Regioselective and Stereoselective Rhodium(II)-Catalyzed C–H Functionalization of Cyclobutanes

Supporting Information

Experimental procedures and characterization data for new compounds.

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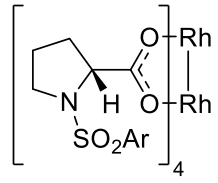
General Considerations: Reactions were carried out under argon in flame-dried or oven-dried glassware unless otherwise specified. Dichloromethane, diethyl ether, tetrahydrofuran, and toluene were purified using a GlassContour solvent system. Chloroform used for C–H functionalization reactions was dried over 4Å molecular sieves and degassed for 1 h with argon and stored under argon for 24 h prior to use. Dichloromethane and 1,2-dichloroethane were distilled under argon from calcium hydride onto molecular sieves and stored under argon for 24 h prior to use. ^{1}H NMR spectra were recorded at either 300 MHz, 400 MHz, 500 MHz, or 600 MHz on Mercury-300, Varian-400, Varian-500, or Bruker 600 spectrometers. ^{13}C NMR spectra were recorded at either 75 MHz, 100 MHz, 126 MHz, or 151 MHz on Mercury-300, Varian-400, Varian-500, or Bruker 600 spectrometers. ^{19}F NMR spectra were recorded at 282 on Varian-300 spectrometer. NMR spectra were obtained from solutions of deuterated chloroform ($CDCl_3$) with residual solvent serving as internal standard (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C). NMR shifts were reported in parts per million (ppm). Abbreviations for signal multiplicity are as follow: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. Coupling constants (*J* values) were calculated directly from the spectra. IR spectra were collected on a Nicolet iS10 FT-IR spectrometer. Mass spectra were taken on a Thermo Finnigan LTQ-FTMS spectrometer with APCI, ESI or NSI. Thin layer chromatographic analysis was performed with glass-backed silica gel plates, visualizing with UV light, and staining with aqueous $KMnO_4$ or cerium molybdate stain. Racemic standards were generated by performing reactions with $Rh_2(OAc)_4$ or from Rh_2(*R*/*S*-DOSP)$_4$ or Rh_2(R/S-2Cl-TPCP)$_4$ which was generated by dissolving an equimolar mixture of the *R* and *S* catalyst in a minimal amount of benzene and lyophilizing.

Figure S1. Catalyst Structures.

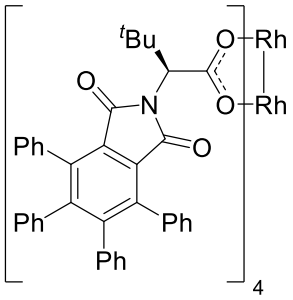
The following catalysts were used in this study and have been prepared previously.

Rh_2(*S*-DOSP)$_4$[1]

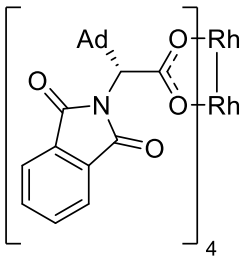


Ar = *p*-$C_{12}H_{25}C_6H_4$

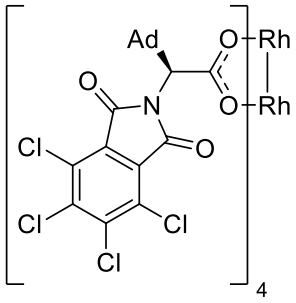
Rh_2(*S*-TPPTTL)$_4$[2]



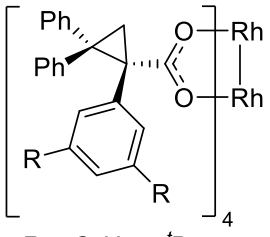
Rh_2(*R*-PTAD)$_4$[3]



Rh_2(*S*-TCPTAD)$_4$[4]

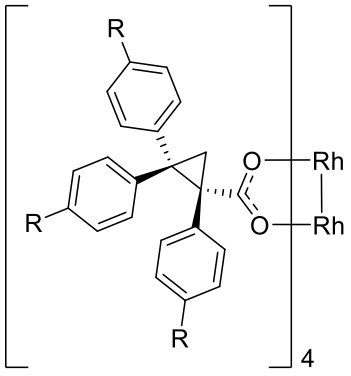


Rh_2(*R*-DiBic)$_4$[5]



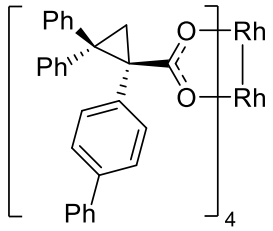
R = C_6H_4-*p*-^{t}Bu

Rh_2(*R*-TriBic)$_4$

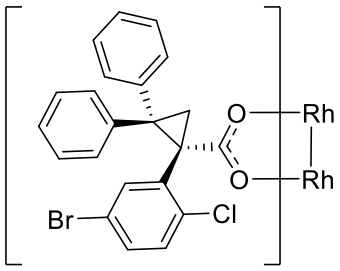


R = C_6H_4-*p*-^{t}Bu

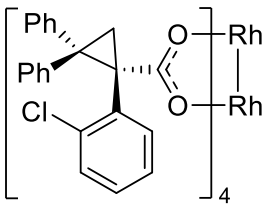
Rh_2(*S*-*p*-Ph-TPCP)$_4$[6]



Rh_2(*S*-2Cl-5Br-TPCP)$_4$[7]



Rh_2(*S*-2Cl-TPCP)$_4$[8]



Synthesis of Substrates and Reagents

Synthesis of Diazos Compounds:

The following diazoacetates were prepared previously:

2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**7**)[9]

2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate[10]

2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate[9]

2,2,2-trichloroethyl 2-(4-acetoxyphenyl)-2-diazoacetate[10]

2,2,2-trichloroethyl 2-diazo-2-(4-fluorophenyl)acetate[9]

2,2,2-trichloroethyl 2-diazo-2-(p-tolyl)acetate[10]

2,2,2-trichloroethyl 2-(4-(tert-butyl)phenyl)-2-diazoacetate[9]

2,2,2-trichloroethyl 2-diazo-2-(3-methoxyphenyl)acetate[10]

2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate[10]

2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate[5]

2,2,2-trichloroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate[10]

Synthesis of Aryl Cyclobutanes

The synthesis of most aryl-substituted cyclobutanes could be accomplished by utilizing a Grignard reagent addition to cyclobutanone followed by reduction of the tertiary alcohol in one step or two steps (elimination followed by hydrogenation). Heteroaryl-substituted cyclobutanes were synthesized as follows:

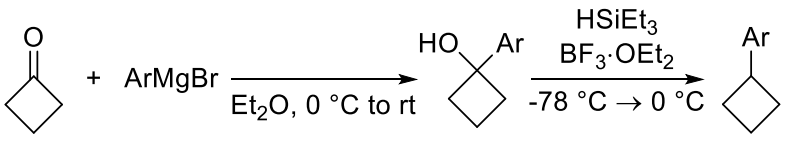
4-cyclobutyl-2,6-dimethylpyridine was prepared according to a literature procedure[11]. Characterization data for this compound were consistent with those reported in the original paper.

5-cyclobutyl-2-methoxypyridine was prepared via the Negishi coupling reaction of 5-bromo-2-methoxypyridine with cyclobutylzinc bromide. Characterization data for the product were consistent with those previously reported in the chemical literature[12].

General Procedure 1 for the Synthesis of Aryl Substituted Cyclobutanes

The aryl substituted cyclobutanes were generated by a two step sequence (Scheme S1).

Scheme S1. Synthesis of aryl cyclobutanes using General Procedure 1.



General Procedure 1, Part A

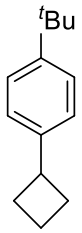
A 3-necked round-bottom flask was equipped with a condenser and addition funnel, and then it was flame-dried under vacuum. After cooling under argon, magnesium (2.5 equiv) was added. The Grignard reagent was formed by the dropwise addition of the corresponding aryl bromide (1.5 equiv) in Et_2O (1 M to the aryl bromide). The Grignard reagent was formed by heating to reflux for 5 h. After formation of the Grignard reagent, the solution was cooled to 0 °C, and then cyclobutanone (1.0 equiv) was added as a solution in ether (0.4 M to cyclobutanone). The reaction mixture was allowed to come to room temperature, and then stirred overnight. The reaction was quenched by the addition of saturated ammonium chloride at 0 °C. The aqueous layer was extracted 3x50 mL ether. The organics were combined and then washed with brine. The organic layer was dried with magnesium sulfate, filtered, and then residual solvent was removed under reduced pressure. The crude material was purified by silica gel chromatography using hexanes/ethyl acetate as eluent.

General Procedure 1, Part B

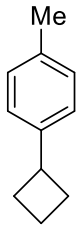
A round-bottom flask was flame-dried and then cooled under argon. The tertiary alcohol was added (1.0 equiv) followed by anhydrous dichloromethane (0.25 M to the tertiary alcohol). Triethylsilane was added, and then the reaction mixture was cooled to -78 °C. Once the mixture was cooled, $BF_3 \cdot OEt_2$ (3.2 equiv) was added dropwise. The reaction mixture was stirred at -78 °C for 30 minutes, and then was stirred at -40 °C for 30 minutes and then was stirred at 0 °C for 60 minutes. The reaction mixture was slowly quenched by an equal volume of saturated sodium bicarbonate at 0 °C. The layers were separated,

and then the aqueous layer was extracted 3 x 50 mL dichloromethane. The organics were combined, dried with magnesium sulfate, filtered, and then the solvent was removed under reduce pressure. The aryl-substituted cyclobutanes were purified by column chromatography on silica gel using pentanes as eluant and/or Kugelrohr distillation.

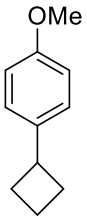
Note: The addition of heteroaromatic-based Grignard reagents was accomplished using methods developed by Senanayake and coworkers.[13]



1-(*Tert*-butyl)-4-cyclobutylbenzene (6). The title compound was prepared by the reduction of 1-(4-(*tert*-butyl)phenyl)cyclobutan-1-ol[14] (5.24 g, 25.6 mmol) as outlined in General Procedure 1. The cyclobutane was purified by column chromatography using pentanes as eluant. This procedure afforded the title compound (4.5 g, 94%) as a colorless oil. The spectrum was consistent with previously reported ^{1}H NMR spectra[15]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 3.52 (p, J = 8.8 Hz, 1H), 2.38–2.26 (m, 2H), 2.22–2.08 (m, 2H), 2.07–1.93 (m, 1H), 1.91–1.77 (m, 1H), 1.32 (s, 9H).

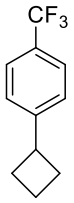


1-Cyclobutyl-4-methylbenzene. The title compound was prepared by the reduction of 1-(p-tolyl)cyclobutan-1-ol[16] (4.1 g, 25 mmol) as outlined in General Procedure 1. The cyclobutane was purified by Kugelrohr distillation (65 °C at 0.5 mmHg). This procedure afforded the title compound (659 mg, 18%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.17 (m, 4H), 3.60 (p, *J* = 8.7 Hz, 1H), 2.49–2.36 (m, 5H), 2.28–2.17 (m, 2H), 2.14–2.03 (m, 1H), 2.00–1.89 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 135.2, 129.0, 126.3, 40.2, 30.1, 21.1, 18.4; IR (neat) 2972, 2937, 2862, 1513, 1444, 1243, 1118. 811, 724 cm^{-1}. MS (APCI+) 147.11736 (147.11683 calcd for $C_{11}H_{15}$, M + H^{+}).

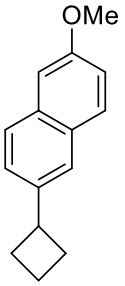


1-cyclobutyl-4-methoxybenzene. The title compound was prepared by the reduction of 1-(4-methoxyphenyl)cyclobutan-1-ol[16] (4.5 g, 25 mmol) as outlined in General Procedure 1. The cyclobutane was purified by Kugelrohr distillation (82-83 °C at 0.5 mmHg). This procedure afforded the title compound (3.05 g, 75%) as a colorless oil. The spectrum was consistent with previously reported ^{1}H NMR spectra[17]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17–7.13 (m, 2H), 6.87–6.82 (m, 2H), 3.79 (s, 3H), 3.54–3.42 (m, 1H), 2.35–2.27 (m, 2H),

2.15–2.04 (m, 2H), 2.04–1.92 (m, 1H), 1.88–1.78 (m, 1H).

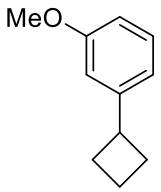


1-cyclobutyl-4-(trifluoromethyl)benzene. The title compound was prepared by the reduction of 1-(4-(trifluoromethyl)phenyl)cyclobutan-1-ol[18] (5.40 g, 25 mmol) as outlined in General Procedure 1. The cyclobutane was purified by Kugelrohr distillation (46 °C at 0.5 mmHg) This procedure afforded the title compound (1.0 g, 20%) as a colorless oil. The spectrum was consistent with previously reported ^{1}H NMR spectra[19]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 3.60 (p, J = 8.7 Hz, 1H), 2.44–2.33 (m, 2H), 2.21–2.11 (m, 2H), 2.11–2.00 (m, 1H), 1.92–1.84 (m, 1H).



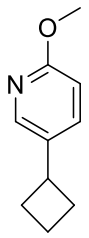
2-cyclobutyl-6-methoxynaphthalene. 1-(6-methoxynaphthalen-2-yl)cyclobutan-1-ol (10.0 g, 88% yield, mp 90–91 °C) was prepared by the addition of (6-methoxynaphthalen-2-yl)magnesium bromide to cyclobutanone using General Procedure 1, Part A. ^{1}H NMR (600 MHz, C_6D_6) δ 7.77 (s, 1H), 7.62 (t, J = 9.9 Hz, 2H), 7.54 (d, J = 8.9 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 6.96 (s, 1H), 3.41 (s, 3H), 2.54–2.45 (m, 2H), 2.39–2.27 (m, 3H), 1.96–1.86 (m, 1H), 1.63–1.53 (m, 1H); ^{13}C NMR (151 MHz, C_6D_6) δ 158.2, 142.1, 134.3, 130.1,

129.1, 127.5, 125.1, 123.4, 119.3, 106.0, 77.0, 54.8, 37.2, 13.5; IR (neat) 3365, 2975, 2938, 1629, 1605, 1484, 1501, 1451, 1386, 1264, 1241, 1176, 1147, 1131, 1112, 1024, 955, 923, 907, cm^{-1}. MS (APCI+) 227.10699 (227.10666 calcd for $C_{15}H_{15}O_2$, M + H^+ - H_2). The title compound was prepared by the reduction of 1-(6-methoxynaphthalen-2-yl)cyclobutan-1-ol (5.71 g, 25 mmol) as outlined in General Procedure 1, Part B. The cyclobutane was purified by eluting the crude material through a plug of silica using hexanes. This procedure afforded the title compound (2.1 g, 41%) as a colorless solid, mp 64–65 °C: ^{1}H NMR (600 MHz, C_6D_6) δ 7.57 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.44 (s, 1H), 7.23 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.17 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.92 (d, *J* = 2.5 Hz, 1H), 3.46 (p, *J* = 8.8 Hz, 1H), 3.36 (s, 3H), 2.20 (qt, *J* = 8.2, 2.3 Hz, 2H), 2.09 (pd, *J* = 9.4, 2.5 Hz, 2H), 1.89–1.79 (m, 1H), 1.76–1.68 (m, 1H); ^{13}C NMR (151 MHz, C_6D_6) δ 157.8, 141.5, 133.8, 129.7, 129.5, 127.2, 126.2, 124.6, 119.2, 106.0, 54.8, 40.8, 30.1, 18.7; IR (neat) 3008, 2961, 2938, 2886, 2861, 1630, 1601, 1483, 1461, 1388, 1352, 1260, 1202, 1162, 1117, 1029, 934, 881, 910, 815 cm^{-1}. MS (APCI+) 211.11202 (211.11174 calcd for $C_{15}H_{15}O$, M + H^+ - H_2).



1-Cyclobutyl-3-methoxybenzene. The title compound was prepared by the reduction of 1-(3-methoxyphenyl)cyclobutan-1-ol[20] (4.46 g, 25 mmol) as outlined in General Procedure 1. The cyclobutane was purified by Kugelrohr distillation (80 °C at 0.5 mmHg). This procedure afforded the title compound (1.14 g, 28%) as a colorless oil. The spectrum

was consistent with previously reported ^{1}H NMR spectra[21]: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.84–6.80 (m, 1H), 6.78 (t, *J* = 1.9 Hz, 1H), 6.72 (dd, *J* = 7.9, 2.9, 1H), 3.81 (s, 3H), 3.56–3.49 (m, 1H), 2.37–2.30 (m, 2H), 2.19–2.10 (m, 2H), 2.05–1.96 (m, 1H), and 1.88–1.81 (m, 1H).



5-cyclobutyl-2-methoxypyridine

A three-necked round bottom flask was charged with freshly ground magnesium turnings (540 mg, 1.00 equiv, 22.2 mmol), dry THF (62 mL), and a magnetic stirbar. Bromocyclobutane (3.09 g, 1.03 equiv, 22.9 mmol) was added dropwise to the stirring mixture as a neat liquid. The flask was heated at reflux for 16 h, which resulted in the near-complete reaction of magnesium to form a clear emerald green solution. At this stage, the mixture was cooled to -78 C using a bath of dry ice/acetone, and a solution of anhydrous zinc(II) bromide (5.00 g, 1.00 equiv, 22.2 mmol) in tetrahydrofuran (19.6 mL, 1.13 M) was added by syringe. The flask was removed from the cooling bath and after stirring at room temperature for 18 h, the mixture was diluted with an additional 35.0 mL THF. 5-bromo-2-methoxypyridine (2.09 g, 1.00 equiv, 11.1 mmol) was then added, followed by [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (812 mg, 10.0 mol%, 1.11 mmol). The mixture was heated at reflux for 16 h. Then it was filtered through silica gel (30 g), washing with additional diethyl ether (400 mL). Concentration of the filtrate gave 2.2 g of crude product as a turbid red oil. Kugelrohr distillation (air

bath temperature 97 °C at 0.6 mmHg) afforded 1.34 g of pure 5-cyclobutyl-2-methoxypyridine (74% yield). The ^{1}H NMR spectrum was consistent with previously reported data[12]: ^{1}H NMR (600 MHz, Chloroform-d) δ 7.95 (s, 1H), 7.44 (dd, 1H), 6.67 (d, 1H), 3.88 (s, 3H), 3.56 – 3.37 (m, 1H), 2.38 – 2.23 (m, 2H), 2.14 – 1.89 (m, 3H), 1.90 – 1.77 (m, 1H).

General Procedure 2 for C–H Functionalization Reactions.

An oven-dried vial was equipped with magnetic stir bar and sealed with septa and cap. This was cooled under vacuum, and then flame-dried once. After cooling to room temperature, the vial was loaded with rhodium catalyst (0.5-1 mol%), the indicated quantity of the cyclobutane substrate, and anhydrous solvent (2.0 mL solvent / 1.0 mmol cyclobutane). The mixture was allowed to stir under argon (the mixture was heated if heat was applied) while the diazo compound was prepared. A solution of the diazo compound was prepared by dissolving in the indicated solvent (3 mL solvent / 0.25 mmol diazo compound) and then this mixture was added dropwise by syringe pump over 3 h. Upon completion of the addition, the reaction was stirred an additional 2-4 h. Residual solvent was removed under reduced pressure (if the reaction was heated, it was allowed to come to room temperature before removing residual solvent), and the crude product was purified by silica gel chromatography.

Procedure for Analyzing Reaction Mixtures during Catalyst Screen

Reactions were conducted according to General Procedure 2 using 3 equiv. of the 1-(*tert*-butyl)-4-cyclobutylbenzene. The d at 3.62 ppm is represented by the *cis* secondary distal functionalization for compound **A**. The s at 3.99 ppm is represented by the tertiary functionalization for compound **B**. The d at 3.89 ppm is represented by the *trans* secondary distal functionalization for compound **C**. The enantioselectivity was determined by HPLC analysis of the material after flash chromatography.

Scheme S2. The reaction of 4-tert-butylphenyl cyclobutane to generate **A** and **B**.

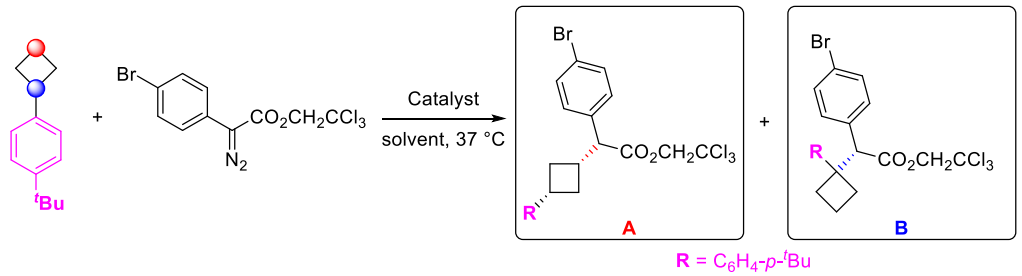
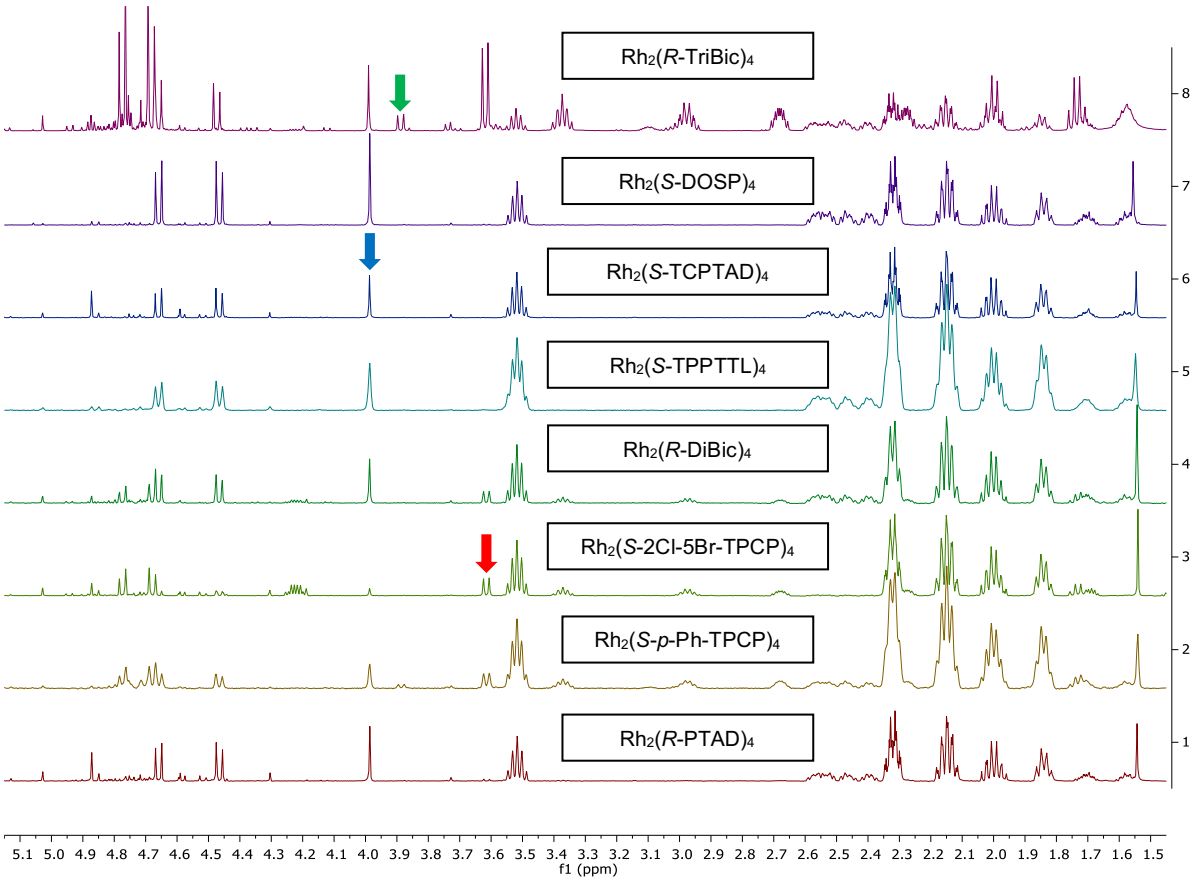


Figure S2. Comparison of crude ^{1}H NMR spectra for C–H Functionalization of Cyclobutanes with Different Catalysts.



(Ratio determined by comparing s at 3.99 ppm (3° C-H insertion product), d at 3.62 (*cis*-C3 insertion product), and d at 3.89 ppm (*trans*-C3 insertion product).

Figure S3. Crude NMR Spectrum using Rh_2(*S*-DOSP)$_4$ as the catalyst.

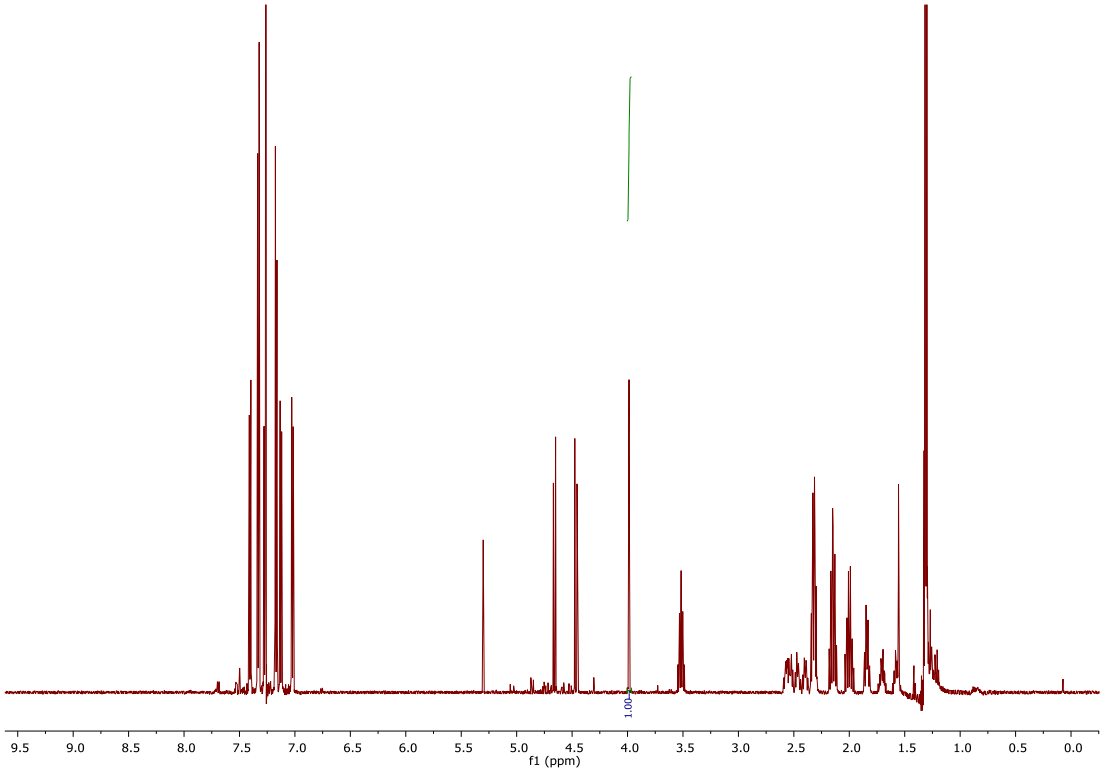


Figure S4. Crude NMR Spectrum using Rh_2(*S*-TCPTAD)$_4$ as the catalyst.

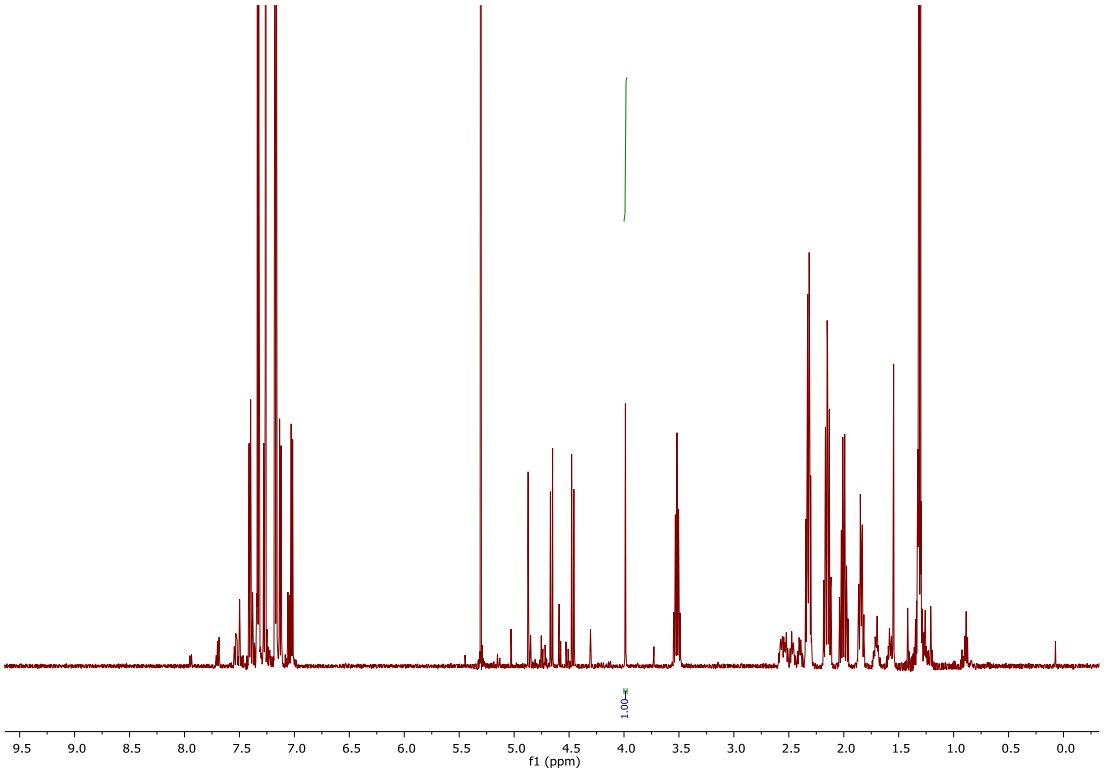


Figure S5. Crude NMR spectrum using Rh_2(*S*-TPPTTL)$_4$ as the catalyst.

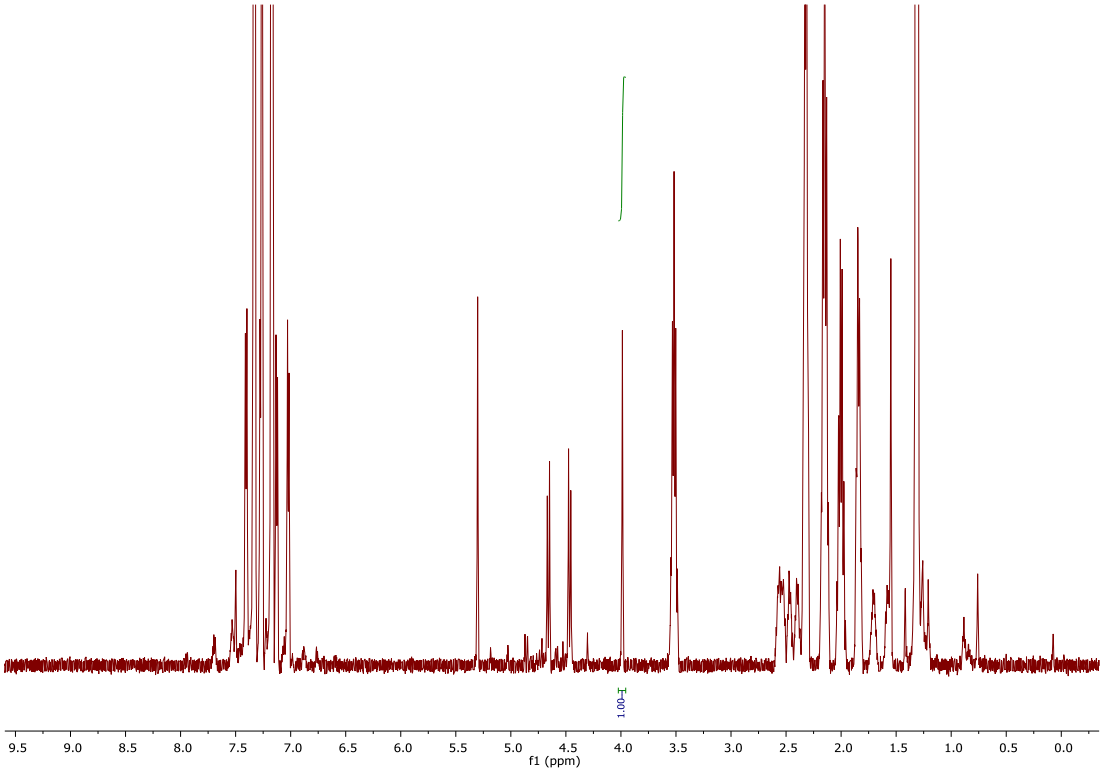


Figure S6. Crude NMR spectrum using Rh_2(*R*-DiBic)$_4$ as the catalyst.

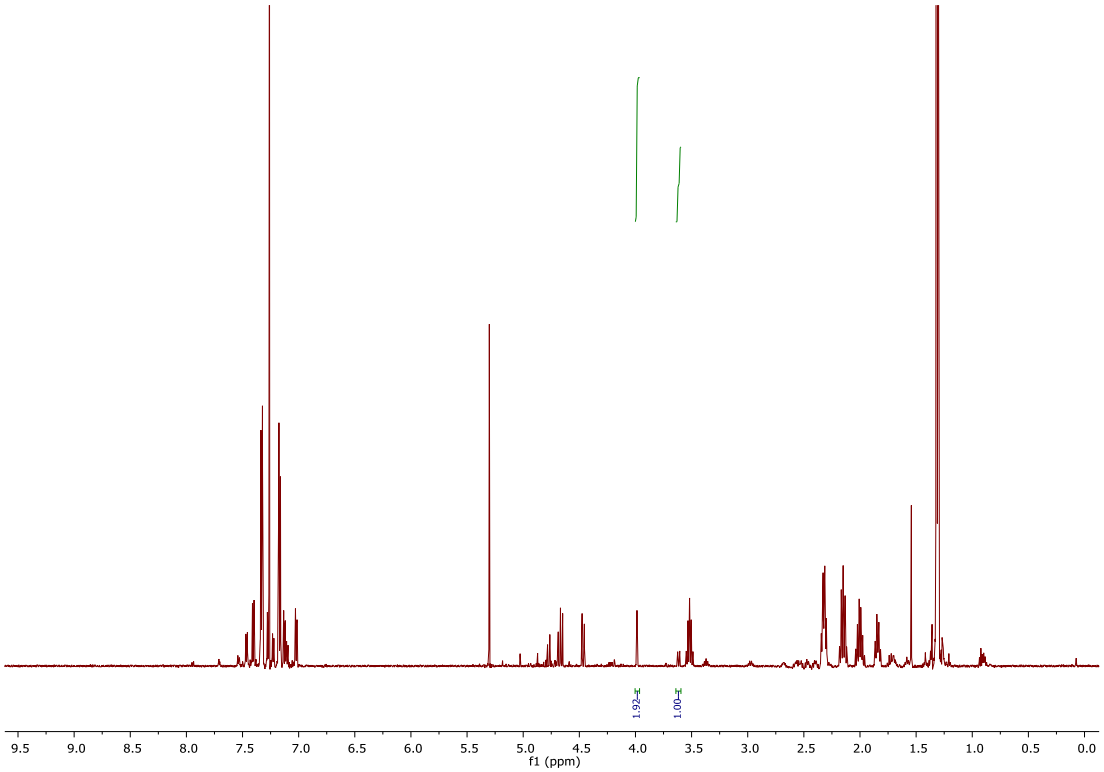


Figure S7. Crude NMR spectrum using Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ as the catalyst.

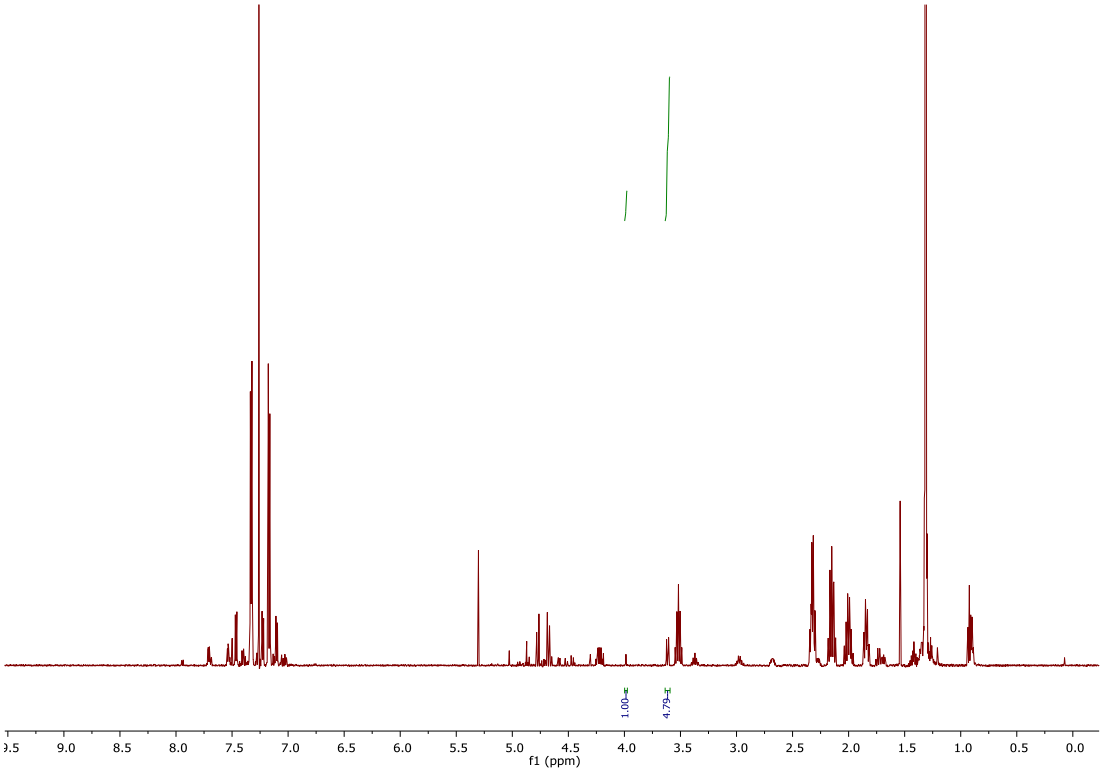


Figure S8. Crude NMR spectrum using Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ as the catalyst.

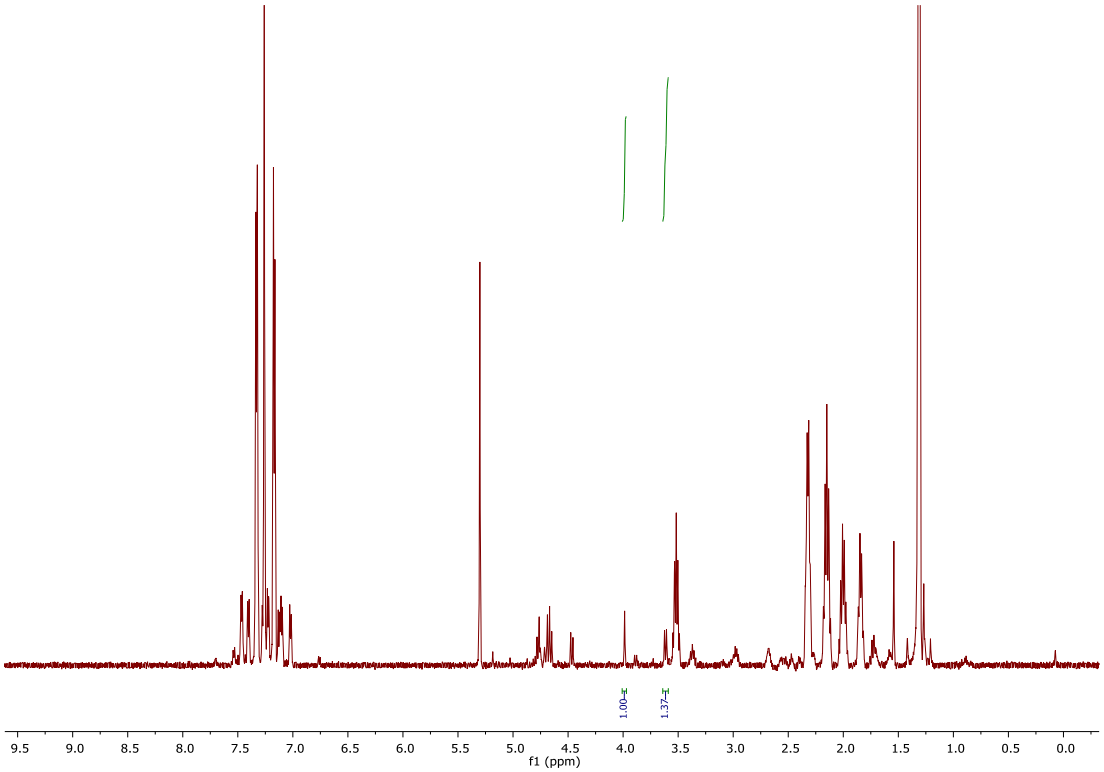


Figure S9. Crude NMR spectrum using Rh_2(*R*-PTAD)$_4$ as the catalyst.

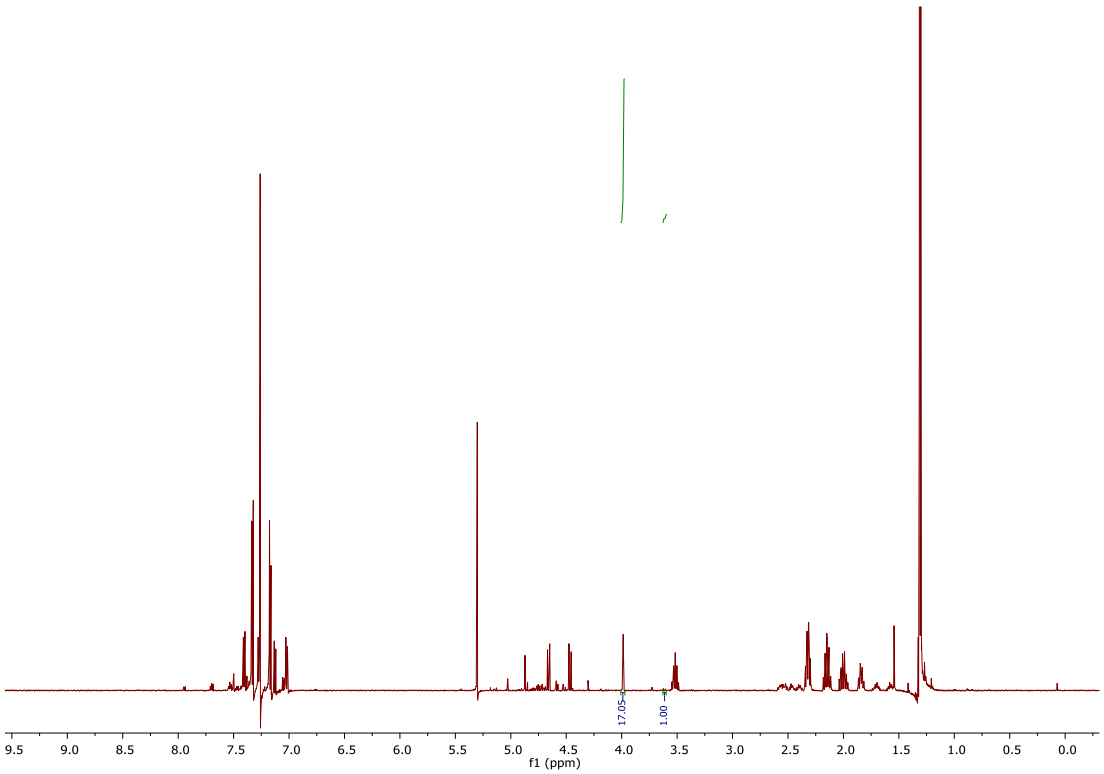
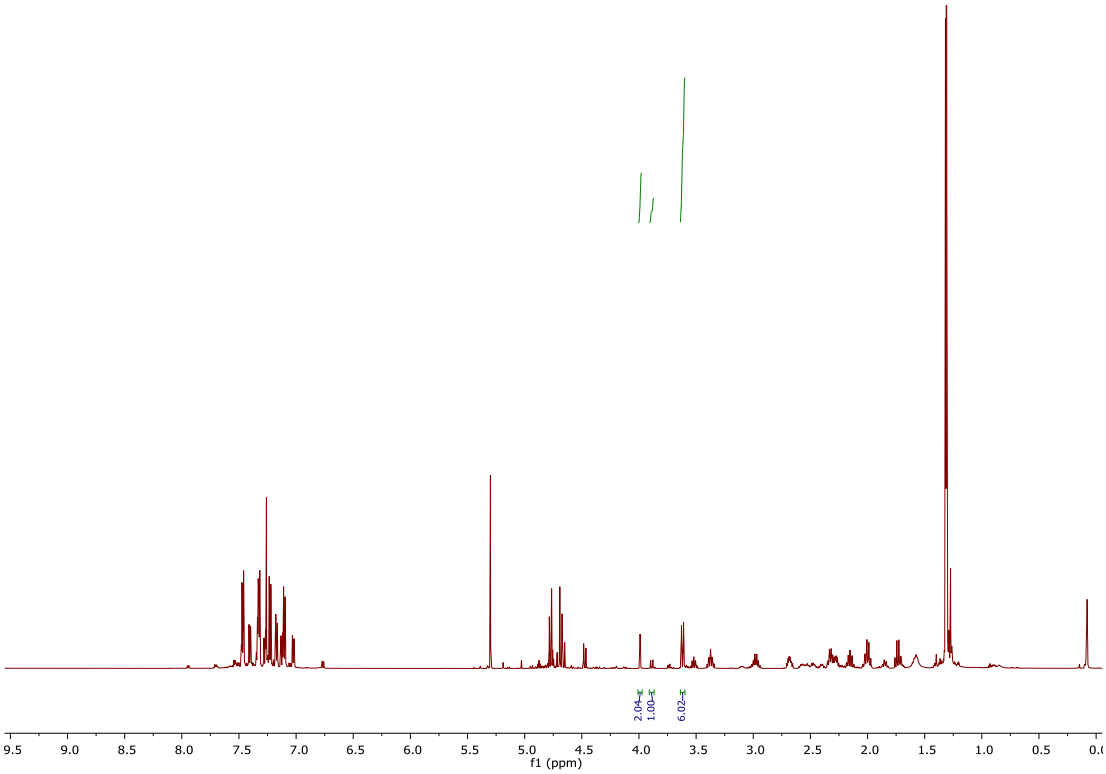
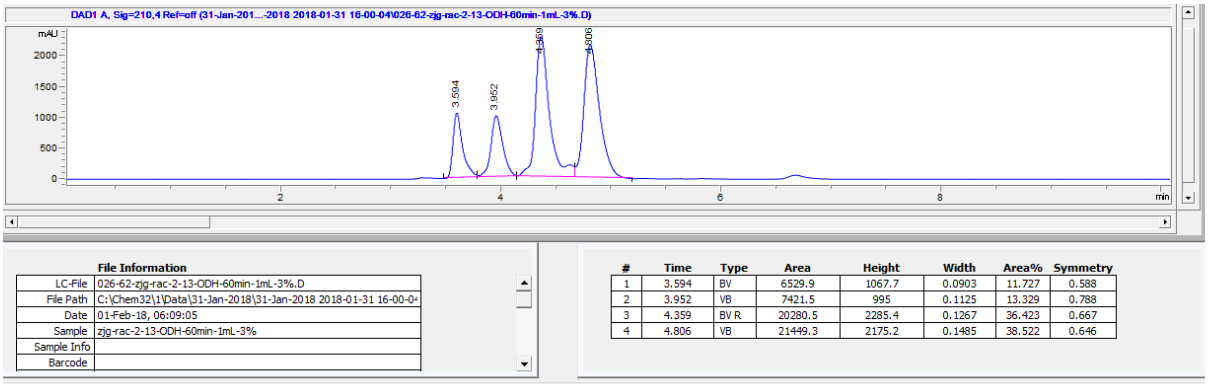


Figure S10. Crude NMR spectrum using Rh_2(*R*-TriBic)$_4$ as the catalyst.



HPLC Traces Generated During Catalyst Screen

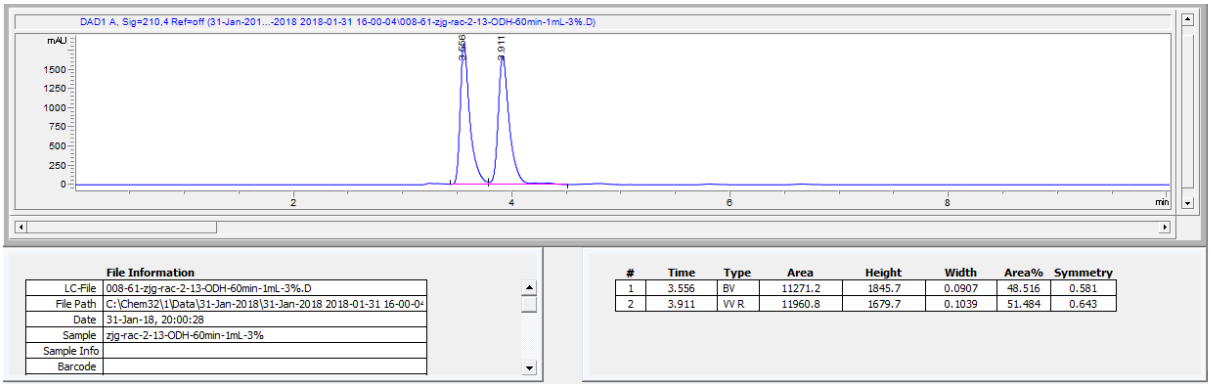
Figure S11. Chiral HPLC trace using Rh_2(*R/S*-2-Cl-TPCP)$_4$ as the catalyst.



File Information	
LC-File	026-62-zjg-rac-2-13-ODH-60min-1mL-3%.D
File Path	C:\Chem32\1\Data\31-Jan-2018\31-Jan-2018 2018-01-31 16-00-0
Date	01-Feb-18, 06:09:05
Sample	zjg-rac-2-13-ODH-60min-1mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.594	BV	6529.9	1067.7	0.0903	11.727	0.588
2	3.952	VB	7421.5	995	0.1125	13.329	0.788
3	4.359	BV R	20280.5	2285.4	0.1267	36.423	0.667
4	4.806	VB	21449.3	2175.2	0.1485	38.522	0.646

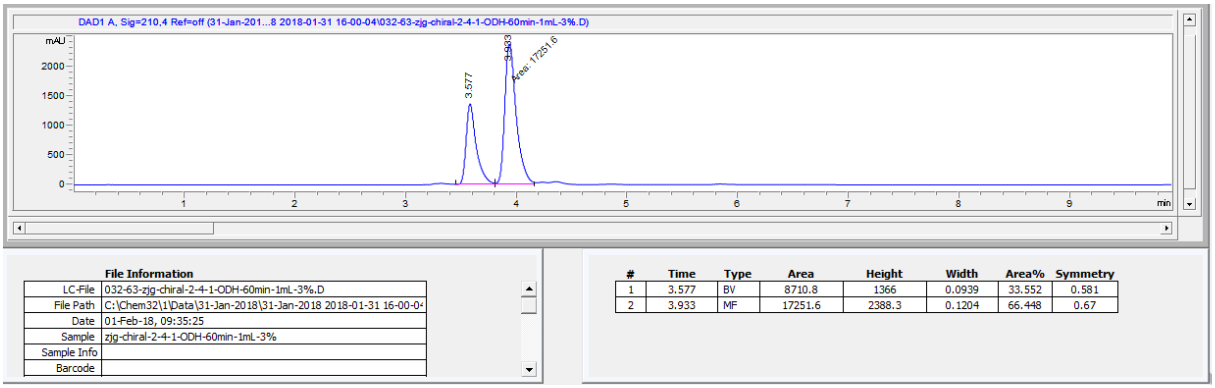
Figure S12. Chiral HPLC trace using Rh_2(*R/S*-TCPTAD)$_4$ as the catalyst.



File Information	
LC-File	008-61-zjg-rac-2-13-ODH-60min-1mL-3%.D
File Path	C:\Chem32\1\Data\31-Jan-2018\31-Jan-2018 2018-01-31 16-00-0
Date	31-Jan-18, 20:00:28
Sample	zjg-rac-2-13-ODH-60min-1mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.556	BV	11271.2	1845.7	0.0907	48.516	0.581
2	3.911	VV R	11960.8	1679.7	0.1039	51.484	0.643

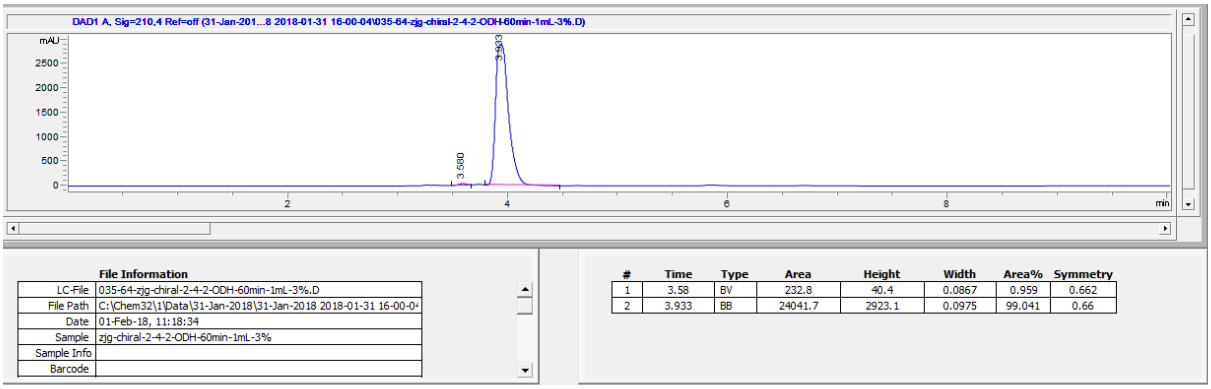
Figure S13. Chiral HPLC trace using Rh_2(*S*-DOSP)$_4$ as the catalyst.



File Information	
LC-File	032-63-zjg-chiral-2-4-1-ODH-60min-1mL-3%.D
File Path	C:\Chem32\1\Data\31-Jan-2018\31-Jan-2018 2018-01-31 16-00-0
Date	01-Feb-18, 09:35:25
Sample	zjg-chiral-2-4-1-ODH-60min-1mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.577	BV	8710.8	1366	0.0939	33.552	0.581
2	3.933	MF	17251.6	2388.3	0.1204	66.448	0.67

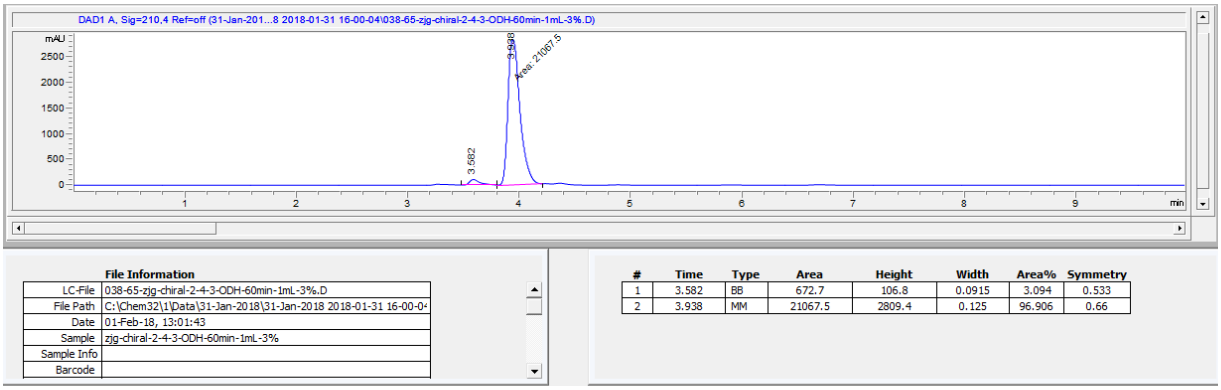
Figure S14. Chiral HPLC trace using Rh_2(*S*-TCPTAD)$_4$ as the catalyst.



File Information	
LC-File	035-64-zjg-chiral-2-4-2-ODH-60min-1mL-3%.D
File Path	C:\Chem32\1\Data\31-Jan-2018\31-Jan-2018 2018-01-31 16-00-0
Date	01-Feb-18, 11:18:34
Sample	zjg-chiral-2-4-2-ODH-60min-1mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.58	BV	232.8	40.4	0.0867	0.959	0.662
2	3.933	BB	24041.7	2923.1	0.0975	99.041	0.66

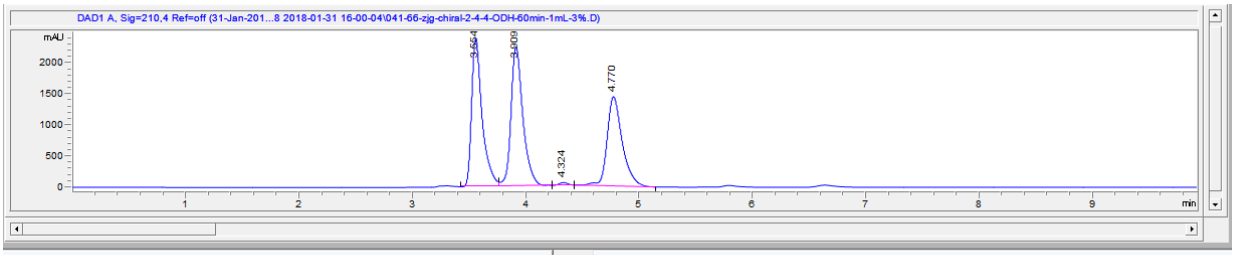
Figure S15. Chiral HPLC trace using Rh2(S-TPPTTL)$_4$ as the catalyst.



File Information	
LC-File	038-65-zjg-chiral-2-4-3-ODH-60min-1mL-3%.D
File Path	C:\Chem32\1\Data\31-Jan-2018\31-Jan-2018 2018-01-31 16-00-0
Date	01-Feb-18, 13:01:43
Sample	zjg-chiral-2-4-3-ODH-60min-1mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.582	BB	672.7	106.8	0.0915	3.094	0.533
2	3.938	MM	21067.5	2809.4	0.125	96.906	0.66

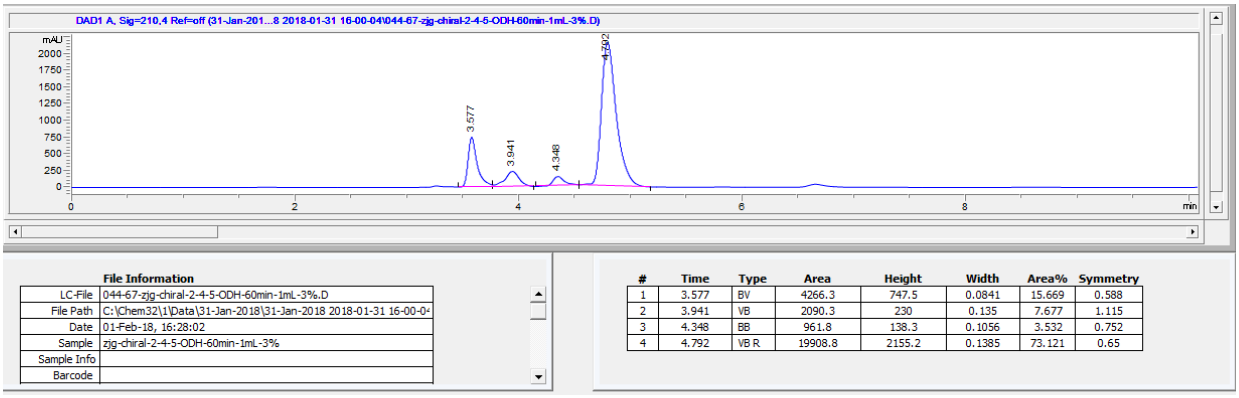
Figure S16. Chiral HPLC trace using Rh_2(*R*-DiBic)$_4$ as the catalyst.



File Information	
LC-File	041-66-zjg-chiral-2-4-4-ODH-60min-1mL-3%.D
File Path	C:\Chem32\1\Data\31-Jan-2018\31-Jan-2018 2018-01-31 16-00-0
Date	01-Feb-18, 14:44:52
Sample	zjg-chiral-2-4-4-ODH-60min-1mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.554	BV	15331.5	2365.4	0.0961	33.880	0.582
2	3.909	VV R	16292.6	2225.5	0.1088	36.004	0.69
3	4.324	BB	226.8	43.6	0.0847	0.501	0.929
4	4.77	VB R	13401	1432.7	0.1387	29.614	0.721

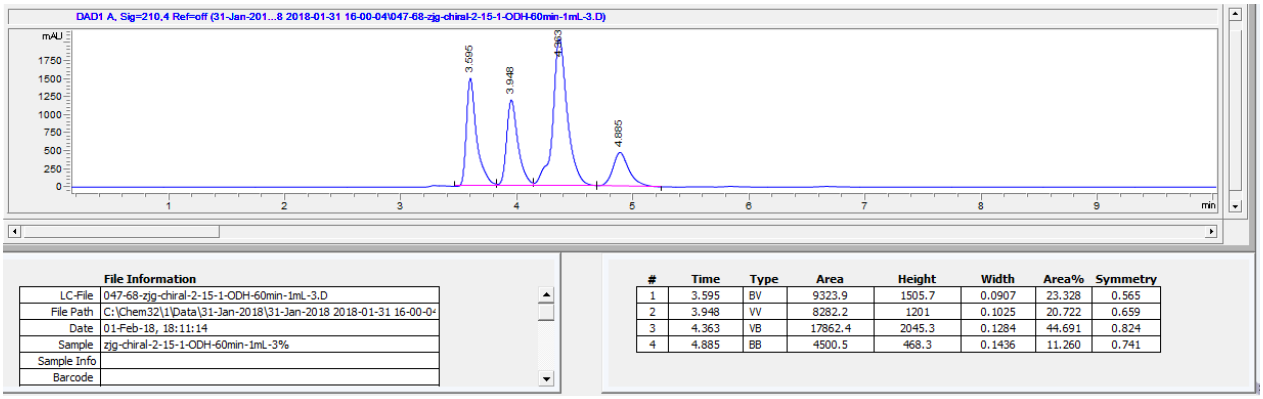
Figure S17. Chiral HPLC trace using Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ as the catalyst.



File Information	
LC-File	044-67-zjg-chiral-2-4-5-ODH-60min-1mL-3%.D
File Path	C:\Chem32\1\Data\31-Jan-2018\31-Jan-2018 2018-01-31 16-00-0
Date	01-Feb-18, 16:28:02
Sample	zjg-chiral-2-4-5-ODH-60min-1mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.577	BV	4266.3	747.5	0.0841	15.669	0.588
2	3.941	VB	2090.3	230	0.135	7.677	1.115
3	4.348	BB	961.8	138.3	0.1056	3.532	0.752
4	4.792	VB R	19908.8	2155.2	0.1385	73.121	0.65

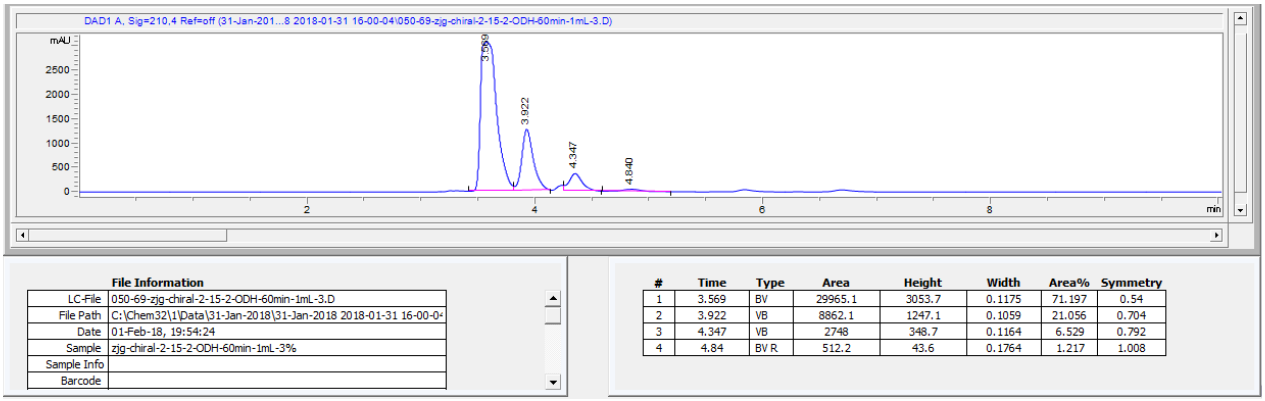
Figure S18. Chiral HPLC trace using Rh_2(*S*-p-PhTPCP)$_4$ as the catalyst.



File Information	
LC-File	047-68-zjg-chiral-2-15-1-ODH-60min-1mL-3.D
File Path	C:\Chem32\1\Data\31-Jan-2018\31-Jan-2018 2018-01-31 16-00-0
Date	01-Feb-18, 18:11:14
Sample	zjg-chiral-2-15-1-ODH-60min-1mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.595	BV	9323.9	1505.7	0.0907	23.328	0.565
2	3.948	VV	8282.2	1201	0.1025	20.722	0.659
3	4.363	VB	17862.4	2045.3	0.1284	44.691	0.824
4	4.885	BB	4500.5	468.3	0.1436	11.260	0.741

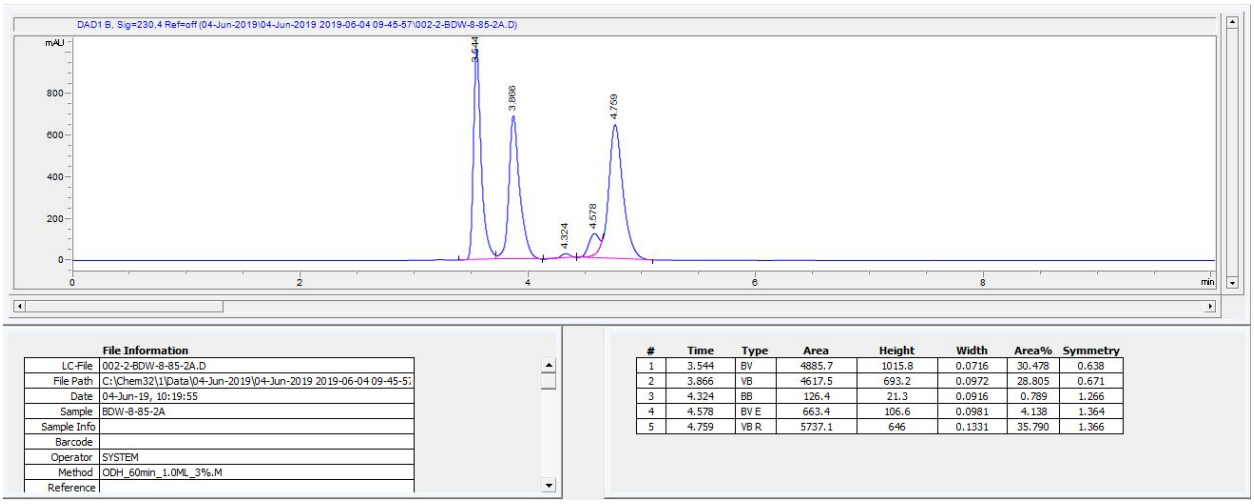
Figure S19. Chiral HPLC trace using Rh_2(*R*-PTAD)$_4$ as the catalyst.



File Information	
LC-File	050-69-zjg-chiral-2-15-2-ODH-60min-1mL-3.D
File Path	C:\Chem32\1\Data\31-Jan-2018\31-Jan-2018 2018-01-31 16-00-0
Date	01-Feb-18, 19:54:24
Sample	zjg-chiral-2-15-2-ODH-60min-1mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.569	BV	29965.1	3053.7	0.1175	71.197	0.54
2	3.922	VB	8862.1	1247.1	0.1059	21.056	0.704
3	4.347	VB	2748	348.7	0.1164	6.529	0.792
4	4.84	BV R	512.2	43.6	0.1764	1.217	1.008

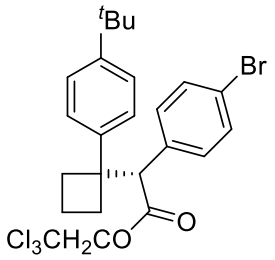
Figure S20. Chiral HPLC trace using Rh_2(*R*-TriBic)$_4$ as the catalyst.



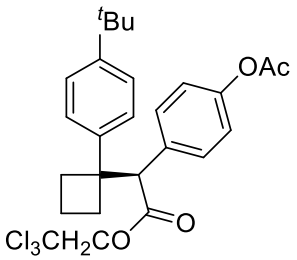
File Information	
LC-File	002-2-BDW-8-85-2A.D
File Path	C:\Chem32\1\Data\04-Jun-2019\04-Jun-2019 2019-06-04 09-45-57
Date	04-Jun-19, 10:19:55
Sample	BDW-8-85-2A
Sample Info	
Barcode	
Operator	SYSTEM
Method	ODH_60min_1.0ML_3%.M
Reference	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.544	BV	4885.7	1015.8	0.0716	30.478	0.638
2	3.866	VB	4617.5	693.2	0.0972	28.805	0.671
3	4.324	BB	126.4	21.3	0.0916	0.789	1.266
4	4.578	BV E	663.4	106.6	0.0981	4.138	1.364
5	4.759	VB R	5737.1	646	0.1331	35.790	1.366

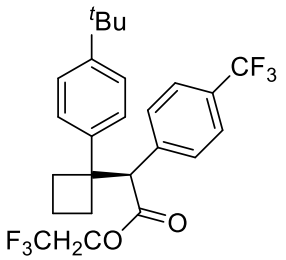
Compound Characterization for C1 Functionalization of Substituted Cyclobutanes



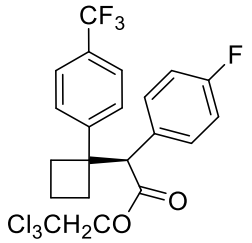
2,2,2-Trichloroethyl (*S*)-2-(4-bromophenyl)-2-(1-(4-(*tert*-butyl)phenyl)cyclobutyl)acetate (8). The general procedure 2 was employed for the C–H functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (47 mg, 0.25 mmol, 1.00 equiv) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol, 2.00 equiv) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (103 mg, 78%) as a colorless solid, mp 70–73 °C: $[\alpha]^{23}_D$ -10.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.46 (d, *J* = 10.6 Hz, 1H), 2.92–2.75 (m, 1H), 1.36–1.27 (m, 1H), 0.91–0.78 (m, 2H), 0.52 (dd, *J* = 14.3, 10.8 Hz, 1H), 0.28 (s, 3H), 0.27 (s, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 140.4, 139.7, 138.3, 136.4, 129.6, 129.0, 128.6, 128.6, 128.1, 127.5, 127.5, 127.4, 127.2, 127.1, 60.5, 57.2, 50.1, 45.8, 40.46, 38.87, 31.0, 23.0, 1 carbon signal is missing due to incidental equivalence; IR (neat) 1488, 1452, 1332, 1153, 1137 cm^{-1}. MS (ESI+) 511.2413 (511.2414 calcd for $C_{32}H_{34}N_2O_2S$, M + H^+). The enantiopurity was determined to be 98% ee by chiral HPLC analysis (Chiralcel ODH, 15 cm x 4.6 mm, 7% IPA/Hexanes, 1.00 mL/min, λ 254 nm, RT= 16.5 and 29.7 min).



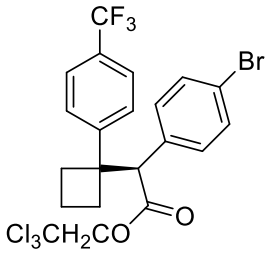
2,2,2-Trichloroethyl (*R*)-2-(4-acetoxyphenyl)-2-(1-(4-(*tert*-butyl)phenyl)cyclobutyl)acetate (10). The general procedure 2 was employed for the C–H functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (47 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-acetoxyphenyl)-2-diazoacetate (176 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (125 mg, 98%) as a colorless solid, mp 70–73 °C: $[\alpha]^{23}_D$ +6.9 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.29 (m, 2H), 7.29–7.26 (m, 2H), 7.06–7.04 (m, 2H), 7.04–7.01 (m, 2H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 11.9 Hz, 1H), 4.01 (s, 1H), 2.63–2.52 (m, 2H), 2.52–2.44 (m 1H), 2.42–2.34 (m, 1H), 2.30 (s, 3H), 1.73–1.64 (m, 1H), 1.58–1.48 (m, 1H), 1.30 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 169.4, 150.4, 149.1, 143.7, 132.8, 131.1, 127.1, 124.7, 121.1, 94.7, 74.4, 60.4, 49.4, 34.5, 32.3, 31.6, 30.4, 21.3, 16.1; IR (film) 2962, 2868, 1751, 1506, 1368, 1271, 1198, 1169, 1133, 1049, 1018, 910, 830, 756, 722 cm^{-1}. MS (APCI-) 509.1066 (509.1059 calcd for $C_{26}H_{28}Cl_3O_4$, M - H$^+$). The enantiopurity was determined to be 96% ee by chiral HPLC analysis (Chiralcel OD-H, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.25 mL/min, λ 230 nm, RT= 25.3 and 27.5 min).



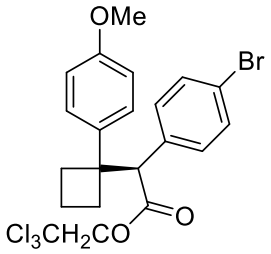
2,2,2-Trifluoroethyl (*R*)-2-(1-(4-(*tert*-butyl)phenyl)cyclobutyl)-2-(4-(trifluoromethyl)phenyl)acetate (11). The general procedure 2 was employed for the C–H functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (94 mg, 0.5 mmol) by reaction of 2,2,2-trifluoroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (312 mg, 1.0 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 0.5 mol%) as catalyst. This procedure afforded the title compound (154 mg, 65%) as a colorless solid, mp 59–62 °C: $[\alpha]^{23}_D$ -6.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.29–7.26 (m, 2H), 6.97–6.94 (m, 2H), 4.37 (dq, *J* = 12.6, 8.5 Hz, 1H), 4.24 (dq, *J* = 12.6, 8.4 Hz, 1H), 4.05 (s, 1H), 2.59–2.53 (m, 1H), 2.53–2.39 (m, 3H), 1.78–1.68 (m, 1H), 1.66–1.56 (m, 1H), 1.31 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 149.5, 142.7, 139.1, 130.4, 130.0 (q, *J* = 33 Hz), 127.0, 124.9 (q, *J* = 3.8 Hz), 124.8, 124.3 (q, *J* = 272 Hz), 122.9 (q, *J* = 277 Hz), 60.5, 60.5 (q, *J* = 37 Hz), 49.7, 34.6, 32.0, 31.5, 30.9, 16.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.55, -73.57 (t, *J* = 8.5 Hz); IR (film) 2965, 1754, 1619, 1509, 1325, 1275, 1164, 1124, 1070, 1019, 980, 837 cm^{-1}. MS (APCI-) 471.1763 (471.1764 calcd for $C_{25}H_{25}O_2F_6$, M - H$^+$). The enantiopurity was determined to be 96% ee by chiral HPLC analysis (Chiralcel OD-H, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.25 mL/min, λ 230 nm, RT= 15.3 and 17.8 min).



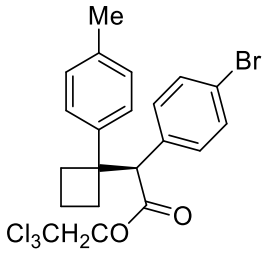
2,2,2-Trichloroethyl (*R*)-2-(4-fluorophenyl)-2-(1-(4-(trifluoromethyl)phenyl)-cyclobutyl)acetate (12). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-diazo-2-(4-fluorophenyl)acetate (156 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (90 mg, 74%) as a colorless oil: $[\alpha]^{23}_D$ +3.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54–7.47 (m, 2H), 7.21–7.12 (m, 4H), 7.03–6.94 (m, 2H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.06 (s, 1H), 2.73–2.54 (m, 2H), 2.51–2.37 (m, 2H), 1.83–1.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 164.3 (d, *J* = 247 Hz), 150.6, 131.6 (d, *J* = 8.1 Hz), 130.3 (d, *J* = 3.4 Hz), 128.6 (q, *J* = 32.8 Hz), 128.1, 124.3 (q, *J* = 272 Hz), 124.65 (q, *J* = 3.8 Hz), 115.2 (d, *J* = 21.5 Hz), 94.6, 74.3, 59.5, 49.7, 32.2, 31.4, 16.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.34, -114.20, -114.33 (m); IR (film) 3046, 2983, 2950, 2869, 1749, 1618, 1606, 1508, 1325, 1228, 1162, 1124, 1114, 1071, 1015, 908, 842, 720 cm^{-1}. MS (ESI-) 516.9926 (516.9924 calcd for $C_{21}H_{17}O_2Cl_4F_4$, M + Cl^-). The enantiopurity was determined to be 96% ee by chiral HPLC (Chiralpak IAU 1.6 um, 100 mm x 3 mm, 0.5% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT= 1.93 and 2.14 min).



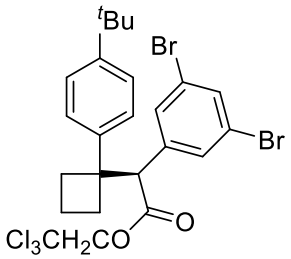
2,2,2-Trichloroethyl (*R*)-2-(4-bromophenyl)-2-(1-(4-(trifluoromethyl)phenyl)cyclobutyl)acetate (13). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (114 mg, 84%) as a colorless oil: $[\alpha]^{23}_D$ -12.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.42–7.39 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.07–7.04 (m, 2H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.05 (s, 1H), 2.69–2.62 (m, 1H), 2.61–2.55 (m, 1H), 2.48–2.40 (m, 2H), 1.80–1.67 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 150.4, 133.6, 131.7, 131.4, 128.7 (q, *J* = 33 Hz), 128.2, 124.7 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272 Hz), 122.4, 94.6, 74.4, 59.8, 49.7, 32.3, 31.5, 16.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.36; IR (film) 2950, 1750, 1618, 1489, 1410, 1325, 1164, 1124, 1071, 1012, 836, 762, 722 cm^{-1}. MS (APCI-) 540.9355 (540.9357 calcd for $C_{21}H_{16}O_2BrCl_3F_3$, M - H$^+$). The enantiopurity was determined to be 98% ee by chiral HPLC analysis (Chiralpak AD-H, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.5 mL/min, λ 210 nm, RT= 9.7 and 10.3 min).



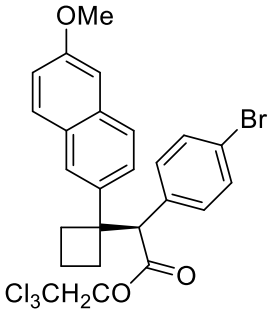
2,2,2-Trichloroethyl (*R*)-2-(4-bromophenyl)-2-(1-(4-methoxyphenyl)cyclobutyl)acetate (14). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-methoxybenzene (41 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (102 mg, 81%) as a colorless oil: $[\alpha]^{23}_D$ -15.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.06–7.04 (m, 2H), 6.99–6.95 (m, 2H), 6.80–6.77 (m, 2H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.00 (s, 1H), 3.79 (s, 3H), 2.66–2.60 (m, 1H), 2.53–2.44 (m, 1H), 2.42–2.35 (m, 2H), 1.79–1.64 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 158.1, 137.9, 134.1, 131.8, 131.1, 128.8, 121.9, 113.1, 94.7, 74.4, 60.5, 55.4, 49.3, 32.3, 31.6, 16.0; IR (film) 2948, 2835, 1748, 1610, 1511, 1488, 1464, 1441, 1409,1372, 1297, 1245, 1178, 1131, 1075, 1032, 1011, 908, 830, 761, 719 cm^{-1}. MS (APCI-) 502.9597 (502.9589 calcd for $C_{21}H_{19}O_3BrCl_3$, M - H$^+$). The enantiopurity was determined to be 91% ee by chiral HPLC analysis (Chiralcel ODH, 25 cm x 4.6 mm, 3% IPA/Hexanes, 1.00 mL/min, λ 210 nm, RT= 4.7 and 6.0 min).



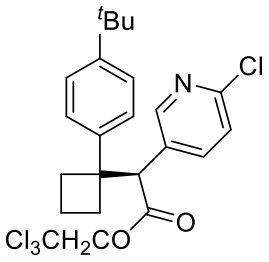
2,2,2-Trichloroethyl (*R*)-2-(4-bromophenyl)-2-(1-(*p*-tolyl)cyclobutyl)acetate (15). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-methylbenzene (37 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (115 mg, 94%) as a colorless oil: $[\alpha]^{23}_D$ -9.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.11–7.04 (m, 4H), 6.97 (d, *J* = 8.2 Hz, 2H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.01 (s, 1H), 2.67–2.60 (m, 1H), 2.55–2.49 (m, 1H), 2.46–2.37 (m, 2H), 2.32 (s, 3H), 1.79–1.70 (m, 1H), 1.70–1.63 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 143.1, 135.9, 134.1, 131.8, 131.1, 128.5, 127.5, 122.0, 94.7, 74.4, 60.4, 49.5, 32.3, 31.3, 21.1, 16.1; IR (film) 2980, 2946, 2866, 1748, 1514, 1488, 1445, 1409, 1371, 1336, 1130, 1075, 1011, 907, 822, 760, 720 cm^{-1}. MS (APCI-) 486.9645 (486.9640 calcd for $C_{21}H_{19}O_2BrCl_3$, M - H^+). The enantiopurity was determined to be 98% ee by chiral HPLC analysis (Chiralcel OJ, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.5 mL/min, λ 210 nm, RT= 10.9 and 13.9 min).



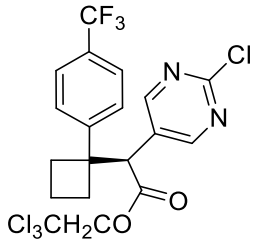
2,2,2-Trichloroethyl (*R*)-2-(1-(4-(*tert*-butyl)phenyl)cyclobutyl)-2-(3,5-dibromophenyl)acetate (16). The general procedure 2 was employed for the C–H functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (47 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-diazo-2-(3,5-dibromophenyl)acetate (226 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (115 mg, 75%) as a colorless oil: $[\alpha]^{23}_D$ -7.3 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (t, *J* = 1.7 Hz, 1H), 7.30–7.27 (m, 2H), 7.16 (d, *J* = 1.7 Hz, 2H), 6.95–6.93 (m, 2H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 3.96 (s, 1H), 2.69–2.62 (m, 1H), 2.50–2.42 (m, 3H), 1.83–1.72 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 149.7, 142.2, 138.8, 133.2, 131.9, 127.3, 124.7, 122.2, 94.6, 74.6, 60.3, 49.7, 34.6, 31.9, 31.6, 31.5, 16.0; IR (film) 2962, 2867, 1750, 1582, 1554, 1509, 1425, 1364, 1334, 1268, 1194, 1136, 1047, 908, 858, 829, 734 cm^{-1}. MS (APCI-) 606.9220 (606.9214 calcd for $C_{24}H_{24}O_2Br_2Cl_3$, M - H^+). The enantiopurity was determined to be 95% ee by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT= 6.9 and 8.2 min).



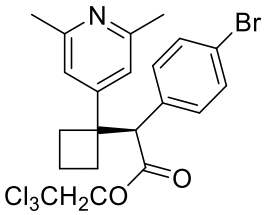
2,2,2-Trichloroethyl (*R*)-2-(4-bromophenyl)-2-(1-(6-methoxynaphthalen-2-yl)cyclobutyl)acetate (17). The general procedure 2 was employed for the C–H functionalization of 2-cyclobutyl-6-methoxynaphthalene (53 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (118 mg, 85%) as a colorless solid, mp 44–49 °C: $[\alpha]^{23}_D$ -17.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.45 (d, *J* = 2.2 Hz, 1H), 7.39–7.36 (m, 2H), 7.17 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.13 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.11–7.07 (m, 3H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.10 (s, 1H), 3.92 (s, 3H), 2.73–2.67 (m, 1H), 2.65–2.58 (m, 1H), 2.58–2.47 (m, 2H), 1.82–1.73 (m, 1H), 1.73–1.66 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 157.8, 141.1, 134.1, 133.2, 131.8, 131.2, 129.5, 128.5, 126.4, 126.2, 122.0, 119.0, 105.6, 94.7, 74.4, 60.4, 55.5, 49.8, 32.2, 31.3, 16.2, 1 carbon signal is missing due to incidental equivalence; IR (film) 2984, 2948, 1749, 1634, 1605, 1488, 1390, 1372, 1338, 1273, 1217, 1131, 1032, 1011, 925, 852, 908, 813, 761, 723 cm^{-1}. MS (APCI-) 552.9750 (552.9745 calcd for $C_{25}H_{21}O_3BrCl_3$, M - H$^+$). The enantiopurity was determined to be 98% ee by chiral HPLC analysis (Chiralpak AD-H, 25 cm x 4.6 mm, 1% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT= 18.3 and 20.2 min).



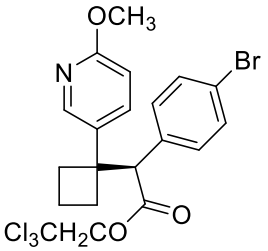
2,2,2-Trichloroethyl (*S*)-2-(1-(4-(*tert*-butyl)phenyl)cyclobutyl)-2-(6-chloropyridin-3-yl)acetate (18). The general procedure 2 was employed for the C–H functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (47 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (164 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (76 mg, 62%) as a viscous oil: $[\alpha]^{23}_D$ -26.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.30–7.26 (m, 2H), 7.19 (d, *J* = 0.7 Hz, 1H), 6.97–6.91 (m, 2H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.09 (s, 1H), 2.74–2.67 (m, 1H), 2.54–2.46 (m, 1H), 2.46–2.37 (m, 2H), 1.82–1.74 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 151.0, 150.8, 149.7, 141.9, 140.3, 129.9, 127.3, 124.9, 123.4, 94.5, 74.7, 57.7, 49.6, 34.6, 32.5, 31.7, 31.5, 16.0; IR (film) 2962, 2868, 1748, 1583, 1562, 1509, 1459, 1395, 1365, 1325, 1141, 1106, 1023, 910, 835, 776, 758, 727 cm^{-1}. MS (APCI-) 486.0572 (486.0567 calcd for $C_{23}H_{24}O_2N_2Cl_4$, M + H$^+$). The enantiopurity was determined to be 94% ee by chiral HPLC (Chiralpak ADH, 25 cm x 4.6 mm, 2% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT= 12.3 and 13.8 min).



2,2,2-Trichloroethyl (*S*)-2-(2-chloropyrimidin-5-yl)-2-(1-(4-(trifluoromethyl)phenyl)-cyclobutyl)acetate (19). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (165 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (45 mg, 36%) as a colorless film: $[\alpha]^{23}_D$ -14.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, Chloroform-d) δ 8.30 (s, 2H), 7.59 – 7.49 (m, 2H), 7.10 – 7.03 (m, 2H), 4.72 (d, J = 11.9 Hz, 1H), 4.63 (d, J = 11.9 Hz, 1H), 4.13 (s, 1H), 2.85 – 2.76 (m, 1H), 2.60 – 2.50 (m, 1H), 2.46 – 2.33 (m, 2H), 1.95 – 1.84 (m, integration of 2H could not be determined due to overlap with an H_2O peak)).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.62, 160.01, 159.11, 147.12, 128.44 (q, *J* = 33.2 Hz), 126.85, 124.22 (q, *J* = 4.0 Hz), 122.82 (q, *J* = 271.9 Hz), 92.94, 73.90, 54.29, 48.71, 31.26, 14.78. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.53; IR (film) 2987, 2953, 2851, 1750, 1618, 1577, 1546, 1401, 1327, 1158, 1126, 1071, 1015, 838, 775, 723 cm^{-1}. MS (ESI-) 498.9777 (486.9767 calcd for $C_{19}H_{14}O_2N_2Cl_4F_3$, M - H$^-$). The enantiopurity was determined to be 88% ee by chiral HPLC (Chiralpak IHU 1.6 um, 100 mm x 3 mm, 5.0% IPA/Hexanes, 0.5 mL/min, λ 230 nm, RT= 2.91 and 3.66 min).

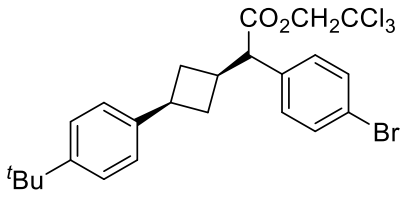


2,2,2-trichloroethyl (*R*)-2-(4-bromophenyl)-2-(1-(2,6-dimethylpyridin-4-yl)cyclobutyl)acetate (20). The general procedure 2 was employed for the C-H functionalization of 4-cyclobutyl-2,6-dimethylpyridine (40.3 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (41 mg, 32%) as a colorless oil: $[\alpha]^{23}_D$ + 4.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, Chloroform-d) δ 7.42 – 7.36 (m, 2H), 7.10 – 7.04 (m, 2H), 6.63 (s, 2H), 4.67 (d, J = 12.0 Hz, 1H), 4.49 (d, J = 11.9 Hz, 1H), 3.94 (s, 1H), 2.60 – 2.46 (m, 2H), 2.43 (s, 6H), 2.41 – 2.28 (m, 2H), 1.73 – 1.55 (m, 2H). ^{13}C NMR (151 MHz, CDCl3) δ 169.89, 157.18, 155.75, 133.43, 131.46, 131.20, 122.19, 119.19, 94.42, 74.30, 59.40, 48.99, 31.61, 30.62, 24.51, 16.01. IR (neat) 2949, 2925, 2854, 1749, 1603, 1561, 1489, 1438, 1408, 1372, 1133, 1075, 1011, 826, 761, 719 cm^{-1}. MS (APCI+) 503.9888 (503.9894 calcd for $C_{21}H_{22}O_2N^{79}Br^{35}Cl_3$, M + H^+) The enantiopurity was determined to be 99% *ee* by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 2.0% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 8.9 and 10.0 min)

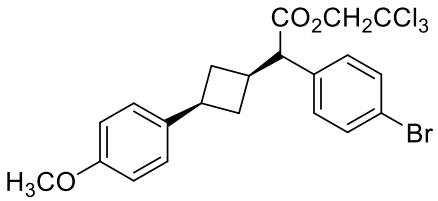


2,2,2-trichloroethyl (R)-2-(4-bromophenyl)-2-(1-(6-methoxypyridin-3-yl)cyclobutyl)acetate (21). The general procedure 2 was employed for the C-H functionalization of 5-cyclobutyl-2-methoxypyridine (40.8 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(*R*-TCPTAD)$_4$ (5.3 mg, 1 mol%) as catalyst. This procedure afforded the title compound (59 mg, 46%) as a colorless oil: $[\alpha]^{23}_D$ – 28.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.82 (d, J = 2.6 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.28 – 7.21 (m, 1H), 7.05 – 6.98 (m, 2H), 6.63 (d, J = 8.6 Hz, 1H), 4.75 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.04 (s, 1H), 3.91 (s, 3H), 2.62 (qd, J = 8.2, 4.3 Hz, 1H), 2.54 – 2.37 (m, 2H), 2.33 (tdd, J = 10.7, 7.8, 2.2 Hz, 1H), 1.79 (p, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.07, 162.61, 146.27, 138.36, 133.49, 133.23, 131.50, 131.19, 122.09, 109.52, 94.52, 74.19, 59.93, 53.39, 47.41, 32.12, 31.68, 16.20. IR (neat) 2980, 2946, 1748, 1604, 1489, 1374, 1286, 1131, 1023, 1011, 908, 827, 721 cm^{-1}. MS (APCI+) XX (XX calcd for $C_{21}H_{22}O_2N^{79}Br^{35}Cl_3$, M + H^+) The enantiopurity was determined to be 99% *ee* by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 0.5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 17.4 and 26.2 min)

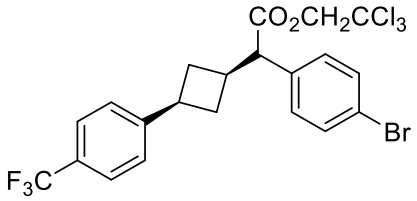
Compound Characterization for C3 Functionalization of Substituted Cyclobutanes



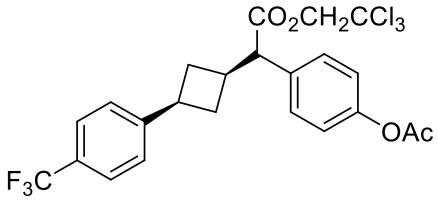
2,2,2-Trichloroethyl (*S*)-2-(4-bromophenyl)-2-((1s,3R)-3-(4-methoxyphenyl)cyclobutyl)acetate (9). The general procedure 2 was employed for the C–H functionalization of 1-(*tert*-butyl)-4-cyclobutylbenzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (94 mg, 71%) as a colorless oil. The ratio of *cis*:*trans* cyclobutane diastereomers was >95:5 by ^{1}HNMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was > 95:5 by ^{1}HNMR $[\alpha]^{20}_D$ +71.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 2H), 7.35–7.29 (m, 2H), 7.24–7.20 (m, 2H), 7.12–7.07 (m, 2H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.43–3.28 (m, 1H), 3.08–2.87 (m, 1H), 2.75–2.58 (m, 1H), 2.34–2.21 (m, 1H), 2.00 (q, *J* = 10.3 Hz, 1H), 1.74 (q, *J* = 10.3 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 148.9, 142.0, 135.4, 131.8, 129.9, 125.9, 125.2, 121.6, 94.8, 74.1, 57.7, 35.24, 34.38, 34.17, 34.12, 31.38; IR (film) 3052, 3024, 2961, 2903, 2864, 1749, 1488, 1364, 1132, 1072, 1010, 909, 827, 759, 716, 568 cm^{-1}. MS (APCI+) 530.0175 (530.0176 calcd for $C_{24}H_{26}O_2BrCl_3$, M +). The enantiopurity was determined to be 92% ee by chiral HPLC (Registech (*R*,*R*)-Whelk, 25 cm x 4.6 mm, 0.5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 9.4 and 11.6 min).



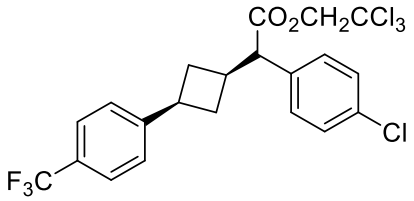
2,2,2-Trichloroethyl (*S*)-2-(4-bromophenyl)-2-((1s,3R)-3-(4-methoxyphenyl)cyclobutyl)acetate (22). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-methoxybenzene (41 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (79 mg, 62%) as a colorless oil. The ratio of *cis*:*trans* cyclobutane diastereomers was >95:5 by ^{1}HNMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was 76:24 by ^{1}HNMR. $[\alpha]^{23}_D$ +63.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.25–7.21 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.86–6.82 (m, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 3.79 (s, 3H), 3.62 (d, *J* = 10.7 Hz, 1H), 3.34 (ddd, *J* = 18.0, 9.9, 8.2 Hz, 1H), 3.01–2.90 (m, 1H), 2.67 (ddt, *J* = 10.3, 7.3, 3.8 Hz, 1H), 2.27 (ddt, *J* = 12.6, 7.6, 3.8 Hz, 1H), 1.95 (q, *J* = 10.2 Hz, 1H), 1.69 (q, *J* = 10.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 158.0, 137.3, 135.5, 131.9, 130.1, 127.4, 121.8, 113.9, 94.9, 74.2, 57.8, 55.5, 35.6, 35.2, 34.6, 34.2; IR (neat) 2959, 2932, 1748, 1610, 1513, 1488, 1297, 1246, 1177, 1136, 1073, 1036, 1011, 829, 800, 760, 720 cm^{-1}. MS (APCI-) 502.9594 (502.9589 calcd for $C_{21}H_{19}O_3BrCl_3$, M - H$^+$). The enantiopurity was determined to be 92% *ee* by chiral HPLC (Chiralpak IH-U, 10 cm x 3.0 mm, 1.6 µm particle size, 5% IPA/Hexanes, 0.35 mL/min, λ 230 nm, RT= 3.2 and 3.6 min).



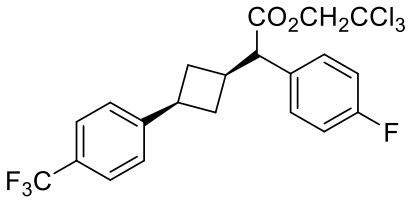
2,2,2-Trichloroethyl (*S*)-2-(4-bromophenyl)-2-((1*s*,3*R*)-3-(4-(trifluoromethyl)phenyl)cyclobutyl)acetate (23). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (118 mg, 87%) as a colorless solid. The ratio of *cis*:*trans* cyclobutane diastereomers was >95:5 by ^{1}HNMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was >95:5 by ^{1}HNMR. mp 83.0-83.5 °C: $[\alpha]^{20}_D$ +71.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.49–7.44 (m, 2H), 7.27–7.19 (m, 4H), 4.76 (d, *J* = 12.0, 0.8 Hz, 1H), 4.68 (d, *J* = 12.0, 0.8 Hz, 1H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.48–3.39 (m, 1H), 3.07–2.95 (m, 1H), 2.78–2.67 (m, 1H), 2.32 (dtd, *J* = 11.1, 7.7, 4.8 Hz, 1H), 2.00 (q, *J* = 10.2 Hz, 1H), 1.73 (q, *J* = 10.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 149.1, 135.2, 132.0, 130.1, 128.4 (q, *J* = 32.4 Hz), 126.7, 125.4 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272 Hz), 121.9, 94.9, 74.2, 57.6, 35.5, 35.1, 34.2, 34.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.30; IR (film) 3046, 2970, 2939, 2861, 1749, 1618, 1488, 1323, 1162, 1120, 1066, 1012, 834, 758, 718 cm^{-1}. MS (APCI+) 541.9424 (541.9424 calcd for $C_{21}H_{17}O_2BrCl_3$, M+). The enantiopurity was determined to be 90% ee by chiral HPLC (Chiralpak OD-H, 25 cm x 4.6 mm, 0.5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 9.96 and 12.96 min).



2,2,2-Trichloroethyl (*R*)-2-(4-acetoxyphenyl)-2-((1*s*,3*S*)-3-(4-(trifluoromethyl)-phenyl)cyclobutyl)acetate (24). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-acetoxyphenyl)-2-diazoacetate (176 mg, 0.50 mmol) using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (121 mg, 92%) as a colorless oil. The ratio of *cis*:*trans* cyclobutane diastereomers was >95:5 by ^{1}HNMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was >95:5 by ^{1}HNMR. $[\alpha]^{23}_D$ +41.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.36–7.32 (m, 2H), 7.24–7.21 (m, 2H), 7.08–7.03 (m, 2H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 3.64 (d, *J* = 10.7 Hz, 1H), 3.50–3.39 (m, 1H), 3.10–2.98 (m, 1H), 2.75–2.67 (m, 1H), 2.42–2.31 (m, 1H), 2.28 (s, 3H), 1.98 (q, *J* = 10.2 Hz, 1H), 1.75 (q, *J* = 10.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.03, 169.33, 150.23, 149.11, 133.60, 129.26, 128.28 (q, *J* = 32.3 Hz), 126.59, 125.24 (q, *J* = 3.3 Hz), 124.31 (q, *J* = 272.1 Hz), 121.83, 94.82, 74.05, 57.48, 35.44, 34.89, 34.20, 34.00, 21.13. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.27; IR (neat) 3042, 2968, 2934, 2860, 1749, 1618, 1507, 1421, 1370, 1323, 1196, 1163, 1120, 1066, 1017, 909, 837, 754, 719 cm^{-1}. MS (ESI-) 557.0082 (557.0087 calcd for $C_{24}H_{16}N_4Cl_4F_3$, M + Cl^-). The enantiopurity was determined to be 66% ee by chiral HPLC (Chiralpak IHU 1.6 um, 100 mm x 3 mm, 5.0% IPA/Hexanes, 0.500 mL/min, λ 230 nm, RT= 3.25 and 3.87 min).

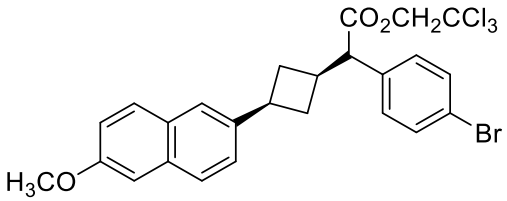


2,2,2-Trichloroethyl (*S*)-2-(4-chlorophenyl)-2-((1*s*,3*R*)-3-(4-(trifluoromethyl)phenyl)cyclobutyl)acetate (25). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-chlorophenyl)-2-diazoacetate (164 mg, 0.50 mmol) using Rh_2(*S*-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (88 mg, 70%) as a colorless oil. The ratio of *cis*:*trans* cyclobutane diastereomers was equal to 95:5 by ^{1}HNMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was >95:5 by ^{1}HNMR. $[\alpha]^{23}_D$ +62.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.33–7.29 (m, 2H), 7.29–7.26 (m, 2H), 7.25–7.21 (m, 2H), 4.76 (d, *J* = 12.0, 1.0 Hz, 1H), 4.68 (d, *J* = 12.0, 1.0 Hz, 1H), 3.62 (d, *J* = 10.6 Hz, 1H), 3.44 (p, *J* = 9.1 Hz, 1H), 3.08–2.97 (m, 1H), 2.78–2.68 (m, 1H), 2.35–2.29 (m, 1H), 2.00 (q, *J* = 10.2 Hz, 1H), 1.73 (q, *J* = 10.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 149.1, 134.7, 133.8, 129.7, 129.1, 128.4 (q, *J* = 32.3 Hz), 126.7, 125.4 (q, *J* = 3.7 Hz), 122.60 (q, *J* = 272 Hz), 94.9, 74.2, 57.6, 35.5, 35.1, 34.3, 34.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.30; IR (neat) 3047, 2970, 2939, 2862, 1749, 1618, 1491, 1323, 1162, 1120, 1066, 1015, 834, 765, 715 cm^{-1}. MS (APCI+) 497.9927 (497.9929 calcd for $C_{21}H_{17}O_2Cl_4F_3$, M +). The enantiomeric excess was determined to be 87% by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 1% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 8.96 and 11.74 min).



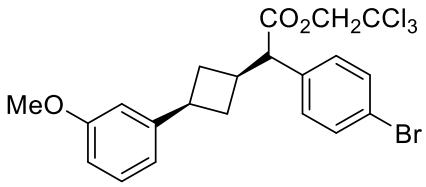
2,2,2-Trichloroethyl (*S*)-2-(4-fluorophenyl)-2-((1*s*,3*R*)-3-(4-(trifluoromethyl)phenyl)cyclobutyl)acetate (26). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-diazo-2-(4-fluorophenyl)acetate (156 mg, 0.50 mmol) using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. Obtained 99 mg of compound **24** as a colorless oil (82% yield.) The ratio of *cis*:*trans* cyclobutane diastereomers was equal to 94:6 by ^{1}HNMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was equal to 93:7 by ^{1}HNMR. $[\alpha]^{23}_D$ +24.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, Chloroform-d) δ 7.53 (d, J = 8.1 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.24 (s, 2H), 7.03 (t, J = 8.6 Hz, 2H), 4.76 (d, J = 12.0 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 3.63 (d, J = 10.7 Hz, 1H), 3.45 (p, J = 9.1 Hz, 1H), 3.03 (qt, J = 10.1, 7.5 Hz, 1H), 2.78 – 2.68 (m, 1H), 2.37 – 2.28 (m, 1H), 2.00 (q, J = 10.2 Hz, 1H), 1.74 (q, J = 10.3 Hz, 1H). ^{13}C NMR (151 MHz, CDCl3) δ 171.11, 162.33 (d, *J* = 246.1 Hz), 149.05, 131.89 (d, *J* = 3.3 Hz), 129.82 (d, *J* = 7.8 Hz), 128.32 (q, *J* = 32.2 Hz), 126.57, 125.25 (q, *J* = 3.3 Hz), 124.38 (q, *J* = 271.8 Hz), 115.65 (d, *J* = 21.7 Hz), 94.79, 74.05, 57.30, 35.42, 34.93, 34.22, 33.93.^{19}F NMR (282 MHz, $CDCl_3$) δ -62.30, -114.59; IR (neat) 3046, 2969, 2940, 2863, 1749, 1618, 1509, 1323, 1225, 1161, 1120, 1066, 1016, 837, 802, 754, 717 cm^{-1}. MS (APCI-) 481.0159 (481.0158 calcd for $C_{21}H_{16}O_2Cl_3F_4$, M – H+). The enantiopurity was determined to be 74% ee by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 1.0% IPA/Hexanes, 1.0 mL/min, λ 210 nm, RT= 8.43

and 10.45 min).



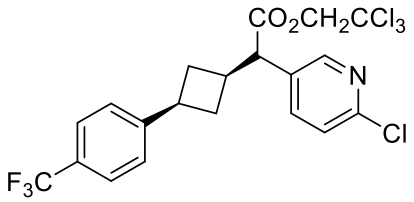
2,2,2-Trichloroethyl (*S*)-2-(4-bromophenyl)-2-((1*s*,3*R*)-3-(6-methoxynaphthalen-2-yl)cyclobutyl)acetate (27). The general procedure 2 was employed for the C–H functionalization of 2-cyclobutyl-6-methoxynaphthalene (53 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (87 mg, 67%) as a colorless solid. Neither the ratio of *cis*:*trans* cyclobutane diastereomers nor the ratio of C3:C1 functionalization products could be accurately determined by ^{1}HNMR due to overlaps. For this experiment, the reported values were determined by isolation. mp 84–89 °C: $[\alpha]^{23}_D$ +80.6 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 3H), 7.29–7.22 (m, 3H), 7.16–7.09 (m, 2H), 4.78 (d, *J* = 11.9 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 3.91 (s, 3H), 3.66 (d, *J* = 10.7 Hz, 1H), 3.53 (p, *J* = 9.1 Hz, 1H), 3.04 (dp, *J* = 17.4, 9.7, 8.6 Hz, 1H), 2.76 (dq, *J* = 15.4, 7.6 Hz, 1H), 2.35 (dq, *J* = 12.4, 7.7, 6.2 Hz, 1H), 2.08 (q, *J* = 10.2 Hz, 1H), 1.82 (q, *J* = 10.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 157.4, 140.3, 135.5, 133.2, 132.0, 130.1, 129.1, 129.0, 127.0, 125.7, 124.2, 121.8, 119.0, 105.8, 94.9, 74.2, 57.8, 55.4, 35.8, 35.3, 34.3, 34.3; IR (film) 3055, 2961, 2934, 2856, 1750, 1634, 1606, 1487, 1266, 1216, 1135, 1073, 1032, 1011, 852, 830, 810, 761, 718 cm^{-1}. MS (NSI+) 554.9899 (554.9891

calcd for $C_{25}H_{23}O_3BrCl_3$, M + H^+). The enantiopurity was determined to be 94% *ee* by chiral HPLC (Chiralpak IH-U, 10 cm x 3.0 mm, 1.6 µm particle size, 5% IPA/Hexanes, 0.35 mL/min, λ 230 nm, RT= 4.4 and 5.7 min).



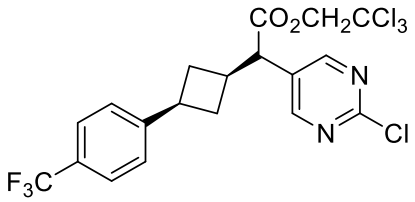
2,2,2-Trichloroethyl (*S*)-2-(4-bromophenyl)-2-((1*s*,3*R*)-3-(3-methoxyphenyl)cyclobutyl)acetate (28). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-3-methoxybenzene (41 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (45 mg, 35%) as a colorless oil. The ratio of *cis*:*trans* cyclobutane diastereomers was equal to 95:5 by ^{1}HNMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was >95:5 by ^{1}HNMR. $[\alpha]^{23}_D$ +63.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52–7.43 (m, 2H), 7.24–7.19 (m, 3H), 6.76–6.71 (m, 2H), 6.69 (s, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 3.79 (s, 3H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.38 (ddd, *J* = 18.1, 10.0, 7.9 Hz, 1H), 2.98 (qt, *J* = 9.9, 7.4 Hz, 1H), 2.69 (dtd, *J* = 10.9, 7.8, 5.0 Hz, 1H), 2.28 (dtd, *J* = 11.1, 7.6, 4.9 Hz, 1H), 1.99 (q, *J* = 10.2 Hz, 1H), 1.73 (q, *J* = 10.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 159.8, 146.9, 135.5, 131.9, 130.1, 129.5, 121.8, 118.8, 112.4, 111.2, 94.9, 74.2, 57.8, 55.3, 35.8, 35.2, 34.2, 34.2; IR (neat) 2962, 2934, 2856, 2834, 1748, 1600, 1582, 1488, 1464, 1453, 1433, 1407, 1371, 1332, 1288, 1259, 1194, 1158, 1134, 1073, 1046,

1011, 910, 865, 824, 803, 763, 754, 719, 696 cm^{-1}. MS (APCI-) 502.9595 (502.9589 calcd for $C_{21}H_{19}O_3BrCl_3$, M - H^+). The enantiopurity was determined to be 88% *ee* by chiral HPLC (Regis Technologies, Inc. (*S*,*S*)-Whelk-01, 25 cm x 4.6 mm, 0.5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 30.5 and 39.5 min).



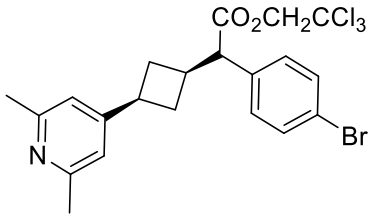
2,2,2-Trichloroethyl (*S*)-2-(6-chloropyridin-3-yl)-2-((1*s*,3*R*)-3-(4-(trifluoromethyl)phenyl)cyclobutyl)acetate (29). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (164 mg, 0.50 mmol) using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (45 mg, 36%) as a colorless oil. The ratio of *cis*:*trans* cyclobutane diastereomers was equal to 93:7 by ^{1}HNMR (By relative integration of the doublets at 3.61 and 3.89 ppm, respectively.) The ratio of C3:C1 functionalization products was 87:13 by ^{1}HNMR. $[\alpha]^{23}_D$ +63.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 2.6 Hz, 1H), 7.70 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 3.68 (d, *J* = 10.7 Hz, 1H), 3.47 (p, *J* = 9.2 Hz, 1H), 3.01 (qt, *J* = 9.9, 7.3 Hz, 1H), 2.76 (dtd, *J* = 15.5, 7.6, 4.9 Hz, 1H), 2.35 (dtd, *J* = 15.6, 7.6, 4.9 Hz, 1H), 2.06 (q, *J* = 10.2 Hz, 1H), 1.74 (q, *J* = 10.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 151.2, 149.6, 148.7, 138.5, 131.0, 128.6 (q, *J* = 32.3 Hz), 126.7, 125.4 (q, *J* = 3.8 Hz), 124.6, 124.4 (q, *J* = 272

Hz), 94.6, 74.3, 54.8, 35.4, 35.1, 34.3, 34.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.34; IR (neat) 3048, 2970, 2936, 2862, 1750, 1618, 1585, 1565, 1461, 1323, 1161, 1104, 1065, 1017, 835, 774, 758, 718 cm^{-1}. MS (APCI+) 499.9969 (499.9960 calcd for $C_{20}H_{17}O_2NCl_4F_3$, M + H^+). The enantiopurity was determined to be 80% *ee* by chiral HPLC (Chiralpak OD-H, 25 cm x 4.6 mm, 5% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 11.2 and 19.2 min).



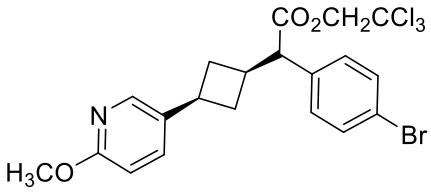
2,2,2-Trichloroethyl (*S*)-2-(2-chloropyrimidin-5-yl)-2-((1*s*,3*R*)-3-(4-(trifluoromethyl)phenyl)cyclobutyl)acetate (30). The general procedure 2 was employed for the C–H functionalization of 1-cyclobutyl-4-(trifluoromethyl)benzene (50 mg, 0.25 mmol) by reaction of 2,2,2-trichloroethyl 2-(2-chloropyrimidin-5-yl)-2-diazoacetate (165 mg, 0.50 mmol) using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (29 mg, 29%) as a colorless oil. The ratio of *cis*:*trans* cyclobutane diastereomers was equal to 94:6 by ^{1}HNMR (By relative integration of the doublets at 3.61 and 3.92 ppm, respectively.) The ratio of C3:C1 functionalization products was 89:11 by ^{1}HNMR. $[\alpha]^{23}_D$ +26.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-d) δ 8.65 (s, 2H), 7.67 – 7.49 (m, 2H), 7.28 – 7.22 (m, 2H), 4.81 (d, J = 11.9 Hz, 1H), 4.75 (d, J = 11.9 Hz, 1H), 3.69 (d, J = 10.6 Hz, 1H), 3.51 (p, J = 9.2 Hz, 1H), 3.02 (dtd, J = 17.4, 9.9, 7.4 Hz, 1H), 2.80 (dtd, J = 12.3, 7.6, 4.8 Hz, 1H), 2.41 (ddd, J = 11.5, 7.9, 4.9 Hz, 1H), 2.12 (q, J = 10.3 Hz, 1H), 1.76 (q, J = 10.3 Hz, 1H). ; ^{13}C NMR

(151 MHz, CDCl3) δ 169.30, 161.02, 159.20, 148.18, 128.62, 128.61 (q, *J* = 32.3 Hz), 126.49, 125.38 (q, *J* = 4.4 Hz), 124.21 (q, *J* = 271.8 Hz), 94.33, 74.41, 52.62, 35.26, 35.00, 34.16, 34.00. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.37; IR (film) 3045, 2974, 2941, 2864, 1750, 1618, 1578, 1547, 1399, 1323, 1155, 1112, 1065, 1016, 908, 837, 774, 729, 714 cm^{-1}. MS (APCI+) 500.9912 (500.9913 calcd for $C_{19}H_{16}O_2N_2Br_2Cl_4F_3$, M + H+). The enantiopurity was determined to be 79% *ee* by chiral HPLC (Chiralpak OD-H, 25 cm x 4.6 mm, 5% IPA/Hexanes, 1.0 mL/min, λ 210 nm, RT = 19.8 and 23.1 min).



2,2,2-trichloroethyl (*S*)-2-(4-bromophenyl)-2-((1*s*,3*R*)-3-(2,6-dimethylpyridin-4-yl)cyclobutyl)acetate (31). The general procedure 2 was employed for the C-H functionalization of 4-cyclobutyl-2,6-dimethylpyridine (40.3 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (97 mg, 77% yield) as a colorless oil. The ratio of *cis*:*trans* cyclobutanes was equal to 85:15 by relative integration of the multiplets at 3.11 and 2.98 ppm in the crude ^{1}HNMR spectrum. The ratio of C3:C1 functionalization products was >95:5 by ^{1}HNMR. $[\alpha]^{23}_D$ + 69.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, Chloroform-d) δ 7.43 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 6.68 (s, 2H), 4.73 (d, J = 11.9 Hz, 1H), 4.65 (d, J = 11.9 Hz, 1H), 3.57 (d, J = 10.7 Hz, 1H), 3.27 (p, J = 9.1 Hz, 1H), 2.98 (qd, J = 10.1, 5.0 Hz, 1H), 2.65 (dtd, J = 12.1, 7.6, 4.7 Hz, 1H), 2.45 (s, 6H), 2.23 (dtd, J = 12.3, 7.6, 4.7 Hz, 1H), 1.93 (q, J = 10.2 Hz, 1H), 1.68

(t, J = 10.3 Hz, 1H). ^{13}C NMR (151 MHz, cdcl3) δ 170.70, 157.56, 154.16, 135.02, 131.81, 129.88, 121.74, 118.08, 94.68, 74.01, 57.41, 34.68, 34.28, 34.10, 33.19, 24.39. IR (neat) 2965, 2926, 2854, 1749, 1606, 1564, 1488, 1136, 1173, 1101, 826, 763, 718 cm^{-1}. MS (ESI+) 503.9894 (503.9894 calcd for $C_{21}H_{22}O_2N^{79}Br^{35}Cl_3$, M + H$^+$) The enantiopurity was determined to be 93% *ee* by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 2.0% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 18.2 and 20.8 min)



2,2,2-trichloroethyl (*S*)-2-(4-bromophenyl)-2-((1*s*,3*R*)-3-(6-methoxypyridin-3-yl)cyclobutyl)acetate (32). The general procedure 2 was employed for the C-H functionalization of 5-cyclobutyl-2-methoxypyridine (40.8 mg, 0.25 mmol) by reaction of 2-(4-bromophenyl)-2-diazoacetate (186 mg, 0.50 mmol) using Rh_2(S-2-Cl-5-BrTPCP)$_4$ (4.8 mg, 1 mol%) as catalyst. This procedure afforded the title compound (69 mg, 54% yield) as a colorless oil. The ratio of *cis*:*trans* cyclobutanes was equal to 92:8 by relative integration of the multiplets at 2.97 and 3.05 ppm in the crude ^{1}HNMR spectrum. The ratio of C3:C1 functionalization products was equal to 78:22 by relative integration of the multiplets at 2.41 and 3.32 ppm in the crude ^{1}HNMR spectrum. [α]$^{23}_D$ + 70.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-d) δ 8.02 – 7.92 (m, 1H), 7.52 – 7.43 (m, 2H), 7.39 (ddd, J = 8.5, 2.5, 0.6 Hz, 1H), 7.29 – 7.19 (m, 2H), 6.68 (dd, J = 8.4, 0.8 Hz, 1H), 4.77 (d, J = 12.0 Hz, 1H), 4.68 (d, J = 11.9 Hz, 1H), 3.90 (s, 2H), 3.62 (d, J = 10.7 Hz, 1H), 3.33 (tt, J = 10.1, 8.0 Hz, 1H), 2.99 (dtt, J = 10.6, 9.6, 7.4 Hz, 1H), 2.73 – 2.62 (m,

1H), 2.33 – 2.21 (m, 1H), 1.95 (q, J = 10.2 Hz, 1H), 1.66 (d, J = 10.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.78, 162.78, 144.50, 136.85, 135.14, 132.67, 131.82, 129.91, 121.74, 110.46, 94.72, 74.06, 57.50, 53.34, 35.17, 34.21, 32.74. IR (neat) 2966, 2944, 2857, 1748, 1607, 1571, 1493, 1374, 1329, 1284, 1258, 1135, 1028, 1012, 830, 761, 721 cm^{-1}. MS (ESI+) X (X calcd for $C_{21}H_{22}O_2N^{79}Br^{35}Cl_3$, M + H^+) The enantiopurity was determined to be 92% *ee* by chiral HPLC (Chiralpak AD-H, 25 cm x 4.6 mm, 3.0% IPA/Hexanes, 1.0 mL/min, λ 230 nm, RT= 10.7 and 20.1 min)

Procedure for Determining Relative Rates of C-H Functionalization

For both Rh_2(*R*-TCPTAD)$_4$ and Rh_2[(*S*)-2-Cl-5-BrTPCP]$_4$ catalysts, reactions were conducted according to General Procedure 2 using an equimolar mixture of 4-tertbutylphenyl cyclobutane (1.50 equiv, 70.6 mg, 0.375 mmol) and either 4-ethyltoluene (1.50 equiv, 45.1 mg, 0.375 mmol) or 4-isopropyltoluene (1.50 equiv, 50.3 mg, 0.375 mmol) with 2,2,2-trichloroethyl 4-bromophenyldiazoacetate (1.00 equiv, 93.1 mg, 0.250 mmol) as the diazo component. On completion of the reaction, the mixtures were concentrated under vacuum and the resulting green oils were analyzed by ^{1}H NMR in $CDCl_3$ solvent containing 0.3% TMS (v/v) with a relaxation delay of 10 s. The relative rates of C-H functionalization were assumed to correspond to the ratios of the products observed in the crude mixture. The signals at the following chemical shifts were used to determine the ratios:

2,2,2-trichloroethyl 2-(4-bromophenyl)-2-(1-(4-(tert-butyl)phenyl)cyclobutyl)acetate: 4.00 ppm, (*s*, 1 H) or 2.48 ppm (*m*, 1 H)

2,2,2-trichloroethyl 2-(4-bromophenyl)-2-(3-(4-(tert-butyl)phenyl)cyclobutyl)acetate: 3.63 ppm (*d*, 1 H)

2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(p-tolyl)butanoate: 3.83 ppm (*d*, 1 H, with overlap of both diastereomers)

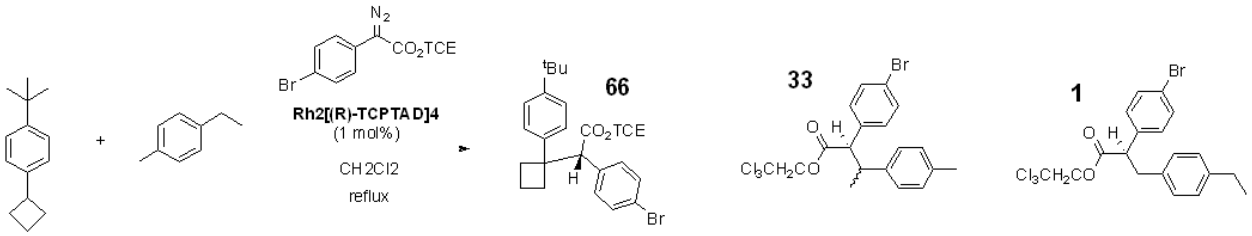
2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(4-ethylphenyl)propanoate: 3.06 ppm (*dd*, 1 H)

2,2,2-trichloroethyl 2-(4-bromophenyl)-3-methyl-3-(p-tolyl)butanoate: 3.99 ppm (*s*, 1 H), 4.46 ppm (*d*, 1 H), or 2.30 ppm (*s*, 3 H)

2,2,2-trichloroethyl 2-(4-bromophenyl)-3-(4-isopropylphenyl)propanoate: 3.06 ppm (*dd*, 1 H)

NMR Spectra for Relative Rates Study

Figure S21. The reaction with 4-tert-butylphenyl cyclobutane and 4-ethyltoluene using $Rh_2[(R)\text{-TCPTAD}]_4$ as the catalyst.



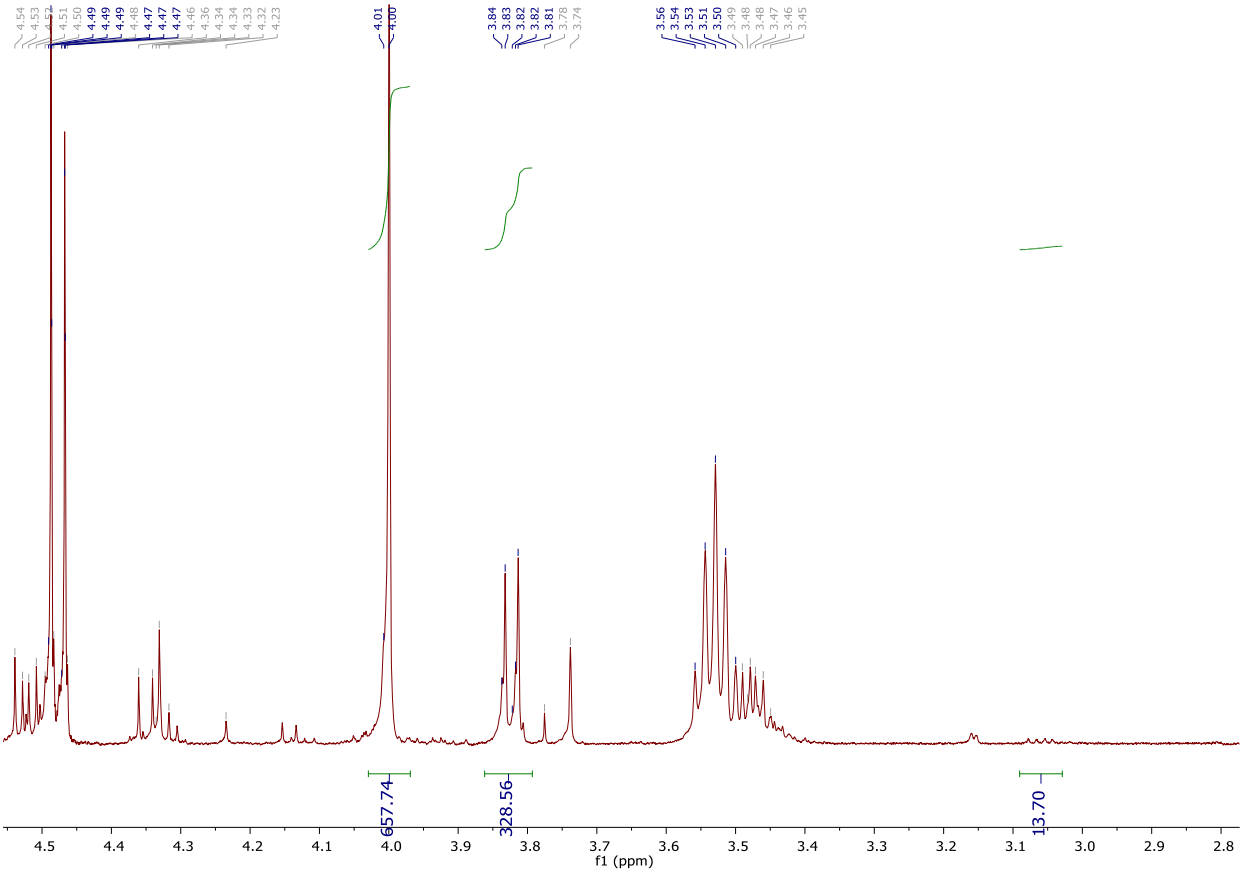


Figure S22. The reaction with 4-tert-butylphenylcyclobutane and 4-isopropyltoluene using Rh_2[(*R*)-TCPTAD]$_4$ as the catalyst.

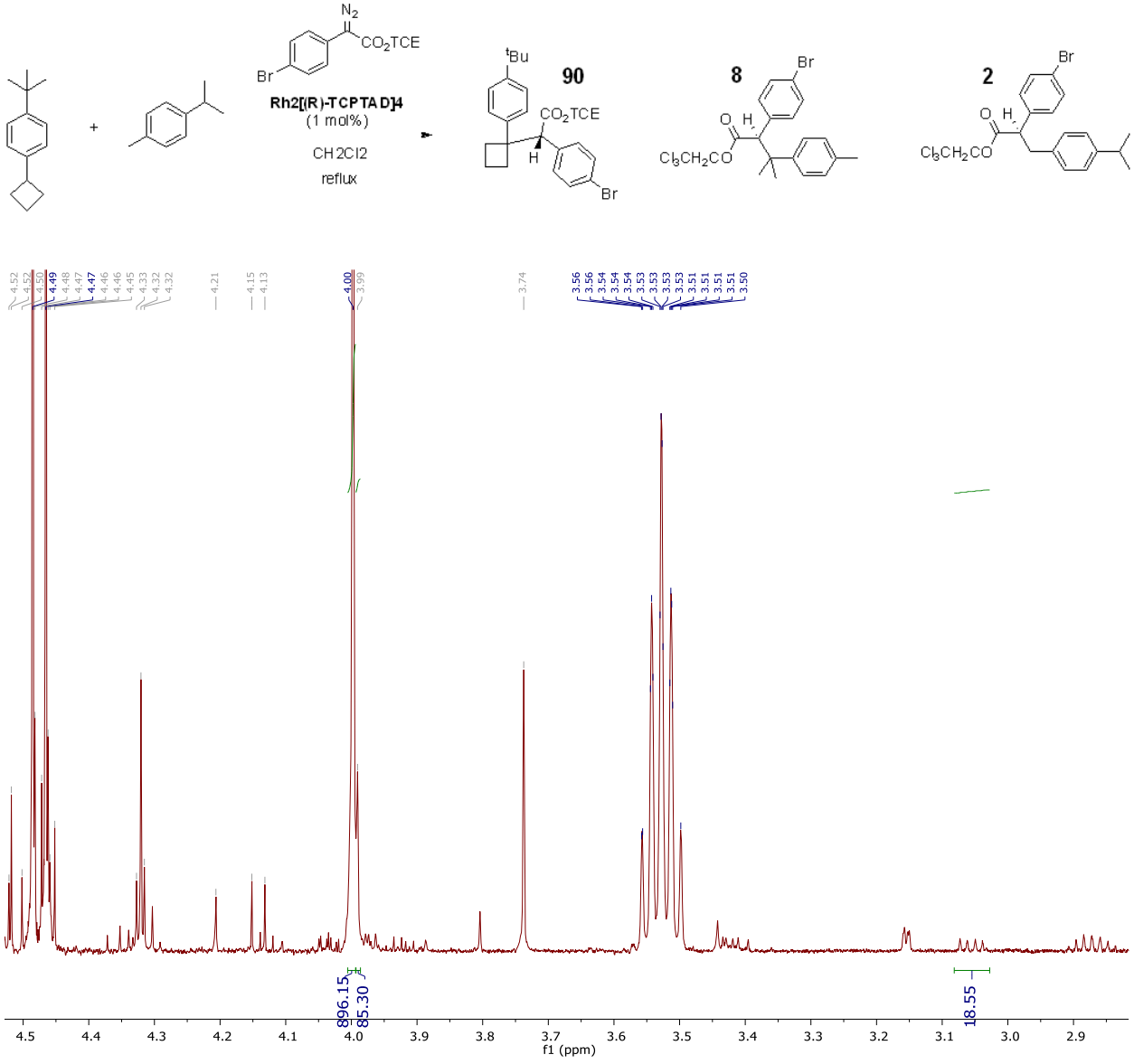


Figure S23. The reaction with 4-tert-butylphenyl cyclobutane and 4-ethyltoluene using Rh_2[(*S*)-2-Cl-5-BrTPCP]$_4$ as the catalyst.

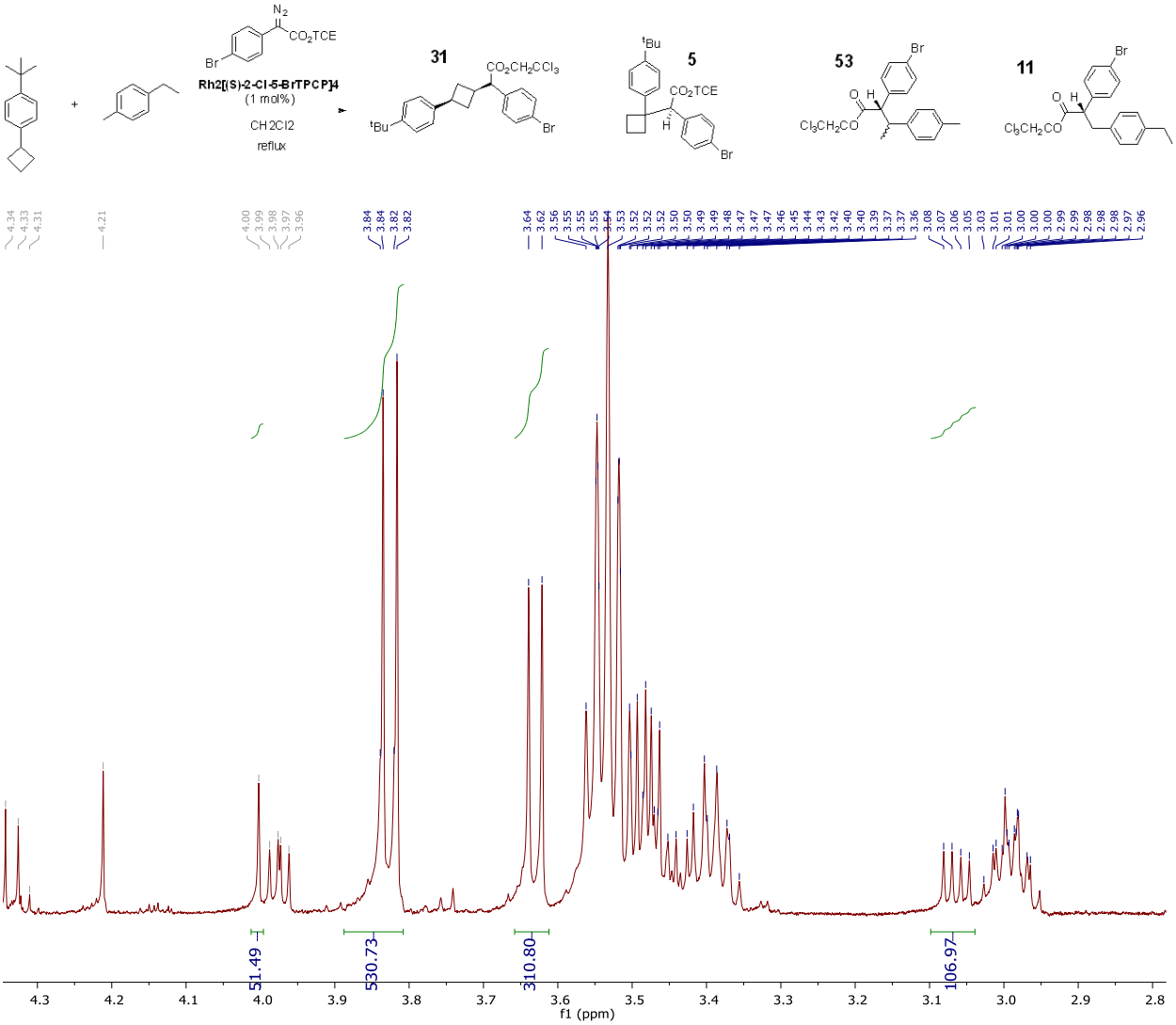
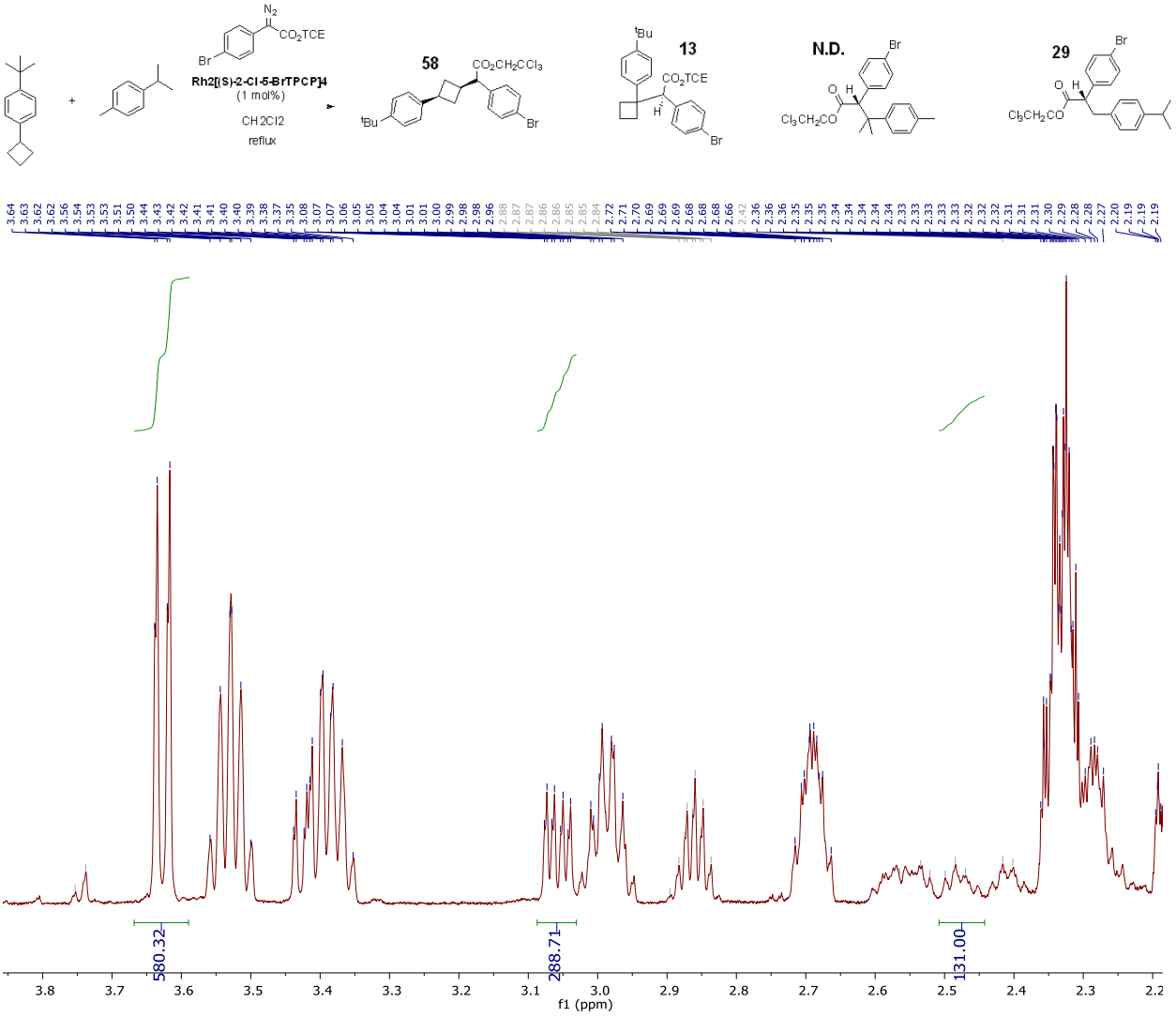


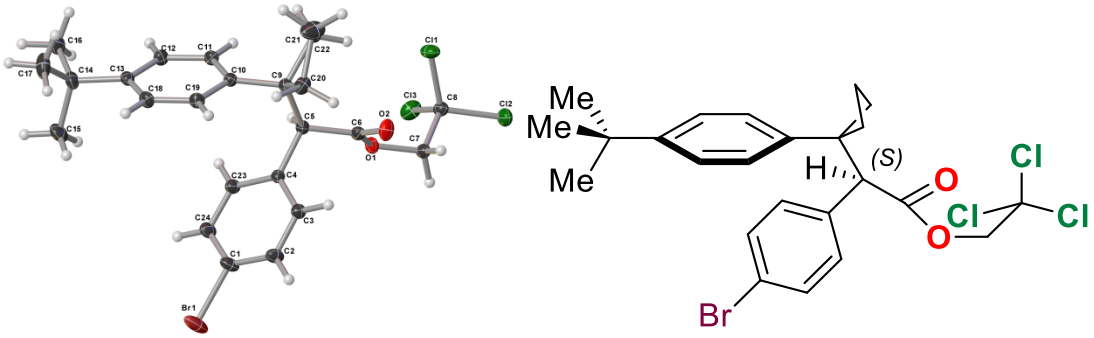
Figure S24. The reaction with 4-tert-butylphenyl cyclobutane and 4-isopropyltoluene using Rh_2[(*S*)-2-Cl-5-BrTPCP]$_4$ as the catalyst.



Determination of Absolute Configuration

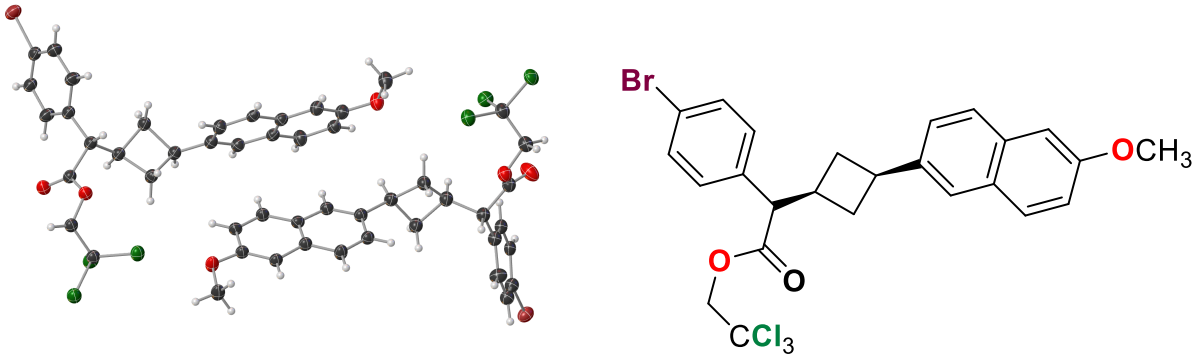
Approximately 10 mg of **8** which was synthesized with Rh_2(*S*-TCPTAD)$_4$ was placed in a 1 dram vial and was dissolved in hexanes. The solution was capped with a slight crack to allow slow evaporation leaving crystals. X-ray crystallographic analysis unveiled that the configuration was *S*.

Figure S25. Solid state structure of compound **8**.



Approximately **50** mg of **25** which was synthesized with Rh_2(*S*-2Cl-5Br-TPCP)$_4$ was placed in a 20 ml vial and dissolved in hexanes. Over time, small needles were formed which were sufficient for determining the absolute and relative configuration. This configuration was confirmed by nOe analysis.

Figure S26. Solid state structure of compound **26**.



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Nuclear Magnetic Resonance Spectra

Figure S27. ^{1}H NMR Spectrum of 1-cyclobutyl-4-methylbenzene in $CDCl_3$.

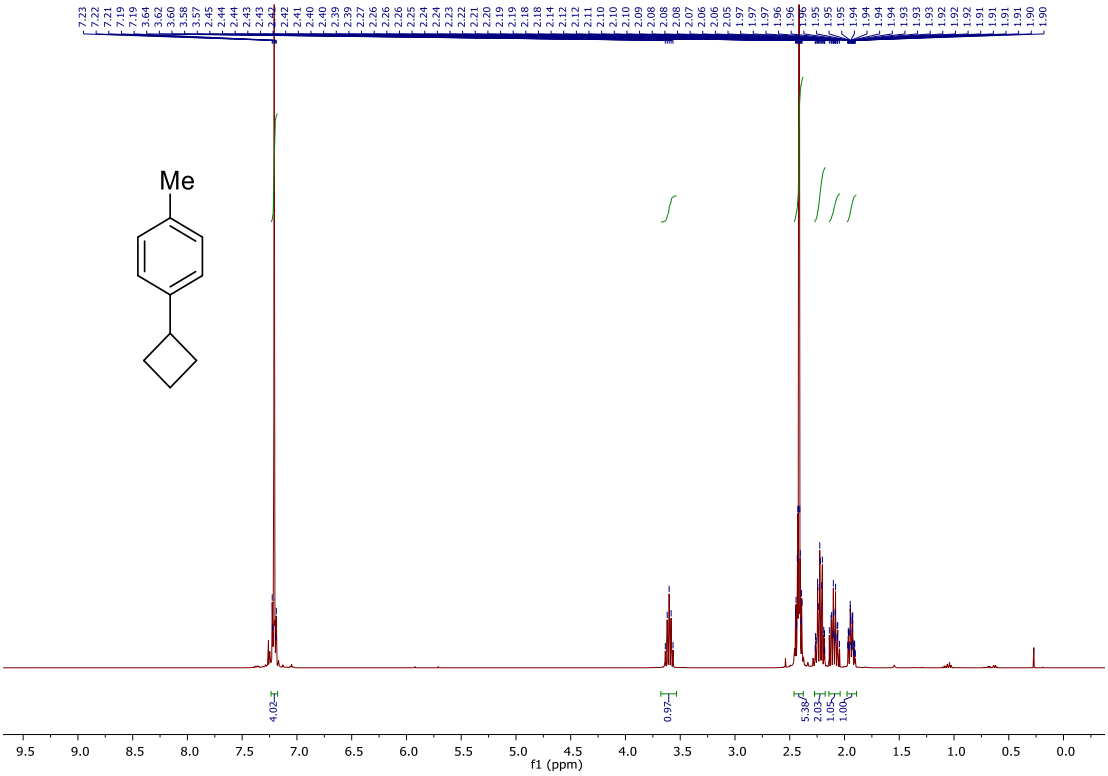


Figure S28. ^{13}C NMR spectrum of 1-cyclobutyl-4-methylbenzene in $CDCl_3$.

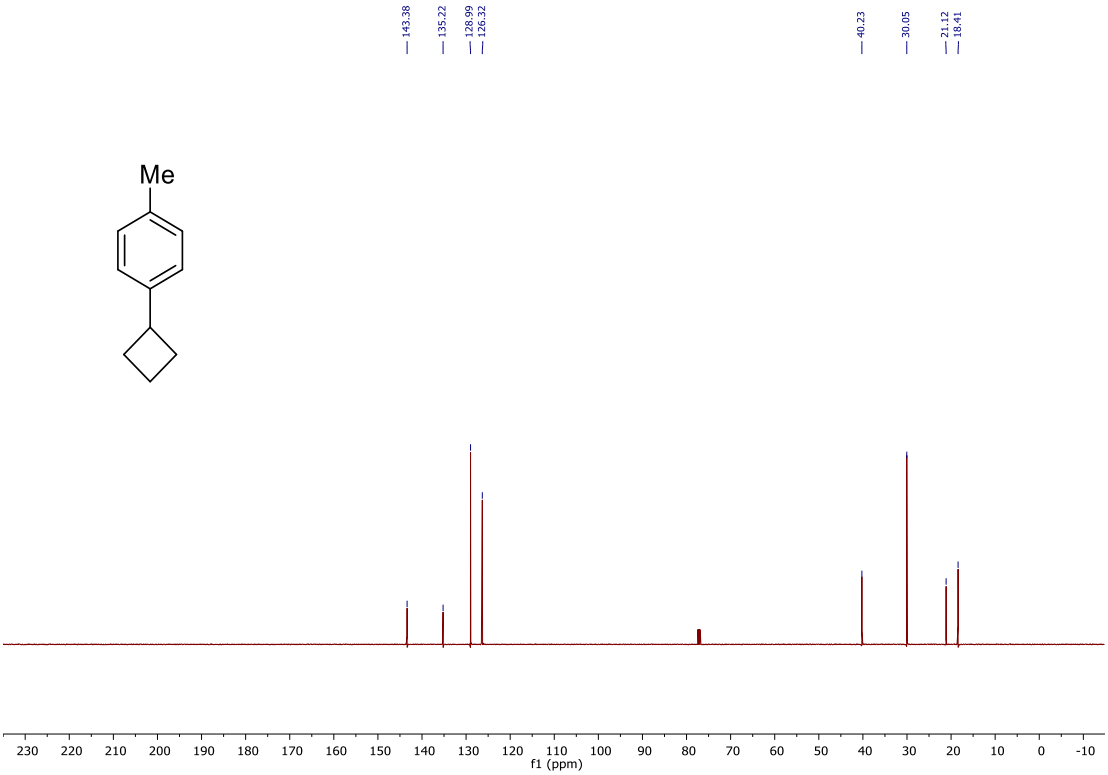


Figure S29. ^{1}H NMR spectrum of 1-(6-methoxynaphthalen-2-yl)cyclobutan-1-ol in C_6D_6.

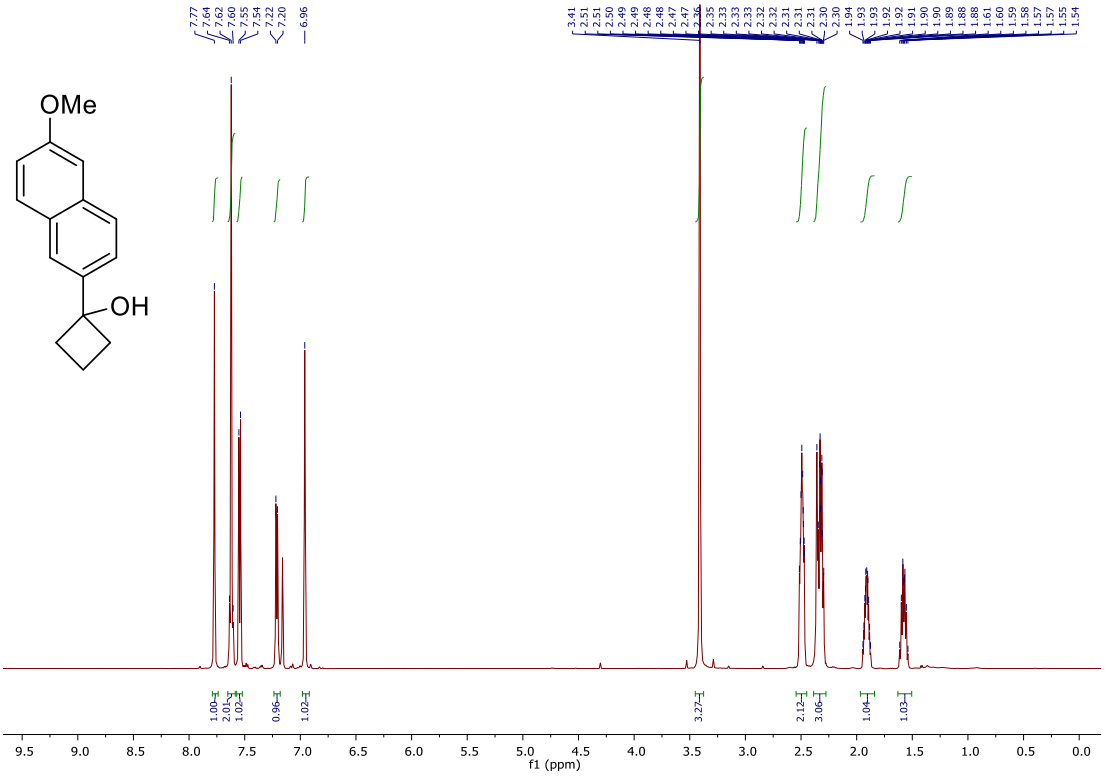


Figure S30. ^{13}C NMR spectrum of 1-(6-methoxynaphthalen-2-yl)cyclobutan-1-ol in C_6D_6.

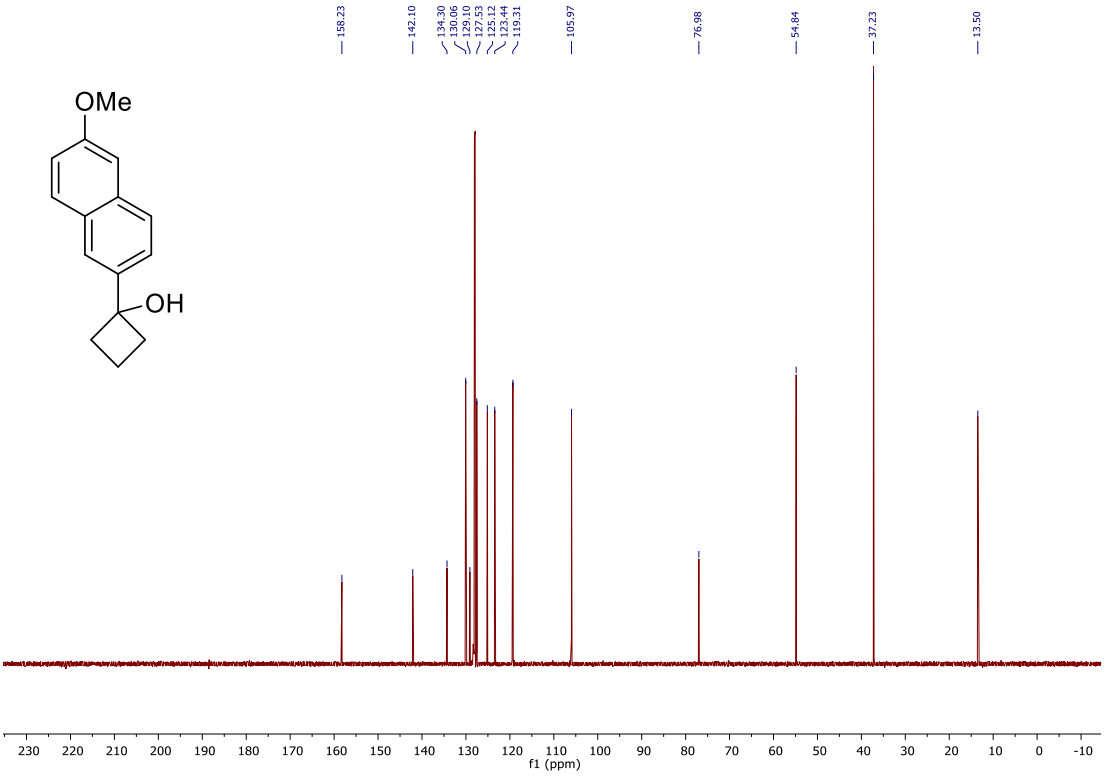


Figure S31. ^{1}H NMR Spectrum of 1-(6-methoxynaphthalen-2-yl)cyclobutane in C_6D_6.

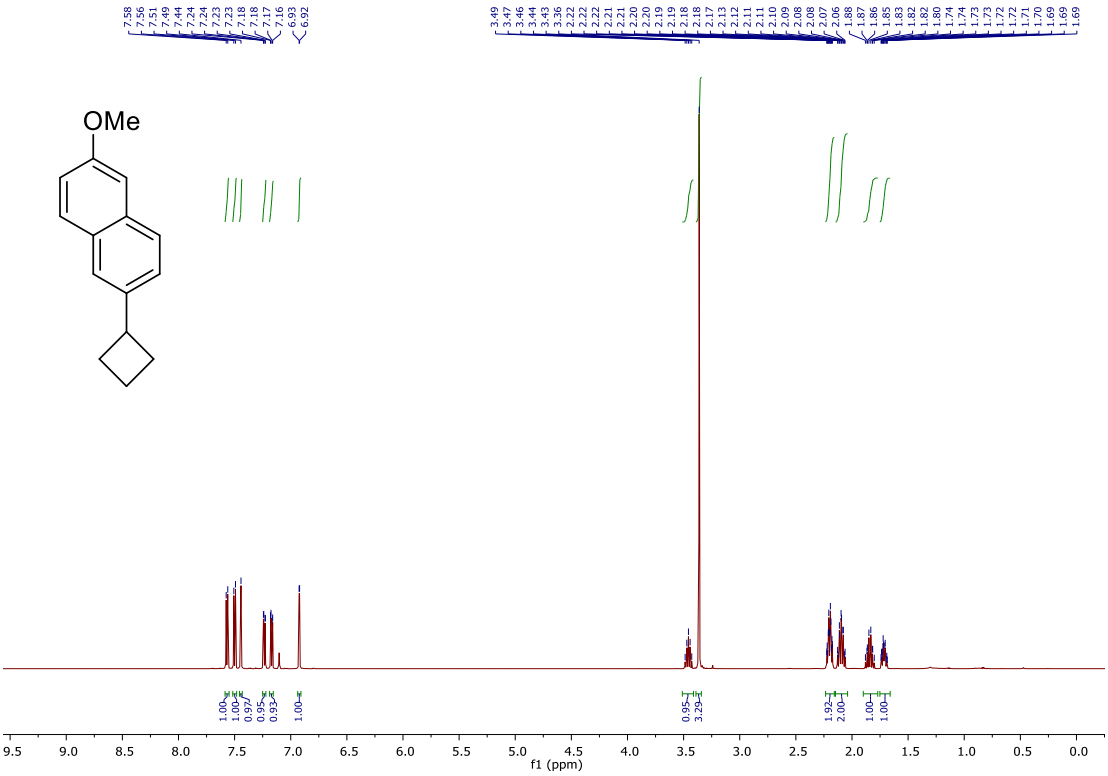


Figure S32. ^{1}H NMR Spectrum of 1-(6-methoxynaphthalen-2-yl)cyclobutane in C_6D_6.

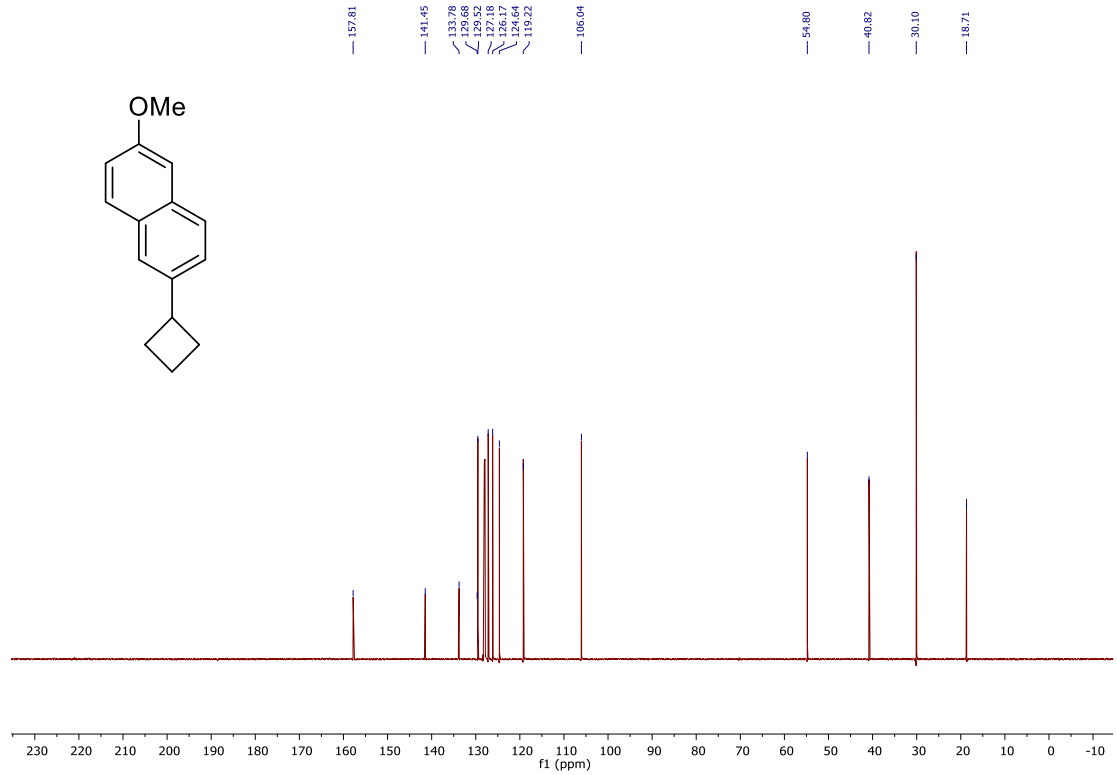


Figure S33. ^{1}H NMR Spectrum of compound **10** in $CDCl_3$.

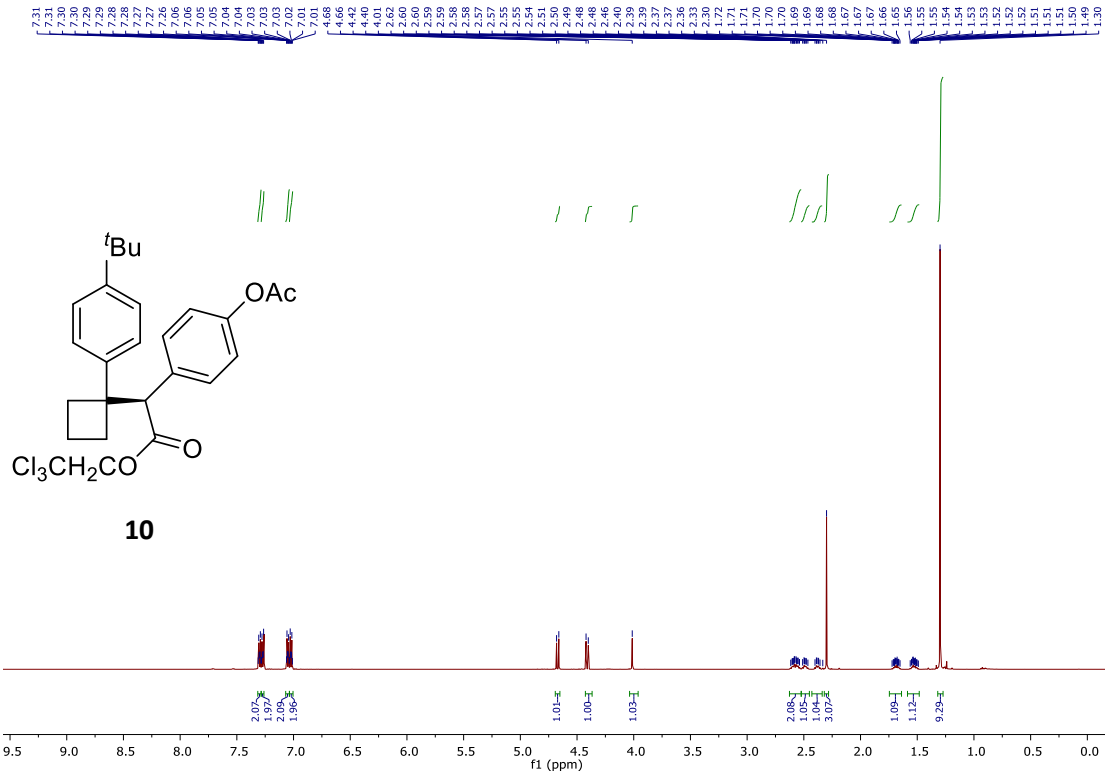


Figure S34. ^{13}C NMR spectrum of compound **10** in $CDCl_3$.

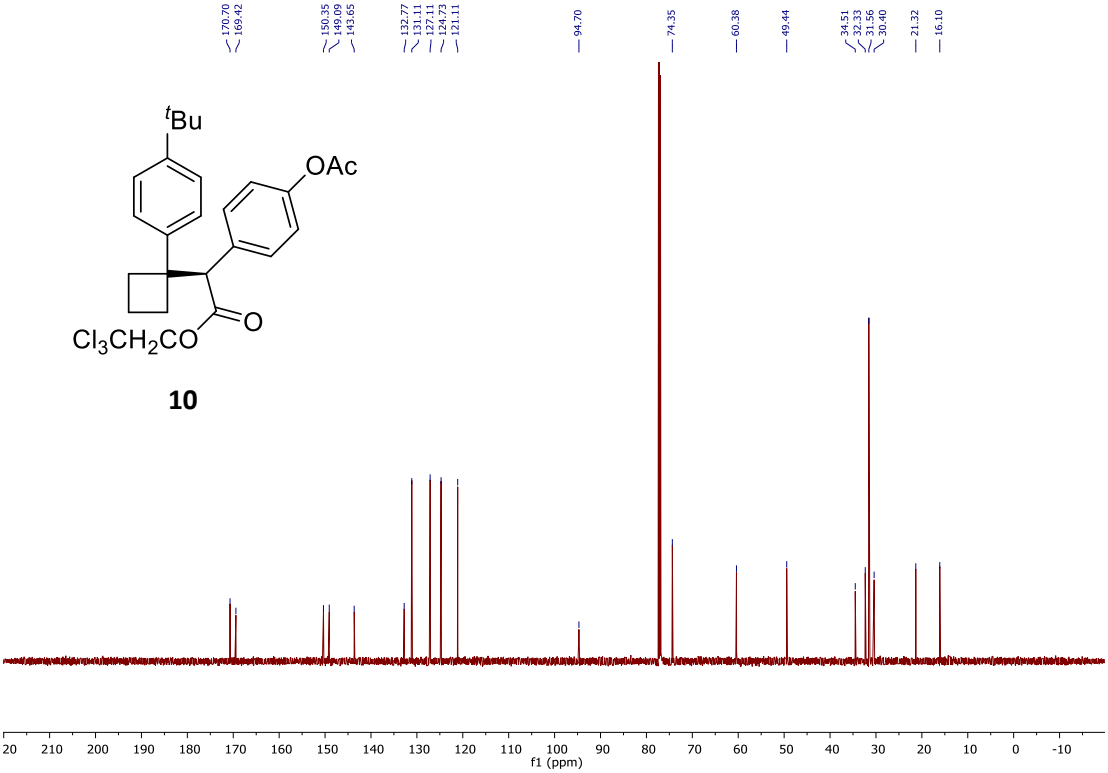


Figure S35. ^{1}H NMR Spectrum of compound **11** in $CDCl_3$.

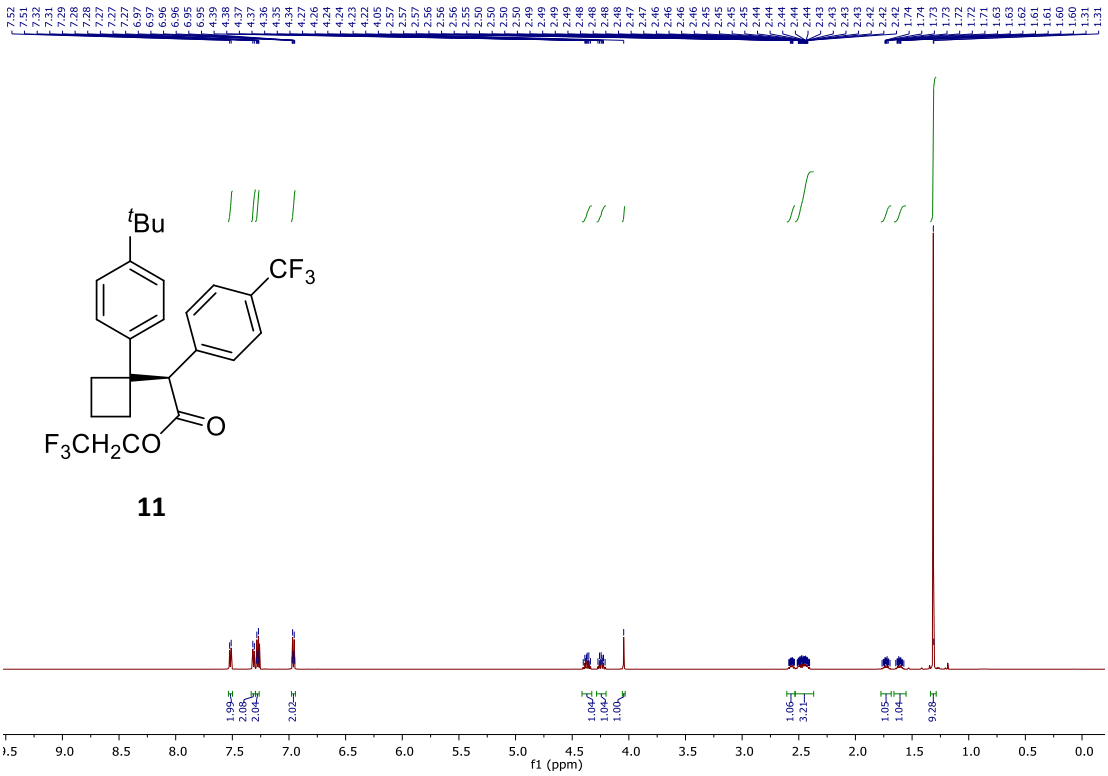


Figure S36. ^{13}C NMR spectrum of compound **11** in $CDCl_3$.

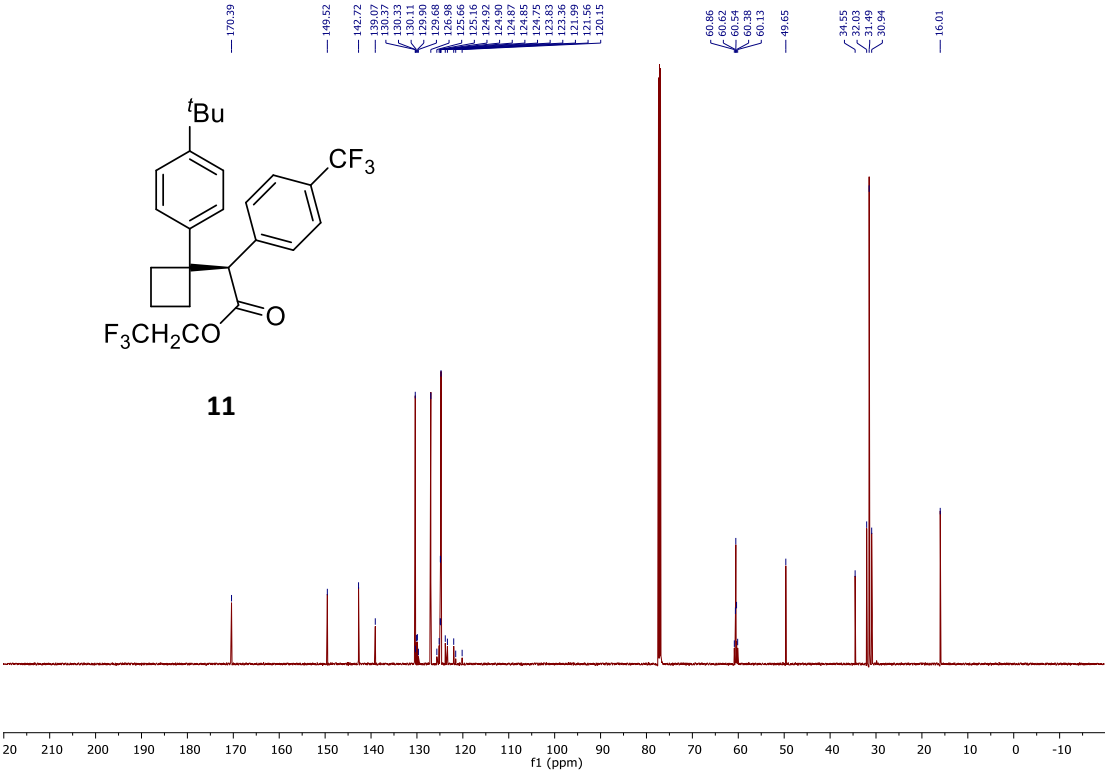


Figure S37. ^{19}F NMR spectrum of compound **11** in $CDCl_3$.

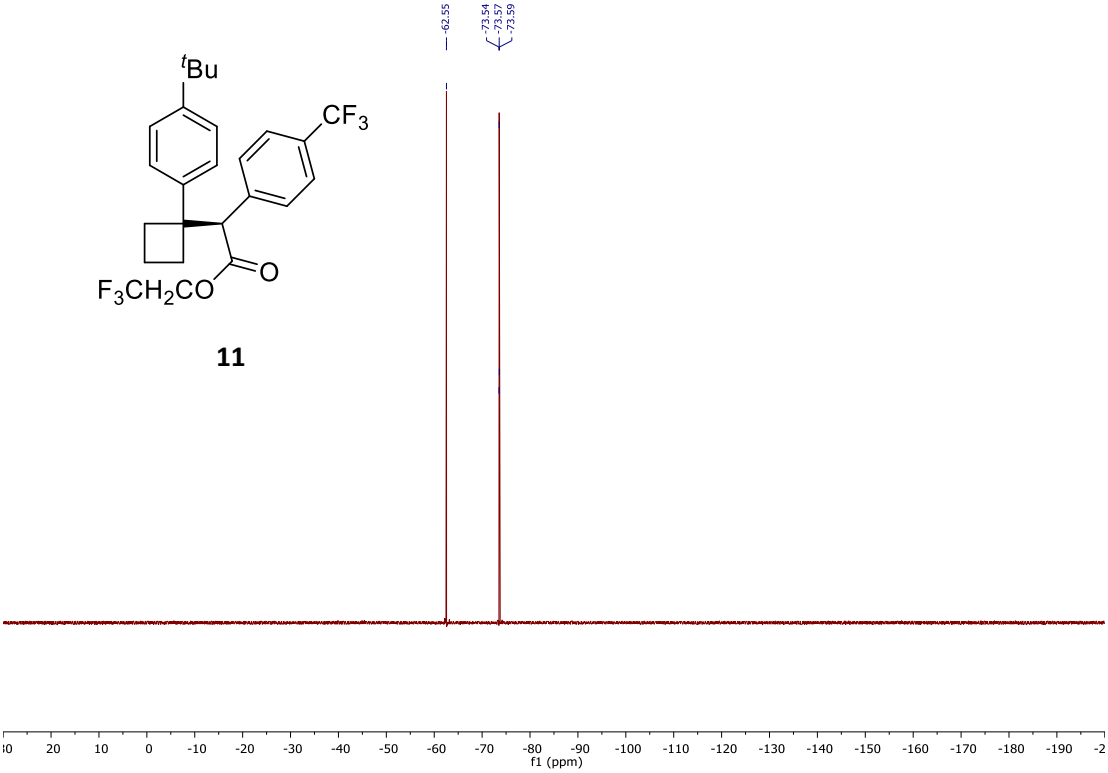


Figure S38. ^{1}H NMR Spectrum of compound **12** in $CDCl_3$.

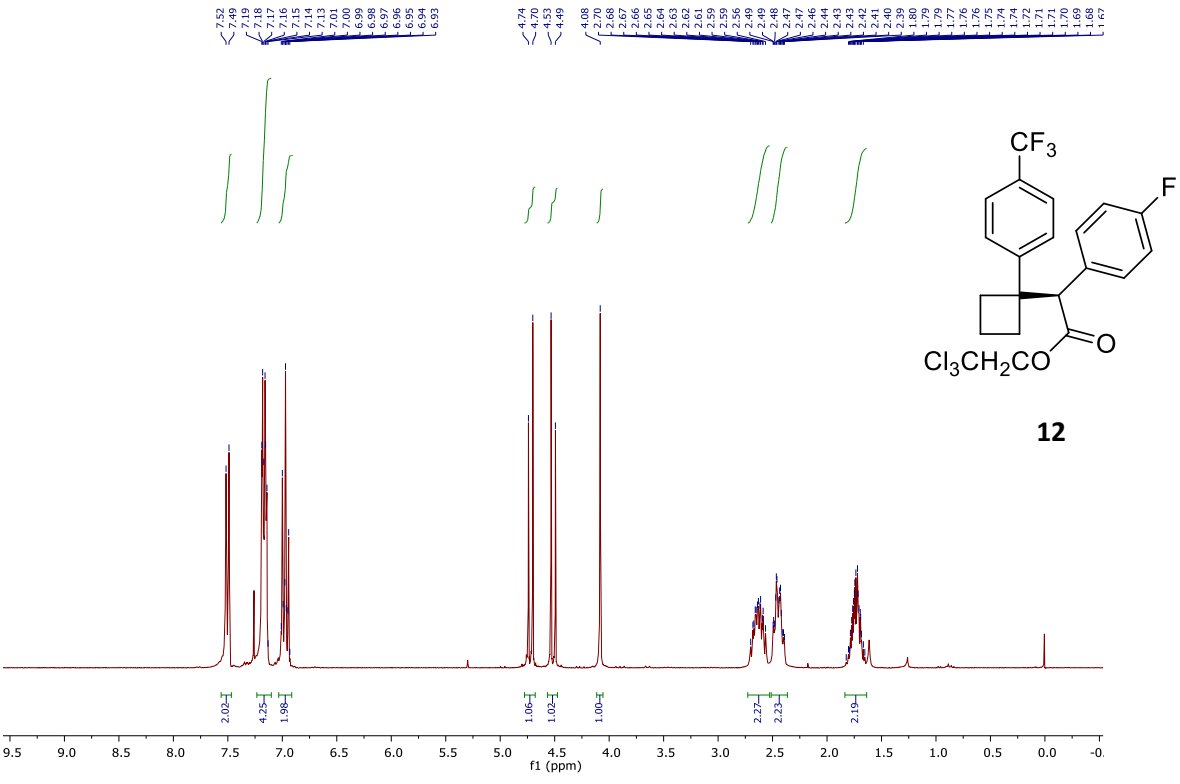


Figure S39. ^{13}C NMR spectrum of compound **12** in $CDCl_3$.

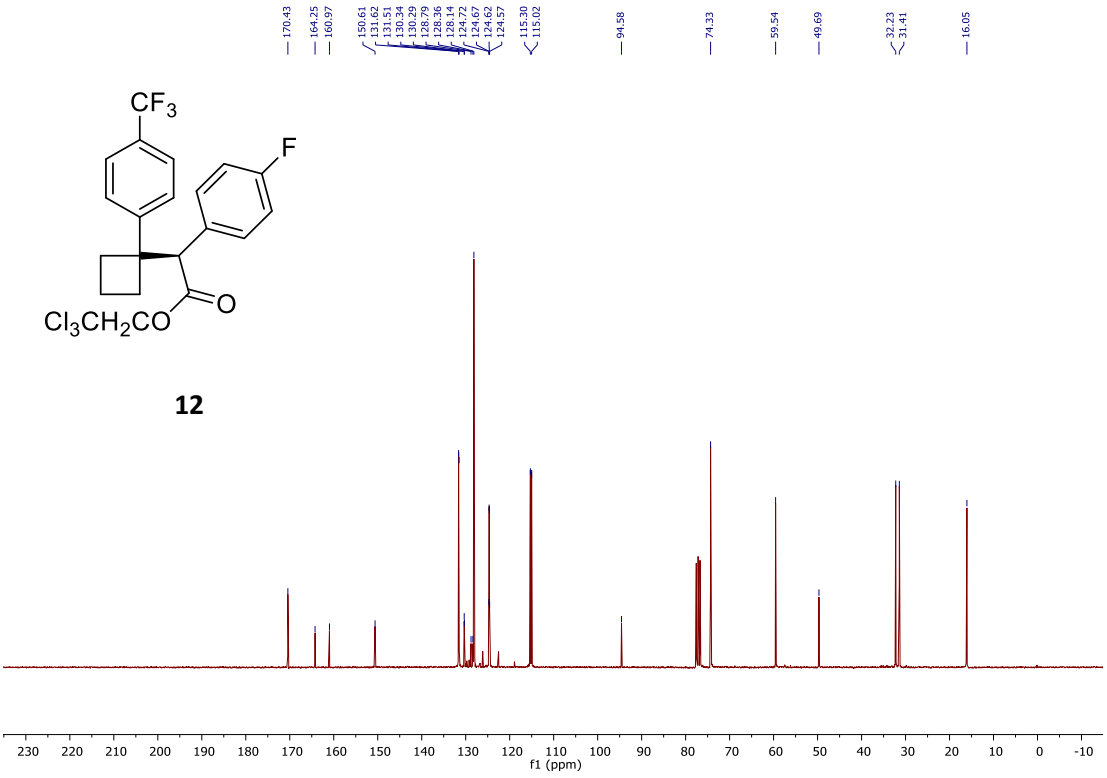


Figure S40. ^{19}F NMR spectrum of compound **12** in $CDCl_3$.

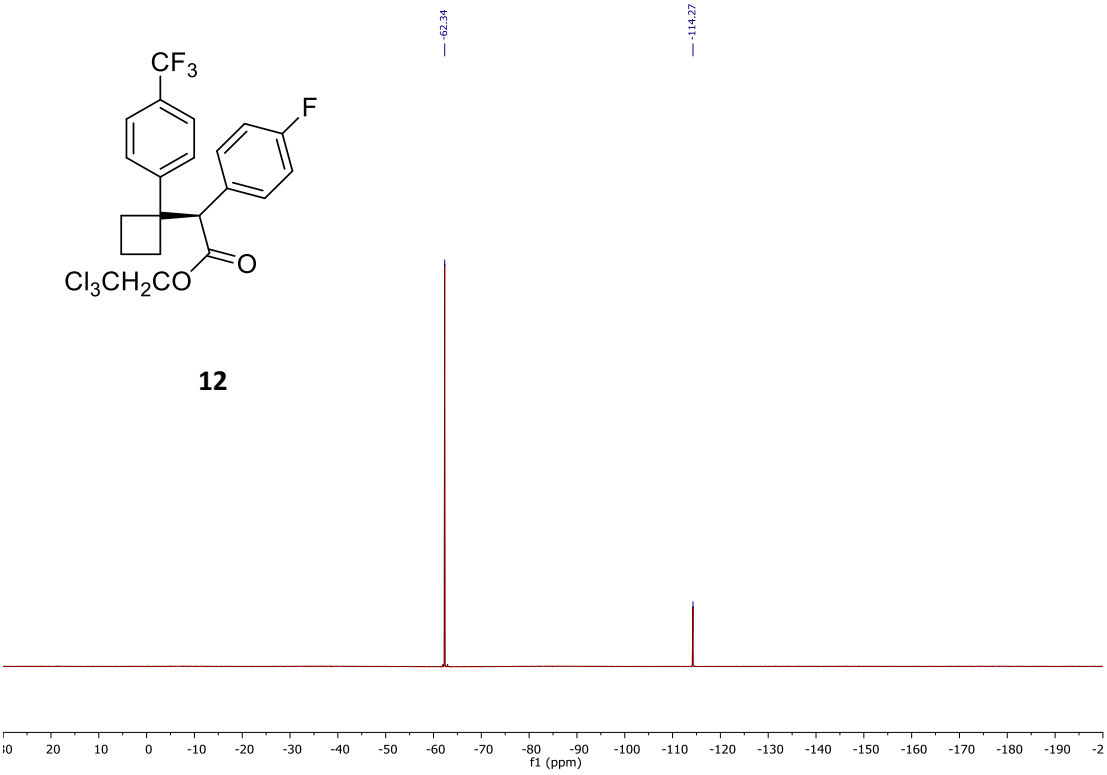


Figure S41. ^{1}H NMR Spectrum of compound **13** in $CDCl_3$.

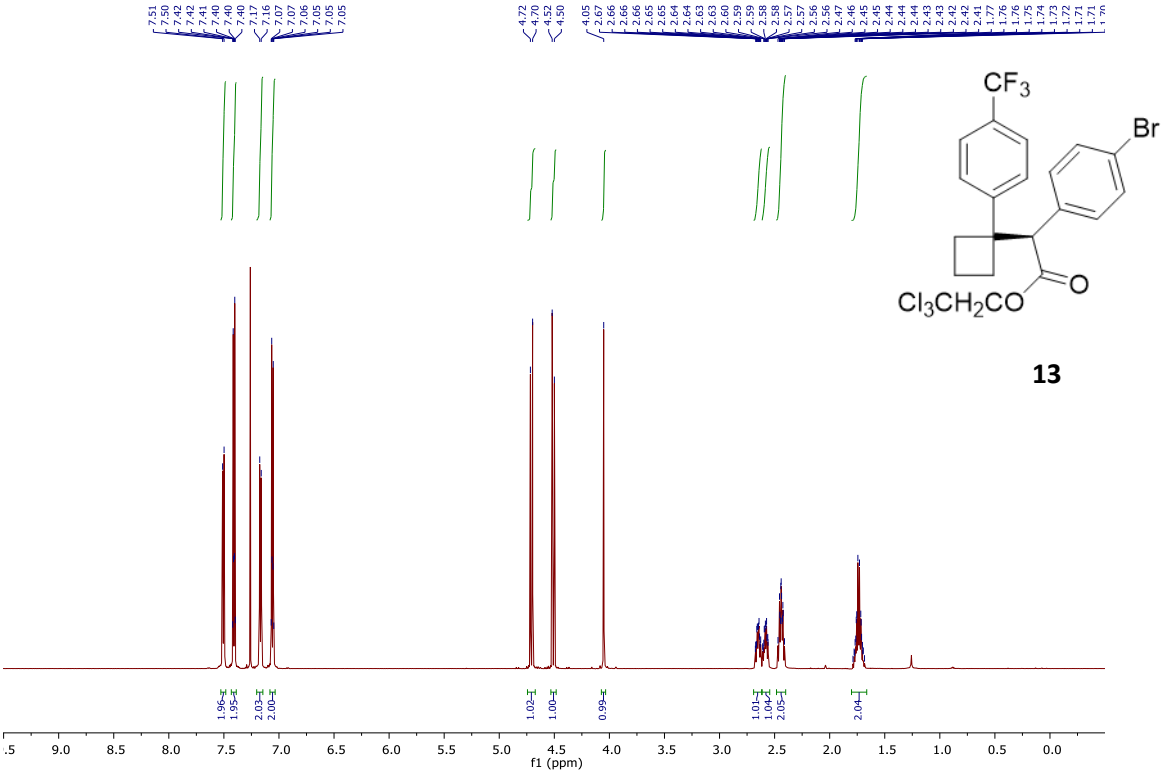


Figure S42. ^{13}C NMR spectrum of compound **13** in $CDCl_3$.

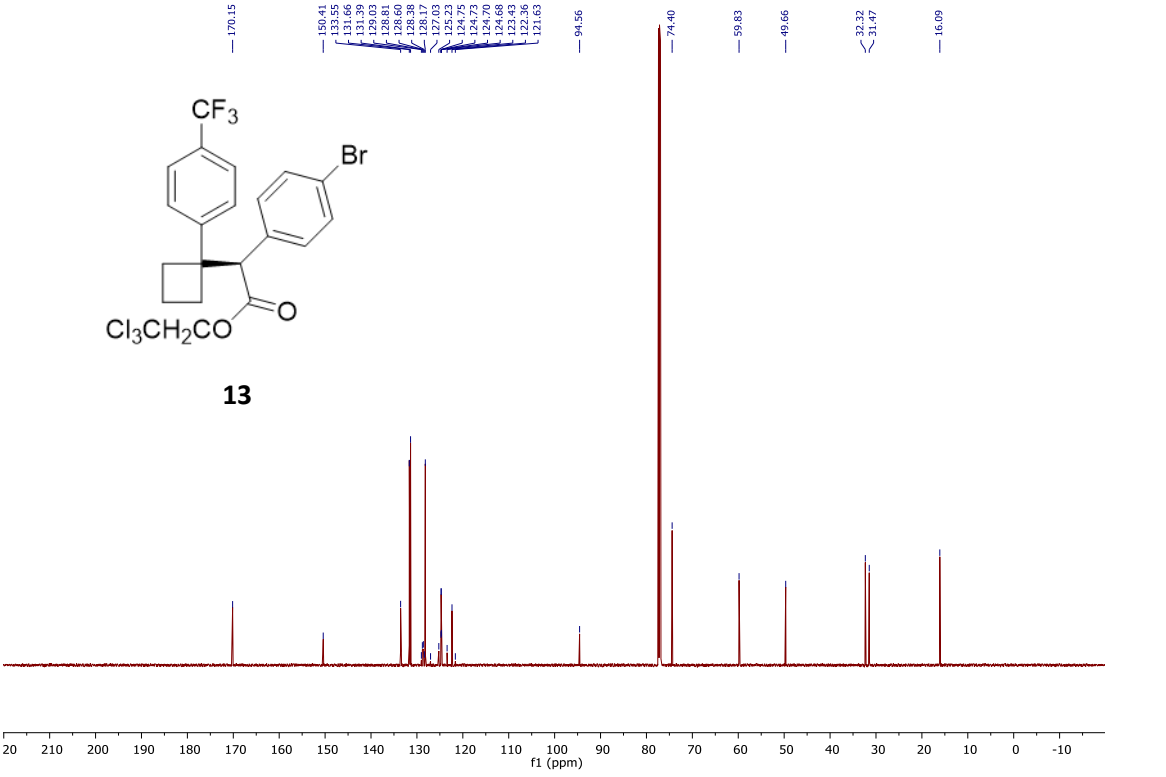
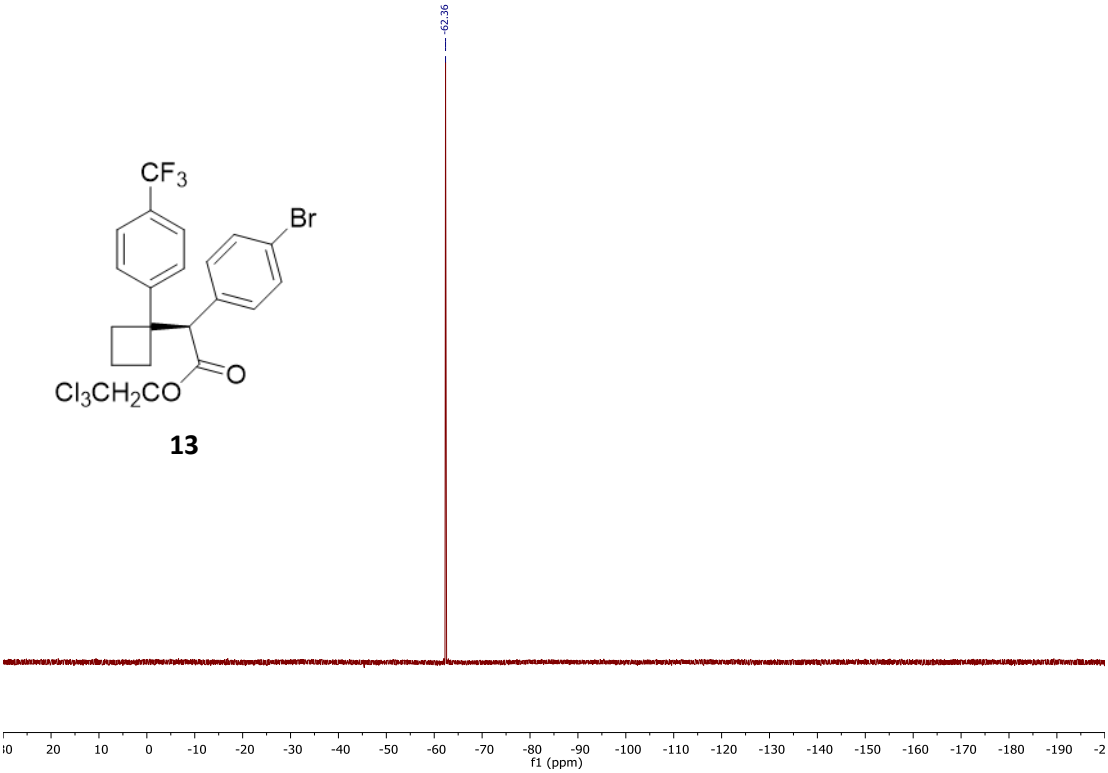
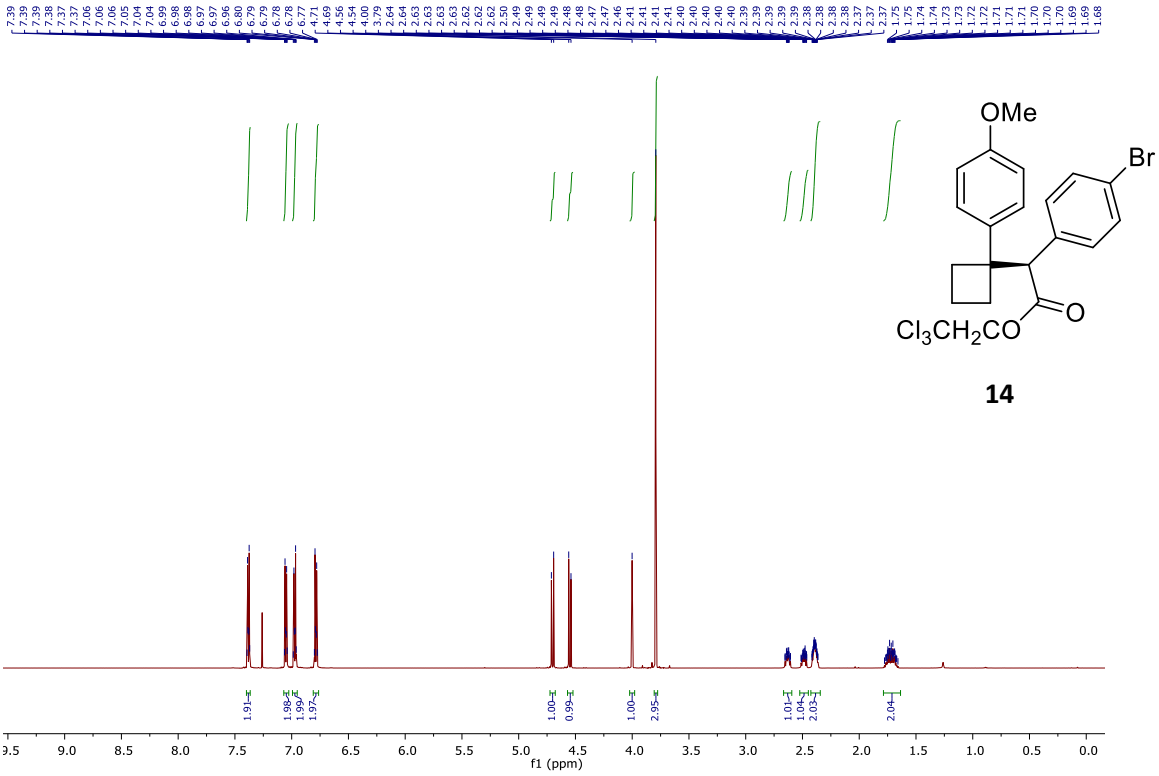


Figure S43. ^{19}F NMR spectrum of compound **13** in $CDCl_3$.



13

Figure S44. ^{1}H NMR Spectrum of compound **14** in $CDCl_3$.



14

Figure S45. ^{13}C NMR spectrum of compound **14** in $CDCl_3$.

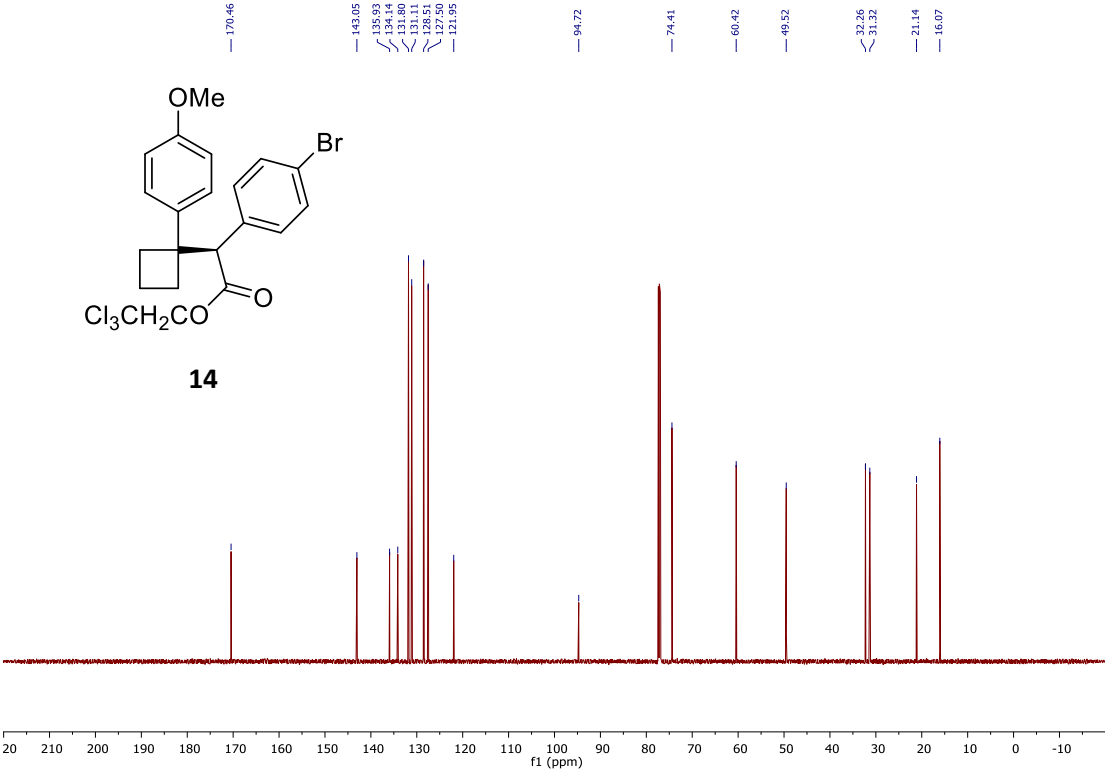


Figure S46. ^{1}H NMR Spectrum of compound **15** in $CDCl_3$.

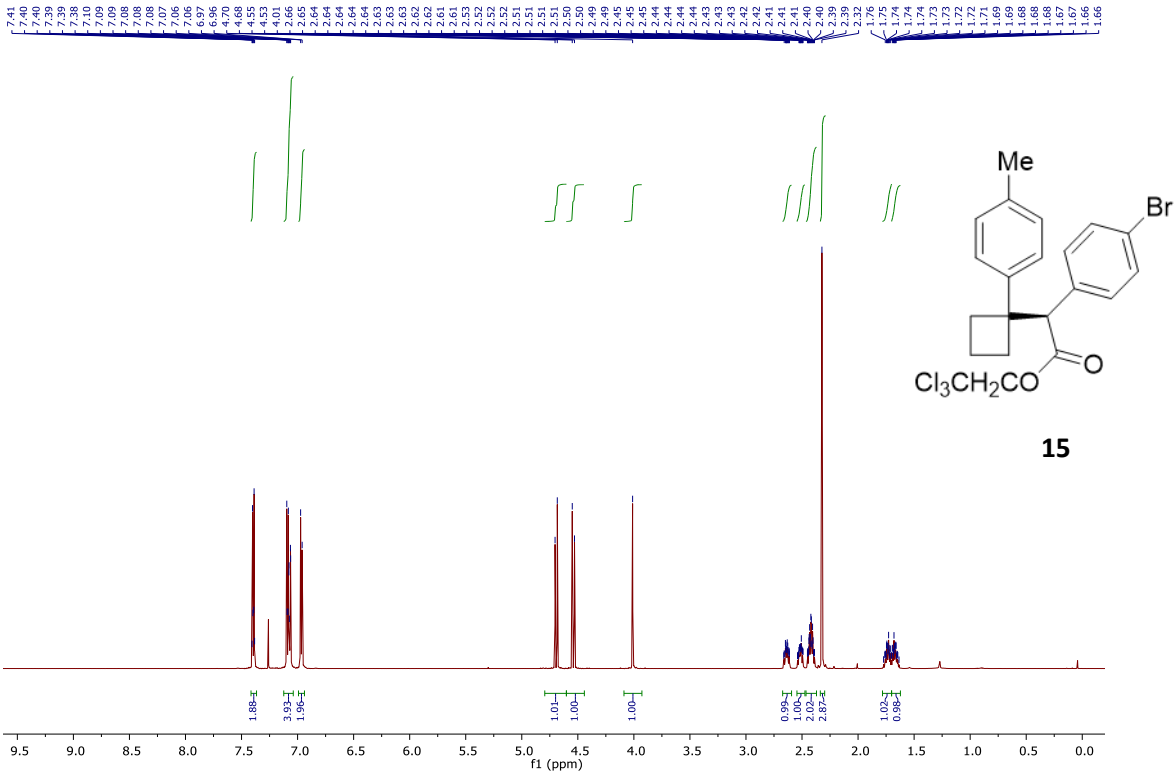


Figure S47.[13]C NMR Spectrum of compound **15** in $CDCl_3$.

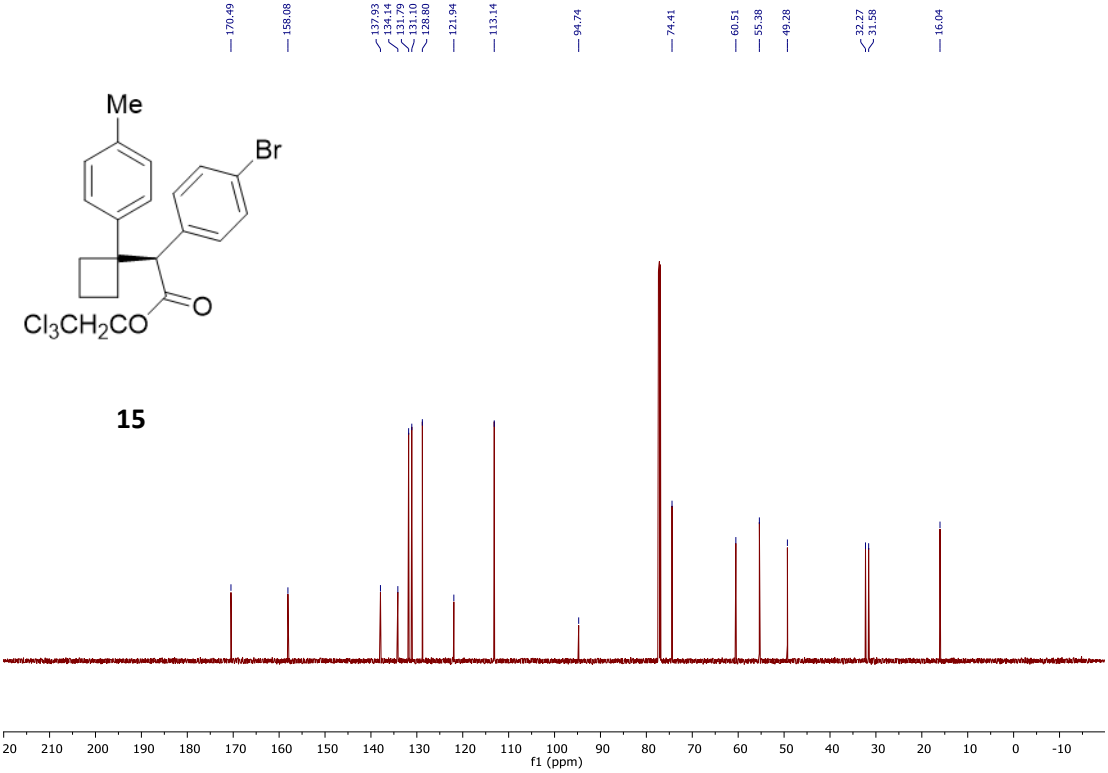


Figure S48. [1]H NMR Spectrum of compound **16** in $CDCl_3$.

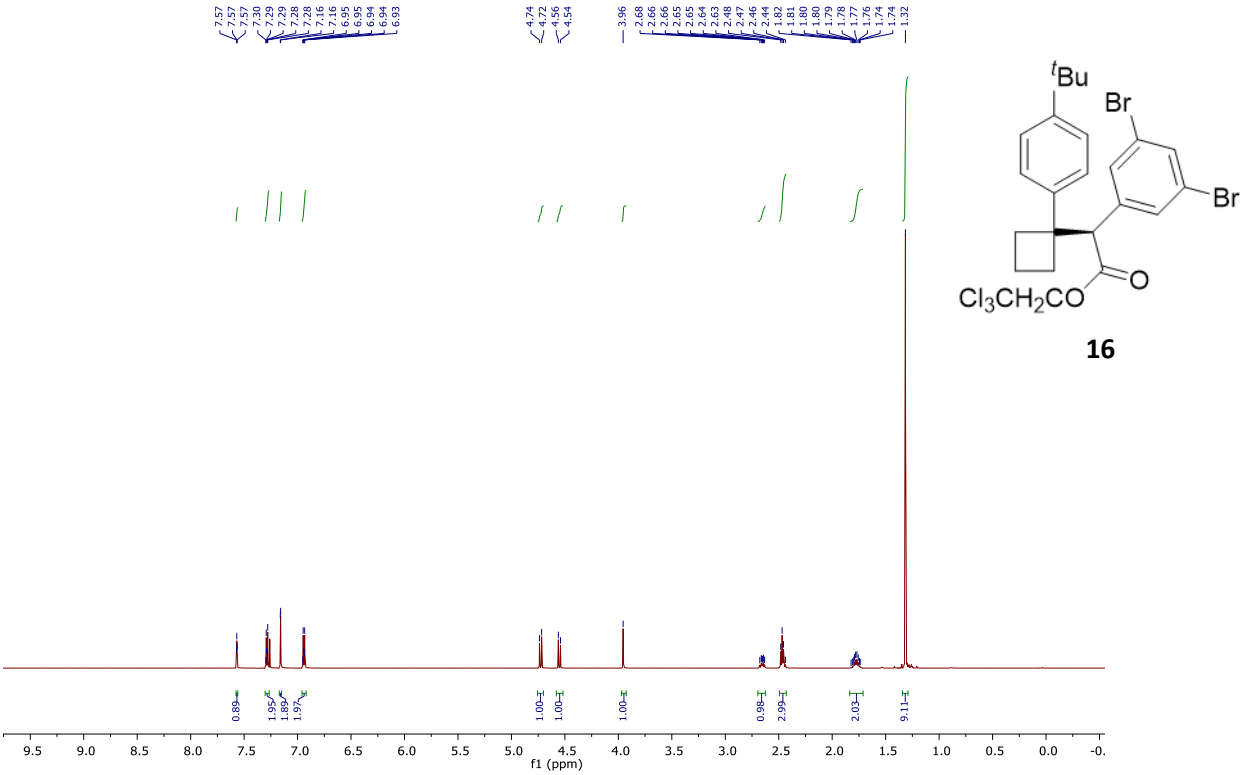


Figure S49. ^{13}C NMR spectrum of compound **16** in $CDCl_3$.

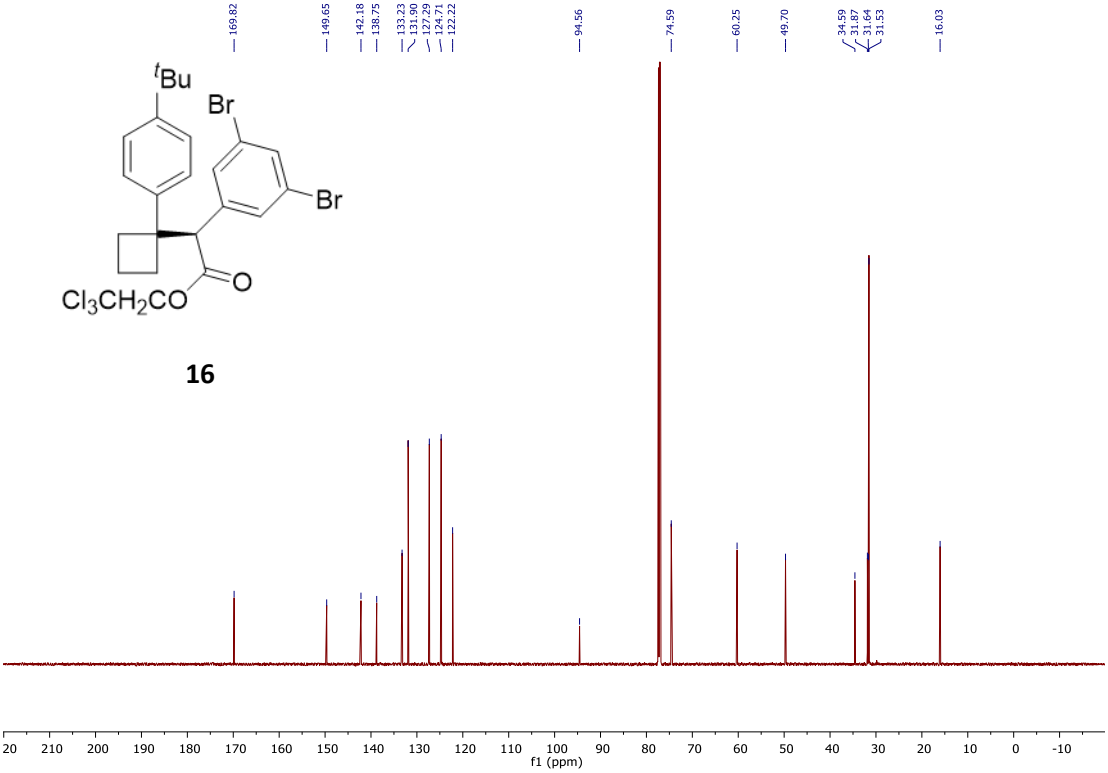


Figure S50. ^{1}H NMR Spectrum of compound **17** in $CDCl_3$.

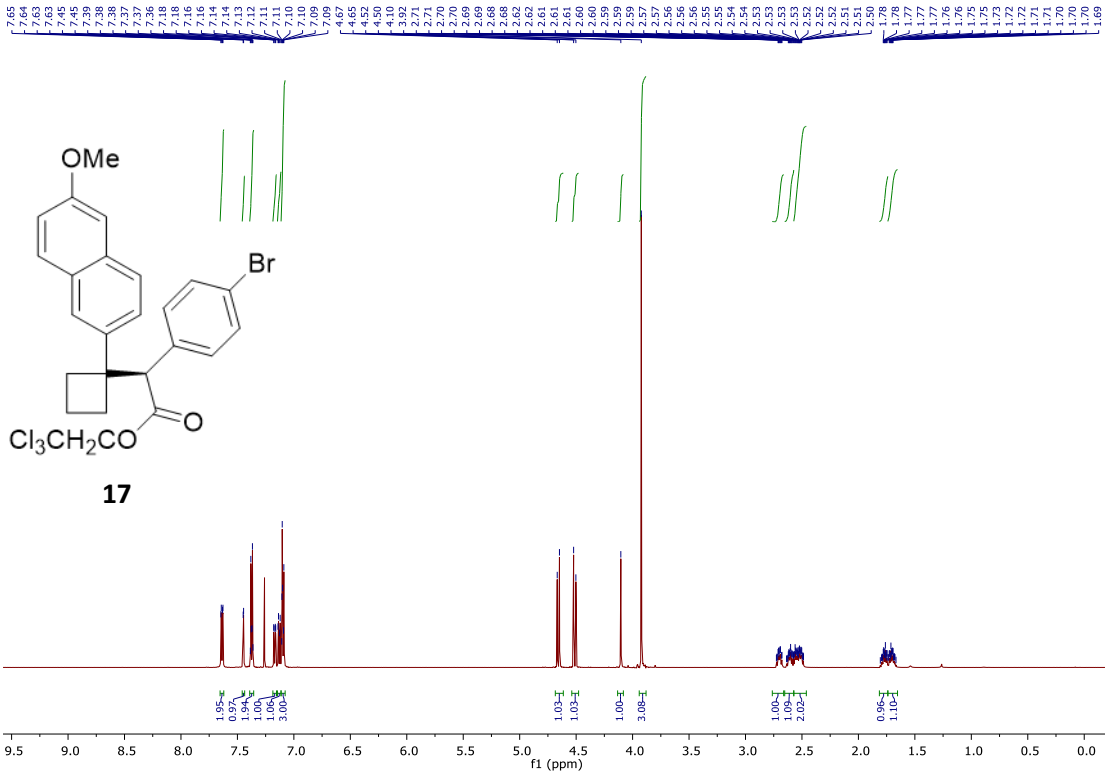


Figure S51. ^{13}C NMR spectrum of compound **17** in $CDCl_3$.

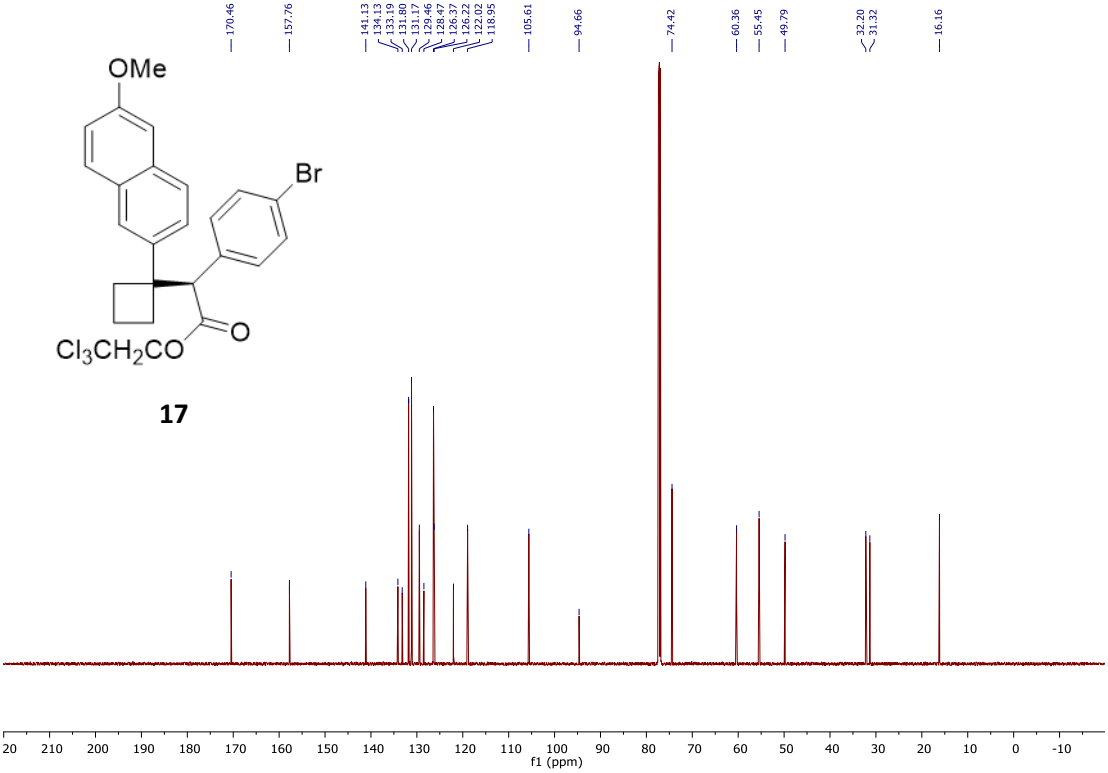


Figure S52. ^{1}H NMR Spectrum of compound **18** in $CDCl_3$.

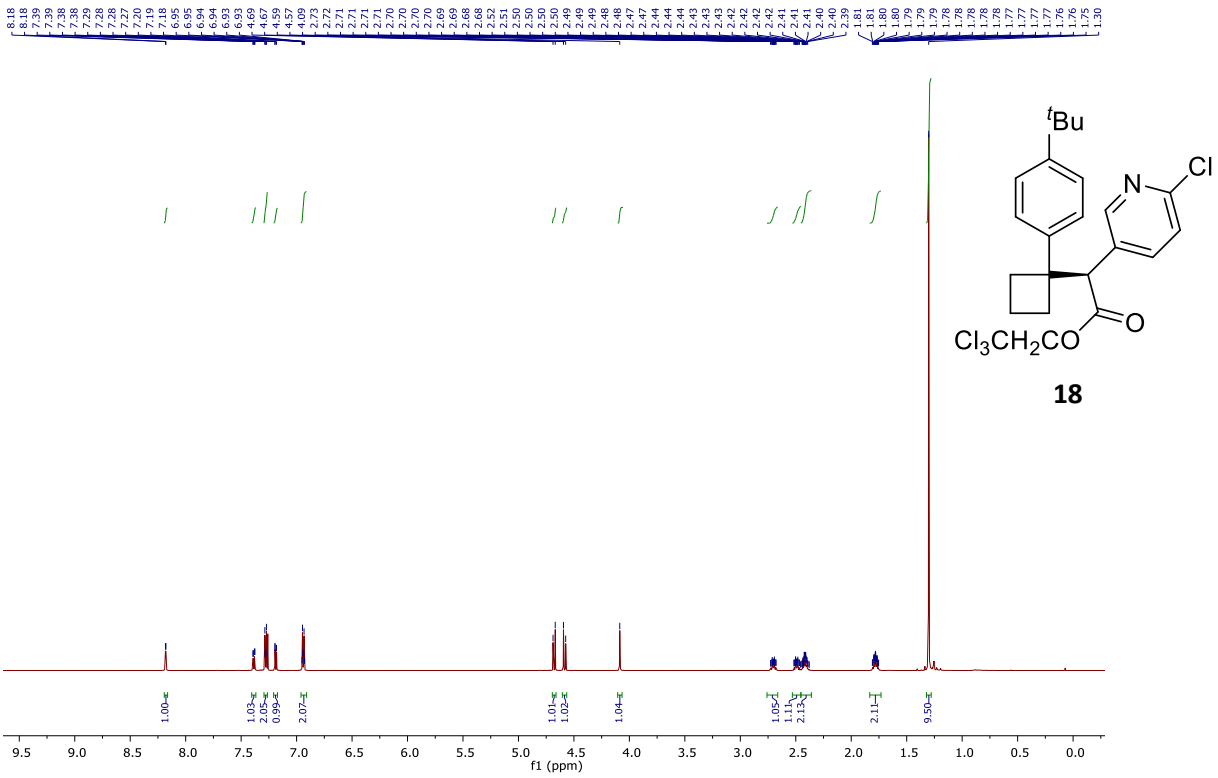


Figure S53. ^{13}C NMR spectrum of compound **18** in $CDCl_3$.

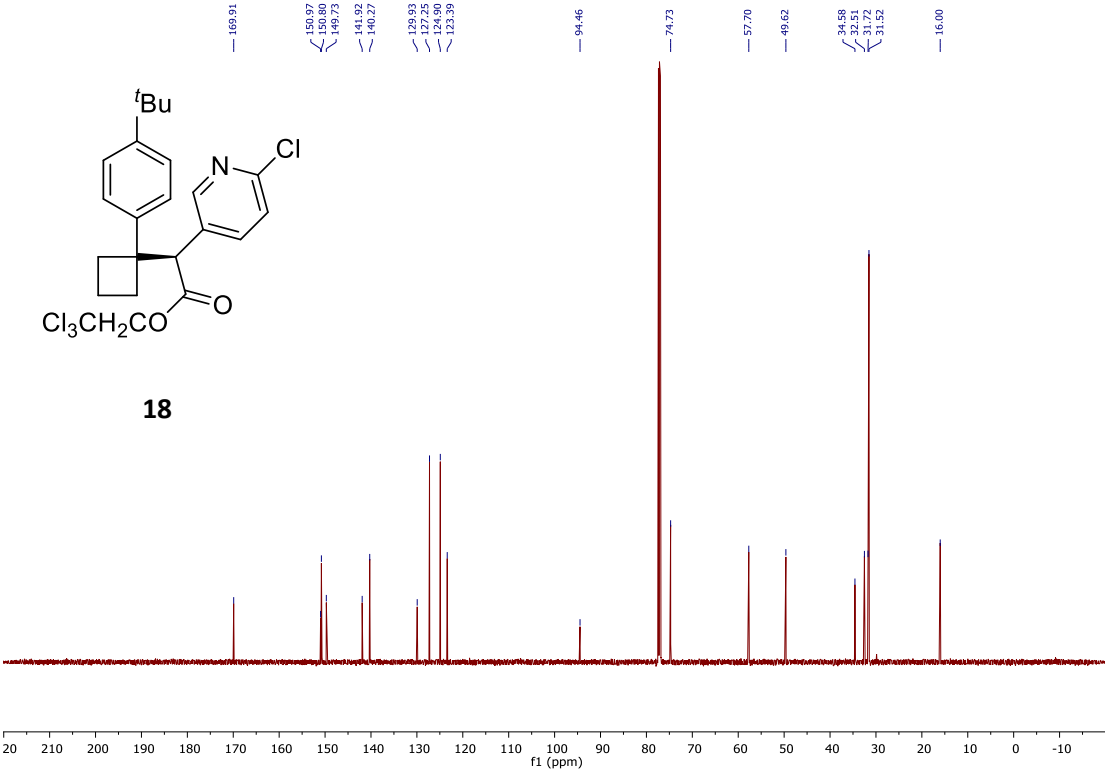


Figure S54. ^{1}H NMR Spectrum of compound **19** in $CDCl_3$.

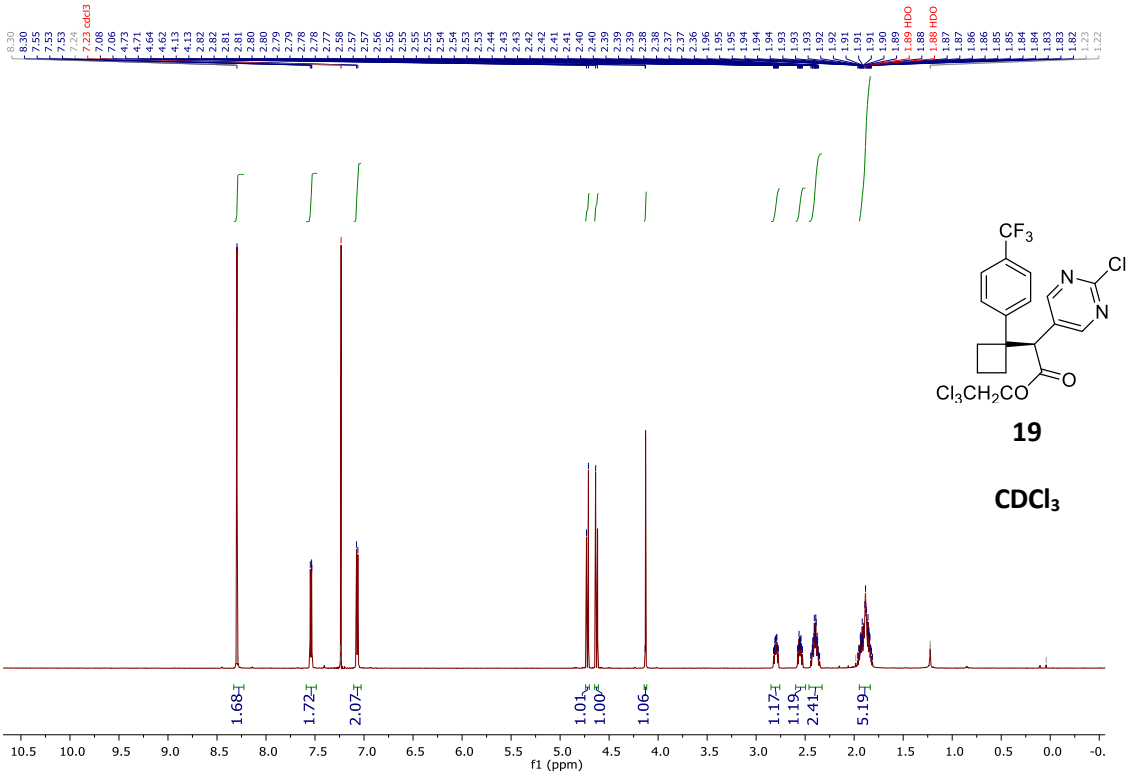


Figure S55. ^{13}C NMR spectrum of compound **19** in $CDCl_3$.

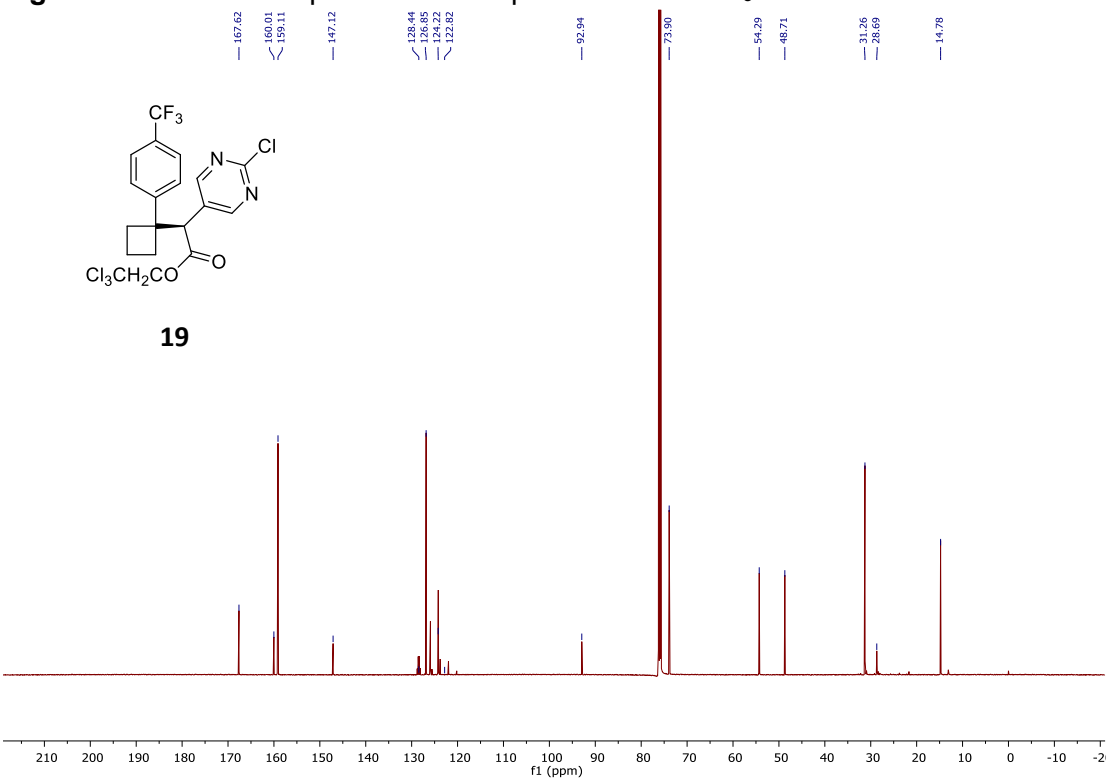


Figure S56. ^{19}F NMR spectrum of compound **1** in $CDCl_3$.

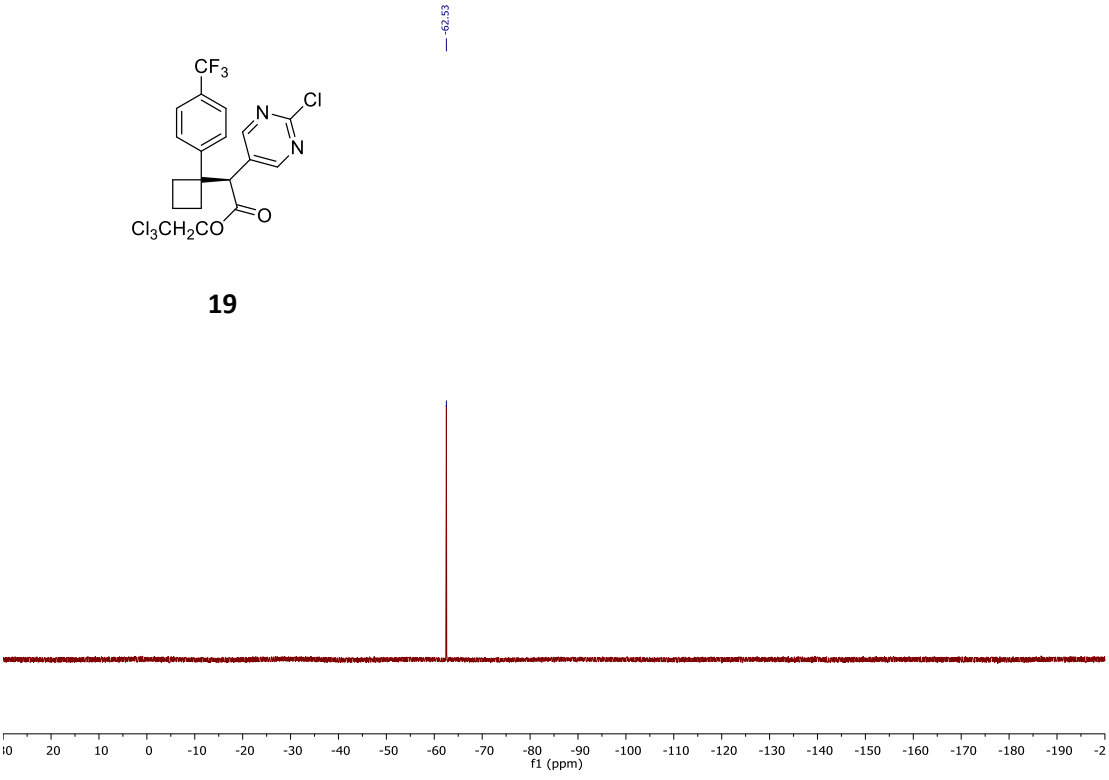


Figure S57. ^{1}H NMR Spectrum of compound **20** in $CDCl_3$.

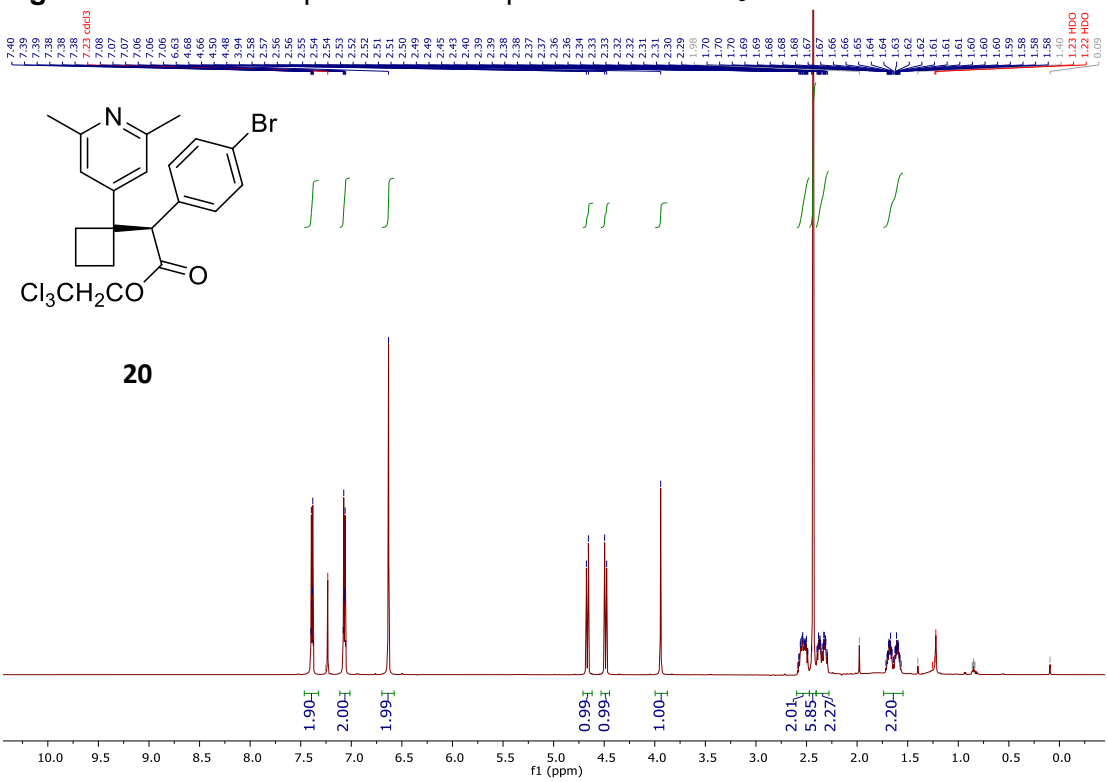


Figure S58. ^{13}C NMR spectrum of compound **20** in $CDCl_3$.

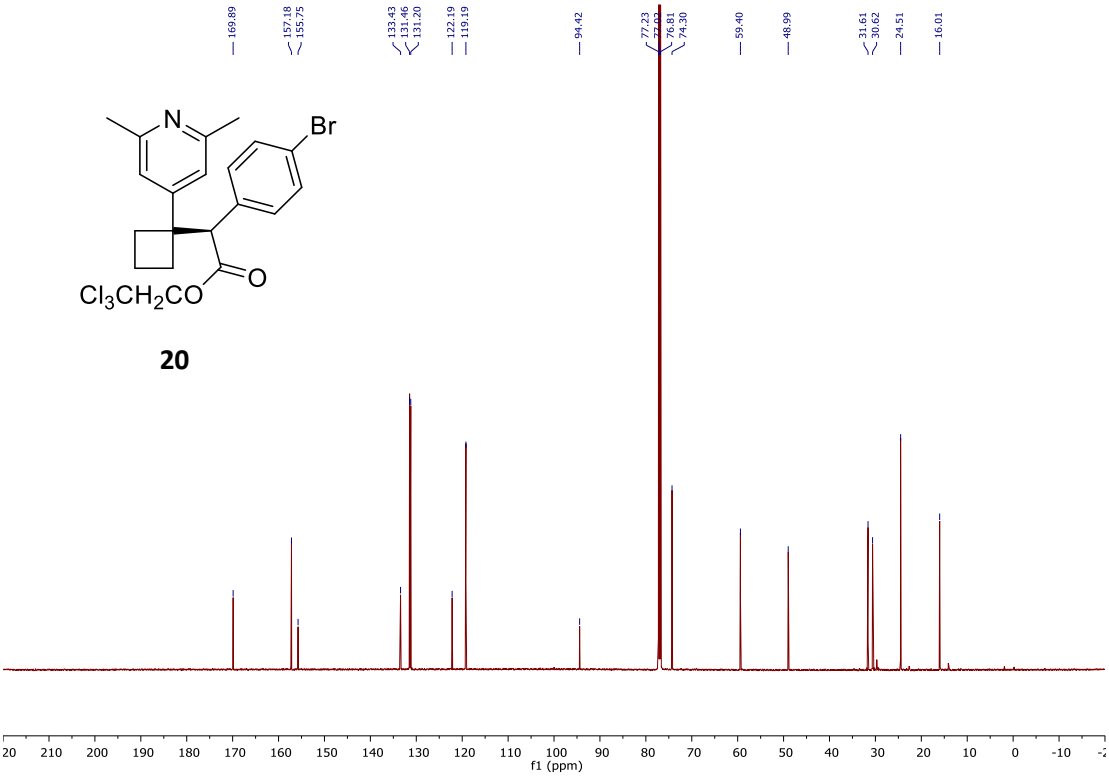


Figure S59. ^{1}H NMR Spectrum of compound **21** in $CDCl_3$.

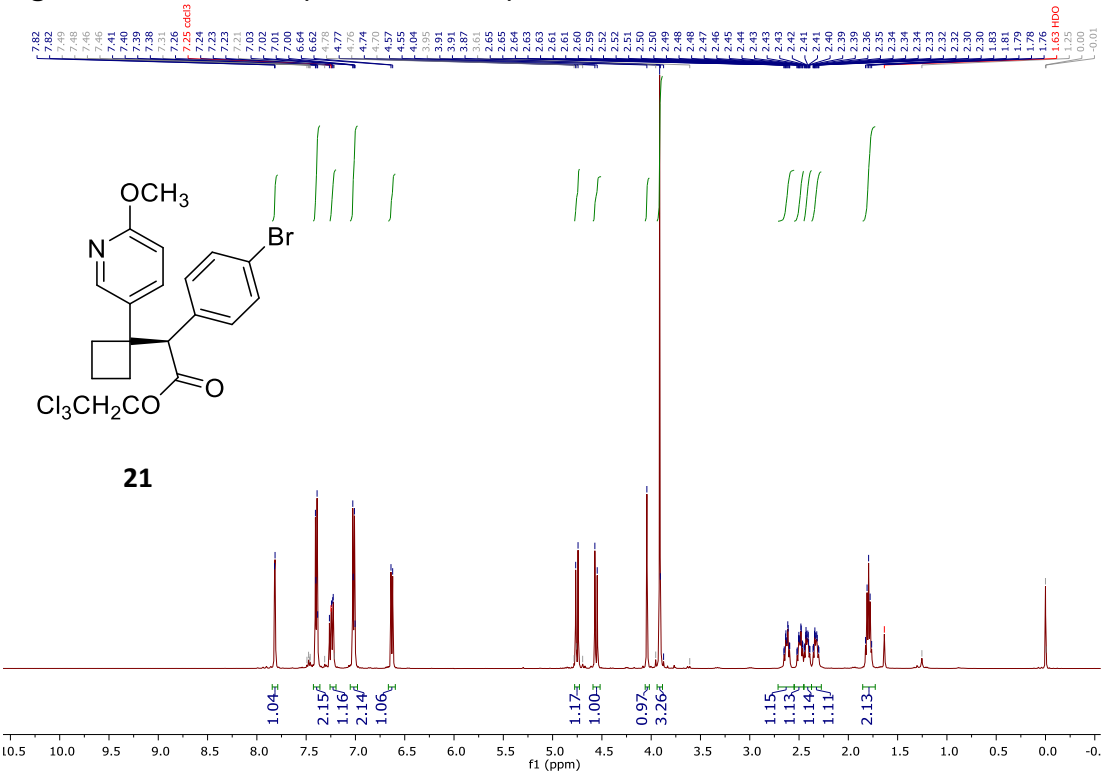


Figure S60. ^{13}C NMR spectrum of compound **21** in $CDCl_3$.

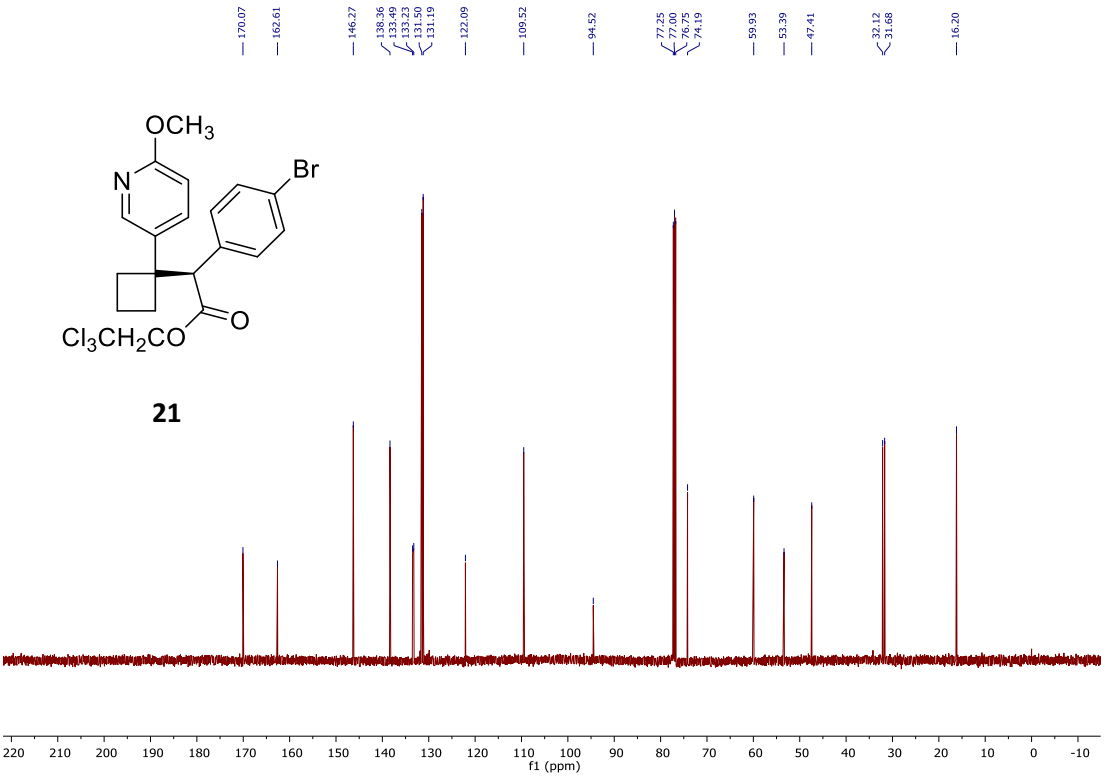


Figure S61. ^{1}H NMR Spectrum of compound **9** in $CDCl_3$.

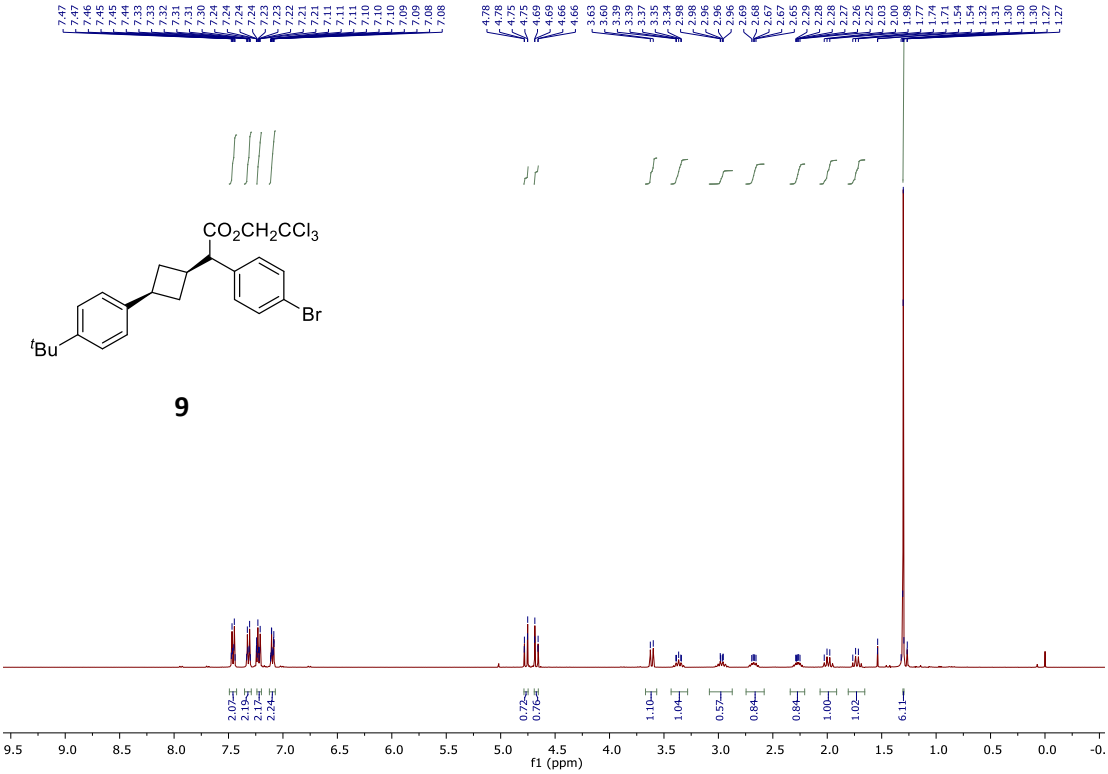


Figure S62. ^{13}C NMR spectrum of compound **9** in $CDCl_3$.

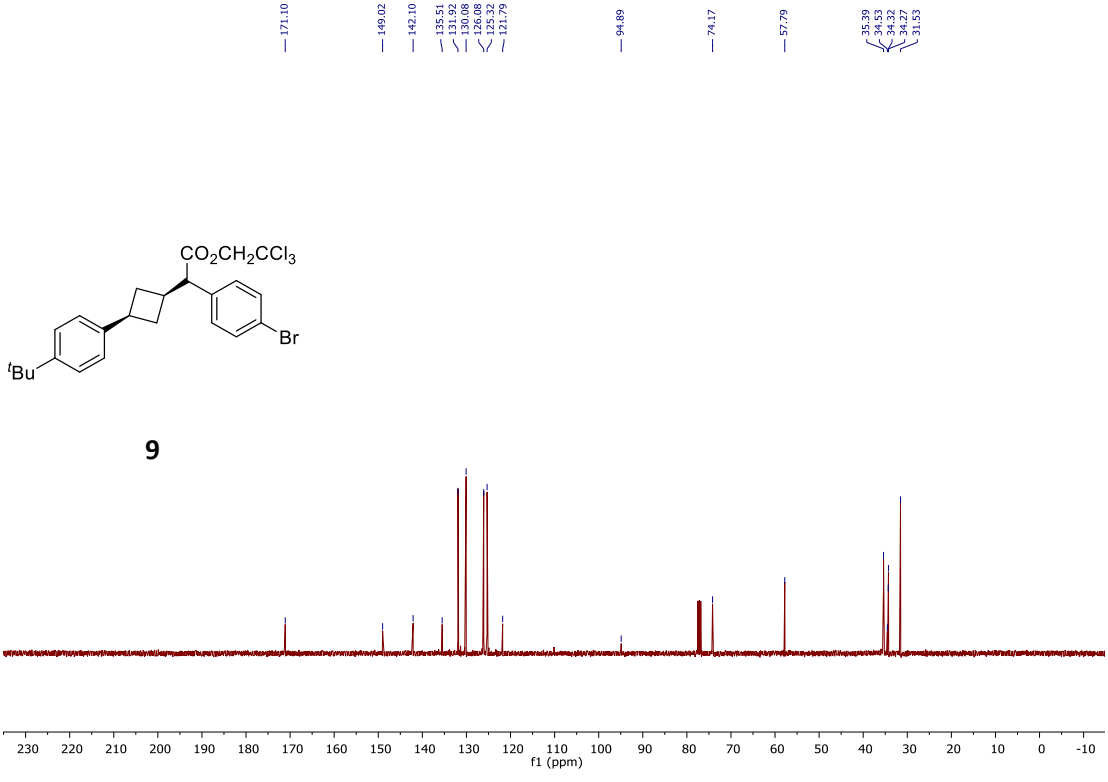


Figure S63. ^{1}H NMR Spectrum of compound **22** in $CDCl_3$.

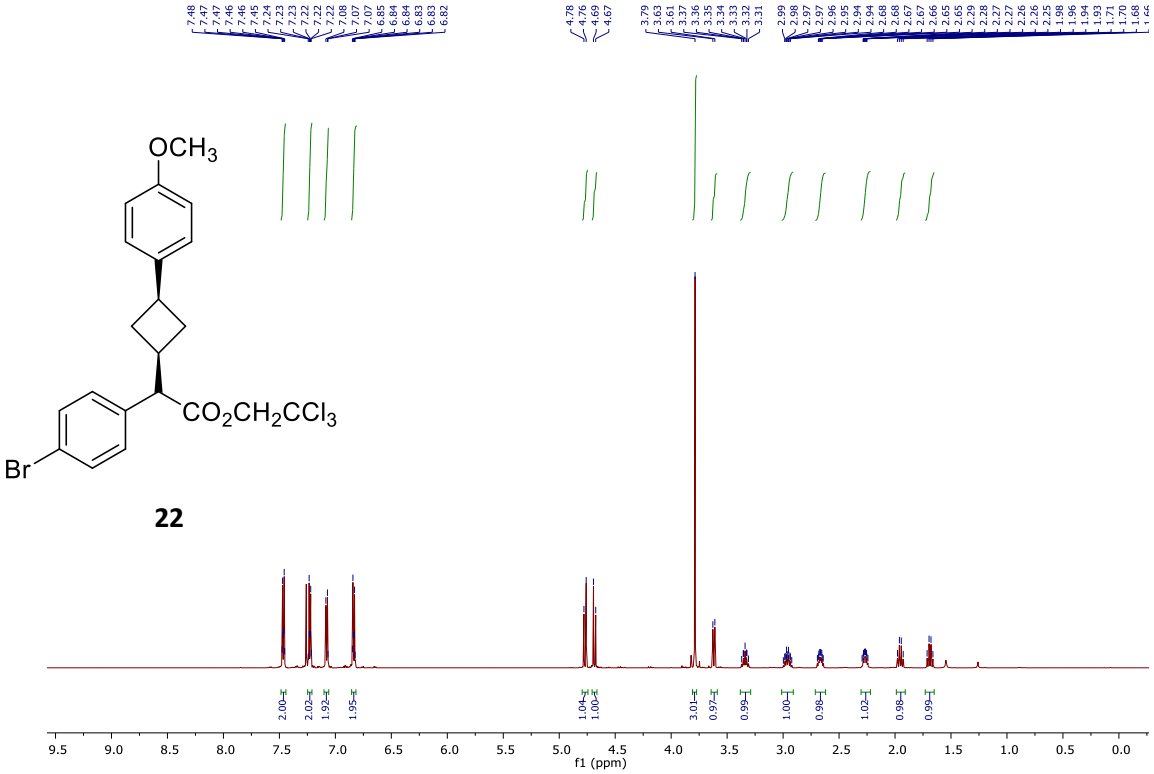


Figure S64. ^{13}C NMR spectrum of compound **22** in $CDCl_3$.

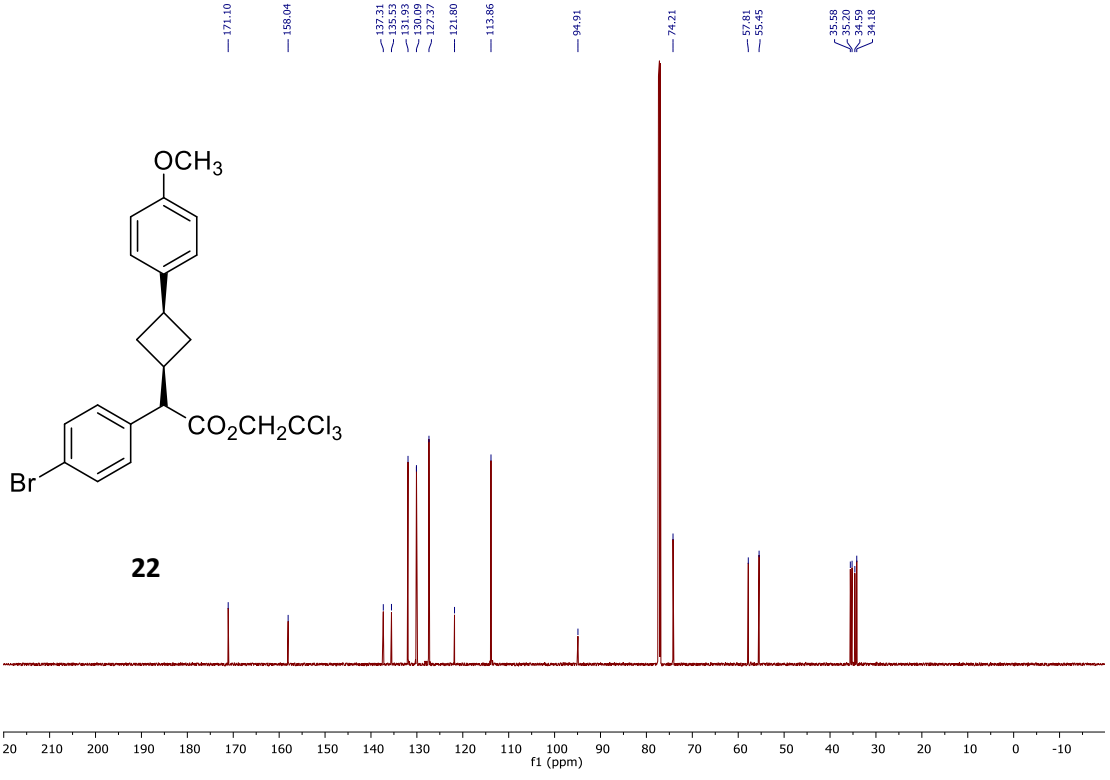


Figure S65. ^{1}H NMR Spectrum of compound **23** in $CDCl_3$.

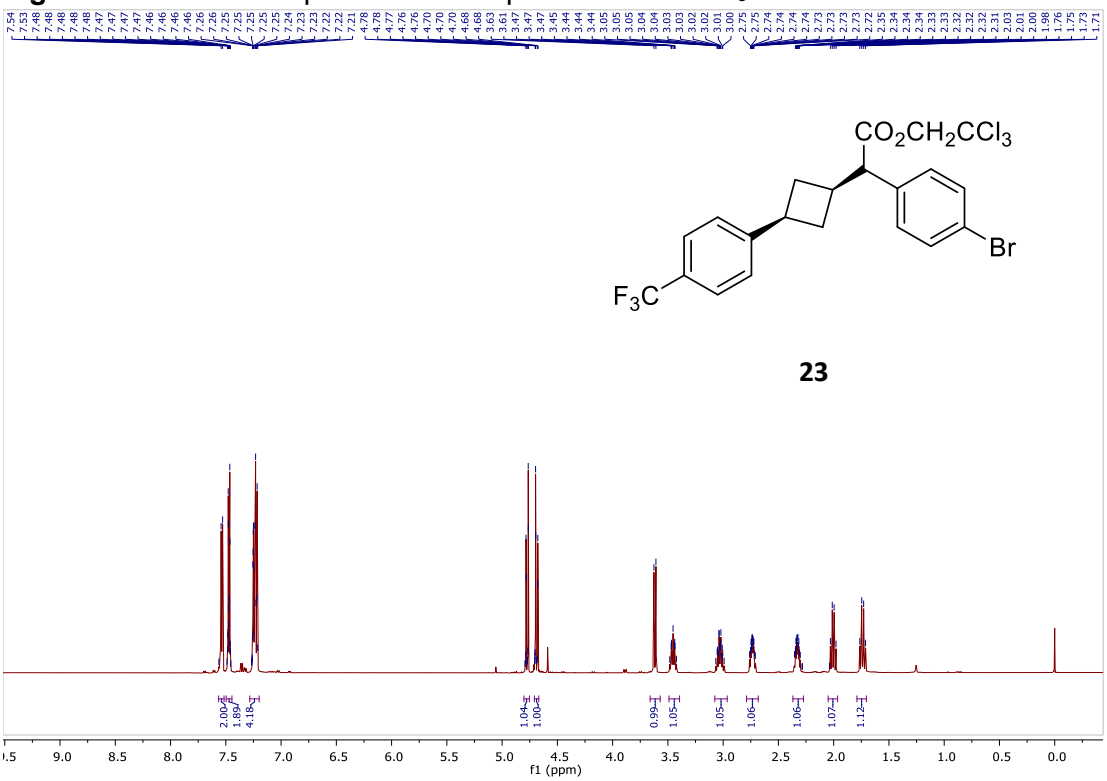


Figure S66. ^{13}C NMR spectrum of compound **23** in $CDCl_3$.

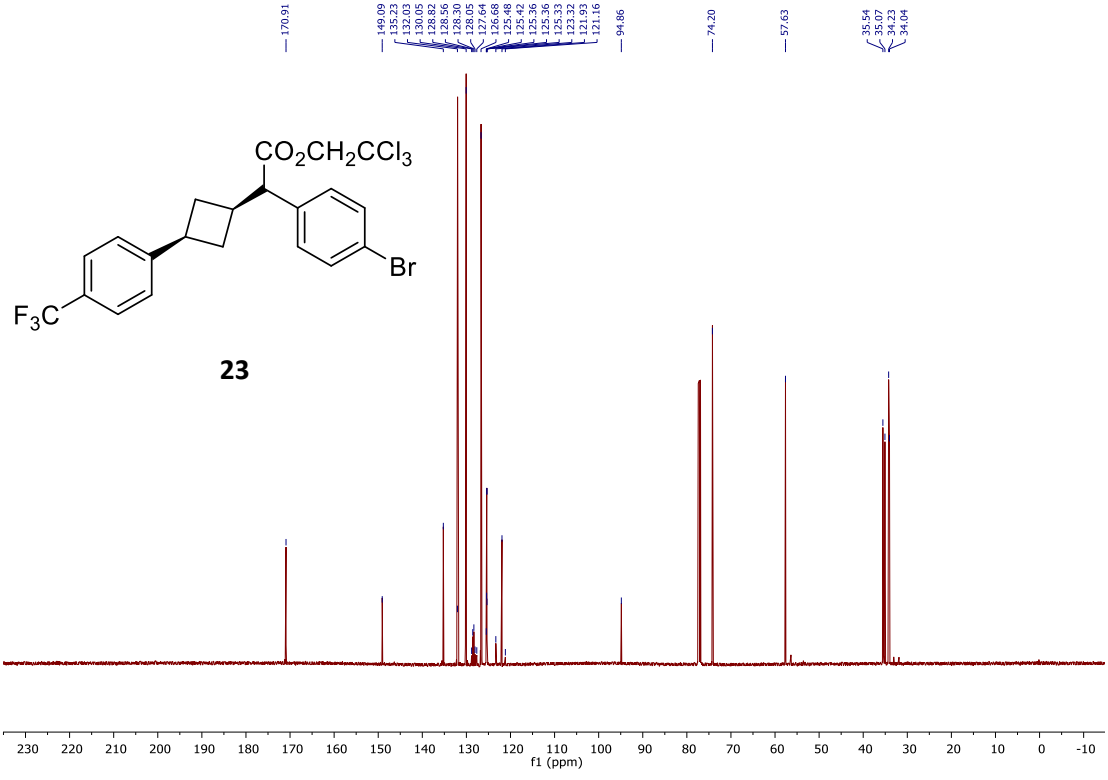


Figure S67. ^{19}F NMR spectrum of compound **23** in $CDCl_3$.

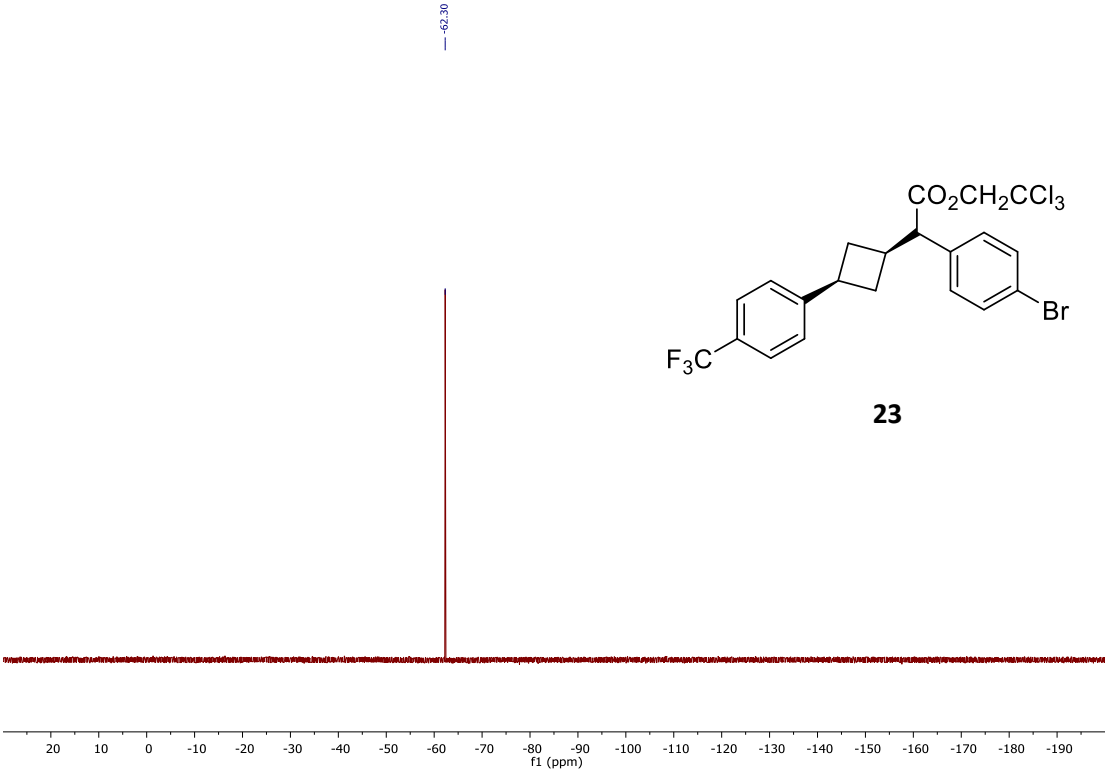


Figure S68. ^{1}H NMR Spectrum of compound **24** in $CDCl_3$.

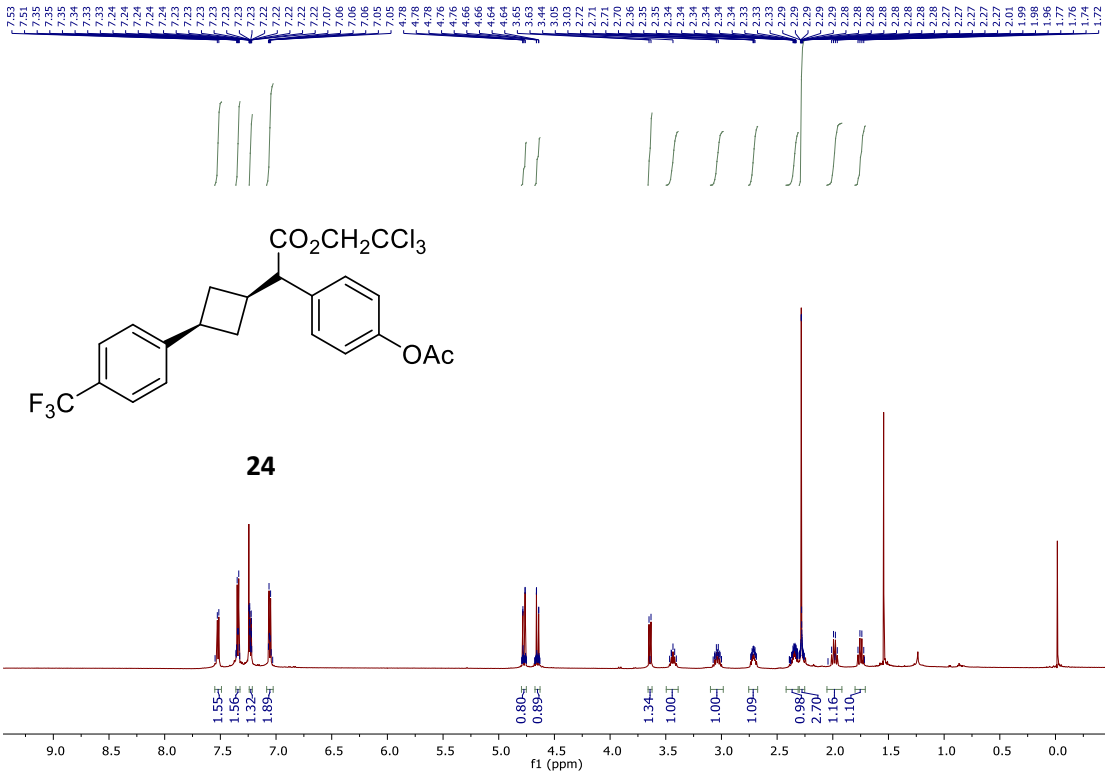


Figure S69. ^{13}C NMR spectrum of compound **24** in $CDCl_3$.

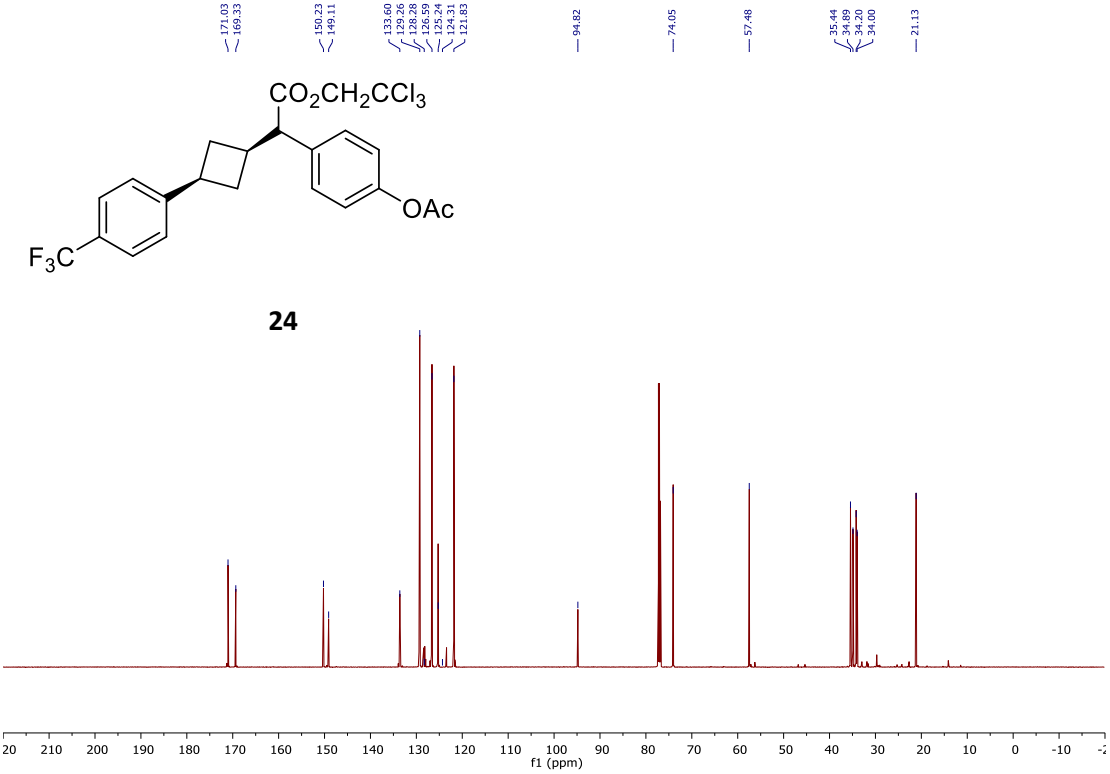


Figure S70. ^{19}F NMR spectrum of compound **24** in $CDCl_3$.

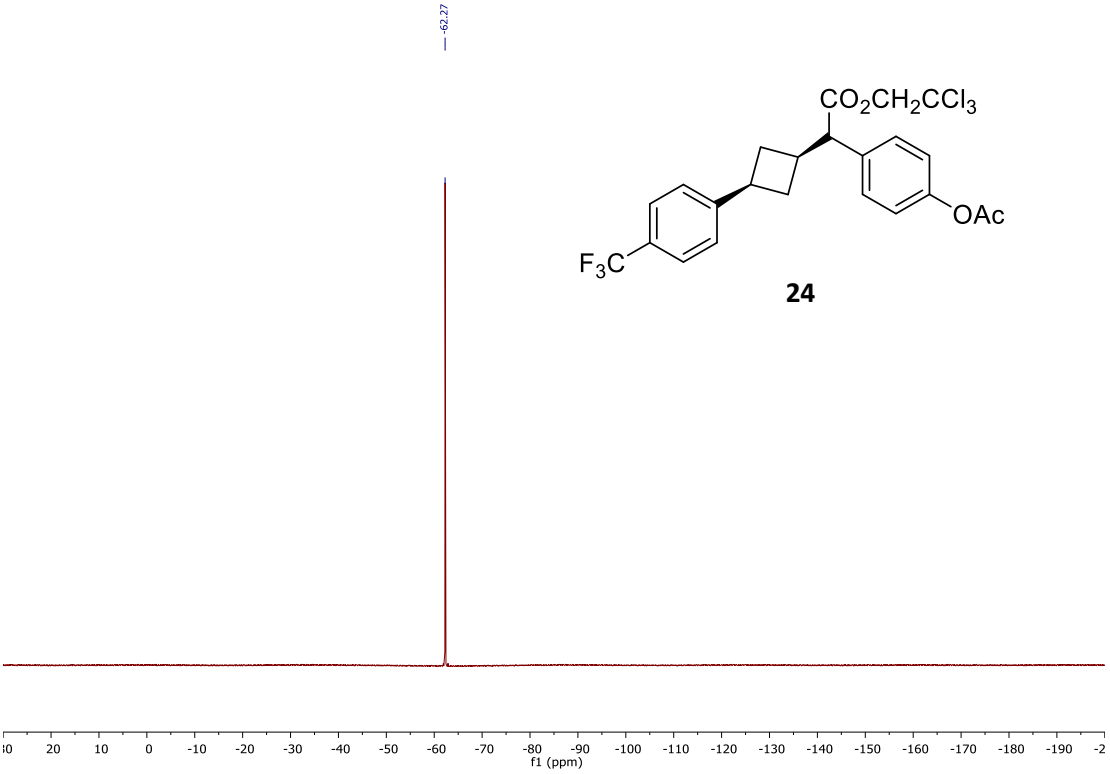


Figure S71. ^{1}H NMR Spectrum of compound **25** in $CDCl_3$.

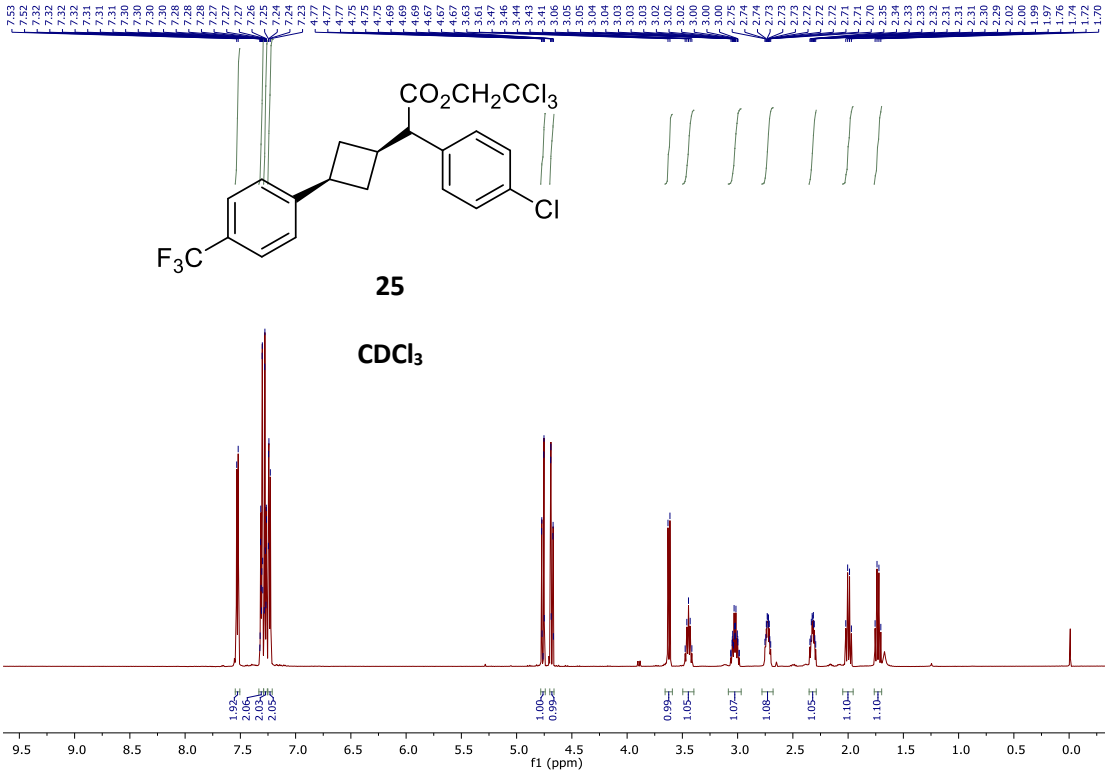


Figure S72. ^{13}C NMR spectrum of compound **25** in $CDCl_3$.

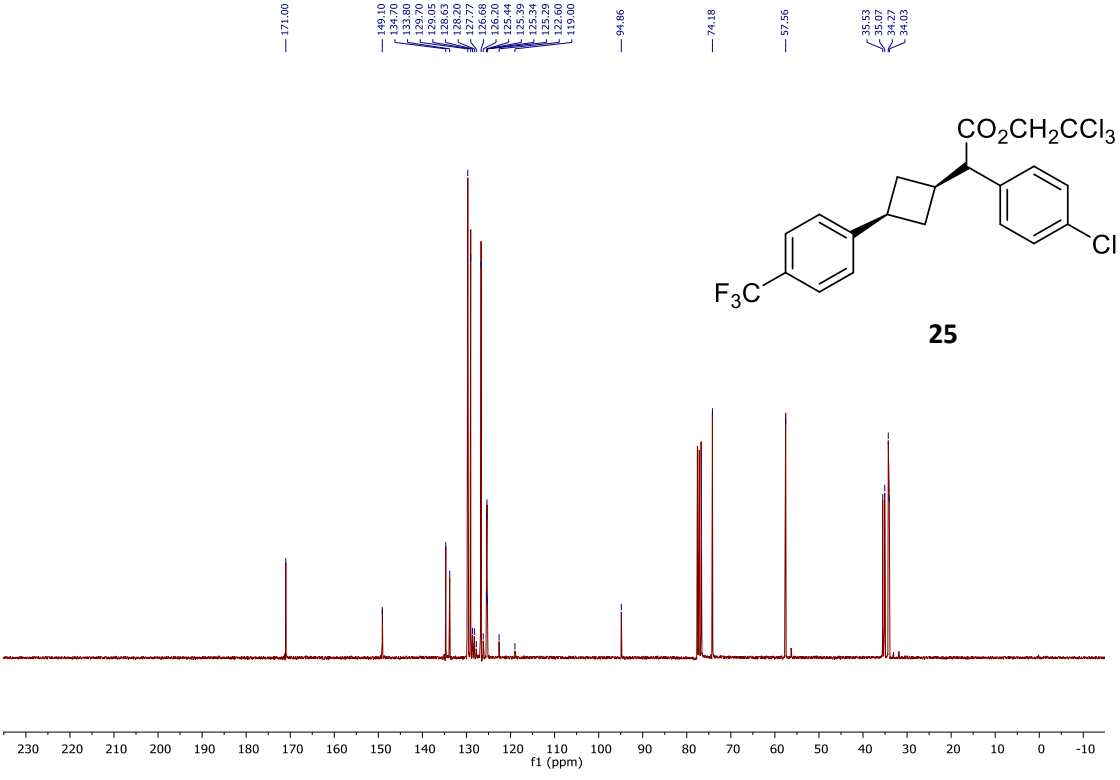


Figure S73. ^{19}F NMR spectrum of compound **25** in $CDCl_3$.

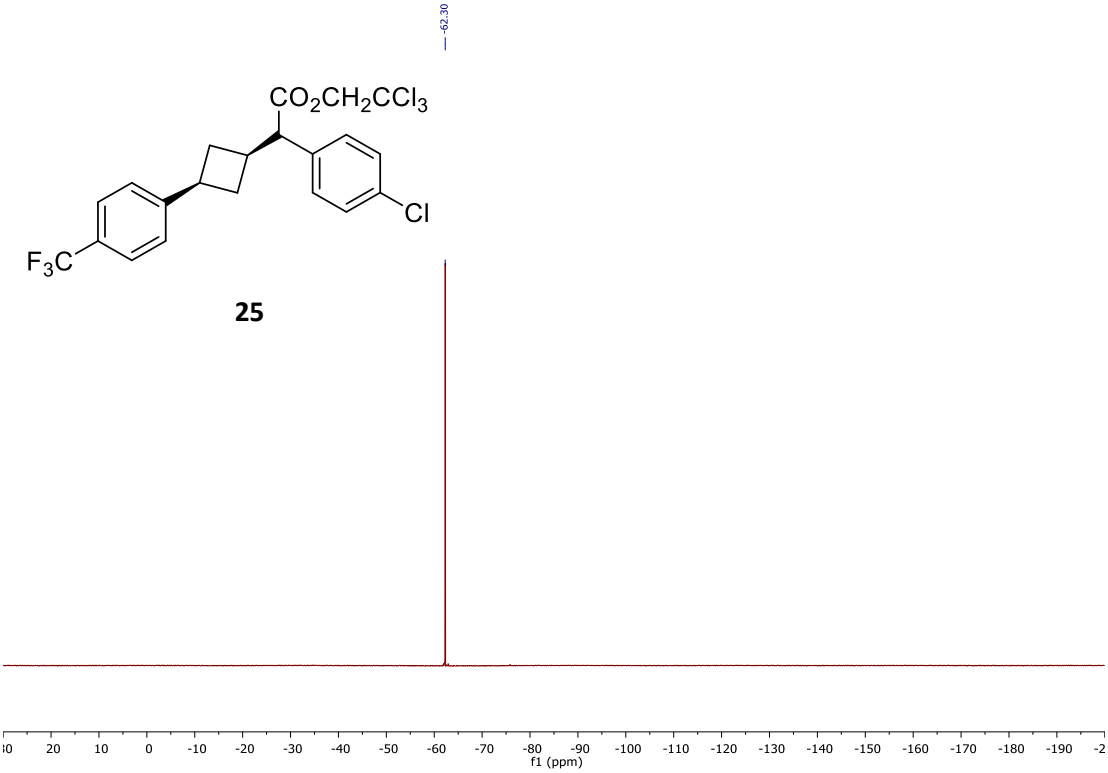


Figure S74. ^{1}H NMR Spectrum of compound **26** in $CDCl_3$.

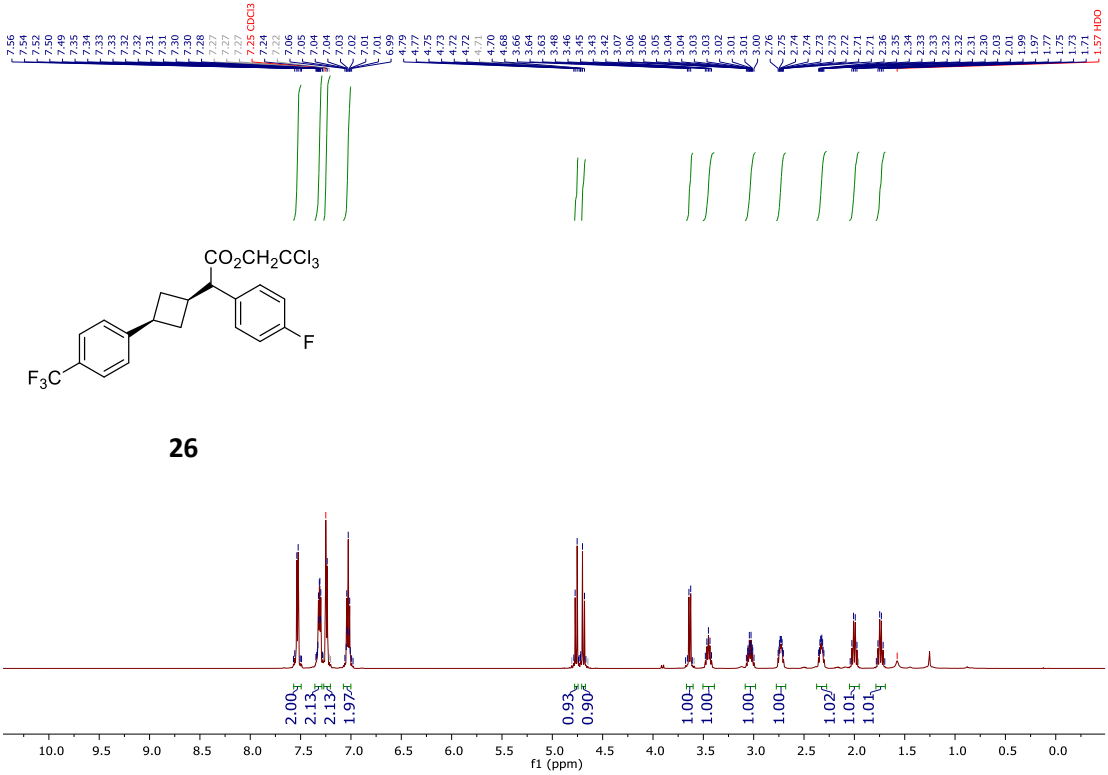


Figure S75. ^{13}C NMR spectrum of compound **26** in $CDCl_3$.

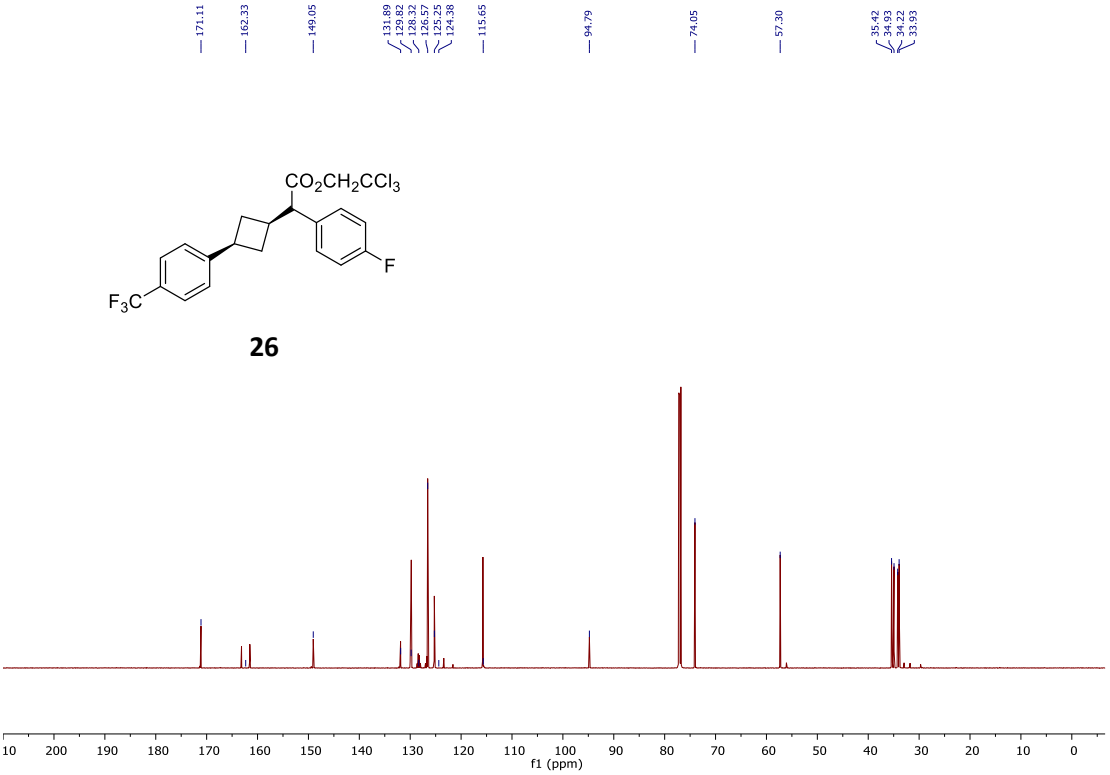


Figure S76. ^{19}F NMR spectrum of compound **26** in $CDCl_3$.

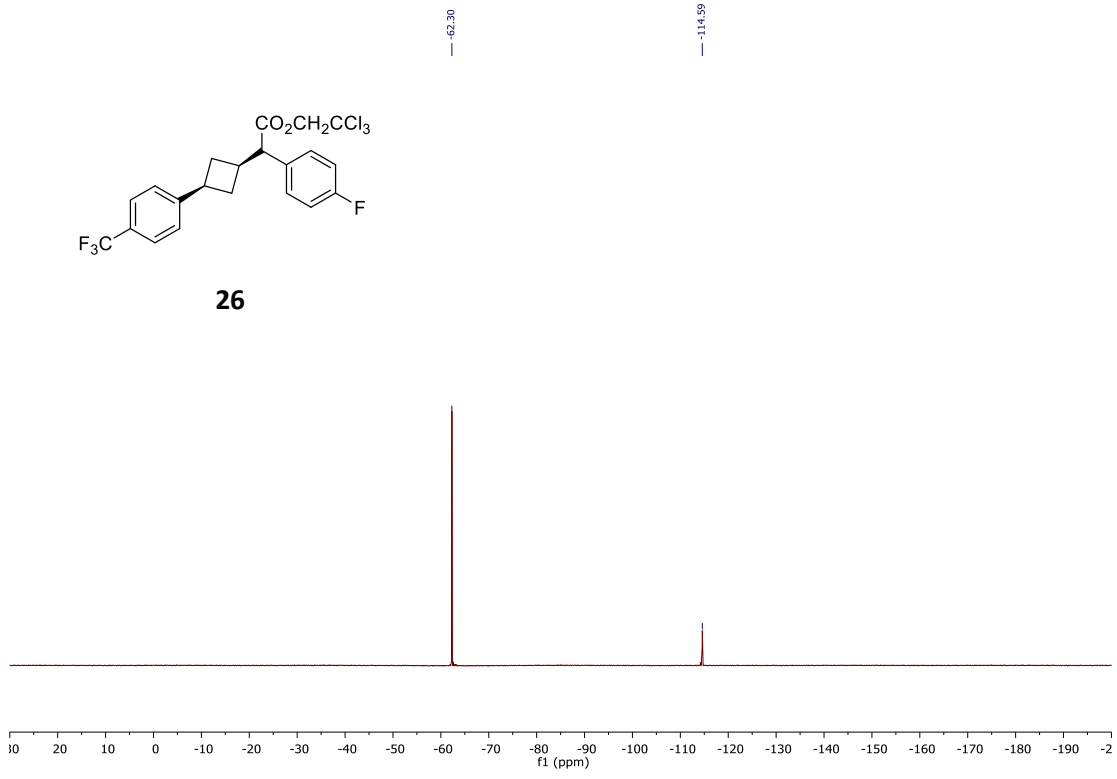


Figure S77. ^{1}H NMR Spectrum of compound **27** in $CDCl_3$.

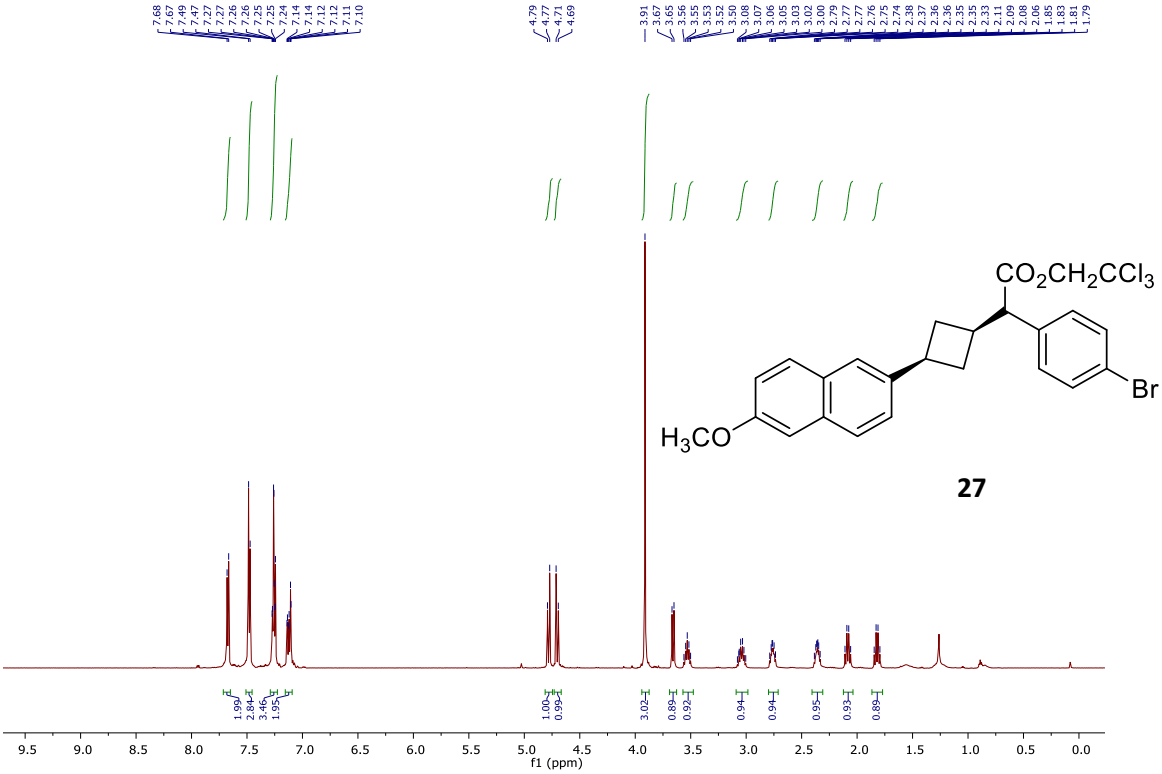


Figure S78. ^{13}C NMR spectrum of compound **27** in $CDCl_3$.

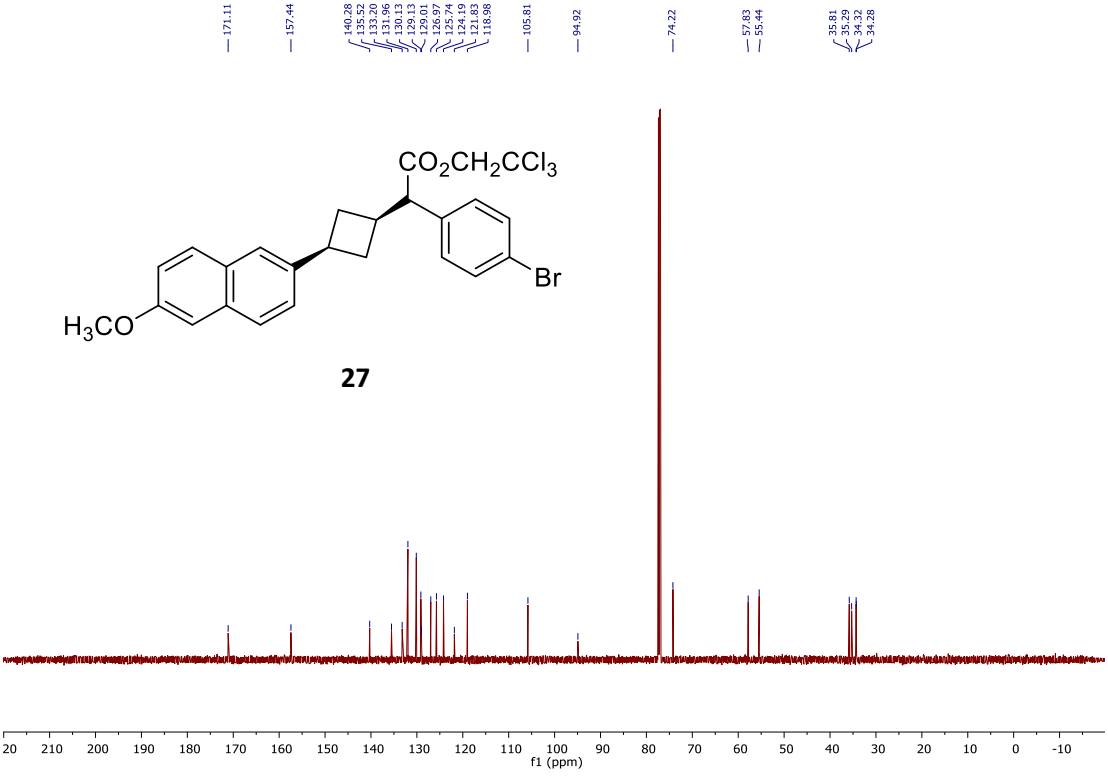


Figure S79. ^{1}H NMR Spectrum of compound **28** in $CDCl_3$.

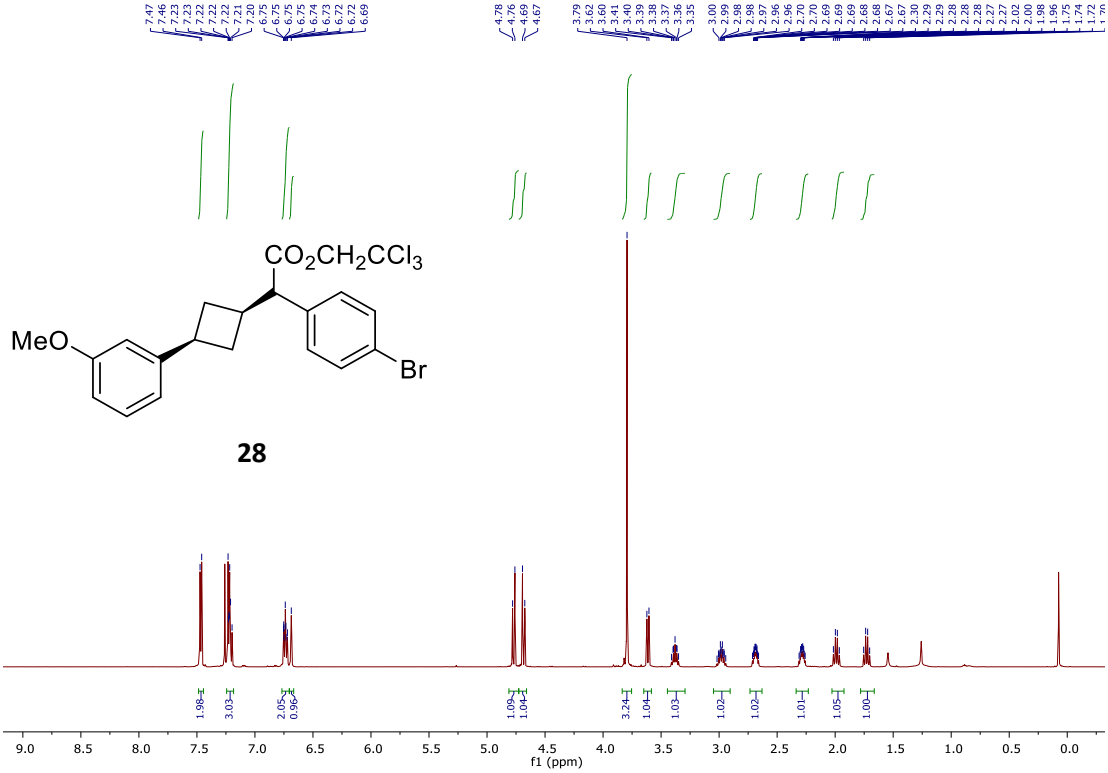


Figure S80. ^{13}C NMR spectrum of compound **28** in $CDCl_3$.

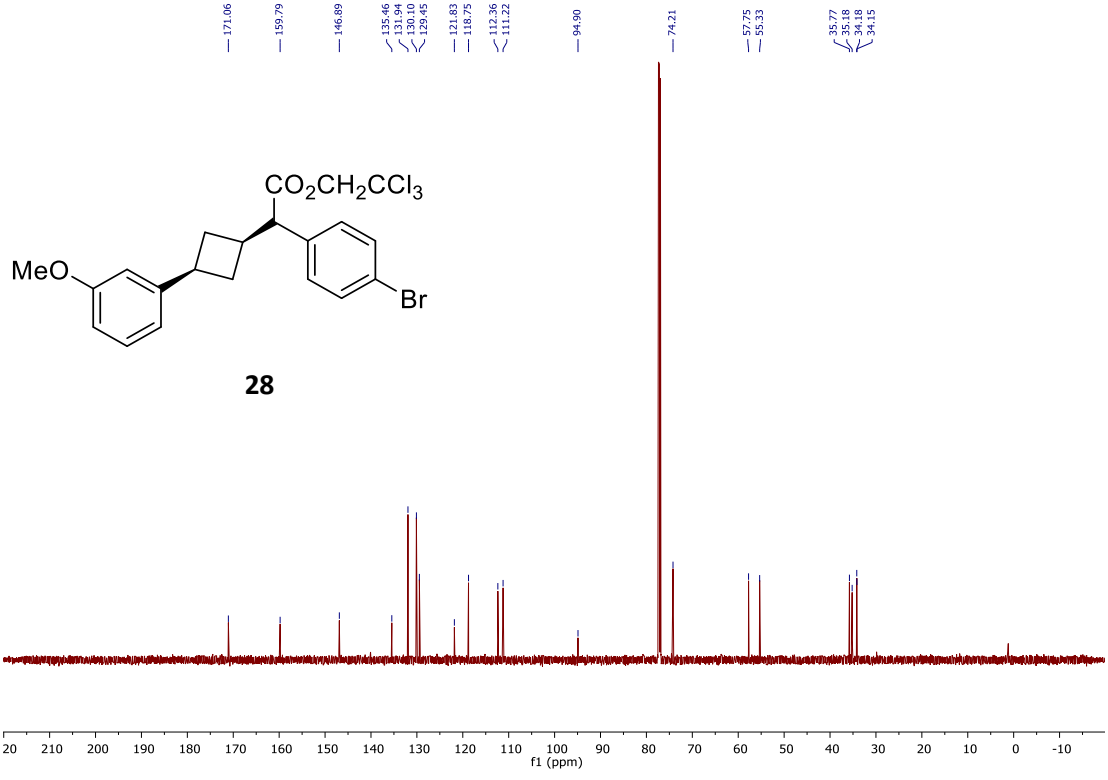


Figure S81. ^{1}H NMR Spectrum of compound **29** in $CDCl_3$.

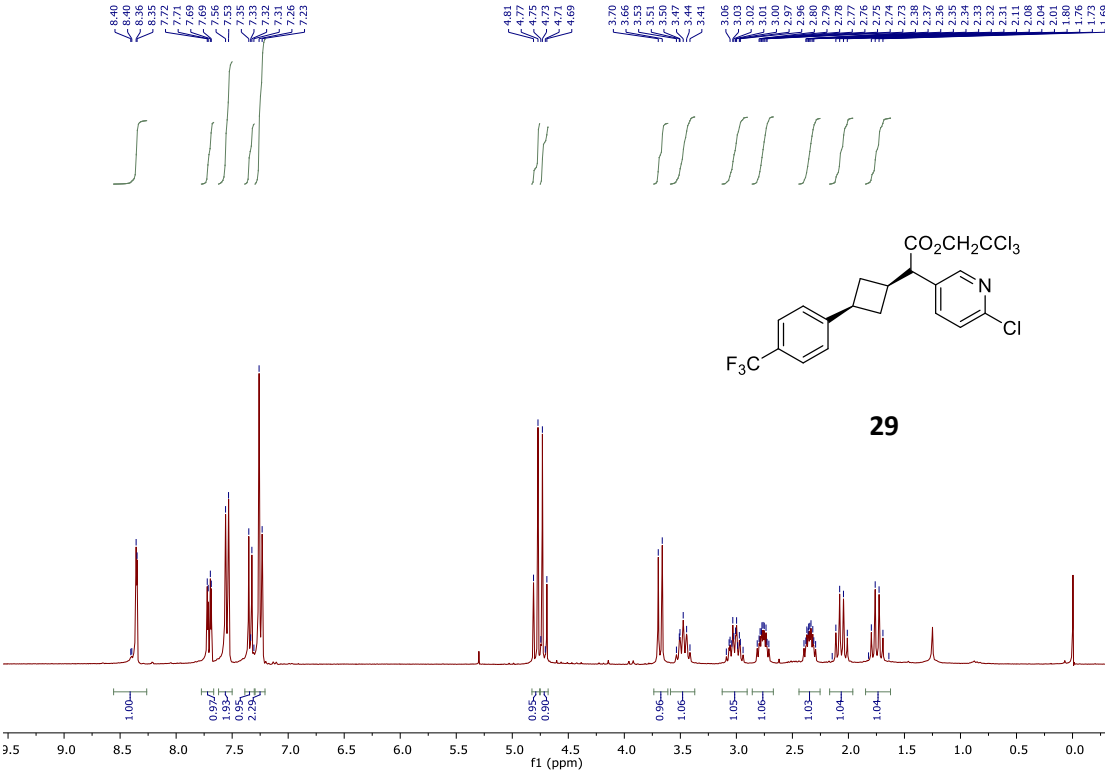


Figure S82. ^{13}C NMR spectrum of compound **29** in $CDCl_3$.

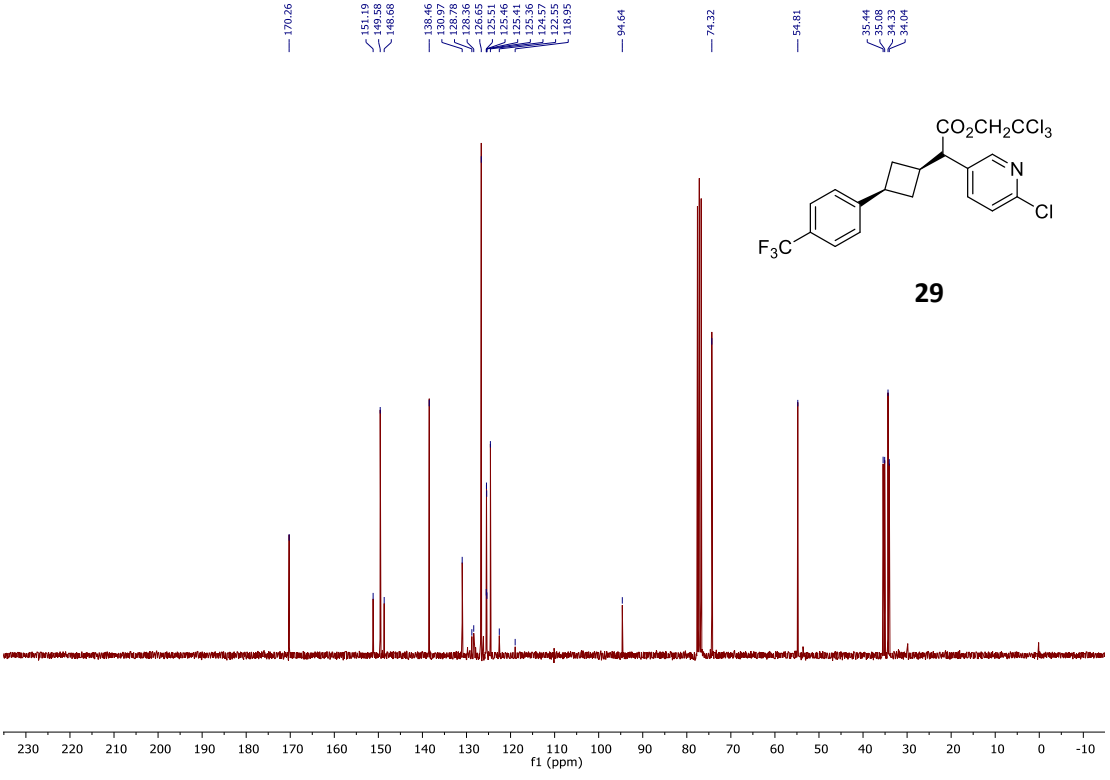


Figure S83. ^{19}F NMR spectrum of compound **29** in $CDCl_3$.

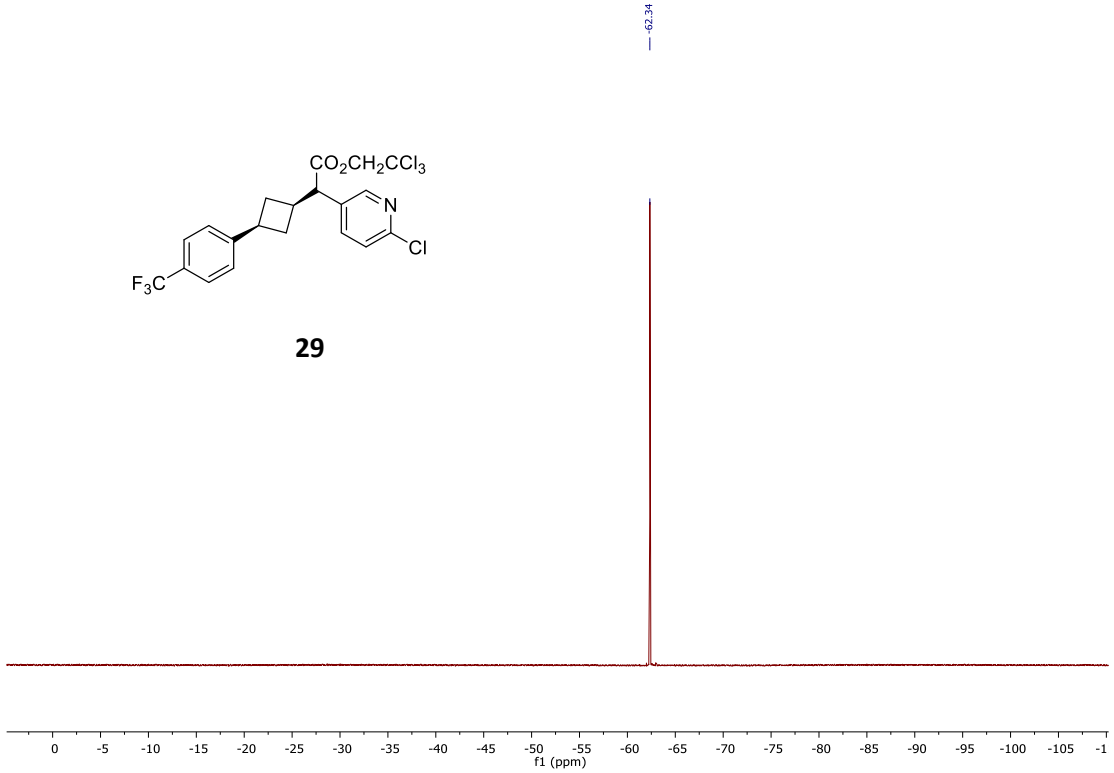


Figure S84. ^{1}H NMR Spectrum of compound **30** in $CDCl_3$.

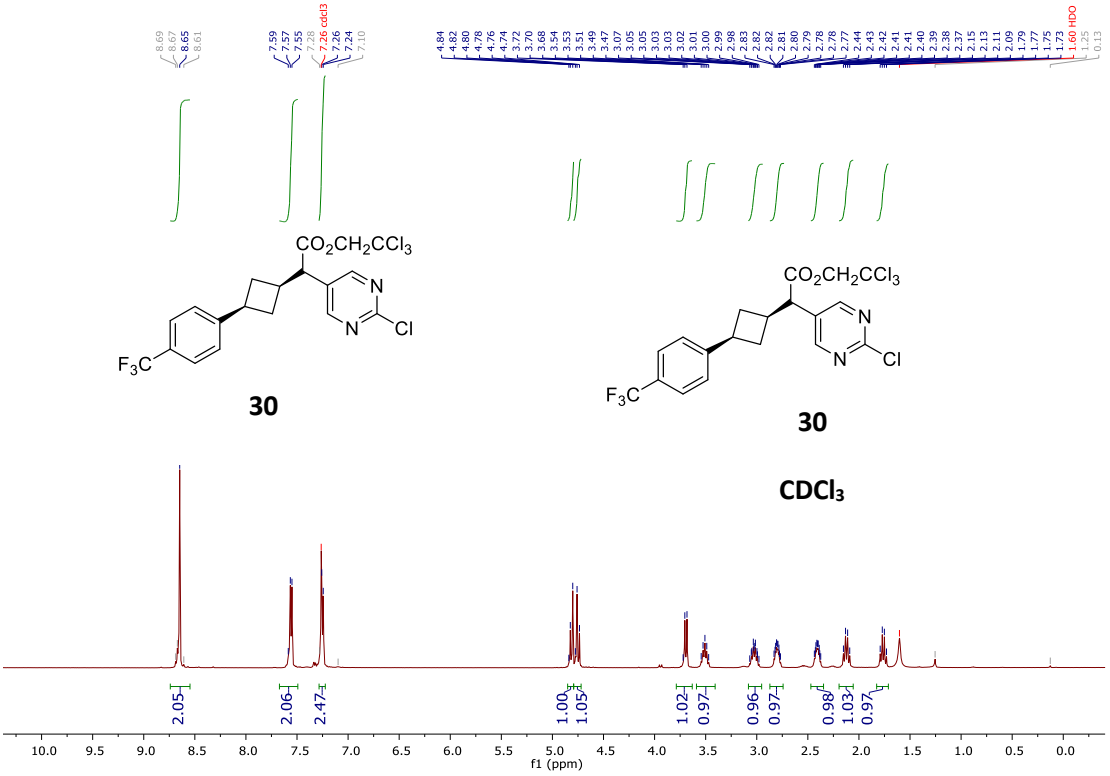


Figure S85. ^{13}C NMR spectrum of compound **30** in $CDCl_3$.

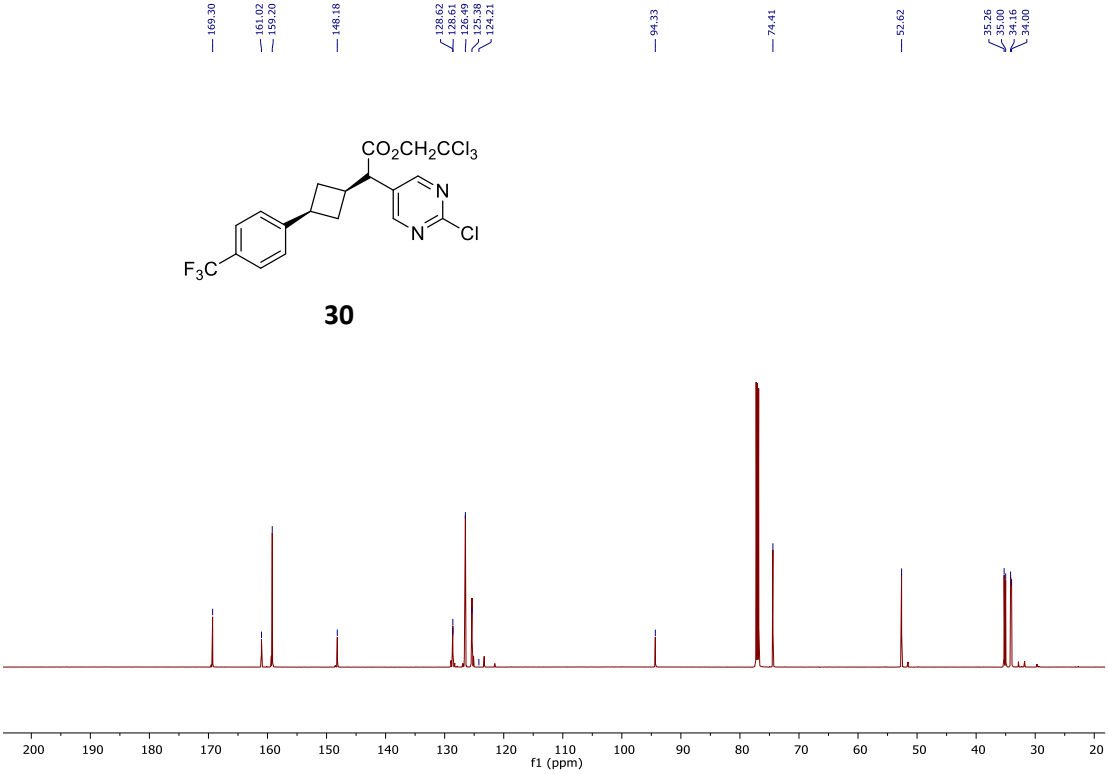


Figure S86. ^{19}F NMR spectrum of compound **30** in $CDCl_3$.

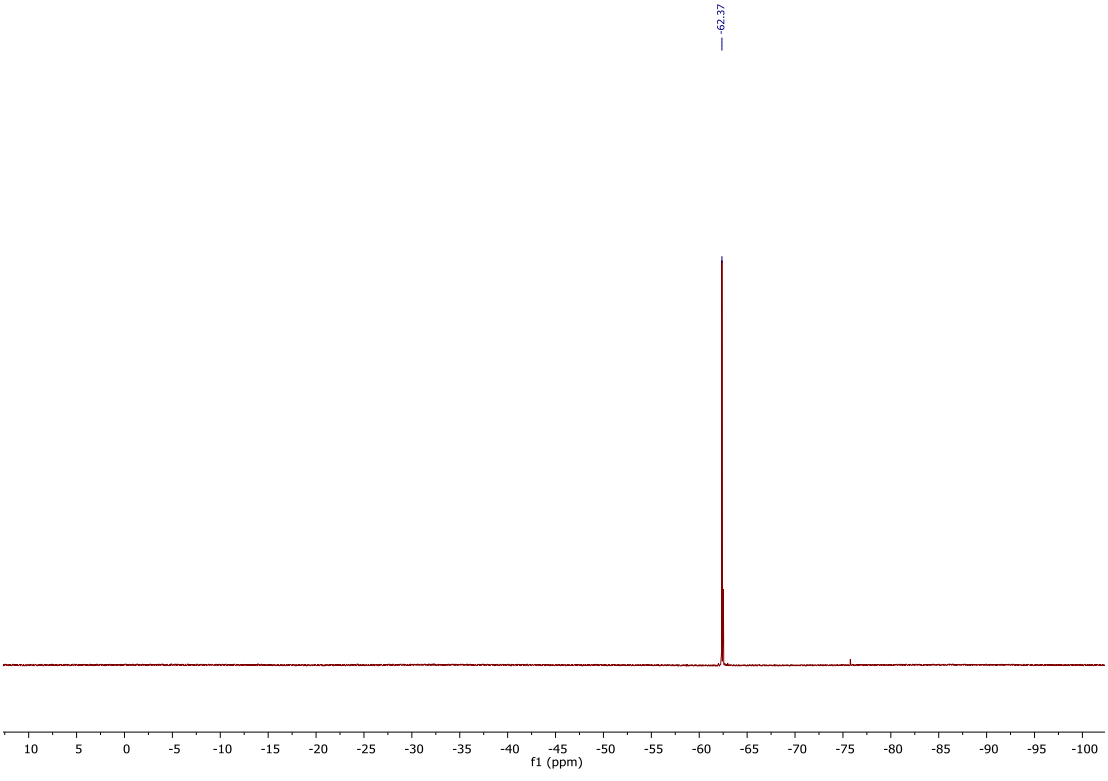


Figure S87. ^{1}H NMR Spectrum of compound **31** in $CDCl_3$.

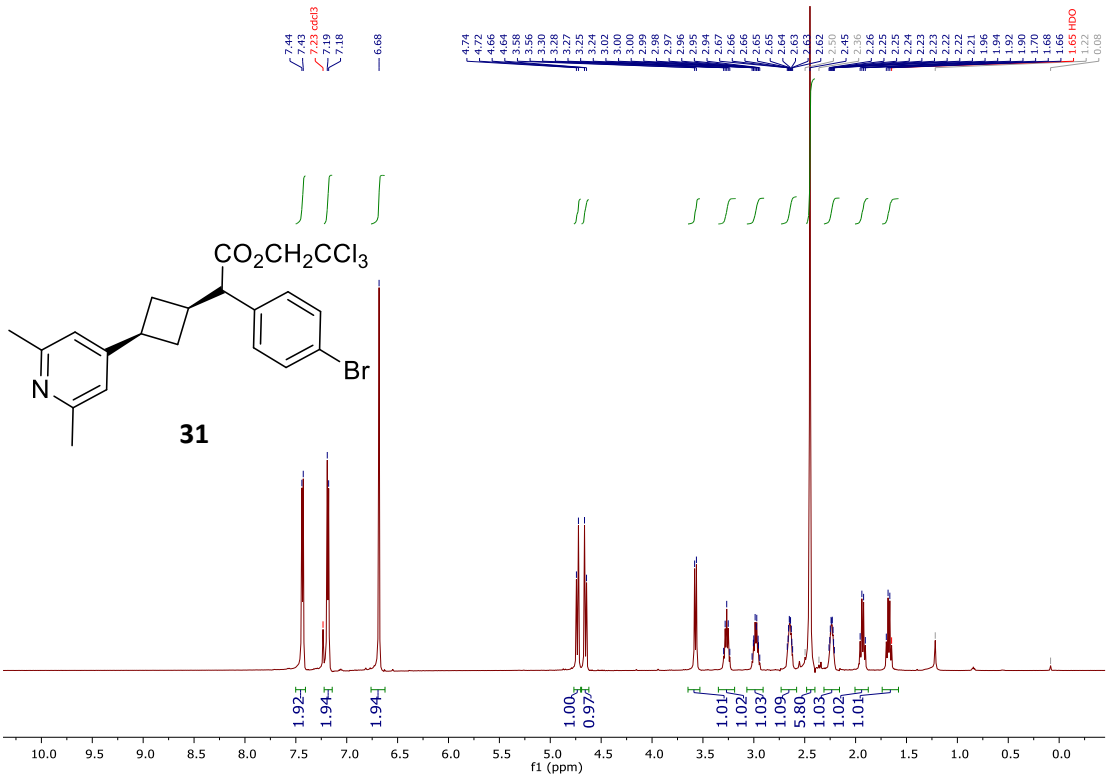


Figure S88. ^{13}C NMR spectrum of compound **31** in $CDCl_3$.

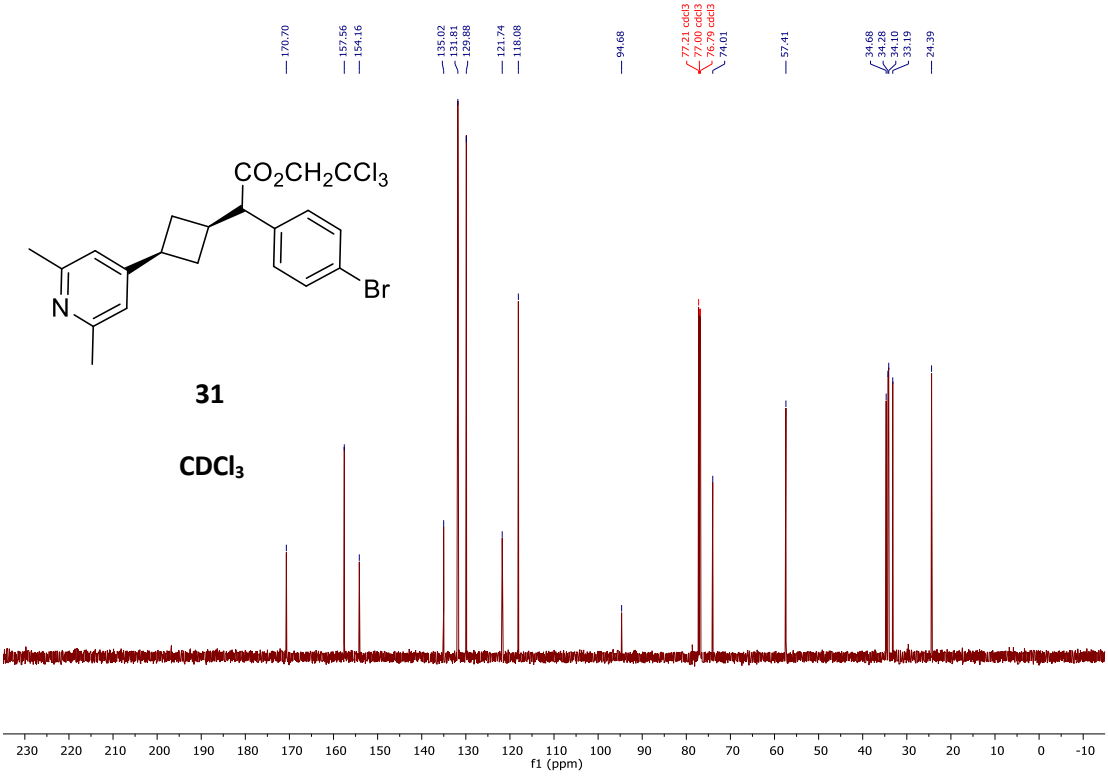


Figure S89. ^{1}H NMR Spectrum of compound **32** in $CDCl_3$.

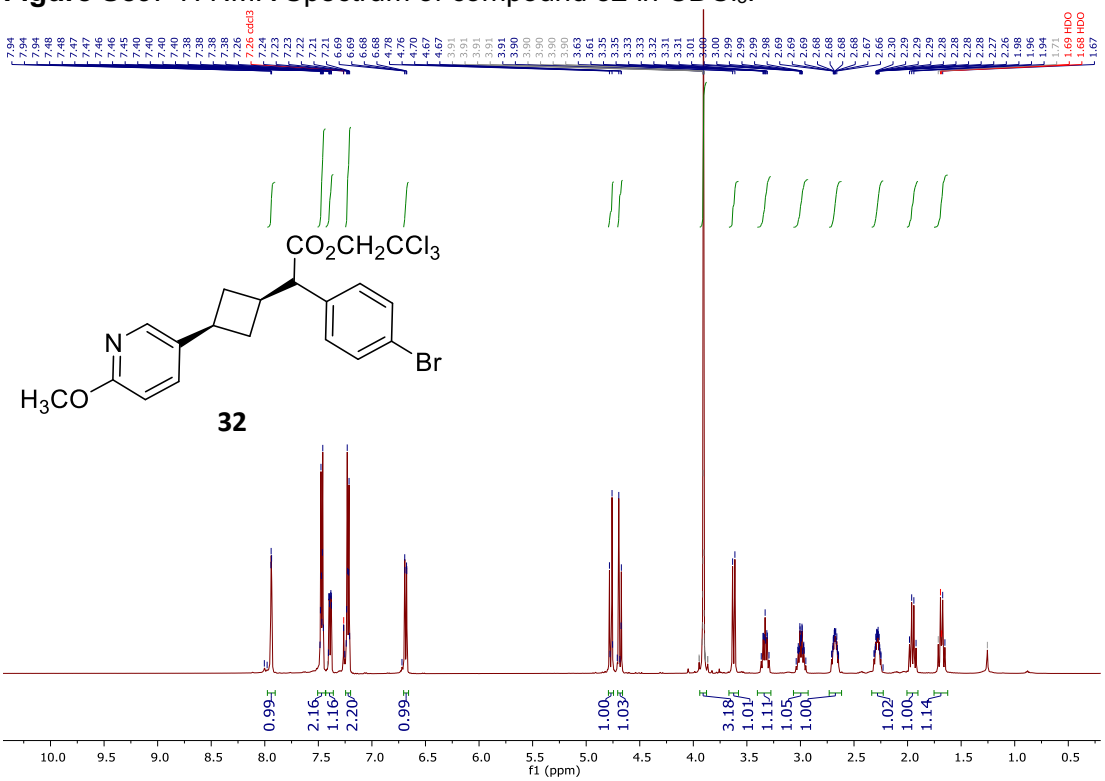
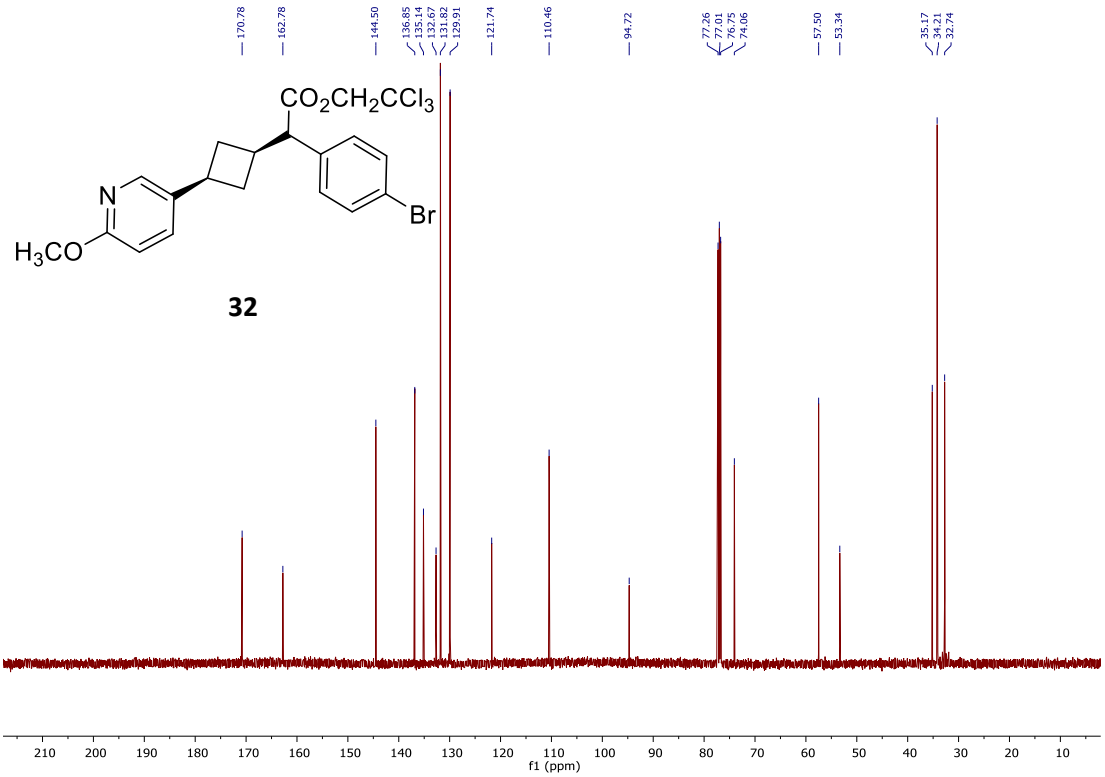


Figure S90. ^{13}C NMR spectrum of compound **32** in $CDCl_3$.



Chiral High Performance Liquid Chromatography Data

Figure S91. Chiral HPLC trace for *rac*-**XX** prepared using Rh_2[(R/S)-TCPTAD]$_4$

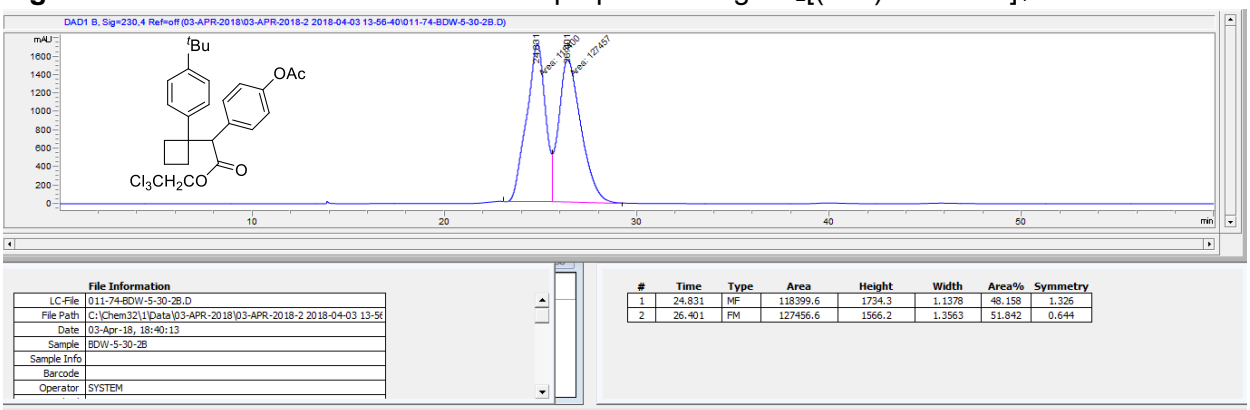


Figure S92. Chiral HPLC trace of compound **10** prepared using Rh_2[(R)-TCPTAD]$_4$

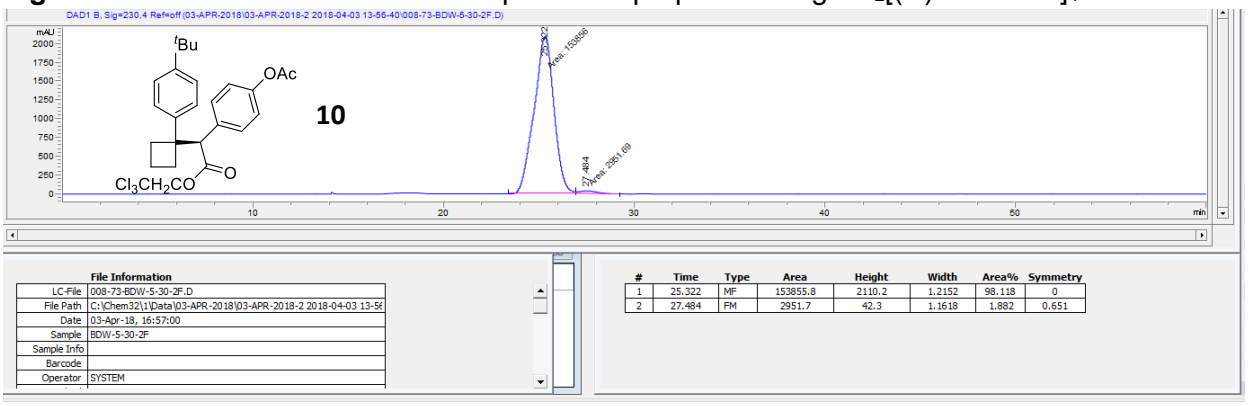
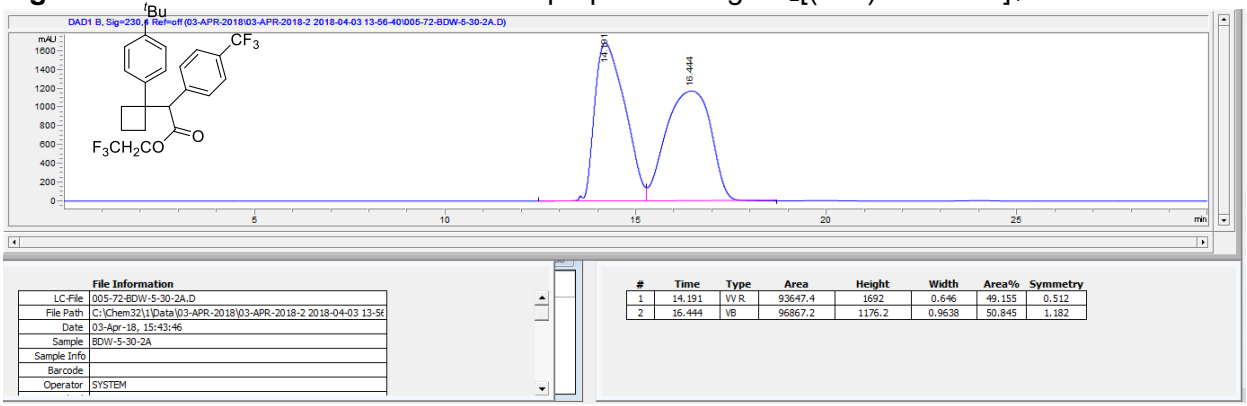


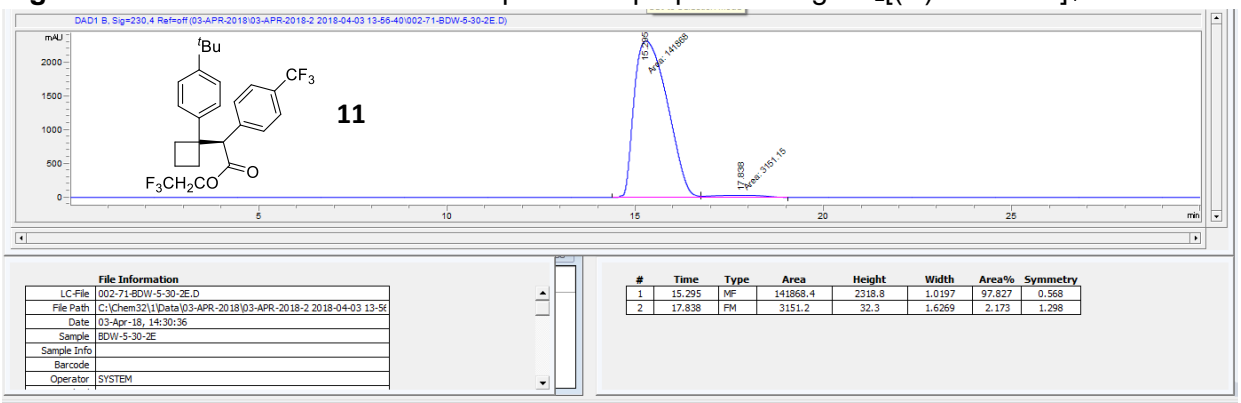
Figure S93. Chiral HPLC trace for *rac*-**11** prepared using Rh_2[(R/S)-TCPTAD]$_4$



File Information	
LC-File	005-72-BDW-5-30-2A.D
File Path	C:\Chem32\1\Data\03-APR-2018\03-APR-2018-2 2018-04-03 13-5
Date	03-Apr-18, 15:43:46
Sample	BDW-5-30-2A
Sample Info	
Barcode	
Operator	SYSTEM

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.191	VV R	93647.4	1692	0.646	49.155	0.512
2	16.444	VB	96867.2	1176.2	0.9638	50.845	1.182

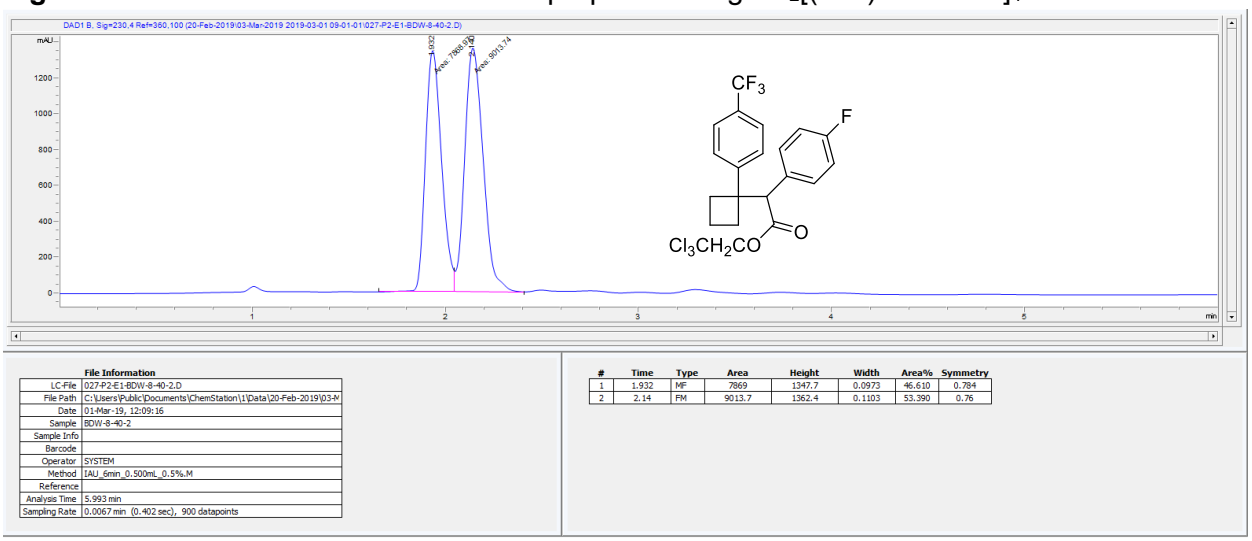
Figure S94. Chiral HPLC trace of compound **11** prepared using Rh_2[(R)-TCPTAD]$_4$



File Information	
LC-File	002-71-BDW-5-30-2E.D
File Path	C:\Chem32\1\Data\03-APR-2018\03-APR-2018-2 2018-04-03 13-5
Date	03-Apr-18, 14:30:36
Sample	BDW-5-30-2E
Sample Info	
Barcode	
Operator	SYSTEM

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.295	MF	141868.4	2318.8	1.0197	97.827	0.568
2	17.838	FM	3151.2	32.3	1.6269	2.173	1.298

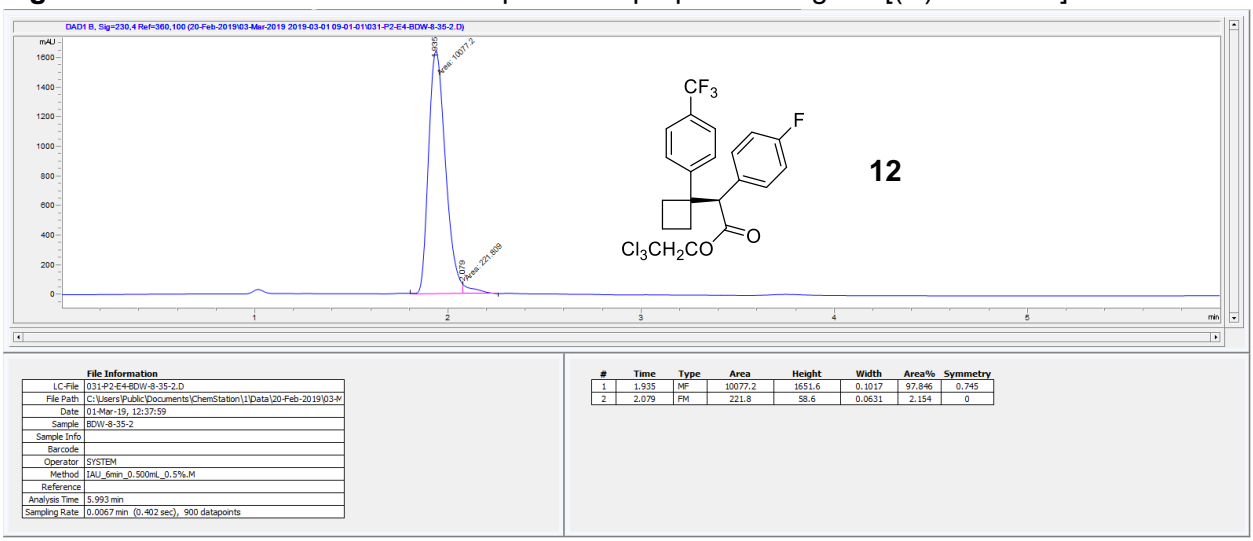
Figure S95. Chiral HPLC trace for *rac*-**12** prepared using Rh_2[(R/S)-TCPTAD]$_4$



File Information	
LC-File	027-P2-E1-BDW-8-40-2.D
File Path	C:\Users\Public\Documents\ChemStation\1\Data\20-Feb-2019\03-M
Date	01-Mar-19, 12:09:16
Sample	BDW-8-40-2
Sample Info	
Barcode	
Operator	SYSTEM
Method	IAU_6min_0.500mL_0.5%.M
Reference	
Analysis Time	5.993 min
Sampling Rate	0.0067 min (0.402 sec), 900 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.932	MF	7869	1347.7	0.0973	46.610	0.784
2	2.14	FM	9013.7	1362.4	0.1103	53.390	0.76

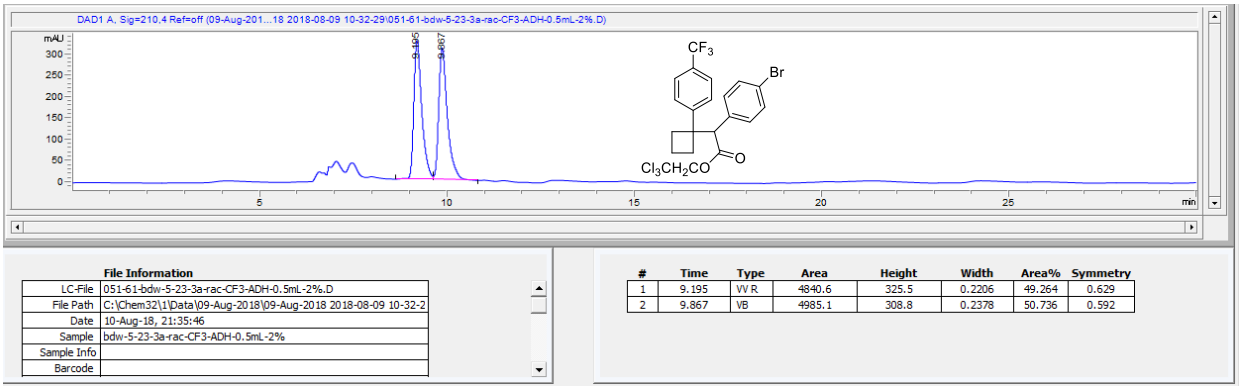
Figure S96. Chiral HPLC trace of compound **12** prepared using Rh_2[(R)-TCPTAD]$_4$



File Information	
LC-File	031-P2-E4-BDW-8-35-2.D
File Path	C:\Users\Public\Documents\ChemStation\1\Data\20-Feb-2019\03-M
Date	01-Mar-19, 12:37:59
Sample	BDW-8-35-2
Sample Info	
Barcode	
Operator	SYSTEM
Method	IAU_6min_0.500mL_0.5%.M
Reference	
Analysis Time	5.993 min
Sampling Rate	0.0067 min (0.402 sec), 900 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.935	MF	10077.2	1651.6	0.1017	97.846	0.745
2	2.079	FM	221.8	58.6	0.0631	2.154	0

Figure S97. Chiral HPLC trace for *rac*-**13** prepared using Rh_2[(R/S)-TCPTAD]$_4$

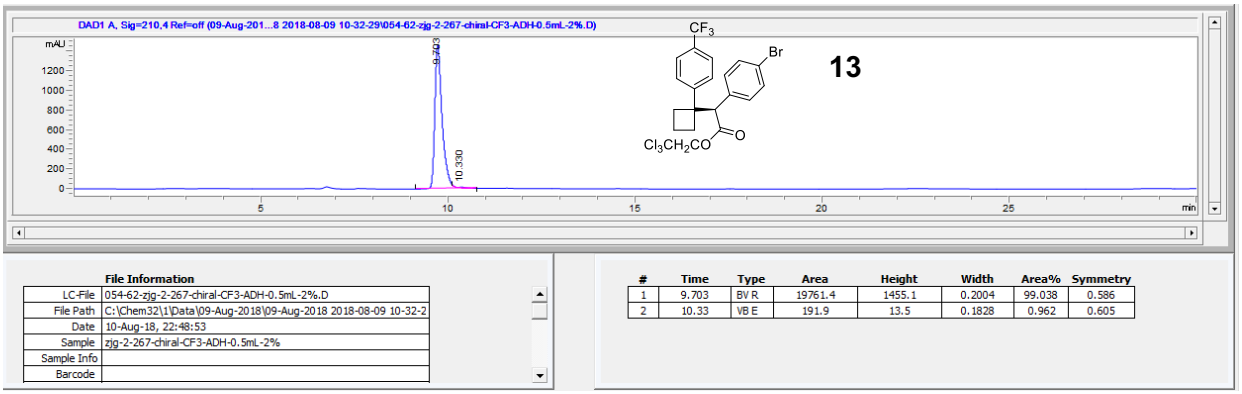


File Information

LC-File	051-61-bdw-5-23-3a-rac-CF3-ADH-0.5mL-2%.D
File Path	C:\Chem32\1\Data\09-Aug-2018\09-Aug-2018 2018-08-09 10-32-2
Date	10-Aug-18, 21:35:46
Sample	bdw-5-23-3a-rac-CF3-ADH-0.5mL-2%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.195	VV R	4840.6	325.5	0.2206	49.264	0.629
2	9.867	VB	4985.1	308.8	0.2378	50.736	0.592

Figure S98. Chiral HPLC trace of compound **13** prepared using Rh_2[(R)-TCPTAD]$_4$

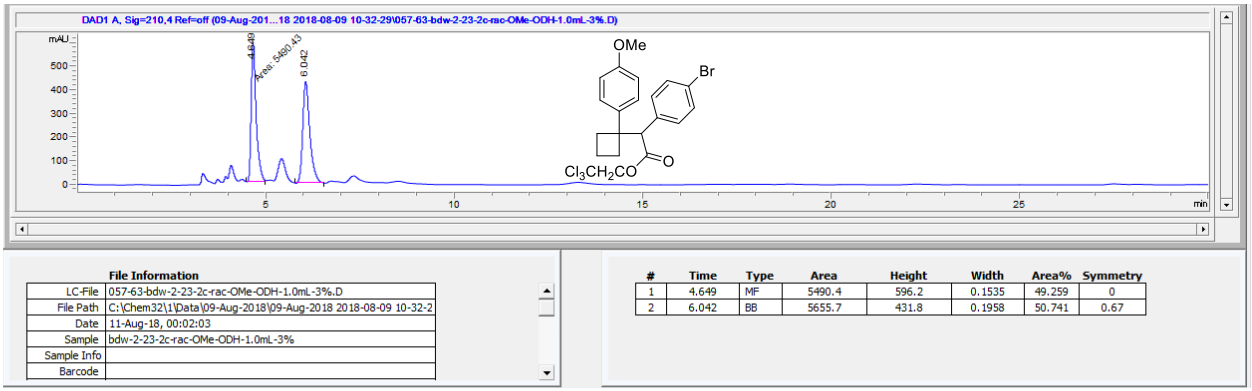


File Information

LC-File	054-62-zjg-2-267-chiral-CF3-ADH-0.5mL-2%.D
File Path	C:\Chem32\1\Data\09-Aug-2018\09-Aug-2018 2018-08-09 10-32-2
Date	10-Aug-18, 22:48:53
Sample	zjg-2-267-chiral-CF3-ADH-0.5mL-2%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.703	BV R	19761.4	1455.1	0.2004	99.038	0.586
2	10.33	VB E	191.9	13.5	0.1828	0.962	0.605

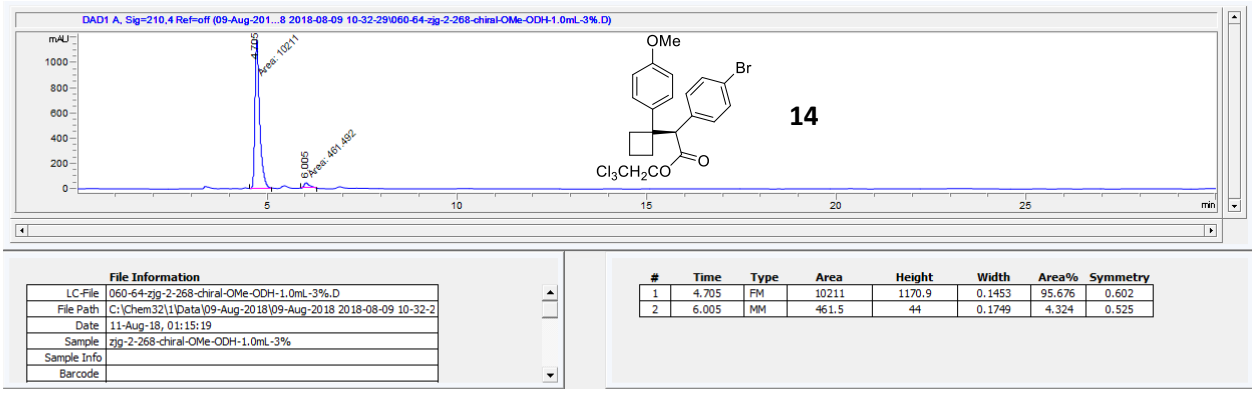
Figure S99. Chiral HPLC trace for *rac*-14 prepared using Rh_2[(R/S)-TCPTAD]$_4$



File Information	
LC-File	057-63-bdw-2-23-2c-rac-OMe-ODH-1.0mL-3%.D
File Path	C:\Chem32\1\Data\09-Aug-2018\09-Aug-2018 2018-08-09 10-32-2
Date	11-Aug-18, 00:02:03
Sample	bdw-2-23-2c-rac-OMe-ODH-1.0mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.649	MF	5490.4	596.2	0.1535	49.259	0
2	6.042	BB	5655.7	431.8	0.1958	50.741	0.67

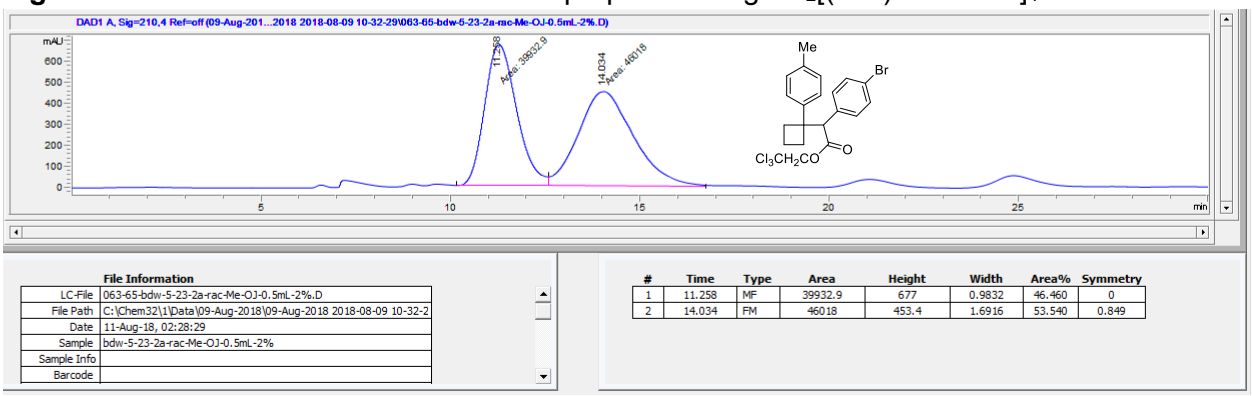
Figure S100. Chiral HPLC trace of compound **14** prepared using Rh_2[(R)-TCPTAD]$_4$



File Information	
LC-File	060-64-zjg-2-268-chiral-OMe-ODH-1.0mL-3%.D
File Path	C:\Chem32\1\Data\09-Aug-2018\09-Aug-2018 2018-08-09 10-32-2
Date	11-Aug-18, 01:15:19
Sample	zjg-2-268-chiral-OMe-ODH-1.0mL-3%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.705	FM	10211	1170.9	0.1453	95.676	0.602
2	6.005	MM	461.5	44	0.1749	4.324	0.525

Figure S101. Chiral HPLC trace for *rac*-**15** prepared using Rh_2[(R/S)-TCPTAD]$_4$

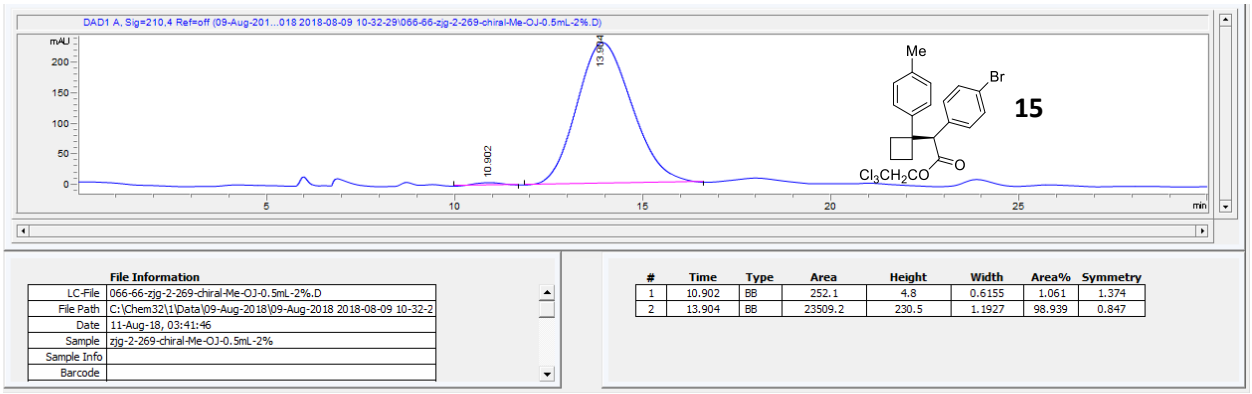


File Information

LC-File	063-65-bdw-5-23-2a-rac-Me-OJ-0.5mL-2%.D
File Path	C:\Chem32\1\Data\09-Aug-2018\09-Aug-2018 2018-08-09 10-32-2
Date	11-Aug-18, 02:28:29
Sample	bdw-5-23-2a-rac-Me-OJ-0.5mL-2%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.258	MF	39932.9	677	0.9832	46.460	0
2	14.034	FM	46018	453.4	1.6916	53.540	0.849

Figure S102. Chiral HPLC trace of compound **15** prepared using Rh_2[(R)-TCPTAD]$_4$

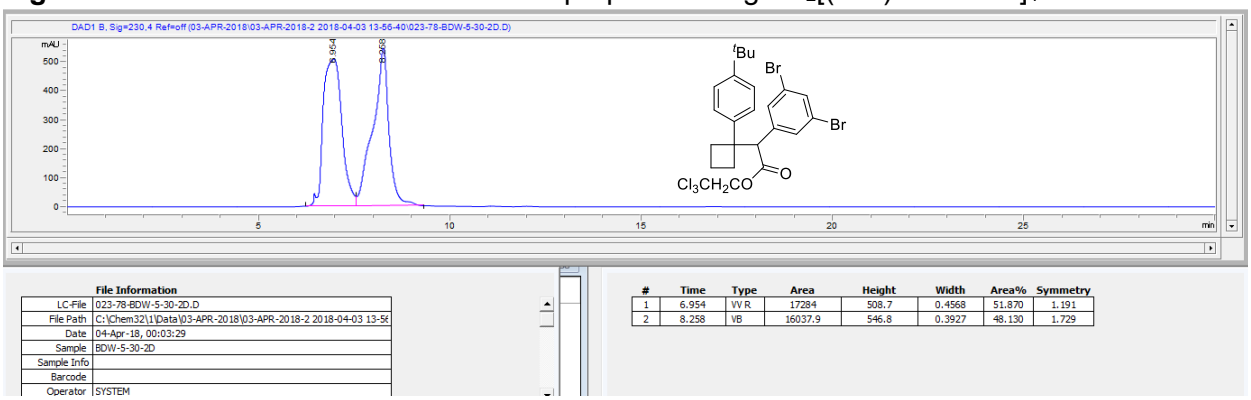


File Information

LC-File	066-66-zjg-2-269-chiral-Me-OJ-0.5mL-2%.D
File Path	C:\Chem32\1\Data\09-Aug-2018\09-Aug-2018 2018-08-09 10-32-2
Date	11-Aug-18, 03:41:46
Sample	zjg-2-269-chiral-Me-OJ-0.5mL-2%
Sample Info	
Barcode	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.902	BB	252.1	4.8	0.6155	1.061	1.374
2	13.904	BB	23509.2	230.5	1.1927	98.939	0.847

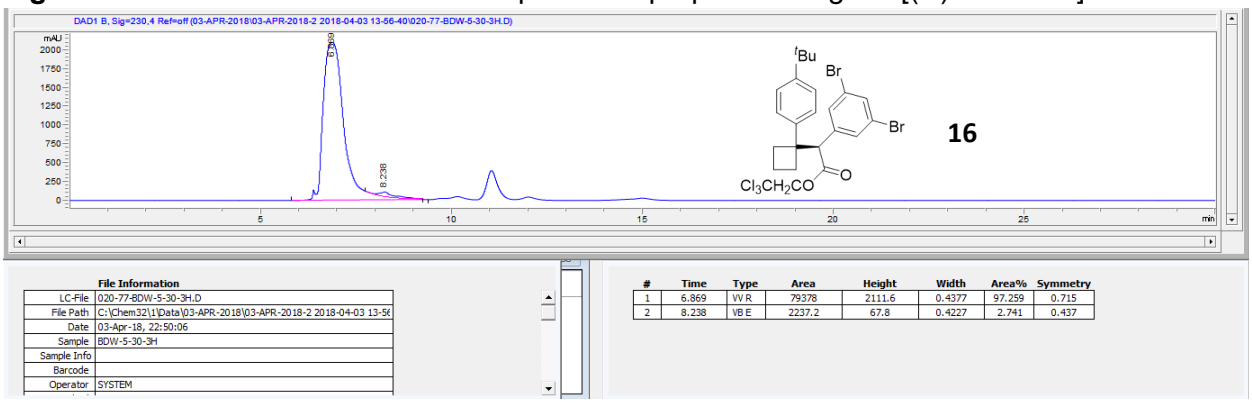
Figure S103. Chiral HPLC trace for *rac*-**16** prepared using Rh_2[(R/S)-TCPTAD]$_4$



File Information	
LC-File	023-78-BDW-5-30-2D.D
File Path	C:\Chem32\1\Data\03-APR-2018\03-APR-2018-2 2018-04-03 13-5
Date	04-Apr-18, 00:03:29
Sample	BDW-5-30-2D
Sample Info	
Barcode	
Operator	SYSTEM

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.954	VV R	17284	508.7	0.4568	51.870	1.191
2	8.258	VB	16037.9	546.8	0.3927	48.130	1.729

Figure S104. Chiral HPLC trace of compound **16** prepared using Rh_2[(R)-TCPTAD]$_4$



File Information	
LC-File	020-77-BDW-5-30-3H.D
File Path	C:\Chem32\1\Data\03-APR-2018\03-APR-2018-2 2018-04-03 13-5
Date	03-Apr-18, 22:50:06
Sample	BDW-5-30-3H
Sample Info	
Barcode	
Operator	SYSTEM

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.869	VV R	79378	2111.6	0.4377	97.259	0.715
2	8.238	VB E	2237.2	67.8	0.4227	2.741	0.437

Figure S105. Chiral HPLC trace for *rac*-**17** prepared using Rh_2[(R/S)-TCPTAD]$_4$

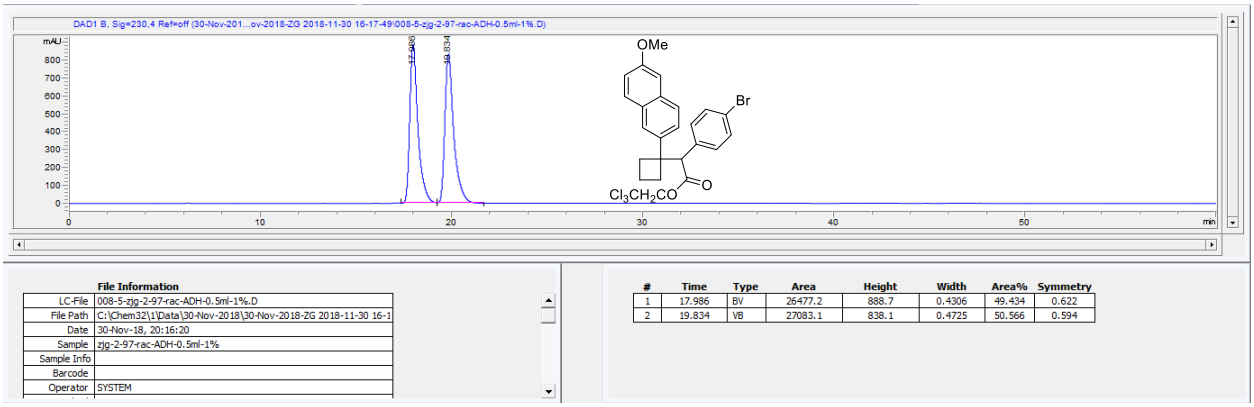


Figure S106. Chiral HPLC trace of compound **17** prepared using Rh_2[(R)-TCPTAD]$_4$

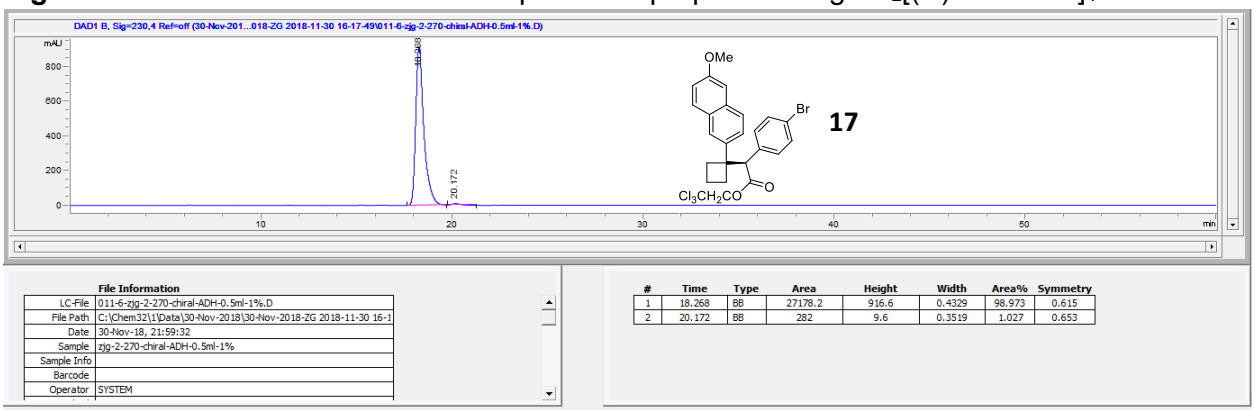
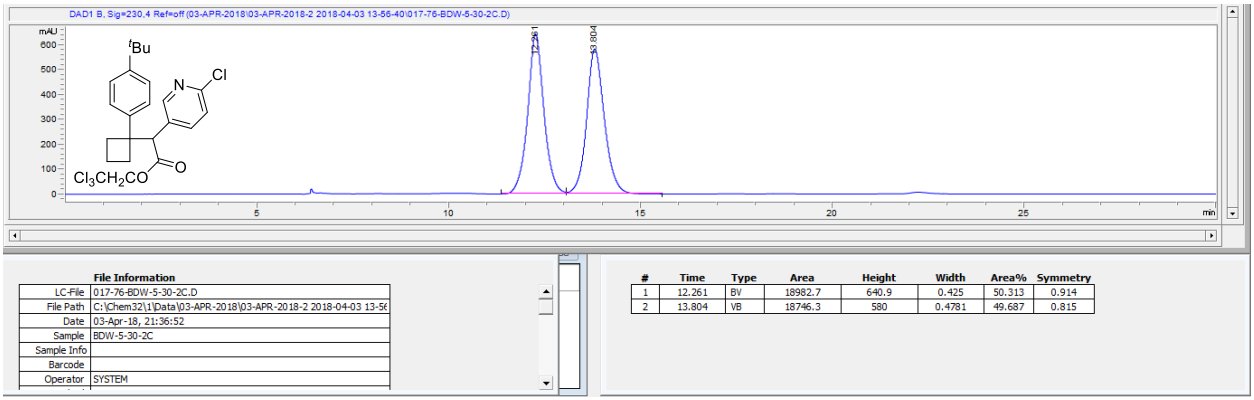


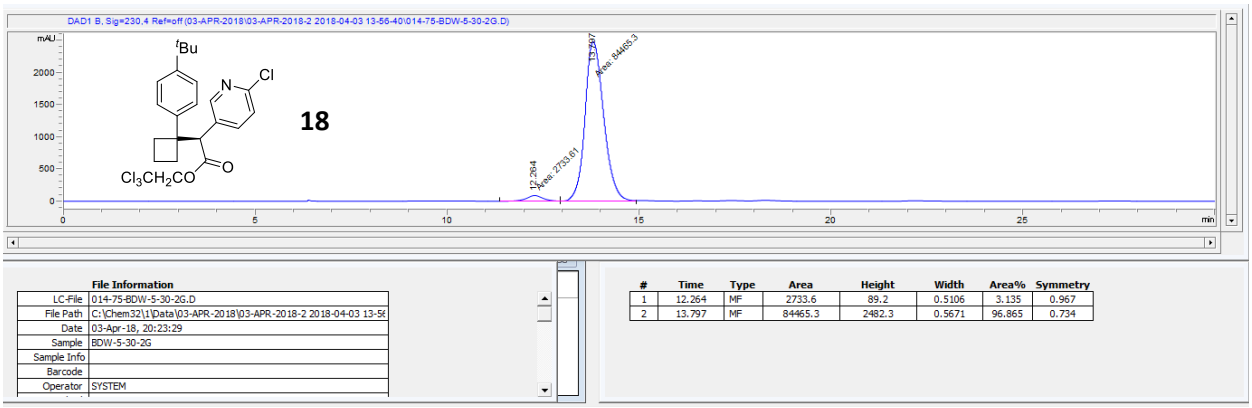
Figure S107. Chiral HPLC trace for *rac*-**18** prepared using Rh_2[(R/S)-TCPTAD]$_4$



File Information	
LC-File	017-76-BDW-5-30-2C.D
File Path	C:\Chem32\1\Data\03-APR-2018\03-APR-2018-2 2018-04-03 13-5(
Date	03-Apr-18, 21:36:52
Sample	BDW-5-30-2C
Sample Info	
Barcode	
Operator	SYSTEM

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.261	BV	18982.7	640.9	0.425	50.313	0.914
2	13.804	VB	18746.3	580	0.4781	49.687	0.815

Figure S108. Chiral HPLC trace of compound **18** prepared using Rh_2[(R)-TCPTAD]$_4$



File Information	
LC-File	014-75-BDW-5-30-2G.D
File Path	C:\Chem32\1\Data\03-APR-2018\03-APR-2018-2 2018-04-03 13-5(
Date	03-Apr-18, 20:23:29
Sample	BDW-5-30-2G
Sample Info	
Barcode	
Operator	SYSTEM

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.264	MF	2733.6	89.2	0.5106	3.135	0.967
2	13.797	MF	84465.3	2482.3	0.5671	96.865	0.734

Figure S109. Chiral HPLC trace for *rac*-**19** prepared using Rh_2[(R/S)-TCPTAD]$_4$

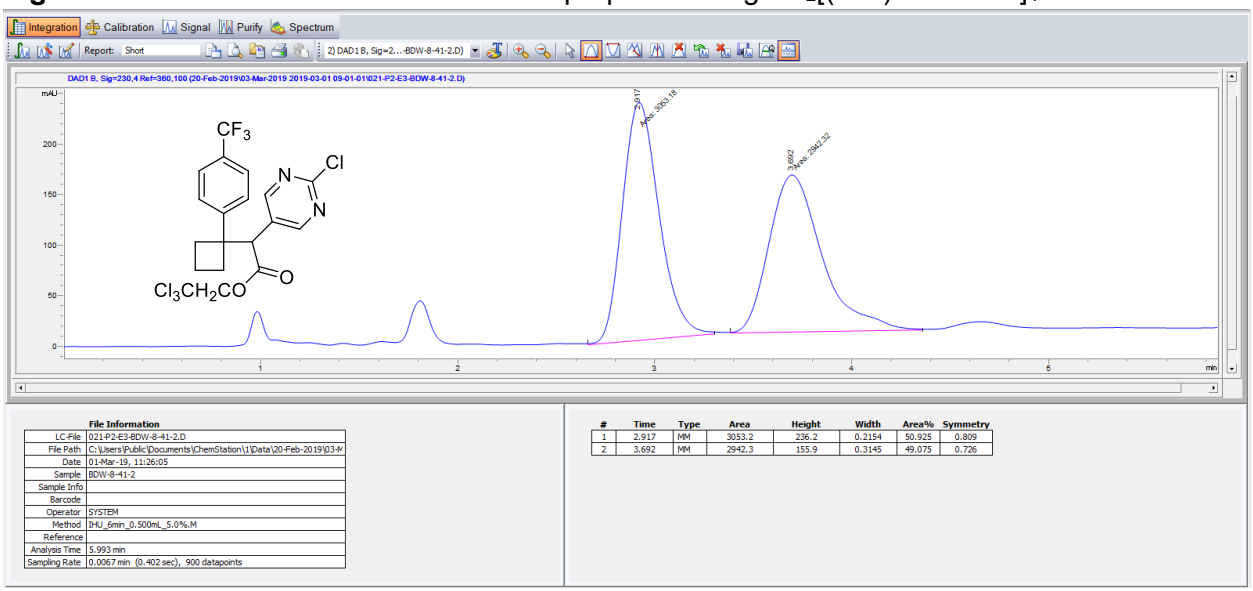


Figure S110. Chiral HPLC trace of compound **19** prepared using Rh_2[(R)-TCPTAD]$_4$

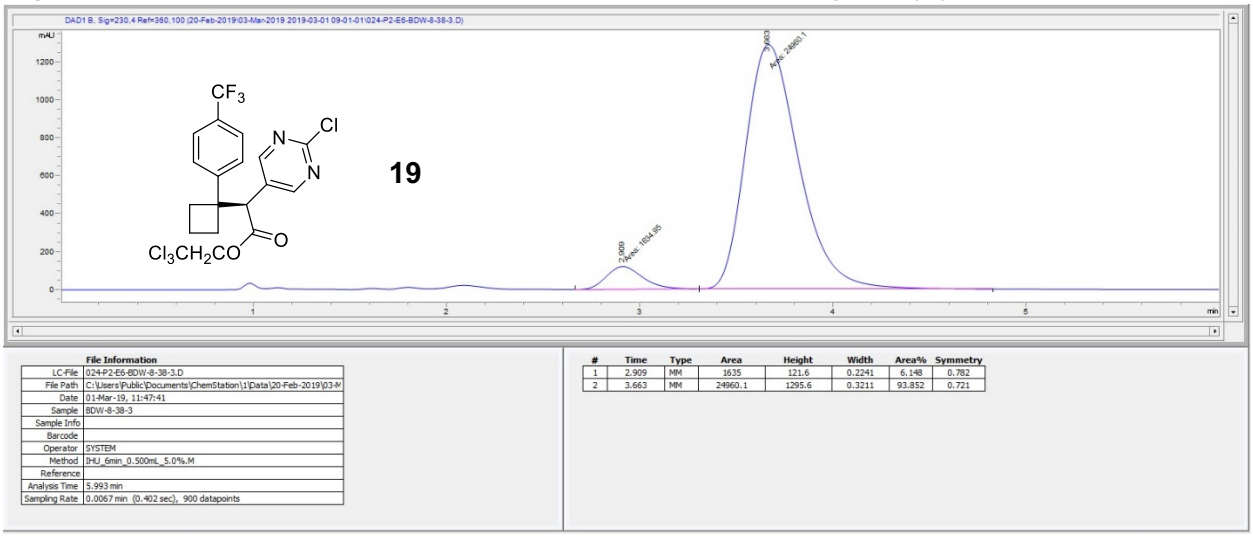


Figure S111. Chiral HPLC trace for *rac*-**20** prepared using Rh_2[(R/S)-TCPTAD]$_4$

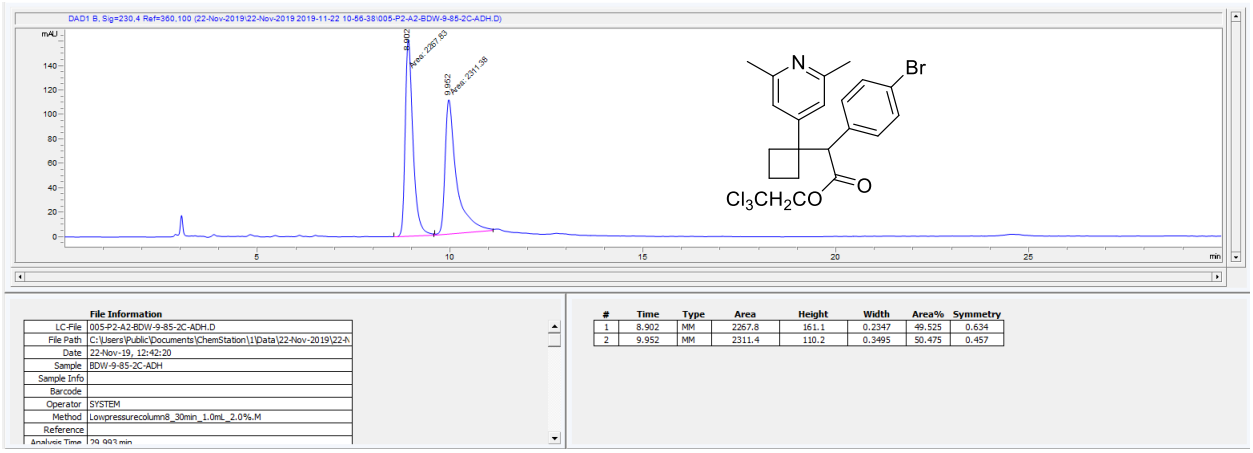


Figure S112. Chiral HPLC trace of compound **20** prepared using Rh_2[(R)-TCPTAD]$_4$

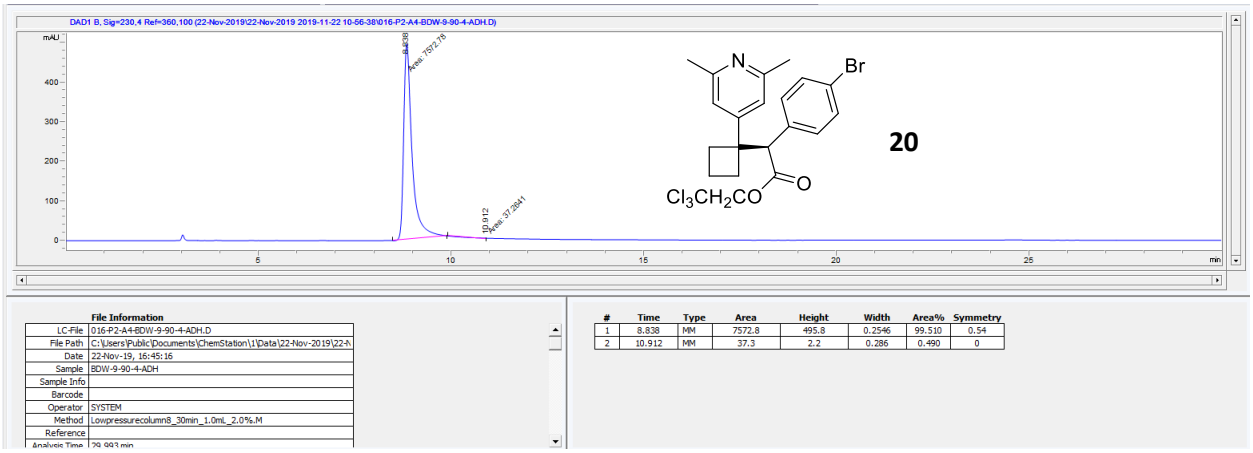
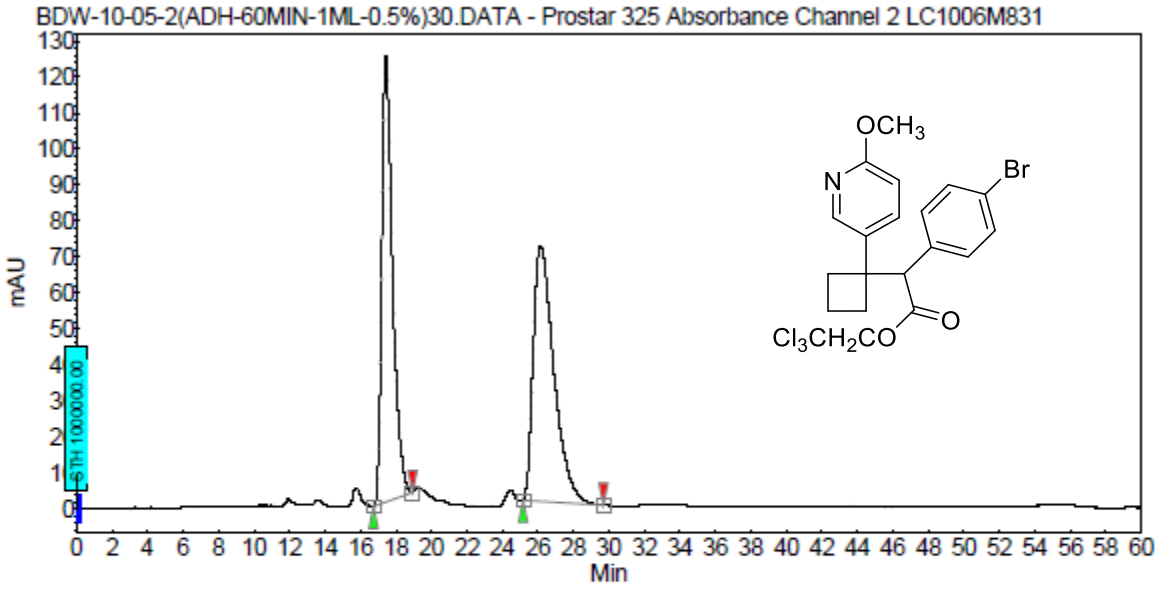


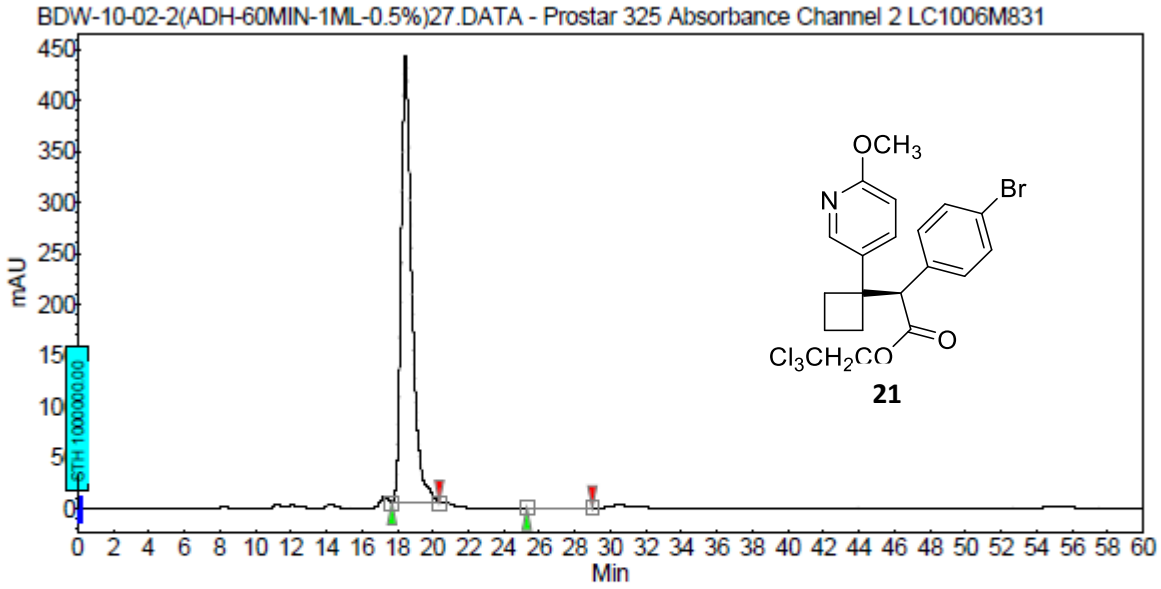
Figure S113. Chiral HPLC trace for *rac*-**21** prepared using Rh_2[(R/S)-TCPTAD]$_4$



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.44	47.48	123.9	86.6	47.482
2	UNKNOWN	26.16	52.52	71.1	95.8	52.518
Total			100.00	194.9	182.4	100.000

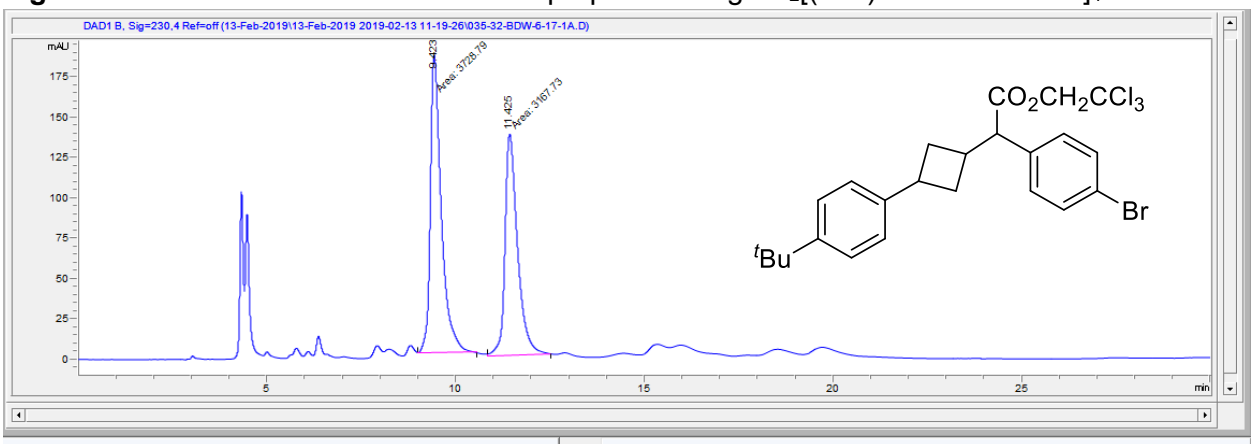
Figure S114. Chiral HPLC trace of compound **21** prepared using Rh_2[(R)-TCPTAD]$_4$



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	18.46	99.83	436.8	306.4	99.826
1	UNKNOWN	27.09	0.17	0.3	0.5	0.174
Total			100.00	437.1	306.9	100.000

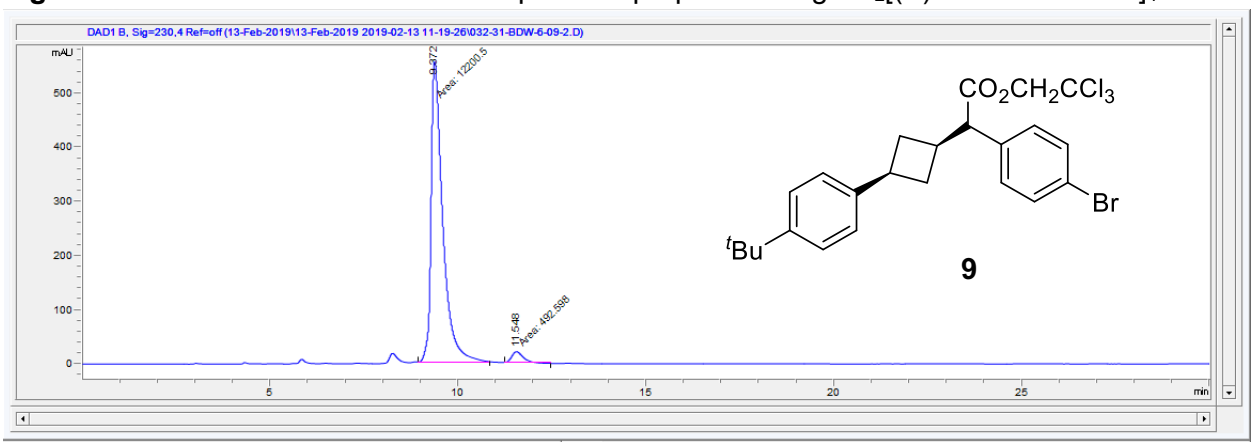
Figure S115. Chiral HPLC trace for *rac*-**9** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	035-32-BDW-6-17-1A.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	14-Feb-19, 01:15:15
Sample	BDW-6-17-1A
Sample Info	
Barcode	
Operator	SYSTEM
Method	WHELK_30min_1.0ML_0.5%.M
Reference	
Analysis Time	30.002 min
Sampling Rate	0.0017 min (0.102 sec), 18002 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.423	MM	3728.8	184.1	0.3376	54.068	0.526
2	11.425	MM	3167.7	136.8	0.3859	45.932	0.593

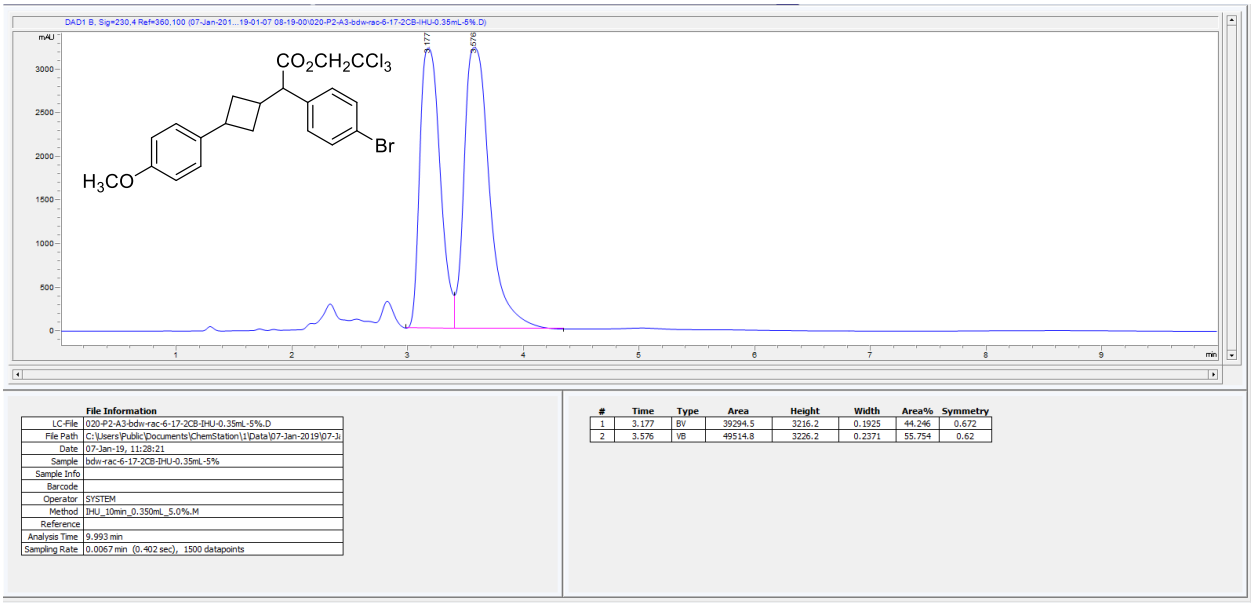
Figure S116. Chiral HPLC trace of compound **9** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	032-31-BDW-6-09-2.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	14-Feb-19, 00:02:10
Sample	BDW-6-09-2
Sample Info	
Barcode	
Operator	SYSTEM
Method	WHELK_30min_1.0ML_0.5%.M
Reference	
Analysis Time	30.002 min
Sampling Rate	0.0017 min (0.102 sec), 18002 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.372	MM	12200.5	556.3	0.3655	96.119	0.434
2	11.548	MM	492.6	21.6	0.3806	3.881	0.68

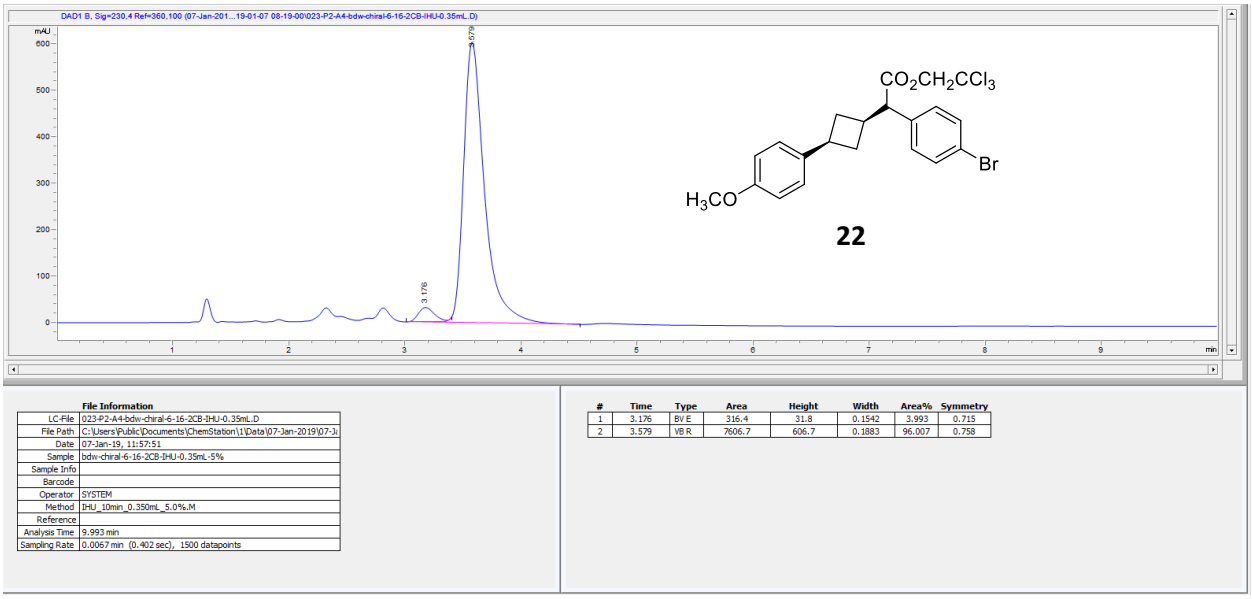
Figure S117. Chiral HPLC trace for *rac*-**22** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	020-P2-A3-bdw-rac-6-17-2CB-IHU-0.35mL-5%.D
File Path	C:\Users\Public\Documents\ChemStation\1\Data\07-Jan-2019\07-J
Date	07-Jan-19, 11:28:21
Sample	bdw-rac-6-17-2CB-IHU-0.35mL-5%
Sample Info	
Barcode	
Operator	SYSTEM
Method	IHU_10min_0.350mL_5.0%.M
Reference	
Analysis Time	9.993 min
Sampling Rate	0.0067 min (0.402 sec), 1500 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.177	BV	39294.5	3216.2	0.1925	44.246	0.672
2	3.576	VB	49514.8	3226.2	0.2371	55.754	0.62

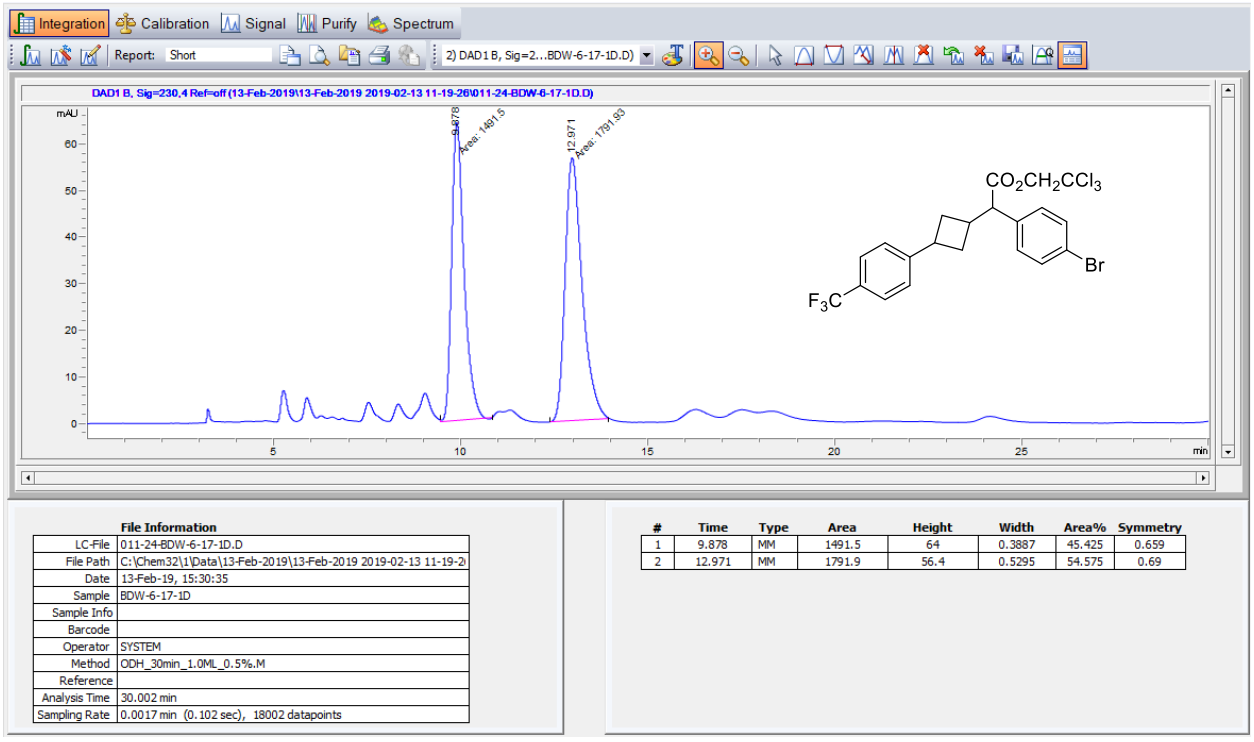
Figure S118. Chiral HPLC trace of compound **22** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	023-P2-A4-bdw-chiral-6-16-2CB-IHU-0.35mL.D
File Path	C:\Users\Public\Documents\ChemStation\1\Data\07-Jan-2019\07-J
Date	07-Jan-19, 11:57:51
Sample	bdw-chiral-6-16-2CB-IHU-0.35mL-5%
Sample Info	
Barcode	
Operator	SYSTEM
Method	IHU_10min_0.350mL_5.0%.M
Reference	
Analysis Time	9.993 min
Sampling Rate	0.0067 min (0.402 sec), 1500 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.176	BV E	316.4	31.8	0.1542	3.993	0.715
2	3.579	VB R	7606.7	606.7	0.1883	96.007	0.758

Figure S119. Chiral HPLC trace for *rac*-**23** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$

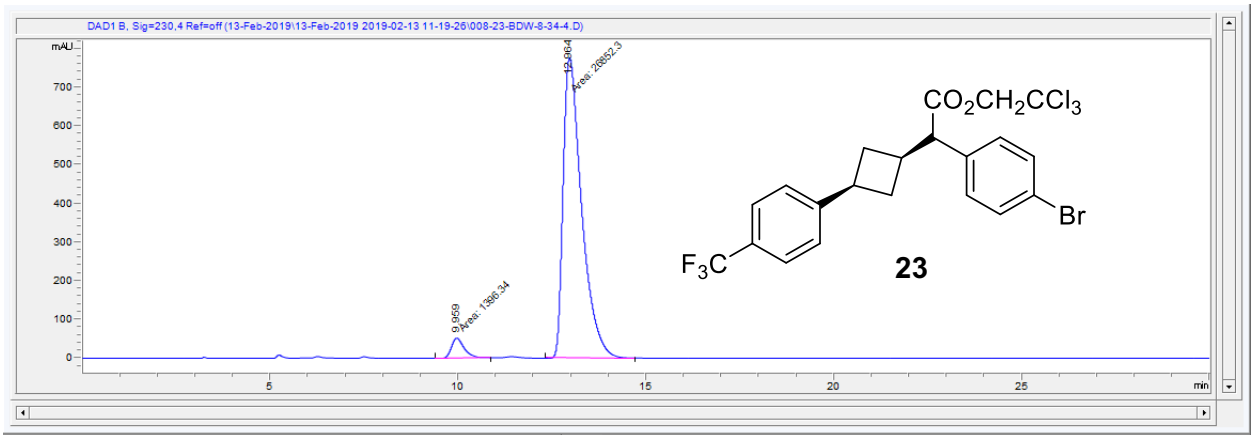


File Information

LC-File	011-24-BDW-6-17-1D.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	13-Feb-19, 15:30:35
Sample	BDW-6-17-1D
Sample Info	
Barcode	
Operator	SYSTEM
Method	ODH_30min_1.0ML_0.5%.M
Reference	
Analysis Time	30.002 min
Sampling Rate	0.0017 min (0.102 sec), 18002 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.878	MM	1491.5	64	0.3887	45.425	0.659
2	12.971	MM	1791.9	56.4	0.5295	54.575	0.69

Figure S120. Chiral HPLC trace of compound **XX** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$

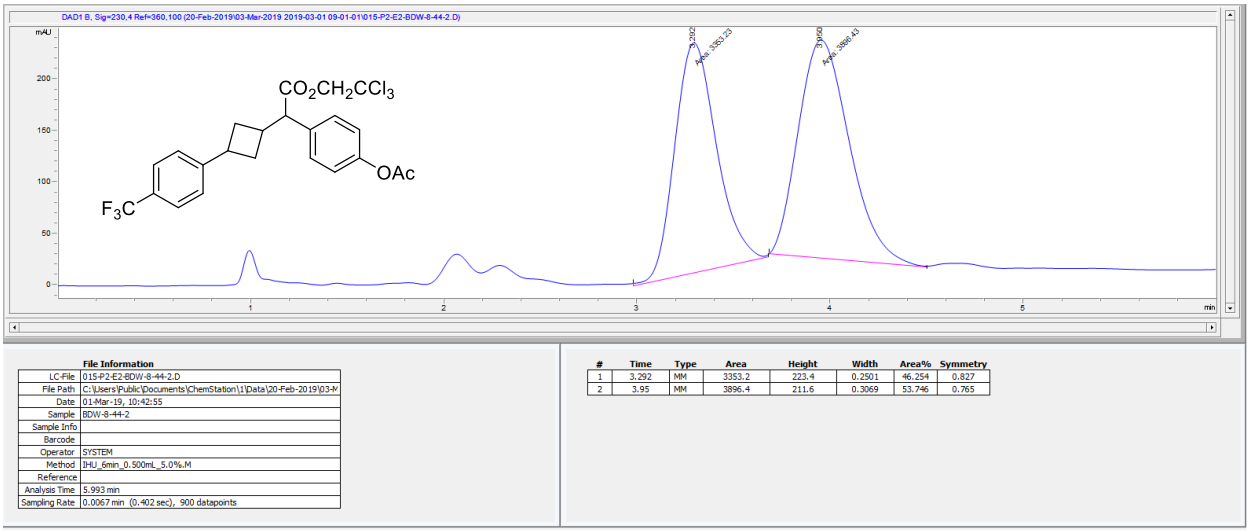


File Information

LC-File	008-23-BDW-8-34-4.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	13-Feb-19, 14:17:29
Sample	BDW-8-34-4
Sample Info	
Barcode	
Operator	SYSTEM
Method	ODH_30min_1.0ML_0.5%.M
Reference	
Analysis Time	30.003 min
Sampling Rate	0.0017 min (0.102 sec), 18003 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.959	MM	1396.3	54.3	0.4288	4.943	0.726
2	12.964	MM	26852.3	781.1	0.573	95.057	0.508

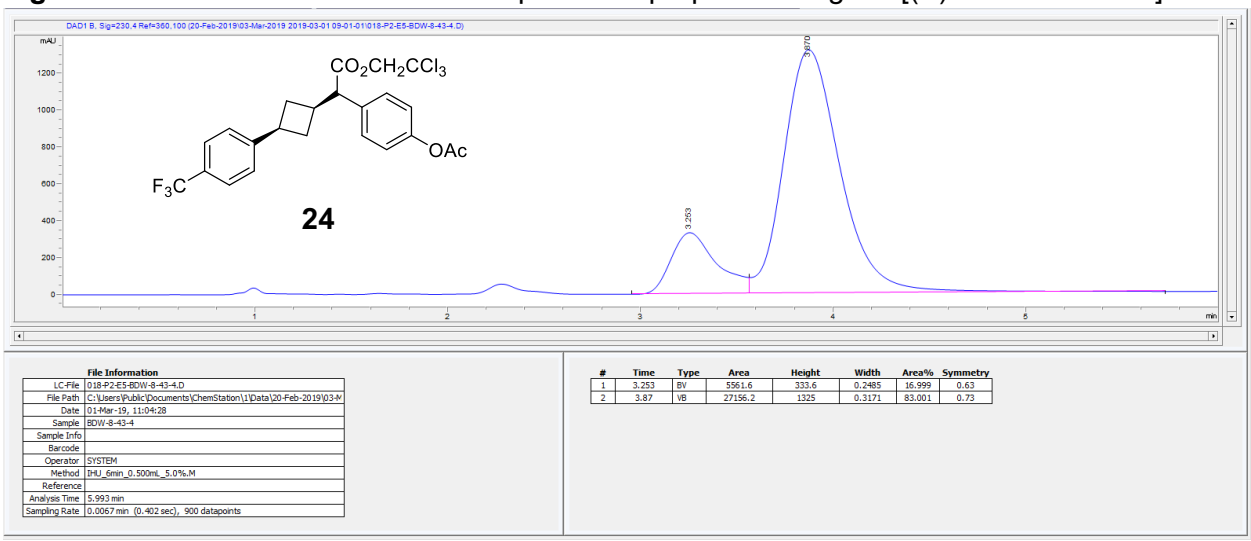
Figure S121. Chiral HPLC trace for *rac*-**24** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	015-P2-E2-BDW-8-44-2.D
File Path	C:\Users\Public\Documents\ChemStation\1\Data\20-Feb-2019\03-M
Date	01-Mar-19, 10:42:55
Sample	BDW-8-44-2
Sample Info	
Barcode	
Operator	SYSTEM
Method	IHU_6min_0.500mL_5.0%.M
Reference	
Analysis Time	5.993 min
Sampling Rate	0.0067 min (0.402 sec), 900 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.292	MM	3353.2	223.4	0.2501	46.254	0.827
2	3.95	MM	3896.4	211.6	0.3069	53.746	0.765

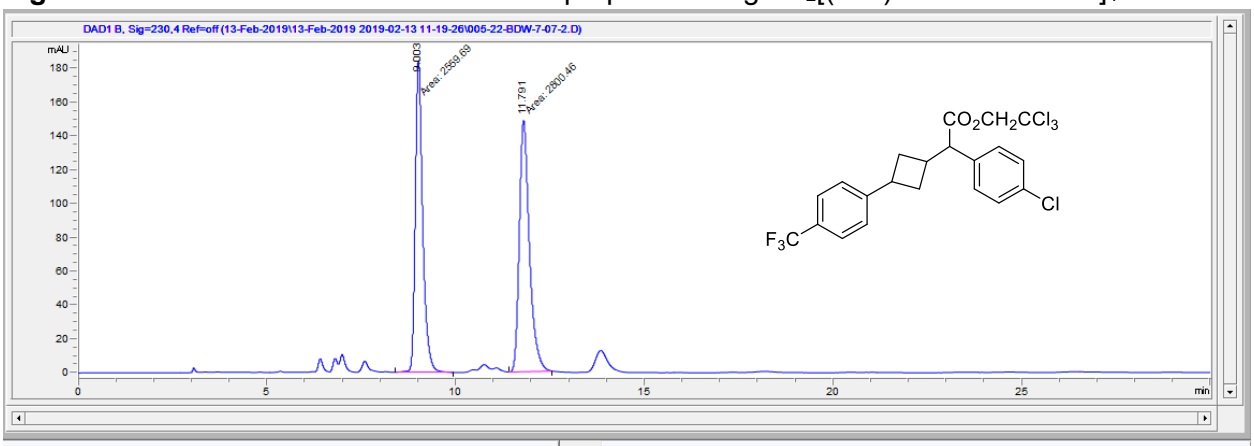
Figure S122. Chiral HPLC trace of compound **24** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	018-P2-E5-BDW-8-43-4.D
File Path	C:\Users\Public\Documents\ChemStation\1\Data\20-Feb-2019\03-M
Date	01-Mar-19, 11:04:28
Sample	BDW-8-43-4
Sample Info	
Barcode	
Operator	SYSTEM
Method	IHU_6min_0.500mL_5.0%.M
Reference	
Analysis Time	5.993 min
Sampling Rate	0.0067 min (0.402 sec), 900 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.253	BV	5561.6	333.6	0.2485	16.999	0.63
2	3.87	VB	27156.2	1325	0.3171	83.001	0.73

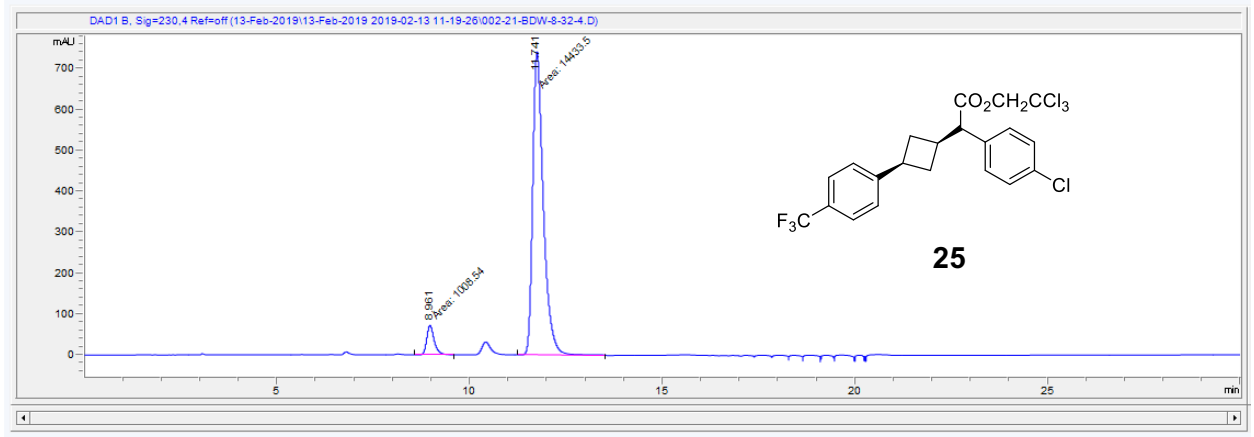
Figure S123. Chiral HPLC trace for *rac*-**25** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	005-22-BDW-7-07-2.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	13-Feb-19, 13:04:21
Sample	BDW-7-07-2
Sample Info	
Barcode	
Operator	SYSTEM
Method	ADH_30min_1.0ML_1.0%.M
Reference	
Analysis Time	30.002 min
Sampling Rate	0.0017 min (0.102 sec), 18002 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.003	MM	2559.7	185.1	0.2304	47.754	0.702
2	11.791	MM	2800.5	149.1	0.313	52.246	0.701

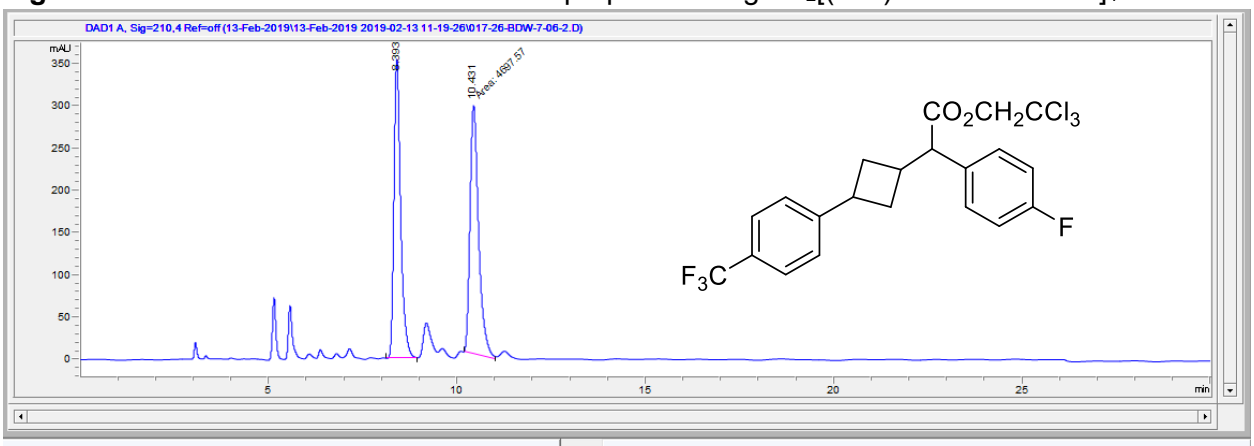
Figure S124. Chiral HPLC trace of compound **25** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	002-21-BDW-8-32-4.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	13-Feb-19, 11:51:19
Sample	BDW-8-32-4
Sample Info	
Barcode	
Operator	SYSTEM
Method	ADH_30min_1.0ML_1.0%.M
Reference	
Analysis Time	30.002 min
Sampling Rate	0.0017 min (0.102 sec), 18002 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.961	MM	1008.5	72.9	0.2306	6.531	0.715
2	11.741	MM	14433.5	742	0.3242	93.469	0.628

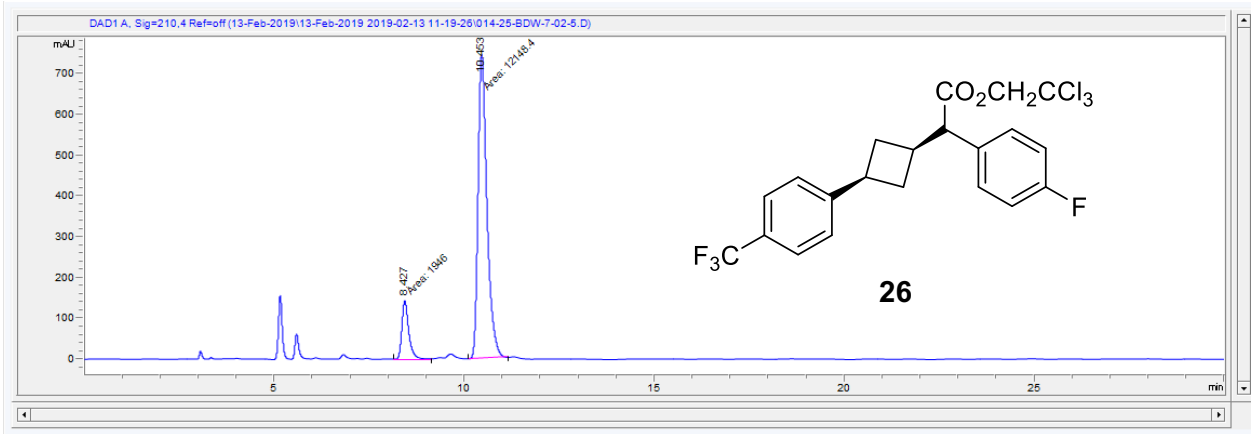
Figure S125. Chiral HPLC trace for *rac*-**25** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	017-26-BDW-7-06-2.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	13-Feb-19, 17:56:42
Sample	BDW-7-06-2
Sample Info	
Barcode	
Operator	SYSTEM
Method	ADH_30min_1.0ML_1.0%.M
Reference	
Analysis Time	30.003 min
Sampling Rate	0.0017 min (0.102 sec), 18003 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.393	BV	4401.3	355.5	0.1854	48.372	0.674
2	10.431	MM	4697.6	295.5	0.265	51.628	0.677

Figure S126. Chiral HPLC trace of compound **26** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	014-25-BDW-7-02-5.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	13-Feb-19, 16:43:38
Sample	BDW-7-02-5
Sample Info	
Barcode	
Operator	SYSTEM
Method	ADH_30min_1.0ML_1.0%.M
Reference	
Analysis Time	30.002 min
Sampling Rate	0.0017 min (0.102 sec), 18002 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.427	MM	1946	145.9	0.2223	13.807	0.659
2	10.453	MM	12148.4	748.2	0.2706	86.193	0.667

Figure S127. Chiral HPLC trace for *rac*-**27** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$

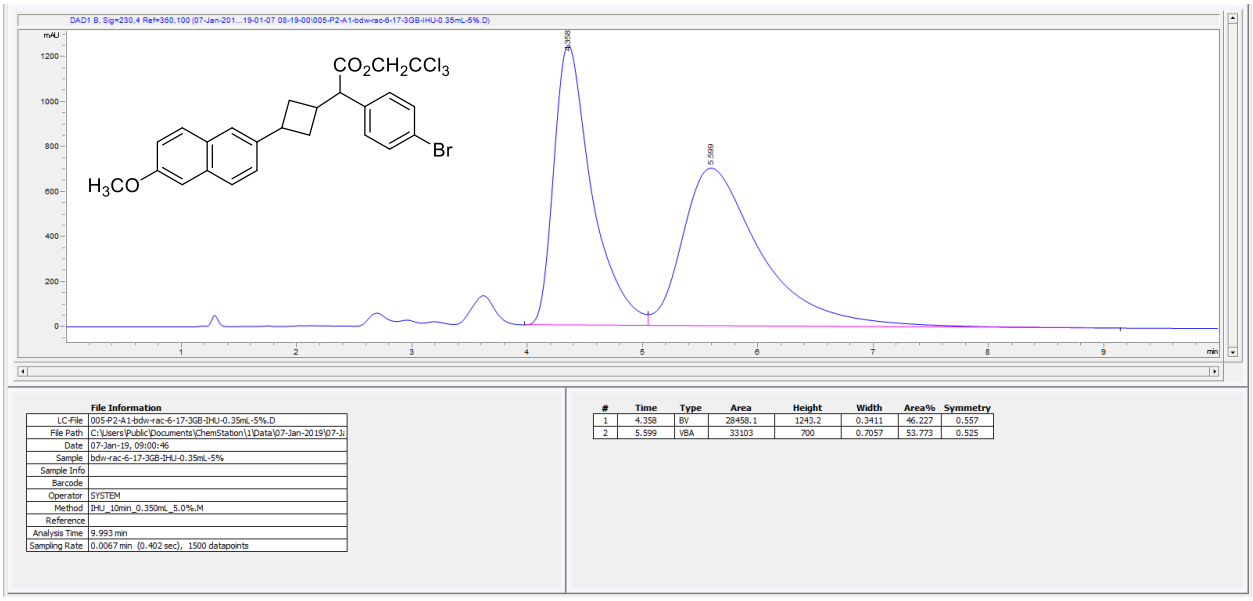


Figure S128. Chiral HPLC trace of compound **27** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$

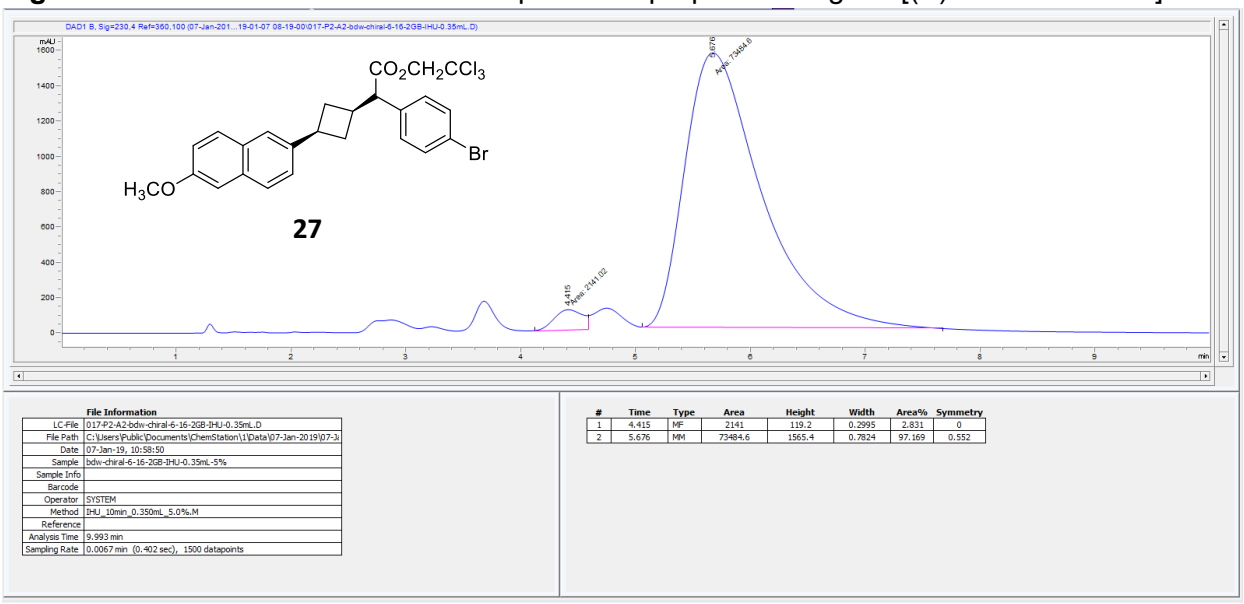
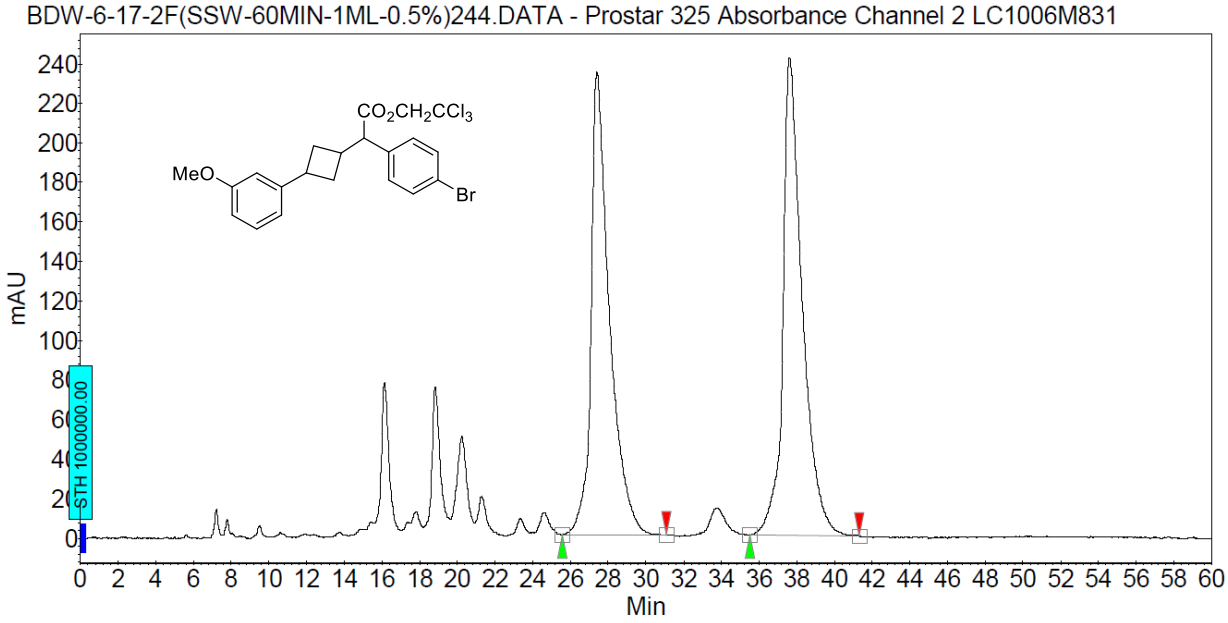


Figure S129. Chiral HPLC trace for *rac*-**28** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$

Chromatogram :
BDW-6-17-2F(SSW-60MIN-1ML-0.5%)244_channe
l2

System : Prostar LC System
Method : OD_30min_1mL_0.5%_230nm
User : User1

Acquired : 9/5/2018 10:55:19 PM
Processed : 1/7/2019 10:34:17 AM
Printed : 1/7/2019 10:36:26 AM



Peak results :

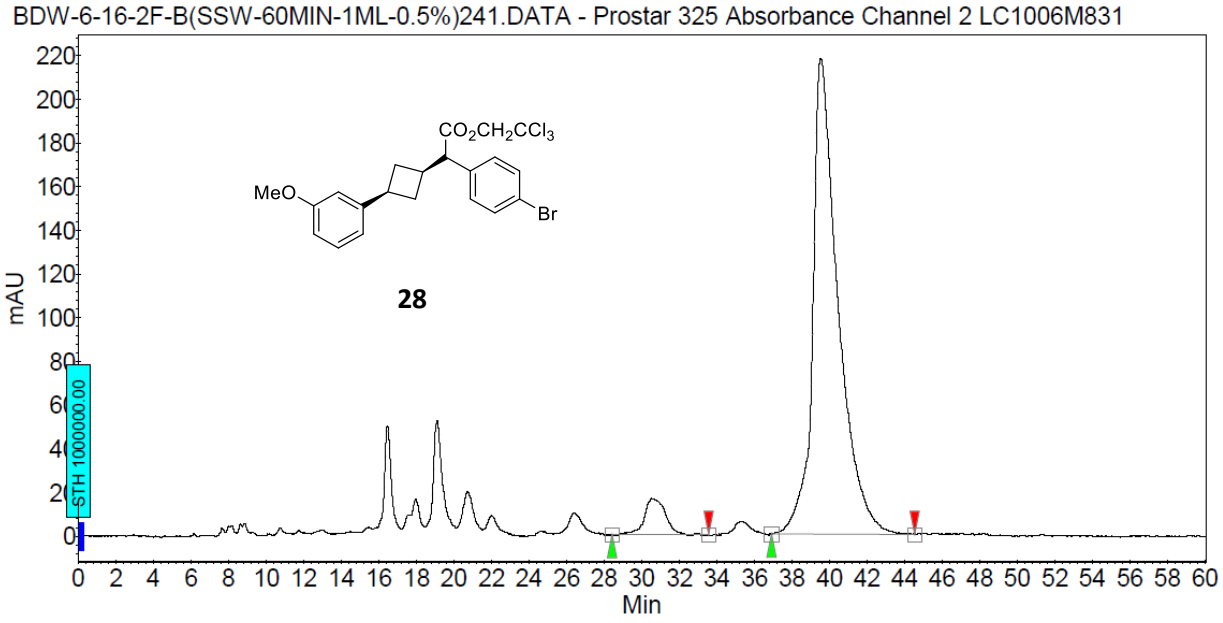
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	27.40	47.90	233.9	265.1	47.896
2	UNKNOWN	37.61	52.10	241.6	288.4	52.104
Total			100.00	475.5	553.4	100.000

Figure S130. Chiral HPLC trace of compound **28** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$

Chromatogram :
BDW-6-16-2F-B(SSW-60MIN-1ML-0.5%)241_channel2

System : Prostar LC System
Method : OD_30min_1mL_0.5%_230nm
User : User1

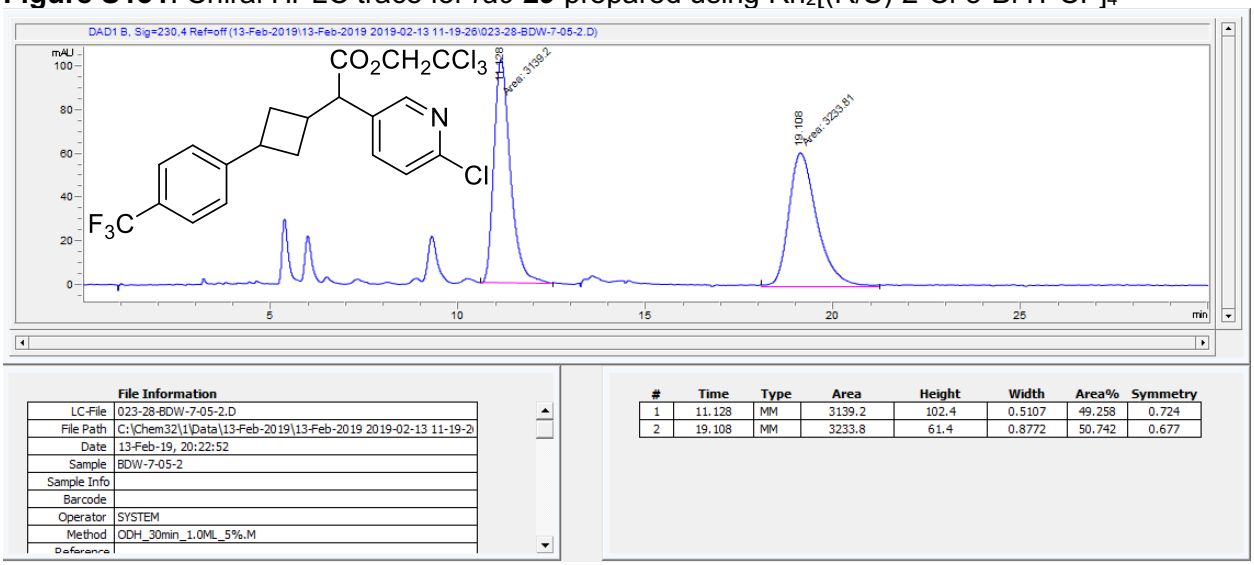
Acquired : 9/5/2018 9:06:28 PM
Processed : 9/6/2018 11:19:50 AM
Printed : 1/7/2019 10:36:18 AM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	30.50	5.85	16.5	21.2	5.847
1	UNKNOWN	39.53	94.15	217.6	341.7	94.153
Total			100.00	234.0	363.0	100.000

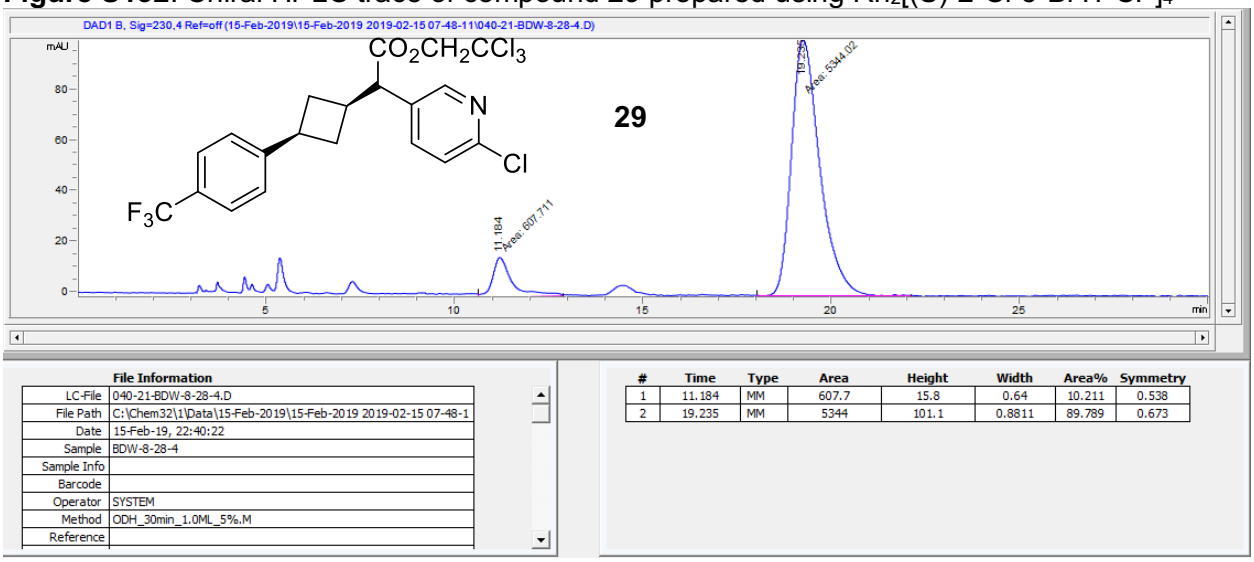
Figure S131. Chiral HPLC trace for *rac*-**29** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	023-28-BDW-7-05-2.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	13-Feb-19, 20:22:52
Sample	BDW-7-05-2
Sample Info	
Barcode	
Operator	SYSTEM
Method	ODH_30min_1.0ML_5%.M
Reference	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.128	MM	3139.2	102.4	0.5107	49.258	0.724
2	19.108	MM	3233.8	61.4	0.8772	50.742	0.677

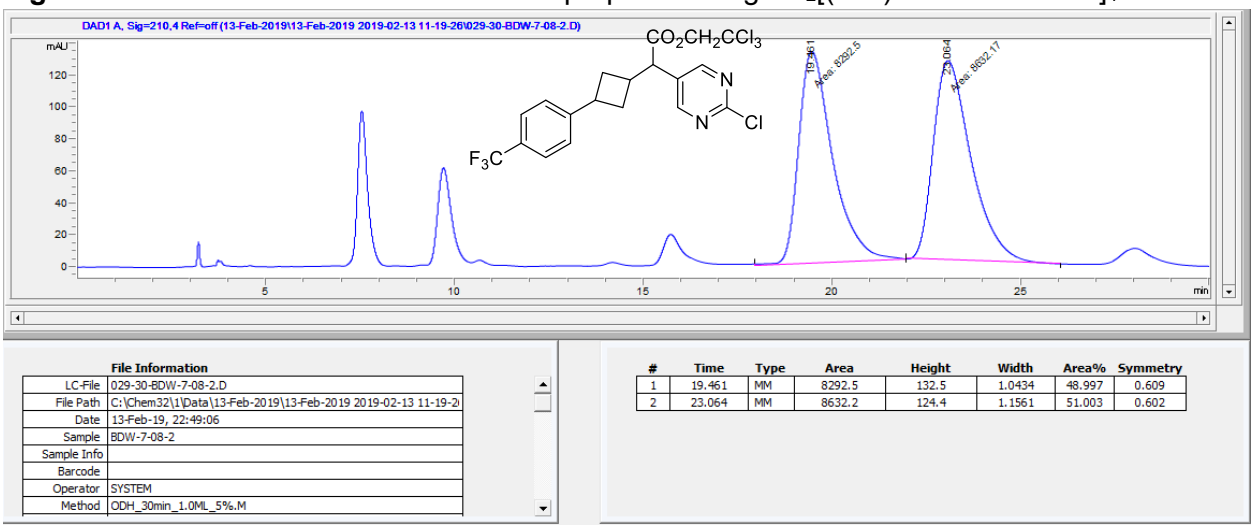
Figure S132. Chiral HPLC trace of compound **29** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	040-21-BDW-8-28-4.D
File Path	C:\Chem32\1\Data\15-Feb-2019\15-Feb-2019 2019-02-15 07-48-1
Date	15-Feb-19, 22:40:22
Sample	BDW-8-28-4
Sample Info	
Barcode	
Operator	SYSTEM
Method	ODH_30min_1.0ML_5%.M
Reference	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.184	MM	607.7	15.8	0.64	10.211	0.538
2	19.235	MM	5344	101.1	0.8811	89.789	0.673

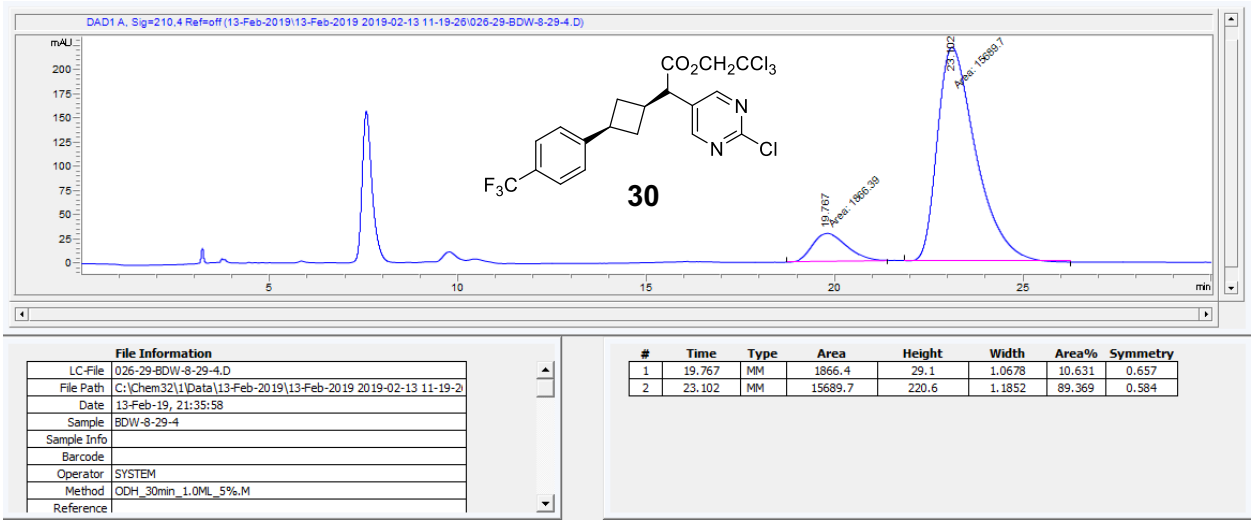
Figure S133. Chiral HPLC trace for *rac*-**30** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	029-30-BDW-7-08-2.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	13-Feb-19, 22:49:06
Sample	BDW-7-08-2
Sample Info	
Barcode	
Operator	SYSTEM
Method	ODH_30min_1.0ML_5%.M

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.461	MM	8292.5	132.5	1.0434	48.997	0.609
2	23.064	MM	8632.2	124.4	1.1561	51.003	0.602

Figure S134. Chiral HPLC trace of compound **30** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$



File Information	
LC-File	026-29-BDW-8-29-4.D
File Path	C:\Chem32\1\Data\13-Feb-2019\13-Feb-2019 2019-02-13 11-19-2
Date	13-Feb-19, 21:35:58
Sample	BDW-8-29-4
Sample Info	
Barcode	
Operator	SYSTEM
Method	ODH_30min_1.0ML_5%.M
Reference	

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.767	MM	1866.4	29.1	1.0678	10.631	0.657
2	23.102	MM	15689.7	220.6	1.1852	89.369	0.584

Figure S135. Chiral HPLC trace for *rac*-**31** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$

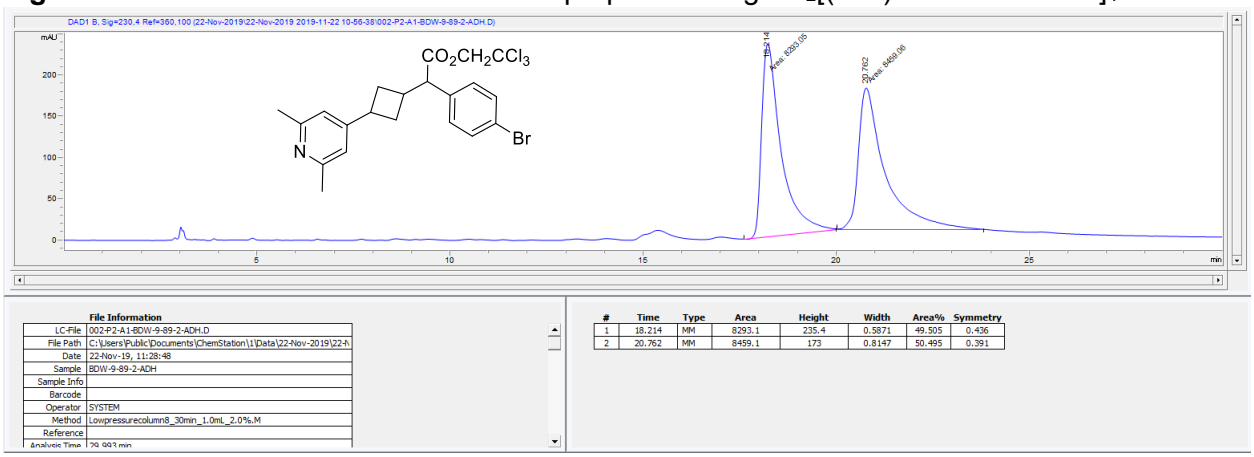


Figure S136. Chiral HPLC trace of compound **31** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$

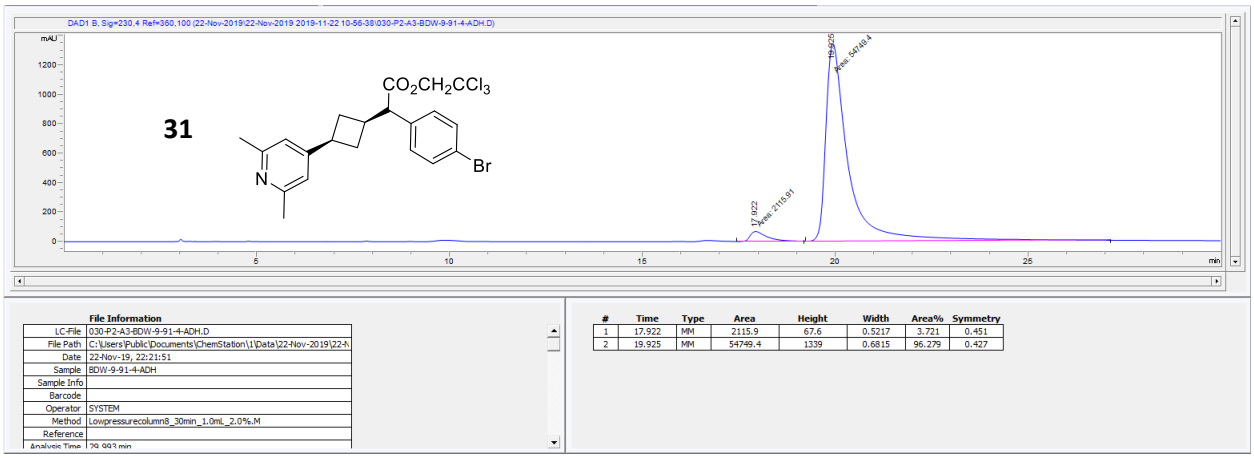
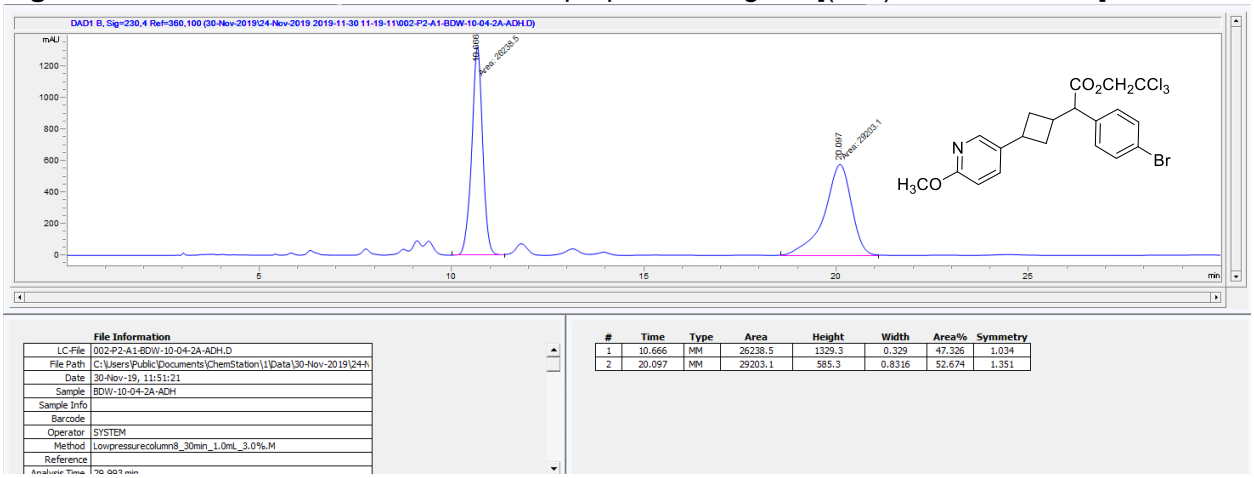


Figure S137. Chiral HPLC trace for *rac*-**32** prepared using Rh_2[(R/S)-2-Cl-5-BrTPCP]$_4$

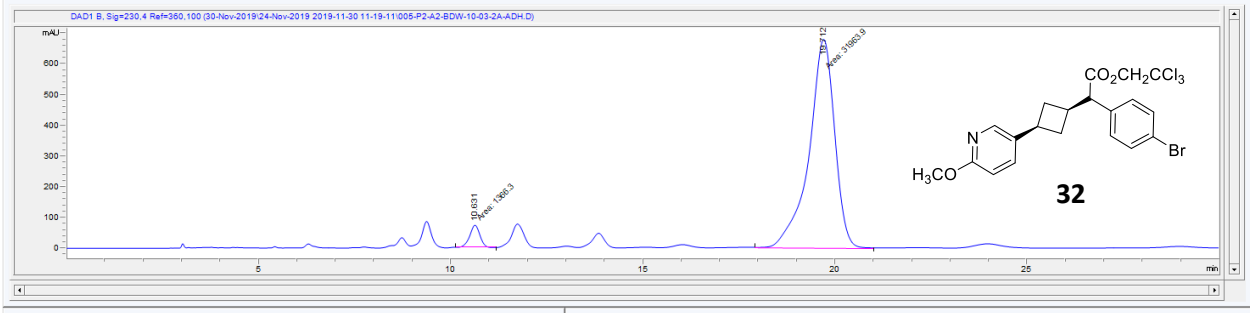


File Information

LC-File	002-P2-A1-BDW-10-04-2A-ADH.D
File Path	C:\Users\Public\Documents\ChemStation\1\Data\30-Nov-2019\24-N
Date	30-Nov-19, 11:51:21
Sample	BDW-10-04-2A-ADH
Sample Info	
Barcode	
Operator	SYSTEM
Method	Lowpressurecolumn8_30min_1.0mL_3.0%.M
Reference	
Analysis Time	29.983 min

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.666	MM	26238.5	1329.3	0.329	47.326	1.034
2	20.097	MM	29203.1	585.3	0.8316	52.674	1.351

Figure S138. Chiral HPLC trace of compound **32** prepared using Rh_2[(S)-2-Cl-5-BrTPCP]$_4$



File Information

LC-File	005-P2-A2-BDW-10-03-2A-ADH.D
File Path	C:\Users\Public\Documents\ChemStation\1\Data\30-Nov-2019\24-N
Date	30-Nov-19, 13:04:53
Sample	BDW-10-03-2A-ADH
Sample Info	
Barcode	
Operator	SYSTEM
Method	Lowpressurecolumn8_30min_1.0mL_3.0%.M
Reference	
Analysis Time	29.987 min

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.631	MM	1366.3	72.8	0.3129	4.099	1.051
2	19.712	MM	31963.9	682.5	0.7805	95.901	1.297