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Supporting Information

Chiral Heterobimetallic Bismuth–Rhodium Paddlewheel Catalysts: A Conceptually New Approach to Asymmetric Cyclopropanation

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SUPPORTING CRYSTALLOGRAPHIC INFORMATION

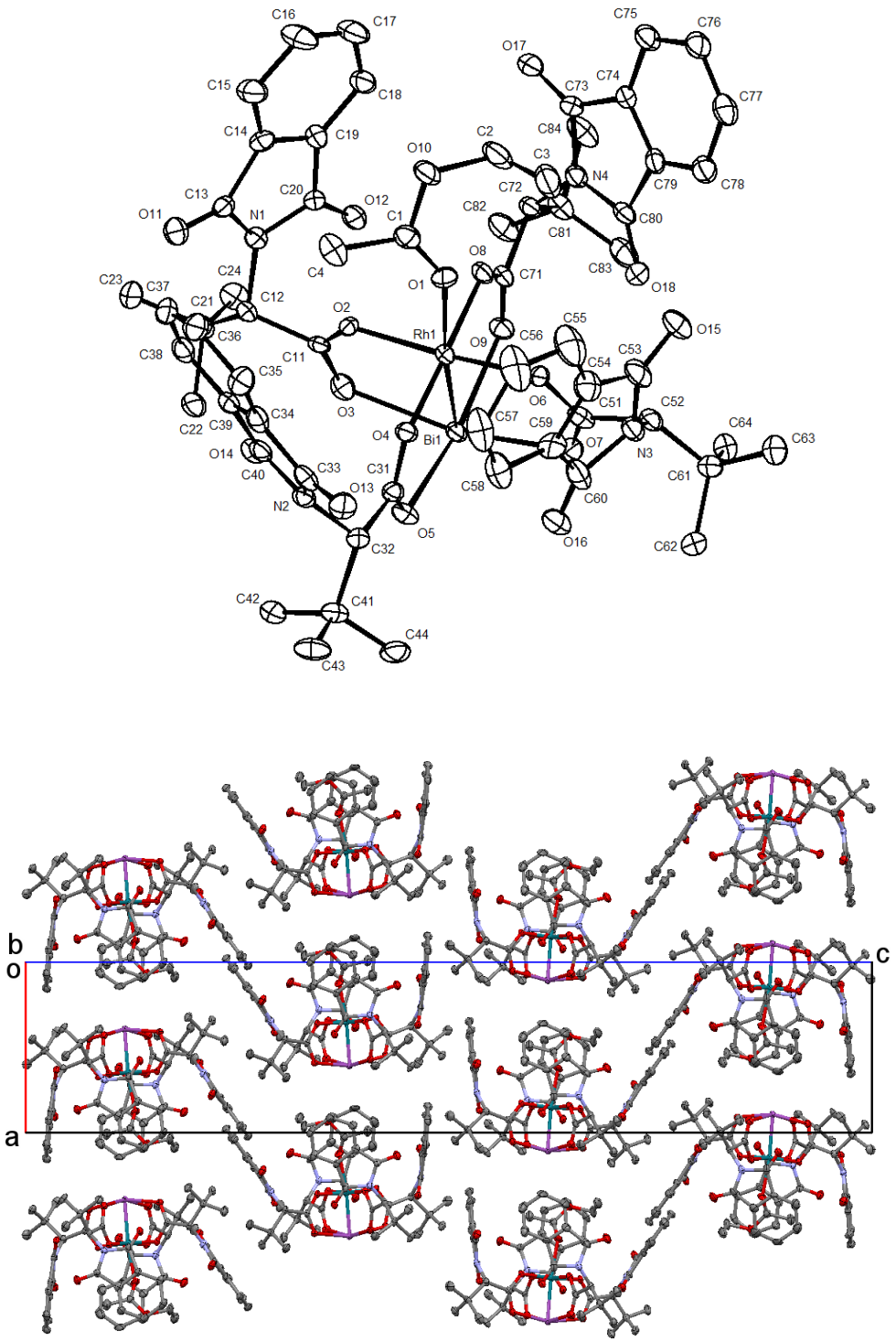


Figure S-1. Molecular structure of **5a**·EtOAc (top) and the packing of molecules in the unit cell (bottom); atomic displacement ellipsoids shown at the 50 % probability level, H atoms omitted for clarity.

X-ray Crystal Structure Analysis of 5a·EtOAc: $C_{60}H_{64}BiN_4O_{18}Rh$, M_r = 1441.04 g · mol^{-1}, yellow plate from pentane, crystal size 0.03 x 0.12 x 0.13 mm^3, orthorhombic, space group $P2_12_12_1$, a = 9.7944(13) Å, b = 12.6243(12) Å, c = 48.615(3) Å, V = 6011.1(10) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.592 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 3.273 mm^{-1}, Gaussian absorption correction (T_{min} = 0.6492, T_{max} = 0.9046), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.632 < θ < 33.240°, 85382 measured reflections, 22090 independent reflections, 18393 reflections with $I > 2\sigma(I)$, R_{int} = 0.081.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.64	338	353	95.8	6.58	75.05	28.77	0.0683	0.0330
2.64 - 1.78	771	771	100.0	7.41	62.88	28.27	0.0711	0.0320
1.78 - 1.41	1139	1139	100.0	7.31	39.23	25.16	0.0708	0.0340
1.41 - 1.23	1124	1124	100.0	6.74	28.58	22.78	0.0710	0.0371
1.23 - 1.12	1124	1126	99.8	6.11	24.07	20.57	0.0742	0.0408
1.12 - 1.04	1132	1133	99.9	5.72	22.14	19.40	0.0774	0.0440
1.04 - 0.98	1065	1065	100.0	5.33	19.08	17.63	0.0806	0.0480
0.98 - 0.93	1163	1165	99.8	5.06	15.12	15.38	0.0867	0.0545
0.93 - 0.89	1074	1077	99.7	4.75	12.87	13.69	0.0938	0.0618
0.89 - 0.85	1355	1360	99.6	4.16	11.04	11.64	0.1013	0.0740
0.85 - 0.82	1126	1135	99.2	3.01	10.03	9.15	0.1049	0.0960
0.82 - 0.80	858	878	97.7	2.54	9.65	8.16	0.1034	0.1092
0.80 - 0.77	1478	1524	97.0	2.32	8.47	7.03	0.1098	0.1251
0.77 - 0.75	1044	1090	95.8	2.16	8.13	6.47	0.1197	0.1360
0.75 - 0.73	1215	1283	94.7	2.04	6.93	5.53	0.1289	0.1613
0.73 - 0.72	670	715	93.7	1.94	6.09	4.88	0.1453	0.1835
0.72 - 0.70	1298	1424	91.2	1.85	5.54	4.37	0.1617	0.2040
0.70 - 0.68	1549	1719	90.1	1.73	4.41	3.49	0.1853	0.2655
0.68 - 0.67	808	914	88.4	1.62	3.84	2.89	0.2212	0.3207
0.67 - 0.66	813	943	86.2	1.59	3.48	2.70	0.2371	0.3578
0.66 - 0.65	994	1221	81.4	1.41	3.26	2.34	0.2523	0.4076
0.75 - 0.65	7347	8219	89.4	1.74	4.86	3.80	0.1713	0.2442
Inf - 0.65	22138	23159	95.6	3.69	15.62	11.76	0.0802	0.0712

The structure was solved by direct methods (*SHELXS*) and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.067 [$I > 2\sigma(I)$], wR_2 = 0.155, 771 parameters. There are four peaks of positive residual density about each Bi1 and Rh1 atom perpendicular to the c axis and peaks of negative residual density about each of Bi1 and Rh1 atoms perpendicular to the a axis. We have no explanation for this

apart from the fact that the diffraction data were collected to the relatively high resolution of 0.65 Å, indicating that the metal atoms may be showing the effects of anharmonic atomic displacement. Reducing the resolution of the diffraction data reduces the residual electron density about the metals.

For example, a cutoff of 0.8 Å reduces the maximum residual electon density about Bi1 to 2.79 eÅ^{-3}. The crystal Gaussian face-based absorption correction was checked and appears to be correctly undertaken. We cannot rule out that the compound crystallized as a mixture of isomers. The Flack

parameter *x* = -0.026(4) was determined using 6518 quotients [(*I*+)-(*I*-)]/[(*I*+)+(*I*-)] (Parsons, Flack and Wagner, *Acta Cryst*. 2013, **B69**, 249-259). H atoms riding, *S* = 1.105, residual electron density 3.26 (0.95 Å from Bi1/ -4.19 (0.73 Å from Bi1) e Å^{-3}. **CCDC-1887484**.

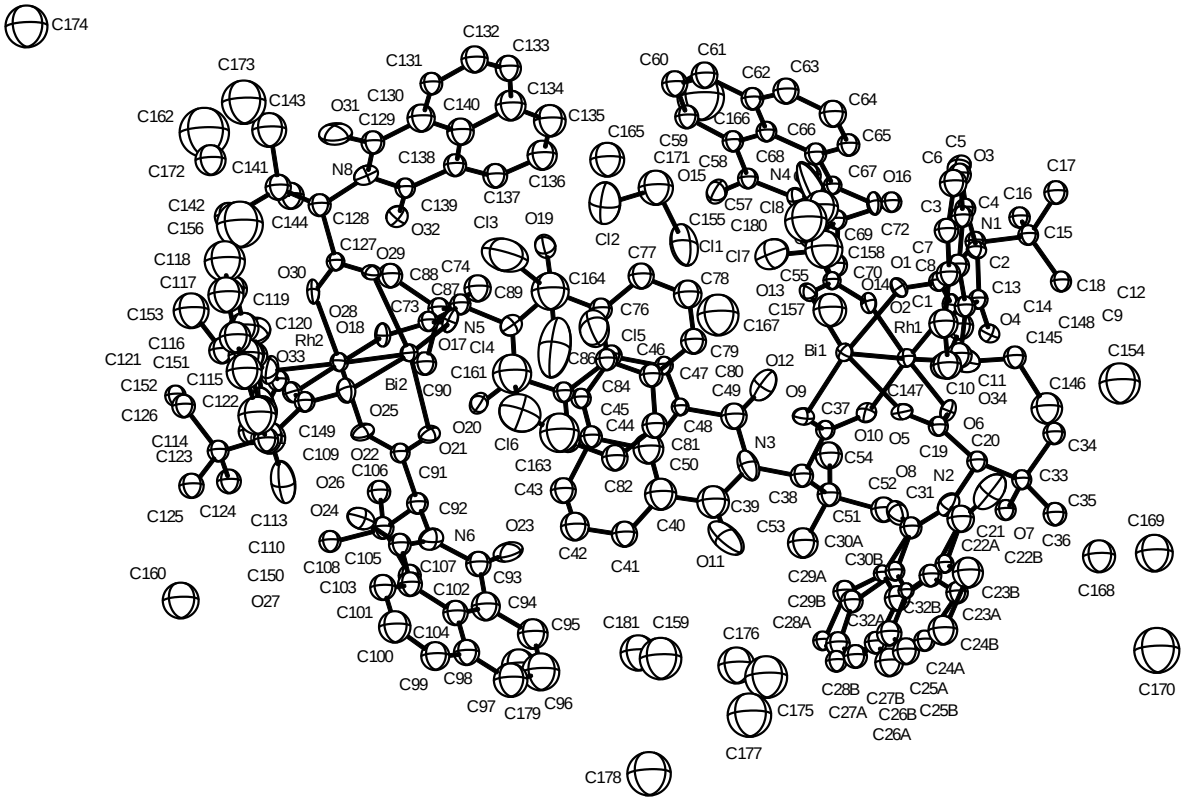


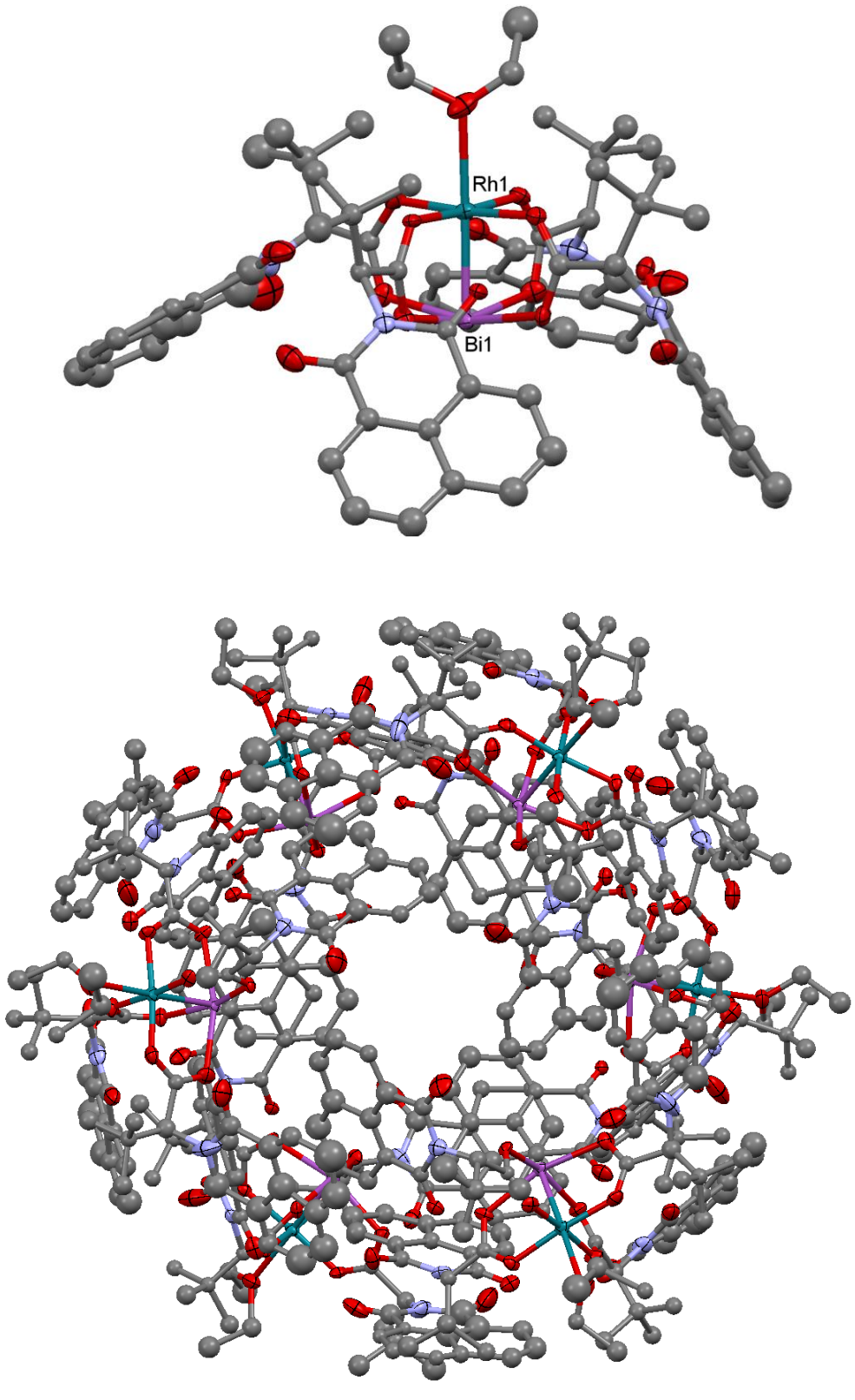
Figure S-2. Molecular structure of **5b**·Et_2O; atomic displacement ellipsoids shown at the 50 % probability level, H atoms omitted for clarity. Note that not all atoms have 100 % occupancy.

X-ray Crystal Structure Analysis of 5b·Et_2O: [$C_{79.49}H_{64.6}BiCl_{1.73}N_4O_{17}Rh$], M_r = 1720.89 g · mol^{-1}, yellow block from dichloromethane/diethylether, crystal size 0.19 x 0.20 x 0.21 mm^3, cubic, space group *P*23, *a* = 36.864(4) Å, *V* = 50098(18) Å^3, *T* = 100(2) K, *Z* = 24, D_{calc} = 1.369 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 2.421 mm^{-1}, Gaussian absorption correction (T_{min} = 0.52413, T_{max} = 0.59397), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.591 < θ < 28.879°, 325530 measured reflections, 43501 independent reflections, 37286 reflections with $I > 2\sigma(I)$, R_{int} = 0.062.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.20	183	205	89.3	31.72	80.51	70.90	0.0521	0.0165
3.20 - 2.10	429	429	100.0	44.55	51.44	79.07	0.0629	0.0115
2.10 - 1.64	611	611	100.0	45.55	35.75	70.03	0.0707	0.0120
1.64 - 1.42	610	610	100.0	42.51	27.20	60.56	0.0785	0.0137
1.42 - 1.28	645	645	100.0	40.06	20.71	53.29	0.0809	0.0164
1.28 - 1.18	644	644	100.0	37.80	18.13	48.49	0.0854	0.0182
1.18 - 1.11	599	599	100.0	35.71	16.40	43.38	0.0925	0.0200
1.11 - 1.05	638	638	100.0	34.24	13.71	37.88	0.1046	0.0229
1.05 - 1.01	528	528	100.0	32.20	11.73	32.41	0.1145	0.0263
1.01 - 0.96	759	759	100.0	30.68	10.30	28.49	0.1280	0.0302
0.96 - 0.93	543	543	100.0	29.12	9.01	24.73	0.1447	0.0350
0.93 - 0.90	606	606	100.0	27.70	7.13	20.39	0.1763	0.0438
0.90 - 0.87	703	703	100.0	26.15	6.74	18.05	0.1867	0.0489
0.87 - 0.85	513	513	100.0	22.34	6.80	15.83	0.1999	0.0551
0.85 - 0.83	582	582	100.0	16.45	5.57	11.89	0.2448	0.0775
0.83 - 0.81	634	634	100.0	13.38	5.66	10.39	0.2419	0.0880
0.81 - 0.79	681	681	100.0	11.49	5.32	9.03	0.2512	0.1008
0.79 - 0.77	764	764	100.0	11.08	4.82	7.93	0.2745	0.1144
0.77 - 0.76	414	414	100.0	10.64	4.66	7.42	0.2788	0.1233
0.76 - 0.74	1103	1103	100.0	10.21	3.98	6.29	0.3248	0.1462
0.84 - 0.74	3895	3895	100.0	11.55	4.81	8.20	0.2713	0.1128
Inf - 0.74	12189	12211	99.8	26.66	14.01	29.82	0.0936	0.0306

The structure was solved by dual space methods (*SHELXT*) and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.051 [$I > 2\sigma(I)$], wR_2 = 0.133, 1270 parameters. A number of low-angle reflections were shadowed by the beamstop and removed from the dataset before the final refinement cycles. In order to achieve a good data to parameter ratio and a good estimate of atomic positions, carbon atoms were refined with isotropic atomic displacement parameters. Rh, Bi, O and N atoms were refined with anisotropic atomic displacement parameters. One N(1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl) group in one of the complexes and one of the ethyl groups of a diethylether group bound to a Rh atom is slightly disordered. The crystal contains disordered solvent (presumably dichloromethane and diethylether). The solvent was modelled by C and Cl atoms of various occupancies. The Cl atoms were refined with anisotropic atomic displacement parameters. In parts of the solvent region of the crystal, the disorder was so great that no residual electron density could be observed. Bond distances and angles should be interpreted with caution. At convergence, approximately 2.3 % of the unit cell volume is occupied by voids (probe radius 1.2 A, grid spacing 0.7 A). The Flack parameter x = 0.0131(16) was determined using 14739 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, *Acta Cryst*. 2013, **B69**, 249-259). The crystal is partially [44.87(9)%] twinned (TWIN 0 1 0 1 0 0 0 0 -1). H atoms riding, S = 1.047, residual electron density 1.08 (0.59 Å from C44)/ -1.02 (2.66 Å from C167) e Å^{-3}. **CCDC-1887485**.



(a) (b)

Figure S-3. Top: one molecule of **5b**·Et_2O, showing the calyx-arrangement of the ligands about Bi1 (cf. **5a**·EtOAc in Fig. 1 of the main text); bottom: the hexamer of **5b**·Et_2O, viewed down the 3-fold axis of the crystal. 50% atomic displacement parameters; H atoms and solvent omitted for clarity.

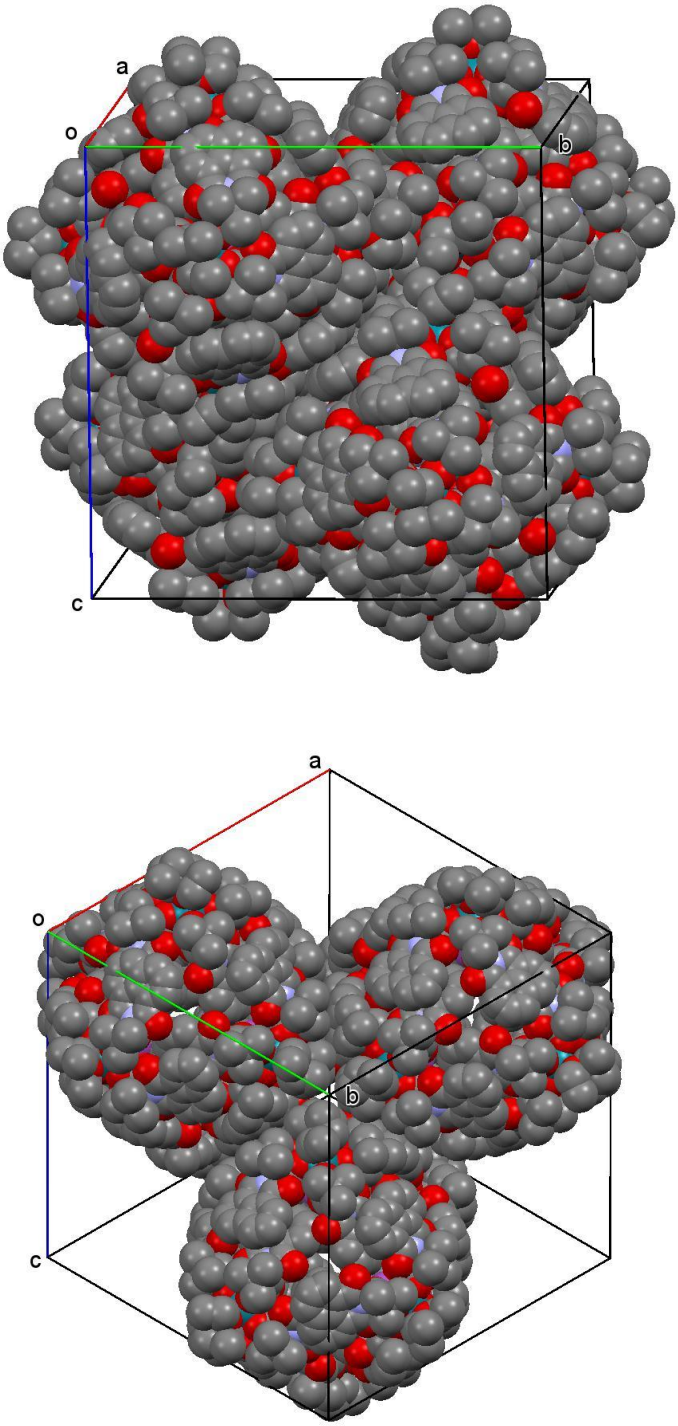


Figure S-4. The cubic-close-packing arrangement of the approximately spherical **5b**·Et_2O hexamers in the unit cell; space filling model based on atomic van der Waals radii; H atoms and solvent omitted for clarity.

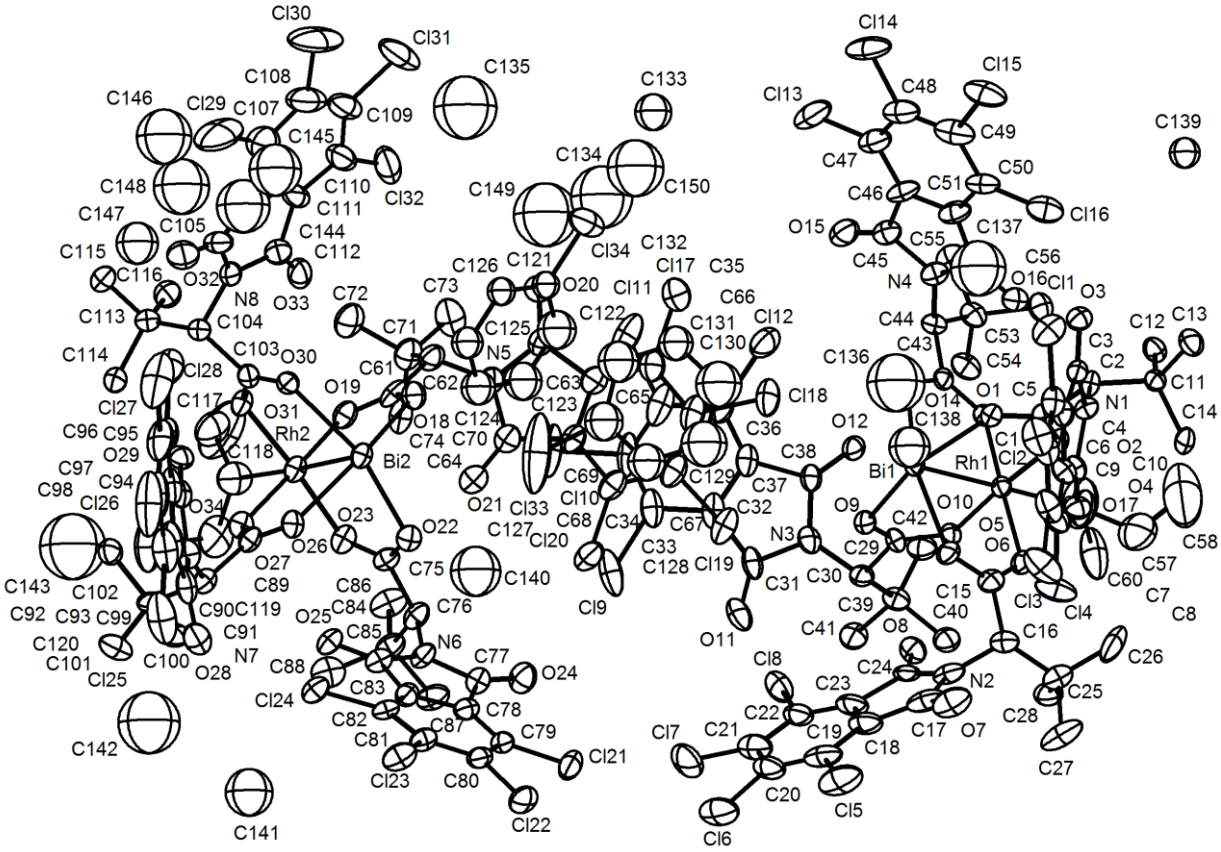


Figure S-5. Molecular structure of **5c**·Et_2O; atomic displacement ellipsoids shown at the 50 % probability level, H atoms omitted for clarity. Note that not all atoms have 100 % occupancy.

X-ray Crystal Structure Analysis of 5c·Et$_2$O: [$C_{69.47}H_{51.3}BiCl_{16.5}N_4O_{17}Rh$], M_r = 2110.86 g · mol^{-1}, yellow prism from chlorobenzene/dichloromethane/diethylether, crystal size 0.080 x 0.090 x 0.161 mm^3, cubic, space group *P*23, a = 37.9749(17) Å, V = 54763(7) Å^3, T = 100(2) K, Z = 24, D_{calc} = 1.536 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 2.649 mm^{-1}, Gaussian absorption correction (T_{min} = 0.72660, T_{max} = 0.81845), Bruker AXS Kappa Mach3 IμS Apex-II diffractometer, 2.211 < θ < 30.640°, 1530089 measured reflections, 56469 independent reflections, 49531 reflections with $I > 2\sigma(I)$, R_{int} = 0.110.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.97	449	462	97.2	40.37	76.64	62.93	0.0316	0.0177
2.97 - 1.95	1056	1056	100.0	77.44	64.99	88.88	0.0435	0.0106
1.95 - 1.53	1510	1510	100.0	83.08	38.95	79.30	0.0550	0.0109
1.53 - 1.33	1504	1504	100.0	76.03	28.30	67.50	0.0749	0.0129
1.33 - 1.20	1582	1582	100.0	68.17	19.62	53.48	0.0957	0.0157
1.20 - 1.11	1553	1553	100.0	61.82	18.22	46.28	0.1073	0.0183
1.11 - 1.05	1340	1340	100.0	57.65	14.77	38.75	0.1246	0.0217
1.05 - 0.99	1691	1691	100.0	54.52	11.87	32.11	0.1516	0.0266

0.99 - 0.95	1352	1352	100.0	51.95	10.32	27.98	0.1709	0.0310
0.95 - 0.91	1622	1622	100.0	49.84	8.47	23.02	0.2090	0.0382
0.91 - 0.88	1428	1428	100.0	48.07	7.29	19.77	0.2389	0.0453
0.88 - 0.85	1595	1595	100.0	46.30	6.32	16.91	0.2810	0.0540
0.85 - 0.82	1861	1861	100.0	44.60	5.76	14.91	0.3101	0.0621
0.82 - 0.80	1408	1408	100.0	42.98	5.39	13.20	0.3348	0.0698
0.80 - 0.78	1530	1530	100.0	41.92	4.74	11.43	0.3746	0.0815
0.78 - 0.76	1667	1667	100.0	40.62	4.60	10.67	0.3955	0.0878
0.76 - 0.75	941	941	100.0	39.59	3.83	8.68	0.4495	0.1082
0.75 - 0.73	2020	2020	100.0	38.57	3.55	7.82	0.4855	0.1210
0.73 - 0.72	1063	1063	100.0	37.50	3.13	6.81	0.5304	0.1415
0.72 - 0.70	2720	2723	99.9	34.02	2.51	5.12	0.6104	0.2006
0.80 - 0.70	9941	9944	100.0	38.17	3.61	8.09	0.4674	0.1217
Inf - 0.70	29892	29908	99.9	51.16	13.58	28.88	0.1161	0.0296

The structure was solved by direct methods (*SHELXS*) and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.037 [$I > 2\sigma(I)$], wR_2 = 0.095, 1920 parameters, 54 restraints. Several low-angle reflections were shadowed by the beamstop and removed from the data set before the final refinement cycles. In order to achieve a good data to parameter ratio and a good estimate of atomic positions, the carbon atoms of the solvent were refined with isotropic atomic displacement parameters. Rh, Bi, Cl, O, C and N atoms were refined with anisotropic atomic displacement parameters. The carbon atoms C61, C62, C63 and C64 in the main residues were restrained to be isotropic with a standard deviation of 0.01. As in the case of **5b**·Et_2O, six Rh-Bi complexes associate, presumably by van der Waals interactions, to create a spherical hollow capsule. The capsules cubic close-pack to form a three dimensional lattice. The space within the capsules and between the capsules is occupied by partially disordered solvent, which was modelled by resolved solvent and variously occupied C atoms, whose positions were refined. The C atoms of the solvent chlorobenzene molecules were constrained to be a regular hexagon with a C-C distance of 1.39 A. In parts of the solvent region of the crystal, the disorder was so great that no residual electron density could be observed. Approximately four percent of the unit cell volume (4.1%) contained no residual electron density at convergence of least-squares refinement (probe radius 1.2 A, grid spacing 0.7 A). The Rh-Bi complexes contain substituents that exhibit large conformational flexibility. Owing to the partially disordered solvent, the outer regions of the molecules adopt slightly different positions in the lattice, resulting in large variation in the atomic displacement parameters of the C atoms in the non-solvent region. Bond distances and angles should therefore be interpreted with caution. The Flack parameter x = -0.0139(8) was determined using 21163 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, *Acta Cryst*. 2013, **B69**, 249-259). The crystal is twinned (TWIN 0 1 0 1 0 0 0 0 -1, 50.67(5)%). H atoms riding, S = 1.085, residual electron density 1.32 (0.69 Å from Bi1)/ -0.93 (0.57 Å from Bi2) e $Å^{-3}$. **CCDC-1887486**.

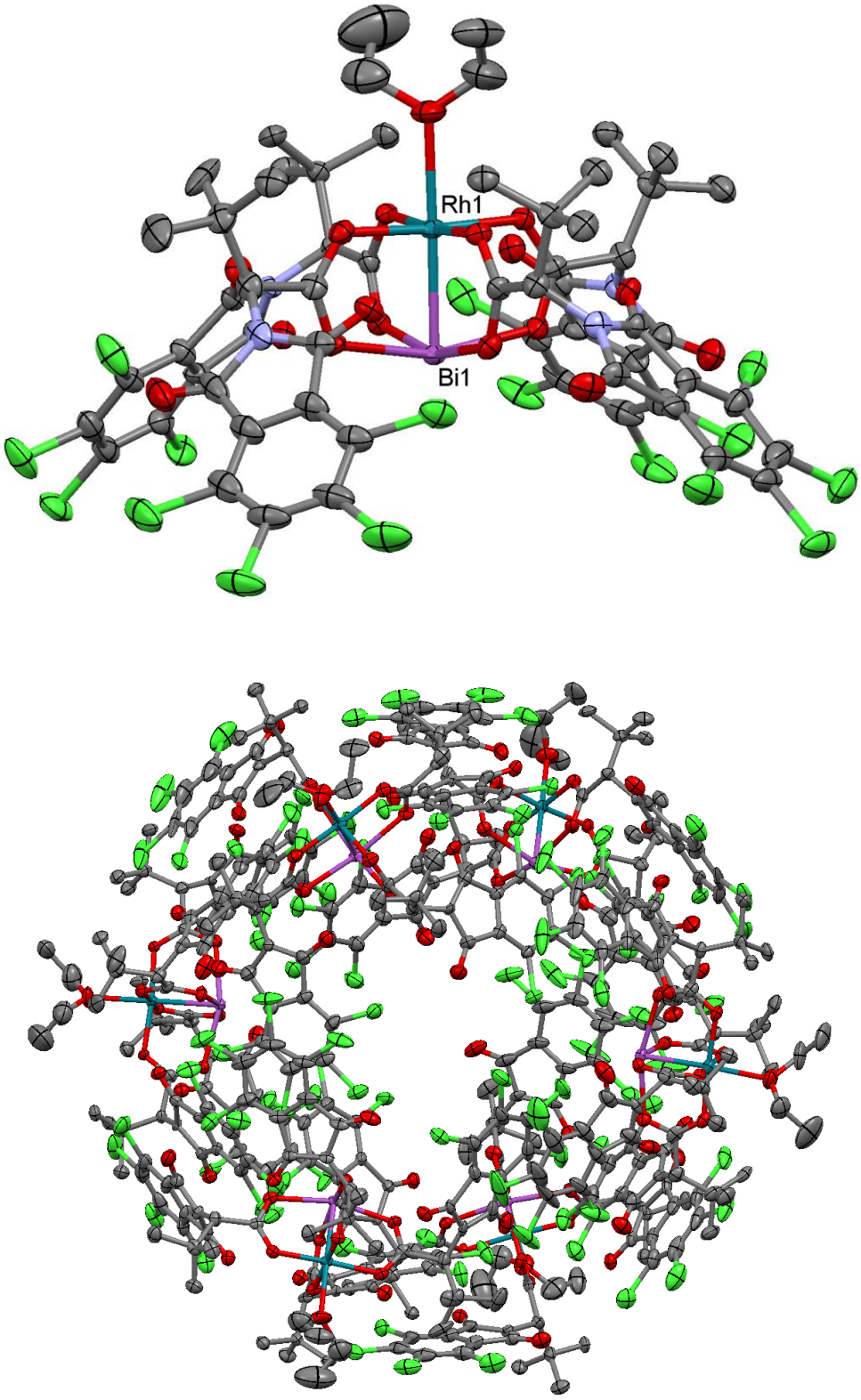


Figure S-6. Top: one molecule of **5c**·Et_2O, showing the arrangement of the ligands (cf. **5a**·EtOAc in Fig. 1 of the main text); bottom: general view of the hexamer of **5c**·Et_2O; 50% atomic displacement parameters, H atoms and solvent omitted for clarity.

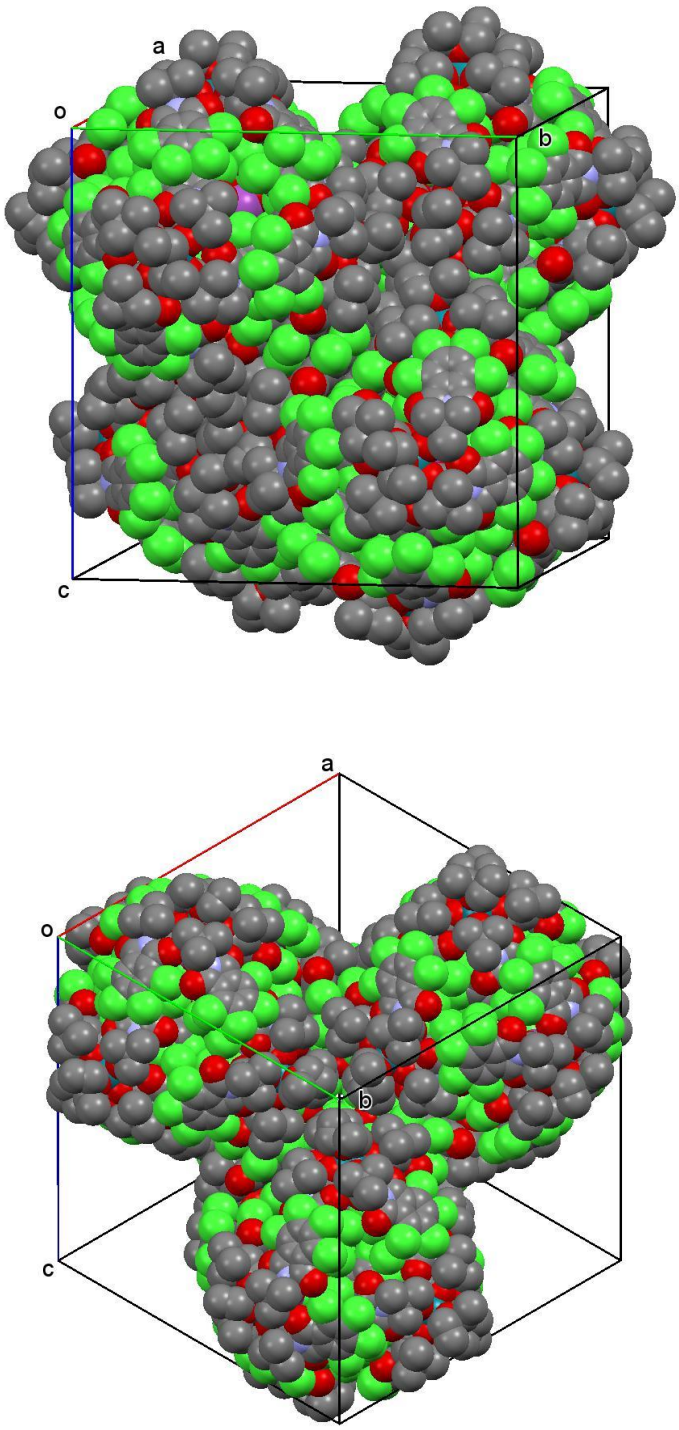


Figure S-7. The cubic-close-packing arrangement of the approximately spherical **5c**·Et_2O hexamers in the unit cell; space filling model based on atomic van der Waals radii; solvent and H atoms omitted for clarity.

^{1}H DOSY NMR. Diffusion coefficients were obtained from TopSpin's Relaxation Module. Hydrodynamic radii were calculated with the Stokes-Einstein equation using the following parameters: $K_B = 1.381 \times 10^{-23}\ m^2kgs^{-2}K^{-1}$; $T = 298K$; $\eta_{DCM} = 0.413cP = 4.1 \times 10^{-4}\ kgm^{-1}s^{-1}$.

The recorded spectra showed that all three samples have essentially the same hydrodynamic radius in CD_2Cl_2 solution (7.4 Å) – consistent with each complex existing as a single paddlewheel in solution. Therefore, the complex crystal structures do not have immediate implications for the active site of these precatalsts but clearly explain the trends in solubility which limit the availability of the catalyst in solution due to the requirement of breaking so many intermolecular contacts.

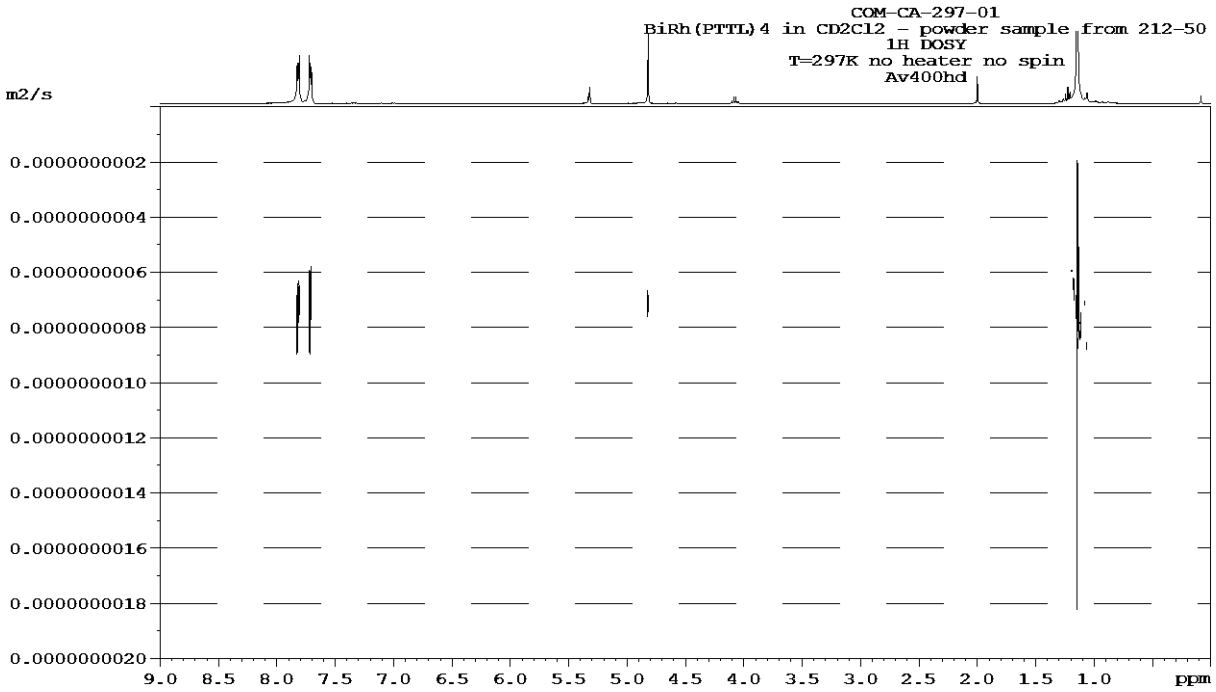


Figure S-8. ^{1}H NMR DOSY Data for [BiRh(PTTL)$_4$] (**5a**).

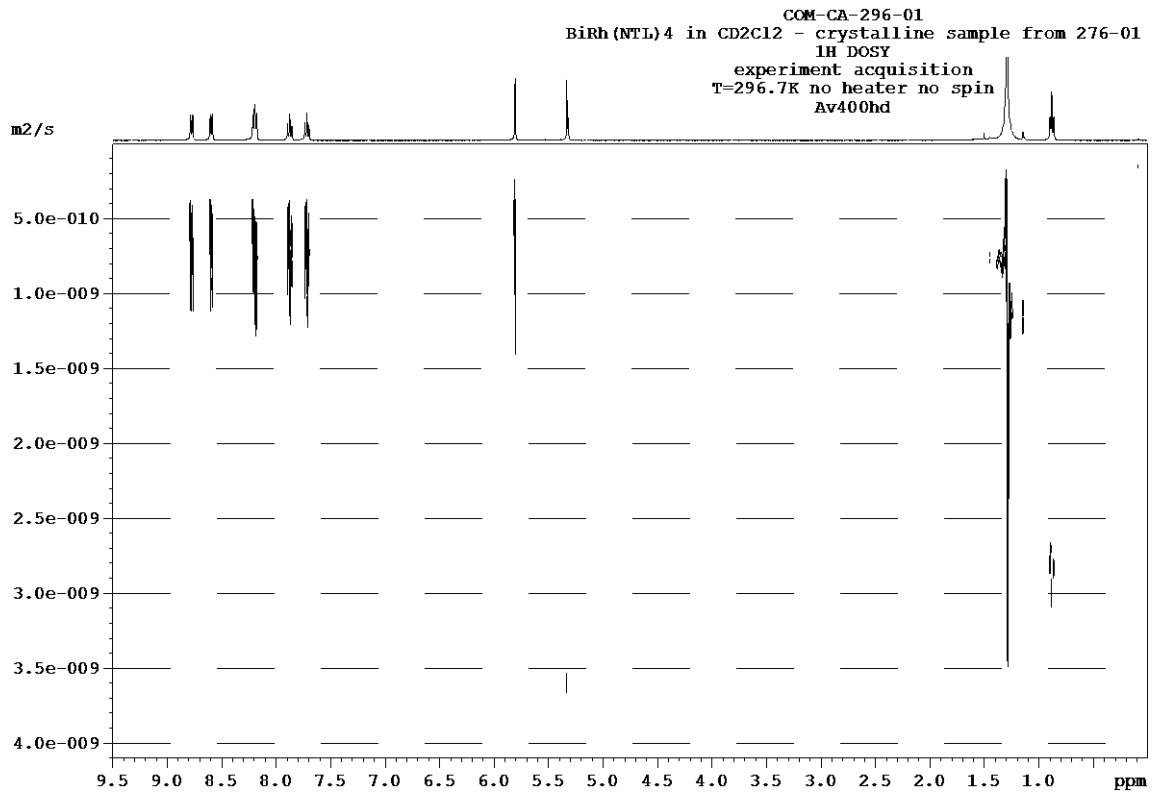


Figure S-9. ^{1}H NMR DOSY Data for [BiRh(NTTL)$_4$] (**5b**).

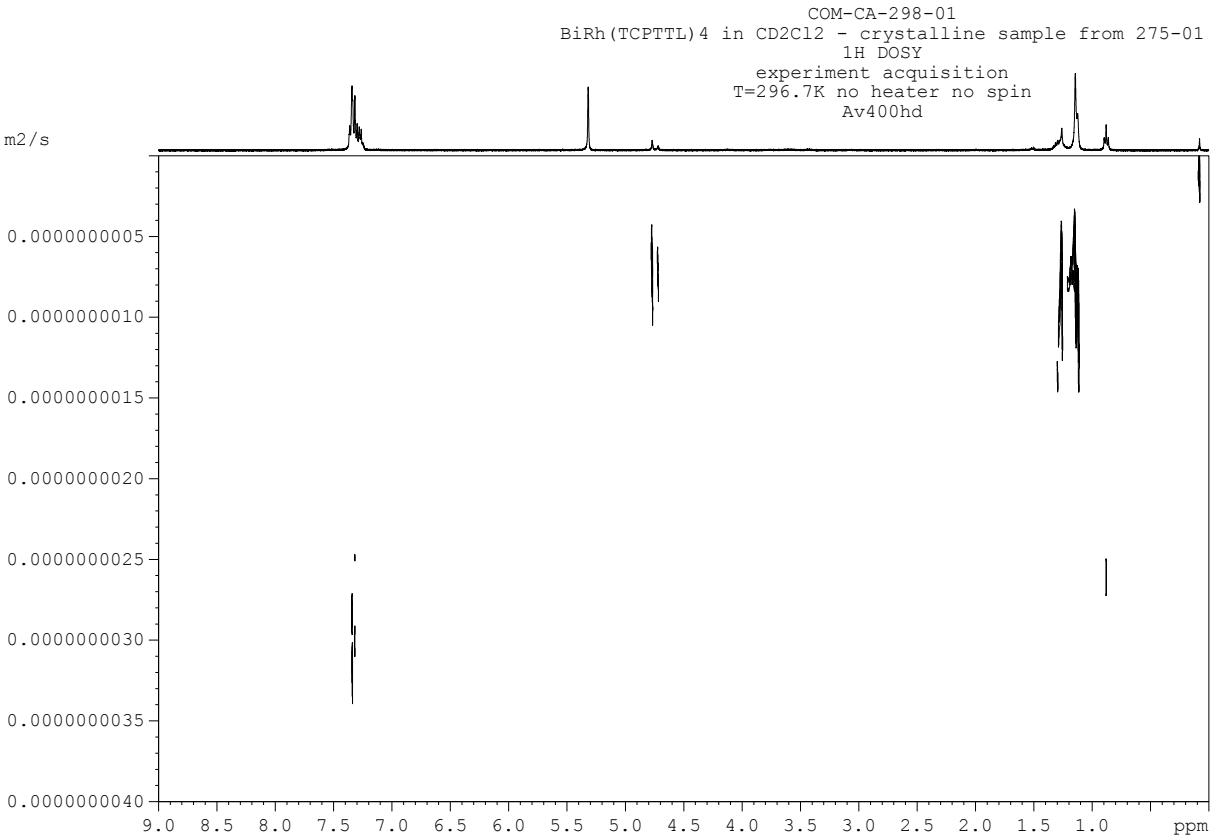


Figure S-10. ^{1}H NMR DOSY Data for [BiRh(TCPTTL)$_4$] (**5c**).

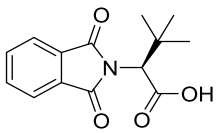
PREPARATION AND CHARACTERIZATION OF THE HETEROBIMETALLIC PADDLEWHEEL COMPLEXES

General. All reactions were carried out under Argon in flame-dried glassware, ensuring rigorously inert conditions. The solvents were purified by distillation over the indicated drying agents and were stored and handled under Argon: THF (Mg/anthracene), Et_2O (Mg/anthracene), CH_2Cl_2 (CaH_2), chlorobenzene (CaH_2), Ph_2O (CaH_2, stored over MS 4Å), hexane (Na/K), pentane (Na/K), toluene (Na/K), MeOH (Mg). NMR spectra were recorded on Bruker AV300 or AV400 spectrometers at 298 K unless otherwise indicated with the chemical shifts (δ) given in ppm relative to TMS and the coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CD_2Cl_2: ^1H = 5.32 ppm, ^{13}C = 53.8 ppm; C_6D_6: ^1H = 7.16 ppm, ^{13}C = 128.0 ppm; $CDCl_3$: ^1H = 7.26 ppm, ^{13}C = 77.0 ppm). ^{19}F NMR resonances were referenced to $C_6H_5CF_3$ (−63.72 ppm) as internal standard.[1] IR: Bruker ALPHA Platinum-ATR, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS: Finnigan MAT 8200 (EI, 70 eV), Bruker ESQ 3000 (ESI), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Finnigan Mat 95. Thin layer chromatography (TLC): Macherey-Nagel pre-coated plates (POLYGRAM®SIL/UV254). Flash chromatography: Merck silica gel 60 (40−63 µm) with technical grade solvents.

Unless stated otherwise, commercially available compounds (Aldrich, Strem, TCI) were used as received. The quality of commercial samples of $Rh_2(TFA)_4$ was checked by ^{19}F NMR for purity and upgraded, if necessary.[2]

Ligands

(*S*)-PTTL-H. To a stirring solution of phthaloyl anhydride (1.859 g, 12.551 mmol) and (L)-*tert*-leucine



(1.658 g, 12.640 mmol) in toluene (60 mL) was added NEt_3 (0.6 mL, 4.3 mmol) and the resulting suspension heated to reflux such that 35 mL of solvent was removed by distillation over 40 minutes. After cooling to ambient temperature, HCl (3 M, 8 mL, 24 mmol) was added and the product extracted into EtOAc. The organic phase was washed with brine and dried over Na_2SO_4, the solvent was evaporated and the residue dried in vacuo. The product was purified by recrystallization from EtOAc/hexane to yield a white powder

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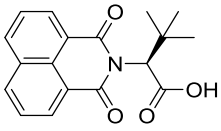
1 The use of $C_6H_5CF_3$ referenced to −63.72 ppm as internal standard was deemed necessary since the literature data are poorly referenced or the reference chosen is ill-defined; for an informative treatise addressing this critical issue, see: C. P. Rosenau, B. J. Jelier, A. D. Gossert, A. Togni, Exposing the Origins of Irreproducibility in Fluorine NMR Spectroscopy. *Angew. Chem. Int. Ed*. **2018,** *57*, 9528-9533.

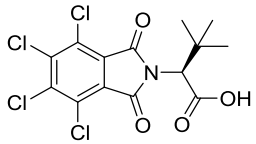
2 Mixed OAc/TFA complexes are common impurities in commercial samples of $Rh_2(TFA)_4$ and appear as a series of ^{19}F resonances instead of the expected singlet ($^{19}F\{^1H\}$ NMR (282.4 MHz, C_6D_6): δ = −76.2 ppm; $^{19}F\{^1H\}$ NMR referenced internally to $PhCF_3$: δ = −63.72 ppm); such samples can be purified by refluxing the material in trifluoroacetic acid, evaporation of all volatiles and thorough drying of the residue.

(1.525 g, 47 %). Spectroscopic data matched those reported in the literature.[3] Additional data: IR (solid): $\tilde{\nu}$ = 3220, 2966, 2900, 1755, 1701, 1465, 1389, 1365, 1332, 1215, 1147, 1105, 1085, 962, 900, 846, 792, 770, 754, 714, 652, 532, 516 cm^{-1}; HRMS (ESI^+): calcd. for $[C_{14}H_{15}NO_4Na]^+$: 284.08933; found 284.08937.

(*S*)-NTTL-H.[5] A solution of 1,8-naphthalic anhydride (0.999 g, 5.041 mmol) and (L)-*tert*-leucine (0.660 g, 5.032 mmol) in DMF (40 mL) was stirred at 383 K (bath temperature) for 26 h. After cooling to ambient temperature, EtOAc (160 mL) was added, the organic phase was washed with brine, dried over $MgSO_4$ and evaporated, yielding a yellow oil which crystallized upon standing. The product was purified by flash chromatography (SiO_2, hexanes/EtOAc, 1:1), followed by recrystallization from CH_2Cl_2/pentane to yield an off-white powder (1.180 g, 75 %). The spectroscopic data matched those reported in the literature.[4] Additional data: IR (solid): $\tilde{\nu}$ = 2911, 1722, 1707, 1665, 1587, 1378, 1337, 1263, 1237, 1178, 1151, 1113, 982, 907, 847, 775, 737, 692, 502 cm^{-1}. HRMS (ESI^+): calcd. for $[C_{18}H_{17}NO_4Na]^+$: 334.10498; found 334.10508.



(*S*)-TCPTTL-H.[5] A stirring solution of tetrachlorophthaloyl anhydride (1.434 g, 5.016 mmol) and (L)-*tert*-leucine (0.659 g, 5.024 mmol) in DMF (40 mL) was heated to 383 K (bath temperature) for 26 h. After cooling to ambient temperature, EtOAc (160 mL) was added and the organic phase was washed with brine, dried over $MgSO_4$ and evaporated. The residue was dried in vacuo, yielding a yellow oil which crystallised upon standing. The product was purified by flash chromatography (SiO_2, hexanes/EtOAc, 5:2), followed by recrystallization from CH_2Cl_2/pentane to yield an off-white powder (0.729 g, 37 %). The spectroscopic data matched those reported in the literature.[6] Additional data: IR (solid): $\tilde{\nu}$ = 1721, 1385, 1369, 1344, 1280, 1201, 1117, 912, 867, 811, 776, 736, 645, 531, 510 cm^{-1}; HRMS (ESI^+): calcd. for $[C_{14}H_{11}NO_4Cl_4Na]^+$: 419.93344; found 419.93364.



Complexes

$[Bi(TFA)_3]$. To a stirring suspension of Bi_2O_3 (0.595 g, 1.28 mmol) in CH_2Cl_2 (3 mL) was added trifluoroacetic acid (TFAH, 2.30 g, 20 mmol) and trifluoroacetic acid anhydride (2.10 g, 10 mmol), slowly leading to the formation of a homogeneous solution. After ≈ 5 d under Ar, all Bi_2O_3 had dissolved;[7] at this point, all volatile materials were removed and the residue was extracted into

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3 H. Tsutsui, T. Abe, S. Nakamura, M. Anada, S. Hashimoto, *Chem. Pharm. Bull*. **2005**, *53*, 1366-1368.

4 C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd, P. Dauban, *J. Am. Chem. Soc*. **2008**, *130*, 343–350.

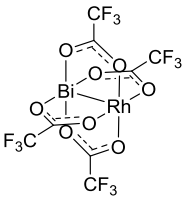
5 V. N. G. Lindsay, A. B. Charette, *ACS Catal.* **2012**, *2*, 1221-1225.

6 Y. Hoshino, H. Yamamoto, *J. Am. Chem. Soc*. **2000**, 122, 10452-10453.

7 Depending on the quality and grain size of Bi_2O_3, the dissolution proceeds at significantly different rates (1-5 d); in cases, where solid material was left after 5 d, additional trifluoroacetic acid and trifluoroacetic

toluene (15 mL). The solution was concentrated and the product reprecipitated with toluene and pentane, washed with pentane and dried thoroughly (373 K, 10^{-3} mbar, 1 h)[8] to yield a fine white powder (0.850 g, 66 %). $^{19}F\{^{1}H\}$ NMR (282.4 MHz, C_6D_6): δ = −75.8 (s, CF_3) ppm).[1]

[BiRh(TFA)$_4$] (7). *The product is highly air- and moisture sensitive and must be kept and handled with appropriate precautions under Ar. In pure form, however, it is stable under Ar at ambient temperature for extended periods of time.*



A flame-dried 50 mL Schlenk flask was charged with thoroughly dried Bi(TFA)$_3$ (0.255 g, 0.465 mmol)[8] under Ar. A solution of Rh_2(TFA)$_4$ (0.292 g, 0.444 mmol)[2] in dry toluene (20.0 mL) was added, followed by freshly distilled Ph_2O (0.7 mL, 4.4 mmol), Bi metal (0.436 g, 2.086 mmol), TFAH (35.0 µL, 0.46 mmol) and finally $PhCF_3$ (27.0 µL, 0.22 mmol; internal standard for quantitative aliquot analysis).[1] The flask was placed in a pre-heated oil bath (388 K – 398 K)[9] and the mixture vigorously stirred until ^{19}F NMR spectra of aliquots indicated that the Rh_2(TFA)$_4$ was completely consumed. Heating is immediately stopped at this point. The mixture was cannula filtered to a fresh 50 mL Schlenk flask and all volatile materials were removed to give a green oil, from which yellow microcrystalline material began to precipitate. Ph_2O was removed by Schlenk-to-Schlenk vacuum transfer (333 K, 10^{-3} mbar): to this end, the product-containing Schlenk flask was gently heated to ~50°C, whereas the receiving flask was cooled with liquid nitrogen. This set-up causes the Ph_2O to slowly condense over, leaving a greasy yellow residue behind. The product was then isolated by sublimation (373-393 K, 10^{-3} mbar, 253 K cold finger) and the sublimed material transferred into a Schlenk flask under Ar by washing the cold finger with CH_2Cl_2 before quickly evaporating the solvent.[10,11] The yellow product was then washed with pentane and dried to yield a fine yellow powder (0.339 g, 50 %). $^{19}F\{^{1}H\}$ NMR (282 MHz, C_6D_6, $C_6H_5CF_3$ as internal standard): δ −74.2 ppm.

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acid anhydride were added and stirring continued; otherwise, any remaining residue has to be removed by canula filtration prior to evaporation of the volatile materials.

8 Thorough drying of Bi(TFA)$_3$ is important to remove excess acid since the complex seems to associate to TFAH; accurate monitoring of this drying process by ^{19}F NMR is recommended

9 Over-heating should be avoided; the literature just says 'reflux' which is potentially misleading for such a solvent mixture.

10 Although the complex is said to be unstable in CH_2Cl_2 over prolonged periods of time, this solvent proved convenient to use; to avoid any decomposition, however, care must be taken to evaporate it quickly and thoroughly.

11 The residual grey material could not be identified.

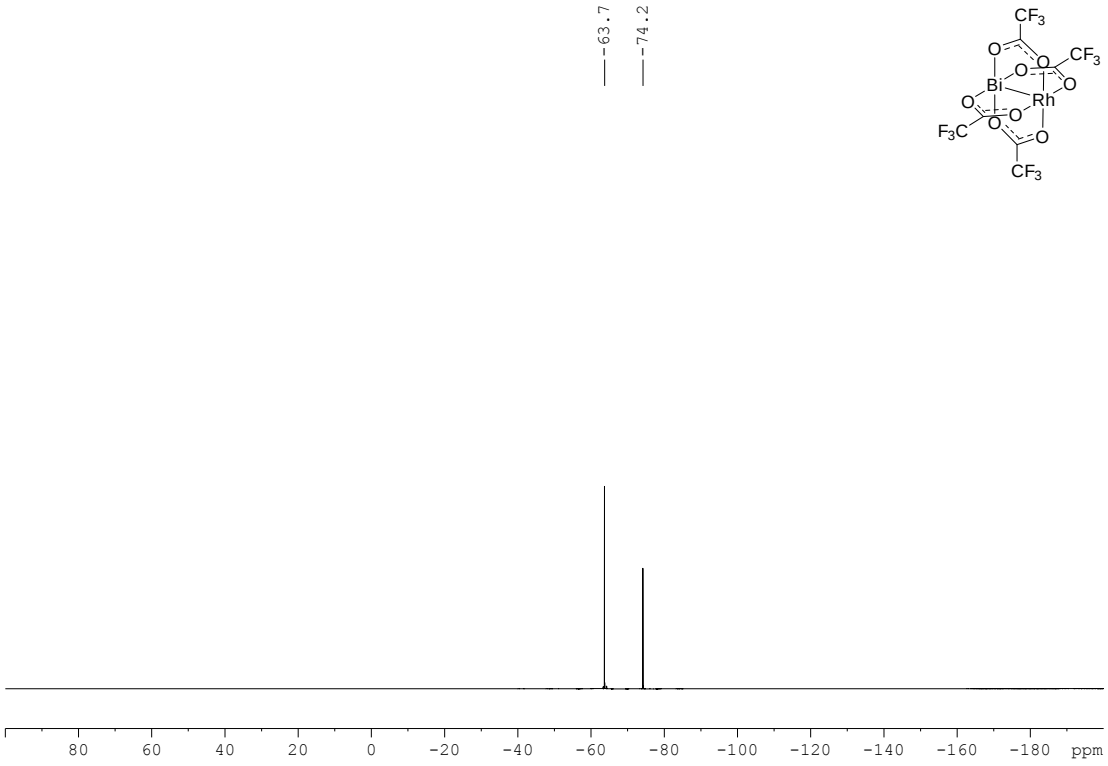
[BiRh((S)-PTTL)$_4$]·EtOAc (5a·EtOAc). A solution of BiRh(TFA)$_4$ (0.330 g, 0.432 mmol) in toluene (15 mL) was added to a 50 mL Schlenk flask containing (*S*)-PTTL-H (0.554 g, 2.120 mmol). Between the Schlenk flask and the reflux condenser was placed a returning-arm frit (or Soxhlet extractor) filled with oven-dried K_2CO_3 (≈ 3.0 g). The flask was placed in a preheated oil bath (413 K) and the mixture was stirred at reflux temperature. The reaction was monitored by $^{19}F\{^1H\}$ NMR analysis of aliquots until the recorded spectra showed that all TFA residues were consumed (about 4 h).[1] The solution was cooled, concentrated and the sticky yellow residue was triturated with pentane and dried to a yellow powder. The complex was then extracted into EtOAc and the combined organic phases were washed with saturated aqueous $NaHCO_3$ to remove acidic residues. After washing with brine and drying over $MgSO_4$, a fine yellow powder was obtained upon removal of volatiles (0.590 g, 95 %). ^1H NMR analysis showed one equivalent of EtOAc to remain bound to the complex, even after drying at 10^{-3} mbar. Crystals suitable for X-ray diffraction studies were grown from a saturated EtOAc solution layered with pentane. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (m, 8 H, 4-ArH), 7.67 (m, 8 H, 5-ArH), 4.87 (s, 4 H, CH), 4.12 (q, 7.1 Hz, 2 H, C$\underline{H_2}$CH$_3$), 2.04 (s, 3 H, C(O)CH$_3$), 1.25 (t, 7.1 Hz, 3 H, CH$_2$C$\underline{H_3}$), 1.16 (s, 36 H, ^{t}Bu) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 181.7 (OCO), 171.2 (CH$_3$$\underline{C}$O), 167.8 (NCO), 133.7 (5-Ar), 131.9 (3-Ar), 123.4 (4-Ar), 61.3 (CH), 60.4 ($\underline{C}$H$_2$CH$_3$), 35.8 ($\underline{C}$(CH$_3$)$_3$), 28.0 (C($\underline{C}$H$_3$)$_3$), 21.0 ($\underline{C}$H$_3$CO), 14.2 (CH$_2$$\underline{C}H_3$) ppm ; IR (solid): $\tilde{\nu}$ = 2959, 2907, 2872, 1776, 1714, 1594, 1480, 1467, 1376, 1345, 1330, 1295, 1264, 1189, 1105, 1087, 1041, 902, 869, 782, 734, 718, 665, 605, 531, 488, 423 cm^{-1}; HRMS (ESI$^+$): calcd. for $[C_{56}H_{56}BiN_4O_{16}RhNa]^+$: 1375.2442; found 1375.24521.

[BiRh((*S*)-NTTL)$_4$] (5b). To a mixture of [BiRh(TFA)$_4$] (0.214 g, 0.280 mmol) and (*S*)-NTTL-H (0.460 g, 1.478 mmol) in a 50 mL Schlenk flask was added toluene (15 mL). Between the Schlenk flask and the reflux condenser was placed a returning-arm frit (or Soxhlet extractor) filled with oven-dried K_2CO_3 (≈ 3.0 g). The flask was placed in an oil bath and the mixture stirred at a bath temperature of 413 K until $^{19}F\{^1H\}$ NMR analysis of aliquots confirmed that all TFA residues were consumed (ca. 4h).[1] The solution was cooled, concentrated and the sticky yellow residue was stirred with pentane and dried to a yellow powder. The complex was then extracted into CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ to remove acidic residues. After washing with brine and drying over $MgSO_4$, a fine yellow powder was obtained upon removal of volatiles (0.370 g, 85 %). Crystals suitable for X-ray diffraction studies were grown from a CH_2Cl_2 solution layered with pentane or Et_2O. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, 7.4 Hz, 4 H, 2-ArH), 8.59 (d, 7.4 Hz, 4 H 7-ArH), 8.12 (overlapping, 8 H, 4-ArH and 5-ArH), 7.85 (m, 4 H, 3-ArH), 7.67 (m, 4 H, 6-ArH), 5.83 (s, 4 H, CH), 1.30 (s, 36 H, ^{t}Bu) ppm; $^{13}C\{^1H\}$ NMR (100

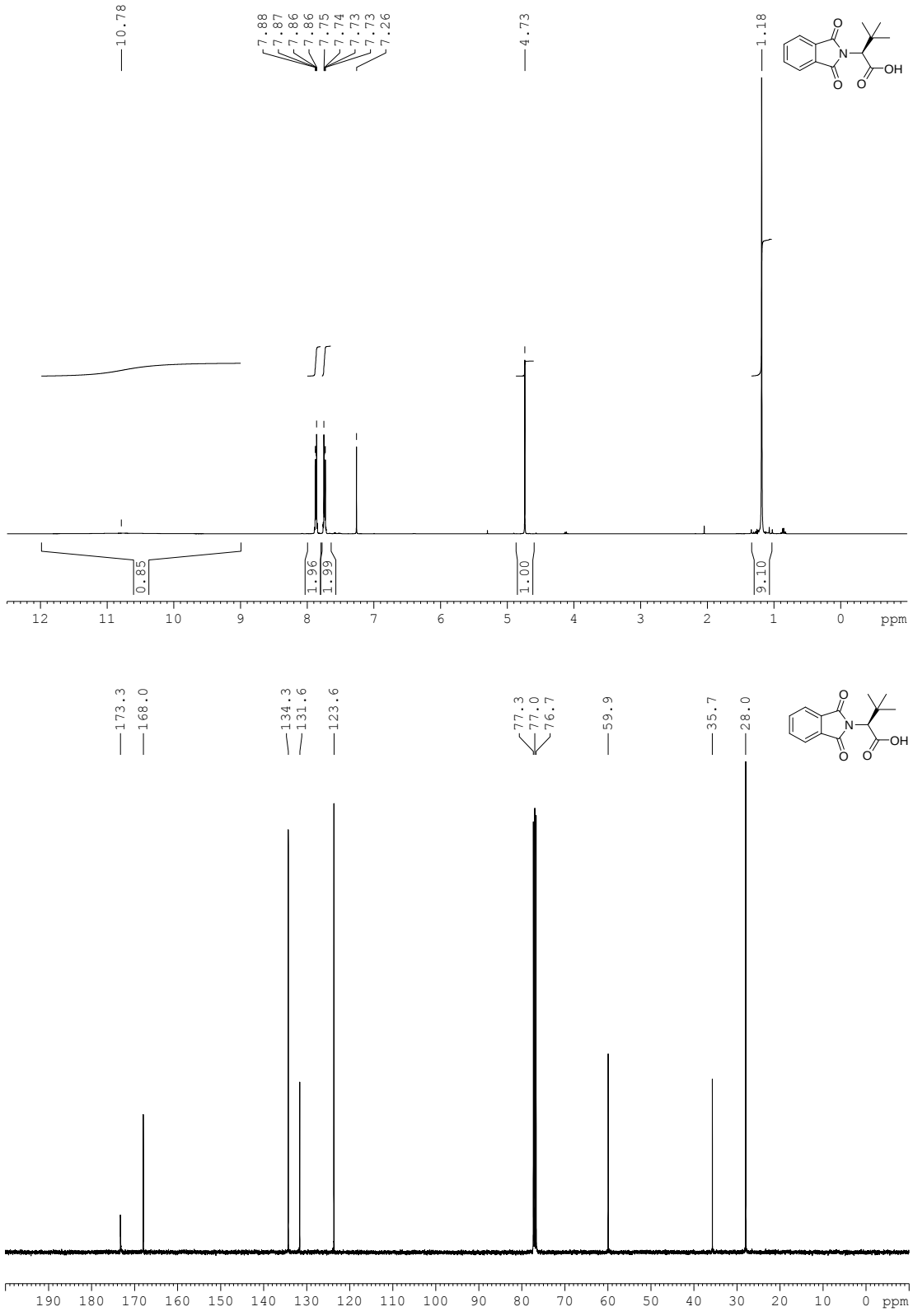
MHz, $CDCl_3$): δ = 182.1 (OCO), 164.8 (NCO), 163.1 (NCO), 133.5 (Ar), 133.1 (Ar), 132.1 (Ar), 131.4 (Ar), 131.2 (Ar), 128.1 (Ar), 127.5 (Ar), 126.5 (Ar), 123.1 (Ar), 122.8 (Ar), 61.7 (CH), 36.3 ($\underline{C}(CH_3)_3$), 28.9 ($C(\underline{C}H_3)_3$) ppm; IR (solid): $\tilde{\nu}$ = 2968, 2929 2868, 1703, 1662, 1586, 1482, 1394, 1374, 1337, 1302, 1235, 1179, 1148, 1110, 1074, 1015, 997, 906, 844, 783, 736, 711, 623, 576, 536, 492, 426 cm^{-1}; HRMS (ESI^+): calcd. for $[C_{72}H_{64}Bi_1N_4O_{16}RhNa]^+$: 1575.3068; found 1575.30651.

[BiRh((*S*)-TCPTTL)$_4$] (5c). To a mixture of [BiRh(TFA)$_4$] (0.224 g, 0.293 mmol) and (*S*)-TCPTTL-H (0.540 g, 1.353 mmol) in a 50 mL Schlenk flask was added toluene (15 mL). Between the Schlenk flask and the reflux condenser was placed a returning-arm frit (or Soxhlet extractor) filled with oven-dried K_2CO_3 (≈ 3.0 g). The flask was placed in a pre-heated oil bath (413 K) and the resulting solution stirred at this temperature until $^{19}F\{^1H\}$ NMR spectra of aliquots confirmed that all TFA residues were consumed (ca. 4 h).[1] The solution was cooled, concentrated and the sticky yellow residue was stirred with pentane and dried to a yellow powder. The complex was then extracted into much toluene and washed with saturated aqueous $NaHCO_3$ to remove acidic residues. After washing with brine and drying with $MgSO_4$, a fine yellow powder was obtained upon removal of volatiles (0.432 g, 77 %). Crystals suitable for X-ray diffraction studies were grown from a PhCl solution layered with either pentane or Et_2O. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.79 (s, 4 H, CH), 1.14 (s, 36 H, ^{t}Bu) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 181.3 (OCO), 163.1 (NCO), 61.8 (CH), 36.0 ($\underline{C}(CH_3)_3$), 27.9 ($C(\underline{C}H_3)_3$) ppm (aromatic signals were not observed); IR (solid): $\tilde{\nu}$ = 2962, 2871, 1782, 1725, 1600, 1477, 1397, 1370, 1352, 1327, 1294, 1196, 1121 1082, 1022, 995, 912, 872, 823, 782, 752, 738, 701, 684, 610, 526, 494, 468, 421 cm^{-1}; HRMS (ESI^+): calcd. for $[C_{56}H_{40}BiCl_{16}N_4O_{16}RhNa]^+$: 1918.6207; found 1918.61880.

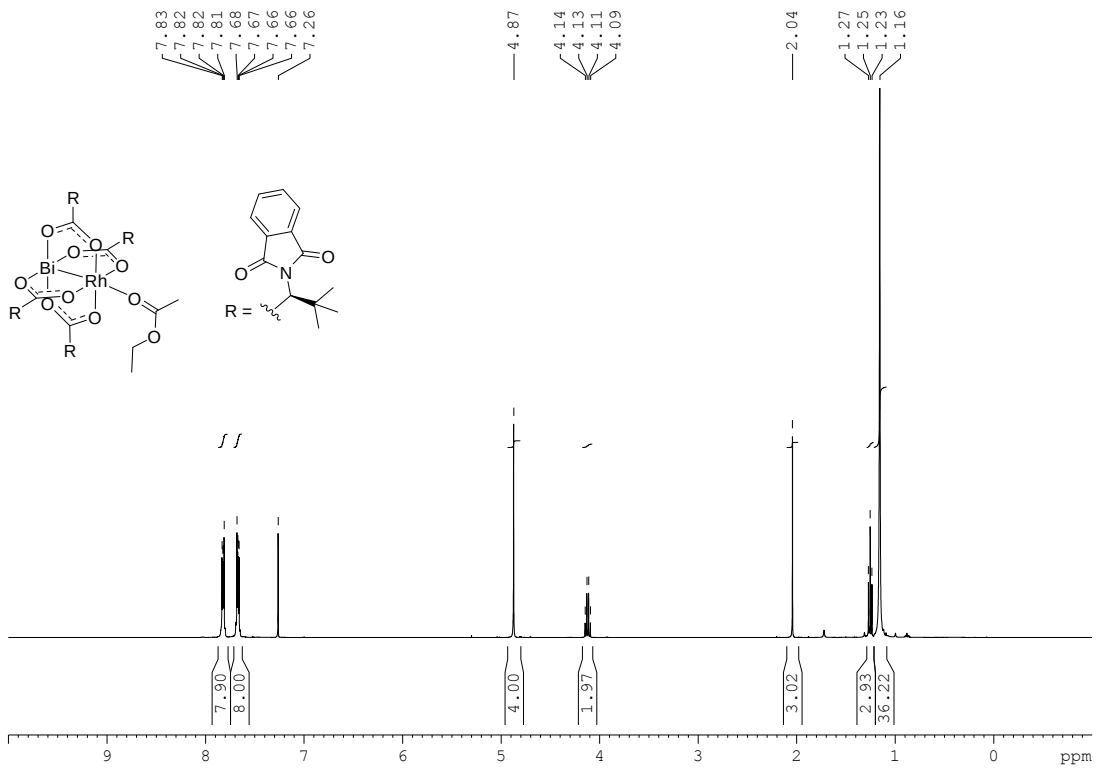
[BiRh(TFA)$_4$]: ^{19}F NMR (282 MHz, CDCl$_3$)

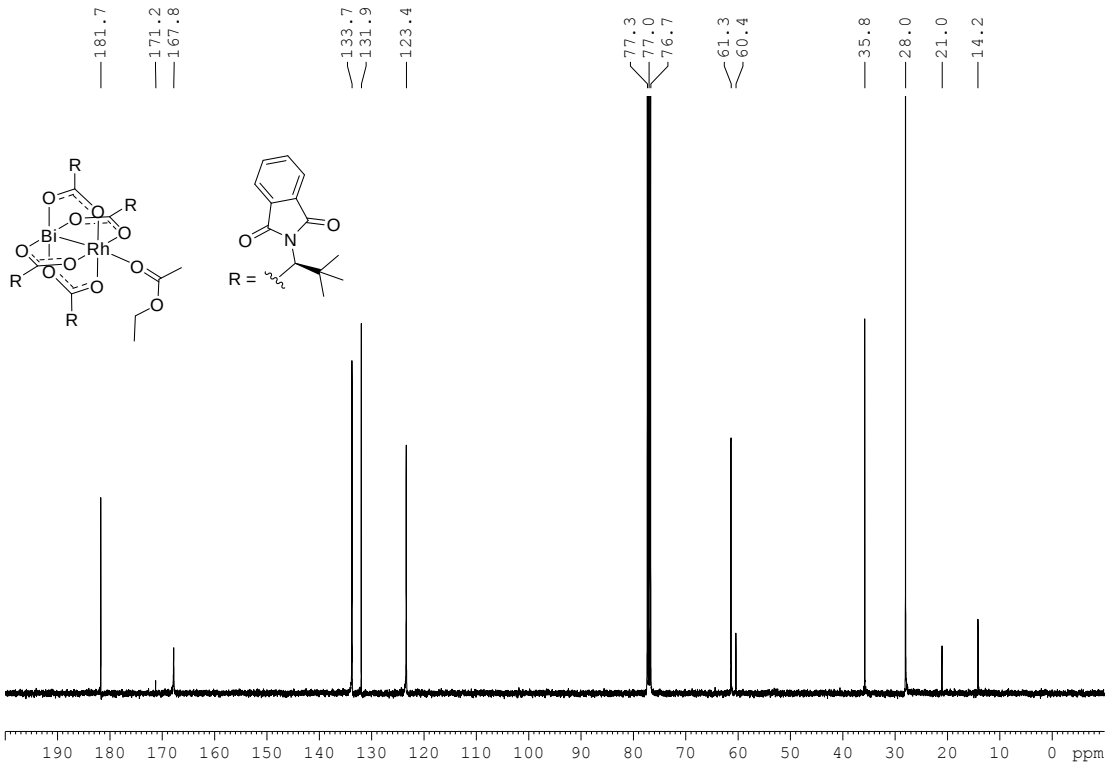


(S)-PTTL-H (^{1}H NMR (400 MHz, top); ^{13}C NMR (100 MHz, bottom, $CDCl_3$ each)

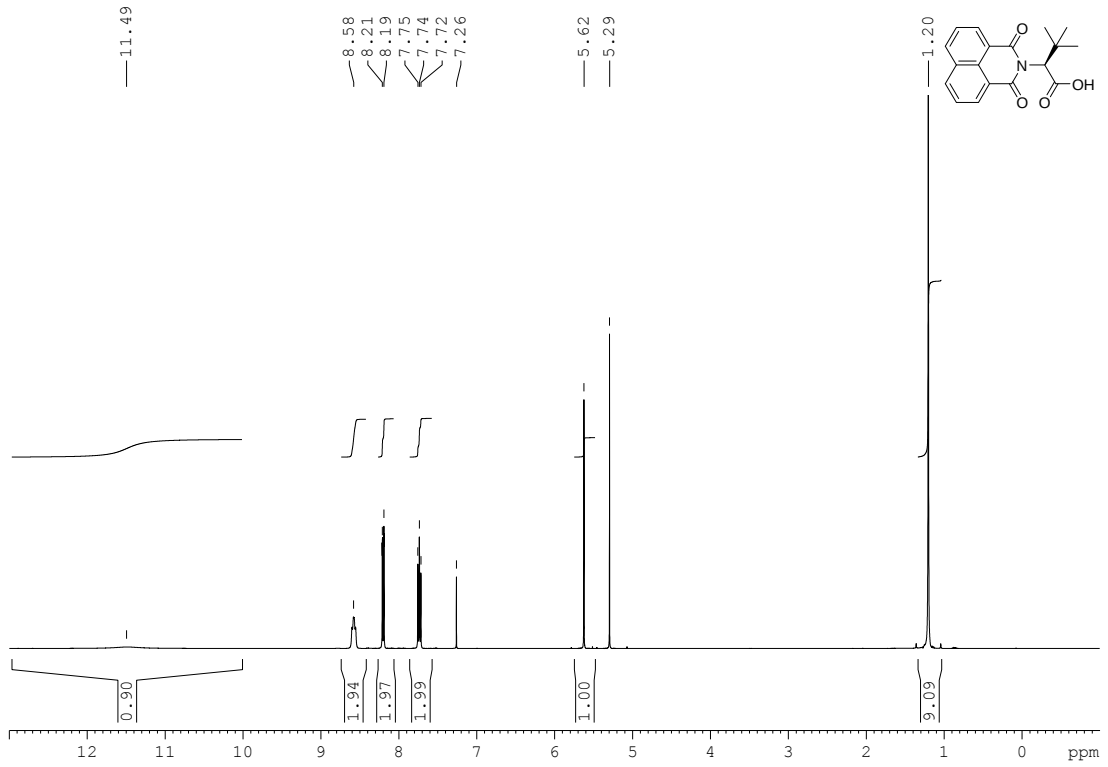


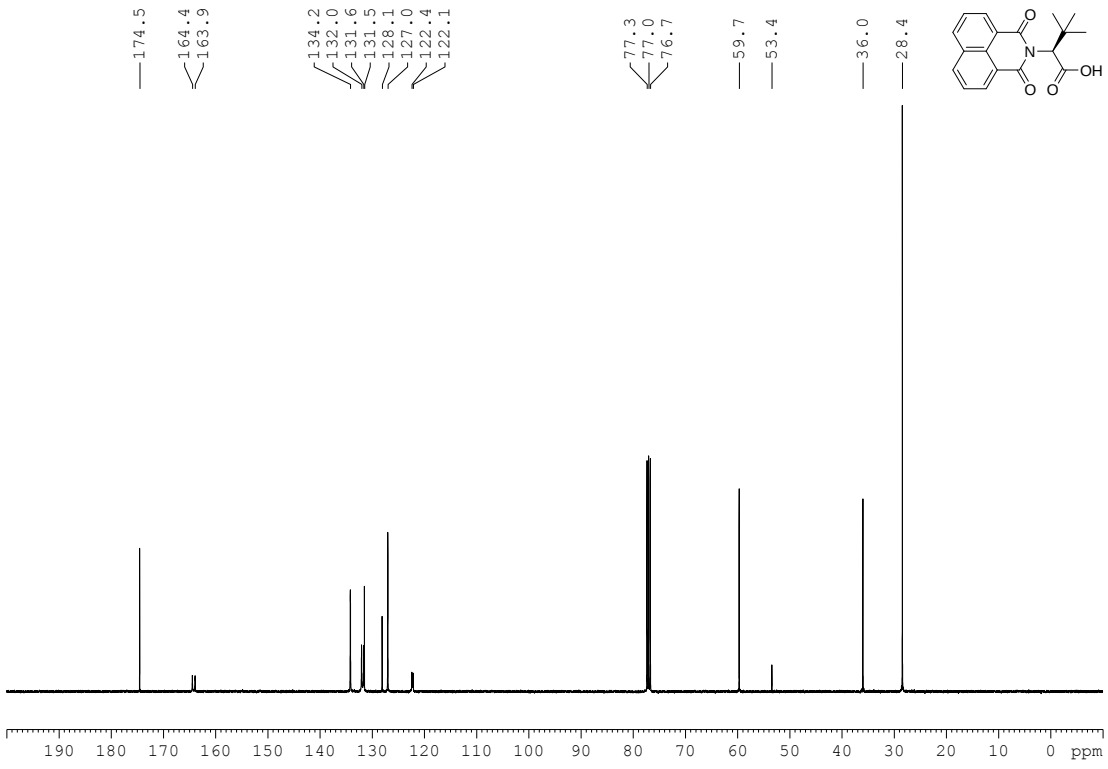
[BiRh((S)-PTTL)$_4$·EtOAc] (^{1}H NMR (400 MHz, top); ^{13}C NMR (100 MHz, bottom, $CDCl_3$ each)



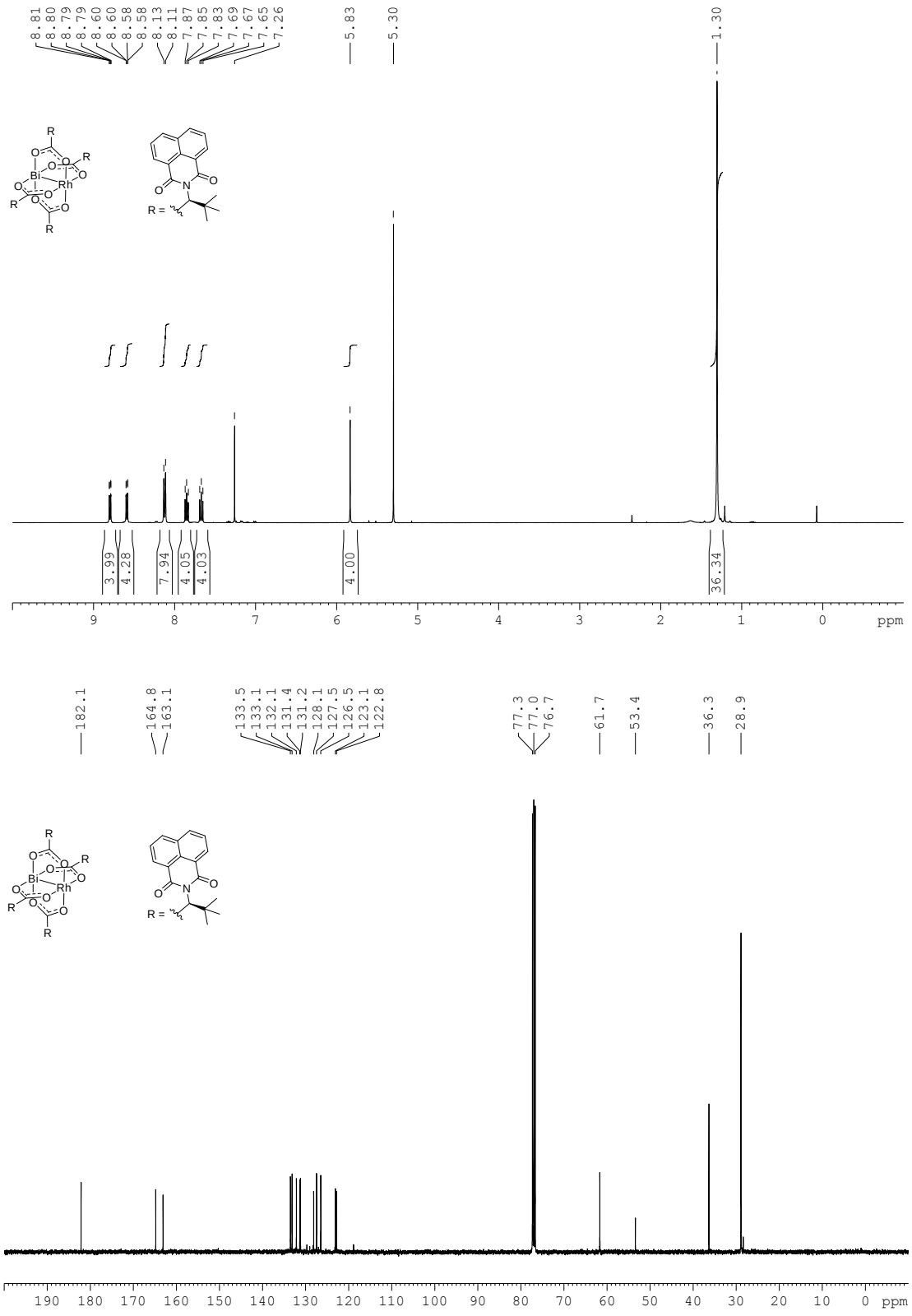


(*S*)-NTTL-H (^{1}H NMR (400 MHz, top); ^{13}C NMR (100 MHz, bottom, $CDCl_3$ each)

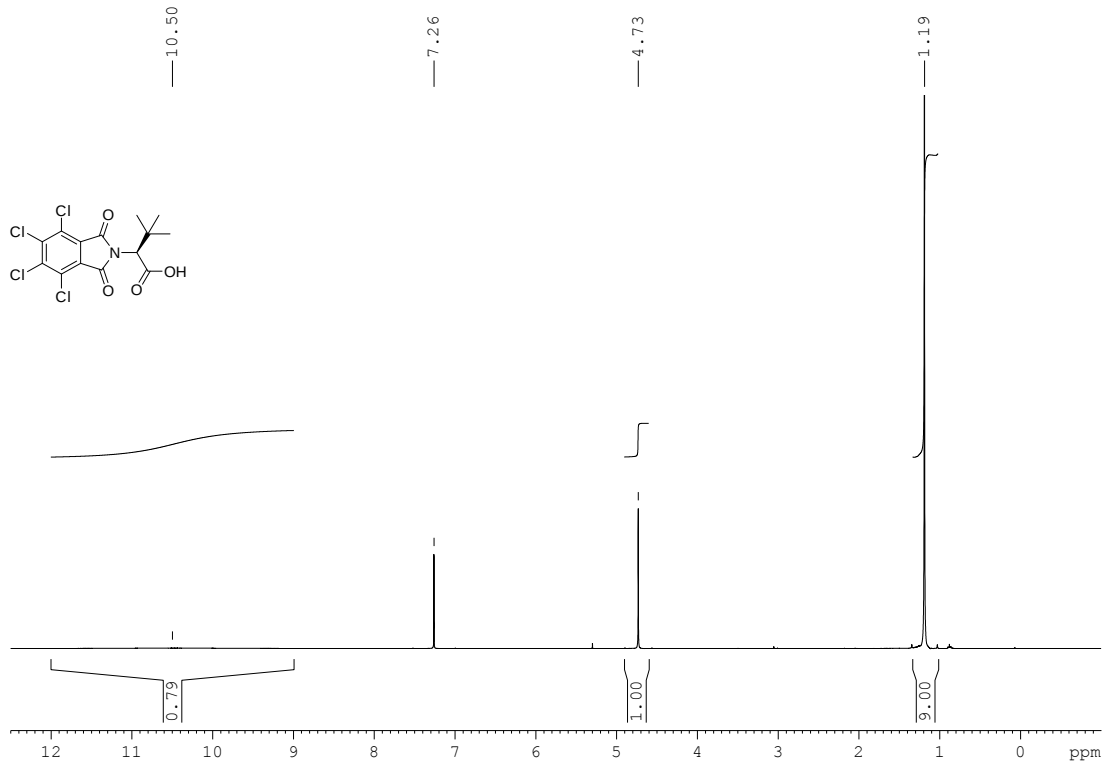


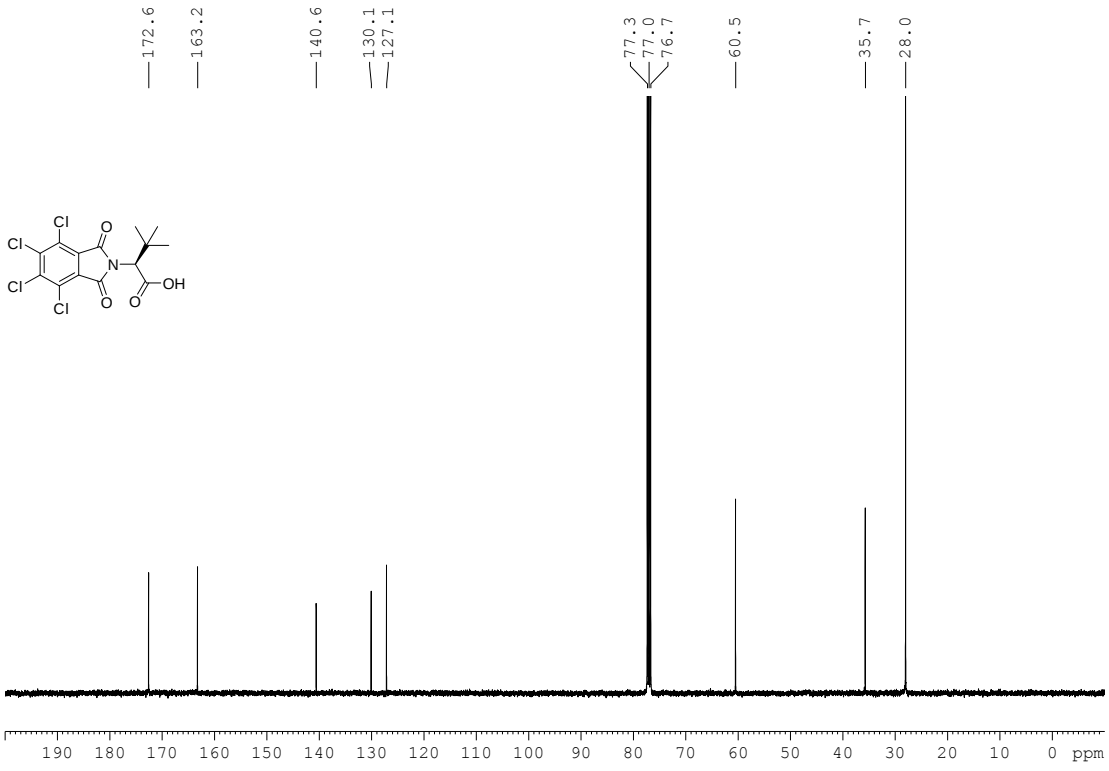


[BiRh((*S*)-NTTL)$_4$] (^{1}H NMR (400 MHz, top); ^{13}C NMR (100 MHz, bottom, $CDCl_3$ each)

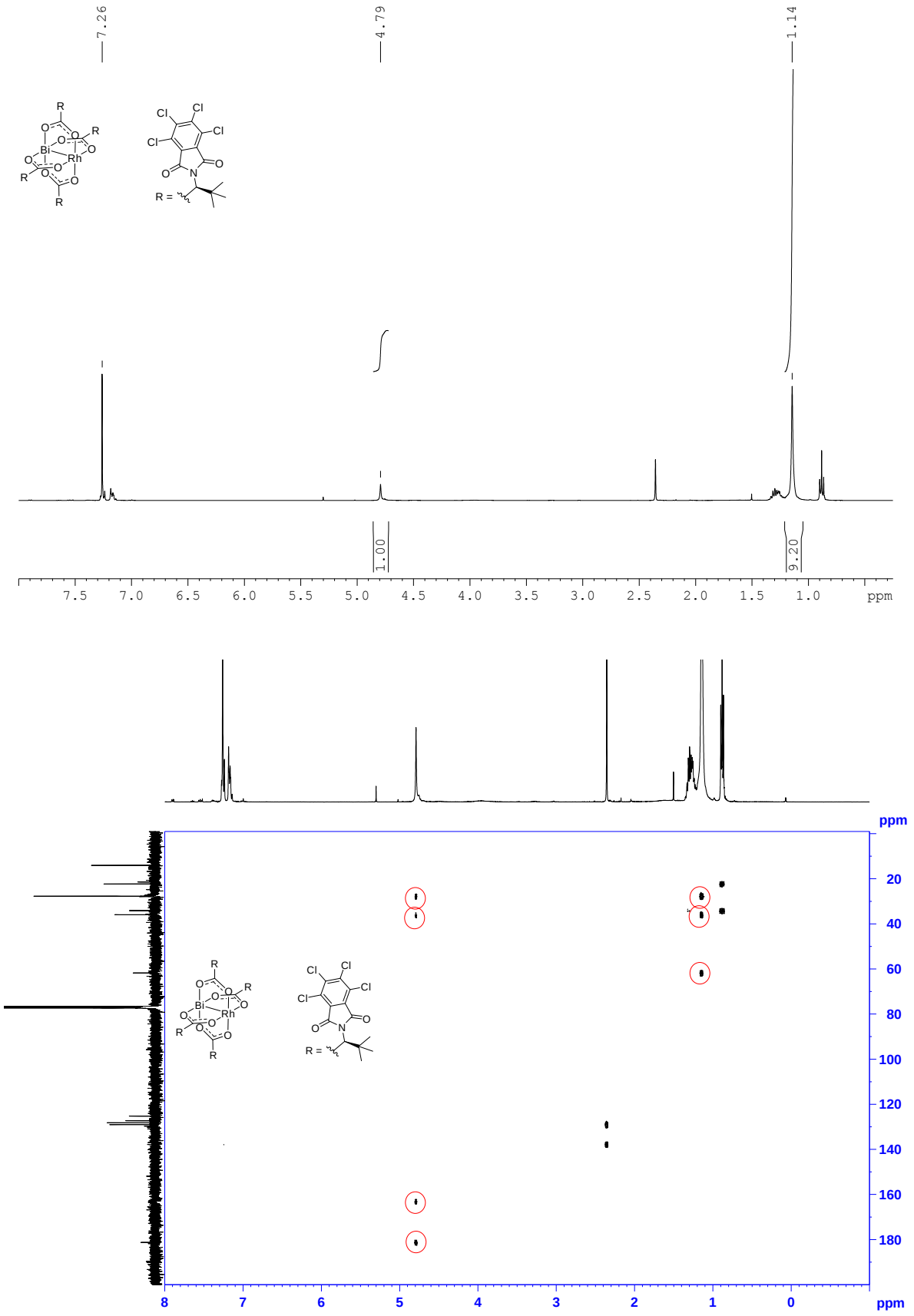


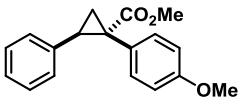
(S)-TCPTTL-H (^{1}H NMR (400 MHz, top); ^{13}C NMR (100 MHz, bottom, $CDCl_3$ each)





[BiRh((*S*)-TCPTTL)$_4$] (^{1}H NMR (400 MHz, top); HMBC (bottom, $CDCl_3$ each)



Representative Procedure for Cyclopropanation Reactions using [BiRh(S-PTTL)$_4$]. Methyl (1*S*,2*R*)-1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (4a). 

A solution of the diazo compound **2** (33.4 mg, 0.162 mmol) in pentane (2 mL) was added to a solution of [BiRh((S)-PTTL)$_4$]·EtOAc (**5a**·EtOAc) (2.3 mg, 0.0016 mmol) and styrene (93 µL, 0.81 mmol) in pentane (3 mL) at −10°C. The resulting mixture was stirred for 7 h at −40°C before all volatile materials were evaporated under reduced pressure. The residue was purified by flash chromatography (silica, hexane/EtOAc, 20:1) to give the title compound as a colorless amorphous solid (31.2 mg, 84%, 95% *ee*). The optical purity was determined by HPLC (Chiralpak IB, ∅ 4.6 mm, 2% 2-propanol in *n*-heptane, 1 mL/min, 20 min, UV 225 nm): t_R 7.65 min (major) and t_R 8.48 min (minor); $[\alpha]_D^{20}$ = +4.6 (c = 1.6, $CHCl_3$) [ref.:[12] $[\alpha]_D^{20}$ = +5.1 (c = 1, $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 – 7.04 (m, 3H), 6.96 – 6.91 (m, 2H), 6.80 – 6.74 (m, 2H), 6.69 – 6.63 (m, 2H), 3.72 (s, 3H), 3.66 (s, 3H), 3.07 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.12 (dd, *J* = 9.4, 4.8 Hz, 1H), 1.82 (dd, *J* = 7.2, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.8, 158.6, 136.6, 133.0, 128.2, 127.8, 126.9, 126.4, 113.3, 55.2, 52.8, 36.8, 33.3, 20.9. The recorded data are consistent with those reported in the literature.[12]

With other substrates, the reaction had to be carried out at −10°C for solubility reasons.

Representative Procedure for Cyclopropanation Reactions using [Rh$_2$(S-PTTL)$_4$]. Methyl (1*S*,2*R*)-1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (4a). A solution of the **t**he diazo compound **2** (20.3 mg, 0.098 mmol) in pentane (2 mL) was added to a solution of [Rh$_2$((S)-PTTL)$_4$] (**1a**) (1.4 mg, 0.001 mmol) and styrene (56.5 µL, 0.49 mmol) in pentane (2 mL) at −40°C. The resulting mixture was stirred for 4 h at −40°C before all volatile materials were evaporated under reduced pressure. The residue was purified by flash chromatography (silica, hexane/EtOAc, 20:1) to give the title compound as a colorless amorphous solid (25.6 mg, 92%, 79% *ee*).

Representative Procedure for the Synthesis of Racemic Cyclopropanes. Methyl *rac*-1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (*rac*-4a). A solulution of the diazo compound **2** (31.1 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) was added to a solution of [Rh$_2$(OAc)$_4$] (2 mg, 0.0045 mmol) and styrene (86.7 µL, 0.754 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was stirred for 2 h at ambient temperature before all volatile materials were evaporated under reduced pressure. The residue was purified by flash chromatography (silica, hexane/EtOAc, 20:1) to give *rac*-**4a** as a colorless amorphous solid.

The following compounds were prepared analogously:

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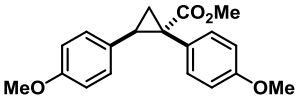
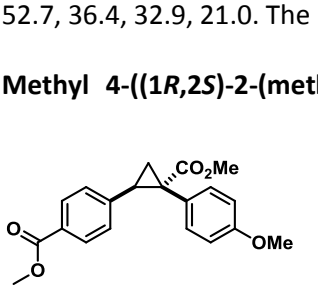
[12] K. M. Chepiga, C. Qin, J. S. Alford, S. Chennamadhavuni, T. M. Gregg, J. P. Olson, H. M. L. Davies *Tetrahedron* **2013**, *69*, 5765-5771.

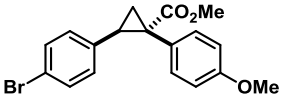
Methyl (1*S*,2*R*)-1,2-bis(4-methoxyphenyl)cyclopropane-1-carboxylate (4b): Colorless amorphous solid: with **Rh_2(*S*-PTTL)$_4$**: 88% yield, 59% *ee*; with **BiRh(*S*-PTTL)$_4$** at −10°C: 91% yield, 73% *ee* [HPLC (Chiralpak IC-3, ∅ 4.6 mm, 5% 2-propanol in *n*-heptane, 1 mL/min, 20 min, UV 230 nm): t_R 10.37 min (major) and t_R 11.57 (minor)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 – 6.91 (m, 2H), 6.72 – 6.65 (m, 4H), 6.64 – 6.59 (m, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 3.65 (s, 3H), 3.02 (dd, *J* = 9.4, 7.3 Hz, 1H), 2.10 (dd, *J* = 9.5, 4.8 Hz, 1H), 1.75 (dd, *J* = 7.4, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.9, 158.5, 158.2, 133.1, 129.2, 128.6, 127.1, 113.3, 113.3, 55.3, 55.2, 52.7, 36.4, 32.9, 21.0. The recorded data are consistent with those reported in the literature.[13]



Methyl 4-((1*R*,2*S*)-2-(methoxycarbonyl)-2-(4-methoxyphenyl)cyclopropyl)benzoate (4c): Colorless amorphous solid: with **Rh_2(*S*-PTTL)$_4$**: 68% yield, 65% *ee*; with **BiRh(*S*-PTTL)$_4$** at −10°C: 92% yield, 88% *ee* [HPLC (Chiralpak IC-3, ∅ 4.6 mm, 10% 2-propanol in *n*-heptane, 1 mL/min, 30 min, UV 230 nm): t_R 17.20 min (minor) and t_R 20.04 (major)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 – 6.91 (m, 2H), 6.83 – 6.74 (m, 4H), 6.70 – 6.66 (m, 2H), 3.73 (s, 3H), 3.66 (s, 3H), 3.06 (dd, *J* = 9.4, 7.2 Hz, 1H), 2.23 (s, 2H), 2.12 (dd, *J* = 9.4, 4.9 Hz, 1H), 1.77 (dd, *J* = 7.2, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.6, 169.4, 158.6, 149.2, 134.3, 133.0, 129.1, 126.7, 120.9, 113.4, 55.2, 52.8, 36.8, 32.7, 21.2, 21.2; IR ($CHCl_3$): $\tilde{\nu}$ = 3013, 2953, 2838, 1760, 1713, 1612, 1513, 1245, 1159, 1032, 752, 565; EI *m/z* (%): 340 (57), 281 (21), 266 (76), 239 (100), 137 (25); HRMS (ESI$^+$) *m/z* calcd. for $C_{20}H_{21}O_5$ $[M+H]^+$: 341.13861, found: 341.13858.



Methyl (1*S*,2*R*)-2-(4-bromophenyl)-1-(4-methoxyphenyl)cyclopropane-1-carboxylate (4d): Colorless amorphous solid: with **Rh_2(*S*-PTTL)$_4$**: 93% yield, 76% *ee*; with **BiRh(*S*-PTTL)$_4$** at −10°C: 68% yield, 92% *ee* [HPLC (Chiralpak IC-3, ∅ 4.6 mm, 2% 2-propanol in *n*-heptane, 1 mL/min, 20 min, UV 230 nm): t_R 9.34 min (major) and t_R 10.70 min (minor)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 – 7.16 (m, 2H), 6.95 – 6.90 (m, 2H), 6.72 – 6.67 (m, 2H), 6.65 – 6.61 (m, 2H), 3.74 (s, 3H), 3.66 (s, 3H), 3.01 (dd, *J* = 9.3, 7.2 Hz, 1H), 2.12 (dd, *J* = 9.4, 4.9 Hz, 1H), 1.76 (dd, *J* = 7.2, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.5, 158.7, 135.9, 133.0, 130.9, 129.8, 126.5, 120.3, 113.5, 77.5, 77.4, 77.2, 76.8, 55.2, 52.8, 36.9, 32.6, 21.1; IR (solid): $\tilde{\nu}$ = 3004, 2951, 2836, 1713, 1515, 1253, 1159, 1032, 800, 751, 558; EI *m/z* (%): 360 (78), 345 (18), 330 (40), 301 (86), 249 (46), 222 (100), 207 (23), 178 (32), 110 (30); HRMS (ESI$^+$) *m/z* calcd. for $C_{18}H_{18}O_3$ $[M+H]^+$: 361.04372, found: 361.04340.



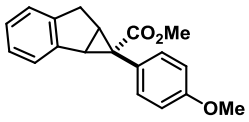
[13] H. M. L. Davies, S. A. Panaro, *Tetrahedron* **2000**, *56*, 4871-4880.

Methyl (1*S*,2*R*)-2-(4-fluorophenyl)-1-(4-methoxyphenyl)cyclopropane-1-carboxylate (4e): Colorless amorphous solid: with **Rh_2(*S*-PTTL)$_4$**: 94% yield, 78% *ee*; with **BiRh(*S*-PTTL)$_4$** at −10°C: 78% yield, 92% *ee* [HPLC (Chiralpak IC-3, ∅ 4.6 mm, 5% 2-propanol in *n*-heptane, 1 mL/min, 13 min, UV 230 nm): t_R 6.31 min (major) and t_R 6.99 min (minor)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 – 6.89 (m, 2H), 6.80 – 6.71 (m, 4H), 6.69 – 6.65 (m, 2H), 3.73 (s, 3H), 3.66 (s, 3H), 3.05 (dd, *J* = 9.4, 7.2 Hz, 1H), 2.11 (dd, *J* = 9.4, 4.9 Hz, 1H), 1.76 (dd, *J* = 7.2, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.7, 162.8, 160.4, 158.6, 133.0, 132.4, 132.3, 129.6, 129.5, 126.7, 114.9, 114.7, 113.4, 55.2, 52.8, 36.6, 32.6, 21.0; IR ($CHCl_3$): $\tilde{\nu}$ = 3015, 2953, 1712, 1513, 1246, 1160, 838, 751, 539; EI *m/z* (%): 300 (46), 268 (49), 241 (90), 225 (44), 196 (45), 133 (100), 109 (52); HRMS (ESI$^+$) *m/z* calcd. for $C_{18}H_{17}O_3F$ $[M+H]^+$: 300.11581, found: 300.11562.

Methyl (1*S*,2*R*)-2-(4-(*tert*-butyl)phenyl)-1-(4-methoxyphenyl)cyclopropane-1-carboxylate (4f): Colorless amorphous solid: with **Rh_2(*S*-PTTL)$_4$**: 90% yield, 95% *ee*; with **BiRh(*S*-PTTL)$_4$**: 95% yield, 98% *ee* [HPLC (Chiralpak IC-3, ∅ 4.6 mm, 2% 2-propanol in *n*-heptane, 1 mL/min, 14 min, UV 230 nm): t_R 7.38 min (major) and t_R 9.60 (minor)]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.11 – 7.06 (m, 2H), 6.96 – 6.91 (m, 2H), 6.70 – 6.65 (m, 4H), 3.73 (s, 3H), 3.66 (s, 3H), 3.03 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.11 (dd, *J* = 9.4, 4.8 Hz, 1H), 1.77 (dd, *J* = 7.3, 4.8 Hz, 1H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.9, 158.5, 149.3, 133.6, 133.1, 127.8, 127.2, 124.7, 113.2, 55.2, 52.7, 36.7, 34.4, 33.1, 31.4, 21.3; IR (solid): $\tilde{\nu}$ = 3018, 2961, 1713, 1515, 1246, 1215, 752, 667, 571; EI *m/z* (%): 338 (100), 279 (61), 250 (77), 221 (35), 177 (32), 117 (22), 57 (41); HRMS (ESI$^+$) *m/z* calcd. for $C_{22}H_{27}O_3$ $[M+H]^+$: 339.19558, found: 339.19547.

Methyl (1*S*,2S)-2-(2-bromophenyl)-1-(4-methoxyphenyl)cyclopropane-1-carboxylate (4g): Colorless amorphous solid: with **Rh_2(*S*-PTTL)$_4$**: 65% yield, 78% *ee*; **BiRh(*S*-PTTL)$_4$**: 79% yield, 93% *ee* [HPLC (Chiralpak IC-3, ∅ 4.6 mm, 2% 2-propanol in *n*-heptane, 1 mL/min, 15 min, UV 230 nm): t_R 9.87 min (minor) and t_R 11.12 (major)]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 – 7.47 (m, 1H), 7.09 – 6.99 (m, 2H), 6.96 – 6.85 (m, 2H), 6.67 – 6.58 (m, 2H), 6.57 – 6.45 (m, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.32 (dd, *J* = 9.2, 7.5 Hz, 1H), 2.09 (dd, *J* = 9.1, 5.0 Hz, 1H), 1.97 (dd, *J* = 7.5, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.4, 158.5, 136.1, 132.5, 128.1, 127.9, 127.2, 126.9, 113.2, 55.2, 52.8, 36.0, 34.3, 19.2; IR ($CHCl_3$): $\tilde{\nu}$ = 2951, 2837, 1718, 1613, 1516, 1437, 1253, 1164, 1032, 747, 561; EI *m/z* (%): 360 (16), 301 (62), 249 (53), 222 (100), 178 (66), 152 (21), 133 (15); HRMS (GC-EI) *m/z* calcd. for $C_{18}H_{17}O_3Br$: 360.03571, found: 360.03557.

Methyl (1*S*,1a*R*,6a*R*)-1-(4-methoxyphenyl)-1,1a,6,6a-tetrahydrocyclopropa[a]indene-1-carboxylate

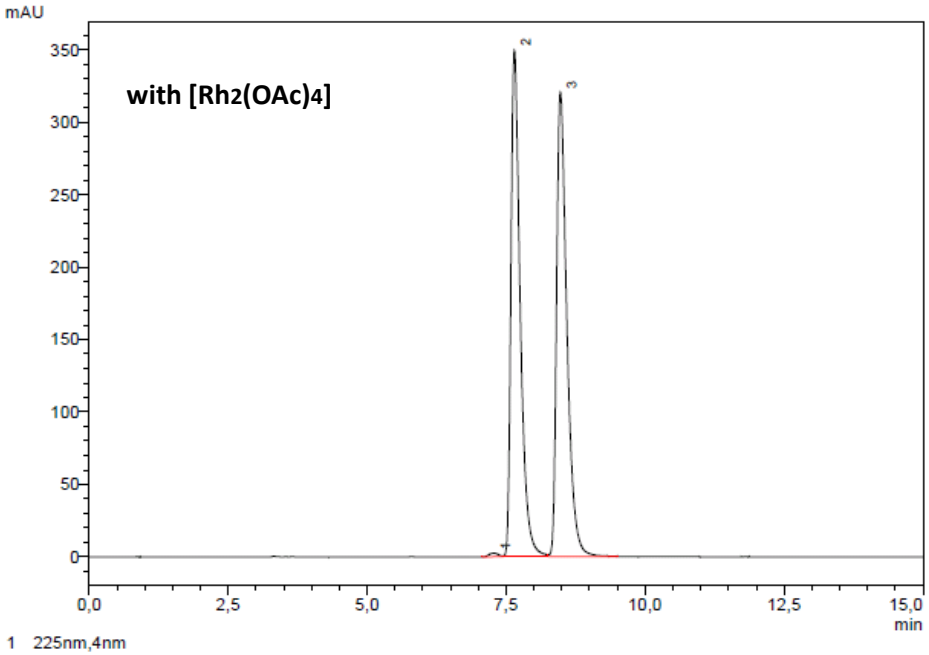


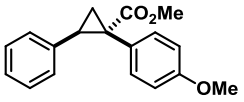
(4h): Colorless amorphous solid: with **Rh_2(*S*-PTTL)$_4$**: 90% yield, 90% *ee*; with **BiRh(*S*-PTTL)$_4$** at −10°C: 91% yield, 96% *ee* [HPLC (Chiralpak IC-3, ∅ 4.6 mm, 5% 2-propanol in *n*-heptane, 1 mL/min, 16 min, UV 230 nm): t_R 7.77 min (minor) and t_R 8.67 (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.92 (td, *J* = 7.5, 1.4 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 9.0 Hz, 2H), 3.67 (s, 3H), 3.63 (s, 3H), 3.44 (dd, *J* = 6.8, 1.3 Hz, 1H), 3.21 (dd, *J* = 17.9, 6.8 Hz, 1H), 2.83 (t, *J* = 6.7 Hz, 1H), 2.72 (d, *J* = 17.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.5, 158.1, 143.3, 141.6, 133.3, 126.4, 126.2, 125.0, 124.3, 124.3, 113.1, 55.1, 52.7, 40.9, 37.7, 33.3, 32.3; IR ($CHCl_3$): $\tilde{\nu}$ = 3021, 2951, 2836, 1711, 1612, 1514, 1242, 1219, 1173, 1032, 751, 550; EI *m/z* (%): 294 (44), 262 (41), 234 (100), 219 (65), 203 (67), 191 (60), 165 (41), 117 (36); HRMS (EI): *m/z* calcd. for $C_{19}H_{18}O_3$: 294.12537, found: 294.12505.

Methyl (1*S*,2*R*)-1-(4-fluorophenyl)-2-phenylcyclopropane-1-carboxylate (4i): Colourless amorphous solid: with **Rh_2(*S*-PTTL)$_4$** (at −40°C): 90% yield, 32% ee; with **BiRh(*S*-PTTL)$_4$**: 93% yield, 35% ee [HPLC (Chiralpak IB, ∅ 4.6 mm, 2% 2-propanol in *n*-heptane, 1 mL/min, 10 min, UV 220 nm): t_R 5.67 min (minor) and t_R 6.31 (major)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (dd, *J* = 4.8, 2.0 Hz, 3H), 7.02 – 6.96 (m, 2H), 6.82 (t, *J* = 8.7 Hz, 2H), 6.79 – 6.74 (m, 2H), 3.67 (s, 3H), 3.11 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.15 (dd, *J* = 9.4, 4.9 Hz, 1H), 1.85 (dd, *J* = 7.4, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.2, 163.1, 160.6, 136.2, 133.6, 133.5, 130.8, 130.7, 128.2, 128.2, 128.0, 128.0, 126.6, 114.9, 114.7, 52.8, 36.7, 33.3, 20.6; ^{19}F (282 MHz, $CDCl_3$): δ = −115,0; IR (solid): $\tilde{\nu}$ = 3033, 2952, 1719, 1605, 1513, 1434, 1259, 1221, 1161, 1089, 745, 697, 550; EI *m/z* (%): 270 (63), 238 (60), 211 (100), 196 (26), 183 (18), 133 (56), 121 (70), 115 (46), 91 (35); HRMS (GC-EI) *m/z* calcd. for $C_{17}H_{15}O_2F$: 270.10524, found: 270.10506.

Methyl (1*S*,2*R*)-1-(benzo[d][1,3]dioxol-5-yl)-2-phenylcyclopropane-1-carboxylate (4j): Colorless amorphous solid: with **Rh_2(*S*-PTTL)$_4$**: 80% yield, 59% *ee*; with **BiRh(*S*-PTTL)$_4$**: 87% yield, 73% *ee* [HPLC (Chiralpak IB, ∅ 4.6 mm, 5% 2-propanol in *n*-heptane, 1 mL/min, 15 min, UV 225 nm): t_R 6.86 min (major) and t_R 8.01 (minor)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 – 7.06 (m, 3H), 6.87 – 6.76 (m, 2H), 6.70 – 6.39 (m, 3H), 5.86 (d, *J* = 6.8 Hz, 2H), 3.67 (s, 3H), 3.07 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.10 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.81 (dd, *J* = 7.3, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.5, 147.1, 146.6, 136.4, 128.6, 128.2, 127.9, 126.5, 125.4, 112.4, 107.7, 101.0, 52.8, 37.2, 33.4, 21.1; IR (solid): $\tilde{\nu}$ = 2951, 2894, 1712, 1490, 1435, 1249, 1229, 1210, 1143, 1035, 934, 696, 630; EI *m/z* (%): 296 (50), 264 (94), 237 (60), 207 (70), 178 (100), 165 (19), 152 (32), 121 (27), 89 (21), 77 (18); HRMS (GC-EI) *m/z* calcd. for $C_{18}H_{16}O_4$: 296.10447, found: 296.10431.

Asymmetric Cyclopropenation. Methyl (*R*)-1-(4-methoxyphenyl)-2-phenylcycloprop-2-ene-1-carboxylate (4k):[14] A solution of methyl 2-diazo-2-(4-methoxyphenyl)acetate (25 mg, 0,121 mmol) in pentane (2 mL) was added to a solution of BiRh(*S*-PTTL)$_4$ or Rh$_2$(*S*-PTTL)$_4$ (1 mol%) and phenylacetylene (67 µL, 0,610 mmol) in pentane (2 mL) at –10 °C. After stirring for 2 h, all volatile materials were evaporated and the residue was purified by flash chromatography (silica, hexane/ethyl acetate, 10:1) to give the title compound as a yellow syrup: with **Rh$_2$(*S*-PTTL)$_4$**: 45% yield, 72% ee; with **BiRh(*S*-PTTL)$_4$**: 56% yield, 92% ee [HPLC (Chiralpak IB, ∅ 4.6 mm, 2% 2-propanol in *n*-heptane, 1 mL/min, 10 min, UV 230 nm): t_R 12.20 min (major) and t_R 14.10 (minor)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.46 – 7.38 (m, 3H), 7.33 – 7.29 (m, 2H), 7.21 (s, 1H), 6.85 – 6.81 (m, 2H), 3.77 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.4, 158.4, 133.2, 130.1, 130.0, 129.4, 129.0, 125.7, 117.8, 113.7, 100.7, 55.4, 52.4, 33.1; IR (solid): $\tilde{\nu}$ = 3131, 2950, 2836, 1716, 1611, 1511, 1446, 1287, 1246, 1221, 1177, 1025, 833, 769, 700; EI *m/z* (%): 280 (38), 248 (14), 221 (100), 206 (24), 178 (50), 152 (13), 59 (8); HRMS (GC-EI) *m/z* calcd. for $C_{18}H_{16}O_3$: 280.10930, found: 280.10939.

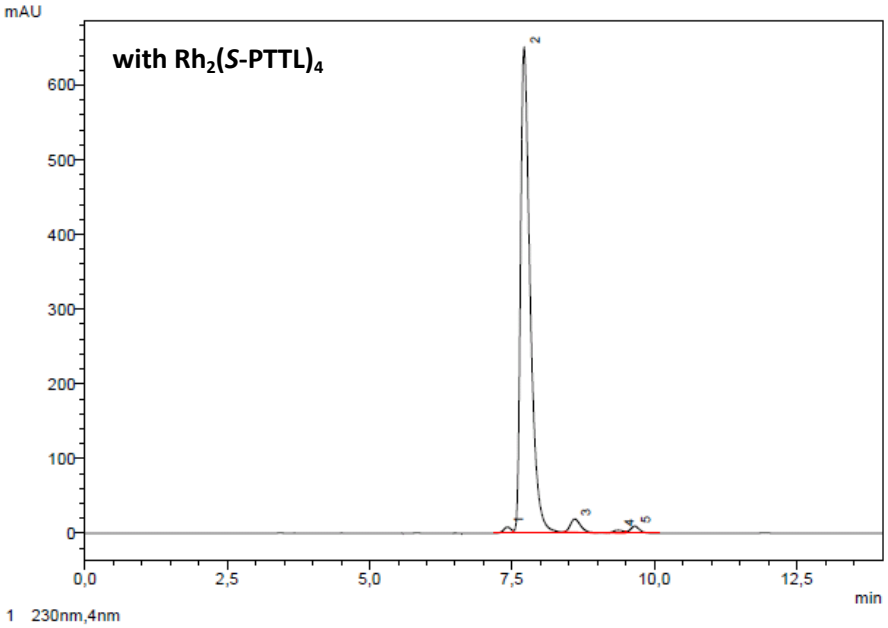




PDA Ch1 225nm

Peak #	Ret. Time	Area %
1	7,28	0,36
2	7,65	49,46
3	8,48	50,18
Total		100,00

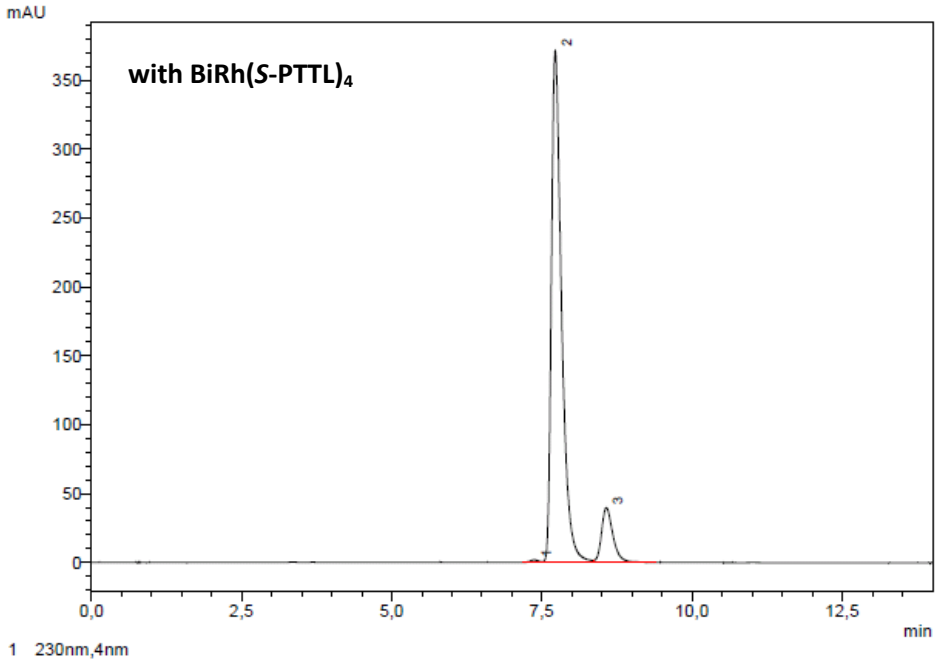
[14] H. M. L. Davies, G. H. Lee, *Org. Lett*. **2004**, *6*, 1233-1236.



1 230nm,4nm

PDA Ch1 230nm

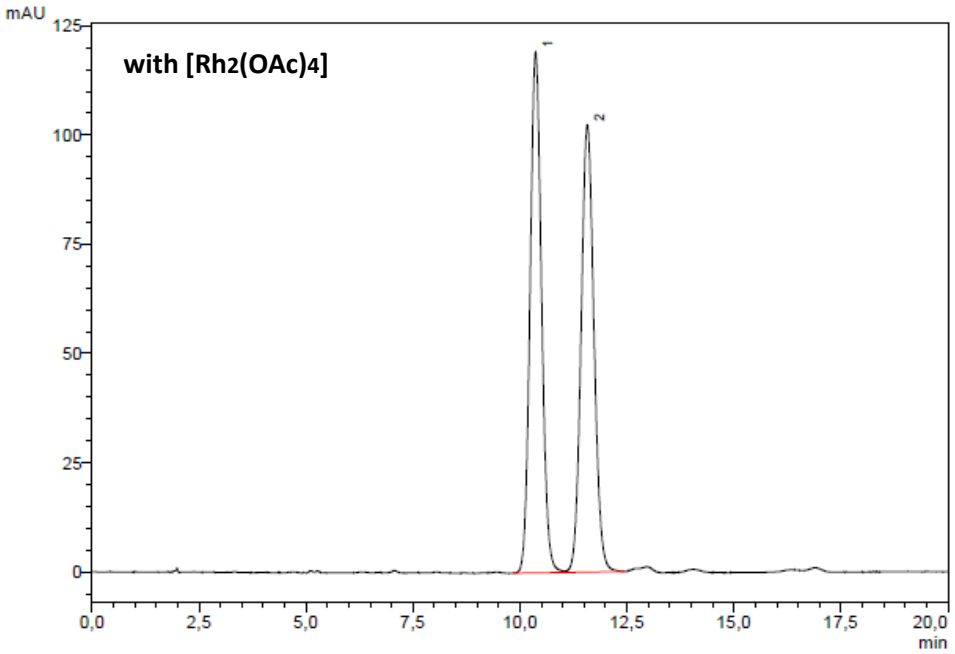
Peak #	Ret. Time	Area %
1	7,42	0,96
2	7,71	94,51
3	8,60	2,67
4	9,37	0,58
5	9,65	1,28
Total		100,00

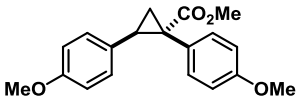


1 230nm,4nm

PDA Ch1 230nm

Peak #	Ret. Time	Area %
1	7,37	0,34
2	7,72	88,97
3	8,57	10,69
Total		100,00

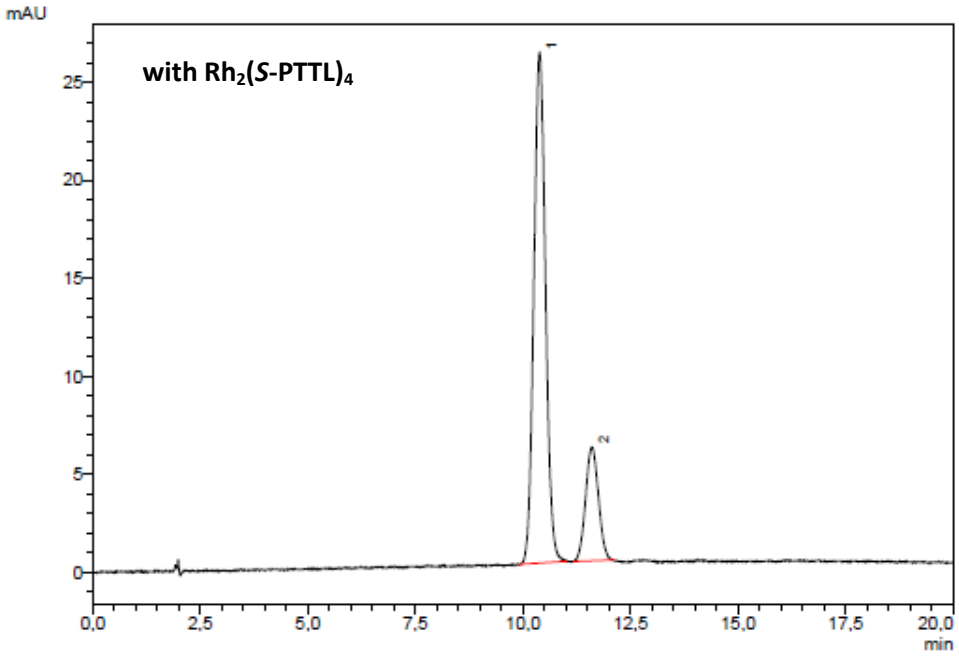




1 230nm,4nm

PDA Ch1 230nm

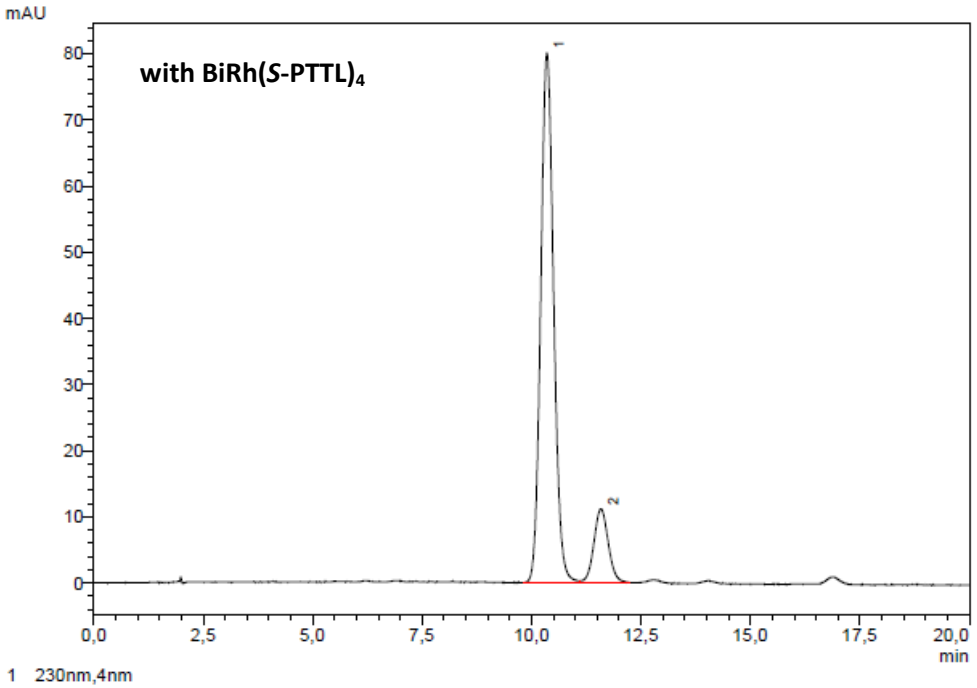
Peak #	Ret. Time	Area %
1	10,37	50,90
2	11,57	49,10
Total		100,00



1 230nm,4nm

PDA Ch1 230nm

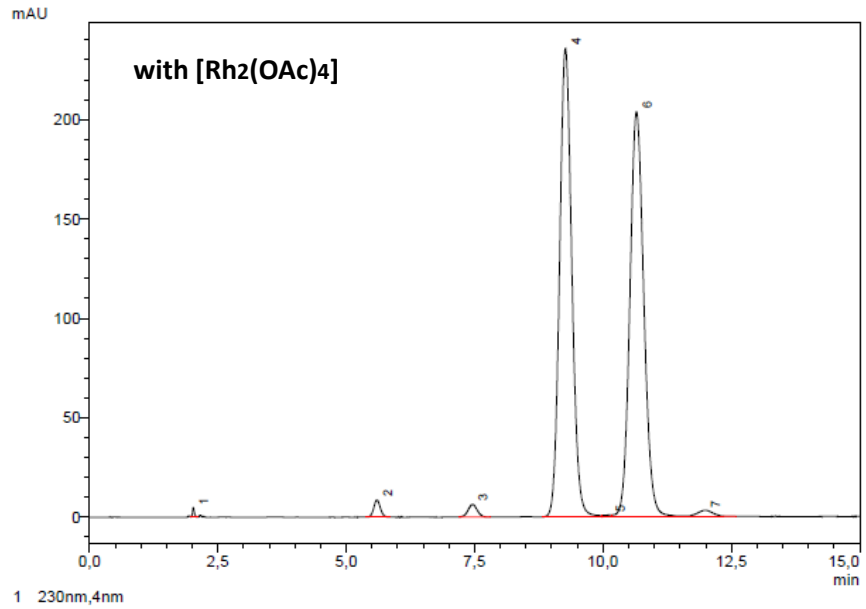
Peak #	Ret. Time	Area %
1	10,39	80,23
2	11,61	19,77
Total		100,00

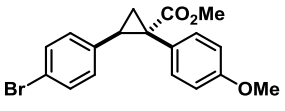


1 230nm,4nm

PDA Ch1 230nm

Peak #	Ret. Time	Area %
1	10,35	86,61
2	11,59	13,39
Total		100,00

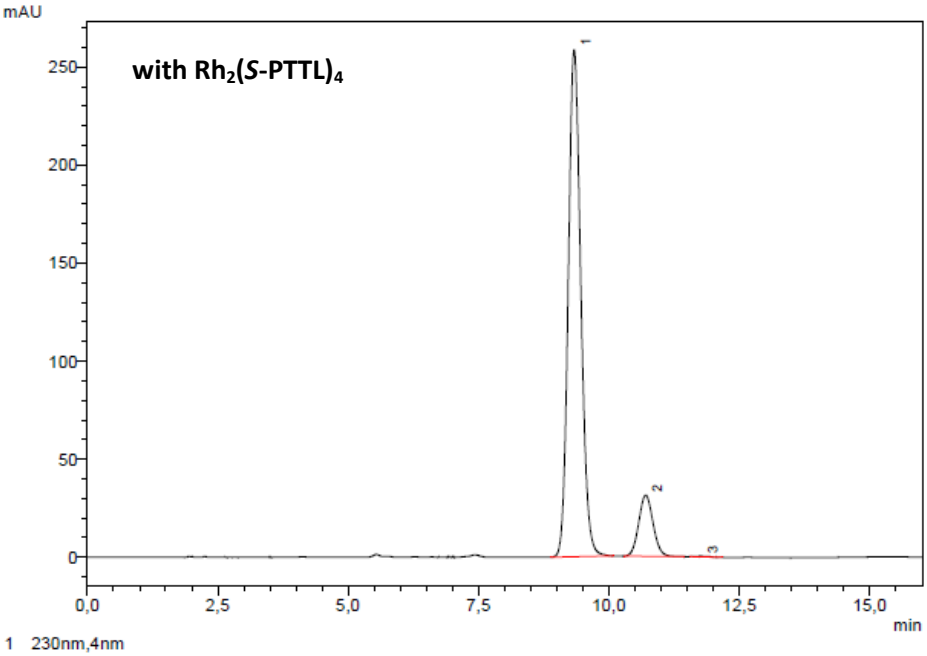




1 230nm,4nm

PDA Ch1 230nm

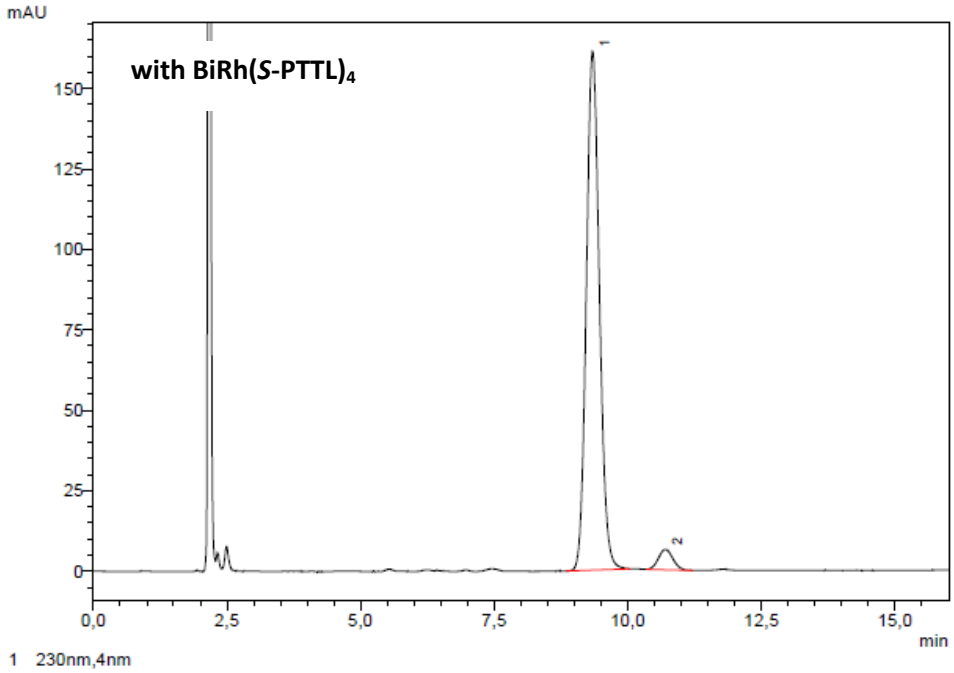
Peak #	Ret. Time	Area %	Name
1	2,02	0,14	
2	5,60	0,95	
3	7,46	0,96	
4	9,27	48,78	1. Enantiomer
5	10,14	0,12	
6	10,65	48,18	2. Enantiomer
7	11,99	0,85	
Total		100,00	



1 230nm,4nm

PDA Ch1 230nm

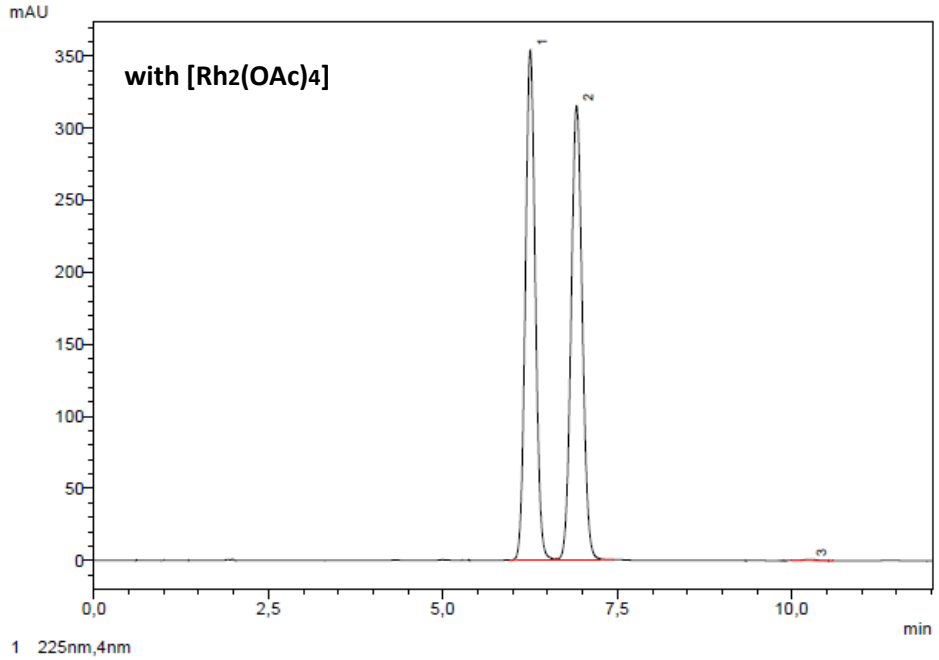
Peak #	Ret. Time	Area %
1	9,33	87,81
2	10,70	12,06
3	11,77	0,13
Total		100,00

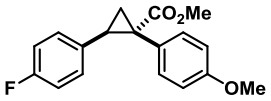


1 230nm,4nm

PDA Ch1 230nm

Peak #	Ret. Time	Area %
1	9,34	95,82
2	10,70	4,18
Total		100,00

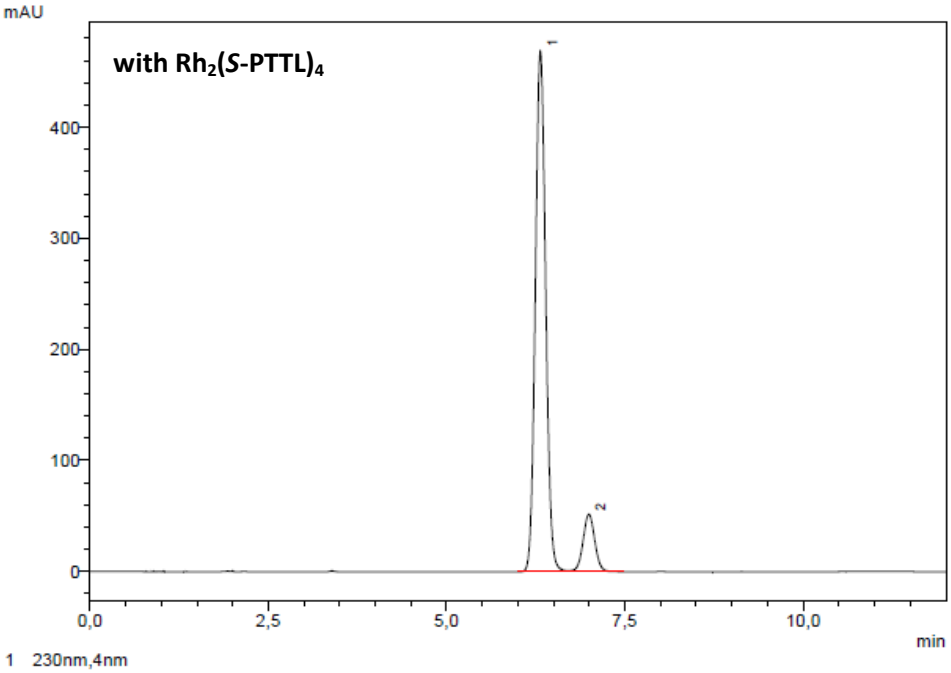




1 225nm,4nm

PDA Ch1 225nm

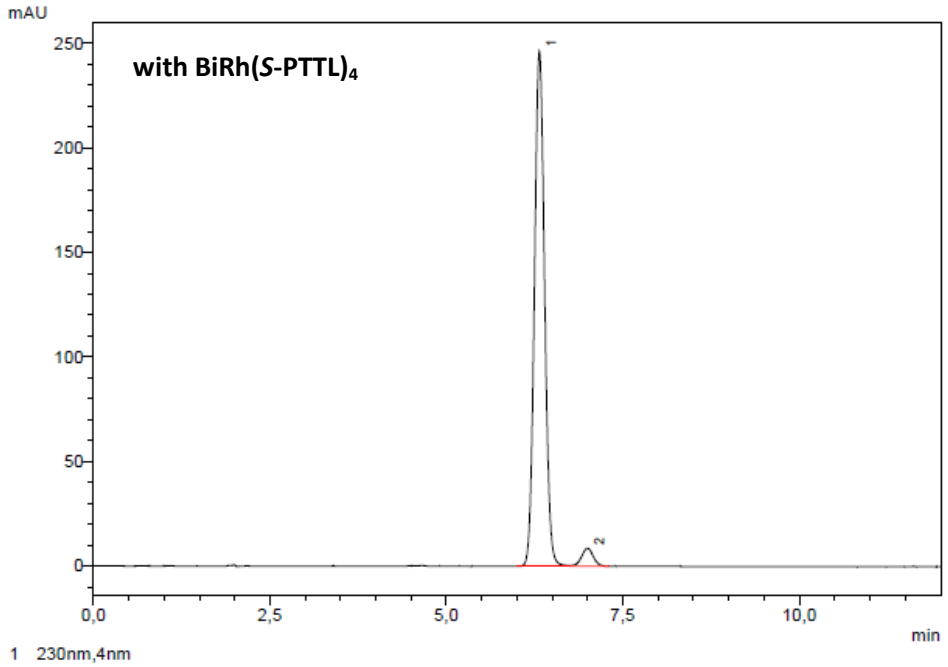
Peak #	Ret. Time	Area %	Name
1	6,25	49,90	1. Enantiomer
2	6,91	49,96	2. Enantiomer
3	10,25	0,14	
Total		100,00	



1 230nm,4nm

PDA Ch1 230nm

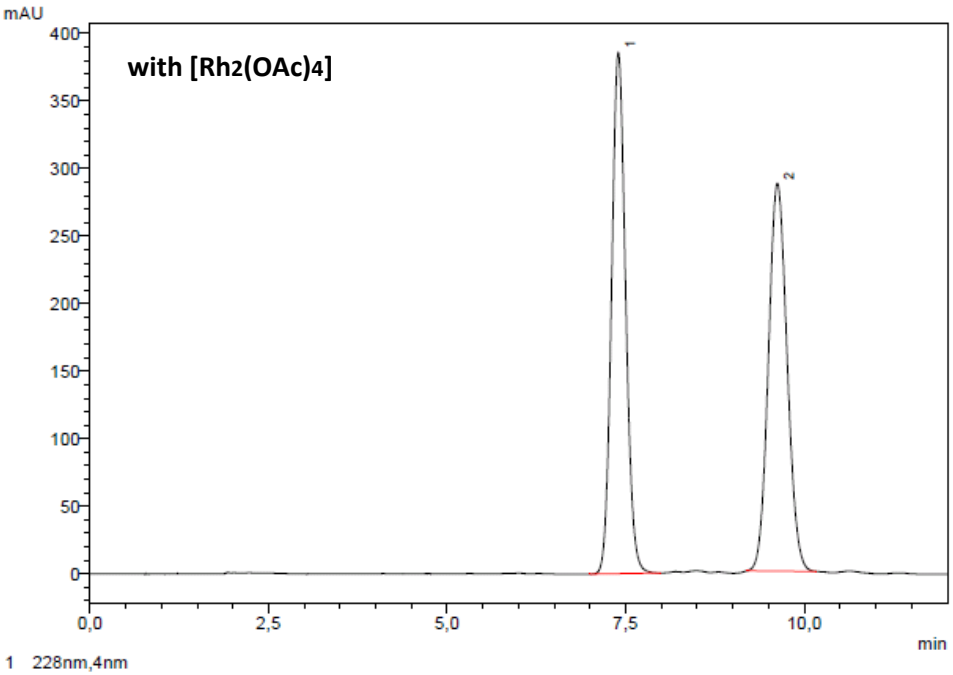
Peak #	Ret. Time	Area %
1	6,31	88,82
2	6,99	11,18
Total		100,00

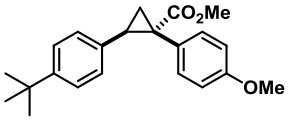


1 230nm,4nm

PDA Ch1 230nm

Peak #	Ret. Time	Area %
1	6,32	96,15
2	7,00	3,85
Total		100,00

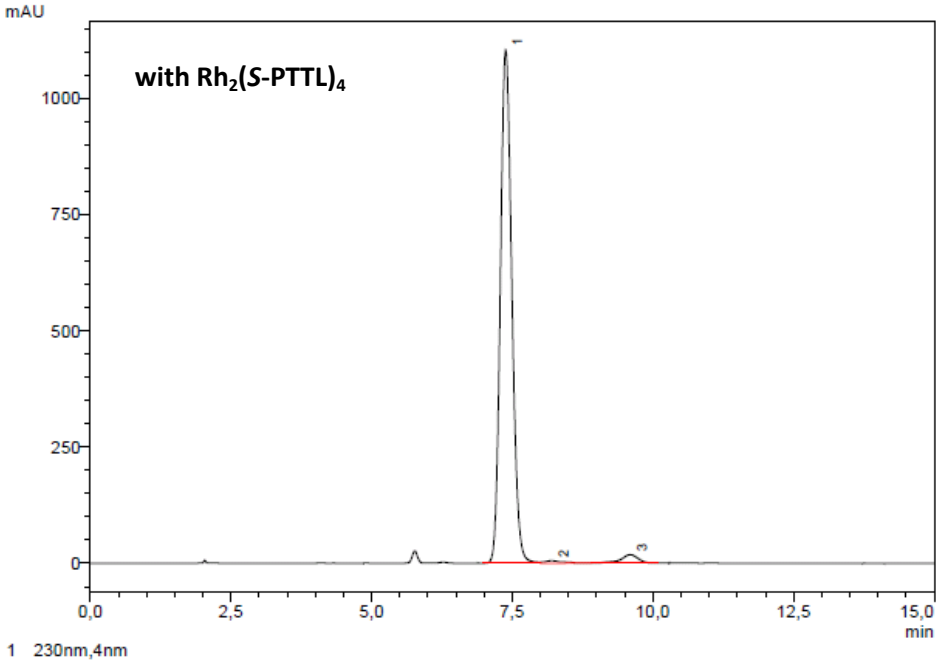




1 228nm,4nm

PDA Ch1 228nm

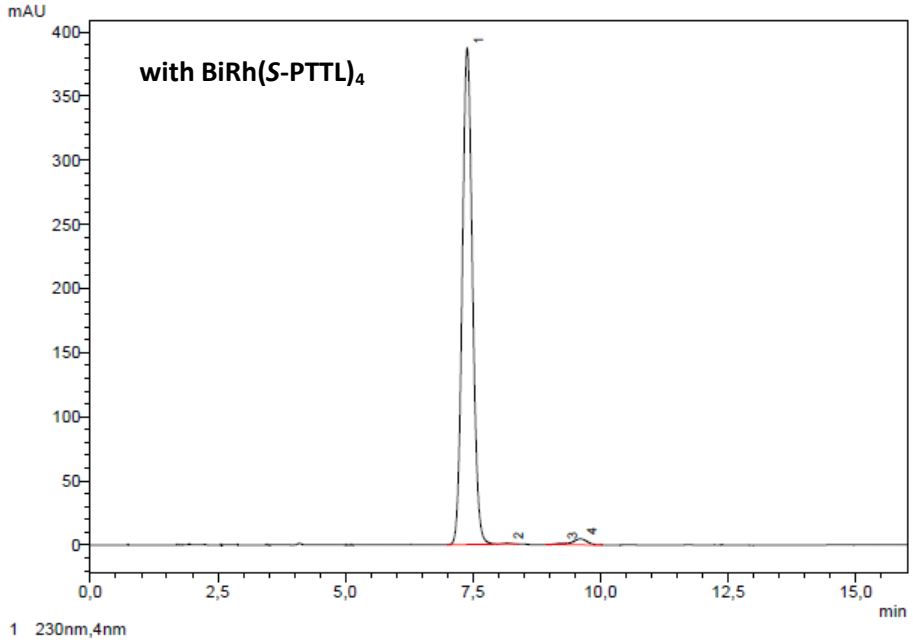
Peak #	Ret. Time	Area %
1	7,40	50,32
2	9,62	49,68
Total		100,00



1 230nm,4nm

PDA Ch1 230nm

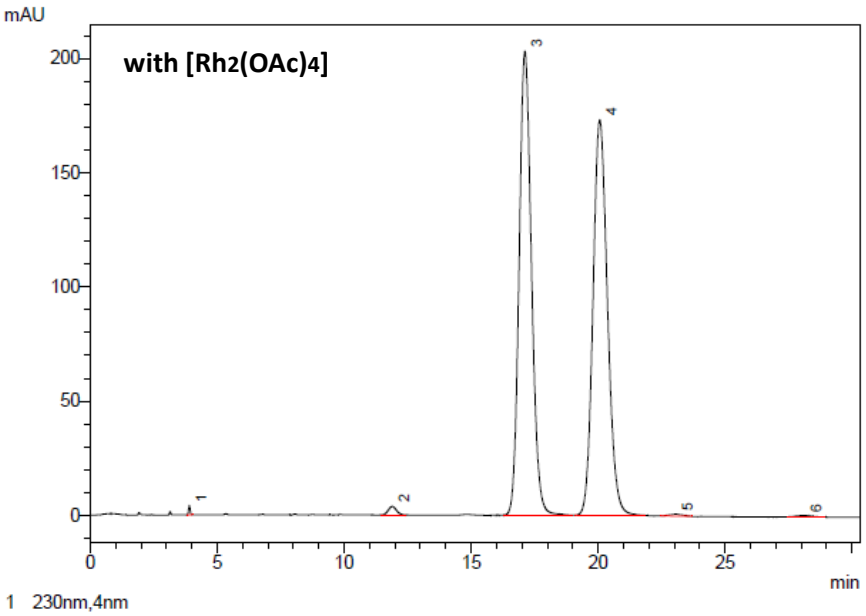
Peak #	Ret. Time	Area %
1	7,38	96,76
2	8,20	0,78
3	9,60	2,46
Total		100,00

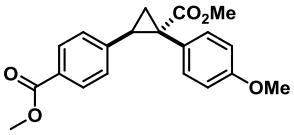


1 230nm,4nm

PDA Ch1 230nm

Peak #	Ret. Time	Area %
1	7,38	97,85
2	8,17	0,19
3	9,22	0,36
4	9,60	1,60
Total		100,00

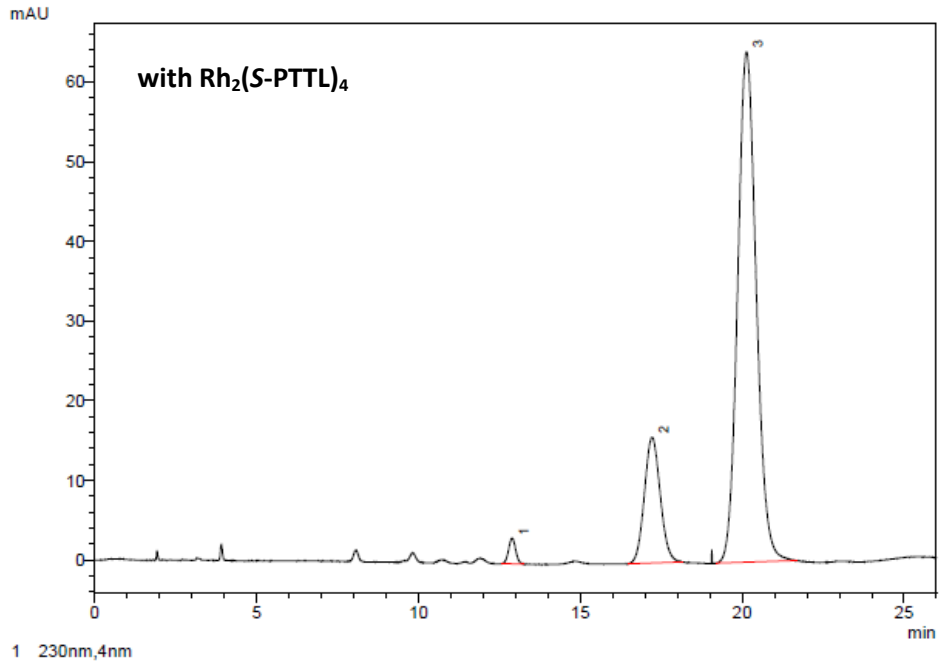




1 230nm,4nm

PDA Ch1 230nm

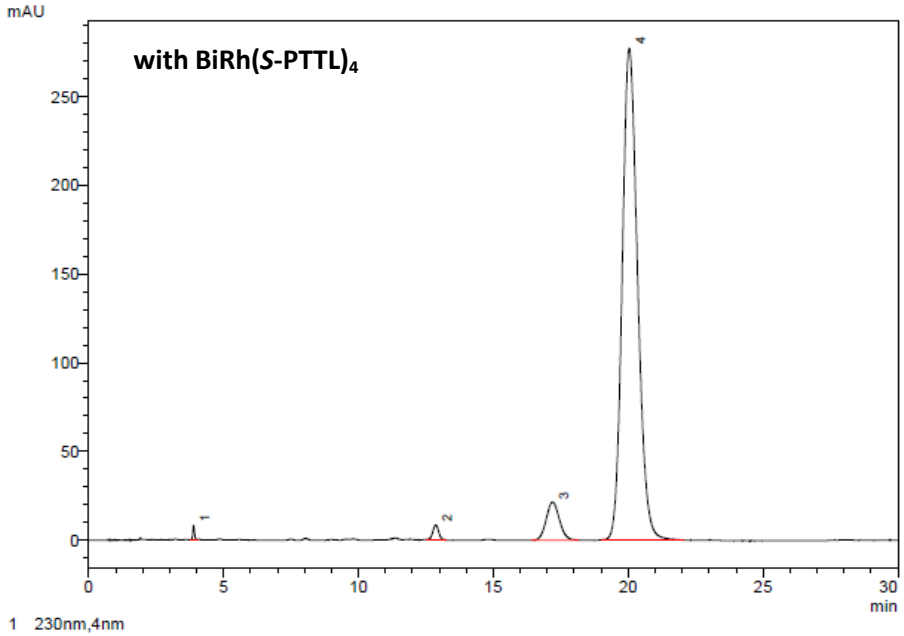
Peak #	Ret. Time	Area %	Name
1	3.90	0.13	
2	11.89	0.60	
3	17.12	49.49	1. Enantiomer
4	20.06	49.37	2. Enantiomer
5	23.04	0.20	
6	28.11	0.21	
Total		100.00	



1 230nm,4nm

PDA Ch1 230nm

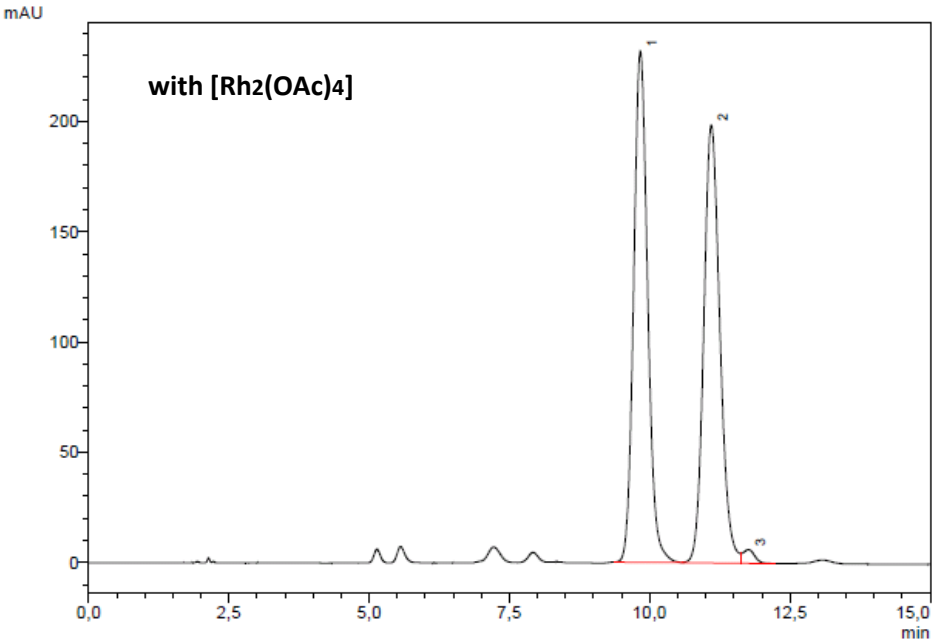
Peak #	Ret. Time	Area %
1	12,89	1,55
2	17,21	17,07
3	20,13	81,38
Total		100,00

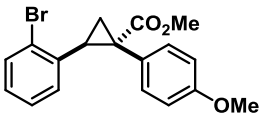


1 230nm,4nm

PDA Ch1 230nm

Peak #	Ret. Time	Area %
1	3,89	0,31
2	12,87	1,05
3	17,20	6,12
4	20,04	92,51
Total		100,00

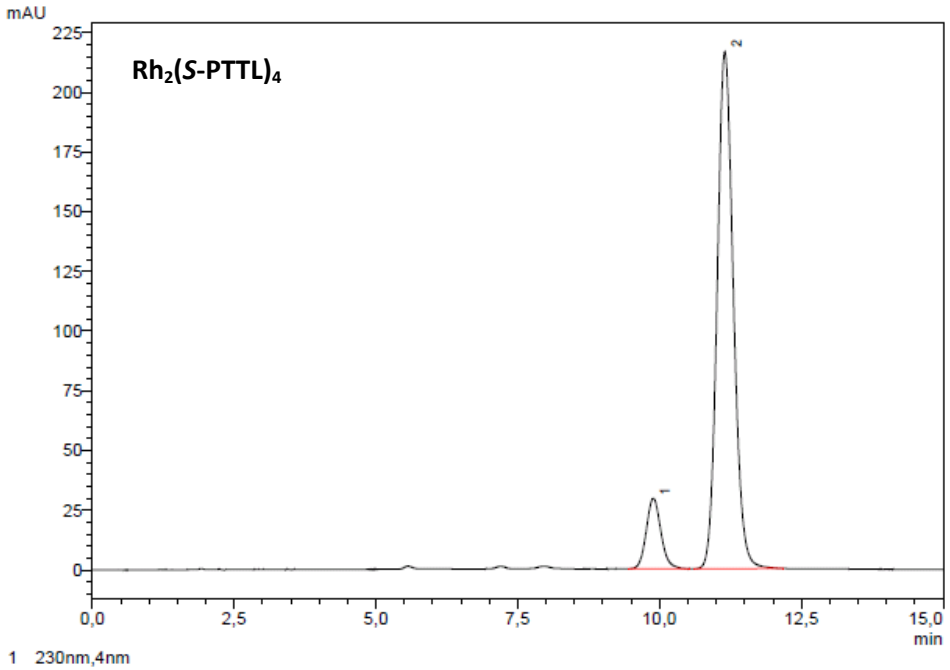




1 230nm,4nm

PDA Ch1 230nm

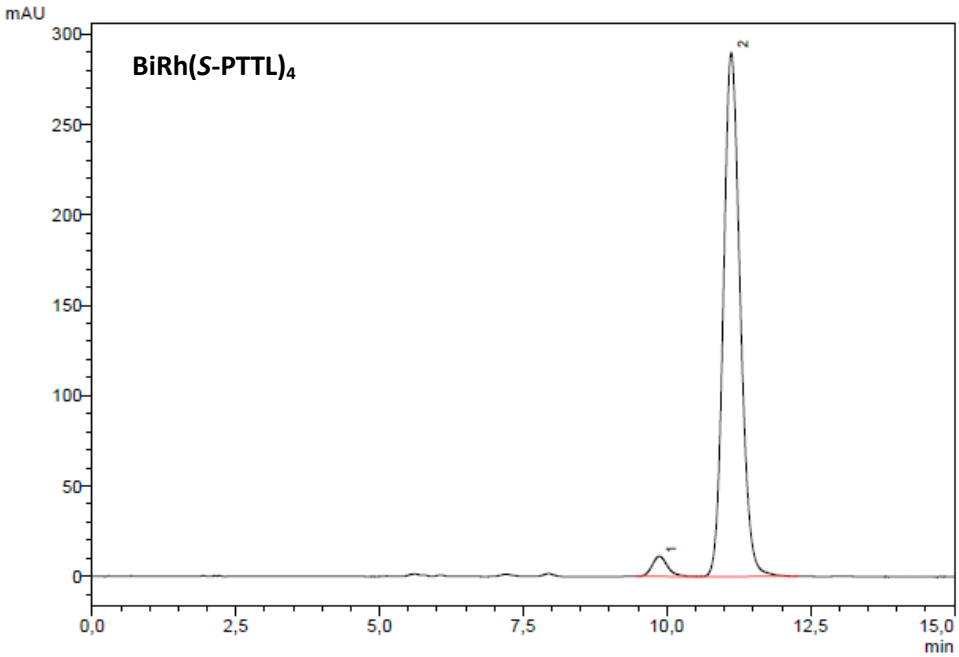
Peak #	Ret. Time	Area %
1	9,83	49,72
2	11,10	49,14
3	11,77	1,14
Total		100,00



1 230nm,4nm

PDA Ch1 230nm

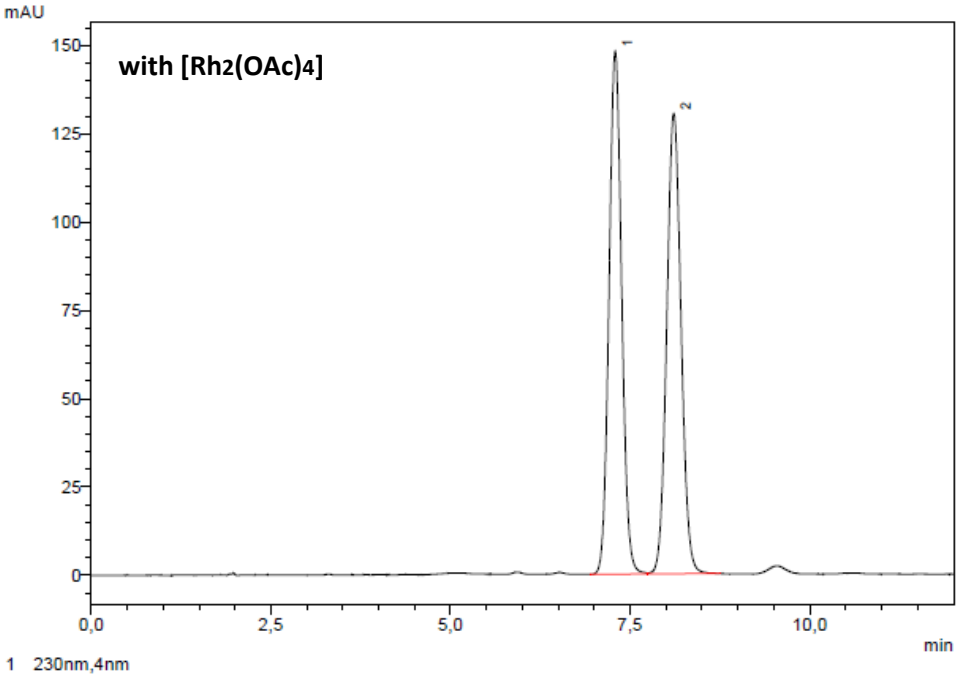
Peak #	Ret. Time	Area %
1	9,89	10,94
2	11,15	89,06
Total		100,00

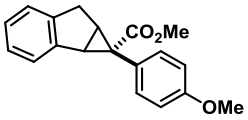


1 230nm,4nm

PDA Ch1 230nm

Peak #	Ret. Time	Area %
1	9,87	3,42
2	11,12	96,58
Total		100,00

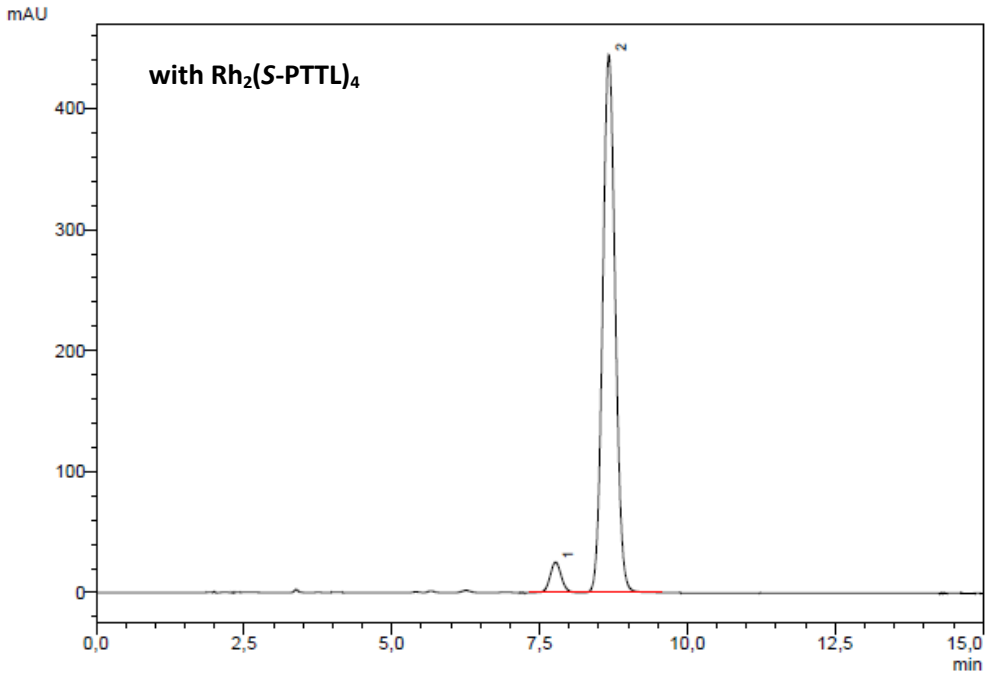




1 230nm,4nm

PDA Ch1 230nm

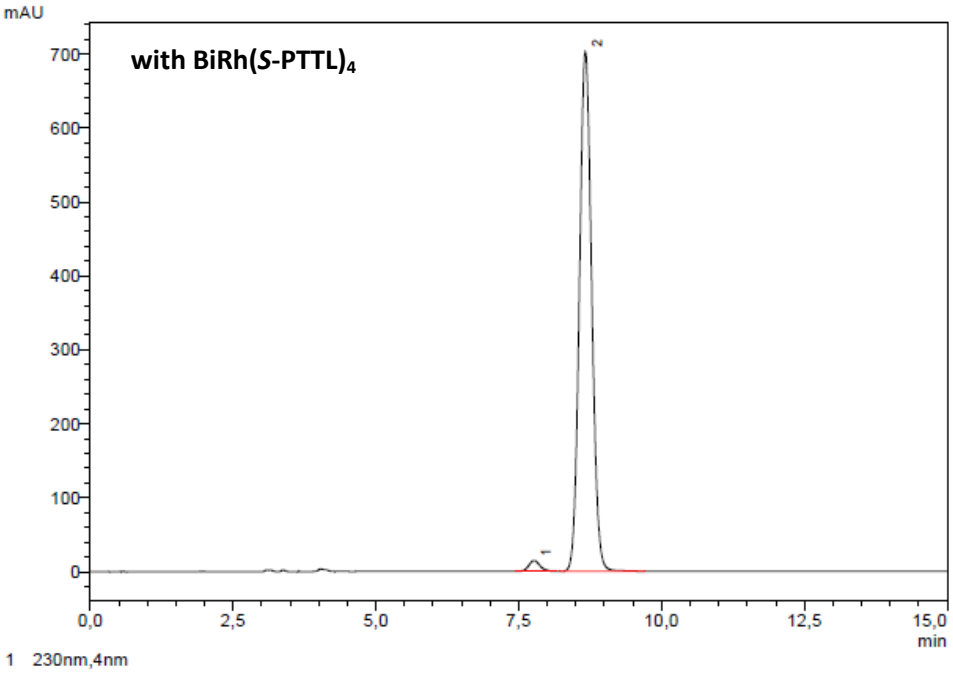
Peak #	Ret. Time	Area %
1	7,29	50,09
2	8,11	49,91
Total		100,00



1 230nm,4nm

PDA Ch1 230nm

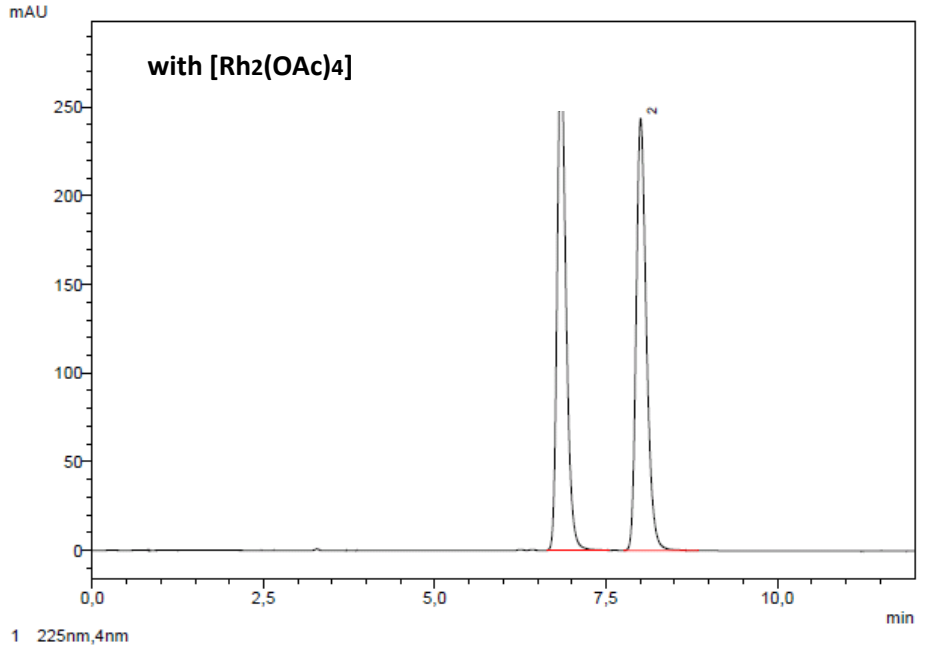
Peak #	Ret. Time	Area %
1	7,77	4,84
2	8,67	95,16
Total		100,00

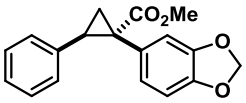


1 230nm,4nm

PDA Ch1 230nm

Peak #	Ret. Time	Area %
1	7,77	1,86
2	8,67	98,14
Total		100,00

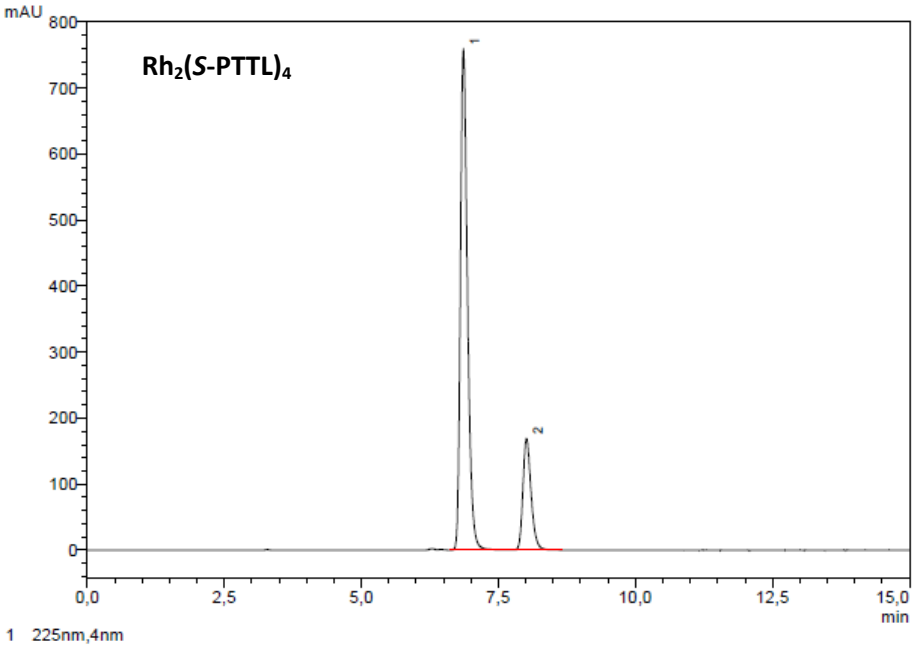




1 225nm,4nm

PDA Ch1 225nm

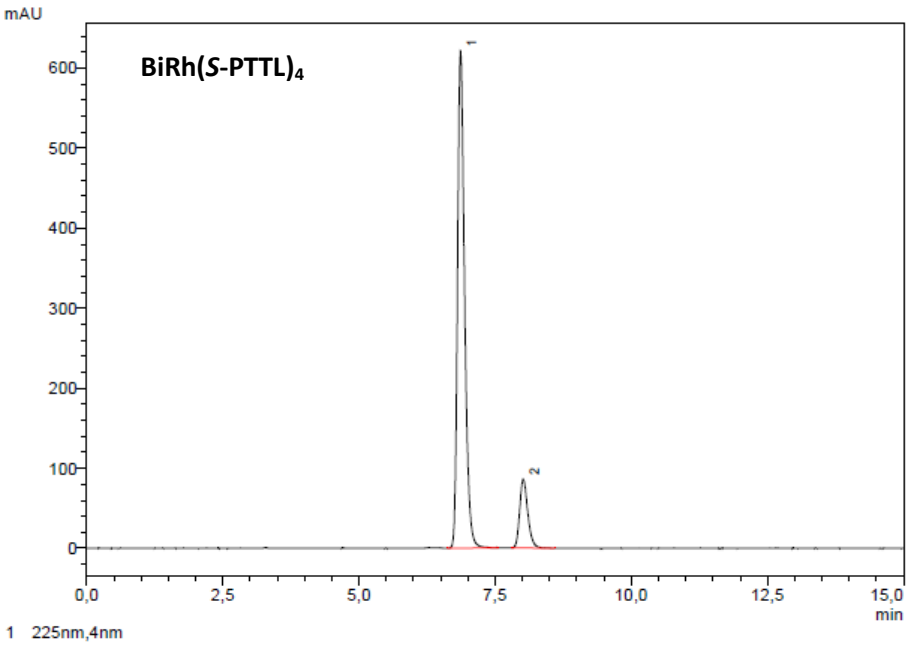
Peak #	Ret. Time	Area %	Name
1	6,84	50,22	1. Enantiomer
2	8,00	49,78	2. Enantiomer
Total		100,00	



1 225nm,4nm

PDA Ch1 225nm

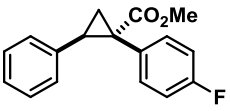
Peak #	Ret. Time	Area %
1	6,86	79,65
2	8,01	20,35
Total		100,00

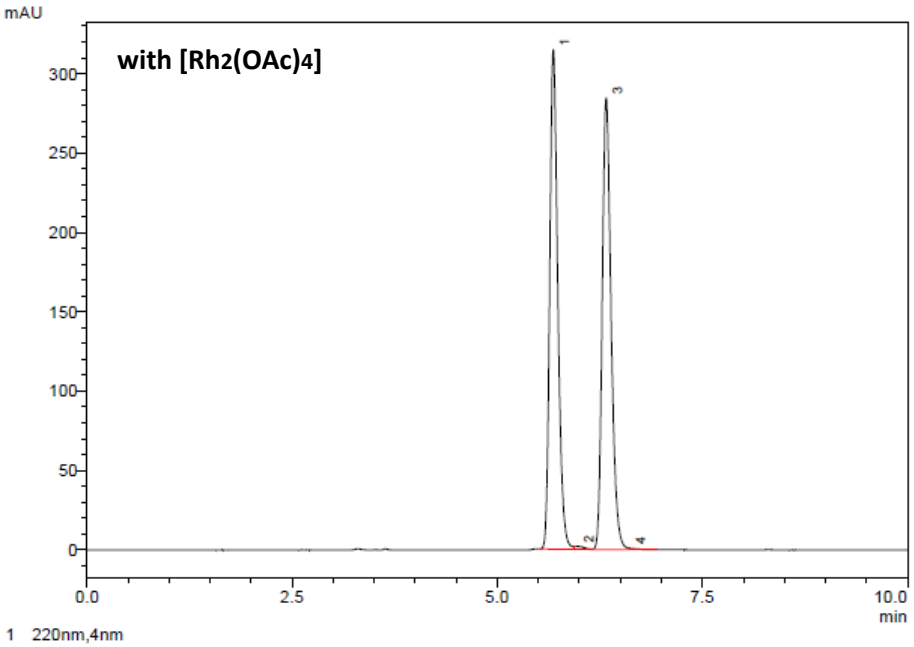


1 225nm,4nm

PDA Ch1 225nm

Peak #	Ret. Time	Area %
1	6,86	86,28
2	8,02	13,72
Total		100,00

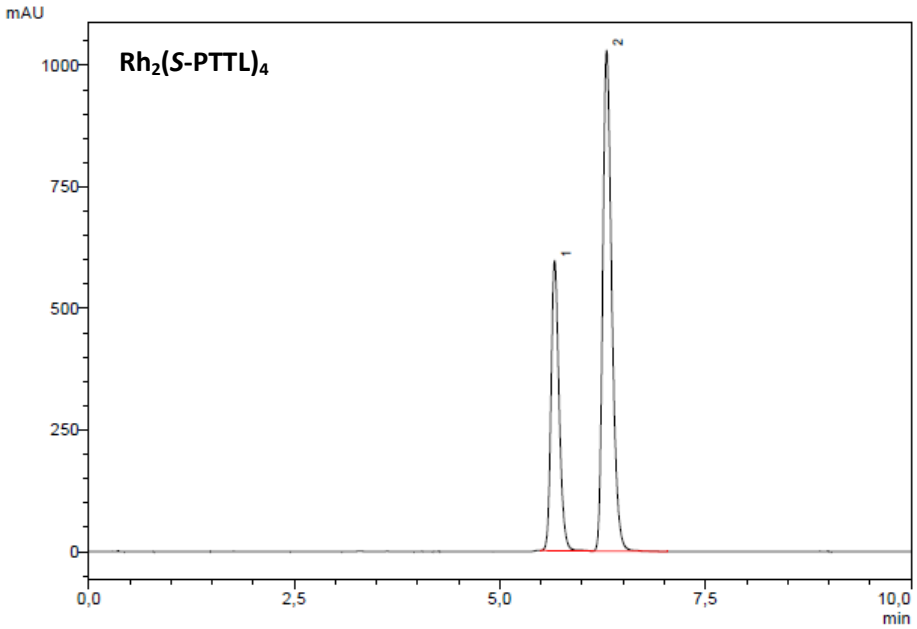




1 220nm,4nm

PDA Ch1 220nm

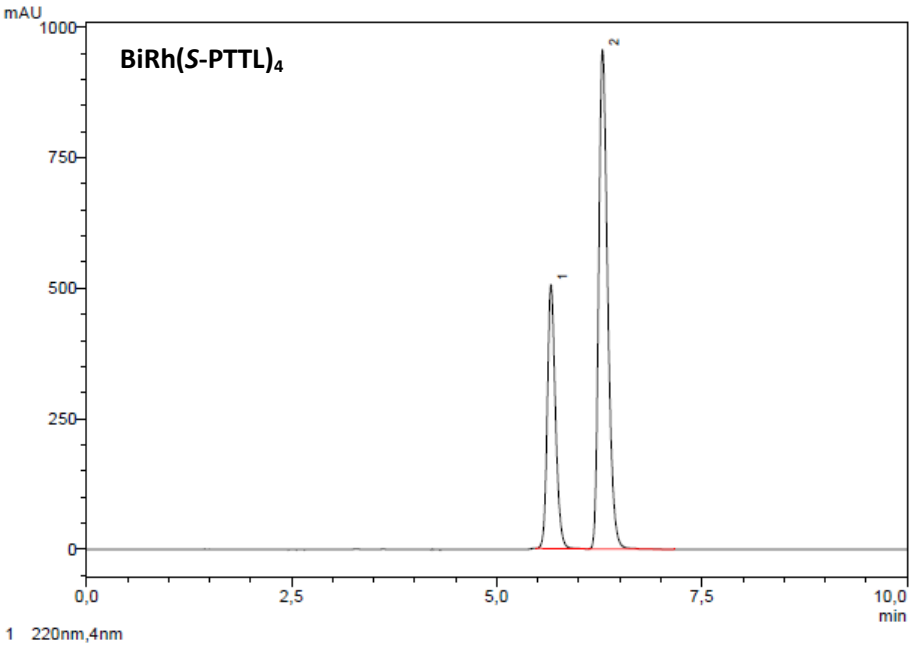
Peak #	Ret. Time	Area %	Name
1	5.68	49.90	1. Enantiomer
2	5.98	0.34	
3	6.33	49.63	2. Enantiomer
4	6.61	0.13	
Total		100.00	



1 220nm,4nm

PDA Ch1 220nm

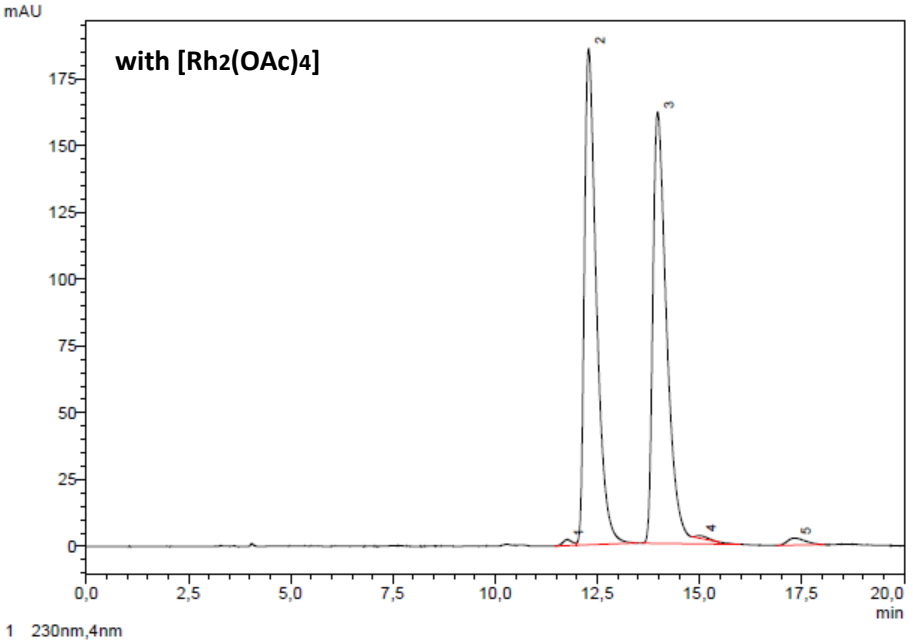
Peak #	Ret. Time	Area %
1	5,67	33,94
2	6,30	66,06
Total		100,00

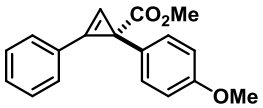


1 220nm,4nm

PDA Ch1 220nm

Peak #	Ret. Time	Area %
1	5,66	32,29
2	6,29	67,71
Total		100,00

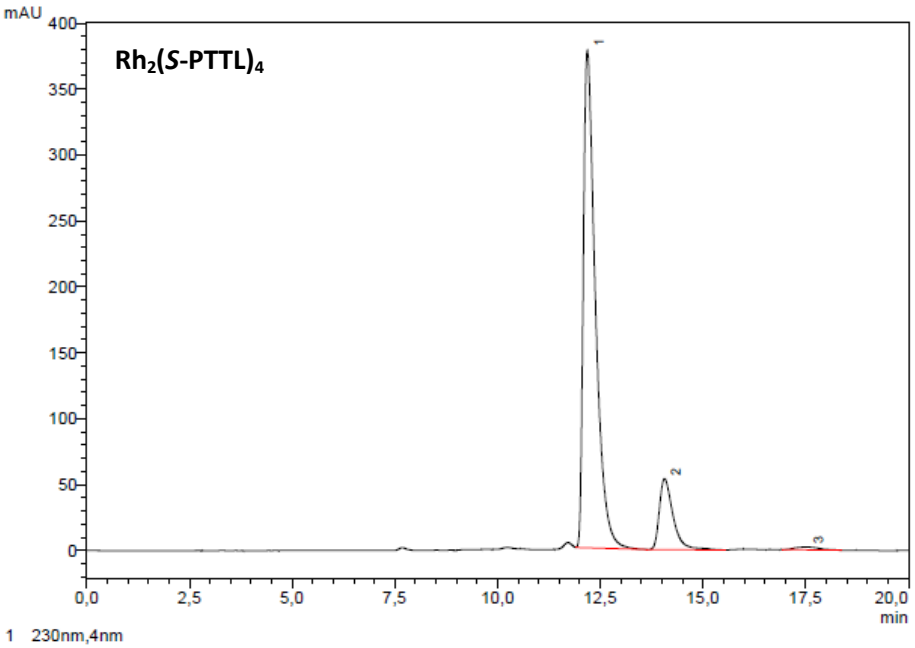




1 230nm,4nm

PDA Ch1 230nm

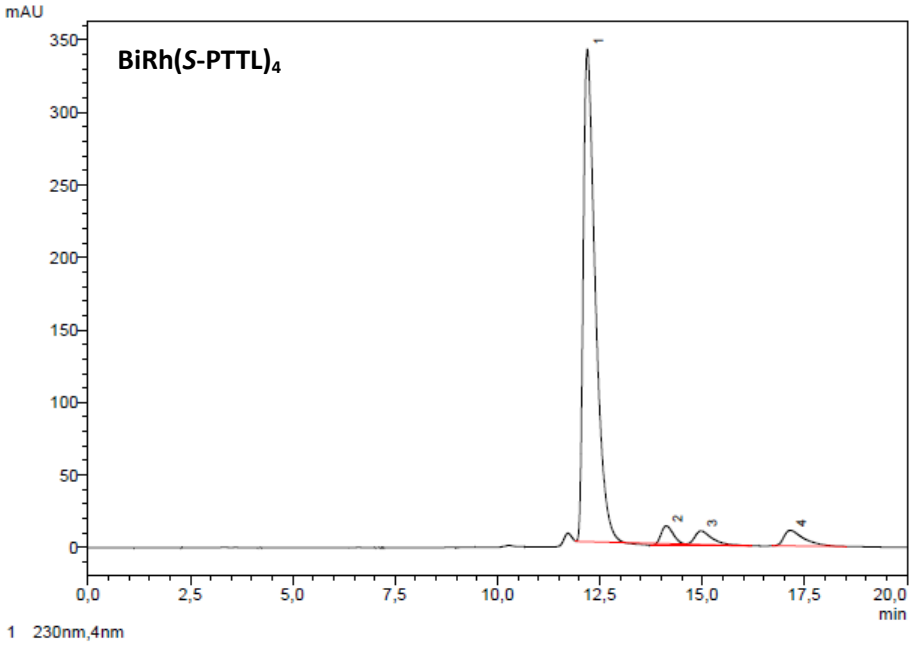
Peak #	Ret. Time	Area %
1	11,77	0,46
2	12,29	48,88
3	13,98	49,36
4	15,00	0,25
5	17,32	1,05
Total		100,00



1 230nm,4nm

PDA Ch1 230nm

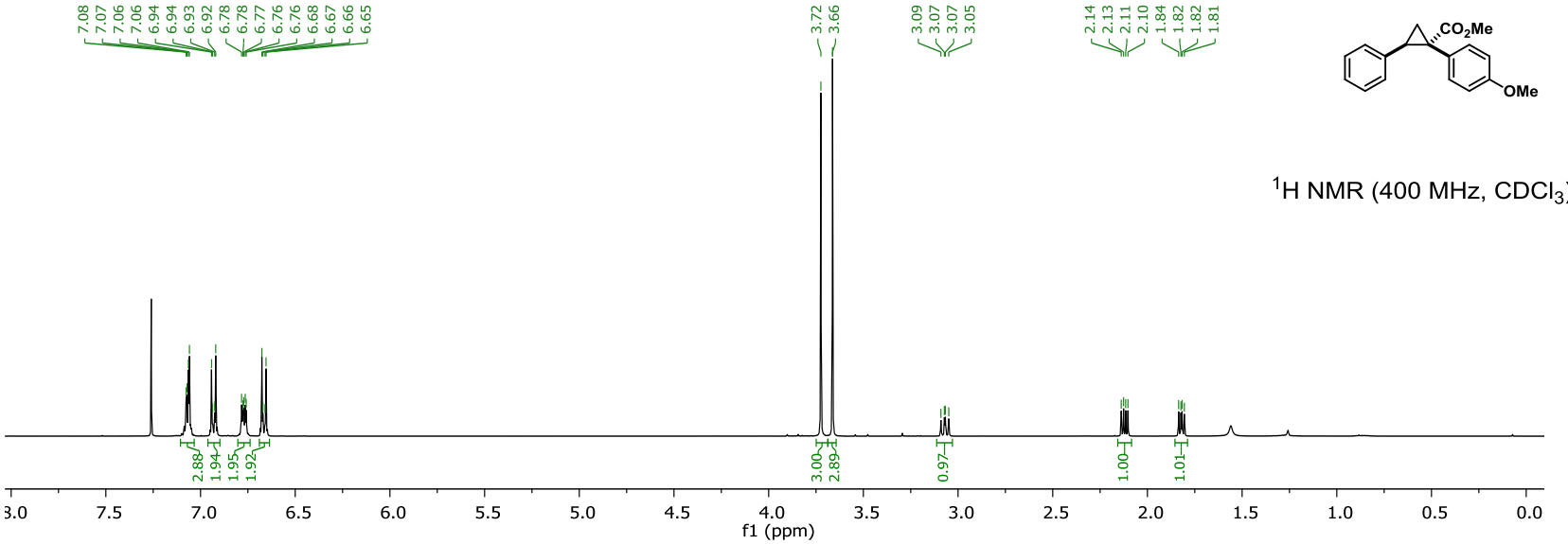
Peak #	Ret. Time	Area %
1	12,19	85,12
2	14,07	13,90
3	17,54	0,98
Total		100,00



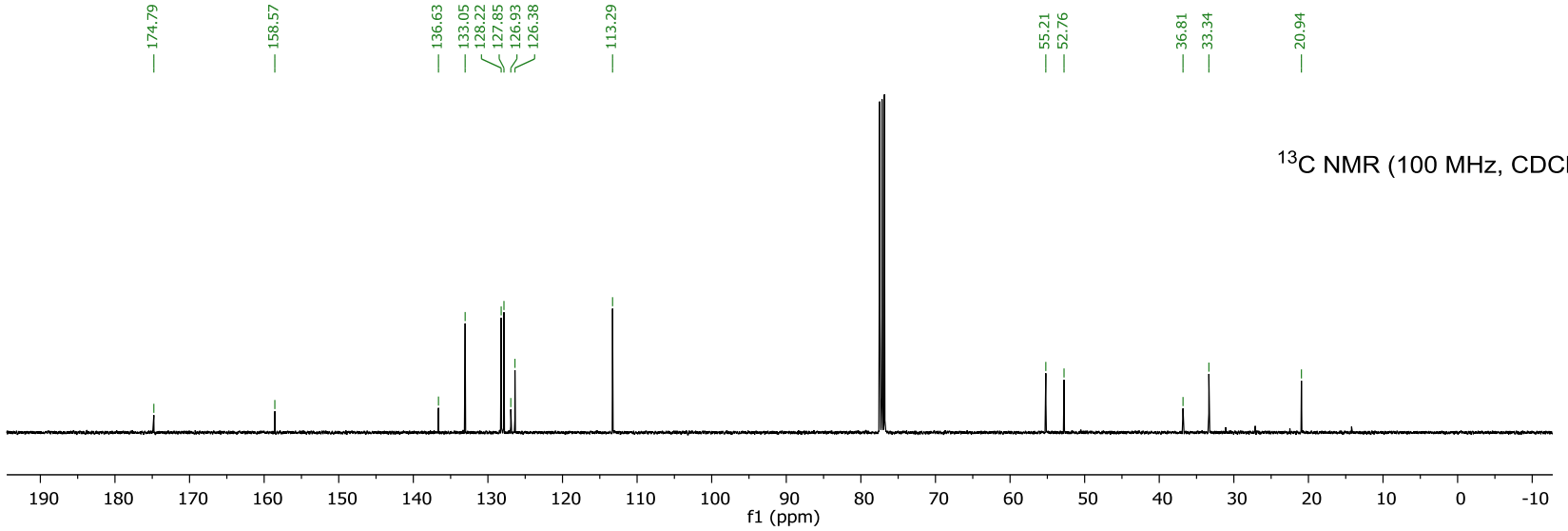
1 230nm,4nm

PDA Ch1 230nm

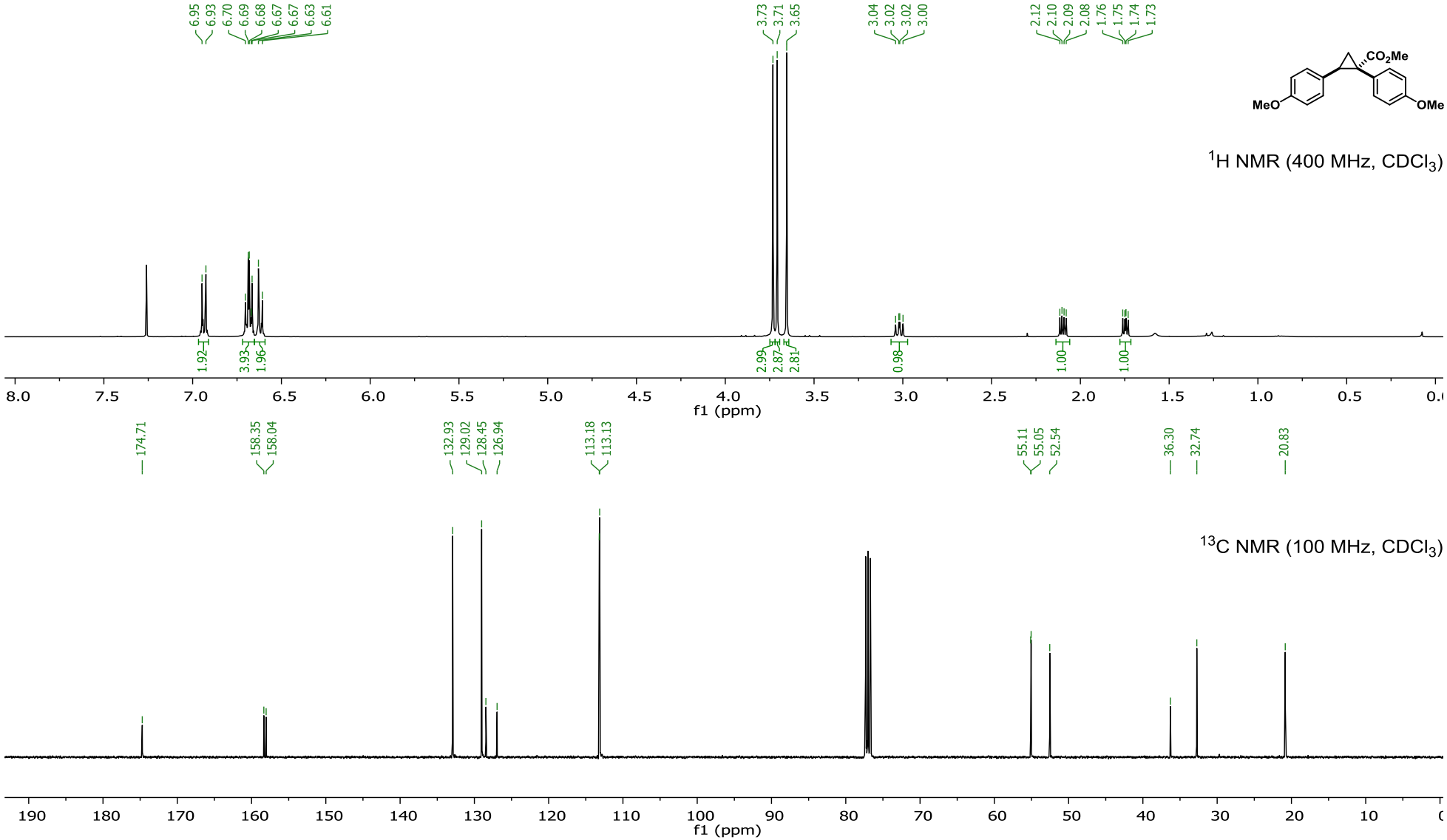
Peak #	Ret. Time	Area %
1	12,20	87,58
2	14,13	3,73
3	14,97	3,99
4	17,15	4,70
Total		100,00

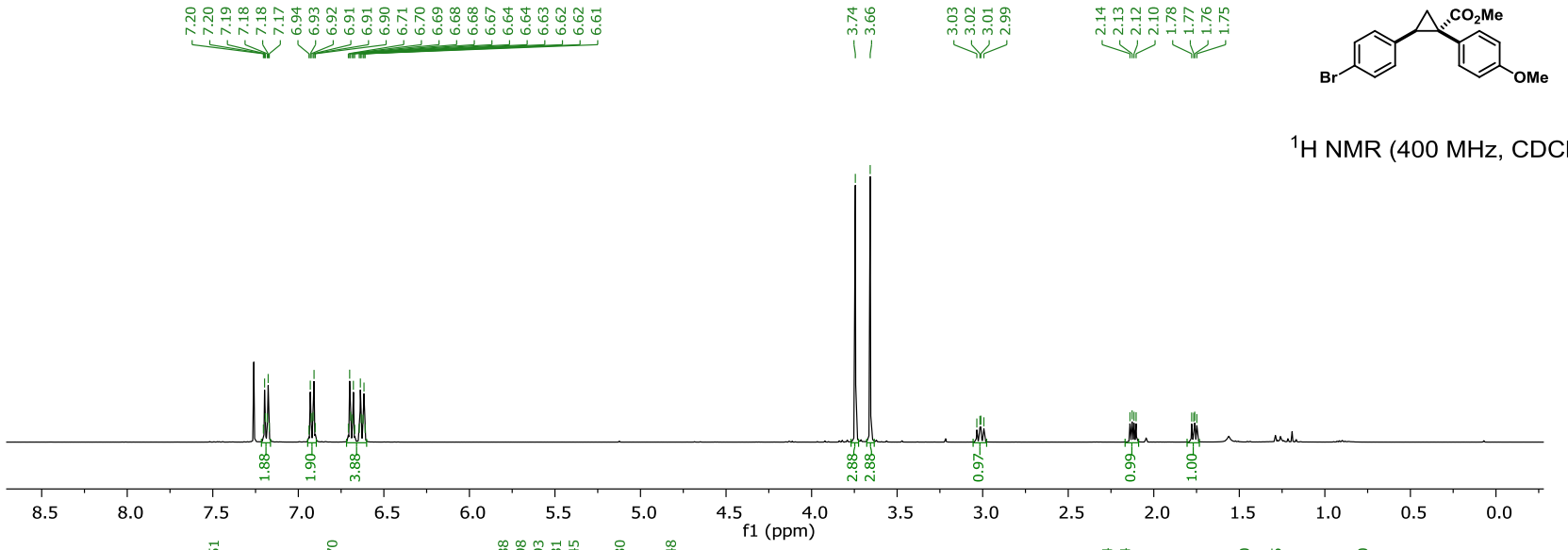


^{1}H NMR (400 MHz, $CDCl_3$)

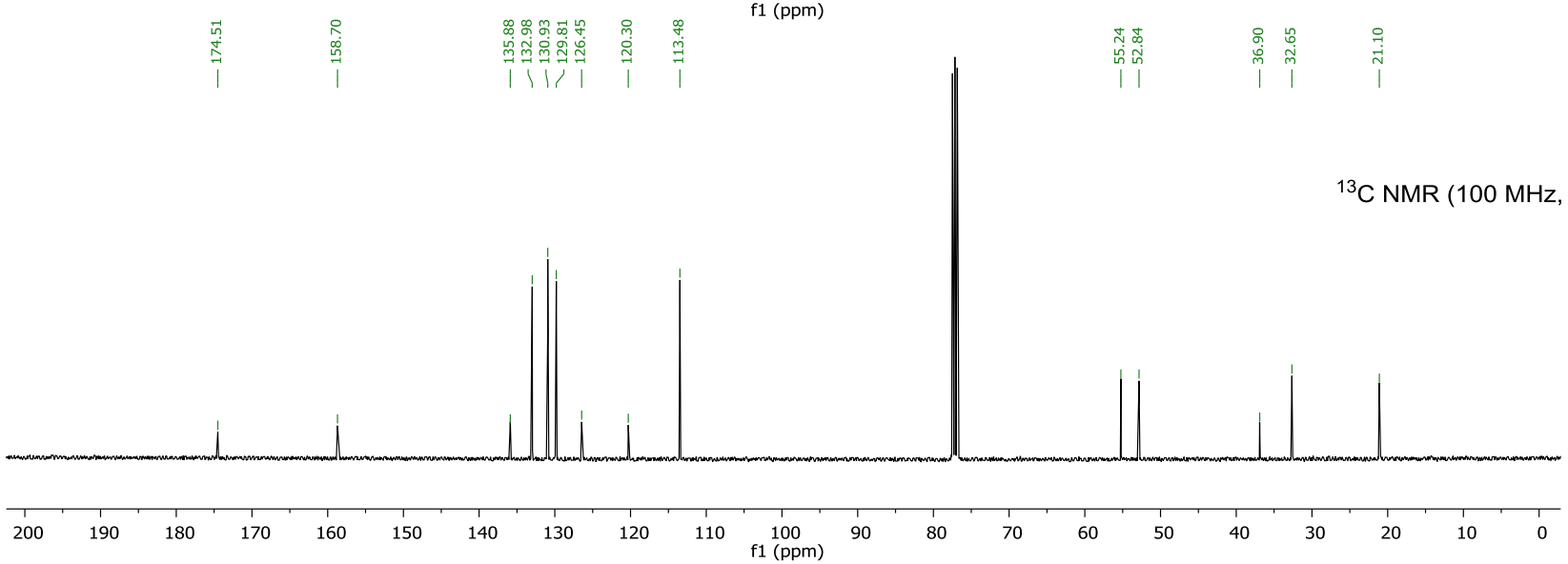


^{13}C NMR (100 MHz, $CDCl_3$)

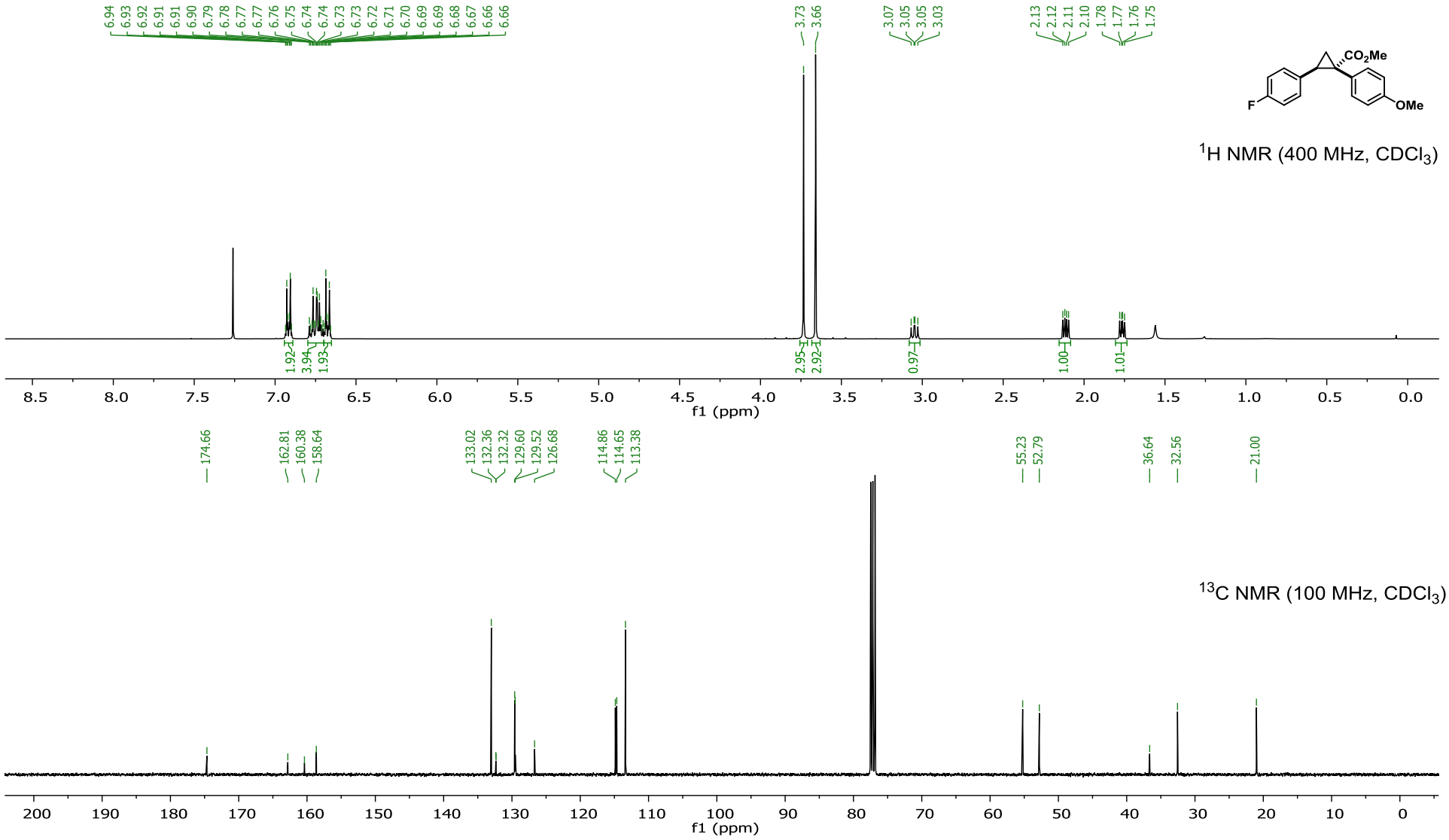

6.95
6.93
6.70
6.69
6.68
6.67
6.67
6.63
6.61
3.73
3.71
3.65
3.04
3.02
3.02
3.00
2.12
2.10
2.09
2.08
1.76
1.75
1.74
1.73
CO2Me
MeO
OMe
1H NMR (400 MHz, CDCl3)
1.92
3.93
1.96
2.99
2.87
2.81
0.98
1.00
1.00
f1 (ppm)
174.71
158.35
158.04
132.93
129.02
128.45
126.94
113.18
113.13
55.11
55.05
52.54
36.30
32.74
20.83
13C NMR (100 MHz, CDCl3)
f1 (ppm)

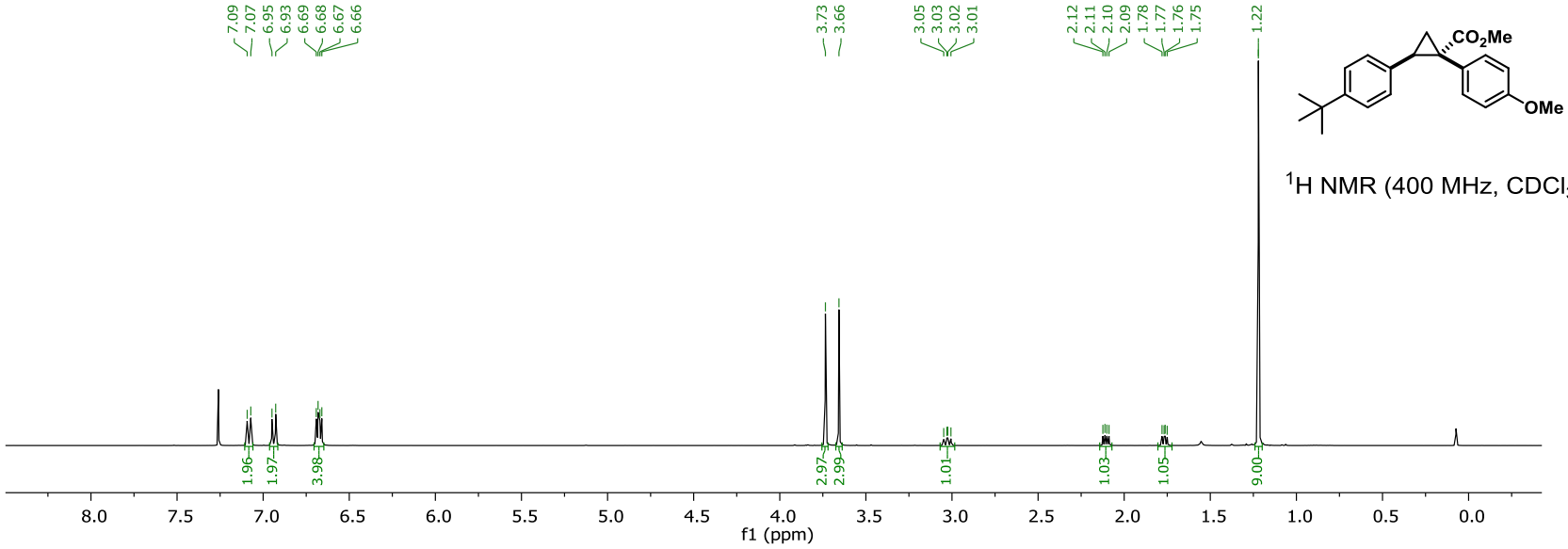


^{1}H NMR (400 MHz, $CDCl_3$)

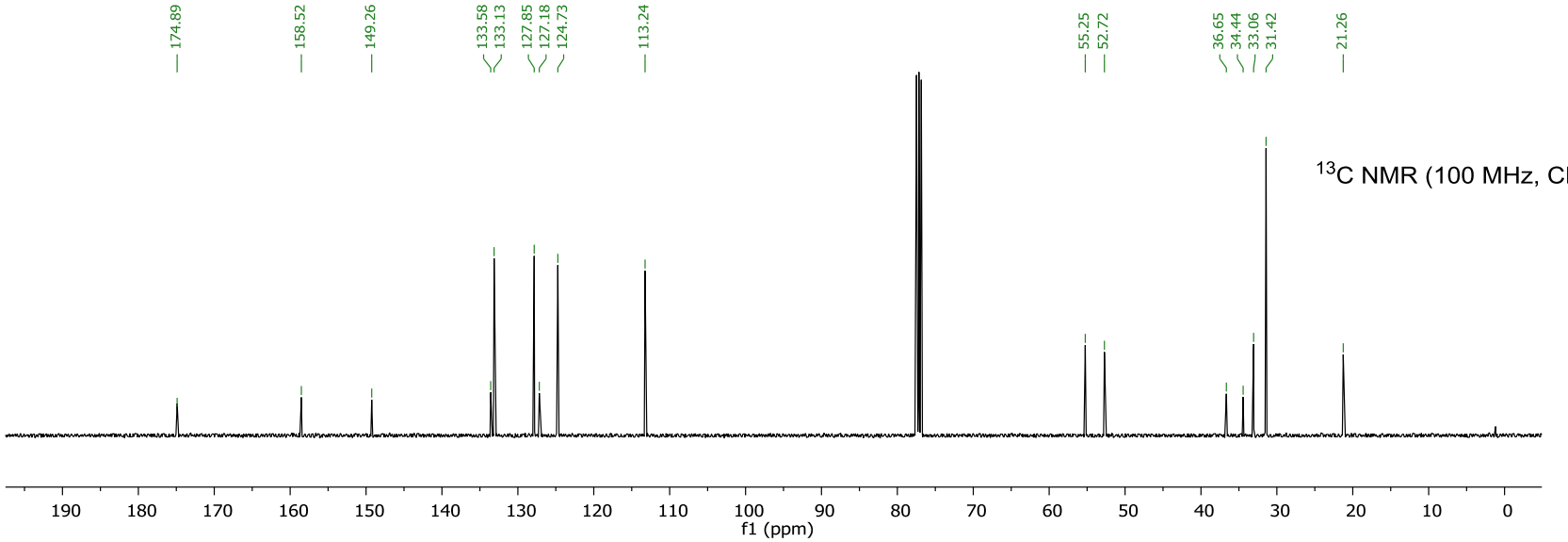


^{13}C NMR (100 MHz, $CDCl_3$)

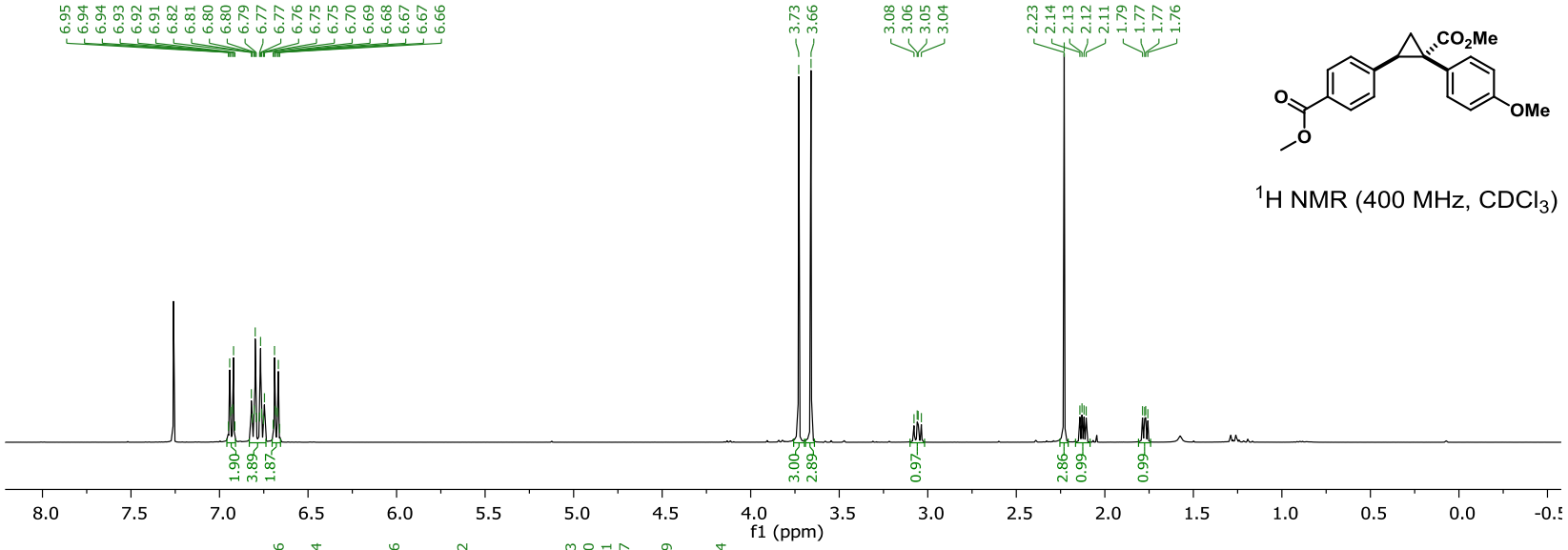

6.94 6.93 6.92 6.91 6.91 6.90 6.79 6.78 6.77 6.77 6.76 6.75 6.74 6.74 6.73 6.73 6.72 6.71 6.70 6.69 6.69 6.68 6.67 6.66 6.66
3.73 3.66
3.07 3.05 3.05 3.03
2.13 2.12 2.11 2.10
1.78 1.77 1.76 1.75
CO2Me
F
OMe
1H NMR (400 MHz, CDCl3)
1.92 3.94 1.93 2.95 2.92 0.97 1.00 1.01
f1 (ppm)
174.66 162.81 160.38 158.64 133.02 132.36 132.32 129.60 129.52 126.68 114.86 114.65 113.38 55.23 52.79 36.64 32.56 21.00
13C NMR (100 MHz, CDCl3)
f1 (ppm)



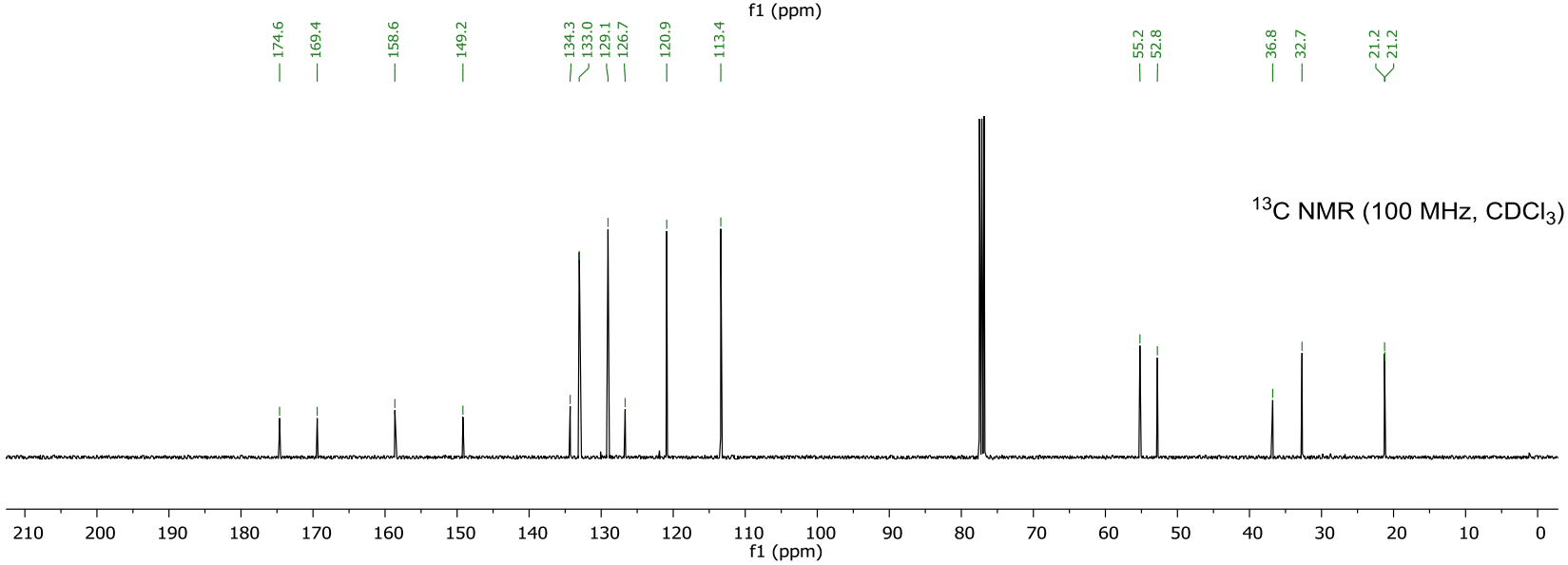
^{1}H NMR (400 MHz, $CDCl_3$)



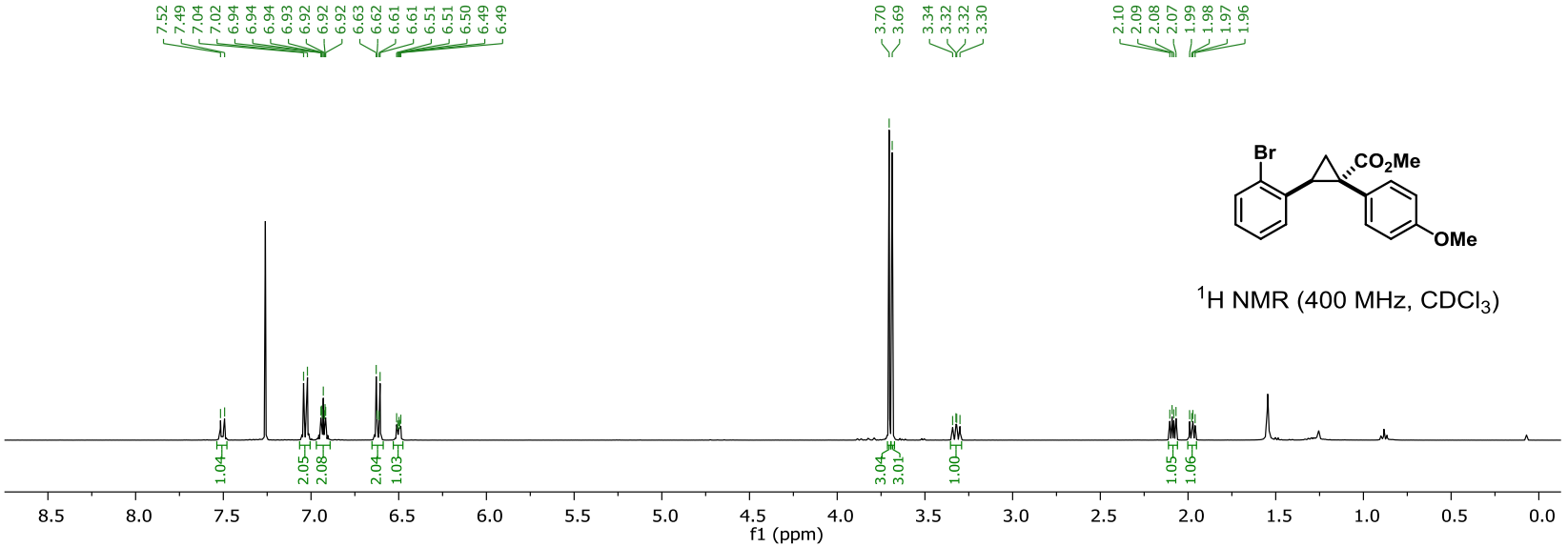
^{13}C NMR (100 MHz, $CDCl_3$)



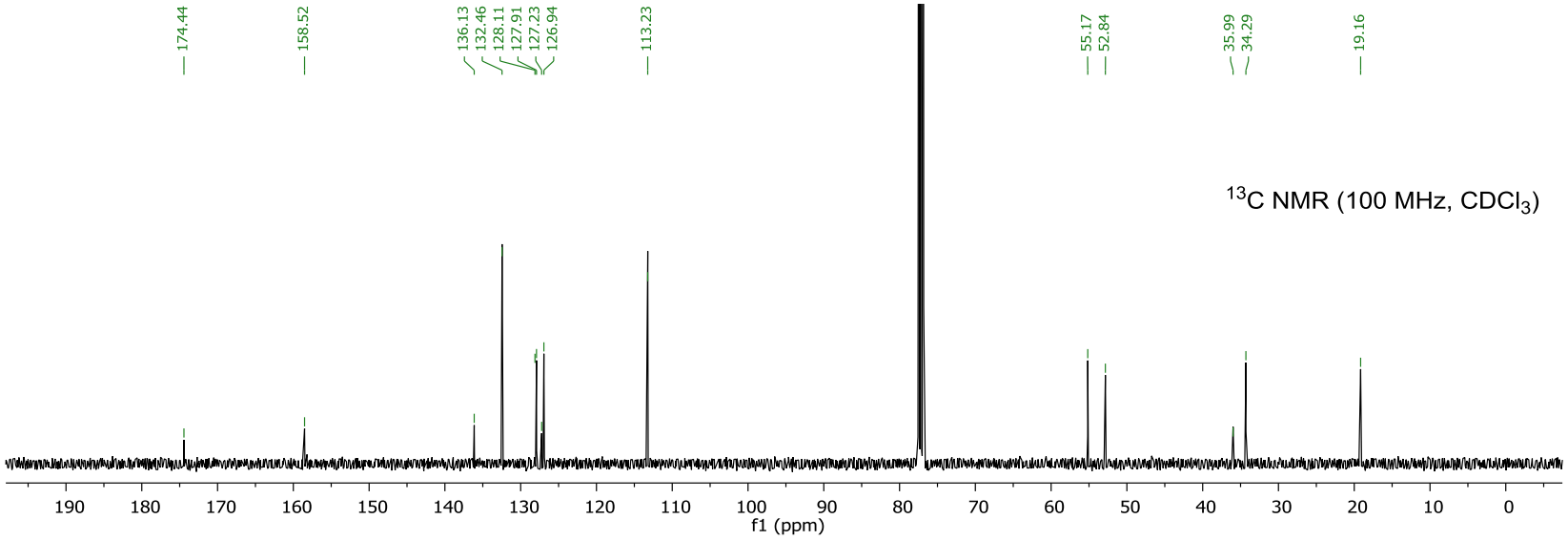
^{1}H NMR (400 MHz, $CDCl_3$)



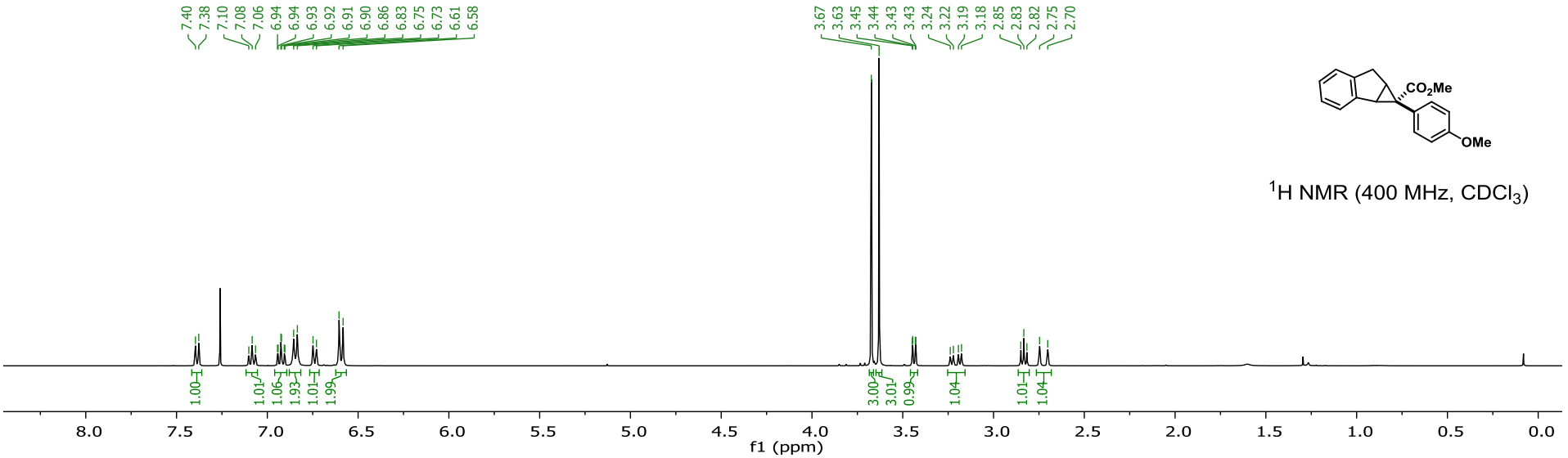
^{13}C NMR (100 MHz, $CDCl_3$)



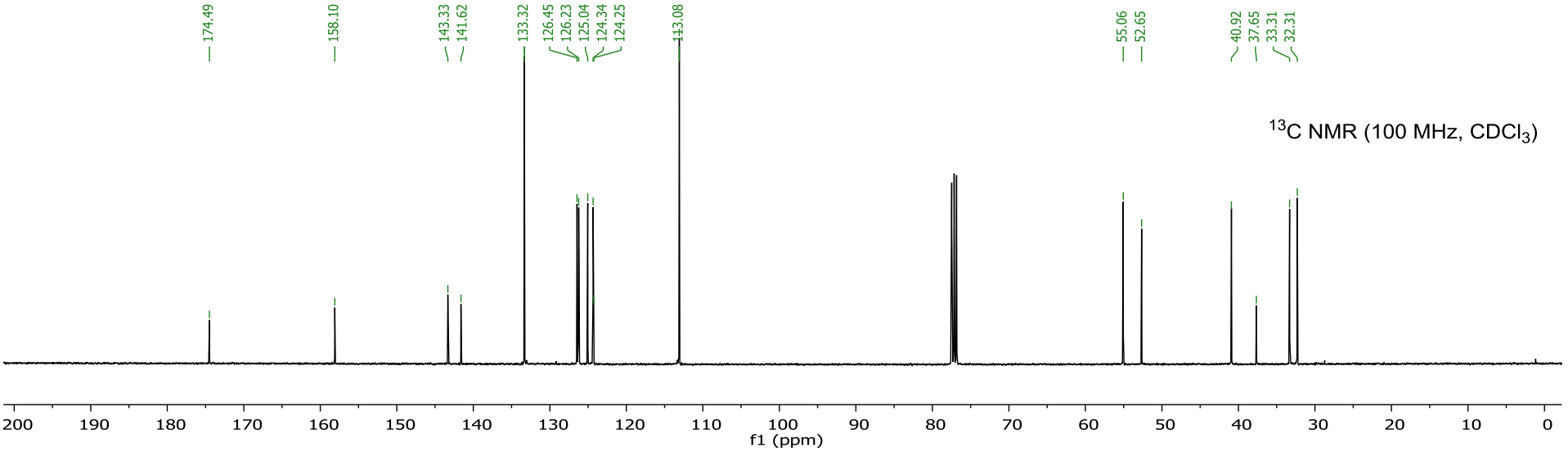
^{1}H NMR (400 MHz, $CDCl_3$)



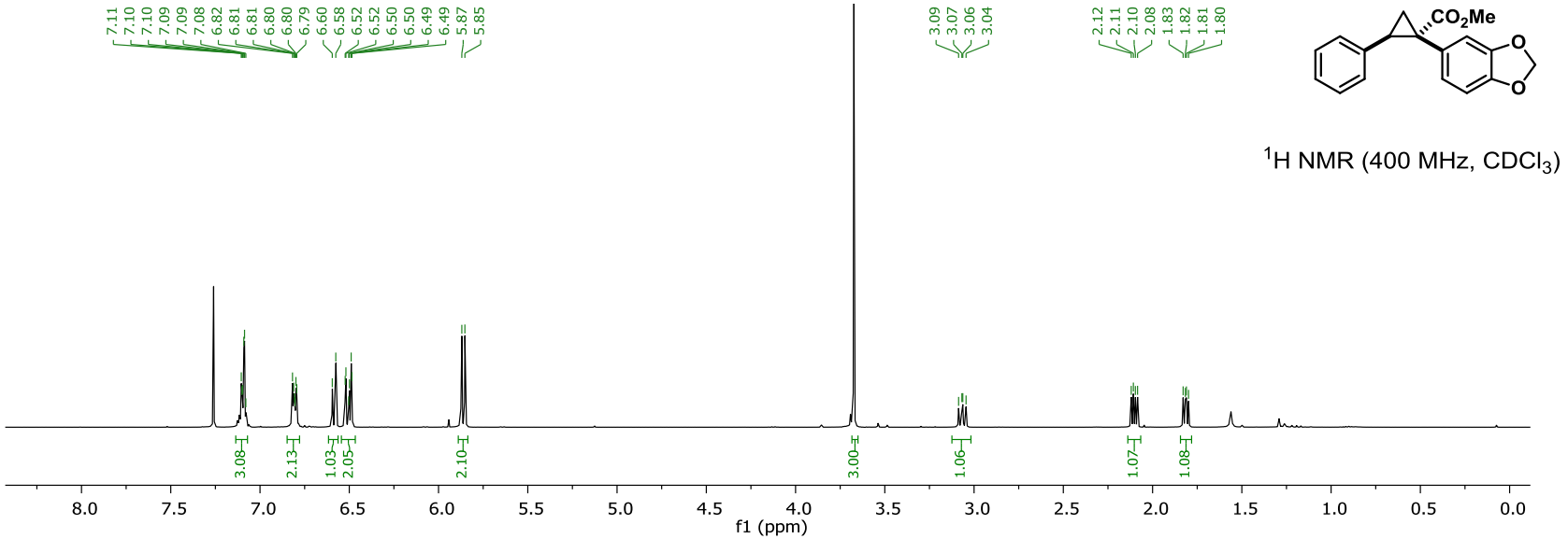
^{13}C NMR (100 MHz, $CDCl_3$)



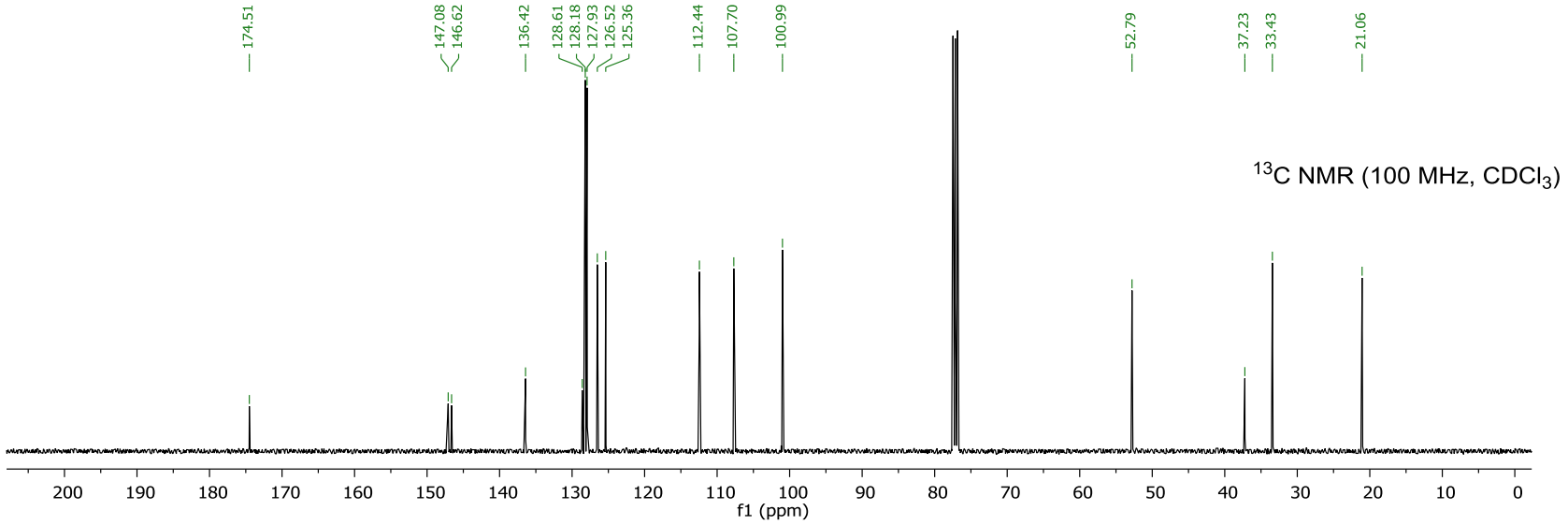
^{1}H NMR (400 MHz, $CDCl_3$)



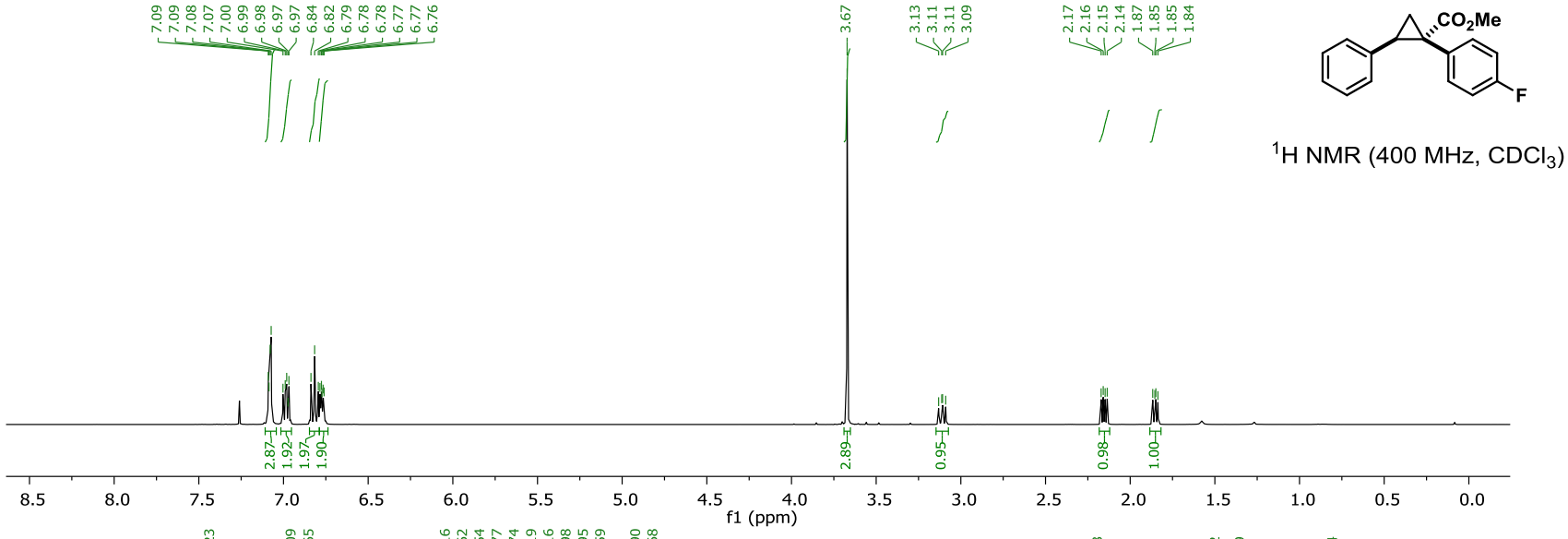
^{13}C NMR (100 MHz, $CDCl_3$)



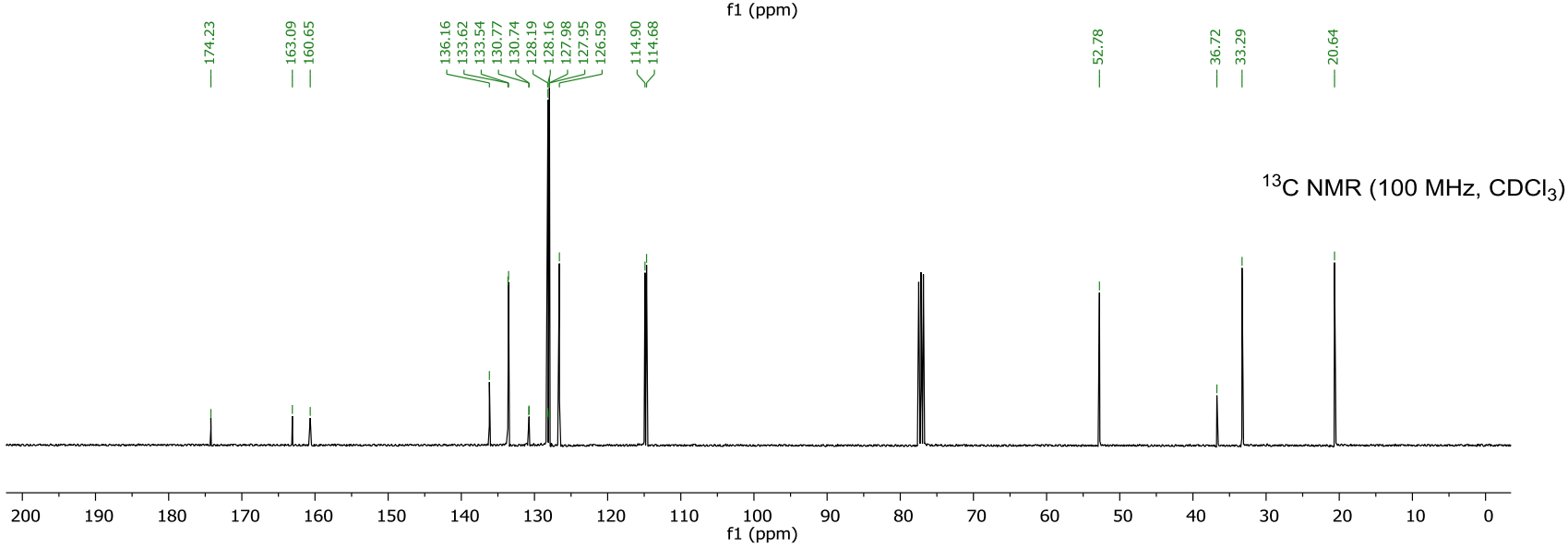
^{1}H NMR (400 MHz, $CDCl_3$)



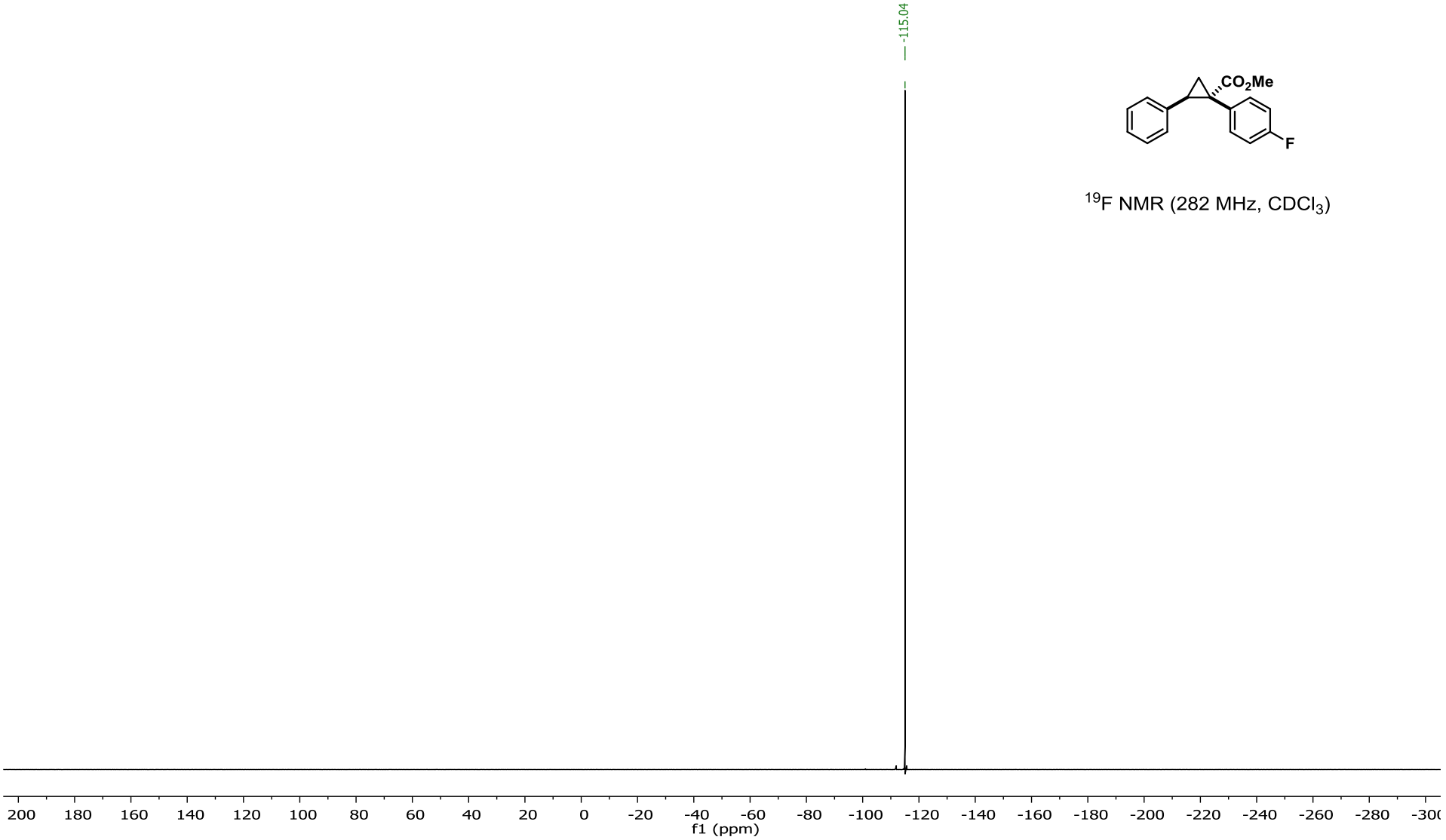
^{13}C NMR (100 MHz, $CDCl_3$)



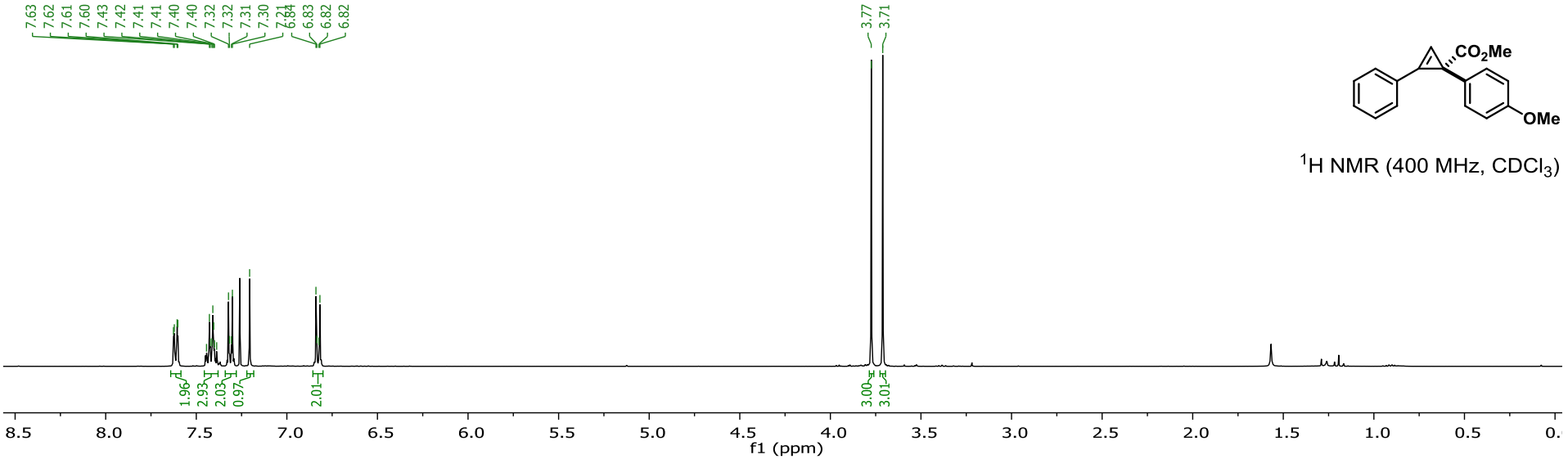
^{1}H NMR (400 MHz, $CDCl_3$)



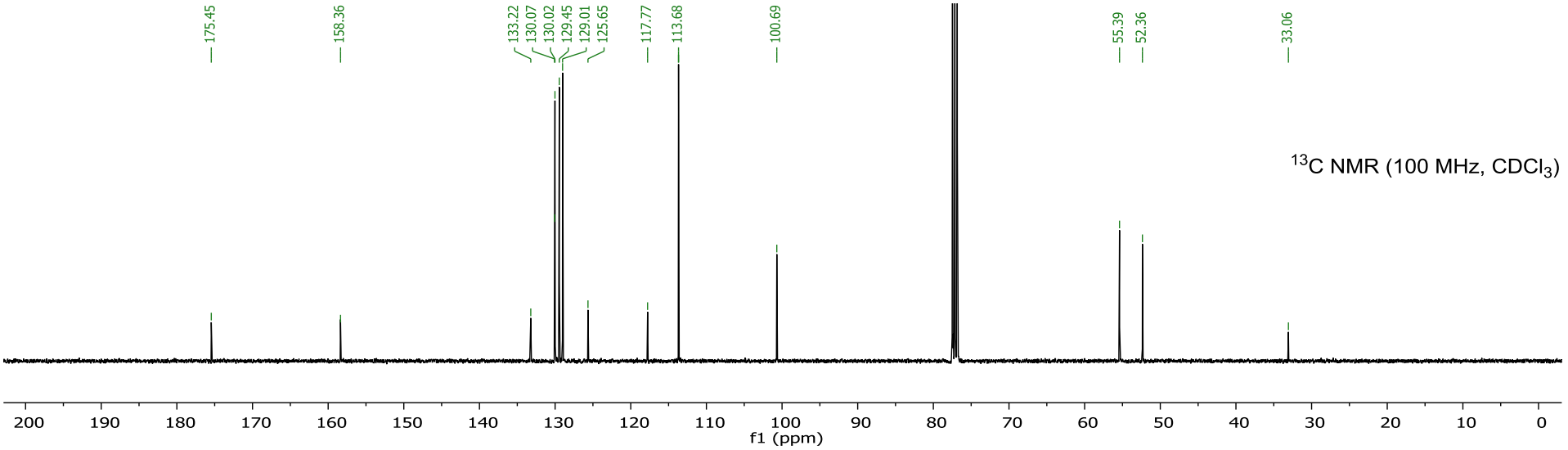
^{13}C NMR (100 MHz, $CDCl_3$)



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



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



^{13}C NMR (100 MHz, $CDCl_3$)