Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Mechanochemical Simmons-Smith Cyclopropanation via Ball-Milling-Enabled Activation of Zinc(0)

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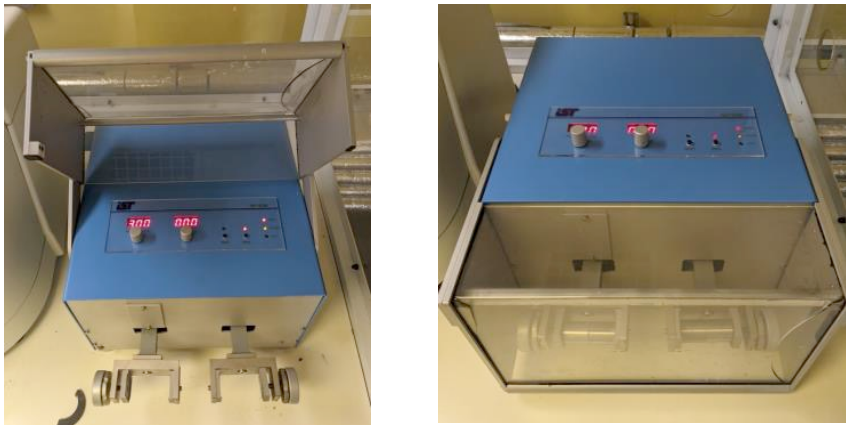
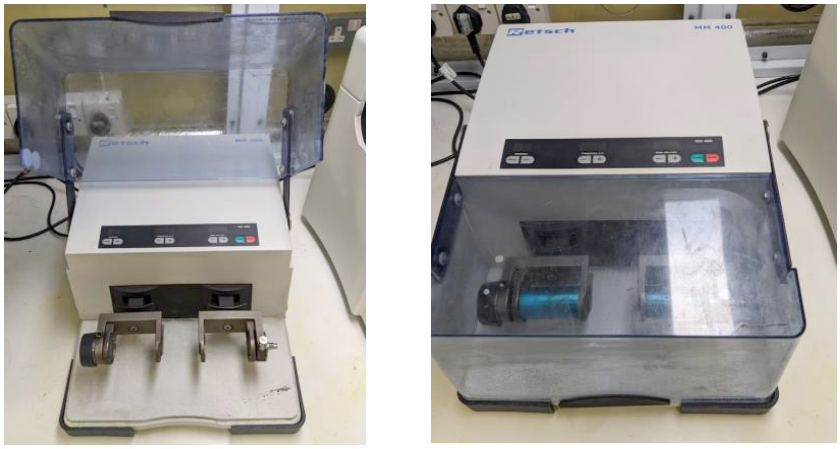
1. General Experimental and Mechanochemistry Equipment

Mixer mills: Mechanochemical reactions (1.00-10.00 mmol) were conducted using an Insolido Tech IST636 mixer mill (see www.insolidotech.org for more details) or a Retsch MM400 mixer mill (see www.retsch.com for more details). Mechanochemical reactions performed above the room temperature were conducted using our in-house designed and prototyped PID-controlled jar heater.



Insolido Tech IST636 mixer mill.



Retsch MM400 mixer mill.

PID-controlled jar heater. - For more information click here

Stainless steel jars: Mechanochemical reactions were conducted using Formtech Scientific SMARTSNAP™ stainless steel grinding jars with Teflon seals (for further details see www.formtechscientific.com) at either 30 mL (left, for 10.00 mmol reaction and cholesterol cyclopropanation) or 15 mL (right, for 1.00-2.00 mmol reactions).

Stainless steel balls: Stainless steel balls were purchased from Bearing Boys limited (www.bearingboys.co.uk) and either 8.56 g (9 g, 12.7 mm, for cholesterol cyclopropanation), 7.22 g (7 g, 12 mm, for 10.00 mmol reactions) or 4.18 g (4 g, 10 mm, for 1.00-2.00 mmol reactions).

Formtech Scientific SMARTSNAP™ stainless steel grinding jars & Stainless steel balls.

Analytical equipment: **^{1}H NMR**, **^{13}C NMR** and **^{19}F NMR** spectra were obtained on a Bruker Avance 400 at 400.13 MHz (^{1}H NMR at 400 MHz, ^{13}C NMR at 101 MHz), Bruker Avance 500 fitted with a cryoprobe, at 500 MHz (^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz) and Bruker Avance Neo 700 at 700 MHz (^{19}F NMR at 659 MHz, $CDCl_3$). Chemical shifts are referenced to residual protium in the deuterated solvent. NMR data are presented in the following format: chemical shift (multiplicity [app = apparent, br = broad, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, m = multiplet], coupling constant [in Hz], number of equivalent nuclei by integration). Spin-spin coupling constants J are given in Hz and refer to apparent multiplicities rather than true coupling constants. Data are reported as: chemical shift, multiplicity and integration. NMR yields were obtained using 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard.

High resolution mass spectral (**HRMS**) data were obtained on a Thermo Orbitrap Exactive Plus Mass Spectrometer coupled to a Vanquisher Liquid Chromatograph. Ions were obtained and analysed by heated electrospray ionisation (HESI) and atmospheric solids analysis probe (ASAP). Samples were analysed as solutions in methanol.

Infrared spectra were recorded on an Agilent Cary 630 FTIR spectrometer.

Analytical thin-layer chromatography was performed on Merck silica gel 60zf F254 plates and visualized with UV light (254 or 365 nm), permanganate, phosphomolybdic acid or *p*-anisaldehyde stain.

Flash chromatography was performed on a Biotage Selekt or Isolera One. In the case of alumina gel, chromatography was performed manually. With the exception of those purified on alumina, samples were dried onto silica gel prior to addition to column. Solvents were removed under reduced pressure using Heidolph Rotavapor apparatus.

Reagents: Unless otherwise stated all reagents were purchased from commercial sources and used without further purifications.

Reactions in solution involving air- and moisture-sensitive reagents: All reactions involving air- and moisture-sensitive reagents were conducted in oven-dried glassware under inert nitrogen or argon atmosphere.

2. Legend of Symbols Used in Main Text

Reaction performed in a mixer mill.

Reaction performed in a mixer mill equipped with the PID-controlled jar heater.

Reaction performed in a planetary mill.

Reaction performed in solution/suspension at room temperature in a round bottom flask.

Reaction performed in neat conditions at room temperature in a round bottom flask.

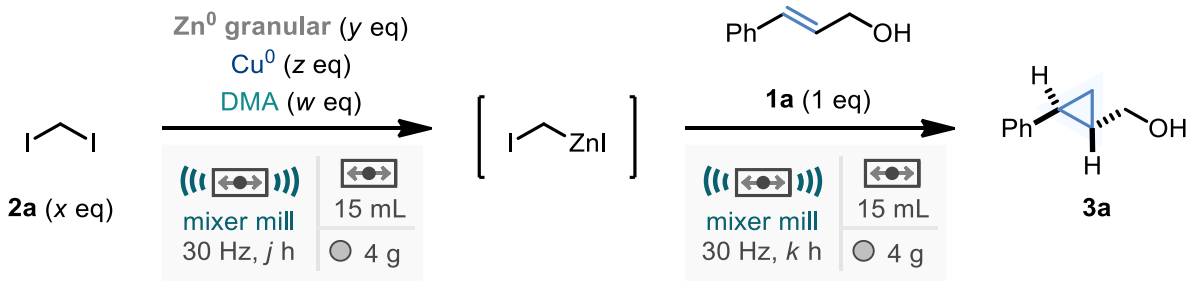
Reaction performed in solution/suspension in a heated round bottom flask.

3. Full Optimization Details & Control Experiments

1st round of reaction optimization:

General procedure for the mechanochemical synthesis of zinc carbenoid followed by Simmons-Smith cyclopropanation:

To a 15 mL stainless jar charged with one 4 g stainless steel ball, zinc metal, *N*,*N*-dimethylacetamide (DMA) and diiodomethane were added and milled at 30 Hz for *j* h at room temperature in a Retsch/Insolido Tech mixer mill. After this time the jar was opened and **1a** (1.00 mmol) was added and further milled for *k* h at 30 Hz. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure in presence of 1.00 mL of 0.33 M solution of 1,3,5-trimethoxybenzene in toluene to give the crude product that was analysed by ^{1}H NMR.



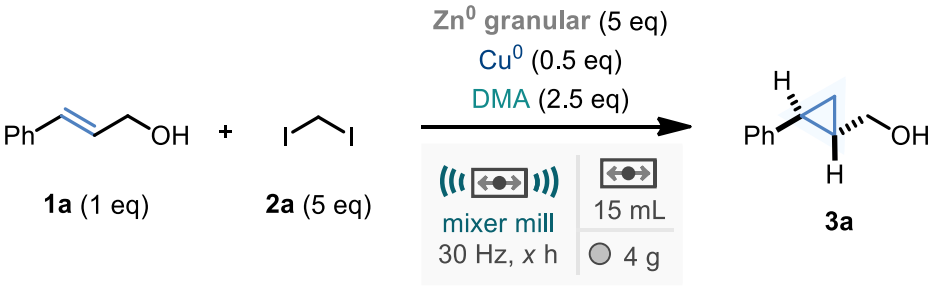
Entry	Zn eq	Cu eq	CH_2I_2 eq	DMA eq	Time (*j* + *k*)	% 1a	% 3a
1	4	4	4	6	2+1	60	14
2	5	5	5	7.5	2+1	54	18
3	5	5	5	5	2+1	6	76
4	5	5	5	2.5	2+1	13	79
5	5	5	5	1.5	2+1	7	56
6	5	5	4	2.5	2+1	18	63
7	5	2.5	5	2.5	2+1	3	79
8	5	1	5	2.5	2+1	7	75
9	5	0.5	5	2.5	2+1	5	85
10	5	0.5	5	2.5	1+2	0	84

Table 1. First round of reaction optimization. Yields were calculated by ^{1}H NMR in presence of 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard.

Optimization of the reaction time (*one-pot* procedure):

General procedure for the one-pot cyclopropanation reaction:

To a 15 mL stainless jar charged with one 4 g stainless steel ball, **1a** (1.00 mmol), zinc metal, LAG and diiodomethane were added and milled at 30 Hz for 1 h at room temperature in a Retsch/Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure in presence of 1.00 mL of 0.33 M solution of 1,3,5-trimethoxybenzene in toluene to give the crude product that was analysed by ^{1}H NMR.

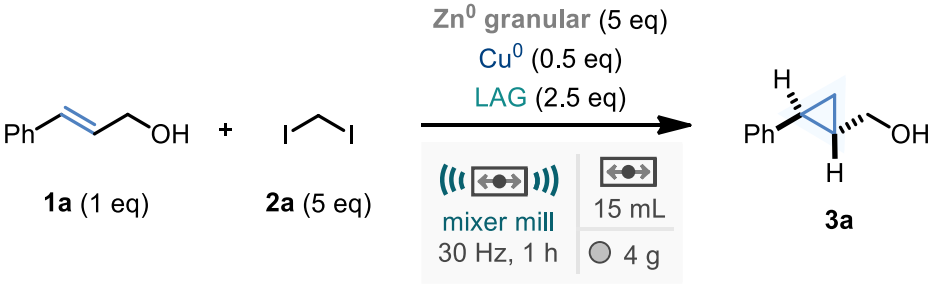


Entry	Time (h)	% 1a	% 3a
1	3	0	80
2	2	0	72
3	1	0	76

Table 2. Optimization of the one-pot cyclopropanation procedure. Yields were calculated by ^{1}H NMR in presence of 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard.

: By switching the reactor of **Entry 3**, **Table 2**, from a mixer mill to round bottom flask (under Ar), preserving the reaction conditions (1h, rt) and the work-up, only 1% conversion was obtained, together with 75% recovery of the starting material.

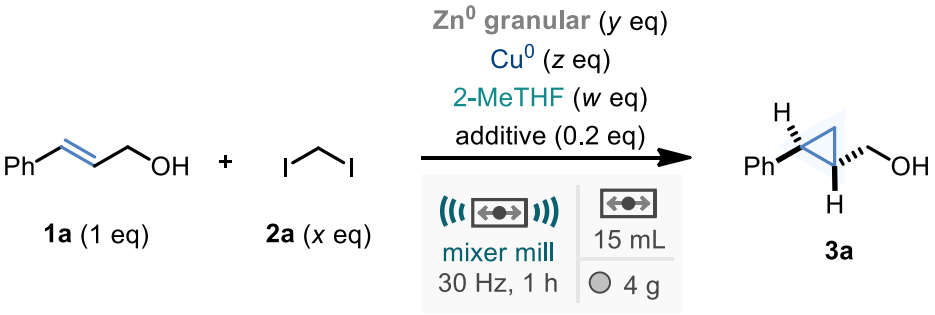
LAG screening:



Entry	LAG	% 1a	% 3a
1	DMA	0	80
2	DMSO	0	79
3	DMF	0	68
4	2-MeTHF	0	83
5	EtOAc	0	81
6	None	0	59

Table 3. LAG screening. Yields were calculated by ^{1}H NMR in presence of 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard.

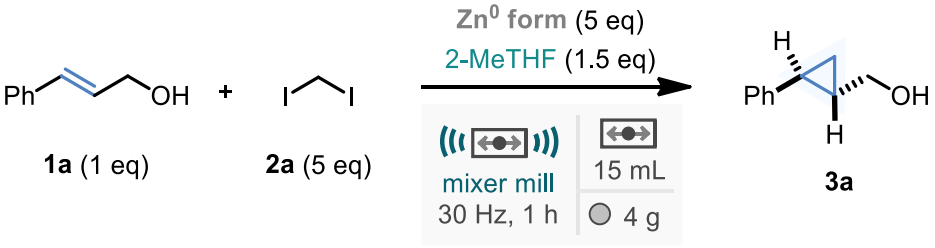
2nd round of reaction optimization:



Entry	Zn eq	Cu eq	CH_2I_2 eq	2-MeTHF eq	additive	% 1a	% 3a
1	5	2.5	5	2.5	-	0	83
2	5	-	5	2.5	-	0	77
3	5	-	5	2.5	TFA	0	73
4	5	-	5	2.5	ZnI_2	0	80
5	5	-	5	1.5	-	0	90
6	5	-	5	0.5	-	0	70
7	5	-	4	1.5	-	12	64
8	4	-	4	1.5		1	69

Table 4. Second round of reaction optimization. Yields were calculated by ^{1}H NMR in presence of 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard.

Zinc form screening:



Entry	Zinc form	% 1a	% 3a
1	granular (20-30 mesh)	0	90
2	Mossy	2	96
3	Wire	0	80
4	Foil	0	77
5	Powder	0	57
6	Shot	0	51
7	Brass	87	6

Table 5. Zinc form screening. Yields were calculated by ^{1}H NMR in presence of 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard.

Carbenoid precursor screening:

General procedure:

To a 15 mL stainless jar charged with one 4 g stainless steel ball, **1a** (1.00 mmol), zinc granular (327 mg, 5.00 mmol, 5.00 eq), 2-MeTHF (151 µL, 1.50 mmol, 1.50 eq) and di-/tri-haloalkane **2a-f** (5.00 mmol, 5.00 eq) were added and milled at 30 Hz for 1 h at room temperature in a Retsch/Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where

the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure in presence of 1.00 mL of 0.33 M solution of 1,3,5-trimethoxybenzene in toluene to give the crude product that was analysed by ^1H NMR.

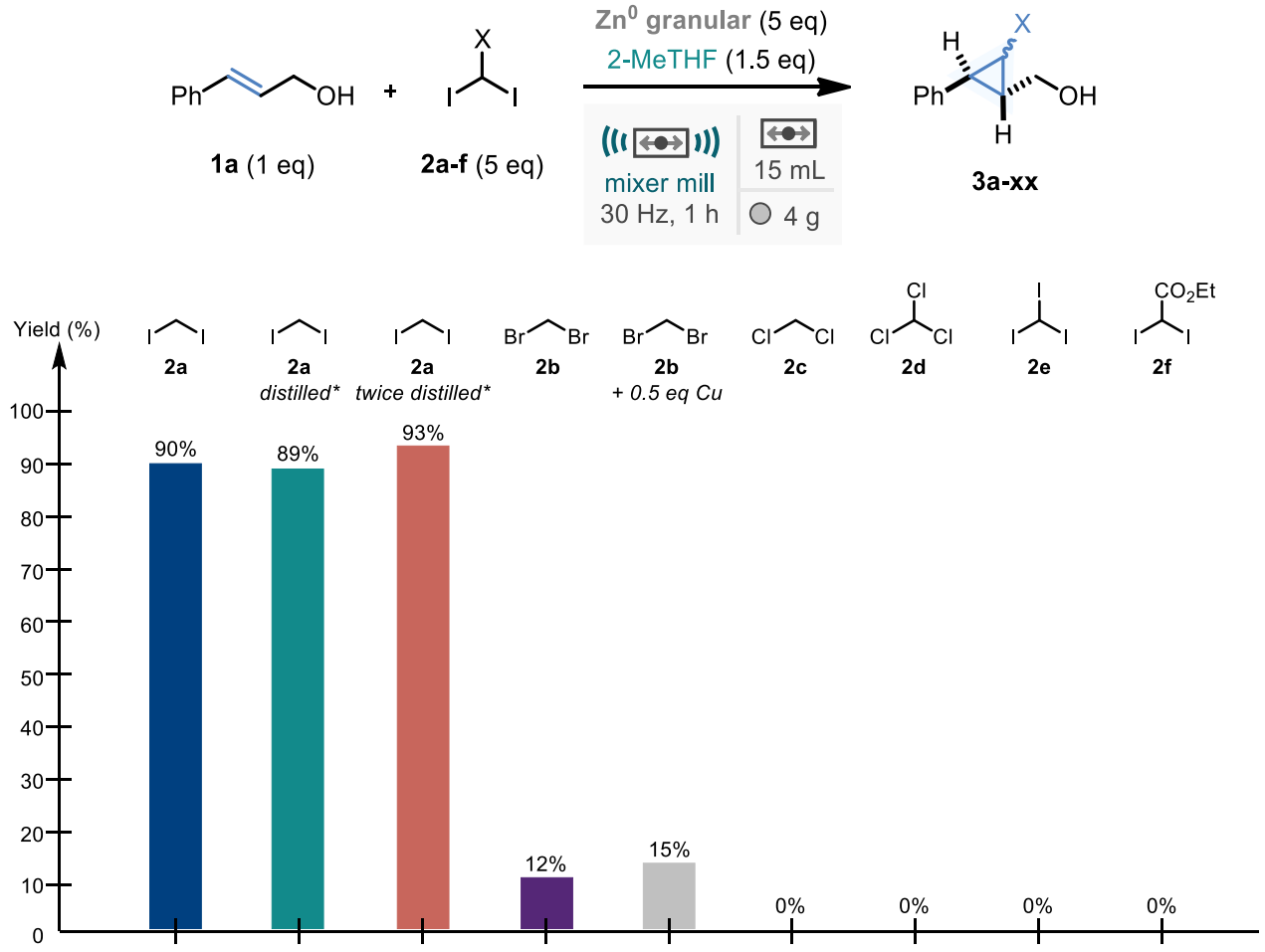
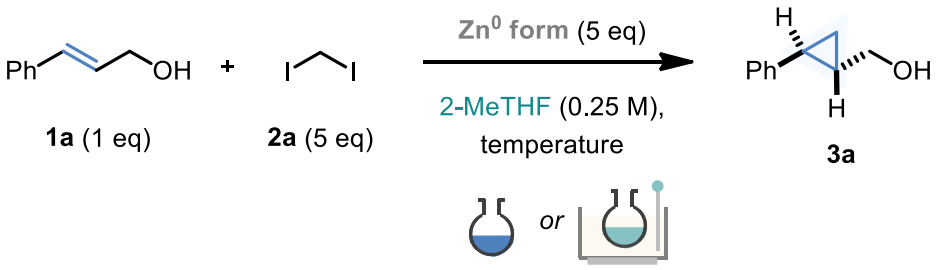


Table 6. Carbenoid precursor screening. Yields were calculated by ^1H NMR in presence of 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard. *Distillation of diiodomethane was performed using a short-path distillation apparatus under high vacuum (Schlenk line). Pure diiodomethane (stabilizer-free) was collected as an orange/red oil (b.p. = 45-50 °C) characterized by a pronounced photo-lability.

Benchmark experiments in round bottom flask & planetary mill:

General procedure in round bottom flask:

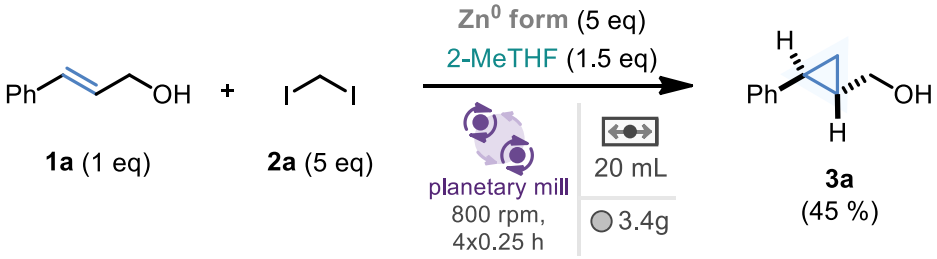
1a (1.00 mmol), zinc (327 mg, 5.00 mmol, 5.00 eq), 2-MeTHF (4.00 mL) and diiodomethane (403 µL, 5.00 mmol, 5.00 eq) were added to a 10 mL round bottom flask and refluxed for 1 h. After this time, the reaction mixture was rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure in presence of 1.00 mL of 0.33 M solution of 1,3,5-trimethoxybenzene in toluene to give the crude product that was analysed by ^1H NMR.



Entry	Zn form	Cu powder (0.5 eq)	Inert atmosphere (Ar)	Temperature	% 1a	% 3a
1	granular	Yes	Yes	rt	85	0
2	granular	Yes	Yes	reflux	5	95
3	granular	No	Yes	reflux	3	74
4	granular	No	No	reflux	5	79
5	mossy	No	No	reflux	10	85
6	wire	No	No	reflux	traces	39
7	foil	No	No	reflux	5	83
8	granular (pre-milled)	No	No	rt	94	0

Table 7. Benchmark experiments in round bottom flask. Yields were calculated by ^{1}H NMR in presence of 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard.

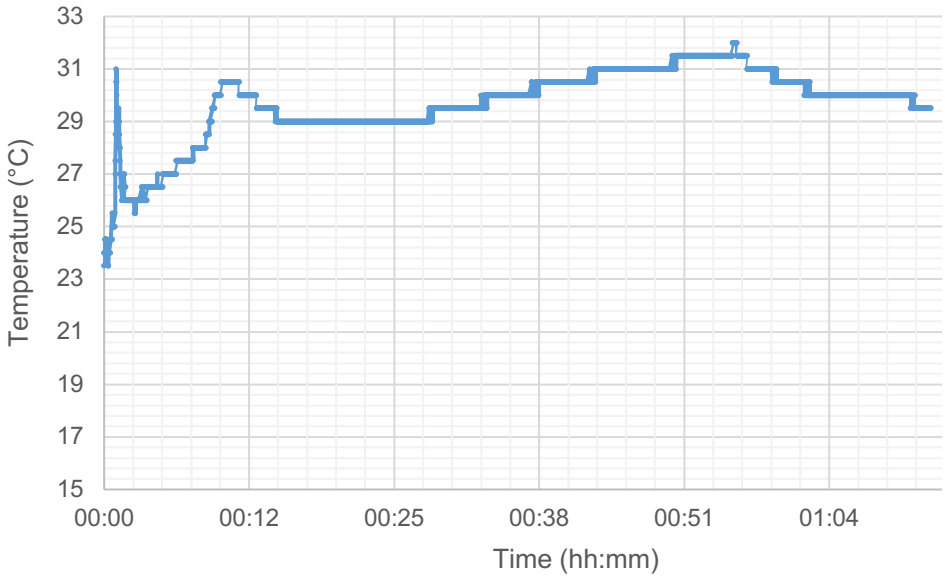
Cyclopropanation of 1a in planetary mill:



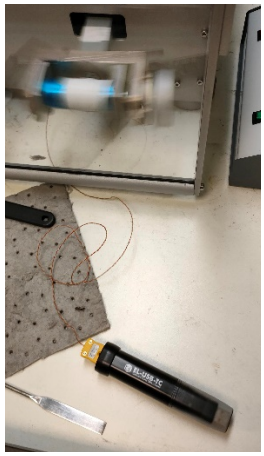
To a 20 mL zirconia jar charged with one 3.4 g zirconia ball, **1a** (1.00 mmol), zinc granular (327 mg, 5.00 mmol, 5.00 eq), 2-MeTHF (151 µL, 1.50 mmol, 1.50 eq) and diiodomethane (403 µL, 5.00 mmol, 5.00 eq) were added and milled at 800 rpm for 1 h (4 x 20 minute cycles) at room temperature in a Fritsch Pulverisette 7 classic line planetary mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure in presence of 1.00 mL of 0.33 M solution of 1,3,5-trimethoxybenzene in toluene to give the crude product that was analysed by ^{1}H NMR.

NMR analysis showed the presence of the desired product in 45% yield together with 35% unreacted starting material.

Thermal profile of the optimized reaction:



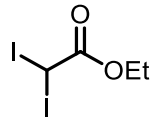
Thermal data were recorded by using a data-logger connected outside the jar during the milling period (1 h). The temperature never reached 33 °C during the reaction time.



Data-logger connected to the jar.

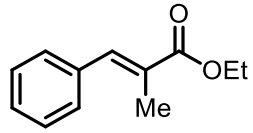
4. Synthesis of Starting Materials

Ethyl 2,2-diiodoacetate (2f)



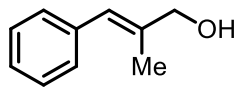
The title compound was prepared using the following procedure adapted from literature.[1] Ethyl diazoacetate (2.42 mL, 20.00 mmol) was added to a 100 mL round bottom flask and dissolved in anhydrous CH_2Cl_2 (20.00 mL). The resulting solution was cooled to 0°C and iodine (5.58 g, 22.00 mmol, 1.10 eq) was added portion-wise under inert flux of N_2. When a violet coloration persisted and gas evolution ceased a saturated aqueous solution of sodium thiosulfate (20.00 mL). The resulting biphasic mixture was transferred to a separatory funnel and the aqueous layer was extracted with CH_2Cl_2 (2 x 20.00 mL). The combined organic layers were dried over anhydrous $NaSO_4$. After the removal of the volatiles *in vacuo* the desired product was obtained quantitatively as photo- and thermo-labile yellow-orange oil (6.80 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.33 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.5, 63.7, 13.8, -45.3. The NMR data is consistent with literature.[2]

(*E*)-Ethyl 2-methyl-3-phenylacrylate



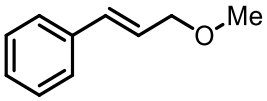
The title compound was prepared using the following procedure. α-Methylcinnamic acid (811 mg, 5.00 mmol) was added to a 50 mL round bottom flask and dissolved in absolute ethanol (8.00 mL). Concentrated sulphuric acid (0.13 mL) was added and the mixture was refluxed for 14 h. After this time, water (20.00 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 x 20.00 mL). The combined organic layers were washed with a saturated solution of $NaHCO_3$ (20.00 mL), Brine (20.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was obtained as a colourless oil that was used without further purification (951 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (q, *J* = 1.6 Hz, 1H), 7.15 – 7.31 (m, 5H), 4.14 (d, *J* = 7.0 Hz, 2H), 1.99 (d, *J* = 1.5 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.1, 139.0, 136.3, 130.0, 129.0, 128.7, 128.6, 61.3, 14.7, 14.4. The NMR data is consistent with literature.[3]

(*E*)-2-Methyl-3-phenylprop-2-en-1-ol (1b)



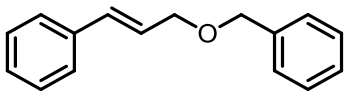
The title compound was prepared using the following procedure. (*E*)-Ethyl 2-methyl-3-phenylacrylate (951 mg, 5.00 mmol) was added to a 100 mL round bottom flask and dissolved in anhydrous THF (20.00 mL). The resulting solution was cooled to 0°C and DIBAL-H 1.0 M in THF (12.50 mL, 12.50 mmol, 2.5 eq) was slowly added dropwise under inert flux of N_2. After 2 h, water (20.00 mL) and 1.0 M HCl (10.00 mL) were added. The resulting suspension was extracted with Et_2O (3 x 20.00 mL). The combined organic layers were washed with Brine (20.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 20 %). The desired product was obtained as a yellowish oil in 98 % yield over two steps (726 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.31 (m, 2H), 7.23 (td, *J* = 7.1, 1.4 Hz, 1H), 6.53 (s, 1H), 4.20 (d, *J* = 1.5 Hz, 2H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.60 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.8, 137.7, 129.0, 128.3, 126.6, 125.2, 69.1, 15.4. The NMR data is consistent with literature.[4]

(*E*)-(3-Methoxyprop-1-en-1-yl)benzene (1c)



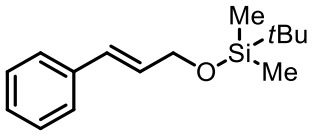
The title compound was prepared using the following procedure. (*E*)-Cinnamyl alcohol (13.42 g, 100.00 mmol) was added to an oven-dried 250 mL round bottom flask and dissolved in anhydrous THF (100.00 mL). The resulting solution was cooled to 0°C and NaH (60 % dispersion in mineral oil) (4.20 g, 105.00 mmol, 1.05 eq) was added portion-wise. After 15 min iodomethane (6.50 mL, 110.00 mmol, 1.10 eq) was added and the resulting mixture was allowed to reach spontaneously the room temperature. After 2.5 h water (60.00 mL) was added and the resulting mixture was extracted with hexane (2 x 50.00 mL). The combined organic layers were washed with Brine (60.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 5 %). The desired product was obtained as a yellowish oil quantitatively (14.82 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.49 (m, 2H), 7.29 – 7.38 (m, 2H), 7.21 – 7.30 (m, 1H), 6.63 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.31 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.11 (dd, *J* = 6.2, 1.5 Hz, 2H), 3.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.8, 132.6, 128.7, 127.8, 126.6, 126.0, 73.2, 58.1. The NMR data is consistent with literature.[5]

(*E*)-(3-(Benzyloxy)prop-1-en-1-yl)benzene (1d)



The title compound was prepared using the following procedure. (*E*)-Cinnamyl alcohol (671 mg, 5.00 mmol) was added to an oven-dried 50 mL round bottom flask and dissolved in anhydrous THF (5.00 mL). The resulting solution was cooled to 0°C and NaH (60 % dispersion in mineral oil) (210 mg, 5.50 mmol, 1.05 eq) was added portion-wise. After 15 min benzyl bromide (653 µL, 5.25 mmol, 1.10 eq) was added and the resulting mixture was allowed to reach spontaneously the room temperature. After 2.5 h water (60.00 mL) was added and the resulting mixture was extracted with hexane (2 x 50.00 mL). The combined organic layers were washed with Brine (60.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 10 %). The desired product was obtained as a yellowish oil in 99 % yield (1.11 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 – 7.45 (m, 10H), 6.56 – 6.69 (m, 1H), 6.35 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.59 (s, 2H), 4.21 (dd, *J* = 6.1, 1.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.4, 136.8, 132.7, 128.7, 128.6, 128.0, 127.8, 127.8, 126.6, 126.2, 72.3, 70.9. The NMR data is consistent with literature.[6]

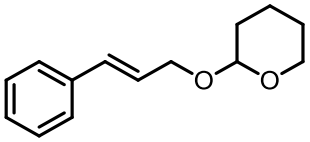
(*E*)-*tert*-Butyl(cinnamyloxy)dimethylsilane (1e)



The title compound was prepared using the following procedure. (*E*)-Cinnamyl alcohol (2.68 g, 20.00 mmol) was added to a 250 mL round bottom flask and was dissolved in DMF (60.00 mL). Imidazole (2.04 g, 30.00 mmol, 1.50 eq) and *tert*-butyldimethylchlorosilane (4.49 g, 29.80 mmol, 1.49 eq) were added under inert flux of N_2. After 14 h at room temperature, the resulting mixture was rinsed with hexane (60.00 mL) and washed with water (60.00 mL) and Brine (60.00 mL). The resulting organic layer was dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 5 %). The desired product was obtained as a pale yellow oil in 96 % yield (4.77 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.19 – 7.25 (m, 1H), 6.53 – 6.66 (m, 1H), 6.29 (d, *J* = 15.8 Hz,

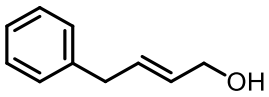
1H), 4.36 (dd, *J* = 5.1, 1.8 Hz, 2H), 0.94 (s, 9H), 0.11 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.2, 129.6, 129.3, 128.6, 127.4, 126.5, 64.0, 26.1, 18.6, -5.0. The NMR data is consistent with literature.[7]

(±)-(*E*)-2-(Cinnamyloxy)tetrahydro-2*H*-pyran (1f)



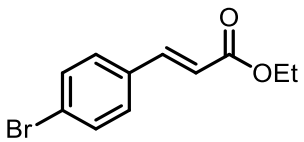
The title compound was prepared using the following procedure. (*E*)-Cinnamyl alcohol (805 mg, 6.00 mmol) was added to an oven-dried 50 mL round bottom flask and dissolved in anhydrous CH_2Cl_2 (20.00 mL). 2,3-Dihydro-4*H*-pyran (821 µL, 9.00 mmol, 1.50 eq) and pyridinium *p*-toluensulfonate (151 mg, 0.60 mmol, 0.10 eq) were added and the resulting mixture was stirred at room temperature under Ar atmosphere for 4 h. After this time, the resulting solution was washed with water (10.00 mL) and Brine (10.00 mL). The resulting organic layer was dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 3-5 %). The desired product was obtained as a colourless oil in 99 % yield (1.30 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 – 7.50 (m, 5H), 6.59 – 6.69 (m, 1H), 6.35 (dt, *J* = 15.8, 6.1 Hz, 1H), 4.74 (t, *J* = 3.7 Hz, 1H), 4.43 (ddd, *J* = 13.0, 5.7, 1.6 Hz, 1H), 4.19 (ddd, *J* = 12.9, 6.6, 1.4 Hz, 1H), 3.94 (ddd, *J* = 11.2, 8.1, 3.1 Hz, 1H), 3.50 – 3.66 (m, 1H), 1.89 (ddt, *J* = 11.9, 8.5, 4.7 Hz, 1H), 1.70 – 1.83 (m, 1H), 1.47 – 1.70 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.9, 132.5, 128.6, 127.7, 126.6, 126.1, 98.0, 67.8, 62.7, 30.8, 25.6, 19.6. The NMR data is consistent with literature.[8]

(*E*)-4-Phenylbut-2-en-1-ol (1g)



The title compound was prepared using the following procedure. **1u** (761 mg, 4.00 mmol) was added to a 100 mL round bottom flask and dissolved in anhydrous THF (20.00 mL). The resulting solution was cooled to 0°C and DIBAL-H 1.0 M in THF (10.00 mL, 10.00 mmol, 2.5 eq) was slowly added dropwise under inert flux of N_2. After 2 h, water (20.00 mL) and 1.0 M HCl (10.00 mL) were added. The resulting suspension was extracted with Et_2O (3 x 20.00 mL). The combined organic layers were washed with Brine (20.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 30 %). The desired product was obtained as a yellowish oil in 93 % yield (551 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.3 Hz, 2H), 7.17 (d, *J* = 10.1 Hz, 3H), 5.77 – 5.88 (m, 1H), 5.61 – 5.74 (m, 1H), 4.09 (s, 2H), 3.35 (d, *J* = 6.8 Hz, 2H), 1.28 – 1.38 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 131.7, 130.5, 128.7, 128.6, 126.3, 63.7, 38.8. The NMR data is consistent with literature.[9]

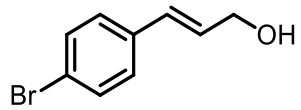
(*E*)-Ethyl 3-(4-bromophenyl)acrylate



The title compound was prepared using the following procedure. NaH (60 % dispersion in mineral oil) (800 mg, 20.00 mmol, 2.00 eq) was added to an oven-dried 250 mL round bottom flask and suspended in anhydrous THF (50.00 mL) and cooled to 0°C. Triethyl phosphonoacetate (3.00 mL, 15.00 mmol, 1.5 eq) was added dropwise and the resulting suspension was stirred for 30 min. After this time, a solution of 4-bromobenzaldehyde (1.85 g, 10.00 mmol) in anhydrous THF (40.00 mL) was added dropwise and the resulting mixture was allowed to reach spontaneously the room temperature. After 1 h the reaction was quenched with water (20.00 mL) and extracted with Et_2O (2 x 20.00 mL). The combined organic layers were washed with Brine (50.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 30 %). The desired product was obtained as a yellowish wax in 84

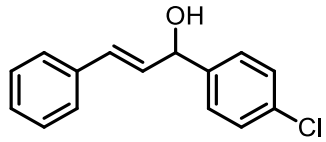
% yield (2.14 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 16.0 Hz, 1H), 7.48 – 7.55 (m, 2H), 7.36 – 7.42 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 143.3, 133.5, 132.3, 129.6, 124.6, 119.1, 60.8, 14.4. The NMR data is consistent with literature.[10]

(*E*)-3-(4-Bromophenyl)prop-2-en-1-ol (1h)



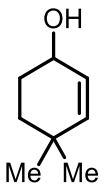
The title compound was prepared using the following procedure. (*E*)-ethyl 3-(4-bromophenyl)acrylate (852 mg, 4.00 mmol) was added to a 100 mL round bottom flask and dissolved in anhydrous THF (20.00 mL). The resulting solution was cooled to 0°C and DIBAL-H 1.0 M in THF (10.00 mL, 10.00 mmol, 2.5 eq) was slowly added dropwise under inert flux of N_2. After 2.5 h, water (10.00 mL) and 1.0 M HCl (20.00 mL) were added. The resulting suspension was extracted with Et_2O (3 x 30.00 mL). The combined organic layers were washed with Brine (40.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 35 %). The desired product was obtained as a white wax in 76 % yield (647 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.51 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.47 – 6.62 (m, 1H), 6.22 – 6.44 (m, 1H), 4.31 (dd, *J* = 5.5, 1.6 Hz, 2H), 1.70 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.7, 131.8, 129.9, 129.4, 128.1, 121.5, 63.6. The NMR data is consistent with literature.[11]

(±)-(*E*)-1-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol (1i)



The title compound was prepared using the following procedure. (*E*)-4'-Chlorochalcone (1.21 g, 5.00 mmol) was added to a 50 mL round bottom flask and dissolved in MeOH (20.00 mL). Cerium trichloride heptahydrate (1.86 g, 5.00 mmol, 1 eq) was added and the resulting mixture was stirred until the salt was completely dissolved. Thus, $NaBH_4$ (189 mg, 5.00 mmol, 1 eq) was added portion-wise at room temperature. After 5 min water (15.00 mL) was added and the resulting mixture was extracted with Et_2O (3 x 20.00 mL). The combined organic layers were washed with Brine (20.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 10 %). The desired product was obtained as a colourless oil in 85 % yield (1.04 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.43 (m, 9H), 6.68 (d, *J* = 15.8 Hz, 1H), 6.33 (dd, *J* = 15.9, 6.7 Hz, 1H), 5.37 (d, *J* = 6.7 Hz, 1H), 2.06 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.3, 136.4, 133.6, 131.2, 131.1, 128.9, 128.8, 128.1, 127.8, 126.8, 74.6. The NMR data is consistent with literature.[12]

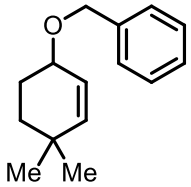
(±)-4,4-Dimethylcyclohex-2-enol (1j)



The title compound was prepared using the following procedure. 4,4-Dimethylcyclohex-2-en-1-one (654 µL, 5.00 mmol) was added to a 50 mL round bottom flask and dissolved in MeOH (20.00 mL). Cerium trichloride heptahydrate (1.86 g, 5.00 mmol, 1 eq) was added and the resulting mixture was stirred until the salt was completely dissolved. Thus, $NaBH_4$ (189 mg, 5.00 mmol, 1 eq) was added portion-wise at room temperature. After 5 min water (15.00 mL) was added and the resulting mixture was extracted with Et_2O (3 x 20.00 mL). The combined organic layers were washed with Brine (20.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was obtained as a colourless oil that was used without further purification (630 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.59 (dd, *J* = 10.0, 3.1 Hz, 1H), 5.52 (d, *J* = 10.0 Hz, 1H), 4.14 (dddd, *J* = 6.6,

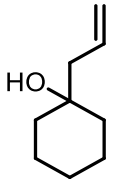
5.0, 3.2, 1.4 Hz, 1H), 1.91 (dddd, *J* = 13.2, 8.1, 5.0, 2.9 Hz, 1H), 1.36 – 1.68 (m, 4H), 1.01 (s, 3H), 0.96 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.8, 127.4, 66.0, 33.7, 32.0, 29.4, 29.3, 29.2. The NMR data is consistent with literature.[13]

(±)-(((4,4-Dimethylcyclohex-2-en-1-yl)oxy)methyl)benzene (1k)



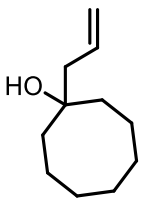
The title compound was prepared using the following procedure. **1j** (719 mg, 5.69 mmol) was added to an oven-dried 50 mL round bottom flask and dissolved in anhydrous THF (10.00 mL). The resulting solution was cooled to 0°C and NaH (60 % dispersion in mineral oil) (224 mg, 5.60 mmol, 1.05 eq) was added portion-wise. After 15 min benzyl bromide (1.49 mL, 12.54 mmol, 2.20 eq) was added and the resulting mixture was allowed to reach spontaneously the room temperature. After 3.5 h water (60.00 mL) was added and the resulting mixture was extracted with hexane (2 x 50.00 mL). The combined organic layers were washed with Brine (60.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 7 %). The desired product was obtained as a colourless oil in 52 % yield (635 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.39 (m, 4H), 7.26 – 7.29 (m, 1H), 5.66 (dd, *J* = 10.1, 2.9 Hz, 1H), 5.56 (d, *J* = 10.1 Hz, 1H), 4.51 – 4.65 (m, 2H), 3.91 (dddd, *J* = 6.9, 4.9, 3.0, 1.5 Hz, 1H), 1.89 (dddd, *J* = 13.2, 8.2, 5.1, 3.1 Hz, 1H), 1.75 (dddd, *J* = 13.2, 10.1, 6.9, 3.1 Hz, 1H), 1.53 – 1.67 (m, 1H), 1.40 (ddd, *J* = 13.3, 10.1, 3.1 Hz, 1H), 1.02 (s, 3H), 0.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.0, 139.1, 128.5, 127.8, 127.6, 125.4, 72.8, 70.2, 34.1, 32.2, 29.5, 29.1, 25.7. **IR** (thin film): ν_{max}: 3064, 3027, 2952, 2863, 1703, 1651, 1603 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_{15}H_{19}O$ 215.1431, found: 215.1424.

1-Allylcyclohexanol (1l)



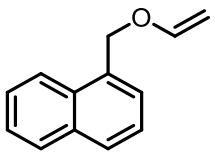
The title compound was prepared using the following procedure. Cyclohexanone (518 µL, 5.00 mmol), zinc powder (980 mg, 1.50 mmol, 3.00 eq) and ammonium acetate (1.05 mg, 1.50 mmol, 3.00 eq) were added to a 100 mL round bottom flask and dissolved/suspended in anhydrous THF (20.00 mL). Allyl bromide (1.30 mL, 1.50 mmol, 3.00 eq) was added at room temperature over 5 minutes. After 30 min a white suspension was formed and 1.0 M HCl (30.00 mL) was added. The resulting mixture was extracted with Et_2O (3 x 20.00 mL). The combined organic layers were washed with Brine (20.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was obtained as a colourless oil that was used without further purification (701 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 17.5, 10.2, 7.5 Hz, 1H), 5.01 – 5.22 (m, 2H), 2.21 (d, *J* = 7.5 Hz, 2H), 1.31 – 1.67 (m, 10H), 1.15 – 1.33 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.8, 118.8, 71.1, 46.8, 37.5, 25.9, 22.3. The NMR data is consistent with literature.[14]

1-Allylcyclooctanol (1m)



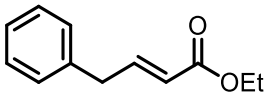
The title compound was prepared using the following procedure. Cyclooctanone (631 mg, 5.00 mmol), zinc powder (980 mg, 1.50 mmol, 3.00 eq) and ammonium acetate (1.05 mg, 1.50 mmol, 3.00 eq) were added to a 100 mL round bottom flask and dissolved/suspended in anhydrous THF (20.00 mL). Allyl bromide (1.30 mL, 1.50 mmol, 3.00 eq) was added at room temperature over 5 minutes. After 30 min a white suspension was formed and 1.0 M HCl (30.00 mL) was added. The resulting mixture was extracted with Et_2O (3 x 20.00 mL). The combined organic layers were washed with Brine (20.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 15 %). The desired product was obtained as a colourless oil in 89 % yield (749 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.89 (ddt, *J* = 17.5, 10.2, 7.4 Hz, 1H), 5.03 – 5.21 (m, 2H), 2.21 (d, *J* = 7.4 Hz, 2H), 1.29 – 1.82 (m, 15H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.2, 118.8, 74.6, 46.1, 36.3, 28.4, 25.1, 22.3. The NMR data is consistent with literature.[15]

1-((Vinyloxy)methyl)naphthalene (1t)



The title compound was prepared using the following procedure adapted from literature.[16] 1-Naphtalenemethanol (3.16 g, 20.00 mmol), palladium acetate (22 mg, 0.10 mmol, 0.005 eq) and 1,10-phenanthroline (18 mg, 0.10 mmol, 0.005 eq) were added to a 250 mL round bottom flask and dissolved in butyl vinyl ether (52.00 mL). The resulting solution was stirred at 75 h for 48 h. After this time the reaction mixture was filtered through a pad of Celite and the solvent was removed *in vacuo*. The crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 2 %). The desired product was obtained as a yellowish oil in 96 % yield (3.54 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.74 (m, 2H), 7.19 – 7.42 (m, 4H), 6.47 (dd, *J* = 14.1, 6.8 Hz, 1H), 4.99 (s, 2H), 4.26 (d, *J* = 14.4 Hz, 1H), 3.98 (d, *J* = 6.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 133.9, 132.4, 131.7, 129.1, 128.7, 126.7, 126.5, 126.0, 125.3, 123.7, 87.5, 68.7. The NMR data is consistent with literature.[17]

(*E*)-Ethyl 4-phenylbut-2-enoate (1u)



The title compound was prepared using the following procedure.
(Carbethoxymethylene)triphenylphosphorane (3.48 g, 10.00 mmol, 1.00 eq) was added to 250 mL round bottom flask and dissolved in anhydrous CH_2Cl_2 (50.00 mL). Phenylacetaldehyde (1.11 mL, 10.00 mmol) was added and the resulting solution was stirred at room temperature for 14 h. After this time, the solvent was removed *in vacuo* and the crude product was further purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Hexane, 30 %). The desired product was obtained as a colourless oil in 75 % yield (1.43 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.3 Hz, 2H), 7.29 (d, *J* = 5.8 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.09 – 7.19 (m, 1H), 5.86 (d, *J* = 15.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.56 (d, *J* = 6.8 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 147.3, 137.8, 128.9, 128.8, 126.7, 122.5, 60.3, 38.5, 14.3. The NMR data is consistent with literature.[18]

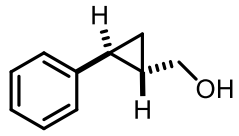
5. Synthesis of Cyclopropanes

General Procedure A: Mechanochemical Simmons-Smith Reaction (1.00 mmol scale)

To a 15 mL stainless jar charged with one 4 g stainless steel ball, alkene (1.00 mmol), zinc metal (327 mg, 5.00 mmol, 5.00 eq), 2-MeTHF (151 μL, 1.50 mmol, 1.50 eq) and diiodomethane (403 μL, 5.00 mmol, 5.00 eq) were added and milled at 30 Hz for 1 h at room temperature in a Retsch/Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product that was further purified by silica gel flash column chromatography using the noted solvent systems.

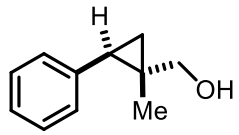
Note: EtOAc can be used in place of CH_2Cl_2 for work-up procedures (see section 7.3: Scale-up).

(±)-(*E*)-(2-Phenylcyclopropyl)methanol (3a)



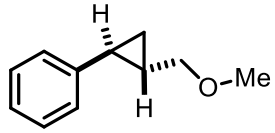
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 20 %) as a yellowish oil in 94 % yield (134 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 – 7.21 (m, 2H), 7.07 (t, *J* = 6.7 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 2H), 3.52 (dd, *J* = 6.7, 3.9 Hz, 2H), 1.68 – 1.77 (m, 1H), 1.62 (s, 1H), 1.36 (h, *J* = 6.6 Hz, 1H), 0.86 (td, *J* = 9.2, 4.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 128.4, 125.9, 125.8, 66.6, 25.4, 21.4, 13.9. The NMR data is consistent with literature.[19]

(±)-(*E*)-(1-Methyl-2-phenylcyclopropyl)methanol (3b)



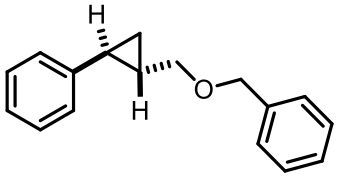
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 10-20 %) as a yellowish oil in 81 % yield (131 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 – 7.23 (m, 2H), 7.06 – 7.14 (m, 3H), 3.47 (d, *J* = 2.5 Hz, 2H), 1.97 (dd, *J* = 8.8, 5.9 Hz, 1H), 1.61 (s, 1H), 0.85 (dd, *J* = 8.8, 5.0 Hz, 1H), 0.79 (d, *J* = 6.9 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.9, 129.2, 128.1, 126.0, 71.8, 26.9, 25.3, 15.9, 15.3. The NMR data is consistent with literature.[20]

(±)-(*E*)-(2-(Methoxymethyl)cyclopropyl)benzene (3c)



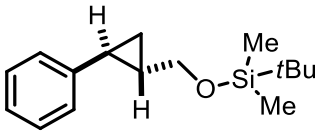
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 5 %) as a pale-yellow oil in 85 % yield (137 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 3.35 – 3.49 (m, 5H), 1.85 (dt, *J* = 9.1, 4.9 Hz, 1H), 1.40 – 1.50 (m, 1H), 0.91 – 1.06 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.6, 128.4, 125.9, 125.6, 76.1, 58.4, 22.5, 21.5, 14.0. The NMR data is consistent with literature.[21]

(±)-(*E*)-(2-((Benzyloxy)methyl)cyclopropyl)benzene (3d)



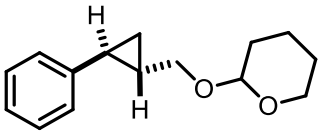
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 5 %) as a colourless oil in 94 % yield (224 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.47 (m, 8H), 7.20 (td, *J* = 6.2, 2.5 Hz, 1H), 7.08 – 7.16 (m, 2H), 4.61 (q, *J* = 2.0 Hz, 2H), 3.59 (ddd, *J* = 8.3, 6.5, 1.9 Hz, 1H), 3.49 (ddd, *J* = 9.9, 6.9, 2.1 Hz, 1H), 1.86 (ddt, *J* = 7.0, 5.0, 2.1 Hz, 1H), 1.52 (dddd, *J* = 8.6, 6.6, 4.4, 2.3 Hz, 1H), 0.95 – 1.07 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.7, 138.5, 128.5, 128.4, 127.8, 127.7, 125.9, 125.7, 73.6, 72.6, 22.7, 21.5, 14.3. The NMR data is consistent with literature.[22]

(±)-(*E*)-*t*ert-Butyldimethyl((2-phenylcyclopropyl)methoxy)silane (3e)



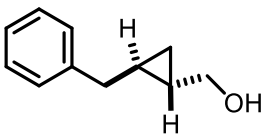
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Hexane, 20 %) as a yellowish oil in 92 % yield (240 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 6.9 Hz, 2H), 3.66 (dd, *J* = 10.7, 5.7 Hz, 1H), 3.57 (dd, *J* = 10.7, 6.0 Hz, 1H), 1.68 – 1.81 (m, 1H), 1.24 – 1.37 (m, 1H), 0.81 – 0.91 (m, 11H), 0.02 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.1, 128.3, 125.9, 125.4, 65.9, 26.1, 25.3, 20.8, 18.5, 13.7, -5.0. The NMR data is consistent with literature.[23]

(±)-(*E*)-2-((2-Phenylcyclopropyl)methoxy)tetrahydro-2H-pyran (3f)



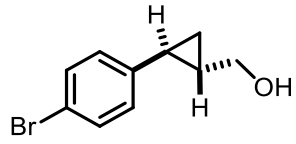
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 3-5 %) as a colourless oil in 28 % yield (mixture of stereoisomers) (65 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 (td, *J* = 8.2, 2.7 Hz, 2H), 7.13 – 7.19 (m, 1H), 7.05 – 7.13 (m, 2H), 4.62 – 4.82 (m, 1H), 3.42 – 3.96 (m, 4H), 1.71 – 1.93 (m, 3H), 1.38 – 1.67 (m, 4H), 0.87 – 1.05 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.9, 142.9, 142.6, 128.4, 128.4, 126.0, 125.9, 125.7, 125.6, 126.6, 98.5, 98.3, 94.8, 94.8, 71.4, 71.4, 70.9, 70.8, 62.4, 30.8, 25.6, 22.7, 22.7, 21.7, 21.6, 21.3, 19.7, 19.7, 14.6, 14.2, 14.2. **IR** (thin film): ν_{max}: 3064, 3027, 2941, 2870, 1729, 1603 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M\text{-THPO}]^+$ Calcd for $C_{10}H_{11}$ 131.0861, found: 131.0855.

(±)-(*E*)-(2-Benzylcyclopropyl)methanol (3g)



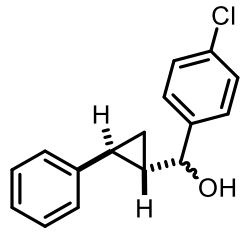
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 30-40 %) as a colourless oil in 94 % yield (153 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.97 – 7.14 (m, 5H), 3.25 (dd, *J* = 6.9, 2.8 Hz, 2H), 2.40 (d, *J* = 8.8 Hz, 2H), 1.47 (s, 1H), 0.82 (ddd, *J* = 12.0, 7.3, 4.9 Hz, 1H), 0.69 – 0.77 (m, 1H), 0.25 – 0.33 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 128.4, 128.3, 126.1, 66.9, 39.3, 21.3, 18.2, 10.1. **IR** (thin film): ν_{max}: 3340, 3064, 3027, 2997, 2915, 2870, 1603 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M\text{-}H_2O\text{+H}]^+$ Calcd for $C_{11}H_{13}$ 145.1012, found: 145.1010.

(±)-(*E*)-(2-(4-Bromophenyl)cyclopropyl)methanol (3h)



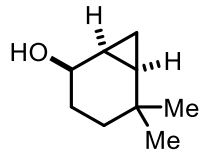
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 35 %) as a colourless oil in 57 % yield (130 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 3.62 (d, *J* = 6.6 Hz, 2H), 1.79 (dt, *J* = 9.2, 5.1 Hz, 1H), 1.60 (s, 1H), 1.41 (d, *J* = 6.3 Hz, 1H), 0.94 (dt, *J* = 8.3, 5.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.6, 131.5, 127.7, 119.3, 66.5, 25.5, 20.9, 14.0. The NMR data is consistent with literature.[24]

***anti-* & *syn*-(±)-(*E*)-(4-Chlorophenyl)(2-phenylcyclopropyl)methanol (3i)**



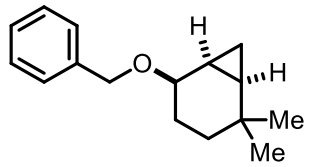
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 15 %) as two yellow oils in 44 % overall yield (2:3, *anti*/*syn*) (45+68 mg). RfI (less polar *anti* isomer): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.34 (m, 6H), 7.06 – 7.12 (m, 1H), 6.97 – 7.04 (m, 2H), 4.23 (d, *J* = 7.7 Hz, 1H), 2.01 (dt, *J* = 9.3, 4.9 Hz, 1H), 1.39 – 1.54 (m, 2H), 1.00 (dt, *J* = 8.9, 5.4 Hz, 1H), 0.93 (dt, *J* = 8.7, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 142.0, 133.5, 128.8, 128.6, 127.5, 126.0, 126.0, 76.9, 30.8, 22.0, 13.6. **IR** (thin film): ν_{max}: 3369, 3064, 3027, 2922, 2870, 1603 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{15}ClONa$ 281.0709, found: 281.0722. RfII (more polar *syn* isomer): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.28 (m, 2H), 7.12 – 7.18 (m, 1H), 6.97 – 7.04 (m, 2H), 4.33 (d, *J* = 7.6 Hz, 1H), 1.96 – 2.10 (m, 2H), 1.45 – 1.54 (m, 1H), 1.18 (dt, *J* = 8.9, 5.3 Hz, 1H), 1.07 (dt, *J* = 8.4, 5.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.0, 141.8, 133.4, 128.7, 128.5, 127.5, 126.1, 126.0, 76.4, 30.3, 21.2, 13.7. **IR** (thin film): ν_{max}: 3347, 3064, 3027, 2874, 1603 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_{16}H_{14}ClO$ 257.0728, found: 257.0722.

***syn*-(±)-5,5-Dimethylbicyclo[4.1.0]heptan-2-ol (3j)**



Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 10-20 %) as a colourless oil in 84 % yield (117 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.22 (q, *J* = 6.1 Hz, 1H), 1.55 (ddt, *J* = 13.4, 7.2, 2.7 Hz, 1H), 1.43 (s, 1H), 1.27 – 1.40 (m, 1H), 1.14 (ddt, *J* = 15.3, 9.1, 4.7 Hz, 2H), 0.91 – 1.06 (m, 7H), 0.84 (td, *J* = 8.5, 6.2 Hz, 1H), 0.38 (ddd, *J* = 10.7, 7.0, 4.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 65.9, 33.2, 31.1, 29.5, 27.4, 27.3, 25.4, 18.6, 3.7. **IR** (thin film): ν_{max}: 3358, 3071, 3008, 2952, 2866, 1685 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_9H_{15}O$ 139.1118, found: 139.1113.

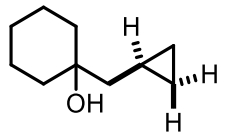
***syn*-(±)-5-(Benzyloxy)-2,2-dimethylbicyclo[4.1.0]heptane (3k)**



Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Hexane, 30 %) as a colourless oil in 40 % yield (92 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 – 7.21 (m, 4H), 7.04 – 7.10 (m, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.29 (d, *J* = 11.9 Hz, 1H), 3.77 (dt, *J* = 6.6, 4.7 Hz, 1H), 1.38 (dddd, *J* = 14.6,

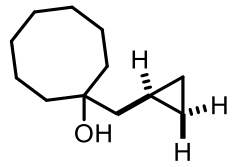
11.5, 5.6, 3.4 Hz, 1H), 1.17 (dddd, *J* = 14.3, 7.1, 4.5, 3.0 Hz, 1H), 1.08 (tdd, *J* = 8.5, 6.7, 5.3 Hz, 1H), 0.99 (ddd, *J* = 14.1, 11.5, 3.0 Hz, 1H), 0.86 (s, 3H), 0.78 (s, 4H), 0.62 (td, *J* = 8.5, 6.2 Hz, 1H), 0.18 – 0.39 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.4, 128.4, 127.8, 127.4, 71.3, 69.3, 31.8, 30.2, 30.1, 28.0, 25.3, 25.0, 14.8, 4.3. **IR** (thin film): ν_{max}: 3064, 3004, 2952, 2863, 1707 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_{16}H_{21}O$ 299.1587, found: 229.1588.

1-(Cyclopropylmethyl)cyclohexanol (3l)



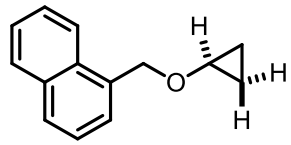
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 25 %) as a colourless oil in 80 % yield (124 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.39 – 1.67 (m, 10H), 1.35 (d, *J* = 6.9 Hz, 2H), 1.23 (qt, *J* = 9.8, 3.8 Hz, 1H), 0.73 (dtt, *J* = 12.4, 7.3, 3.7 Hz, 1H), 0.40 – 0.48 (m, 2H), 0.00 – 0.06 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 72.4, 47.2, 37.6, 26.0, 22.3, 5.4, 4.2. The NMR data is consistent with literature.[25]

1-(Cyclopropylmethyl)cyclooctanol (3m)



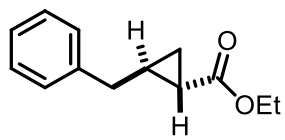
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 15 %) as a colourless oil in 60 % yield (110 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.77 (dd, *J* = 12.6, 10.1 Hz, 2H), 1.53 – 1.67 (m, 8H), 1.32 – 1.51 (m, 7H), 0.68 – 0.79 (m, 1H), 0.41 – 0.47 (m, 2H), 0.01 – 0.08 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 75.8, 46.3, 36.3, 28.4, 25.0, 22.4, 5.5, 4.2. **IR** (thin film): ν_{max}: 3410, 3075, 3000, 2915, 2851 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_{12}H_{21}O$ 181.1587, found: 181.0300.

1-(Cyclopropoxymethyl)naphthalene (3t)



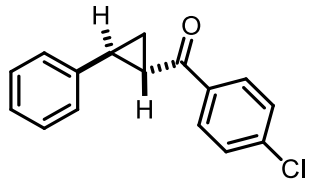
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 4 %) as a yellowish oil in 95 % yield (189 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.78 – 7.92 (m, 2H), 7.37 – 7.58 (m, 4H), 5.01 (s, 2H), 3.41 (tt, *J* = 6.1, 3.0 Hz, 1H), 0.70 (dt, *J* = 5.2, 3.1 Hz, 2H), 0.52 (dd, *J* = 6.0, 1.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.9, 133.8, 131.9, 128.7, 128.7, 126.7, 126.3, 125.9, 125.4, 124.1, 71.3, 53.3, 5.8. **IR** (thin film): ν_{max}: 3045, 3004, 2922, 2855, 1688, 1595, 1510 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}O$ 199.1123, found: 199.1117.

(±)-(*E*)-Ethyl 2-benzylcyclopropanecarboxylate (3u)



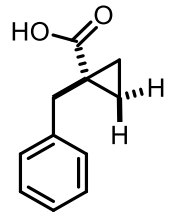
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Hexane, 30 %) as a colourless oil in 34 % yield (130 mg of 1:1 mixture of product and starting material). **^{1}H NMR** (400 MHz, CDCl3) δ 7.21-7.37 (m, 5H), 4.15 (q, *J* = 5 Hz, 2H), 2.80 (dd, *J* = 5, 15 Hz, 1H), 2.61 (dd, *J* = 5 & 10 Hz, 1H), 1.74 (m, 1H), 1.55 (m, 1H), 1.29 (m, 4H), 0.87 (m, 1H). **^{13}C NMR** (101 MHz, CDCl3) δ 174.1, 140.2, 128.4, 128.4, 126.3, 60.4, 38.4, 23.0, 20.2, 15.3, 14.3. The NMR data is consistent with literature.[26]

(±)-(*E*)-(4-Chlorophenyl)(2-phenylcyclopropyl)methanone (3v)



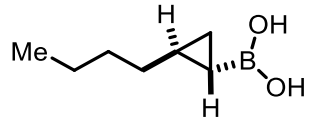
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Hexane, 20-30 %) as a colourless oil in 32 % yield (82 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.06 – 7.12 (m, 2H), 2.71 – 2.80 (m, 1H), 2.57 – 2.67 (m, 1H), 1.85 (t, *J* = 3.9 Hz, 1H), 1.50 – 1.53 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.5, 140.4, 139.5, 136.1, 129.7, 129.0, 128.7, 126.8, 126.3, 30.4, 29.4, 19.5. The NMR data is consistent with literature.[27]

1-Benzylcyclopropanecarboxylic acid (3x)



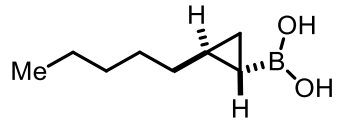
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 20-30 %) as colourless oil in 40 % yield (71 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.23 (bs, 1H), 7.00 – 7.29 (m, 5H), 2.92 (s, 2H), 1.29 (q, *J* = 4.2 Hz, 2H), 0.81 (q, *J* = 4.1 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 182.3, 139.3, 129.3, 128.3, 126.4, 37.8, 23.7, 16.2. The NMR data is consistent with literature.[28]

(±)-(*E*)-(2-Butylcyclopropyl)boronic acid (3y)



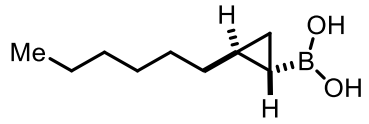
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 30 %) as a colourless oil in 38 % yield (54 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.18 – 1.43 (m, 7H), 0.97 (q, *J* = 6.3 Hz, 1H), 0.89 (t, *J* = 7.1 Hz, 4H), 0.72 (t, *J* = 6.7 Hz, 1H), 0.44 (dt, *J* = 8.8, 4.4 Hz, 1H), -0.46 – -0.35 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 35.0, 32.1, 22.7, 19.6, 14.3, 12.6, 4.0. **IR** (thin film): ν_{max}: 3228, 3000, 2959, 2922, 2855 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_7H_{14}{}^{11}BO_2$ 141.1082, found: 141.1082.

(±)-(*E*)-(2-Pentylcyclopropyl)boronic acid (3z)



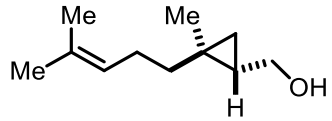
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 30 %) as a white wax in 54 % yield (84 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.18 – 1.44 (m, 9H), 0.97 (m, 1H), 0.88 (t, *J* = 6.9 Hz, 4H), 0.71 (tt, *J* = 5.7, 3.0 Hz, 1H), 0.43 (ddd, *J* = 8.8, 5.5, 3.0 Hz, 1H), -0.40 (dt, *J* = 8.8, 5.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 35.3, 31.9, 29.6, 22.8, 19.7, 14.2, 12.6, 4.0. **IR** (thin film): ν_{max}: 3228, 3071, 3000, 2959, 2922, 2855 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_8H_{16}{}^{11}BO_2$ 155.1238, found: 155.1239.

(±)-(*E*)-(2-Hexylcyclopropyl)boronic acid (3aa)



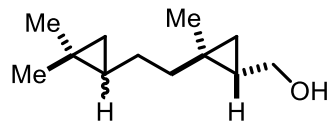
Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 30 %) as a colourless oil in 58 % yield (98 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.17 – 1.44 (m, 11H), 0.96 (m, 1H), 0.88 (t, *J* = 6.9 Hz, 4H), 0.40 – 0.47 (m, 1H), 0.68 – 0.74 (m, 1H), -0.41 (dt, *J* = 8.8, 5.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 35.3, 32.0, 29.8, 29.3, 22.8, 19.7, 14.3, 12.6, 4.0. **IR** (thin film): ν_{max}: 3224, 3075, 3000, 2922, 2855 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_9H_{18}{}^{11}BO_2$ 169.1395, found: 169.1405.

(±)-(*E*)-(2-Methyl-2-(4-methylpent-3-en-1-yl)cyclopropyl)methanol (3ab')



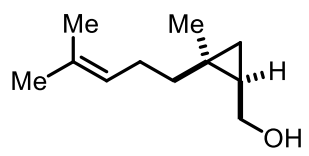
The title compound was prepared using the following procedure. To a 15 mL stainless jar charged with one 4 g stainless steel ball, geraniol (351 µL, 2.00 mmol), zinc metal (327 mg, 5.00 mmol, 2.50 eq), 2-MeTHF (151 µL, 1.50 mmol, 0.75 eq) and diiodomethane (403 µL, 5.00 mmol, 2.50 eq) were added and milled at 30 Hz for 1 h at room temperature in a Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product that was further purified by silica gel flash column chromatography (Eluent: EtOAc/Hexane, 10-20 %) as a colourless oil in 84 % yield (283 mg). The minor regioisomeric impurity (>5%) was detected by NMR. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.11 (t, *J* = 7.4 Hz, 1H), 3.72 (dt, *J* = 11.7, 6.1 Hz, 1H), 3.49 (td, *J* = 10.7, 3.9 Hz, 1H), 2.07 (q, *J* = 8.1 Hz, 2H), 1.68 (s, 3H), 1.61 (s, 3H), 1.37 (dt, *J* = 14.9, 8.0 Hz, 1H), 0.97 – 1.27 (m, 5H), 0.91 (dq, *J* = 9.7, 4.8 Hz, 1H), 0.51 (dd, *J* = 8.9, 4.5 Hz, 1H), 0.12 (t, *J* = 5.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.5, 124.8, 64.1, 41.2, 26.4, 25.8, 25.6, 20.0, 17.8, 17.7, 17.2. The NMR data is consistent with literature.[29]

***syn-* + *anti*-(±)-(*E*)-(2-(2-(2,2-Dimethylcyclopropyl)ethyl)-2-methylcyclopropyl)methanol (3ab'')**



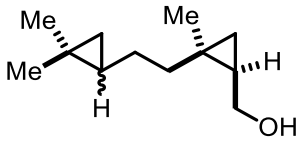
The title compound was prepared using the following procedure. To a 15 mL stainless jar charged with one 4 g stainless steel ball, geraniol (175 µL, 1.00 mmol), zinc metal (490 mg, 7.50 mmol, 7.50 eq), 2-MeTHF (151 µL, 1.50 mmol, 1.50 eq) and diiodomethane (604 µL, 7.50 mmol, 7.50 eq) were added and milled at 30 Hz for 1 h at room temperature in a Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product that was further purified by silica gel flash column chromatography (Eluent: EtOAc/Hexane, 10-20 %) as a colourless oil in 60 % yield (110 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.69 (ddd, *J* = 11.8, 6.8, 5.3 Hz, 1H), 3.51 (ddd, *J* = 11.5, 8.5, 5.0 Hz, 1H), 0.76 – 1.44 (m, 15H), 0.36 – 0.53 (m, 2H), 0.33 (dd, *J* = 8.6, 4.0 Hz, 1H), 0.11 (t, *J* = 4.8 Hz, 1H), -0.16 (t, *J* = 4.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 64.1, 41.7, 41.7, 27.8, 27.2, 26.3, 26.2, 24.7, 24.7, 20.2, 20.1, 19.9, 19.8, 19.8, 17.9, 17.9, 17.3, 17.2, 15.5. The NMR data is consistent with literature.[29]

(±)-(*Z*)-(2-Methyl-2-(4-methylpent-3-en-1-yl)cyclopropyl)methanol (3ac')



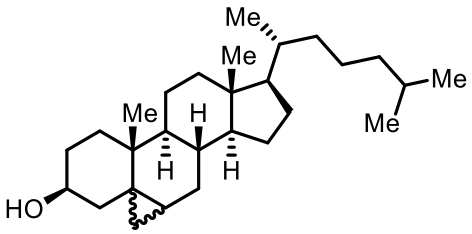
The title compound was prepared using the following procedure. To a 15 mL stainless jar charged with one 4 g stainless steel ball, nerol (350 µL, 2.00 mmol), zinc metal (327 mg, 5.00 mmol, 2.50 eq), 2-MeTHF (151 µL, 1.50 mmol, 0.75 eq) and diiodomethane (403 µL, 5.00 mmol, 2.50 eq) were added and milled at 30 Hz for 1 h at room temperature in a Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product that was further purified by silica gel flash column chromatography (Eluent: EtOAc/Hexane, 10-20 %) as a colourless oil in 76 % yield (254 mg). The minor regioisomeric impurity (>5%) was detected by NMR. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.12 (tt, *J* = 6.6, 3.3 Hz, 1H), 3.52 – 3.68 (m, 2H), 1.99 – 2.14 (m, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.36 (m, 2H), 0.96 – 1.13 (m, 4H), 0.91 (qd, *J* = 7.8, 5.3 Hz, 1H), 0.46 (dd, *J* = 8.5, 4.4 Hz, 1H), 0.13 (t, *J* = 4.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 131.7, 124.7, 63.6, 34.3, 27.4, 25.8, 25.8, 24.5, 20.3, 17.7, 17.6. The NMR data is consistent with literature.[29]

***syn-* + *anti-*(±)-(*Z*)-(2-(2-(2,2-Dimethylcyclopropyl)ethyl)-2-methylcyclopropyl)methanol (3ac")**



Prepared according to general procedure **A**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 10-20 %) as a colourless oil in 54 % yield (98 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.54 – 3.69 (m, 2H), 1.31 – 1.53 (m, 4H), 1.25 (s, 1H), 0.94 – 1.07 (m, 9H), 0.91 (qd, *J* = 7.7, 5.3 Hz, 1H), 0.45 (tt, *J* = 12.5, 5.4 Hz, 2H), 0.32 – 0.38 (m, 1H), 0.15 (t, *J* = 5.1 Hz, 1H), -0.14 (q, *J* = 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 63.8, 63.8, 34.7, 24.6, 27.8, 27.6, 27.5, 27.4, 25.0, 24.6, 20.6, 20.4, 20.0, 19.9, 19.8, 17.8, 15.6. The NMR data is consistent with literature.[29]

5α,6α- + 5β,6β-Cyclopropa-[5,6]-cholest-5-en-3β-ol (3ad)



The title compound was prepared using the following procedure. In a 30 mL stainless jar charged with one 9 g stainless steel ball, cholesterol (387 mg, 1.00 mmol), zinc metal (327 mg, 5.00 mmol, 5.00 eq), sand (2.18 g, 1 me), 2-MeTHF (151 µL, 1.50 mmol, 1.50 eq) and diiodomethane (403 µL, 5.00 mmol, 5.00 eq) were added and milled at 30 Hz for 1 h at 75°C in a Retsch mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was vacuum filtered and transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product that was further purified by silica gel flash column chromatography (Eluent: EtOAc/Hexane, 10-20 %). The resulting inseparable mixture of **3ad** and cholesterol was put to a 50 mL round bottom flask and dissolved in anhydrous CH_2Cl_2 (5.00 mL). The resulting solution was cooled to 0 °C and 3-chloroperbenzoic acid (70 % purity) (123 mg, 0.50 mmol, 0.50 eq) was added. After 1 h NaOH 1.0 M (30.00 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (2 x 20.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the crude product was further purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 15 %). The desired product was obtained as a colourless oil in 30 % overall yield (3:2, α/β) (119 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.86 (dq, *J* = 11.0, 5.5 Hz, 1H), 1.73 – 2.06 (m, 5H), 0.66 – 1.72 (m, 36H), 0.61 (d, *J* = 7.7 Hz, 4H), 0.32 (dt, *J* = 9.7, 4.6 Hz, 1H), -0.08 (dd, *J* = 8.5, 4.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 70.3, 68.5, 57.8, 57.1, 56.4, 56.1, 49.2, 44.3, 44.3, 43.1, 42.7, 42.4, 40.2, 39.8, 39.6, 36.3, 36.3, 35.9, 35.5, 33.9, 33.9, 33.1, 32., 30.9, 30.8, 30.8, 30.7, 28.8, 28.4, 28.3, 28.1, 24.4, 24.1, 24.1, 23.9, 23.0, 22.7, 22.4, 21.9, 21.6, 21.3, 18.8, 17.9, 16.8, 16.6, 12.6, 12.2, 12.1. **IR** (thin film): ν_{max}: 3358, 3064, 2930, 2866, 1729 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{49}O$ 401.3778, found: 401.3770.

5.1. Synthesis of cyclopropanes from silyl enol ethers

All t-butyldimethylsilyl enol ether proved to be extremely unstable, thus they were used after a very fast chromatography/filtration through a short pad (7-10 cm) of alumina gel.

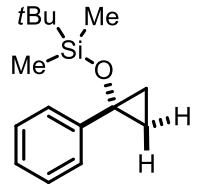
General Procedure B: Mechanochemical Simmons-Smith Reaction of Acetophenone Derivatives

Acetophenone (or its *meta*-substituted derivative) (10.00 mmol), *t*-butyldimethylchlorosilane (2.86 g, 19.00 mmol, 1.90 eq) and trimethylamine (2.05 mL, 15.00 mmol, 1.50 eq) were added to a 250 mL round bottom flask and dissolved in acetonitrile (40.00 mL). A solution of sodium iodide (2.25 g, 15.00 mmol, 1.50 eq) in acetonitrile (18.00 mL) was added dropwise under Ar atmosphere and the resulting mixture was heated to 70°C. After 7 h the crude mixture was cooled, vacuum filtered and concentrated. The intermediate silyl enol ether was obtained after a fast filtration through a pad (7-10 cm) of alumina gel (Eluent: CH_2Cl_2/Hexane, 5-30 %) and used without further purification or characterization because of its instability. Then, to a 15 mL stainless jar charged with one 4 g stainless steel ball, silyl enol ether (1.00 mmol), zinc metal (327 mg, 5.00 mmol, 5.00 eq), 2-MeTHF (151 µL, 1.50 mmol, 1.50 eq) and diiodomethane (403 µL, 5.00 mmol, 5.00 eq) were added and milled at 30 Hz for 1 h at room temperature in a Retsch/Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product that was further purified by silica gel flash column chromatography using the noted solvent systems.

General Procedure C: Mechanochemical Simmons-Smith Reaction of Other TBS Enol Ethers

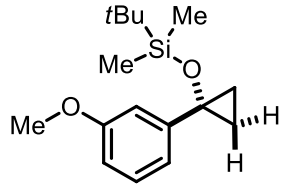
Ketone (5.00 mmol) was added to a 50 mL round bottom flask and dissolved in acetonitrile (20.00 mL). Triethylamine (809 µL, 8.00 mmol, 1.60 eq), *t*-butyldimethylchlorosilane (1.21 g, 8.00 mmol, 1.60 eq) and sodium iodide (1.20 g, 8.00 mmol, 1.60 eq) were added in this order under inert flux of N_2 and the resulting mixture was stirred at room temperature for 16 h. After this time the resulting brown suspension was extracted with hexane (3 x 30.00 mL) and the combined organic layers were washed with a saturated solution of $NaHCO_3$ (20.00 mL), Brine (20.00 mL) and dried over anhydrous $MgSO_4$. After the removal of the volatiles *in vacuo* the intermediate silyl enol ether was obtained after a fast filtration through a pad (7-10 cm) of alumina gel (Eluent: EtOAc/Hexane, 1-5 %) and used without further purification or characterization because of its instability. Then, to a 15 mL stainless jar charged with one 4 g stainless steel ball, silyl enol ether (1.00 mmol), zinc metal (327 mg, 5.00 mmol, 5.00 eq), 2-MeTHF (151 µL, 1.50 mmol, 1.50 eq) and diiodomethane (403 µL, 5.00 mmol, 5.00 eq) were added and milled at 30 Hz for 1 h at room temperature in a Retsch/Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product that was further purified by silica gel flash column chromatography using the noted solvent systems.

***tert*-Butyldimethyl(1-phenylcyclopropoxy)silane (3n)**



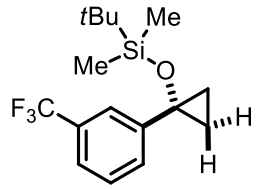
Prepared according to general procedure **B**. Purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Petroleum ether, 5 %) as a colourless oil in 91 % yield (226 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.37 (m, 4H), 7.20 (t, *J* = 6.1 Hz, 1H), 1.17 (d, *J* = 5.3 Hz, 2H), 0.88 (s, 9H), 0.97 – 1.03 (m, 2H), -0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 128.1, 126.4, 125.7, 58.1, 26.0, 18.1, 16.7, -3.4. **IR** (thin film): ν_{max}: 3086, 3065, 3027, 2956, 2889, 2855, 1688, 1603 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{25}OSi$ 249.1675, found: 249.1668.

***tert*-Butyl(1-(3-methoxyphenyl)cyclopropoxy)dimethylsilane (3o)**



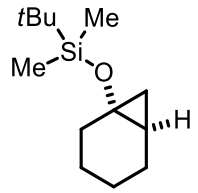
Prepared according to general procedure **B**. Purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Petroleum ether, 0-10 %) as a colourless oil in 68 % yield (189 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 3.82 (s, 3H), 1.17 (d, *J* = 4.8 Hz, 2H), 0.99 (d, *J* = 5.6 Hz, 2H), 0.89 (s, 9H), 0.02 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 146.6, 129.1, 117.5, 112.0, 111.5, 58.0, 55.3, 26.0, 18.1, 17.0, -3.3. **IR** (thin film): ν_{max}: 3086, 3004, 2952, 2889, 2855, 1685, 1580 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M\text{-TBSO}]^+$ Calcd for $C_{10}H_{11}O$ 147.0810, found: 147.0803.

***tert*-Butyldimethyl(1-(3-(trifluoromethyl)phenyl)cyclopropoxy)silane (3p)**



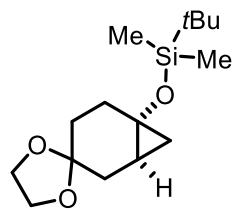
Prepared according to general procedure **B**. Purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Petroleum ether, 10 %) as a colourless oil in 53 % yield (168 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.30 – 7.51 (m, 3H), 1.25 (d, *J* = 5.6 Hz, 2H), 0.97 – 1.09 (m, 2H), 0.89 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.2, 130.8, 130.4, 128.7, 128.1, 125.8, 123.2, 123.1, 123.0, 122.5, 122.3, 57.7, 25.9, 18.1, 17.4, -3.4. **^{19}F NMR** (659 MHz, $CDCl_3$) δ -62.66 (s). **IR** (thin film): ν_{max}: 2956, 2892, 2859 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}OF_3Si$ 317.1549, found: 317.1540.

(±)-(bicyclo[4.1.0]heptan-1-yloxy)(*tert*-butyl)dimethylsilane (3q)



Prepared according to general procedure **C**. Purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Hexane, 10 %) as a colourless oil in 56 % yield (127 mg). **^{1}H NMR** (500 MHz, C_6D_6) δ 2.06 (dt, *J* = 13.1, 5.2 Hz, 1H), 1.90 (dddd, *J* = 14.9, 7.5, 5.7, 1.6 Hz, 2H), 1.26 – 1.36 (m, 2H), 0.97 (s, 9H), 1.03 – 1.19 (m, 3H), 0.82 – 0.91 (m, 2H), 0.21 (dd, *J* = 6.3, 5.3 Hz, 1H), 0.13 (d, *J* = 2.2 Hz, 6H). **^{13}C NMR** (126 MHz, C_6D_6) δ 56.4, 32.9, 26.0, 25.0, 22.2, 21.9, 19.7, 19.1, 17.9, -3.0, -3.2. **IR** (thin film): ν_{max}: 2930, 2855 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_{13}H_{25}OSi$ 225.1670, found: 225.1667.

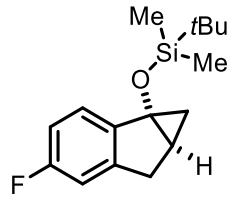
(±)-*tert*-Butyldimethyl(spiro[bicyclo[4.1.0]heptane-3,2'-[1,3]dioxolan]-6-yloxy)silane (3r)



Prepared according to general procedure **C**. Purified by silica gel flash chromatography (Eluent: EtOAc/Hexane, 5-10 %) as a colourless oil in 77 % yield (219 mg). **^{1}H NMR** (500 MHz, C_6D_6) δ 3.37 – 3.52 (m, 4H), 2.41 (dddd, *J* = 13.0, 11.6, 5.4, 1.3 Hz, 1H), 2.09 – 2.23 (m, 2H), 1.63 (dd, *J* = 14.5, 1.5 Hz, 1H), 1.56 (dtd, *J* = 13.5, 5.0, 2.1

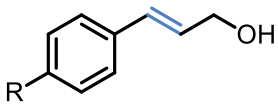
Hz, 1H), 1.11 – 1.27 (m, 2H), 0.85 – 1.01 (m, 10H), 0.41 (t, *J* = 5.8 Hz, 1H), 0.17 (d, *J* = 3.6 Hz, 6H). **^{13}C NMR** (126 MHz, C_6D_6) δ 107.8, 64.3, 63.9, 55.8, 34.9, 30.9, 30.4, 26.0, 18.9, 18.8, 17.9, -3.2, -3.3, -3.2. **IR** (thin film): ν_{max}: 2952, 2885, 2855 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M+CH_3OH+H]^+$ Calcd for $C_{16}H_{33}O_4Si$ 317.2143, found: 317.1540.

(±)-*tert*-Butyl((-4-fluoro-1,1a,6,6a-tetrahydrocyclopropa[a]inden-1a-yl)oxy)dimethylsilane (3s)



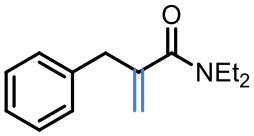
Prepared according to general procedure **C**. Purified by silica gel flash chromatography (Eluent: CH_2Cl_2/Hexane, 30 %) as a colourless oil in 60 % yield (166 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.3, 5.3 Hz, 1H), 6.87 (td, *J* = 8.7, 2.4 Hz, 1H), 6.79 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.20 (dd, *J* = 17.3, 6.4 Hz, 1H), 2.66 (d, *J* = 17.3 Hz, 1H), 1.98 (ddd, *J* = 10.0, 6.4, 4.4 Hz, 1H), 1.40 (dd, *J* = 9.5, 5.1 Hz, 1H), 0.91 (s, 9H), 0.37 (t, *J* = 4.8 Hz, 1H), 0.02 (d, *J* = 11.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 161.0, 142.7, 142.7, 141.4, 141.3, 123.5, 123.4, 113.3, 133.0, 112.6, 112.4, 67.7, 34.5, 34.5, 25.9, 24.5, 23.2, 18.0, -3.5, -4.0. **^{19}F NMR** (659 MHz, $CDCl_3$) δ -117.31 (td, *J* = 9.0, 5.1 Hz). **IR** (thin film): ν_{max}: 3068, 2956, 2855, 1595 cm^{-1}. **HRMS** (ASAP-HESI) m/z: $[M-H]^+$ Calcd for $C_{16}H_{22}FOSi$ 277.1419, found: 277.1417.

6. Unsuccessful and Low Yielding Substrates



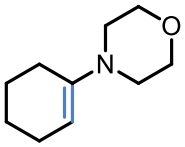
Nitrogen-containing (E)-cinnamyl alcohols

R = NO_2, no reaction
R = NMe_2, no reaction



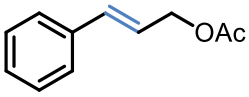
, -Unsaturated amide

no reaction



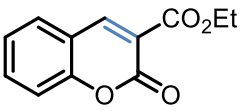
Enamine

decomposition



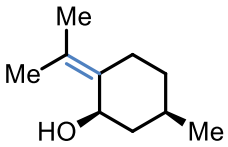
(E)-Cinnamyl acetate

no reaction



Coumarin carboxylate

4 %



Tetrasubstituted alkenol

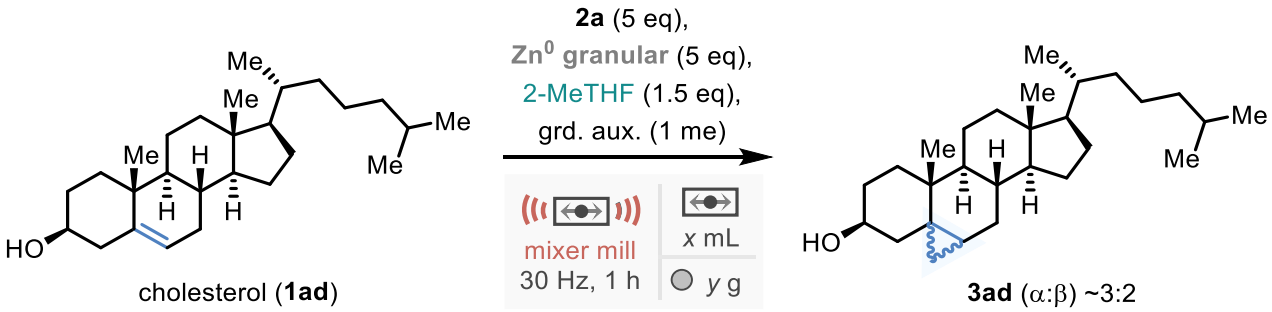
decomposition

7. Further Studies

7.1. Cholesterol cyclopropanation optimization

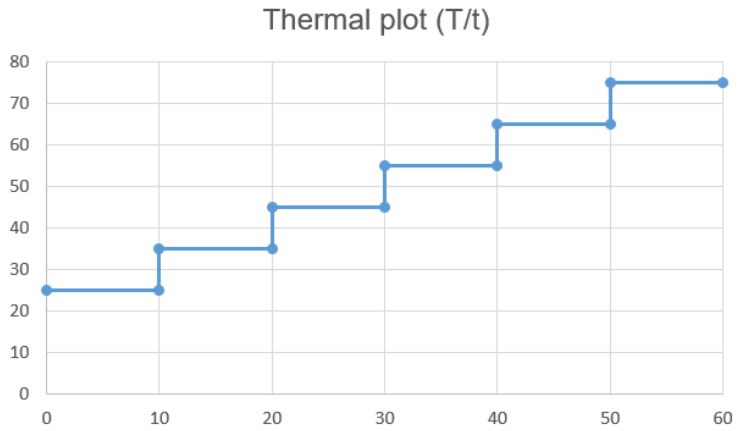
General procedure:

In a stainless jar charged with one stainless steel ball, cholesterol (387 mg, 1.00 mmol), zinc metal (327 mg, 5.00 mmol, 5.00 eq), grinding auxiliary (grd. aux.), 2-MeTHF (151 µL, 1.50 mmol, 1.50 eq) and diiodomethane (403 µL, 5.00 mmol, 5.00 eq) were added and milled at 30 Hz for 1 h in a Retsch mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was vacuum filtered and transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure in presence of 1.00 mL of 0.33 M solution of 1,3,5-trimethoxybenzene in toluene to give the crude product that was analysed by ^1H NMR.



Entry	Jar volume (mL)	Ball size (g)	Temperature (°C)	Grd. aux.	% 1ad	% 3ad
1	15	4	rt	none	82	0
2	15	4	75	none	38	38
3	15	9	75	none	42	20
4	30	9	75	NaCl	36	46
5	30	9	75	sand	16	51
6	30	9	55	sand	57	35
7	30	9	65	sand	28	47
8	30	9	85	sand	17	36
9	30	9	85[a]	sand	82	0
10	30	9	75	celite	72	0
11	30	9	75	silica	74	2
12	30	9	75[b]	sand	37	34

Table 8. Optimization of cholesterol cyclopropanation. Yields were calculated by ^1H NMR in presence of 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard.[a]: DMSO was used instead of 2-MeTHF.



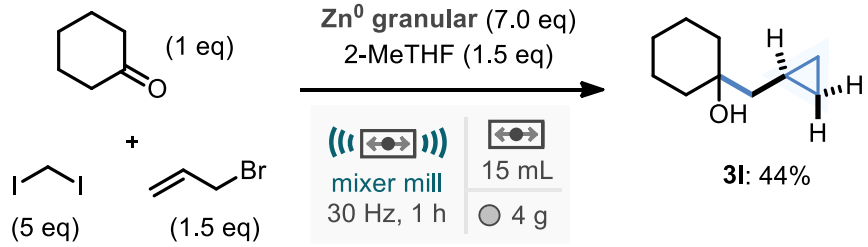
[b]: Thermal plot of **Entry 12**, **Table 8**.

Extending the reaction period of the optimized conditions (**Entry 5**, **Table 8**) proved to be inefficient in terms of conversion as the crude mixture clumped around the ball thus preventing the milling.

Reaction appearance before work-up.

: By running the reaction in a round bottom flask in a 0.25 M refluxing solution in 2-MeTHF (see **Entry 1**, **Table 8**, for conditions) for 1 hour, 97% of the starting material was recovered. This result was consistent with literature precedents.[30]

7.2. Tandem/one-pot organozinc reactions via ball milling

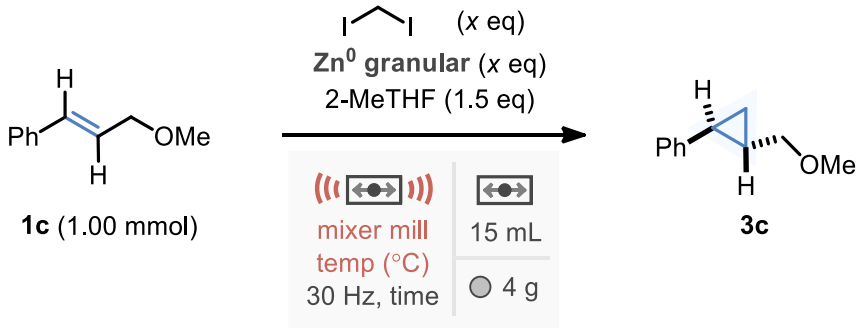


To a 15 mL stainless jar charged with one 4 g stainless steel ball, cyclohexanone (103 µL, 1.00 mmol), zinc metal (458 mg, 7.00 mmol, 7.00 eq), 2-MeTHF (151 µL, 1.50 mmol, 1.50 eq), allyl bromide (130 µL, 1.50 mmol, 1.50 eq) and diiodomethane (403 µL, 5.00 mmol, 5.00 eq) were added and milled at 30 Hz for 3 h at room temperature in an Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product that was further purified by silica gel flash column chromatography (Eluent: EtOAc/Hexane, 25 %) as a colourless oil in 44 % yield. NMR data were consistent with those previously reported for **3l**.

7.3. Scale-up of the mechanochemical Simmons-Smith reaction

Optimization of the reaction on 1c (1.00 mmol scale):

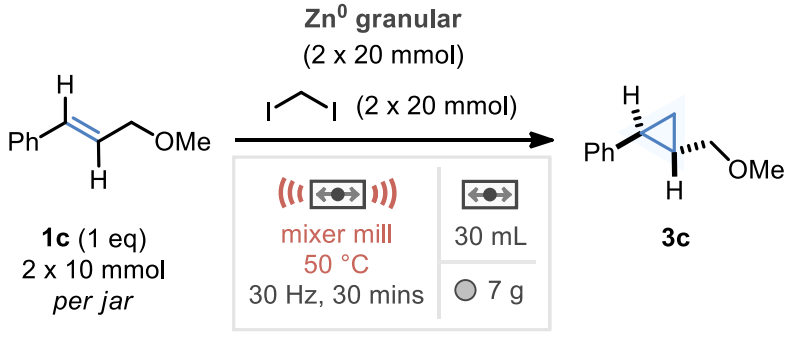
To a 15 mL stainless jar charged with one 4 g stainless steel ball, **1c** (1.00 mmol), zinc metal (*x* eq), 2-MeTHF (151 µL, 1.50 mmol, 1.50 eq) and diiodomethane (*x* eq) were added and milled at 30 Hz for 1 h at room temperature in a Retsch/Insolido Tech mixer mill. After the milling period the jar was opened and rinsed from the jar into a conical flask using CH_2Cl_2 (20.00 mL). 1.0 M HCl (10.00 mL) was added to the flask and stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 15.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure in presence of 1.00 mL of 0.33 M solution of 1,3,5-trimethoxybenzene in toluene to give the crude product that was analysed by ^{1}H NMR.



Entry	SSReag eq (*x*)	Time (minutes)	Temperature (°C)	% 1c	% 3c
1	5.0	60	rt	0	85[a]
2	2.5	60	rt	0	75
3	1.5	60	rt	76	0
4	2.0	60	rt	43	32
5	2.0	60	50	0	72
6	1.5	60	50	7	46
7	2.0	30	50	0	75
8	2.0	15	50	5	73
9	2.0	20	50	0	80
10	Like **Entry 9** but without 2-MeTHF			0	79

Table 9. Optimization of **1c** cyclopropanation on 1.00 mmol scale. Yields were calculated by ^{1}H NMR in presence of 0.33 mmol of 1,3,5-trimethoxybenzene as an internal standard.[a]: isolated yield.

Scale-up (2 x 10.00 mmol scale):



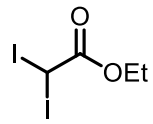
In two 30 mL stainless steel jars charged with one 7 g stainless steel ball, **1c** (1.48 g, 10.00 mmol), zinc metal (1.31 g, 20.00 mmol, 2.00 eq) and diiodomethane (1.61 mL, 20.00 mmol, 2.00 eq) were added in each jar and milled at 30 Hz for 20 minutes at 50°C in a Retsch mixer mill. After the milling period the jars were opened and rinsed from the jars into a single conical flask using EtOAc (80.00 mL). 1.0 M HCl (60.00 mL) was added to the flask and

stirred for 10 minutes. The resulting biphasic mixture was transferred to a separating funnel where the layers were separated. The aqueous layer was extracted with EtOAc (2 x 40.00 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product that was further purified by silica gel flash column chromatography (Eluent: EtOAc/Hexane, 10 %) as a colourless oil in 75 % yield. NMR data were consistent with those previously reported for **3c**.

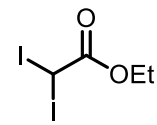
Appearance of the reaction mixture after milling.

8. NMR Spectra

Ethyl 2,2-diiodoacetate (2f)

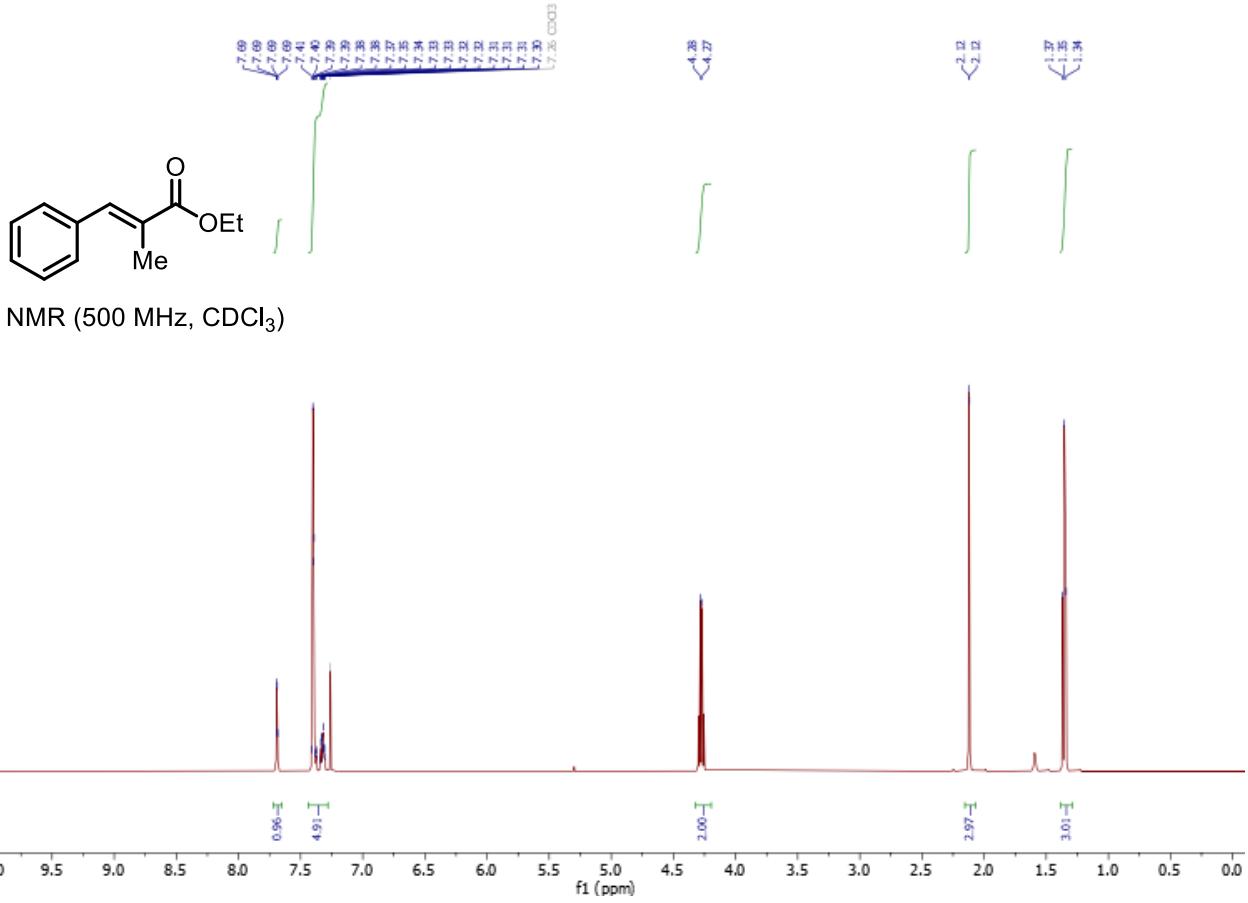


^{1}H NMR (500 MHz, $CDCl_3$)

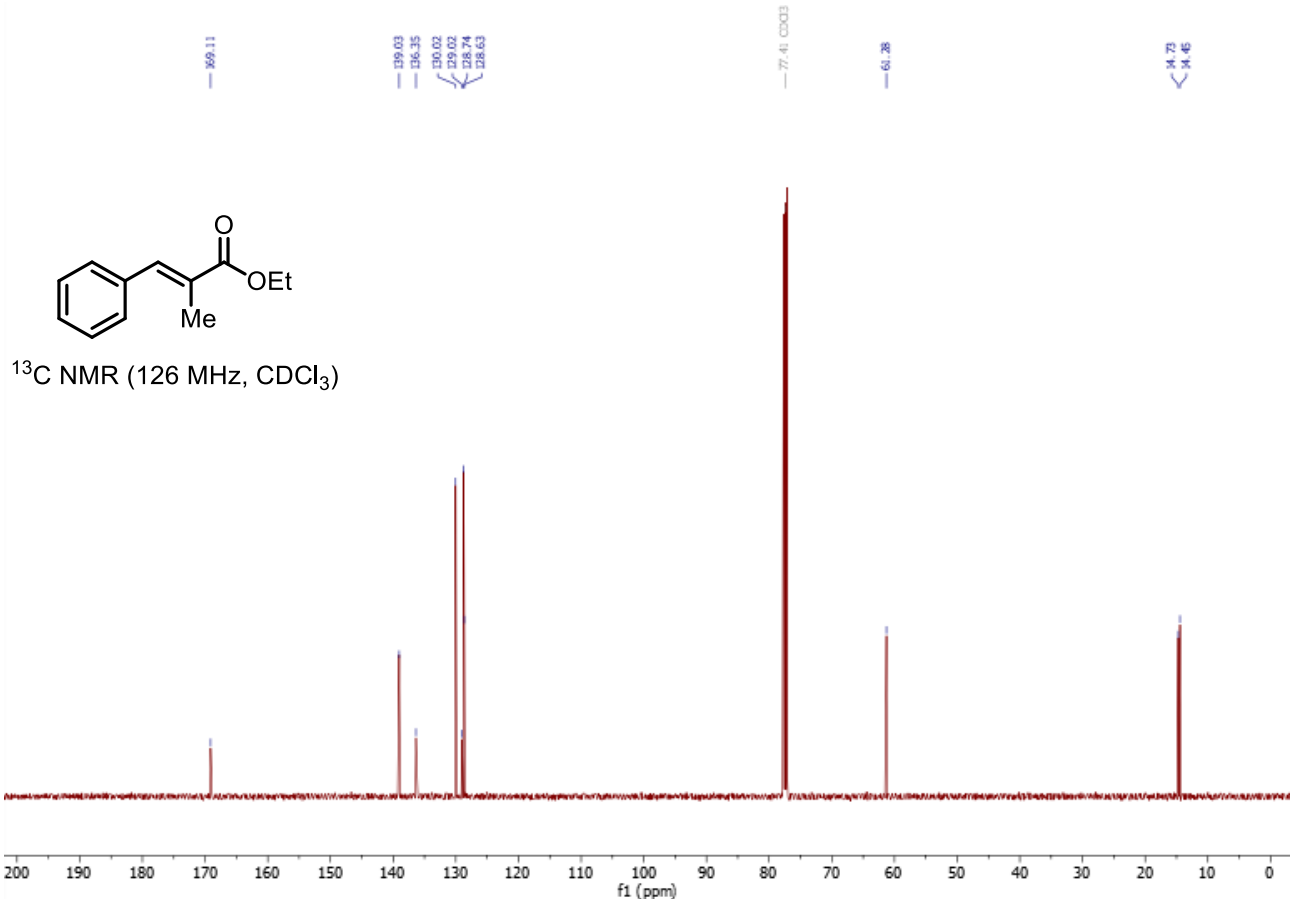


^{13}C NMR (126 MHz, $CDCl_3$)

(*E*)-Ethyl 2-methyl-3-phenylacrylate

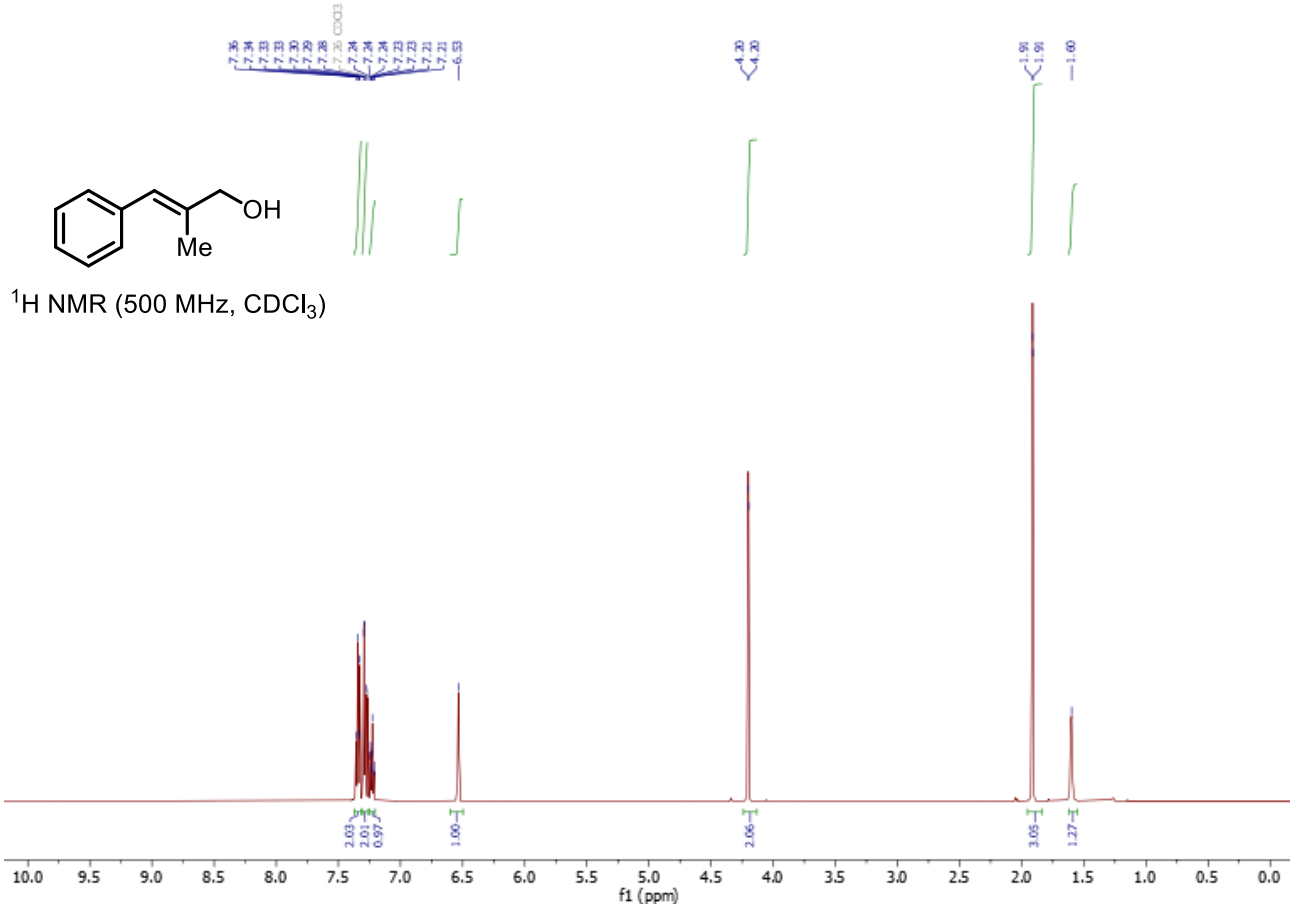


^{1}H NMR (500 MHz, $CDCl_3$)

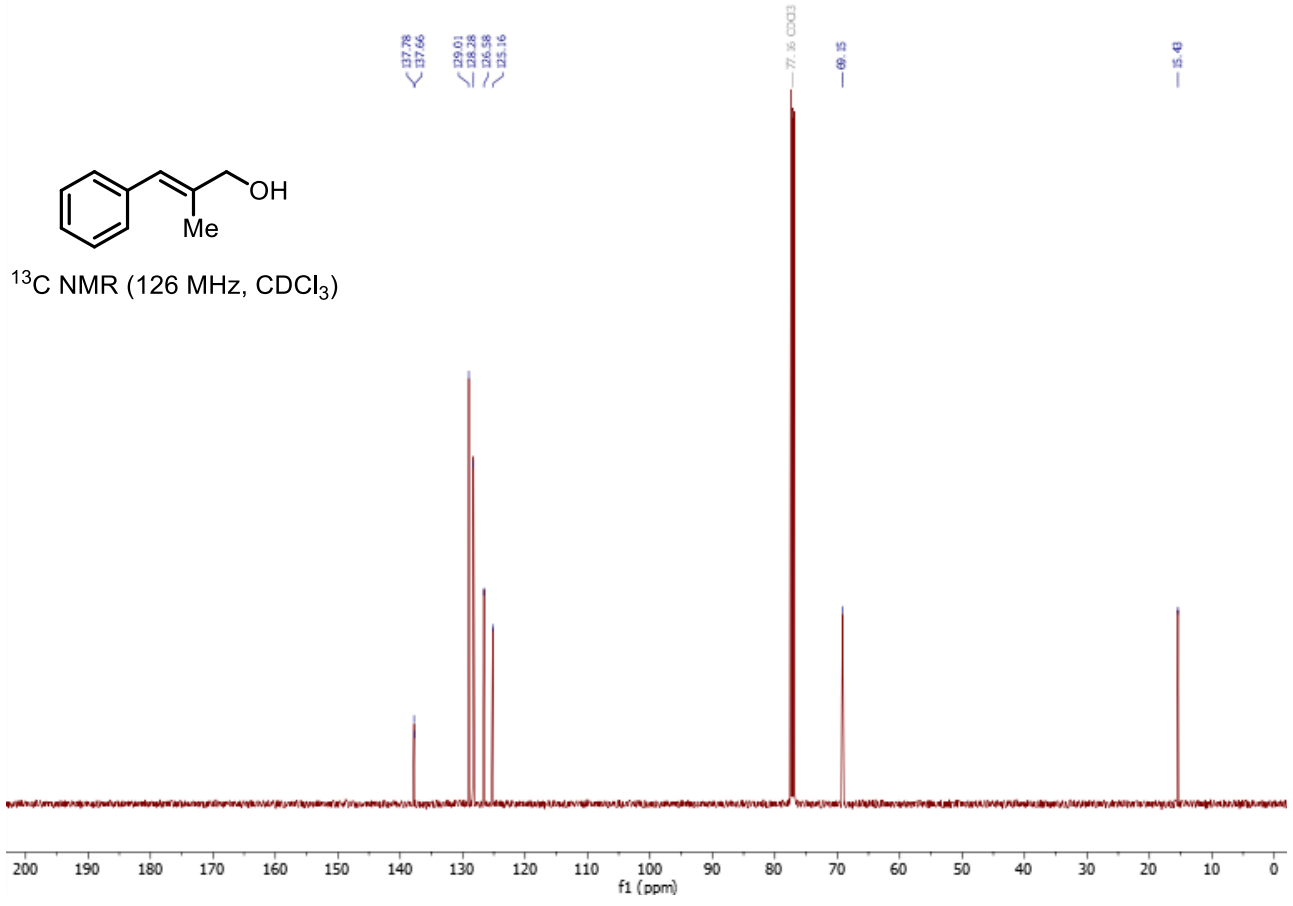


^{13}C NMR (126 MHz, $CDCl_3$)

(*E*)-2-Methyl-3-phenylprop-2-en-1-ol (1b)

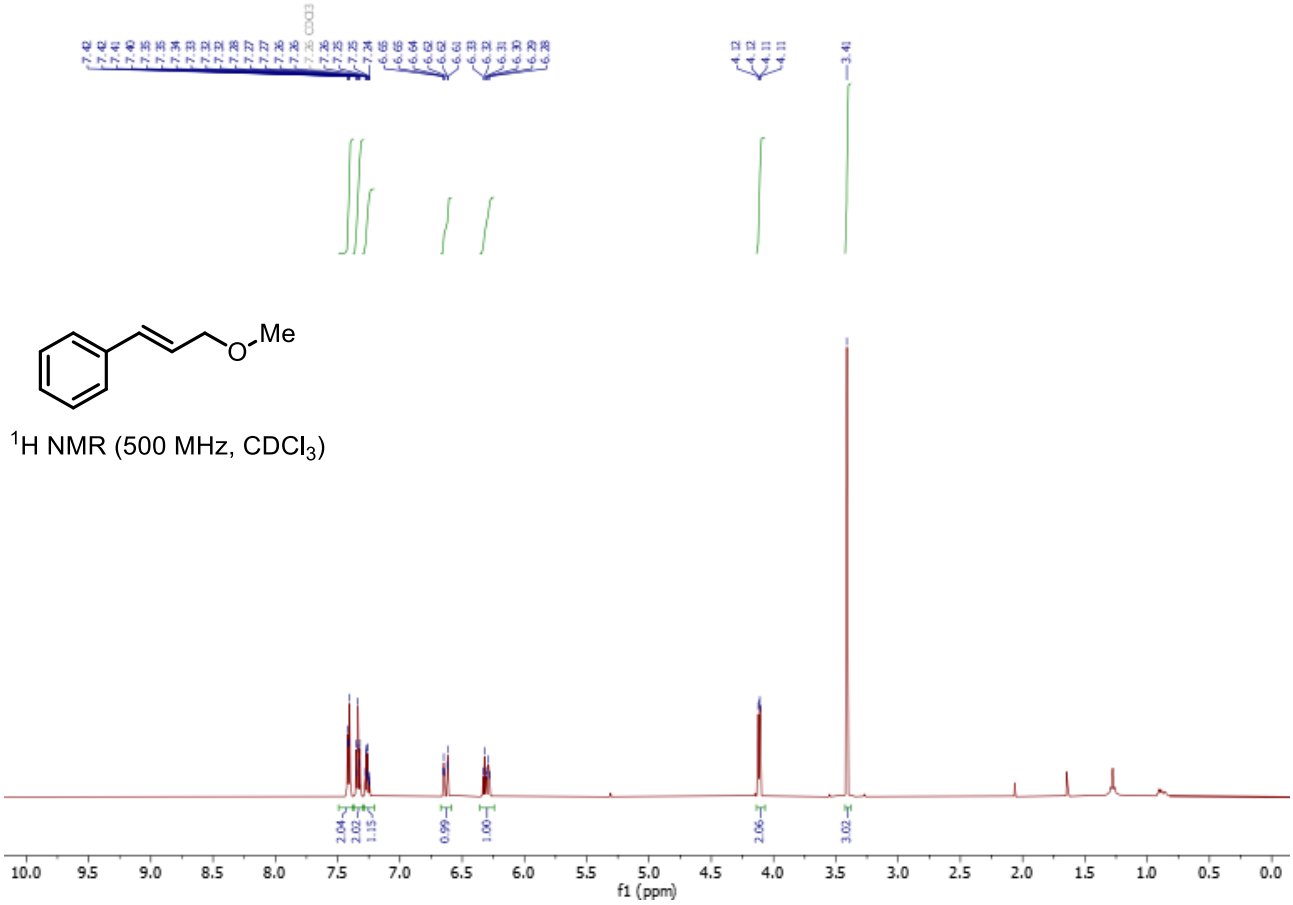


^{1}H NMR (500 MHz, $CDCl_3$)

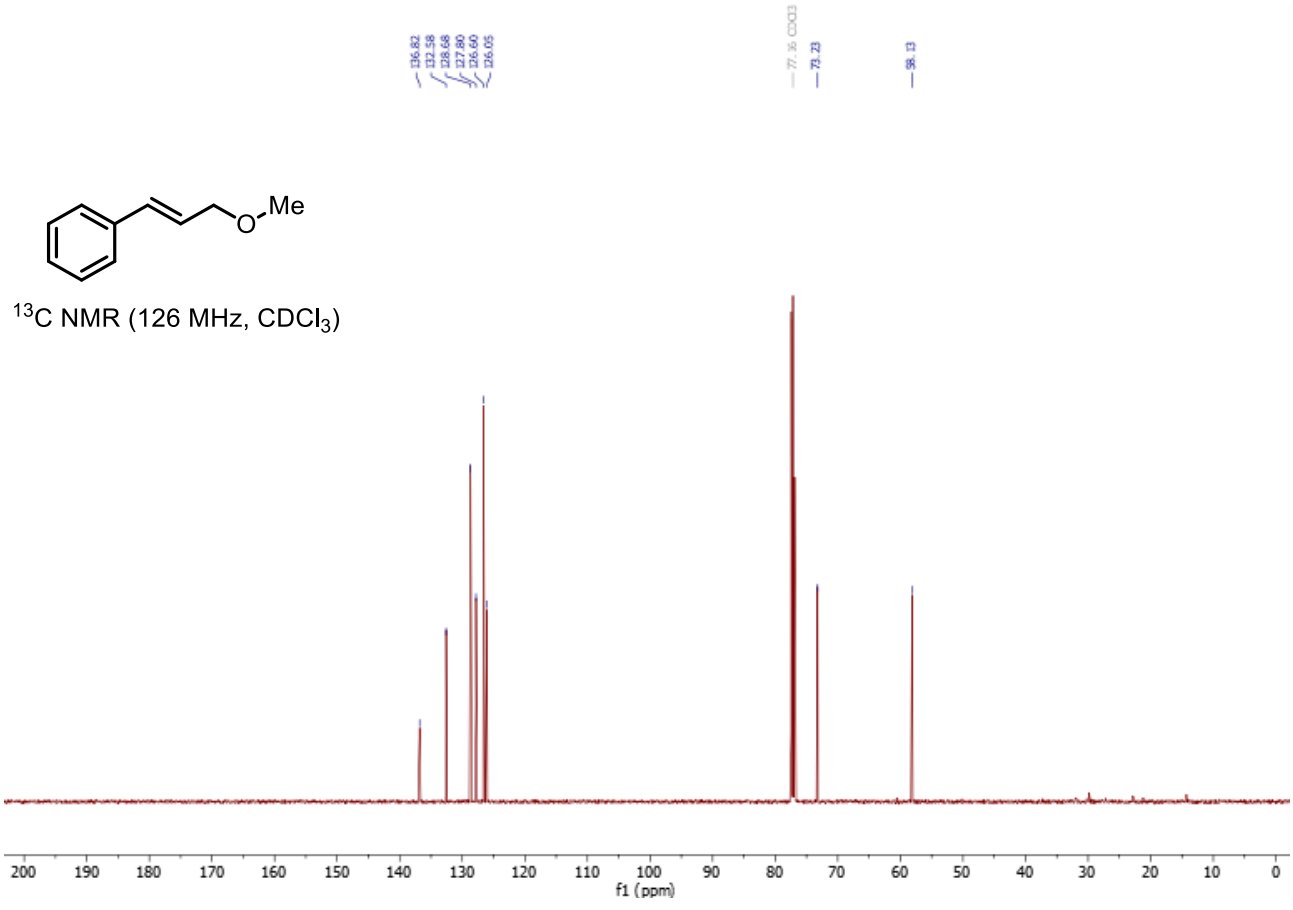


^{13}C NMR (126 MHz, $CDCl_3$)

(*E*)-(3-Methoxyprop-1-en-1-yl)benzene (1c)

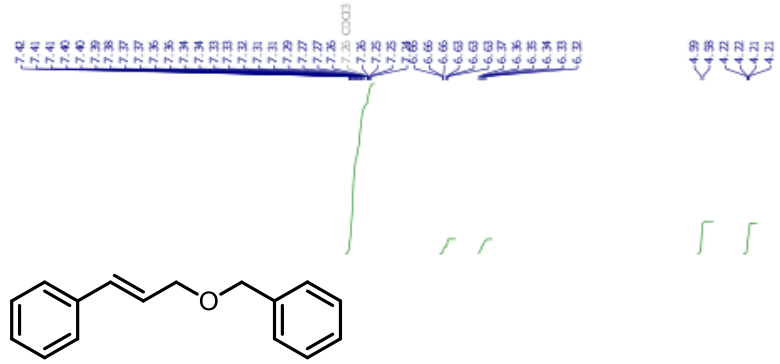


^{1}H NMR (500 MHz, $CDCl_3$)

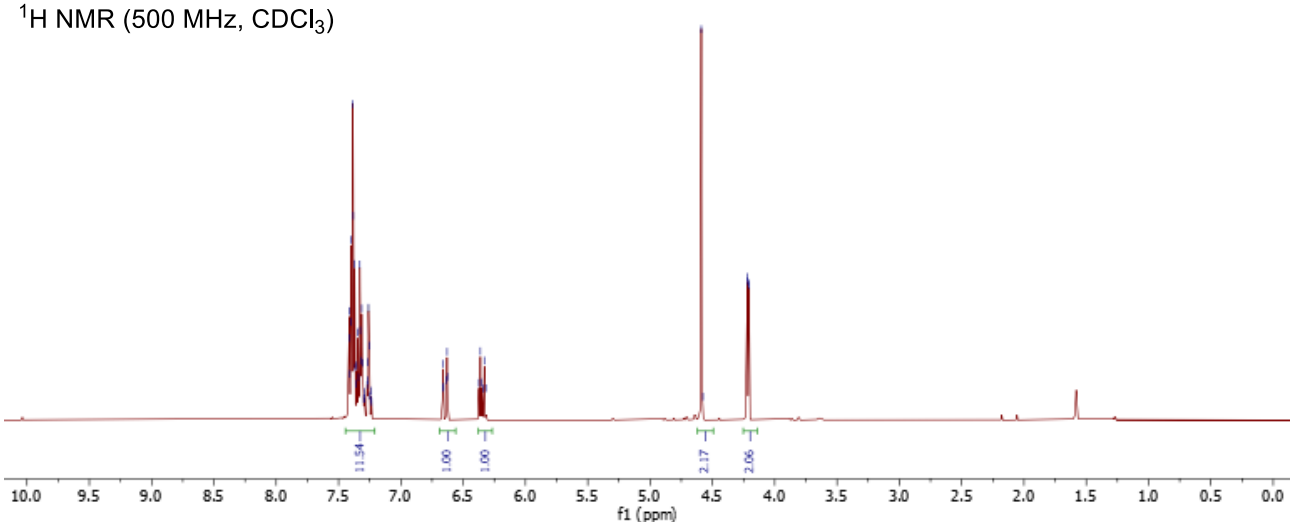


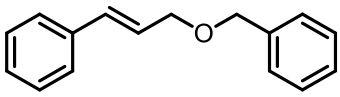
^{13}C NMR (126 MHz, $CDCl_3$)

(*E*)-(3-(Benzyloxy)prop-1-en-1-yl)benzene (1d)



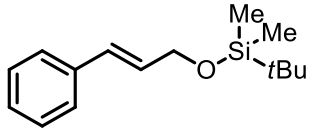
^{1}H NMR (500 MHz, $CDCl_3$)



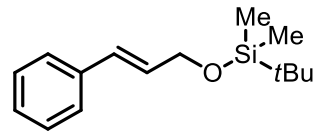


^{13}C NMR (126 MHz, $CDCl_3$)

(*E*)-*tert*-Butyl(cinnamyloxy)dimethylsilane (1e)

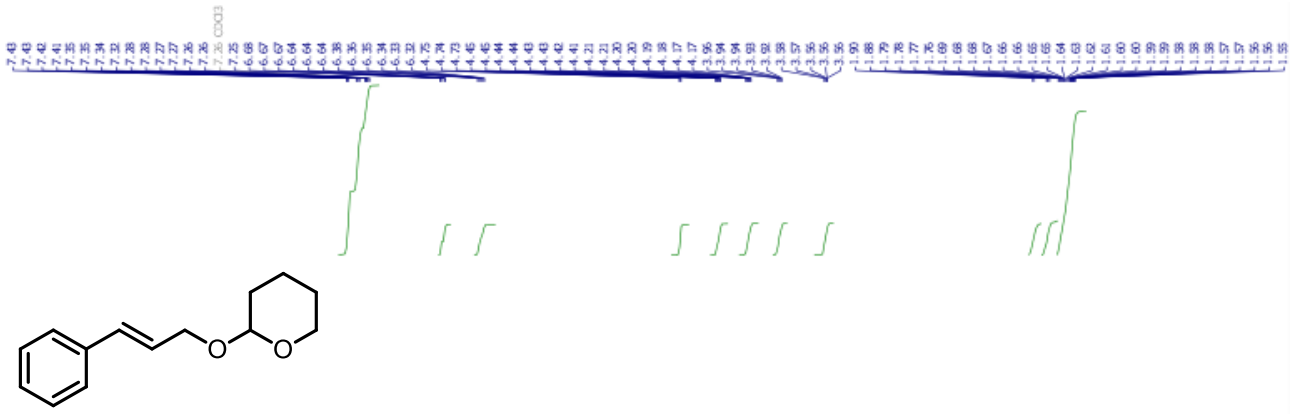


^{1}H NMR (500 MHz, $CDCl_3$)

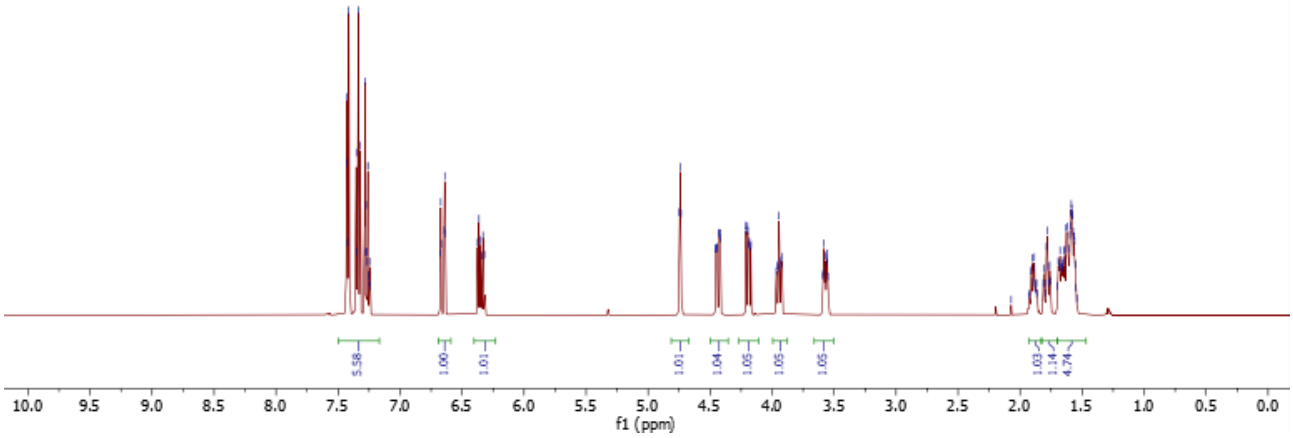


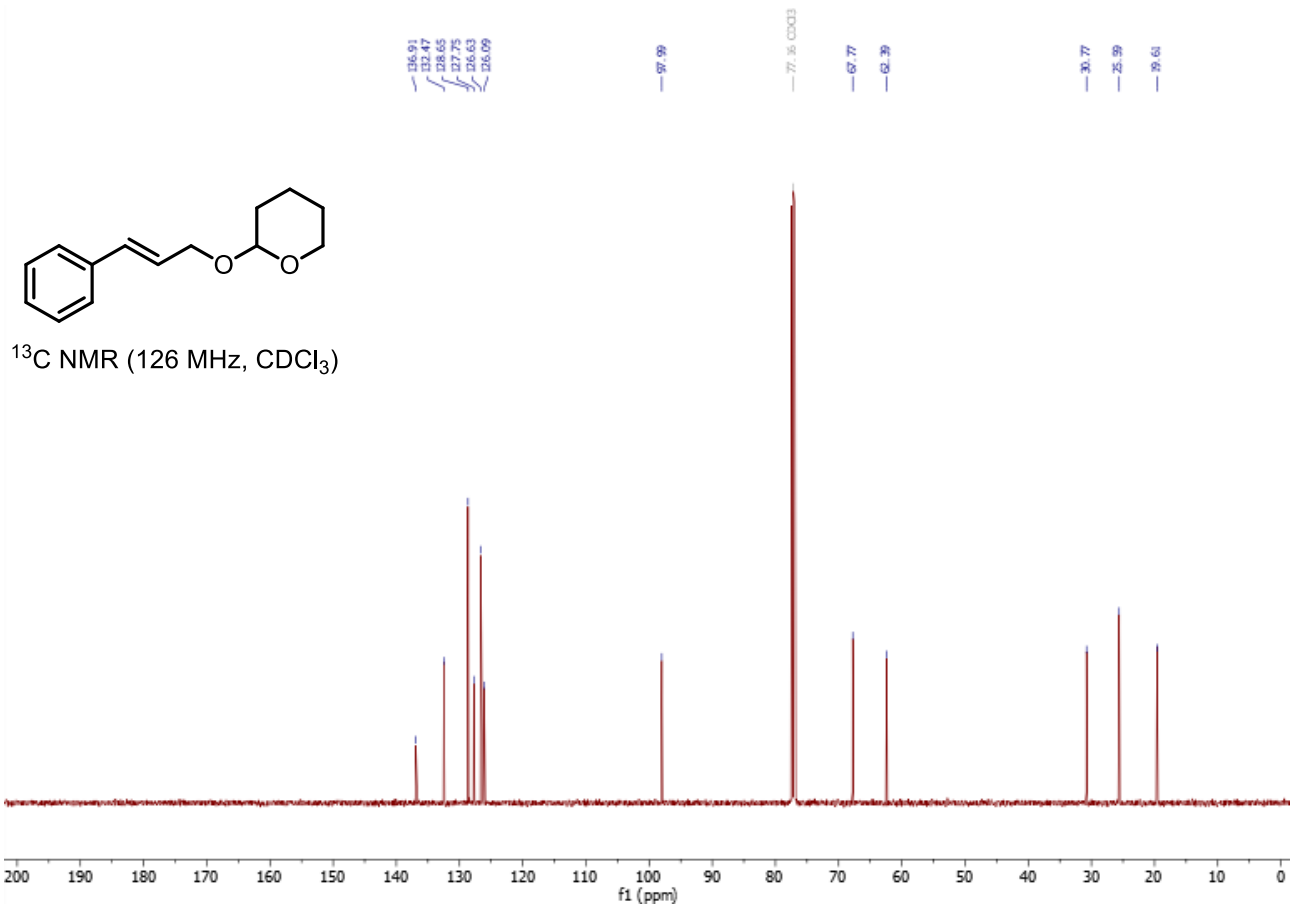
^{13}C NMR (126 MHz, $CDCl_3$)

(±)-(*E*)-2-(Cinnamyloxy)tetrahydro-2*H*-pyran (1f)



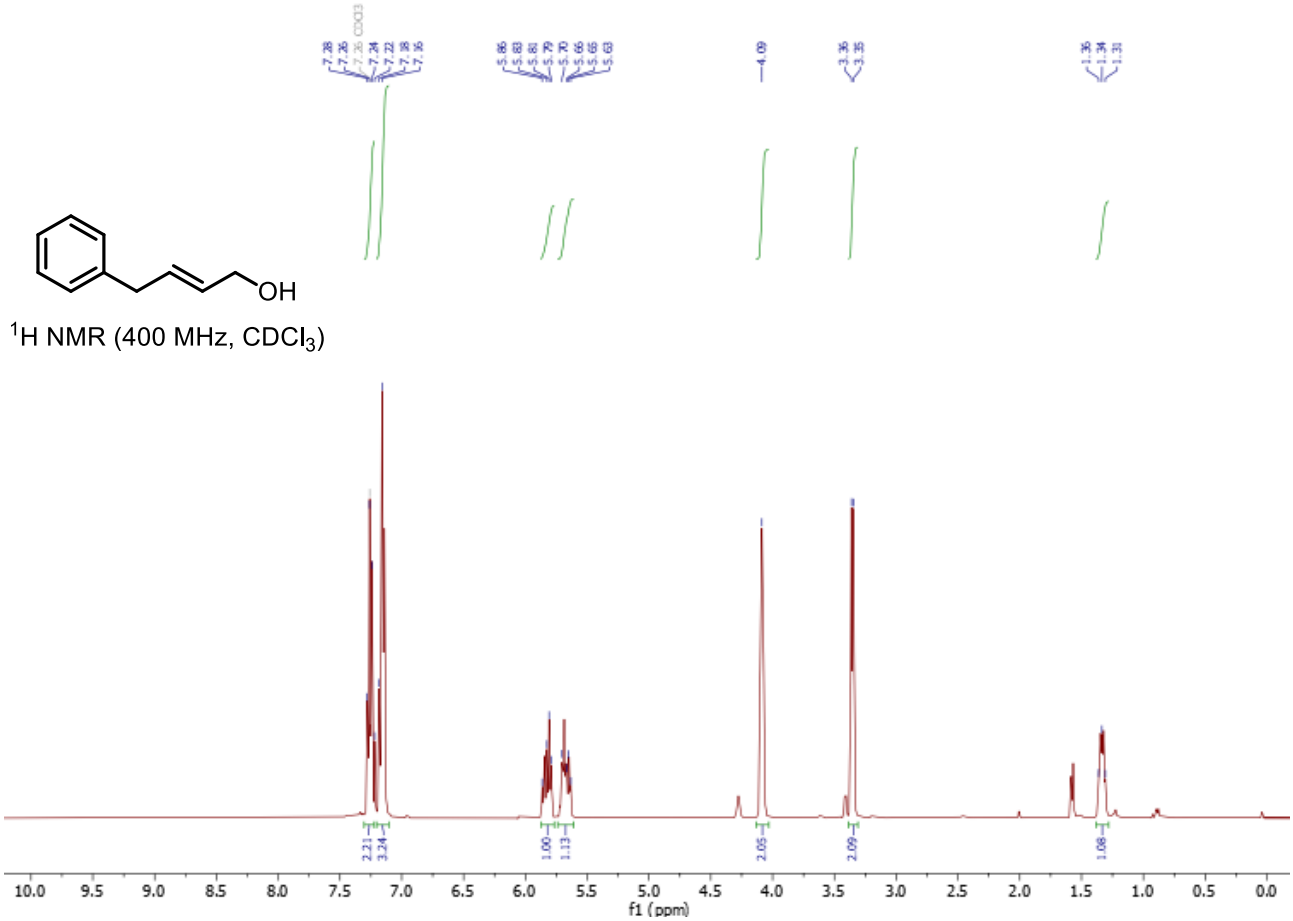
^{1}H NMR (500 MHz, $CDCl_3$)



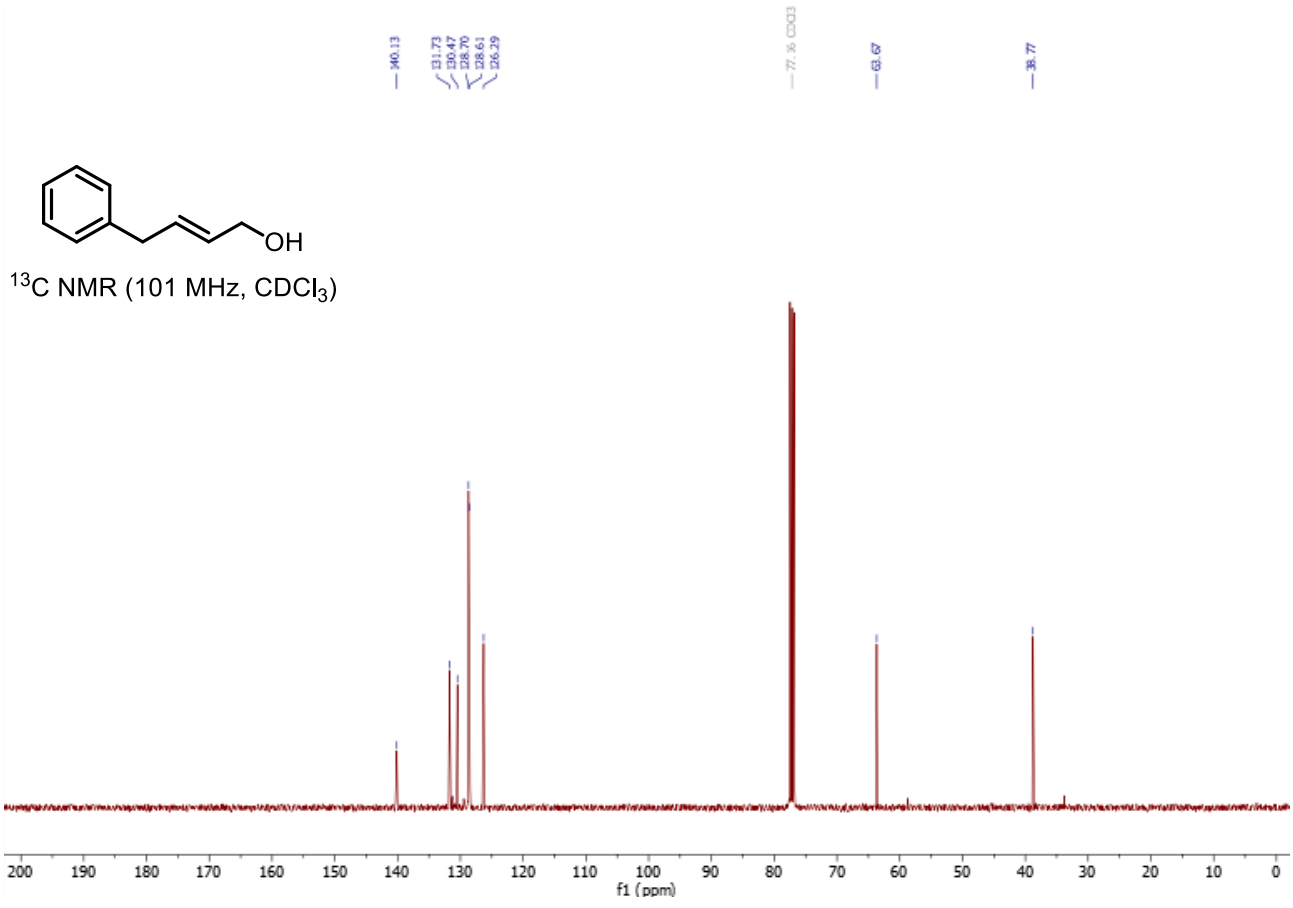


^{13}C NMR (126 MHz, $CDCl_3$)

(*E*)-4-Phenylbut-2-en-1-ol (1g)

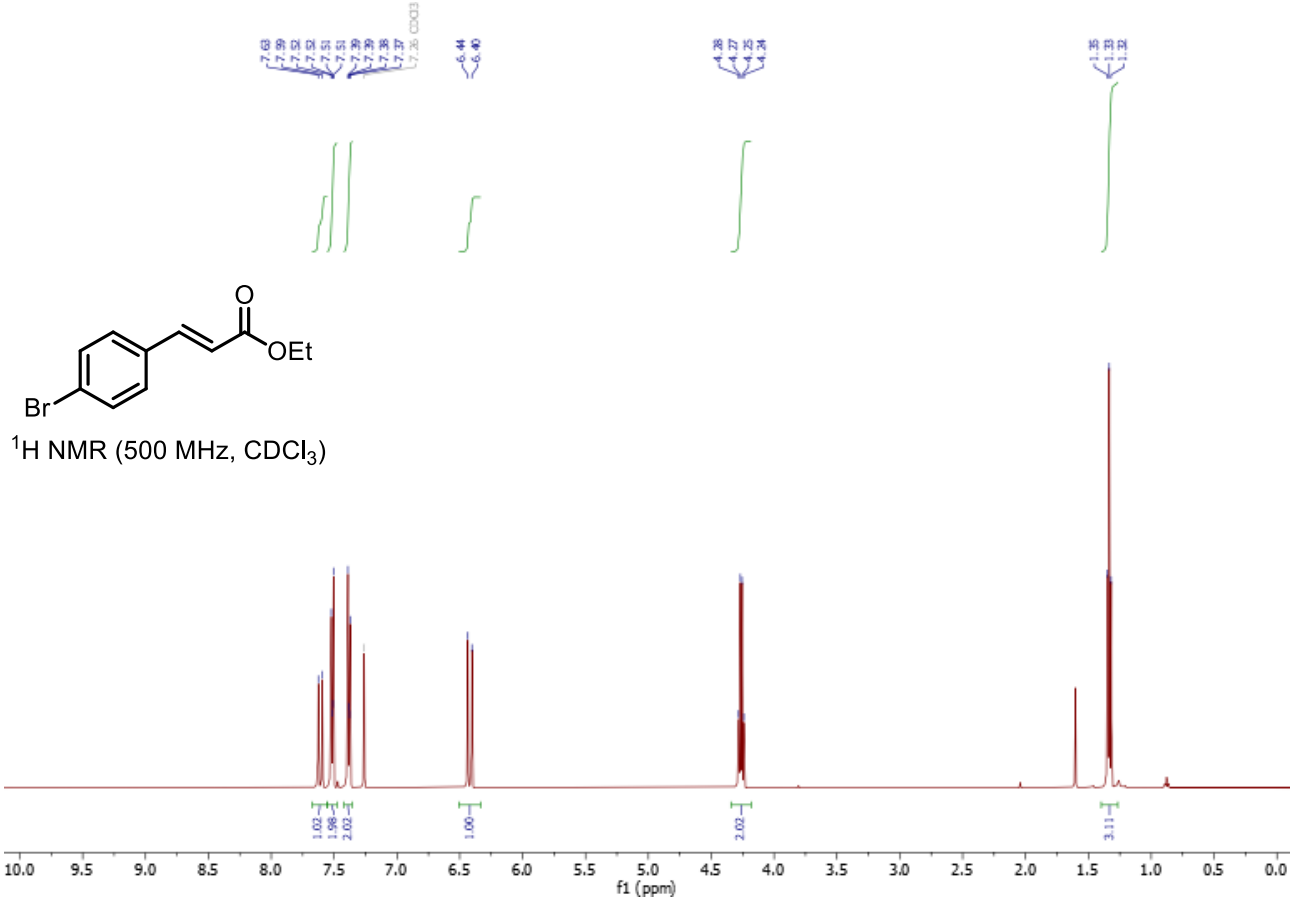


^{1}H NMR (400 MHz, $CDCl_3$)

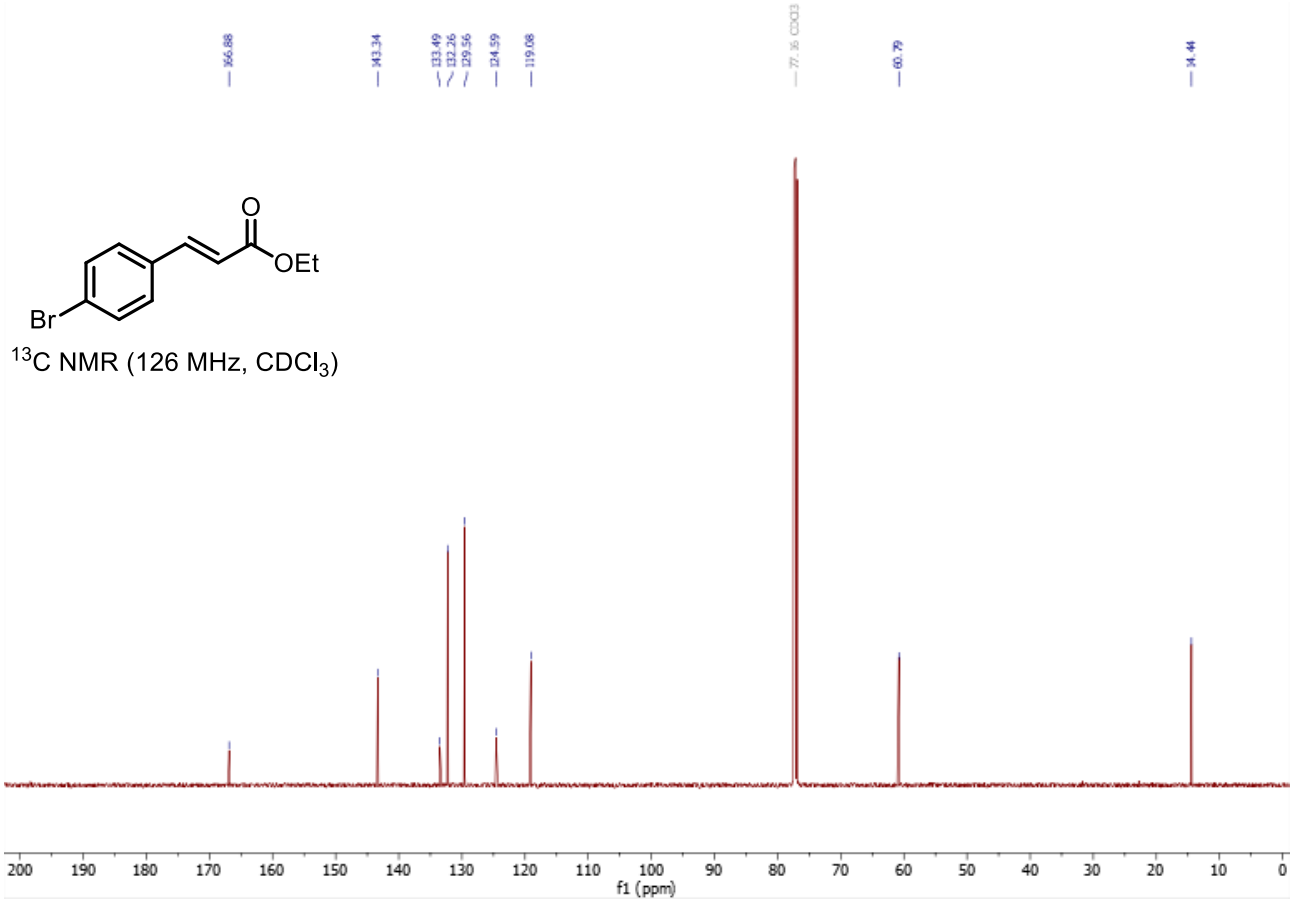


^{13}C NMR (101 MHz, $CDCl_3$)

(*E*)-Ethyl 3-(4-bromophenyl)acrylate

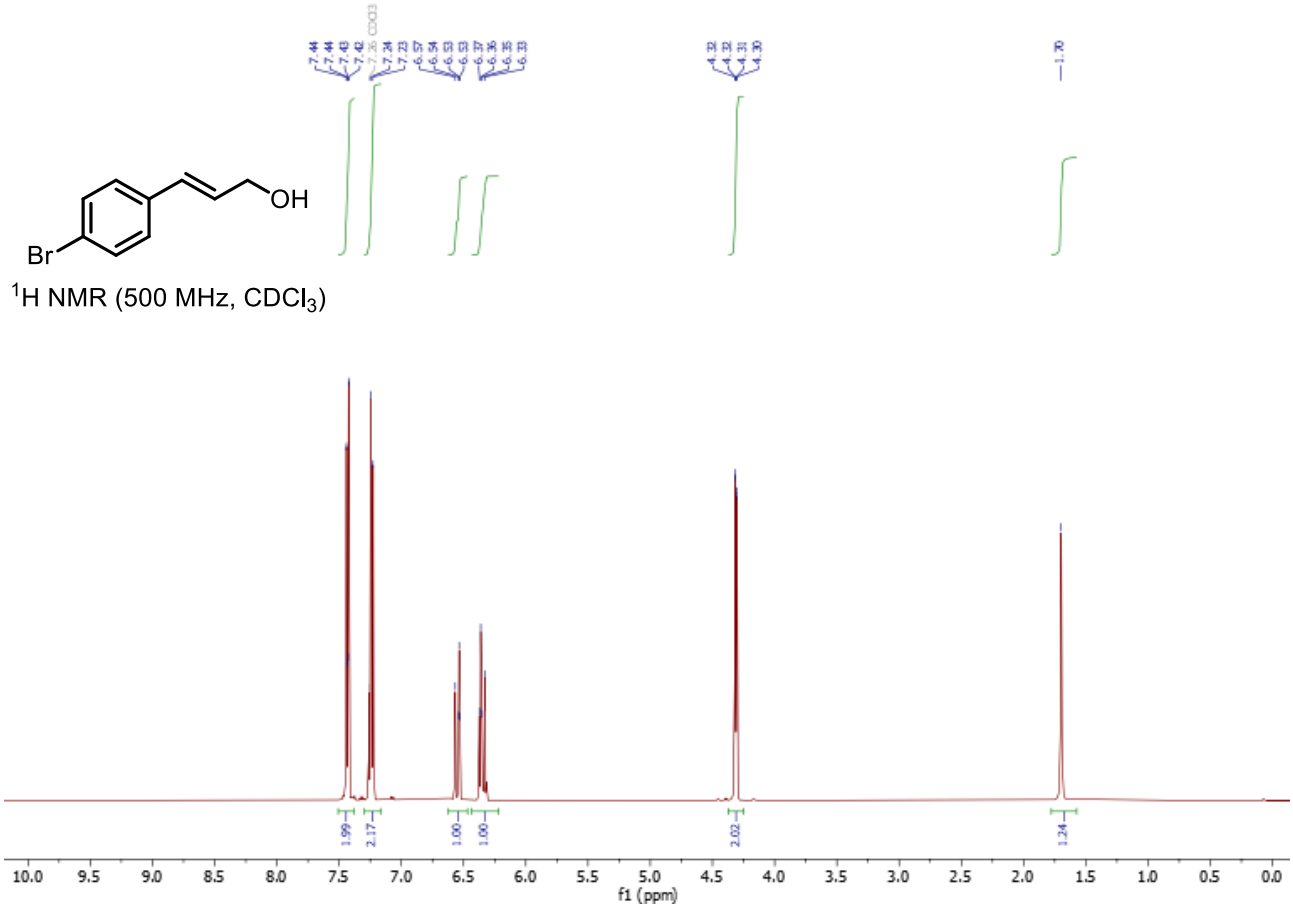


^{1}H NMR (500 MHz, $CDCl_3$)

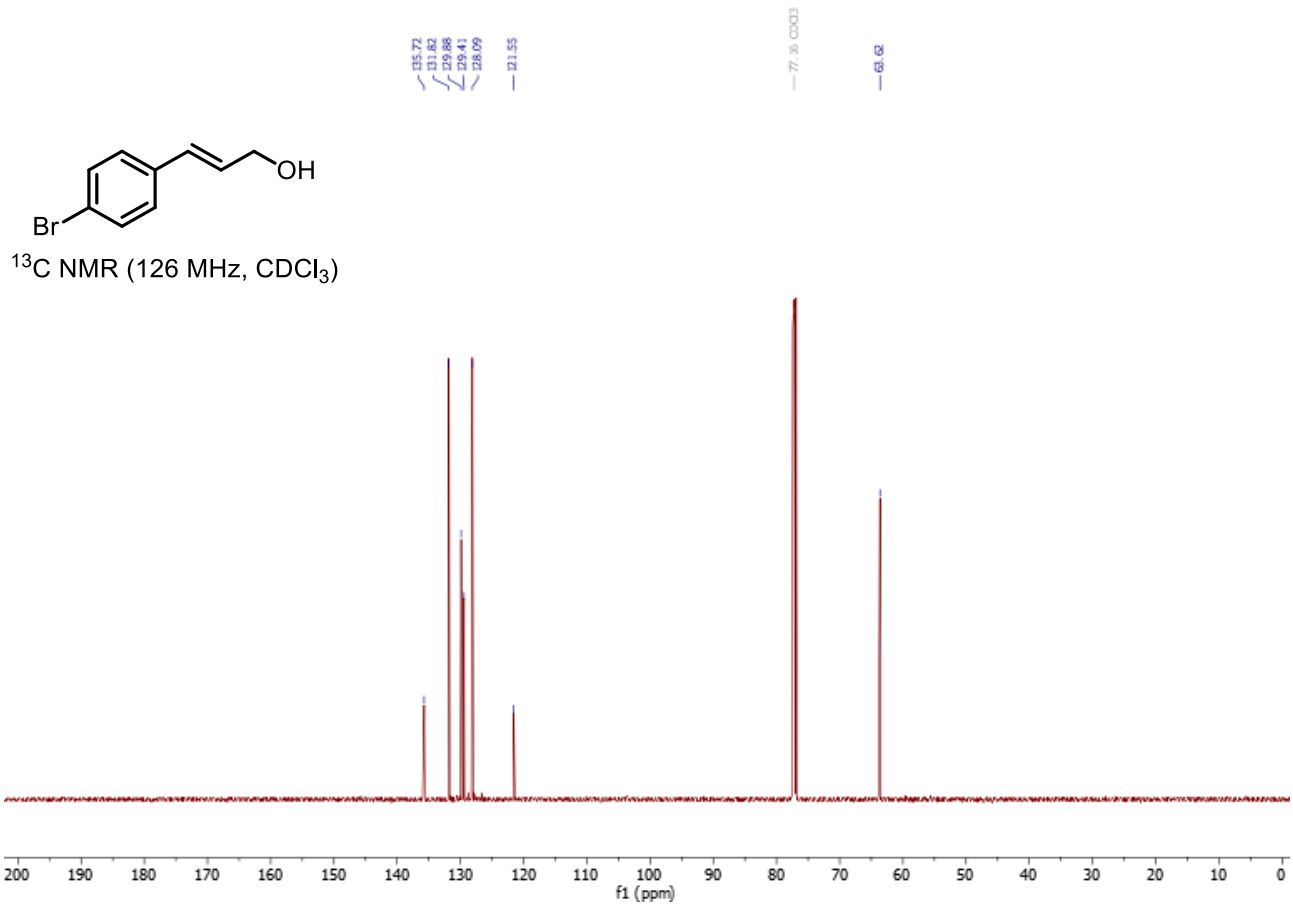


^{13}C NMR (126 MHz, $CDCl_3$)

(*E*)-3-(4-Bromophenyl)prop-2-en-1-ol (1h)



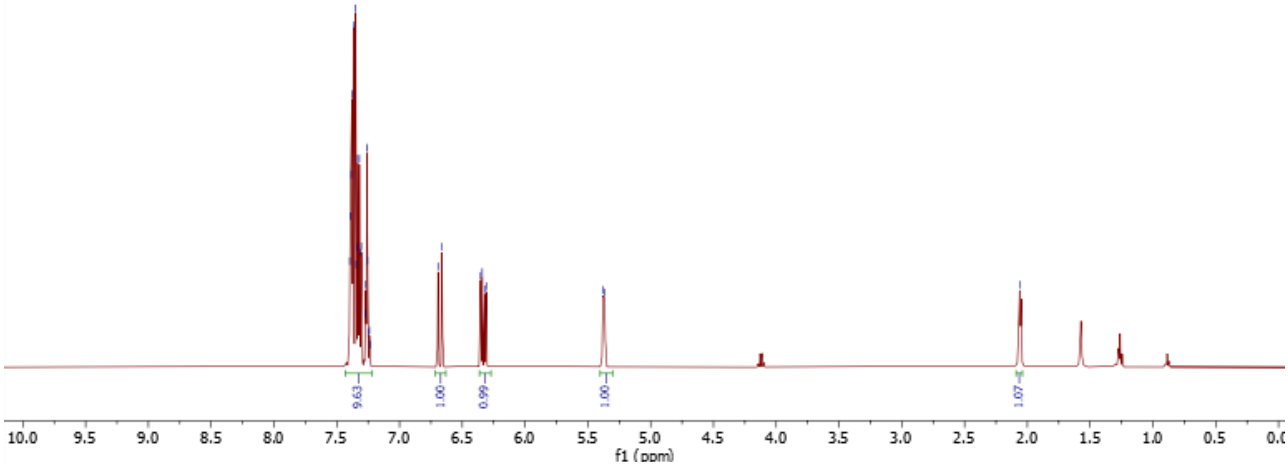
^{1}H NMR (500 MHz, $CDCl_3$)

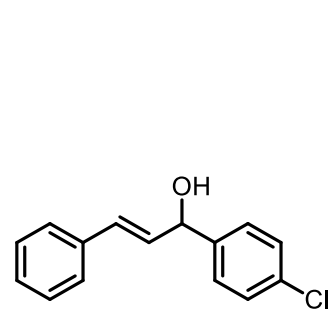


^{13}C NMR (126 MHz, $CDCl_3$)

(±)-(*E*)-1-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol (1i)

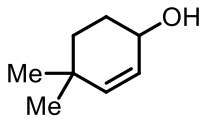
^{1}H NMR (500 MHz, $CDCl_3$)



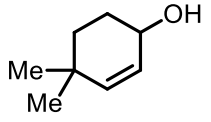


^{13}C NMR (126 MHz, $CDCl_3$)

(±)-4,4-Dimethylcyclohex-2-enol (1j)

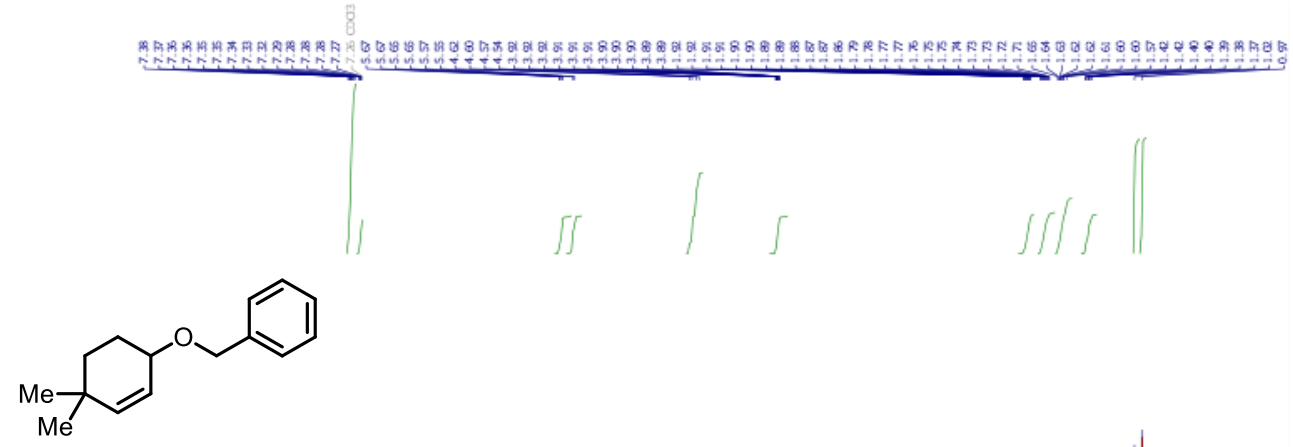


^{1}H NMR (500 MHz, $CDCl_3$)

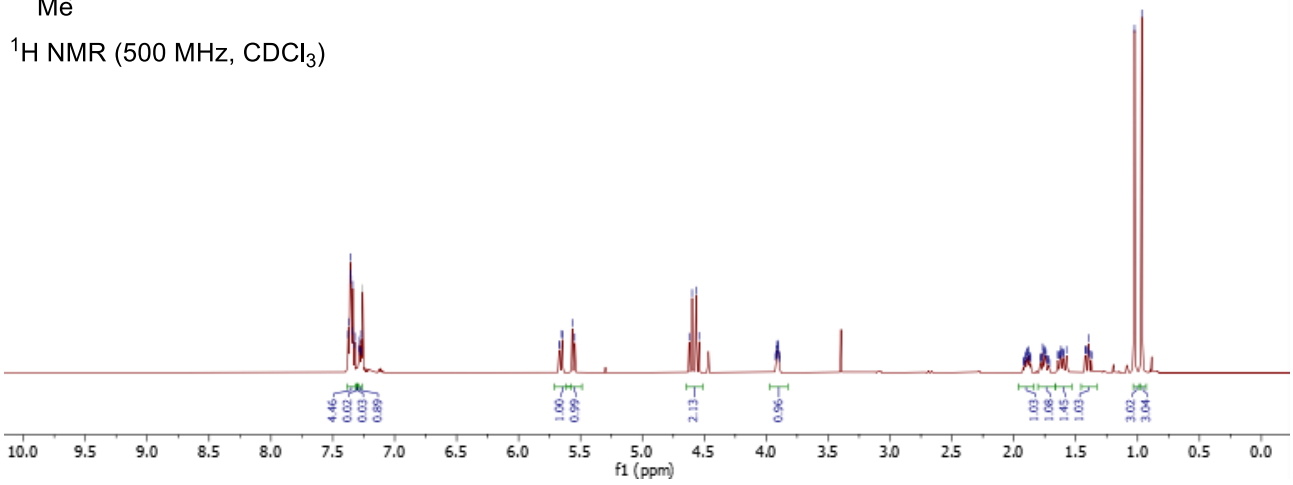


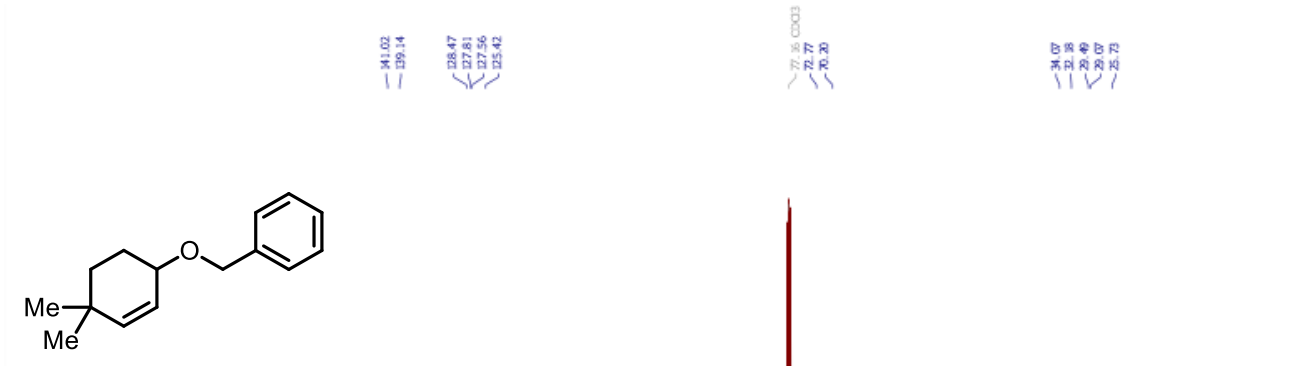
^{13}C NMR (126 MHz, $CDCl_3$)

(±)- (((4,4-Dimethylcyclohex-2-en-1-yl)oxy)methyl)benzene (1k)

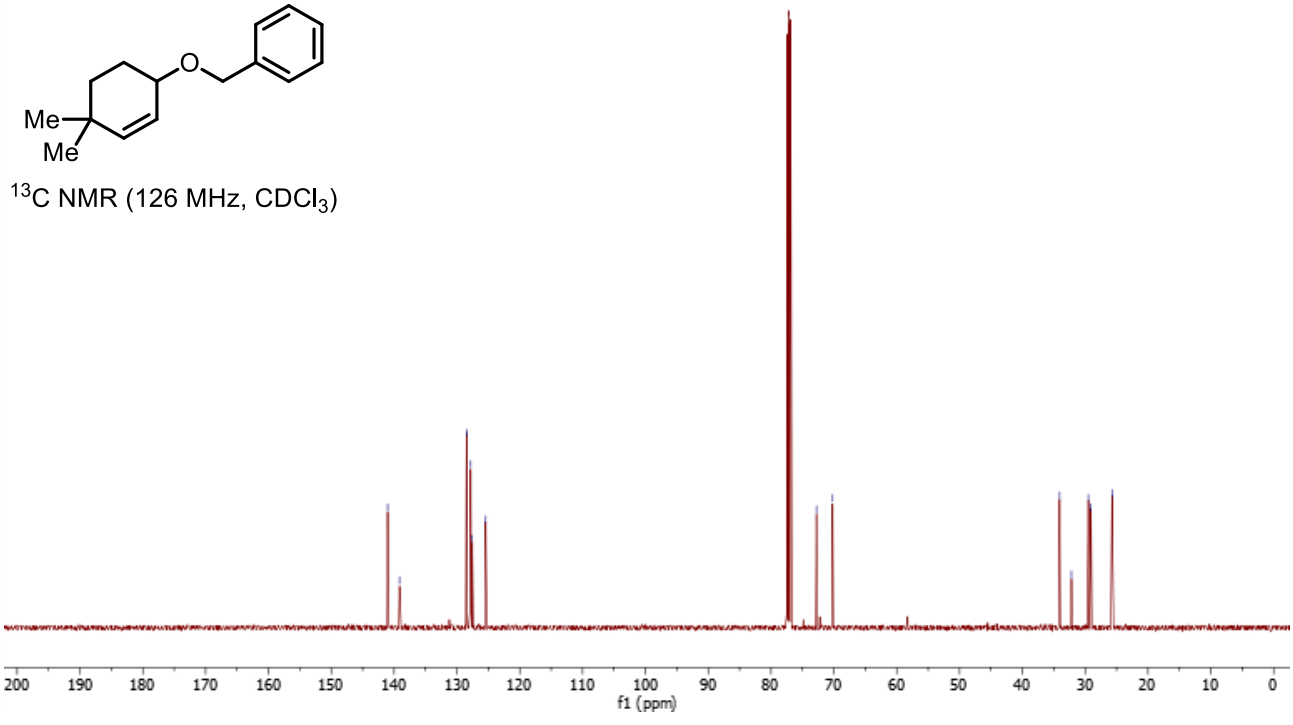


^{1}H NMR (500 MHz, $CDCl_3$)

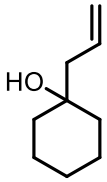




^{13}C NMR (126 MHz, $CDCl_3$)

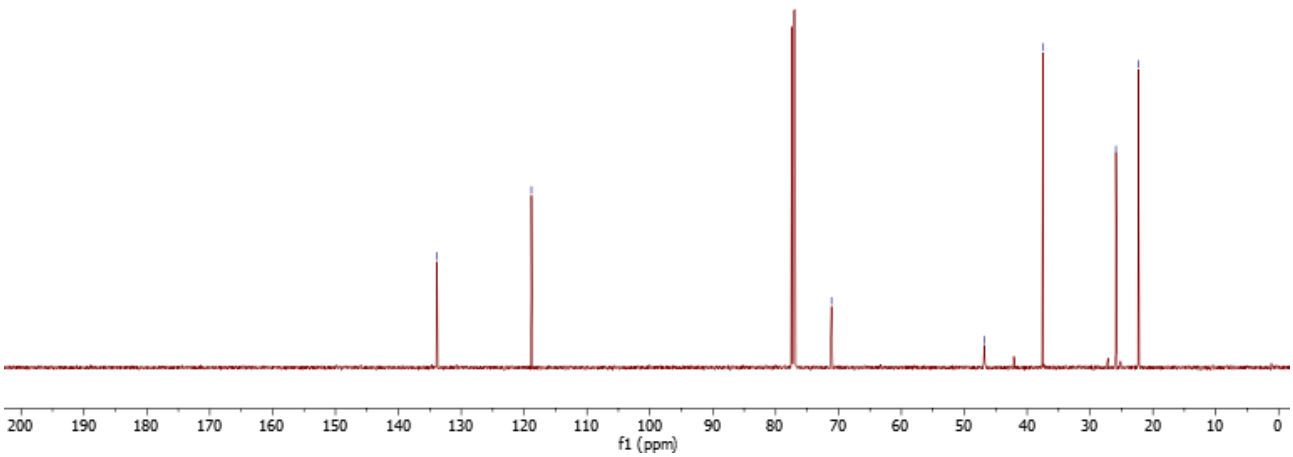


1-Allylcyclohexanol (1l)

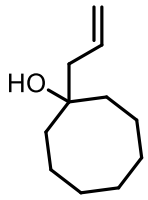


^{1}H NMR (500 MHz, $CDCl_3$)

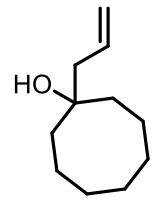
^{13}C NMR (126 MHz, $CDCl_3$)



1-Allylcyclooctanol (1m)

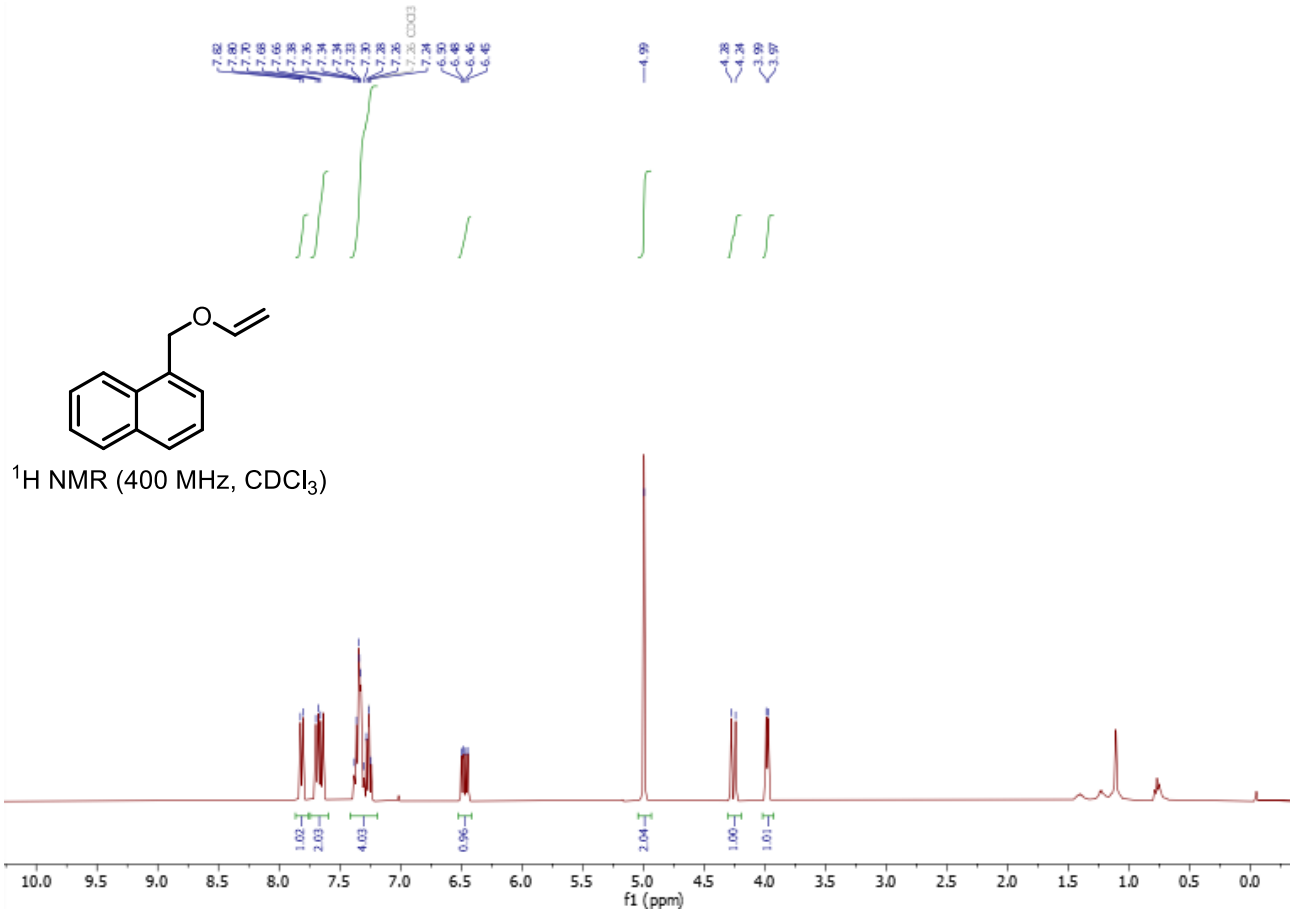


^{1}H NMR (500 MHz, $CDCl_3$)

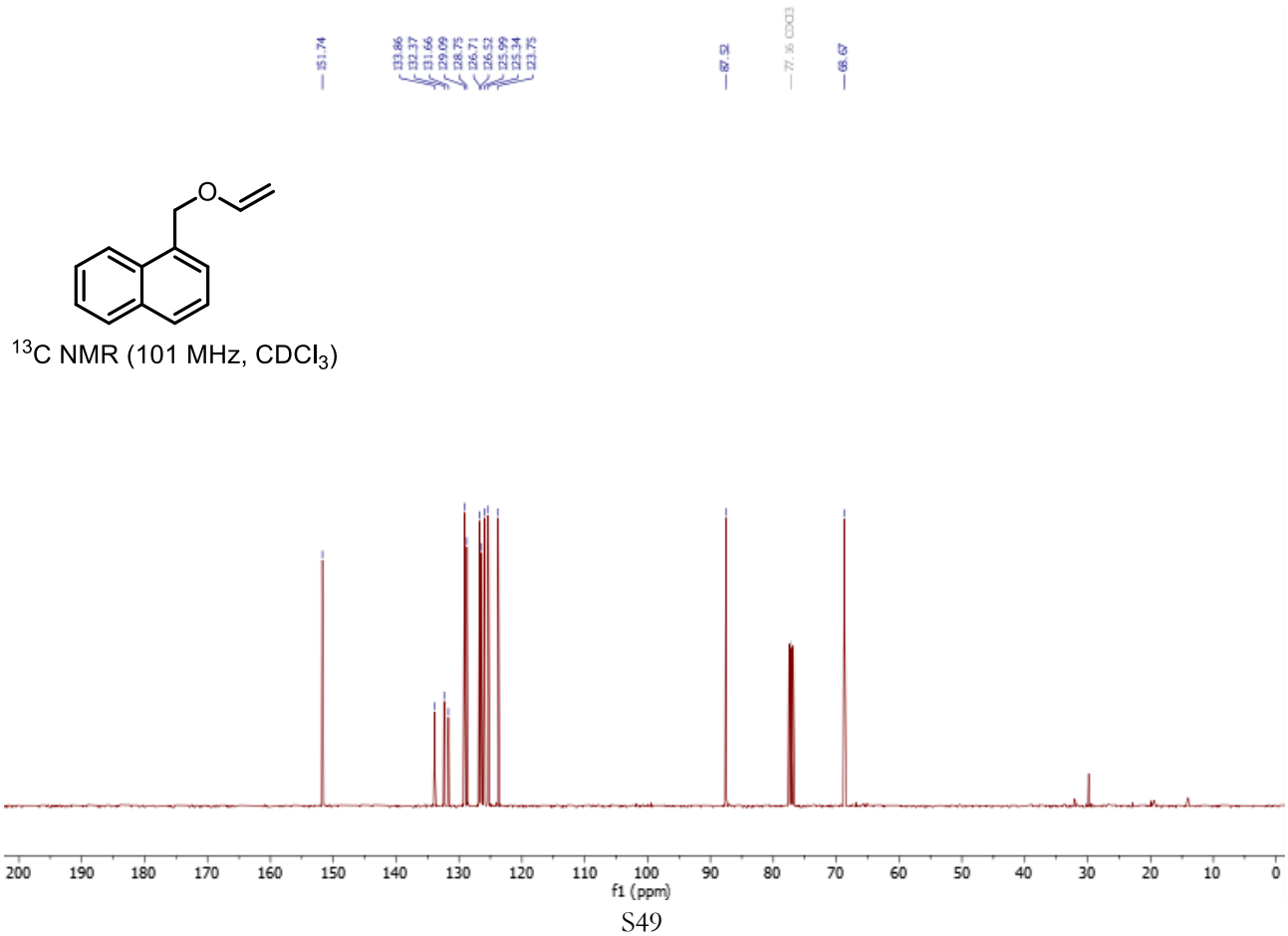


^{13}C NMR (126 MHz, $CDCl_3$)

1-((Vinyloxy)methyl)naphthalene (1t)

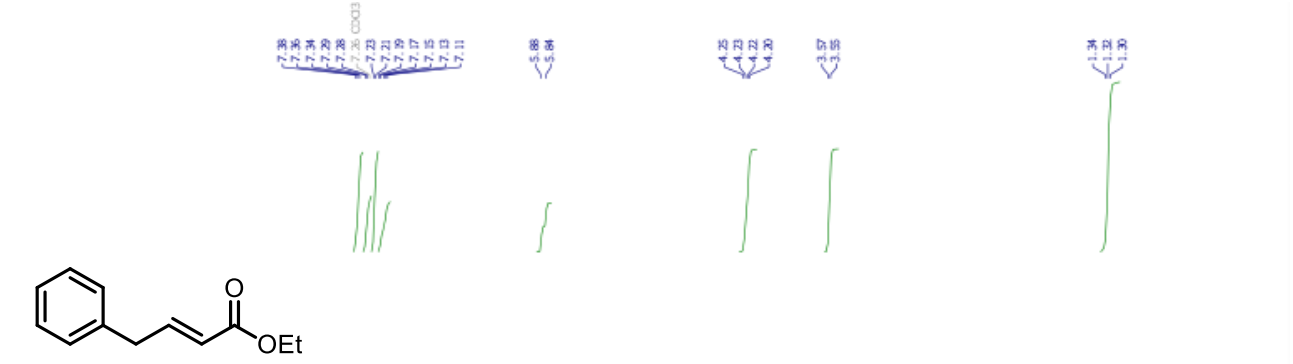


^{1}H NMR (400 MHz, $CDCl_3$)

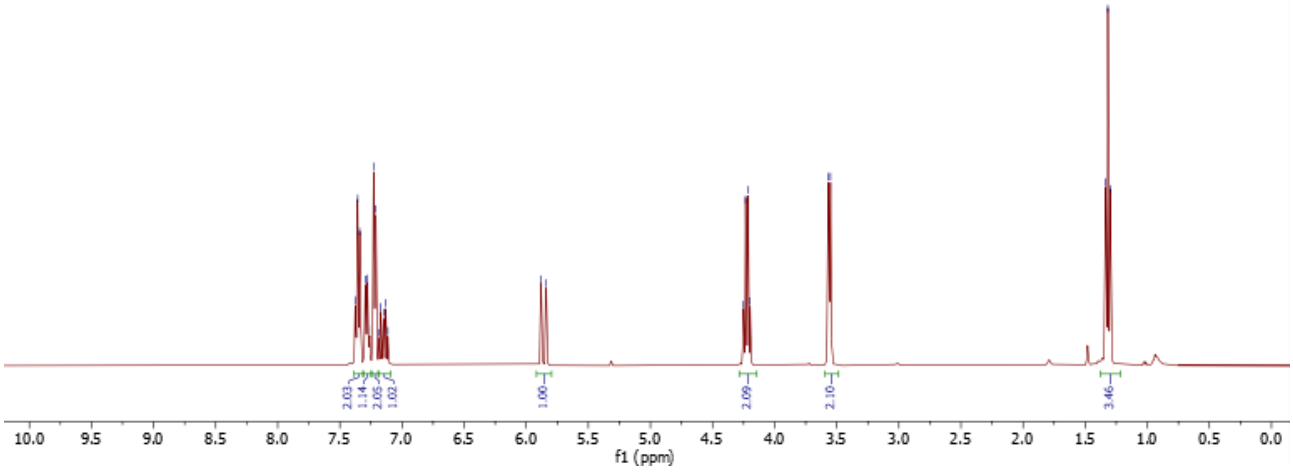


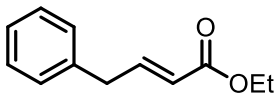
^{13}C NMR (101 MHz, $CDCl_3$)

(*E*)-Ethyl 4-phenylbut-2-enoate (1u)

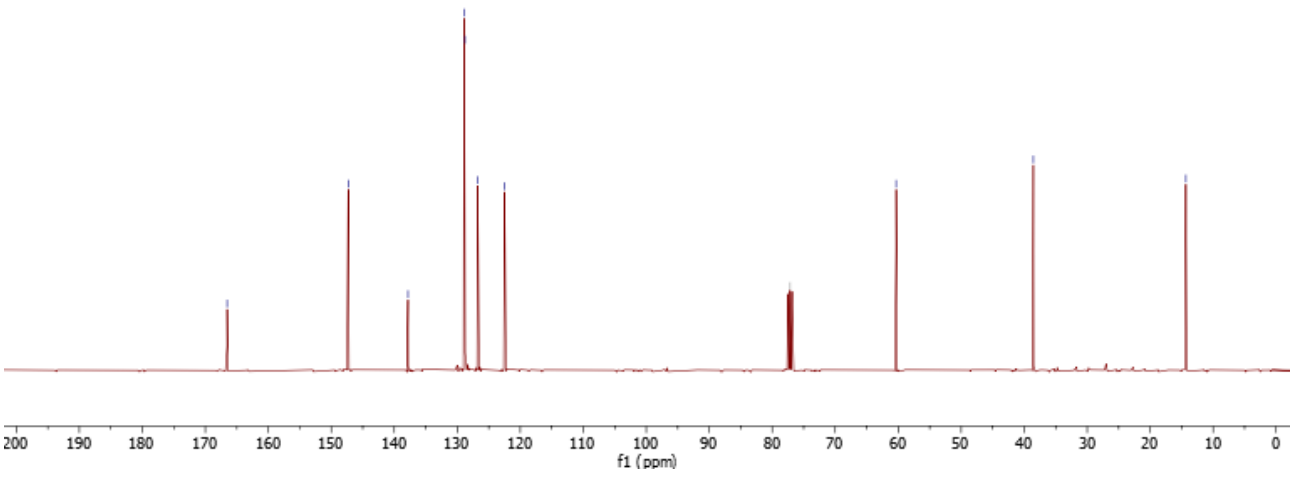


^{1}H NMR (400 MHz, $CDCl_3$)

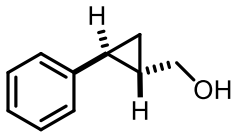




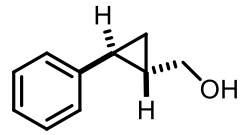
^{13}C NMR (101 MHz, $CDCl_3$)



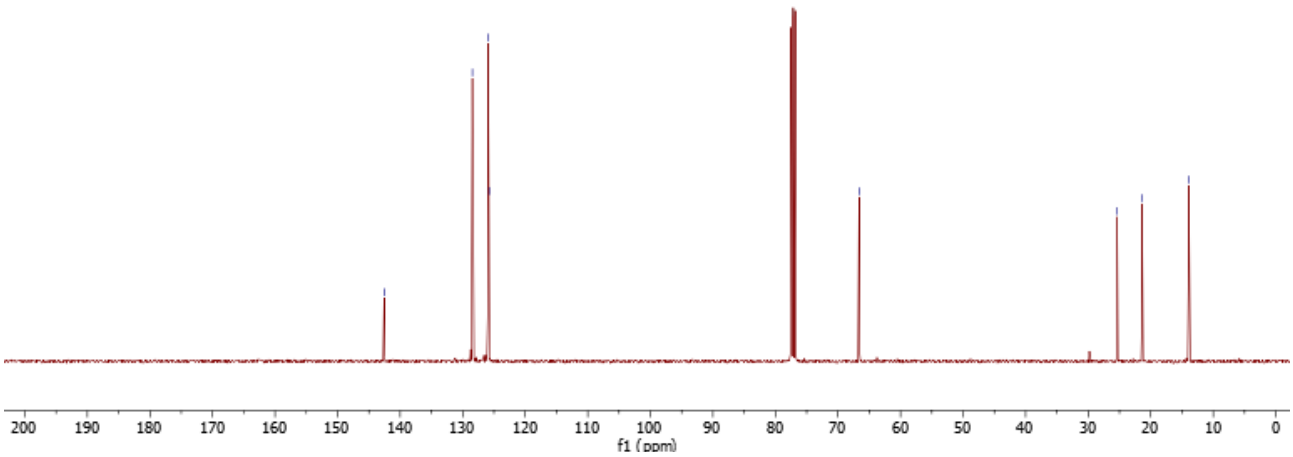
(±)-(*E*)-(2-Phenylcyclopropyl)methanol (3a)



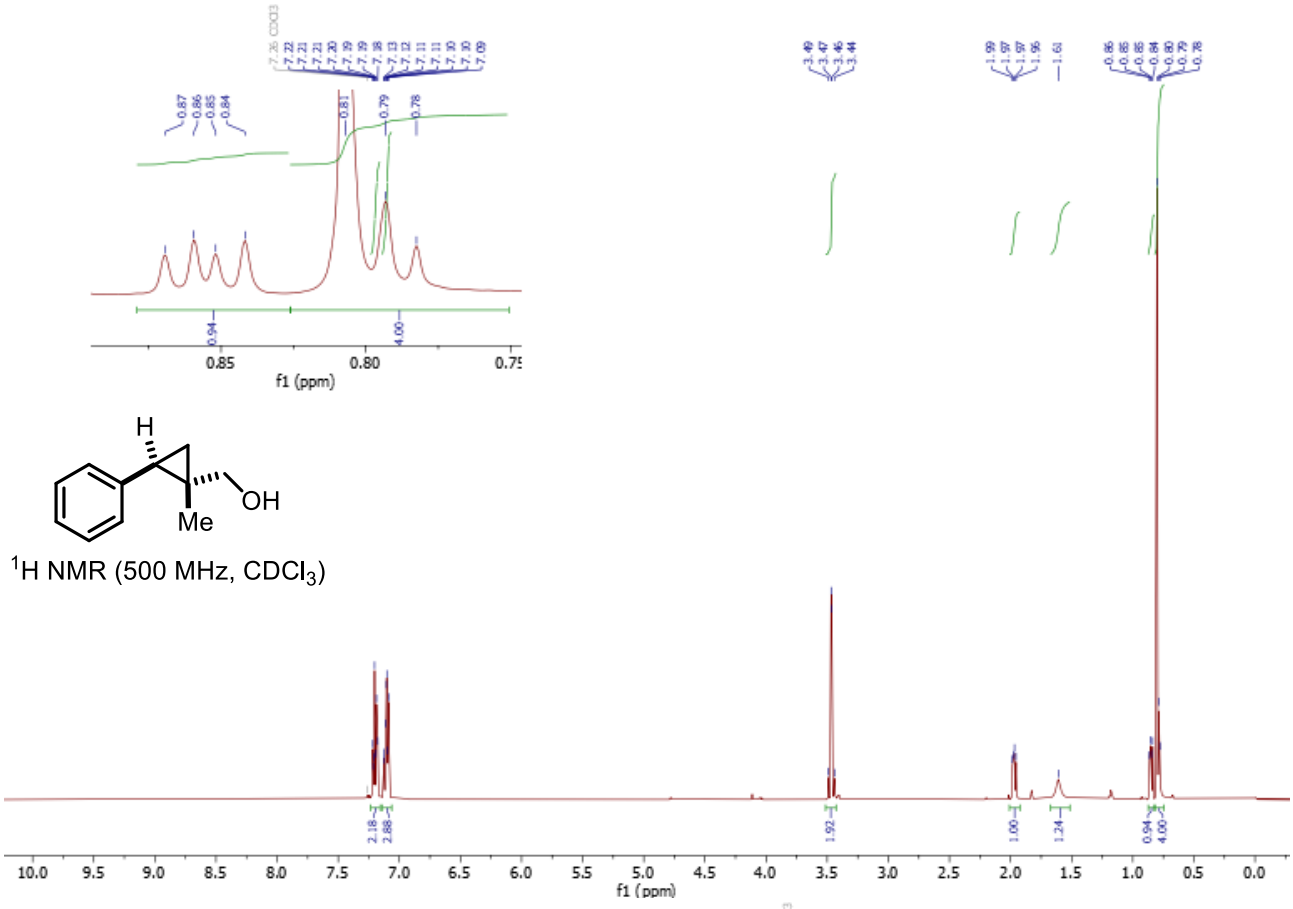
^{1}H NMR (400 MHz, $CDCl_3$)



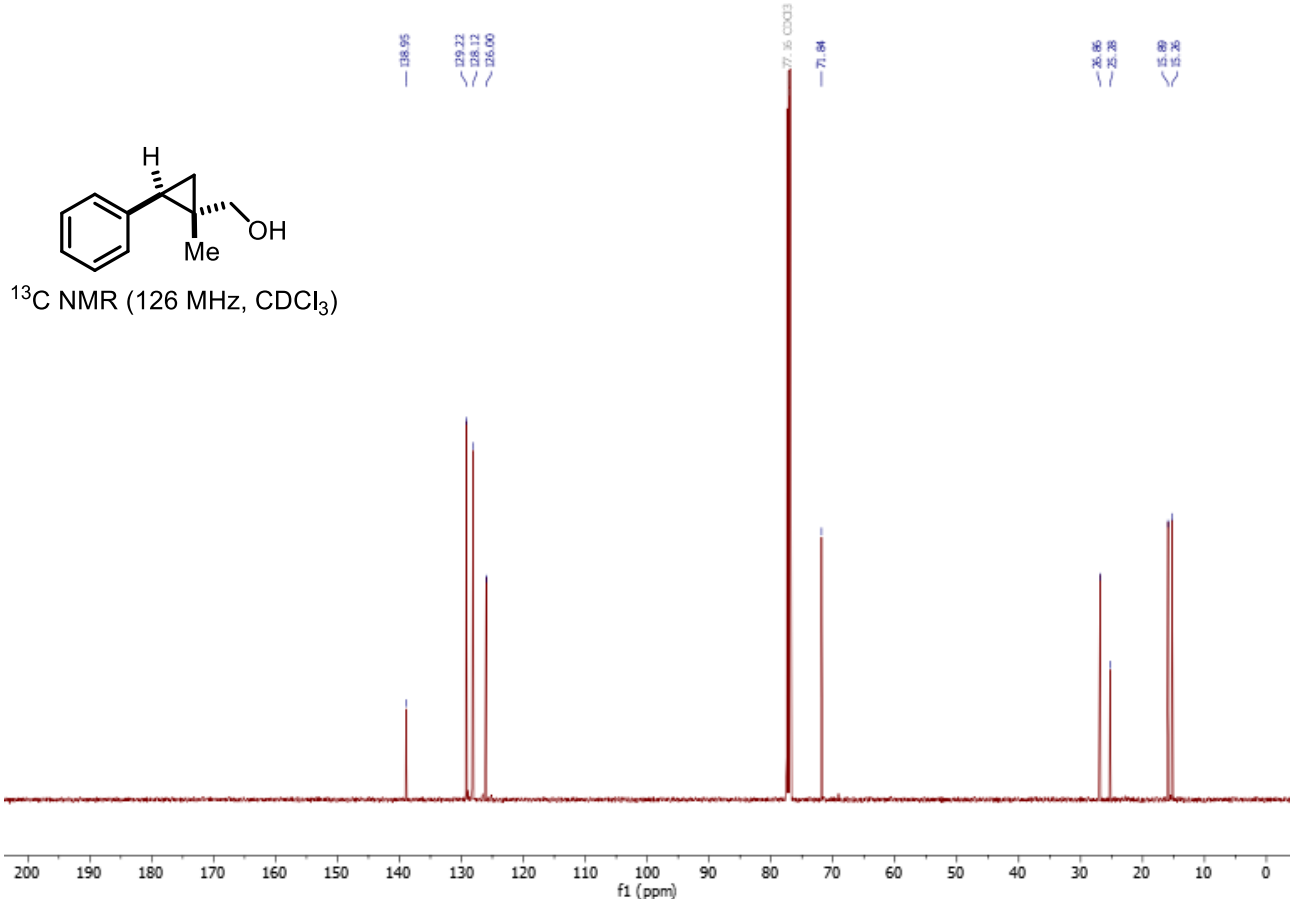
^{13}C NMR (101 MHz, $CDCl_3$)



(±)-(*E*)-(1-Methyl-2-phenylcyclopropyl)methanol (3b)

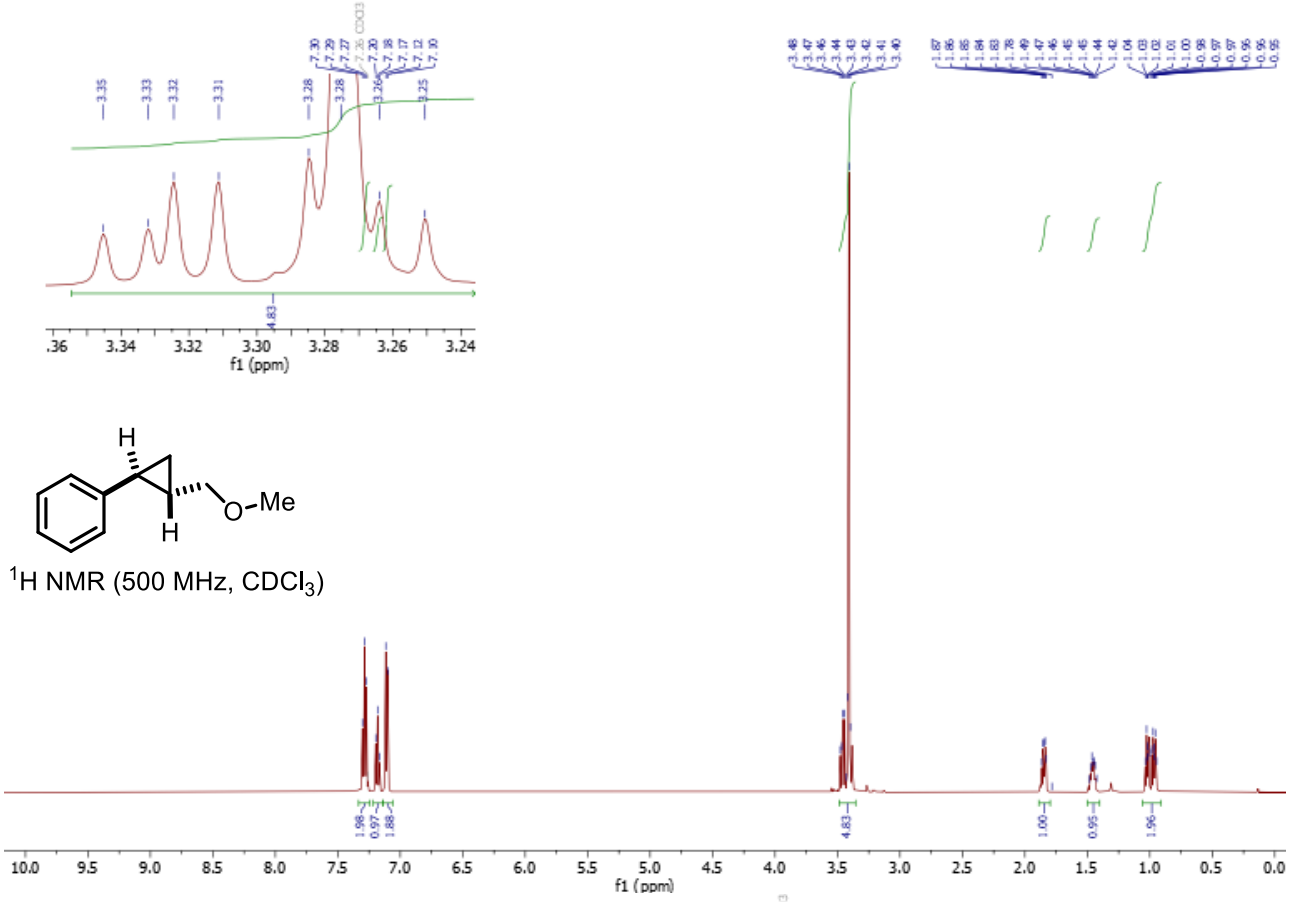


^{1}H NMR (500 MHz, $CDCl_3$)

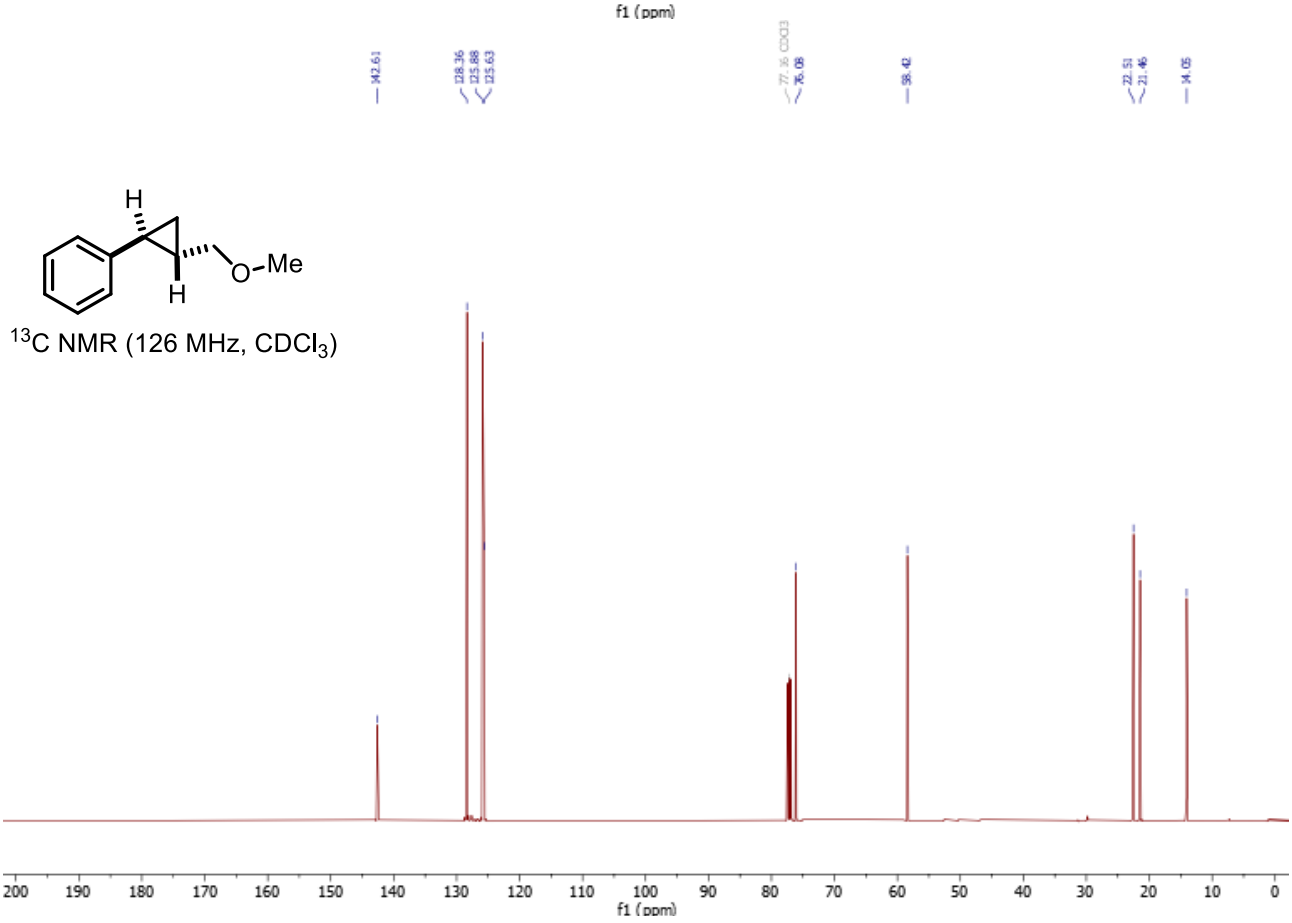


^{13}C NMR (126 MHz, $CDCl_3$)

(±)-(*E*)-(2-(Methoxymethyl)cyclopropyl)benzene (3c)

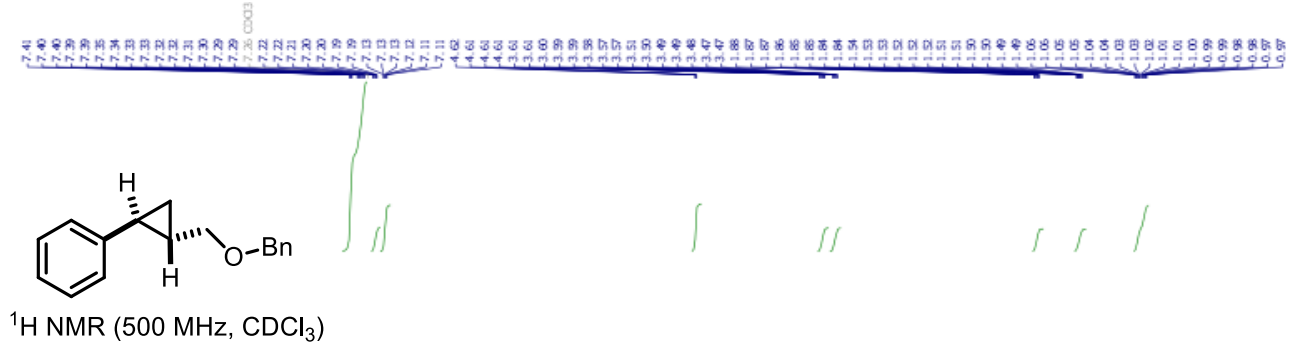


^{1}H NMR (500 MHz, $CDCl_3$)

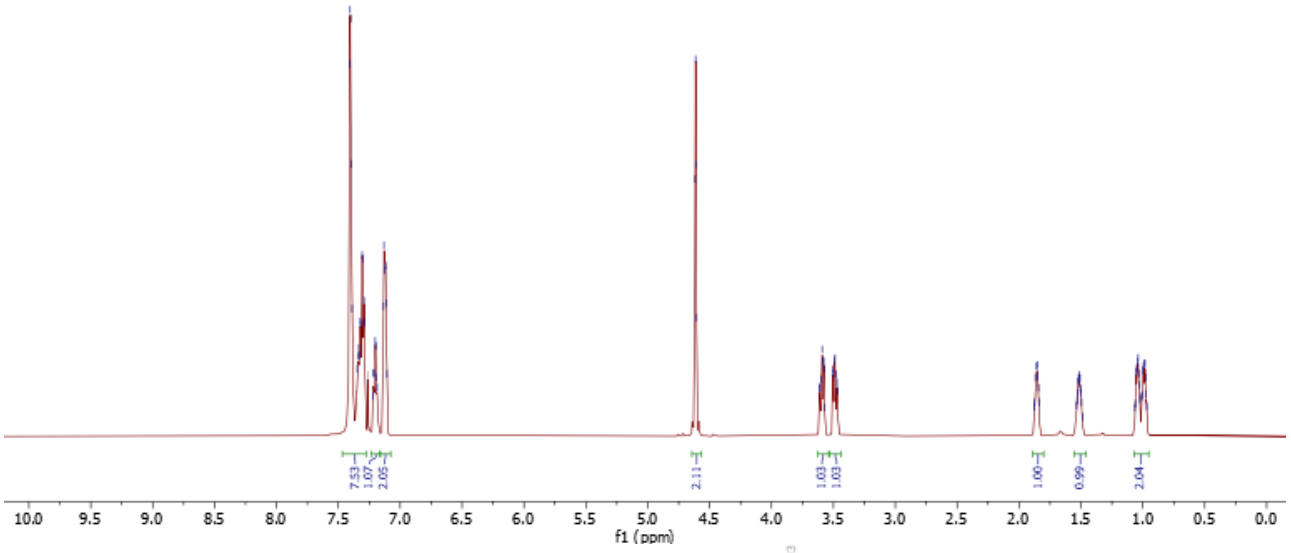


^{13}C NMR (126 MHz, $CDCl_3$)

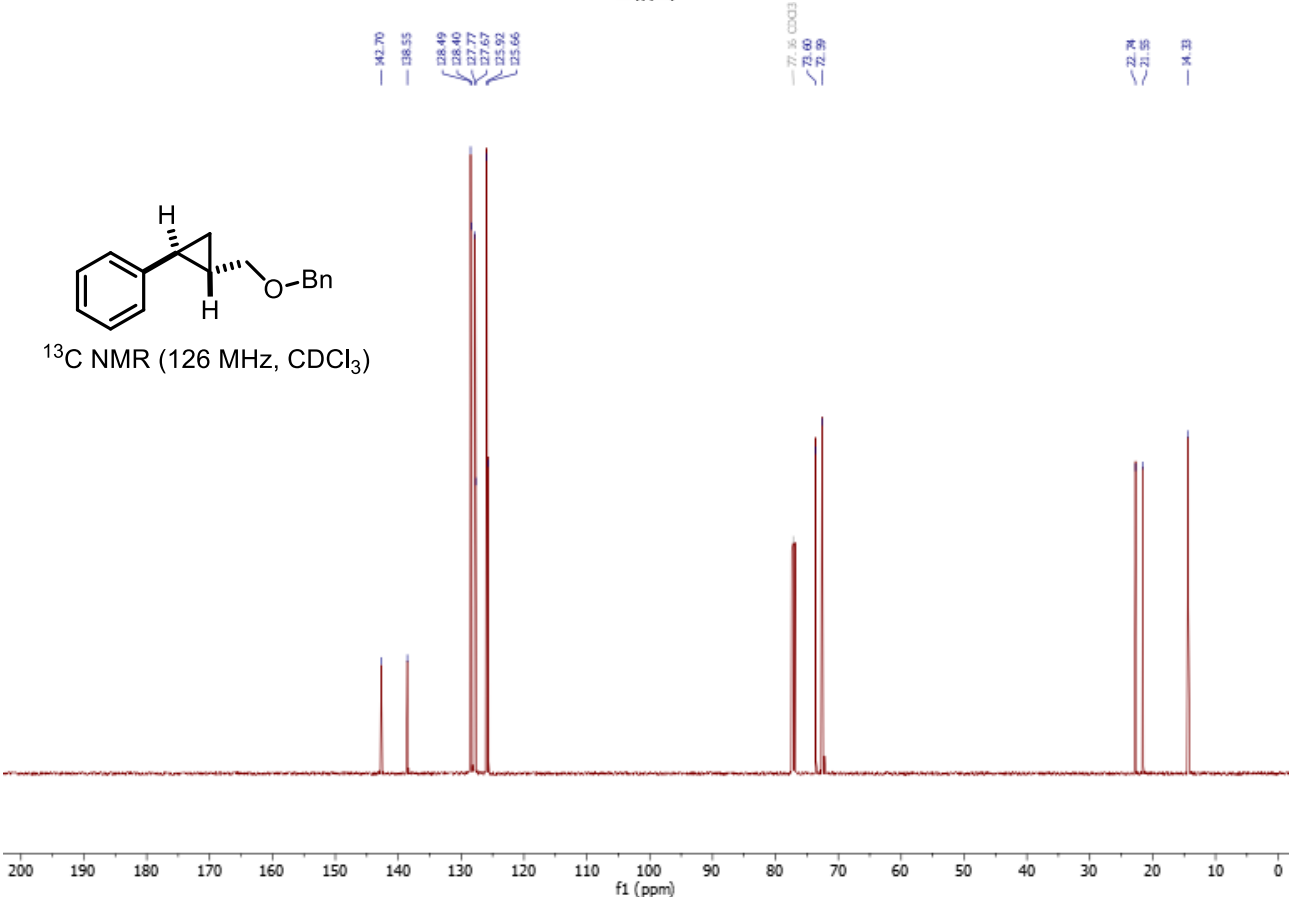
(±)-(*E*)-(2-((Benzyloxy)methyl)cyclopropyl)benzene (3d)



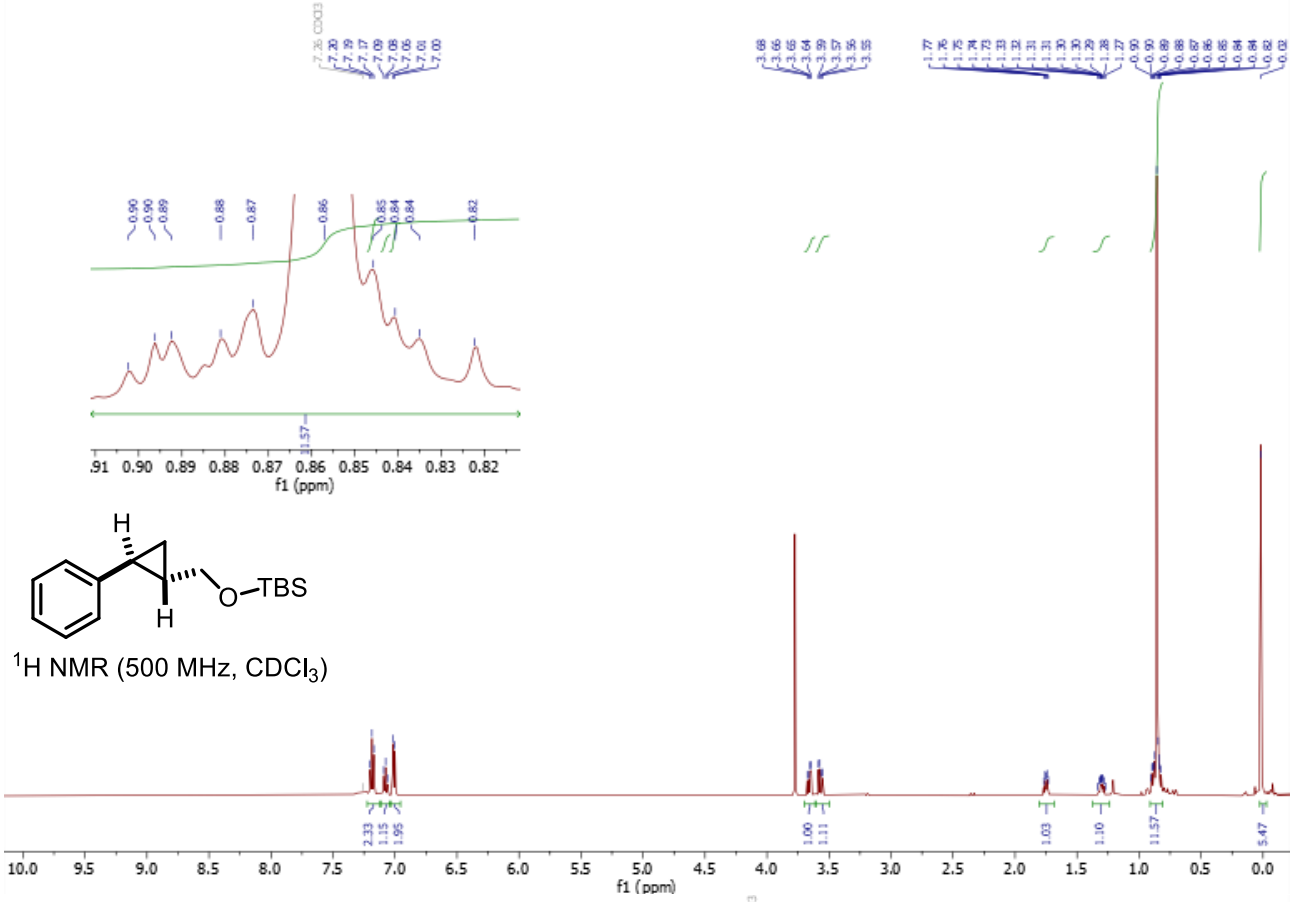
^{1}H NMR (500 MHz, $CDCl_3$)

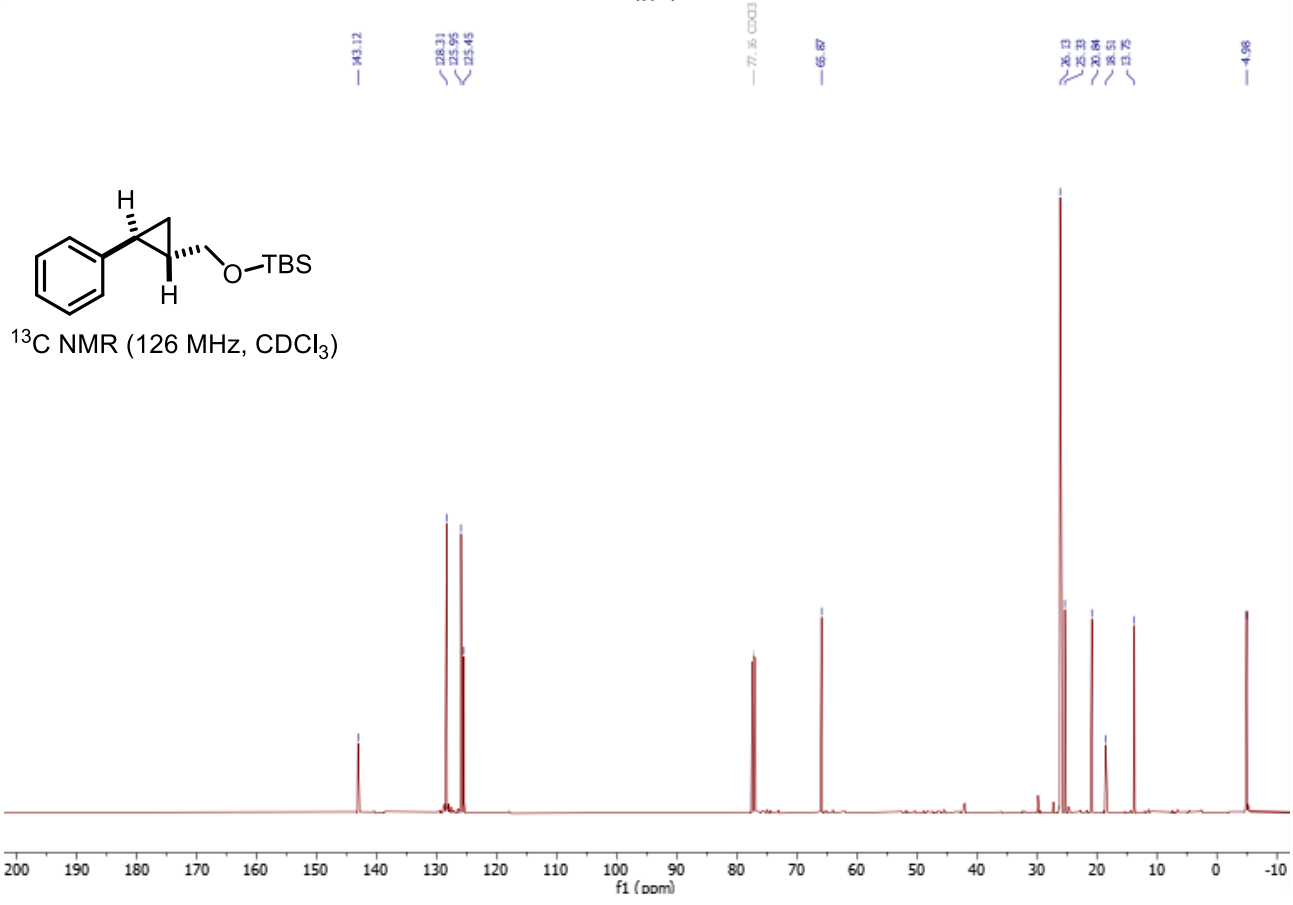


^{13}C NMR (126 MHz, $CDCl_3$)

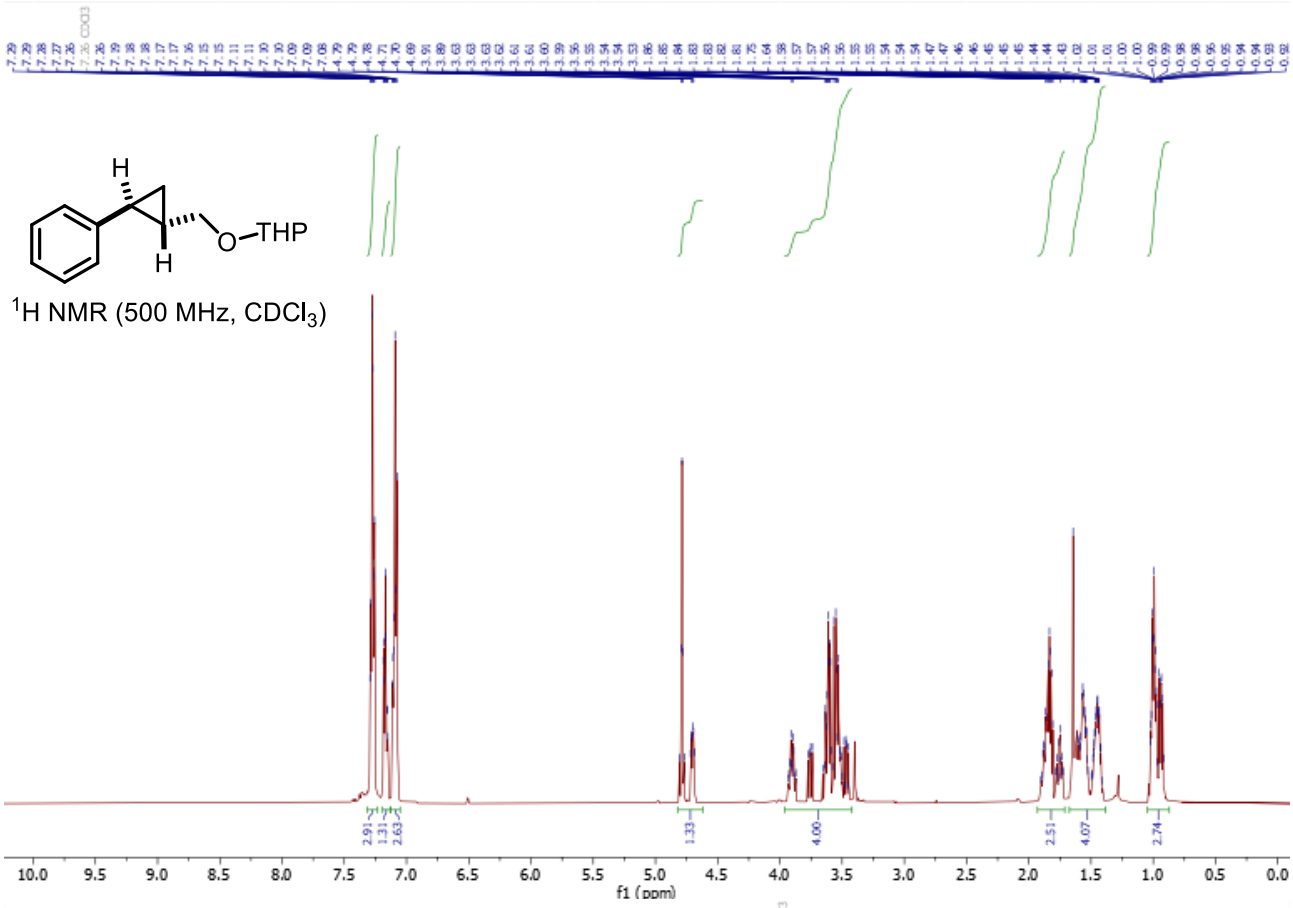


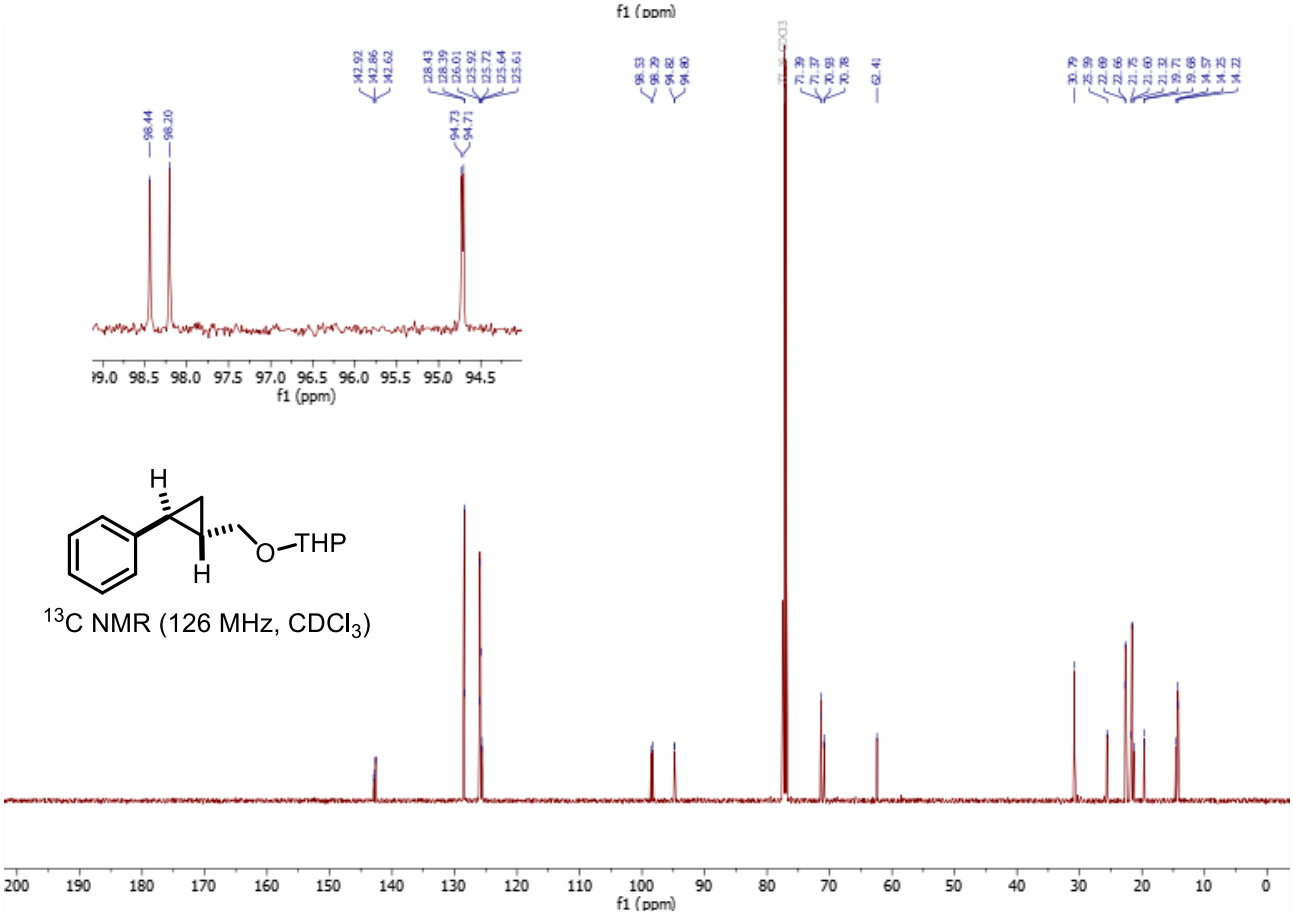
(±)-(*E*)-*t*ert-Butyldimethyl((2-phenylcyclopropyl)methoxy)silane (3e)



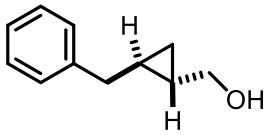


(±)-(*E*)-2-((2-Phenylcyclopropyl)methoxy)tetrahydro-2H-pyran (3f)

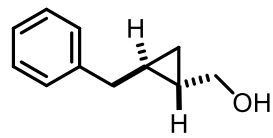




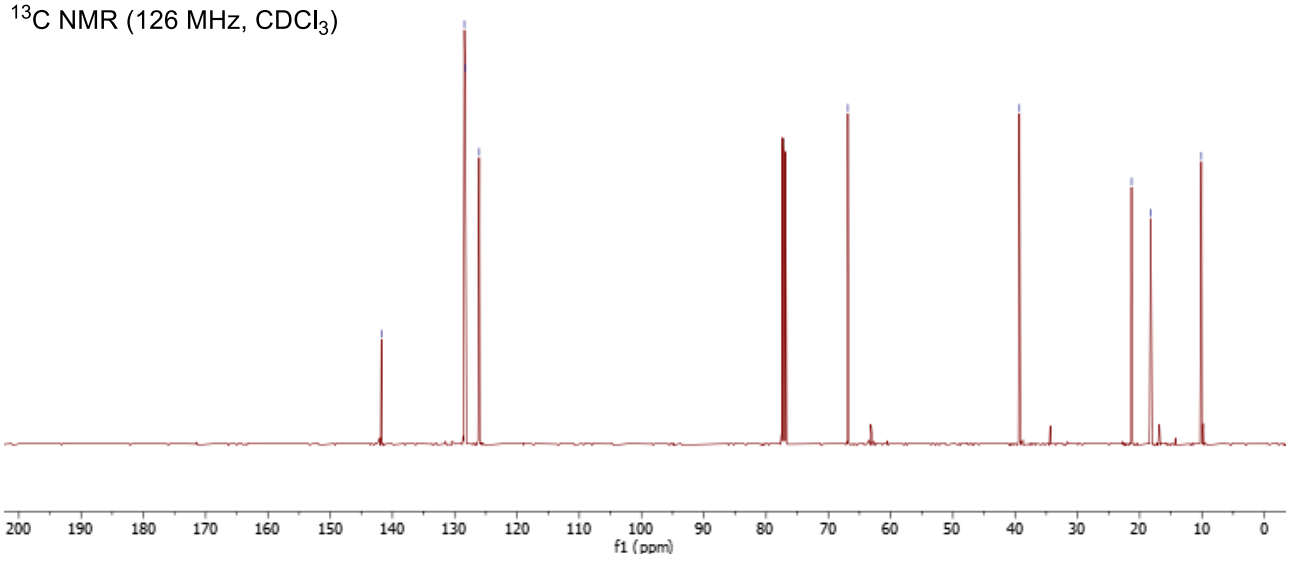
(±)-(*E*)-(2-Benzylcyclopropyl)methanol (3g)



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

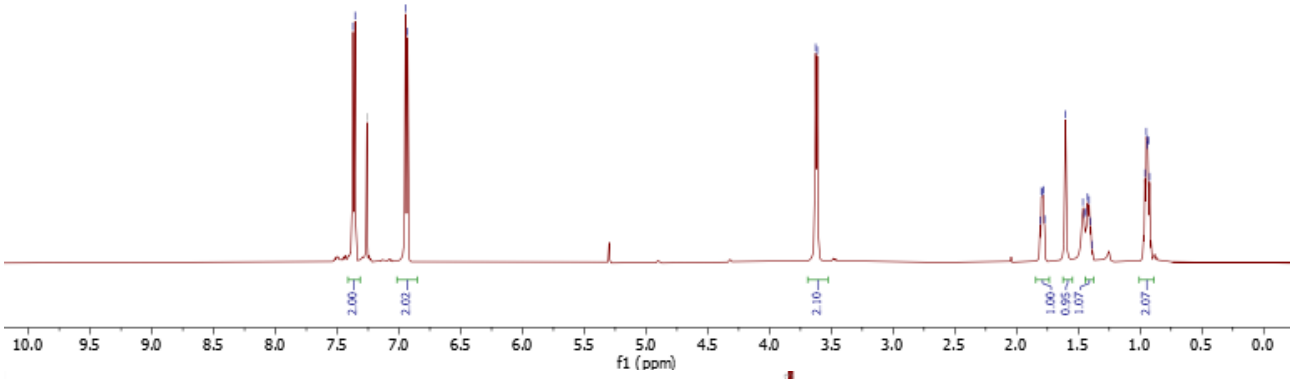


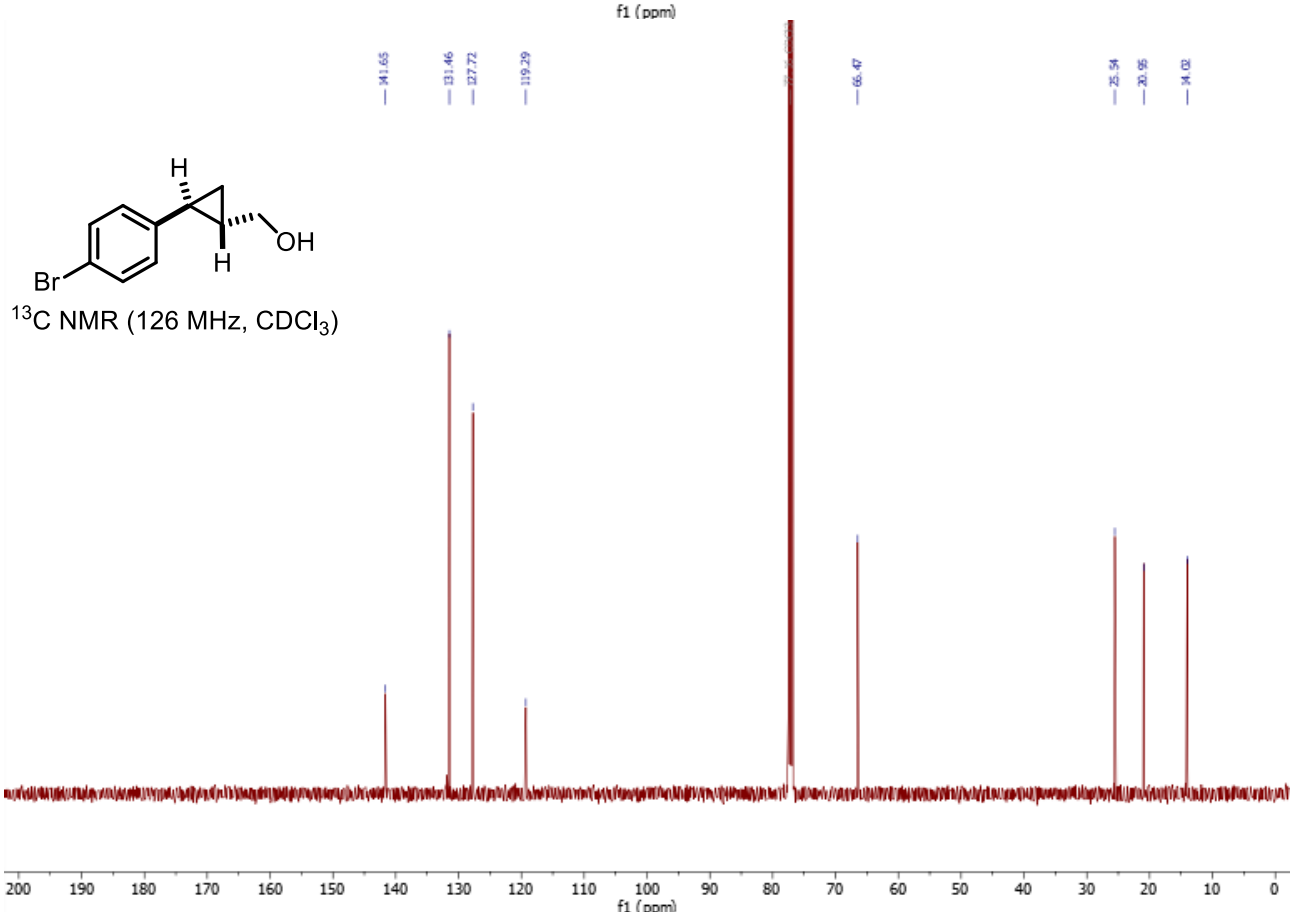
^{13}C NMR (126 MHz, $CDCl_3$)



(±)-(*E*)-(2-(4-Bromophenyl)cyclopropyl)methanol (3h)

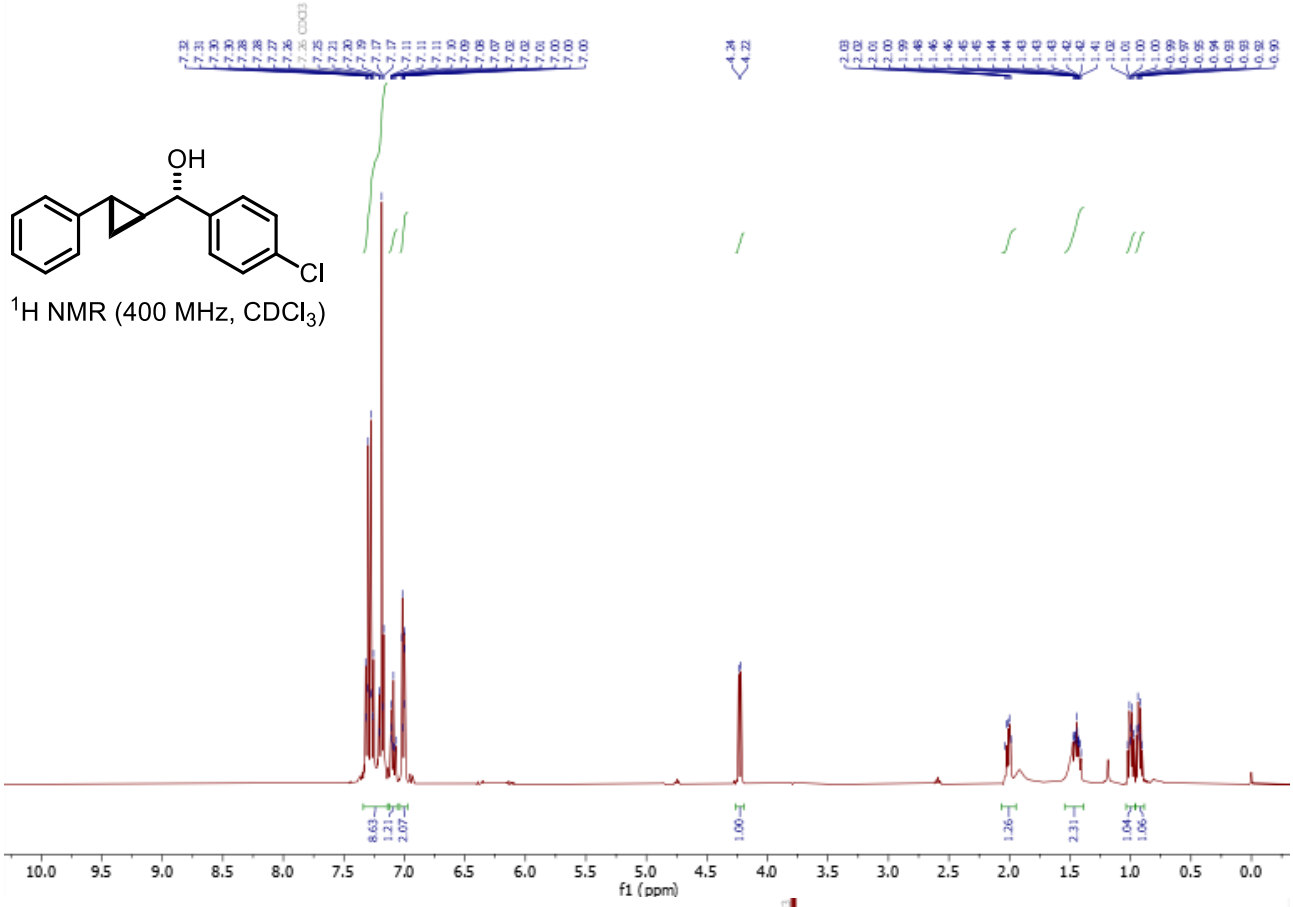
^{1}H NMR (500 MHz, $CDCl_3$)

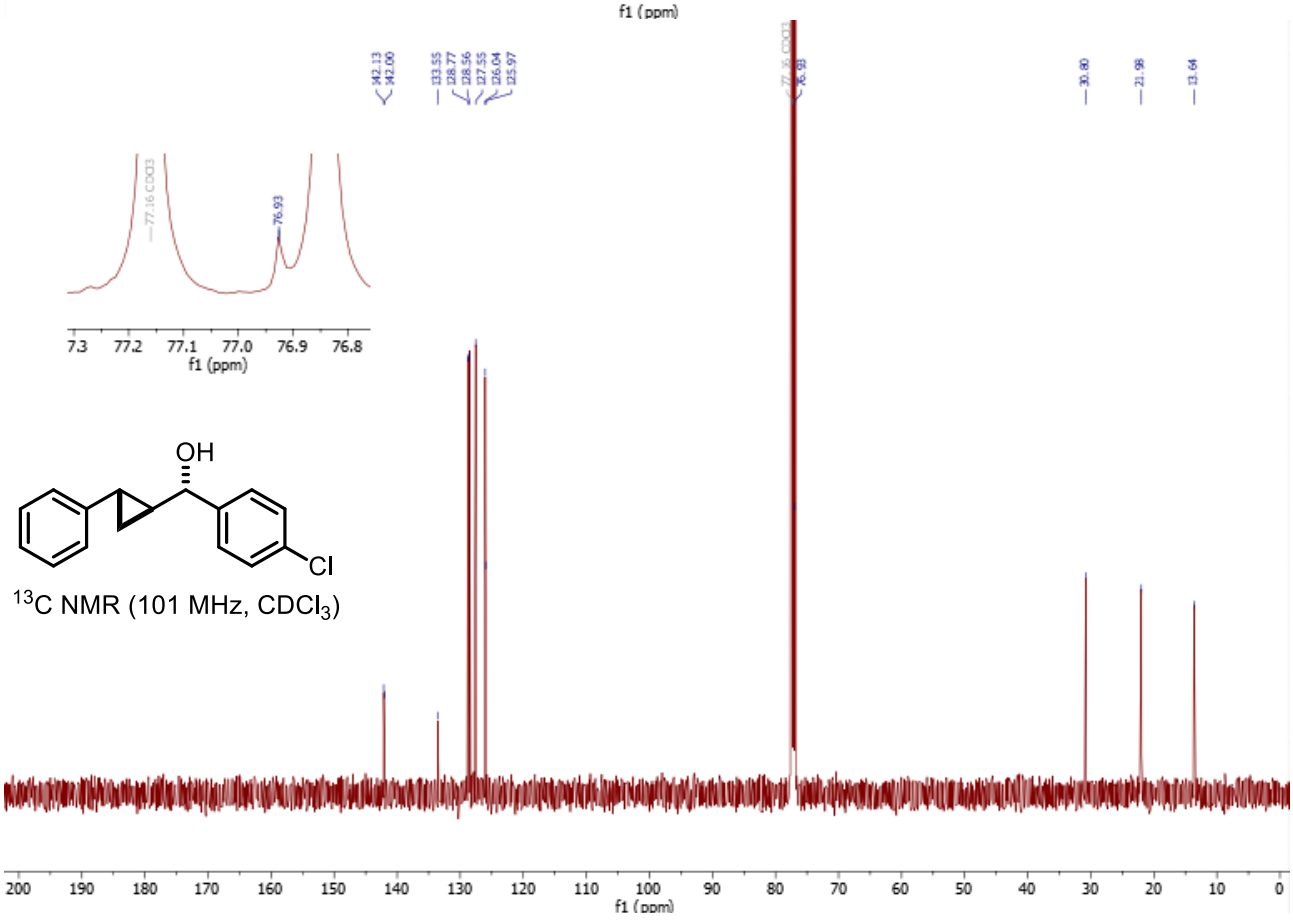




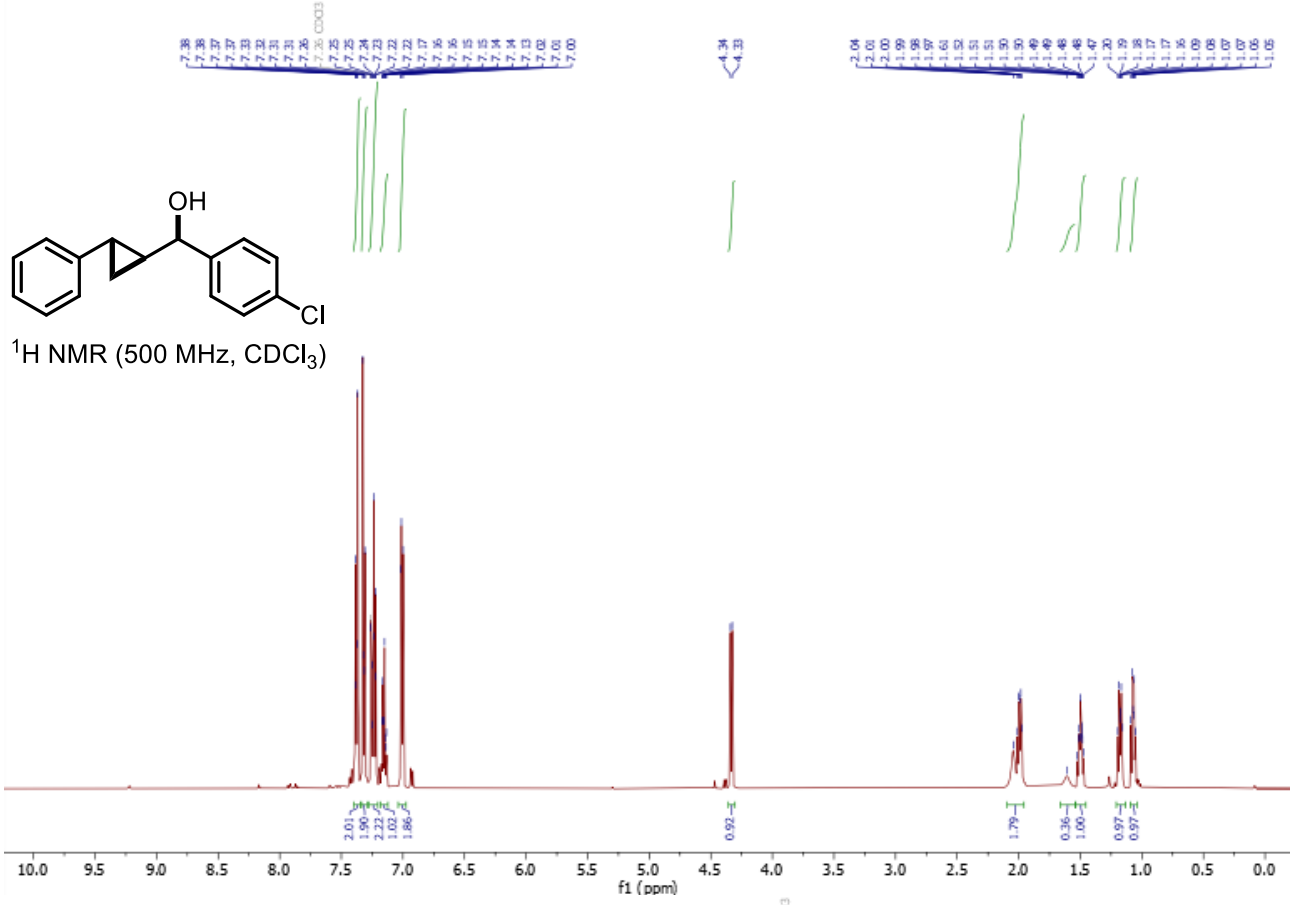
^{13}C NMR (126 MHz, $CDCl_3$)

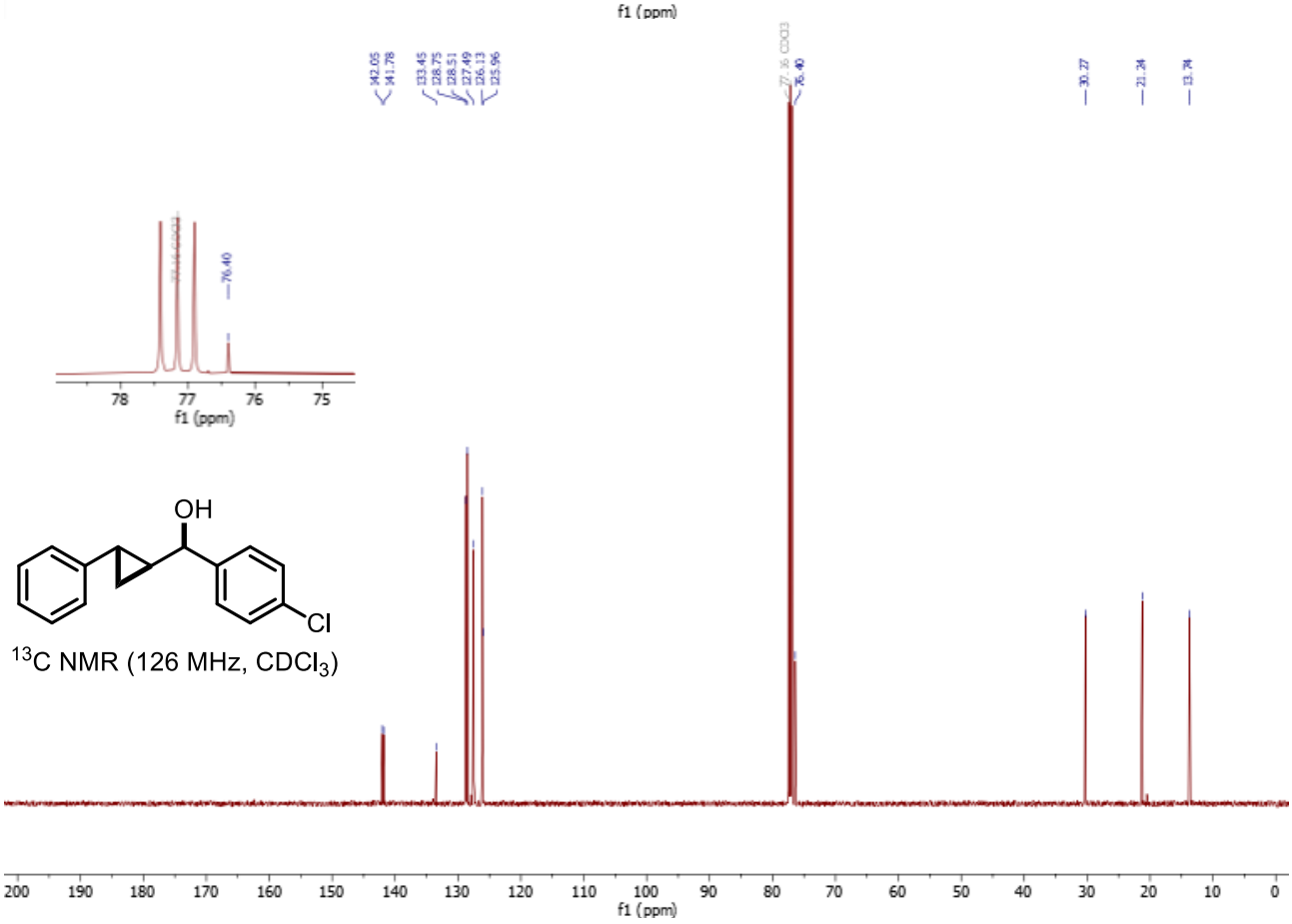
***anti*-(±)-(*E*)-(4-Chlorophenyl)(2-phenylcyclopropyl)methanol (*anti*-3i)**[31]



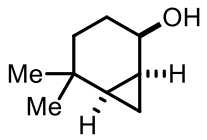


syn-(±)-(*E*)-(4-Chlorophenyl)(2-phenylcyclopropyl)methanol (*syn*-3i)[31]

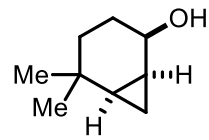




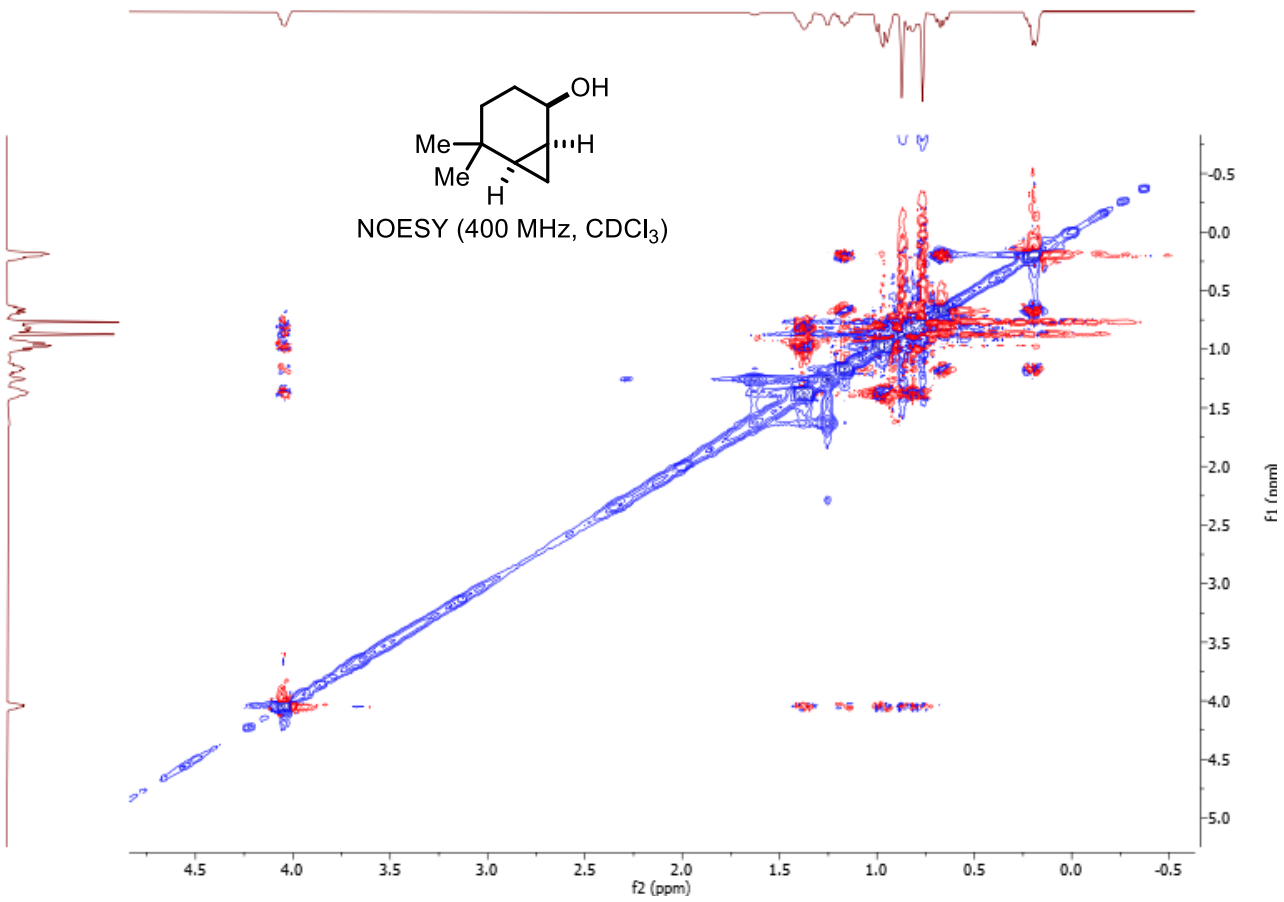
***syn*-(±)-5,5-Dimethylbicyclo[4.1.0]heptan-2-ol (3j)**



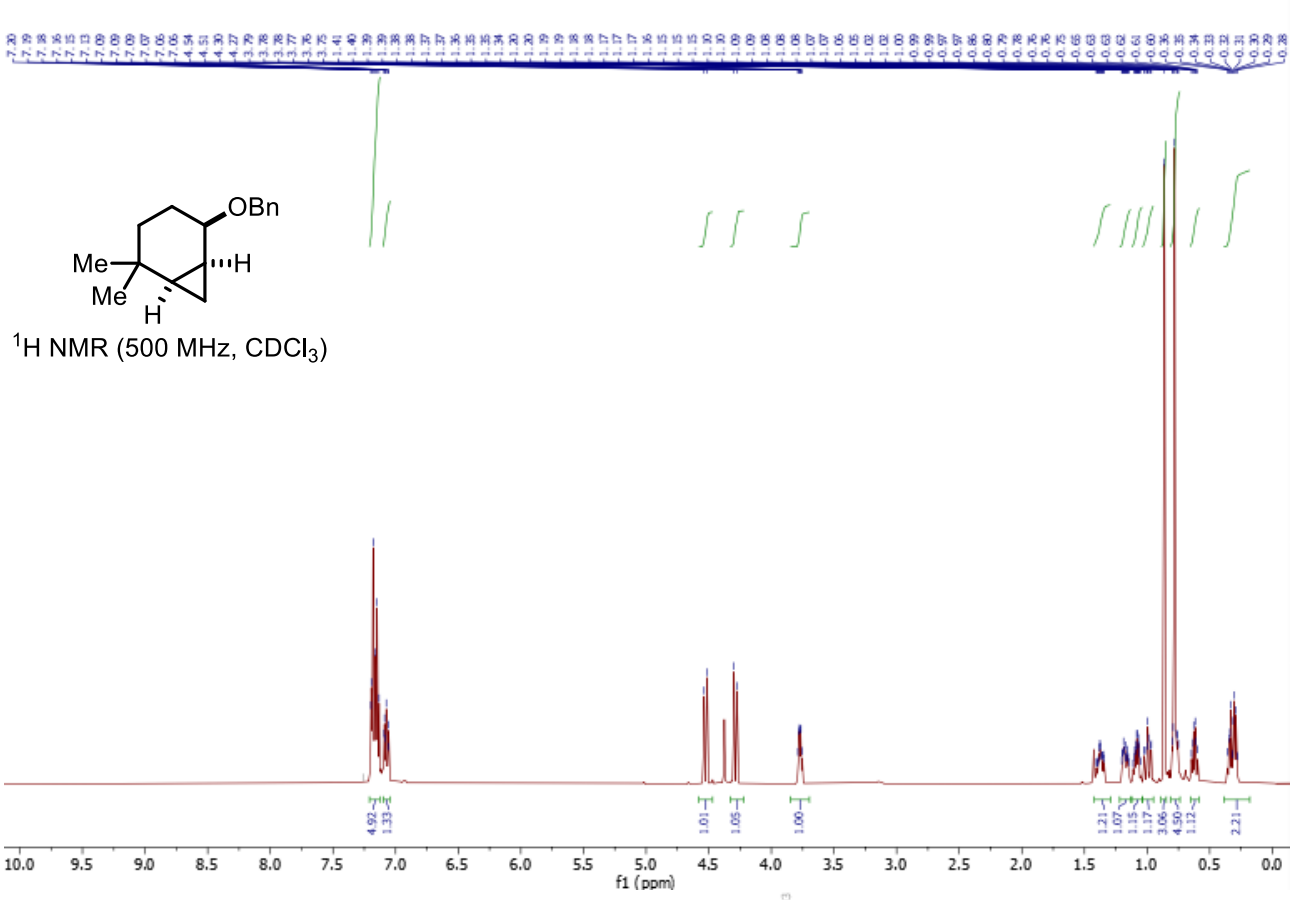
^{1}H NMR (400 MHz, $CDCl_3$)



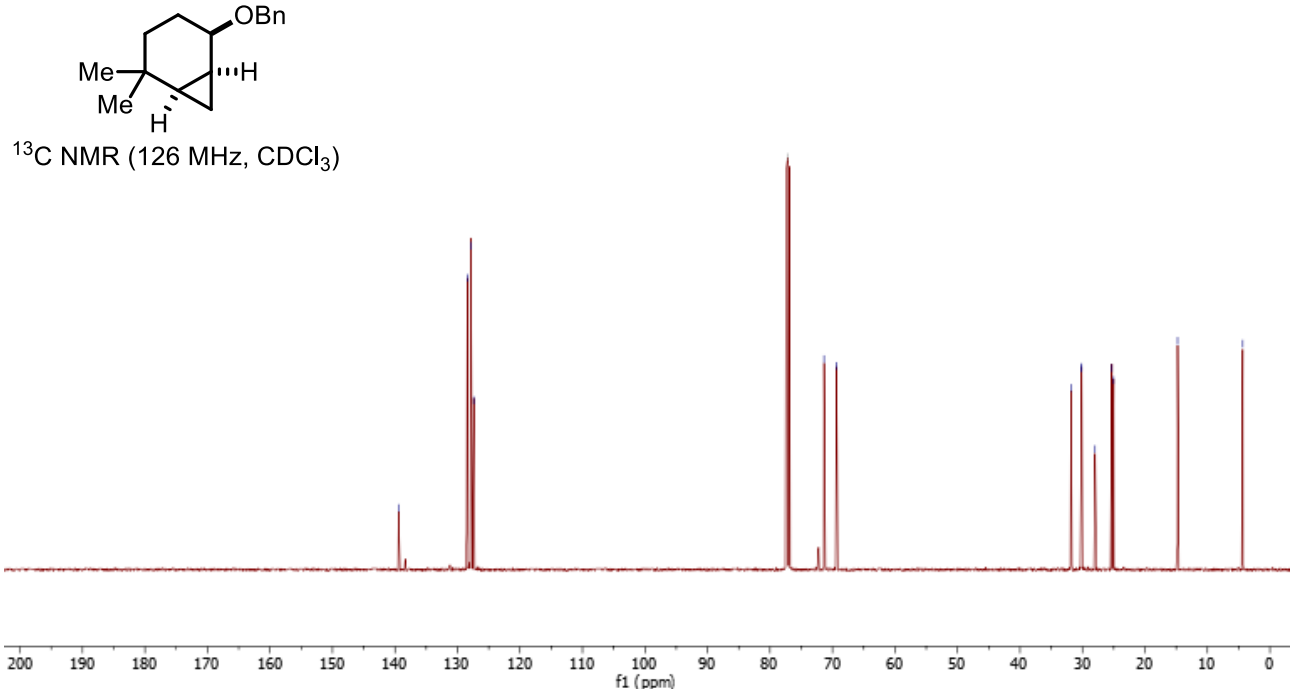
^{13}C NMR (101 MHz, $CDCl_3$)


OH
Me
Me
H
H
NOESY (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

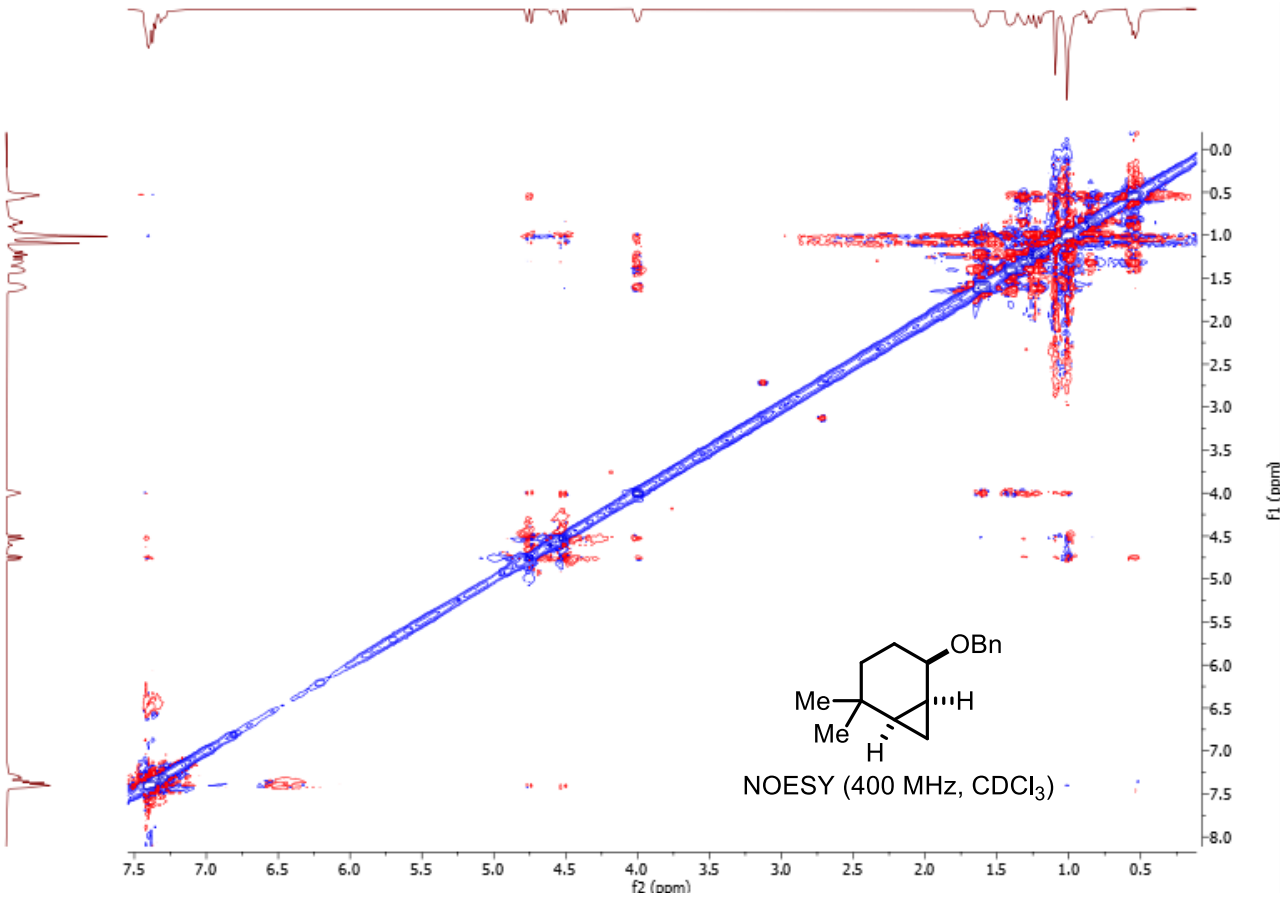
***syn*-(±)-5-(Benzyloxy)-2,2-dimethylbicyclo[4.1.0]heptane (3k)**



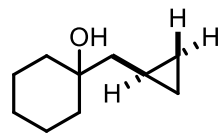
^{1}H NMR (500 MHz, $CDCl_3$)



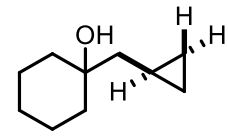
^{13}C NMR (126 MHz, $CDCl_3$)


OBn
Me
Me
H
H
NOESY (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

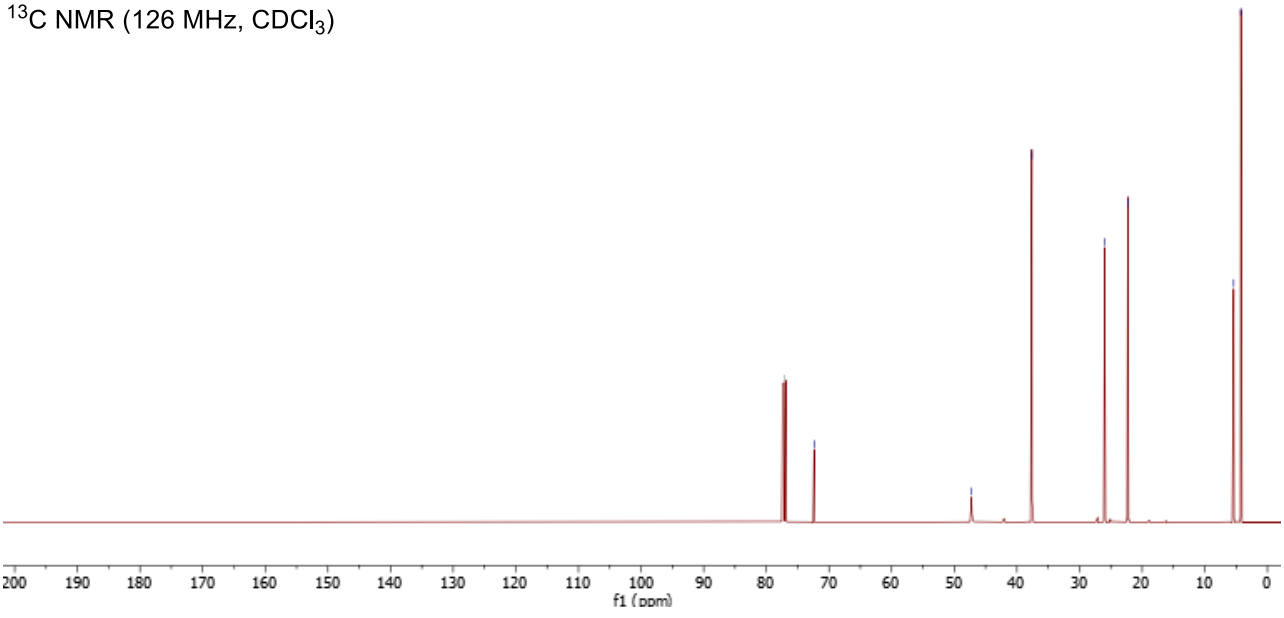
1-(Cyclopropylmethyl)cyclohexanol (3l)



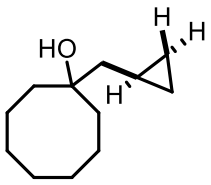
^{1}H NMR (500 MHz, $CDCl_3$)



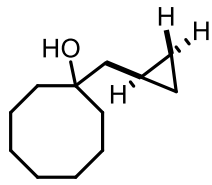
^{13}C NMR (126 MHz, $CDCl_3$)



1-(Cyclopropylmethyl)cyclooctanol (3m)

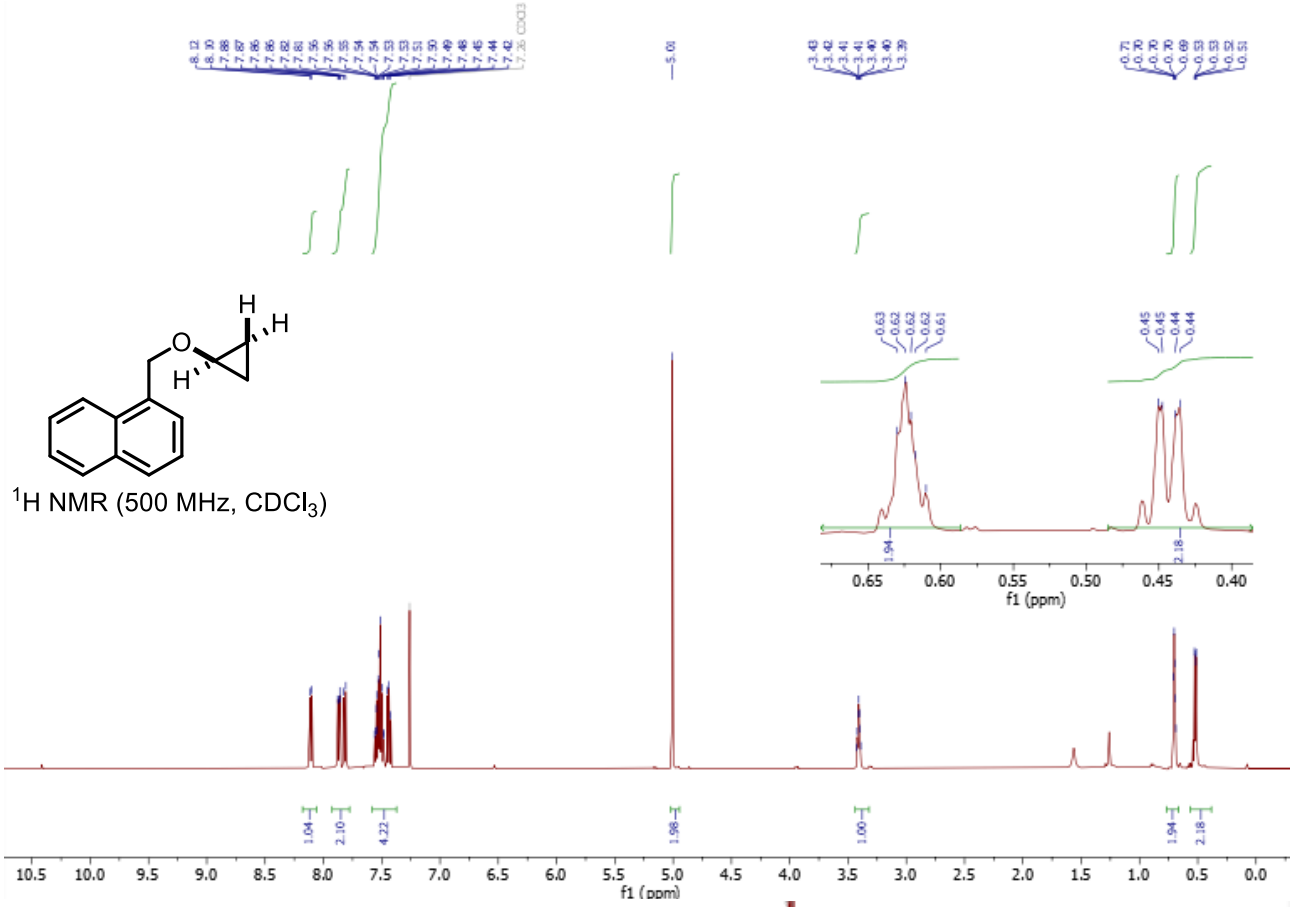


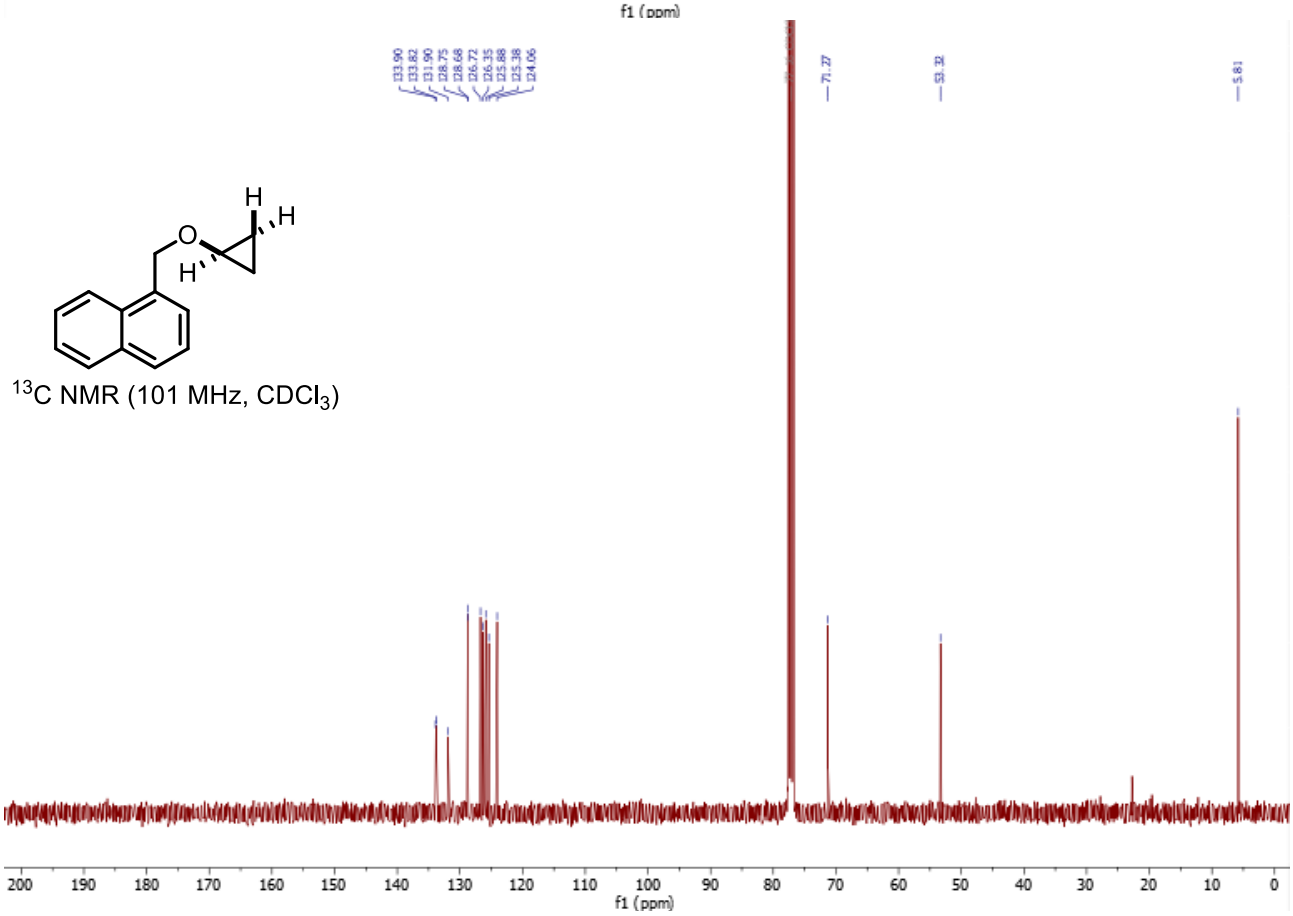
^{1}H NMR (500 MHz, $CDCl_3$)



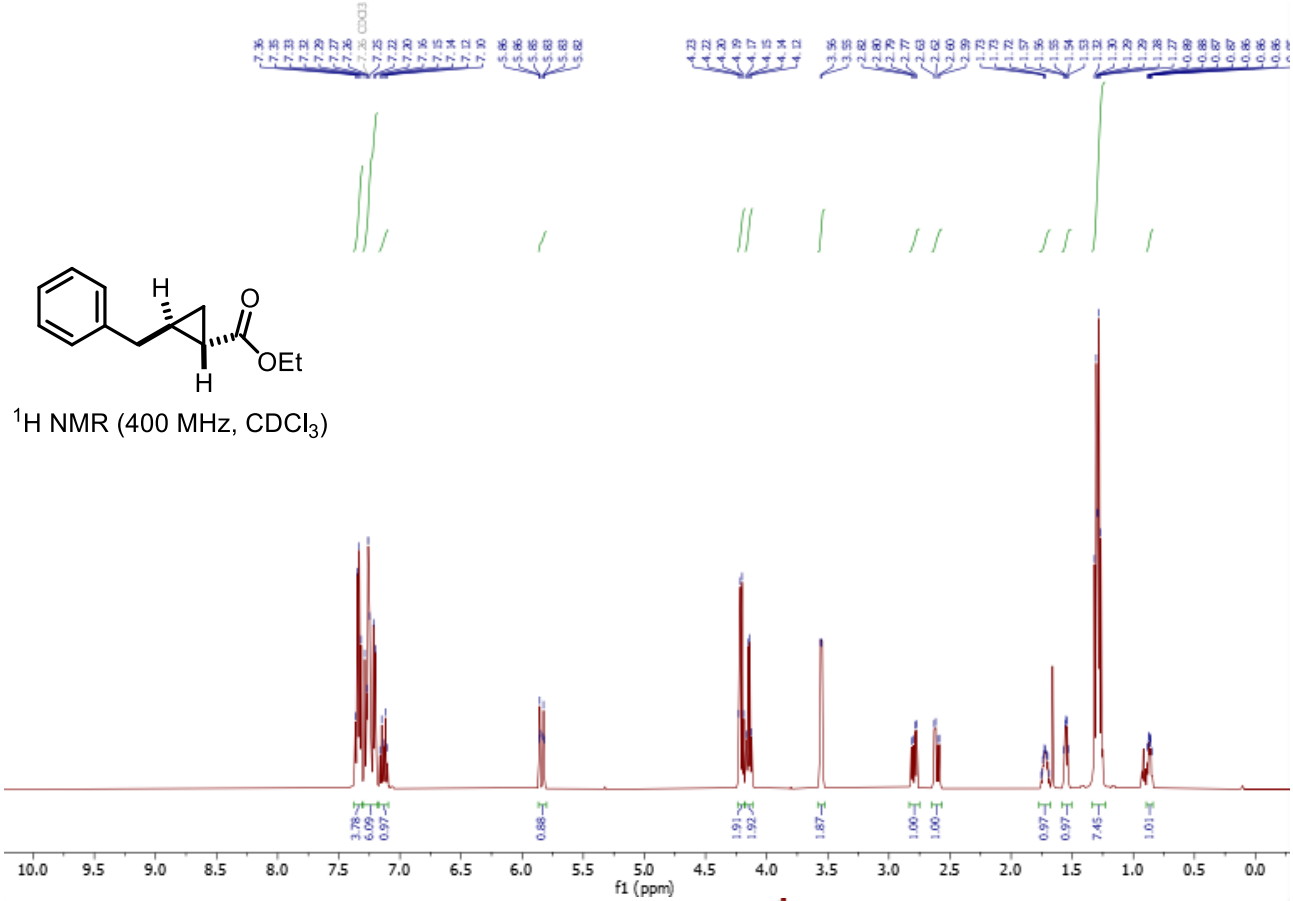
^{13}C NMR (126 MHz, $CDCl_3$)

1-(Cyclopropoxymethyl)naphthalene (3t)

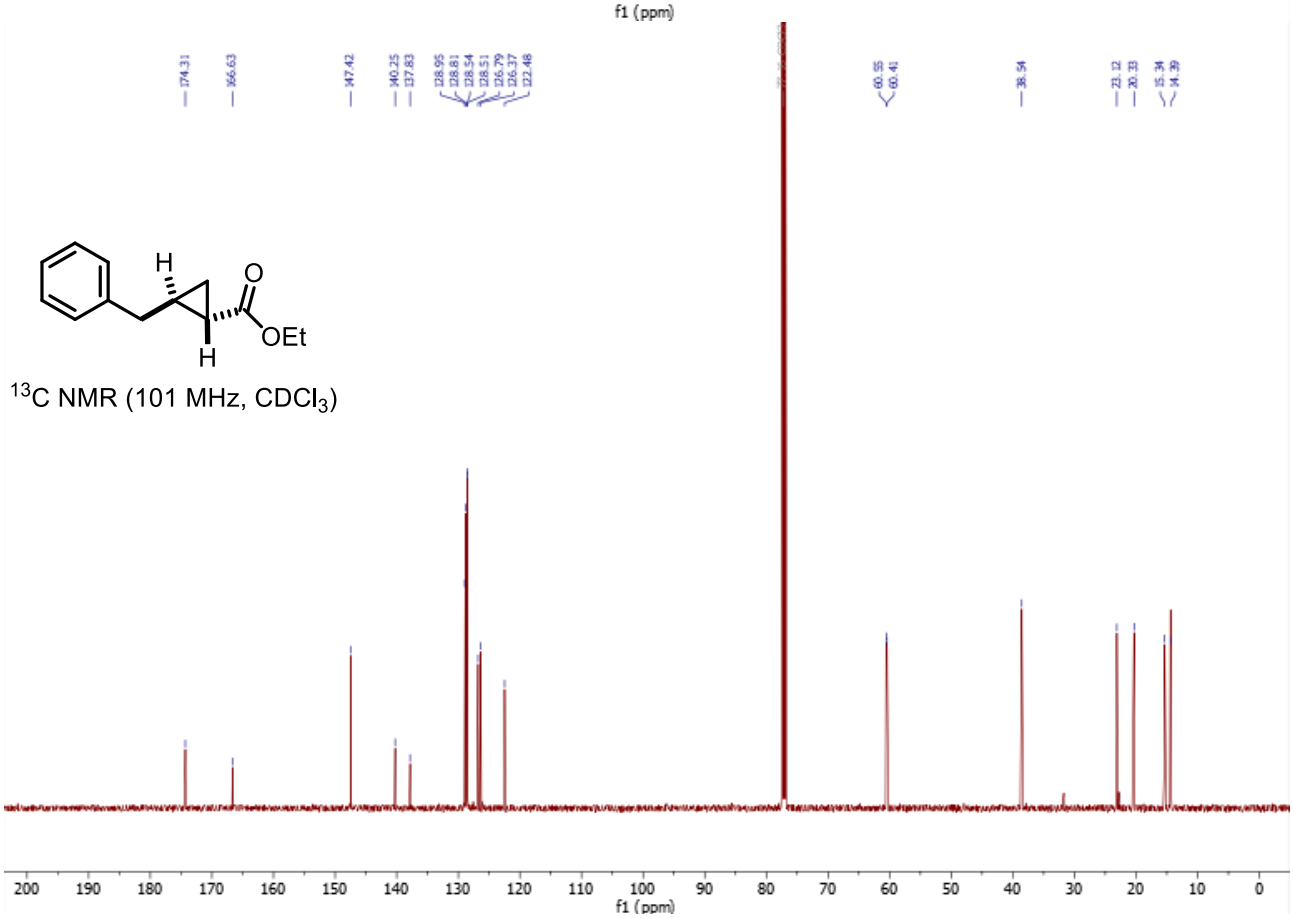




(±)-(*E*)-Ethyl 2-benzylcyclopropanecarboxylate (3u)



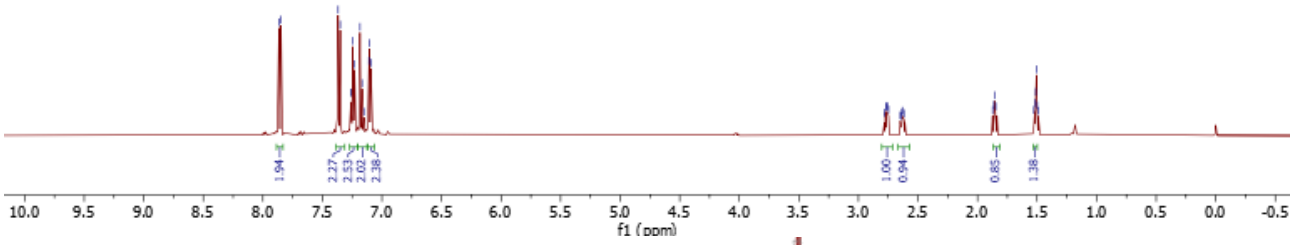
^{1}H NMR (400 MHz, $CDCl_3$)

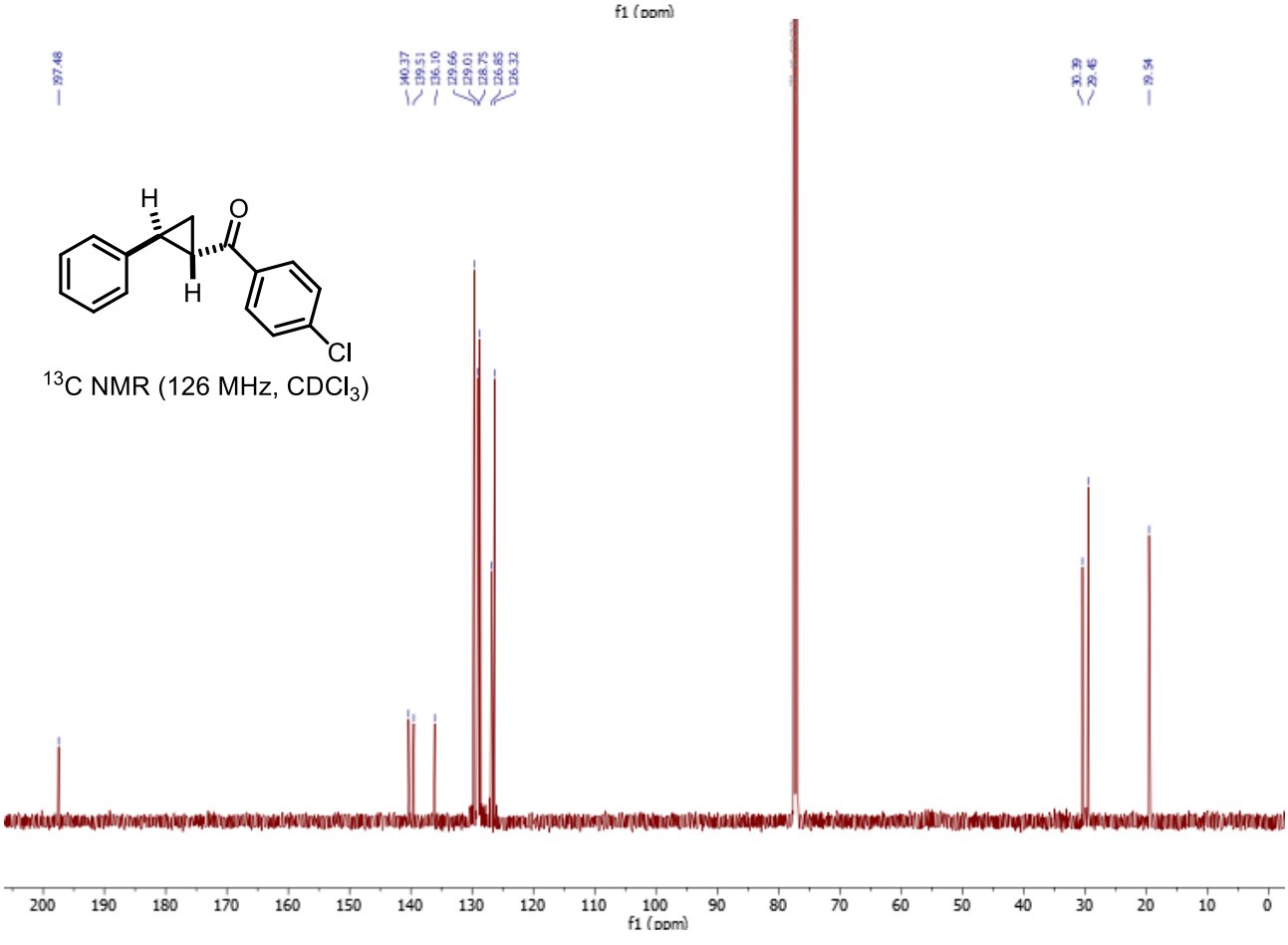


^{13}C NMR (101 MHz, $CDCl_3$)

(±)-(*E*)-(4-Chlorophenyl)(2-phenylcyclopropyl)methanone (3v)

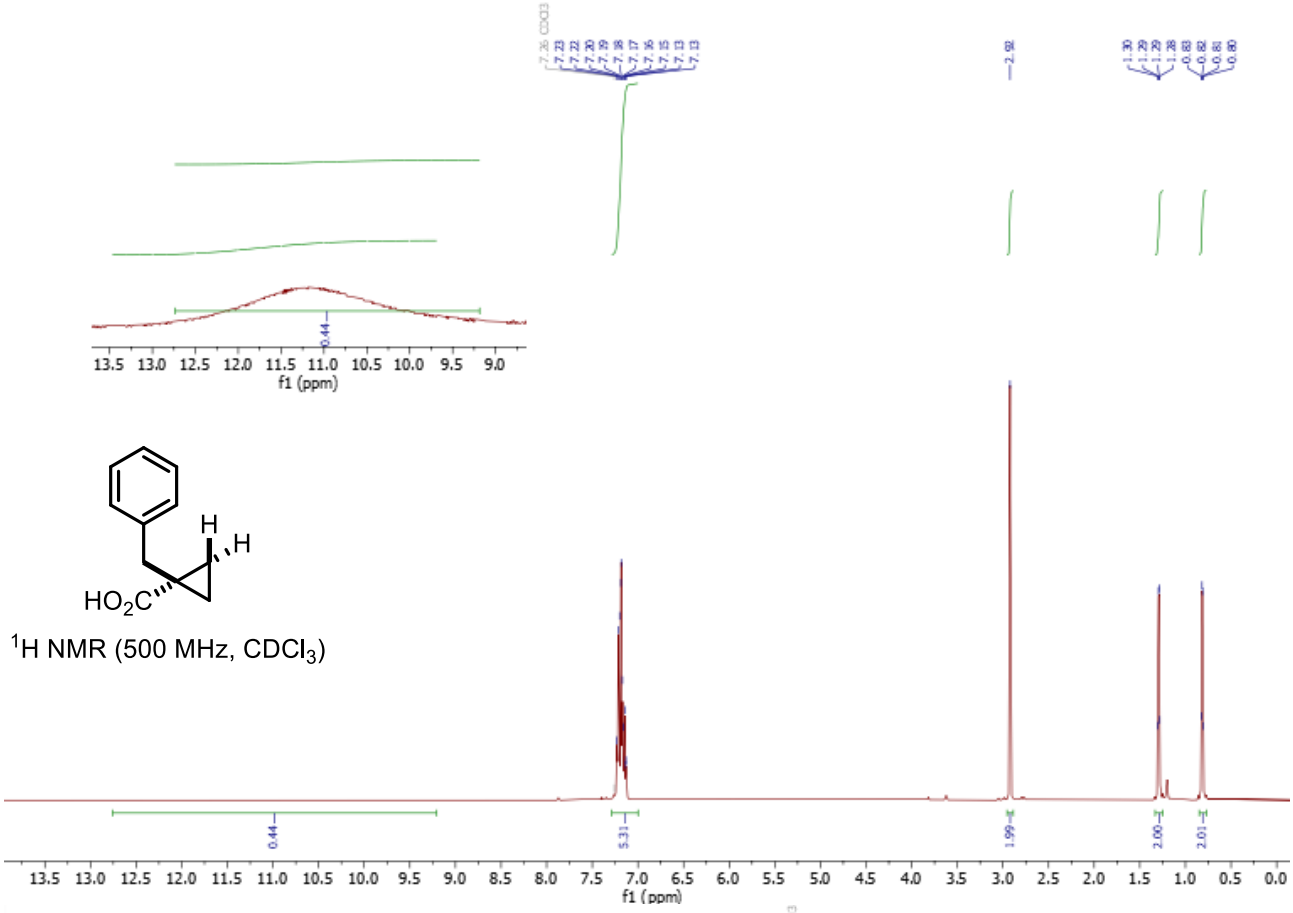
^{1}H NMR (500 MHz, $CDCl_3$)



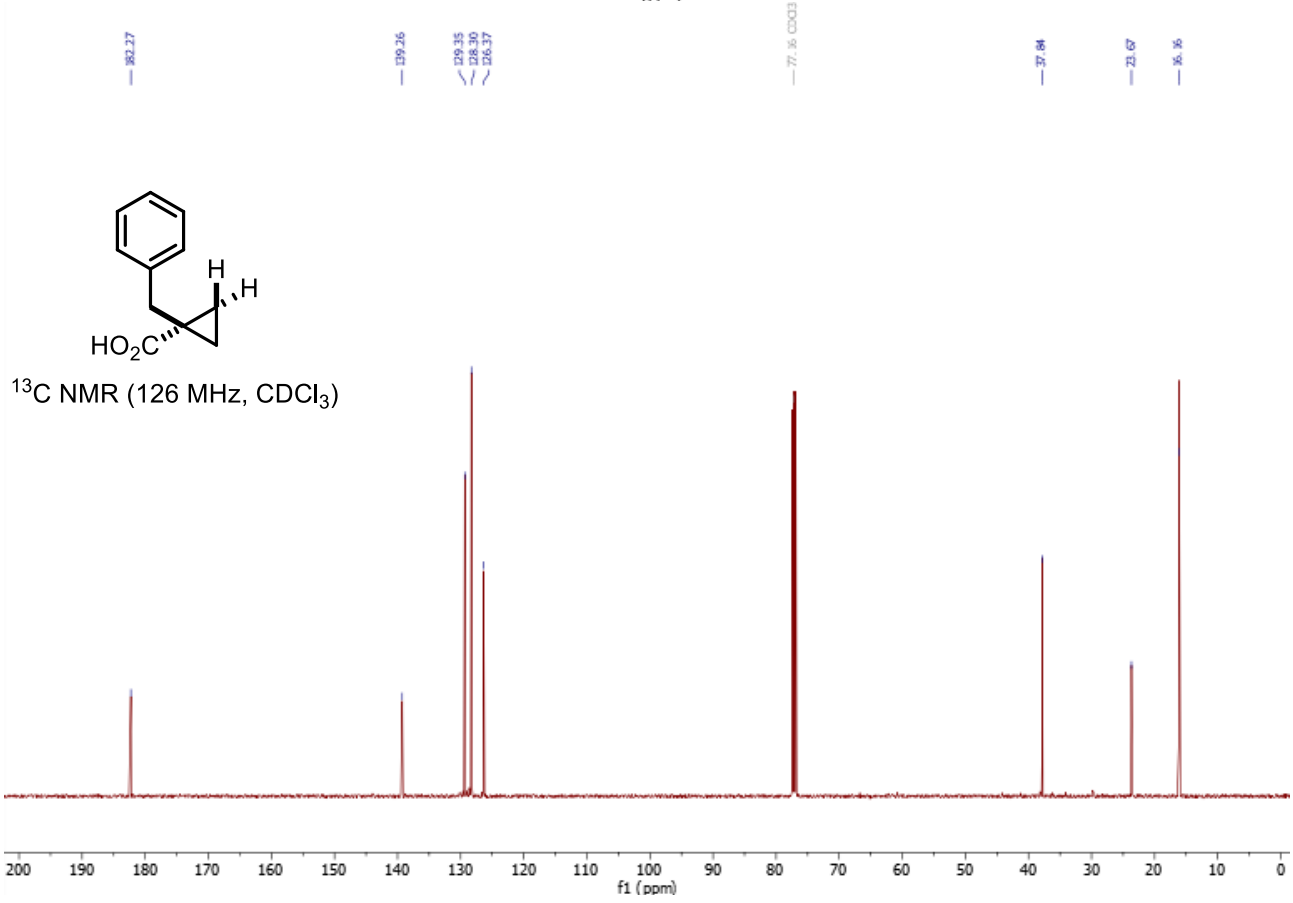


^{13}C NMR (126 MHz, $CDCl_3$)

1-Benzylcyclopropanecarboxylic acid (3x)

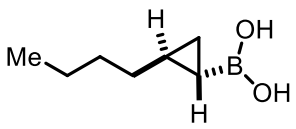


^{1}H NMR (500 MHz, $CDCl_3$)

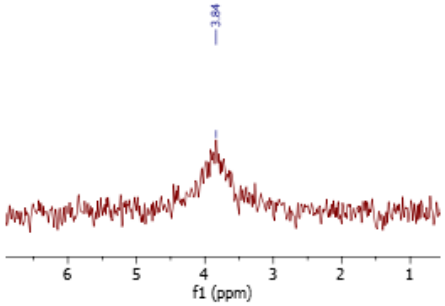


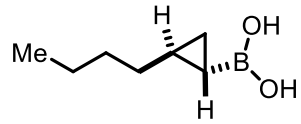
^{13}C NMR (126 MHz, $CDCl_3$)

(±)-(*E*)-(2-Butylcyclopropyl)boronic acid (3y)



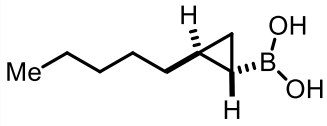
^{1}H NMR (400 MHz, $CDCl_3$)



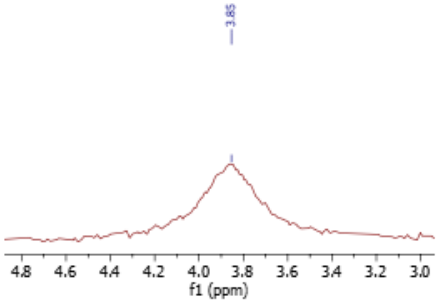


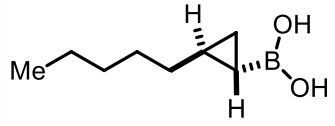
^{13}C NMR (101 MHz, $CDCl_3$)

(±)-(*E*)-(2-Pentylcyclopropyl)boronic acid (3z)



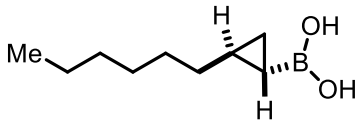
^{1}H NMR (500 MHz, $CDCl_3$)



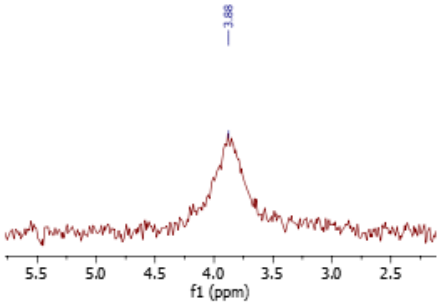


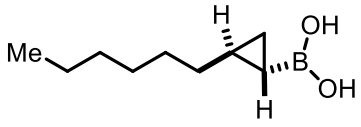
^{13}C NMR (126 MHz, $CDCl_3$)

(±)-(*E*)-(2-Hexylcyclopropyl)boronic acid (3aa)



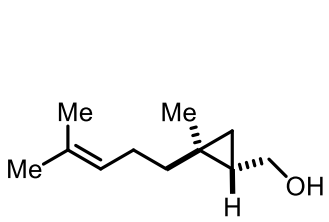
^{1}H NMR (500 MHz, $CDCl_3$)



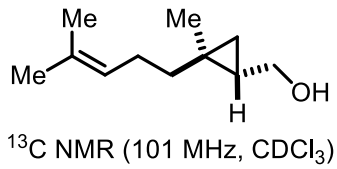


^{13}C NMR (126 MHz, $CDCl_3$)

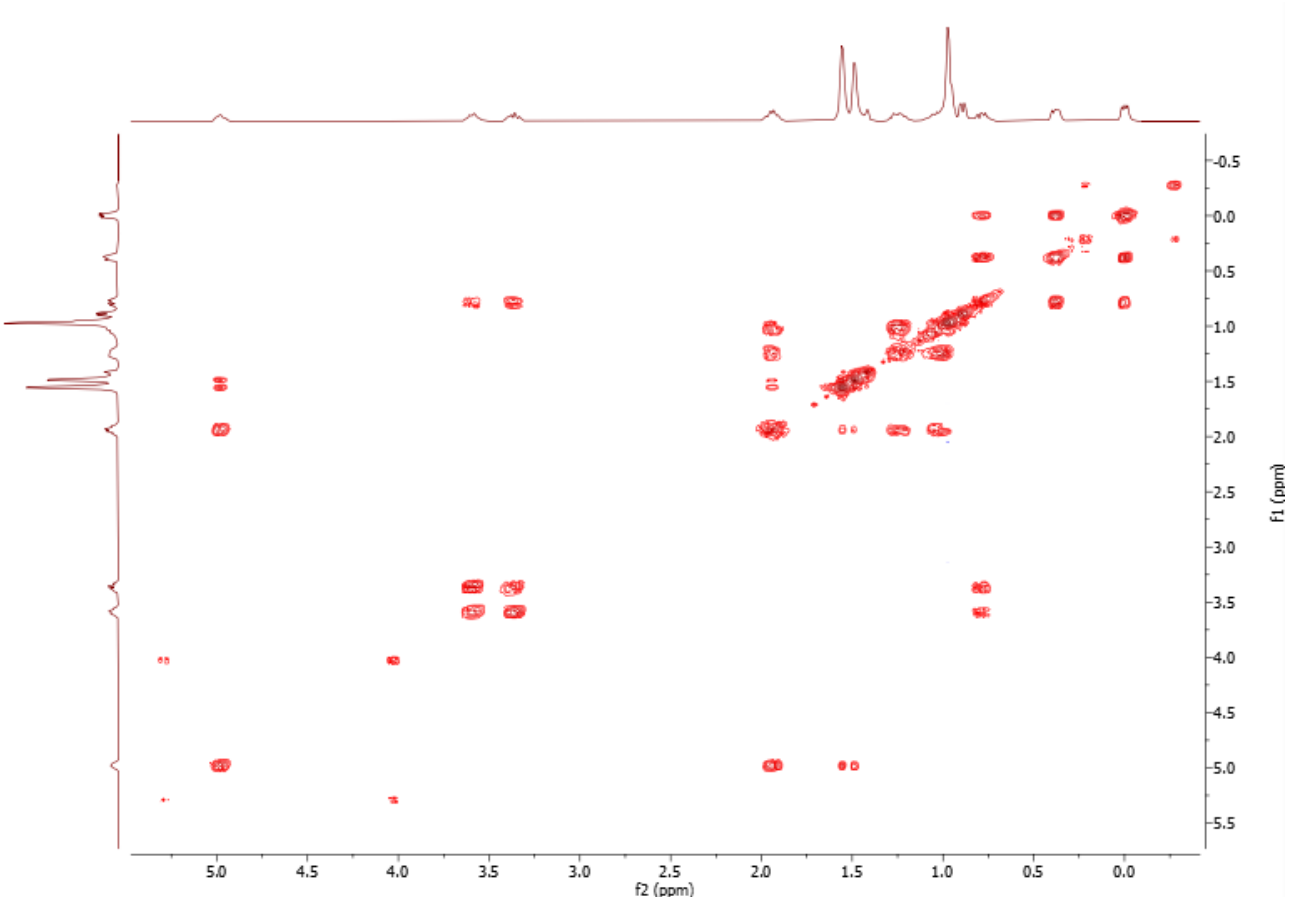
(±)-(*E*)-(2-Methyl-2-(4-methylpent-3-en-1-yl)cyclopropyl)methanol (3ab')

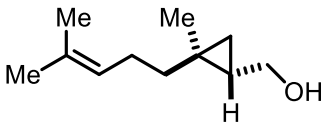


^{1}H NMR (400 MHz, $CDCl_3$)



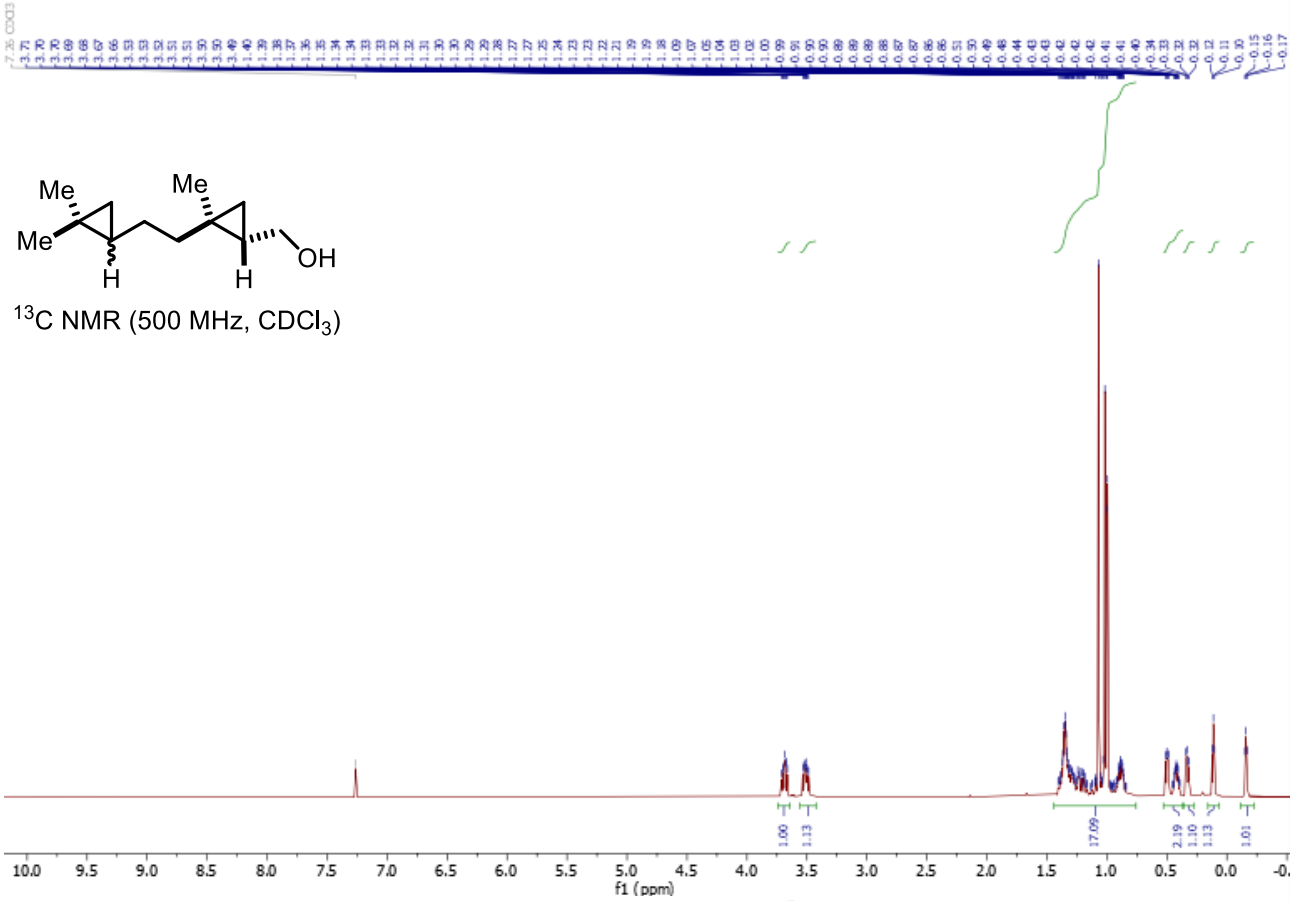
^{13}C NMR (101 MHz, $CDCl_3$)



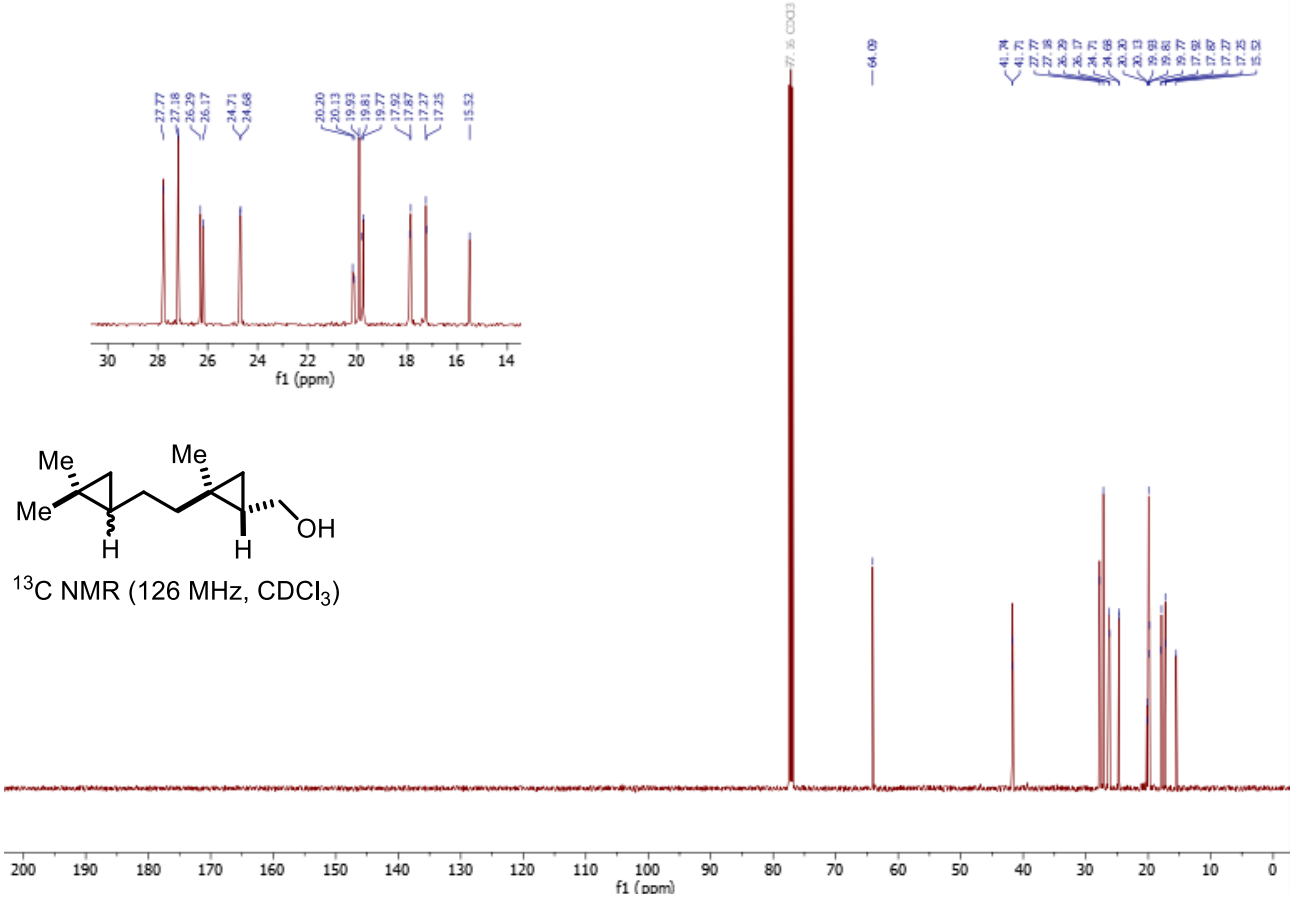


COSY (400 MHz, $CDCl_3$)

***syn-* + *anti*-(±)-(*E*)-(2-(2-(2,2-Dimethylcyclopropyl)ethyl)-2-methylcyclopropyl)methanol (3ab")**

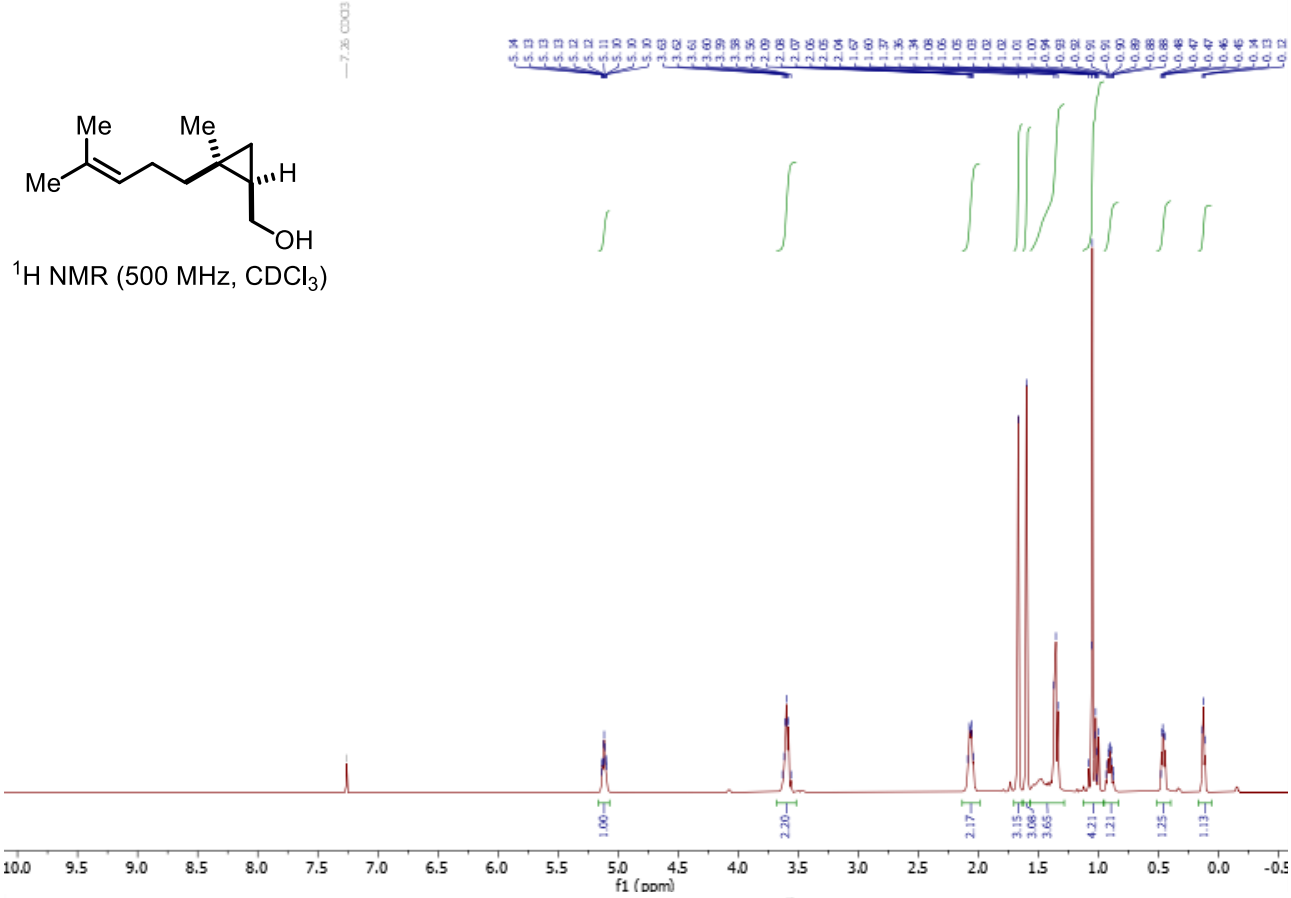


^{13}C NMR (500 MHz, $CDCl_3$)

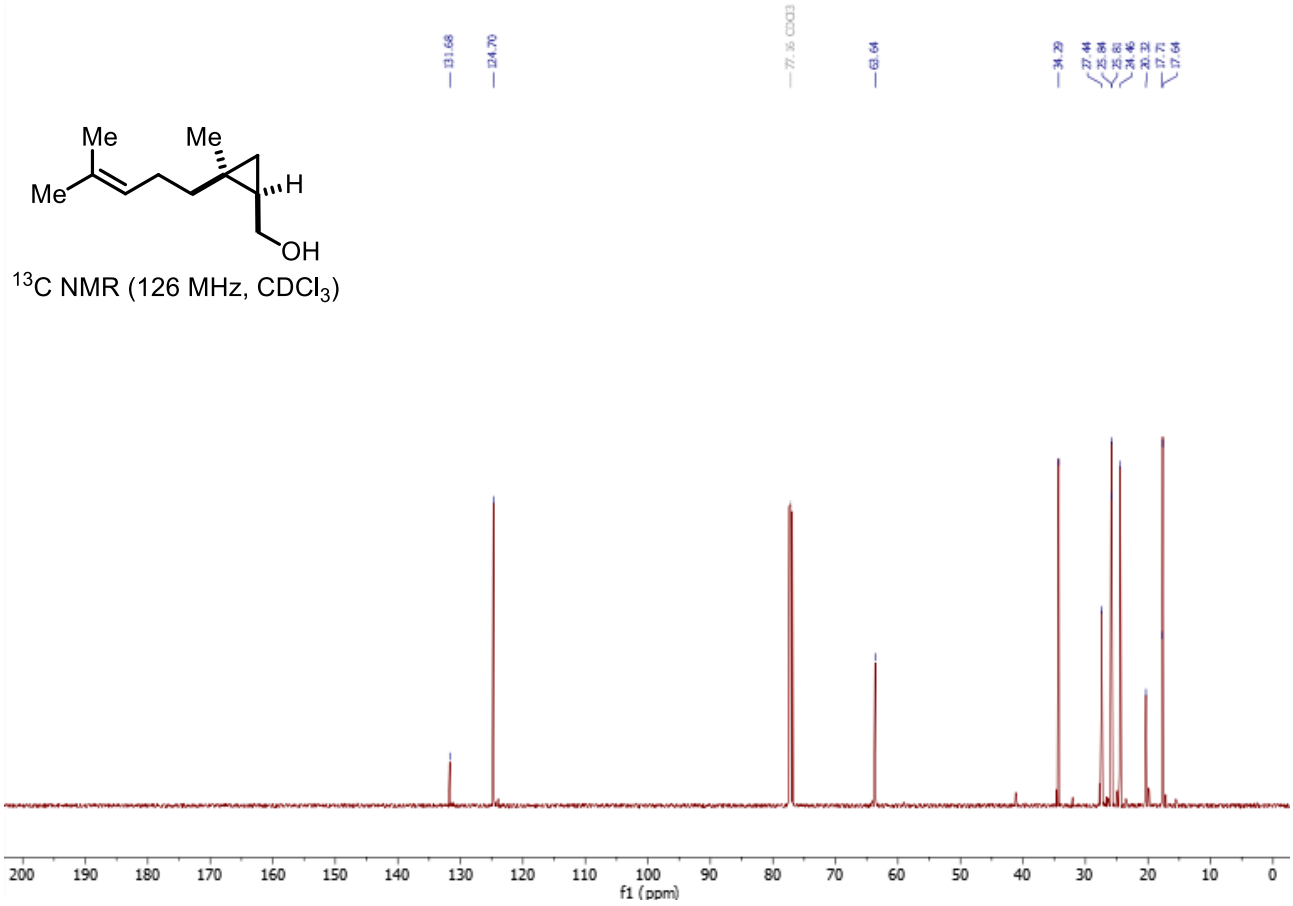


^{13}C NMR (126 MHz, $CDCl_3$)

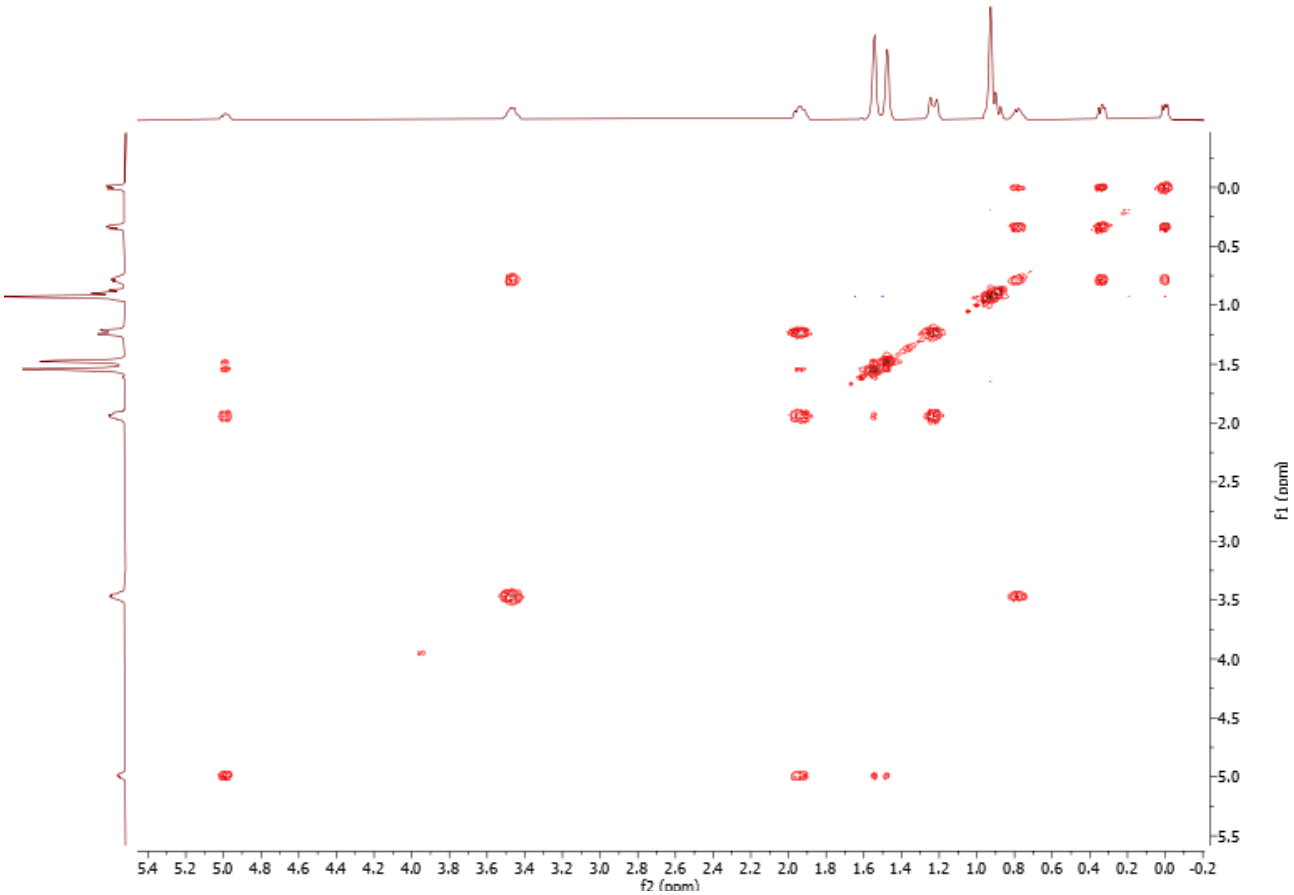
(±)-(*Z*)-(2-Methyl-2-(4-methylpent-3-en-1-yl)cyclopropyl)methanol (3ac')

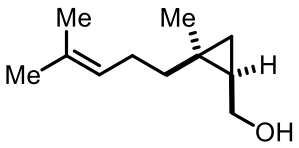


^{1}H NMR (500 MHz, $CDCl_3$)



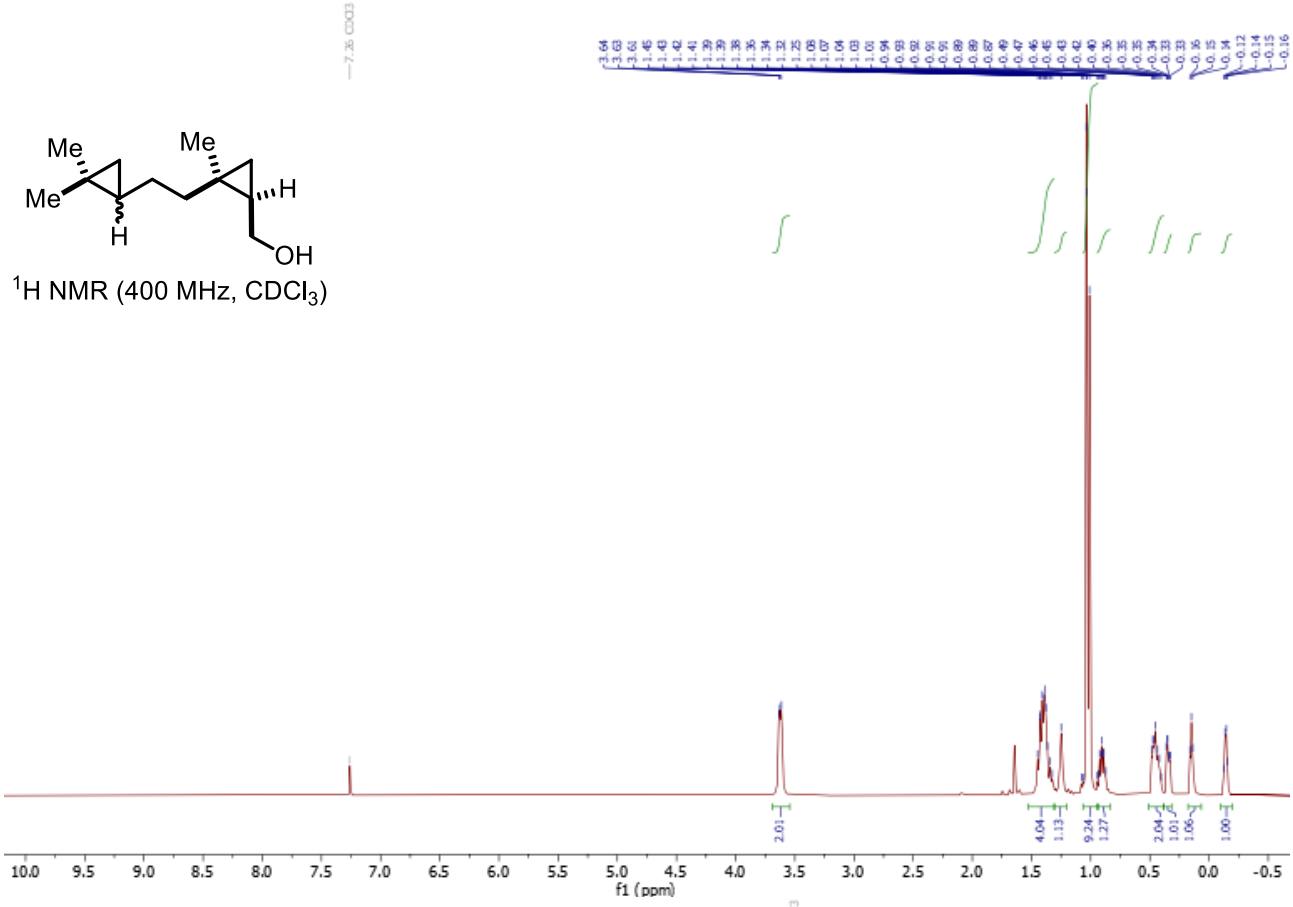
^{13}C NMR (126 MHz, $CDCl_3$)



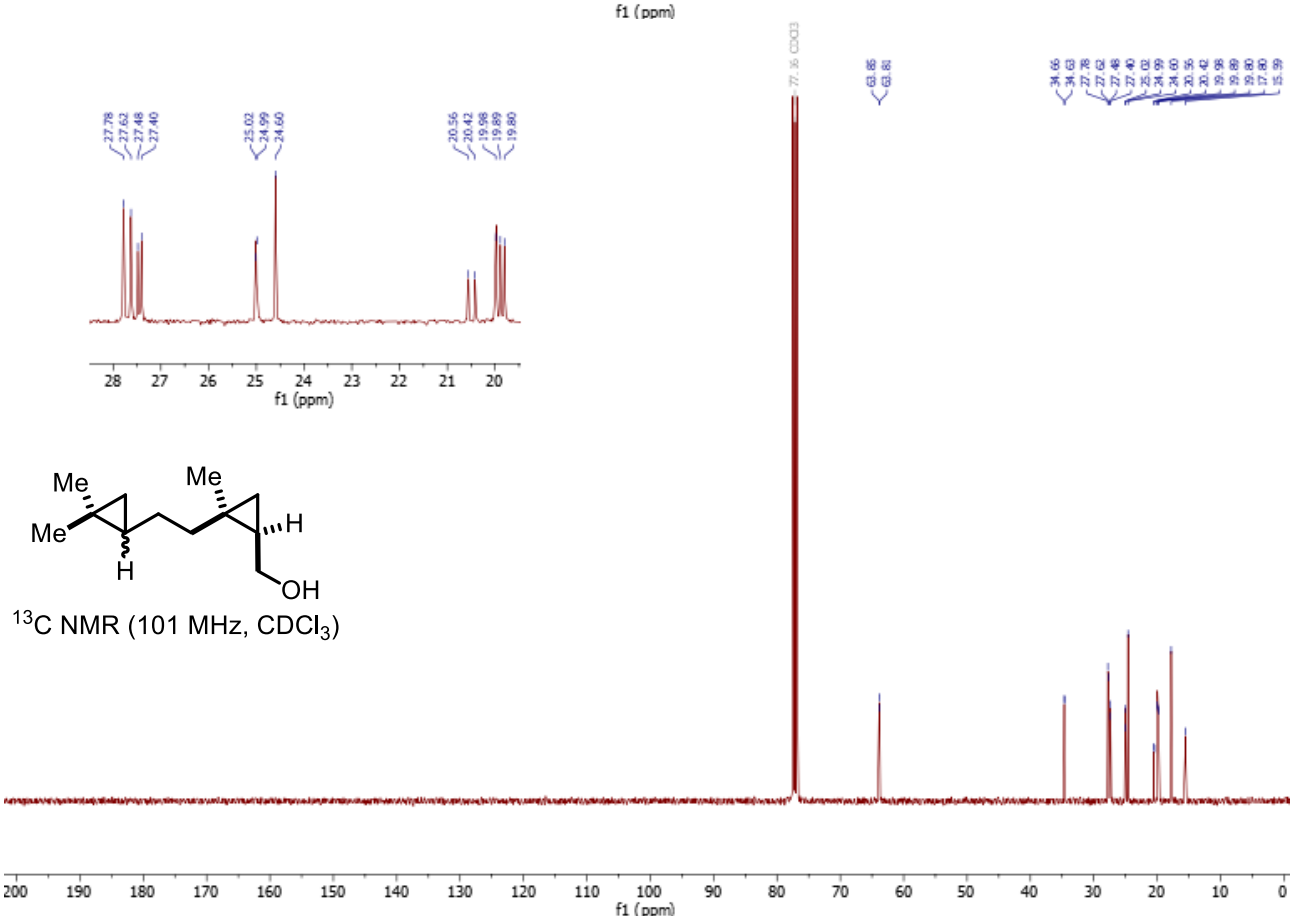


COSY (500 MHz, $CDCl_3$)

***syn-* + *anti*-(±)-(*Z*)-(2-(2-(2,2-Dimethylcyclopropyl)ethyl)-2-methylcyclopropyl)methanol (3ac")**

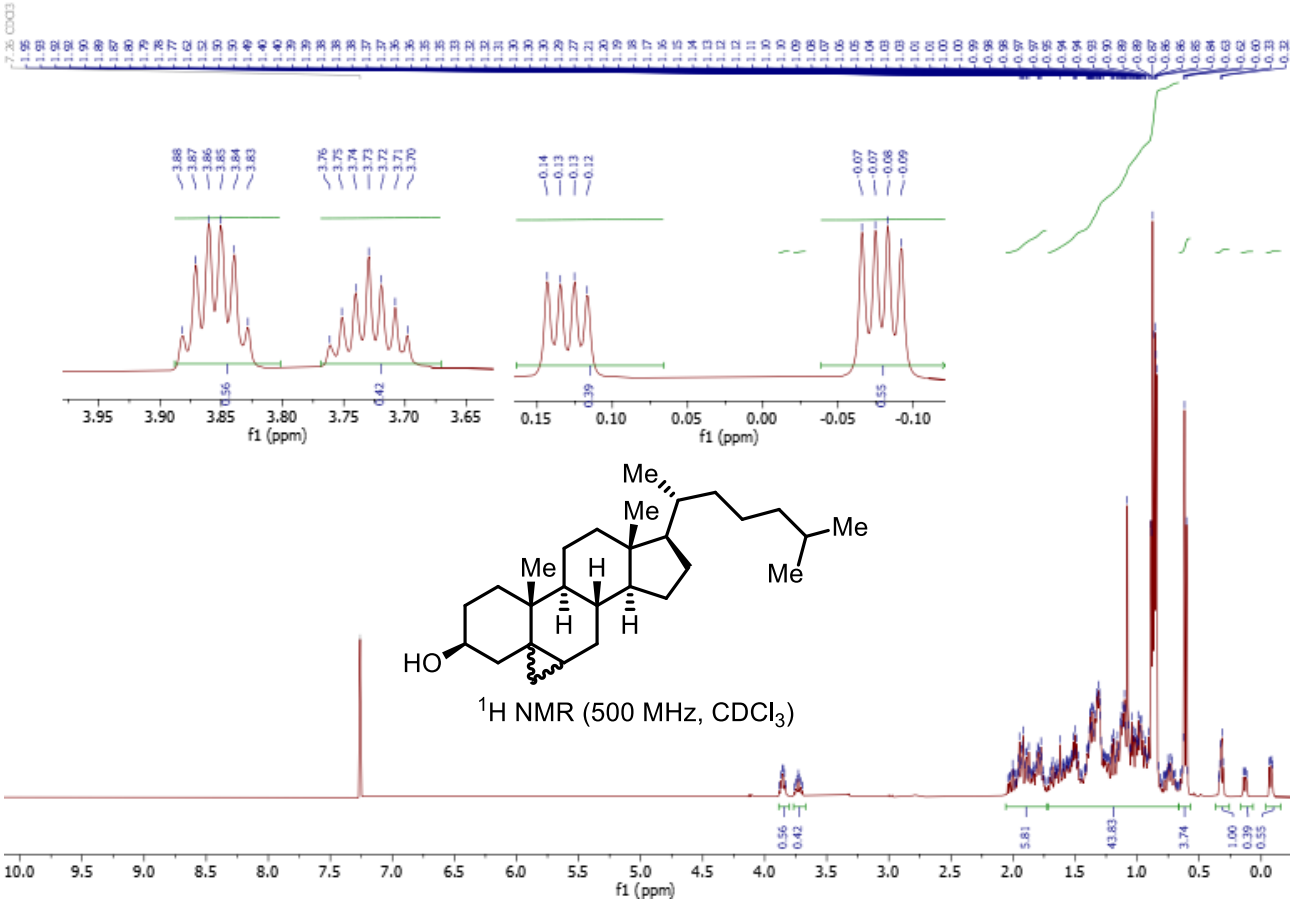


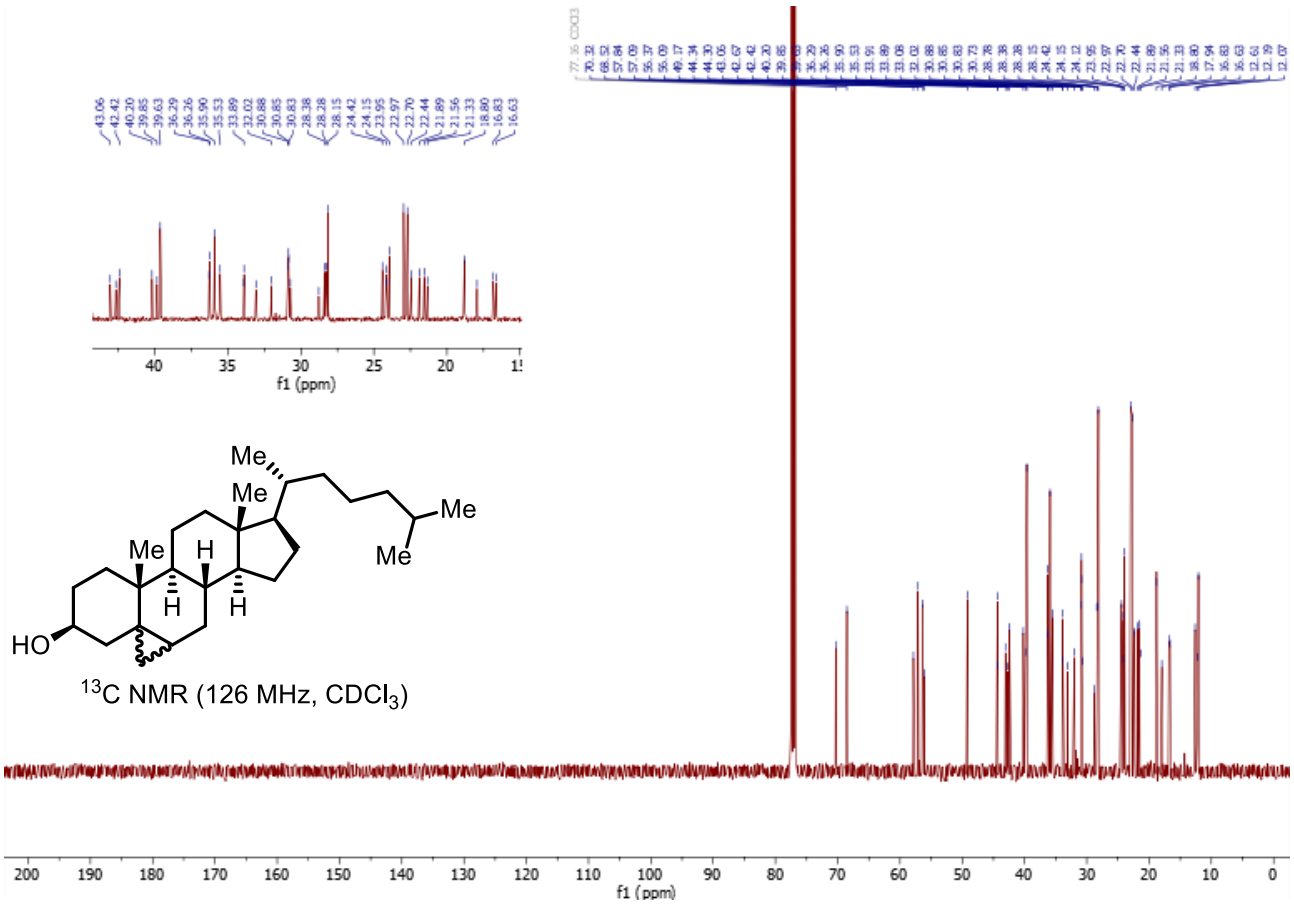
^{1}H NMR (400 MHz, $CDCl_3$)



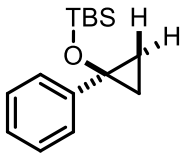
^{13}C NMR (101 MHz, $CDCl_3$)

5α,6α- + 5β,6β-Cyclopropa-[5,6]-cholest-5-en-3β-ol (3ad)

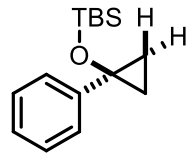




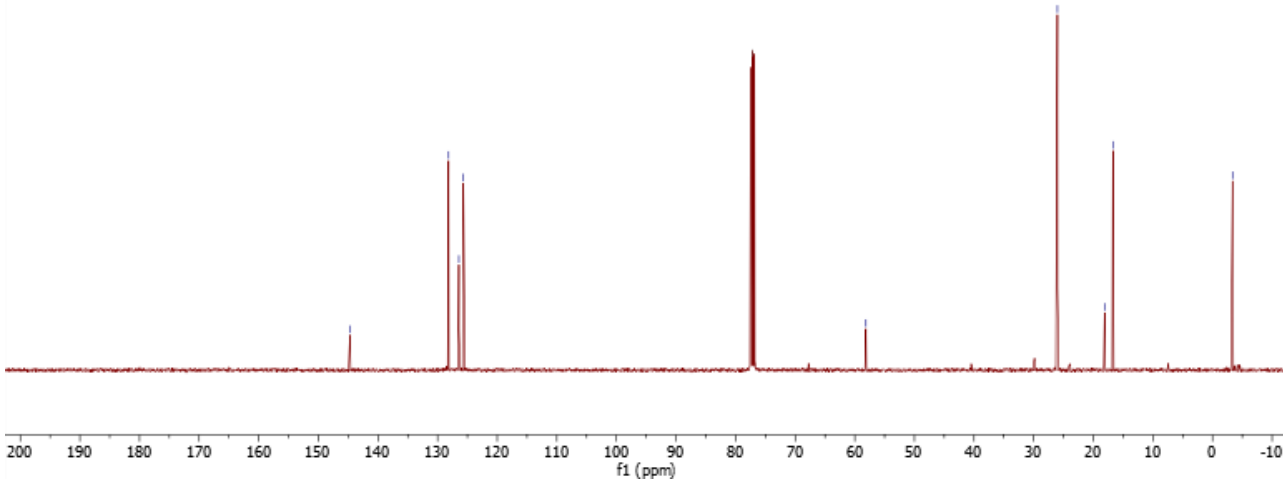
***tert*-Butyldimethyl(1-phenylcyclopropoxy)silane (3n)**



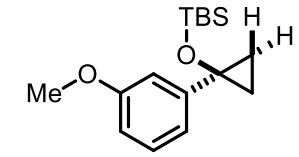
^{1}H NMR (400 MHz, $CDCl_3$)



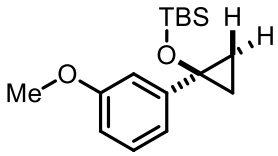
^{13}C NMR (101 MHz, $CDCl_3$)



***tert*-Butyl(1-(3-methoxyphenyl)cyclopropoxy)dimethylsilane (3o)**

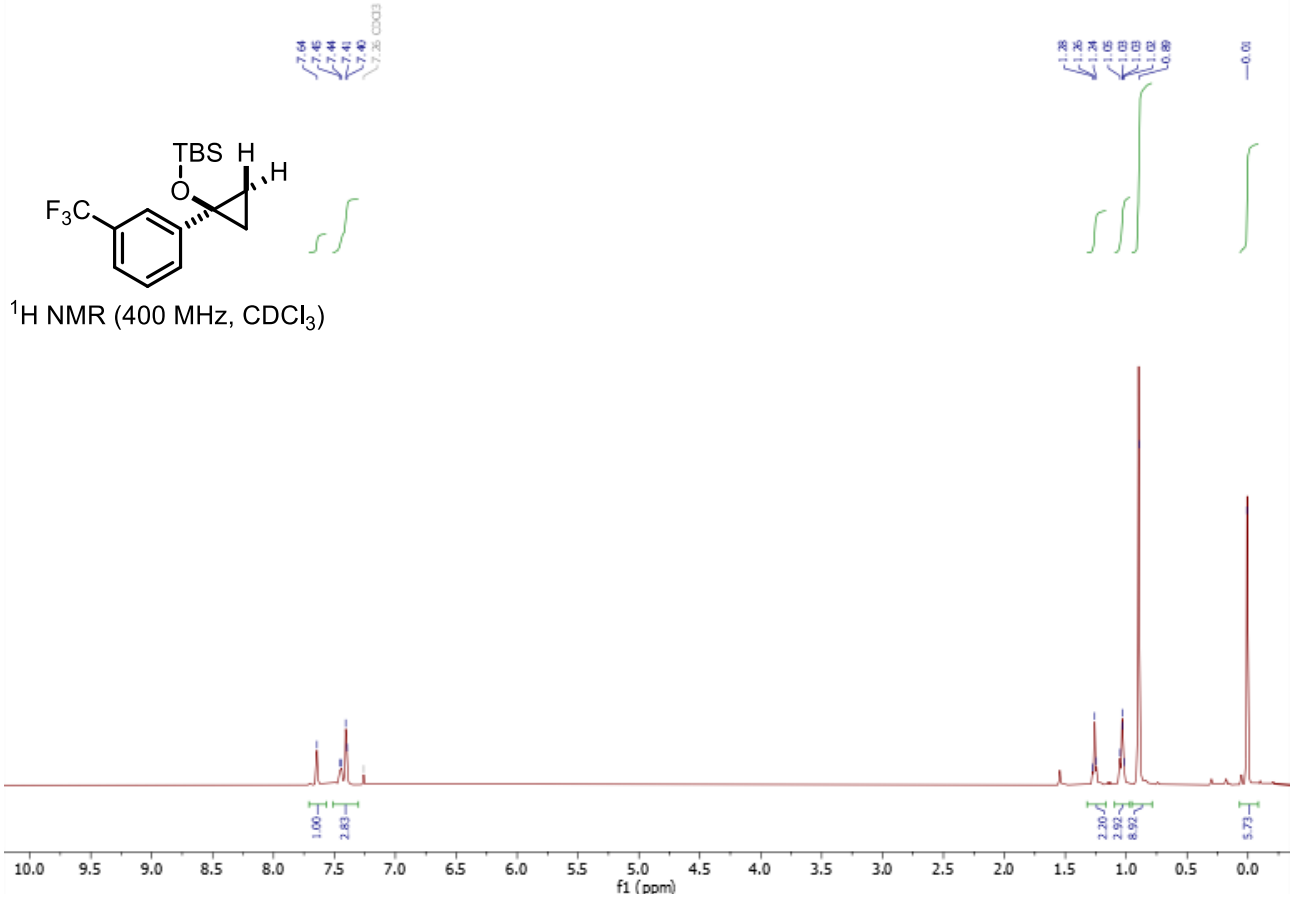


^{1}H NMR (400 MHz, $CDCl_3$)

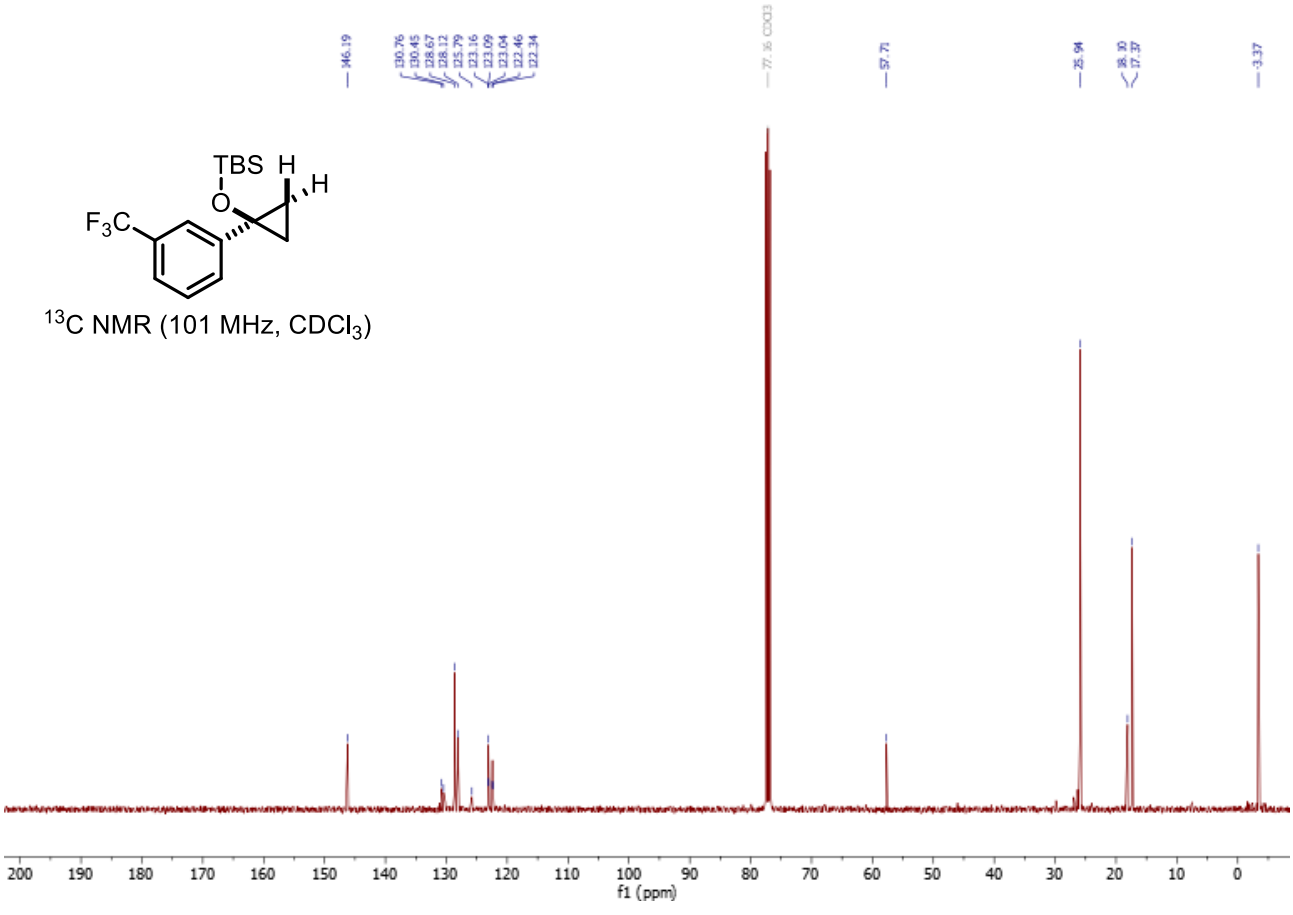


^{13}C NMR (101 MHz, $CDCl_3$)

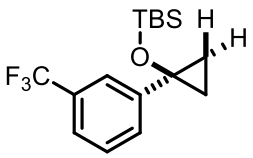
***tert*-Butyldimethyl(1-(3-(trifluoromethyl)phenyl)cyclopropoxy)silane (3p)**



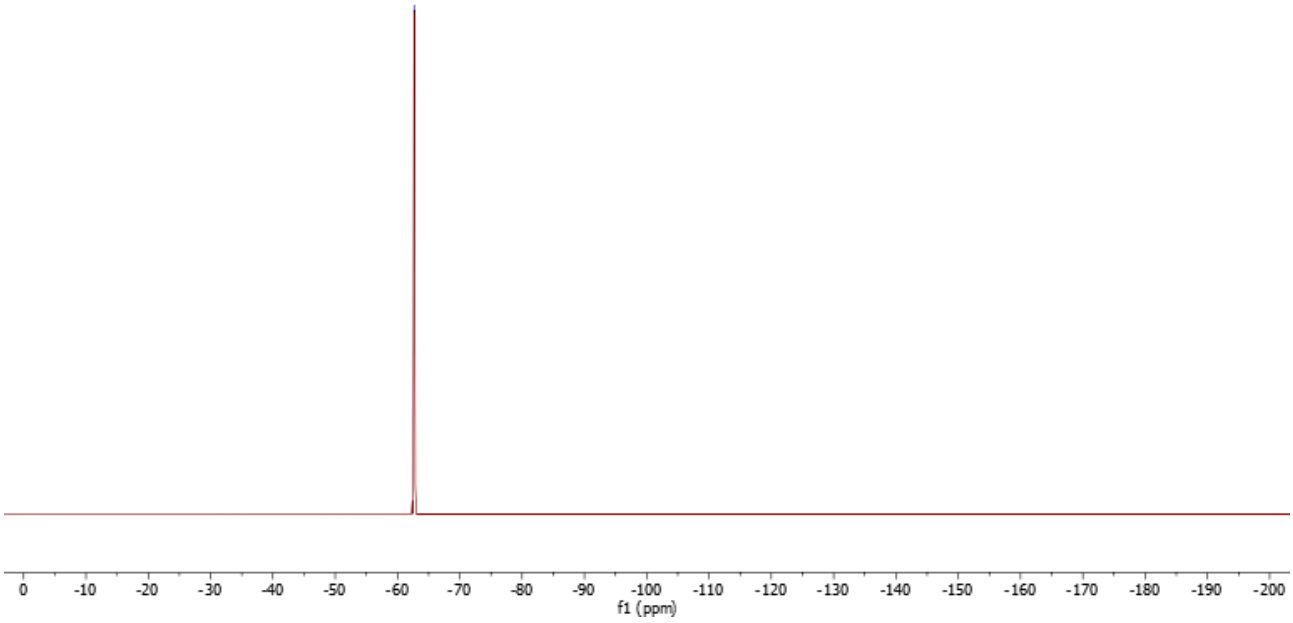
^{1}H NMR (400 MHz, $CDCl_3$)



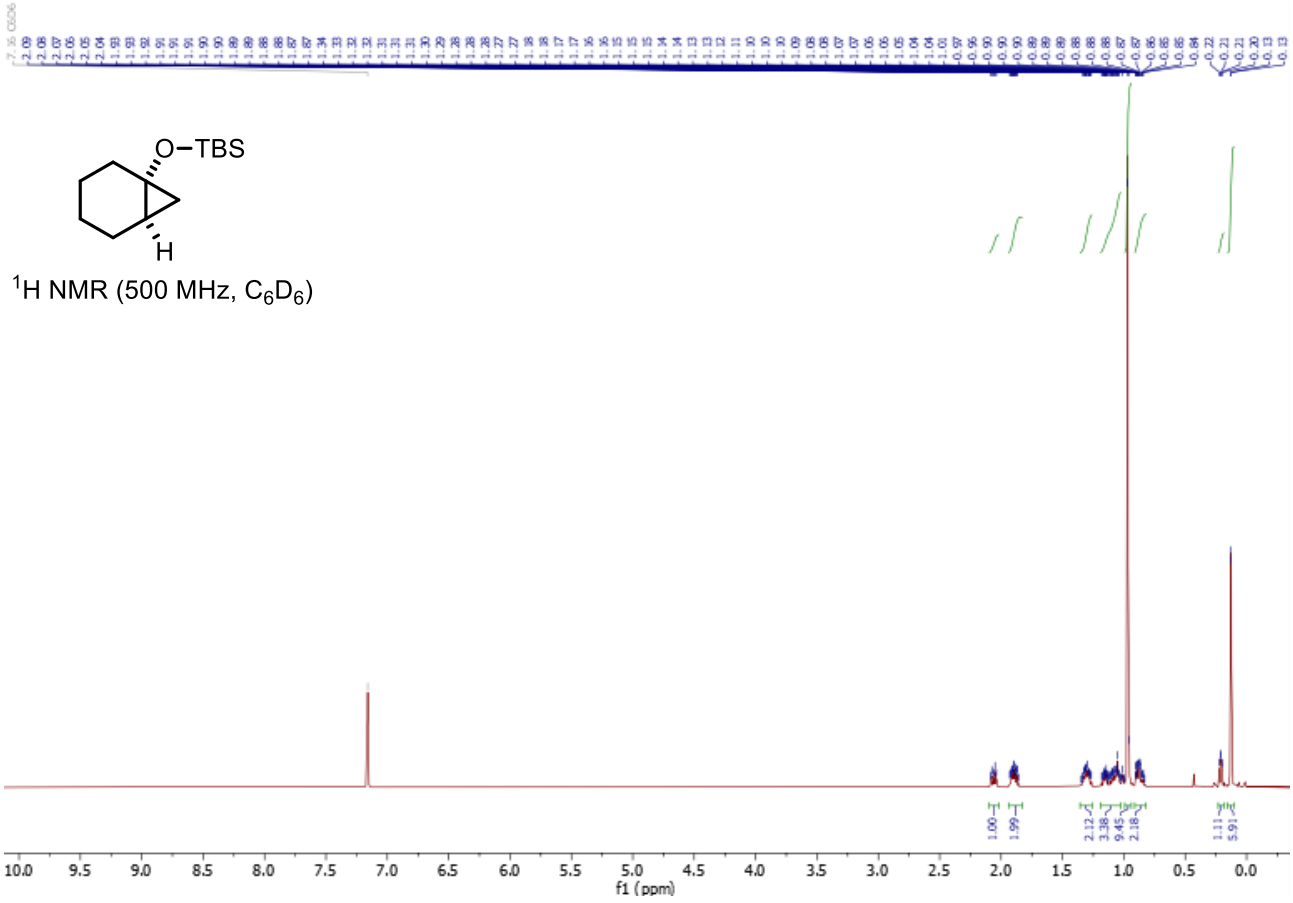
^{13}C NMR (101 MHz, $CDCl_3$)



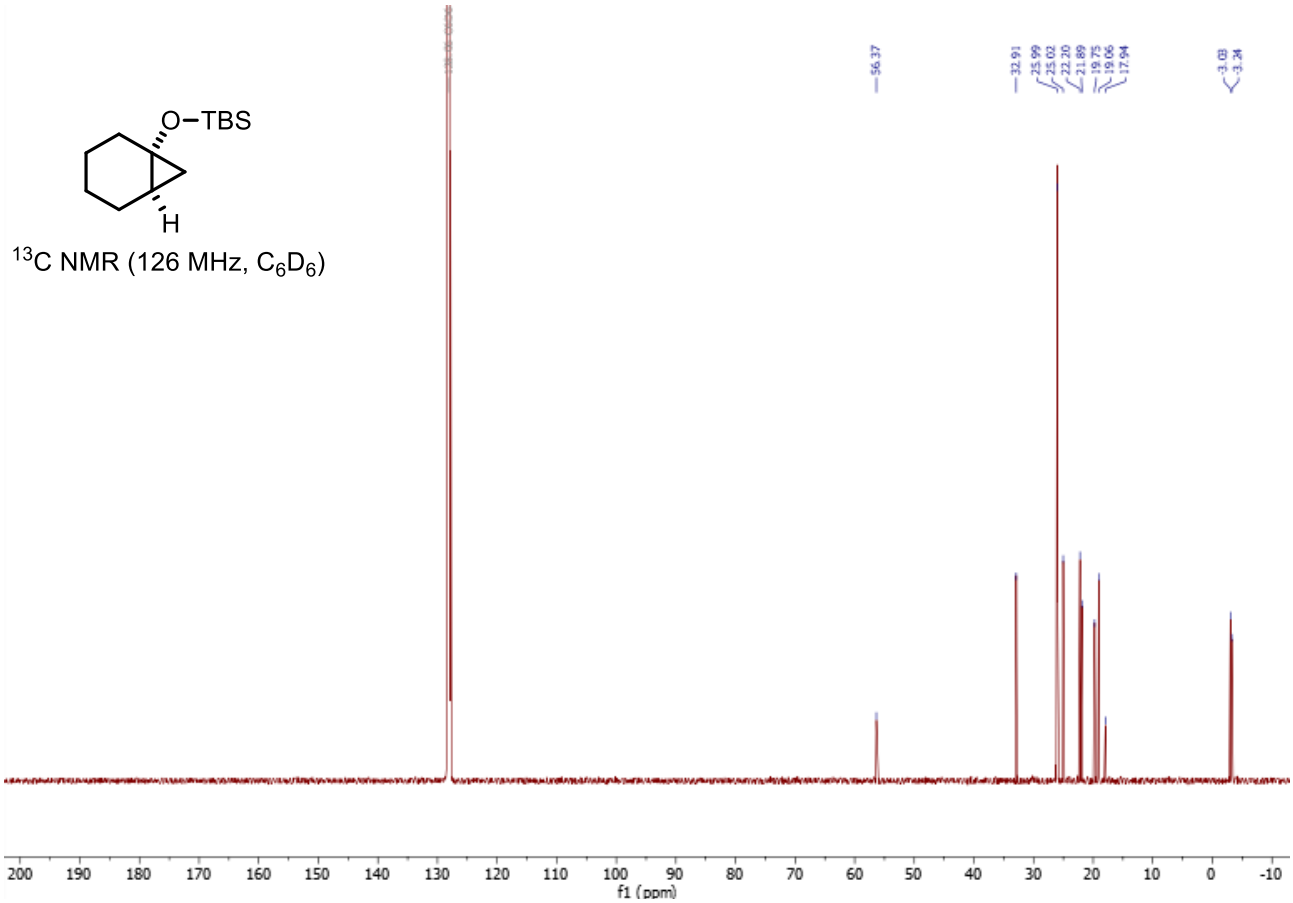
^{19}F NMR (659 MHz, $CDCl_3$)



(±)-(bicyclo[4.1.0]heptan-1-yloxy)(*tert*-butyl)dimethylsilane (3q)

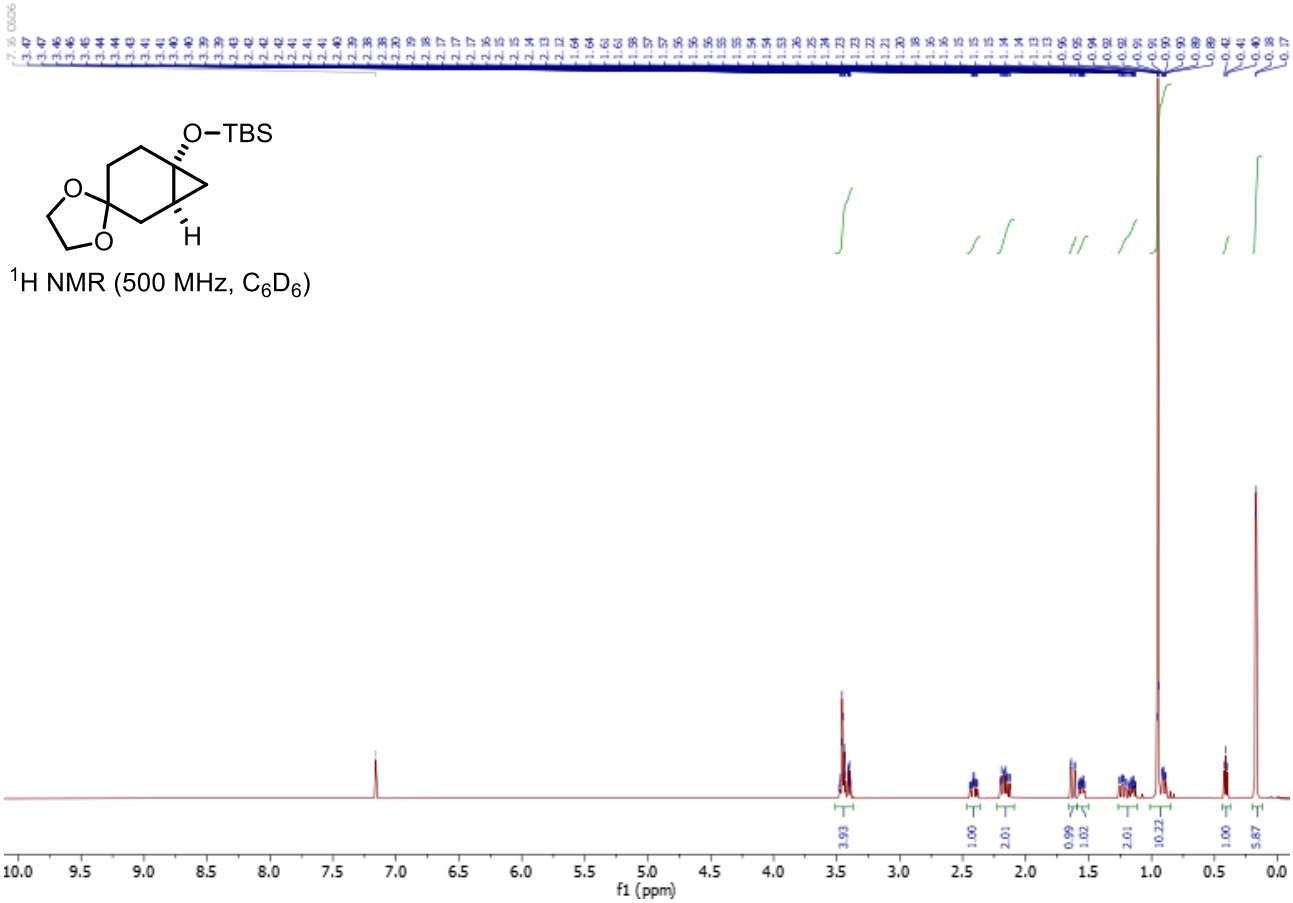


^{1}H NMR (500 MHz, C_6D_6)

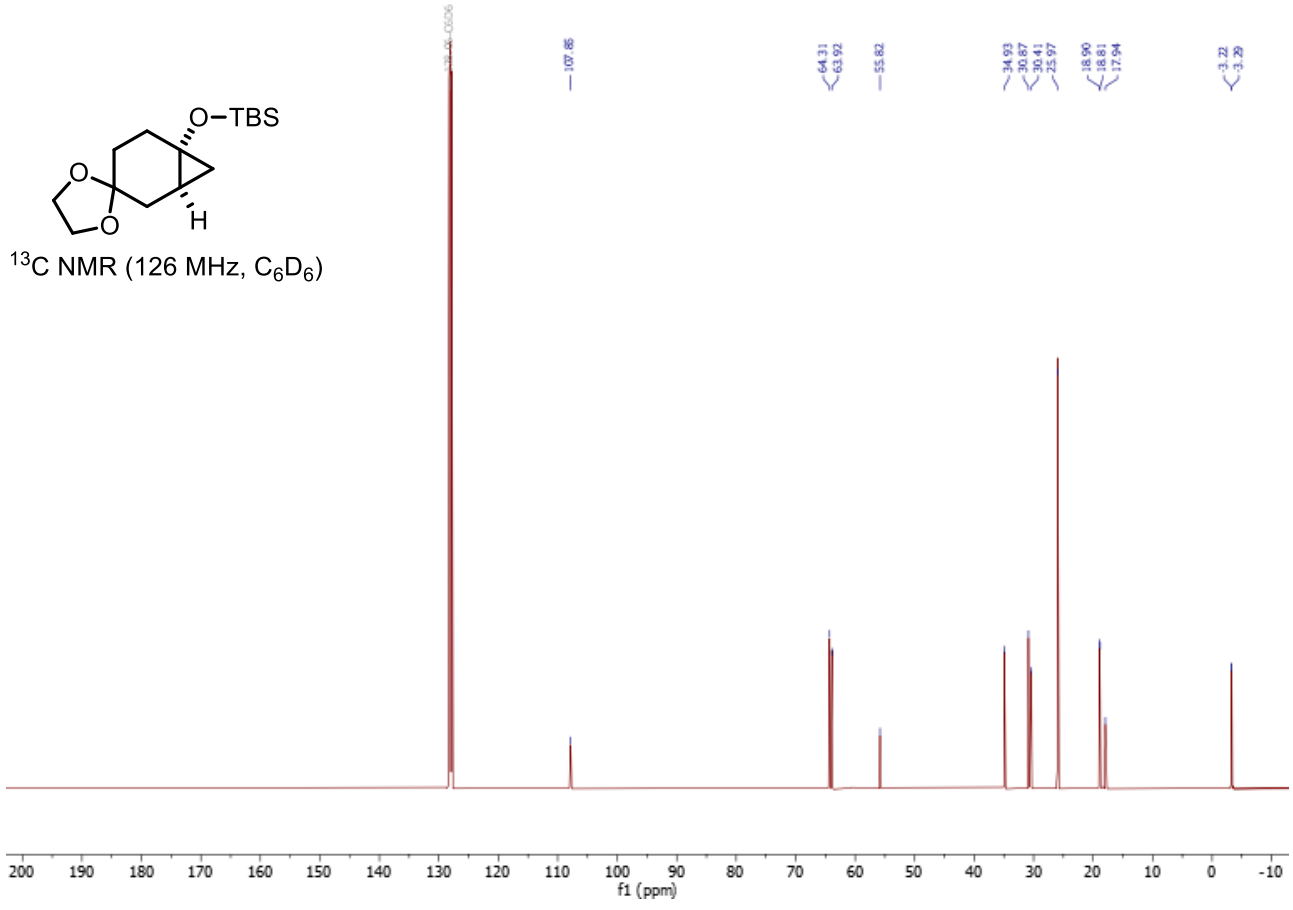


^{13}C NMR (126 MHz, C_6D_6)

(±)-*tert*-Butyldimethyl(spiro[bicyclo[4.1.0]heptane-3,2'-[1,3]dioxolan]-6-yloxy)silane (3r)

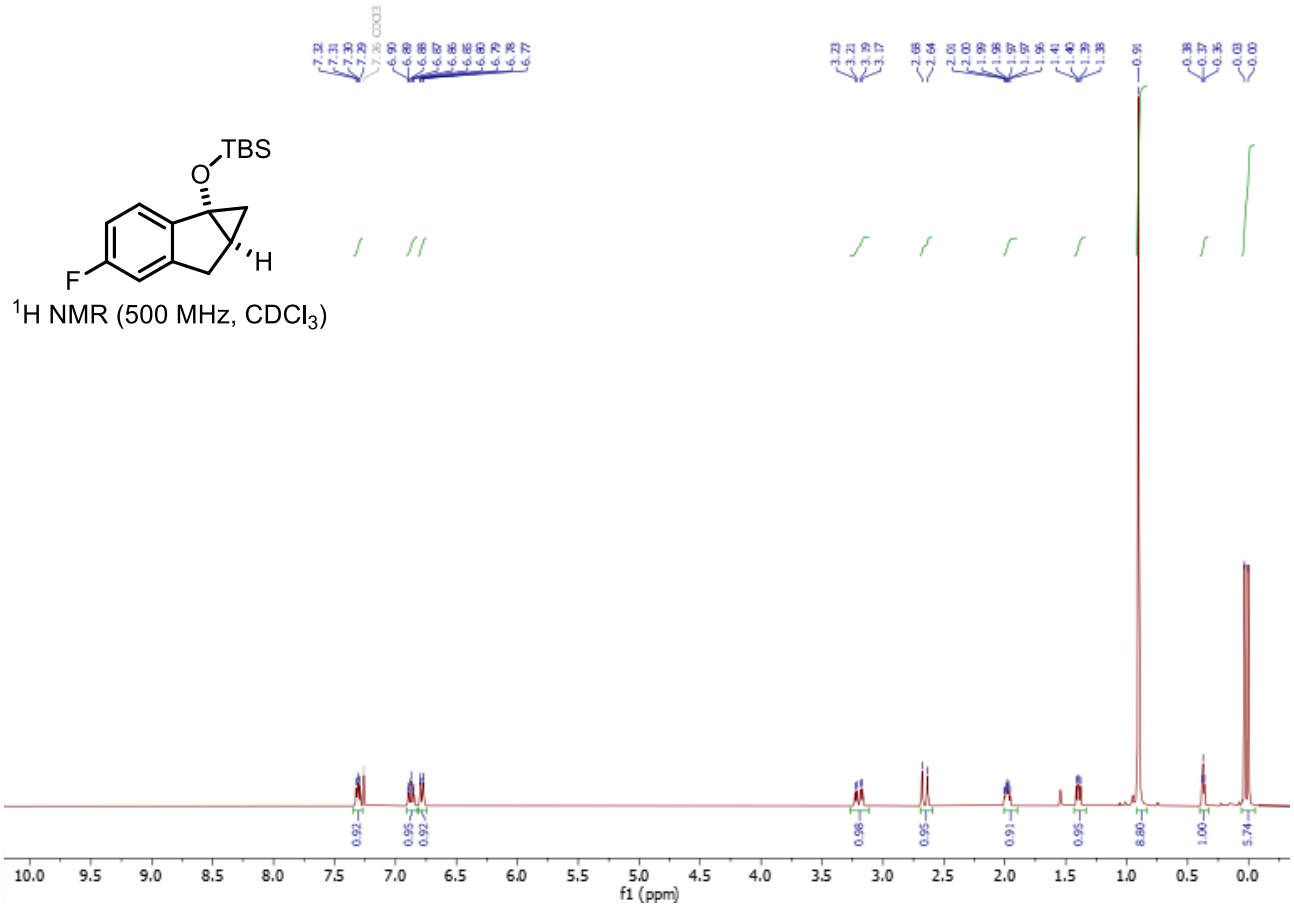


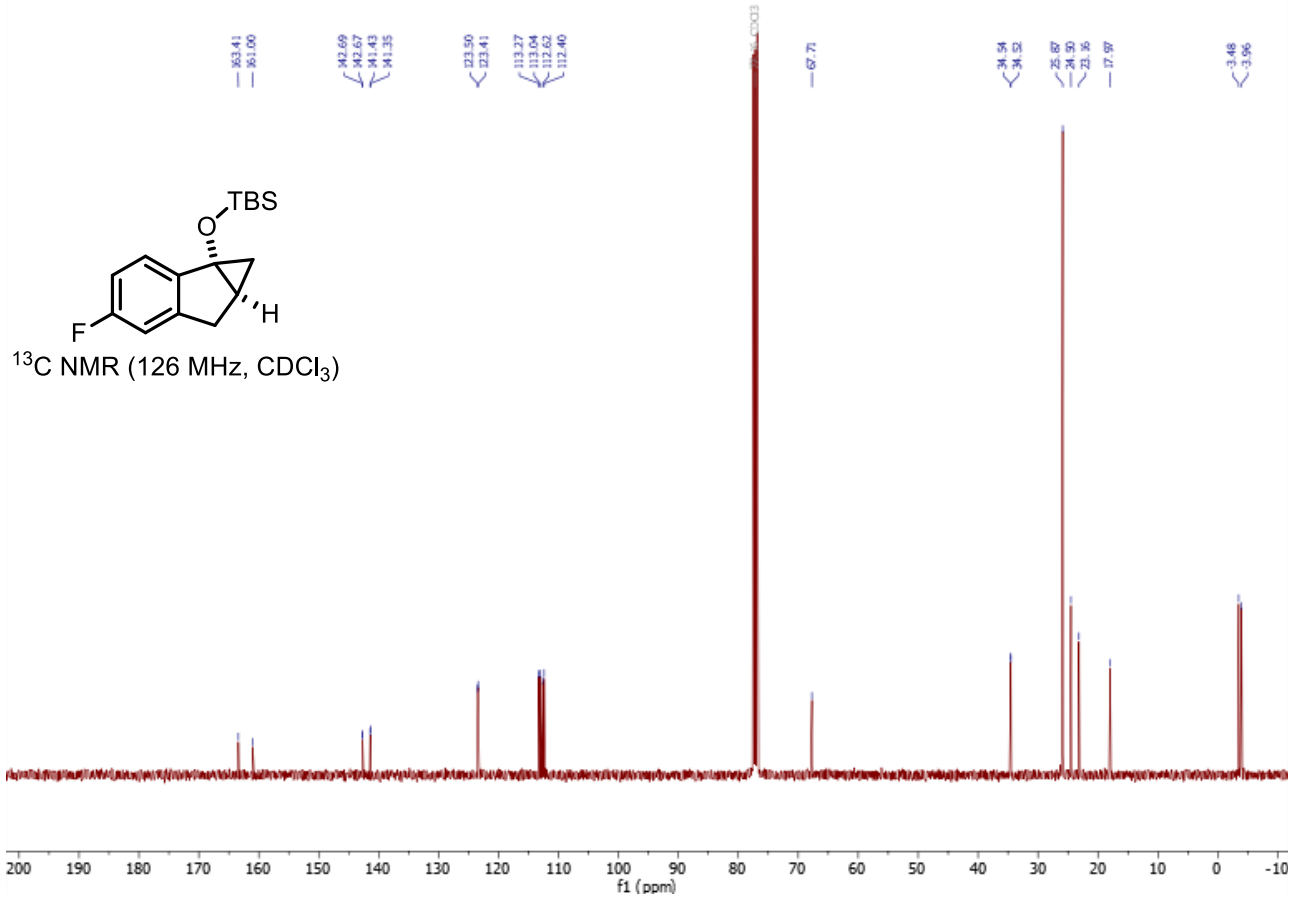
^{1}H NMR (500 MHz, C_6D_6)

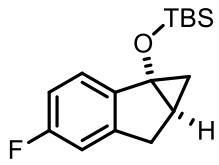


^{13}C NMR (126 MHz, C_6D_6)

(±)-*tert*-Butyl((-4-fluoro-1,1a,6,6a-tetrahydrocyclopropa[a]inden-1a-yl)oxy)dimethylsilane (3t)







^{19}F NMR (659 MHz, $CDCl_3$)

9. References

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