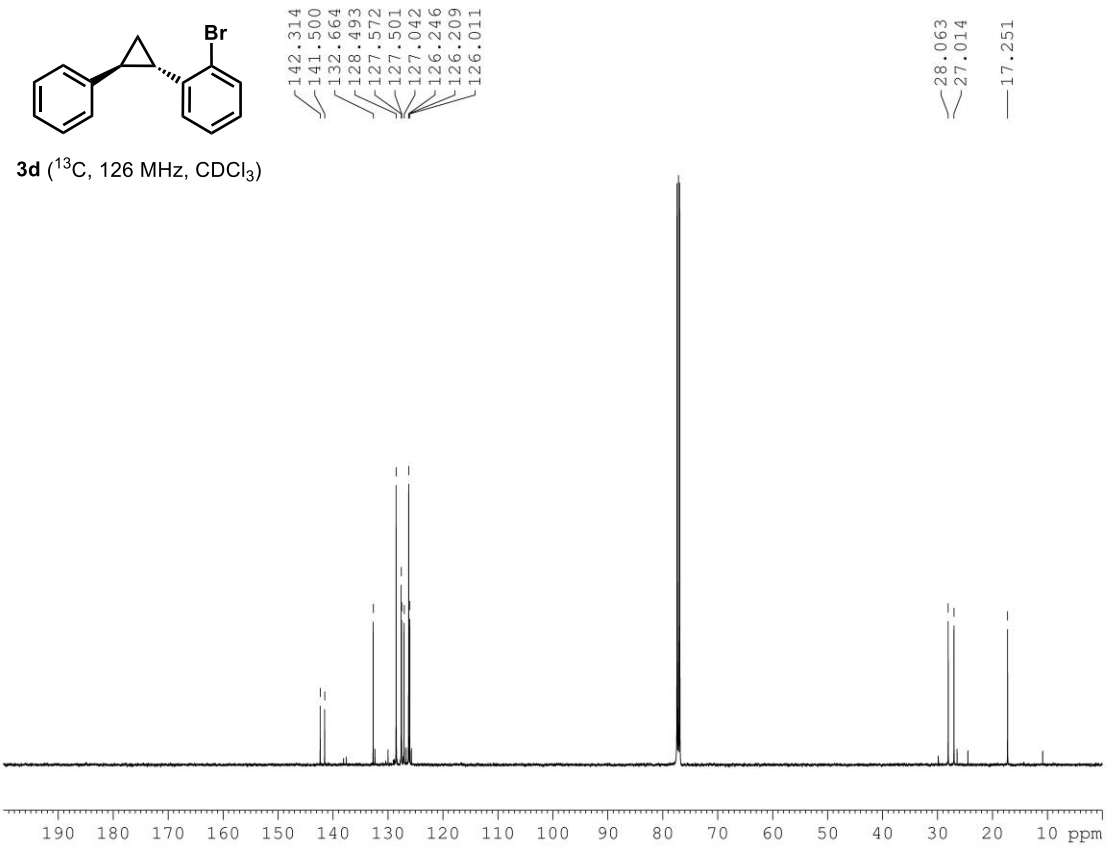
3c (^{1}H, 400 MHz, $CDCl_3$)



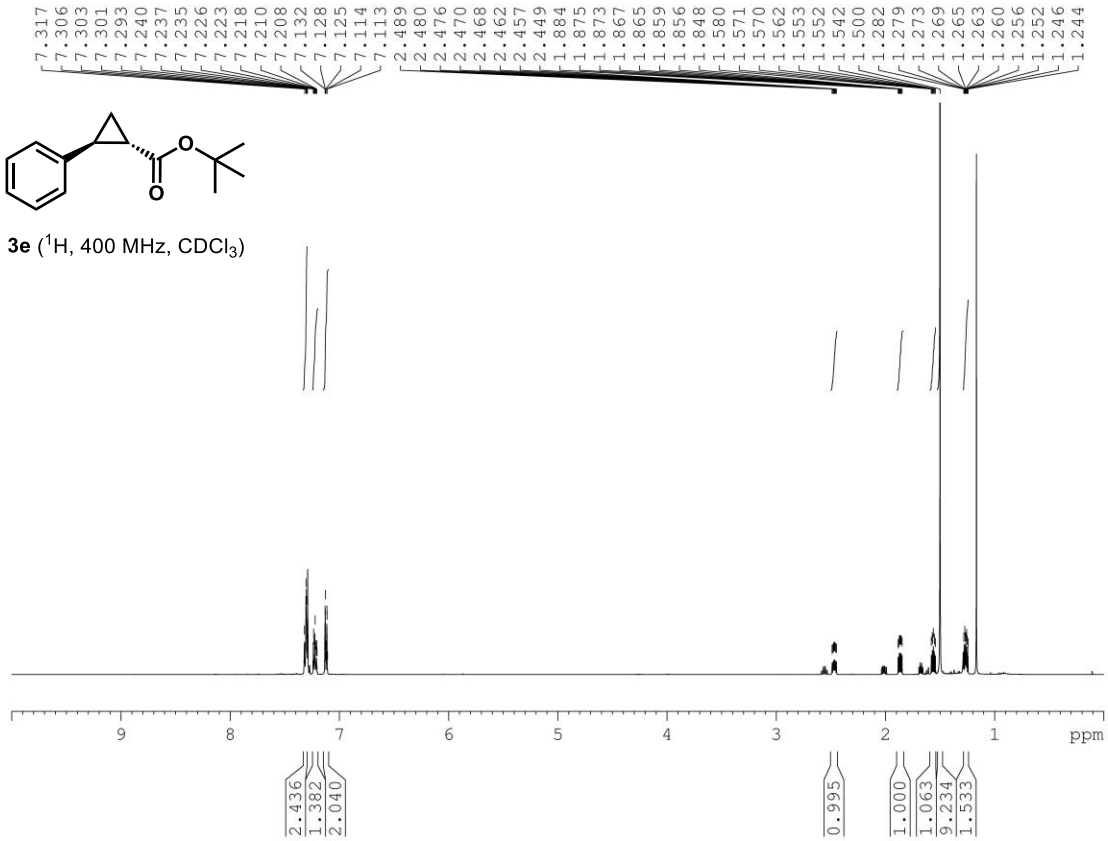
3c (^{13}C, 126 MHz, $CDCl_3$)



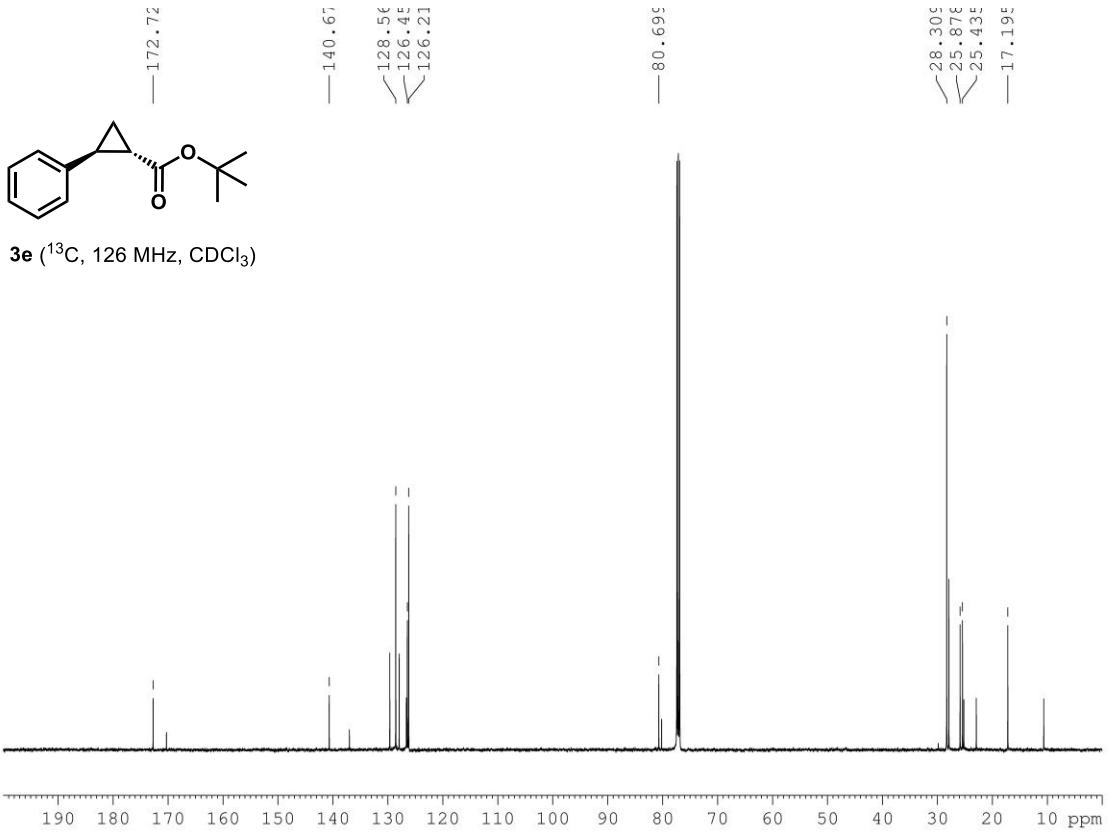
3d (^{1}H, 400 MHz, $CDCl_3$)



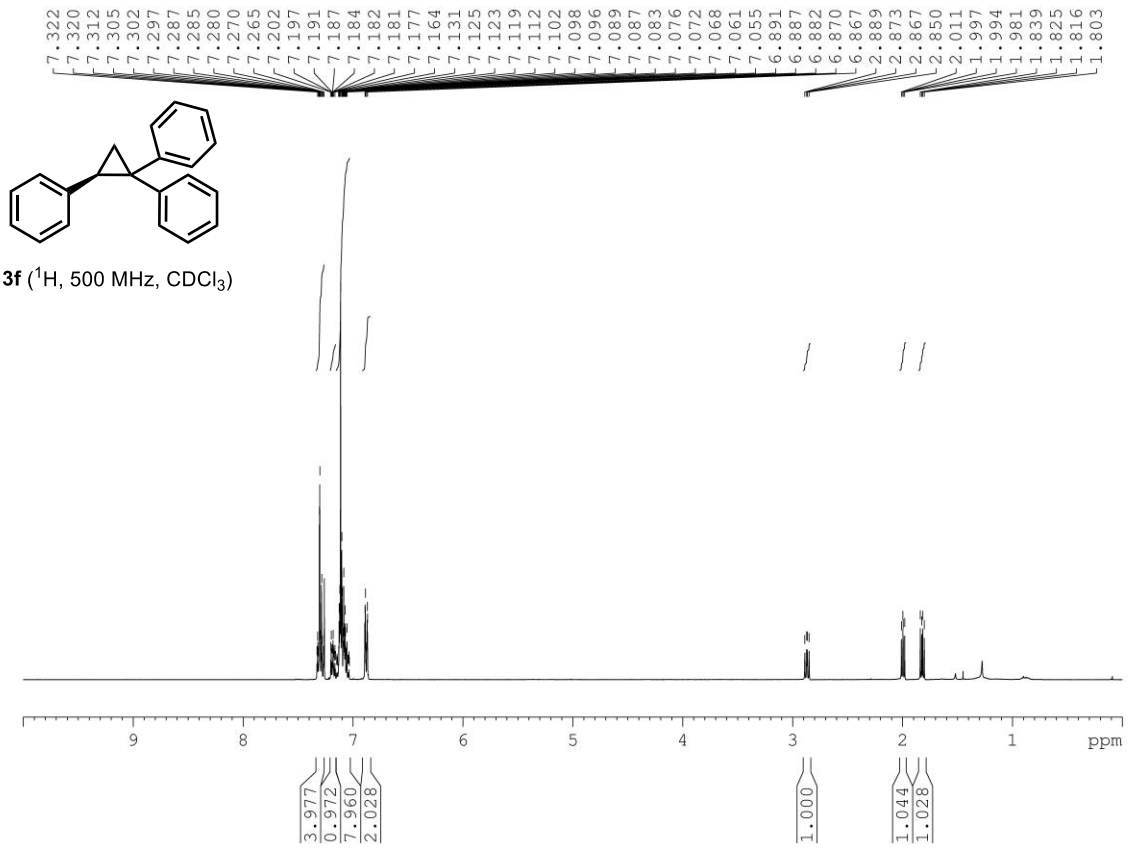
3d (^{13}C, 126 MHz, $CDCl_3$)



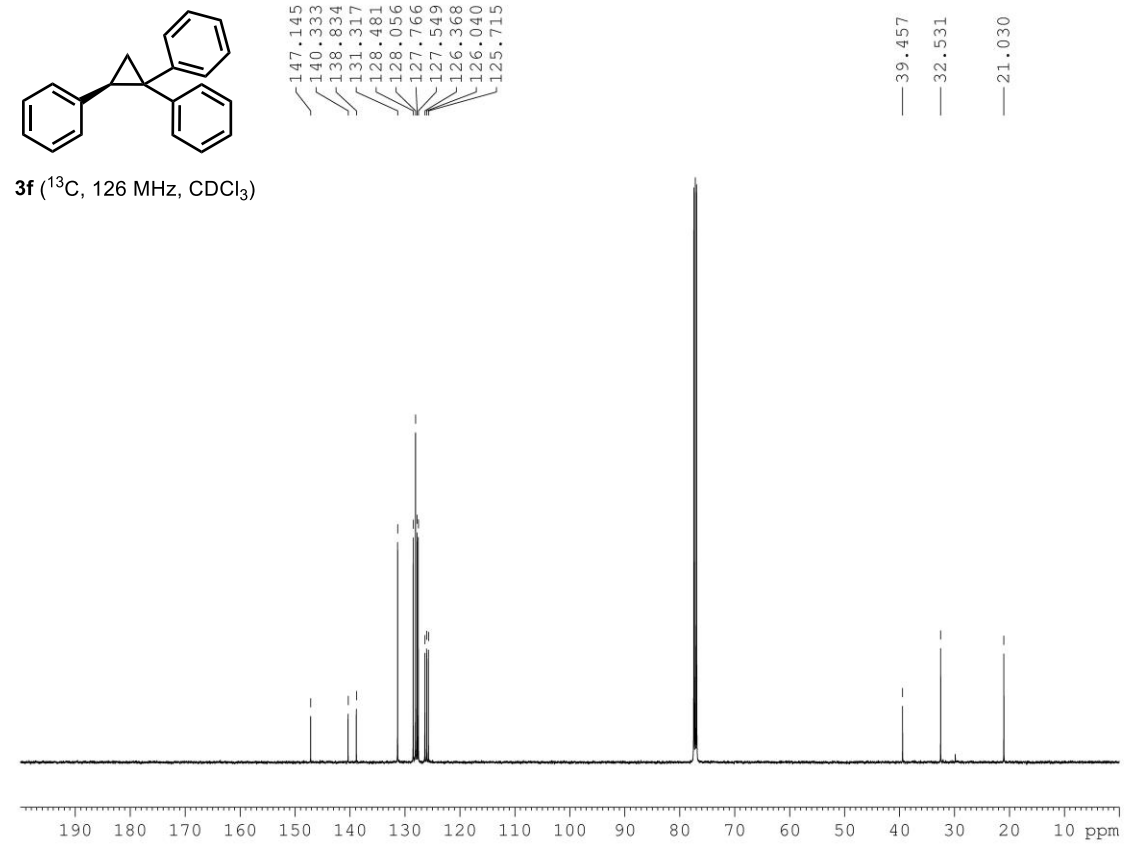
3e (^{1}H, 400 MHz, $CDCl_3$)



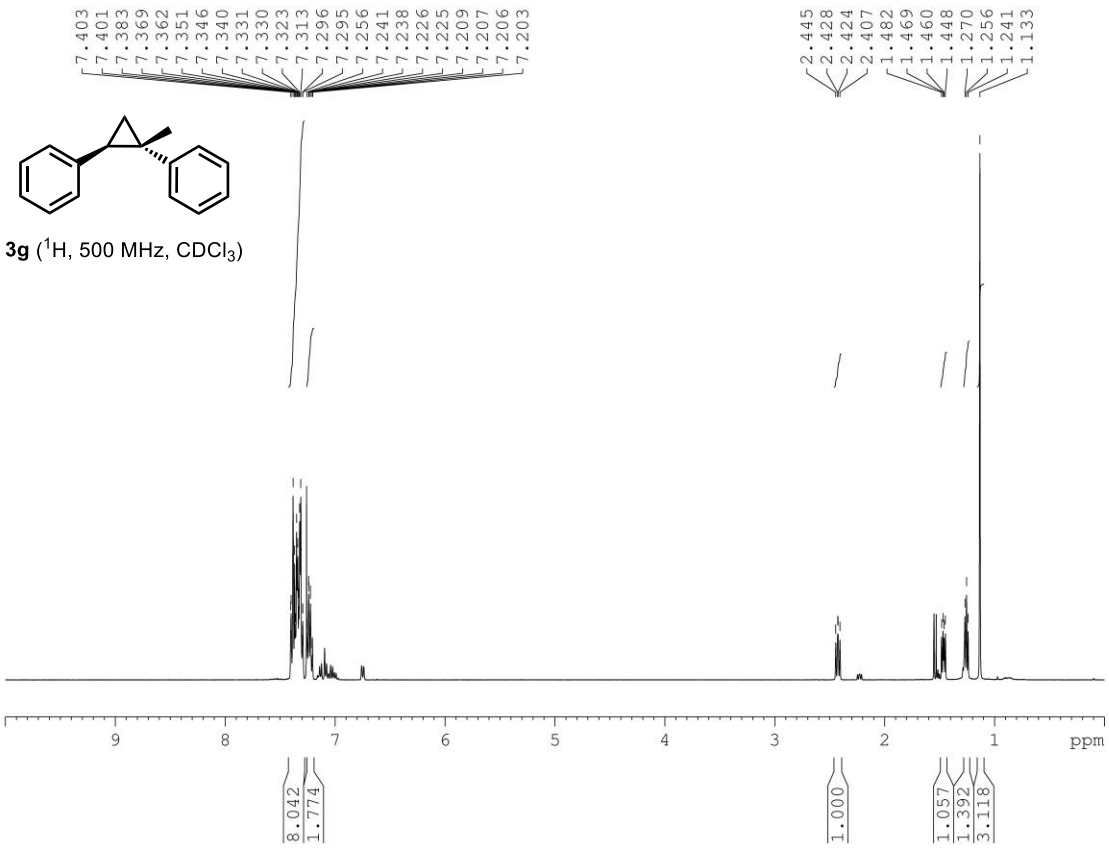
3e (^{13}C, 126 MHz, $CDCl_3$)



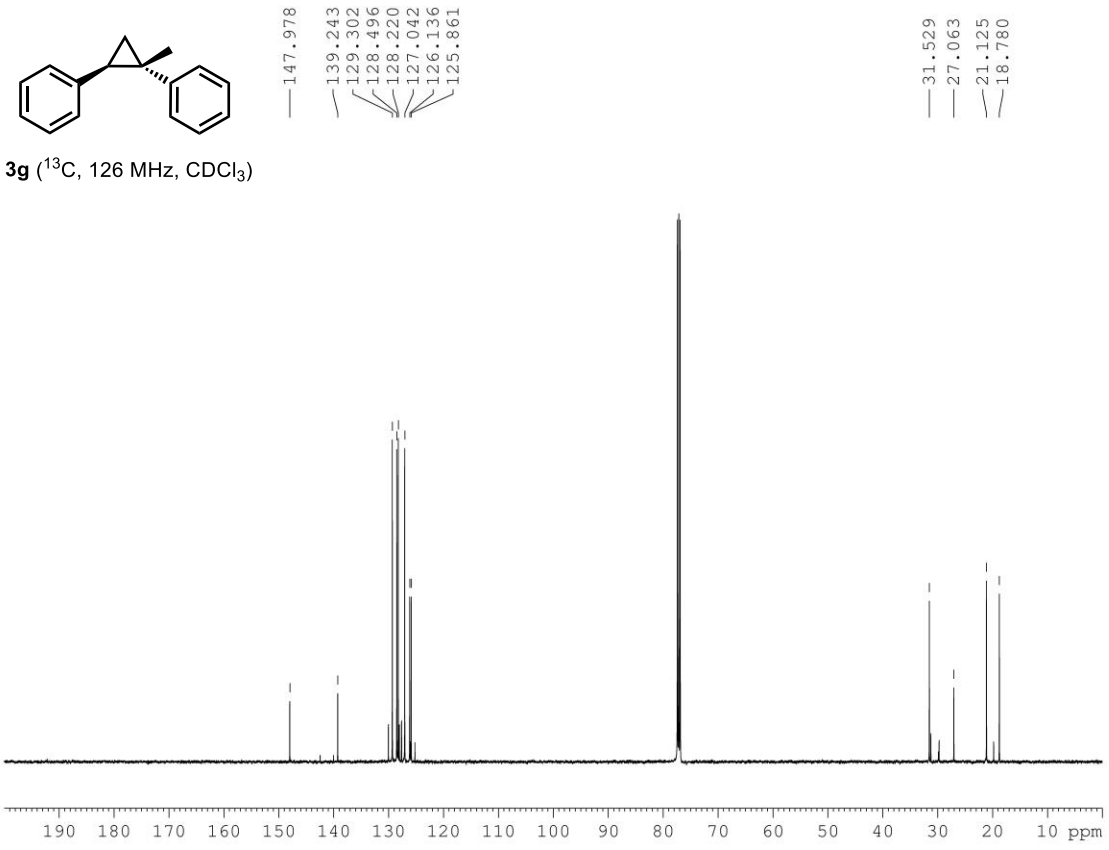
3f (^{1}H, 500 MHz, $CDCl_3$)



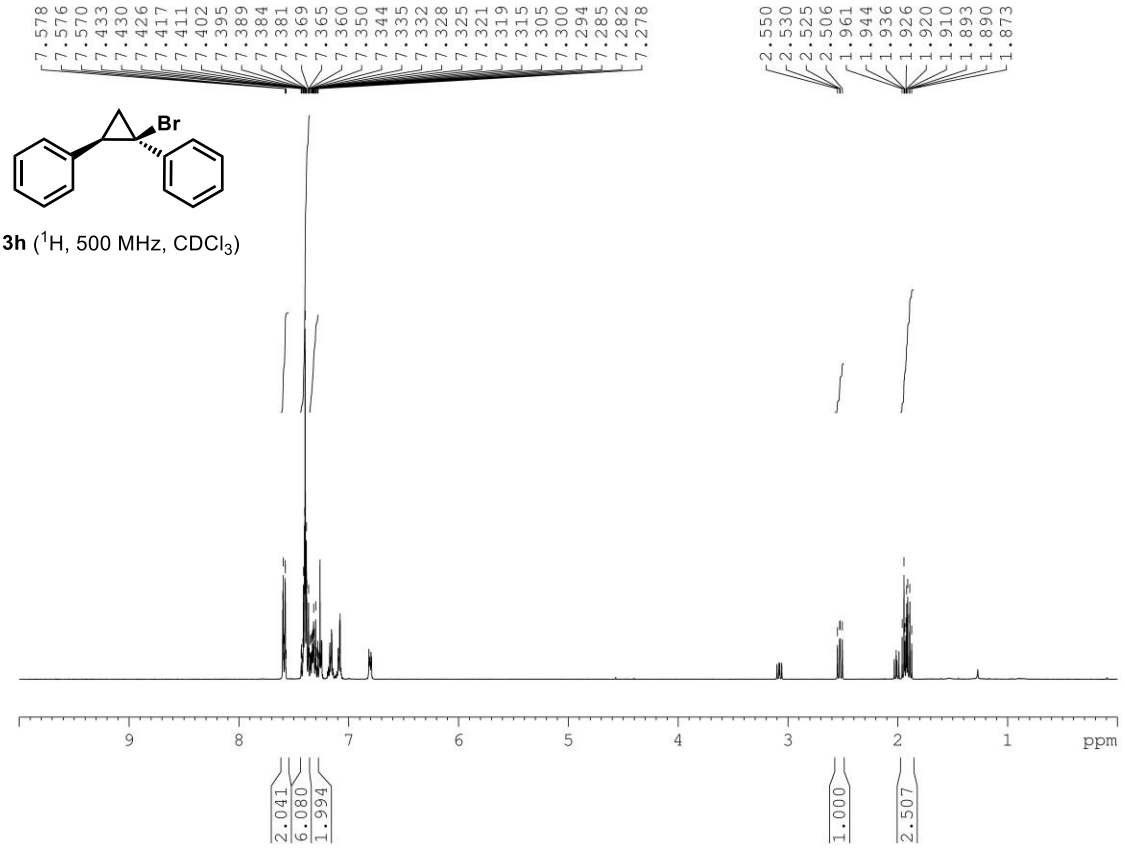
3f (^{13}C, 126 MHz, $CDCl_3$)



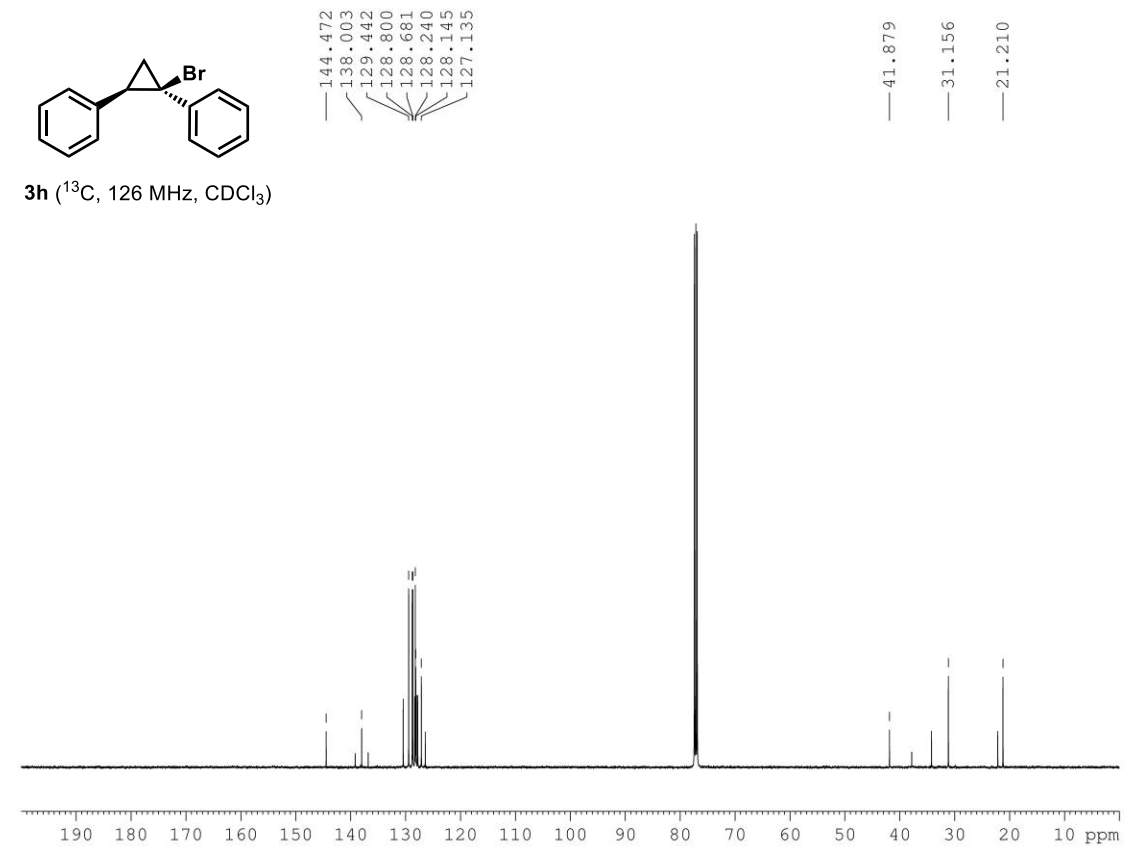
3g (^{1}H, 500 MHz, $CDCl_3$)



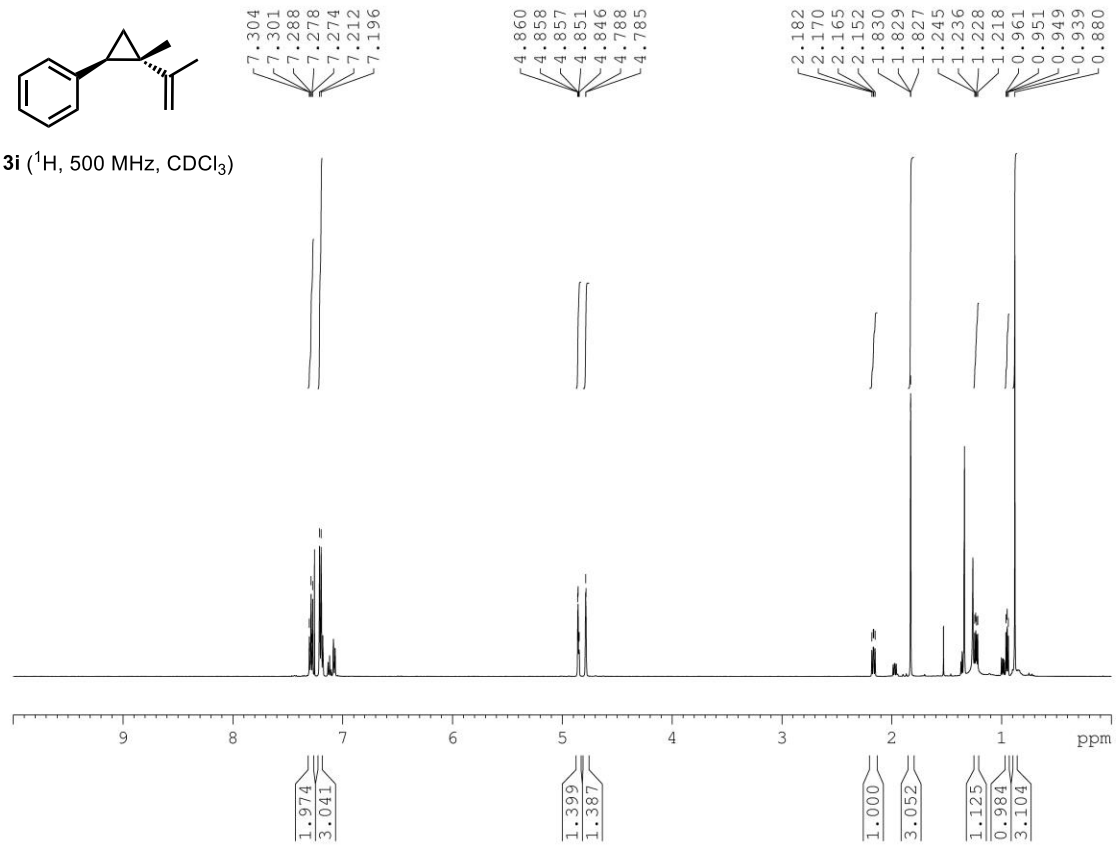
3g (^{13}C, 126 MHz, $CDCl_3$)



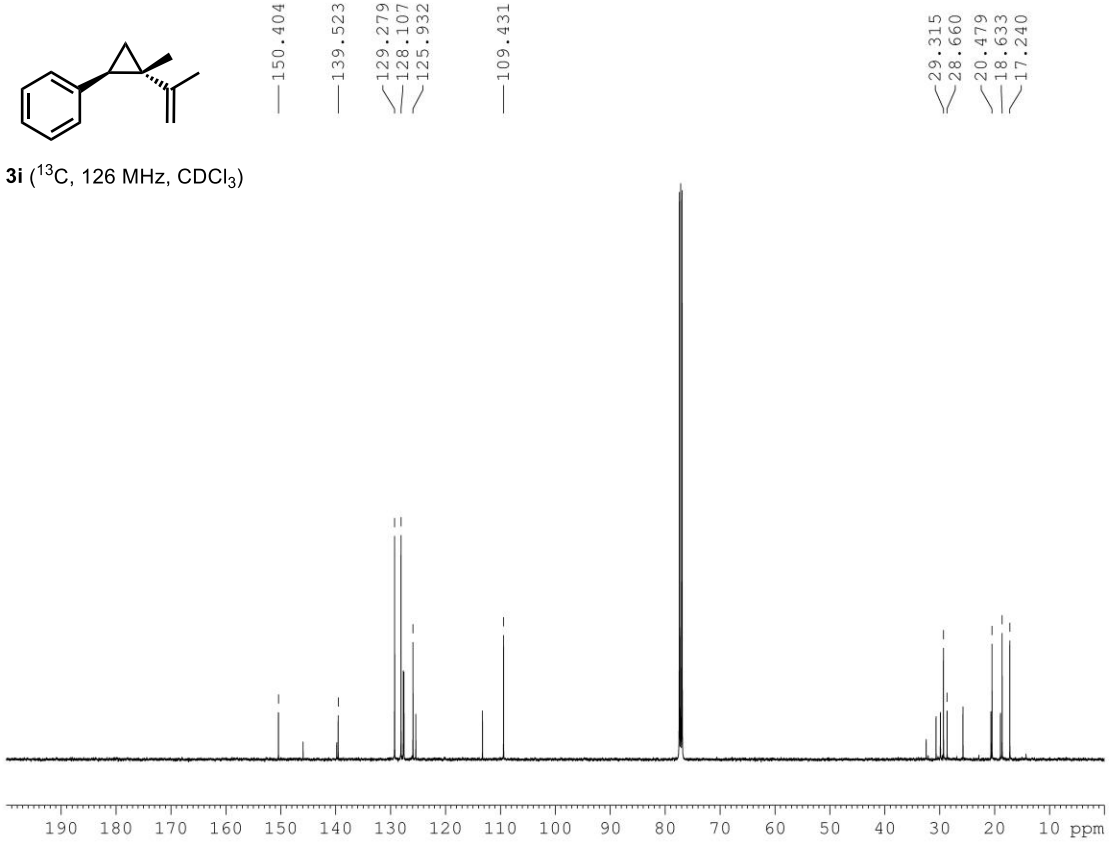
3h (^{1}H, 500 MHz, $CDCl_3$)



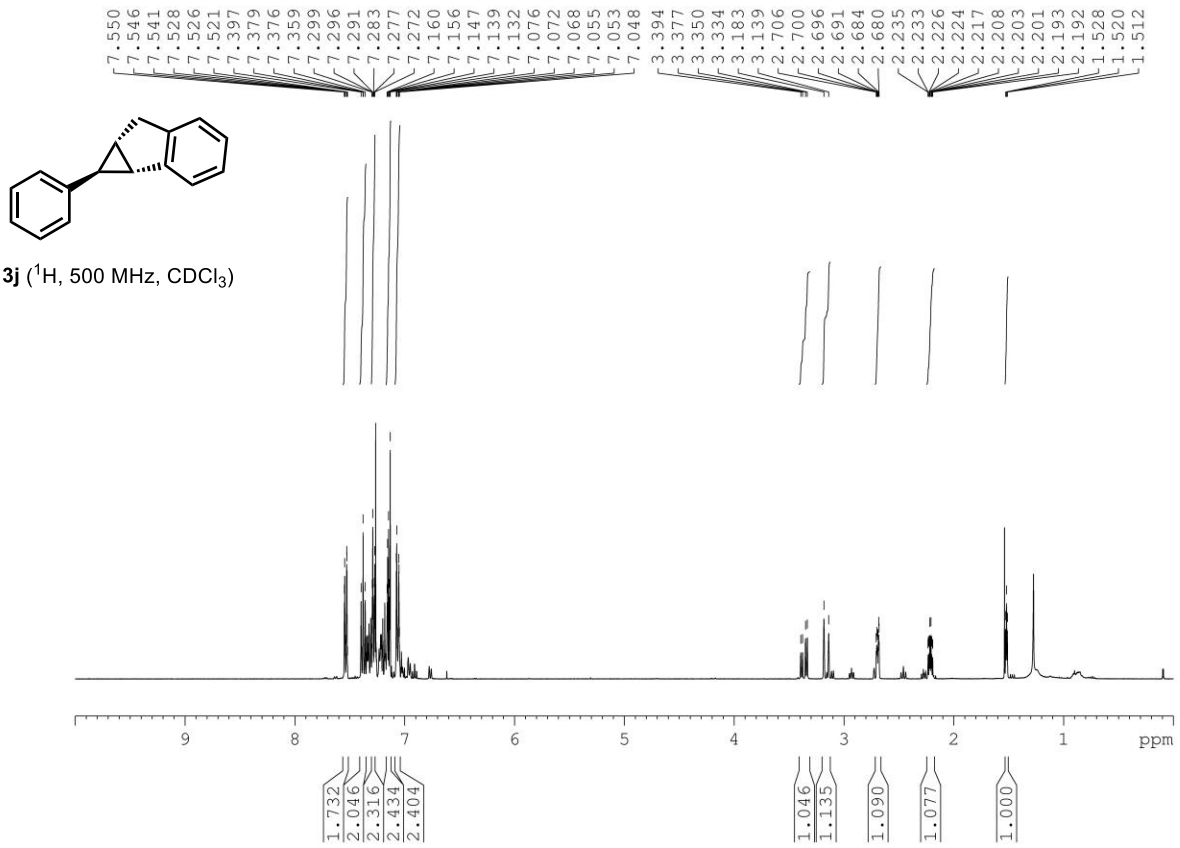
3h (^{13}C, 126 MHz, $CDCl_3$)



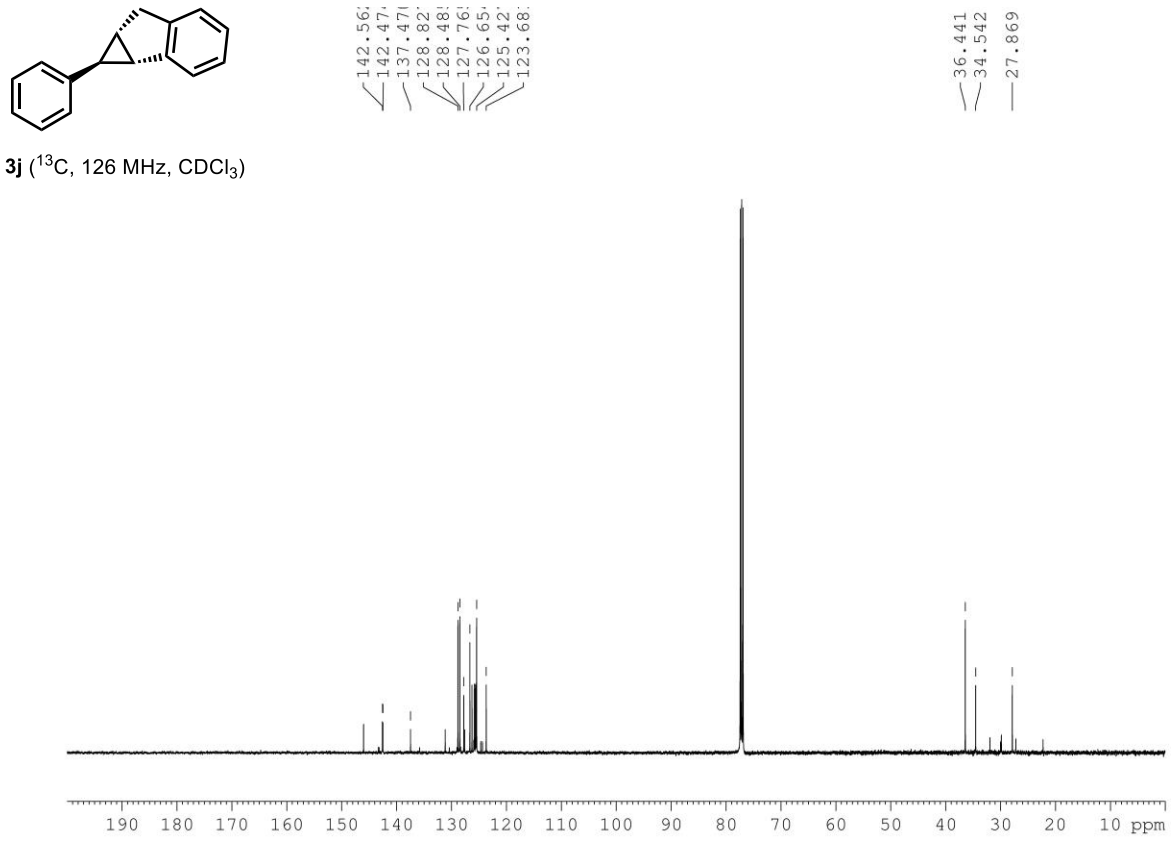
3i (^{1}H, 500 MHz, $CDCl_3$)



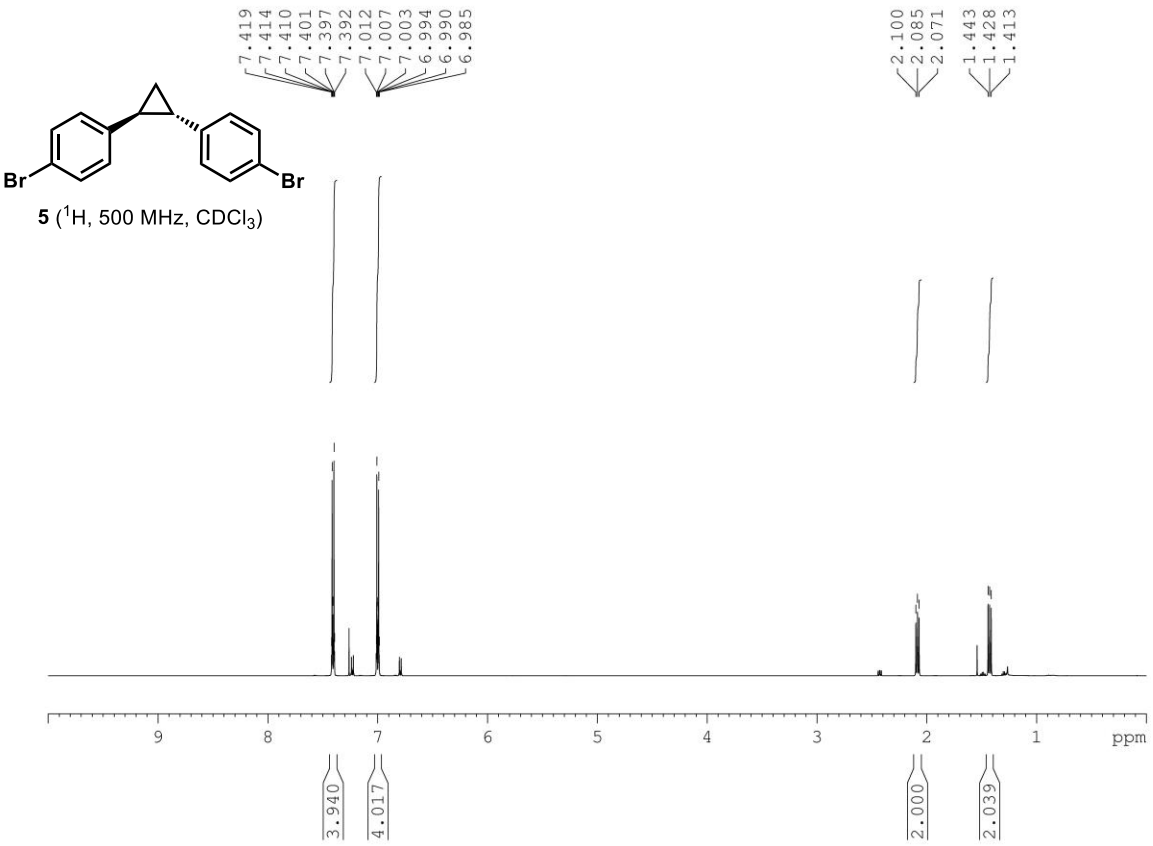
3i (^{13}C, 126 MHz, $CDCl_3$)



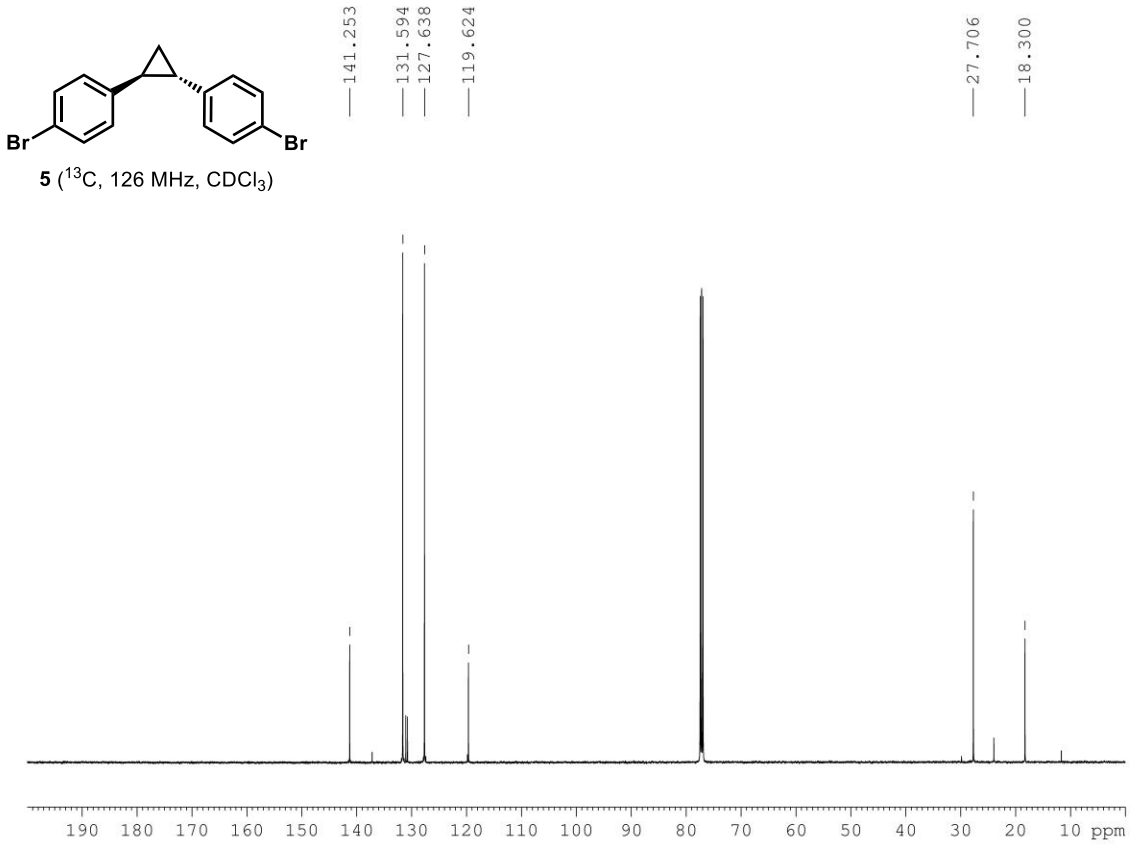
3j (^{1}H, 500 MHz, $CDCl_3$)



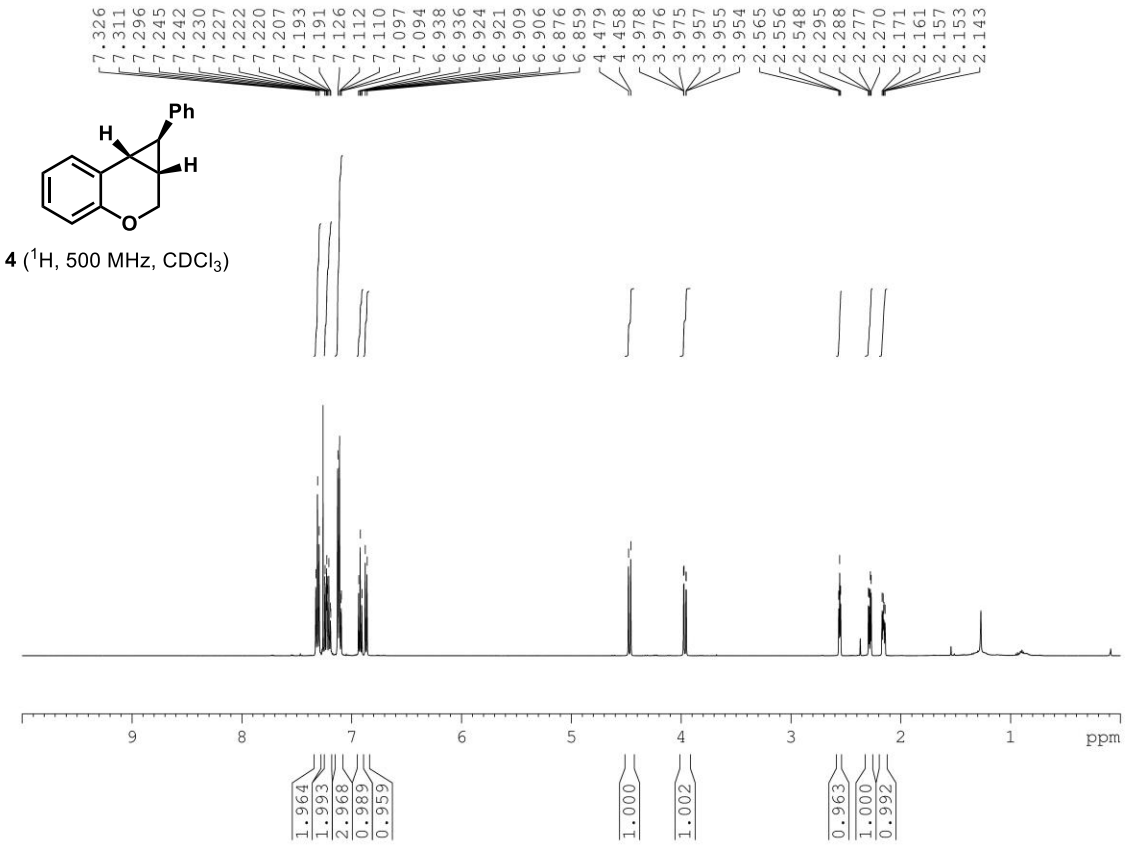
3j (^{13}C, 126 MHz, $CDCl_3$)



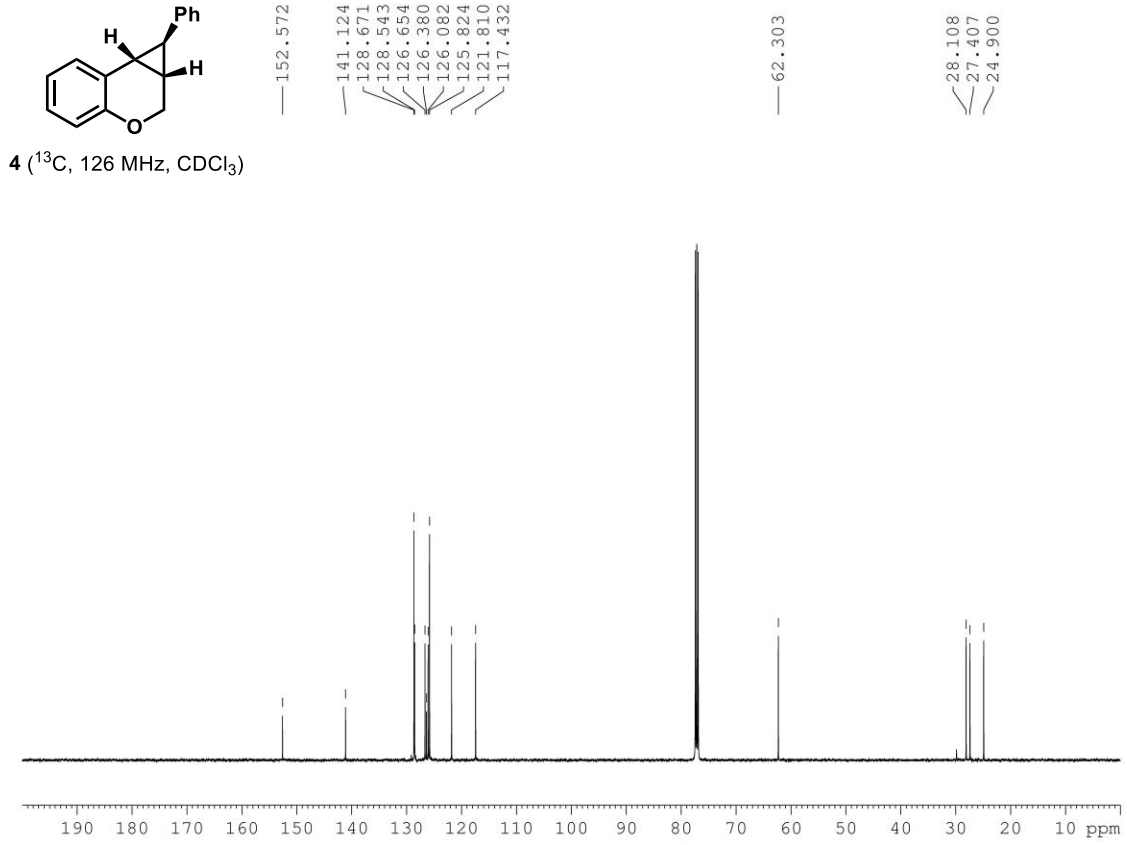
5 (^{1}H, 500 MHz, $CDCl_3$)



5 (^{13}C, 126 MHz, $CDCl_3$)



4 (^{1}H, 500 MHz, $CDCl_3$)



4 (^{13}C, 126 MHz, $CDCl_3$)