Supporting Information for:

Non-stabilized diazoalkane synthesis *via* the oxidation of free hydrazones by iodosylbenzene and application in *in situ* MIRC cyclopropanation

Emmanuelle M. D. Allouche and André B. Charette*

Centre in Green Chemistry and Catalysis (CGCC),
Department of Chemistry, Université de Montréal,
P.O. Box 6128, Station Downtown, Montreal, Quebec, Canada H3C 3J7.

Table of contents

1. General Information

Unless otherwise stated, all alkenes and hydrazones syntheses along with cyclopropanation reactions were run under an argon atmosphere with oven-dried glassware using standard techniques for manipulating air-sensitive compound.[1] Dry CH_2Cl_2 was obtained by filtration under argon through an alumina drying column on a filtration system. EtOAc 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) or using cerium ammonium molybdate stain. 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 spectrometer (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 (ppm) and recorded in $CDCl_3$, using the residual $CHCl_3$ as reference (^{1}H: δ7.26 ppm, ^{13}C: δ77.16 ppm). The data is reported as follows: chemical shift (ppm), multiplicity (s = singlet, br = broad singlet, app. s = apparent singulet, d = doublet, , app. d = apparent 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 sept = septuplet, and m = multiplet, app. m = apparent 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). When ambiguous, proton and carbon assignments were established through COSY, HSQC, and/or DEPT experiments. The relative stereochemistry was verified by NOE experiments when necessary. 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

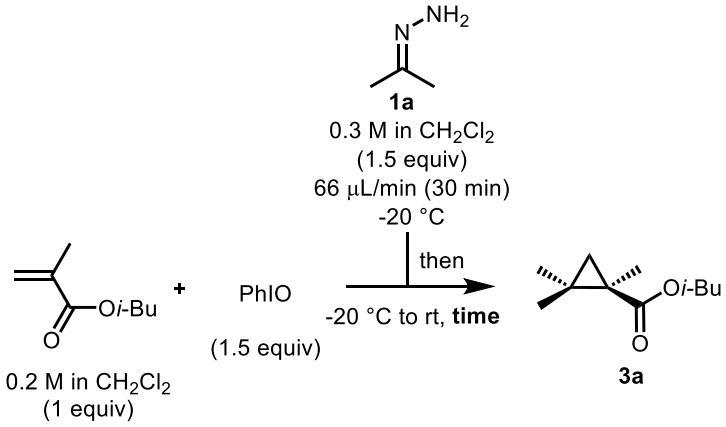
Commercially available reagents were used as supplied or purified by standard techniques where necessary. Non-commercial starting materials were synthesized according to literature procedures.

Caution: Diazoalkanes are toxic, irritating and explosive (shock-sensitive), therefore extreme care should be taken when handling them. No incident occurred during this study as the diazo compounds that are generated are consumed right away in the subsequent cyclopropanation step. Moreover, alkyl diazo compounds decompose very rapidly at room-temperature, hence allowing to bypass the quench step. Nevertheless, if traces are believed to remain, reactions must be quenched using an hydrochloric acid solution prior to work-up.

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

3. Optimization

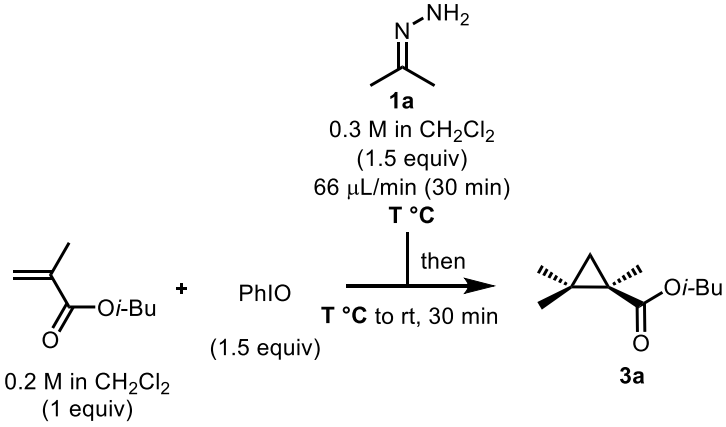
Post-addition reaction time



Entry	time	Yield (%)
1	2 hours	91%[a]
2	30 min	92%[a]
3	15 min	73% [a]

[a] Determined by ^{1}H NMR (Ph_3CH used as internal standard).

Temperature



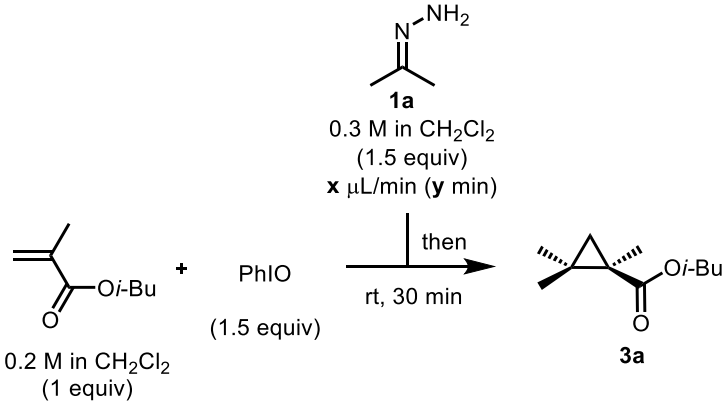
Entry	T °C	Yield (%)
1	-20 °C	92%[a]
2	0 °C	87%[a]
3	rt	quant.[b]

quant. = quantitative yield

[a] Determined by ^{1}H NMR (Ph_3CH used as internal standard).

[b] Isolated yield.

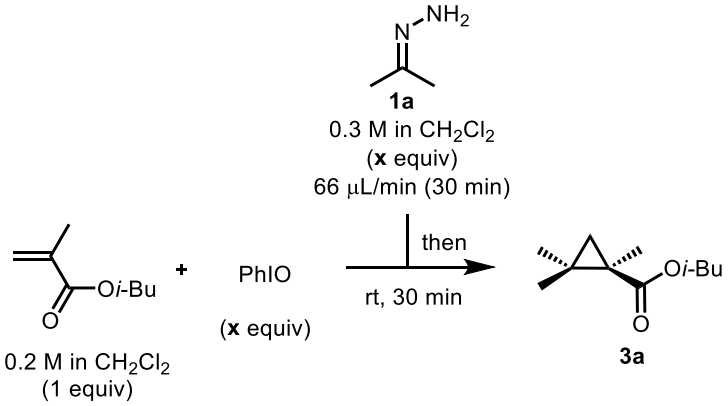
Rate of addition



Entry	Rate of addition (total addition time)	Yield (%)
1	133 μL/min (15 min)	97%[a]
2	66 μL/min (30 min)	quant.[b]
3	47 μL/min (45 min)	quant.[b]

quant. = quantitative yield
[a] Determined by ^{1}H NMR (Ph_3CH used as internal standard).
[b] Isolated yield.

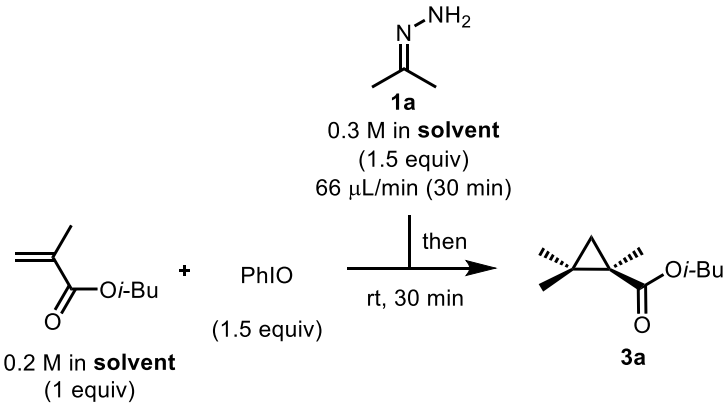
Equivalents of PhIO and hydrazone 1a



Entry	equivalents	Yield (%)
1	1.1 equiv	53%[a]
2	1.5 equiv	quant.[b]

quant. = quantitative yield
[a] Determined by ^{1}H NMR (Ph_3CH used as internal standard).
[b] Isolated yield.

Solvent



Entry	solvent	Yield (%)
1	CH_2Cl_2	quant.[b]
2	EtOAc	quant.[b]
3	MeCN	95%[a]

quant. = quantitative yield
[a] Determined by ^1H NMR (Ph_3CH used as internal standard).
[b] Isolated yield.

4. Experimental Procedures and Characterization Data

1. Preparation of iodosylbenzene

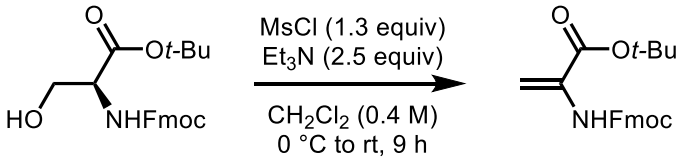
Following a modified literature procedure,[2] iodosylbenzene diacetate (6.0 g, 18.3 mmol, 1.0 equiv) was placed in a 125 mL Erlenmeyer flask, and 110 mL of a 3M sodium hydroxide solution (329 mmol, 18.0 equiv) was added over a 5-minute period under vigorous stirring. The reaction mixture was stirred for an additional 45 minutes. The crude solid was then collected on a fritted funnel and washed with water until neutral pH, and the residual solid was then copiously washed with $CHCl_3$ (250 mL). After being thoroughly dried under reduced pressure overnight, the solid was grounded and put back under strong vacuum for an additional 2 hours. The iodosylbenzene was therefore obtained as a slightly yellow solid (3.21 − 3.29 g, 14.6 – 15.0 mmol, 80 − 82%). Characterization data match the literature.

[2] H. Saltzman, J. G. Sharefkin, *Org. Synth.,* 1963, **43**, 60.

2. Starting alkenes synthesis

Alkenes **3**, **4**, **5**, **6**, **7**, **8**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, **17** were either commercially available or synthesized according to literature procedures. Characterization data match the literature.

Procedure for the synthesis of 9



***tert*-butyl 2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)acrylate (9)**

N-α-Fmoc-L-serine *tert*-butyl ester (synthesized according a literature procedure[3]) (500 mg, 1.30 mmol, 1.0 equiv) was weighed in a flame-dried 25 mL round-bottomed flask equipped with a magnetic stirrer and dissolved with 3.2 mL of anhydrous dichloromethane. The reaction mixture was then cooled down to 0 °C and methanesulfonyl chloride (130 μL, 1.70 mmol, 1.3 equiv) was added. After 5 minutes of stirring under argon at the same temperature, distilled triethylamine (450 μL, 3.26 mmol, 2.5 equiv) was added dropwise. The cooling bath was then removed and the reaction was stirred for 9 hours at room temperature. The reaction mixture was then quenched with cold water and extracted three times with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (20% ethyl acetate in hexanes) to afford 271 mg (0.74 mmol, 57%) of the desired alkene **9** as a clear sticky oil.

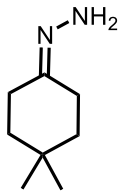
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.32 (td, *J* = 7.5, 1.1 Hz, 2H), 7.29 (br, 1H), 6.16 (br, 1H), 5.70 (s, 1H), 4.44 (d, *J* = 7.1 Hz, 2H), 4.25 (t, *J* = 7.1 Hz, 1H), 1.54 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.06 (Cq), 153.39 (Cq), 143.84 (Cq), 141.47 (Cq), 132.22 (Cq), 127.94 (CH), 127.28 (CH), 125.18 (CH), 120.20 (CH), 105.19 (CH_2), 83.09 (Cq), 67.25 (CH_2), 47.14 (CH), 28.10 (CH_3). **FTIR (cm^{-1}) (neat):** 3409, 3066, 2978, 2934, 1736, 1702, 1511, 1330, 1160, 1079, 1062, 739. **HRMS (ESI, Pos)** calculated for $C_{22}H_{23}NO_4Na$ $[M+Na]^+$: 388.15193 m/z, found 388.15132 m/z.

[3] D. M. Rothman, M. E. Vazquez, E. M. Vogel, B. Imperiali, *J. Org. Chem.*, 2003, **68**, 6795.

3. Hydrazones synthesis

Hydrazones **1a**, **1b**, **1c**, **1d, 1e, 1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1o**, **1p, 1q, 1r** and **1s** were synthesized according to literature procedures. Characterization data match the literature. Crude hydrazones were used directly in the next step without further purification. Some hydrazones may be contaminated by small amounts of the unwanted azines along with traces of solvent (more thorough evaporation would lead the preferential formation of the azine). Purities were determined by ^{1}H NMR prior to use and taken into account for the following steps.

Procedure for the synthesis of hydrazone 1f

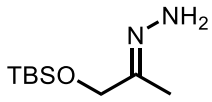


(4,4-dimethylcyclohexylidene)hydrazine (1f)

To a flame-dried 20 mL glass microwave vial equipped with a magnetic stirrer, 4,4-dimethylcyclohexanone (1.4 mL, 10.0 mmol, 1 equiv) was added dropwise to hydrazine monohydrate (5.0 mL, 100.0 mmol, 10 equiv). The vial was then sealed with a pressure cap, put into a 100 °C oil-bath and the reaction mixture was stirred at this temperature overnight. The reaction mixture was then cooled down to room temperature, poured into water and extracted with CH_2Cl_2 (x3). The combined organic layers were washed with brine (x3) and dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum at room temperature to give 1.18 g (8.4 mmol, 84%) of the crude hydrazone as a yellow liquid (75% purity by ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (br, 1H), 2.24 (td, *J* = 6.6, 4.4 Hz, 4H), 1.45 (dt, *J* = 9.1, 6.9 Hz, 4H), 0.99 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.26 (Cq), 39.19 (CH_2), 37.81 (CH_2), 31.29 (CH_2), 30.41 (Cq), 27.94 (CH_3), 20.70 (CH_2).

Procedure for the synthesis of hydrazone 1m



(1-((*tert*-butyldimethylsilyl)oxy)propan-2-ylidene)hydrazine (1n)

1-((*tert*-butyldimethylsilyl)oxy)propan-2-one (synthesized according a literature procedure[4]) (600.0 mg, 3.2 mmol, 1 equiv) was weighed in an oven-dried 5 mL glass microwave vial equipped with a magnetic stirrer. The vial was sealed with a pressure cap and hydrazine monohydrate (790 μL, 16.0 mmol, 5 equiv) was added at once. The reaction mixture was then put into a 100 °C oil-bath and stirred at this temperature overnight. The reaction mixture was then cooled down to room temperature, poured into water and extracted with CH_2Cl_2 (x3). The combined organic layers were washed with brine (x3) and dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum at room temperature to give 576 mg (2.88 mmol, 90%) of the crude hydrazone as a clear liquid (82% purity by ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (br, 2H), 4.13 (s, 2H), 1.78 (s, 3H), 0.90 (s, 9H), 0.07 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 150.64 (Cq), 67.88 (CH_2), 26.00 (CH_3), 18.44 (Cq), 10.87 (CH_3), -5.17 (CH_3).

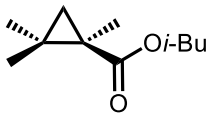
[4] M. S. Davey, R. Malde, R. C. Mykura, A. T. Baker, T. E. Taher, C. S. Le Duff, B. E. Willcox, Y. Mehellou, *J. Med. Chem.,* 2018, **61**, 2111.

4. Cyclopropanes synthesis

General procedure for MIRC-type cyclopropanation reaction

In an oven-dried 5 mL glass microwave vial equipped with a magnetic stirrer were weighed iodosylbenzene (133.0 mg, 0.60 mmol, 1.5 equiv) along with the chosen substrate (0.40 mmol, 1.0 equiv) if solid. The flask was then capped and flushed with argon during few minutes, after which the chosen solvent (2 mL) was added. If liquid, the chosen substrate was added at this moment via micropipette, and the flask was purged again with argon during few minutes. A freshly prepared 2 mL hydrazone solution (0.60 mmol, 1.5 equiv) in the chosen solvent was then added over 30 minutes using a syringe pump set to 4 mL/hour (= 66 μL/min), causing an instantaneous gas evolution released thanks to the presence of the argon inlet. The reaction mixture was vigorously stirred for an additional 30 minutes (for the Michael acceptors scope) or for an additional 2-hour (for the hydrazones scope). The reaction mixture was then filtrated over a short pad of celite® and copiously washed with the chosen solvent, followed by evaporation under reduced pressure. For more stable diazo compounds (products **8n**, **8o**, **8p**, **8q**), an acidic work-up was necessary: the reaction mixture was quenched with a 2M HCl aqueous solution and diluted with the chosen solvent. The layers were separated and the aqueous one was extracted three times with the chosen solvent. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography.

Characterization data



(±)-isobutyl (*R*)-1,2,2-trimethylcyclopropane-1-carboxylate (3a)

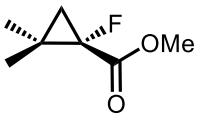
Synthesized in EtOAc from acetone hydrazone **1a** (84.7% purity) (50.9 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellowish oil (73.4 mg, 0.40 mmol, 100%). **Rf** (10% ethyl acetate in hexanes) = 0.33. The characterization data match the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (d, *J* = 6.7 Hz, 2H), 2.02 (d, *J* = 12.9 Hz, 1H), 1.96 (sept, *J* = 6.7 Hz, 1H), 1.63 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 1.32 (d, *J* = 13.0 Hz, 1H), 0.93 (d, *J* = 0.7 Hz, 3H), 0.92 (d, *J* = 0.7 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.37 (Cq), 96.47 (Cq), 92.20 (Cq), 71.84 (CH_2), 41.76 (CH_2), 27.84 (CH), 27.69 (CH_3), 26.80 (CH_3), 23.96 (CH_3), 19.13 (CH_3).

Procedure for the reaction run under air with from-the-bottle ethyl acetate

In a 5 mL glass microwave vial equipped with a magnetic stirrer was weighted iodosylbenzene (133.0 mg, 0.60 mmol, 1.5 equiv). From-the-bottle ethyl acetate (2 mL) was then added along with isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) via micropipette. A freshly prepared 2 mL acetone hydrazone **1a** solution (84.7% purity) (50.9 mg, 0.60 mmol, 1.5 equiv) in from-the-bottle ethyl acetate was then added over 30 minutes using a syringe pump set to 4 mL/hour (= 66 μL/min), causing an instantaneous gas evolution. The reaction mixture was vigorously stirred for an additional 30 minutes. The reaction mixture was then quenched with a 2M HCl aqueous solution and diluted with ethyl acetate. The layers were separated and the aqueous one was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellowish oil (59.8 mg, 0.324 mmol, 81%).

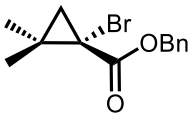
[5] P. Rulliere, G. Benoit, E. M. D. Allouche, A. B. Charette, *Angew. Chem., Int. Ed.,* 2018, **57**, 5777.



(±)-methyl (*S*)-1-fluoro-2,2-dimethylcyclopropane-1-carboxylate (4a)

Synthesized in CH_2Cl_2 from acetone hydrazone **1a** (94.3% purity) (45.5 mg, 0.60 mmol, 1.5 equiv) and methyl 2-fluoroacrylate (39 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellow oil (49.7 mg, 0.344 mmol, 86%). **Rf** (10% ethyl acetate in hexanes) = 0.36. The characterization data match the literature.[5]

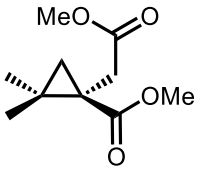
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 3H), 2.09 (dd, *J* = 22.5, 14.4 Hz, 1H), 1.75 (dd, *J* = 25.6, 14.4 Hz, 1H), 1.52 (s, 3H), 1.49 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.38 (d, *J* = 30.0 Hz, Cq), 122.96 (d, *J* = 221.1 Hz, Cq), 93.32 (Cq), 53.64 (CH_3), 39.86 (d, *J* = 21.7 Hz, CH_2), 27.07 (CH_3), 25.84 (d, *J* = 4.1 Hz, CH_3).



(±)-benzyl (*S*)-1-bromo-2,2-dimethylcyclopropane-1-carboxylate (5a)

Synthesized in CH_2Cl_2 from acetone hydrazone **1a** (84.7% purity) (51.4 mg, 0.60 mmol, 1.5 equiv) and benzyl 2-bromoacrylate (97.1 mg, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellow oil (61.9 mg, 0.22 mmol, 54%). **Rf** (10% ethyl acetate in hexanes) = 0.30.

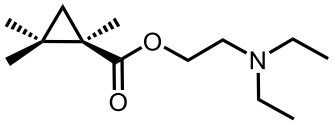
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 5.31 (d, *J* = 2.2 Hz, 2H), 2.40 (d, *J* = 14.9 Hz, 1H), 2.18 (d, *J* = 14.9 Hz, 1H), 1.51 (s, 3H), 1.43 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.45 (Cq), 134.71 (Cq), 128.82 (CH), 128.33 (CH), 92.31 (Cq), 91.33 (Cq), 68.97 (CH_2), 44.52 (CH_2), 26.91 (CH_3), 25.13 (CH_3). **FTIR (cm^{-1}) (neat):** 2975, 2930, 2874, 1719, 1454, 1381, 1270, 594. **HRMS (ESI, Pos)** calculated for $C_{13}H_{15}Br_1O_2Na$ $[M+Na]^+$: 305.01476 m/z, found 305.01531 m/z.



(±)-methyl (*S*)-1-(2-methoxy-2-oxoethyl)-2,2-dimethylcyclopropane-1-carboxylate (6a)

Synthesized in EtOAc from acetone hydrazone **1a** (82.0% purity) (54.2 mg, 0.60 mmol, 1.5 equiv) and dimethyl itaconate (57 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 30% ethyl acetate in hexanes) yielded a yellow oil (82.0 mg, 0.40 mmol, 100%). **Rf** (30% ethyl acetate in hexanes) = 0.32. The characterization data match the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.69 (s, 3H), 3.55 (d, *J* = 16.7 Hz, 1H), 2.64 (d, *J* = 16.7 Hz, 1H), 2.26 (d, *J* = 13.5 Hz, 1H), 1.48 (s, 3H), 1.47 (d, *J* = 13.4 Hz, 1H), 1.44 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.25 (Cq), 169.64 (Cq), 98.35 (Cq), 93.65 (Cq), 53.29 (CH_3), 52.18 (CH_3), 41.08 (CH_2), 39.25 (CH_2), 27.79 (CH_3), 26.66 (CH_3).

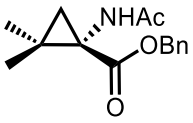


(±)-2-(diethylamino)ethyl (*R*)-1,2,2-trimethylcyclopropane-1-carboxylate (7a)

Synthesized in EtOAc from acetone hydrazone **1a** (82.0% purity) (52.6 mg, 0.60 mmol, 1.5 equiv) and 2-(diethylamino)ethyl methacrylate (81 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% dichloromethane to 10% methanol in dichloromethane) yielded a reddish oil (90.6 mg, 0.40 mmol, 100%). **Rf** (10% methanol in dichloromethane) = 0.31.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.27 – 4.19 (m, 2H), 2.71 (t, *J* = 6.2 Hz, 2H), 2.56 (q, *J* = 7.0 Hz, 4H), 2.03 (d, *J* = 13.0 Hz, 1H), 1.62 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.31 (d, *J* = 13.0 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.40 (Cq), 96.30 (Cq), 92.15 (Cq), 63.93 (CH_2), 51.09 (CH_2), 47.66 (CH_2), 41.71 (CH_2), 27.67 (CH_3), 26.79 (CH_3), 23.99 (CH_3), 12.08 (CH_3). **FTIR (cm^{-1}) (neat):** 2969, 2933, 2873, 1734, 1454, 1376, 1292, 1244, 1160, 1067. **HRMS (ESI, Pos)** calculated for $C_{13}H_{26}NO_2$ $[M+H]^+$: 228.19581 m/z, found 228.19654 m/z.

[6] E. Leonel, J.-P. Paugam, S. Condon-Gueugnot, J.-Y. Nedelec, *Tetrahedron* 1998, **54**, 3207. S. Sengmany, E. Léonel, J.-P. Paugam, J.-Y. Nédélec, *Tetrahedron* 2002**, 58**, 271.



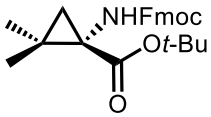
(±)-benzyl (*S*)-1-acetamido-2,2-dimethylcyclopropane-1-carboxylate (8a)

Synthesized in EtOAc from acetone hydrazone **1a** (95.9% purity) (45.8 mg, 0.61 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (89.1 mg, 0.405 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 50% ethyl acetate in hexanes) yielded a yellow solid (110.5 mg, 0.405 mmol, 100%). **Rf** (50% ethyl acetate in hexanes) = 0.26. The characterization data match the literature.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 3H), 7.30 – 7.28 (m, 2H), 7.17 (br, 1H), 5.26 (d, *J* = 12.0 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 2.05 (s, 3H), 1.95 (d, *J* = 1.02 Hz, 2H), 1.65 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.18 (Cq), 167.80 (Cq), 134.23 (Cq), 129.07 (CH), 128.89 (CH), 128.63 (CH), 104.09 (Cq), 95.20 (Cq), 69.03 (CH_2), 38.40 (CH_2), 26.38 (CH_3), 26.20 (CH_3), 23.89 (CH_3).

Procedure for the 6-fold scale-up reaction run under air with from-the-bottle ethyl acetate

In a 50 mL round-bottom flask equipped with a magnetic stirrer were weighted iodosylbenzene (816.0 mg, 3.63 mmol, 1.5 equiv) along with benzyl 2-acetamidoacrylate (531.0 mg, 2.42 mmol, 1.0 equiv). From-the-bottle ethyl acetate (12 mL) was then added. A freshly prepared 12 mL acetone hydrazone **1a** solution (67.0% purity) (391 mg, 3.63 mmol, 1.5 equiv) in from-the-bottle ethyl acetate was then added over 3 hours using a syringe pump set to 4 mL/hour (= 66 μL/min), causing an instantaneous gas evolution. The reaction mixture was vigorously stirred overnight. The reaction mixture was then quenched with a 2M HCl aqueous solution and diluted with ethyl acetate. The layers were separated and the aqueous one was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure.The crude product was then purified by silica gel chromatography (using a gradient from 100% hexanes to 50% ethyl acetate in hexanes) yielded a yellow solid (500 mg, 1.91 mmol, 79%).



(±)-*tert*-butyl (*S*)-1-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-2,2-dimethylcyclopropane-1-carboxylate (9a)

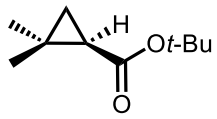
Synthesized in CH_2Cl_2 from acetone hydrazone **1a** (67.3% purity) (50.7 mg, 0.473 mmol, 1.5 equiv) and *tert*-butyl 2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)acrylate **9** (115.0 mg, 0.316 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 20% ethyl acetate in hexanes) yielded a white solid (129.0 mg, 0.316 mmol, 100%). **Rf** (20% ethyl acetate in hexanes) = 0.48. **mp**: 56 – 110 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 8.2 Hz, 2H), 7.40 (tt, *J* = 7.5, 0.82 Hz, 2H), 7.31 (tt, *J* = 8.1, 1.4 Hz, 2H), 6.73 (br, 1H), 4.38 – 4.30 (m, 2H), 4.21 (t, *J* = 7.1 Hz, 1H), 1.91 (app. s, 2H), 1.68 (s, 3H), 1.50 (s, 3H), 1.49 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.77 (Cq), 153.79 (Cq), 143.97 (Cq), 143.73 (Cq), 141.45 (Cq), 127.88 (CH), 127.23 (CH), 125.29 (CH), 125.25 (CH), 120.14 (CH), 104.20 (Cq), 94.43 (Cq), 85.24 (Cq), 67.12 (CH_2), 47.13 (CH), 38.57 (CH_2), 27.93 (CH_3), 26.56 (CH_3), 26.33 (CH_3). **FTIR (cm^{-1}) (neat):** 3413, 2977, 1725, 1495, 1314, 1147, 739. **HRMS (ESI, Pos)** calculated for $C_{25}H_{30}NO_4$ $[M+H]^+$: 408.21693 m/z, found 408.21672 m/z.

(±)-(*R*)-1,2,2-trimethylcyclopropane-1-carbonitrile (10a)

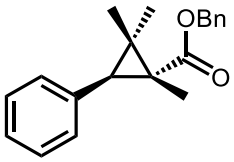
Synthesized in CH_2Cl_2 from acetone hydrazone **1a** (82.0% purity) (53.5 mg, 0.60 mmol, 1.5 equiv) and methacrylonitrile (34 μL, 0.405 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellow oil (37.1 mg, 0.34 mmol, 84%). **Rf** (10% ethyl acetate in hexanes) = 0.13.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (d, *J* = 13.3 Hz, 1H), 1.80 (s, 3H), 1.52 (s, 3H), 1.45 (s, 3H), 1.43 (d, *J* = 13.3 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 119.32 (Cq), 94.18 (Cq), 83.76 (Cq), 43.35 (CH_2), 27.15 (CH_3), 26.22 (CH_3), 25.39 (CH_3). **FTIR (cm^{-1}) (neat):** 2960, 2929, 2874, 2230, 1450, 1384, 1211, 1116. **HRMS (ESI, Pos)** calculated for $C_7H_{12}N_1$ $[M+H]^+$: 110.09643 m/z, found 110.09616 m/z.



(±)-tert-butyl (*R*)-2,2-dimethylcyclopropane-1-carboxylate (11a)

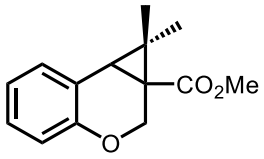
Synthesized in CH_2Cl_2 from acetone hydrazone **1a** (77.5% purity) (55.8 mg, 0.60 mmol, 1.5 equiv) and *tert*-butyl acrylate (58 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. The desired product was observed in 27% (determined by ^{1}H NMR, using triphenylmethane as internal standard). However full conversion of the starting material was confirmed by NMR. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a mixture of the desired cyclopropane with the corresponding pyrazole. **Rf** (10% ethyl acetate in hexanes) = 0.38.



(±)-benzyl (1*R*,3*S*)-1,2,2-trimethyl-3-phenylcyclopropane-1-carboxylate (12a)

Synthesized in EtOAc from acetone hydrazone **1a** (95.9% purity) (45.5 mg, 0.60 mmol, 1.5 equiv) and trans-β-methylstyrene (116 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 4% ethyl acetate in hexanes) yielded a yellow oil (61.9 mg, 0.21 mmol, 52%). **Rf** (4% ethyl acetate in hexanes) = 0.14.

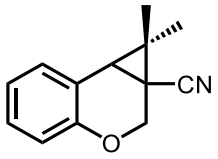
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38– 7.30 (m, 5H), 7.27 – 7.24 (m, 3H), 6.97 – 6.93 (m, 2H), 5.25 (d, *J* = 12.3 Hz, 1H), 5.20 (d, *J* = 12.3 Hz, 1H), 3.27 (s, 1H), 1.54 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.12 (Cq), 135.44 (Cq), 135.42 (Cq), 130.95 (CH), 128.73 (CH), 128.57 (CH), 128.40 (CH), 128.28 (CH), 127.47 (CH), 96.64 (Cq), 92.21 (Cq), 67.56 (CH_2), 55.49 (CH), 27.56 (CH_3), 23.51 (CH_3), 20.00 (CH_3). **FTIR (cm^{-1}) (neat):** 3063, 2974, 2932, 2871, 1731, 1455, 1377, 1106, 751, 697. **HRMS (ESI, Pos)** calculated for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.16926 m/z, found 295.17047 m/z.



(±)-methyl 1,1-dimethyl-1,7b-dihydrocyclopropa[*c*]chromene-1a(2*H*)-carboxylate (13a)

Synthesized in EtOAc from acetone hydrazone **1a** (89.0% purity) (48.7 mg, 0.60 mmol, 1.5 equiv) and methyl 2*H*-chromene-3-carboxylate (76.2 mg, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellowish solid (93.0 mg, 0.40 mmol, 100%). **Rf** (10% ethyl acetate in hexanes) = 0.36. **mp**: 70 - 76 °C.

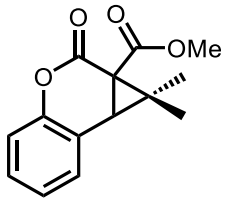
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.9, 1.7 Hz, 1H), 7.07 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.99 (td, *J* = 7.5, 1.2 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 3H), 3.37 (s, 1H), 1.65 (s, 3H), 0.94 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.56 (Cq), 155.48 (Cq), 129.94 (CH), 128.43 (CH), 123.23 (Cq), 122.90 (CH), 117.76 (CH), 101.09 (Cq), 97.32 (Cq), 68.52 (CH_2), 53.52 (CH_3), 43.97 (CH), 28.86 (CH_3), 23.68 (CH_3). **FTIR (cm^{-1}) (neat):** 2977, 2927, 2854, 1732, 1490, 1454, 1433, 1273, 1220, 1023, 954, 760. **HRMS (ESI, Pos)** calculated for $C_{14}H_{17}O_3$ $[M+H]^+$: 233.11722 m/z, found 233.11755 m/z.



(±)-1,1-dimethyl-1,7b-dihydrocyclopropa[*c*]chromene-1a(2*H*)-carbonitrile (14a)

Synthesized in EtOAc from acetone hydrazone **1a** (89% purity) (48.9 mg, 0.60 mmol, 1.5 equiv) and 2*H*-chromene-3-carbonitrile (63.2 mg, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a white solid (80.0 mg, 0.40 mmol, 100%). **Rf** (10% ethyl acetate in hexanes) = 0.44. **mp**: 52 - 56 °C.

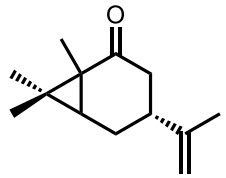
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.20 (m, 1H), 7.08 – 7.03 (m, 2H), 6.95 – 6.93 (m, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.28 (d, *J* = 11.7 Hz, 1H), 3.29 (s, 1H), 1.68 (s, 3H), 1.03 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.69 (Cq), 129.92 (CH), 129.22 (CH), 123.50 (CH), 120.47 (Cq), 118.24 (CH), 116.40 (Cq), 98.61 (Cq), 87.78 (Cq), 68.35 (CH_2), 46.30 (CH), 28.99 (CH_3), 23.57 (CH_3). **FTIR (cm^{-1}) (neat):** 2956, 2922, 2851, 1459, 1225, 1036, 1024, 761. **HRMS (ESI, Pos)** calculated for $C_{13}H_{13}N_1O_1Na$ $[M+Na]^+$: 222.08894 m/z, found 222.08917 m/z.



(±)-methyl 1,1-dimethyl-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1a(2*H*)-carboxylate (15a)

Synthesized in CH_2Cl_2 from acetone hydrazone **1a** (77.5% purity) (56.1 mg, 0.60 mmol, 1.5 equiv) and methyl 2-oxo-2*H*-chromene-3-carboxylate (82.1 mg, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 4% ethyl acetate in hexanes) yielded a yellowish solid (76.5 mg, 0.31 mmol, 77%). **Rf** (10% ethyl acetate in hexanes) = 0.23. **mp**: 66 - 76 °C.

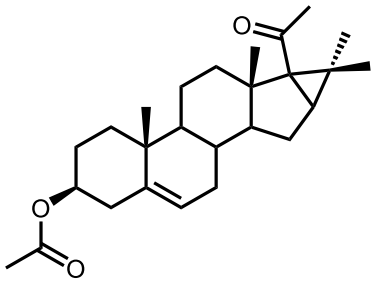
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.34 – 7.29 (m, 2H), 7.24 – 7.19 (m, 2H), 3.79 (s, 3H), 1.62 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.02 (Cq), 163.80 (CH), 160.79 (Cq), 151.22 (Cq), 136.65 (Cq), 128.79 (CH), 125.89 (CH), 125.50 (CH), 123.23 (Cq), 122.03 (CH), 52.90 (CH), 37.67 (Cq), 26.83 (CH_3). **FTIR (cm^{-1}) (neat):** 2953, 2924, 2854, 1729, 1717, 1437, 1239, 1048, 1033, 756. **HRMS (ESI, Pos)** calculated for $C_{14}H_{15}O_4$ $[M+H]^+$: 247.09649 m/z, found 247.09636 m/z.



(4*R*)-1,7,7-trimethyl-4-(prop-1-en-2-yl)bicyclo[4.1.0]heptan-2-one (16a)

Synthesized in CH_2Cl_2 from acetone hydrazone **1a** (77.5% purity) (55.2 mg, 0.60 mmol, 1.5 equiv) and (*R*)-(-)-carvone (62 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 30% ethyl acetate in hexanes) yielded a yellow oil (39.5 mg, 0.21 mmol, 52%). **Rf** (10% ethyl acetate in hexanes) = 0.07.

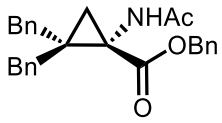
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.72 (s, 1H), 2.55 – 2.39 (m, 3H), 1.90 – 1.75 (m, 3H), 1.73 (s, 3H), 1.69 (s, 3H), 1.48 (s, 3H), 1.24 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 208.79 (Cq), 146.51 (Cq), 110.82 (CH_2), 96.51 (Cq), 92.14 (Cq), 48.34 (CH), 43.60 (CH_2), 41.18 (CH), 28.02 (CH_3), 27.21 (CH_2), 24.02 (CH_3), 21.76 (CH_3), 20.50 (CH_3). **FTIR (cm^{-1}) (neat):** 3078, 2970, 2928, 2871, 1711, 1645, 1453, 1373, 1230, 1101, 892. **HRMS (ESI, Pos)** calculated for $C_{13}H_{21}O_1$ $[M+H]^+$: 193.1587 m/z, found 193.158 m/z.



(4S,6a*R*, 8a*S*)-8b-acetyl-6a,8a,9,9-tetramethyl-1,3,4,5,6,6a,6b,7,8,8a,8b,9,9a,10,10a,10b-hexadecahydrocyclopropa[3,4]cyclopenta[1,2-a]phenanthren-4-yl acetate (17a)

Synthesized in EtOAc from acetone hydrazone **1a** (77.5% purity) (56.8 mg, 0.61 mmol, 1.5 equiv) and (3*S*,10*R*,13*S*)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1*H*-cyclopenta[a]phenanthren-3-yl acetate (145 mg, 0.41 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 20% ethyl acetate in hexanes) yielded a yellowish solid (83.5 mg, 0.21 mmol, 51%). **Rf** (20% ethyl acetate in hexanes) = 0.43. **mp**: 138 - 142 °C.

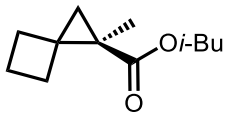
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.32 (d, *J* = 5.1 Hz, 1H), 4.60 – 4.53 (m, 1H), 2.60 (d, *J* = 9.1 Hz, 1H), 2.42 (s, 3H), 2.33 – 2.21 (m, 3H), 2.14 (td, *J* = 13.0, 3.6 Hz, 1H), 2.02 (s, 3H), 1.95 (ddd, *J* = 11.7, 4.9, 2.2 Hz, 1H), 1.87 – 1.82 (m, 2H), 1.70 – 1.65 (m, 2H), 1.61 – 1.52 (m, 2H), 1.50 – 1.45 (m, 2H), 1.44 (s, 3H), 1.26 – 1.19 (m, 1H), 1.14 – 1.07 (m, 1H), 1.01 (s, 3H), 1.00 (s, 3H), 0.93 – 0.82 (m, 1H), 0.78 (s, 3H), 0.51 (ddd, *J* = 13.9, 10.0, 5.9 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 203.45 (Cq), 170.64 (Cq), 139.91 (Cq), 121.94 (CH), 121.30 (Cq), 91.40 (Cq), 73.85 (CH), 51.76 (CH), 49.27 (CH), 48.32 (Cq), 42.32 (CH), 38.10 (CH_2), 37.01 (CH_2), 36.63 (Cq), 33.67 (CH_2), 31.85 (CH_2), 31.38 (CH_3), 29.98 (CH), 27.95 (CH_2), 27.85 (CH_3), 27.77 (CH_2), 21.86 (CH_3), 21.54 (CH_3), 20.88 (CH_2), 19.34 (CH_3), 15.74 (CH_3). **FTIR (cm^{-1}) (neat):** 2958, 2924, 2852, 1731, 1707, 1455, 1361, 1244, 1031, 805. **HRMS (ESI, Pos)** calculated for $C_{26}H_{39}O_3$ $[M+H]^+$: 399.28937 m/z, found 399.28972 m/z.



(±)-benzyl (*S*)-1-acetamido-2,2-dibenzylcyclopropane-1-carboxylate (8b)

Synthesized in EtOAc from dibenzyl ketone hydrazone **1b** (93.9% purity) (145.0 mg, 0.61 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (88.7 mg, 0.405 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 50% ethyl acetate in hexanes) yielded a yellow oil (160.6 mg, 0.39 mmol, 96%). **Rf** (50% ethyl acetate in hexanes) = 0.68.

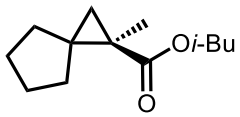
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 3H), 7.28 – 7.22 (m, 8H), 7.19 – 7.16 (m, 2H), 7.00 – 6.98 (m, 2H), 5.08 (d, *J* = 12.3 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H). 4.65 (br, 1H), 3.62 (d, *J* = 13.9 Hz, 1H), 3.30 (d, *J* = 13.7 Hz, 1H), 3.14 (d, *J* = 13.7 Hz, 1H), 2.83 (d, *J* = 13.9 Hz, 1H), 2.42 (d, *J* = 14.4 Hz, 1H), 1.58 (s, 3H), 1.55 (d, *J* = 14.5 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.84 (Cq), 166.71 (Cq), 136.27 (Cq), 135.69 (Cq), 135.20 (Cq), 131.37 (CH), 130.89 (CH), 128.68 (CH), 128.57 (CH), 128.51 (CH), 128.46 (CH), 128.34 (CH), 127.26 (CH), 127.15 (CH), 104.21 (Cq), 101.99 (Cq), 68.23 (CH_2), 44.91 (CH_2), 43.19 (CH_2), 33.44 (CH_2), 22.75 (CH_3). **FTIR (cm^{-1}) (neat):** 3263, 3029, 2955, 2924, 2854, 1737, 1658, 1495, 1454, 1371, 1276, 1255, 1215, 1116, 752, 735, 696. **HRMS (ESI, Pos)** calculated for $C_{27}H_{28}NO_3$ $[M+H]^+$: 414.20637 m/z, found 414.20659 m/z.



(±)-isobutyl (*R*)-1-methylspiro[2.3]hexane-1-carboxylate (3c)

Synthesized in EtOAc from cyclobutanone hydrazone **1c** (81.8% purity) (61.5 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellow liquid (55.6 mg, 0.285 mmol, 100%). **Rf** (10% ethyl acetate in hexanes) = 0.37.

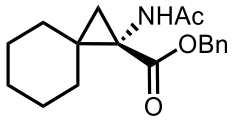
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (dd, *J* = 8.2, 4.4 Hz, 1H), 3.89 (dd, *J* = 8.2, 4.3 Hz, 1H), 2.68 – 2.61 (m, 2H), 2.45 – 2.37 (m, 1H), 2.27 – 2.19 (m, 2H), 2.16 (d, *J* = 13.3 Hz, 1H), 2.04 – 1.97 (m, 1H), 1.97 – 1.89 (m, 1H), 1.54 (d, *J* = 13.3 Hz, 1H), 1.52 (s, 3H), 0.91 (d, *J* = 1.2 Hz, 3H), 0.90 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.00 (Cq), 94.45 (Cq), 94.12 (Cq), 71.74 (CH_2), 41.29 (CH_2), 32.94 (CH_2), 32.80 (CH_2), 27.81 (CH), 22.60 (CH_3), 19.11 (CH_3), 19.10 (CH_3), 16.49 (CH_2). **FTIR (cm^{-1}) (neat):** 2962, 2935, 2875, 1733, 1469, 1455, 1262, 1169, 1129, 990, 893. **HRMS (ESI, Pos)** calculated for $C_{12}H_{21}O_2$ $[M+H]^+$: 197.15361 m/z, found 197.15372 m/z.



(±)-isobutyl (R)-1-methylspiro[2.4]heptane-1-carboxylate (3d)

Synthesized in EtOAc from cyclopentatone hydrazone **1d** (86.2% purity) (68.1 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellowish liquid (83.9 mg, 0.40 mmol, 100%). **Rf** (10% ethyl acetate in hexanes) = 0.42.

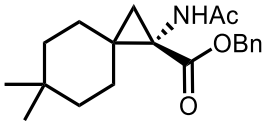
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (dd, *J* = 7.7, 3.7 Hz, 1H), 3.91 (dd, *J* = 7.7, 3.7 Hz, 1H), 2.18 – 2.08 (m, 2H), 2.10 (d, *J* = 13.0 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.99 – 1.92 (m, 1H), 1.83 – 1.74 (m, 2H), 1.68 – 1.61 (m, 2H), 1.58 (s, 3H), 1.44 (d, *J* = 13.0 Hz, 1H), 0.93 (d, *J* = 1.2 Hz, 3H), 0.91 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.42 (Cq), 100.74 (Cq), 94.89 (Cq), 71.75 (CH_2), 41.66 (CH_2), 39.09 (CH_2), 38.60 (CH_2), 27.84 (CH), 25.95 (CH_2), 25.73 (CH_2), 23.10 ((CH_3), 19.14 ((CH_3), 19.13 ((CH_3). **FTIR (cm^{-1}) (neat):** 2959, 2874, 1733, 1449, 1376, 1176, 1145, 991, 890. **HRMS (ESI, Pos)** calculated for $C_{13}H_{23}O_2$ $[M+H]^+$: 211.16926 m/z, found 211.16995 m/z.



(±)-benzyl (S)-1-acetamidospiro[2.5]octane-1-carboxylate (8e)

Synthesized in EtOAc from cyclohexanone hydrazone **1d** (70.7% purity) (96.7 mg, 0.61 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (89.6 mg, 0.41 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 30% ethyl acetate in hexanes) yielded a yellowish oil (122.6 mg, 0.41 mmol, 100%). **Rf** (50% ethyl acetate in hexanes) = 0.53.

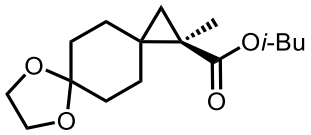
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 3H), 7.29 – 7.27 (m, 2H), 7.12 (br, 1H), 5.27 (d, *J* = 12.1 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 2.23 – 2.15 (m, 1H), 2.04 (s, 3H), 1.99 (d, *J* = 13.3 Hz, 1H), 1.97 – 1.88 (m, 3H), 1.88 (d, *J* = 13.2 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.49 – 1.39 (m, 2H), 1.34 – 1.24 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.25 (Cq), 167.79 (Cq), 134.35 (Cq), 128.99 (CH), 128.85 (CH), 128.53 (CH), 102.83 (Cq), 99.64 (Cq), 68.90 (CH_2), 36.34 (CH_2), 34.50 (CH_2), 34.32 (CH_2), 25.33 (CH_2), 23.86 (CH_3), 23.56 (CH_2), 23.18 (CH_2). **FTIR (cm^{-1}) (neat):** 3268, 3033, 2929, 2855, 1730, 1660, 1519, 1447, 1372, 1302, 1272, 1236, 1161, 1141, 736, 697. **HRMS (ESI, Pos)** calculated for $C_{18}H_{24}N_1O_3$ $[M+H]^+$: 302.17507 m/z, found 302.17505 m/z.



(±)-benzyl (*S*)-1-acetamido-6,6-dimethylspiro[2.5]octane-1-carboxylate (8f)

Synthesized in EtOAc from 4,4-dimethyl cyclohexanone hydrazone **1e** (75.0% purity) (113.0 mg, 0.606 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (88.6 mg, 0.404 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 50% ethyl acetate in hexanes) yielded a yellowish oil (121.9 mg, 0.37 mmol, 92%). **Rf** (10% ethyl acetate in hexanes) = 0.60.

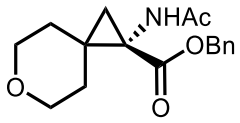
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 3H), 7.27 – 7.25 (m, 2H), 5.25 (d, *J* = 12.1 Hz, 1H), 5.13 (d, *J* = 12.1 Hz, 1H), 2.35 – 2.28 (m, 1H), 2.10 – 2.06 (m, 1H), 2.01 (s, 3H), 2.01 (d, *J* = 13.2 Hz, 1H), 1.84 (d, *J* = 13.3 Hz, 1H), 1.82 – 1.77 (m, 1H), 1.63 – 1.58 (m, 1H), 1.54 – 1.49 (m, 1H), 1.40 – 1.35 (m, 1H), 1.21 – 1.12 (m, 2H), 1.02 (s, 3H), 0.92 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.25 (Cq), 167.77 (Cq), 134.37 (Cq), 128.98 (CH), 128.84 (CH), 128.51 (CH), 102.83 (Cq), 99.62 (Cq), 68.89 (CH_2), 36.33 (CH_2), 36.27 (CH_2), 35.96 (CH_2), 30.58 (CH_2), 30.50 (CH_2), 29.38 (Cq), 23.80 (CH_3). **FTIR (cm^{-1}) (neat):** 3282, 3033, 2946, 2927, 2863, 1741, 1661, 1519, 1454, 1367, 1302, 1269, 1239, 1129, 735, 697. **HRMS (ESI, Neg)** calculated for $C_{20}H_{26}N_1O_3$ $[M+H]^-$: 328.19182 m/z, found 328.19111 m/z.



(±)-isobutyl (*R*)-1-methyl-7,10-dioxadispiro[2.2.4^{6}.2^{3}]dodecane-1-carboxylate (3g)

Synthesized in EtOAc from cyclohexanedione monoethylene ketal hydrazone **1f** (81.1% purity) (127.0 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellowish oil (113.0 mg, 0.40 mmol, 100%). **Rf** (10% ethyl acetate in hexanes) = 0.17.

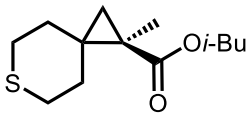
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 – 3.95 (m, 4H), 3.93 (app. d, *J* = 6.7 Hz, 2H), 2.21 – 2.06 (m, 4H), 2.03 (d, *J* = 13.0 Hz, 1H), 1.95 (sept, *J* = 13.4, 6.7 Hz, 1H), 1.69 – 1.63 (m, 4H), 1.63 (s, 3H), 1.31 (d, *J* = 13.0 Hz, 1H), 0.92 (d, *J* = 1.1 Hz, 3H), 0.91 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.25 (Cq), 107.98 (Cq), 95.31 (Cq), 95.13 (Cq), 71.88 (CH_2), 64.58 (CH_2), 64.54 (CH_2), 39.46 (CH_2), 34.52 (CH_2), 33.41 (CH_2), 32.22 (CH_2), 32.12 (CH_2), 27.83 (CH), 24.18 (CH_3), 19.12 (CH_3). **FTIR (cm^{-1}) (neat):** 2957, 2876, 1732, 1445, 1372, 1267, 1236, 1164, 1144, 1098, 1036, 889, 662. **HRMS (ESI, Pos)** calculated for $C_{16}H_{27}O_4$ $[M+H]^+$: 283.19039 m/z, found 283.19072 m/z.



(±)-benzyl (*S*)-1-acetamido-6-oxaspiro[2.5]octane-1-carboxylate (8h)

Synthesized in EtOAc from tetrahydro-4H-pyran-4-one hydrazone **1g** (44.3% purity) (158.0 mg, 0.615 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (89.9 mg, 0.410 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 50% ethyl acetate in hexanes) yielded a yellowish solid (110.1 mg, 0.365 mmol, 89%). **Rf** (50% ethyl acetate in hexanes) = 0.17. **mp**: 82 - 86 °C.

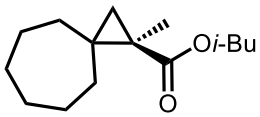
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 3H), 7.27 – 7.25 (m, 2H), 5.27 (d, *J* = 12.0 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 4.15 (ddd, *J* = 11.7, 6.1, 3.9 Hz, 1H), 4.02 (ddd, *J* = 11.6, 6.2, 3.9 Hz, 1H), 3.62 – 3.50 (m, 2H), 2.52 – 2.45 (m, 1H), 2.11 – 2.07 (m, 1H), 2.05 (s, 3H), 2.03 – 2.00 (m, 1H), 1.98 (d, *J* = 5.2 Hz, 2H), 1.57 – 1.51 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.29 (Cq), 167.48 (Cq), 134.04 (Cq), 129.22 (CH), 128.94 (CH), 128.62 (CH), 102.83 (Cq), 96.32 (Cq), 69.19 (CH_2), 65.41 (CH_2), 65.28 (CH_2), 36.62 (CH_2), 35.20 (CH_2), 34.78 (CH_2), 23.91 (CH_3). **FTIR (cm^{-1}) (neat):** 3280, 2961, 2923, 2851, 1741, 1678, 1512, 1303, 1249, 1208, 1142, 1102, 956, 841, 754, 696, 584, 492. **HRMS (ESI, Pos)** calculated for $C_{17}H_{22}N_1O_4$ $[M+H]^+$: 304.15433 m/z, found 304.15303 m/z.



(±)-isobutyl (*R*)-1-methyl-6-thiaspiro[2.5]octane-1-carboxylate (3i)

Synthesized in EtOAc from tetrahydrothiopyran-4-one hydrazone **1h** (83.7% purity) (93.1 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellowish oil (96.7 mg, 0.40 mmol, 100%). **Rf** (10% ethyl acetate in hexanes) = 0.45.

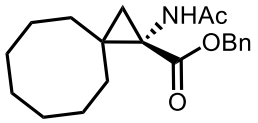
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (dd, *J* = 7.8, 3.9 Hz, 1H), 3.92 (dd, *J* = 7.8, 3.8 Hz, 1H), 3.09 – 2.99 (m, 2H), 2.66 – 2.59 (m, 2H), 2.32 – 2.22 (m, 2H), 2.01 (d, *J* = 13.0 Hz, 1H), 2.01 – 1.91 (m, 1H), 1.82 – 1.76 (m, 2H), 1.64 (s, 3H), 1.25 (d, *J* = 13.1 Hz, 1H), 0.93 (d, *J* = 0.9 Hz, 3H), 0.91 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.03 (Cq), 95.83 (Cq), 95.26 (Cq), 72.00 (CH_2), 39.93 (CH_2), 37.62 (CH_2), 36.41 (CH_2), 27.84 (CH), 25.44 (CH_2), 25.43 (CH_2), 24.32 (CH_3), 19.12 (CH_3). **FTIR (cm^{-1}) (neat):** 2959, 2933, 2874, 1731, 1431, 1377, 1273, 1173, 1147, 1116, 988, 892. **HRMS (ESI, Pos)** calculated for $C_{13}H_{23}O_2S_1$ $[M+H]^+$: 243.14133 m/z, found 243.14077 m/z.



(±)-isobutyl (*R*)-1-methylspiro[2.6]nonane-1-carboxylate (3j)

Synthesized in EtOAc from cycloheptanone hydrazone **1j** (83.1% purity) (90.8 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellow liquid (95.0 mg, 0.40 mmol, 100%). **Rf** (10% ethyl acetate in hexanes) = 0.58.

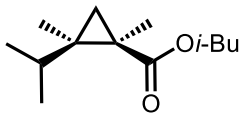
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (app. d, *J* = 6.6 Hz, 2H), 2.11 (ddd, *J* = 14.3, 10.3, 2.2 Hz, 1H), 2.06 – 2.00 (m, 1H), 2.02 (d, *J* = 13.1 Hz, 1H), 1.95 (sept, *J* = 13.4, 6.7 Hz, 1H), 1.93 – 1.83 (m, 2H), 1.74 – 1.56 (m, 4H), 1.61 (s, 3H), 1.54 – 1.48 (m, 4H), 1.30 (d, *J* = 13.0 Hz, 1H), 0.93 (d, *J* = 1.4 Hz, 3H), 0.91 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.64 (Cq), 99.48 (Cq), 95.27 (Cq), 71.79 (CH_2), 41.07 (CH_2), 39.46 (CH_2), 38.24 (CH_2), 29.57 (CH_2), 29.54 (CH_2), 27.83 (CH), 24.08 (CH_3), 23.96 (CH_2), 23.85 (CH_2), 19.13 (CH_3). **FTIR (cm^{-1}) (neat):** 2926, 2856, 1733, 1453, 1264, 1155, 991, 855. **HRMS (ESI, Pos)** calculated for $C_{15}H_{27}O_2$ $[M+H]^+$: 239.20056 m/z, found 239.20133 m/z.



(±)-benzyl (*S*)-1-acetamidospiro[2.7]decane-1-carboxylate (8k)

Synthesized in EtOAc from cyclooctatone hydrazone **1k** (88.9% purity) (95.4 mg, 0.60 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (88.4 mg, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 50% ethyl acetate in hexanes) yielded a yellowish solid (81.8 mg, 0.25 mmol, 62%). **Rf** (50% ethyl acetate in hexanes) = 0.51. **mp**: 58 - 62 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 5.97 (br, 1H), 5.15 (d, *J* = 12.3 Hz, 1H), 5.09 (d, *J* = 12.3 Hz, 1H), 1.98 (s, 3H), 1.90 (d, *J* = 5.6 Hz, 1H), 1.74 – 1.36 (m, 14H), 1.04 (d, *J* = 5.6 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.33 (Cq), 135.95 (Cq), 128.65 (CH), 128.44 (CH), 128.36 (CH), 67.29 (CH_2), 44.32 (Cq), 35.37 (Cq), 33.50 (CH_2), 29.33 (CH_2), 28.76 (CH_2), 27.50 (CH_2), 26.03 (CH_2), 25.54 (CH_2), 25.41 (CH_2), 24.37 (CH_2), 23.44 (CH_3). **FTIR (cm^{-1}) (neat):** 3237, 3034, 2922, 2853, 1727, 1637, 1543, 1449, 1373, 1284, 1164, 725, 692, 460. **HRMS (ESI, Pos)** calculated for $C_{20}H_{28}N_1O_3$ $[M+H]^+$: 330.20637 m/z, found 330.20547 m/z.



(±)-isobutyl (1*R*,2*R*)-2-isopropyl-1,2-dimethylcyclopropane-1-carboxylate (3l)

Synthesized in EtOAc from 3-methylbutan-2-one hydrazone **1l** (91.6% purity) (65.4 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellow liquid (84.6 mg, 0.40 mmol, 100%) as a mixture of diastereomers (1.4:1). **Rf** (10% ethyl acetate in hexanes) = 0.65, 0.59.

FTIR (cm^{-1}) (neat): 2963, 2935, 2875, 1733, 1467, 1375, 1172, 1145, 991, 896. **HRMS (ESI, Pos)** calculated for $C_{13}H_{25}O_2$ $[M+H]^+$: 213.18491 m/z, found 213.18539 m/z.

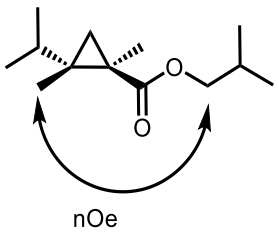
Characterization data for the major diastereomer:

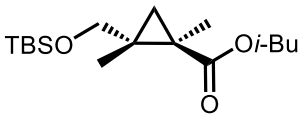
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.93 (app. d, *J* = 6.6 Hz, 2H), 2.22 – 2.12 (m, 1H), 2.01 – 1.92 (m, 1H), 1.82 (d, *J* = 13.2 Hz, 1H), 1.65 (s, 3H), 1.31 (d, *J* = 13.3 Hz, 1H), 1.30 (s, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.94 – 0.92 (app. m, 6H), 0.79 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.57 (Cq), 99.57 (Cq), 95.85 (Cq), 71.88 (CH_2), 36.51 (CH_2), 35.36 (CH), 27.85 (CH), 23.39 (CH_3), 22.68 (CH_3), 19.15 (CH_3), 18.05 (CH_3), 18.02 (CH_3).

Characterization data for the minor diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96 (dd, *J* = 6.7, 2.9 Hz, 2H), 2.22 – 2.12 (m, 1H), 2.07 (d, *J* = 13.1 Hz, 1H), 2.01 – 1.92 (m, 1H), 1.60 (s, 3H), 1.32 (s, 3H), 1.17 (d, *J* = 13.2 Hz, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.94 – 0.92 (app. m, 6H), 0.79 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.71 (Cq), 98.73 (Cq), 95.79 (Cq), 71.86 (CH_2), 36.50 (CH_2), 35.52 (CH), 27.85 (CH), 24.22 (CH_3), 23.39 (CH_3), 19.15 (CH_3), 17.98 (CH_3), 17.91 (CH_3).

The relative stereochemistry was verified by NOE experiment:





(±)-isobutyl (1*R*,2*S*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-1,2-dimethylcyclopropane-1-carboxylate (3m)

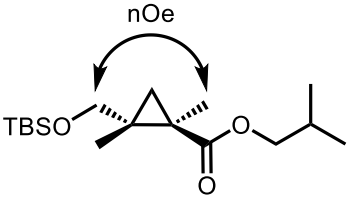
Synthesized in EtOAc from (1-((*tert*-butyldimethylsilyl)oxy)propan-2-ylidene)hydrazine **1n** (82.0% purity) (148.0 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellow liquid (122.0 mg, 0.388 mmol, 97%) as a mixture of diastereomers (2.4:1). **Rf** (10% ethyl acetate in hexanes) = 0.26, 0.39.

FTIR (cm^{-1}) (neat): 2957, 2931, 2858, 1736, 1471, 1463, 1289, 1167, 1103, 834, 776. **HRMS (ESI, Pos)** calculated for $C_{17}H_{35}O_3Si$ $[M+H]^+$: 315.235 m/z, found 315.2353 m/z.

Characterization data for the major diastereomer:

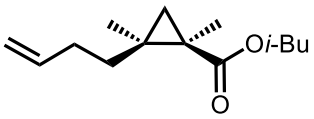
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (d, *J* = 10.5 Hz, 1H), 3.93 (dd, *J* = 6.6, 2.2 Hz, 2H), 3.58 (d, *J* = 10.5 Hz, 1H), 2.03 – 1.90 (app. m, 1H), 1.82 (d, *J* = 12.6 Hz, 1H), 1.69 (d, *J* = 12.7 Hz, 1H), 1.65 (s, 3H), 1.32 (s, 3H), 0.93 (app. s, 3H), 0.90 (d, *J* = 1.4 Hz, 3H), 0.86 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.59 (Cq), 97.53 (Cq), 97.24 (Cq), 71.81 (CH_2), 67.46 (CH_2), 35.88 (CH_2), 27.88 (CH), 26.04 (CH_3), 22.71 (CH_3), 21.56 (CH_3), 19.17 (CH_3), 19.15 (CH_3), 18.57 (CH_2), -5.19 (CH_3), -5.39 (CH_3).

The relative stereochemistry was verified by NOE experiment:



Characterization data for the minor diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (dd, *J* = 10.6, 6.8 Hz, 1H), 3.90 (dd, *J* = 10.6, 6.7 Hz, 1H), 3.85 (d, *J* = 10.1 Hz, 1H), 3.70 (d, *J* = 10.1 Hz, 1H), 2.34 (d, *J* = 13.0 Hz, 1H), 2.03 – 1.90 (app. m, 1H), 1.62 (s, 3H), 1.38 (s, 3H), 1.20 (d, *J* = 13.0 Hz, 1H), 0.95 (d, *J* = 1.3 Hz, 3H), 0.94 (d, *J* = 1.4 Hz, 3H), 0.85 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.51 (Cq), 96.64 (Cq), 96.24 (Cq), 71.67 (CH_2), 67.53 (CH_2), 36.25 (CH_2), 27.88 (CH), 25.96 (CH_3), 25.19 (CH_3), 22.51 (CH_3), 19.20 (CH_3), -5.15 (CH_3), -5.35 (CH_3).



(±)-isobutyl (1*R*,2*S*)-2-(but-3-en-1-yl)-1,2-dimethylcyclopropane-1-carboxylate (3n)

Synthesized in EtOAc from hex-5-en-2-ylidenehydrazine **1m** (87.5% purity) (76.7 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded an orange liquid (88.1 mg, 0.588 mmol, 98%) as a mixture of diastereomers (1:1). **Rf** (10% ethyl acetate in hexanes) = 0.40, 0.50.

FTIR (cm^{-1}) (neat): 2966, 2934, 2875, 1733, 1452, 1376, 1288, 1160, 992, 910. **HRMS (ESI, Pos)** calculated for $C_{14}H_{25}O_2$ $[M+H]^+$: 225.18491 m/z, found 225.18503 m/z.

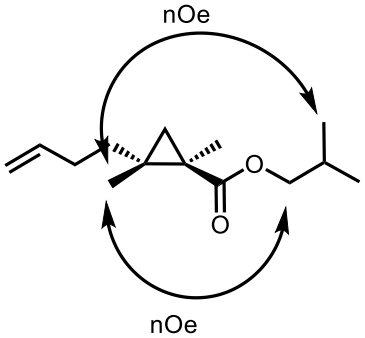
Characterization data for one diastereomer:

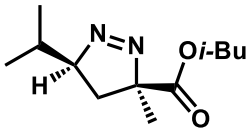
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 – 5.76 (app. m, 1H), 5.07 – 4.95 (app. m, 2H), 3.96 – 3.93 (app. m, 2H), 2.21 – 2.12 (app. m, 1H), 2.09 (d, *J* = 13.1 Hz, 1H), 2.05 – 1.76 (app. m, 4H), 1.65 (s, 3H), 1.41 (s, 3H), 1.27 (d, *J* = 13.1 Hz, 1H), 0.94 (app. s, 3H), 0.92 (app. s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.35 (Cq), 137.85 (CH), 115.20 (CH_2), 96.29 (Cq), 95.53 (Cq), 71.91 (CH_2), 39.49 (CH_2), 39.26 (CH_2), 28.96 (CH_2), 27.85 (CH), 24.84 (CH_3), 23.76 (CH_3), 19.16 (CH_3).

Characterization data for the other diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 – 5.76 (app. m, 1H), 5.07 – 4.95 (app. m, 2 H), 3.96 – 3.93 (app. m, 2H), 2.21 – 2.12 (app. m, 1H), 1.96 (d, *J* = 13.1 Hz, 1H), 2.05 – 1.76 (app. m, 4H), 1.61 (s, 3H), 1.38 (s, 3H), 1.35 (d, *J* = 13.1 Hz, 1H), 0.94 (app. s, 3H), 0.93 (app. s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.42 (Cq), 137.98 (CH), 115.01 (CH_2), 96.34 (Cq), 95.14 (Cq), 71.91 (CH_2), 39.40 (CH_2), 38.72 (CH_2), 28.80 (CH_2), 27.85 (CH), 25.67 (CH_3), 24.14 (CH_3), 19.16 (CH_3).

The relative stereochemistry vas verified by NOE experiment:





(±)-isobutyl (3*R*,5*S*)-5-isopropyl-3-methyl-4,5-dihydro-3*H*-pyrazole-3-carboxylate (17o)

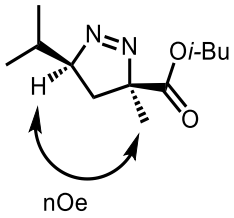
Synthesized in EtOAc from isobutyraldehyde hydrazone **1m** (78.0% purity) (66.1 mg, 0.60 mmol, 1.5 equiv) and isobutyl methacrylate (64 μL, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. Flash chromatography (using a gradient from 100% hexanes to 10% ethyl acetate in hexanes) yielded a yellow liquid (70.7 mg, 0.31 mmol, 78%) as a mixture of diastereomers (1.4:1). **Rf** (10% ethyl acetate in hexanes) = 0.65.

FTIR (cm^{-1}) (neat): 2962, 2935, 2875, 1734, 1468, 1371, 1281, 1173, 1147, 991, 891. **HRMS (ESI, Pos)** calculated for $C_{12}H_{23}N_2O_2$ $[M+H]^+$: 227.1754 m/z, found 227.17578 m/z.

Characterization data for the major diastereomer:

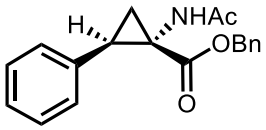
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.32 (td, *J* = 8.5, 7.2 Hz, 1H), 4.00 (dd, *J* = 8.2, 4.3 Hz, 1H), 3.97 (dd, *J* = 8.2, 4.2 Hz, 1H), 2.21 – 2.14 (m, 1H), 2.02 – 1.89 (m, 1H), 1.73 – 1.69 (app. m, 1H), 1.65 – 1.60 (app. m, 1H), 1.42 (s, 3H), 1.20 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 1.5 Hz, 3H), 0.93 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.68 (Cq), 95.18 (CH), 94.39 (Cq), 71.78 (CH_2), 31.50 (CH_2), 31.42 (CH), 27.86 (CH), 21.14 (CH_3), 20.28 (CH_3), 19.15 (CH_3), 19.14 (CH_3), 19.11 (CH_3).

The relative stereochemistry was verified by NOE experiment:



Characterization data for the minor diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.40 (td, *J* = 8.7, 7.1 Hz, 1H), 3.90 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.87 (dd, *J* = 7.9, 3.9 Hz, 1H), 2.24 – 2.14 (app. m, 2H), 2.02 – 1.89 (m, 1H), 1.72 (s, 3H), 1.19 (d, *J* = 6.7 Hz, 3H), 1.01 (dd, *J* = 13.0, 8.9 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 1.4 Hz, 3H), 0.90 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.52 (Cq), 97.28 (CH), 95.37 (Cq), 71.71 (CH_2), 32.57 (CH_2), 31.54 (CH), 27.81 (CH), 22.86 (CH_3), 20.25 (CH_3), 19.27 (CH_3), 19.19 (CH_3), 19.11 (CH_3).



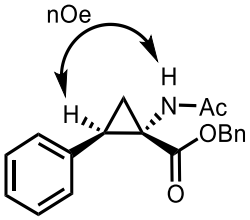
(±)-benzyl (1*S*,2*R*)-1-acetamido-2-phenylcyclopropane-1-carboxylate (8p)

Synthesized in EtOAc from benzaldehyde hydrazone **1q** (93.4% purity) (78.8 mg, 0.612 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (89.5 mg, 0.408 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. The crude mixture was purified by flash chromatography using a gradient from 100% hexanes to 50% ethyl acetate in hexanes.

The major cyclopropane was isolated as am orangish solid (101.2 mg, 0.326 mmol, 80%). **Rf** (50% ethyl acetate in hexanes) = 0.24. **mp**: 80 - 84 °C.

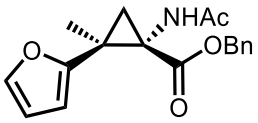
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.33 (m, 2H), 7.25 – 7.21 (m, 6H), 6.93 – 6.91 (m, 2H), 6.32 (br, 1H), 4.87 (d, *J* = 12.3 Hz, 1H), 4.66 (d, *J* = 12.3 Hz, 1H), 2.85 (t, *J* = 9.1 Hz, 1H), 2.25 (dd, *J* = 8.5, 5.6 Hz, 1H), 2.04 (s, 3H), 1.63 (dd, *J* = 9.7, 5.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.28 (Cq), 169.71 (Cq), 135.45 (Cq), 135.29 (Cq), 129.49 (CH), 128.40 (CH), 128.24 (CH), 128.21 (CH), 128.10 (CH), 127.25 (CH), 67.06 (CH_2), 40.70 (Cq), 35.01 (CH), 23.40 (CH_3), 20.70 (CH_2). **FTIR (cm^{-1}) (neat):** 3320, 3058, 3033, 2957, 2923, 2853, 1725, 1650, 1527, 1277, 1213, 1163, 752, 726, 699, 587. **HRMS (ESI, Pos)** calculated for $C_{19}H_{20}N_1O_3$ $[M+H]^+$: 310.14377 m/z, found 310.14439 m/z.

The relative stereochemistry was verified by NOE experiment:



The minor cyclopropane was isolated as a yellow solid (18.6 mg, 0.061 mmol, 15%). **Rf** (50% ethyl acetate in hexanes) = 0.38. **mp**: 64 - 68 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 8H), 7.17 – 7.14 (m, 2H), 5.34 (br, 1H), 5.19 (d, *J* = 12.5 Hz, 1H), 5.16 (d, *J* = 12.5 Hz, 1H), 2.96 (t, *J* = 8.92 Hz, 1H), 2.26 (dd, *J* = 9.6, 6.0 Hz, 1H), 1.83 (s, 3H), 1.76 (dd, *J* = 8.1, 6.0 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.65 (Cq), 171.42 (Cq), 135.79 (Cq), 134.29 (Cq), 128.81 (CH), 128.72 (CH), 128.65 (CH), 128.40 (CH), 128.06 (CH), 127.69 (CH), 67.49 (CH_2), 39.27 (Cq), 32.65 (CH), 23.09 (CH_3), 21.37 (CH_2). **FTIR (cm^{-1}) (neat):** 3340, 2953, 2920, 2853, 1716, 1660, 1515, 1455, 1391, 1330, 1264, 1250, 1159, 746, 698, 603, 579. **HRMS (ESI, Pos)** calculated for $C_{19}H_{20}N_1O_3$ $[M+H]^+$: 310.14377 m/z, found 310.14301 m/z.



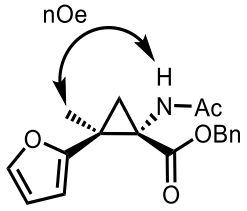
(±)-benzyl (1*S*,2*S*)-1-acetamido-2-(furan-2-yl)-2-methylcyclopropane-1-carboxylate (8q)

Synthesized in EtOAc from 1-(furan-2-yl)ethan-1-one hydrazone **1n** (97.7% purity) (76.5 mg, 0.60 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (88 mg, 0.40 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. The crude mixture was purified by flash chromatography using a gradient from 100% hexanes to 50% ethyl acetate in hexanes.

The major cyclopropane was isolated as an orange oil (93.6 mg, 0.296 mmol, 74%). **Rf** (50% ethyl acetate in hexanes) = 0.26.

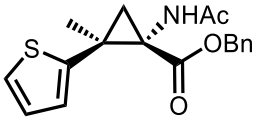
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 3H), 7.16 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.14 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.26 (br, 1H), 6.20 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.08 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.99 (d, *J* = 12.3 Hz, 1H), 4.73 (d, *J* = 12.3 Hz, 1H), 2.49 (d, *J* = 6.0 Hz, 1H), 2.05 (s, 3H), 1.53 (s, 3H), 1.43 (d, *J* = 6.0 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.48 (Cq), 169.52 (Cq), 154.04 (Cq), 141.46 (CH), 135.58 (Cq), 128.48 (CH), 128.38 (CH), 128.23 (CH), 110.35 (CH), 107.52 (CH), 67.34 (CH_2), 43.63 (Cq), 29.47 (Cq), 26.33 (CH_2), 23.47 (CH_3), 20.40 (CH_3). **FTIR (cm^{-1}) (neat):** 3266, 3035, 2931, 2855, 1728, 1665, 1526, 1501, 1455, 1372, 1311, 1265, 1186, 1159, 1111, 1098, 730, 696. **HRMS (ESI, Pos)** calculated for $C_{18}H_{20}N_1O_4$ $[M+H]^+$: 314.13868 m/z, found 314.13799 m/z.

The relative stereochemistry was verified by NOE experiment:



The minor cyclopropane was isolated as a yellow oil (19.2 mg, 0.06 mmol, 15%). **Rf** (50% ethyl acetate in hexanes) = 0.38.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 6H), 6.35 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.16 (dd, *J* = 3.3, 0.8 Hz, 1H), 5.54 (br, 1H), 5.20 (d, *J* = 12.54 Hz, 1H), 5.17 (d, *J* = 12.54 Hz, 1H), 2.17 (d, *J* = 6.1 Hz, 1H), 1.84 (d, *J* = 6.1 Hz, 1H), 1.81 (s, 3H), 1.50 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.96 (Cq), 169.92 (Cq), 153.97 (Cq), 142.20 (CH), 135.81 (Cq), 128.69 (CH), 128.43 (CH), 128.34 (CH), 110.85 (CH), 108.09 (CH), 67.55 (CH_2), 43.83 (Cq), 30.09 (Cq), 26.69 (CH_2), 23.04 (CH_3), 17.10 (CH_3). **FTIR (cm^{-1}) (neat):** 3292, 3034, 2926, 2854, 1723, 1668, 1499, 1321, 1263, 1175, 1124, 732, 697, 597. **HRMS (ESI, Pos)** calculated for $C_{18}H_{20}N_1O_4$ $[M+H]^+$: 314.13868 m/z, found 314.1374 m/z.



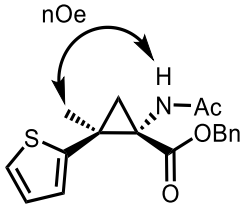
(±)-benzyl (1*S*,2*S*)-1-acetamido-2-methyl-2-(thiophen-2-yl)cyclopropane-1-carboxylate (8r)

Synthesized in EtOAc from 1-(furan-2-yl)ethan-1-one **1o** (97.0% purity) (88.1 mg, 0.61 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (89.1 mg, 0.406 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. The crude mixture was purified by flash chromatography using a gradient from 100% hexanes to 50% ethyl acetate in hexanes.

The major cyclopropane was isolated as a yellow oil (113.1 mg, 0.341 mmol, 84%). **Rf** (50% ethyl acetate in hexanes) = 0.44.

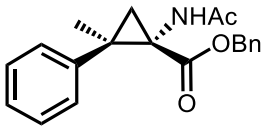
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 3H), 7.09 (dd, *J* = 4.3, 2.1 Hz, 1H), 7.05 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.86 – 6.80 (m, 2H), 6.28 (br, 1H), 4.91 (d, *J* = 12.2 Hz, 1H), 4.65 (d, *J* = 12.2 Hz, 1H), 2.52 (d, *J* = 5.9 Hz, 1H), 2.06 (s, 3H), 1.59 (s, 3H), 1.46 (d, *J* = 5.9 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.46 (Cq), 169.56 (Cq), 145.11 (Cq), 135.46 (Cq), 128.48 (CH), 128.45 (CH), 128.23 (CH), 126.63 (CH), 126.11 (CH), 124.41 (CH), 67.36 (CH_2), 44.93 (Cq), 31.31 (Cq), 27.86 (CH_2), 24.28 (CH_3), 23.47 (CH_3). **FTIR (cm^{-1}) (neat):** 3274, 3034, 2928, 1726, 1665, 1524, 1454, 1372, 1307, 1266, 1178, 1111, 732, 694. **HRMS (ESI, Pos)** calculated for $C_{18}H_{20}N_1O_3S_1$ $[M+H]^+$: 330.11584 m/z, found 330.11622 m/z.

The relative stereochemistry was verified by NOE experiment:



The minor cyclopropane was isolated as a yellow oil (23.1 mg, 0.069 mmol, 17%). **Rf** (10% ethyl acetate in hexanes) = 0.33.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 5H), 7.22 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.99 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.86 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.50 (br, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.18 (d, *J* = 12.4 Hz, 1H), 2.26 (d, *J* = 6.3 Hz, 1H), 1.79 (s, 3H), 1.75 (d, *J* = 6.3 Hz, 1H), 1.58 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.94 (Cq), 170.01 (Cq), 144.55 (Cq), 135.84 (Cq), 128.69 (CH), 128.42 (CH), 128.33 (CH), 127.41 (CH), 126.07 (CH), 125.05 (CH), 67.55 (CH_2), 44.05 (Cq), 31.38 (Cq), 28.69 (CH_2), 22.96 (CH_3), 20.76 (CH_3). **FTIR (cm^{-1}) (neat):** 3304, 3033, 2926, 2873, 1723, 1669, 1497, 1455, 1373, 1310, 1254, 1172, 1112, 736, 697. **HRMS (ESI, Pos)** calculated for $C_{18}H_{20}N_1O_3S_1$ $[M+H]^+$: 330.11584 m/z, found 330.11639 m/z.



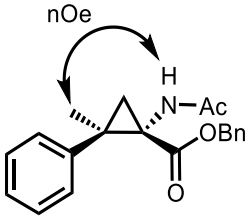
(±)-benzyl (1*S*,2*R*)-1-acetamido-2-methyl-2-phenylcyclopropane-1-carboxylate (8s)

Synthesized in EtOAc from acetophenone hydrazone **1p** (95.7% purity) (85.2 mg, 0.608 mmol, 1.5 equiv) and benzyl 2-acetamidoacrylate (88.8 mg, 0.405 mmol, 1.0 equiv) using the general procedure for the cyclopropanation reaction. The crude mixture was purified by flash chromatography using a gradient from 100% hexanes to 50% ethyl acetate in hexanes.

The major cyclopropane was isolated as a yellowish oil (99.7 mg, 0.308 mmol, 76%). **Rf** (50% ethyl acetate in hexanes) = 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 8H), 6.90 (dd, *J* = 6.7, 2.5 Hz, 2H), 6.21 (br, 1H), 4.83 (d, *J* = 12.2 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 2.39 (d, *J* = 5.6 Hz, 1H), 2.09 (s, 3H), 1.52 (s, 3H), 1.34 (d, *J* = 5.7 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.61 (Cq), 170.40 (Cq), 141.97 (Cq), 135.39 (Cq), 128.57 (CH), 128.48 (CH), 128.37 (CH), 128.12 (CH), 127.02 (CH), 67.10 (CH_2), 43.86 (Cq), 37.26 (Cq), 26.52 (CH_2), 24.37 (CH_3), 23.48 (CH_3). **FTIR (cm^{-1}) (neat):** 3281, 3059, 3029, 2922, 1725, 1665, 1526, 1496, 1446, 1309, 1265, 1185, 1084, 732, 697. **HRMS (ESI, Pos)** calculated for $C_{20}H_{22}N_1O_3$ $[M+H]^+$: 324.15942 m/z, found 324.1588 m/z.

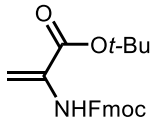
The relative stereochemistry was verified by NOE experiment:



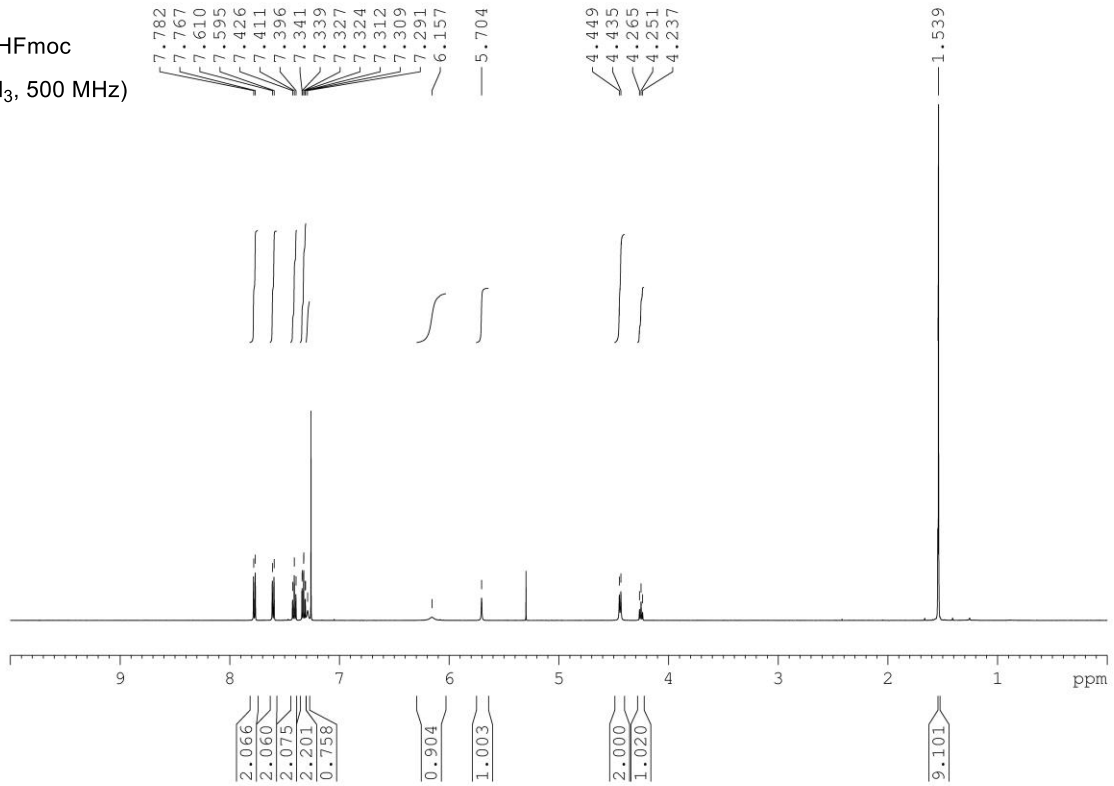
The minor cyclopropane was isolated as a yellowish oil (24.2 mg, 0.073 mmol, 18%). **Rf** (50% ethyl acetate in hexanes) = 0.56.

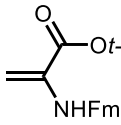
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 8H), 7.25 – 7.19 (m, 2H), 5.28 (br, 1H), 5.23 (d, *J* = 12.3 Hz, 1H), 5.20 (d, *J* = 12.3 Hz, 1H), 2.15 (d, *J* = 6.0 Hz, 1H), 1.69 (s, 3H), 1.67 (d, *J* = 6.0 Hz, 1H), 1.49 (s, *J* = 2.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.69 (Cq), 170.44 (Cq), 140.51 (Cq), 136.01 (Cq), 129.37 (CH), 128.68 (CH), 128.38 (CH), 128.35 (CH), 128.16 (CH), 127.72 (CH), 67.44 (CH_2), 42.82 (Cq), 35.86 (Cq), 26.73 (CH_2), 22.95 (CH_3), 21.24 (CH_3). **FTIR (cm^{-1}) (neat):** 3272, 3059, 3031, 2957, 2927, 2854, 1724, 1668, 1496, 1454, 1446, 1253, 1170, 1123, 1080, 1066, 735, 697. **HRMS (ESI, Pos)** calculated for $C_{20}H_{22}N_1O_3$ $[M+H]^+$: 324.15942 m/z, found 324.15828 m/z.

5. NMR spectra

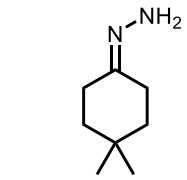


9 (^{1}H, $CDCl_3$, 500 MHz)

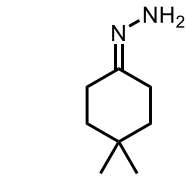




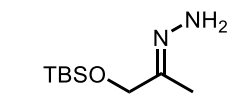
9 (^{13}C, $CDCl_3$, 126 MHz)



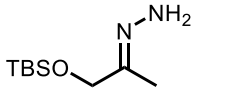
1f (^{1}H, $CDCl_3$, 400 MHz)



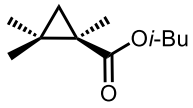
1f (^{13}C, $CDCl_3$, 75 MHz)



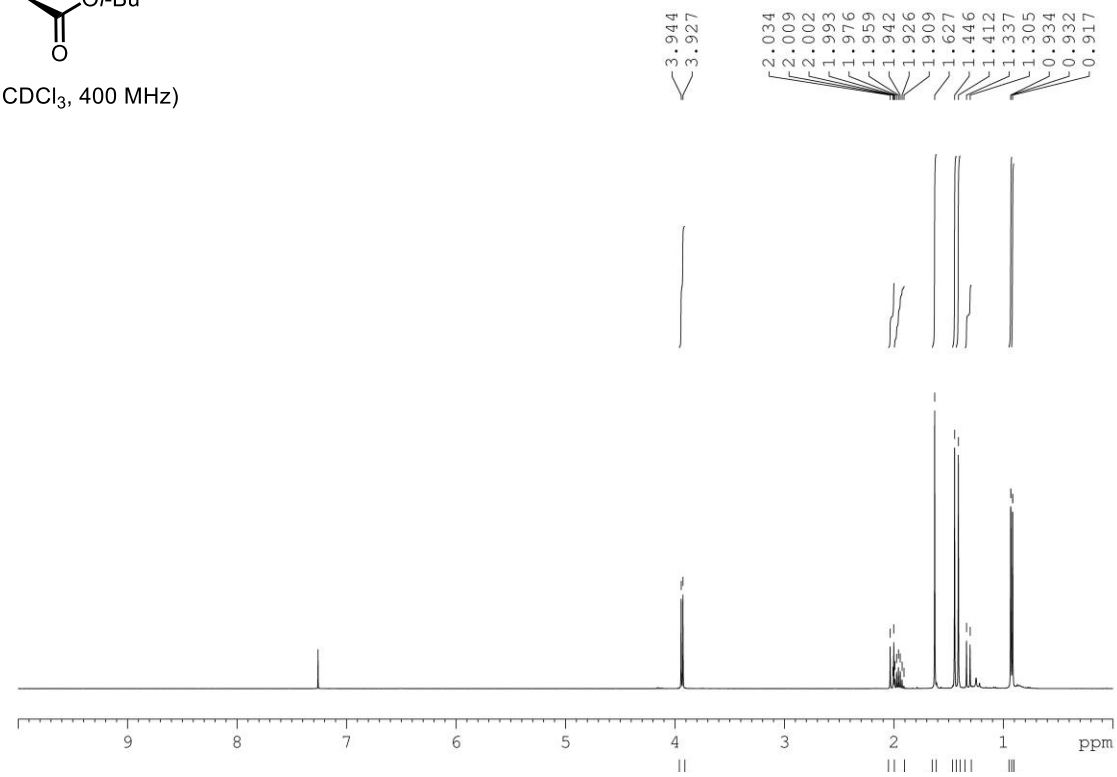
1m (^{1}H, $CDCl_3$, 300 MHz)

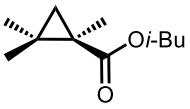


1m (^{13}C, $CDCl_3$, 75 MHz)

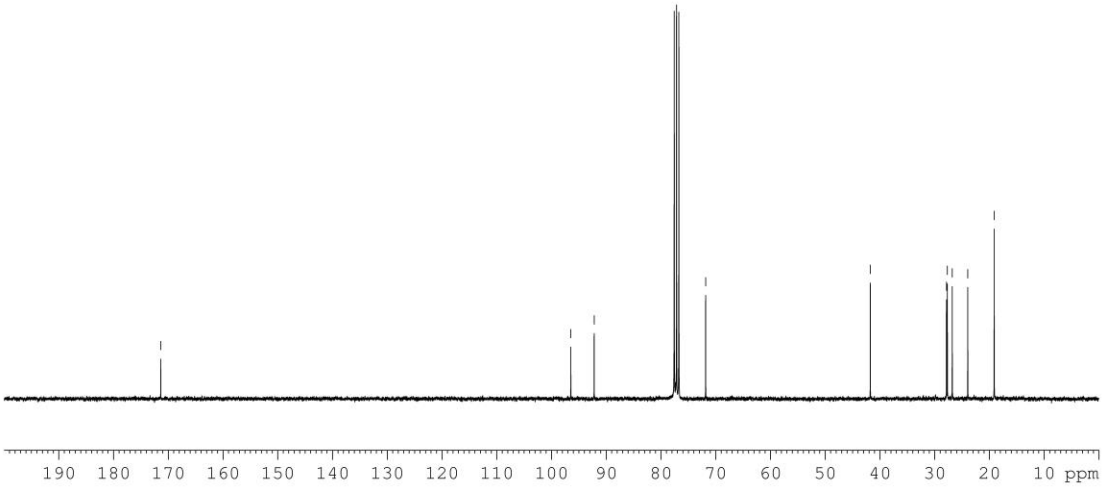


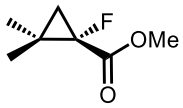
3a (^{1}H, $CDCl_3$, 400 MHz)



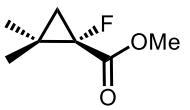


3a (^{13}C, $CDCl_3$, 75 MHz)

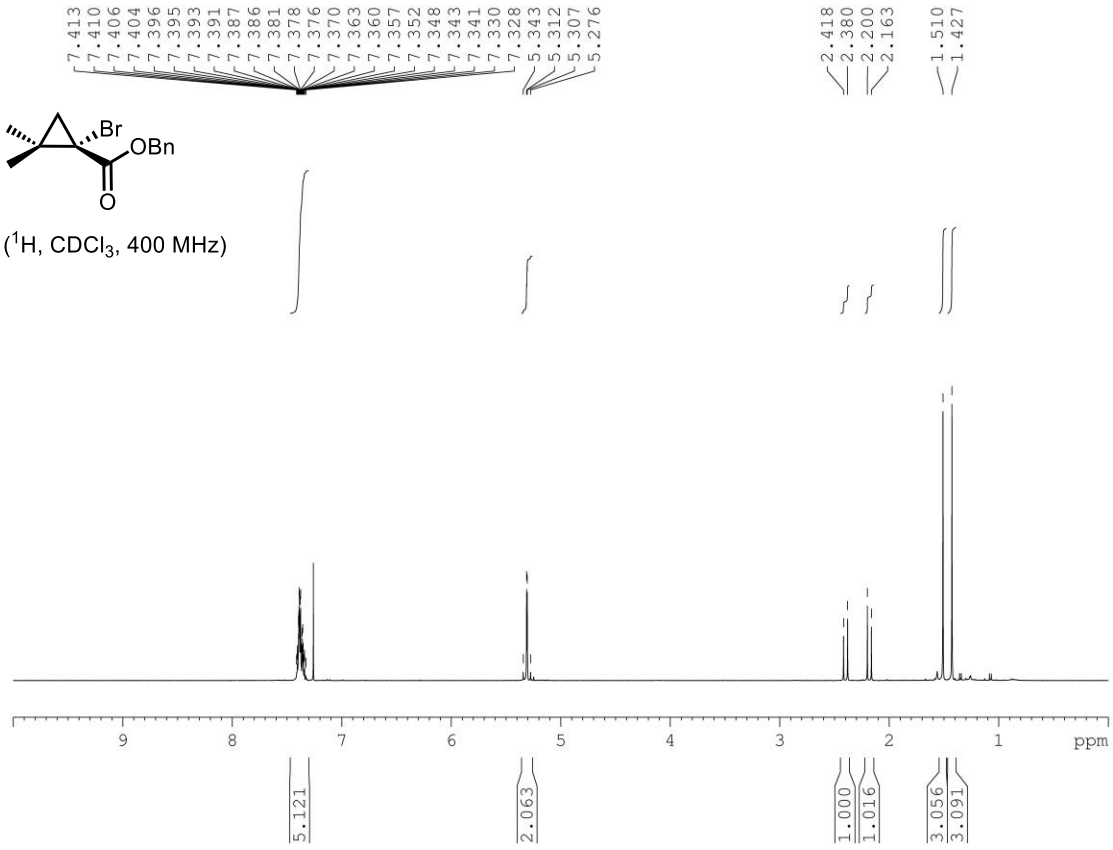




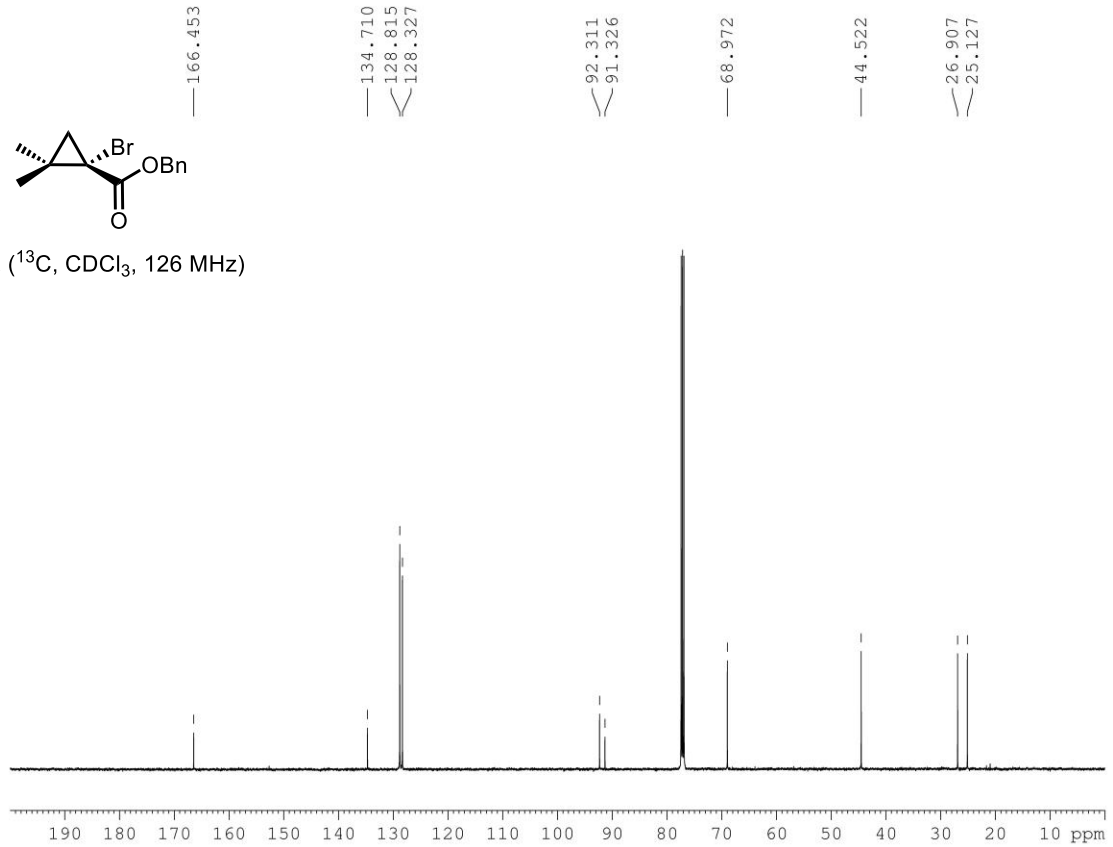
4a (^{1}H, $CDCl_3$, 500 MHz)



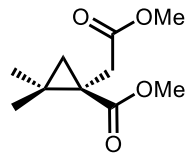
4a (^{13}C, $CDCl_3$, 126 MHz)



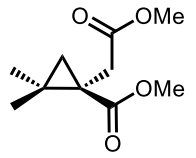
5a (^{1}H, $CDCl_3$, 400 MHz)



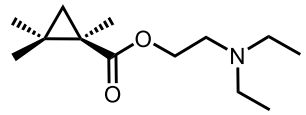
5a (^{13}C, $CDCl_3$, 126 MHz)



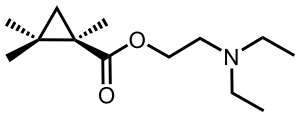
6a (^{1}H, $CDCl_3$, 400 MHz)



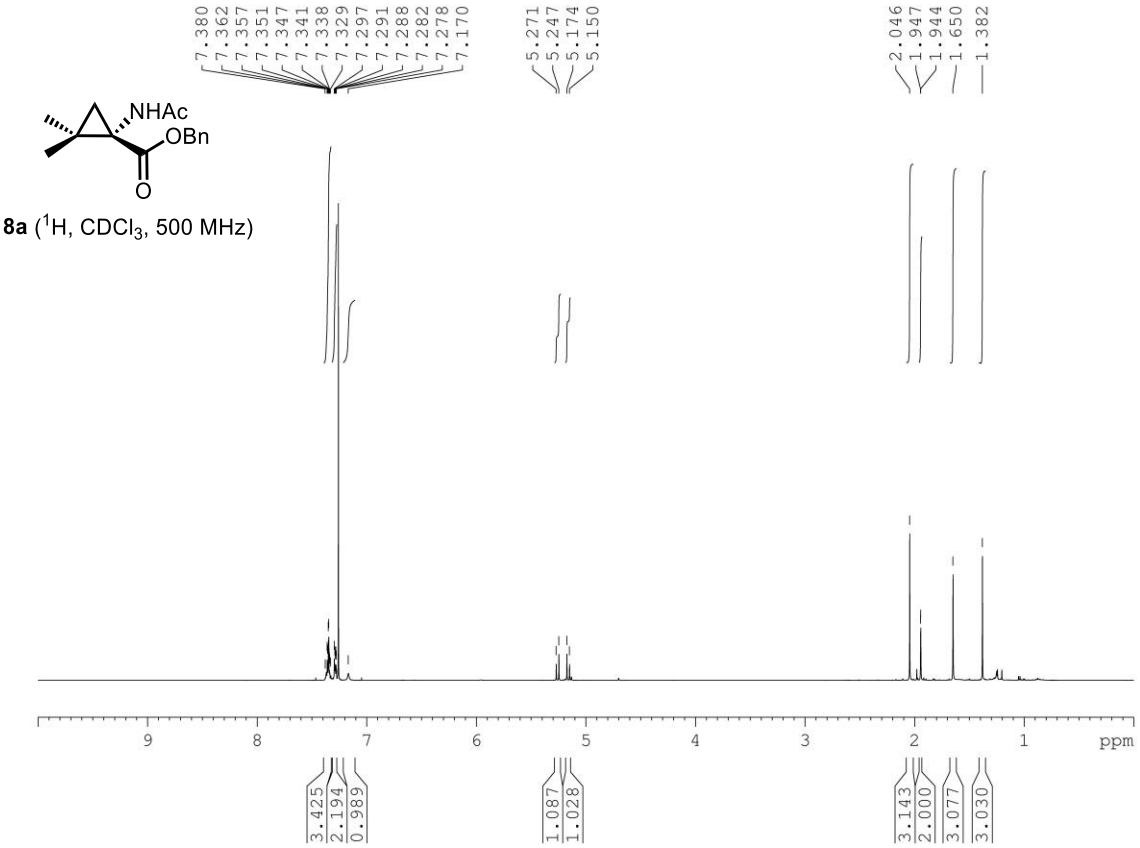
6a (^{13}C, $CDCl_3$, 126 MHz)



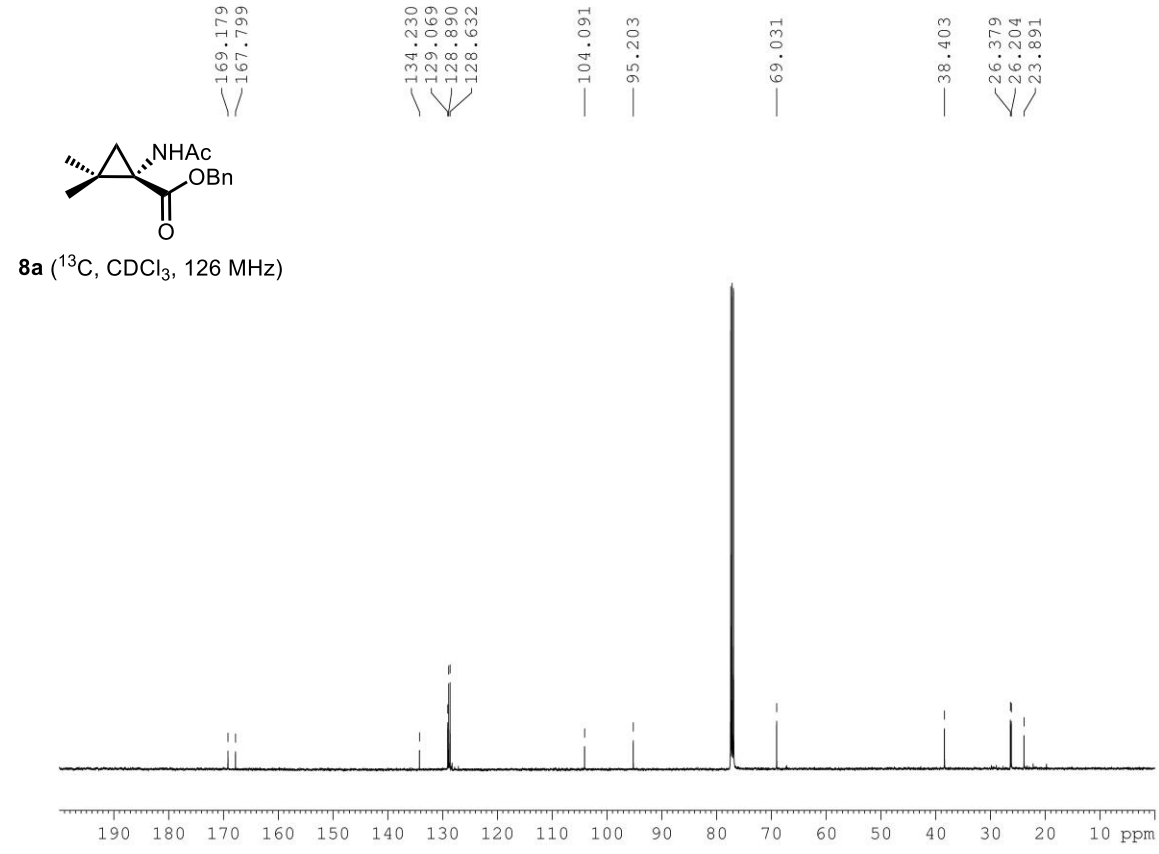
7a (^{1}H, $CDCl_3$, 500 MHz)



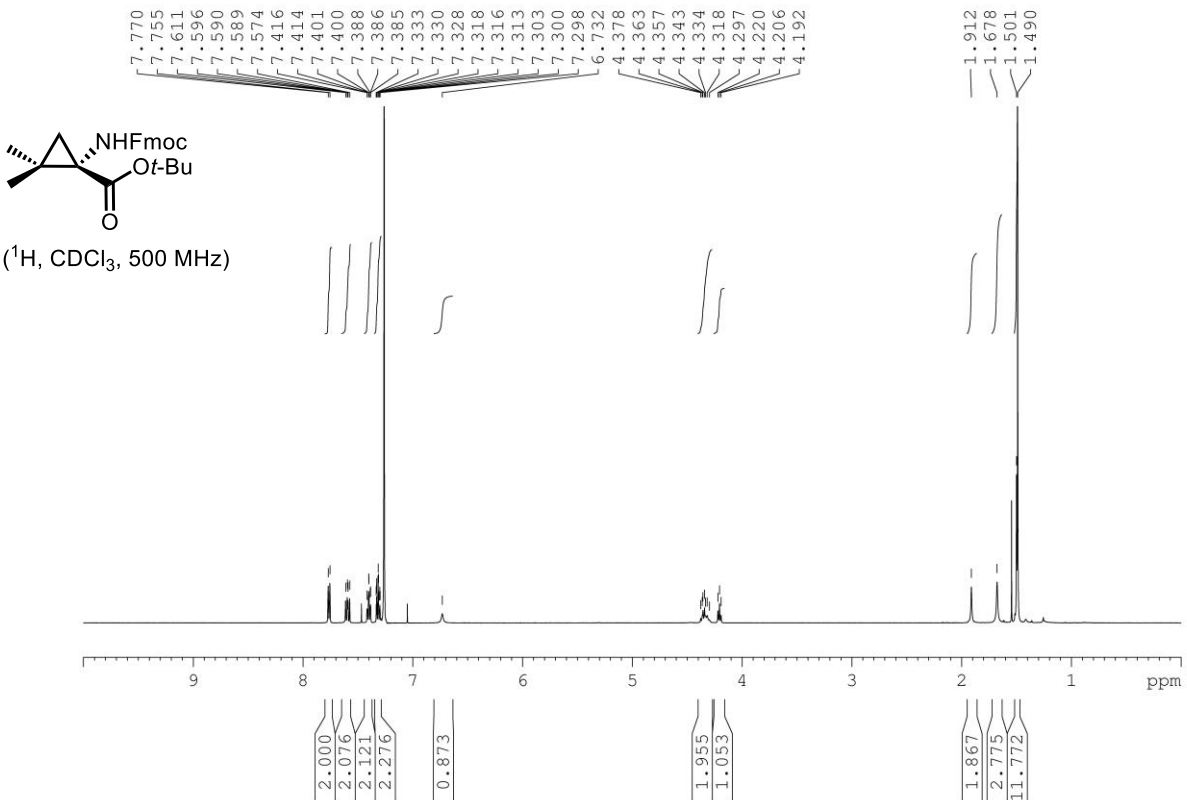
7a (^{13}C, $CDCl_3$, 126 MHz)



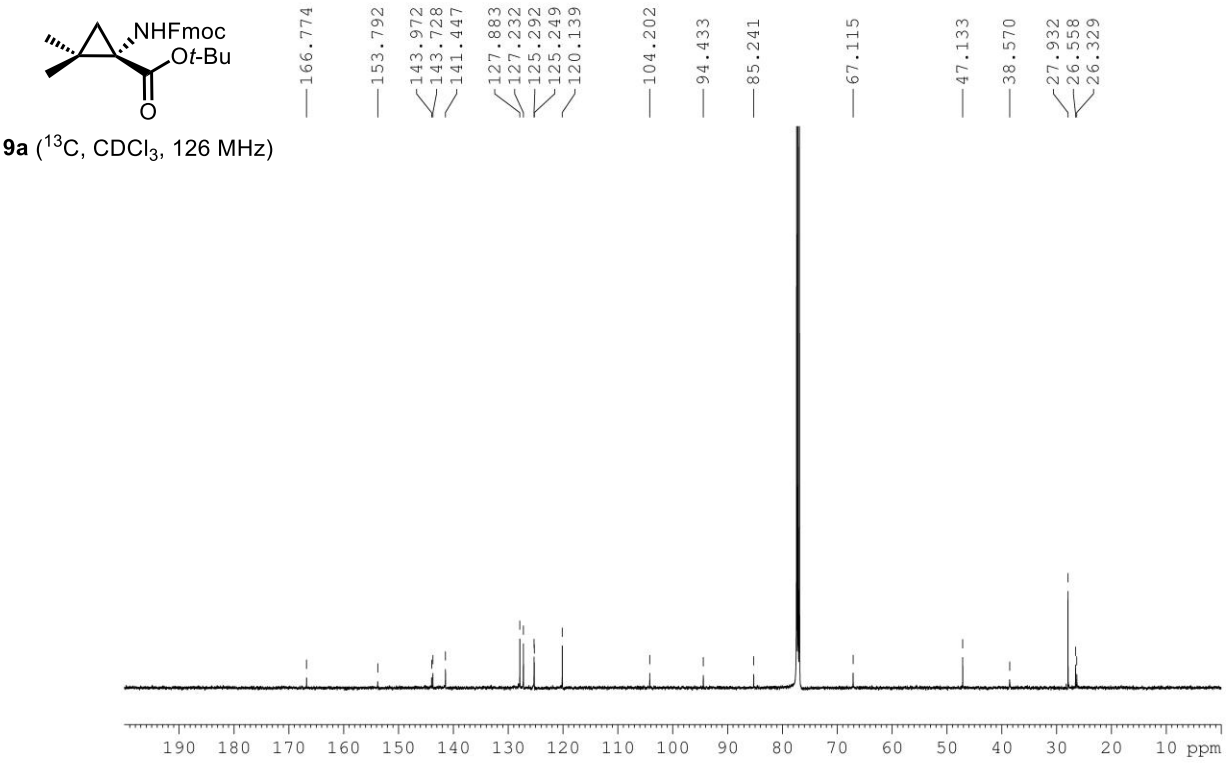
8a (^{1}H, $CDCl_3$, 500 MHz)



8a (^{13}C, $CDCl_3$, 126 MHz)



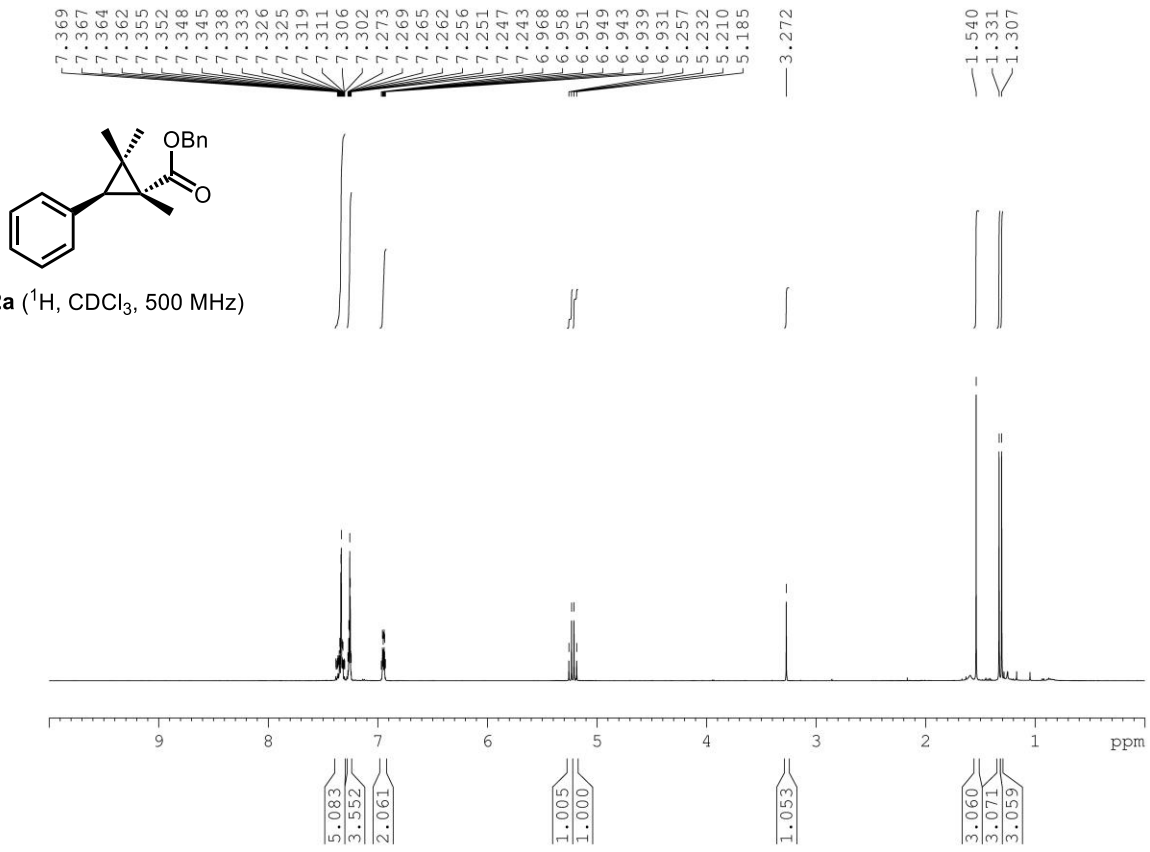
9a (^{1}H, $CDCl_3$, 500 MHz)



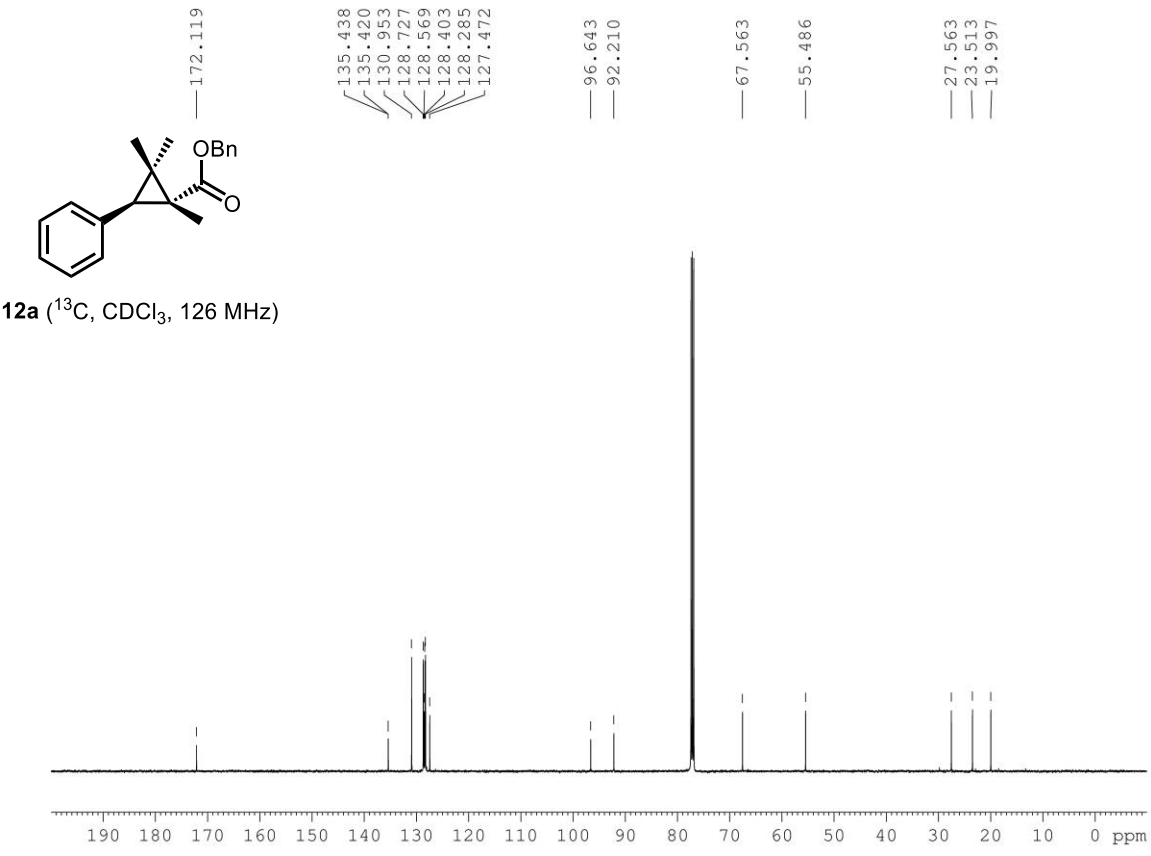
9a (^{13}C, $CDCl_3$, 126 MHz)

10a (^{1}H, $CDCl_3$, 500 MHz)

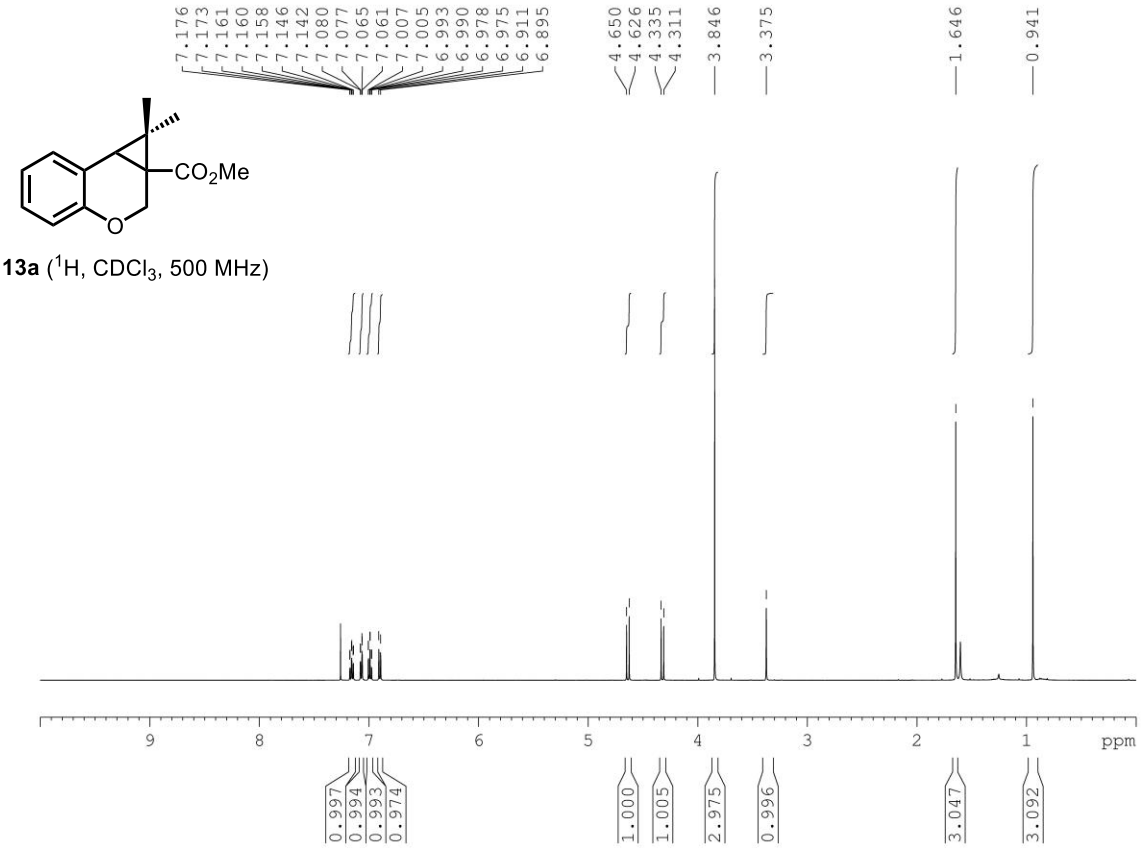
10a (^{13}C, $CDCl_3$, 126 MHz)



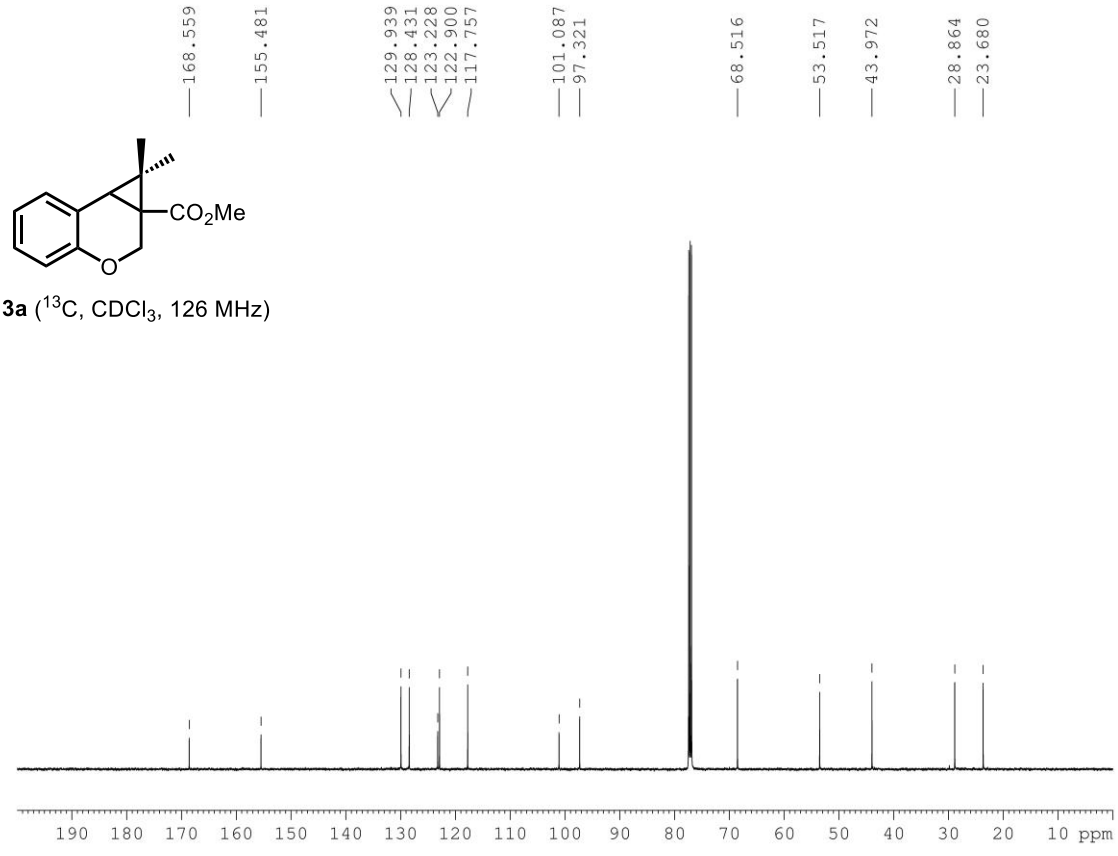
12a (^{1}H, $CDCl_3$, 500 MHz)



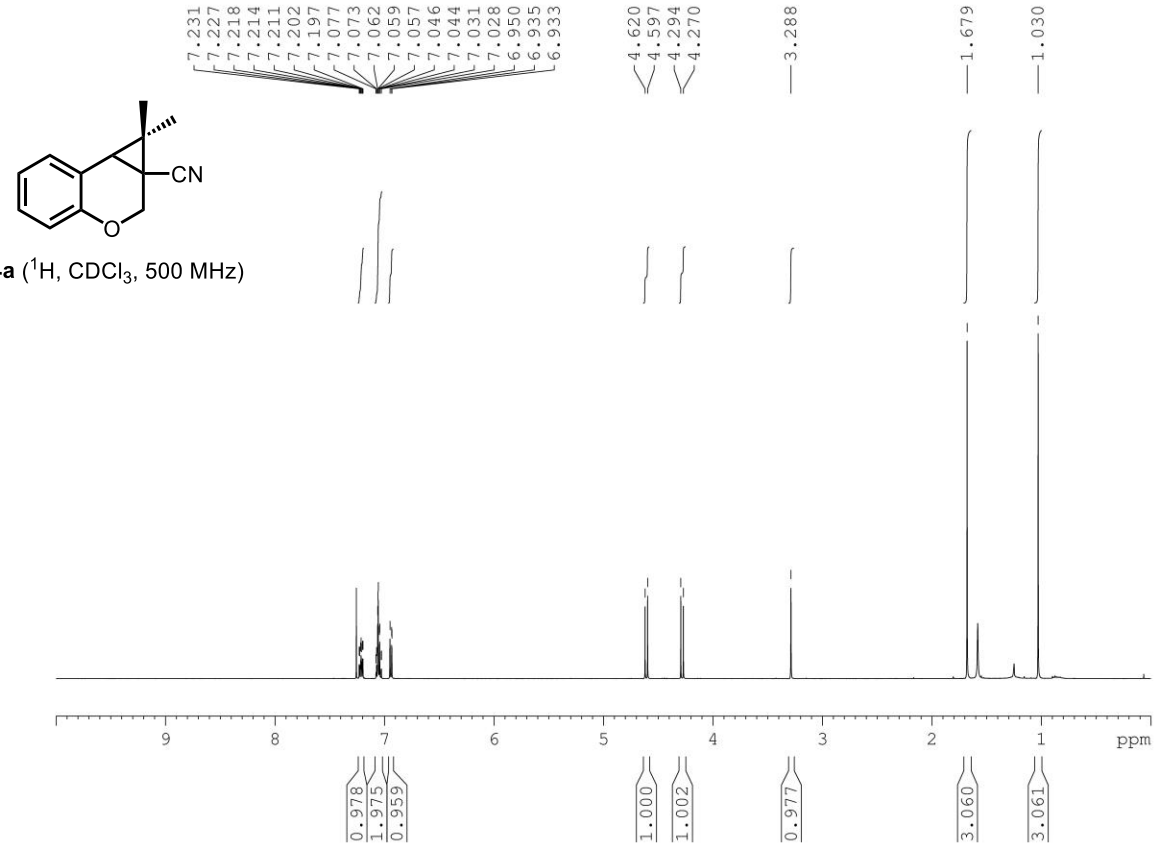
12a (^{13}C, $CDCl_3$, 126 MHz)



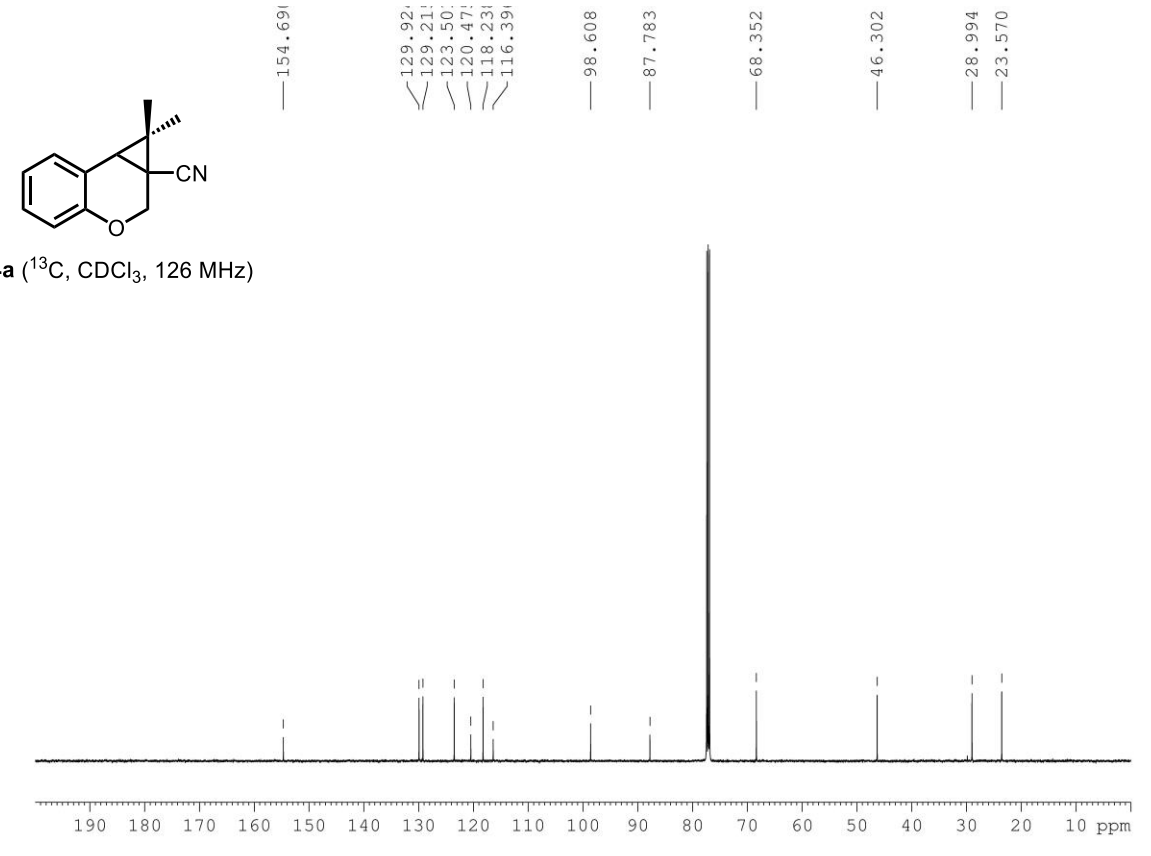
13a (^{1}H, $CDCl_3$, 500 MHz)



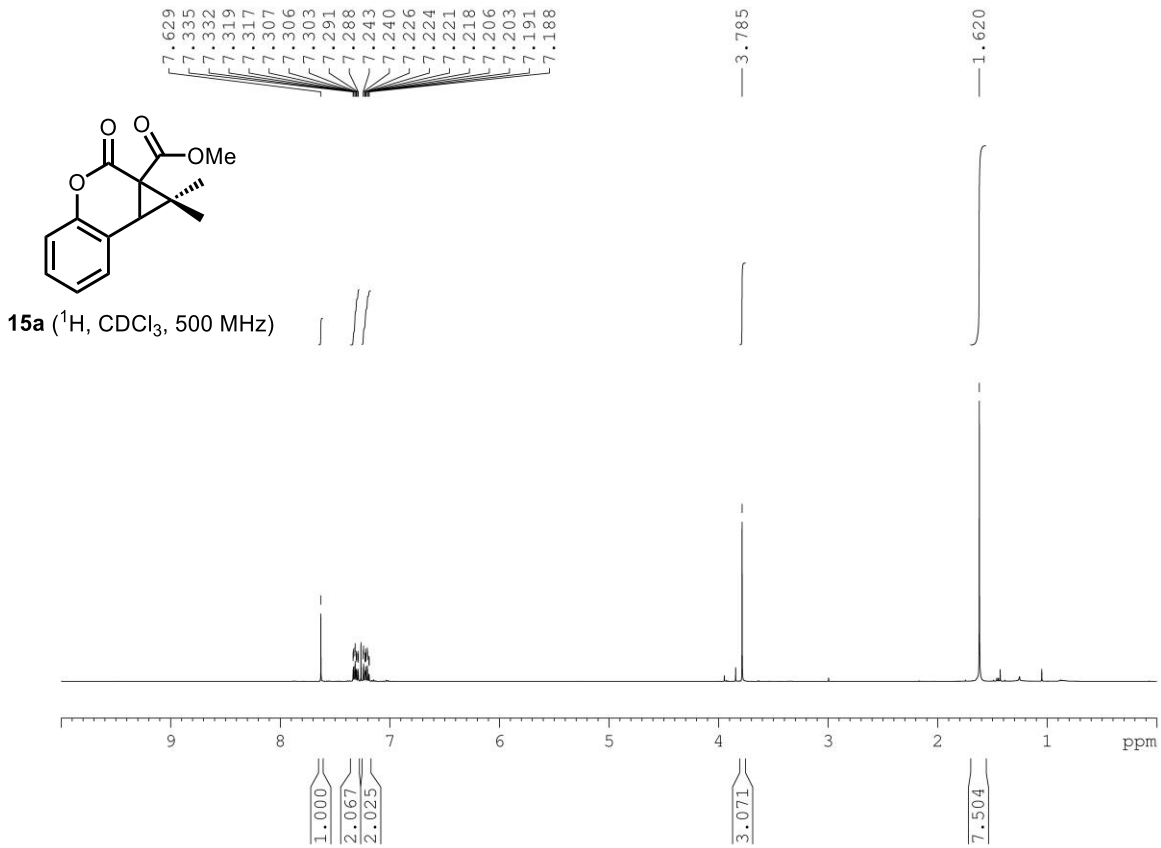
13a (^{13}C, $CDCl_3$, 126 MHz)



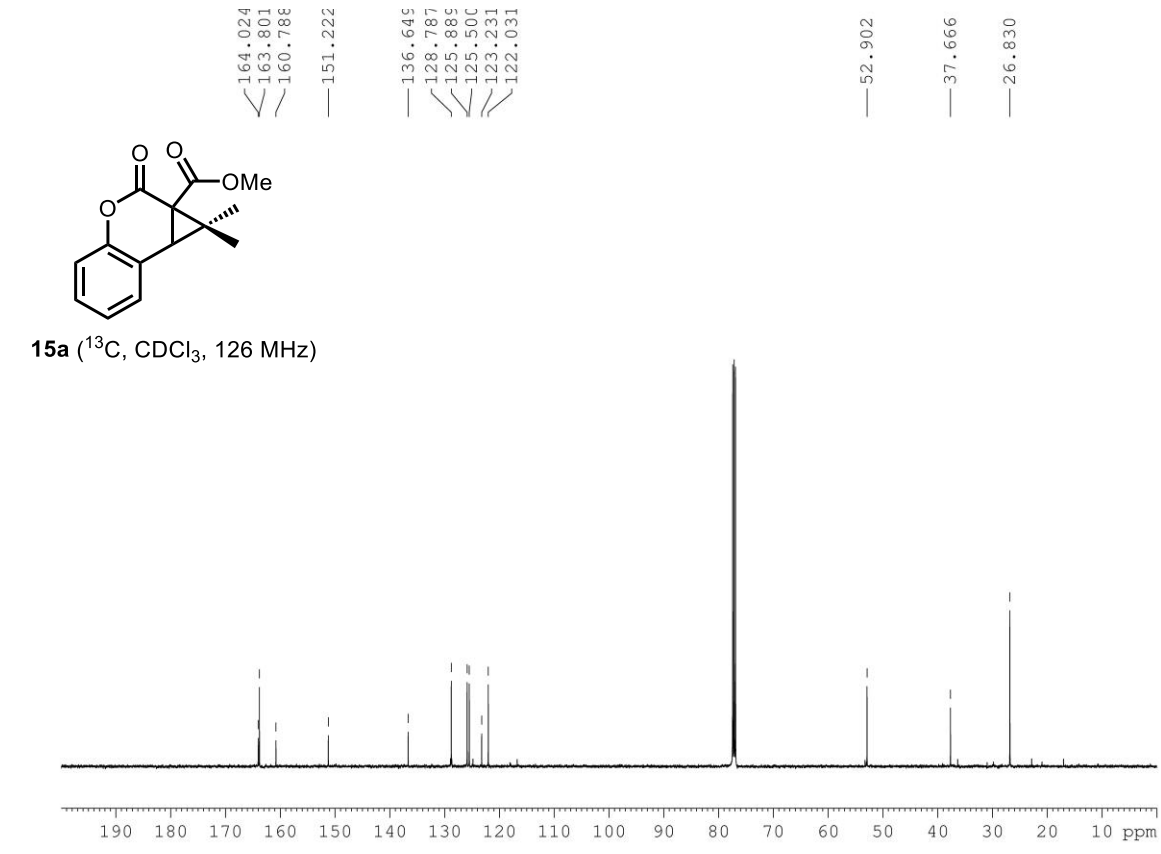
14a (^{1}H, $CDCl_3$, 500 MHz)



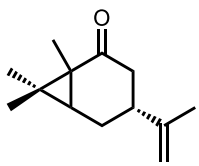
14a (^{13}C, $CDCl_3$, 126 MHz)



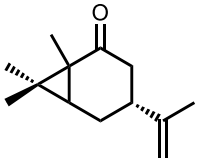
15a (^{1}H, $CDCl_3$, 500 MHz)



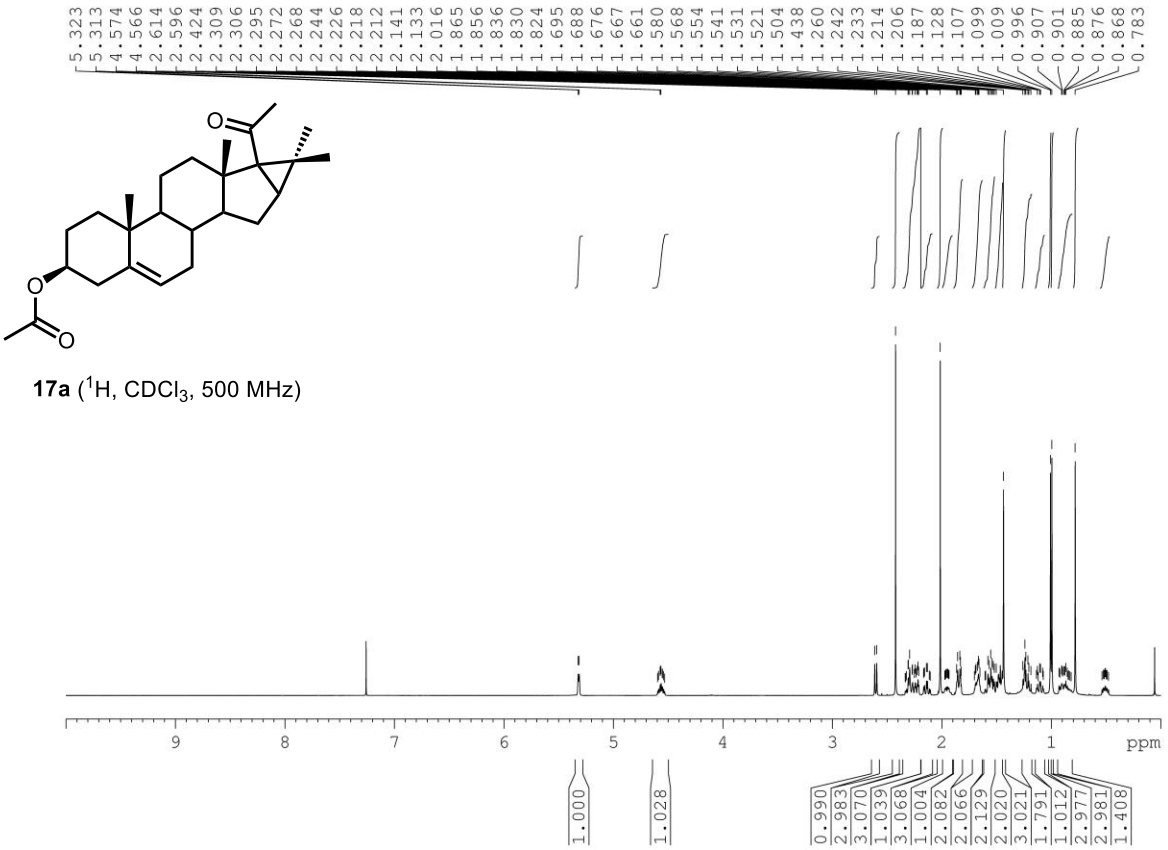
15a (^{13}C, $CDCl_3$, 126 MHz)



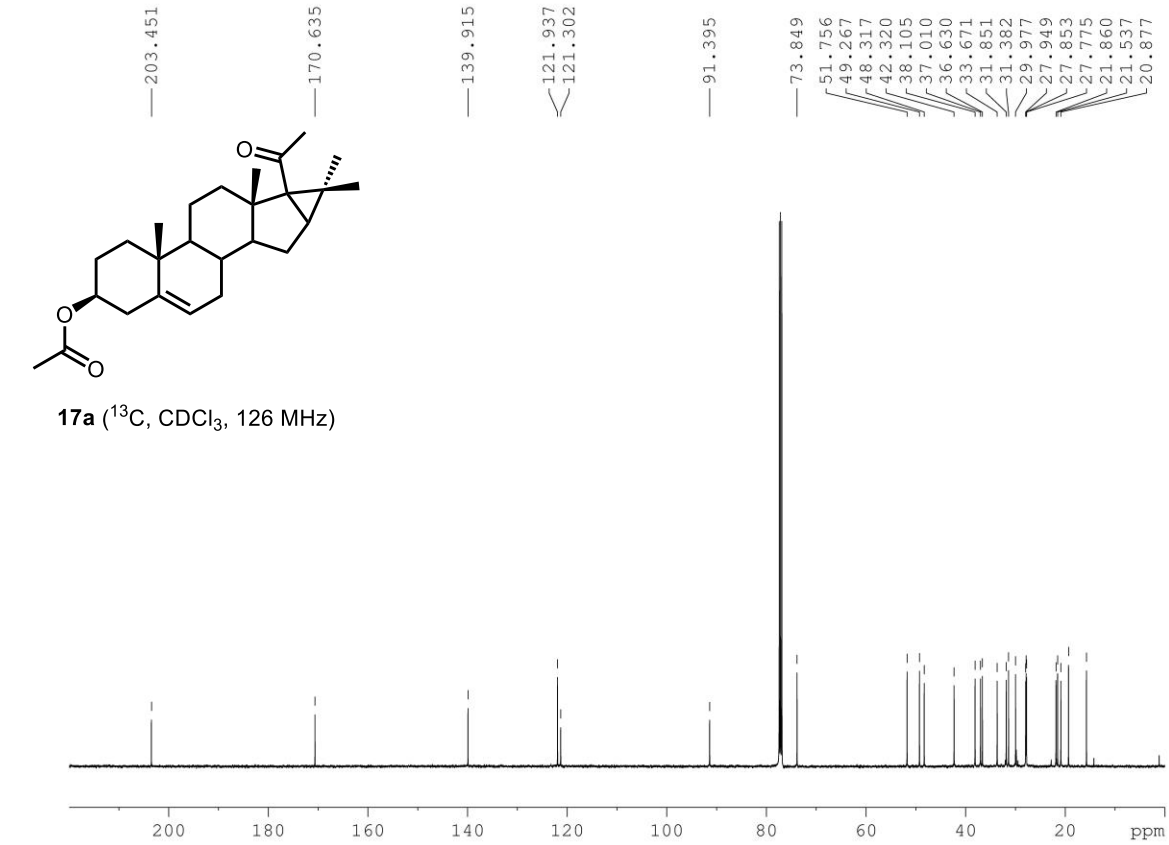
16a (^{1}H, $CDCl_3$, 400 MHz)



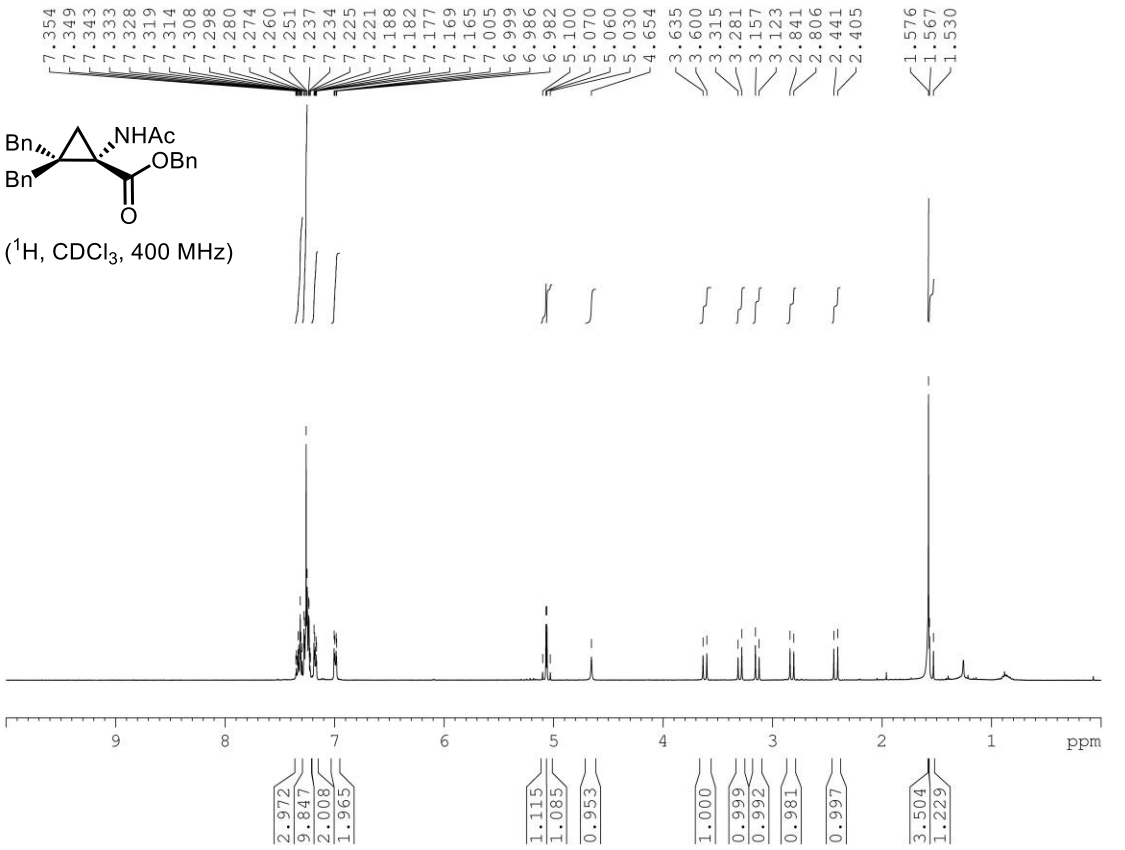
16a (^{13}C, $CDCl_3$, 126 MHz)



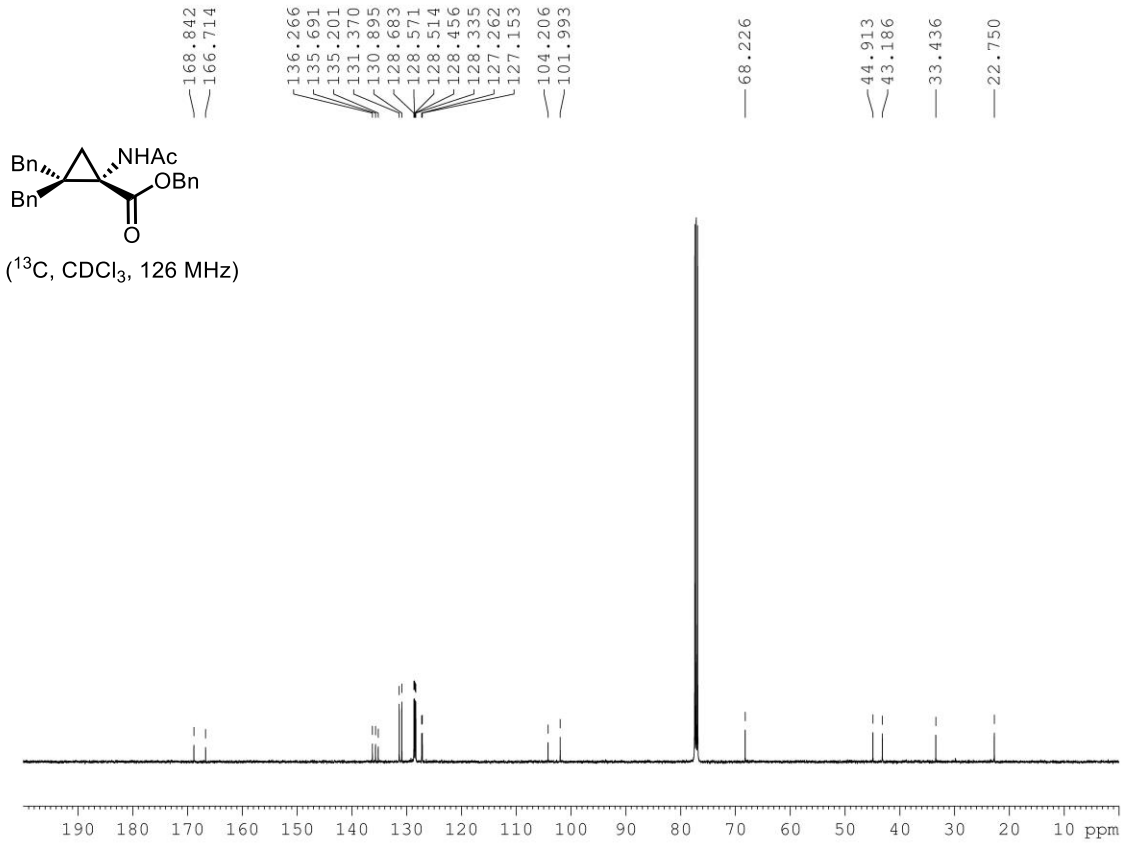
17a (^{1}H, $CDCl_3$, 500 MHz)



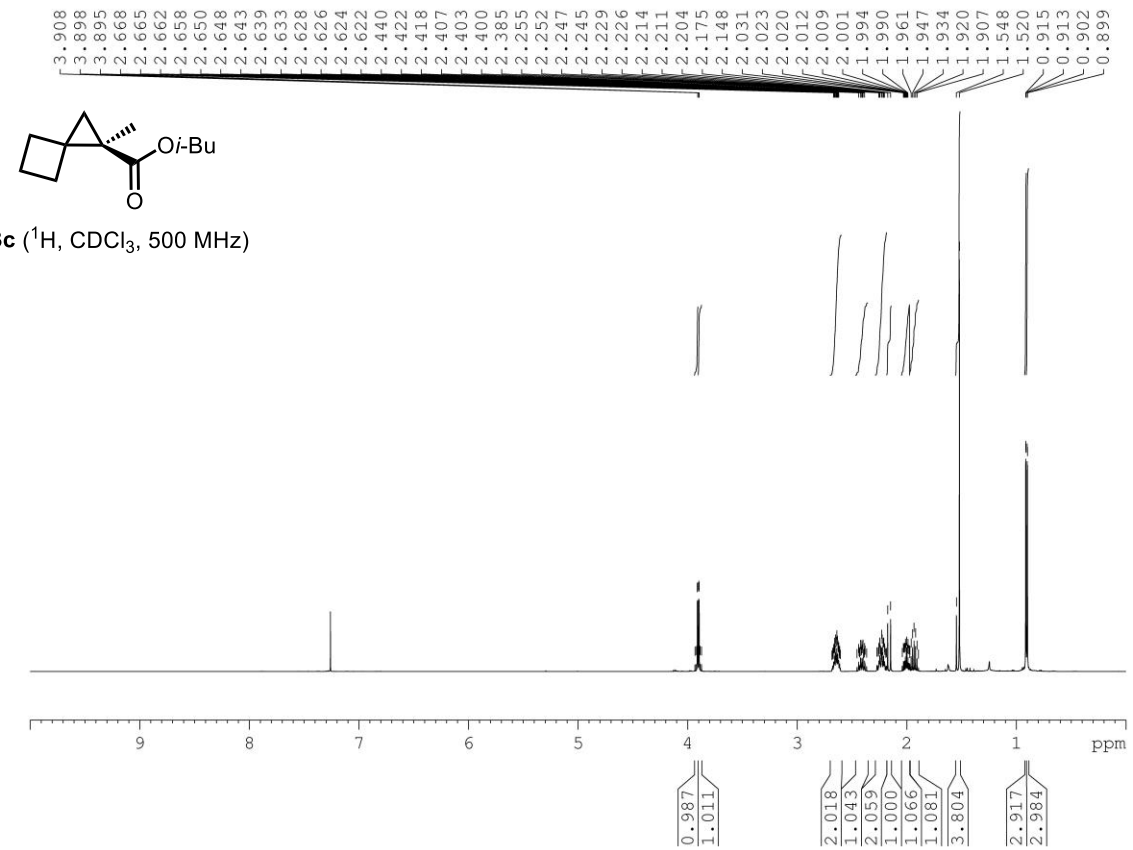
17a (^{13}C, $CDCl_3$, 126 MHz)



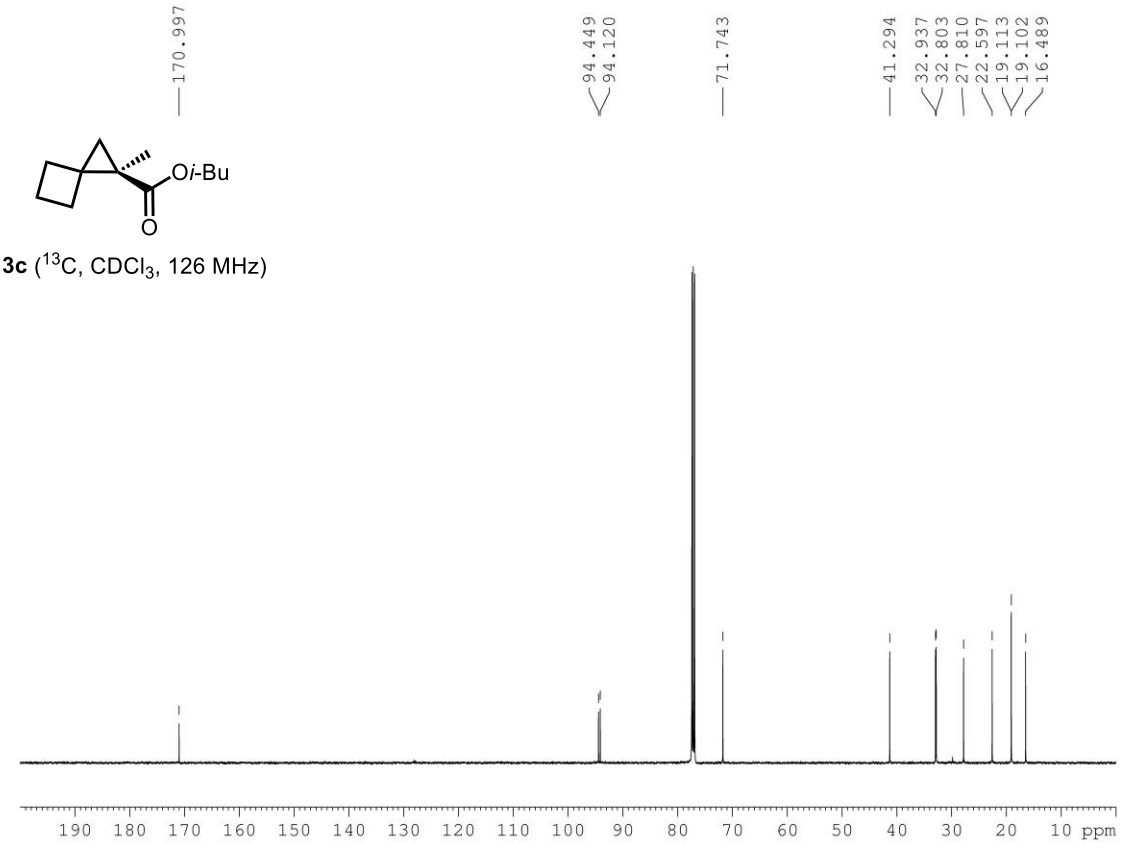
8b (^{1}H, $CDCl_3$, 400 MHz)



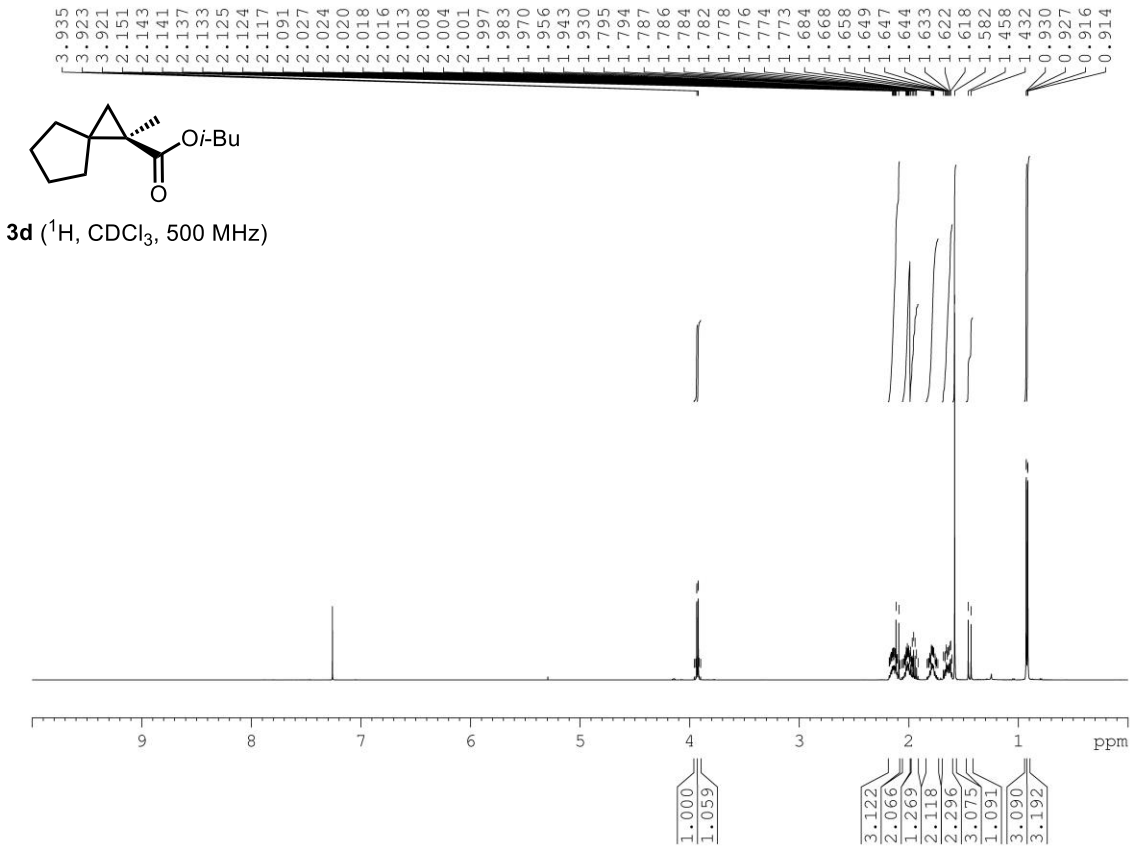
8b (^{13}C, $CDCl_3$, 126 MHz)



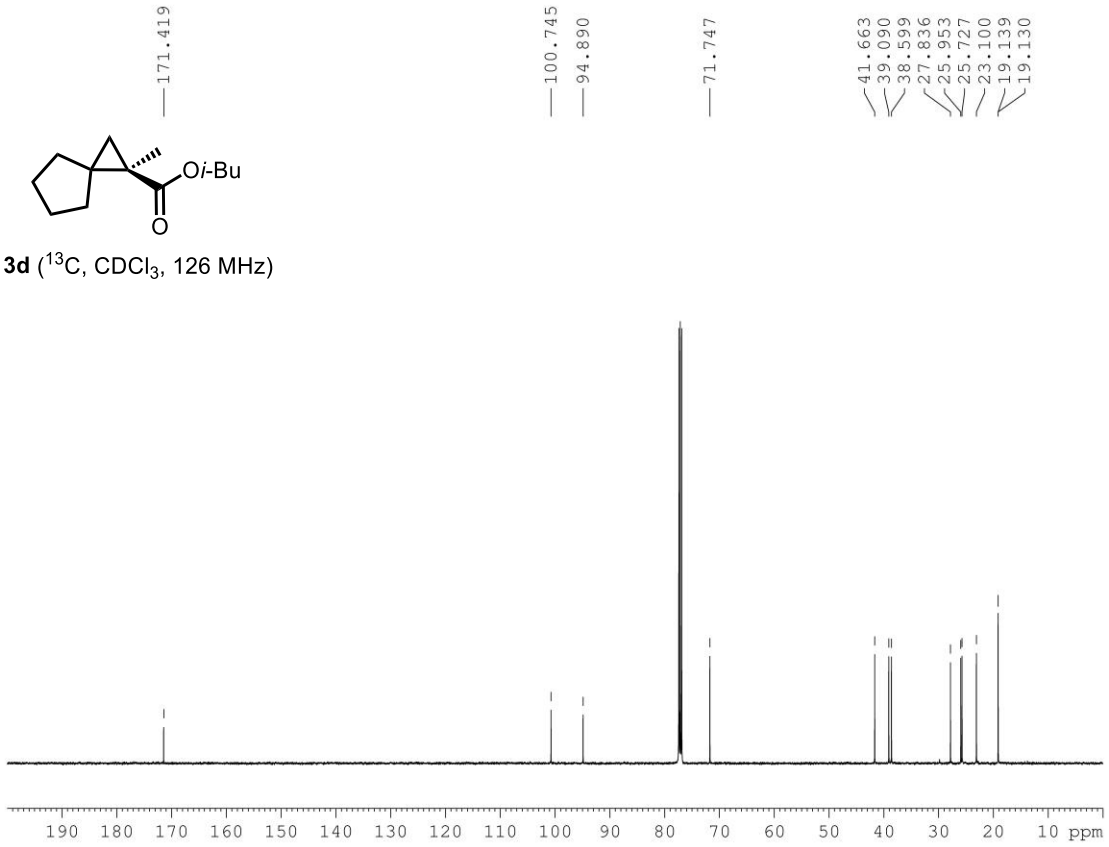
3c (^{1}H, $CDCl_3$, 500 MHz)



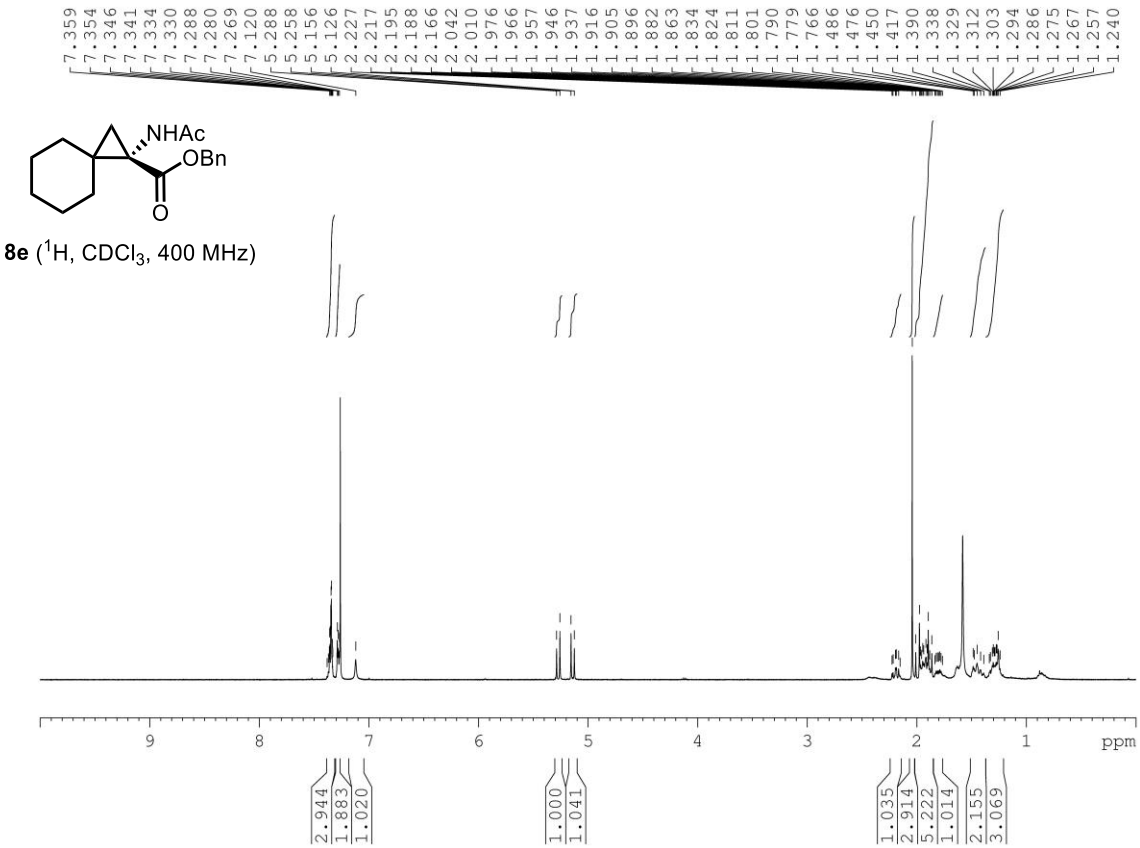
3c (^{13}C, $CDCl_3$, 126 MHz)



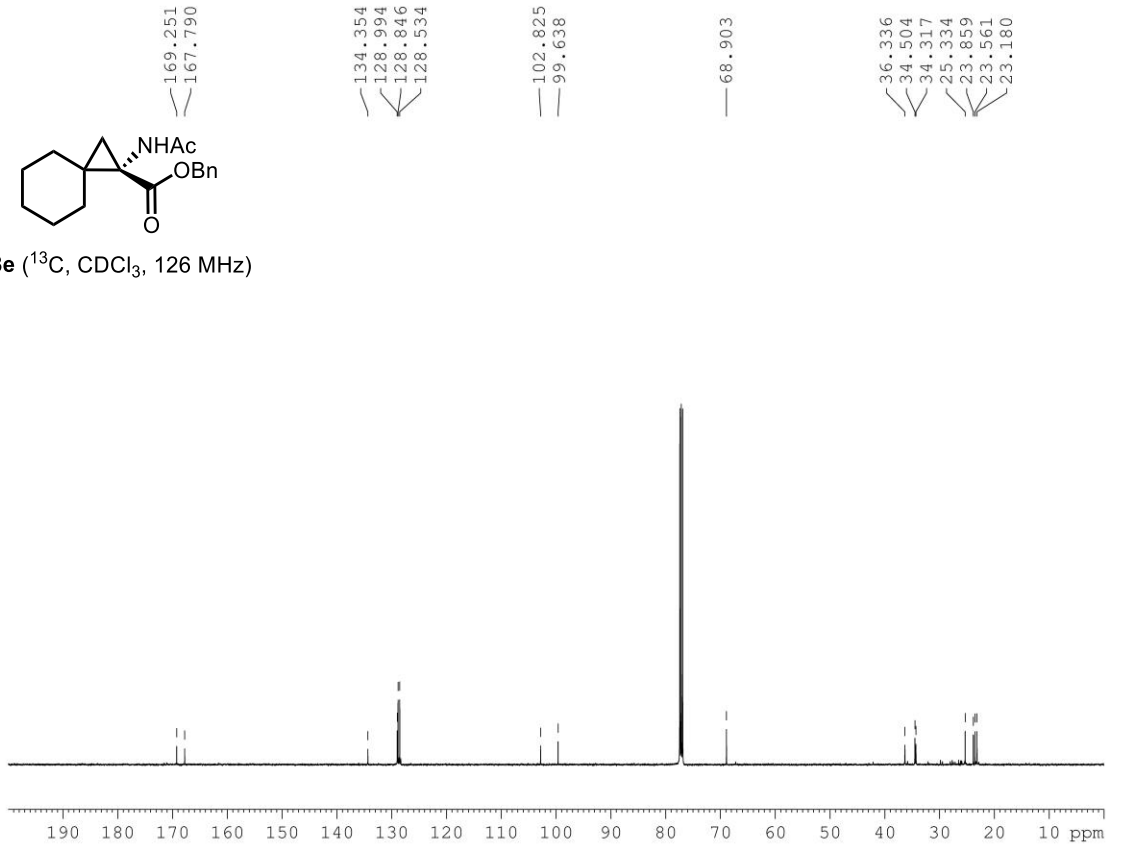
3d (^{1}H, $CDCl_3$, 500 MHz)



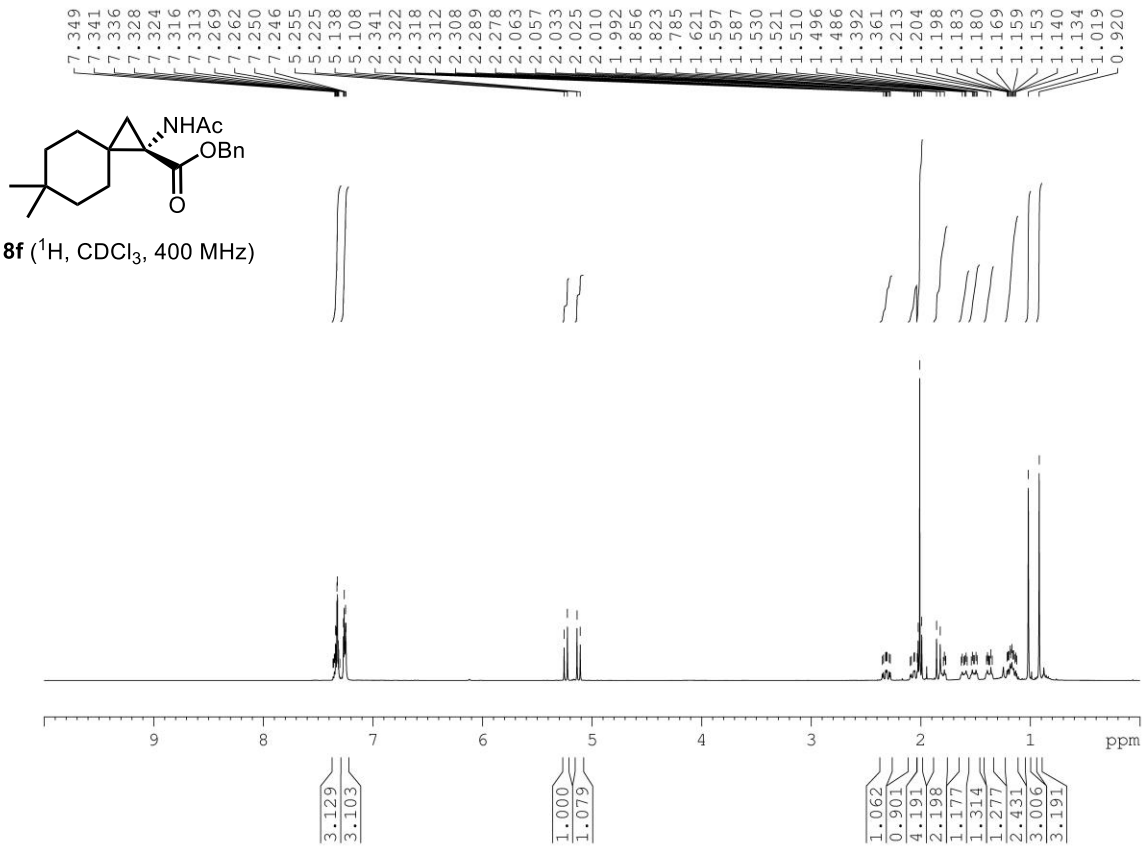
3d (^{13}C, $CDCl_3$, 126 MHz)



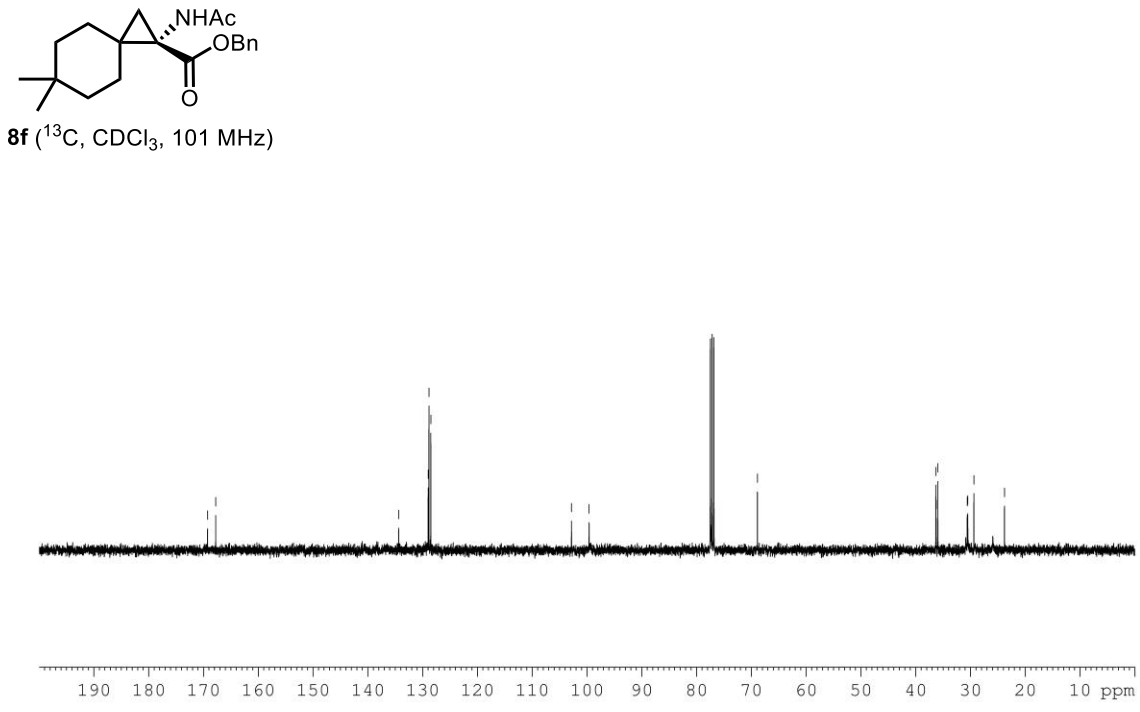
8e (^{1}H, $CDCl_3$, 400 MHz)



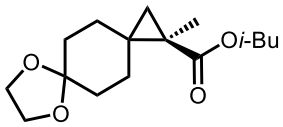
8e (^{13}C, $CDCl_3$, 126 MHz)



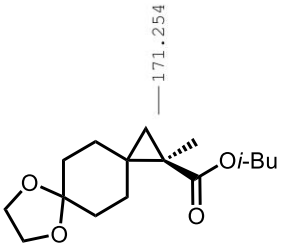
8f (^{1}H, $CDCl_3$, 400 MHz)



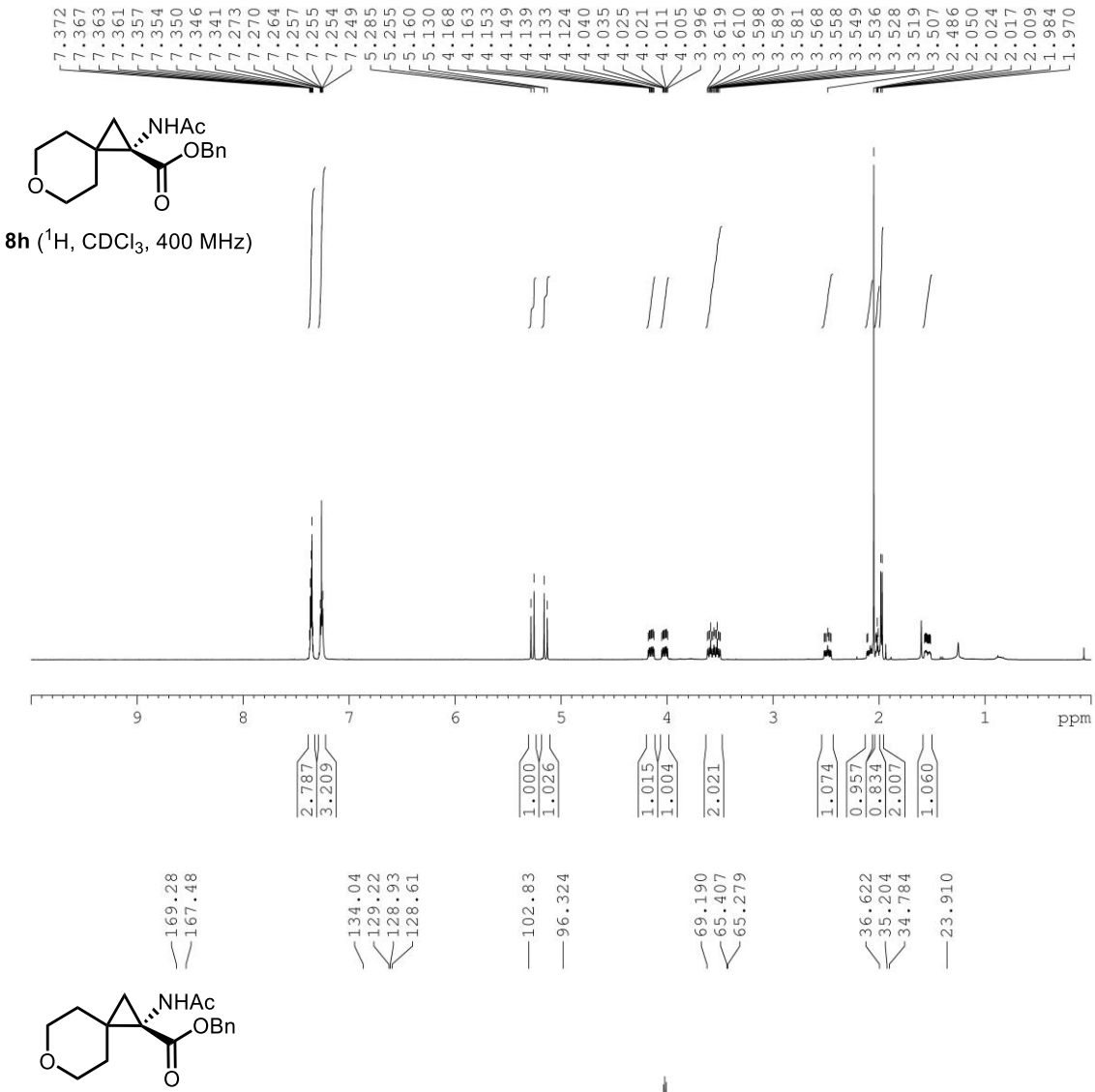
8f (^{13}C, $CDCl_3$, 101 MHz)



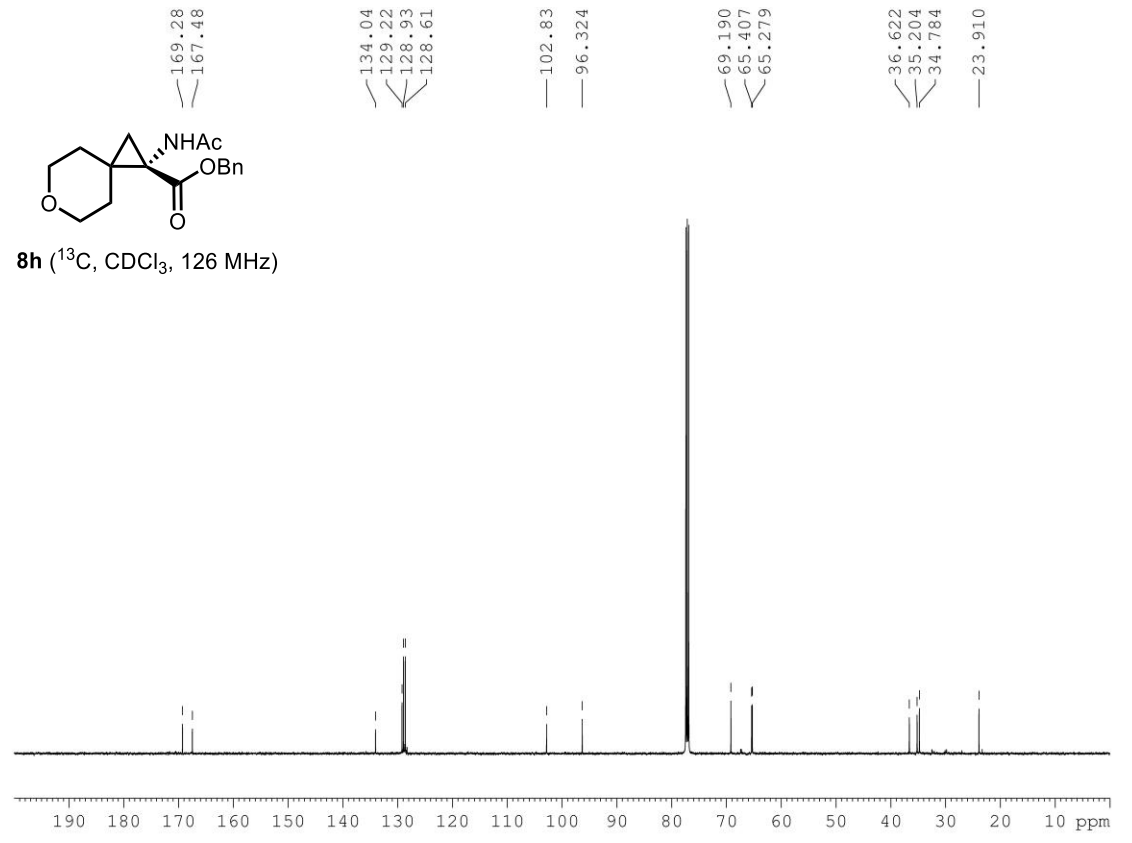
3g (^{1}H, $CDCl_3$, 500 MHz)



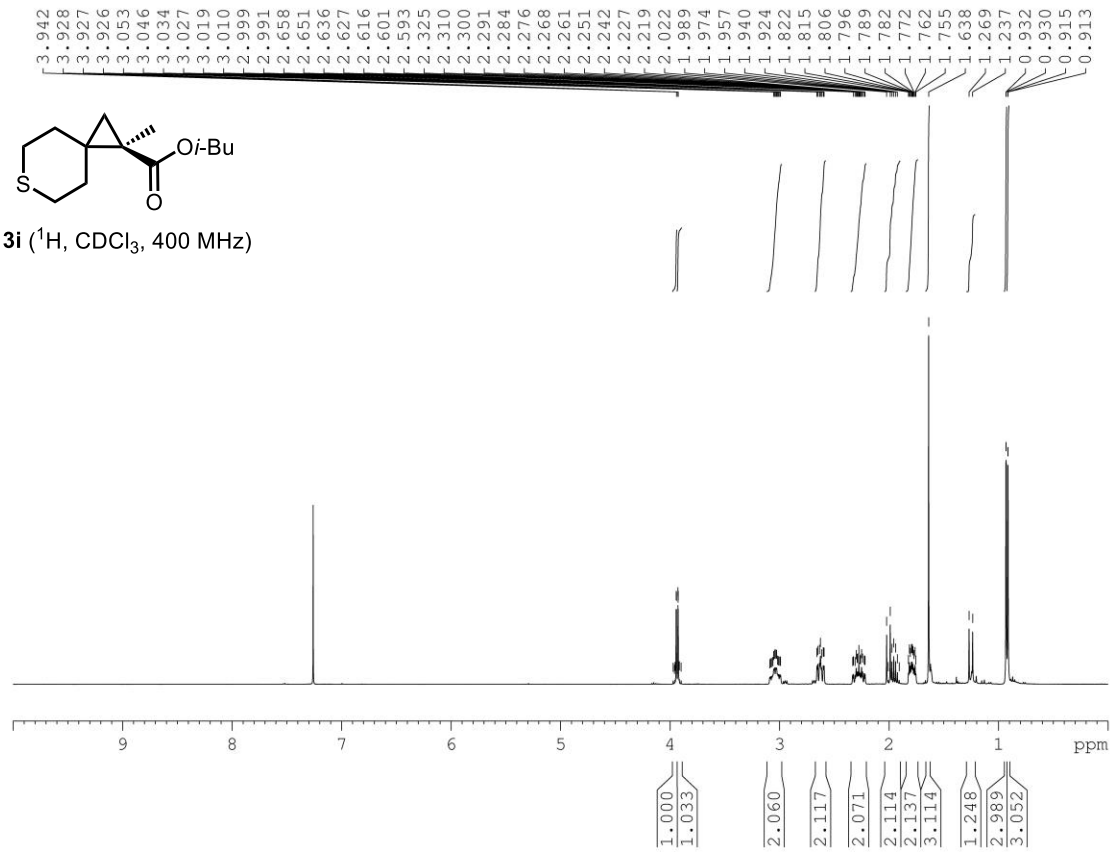
3g (^{13}C, $CDCl_3$, 126 MHz)



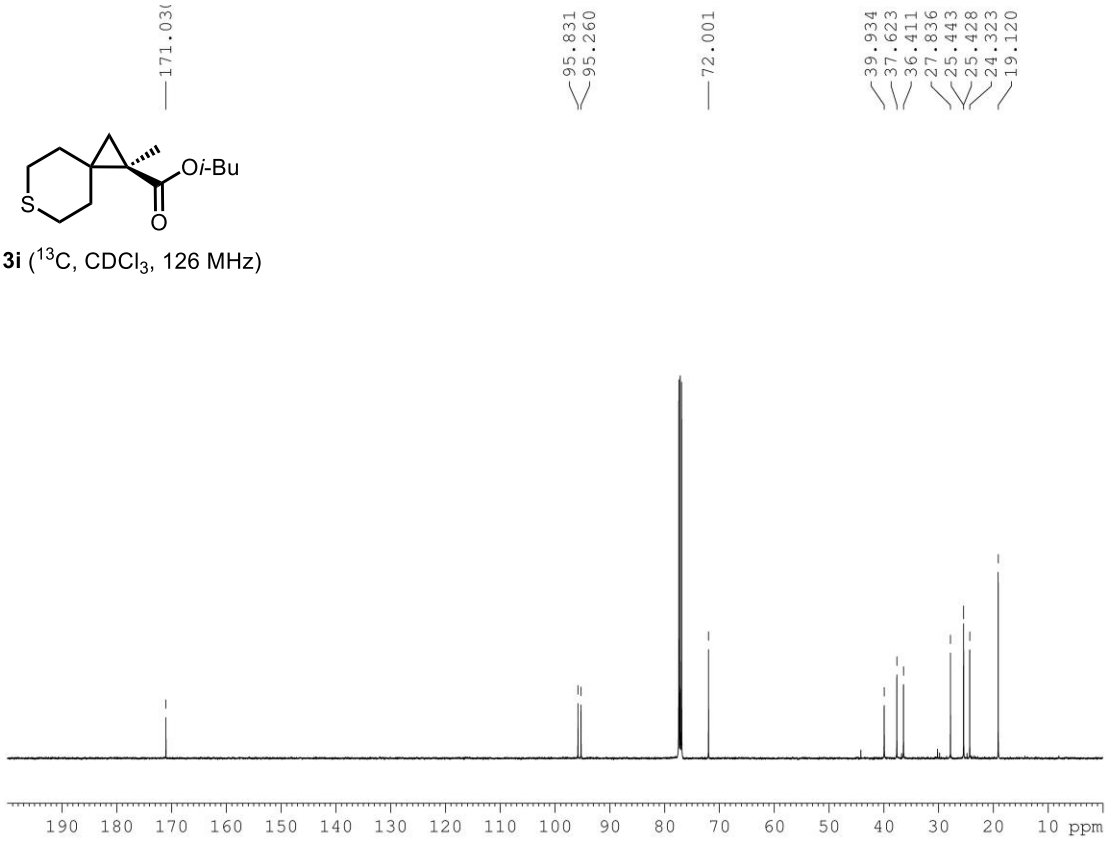
8h (^{1}H, $CDCl_3$, 400 MHz)



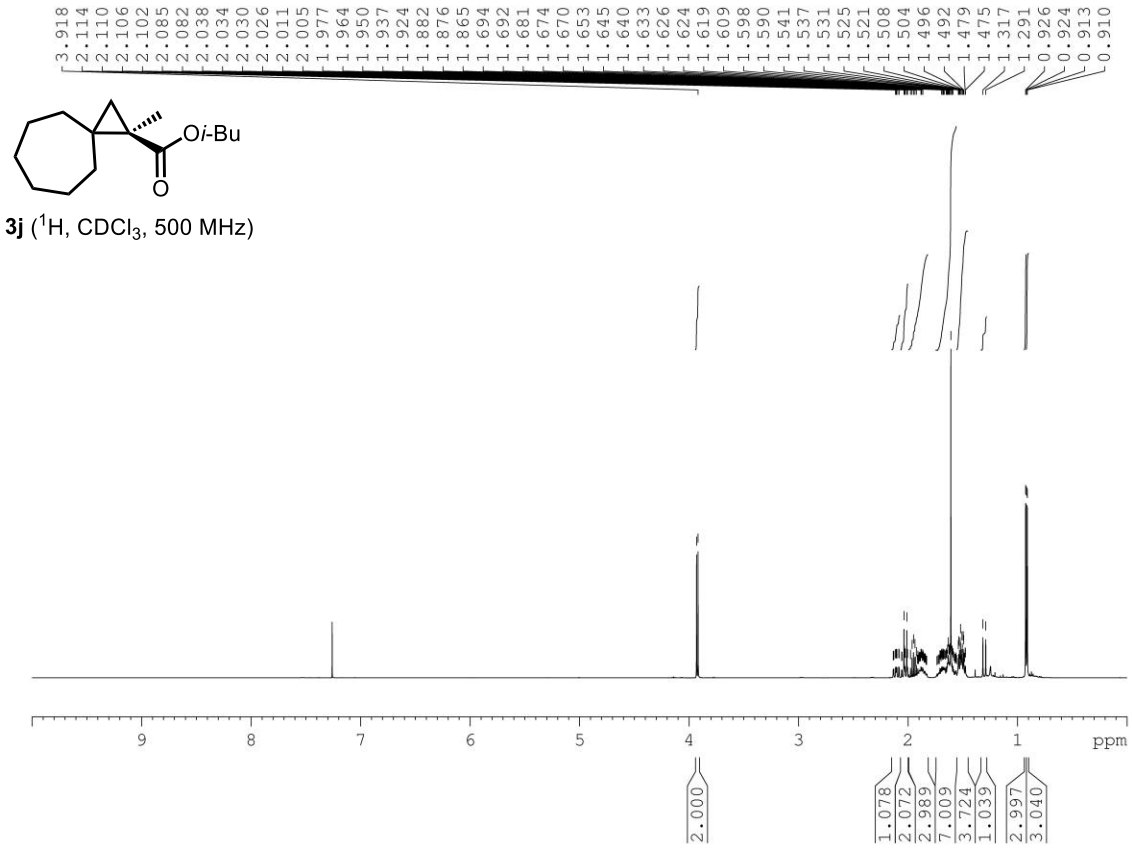
8h (^{13}C, $CDCl_3$, 126 MHz)



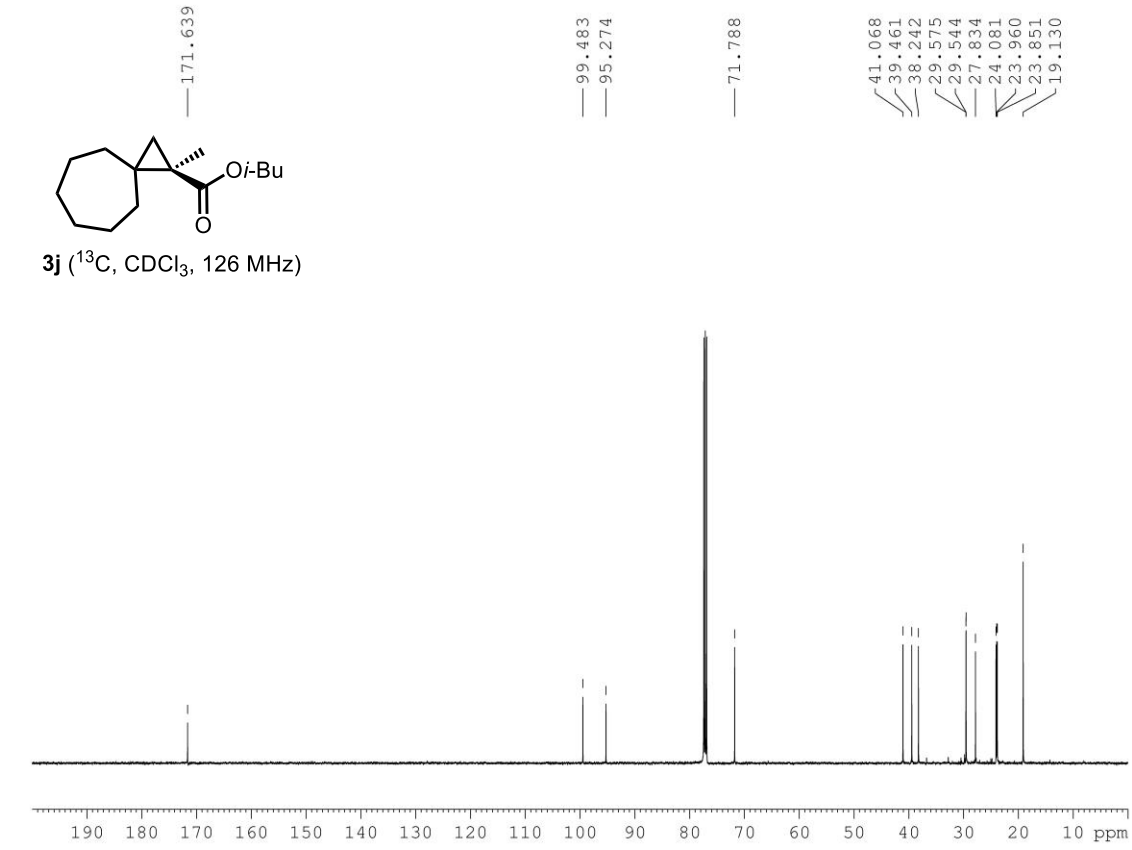
3i (^{1}H, $CDCl_3$, 400 MHz)



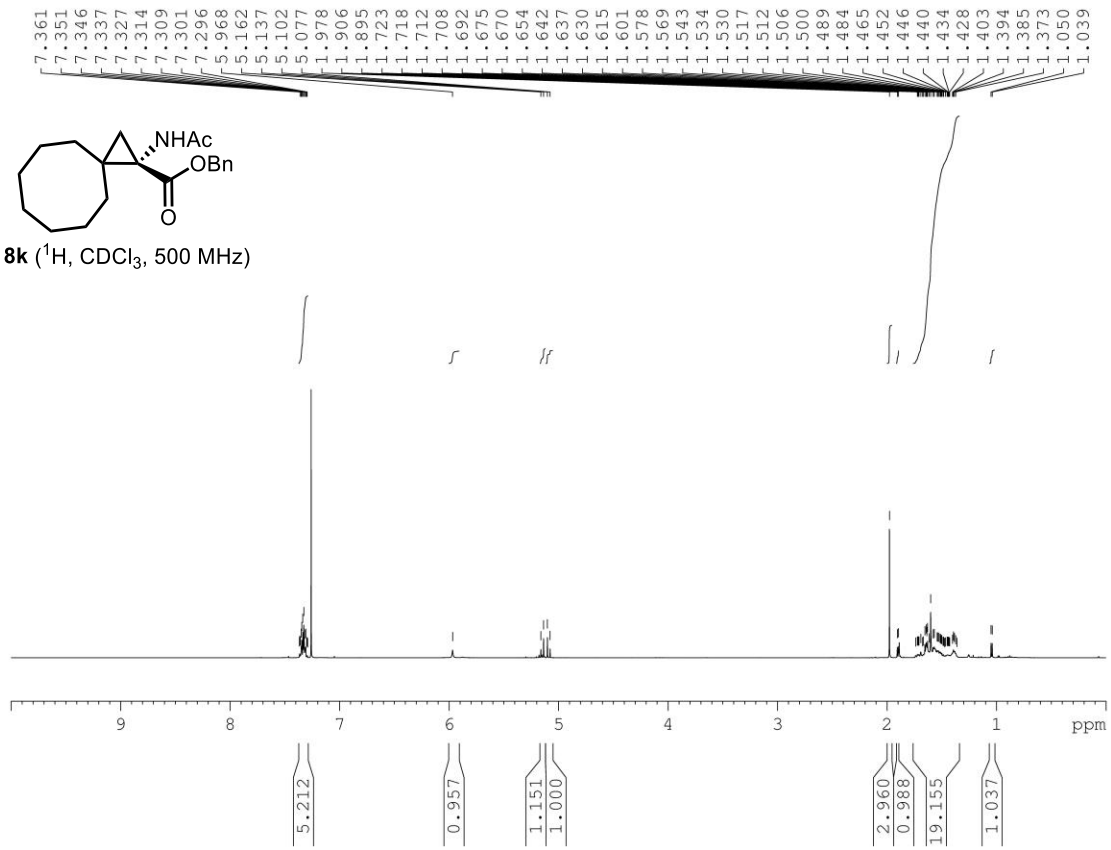
3i (^{13}C, $CDCl_3$, 126 MHz)



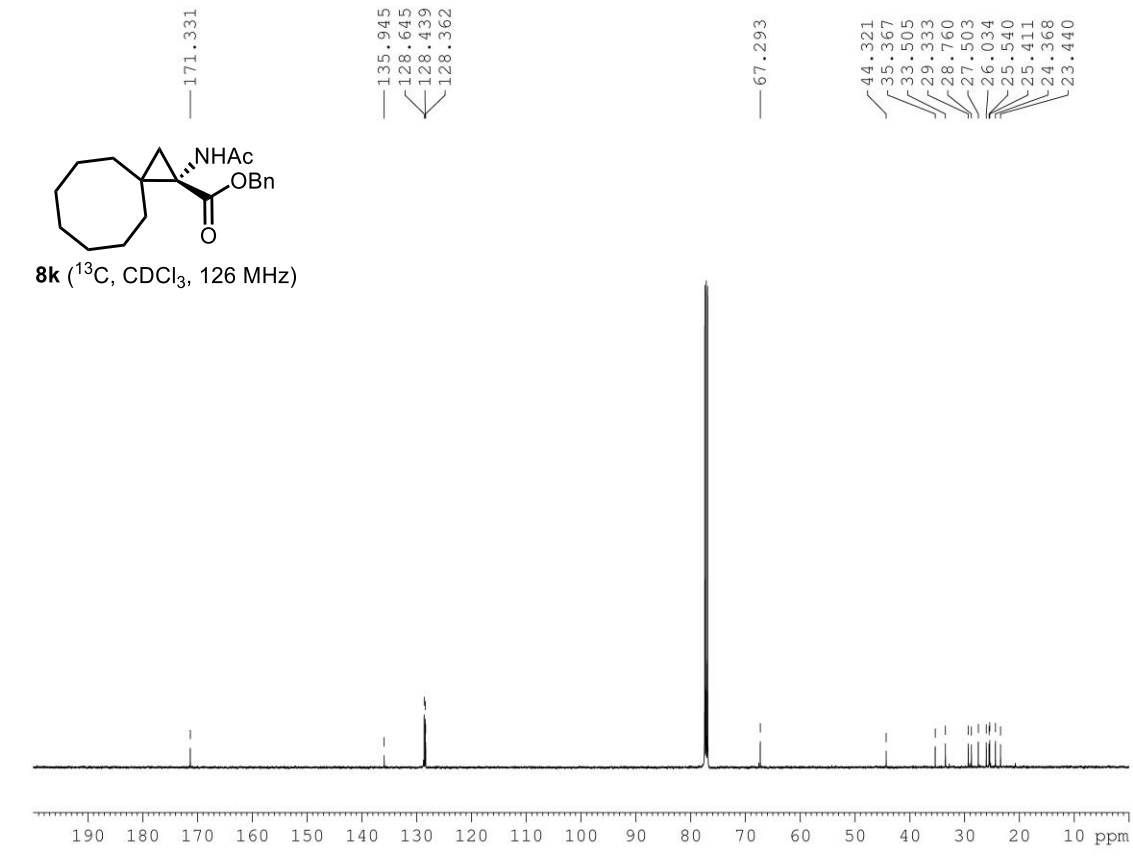
3j (^{1}H, $CDCl_3$, 500 MHz)



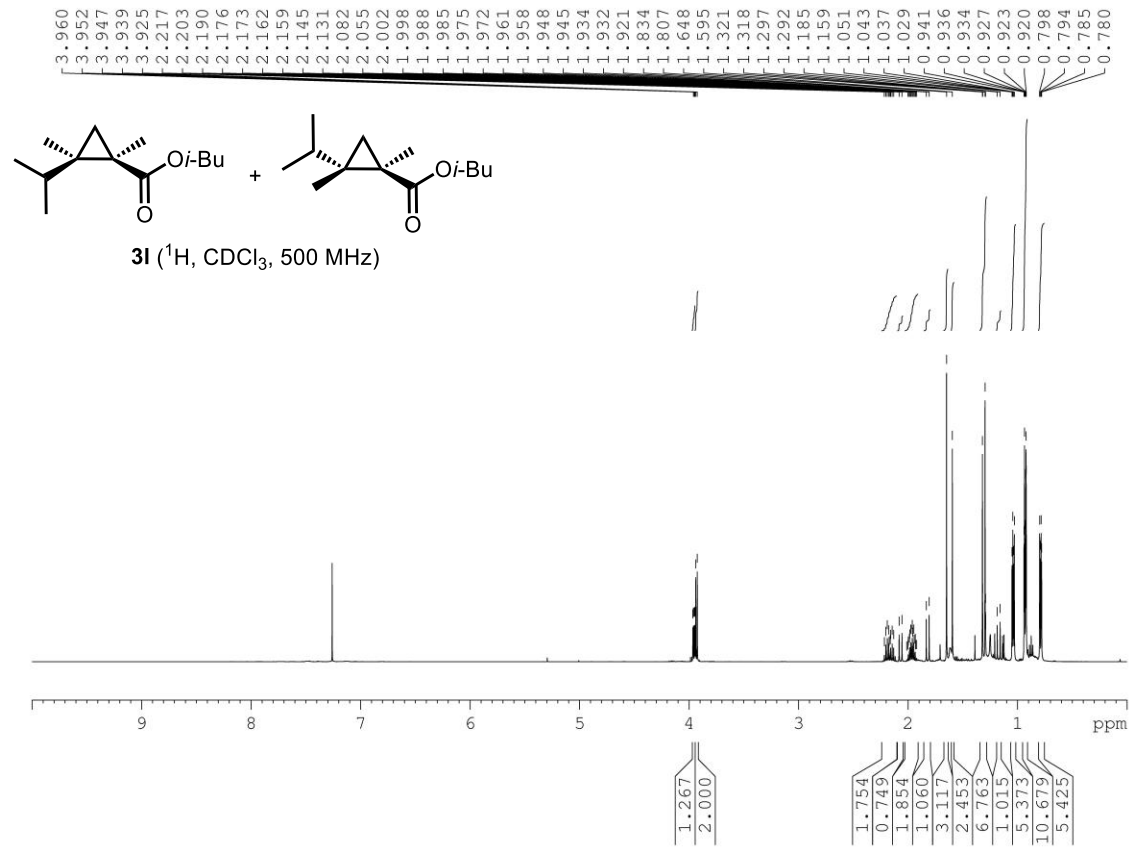
3j (^{13}C, $CDCl_3$, 126 MHz)



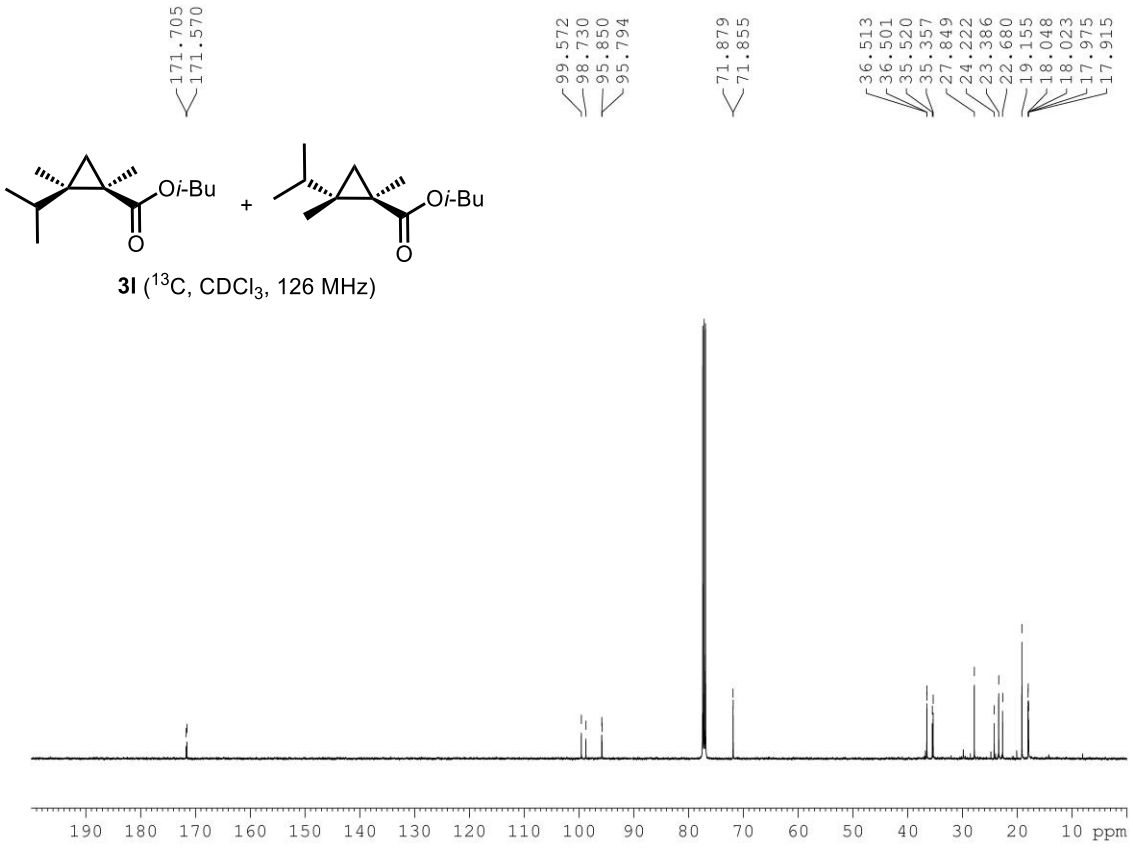
8k (^{1}H, $CDCl_3$, 500 MHz)



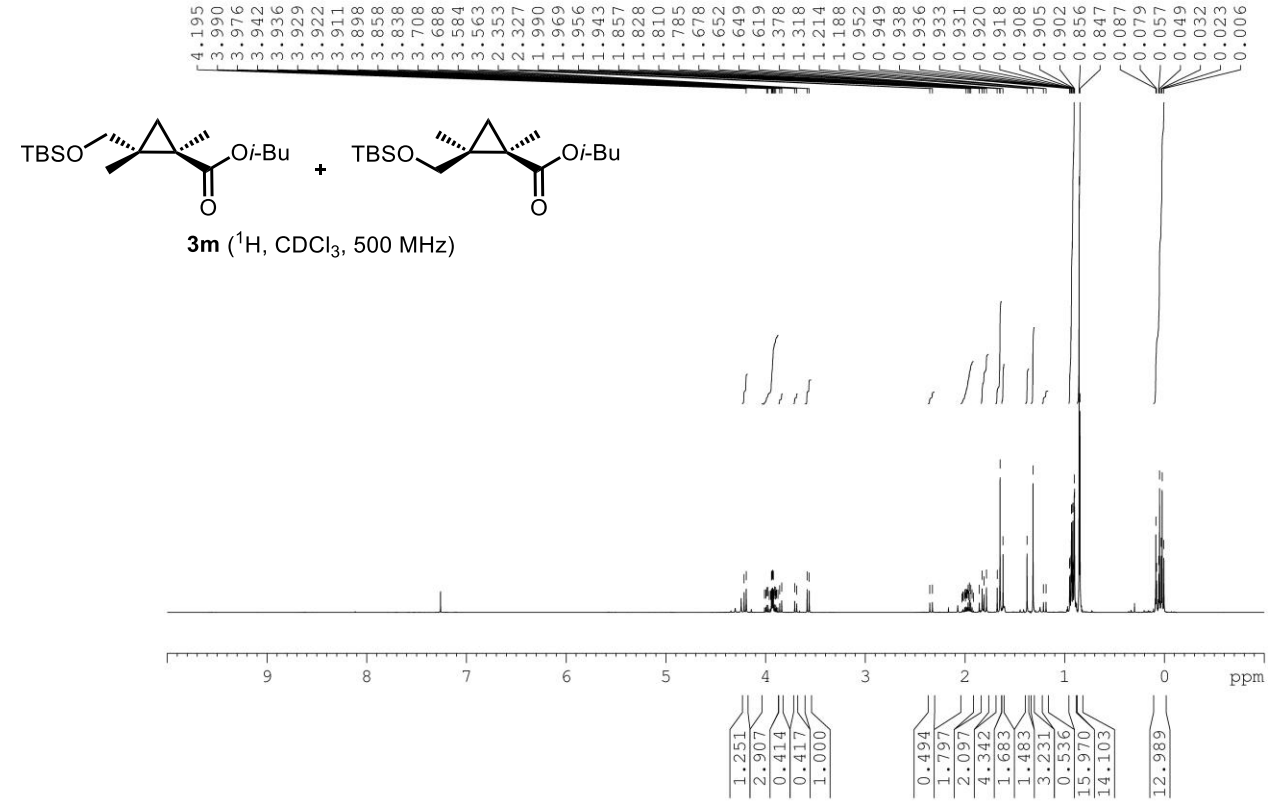
8k (^{13}C, $CDCl_3$, 126 MHz)



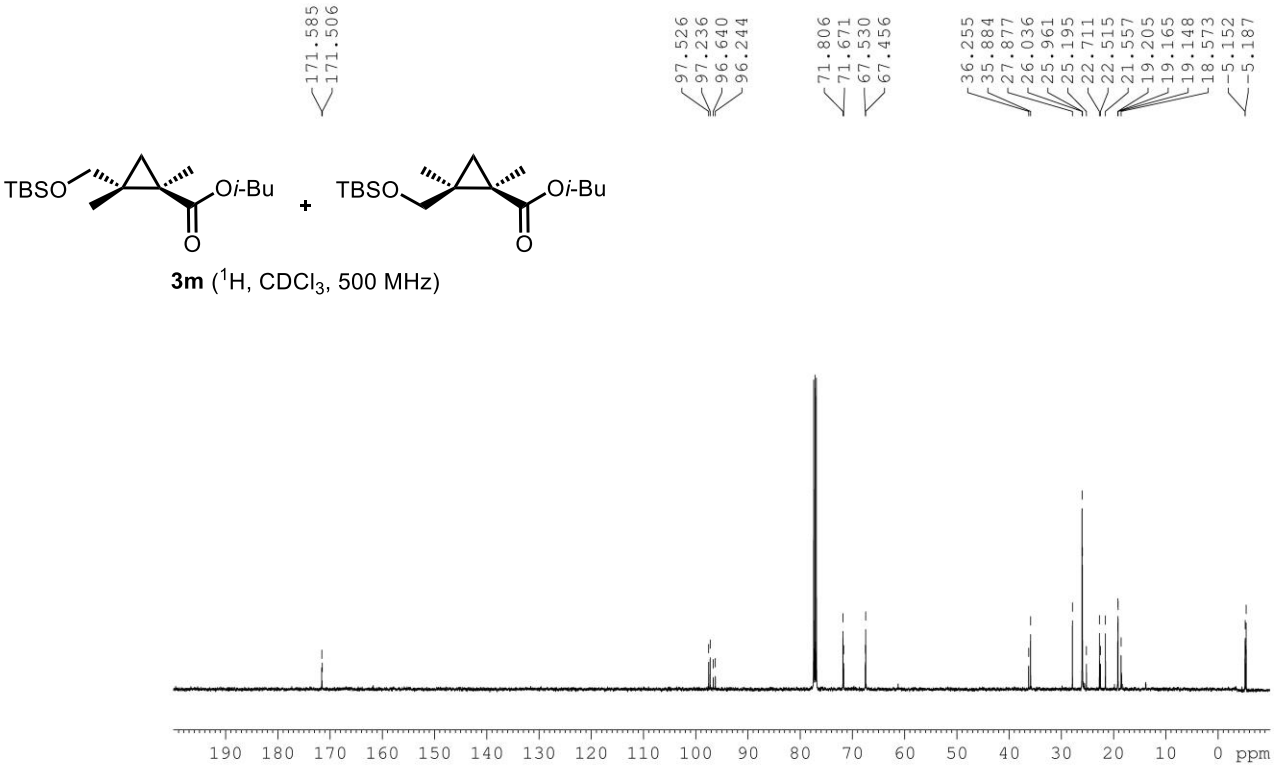
3l (^{1}H, $CDCl_3$, 500 MHz)



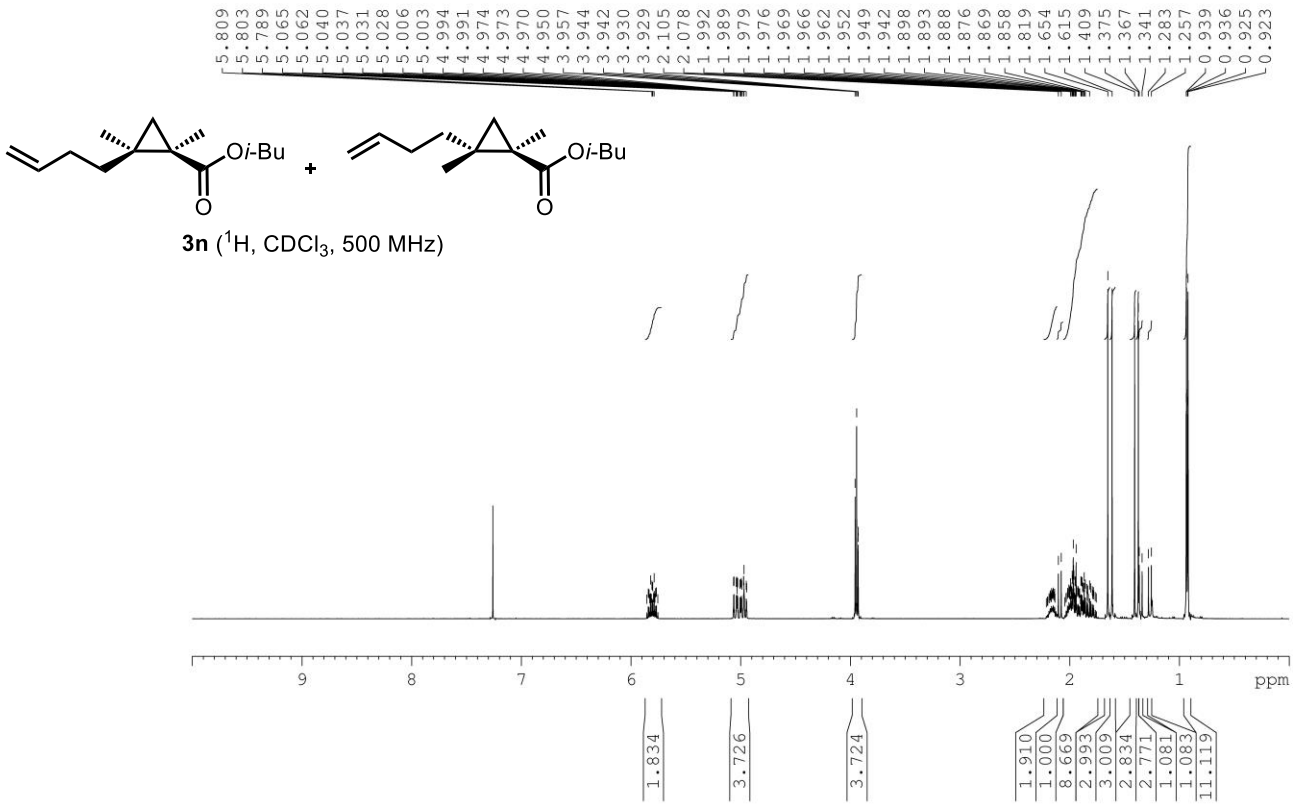
3l (^{13}C, $CDCl_3$, 126 MHz)



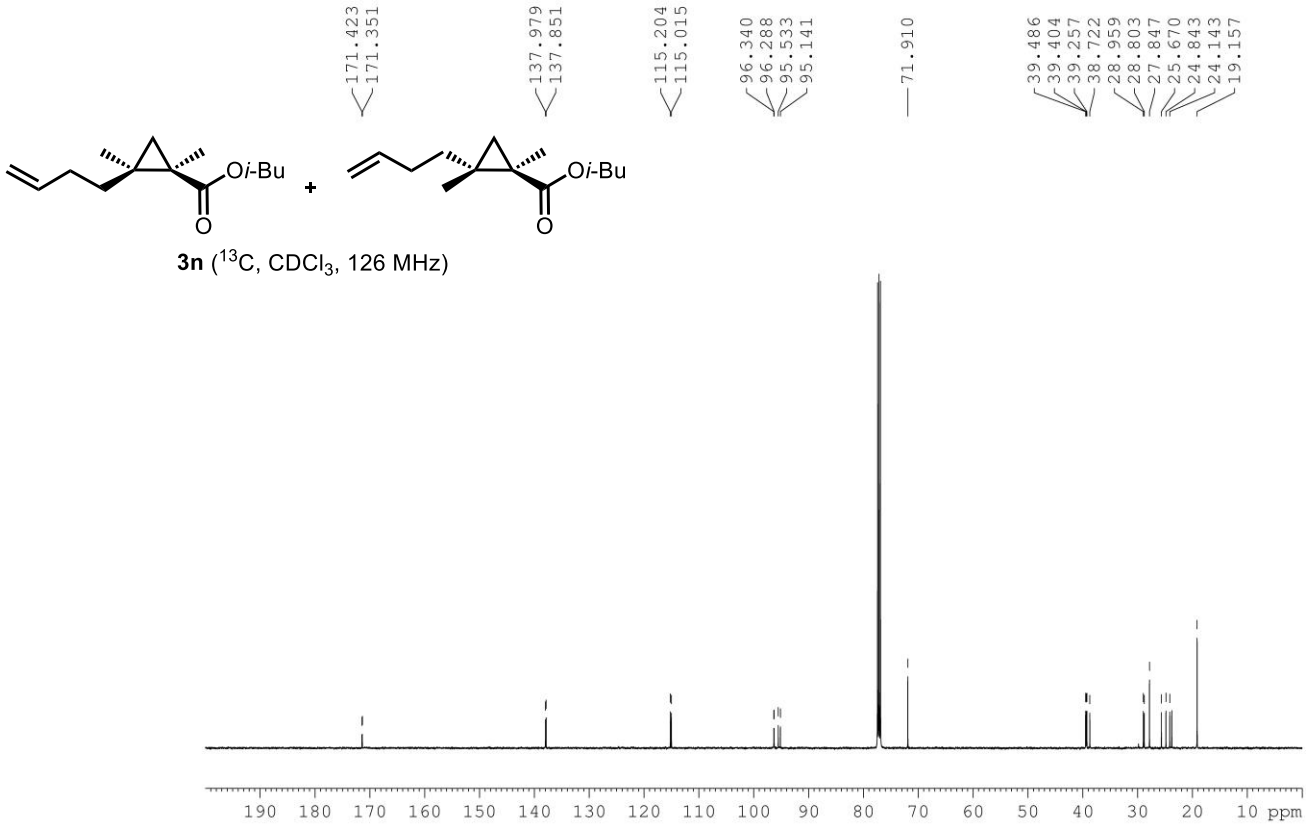
3m (^{1}H, $CDCl_3$, 500 MHz)



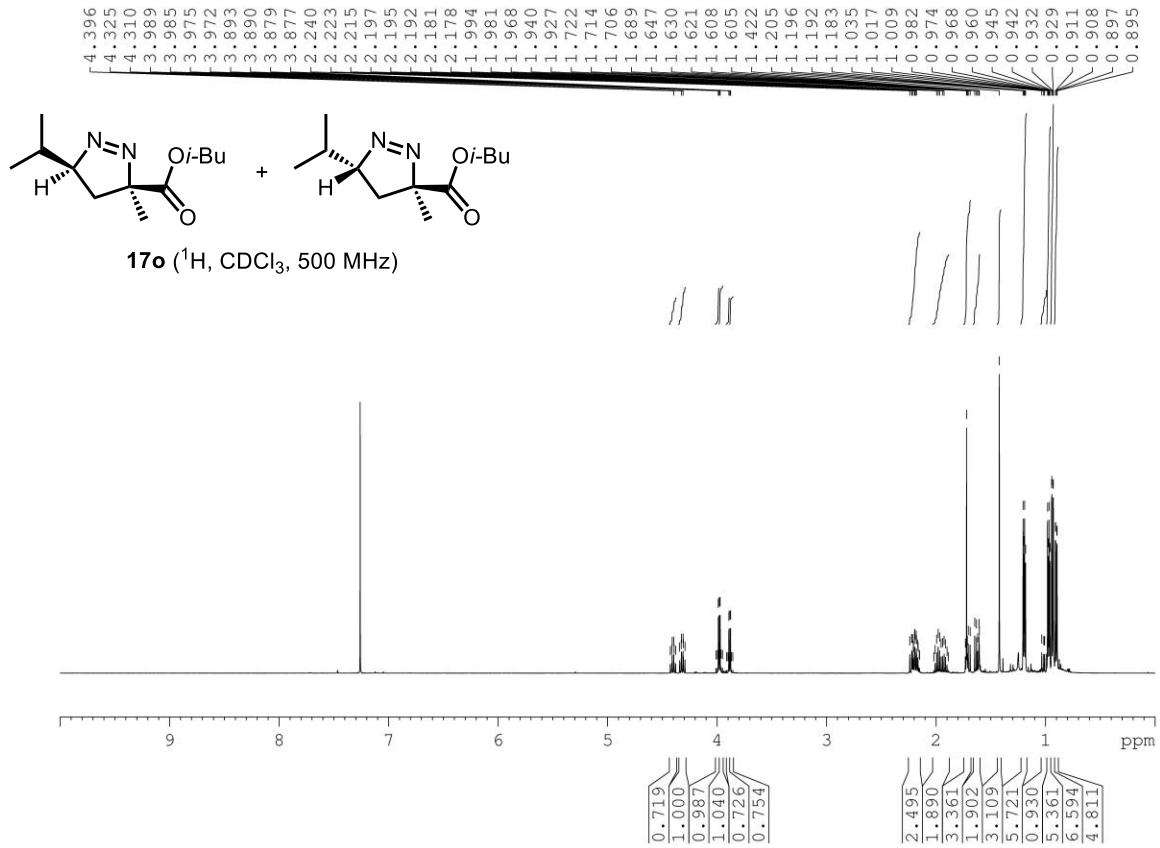
3m (^{1}H, $CDCl_3$, 500 MHz)



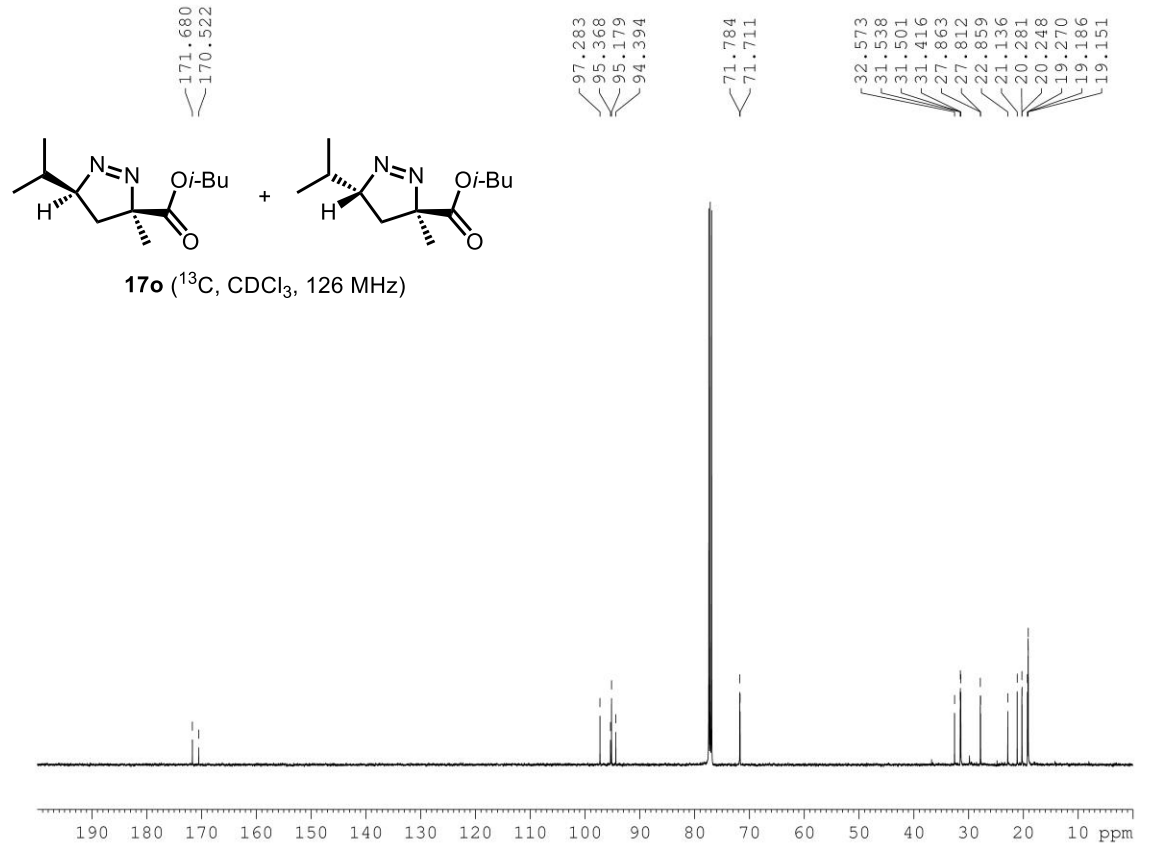
3n (^{1}H, $CDCl_3$, 500 MHz)



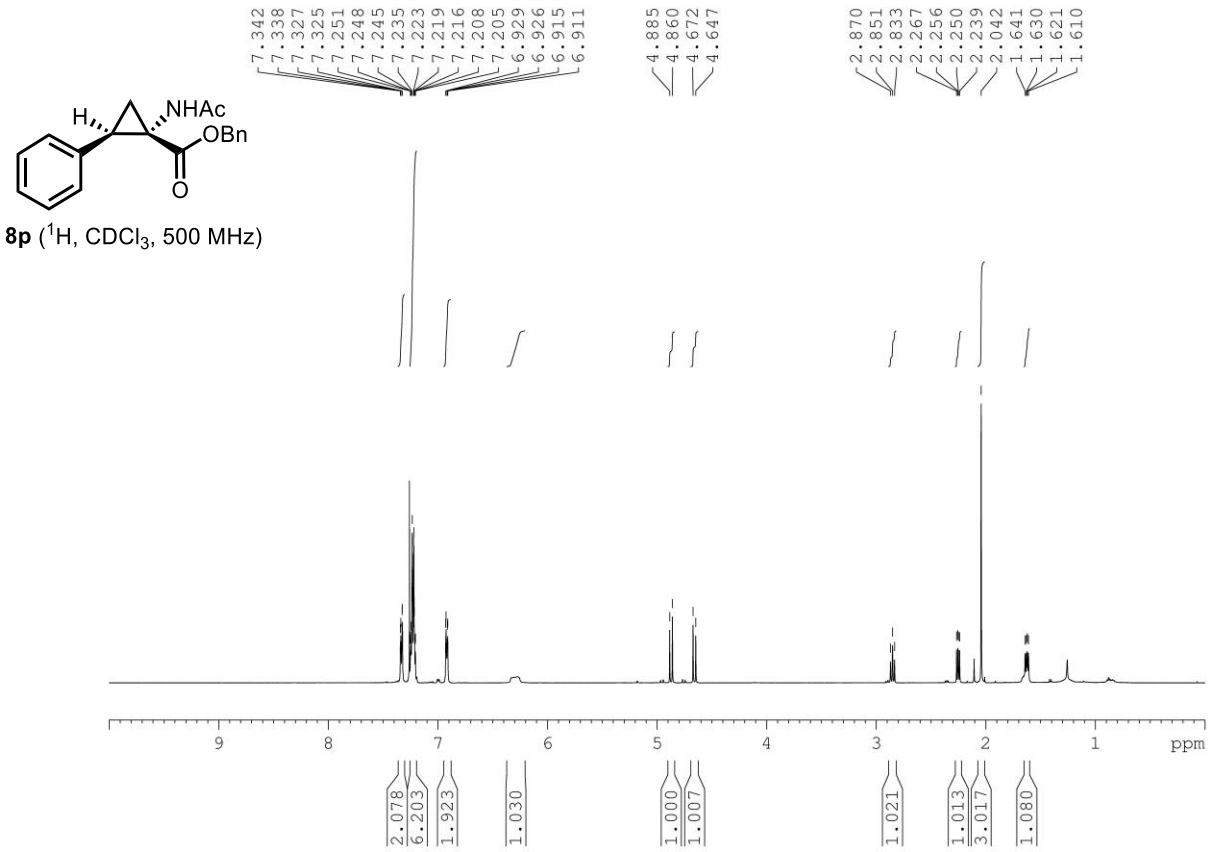
3n (^{13}C, $CDCl_3$, 126 MHz)



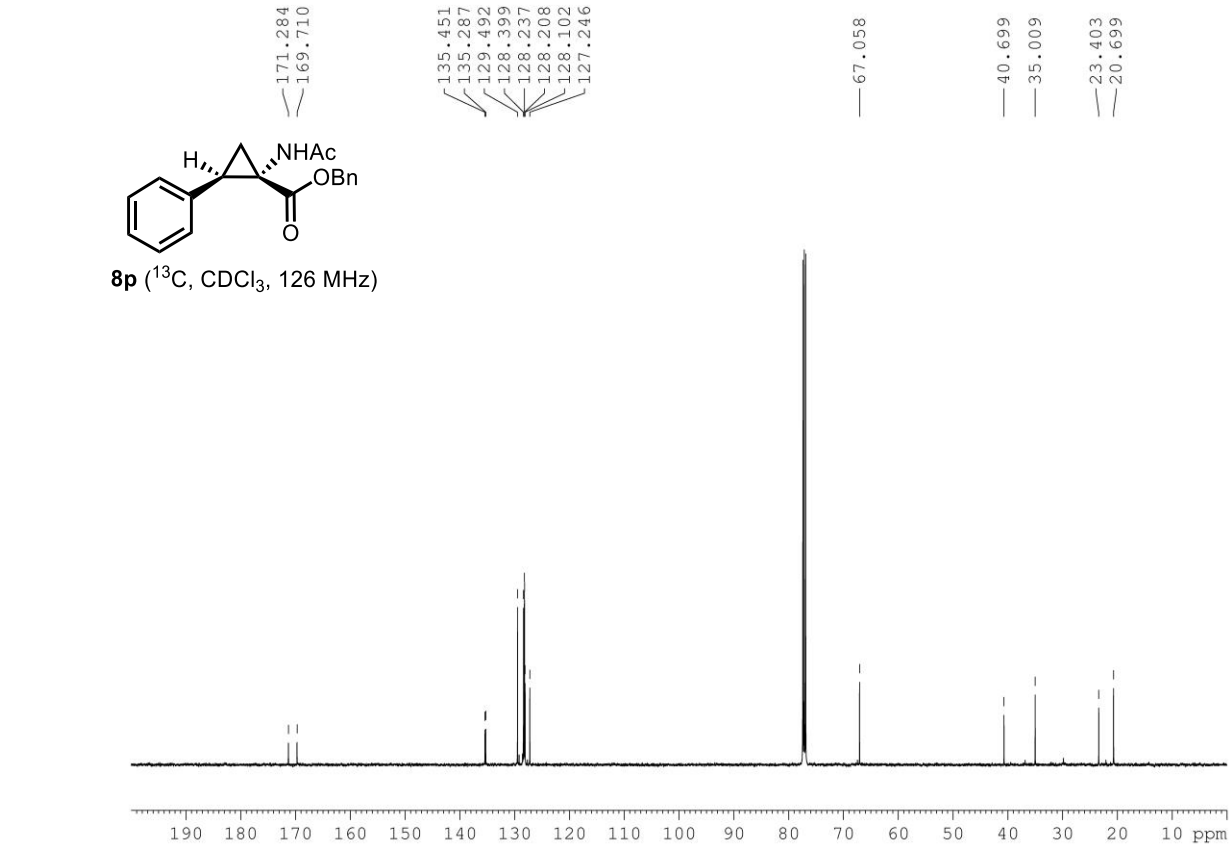
17o (^{1}H, $CDCl_3$, 500 MHz)



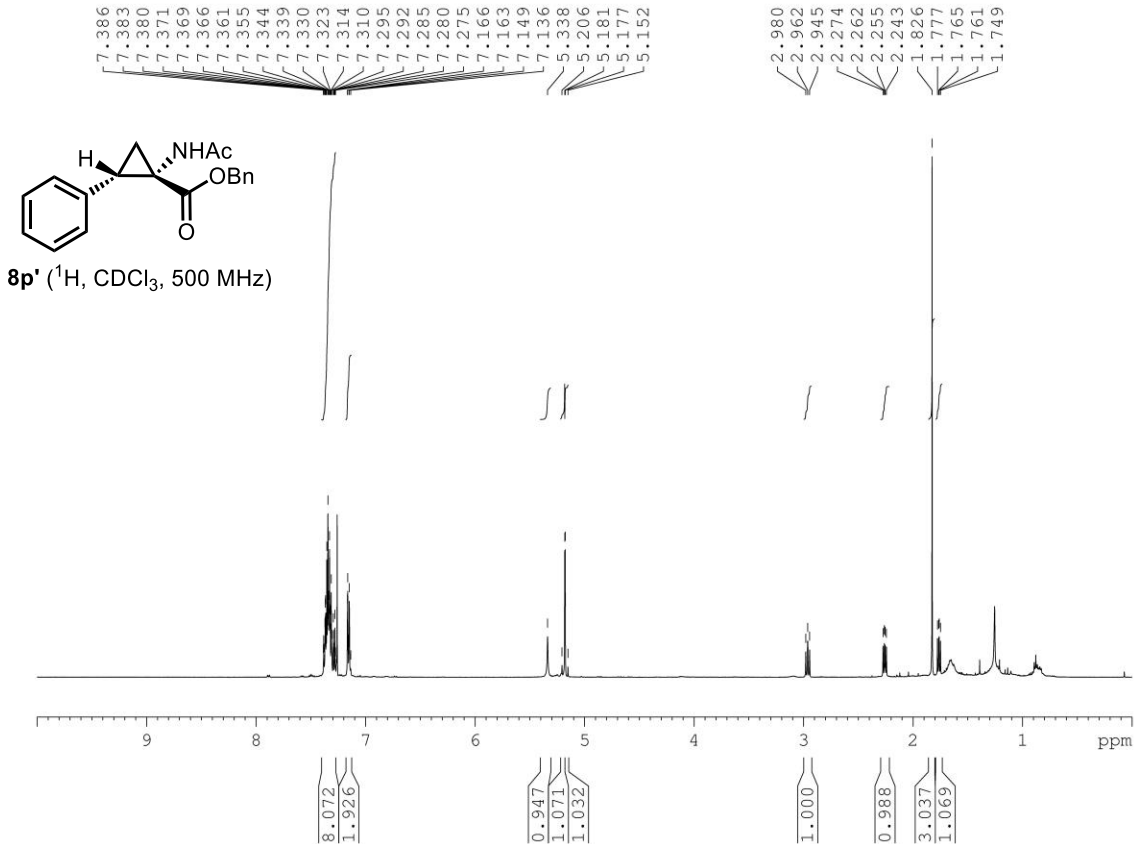
17o (^{13}C, $CDCl_3$, 126 MHz)



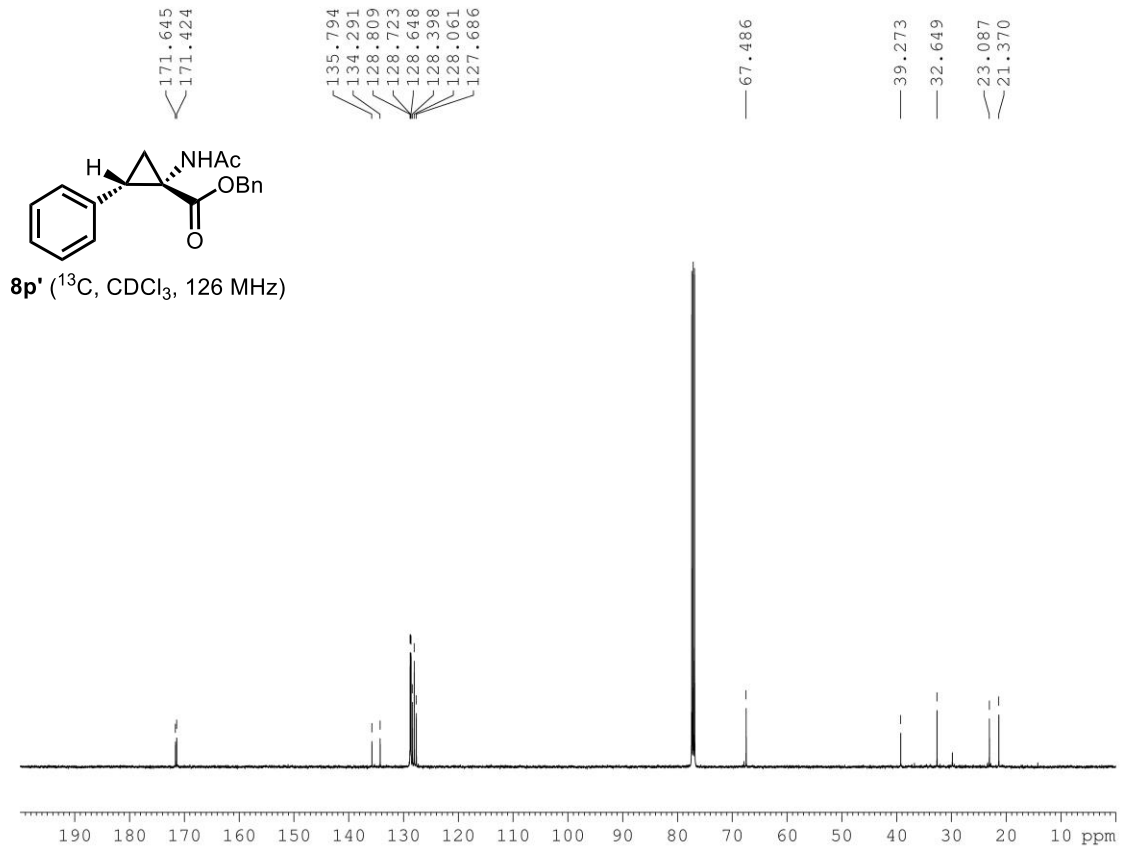
8p (^{1}H, $CDCl_3$, 500 MHz)



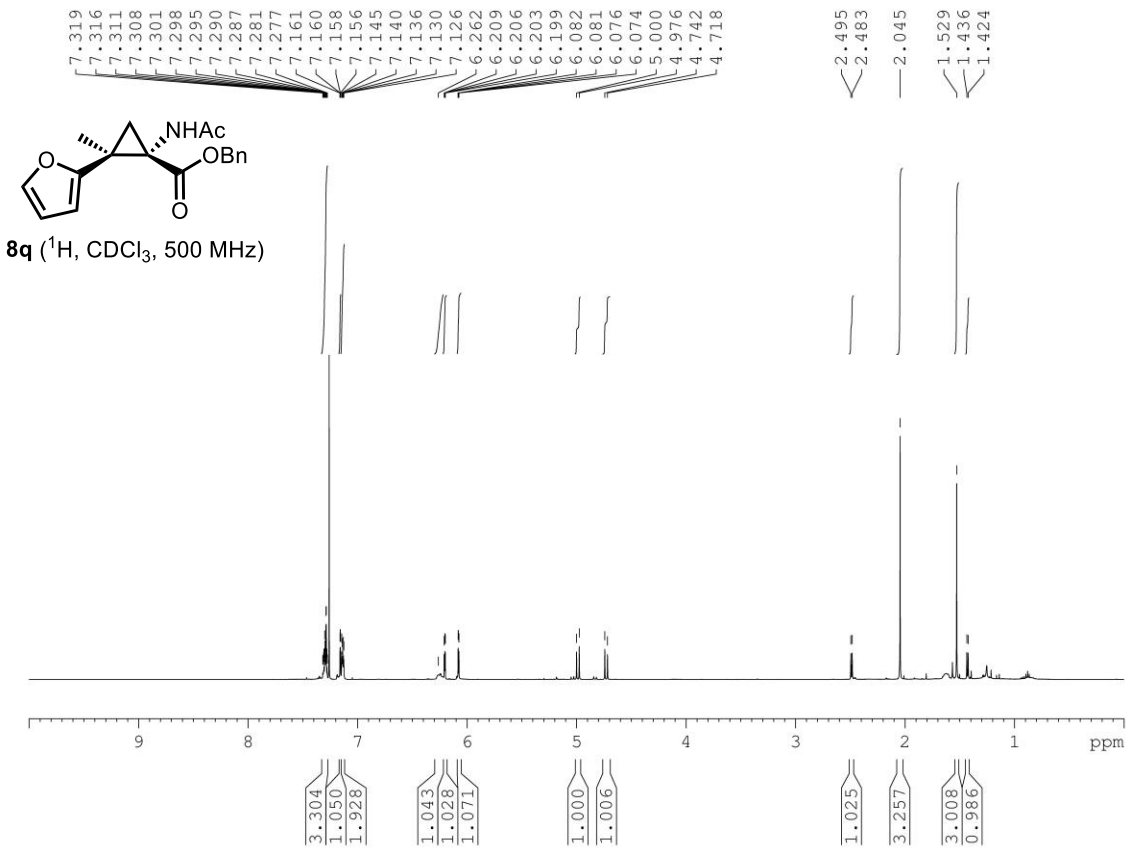
8p (^{13}C, $CDCl_3$, 126 MHz)



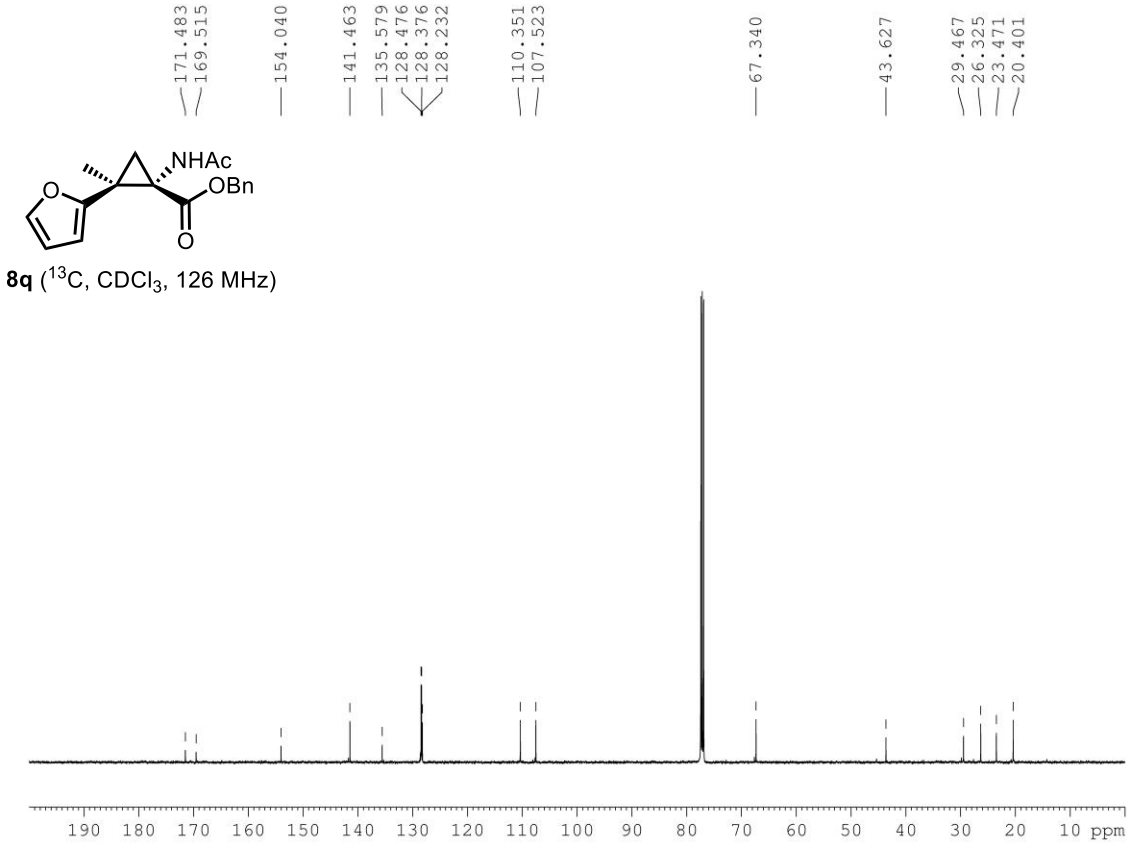
8p' (^{1}H, $CDCl_3$, 500 MHz)



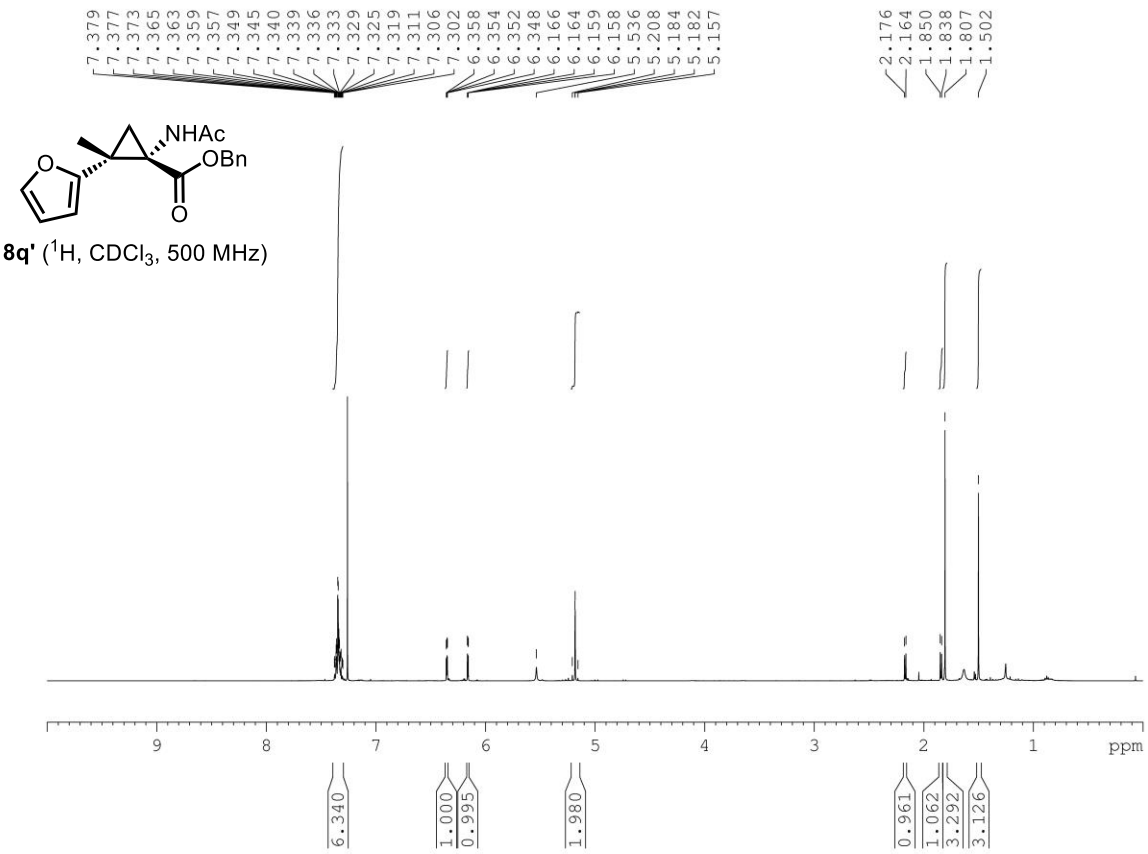
8p' (^{13}C, $CDCl_3$, 126 MHz)



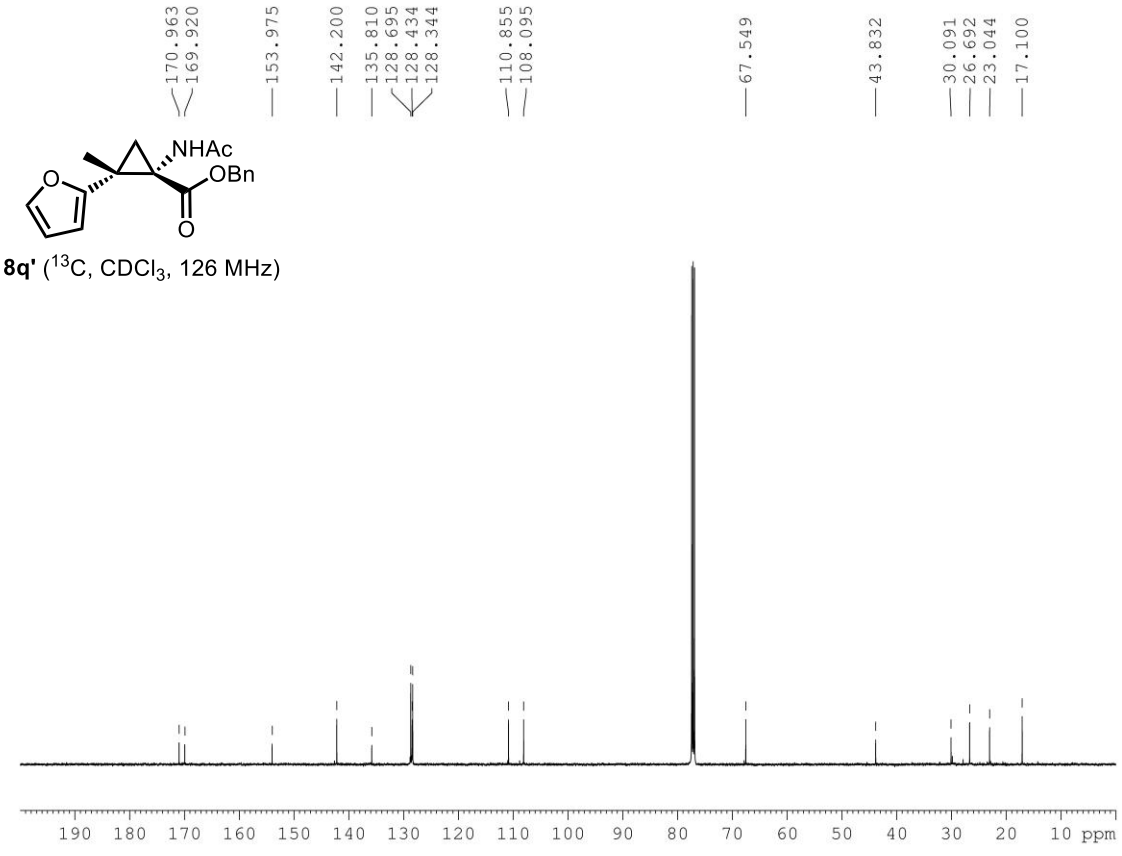
8q (^{1}H, $CDCl_3$, 500 MHz)



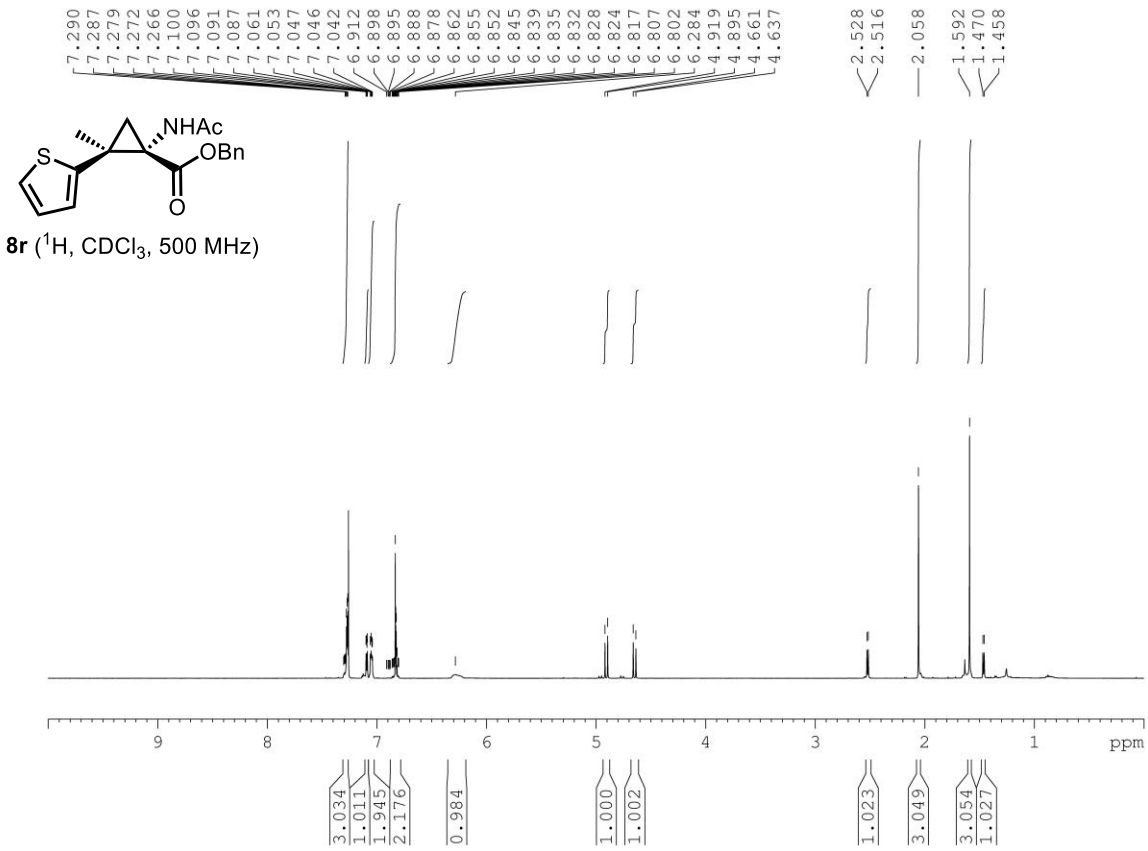
8q (^{13}C, $CDCl_3$, 126 MHz)



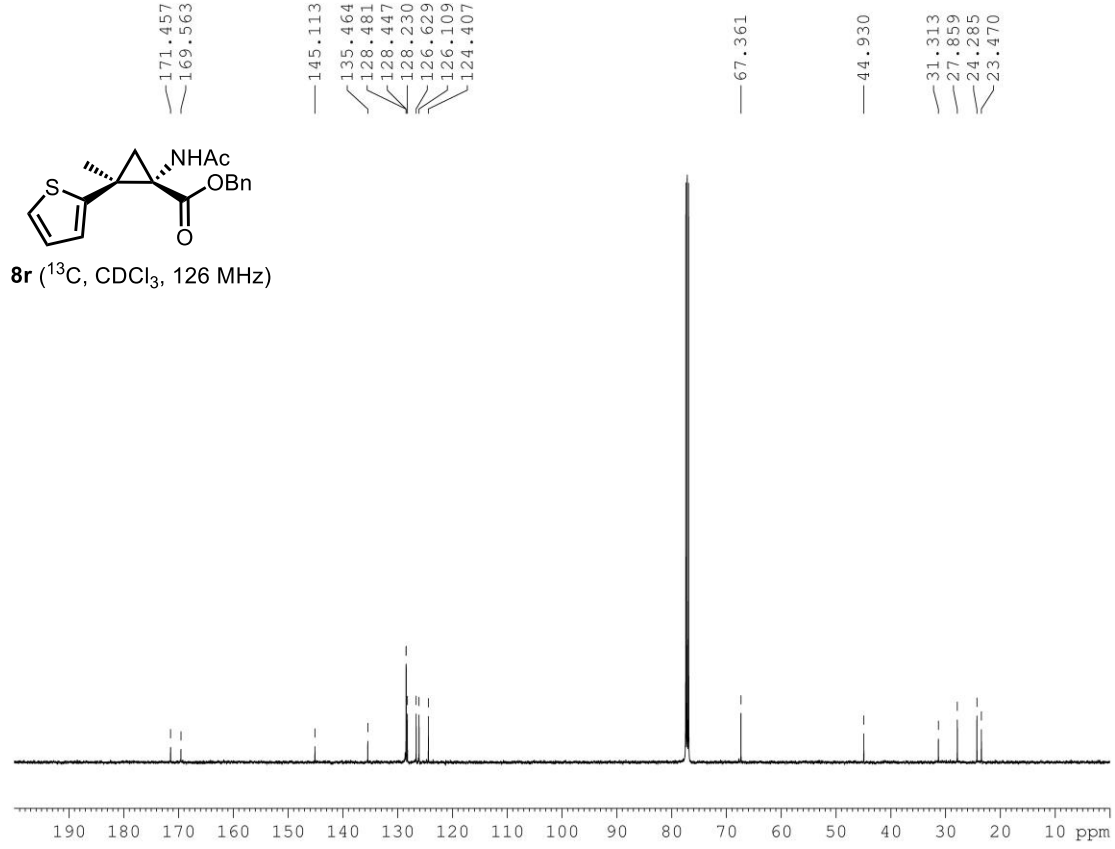
8q' (^{1}H, $CDCl_3$, 500 MHz)



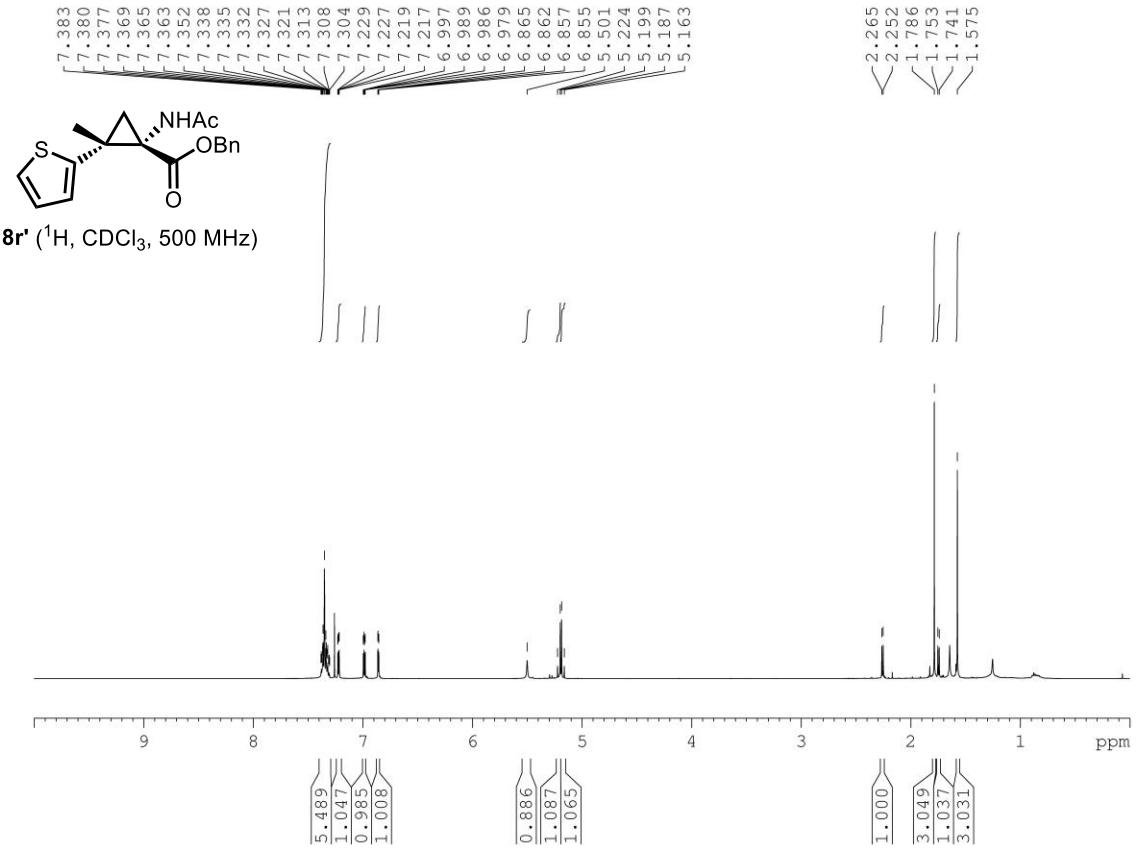
8q' (^{13}C, $CDCl_3$, 126 MHz)



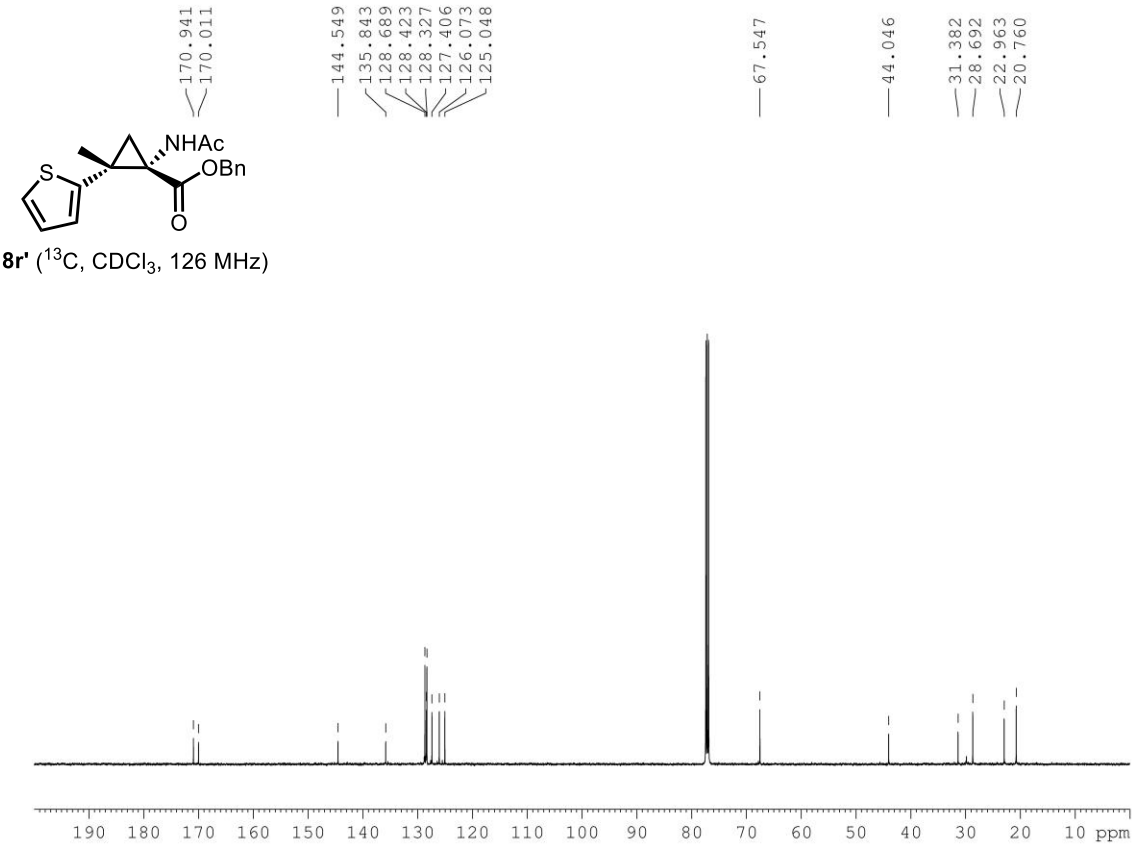
8r (^{1}H, $CDCl_3$, 500 MHz)



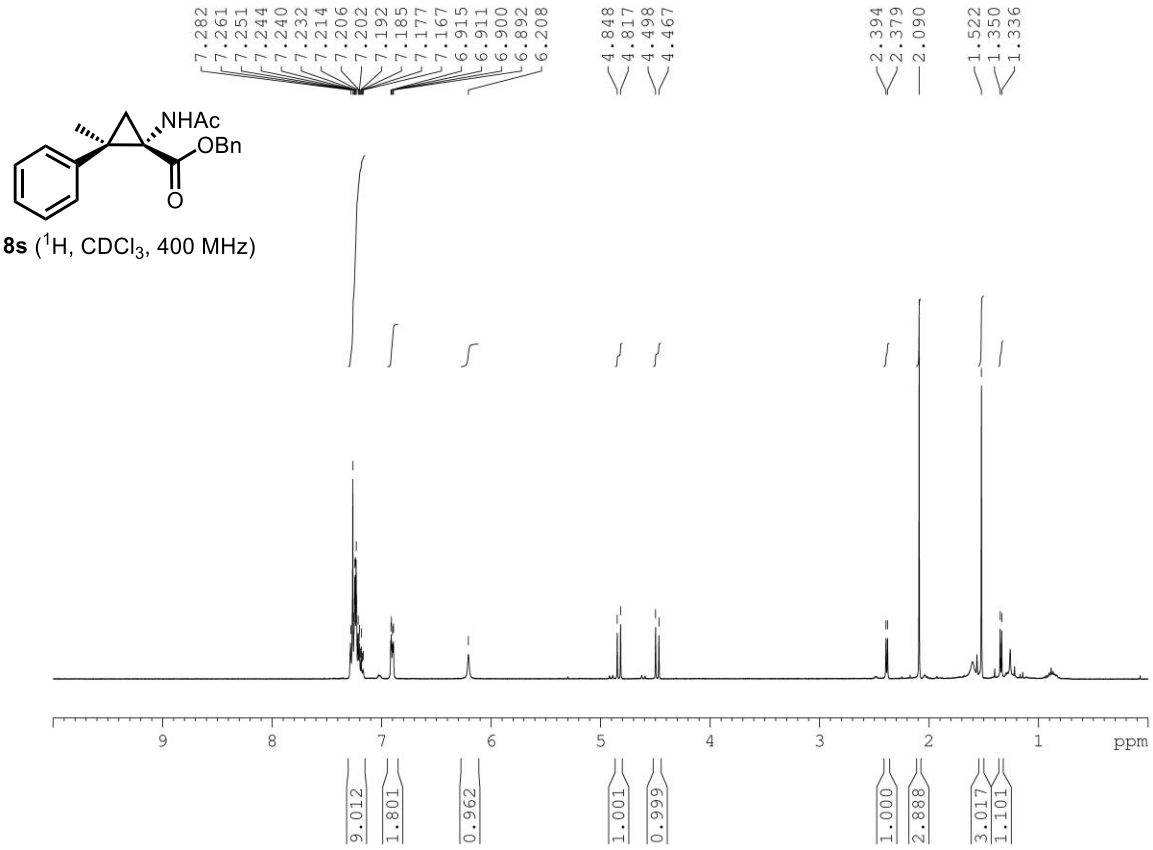
8r (^{13}C, $CDCl_3$, 126 MHz)



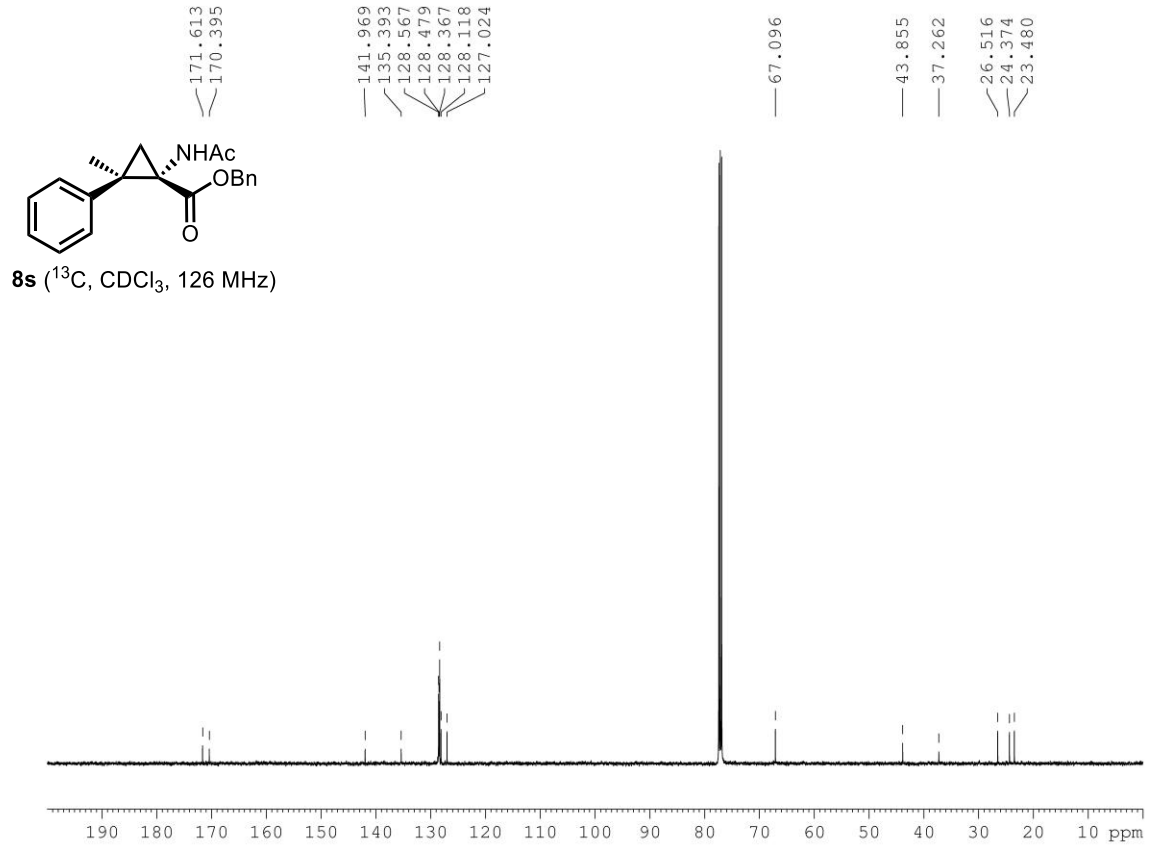
8r' (^{1}H, $CDCl_3$, 500 MHz)



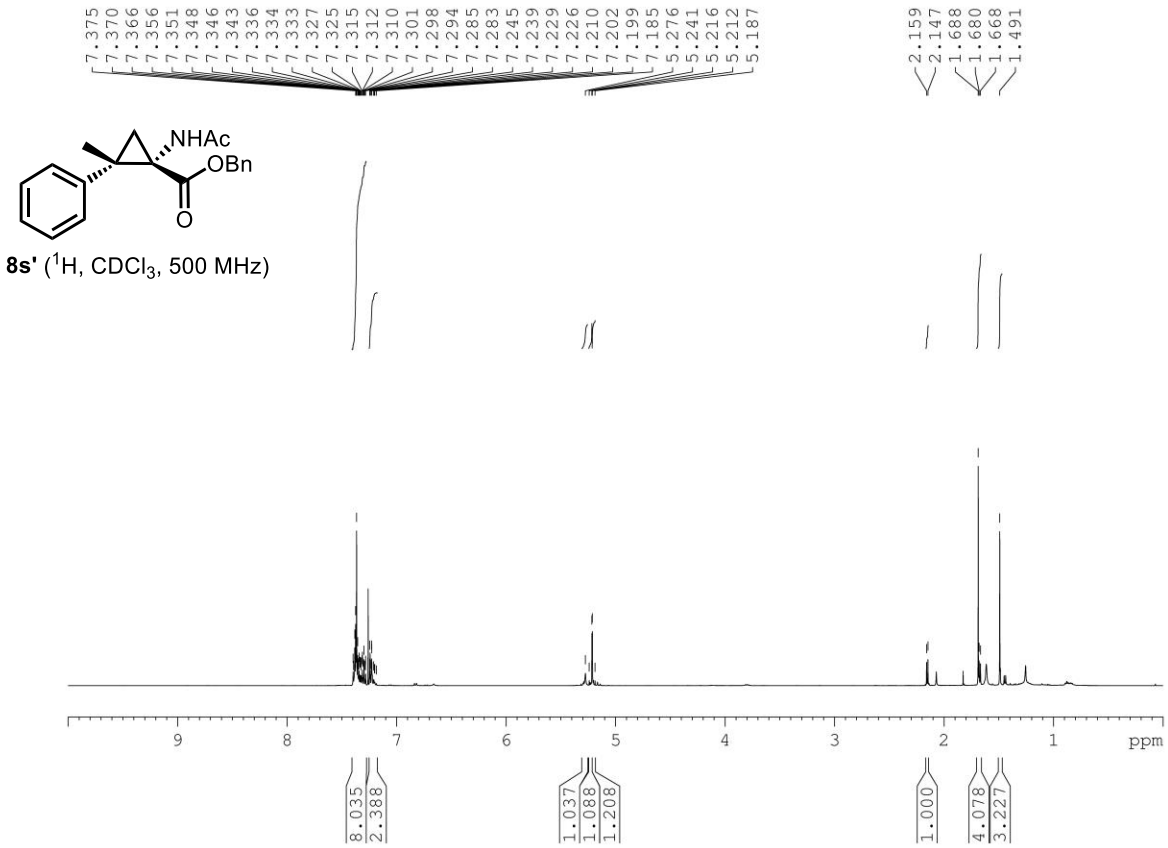
8r' (^{13}C, $CDCl_3$, 126 MHz)



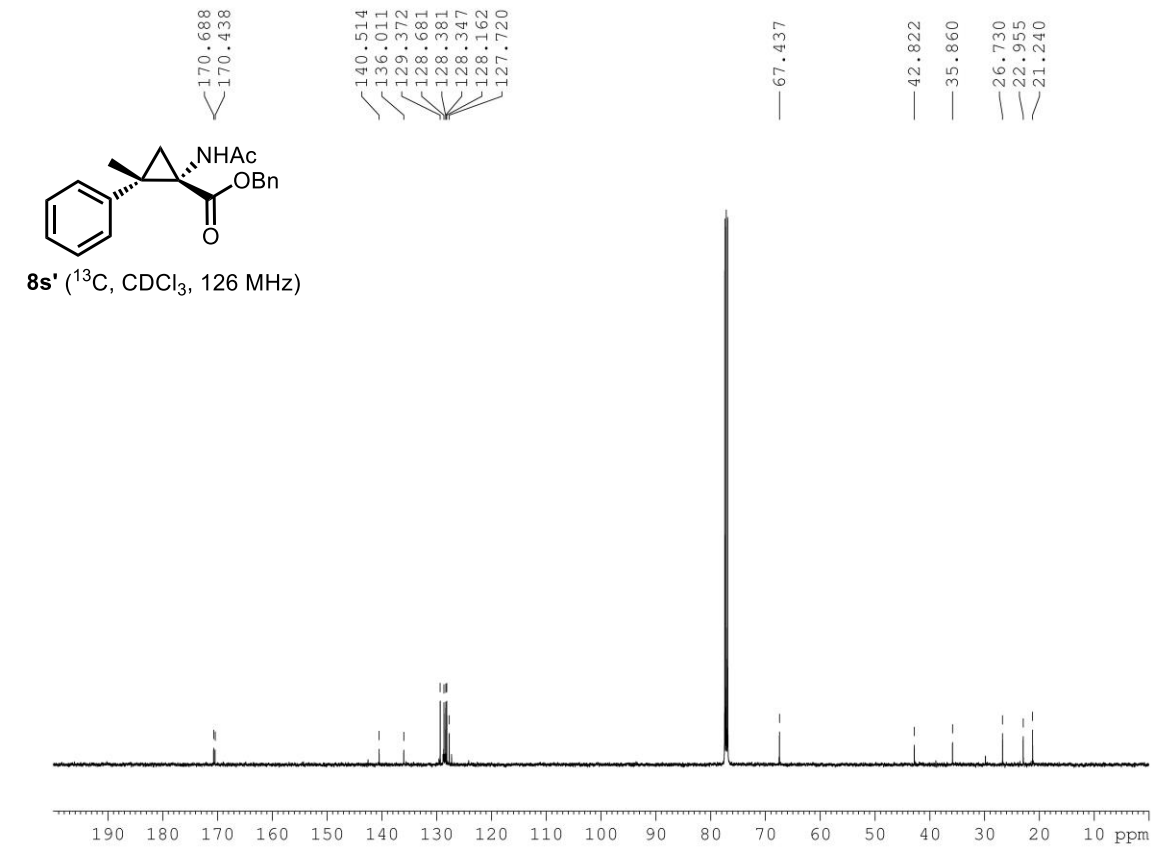
8s (^{1}H, $CDCl_3$, 400 MHz)



8s (^{13}C, $CDCl_3$, 126 MHz)



8s' (^{1}H, $CDCl_3$, 500 MHz)



8s' (^{13}C, $CDCl_3$, 126 MHz)