Electronic Supplementary Material (ESI) for ChemComm.

Chiral BINOL-Based Borate Counterions: From Cautionary Tale on Anion Stability to Enantioselective Cu-Catalyzed Cyclopropanation

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Supporting Information

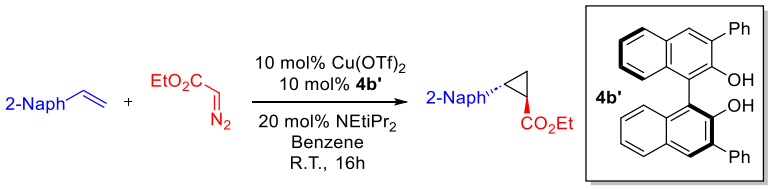
Table of Contents

I. General Considerations

All manipulations were conducted either in a glovebox under a nitrogen atmosphere operating at H_2O < 0.1 ppm and O_2 < 5.0 ppm (typically < 0.1 ppm O_2) on a schlenk line, 5.0 purity for nitrogen or argon was used (from Linde), or as noted in each procedure. Unless otherwise noted, all reagents were purchased from commercial sources. All solvents were dried by using a solvent purifier system and stored over activated 4Å molecular sieves inside the glovebox to ensure the water level is below 5 ppm. Nuclear magnetic resonance (NMR) characterization was performed on 400 MHz or 500 MHz spectrometers for proton, 126 MHz or 201 MHz for carbon. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent. Mass spectra were recorded on a high-resolution electrospray ionization quadrupole mass spectrometer. Enantiomeric ratios were measured on Agilent Technologies 1200 series HPLC with diode array detector using CHIRALCEL OJ-H, AS-H, IB, IC columns, (250 x 4.6 mm i.d., 5μm), at room temperature using HPLC grade hexanes/2-isopropanol as the mobile phase.

II. Supplementary Table

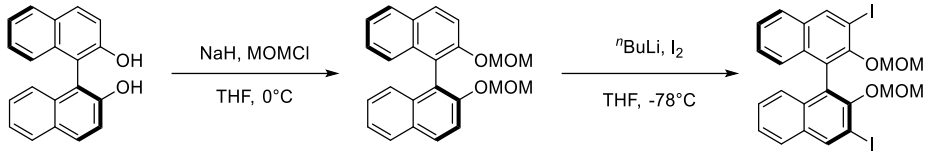
Table S1. Catalytic Cyclopropanation with 4b'



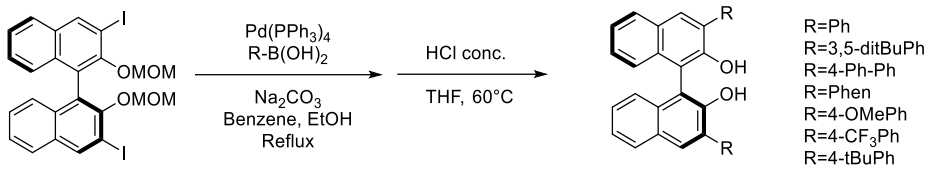
Condition variations	Yield	d.r.	e.r.
No variation	96%	86:14	94:6
Under N_2	98%	88:12	94:6
toluene instead of benzene solvent	95%	88:12	95:5
4.4 mmol scale	97%	87:13	94:6

III. Synthesis of BINOL derivatives

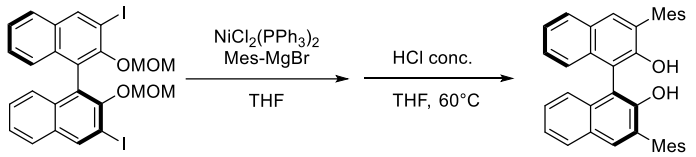
Synthesis of (S)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene



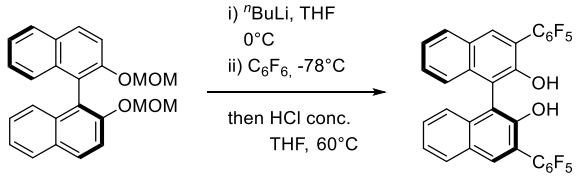
Synthesis of 3,3'-substituted Binol derivatives



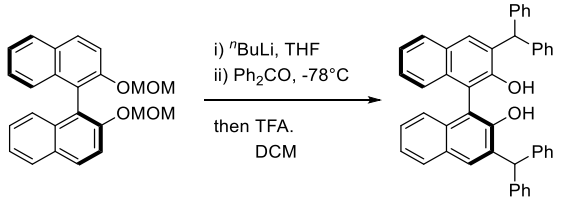
Synthesis of (S)-3,3'-dimesityl-[1,1'-binaphthalene]-2,2'-diol



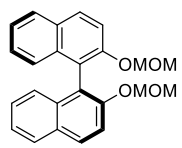
Synthesis of (S)-3,3'-bis(perfluorophenyl)-[1,1'-binaphthalene]-2,2'-diol



Synthesis of (S)-3,3'-dibenzhydryl-[1,1'-binaphthalene]-2,2'-diol



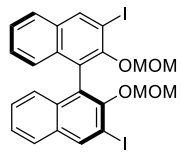
Synthetic procedures of BINOL derivatives



(S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene. In a 500 mL round bottom flask on the Schlenk line, to a solution of NaH (60% in oil, 9.51 g, 237 mmol) in THF (172 mL, 0.23 M) was added (S)-[1,1'-binaphthalene]-2,2'-diol (10.0 g, 39.6 mmol) slowly over 5 minutes at 0°C. The resultant mixture was stirred at 0°C for 1 h. CH_3OCH_2Br (9.03 mL, 119 mmol) was added dropwise and the mixture was stirred at 0°C for 10 min. The mixture was quenched with sat. aq. NH_4Cl (100 mL) and extracted with ethyl acetate (200 mL). The combined organic layers were then dried over $MgSO_4$, filtered, and the solvent removed in vacuo. The residue was purified by silica gel flash column chromatography (gradient eluent: 0-5% of ethyl acetate/hexanes) to afford (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene as a white solid (11.8 g, 90%). Spectral data correlated with that previously reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 9.1 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.22 (t, *J* = 7.1 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 5.09 – 4.96 (m, 4H), 3.14 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.81, 134.17, 130.04, 129.53, 128.01, 126.43, 125.71, 124.21, 121.47, 117.46, 95.39, 55.97.

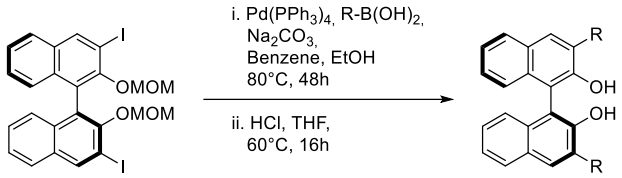


(S)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene. In a 500 mL round bottom flask on the Schlenk line, to a solution of (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (3.00 g, 8.01 mmol) in THF (200 mL, 0.04M) was added ^{n}BuLi (2.5 M in hexanes, 9.61 mL, 24.0 mmol) at 0°C dropwise over 5 minutes. The resultant mixture was warmed up to room temperature and stirred for 2 h. The reaction was then cooled to -78°C, and iodine (6.10 g, 24.0 mmol) was added over a period of 2 minutes. The resultant mixture was warmed to room temperature and stirred for 4 h. The mixture was quenched with sat. aq. $Na_2S_2O_3$ (200 mL) and extracted with ethyl acetate (300 mL). The combined organic layers were then dried over $MgSO_4$, filtered, and the solvent removed in vacuo. The residue was purified by silica gel flash column chromatography (gradient eluent: 0-3% of ethyl acetate/hexanes) to afford (S)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene as a pale-yellow solid (4.70 g, 93%). Spectral data correlated with that previously reported in the literature.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.42 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H), 7.30 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 4.81 – 4.69 (m, 4H), 2.60 (s, 6H).

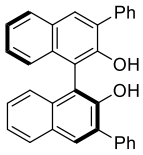
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.31, 140.17, 133.98, 132.36, 127.26, 126.89, 126.67, 126.39, 125.99, 99.56, 92.61, 56.66.

General method A: Suzuki coupling (for non ortho-substituted aromatic rings)



R=Ph
R=3,5-ditBuPh
R=4-Ph-Ph
R=Phen
R=4-OMePh
R=4-CF_3Ph
R=4-tBuPh

In a 25 mL Teflon sealed Schlenk flask inside the glovebox, (S)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (0.48 mmol, 1.00 eq), boronic acid (1.92 mmol, 4 eq), $Pd(PPh_3)_4$ (55.5 mg, 0.05 mmol, 0.10 eq) were mixed in benzene (2 mL, 0.24 M). On the Schlenk line, 1.25 mL of an aqueous solution of Na_2CO_3 (2M, 2.49 mmol, 5.20 eq) and ethanol (0.12 mL, 4.0M) were added. The mixture was stirred at reflux for 48h. After cooling to r.t., the reaction mixture was transfered to a separatory funnel with water (25 mL) and CH_2Cl_2 (25 mL), and the organic layer was collected. The aqueous layer was extracted with CH_2Cl_2 (2 x 25 mL), and the organic layers were combined and washed with water (25 mL). The organic layer was then passed through a silica pad, dried over $MgSO_4$, filtered, and the solvent removed in vacuo. The crude residue was then dissolved in THF (2.4 mL, 0.2M) and conc. HCl (7.68 mmol, 16 eq) was added dropwise to the solution over 5 minutes. The reaction mixture was stirred at 60°C for 16h. The crude mixture was extracted with ethyl acetate (20 mL) and washed with 10% aqueous Na_2CO_3 (20 mL) and brine (2 x 20 mL) and then dried over $MgSO_4$, filtered, and the solvent removed in vacuo. The crude product was purified by silica gel flash column chromatography.



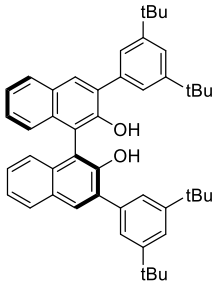
(S)-3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diol.

The product was prepared using general method A using phenylboronic acid. Purification conditions: 0-10% of ethyl acetate/hexanes to afford (S)-3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diol as a white solid (187 mg, 89%).

Spectral data correlated with that previously reported in the literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.75 – 7.72 (m, 4H), 7.50 (t, *J* = 7.4 Hz, 4H), 7.43 – 7.37 (m, 4H), 7.32 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.35 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.28, 137.62, 133.11, 131.55, 130.82, 129.76, 129.60, 128.64, 128.60, 127.92, 127.50, 124.48, 124.44, 112.55.

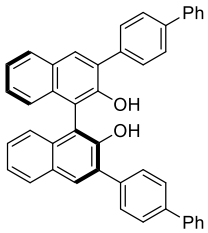


(S)-3,3'-bis(3,5-di-tert-butylphenyl)-[1,1'-binaphthalene]-2,2'-diol

The product was prepared using general method A using 3,5-ditBu-phenylboronic acid. Purification conditions: 0-8% of ethyl acetate/hexanes to afford (S)-3,3'- bis(3,5-di-tert-butylphenyl)-[1,1'-binaphthalene]-2,2'-diol as a white solid (293 mg, 92%). Spectral data correlated with that previously reported in the literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.93 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 1.8 Hz, 4H), 7.49 (t, *J* = 1.8 Hz, 2H), 7.39 (ddd, *J* = 8.1, 6.7, 1.4 Hz, 2H), 7.32 (ddd, *J* = 8.0, 6.7, 1.3, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 5.48 (s, 2H), 1.39 (s, 36H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.17, 150.17, 136.59, 133.16, 131.71, 131.10, 129.55, 128.48, 127.14, 124.67, 124.25, 124.07, 122.11, 113.14, 35.16, 31.69.

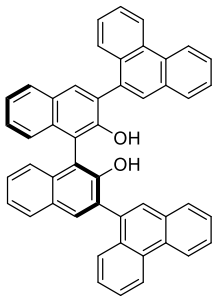


(S)-3,3'-di([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol

The product was prepared using general method A using 4-phenyl-phenylboronic acid. Purification conditions: 0-10% of ethyl acetate/hexanes to afford (S)-3,3'-di([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol as a white solid (213 mg, 75%). Spectral data correlated with that previously reported in the literature.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 4H), 7.74 (d, *J* = 8.4 Hz, 4H), 7.68 (d, *J* = 7.0 Hz, 4H), 7.48 (t, *J* = 7.7 Hz, 4H), 7.44 – 7.33 (m, 6H), 7.27 (d, *J* = 7.9 Hz, 2H), 5.42 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.40, 140.91, 140.77, 136.59, 133.10, 131.56, 130.41, 130.17, 129.68, 128.97, 128.65, 127.60, 127.57, 127.36, 127.30, 124.57, 124.43, 112.47.

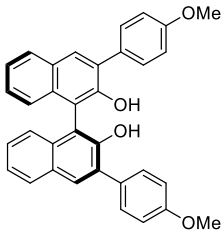


(S)-3,3'-di(phenanthren-9-yl)-[1,1'-binaphthalene]-2,2'-diol

The product was prepared using general method A using 9-phenanthrylboronic acid. Purification conditions: 0-10% of ethyl acetate/hexanes to afford (S)-3,3'-di(phenanthren-9-yl)-[1,1'-binaphthalene]-2,2'-diol as a white solid (196 mg, 64%). Spectral data correlated with that previously reported in the literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 – 8.74 (m, 4H), 8.10 – 8.08 (m, 2H), 7.99 – 7.86 (m, 6H), 7.77 – 7.41 (m, 16H), 5.32 – 5.22 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.79, 134.16, 133.86, 132.21, 131.67, 131.35, 130.65, 129.61, 129.46, 129.04, 128.97, 128.65, 128.54, 127.53, 127.23, 127.06, 126.97, 124.88, 124.66, 124.48, 123.15, 123.04, 122.80, 113.12.

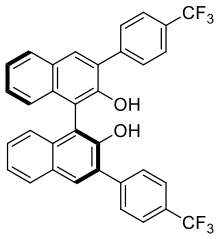


(S)-3,3'-bis(4-methoxyphenyl)-[1,1'-binaphthalene]-2,2'-diol

The product was prepared using general method A using 4-methoxyphenylboronic acid. Purification conditions: 0-15% of ethyl acetate/hexanes to afford (S)-3,3'-bis(4-methoxyphenyl)-[1,1'-binaphthalene]-2,2'-diol as a white solid (208 mg, 87%). Spectral data correlated with that previously reported in the literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 4H), 7.38 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.30 (ddd, *J* = 8.2, 6.8, 1.3, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 4H), 5.36 (s, 2H), 3.87 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.47, 150.38, 132.89, 131.08, 130.91, 130.44, 129.92, 129.64, 128.46, 127.25, 124.43, 124.40, 114.11, 112.53, 55.51.

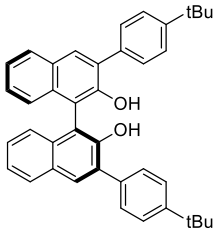


(S)-3,3'-bis(4-(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol

The product was prepared using general method A using 4-(trifluoromethyl)phenylboronic acid. Purification conditions: 0-10% of ethyl acetate/hexanes to afford (S)-3,3'-bis(4-(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol as a white solid (190 mg, 69%). Spectral data correlated with that previously reported in the literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 4H), 7.74 (d, *J* = 8.1 Hz, 4H), 7.44 (ddd, *J* = 8.1, 6.9, 1.3, 2H), 7.37 (ddd, *J* = 8.2, 6.8, 1.3, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.32 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.23, 141.30, 133.22, 132.21, 130.13, 129.76, 129.60, 129.48, 128.86, 128.21, 125.39, 124.95, 124.24, 112.08.



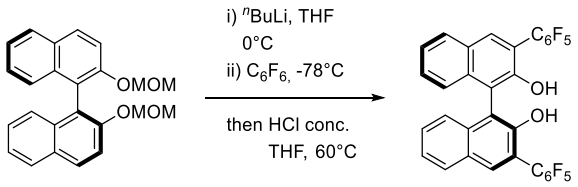
(S)-3,3'-bis(4-(tert-butyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol

The product was prepared using general method A using 4-(tert-butyl)phenylboronic acid. Purification conditions: 0-8% of ethyl acetate/hexanes to afford (S)-3,3'-bis(4-(tert-butyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol as a white solid (174 mg, 66%). Spectral data correlated with that previously reported in the literature.[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 4H), 7.38 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 2H), 7.30 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.38 (s, 2H), 1.38 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.91, 150.38, 134.61, 133.01, 131.33, 130.66, 129.63, 129.38, 128.53, 127.32, 125.65, 124.38, 112.57, 34.80, 31.51.

Synthesis of (S)-3,3'-bis(perfluorophenyl)-[1,1'-binaphthalene]-2,2'-diol



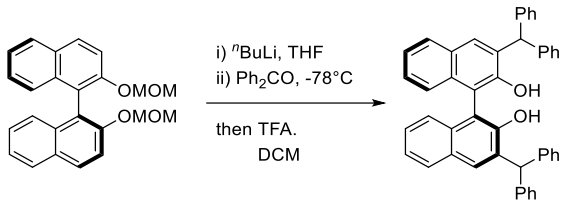
In a 100 mL round bottom flask on the Schlenk line, to a solution of (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (1.60 mmol, 1.00 eq) in THF (40 mL, 0.04M) was added n-

BuLi (2.5 M in hexane, 4.80 mmol, 3.00 eq) at 0°C over 5 minutes. The resultant mixture was warmed to room temperature and stirred for 2 h. Then, the reaction was cooled to -78°C, and C_6F_6 (4.80 mmol, 3.00 eq) was added. The resultant mixture was warmed to room temperature and stirred for 4 h. The mixture was quenched with sat. aq. $Na_2S_2O_3$ (50 mL) and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent removed in vacuo. The crude residue was then dissolved in THF (8.0 mL, 0.2M) and conc. HCl (25.6 mmol, 16 eq) was added dropwise to the solution over 5 minutes. The reaction mixture was stirred at 60°C for 16h. The residue was extracted with ethyl acetate (15 mL) and washed with 10% aqueous Na_2CO_3 (15 mL) and brine (2x 15 mL) and then dried over $MgSO_4$, filtered, and the solvent removed in vacuo. The crude product was purified by silica gel flash column chromatography (0-8% of ethyl acetate/hexanes) to afford (S)-3,3'-bis(perfluorophenyl)-[1,1'-binaphthalene]-2,2'-diol as a white solid (296 mg, 30%). Spectral data correlated with that previously reported in the literature.[9]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.43 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.26 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.50, 145.70, 143.84, 134.28, 133.77, 129.12, 129.10, 129.05, 125.24, 124.18, 115.90, 112.04, 112.04, 111.47.

Synthesis of (S)-3,3'-dibenzhydryl-[1,1'-binaphthalene]-2,2'-diol



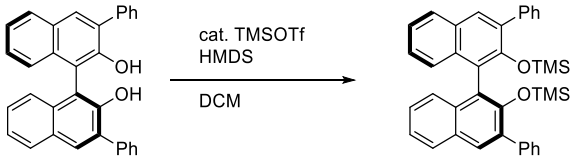
In a 50 mL round bottom flask on the Schlenk line, (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (0.80 mmol, 1.00 eq) was dissolved in THF (3 mL, 0.27M). ^{n}BuLi (2.50 M in hexane; 2.88 mmol, 3.60 eq) was then added at room temperature over 5 minutes. The mixture was stirred for 2 h. After cooling to –78 °C, benzophenone (3.45 mmol, 4.30 eq) in THF (1.5 mL, 0.53M) was added over 5 minutes. The reaction mixture was stirred for 2 h at –78 °C and then at room temperature for 2 h. After addition of aqueous 15 mL of 5% NH_4Cl, the organic phase was extracted with ethyl acetate (3 x 15 mL), dried over $MgSO_4$, filtered, and the solvent removed in vacuo. The crude residue was then dissolved in CH_2Cl_2 (27 mL, 0.03M) and CF_3COOH (2.80 mmol, 3.50 eq) was

added. The reaction mixture was stirred for 24 h at room temperature. After neutralization with saturated aqueous $NaHCO_3$, the organic layer was separated, dried over $MgSO_4$, filtered, and the solvent removed in vacuo. The crude residue was purified by silica gel flash column chromatography (0-7% of ethyl acetate/hexanes) to afford (S)-3,3'-dimesityl-[1,1'-binaphthalene]-2,2'-diol as a white solid (204 mg, 41%). Spectral data correlated with that previously reported in the literature.[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.4 Hz, 2H), 7.43 (s, 2H), 7.36 – 7.24 (m, 16H), 7.22 – 7.19 (m, 8H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.04 (s, 2H), 5.13 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.37, 143.26, 143.06, 133.13, 132.38, 131.53, 129.66, 129.48, 129.18, 128.62, 128.55, 128.49, 127.16, 126.67, 126.57, 124.16, 124.01, 111.29, 51.07.

Synthesis of (S)-((3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diyl)bis(oxy))bis(trimethylsilane) (4b)



In a 20 mL vial inside the glovebox, a solution of (S)-3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diol (907 mg, 2.07 mmol) and hexamethyldisilazane (4.34 mL, 20.69 mmol, 10.0 eq) were dissolved in anhydrous dichloromethane (9.0 mL, 0.23 M). Trimethylsilyl trifluoromethanesulfonate (0.24 mL, 0.78 mmol, 0.38 eq) was added over 1 minute. After stirring for 16h at room temperature, the reaction mixture was concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (0-2% of ethyl acetate/hexanes) to afford (S)-((3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diyl)bis(oxy))bis(trimethylsilane) as a white solid (788 mg, 73%).

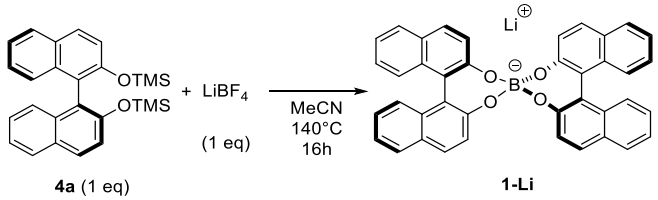
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.84 (m, 4H), 7.65 – 7.62 (m, 4H), 7.48 – 7.43 (m, 4H), 7.39 – 7.31 (m, 4H), 7.23 – 7.17 (m, 4H), -0.69 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.73, 140.30, 136.05, 134.21, 130.46, 130.07 (d), 129.89, 128.25, 128.13, 127.30, 126.51, 125.97, 124.05, 123.73, 0.11 (d).

HRMS calculated for $C_{38}H_{38}O_2NaSi_2$ (M+Na): 605.23025, found: 605.22971.

IV. Synthesis of Borate Anions

IV.A Reaction of $LiBF_4$ with 4a

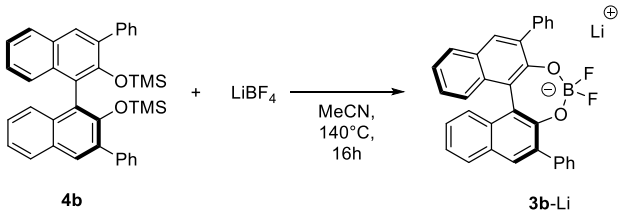


Inside the glovebox, $LiBF_4$ (6 mg, 0.06 mmol) and **4a** (28 mg, 0.060 mmol) were mixed in acetonitrile (1.3 mL, 0.05M) in a J Young NMR tube. Dimethylsulfone (3 mg, 0.030 mmol) was added as an internal standard. The reaction was sealed, brought out of the glovebox and heated to 140 °C for 16h. The ^{1}H NMR analysis shows the formation of **1**-Li in 74% yield. ^{1}H and ^{11}B NMR of **1-Li** matches that previously reported for **1**$^-$.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 4H), 7.98 (d, *J* = 8.2 Hz, 4H), 7.46 (d, *J* = 8.7 Hz, 4H), 7.35 (ddd, *J* = 8.1, 5.7, 2.2 Hz, 4H), 7.23 – 7.17 (m, 8H).

^{11}B NMR (128 MHz, $CDCl_3$) δ 8.87.

IV.B Reaction of $LiBF_4$ with 4b



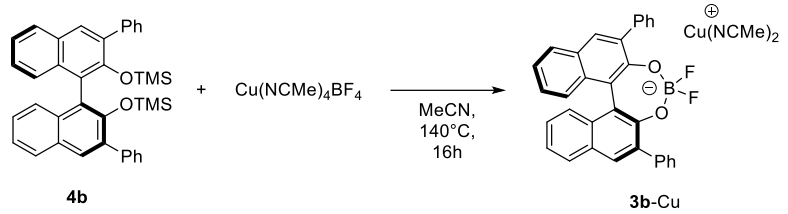
Inside the glovebox, $LiBF_4$ (3 mg, 0.032 mmol) and **4b** (19 mg, 0.032 mmol) were mixed in acetonitrile (0.7 mL, 0.05M) in a J Young NMR tube. Dimethylsulfone (3 mg, 0.032 mmol) was added as an internal standard. The reaction was sealed, brought out of the glovebox and heated to 140 °C for 16h. The ^{1}H NMR analysis shows the formation of **3b**-Li in 77 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 4H), 7.87 (d, *J* = 7.2 Hz, 4H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 2H), 7.16 (ddd, *J* = 8.1, 6.6, 1.3 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ 3.52.

^{19}F NMR (376 MHz, CD_3CN) δ -145.3.

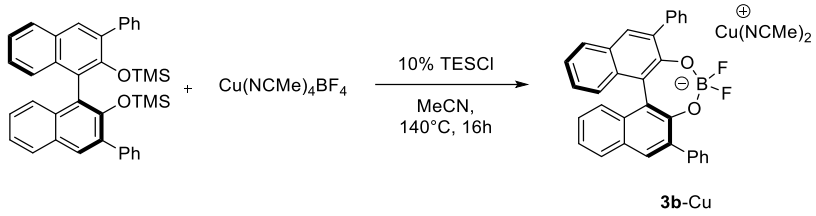
IV.C Reaction of $Cu(NCMe)_4BF_4$ with 4b



Inside the glovebox, $Cu(NCMe)_4BF_4$ (10 mg, 0.032 mmol) and **4b** (56 mg, 0.10 mmol) were mixed in acetonitrile (0.7 mL, 0.05M) in a J Young NMR tube. Dimethylsulfone (3 mg, 0.03 mmol) was added as an internal standard. The reaction was sealed, brought out of the glovebox and heated to 140°C for 16h. ^{1}H NMR analysis shows the formation of **3b-Cu** in 92% yield.

See III.D for characterization.

IV.D Synthesis of 3b



In a 5 mL Teflon cap sealable Schlenk flask inside the glovebox, $Cu(NCMe)_4BF_4$ (10 mg, 0.030 mmol) and (S)-((3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diyl)bis(oxy))bis(trimethylsilane) (56 mg, 0.10 mmol) were mixed in acetonitrile (0.64 mL, 0.05M in copper). Et_3SiCl (0.53 uL, 0.0030 mmol) was then added. The reaction was sealed, brought out of the glovebox and heated to 140°C for 16h. The mixture was brought back into a glovebox and transferred into a 20 mL vial with an added 2 mL acetonitrile. The acetonitrile solution was washed with pentane (3x 7 mL). The acetonitrile solvent was removed in vacuo, benzene (0.7 mL) was added to dissolve **3b-Cu**, and the solution was left at room temperature for 16h, leading to the formation of off-white crystals. The benzene was removed, the crystals washed with pentane (2x 2 mL), and dried in vacuo to afford **3b-Cu** (15 mg, 77%). In a separate experiment, dimethylsulfone (3 mg, 0.03 mmol) was added after the reaction as an externalstandard, which showed the formation **3b-Cu** by ^{1}H NMR analysis in 96% yield.

^{1}H NMR (500 MHz, CD_3CN) δ 7.91 – 7.87 (m, 8H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.37 – 7.34 (m, 2H), 7.29 (ddd, *J* = 8.0, 6.7, 1.3 Hz, 2H), 7.14 (ddd, *J* = 8.0, 6.7, 1.3 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (126 MHz, CD_3CN) δ 141.20, 136.75, 133.88, 131.14, 130.05, 129.70, 129.27, 129.06, 128.56, 127.48, 126.76, 125.83, 123.74, 123.67.

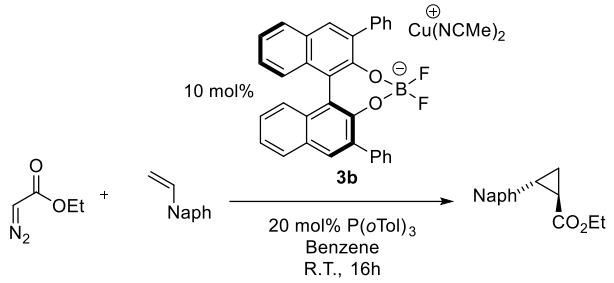
^{19}F NMR (376 MHz, CD_3CN) δ -142.58 (q, *J* = 10 Hz).

^{11}B NMR (128 MHz, CD_3CN) δ 4.29 (t, *J* = 9.7 Hz).

HRMS calculated for $C_{32}H_{20}BF_2O_2$: 485.1530, found: 485.1516.

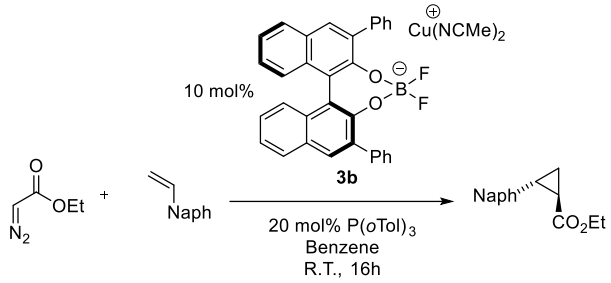
V. Catalytic Cyclopropanation

Typical procedure for cyclopropanation with 3b-Cu (Table 1) Method A



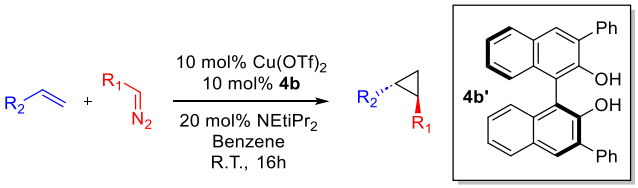
In an 8 mL microwave cap sealable tube inside the glovebox, 2-vinylnaphthalene (21 mg, 0.14 mmol, 5.2 eq), **3b-Cu** (2 mg, 0.0030 mmol, 0.10 eq) and P(*o*Tol)$_3$ (2 mg, 0.0030 mmol, 0.20 eq) were mixed in benzene (0.14 mL, 0.19 M) for 15 minutes. A septa cap was installed on the tube using a press. The mixture was then brought outside the glovebox and connected to a nitrogen line with a needle. In a separate 8 mL microwave cap sealable tube inside the glovebox, benzene (0.1 mL, 0.27 M) was added and the septa cap was installed using a press. The second tube was brought outside the glovebox, connected to a nitrogen line with a needle, and ethyl diazoacetate (22 µL, 0.026 mmol, 1.00 eq, 15% in toluene) was added. The solution of ethyl diazoacetate in benzene was then added to the tube containing the olefin, ligand and catalyst by syringe over the course of 10 min. The reaction mixture was allowed to stir for an additional 16h at room temperature. The reaction solution was then filtered through a pad of basic alumina using ethyl acetate and the solvent removed in vacuo. A small amount of the crude mixture was taken and ^{1}H NMR analysis used to determine the diastereomeric ratios of the trans and cis isomers (80:20, respectively) by comparison to literature reported chemical shifts. The product was purified by silica gel flash column chromatography (0-2% of ethyl acetate/hexanes). A sample of the pure trans ethyl 2-(naphthalen-2-yl)cyclopropane-1-carboxylate was collected for chiral HPLC (83:17, (R,R):(S,S)) and ^{1}H/^{13}C NMR analysis (see characterization section for details). All the fractions for ethyl 2-(naphthalen-2-yl)cyclopropane-1-carboxylate were combined to afford a white solid (3 mg, 42% yield).

Typical procedure for cyclopropanation with 3b-Cu under inert atmosphere (Figure 3) Method B



In an 8 mL microwave cap sealable tube inside the glovebox, 2-vinylnaphthalene (21 mg, 0.14 mmol, 5.2 eq), **3b-Cu** (2 mg, 0.0030 mmol, 0.10 eq) and P(*o*Tol)$_3$ (2 mg, 0.0030 mmol, 0.20 eq) were mixed in benzene (0.14 mL, 0.19 M) for 15 minutes. A solution of ethyl diazoacetate (22 µL, 0.026 mmol, 1.00 eq, 15% in toluene) in benzene (0.1 mL, 0.27 M) was added to the mixture by syringe over the course of 10 min. The reaction mixture was allowed to stir for an additional 16h at room temperature. The reaction solution was then filtered through a pad of basic alumina using ethyl acetate and the solvent removed in vacuo. A small amount of the crude mixture was taken and ^{1}H NMR analysis used to determine the diastereomeric ratios of the trans and cis isomers (75:25, respectively) by comparison to literature reported chemical shifts. The product was purified by silica gel flash column chromatography (0-2% of ethyl acetate/hexanes). A sample of the pure trans ethyl 2-(naphthalen-2-yl)cyclopropane-1-carboxylate was collected for chiral HPLC (64:36, (R,R):(S,S)) and ^{1}H/^{13}C NMR analysis (see characterization section for details). All the fractions for ethyl 2-(naphthalen-2-yl)cyclopropane-1-carboxylate were combined to afford a white solid (2 mg, 29% yield).

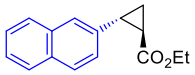
Typical procedure for cyclopropanation with Cu(OTf)$_2$ and 4b' (Figure 3, Table 3)



In a 4 mL vial inside the glovebox, 4-cyanostyrene (51 mg, 0.39 mmol, 3.00 eq), Cu(OTf)$_2$ (5 mg, 0.010 mmol, 0.10 eq), **4b'** (6 mg, 0.010 mmol, 0.10 eq) and ^{i}Pr$_2$NEt (3 mg, 0.030 mmol, 0.20 eq) were mixed in benzene (1.3 mL, 0.10 M) for 15 minutes. A solution of ethyl diazoacetate (111 µL,

15% in toluene, 0.13 mmol, 1.00 eq) in benzene (0.5 mL, 0.27 M) was added to the mixture by syringe over the course of 10 min. The reaction mixture was allowed to stir for an additional 16h at room temperature. The reaction solution was then filtered through a pad of basic alumina using ethyl acetate and the solvent removed in vacuo. A small amount of the crude mixture was taken and ^{1}H NMR analysis used to determine the diastereomeric ratios of the trans and cis isomers (86:14, respectively) by comparison to literature reported chemical shifts. The product was purified by silica gel flash column chromatography (0-2% of ethyl acetate/hexanes). A sample of the pure trans ethyl 2-(4-cyanophenyl)cyclopropane-1-carboxylate was collected for chiral HPLC 96:4, (R,R):(S,S) and ^{1}H/^{13}C NMR analysis (see characterization section for details). All the fractions for ethyl 2-(4-cyanophenyl)cyclopropane-1-carboxylate were combined to afford a white solid (21 mg, 75% yield).

Characterization Data for Cyclopropanes (Table 3)



Ethyl (1R,2R)-2-(naphthalen-2-yl)cyclopropane-1-carboxylate (5a). The product was prepared using Cu(OTf)$_2$/**4b'** as described above with 2-vinylnaphthalene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (86:14, respectively). Purification conditions: 0-2% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-(naphthalen-2-yl)cyclopropane-1-carboxylate was collected for chiral HPLC and ^{1}H/^{13}C NMR analysis. Spectral data correlated with that previously reported in the literature.[14] All the fractions for ethyl 2-(naphthalen-2-yl)cyclopropane-1-carboxylate were combined to afford a white solid (30 mg, 96%).

HPLC: IC column, 1mL/min, 0.7% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 10.4 and 11.7 min, e.r.: 94:6, (R,R):(S,S).

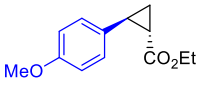
Reaction in toluene solvent: yield: 95%, d.r.: 88:12, e.r.: 95:5, (R,R):(S,S).

Reaction under N_2 on a Schlenk line: yield: 98%, d.r.: 88:12, e.r.: 94:6, (R,R):(S,S).

Large scale reaction: yield: 95% (1.0 g, 4.2 mmol), d.r.: 87:13, e.r. 94:6, (R,R):(S,S).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 3H), 7.57 (s, 1H), 7.48 – 7.41 (m, 2H), 7.20 (dd, *J* = 8.4, 1.9 Hz, 1H), 4.19 (qd, *J* = 7.1, 0.9 Hz, 2H), 2.69 (ddd, *J* = 10.1, 6.5, 4.1 Hz, 1H), 2.01 (ddd, *J* = 8.4, 5.3, 4.2 Hz, 1H), 1.67 (ddd, *J* = 9.1, 5.3, 4.6 Hz, 1H), 1.43 (ddd, *J* = 8.4, 6.5, 4.6 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H).

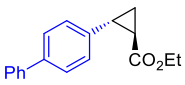
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.55, 137.67, 133.50, 132.42, 128.31, 127.76, 127.54, 126.40, 125.63, 124.92, 124.71, 60.90, 26.56, 24.28, 17.17, 14.42.



Ethyl (1S,2S)-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (5b). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-methoxystyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (86:14, respectively). Purification conditions: 0-5% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-(4-methoxyphenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and ^{1}H/^{13}C NMR analysis. Spectral data correlated with that previously reported in the literature.[14] All the fractions for ethyl 2-(4-methoxyphenyl)cyclopropane-1-carboxylate were combined to afford a white solid (14 mg, 48%). HPLC: OJ-H column, 1mL/min, 0.3% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 60.1 and 64.9 min, e.r.: 89:11, (S,S):(R,R).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* =8.7 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 2.48 (ddd, *J* = 9.2, 6.5, 4.1 Hz, 1H), 1.82 (ddd, *J* = 8.4, 5.2, 4.2 Hz, 1H), 1.55 (ddd, *J* = 9.2, 5.3, 4.5 Hz, 1H), 1.29 – 1.23 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.72, 158.48, 132.25, 127.52, 114.06, 60.79, 55.48, 25.77, 24.02, 16.89, 14.43.

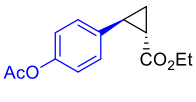


Ethyl (1R,2R)-2-([1,1'-biphenyl]-4-yl)cyclopropane-1-carboxylate (5c). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-phenylstyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (87:13, respectively). Purification conditions: 0-2% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-([1,1'-biphenyl]-4-yl)cyclopropane-1-carboxylate was collected for chiral HPLC and ^{1}H/^{13}C NMR analysis. Spectral data correlated with that previously reported in the literature.[15] All the fractions for ethyl 2-(4-methoxyphenyl)cyclopropane-1-carboxylate were combined to afford a white solid (31 mg, 89%). HPLC: IC column, 1mL/min, 0.7% iPrOH/Hexanes, 254 nm UV detector. RetTime: 11.4 and 13.0 min, e.r.: 97:3, (R,R):(S,S).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 2H), 7.53 – 7.50 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.32 (m, 1H), 7.19 – 7.16 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.56 (ddd, *J* = 9.2, 6.5, 4.2 Hz,

1H), 1.94 (ddd, *J* = 8.4, 5.3, 4.1 Hz, 1H), 1.64 (ddd, *J* = 9.2, 5.4, 4.1 Hz, 1H), 1.35 (ddd, *J* = 8.4, 6.5, 4.6 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.52, 140.91, 139.64, 139.43, 128.92, 127.36, 127.34, 127.12, 126.73, 60.89, 26.07, 24.45, 17.26, 14.43.

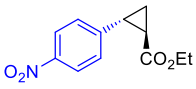


Ethyl (1S,2S)-2-(4-acetoxyphenyl)cyclopropane-1-carboxylate (5d). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-acetoxystyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (87:13, respectively). Purification conditions: 0-4% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-(4-acetoxyphenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and ^{1}H/^{13}C NMR analysis. Spectral data correlated with that previously reported in the literature.[14] All the fractions for ethyl 2-(4-acetoxyphenyl)cyclopropane-1-carboxylate were combined to afford a white solid (16 mg, 50%).

HPLC: OJ-H column, 1mL/min, 0.4% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 11.2 and 14.1 min, e.r.: 94:6, (S,S):(R,R).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.51 (ddd, *J* = 9.2, 6.5, 4.2 Hz, 1H), 2.29 (s, 3H), 1.87 (ddd, *J* = 8.3, 5.3, 4.2 Hz, 1H), 1.61 – 1.57 (m, 1H), 1.31 – 1.26 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.43, 169.71, 149.36, 137.86, 127.41, 121.72, 60.90, 25.77, 24.26, 21.25, 17.08, 14.41.

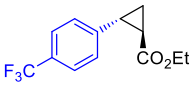


Ethyl (1R,2R)-2-(4-nitrophenyl)cyclopropane-1-carboxylate (5e). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-nitrostyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (92:8, respectively). Purification conditions: 0-3% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-(4-nitrophenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and ^{1}H/^{13}C NMR analysis. Spectral data correlated with that previously reported in the literature.[16] All the fractions for ethyl 2-(4-nitrophenyl)cyclopropane-1-carboxylate were combined to afford a colorless oil (25 mg, 80%).

HPLC: AS-H column, 1mL/min, 1.8% ^{i}PrOH/Hexanes, 220 nm UV detector. RetTime: 21.2 and 25.0 min, e.r.: 92:8, (R,R):(S,S).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 4.19 (qd, *J* = 7.2, 1.3 Hz, 2H), 2.60 (ddd, *J* = 9.2, 6.4, 4.2 Hz, 1H), 2.00 (ddd, *J* = 8.6, 5.5, 4.2 Hz, 1H), 1.72 (ddd, *J* = 9.1, 5.5, 4.8 Hz, 1H), 1.38 (ddd, *J* = 8.6, 6.4, 4.8 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.61, 148.30, 146.73, 126.89, 123.94, 61.25, 25.83, 25.26, 17.99, 14.37.



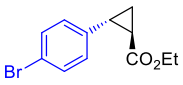
Ethyl (1R,2R)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1-carboxylate (5f). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-trifluoromethylstyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (91:9, respectively). Purification conditions: 0-4% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and ^{1}H/^{13}C NMR analysis. Spectral data correlated with that previously reported in the literature.[14] All the fractions for ethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1-carboxylate were combined to afford a colorless oil (16 mg, 48%).

HPLC: OJ-H column, 1mL/min, 0.3% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 19.3 and 24.3 min, e.r.: 97:3, (R,R):(S,S).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.56 (ddd, *J* = 9.3, 6.5, 4.2 Hz, 1H), 1.94 (ddd, *J* = 8.5, 5.4, 4.2 Hz, 1H), 1.66 (ddd, *J* = 9.2, 5.4, 4.7 Hz, 1H), 1.34 (ddd, *J* = 8.5, 6.4, 4.7 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.04, 144.51 (q, *J* = 1.3 Hz), 129.04, 128.79, 126.57, 125.56 (q, *J* = 3.8 Hz), 123.23, 61.08, 25.84, 24.66, 17.45, 14.39.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.44



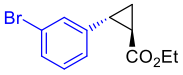
Ethyl (1R,2R)-2-(4-bromophenyl)cyclopropane-1-carboxylate (5g). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-bromostyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (84:16, respectively). Purification conditions: 0-2% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-(4-bromophenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and ^{1}H/^{13}C NMR analysis. Spectral data correlated with that

previously reported in the literature.[14] All the fractions for ethyl 2-(4-bromophenyl)cyclopropane-1-carboxylate were combined to afford a colorless oil (29 mg, 83%).

HPLC: OJ-H column, 1mL/min, 0.3% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 31.6 and 35.3 min, e.r.: 96:4, (R,R):(S,S).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 4.17 (qd, *J* = 7.2, 0.8 Hz, 2H), 2.47 (ddd, *J* = 9.2, 6.4, 4.2 Hz, 1H), 1.86 (ddd, *J* = 8.5, 5.3, 4.2 Hz, 1H), 1.60 (ddd, *J* = 9.2, 5.4, 4.6 Hz, 1H), 1.29 – 1.25 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.26, 139.34, 131.66, 128.10, 120.30, 60.98, 25.70, 24.30, 17.14, 14.40.

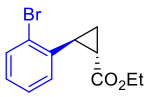


Ethyl (1R,2R)-2-(3-bromophenyl)cyclopropane-1-carboxylate (5h). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 3-bromostyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (81:19, respectively). Purification conditions: 0-2% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-(3-bromophenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and ^{1}H/^{13}C NMR analysis. Spectral data correlated with that previously reported in the literature.[17] All the fractions for ethyl 2-(3-bromophenyl)cyclopropane-1-carboxylate were combined to afford a colorless oil (30 mg, 83%).

HPLC: OJ-H column, 1mL/min, 0.2% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 22.9 and 25.5, e.r.: 97:3, (R,R):(S,S).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.23 (dd, *J* = 1.9, 1.9 Hz, 1H), 7.14 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.03 (ddd, *J* = 7.7, 1.4, 1.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.48 (ddd, *J* = 9.2, 6.5, 4.2 Hz, 1H), 1.89 (ddd, *J* = 8.5, 5.4, 4.2 Hz, 1H), 1.60 (ddd, *J* = 9.2, 5.4, 4.7 Hz, 1H), 1.31 – 1.26 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.16, 142.69, 130.11, 129.73, 129.44, 125.15, 122.73, 61.00, 25.72, 24.33, 17.12, 14.39.



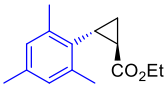
Ethyl (1S,2S)-2-(2-bromophenyl)cyclopropane-1-carboxylate (5i). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 2-bromostyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (90:10, respectively). Purification conditions: 0-2% of ethyl acetate/hexanes. A sample

of the pure trans ethyl 2-(2-bromophenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and $^{1}H/^{13}C$ NMR analysis. Spectral data correlated with that previously reported in the literature.[18] All the fractions for ethyl 2-(2-bromophenyl)cyclopropane-1-carboxylate were combined to afford a colorless oil (14 mg, 40%).

HPLC: OJ-H column, 1mL/min, 0.2% iPrOH/Hexanes, 230 nm UV detector. RetTime: 13.3 and 14.8 min, e.r.: 97:3, (S,S):(R,R).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.23 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H), 7.09 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1H), 7.02 (dd, *J* = 7.9, 1.7 Hz, 1H), 4.27 – 4.15 (m, 2H), 2.73 – 2.68 (m, 1H), 1.79 (ddd, *J* = 8.4, 5.3, 4.5 Hz, 1H), 1.63 (ddd, *J* = 9.0, 5.3, 4.6 Hz, 1H), 1.35 – 1.28 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.42, 139.23, 132.77, 128.32, 127.65, 127.50, 126.43, 60.87, 27.13, 23.31, 15.83, 14.48.

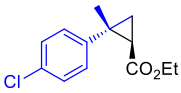


Ethyl (1R,2R)-2-mesitylcyclopropane-1-carboxylate (5j). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 2,4,6-trimethylstyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (85:15, respectively). Purification conditions: 0-1% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-mesitylcyclopropane-1-carboxylate was collected for chiral HPLC and $^{1}H/^{13}C$ NMR analysis. Spectral data correlated with that previously reported in the literature.[15] All the fractions for ethyl 2-mesitylcyclopropane-1-carboxylate were combined to afford a colorless oil (23 mg, 75%).

HPLC: OJ-H column, 1mL/min, 0.2% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 6.5 and 7.4 min, e.r.: 87:13, (R,R):(S,S).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (s, 2H), 4.28 – 4.17 (m, 2H), 2.34 (s, 6H), 2.32 – 2.28 (m, 1H), 2.25 (s, 3H), 1.72 (ddd, *J* = 8.4, 8.4, 4.9 Hz, 1H), 1.66 (ddd, *J* = 9.2, 5.0, 4.1 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.13 (ddd, *J* = 8.4, 7.2, 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.49, 138.52, 136.51, 133.28, 129.04, 60.74, 23.32, 23.29, 20.94, 20.59, 17.73, 14.55.



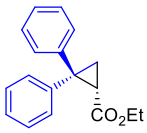
Ethyl (1R,2R)-2-(4-chlorophenyl)-2-methylcyclopropane-1-carboxylate (5k). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-

chloro-alpha-methylstyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (75:25, respectively). Purification conditions: 0-2% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-(4-chlorophenyl)-2-methylcyclopropane-1-carboxylate was collected for chiral HPLC and ^{1}H/^{13}C NMR analysis. Spectral data correlated with that previously reported in the literature.[19] All the fractions ethyl 2-(4-chlorophenyl)-2-methylcyclopropane-1-carboxylate were combined to afford a white solid (23 mg, 72%).

HPLC: IB column, 1mL/min, 0.3% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 8.9 and 9.7 min, e.r.: 89:11, (R,R):(S,S).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 4H), 4.25 – 4.15 (m, 2H), 1.92 (dd, *J* = 8.4, 6.0 Hz, 1H), 1.50 (s, 3H), 1.45 (dd, *J* = 6.0, 4.8 Hz, 1H), 1.38 (dd, *J* = 8.4, 4.8 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.05, 144.59, 132.36, 128.91, 128.71, 60.77, 30.13, 27.98, 20.88, 19.97, 14.56.

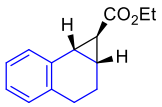


Ethyl (S)-2,2-diphenylcyclopropane-1-carboxylate (5l). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 1,1-diphenylethylene and ethyl diazoacetate. Purification conditions: 0-4% of ethyl acetate/hexanes to afford ethyl 2,2-diphenylcyclopropane-1-carboxylate as a white solid (19 mg, 54%). Spectral data correlated with that previously reported in the literature. [20]

HPLC: OJ-H column, 1mL/min, 0.7% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 30.2 and 41.2 min, e.r.: 97:3, (S):(R).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 2H), 7.28 – 7.15 (m, 8H), 3.97 – 3.85 (m, 2H), 2.54 (dd, *J* = 8.1, 5.9 Hz, 1H), 2.17 (dd, *J* = 5.9, 4.8 Hz, 1H), 1.59 (dd, *J* = 8.2, 4.8 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.80, 145.03, 140.41, 129.91, 128.59, 128.42, 127.73, 127.10, 126.65, 60.58, 39.96, 29.19, 20.26, 14.15.



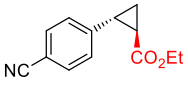
Ethyl (1S)-1a,2,3,7b-tetrahydro-1H-cyclopropa[a]naphthalene-1-carboxylate (5m). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 1,2-dihydronaphthalene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the

diastereomeric ratios of the trans and cis isomers (91:9, respectively). Purification conditions: 0-2% of ethyl acetate/hexanes. A sample of the pure trans ethyl 1a,2,3,7b-tetrahydro-1H-cyclopropa[a]naphthalene-1-carboxylate was collected for chiral HPLC and $^{1}H/^{13}C$ NMR analysis. Spectral data correlated with that previously reported in the literature.[21] All the fractions for ethyl 1a,2,3,7b-tetrahydro-1H-cyclopropa[a]naphthalene-1-carboxylate were combined to afford a white solid (16 mg, 57%). The major trans product was used for characterization and enantiomeric ratio determination. Spectral data correlated with that previously reported in the literature.

HPLC: OJ-H column, 1mL/min, 0.4% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 10.8 and 14.4 min, e.r.: 92:8, (S):(R).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 6.8 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.02 (d, *J* = 7.2 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.65 (dd, *J* = 16.3, 5.7 Hz, 1H), 2.55 (dd, *J* = 9.0, 3.6 Hz, 1H), 2.46 (ddd, *J* = 16.1, 15.0, 6.2 Hz, 1H), 2.22 – 2.16 (m, 2H), 2.08 – 2.05 (m, 1H), 1.80 (dddd, *J* = 13.7, 10.6, 5.7, 2.9 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.37, 135.22, 133.91, 128.98, 128.76, 126.40, 126.12, 60.72, 26.53, 25.50, 24.41, 23.28, 18.72, 14.42.

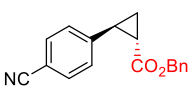


Ethyl (1R,2R)-2-(4-cyanophenyl)cyclopropane-1-carboxylate (5n). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-cyanostyrene and ethyl diazoacetate. ^{1}H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (86:14, respectively). Purification conditions: 0-4% of ethyl acetate/hexanes. A sample of the pure trans ethyl 2-(4-cyanophenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and $^{1}H/^{13}C$ NMR analysis. Spectral data correlated with that previously reported in the literature.[12] All the fractions for ethyl 2-(4-cyanophenyl)cyclopropane-1-carboxylate were combined to afford a colorless oil (21 mg, 75%).

HPLC: AS-H column, 1mL/min, 1.8% ^{i}PrOH/Hexanes, 254 nm UV detector. RetTime: 24.7 and 32.2 min, e.r.: 96:4, (R,R):(S,S).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.18 (qd, *J* = 7.1, 1.0 Hz, 2H), 2.54 (ddd, *J* = 9.3, 6.4, 4.1 Hz, 1H), 1.95 (ddd, *J* = 8.6, 5.5, 4.1 Hz, 1H), 1.69 (ddd, *J* = 9.3, 5.5, 4.8 Hz, 1H), 1.36 – 1.30 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.57, 145.95, 132.29, 126.79, 118.79, 110.21, 61.04, 25.84, 24.85, 17.56, 14.22.



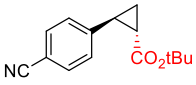
Benzyl (1S,2S)-2-(4-cyanophenyl)cyclopropane-1-carboxylate (5o). The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-cyanostyrene and benzyl diazoacetate. ^1H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (95:5, respectively). Purification conditions: 0-5% of ethyl acetate/hexanes. A sample of the pure trans benzyl 2-(4-cyanophenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and $^1H/^{13}C$ NMR analysis. All the fractions for benzyl 2-(4-cyanophenyl)cyclopropane-1-carboxylate were combined to afford a colorless oil (25 mg, 67%).

HPLC: IB column, 1mL/min, 3% ^{i}PrOH/Hexanes, 254 nm UV detector. RetTime: 14.8 and 15.3 min, e.r.: 97:3, (S,S):(R,R).

^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.32 (m, 5H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.19 – 5.14 (m, 2H), 2.58 (ddd, *J* = 9.2, 6.4, 4.2 Hz, 1H), 2.02 (ddd, *J* = 8.5, 5.5, 4.1 Hz, 1H), 1.73 (ddd, *J* = 9.2, 5.1, 5.1 Hz, 1H), 1.37 (ddd, *J* = 8.6, 6.5, 4.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.57, 145.88, 135.74, 132.44, 128.78, 128.56, 128.47, 126.93, 110.40, 67.05, 26.20, 24.94, 17.90.

HRMS calculated for $C_{18}H_{16}O_2N$ (M+H): 278.11756, found: 278.11685.



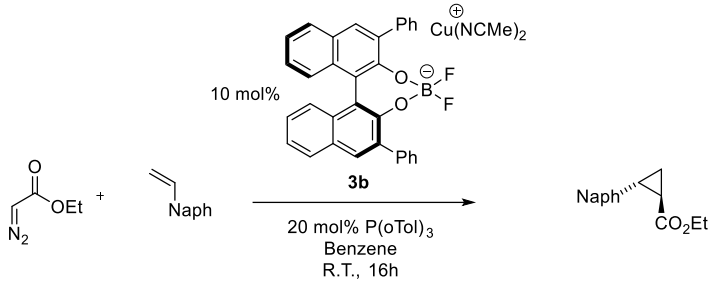
***tert*-butyl (1S,2S)-2-(4-cyanophenyl)cyclopropane-1-carboxylate (5p)**. The product was prepared using $Cu(OTf)_2$/**4b'** as described above with 4-cyanostyrene and benzyl diazoacetate. ^1H NMR analysis was used to determine the diastereomeric ratios of the trans and cis isomers (93:7, respectively). Purification conditions: 0-5% of ethyl acetate/hexanes. A sample of the pure trans *tert* butyl 2-(4-cyanophenyl)cyclopropane-1-carboxylate was collected for chiral HPLC and $^1H/^{13}C$ NMR analysis. Spectral data correlated with that previously reported in the literature.[13] All the fractions for *tert* butyl 2-(4-cyanophenyl)cyclopropane-1-carboxylate were combined to afford a colorless oil (24 mg, 76%).

HPLC: AS-H column, 1mL/min, 1% ^{i}PrOH/Hexanes, 230 nm UV detector. RetTime: 10.7 and 12.0 min, e.r.: 96:4, (S,S):(R,R).

^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 2.46 (ddd, *J* = 9.1, 6.3, 4.2 Hz, 1H), 1.88 (ddd, *J* = 8.5, 5.5, 4.2 Hz, 1H), 1.61 (ddd, *J* = 9.2, 5.5, 4.7 Hz, 1H), 1.47 (s, 9H), 1.26 (ddd, *J* = 8.5, 6.3, 4.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.85, 146.52, 132.37, 126.86, 119.02, 110.13, 81.30, 28.26, 26.11, 25.60, 17.78.

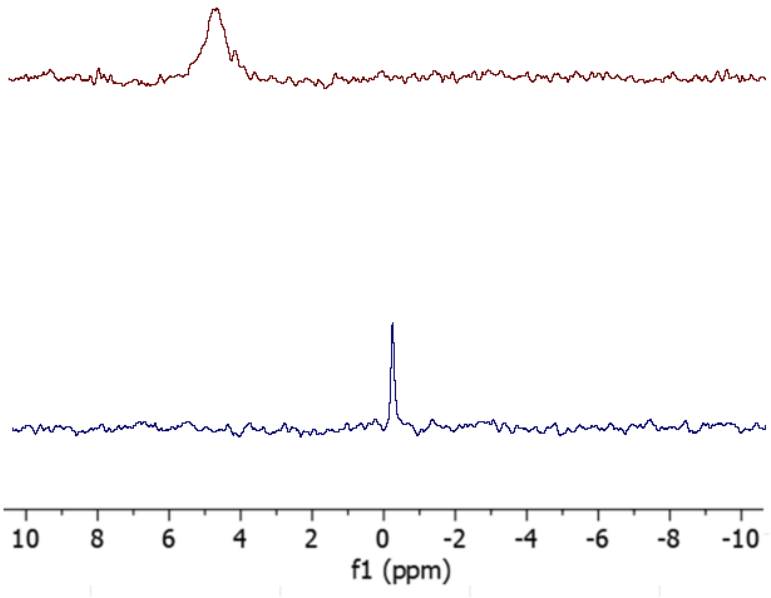
VI. Control experiments using 3b-Cu in catalytic cyclopropanation (Figure 3)



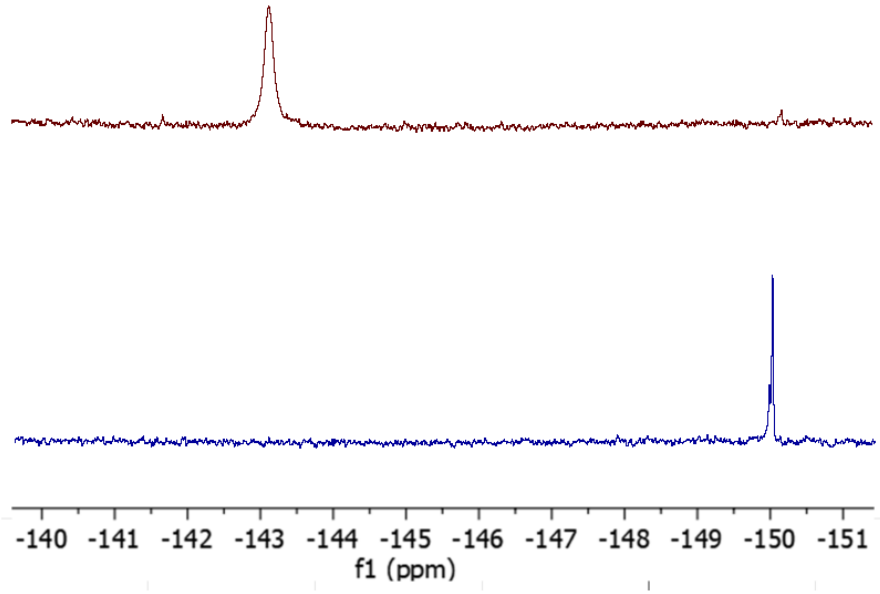
V.A *Determination of fate of* **3b-Cu** *after catalysis via Method A (Figure 3A)*

In an 8 mL microwave cap sealable tube inside the glovebox, 2-vinylnaphthalene (21 mg, 0.14 mmol, 5.2 eq), **3b-Cu** (2 mg, 0.0030 mmol, 0.10 eq) and P(*o*Tol)$_3$ (2 mg, 0.0030 mmol, 0.20 eq) were mixed in benzene (0.14 mL, 0.19 M) for 15 minutes. ^{11}B and ^{19}F NMR spectra were obtained on the initial catalytic mixture by transferring the solution to a J Young NMR tube for analysis. The NMR tube was then returned to the glovebox, the solution transferred back into the 8 mL microwave cap sealable tube and the septa cap was installed on the tube using a press. The mixture was then brought outside the glovebox and connected to a nitrogen line with a needle. In a separate 8 mL microwave cap sealable tube inside the glovebox, benzene (0.1 mL, 0.27 M) was added and the septa cap was installed using a press. The second tube was brought outside the glovebox, connected to a nitrogen line with a needle, and ethyl diazoacetate (22 µL, 0.026 mmol, 1.00 eq, 15% in toluene) was added. The solution of ethyl diazoacetate in benzene was then added to the tube containing the olefin and catalyst over the course of 10 min with a syringe. The reaction mixture was allowed to stir for an additional 16h at room temperature. The mixture was brought inside the glovebox and transferred to a J Young NMR tube. ^{11}B and ^{19}F NMR analysis shows the complete disappearance of **3b-Cu** and formation of BF_4^-.

^{11}B NMR (128 MHz, C_6D_6):



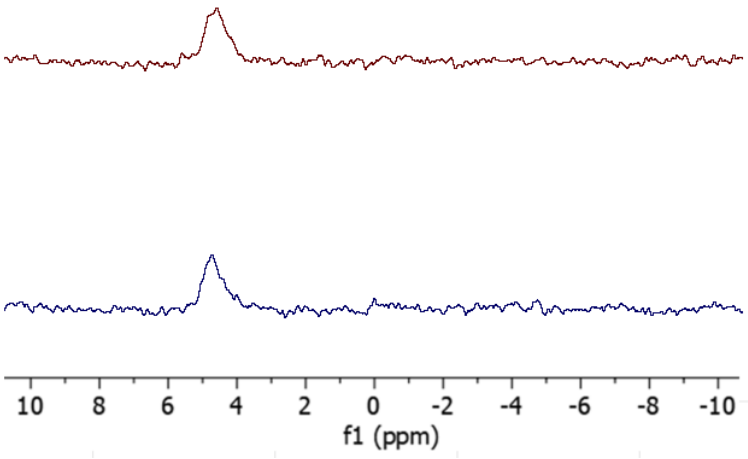
^{19}F NMR (376 MHz, C_6D_6):



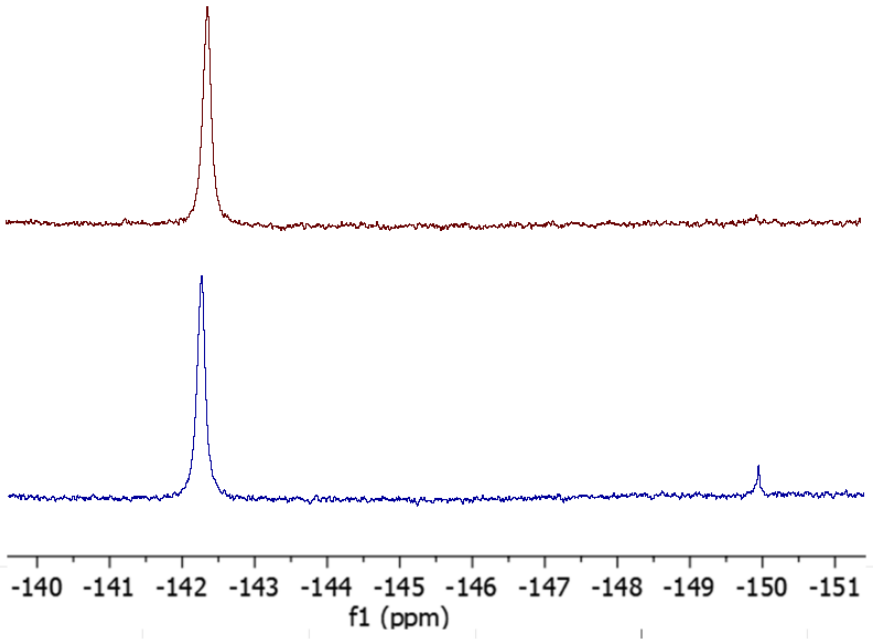
*VI.B Determining fate of **3b-Cu** after catalysis under inert conditions (Method B) (Figure 3A)*

In an 8 mL microwave cap sealable tube inside the glovebox, 2-vinylnaphthalene (21 mg, 0.14 mmol, 5.2 eq), **3b-Cu** (2 mg, 0.0030 mmol, 0.10 eq) and P(*o*Tol)$_3$ (2 mg, 0.0030 mmol, 0.20 eq) were mixed in benzene (0.14 mL, 0.19 M) for 15 minutes. ^{11}B and ^{19}F NMR spectra were obtained on the initial catalytic mixture by transferring the solution to a J Young NMR tube for analysis. The NMR tube was then returned to the glovebox, the solution transferred back into the 8 mL tube and a solution of ethyl diazoacetate (22 µL, 0.026 mmol, 1.00 eq, 15% in toluene) in benzene (0.1 mL, 0.27 M) was added to the mixture by syringe over the course of 10 min. The reaction mixture was allowed to stir for an additional 16h at room temperature. The mixture was then transferred to a J Young NMR tube, and ^{11}B and ^{19}F NMR analysis shows that **3b-Cu** remains after catalysis.

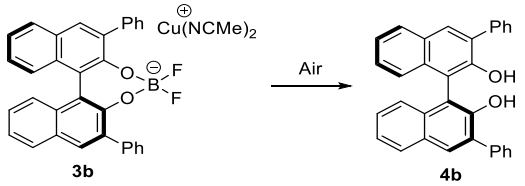
^{11}B NMR (128 MHz, C_6D_6):



^{19}F NMR (376 MHz, C_6D_6):



VI.C Decomposition of **3b-Cu** under aerobic conditions



In a 4 mL vial inside the glovebox, **3b-Cu** (4 mg, 0.0060 mmol, 1.0 eq) and P(*o*Tol)$_3$ (4 mg, 0.010 mmol, 2.0 eq) were mixed in benzene (0.14 mL, 0.19M) for 1h. Dimethlylsulfone (2 mg, 0.020 mmol, 3.0 eq) was added as an internal standard. The reaction mixture was brought outside the glovebox and exposed to air for 16h by removing the cap. The solution was then dilute in 0.6 mL with C_6D_6 and ^{1}H NMR analysis shows conversion of **3b-Cu** to **4b'** in 99% yield.

VII. Crystallographic data

X-ray crystal structure of **3b**:

X-ray quality crystals of **3b** were grown by adding 0.7 mL of benzene to the crude mixture and allowing the crystals to slowly grow overnight at room temperature. Suitable crystals for x-ray analysis were taken out of a glovebox and submerged in paratone oil, placed onto a mounting loop. Single crystal X-ray diffraction (SCXRD) data were measured on a Bruker D8 Venture diffractometer equipped with a Photon 200 area detector, and IμS microfocus X-ray source (Bruker AXS, CuKα source). Data were collected in a series of φ- and ω-scans. APEX3 software was used for data collection, integration and reduction.[22] Multi-scan absorption correction was applied using SADABS-2016/2.[23] Intrinsic phasing was used to generate the initial solutions. Final solution refinements were solved by full-matrix least-squares methods on F of all data,[23] by using SHELXLE software.[24,25] All of the nonhydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom thermal parameters were constrained to ride on the carrier atom. Measurements for **3b** were performed at 25(2)°C. The ORTEP representations of the structures were produced by MERCURY 4.0.[26] Olex2 was used to generate the data tables and report.[27] The structure was deposited in the Cambridge Crystallographic Data Centre (CCDC) data base under the deposition number 2215833.

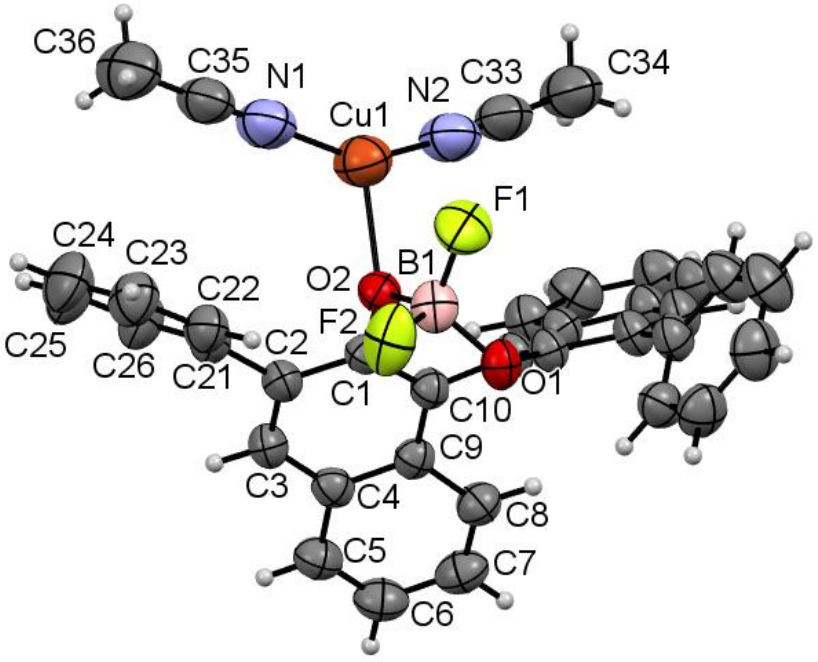


Table 1 Crystal data and structure refinement for AL1_a.

Identification code	AL1_a
Empirical formula	$C_{36}H_{26}BCuF_2N_2O_2$
Formula weight	630.94
Temperature/K	298(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.0757(3)
b/Å	14.0725(3)
c/Å	19.5245(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3043.14(13)
Z	4
ρ_{calc}g/cm^3	1.377
μ/mm^{-1}	1.408
F(000)	1296.0
Crystal size/mm^3	0.300 × 0.160 × 0.130
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.744 to 144.984
Index ranges	$-13 \le h \le 13$, $-17 \le k \le 17$, $-23 \le l \le 24$
Reflections collected	52720
Independent reflections	6032 [R_{int} = 0.1495, R_{sigma} = 0.0786]
Data/restraints/parameters	6032/0/399
Goodness-of-fit on F^2	1.106
Final R indexes [I>=2σ (I)]	R_1 = 0.0737, wR_2 = 0.1814
Final R indexes [all data]	R_1 = 0.1001, wR_2 = 0.2277
Largest diff. peak/hole / e Å^{-3}	0.43/-0.97
Flack parameter	-0.02(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for AL1_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cu1	4493.2(13)	1589.3(10)	6550.1(7)	90.0(5)
F1	5645(4)	3183(4)	6086(2)	90.5(14)
O1	5316(3)	4470(3)	6856(2)	54.5(9)
N1	3482(8)	1129(6)	5865(5)	94(2)
C1	3373(4)	3336(4)	7353(3)	44.5(10)

B1	4779(7)	3751(6)	6418(4)	60.5(16)
F2	4096(5)	4236(4)	5937(2)	93.3(15)
O2	4013(3)	3053(3)	6789.8(19)	51.2(9)
N2	5687(8)	1319(5)	7188(4)	90(2)
C2	2098(5)	3243(4)	7347(3)	49.4(12)
C3	1462(5)	3566(4)	7905(3)	53.0(13)
C4	2034(5)	4001(4)	8469(3)	49.2(11)
C5	1359(6)	4398(5)	9014(3)	60.8(14)
C6	1913(6)	4838(5)	9549(4)	66.5(16)
C7	3169(7)	4907(5)	9560(4)	65.3(16)
C8	3854(6)	4533(4)	9049(3)	55.8(13)
C9	3307(5)	4057(4)	8482(3)	46.5(11)
C10	3987(5)	3680(4)	7926(3)	45.7(11)
C11	5326(5)	3696(4)	7934(3)	48.0(11)
C12	5939(5)	4166(4)	7414(3)	48.9(11)
C13	7195(5)	4359(4)	7453(3)	52.2(12)
C14	7819(5)	4001(5)	8005(3)	59.2(14)
C15	7275(5)	3427(4)	8506(3)	55.9(12)
C16	7943(6)	2997(5)	9046(4)	65.6(16)
C17	7411(7)	2439(6)	9517(4)	73.7(19)
C18	6170(7)	2256(6)	9476(4)	72.4(18)
C19	5481(6)	2660(5)	8968(3)	60.1(14)
C20	6003(5)	3270(4)	8477(3)	51.5(12)
C21	1420(5)	2804(5)	6772(3)	57.9(14)
C22	1567(6)	3088(5)	6094(4)	64.8(15)
C23	816(7)	2728(6)	5575(4)	79(2)
C24	-59(9)	2079(7)	5737(5)	96(3)
C25	-205(9)	1785(7)	6399(5)	97(3)
C26	530(7)	2131(6)	6912(4)	74.8(18)
C27	7827(5)	4956(5)	6936(3)	58.0(14)
C28	8935(6)	4676(6)	6683(4)	72.0(19)
C29	9562(7)	5257(7)	6225(5)	85(2)
C30	9091(7)	6115(7)	6034(5)	83(2)
C31	7991(7)	6403(5)	6275(4)	74.2(19)
C32	7357(6)	5828(5)	6726(4)	62.7(15)
C33	6459(9)	1115(6)	7543(5)	85(2)
C34	7429(11)	837(7)	8004(6)	111(4)
C35	2843(9)	823(6)	5461(5)	86(2)
C36	2028(11)	411(10)	4972(6)	118(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for AL1_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	100.9(9)	82.7(8)	86.3(8)	-12.1(6)	-7.5(7)	10.0(7)
F1	83(3)	110(3)	78(3)	-20(2)	34(2)	-7(3)
O1	48.8(19)	62(2)	53(2)	9.9(17)	-4.9(16)	-6.3(18)
N1	99(5)	80(4)	104(5)	-12(4)	-15(5)	24(4)
C1	43(2)	46(3)	44(2)	-1(2)	1.8(19)	2(2)
B1	62(4)	75(4)	44(3)	7(3)	2(3)	-5(3)
F2	106(3)	104(3)	69(3)	34(2)	-33(2)	-25(3)
O2	49.5(18)	55(2)	48.7(19)	-2.7(16)	6.6(15)	1.0(16)
N2	106(5)	69(4)	97(5)	-8(3)	-6(5)	17(4)
C2	44(2)	50(3)	54(3)	-1(2)	-2(2)	1(2)
C3	43(3)	57(3)	60(3)	-2(2)	1(2)	-3(2)
C4	48(3)	45(3)	54(3)	4(2)	4(2)	2(2)
C5	60(3)	61(3)	62(3)	-3(3)	8(3)	7(3)
C6	76(4)	67(4)	57(3)	-6(3)	14(3)	10(3)
C7	85(4)	58(4)	53(3)	-7(3)	-2(3)	2(3)
C8	60(3)	57(3)	51(3)	-4(2)	-1(3)	-1(3)
C9	49(3)	43(2)	47(3)	3(2)	-1(2)	-2(2)
C10	43(2)	50(3)	44(3)	-2(2)	-2(2)	0(2)
C11	45(3)	52(3)	47(3)	6(2)	-2(2)	0(2)
C12	44(3)	53(3)	49(3)	4(2)	-4(2)	2(2)
C13	40(2)	61(3)	55(3)	6(3)	2(2)	1(2)
C14	43(3)	70(4)	65(4)	6(3)	-2(2)	-2(3)
C15	51(3)	61(3)	55(3)	6(3)	-8(2)	4(3)
C16	60(3)	71(4)	65(4)	5(3)	-15(3)	9(3)
C17	77(5)	76(4)	69(4)	16(3)	-13(3)	11(4)
C18	82(4)	72(4)	63(4)	18(3)	-5(3)	8(4)
C19	59(3)	65(3)	57(3)	9(3)	-2(3)	0(3)
C20	49(2)	54(3)	51(3)	3(2)	-3(2)	3(2)
C21	52(3)	55(3)	66(4)	-8(3)	-8(3)	-1(3)
C22	63(3)	66(4)	65(4)	-7(3)	-13(3)	2(3)
C23	84(5)	84(5)	69(4)	-7(4)	-19(4)	-3(4)
C24	94(6)	101(6)	93(6)	-26(5)	-32(5)	-15(5)
C25	95(6)	99(6)	98(6)	-21(5)	-13(5)	-35(5)
C26	74(4)	74(4)	77(4)	-8(3)	-8(4)	-21(4)
C27	45(3)	63(3)	66(3)	4(3)	3(3)	-3(3)
C28	54(3)	81(4)	80(5)	15(4)	16(3)	4(3)
C29	57(4)	106(6)	91(5)	14(5)	18(4)	0(4)
C30	73(4)	90(5)	86(5)	17(4)	11(4)	-19(4)
C31	78(4)	61(4)	84(5)	10(3)	-3(4)	-11(3)

C32	58(3)	56(3)	74(4)	4(3)	6(3)	-2(3)
C33	97(6)	63(4)	96(6)	-12(4)	-8(5)	12(4)
C34	123(8)	88(6)	121(8)	-25(6)	-38(7)	23(6)
C35	89(5)	81(5)	87(5)	-14(4)	-12(5)	28(4)
C36	131(9)	122(8)	100(7)	-28(7)	-35(7)	27(7)

Table 4 Bond Lengths for AL1_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N2	1.856(9)	C11	C20	1.429(8)
Cu1	N1	1.862(9)	C12	C13	1.419(8)
Cu1	O2	2.178(4)	C13	C14	1.377(9)
F1	B1	1.407(9)	C13	C27	1.488(9)
O1	C12	1.358(7)	C14	C15	1.404(9)
O1	B1	1.454(9)	C15	C16	1.424(8)
N1	C35	1.143(12)	C15	C20	1.427(8)
C1	O2	1.368(6)	C16	C17	1.344(11)
C1	C10	1.396(7)	C17	C18	1.401(11)
C1	C2	1.418(7)	C18	C19	1.375(9)
B1	F2	1.385(8)	C19	C20	1.412(8)
B1	O2	1.487(8)	C21	C22	1.393(10)
N2	C33	1.138(12)	C21	C26	1.394(10)
C2	C3	1.374(8)	C22	C23	1.405(10)
C2	C21	1.483(8)	C23	C24	1.368(13)
C3	C4	1.411(8)	C24	C25	1.368(14)
C4	C9	1.413(7)	C25	C26	1.380(11)
C4	C5	1.415(8)	C27	C28	1.380(9)
C5	C6	1.361(10)	C27	C32	1.395(9)
C6	C7	1.394(10)	C28	C29	1.397(11)
C7	C8	1.361(9)	C29	C30	1.366(13)
C8	C9	1.428(8)	C30	C31	1.367(12)
C9	C10	1.423(8)	C31	C32	1.386(10)
C10	C11	1.484(7)	C33	C34	1.455(14)
C11	C12	1.390(8)	C35	C36	1.436(14)

Table 5 Bond Angles for AL1_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Cu1	N1	147.1(3)	C20	C11	C10	121.7(5)
N2	Cu1	O2	102.9(2)	O1	C12	C11	119.2(5)

N1	Cu1	O2	109.7(3)	O1	C12	C13	118.7(5)
C12	O1	B1	117.4(5)	C11	C12	C13	122.1(5)
C35	N1	Cu1	177.5(9)	C14	C13	C12	117.6(5)
O2	C1	C10	119.5(4)	C14	C13	C27	120.1(5)
O2	C1	C2	118.8(5)	C12	C13	C27	122.2(5)
C10	C1	C2	121.6(5)	C13	C14	C15	122.8(5)
F2	B1	F1	109.9(6)	C14	C15	C16	122.6(5)
F2	B1	O1	106.2(6)	C14	C15	C20	119.0(5)
F1	B1	O1	112.9(6)	C16	C15	C20	118.5(6)
F2	B1	O2	110.1(5)	C17	C16	C15	121.8(6)
F1	B1	O2	103.8(6)	C16	C17	C18	119.9(6)
O1	B1	O2	113.9(5)	C19	C18	C17	120.6(7)
C1	O2	B1	119.8(5)	C18	C19	C20	121.0(6)
C1	O2	Cu1	125.0(3)	C19	C20	C15	118.1(5)
B1	O2	Cu1	112.3(4)	C19	C20	C11	122.9(5)
C33	N2	Cu1	175.0(8)	C15	C20	C11	118.9(5)
C3	C2	C1	118.1(5)	C22	C21	C26	117.6(6)
C3	C2	C21	118.6(5)	C22	C21	C2	122.7(6)
C1	C2	C21	123.3(5)	C26	C21	C2	119.5(6)
C2	C3	C4	122.2(5)	C21	C22	C23	120.8(7)
C3	C4	C9	119.0(5)	C24	C23	C22	119.6(8)
C3	C4	C5	121.4(5)	C25	C24	C23	120.3(8)
C9	C4	C5	119.5(5)	C24	C25	C26	120.6(8)
C6	C5	C4	121.2(6)	C25	C26	C21	121.1(8)
C5	C6	C7	119.6(6)	C28	C27	C32	118.5(6)
C8	C7	C6	121.2(6)	C28	C27	C13	120.0(6)
C7	C8	C9	121.0(6)	C32	C27	C13	121.3(5)
C4	C9	C10	119.6(5)	C27	C28	C29	120.3(7)
C4	C9	C8	117.6(5)	C30	C29	C28	120.1(7)
C10	C9	C8	122.8(5)	C29	C30	C31	120.6(7)
C1	C10	C9	118.9(5)	C30	C31	C32	119.8(7)
C1	C10	C11	120.0(5)	C31	C32	C27	120.7(6)
C9	C10	C11	121.0(5)	N2	C33	C34	178.6(11)
C12	C11	C20	119.0(5)	N1	C35	C36	177.8(12)
C12	C11	C10	119.2(5)				

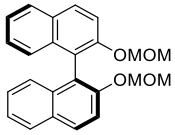
Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for AL1_a.

Atom	***x***	***y***	***z***	**U(eq)**
H3	627.47	3496.03	7910.21	64

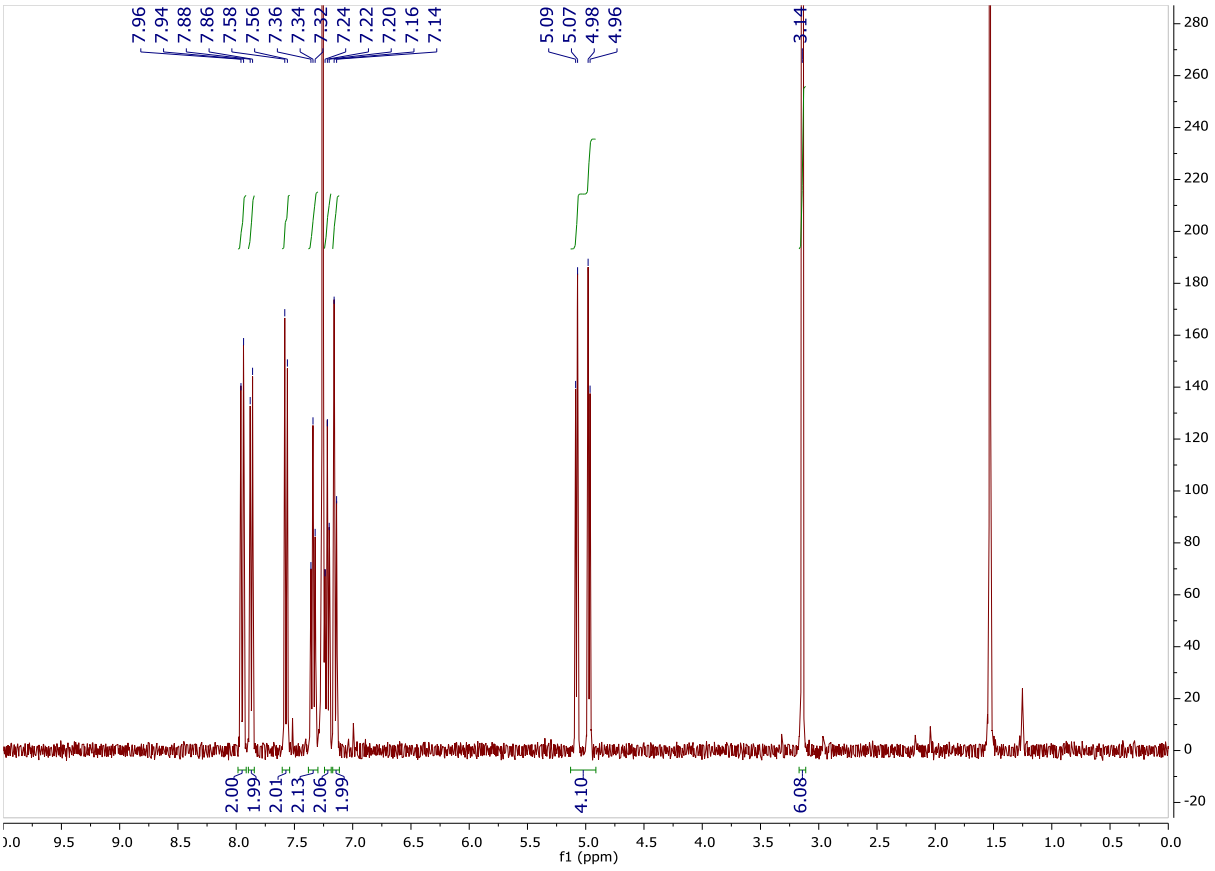
H5	520.61	4358.21	9005.94	73
H6	1457.55	5090.64	9905.28	80
H7	3544.83	5214.44	9924.19	78
H8	4689.98	4587.01	9068.29	67
H14	8634.86	4144.28	8048.05	71
H16	8769.93	3104.62	9074.79	79
H17	7866.82	2175.18	9868.97	88
H18	5808.5	1856.64	9795.65	87
H19	4658.28	2529.87	8947.95	72
H22	2169.91	3521.78	5983.45	78
H23	913.8	2929.01	5125.06	95
H24	-555.72	1837.99	5394.51	115
H25	-806.03	1346.65	6504.42	117
H26	429.6	1912.39	7357.54	90
H28	9265.27	4097.8	6817.2	86
H29	10302.18	5060.81	6049.74	102
H30	9521.56	6505.69	5738.1	100
H31	7669.51	6982.62	6137.56	89
H32	6610.48	6026.17	6890.34	75
H34A	7736.37	226.92	7869.9	166
H34B	7124.25	800.91	8464.01	166
H34C	8065.15	1298.94	7983.43	166
H36A	2262.14	-234.18	4882.28	177
H36B	2054.38	769.31	4554.16	177
H36C	1222.04	421.27	5153.17	177

VIII. Characterization (NMR, HPLC, X-Ray)

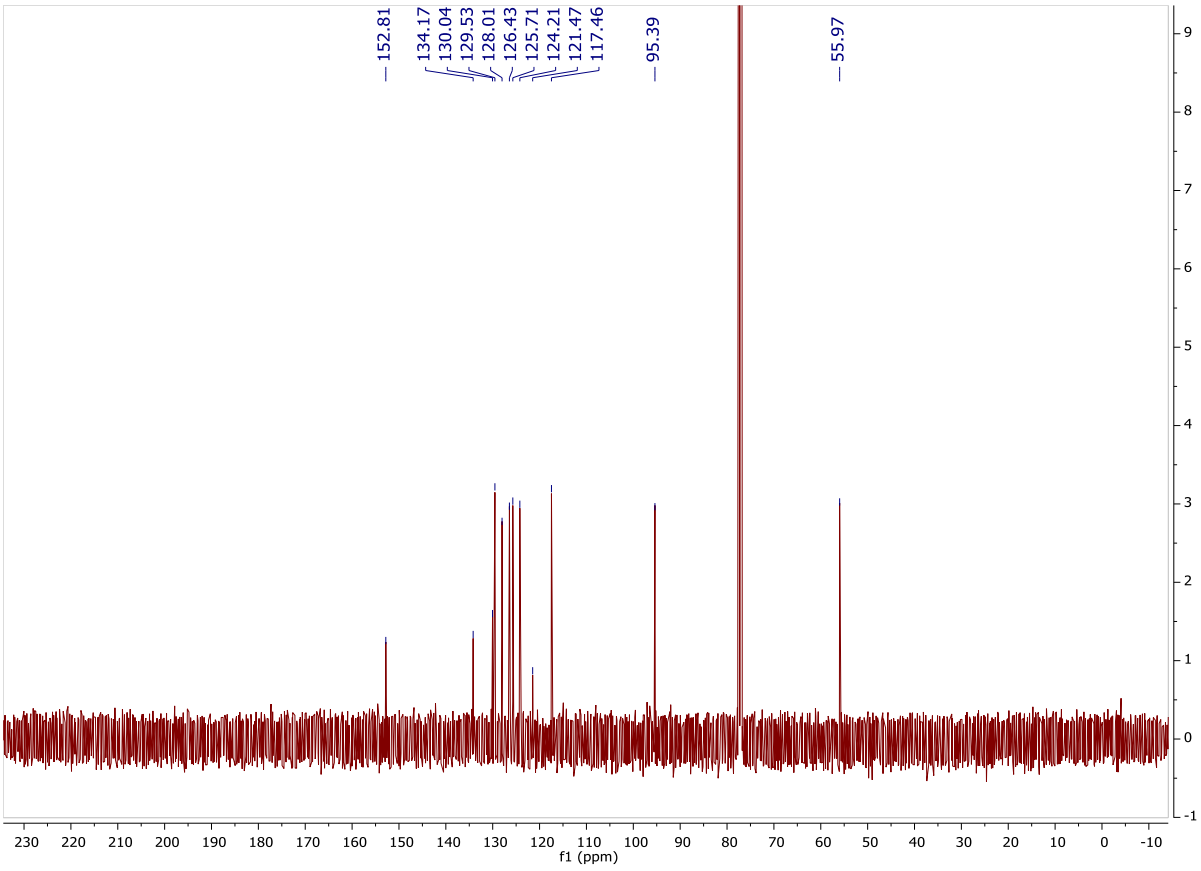
(S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene.



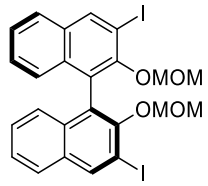
^{1}H NMR (500 MHz, $CDCl_3$):



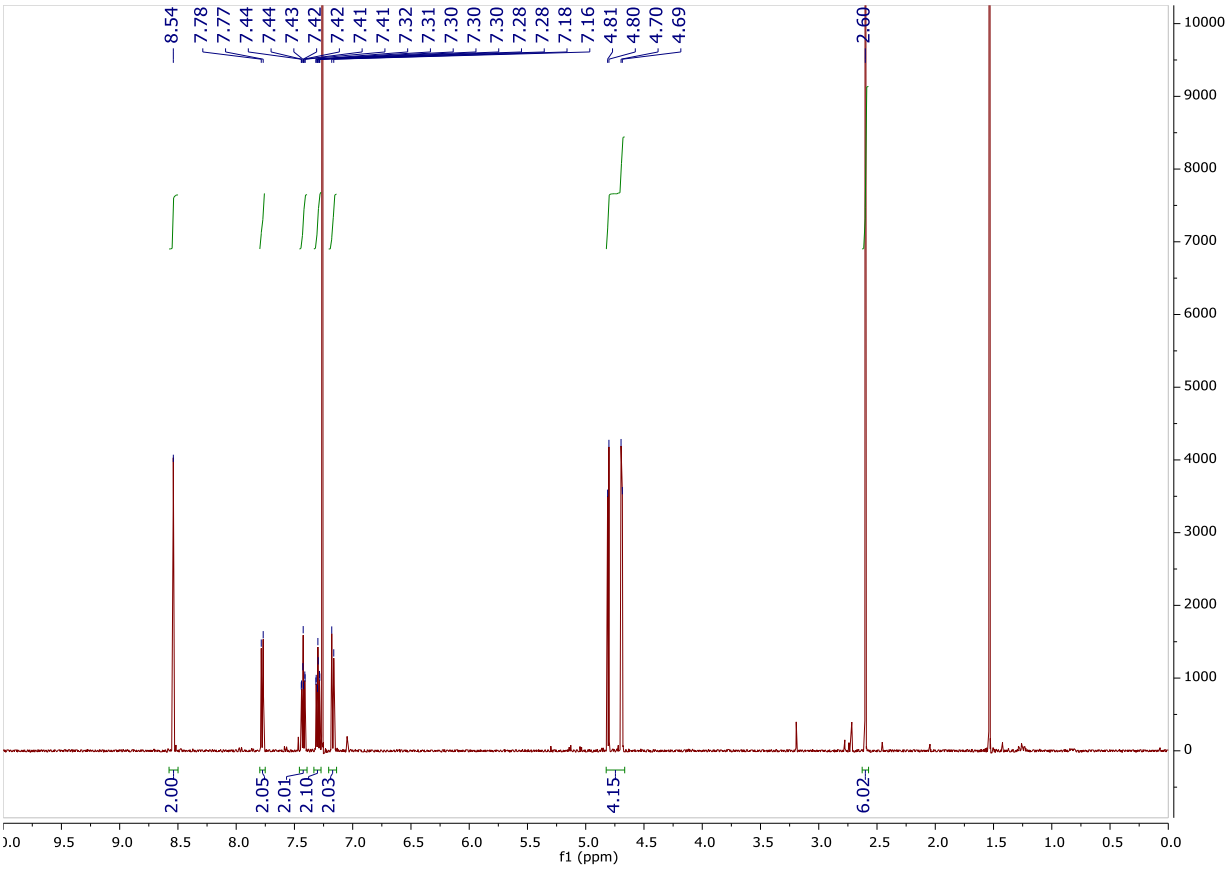
^{13}C NMR (126 MHz, $CDCl_3$):



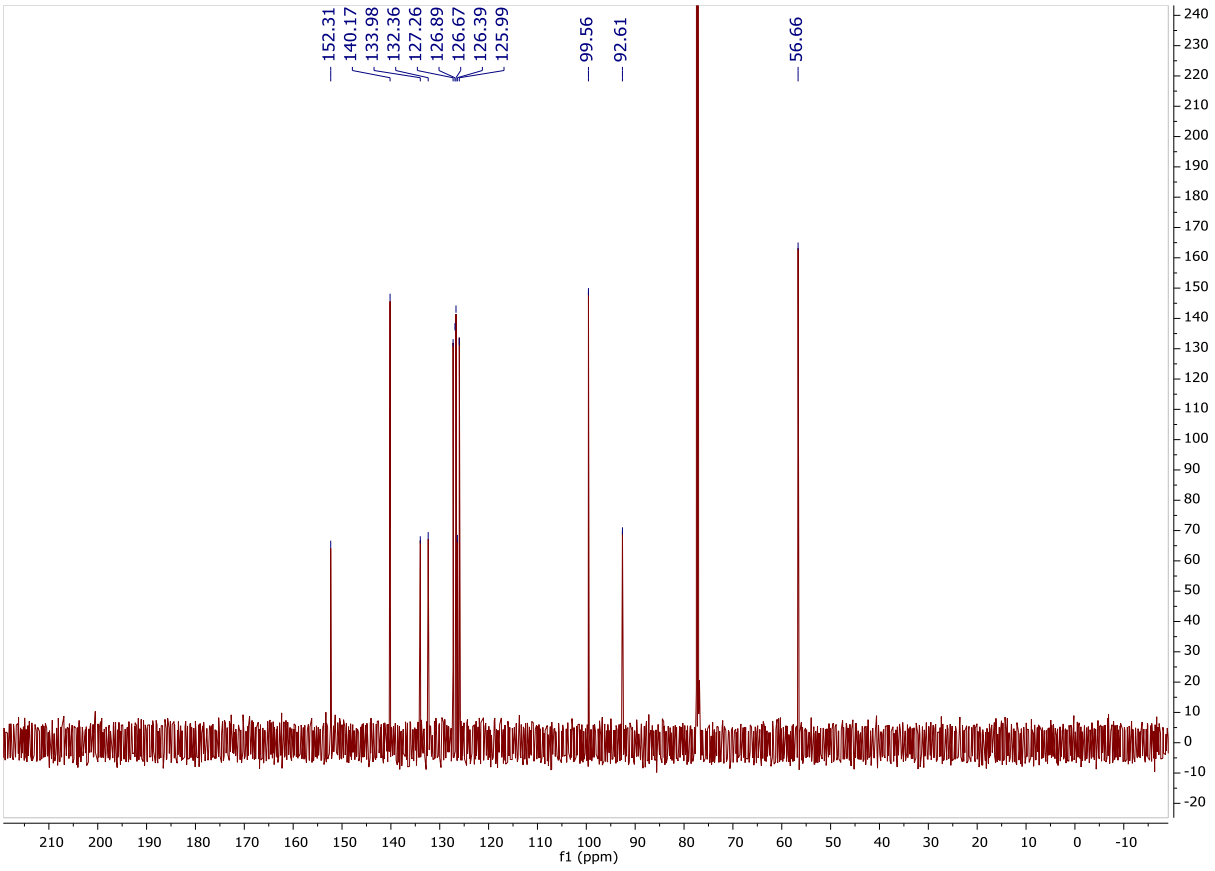
(S)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene



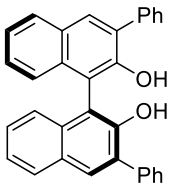
^{1}H NMR (500 MHz, $CDCl_3$):



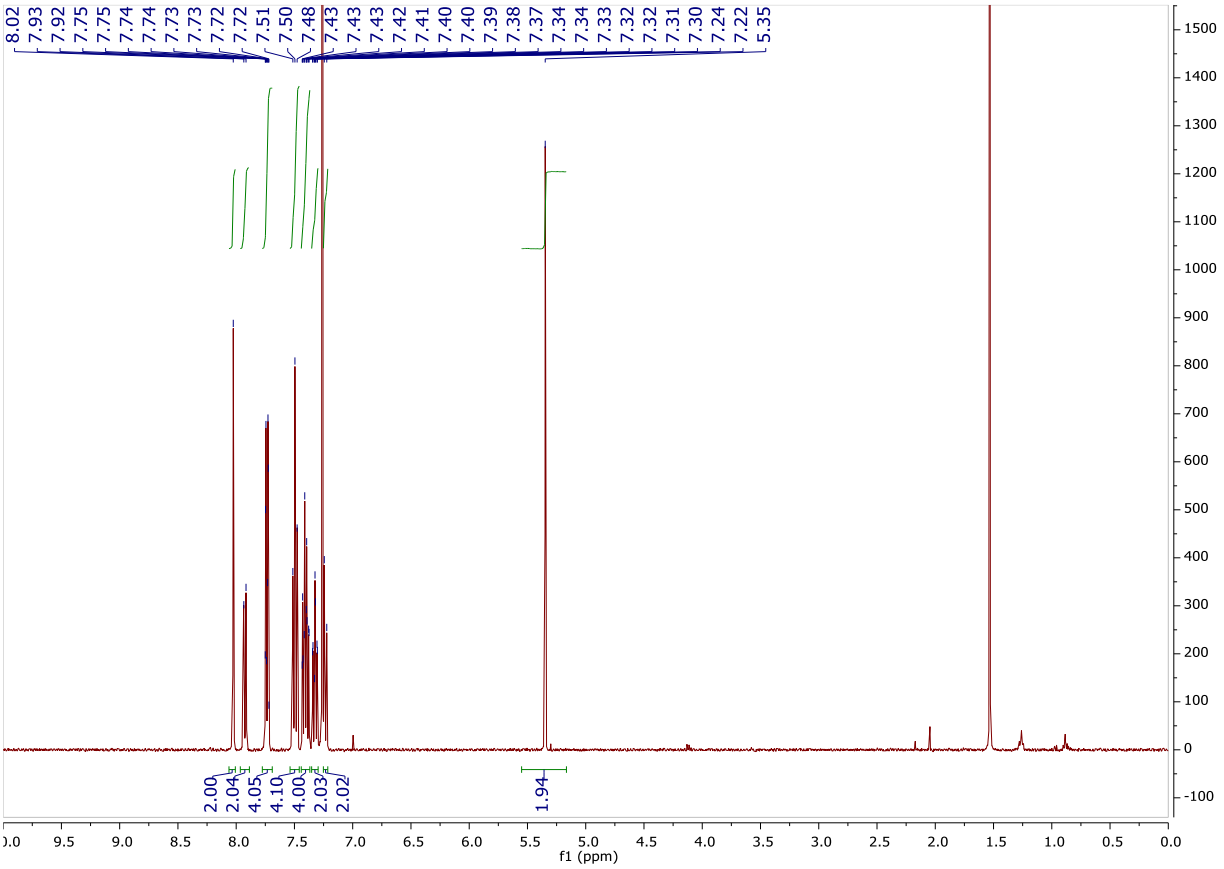
^{13}C NMR (126 MHz, $CDCl_3$):



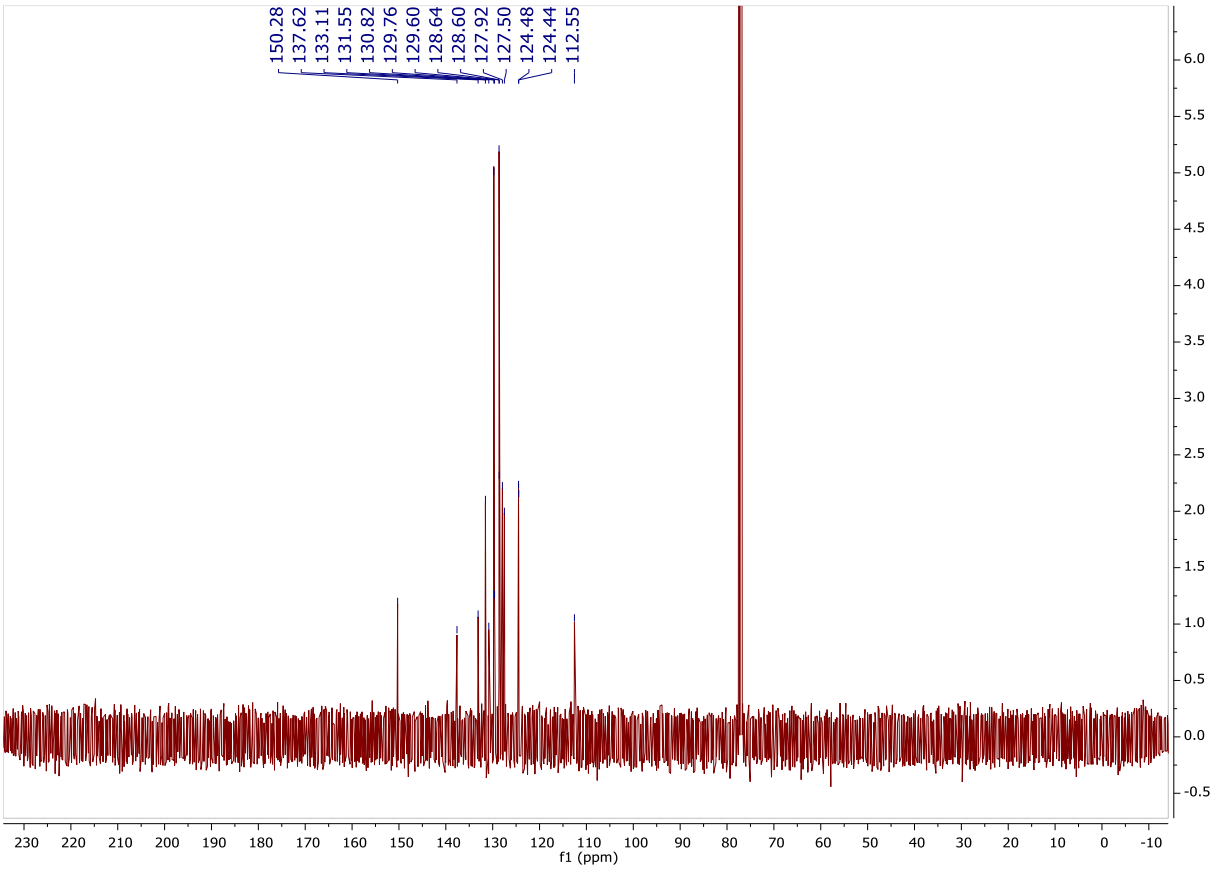
(S)-3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diol.



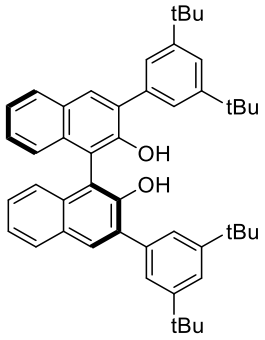
^{1}H NMR (500 MHz, $CDCl_3$):



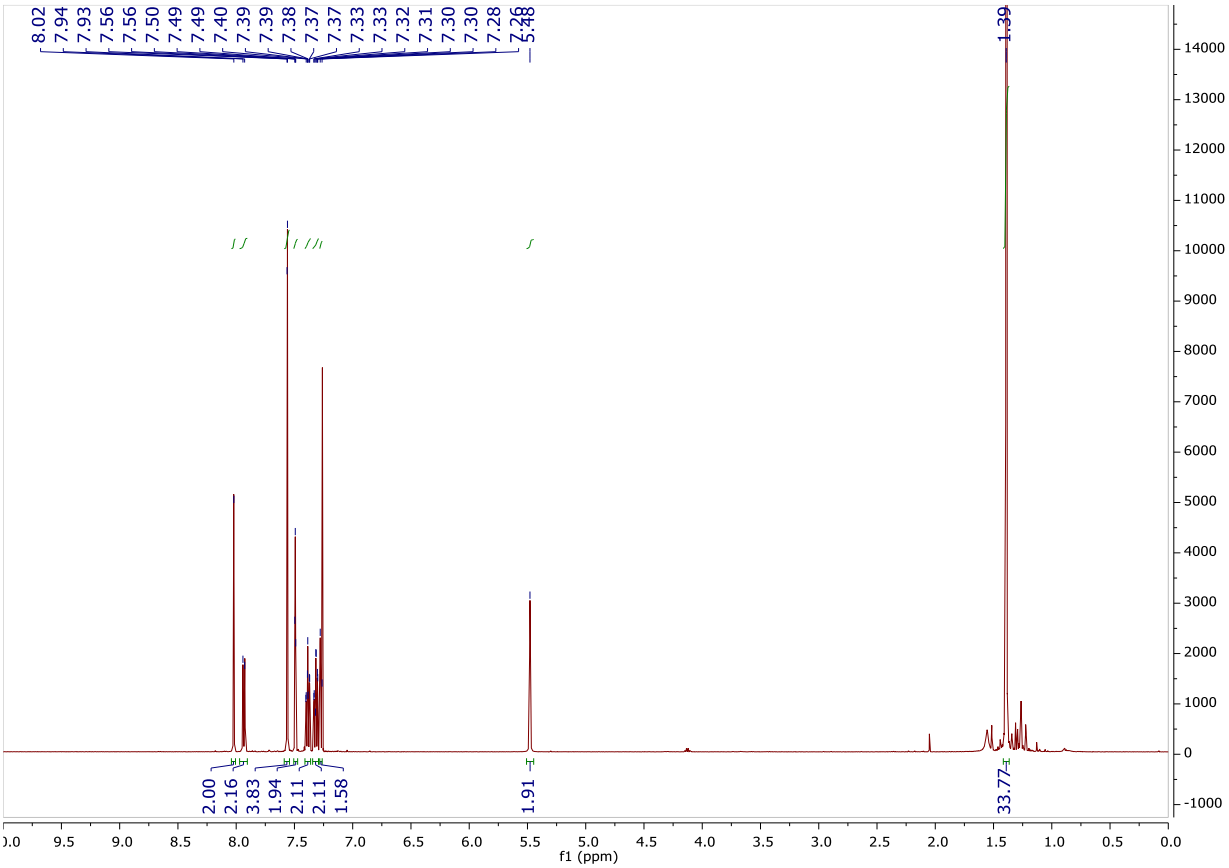
^{13}C NMR (126 MHz, $CDCl_3$):



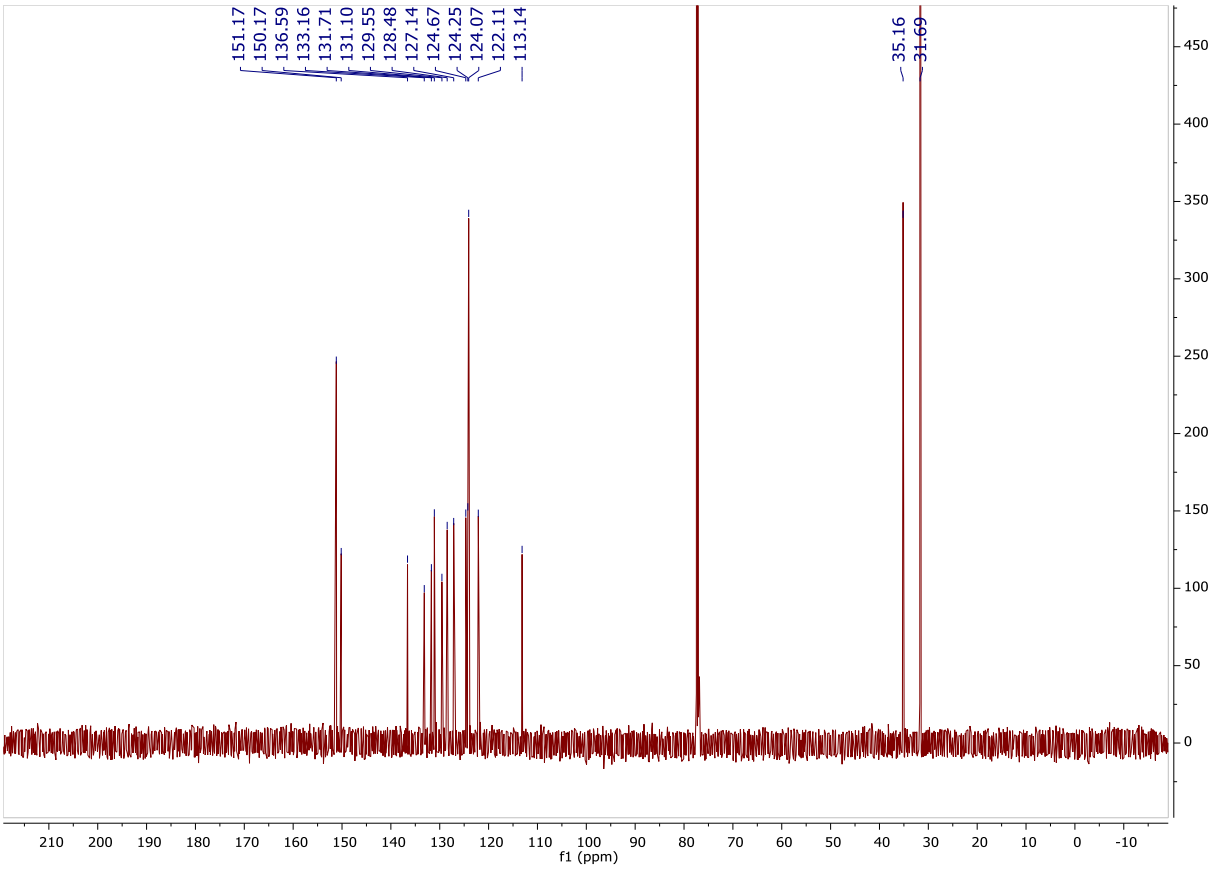
(S)-3,3'-bis(3,5-di-tert-butylphenyl)-[1,1'-binaphthalene]-2,2'-diol



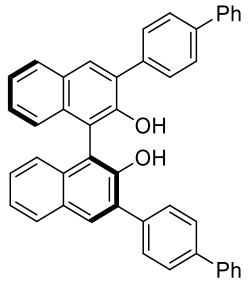
^{1}H NMR (500 MHz, $CDCl_3$):



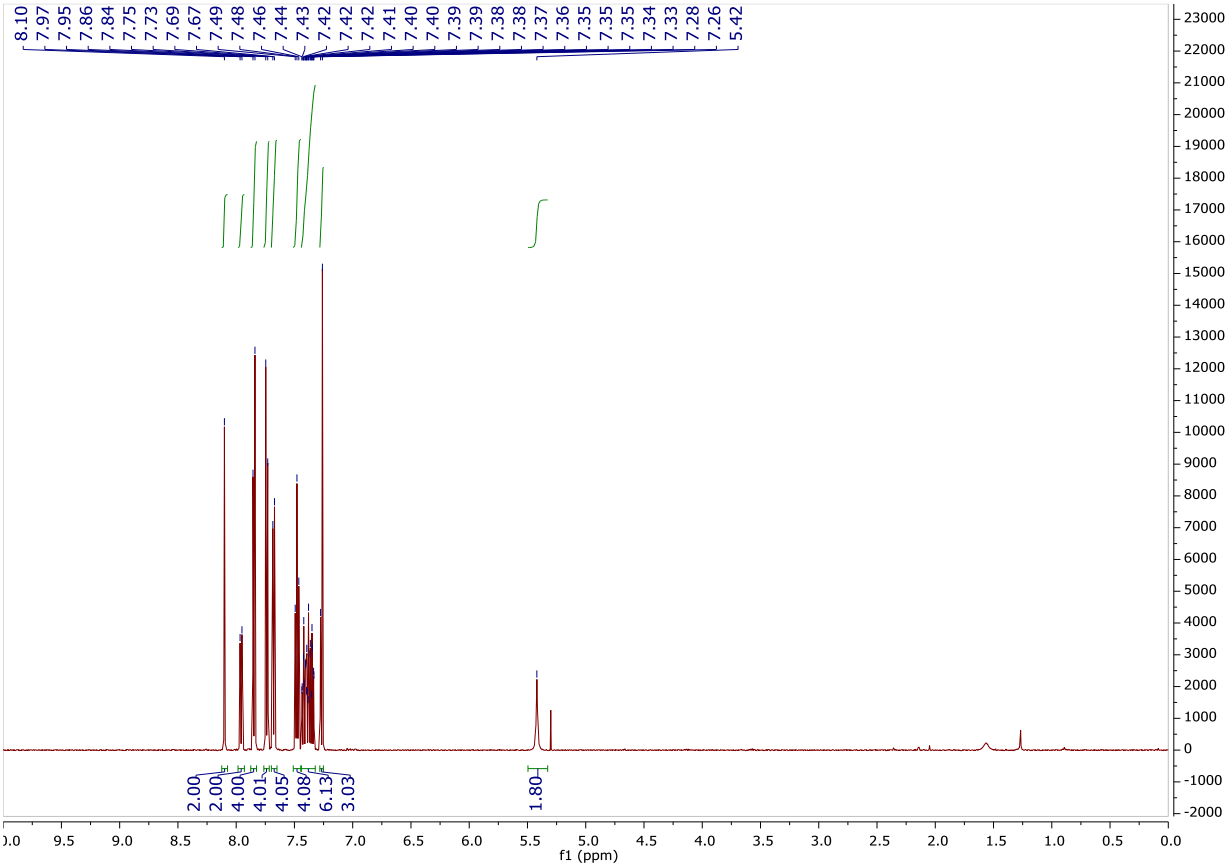
^{13}C NMR (126 MHz, $CDCl_3$):



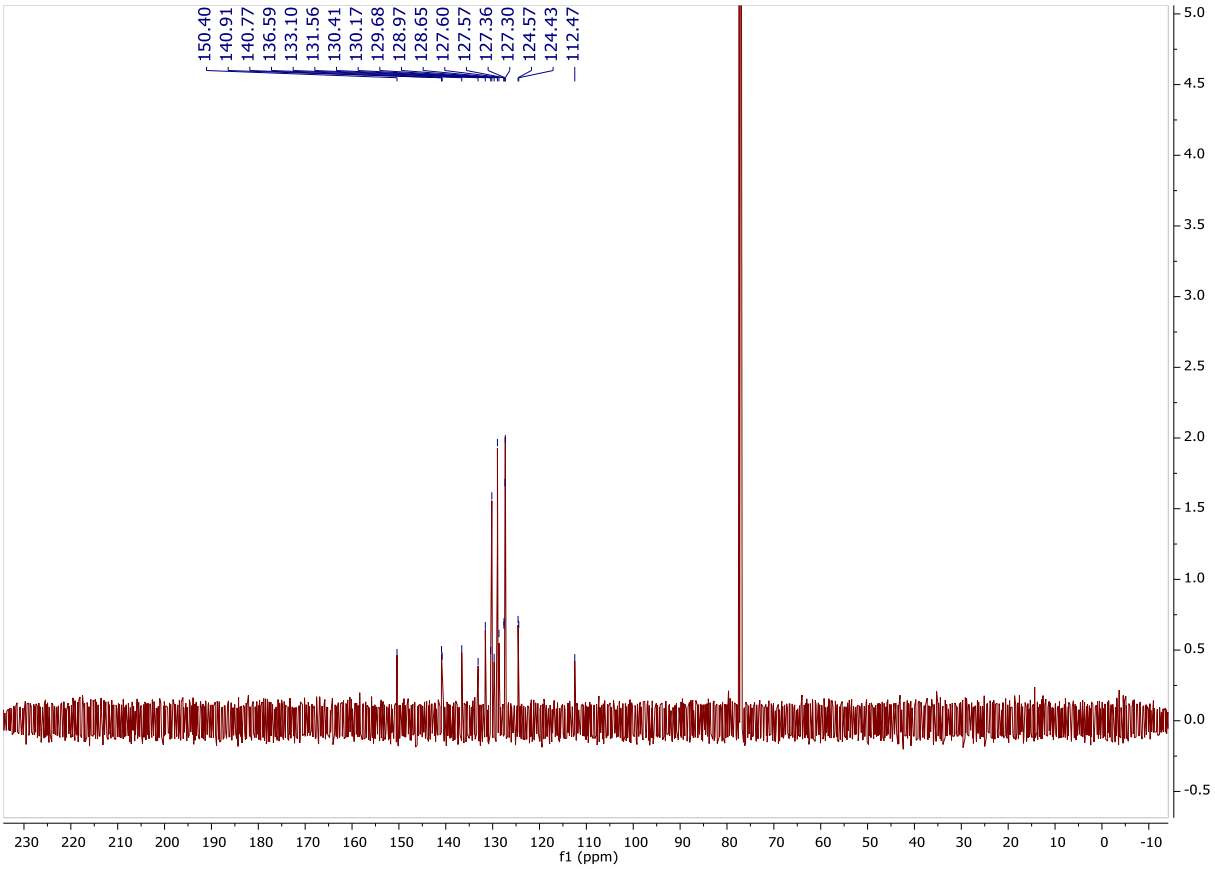
(S)-3,3'-di([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol



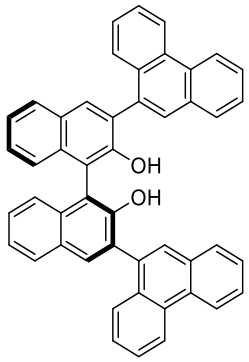
^{1}H NMR (500 MHz, $CDCl_3$):



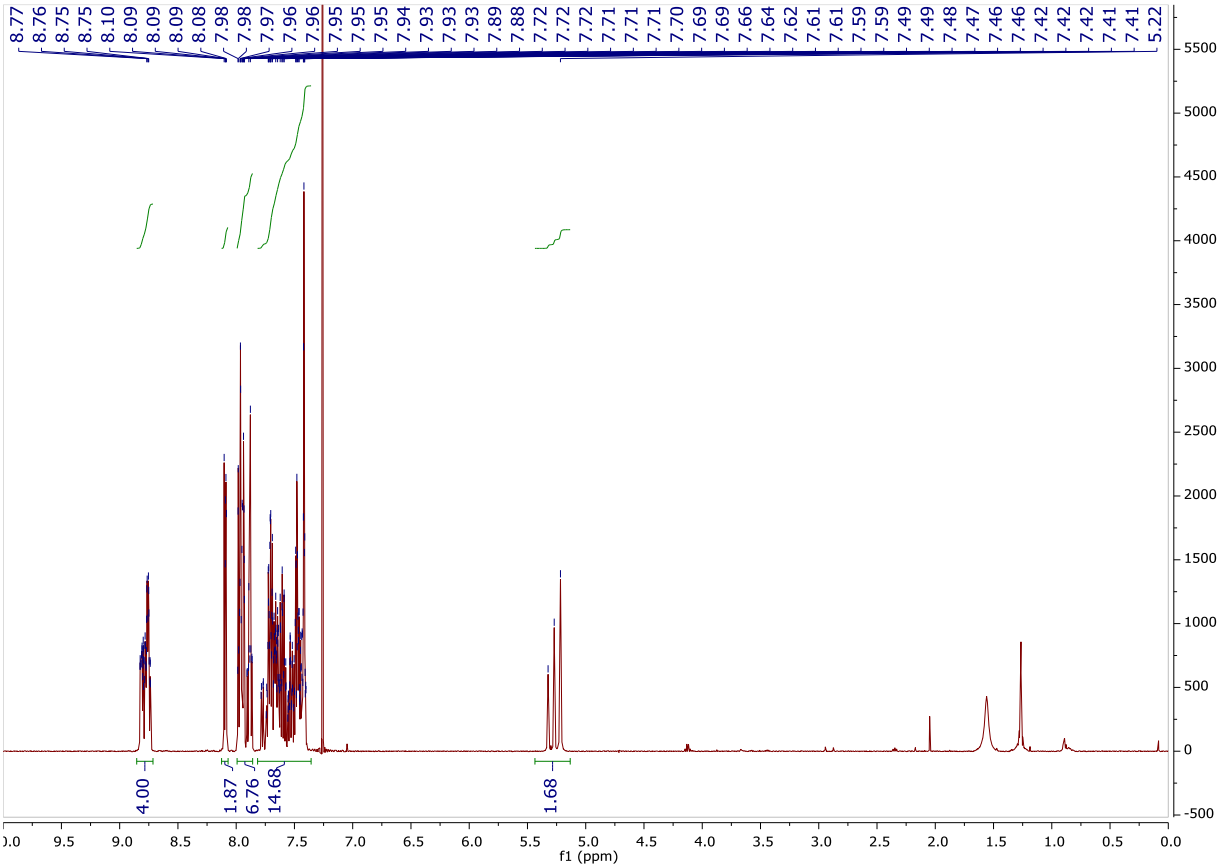
^{13}C NMR (126 MHz, $CDCl_3$):



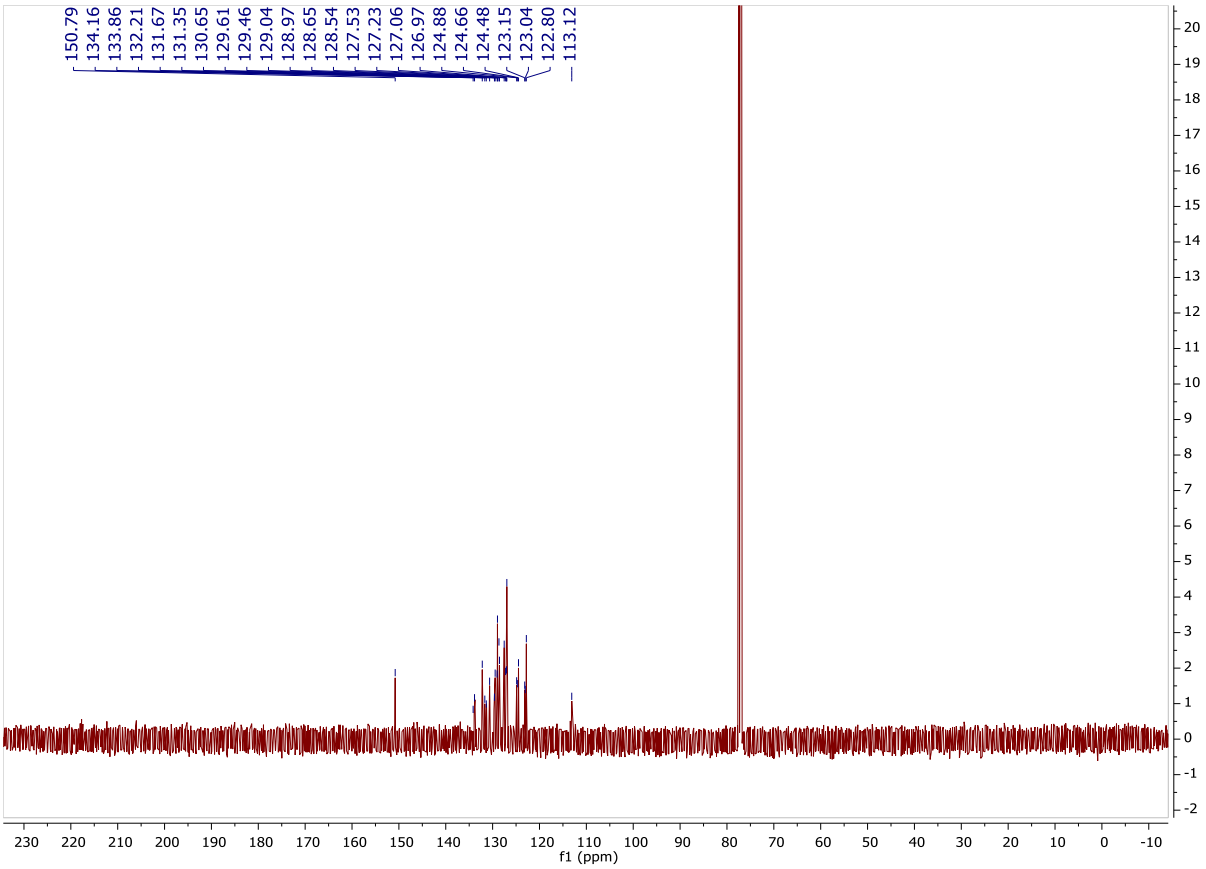
(S)-3,3'-di(phenanthren-9-yl)-[1,1'-binaphthalene]-2,2'-diol



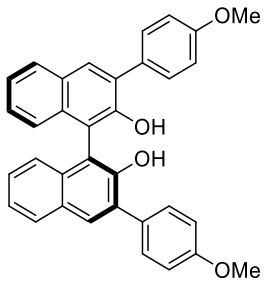
^{1}H NMR (500 MHz, $CDCl_3$):



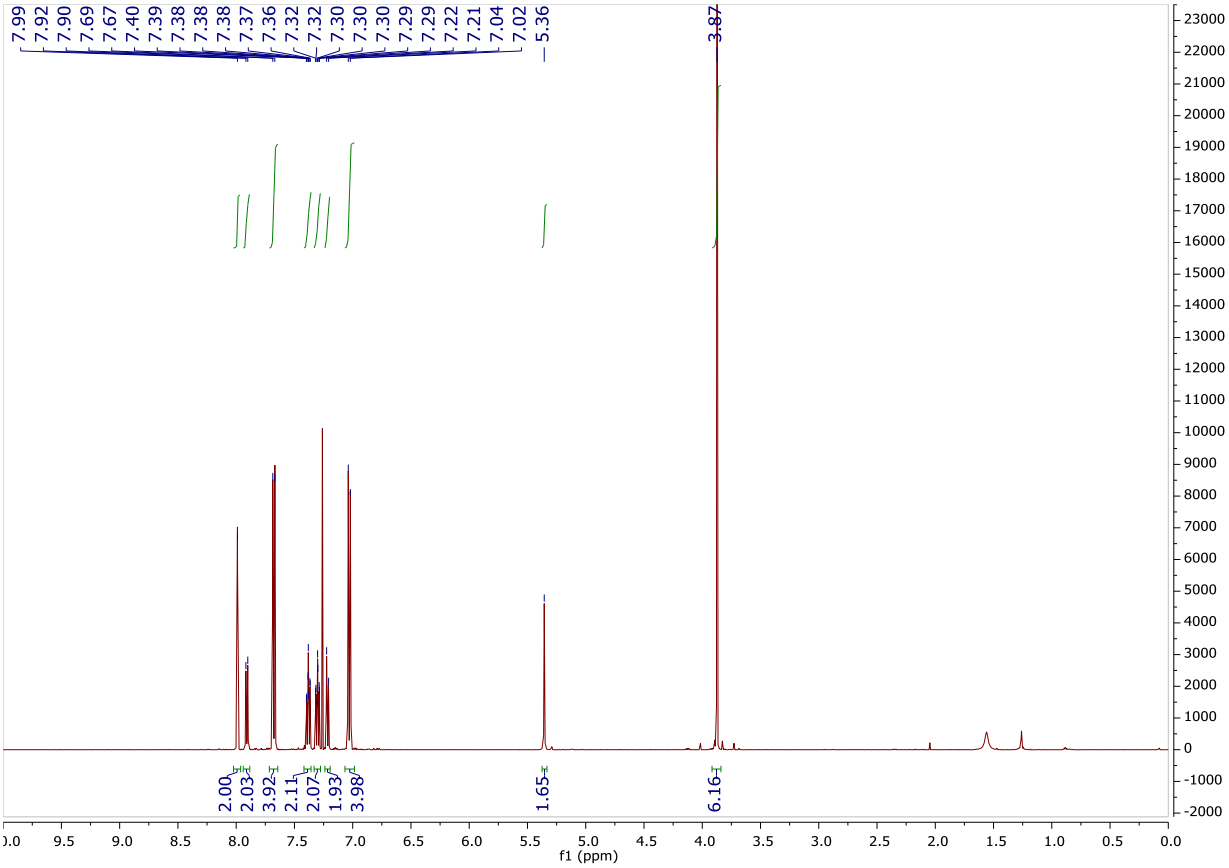
^{13}C NMR (126 MHz, $CDCl_3$):



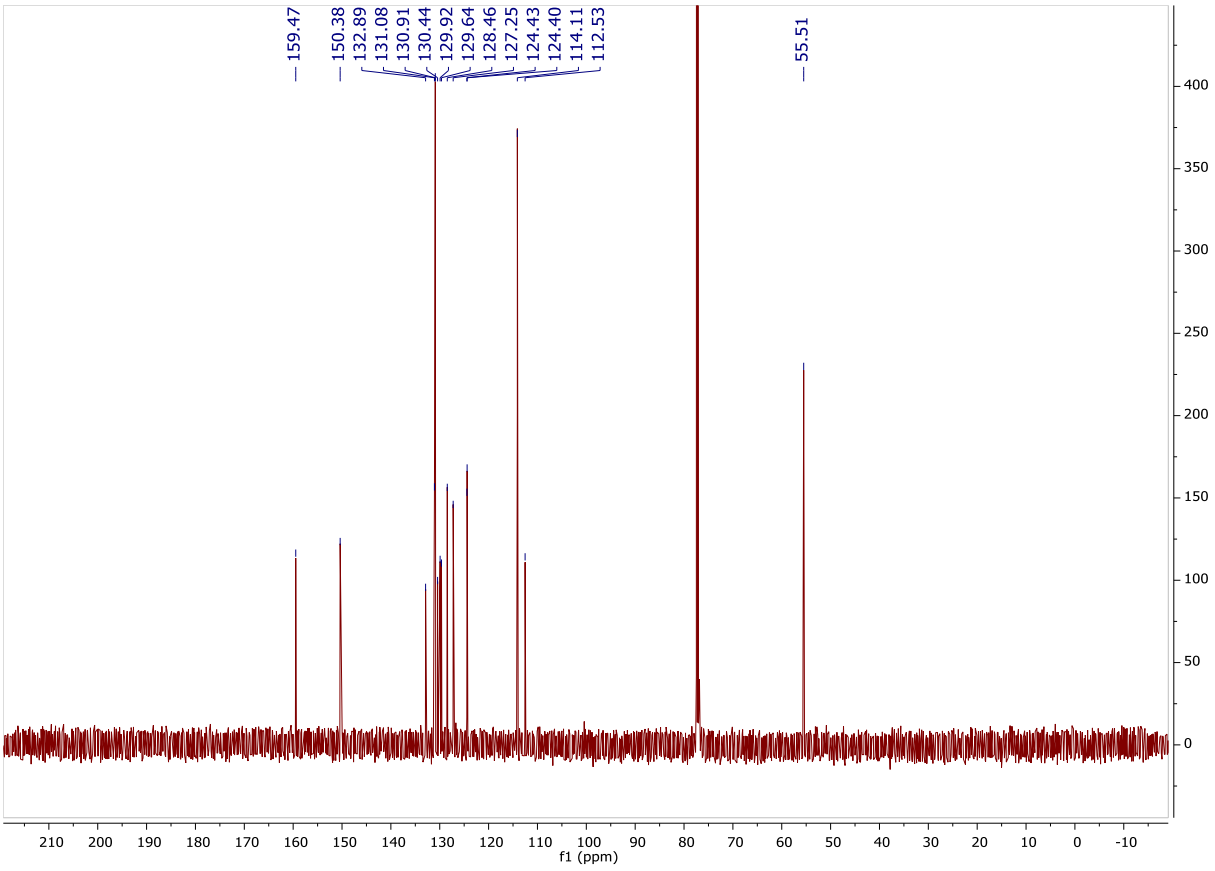
(S)-3,3'-bis(4-methoxyphenyl)-[1,1'-binaphthalene]-2,2'-diol



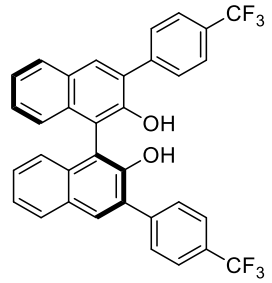
^{1}H NMR (500 MHz, $CDCl_3$):



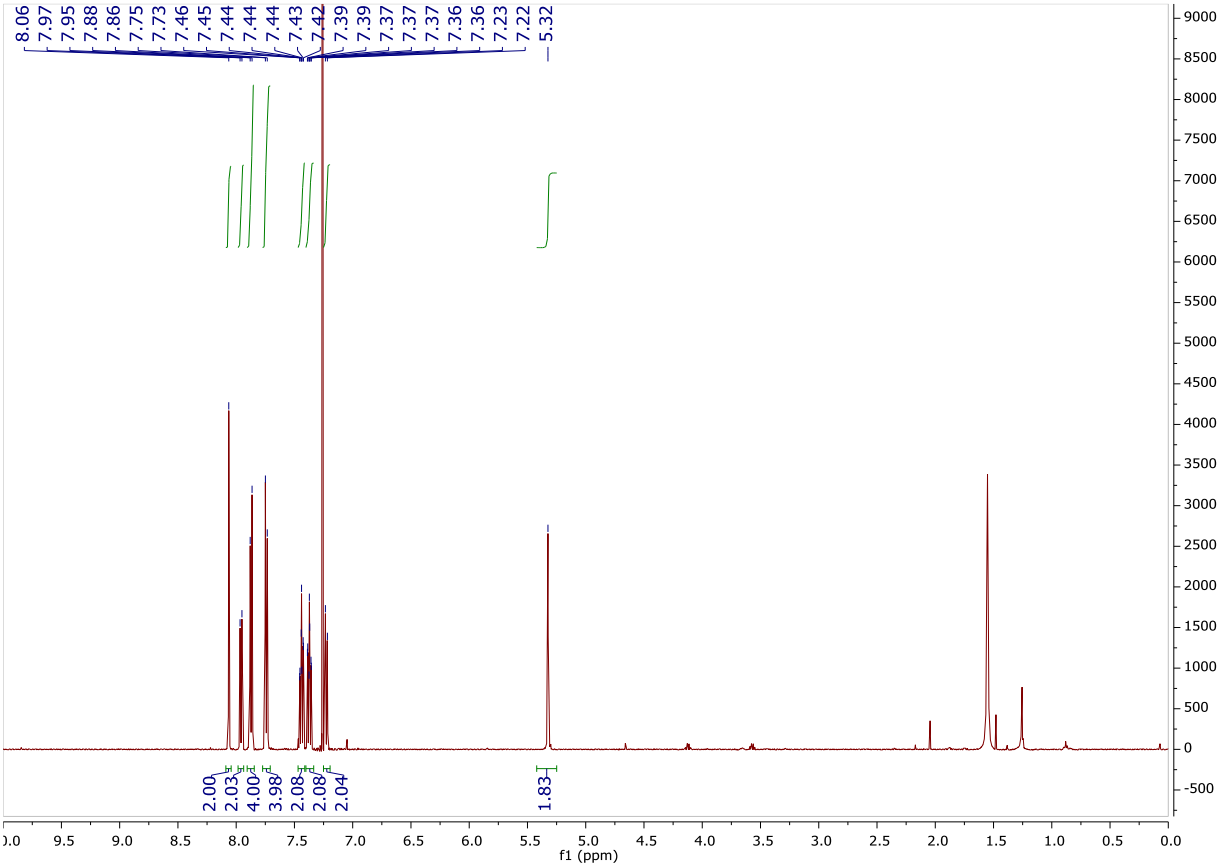
^{13}C NMR (126 MHz, $CDCl_3$):



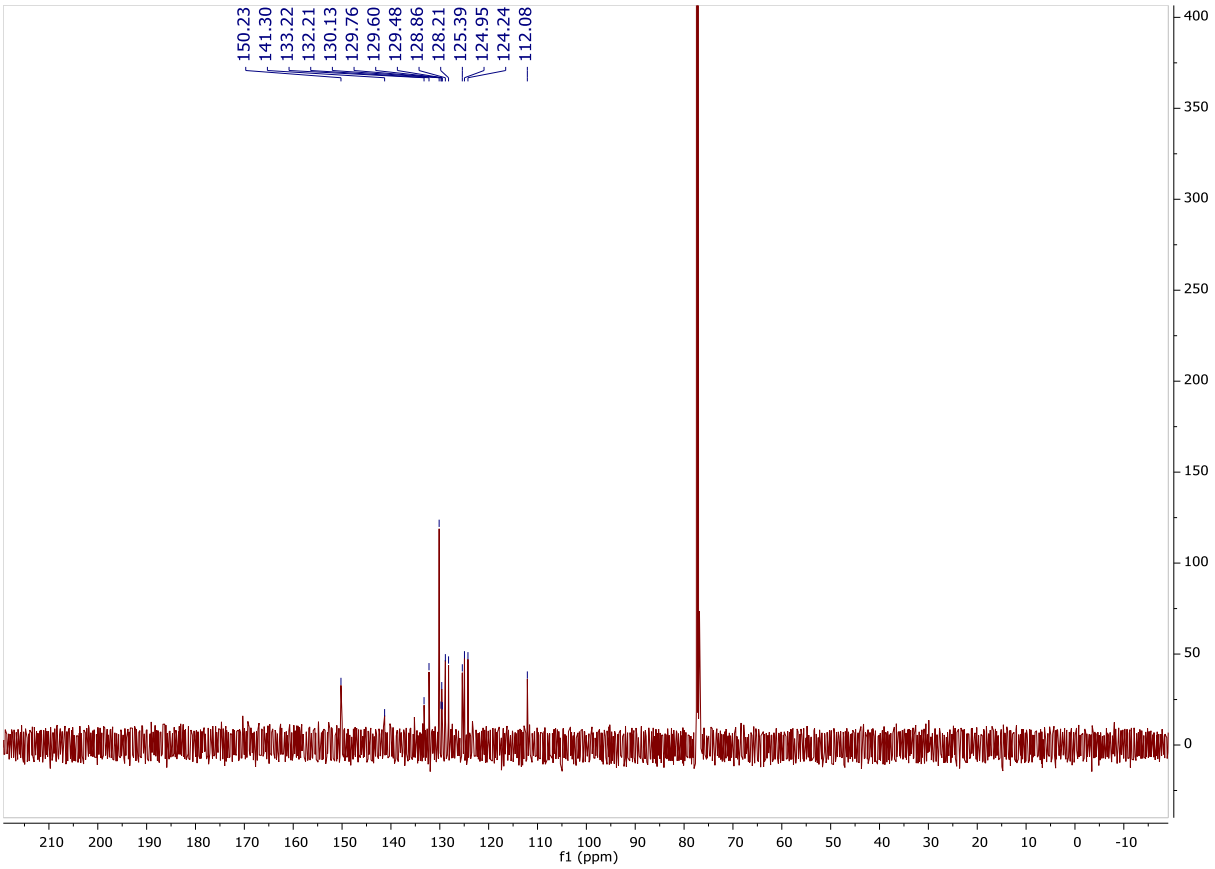
(S)-3,3'-bis(4-(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol



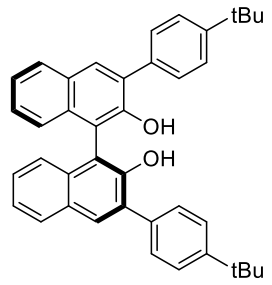
^{1}H NMR (500 MHz, $CDCl_3$):



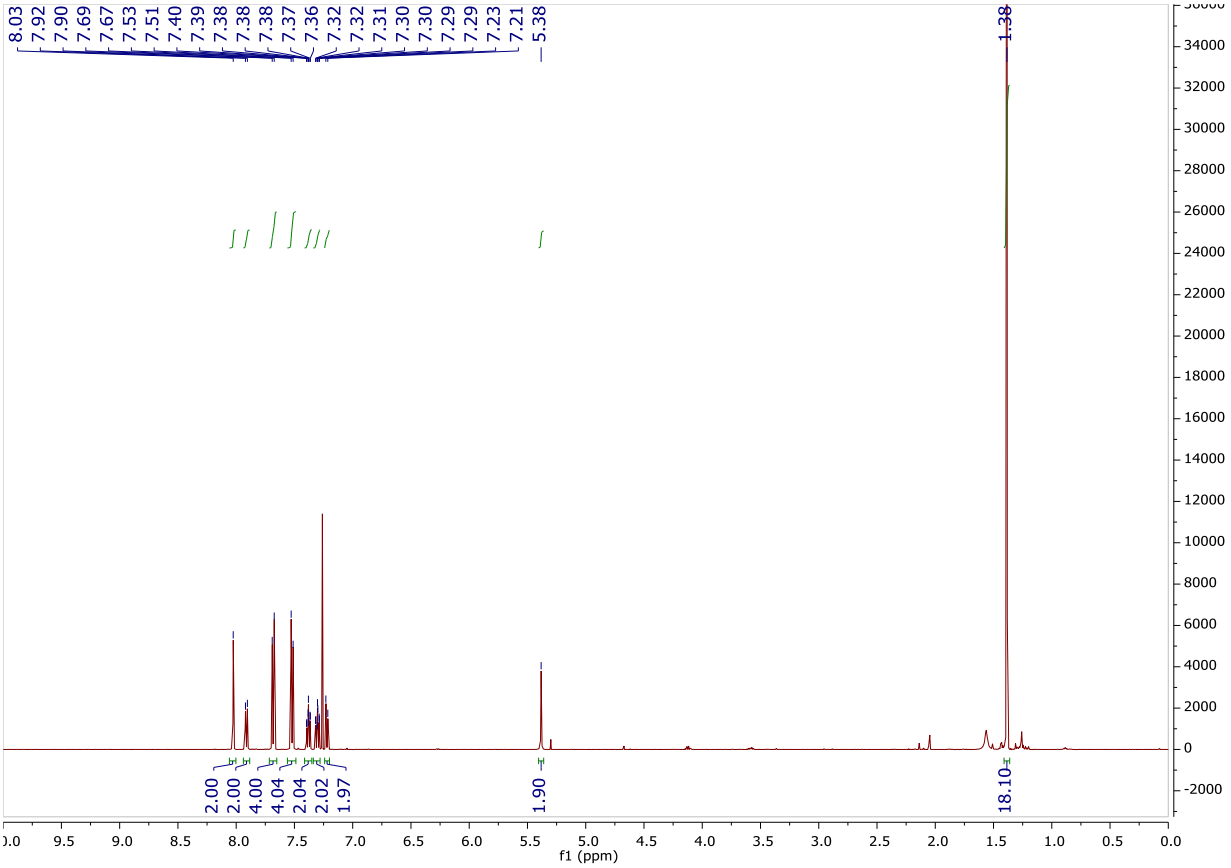
^{13}C NMR (126 MHz, $CDCl_3$):



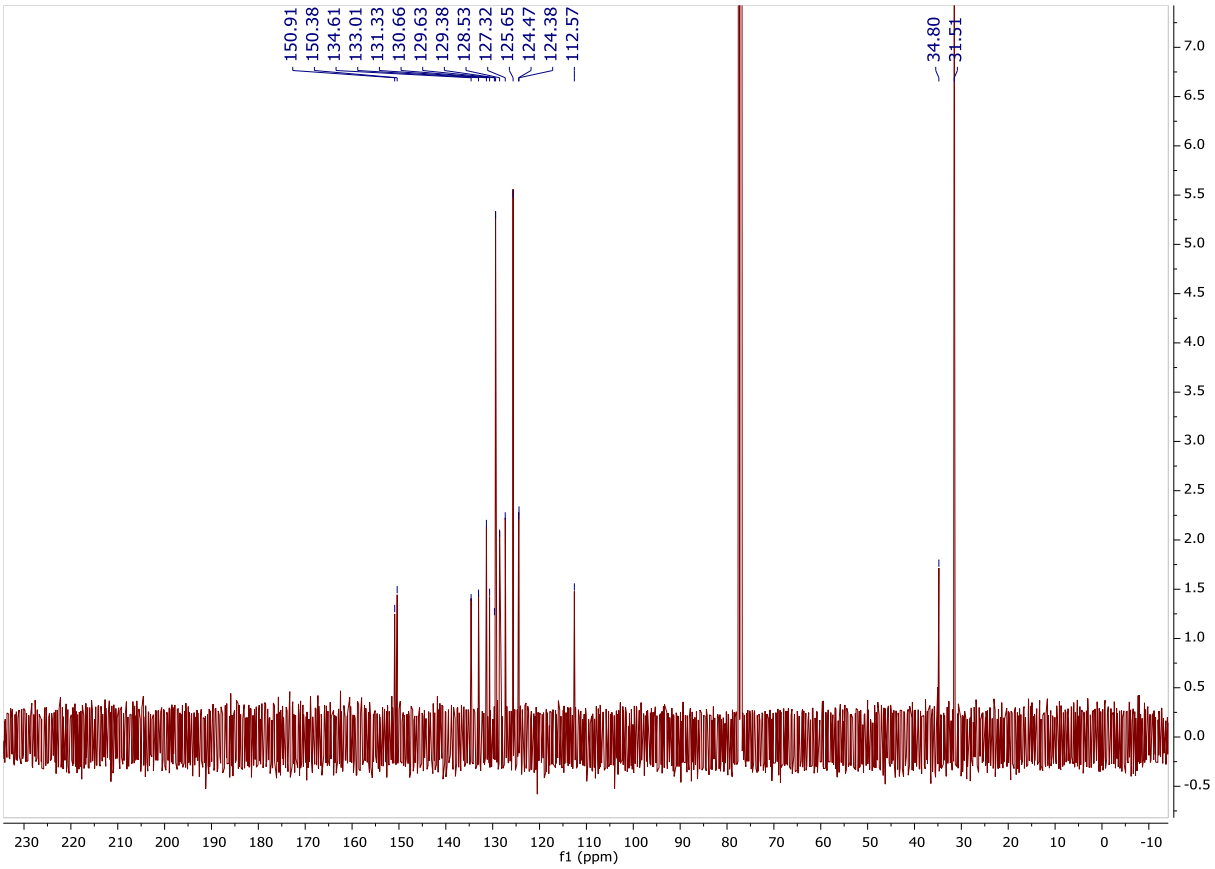
(S)-3,3'-bis(4-(tert-butyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol



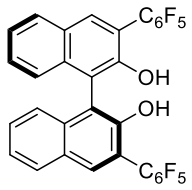
^{1}H NMR (500 MHz, $CDCl_3$):



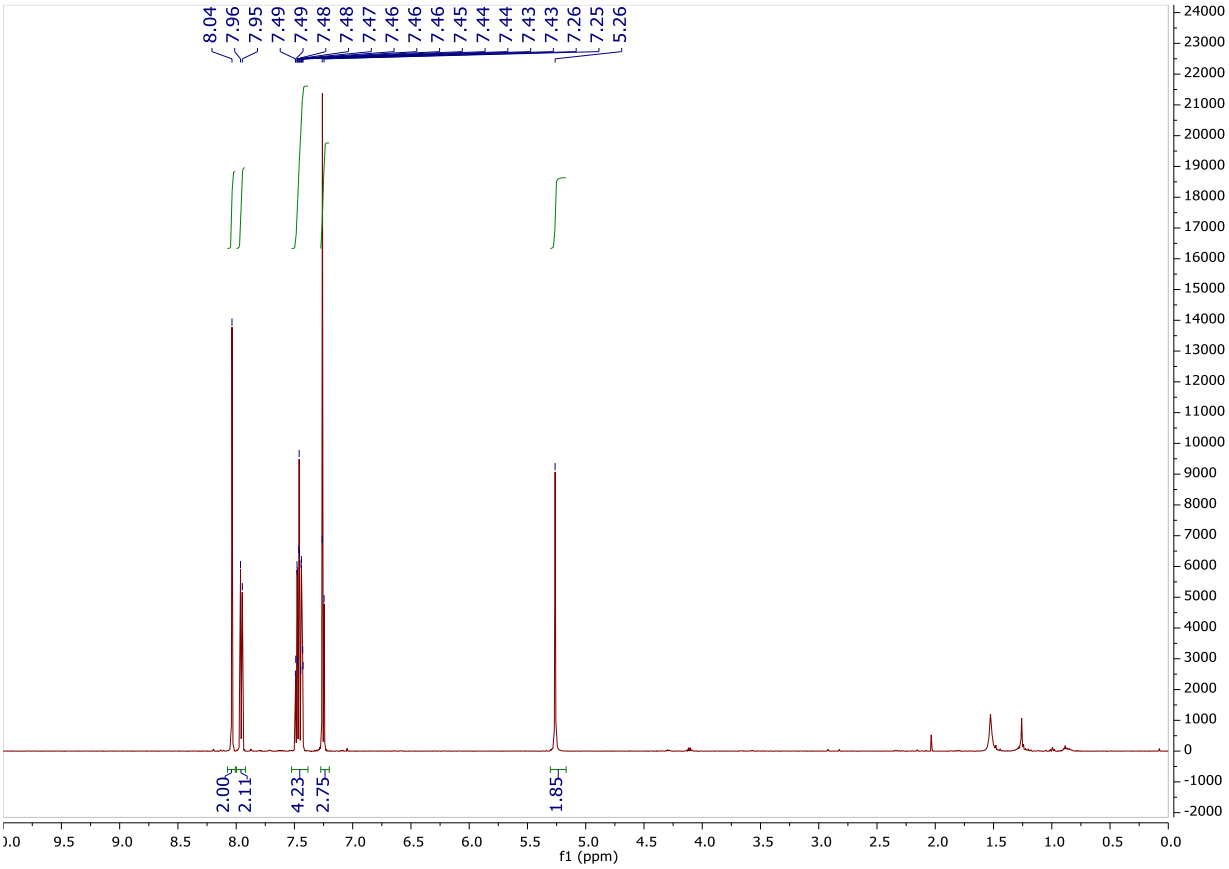
^{13}C NMR (126 MHz, $CDCl_3$):



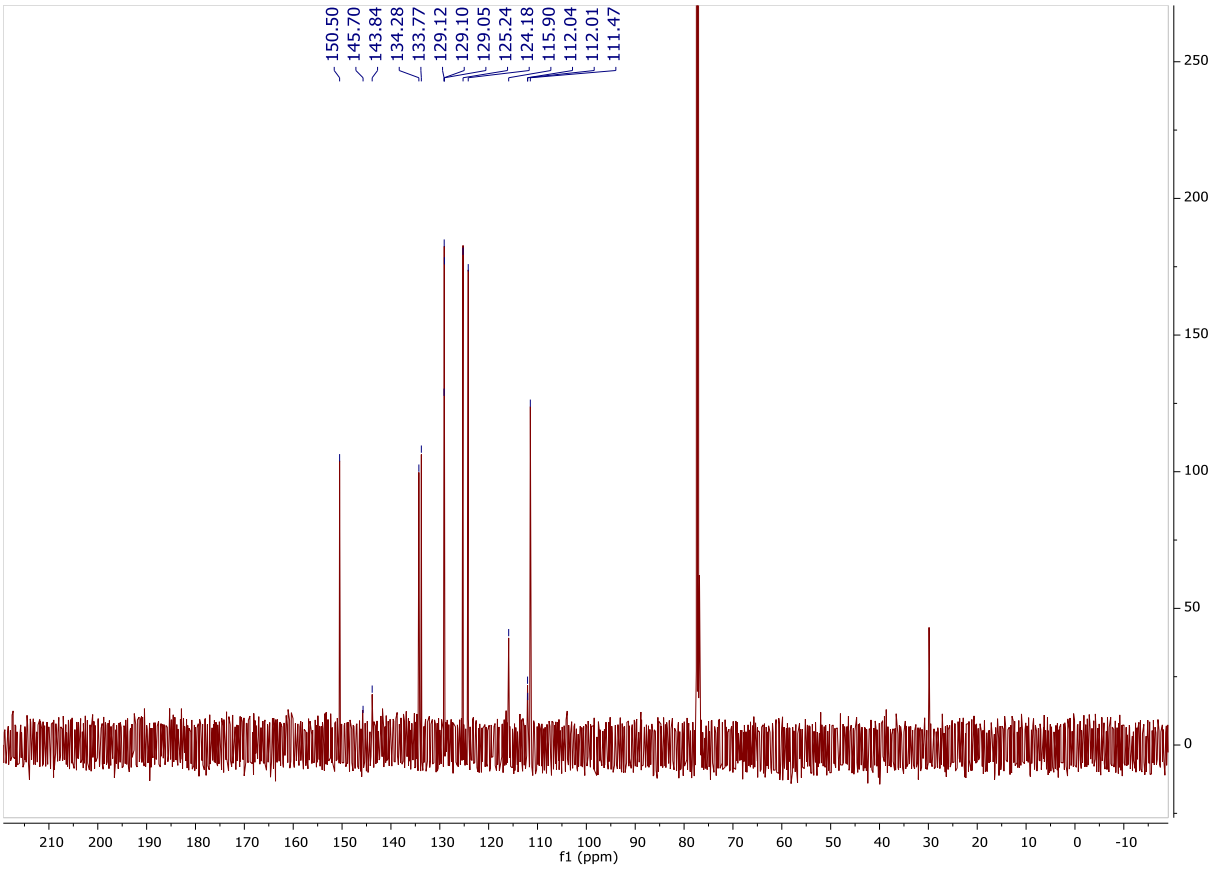
(S)-3,3'-bis(perfluorophenyl)-[1,1'-binaphthalene]-2,2'-diol



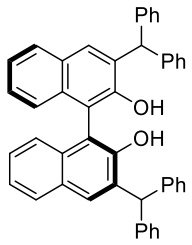
^{1}H NMR (500 MHz, $CDCl_3$):



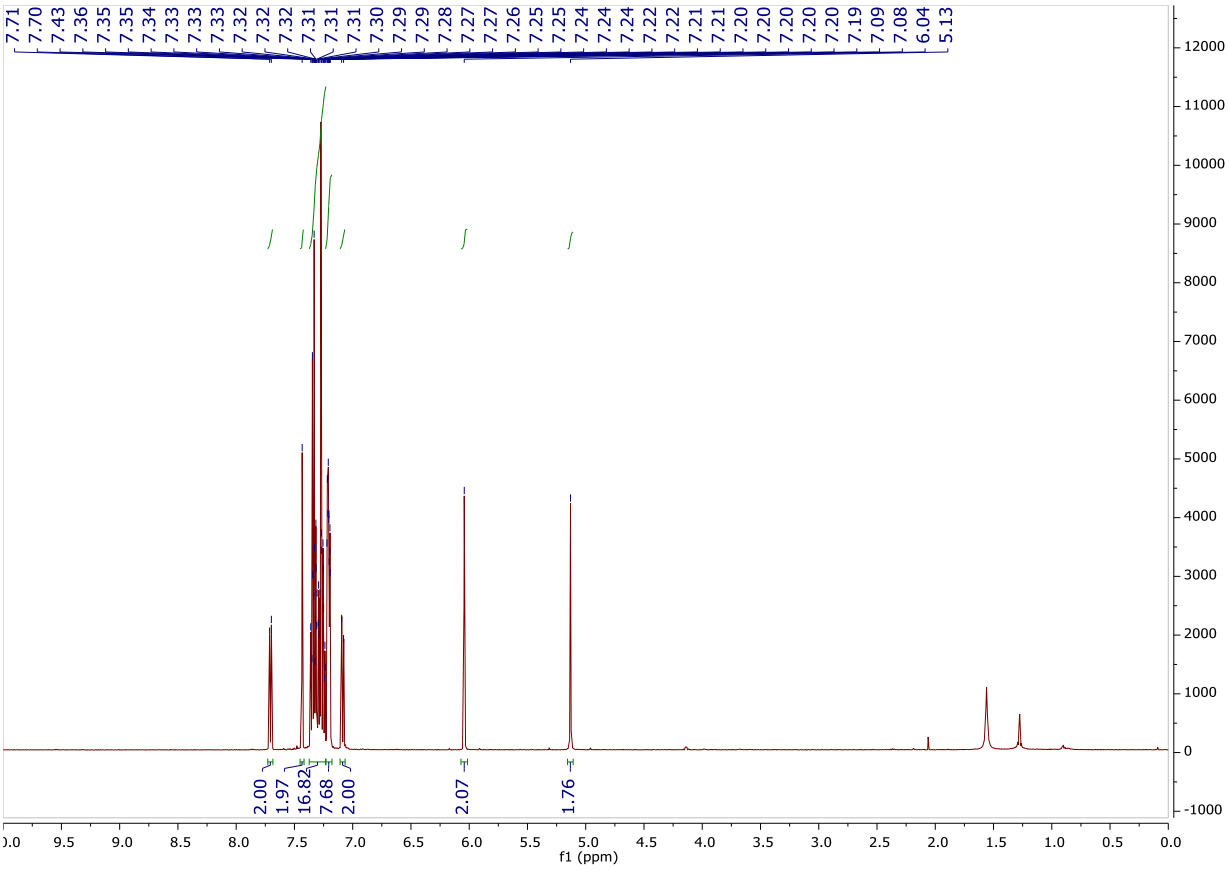
^{13}C NMR (126 MHz, $CDCl_3$):



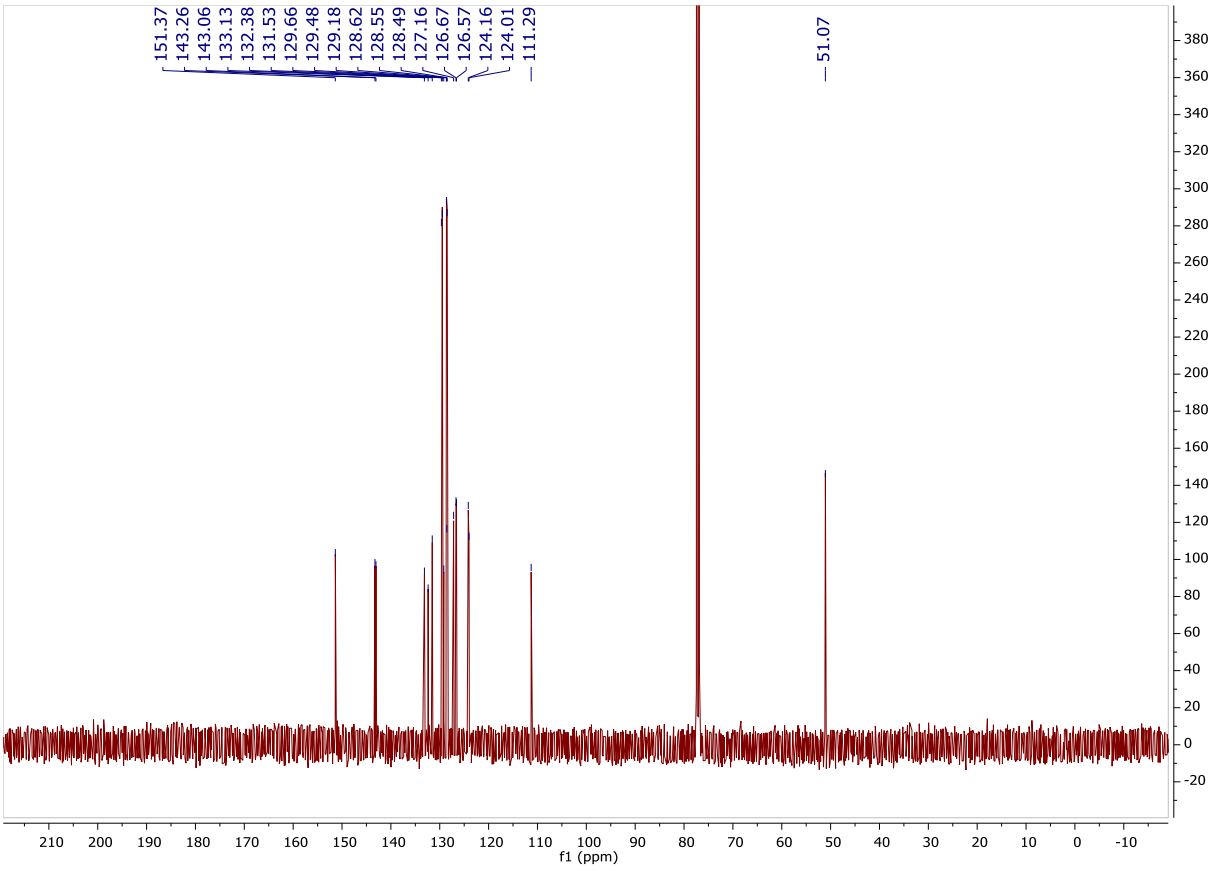
Synthesis of (S)-3,3'-dibenzhydryl-[1,1'-binaphthalene]-2,2'-diol



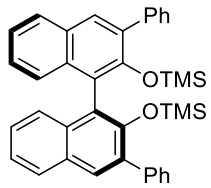
^{1}H NMR (500 MHz, $CDCl_3$):



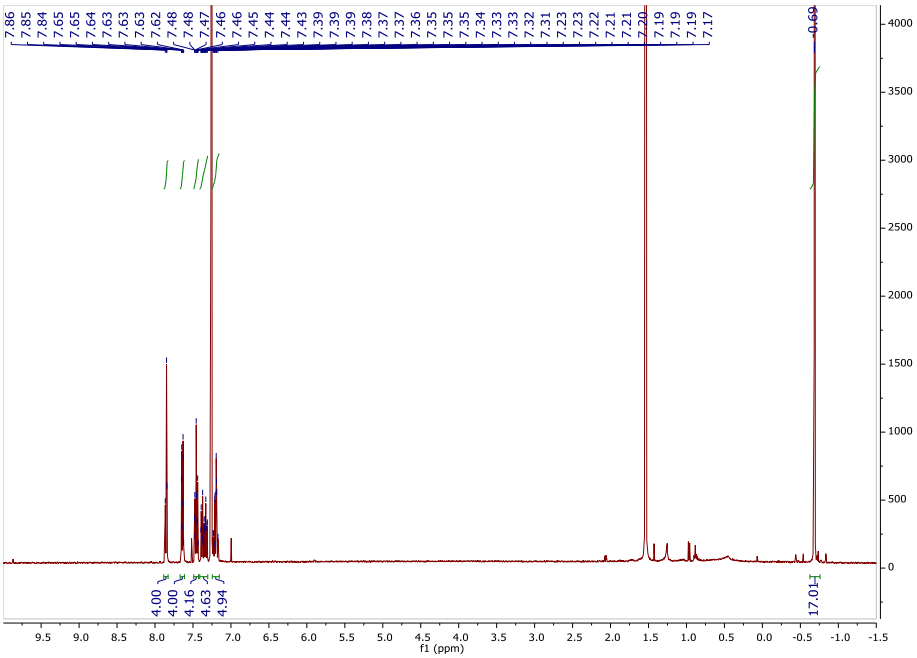
^{13}C NMR (126 MHz, $CDCl_3$):



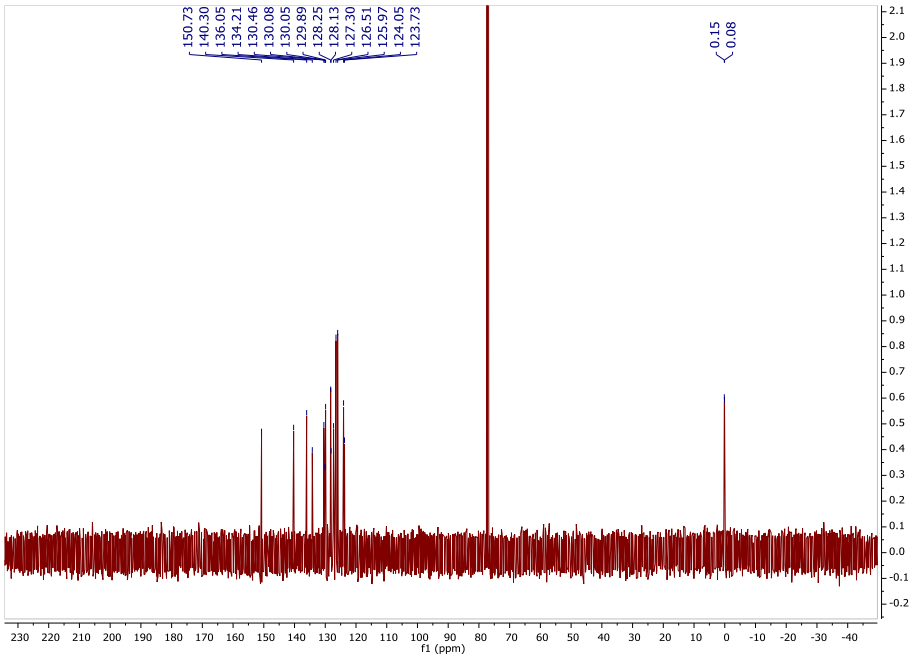
(S)-((3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diyl)bis(oxy))bis(trimethylsilane) (4b')



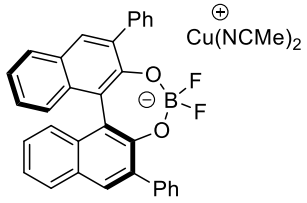
^{1}H NMR (500 MHz, $CDCl_3$):



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

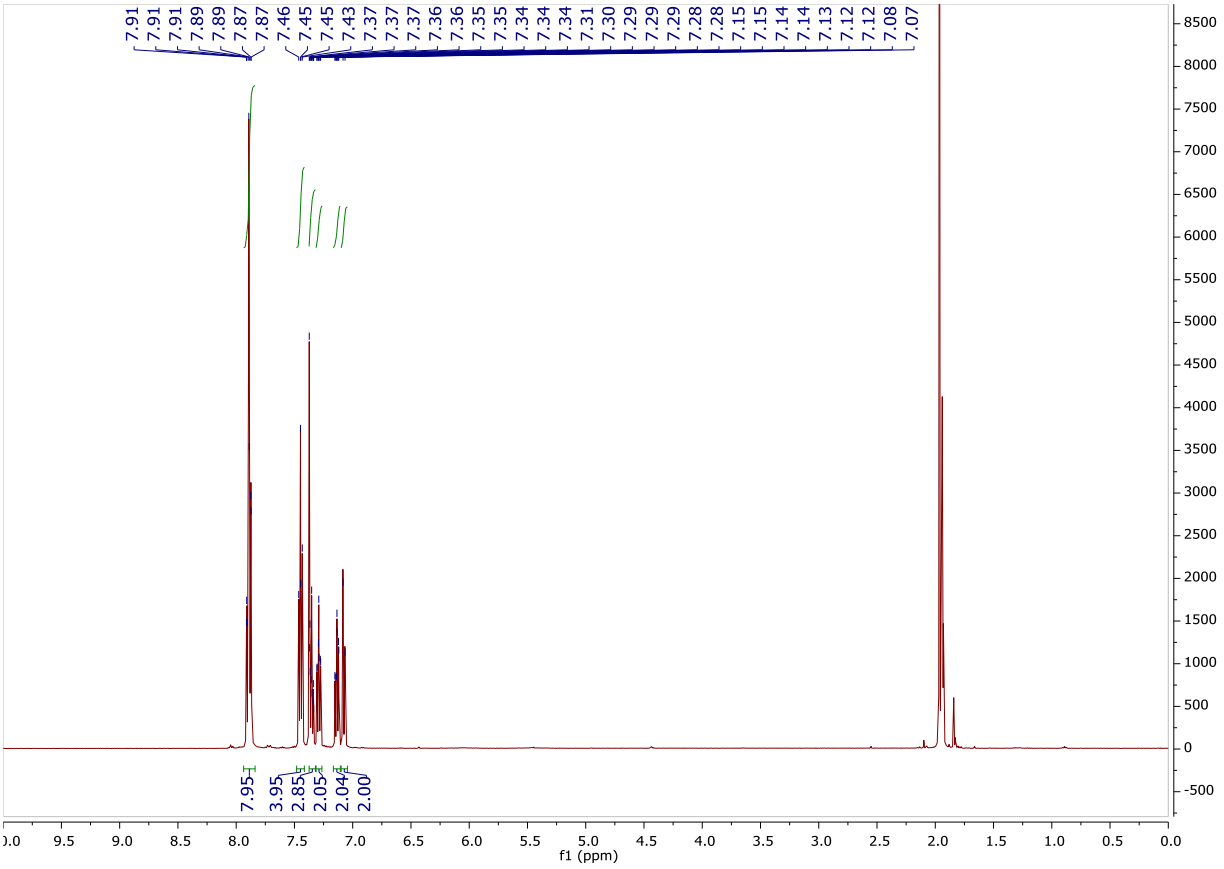


Bis(acetonitrile)copper 4,4-difluoro-2,6-diphenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaborepin-4-uide) (3b)

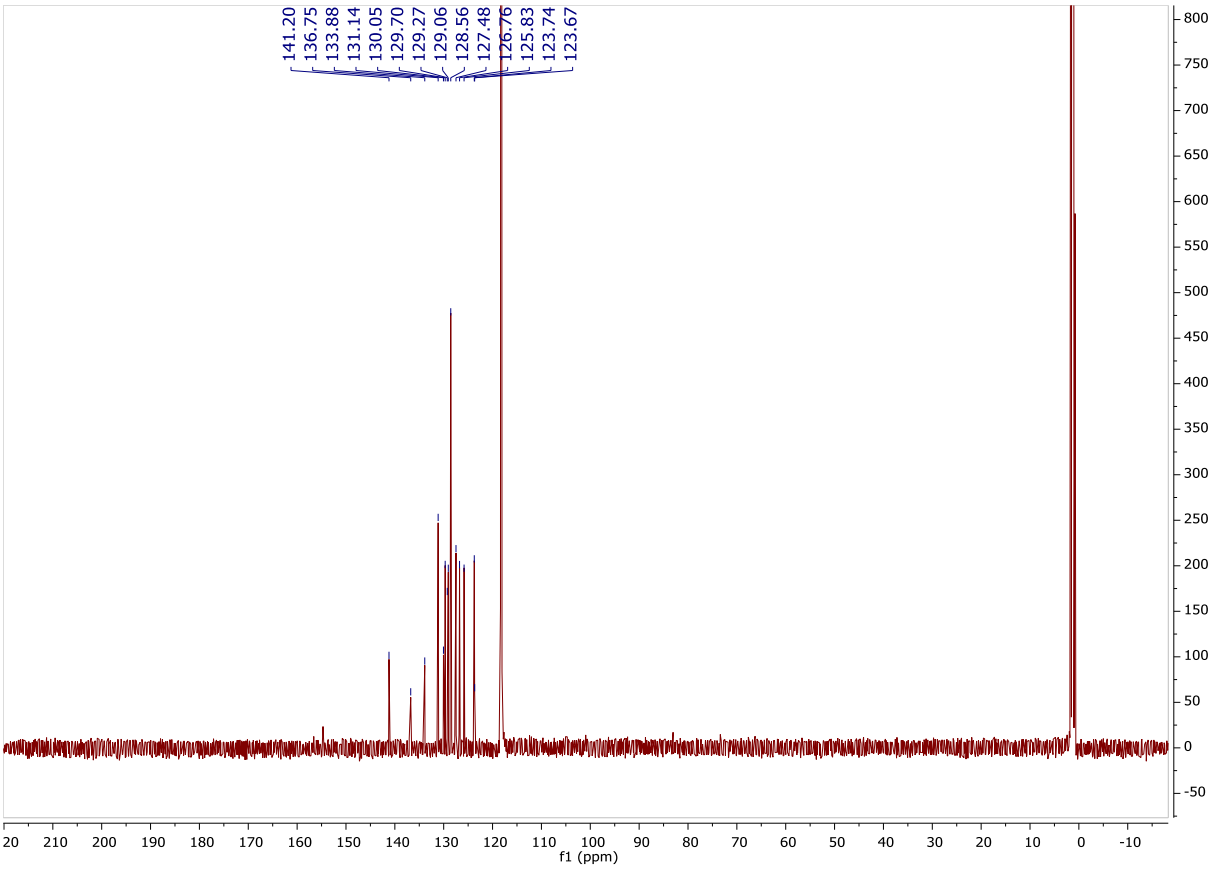


3b

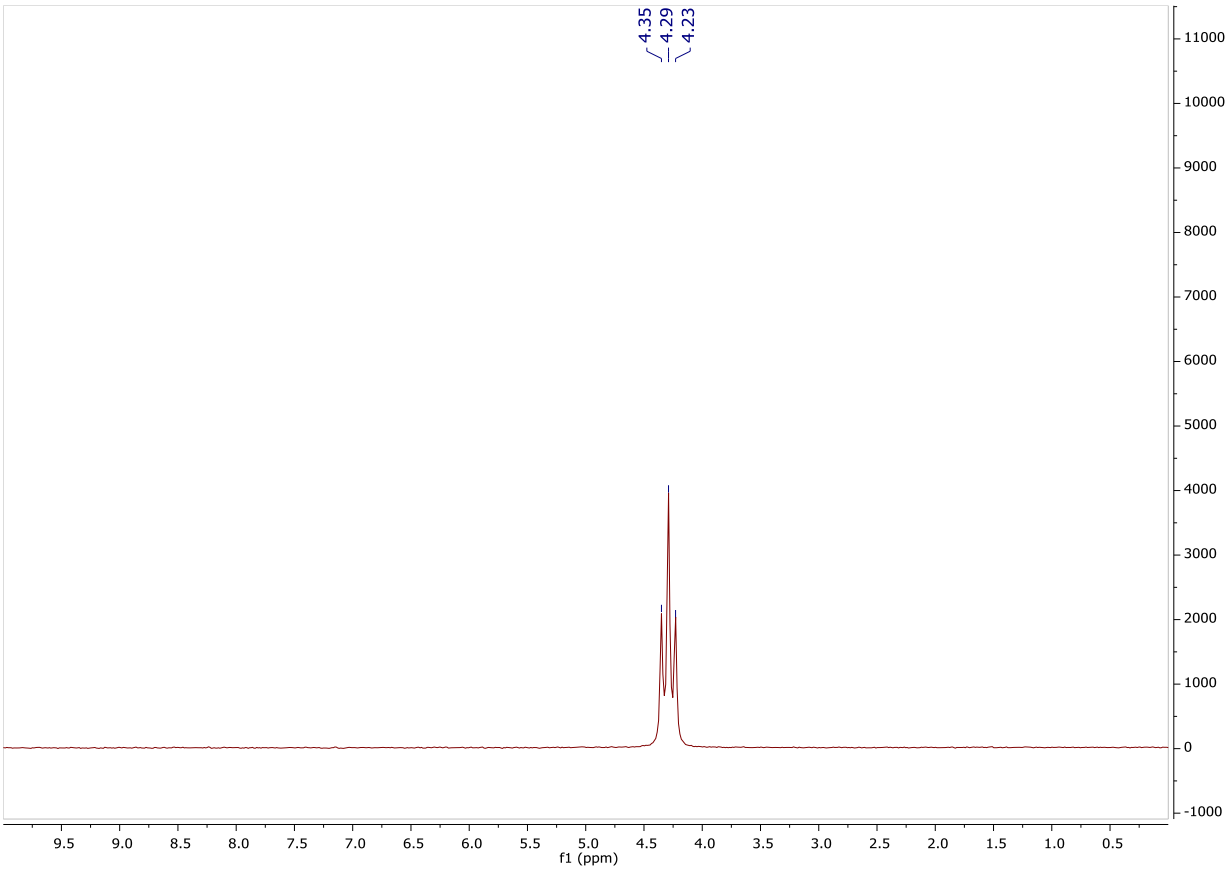
^{1}H NMR (500 MHz, CD_3CN):



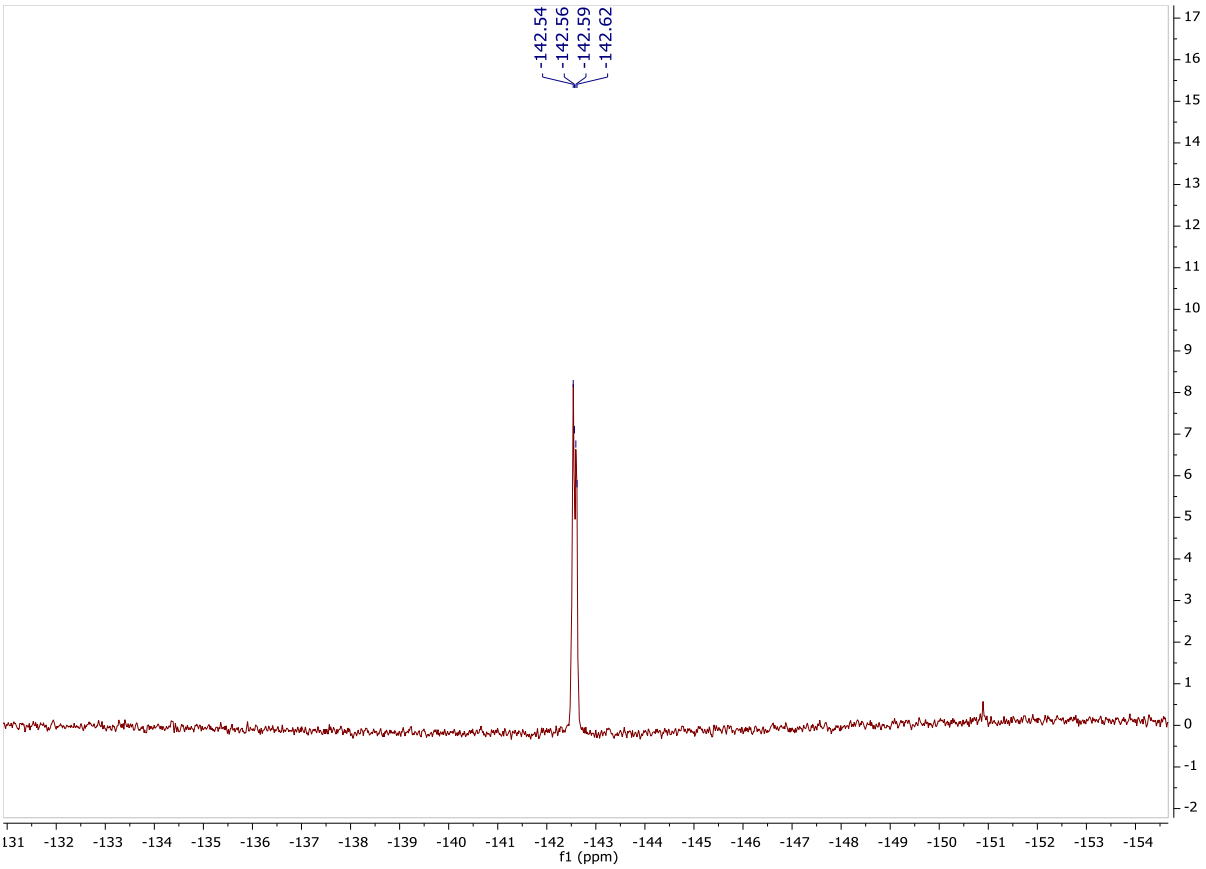
^{13}C NMR (126 MHz, CD_3CN):



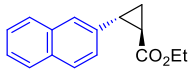
^{11}B NMR (128 MHz, CD_3CN):



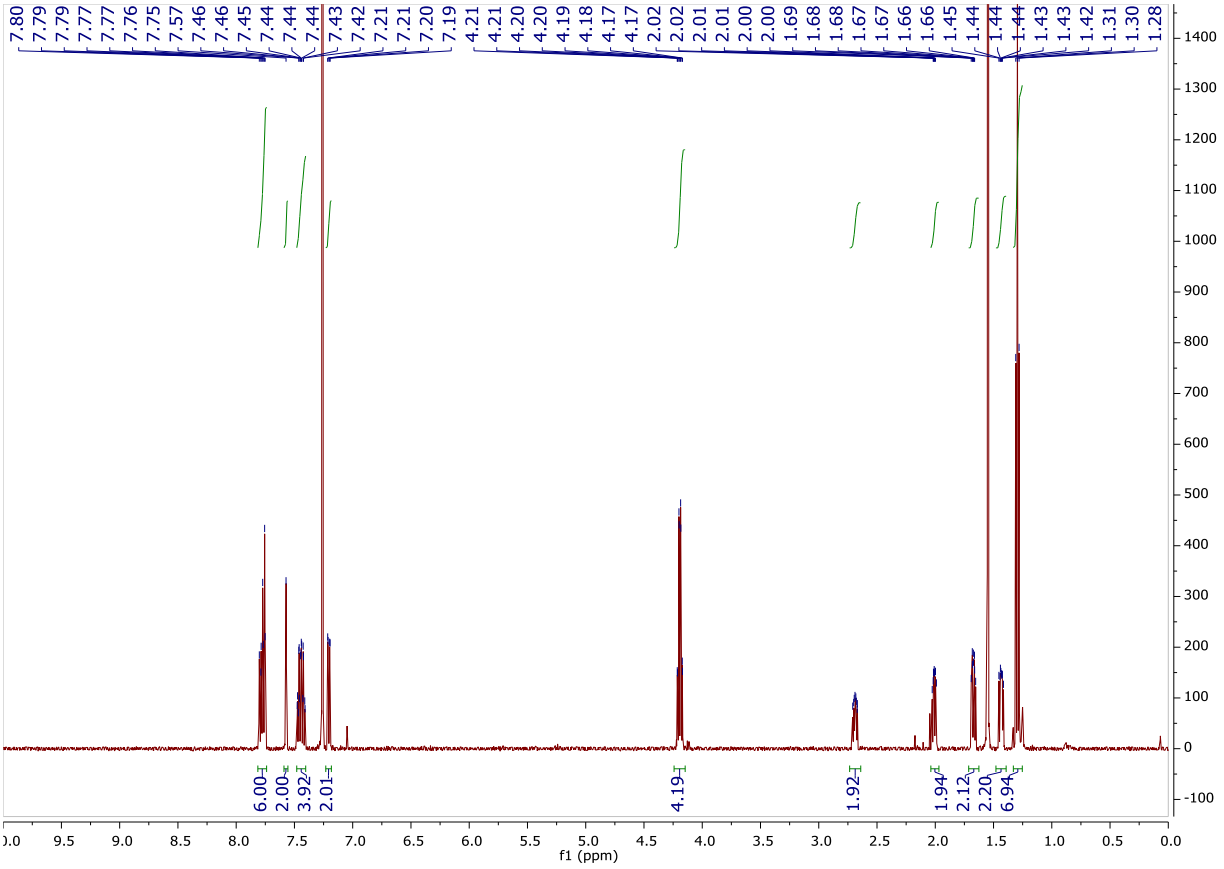
^{19}F NMR (376 MHz, CD_3CN):



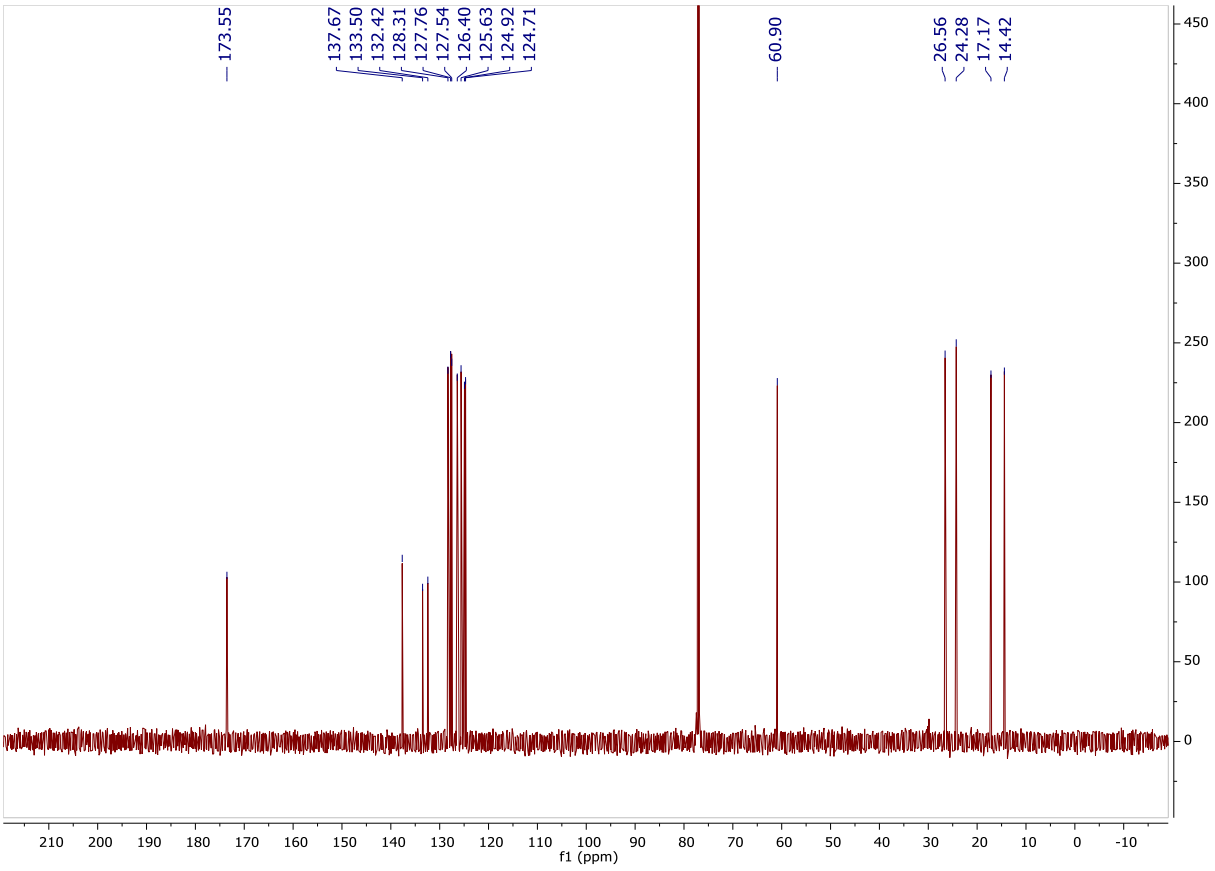
Ethyl (1R,2R)-2-(naphthalen-2-yl)cyclopropane-1-carboxylate (5a).



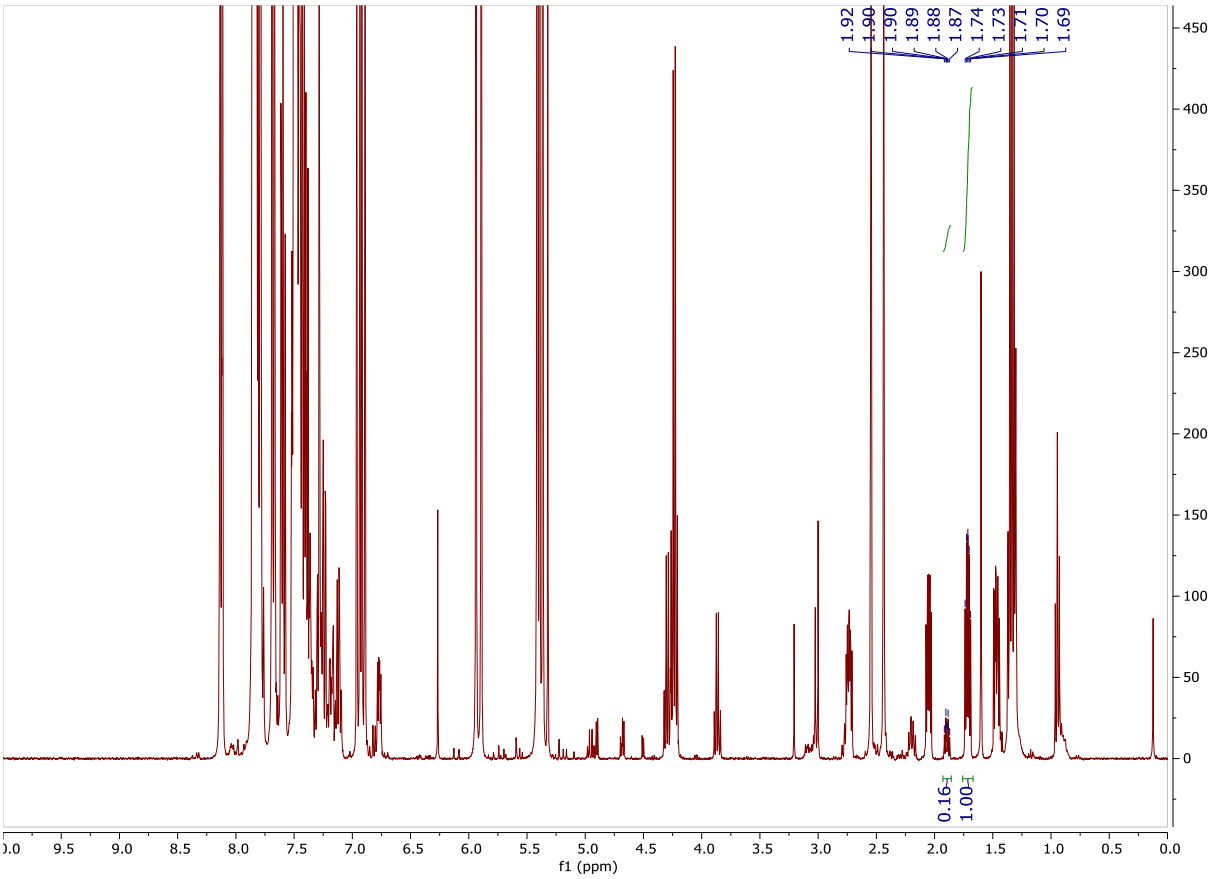
^{1}H NMR (500 MHz, $CDCl_3$):



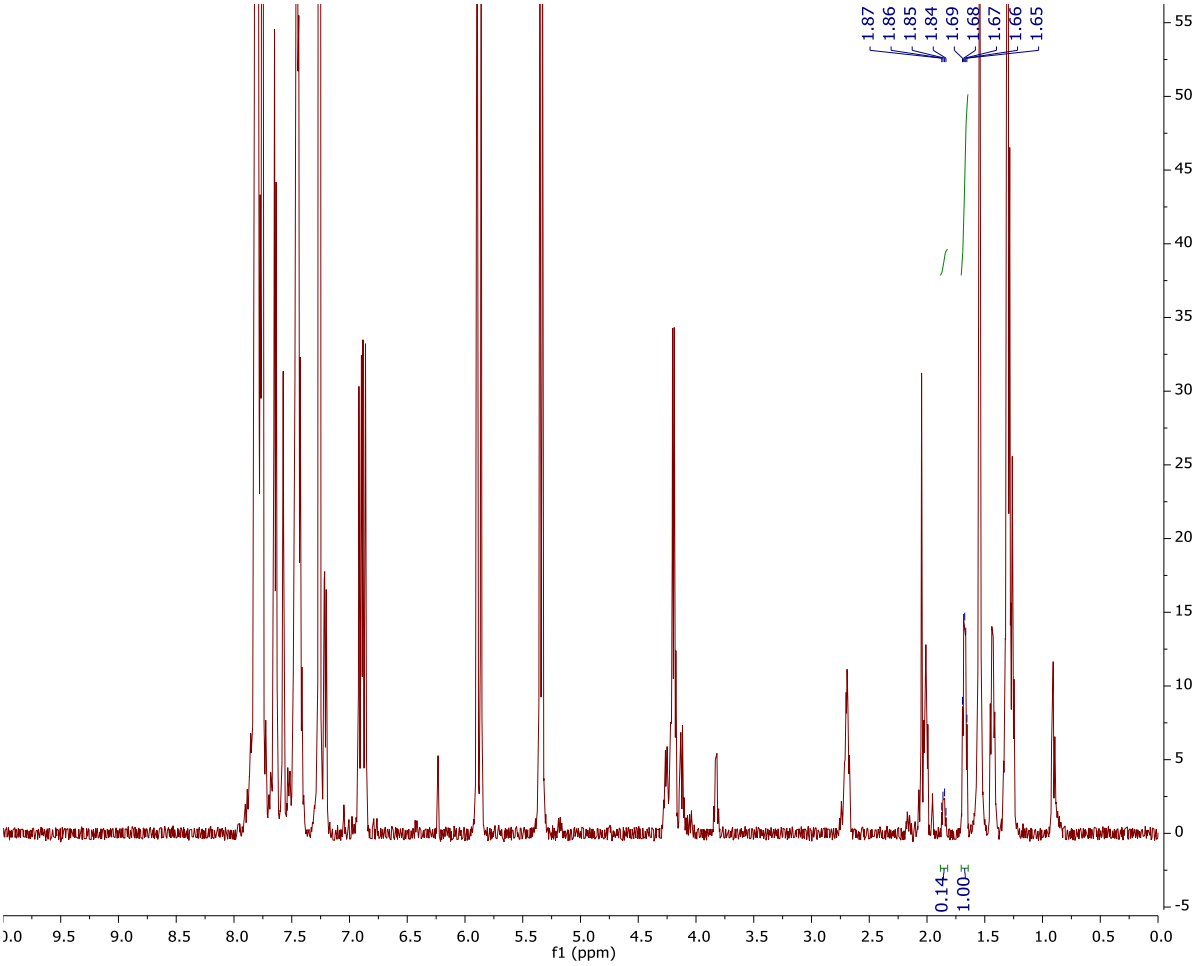
^{13}C NMR (126 MHz, $CDCl_3$):



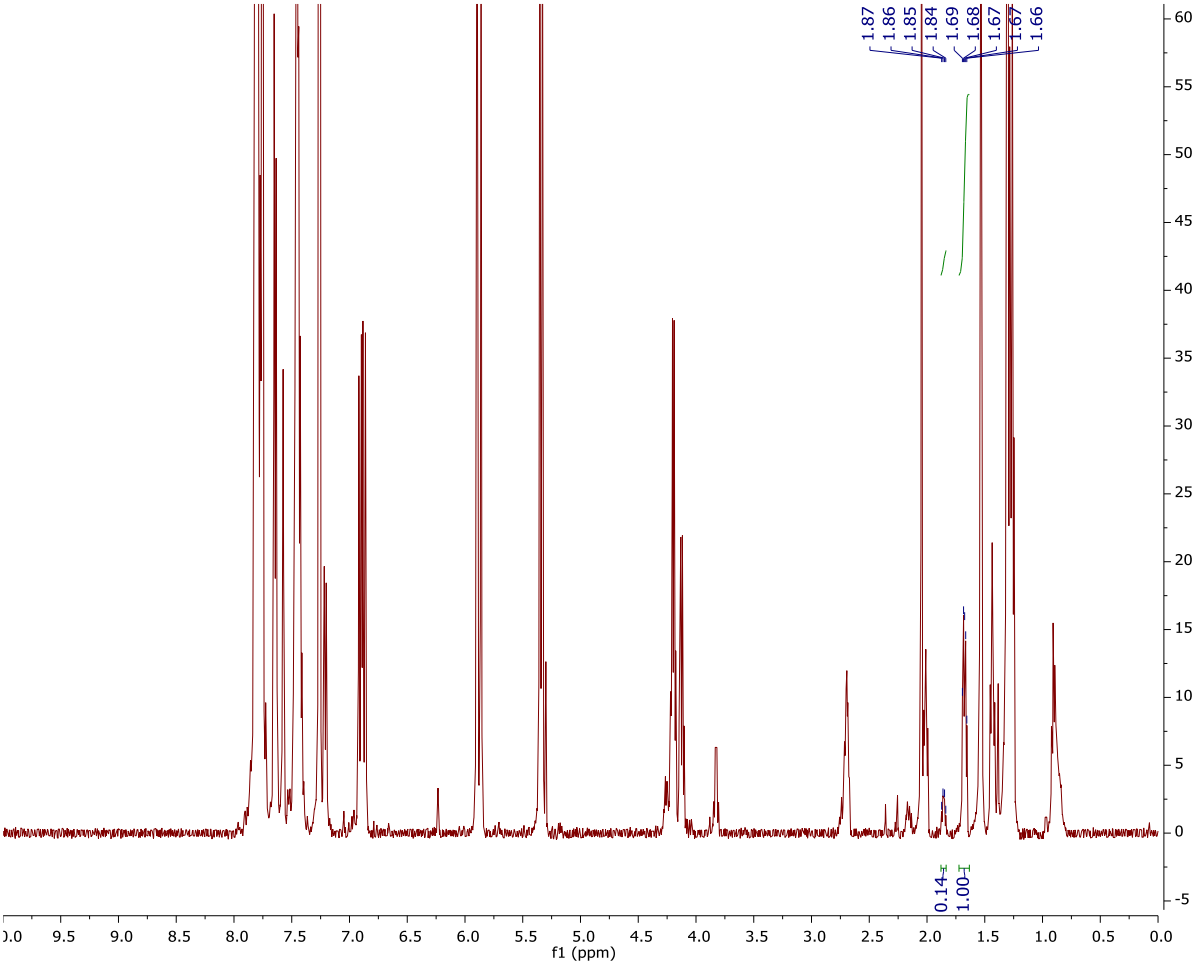
Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Cis (1.89 ppm), Trans (1.71 ppm), Ratio: 86:14.



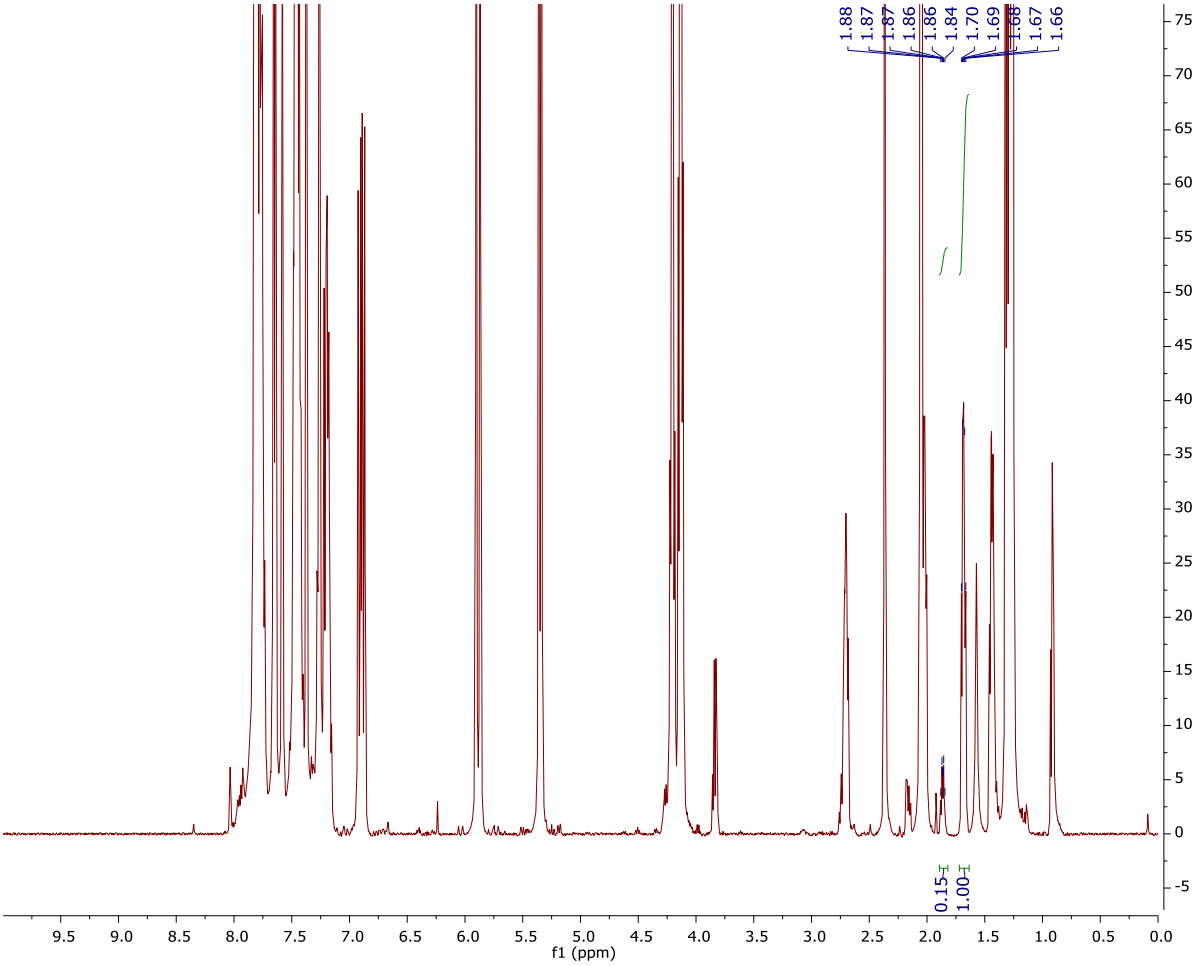
Diastereomeric ratios NMR for reaction in Toluene ($CDCl_3$, 500 MHz): Cis (1.86 ppm), Trans (1.67 ppm), Ratio: 88:12.



Diastereomeric ratios NMR for Schlenk line reaction ($CDCl_3$, 500 MHz): Cis (1.86 ppm), Trans (1.67 ppm), Ratio: 88:12.

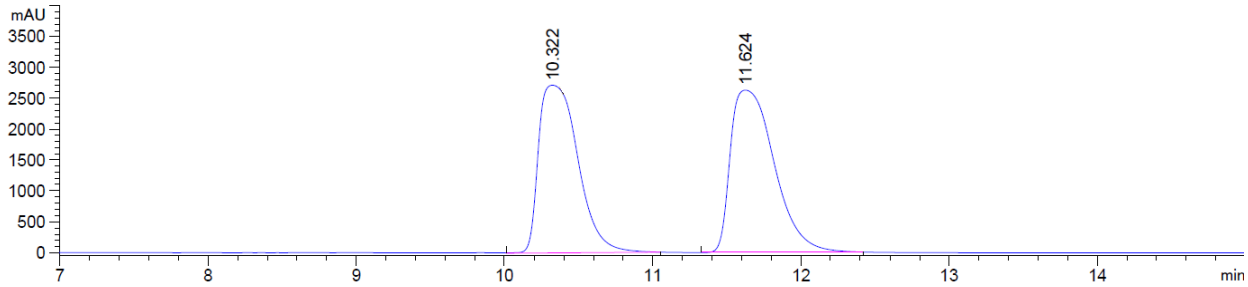


Diastereomeric ratios NMR for 1 gram scale reaction ($CDCl_3$, 500 MHz): Cis (1.86 ppm), Trans (1.67 ppm), Ratio: 87:13.



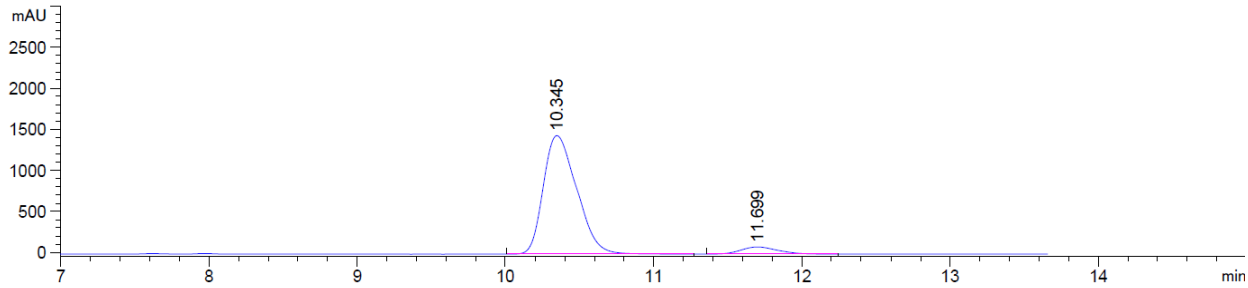
HPLC conditions: IC column, 1mL/min, 0.7% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



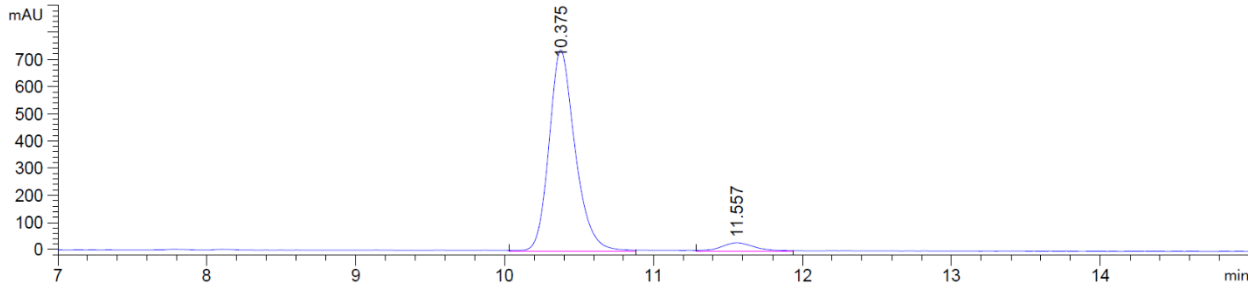
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	10.3	50279.4	48.2
2	11.6	53936.0	51.8

HPLC (Chiral)



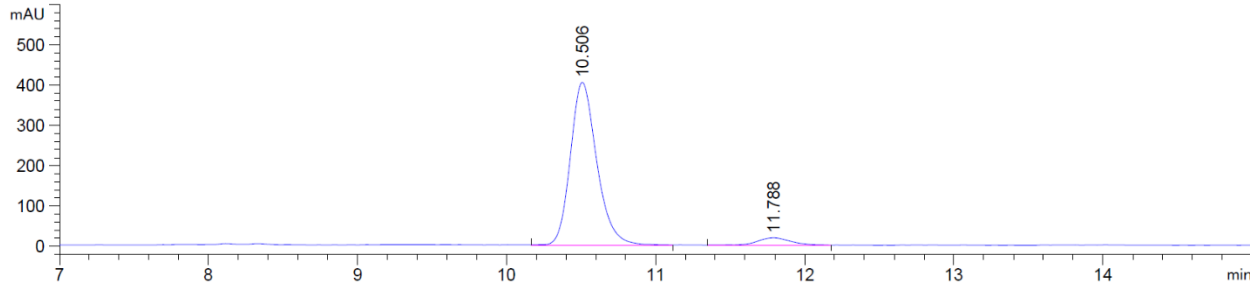
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	10.4	22633.6	93.7
2	11.7	1532.16	6.3

HPLC (Chiral) for reaction in Toluene



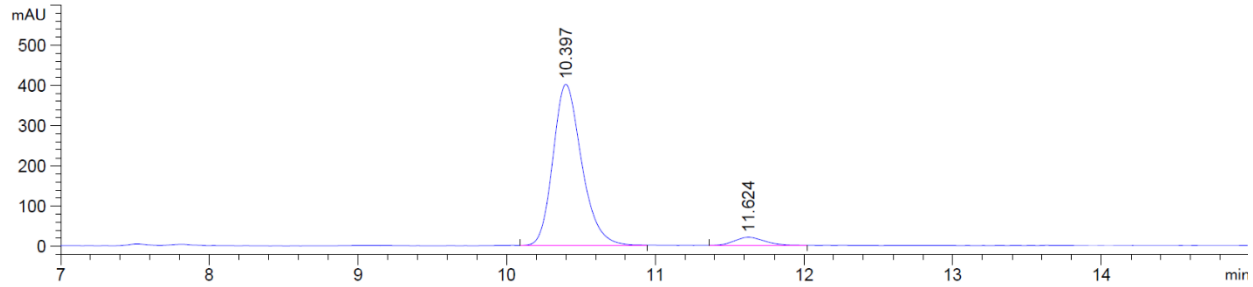
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	10.4	9014.30	94.9
2	11.6	488.901	5.1

HPLC (Chiral) for Schlenk line reaction



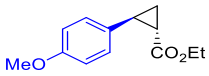
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	10.5	5002.70	94.3
2	11.8	301.076	5.7

HPLC (Chiral) for 1 gram scale reaction

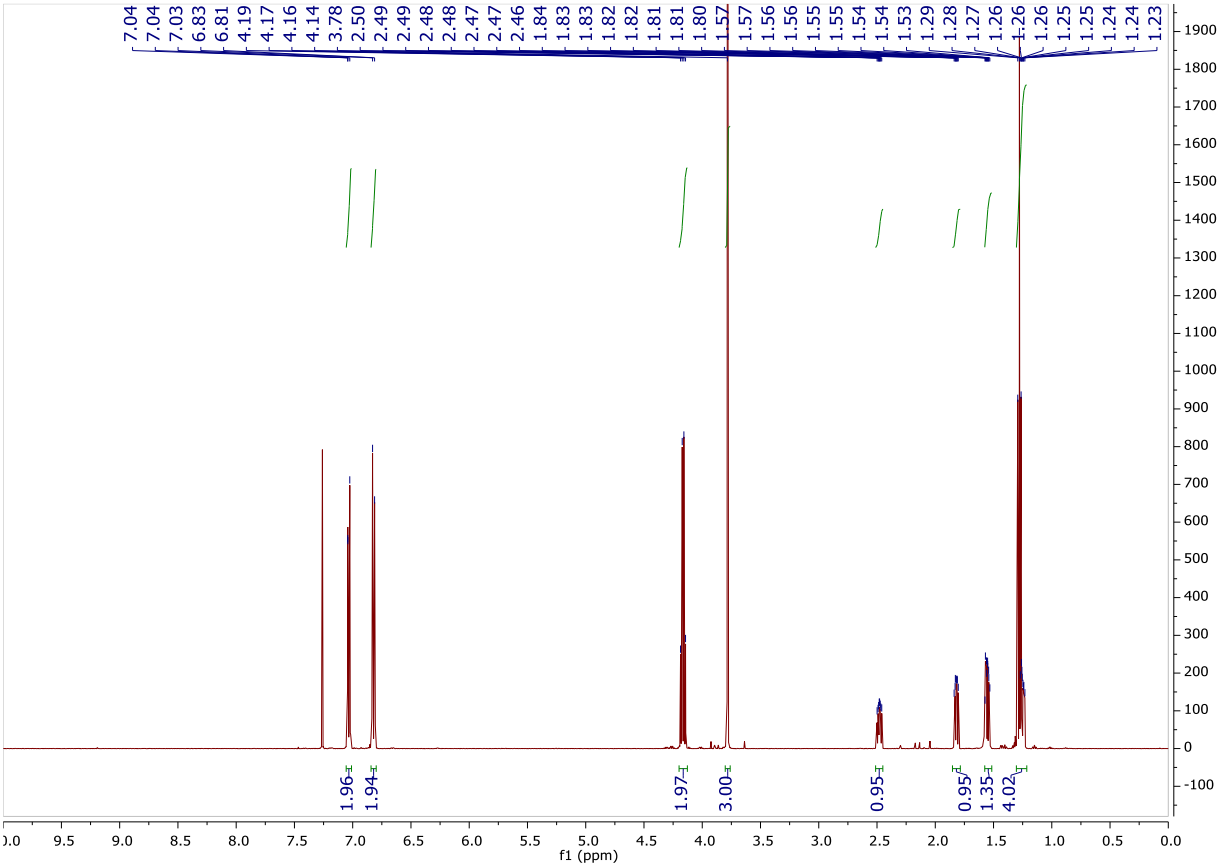


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	10.4	5423.30	94.4
2	11.6	322.554	5.6

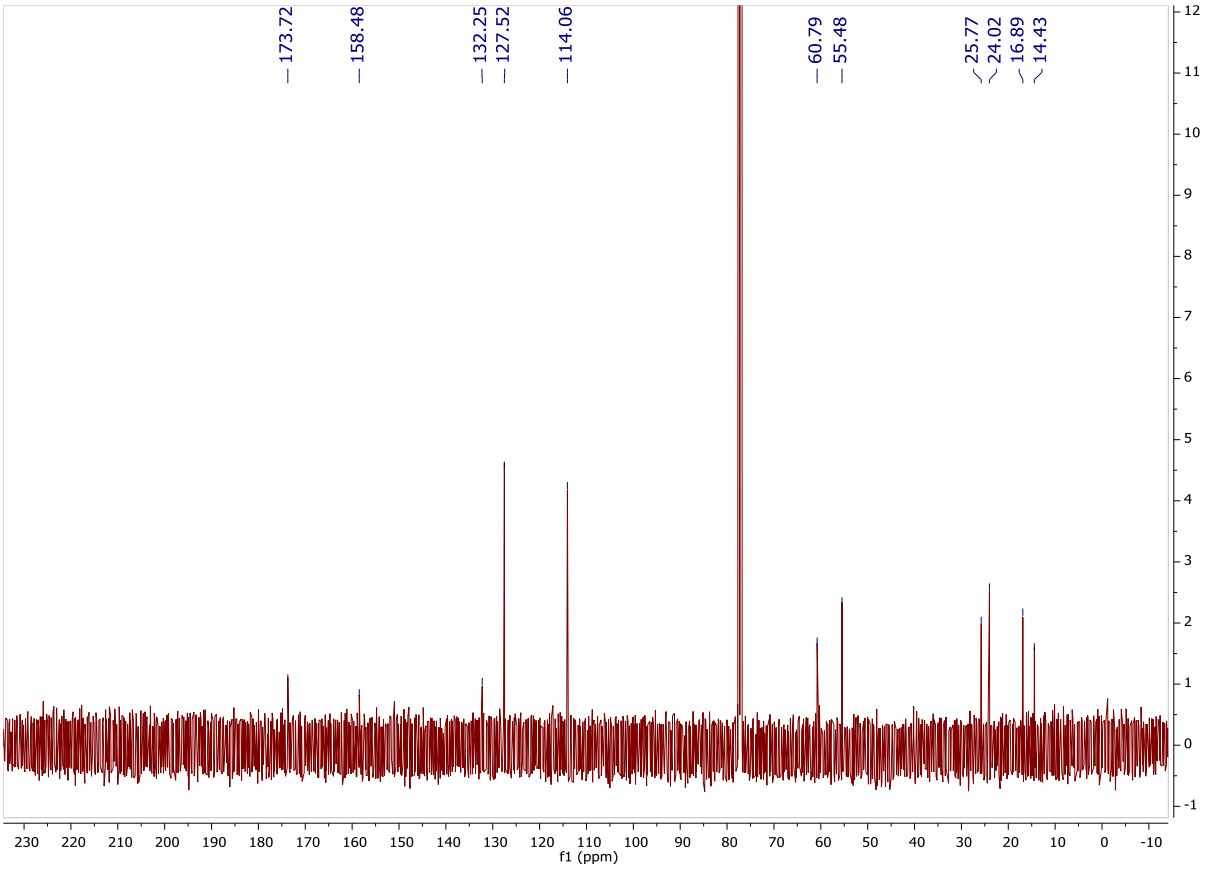
Ethyl (1S,2S)-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (5b).



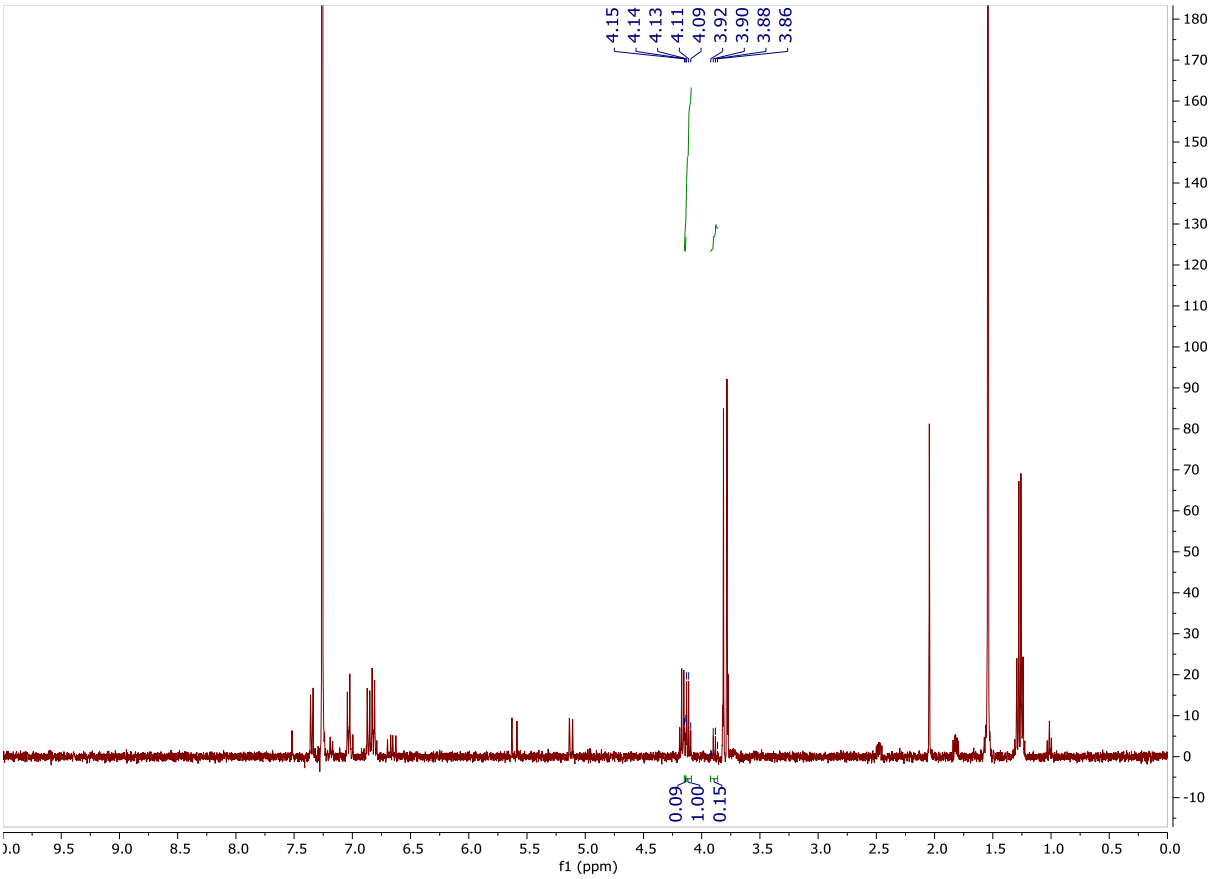
^{1}H NMR (500 MHz, $CDCl_3$):



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

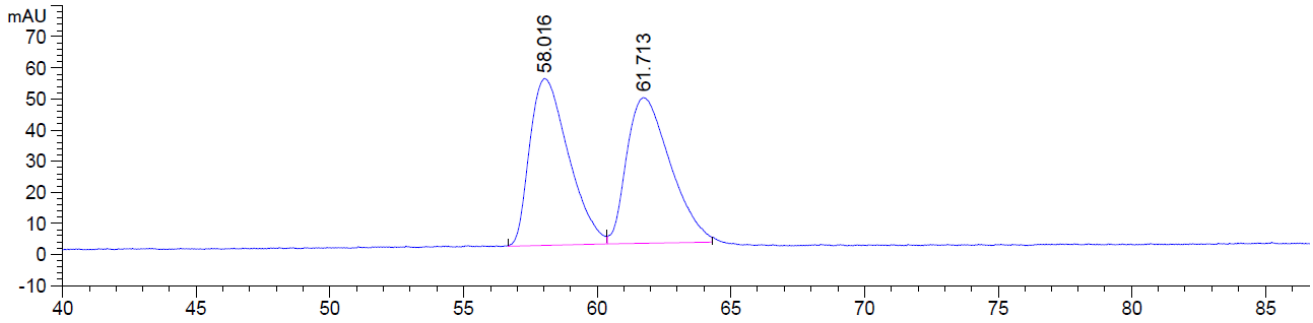


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Trans (4.13 ppm), Cis (3.89 ppm), Ratio: 86:14.



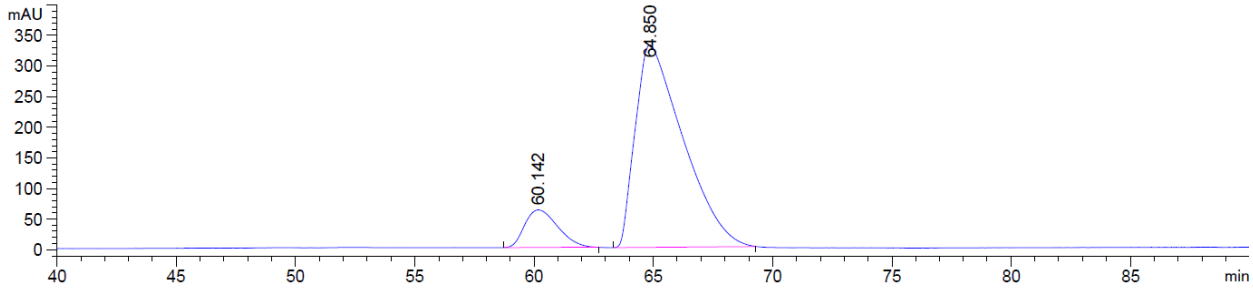
HPLC conditions: OJ-H column, 1mL/min, 0.3% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



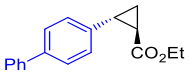
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	58.0	5425.61	50.4
2	61.7	5344.12	49.6

HPLC (Chiral)

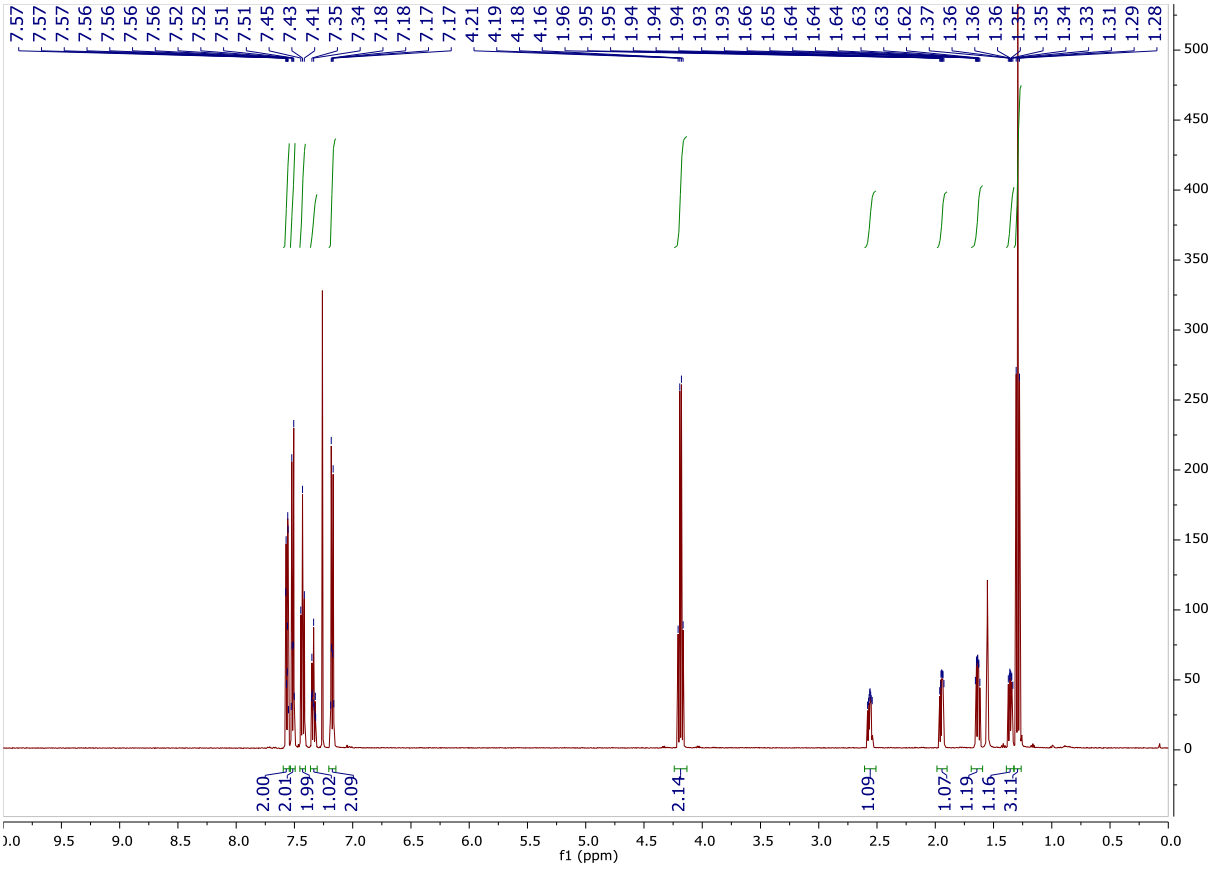


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	60.1	5970.71	11.5
2	64.9	46105.2	88.5

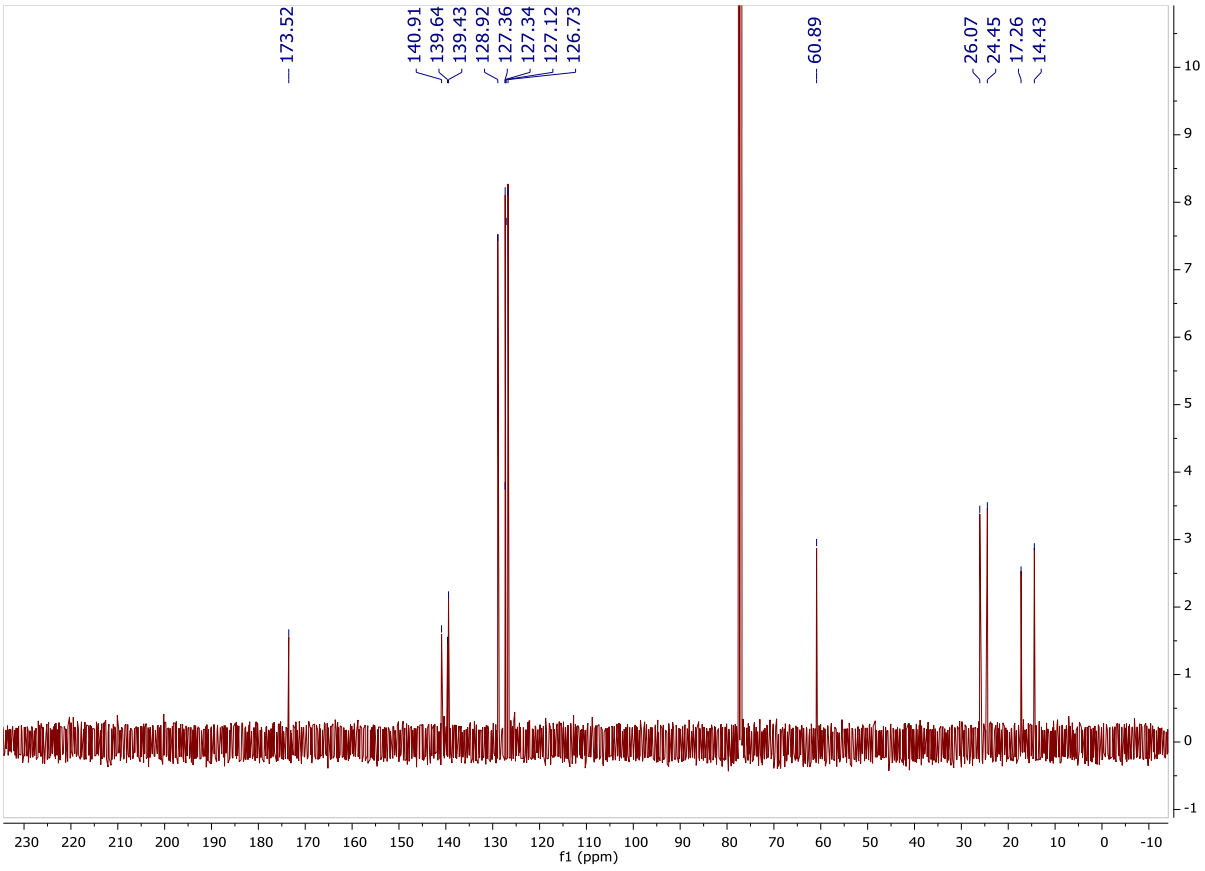
Ethyl (1R,2R)-2-([1,1'-biphenyl]-4-yl)cyclopropane-1-carboxylate (5c).



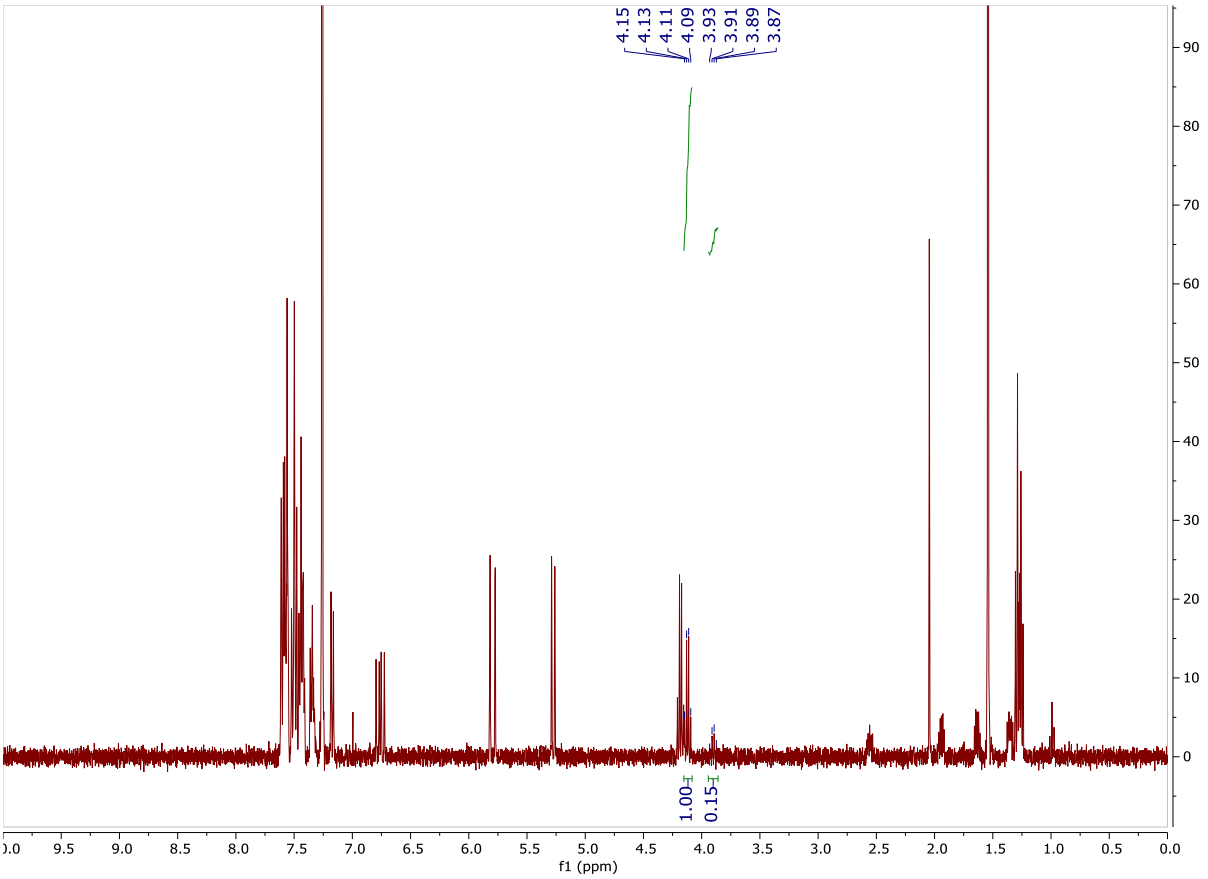
^{1}H NMR (500 MHz, $CDCl_3$):



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

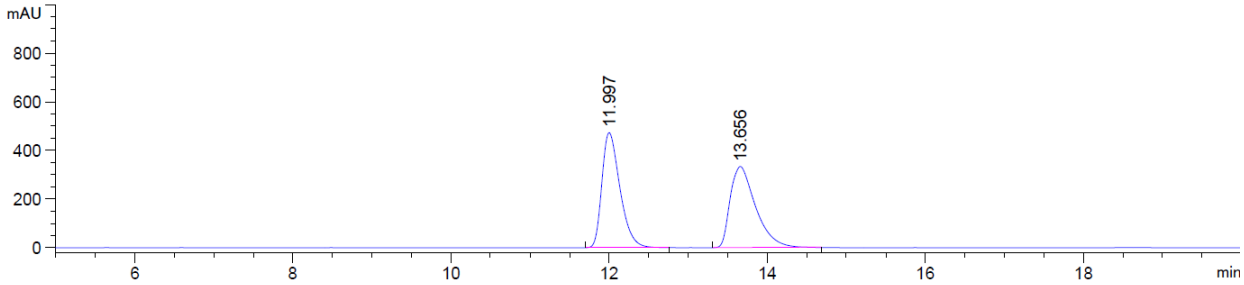


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Trans (4.12 ppm), Cis (3.90 ppm), Ratio: 87:13.



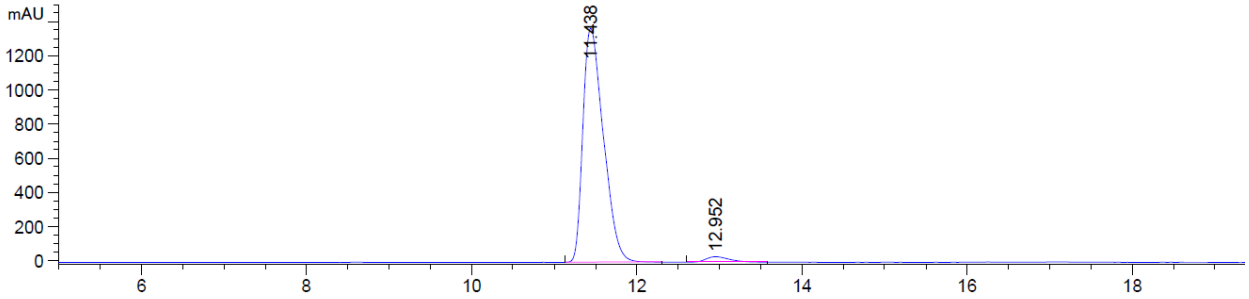
HPLC conditions: IC column, 1mL/min, 0.7% iPrOH/Hexanes, 254 nm UV detector.

HPLC (Racemic)



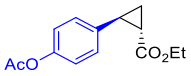
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	12.0	7498.08	50.1
2	13.7	7456.15	49.9

HPLC (Chiral)

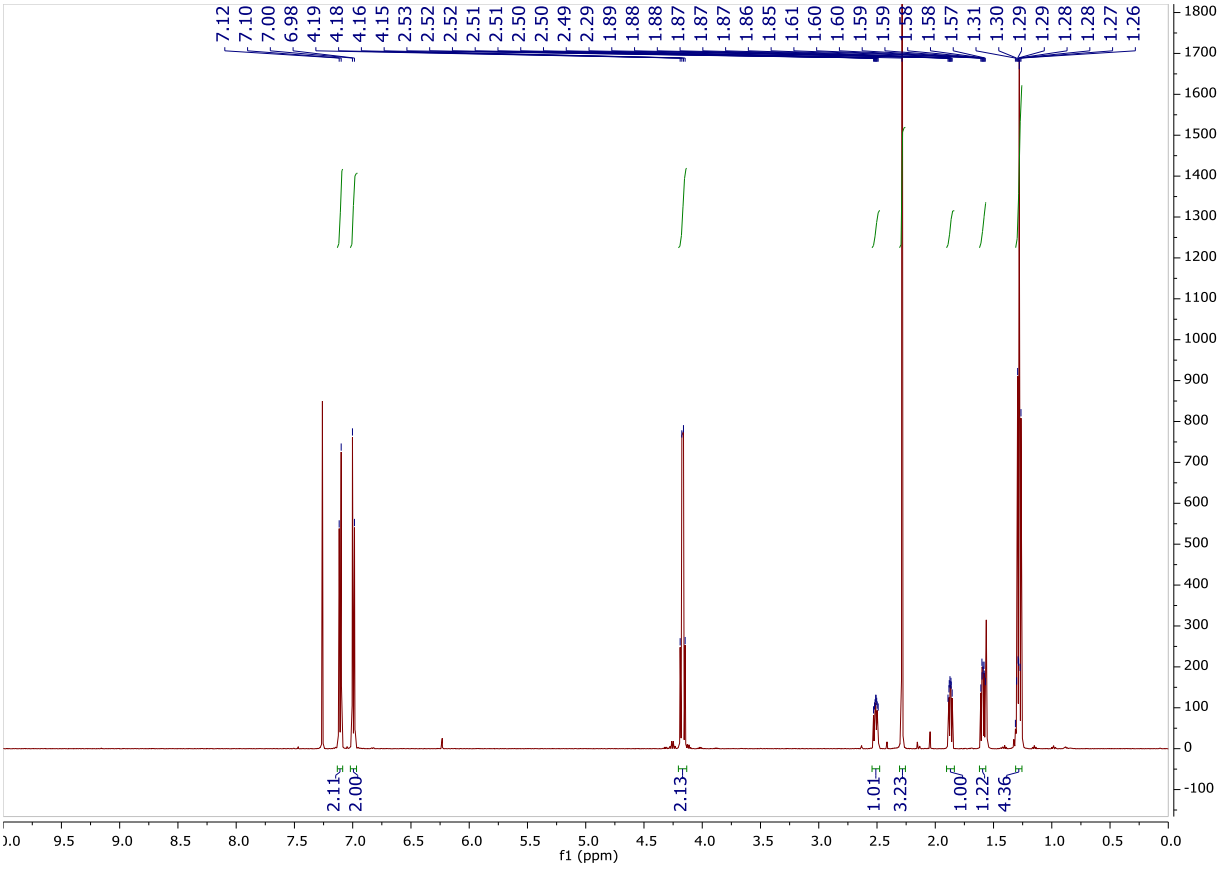


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	11.4	23623.7	97.3
2	13.0	652.098	2.7

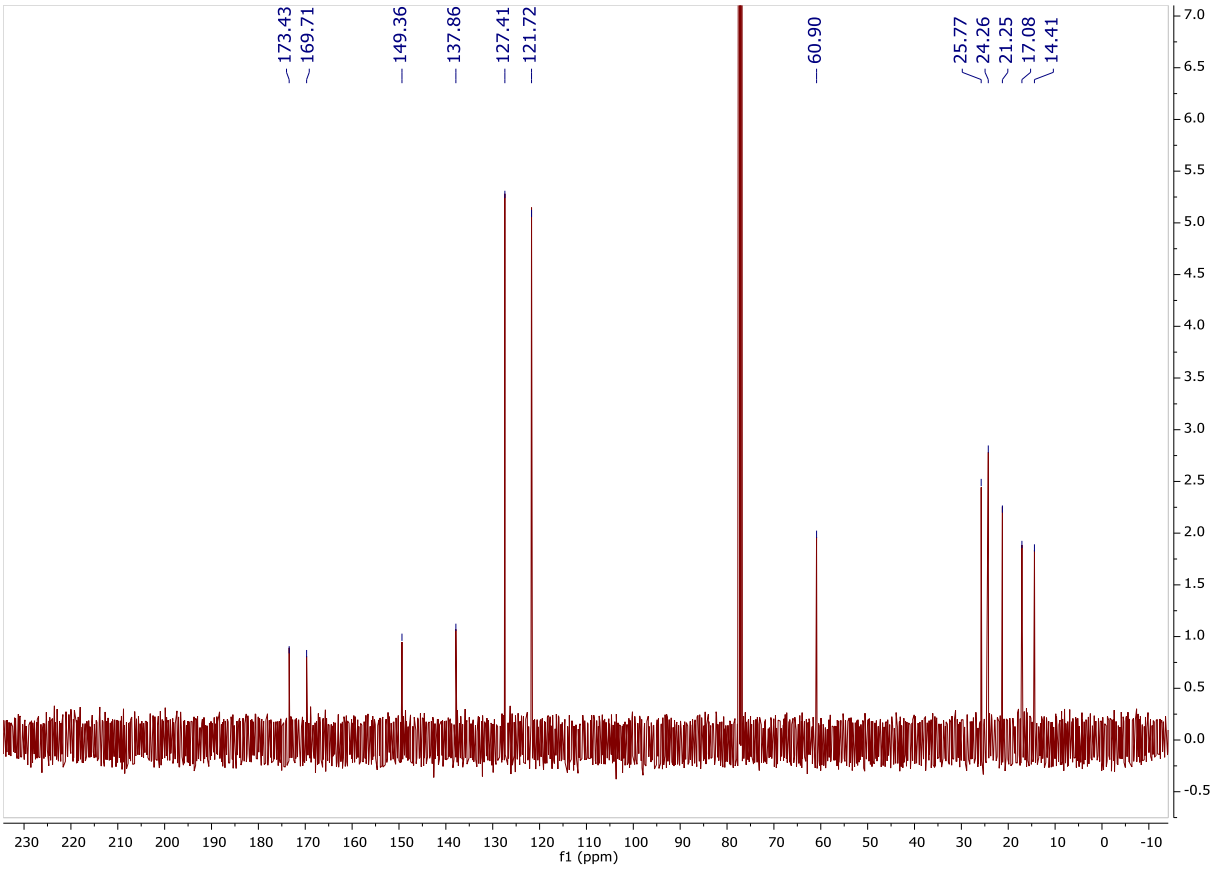
Ethyl (1S,2S)-2-(4-acetoxyphenyl)cyclopropane-1-carboxylate (5d).



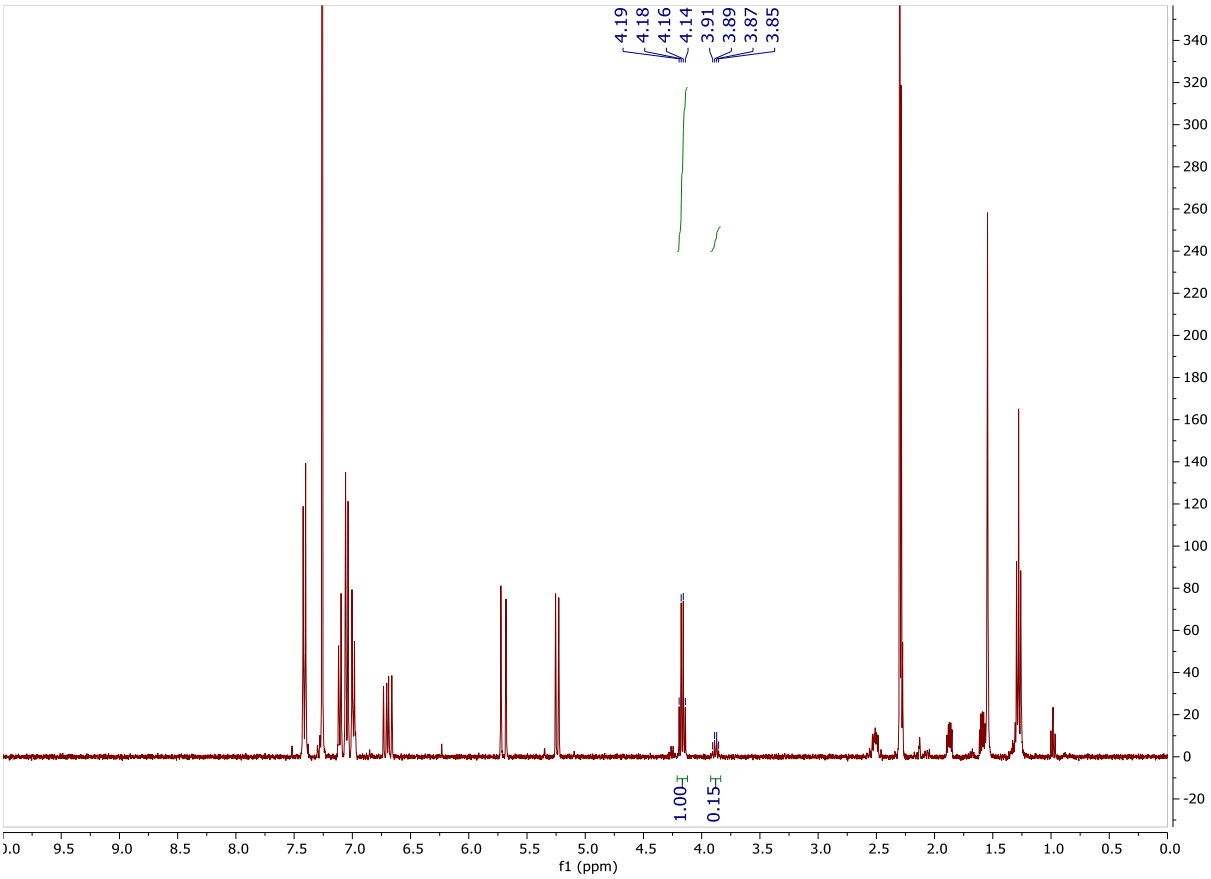
^{1}H NMR (500 MHz, $CDCl_3$):



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

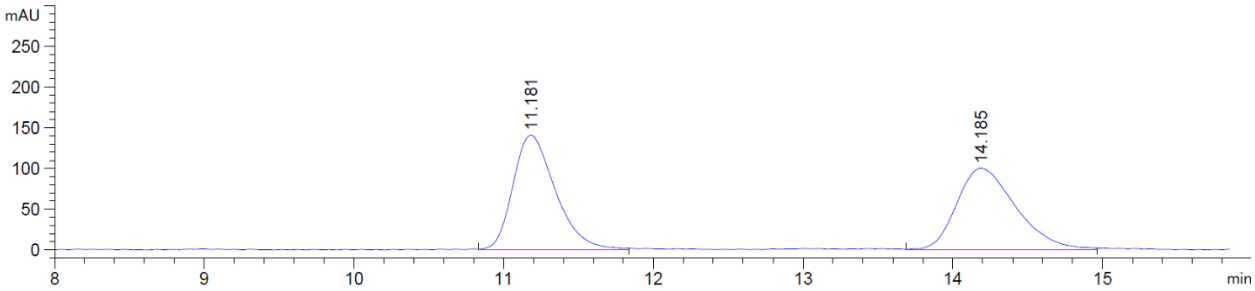


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Trans (4.17 ppm), Cis (3.88 ppm), Ratio: 87:13.



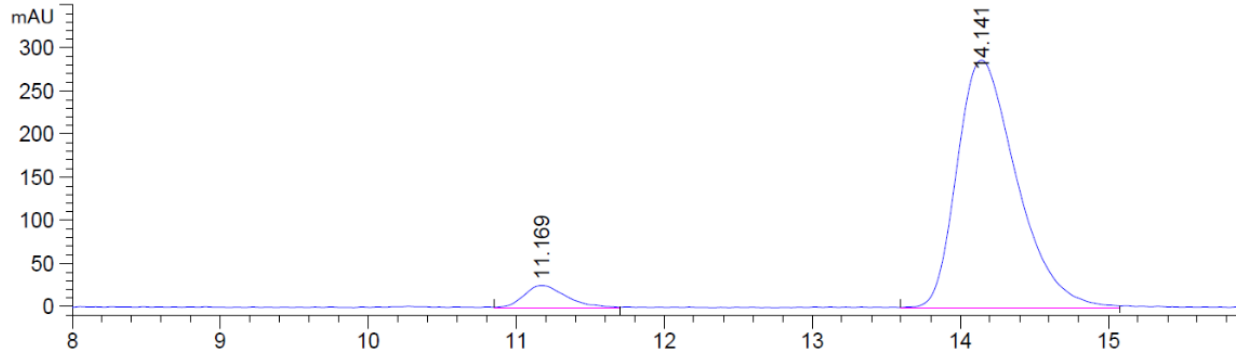
HPLC conditions: AS-H column, 1mL/min, 1.8% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



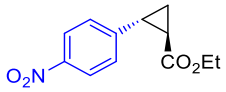
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	11.2	2789.97	50.3
2	14.2	2761.96	49.7

HPLC (Chiral)

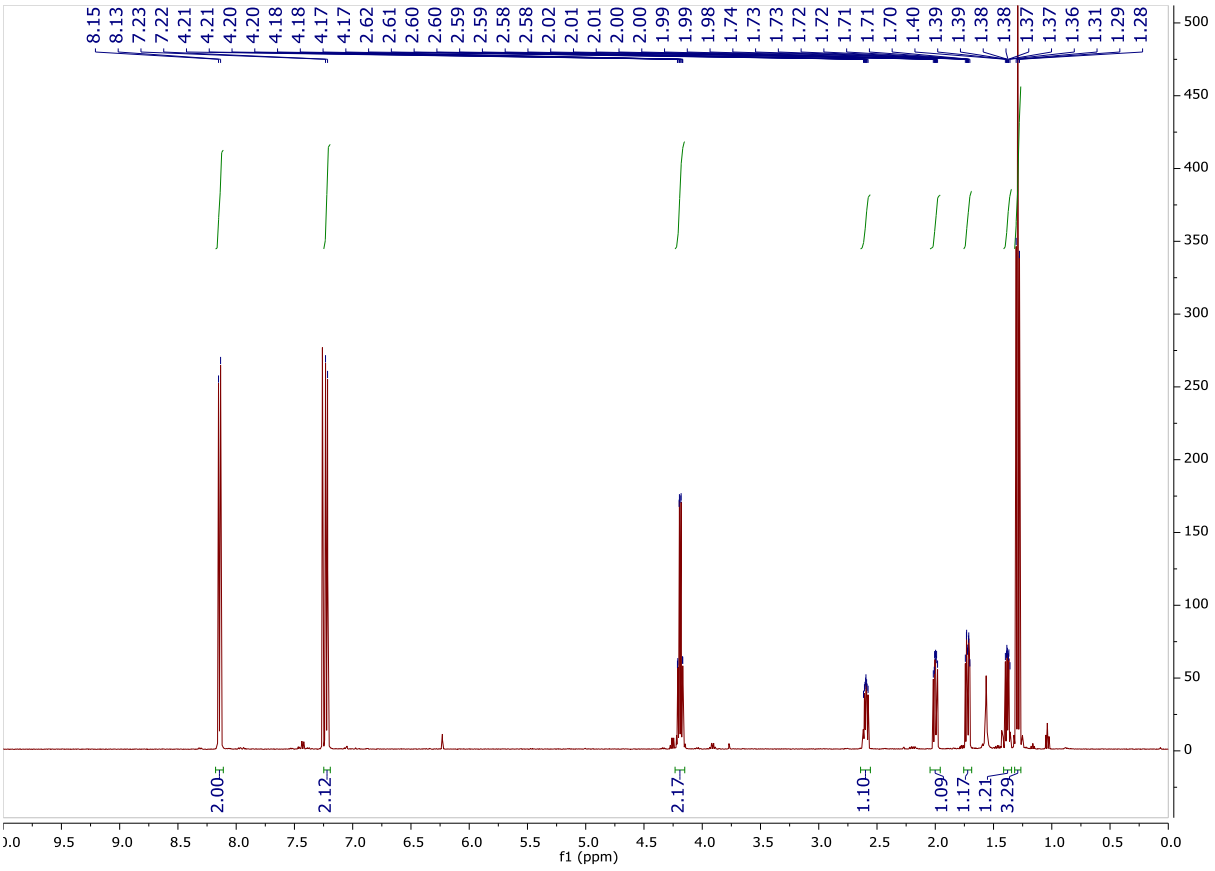


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	11.2	513.057	6.0
2	14.1	8047.97	94.0

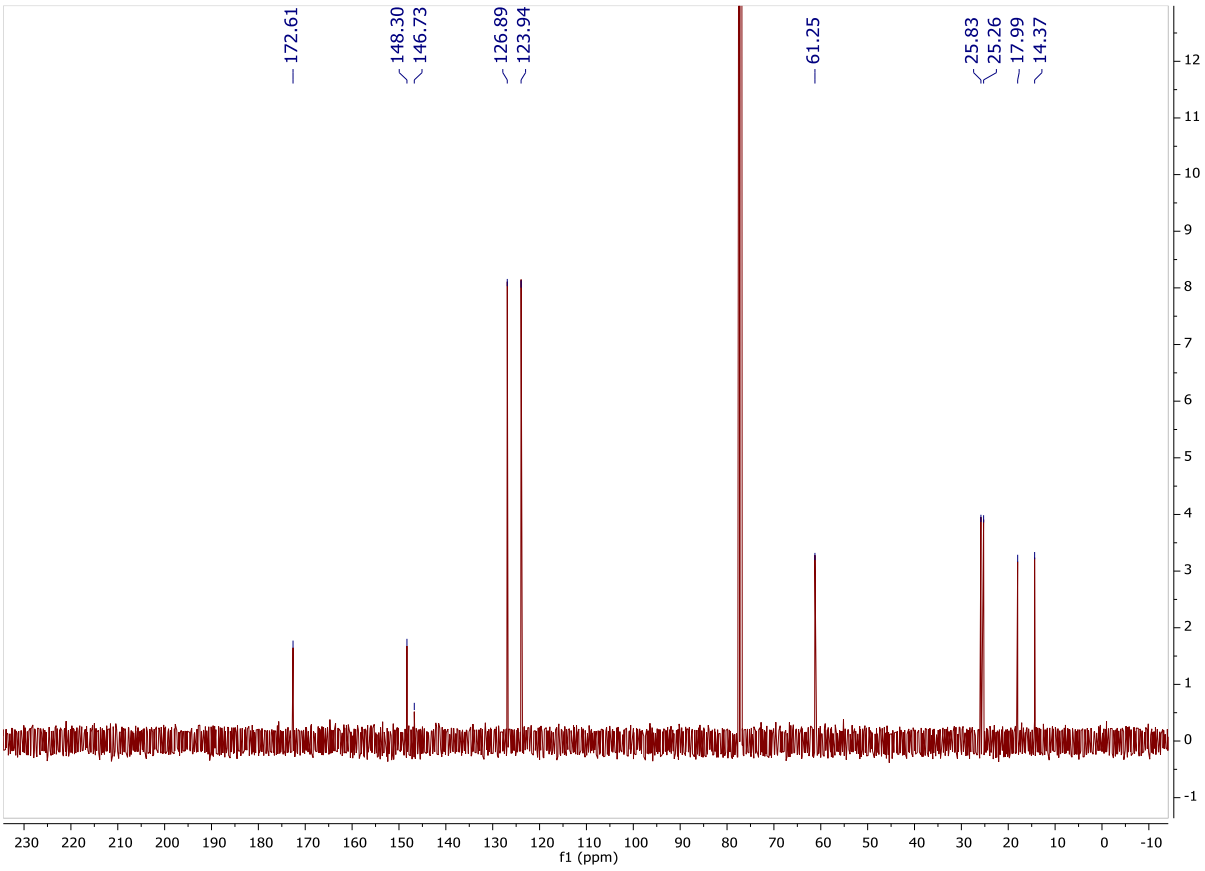
Ethyl (1R,2R)-2-(4-nitrophenyl)cyclopropane-1-carboxylate (5e).



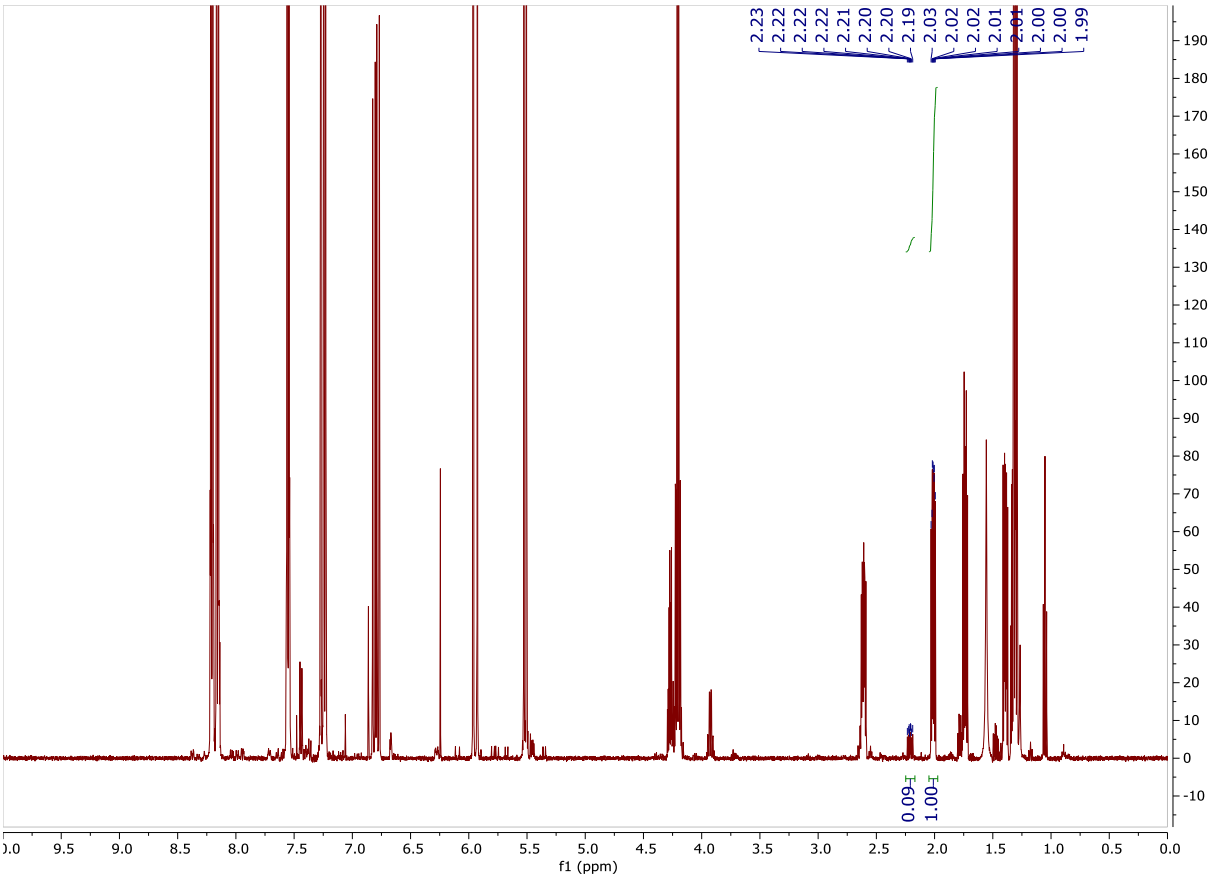
^{1}H NMR (500 MHz, $CDCl_3$):



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

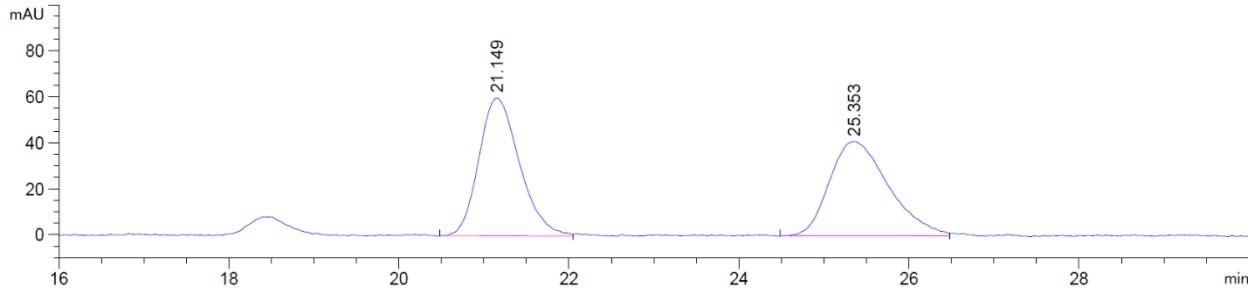


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Cis (2.21 ppm), Trans (2.01 ppm), Ratio: 92:8.



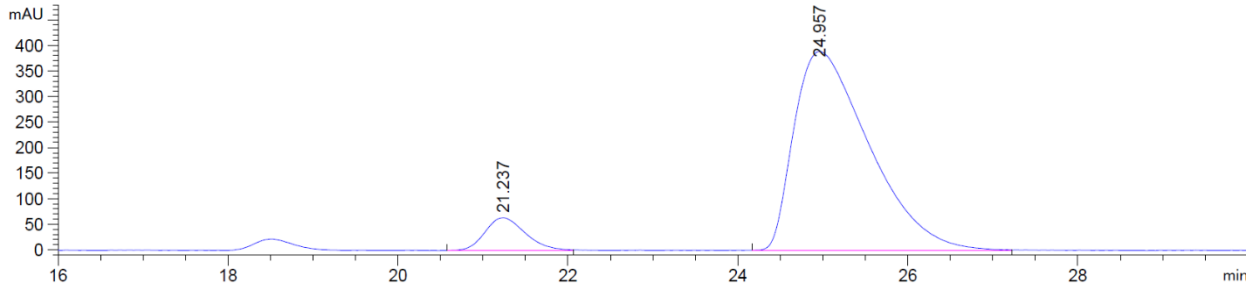
HPLC conditions: AS-H column, 1mL/min, 1.8% ^{i}PrOH/Hexanes, 220 nm UV detector.

HPLC (Racemic)



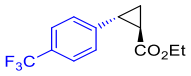
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	21.2	2003.62	49.9
2	25.4	2013.51	50.1

HPLC (Chiral)

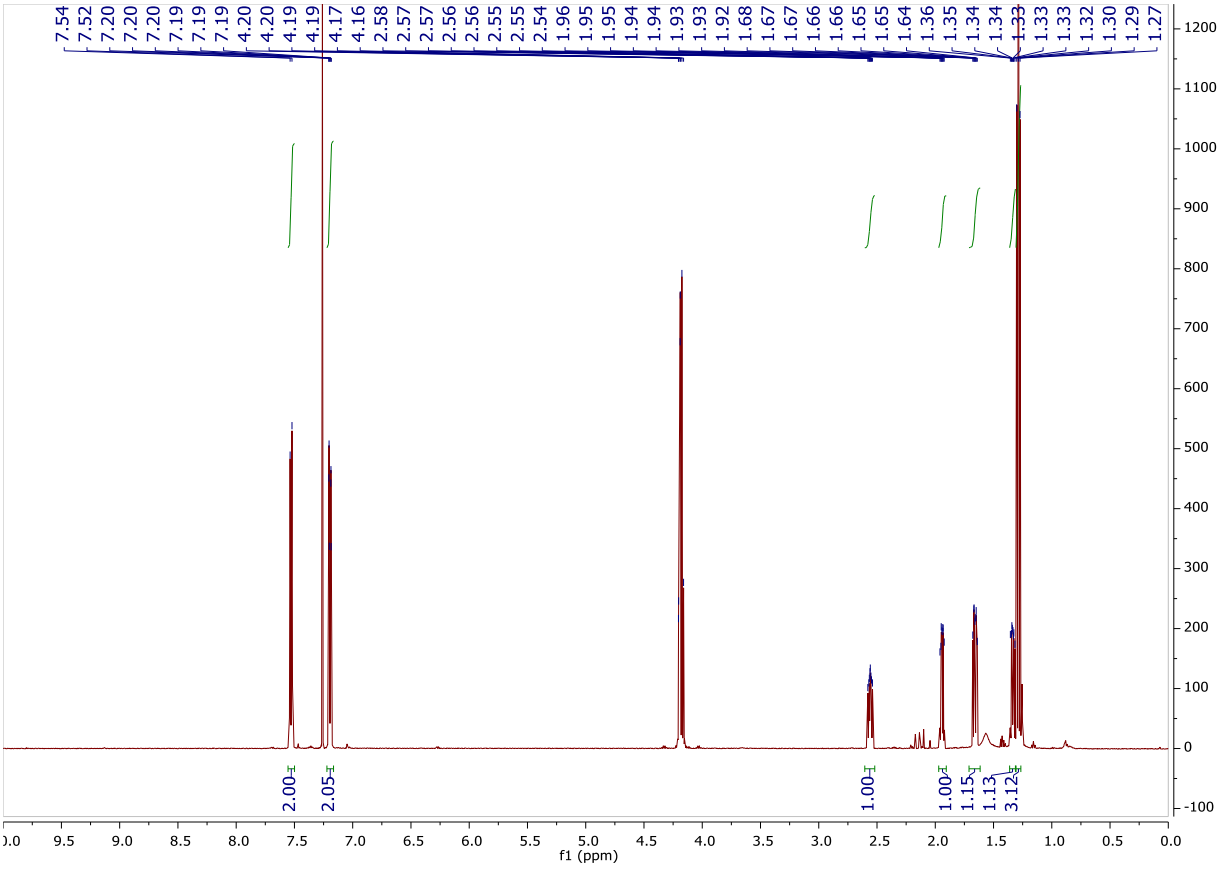


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	21.2	2130.41	8.2
2	25.0	23999.7	91.8

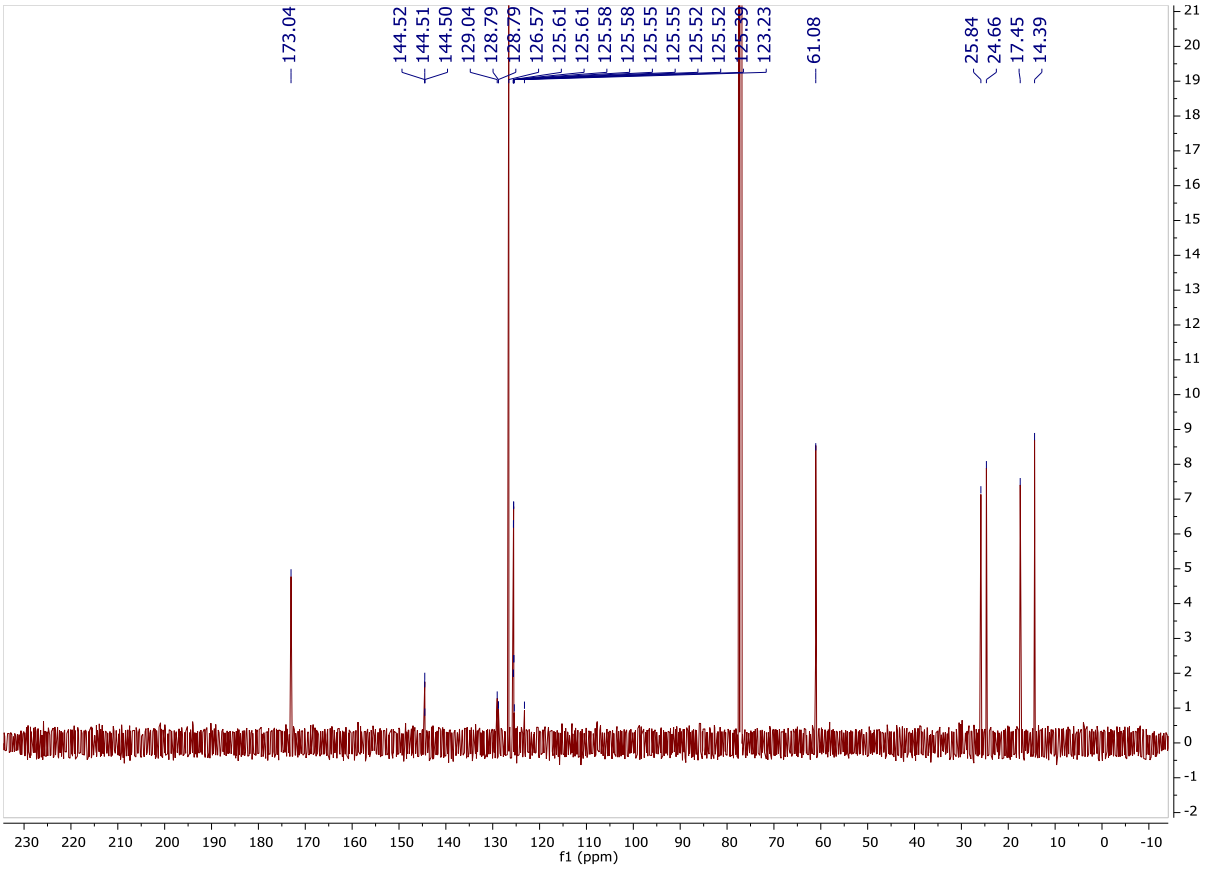
Ethyl (1R,2R)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1-carboxylate (5f).



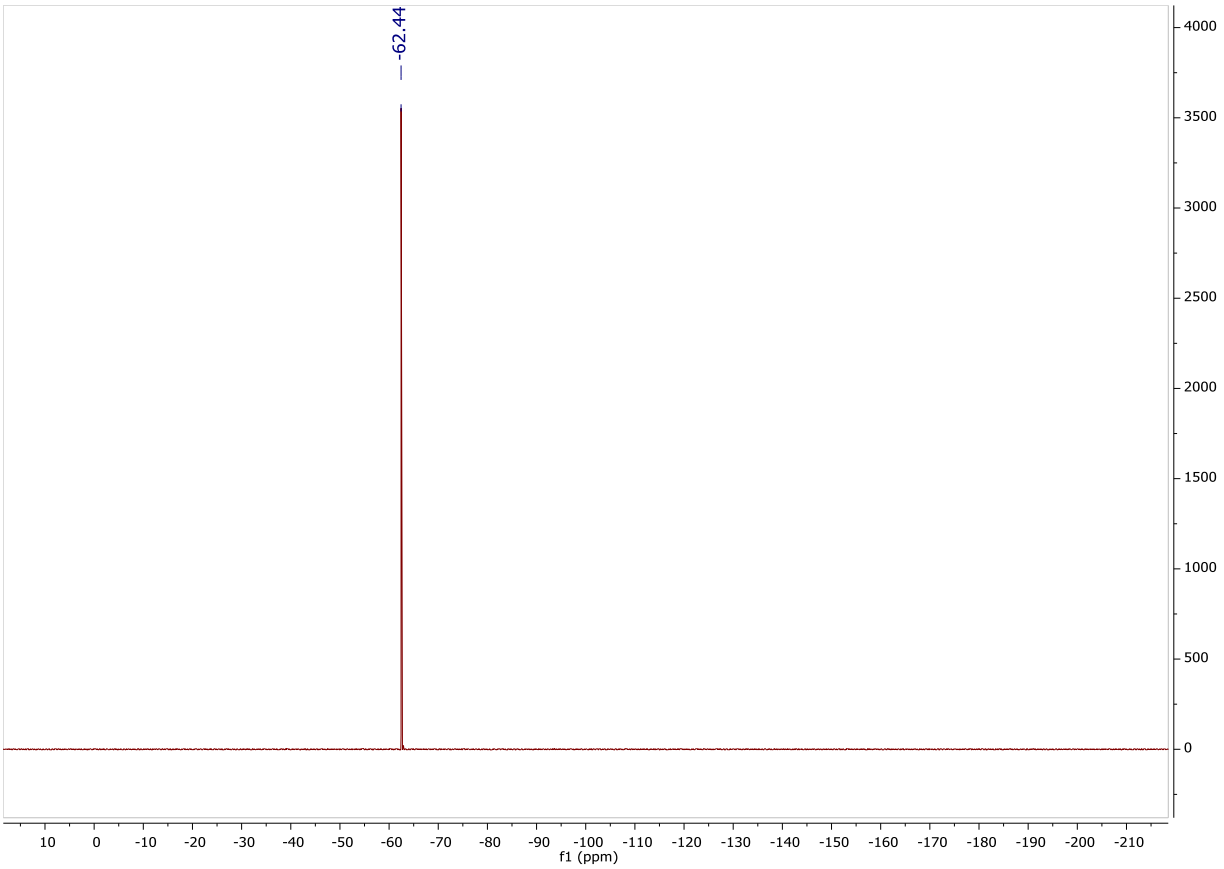
^{1}H NMR (500 MHz, $CDCl_3$):



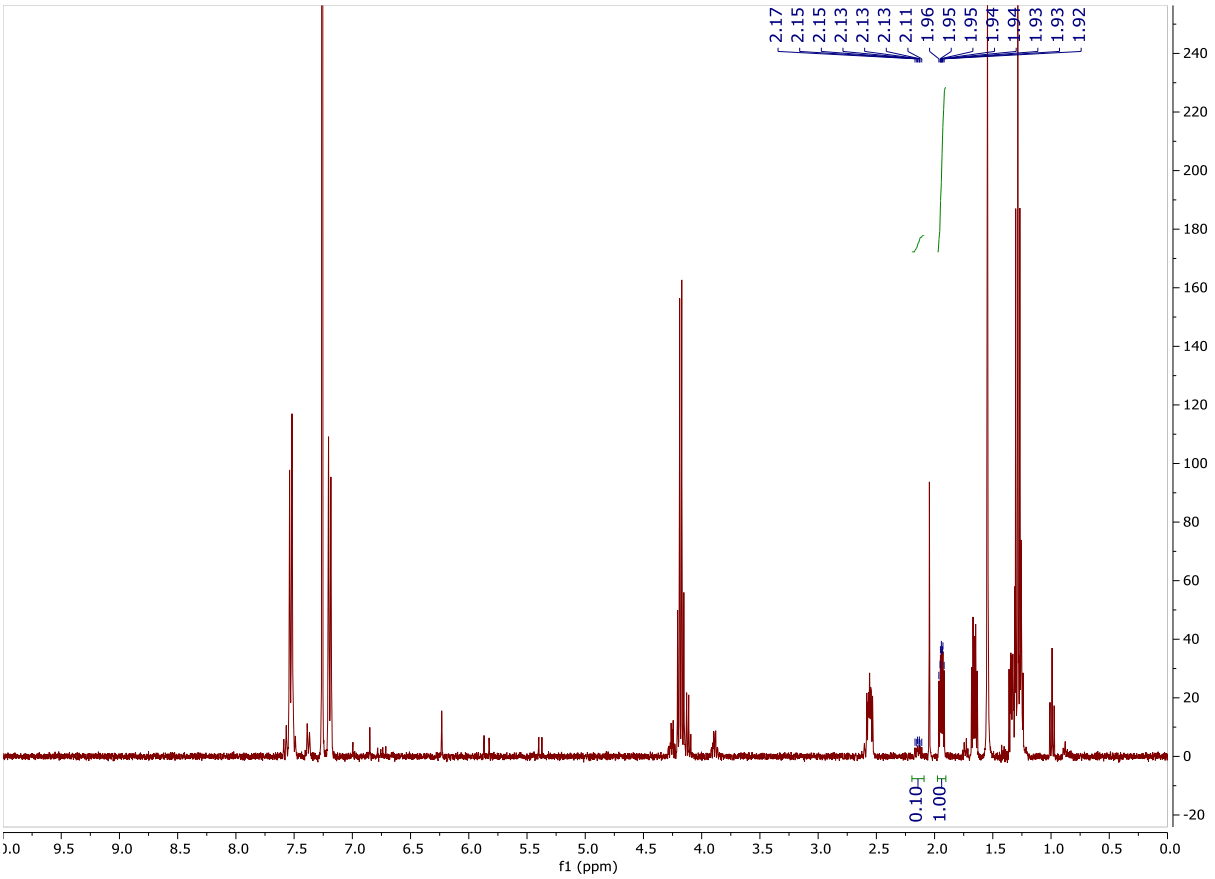
^{13}C NMR (126 MHz, $CDCl_3$):



^{19}F NMR (471 MHz, $CDCl_3$):

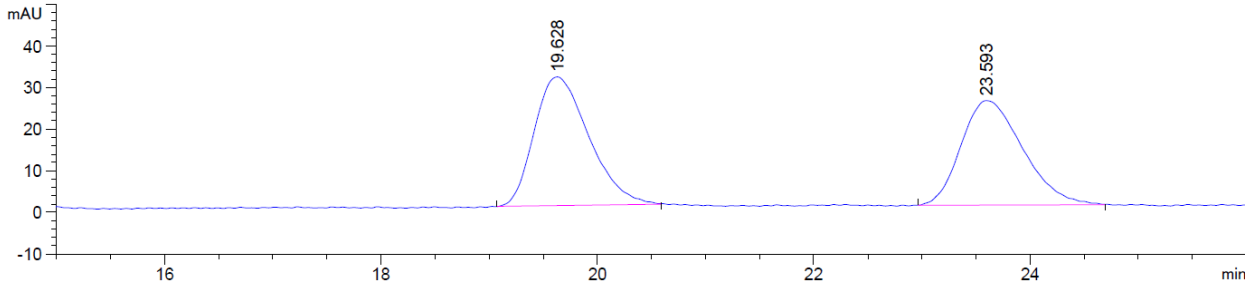


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Cis (2.13 ppm), Trans (1.94 ppm), Ratio: 91:9.



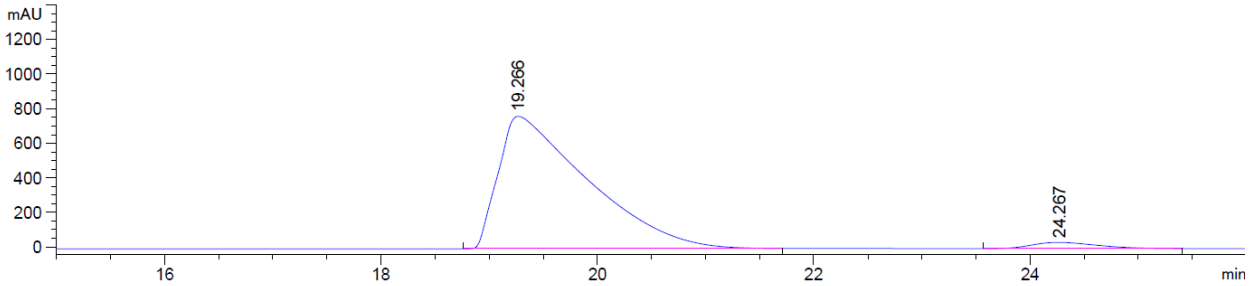
HPLC conditions: OJ-H column, 1mL/min, 0.3% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



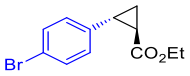
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	19.6	1091.74	52.1
2	23.6	1002.40	47.9

HPLC (Chiral)

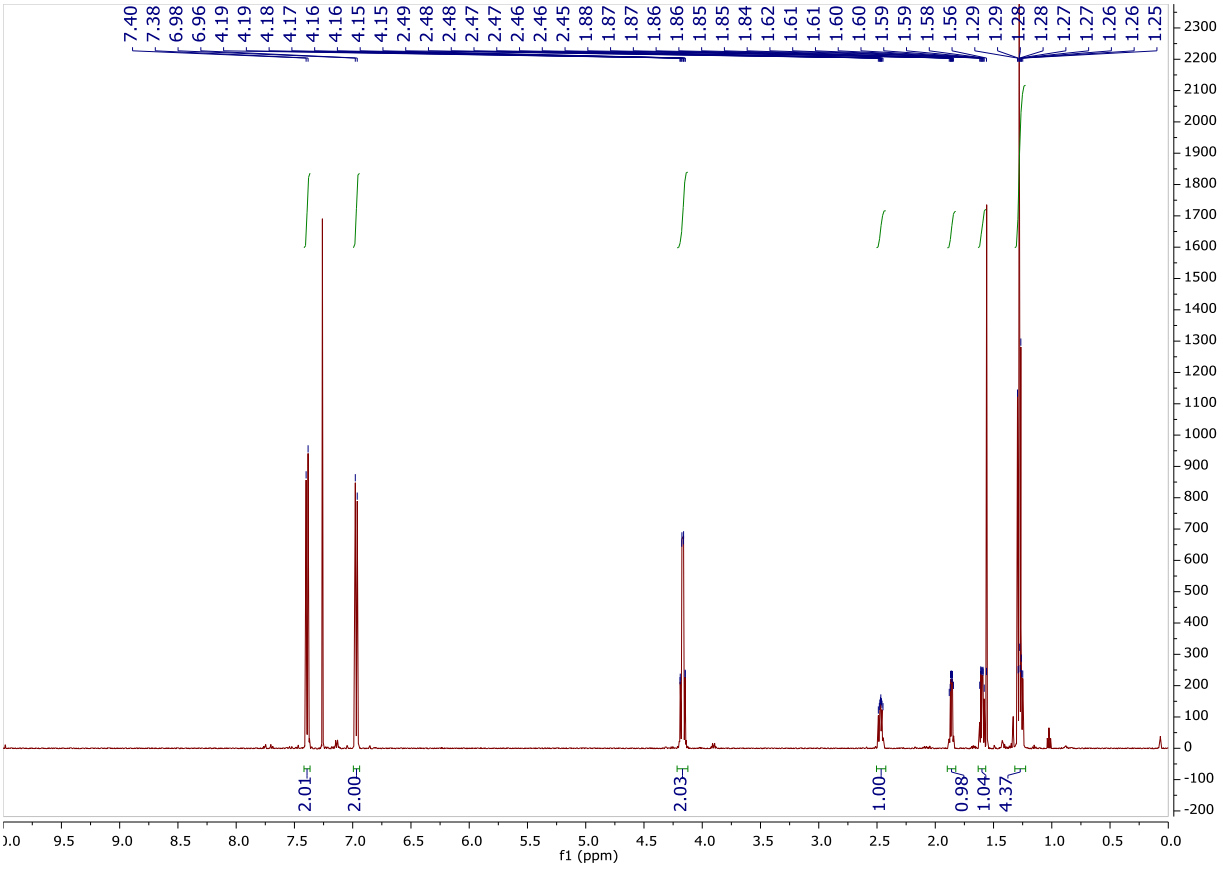


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	19.3	43725.9	96.6
2	24.3	1534.56	3.4

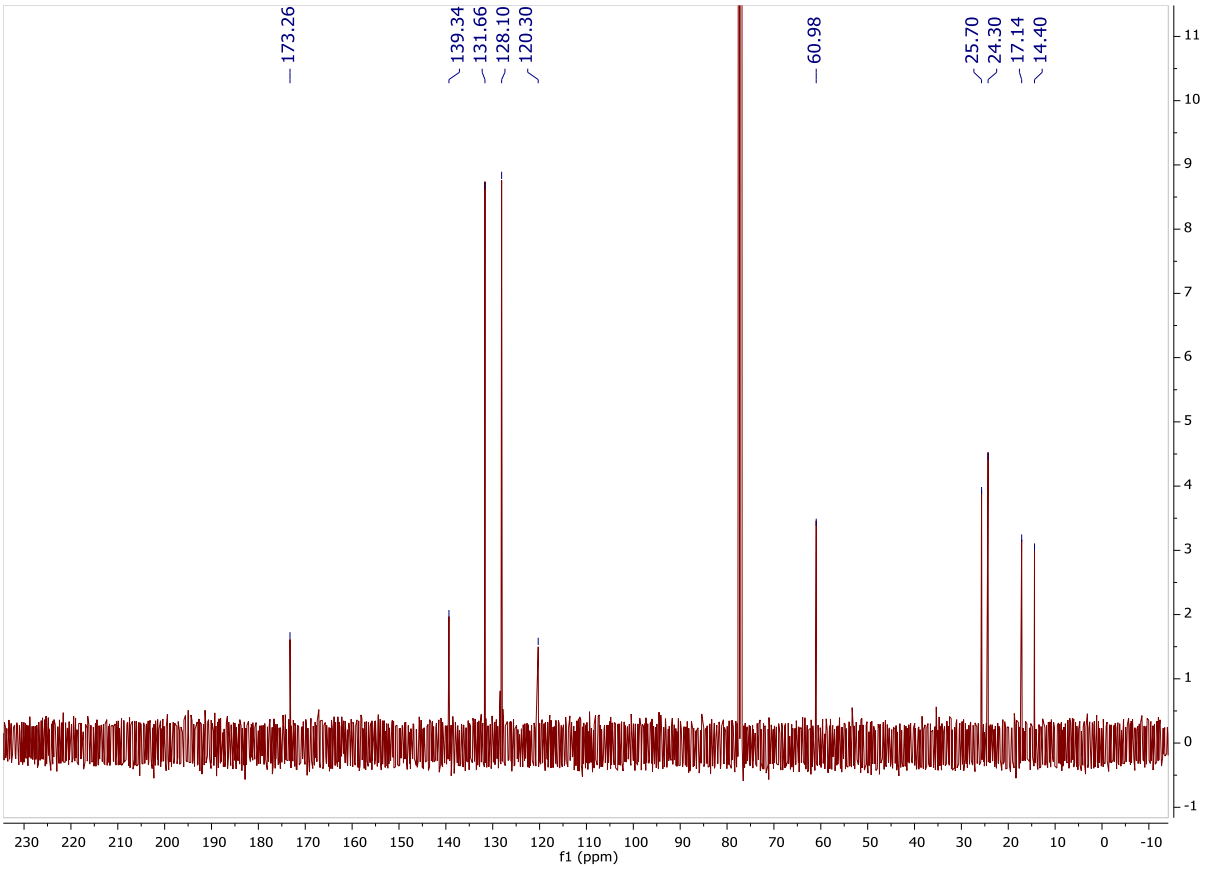
Ethyl (1R,2R)-2-(4-bromophenyl)cyclopropane-1-carboxylate (5g).



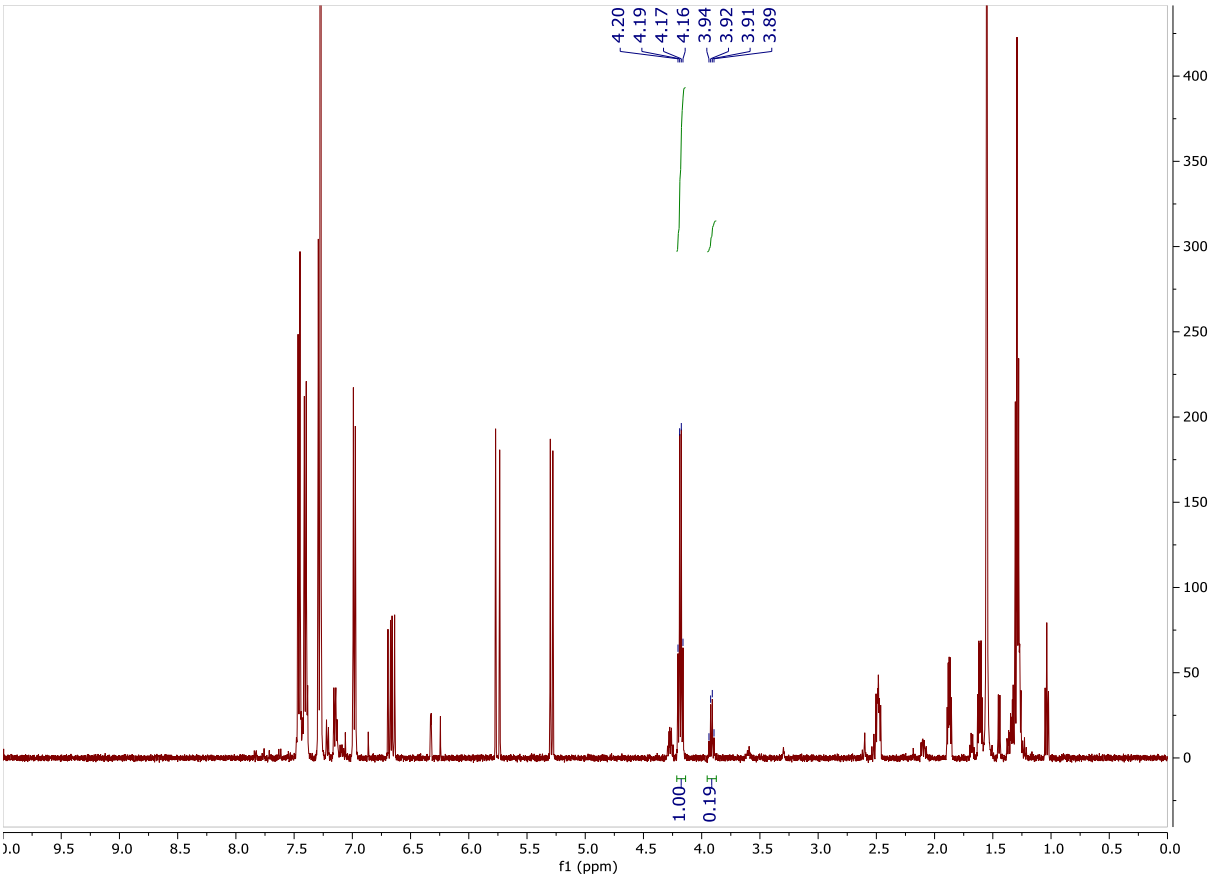
^{1}H NMR (500 MHz, $CDCl_3$):



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

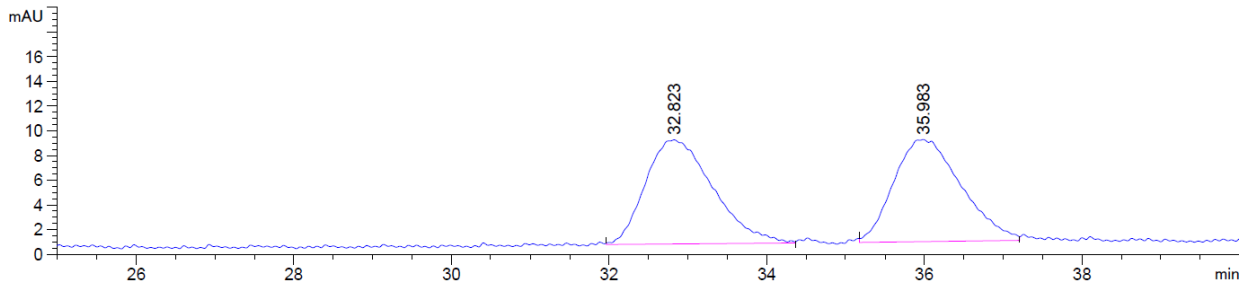


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Trans (4.18 ppm), Cis (3.91 ppm), Ratio: 84:16.



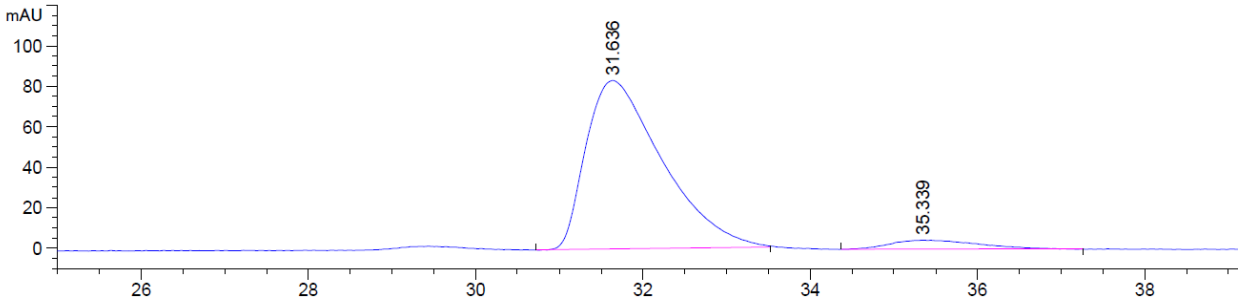
HPLC conditions: OJ-H column, 1mL/min, 0.3% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



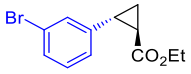
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	32.8	503.365	50.4
2	36.0	494.443	49.6

HPLC (Chiral)

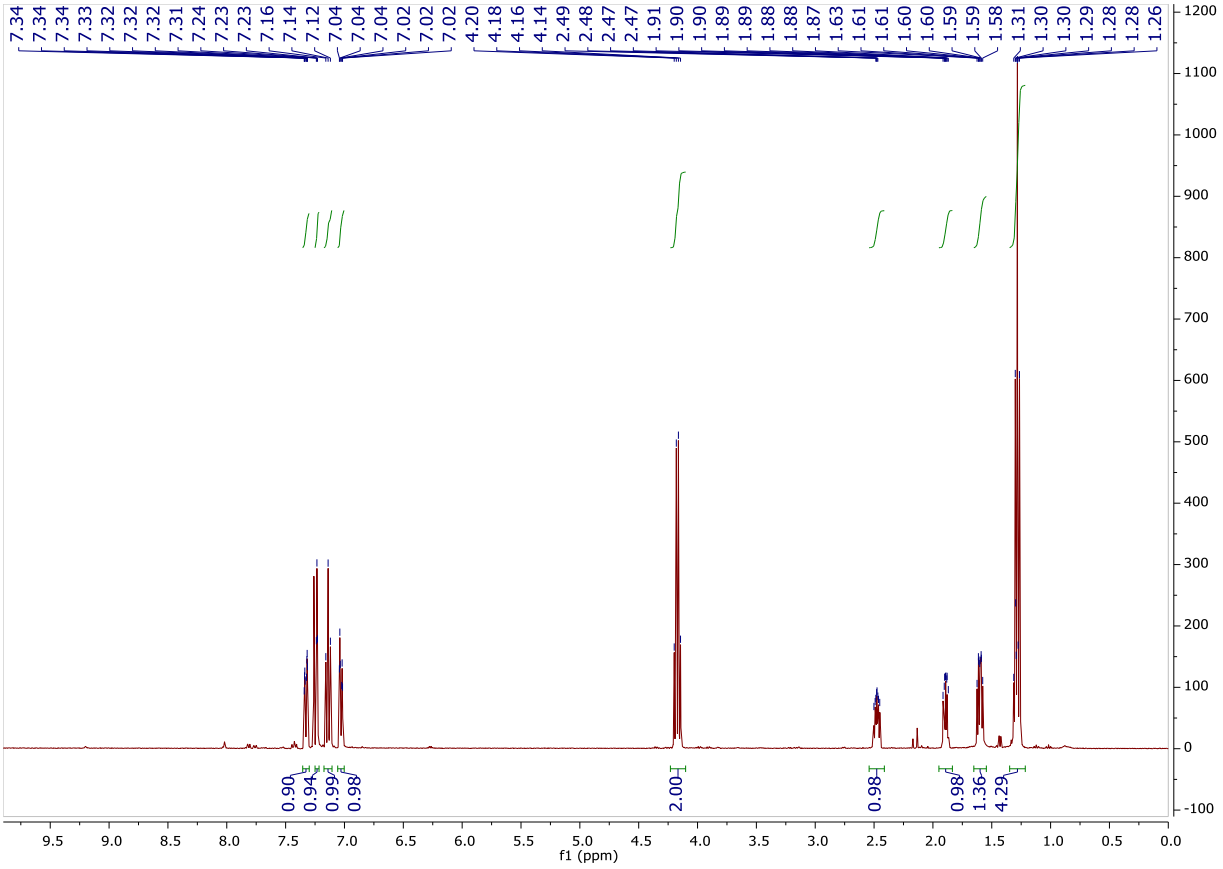


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	31.6	90109.6	95.6
2	35.3	4140.4	4.4

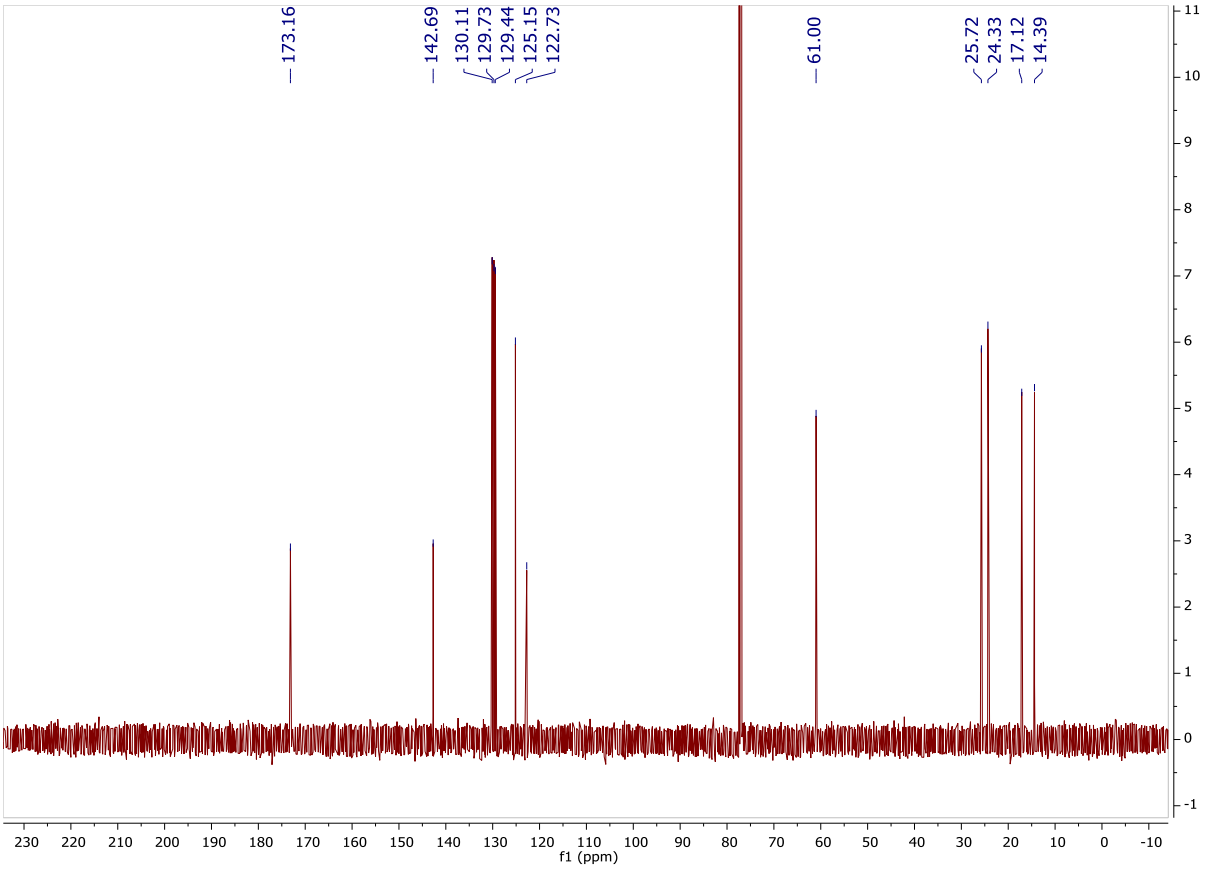
Ethyl (1R,2R)-2-(3-bromophenyl)cyclopropane-1-carboxylate (5h).



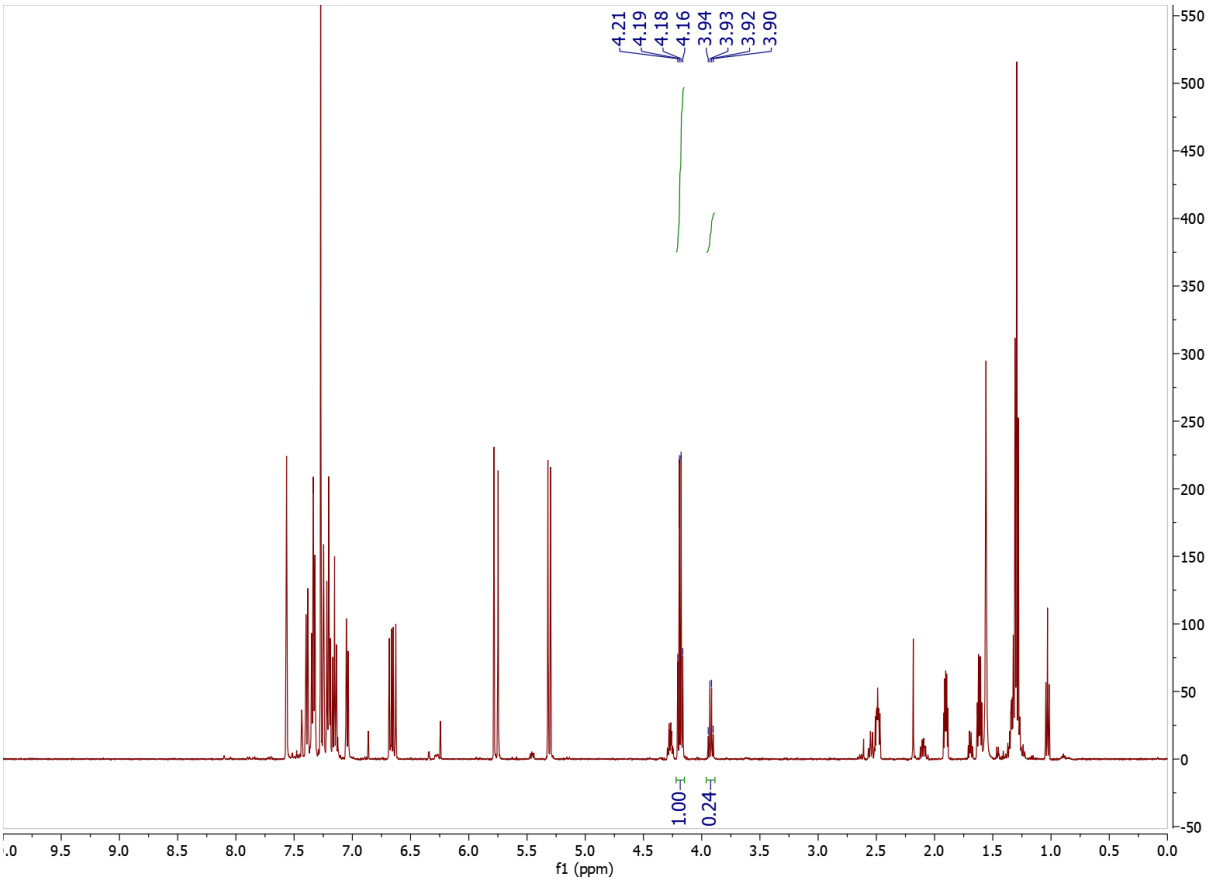
^{1}H NMR (500 MHz, $CDCl_3$):



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

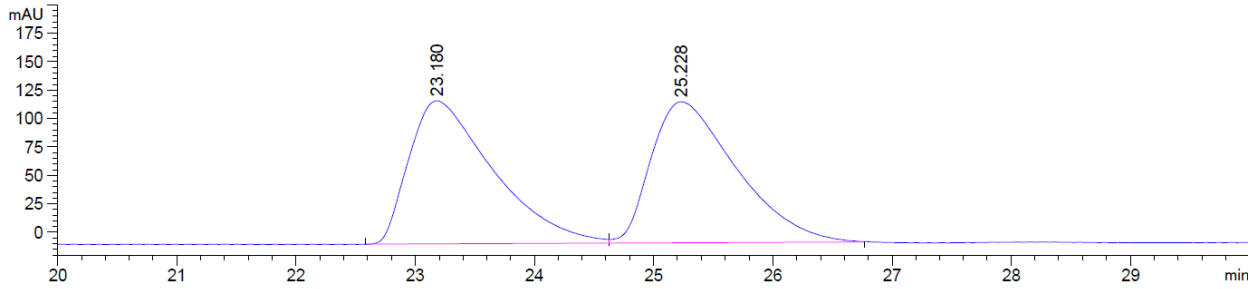


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Trans (4.18 ppm), Cis (3.93 ppm), Ratio: 81:19.



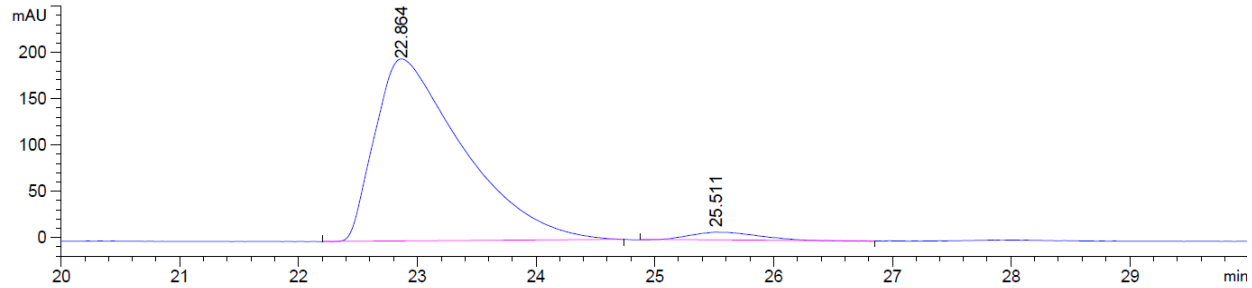
HPLC conditions: OJ-H column, 1mL/min, 0.2% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



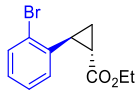
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	23.2	6180.60	50.0
2	25.2	6191.27	50.0

HPLC (Chiral)

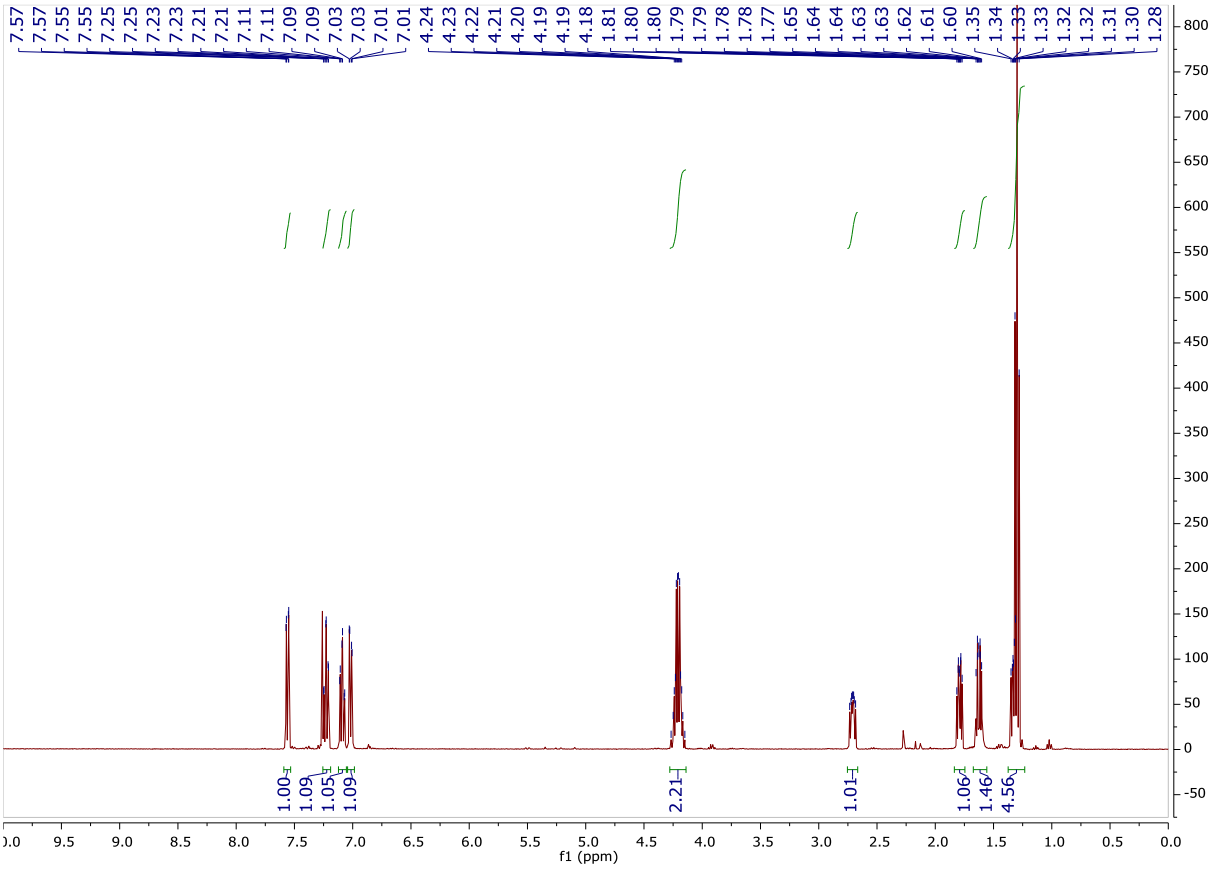


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	22.9	10145.8	96.7
2	25.5	348.810	3.3

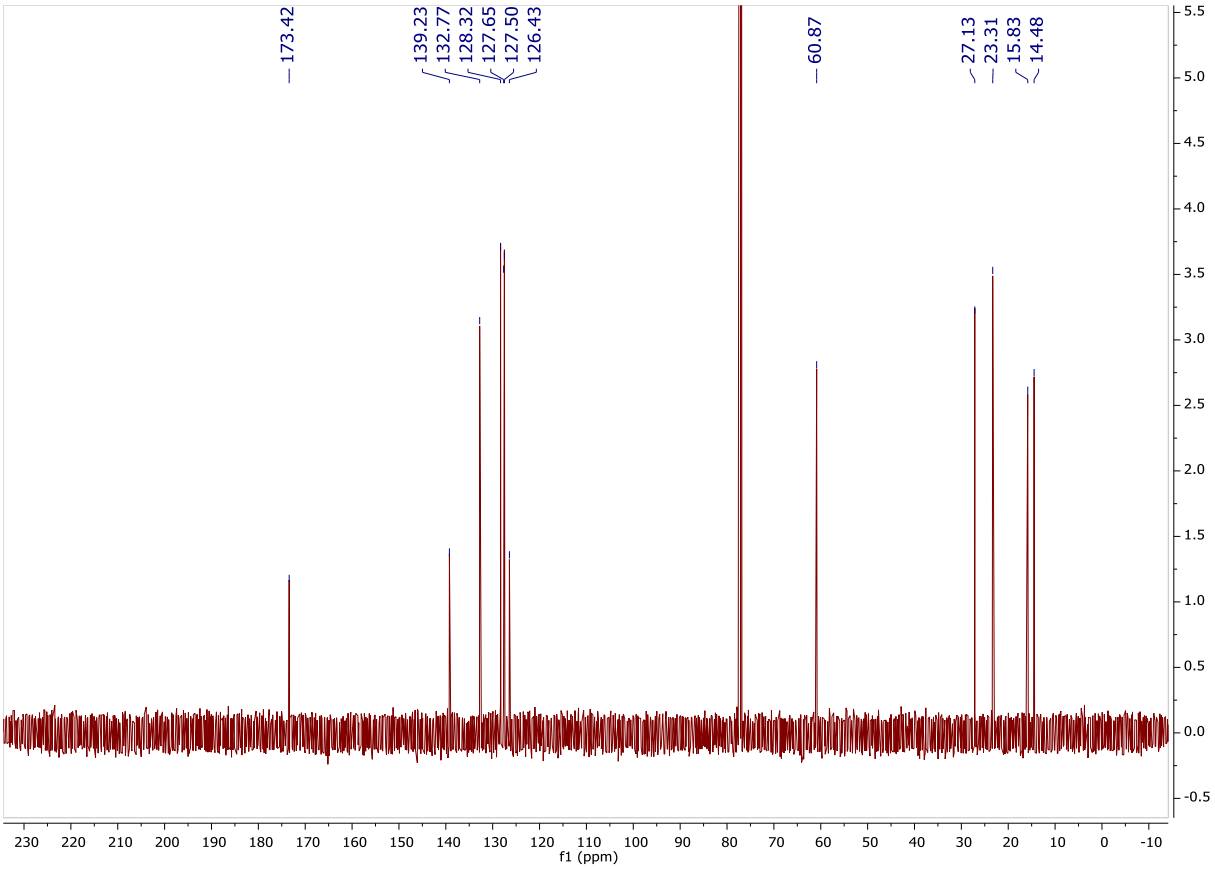
Ethyl (1S,2S)-2-(2-bromophenyl)cyclopropane-1-carboxylate (5i).



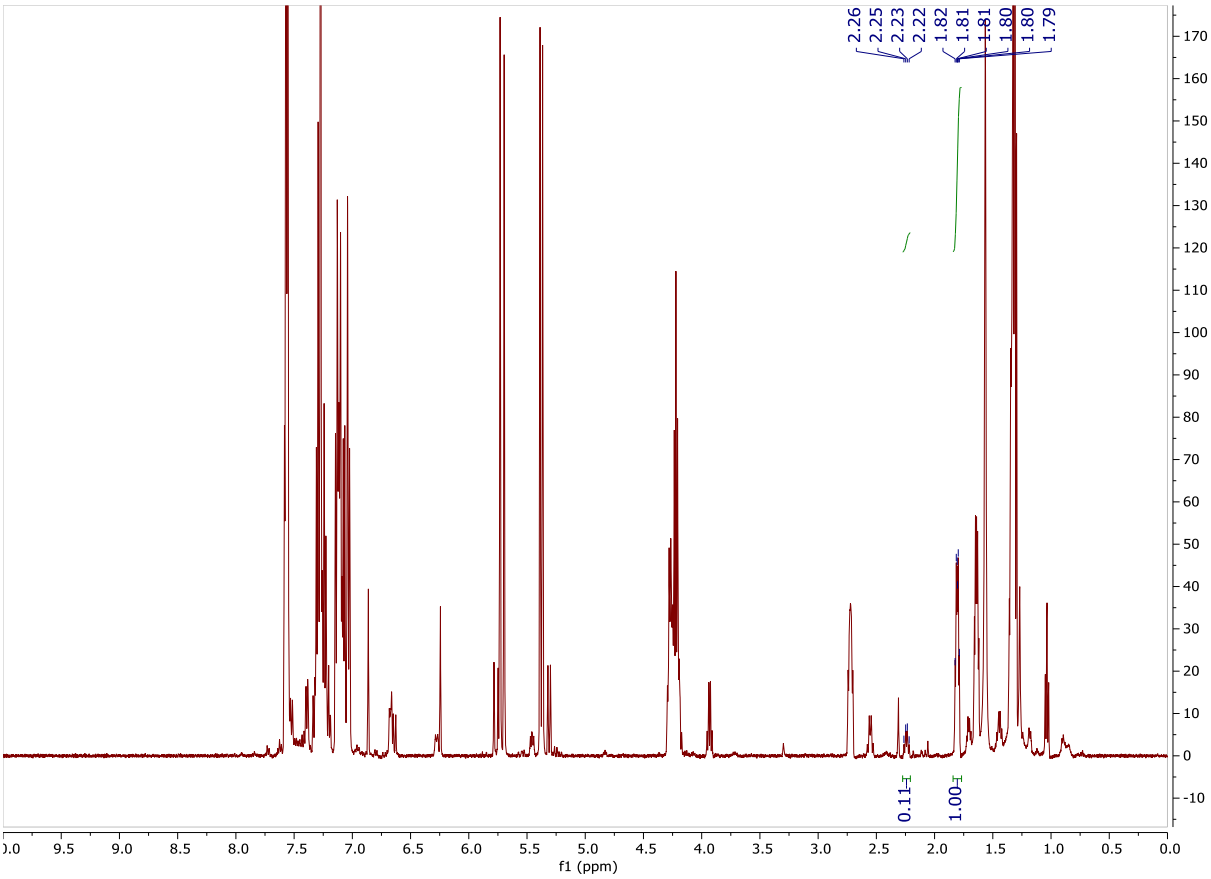
^{1}H NMR (500 MHz, $CDCl_3$):



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

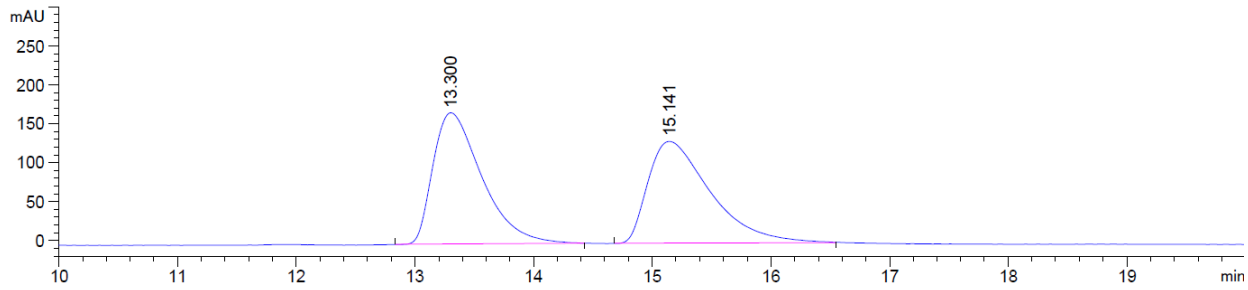


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Cis (2.24 ppm), Trans (1.80 ppm), Ratio: 90:10.



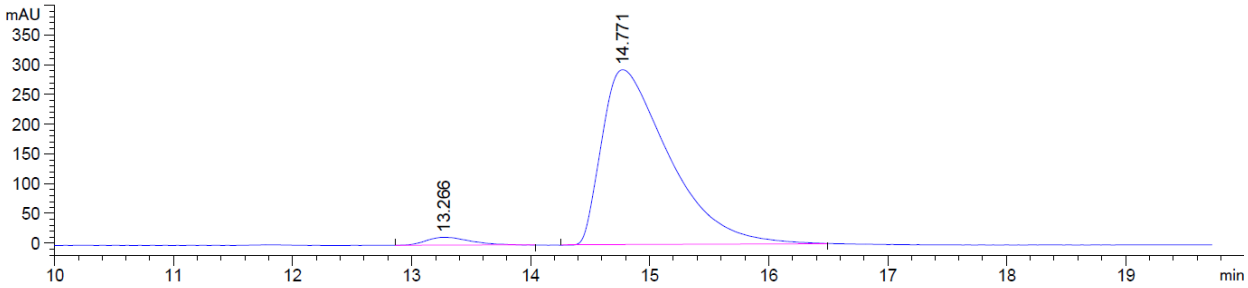
HPLC conditions: OJ-H column, 1mL/min, 0.2% iPrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



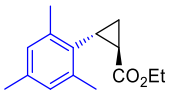
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	13.3	4870.65	50.4
2	15.1	4792.84	49.6

HPLC (Chiral)

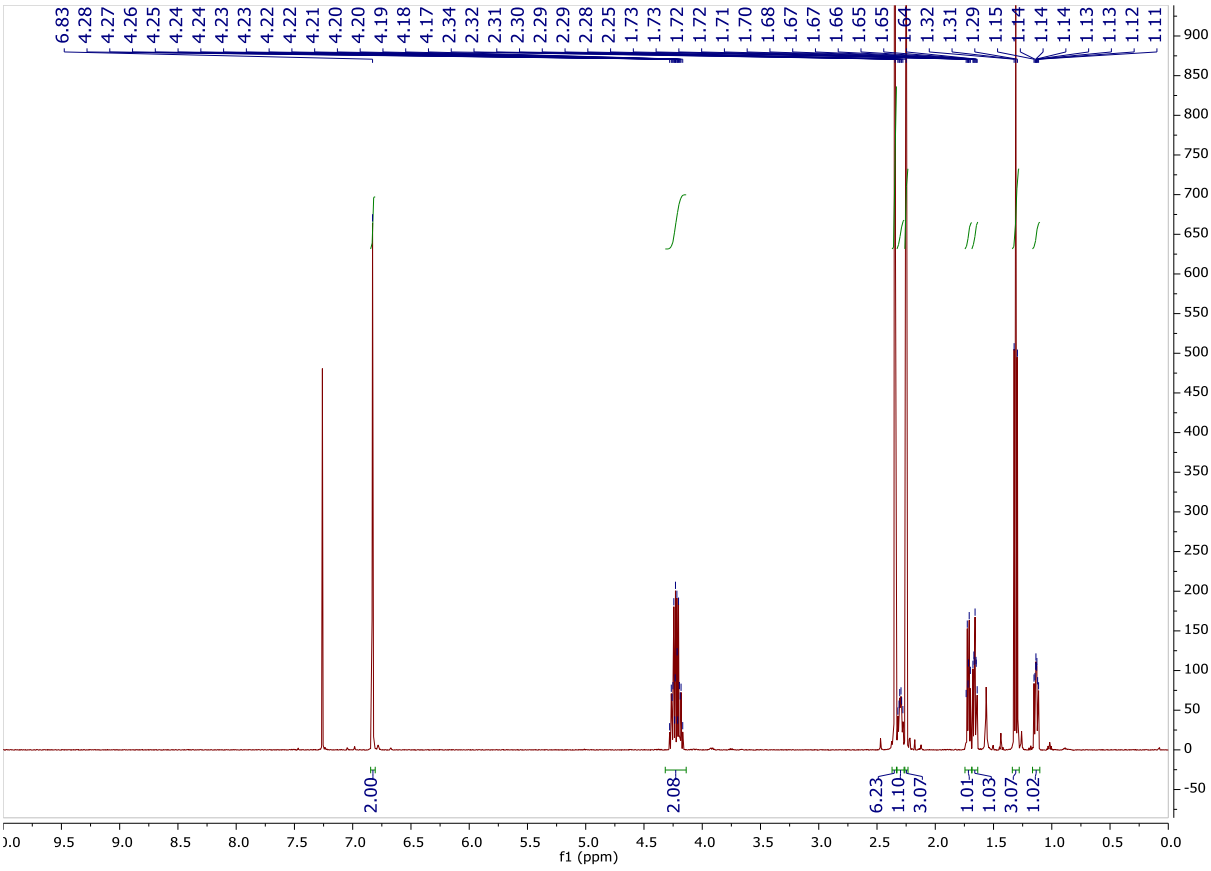


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	13.3	364.452	3.1
2	14.8	11573.2	96.9

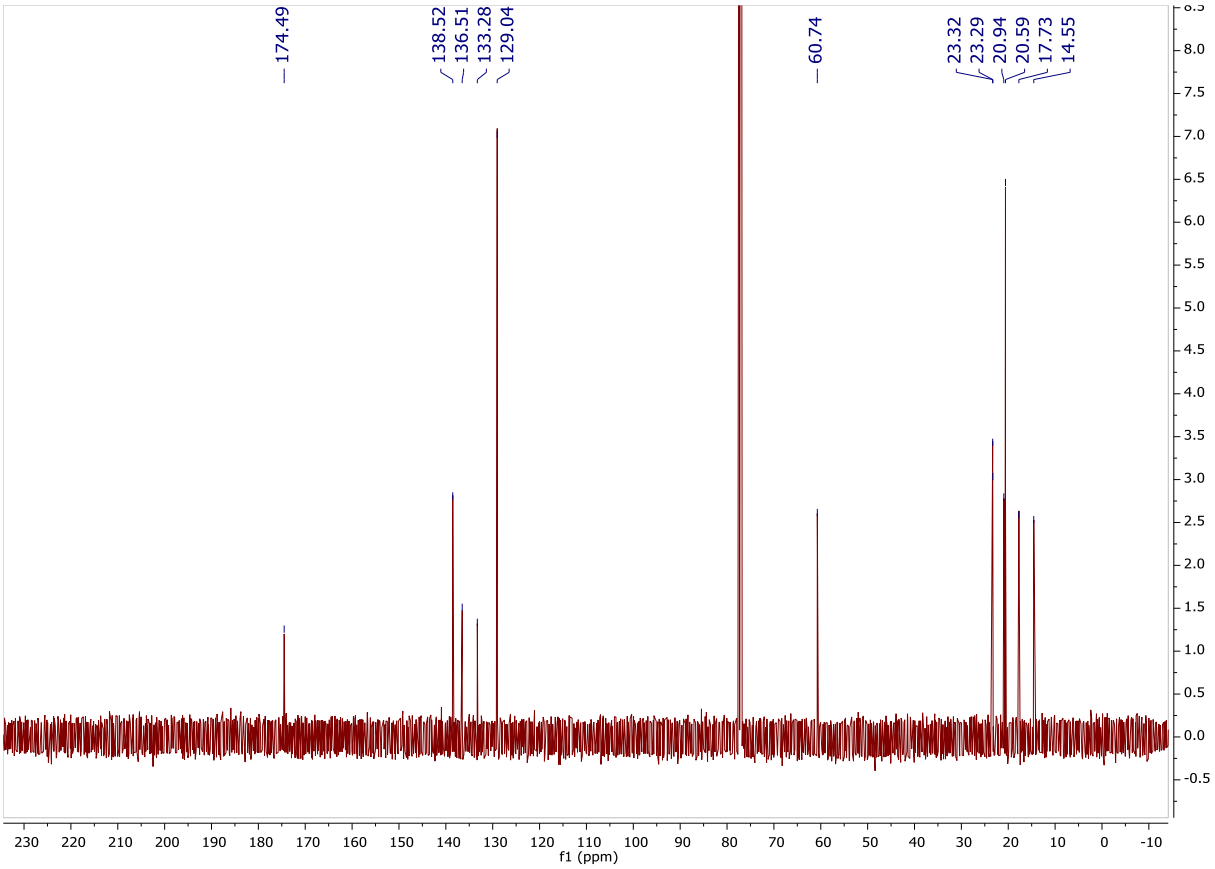
Ethyl (1R,2R)-2-mesitylcyclopropane-1-carboxylate (5j).



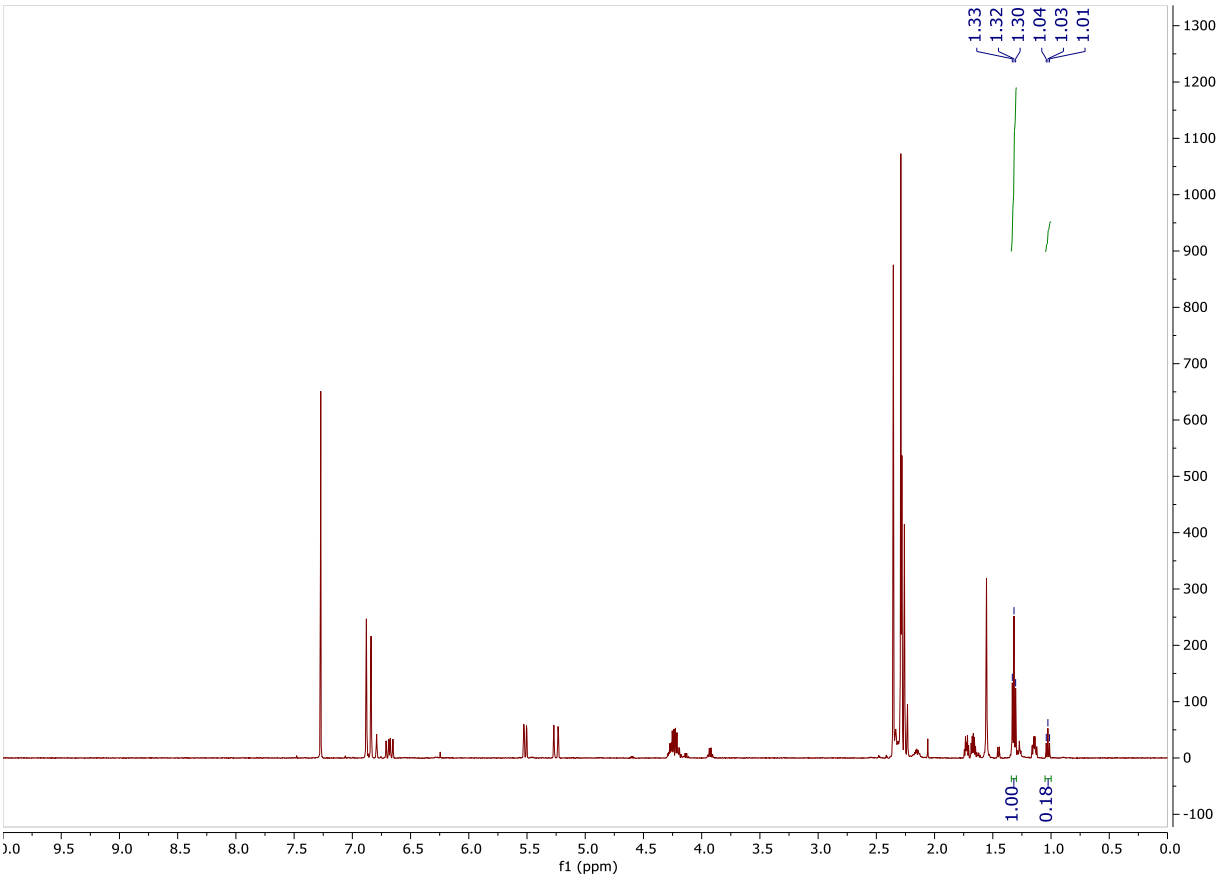
^{1}H NMR (500 MHz, $CDCl_3$):



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

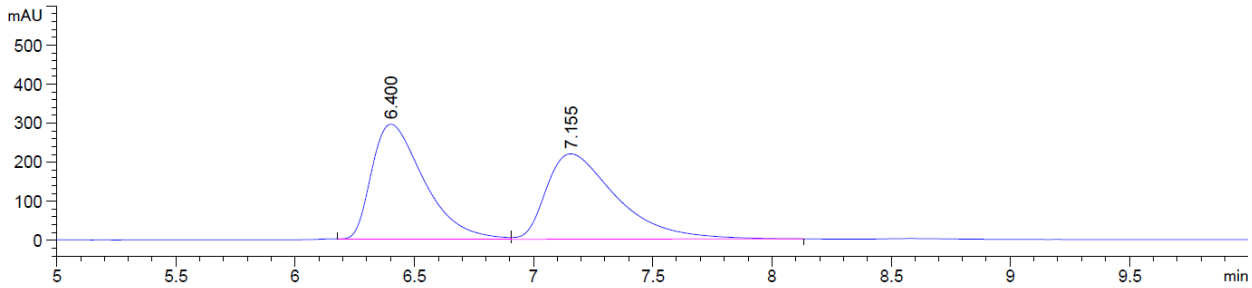


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Trans (1.32 ppm), Cis (1.03 ppm), Ratio: 85:15.



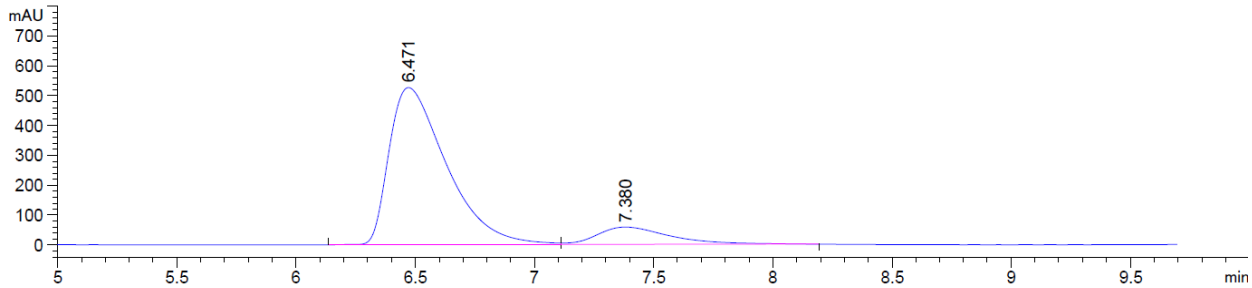
HPLC conditions: OJ-H column, 1mL/min, 0.2% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



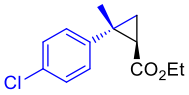
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	6.4	4544.25	50.1
2	7.2	4524.25	49.9

HPLC (Chiral)

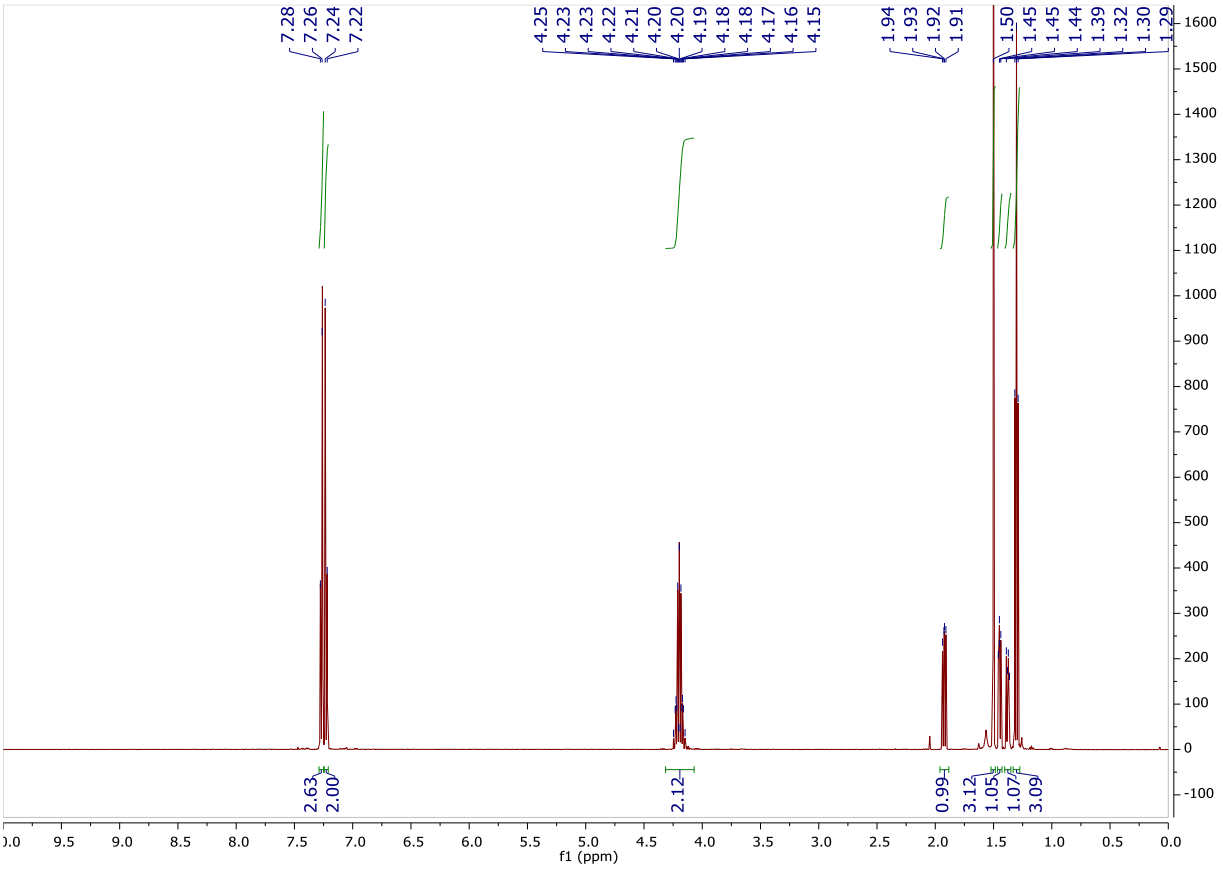


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	6.5	8809.21	87.4
2	7.4	1267.24	12.6

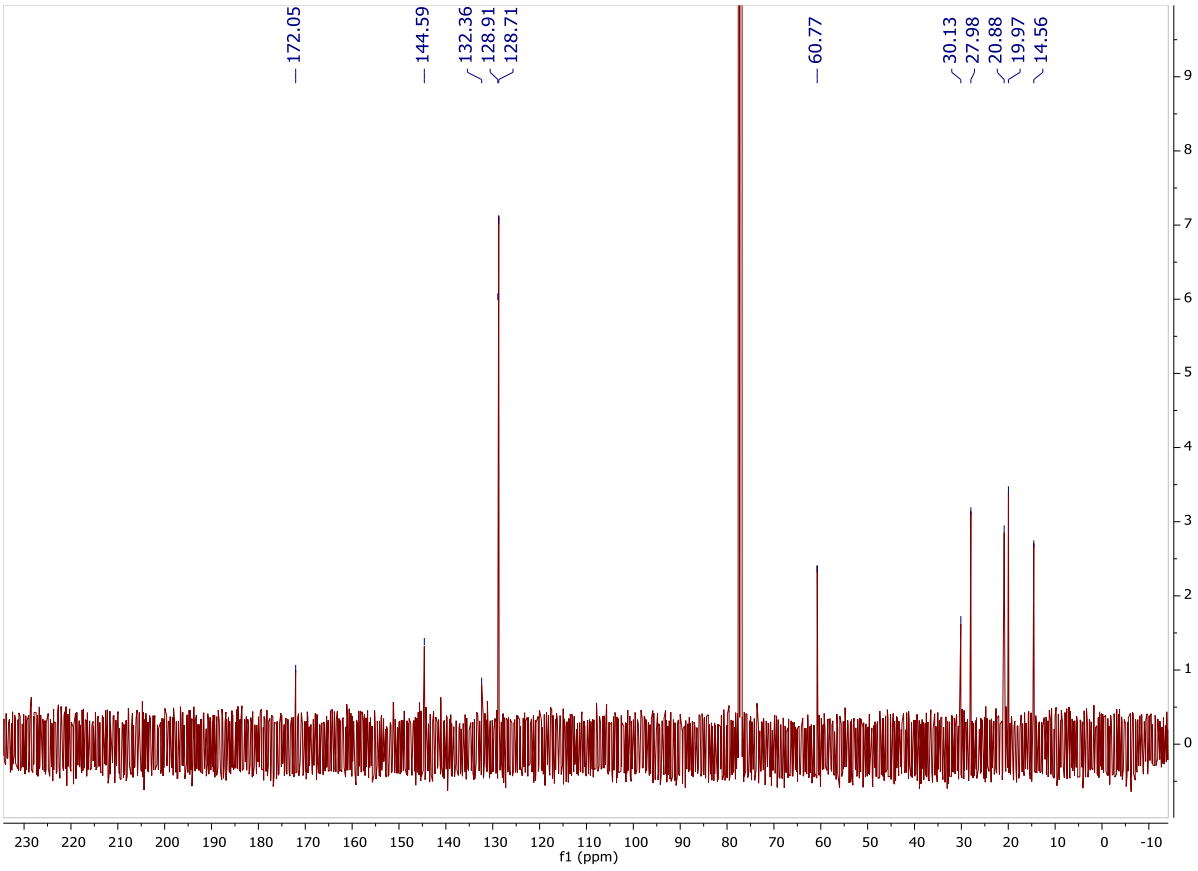
Ethyl (1R,2R)-2-(4-chlorophenyl)-2-methylcyclopropane-1-carboxylate (5k).



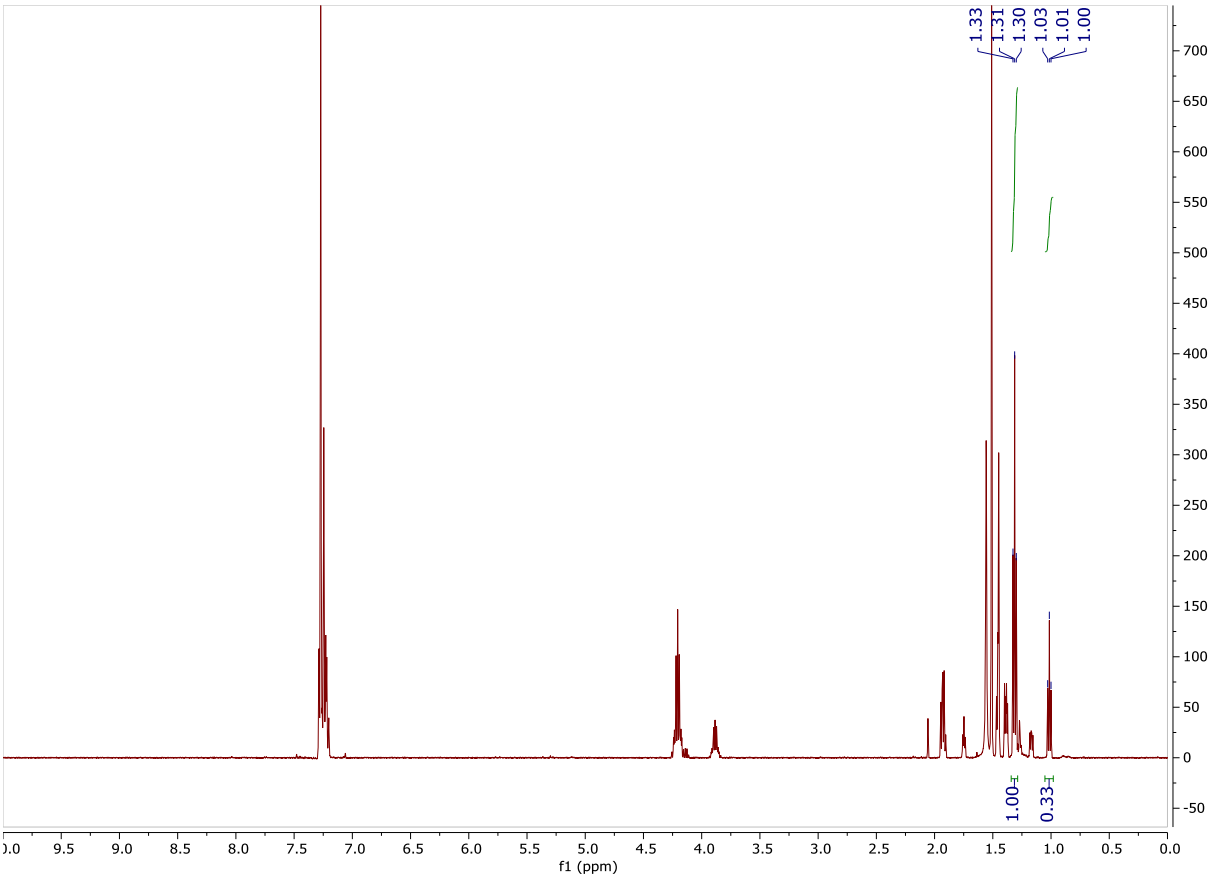
^{1}H NMR (500 MHz, $CDCl_3$):



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

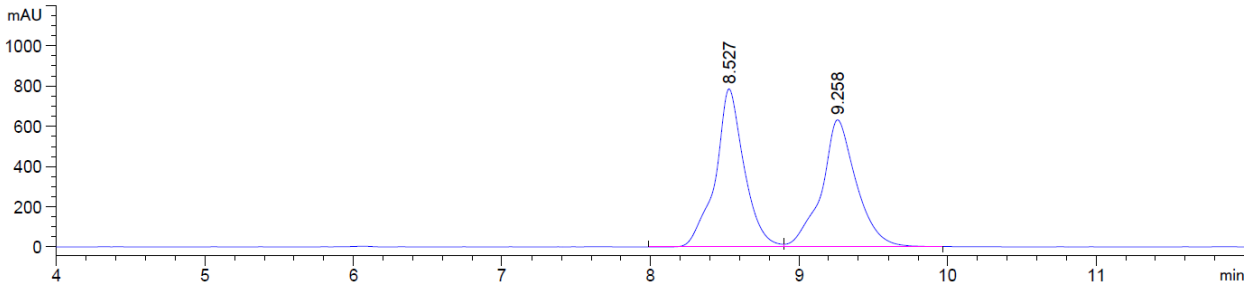


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Trans (1.31 ppm), Cis (1.01 ppm), Ratio: 75:25.



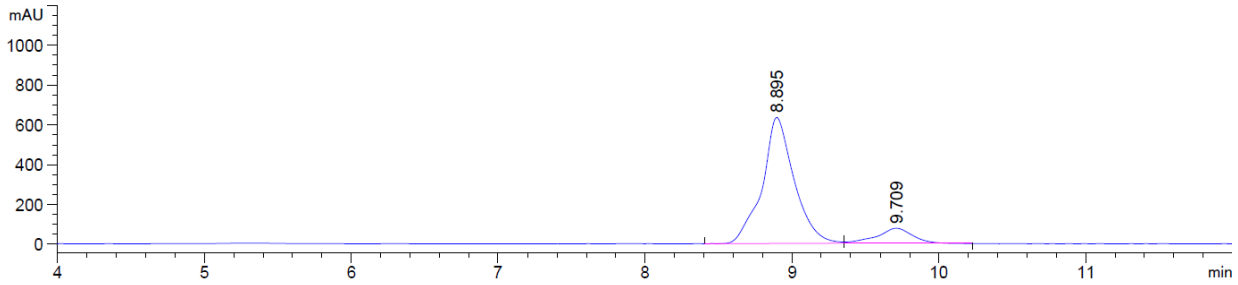
HPLC conditions: IB column, 1mL/min, 0.3% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



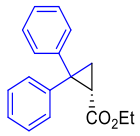
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	8.5	10617.7	50.5
2	9.3	10387.9	49.5

HPLC (Chiral)

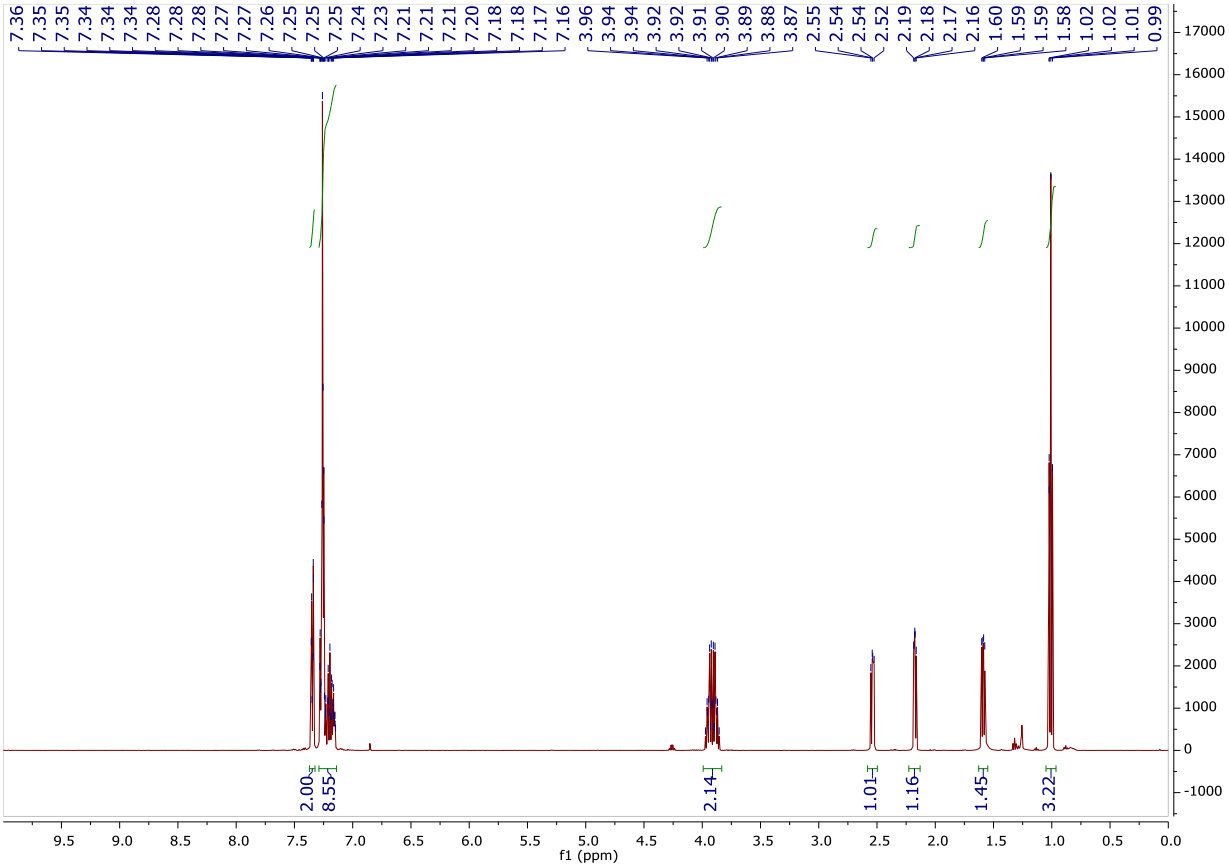


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	8.9	21716.3	89.4
2	9.7	2580.50	10.6

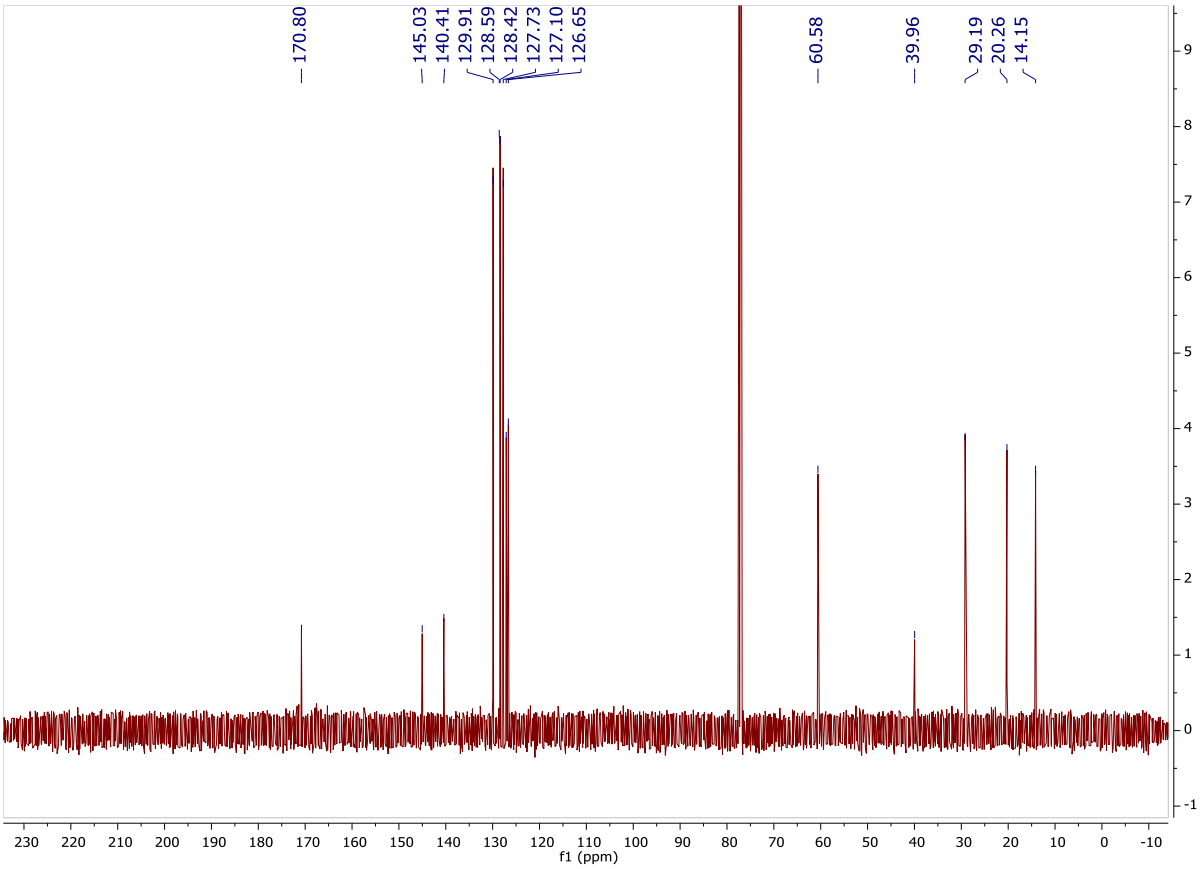
Ethyl (S)-2,2-diphenylcyclopropane-1-carboxylate (5l).



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

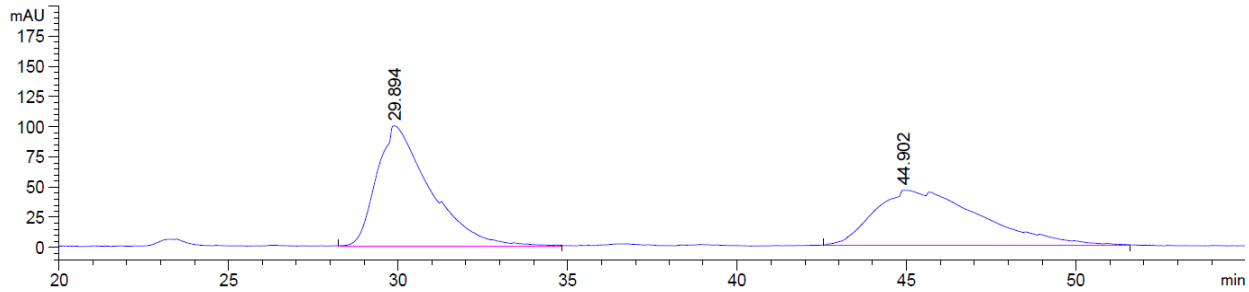


^{13}C NMR (126 MHz, $CDCl_3$):



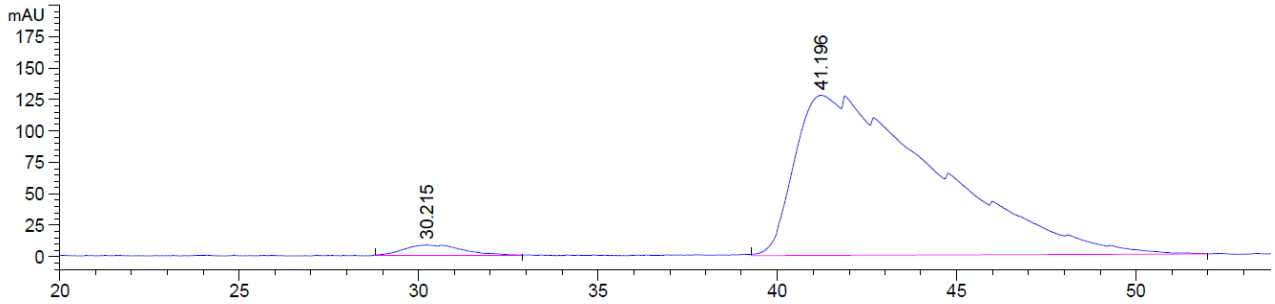
HPLC conditions: OJ-H column, 1mL/min, 0.7% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



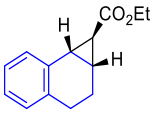
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	29.9	10908.2	51.8
2	44.9	10134.4	48.2

HPLC (Chiral)

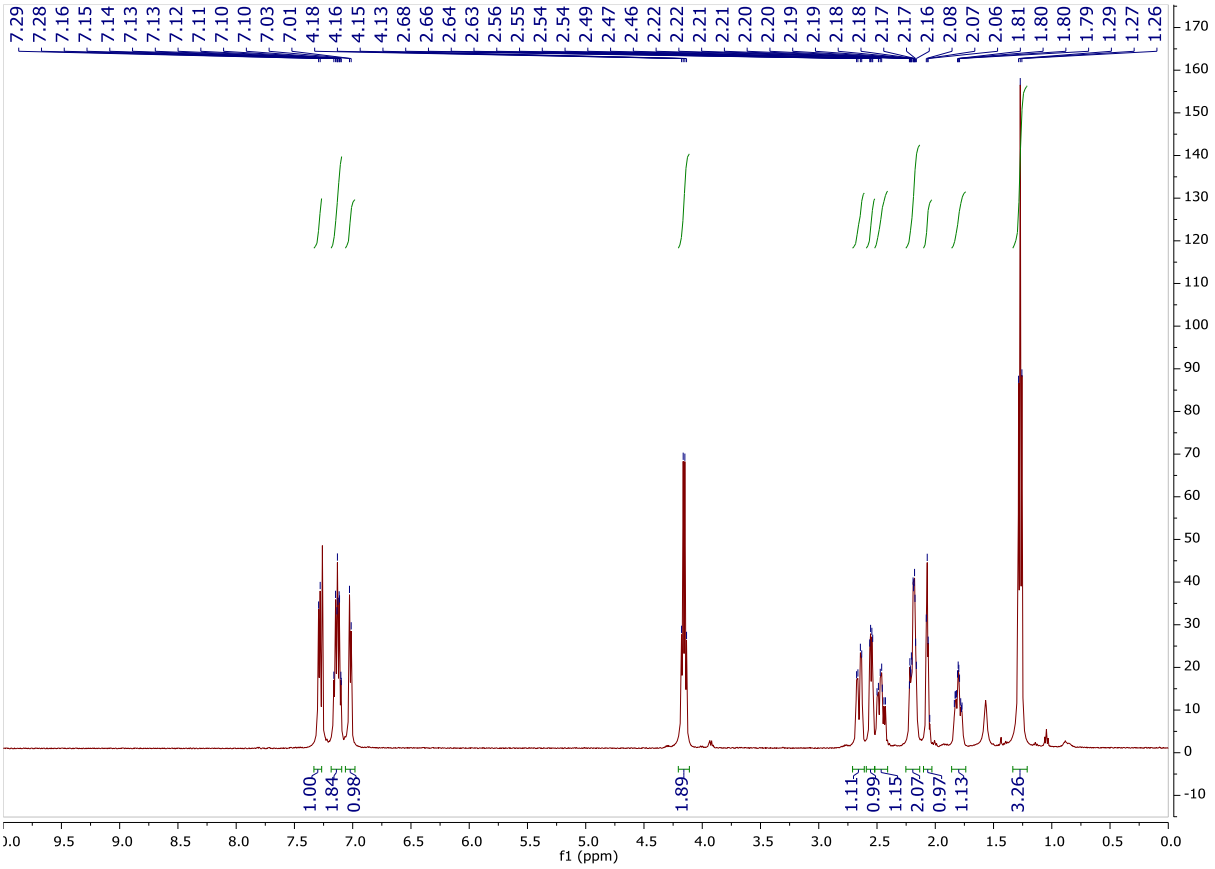


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	30.2	1069.77	2.9
2	41.3	35755.0	97.1

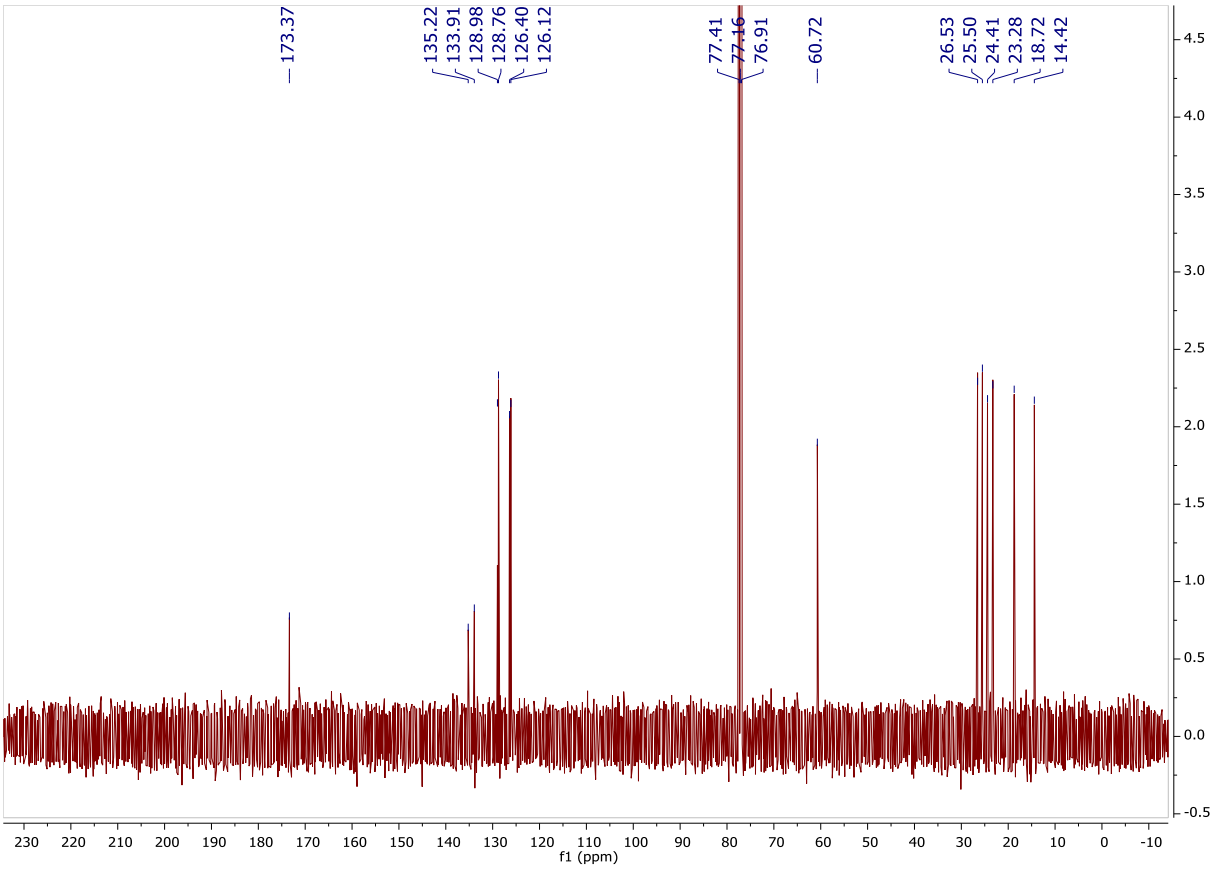
Ethyl (1S)-1a,2,3,7b-tetrahydro-1H-cyclopropa[a]naphthalene-1-carboxylate (5m).



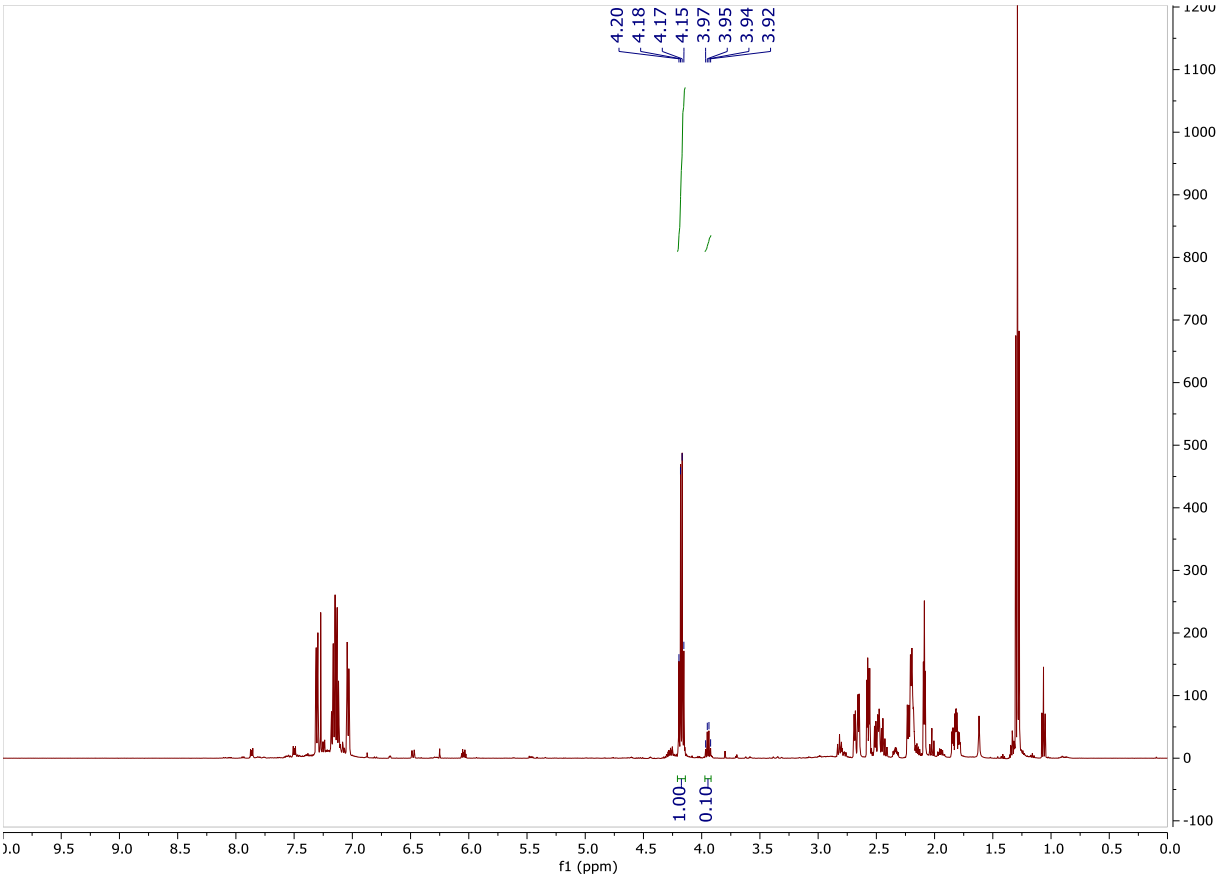
^{1}H NMR (500 MHz, $CDCl_3$):



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

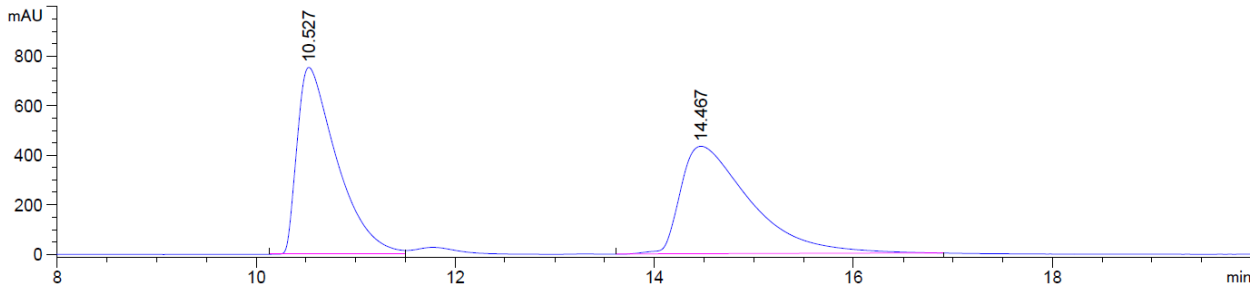


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Trans (4.18 ppm), Cis (3.95 ppm), Ratio: 91:9.



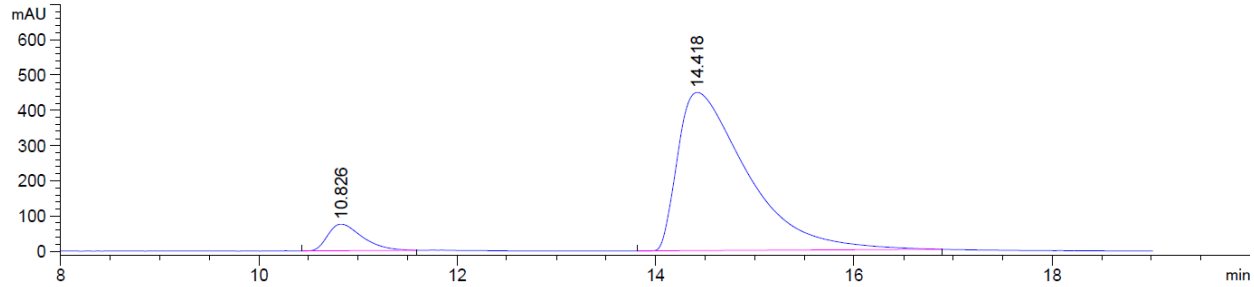
HPLC conditions: OJ-H column, 1mL/min, 0.4% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



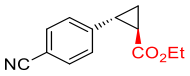
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	10.5	20943.3	49.6
2	14.5	21303.4	50.4

HPLC (Chiral)

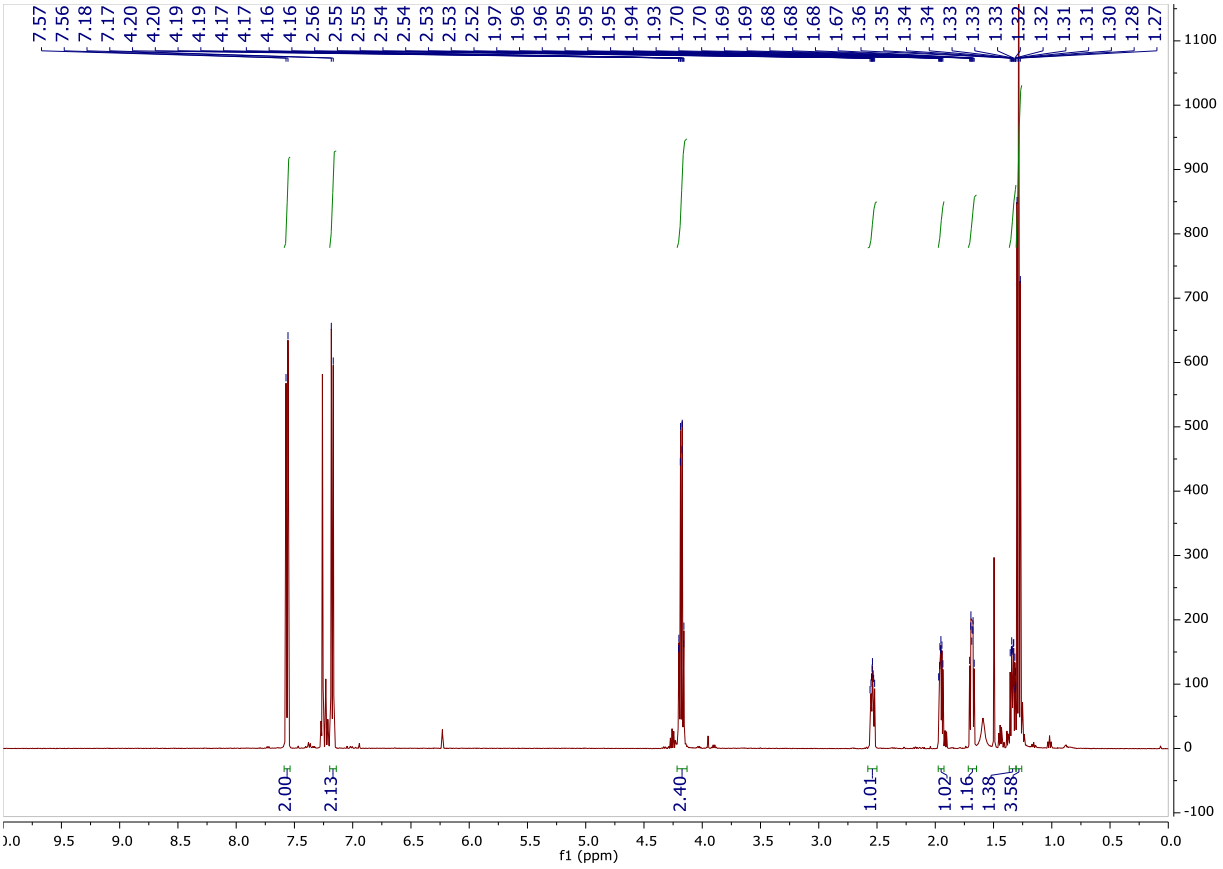


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	10.8	1843.01	7.7
2	14.4	21940.6	92.3

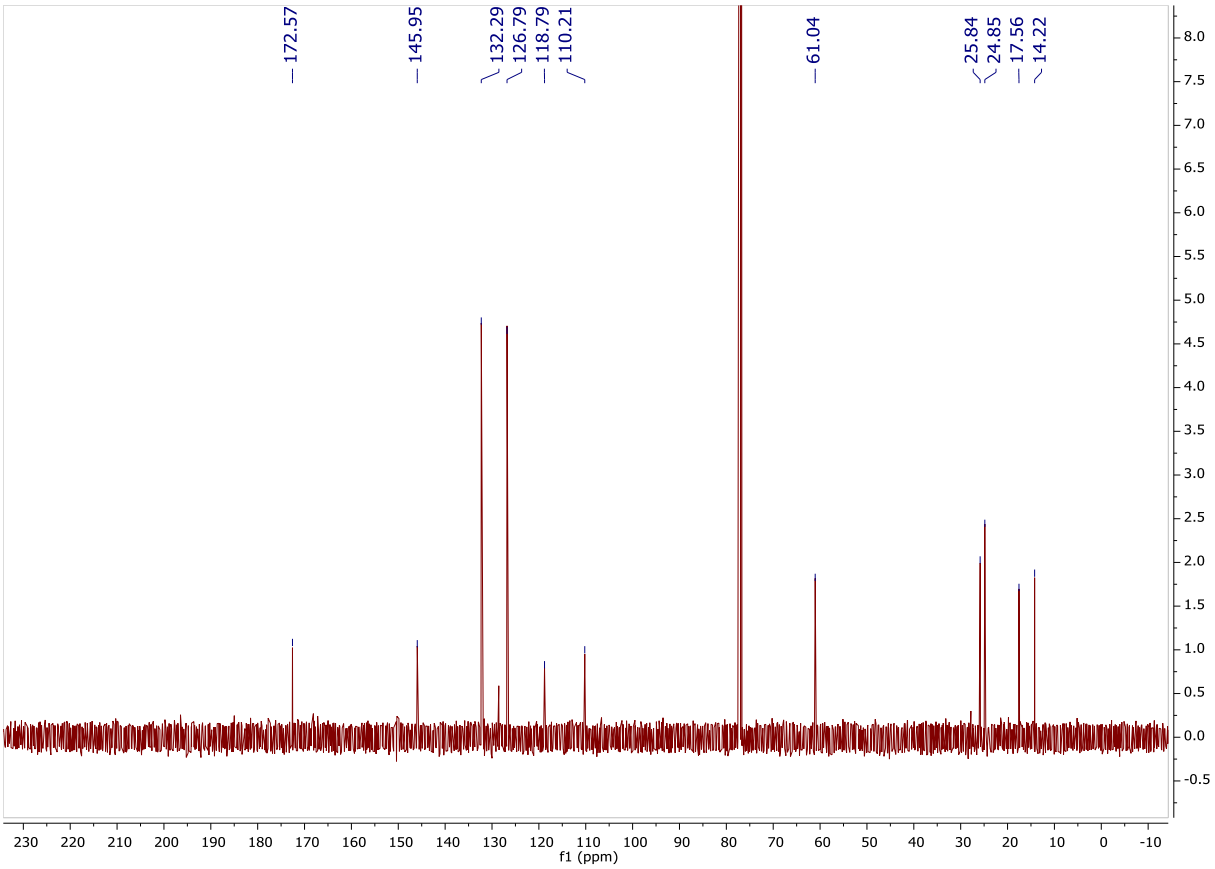
Ethyl (1R,2R)-2-(4-cyanophenyl)cyclopropane-1-carboxylate (5n).



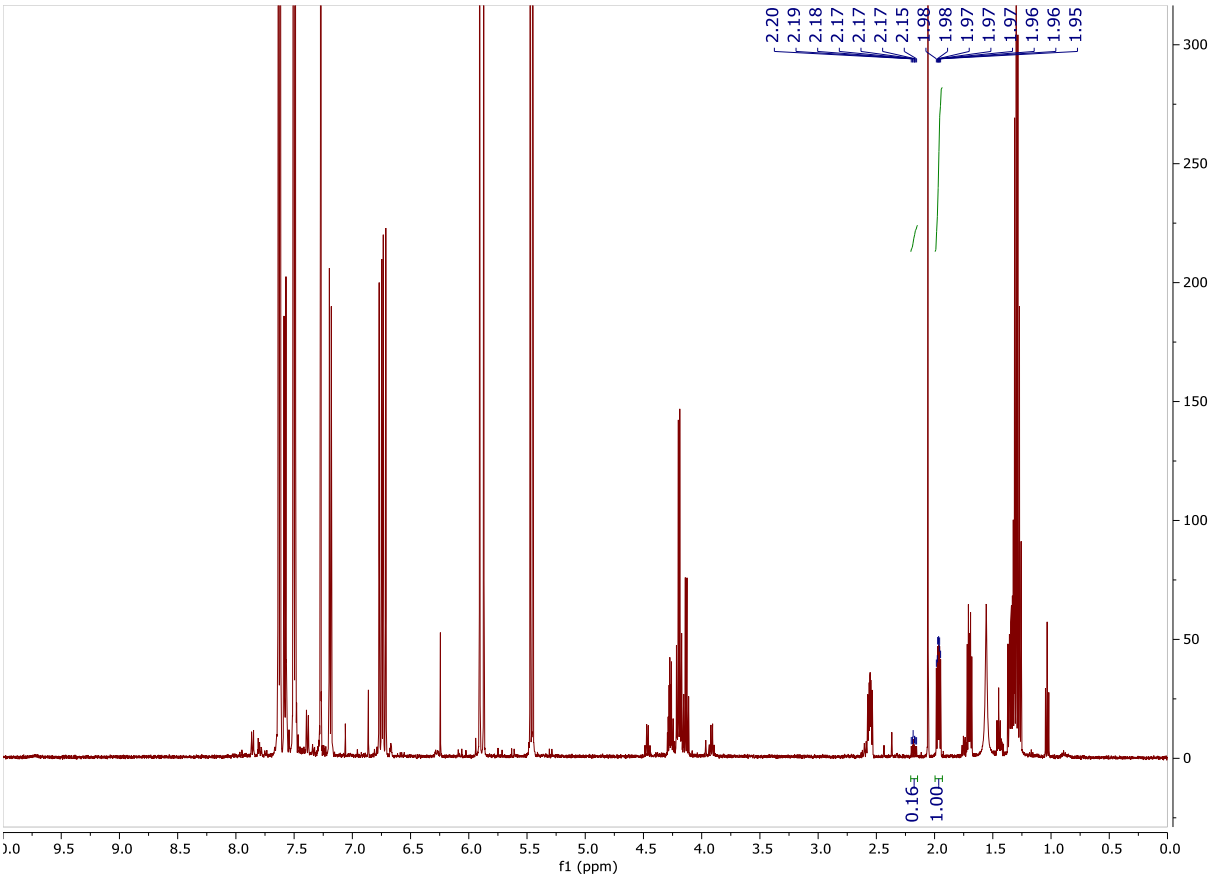
^{1}H NMR (500 MHz, $CDCl_3$):



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

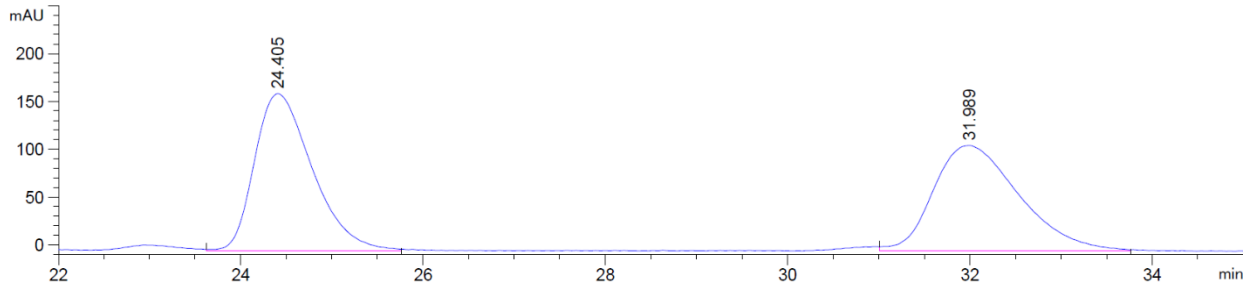


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Cis (2.17 ppm), Trans (1.97 ppm). Ratio: 86:14.



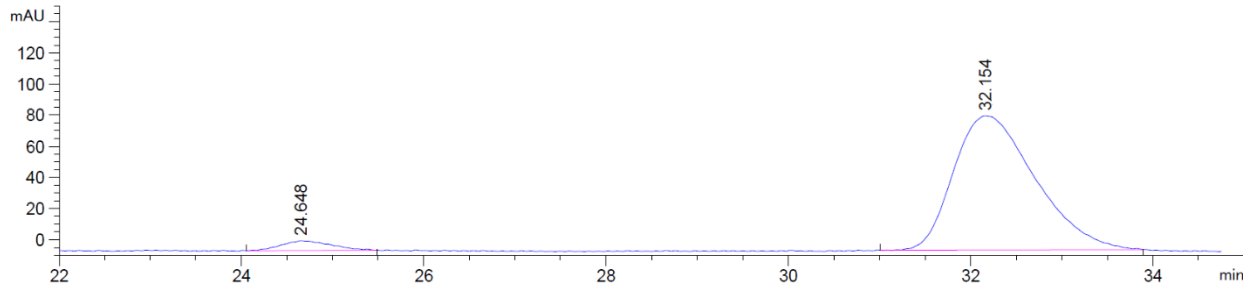
HPLC conditions: AS-H column, 1mL/min, 1.8% ^{i}PrOH/Hexanes, 254 nm UV detector.

HPLC (Racemic)



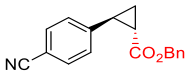
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	24.4	7281.75	50.0
2	32.0	7280.48	50.0

HPLC (Chiral)

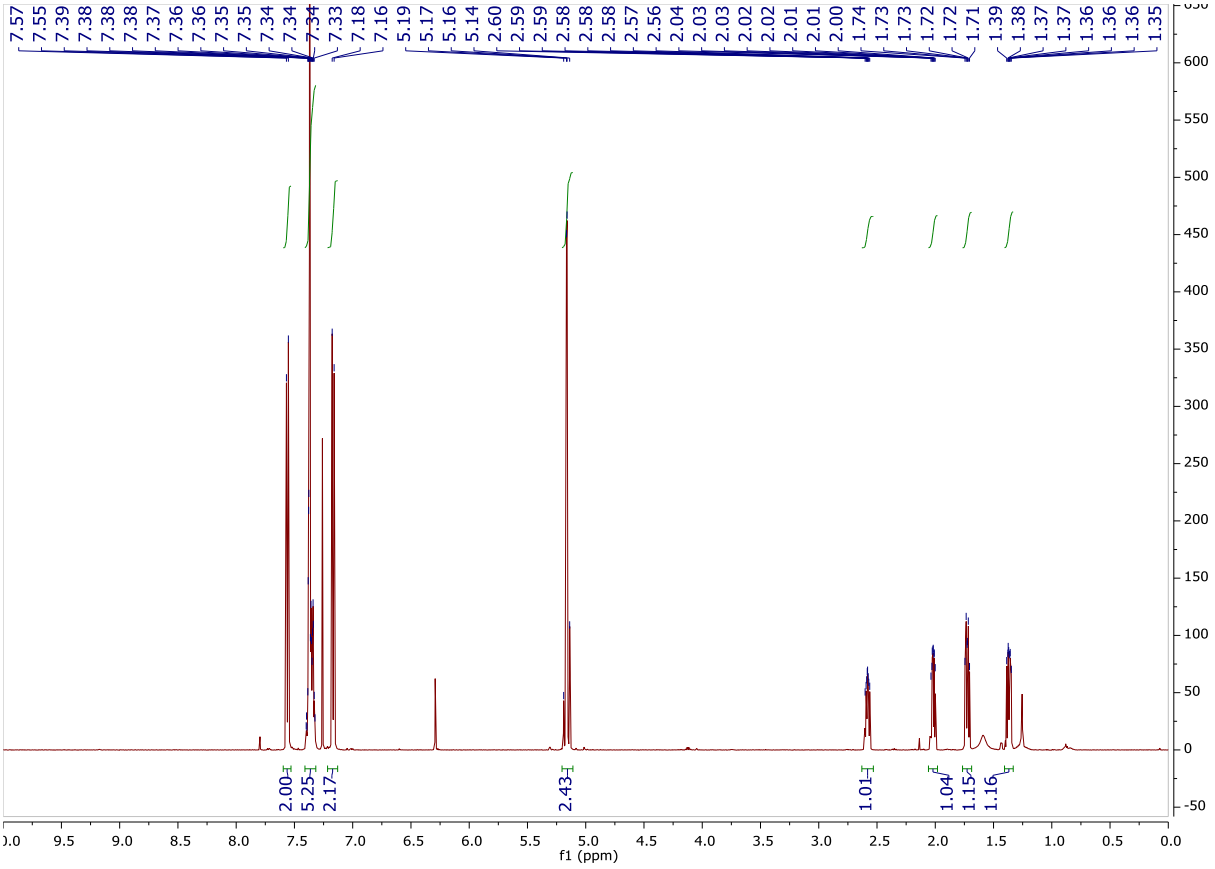


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	24.7	251.275	4.5
2	32.2	5386.37	95.5

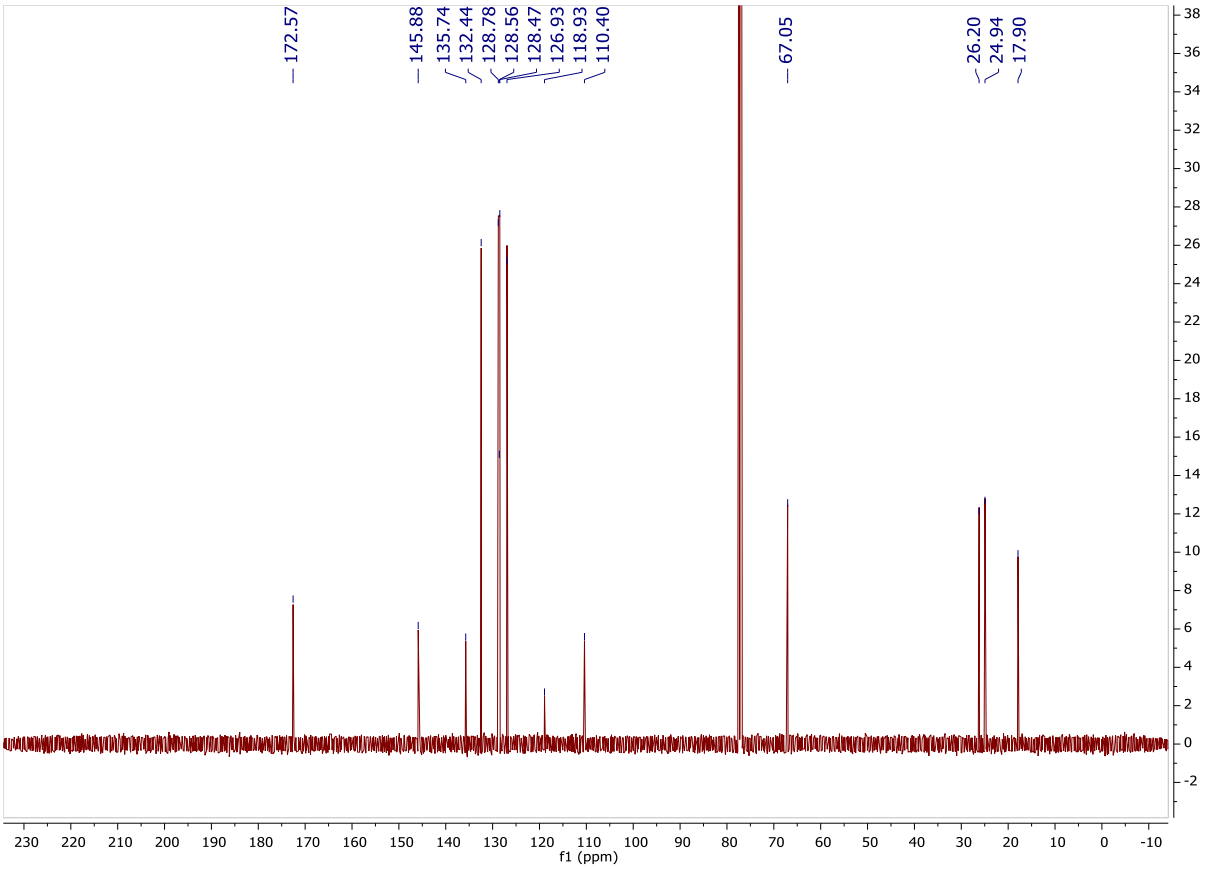
Benzyl (1S,2S)-2-(4-cyanophenyl)cyclopropane-1-carboxylate (5o).



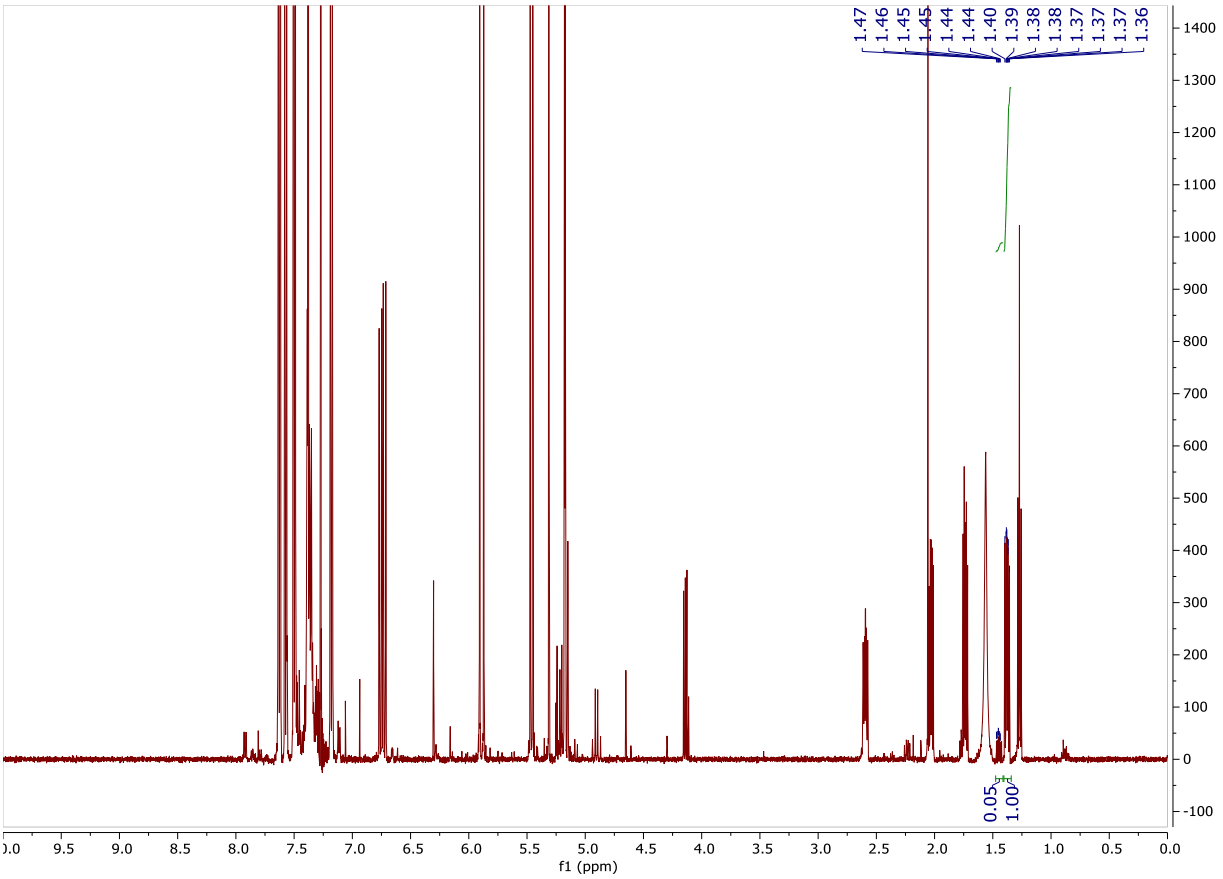
^{1}H NMR (500 MHz, $CDCl_3$):



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

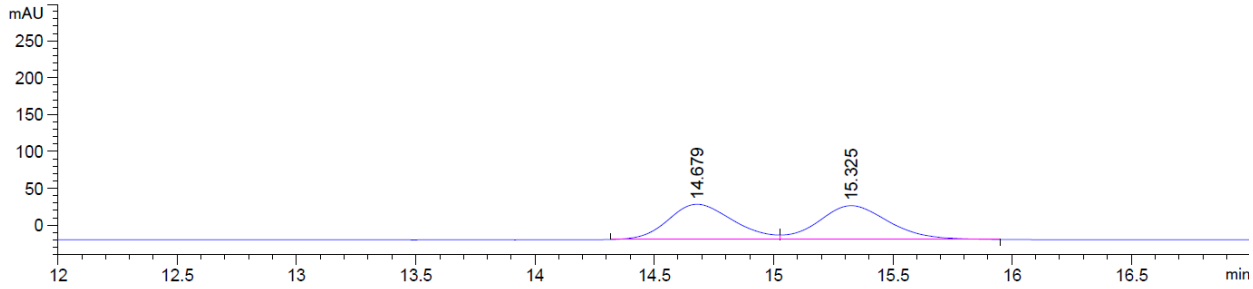


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Cis (1.45 ppm), Trans (1.38 ppm), Ratio: 95:5.



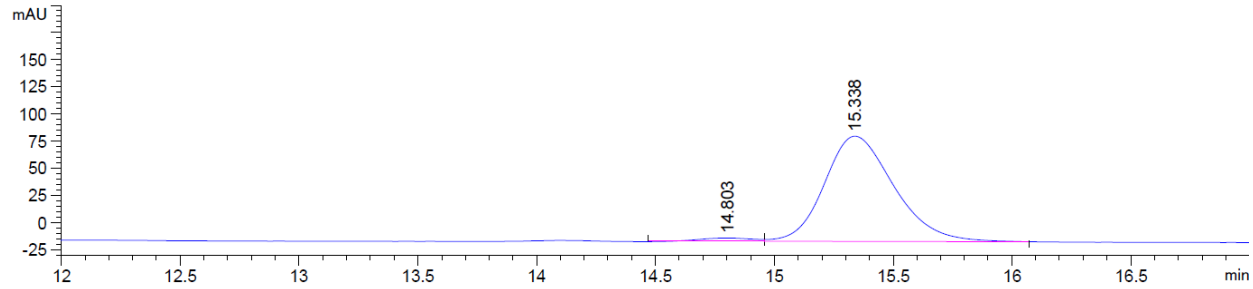
HPLC conditions: IB column, 1mL/min, 3% ^{i}PrOH/Hexanes, 254 nm UV detector.

HPLC (Racemic)



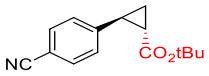
Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	14.7	918.374	49.2
2	15.3	949.119	50.8

HPLC (Chiral)

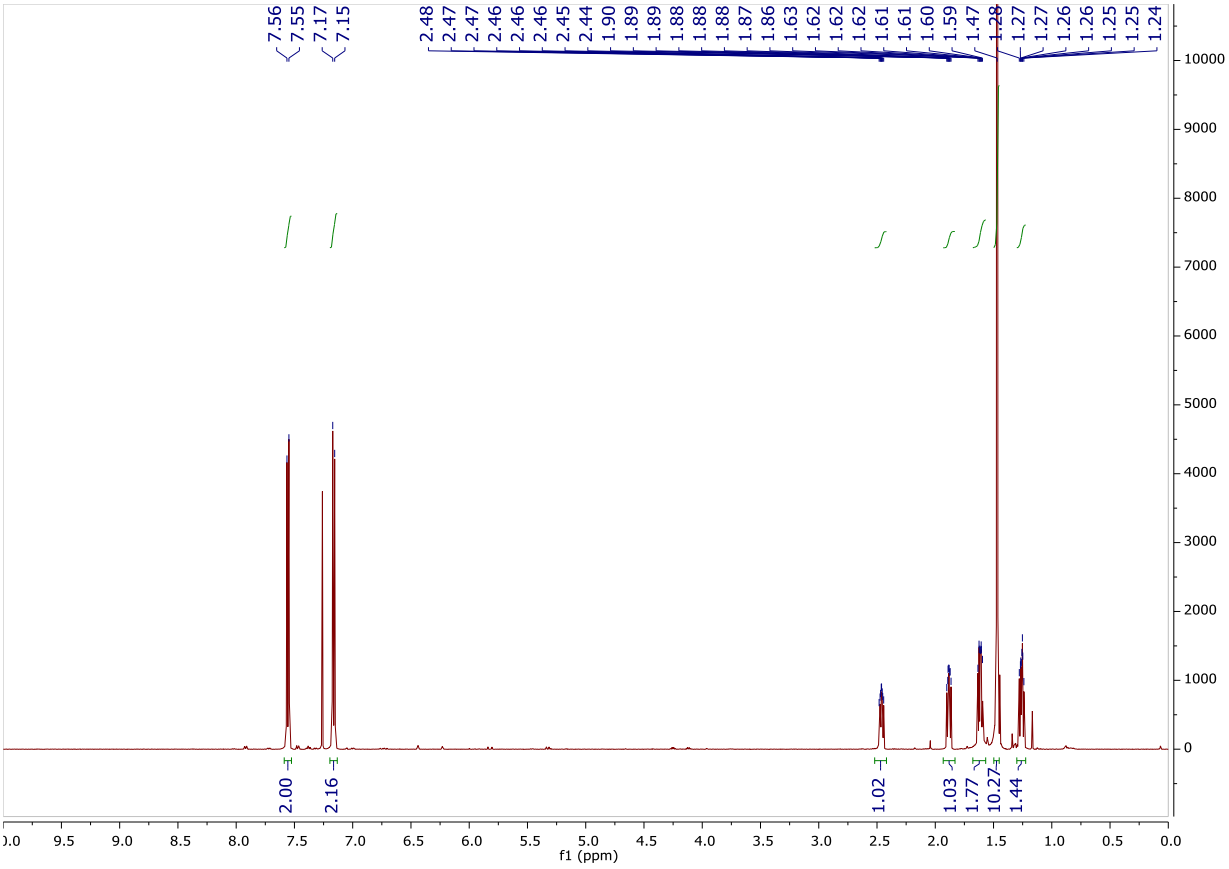


Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	14.8	56.5436	2.8
2	15.3	1992.39	97.2

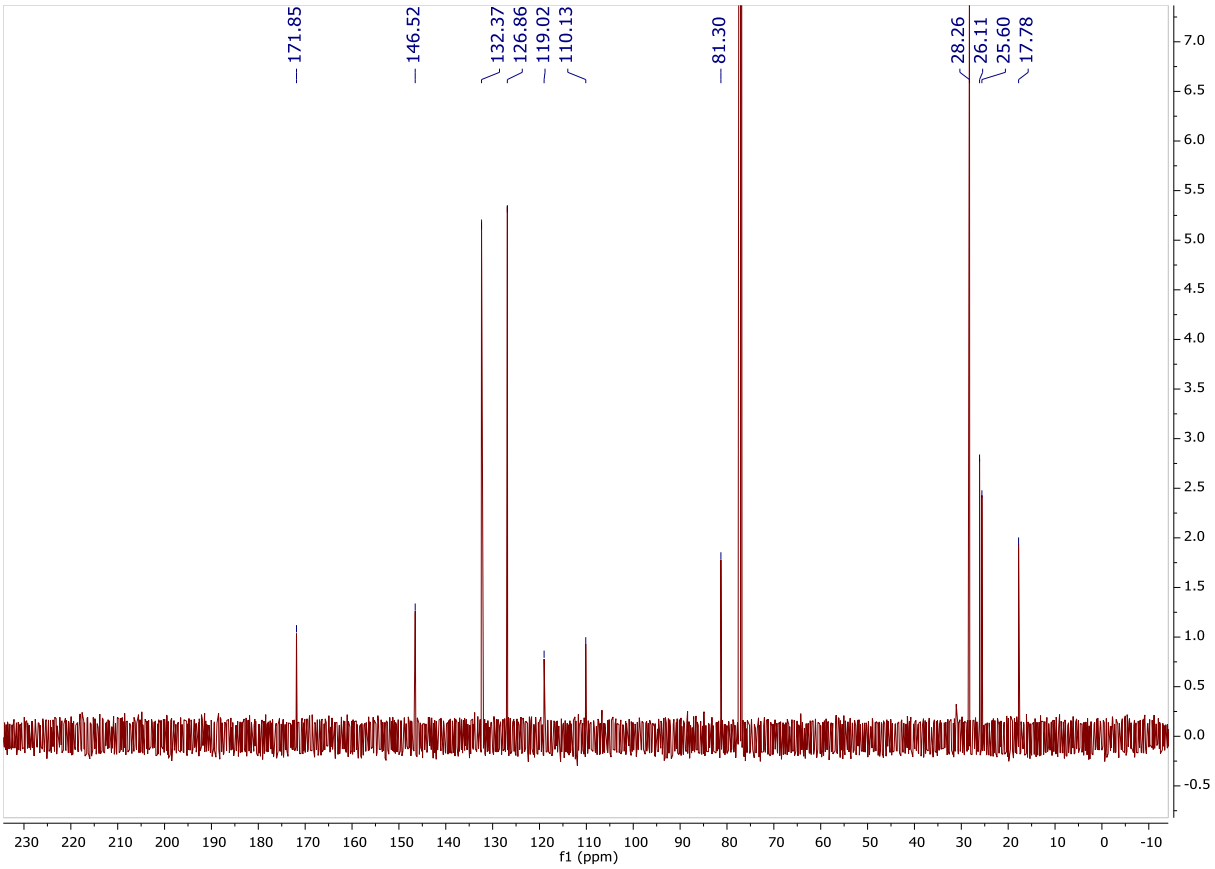
***tert*-butyl (1S,2S)-2-(4-cyanophenyl)cyclopropane-1-carboxylate (5p).**



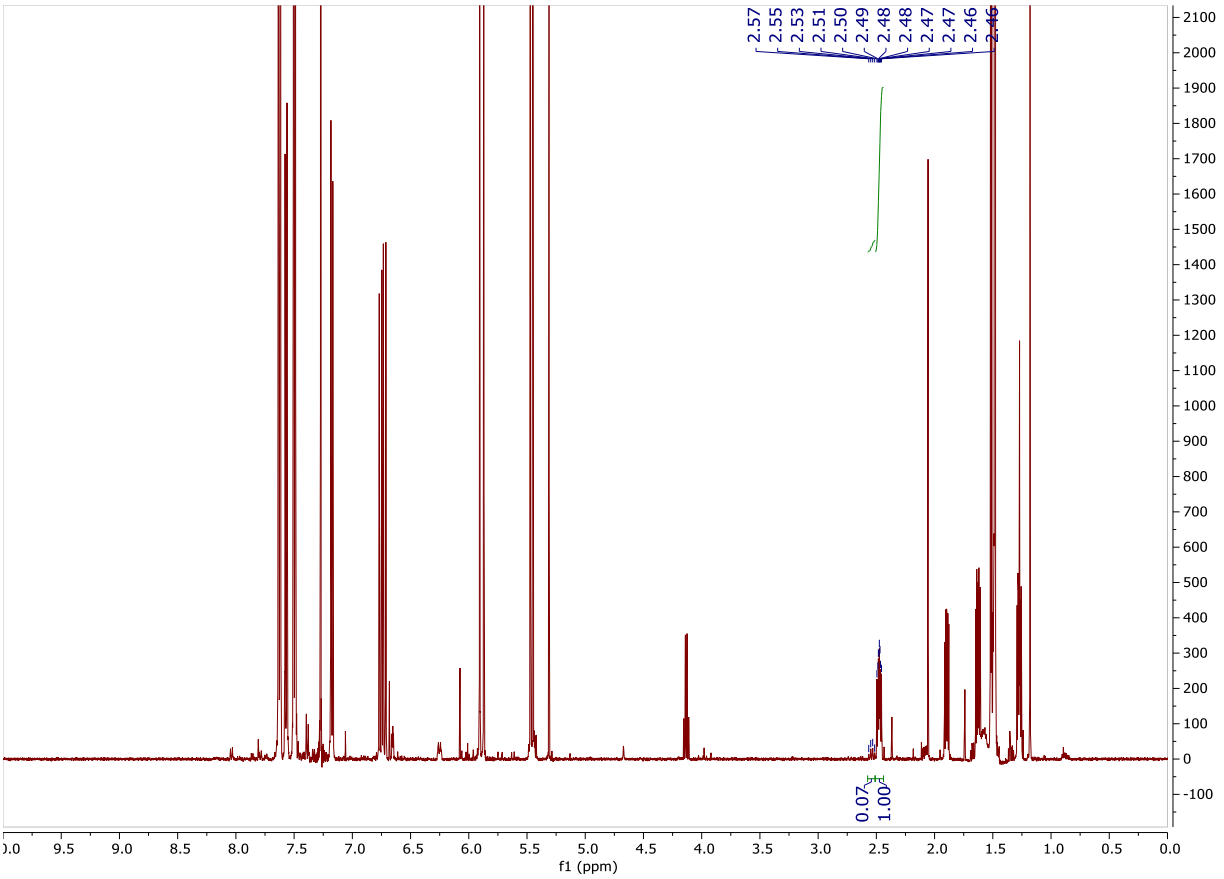
^{1}H NMR (500 MHz, $CDCl_3$):



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

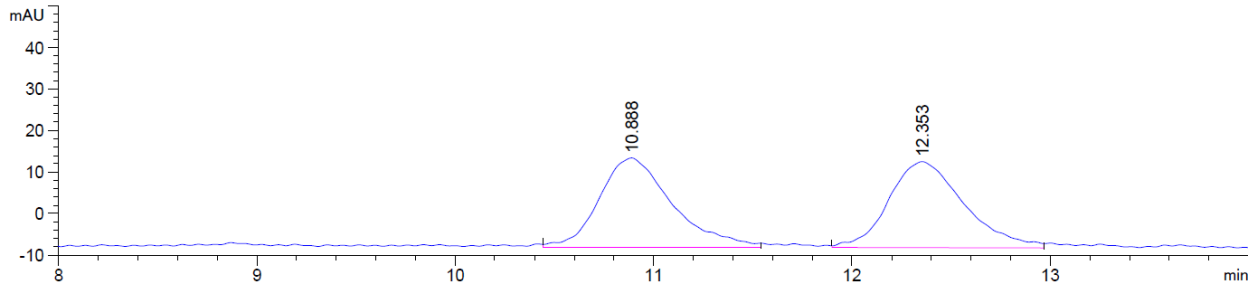


Diastereomeric ratios NMR ($CDCl_3$, 500 MHz): Cis (2.54 ppm), Trans (2.48 ppm), Ratio: 93:7.



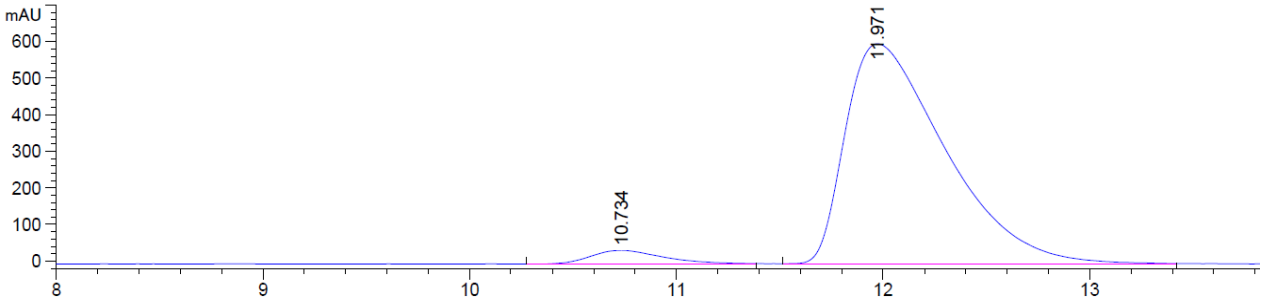
HPLC conditions: AS-H column, 1mL/min, 1% ^{i}PrOH/Hexanes, 230 nm UV detector.

HPLC (Racemic)



Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	10.9	553.481	50.2
2	12.4	548.232	49.8

HPLC (Chiral)



Peak #	RetTime (min)	Area (mAU*s)	Area (%)
1	10.7	924.450	95.6
2	12.0	20227.8	4.4

IX. References

(1) C. Simonin, M. Awale, M. Brand, R. van Deursen, J. Schwartz, M. Fine, G. Kovacs, P. Häfliger, G. Gyimesi, A. Sithampari, R.-P. Charles, M. A. Hediger and J.-L. Reymond, Angewandte Chemie International Edition, 2015, 54, 14748–14752.
(2) S. Narute, R. Parnes, F. D. Toste and D. Pappo, J. Am. Chem. Soc., 2016, 138, 16553–16560.
(3) H.-R. Tong, W. Zheng, X. Lv, G. He, P. Liu and G. Chen, ACS Catal., 2020, 10, 114–120.
(4) T. R. Wu, L. Shen and J. M. Chong, Org. Lett., 2004, 6, 2701–2704.
(5) K. B. Simonsen, K. V. Gothelf and K. A. Jørgensen, J. Org. Chem., 1998, 63, 7536–7538.
(6) Y. Zhang, Z. Zhang, S. Ma, J. Jia, H. Xia and X. Liu, J. Mater. Chem. A, 2021, 9, 25369–25373.
(7) I. Ahmed and D. A. Clark, Org. Lett., 2014, 16, 4332–4335.
(8) A. Jolit, P. M. Walleser, G. P. A. Yap and M. A. Tius, Angewandte Chemie International Edition, 2014, 53, 6180–6183.
(9) R. Singh, C. Czekelius, R. R. Schrock, P. Müller and A. H. Hoveyda, Organometallics, 2007, 26, 2528–2539.
(10) Y.-L. Zhang, F. Zhang, W.-J. Tang, Q.-L. Wu and Q.-H. Fan, Synlett, 2006, 2006, 1250–1254.
(11) D. B. Llewellyn, D. Adamson and B. A. Arndtsen, Org. Lett., 2000, 2, 4165–4168.
(12) A. Solladié-Cavallo, A. Diep-Vohuule and T. Isarno, Angewandte Chemie International Edition, 1998, 37, 1689–1691.
(13) K. Kisiel, R. Loska and M. Mąkosza, Synthesis, 2022, 54, 2289–2297.
(14) Y. Chen and X. P. Zhang, *J. Org. Chem.*, 2007, **72**, 5931–5934.
(15) A. G. Herraiz and M. G. Suero, *Chem. Sci.*, 2019, **10**, 9374–9379.
(16) O. V. Hryschuk, Y. Yurov, A. V. Tymtsunik, V. O. Kovtunenko, I. V. Komarov and O. O. Grygorenko, *Advanced Synthesis & Catalysis*, 2019, **361**, 5428–5439.
(17) S. S. Hixson, L. A. Franke, J. A. Gere and Y. De. Xing, *J. Am. Chem. Soc.*, 1988, **110**, 3601–3610.
(18) S. Tyagi, C. D. Cook, D. A. DiDonato, J. A. Key, B. P. McKillican, W. J. Eberle, T. J. Carlin, D. A. Hunt, S. J. Marshall and N. L. Bow, *J. Org. Chem.*, 2015, **80**, 11941–11947.
(19) S. Fantauzzi, E. Gallo, E. Rose, N. Raoul, A. Caselli, S. Issa, F. Ragaini and S. Cenini, *Organometallics*, 2008, **27**, 6143–6151.
(20) M. Z. Gao, B. Wang, D. Kong, R. A. Zingaro, A. Clearfield and Z. L. Xu, *Synthetic Communications*, 2005, **35**, 2665–2673.
(21) K. Nishikawa, H. Fukuda, M. Abe, K. Nakanishi, Y. Tazawa, C. Yamaguchi, S. Hiradate, Y. Fujii, K. Okuda and M. Shindo, *Phytochemistry*, 2013, **96**, 223–234.
(22) Bruker. APEX3; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
(23) L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J Appl Cryst*, 2015, **48**, 3–10.
(24) Sheldrick, G. M. Acta Cryst. C71, 2015, 3-8.
(25) C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J Appl Cryst*, 2011, **44**, 1281–1284.
(26) C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J Appl Cryst*, 2020, **53**, 226–235.
(27) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. a. K. Howard and H. Puschmann, *J Appl Cryst*, 2009, **42**, 339–341.