SUPPORTING INFORMATION

A New Ligand Design Based on London Dispersion Empowers Chiral Bismuth-Rhodium Paddlewheel Catalysts

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Supporting Crystallographic Data

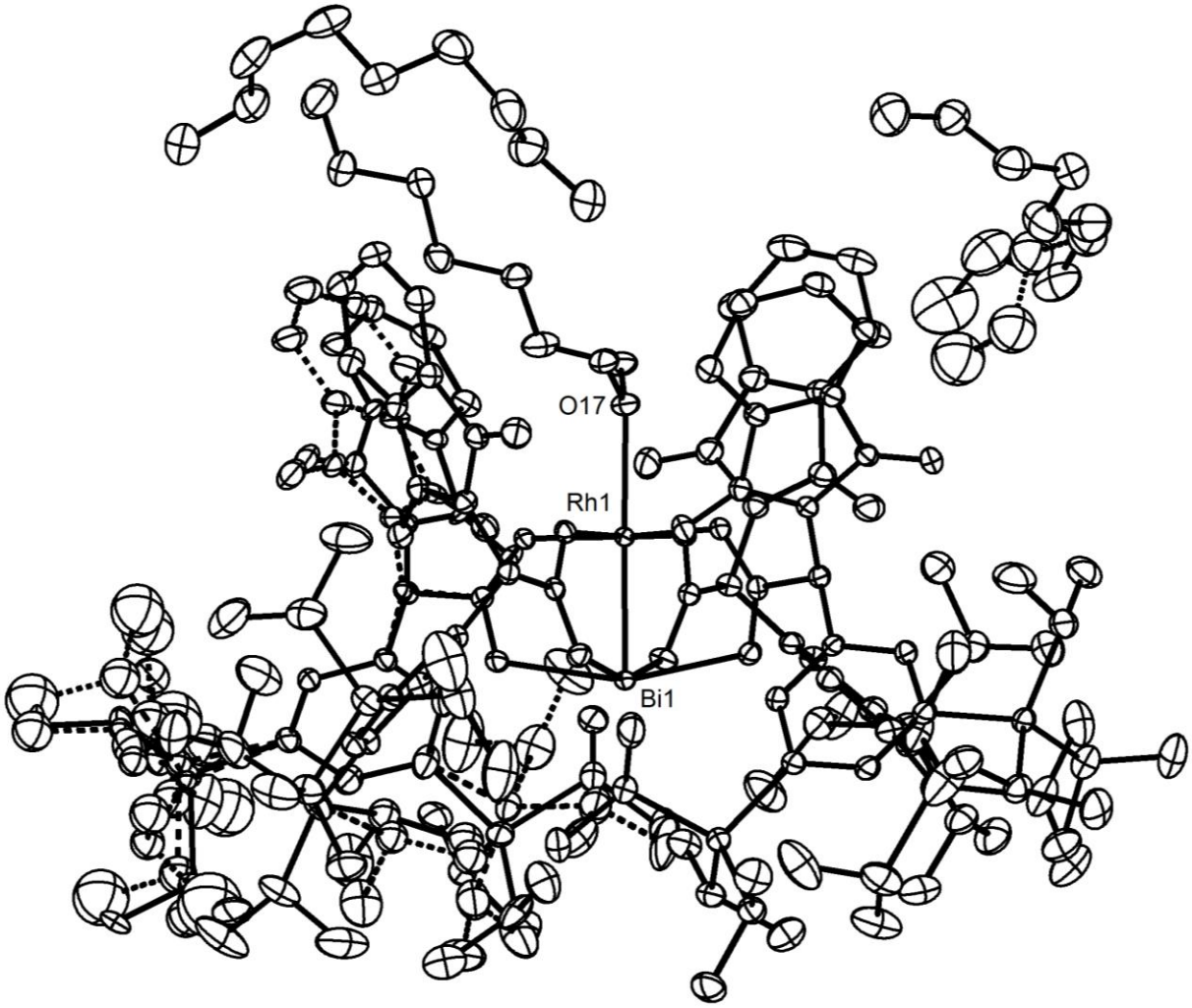
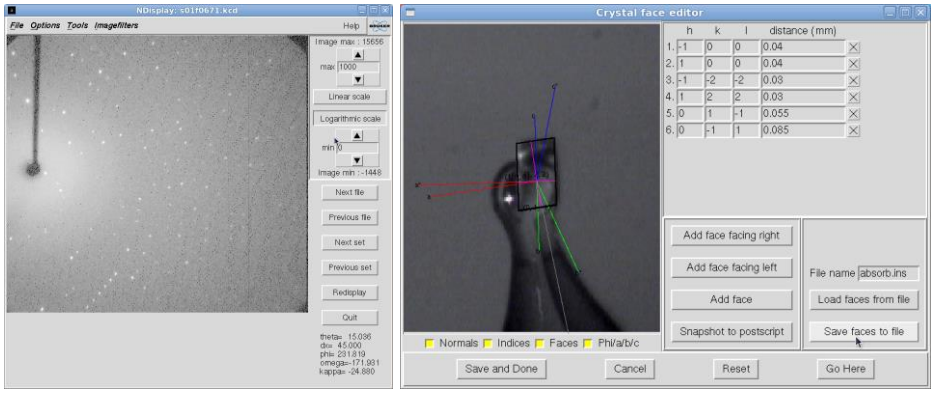


Figure S1. Molecular structure of complex **3a**. Atomic displacement ellipsoids are shown at the 50 % probability level. Disordered parts of the molecule are shown with dashed bonds. H atoms are omitted for clarity.

X-ray Crystal Structure Analysis of Complex 3a: C_{142} H_{214} Bi N_4 O_{19} Rh Si_8 · 2(C_6 H_{14} O_3), M_r = 3086.11 g · mol^{-1}, yellow plate, crystal size 0.06 x 0.08 x 0.14 mm^3, triclinic, space group *P*-1 [2], a = 17.791(3) Å, b = 22.062(4) Å, c = 24.399(2) Å, α = 69.943(11)°, β = 72.801(14)°, γ = 66.640(9)°, V = 8116(2) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.263 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*α) = 1.308 mm^{-1}, face-indexed absorption correction (*SADABS*, T_{min} = 0.71878, T_{max} = 0.86434), Bruker-AXS Mach3 diffractometer with Kappa-CCD detector and FR591 molybdenum rotating

anode X-ray source equipped with Incoatec Helios X-ray optics, 2.630 < θ < 33.073°, 430062 measured reflections, 61295 independent reflections, 48905 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0812$, 99.6 % coverage with an average redundancy of 6.99 to 0.65 Å resolution.



INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.61	923	958	96.3	11.15	59.39	66.18	0.0440	0.0118
2.61 - 1.76	2159	2159	100.0	10.16	43.46	52.27	0.0344	0.0141
1.76 - 1.40	3079	3081	99.9	9.85	26.81	41.89	0.0406	0.0174
1.40 - 1.22	3153	3153	100.0	9.60	20.38	35.30	0.0483	0.0209
1.22 - 1.11	3038	3038	100.0	9.27	17.12	30.68	0.0548	0.0246
1.11 - 1.03	3171	3171	100.0	8.73	15.04	26.30	0.0603	0.0291
1.03 - 0.97	3066	3066	100.0	8.14	12.51	21.89	0.0722	0.0358
0.97 - 0.92	3196	3196	100.0	7.73	10.44	18.18	0.0861	0.0434
0.92 - 0.88	3120	3120	100.0	7.39	9.26	15.84	0.0976	0.0505
0.88 - 0.85	2707	2707	100.0	7.11	8.21	13.92	0.1086	0.0586
0.85 - 0.82	3162	3162	100.0	6.75	7.58	12.49	0.1240	0.0668
0.82 - 0.79	3664	3664	100.0	6.47	6.91	10.99	0.1364	0.0763
0.79 - 0.77	2778	2778	100.0	6.15	6.61	10.23	0.1495	0.0841
0.77 - 0.75	3031	3031	100.0	5.87	5.90	8.83	0.1782	0.0987
0.75 - 0.73	3442	3442	100.0	5.69	5.28	7.74	0.1966	0.1133
0.73 - 0.71	3718	3718	100.0	5.46	4.69	6.66	0.2200	0.1331
0.71 - 0.70	2142	2142	100.0	5.26	4.30	5.91	0.2394	0.1503
0.70 - 0.68	4479	4479	100.0	5.12	3.84	5.20	0.2757	0.1760
0.68 - 0.67	2451	2451	100.0	4.91	3.44	4.42	0.3069	0.2094
0.67 - 0.66	2595	2595	100.0	4.85	3.23	3.95	0.3408	0.2391
0.66 - 0.65	2221	2427	91.5	4.29	3.08	3.57	0.3561	0.2677
0.75 - 0.65	21048	21254	99.0	5.13	4.07	5.53	0.2566	0.1680
Inf - 0.65	61295	61538	99.6	6.99	11.24	17.20	0.0772	0.0497

A number of low-angle refections were shadowed by the beamstop and removed from the dataset before the final refinement cycles. Part of one solvent diglyme molecule, one 1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl group, one isopropyl group on one otherwise not disordered tris-isopropylsilyl group and two tris-isopropylsilyl groups are disordered. One of the tris-isopropylsilyl groups is disordered over two positions (50:50 percent) and one over three positions (60:25:15 percent). The part of the diglyme molecule that is disordered is disordered over two positions (70:30 percent). Atoms of disordered parts were refined with anisotropic atomic displacement parameters when possible, whereby atoms of minor components and atoms in disordered groups in close proximity were refined with isotropic atomic displacment parameters in order to avoid high correlations. For the minor component of one tris-isopropylsilyl group (occupancy 0.15, third of three components, residue 9), the C-C distances of two isopropyl groups were restrained to be equal with an effective standard deviation of 0.005 and the atomic displacement parameters of the carbon atoms of two isopropyl groups were constrained to be equal. The second parameter of WGHT in SHELXL is 10.35 which can be attributed to the disorder in the structure. The environments of the carbon atoms range from tightly-bound atoms close to the centre of the complex to disordered atoms at the periphery. As a result, non-solvent carbon atoms have an Ueq(max)/Ueq(min) range of 10.0. The diffraction data were collected to a resolution of 0.65 Å. We cannot rule out that the residual electron density close to the bismuth atom is a result of anharmonic displacement of the heavy atom (83 electrons) since the diffraction data were corrected for the effects of absorption using indexed faces. In all, diffraction data were collected from six crystals, four were of the enantiopure (99.9% ee) and two racemates. The enantiopure crystals diffracted poorly. The quality of the diffraction data from one of the two racemate crystals (the current crystal) was by far the best. The crystals contain bound (to the rhodium atom) as well as solvent diglyme. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2. Hydrogen atoms were refined using a riding model. Refinement of the structure resulted in $R1$ = 0.0442 for 48905 [$I > 2\sigma(I)$] and 0.0670 for all 61295 data, 2074 parameters refined, 4 restraints (C-C bond lengths in two disordered minor component isopropyl groups), $wR2$ = 0.0833, *GooF* = S = 1.069, residual electron density +1.01 (0.58 Å from Bi1) / –2.81 (0.74 Å from Bi1) e · Å^{-3}. **CCDC-2063745**.

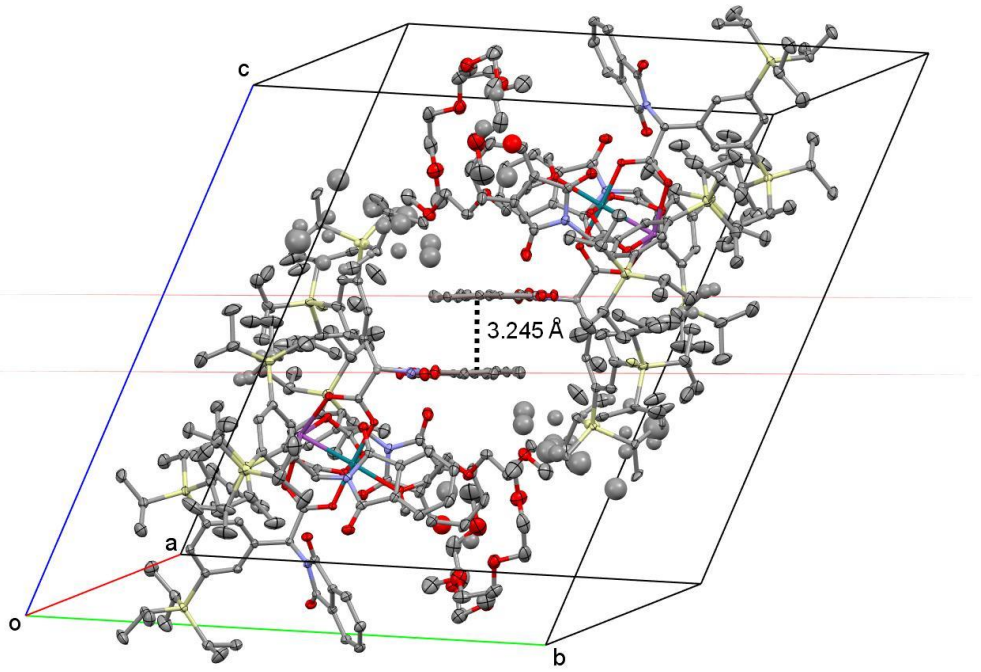


Figure S2. Packing of the molecules of complex **3a** within the triclinic unit cell, showing the arrangement of disordered phthalimido groups on two adjacent molecules.

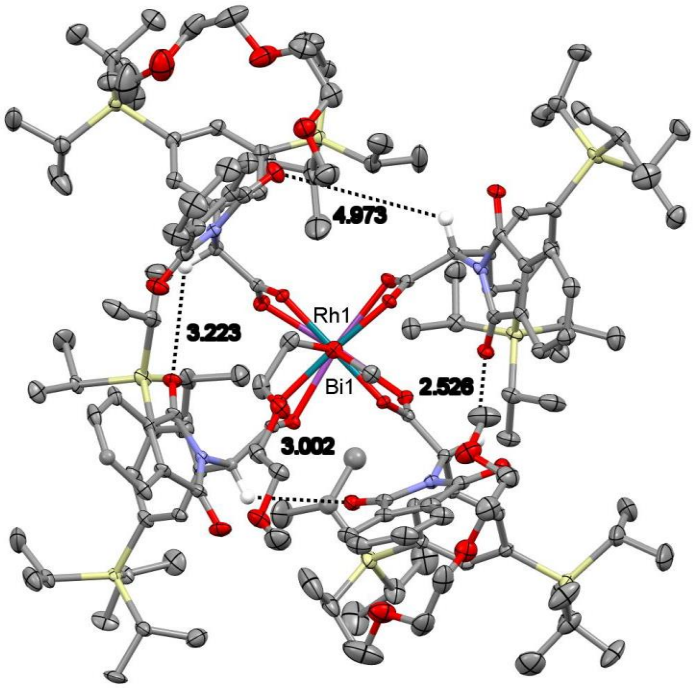


Figure S3. Major component of complex **3a** viewed along the Rh-Bi vector showing possible intramolecular C-H···O interactions between methanetriyl hydrogen atoms and oxygen atoms on adjacent phthalimido groups.

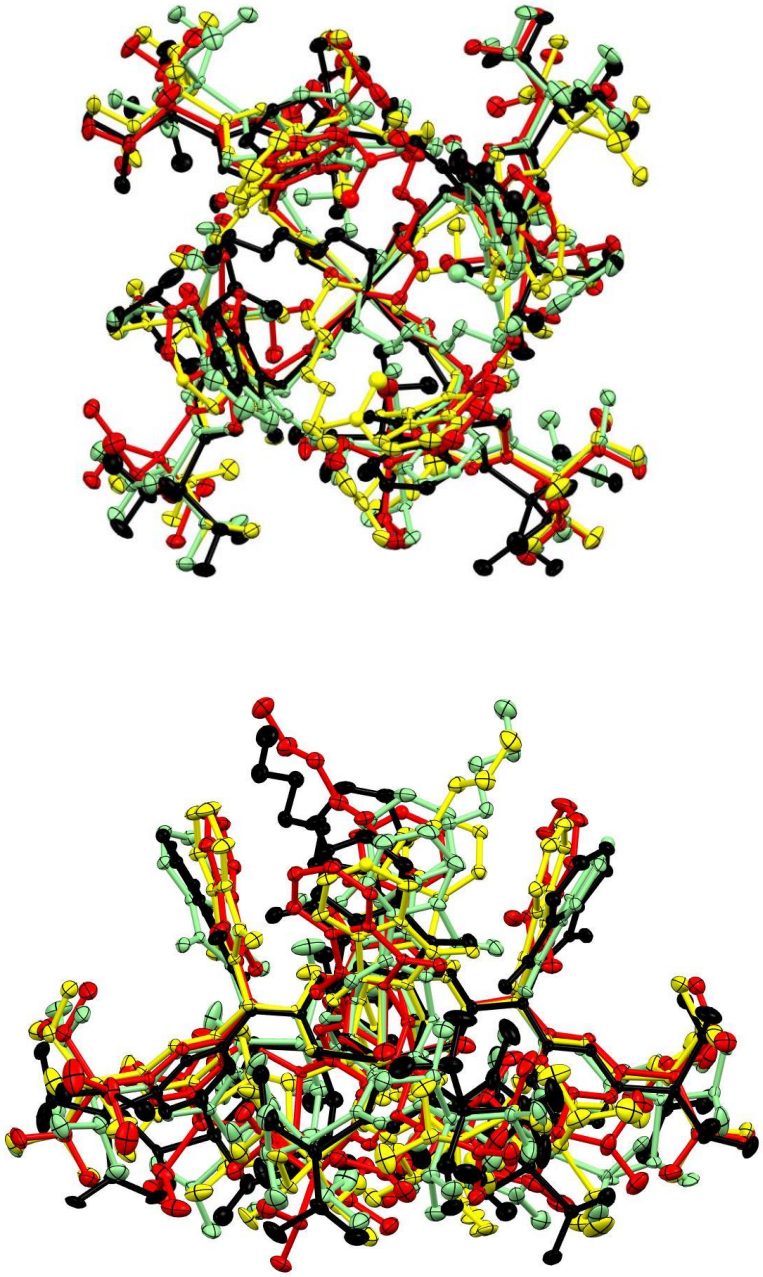


Figure S4. Overlay of central O8RhBi units of four molecules of complex **3a** rotated by respectively 90° about the Rh-Bi direction to illustrate the approximate C_4 symmetry of the molecule (top and side view).

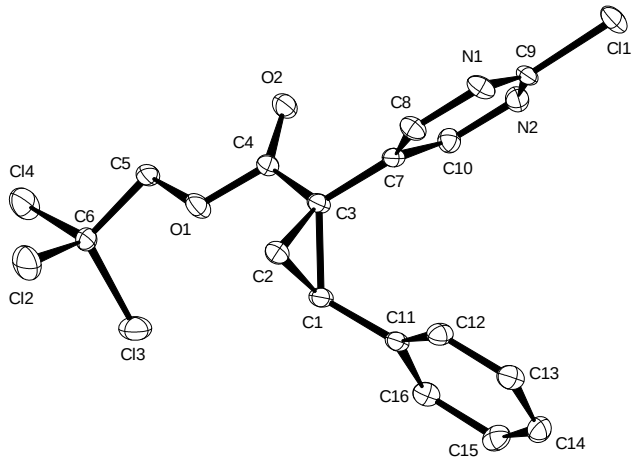


Figure S5. Structure of cyclopropane **S20** in the solid state. H atoms have been removed for clarity.

X-Ray Crystal Structure Analysis of Compound S20. $C_{16}H_{12}Cl_4N_2O_2$, Mr = 406.08 g/mol, colourless plate, crystal size 0.051 x 0.022 x 0.013 mm^3, orthorhombic, space group P212121, [No. 19]**,** *a* = 6.0034(3) Å, *b* = 16.7746(8) Å, *c* = 16.8953(9) Å, *V* = 1701.43(15) $Å^3$, *T* = 100(2) K, *Z* = 4, *Dcalc* = 1.585 $mg \cdot m^{-3}$, *λ* = 0.71073 Å, *μ(Mo-Kα)* = 0.707 mm^{-1}, analytical absorption correction (*Tmin* = 0.95449, *Tmax* = 0. 98702), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and IμS micro focus X-ray source, 1.711 < θ < 31.047°, 52940 measured reflections, 5435 independent reflections, 4897 reflections with *I>2σ(I)*, Rint = 0.0448.

INTENSITY STATISTICS FOR DATASET (Friedel pairs not merged)

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.88	82	82	100.0	16.62	97.34	108.28	0.0200	0.0071
2.88 - 1.87	198	198	100.0	17.58	45.89	101.13	0.0235	0.0079
1.87 - 1.48	272	272	100.0	18.34	27.65	82.38	0.0275	0.0094
1.48 - 1.30	271	271	100.0	17.53	16.96	64.54	0.0389	0.0122
1.30 - 1.18	277	277	100.0	17.37	17.77	60.79	0.0413	0.0131
1.18 - 1.10	267	267	100.0	15.78	14.90	50.39	0.0512	0.0154
1.10 - 1.03	280	280	100.0	12.56	8.86	34.00	0.0746	0.0238
1.03 - 0.97	331	331	100.0	9.92	7.41	26.80	0.0810	0.0302
0.97 - 0.93	270	270	100.0	8.79	7.02	23.91	0.0911	0.0345
0.93 - 0.90	223	223	100.0	7.95	6.50	21.90	0.0870	0.0383
0.90 - 0.87	257	257	100.0	7.53	5.72	18.91	0.0908	0.0441
0.87 - 0.84	304	304	100.0	6.92	5.88	17.86	0.0890	0.0463
0.84 - 0.81	349	349	100.0	6.69	4.55	14.70	0.1068	0.0581
0.81 - 0.79	265	265	100.0	6.66	4.02	12.44	0.1196	0.0654
0.79 - 0.77	278	278	100.0	6.50	3.54	11.26	0.1352	0.0754
0.77 - 0.75	313	313	100.0	6.32	3.46	10.47	0.1480	0.0807
0.75 - 0.74	181	181	100.0	5.75	2.62	8.06	0.1733	0.1036
0.74 - 0.72	382	382	100.0	5.75	2.78	8.21	0.1771	0.1043
0.72 - 0.71	214	214	100.0	5.76	2.65	7.62	0.1823	0.1107

0.71 - 0.70	221	221	100.0	5.63	2.67	7.71	0.1862	0.1135
0.70 - 0.69	228	249	91.6	3.84	2.29	5.76	0.2085	0.1703
0.79 - 0.69	1817	1838	98.9	5.69	2.91	8.61	0.1655	0.1023
Inf - 0.69	5463	5484	99.6	9.69	10.54	29.87	0.0444	0.0258

The structure was solved by dual space methods (SHELXT) and refined by full-matrix least-squares (SHELXL) against F^2 with aspherical scattering factors for all atoms except Cl applied according to Luebben et al. [*Acta Cryst*. (2019). A75, 50-62] to *R1*= 0.0308 [$I > 2\sigma(I)$], *wR2* = 0.0673, 224 parameters, 0 restraints, absolute structure parameter according to Parsons, Flack and Wagner = 0.011(16) [1987 quotients] [Parsons, Flack and Wagner, *Acta Cryst*. B69 (2013) 249-259], GooF = S = 1.041, residual electron density 1.15 e · Å^{-1} [0.82 Å from CL4], -0.74 e · Å^{-1} [0.66 Å from CL4]. **CCDC-2063746**

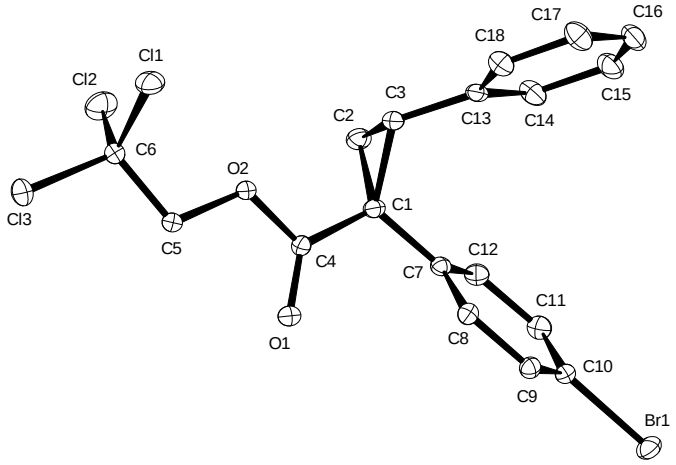


Figure S6. Structure of cyclopropane **S4** in the solid state. H atoms have been removed for clarity

X-Ray Crystal Structure Analysis of Compound S4. $C_{18}H_{14}BrCl_3O_2$, Mr = 448.55 g/mol, colourless plate, crystal size 0.078 x 0.045 x 0.024 mm^3, orthorhombic, space group P212121, [No. 19]**,** *a* = 5.8058(3) Å, *b* = 17.1098(9) Å, *c* = 17.8442(10) Å, *V* = 1772.57(16) Å^3, *T* = 100(2) K, *Z* = 4, *Dcalc* = 1.681 mg·m^{-3} , λ = 0.71073 Å, μ (*Mo-K*α) = 2.779 mm^{-1}, analytical absorption correction (T_{min} = 0.86072, T_{max} = 0.94978), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and IμS micro focus X-ray source, 1.649 < θ < 33.876°, 118713 measured reflections, 7107 independent reflections, 6803 reflections with $I > 2\sigma(I)$, Rint = 0.0393.

INTENSITY STATISTICS FOR DATASET (Friedel pairs not merged)

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.64	107	107	100.0	22.84	86.50	110.25	0.0273	0.0082
2.64 - 1.75	254	254	100.0	27.52	45.56	117.63	0.0267	0.0075
1.75 - 1.38	358	358	100.0	28.05	28.84	109.24	0.0288	0.0079
1.38 - 1.20	369	369	100.0	27.27	23.00	98.14	0.0296	0.0084
1.20 - 1.09	366	366	100.0	25.92	18.07	86.63	0.0351	0.0093
1.09 - 1.01	364	364	100.0	21.01	12.68	70.67	0.0427	0.0117
1.01 - 0.95	361	361	100.0	18.64	10.67	60.33	0.0443	0.0135
0.95 - 0.90	390	390	100.0	16.84	9.08	52.01	0.0478	0.0156
0.90 - 0.87	283	283	100.0	15.91	9.22	49.43	0.0496	0.0165
0.87 - 0.83	401	401	100.0	15.18	8.02	44.59	0.0557	0.0187
0.83 - 0.80	402	402	100.0	14.74	6.32	37.22	0.0615	0.0222
0.80 - 0.78	288	288	100.0	14.22	4.96	31.45	0.0720	0.0272
0.78 - 0.75	485	485	100.0	13.74	4.88	29.29	0.0762	0.0288
0.75 - 0.73	365	365	100.0	13.09	4.26	25.17	0.0872	0.0338
0.73 - 0.71	413	413	100.0	12.76	3.88	22.40	0.0955	0.0380
0.71 - 0.70	240	240	100.0	12.58	3.38	20.37	0.1030	0.0435
0.70 - 0.68	508	508	100.0	12.20	3.16	18.92	0.1130	0.0476
0.68 - 0.67	246	246	100.0	11.85	3.37	18.93	0.1132	0.0481
0.67 - 0.66	298	298	100.0	11.35	2.56	14.56	0.1317	0.0621
0.66 - 0.65	276	276	100.0	11.23	2.52	14.39	0.1383	0.0647
0.65 - 0.64	365	420	86.9	7.49	2.26	10.90	0.1535	0.0998
0.74 - 0.64	2535	2590	97.9	11.41	3.14	17.98	0.1124	0.0520
Inf - 0.64	7139	7194	99.2	16.55	11.08	47.13	0.0391	0.0157

The structure was solved by dual space methods (SHELXT) and refined by full-matrix least-squares (SHELXL) against F^2 with aspherical scattering factors for all atoms except Cl and Br applied according to Luebben et al. [*Acta Cryst*. (2019). A75, 50-62]. H atom postions were calculated and allowed to ride with extended averaged refined C-H distances. *R1*= 0.0164 [$I>2\sigma(I)$], *wR2* = 0.0377, 220 parameters, 0 restraints, absolute structure parameter according to Parsons, Flack and Wagner = -0.0035(11) [2854 quotients] [Parsons, Flack and Wagner, *Acta Cryst*. B69 (2013) 249-259], GooF = S = 1.051, residual electron density 0.67 e · Å^{-1} [0.76 Å from CL3], -0.29 e · Å^{-1} [0.59 Å from CL3]. **CCDC-2063747**

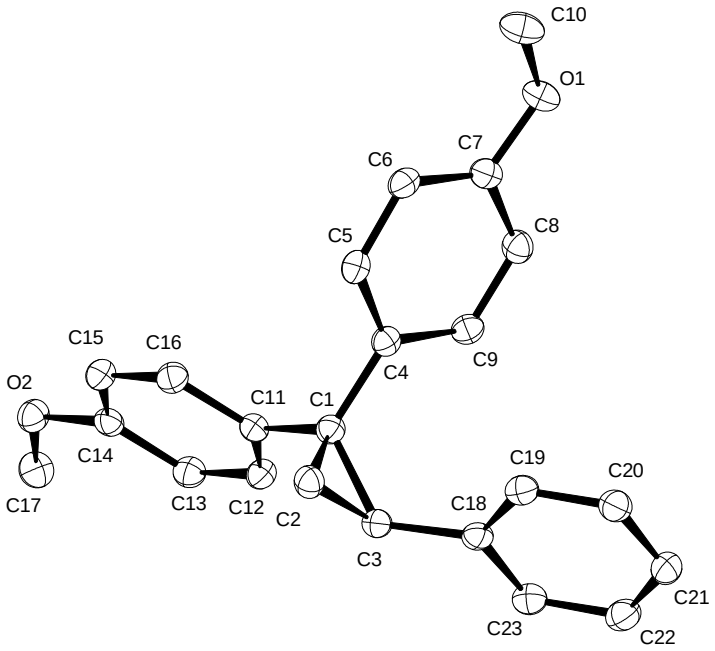


Figure S7. Structure of cyclopropane **S28** in the solid state. H atoms have been removed for clarity.

X-Ray Crystal Structure Analysis of Compound S28. $C_{23}H_{22}O_2$, Mr = 330.40 g/mol, colourless prism, crystal size 0.051 x 0.131 x 0.159 mm^3, monoclinic, space group P21, [No. 4]**,** *a* = 12.3391(7) Å, *b* = 5.8750(3) Å, *c* = 12.7465(7) Å, β = 110.721(2)°, *V* = 846.25(8) $Å^3$, *T* = 100(2) K, *Z* = 2, *Dcalc* = 1.270 $mg·m^{-3}$, λ = 1.54178 Å, μ (*Mo-K*α) = 2.779 mm^{-1}, analytical absorption correction (T_{min} = 0. 92109, T_{max} = 0. 97129), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and Bruker-Nonius FR591 rotating anode X-ray source, 3.707 < θ < 72.462°, 35434 measured reflections, 3412 independent reflections, 3330 reflections with *I>2*σ*(I)*, Rint = 0.0323.

INTENSITY STATISTICS FOR DATASET (Friedel pairs not merged)

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.29	53	53	100.0	13.53	179.81	110.83	0.0207	0.0077
3.29 - 2.22	118	118	100.0	12.88	54.24	105.59	0.0210	0.0083
2.22 - 1.75	173	173	100.0	13.54	35.22	98.59	0.0222	0.0089
1.75 - 1.52	170	170	100.0	10.54	23.17	79.64	0.0226	0.0106
1.52 - 1.38	175	175	100.0	10.83	14.79	67.73	0.0269	0.0118
1.38 - 1.29	164	164	100.0	10.88	11.56	62.36	0.0317	0.0131
1.29 - 1.20	197	197	100.0	9.73	15.25	64.30	0.0299	0.0132
1.20 - 1.14	168	168	100.0	9.70	18.66	60.93	0.0283	0.0128
1.14 - 1.10	153	153	100.0	9.30	13.18	53.41	0.0342	0.0148

1.10 - 1.06	168	168	100.0	10.82	12.35	52.27	0.0474	0.0150
1.06 - 1.02	166	166	100.0	14.17	11.18	51.26	0.0561	0.0156
1.02 - 0.98	206	206	100.0	12.16	6.84	36.02	0.0630	0.0219
0.98 - 0.96	144	144	100.0	12.47	6.04	34.99	0.0666	0.0234
0.96 - 0.93	208	208	100.0	11.96	6.19	32.47	0.0607	0.0226
0.93 - 0.91	139	139	100.0	11.49	4.56	29.06	0.0775	0.0278
0.91 - 0.89	178	178	100.0	9.85	5.31	31.36	0.0633	0.0283
0.89 - 0.87	176	176	100.0	9.85	3.94	26.61	0.0810	0.0310
0.87 - 0.85	192	192	100.0	8.09	3.64	23.12	0.0812	0.0348
0.85 - 0.83	217	217	100.0	7.59	2.96	21.30	0.0962	0.0395
0.83 - 0.82	119	119	100.0	6.29	3.44	23.12	0.0929	0.0395
0.82 - 0.81	136	155	87.7	3.09	3.17	14.75	0.1029	0.0618
0.91 - 0.81	1018	1037	98.2	7.63	3.75	23.66	0.0798	0.0368
Inf - 0.81	3420	3439	99.4	10.32	14.78	48.75	0.0322	0.0136

The structure was solved by dual space methods (SHELXT) and refined by full-matrix least-squares (SHELXL) against F^2 with aspherical scattering factors for all atoms applied according to Luebben et al. [*Acta Cryst*. (2019). A75, 50-62]. H atom postions were calculated and allowed to ride with extended averaged refined C-H distances. *R1*= 0.0210 [$I>2\sigma(I)$], *wR2* = 0.0525, 231 parameters, 1 restraint, absolute structure parameter according to Parsons, Flack and Wagner = -0.04(8) [1459 quotients] [Parsons, Flack and Wagner, *Acta Cryst*. B69 (2013) 249-259], GooF = S = 1.079, residual electron density 0.11 e · Å^{-1} [0.93 Å from C1], -0.12 e · Å^{-1} [1.09 Å from C3]. **CCDC- 2063748**

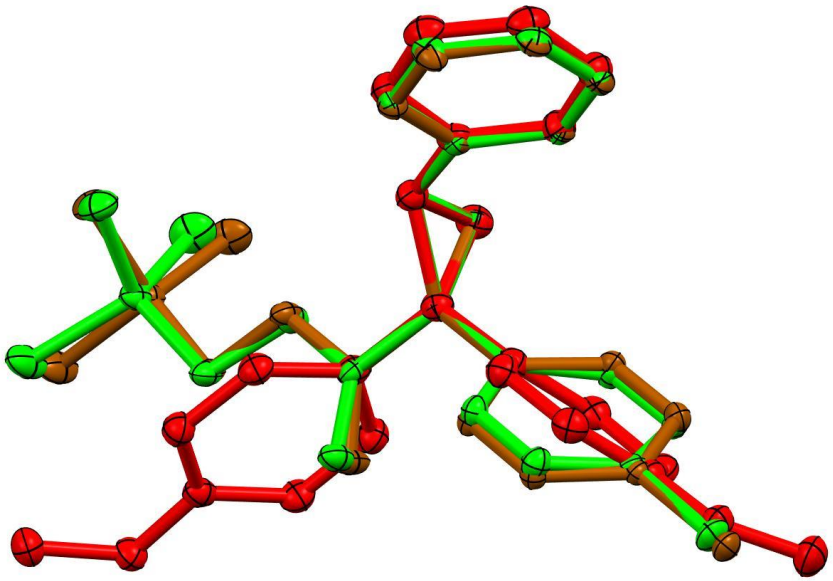


Figure S8. Overlay of the cyclopropane moieties of cyclopropanes **S20** (green), **S4** (brown) and **S28** (red) in their respective crystals, showing the differences in the conformations.

General

Unless stated otherwise, all reactions were carried out under argon atmosphere in flame dried Schlenk glassware. The solvents were purified by distillation over the indicated drying agents under argon: THF (Mg/anthracene), Et_2O (Mg/anthacene), pentane (Na/K), CH_2Cl_2 (CaH_2). MeCN and Et_3N were dried by an absorption solvent purification system based on molecular sieves. Flash chromatography: VWR Chemicals silica gel 40 – 63µm.

NMR spectra were recorded on Bruker DPX 300, AV 400, AV 500 or AV III 600 spectrometers in the solvents indicated; chemical shifts are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.2 ppm; residual $CHCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 54.0 ppm; residual $CHDCl_2$: δ_H = 5.32 ppm). Proton and carbon assignments were established using HSQC, HMBC and NOESY experiments.

IR: Alpha Platinum ATR (Bruker), wavenumbers ($\tilde{\nu}$) in cm^{-1}.

MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker),Thermo Scientific LTQ-FT, or Thermo Scientific Exactive. HRMS: Bruker APEX III FT-MS (7 T magnet), MAT 95 (Finnigan), Thermo Scientific LTQ-FT, or Thermo Scientific Exactive. GC-MS: Shimadzu GCMS-QP2010 Ultra instrument.

HPLC analyses for the determination of enantiomeric excesses were conducted on a Shimadzu LC 2020 instrument equipped with a Shimadzu SPD-M20A UV/VIS detector. Solvents (HPLC grade) were purchased and used as received. The exact conditions are stated separately for each compound.

Optical rotations were measured with an A-Krüss Otronic Model P8000-t polarimeter at a wavelength of 589 nm. The values are given as specific optical rotation with exact temperature, concentration (c/(10 mg/mL)) and solvent.

Unless stated otherwise, all commercially available compounds (abcr, Acros, TCI, Aldrich, Alfa Aesar, Fluoro Chem) were used as received.

Kinetic Studies

General: Reactions were monitored on a Bruker AV 500 NMR spectrometer at −10°C in non-deuterated pentane with coaxial-sample-insert filled with [D_6]-acetone for locking. During the reactions a spectrum was acquired every 3 min. The solvent signals of pentane were suppressed using the WET sequence with selective shaped pulses and ^{13}C decoupling. (Bruker sequence: wetdc).

The acquired spectra were imported into MNOVA 14.1.2 (Mestrelab Research S.L) with the reaction monitoring plugin for further processing. For the data analysis, the baseline of the spectra was corrected with a multiple point baseline correction.

Sample preparation: In flame-dried Schlenk tubes, the following stock solutions were prepared:

Stock solution 1: Methyl p-methoxyphenyldiazoacetate (c = 18 mmol/L) and styrene (c = 91 mmol/L) in pentane

Stock solution 2: Respective [BiRh] catalyst (c = 0.44 mmol/L) in pentane

Typical procedure: A flame-dried NMR tube under Ar was charged with an aliquot of the stock solution 1 (0.4 mL), which was cooled to −50°C in a dry ice/ethanol mixture. The solution was overlaid with an aliquot of stock solution 2 (41 µL) and the walls of the NMR tube were washed with a minimal amount of dry pentane. A capillary of [D_6]-acetone was inserted. The solution was mixed shortly before the start of the measurements and was warmed to −10 °C in the NMR machine. ^{1}H NMR spectra were recorded every 3 min.

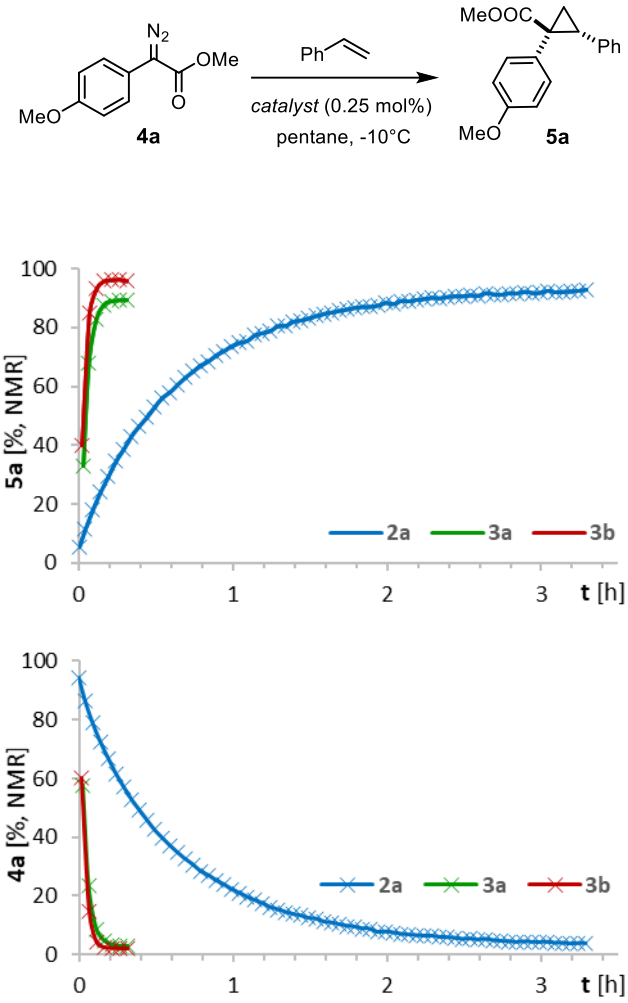


Figure S9. Kinetic data for the formation of the cyclopropane **5a** (top) as well as for the consumption of methyl *p*-methoxyphenyldiazoacetate **4a** (bottom); the reactions were performed with 0.25 mol% of catalyst in pentane at −10°C

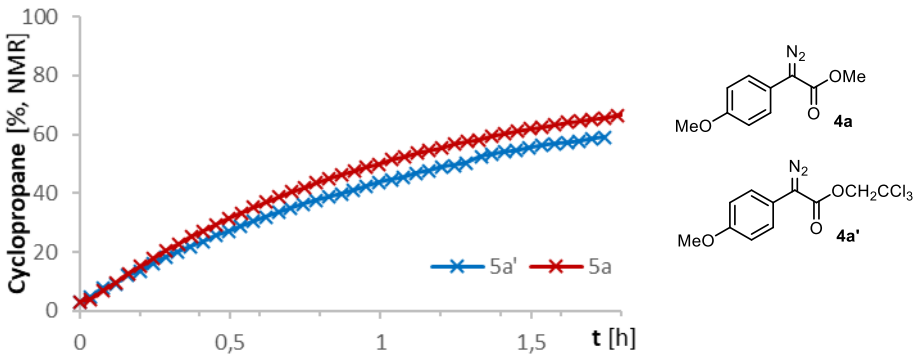


Figure S10. Kinetic data for the formation of cyclopropanes **5a** and **5a'**, showing that methyl 2-(4-methoxyphenyl)-2-diazoacetate (**4a**) and 2,2,2-trichloroethyl 2-(4-methoxyphenyl)-2-diazoacetate (**4a'**) react with very similar rates; the reactions were performed with 0.1 mol% of catalyst **3b** in CH_2Cl_2 at −10°C.

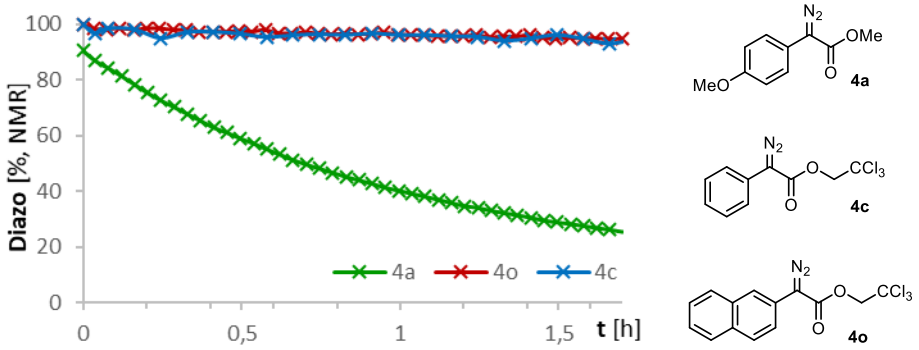
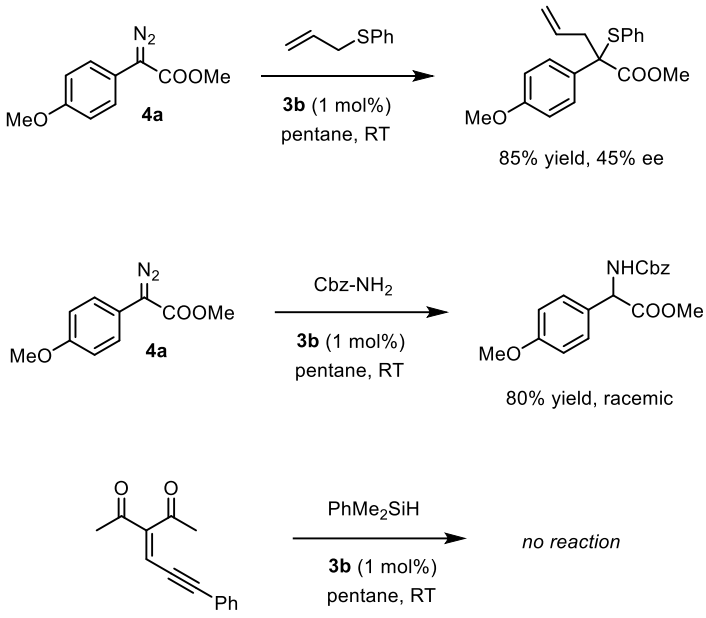


Figure S11. Kinetic data for the consumption of diazo compounds **4a**, **4c** and **4o**, showing the influence of the arene substituent on the reaction rate; the reactions were performed with 0.1 mol% of catalyst **3b** in CH_2Cl_2 at −10°C.

Exploratory Studies

It is well established that chiral dirhodium paddlewheel complexes are hardly adequate for enantioselective –OH or –NH insertion and Doyle-Kirmse reactions, except for special cases or if chiral co-catalysts are added that then largely account for the induction.[1,2,3,4] This inability is inherent and basically rooted in the dissociation of the (chiral) rhodium moiety from the ylide primarily formed before the enantiodetermining [1,2]-H shift does occur.[5] In line with this notion, the few test reactions performed so far with complexes **3** also afforded no or only modest enantioselectivity. Likewise, an attempt at performing an enynone rearrangement/Si–H insertion sequence has so far met with failure.[6] A comprehensive screening, however, has not yet been carried out and must await future studies.

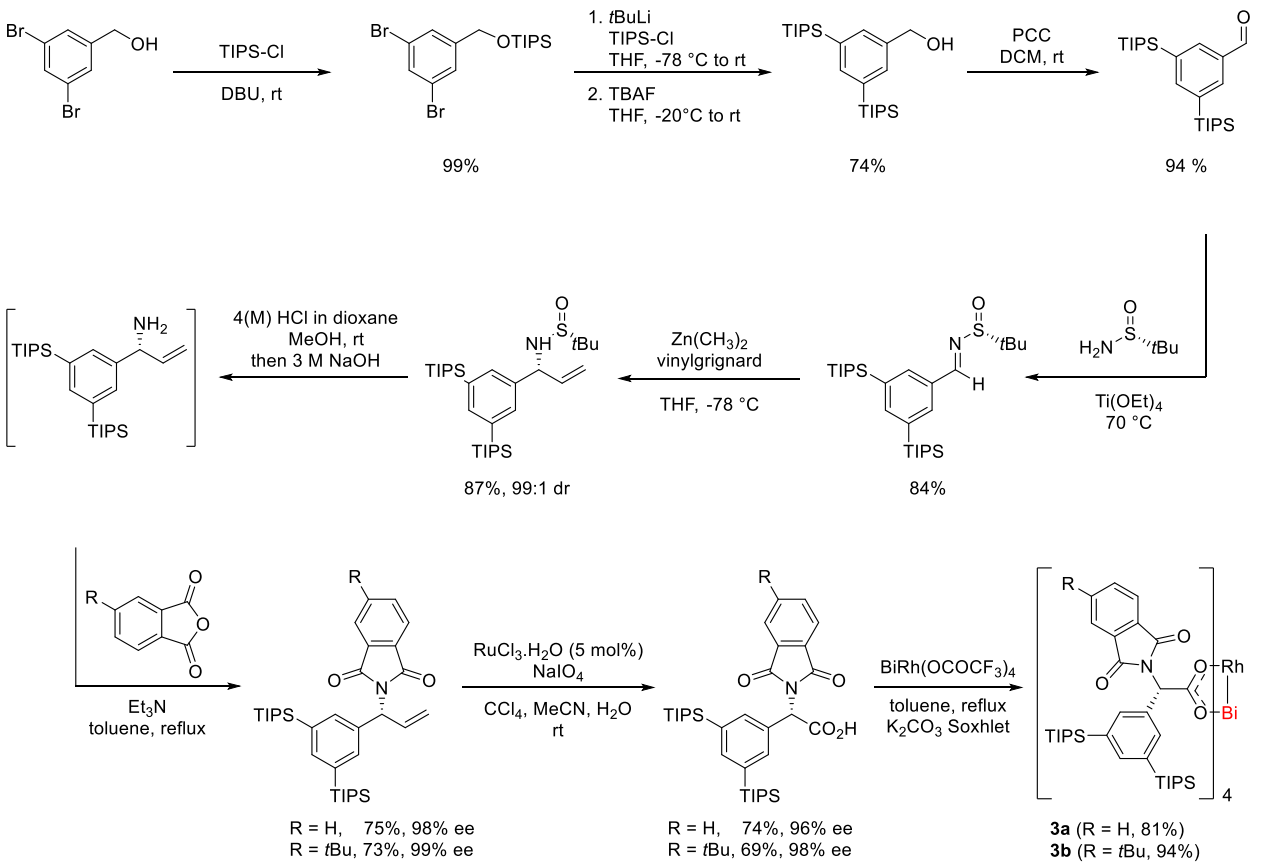


Preparation of Heterobimetallic [BiRh] Complexes

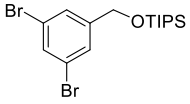
[BiRh(OCOCF$_3$)$_4$]

[BiRh(OCOCF$_3$)$_4$] was prepared by a modified literature procedure.[7] A flame-dried two-necked round bottom flask equipped with a reflux condenser was charged with [Rh$_2$(OCOCF$_3$)$_4$]·2 MeCN (534 mg, 0.722 mmol), which was heated (80°C, 10^{-3} mbar) for 1 h to remove any axially coordinated ligands; during this time, the color of the sample changed from purple to green. Next, Bi(OCOCF$_3$)$_3$ (415 mg, 0.757 mmol),[8] freshly ground Bi metal (817 mg, 3.91 mmol), toluene (40 mL), Ph$_2$O (1.1 mL, 6.93 mmol) and trifluoroacetic acid (200 µL, 2.61 mmol) were added. The mixture was stirred at 115 °C bath temperature. After 16 h, ^{19}F NMR showed full conversion of [Rh$_2$(OCOCF$_3$)$_4$]. At this point, remaining Bi metal was allowed to settle and the supernatant removed via cannula filtration. The yellow filtrate was concentrated in vacuo. Remaining Ph$_2$O was sublimed onto a -30°C-cold sublimation finger at 50°C and 10^{-3} mbar. The residue was purified by flash chromatography (silica), eluting with a toluene/MeCN gradient (100:0 → 90:10) to obtain the title compound as a yellow powder (855 mg, 82%). Characterization data matches with the previously reported data.[7]

Preparation of Complexes 3a and 3b



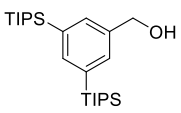
((3,5-Dibromobenzyl)oxy)triisopropylsilane (S1). A 250 mL round bottom Schlenk flask was charged with



3,5-dibromobenzylalcohol (**6**) (3.00 g, 11.28 mmol), chlorotriisopropylsilane (2.9 mL, 13.54 mmol) and CH_2Cl_2 (50 mL). The solution was cooled to 0°C and DBU (2.2 mL, 14.67 mmol) was added dropwise. After the addition was complete, stirring was continued for 2 h at ambient temperature. The reaction was quenched with HCl (1 M, 30 mL) and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography using pentane as eluent yielded the title compound as a colorless oil (4.72 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 1.9, 0.9 Hz, 2H), 4.77 (s, 2H), 1.24 – 1.12 (m, 3H), 1.09 (d, *J* = 6.7 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.8, 132.4, 127.6, 122.9, 63.8, 18.1, 12.1; IR (ATR): ṽ = 2942, 2865, 1587, 1557, 1461, 1425, 1365, 1198, 1117, 1068, 995, 880, 846, 798, 738, 666, cm^{-1}; HRMS (ESI$^+$) for $C_{16}H_{27}OBr_2Si$ $[M+H]^+$: calcd: 421.01927, found: 421.01905.

(3,5-Bis(triisopropylsilyl)phenyl)methanol (7). A flame dried Schlenk flask was charged with ((3,5-dibromobenzyl)oxy)triisopropylsilane **(S1)** (1.013 g, 2.4 mmol) and THF (20 mL). The solution was cooled to −78°C before *tert*-buthylithium (1.6 M in pentane, 6.6 mL, 10.56 mmol) was added dropwise. After the addition was complete, the mixture was warmed to ambient temperature and stirring continued for 1 h. The solution was cooled to −20°C before chlorotriisopropylsilane (1.28 mL, 6.0 mmol) was added

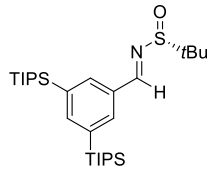
dropwise. The resulting mixture was warmed to ambient temperature and stirring continued for another 24 h. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) solution and the aqueous phase was extracted with methyl *tert*-butyl ether. The combined organic layers were dried over Na_2SO_4 and concentrated. Analysis of the crude reaction mixture indicated a 5:1 ratio of di- and mono-silylated product; this material was used directly in the next step.



Tetrabutylammonium fluoride (1 M in THF, 2.4 mL, 2.4 mmol) was added dropwise to a solution of the crude product in THF (20 mL) at 0°C. The solution was warmed to ambient temperature and stirring was continued for 30 min. The reaction was quenched with saturated aqueous NH_4Cl solution (10 mL) and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated. Purification of the residue by flash chromatography using 10% EtOAc in pentane as eluent yielded the title compound as a white solid after drying in high vacuum (750 mg, 74% over two steps). m.p. = 96-97°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (t, *J* = 1.3 Hz, 1H), 7.46 (d, *J* = 1.1 Hz, 2H), 4.69 (s, 2H), 1.41 (hept, *J* = 7.4 Hz, 6H), 1.07 (d, *J* = 7.5 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.2, 138.6, 134.4, 133.8, 66.4, 18.7, 10.9; IR (ATR): ṽ = 3270, 2940, 2863, 1461, 1383, 1366, 1142, 1014. 994, 882, 788, 714 674, 643, 561, 497 cm^{-1}; HRMS (ESI$^+$) for $C_{25}H_{48}OSi_2Na$ [M+Na]$^+$: calcd: 443.31359, found: 443.31334.

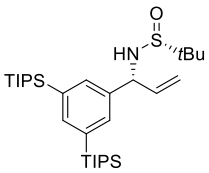
3,5-Bis(triisopropylsilyl)benzaldehyde (S2). A round bottom flask was charged with (3,5-bis(triisopropylsilyl)phenyl)methanol **(7)** (740 mg, 1.758 mmol), silica gel, and CH_2Cl_2 (20 mL). PCC (568 mg, 2.637 mmol) was added to this suspension and the mixture was stirred for 2 h until TLC analysis indicated full conversion. The mixture was concentrated and the residue loaded on top of a silica-gel column, eluting the product-containing fractions with 2% Et_2O in pentane to give the title compound as a white solid (694 mg, 94%). m.p. = 49-50°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1H), 7.96 (d, *J* = 1.3 Hz, 2H), 7.89 (t, *J* = 1.3 Hz, 1H), 1.44 (h, *J* = 7.4 Hz, 6H), 1.08 (d, *J* = 7.5 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.7, 148.6, 137.0, 135.0, 134.6, 18.6, 10.9; IR (ATR): ṽ = 2941, 2863, 1699, 1566, 1461, 1383, 1366, 1248, 1217, 1142, 1120, 1073, 1013, 994, 910, 881, 787, 701, 672, 644, 559, 511, 488 cm^{-1}; HRMS (ESI$^+$) for $C_{25}H_{46}OSi_2Na$ [M+Na]$^+$: calcd: 441.29794, found: 441.29786.

(*R*,*E*)-N-(3,5-Bis(triisopropylsilyl)benzylidene)-2-methylpropane-2-sulfinamide (8). A round bottom flask was charged with 3,5-bis(triisopropylsilyl) benzaldehyde **(S2)** (685 mg, 1.635 mmol), (*R*)-*tert*-butylsulfinamide (218 mg, 1.799 mmol), and THF (20 mL). $Ti(OEt)_4$ (514 µL, 2.45 mmol) was added and the resulting solution was stirred at 75°C for 6 h. The reaction was quenched with brine under vigorous stirring. The resulting suspension was filtered through a plug of Celite® and the filter cake was carefully rinsed with EtOAc. The combined filtrates were washed with brine. The brine layer was extracted once with EtOAc, and the combined organic phases were dried over Na_2SO_4, filtered and concentrated. Purification of the residue by flash chromatography using 5% EtOAc in pentane as eluent yielded the title compound as a white solid (815 mg, 95%). m.p. = 85-86°C; $[\alpha]_D^{20}$ = −19.3 (c = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 7.95 (d, *J* = 1.2 Hz, 2H), 7.77 (t, *J* = 1.3 Hz, 1H), 1.42 (h, *J* = 7.5 Hz, 6H), 1.27 (s, 9H), 1.08 (dd, *J* = 7.5, 3.8 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.7, 146.6, 136.7, 134.7, 132.3, 57.9, 22.8, 18.7, 18.6, 10.9; IR (ATR): ṽ = 2942, 2864, 1595, 1561, 1460, 1362, 1143, 1087, 1013, 995, 919, 878, 793, 750, 704,

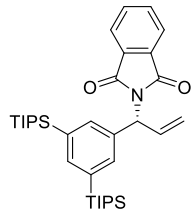


675, 643, 562, 500, 447 cm^{-1}; HRMS (ESI^+) for $C_{29}H_{55}NOSSi_2Na$ $[M+Na]^+$: calcd: 544.34351, found: 544.34338.

(*R*)-N-((*R*)-1-(3,5-Bis(triisopropylsilyl)phenyl)allyl)-2-methylpropane-2-sulfinamide (9). A flame dried Schlenk flask was charged with vinylmagnesium bromide (1 M in THF, 6.66 mL, 6.66 mmol) and dimethylzinc (1.2 M in toluene, 1.85 mL, 2.222 mmol) and the resulting solution was stirred at 0°C for 10 min. The mixture was cooled to −78°C before a solution of compound **8** (2.32 g, 4.44 mmol) in THF (15 mL) was added via syringe pump over a period of 60 min. Stirring was continued for 6 h at −78°C before the reaction was quenched with saturated aqueous NH_4Cl solution at −78°C. The aqueous phase was extracted with EtOAc, and the combined organic layers were dried over Na_2SO_4 and concentrated. NMR analysis of the crude mixture indicated a diastereomeric ratio of ≈99:1. Purification of the residue by flash chromatography using 20% EtOAc in pentane as eluent yielded the title compound as a white solid (2.14 g, 87%). m.p. =109-110°C; $[\alpha]_D^{20}$ = −40.5 (c = 1.65, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (t, *J* = 1.2 Hz, 1H), 7.36 (d, *J* = 1.2 Hz, 2H), 5.84 (ddd, *J* = 17.0, 10.1, 7.8 Hz, 1H), 5.28 (dt, *J* = 17.0, 1.1 Hz, 1H), 5.14 (dt, *J* = 10.1, 1.0 Hz, 1H), 4.89 (d, *J* = 7.8 Hz, 1H), 1.31 (hept, *J* = 7.0 Hz, 6H), 1.18 (s, 9H), 0.99 (dd, *J* = 7.5, 2.4 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.2, 139.4, 138.8, 134.2, 134.1, 117.5, 61.7, 55.7, 22.8, 18.7, 18.7, 10.9; IR (ATR): ṽ = 3712, 2941, 2864, 1462, 1369, 1145, 1048, 1015, 993, 918, 881, 788, 673, 645, 561, 496 cm^{-1}; HRMS (ESI^+) for $C_{31}H_{59}NOSSi_2Na$ $[M+Na]^+$: calcd: 572.37481, found: 572.37492.

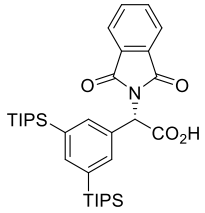


(*R*)-2-(1-(3,5-Bis(triisopropylsilyl)phenyl)allyl)isoindoline-1,3-dione (10a). HCl (4 M in dioxane, 0.56 mL, 2.22 mmol) was added at 0°C to a solution of compound **9** (407 mg, 0.74 mmol) in methanol (HPLC grade, 10 mL). The reaction flask was capped with a rubber septum and the mixture was stirred under air at room temperature for 1 h. The mixture was concentrated under vacuum. Water (20 mL) and CH_2Cl_2 (20 mL) were added to the residue and the pH of the aqueous phase was adjusted to pH ≈ 10 by addition of NaOH (3 M) before it was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuum to give (*R*)-1-(3,5-bis(triisopropylsilyl)phenyl)prop-2-en-1-amine, which was directly used in the next step.

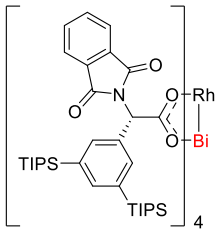


A solution of the crude amine, phthalic anhydride (120 mg, 0.814 mmol) and Et_3N (103 µL, 0.74 mmol) in toluene (20 mL) was stirred at reflux temperature for 36 h, using a Dean-Stark apparatus to collect the released water. Evaporation of the solvent and purification of the residue by flash chromatography using 3% Et_2O in pentane as eluent afforded the title compound as a colorless sticky solid (320 mg, 75% over two steps). m.p. = 86-89°C, $[\alpha]_D^{20}$ = −10.1 (c = 1.07, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.54 (d, *J* = 1.1 Hz, 2H), 7.52 (d, *J* = 1.2 Hz, 1H), 6.65 (ddd, *J* = 17.3, 10.2, 7.3 Hz, 1H), 5.96 (d, *J* = 7.2 Hz, 1H), 5.41 – 5.25 (m, 2H), 1.36 (hept, *J* = 7.5 Hz, 6H), 1.03 (dd, *J* = 7.5, 2.4 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9, 141.8, 136.3, 135.1, 134.9, 134.0, 133.7, 132.2, 123.3, 118.8, 57.6, 18.7, 18.7, 10.9; IR (ATR): ṽ = 2942, 2864, 1714, 1463, 1377, 1348, 1082,1015, 994, 881, 789, 714, 675, 641, 562, 502 cm^{-1}; HRMS (ESI^+) for $C_{35}H_{53}NO_2Si_2Na$ $[M+Na]^+$: calcd: 598.35071, found: 598.35162. The product had an *ee* of 98%. [The *ee* was determined by HPLC analysis: 150 mm Chiralpak IB-N-3, 3 µm, ∅ 4.6 mm, *n*-heptane/i-propanol = 99.9:0.1, v = 1.0 mL/min, λ = 220 nm].

2-(3,5-Bis(triisopropylsilyl)phenyl)-2-(1,3-dioxoisoindolin-2-yl)acetic acid (11a). A round bottom flask

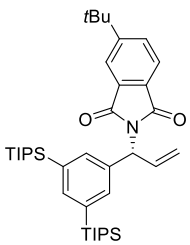


containing a magnetic stir-bar was charged with 2-(1-(3,5-bis(triisopropylsilyl)phenyl)allyl)isoindoline-1,3-dione **(10a)** (308 mg, 0.535 mmol), sodium metaperiodate (571 mg, 2.674 mmol), water (3 mL), acetonitrile (2 mL) and carbon tetrachloride (2 mL). Ruthenium trichloride hydrate (5.5 mg, 0.026 mmol, 5 mol%) was added to this biphasic mixture, which was vigorously stirred for 12 h at ambient temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL), the combined extracts were dried over Na_2SO_4, filtered through a Celite® pad and the filtrate was concentrated. The crude product was purified by flash chromatography using 2% MeOH in CH_2Cl_2 as eluent to afford the title compound as a colorless solid (235 mg, 74%). m.p. = 155-160°C; $[\alpha]_D^{20}$ = –0.4 (c = 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.67 (d, *J* = 1.1 Hz, 2H), 7.57 (s, 1H), 6.07 (s, 1H), 1.39 (p, *J* = 7.4 Hz, 6H), 1.04 (d, *J* = 7.5 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1, 167.1, 142.7, 137.0, 134.3, 133.9, 132.0, 132.0, 123.8, 56.4, 18.6, 18.6, 10.9; IR (ATR): ṽ = 2942, 2864, 1776, 1713, 1464, 1382, 1253, 1234, 1106, 1015, 964, 909, 882, 792, 724, 680, 670, 641, 563, 528, 505 cm^{-1}; HRMS (ESI$^+$) for $C_{34}H_{51}NO_4Si_2Na$ [M+Na]$^+$: calcd: 616.32489, found: 616.32568. The optical purity was 96% *ee* as determined by HPLC analysis: 150 mm Chiralpak IA-3, 3 µm, ∅ 4.6 mm, *n*-heptane/2-propanol/TFA = 95/5/0.05, v = 1.0 mL/min, λ = 220 nm.



Complex 3a. A mixture of [$BiRh(OCOCF_3)_4$] (55.3 mg, 0.072 mmol) and 2(*S*)-(3,5-bis(triisopropylsilyl)phenyl)-2-(1,3-dioxoisoindolin-2-yl)acetic acid **(11a)** (215 mg, 0.362 mmol, 96% *ee*) in dry toluene (25 mL) was stirred at reflux temperature for 3 h, passing the condensed vapor through a Soxhlet apparatus filled with K_2CO_3; at this point, ligand exchange was complete as judged by ^{19}F NMR. The mixture was concentrated in vacuum and the residue was purified by flash chromatography using 4% EtOAc in CH_2Cl_2 as eluent to give the title complex as a yellow solid (157 mg, 81%). $[\alpha]_D^{20}$ = 80.8 (c = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 – 7.81 (m, 8H), 7.65 (s, 8H), 7.63 – 7.57 (m, 8H), 7.49 (s, 4H), 6.38 (s, 4H), 1.41 – 1.25 (m, 24H), 0.98 (dd, *J* = 7.5, 5.3 Hz, 144H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.9, 166.6, 142.0, 137.7, 134.1, 133.7, 132.7, 132.3, 123.5, 57.8, 18.6, 18.6, 10.8; IR (ATR): ṽ = 2942, 2863, 1772, 1715, 1463, 1376, 1333, 1144, 1106, 1015, 993, 881, 806, 782, 738, 724, 712, 675, 643, 561 cm^{-1}; HRMS (ESI$^+$) for $C_{136}H_{200}BiN_4O_{16}Si_8RhNa$ [M+ Na]$^+$: calcd: 2704.18646, found: 2704.18946.

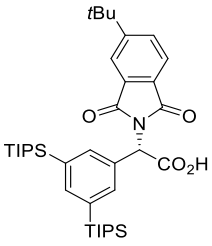
(*R*)-2-(1-(3,5-Bis(triisopropylsilyl)phenyl)allyl)-5-(*tert*-butyl)isoindoline-1,3-dione (10b). HCl (4 M in



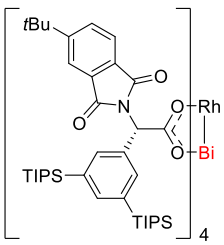
dioxane, 1.68 mL, 6.729 mmol) was added at 0°C under air to a solution of compound **9** (1.234 g, 2.243 mmol) in methanol (HPLC-grade, 20 mL). The flask was capped with a rubber septum and the solution stirred at room temperature for 1 h. The mixture was concentrated under vacuum. Water (20 mL) and CH_2Cl_2 (20 mL) were added to the residue and the pH of the aqueous phase was adjusted to pH ≈ 10 upon addition of aqueous NaOH (3 M) before it was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuum to give (*R*)-1-(3,5-bis(triisopropylsilyl)phenyl)prop-2-en-1-amine, which was used directly in the next step.

5-(*tert*-Butyl)isobenzofuran-1,3-dione (503 mg, 2.467 mmol) and Et_3N (312 µL, 2.243 mmol) were added to the crude amine in toluene (20 mL) and the resulting mixture was stirred at reflux temperature for 36 h while the released water was collected in a Dean-Stark apparatus. Evaporation of the solvent and purification of the residue by flash chromatography using 3% Et_2O in pentane as eluent afforded the title compound as a colorless waxy solid (1.03 g, 73% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.75 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.71 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.51 (d, *J* = 1.2 Hz, 1H), 6.65 (ddd, *J* = 17.3, 10.2, 7.3 Hz, 1H), 6.00 – 5.82 (m, 1H), 5.39 – 5.24 (m, 2H), 1.44 – 1.29 (m, 15H), 1.03 (dd, *J* = 7.5, 2.3 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.3, 167.9, 158.6, 141.8, 136.5, 135.2, 135.1, 133.6, 132.4, 131.0, 129.5, 123.2, 120.5, 118.6, 57.5, 35.9, 31.3, 18.7, 18.6, 10.9; IR (ATR): ṽ = 2942, 2864, 1771, 1714, 1620, 1462, 1369, 1326, 1255, 1135, 1087, 994, 922, 880, 790, 753, 675, 642, 563, 502 cm^{-1}; HRMS (ESI$^+$) for $C_{39}H_{61}NO_2Si_2Na$ [M+Na]$^+$: calcd: 654.41331, found: 654.41370. The product was obtained in 98% *ee* [The *ee* was determined by HPLC analysis: 150 mm Chiralpak IB-N-3, 3 µm, ∅ 4.6 mm, *n*-heptan/2-propanol = 99.9/0.1, v = 1.0 mL/min, 298 K, λ = 220 nm].

(*S*)-2-(3,5-Bis(triisopropylsilyl)phenyl)-2-(5-(*tert*-butyl)-1,3-dioxoisoindolin-2-yl)acetic acid (11b). A round bottom flask containing a magnetic stir-bar was charged with compound **10b** (830 mg, 1.313 mmol), sodium metaperiodate (1.404 g, 6.57 mmol), water (9 mL), acetonitrile (6 mL), and carbon tetrachloride (6 mL). Ruthenium trichloride hydrate (13.6 mg, 5 mol%) was added and the biphasic mixture was vigorously stirred for 12 h at ambient temperature. The mixture was diluted with CH_2Cl_2 (20 mL), the phases were separated, and the aqueous layer repeatedly extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4, filtered through a Celite® pad and the filtrate was concentrated. The crude product was purified by flash chromatography using 2% MeOH in CH_2Cl_2 as eluent to afford the title compound as a colorless solid (590 mg, 69%). m.p. = 117-119°C; $[\alpha]_D^{20}$ = 12.0 (c = 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 1.5 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.64 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.59 (d, *J* = 1.2 Hz, 2H), 7.49 (d, *J* = 1.3 Hz, 1H), 5.97 (s, 1H), 1.38 – 1.24 (m, 15H), 0.96 (d, *J* = 7.5 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.4, 167.6, 167.2, 159.0, 142.6, 137.0, 137.0, 133.8, 132.2, 131.3, 129.3, 123.6, 120.9, 56.4, 35.9, 31.3, 18.7, 18.6, 10.9; IR (ATR): ṽ = 2942, 2864, 1776, 1715, 1462, 1371, 1254, 1138, 1103, 1015, 994, 881, 790, 753, 676, 642, 563, 500 cm^{-1}; HRMS (ESI$^+$) for $C_{38}H_{59}NO_4Si_2Na$ [M+Na]$^+$: calcd: 672.38749, found: 672.38859. The optical purity (98% *ee*) was determined by HPLC analysis: Chiralpak IB-N-3, 3 µm, ∅ 4.6 mm, *n*-heptane/2-propanol/TFA = 99/1/0.05, v = 1.0 mL/min, λ = 220 nm.

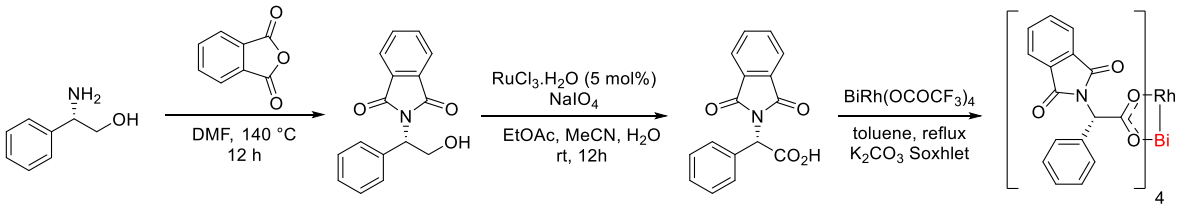


Complex 3b. A solution of [$BiRh(OCOCF_3)_4$] (72 mg, 0.094 mmol) and (*S*)-2-(3,5-bis(triisopropylsilyl)-phenyl)-2-(5-(*tert*-butyl)-1,3-dioxoisoindolin-2-yl)acetic acid **(11b)** (306 mg, 0.471 mmol; 98% *ee*) in toluene (25 mL) was stirred at reflux temperature for 3 h, passing the condensed vapors through a Soxhlet apparatus filled with K_2CO_3. The progress of the reaction was monitored by ^{19}F NMR, which indicated complete conversion of the starting complex after 3 h. The mixture was concentrated in vacuum and the residue was purified by flash chromatography using 60% CH_2Cl_2 in pentane as eluent to furnish the desired complex as a yellow solid (258 mg, 94%). NMR spectra were recorded at 80°C; at lower temperature only very broad signals with poor resolution were observed. $[\alpha]_D^{20}$ = 80.2 (c = 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, 353K): δ = 7.90 (s, 4H), 7.78 – 7.72



(m, 12H), 7.62 (dd, *J* = 7.9, 1.7 Hz, 4H), 7.56 (d, *J* = 1.3 Hz, 4H), 6.38 (s, 4H), 1.42 – 1.33 (m, 60H), 1.04 (dd, *J* = 7.5, 5.7 Hz, 144H); ^{13}C NMR (151 MHz, $CDCl_3$, 353K): δ = 182.1, 167.0, 166.7, 158.3, 142.1, 138.0, 134.6, 133.3, 133.0, 130.5, 130.1, 123.3, 120.7, 58.0, 35.9, 31.4, 18.9, 11.2; IR (ATR): ṽ = 2942, 2864, 1774, 1714, 1462, 1368, 1329, 1104, 1014, 881, 807, 783, 756, 643, 564, 509 cm^{-1}; HRMS (ESI$^+$) for $C_{152}H_{232}BiN_4O_{16}RhSi_8Na$ [M+ Na]$^+$: calcd: 2928.43686, found: 2928.43753.

Control Experiment with the Catalyst Lacking the Peripheral TIPS-Groups: [BiRh(*S*)-PTPG)$_4$]



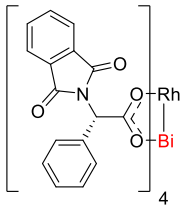
BiRh(*S*-PTPG)$_4$, 97%

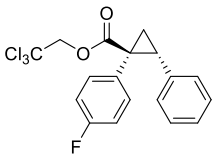
2(*S*)-2-(1,3-Dioxoisoindolin-2-yl)-2-phenylacetic acid was synthesized in a two steps sequence described below. Characterization data matched with the literature reported data.[9]

A mixture of (*S*)-2-amino-2-phenylethan-1-ol (1018 mg, 7.420 mmol) and phthalic anhydride (1099 mg, 7.420 mmol) was stirred at 140 °C for 12 h. After cooling, water was added and the product was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated to give crude (*S*)-2-(2-hydroxy-1-phenylethyl)isoindoline-1,3-dione which was used directly in the next step.

Crude (*S*)-2-(2-hydroxy-1-phenylethyl)isoindoline-1,3-dione thus obtained was dissolved in EtOAc (30 mL) and CH_3CN (30 mL). A solution of $NaIO_4$ (6.51 g, 30.421 mmol) in water (45 mL) and ruthenium trichloride hydrate (33.8 mg, 2.2 mol%) were added and the mixture was vigorously stirred for 12 h. The mixture was then diluted with EtOAc and water and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. Purification opf the residue by flash chromatography using 5% MeOH in CH_2Cl_2 as eluent gave the desired product as a white solid (1.30 mg, 62% yield).

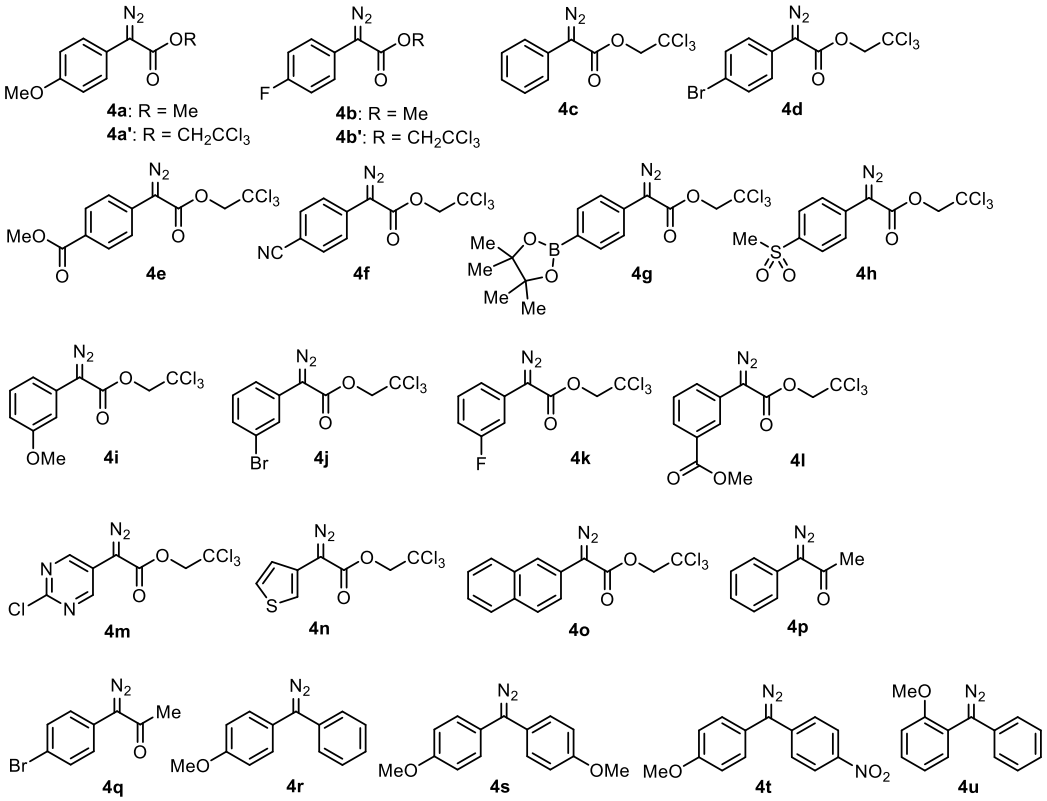
Complex BiRh(*S*-PTPG)$_4$ (S3). A mixture of [$BiRh(OCOCF_3)_4$] (54.3 mg, 0.071 mmol) and 2(*S*)-2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetic acid (100 mg, 0.356 mmol) in dry toluene (25 mL) was stirred at reflux temperature for 3 h, passing the condensed vapor through a Soxhlet apparatus filled with K_2CO_3; at this point, ligand exchange was complete as judged by ^{19}F NMR. The mixture was concentrated in vacuum and the residue was purified by flash chromatography using 2% MeOH in CH_2Cl_2 as eluent to give the title complex as a yellow solid (99 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.38, 3.04 Hz, 8H), 7.59 (dd, *J* = 5.45, 2.83 Hz, 8H), 7.55 – 7.50 (m, 8H), 7.32 – 7.14 (m, 12H), 6.23 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 182.5, 167.1, 136.4, 134.0, 132.1, 130.0, 128.4, 128.2, 123.6, 57.4; IR (ATR): ṽ = 1771, 1712, 1644, 1597, 1467, 1377, 1333, 1260, 1107, 1075, 954, 910, 892, 716, 696, 648, 530 cm^{-1}; HRMS (ESI$^+$) for $C_{64}H_{40}Bi_1N_4O_{16}Rh_1Na_1$ [M + Na]$^+$: calcd: 1455.11904, found: 1455.12001.





Using this complex, cyclopropane **5b'** was obtained at RT in 94% yield and 24% ee.

Diazo Compounds



Diazo compounds **4a**, **4b** are known compounds and were prepared according to the literature procedure.[10] Characterization data matched with the reported data.

Diazo compounds **4a'**, **4b'**, **4c**, **4d** are known compounds and were prepared according to the literature procedure.[11] Characterization data matched with the reported data.

Diazo compounds **4e**, **4g**, **4i**, **4j**, **4m, 4o** are known compounds and were prepared according to the literature procedure.[12] Characterization data matched with the reported data.

Diazo compounds **4p**, **4q** are known compounds and were prepared according to the literature procedure.[13] Characterization data matched with the reported data.

Diazo compounds **4h** was prepared by adapting a literature procedure.[11] Characterization data is given below.

Diazo compounds **4f**, **4k**, **4l** were prepared by adapting a literature procedure.[12] Characterization data is given below.

Diazo compounds **4r**, **4t** are known compounds and were prepared according to the literature procedure.[14] Characterization data matched with the reported data.

Diazo compound **4s** is a known compounds and was prepared according to the literature procedure.[15] Characterization data matched with the reported data.

Diazo compound **4u** is a known compound and was prepared according to the literature procedure.[16] Characterization data matched with the reported data.

2,2,2-Trichloroethyl 2-(4-cyanophenyl)-2-diazoacetate (4f). Prepared from 4-iodobenzonitrile (962 mg, 4.43 mmol) as a yellow solid (735 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.59 (m, 4H), 4.93 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.3, 132.9, 130.8, 123.7, 118.7, 109.5, 94.9, 74.1 (C-N_2 was not detected); IR (ATR): ṽ = 2961, 2220, 2099, 1714, 1602, 1506, 1377, 1343, 1237, 1184, 1136, 1084, 1037, 926, 838, 827, 793, 731, 708, 576, 551, 496; HRMS (ESI$^+$) for $C_{11}H_6Cl_3N_3O_2Na$ $[M+Na^+]^+$: calcd: 339.94178, found: 339.94172.

2,2,2-Trichloroethyl 2-diazo-2-(4-(methylsulfonyl)phenyl)acetate (4h). Prepared from 2-(4-(methylsulfonyl)phenyl)acetic acid (1.52 g, 7.12 mmol) as a yellow solid (560 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 – 7.90 (m, 2H), 7.75 – 7.67 (m, 2H), 4.94 (s, 2H), 3.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.3, 137.7, 131.9, 128.3, 123.8, 94.9, 74.2, 44.7 (C=N_2 was not detected); IR (ATR): ṽ = 2926, 2096, 1702, 1499, 1337, 1304, 1285, 1237, 1147, 1092, 1033, 958, 787, 769, 734, 715, 564, 521, 503; HRMS (ESI$^+$) for $C_{11}H_9N_2O_4SCl_3Na$ $[M+Na^+]^+$: calcd: 392.92408, found: 392.92450.

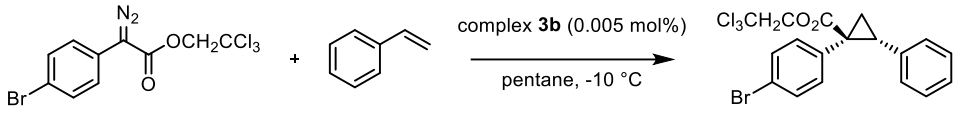
2,2,2-Trichloroethyl 2-diazo-2-(3-fluorophenyl)acetate (4k). Prepared from 1-fluoro-3-iodobenzene (945 mg, 4.26 mmol) as a yellow solid (1.06 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.29 (m, 2H), 7.19 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H), 6.91 (tdd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 4.92 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.6, 162.6 (d, *J* = 79.2 Hz), 130.7 (d, *J* = 9.0 Hz), 127.3 (d, *J* = 9.4 Hz), 119.1 (d, *J* = 3.0 Hz), 113.2 (d, *J* = 21.5 Hz), 111.4 (d, *J* = 25.3 Hz), 95.1, 74.1, (C=N_2 was not detected); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −111.4; IR (ATR): ṽ = 3019, 2093, 1701, 1611, 1580, 1493, 1445, 1383, 1351, 1231, 1211, 1170, 1130, 1090, 1049, 890, 874, 815, 774, 730, 709, 680, 577, 499; HRMS (EI) for $C_{10}H_6N_2O_2Cl_3F$ $[M]^+$: calcd: 309.94734, found: 309.94710.

Methyl 3-(1-diazo-2-oxo-2-(2,2,2-trichloroethoxy)ethyl)benzoate (4l). Prepared from methyl 3-iodobenzoate (806 mg, 3.08 mmol) as a yellow solid (980 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (t, *J* = 1.9 Hz, 1H), 7.89 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.77 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.53 – 7.45 (m, 1H), 4.93 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6, 163.2, 131.2, 129.4, 128.5, 127.5, 125.6, 124.8, 95.1, 74.1, 52.5 (C-N_2 was not detected); IR (ATR): ṽ = 2947, 2865, 2085, 1710, 1385, 1244, 1155, 1052, 783, 751, 707, 676, 581; HRMS (ESI$^+$) for $C_{12}H_9N_2O_4Cl_3Na$ $[M+Na^+]^+$: calcd: 372.95201, found: 372.95244.

Cyclopropanes and Cyclopropenes

General procedure (Small Scale). An oven dried jacketed Schlenk flask equipped with a magnetic stir bar was charged with the [BiRh] catalyst (0.001 mmol, 1 mol%) under argon. The alkene or alkyne substrate (0.5 mmol) and pentane (1 mL) were added and the resulting solution cooled to −10°C. A solution of the diazo compound (0.1 mmol) in pentane (3 mL) was added dropwise over 10 min. The resulting mixture was stirred at −10°C until TLC analysis indicated the complete consumption of the diazo compound. For work up, the mixture was absorbed on silica, which was loaded on top of a silica column. Purification by flash chromatography (*n*-pentane/Et_2O or hexanes/EtOAc) afforded the desired cyclopropane or cyclpropene product.

Gram Scale Reaction with Reduced Catalyst Loading. 2,2,2-Trichloroethyl (1*S*,2*R*)-1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (S4).



An oven dried jacketed Schlenk flask equipped with a magnetic stir bar was charged under argon with complex **3b** (750 µL of 0.2 mmol/L stock solution in pentane, 0.005 mol%), styrene (1.73 mL, 15 mmol) and pentane (5 mL). The resulting solution was cooled to −10°C before a solution of 2,2,2-trichloroethyl 2-diazo-2-(4-bromophenyl)acetate (**4d**) (1.12 g, 3 mmol) in pentane (20 mL) was added dropwise over 30 min. Once the addition was complete, stirring was continued at −10°C for 24 h. The mixture was concentrated in the presence of silica and the loaded silica then added on top of a column of silica gel. The product was eluted with *n*-pentane/Et_2O to give the title compound as a colorless solid (1.31 g, 97%, 98% *ee*). m.p. = 87-89°C; $[\alpha]_D^{20}$ = –4.3 (c = 4.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 – 7.15 (m, 2H), 7.06 – 6.98 (m, 3H), 6.91 – 6.82 (m, 2H), 6.73 (dd, *J* = 6.8, 2.9 Hz, 2H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 3.14 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.21 (dd, *J* = 9.4, 5.2 Hz, 1H), 1.89 (dd, *J* = 7.5, 5.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 135.3, 133.8, 133.1, 131.0, 128.2, 128.2, 127.0, 121.7, 95.1, 74.5, 36.7, 34.1, 20.3; IR (ATR): ṽ = 1731, 1488, 1428, 1363, 1232, 1206, 1149, 1094, 1051, 1009, 969, 804, 804, 770, 710, 695, 575, 549, 500 cm^{-1}; HRMS (ESI$^+$) for $C_{18}H_{14}Cl_3BrO_2Na$ $[M+Na^+]^+$: calcd: 468.91351, found: 468.91346.

The optical purity (98% *ee*) was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, ∅ 4.6 mm, *n*-heptane/i-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 3.45 min, t(major) = 4.04 min.]

When the same compound was prepared according to the general procedure with catalyst **2a**, a yield of 91% and an optical purity of 91% *ee* was obtained.

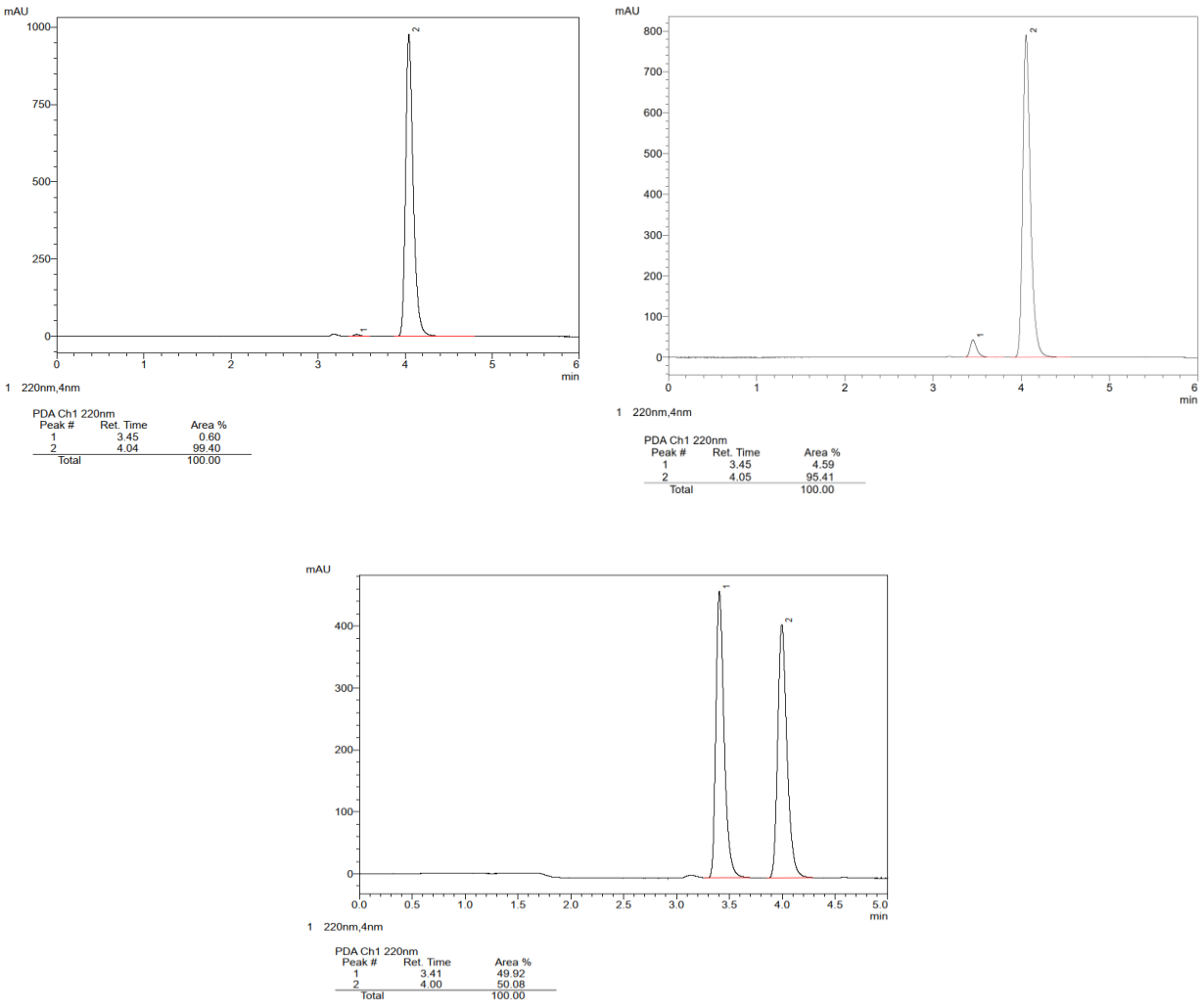
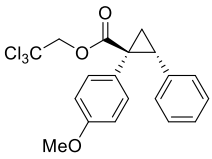


Figure S12. HPLC traces of compound **S4**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

The following compounds were prepared analogously



2,2,2-Trichloroethyl (1*S*,2*R*)-1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (5a'). Prepared according to the general procedure as a colorless oil; with complex **2a**: 90% yield, 98% *ee*; with complex **3b**: 99% yield, >99% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, ∅ 4.6 mm, *n*-heptane/i-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 4.00 min, t(major) = 4.51 min.] $[\alpha]_D^{20}$ = –0.45 (c = 3.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.02 – 6.93 (m, 2H), 6.84 – 6.75 (m, 2H), 6.70 – 6.62 (m, 2H), 4.83 (d, *J* = 11.9 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 3.72 (s, 3H), 3.18 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.26 (dd, *J* = 9.4, 5.0 Hz, 1H), 1.95 (dd, *J* = 7.4, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.5, 158.8, 136.0, 133.2, 128.3, 128.0, 126.7, 125.9, 113.3, 95.3, 74.5, 55.2, 36.7, 34.0, 20.6; IR (ATR): ṽ = 1730, 1612, 1515, 1456, 1441, 1294, 1239, 1209, 1177, 1149, 1109, 1094, 1052, 1032, 970, 831, 797, 770, 744, 712, 695, 613, 572, 553 cm^{-1}; HRMS (ESI$^+$) for $C_{19}H_{18}Cl_3O_3$ [M+H]$^+$: calcd: 399.03160, found: 399.03160.

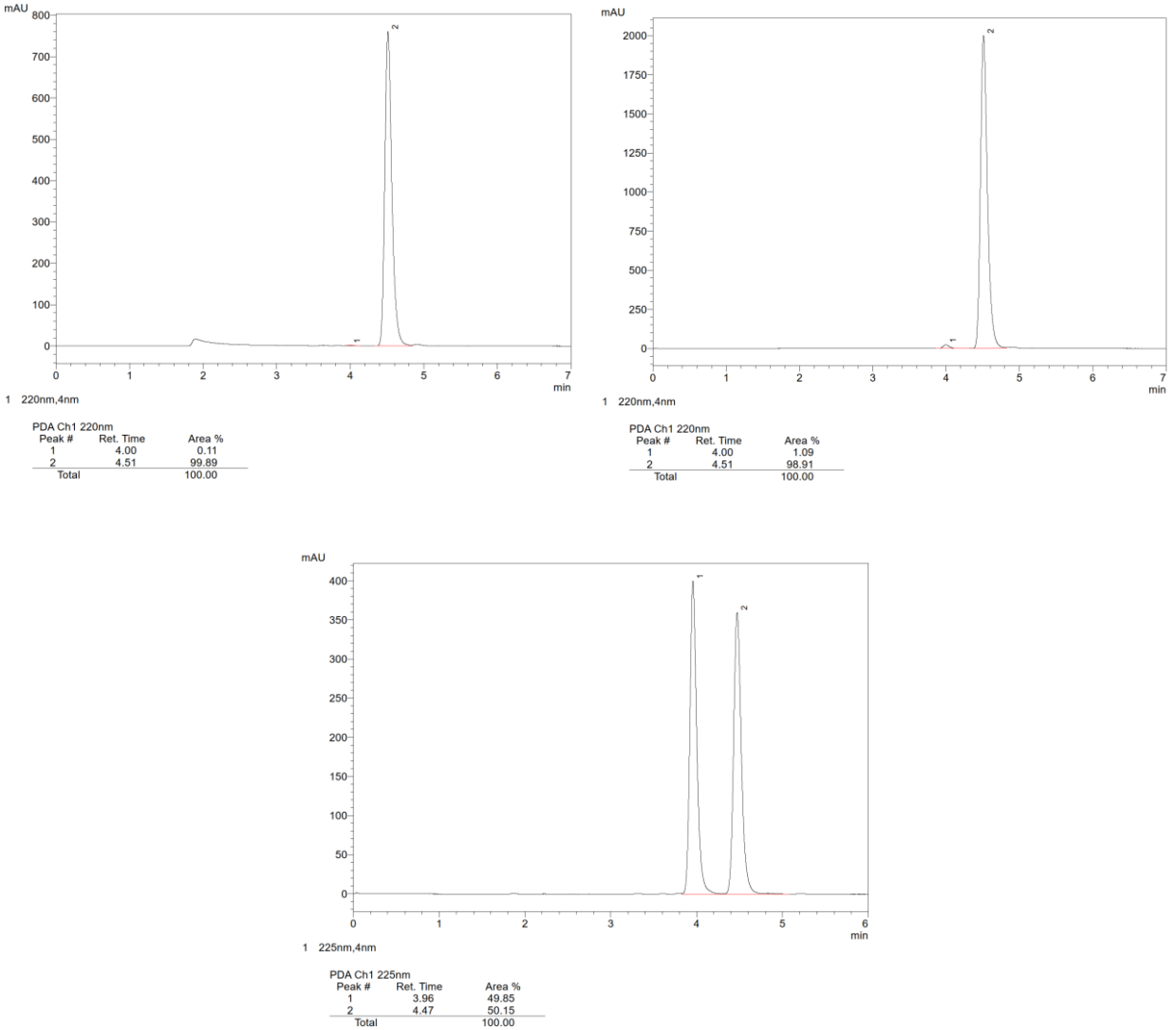
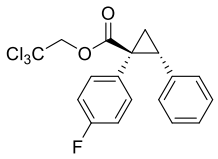


Figure S13. HPLC traces of compound **5a'**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-1-(4-fluorophenyl)-2-phenylcyclopropane-1-carboxylate (5b'). Prepared



according to the general procedure as a white solid; with complex **2a**: 99% yield, 83% *ee*; with complex **3b**: 99% yield, 98% *ee.* [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, ∅ 4.6 mm, *n*-heptane/i-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 3.29 min, t(major) = 3.55 min]. m. p. = 83-85°C; $[\alpha]_D^{20}$ = + 4.6 (c = 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 – 7.08 (m, 3H), 7.06 – 7.00 (m, 2H), 6.87 – 6.77 (m, 4H), 4.83 (dd, *J* = 11.9, 0.7 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 3.22 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.29 (dd, *J* = 9.4, 5.2 Hz, 1H), 1.98 (dd, *J* = 7.4, 5.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1, 163.3, 160.8, 135.5, 133.7 (d, *J* = 8.2 Hz), 129.8 (d, *J* = 3.1 Hz), 128.2 (d, *J* = 15.9 Hz), 126.9, 114.8 (d, *J* = 21.4 Hz), 95.1, 74.5, 36.6, 34.1, 20.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.6; IR (ATR): ṽ = 1733, 1604, 1510, 1437, 1235, 1212, 1152, 1055, 833, 810, 783, 771, 710, 694, 579, 543 cm^{-1}; HRMS (ESI^+) for $C_{18}H_{14}Cl_3FO_2Na$ $[M+Na]^+$: calcd: 408.99356, found: 408.99326.

Control Experiment using the Catalyst without the peripheral TIPS-groups: the use of complex **BiRh(*S*-PTPG)$_4$ (S3)** at room temperature furnished product **5b'** in 94% yield and **24% ee**.

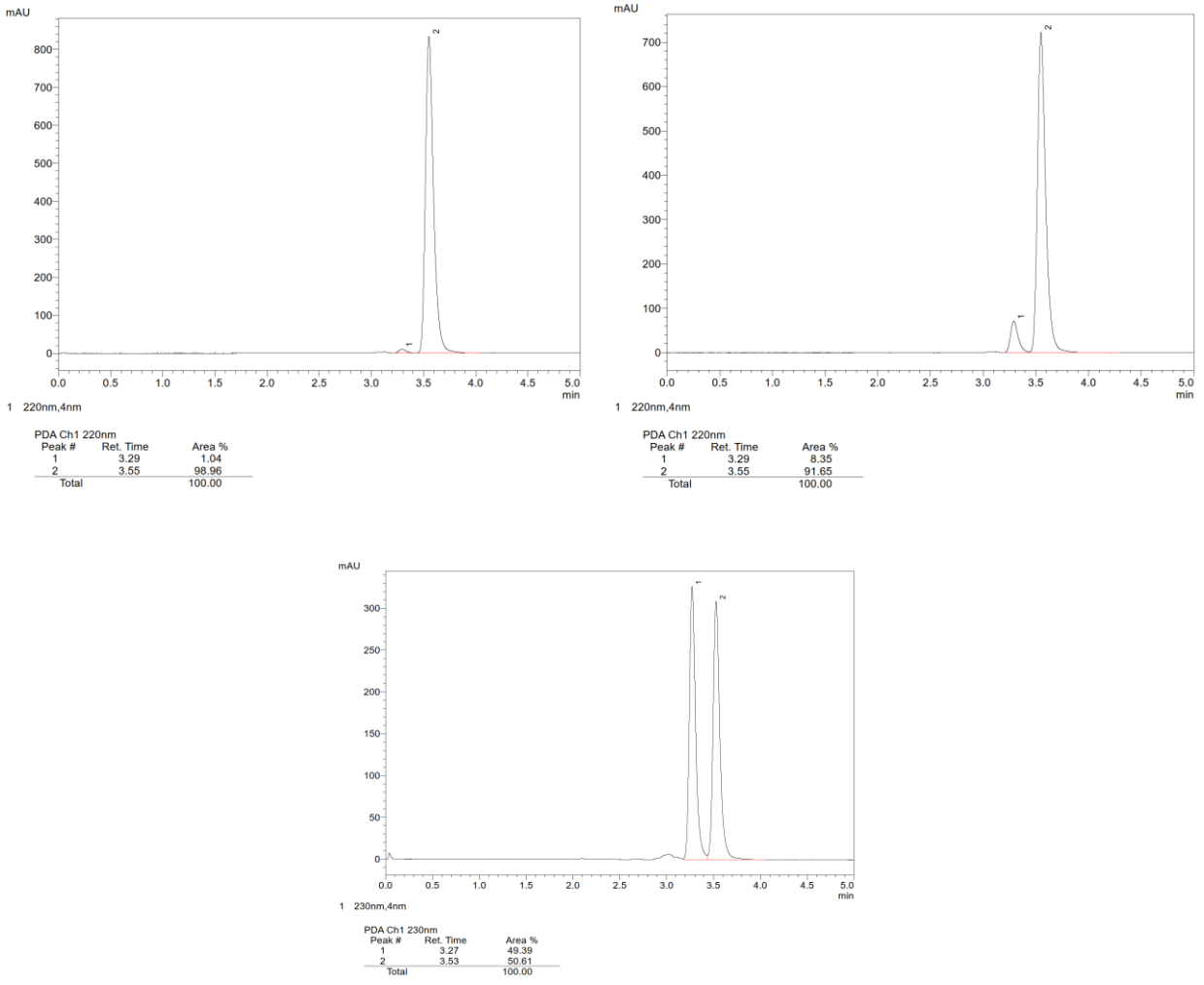
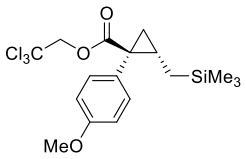


Figure S14. HPLC traces of compound **5b'**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*S*)-1-(4-methoxyphenyl)-2-((trimethylsilyl)methyl)cyclopropane-1-carboxylate (S5). 

Prepared according to the general procedure as a colorless oil; with complex **2a**: 91% yield, 99% *ee;* with complex **3b**: 95% yield, 99% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IC-3, Ø 4.6 mm, n-heptane/2-propanol = 90/10, v = 1.0 mL/min, λ = 220 nm, t(major) = 2.63 min, t(minor) = 3.22 min.] $[\alpha]_D^{20}$ = +35.3 (c = 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 – 7.18 (m, 2H), 6.91 – 6.83 (m, 2H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 3.81 (s, 3H), 1.98 – 1.85 (m, 2H), 1.08 (q, *J* = 3.1 Hz, 1H), 0.85 (ddd, *J* = 14.5, 2.8, 1.3 Hz, 1H), 0.01 (s, 9H), -0.32 – -0.47 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.5, 158.8, 133.0, 127.6, 113.5, 95.4, 74.3, 55.3, 32.9, 26.9, 23.7, 18.3, -1.3; ^{29}Si NMR (99 MHz, $CDCl_3$): δ = 2.4; IR (ATR): ṽ = 2953, 1729, 1516, 1244, 1164, 1123, 1034, 834, 709, 572; HRMS (ESI$^+$) for $C_{17}H_{23}O_3Cl_3Si_1Na_1$ $[M+Na^+]^+$: calcd: 431.03743, found: 431.03706.

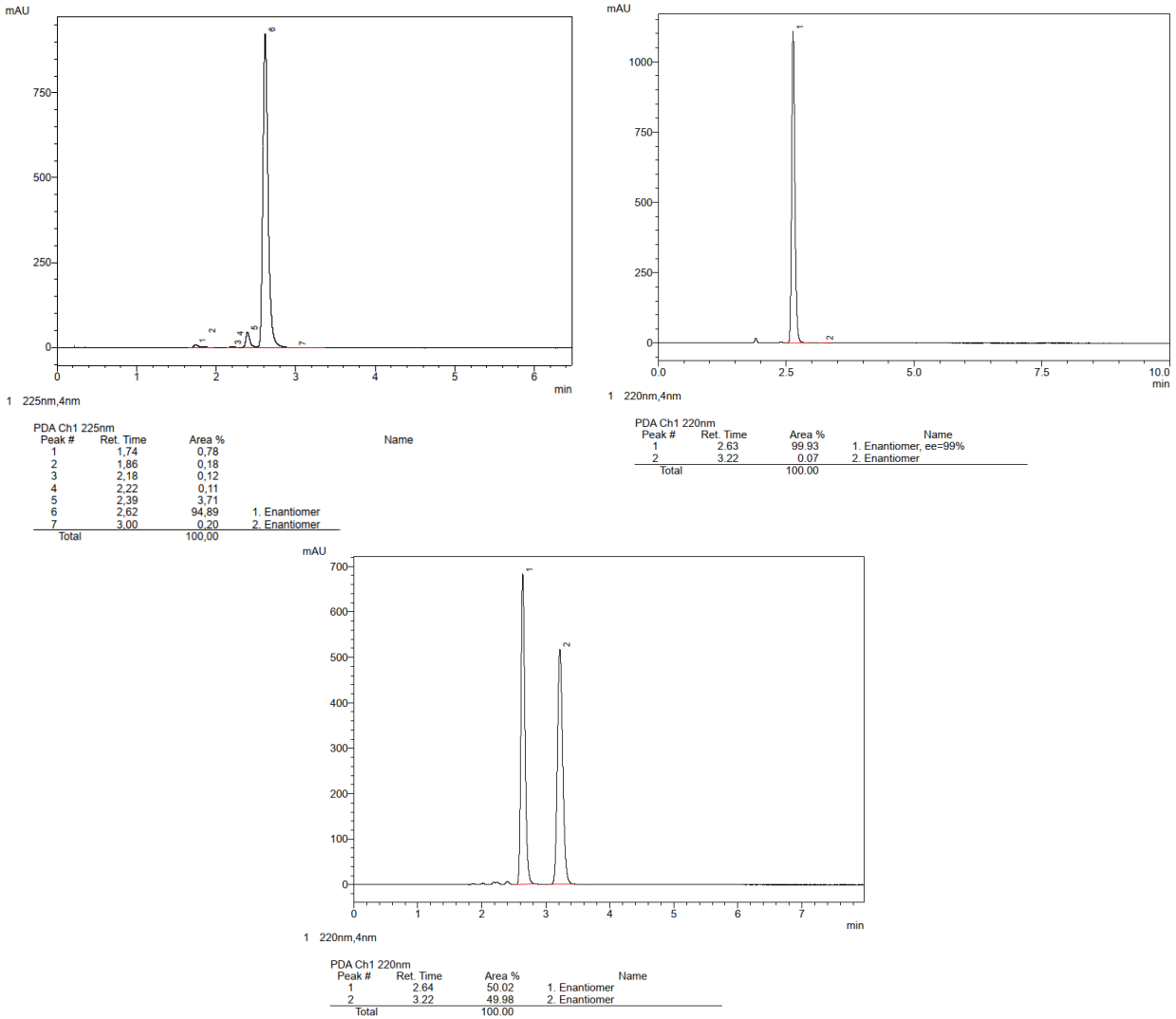


Figure S15. HPLC traces of compound **S5**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*S*)-1-(4-methoxyphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclopropane-1-carboxylate (S6). Prepared to the general procedure as a colorless oil; with complex **2a**: 73% yield, 99% *ee*, with complex **3b**: 45% yield, 98% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IC-3, Ø 4.6 mm, n-heptane/2-propanol = 90/10, v = 1.0 mL/min, λ = 220 nm, t(major) = 2.98 min, t(minor) = 3.54 min.] $[\alpha]_D^{20}$ = −15.6 (c = 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25 – 7.20 (m, 2H), 6.86 – 6.81 (m, 2H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 3.79 (s, 3H), 2.04 – 1.98 (m, 1H), 1.88 (dd, *J* = 9.0, 4.3 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.17 (dd, *J* = 6.9, 4.3 Hz, 1H), 0.68 (dd, *J* = 16.5, 6.6 Hz, 1H), 0.39 (dd, *J* = 16.5, 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.5, 158.9, 132.9, 127.4, 113.5, 95.4, 83.4, 74.2, 55.4, 33.1, 25.9, 25.0, 24.9, 23.0, 12.7; ^{11}B NMR (128 MHz, $CDCl_3$): δ = 33.8; IR (ATR): ṽ = 2978, 1732, 1516, 1322, 1243, 1142, 1035, 967, 795, 709, 574; HRMS (ESI$^+$) for $C_{20}H_{26}O_5Cl_3B_1Na_1$ $[M+Na^+]^+$: calcd: 485.08311, found: 485.08315.

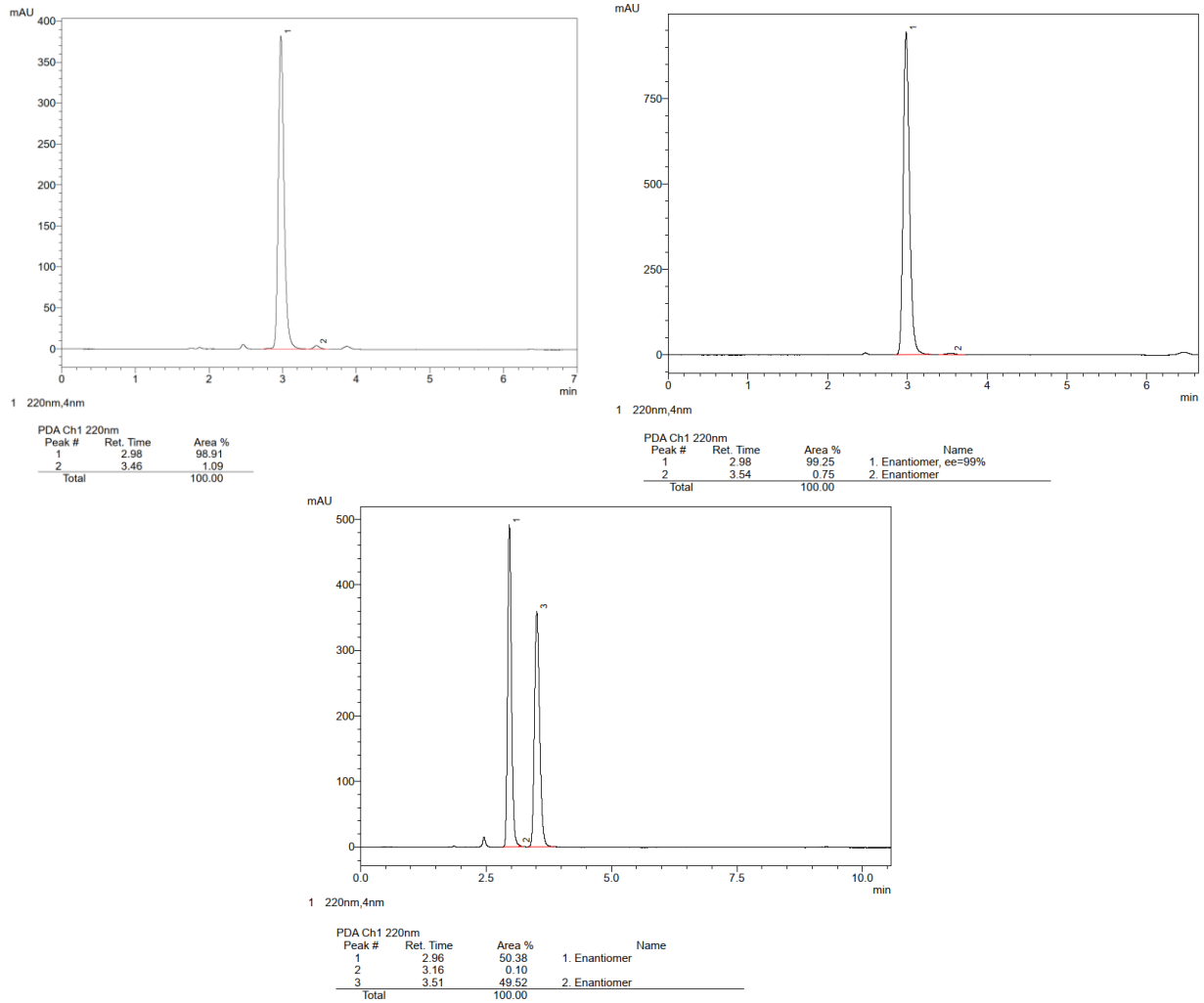
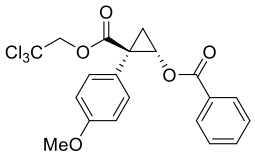


Figure S16. HPLC traces of compound **S6**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

(1*S*,2*R*)-2-(4-methoxyphenyl)-2-((2,2,2-trichloroethoxy)carbonyl)cyclopropyl benzoate (S7). Prepared



according to the general procedure as a colorless oil; with complex **2a**: 57% yield, 96% *ee*; with complex **3b**: 91% yield, 99% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, Ø 4.6 mm, n-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 225 nm, t(major) = 8.17 min, t(minor) = 7.49 min.] $[\alpha]_D^{20}$ = −26.4 (c = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 – 7.61 (m, 2H), 7.53 – 7.44 (m, 1H), 7.36 – 7.23 (m, 4H), 6.85 – 6.77 (m, 2H), 5.13 (dd, *J* = 7.2, 4.6 Hz, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 3.75 (s, 3H), 2.21 (dd, *J* = 7.2, 6.2 Hz, 1H), 1.92 (dd, *J* = 6.3, 4.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9, 166.8, 159.3, 133.4, 132.5, 129.6, 129.3, 128.5, 124.8, 113.8, 95.0, 74.5, 58.5, 55.4, 33.7, 20.3; IR (ATR): ṽ = 2959, 1729, 1516, 1240, 1092, 1031, 796, 708, 575; HRMS (ESI$^+$) for $C_{20}H_{17}O_5Cl_3Na$ $[M+Na^+]^+$: calcd: 465.00338, found: 465.00369.

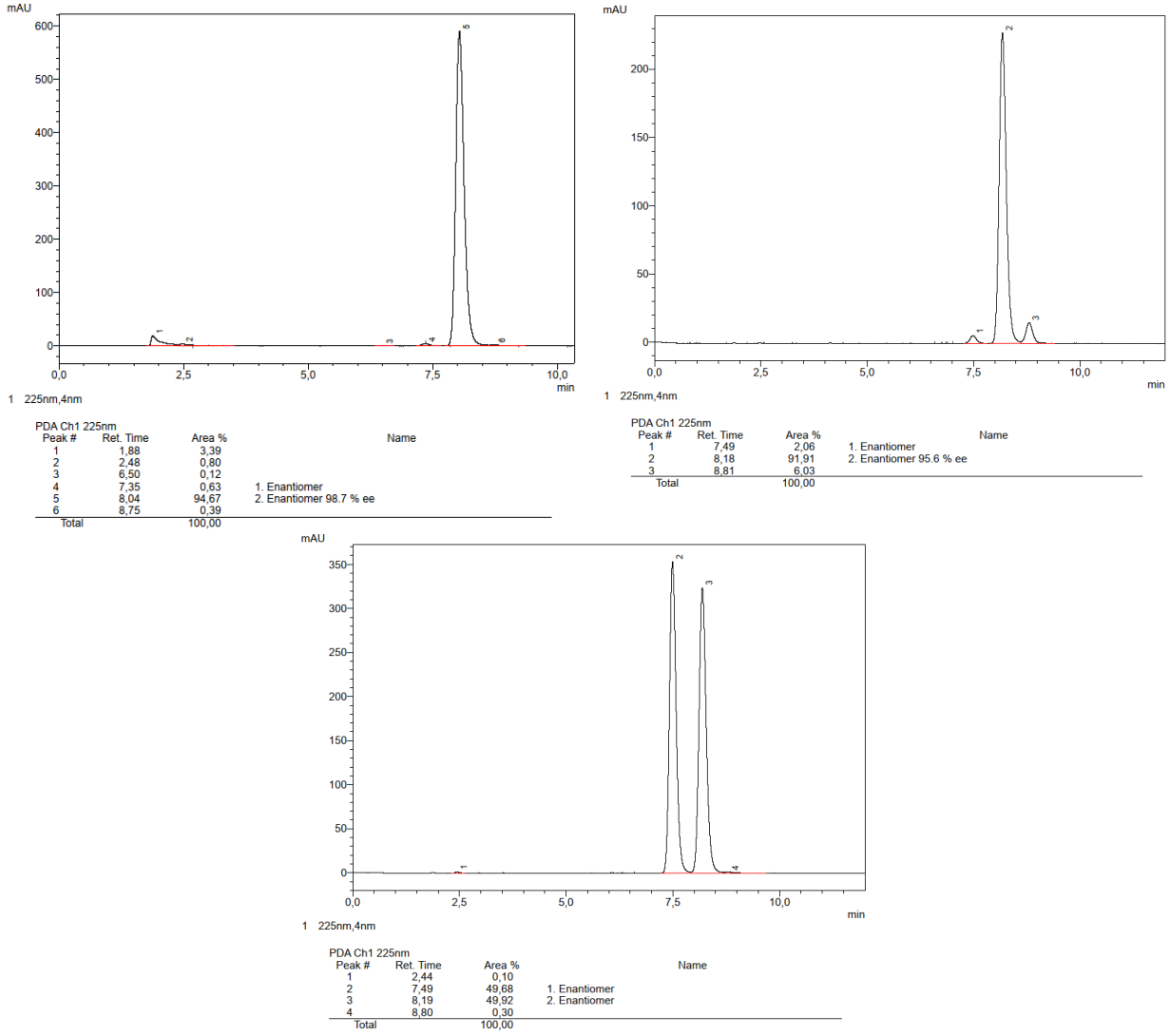


Figure S17. HPLC traces of compound **S7**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-1,2-diphenylcyclopropane-1-carboxylate (S8). Prepared according to the general procedure as a white solid; with complex **2a**: 84% yield, 69% *ee*; with complex **3b**: 87% yield, 96% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, ∅ 4.6 mm, *n*-heptane/i-propanol = 99/1, v = 1.0 mL/min, λ = 220 nm, t(major) = 4.38 min, t(minor) = 7.81 min]. m. p. = 67-70°C; $[\alpha]_D^{20}$ = +8.8 (c = 3.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 – 7.11 (m, 3H), 7.11 – 7.03 (m, 5H), 6.81 (dd, *J* = 6.7, 2.9 Hz, 2H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 3.23 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.29 (dd, *J* = 9.4, 5.1 Hz, 1H), 2.02 (dd, *J* = 7.4, 5.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ =172.2, 135.9, 133.8, 132.2, 128.2, 127.9, 127.8, 127.4, 126.7, 95.2, 74.5, 37.4, 34.0, 20.4; IR (ATR): ṽ = 1730, 1499, 1433, 1378, 1239, 1208, 1149, 1096, 1051, 969, 810, 782, 761, 712, 693, 571, 550 cm^{-1}; HRMS (ESI$^+$) for $C_{18}H_{15}Cl_3O_2Na$ [M+Na]$^+$: calcd: 391.00298, found: 391.00275.

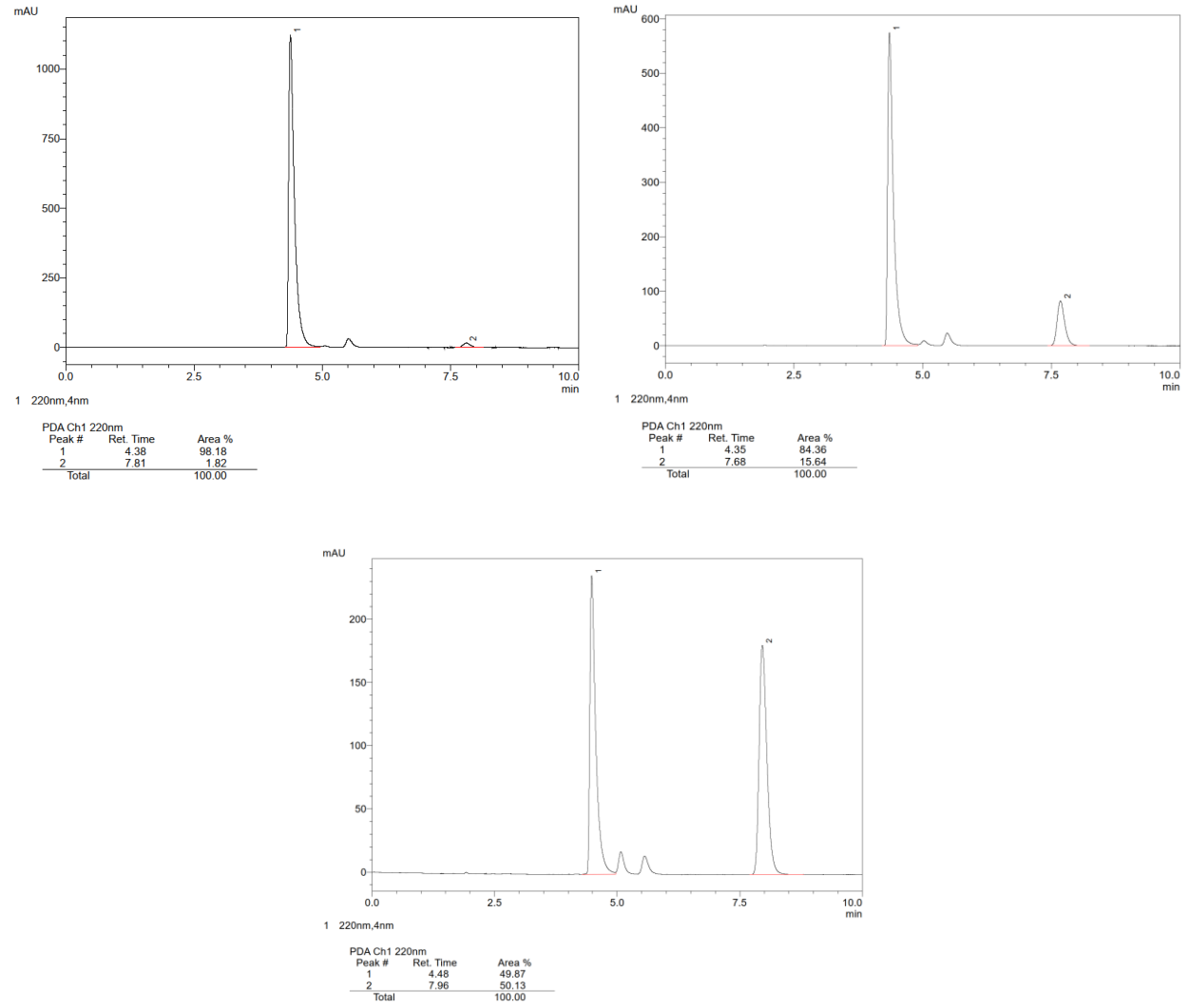
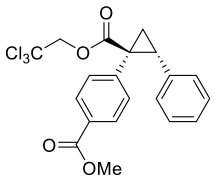


Figure S18. HPLC traces of compound **S8**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

Methyl 4-((1*S*,2*R*)-2-phenyl-1-((2,2,2-trichloroethoxy)carbonyl)cyclopropyl)benzoate (S9). Prepared



according to the general procedure as a colorless oil; with complex **2a**: 89% yield, 82% *ee*; with complex **3b**: 99% yield, 99% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IC-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 90/10, v = 1.0 mL/min, λ = 220 nm, t(major) = 4.78 min, t(minor) = 5.64 min.]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 – 7.76 (m, 2H), 7.21 – 7.10 (m, 2H), 7.10 – 7.04 (m, 3H), 6.85 – 6.75 (m, 2H), 4.83 (d, *J* = 11.9 Hz, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 3.86 (s, 3H), 3.26 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.30 (dd, *J* = 9.4, 5.2 Hz, 1H), 2.09 – 2.01 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.6, 167.0, 139.2, 135.2, 132.2, 129.2, 129.1, 128.2, 127.0, 95.0, 74.6, 60.6, 52.2, 37.2, 34.3, 20.3; IR (ATR): ṽ = 2953, 1718, 1611, 1435, 1275, 1240, 1152, 1105, 809, 752, 705, 573; HRMS (ESI$^+$) for $C_{20}H_{17}Cl_3O_4Na$ [M+Na$^+$]$^+$: calcd: 449.00846, found: 449.00802.

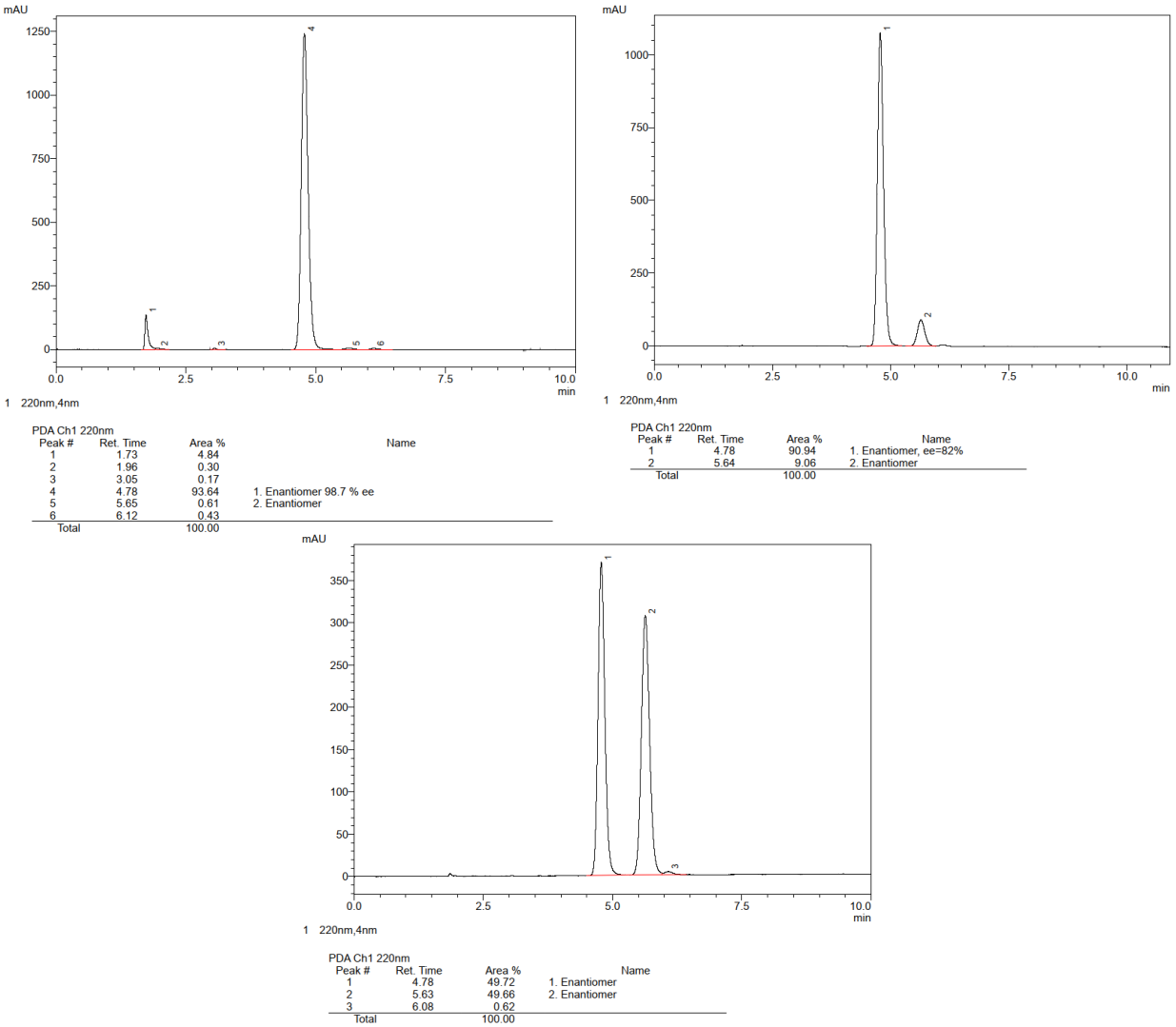
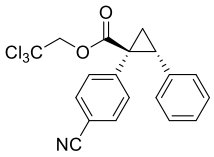


Figure S19. HPLC traces of compound **S9**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-1-(4-cyanophenyl)-2-phenylcyclopropane-1-carboxylate (S10). Prepared



according to the general procedure as a colorless oil; with complex **2a**: 36% yield, 68% *ee*; with complex **3b**: 99% yield, 97% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 90/10, v = 1.0 mL/min, λ = 220 nm, t(major) = 4.66 min, t(minor) = 4.14 min.] $[\alpha]_D^{20}$ = −11.1 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.16 – 7.05 (m, 3H), 6.83 – 6.76 (m, 2H), 4.83 (d, *J* = 11.9 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 3.29 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.33 (dd, *J* = 9.4, 5.4 Hz, 1H), 2.08 – 2.03 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.1, 139.6, 134.8, 132.9, 131.7, 128.3, 128.1, 127.3, 118.8, 111.4, 94.9, 74.6, 37.1, 34.4, 20.1; IR (ATR): ṽ = 2957, 2229, 1732, 1374, 1239, 1152, 1094, 1049, 808, 713, 695, 601, 567; HRMS (EI) for $C_{19}H_{14}NO_2Cl_3$ $[M^+]^+$: calcd: 393.00846, found: 393.00872.

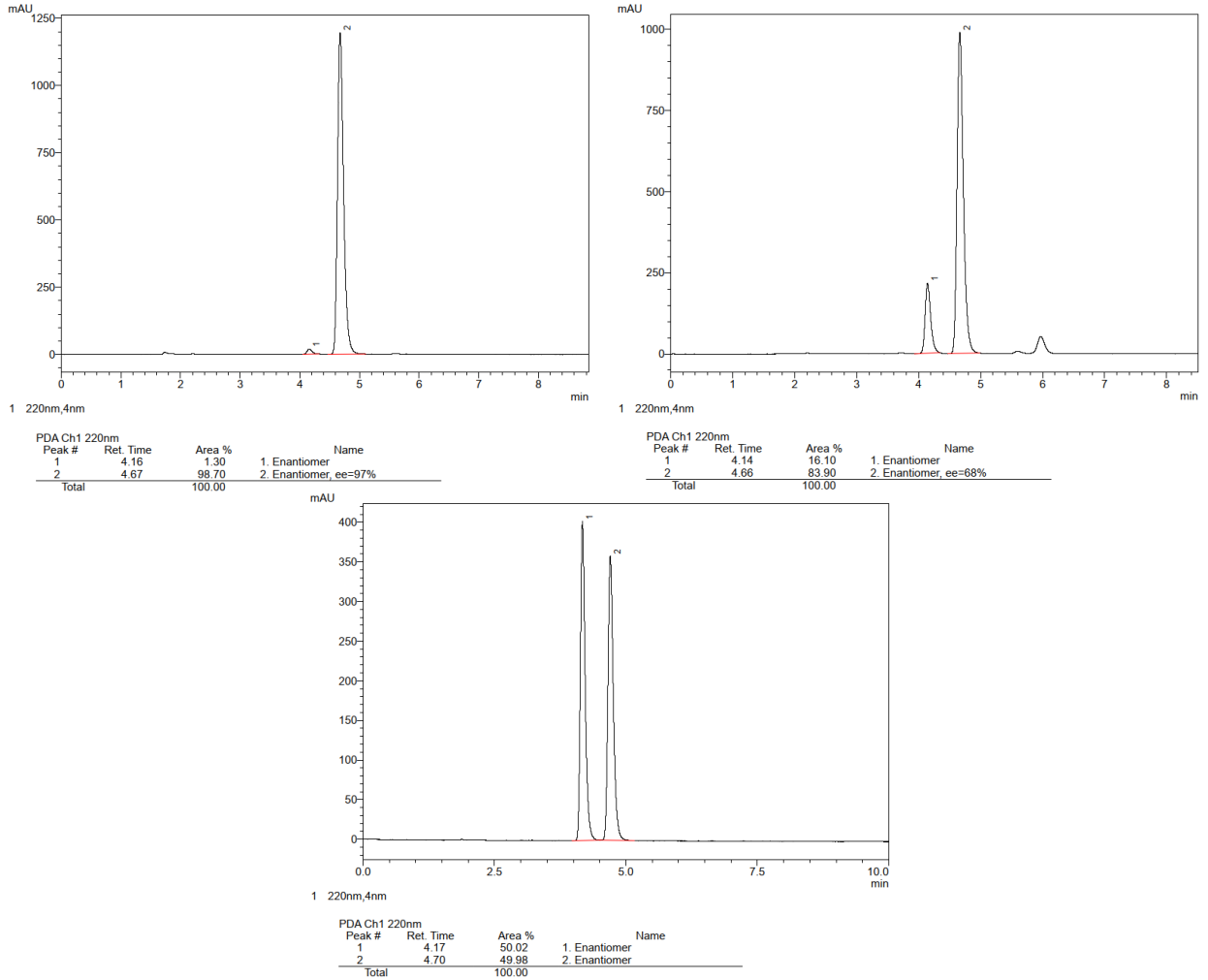


Figure S20. HPLC traces of compound **S10**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-2-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropane-1-carboxylate (S11). Prepared according to the general procedure as a colorless oil; with complex **2a**: 70% yield, 99% *ee*; with complex **3b**: 69% yield, 99% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 225 nm, t(major) = 3.50 min, t(minor) = 5.20 min.] $[\alpha]_D^{20}$ = −4.3 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 – 7.53 (m, 2H), 7.13 – 7.02 (m, 5H), 6.85 – 6.75 (m, 2H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 3.22 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.27 (dd, *J* = 9.4, 5.1 Hz, 1H), 2.07 – 1.97 (m, 1H), 1.31 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1, 136.9, 135.7, 134.3, 131.5, 128.3, 128.1, 126.8, 95.2, 83.9, 74.5, 37.5, 34.2, 25.1, 25.0, 20.4 (C-B was not detected); ^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.3; IR (ATR): $\tilde{\nu}$ = 2977, 1738, 1612, 1397, 1358, 1323, 1238, 1152, 1097, 1052, 1017, 856, 808, 703, 652, 570; HRMS (EI) for $C_{24}H_{26}BO_4Cl_3$ $[M^+]^+$: calcd: 494.09842, found: 494.09923.

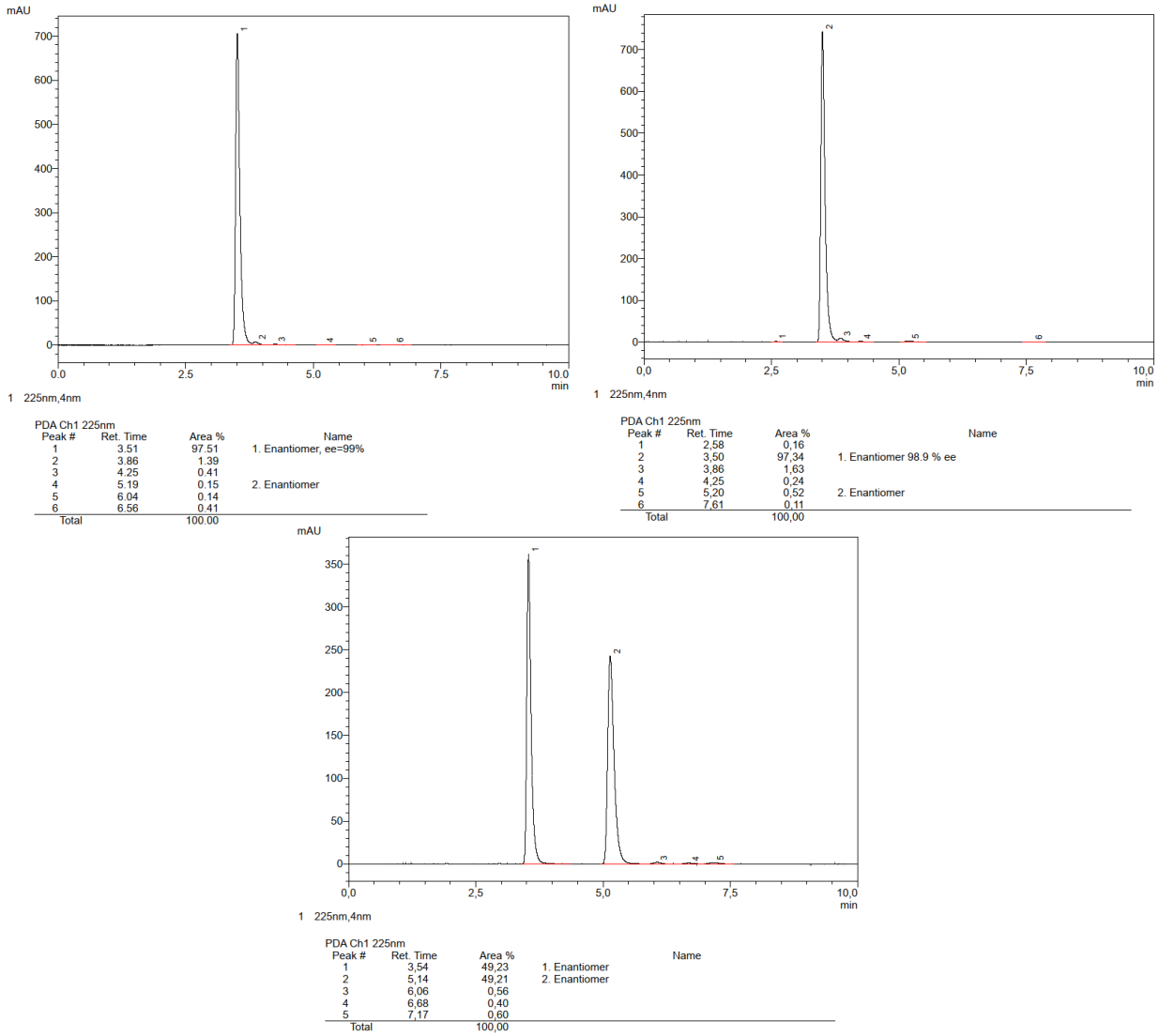
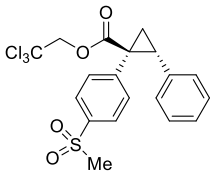


Figure S21. HPLC traces of compound **S11**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-1-(4-(methylsulfonyl)phenyl)-2-phenylcyclopropane-1-carboxylate (S12).



Prepared according to the general procedure in CH_2Cl_2/pentane (1/5) as a colorless oil; with complex **2a**: 56% yield, 97% *ee*; with complex **3b**: 85% yield, 99% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 90/10, v = 1.0 mL/min, λ = 225 nm, t(major) = 14.21 min, t(minor) = 16.22 min.] $[\alpha]_D^{20}$ = +2.5 (c = 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 – 7.65 (m, 2H), 7.31 – 7.24 (m, 2H), 7.13 – 7.04 (m, 3H), 6.84 – 6.75 (m, 2H), 4.82 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 3.31 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.96 (s, 3H), 2.36 (dd, *J* = 9.4, 5.4 Hz, 1H), 2.11 – 2.04 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.1, 140.6, 139.4, 134.7, 133.2, 128.4, 128.1, 127.4, 126.9, 95.0, 74.6, 44.7, 37.0, 34.3, 20.1; IR (ATR): ṽ = 2930, 1732, 1312, 1240, 1149, 1095, 1049, 956, 771, 713, 597, 553; HRMS (ESI$^+$) for $C_{19}H_{17}O_4SCl_3Na$ $[M+Na^+]^+$: calcd: 468.98054, found: 468.98098.

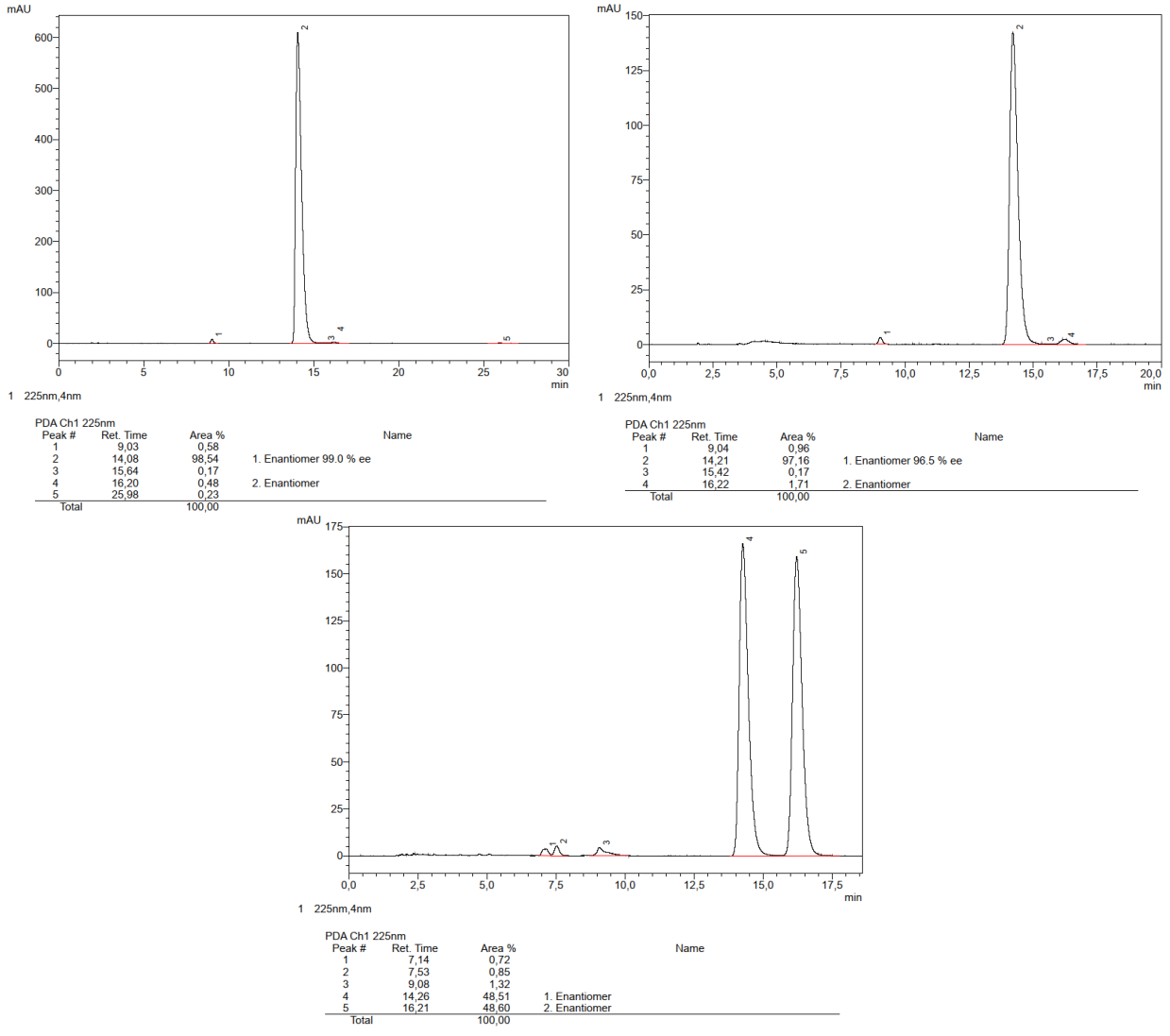


Figure S22. HPLC traces of compound **S12**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*S*)-2-butyl-1-(4-fluorophenyl)cyclopropane-1-carboxylate (S13). Prepared according to the general procedure as a colorless oil; with complex **2a**: 72% yield, 79% *ee*; with complex **3b**: 83% yield, 96% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralcel OJ-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(major) = 3.60 min, t(minor) = 2.83 min.] $[\alpha]_D^{20}$ = +11.8 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.23 (m, 2H), 7.09 – 6.96 (m, 2H), 4.78 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 1.93 (dddd, *J* = 11.0, 8.7, 6.6, 4.5 Hz, 1H), 1.86 (ddd, *J* = 9.1, 4.0, 0.6 Hz, 1H), 1.44 – 1.31 (m, 3H), 1.26 (dtd, *J* = 15.2, 7.5, 1.9 Hz, 2H), 1.18 (dd, *J* = 6.7, 4.0 Hz, 1H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.67 – 0.51 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 162.2 (d, *J* = 245.9 Hz), 133.1 (d, *J* = 8.1 Hz), 131.3 (d, *J* = 3.4 Hz), 115.1 (d, *J* = 21.5 Hz), 95.2, 74.4, 33.0, 31.3, 30.1, 29.7, 22.6, 22.3, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −115.09; IR (ATR): ṽ = 2930, 1733, 1512, 1253, 1222, 1158, 1103, 1046, 837, 804, 755, 719, 573; HRMS (ESI$^+$) for $C_{16}H_{18}O_2FCl_3$ $[M+Na^+]^+$: calcd: 366.03509, found: 366.03536.

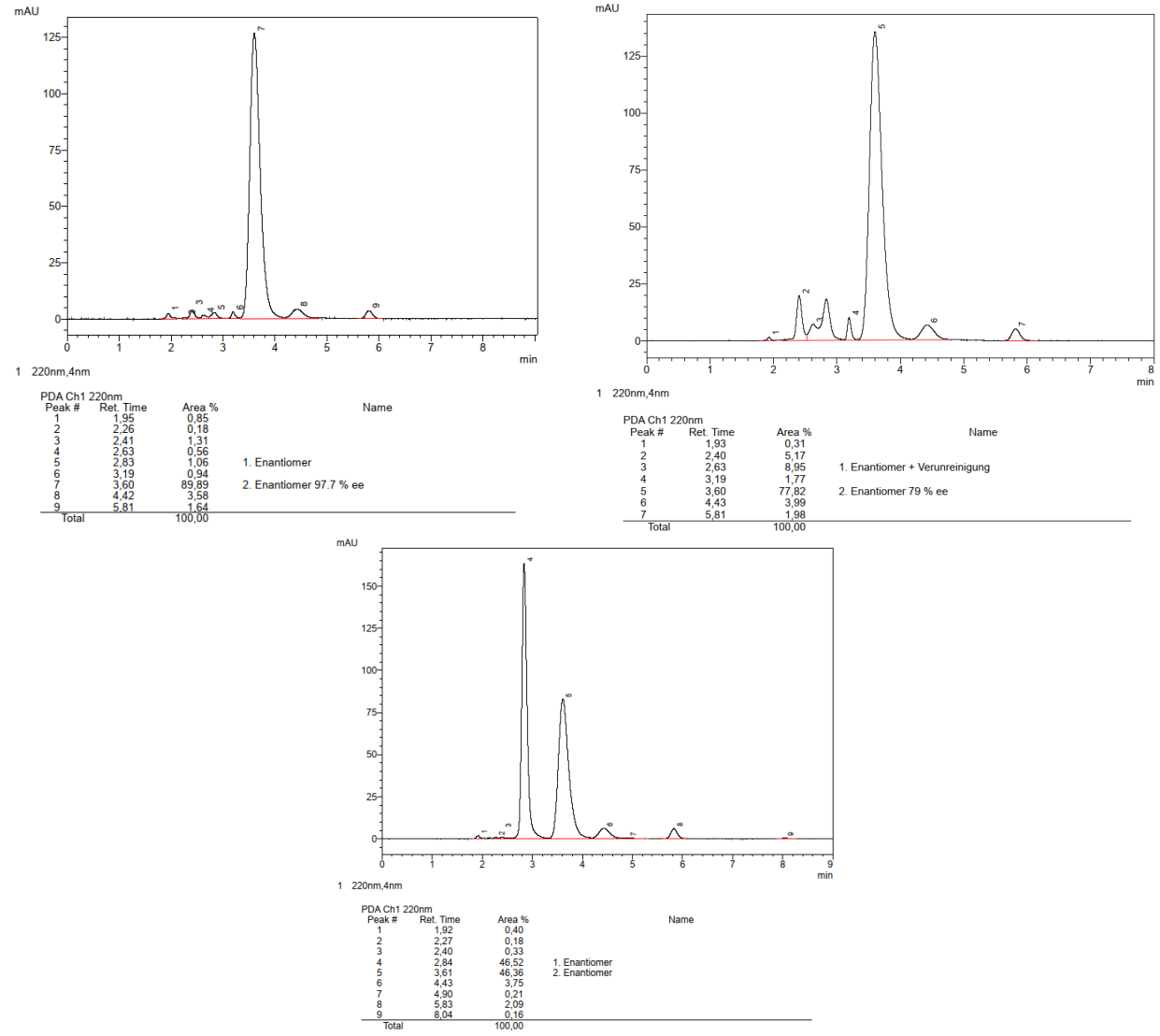
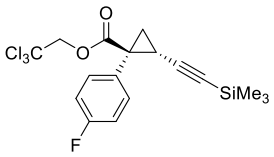


Figure S23. HPLC traces of compound **S13**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*S*)-1-(4-fluorophenyl)-2-((trimethylsilyl)ethynyl)cyclopropane-1-carboxylate (S14). 

Prepared according to the general procedure as a colorless oil; with complex **2a**: 55% yield, 77% *ee*; with complex **3b**: 65% yield, 96% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(major) = 2.53 min, t(minor) = 2.77 min.] $[\alpha]_D^{20}$ = +155.8 (c = 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.30 (m, 2H), 7.08 – 6.97 (m, 2H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H), 2.52 (dd, *J* = 9.3, 6.7 Hz, 1H), 2.12 – 2.02 (m, 1H), 1.65 (dd, *J* = 6.7, 4.4 Hz, 1H), -0.06 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.0, 162.5 (d, *J* = 246.4 Hz), 133.4 (d, *J* = 8.2 Hz), 130.2 (d, *J* = 3.4 Hz), 114.9 (d, *J* = 21.6 Hz), 103.4, 94.8, 88.3, 74.7, 34.9, 24.0, 19.4, -0.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.5; ^{29}Si NMR (60 MHz, $CDCl_3$): δ = -18.3; IR (ATR): ṽ = 2959, 2165, 1738, 1513, 1235, 1159, 1047, 875, 837, 806, 757, 718, 644, 578; HRMS (EI) for $C_{17}H_{18}O_2SiFCl_3$ $[M]^+$: calcd: 406.01202, found: 406.01169.

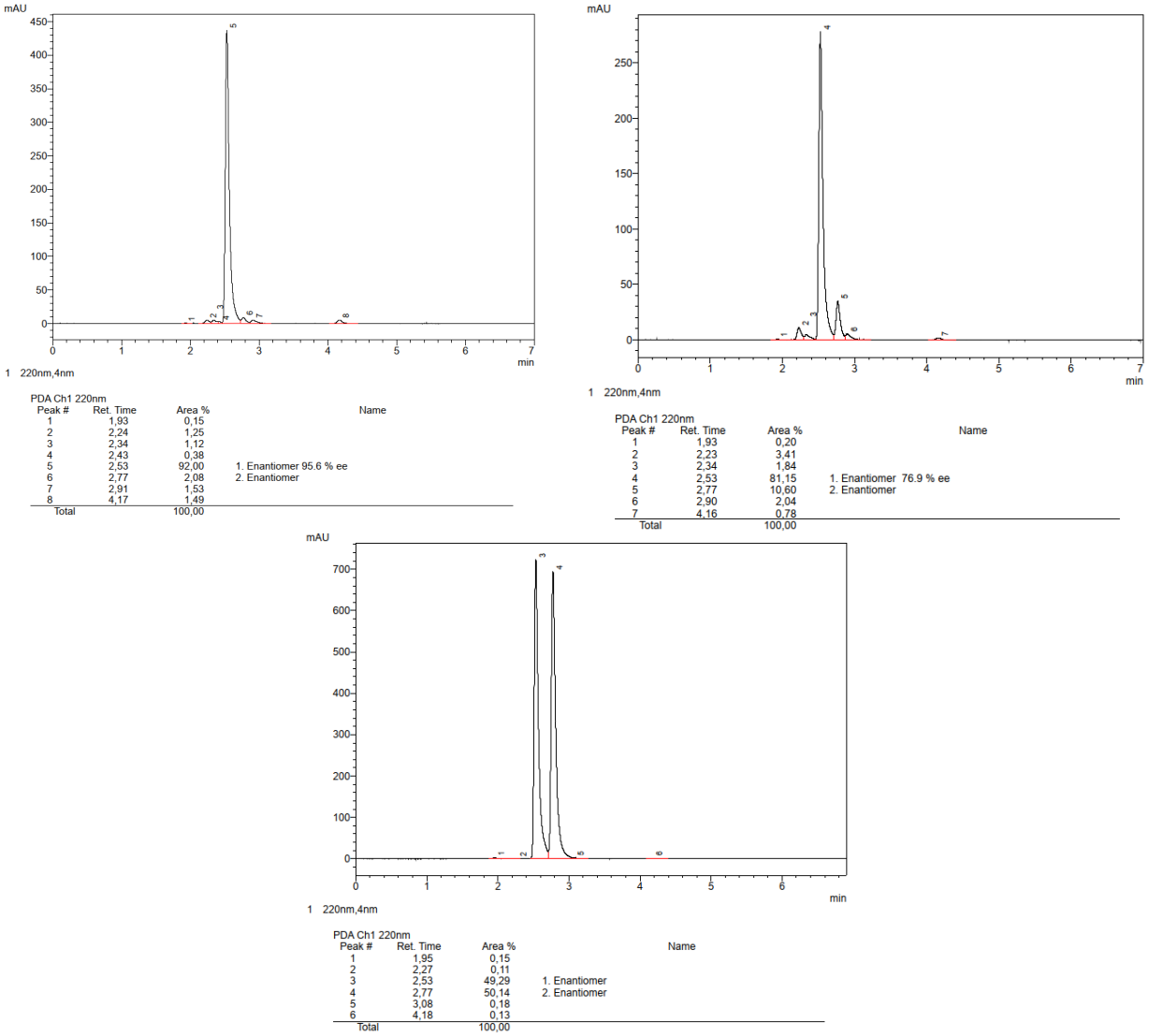
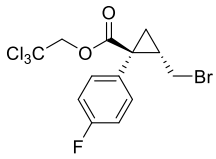


Figure S24. HPLC traces of compound **S14**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*S*)-2-(bromomethyl)-1-(4-fluorophenyl)cyclopropane-1-carboxylate (S15).



Prepared according to the general procedure as a white sticky solid; with complex **2a**: 52% yield, 83% *ee*; with complex **3b**: 89% yield, 99% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak OJ-3R, Ø 4.6 mm, CH_3CN/water = 70/30, v = 0.5 mL/min, λ = 210 nm, t(minor) = 10.62 min, t(major) = 9.78 min]. $[\alpha]_D^{20}$ = −9.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 – 7.32 (m, 2H), 7.13 – 6.98 (m, 2H), 4.80 (d, *J* = 11.9 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 3.02 (d, *J* = 7.5 Hz, 2H), 2.54 – 2.42 (m, 1H), 2.02 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.39 (dd, *J* = 6.8, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 162.7 (d, *J* = 247.4 Hz), 133.3 (d, *J* = 8.4 Hz), 129.1 (d, *J* = 3.2 Hz), 115.5 (d, *J* = 21.6 Hz), 94.9, 74.6, 36.2, 32.2, 30.5, 22.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -113.6; IR (ATR): ṽ = 1734, 1512, 1247, 1223, 1159, 1045, 840, 803, 755, 718, 570, 543; HRMS (ESI$^+$) for $C_{13}H_{11}{}^{79}BrCl_3FO_2Na$ $[M+Na^+]^+$: calcd: 424.88843, found: 424.88844.

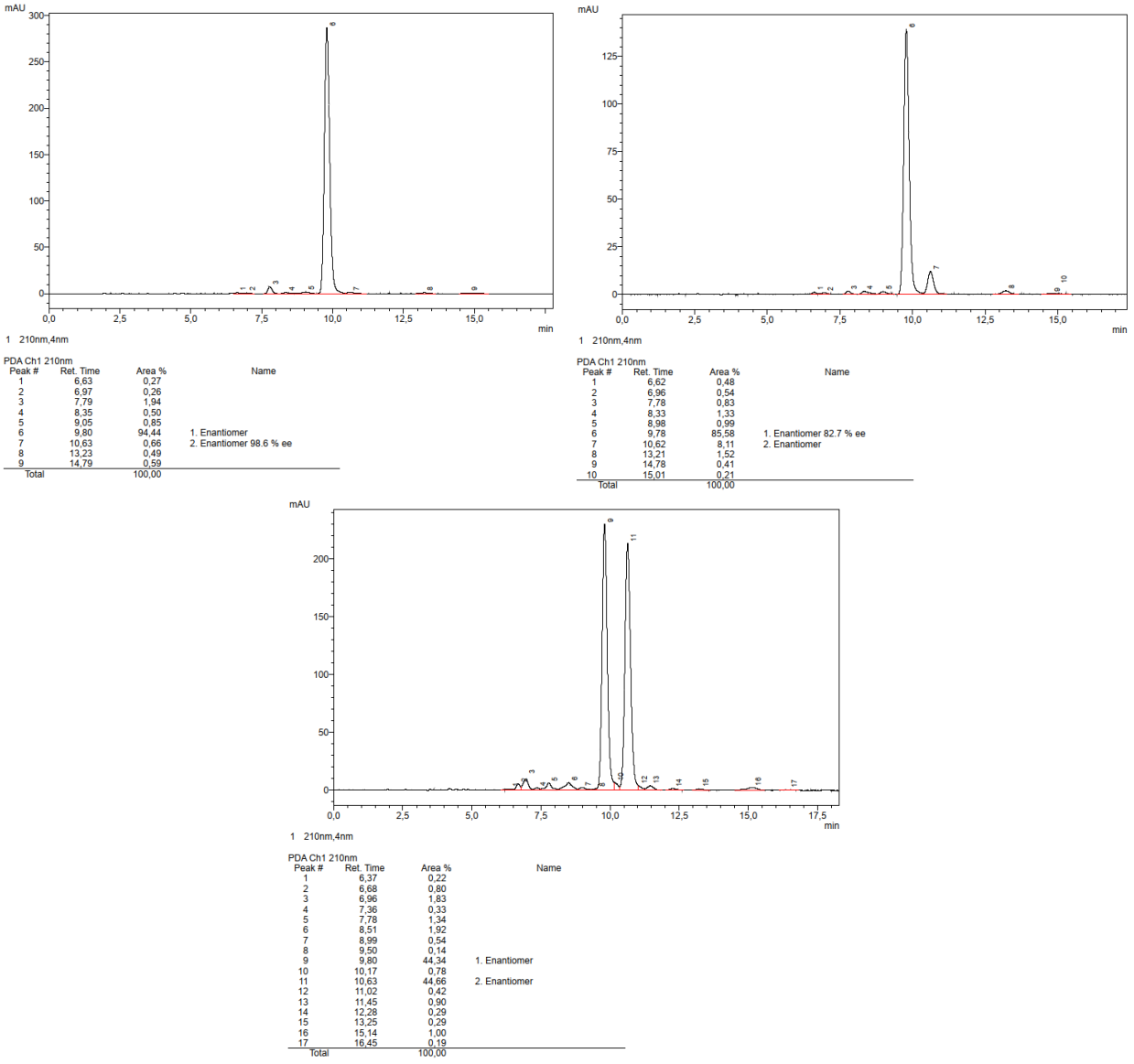
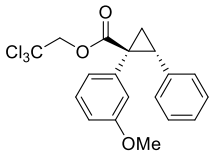


Figure S25. HPLC traces of compound **S15**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-1-(3-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (S16). Prepared



according to the general procedure as a colorless oil; with complex **2a**: 92% yield, 58% *ee*; with complex **3b**: 98% yield, 87% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(major) = 3.93 min, t(minor) = 4.24 min.] $[\alpha]_D^{20}$ = +17.8 (c = 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.85 – 6.80 (m, 2H), 6.68 (dddd, *J* = 7.0, 3.6, 2.1, 1.0 Hz, 2H), 6.56 (dd, *J* = 2.6, 1.6 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 3.59 (s, 3H), 3.20 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.26 (dd, *J* = 9.4, 5.1 Hz, 1H), 2.00 (dd, *J* = 7.5, 5.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 159.0, 135.9, 135.3, 128.7, 128.2, 128.0, 126.8, 124.6, 117.6, 113.6, 95.2, 74.5, 55.2, 37.3, 34.0, 20.5; IR (ATR): ṽ = 2957, 1732, 1584, 1433, 1238, 1147, 1043, 804, 694, 572; HRMS (ESI$^+$) for $C_{19}H_{17}O_3Cl_3Na$ [M+Na$^+$]$^+$: calcd: 421.01355, found: 421.01384.

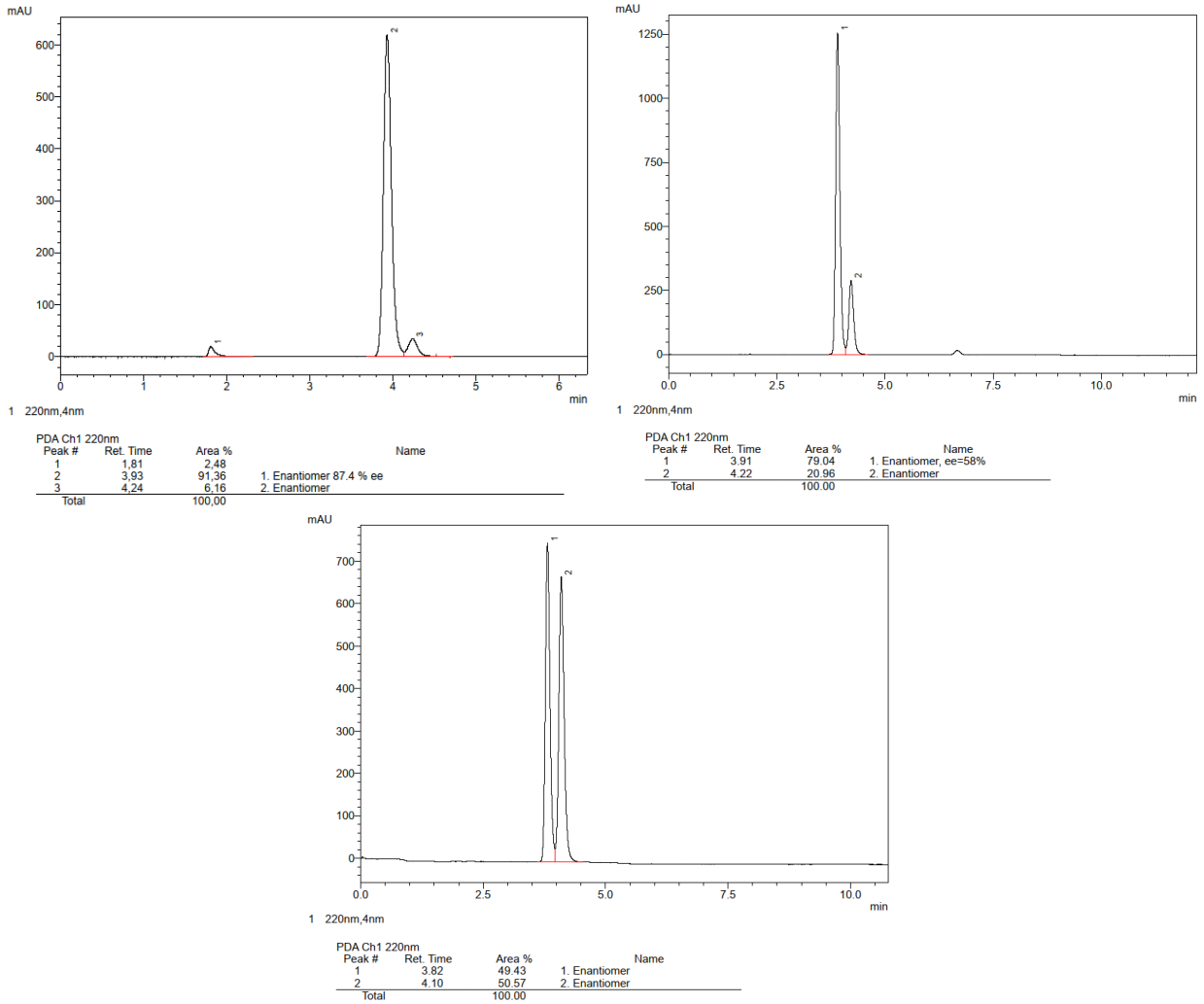
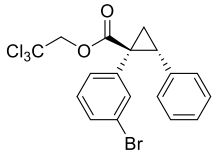


Figure S26. HPLC traces of compound **S16**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-1-(3-bromophenyl)-2-phenylcyclopropane-1-carboxylate (S17). Prepared



according to the general procedure as a colorless oil; with complex **2a**: 98% yield, 74% *ee*; with complex **3b**: 99% yield, 95% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralcel OJ-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 95/5, v = 1.0 mL/min, λ = 220 nm, t(major) = 5.66 min, t(minor) = 4.18 min.] $[\alpha]_D^{20}$ = −10.5 (c = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.21 (m, 2H), 7.17 – 7.06 (m, 3H), 7.02 – 6.91 (m, 2H), 6.86 – 6.79 (m, 2H), 4.85 (d, *J* = 11.8 Hz, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 3.23 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.28 (dd, *J* = 9.4, 5.2 Hz, 1H), 2.00 (dd, *J* = 7.5, 5.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 136.3, 135.2, 135.1, 130.9, 130.6, 129.3, 128.2, 128.2, 127.1, 121.7, 95.1, 74.6, 36.8, 34.2, 20.2; IR (ATR): ṽ = 3032, 1731, 1374, 1238, 1151, 1108, 1049, 813, 765, 697, 572; HRMS (ESI$^+$) for $C_{18}H_{14}O_2{}^{79}BrCl_3Na$ [M+Na$^+$]$^+$: calcd: 468.91351, found: 468.91391.

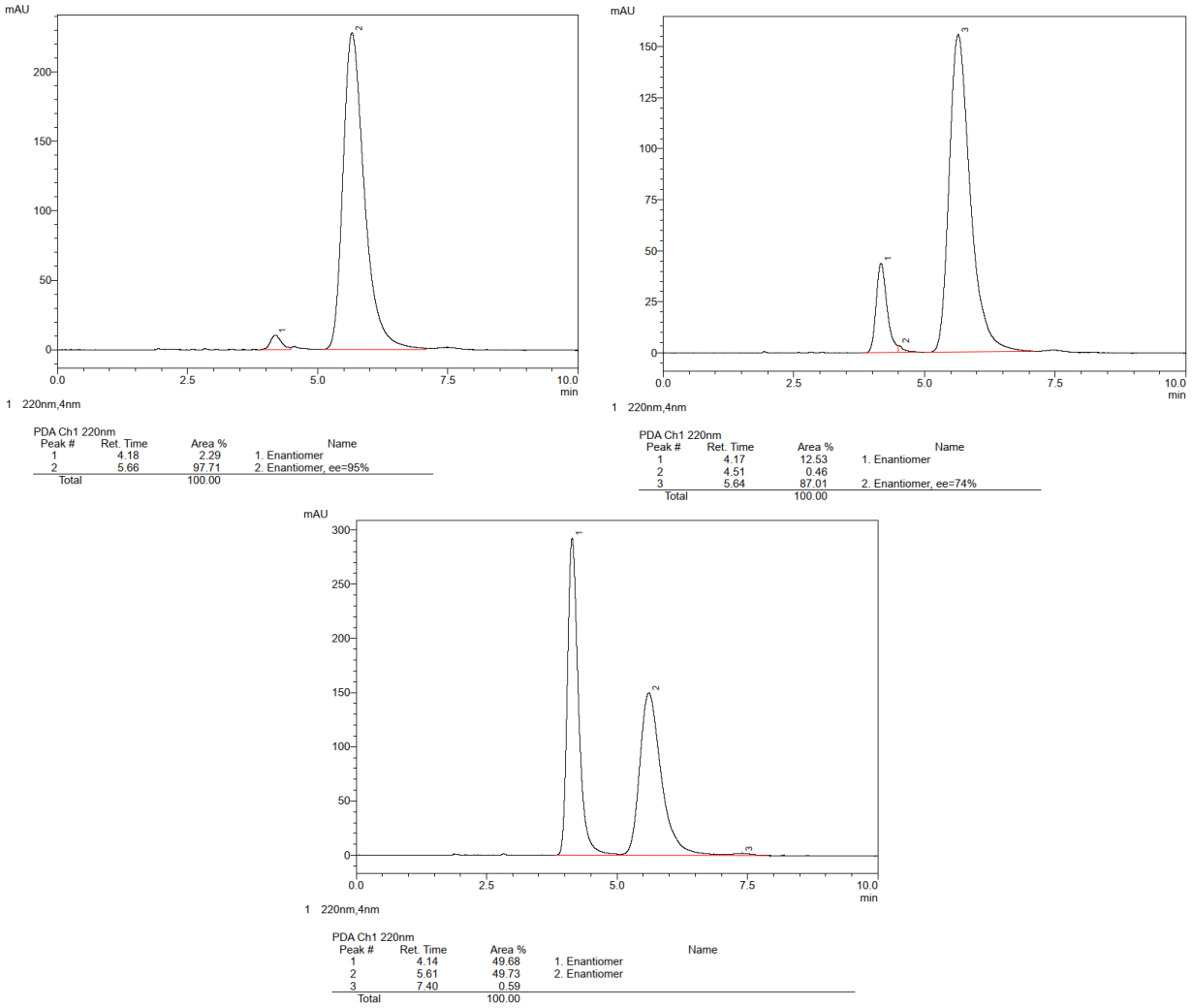
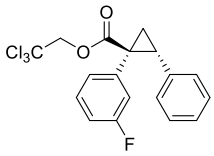


Figure S27. HPLC traces of compound **S17**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-1-(3-fluorophenyl)-2-phenylcyclopropane-1-carboxylate (S18). Prepared



according to the general procedure as a colorless oil; with complex **2a**: 98% yield, 80% *ee*; with complex **3b**: 97% yield, 97% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(major) = 3.83 min, t(minor) = 4.51 min.] $[\alpha]_D^{20}$ = +21.5 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 – 7.04 (m, 4H), 6.81 (d, *J* = 0.5 Hz, 5H), 4.83 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 3.24 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.28 (dd, *J* = 9.4, 5.2 Hz, 1H), 2.01 (dd, *J* = 7.5, 5.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 162.3 (d, *J* = 245.3 Hz), 136.4 (d, *J* = 7.7 Hz), 135.3, 129.2 (d, *J* = 8.4 Hz), 128.2, 128.1, 127.9 (d, *J* = 2.8 Hz), 127.0, 119.1 (d, *J* = 21.5 Hz), 114.5 (d, *J* = 21.1 Hz), 95.1, 74.6, 37.0 (d, *J* = 2.4 Hz), 34.2, 20.3; ^{19}F NMR (470 MHz, $CDCl_3$): δ = −114.2; IR (ATR): ṽ = 3031, 1732, 1588, 1443, 1239, 1217, 1144, 1096, 1048, 806, 742, 711, 692, 571, 524; HRMS (EI) for $C_{18}H_{14}O_2FCl_3$ $[M^+]^+$: calcd: 386.00379, found: 386.00412.

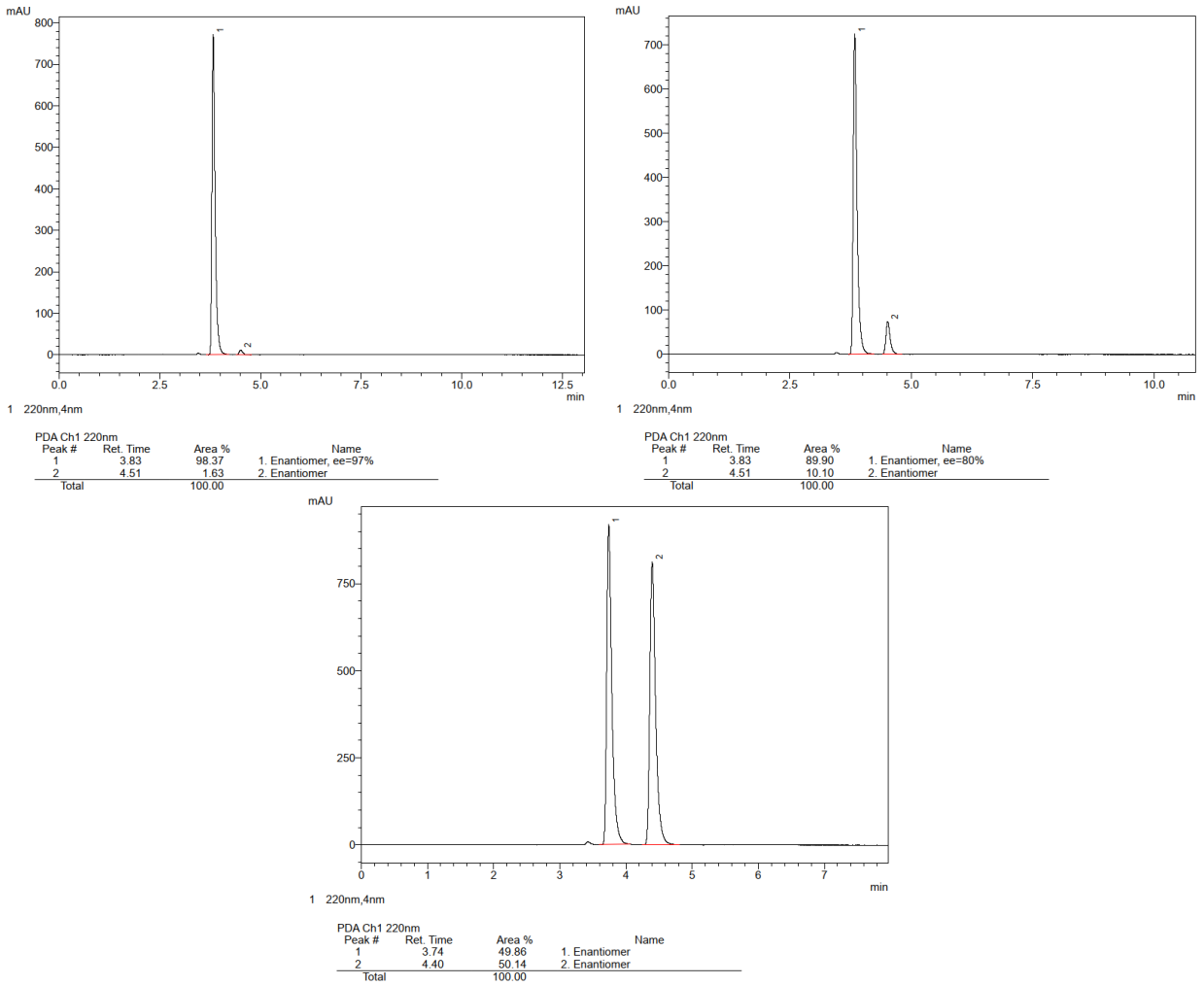
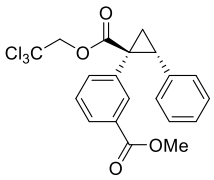


Figure S28. HPLC traces of compound **S18**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

Methyl 3-((1*S*,2*R*)-2-phenyl-1-((2,2,2-trichloroethoxy)carbonyl)cyclopropyl)benzoate (S19). Prepared



according to the general procedure as a colorless oil; with complex **2a**: 99% yield, 85% *ee*; with complex **3b**: 99% yield, 98% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 90/10, v = 1.0 mL/min, λ = 220 nm, t(major) = 4.03 min, t(minor) = 5.26 min.] $[\alpha]_D^{20}$ = +17.8 (c = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dt, *J* = 1.7, 1.0 Hz, 1H), 7.81 (ddd, *J* = 6.0, 2.8, 1.7 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.10 – 7.03 (m, 3H), 6.85 – 6.76 (m, 2H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 3.87 (s, 3H), 3.26 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.32 (dd, *J* = 9.4, 5.3 Hz, 1H), 2.08 (dd, *J* = 7.4, 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.8, 167.0, 137.1, 135.3, 134.5, 132.9, 129.9, 128.8, 128.3, 128.1, 127.9, 127.0, 95.1, 74.6, 52.2, 37.0, 34.2, 20.2; IR (ATR): ṽ = 2952, 1719, 1435, 1287, 1261, 1238, 1207, 1151, 1098, 1052, 806, 778, 749, 714, 698, 572; HRMS (ESI$^+$) for $C_{20}H_{17}O_4Cl_3Na$ [M+Na$^+$]$^+$: calcd: 449.00846, found: 449.00893.

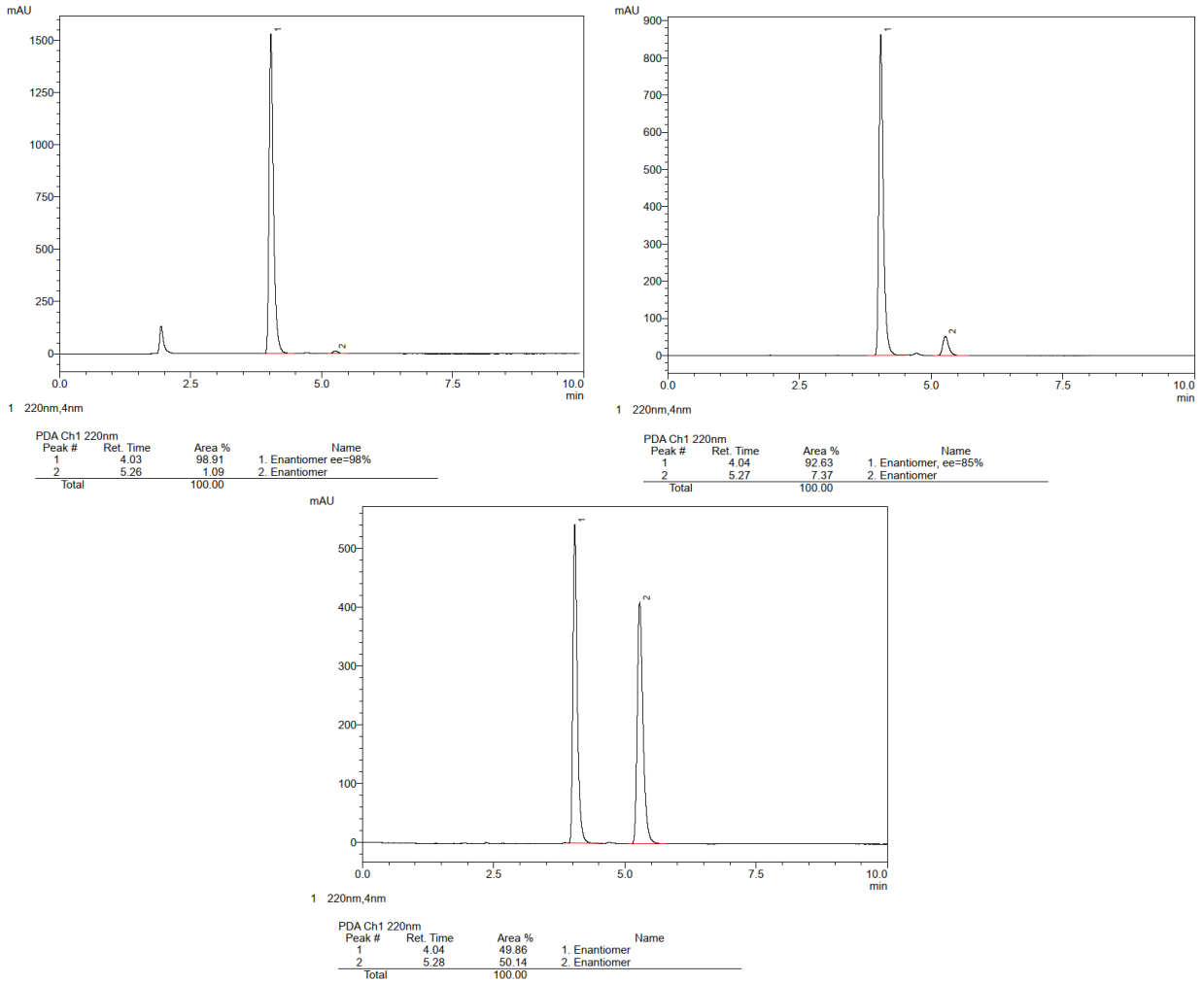
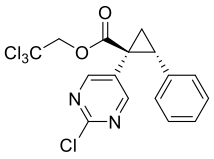


Figure S29. HPLC traces of compound **S19**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-1-(2-chloropyrimidin-5-yl)-2-phenylcyclopropane-1-carboxylate (S20).



Prepared according to the general procedure at room temperature as a colorless oil; with complex **2a**: 82% yield, 91% *ee*; with complex **3b**: 87% yield, 96% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 90/10, v = 1.0 mL/min, λ = 220 nm, t(major) = 7.01 min, t(minor) = 5.39 min.] $[\alpha]_D^{20}$ = −3.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 2H), 7.23 – 7.12 (m, 3H), 6.91 – 6.84 (m, 2H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 3.35 (dd, *J* = 9.4, 7.6 Hz, 1H), 2.41 (dd, *J* = 9.4, 5.6 Hz, 1H), 2.12 – 2.02 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0, 162.2, 160.1, 133.4, 128.8, 128.1, 128.0, 127.2, 94.6, 74.6, 33.9, 31.6, 18.8; IR (ATR): ṽ = 2956, 1727, 1540, 1403, 1244, 1144, 1109, 1082, 1057, 782, 766, 710, 639, 574, 494; HRMS (ESI$^+$) for $C_{16}H_{12}N_2O_2Cl_4Na$ [M+Na$^+$]$^+$: calcd: 426.95451, found: 426.95493.

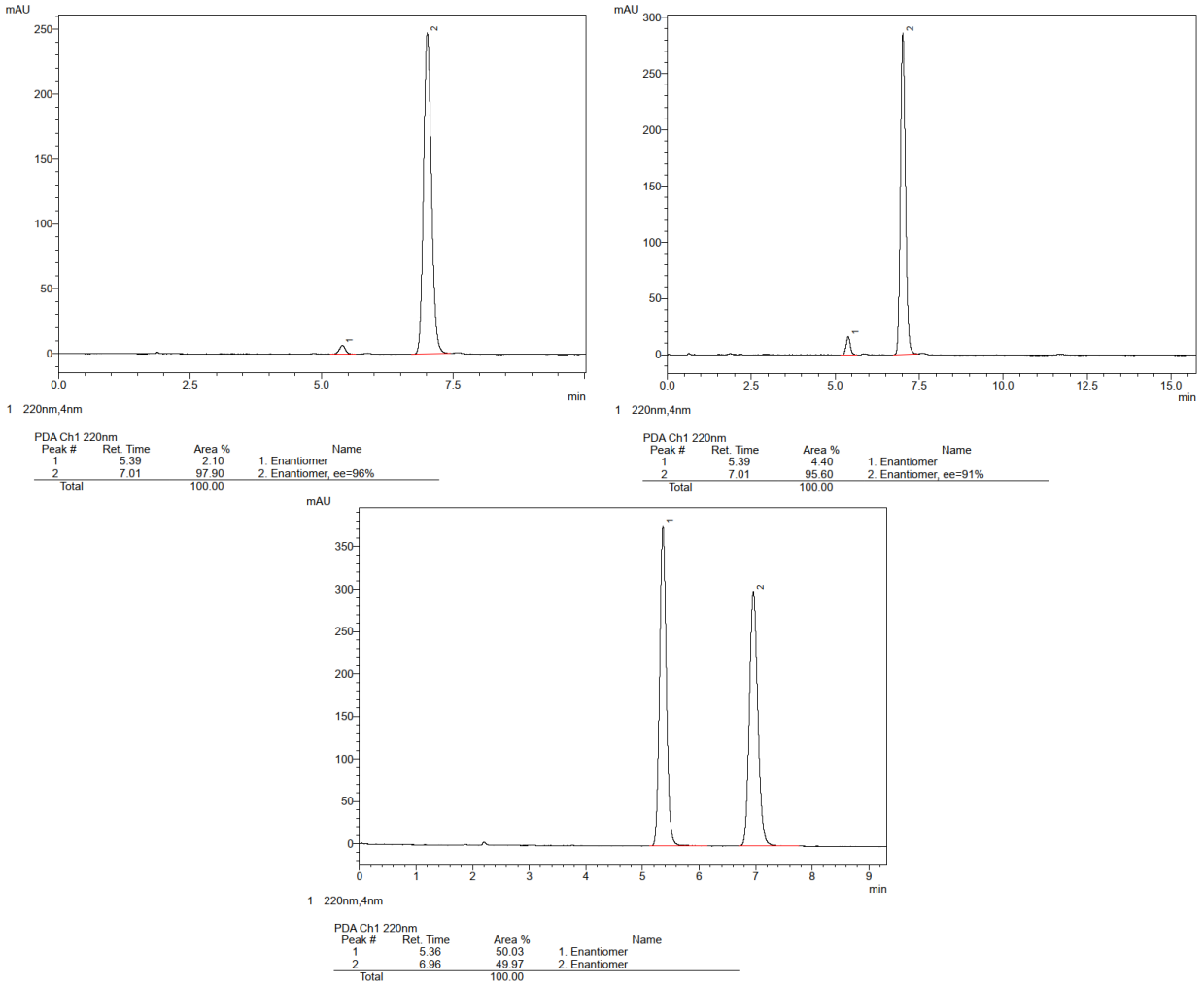
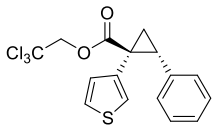


Figure S30. HPLC traces of compound **S20**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-2-phenyl-1-(thiophen-3-yl)cyclopropane-1-carboxylate (S21). Prepared



according to the general procedure as a colorless sticky solid; with complex **2a**: 97% yield, 73% *ee*; with complex **3b**: 99% yield, 94% *ee.* [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, ∅ 4.6 mm, *n*-heptane/i-propanol = 99/1, v = 1.0 mL/min, λ = 220 nm, t(major) = 5.01 min, t(minor) = 9.63 min.] $[\alpha]_D^{20}$ = +4.6 (c = 3.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 – 7.09 (m, 3H), 7.03 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.97 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.89 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.75 (dt, *J* = 5.0, 1.1 Hz, 1H), 4.87 (dd, *J* = 11.9, 0.8 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 3.18 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.28 (dd, *J* = 9.4, 5.1 Hz, 1H), 2.02 (dd, *J* = 7.4, 5.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.8, 135.7, 134.7, 130.4, 128.2, 128.0, 126.9, 125.8, 124.6, 95.2, 74.5, 34.4, 32.4, 20.6; IR (ATR): ṽ = 1730, 1604, 1454, 1433, 1377, 1245, 1213, 1197, 1144, 1095, 1053, 975, 818, 790, 765, 693, 645, 571, 535 cm^{-1}; HRMS (ESI$^+$) for $C_{16}H_{13}Cl_3O_2SNa$ [M+Na]$^+$: calcd: 396.95941, found: 396.95900.

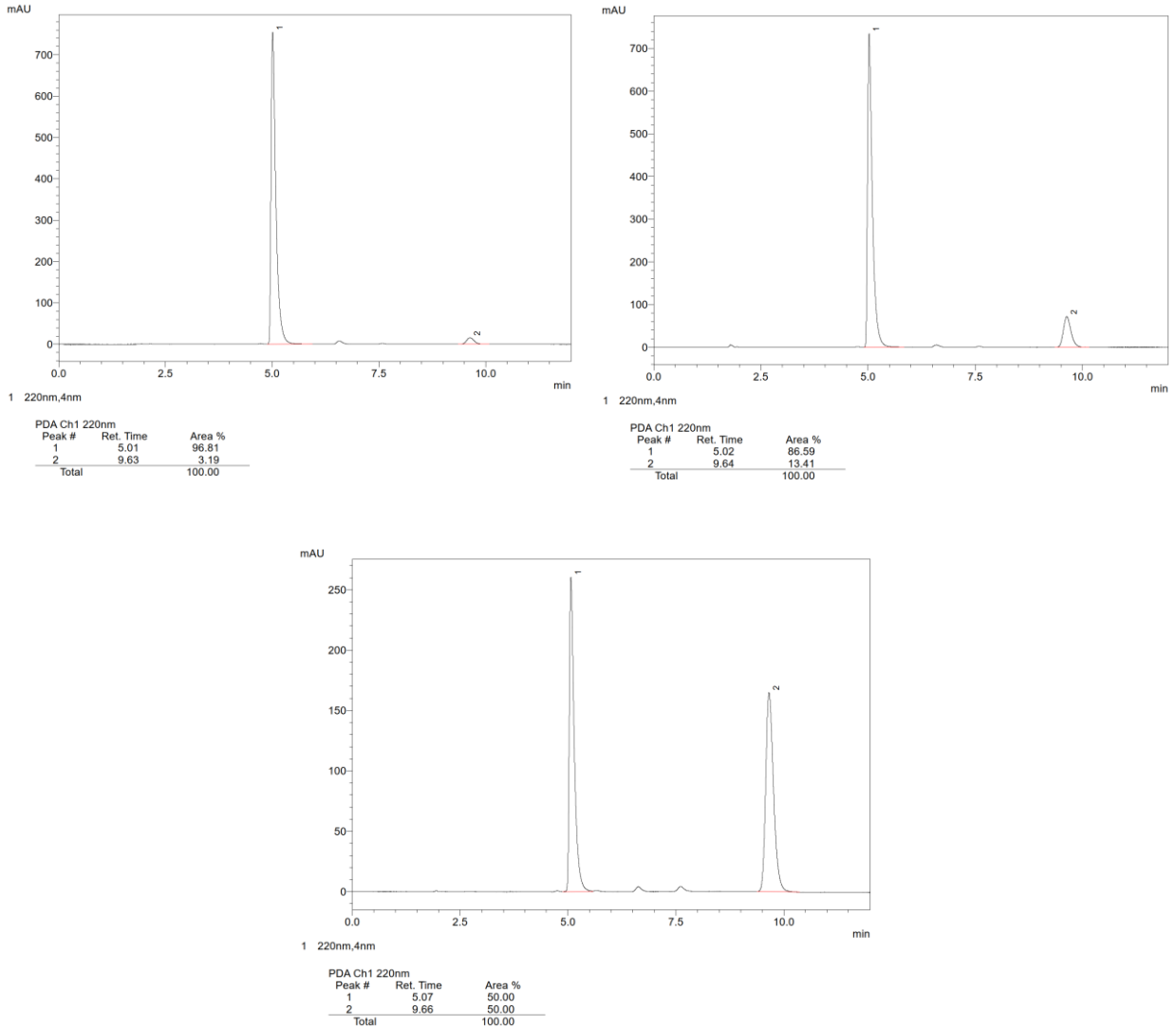
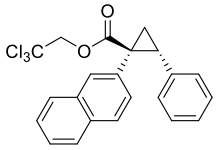


Figure S31. HPLC traces of compound **S21**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (1*S*,2*R*)-1-(naphthalen-2-yl)-2-phenylcyclopropane-1-carboxylate (S22). Prepared



according to the general procedure as a white solid; with complex **2a**: 85% yield, 96% *ee*; with complex **3b**: 91% yield, 99% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, ∅ 4.6 mm, *n*-heptane/i-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 3.89 min, t(major) = 4.29 min]. m. p. = 100-102°C; $[\alpha]_D^{20}$ = −40.2 (c = 3.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 – 7.65 (m, 3H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.42 (dt, *J* = 6.3, 3.4 Hz, 2H), 7.11 (dt, *J* = 8.6, 1.6 Hz, 1H), 7.06 – 6.98 (m, 3H), 6.91 – 6.78 (m, 2H), 4.88 (dd, *J* = 11.9, 1.2 Hz, 1H), 4.63 (dd, *J* = 12.0, 1.0 Hz, 1H), 3.30 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.38 (ddd, *J* = 9.4, 5.1, 1.1 Hz, 1H), 2.21 – 2.10 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ =172.3, 135.7, 133.1, 132.7, 131.7, 130.9, 130.2, 128.3, 128.0, 127.9, 127.7, 127.2, 126.8, 126.0, 125.8, 95.2, 74.5, 37.5, 34.2, 20.5; IR (ATR): ṽ = 1723, 1448, 1376, 1245, 1150, 1129, 1100, 1082, 1054, 979, 966, 908, 866, 834, 800, 748, 715, 964, 652, 575, 546, 478 cm^{-1}; HRMS (ESI^+) for $C_{22}H_{17}Cl_3O_2Na$ $[M+Na]^+$: calcd: 441.01863, found: 441.01828.

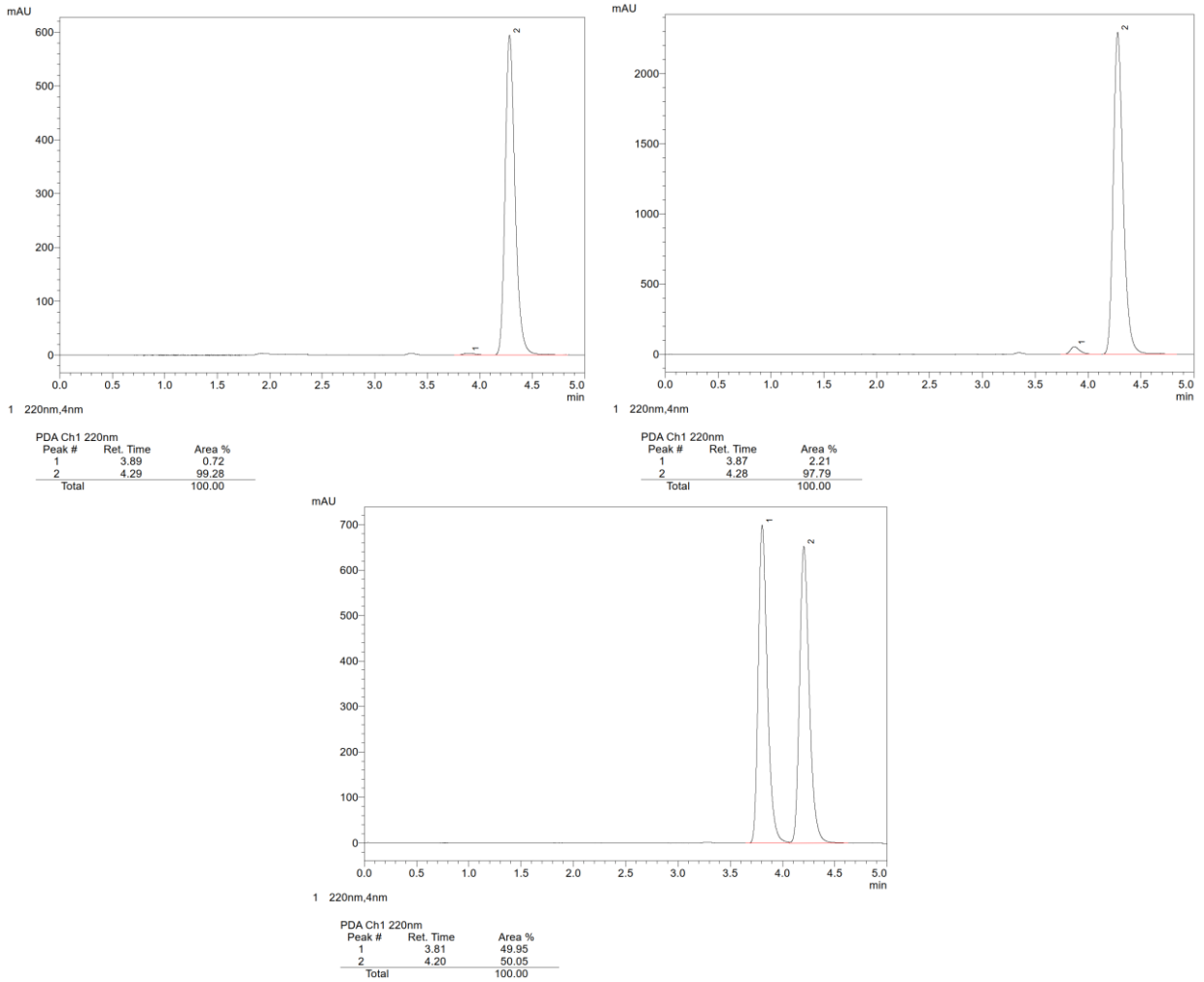


Figure S32. HPLC traces of compound **S22**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (*S*)-1-(4-fluorophenyl)spiro[2.3]hexane-1-carboxylate (S23). Prepared according to the general procedure as a colorless oil; with complex **2a**: 85% yield, 70% *ee*; with complex **3b**: 95% yield, 96% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak OJ-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(major) = 6.14 min, t(minor) = 4.33 min.] $[\alpha]_D^{20}$ = −9.4 (c = 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.23 (m, 2H), 7.07 – 6.96 (m, 2H), 4.87 (dd, *J* = 11.9, 1.1 Hz, 1H), 4.51 (d, *J* = 1.2 Hz, 1H), 2.51 – 2.39 (m, 1H), 2.39 – 2.25 (m, 1H), 2.16 – 2.02 (m, 2H), 2.01 – 1.89 (m, 2H), 1.67 – 1.56 (m, 1H), 1.55 – 1.48 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9, 162.1 (d, *J* = 245.7 Hz), 132.7 (d, *J* = 8.2 Hz), 131.9 (d, *J* = 3.3 Hz), 115.1 (d, *J* = 21.5 Hz), 95.1, 74.4, 37.4, 36.5, 29.5, 28.5, 27.8, 16.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −115.2; IR (ATR): $\tilde{\nu}$ = 2952, 1730, 1512, 1312, 1179, 1092, 1047, 836, 806, 751, 719, 573, 535; HRMS (EI) for $C_{15}H_{14}O_2FCl_3$ $[M]^+$: calcd: 350.00379, found: 350.00410.

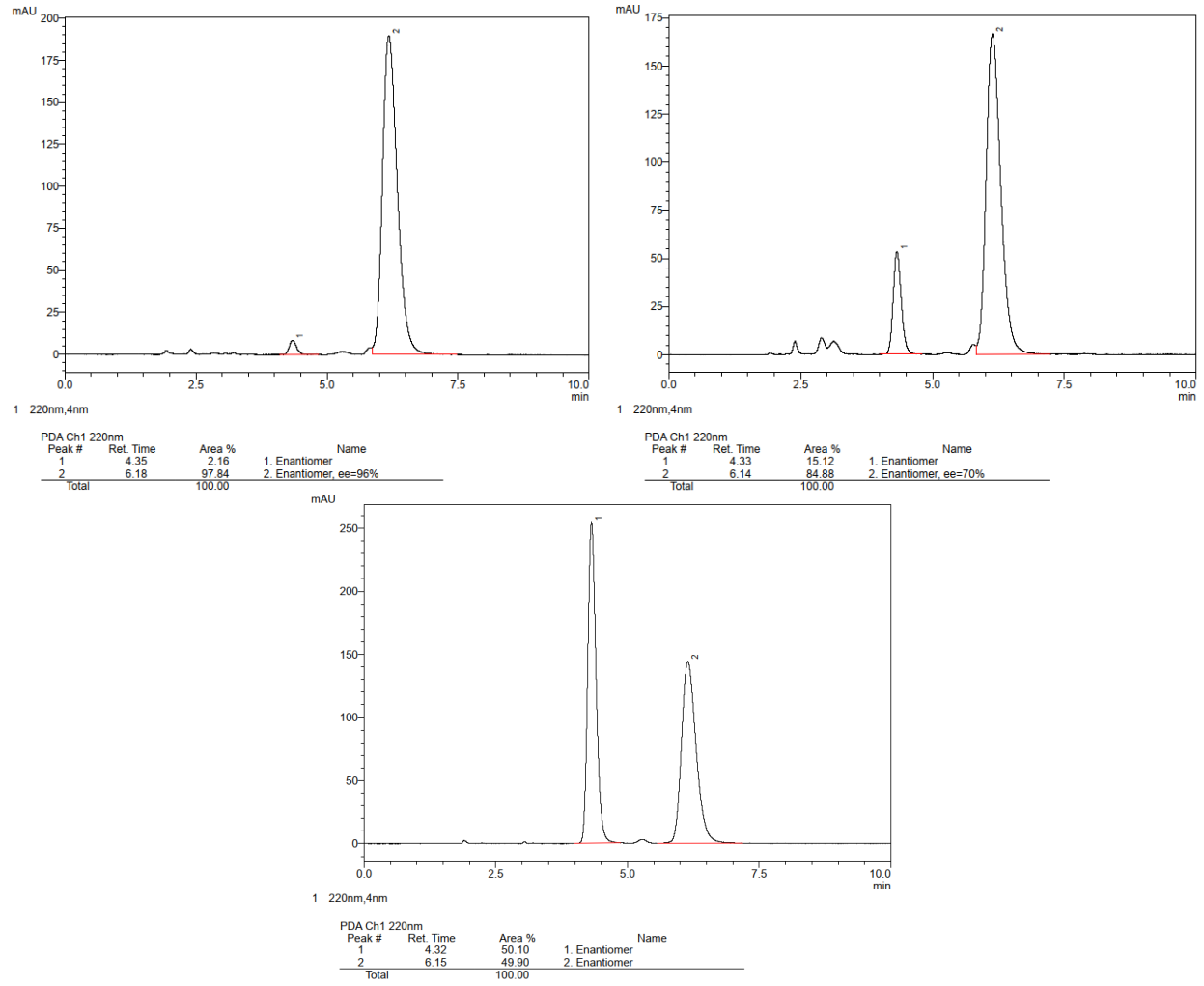


Figure S33. HPLC traces of compound **S23**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (*S*)-1-(4-fluorophenyl)spiro[2.5]octane-1-carboxylate (S24). Prepared according to the general procedure as a colorless oil; with complex **2a**: 80% yield, 74% *ee*; with complex **3b**: 87% yield, 98% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 99.9/0.1, v = 1.0 mL/min, λ = 220 nm, t(major) = 4.94 min, t(minor) = 6.10 min.] $[\alpha]_D^{20}$ = −42.5 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.34 (m, 2H), 7.02 – 6.93 (m, 2H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 1.77 – 1.40 (m, 7H), 1.39 – 1.29 (m, 3H), 1.17 (dd, *J* = 4.9, 1.0 Hz, 1H), 0.70 (dt, *J* = 10.2, 3.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.3, 162.1 (d, *J* = 245.9 Hz), 133.2 (d, *J* = 8.1 Hz), 132.4 (d, *J* = 3.5 Hz), 114.8 (d, *J* = 21.1 Hz), 95.0, 74.7, 39.6, 34.8, 34.1, 31.0, 26.2, 25.9, 25.5, 24.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −115.3; IR (ATR): ṽ = 2929, 1732, 1510, 1225, 1167, 1119, 1051, 837, 804, 756, 718, 575; HRMS (EI) for $C_{17}H_{18}O_2FCl_3$ $[M]^+$: calcd: 378.03509, found: 378.03532.

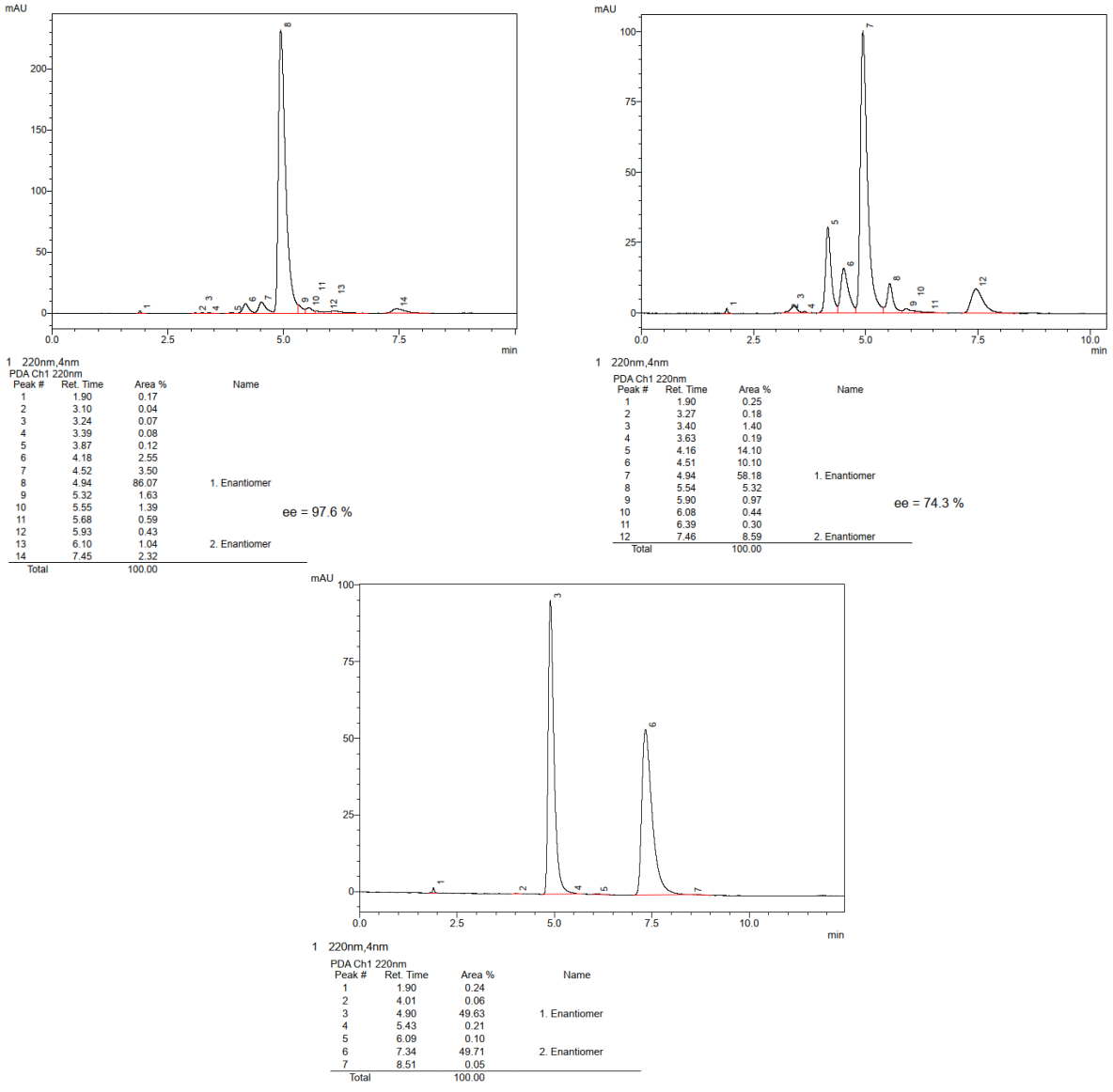


Figure S34. HPLC traces of compound **S24**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

1-((1*S*,2*R*)-1,2-diphenylcyclopropyl)ethan-1-one (S25). Prepared according to the general procedure as a colorless oil; with complex **2a**: 25% yield, 78% *ee*; with complex **3b**: 68% yield, 91% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralcel OJ-3, ∅ 4.6 mm, *n*-heptane/i-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 4.65 min, t(major) = 6.49 min.] $[\alpha]_D^{20}$ = +136.5 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 – 7.15 (m, 3H), 7.10 – 6.98 (m, 5H), 6.79 – 6.73 (m, 2H), 3.15 (dd, *J* = 9.2, 7.3 Hz, 1H), 2.11 (dd, *J* = 9.2, 4.3 Hz, 1H), 2.02 (s, 3H), 1.82 (dd, *J* = 7.3, 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 208.0, 137.0, 136.7, 132.2, 128.3, 128.1, 127.8, 127.4, 126.4, 46.1, 35.1, 30.1, 23.6; IR (ATR): ṽ = 1687, 1600, 1496, 1419, 1372, 1354, 1240, 1207, 1148, 981, 882, 756, 696, 677, 644, 544, 509 cm^{-1}; HRMS (ESI$^+$) for $C_{17}H_{16}ONa$ $[M+Na]^+$: calcd: 259.10933, found: 259.10924.

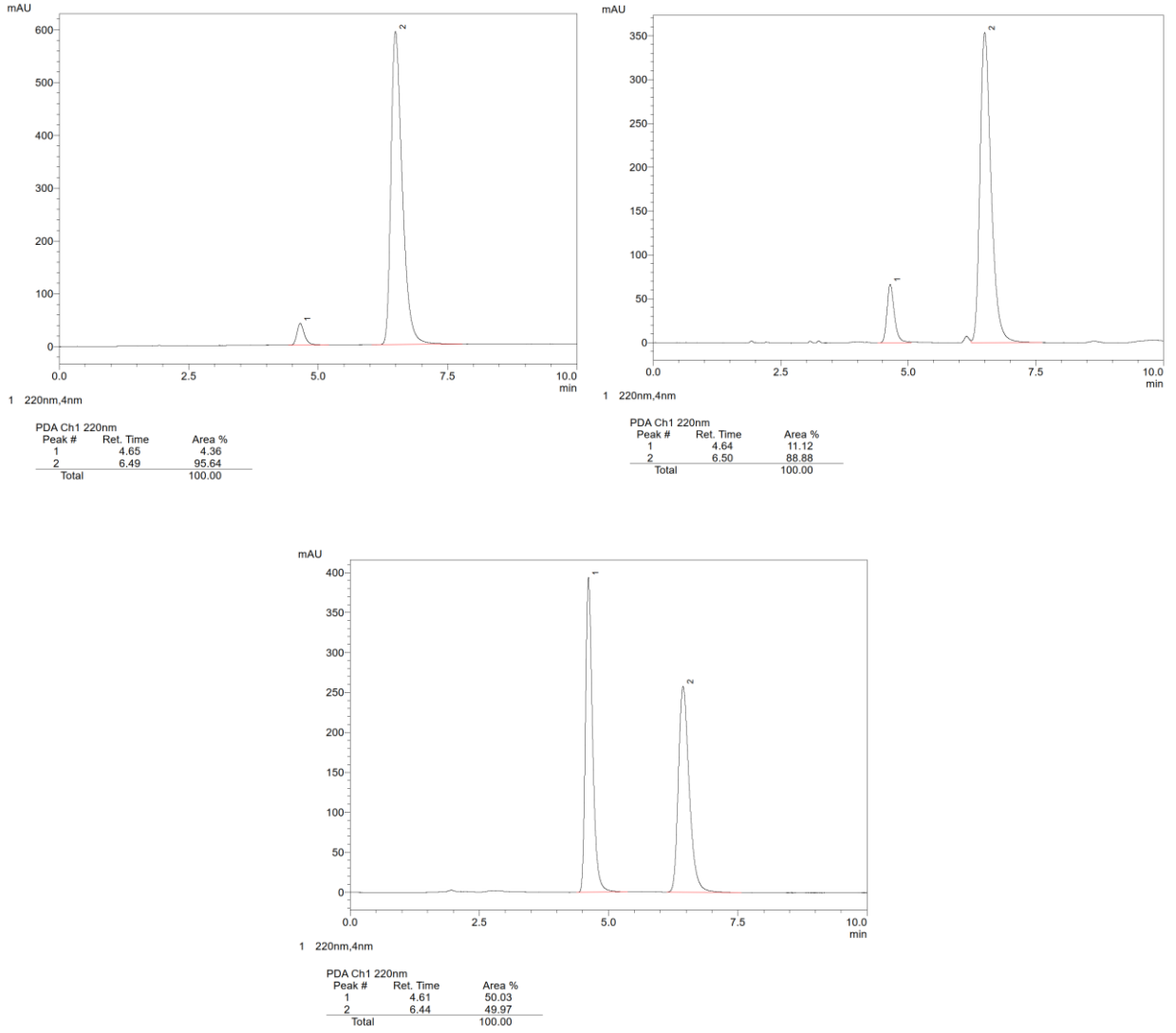


Figure S35. HPLC traces of compound **S25**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

1-((1*S*,2*R*)-1-(4-bromophenyl)-2-phenylcyclopropyl)ethan-1-one (S26). Prepared according to the general procedure as a colorless oil; with complex **2a**: 34% yield, 89% *ee*; with complex **3b**: 75% yield, 92% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralcel OJ-3, ∅ 4.6 mm, *n*-heptane/i-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 5.32 min, t(major) = 10.74 min.] $[\alpha]_D^{20}$ = +44.6 (c = 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.27 (m, 2H), 7.13 – 7.05 (m, 3H), 6.93 – 6.87 (m, 2H), 6.79 – 6.72 (m, 2H), 3.14 (dd, *J* = 9.2, 7.3 Hz, 1H), 2.12 (dd, *J* = 9.2, 4.4 Hz, 1H), 2.00 (s, 3H), 1.78 (dd, *J* = 7.3, 4.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.0, 136.4, 135.9, 133.8, 131.6, 128.1, 128.1, 126.7, 121.7, 45.4, 35.1, 30.0, 23.5; IR (ATR): ṽ = 1687, 1604, 1485, 1445, 1420, 1395, 1354, 1236, 1207, 1147, 1084, 1071, 1010, 982, 836, 773, 747, 695, 613, 541 cm^{-1}; HRMS (ESI$^+$) for $C_{17}H_{15}BrONa$ [M+Na]$^+$: calcd: 337.01986, found: 337.01954.

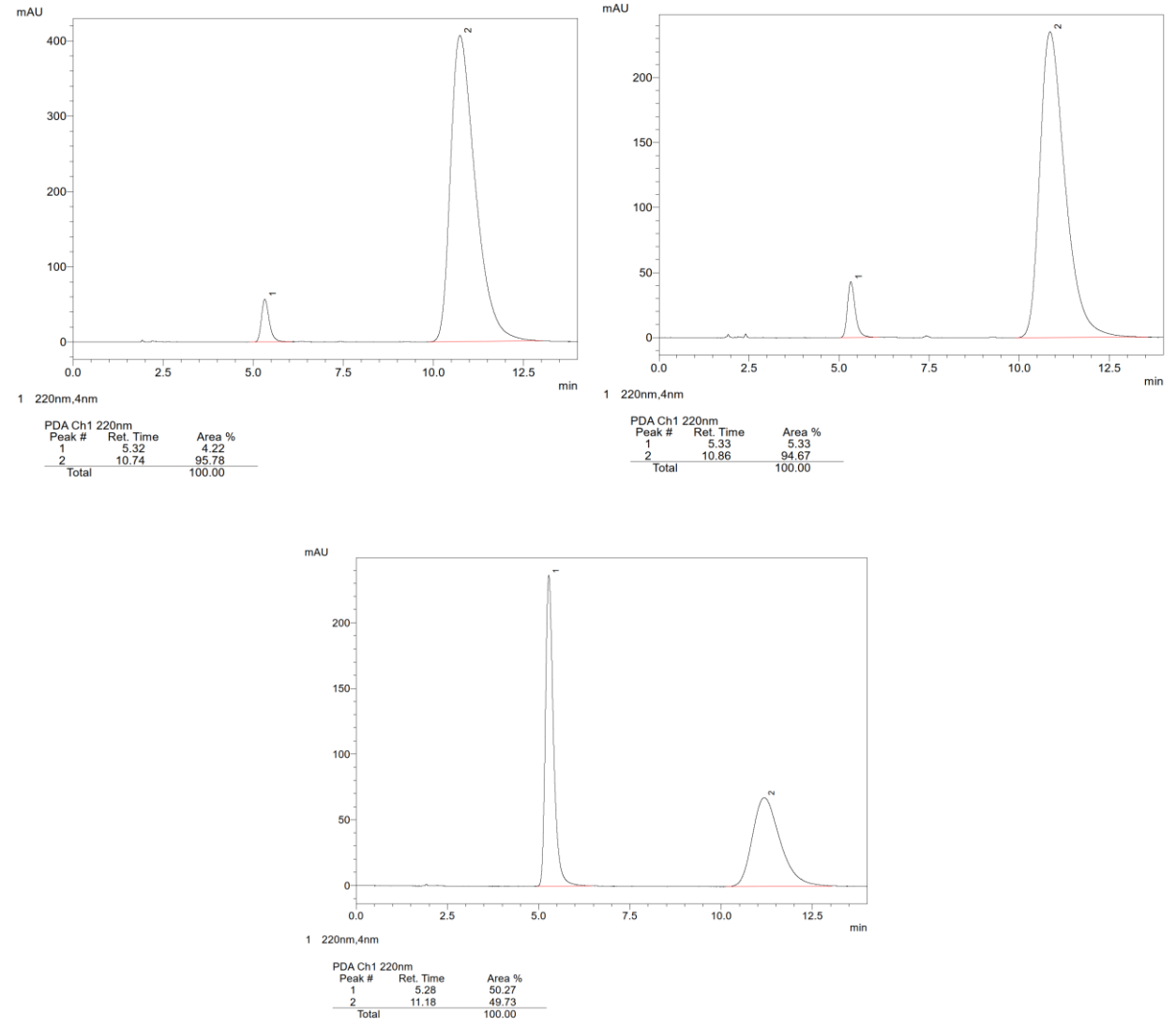


Figure S36. HPLC traces of compound **S26**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

((1*R*,2*R*)-1-(4-Methoxyphenyl)cyclopropane-1,2-diyl)dibenzene (S27). Prepared at room temperature according to the general procedure as a white solid; with complex **3b**: 68% yield, 99% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IG-3, Ø 4.6 mm, n-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 230 nm, t(minor) = 2.93 min, t(major) = 3.49 min]. m. p. = 55-58°C; $[\alpha]_D^{20}$ = +100.9 (c = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.26 (m, 4H), 7.20 – 7.03 (m, 4H), 7.03 – 6.98 (m, 2H), 6.90 – 6.82 (m, 2H), 6.70 – 6.62 (m, 2H), 3.71 (s, 3H), 2.81 (dd, *J* = 9.0, 6.6 Hz, 1H), 1.93 (dd, *J* = 6.6, 5.3 Hz, 1H), 1.80 (dd, *J* = 9.0, 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.1, 147.6, 139.0, 132.5, 132.4, 128.5, 128.1, 127.8, 127.3, 125.9, 125.7, 113.5, 55.2, 38.7, 32.8, 21.4; IR (ATR): ṽ = 3001, 1601, 1510, 1444, 1290, 1242, 1174, 1030, 843, 819, 722, 759, 727, 694, 551, 514; HRMS (EI$^+$) for $C_{22}H_{20}O$ [M]$^+$: calcd: 300.15087, found: 300.15123.

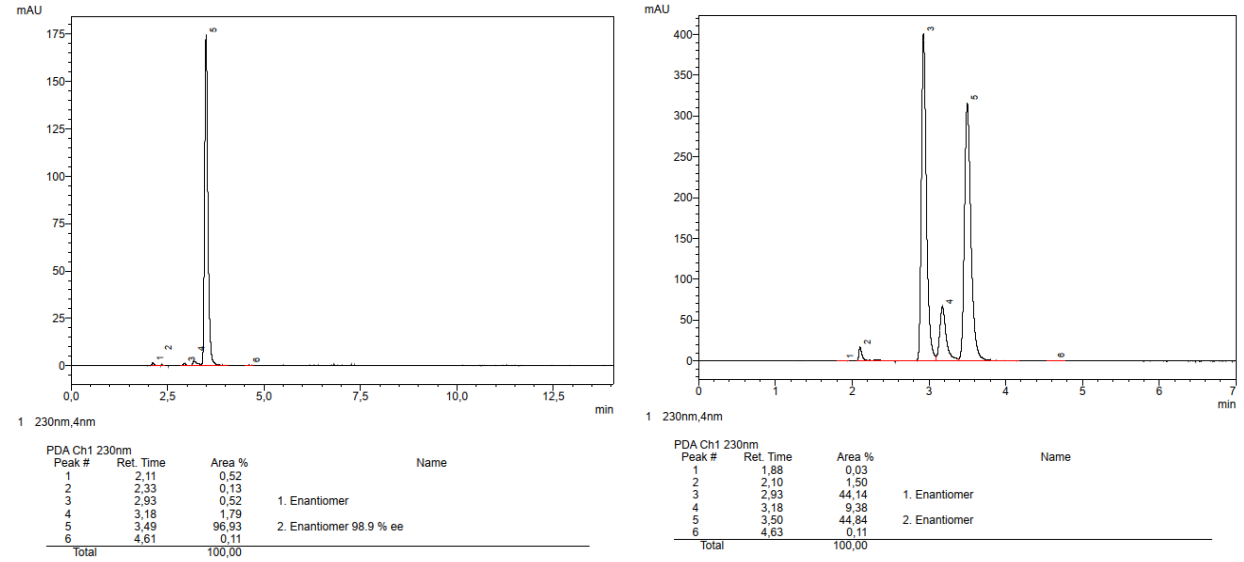
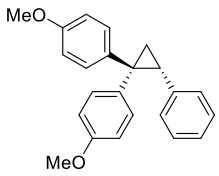


Figure S37. HPLC traces of compound **S27**: with complex **3b** (left); the corresponding racemate (right).

(*R*)-4,4'-(2-Phenylcyclopropane-1,1-diyl)bis(methoxybenzene) (S28). Prepared at room temperature



according to the general procedure in CH_2Cl_2/pentane = 1/9 as a white solid; with complex **3b**: 92% yield, 97% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, Ø 4.6 mm, n-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 4.27 min, t(major) = 4.66 min]. m. p. = 127-131°C; $[\alpha]_D^{20}$ = +105.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.16 (m, 2H), 7.14 – 7.02 (m, 3H), 7.02 – 6.96 (m, 2H), 6.89 – 6.84 (m, 2H), 6.84 – 6.79 (m, 2H), 6.69 – 6.61 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 2.76 (dd, *J* = 9.0, 6.5 Hz, 1H), 1.88 (dd, *J* = 6.5, 5.2 Hz, 1H), 1.73 (dd, *J* = 9.0, 5.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.0, 157.9, 139.9, 139.2, 133.0, 132.1, 128.5, 128.1, 127.8, 125.6, 113.9, 113.5, 55.5, 55.2, 38.1, 32.4, 21.1; IR (ATR): ṽ = 2957, 1716, 1605, 1509, 1455, 1290, 1241, 1173, 1022, 836, 814, 744, 736, 696, 603, 559, 546, 511; HRMS (EI$^+$) for $C_{23}H_{22}O_2$ $[M]^+$: calcd: 330.16143, found: 330.16114.

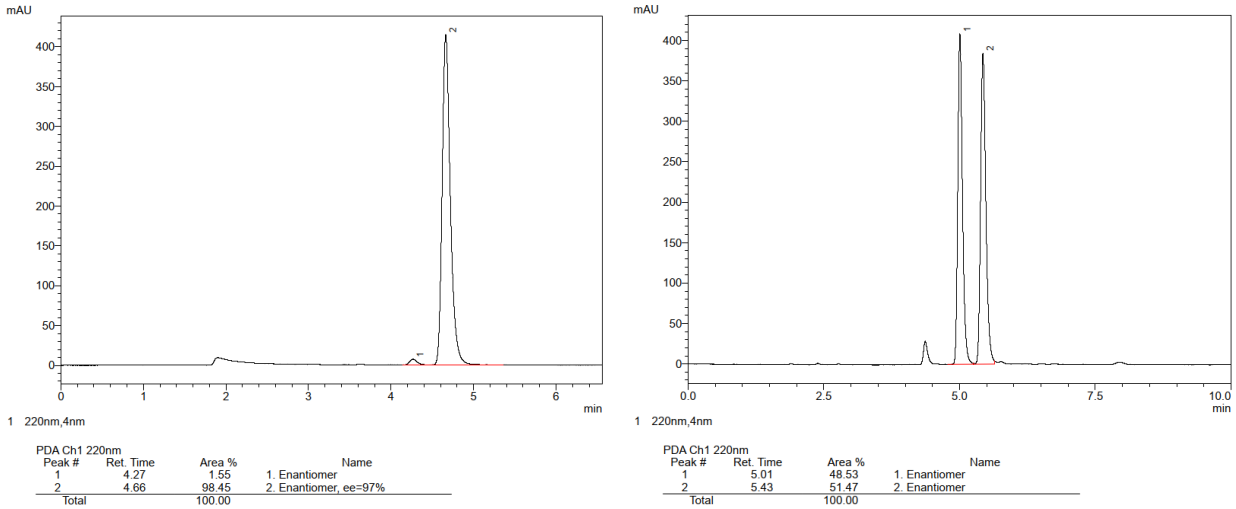
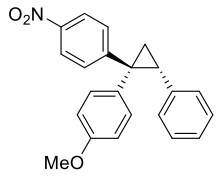


Figure S38. HPLC traces of compound **S28**: with complex **3b** (left); the corresponding racemate (right).

1-Methoxy-4-((1*R*,2*R*)-1-(4-nitrophenyl)-2-phenylcyclopropyl)benzene (S29). Prepared at room



temperature according to the general procedure in CH_2Cl_2 as a white solid; with complex **3b**: 90% yield, 95% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, Ø 4.6 mm, n-heptane/2-propanol = 95/5, v = 1.0 mL/min, λ = 220 nm, t(minor) = 5.15 min, t(major) = 6.19 min]. m. p. = 103-104°C; $[\alpha]_D^{20}$ = +199 (c = 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 – 8.06 (m, 2H), 7.35 – 7.26 (m, 2H), 7.18 – 7.03 (m, 3H), 7.01 – 6.90 (m, 2H), 6.91 – 6.79 (m, 2H), 6.74 – 6.66 (m, 2H), 3.73 (s, 3H), 2.85 (dd, *J* = 9.1, 6.8 Hz, 1H), 2.08 (dd, *J* = 6.9, 5.6 Hz, 1H), 1.89 (dd, *J* = 9.2, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.6, 155.2, 145.9, 137.8, 132.7, 130.5, 128.0, 128.0, 127.4, 126.2, 123.7, 113.9, 55.3, 38.4, 34.5, 22.6; IR (ATR): ṽ = 2924, 1591, 1503, 1455, 1342, 1327, 1295, 1241, 1177, 1109, 1027, 965, 858, 841, 809, 773, 756, 729, 695, 613, 553, 505; HRMS (ESI$^+$) for $C_{22}H_{19}NO_3Na$ $[M+Na]^+$: calcd: 368.12571, found: 368.12568.

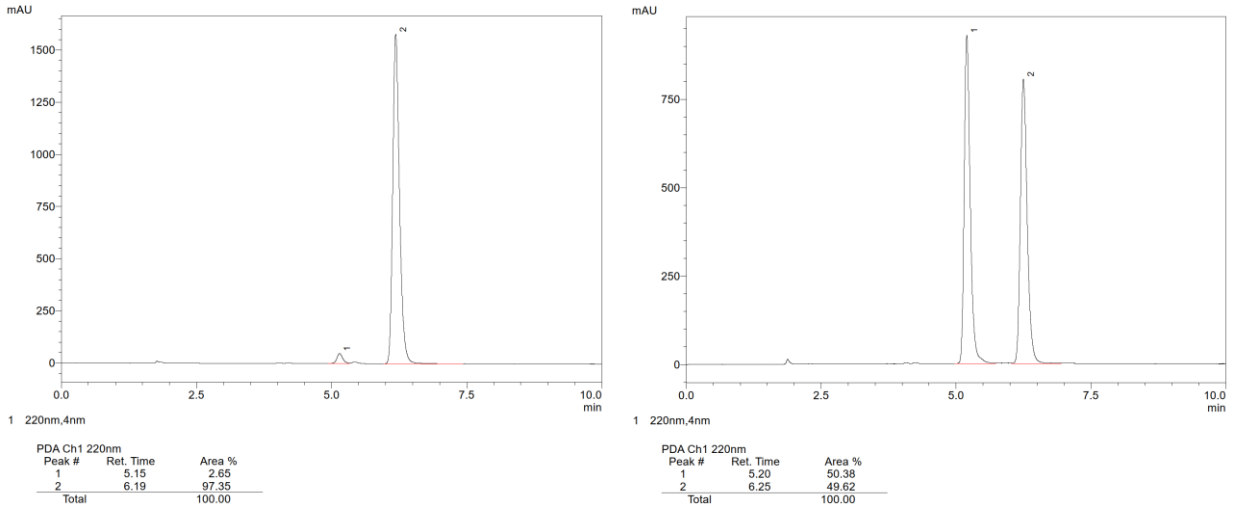
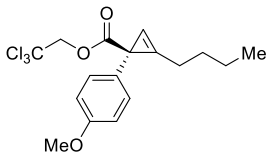


Figure S39. HPLC traces of compound **S29**: with complex **3b** (left); the corresponding racemate (right).

Cyclopropenes.

2,2,2-Trichloroethyl (*S*)-2-butyl-1-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (S30). Prepared



according to the general procedure as a colorless oil: with complex **2a**: 54% yield, 96% *ee*; with complex **3b**: 82% yield, >99% *ee*.. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IC-3, Ø 4.6 mm, n-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(major) = 6.91 min, t(minor) = 9.62 min.] $[\alpha]_D^{20}$ = +13.1 (c = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 – 7.20 (m, 2H), 6.88 – 6.80 (m, 2H), 6.67 (t, *J* = 1.5 Hz, 1H), 4.75 (s, 1H), 4.74 (s, 1H), 3.79 (s, 3H), 2.58 (tt, *J* = 7.2, 1.5 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.45 – 1.28 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.1, 158.3, 133.1, 129.5, 121.1, 113.6, 96.4, 95.6, 74.4, 55.4, 32.3, 29.0, 24.3, 22.4, 13.9; IR (ATR): ṽ = 2933, 2110, 1730, 1610, 1511, 1245, 1169, 1032, 836, 795, 768, 712, 573; HRMS (ESI$^+$) for $C_{17}H_{19}Cl_3O_3Na$ [M+Na$^+$]$^+$: calcd: 399.02920, found: 399.02908.

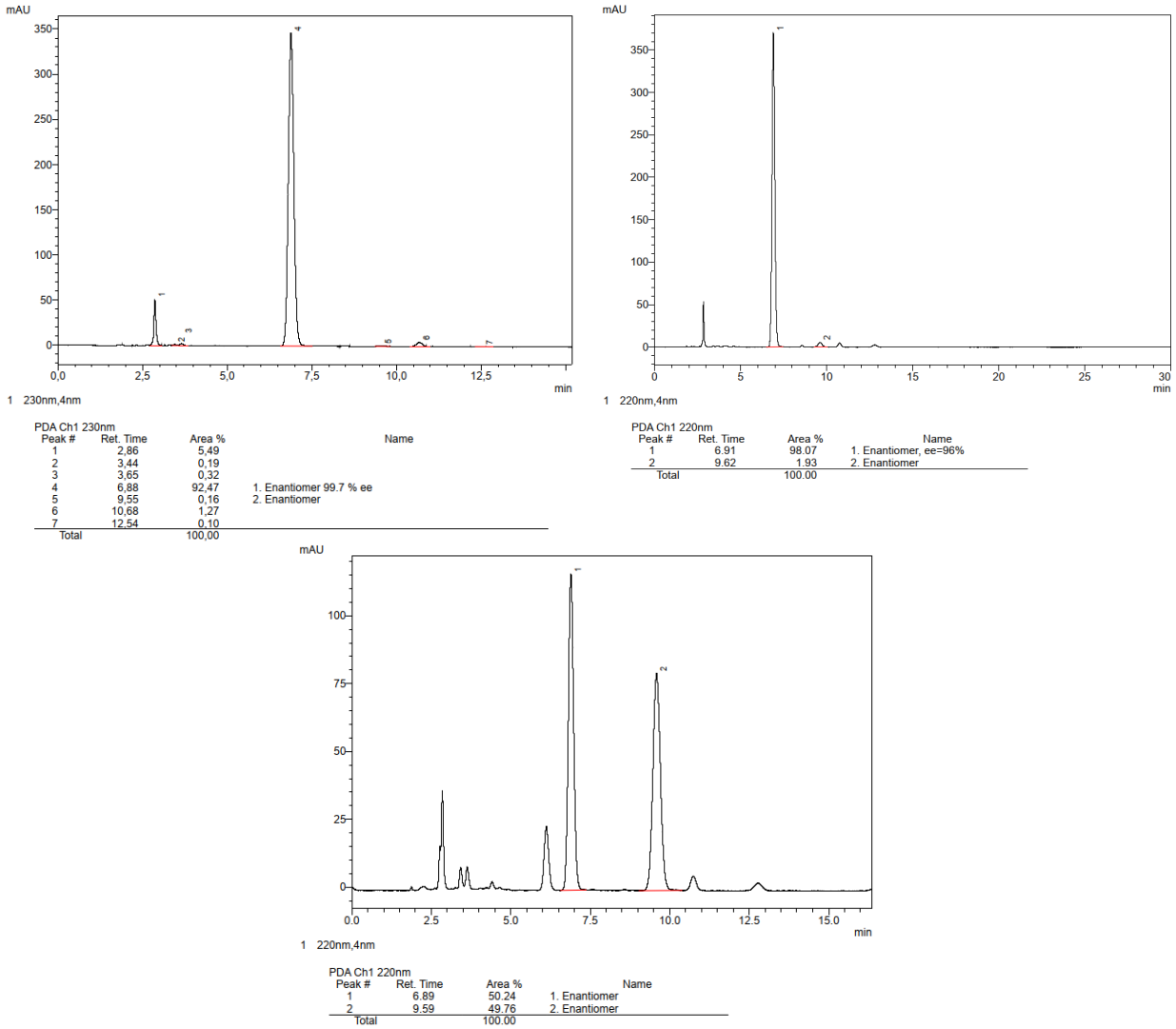


Figure S40. HPLC traces of compound **S30**: with complex **2a** (top, left); with complex **3b** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (*R*)-1-(4-fluorophenyl)-2-((trimethylsilyl)methyl)cycloprop-2-ene-1-carboxylate (S31). Prepared according to the general procedure as a colorless oil: with complex **2a**: 98% yield, 84% *ee*; with complex **3b**: 83% yield, 97% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IC-3, ∅ 4.6 mm, *n*-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(major) = 2.60 min, t(minor) = 2.89 min.] $[\alpha]_D^{20}$ = +39.9 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.24 (m, 2H), 7.02 – 6.94 (m, 2H), 6.54 (t, *J* = 1.1 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 2.07 – 1.90 (m, 2H), -0.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.0, 161.7 (d, *J* = 244.6 Hz), 136.8 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 8.1 Hz), 119.7, 114.9 (d, *J* = 21.1 Hz), 95.5, 93.5, 74.4, 32.7, 14.4, −1.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −116.6; ^{29}Si NMR (79 MHz, $CDCl_3$): δ = 2.0; IR (ATR): ṽ = 2955, 1731, 1603, 1509, 1250, 1175, 1093, 839, 769, 712, 572; HRMS (EI) for $C_{16}H_{18}O_2FCl_3Si$ $[M]^+$: calcd: 394.01202, found: 394.01170.

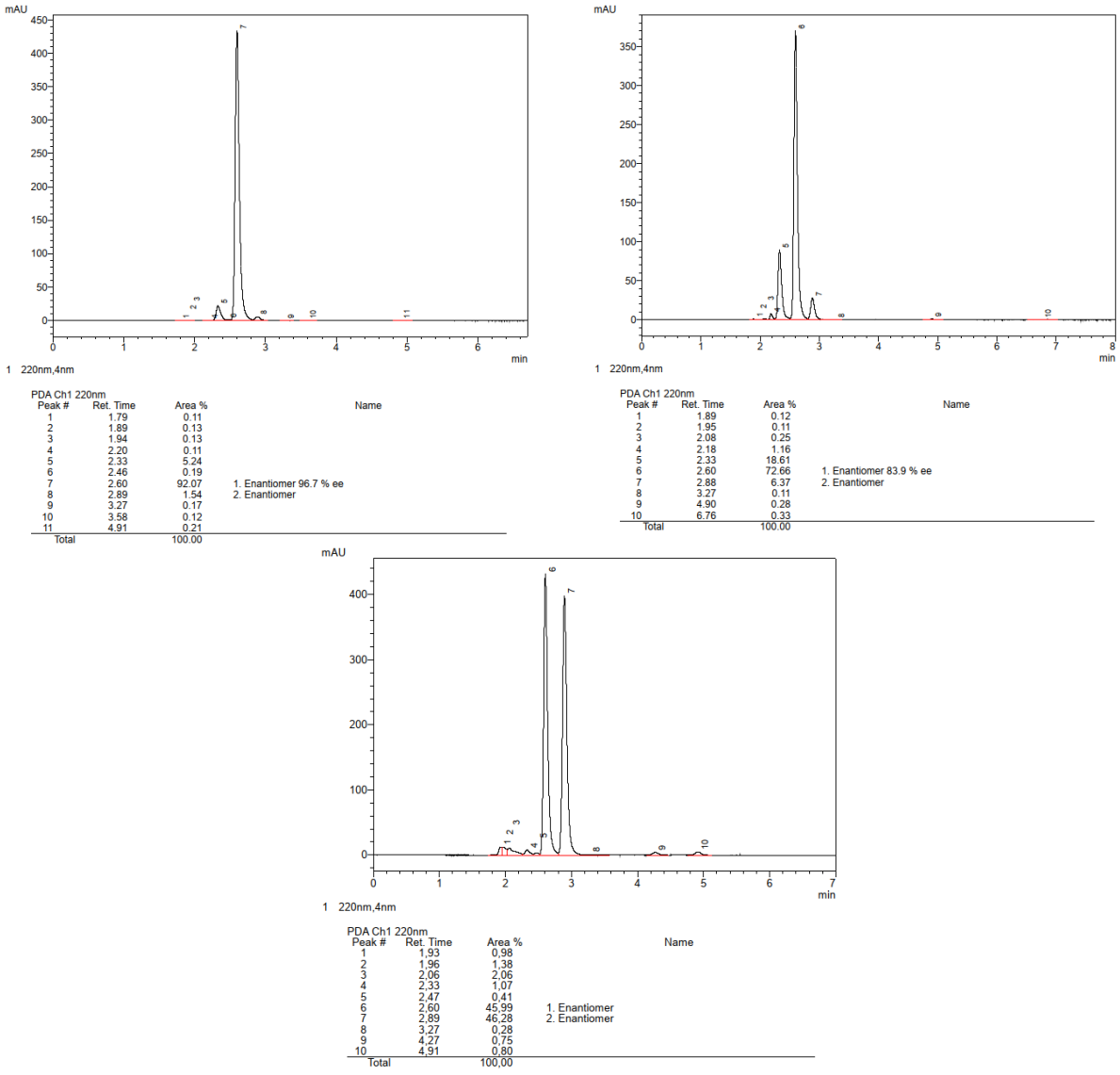
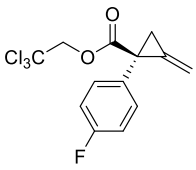


Figure S41. HPLC traces of compound **S31**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

2,2,2-Trichloroethyl (*S*)-1-(4-fluorophenyl)-2-methylenecyclopropane-1-carboxylate was isolated as a side product: with complex **3b**: 17 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 – 7.35 (m, 2H), 7.06 – 6.95 (m, 2H), 6.33 (t, *J* = 2.7 Hz, 1H), 4.76 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 2.64 (dd, *J* = 9.4, 2.7 Hz, 1H), 1.85 (dd, *J* = 9.4, 2.8 Hz, 1H), 0.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.5, 162.3 (d, *J* = 246.4 Hz), 140.6, 133.2 (d, *J* = 3.2 Hz), 131.1 (d, *J* = 8.4 Hz), 119.2, 115.3 (d, *J* = 21.6 Hz), 95.1, 74.4, 30.4, 21.4, -0.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.6.



2,2,2-Trichloroethyl (*R*)-2-(chloromethyl)-1-(4-fluorophenyl)cycloprop-2-ene-1-carboxylate (S32). Prepared according to the general procedure as a colorless oil: with complex **2a**: 81% yield, 77% *ee*; with complex **3b**: 96% yield, 98% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, Ø 4.6 mm, n-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(major) = 5.97 min, t(minor) = 7.60 min.] $[\alpha]_D^{20}$ = +39.9 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.26 (m, 2H), 7.10 (t, *J* = 1.5 Hz, 1H), 7.06 – 6.96 (m, 2H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.60 (dd, *J* = 15.2, 1.6 Hz, 1H), 4.53 (dd, *J* = 15.2, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 162.1 (d, *J* = 245.8 Hz), 134.9 (d, *J* = 3.1 Hz), 130.2 (d, *J* = 8.1 Hz), 117.6, 115.3 (d, *J* = 21.5 Hz), 101.6, 95.2, 74.6, 35.7, 35.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -115.2; IR (ATR): ṽ = 3144, 1733, 1604, 1509, 1274, 1219, 1186, 1159, 1037, 844, 811, 773, 711, 571, 544; HRMS (EI) for $C_{13}H_9O_2FCl_4$ $[M]^+$: calcd: 355.93352, found: 355.93348.

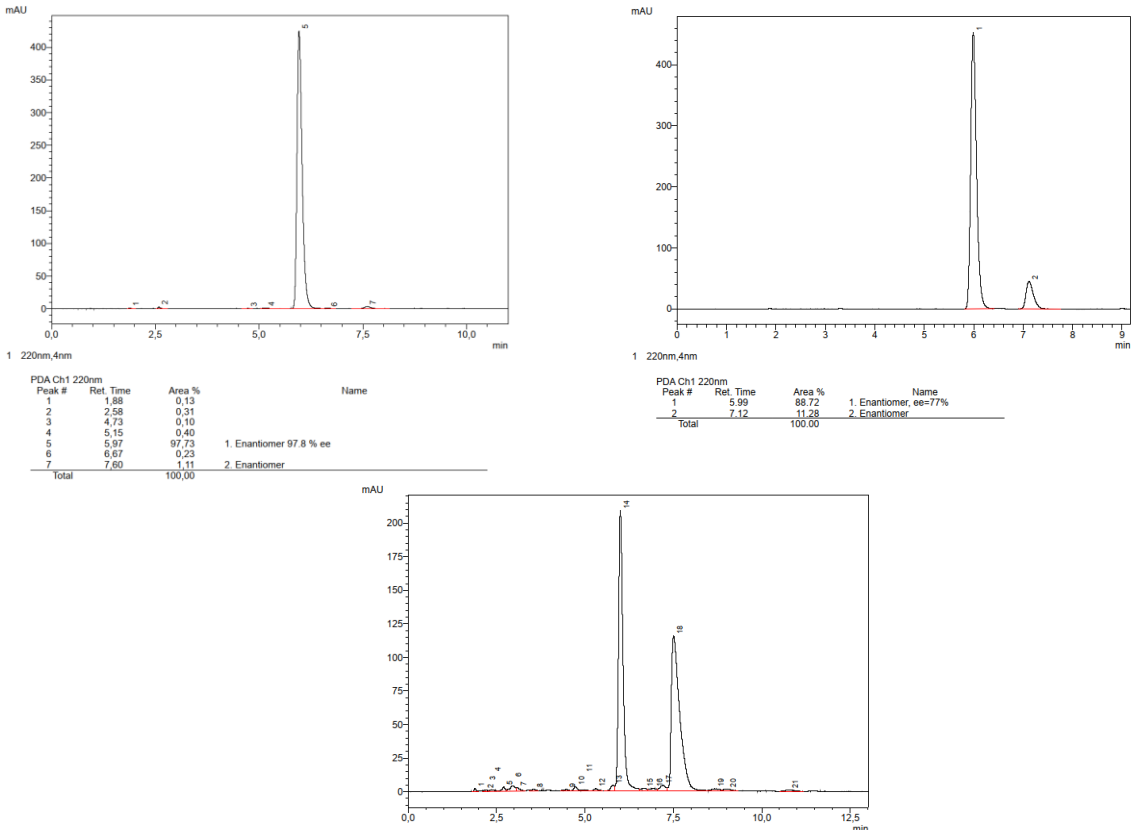
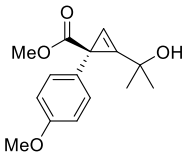


Figure S42. HPLC traces of compound **S32**: complex **2a** (top, left); with complex **3b** (top, right); the corresponding racemate (bottom).

Methyl (*R*)-2-(2-hydroxypropan-2-yl)-1-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (S33).



Prepared at RT according to the general procedure as a colorless oil; with complex **3b**: 72% yield, 94% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, Ø 4.6 mm, n-heptane/2-propanol = 95/5, v = 1.0 mL/min, λ = 220 nm, t(major) = 8.86 min, t(minor) = 8.26 min; The racemic compound was prepared using a racemic mixture of **3b**]. $[\alpha]_D^{20}$ = +67.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 – 7.17 (m, 2H), 6.88 – 6.80 (m, 2H), 6.79 (s, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 1.48 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.3, 158.4, 132.9, 129.4, 127.1, 113.7, 97.0, 69.1, 55.4, 52.5, 34.9, 29.2, 28.4; IR (ATR): ṽ = 3434, 2980, 1715, 1611, 1511, 1460, 1437, 1373, 1288, 1243, 1213, 1175, 1026, 1005, 969, 897, 854, 831, 809, 770, 589, 527; HRMS (ESI$^+$) for $C_{15}H_{18}O_4Na$ [M+Na$^+$]$^+$: calcd: 285.10973, found: 285.10963.

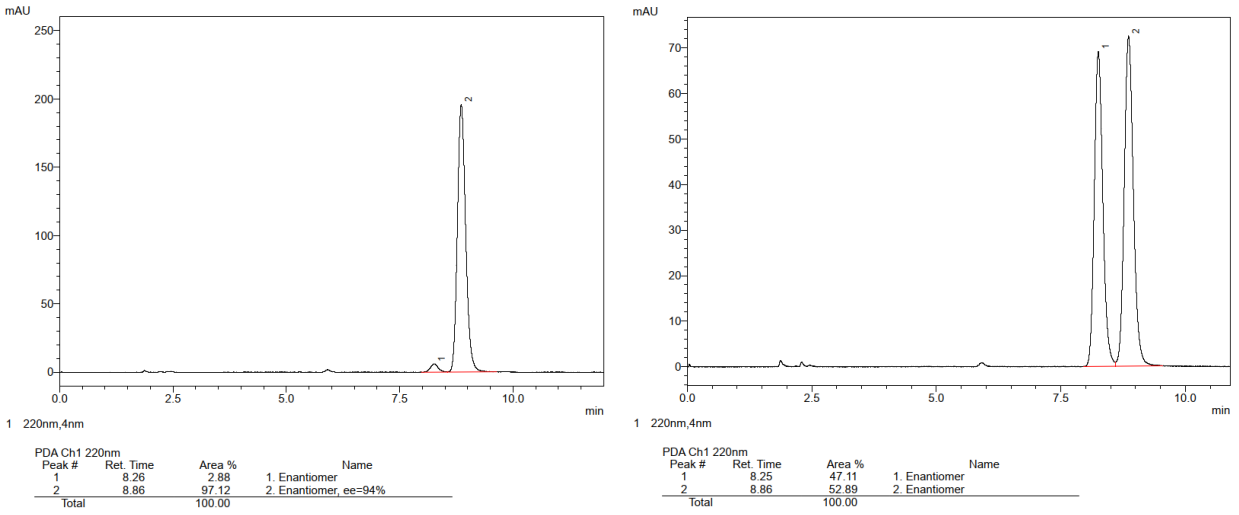


Figure S43. HPLC traces of compound **S33**: with complex **3b** (left); the corresponding racemate (right).

C–H and Si–H Insertion Reactions

General Procedure. An oven dried jacketed Schlenk flask equipped with a magnetic stir bar was charged with the [BiRh] catalyst (0.001 mmol, 1 mol%) under argon. For C-H insertion, cyclohexane (1 mL) was added and a solution of the diazo derivative (0.1 mmol) in cyclohexane was added dropwise over 30 minutes. The resulting mixture was stirred at ambient temperature until TLC analysis indicated the complete consumption of the diazo compound. For Si-H insertion, the silane substrate (0.25 mmol) and pentane (1 mL) were added to the catalyst and the resulting solution was cooled to −10°C. A solution of the diazo compound (0.1 mmol) in pentane (3 mL) was added dropwise over 60 min. The resulting mixture was stirred at −10°C until TLC analysis indicated the complete consumption of the diazo compound. For work up, the mixture was absorbed on silica, which was loaded on top of a silica column. Purification by flash chromatography (n-pentane/Et_2O or hexanes/EtOAc) afforded the desired products.

(+)-2,2,2-Trichloroethyl 2-cyclohexyl-2-(4-methoxyphenyl)acetate (S34). Prepared as a colorless oil at ambient temperature in cyclohexane as the solvent according to the general procedure; with complex **2a**: 49% yield, 85% *ee*; with complex **3b**: 73% yield, 93% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralcel OJ-3, Ø 4.6 mm, n-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 230 nm, t(minor) = 2.98 min, t(major) = 3.57 min]. $[\alpha]_D^{20}$ = +12.5 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.24 (m, 2H), 6.88 – 6.82 (m, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 3.79 (s, 3H), 3.32 (d, *J* = 10.7 Hz, 1H), 2.13 – 1.96 (m, 1H), 1.92 – 1.81 (m, 1H), 1.75 (dtd, *J* = 13.1, 3.6, 1.7 Hz, 1H), 1.69 – 1.55 (m, 2H), 1.43 – 1.23 (m, 2H), 1.22 – 1.03 (m, 3H), 0.76 (dtd, *J* = 14.9, 12.1, 3.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.6, 159.1, 129.9, 129.1, 114.1, 95.1, 74.2, 58.0, 55.4, 40.9, 32.1, 30.4, 26.4, 26.1, 26.0; IR (ATR): ṽ = 2926, 2852, 1745, 1611, 1511, 1448, 1245, 1177, 1119, 1035, 833, 790, 753, 719, 572, 530, 433; HRMS (ESI$^+$) for $C_{17}H_{21}O_3Cl_3Na_1$ [M + Na]$^+$: calcd: 401.04485, found: 401.04528.

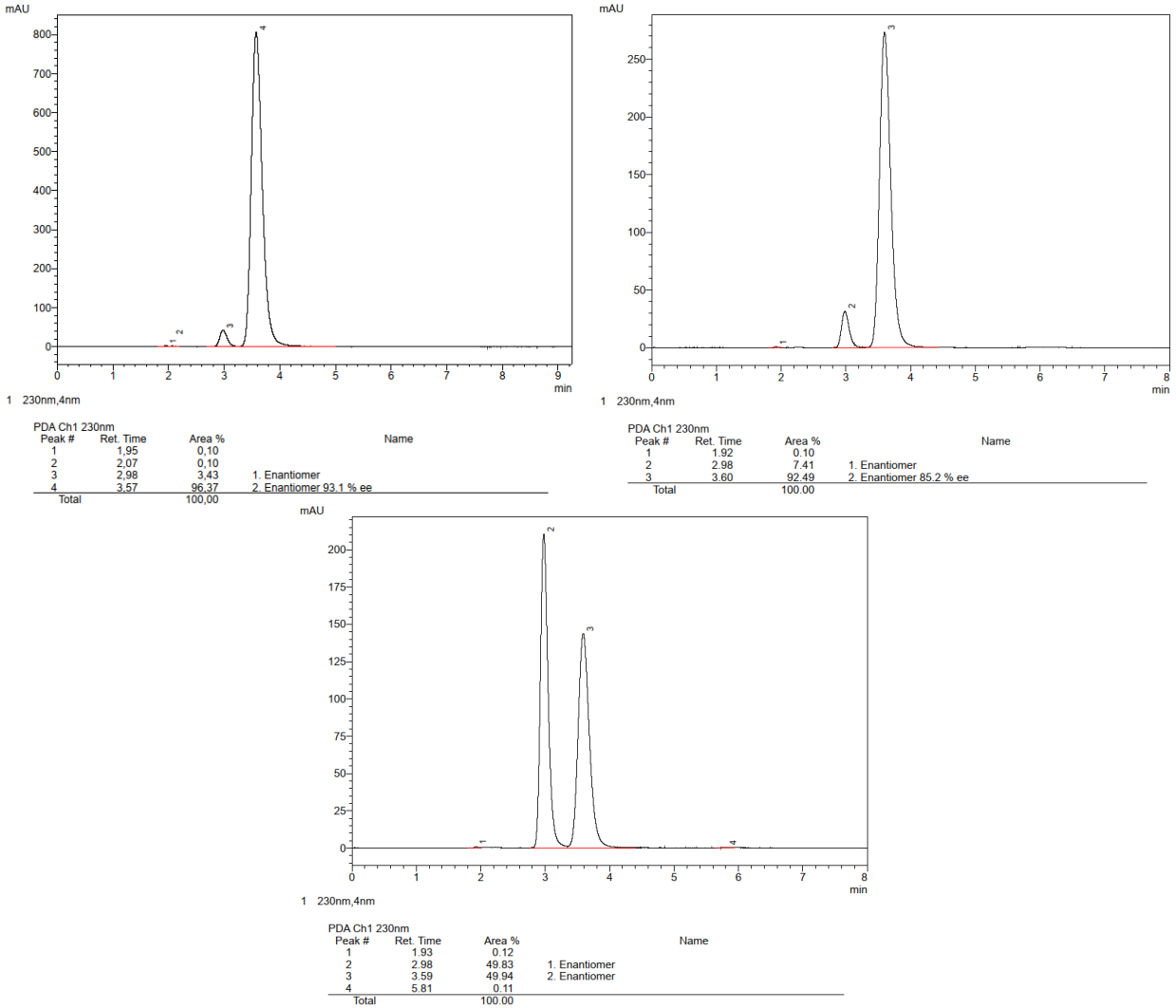
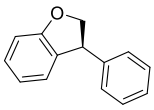


Figure S44. HPLC traces of compound **S34**: with complex **3b** (top, left); with complex **2a** (top, right); the corresponding racemate (bottom).

(S)-3-phenyl-2,3-dihydrobenzofuran (S35). An oven dried jacketed Schlenk flask equipped with a magnetic



stir bar was charged with complex **3b** (3.8 mg, 0.001 mmol, 1 mol%) under argon. Pentane (5 mL) was added and the resulting solution cooled to −10°C. A solution of the diazo compound (39.6 mg, 0.17 mmol) in pentane (3 mL) was added dropwise over 30 min. The resulting mixture was stirred at −10°C for 2 h. For work up, the mixture was absorbed on silica, which was loaded on top of a silica column. Purification by flash chromatography (hexanes/EtOAc = 15/1) afforded the desired product as a colorless solid (93% yield, 94% *ee*). [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralcel OJ-3, Ø 4.6 mm, n-heptane/i-propanol = 95/5, v = 1.0 mL/min, λ = 220 nm, t(minor) = 5.24 min, t(major) = 8.17 min.] mp = 65-66°C; $[\alpha]_D^{20}$ = −21.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.29 (m, 2H), 7.29 – 7.15 (m, 4H), 7.06 – 6.99 (m, 1H), 6.92 – 6.82 (m, 2H), 4.91 (dd, *J* = 9.6, 8.8 Hz, 1H), 4.68 (dd, *J* = 9.5, 7.4 Hz, 1H), 4.43 (dd, *J* = 8.8, 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.4, 143.0, 130.7, 129.0, 128.7, 128.0, 127.2, 125.4, 121.0, 109.8, 79.3, 48.7; IR (ATR): ṽ = 2961, 1594, 1477, 1458, 1229, 1096, 1014, 977, 944, 862, 822, 754, 698, 613, 559, 508, 438; HRMS (EI) for $C_{14}H_{12}O$ $[M]^+$: calcd: 196.08827, found: 196.08820.

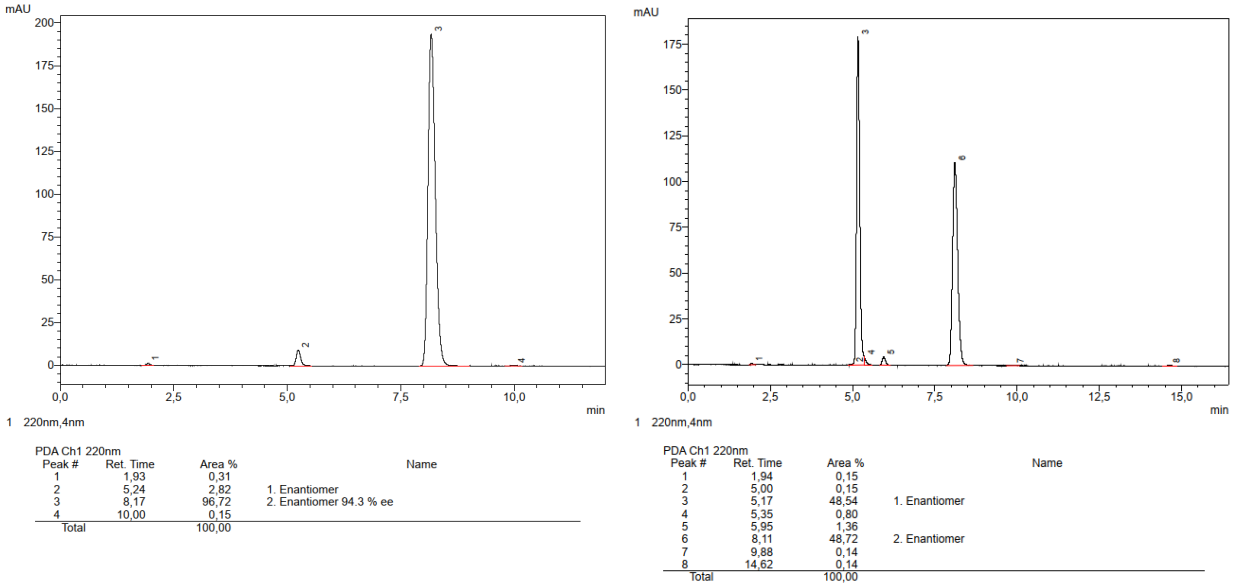


Figure S45. HPLC traces of compound **S35**: with complex **3b** (left); the corresponding racemate (right).

(–)-Methyl-2-(4-methoxyphenyl)-2-(triethylsilyl)acetate (S36). Prepared according to the general procedure as a colorless oil; with complex **2a**: 25% yield, 37% *ee*; with complex **3b**: 84% yield, 94% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, Ø 4.6 mm, n-heptane/2-propanol = 96/4, v = 1.0 mL/min, λ = 220 nm, t(minor) = 2.65 min, t(major) = 3.25 min.] $[\alpha]_D^{20}$ = –95.5 (c = 3.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.22 (m, 2H), 6.87 – 6.78 (m, 2H), 3.78 (s, 3H), 3.66 (s, 3H), 3.47 (s, 1H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.58 (dtd, *J* = 8.3, 7.5, 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.2, 157.8, 129.6, 128.7, 113.7, 55.4, 51.4, 41.8, 7.2, 2.9; IR (ATR): ṽ = 2951, 2877, 1720, 1610, 1509, 1462, 1434, 1338, 1279, 1244, 1197, 1179, 1143, 1037, 1007, 908, 863, 830, 797, 750, 709, 527; HRMS (ESI$^+$) for $C_{16}H_{26}O_3Si_1Na_1$ [M+Na]$^+$: calcd: 317.15434, found: 317.15412.

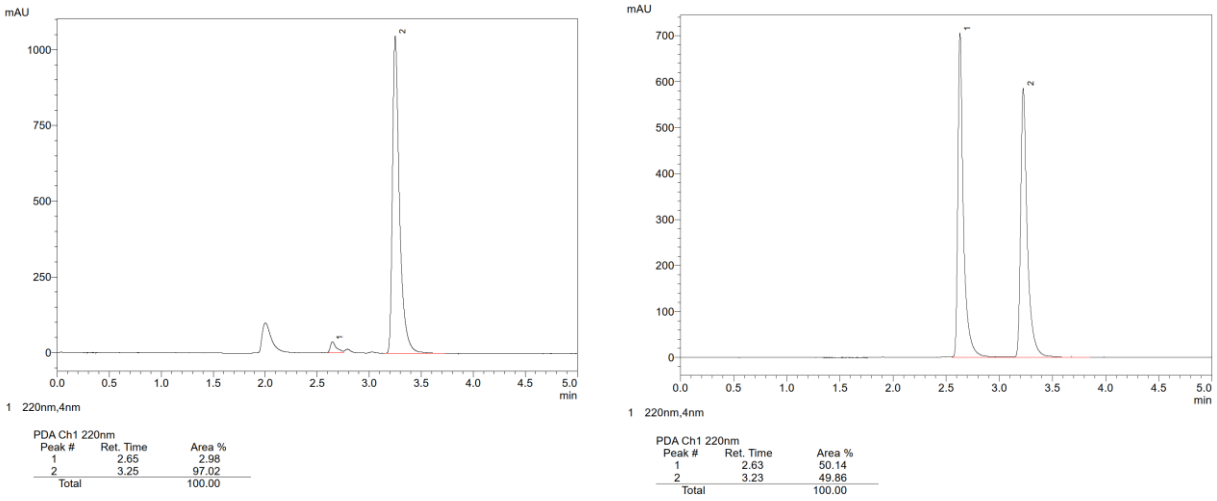


Figure S46. HPLC traces of compound **S36**: with complex **3b** (left); the corresponding racemate (right).

(–)-Methyl-2-(dimethyl(phenyl)silyl)-2-(4-fluorophenyl)acetate (S37). Prepared according to the general procedure as a colorless oil; with complex **3b**: 62% yield, 90% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IB-N-3, Ø 4.6 mm, n-heptane/2-propanol = 99/1, v = 1.0 mL/min, λ = 220 nm, t(minor) = 3.02 min, t(major) = 3.42 min.] $[\alpha]_D^{20}$ = –31.5 (c = 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 77.46 – 7.28 (m, 5H), 7.22 – 7.11 (m, 2H), 6.96 – 6.84 (m, 2H), 3.60 (s, 1H), 3.58 (s, 3H), 0.35 (d, *J* = 5.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2, 161.3 (d, *J* = 243.9 Hz), 135.3, 134.1, 131.7 (d, *J* = 3.0 Hz), 129.9, 129.8, 127.9, 114.9 (d, *J* = 21.1 Hz), 51.5, 45.3, -4.1, -4.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -117.77 IR (ATR): ṽ = 2952, 1718, 1604, 1505, 1430, 1330, 1298, 1274, 1222, 1197, 1146, 1116, 1089, 1014, 912, 867, 835, 814, 785, 732, 698, 661, 520; HRMS (ESI$^+$) for $C_{17}H_{19}F_1O_2Si_1Na_1$ $[M+Na]^+$: calcd: 325.10306, found: 325.10283.

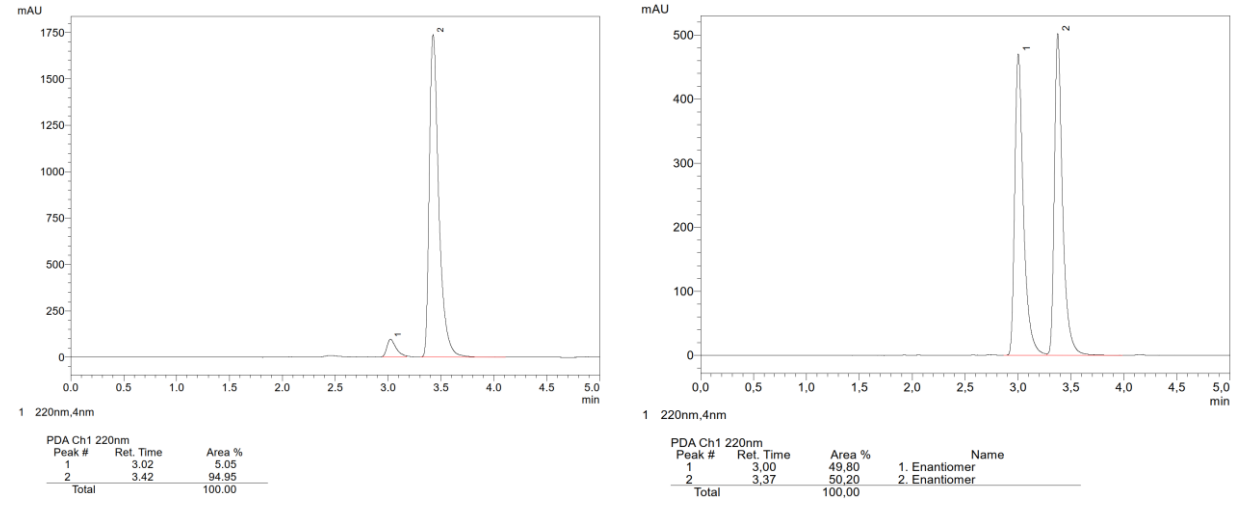


Figure S47. HPLC traces of compound **S37**: with complex **3b** (left); the corresponding racemate (right).

(–)-Methyl-2-(dimethyl(phenyl)silyl)-2-(4-methoxyphenyl)acetate (S38). Prepared according to the general procedure as a colorless oil; with complex **3b**: 91% yield, 95% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IC-3, Ø 4.6 mm, n-heptane/2-propanol = 95/5, v = 1.0 mL/min, λ = 220 nm, t(minor) = 4.17 min, t(major) = 4.74 min.] $[\alpha]_D^{20}$ = –24.9 (c = 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 – 7.28 (m, 5H), 7.17 – 7.09 (m, 2H), 6.82 – 6.74 (m, 2H), 3.78 (s, 3H), 3.55 (d, *J* = 1.2 Hz, 4H), 0.34 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.5, 157.8, 135.8, 134.1, 129.7, 129.5, 128.1, 127.8, 113.6, 55.3, 51.4, 45.0, -3.9, -4.3; IR (ATR): ṽ = 2951, 1717, 1610, 1509, 1463, 1429, 1338, 1304, 1281, 1245, 1198, 1179, 1145, 1115, 1036, 1010, 910, 866, 834, 811, 781, 732, 699, 529; HRMS (ESI$^+$) for $C_{18}H_{22}O_3Si_1Na_1$ [M+Na]$^+$: calcd: 337.12304, found: 337.12274.

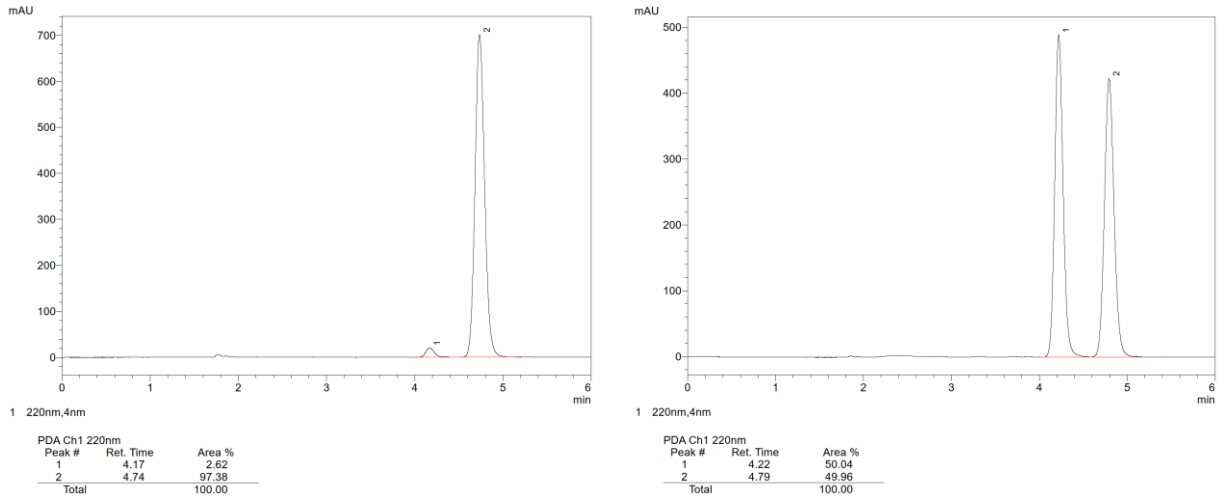


Figure S48. HPLC traces of compound **S38**: with complex **3b** (left); the corresponding racemate (right).

NH-Insertion and Doyle-Kirmse Reaction

(+)-Methyl 2-(4-methoxyphenyl)-2-(phenylthio)pent-4-enoate (S39). An oven dried Schlenk flask equipped with a magnetic stir bar was charged with complex **3b** (2.9 mg, 0.001 mmol, 1 mol%) and allyl phenyl sulfide (22 µL, 0.15 mmol) under argon. Pentane (1 mL) was introduced before a solution of the diazo compound (20.6 mg, 0.1 mmol) in pentane (3 mL) was added dropwise over 30 min. The resulting mixture was stirred at rt for 2 h. For work up, the mixture was absorbed on silica, which was loaded on top of a silica column. Purification by flash chromatography (n-pentane/Et_2O = 7/1) afforded the desired product as a colorless oil. With complex **3b**: 85% yield, 45% *ee*. [The *ee* was determined by HPLC analysis: Daicel 150 mm Chiralpak IA-3, Ø 4.6 mm, n-heptane/2-propanol = 98/2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 4.76 min, t(major) = 5.45 min]. $[\alpha]_D^{20}$ = +47.0 (c = 2.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (ddd, *J* = 6.70, 4.80, 2.69 Hz, 1H), 7.23 – 7.16 (m, 6H), 6.84 – 6.80 (m, 2H), 5.90 (dddd, *J* = 16.78, 10.28, 7.34, 6.32 Hz, 1H), 5.15 – 5.01 (m, 2H), 3.80 (s, 3H), 3.69 (s, 3H), 2.84 (qdt, *J* = 14.45, 6.31, 1.35 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.6, 158.9, 136.9, 133.4, 131.9, 131.0, 129.3, 128.8, 128.6, 118.8, 113.5, 64.2, 55.4, 52.7, 40.7; IR (ATR): ṽ = 1727, 1608, 1581, 1510, 1438, 1250, 1214, 1180, 1121, 1033, 910, 824, 729, 692, 534, 497; HRMS (ESI$^+$) for $C_{19}H_{20}O_3SNa$ [M+Na$^+$]$^+$: calcd: 351.10254, found: 351.10284.

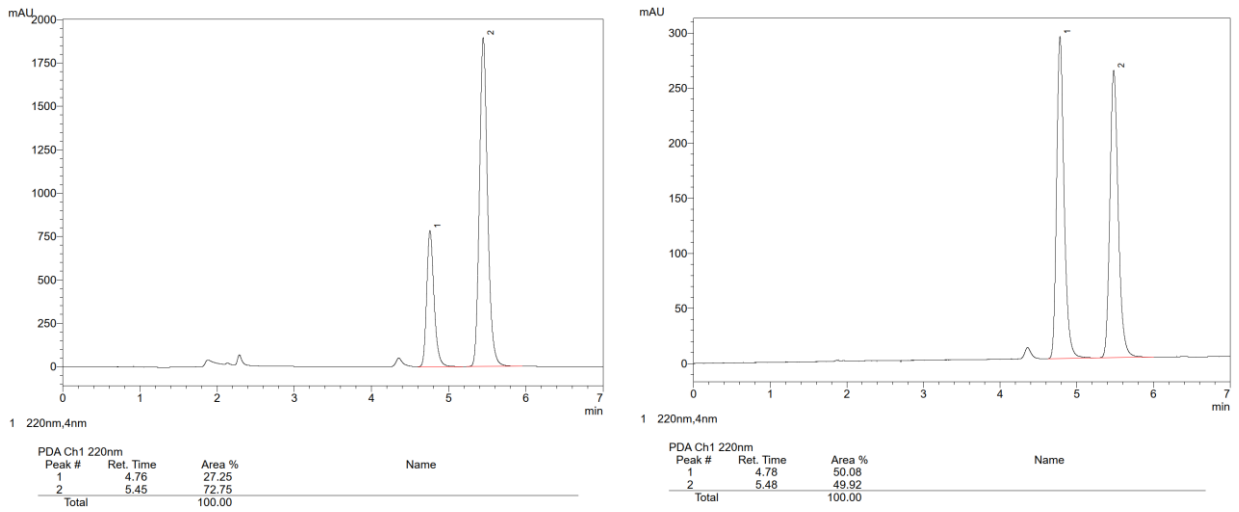


Figure S49. HPLC traces of compound **S39**: with complex **3b** (left); the corresponding racemate (right).

Methyl 2-(((benzyloxy)carbonyl)amino)-2-(4-methoxyphenyl)acetate (S40). An oven dried Schlenk flask equipped with a magnetic stir bar was charged with complex **3b** (2.9 mg, 0.001 mmol, 1 mol%) and benzyl carbamate (22.7 mg, 0.15 mmol) under argon. CH_2Cl_2 (1 mL) was introduced before a solution of the diazo compound (20.6 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) was added dropwise over 30 min. The resulting mixture was stirred at rt for 2 h. For work up, the mixture was absorbed on silica, which was loaded on top of a silica column. Purification by flash chromatography (n-pentane/EtOAc = 3/1) afforded the desired product as a colorless solid. With complex **3b**: 80% yield, 0% *ee* [The *ee* was determined by HPLC analysis: Daicel 150 mm

Chiralpak IA-3, Ø 4.6 mm, n-heptane/2-propanol = 90/10, v = 1.0 mL/min, λ = 220 nm, t_1 = 13.07 min, t_2 = 13.98 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.11 (m, 7H), 6.80 (d, *J* = 8.34 Hz, 2H), 5.71 (d, *J* = 7.24 Hz, 1H), 5.23 (d, *J* = 12.44 Hz, 1H), 5.11 – 4.93 (m, 2H), 3.71 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 159.9, 155.5, 136.3, 128.8, 128.7, 128.5, 128.3, 128.3, 114.5, 67.2, 57.5, 55.4, 52.9; IR (ATR): $\tilde{\nu}$ = 1712, 1611, 1510, 1438, 1323, 1305, 1233, 1212, 1175, 1049, 909, 832, 796, 728, 697, 544; HRMS (ESI$^+$) for $C_{18}H_{19}NO_5SNa$ [M+Na$^+$]$^+$: calcd: 352.11554, found: 352.11544.

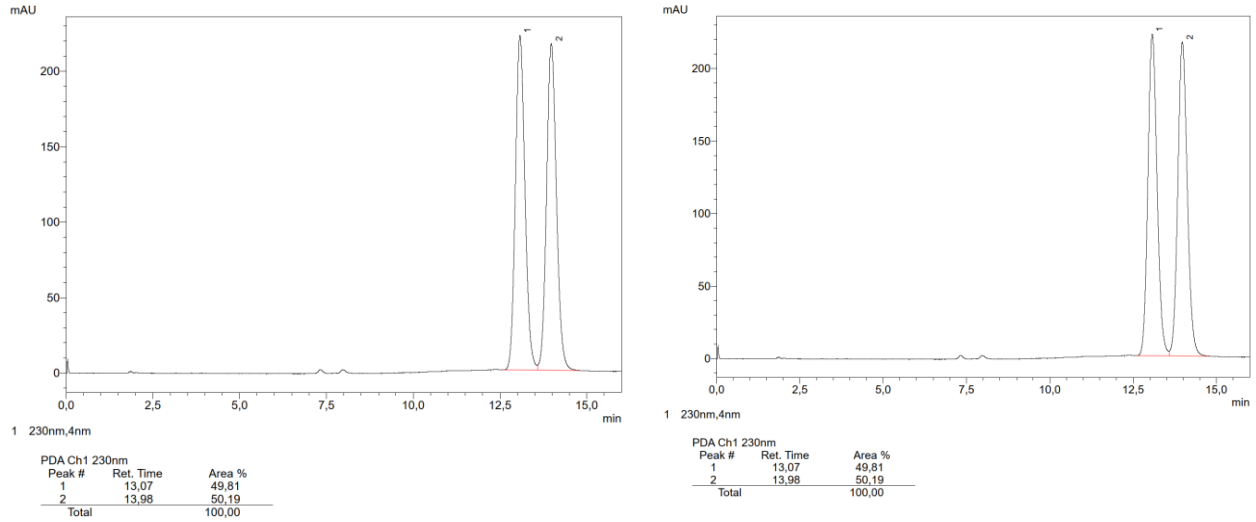


Figure S50. HPLC traces of compound **S40**: with complex **3b** (left); the corresponding racemate (right).

Supporting Computational Information

Computational Details and Methodological Aspects

All calculations were carried out using a development version of the ORCA suite of programs based on version 4.2.[17]

For **3a** and **3b,** geometry optimizations were carried out at the PBE level of theory with and without the inclusion of the D3[18] (with Becke-Johnson damping)[19] dispersion correction. The def2-SVP basis set[20] was used for all atoms. Single point energy calculations at the PBE-D3(BJ)/def2-TZVP level were carried out to compute the relative energy between the PBE-D3/def2-SVP and the PBE/def2-SVP optimized structures, ΔE. ΔE was decomposed into "dispersive" and "non-dispersive" contributions as:

$$\Delta E = \Delta E_{disp} + \Delta E_{no-disp} \quad (1)$$

ΔE_{disp} denotes the contribution to the relative energy from the D3 dispersion correction, whilst $\Delta E_{no-disp}$ represents the contribution from the PBE exchange-correlation functional. Note that previous studies[18,21] showed that ΔE_{disp} typically provides a lower bound for the coupled cluster dispersion computed using accurate techniques like the Local Energy Decomposition (LED) when the PBE exchange correlation functional is used.[21,22]

As ΔE_{disp} is computed by summing up a series of atom-pairwise terms, it can be easily decomposed into contributions from individual functional groups. Herein, we have used this method to quantify the contribution to ΔE_{disp} originating from the interaction between the key functional groups in **3a** and **3b.** In particular, we have used the following equation:

$$\Delta E_{disp} = \Delta E_{disp(TIPS)} + \Delta E_{disp(^{t}\mathrm{Bu})} + \Delta E_{disp(rest)} \quad (2)$$

in which $\Delta E_{disp(TIPS)}$, $\Delta E_{disp(^{t}\mathrm{Bu})}$ and $\Delta E_{disp(rest)}$ denote the contribution to ΔE_{disp} from dispersion forces between the TIPS groups, the ^{t}Bu groups (if present) and the rest of the metal-ligand catalyst, respectively.

Energetic Analysis

The decomposition of ΔE and ΔE_{disp} according to eq. 1 and eq. 2. is shown in **Table S1**. For **3b**, ΔE amounts to -11.6 kcal/mol. Hence, dispersion changes significantly the structure of the system. The pure dispersion contribution to the relative energy, ΔE_{disp}, amounts to -40.4 kcal/mol. Importantly, about 32% of ΔE_{disp} originates from the interaction between the TIPS groups, whilst the interaction between the ^{t}Bu groups contribute with an additional 12%. Similar results were found for **3a**.

Table S1: Decomposition of ΔE and ΔE_{disp} according to eq. 1 and eq. 2. All energies are in kcal/mol.

	3a	**3b**
ΔE	-9.9	-11.6
ΔE_{disp}	-28.3	-40.4
ΔE_{nodisp}	+18.4	+28.8
$\Delta E_{disp(TIPS)}$	-12.6	-12.7
$\Delta E_{disp(^t\mathrm{Bu})}$	(not present)	-4.8
$\Delta E_{disp(rest)}$	-15.7	-22.9

Optimized Structures in XYZ Format

3a at the PBE-D3 level

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366
Coordinates from ORCA-job
  C   2.44574221536528      2.21582006442828      7.28644445874505
  C   2.50852304543049      2.76544372055893      5.99384477127055
  C   1.38560894440541      3.42986446243833      5.47243786063029
  C   0.17997886913238      3.53937437784057      6.19976611201558
  C   0.15810231331351      2.96535720686877      7.49327069080912
  C   1.27285244295571      2.31127247086700      8.06538958938494
  C   3.76295080163153      2.65474953430671      5.14660668121579
  N   4.02051618908023      1.31635650395124      4.62470703485901
  C   4.61193073321718      0.27379382594779      5.37398677328880
  C   4.95572349490502     -0.78905811590941      4.38619880096504
  C   4.58736955173454     -0.33647920874622      3.10610511795966
  C   4.03153450062907      1.04423946642292      3.24027279018546
  C   4.80814343677884     -1.11447617681953      1.96979573549511
  C   5.41775299869726     -2.37180314774312      2.15382435241192
  C   5.79933645899677     -2.81528445700671      3.43509879132160
  C   5.57525992082470     -2.02468689084705      4.58025443482316
  O   4.80736983521400      0.28938619000661      6.58012118237639
  O   3.68167837950952      1.82735897642310      2.37019784048601
  Si  -1.35322700168958      4.40907263845953      5.45883357493492
  C   -1.92563974598746      5.85181792852288      6.60905039606889
  C   -1.71520556544417      5.64167578853736      8.11551973534277
  Si  1.28751755691691      1.57140861389092      9.82023673713467
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  Rh  7.94495916842067      3.04759681718500      6.13097776155848
  O   8.09288617997044      4.74809935310586      5.07153622261842
  C   7.81787130486785      5.89762992972375      5.54878131523007
  C   7.81654057251786      7.01537580819666      4.49045340595893
  N   7.53410995314103      6.41153443039730      3.19230835875059
  C   8.49700160934949      6.32395807382409      2.16964237252866
```

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H	8.65292564677974	14.55606269337121	4.61257659356898
H	9.41753109494556	13.11360387000817	5.34529835162762
H	10.25101055418114	13.99925104122883	4.04301240719680
H	10.53048869520024	12.00950781722886	2.58404926735948
H	9.82419946519978	10.99939266650178	3.86635590402727
H	9.17203688114755	10.91209989212476	2.20309228619530
H	5.26973615476383	7.27283400400585	8.12490514946563
H	3.96006174497870	7.51315710241847	9.31476657714819
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3a at the PBE level

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366
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3b at the PBE-D3 level

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414
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3b at the PBE level

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414
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H	4.15966499115787	-4.48888598940718	12.72682619168647
H	9.00560378372365	3.89058573570628	16.49863663118944
H	3.75279442373246	-0.96832407722622	14.70504791872801
H	2.71277432941388	-2.87811908191077	13.97861555296635
H	10.34272637910477	-0.57453031342647	14.08164840994558
H	6.66659249329705	4.45459136131836	13.36890871899729
H	2.82089905543298	-1.69904243730466	12.63359588604195
H	6.81191992830513	3.43170575053093	11.90847934471943
H	11.41196862349847	2.61334863642032	12.14464875101012
H	8.89186248957223	5.23470299563077	14.61242224383106
H	1.99483532059720	-3.26055608620794	12.38975070661175
H	10.47767329292475	4.70094598960838	13.98048019653993
H	10.94858626935436	0.90979524415395	11.89532615988651
H	7.34773712972568	5.14538647588205	11.87330109126932
H	9.49894550087726	5.87448565471220	13.05828849960320
H	8.90292236160634	-3.04171150871718	12.78216414961359
H	7.89423355194449	-5.83671814931953	11.97775330730199
H	7.41210323551761	-4.38717910108879	11.05845829105562
H	6.16242577472575	-5.50441021765598	11.69300539331200
H	6.25416021352471	-1.84449819141308	10.43249552178366
H	5.11126187634346	-3.86753157740286	10.42455738865839
H	4.11579070314602	-2.38035526485599	10.46227771069855
H	3.32915363177856	-3.97608371824157	10.45796900413245
H	11.91670386158541	-0.06253683913653	14.75845813774279

H	12.48013260173831	1.30290073532617	12.72718463236766
H	8.59792816542516	1.73336062981876	10.89822467098195
H	6.71782793867590	-0.56678024547958	8.56403608055344
H	12.67071550512262	12.13224412366886	12.04110351698474
H	13.28014545394667	10.57276160969906	11.42154193264369
H	12.78836360073276	11.85046646878362	10.27997221034501
H	10.41837472893254	11.68590811599523	11.00126177218930
H	9.31768864897393	3.64389529864203	11.99387913299658
C	11.90522149321759	-4.98081618559285	4.84379687690469
C	13.38844608523391	-3.16830612311983	3.95908433772446
C	14.02370257333964	-4.42593794670387	6.05958866054313
H	13.91029604875449	-3.91968593949060	3.33099927450278
H	12.56485654930049	-2.73165732884581	3.35834198689771
H	14.11126243424335	-2.35770574875247	4.17944422713900
H	12.45868444655248	-5.71987802783620	4.23016112915457
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H	11.04858744422359	-4.62168021036973	4.23815074895092
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H	14.76142345199117	-3.65132685388326	6.34965070197904
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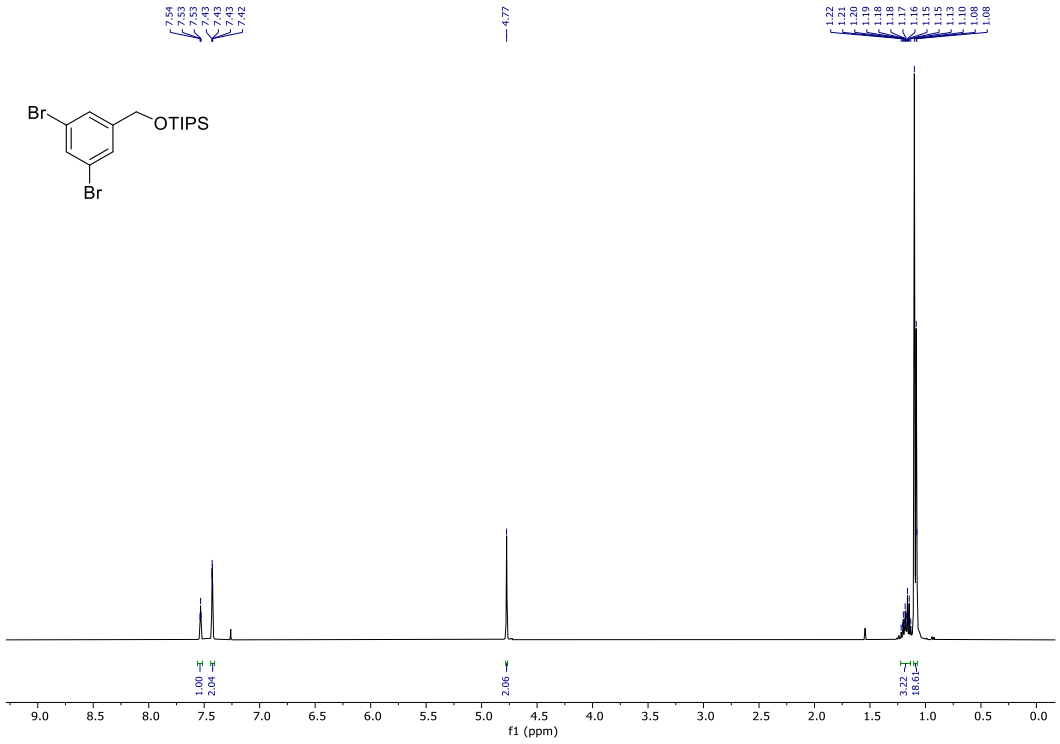
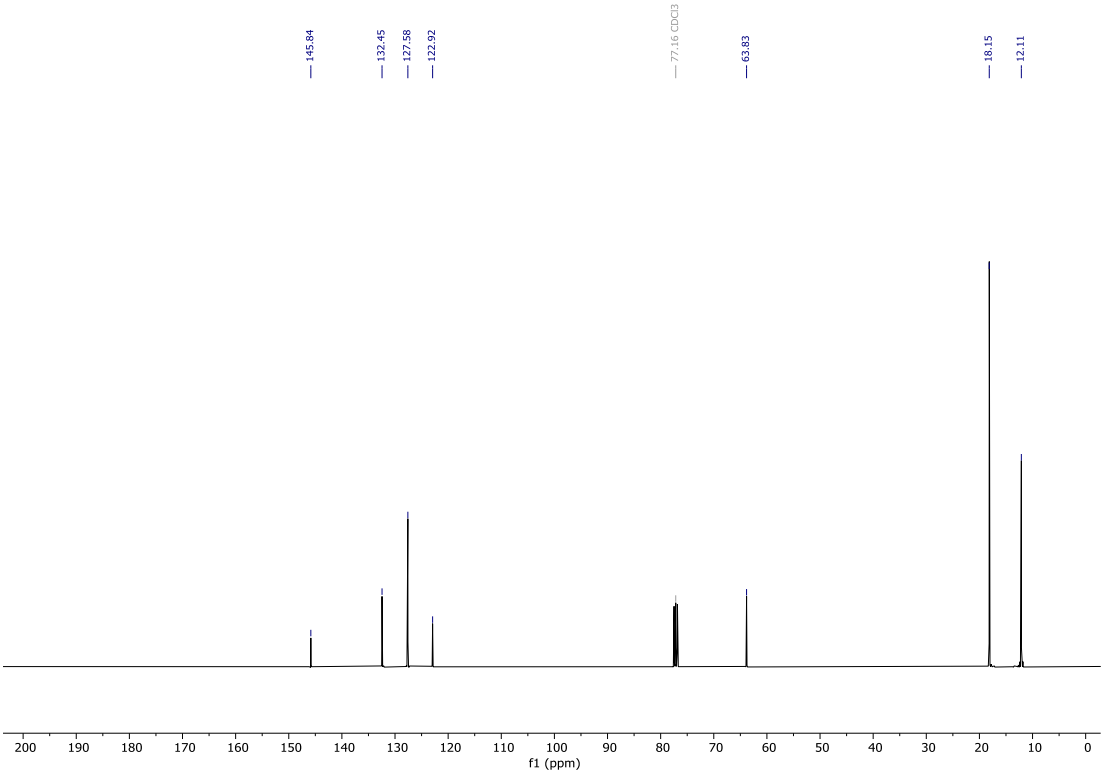
Spectra

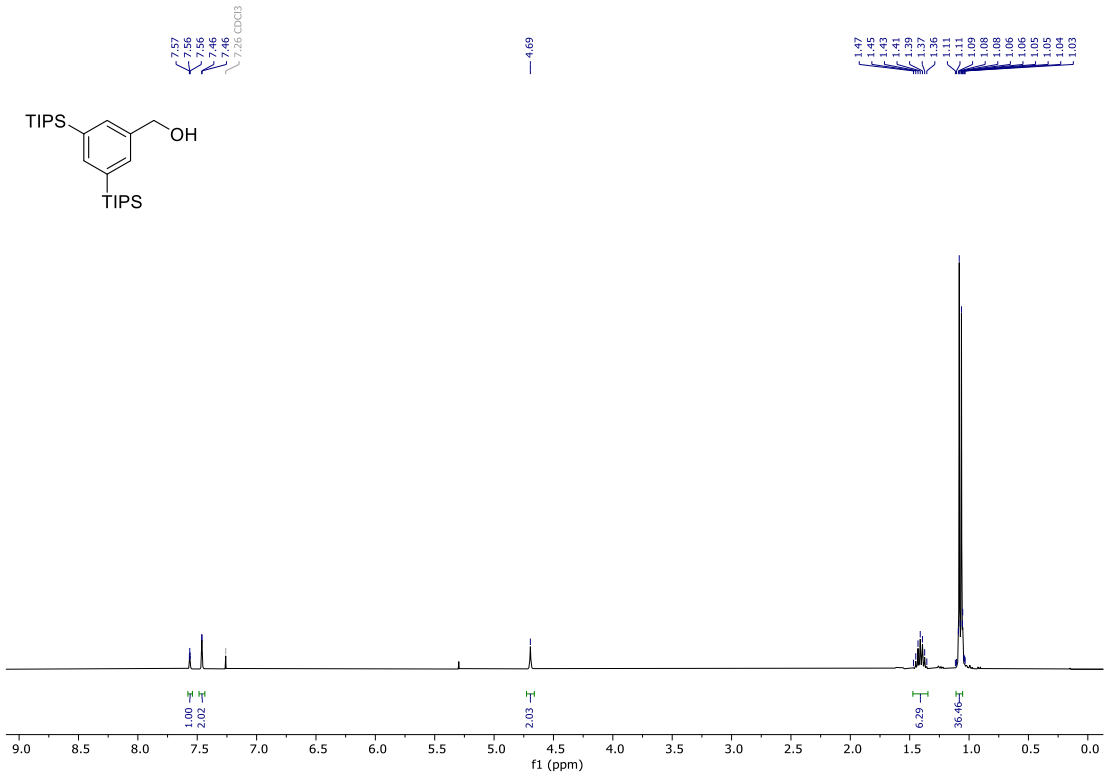
S1: ^{1}H NMR (400 MHz, $CDCl_3$):



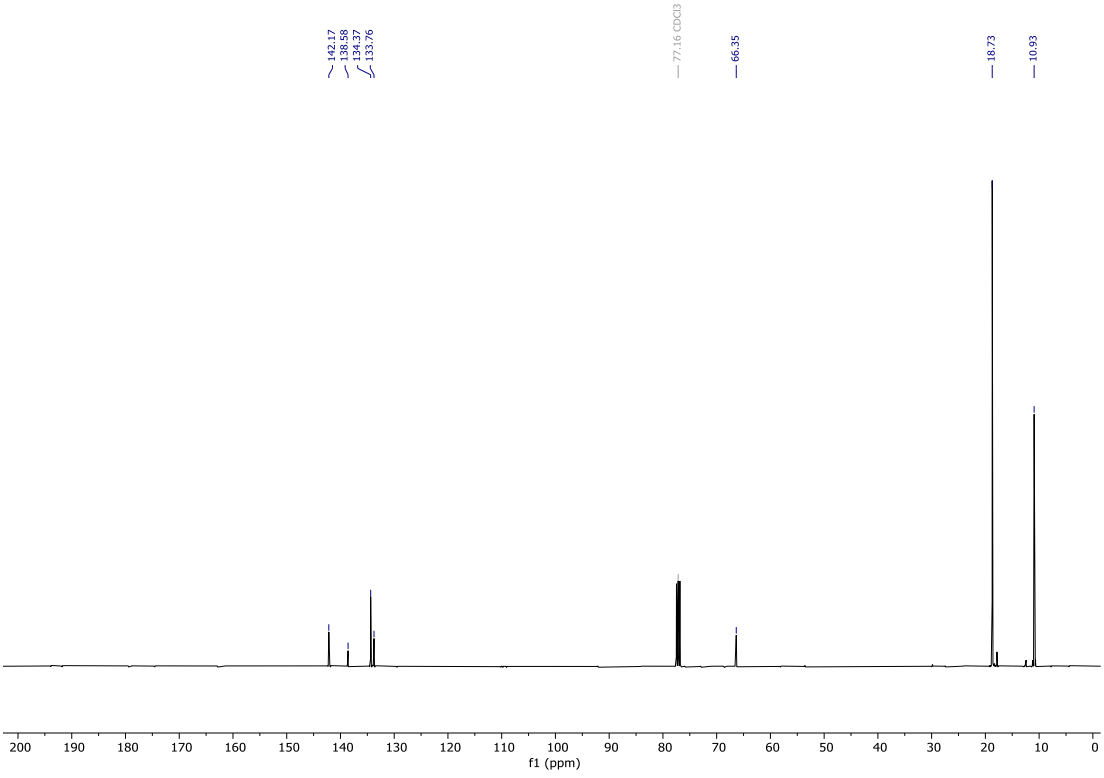
S1: ^{13}C NMR (101 MHz, $CDCl_3$):



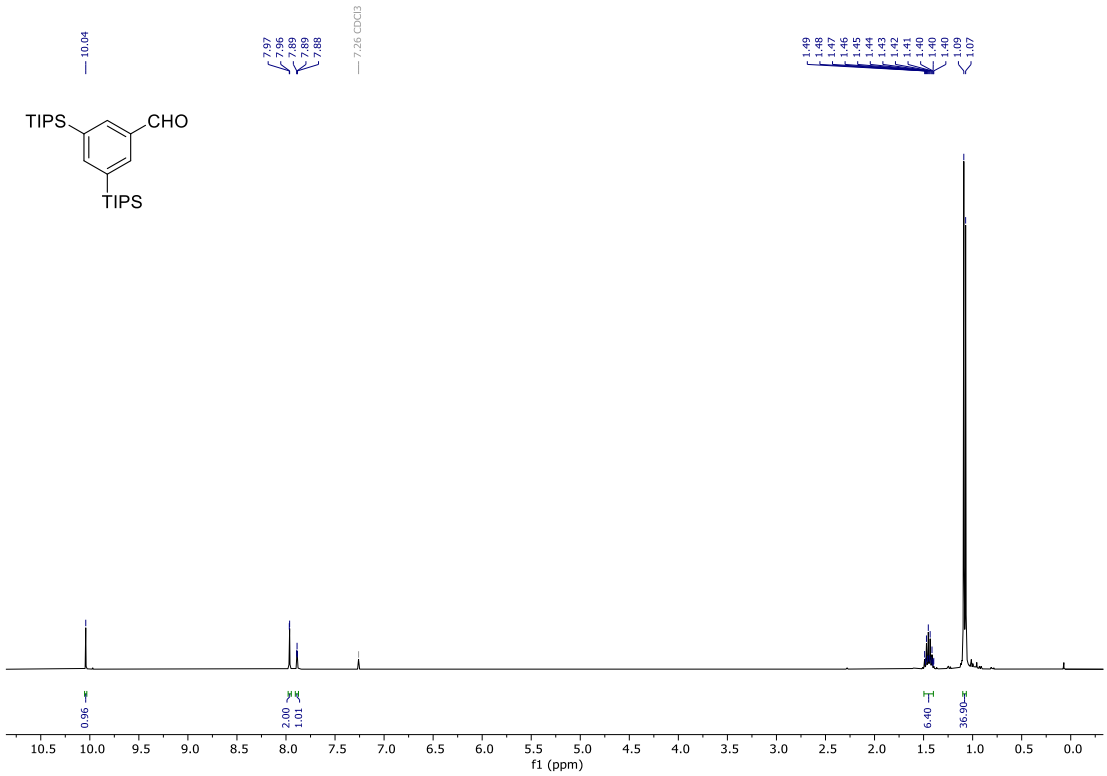
7: ^{1}H NMR (400 MHz, $CDCl_3$):



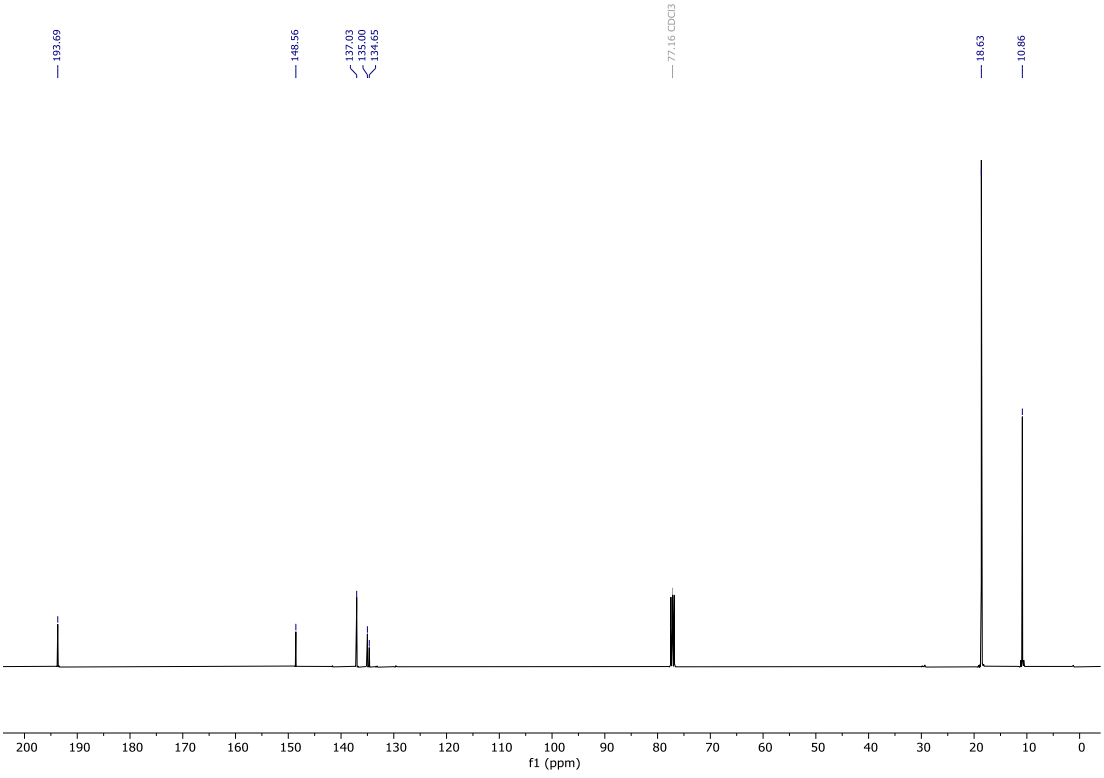
7: ^{13}C NMR (101 MHz, $CDCl_3$):



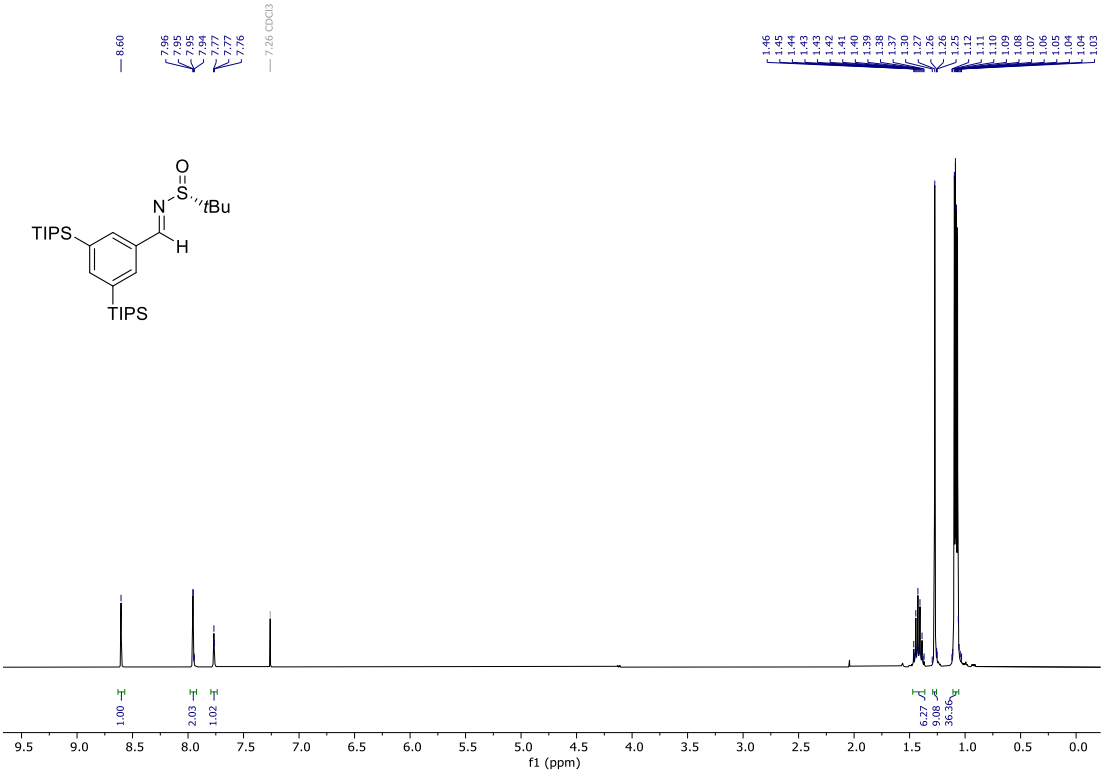
S2: ^{1}H NMR (400 MHz, $CDCl_3$):



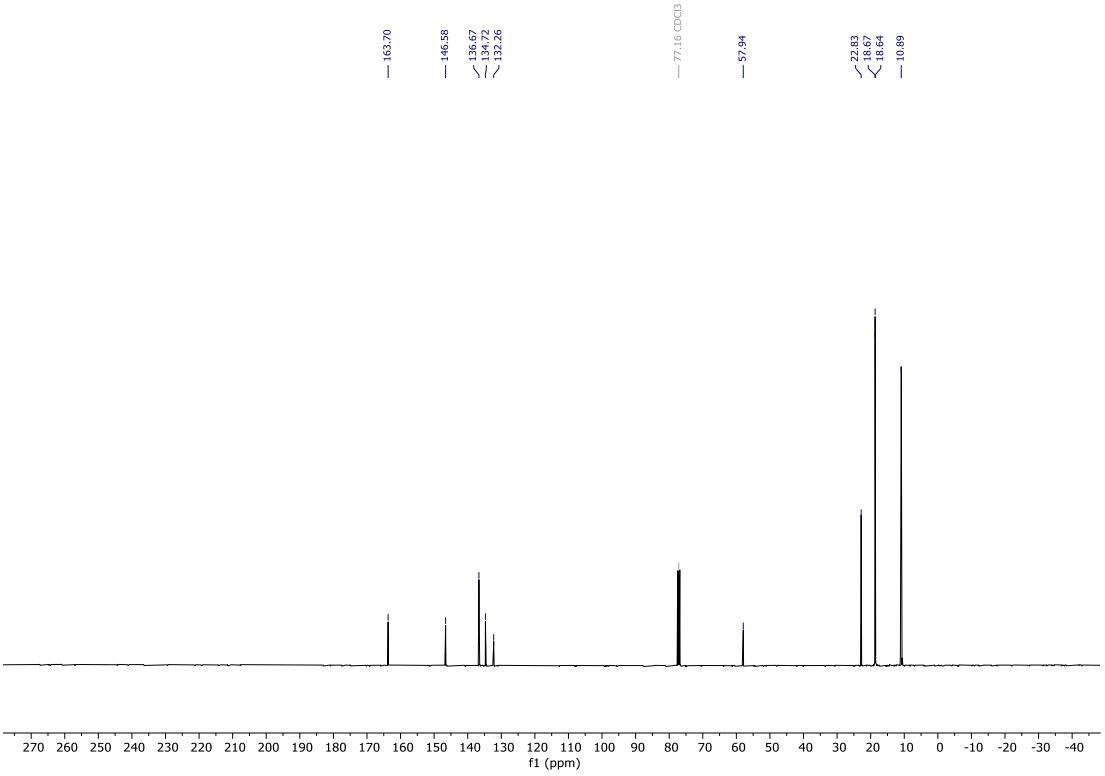
S2: ^{13}C NMR (101 MHz, $CDCl_3$):



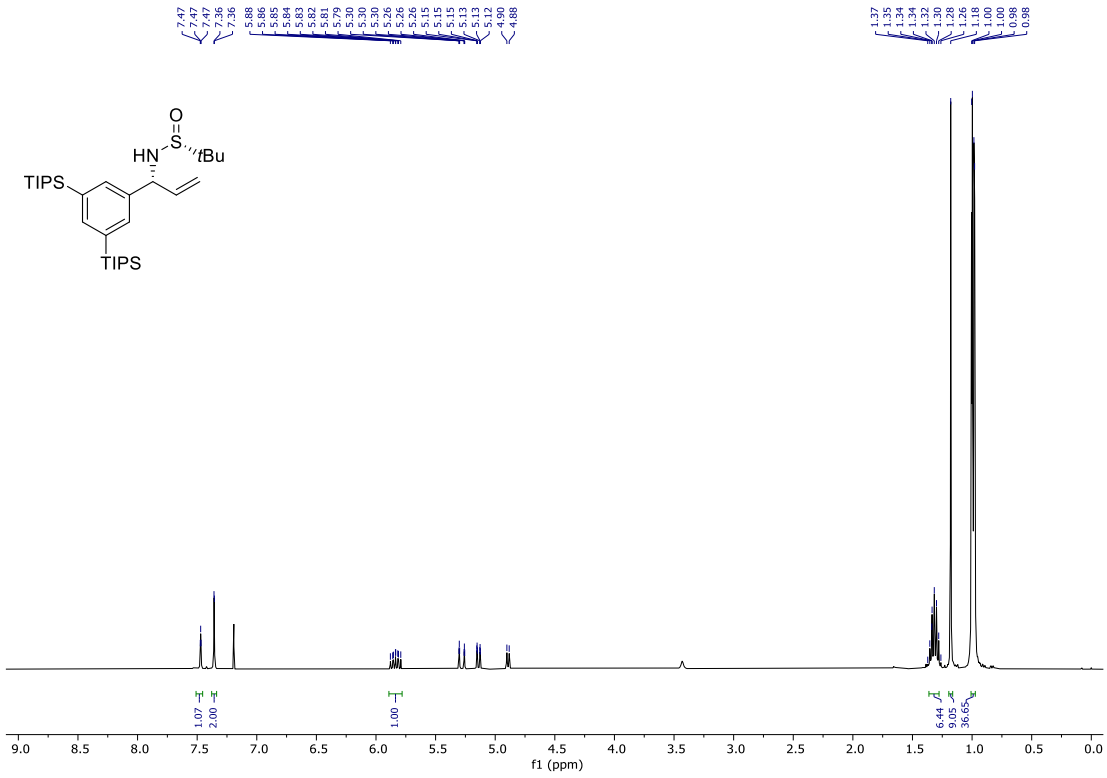
8: ^{1}H NMR (400 MHz, $CDCl_3$):



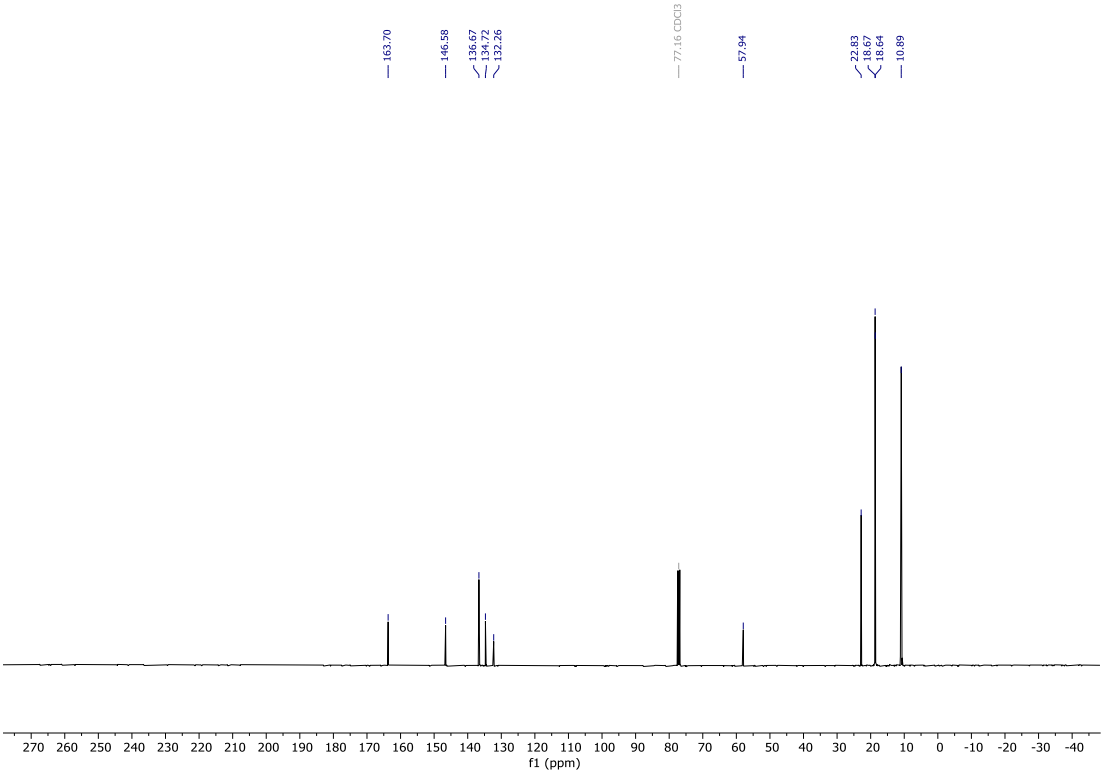
8: ^{13}C NMR (101 MHz, $CDCl_3$):



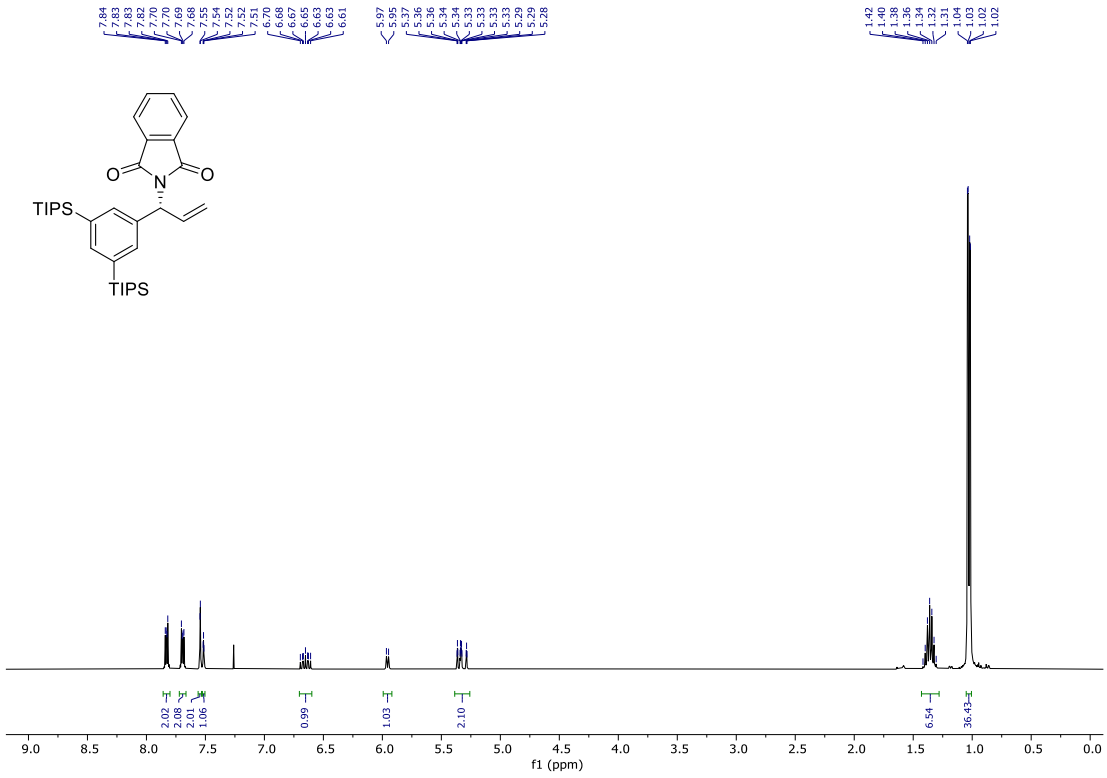
9: ^{1}H NMR (400 MHz, $CDCl_3$):



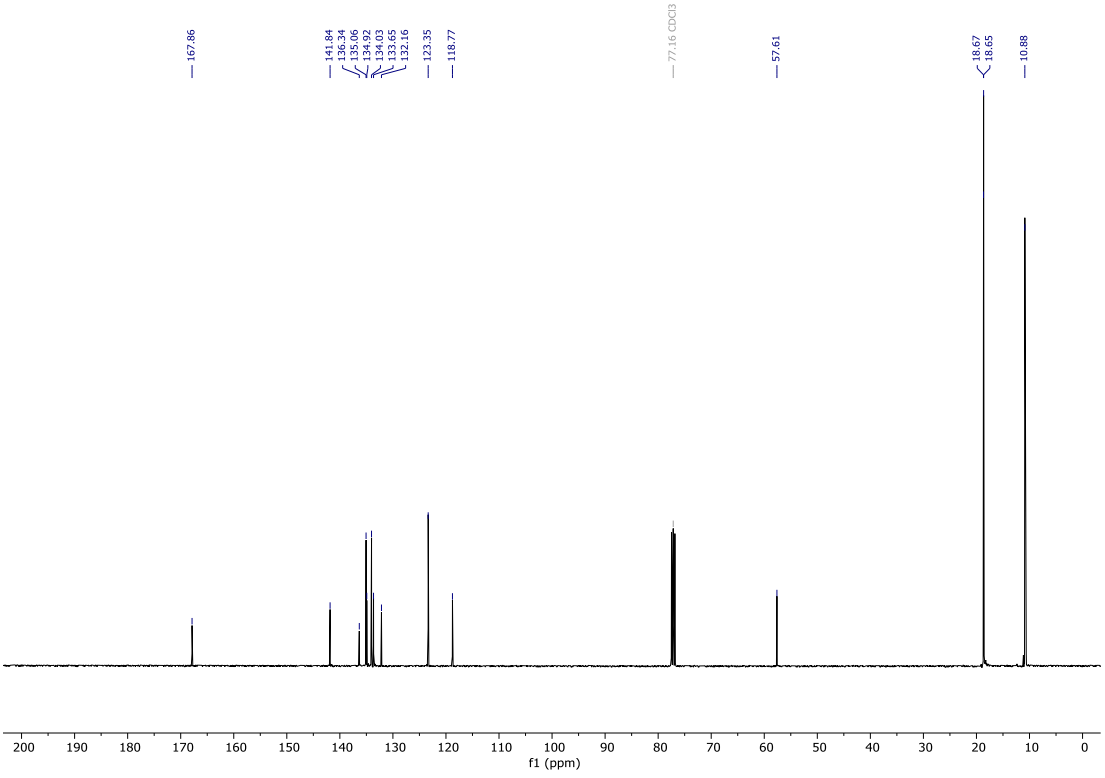
9: ^{13}C NMR (101 MHz, $CDCl_3$):



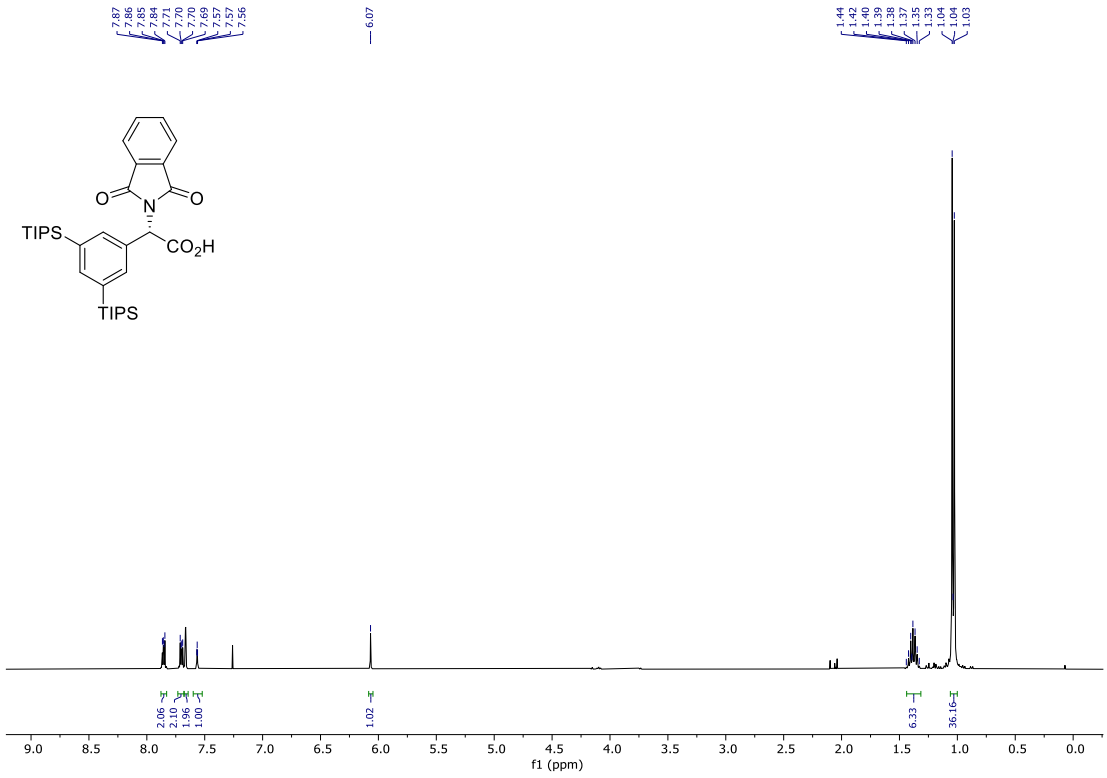
10a: ^{1}H NMR (400 MHz, $CDCl_3$):



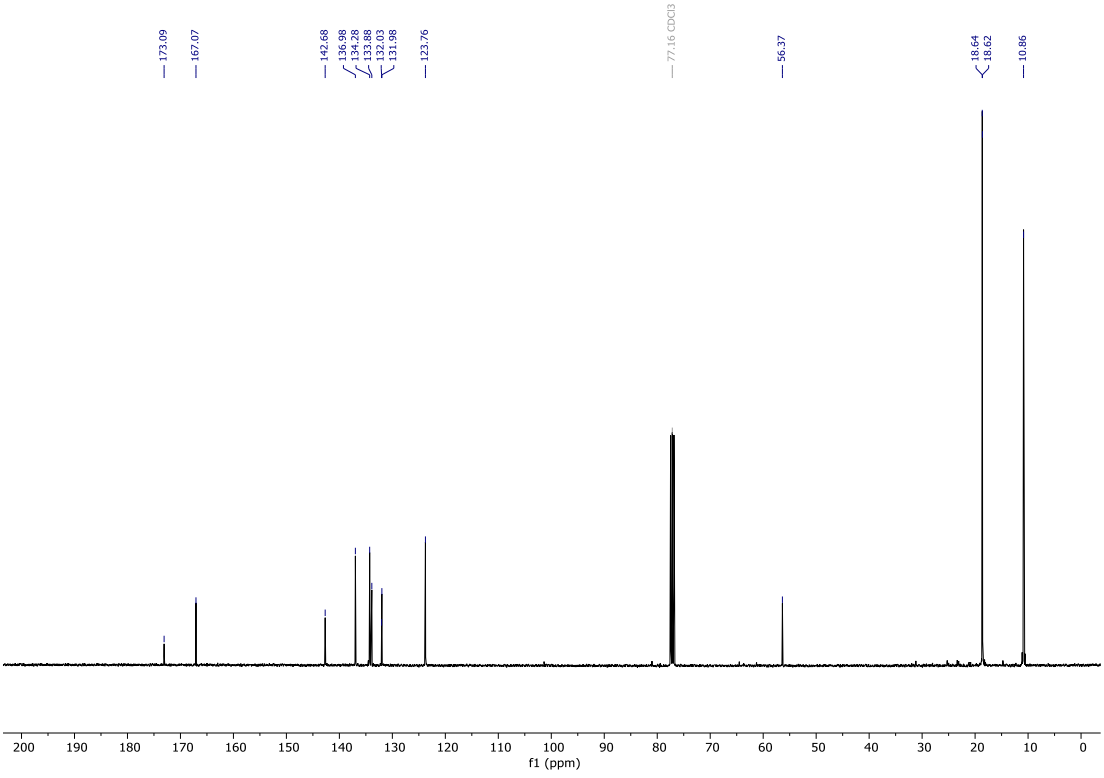
10a: ^{13}C NMR (101 MHz, $CDCl_3$):



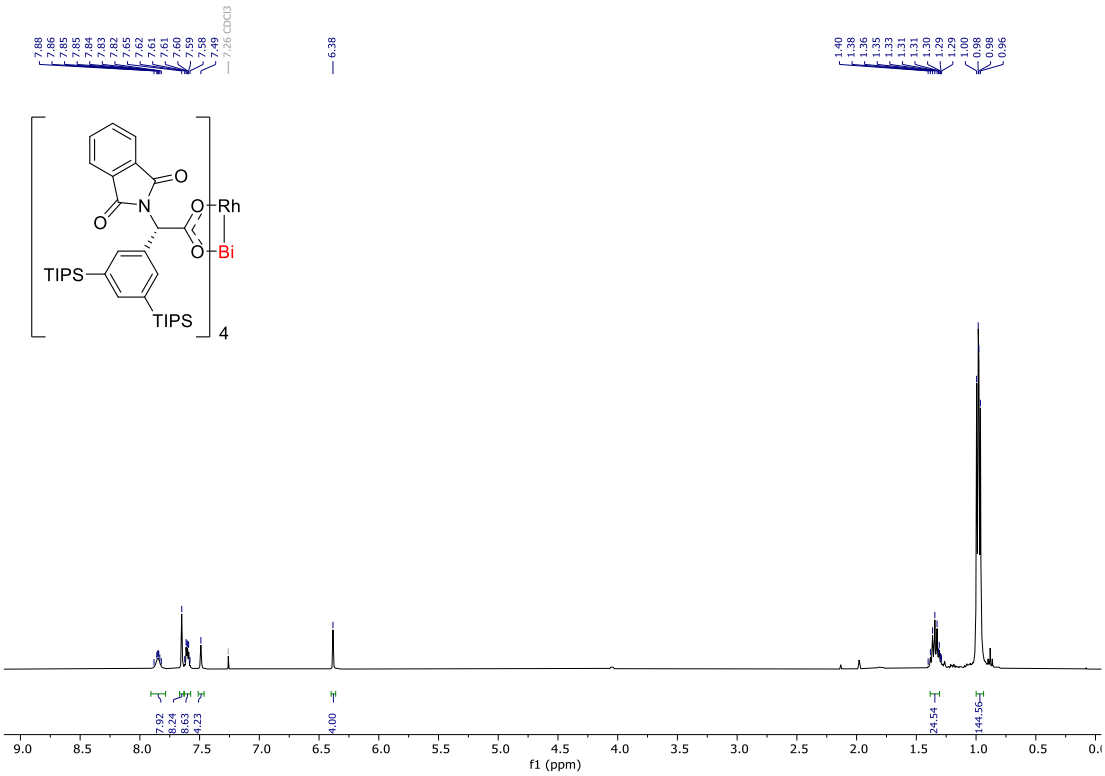
11a: ^{1}H NMR (400 MHz, $CDCl_3$):



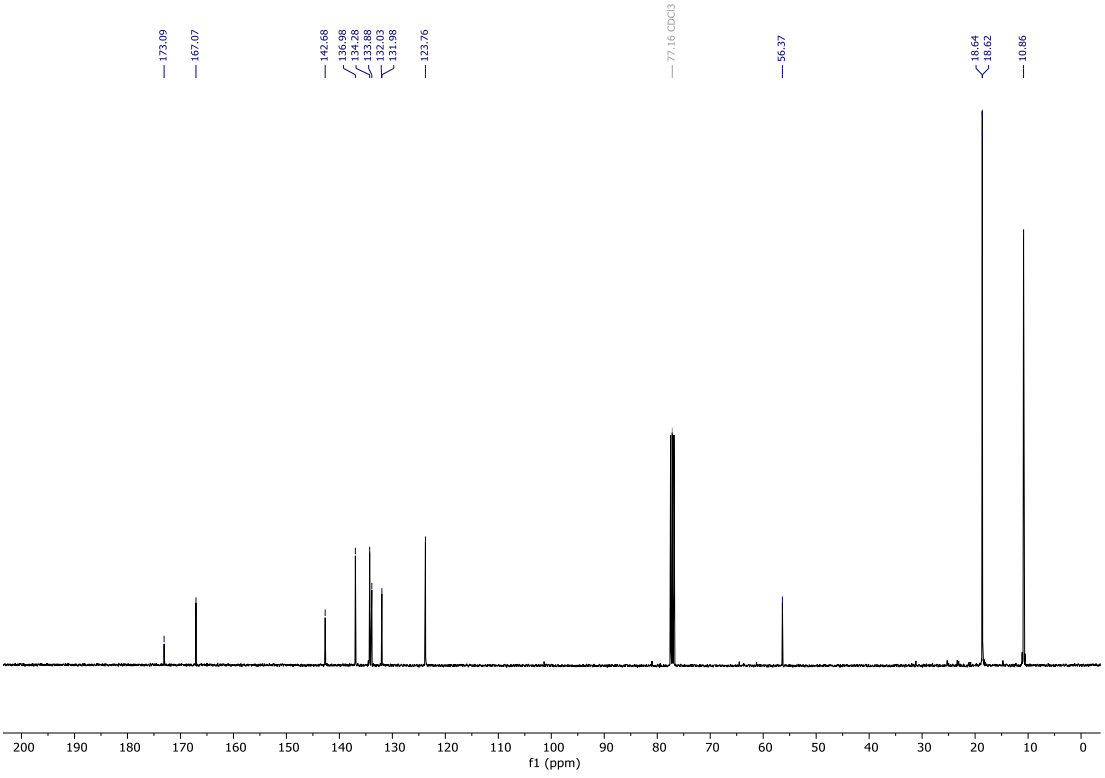
11a: ^{13}C NMR (101 MHz, $CDCl_3$):



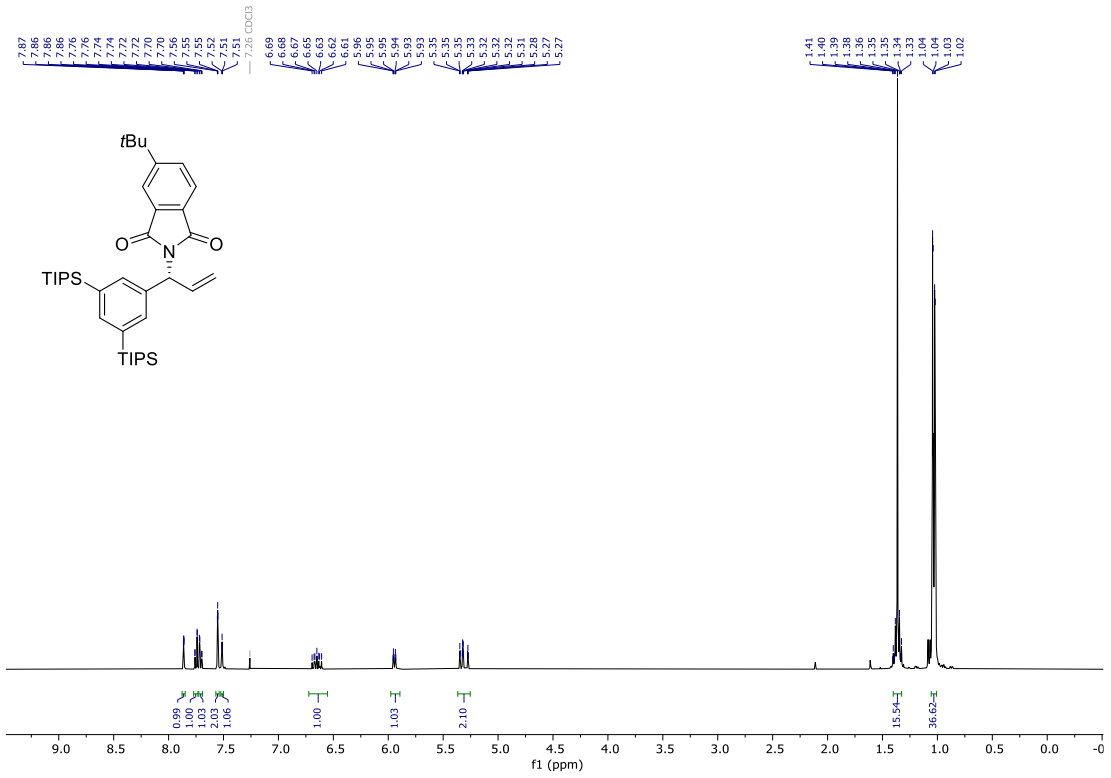
3a: ^{1}H NMR (400 MHz, $CDCl_3$):



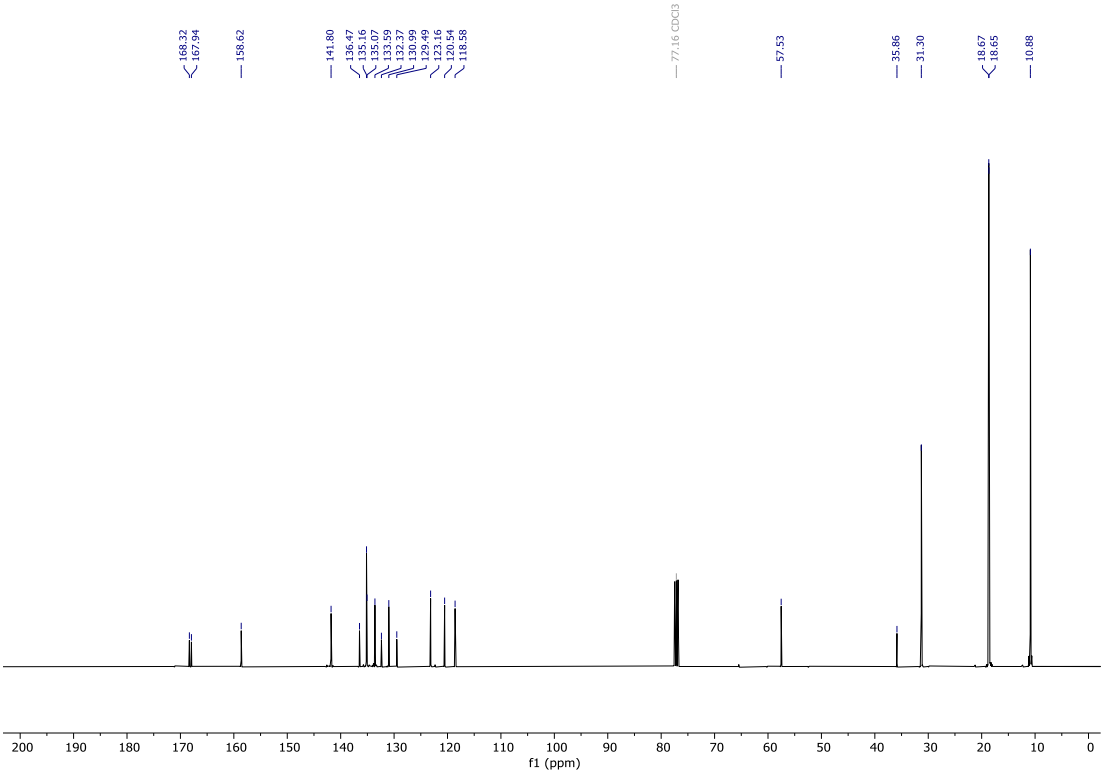
3a: ^{13}C NMR (101 MHz, $CDCl_3$):



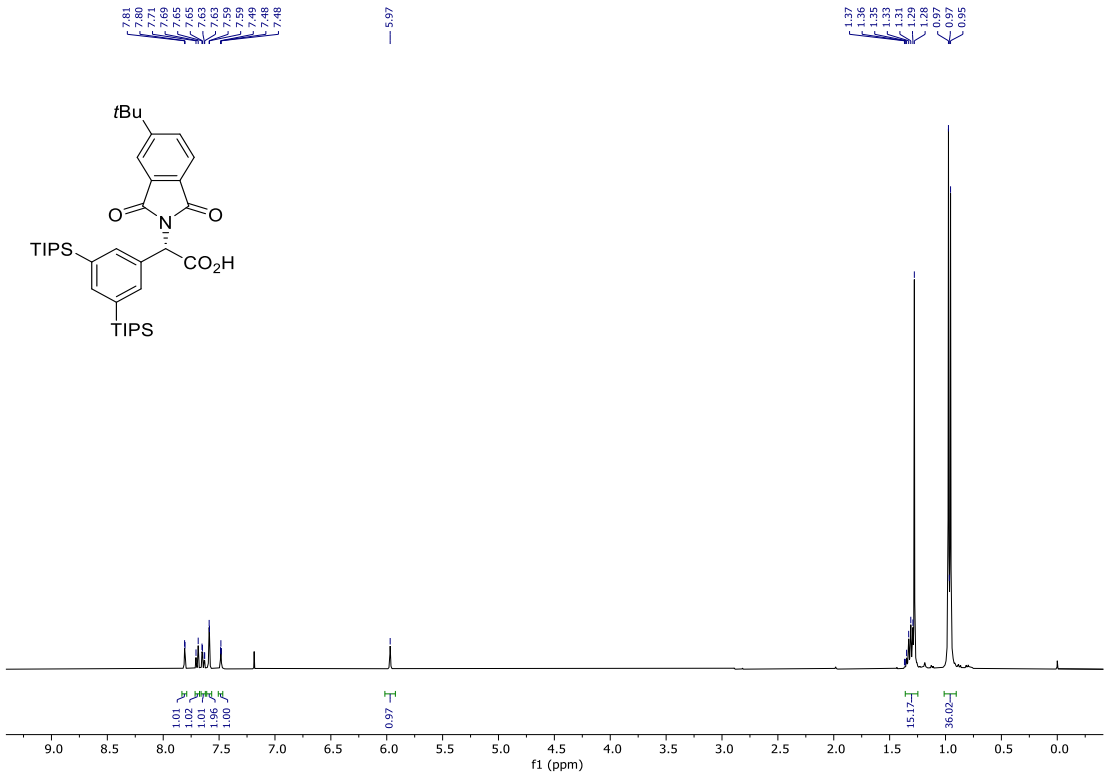
10b: ^{1}H NMR (400 MHz, $CDCl_3$):



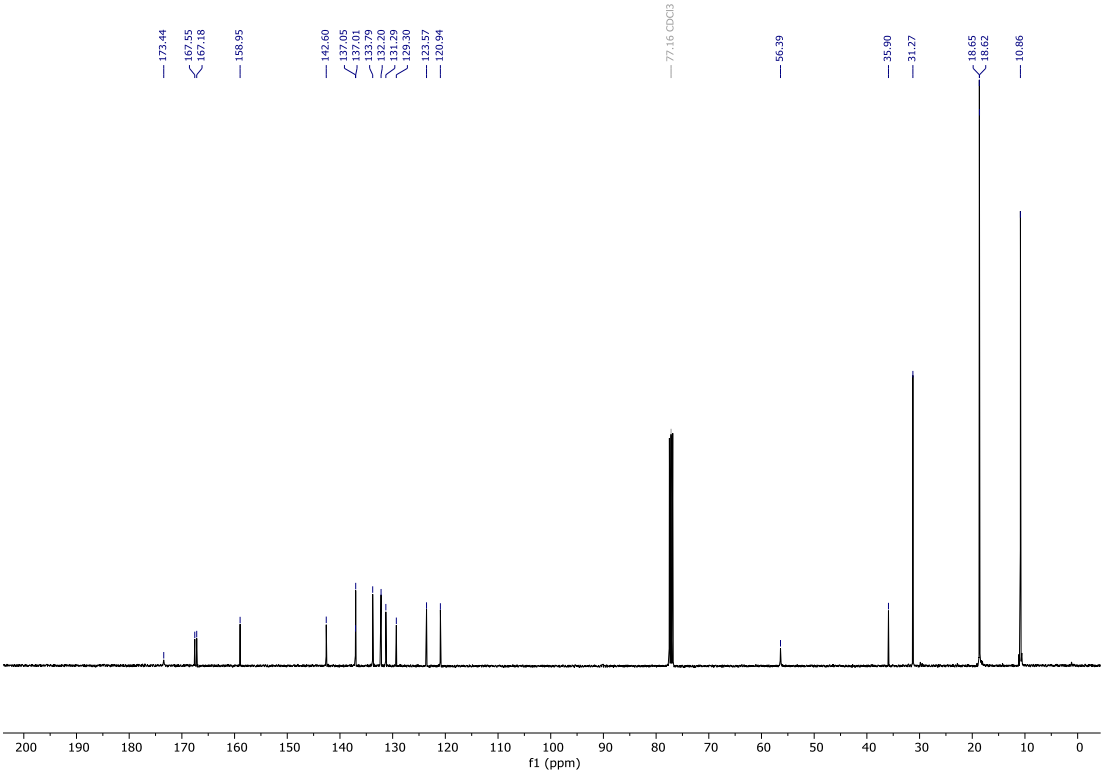
10b: ^{13}C NMR (101 MHz, $CDCl_3$):



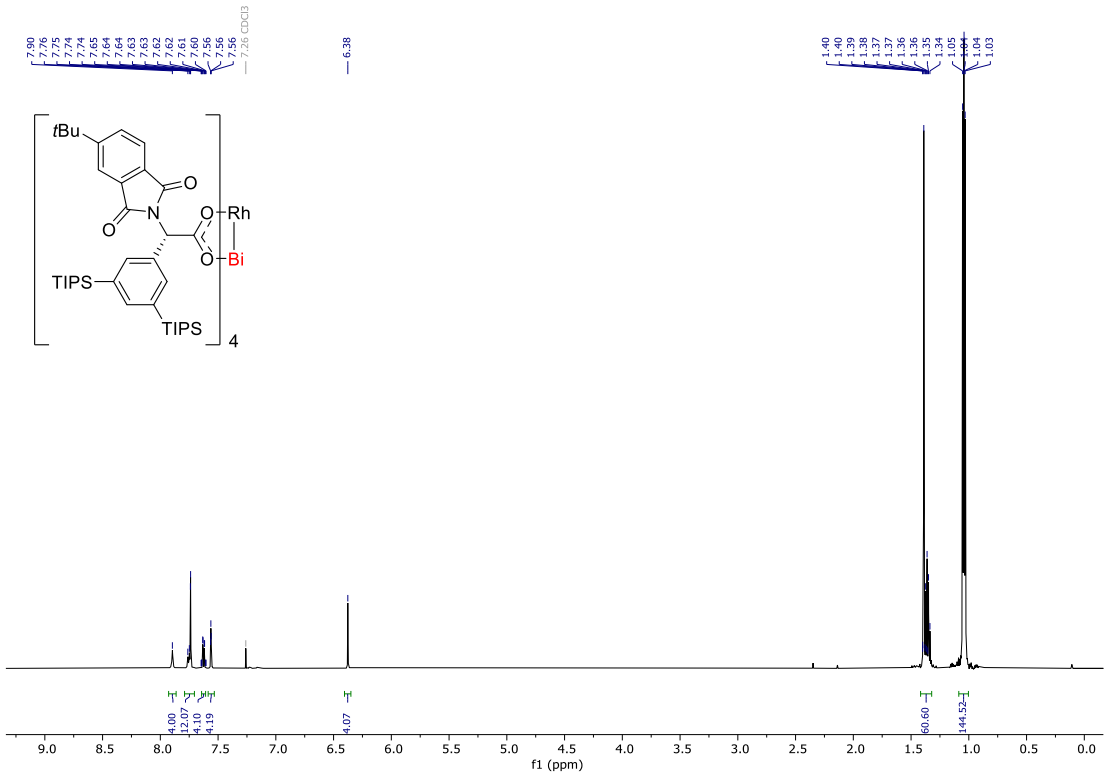
11b: ^{1}H NMR (400 MHz, $CDCl_3$):



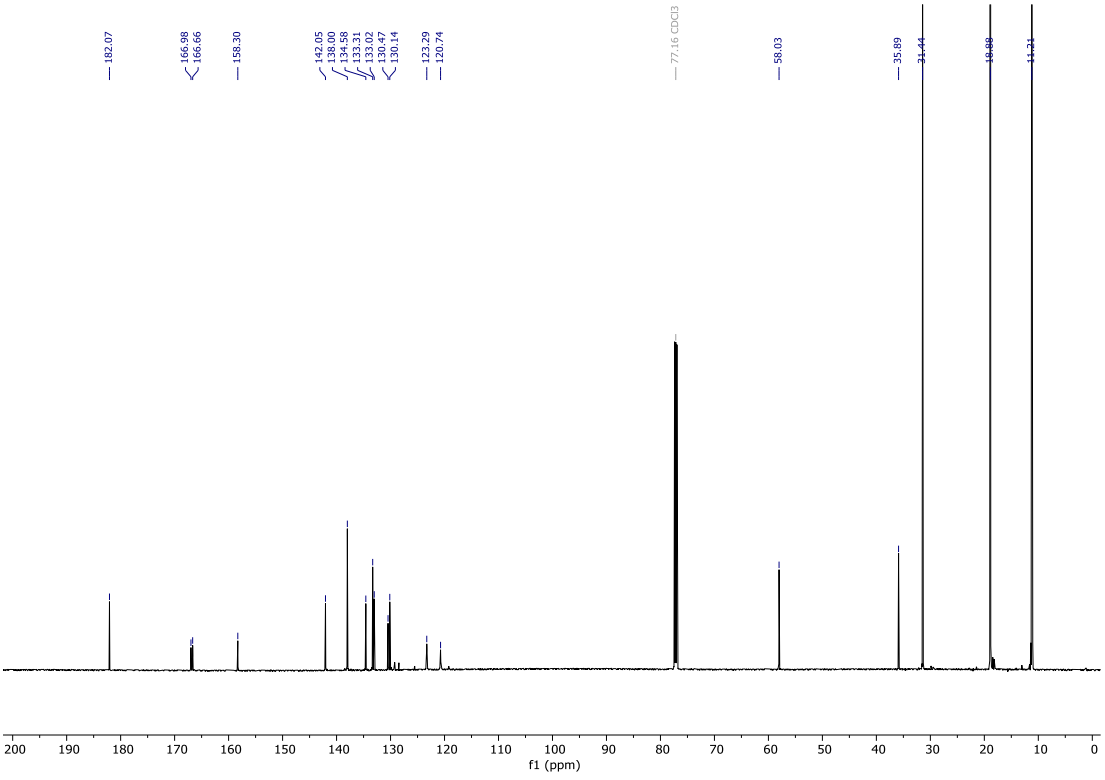
11b: ^{13}C NMR (101 MHz, $CDCl_3$):



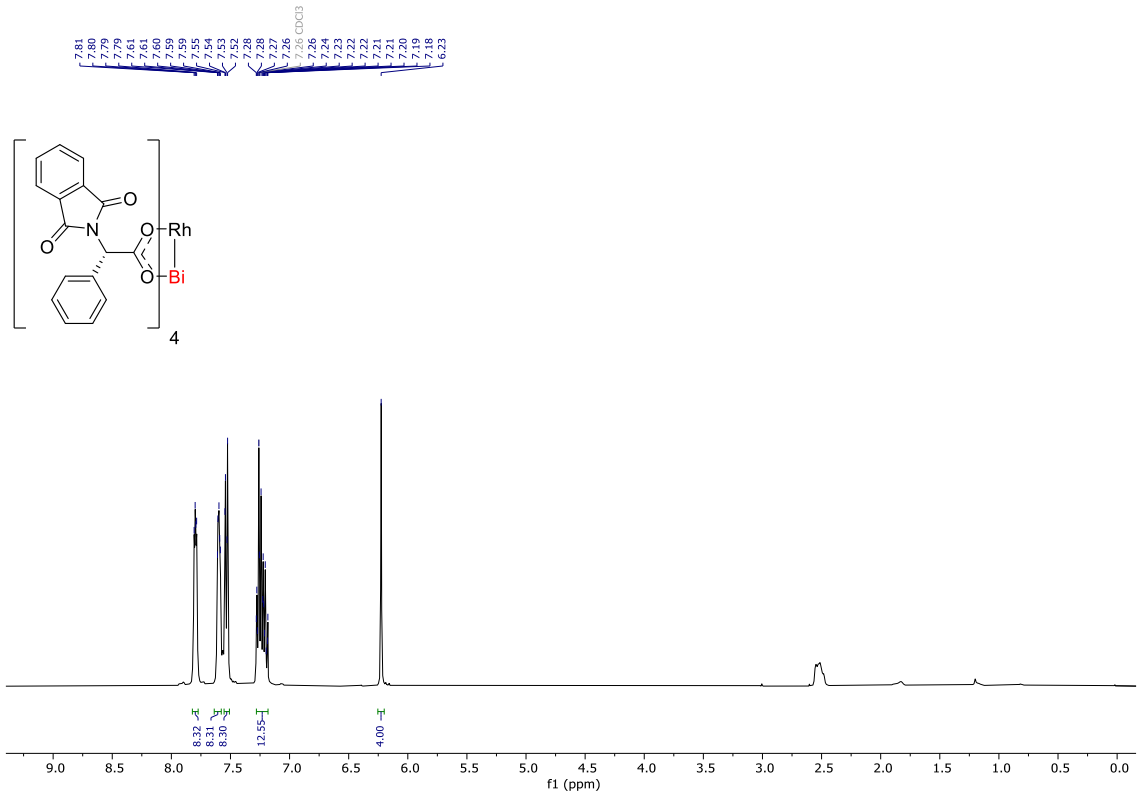
3b: ^{1}H NMR (600 MHz, $CDCl_3$, 353 K):



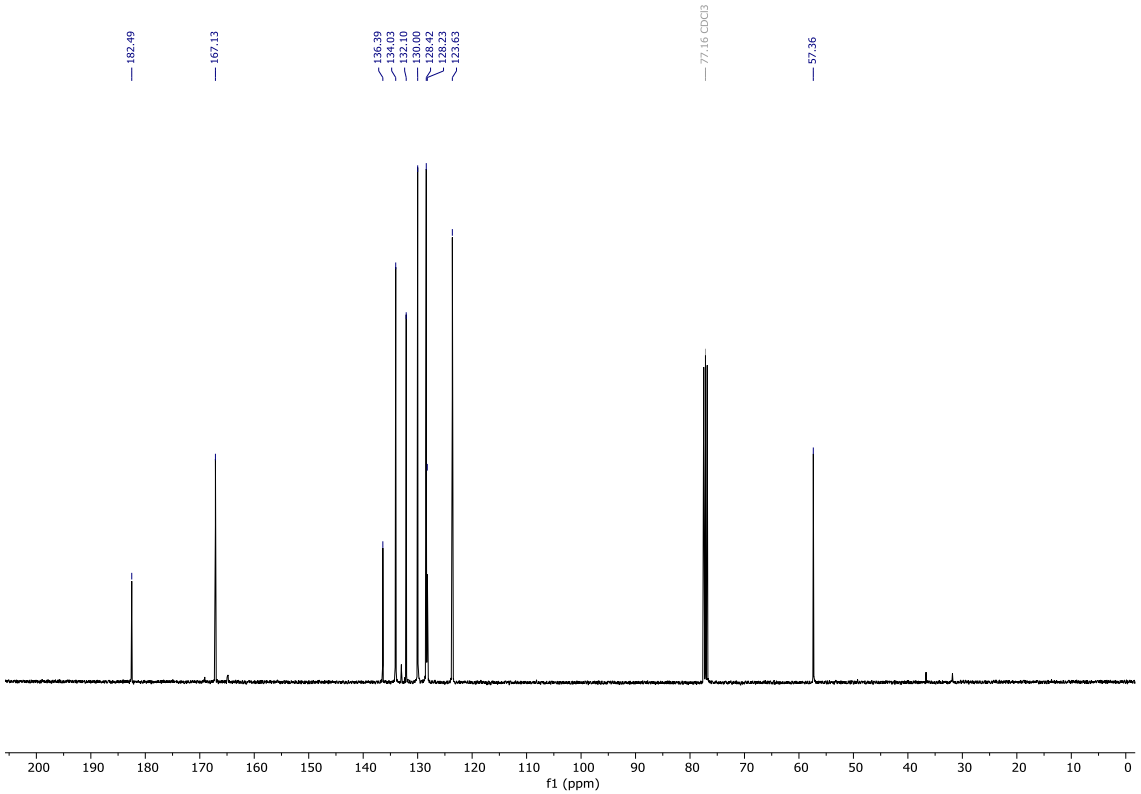
3b: ^{13}C NMR (151 MHz, $CDCl_3$, 353 K):



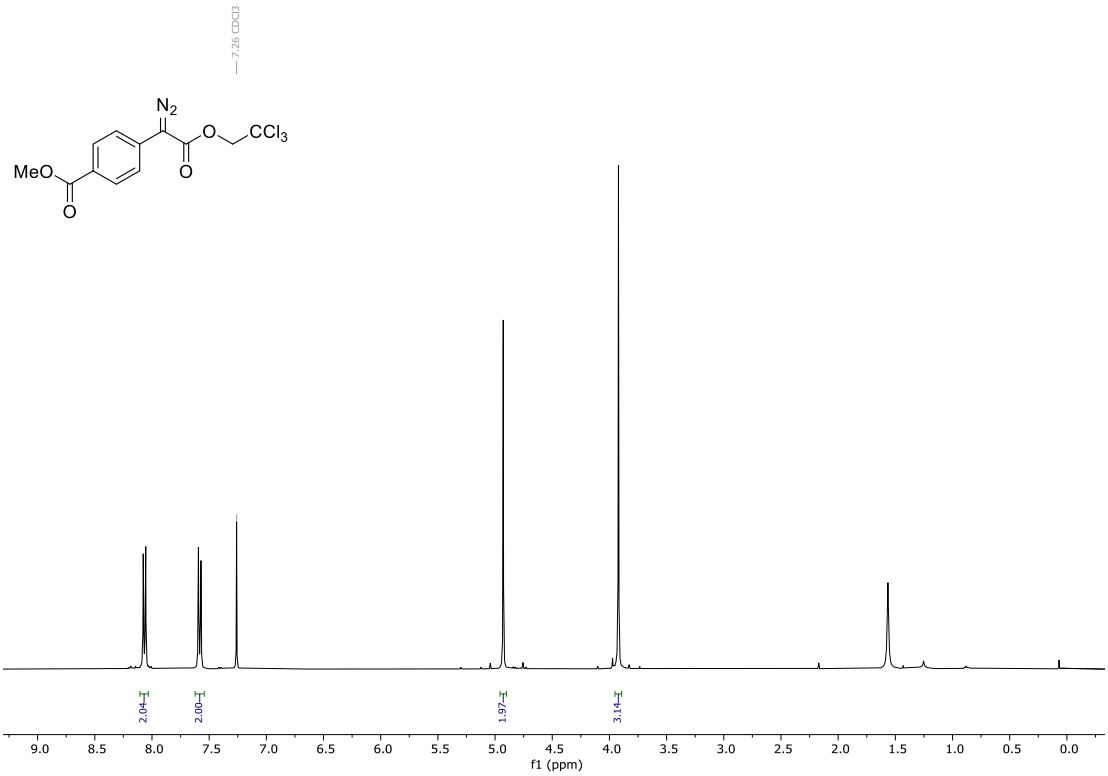
BiRh(*S*-PTPG)$_4$ (S3): ^{1}H NMR (400 MHz, $CDCl_3$):



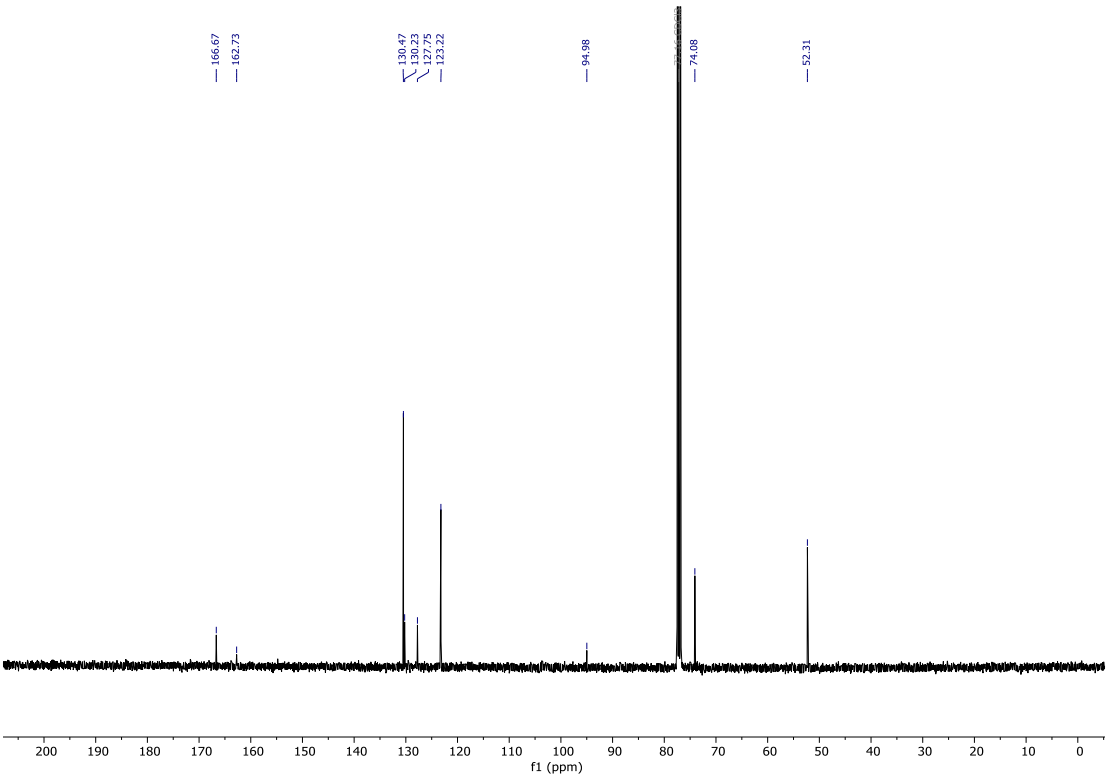
BiRh(*S*-PTPG)$_4$ (S3): ^{13}C NMR (101 MHz, $CDCl_3$):



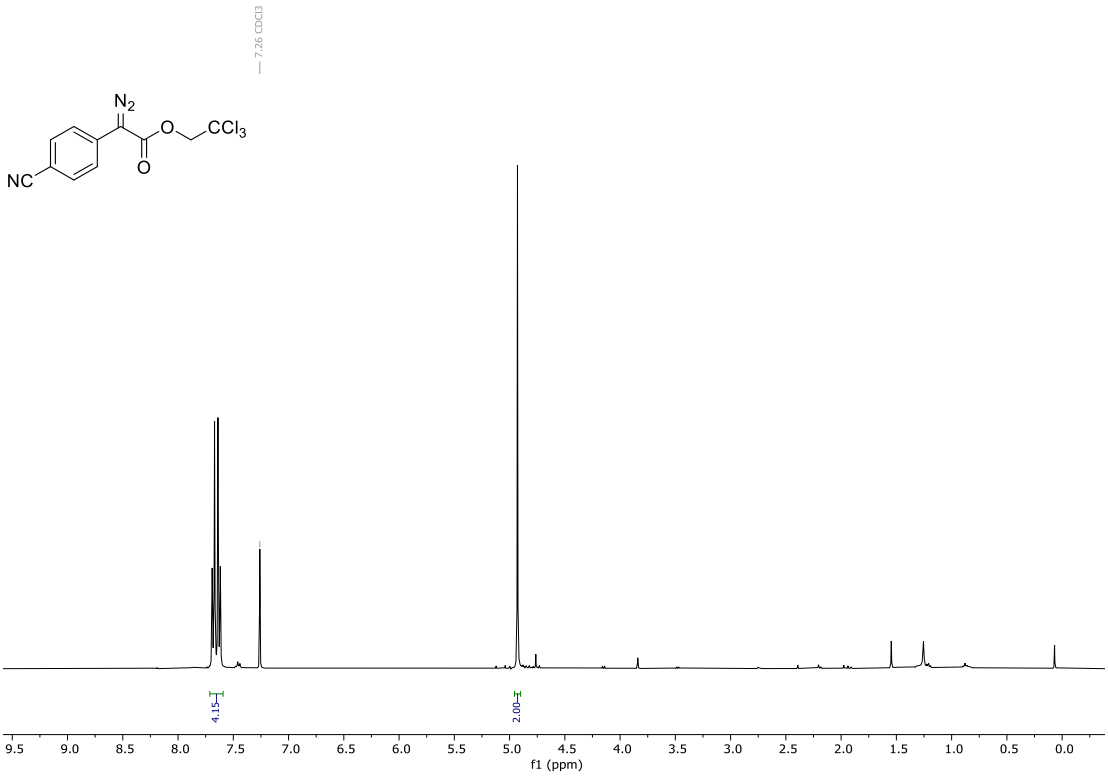
4e: ^{1}H NMR (400 MHz, $CDCl_3$):



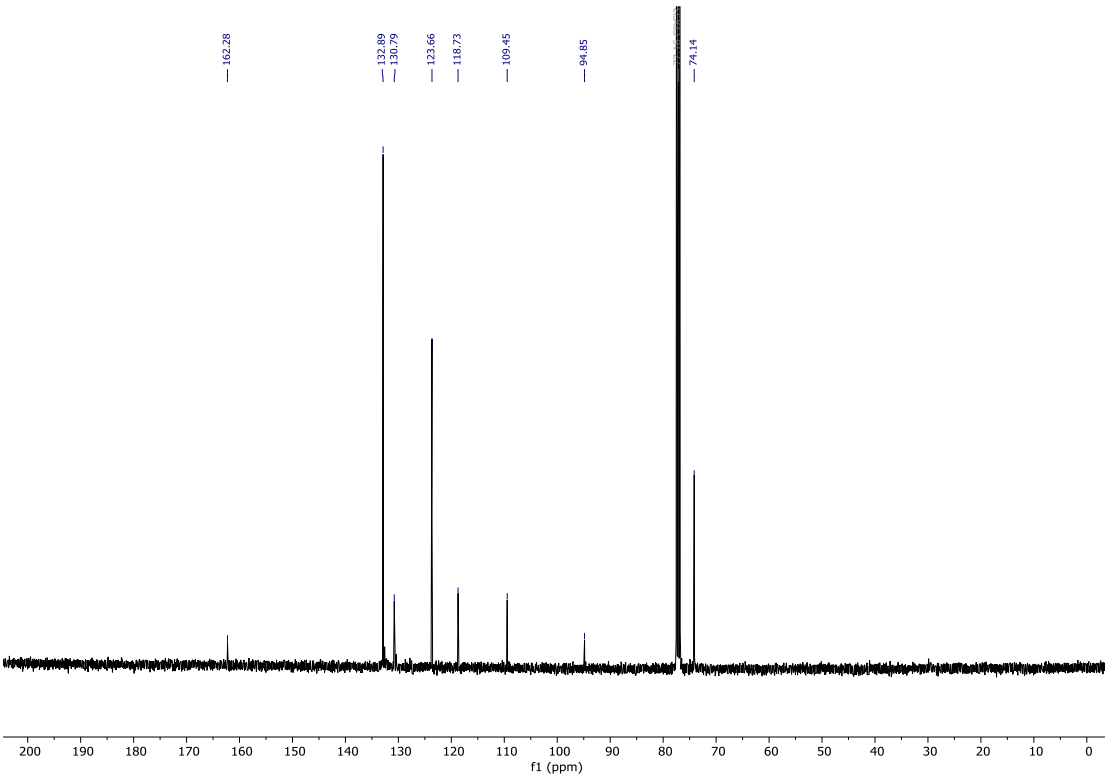
4e: ^{13}C NMR (101 MHz, $CDCl_3$):



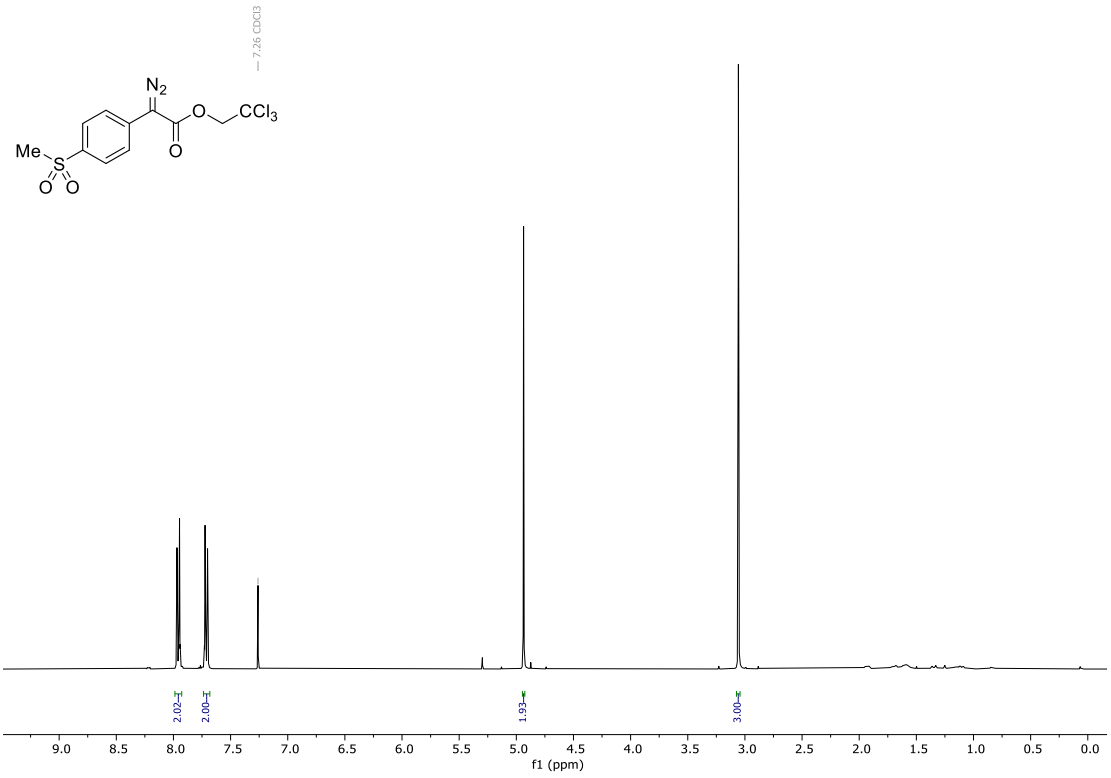
4f: ^{1}H NMR (400 MHz, $CDCl_3$):



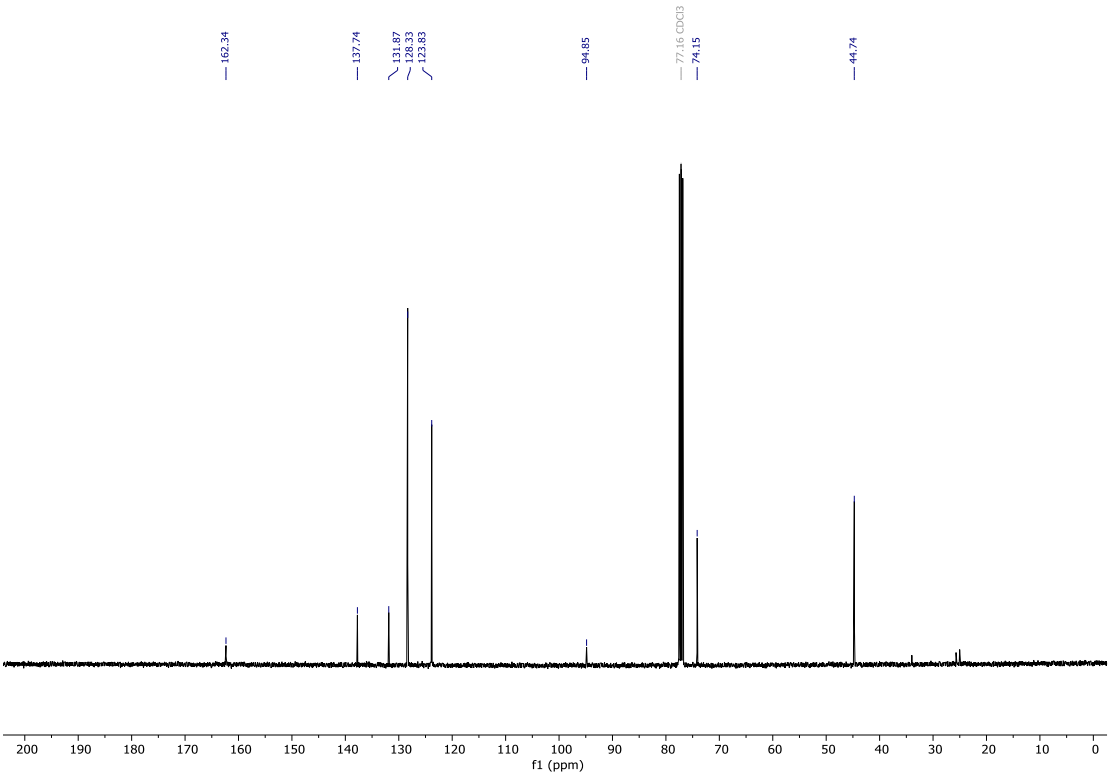
4f: ^{13}C NMR (101 MHz, $CDCl_3$):



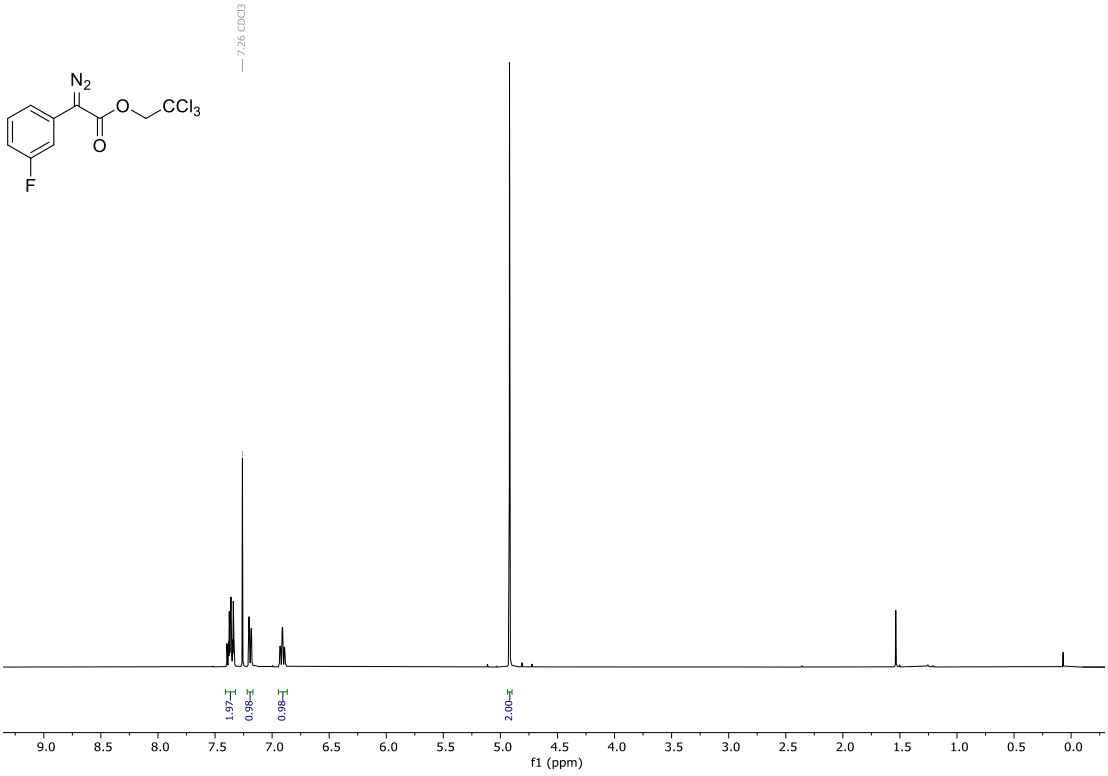
4h: ^{1}H NMR (400 MHz, $CDCl_3$):



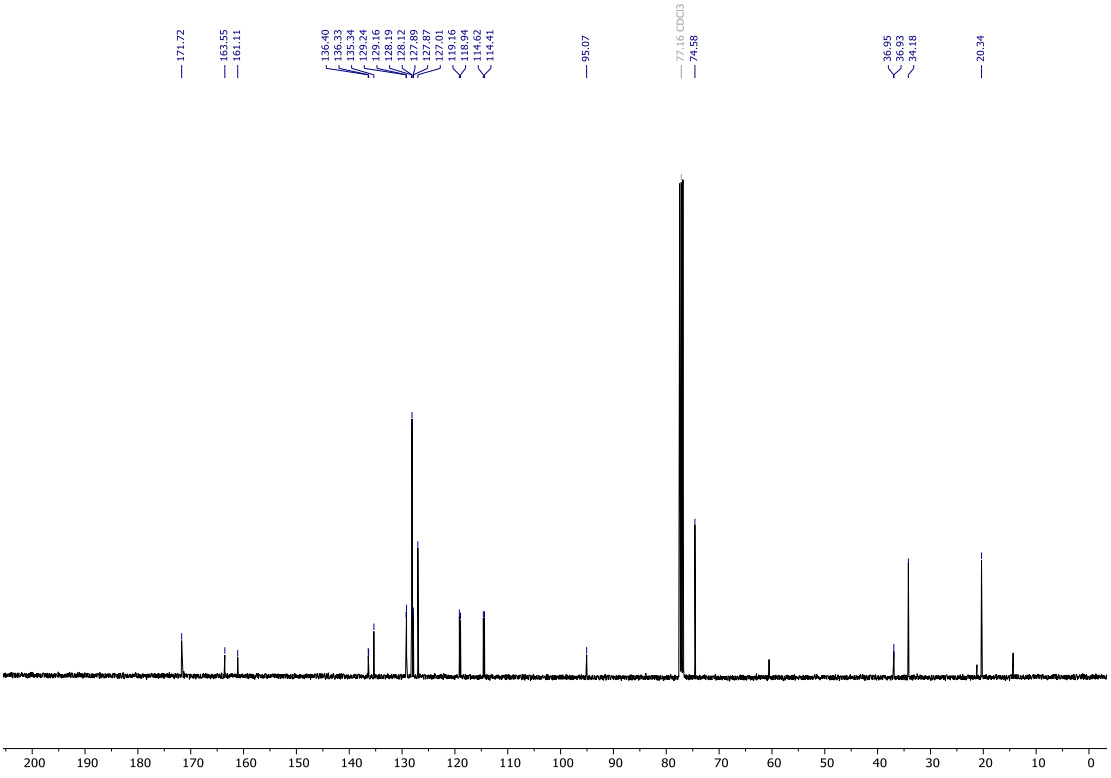
4h: ^{13}C NMR (101 MHz, $CDCl_3$):



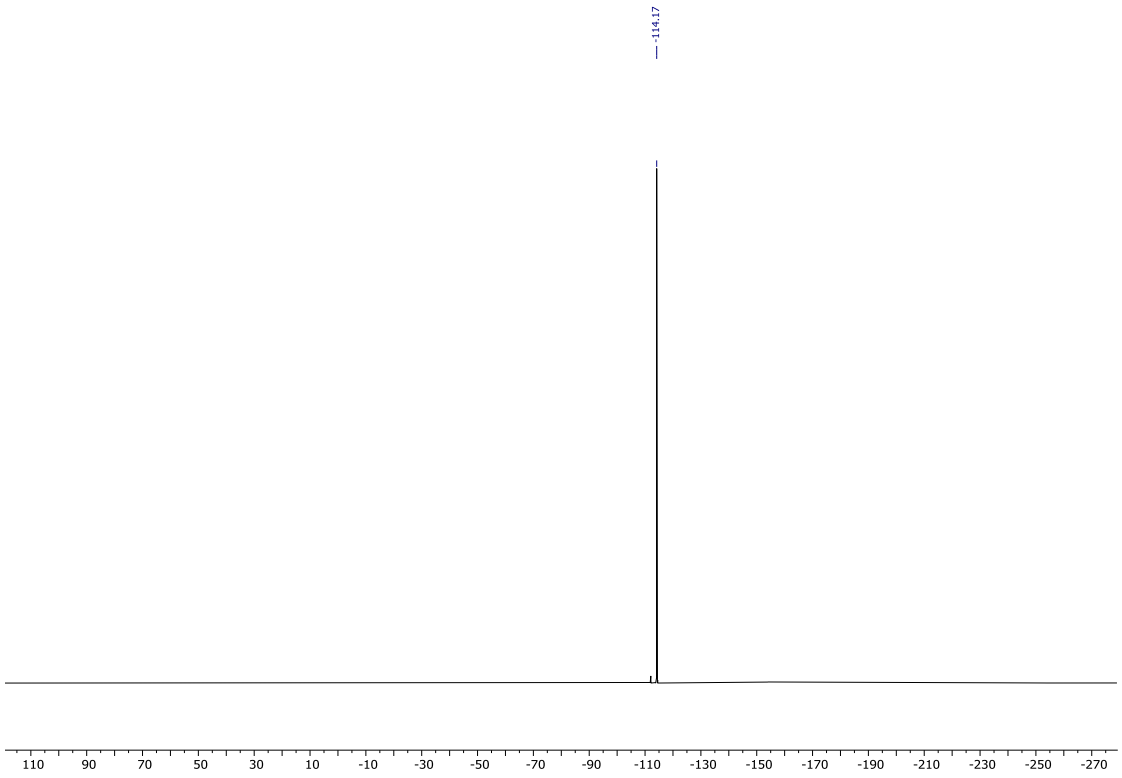
4k: ^{1}H NMR (400 MHz, $CDCl_3$):



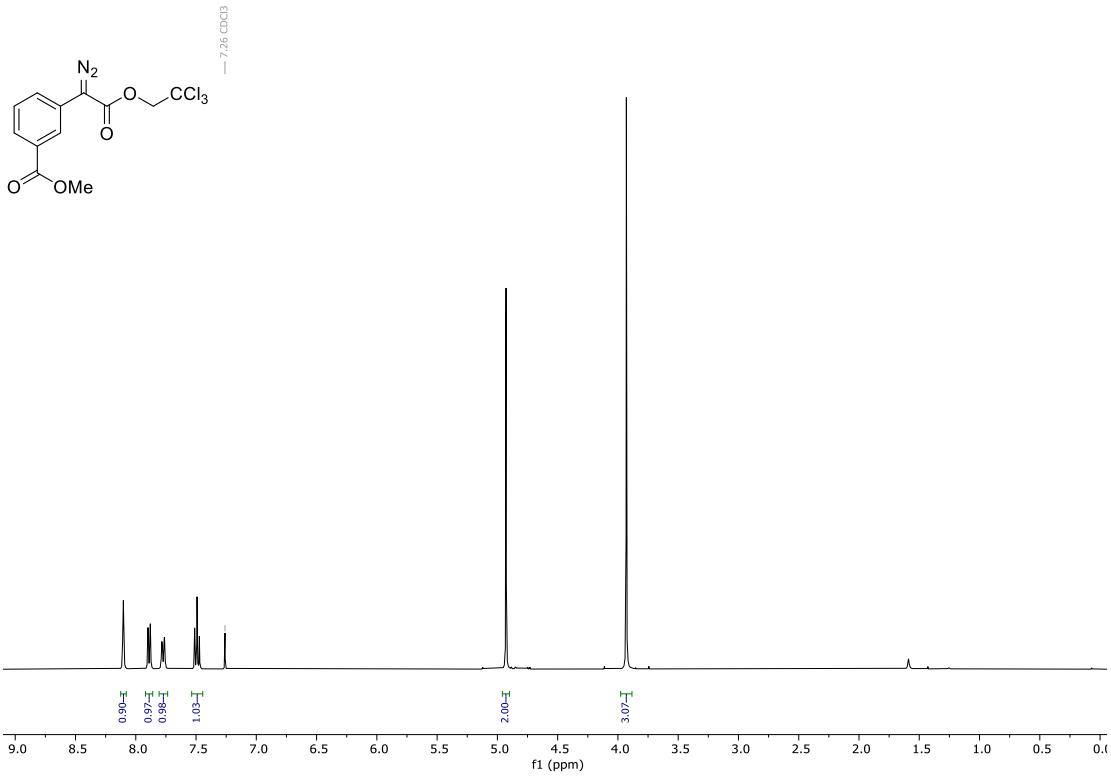
4k: ^{13}C NMR (101 MHz, $CDCl_3$):



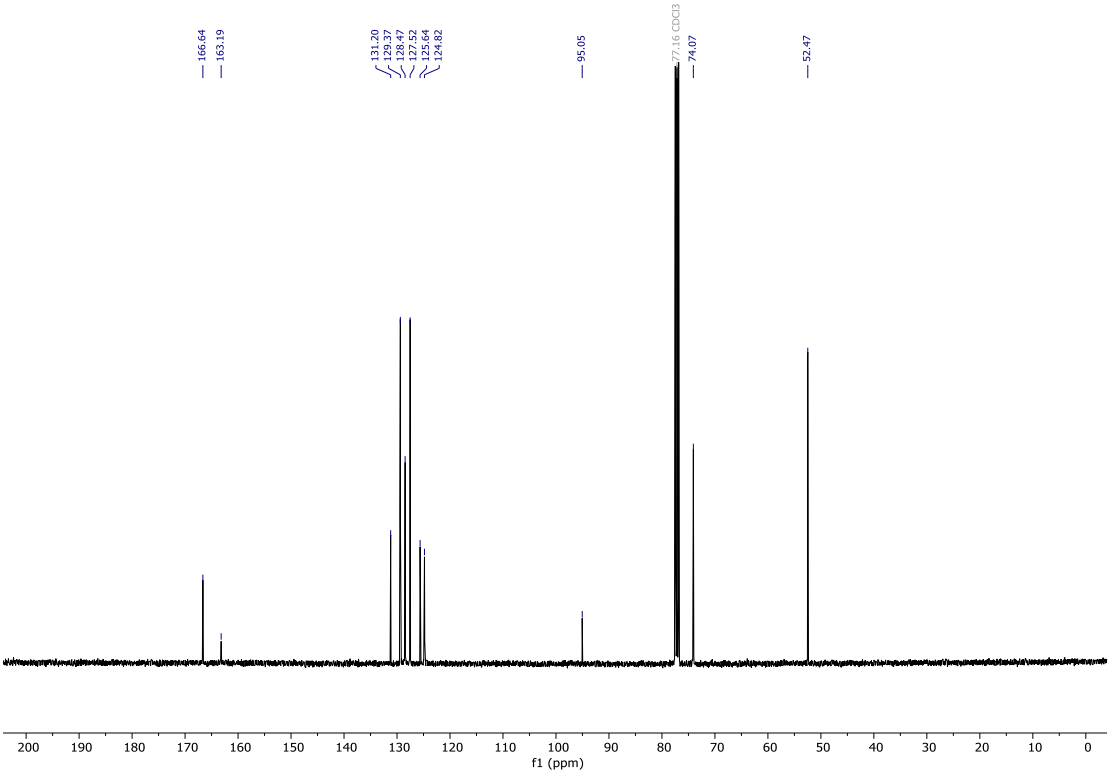
4k: ^{19}F NMR (470 MHz, $CDCl_3$):



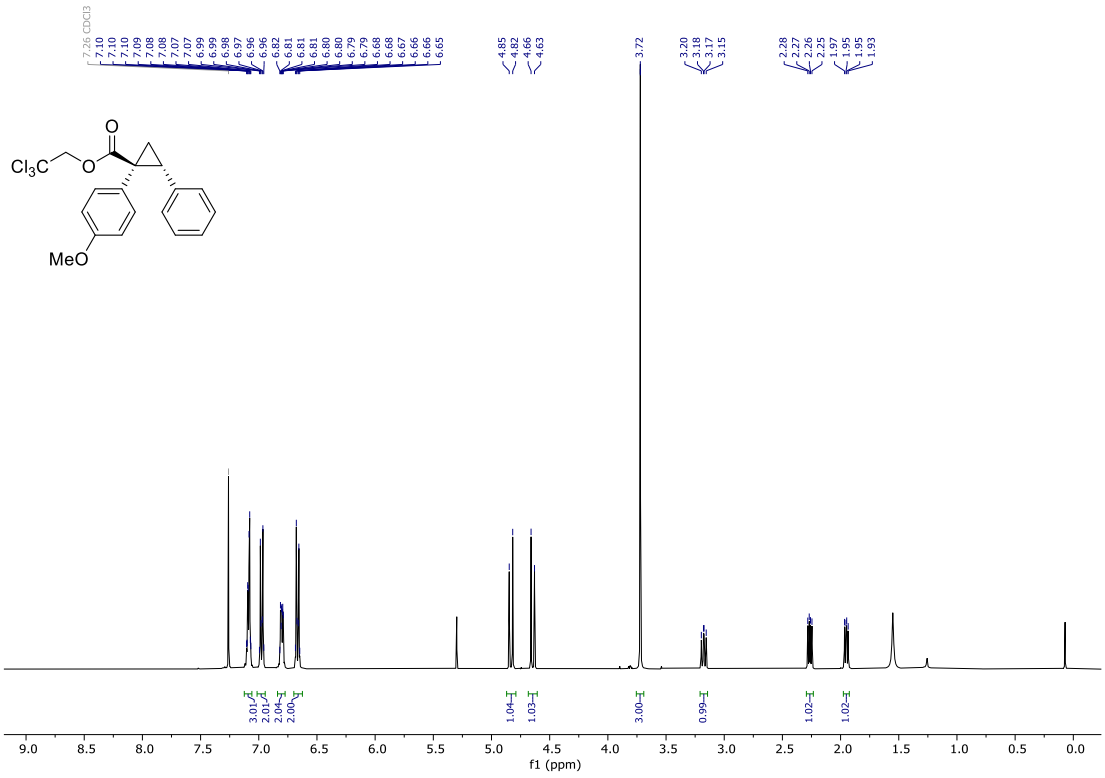
4l: ^{1}H NMR (400 MHz, $CDCl_3$):



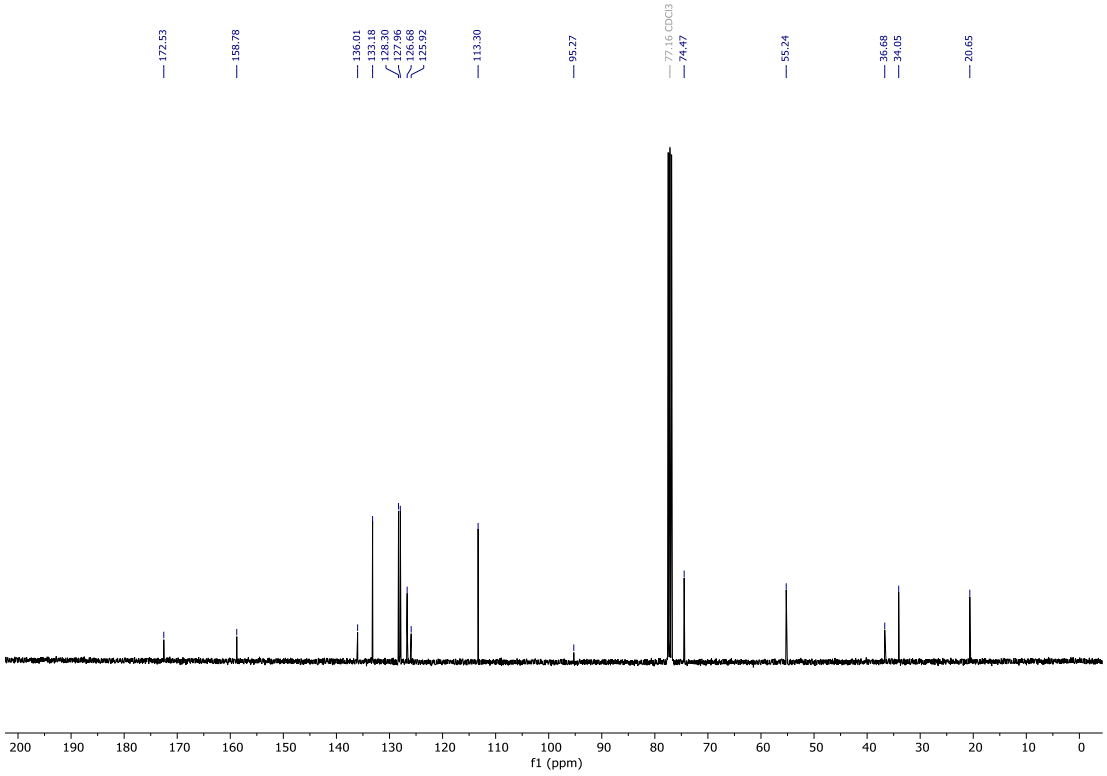
4l: ^{13}C NMR (400 MHz, $CDCl_3$):



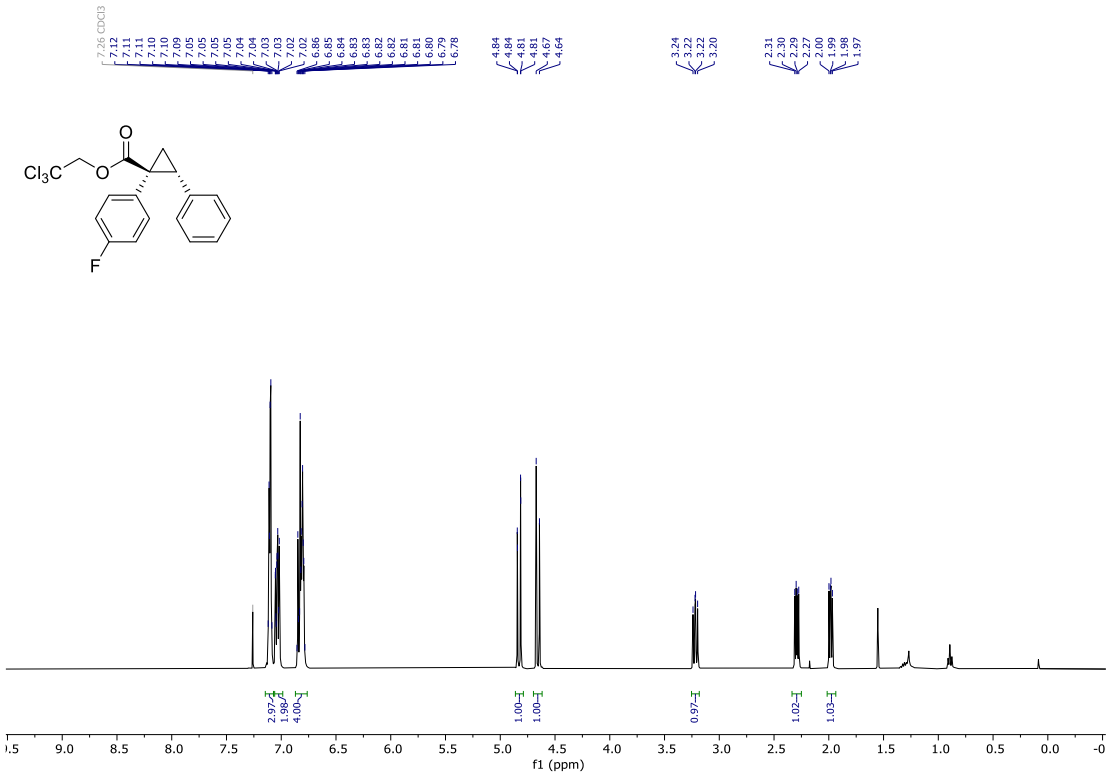
5a': ^{1}H NMR (400 MHz, $CDCl_3$):



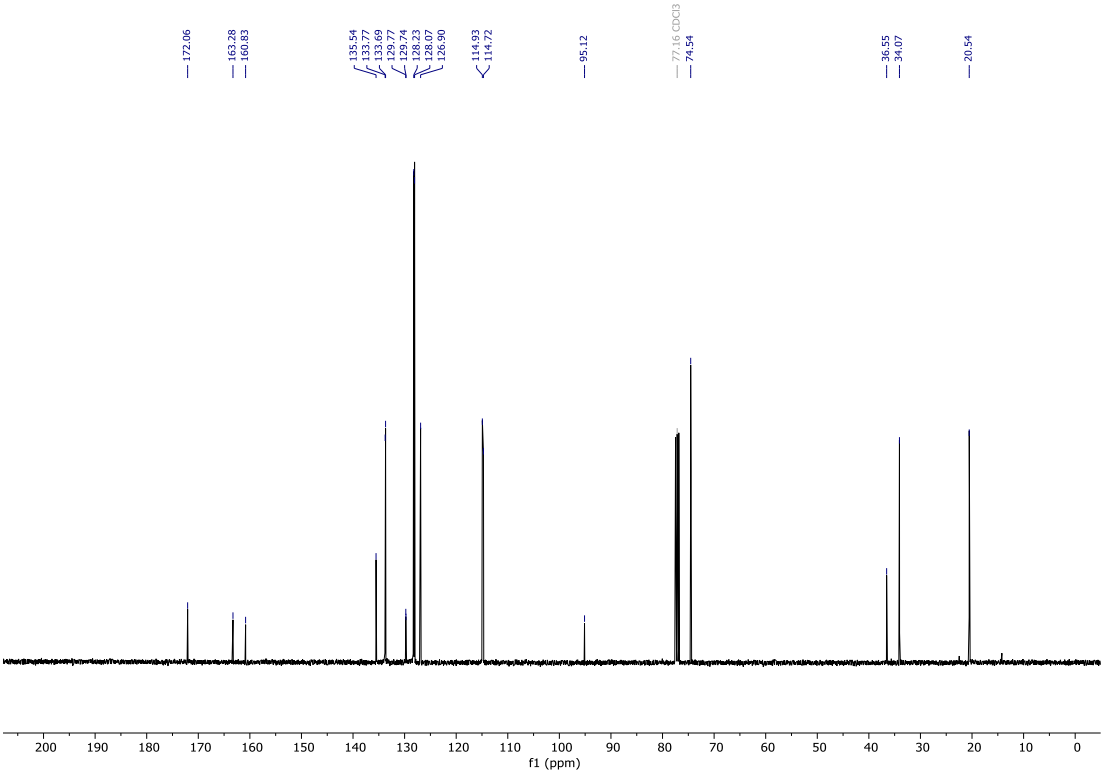
5a': ^{13}C NMR (101 MHz, $CDCl_3$):



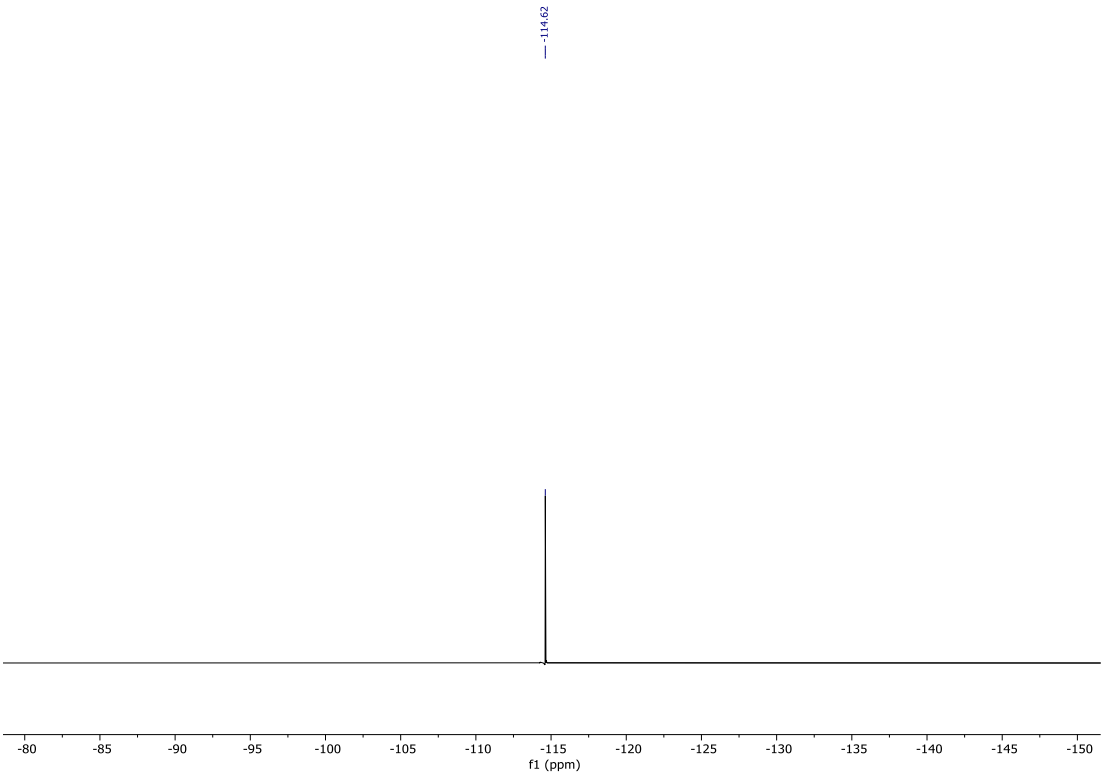
5b': ^{1}H NMR (400 MHz, $CDCl_3$):



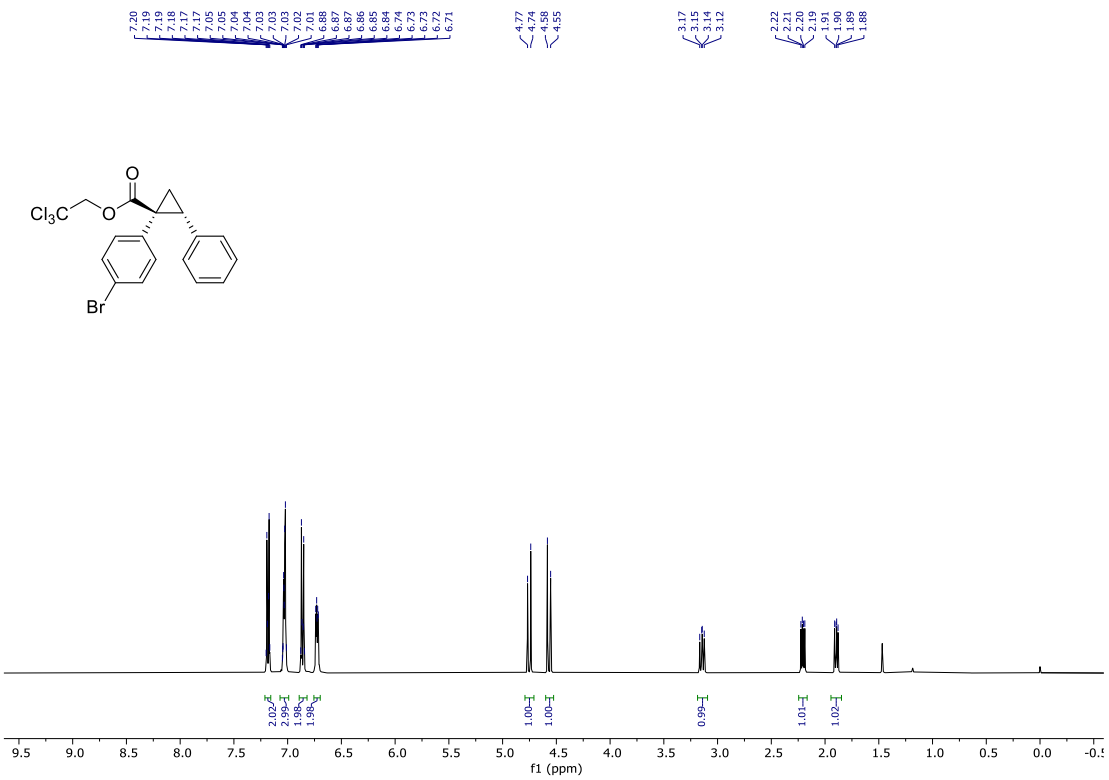
5b': ^{13}C NMR (101 MHz, $CDCl_3$):



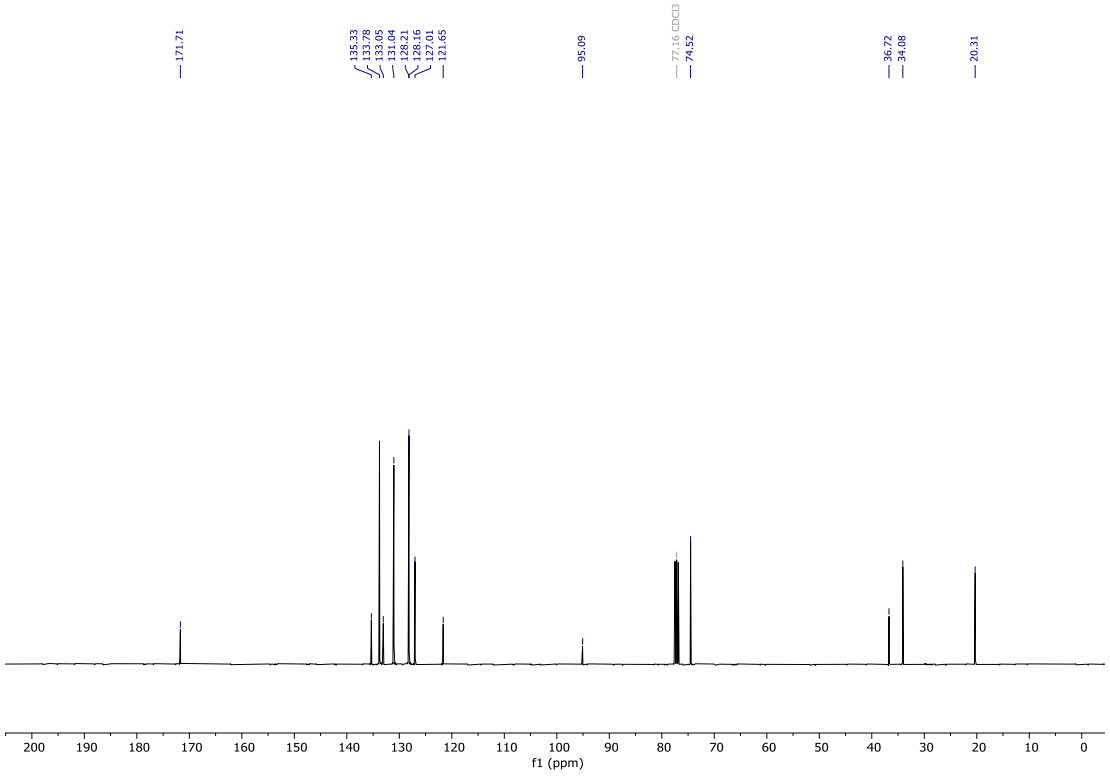
5b': ^{19}F NMR (282 MHz, $CDCl_3$):



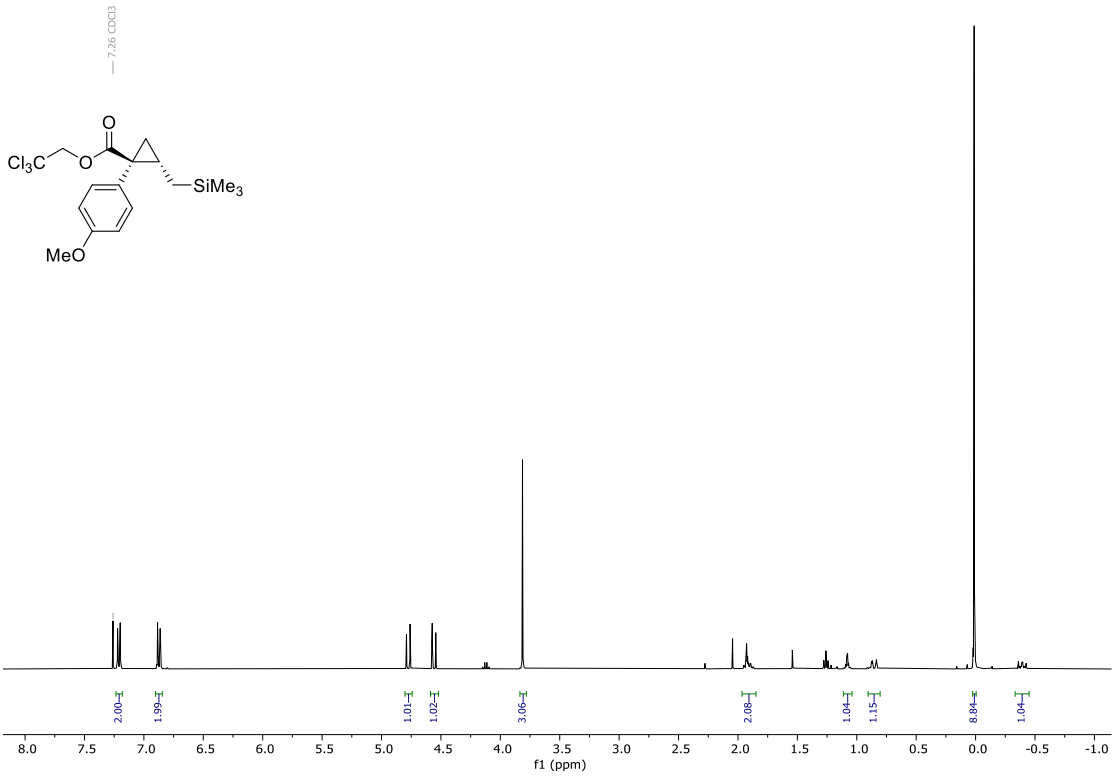
S4: ^{1}H NMR (400 MHz, $CDCl_3$):



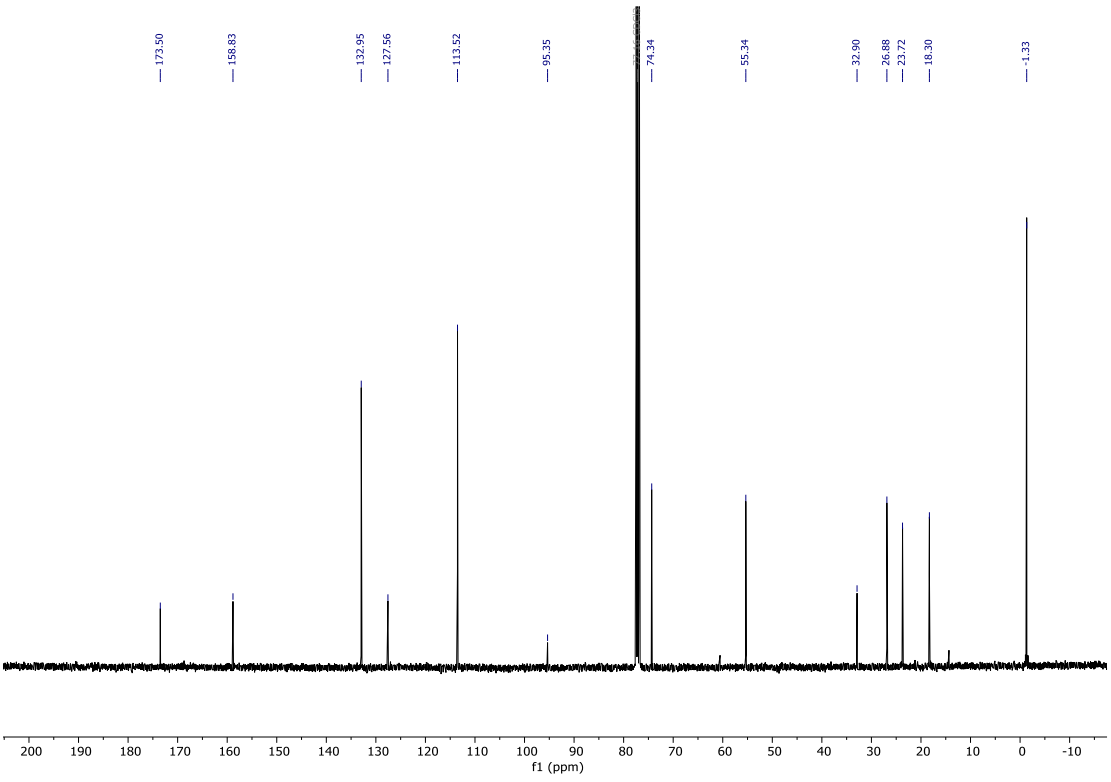
S4: ^{13}C NMR (101 MHz, $CDCl_3$):



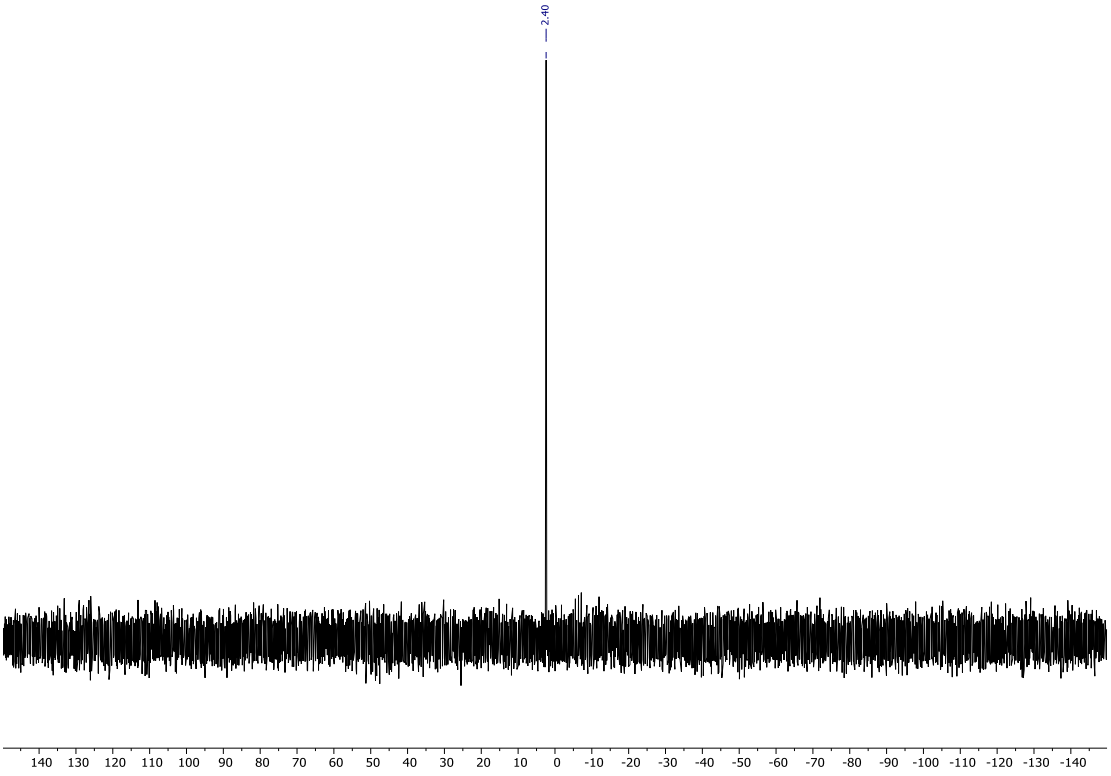
S5: ^{1}H NMR (400 MHz, $CDCl_3$):



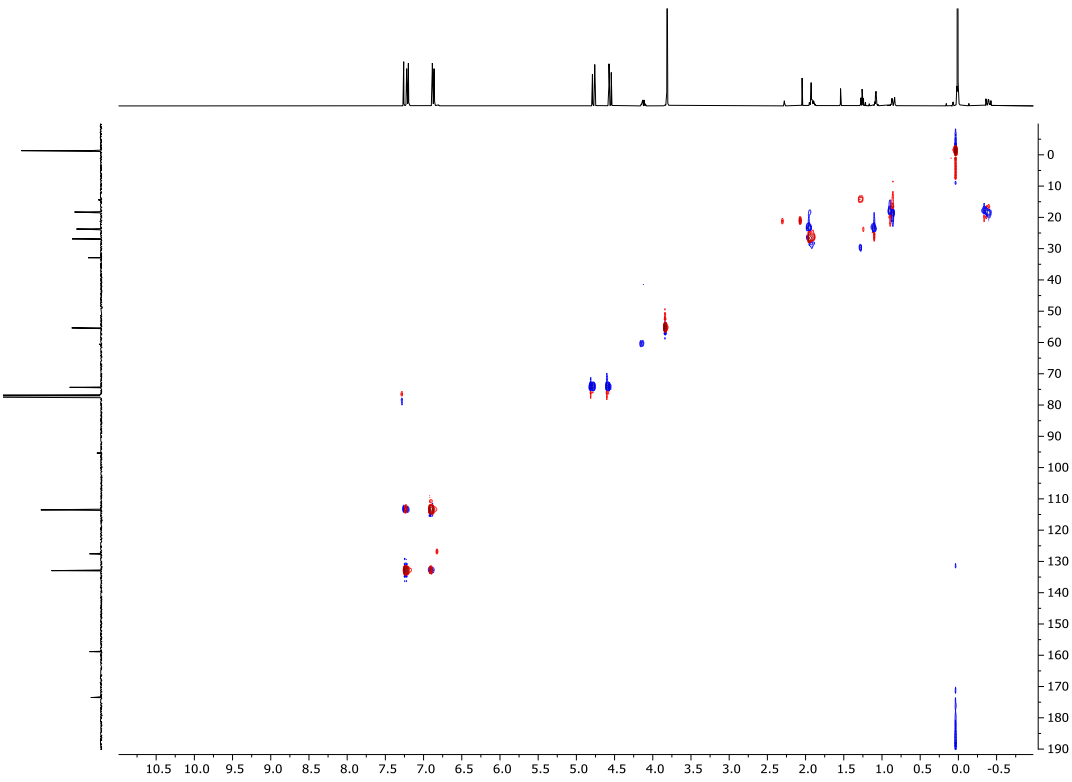
S5: ^{13}C NMR (101 MHz, $CDCl_3$):



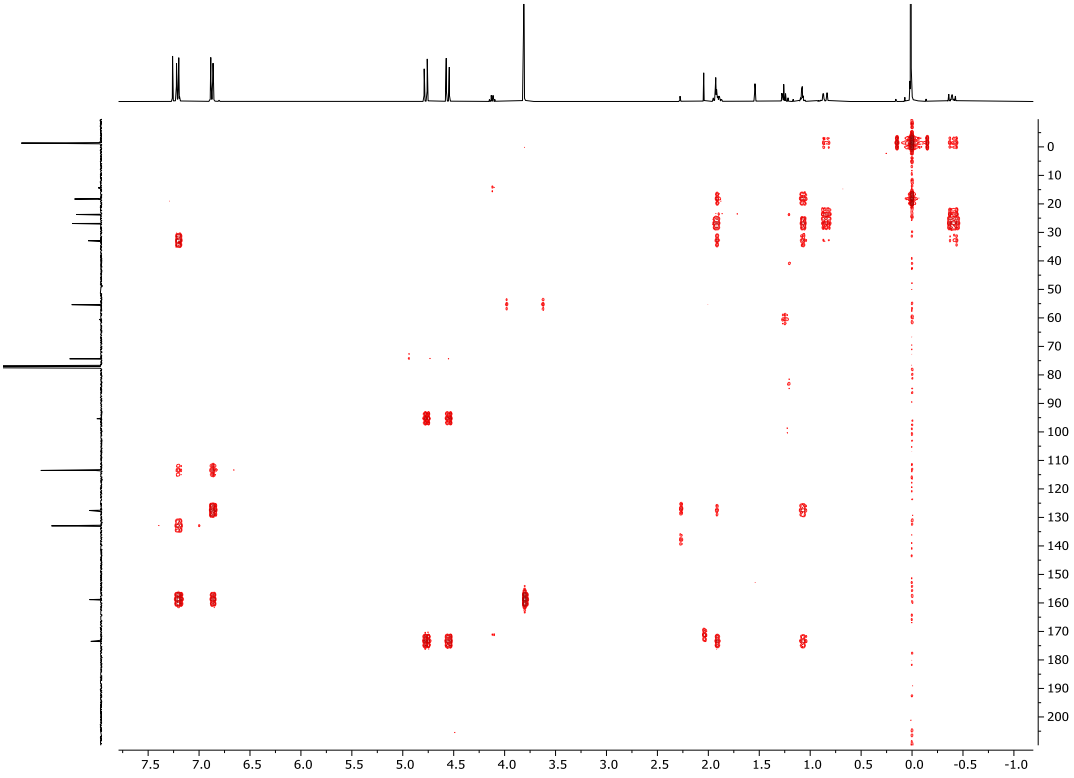
S5: ^{29}Si NMR (99 MHz, $CDCl_3$):



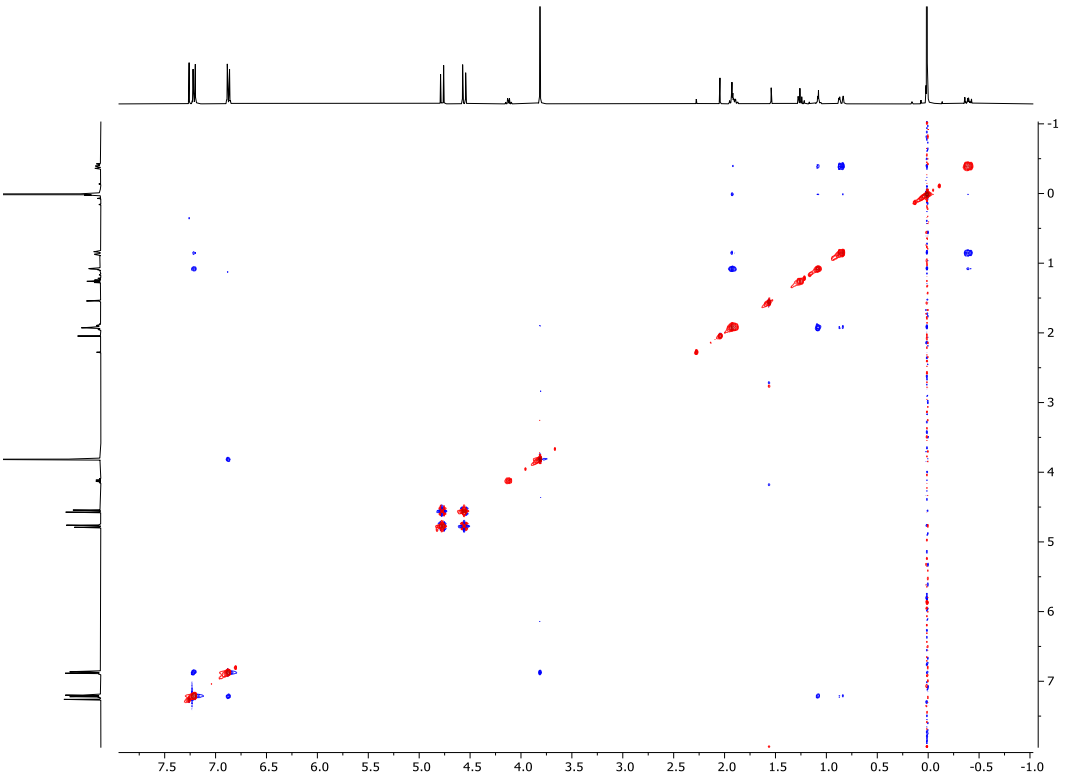
S5: HSQC NMR (400 MHz, 101 MHz, $CDCl_3$):



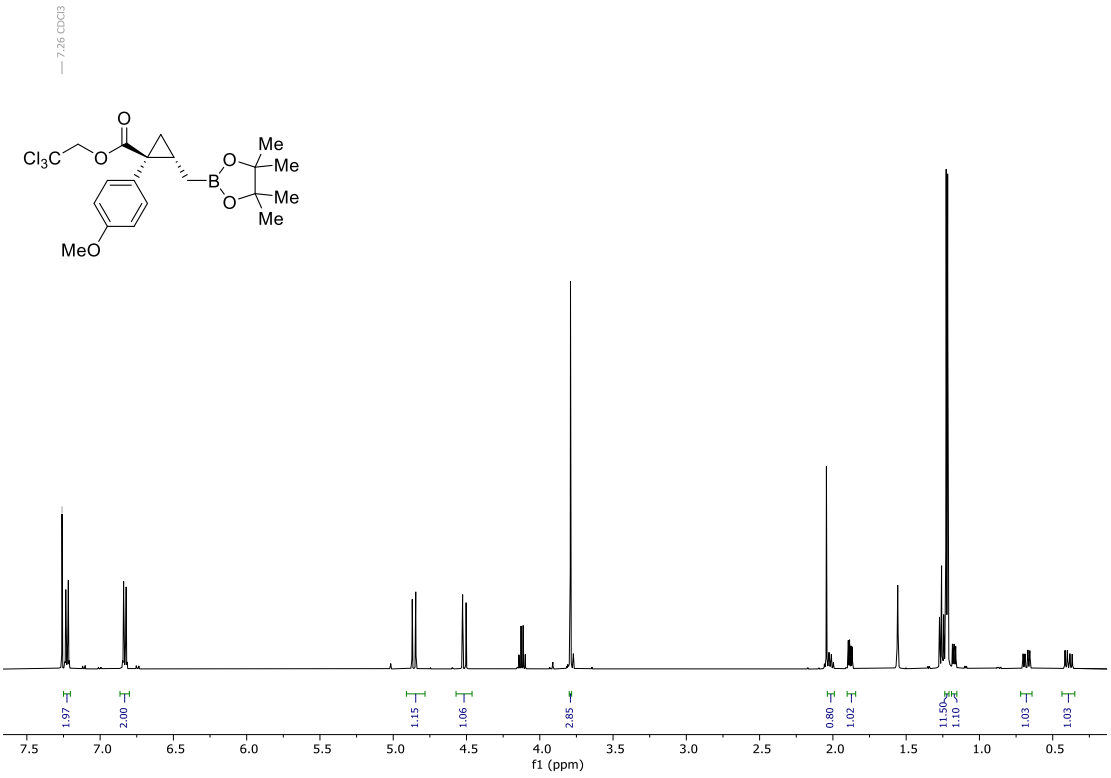
S5: HMBC NMR (400 MHz, 101 MHz, $CDCl_3$):



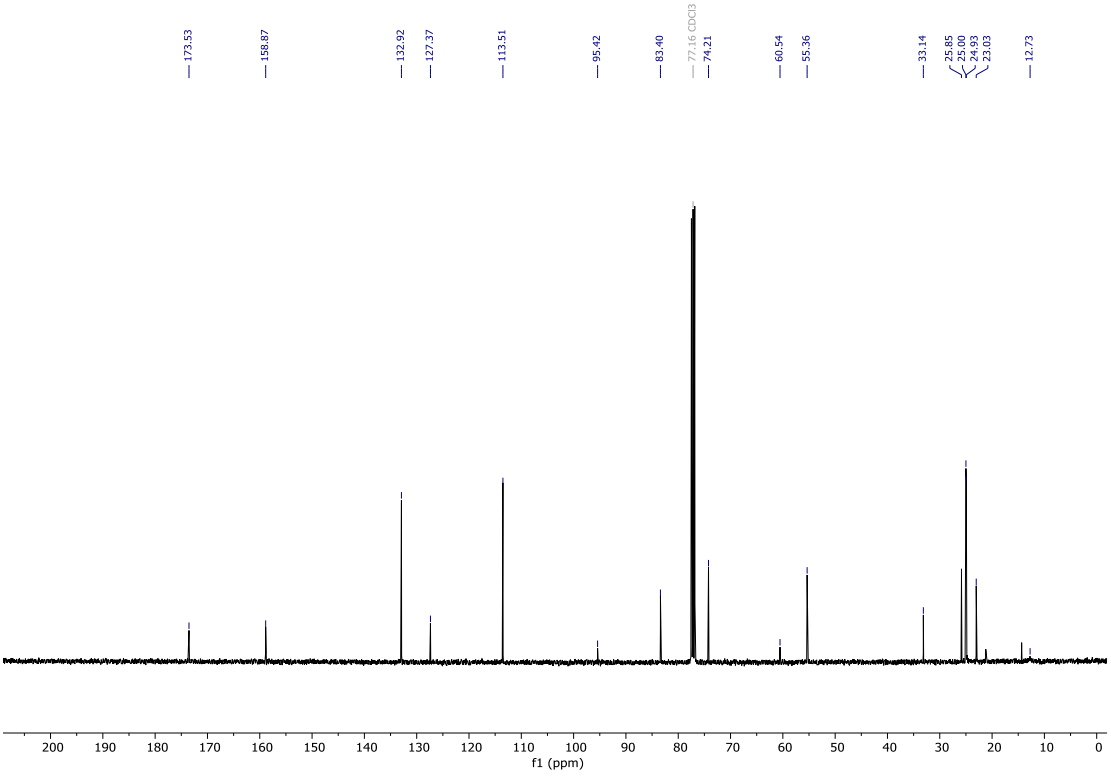
S5: NOESY NMR (400 MHz, $CDCl_3$):



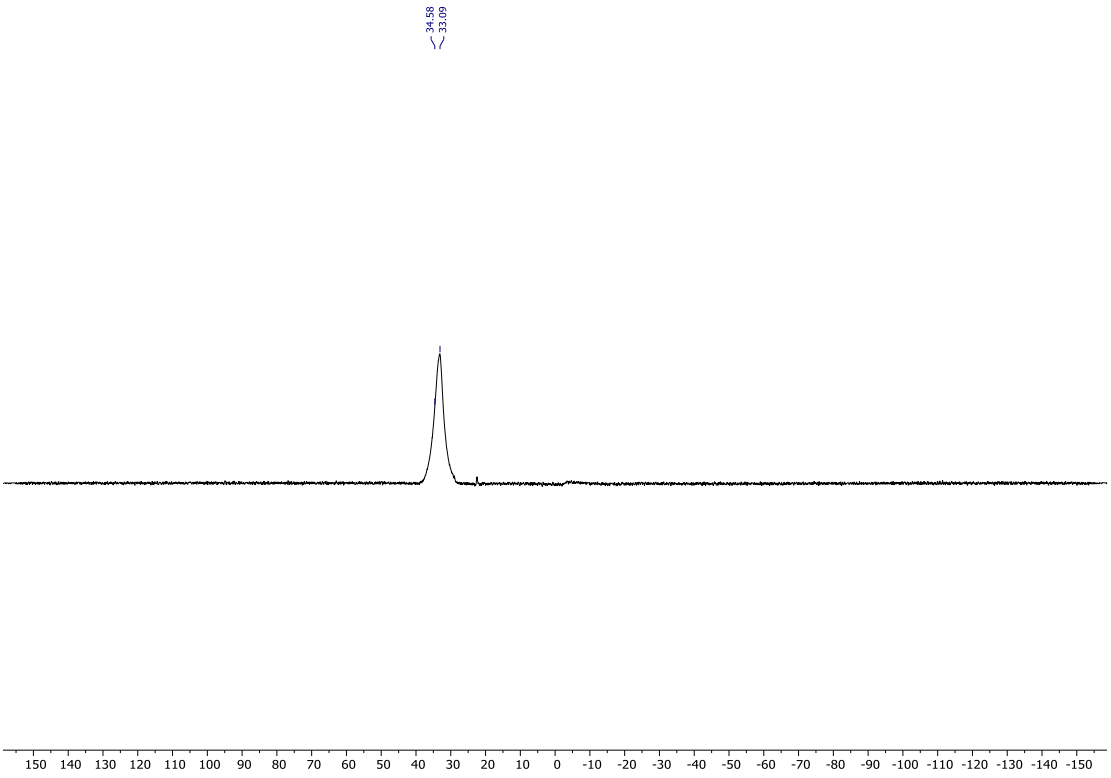
S6: ^{1}H NMR (400 MHz, $CDCl_3$):



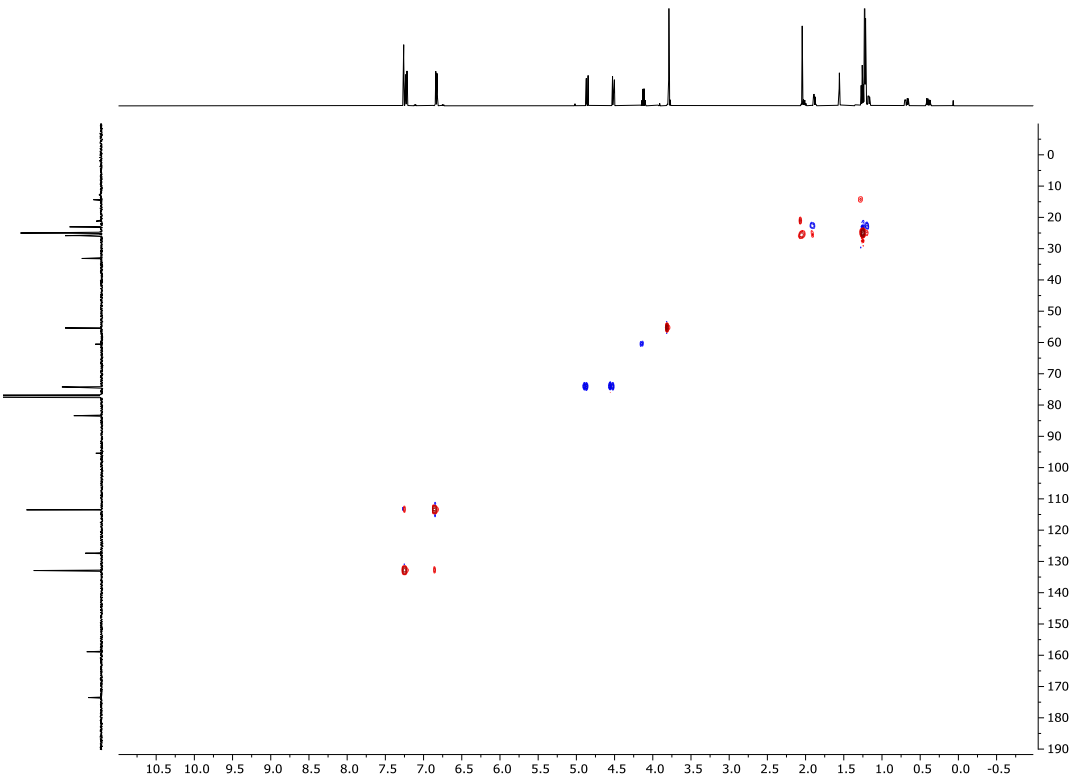
S6: ^{13}C NMR (101 MHz, $CDCl_3$):



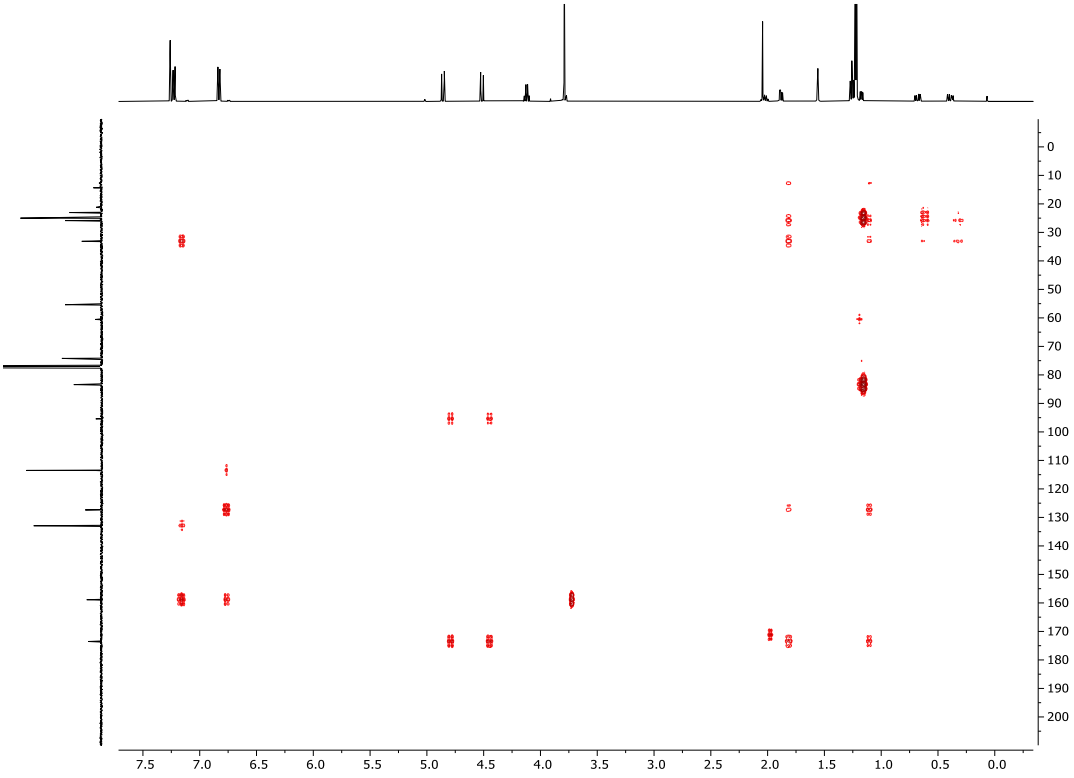
S6: ^{11}B NMR (128 MHz, $CDCl_3$):



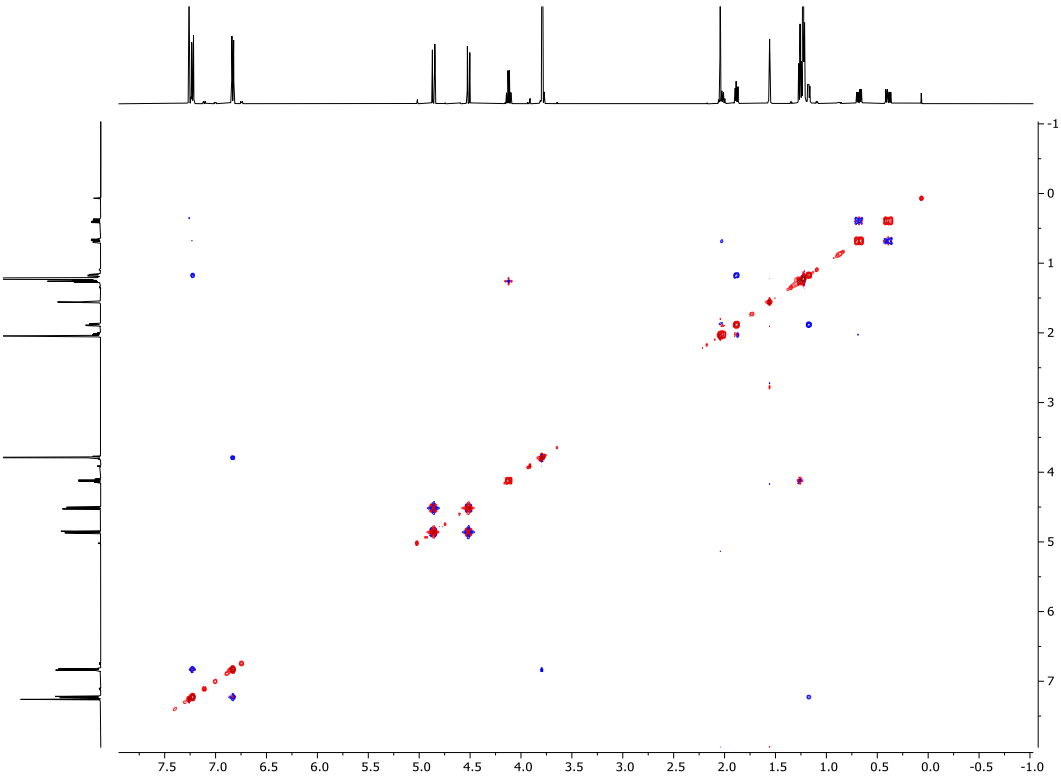
S6: HSQC NMR (400 MHz, 101 MHz, $CDCl_3$):



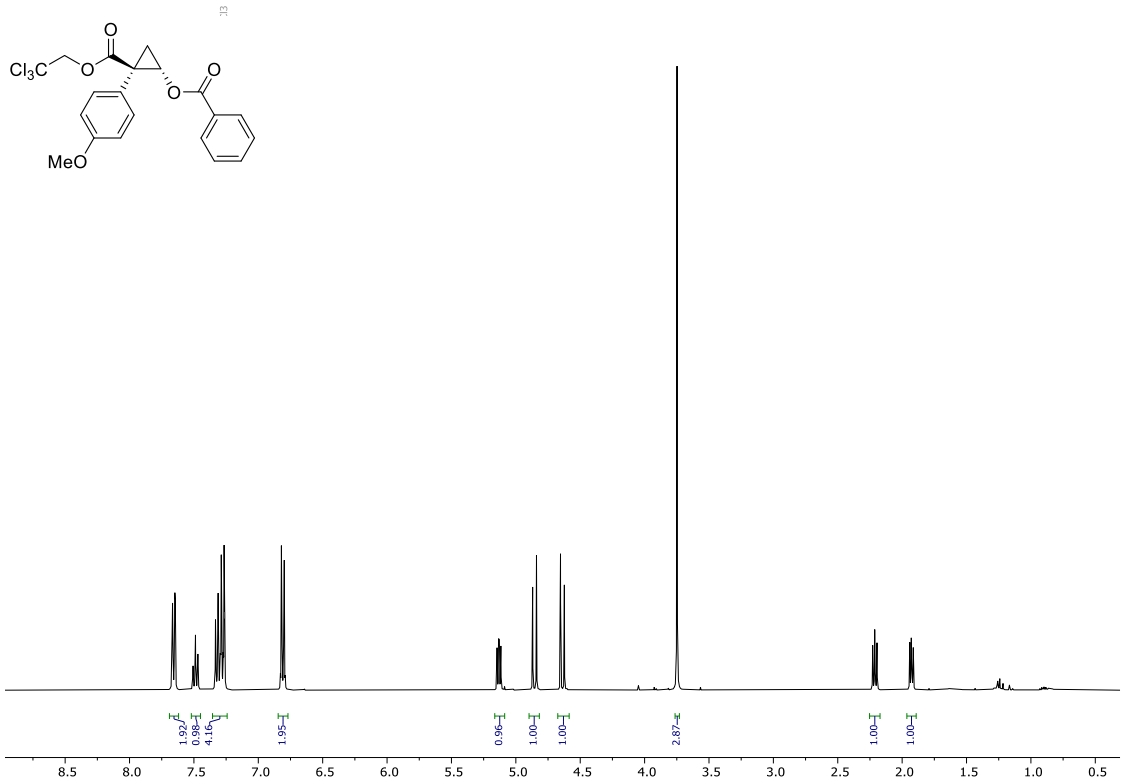
S6: HMBC NMR (400 MHz, 101 MHz, $CDCl_3$):



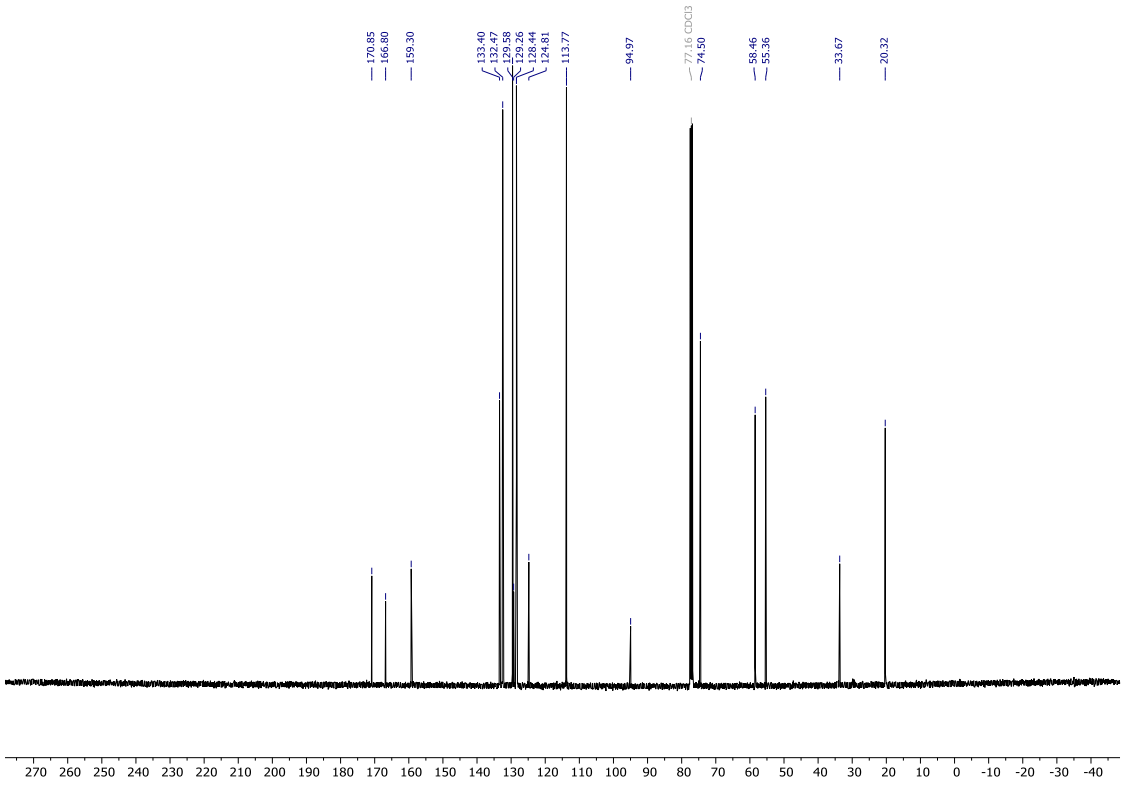
S6: NOESY NMR (400 MHz, $CDCl_3$):



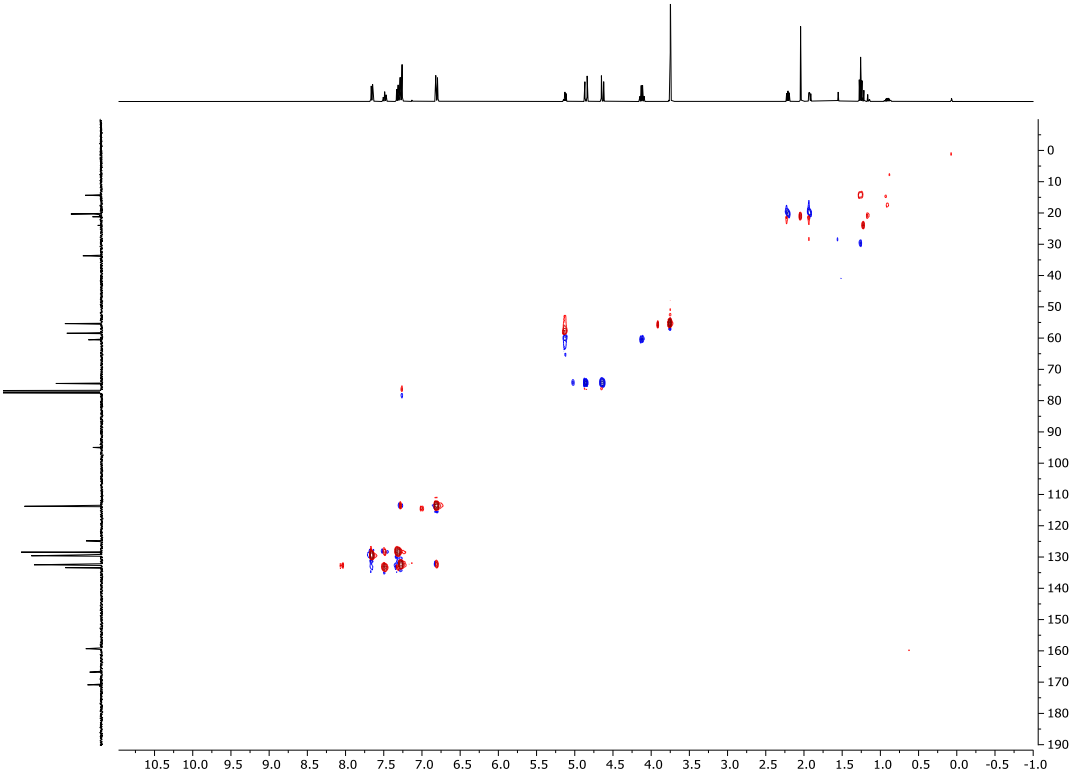
S7: ^{1}H NMR (400 MHz, $CDCl_3$):



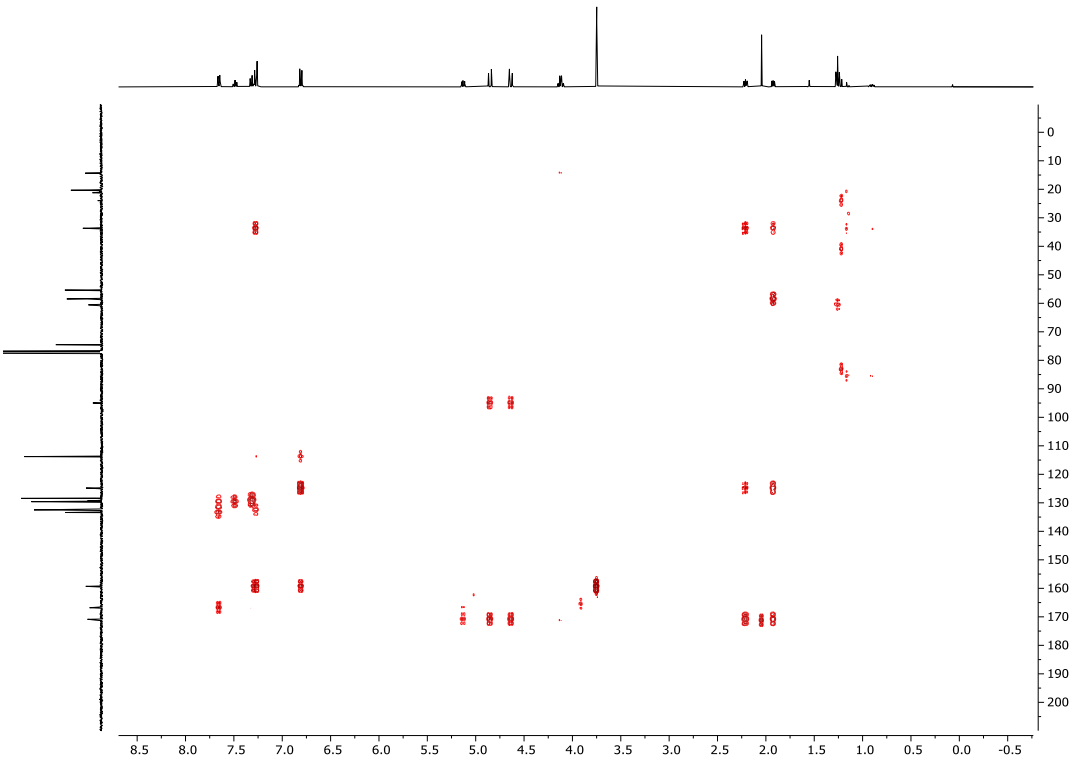
S7: ^{13}C NMR (101 MHz, $CDCl_3$)



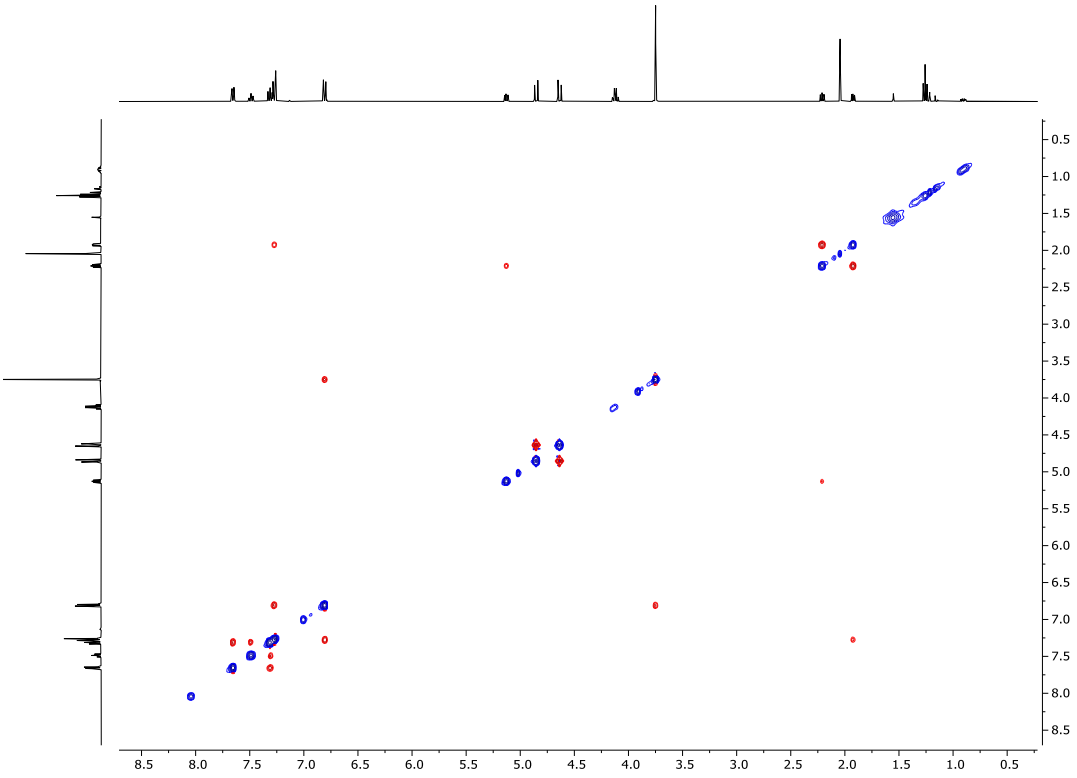
S7: HSQC NMR (400 MHz, 101 MHz, $CDCl_3$):



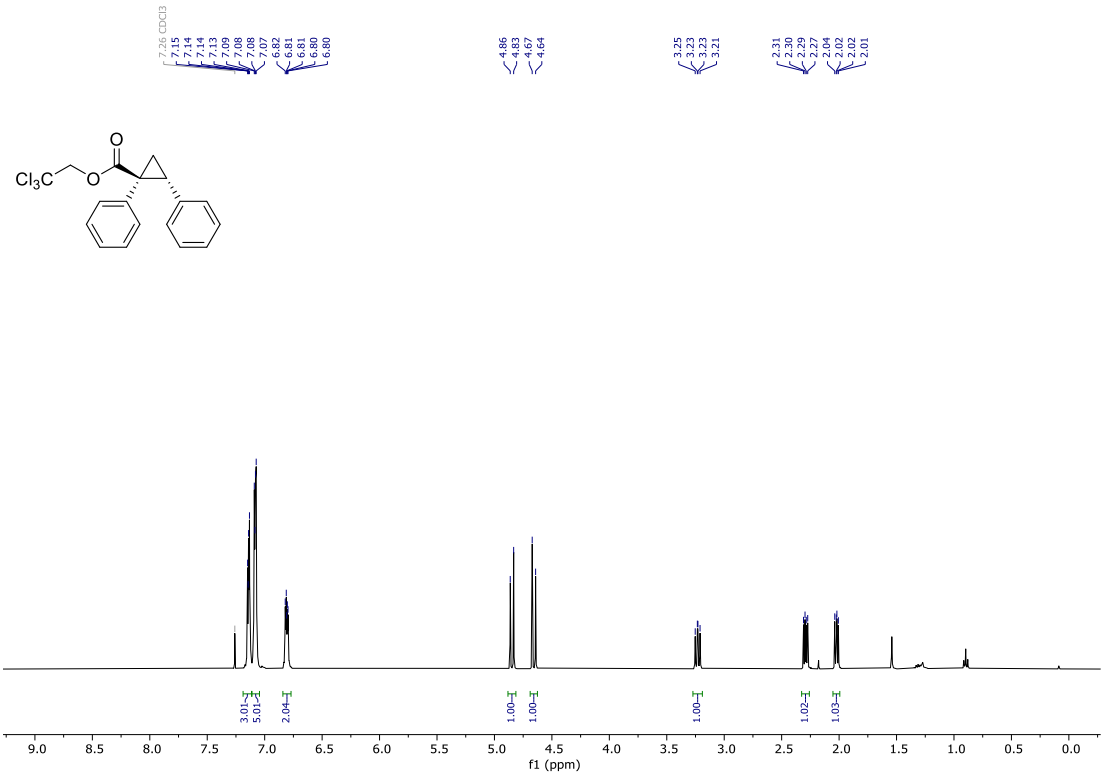
S7: HMBC NMR (400 MHz, 101 MHz, CDCl3):



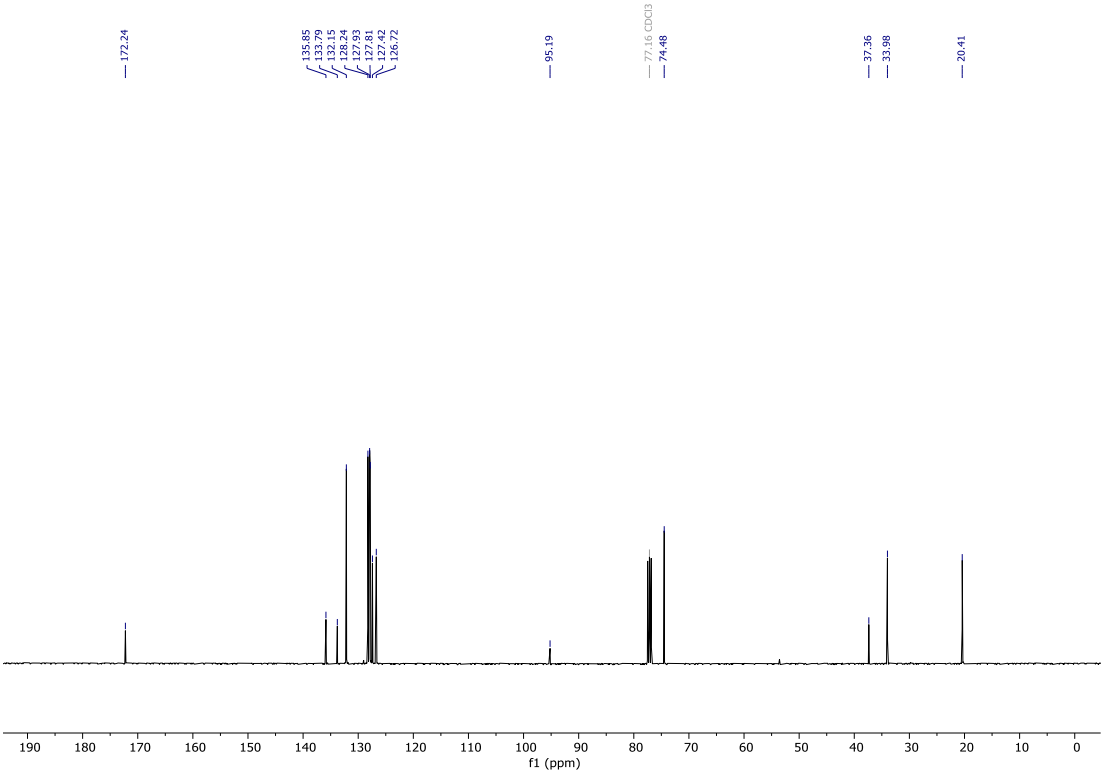
S7: NOESY NMR (500 MHz, $CDCl_3$):



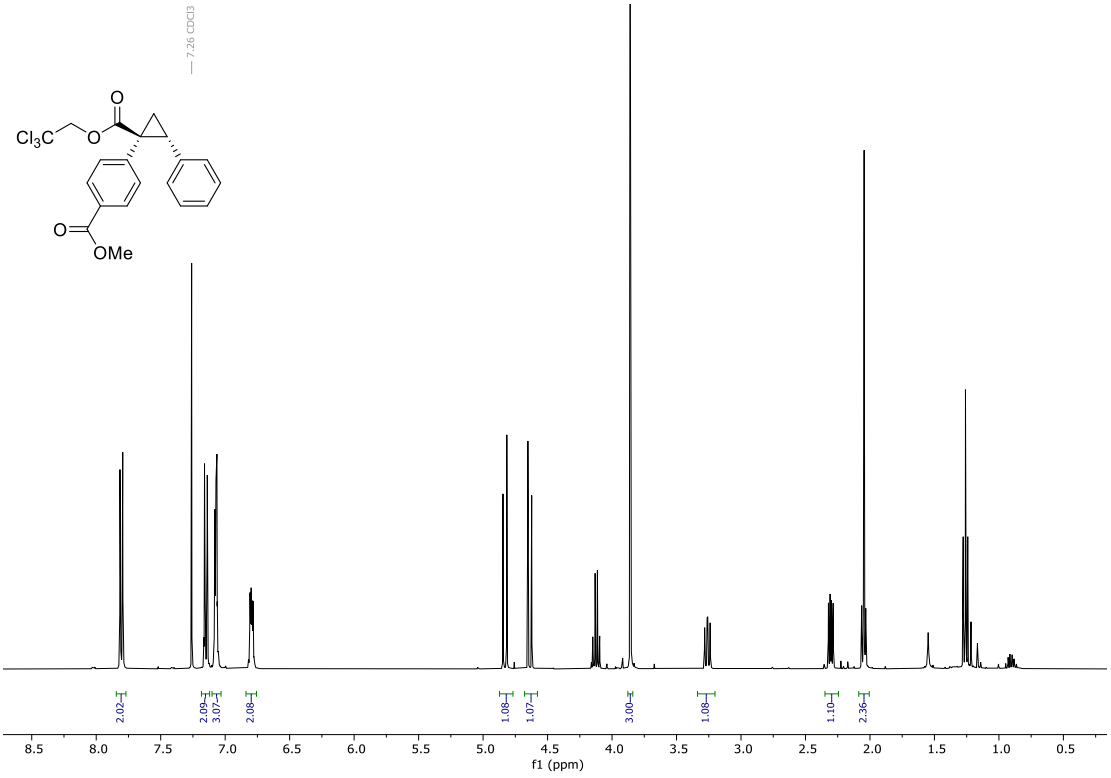
S8: ^{1}H NMR (400 MHz, $CDCl_3$):



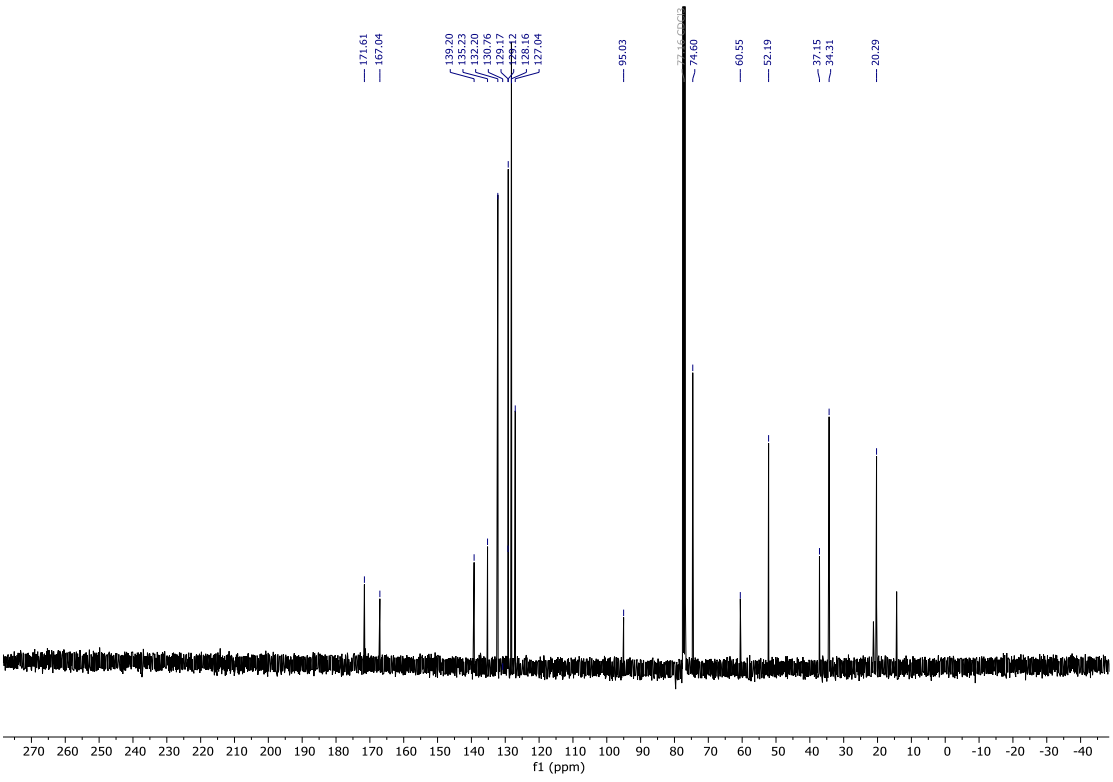
S8: ^{13}C NMR (101 MHz, $CDCl_3$):



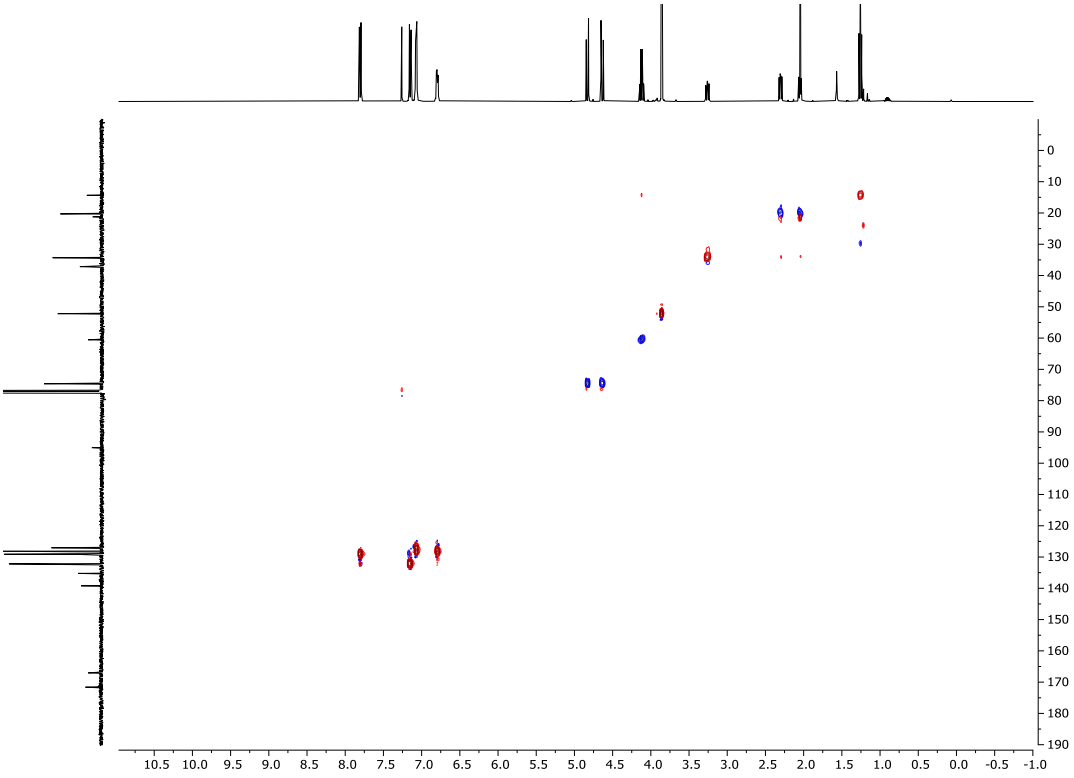
S9: ^{1}H NMR (400 MHz, $CDCl_3$):



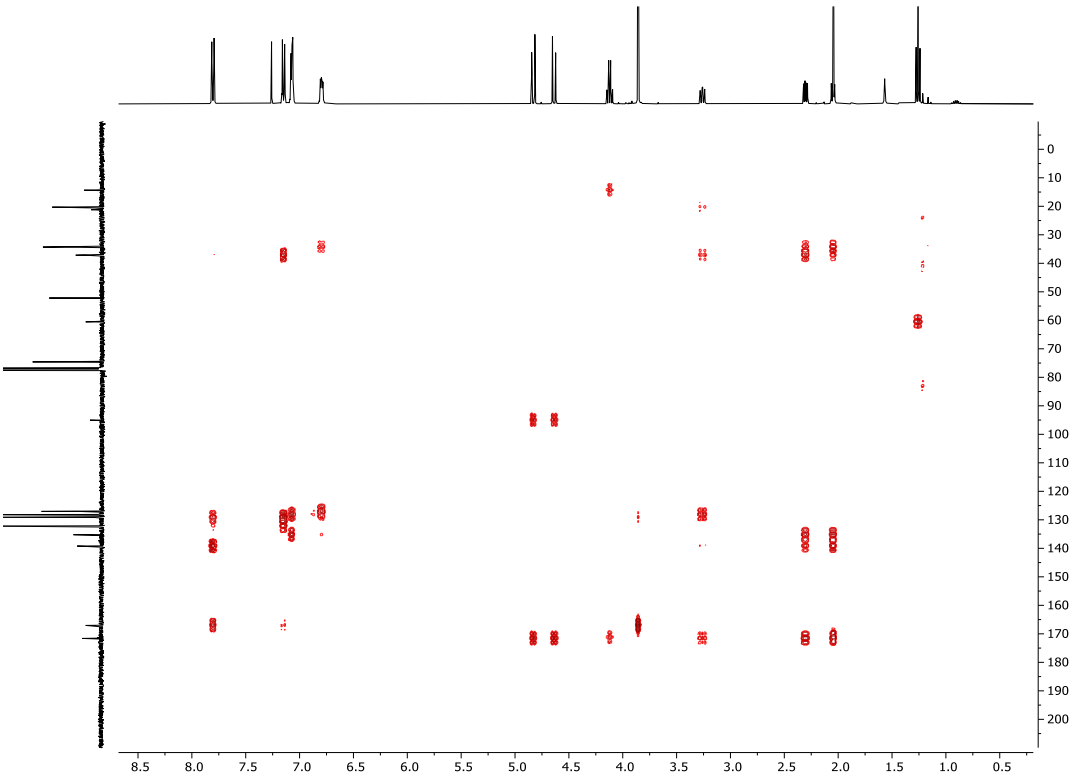
S9: ^{13}C NMR (101 MHz, $CDCl_3$):



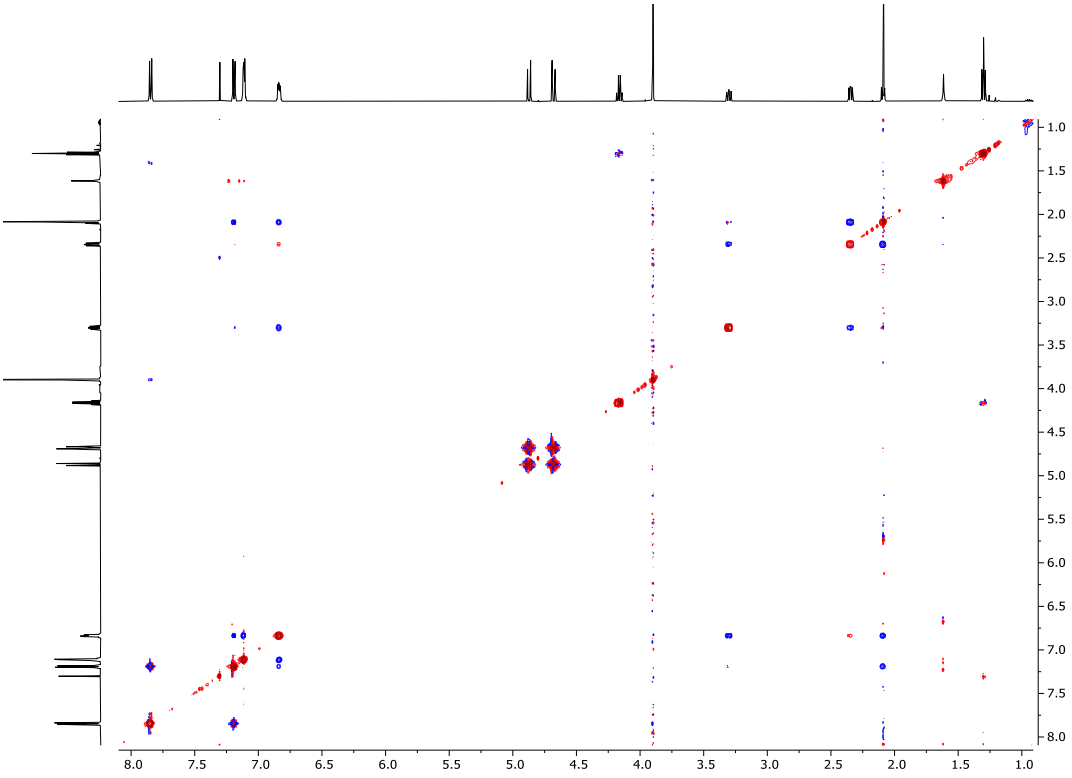
S9: HSQC NMR (400 MHz, 101 MHz, $CDCl_3$):



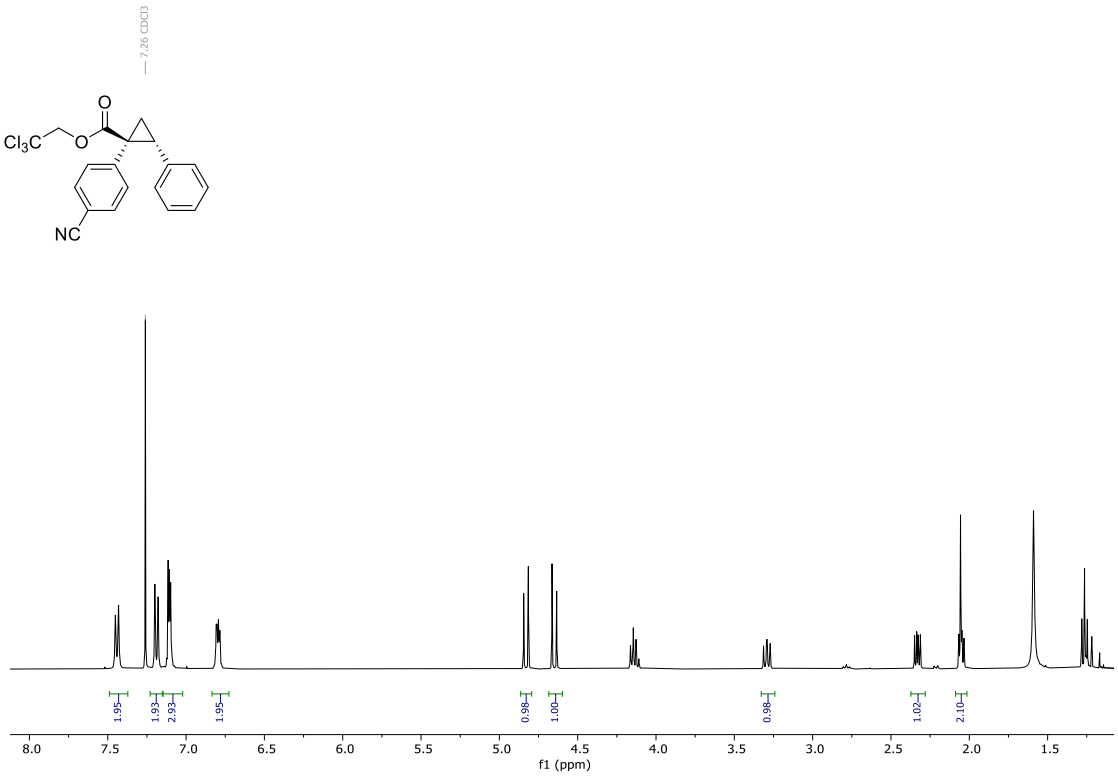
S9: HMBC NMR (400 MHz, 101 MHz, $CDCl_3$):



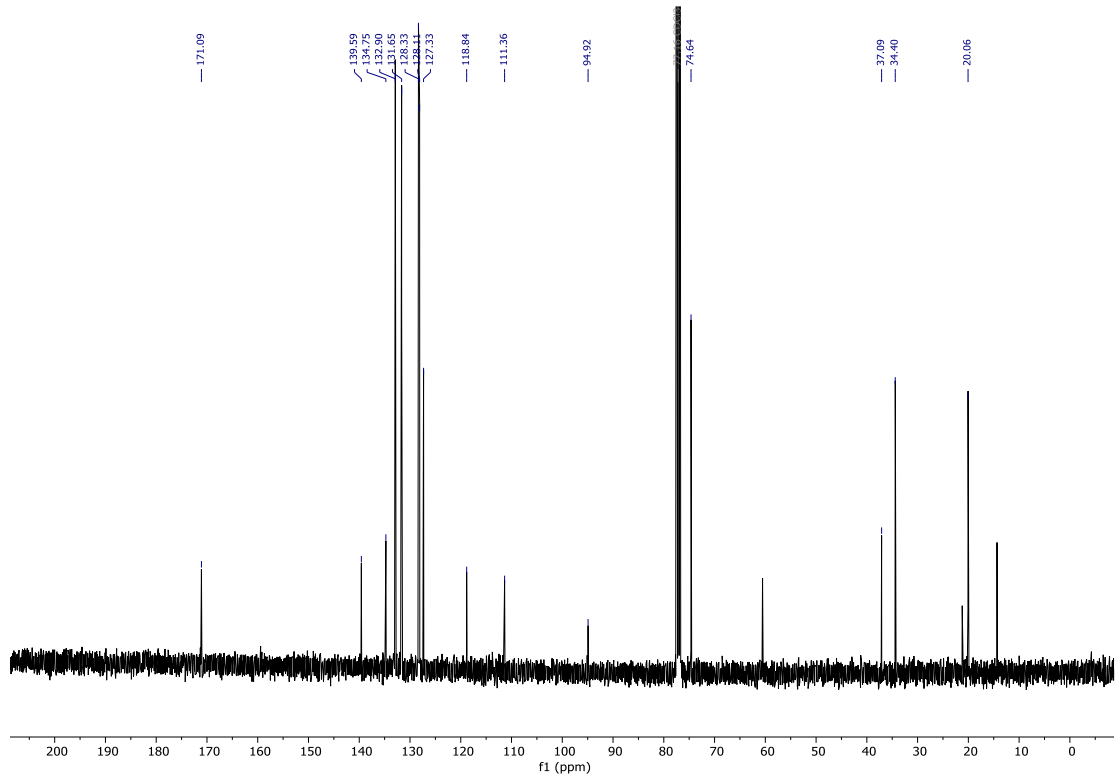
S9: NOESY NMR (400 MHz, $CDCl_3$):



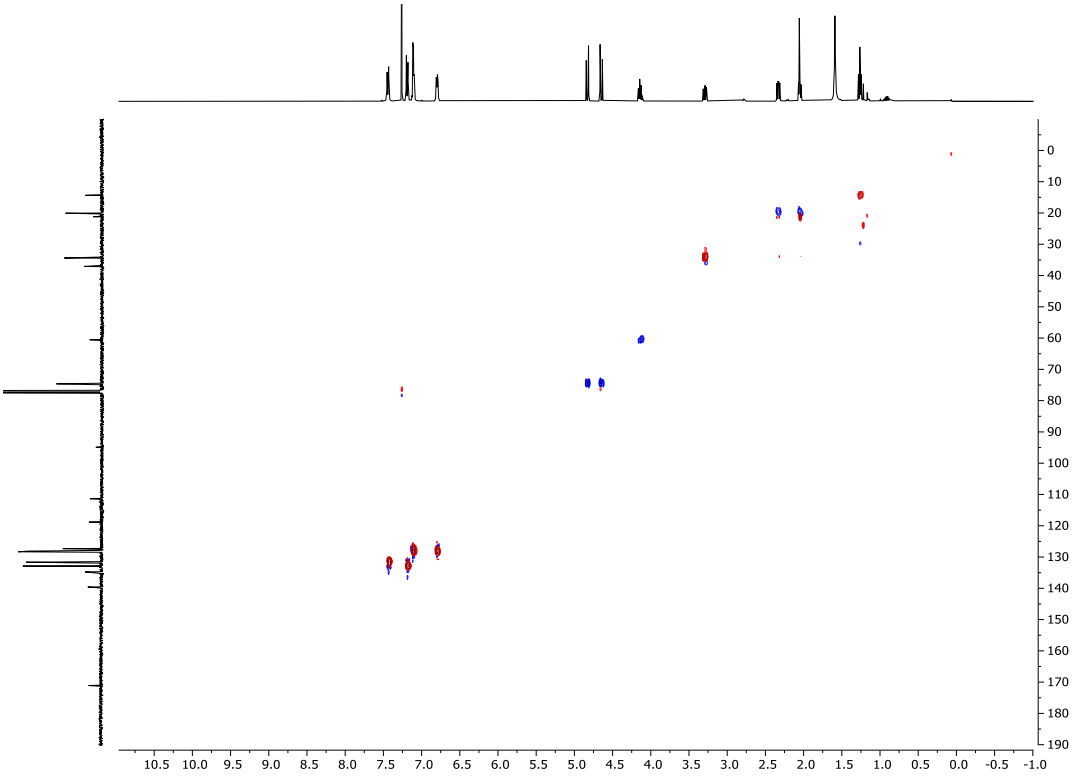
S10: ^{1}H NMR (400 MHz, $CDCl_3$):



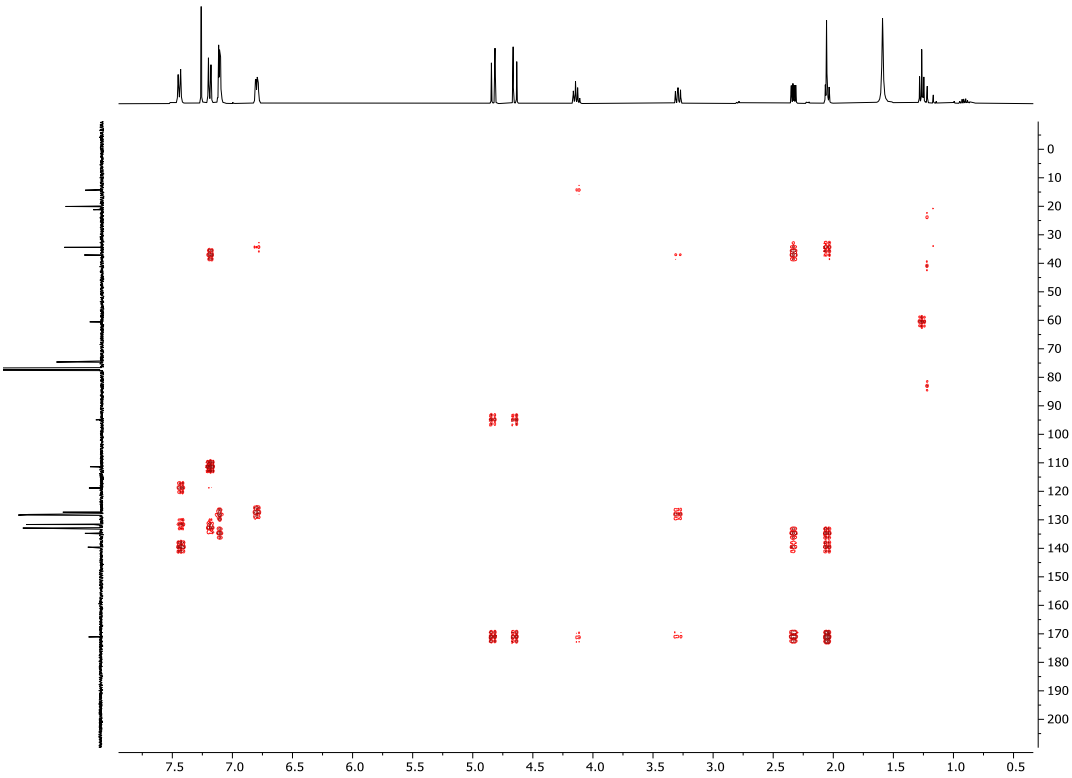
S10: ^{13}C NMR (101 MHz, $CDCl_3$):



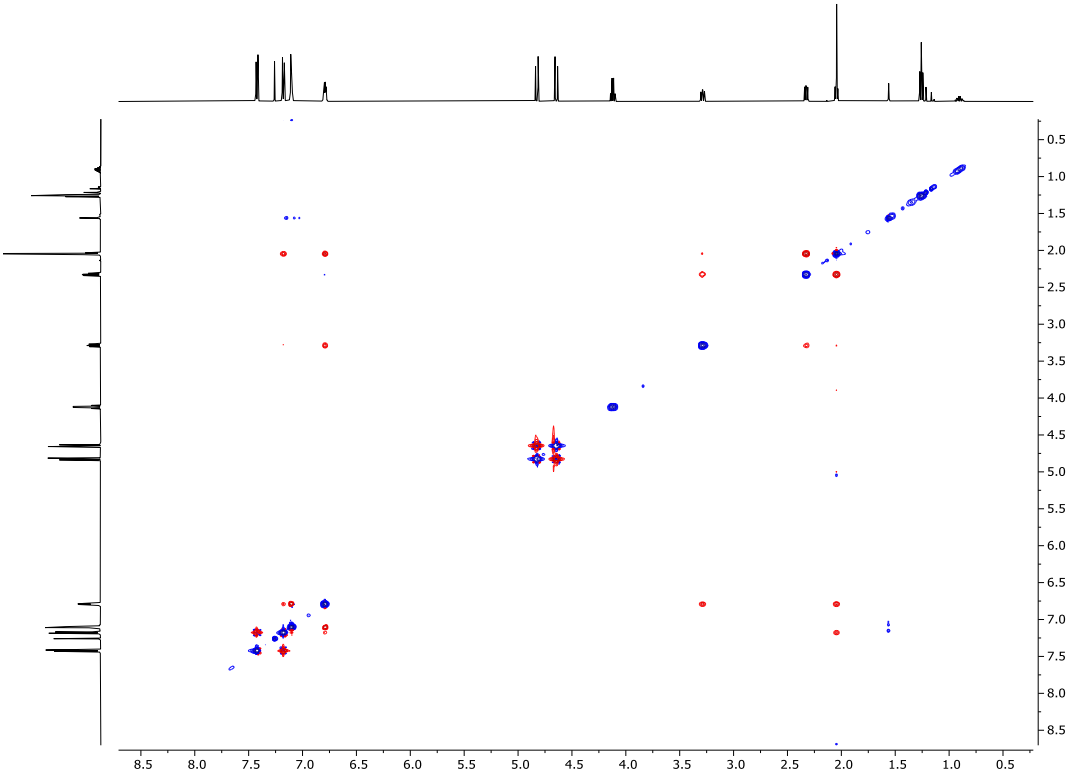
S10: HSQC NMR (400 MHz, 101 MHz, $CDCl_3$):



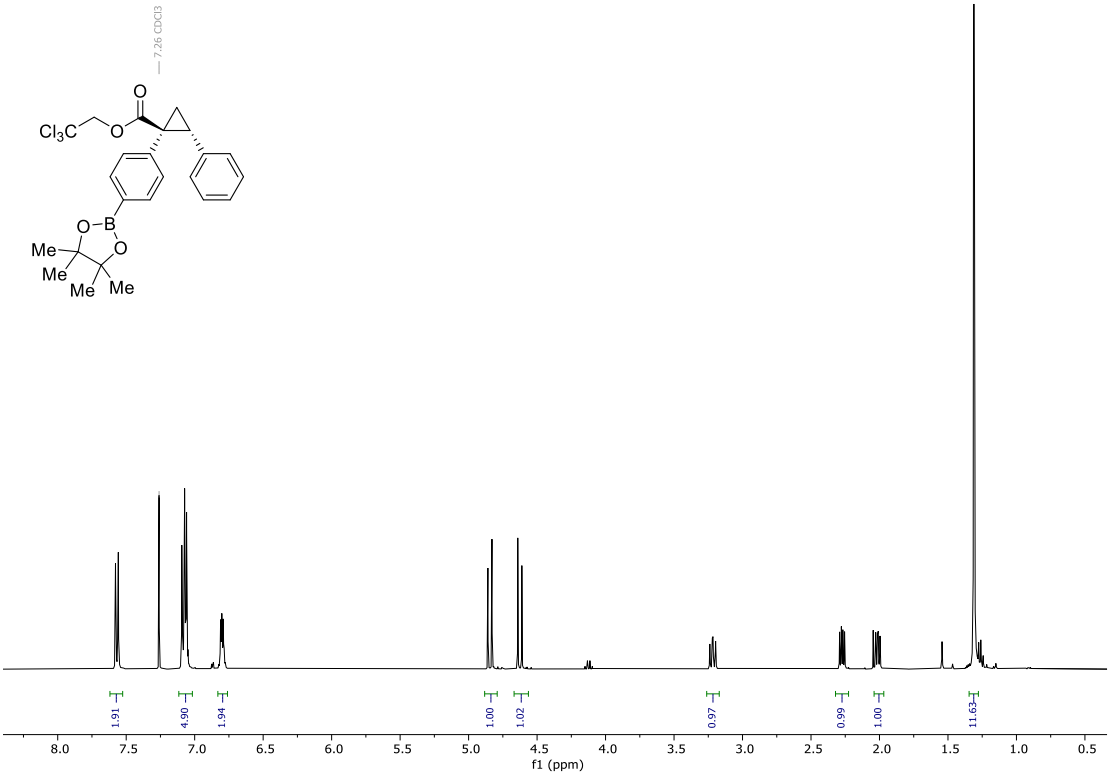
S10: HMBC NMR (400 MHz, 101 MHz, $CDCl_3$):



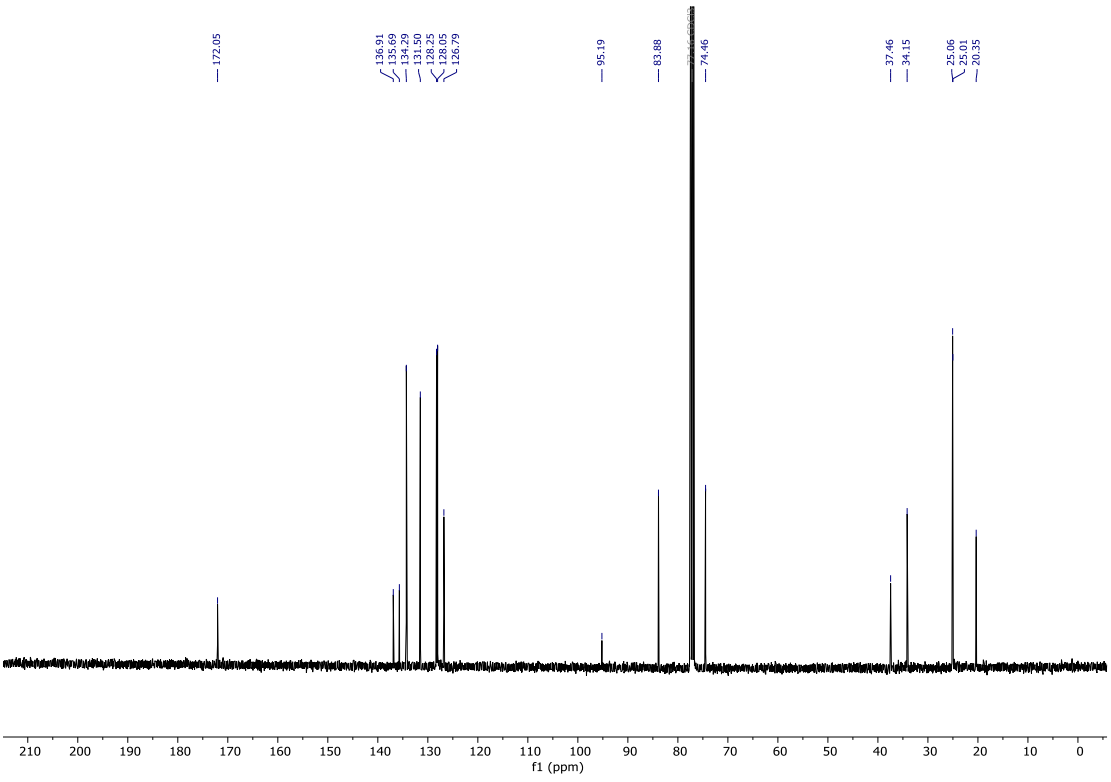
S10: NOESY NMR (500 MHz, $CDCl_3$):



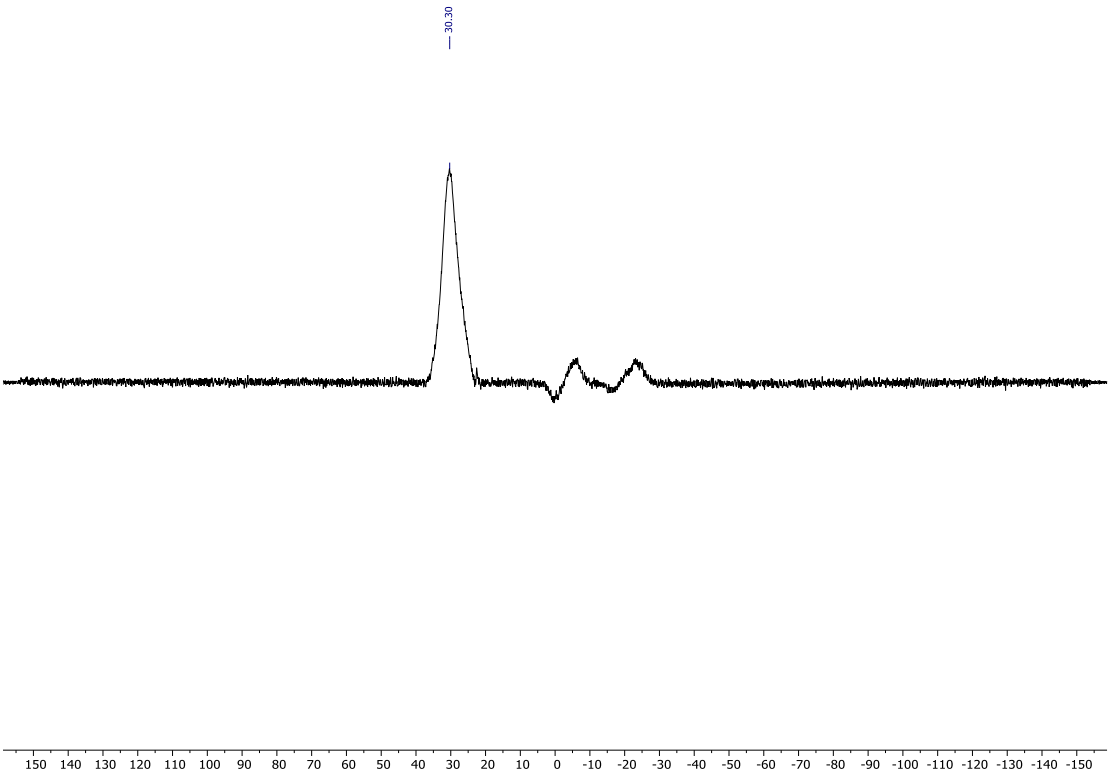
S11: ^{1}H NMR (400 MHz, $CDCl_3$):



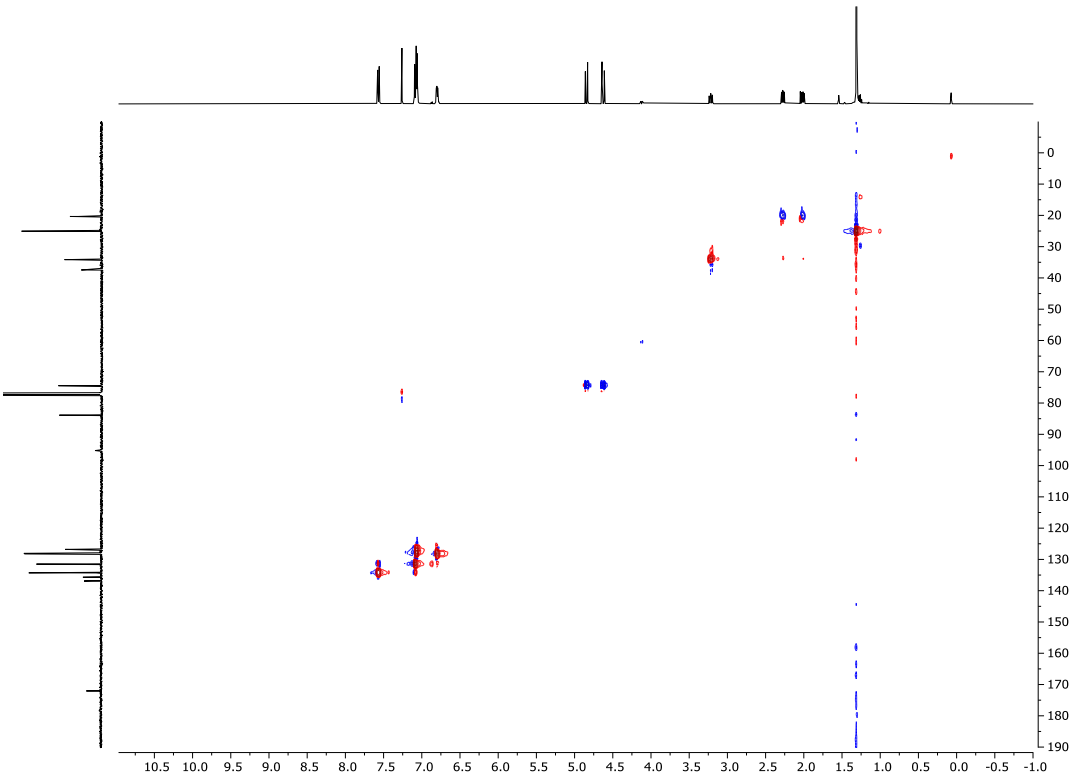
S11: ^{13}C NMR (101 MHz, $CDCl_3$):



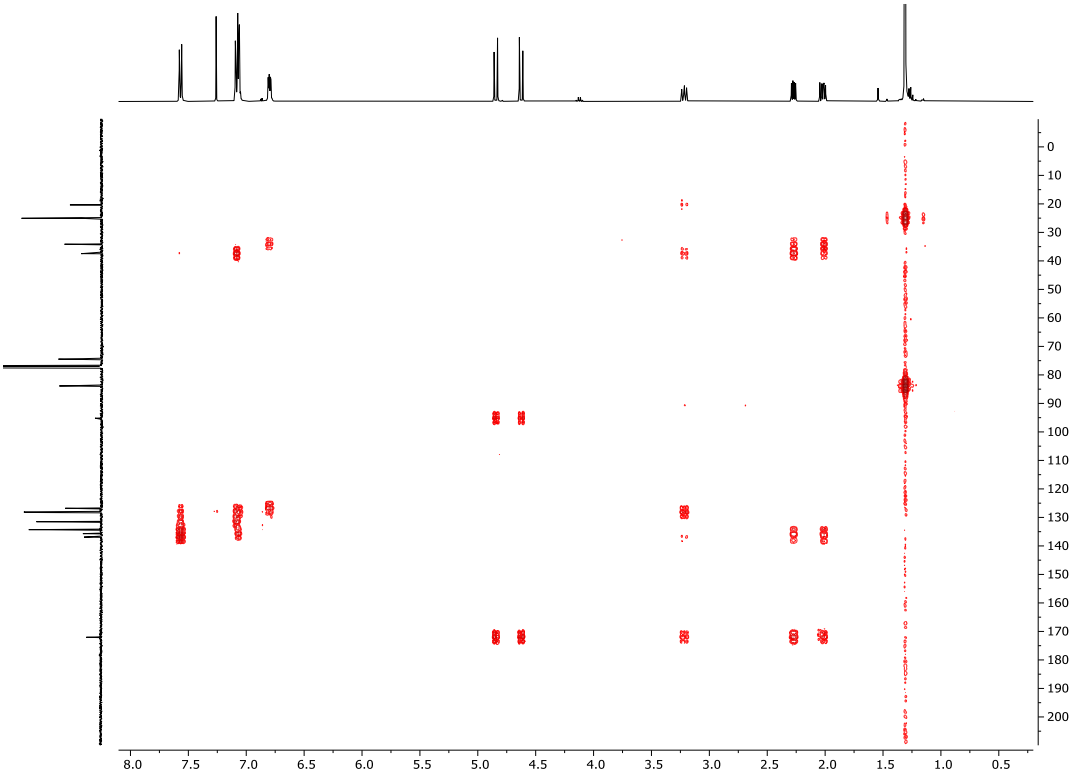
S11: ^{11}B NMR (128 MHz, $CDCl_3$):



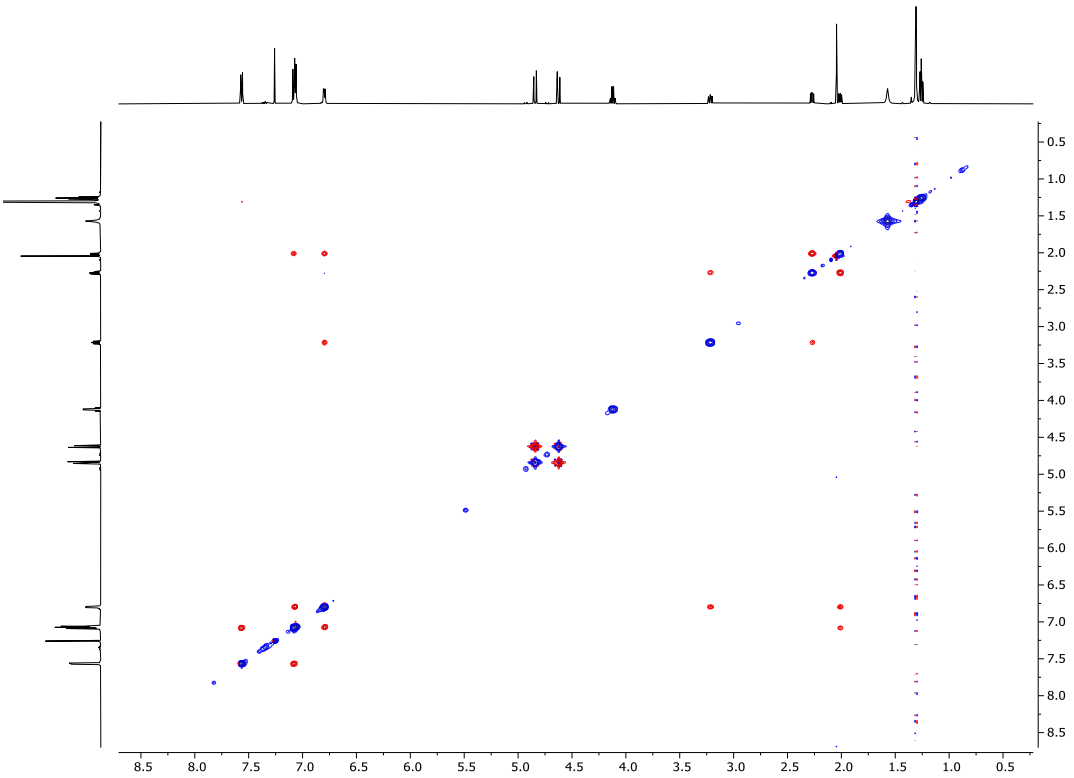
S11: HSQC NMR (400 MHz, 101 MHz, $CDCl_3$):



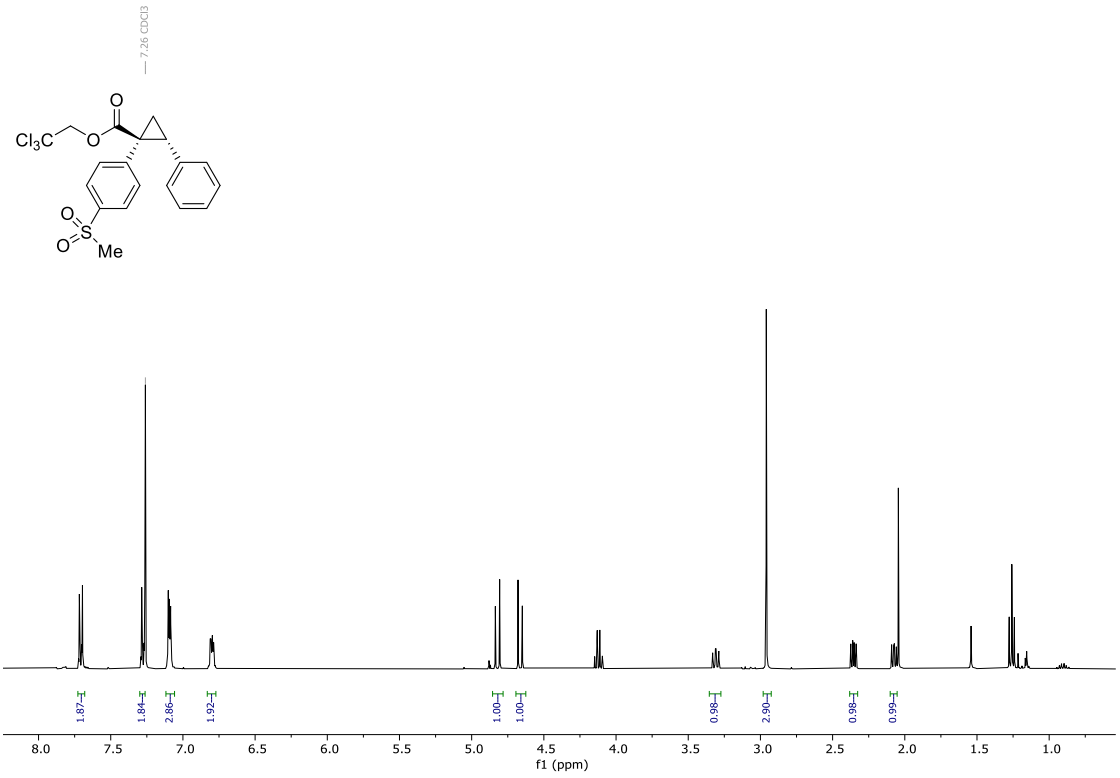
S11: HMBC NMR (400 MHz, 101 MHz, $CDCl_3$):



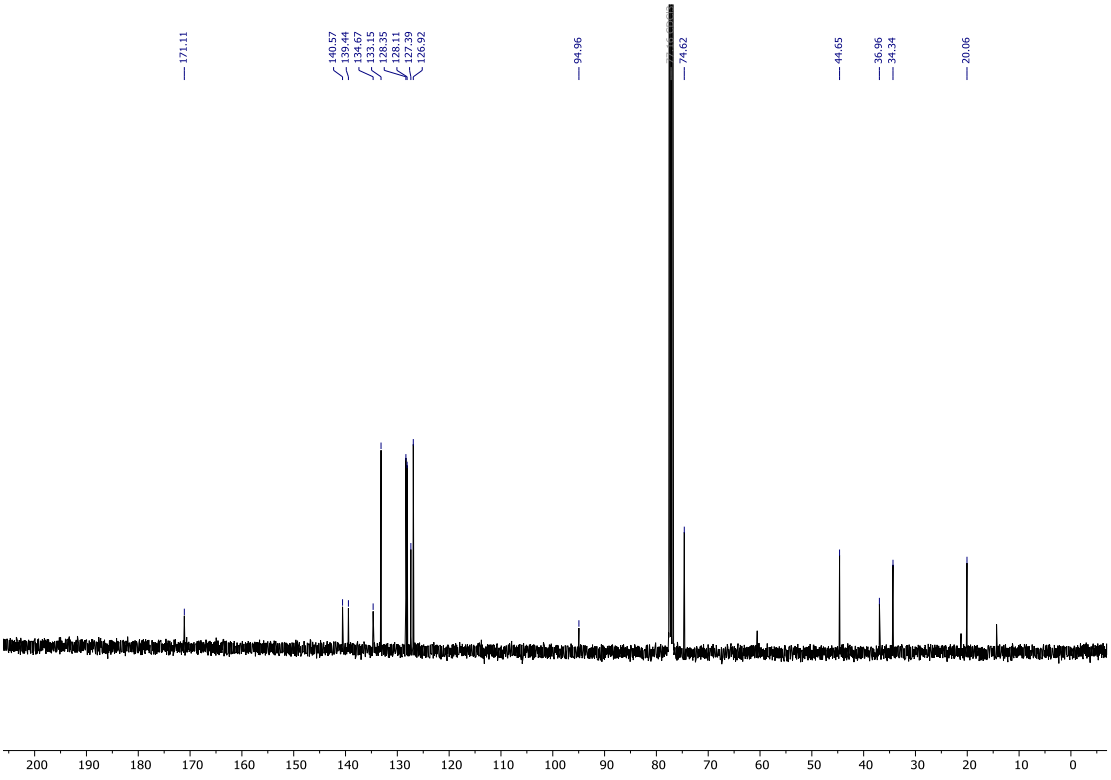
S11: NOESY NMR (400 MHz, $CDCl_3$):



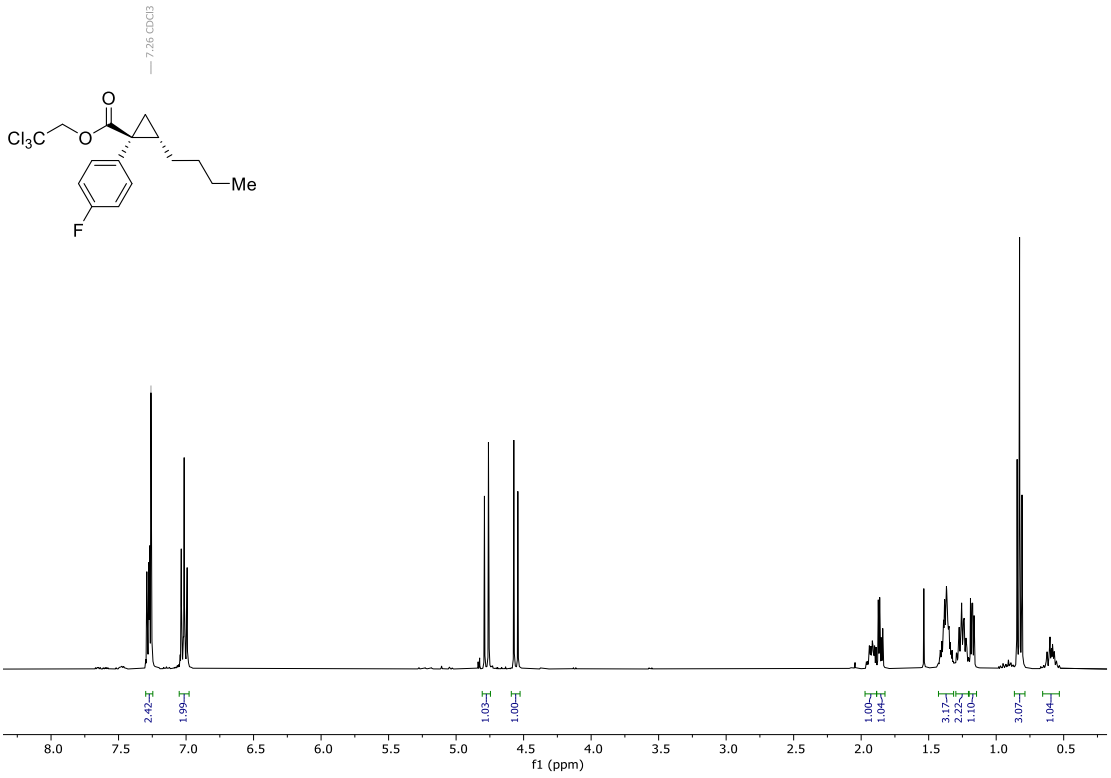
S12: ^{1}H NMR (400 MHz, $CDCl_3$):



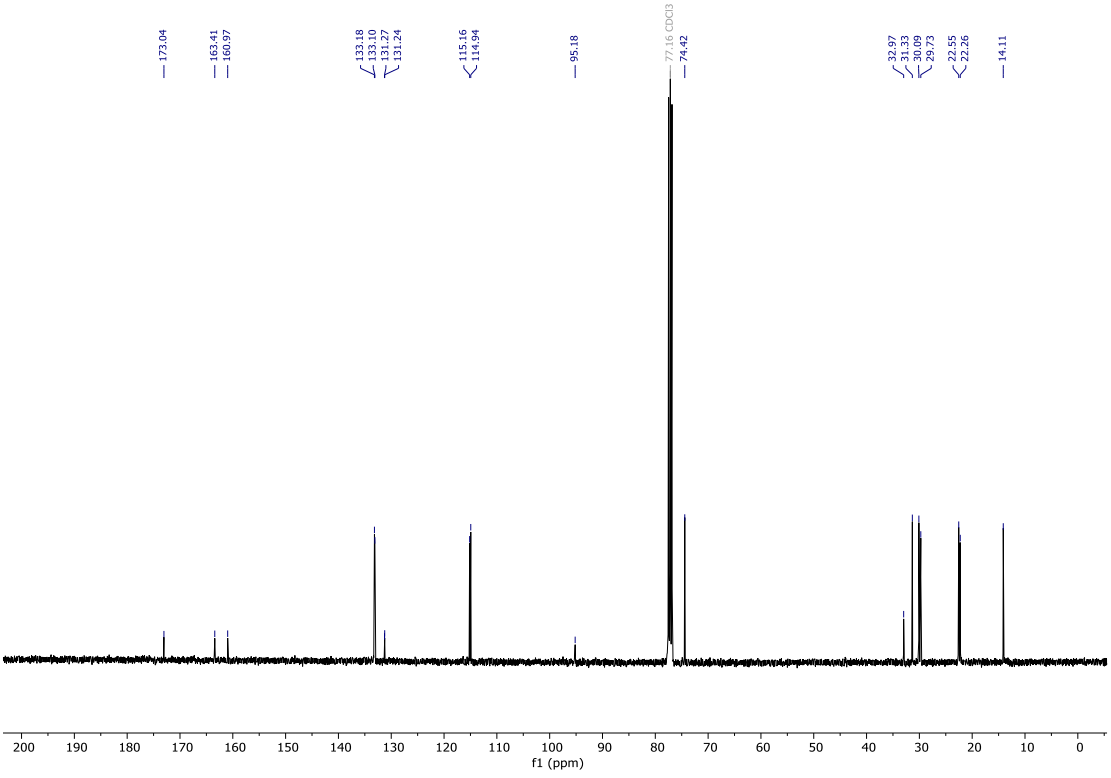
S12: ^{13}C NMR (101 MHz, $CDCl_3$):



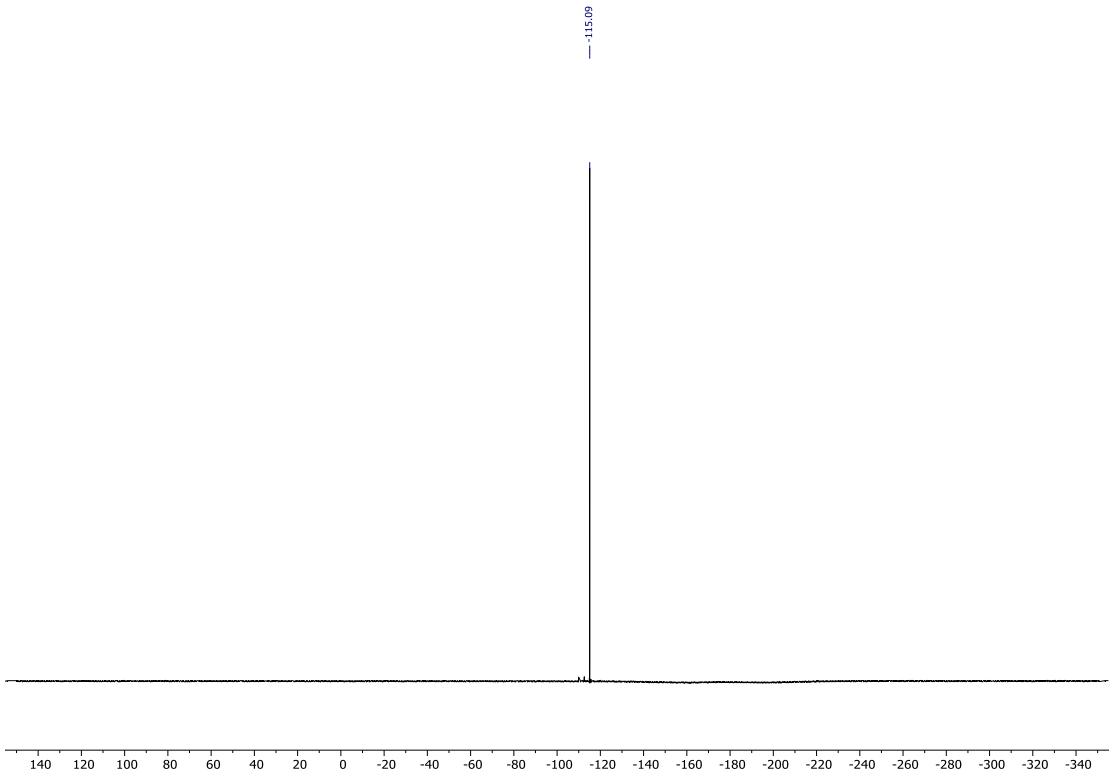
S13: ^{1}H NMR (400 MHz, $CDCl_3$):



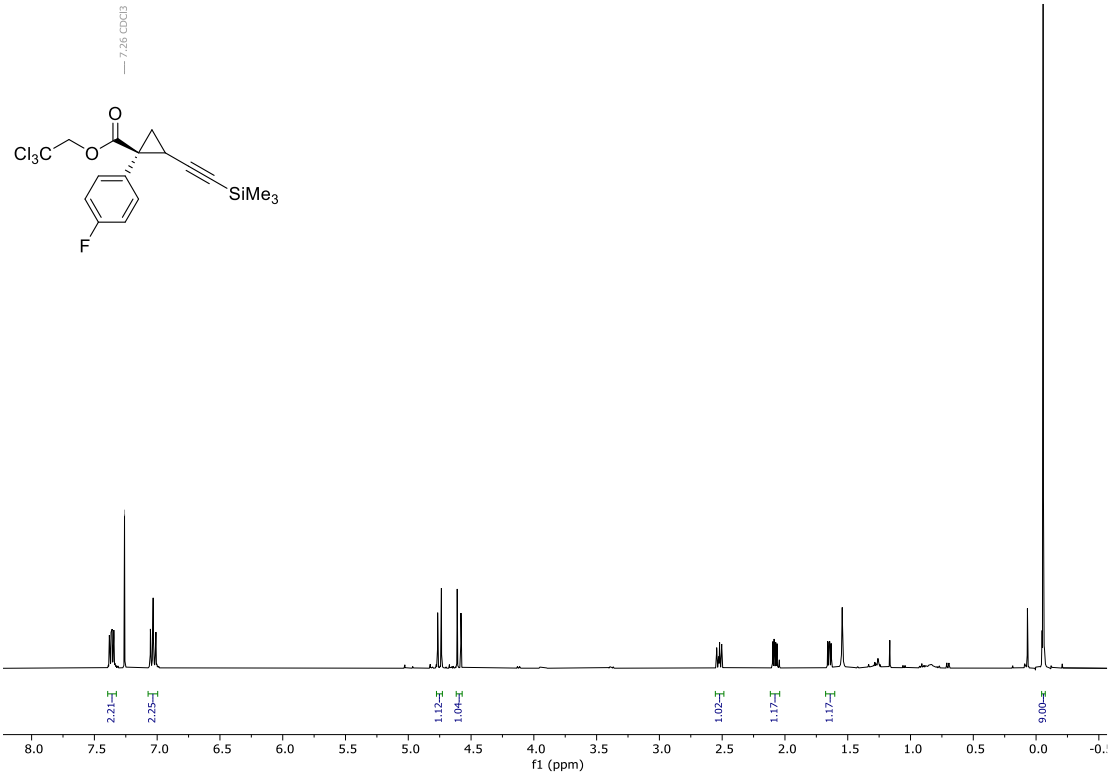
S13: ^{13}C NMR (101 MHz, $CDCl_3$):



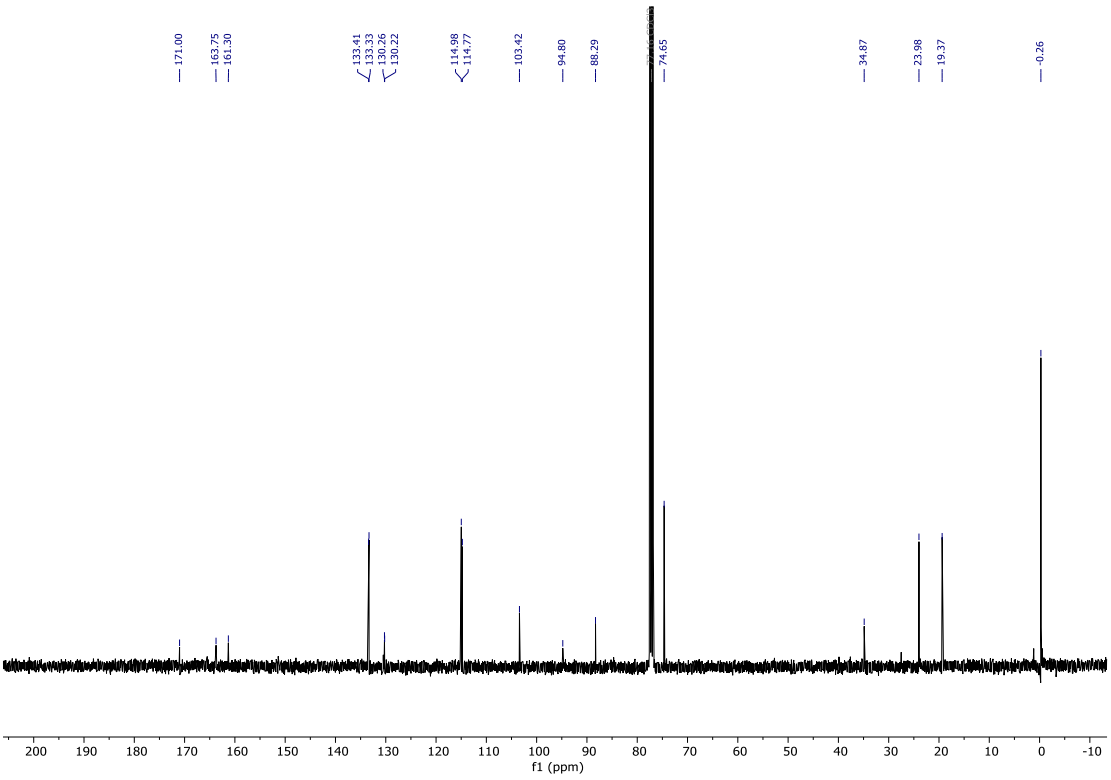
S13: ^{19}F NMR (282 MHz, $CDCl_3$):



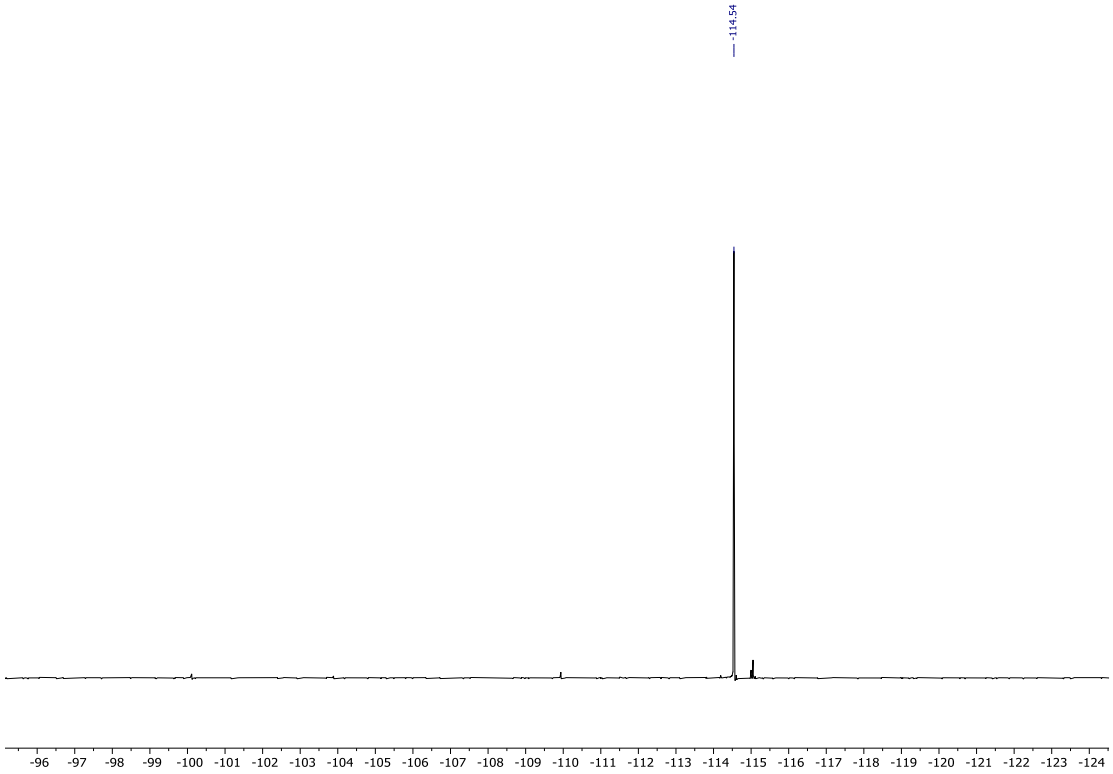
S14: ^{1}H NMR (400 MHz, $CDCl_3$):



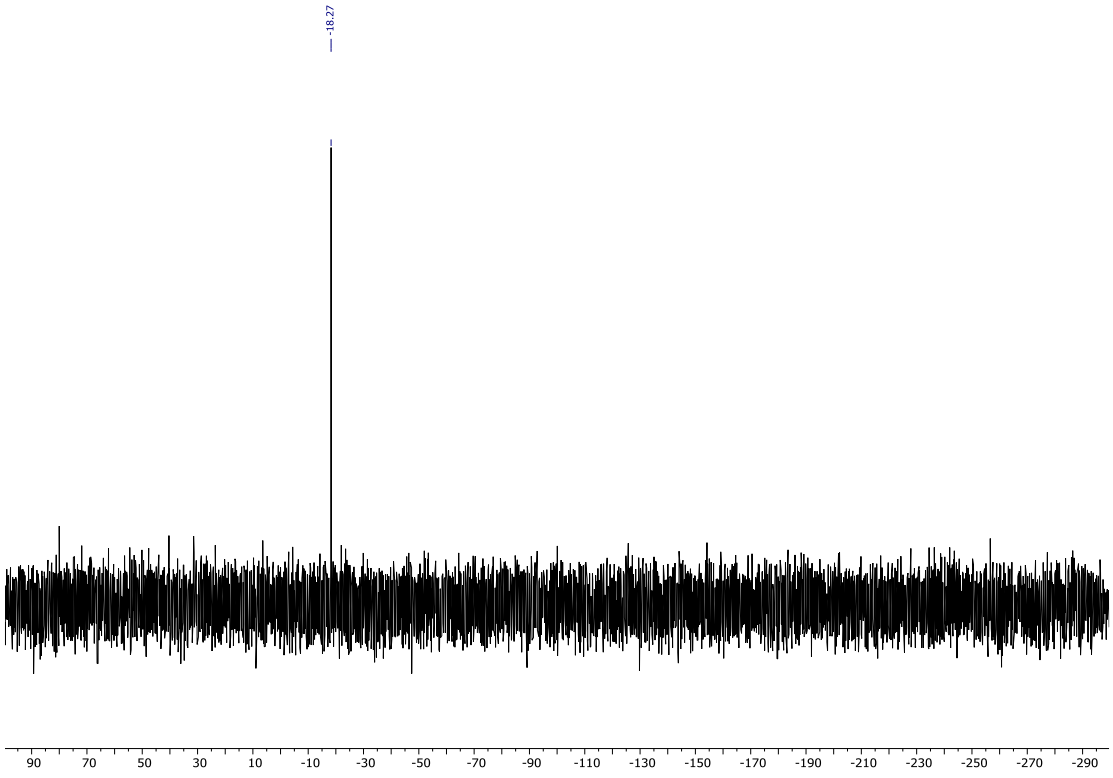
S14: ^{13}C NMR (101 MHz, $CDCl_3$):



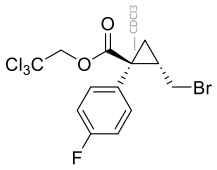
S14: ^{19}F NMR (282 MHz, $CDCl_3$):

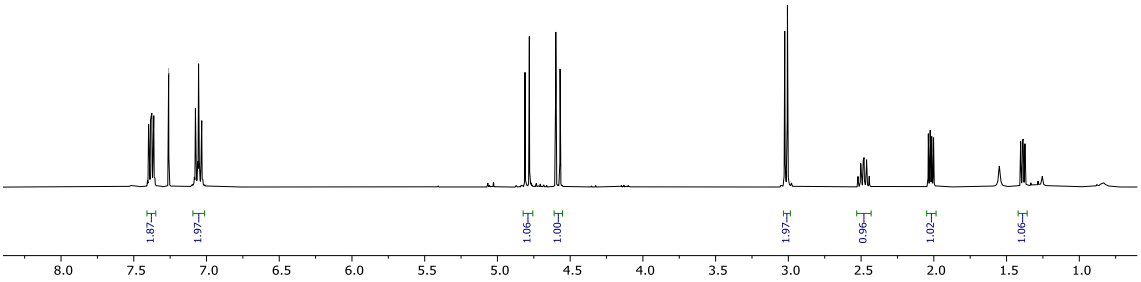


S14: ^{29}Si NMR (60 MHz, $CDCl_3$):

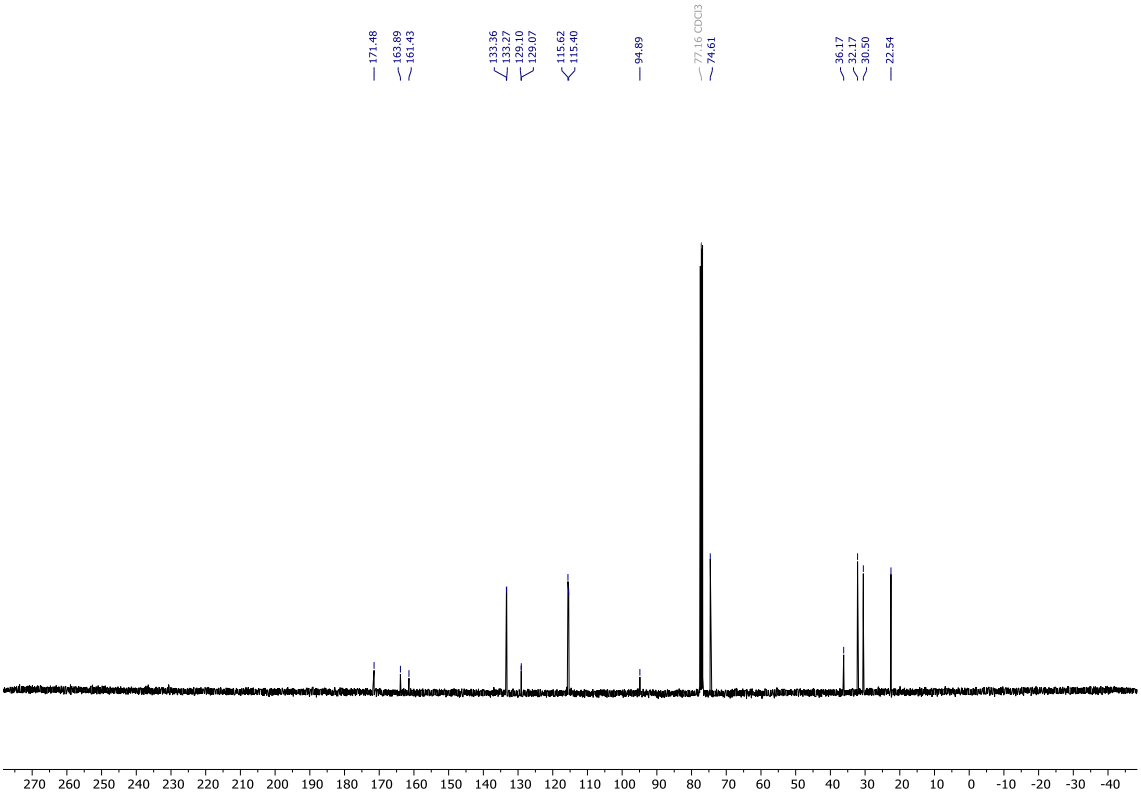


S15: ^{1}H NMR (400 MHz, $CDCl_3$):

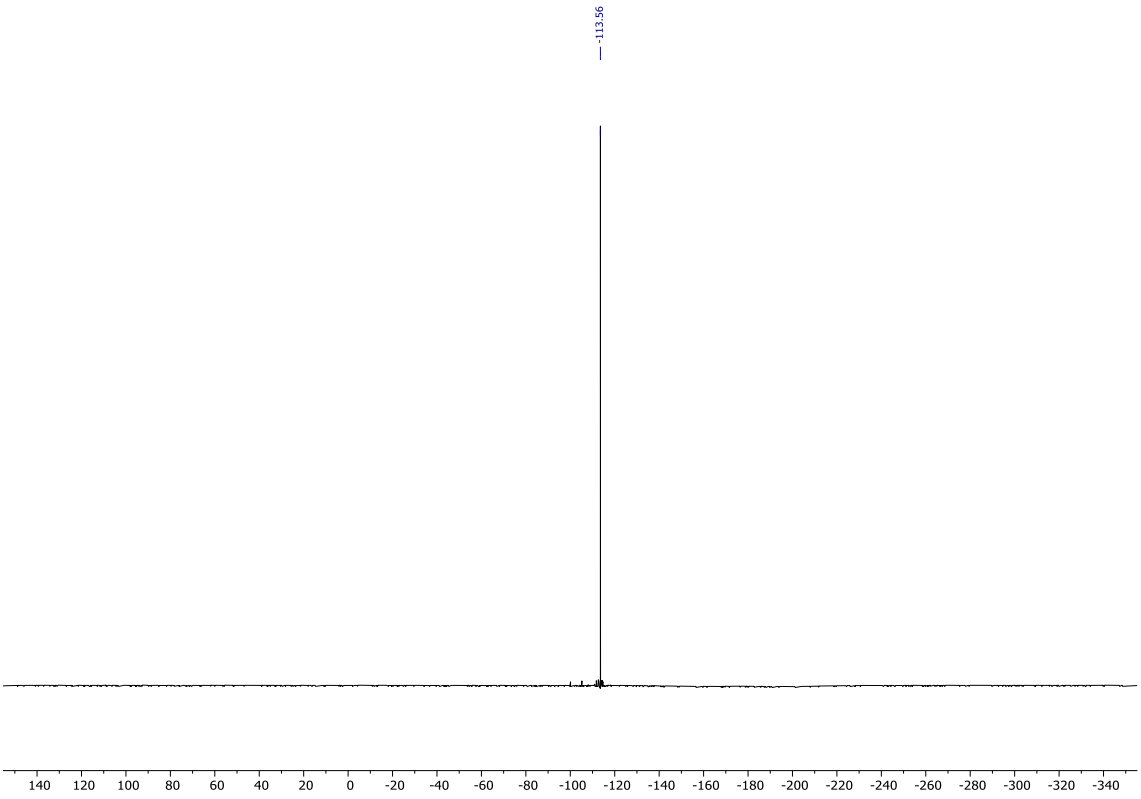




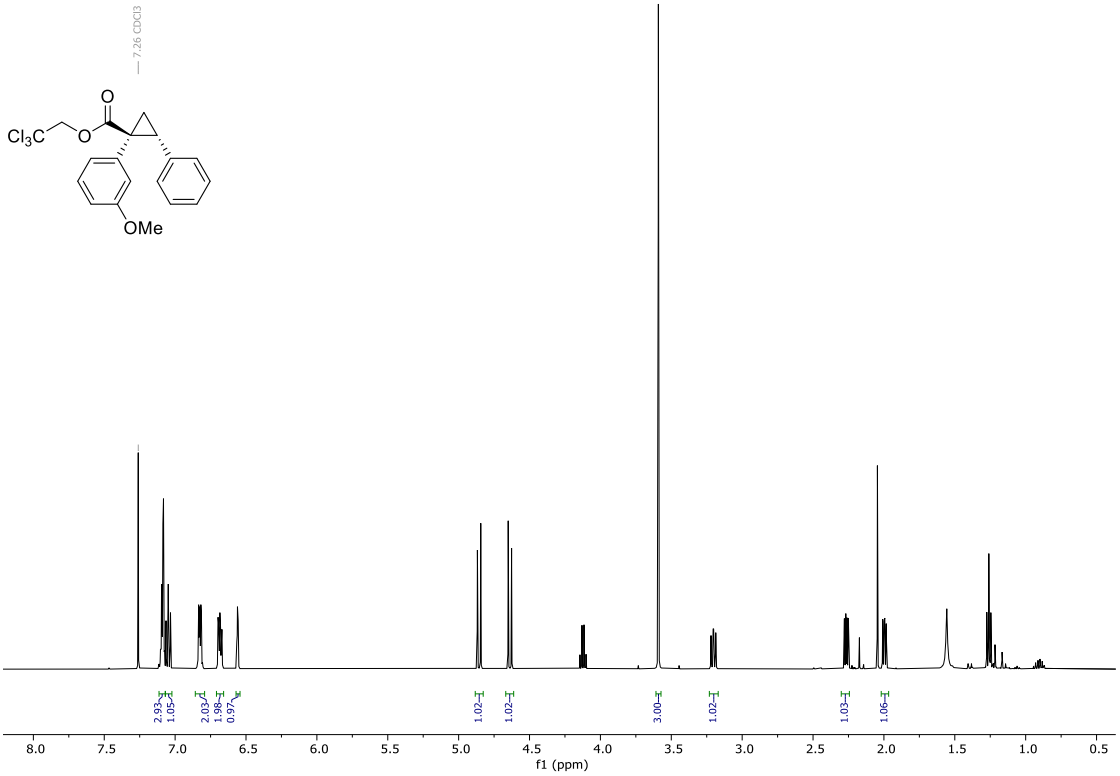
S15: ^{13}C NMR (101 MHz, $CDCl_3$):



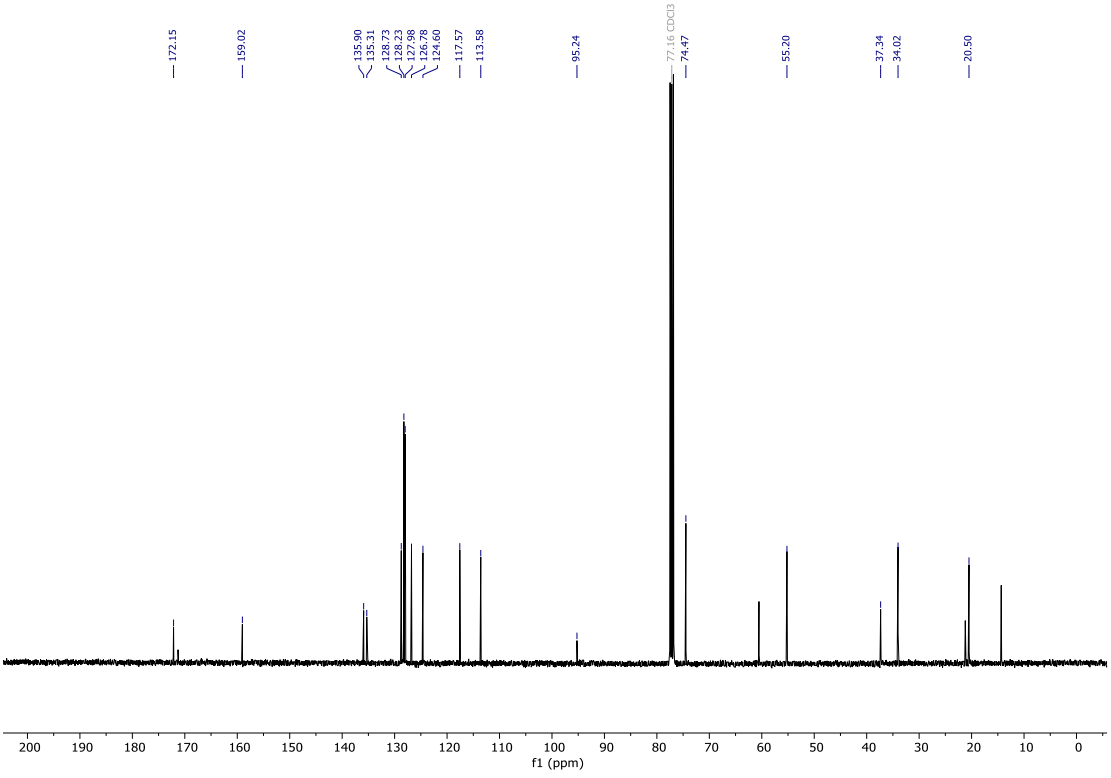
S15: ^{19}F NMR (282 MHz, $CDCl_3$):



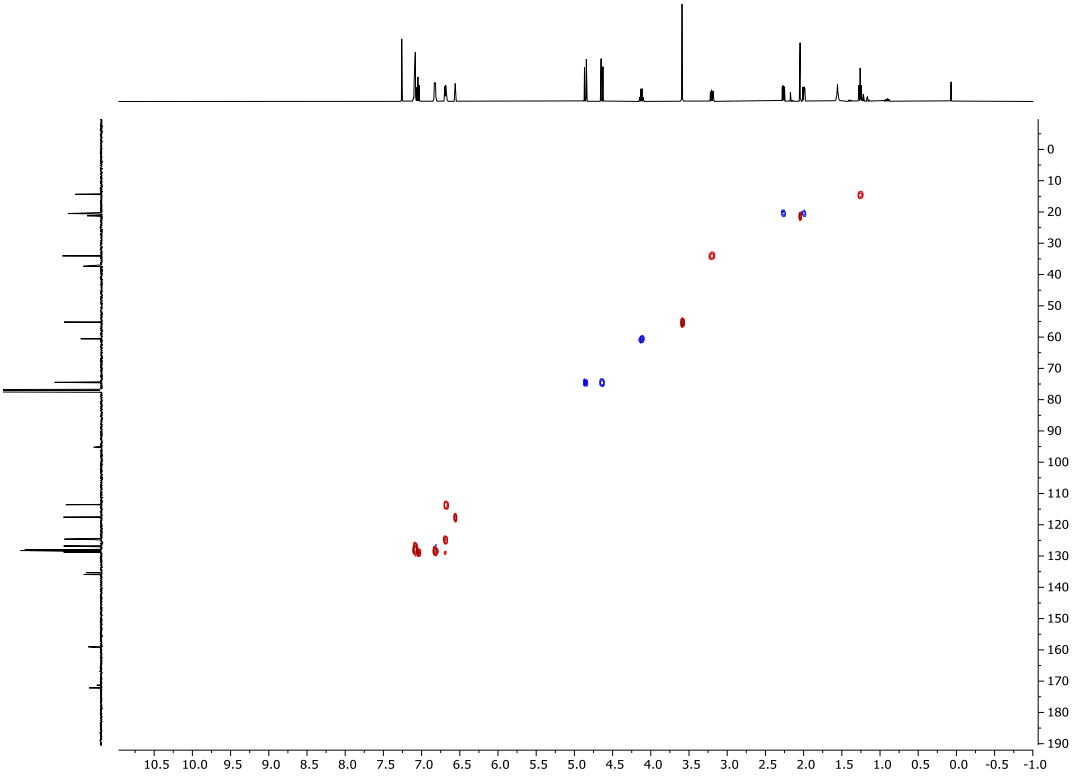
S16: ^{1}H NMR (400 MHz, $CDCl_3$):



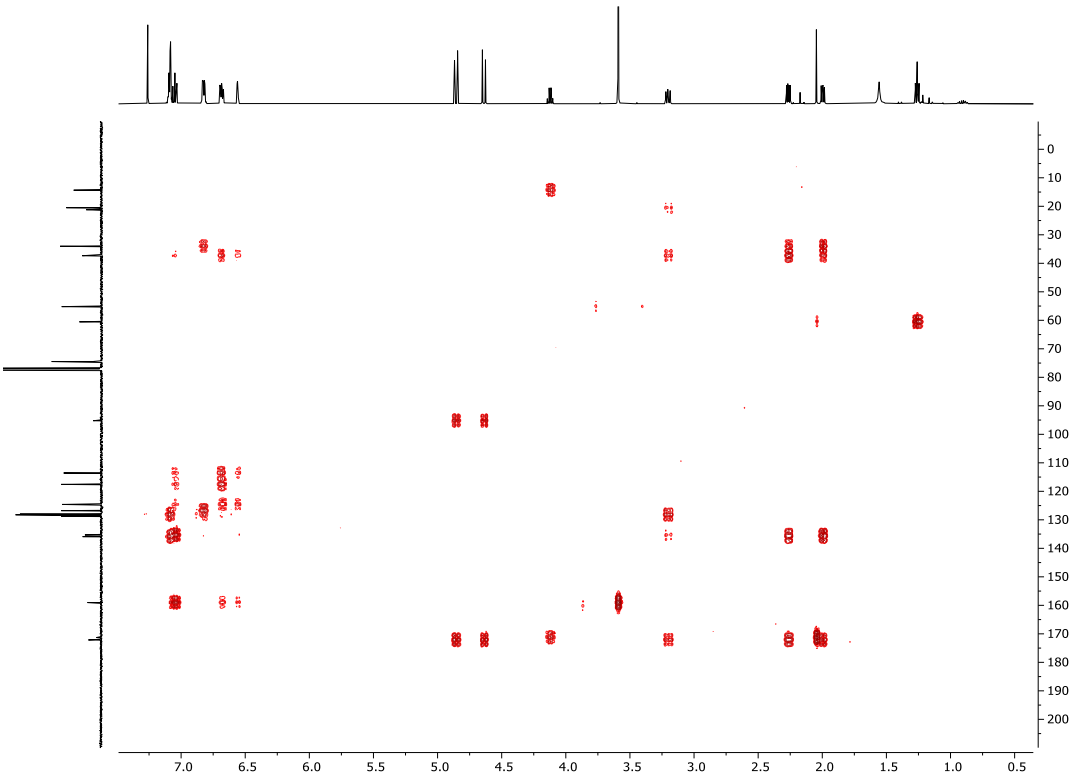
S16: ^{13}C NMR (101 MHz, $CDCl_3$):



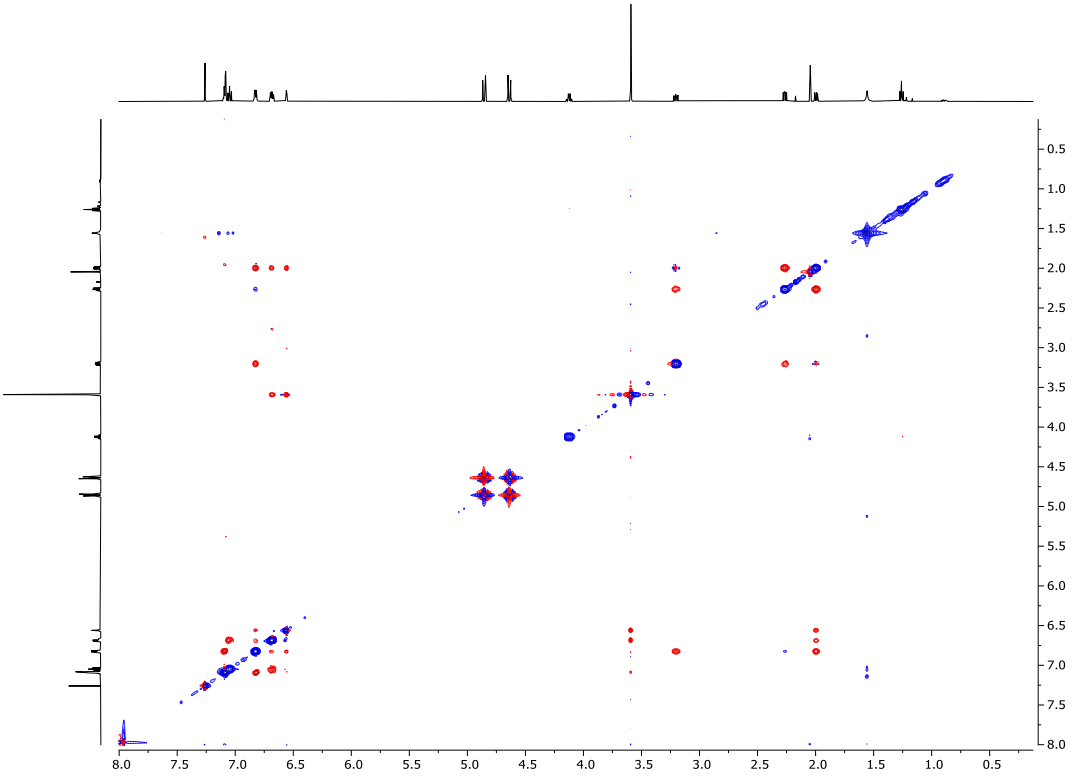
S16: HSQC NMR (400 MHz, 101 MHz, $CDCl_3$):



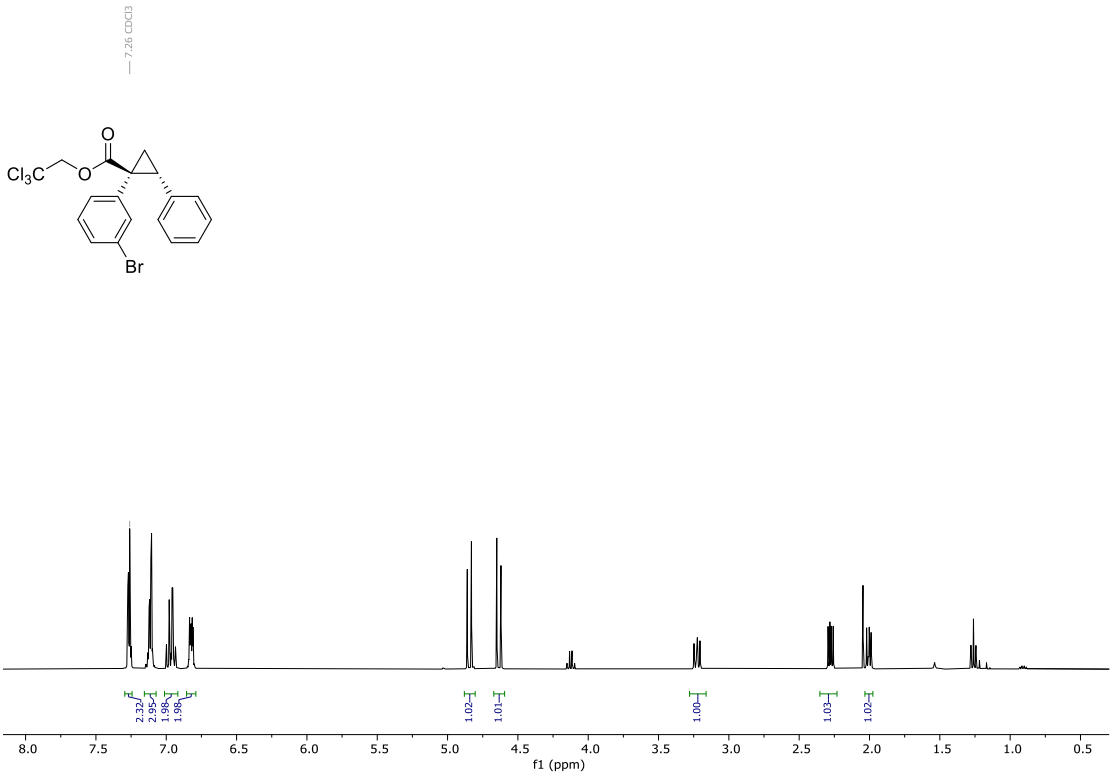
S16: HMBC NMR (400MHz, 101 MHz, $CDCl_3$):



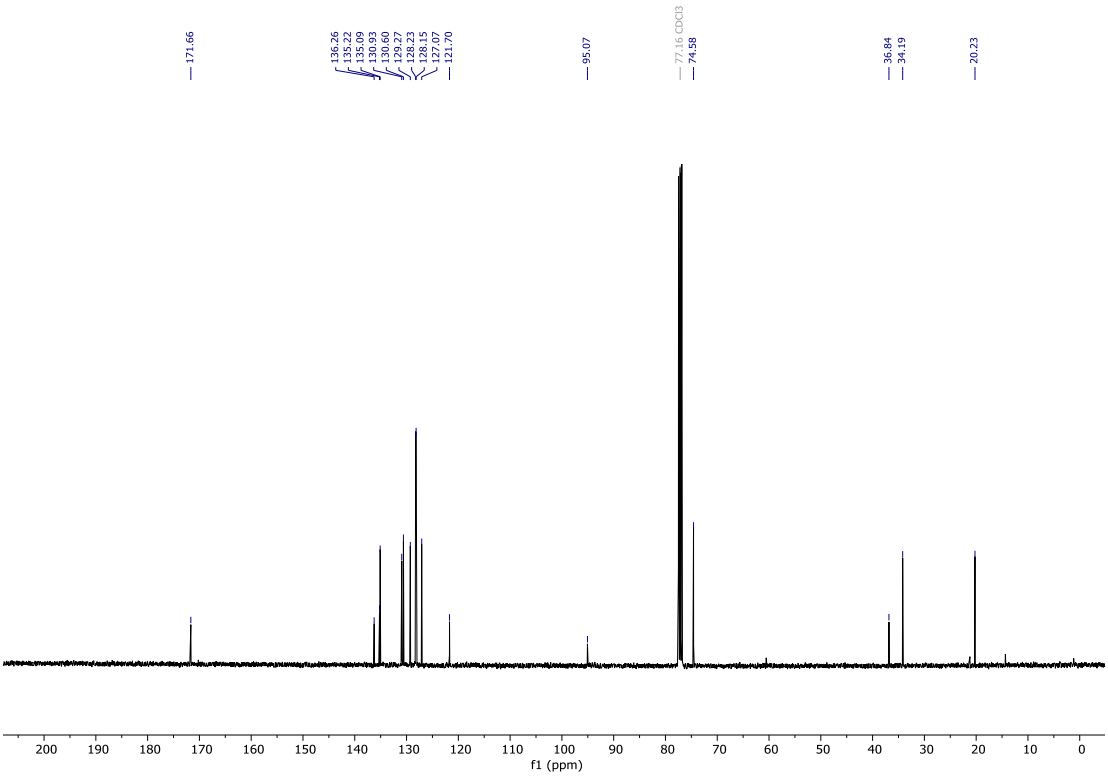
S16: NOESY NMR (500 MHz, $CDCl_3$):



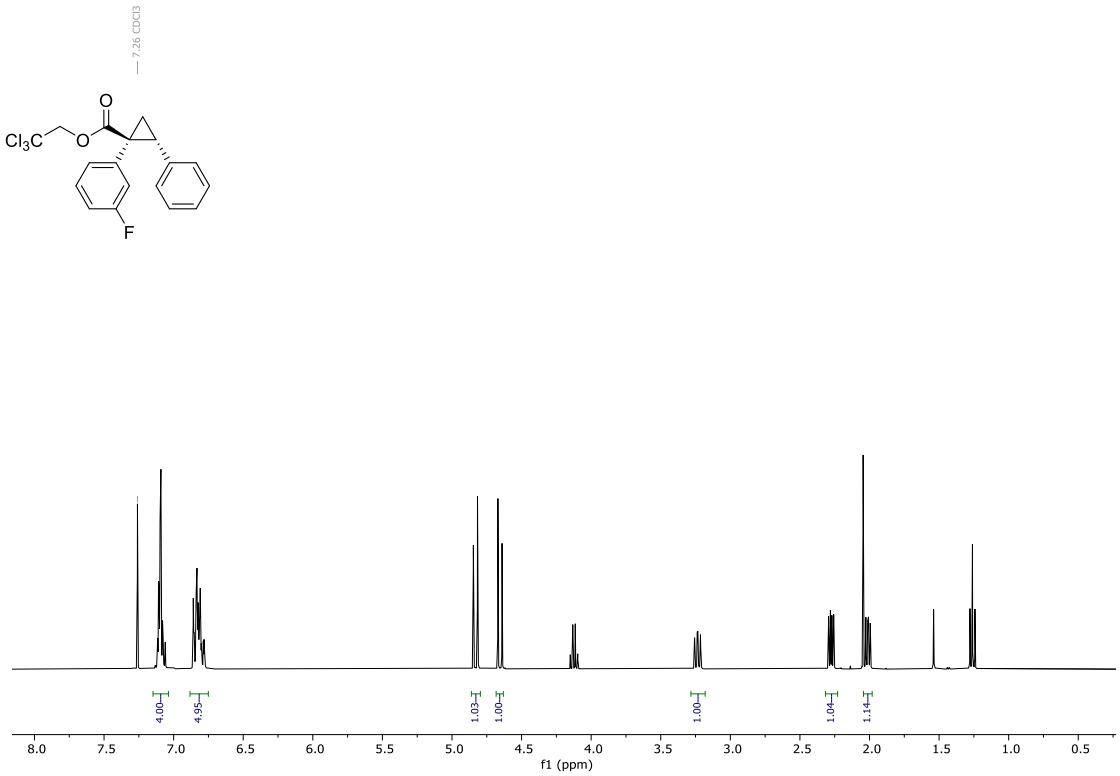
S17: ^{1}H NMR (400 MHz, $CDCl_3$):



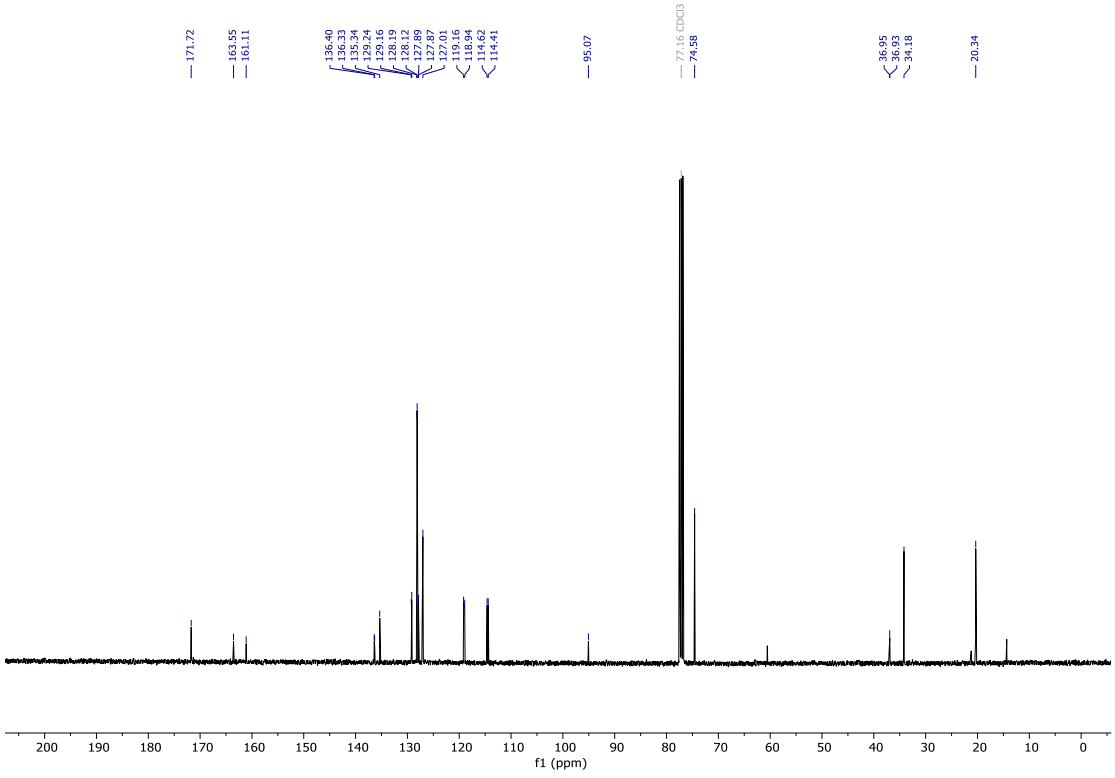
S17: ^{13}C NMR (101 MHz, $CDCl_3$):



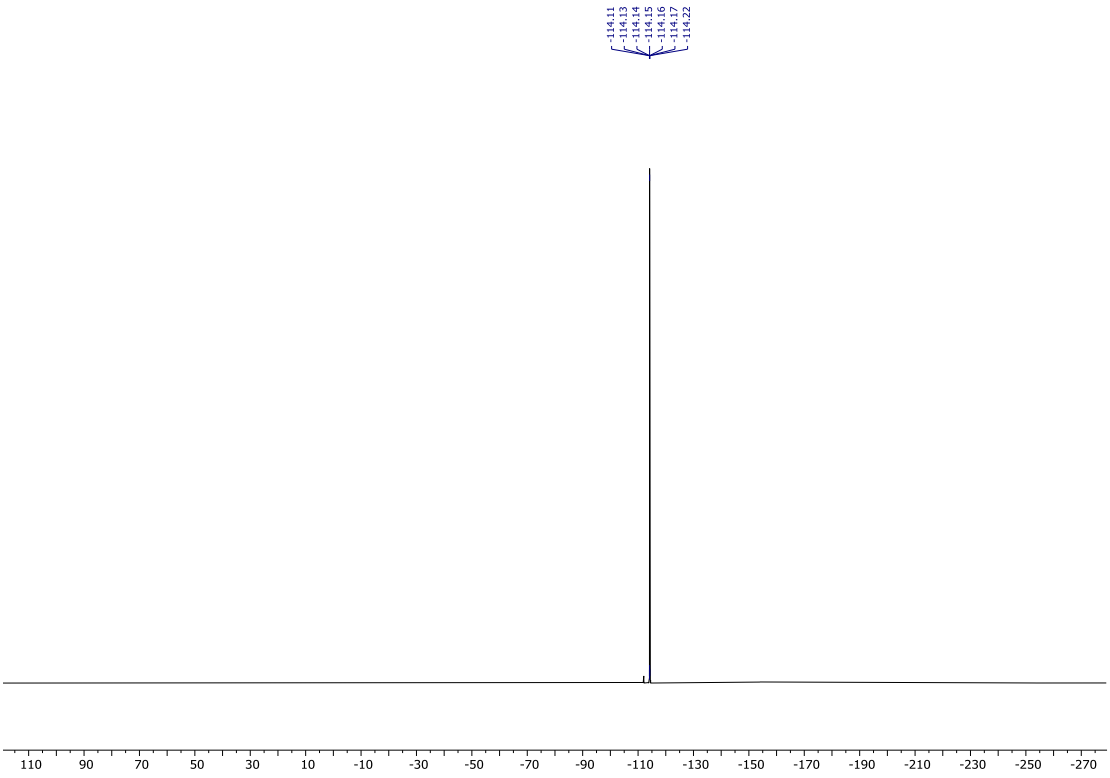
S18: ^{1}H NMR (400 MHz, $CDCl_3$):



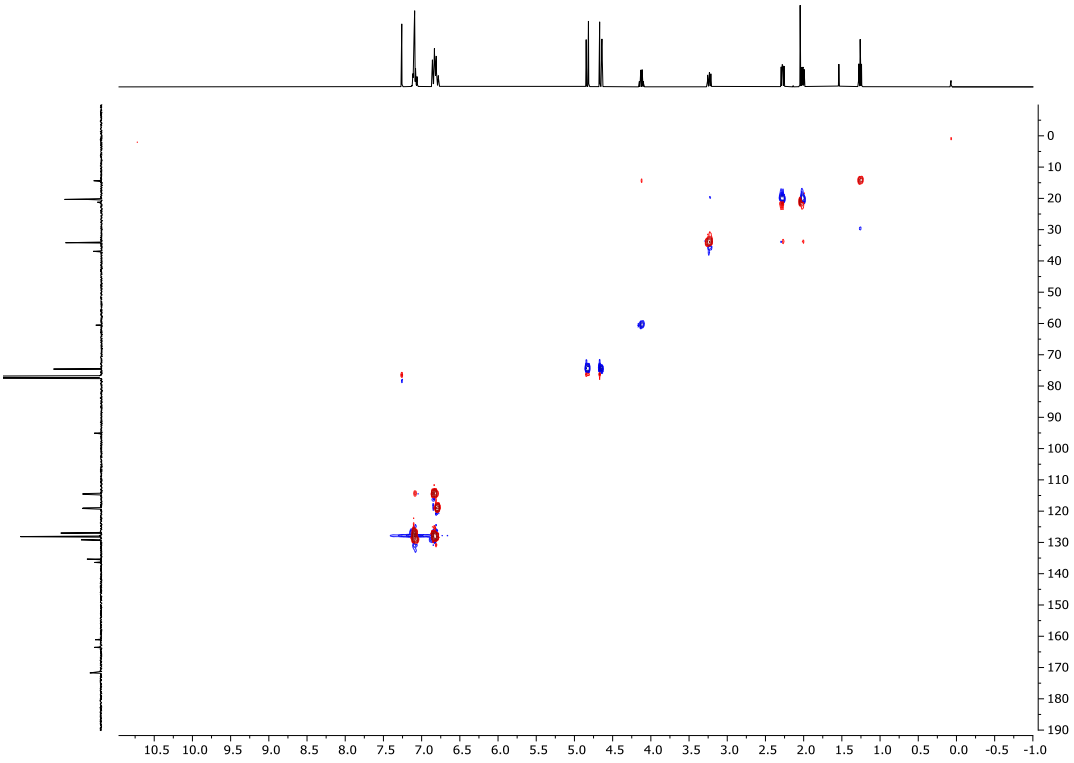
S18: ^{13}C NMR (101 MHz, $CDCl_3$):



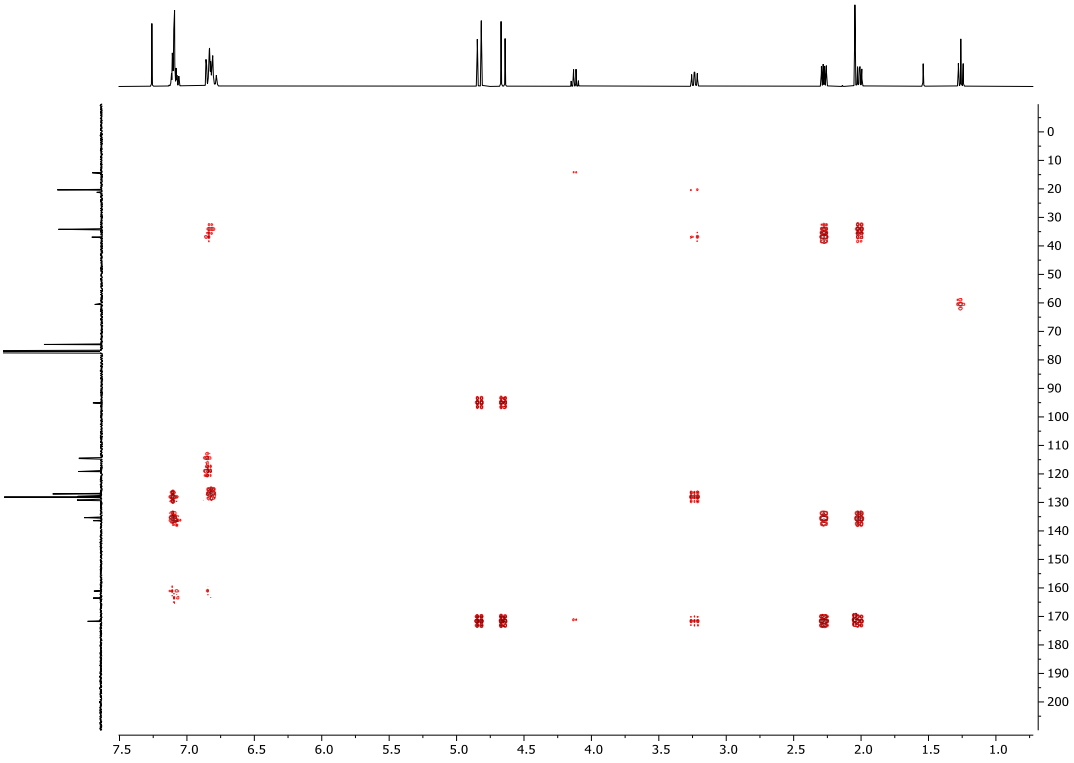
S18: ^{19}F NMR (470 MHz, $CDCl_3$):



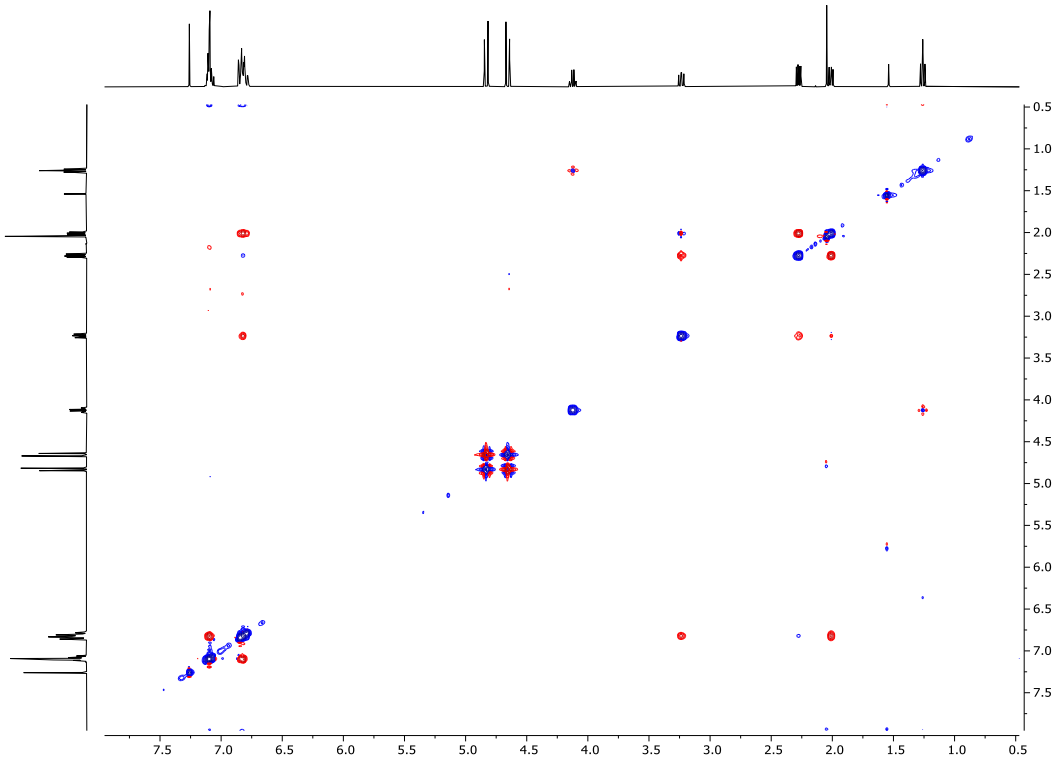
S18: HSQC NMR (400 MHz, 101 MHz, $CDCl_3$):



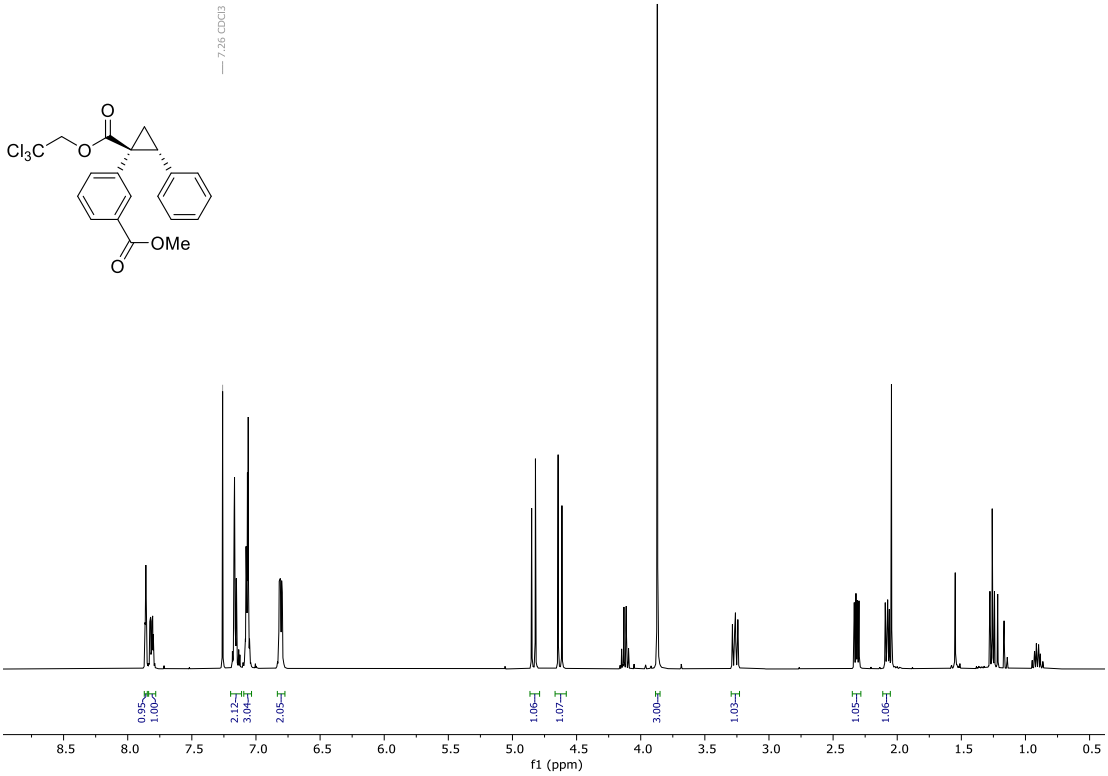
S18: HMBC NMR (400 MHz, 101 MHz, $CDCl_3$):



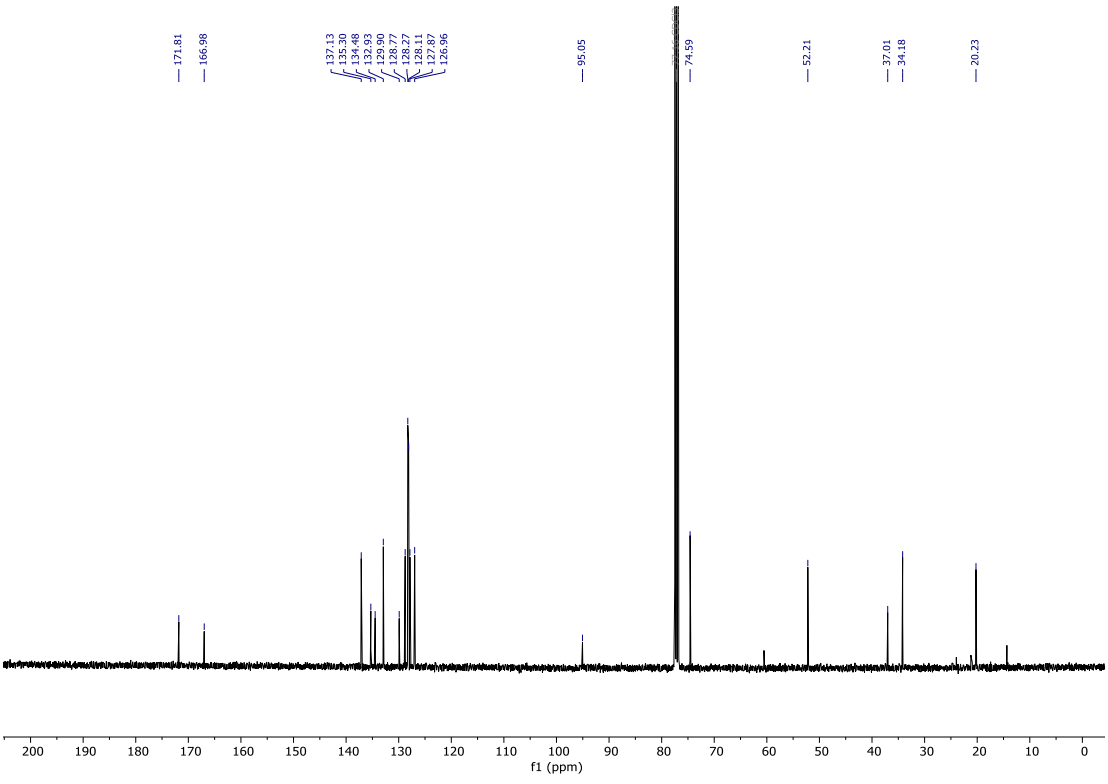
S18: NOESY NMR (500 MHz, $CDCl_3$):



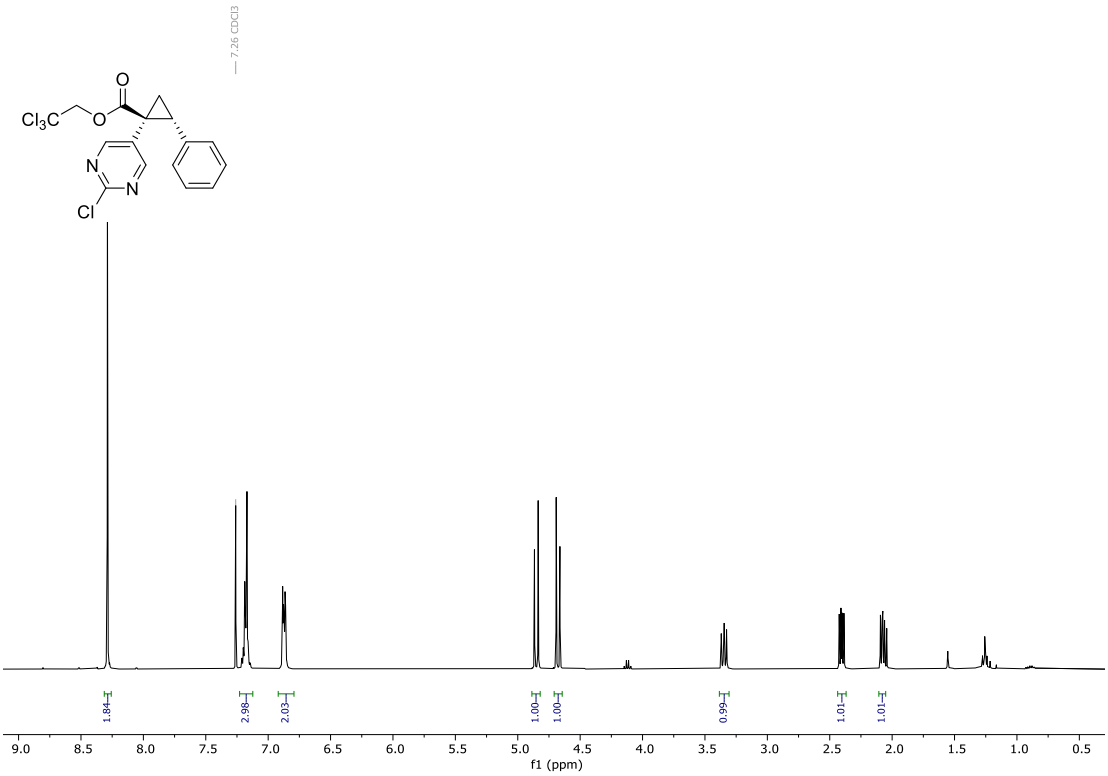
S19: ^{1}H NMR (400 MHz, $CDCl_3$):



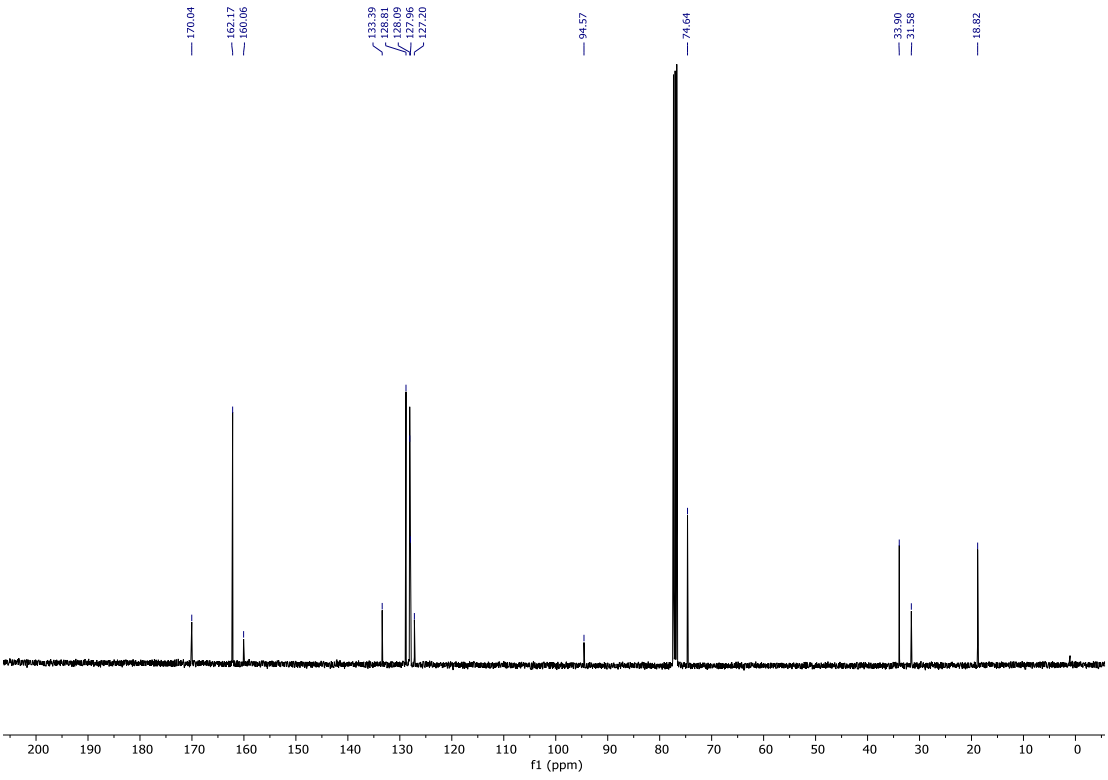
S19: ^{13}C NMR (101 MHz, $CDCl_3$):



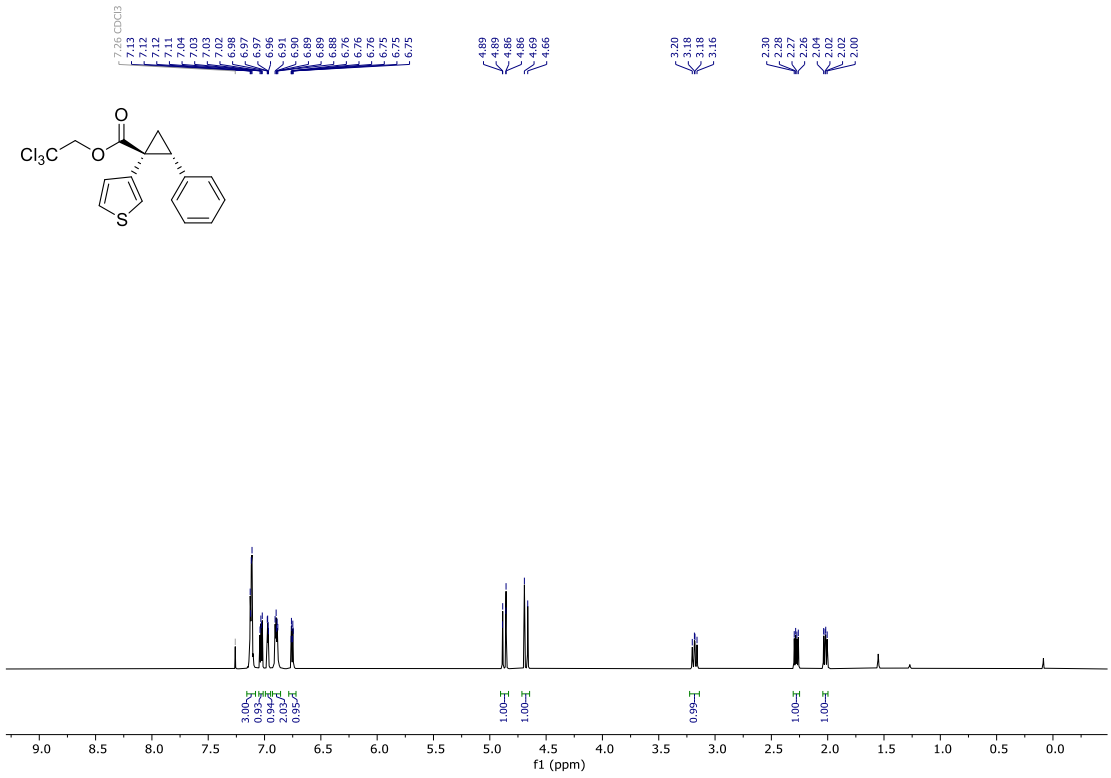
S20: ^{1}H NMR (400 MHz, $CDCl_3$):



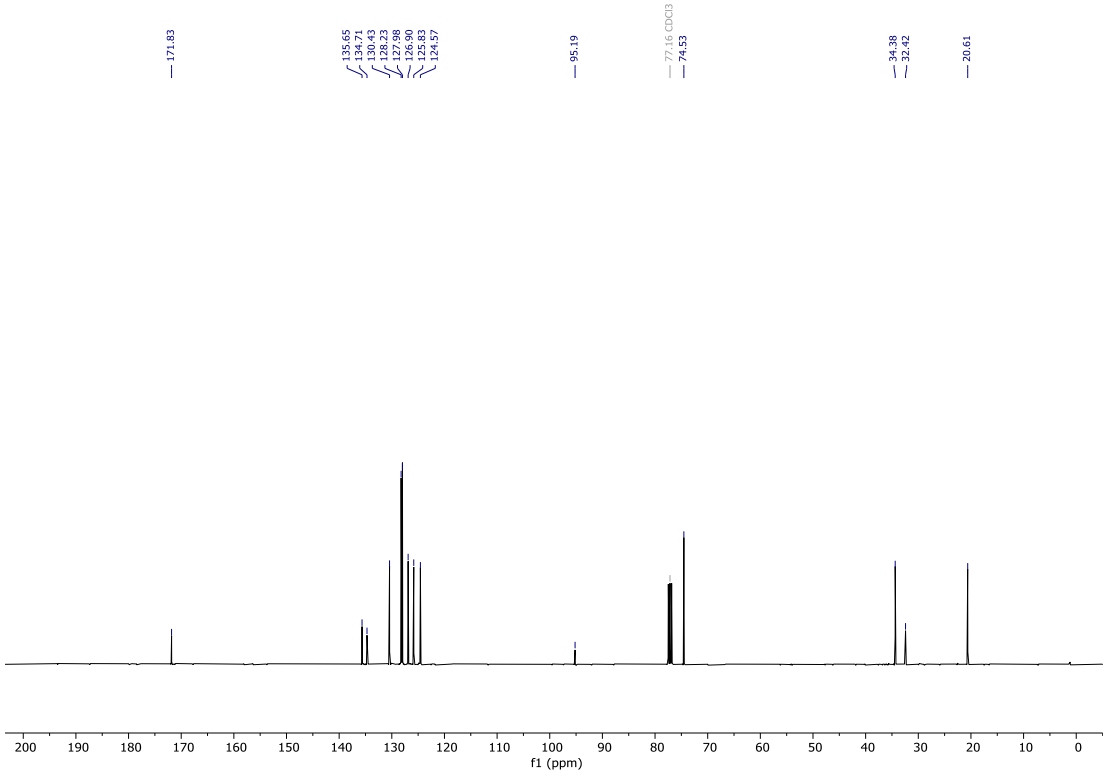
S20: ^{13}C NMR (101 MHz, $CDCl_3$):



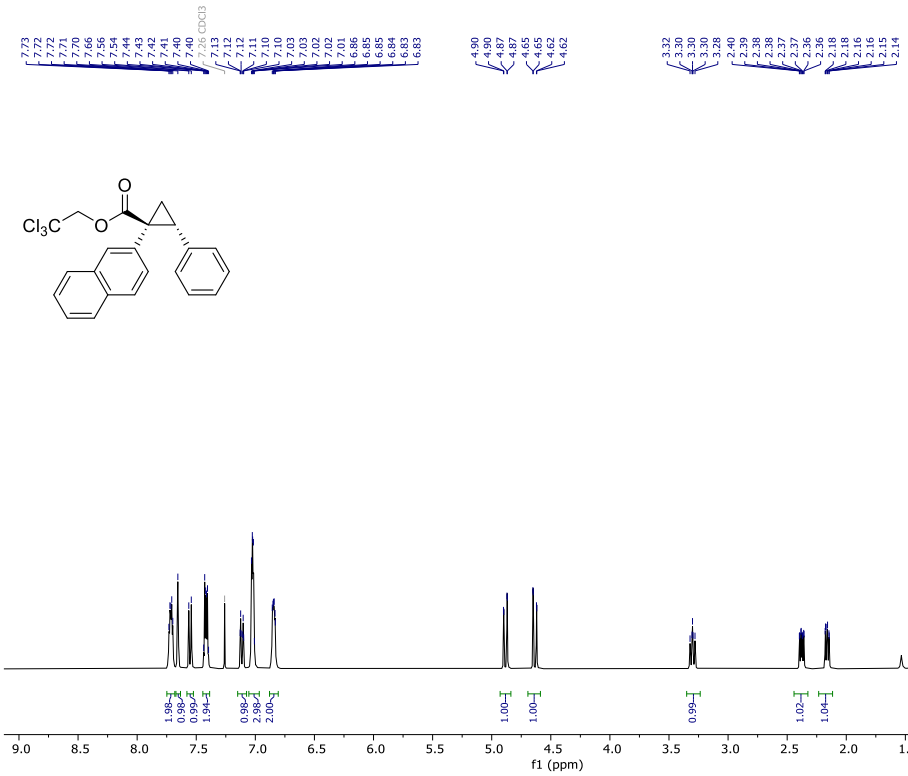
S21: ^{1}H NMR (400 MHz, $CDCl_3$):



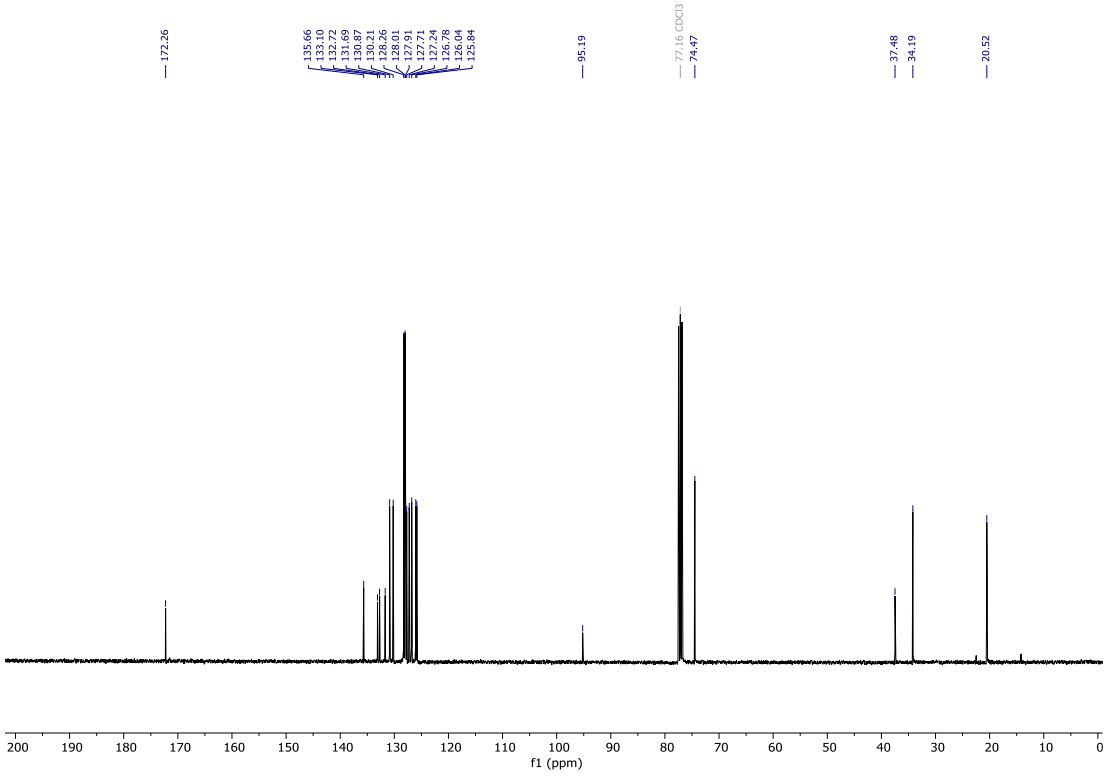
S21: ^{13}C NMR (101 MHz, $CDCl_3$):



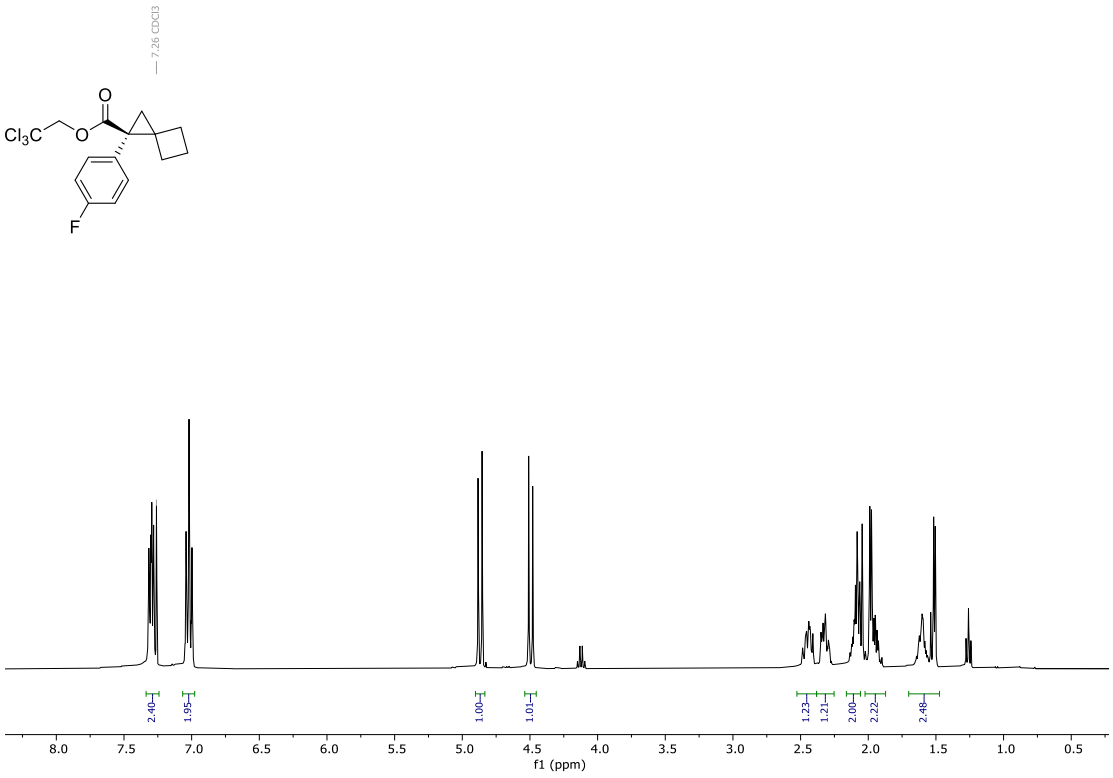
S22: ^{1}H NMR (400 MHz, $CDCl_3$):



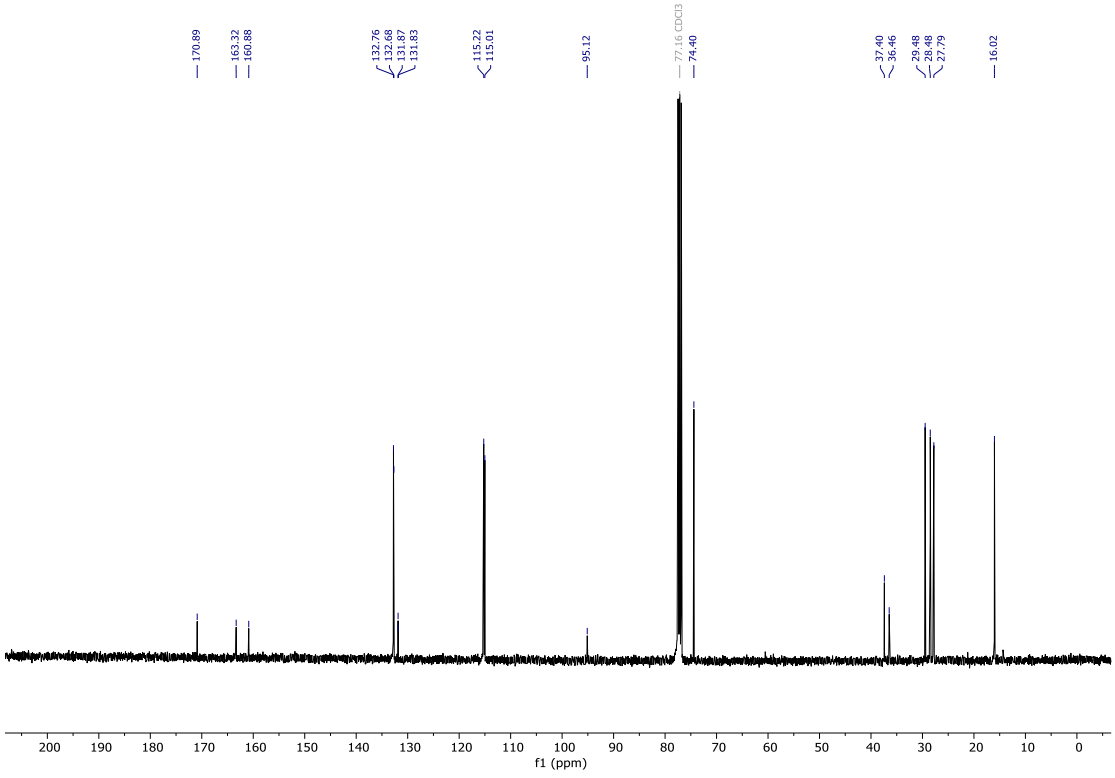
S22: ^{13}C NMR (101 MHz, $CDCl_3$):



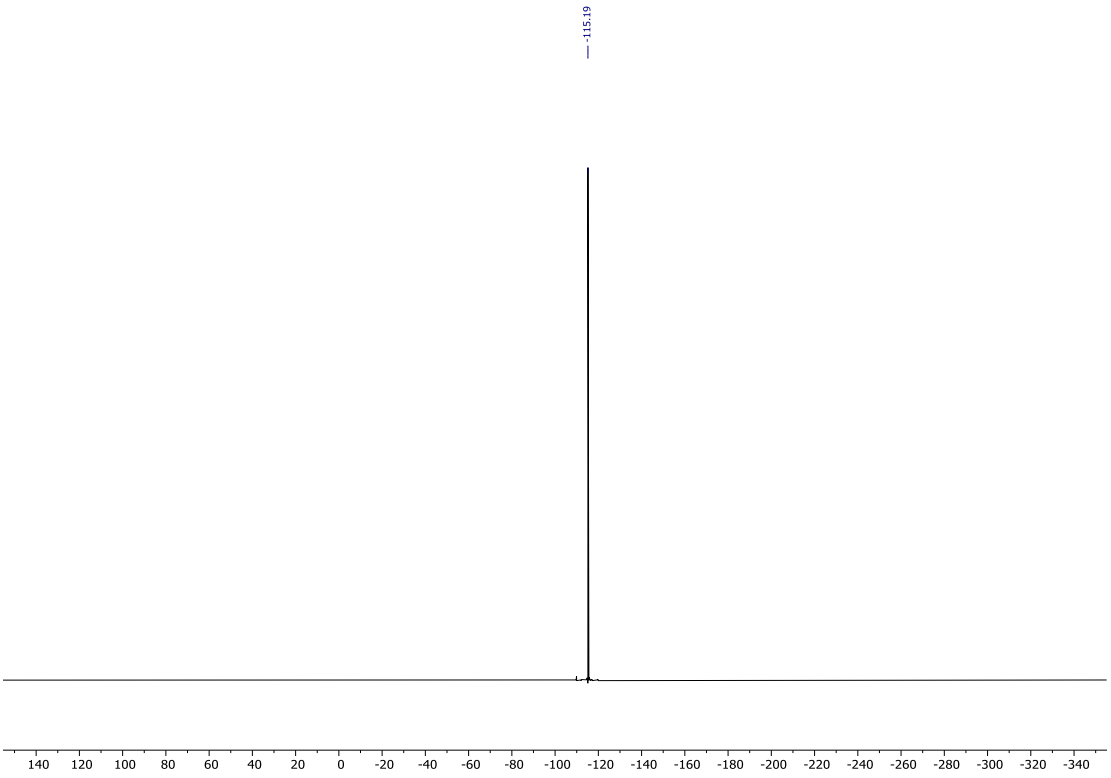
S23: ^{1}H NMR (400 MHz, $CDCl_3$):



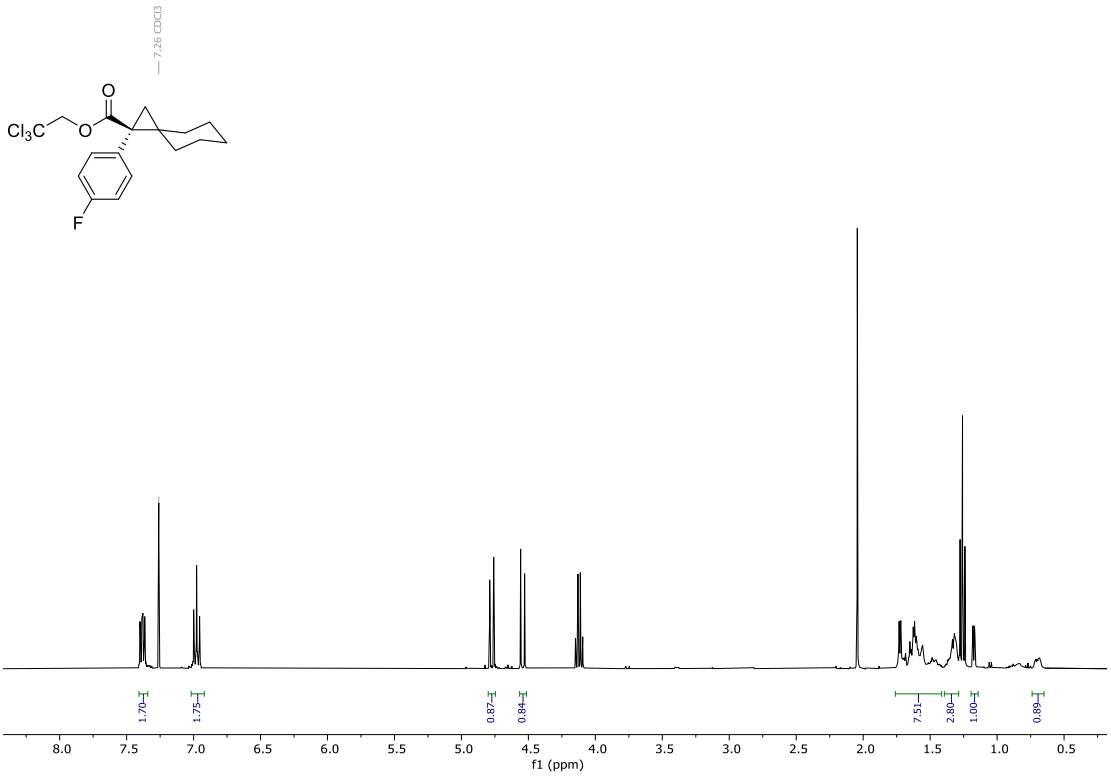
S23: ^{13}C NMR (101 MHz, $CDCl_3$):



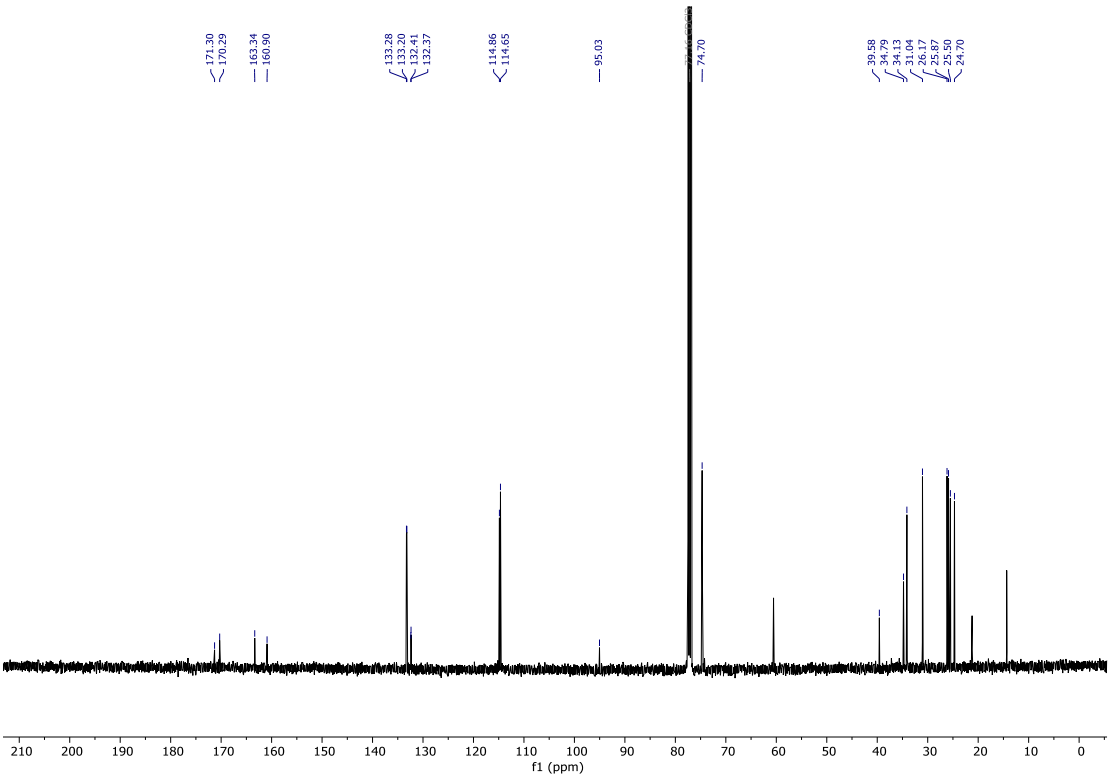
S23: ^{19}F NMR (282 MHz, $CDCl_3$):



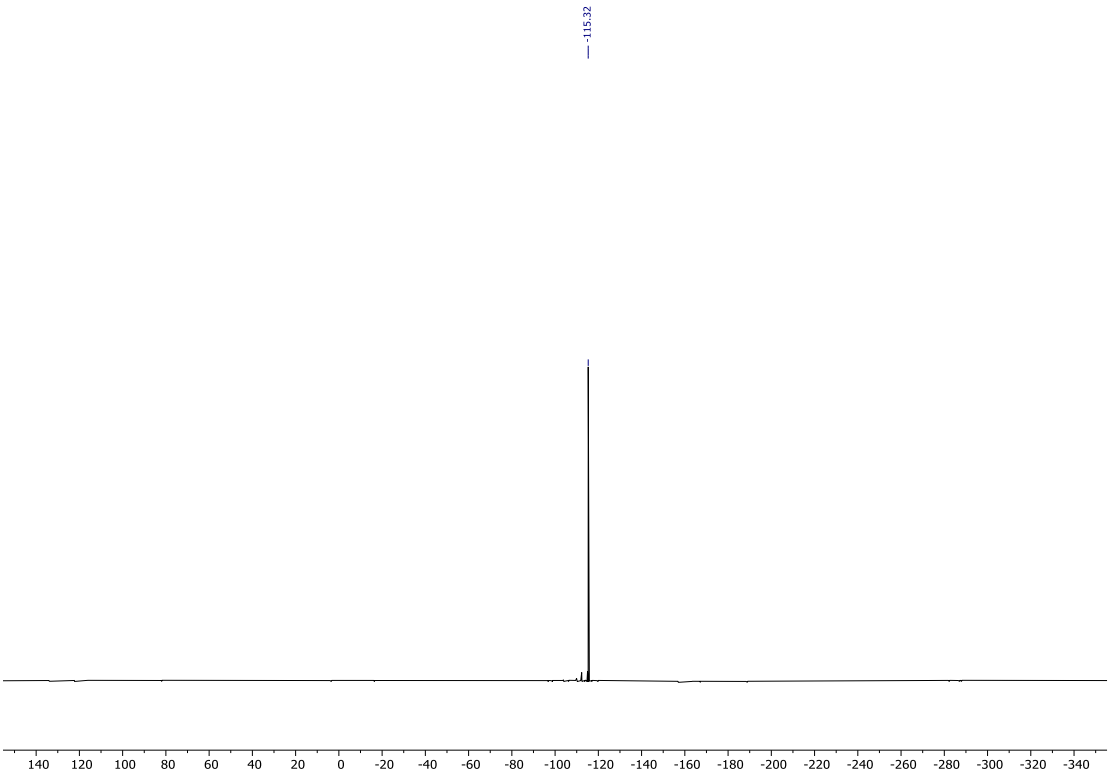
S24: ^{1}H NMR (400 MHz, CDCl3):



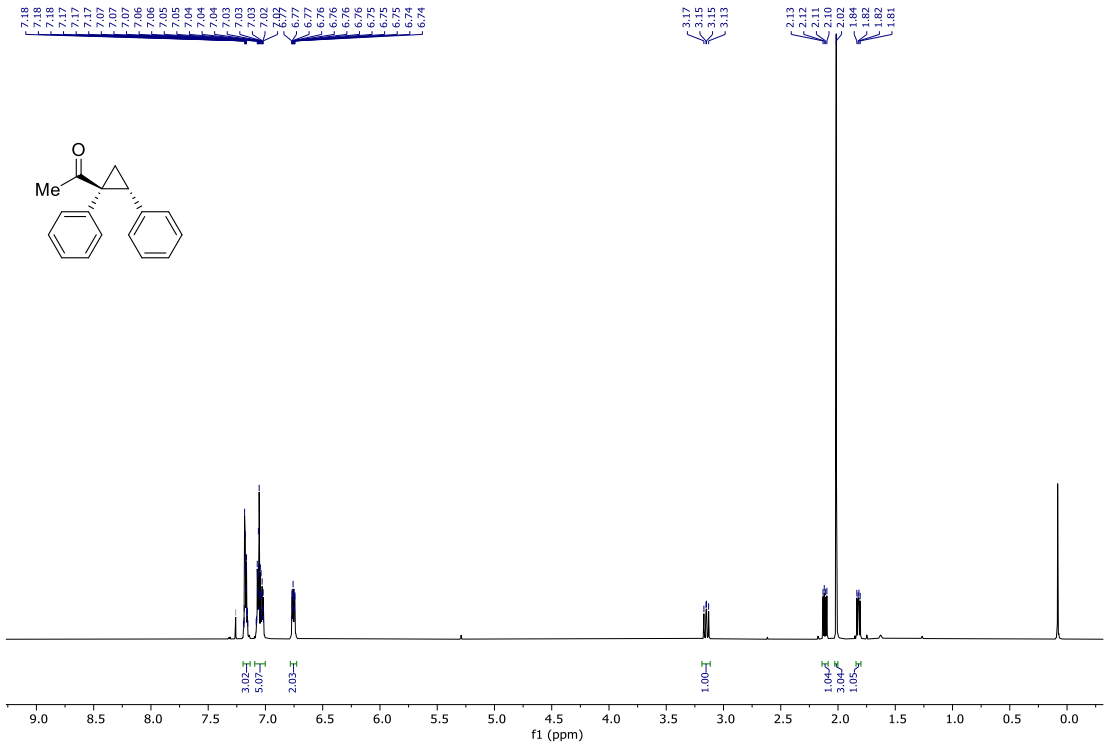
S24: ^{13}C NMR (400 MHz, $CDCl_3$):



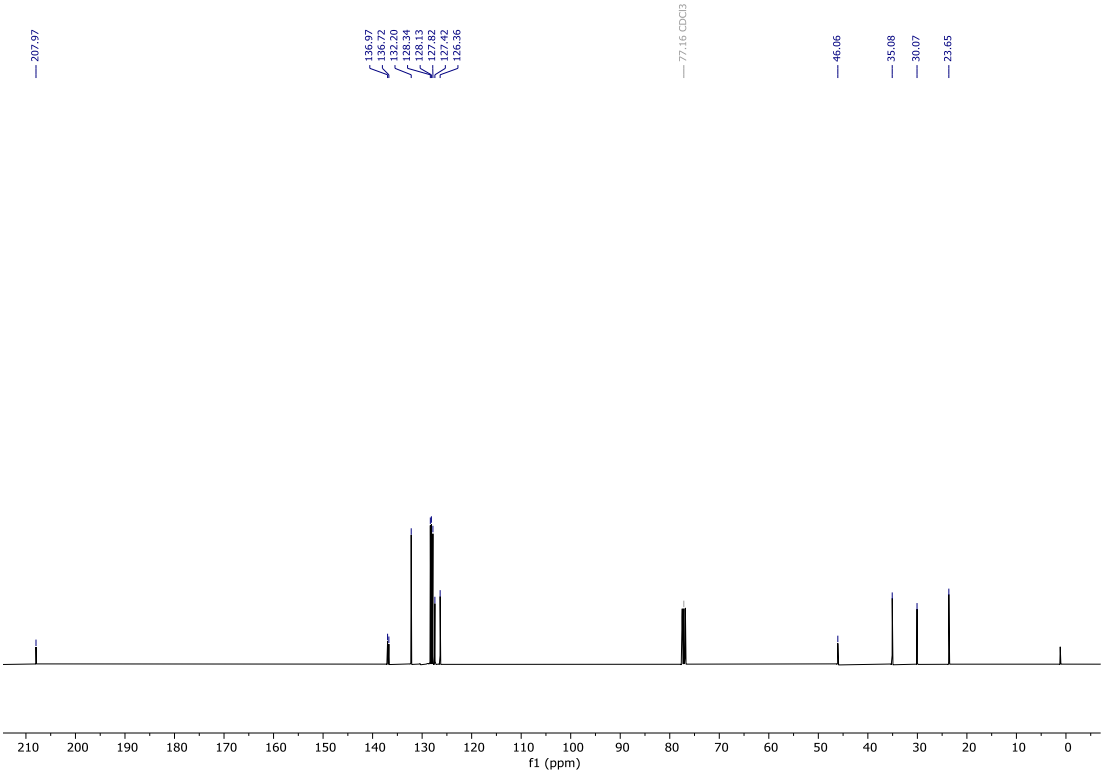
S24: ^{19}F NMR (282 MHz, $CDCl_3$):



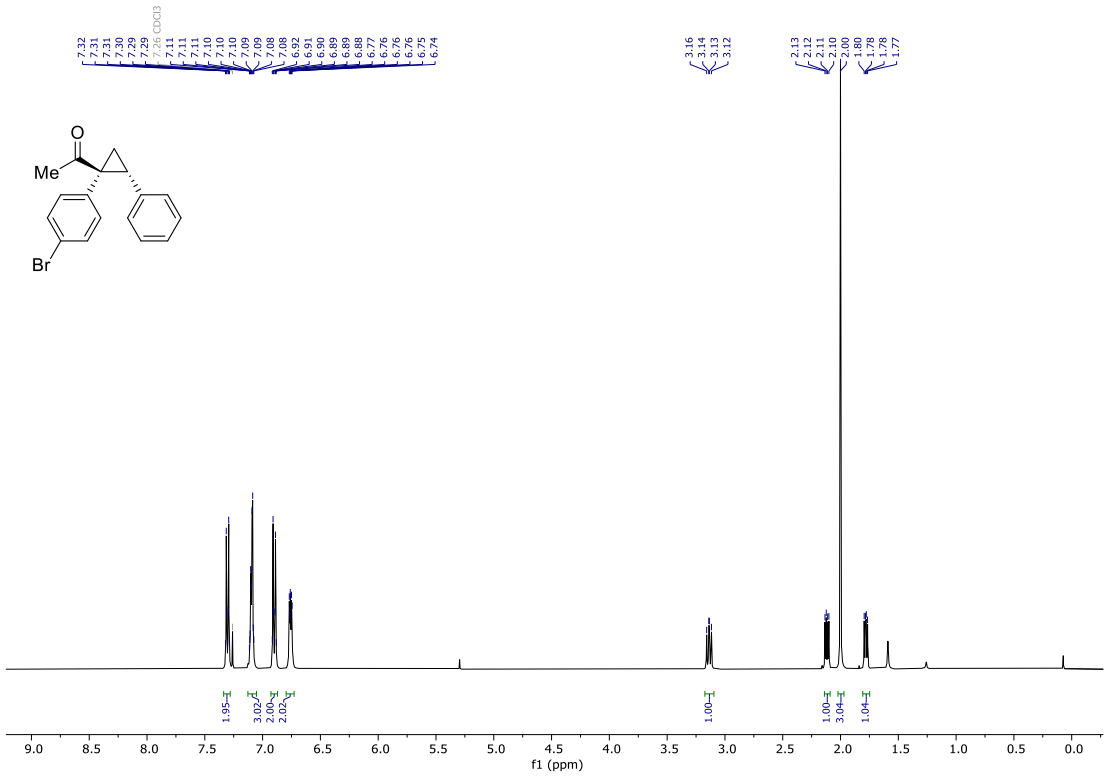
S25: ^{1}H NMR (400 MHz, $CDCl_3$):



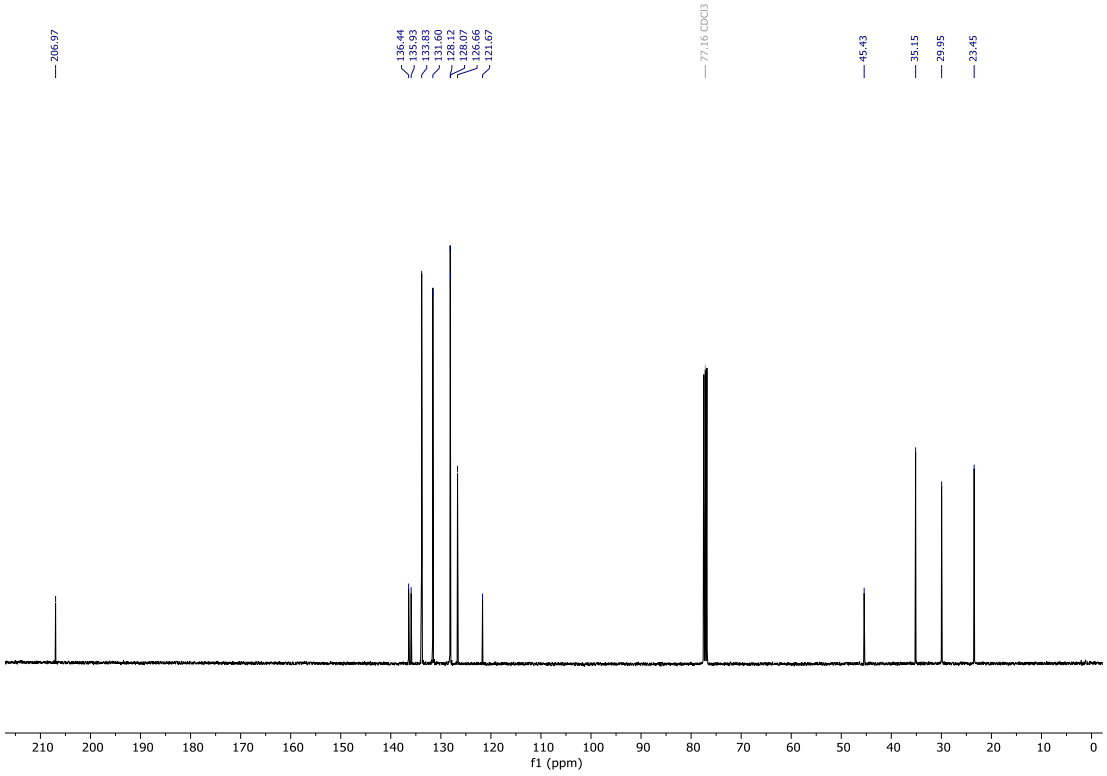
S25: ^{13}C NMR (101 MHz, $CDCl_3$):



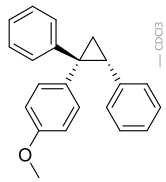
S26: ^{1}H NMR (400 MHz, $CDCl_3$):

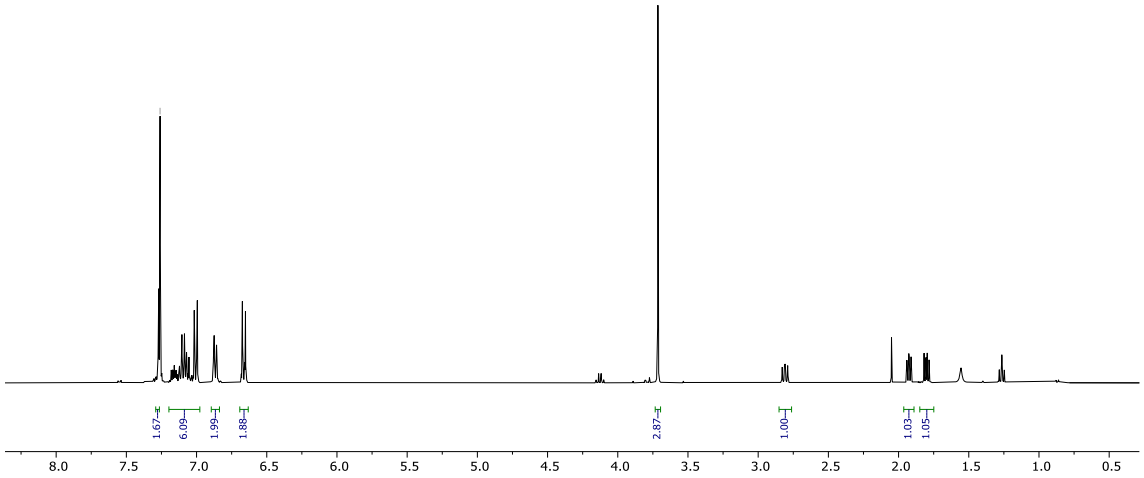


S26: ^{13}C NMR (101 MHz, $CDCl_3$):

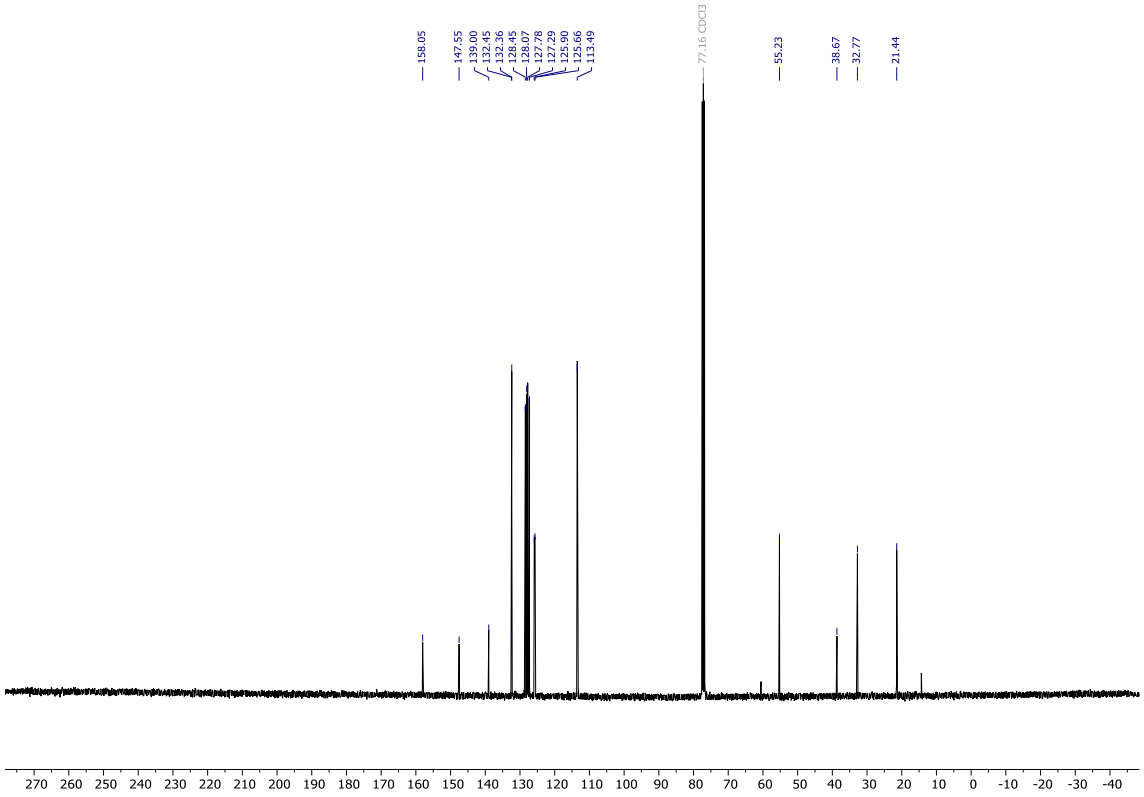


S27: ^{1}H NMR (400MHz, $CDCl_3$):

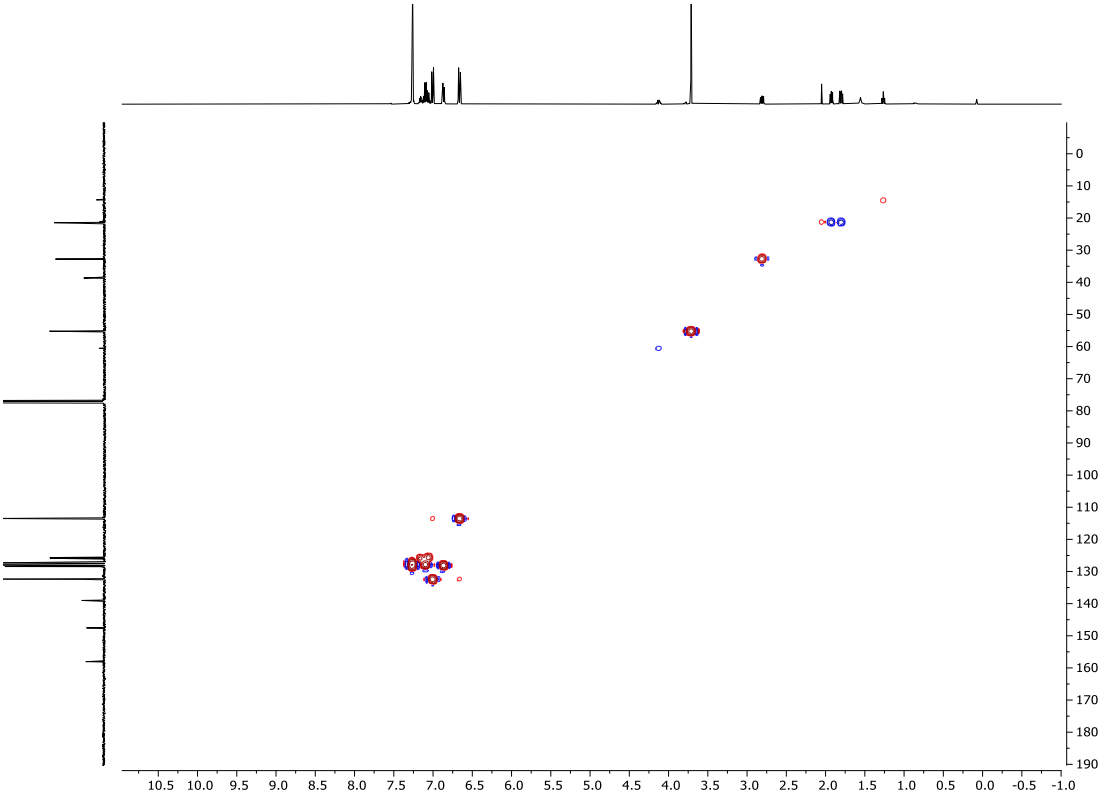




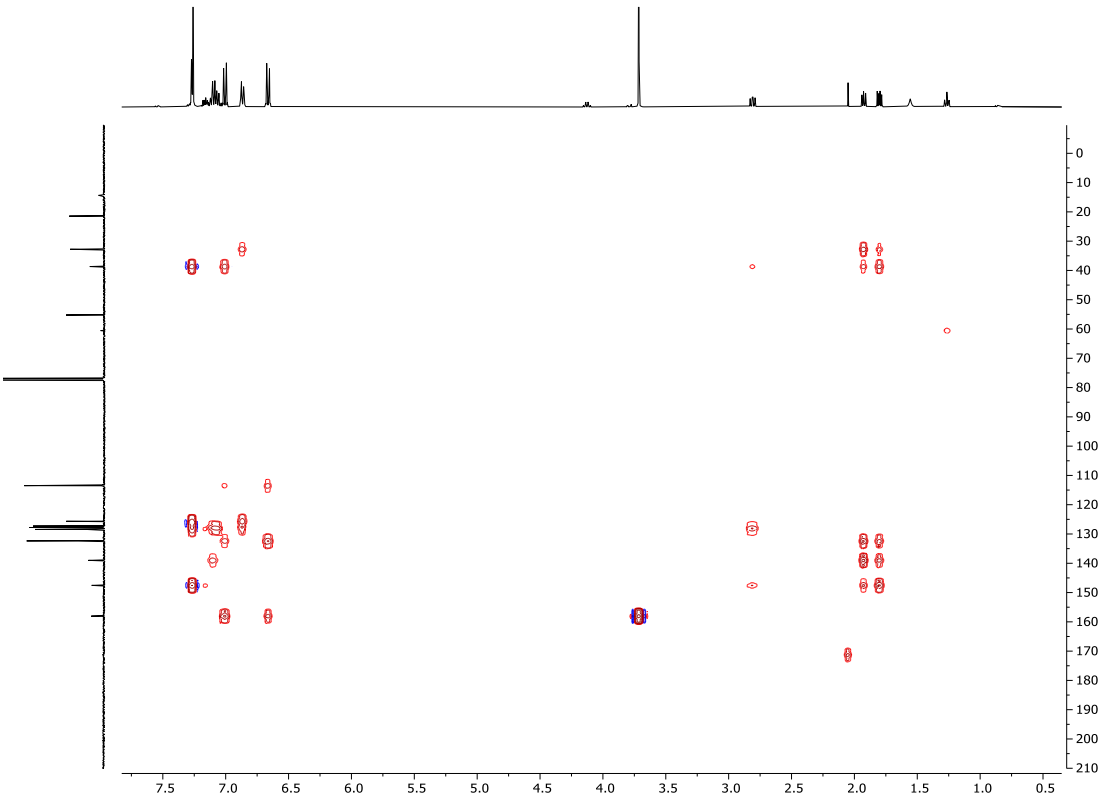
S27: ^{13}C NMR (101 MHz, $CDCl_3$):



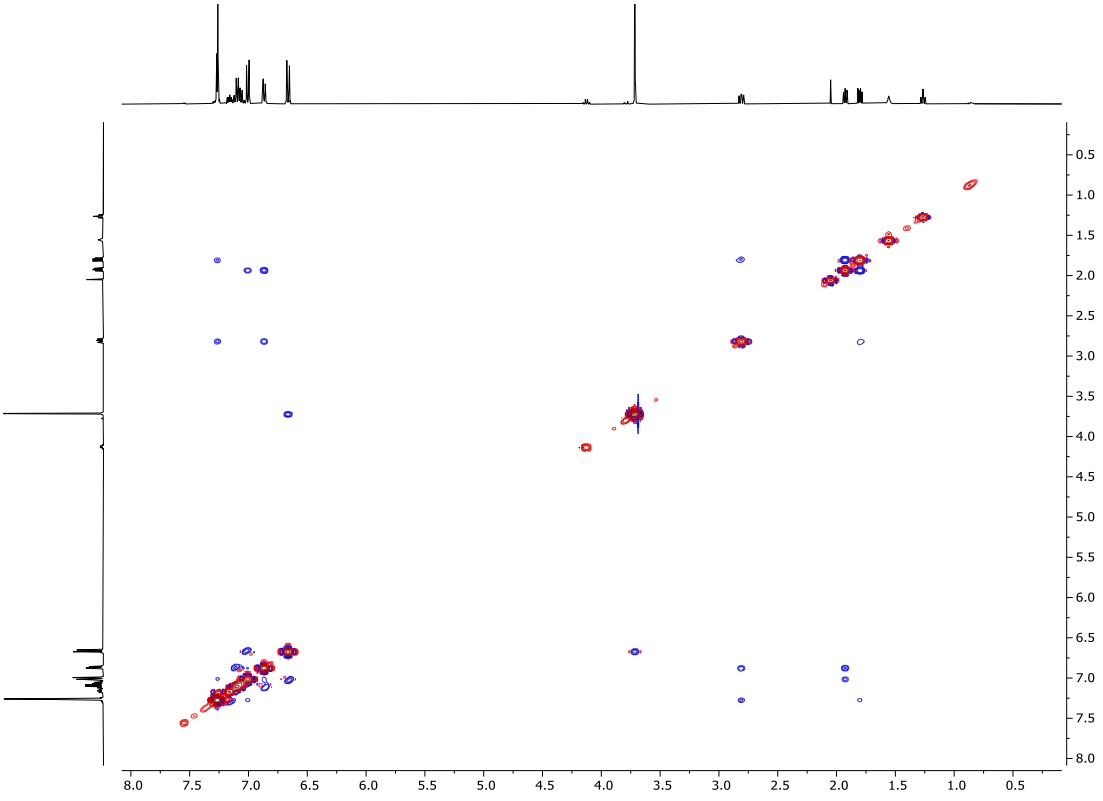
S27: HSQC NMR (400 MHz, 101 MHz, $CDCl_3$):



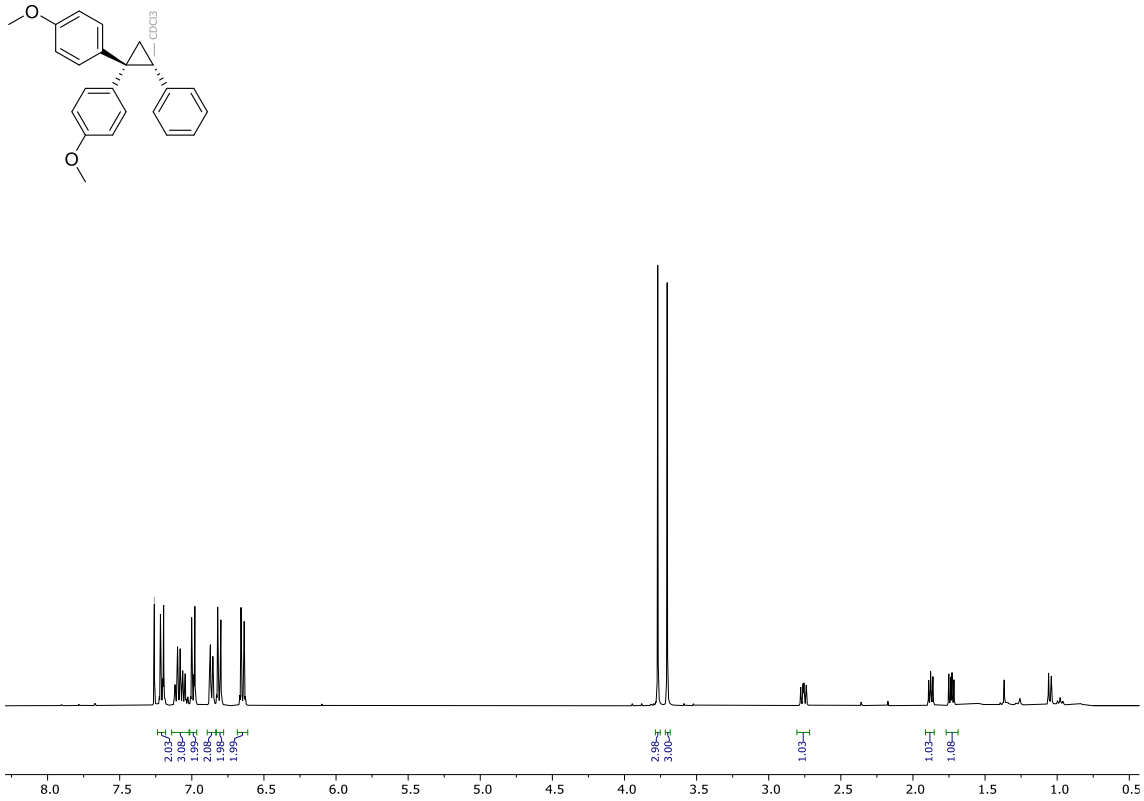
S27: HMBC NMR (400 MHz, 101 MHz, $CDCl_3$):



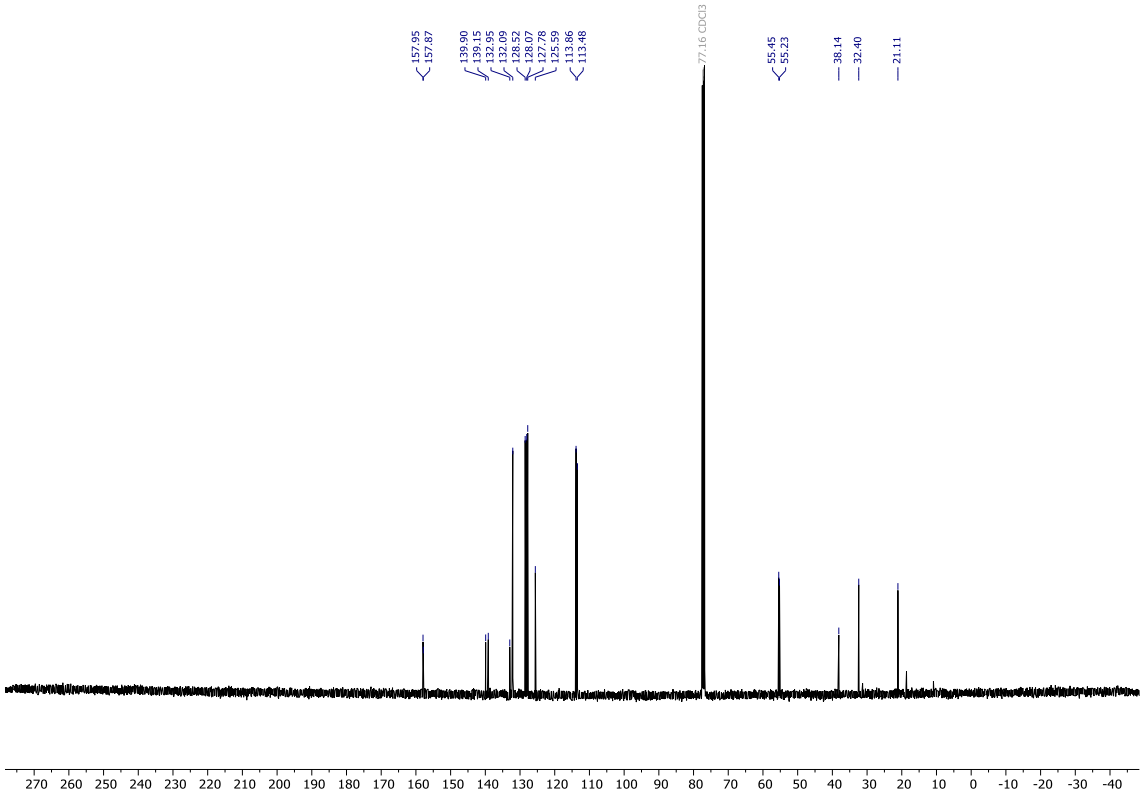
S27: NOESY NMR (400 MHz, $CDCl_3$):



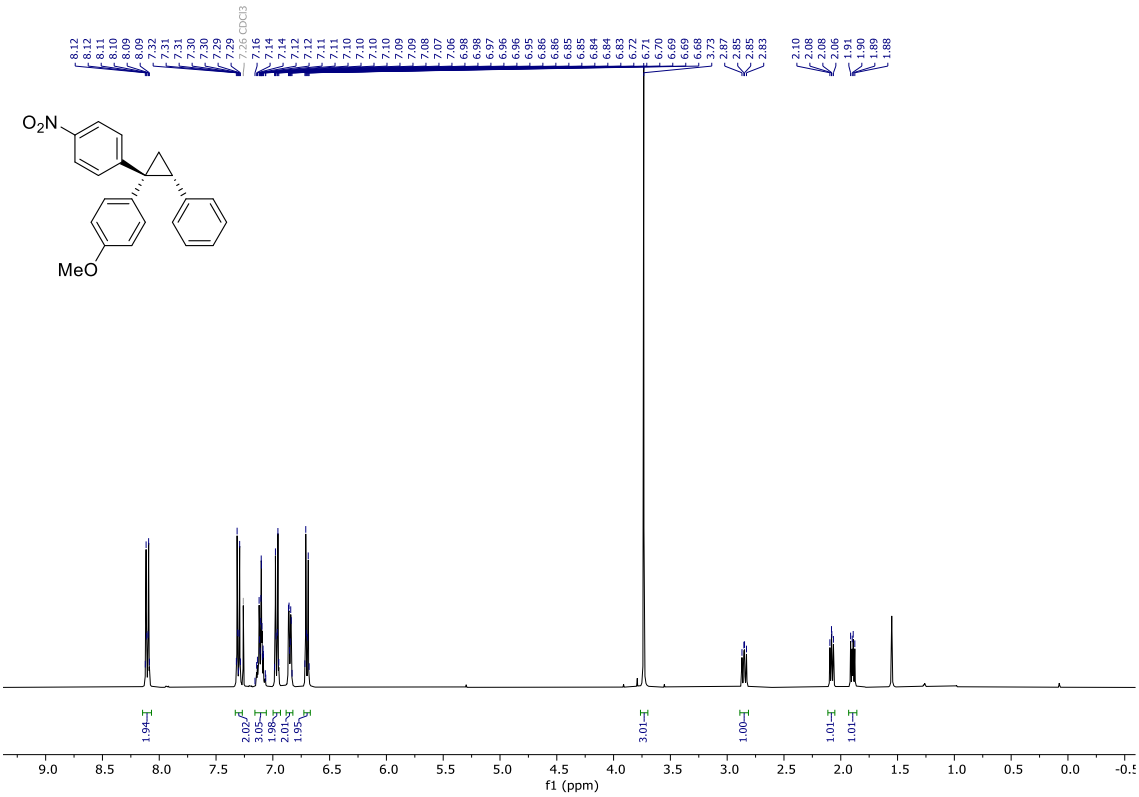
S28: ^{1}H NMR (400 MHz, $CDCl_3$):



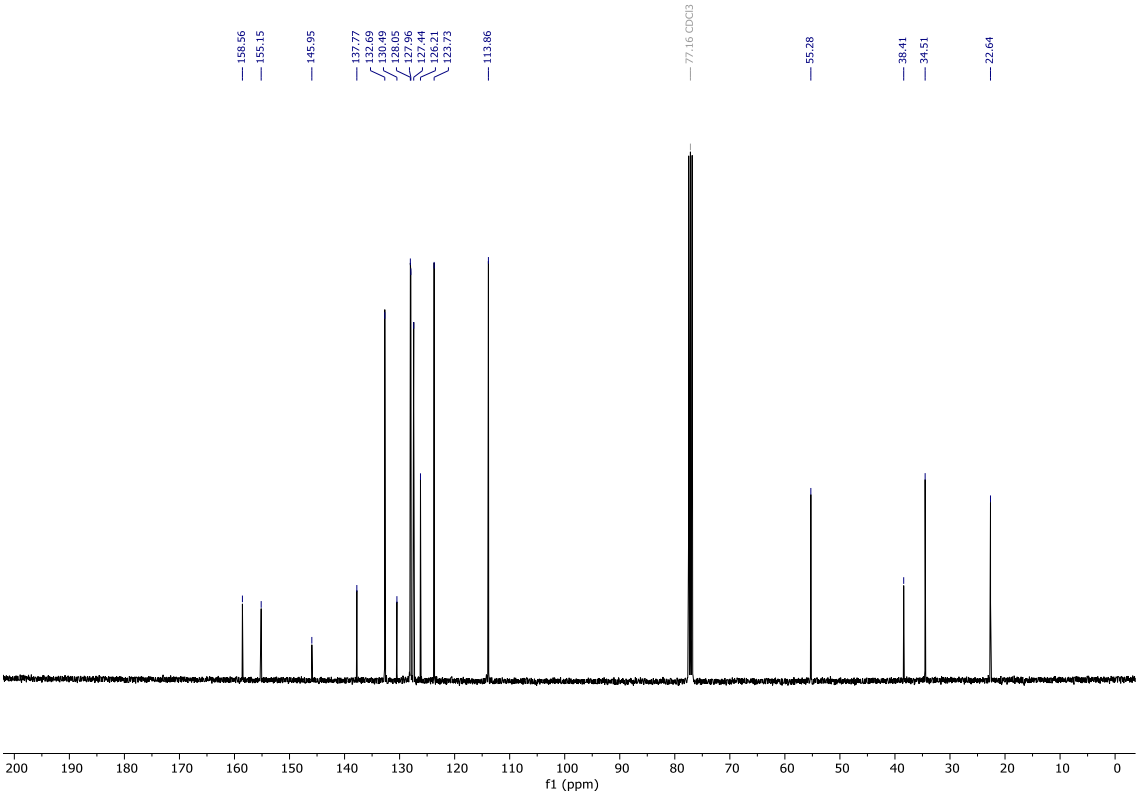
S28: ^{13}C NMR (101 MHz, $CDCl_3$):



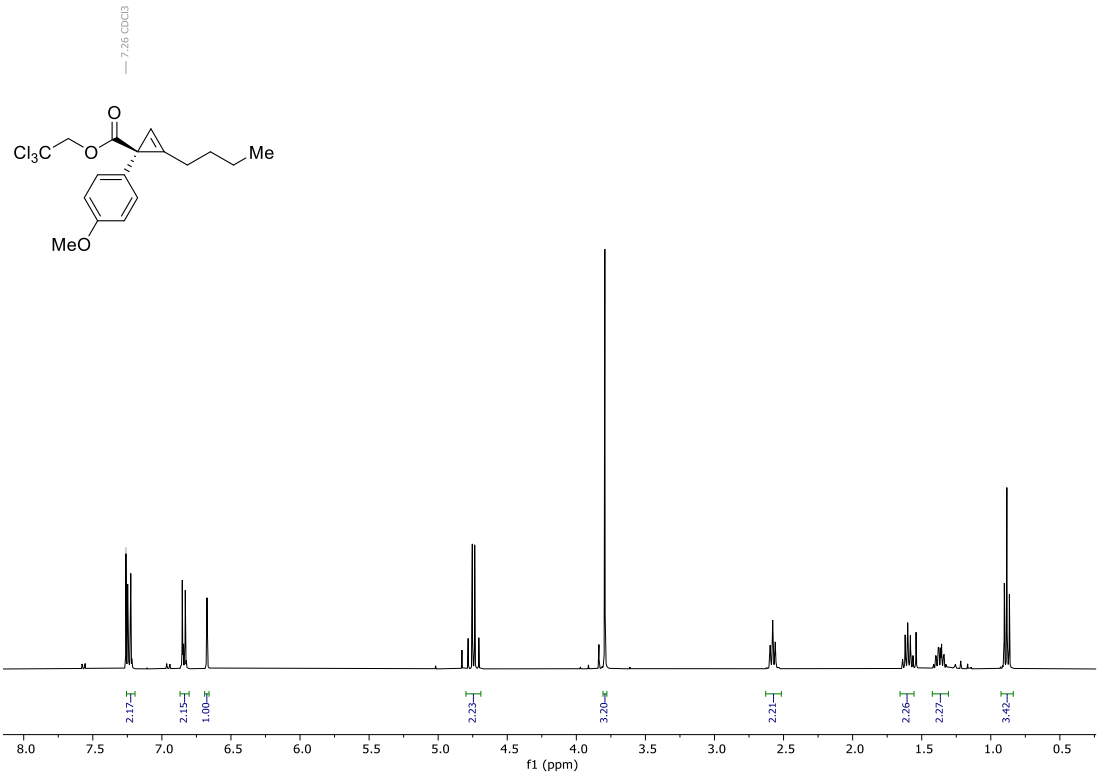
S29: ^{1}H NMR (400 MHz, $CDCl_3$):



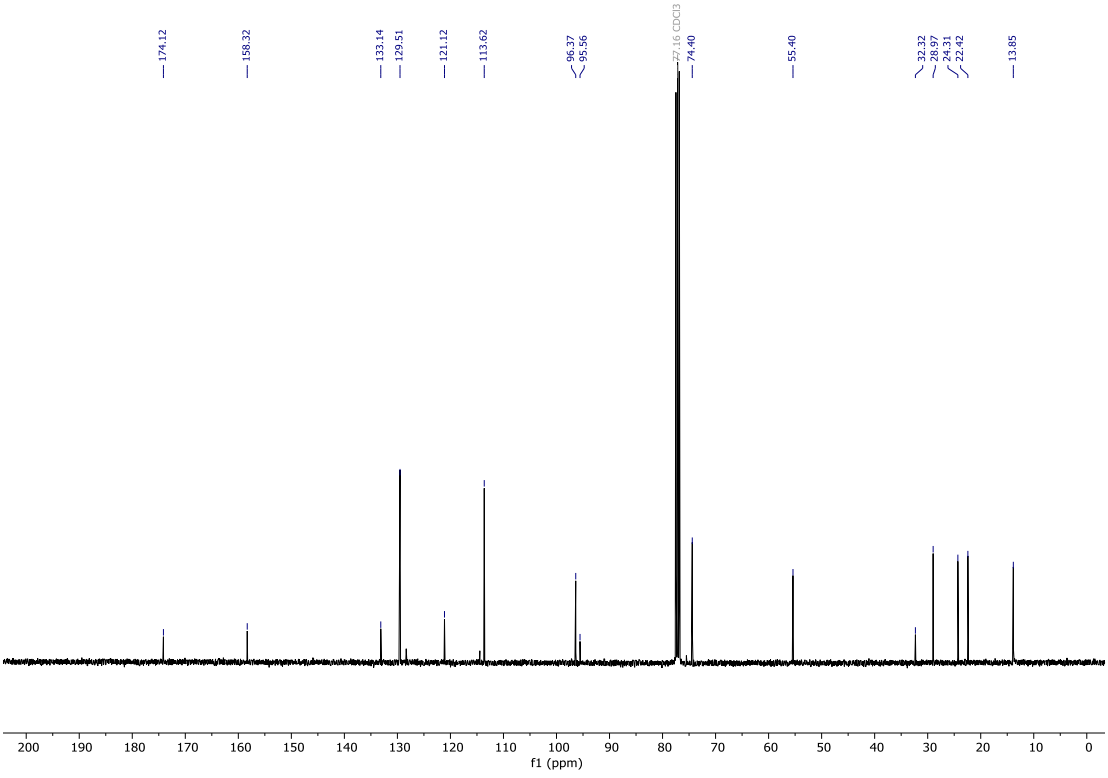
S29: ^{13}C NMR (101 MHz, $CDCl_3$):



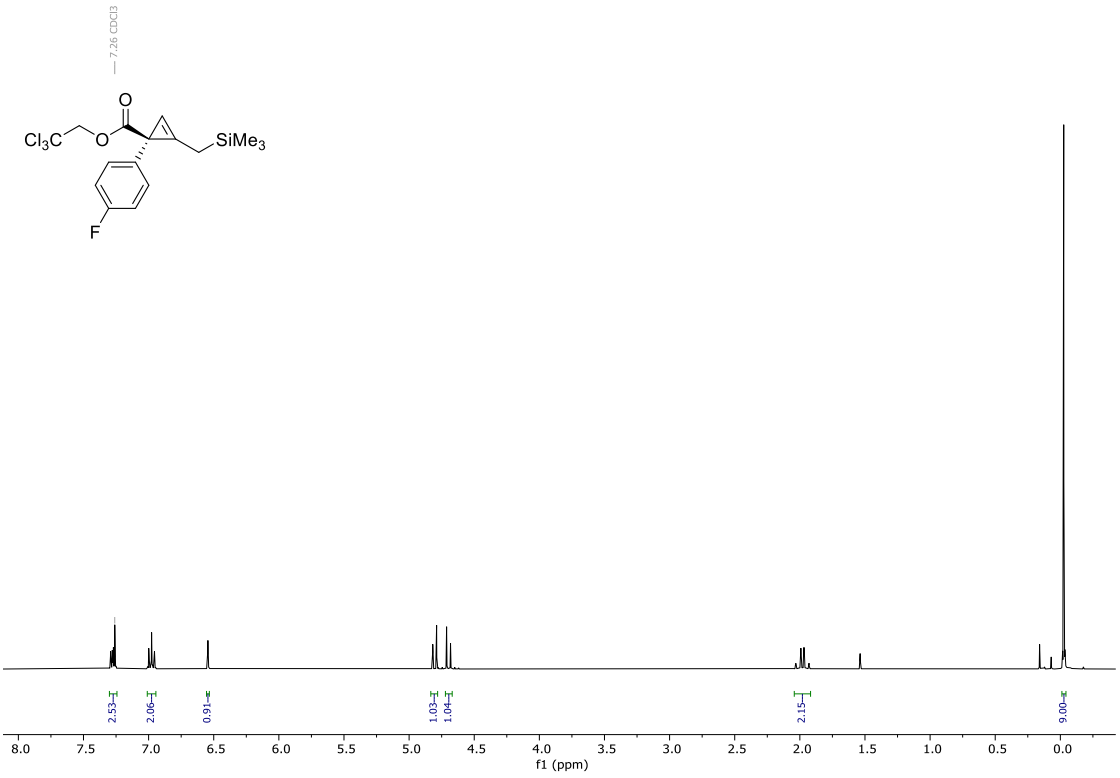
S30: ^{1}H NMR (400 MHz, $CDCl_3$):



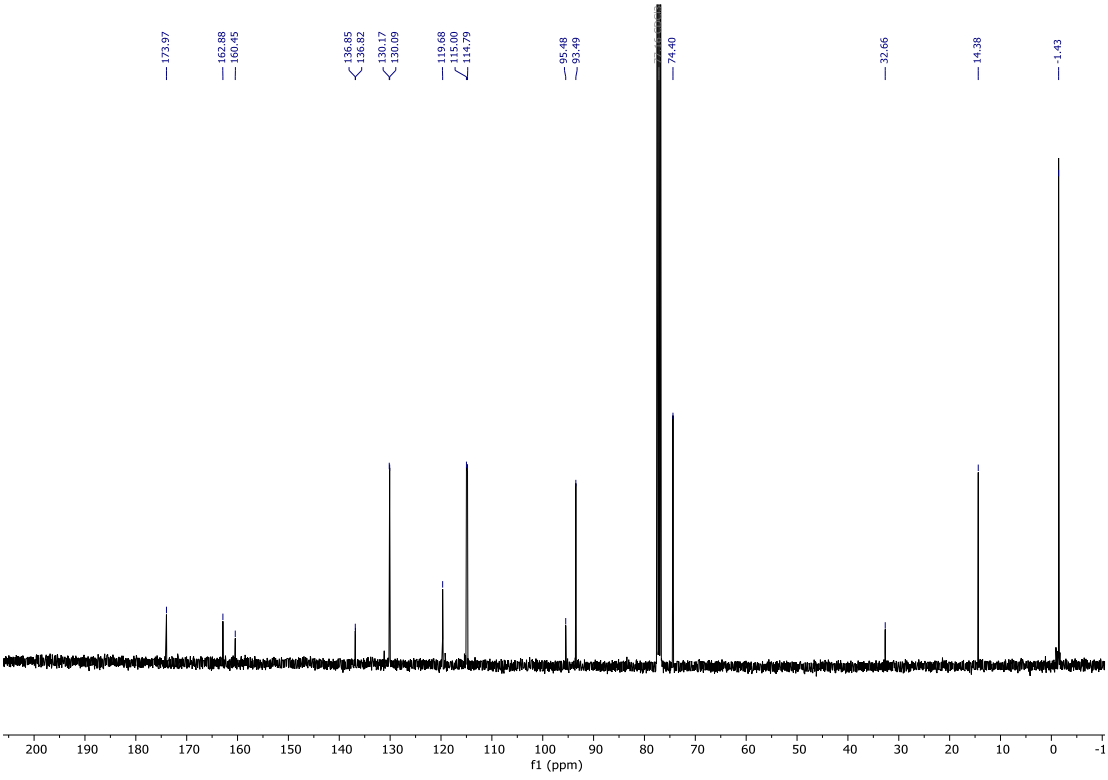
S30: ^{13}C NMR (101 MHz, $CDCl_3$):



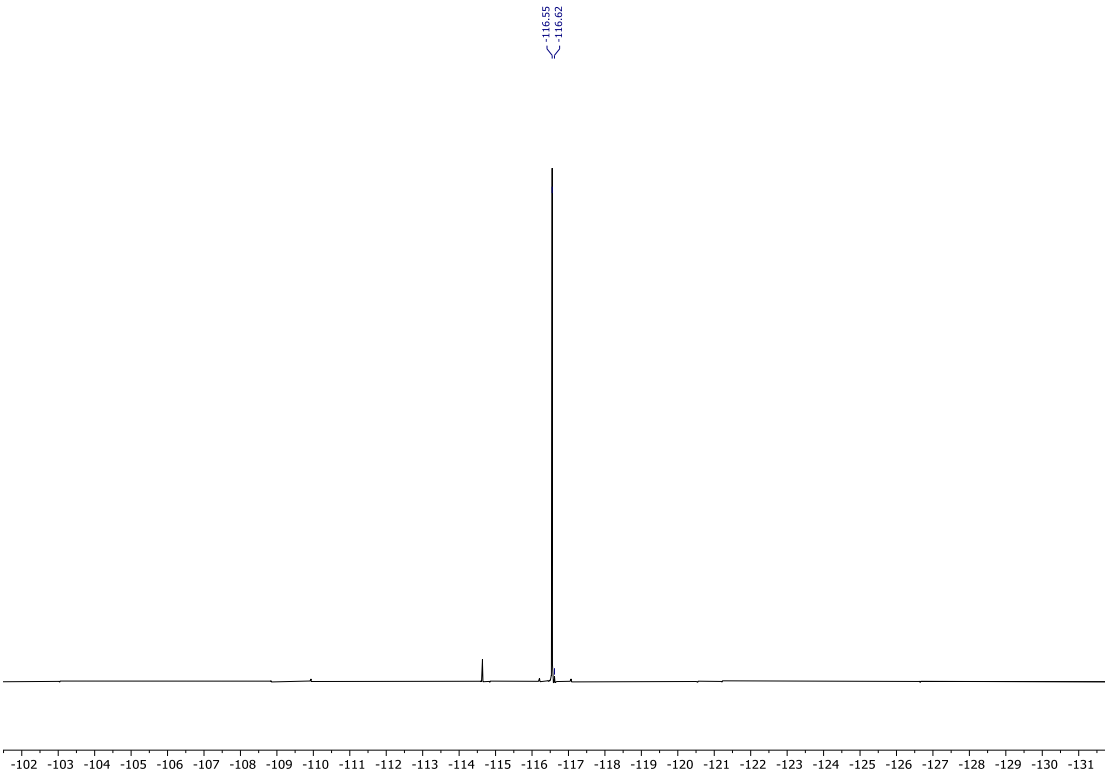
S31: ^{1}H NMR (400 MHz, $CDCl_3$):



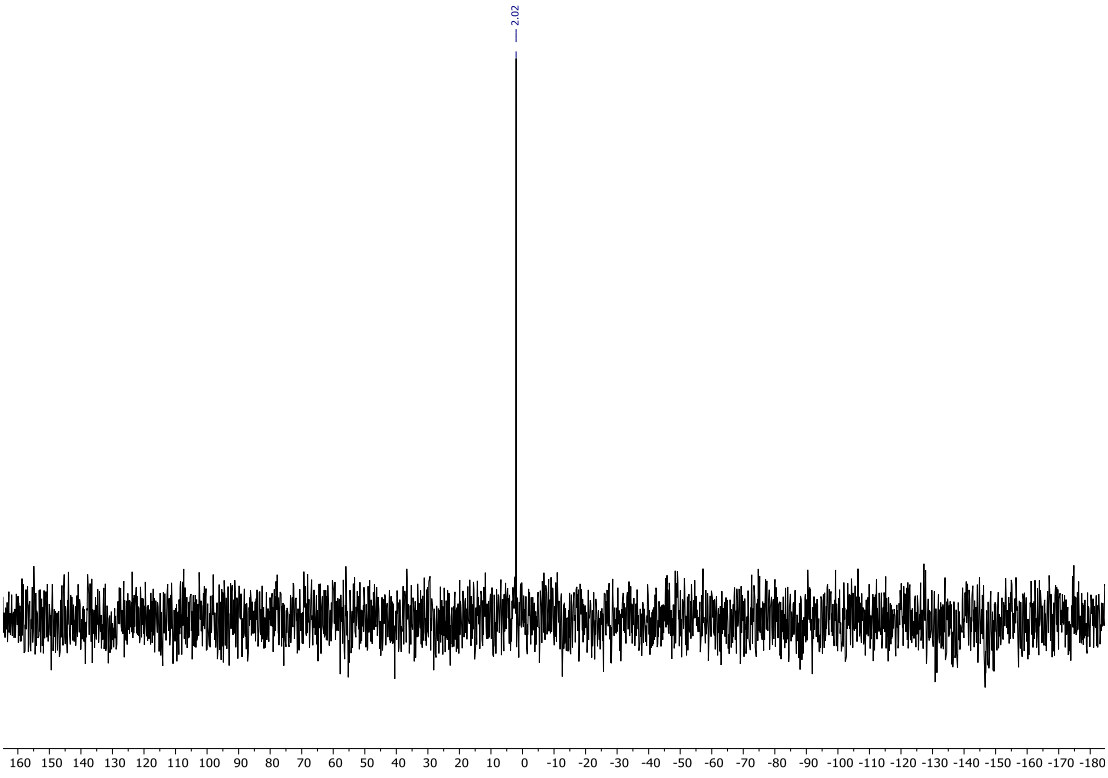
S31: ^{13}C NMR (101 MHz, $CDCl_3$):



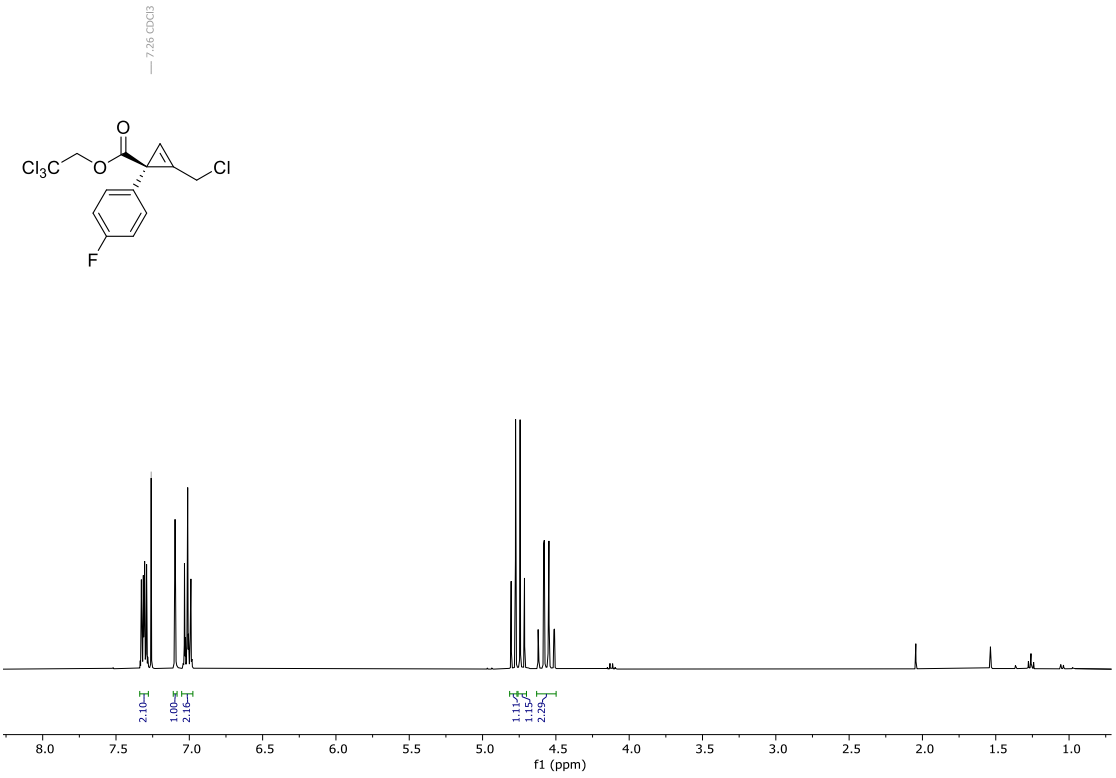
S31: ^{19}F NMR (282 MHz, $CDCl_3$):



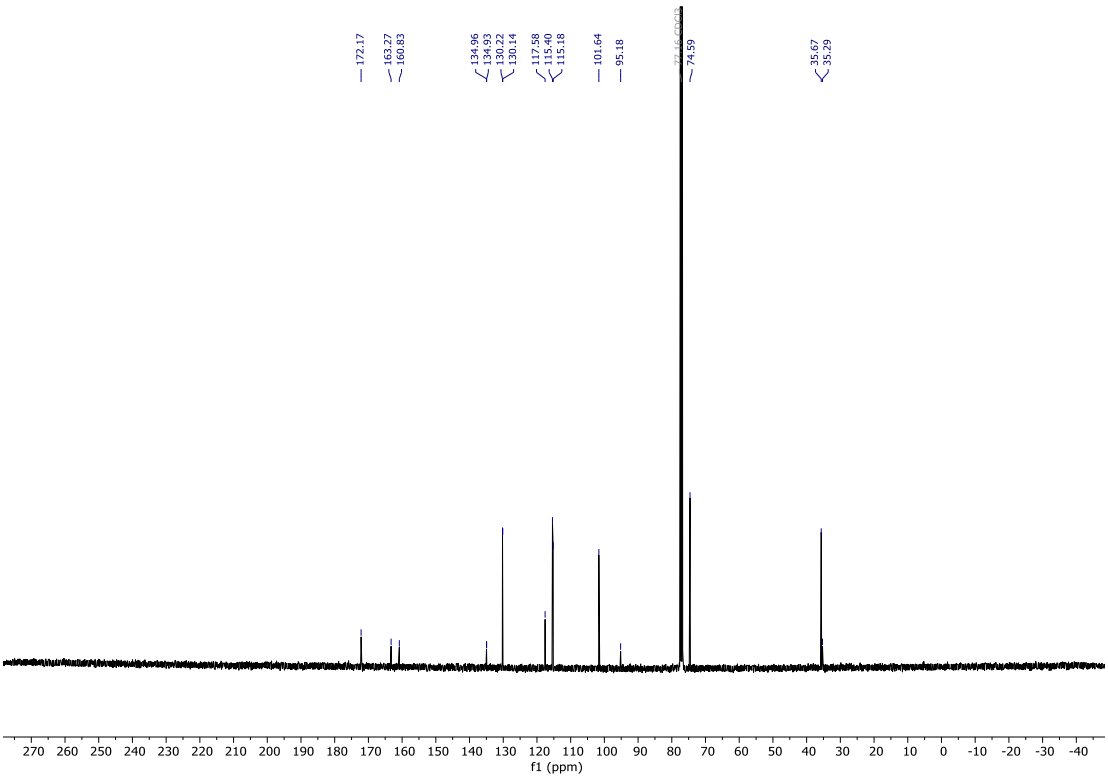
S31: ^{29}Si NMR (79 MHz, $CDCl_3$):



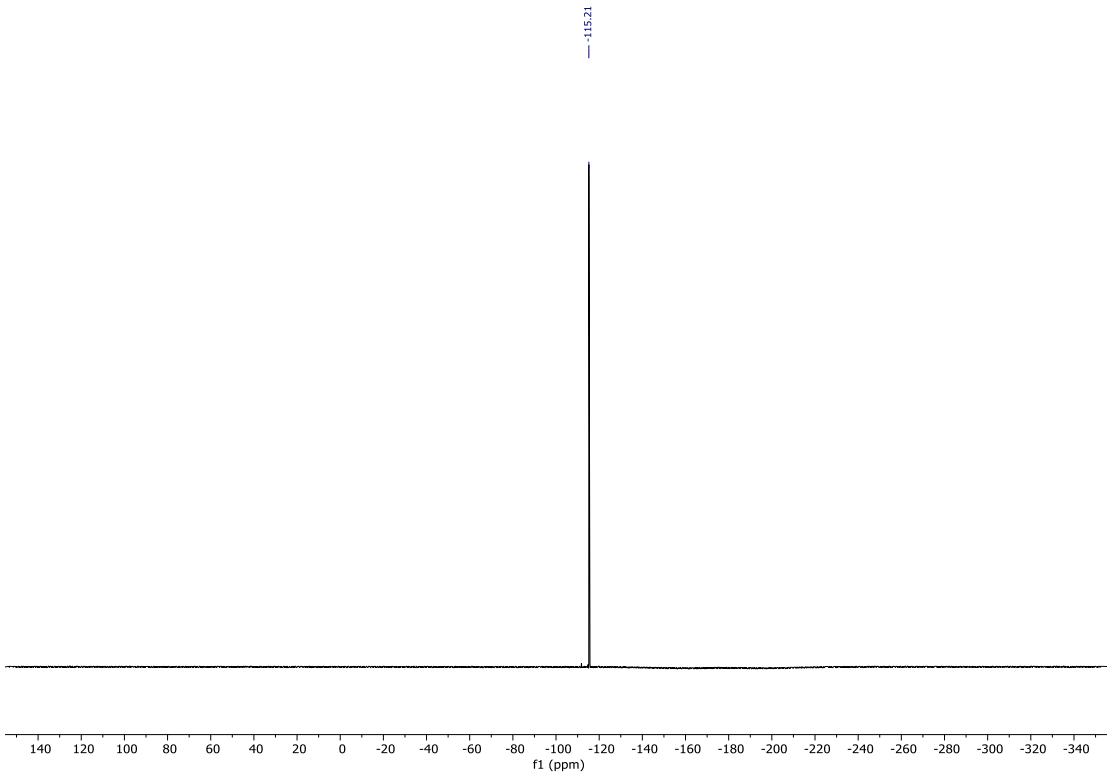
S32: ^{1}H NMR (400 MHz, $CDCl_3$):



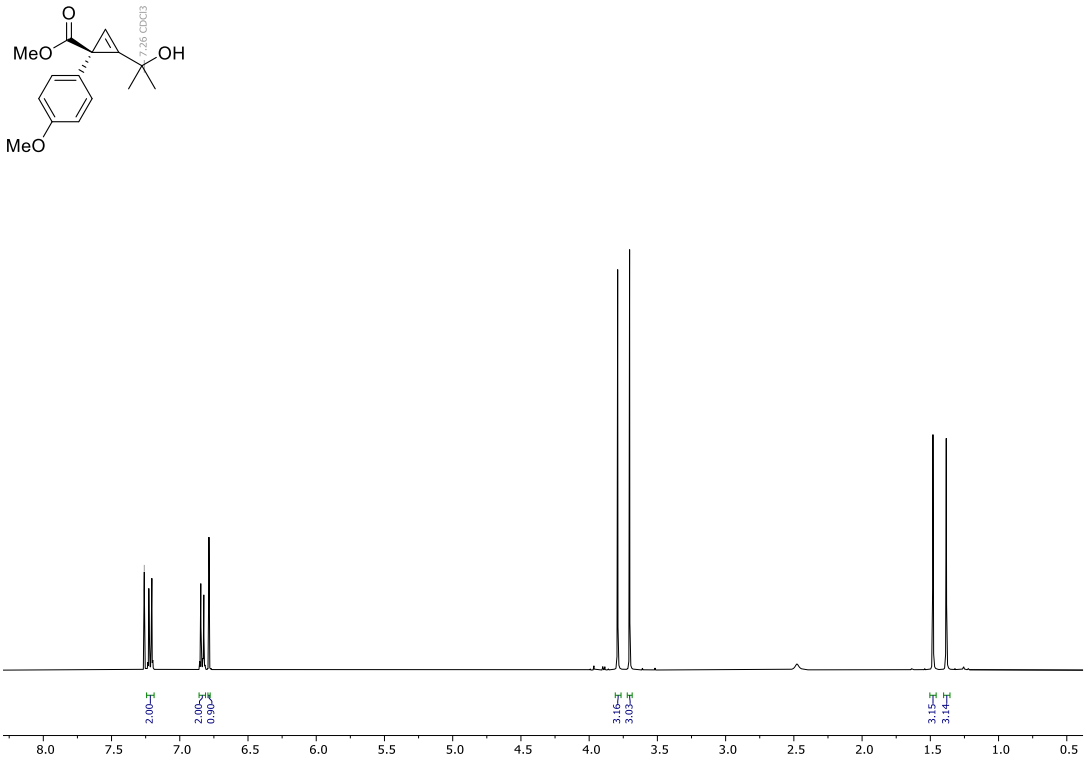
S32: ^{13}C NMR (101 MHz, $CDCl_3$):



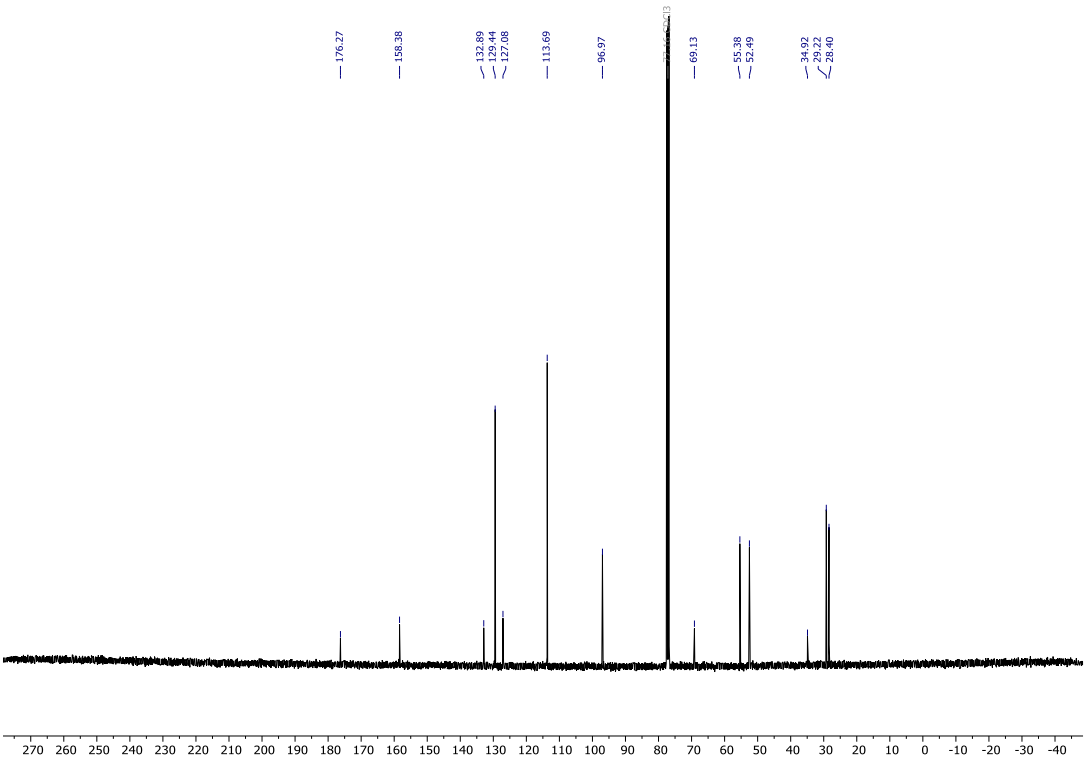
S32: ^{19}F NMR (282 MHz, $CDCl_3$):



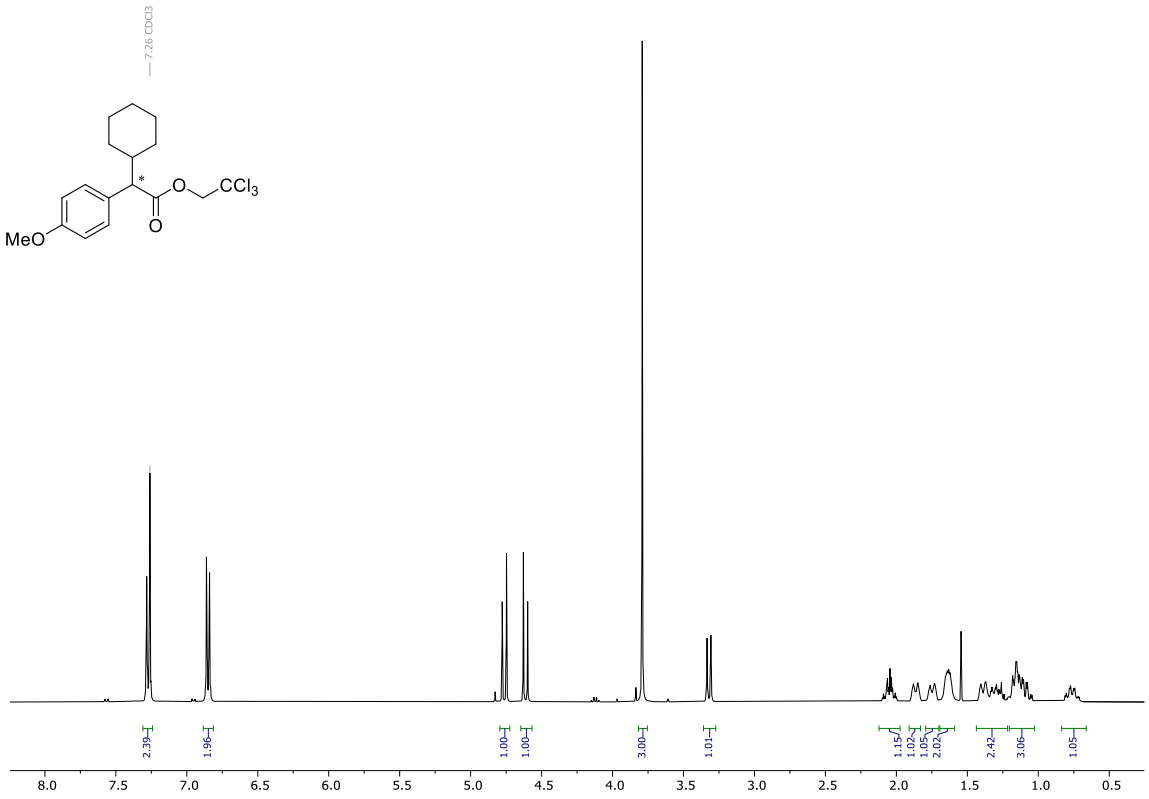
S33: ^{1}H NMR (400 MHz, $CDCl_3$):



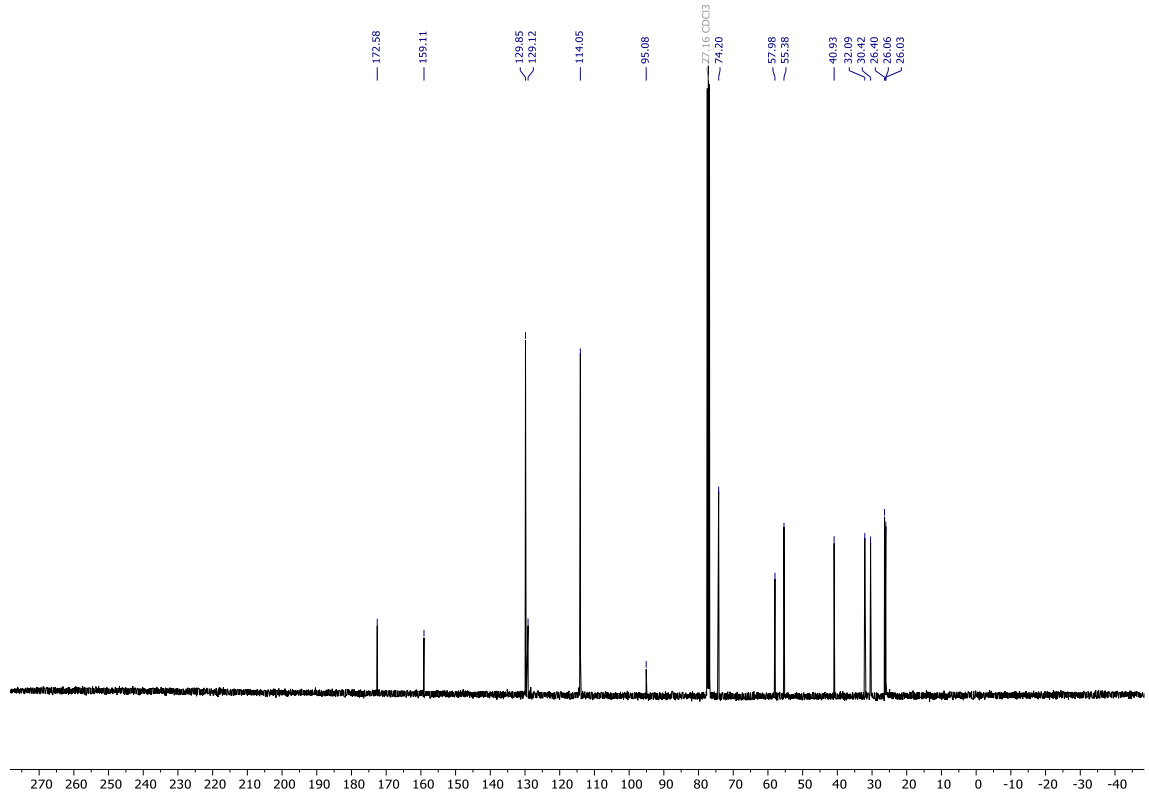
S33: ^{13}C NMR (101 MHz, $CDCl_3$):



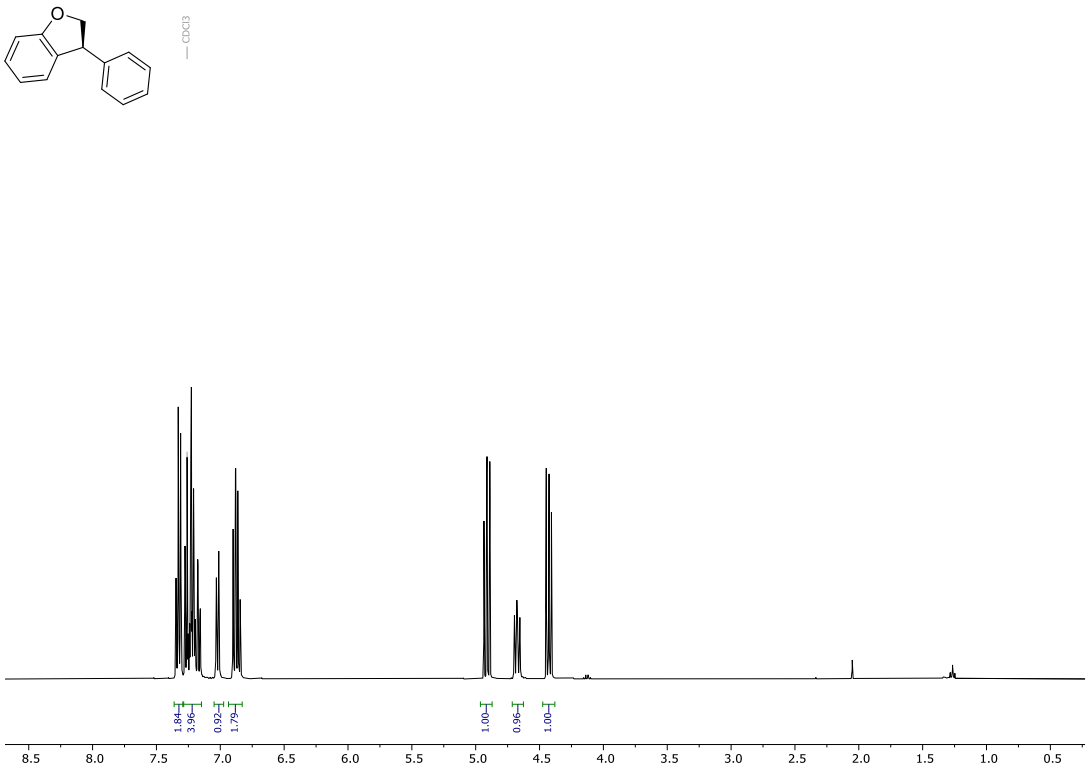
S34: ^{1}H NMR (400 MHz, $CDCl_3$):



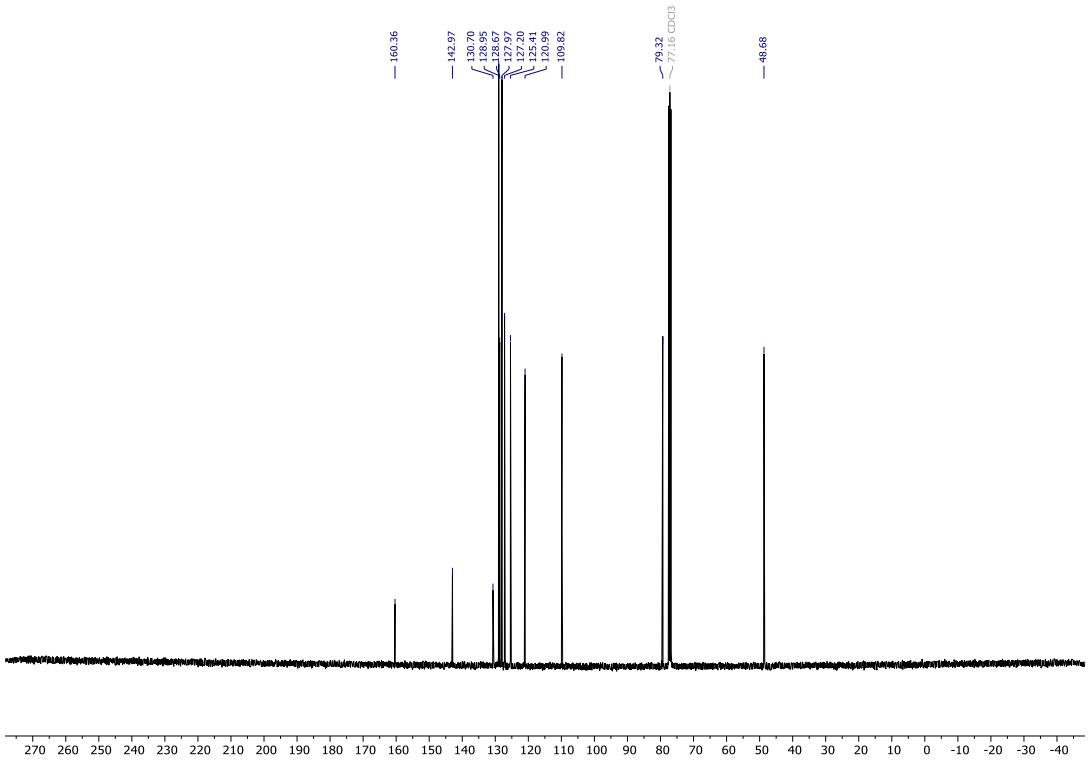
S34: ^{13}C NMR (101 MHz, $CDCl_3$):



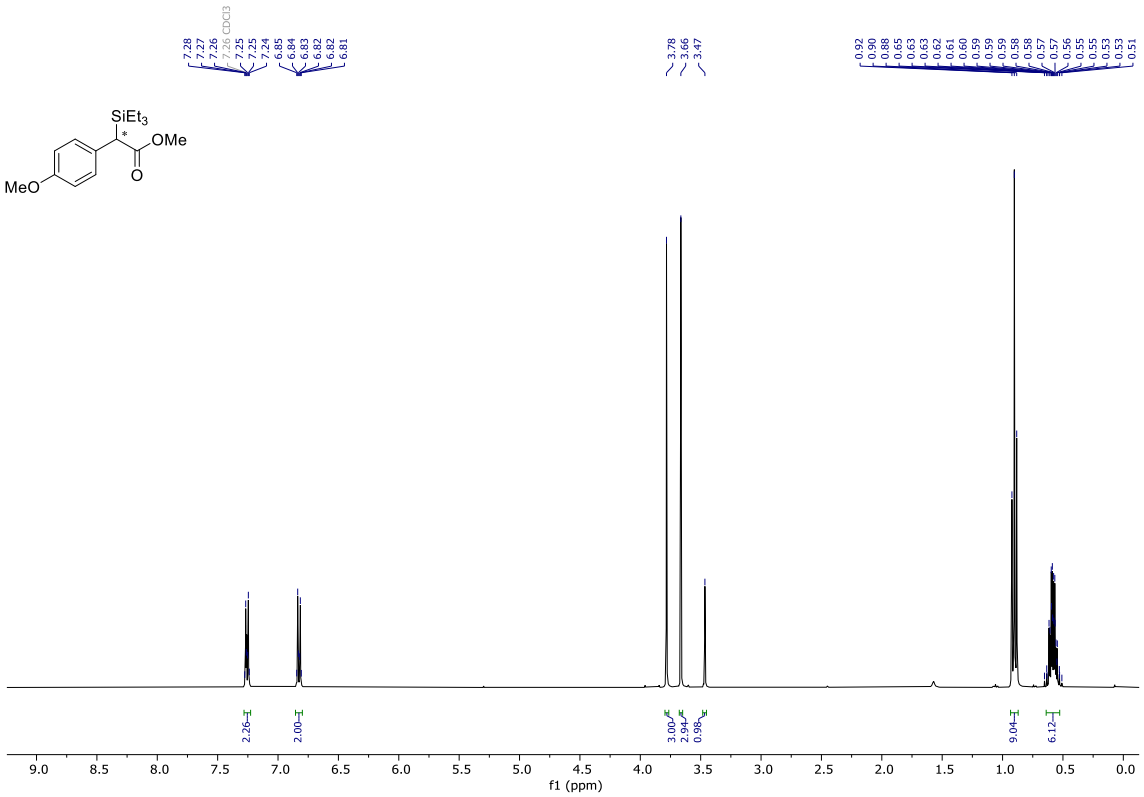
S35: ^{1}H NMR (400 MHz, $CDCl_3$):



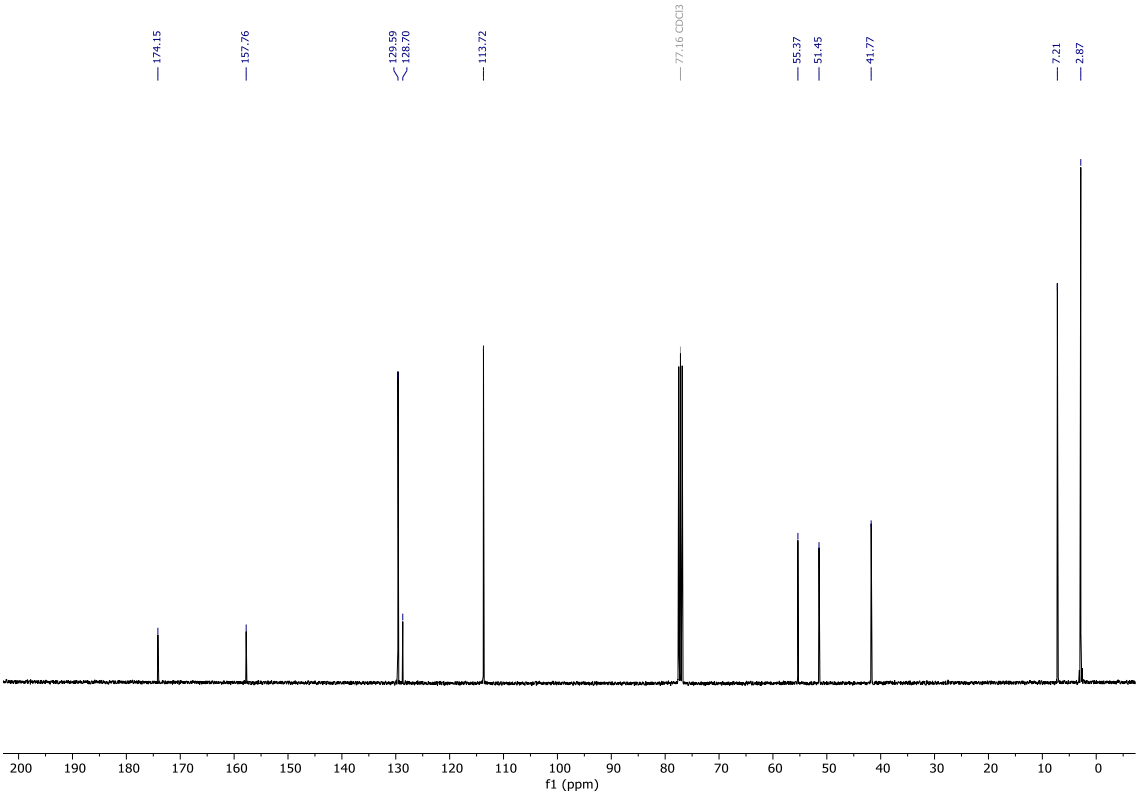
S35: ^{13}C NMR (101 MHz, $CDCl_3$):



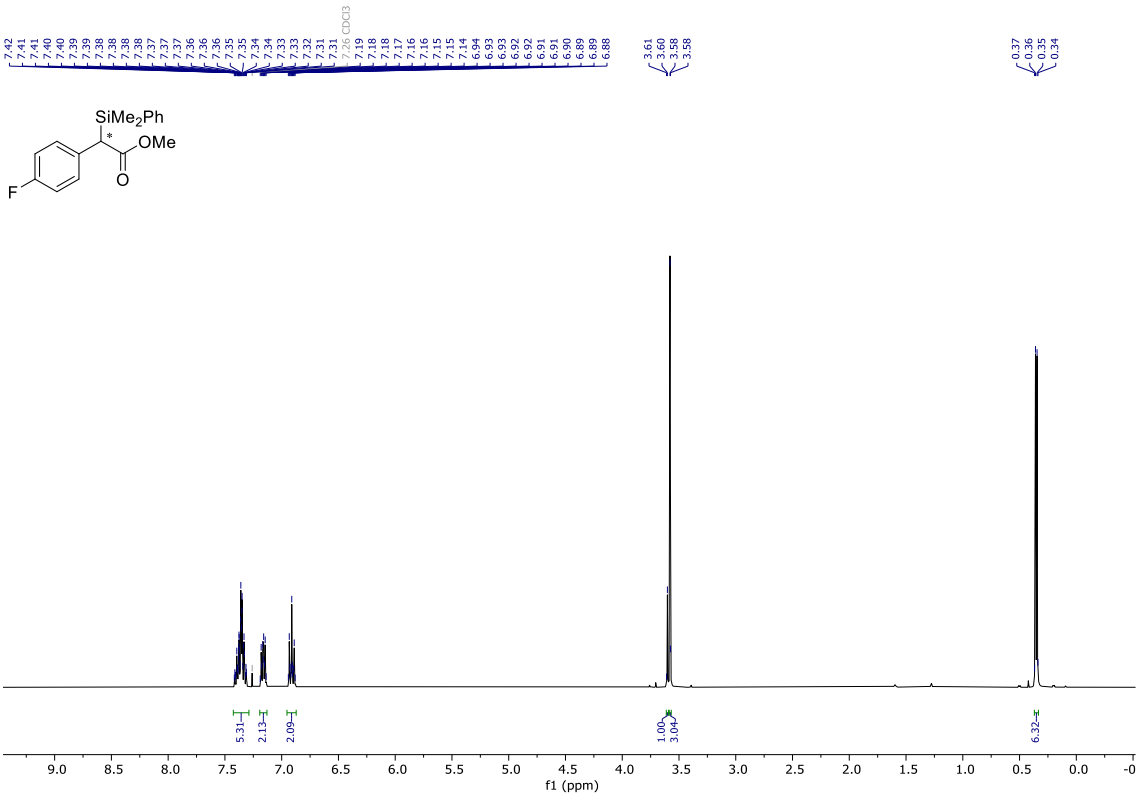
S36: ^{1}H NMR (400 MHz, $CDCl_3$):



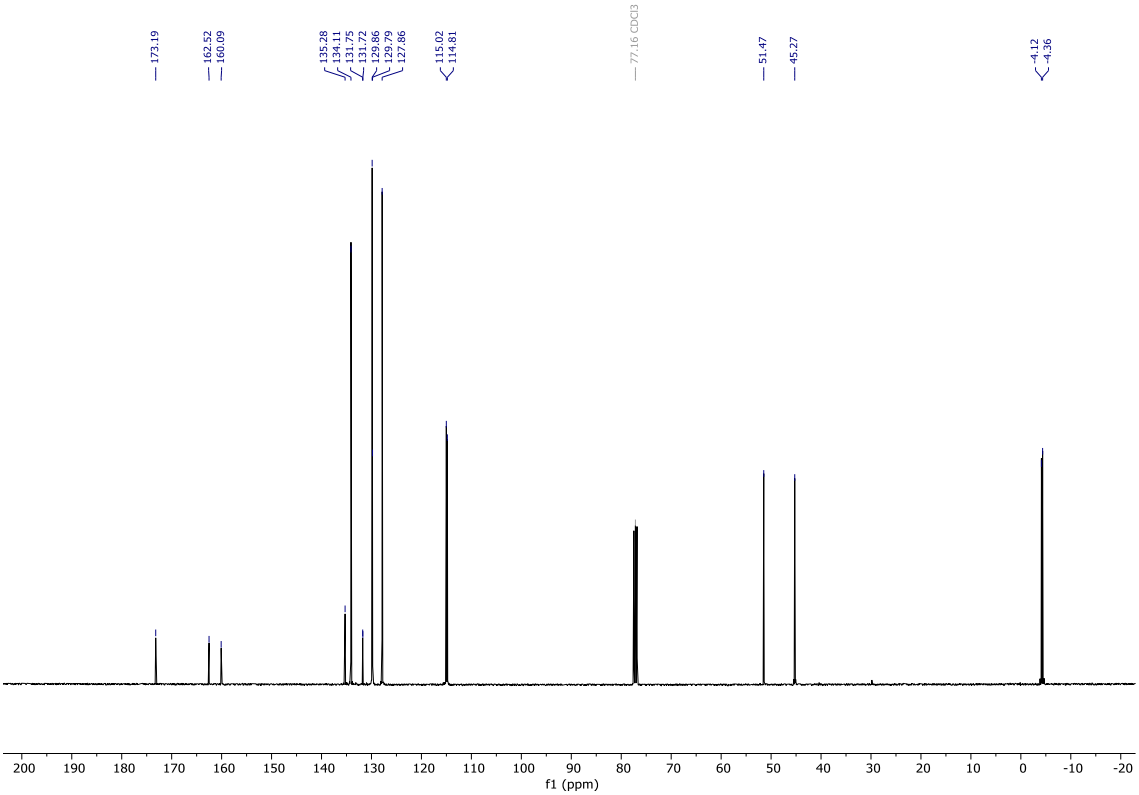
S36: ^{13}C NMR (101 MHz, $CDCl_3$):



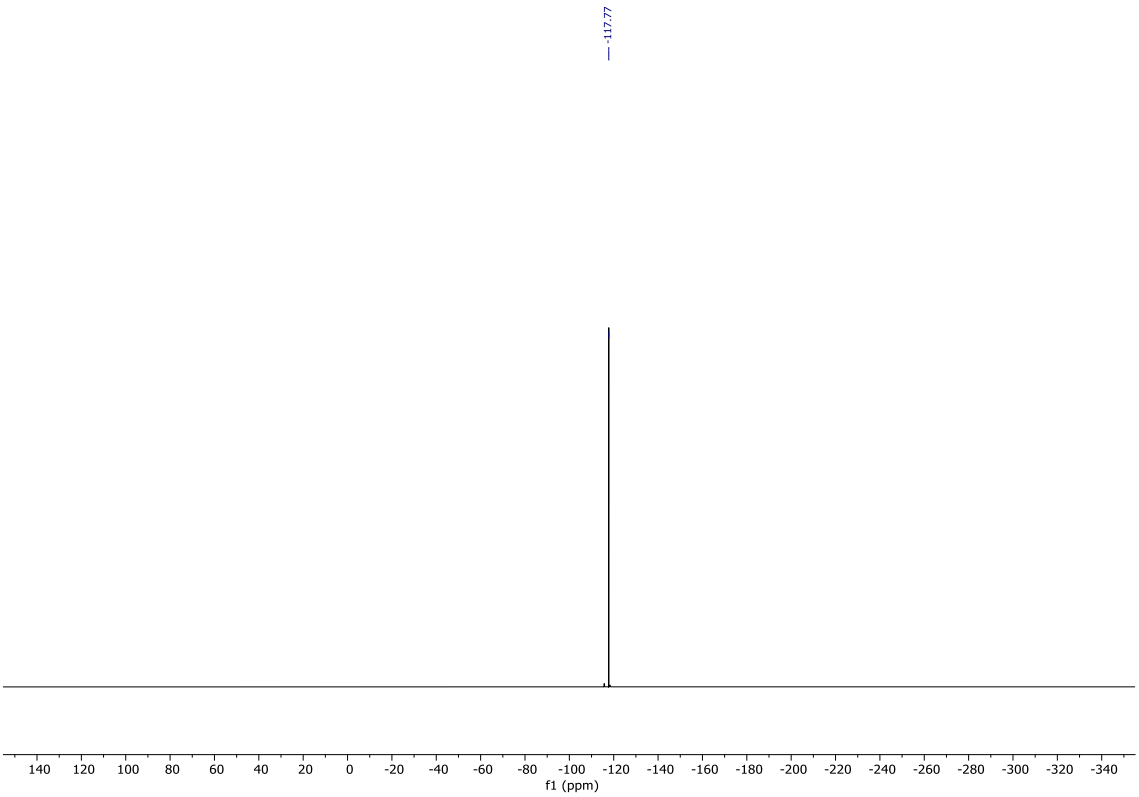
S37: ^{1}H NMR (400 MHz, $CDCl_3$):



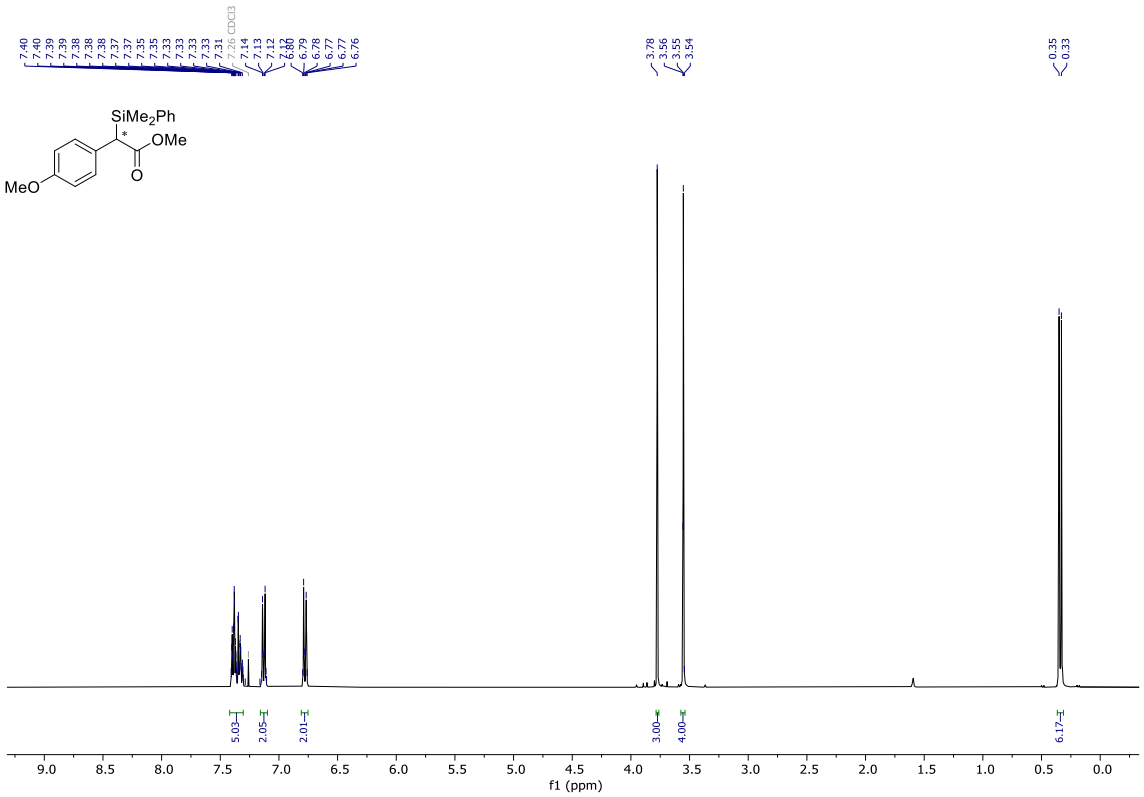
S37: ^{13}C NMR (101 MHz, $CDCl_3$):



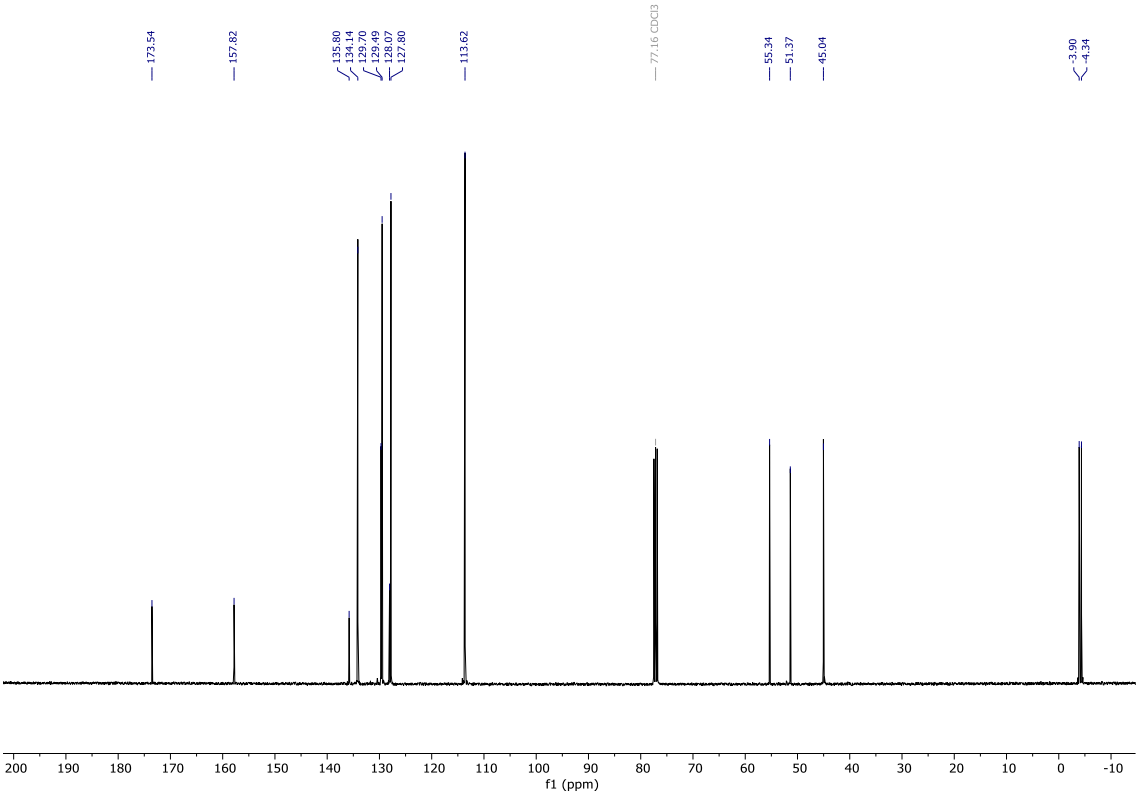
S37: ^{19}F NMR (282 MHz, $CDCl_3$):



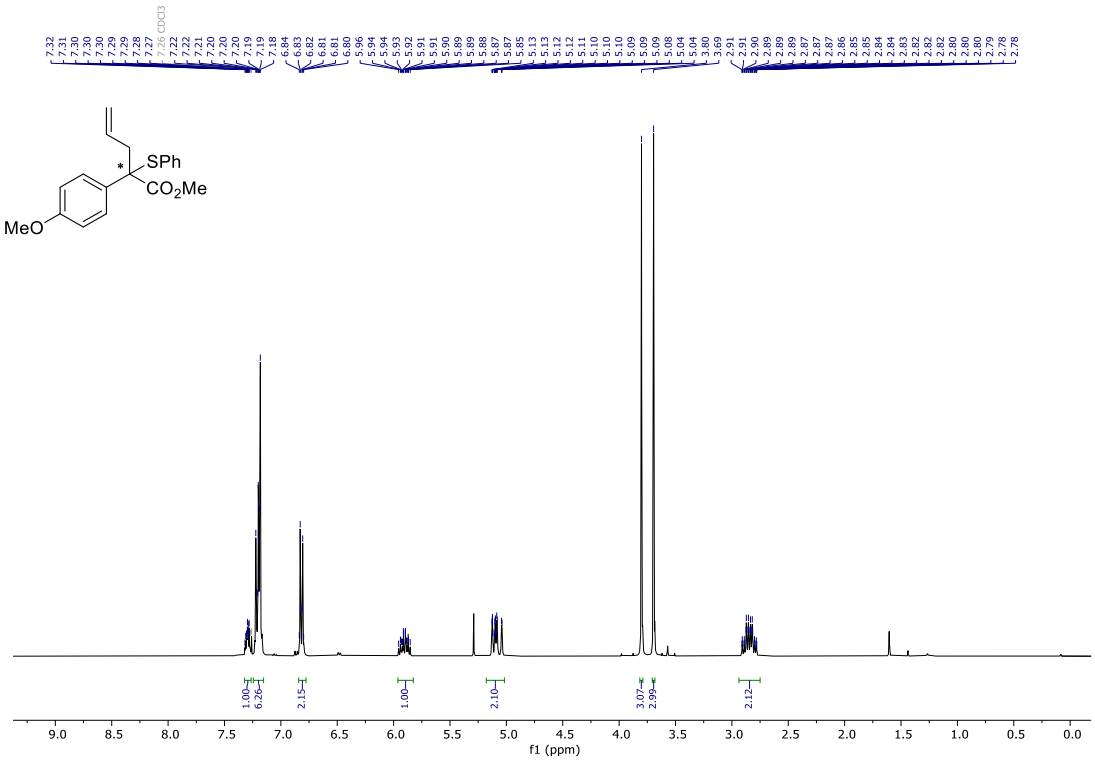
S38: ^{1}H NMR (400 MHz, $CDCl_3$):



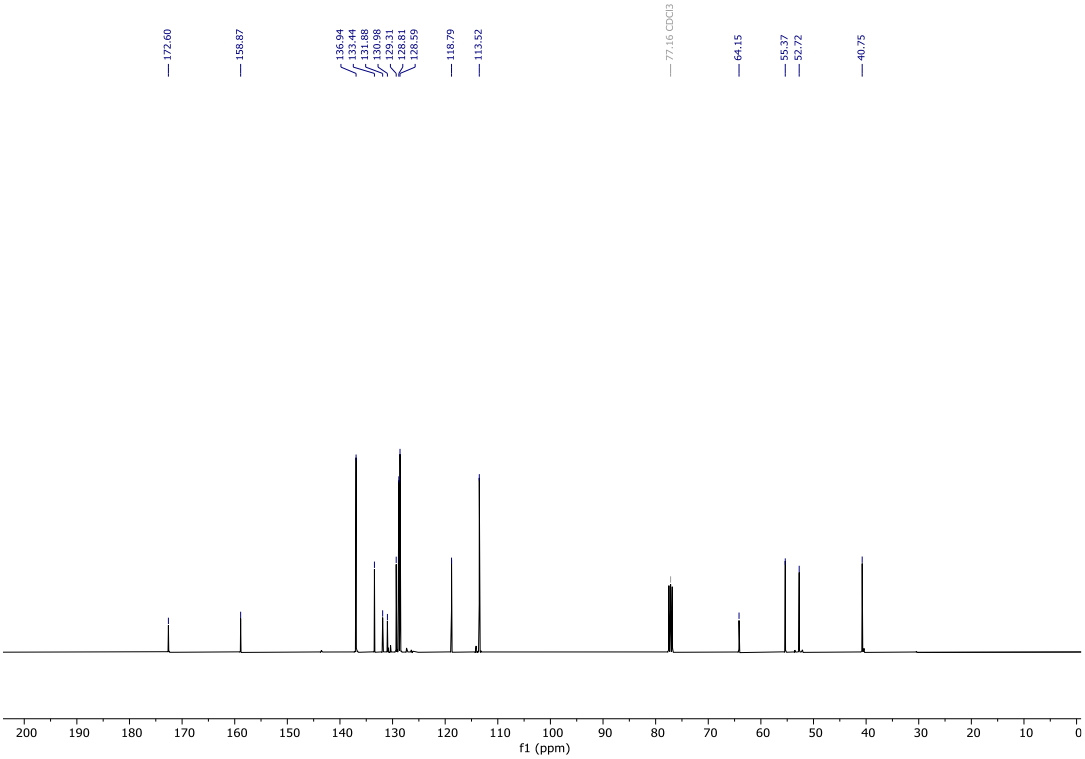
S38: ^{13}C NMR (101 MHz, $CDCl_3$):



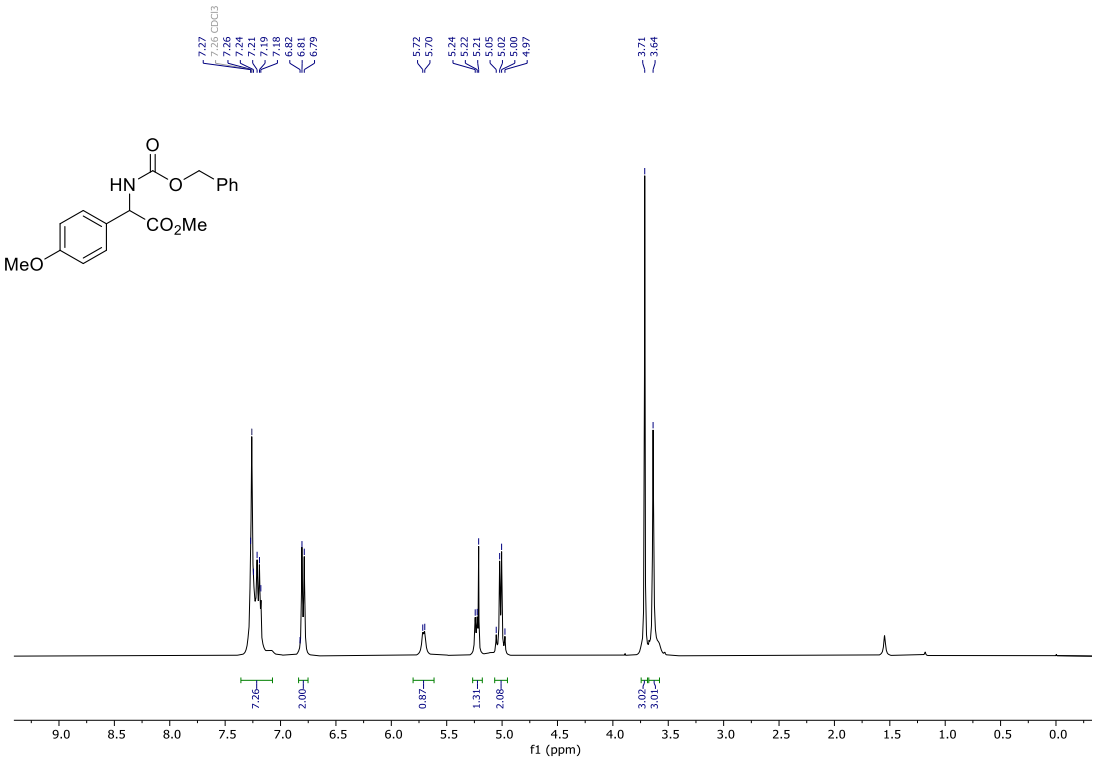
S39: ^{1}H NMR (400 MHz, $CDCl_3$):



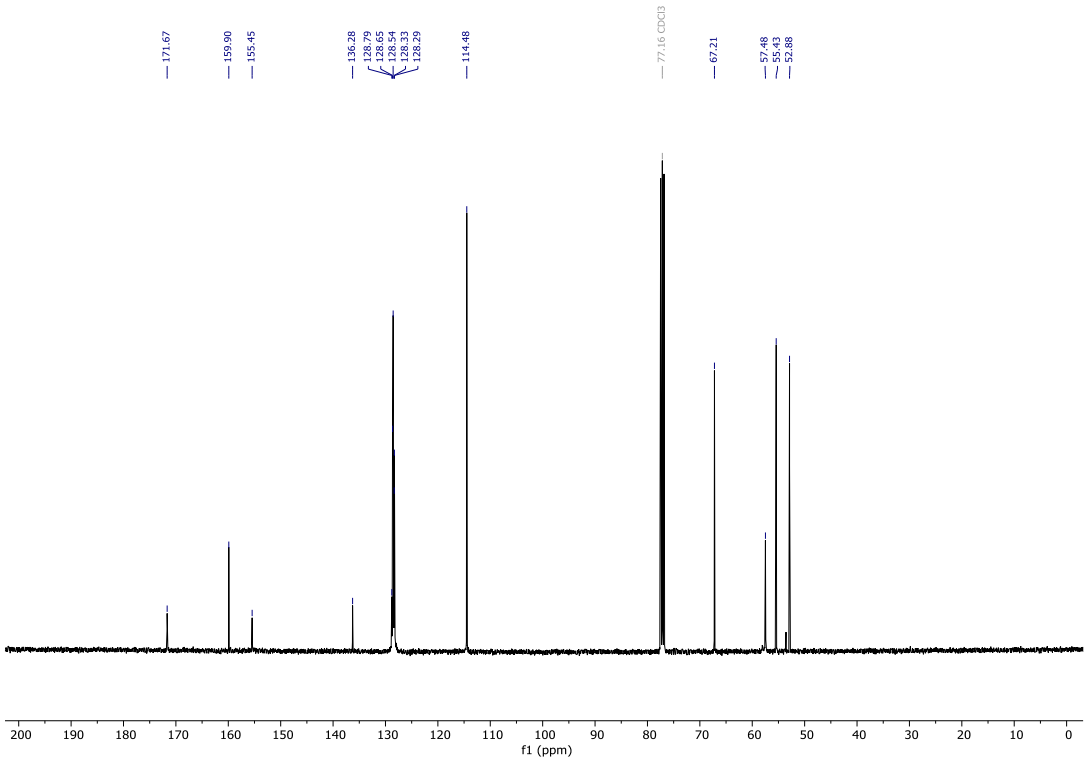
S39: ^{13}C NMR (101 MHz, $CDCl_3$):



S40: ^{1}H NMR (400 MHz, $CDCl_3$):



S40: ^{13}C NMR (101 MHz, $CDCl_3$):



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