SUPPORTING INFORMATION

General Synthesis of Cyclopropanols via Organometallic Addition to 1-Sulfonylcyclopropanols as Cyclopropanone Precursors

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TABLE OF CONTENT OF THE SUPPORTING INFORMATION

GENERAL EXPERIMENTAL CONDITIONS

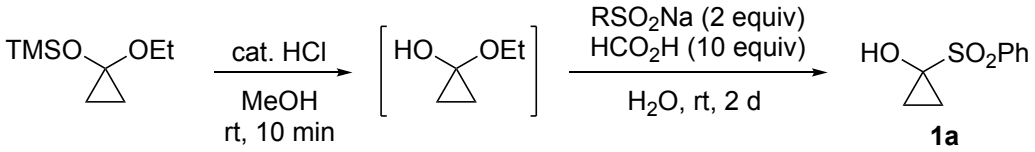
General: Unless stated otherwise, all non-aqueous reactions were performed in oven-dried glassware sealed with microwave caps or rubber septa under a nitrogen or argon atmosphere and were stirred with Teflon-coated magnetic stir bars.[1] Liquid reagents and solvents were transferred via syringe using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O), methanol (MeOH) were dried by passage over a column of activated alumina (JC Meyers Solvent System). Anhydrous 1,4-dioxane, *tert*-butyl methyl ether (*t*-BuOMe), and diisopropyl ether (*i*-Pr_2O) were obtained in Sure Seal bottles from Aldrich and used as received. Anhydrous 1,2-dimethoxyethane (DME) was obtained in Sure Seal bottles from Acros Organics and used as received. All other solvents were used as received unless otherwise noted. Thin layer chromatography (TLC) was performed using Silicycle silica gel 60 F-254 precoated plates (0.25 mm) and visualised by UV irradiation, potassium permanganate or iodine stain. Flash chromatography was performed on a Biotage Isolera One. Sorbent silica gel (particle size 40-63 μm) was used for flash chromatography of the indicated solvent system according to standard techniques.[2] Nuclear magnetic resonance (NMR) spectra (^1H, ^{13}C) were recorded on Bruker spectrometers operating at 600 or 700 MHz for ^1H and 150 or 175 MHz for ^{13}C experiments. Chemical shifts (δ) for ^1H NMR spectra are recorded in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, and integration. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million (ppm) from tetramethylsilane using the central peak of chloroform (δ 77.16 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. Only selected ^1H and ^{13}C spectra are reported. Infrared (IR) spectra were collected on a Thermo Scientific Nicolet iS5 FTIR instrument using attenuated total reflectance (ATR) mode and signals are reported in reciprocal centimeters (cm^{-1}). Only selected IR frequencies are reported. High-resolution mass spectral data (HRMS) were obtained from the NC State University Molecular Education, Technology and Research Innovation Center (METRIC), on a Thermo Fisher Scientific Exactive Plus (ion trap mass analyzer, Orbitrap™) using HESI. Melting Points were taken in a Mettler Toledo apparatus, Model MP50. Enantiomeric excess was determined by HPLC analysis (Agilent Technologies 1100 series, normal phase) using a chiral stationary phase. Optical rotations were determined with a Jasco P-2000 polarimeter at 598 nm. Data are reported as follows $[\alpha]_D^{temp}$, concentration (c in g/100 mL), and solvent.

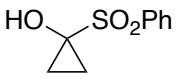
Reagents: Anhydrous $ZnCl_2$, (1-ethoxycycloproxy)trimethylsilane, $PhSO_2Na$, HCO_2H, HCl (5-6N in *i*-PrOH), (*R*)-(+)-propylene oxide, BsCl, BF_3•OEt_2, trimethylsilylmethylmagnesium chloride (1.3 M in THF), methylmagnesium bromide (3.2 M in 2-methyl-THF), *o*-tolylmagnesium chloride (1.4 M in THF/toluene), phenylacetylene, anhydrous lithium chloride, hexylmagnesium bromide (2 M in Et_2O), 4-(*N*,*N*-dimethylamino)phenylmagnesium bromide (0.5 M in THF), benzylmagnesium chloride (2.0 M in THF), 4-methoxyphenylmagnesium bromide (0.5 M in THF), mesitylmagnesium bromide (1.0 M in THF), 3,5-bis(trifluoromethyl)phenylmagnesium bromide (0.5 M in THF), 4-fluorophenylmagnesium bromide (1.0 M in THF), 3-methoxyphenylmagnesium bromide (1.0 M in THF), phenylethynylmagnesium bromide (1.0 M in THF), 2-thienylmagnesium bromide (1.0 M in THF), phenylmagnesium bromide (3.0 M in Et_2O), *n*-BuLi (2.5 M in Hexanes), $Cu(OAc)_2$•H_2O, $PhSO_2Na$, (bromoethynyl)benzene, diethylzinc solution (1M) and CuCN•2LiCl were purchased from commercial sources and used as received. Other Grignard reagents were prepared[3] and titrated[4] according to literature procedures prior to use (see specific procedure, page S7).

1. Shriver, D. F.; Drezdzon, M. A. *The manipulation of air-sensitive compounds*. Wiley: New York; Chichester, 1986.
2. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.
3. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *A Small Scale Approach to Organic Laboratory Techniques*. Mary Finch: Belmont, 2011.
4. Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 0890-0891.

EXPERIMENTAL PROCEDURES AND CHARACTERIZATION DATA

Synthesis of 1-sulfonylcyclopropanols 1a-1c used as starting materials

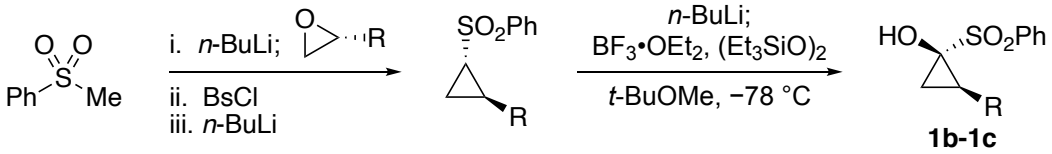


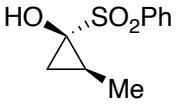


1-(phenylsulfonyl)cyclopropanol (1a) was prepared according to a previously reported procedure.[5] A flame-dried microwave vial was charged with (1-ethoxycycloproxy)trimethylsilane (500 mg, 2.87 mmol, 1.0 equiv) and dry MeOH (1.5 mL). HCl (1 drop, 5-6 N solution in *i*-PrOH) was added, and the reaction was stirred at room temperature for 10 minutes and monitored by TLC (10% EtOAc in hexanes, R_f = 0.3). To the resulting solution containing the cyclopropanone hemiketal intermediate in methanol was successively added H_2O (3.0 mL), sodium benzenesulfinate (942 mg, 5.74 mmol, 2.0 equiv) and formic acid (1.08 ml, 28.7 mmol, 10 equiv). After stirring at room temperature for 48 hours, H_2O was added and the reaction mixture was extracted three times with CH_2Cl_2, the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under vacuum, affording the pure 1-sulfonylcyclopropanol **1a** (523 mg, 92%) as a white solid which was used without further purification.

On gram scale: Starting with (1-ethoxycycloproxy)trimethylsilane (4.0 g, 22.9 mmol, 1.0 equiv), sodium benzenesulfinate (7.5 g, 45.8 mmol, 2.0 equiv), HCl (5 drops, 5-6N in *i*-PrOH) and formic acid (8.64 mL, 229.0 mmol, 10 equiv), affording 1-sulfonylcyclopropanol **1a** (4.1 g, 90%) as a white solid. All analyses were consistent with the previously reported data.[6]

5. Poteat, C. M.; Jang, Y.; Jung, M.; Johnson, J. D.; Williams, R. G.; Lindsay, V. N. G. *Angew. Chem. Int. Ed.* **2020**. DOI: 10.1002/anie.202006786.
6. Liu, J.; An, Y.; Jiang, H.-Y.; Chen, Z. *Tetrahedron Lett.* **2008**, *3*, 490-494.

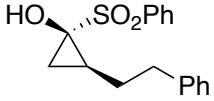




(1*S*,2*S*)-2-methyl-1-(phenylsulfonyl)cyclopropan-1-ol (1b) was prepared according to a previously reported procedure.[5] To an oven-dried 50 mL round-bottomed flask containing a solution of methyl phenyl sulfone[7] (500 mg, 3.20 mmol, 1.0 equiv) in dry THF (20 mL) under N_2 was added *n*-BuLi (1.3 mL (2.5M solution in hexanes), 3.36 mmol, 1.05 equiv) dropwise at –78 °C and stirred for 30 min at the same temperature. To the reaction mixture was added (*R*)-(+)-propylene oxide (0.22 mL, 3.20 mmol, 1.0 equiv) and the solution was warmed to room temperature. After the starting material was consumed (3 hours by TLC analysis), the solution was cooled back to –78 °C and benzenesulfonyl chloride (0.41 mL, 3.2 mmol, 1.0 equiv) was added dropwise. After 30 min, the reaction was warmed to 0 °C and kept at this temperature for 3 hours. The resulting solution was cooled to –78 °C again and *n*-BuLi (1.3 mL (2.5M solution in hexanes), 3.36 mmol, 1.05 equiv) was added dropwise, and the solution was left to slowly warm to room temperature overnight. The resulting mixture was quenched with H_2O and extracted twice with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The sulfonylcyclopropane intermediate (410 mg, 66% yield, >99:1 dr, >99% ee) was isolated as a colorless oil after purification by flash chromatography, eluting with 0-60% EtOAc in hexanes (elution gradient). All analyses were consistent with previously reported data.[5,8,9]

An oven-dried 5 mL microwave vial equipped with a magnetic stirbar was charged with the sulfonylcyclopropane intermediate (45 mg, 0.23 mmol, 1.0 equiv), capped and flushed with N_2. Anhydrous *t*-BuOMe (0.6 mL) was added and the solution was cooled to –78 °C. To the resulting solution was added *n*-BuLi (92 µL (2.5M solution in hexanes), 0.23 mmol, 1.0 equiv) and the mixture was stirred at –78 °C for 45 minutes. BF_3•OEt_2 (0.33 mL, 1.25 mmol, 5.4 equiv) was added dropwise at –78°C, followed by a solution of peroxybis(triethylsilane)[5,10] (74 mg, 0.28 mmol, 1.2 equiv) in *t*-BuOMe (0.1 mL). The reaction mixture was stirred for 1 hour at –78 °C and then quenched by addition of a solution of acetic acid in toluene (0.25 mL, PhMe:AcOH = 5:1), warmed and stirred for 1 h at room temperature. To the resulting solution was added aq. sat. NH_4Cl and the mixture was extracted three times with EtOAc. The combined organic fractions were dried on $MgSO_4$ and concentrated under vacuum to afford the crude product **1b**, which was purified by flash chromatography (10% EtOAc in hexanes containing 0.5% AcOH) to afford the pure 1-sulfonylcyclopropanol **1b** (41 mg, 84% yield, >99:1 dr, >99%ee). All analyses were consistent with previously reported data.[5]

7. Yu, B.; Liu, A.-H.; He, L.-N.; Li, B.; Diao, Z.-F.; Li, Y.-N. *Green Chem.* **2012**, *14*, 957-962.
8. Jankins, T. C.; Fayzullin, R. R.; Khaskin, E. *Organometallics*, **2018**, *37*, 2609-2617.
9. Brandt, A.; Wojtasiewicz, A.; Śnieżek, M.; Mąkosza, M. *Tetrahedron* **2010**, *66*, 3378-3385.
10. Sakamoto, R.; Sakurai, S.; Maruoka, K. *Chem. Commun.* **2017**, *53*, 6484-6487.

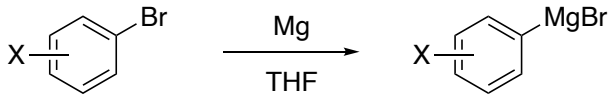


(1*S*,2*S*)-2-phenethyl-1-(phenylsulfonyl)cyclopropan-1-ol (1c) was prepared according to a previously reported procedure.[5] To an oven-dried flask containing methyl phenyl sulfone[7] (453 mg, 2.9 mmol, 1.0 equiv) in dry THF (14 mL) at –78 °C under N_2 was added *n*-BuLi (1.5 mL (2.1M solution in hexanes), 3.2 mmol, 1.1 equiv) and stirred for 30 minutes at the same temperature. To the resulting mixture was added a solution of (*R*)-2-phenethyloxirane[11,12] (474 mg, 3.2 mmol, 1.1 equiv, 96% ee) in dry THF (1.5 mL) dropwise, and the reaction was allowed to warm to room temperature and stirred for 16 hours. The reaction was then cooled to –78 °C and benzenesulfonyl chloride (0.36 mL, 2.9 mmol, 1.0 equiv) was added, then warmed to 0 °C. After 3 hours at that temperature, the reaction was cooled to –78 °C again and *n*-BuLi (1.5 mL (2.1M solution in hexanes), 3.2 mmol, 1.1 equiv) was added, and the mixture was warmed to room temperature and stirred for 3 hours. After this time, the reaction was quenched with aq. sat. NH_4Cl and extracted three times with Et_2O. Combined organic layers were dried over Na_2SO_4 and concentrated, to afford the crude sulfonylcyclopropane which was purified by flash chromatography, eluting with 0-20% EtOAc in hexanes (elution gradient), furnishing the pure sulfonylcyclopropane intermediate (560 mg, 67% yield, >99:1 dr, 95% ee) as a pale yellow oil. All analyses were consistent with previously reported data.[5]

An oven-dried 20 mL microwave vial equipped with a magnetic stirbar was charged with the sulfonylcyclopropane intermediate (550 mg, 1.92 mmol, 1.0 equiv), capped and flushed with N_2. Anhydrous *t*-BuOMe (9.5 mL) was added and the solution was cooled to –78 °C. To the resulting solution was added *n*-BuLi (1.09 mL (2.1M solution in hexanes), 2.30 mmol, 1.2 equiv) and the mixture was stirred at –78 °C for 45 minutes. BF_3•OEt_2 (2.78 mL, 10.37 mmol, 5.4 equiv) was added dropwise at –78°C, followed by a solution of peroxybis(triethylsilane)[5,10] (604 mg, 2.30 mmol, 1.2 equiv) in *t*-BuOMe (1.0 mL). The reaction mixture was stirred for 30 minutes at –78 °C and then quenched by addition of a solution of acetic acid in toluene (2.5 mL, PhMe:AcOH = 5:1), warmed and stirred for 1 h at room temperature. To the resulting solution was added aq. sat. NH_4Cl and the mixture was extracted three times with EtOAc. The combined organic fractions were dried on $MgSO_4$ and concentrated under vacuum to afford the crude product **1c**, which was purified by flash chromatography (10% EtOAc in hexanes containing 0.5% AcOH) to furnish the pure 1-sulfonylcyclopropanol **1c** (382 mg, 66% yield, >99:1 dr, 96% ee). All analyses were consistent with previously reported data.[5]

11. Kurosaki, Y.; Fukuda, T.; Iwao, M. *Tetrahedron* **2005**, *61*, 3289-3303.
12. Made from (*R*)-epichlorohydrin using the following procedure: Deng, H.; Cao, W.; Liu, R.; Zhang, Y.; Liu, B. *Angew. Chem. Int. Ed.* **2017**, *56*, 5849-5852.

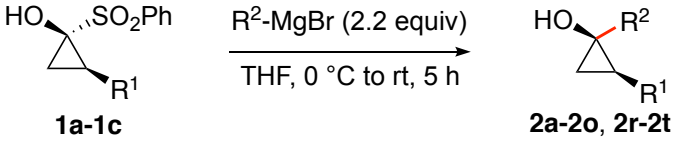
Synthesis and titration of Grignard reagents



The Grignard reagents used for products **2b**, **2e**, **2g**, **2i** and **2k** were prepared according to the following literature procedure (for all other Grignard reagents, refer to the 'Reagents' section, p. S3):[3]
Mg turnings (1.50 equiv) were charged in an oven-dried microwave vial equipped with a magnetic stir bar and heated with a heat gun under vacuum, cooled down, and backfilled with nitrogen. The process was repeated two more times and dry THF was added. In a separate oven-dried round bottom flask, a 1M solution of the bromoarene (1.00 equiv) in dry THF was prepared, 30% of this solution was added to the vial containing Mg turnings and heated. Once the reaction has visibly started, as typically noticed by a change of color, refluxing, heat release or gas evolution on the magnesium surface, the remaining 70% of the bromoarene solution was added dropwise. Upon completion of the reaction, the Grignard reagent solution thus obtained is then titrated according to the following literature procedure:[4]

Grignard titration:
Iodine is charged in an oven-dried microwave vial containing a magnetic stir bar, capped, the system is flushed with nitrogen and a saturated solution of LiCl in dry THF is added. The mixture is cooled to 0 °C, and the organometallic reagent is added dropwise until a clear solution is obtained. Initial and final volumes were recorded, and the molar concentration is obtained by dividing the mmols of iodine used by the total volume (in mL) of Grignard reagent solution consumed.

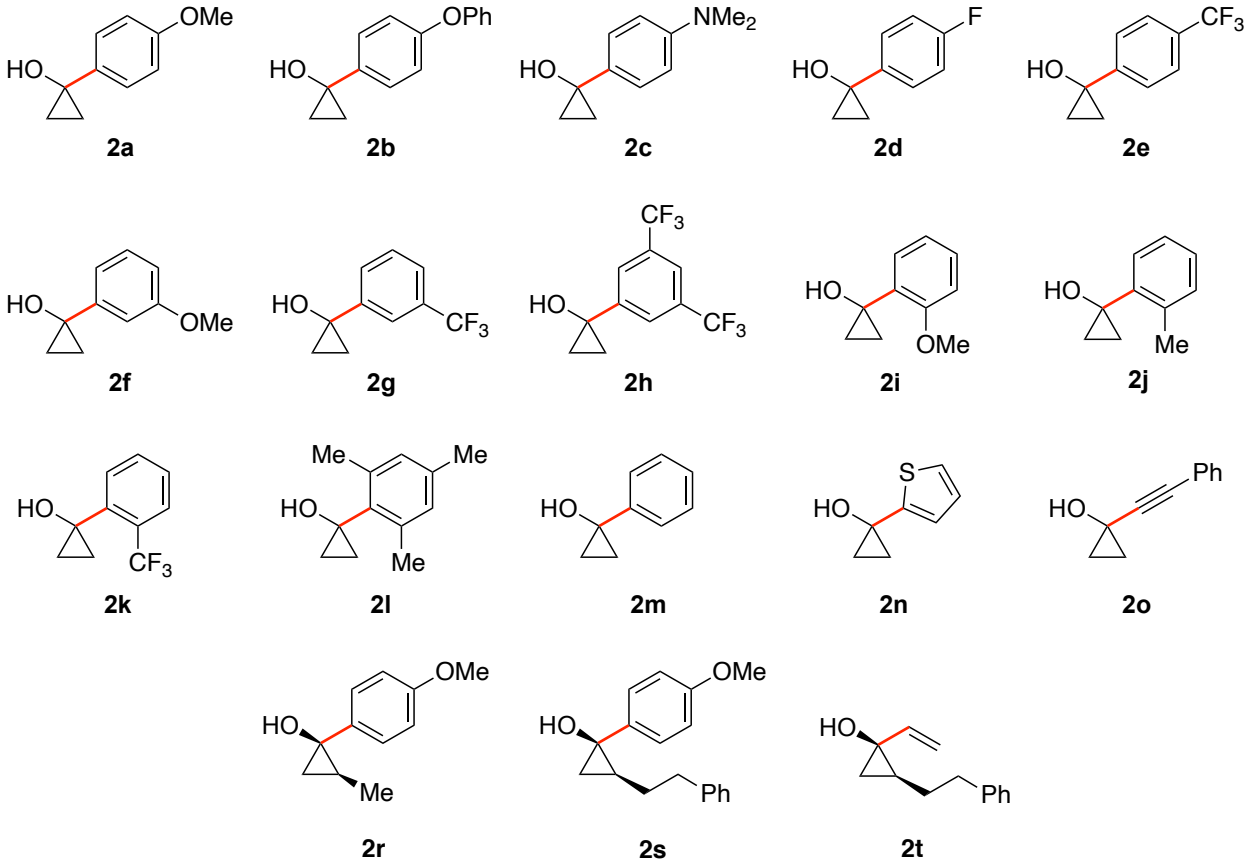
GENERAL PROCEDURE A: Synthesis of 1-substituted cyclopropanols 2a-2o and 1,2-disubstituted cyclopropanols 2r-2t (Grignard reagent as sacrificial base)



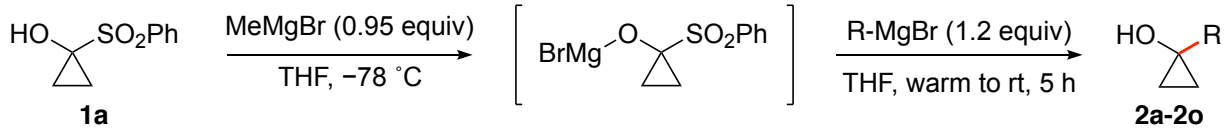
1a-1c **2a-2o**, **2r-2t**

An oven-dried microwave vial equipped with a magnetic stir bar was charged with 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv) and dissolved in dry THF (2.5 mL). The resulting solution was cooled down to 0 °C using a water/ice bath (or to –78 °C using a dry ice/acetone bath, see specific procedures). The Grignard reagent (0.555 mmol, 2.20 equiv) was then added dropwise. After the addition was complete, the reaction mixture was removed from the bath and stirred at room temperature for the indicated time. Note: all reactions must be stirred at least 5 hours at room temperature to avoid the presence of residual dimeric side product in the crude mixture. The reaction mixture was quenched at 0 °C with a saturated solution of NH_4Cl, then diluted in hexanes and ethyl acetate and filtered through celite on top of a silica pad using EtOAc as an eluent or extracted with EtOAc and dried with Na_2SO_4. The filtrate was concentrated and the resulting residue was purified by flash chromatography using EtOAc/Hexanes or Et_2O/Hexanes to give pure cyclopropanol products **2a-2o** and **2r-2t**. See specific procedures for details.

Cyclopropanols prepared using general procedure A

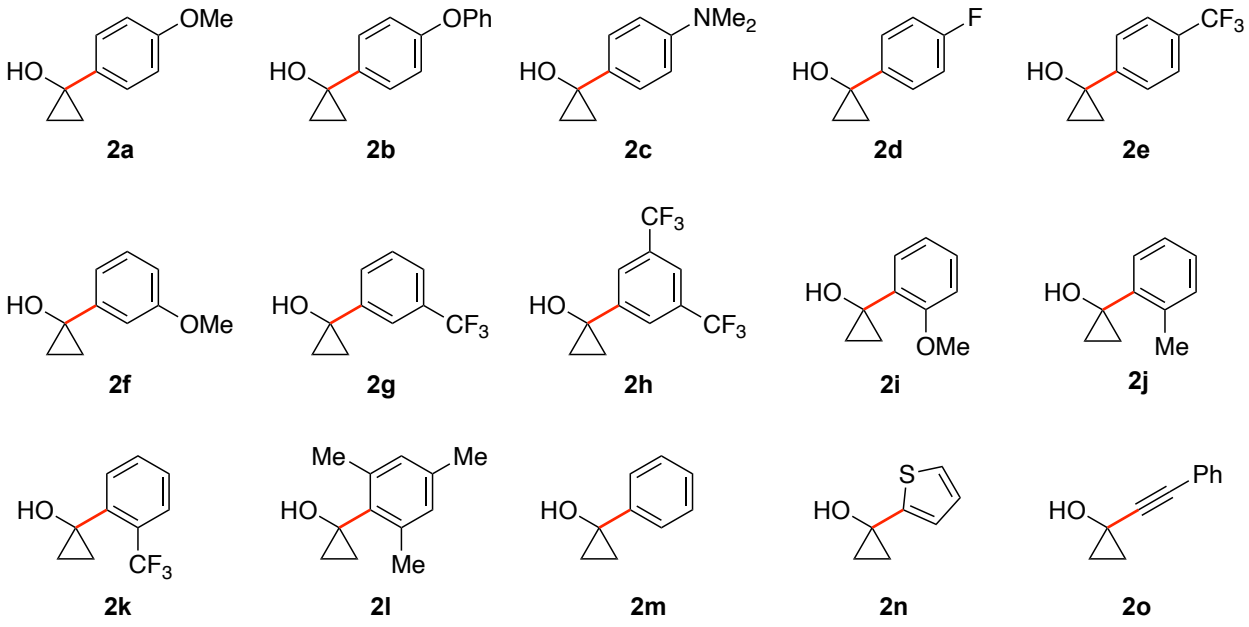


GENERAL PROCEDURE B: Synthesis of 1-substituted cyclopropanols 2a-2o (Grignard economy by using an external base)

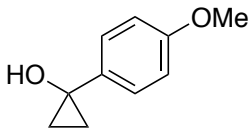


An oven-dried microwave vial equipped with a magnetic stir bar was charged with 1-(phenylsulfonyl)cyclopropanol (50.0 mg, 0.252 mmol, 1.00 equiv) and dissolved in dry THF (2.5 mL). The resulting solution was cooled down to –78 °C using an acetone/dry ice bath. MeMgBr (3.20 M, 0.240 mmol, 0.950 equiv) was added dropwise –78 °C, followed by the Grignard reagent (0.303 mmol, 1.20 equiv), maintaining vigorous stirring throughout. After the addition was complete, the reaction mixture was removed from the bath and stirred at room temperature for the indicated time. Note: all reactions must be stirred at least 5 hours at room temperature to avoid the presence of residual dimeric side product in the crude mixture. The reaction mixture was quenched at 0 °C with a saturated solution of NH_4Cl, then diluted with hexanes and ethyl acetate and filtered through celite on top of a silica pad using EtOAc as an eluent. The filtrate was concentrated and the resulting residue was purified by flash chromatography using EtOAc/Hexanes or Et_2O/Hexanes to give pure cyclopropanol products **2a-2o**. See specific procedures for details.

Cyclopropanols prepared using general procedure B



Specific procedures and characterization data for cyclopropanols 2a-2o and 2r-2t

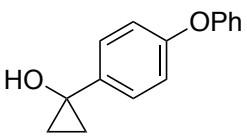


1-(4-methoxyphenyl)cyclopropan-1-ol (2a). Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 4-methoxyphenylmagnesium bromide (1.1 mL (0.500 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2a** (38.0 mg, 91% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient).

On larger scale: Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (500 mg, 2.52 mmol, 1.00 equiv), 4-methoxyphenylmagnesium bromide (11.1 mL (0.500 M sln), 5.55 mmol, 2.20 equiv) added at 0 ºC in dry THF (25.0 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2a** (389 mg, 94% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient).

Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv) and 4-methoxyphenylmagnesium bromide (606 µL (0.500 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2a** (35.7 mg, 86% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient).

On larger scale: Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (500 mg, 2.52 mmol, 1.00 equiv), methylmagnesium bromide (750 µL (3.2 M sln), 2.40 mmol, 0.95 equiv) and 4-methoxyphenylmagnesium bromide (6.06 mL (0.50 M sln), 3.03 mmol, 1.20 equiv) added at –78 ºC in dry THF (25.0 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2a** (364 mg, 88% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 2.25 (s (br), OH), 1.21-1.19 (m, 2H), 0.98-0.96 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.6, 136.2, 126.5, 113.9, 56.9, 55.5, 16.9. All other analyses were consistent with previously reported data.[13]

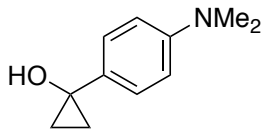


1-(4-phenoxyphenyl)cyclopropan-1-ol (2b). The Grignard reagent was prepared according to the procedure described on page S7. Mg turnings (1.50 mmol, 1.50 equiv) and 1-bromo-4-phenoxybenzene (1.00 mmol, 1.00 equiv) in dry THF (1.0 mL). Titration: 0.340 M.

Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 4-phenoxyphenylmagnesium bromide (1.65 mL (0.340 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2b** (49.1 mg, 86% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient).

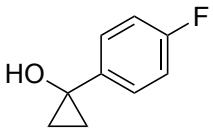
Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), 4-phenoxyphenylmagnesium bromide (891 µL (0.340 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2b** (46.2 mg, 81% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient). **R_f** 0.33 (20% EtOAc in hexanes). **mp** 70-71 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.01-6.97 (m, 4H), 2.31 (s (br), OH), 1.26-1.24 (m, 2H), 1.03-1.01 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.5, 156.0, 139.2, 129.9, 126.4, 123.3, 119.0, 118.8, 56.7, 17.5. **IR** (neat) 3334, 3039, 1898, 1671, 1587, 1508, 1483, 1406, 1224, 1166, 1092, 1022, 1012, 971, 862, 826, 787, 753, 691, 552. **HRMS** (HESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{15}O_2$ 227.1067; Found 227.1063.

13. Jia, K.; Zhang, F.; Huang, H.; Chen, Y. *J. Am. Chem. Soc.* **2016**, *138*, 1514-1517.



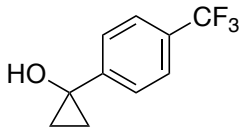
1-(4-(dimethylamino)phenyl)cyclopropan-1-ol (2c). Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 4-(*N*,*N*-dimethyl)anilinemagnesium bromide (1.1 mL (0.50 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2c** (37.5 mg, 84% yield) as a light yellow solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient).

Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), 4-(*N*,*N*-dimethyl)anilinemagnesium bromide (606 µL (0.50 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2c** (32.3 mg, 72% yield) as a white yellow solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient). $\mathbf{R_f}$ 0.22 (20% EtOAc in hexanes). **mp** 109-112 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.3 Hz, 2H), 2.94 (s, 6H), 2.22 (s (br), OH), 1.17-1.15 (m, 2H), 0.96-0.94 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.8, 131.8, 126.6, 112.8, 57.1, 40.9, 16.2. **IR** (neat) 3297, 3091, 3007, 2879, 2851, 2799, 1872, 1616, 1561, 1526, 1443, 1355,1229, 1193, 1012, 870, 810, 551, 492. **HRMS** (HESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{17}ON$ 178.1226; Found 178.1228.



1-(4-fluorophenyl)cyclopropan-1-ol (2d). Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 4-fluorophenylmagnesium bromide (555 µL (1.0 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2d** (36.1 mg, 94% yield) as a clear solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient).

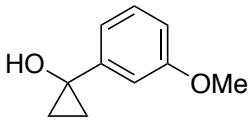
Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), 4-fluorophenylmagnesium bromide (303 µL (1.0 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2d** (32.9 mg, 86% yield) as a clear solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient). $\mathbf{R_f}$ 0.31 (20% EtOAc in hexanes) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 2.61 (s (br), OH), 1.23-1.21 (m, 2H), 0.99-0.97 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.8 (d, *J* = 244.6 Hz), 140.0 (d, *J* = 3.0 Hz), 126.6 (d, *J* = 7.5 Hz), 115.3 (d, *J* = 21.1 Hz), 56.6, 17.6. **^{19}F NMR** (564 MHz, $CDCl_3$) δ –116.7 (s, 1F). All other analyses were consistent with previously reported data.[13]



1-(4-(trifluoromethyl)phenyl)cyclopropan-1-ol (2e). The Grignard reagent was prepared according to the procedure described on page S7. Mg turnings (3.00 mmol, 1.5 equiv) and 4-bromobenzotrifluoride (2.00 mmol, 1.00 equiv) in 5 mL of dry THF. Titration: 0.280 M. Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 4-(trifluoromethyl)phenylmagnesium bromide (2.0 mL (0.280 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2e** (45.4 mg, 89% yield) as a white solid after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient).

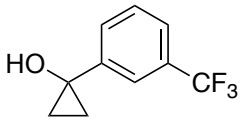
Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), 4-(trifluoromethyl)phenylmagnesium bromide (1.1 mL (0.280 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2e** (38.8 mg, 76% yield) as a white solid after purification

by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). **R_f** 0.33 (20% EtOAc in hexanes). **mp** 67-69 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.42 (s (br), OH), 1.37–1.35 (m, 2H), 1.12-1.10 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.9, 128.6 (q, *J* = 32.4 Hz), 125.4 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272.0 Hz), 124.3, 56.4, 19.2. **^{19}F NMR** (564 MHz, $CDCl_3$) δ –62.4 (s, 3F). **HRMS** (HESI) *m/z*: $[M–H]^-$ Calcd for $C_{10}H_8F_3O$ 201.0533; Found 201.0533. All other analyses were consistent with previously reported data.[14]



1-(3-methoxyphenyl)cyclopropan-1-ol (2f). Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 3-methoxyphenylmagnesium bromide (555 µL (1.0 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2f** (36.9 mg, 89% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient).

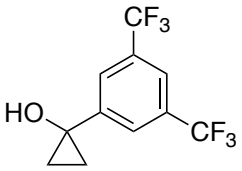
Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), 3-methoxyphenylmagnesium bromide (303 µL (1.0 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2f** (36.4 mg, 88% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient). **R_f** 0.34 (20% EtOAc in hexanes). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.9 Hz, 1H), 6.91 (s, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 3H), 2.56 (s (br), OH), 1.26-1.24 (m, 2H), 1.05-1.03 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.8, 146.3, 129.5, 116.6, 111.8, 110.6, 56.6, 55.3, 18.1. All other analyses were consistent with previously reported data.[13]



1-(3-(trifluoromethyl)phenyl)cyclopropan-1-ol (2g). The Grignard reagent was prepared according to the procedure described on page S7. Mg turnings (3.00 mmol, 1.50 equiv) and 3-bromobenzotrifluoride (2.00 mmol, 1.00 equiv) in (5.00 mL) of dry THF. Titration: 0.300 M. Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), (3-(trifluoromethyl)phenyl)magnesium bromide (1.85 mL (0.30 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2g** (43.3 mg, 85% yield) as a white solid after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient).

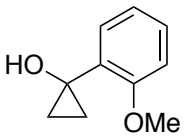
Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), (3-(trifluoromethyl)phenyl)magnesium bromide (1.0 mL (0.30 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2g** (36.7 mg, 72% yield) as a white solid after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). **R_f** 0.38 (20% EtOAc in hexanes). **mp** 50-51 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.48-7.42 (m, 3H), 2.48 (s (br), OH), 1.35-1.33 (m, 2H), 1.10-1.08 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.7, 130.9 (q, *J* = 32.2 Hz), 128.9, 127.5, 124.3 (q, *J* = 272.7 Hz), 123.3 (q, *J* = 3.8 Hz), 121.3 (q, *J* = 3.8 Hz), 56.4, 18.7. **^{19}F NMR** (564 MHz, $CDCl_3$) δ –62.6 (s, 3F). **IR** (neat) 3306, 2850, 1953, 1828, 1617, 1599, 1494, 1437, 1245, 1288, 1237, 1155, 1106, 1013, 971, 894, 868, 803, 792, 696. **HRMS** (HESI) *m/z*: $[M–H]^-$ Calcd for $C_{10}H_8F_3O$ 201.0533; Found 201.0535.

14. He, X.-P.; Shu, Y.-J.; Dai, J.-J.; Zhang, W.-M.; Feng, Y.-S.; Xu, H.-J. *Org. Biomol. Chem.* **2015**, *13*, 7159-7163.



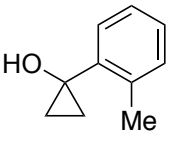
1-(3,5-bis(trifluoromethyl)phenyl)cyclopropan-1-ol (2h). Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 3,5-bis(trifluoromethyl)phenylmagnesium bromide (1.1 mL (0.500 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2h** (45.0 mg, 66% yield) as a white solid after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient).

Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), 3,5-bis(trifluoromethyl)phenylmagnesium bromide (606 µL (0.500 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2h** (42.2 mg, 62% yield) as a white solid after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). **R_f** 0.43 (20% EtOAc in hexanes). **mp** 108-109 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.72 (s, 2H), 2.42 (s (br), OH), 1.45-1.43 (m, 2H), 1.17-1.15 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.6, 131.8 (q, J = 33.2 Hz), 124.3, (q, J = 3.9 Hz), 123.5 (q, J = 273.0 Hz), 120.3 (qn, J = 3.8 Hz), 56.2, 19.5. **^{19}F NMR** (564 MHz, $CDCl_3$) δ –62.9 (s, 6F). **IR** (neat) 3319, 1800, 1624, 1385, 1280, 1243, 1188, 1160, 1116, 1016, 979, 899, 867, 845, 795, 680. **HRMS** (HESI) *m/z*: $[M–H]^-$ Calcd for $C_{11}H_7F_6O$ 269.0407; Found 269.0404.



1-(2-methoxyphenyl)cyclopropan-1-ol (2i). The Grignard reagent was prepared according to the procedure described on page S7. Mg turnings (1.51 mmol, 6.00 equiv) and 2-bromoanisole (1.01 mmol, 4.00 equiv) in (5.00 mL) of dry THF. Titration: 0.290 M. Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), (2-methoxyphenyl)magnesium bromide (1.79 mL (0.310 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2i** (30.6 mg, 74% yield) as a colorless oil after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient).

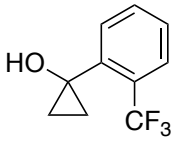
Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), (2-methoxyphenyl)magnesium bromide (977 µL (0.310 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2i** (21.5 mg, 52% yield) as a colorless oil after purification by flash chromatography, eluting with 0-40% EtO_2 in hexanes (elution gradient). **R_f**: 0.32 (20% EtOAc in hexanes). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (d, J = 7.5 Hz, 1H), 7.21 (d, J = 6.9 Hz, 1H), 6.93-6.89 (m, 2H), 3.94 (s, 3H), 3.60 (s (br), OH), 1.15-1.09 (m, 2H), 0.96-0.89 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.6, 130.5, 128.9, 127.4, 120.6, 110.6, 55.6, 55.4, 13.6. All analyses were consistent with the previously reported data.[14]



1-(*o*-tolyl)cyclopropan-1-ol (2j). Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), *o*-tolylmagnesium chloride (396 µL (1.40 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2j** (30.7 mg, 82% yield) as a white solid after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient).

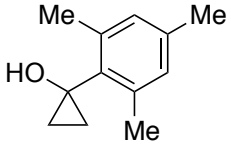
Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), *o*-tolylmagnesium chloride (216 µL (1.40 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2j** (27.6 mg, 74% yield) as a white solid after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). **R_f** 0.42 (20% EtOAc in hexanes). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35-7.34 (m, 1H), 7.23-7.21 (m, 2H), 7.17 -7.15 (m, 1H), 2.57 (s, 3H), 2.18 (s (br), OH), 1.17-1.15

(m, 2H), 0.94-0.92 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.0, 139.1, 130.7, 128.6, 128.2, 125.7, 57.5, 19.3, 13.9. All other analyses were consistent with previously reported data.[15]



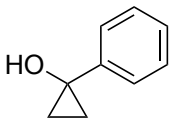
1-(2-(trifluoromethyl)phenyl)cyclopropan-1-ol (2k). The Grignard reagent was prepared according to the procedure described on page S7. Mg turnings (1.51 mmol, 6.00 equiv) and 2-bromobenzotrifluoride (1.01 mmol, 4.00 equiv) in (2.00 mL) of dry THF. Titration: 0.600 M. Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 2-(trifluoromethyl)phenylmagnesium bromide (925 µL (0.600 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2k** (22.4 mg, 44% yield) as a colorless oil after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient).

Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), 2-(trifluoromethyl)phenylmagnesium bromide (689 µL (0.440 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2k** (20.4 mg, 40% yield) as a colorless oil after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). **R_f** 0.36 (20% EtOAc in hexanes). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (t, J = 8.4 Hz, 2H), 7.55 (t, J = 7.7 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 2.62 (s (br), OH), 1.26-1.24 (m, 2H), 1.06-1.04 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.9, 132.3, 132.0, 129.5 (q, J = 30.8 Hz), 128.4, 126.8 (q, J = 5.8 Hz), 124.8 (q, J = 273.6 Hz), 56.3, 14.8. **^{19}F NMR** (564 MHz, $CDCl_3$) δ –57.9 (s, 3F). **IR** (neat) 3385, 1607, 1581, 1450, 1310, 1270, 1224, 1165, 1103, 1049, 1037, 1021, 958, 939, 871, 766, 700, 647, 599, 549.



1-mesitylcyclopropan-1-ol (2l). Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 2-mesitylmagnesium bromide (555 µL (1.00 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2l** (39.1 mg, 88% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient).

Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), 2-mesitylmagnesium bromide (303 µL (1.00 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 16 h, affording cyclopropanol **2l** (41.8 mg, 94% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient). **R_f** 0.45 (20% EtOAc in hexanes). **mp** 96-99 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.86 (s, 2H), 2.49 (s, 6H), 2.26 (s, 3H), 1.94 (s (br), OH), 1.23-1.21 (m, 2H), 0.88-0.85 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.6, 137.8, 135.0, 129.4, 54.2, 21.0, 20.2, 16.0. **IR** (neat) 3382, 3005, 2920, 2854, 2114, 1611, 1573, 1450, 1374, 1223, 1081, 1021, 965, 864, 851. **HRMS** (HESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{17}O$ 177.1274; Found 177.1272.

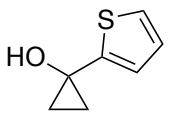


1-phenylcyclopropan-1-ol (2m). Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), phenylmagnesium bromide (173 µL (3.20 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h, affording cyclopropanol **2m** (28.1 mg, 83% yield) as colorless oil by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient).

Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), phenylmagnesium bromide (95 µL (3.20 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 5 h,

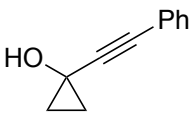
15. Ren, S.; Feng, C.; Loh, T.-P. *Org. Biomol. Chem.* **2015**, *13*, 5105-5109.

affording cyclopropanol **2m** (28.8 mg, 85% yield) as a colorless oil after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). $\mathbf{R_f}$ 0.39 (20% EtOAc in hexanes). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35-7.30 (m, 4H), 7.25-7.22 (m, 1H), 2.48 (s (br), OH), 1.28-1.26 (m, 2H), 1.06-1.04 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.4, 128.5, 126.5, 124.5, 56.7, 18.0. All other analyses were consistent with previously reported data.[13]



1-(thiophen-2-yl)cyclopropan-1-ol (2n). Following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 2-thienylmagnesium bromide (555 µL (1.00 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC in dry THF (2.50 mL) and the reaction run at rt for 16 h, affording cyclopropanol **2n** (31.8 mg, 90% yield) as colorless oil after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient).

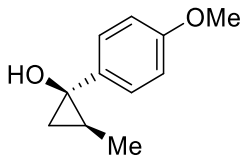
Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), 2-thienylmagnesium bromide (303 µL (1.00 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 16 h, affording cyclopropanol **2n** (28.6 mg, 81% yield) as a white solid after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). $\mathbf{R_f}$ 0.39 (20% EtOAc in hexanes). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.18 (d, J = 5.0 Hz, 1H), 6.95-6.92 (m, 1H), 6.87 (d, J = 3.4 Hz, 1H), 2.74 (s (br), OH), 1.31-1.28 (m, 2H), 1.08-1.06 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.4, 127.0, 123.9, 122.3, 54.5, 18.5. **IR** (neat) 3313, 3087, 3004, 2916, 2849, 2160, 1648, 1443, 1413, 1352, 1290, 1255, 1212, 1086, 1038, 1010, 966, 928, 887, 845, 824, 693, 599, 533, 502. **HRMS** (HESI) *m/z*: $[M+H]^+$ Calcd for C_7H_9SO 141.0369; Found 141.0366.



1-(phenylethynyl)cyclopropan-1-ol (2o). An oven-dried microwave vial was charged with phenylacetylene (72.0 µL, 0.555 mmol, 2.20 equiv) and dissolved in dry THF (1.0 mL). The solution was cooled to –78 °C, *n*-BuLi (227 µL (2.50 M sln), 0.568 mmol, 2.25 equiv) was added dropwise, and the resulting mixture was stirred for 1 h at the same temperature. A separate oven-dried microwave vial was charged with 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), flushed with nitrogen and dry THF (2.50 mL) was added. This solution was cooled to –78 °C, and the (phenylethynyl)lithium solution prepared was added dropwise. After the addition was complete, the reaction mixture was removed from the bath and stirred at room temperature for 5 h. The reaction mixture was quenched at 0 °C with a saturated solution of NH_4Cl, then diluted in hexanes and ethyl acetate and filtered through celite on top of a silica pad using EtOAc as an eluent. The filtrate was concentrated, and the resulting residue was purified by flash chromatography using EtOAc/Hexanes (0-40 % elution gradient) to afford cyclopropanol **2o** (30.3 mg, 76% yield) as a colorless oil.

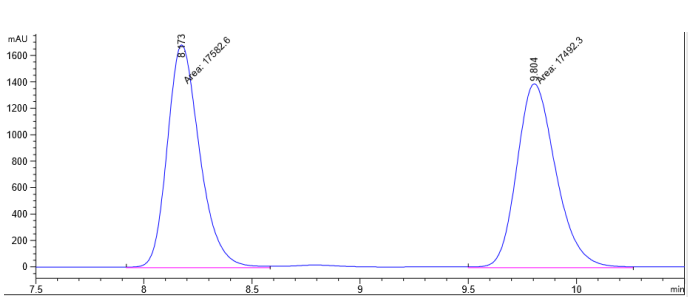
Following general procedure B, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), methylmagnesium bromide (75 µL (3.2 M sln), 0.24 mmol, 0.95 equiv), phenylethynylmagnesium bromide (303 µL (1.00 M sln), 0.303 mmol, 1.20 equiv) added at –78 ºC in dry THF (2.50 mL) and the reaction run at rt for 16 h, affording cyclopropanol **2o** (28.3 mg, 71% yield) as a colorless oil after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). $\mathbf{R_f}$ 0.39 (20% EtOAc in hexanes). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42-7.41 (m, 2H), 7.30-7.29 (m, 3H), 2.68 (s (br), OH), 1.19-1.17 (m, 2H), 1.11-1.09 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 131.7, 128.4, 128.3 122.9, 90.9, 82.5, 46.2, 17.8. All other analyses were consistent with previously reported data.[16]

16. Stephen, A. Hashmi, K.; Wang, T.; Shi, S.; Rudolph, M. *J. Org. Chem.* **2012**, *77*, 7761-7767.



(1*R*,2*S*)-1-(4-methoxyphenyl)-2-methylcyclopropan-1-ol (2r). Following modified general procedure A, (1*S*,2*S*)-2-methyl-1-(phenylsulfonyl)cyclopropan-1-ol **1b**[5] (53.5 mg, 0.252 mmol, 1.0 equiv, >99% ee) was dissolved in dry THF (2.5 mL) at –78 °C and 4-methoxyphenylmagnesium bromide (1.51 mL (0.5 M sln), 0.756 mmol, 3.0 equiv) was added dropwise. After the addition was complete, the reaction mixture was removed from the bath and stirred at room temperature for 1 h. After this time, the reaction was quenched at 0 °C with aq. sat. NH_4Cl, extracted with EtOAc, and dried over Na_2SO_4. The crude mixture was purified by flash chromatography, eluting with 0-20% EtOAc in hexanes (elution gradient) to afford product **2r** (38.1 mg, 85% yield, 94% ee) as a colorless oil. Enantiomeric excess was determined by HPLC analysis on chiral stationary phase (Chiralcel AD-H 25 cm, 10% *i*-PrOH, 1 mL/min, 23 °C, 43 bar, 214 nm, t_r (major) 8.2 min, t_r (minor) 9.8 min). **$[\alpha]_D^{20}$** = +51.6 (*c* 0.58, $CHCl_3$). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.24-7.22 (m, 2H), 6.88-6.86 (m, 2H), 3.80 (s, 3H), 2.05 (s (br), OH), 1.31 (d, *J* = 5.9 Hz, 3H), 1.21-1.13 (m, 2H) 0.76-0.74 (m, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 158.4, 137.5, 125.9, 113.9, 59.3, 55.5, 23.3, 21.1, 12.7. **IR** (neat) 3385, 2928, 2835, 1611, 1513, 1247, 1180, 1033, 829. **HRMS** (HESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{15}O_2$ 179.1067; Found 179.1064.

HPLC trace:



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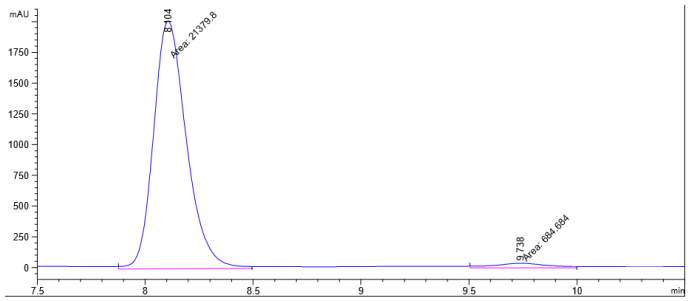

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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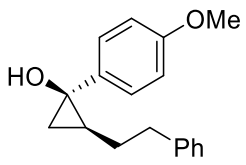
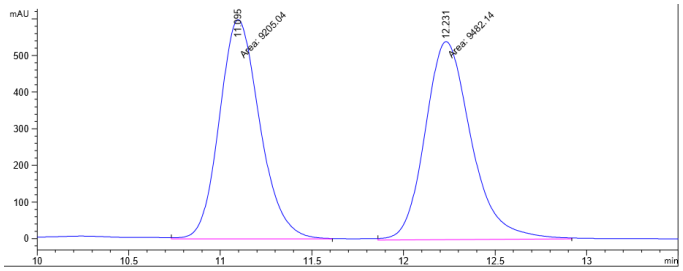


(1*R*,2*S*)-1-(4-methoxyphenyl)-2-phenethylcyclopropan-1-ol (2s). Following modified general procedure A, (1*S*,2*S*)-2-phenethyl-1-(phenylsulfonyl)cyclopropan-1-ol **1c**[5] (76.2 mg, 0.252 mmol, 1.0 equiv) was dissolved in dry THF (2.5 mL) at –78 °C and 4-methoxyphenylmagnesium bromide (1.51 mL (0.5 M sln), 0.756 mmol, 3.0 equiv) was added dropwise. After the addition was complete, the reaction mixture was removed from the bath and stirred at room temperature for 1 h. After this time, the reaction was quenched at 0 °C with aq. sat. NH_4Cl, extracted with EtOAc, and dried over Na_2SO_4. The crude mixture was purified by flash chromatography, eluting with 0-20% EtOAc in hexanes (elution gradient) to afford product **2s** (61.6 mg, 91% yield, 96% ee) as a white solid. Enantiomeric excess was determined by HPLC analysis on chiral stationary phase (Chiralcel AD-H 25 cm, 10% *i*-PrOH, 1 mL/min, 23 °C, 43 bar, 214 nm, t_r (major) 11.1 min, t_r (minor) 12.2 min). **$[\alpha]_D^{20}$** = +95.4 (*c* 1.03, $CHCl_3$). **mp** 80-82 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 7.20-7.17 (m, 3H), 7.09-7.05 (m, 2H), 6.85-6.82 (m, 2H), 3.80 (s, 3H), 2.85-2.82 (m, 1H), 2.73-2.69 (m, 1H), 2.12-2.06 (m, 1H), 1.92-1.86 (m, 1H), 1.46 (s (br), OH) 1.17-1.10 (m, 2H), 0.80-0.78 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.3, 142.4, 137.4, 128.8, 128.6, 126.0, 125.8, 113.7, 59.4, 55.5, 36.3, 30.3, 27.9, 22.3. **IR** (neat) 3388, 2998, 2906, 2836, 1612, 1513, 1248, 1180, 1031, 821, 702, 571. **HRMS** (HESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{21}O_2$ 269.1536; Found 269.1531.

HPLC trace:



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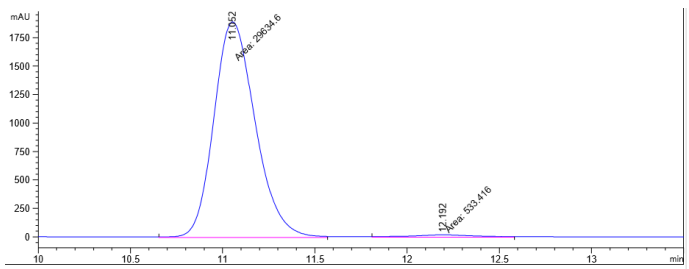

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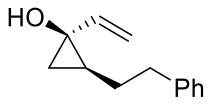
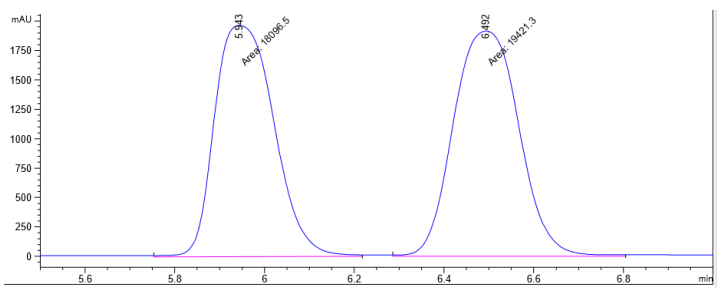
2	12.192	MM	0.4281	533.41589	20.76600	1.7682



(1*S*,2*S*)-2-phenethyl-1-vinylcyclopropan-1-ol (2t). Following modified general procedure A, (1*S*,2*S*)-2-phenethyl-1-(phenylsulfonyl)cyclopropan-1-ol **1c**[5] (76.2 mg, 0.252 mmol, 1.0 equiv) was dissolved in dry THF (2.5 mL) at –78 °C and vinylmagnesium bromide (756 µL (1.0 M sln), 0.756 mmol, 3.0 equiv) was added dropwise. After the addition was complete, the reaction mixture was removed from the bath and stirred at room temperature for 1 h. After this time, the reaction was quenched at 0 °C with aq. sat. NH_4Cl, extracted with EtOAc, and dried over Na_2SO_4. The crude mixture was purified by flash chromatography, eluting with 0-20% EtOAc in hexanes (elution gradient) to afford product **2t** (35.7 mg, 75% yield, 96% ee) as a colorless oil. Enantiomeric excess was determined by HPLC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 10% *i*-PrOH, 1 mL/min, 23 °C, 43 bar, 214 nm, t_r (minor) 5.9 min), t_r (major) 6.5 min. **$[\alpha]_D^{20}$** = -6.1 (*c* 2.33, $CHCl_3$). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.18 (m, 3H), 5.47 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.96 (d, *J* = 10.7 Hz, 1H), 2.82-2.78 (m, 1H), 2.66-2.62 (m, 1H), 2.04-2.00 (m, 1H), 1.78-1.73 (m, 1H), 1.08 (s (br), OH) 0.92-0.86 (m, 2H), 0.66-0.64 (m, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 143.3, 142.3, 128.8, 128.6, 126.1, 109.7, 59.1, 36.2, 29.9, 26.9, 21.1. **IR** (neat) 3358, 3025, 2924, 2856, 1638, 1495, 1279, 901, 699. **HRMS** (HESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{17}O$ 189.1274; Found 189.1270.

HPLC trace:



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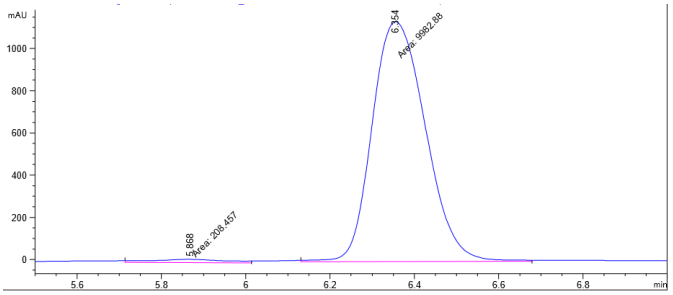

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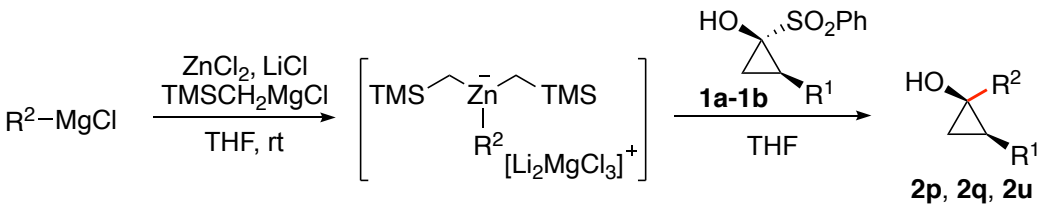
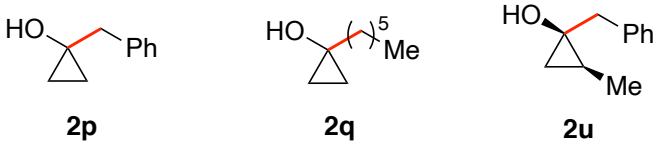
2	6.354	MM	0.1463	9982.87988	1137.29065	97.9546

GENERAL PROCEDURE C: Synthesis of 1-alkyl-substituted cyclopropanols 2p, 2q and 2u



The transmetallation step was effected following a modified literature procedure.[17] In an inert atmosphere glove-box, an oven-dried microwave vial equipped with a magnetic stirbar was charged with anhydrous $ZnCl_2$ (41.3, mg, 0.303 mmol, 1.20 equiv.) and LiCl (64.1 mg, 1.51 mmol 6.00 equiv), the vial was capped and taken out of the glove-box, put under vacuum and heated at 100 °C for 1 h. The vial was allowed to cool down to room temperature under nitrogen, and $TMSCH_2MgCl$ (465 μL (1.30 M sln in THF), 0.605 mmol, 2.40 equiv) was added and the resulting mixture was stirred at room temperature for 15 minutes. After this time, the Grignard reagent (0.555 mmol, 2.20 equiv) was added and the resulting mixture was stirred for 45 minutes at room temperature (note: if the Grignard solution concentration is > 1 M, it was diluted with dry THF to 1 M prior to transmetallation). The resulting mixture was cooled down to 0 °C and a solution of 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv.) in dry THF (1.0 mL) was added dropwise. The bath was removed after the addition and the reaction was stirred at room temperature for the indicated time (note: the reaction must be stirred at least 5 hours at room temperature to avoid the presence of dimeric side product **3** in the crude mixture). The resulting reaction mixture was diluted with hexane and ethyl acetate and filtered through a plug of silica and celite eluting with ethyl acetate (or indicated solvent). The filtrate was concentrated, and the resulting crude product was purified by flash chromatography using ethyl acetate (or diethyl ether) in hexanes to give cyclopropanols **2p**, **2q** and **2u**. See specific procedures for details.

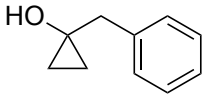
Cyclopropanols prepared using general procedure C



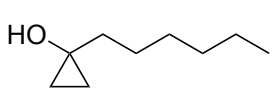
2p **2q** **2u**

17. Hatano, M.; Ito, O.; Suzuki, S.; Ishihara, K. *J. Org. Chem.* **2010**, *75*, 5008-5016.

Specific procedures and characterization data for cyclopropanols 2p, 2q and 2u

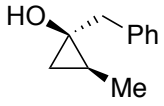


1-benzylcyclopropan-1-ol (2p). Following general procedure C, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), $ZnCl_2$ (41.3 mg, 0.303 mmol, 1.20 equiv), LiCl (64.1 mg, 1.51 mmol, 6.00 equiv), $TMSCH_2MgCl$ (465 µL (1.30 M sln in THF), 0.605 mmol 2.40 equiv), benzylmagnesium chloride (555 µL (1.00 M sln), 0.555 mmol, 2.20 equiv) added at 0 °C and the reaction stirred at room temperature for 12 h, affording cyclopropanol **2p** (28.4 mg, 76% yield) as a clear oil after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). $\mathbf{R_f}$ 0.35 (20% EtOAc in hexanes). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 2.89 (s, 2H), 1.90 (s (br), OH), 0.84-0.82 (m, 2H), 0.66-0.64 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.7, 129.6, 128.7, 126.8, 56.3, 44.3, 13.4. All other analyses were consistent with previously reported data.[18]



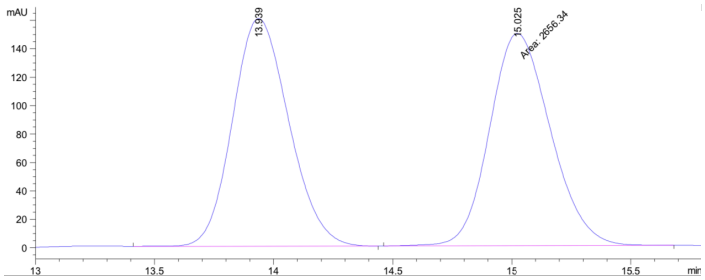
1-hexylcyclopropan-1-ol (2q). Following general procedure C, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv.), $ZnCl_2$ (41.3 mg, 0.303 mmol, 1.20 equiv), LiCl (64.1 mg, 1.51 mmol, 6.00 equiv), $TMSCH_2MgCl$ (465 µL (1.30 M sln in THF), 0.605 mmol 2.40 equiv), hexylmagnesium bromide (555 µL (1.00 M sln), 0.555 mmol, 2.20 equiv) added at 0 °C and the reaction stirred at room temperature for 14 h, affording cyclopropanol **2q** (23.3 mg, 65% yield) as a colorless oil after purification by flash chromatography, eluting with 0-40% Et_2O in hexanes (elution gradient). $\mathbf{R_f}$ 0.53 (20% EtOAc in hexanes). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.85 (s (br), OH), 1.56-1.53 (m, 2H), 1.51-1.46 (m, 2H), 1.36-1.25 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H), 0.73-0.71 (m, 2H), 0.44-0.42 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 56.0, 38.4, 32.0, 29.5, 26.0, 22.8, 14.2, 13.6. **IR** (neat) 3313, 3083, 3004, 2957, 2927, 2856, 1466, 1305, 1270, 1237, 1097, 1008, 955, 928, 736. **HRMS** (HESI) *m/z*: $[M+H]^+$ Calcd for $C_9H_{19}O$ 143.1430; Found 143.1430.

18. Konik, Y. A.; Zoltán-Elek, G.; Kaabel, S.; Järving, I.; Lopp, M.; Kananovich, D. G. *Org. Biomol. Chem.* **2017**, *15*, 8334-8340.

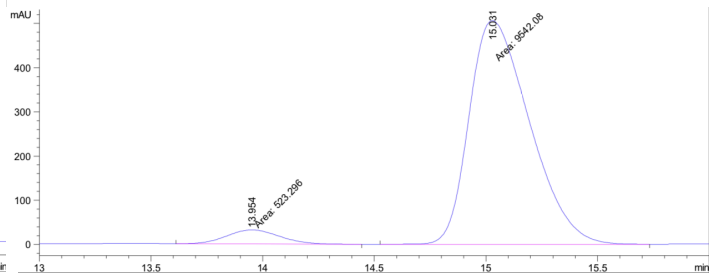


(1*S*,2*S*)-1-benzyl-2-methylcyclopropan-1-ol (2u). In an inert atmosphere glove-box, an oven-dried microwave vial equipped with a magnetic stirbar was charged with anhydrous $ZnCl_2$ (41.3, mg, 0.303 mmol, 1.20 equiv.) and LiCl (64.1 mg, 1.51 mmol 6.00 equiv), the vial was capped and taken out of the glove-box, put under vacuum and heated at 100 °C for 1 h. The vial was allowed to cool down to room temperature under nitrogen, and $TMSCH_2MgCl$ (465 µL (1.30 M sln in THF), 0.605 mmol, 2.40 equiv) was added and the resulting mixture was stirred at room temperature for 15 minutes. After this time, benzylmagnesium chloride (555 µL (1.00 M sln), 0.555 mmol, 2.20 equiv) was added and the resulting mixture was stirred for 45 minutes at room temperature. The resulting mixture was cooled down to –20 °C and a solution of (1*S*,2*S*)-2-methyl-1-(phenylsulfonyl)cyclopropan-1-ol **1b**[5] (53 mg, 0.252 mmol, 1.0 equiv, >99% ee) in dry THF (1.0 mL) was added dropwise, and the reaction was stirred at –20 °C for 6 h. After this time, the reaction was quenched with aq. sat. NH_4Cl, diluted with ethyl acetate and filtered through a plug of silica and celite eluting with ethyl acetate. The filtrate was concentrated and the resulting crude product was purified by flash chromatography using Et_2O in hexanes (0-50 % elution gradient) to afford cyclopropanol **2u** as a white solid (25.4 mg, 62% yield, 90% ee). Enantiomeric excess was determined by HPLC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 2% *i*-PrOH in Hexanes, 1 mL/min, 23 °C, 43 bar, 214 nm, t_r (minor) 13.9 min, t_r (major) 15.0 min). **$[\alpha]_D^{21}$** = +114.8 (*c* 1.00, $CHCl_3$). **mp** 40-42 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34-7.24 (m, 5H), 2.92 (d, *J* = 14.2 Hz, 1H), 2.80 (d, *J* = 14.3 Hz, 1H), 1.68 (s (br), OH), 1.16 (d, *J* = 6.2 Hz, 3H), 0.95-0.89 (m, 1H), 0.79-0.76 (m, 1H), 0.35 (t, *J* = 5.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.9, 129.4, 128.7, 126.7, 59.0, 45.3, 19.3, 18.5, 12.5. **IR** (neat) 3299, 3216, 3064, 3013, 2952, 1603, 1451, 1275, 991, 703, 659. **HRMS** (HESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{15}O$ 163.1117; Found 163.1116.

HPLC trace:

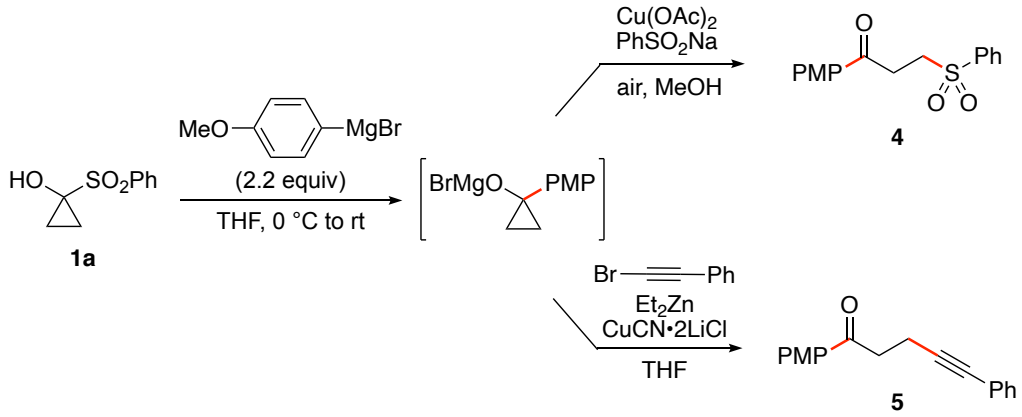


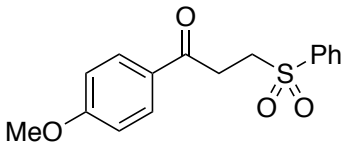
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.939	BB	0.2558	2632.50269	160.20461	49.7747
2	15.025	MM	0.2963	2656.33862	149.41489	50.2253



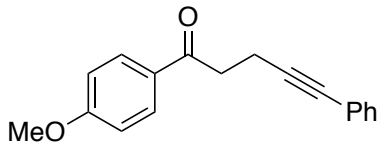
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.954	MM	0.2743	523.29584	31.79291	5.1990
2	15.031	MM	0.3142	9542.08301	506.18121	94.8010

One-pot homoenolate chemistry





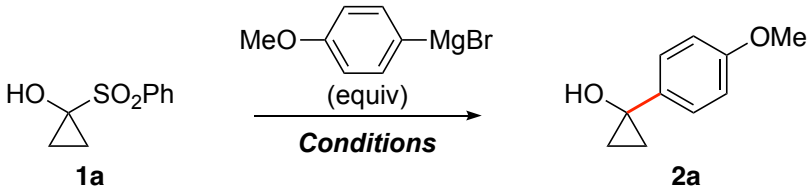
1-(4-methoxyphenyl)-3-(phenylsulfonyl)propan-1-one (4). Addition step: following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 4-methoxyphenylmagnesium bromide (1.11 mL (0.500 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC, in dry THF (2.50 mL) for 5 h at room temperature. Sulfonylation step:[19] In a separate flask equipped with a magnetic stirbar, $Cu(OAc)_2•H_2O$ (50.3 mg, 0.252 mmol, 1.00 equiv) and phenylsulfinic sodium salt (62.1 mg, 0.378 mmol, 1.50 equiv) were dissolved in MeOH (2.0 mL). The Grignard addition reaction mixture (not quenched) was transferred via syringe to this solution and stirred at room temperature, open to air and followed by TLC (20% EtOAc/hexanes). When all the cyclopropanol intermediate **2a** was consumed, the reaction was quenched sequentially with aq. sat. NH_4Cl (1 mL) and 1M HCl (1 mL). The resulting mixture was extracted three times with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated. Flash chromatography using 0-40 % EtOAc/hexanes (elution gradient) provided the pure γ-ketosulfone **4** (31.2 mg, 41% yield) as a white solid. All analyses were consistent with previously reported data.[20]



1-(4-methoxyphenyl)-5-phenylpent-4-yn-1-one (5). Addition step: following general procedure A, using 1-(phenylsulfonyl)cyclopropanol **1a** (50.0 mg, 0.252 mmol, 1.00 equiv), 4-methoxyphenylmagnesium bromide (1.11 mL (0.500 M sln), 0.555 mmol, 2.20 equiv) added at 0 ºC, in dry THF (2.50 mL) for 5 h at room temperature. Alkynylation step:[21], diethyl zinc solution (252 µL (1M sln), 0.252 mmol, 1 equiv) was added to the (unquenched) Grignard addition mixture at room temperature and stirred for 10 minutes. After this time, CuCN•2LiCl (65 mg, 0.373 mmol, 1.5 equiv) was added and the resulting mixture was stirred for 10 minutes at room temperature. A solution of (bromoethynyl)benzene (137 mg, 0.757 mmol, 3.00 equiv) in dry THF (1.0 mL) was added at room temperature and the reaction was followed by TLC (20% EtOAc/hexanes). When all the cyclopropanol intermediate **2a** was consumed, the reaction was quenched with aq. sat. NH_4Cl (2 mL) and stirred for 15 minutes at room temperature. Et_2O (3 mL) was added and stirred for 30 minutes. Layers were separated and the aqueous layer was extracted twice with Et_2O. Combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. Flash chromatography using 0-40 % EtOAc/hexanes (elution gradient) provided β,γ-alkynylketone **5** (32.0 mg, 48% yield). All analyses were consistent with previously reported data.[22]

19. Konik, J. A.; Gábor Zoltán, E.; Kaabel, S.; Järving, I.; Lopp, M.; Kananovich, D. G. *Org. Biomol. Chem.* **2017**, *15*, 8334-8340.
20. Vellakkaran, M.; Andappan, M.; Nagaiah, K.; Nanubolu, J. B. *Eur. J. Org. Chem.* **2016**, 3575-3583.
21. Murali, R. V. N. S.; Rao, N. N.; Cha, J. K. *Org. Lett.* **2015**, *17*, 3854-3856.
22. Chen, L.; Li, C-J. *Org. Lett.* **2004**, *18*, 3151-3153.

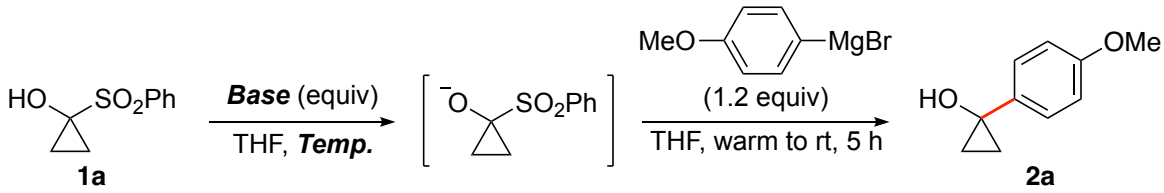
Method A optimization: Grignard as sacrificial base



Entry	Grignard (equiv)	Temp. (°C)	Conc. (M)	Solvent	Time (h)	Yield (%)[a]
1	2.00	0 to rt	1.0	*t*-BuOMe	5	78
2	2.00	0 to rt	1.0	Et_2O	5	63
3	2.00	0 to rt	1.0	THF	5	75
4	2.00	–78	1.0	THF	5	ND[b,c]
5	2.00	0	1.0	THF	5	71[b,c,d]
6	2.00	0 to rt	0.10	THF	5	86
7	2.20	0 to rt	1.0	THF	5	89
8	2.00	0 to rt	1.0	THF	2	62[b,d]
9	**2.20**	**0 to rt**	**0.10**	**THF**	**5**	**91**

[a]Isolated yield of **2a** unless otherwise noted. [b]**2a** could not be isolated due to the presence of unseparable dimeric product. [c]Reaction was quenched at low temperature. [d]Yield determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as standard.

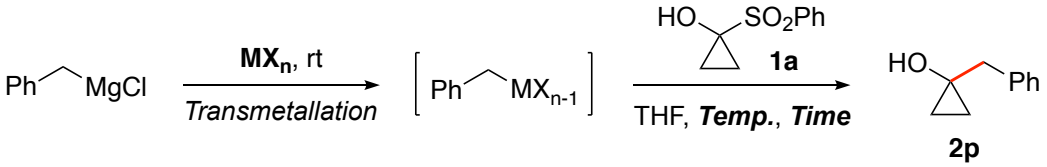
Method B optimization: Grignard economy via the use of an external base



Entry	Base (equiv)	Temp. (°C)	Time (h)	Yield (%)[a]
1	LDA (1.00)	0	5	10
2	LDA (1.00)	–78	5	15
3	NaH (1.00)	0	5	7
4	Et_3N (1.00)	0	5	7
5	MeMgBr (1.00)	0	5	60
6	MeMgBr (1.00)	–78	5	79
7	MeMgBr (0.95)	–78	5	86 (86)[b]
8	(*n*-Bu)$_2$Mg (0.95)	–78	5	92

[a]Yield on 0.25 mmol scale determined by ^{1}H NMR using 1,3,5-trimethoxy-benzene as standard. [b]Isolated yield in parentheses.

Method C optimization: access to 1-alkylsubstituted cyclopropanols via transmetallation

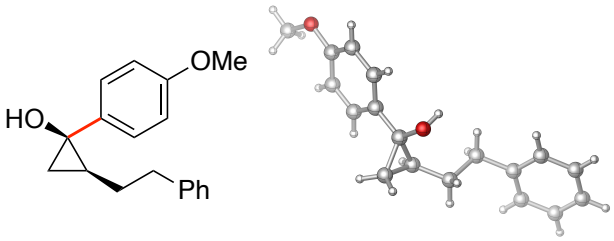


Entry	MX_n (equiv)	Temp. (°C)	Grignard (equiv)	Time (h)	Yield (%)[a]
1	none	rt	2.20	5	<20[b]
2	$CeCl_3$ (2.20)	rt	2.20	12	15
3[c]	$CeCl_3$ (2.20)	0	2.20	5	30
4	CuBr (2.20)	0 to rt	2.20	4	20
5	$CuBr_2$ (2.20)	0 to rt	2.20	4	< 5
6	CuCN (2.20)	0 to rt	2.20	5	20
7	$FeCl_2$ (2.20)	rt	2.20	5	27
8[d]	Bn_2Zn (2.20)	0 to rt	---	5	47
9[d]	Bn_2Zn (2.20)	50	---	5	58
10[c]	Et_2Zn (2.10)	0	2.10	5	61 (56)[e]
11[c]	Et_2Zn (2.10)	–78 to rt	2.10	5	10
12[c]	Et_2Zn (2.10)	–78 to rt	2.10	12	53
13[c]	Et_2Zn (2.10)	rt	2.10	5	50
14[f]	$(TMSCH_2)_2Zn$ (0.10)	0	2.30	5	10
15[g]	$(TMSCH_2)_2Zn$ (2.20)	0	2.20	5	66
16[g]	$(TMSCH_2)_2Zn$ (2.20)	–78 to rt	2.20	12	59
17[g]	$(TMSCH_2)_2Zn$ (2.20)	rt	2.20	5	63
18[g,h]	$(TMSCH_2)_2Zn$ (2.20)	0	2.20	5	14
19[i]	$(TMSCH_2)_2Zn$ (0.50)	0	2.20	5	40
20[j]	$(TMSCH_2)_2Zn$ (1.20)	0 to rt	2.20	5	72
21[j]	**$(TMSCH_2)_2Zn$ (1.20)**	**0 to rt**	**2.20**	**12**	**(76)**[e]

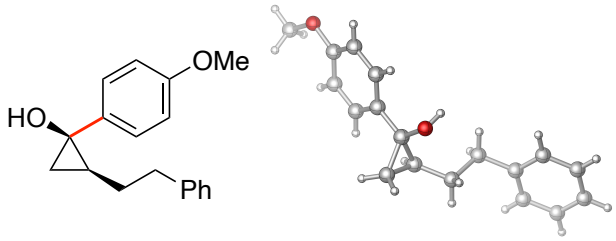
[a]NMR yield determined using 1,3,5-trimethoxybenzene as internal standard. [b]Significant decomposition observed by ^1H NMR. [c]Syringe pump addition of organometallic reagent. [d]Prepared *in situ* from $Zn(OMe)_2$ (2.2 equiv) and BnMgCl (2.2 equiv).[23] [e]Isolated yield in parenthesis. [f]Prepared *in situ* from $ZnCl_2$ (10 mol%), $TMSCH_2MgCl$ (20 mol%), LiCl (110 mol%). [g]Prepared *in situ* from $ZnCl_2$ (2.20 equiv), $TMSCH_2MgCl$ (4.40 equiv), LiCl (13.0 equiv). [h]Complex stirred for 3 h prior to addition of **1a**. [i]Prepared *in situ* from $ZnCl_2$ (50 mol%), $TMSCH_2MgCl$ (1 equiv), LiCl (5.5 equiv). [j]Prepared *in situ* from $ZnCl_2$ (1.20 equiv), $TMSCH_2MgCl$ (2.40 equiv) and LiCl (6.0 equiv)

23. Côté, A.; Charette, A. B. *J. Am. Chem. Soc.* **2008**, *130*, 2771-2773.

X-ray data of chiral cyclopropanol 2s

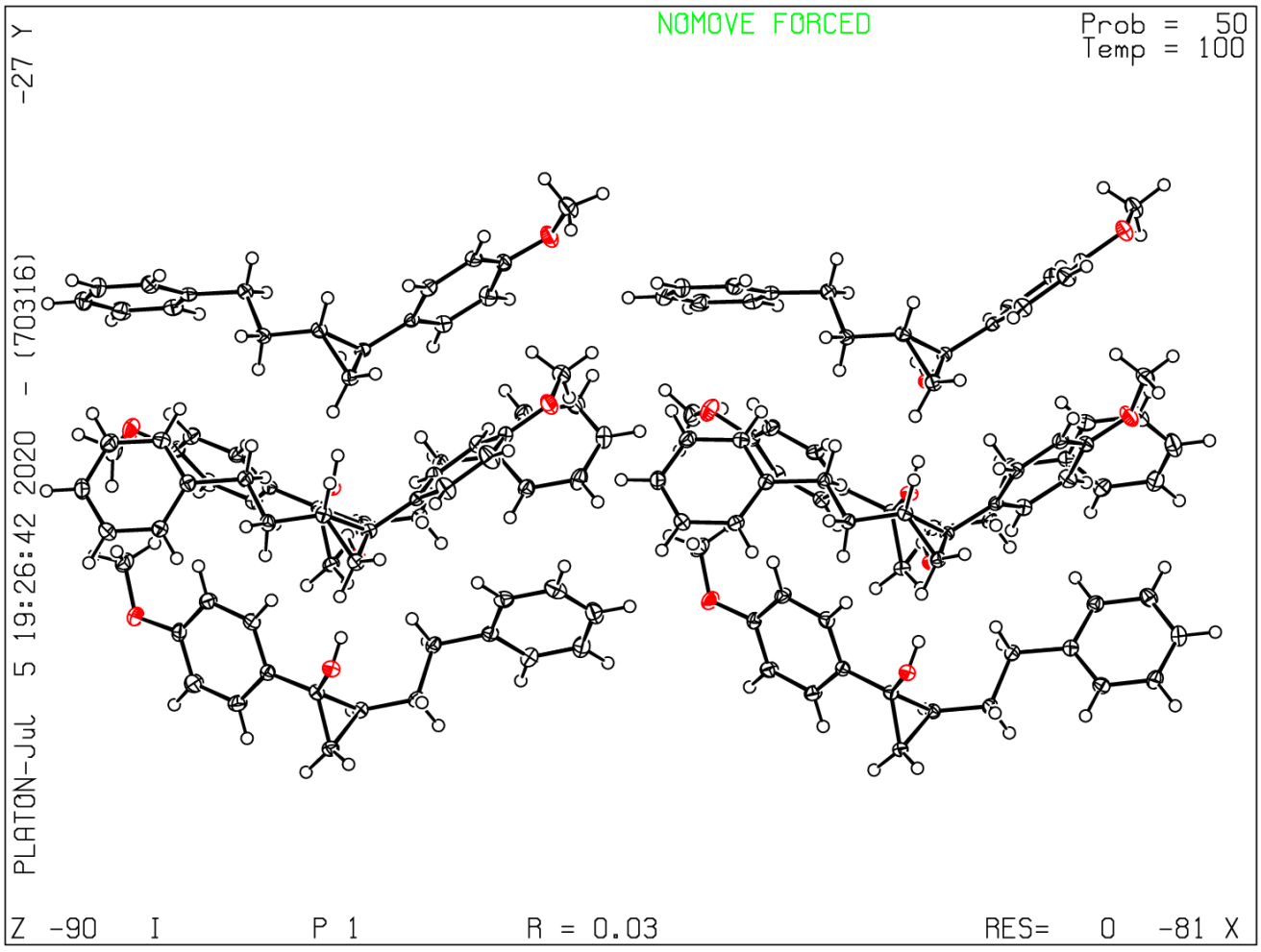


Identification code	rs013	
Chemical formula	$C_{18}H_{20}O_2$	
Formula weight	268.34 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.072 x 0.150 x 0.396 mm	
Crystal habit	colorless rod	
Crystal system	triclinic	
Space group	P 1	
Unit cell dimensions	a = 10.4813(4) Å	α = 98.118(2)°
	b = 10.5687(5) Å	β = 90.124(2)°
	c = 29.7666(13) Å	γ = 119.678(2)°
Volume	2826.1(2) $Å^3$	
Z	8	
Density (calculated)	1.261 g/cm^3	
Absorption coefficient	0.634 mm^{-1}	
F(000)	1152	
Diffractometer	Bruker D8 VENTURE κ-geometry diffractometer	
Radiation source	Incoatec IμS 3.0 microfocus sealed tube (Cu Kα, λ = 1.54178 Å)	
Theta range for data collection	3.01 to 80.14°	
Index ranges	-13<=h<=12, -13<=k<=11, -37<=l<=38	
Reflections collected	98059	
Independent reflections	23041 [R(int) = 0.0316]	
Coverage of independent reflections	98.1%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9560 and 0.7870	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5 (Sheldrick, 2015)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2015)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	23041 / 31 / 1474	
Goodness-of-fit on F2	1.042	
Δ/σmax	0.001	
Final R indices	22688 data; I>2σ(I)	R1 = 0.0274, wR2 = 0.0725
	all data	R1 = 0.0281, wR2 = 0.0731
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0415P)^2+0.3077P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.01(3)	
Largest diff. peak and hole	0.184 and -0.185 $eÅ^{-3}$	
R.M.S. deviation from mean	0.034 $eÅ^{-3}$	



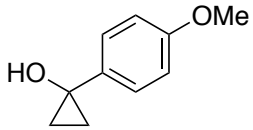
Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexanes into a concentrated solution of **2s** in CH_2Cl_2

ORTEP for 2s:



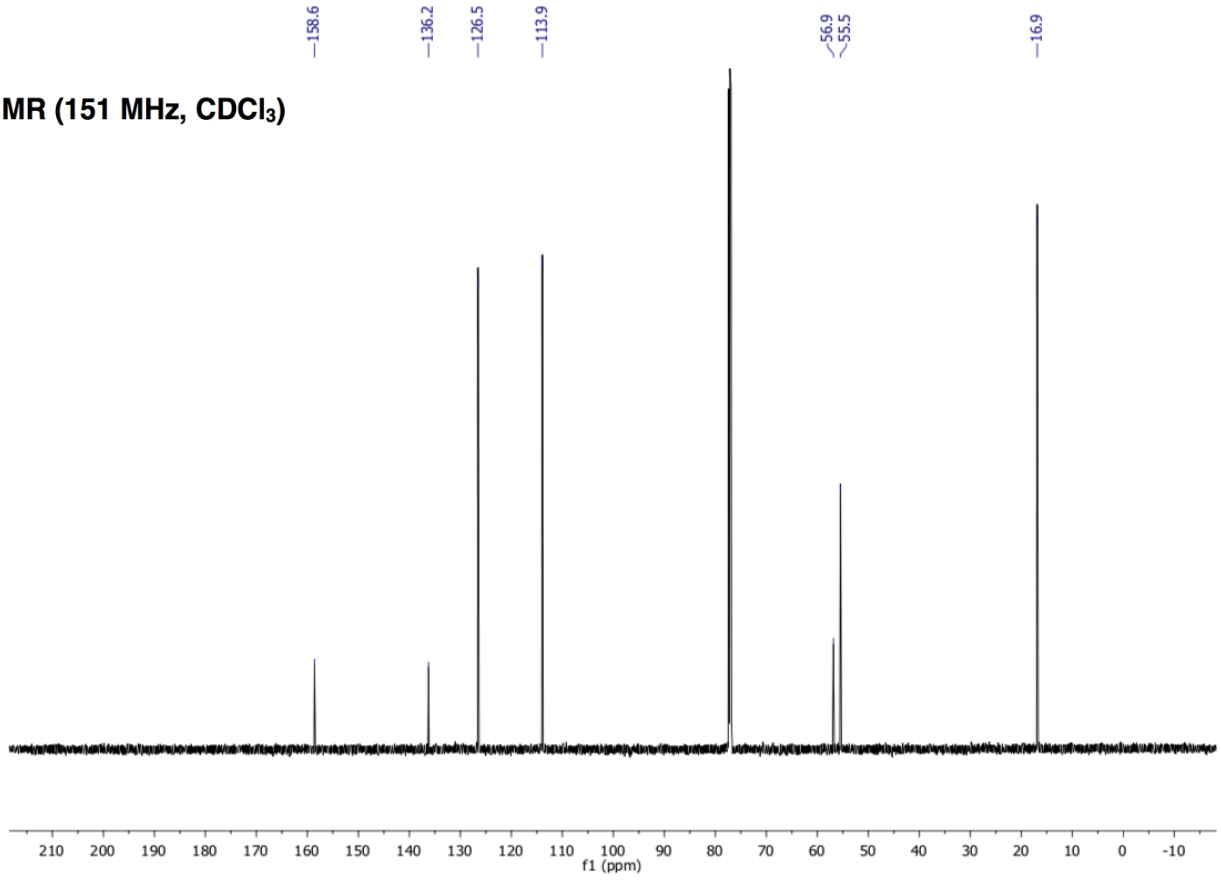
^{1}H and ^{13}C NMR SPECTRA

^{1}H NMR (600 MHz, $CDCl_3$)

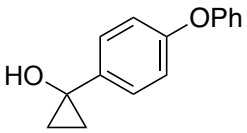


2a

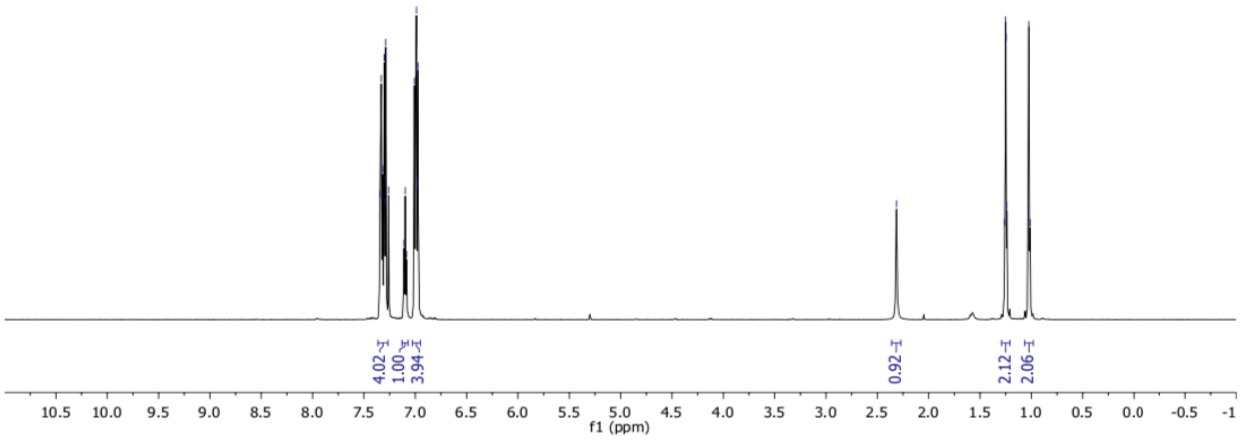
^{13}C NMR (151 MHz, $CDCl_3$)



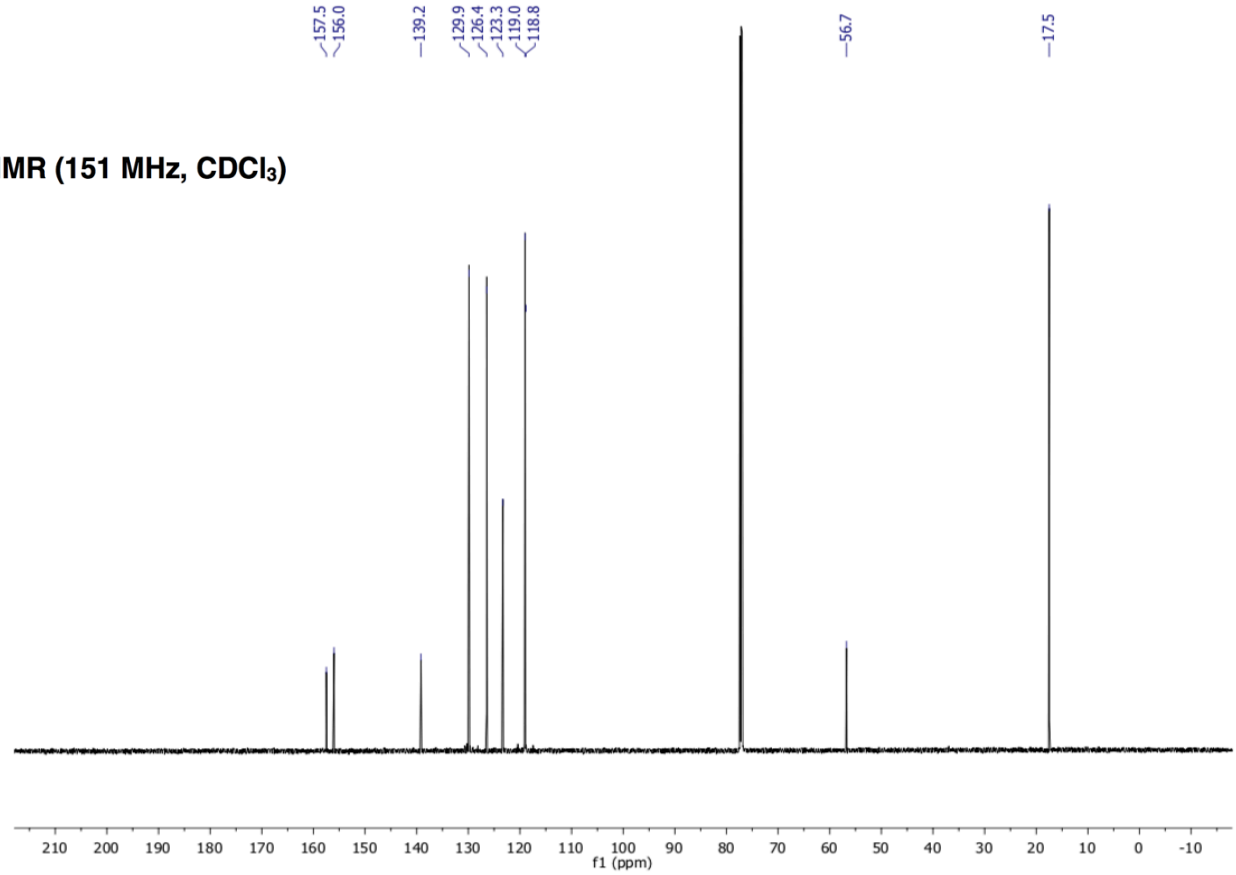
^{1}H NMR (600 MHz, $CDCl_3$)



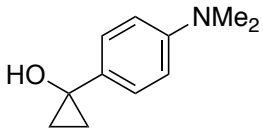
2b



^{13}C NMR (151 MHz, $CDCl_3$)

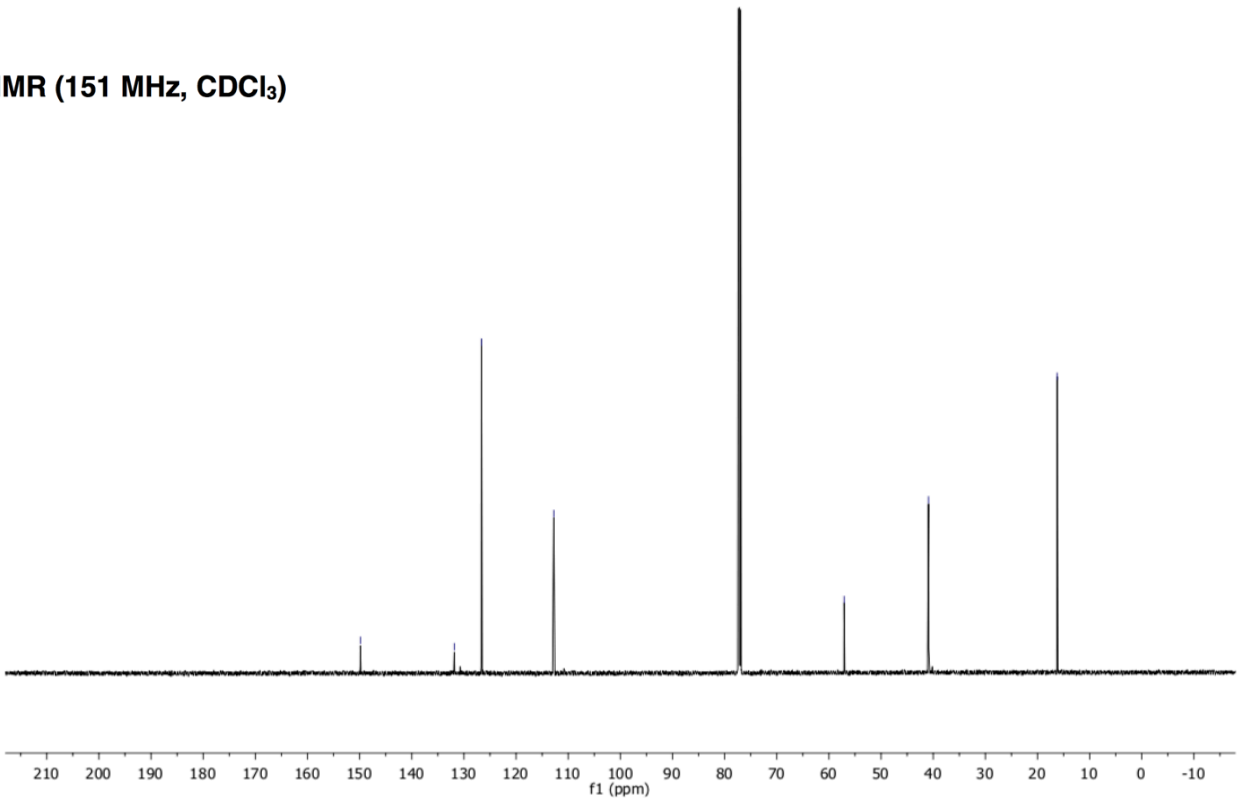


^{1}H NMR (600 MHz, $CDCl_3$)

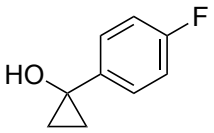


2c

^{13}C NMR (151 MHz, $CDCl_3$)

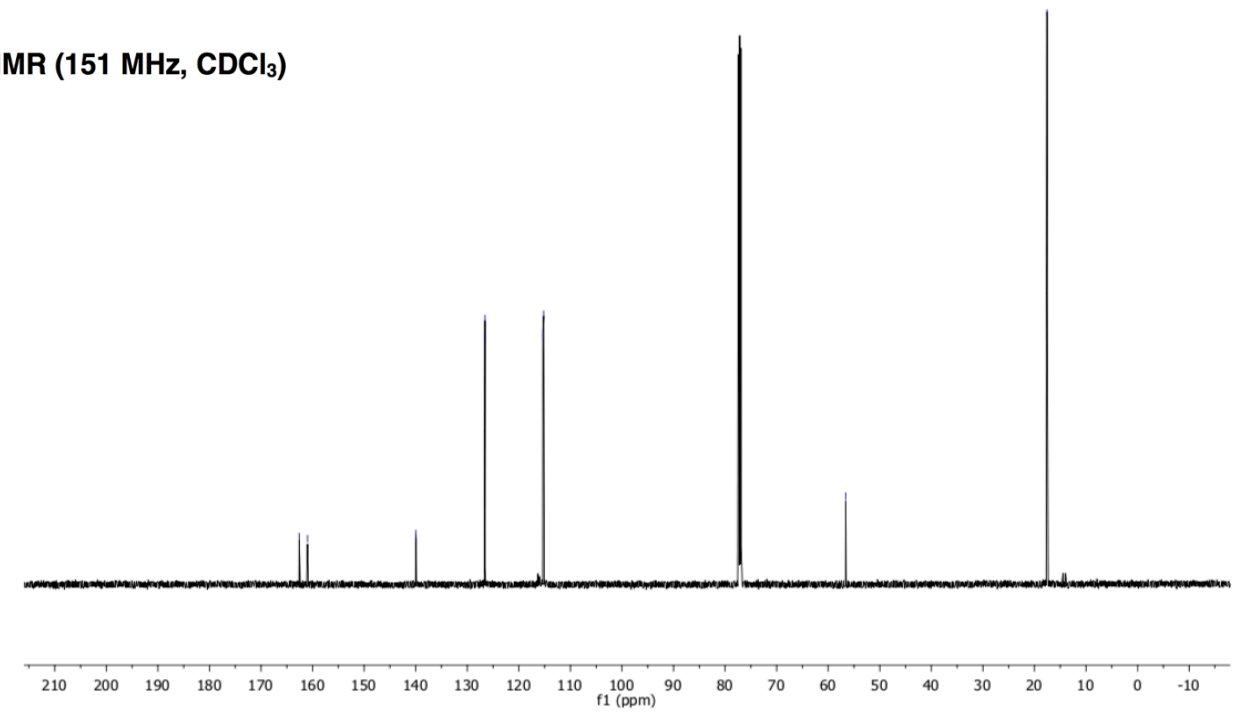


^{1}H NMR (600 MHz, $CDCl_3$)

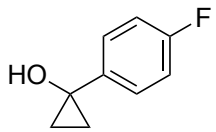


2d

^{13}C NMR (151 MHz, $CDCl_3$)

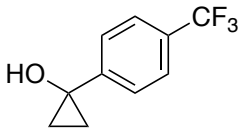


^{19}F NMR (564 MHz, $CDCl_3$)



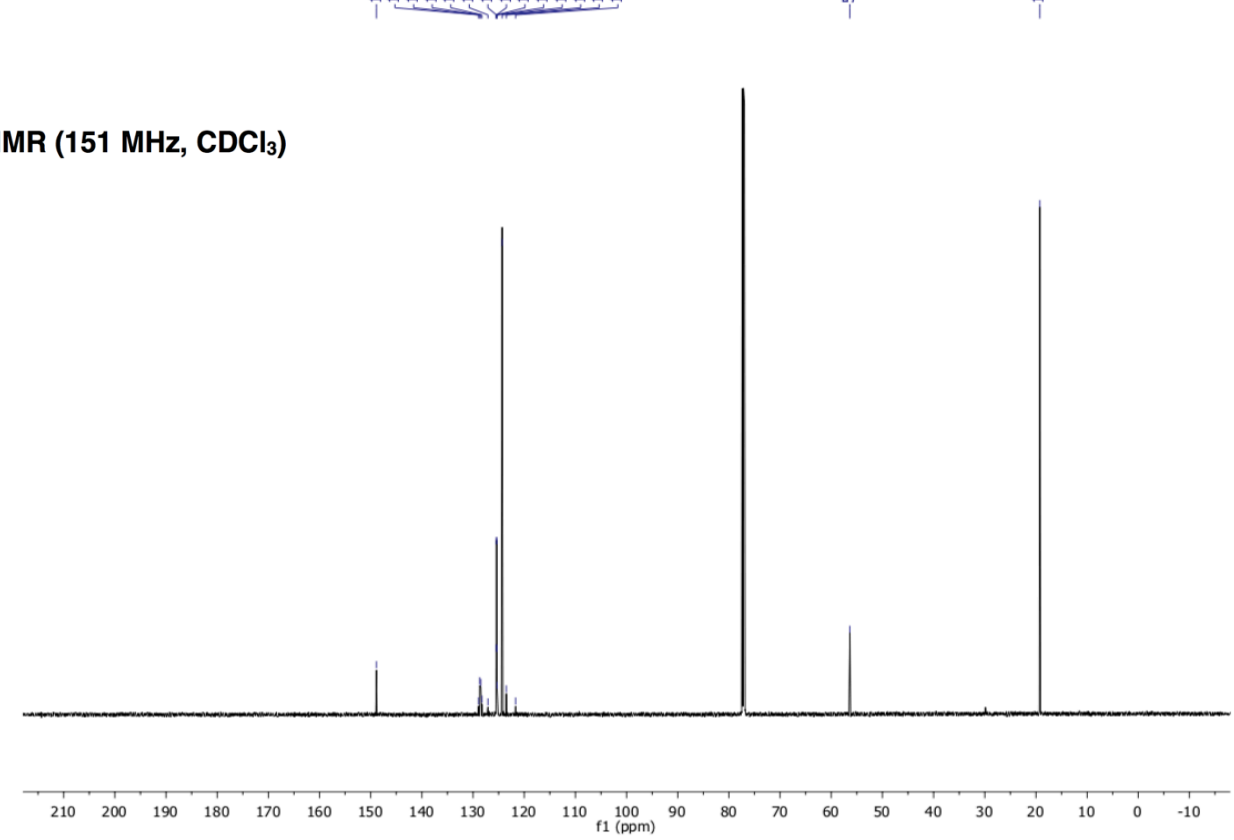
2d

^{1}H NMR (600 MHz, $CDCl_3$)

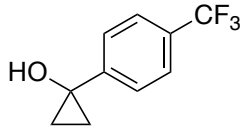


2e

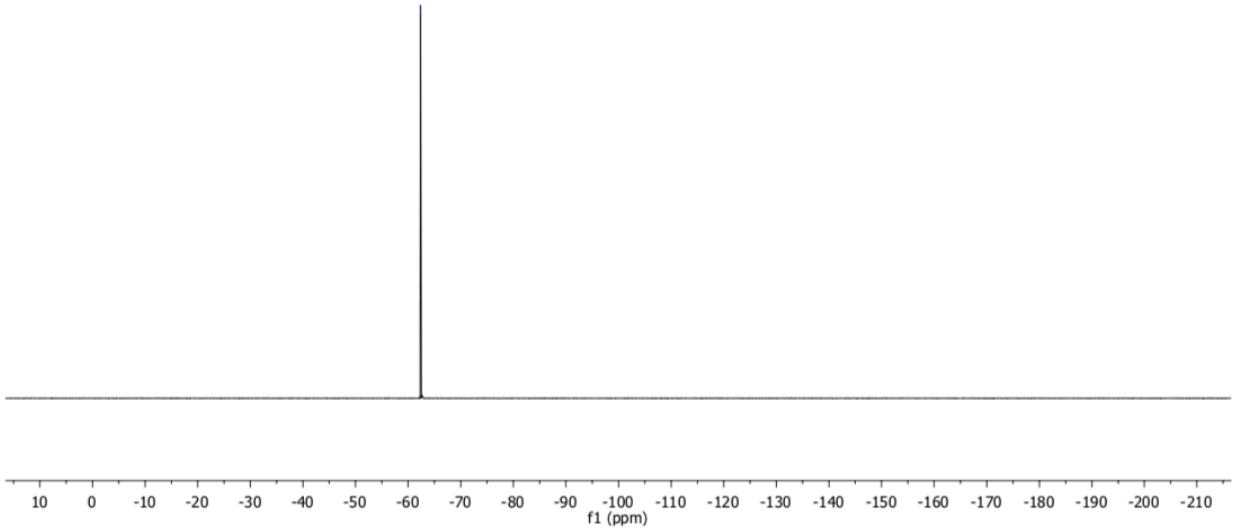
^{13}C NMR (151 MHz, $CDCl_3$)



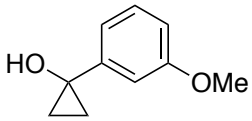
^{19}F NMR (564 MHz, $CDCl_3$)



2e

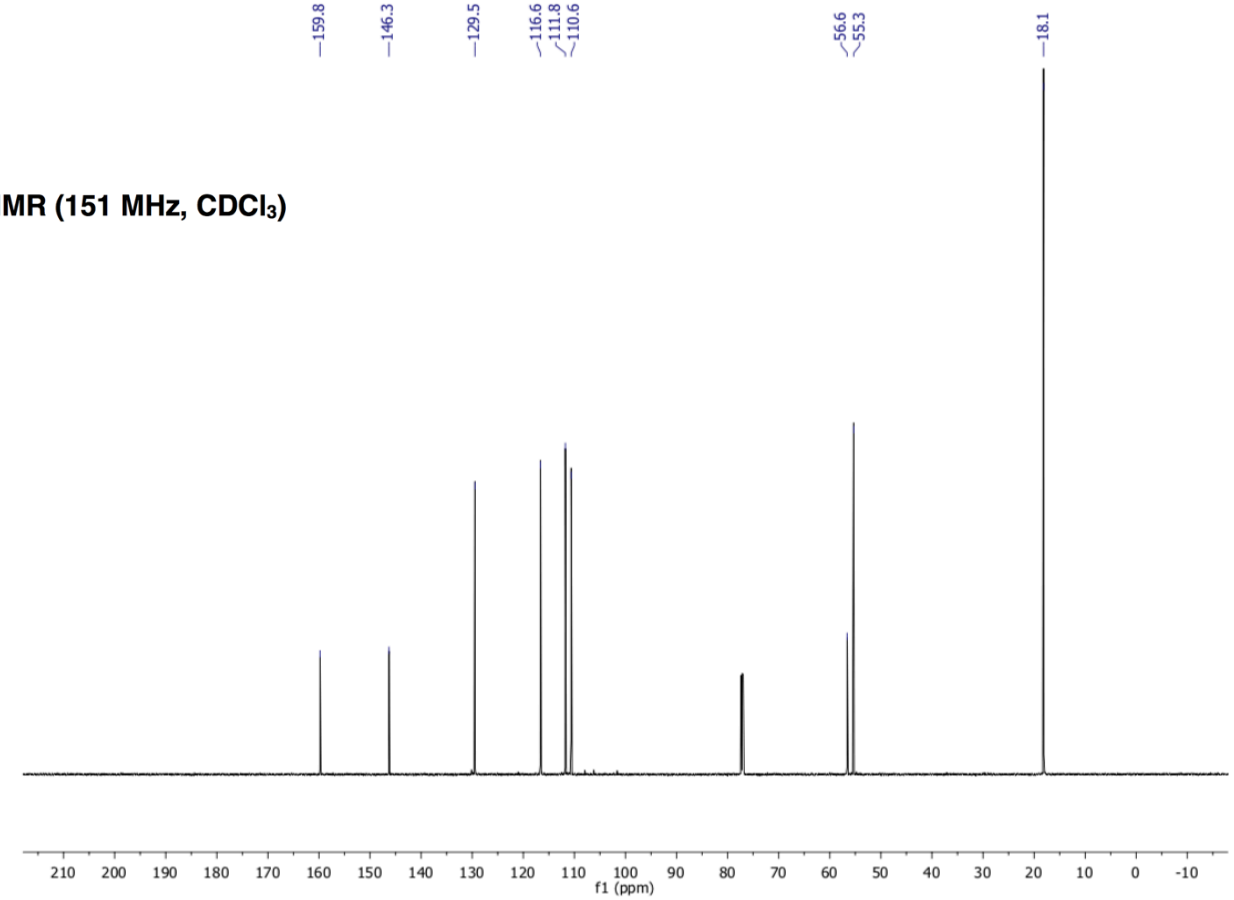


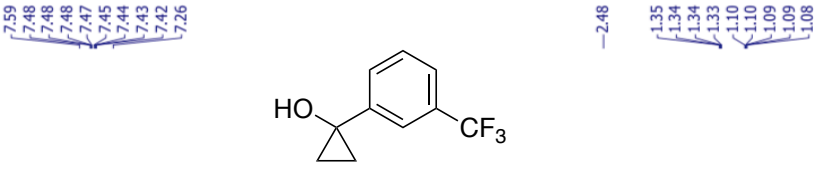
^{1}H NMR (600 MHz, $CDCl_3$)



2f

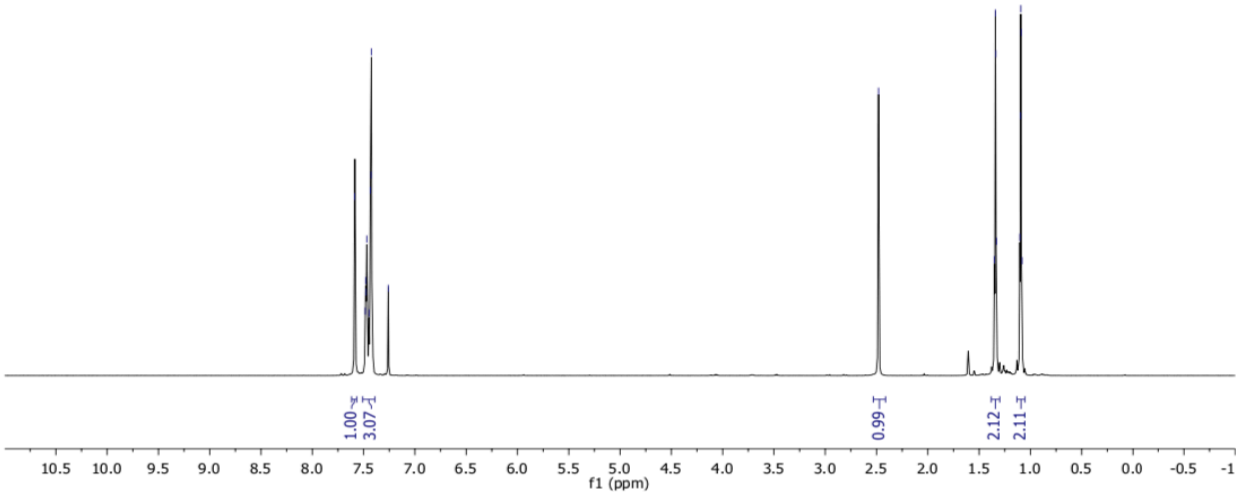
^{13}C NMR (151 MHz, $CDCl_3$)



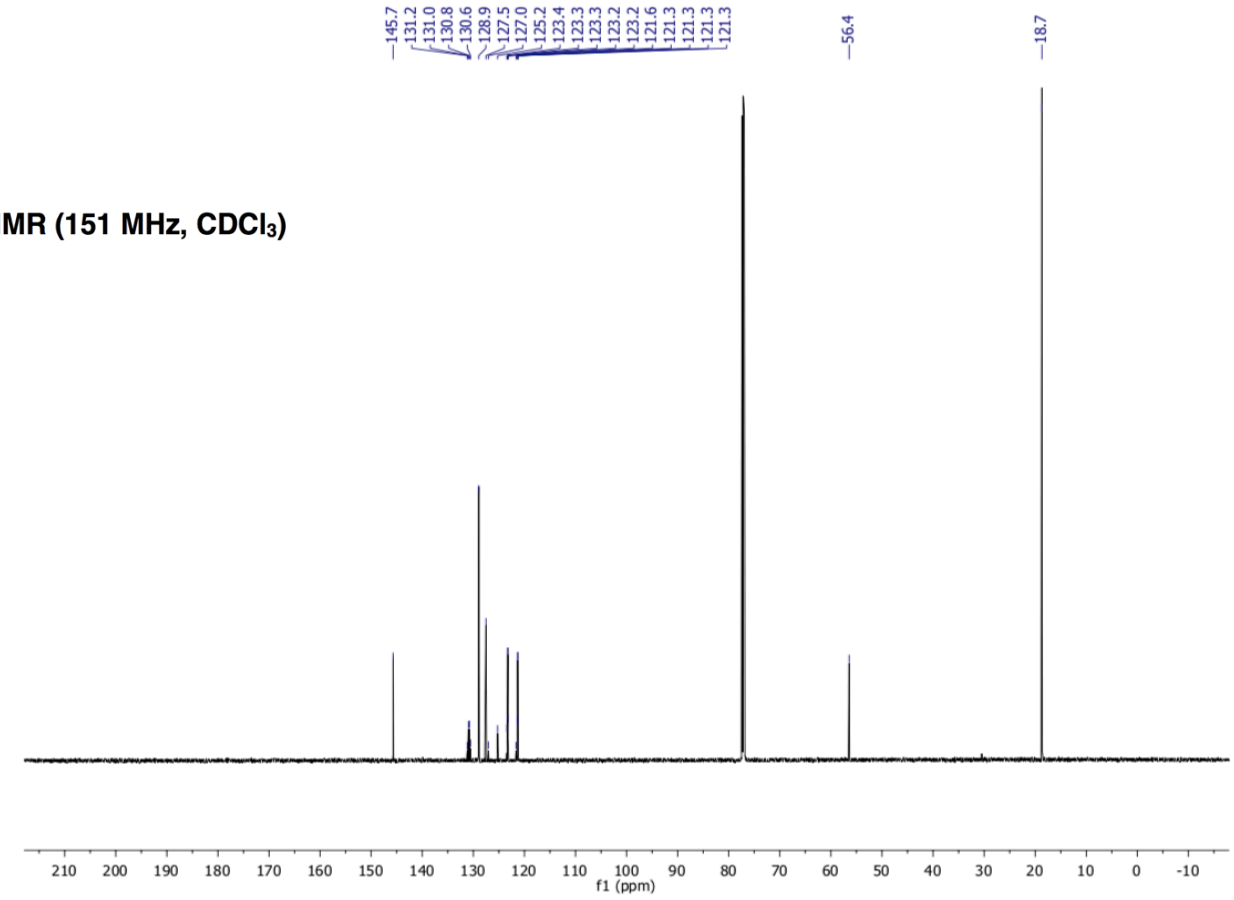


2g

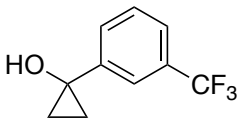
^{1}H NMR (600 MHz, $CDCl_3$)



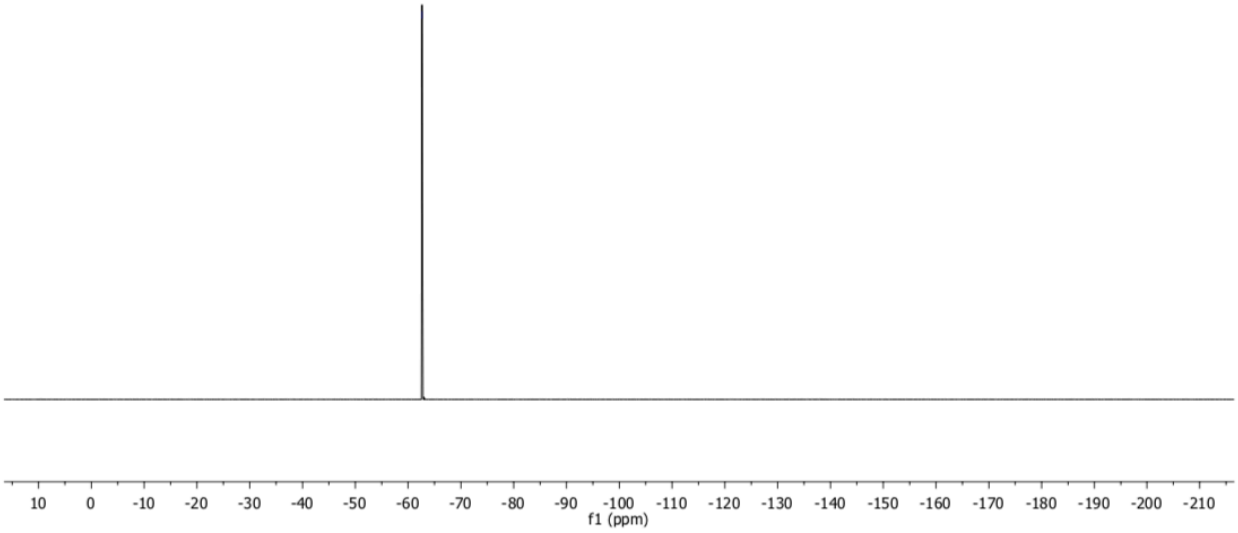
^{13}C NMR (151 MHz, $CDCl_3$)



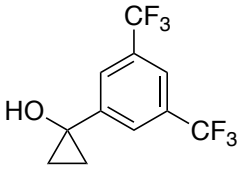
^{19}F NMR (564 MHz, $CDCl_3$)



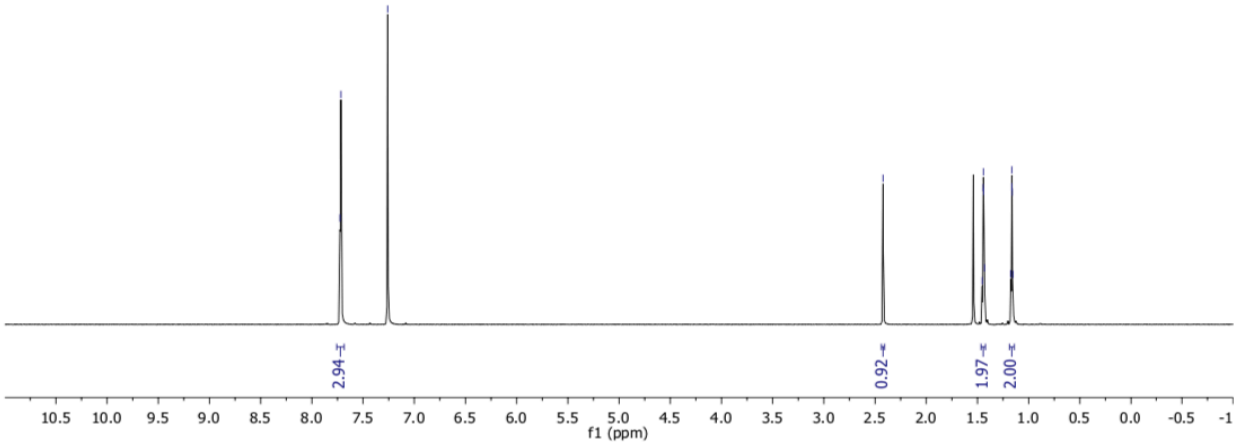
2g



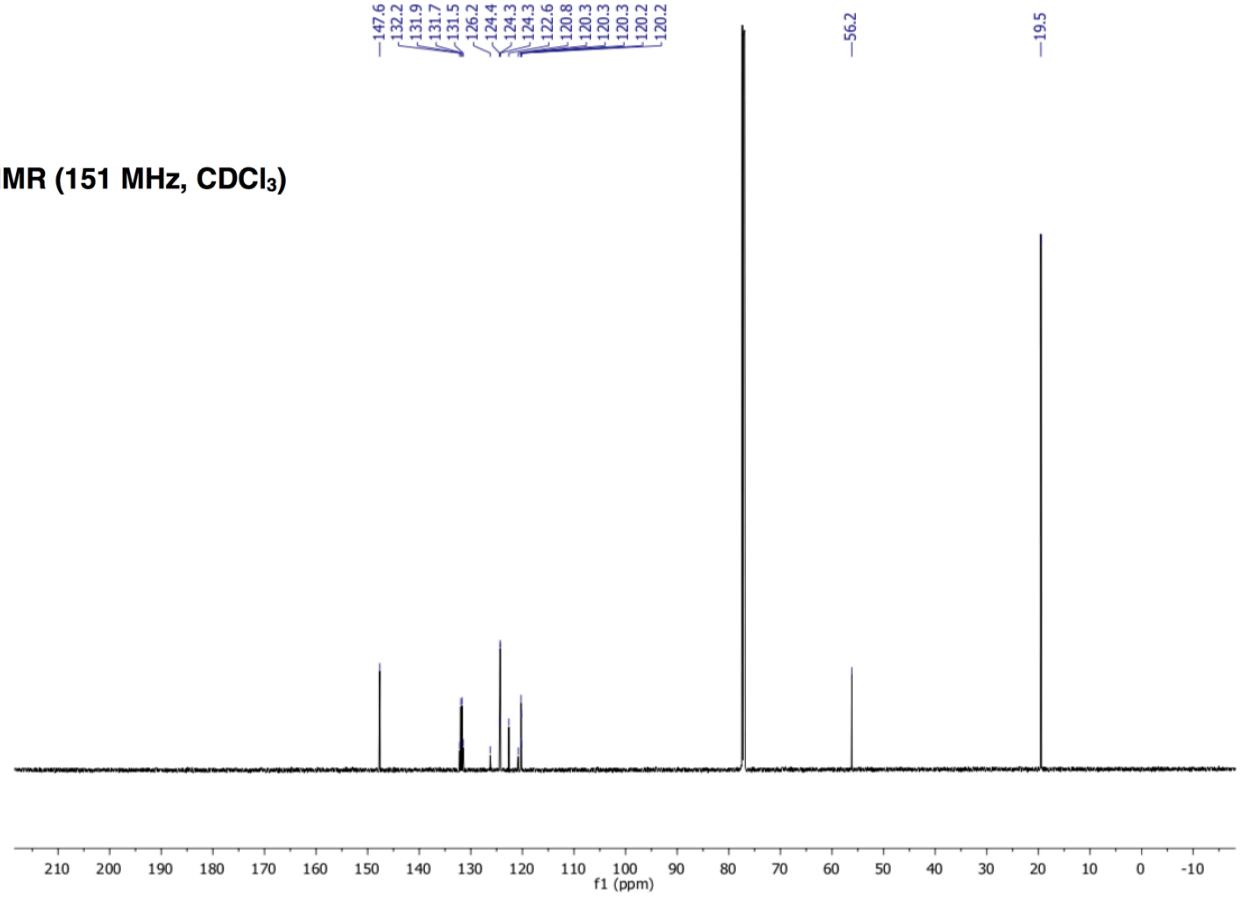
^{1}H NMR (600 MHz, $CDCl_3$)



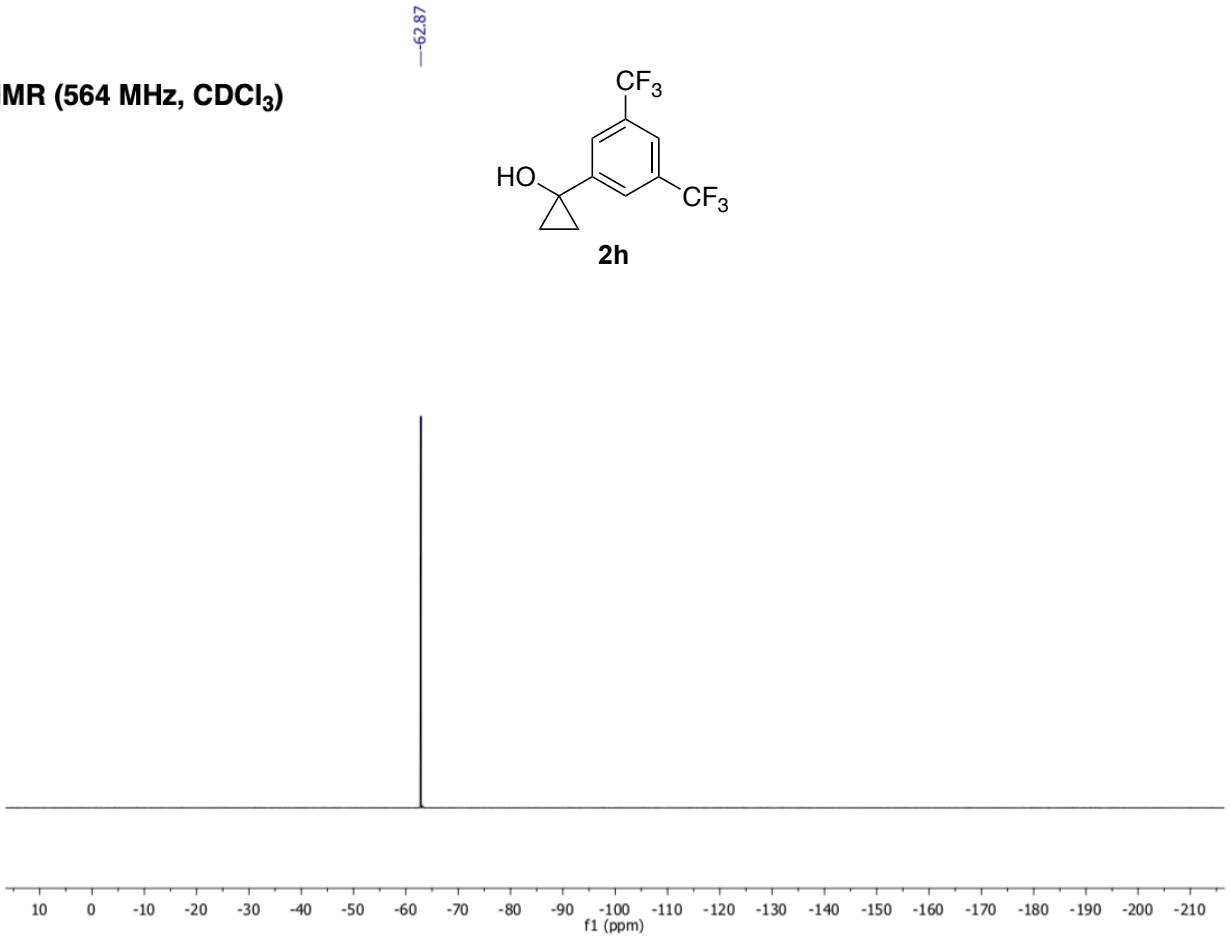
2h



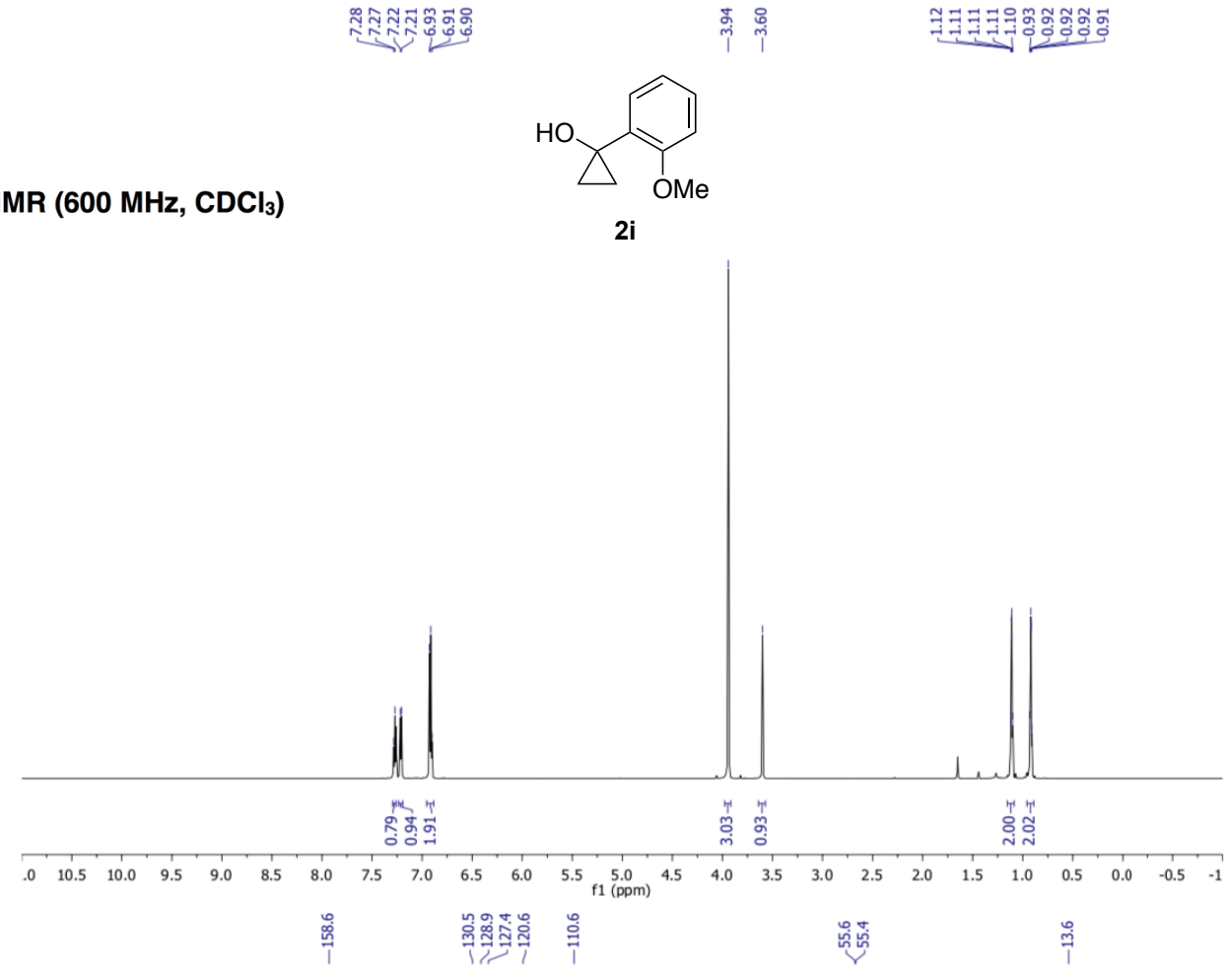
^{13}C NMR (151 MHz, $CDCl_3$)



^{19}F NMR (564 MHz, $CDCl_3$)



2h

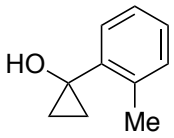


2i

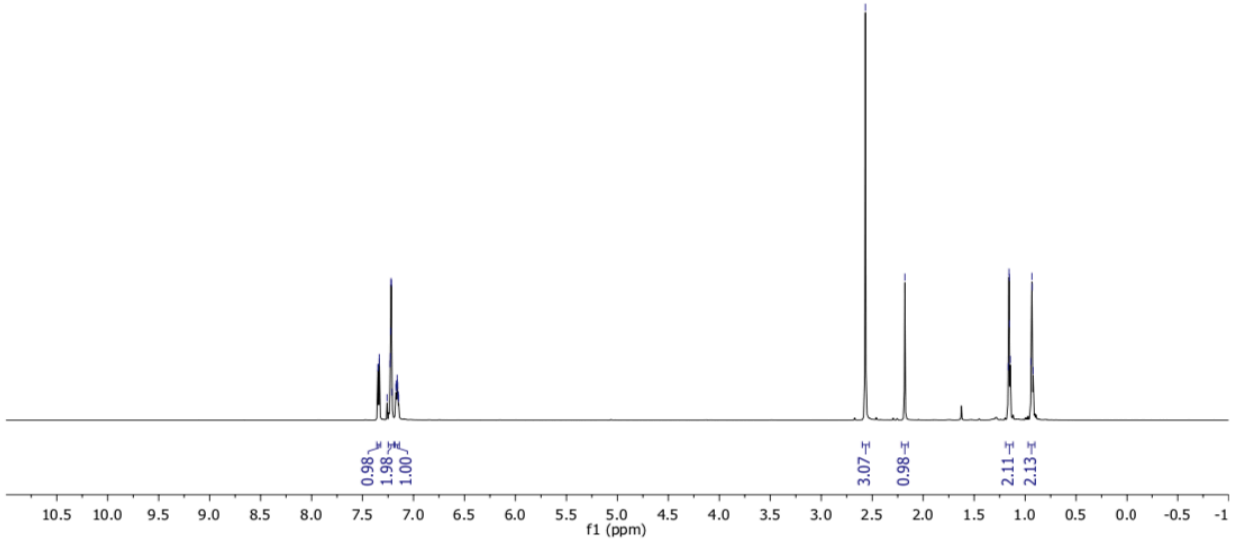
^{1}H NMR (600 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$)

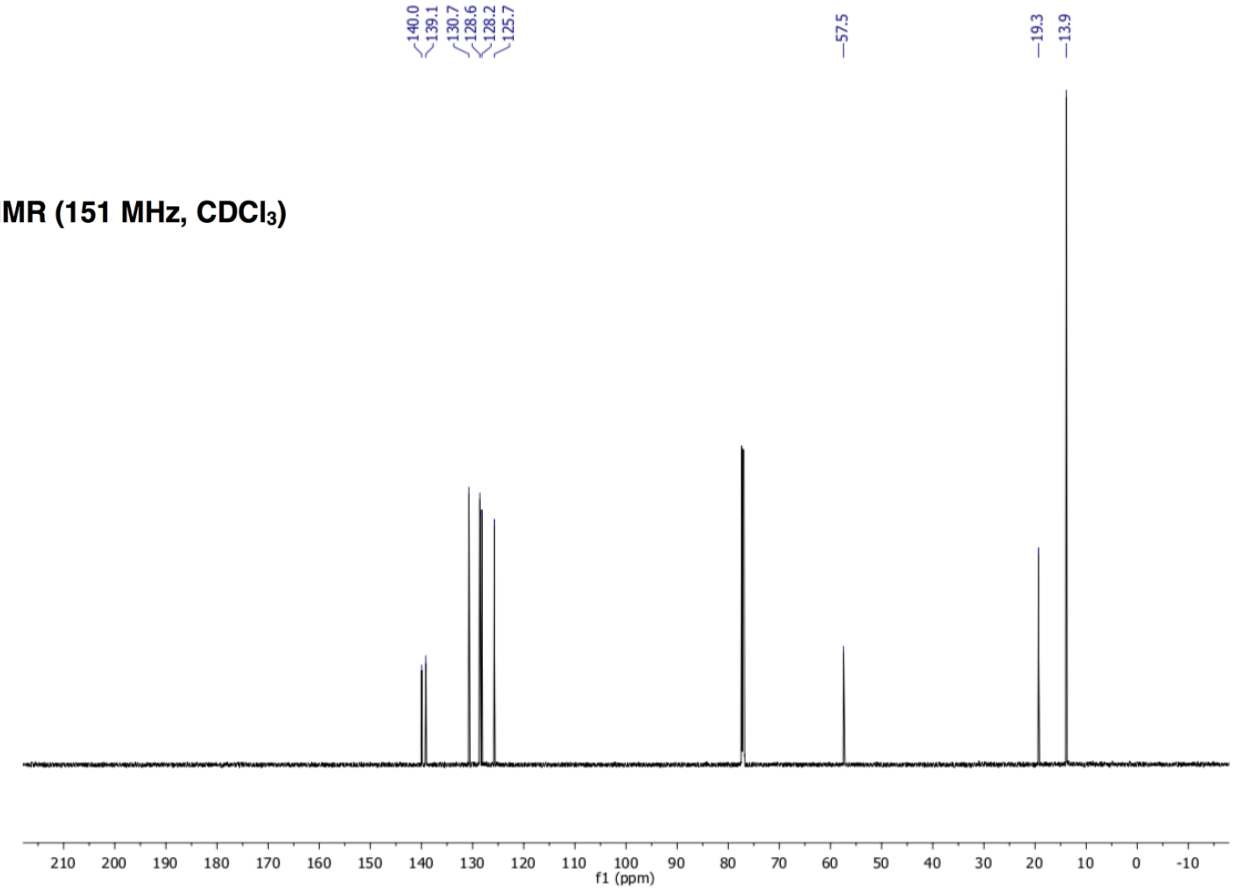
^{1}H NMR (600 MHz, $CDCl_3$)



2j



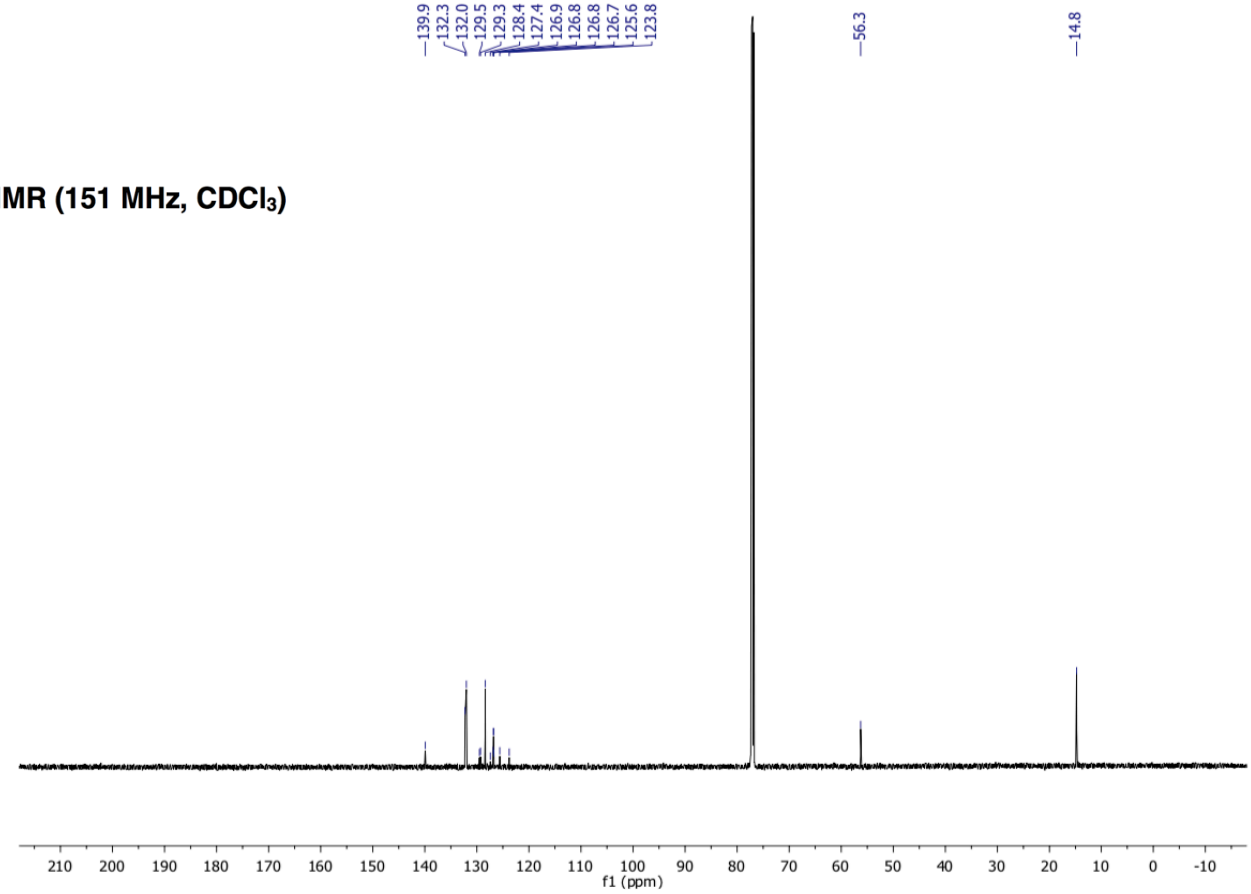
^{13}C NMR (151 MHz, $CDCl_3$)



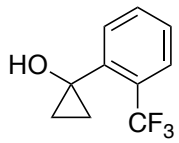
^{1}H NMR (600 MHz, $CDCl_3$)

2k

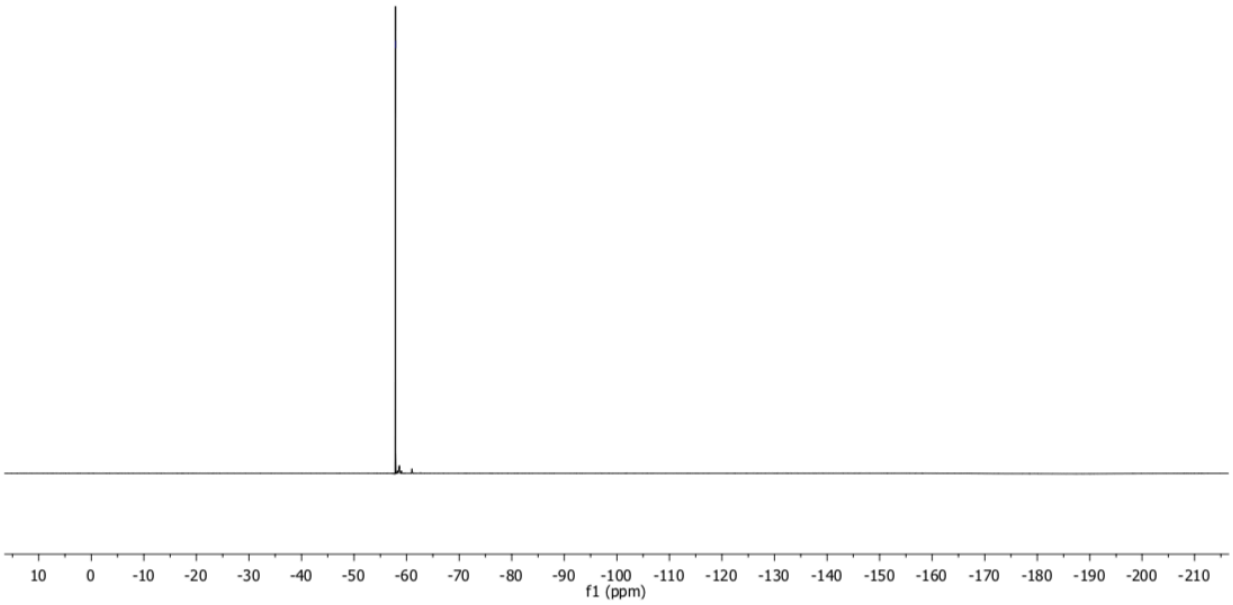
^{13}C NMR (151 MHz, $CDCl_3$)



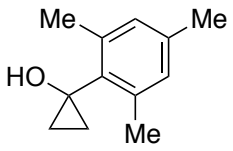
^{19}F NMR (564 MHz, $CDCl_3$)



2k

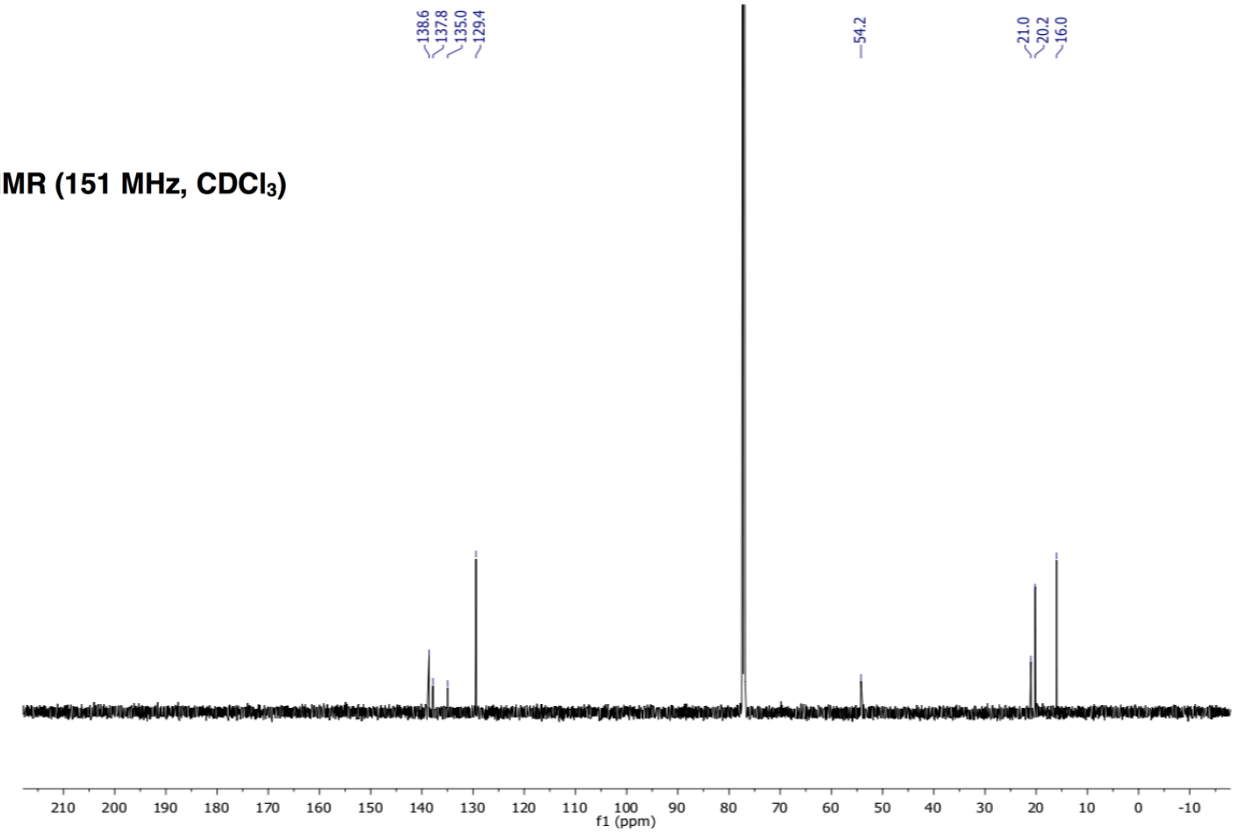


^{1}H NMR (600 MHz, $CDCl_3$)

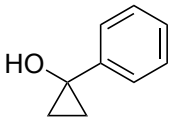


2l

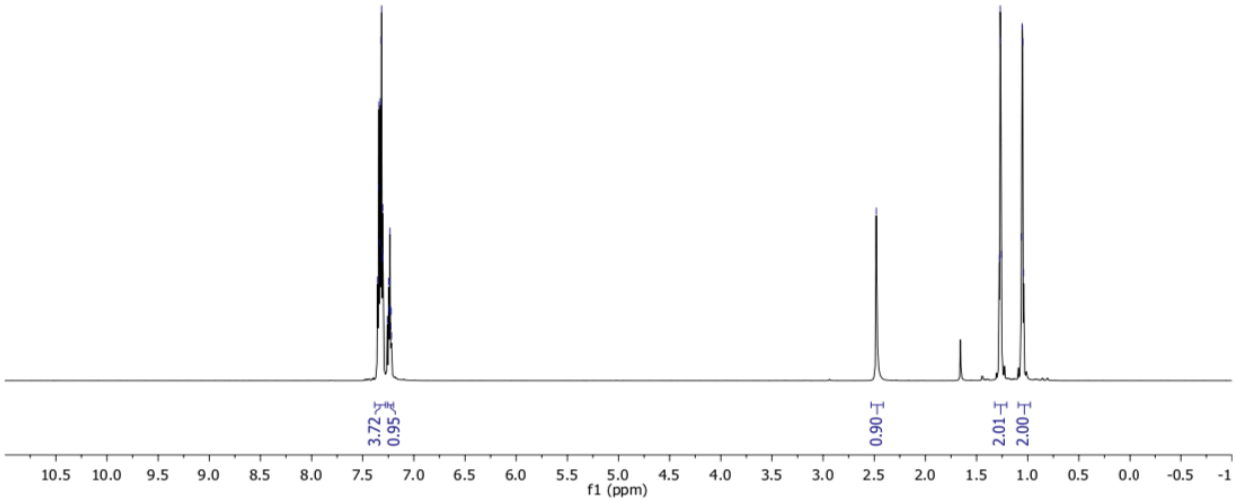
^{13}C NMR (151 MHz, $CDCl_3$)



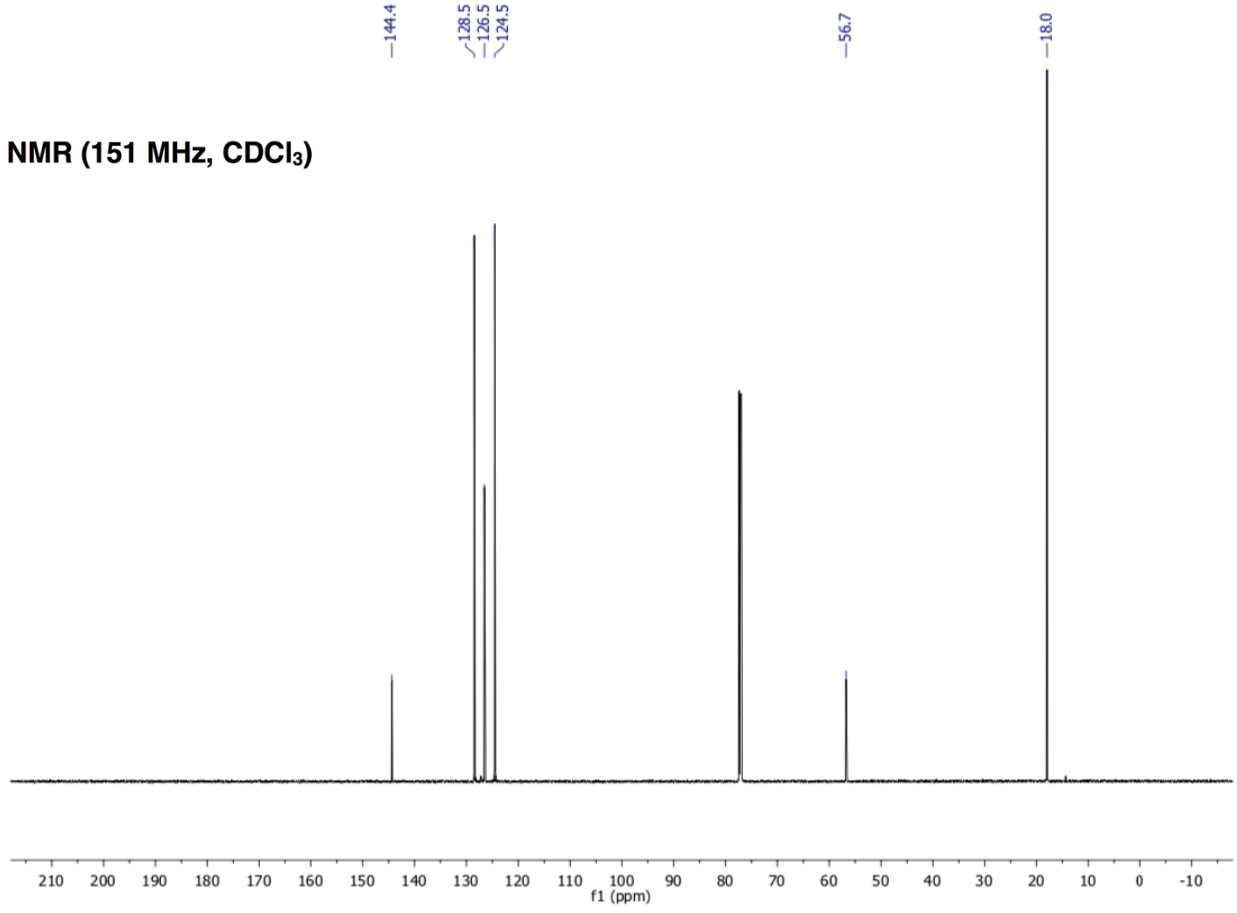
^{1}H NMR (600 MHz, $CDCl_3$)

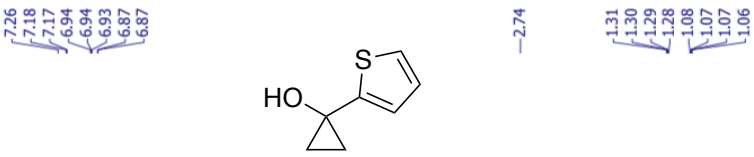


2m

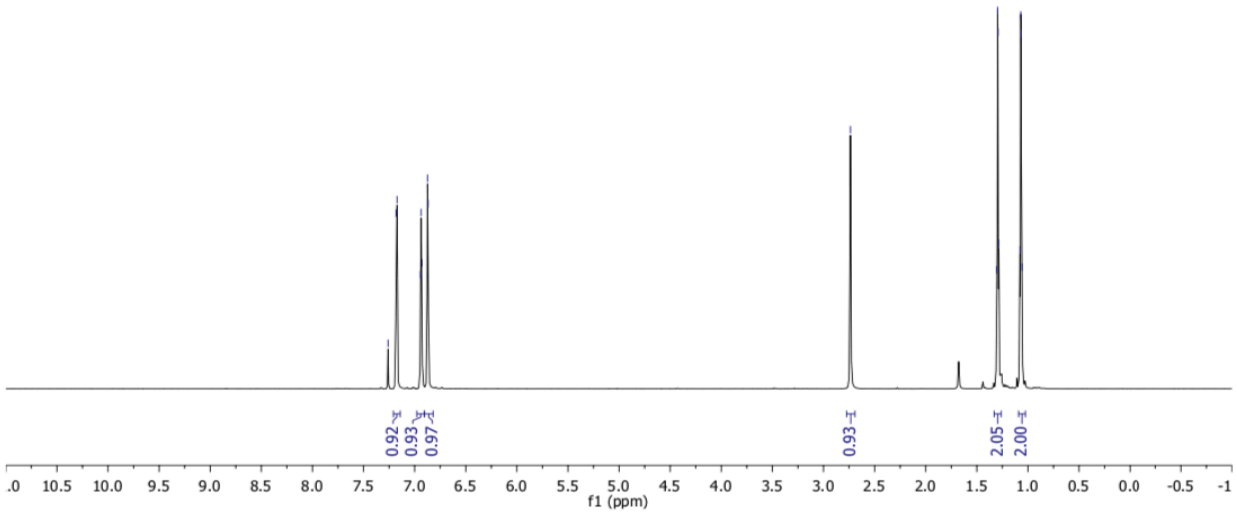


^{13}C NMR (151 MHz, $CDCl_3$)

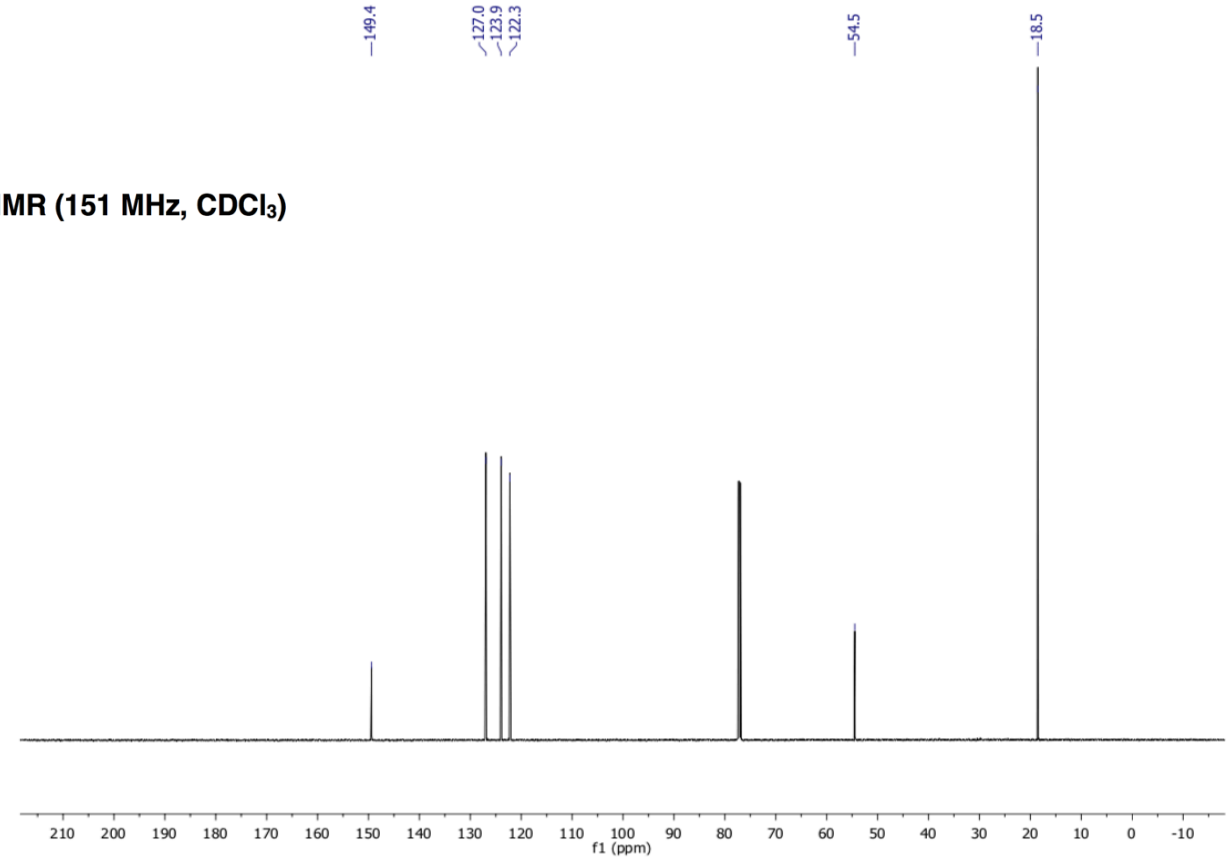


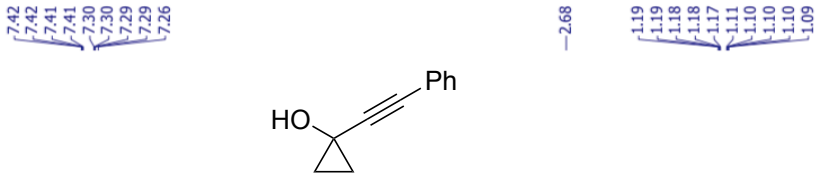


^{1}H NMR (600 MHz, $CDCl_3$) **2n**



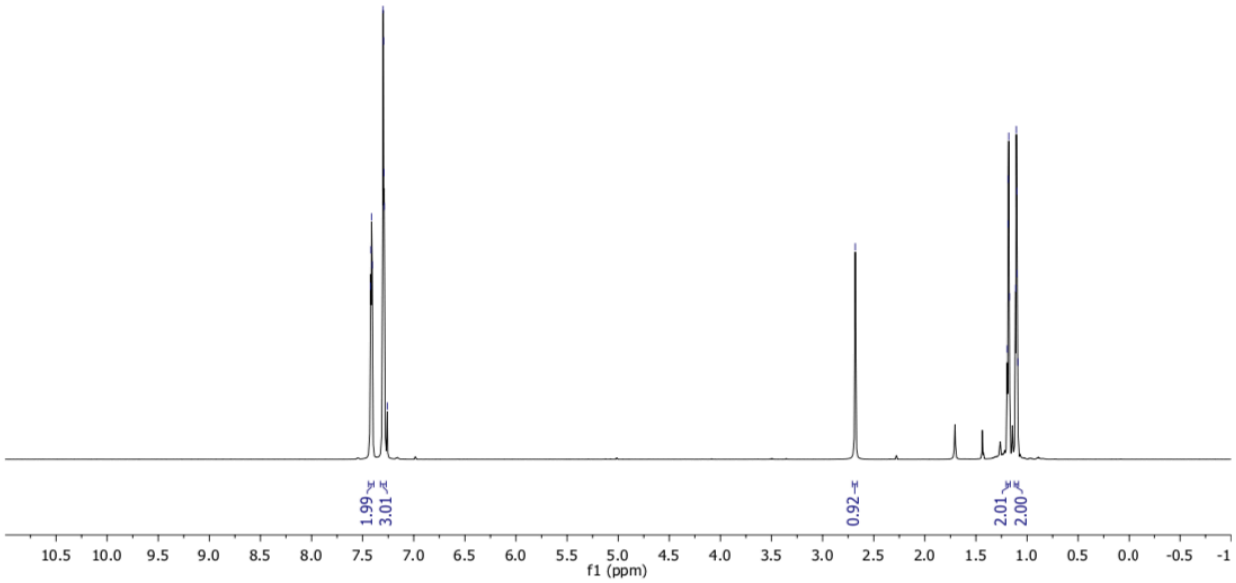
^{13}C NMR (151 MHz, $CDCl_3$)



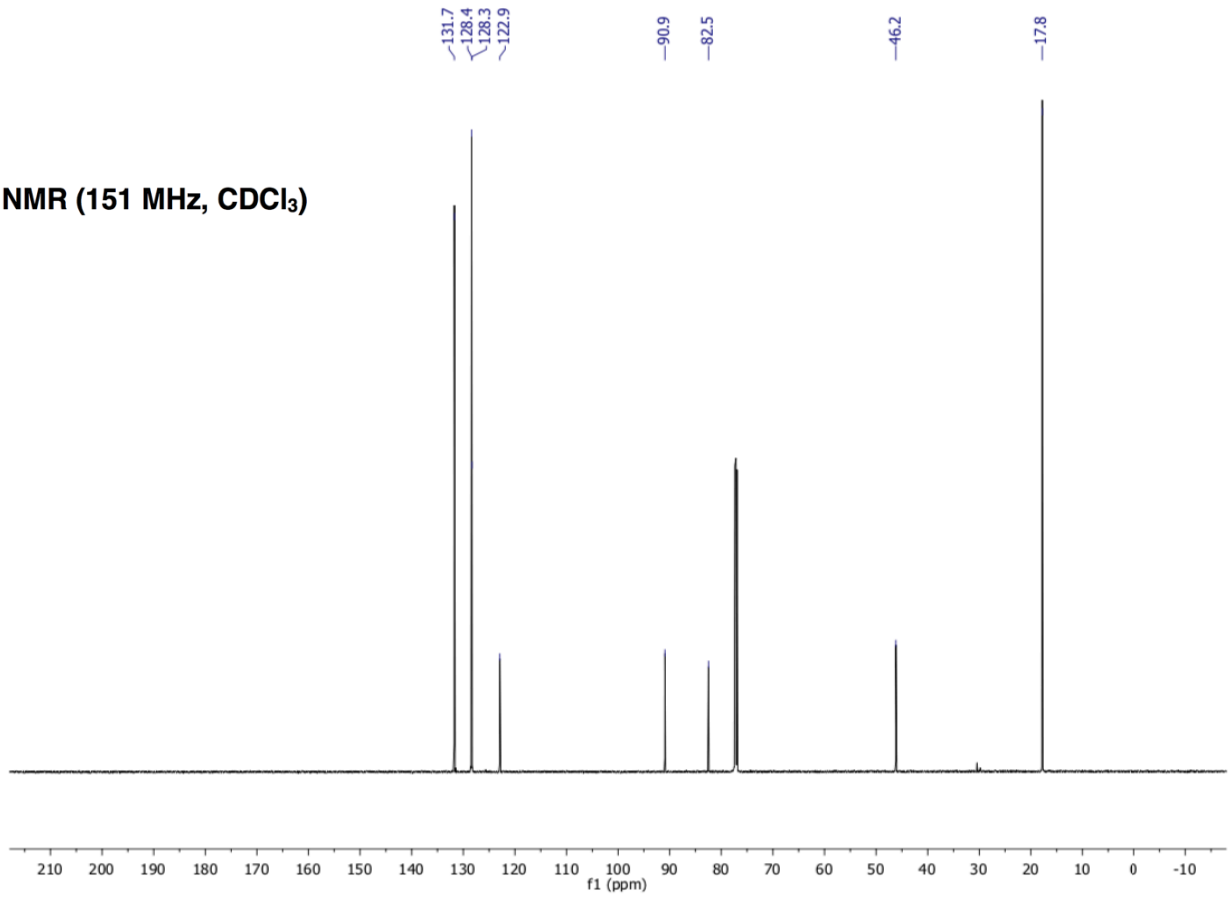


2o

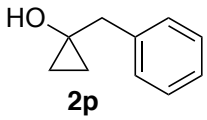
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

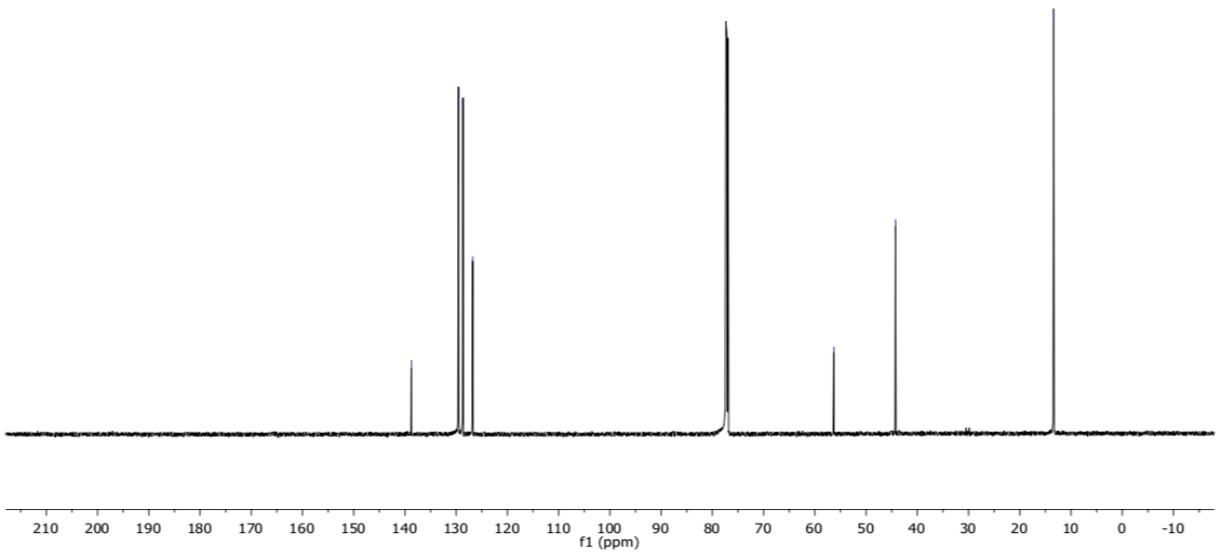


^{1}H NMR (600 MHz, $CDCl_3$)

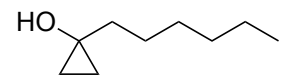


2p

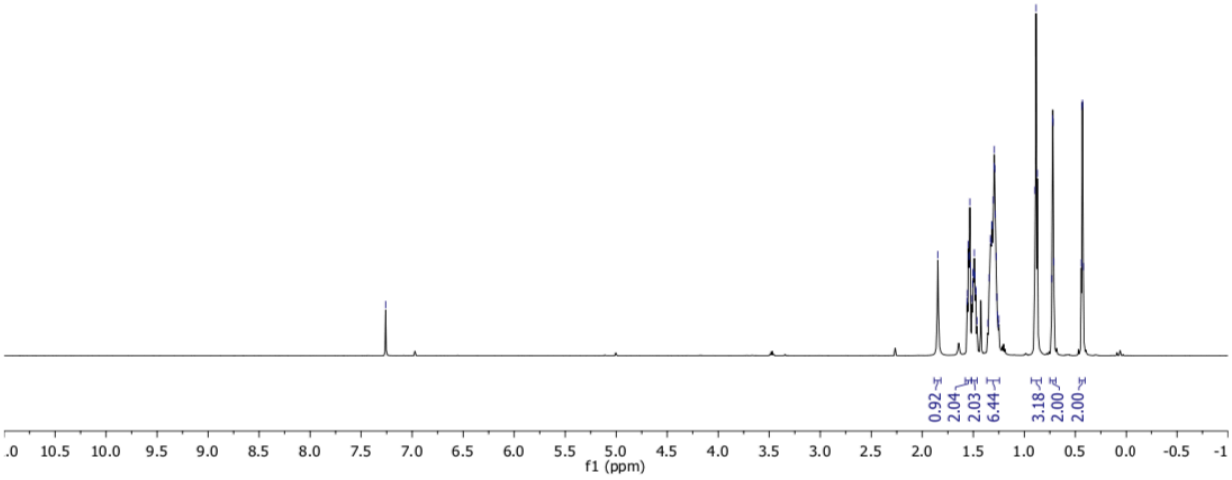
^{13}C NMR (151 MHz, $CDCl_3$)



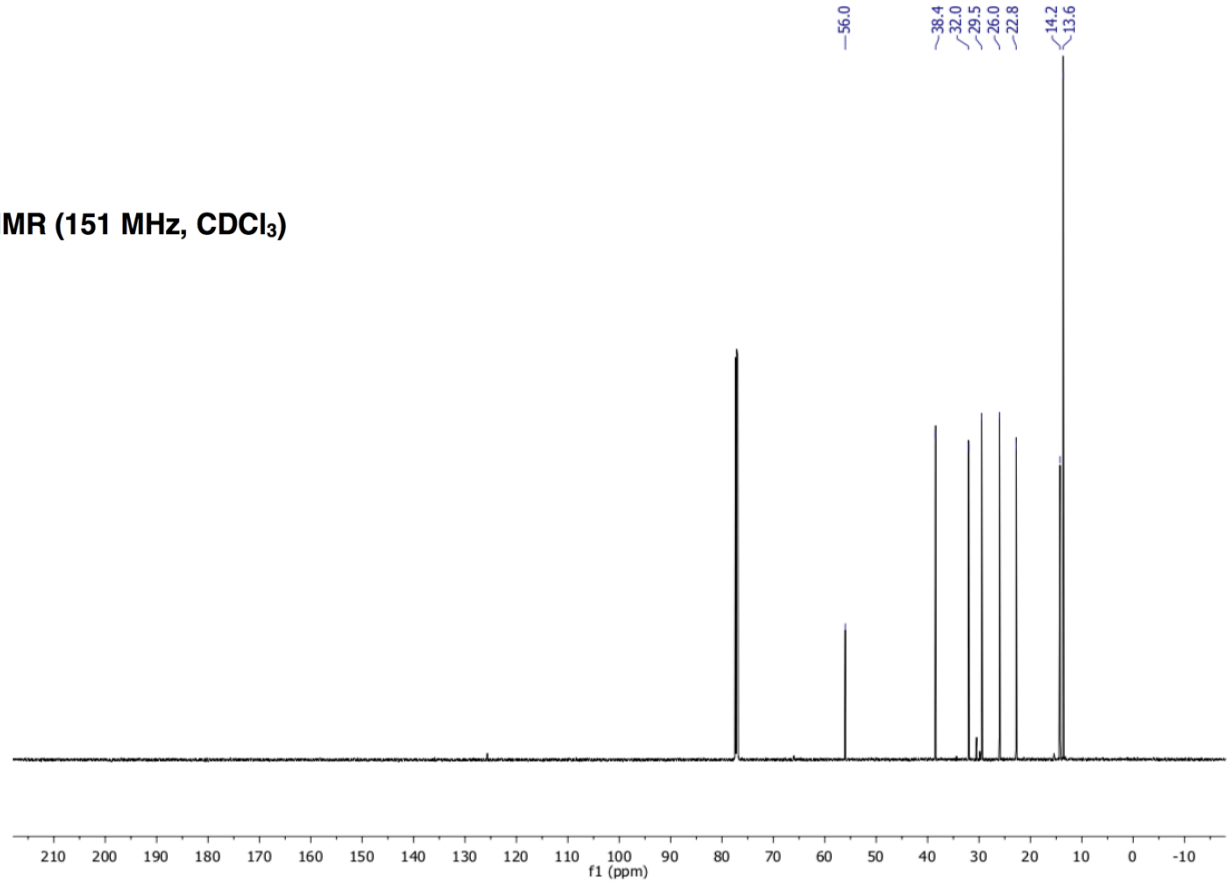
^{1}H NMR (600 MHz, $CDCl_3$)



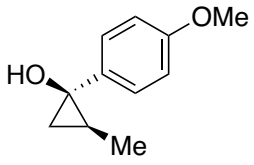
2q



^{13}C NMR (151 MHz, $CDCl_3$)

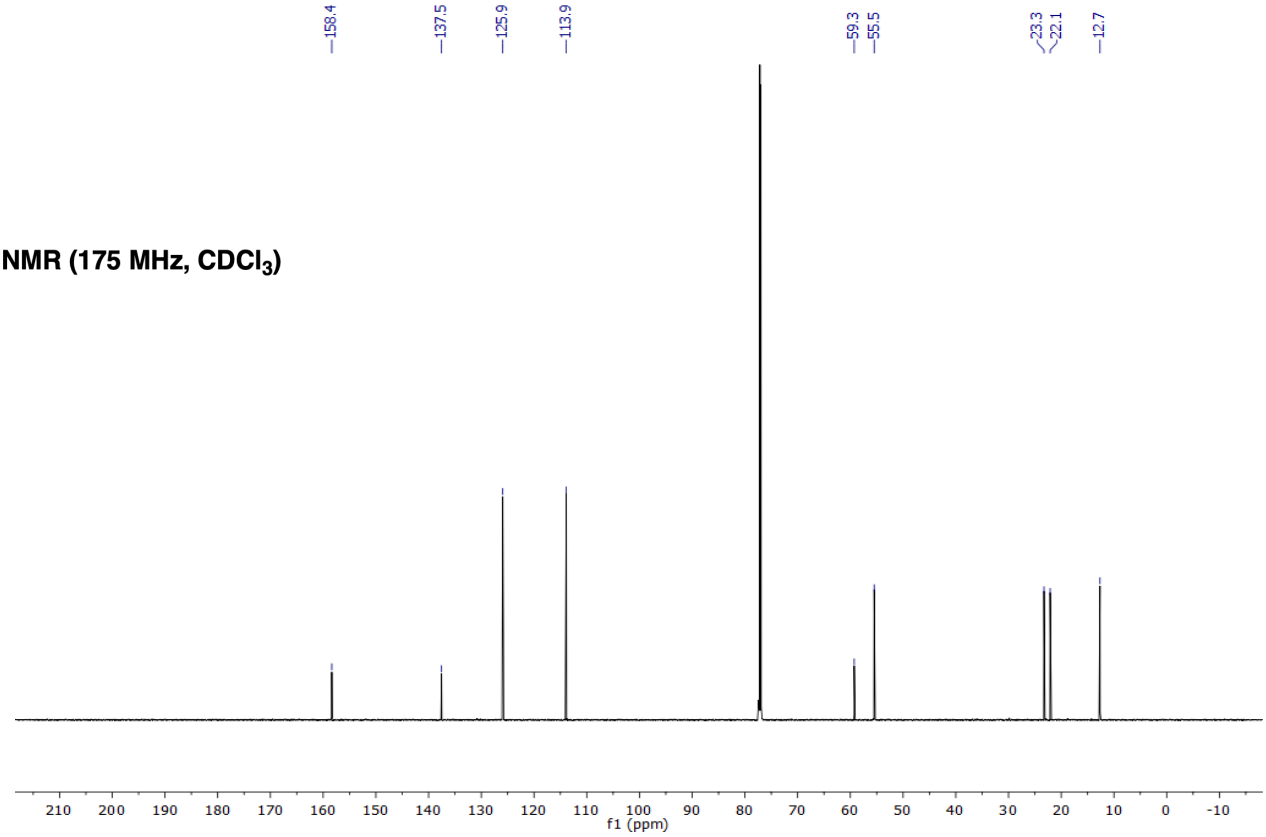


^{1}H NMR (700 MHz, $CDCl_3$)

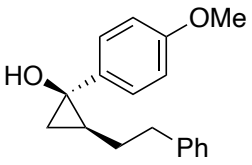


2r

^{13}C NMR (175 MHz, $CDCl_3$)

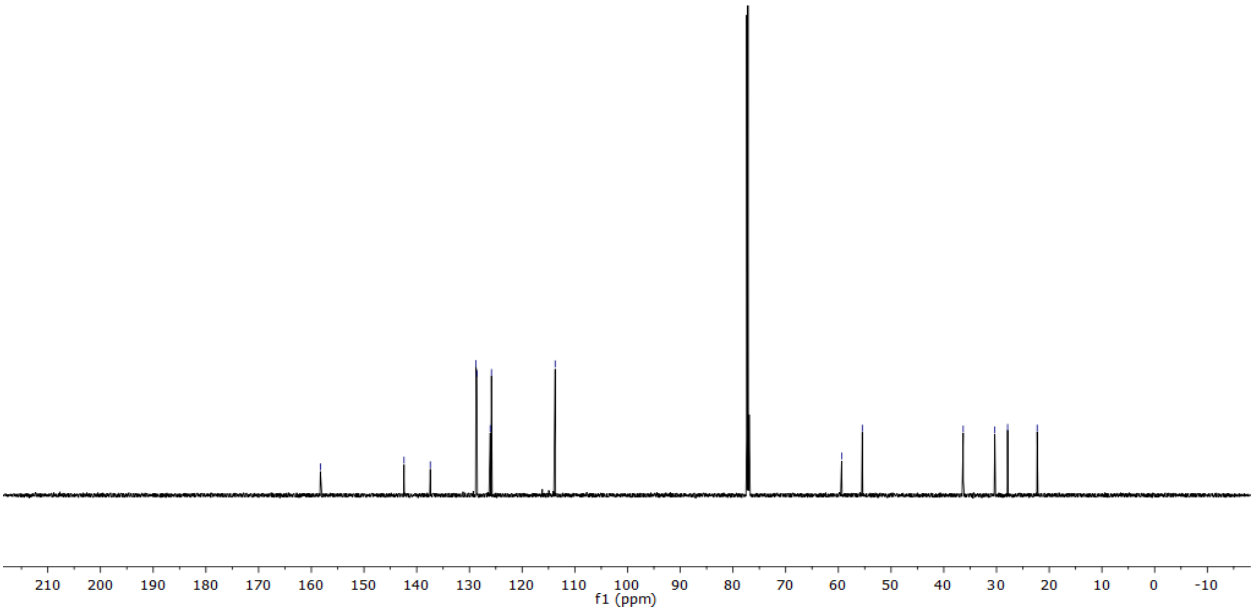


^{1}H NMR (600 MHz, $CDCl_3$)

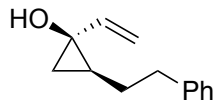


2s

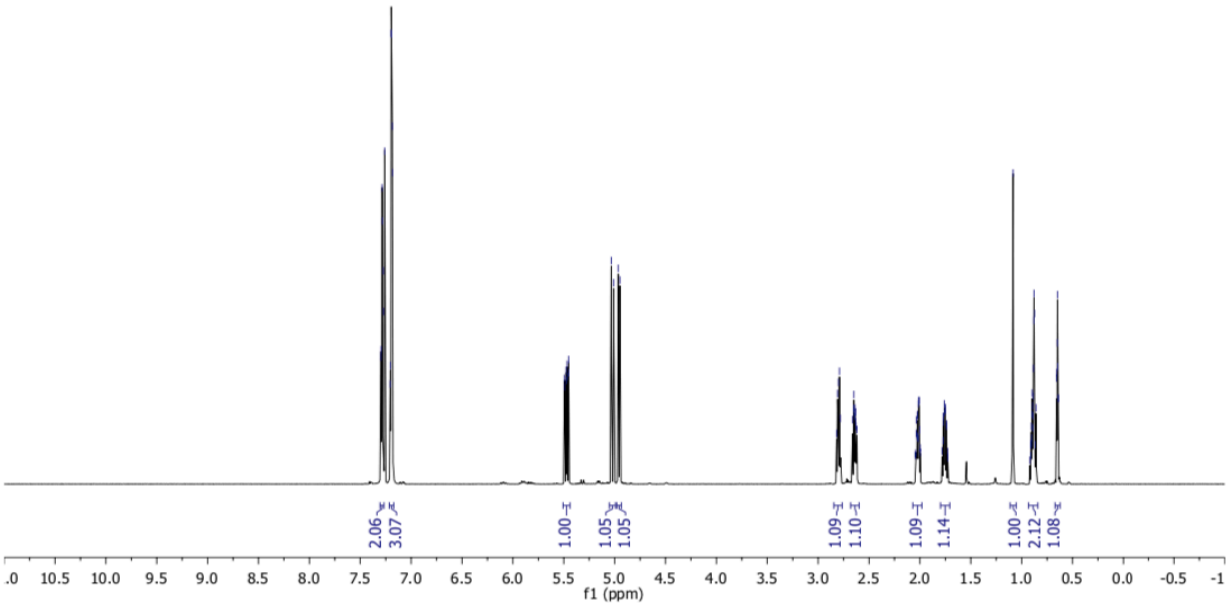
^{13}C NMR (151 MHz, $CDCl_3$)



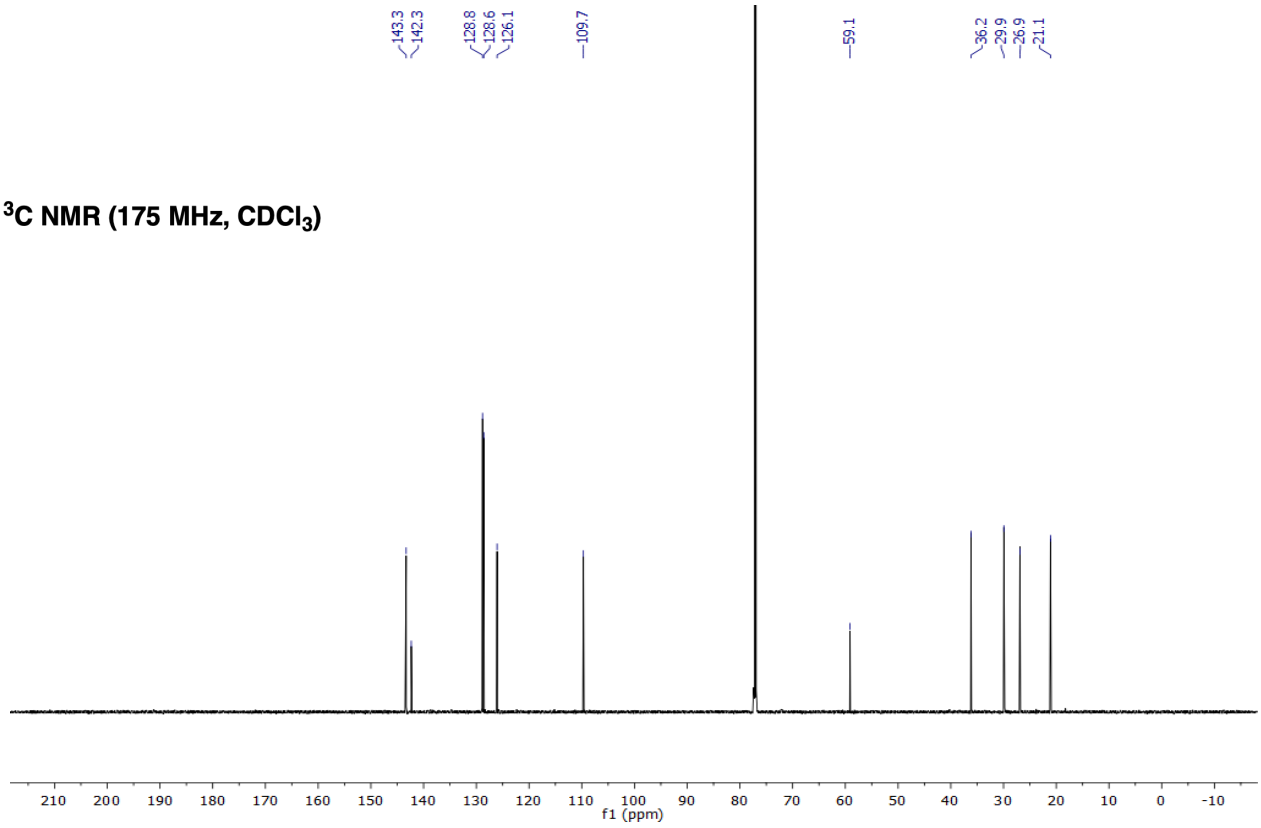
^{1}H NMR (700 MHz, $CDCl_3$)



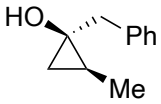
2t



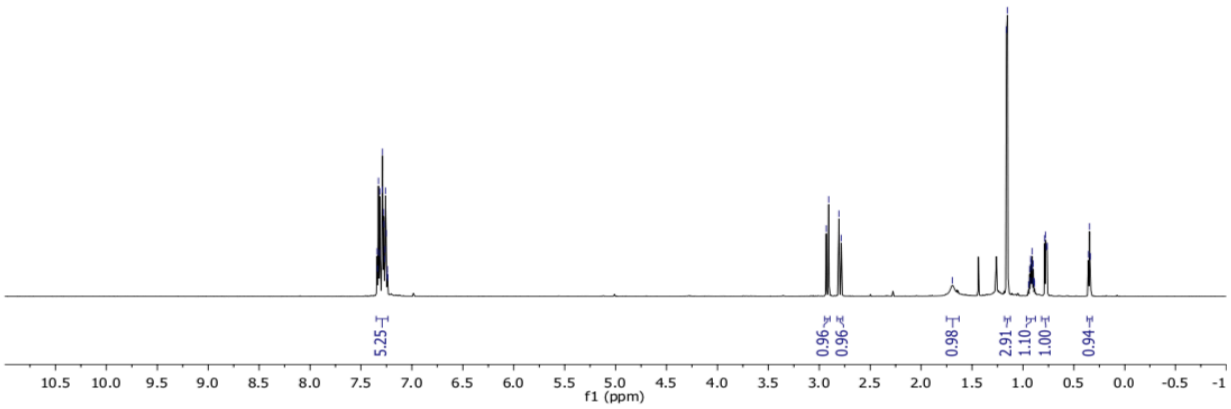
^{13}C NMR (175 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



2u



^{13}C NMR (151 MHz, $CDCl_3$)