Electronic Supplementary Information (ESI)

Cp*Rh(III)-Catalyzed Electrophilic Amination of Arylboronic Acids with Azo compounds for Synthesis of Arylhydrazides

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1. General Experimental Section

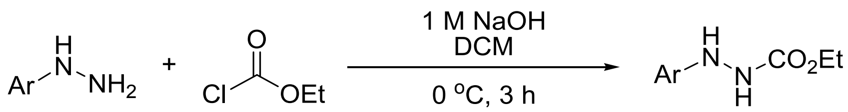
All the reactions were performed under a nitrogen atmosphere. All the solvents were freshly distilled and dried according to the standard methods prior to use.[1] $[Cp^*RhCl_2]_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl), $[Cp^*Rh(OAc)_2]$, $[Cp^*Rh(MeCN)_3(SbF_6)_2]$, $[Rh(COD)Cl]_2$ (COD = cyclooctadiene) and $[Rh(COD)(OH)]_2$ were synthesized by the literature methods.[2] Arylboronic acids, potassium phenyltrifluoroborate, phenylboronic acid pinacol eater, boric acid and diethyl azodicarboxylate (DEAD) were obtained commercially, and were used without purification.

Thin layer chromatography was performed on silica gel plates. Flash column chromatography was performed on silica gel (Merck, 230-400 mesh). ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker DPX-400 MHz spectrometer. The chemical shift (δ) values were given in ppm and were referenced to residual solvent peaks, carbon multiplicities were determined by DEPT-135 and DEPT-90 experiments. Coupling constants (*J*) were reported in hertz (Hz). Mass spectra and high resolution mass spectra (HRMS) were obtained on a VG MICROMASS Fison VG platform, a Finnigan Model Mat 95 ST instrument, or a Bruker APEX 47e FT-ICR mass spectrometer. X-ray crystallographic study was performed by a Bruker CCD area detector diffractometer.

2. Experimental Procedures and Physical Characterization

2.1 General procedure for preparation of ethyl arylhydrazinecarboxylates

Scheme S1. General procedure for ethyl arylhydrazinecarboxylates preparation



Arylhydrazine (10.0 mmol) in anhydrous DCM (15 mL) was placed in a 100 mL 2-neck round bottom flask, and the mixture was immersed into an ice-bath. Ethyl chloroformate (10.0 mmol) was diluted with anhydrous DCM (5 mL) and was added dropwise via a dropping funnel. When half of the ethyl chloroformate was added, 1 M NaOH (10 mL) was added dropwise via another dropping funnel. The reaction mixture was stirred for 3 h. The reaction mixture was diluted with DCM (10 mL), followed by acidification with 1 M HCl (10 mL). After washing with deionized water (20 mL), the aqueous layer was extracted with DCM (20 mL × 3). The combined organic layers were dried over $MgSO_4$ and concentrated by rotary evaporation.

2.2.1 Method A:

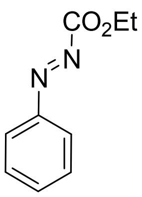
Preparation of ethyl arylazocarboxylates by NBS oxidation

To a mixture of arylhydrazides obtained from 2.1 (10.0 mmol) was dissolved in anhydrous toluene (50 mL). Pyridine (12.75 mmol) and NBS (12.75 mmol) were added sequentially. The reaction mixture was stirred vigorously at room temperature for 15 min. The reaction mixture was diluted with toluene (50 mL), washed with deionized water (50 mL), saturated $Na_2S_2O_3$ (30 mL), 1 M HCl (15 mL × 2), saturated $NaHCO_3$ solution (30 mL) and deionized water (50 mL). The organic layer was dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by flash column chromatography to afford the corresponding azo compounds.

2.2.2 Method B:

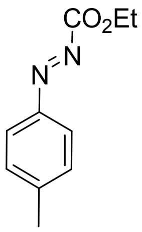
Preparation of ethyl arylazocarboxylates by CAN oxidation

A solution of CAN (22.1 mmol) in MeOH (30 mL) was added dropwise under stirring into the solution of ethyl arylhydraiznecarboxylate (10.0 mmol) in MeOH (30 mL). The reaction mixture was stirred vigorously for 5 min. The reaction mixture was diluted with deionized water (30 mL), and the product was extracted with DCM (20 mL × 3). The combined organic layers were washed with saturated $NaHCO_3$ solution (20 mL), brine (20 mL), dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by flash column chromatography to afford the corresponding azo compounds.



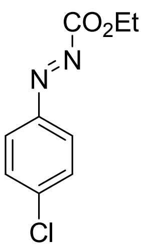
3a

Eluent: n-hexane / ethyl acetate 15:1, R_F = 0.5. The product was obtained as a red oil (77% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.52 (t, J =7.1 Hz, 2H), 4.52 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.2 (CO), 151.6 (C), 133.8 (CH), 129.3 (CH), 123.7 (CH), 64.4 (CH_2), 14.2 (CH_3). IR (KBr): 3488 (br, w), 2985 (m), 1758 (s), 1454 (m), 1244 (s), 1191 (s), 1146 (s), 973 (w), 778 (m), 685 (s) HRMS (ESI) calcd. for $C_9H_{10}N_2O_2Na$ (M+Na) 201.0634, found 201.0636.



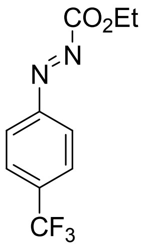
3b

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.8. The product was obtained as a red oil (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.84 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.52 (q, J = 6.8 Hz 2H), 2.44 (s, 3 H), 1.46 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.2 (CO), 149.9 (C), 145.2 (C), 130.0 (CH), 123.9 (CH), 64.4 (CH_2), 21.8 (CH_3), 14.2 (CH_3). IR (KBr): 3487 (br, w), 2971 (w), 1755 (s), 1508 (m), 1247 (s), 1197 (s), 1148 (s), 827 (m). HRMS (ESI) calcd. for $C_{10}H_{12}N_2O_2Na$ (M+Na) 215.0791, found 215.0785.



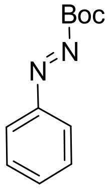
3c

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.8. The product was obtained as a red oil (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.87 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 4.51 (q, J = 7.2 Hz, 2H), 1.46 (t, J = 7.2Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.0 (CO), 149.9 (C), 140.1 (C), 129.7 (CH), 125.0 (CH), 64.6 (CH_2), 14.2 (CH_3). IR (KBr): 3490 (br, w), 2983 (w), 1760 (s), 1500 (s), 1245 (s), 839 (m), 779 (m). HRMS (ESI) calcd. for $C_9H_9ClN_2O_2Na$ (M+Na) 235.0245, found 235.0255.



3d

Eluent: n-hexane / ethyl acetate 75:25, R_F = 0.7. The product was obtained as a red oil (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.01 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 4.54 (m, 2H), 1.48 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.8 (CO), 153.2 (C), 134.7 (q, J = 32.3 Hz, C), [127.5, 124.8, 122.1, 119.4 (q, J = 270.0 Hz, CF_3)], 126.5 (q, J = 3.6 Hz, CH), 123.8 (CH), 64.8 (CH_2), 14.1 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.0. IR (KBr): 3490 (br, w), 2986 (w), 1762 (s), 1324 (s), 1247 (s), 1064 (s), 851 (m), 748 (w), 596 (w). HRMS (ESI) calcd. for $C_{10}H_9F_3N_2O_2Na$ (M+Na) 269.0508, found 269.0517.

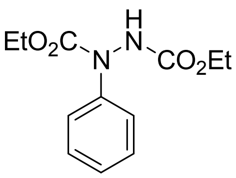


3e

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.7. The product was obtained as a red oil (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.90 (d, J = 6.9 Hz, 2H), 7.55 (t, J = 6.9 Hz, 1H), 7.50 (t, J = 6.8 Hz, 2H), 1.66 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.2 (CO), 151.6 (C), 133.3 (CH), 129.2 (CH), 123.5 (CH), 84.9 (C), 27.8 (CH_3). IR (KBr): 3484 (br, w), 3063 (w), 2983 (m), 2933 (w), 1751 (s), 1507 (m), 1272 (s), 1256 (s), 842 (m), 780 (m), 685 (m). HRMS (ESI) calcd. for $C_{11}H_{14}N_2O_2Na$ (M+Na) 229.0947, found 229.0954.

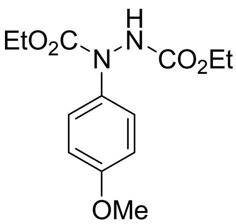
2.3 General procedure for the Rh-catalyzed electrophilic amination

To a mixture of arylboronic acid (0.3 mmol) and [Cp*Rh(OAc)$_2$] (2 mol%) in a reaction vial (8 mL), azo compound (0.2 mmol) in anhydrous DMF (1 mL) was added. The reaction mixture was stirred at 40 ^{o}C under N_2 atmosphere for 4 h. The reaction mixture was diluted with ethyl acetate (5 mL) followed by filtration with a short pad of silica gel. The reaction mixture was concentrated by rotary evaporation. The residue was purified by flash column chromatography.



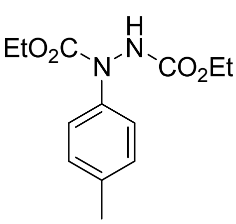
2a

Eluent: n-hexane / ethyl acetate 6:4, R_F = 0.6. The product was obtained as a pale yellow oil (99% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.43 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 8.0 Hz, 1H), 7.04 (br, s, 1H), 4.28–4.21(m, 4H), 1.28 (t, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 156.4 (CO), 154.9 (CO), 141.7 (C), 128.6 (CH), 126.4 (CH), 124.4 (CH), 63.0 (CH$_2$), 62.3 (CH$_2$), 14.4 (CH$_3$). IR (KBr): 3303 (br, m), 2984 (m), 1724 (s), 1340 (s), 1304 (s), 1237 (s), 1062 (s). HRMS (ESI) calcd. for $C_{12}H_{16}N_2O_4Na$ (M+Na) 275.1002, found 275.1002.



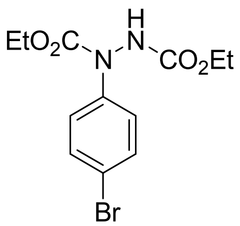
2b

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.3. The product was obtained as a pale yellow oil (99% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.32 (d, J = 6.8 Hz, 2H), 7.19 (s, 1H), 6.85 (d, J = 9.2 Hz, 2H), 4.24–4.18 (m, 4H), 3.79 (s, 3H), 1.26 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 158.2 (CO), 156.4 (CO), 134.8 (C), 126.8 (C), 113.9 (CH), 62.9 (CH$_2$), 62.2 (CH$_2$), 55.4 (CH$_3$), 14.5 (CH$_3$). IR (KBr): 3296 (s), 2993 (m), 2973 (w), 1734 (s), 1712 (s), 1340 (m), 1251 (s). HRMS (ESI) calcd. for $C_{13}H_{18}N_2O_5Na$ (M+Na) 305.1108, found 305.1104.



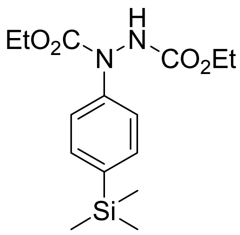
2c

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.3. The product was obtained as an orange oil (99% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.34 (br, s, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 4.25–4.18 (m, 4H), 2.32 (s, 3H), 1.26 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 156.4 (CO), 155.2 (CO), 139.2 (C), 136.3 (C), 129.2 (CH), 124.6 (CH), 62.9 (CH$_2$), 62.2 (CH$_2$), 20.9 (CH$_3$), 14.4 (CH$_3$). IR (KBr): 3306 (br, m), 2983 (m), 1721 (s), 1375 (s), 1336 (s), 1303 (s), 1235 (s), 1198 (m). HRMS (ESI) calcd. for $C_{13}H_{18}N_2O_4Na$ (M+Na) 289.1159, found 289.1156.



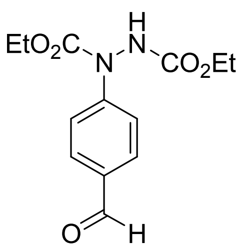
2d

Eluent: n-hexane / ethyl acetate 6:4, R_F = 0.6. The product was obtained as an orange oil (98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.06 (br, s, 1H), 4.28–4.20 (m, 4H), 1.27 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 156.3 (CO), 140.7 (C), 131.7 (CH), 63.3 (CH_2), 62.5 (CH_2), 14.4 (CH_3), 14.4 (CH_3). IR (KBr): 3305 (br, s), 2983 (m), 2929 (w), 2907 (w), 2866 (w), 1724 (s), 1321 (s), 1236 (s), 1063 (s), 510 (m). HRMS (ESI) calcd. for $C_{12}H_{16}BrN_2O_4$ (M+H) 331.0288, found 331.0292.



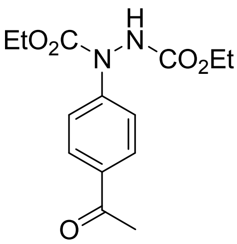
2e

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.4. The product was obtained as a clear oil (98% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ_H 7.76 (br, s, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.48(d, J = 8.2 Hz, 2H), 4.31–4.22 (m, 4H), 1.34–1.29 (m, 6H), 0.34 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ_C 156.4 (CO), 154.8 (CO), 142.4 (C), 138.2 (C), 133.7 (CH), 122.9 (CH), 63.0 (CH_2), 62.2 (CH_2), 14.3 (CH_3), 14.2 (CH_3), -1.4 (CH_3). IR (KBr): 3299 (br, m), 2983 (m), 2956 (m), 1728 (m), 1596 (m), 1505 (m), 1248 (m), 1183 (m), 1063 (m), 851 (m), 7575 (m), 727 (m), 620 (w), 523 (m). HRMS (ESI) calcd. for $C_{15}H_{25}N_2O_4Si$ (M+H) 325.1578 , found 325.1566.



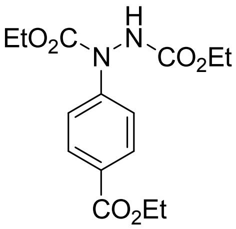
2f

Eluent: n-hexane / ethyl acetate 6:4, R_F = 0.4. The product was obtained as an orange oil (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.96 (s, 1H), 7.85 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.04 (br, s, 1H), 4.33–4.23 (m, 4H), 1.34–1.30 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 191.1 (CHO), 156.2 (CO), 154.0 (CO), 146.8 (C), 133.2 (C), 130.4 (CH), 63.6 (CH_2), 62.8 (CH_2), 14.4 (CH_3), 14.3 (CH_3). IR (KBr): 3466 (br, s), 2984 (w), 1731 (s), 1602 (s), 1317 (s), 1298 (s), 1238 (m), 1198 (m). HRMS (ESI) calcd. for $C_{13}H_{17}N_2O_5$ (M+H) 281.1132, found 281.1133.



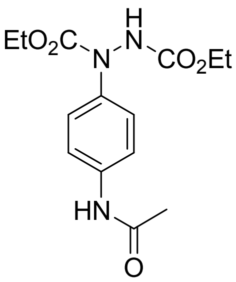
2g

Eluent: n-hexane / ethyl acetate 6:4, R_F = 0.4. The product was obtained as a yellow solid (93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.92 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.17 (br, s, 1H), 4.31–4.21 (m, 4H), 2.57 (s, 3H), 1.33 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 197.1 (CO), 156.2 (CO), 145.7 (C), 129.0 (CH), 122.1 (C), 63.4 (CH_2), 62.6 (CH_2), 26.5 (CH_3), 14.4 (CH_3), 14.3 (CH_3). IR (KBr): 3307 (s), 2986 (m), 2953 (w), 1750 (s), 1686 (s), 1508 (s), 1231 (s), 1209 (s), 1067 (s). HRMS (ESI) calcd. for $C_{14}H_{19}N_2O_5$ (M+H) 295.1288, found 295.1291.



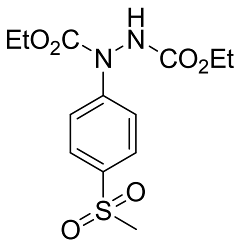
2h

Eluent: n-hexane / ethyl acetate 6:4, R_F = 0.5. The product was obtained as an orange oil (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.00 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.10 (br, s, 1H), 4.36 (q, J = 7.2 Hz, 2H), 4.30–4.21 (m, 4H), 1.38 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 166.0 (CO), 156.2 (CO), 154.2 (CO), 145.5 (C), 130.2 (CH), 122.2 (C), 63.4 (CH_2), 62.6 (CH_2), 61.0 (CH_2), 14.4 (CH_3), 14.3 (CH_3), 14.3 (CH_3). IR (KBr): 3457 (br, m), 2983 (m), 1717 (s), 1371 (m), 1276 (s), 1234 (m). HRMS (ESI) calcd. for $C_{15}H_{20}N_2O_6Na$ (M+Na) 347.1214, found 347.1214.



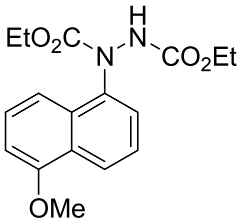
2i

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.3. The product was obtained as a white solid (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.17 (br, s, 1H), 7.56 (br, s, 1H), 7.35 (d, J = 6.8 Hz, 2H), 7.25 (d, J = 9.2 Hz, 2H), 4.23–4.16 (m, 4H), 2.09 (s, 3H), 1.27–1.23 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.0 (CO), 156.4 (CO), 155.1 (CO), 137.5 (C), 136.4 (C), 124.9 (CH), 120.3 (CH), 63.0 (CH_2), 62.3 (CH_2), 24.3 (CH_3), 14.4 (CH_3), 14.4 (CH_3). IR (KBr): 3297 (s), 2986 (w), 1747 (s), 1710 (s), 1666 (s), 1519 (s), 1308 (m), 1261 (s), 1197 (m), 1066 (m). HRMS (ESI) calcd. for $C_{14}H_{20}N_3O_5$ (M+H) 310.1397, found 310.1398.



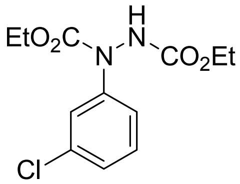
2j

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.5. The product was obtained as an off-while solid (86% yield). [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.90 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.00 (br, s, 1H), 4.34–4.24 (m, 4H), 3.04 (s, 3H), 1.35–1.26 (m, 6H). [13]C NMR (100 MHz, $CDCl_3$): δ_C 156.2 (CO), 153.9 (CO), 146.3 (C), 136.5 (C), 128.1 (CH), 63.7 (CH_2), 62.8 (CH_2), 44.6 (CH_3), 14.4 (CH_3), 14.3 (CH_3). IR (KBr): 3298 (m), 2987 (m), 2913 (w), 1748 (s), 1727 (s), 1291 (s), 1276 (s), 1064 (s). HRMS (ESI) calcd. for $C_{13}H_{19}N_2O_6S$ (M+H) 331.0958, found 331.0963.



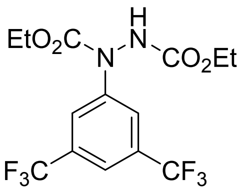
2k

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.2. The product was obtained as an orange solid (99% yield). [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.80 (s, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.18 (s, 1H), 7.15–7.11 (m, 2H), 4.30–4.19 (m, 4H), 3.91 (s, 3H), 1.31–1.27 (m, 6H). [13]C NMR (100 MHz, $CDCl_3$): δ_C 157.9 (CO), 156.5 (CO), 137.3 (C), 133.1 (C), 129.5 (CH), 128.7 (C), 127.2 (CH), 119.3 (CH), 105.6 (CH), 63.1 (CH_2), 62.3 (CH_2), 55.4 (CH_3), 14.5 (CH_3). IR (KBr): 3289 (s), 2983 (m), 1756 (s), 1716 (s), 1328 (s), 1229 (s), 1178 (s), 1060 (s). HRMS (ESI) calcd. for $C_{17}H_{20}N_2O_5Na$ (M+Na) 355.1264, found 355.1263.



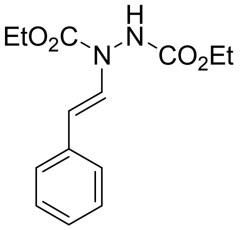
2l

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.7. The product was obtained as a clear oil (97% yield). [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.47 (s, 1H), 7.35 (d, *J* = 8 Hz, 1H), 7.25 (t, *J* = 8 Hz, 1H), 7.17 (d, *J* = 8 Hz, 1H), 7.11 (s, 1H), 4.29–4.21 (m, 4H), 1.29 (t, *J* = 6.8 Hz, 6H). [13]C NMR (100 MHz, $CDCl_3$): δ_C 156.3 (CO), 154.5 (CO), 142.7 (CH), 134.2 (CH), 129.6 (CH), 126.2 (CH), 123.9 (C), 121.8 (C), 63.3 (CH_2), 62.5 (CH_2), 14.4 (CH_3), 14.4 (CH_3). IR (KBr): 3298 (br, s), 3072 (w), 2983 (m), 2932 (w), 2904 (w), 2866 (w), 1727 (s), 1329 (s), 1237 (s), 780 (m), 760 (m). HRMS (ESI) calcd. for $C_{12}H_{16}N_2O_4ClNa$ (M+Na) 309.0613, found 309.0615.



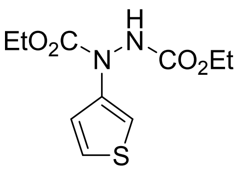
2m

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.7. The product was obtained as an orange solid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98 (s, 2H), 7.68 (s, 1H), 6.97 (br, s, 1H), 4.35–4.27 (m, 4H), 1.33 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 156.2 (CO), 153.8 (CO), 143.0 (C), 132.0 (q, J = 30 Hz, CCF_3), 124.4 (CH), 121.7 (CH), 119.0 (CH), 63.9 (CH_2), 63.0 (CH_2), 14.8 (CH_3), 14.3 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.0. IR (KBr): 3261 (m), 3031 (w), 2983 (w), 2923 (w), 1731 (s), 1279 (s), 1170 (s), 1122 (s), 887 (m), 684 (m). HRMS (ESI) calcd. for $C_{14}H_{13}F_6N_2O_4$ (M+H) 387.0785, found 387.0786.



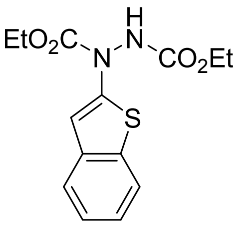
2n

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.3. The product was obtained as a white solid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.54 (d, J = 15.6 Hz, 1H), 7.32–7.28 (m, 3H), 7.17 (d, J = 6.8 Hz, 1H), 6.80 (1H), 6.14 (s, 1H), 4.26 (m, 4H), 1.32 (br, s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 153.3 (CO), 136.0 (C), 128.6 (CH), 126.5 (CH), 126.3 (CH), 125.8 (CH), 110.2 (CH), 62.6 (CH_2), 14.4 (CH_3). IR (KBr): 3280 (m), 3078 (w), 3018 (w), 2981 (w), 2929 (w), 1748 (s), 1692 (s), 1654 (s), 1330 (m), 1301 (s), 1278 (m). HRMS (ESI) calcd. for $C_{14}H_{18}N_2O_4Na$ (M+Na) 301.1159, found 301.1160.



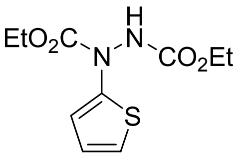
2o

Eluent: n-hexane / ethyl acetate 6:4, R_F = 0.6. The product was obtained as an orange solid (93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.21–7.18 (m, 3H), 7.04 (br, s, 1H), 4.30–4.21 (m, 4H), 1.30 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 140.2 (C), 124.4 (CH), 63.2 (CH_2), 62.4 (CH_2), 14.5 (CH_3), 14.4 (CH_3). IR (KBr): 3274 (m), 1707 (m), 1632 (m), 1597 (m), 1269 (m), 1246 (m), 744 (m). HRMS (ESI) calcd. for $C_{10}H_{15}N_2O_4S$ (M+H) 259.0747, found 259.0749.



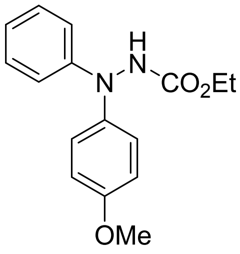
2p

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.5. The product was obtained as an orange solid (45% yield). [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.71 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.4 Hz, 1H), 7.25 (t, J = 7.3 Hz, 1H), 7.09 (br, s, 2H), 4.35 (q, J = 7.1 Hz, 2H), 4.29–4.27 (m, 2H), 1.35 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 144.1 (C), 137.9 (C), 124.5 (CH), 123.6 (C), 122.9 (C), 121.7 (CH), 64.0 (CH_2), 62.8 (CH_2), 14.4 (CH_3), 14.4 (CH_3). IR (KBr): 3299 (m), 2970 (w), 1747 (s), 1693 (s), 1354 (s), 1302 (s), 1233 (m). HRMS (ESI) calcd. for $C_{14}H_{17}N_2O_4S$ (M+H) 309.0904, found 309.0907.



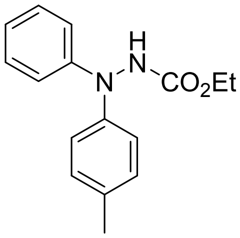
2q

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.3. The product was obtained as a purple oil (20% yield). [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.05 (br, s, 1H), 7.00 (br, s, 1H), 6.86–6.84 (m, 2H), 4.31–4.22 (m, 4H), 1.30 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 155.7 (CO), 153.8 (CO), 144.1 (C), 124.9 (CH), 63.6 (CH_2), 62.6 (CH_2), 14.4 (CH_3), 14.4 (CH_3). IR (KBr): 3414 (m), 2980 (w), 1718 (s), 1331 (s), 1309 (s), 1244 (s), 1061 (m). HRMS (ESI) calcd. for $C_{10}H_{15}N_2O_4S$ (M+H) 281.0566, found 281.0563.



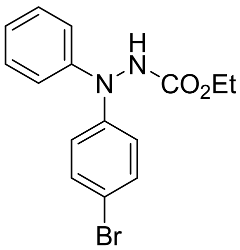
4aa

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.5. The product was obtained as an orange solid (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26–7.20 (m, 4H), 7.03 (s, 1H), 6.92–6.87 (m, 5H), 4.19 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.02 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.5 (CO), 139.0 (C), 128.9 (CH), 125.5 (C), 125.0 (C), 120.7 (CH), 115.4 (CH), 114.6 (CH), 61.8 (CH_2), 55.5 (CH_3), 14.5 (CH_3). IR (KBr): 3285 (m), 2955 (w), 2930 (w), 1707 (s), 1508 (s), 1280 (m), 1247 (s). HRMS (ESI) calcd. for $C_{16}H_{19}N_2O_3$ (M+H) 287.1390, found 287. 1387.



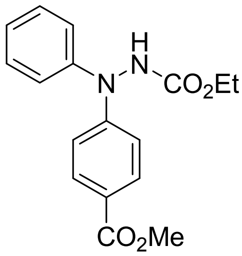
4ba

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.6. The product was obtained as a pale yellow solid (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26 (t, J = 8.4 Hz, 2H), 7.13 (s, 4H), 7.05 (d, J = 7.6 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 4.21–4.19 (m, 2H), 2.33 (s, 3H) 1.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 146.8 (CO), 143.6 (C), 133.6 (C), 131.9 (C), 129.8 (CH), 129.0 (CH), 121.9 (CH), 121.4 (CH), 117.7 (CH), 61.9 (CH_2), 20.8 (CH_3), 14.5 (CH_3). IR (KBr): 3279 (s), 3024 (w), 2980 (w), 2904 (w), 1709 (s), 1510 (s), 1247 (s), 1049 (s). HRMS (ESI) calcd. for $C_{16}H_{19}N_2O_2$ (M+H) 271.1441, found 271.1441.



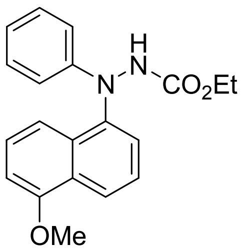
4ca

Eluent: n-hexane / ethyl acetate 9:1, R_F = 0.2. The product was obtained as a yellow solid (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36 (d, J = 8.8 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.16 (d, J = 6.9 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 6.99 (d, J = 8.7 Hz, 2H), 6.85 (br, s, 1H), 4.20 (m, 2H), 1.28 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 145.5 (CO), 132.2 (C), 132.1 (C), 132.0 (CH), 131.0 (C), 129.3 (CH), 123.9 (CH), 120.3 (CH), 62.1 (CH_2), 14.5 (CH_3). IR (KBr): 3270 (s), 2977 (w), 1707 (s), 1250 (s), 607 (m), 502 (m). HRMS (ESI) calcd. for $C_{15}H_{14}BrN_2O_2$ (M-H) 333.0244, found 333.0250.



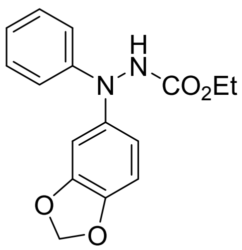
4da

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.4. The product was obtained as a yellow oil (44% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.91 (d, J = 8.8 Hz, 2H), 7.41–7.35 (m, 4H), 7.21 (t, J = 7.1 Hz, 1H), 7.07 (br, s, 1H), 6.98 (d, J = 8.2 Hz, 2H), 4.21 (m, 2H), 3.87 (s, 3H), 1.30–1.14 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 166.9 (CO), 155.7 (CO), 150.6 (C), 144.4 (C), 131.0 (CH), 129.5 (CH), 125.9 (CH), 123.9 (CH), 122.2 (C), 114.5 (CH), 62.1 (CH_2), 51.8 (CH_3), 14.5 (CH_3). IR (KBr): 3280 (m), 2983 (w), 2951 (w), 1716 (s), 1607 (s), 1592 (s), 1277 (s), 1230 (s). HRMS (ESI) calcd. for C_{17}H19N$_2$O4 (M+H) 315.1345, found 315.1343.



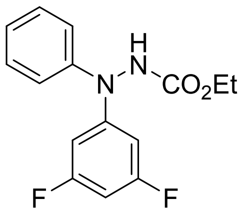
4ea

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.3. The product was obtained as a pink solid (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.68 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.56 (br, s, 1H), 7.36 (d, J = 6.4 Hz, 1H), 7.31–7.28 (m, 2H), 7.12 (d, J = 8.8 Hz, 4H), 7.02–6.99 (m, 2H), 4.23–4.22 (m, 2H), 3.92 (s, 3H), 1.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 157.1 (CO), 146.7 (C), 141.8 (C), 132.0 (C), 131.7 (C), 129.5 (CH), 129.1 (CH), 128.8 (CH), 127.8 (CH), 122.3 (CH), 119.2 (CH), 118.1 (CH), 117.8 (C), 117.0 (C), 105.9 (CH), 61.9 (CH_2), 55.4 (CH_3), 14.5 (CH_3). IR (KBr): 3289 (s), 2983 (w), 2929 (w), 1708 (s), 1247 (s). HRMS (ESI) calcd. for $C_{20}H_{21}N_2O_3$ (M+H) 337.1547, found 337.1545.



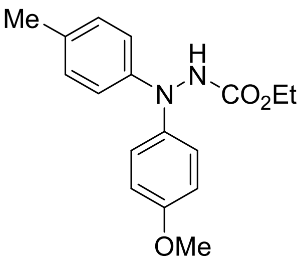
4fa

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.2. The product was obtained as a purple solid (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.23 (t, J = 7.6 Hz, 2H), 7.03 (br, s, 1H), 6.95–6.90 (m, 3H), 6.83–6.76 (m, 3H), 5.96 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 1.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 155.9 (CO), 148.2 (C), 147.2 (C), 145.0 (C), 140.4 (C), 131.8 (CH), 129.0 (CH), 121.2 (CH), 116.2 (CH), 108.4 (CH), 105.3 (CH), 101.4 (CH_2), 61.9 (CH_2), 14.5 (CH_3). IR (KBr): 3279 (s), 2983 (w), 2929 (w), 2879 (w), 1709 (s), 1243 (m), 1217 (s), 1039 (m). HRMS (ESI) calcd. for $C_{16}H_{16}N_2O_4Na$ (M+Na) 323.1002, found 323.1004.



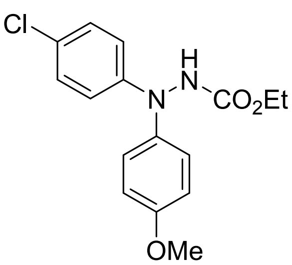
4ga

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.3. The product was obtained as an orange solid (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.30 (t, J = 8.4 Hz, 1H), 7.11 (d, J = 6.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 3H), 6.96 (t, J = 7.6 Hz, 1H), 6.81 (t, J = 8.8 Hz, 1H), 6.44 (br, s, 1H), 5.86 (br, s, 1H), 4.17 (q, J = 7.2 Hz, 2H), 1.26 (br, s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 164.5 (d, J = 13Hz, CH), 162.0 (d, J = 13 Hz, CH), 156.8 (C), 144.7 (C), 141.7 (C), 130.1 (CH), 129.5 (CH), 120.8 (C), 112.4 (t, J = 25 Hz, C), 103.0 (t, J = 25 Hz, C), 62.0 (CH_2), 14.5 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ_F -108.9. IR (KBr): 3238 (s), 3081 (w), 2989 (w), 1725 (m), 1625 (s), 1284 (s), 1251 (s), 755 (s). HRMS (ESI) calcd. for $C_{15}H_{15}F_2N_2O_2$ (M+H) 293.1096, found 293.1102.



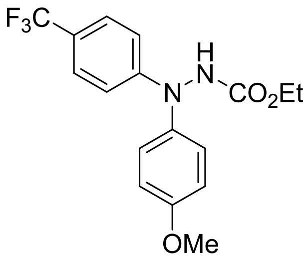
4ab

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.5. The product was obtained as a white solid (93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.17 (m, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.97 (s, 1H), 6.88–6.85 (m, 4H), 4.21–4.16 (m, 2H), 3.80 (s, 3H), 2.28 (s, 3H), 1.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 156.6 (CO), 145.0 (C), 139.7 (C), 130.8 (C), 129.6 (CH), 123.9 (C), 123.6 (C), 116.8 (C), 114.5 (CH), 61.7 (CH_2), 55.5 (CH_3), 20.6 (CH_3), 14.5 (CH_3). IR (KBr): 3293 (m), 2983 (w), 2832 (w), 1711 (s), 1507 (s), 1244 (s), 815 (m), 586 (w). HRMS (ESI) calcd. for $C_{17}H_{20}N_2O_3Na$ (M+Na) 323.1366, found 323.1364.



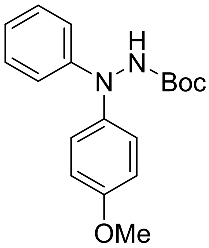
4ac

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.5. The product was obtained as a white solid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26 (s, 2H), 7.23 (s, 1H), 7.17 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.9 Hz, 2H), 4.19 (t, J = 7.2 Hz, 2H), 3.81 (s, 3H), 1.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 157.5 (CO), 155.9 (C), 146.3 (C), 138.4 (C), 128.8 (CH), 125.8 (C), 125.3 (C), 116.3 (CH), 114.7 (CH), 61.9 (CH_2), 55.5 (CH_3), 14.5 (CH_3). IR (KBr): 3292 (s), 2976 (w), 2838 (w), 1707 (s), 838 (m), 824 (s), 617 (m), 581 (m), 541 (m). HRMS (ESI) calcd. for $C_{16}H_{17}ClN_2O_3Na$ (M+Na) 343.0820, found 343.0820.



4ad

Eluent: n-hexane / ethyl acetate 7:3, R_F = 0.6. The product was obtained as a white solid (78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (d, *J* = 8.6 Hz, 2H), 7.30 (br, d, 2H), 7.07 (s, 1H), 6.92 (d, *J* = 8.9, 2H), 6.86 (d, *J* = 8.44 Hz, 2H), 4.20 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.28 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 158.4 (CO), 155.7 (C), 150.4 (C), 137.4 (C), 127.5 (CH), 126.3 (q, J = 3.65 Hz, CH), 123.3 (C), 121.6 (q, *J* = 32.4 Hz, C), 115.0 (CH), 113.2 (CH), 62.1 (CH_2), 55.5 (CH_3), 14.5 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ_F -61.4. IR (KBr): 3269 (m), 2980 (w), 2838 (w), 1716 (s), 1615 (m), 1509 (s), 1325 (s), 1251 (s), 1117 (s), 1069 (m), 833 (m), 586 (w), 539 (w). HRMS (ESI) calcd. for $C_{17}H_{17}F_3N_2O_3Na$ (M+Na) 377.1083, found 377.1083.

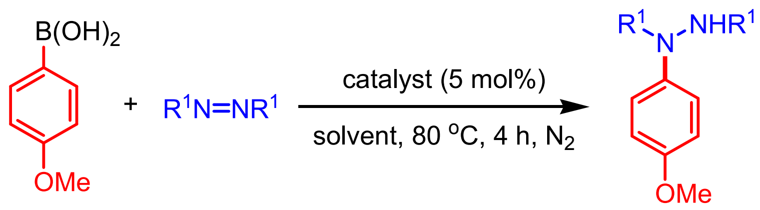


4ae

Eluent: n-hexane / ethyl acetate 8:2, R_F = 0.5. The product was obtained as a white solid (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26–7.20 (m, 4H), 6.92–6.87 (m, 5H), 6.82 (s, 1H), 3.81 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 155.0 (CO), 147.5 (C), 139.1 (C), 128.9 (CH), 125.1 (CH), 124.4 (C), 120.6 (CH), 115.4 (CH), 114.6 (CH), 55.5 (CH_3), 28.3 (CH_3). IR (KBr): 3327 (s), 2965 (m), 2834 (w), 1707 (s), 1597 (m), 1030 (s), 836 (s), 749 (s), 690 (m), 578 (m). HRMS (ESI) calcd. for $C_{18}H_{22}N_2O_3Na$ (M+Na) 337.1523, found 337.1523.

3. Results for Optimization Studies

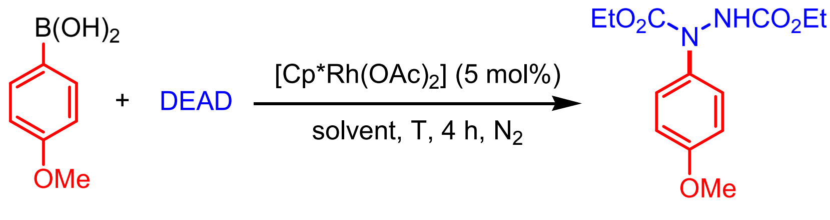
Table S1. Catalyst screening[a]



Entry	R^1	Catalyst	Solvent	Yield/ %
1	CO_2Et	$[Cp^*Rh(OAc)_2]$	THF	85
2	$CO_2{}^tBu$	$[Cp^*Rh(OAc)_2]$	THF	42
3	Ph	$[Cp^*Rh(OAc)_2]$	THF	0
4	CO_2Et	$[Cp^*RhCl_2]_2$	THF	10
5[b]	CO_2Et	$[Cp^*RhCl_2]_2$	THF	40
6[c]	CO_2Et	$[Cp^*RhCl_2]_2$	THF	0
7[d]	CO_2Et	$[Cp^*RhCl_2]_2$	THF	8
8	CO_2Et	$[Cp^*Rh(MeCN)_3(SbF_6)_2]$	THF	85
9	CO_2Et	$[Cp^*IrCl_2]_2$	THF	0
10[b]	CO_2Et	$[Cp^*IrCl_2]_2$	THF	9
11[e]	CO_2Et	$[Rh(COD)Cl]_2$	THF	11
12	CO_2Et	$[Rh(COD)(OH)]_2$	DMF	0
13[f]	CO_2Et	$[Ir(COD)Cl]_2$	THF	0
14	CO_2Et	$[Pd(PPh_3)_4]$	DCE	0
15	CO_2Et	$[Pd_2(dba)_3{\cdot}CHCl_3]$	DCE	27

[a]Conditions: **1** (0.3 mmol), **2** (0.2 mmol), catalyst (5 mol% on metal basis) in solvent (1 mL) at 80 °C for 4 h under N_2 atmosphere. [b]AgOAc (1.1 equiv) was added. [c]PivOH (1.1 equiv) was added. [d]Zn (50 mol%) was added. [e]CsOAc (1.1 equiv) was added. [f]Bathocuproine (10 mol%) and KOPiv (1.1 equiv) were added.

Table S2. Reaction Optimization[a]



Entry	Solvent	Temp/ °C	Yield/ %
1	H_2O	80	39
2	^{t}BuOH	80	64
3	MeOH	80	18
4	MeCN	80	3
5	acetone	80	64
6	EA	80	51
7	dioxane	80	50
8	toluene	80	14
9	DCE	80	31
10	n-hexane	80	24
11	TBME	80	28
12	DMA	80	92
13	DMPU	80	95
14	DMF	80	99
15	THF	100	70
16	THF	60	82
17	THF	50	55
18	DMF	60	99
19	DMF	40	98
20[b]	DMF	40	99

[a]Conditions: **1** (0.3 mmol), **2** (0.2 mmol), [Cp*Rh(OAc)$_2$] (5 mol%) in solvent (1 mL) for 4 h under N_2 atmosphere. [b][Cp*Rh(OAc)$_2$] (2 mol%) was used.

4. Synthesis of [Cp*Rh^{III}] complexes

4.1 Synthesis of [Cp*RhCl$_2$(PPh$_3$)]

A mixture of [Cp*RhCl$_2$]$_2$ (0.95 mmol) and triphenylphosphine (2.28 mmol) was dissolved in anhydrous DCM (30 mL). The reaction mixture was stirred for 1 h under room temperature. The reaction mixture was filtered and rinsed with DCM (5 mL) to afford 99% of the pure complex as a red powder.

[Cp*RhCl$_2$(PPh$_3$)] was isolated as a red powder (99% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 7.82–7.80 (m, 6H), 7.37 (m, 9H), 1.36 (d, J = 3.4 Hz, 15H), ^{13}C NMR (CDCl$_3$, 100 MHz); δ_C 134.8 (CH), 134.7 (CH), 130.4 (C), 127.9 (CH), 99.16 (d, J = 4.1 Hz, C), 8.8 (CH$_3$). ^{31}P NMR (CDCl$_3$, 162 MHz); δ_p 30.0 (d, J = 144.5 Hz). HRMS (ESI) calcd. for C$_{28}$H$_{30}$ClPRh (M+ = [Cp*RhCl(PPh$_3$)]$^+$) 535.0829, found 535.0834.

4.2.1 Synthesis of [Cp*Rh(Ph)(Br)(PPh$_3$)] (5a)

To a 10 mL-Schlenk tube, [Cp*RhCl$_2$(PPh$_3$)] (0.28 mmol) in anhydrous THF (5 mL) was added and immersed into an ice-bath. 2.7 M Phenylmagnesium bromide (0.27 mL) was added slowly via a syringe for 30 min. The reaction mixture was stirred for 2 h at 0 °C under nitrogen atmosphere. The excess Grignard reagent was hydrolyzed with aqueous ammonium chloride and the mixture was filtered. The organic layer was washed with water (10 mL) and dried over anhydrous magnesium sulfate. After the solvent was removed in *vacuo*, the residue was purified by flash column chromatography on silica gel using (n-hexane / ethyl acetate = 7 : 3, v / v) as eluent.. Recrystallization of the complex from diethyl ether affords 71% of the pure complex as a red crystal.

[Cp*Rh(Ph)(Br)(PPh$_3$)] was isolated as a red crystal (71% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 7.85 (t, J = 8.5 Hz, 2H), 7.42–7.40 (m, 7H), 7.19–7.15 (m, 4H), 6.99 (m, 3H), 6.91–6.81 (m, 4H), 1.37 (d, J = 2.3 Hz, 15H), ^{13}C NMR (CDCl$_3$, 100 MHz); δ_C 157.6 (d, J = 21 Hz, C), 140.5 (C), 136.0 (d, J = 37 Hz, CH), 134.6 (CH), 131.0 (d, J = 26 Hz, CH), 130.3 (CH), 128.5 (d, J = 77 Hz, CH), 123.1 (CH), 101.4 (t, J = 4 Hz, C), 9.8 (CH$_3$). ^{31}P NMR (CDCl$_3$, 162 MHz); δ_P 39.8 (d, J = 160.3 Hz). HRMS (ESI) calcd. for C$_{34}$H$_{35}$PRh (M+ = [Cp*Rh(Ph)(PPh$_3$)]$^+$) 577.1531, found 577.1516.

4.2.2 Synthesis of [Cp*Rh(Ph)(Cl)(PPh_3)] (5b)

To a 200 mL-Schlenk flask, [Cp*RhCl_2(PPh_3)] (5 mmol) and PhB$(OH)_2$ (10 mmol) were added. The flask was evacuated and back-filled with N_2 for three times. Distilled THF (50 mL) and NEt_3 (50 mL) were added to the reaction flask. The reaction mixture was stirred at 50 °C for 2 h. After that, solvents were removed by rotary evaporation, and the residue was re-dissolved in a small amount of dichloromethane (DCM). The dissolved mixture was then purified by flash column chromatography on silica gel using (n-hexane / ethyl acetate = 7 : 3, v / v) as eluent. Recrystallization of the complex from diethyl ether affords 83% of the pure complex as red crystal.

[Cp*Rh(Ph)(Cl)(PPh_3)] was isolated as a red crystal (83% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.84–7.43 (m, 9H), 7.19–6.98 (m, 8H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.61–6.47 (m, 2H), 1.31 (d, *J* = 2.4 Hz, 15H), ^{13}C NMR ($CDCl_3$, 100 MHz); δ_C 157.6 (d, *J* = 21 Hz, C), 140.5 (C), 136.0 (d, *J* = 37 Hz, CH), 134.6 (CH), 131.0 (d, *J* = 26 Hz, CH), 130.3 (CH), 128.5 (d, *J* = 77 Hz, CH), 123.1 (CH), 101.4 (t, *J* = 4 Hz, C), 9.8 (CH_3). ^{31}P NMR ($CDCl_3$, 162 MHz); δ_P 39.8 (d, *J* = 159.1 Hz). HRMS (ESI) calcd. for $C_{34}H_{35}PRh$ (M+ = $[Cp^*Rh(Ph)(PPh_3)]^+$) 577.1531, found 577.1516.

5. X-ray Crystallographic Data

Figure S1. Molecular structure of 2-(4-methoxyphenyl)-2-phenyl-, 1-ethyl hydrazinecarboxylic acid ester (**4aa**)
(CCDC number = 1455771)

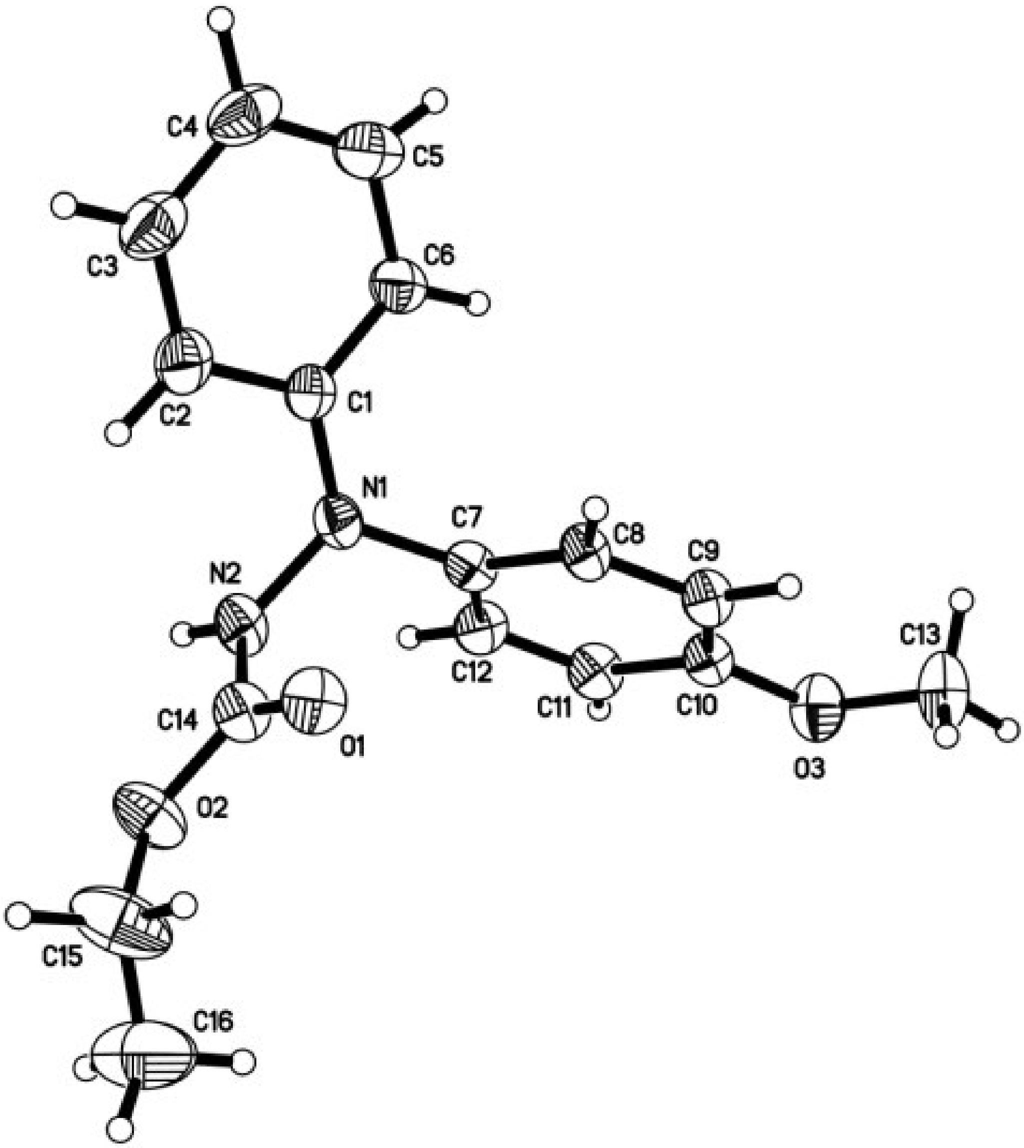


Table S3. Crystal data and structure refinement for 2-(4-methoxyphenyl)-2-phenyl-, 1-ethyl hydrazinecarboxylic acid ester

CCDC number	1455771	
Identification code	lyf1	
Empirical formula	$C_{16} H_{18} N_2 O_3$	
Formula weight	286.32	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pc2(1)b	
Unit cell dimensions	a = 9.7693(4) Å	α= 90°.
	b = 16.4783(7) Å	β= 90°.
	c = 19.4329(7) Å	γ = 90°.
Volume	3128.3(2) $Å^3$	
Z	8	
Density (calculated)	1.216 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	1216	
Crystal size	0.60 x 0.42 x 0.42 mm^3	
Theta range for data collection	2.08 to 27.43°.	
Index ranges	-12<=h<=12, -19<=k<=21, -25<=l<=22	
Reflections collected	32425	
Independent reflections	6403 [R(int) = 0.0756]	
Completeness to theta = 27.43°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6050	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6403 / 4 / 399	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0681, wR2 = 0.1709	
R indices (all data)	R1 = 0.1627, wR2 = 0.2424	
Absolute structure parameter	-1(2)	
Extinction coefficient	0.0053(5)	
Largest diff. peak and hole	0.481 and -0.175 e.$Å^{-3}$	

Table S4. Bond lengths [Å] and angles [°] for 2-(4-methoxyphenyl)-2-phenyl-, 1-ethyl hydrazinecarboxylic acid ester

O(1)-C(14)	1.210(4)
O(2)-C(14)	1.344(5)
O(2)-C(15)	1.438(6)
O(3)-C(10)	1.387(5)
O(3)-C(13)	1.428(6)
N(1)-C(1)	1.386(5)
N(1)-N(2)	1.404(4)
N(1)-C(7)	1.452(5)
N(2)-C(14)	1.316(5)
N(2)-H(2A)	0.8600
C(1)-C(6)	1.383(6)
C(1)-C(2)	1.395(6)
C(2)-C(3)	1.343(6)
C(2)-H(2B)	0.9300
C(3)-C(4)	1.368(8)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.384(8)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.367(5)
C(5)-H(5A)	0.9300
C(6)-H(6A)	0.9300
C(7)-C(12)	1.382(5)
C(7)-C(8)	1.389(5)
C(8)-C(9)	1.370(5)
C(8)-H(8A)	1.06(3)
C(9)-C(10)	1.381(5)
C(9)-H(9A)	0.9300
C(10)-C(11)	1.390(5)
C(11)-C(12)	1.356(6)
C(11)-H(11A)	0.9300
C(12)-H(12A)	0.9300
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(15)-C(16)	1.347(8)

C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
O(4)-C(30)	1.212(4)
O(5)-C(30)	1.349(5)
O(5)-C(31)	1.436(5)
O(6)-C(26)	1.371(4)
O(6)-C(29)	1.429(5)
N(3)-C(17)	1.401(5)
N(3)-N(4)	1.406(4)
N(3)-C(23)	1.430(4)
N(4)-C(30)	1.323(5)
N(4)-H(4B)	0.8600
C(17)-C(22)	1.384(5)
C(17)-C(18)	1.385(5)
C(18)-C(19)	1.377(6)
C(18)-H(18A)	0.97(3)
C(19)-C(20)	1.375(6)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.356(7)
C(20)-H(20A)	0.9300
C(21)-C(22)	1.376(6)
C(21)-H(21A)	0.9300
C(22)-H(22A)	0.9300
C(23)-C(28)	1.368(4)
C(23)-C(24)	1.375(5)
C(24)-C(25)	1.383(5)
C(24)-H(24A)	0.84(3)
C(25)-C(26)	1.381(5)
C(25)-H(25A)	1.13(4)
C(26)-C(27)	1.389(5)
C(27)-C(28)	1.375(5)
C(27)-H(27A)	0.9300
C(28)-H(28A)	0.87(3)
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600

C(29)-H(29C)	0.9600
C(31)-C(32)	1.346(7)
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600

C(14)-O(2)-C(15)	117.0(4)
C(10)-O(3)-C(13)	118.3(4)
C(1)-N(1)-N(2)	119.4(3)
C(1)-N(1)-C(7)	124.5(3)
N(2)-N(1)-C(7)	114.5(3)
C(14)-N(2)-N(1)	119.2(3)
C(14)-N(2)-H(2A)	120.4
N(1)-N(2)-H(2A)	120.4
C(6)-C(1)-N(1)	120.5(4)
C(6)-C(1)-C(2)	117.4(4)
N(1)-C(1)-C(2)	121.9(4)
C(3)-C(2)-C(1)	120.0(5)
C(3)-C(2)-H(2B)	120.0
C(1)-C(2)-H(2B)	120.0
C(2)-C(3)-C(4)	123.9(6)
C(2)-C(3)-H(3A)	118.0
C(4)-C(3)-H(3A)	118.0
C(5)-C(4)-C(3)	116.0(5)
C(5)-C(4)-H(4A)	122.0
C(3)-C(4)-H(4A)	122.0
C(4)-C(5)-C(6)	121.8(5)
C(4)-C(5)-H(5A)	119.1
C(6)-C(5)-H(5A)	119.1
C(1)-C(6)-C(5)	120.8(5)
C(1)-C(6)-H(6A)	119.6
C(5)-C(6)-H(6A)	119.6
C(12)-C(7)-C(8)	119.5(4)
C(12)-C(7)-N(1)	119.2(3)
C(8)-C(7)-N(1)	121.2(3)
C(9)-C(8)-C(7)	120.5(3)

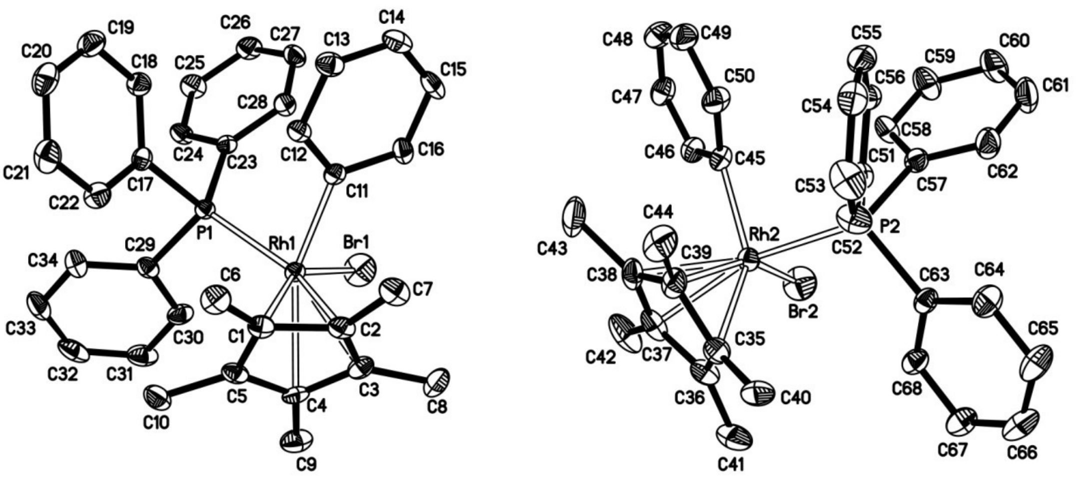
C(9)-C(8)-H(8A)	111.6(16)
C(7)-C(8)-H(8A)	127.9(16)
C(8)-C(9)-C(10)	119.7(3)
C(8)-C(9)-H(9A)	120.2
C(10)-C(9)-H(9A)	120.2
C(9)-C(10)-O(3)	124.7(3)
C(9)-C(10)-C(11)	119.5(4)
O(3)-C(10)-C(11)	115.8(3)
C(12)-C(11)-C(10)	120.8(4)
C(12)-C(11)-H(11A)	119.6
C(10)-C(11)-H(11A)	119.6
C(11)-C(12)-C(7)	120.0(3)
C(11)-C(12)-H(12A)	120.0
C(7)-C(12)-H(12A)	120.0
O(3)-C(13)-H(13A)	109.5
O(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
O(3)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(1)-C(14)-N(2)	125.7(4)
O(1)-C(14)-O(2)	125.1(4)
N(2)-C(14)-O(2)	109.2(3)
C(16)-C(15)-O(2)	111.6(6)
C(16)-C(15)-H(15A)	109.3
O(2)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15B)	109.3
O(2)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(30)-O(5)-C(31)	116.3(3)
C(26)-O(6)-C(29)	117.5(3)
C(17)-N(3)-N(4)	117.3(3)

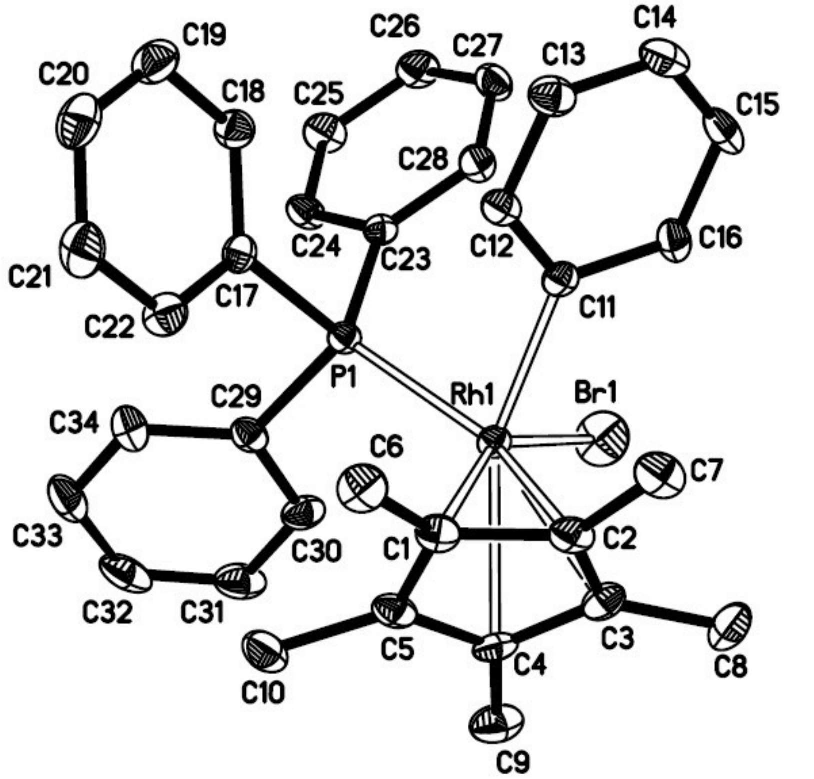
C(17)-N(3)-C(23)	124.9(3)
N(4)-N(3)-C(23)	115.6(3)
C(30)-N(4)-N(3)	119.8(3)
C(30)-N(4)-H(4B)	120.1
N(3)-N(4)-H(4B)	120.1
C(22)-C(17)-C(18)	118.6(4)
C(22)-C(17)-N(3)	121.2(3)
C(18)-C(17)-N(3)	120.1(3)
C(19)-C(18)-C(17)	120.0(4)
C(19)-C(18)-H(18A)	115(2)
C(17)-C(18)-H(18A)	124(2)
C(20)-C(19)-C(18)	121.0(5)
C(20)-C(19)-H(19A)	119.5
C(18)-C(19)-H(19A)	119.5
C(21)-C(20)-C(19)	118.7(5)
C(21)-C(20)-H(20A)	120.6
C(19)-C(20)-H(20A)	120.6
C(20)-C(21)-C(22)	121.5(4)
C(20)-C(21)-H(21A)	119.2
C(22)-C(21)-H(21A)	119.2
C(21)-C(22)-C(17)	120.0(4)
C(21)-C(22)-H(22A)	120.0
C(17)-C(22)-H(22A)	120.0
C(28)-C(23)-C(24)	118.9(3)
C(28)-C(23)-N(3)	122.5(3)
C(24)-C(23)-N(3)	118.6(3)
C(23)-C(24)-C(25)	121.2(3)
C(23)-C(24)-H(24A)	120(2)
C(25)-C(24)-H(24A)	119(2)
C(26)-C(25)-C(24)	119.0(3)
C(26)-C(25)-H(25A)	126(2)
C(24)-C(25)-H(25A)	114(2)
O(6)-C(26)-C(25)	115.9(3)
O(6)-C(26)-C(27)	123.8(3)
C(25)-C(26)-C(27)	120.3(3)
C(28)-C(27)-C(26)	119.0(3)
C(28)-C(27)-H(27A)	120.5
C(26)-C(27)-H(27A)	120.5

C(23)-C(28)-C(27)	121.5(3)
C(23)-C(28)-H(28A)	126.1(19)
C(27)-C(28)-H(28A)	112.3(19)
O(6)-C(29)-H(29A)	109.5
O(6)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
O(6)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
O(4)-C(30)-N(4)	126.3(4)
O(4)-C(30)-O(5)	124.9(4)
N(4)-C(30)-O(5)	108.9(3)
C(32)-C(31)-O(5)	111.0(5)
C(32)-C(31)-H(31A)	109.4
O(5)-C(31)-H(31A)	109.4
C(32)-C(31)-H(31B)	109.4
O(5)-C(31)-H(31B)	109.4
H(31A)-C(31)-H(31B)	108.0
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5

Symmetry transformations used to generate equivalent atoms:

Figure S2a. Molecular structure of Rhodium, bromo-(1,2,3,4,5-pentamethylcyclopentadienyl)phenyl(triphenylphosphine) complex (**5a**) (CCDC number = 1455769)

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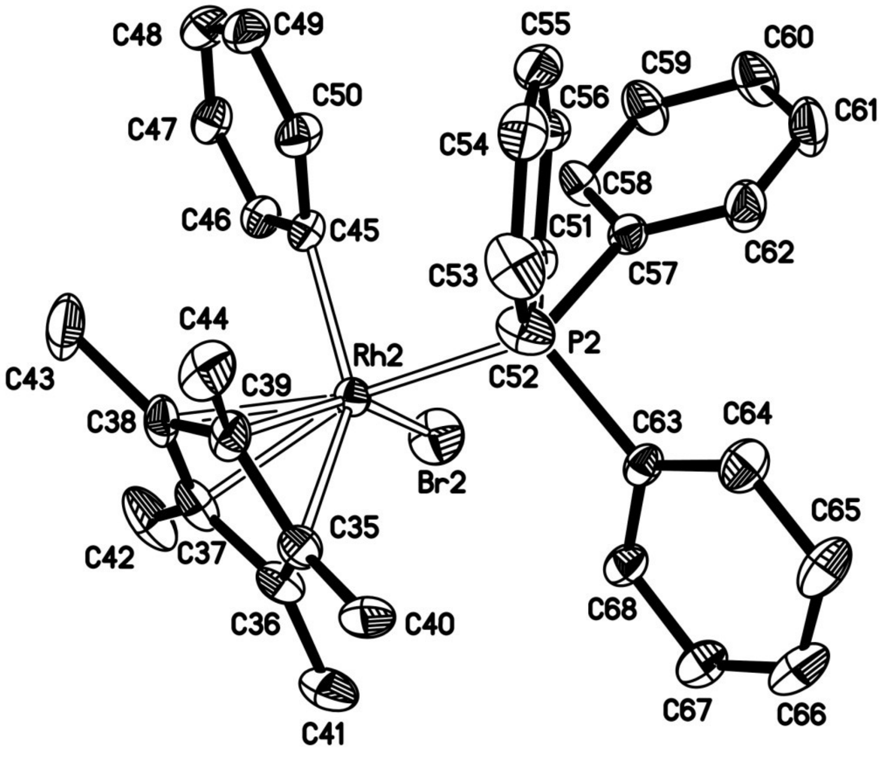
C3
C8
C10
C9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P2
C52
C43
Rh2
C39
C38
C63
C64
Br2
C65
C42
C37
C35
C68
C36
C40
C41
C67
C66

Table S5. Crystal data and structure refinement for Rhodium, bromo-(1,2,3,4,5-pentamethylcyclopentadienyl)phenyl(triphenylphosphine) complex

CCDC number	1455769	
Identification code	lyf5	
Empirical formula	$RhBr(C_{10}H_{15})(C_6H_5)P(C_6H_5)_3$	
Formula weight	657.41	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4383(2) Å	α= 104.905(2)°.
	b = 15.6767(4) Å	β= 100.8330(10)°.
	c = 19.2505(5) Å	γ = 98.7530(10)°.
Volume	2922.39(12) Å^3	
Z	4	
Density (calculated)	1.494 Mg/m^3	
Absorption coefficient	2.027 mm^{-1}	
F(000)	1336	
Crystal size	0.32 x 0.18 x 0.10 mm^3	
Theta range for data collection	1.38 to 27.52°.	
Index ranges	-13<=h<=13, -20<=k<=20, -25<=l<=24	
Reflections collected	80719	
Independent reflections	13409 [R(int) = 0.0940]	
Completeness to theta = 27.52°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8230 and 0.5631	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13409 / 6 / 667	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0825, wR2 = 0.2105	
R indices (all data)	R1 = 0.1486, wR2 = 0.2502	
Largest diff. peak and hole	1.191 and -1.215 e.Å^{-3}	

Table S6. Bond lengths [Å] and angles [°] for Rhodium, bromo-(1,2,3,4,5-pentamethylcyclopentadienyl)phenyl(triphenylphosphine) complex

Rh(1)-C(11)	2.067(4)
Rh(1)-C(1)	2.192(4)
Rh(1)-C(2)	2.232(4)
Rh(1)-C(3)	2.242(5)
Rh(1)-C(4)	2.292(4)
Rh(1)-C(5)	2.294(4)
Rh(1)-P(1)	2.2983(11)
Rh(1)-Br(1)	2.4778(9)
P(1)-C(17)	1.820(5)
P(1)-C(23)	1.830(4)
P(1)-C(29)	1.837(5)
C(1)-C(2)	1.435(7)
C(1)-C(5)	1.457(7)
C(1)-C(6)	1.489(8)
C(2)-C(3)	1.411(8)
C(2)-C(7)	1.496(7)
C(3)-C(4)	1.439(7)
C(3)-C(8)	1.515(8)
C(4)-C(5)	1.396(8)
C(4)-C(9)	1.516(8)
C(5)-C(10)	1.491(8)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600

C(10)-H(10C)	0.9600
C(11)-C(12)	1.375(7)
C(11)-C(16)	1.406(6)
C(12)-C(13)	1.392(7)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.360(8)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.357(9)
C(14)-H(14A)	0.9300
C(15)-C(16)	1.412(7)
C(15)-H(15A)	0.9300
C(16)-H(16A)	0.9300
C(17)-C(18)	1.380(6)
C(17)-C(22)	1.403(6)
C(18)-C(19)	1.400(8)
C(18)-H(18A)	0.9300
C(19)-C(20)	1.352(7)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.362(8)
C(20)-H(20A)	0.9300
C(21)-C(22)	1.370(9)
C(21)-H(21A)	0.9300
C(22)-H(22A)	0.9300
C(23)-C(28)	1.372(6)
C(23)-C(24)	1.400(6)
C(24)-C(25)	1.364(6)
C(24)-H(24A)	0.9300
C(25)-C(26)	1.372(8)
C(25)-H(25A)	0.9300
C(26)-C(27)	1.364(8)
C(26)-H(26A)	0.9300
C(27)-C(28)	1.382(6)
C(27)-H(27A)	0.9300
C(28)-H(28A)	0.9300
C(29)-C(34)	1.368(7)
C(29)-C(30)	1.385(8)
C(30)-C(31)	1.380(8)
C(30)-H(30A)	0.9300

C(31)-C(32)	1.354(10)
C(31)-H(31A)	0.9300
C(32)-C(33)	1.359(10)
C(32)-H(32A)	0.9300
C(33)-C(34)	1.376(8)
C(33)-H(33A)	0.9300
C(34)-H(34A)	0.9300
Rh(2)-C(45)	2.060(4)
Rh(2)-C(39)	2.202(5)
Rh(2)-C(37)	2.211(6)
Rh(2)-C(38)	2.221(6)
Rh(2)-C(36)	2.264(5)
Rh(2)-C(35)	2.298(5)
Rh(2)-P(2)	2.3194(14)
Rh(2)-Br(2)	2.4911(10)
P(2)-C(51)	1.836(5)
P(2)-C(57)	1.852(4)
P(2)-C(63)	1.853(5)
C(35)-C(36)	1.391(9)
C(35)-C(39)	1.462(8)
C(35)-C(40)	1.479(8)
C(36)-C(37)	1.438(8)
C(36)-C(41)	1.498(9)
C(37)-C(38)	1.396(10)
C(37)-C(42)	1.485(10)
C(38)-C(39)	1.441(9)
C(38)-C(43)	1.540(10)
C(39)-C(44)	1.476(10)
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
C(41)-H(41A)	0.9600
C(41)-H(41B)	0.9600
C(41)-H(41C)	0.9600
C(42)-H(42A)	0.9600
C(42)-H(42B)	0.9600
C(42)-H(42C)	0.9600
C(43)-H(43A)	0.9600

C(43)-H(43B)	0.9600
C(43)-H(43C)	0.9600
C(44)-H(44A)	0.9600
C(44)-H(44B)	0.9600
C(44)-H(44C)	0.9600
C(45)-C(50)	1.361(8)
C(45)-C(46)	1.401(7)
C(46)-C(47)	1.361(7)
C(46)-H(46A)	0.9300
C(47)-C(48)	1.343(9)
C(47)-H(47A)	0.9300
C(48)-C(49)	1.377(9)
C(48)-H(48A)	0.9300
C(49)-C(50)	1.403(8)
C(49)-H(49A)	0.9300
C(50)-H(50A)	0.9300
C(51)-C(52)	1.376(7)
C(51)-C(56)	1.384(7)
C(52)-C(53)	1.422(10)
C(52)-H(52A)	0.9300
C(53)-C(54)	1.361(9)
C(53)-H(53A)	0.9300
C(54)-C(55)	1.329(7)
C(54)-H(54A)	0.9300
C(55)-C(56)	1.406(8)
C(55)-H(55A)	0.9300
C(56)-H(56A)	0.9300
C(57)-C(58)	1.370(7)
C(57)-C(62)	1.374(8)
C(58)-C(59)	1.383(7)
C(58)-H(58A)	0.9300
C(59)-C(60)	1.348(9)
C(59)-H(59A)	0.9300
C(60)-C(61)	1.361(9)
C(60)-H(60A)	0.9300
C(61)-C(62)	1.370(8)
C(61)-H(61A)	0.9300
C(62)-H(62A)	0.9300

C(63)-C(68)	1.375(7)
C(63)-C(64)	1.409(7)
C(64)-C(65)	1.378(8)
C(64)-H(64A)	0.9300
C(65)-C(66)	1.375(9)
C(65)-H(65A)	0.9300
C(66)-C(67)	1.373(9)
C(66)-H(66A)	0.9300
C(67)-C(68)	1.385(7)
C(67)-H(67A)	0.9300
C(68)-H(68A)	0.9300
C(11)-Rh(1)-C(1)	101.20(17)
C(11)-Rh(1)-C(2)	88.97(16)
C(1)-Rh(1)-C(2)	37.83(19)
C(11)-Rh(1)-C(3)	113.02(18)
C(1)-Rh(1)-C(3)	62.41(19)
C(2)-Rh(1)-C(3)	36.78(19)
C(11)-Rh(1)-C(4)	149.06(17)
C(1)-Rh(1)-C(4)	61.87(18)
C(2)-Rh(1)-C(4)	61.52(18)
C(3)-Rh(1)-C(4)	37.00(18)
C(11)-Rh(1)-C(5)	138.58(18)
C(1)-Rh(1)-C(5)	37.82(18)
C(2)-Rh(1)-C(5)	61.90(17)
C(3)-Rh(1)-C(5)	60.90(18)
C(4)-Rh(1)-C(5)	35.44(19)
C(11)-Rh(1)-P(1)	87.50(12)
C(1)-Rh(1)-P(1)	113.07(14)
C(2)-Rh(1)-P(1)	148.85(15)
C(3)-Rh(1)-P(1)	159.35(13)
C(4)-Rh(1)-P(1)	122.38(14)
C(5)-Rh(1)-P(1)	102.49(13)
C(11)-Rh(1)-Br(1)	95.86(12)
C(1)-Rh(1)-Br(1)	151.59(14)
C(2)-Rh(1)-Br(1)	121.09(15)
C(3)-Rh(1)-Br(1)	90.06(14)
C(4)-Rh(1)-Br(1)	92.26(13)

C(5)-Rh(1)-Br(1)	123.80(14)
P(1)-Rh(1)-Br(1)	90.06(4)
C(17)-P(1)-C(23)	100.71(19)
C(17)-P(1)-C(29)	103.6(2)
C(23)-P(1)-C(29)	102.05(19)
C(17)-P(1)-Rh(1)	116.82(14)
C(23)-P(1)-Rh(1)	120.23(15)
C(29)-P(1)-Rh(1)	111.17(15)
C(2)-C(1)-C(5)	107.2(5)
C(2)-C(1)-C(6)	123.4(5)
C(5)-C(1)-C(6)	127.0(5)
C(2)-C(1)-Rh(1)	72.6(2)
C(5)-C(1)-Rh(1)	74.9(2)
C(6)-C(1)-Rh(1)	131.6(3)
C(3)-C(2)-C(1)	107.7(4)
C(3)-C(2)-C(7)	127.3(5)
C(1)-C(2)-C(7)	125.1(5)
C(3)-C(2)-Rh(1)	72.0(3)
C(1)-C(2)-Rh(1)	69.6(2)
C(7)-C(2)-Rh(1)	124.7(3)
C(2)-C(3)-C(4)	108.6(5)
C(2)-C(3)-C(8)	125.8(5)
C(4)-C(3)-C(8)	125.4(5)
C(2)-C(3)-Rh(1)	71.2(3)
C(4)-C(3)-Rh(1)	73.4(3)
C(8)-C(3)-Rh(1)	125.0(3)
C(5)-C(4)-C(3)	108.4(5)
C(5)-C(4)-C(9)	128.0(5)
C(3)-C(4)-C(9)	123.6(5)
C(5)-C(4)-Rh(1)	72.4(2)
C(3)-C(4)-Rh(1)	69.6(2)
C(9)-C(4)-Rh(1)	126.2(3)
C(4)-C(5)-C(1)	107.9(4)
C(4)-C(5)-C(10)	127.2(5)
C(1)-C(5)-C(10)	124.5(5)
C(4)-C(5)-Rh(1)	72.2(2)
C(1)-C(5)-Rh(1)	67.3(2)
C(10)-C(5)-Rh(1)	131.1(3)

C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5
C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	117.1(4)
C(12)-C(11)-Rh(1)	122.4(3)
C(16)-C(11)-Rh(1)	120.2(4)
C(11)-C(12)-C(13)	122.0(5)
C(11)-C(12)-H(12A)	119.0
C(13)-C(12)-H(12A)	119.0
C(14)-C(13)-C(12)	120.9(5)
C(14)-C(13)-H(13A)	119.5

C(12)-C(13)-H(13A)	119.5
C(15)-C(14)-C(13)	118.8(5)
C(15)-C(14)-H(14A)	120.6
C(13)-C(14)-H(14A)	120.6
C(14)-C(15)-C(16)	121.6(5)
C(14)-C(15)-H(15A)	119.2
C(16)-C(15)-H(15A)	119.2
C(11)-C(16)-C(15)	119.6(5)
C(11)-C(16)-H(16A)	120.2
C(15)-C(16)-H(16A)	120.2
C(18)-C(17)-C(22)	117.3(5)
C(18)-C(17)-P(1)	122.9(3)
C(22)-C(17)-P(1)	119.4(3)
C(17)-C(18)-C(19)	121.1(4)
C(17)-C(18)-H(18A)	119.5
C(19)-C(18)-H(18A)	119.5
C(20)-C(19)-C(18)	119.8(5)
C(20)-C(19)-H(19A)	120.1
C(18)-C(19)-H(19A)	120.1
C(19)-C(20)-C(21)	120.3(6)
C(19)-C(20)-H(20A)	119.8
C(21)-C(20)-H(20A)	119.8
C(20)-C(21)-C(22)	120.8(5)
C(20)-C(21)-H(21A)	119.6
C(22)-C(21)-H(21A)	119.6
C(21)-C(22)-C(17)	120.7(5)
C(21)-C(22)-H(22A)	119.7
C(17)-C(22)-H(22A)	119.7
C(28)-C(23)-C(24)	117.1(3)
C(28)-C(23)-P(1)	123.4(3)
C(24)-C(23)-P(1)	119.5(3)
C(25)-C(24)-C(23)	122.0(4)
C(25)-C(24)-H(24A)	119.0
C(23)-C(24)-H(24A)	119.0
C(24)-C(25)-C(26)	119.5(5)
C(24)-C(25)-H(25A)	120.2
C(26)-C(25)-H(25A)	120.2
C(27)-C(26)-C(25)	119.9(4)

C(27)-C(26)-H(26A)	120.1
C(25)-C(26)-H(26A)	120.1
C(26)-C(27)-C(28)	120.5(5)
C(26)-C(27)-H(27A)	119.8
C(28)-C(27)-H(27A)	119.8
C(23)-C(28)-C(27)	121.0(4)
C(23)-C(28)-H(28A)	119.5
C(27)-C(28)-H(28A)	119.5
C(34)-C(29)-C(30)	118.3(5)
C(34)-C(29)-P(1)	124.3(4)
C(30)-C(29)-P(1)	117.2(4)
C(31)-C(30)-C(29)	120.5(6)
C(31)-C(30)-H(30A)	119.7
C(29)-C(30)-H(30A)	119.7
C(32)-C(31)-C(30)	119.2(6)
C(32)-C(31)-H(31A)	120.4
C(30)-C(31)-H(31A)	120.4
C(31)-C(32)-C(33)	121.8(6)
C(31)-C(32)-H(32A)	119.1
C(33)-C(32)-H(32A)	119.1
C(32)-C(33)-C(34)	118.8(6)
C(32)-C(33)-H(33A)	120.6
C(34)-C(33)-H(33A)	120.6
C(29)-C(34)-C(33)	121.4(6)
C(29)-C(34)-H(34A)	119.3
C(33)-C(34)-H(34A)	119.3
C(45)-Rh(2)-C(39)	103.2(2)
C(45)-Rh(2)-C(37)	105.4(2)
C(39)-Rh(2)-C(37)	63.2(2)
C(45)-Rh(2)-C(38)	85.9(2)
C(39)-Rh(2)-C(38)	38.0(2)
C(37)-Rh(2)-C(38)	36.7(3)
C(45)-Rh(2)-C(36)	142.8(2)
C(39)-Rh(2)-C(36)	62.4(2)
C(37)-Rh(2)-C(36)	37.5(2)
C(38)-Rh(2)-C(36)	61.4(2)
C(45)-Rh(2)-C(35)	141.0(2)
C(39)-Rh(2)-C(35)	37.9(2)

C(37)-Rh(2)-C(35)	61.3(2)
C(38)-Rh(2)-C(35)	61.5(2)
C(36)-Rh(2)-C(35)	35.5(2)
C(45)-Rh(2)-P(2)	92.85(15)
C(39)-Rh(2)-P(2)	108.17(17)
C(37)-Rh(2)-P(2)	161.02(15)
C(38)-Rh(2)-P(2)	143.53(18)
C(36)-Rh(2)-P(2)	123.85(16)
C(35)-Rh(2)-P(2)	101.15(15)
C(45)-Rh(2)-Br(2)	92.33(15)
C(39)-Rh(2)-Br(2)	153.78(18)
C(37)-Rh(2)-Br(2)	92.51(18)
C(38)-Rh(2)-Br(2)	124.70(18)
C(36)-Rh(2)-Br(2)	92.57(16)
C(35)-Rh(2)-Br(2)	123.02(16)
P(2)-Rh(2)-Br(2)	91.77(4)
C(51)-P(2)-C(57)	102.2(2)
C(51)-P(2)-C(63)	102.8(2)
C(57)-P(2)-C(63)	102.0(2)
C(51)-P(2)-Rh(2)	115.38(17)
C(57)-P(2)-Rh(2)	120.13(18)
C(63)-P(2)-Rh(2)	112.17(16)
C(36)-C(35)-C(39)	108.3(5)
C(36)-C(35)-C(40)	127.1(5)
C(39)-C(35)-C(40)	124.1(6)
C(36)-C(35)-Rh(2)	70.9(3)
C(39)-C(35)-Rh(2)	67.5(3)
C(40)-C(35)-Rh(2)	133.7(4)
C(35)-C(36)-C(37)	108.7(6)
C(35)-C(36)-C(41)	126.6(6)
C(37)-C(36)-C(41)	124.4(6)
C(35)-C(36)-Rh(2)	73.6(3)
C(37)-C(36)-Rh(2)	69.3(3)
C(41)-C(36)-Rh(2)	127.5(4)
C(38)-C(37)-C(36)	107.8(5)
C(38)-C(37)-C(42)	126.2(6)
C(36)-C(37)-C(42)	125.6(7)
C(38)-C(37)-Rh(2)	72.0(4)

C(36)-C(37)-Rh(2)	73.3(3)
C(42)-C(37)-Rh(2)	125.5(4)
C(37)-C(38)-C(39)	109.2(5)
C(37)-C(38)-C(43)	127.2(6)
C(39)-C(38)-C(43)	123.6(7)
C(37)-C(38)-Rh(2)	71.2(3)
C(39)-C(38)-Rh(2)	70.3(3)
C(43)-C(38)-Rh(2)	125.8(4)
C(38)-C(39)-C(35)	105.6(6)
C(38)-C(39)-C(44)	125.7(6)
C(35)-C(39)-C(44)	126.6(5)
C(38)-C(39)-Rh(2)	71.7(3)
C(35)-C(39)-Rh(2)	74.6(3)
C(44)-C(39)-Rh(2)	131.2(4)
C(35)-C(40)-H(40A)	109.5
C(35)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(35)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(36)-C(41)-H(41A)	109.5
C(36)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(36)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(37)-C(42)-H(42A)	109.5
C(37)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(37)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(38)-C(43)-H(43A)	109.5
C(38)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
C(38)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5

C(39)-C(44)-H(44A)	109.5
C(39)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(39)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(50)-C(45)-C(46)	115.7(4)
C(50)-C(45)-Rh(2)	124.2(4)
C(46)-C(45)-Rh(2)	119.0(4)
C(47)-C(46)-C(45)	123.0(5)
C(47)-C(46)-H(46A)	118.5
C(45)-C(46)-H(46A)	118.5
C(48)-C(47)-C(46)	120.4(5)
C(48)-C(47)-H(47A)	119.8
C(46)-C(47)-H(47A)	119.8
C(47)-C(48)-C(49)	119.3(5)
C(47)-C(48)-H(48A)	120.4
C(49)-C(48)-H(48A)	120.4
C(48)-C(49)-C(50)	119.9(6)
C(48)-C(49)-H(49A)	120.0
C(50)-C(49)-H(49A)	120.0
C(45)-C(50)-C(49)	121.6(5)
C(45)-C(50)-H(50A)	119.2
C(49)-C(50)-H(50A)	119.2
C(52)-C(51)-C(56)	118.9(5)
C(52)-C(51)-P(2)	119.2(4)
C(56)-C(51)-P(2)	121.9(3)
C(51)-C(52)-C(53)	119.4(5)
C(51)-C(52)-H(52A)	120.3
C(53)-C(52)-H(52A)	120.3
C(54)-C(53)-C(52)	120.8(5)
C(54)-C(53)-H(53A)	119.6
C(52)-C(53)-H(53A)	119.6
C(55)-C(54)-C(53)	119.2(6)
C(55)-C(54)-H(54A)	120.4
C(53)-C(54)-H(54A)	120.4
C(54)-C(55)-C(56)	122.2(5)
C(54)-C(55)-H(55A)	118.9

C(56)-C(55)-H(55A)	118.9
C(51)-C(56)-C(55)	119.4(4)
C(51)-C(56)-H(56A)	120.3
C(55)-C(56)-H(56A)	120.3
C(58)-C(57)-C(62)	118.2(4)
C(58)-C(57)-P(2)	121.1(4)
C(62)-C(57)-P(2)	120.6(4)
C(57)-C(58)-C(59)	119.6(5)
C(57)-C(58)-H(58A)	120.2
C(59)-C(58)-H(58A)	120.2
C(60)-C(59)-C(58)	121.5(6)
C(60)-C(59)-H(59A)	119.2
C(58)-C(59)-H(59A)	119.2
C(59)-C(60)-C(61)	119.3(5)
C(59)-C(60)-H(60A)	120.4
C(61)-C(60)-H(60A)	120.4
C(60)-C(61)-C(62)	120.0(7)
C(60)-C(61)-H(61A)	120.0
C(62)-C(61)-H(61A)	120.0
C(61)-C(62)-C(57)	121.4(6)
C(61)-C(62)-H(62A)	119.3
C(57)-C(62)-H(62A)	119.3
C(68)-C(63)-C(64)	118.2(5)
C(68)-C(63)-P(2)	119.1(4)
C(64)-C(63)-P(2)	122.8(4)
C(65)-C(64)-C(63)	121.0(6)
C(65)-C(64)-H(64A)	119.5
C(63)-C(64)-H(64A)	119.5
C(66)-C(65)-C(64)	119.5(6)
C(66)-C(65)-H(65A)	120.2
C(64)-C(65)-H(65A)	120.2
C(67)-C(66)-C(65)	120.0(6)
C(67)-C(66)-H(66A)	120.0
C(65)-C(66)-H(66A)	120.0
C(66)-C(67)-C(68)	120.7(6)
C(66)-C(67)-H(67A)	119.7
C(68)-C(67)-H(67A)	119.7
C(63)-C(68)-C(67)	120.5(5)

C(63)-C(68)-H(68A)	119.8
C(67)-C(68)-H(68A)	119.8

Symmetry transformations used to generate equivalent atoms:

Figure S2b. Molecular structure of Rhodium, chloro-(1,2,3,4,5-pentamethylcyclopentadienyl)phenyl(triphenylphosphine) complex (**5b**) (CCDC number = 1455768)

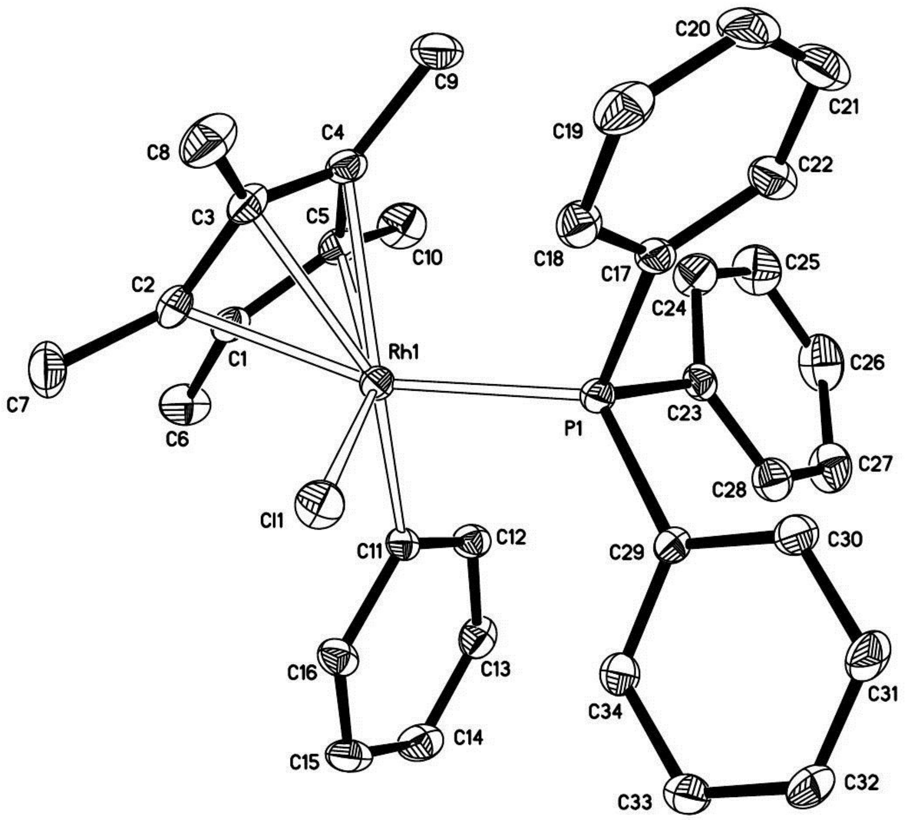


Table S7. Crystal data and structure refinement for Rhodium, chloro-(1,2,3,4,5-pentamethylcyclopentadienyl)phenyl(triphenylphosphine) complex

CCDC number	1455768	
Identification code	nfn22	
Empirical formula	$RhCl(C_{16}H_{20})P(C_6H_5)_3$	
Formula weight	612.95	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4496(3) Å	α= 104.775(2)°.
	b = 15.6045(5) Å	β= 100.930(2)°.
	c = 19.2722(6) Å	γ = 98.868(2)°.
Volume	2914.84(15) $Å^3$	
Z	4	
Density (calculated)	1.397 Mg/m^3	
Absorption coefficient	0.754 mm^{-1}	
F(000)	1264	
Crystal size	0.18 x 0.16 x 0.10 mm^3	
Theta range for data collection	1.38 to 27.58°.	
Index ranges	-13<=h<=13, -20<=k<=20, -25<=l<=25	
Reflections collected	66539	
Independent reflections	12997 [R(int) = 0.0884]	
Completeness to theta = 27.58°	96.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5939	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12997 / 0 / 745	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0611, wR2 = 0.1183	
R indices (all data)	R1 = 0.1110, wR2 = 0.1373	
Largest diff. peak and hole	0.847 and -0.601 e.$Å^{-3}$	

Table S8. Bond lengths [Å] and angles [°] for Rhodium, chloro-(1,2,3,4,5-pentamethylcyclopentadienyl)phenyl(triphenylphosphine) complex

Rh(1)-C(11)	2.054(3)
Rh(1)-C(5)	2.201(3)
Rh(1)-C(1)	2.229(3)
Rh(1)-C(2)	2.229(4)
Rh(1)-C(3)	2.280(3)
Rh(1)-C(4)	2.292(3)
Rh(1)-P(1)	2.2939(10)
Rh(1)-Cl(1)	2.4074(10)
P(1)-C(23)	1.821(4)
P(1)-C(29)	1.834(3)
P(1)-C(17)	1.836(4)
C(1)-C(2)	1.405(6)
C(1)-C(5)	1.440(6)
C(1)-C(6)	1.508(6)
C(2)-C(3)	1.447(6)
C(2)-C(7)	1.502(6)
C(3)-C(4)	1.389(6)
C(3)-C(8)	1.501(6)
C(4)-C(5)	1.447(6)
C(4)-C(9)	1.513(6)
C(5)-C(10)	1.499(6)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600

C(10)-H(10C)	0.9600
C(11)-C(12)	1.384(5)
C(11)-C(16)	1.399(5)
C(12)-C(13)	1.380(5)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.369(6)
C(13)-H(13A)	0.88(4)
C(14)-C(15)	1.364(7)
C(14)-H(14A)	0.9300
C(15)-C(16)	1.387(6)
C(15)-H(15A)	0.9300
C(16)-H(16A)	0.95(3)
C(17)-C(18)	1.372(6)
C(17)-C(22)	1.394(6)
C(18)-C(19)	1.385(6)
C(18)-H(18A)	0.88(3)
C(19)-C(20)	1.366(7)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.358(8)
C(20)-H(20A)	0.85(4)
C(21)-C(22)	1.376(6)
C(21)-H(21A)	0.9300
C(22)-H(22A)	0.89(4)
C(23)-C(24)	1.376(5)
C(23)-C(28)	1.391(5)
C(24)-C(25)	1.383(7)
C(24)-H(24A)	0.9300
C(25)-C(26)	1.358(7)
C(25)-H(25A)	0.87(3)
C(26)-C(27)	1.372(6)
C(26)-H(26A)	0.86(5)
C(27)-C(28)	1.384(6)
C(27)-H(27A)	0.9300
C(28)-H(28A)	0.83(3)
C(29)-C(30)	1.379(5)
C(29)-C(34)	1.386(5)
C(30)-C(31)	1.379(5)
C(30)-H(30A)	0.94(3)

C(31)-C(32)	1.355(6)
C(31)-H(31A)	0.84(4)
C(32)-C(33)	1.353(6)
C(32)-H(32A)	0.84(3)
C(33)-C(34)	1.387(5)
C(33)-H(33A)	0.82(3)
C(34)-H(34A)	0.87(3)
Rh(2)-C(45)	2.059(4)
Rh(2)-C(35)	2.198(4)
Rh(2)-C(38)	2.209(5)
Rh(2)-C(39)	2.232(4)
Rh(2)-C(37)	2.270(4)
Rh(2)-C(36)	2.296(4)
Rh(2)-P(2)	2.3194(11)
Rh(2)-Cl(2)	2.4153(11)
P(2)-C(57)	1.832(4)
P(2)-C(63)	1.836(4)
P(2)-C(51)	1.844(4)
C(35)-C(39)	1.431(7)
C(35)-C(36)	1.450(6)
C(35)-C(40)	1.489(7)
C(36)-C(37)	1.397(6)
C(36)-C(41)	1.500(6)
C(37)-C(38)	1.460(6)
C(37)-C(42)	1.504(7)
C(38)-C(39)	1.424(7)
C(38)-C(43)	1.482(7)
C(39)-C(44)	1.489(7)
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
C(41)-H(41A)	0.9600
C(41)-H(41B)	0.9600
C(41)-H(41C)	0.9600
C(42)-H(42A)	0.9600
C(42)-H(42B)	0.9600
C(42)-H(42C)	0.9600
C(43)-H(43A)	0.9600

C(43)-H(43B)	0.9600
C(43)-H(43C)	0.9600
C(44)-H(44A)	0.9600
C(44)-H(44B)	0.9600
C(44)-H(44C)	0.9600
C(45)-C(50)	1.385(6)
C(45)-C(46)	1.391(5)
C(46)-C(47)	1.387(6)
C(46)-H(46A)	0.96(4)
C(47)-C(48)	1.345(7)
C(47)-H(47A)	0.9300
C(48)-C(49)	1.371(6)
C(48)-H(48A)	0.9300
C(49)-C(50)	1.380(6)
C(49)-H(49A)	0.9300
C(50)-H(50A)	0.9300
C(51)-C(56)	1.380(6)
C(51)-C(52)	1.403(6)
C(52)-C(53)	1.389(7)
C(52)-H(52A)	0.9300
C(53)-C(54)	1.376(8)
C(53)-H(53A)	0.9300
C(54)-C(55)	1.369(8)
C(54)-H(54A)	0.84(4)
C(55)-C(56)	1.380(6)
C(55)-H(55A)	0.9300
C(56)-H(56A)	0.9300
C(57)-C(58)	1.384(6)
C(57)-C(62)	1.389(6)
C(58)-C(59)	1.384(6)
C(58)-H(58A)	0.94(3)
C(59)-C(60)	1.348(6)
C(59)-H(59A)	0.9300
C(60)-C(61)	1.352(7)
C(60)-H(60A)	0.9300
C(61)-C(62)	1.378(7)
C(61)-H(61A)	0.9300
C(62)-H(62A)	0.89(3)

C(63)-C(64)	1.366(6)
C(63)-C(68)	1.403(6)
C(64)-C(65)	1.394(6)
C(64)-H(64A)	0.9300
C(65)-C(66)	1.346(7)
C(65)-H(65A)	0.9300
C(66)-C(67)	1.345(7)
C(66)-H(66A)	0.81(4)
C(67)-C(68)	1.387(6)
C(67)-H(67A)	0.9300
C(68)-H(68A)	0.9300

C(11)-Rh(1)-C(5)	101.63(14)
C(11)-Rh(1)-C(1)	88.93(13)
C(5)-Rh(1)-C(1)	37.93(14)
C(11)-Rh(1)-C(2)	112.54(14)
C(5)-Rh(1)-C(2)	62.52(15)
C(1)-Rh(1)-C(2)	36.75(15)
C(11)-Rh(1)-C(3)	149.04(13)
C(5)-Rh(1)-C(3)	61.76(15)
C(1)-Rh(1)-C(3)	61.67(14)
C(2)-Rh(1)-C(3)	37.40(14)
C(11)-Rh(1)-C(4)	138.77(14)
C(5)-Rh(1)-C(4)	37.51(14)
C(1)-Rh(1)-C(4)	61.78(14)
C(2)-Rh(1)-C(4)	61.06(14)
C(3)-Rh(1)-C(4)	35.37(15)
C(11)-Rh(1)-P(1)	87.53(10)
C(5)-Rh(1)-P(1)	113.40(11)
C(1)-Rh(1)-P(1)	149.17(11)
C(2)-Rh(1)-P(1)	159.86(11)
C(3)-Rh(1)-P(1)	122.50(11)
C(4)-Rh(1)-P(1)	103.00(10)
C(11)-Rh(1)-Cl(1)	94.90(10)
C(5)-Rh(1)-Cl(1)	152.37(11)
C(1)-Rh(1)-Cl(1)	121.74(11)
C(2)-Rh(1)-Cl(1)	90.76(11)
C(3)-Rh(1)-Cl(1)	93.07(11)

C(4)-Rh(1)-Cl(1)	124.57(11)
P(1)-Rh(1)-Cl(1)	89.09(4)
C(23)-P(1)-C(29)	101.45(16)
C(23)-P(1)-C(17)	104.39(18)
C(29)-P(1)-C(17)	100.71(16)
C(23)-P(1)-Rh(1)	116.22(12)
C(29)-P(1)-Rh(1)	120.81(12)
C(17)-P(1)-Rh(1)	111.03(12)
C(2)-C(1)-C(5)	107.8(3)
C(2)-C(1)-C(6)	127.0(4)
C(5)-C(1)-C(6)	125.2(4)
C(2)-C(1)-Rh(1)	71.6(2)
C(5)-C(1)-Rh(1)	70.0(2)
C(6)-C(1)-Rh(1)	125.0(2)
C(1)-C(2)-C(3)	108.3(4)
C(1)-C(2)-C(7)	126.6(4)
C(3)-C(2)-C(7)	124.8(4)
C(1)-C(2)-Rh(1)	71.6(2)
C(3)-C(2)-Rh(1)	73.2(2)
C(7)-C(2)-Rh(1)	126.0(3)
C(4)-C(3)-C(2)	108.2(4)
C(4)-C(3)-C(8)	128.0(4)
C(2)-C(3)-C(8)	123.7(4)
C(4)-C(3)-Rh(1)	72.8(2)
C(2)-C(3)-Rh(1)	69.4(2)
C(8)-C(3)-Rh(1)	126.8(3)
C(3)-C(4)-C(5)	108.4(3)
C(3)-C(4)-C(9)	125.9(4)
C(5)-C(4)-C(9)	125.5(4)
C(3)-C(4)-Rh(1)	71.8(2)
C(5)-C(4)-Rh(1)	67.82(19)
C(9)-C(4)-Rh(1)	130.3(3)
C(1)-C(5)-C(4)	107.0(4)
C(1)-C(5)-C(10)	124.4(4)
C(4)-C(5)-C(10)	126.5(4)
C(1)-C(5)-Rh(1)	72.09(19)
C(4)-C(5)-Rh(1)	74.7(2)
C(10)-C(5)-Rh(1)	131.4(3)

C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5
C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	115.6(3)
C(12)-C(11)-Rh(1)	123.0(3)
C(16)-C(11)-Rh(1)	121.2(3)
C(13)-C(12)-C(11)	122.1(4)
C(13)-C(12)-H(12A)	118.9
C(11)-C(12)-H(12A)	118.9
C(14)-C(13)-C(12)	121.1(4)
C(14)-C(13)-H(13A)	118(2)

C(12)-C(13)-H(13A)	121(2)
C(15)-C(14)-C(13)	118.4(4)
C(15)-C(14)-H(14A)	120.8
C(13)-C(14)-H(14A)	120.8
C(14)-C(15)-C(16)	120.7(4)
C(14)-C(15)-H(15A)	119.6
C(16)-C(15)-H(15A)	119.6
C(15)-C(16)-C(11)	121.9(4)
C(15)-C(16)-H(16A)	125.2(19)
C(11)-C(16)-H(16A)	112.9(19)
C(18)-C(17)-C(22)	118.4(4)
C(18)-C(17)-P(1)	118.1(3)
C(22)-C(17)-P(1)	123.5(3)
C(17)-C(18)-C(19)	120.1(4)
C(17)-C(18)-H(18A)	118(2)
C(19)-C(18)-H(18A)	122(2)
C(20)-C(19)-C(18)	120.4(5)
C(20)-C(19)-H(19A)	119.8
C(18)-C(19)-H(19A)	119.8
C(21)-C(20)-C(19)	120.4(5)
C(21)-C(20)-H(20A)	122(3)
C(19)-C(20)-H(20A)	118(3)
C(20)-C(21)-C(22)	119.7(5)
C(20)-C(21)-H(21A)	120.2
C(22)-C(21)-H(21A)	120.2
C(21)-C(22)-C(17)	121.0(5)
C(21)-C(22)-H(22A)	119(2)
C(17)-C(22)-H(22A)	120(2)
C(24)-C(23)-C(28)	117.8(4)
C(24)-C(23)-P(1)	119.4(3)
C(28)-C(23)-P(1)	122.6(3)
C(23)-C(24)-C(25)	120.8(4)
C(23)-C(24)-H(24A)	119.6
C(25)-C(24)-H(24A)	119.6
C(26)-C(25)-C(24)	120.4(4)
C(26)-C(25)-H(25A)	122(3)
C(24)-C(25)-H(25A)	117(3)
C(25)-C(26)-C(27)	120.5(5)

C(25)-C(26)-H(26A)	121(3)
C(27)-C(26)-H(26A)	118(3)
C(26)-C(27)-C(28)	119.1(4)
C(26)-C(27)-H(27A)	120.5
C(28)-C(27)-H(27A)	120.5
C(27)-C(28)-C(23)	121.4(4)
C(27)-C(28)-H(28A)	120(3)
C(23)-C(28)-H(28A)	119(3)
C(30)-C(29)-C(34)	117.7(3)
C(30)-C(29)-P(1)	119.9(3)
C(34)-C(29)-P(1)	122.3(3)
C(31)-C(30)-C(29)	121.2(4)
C(31)-C(30)-H(30A)	121(2)
C(29)-C(30)-H(30A)	118(2)
C(32)-C(31)-C(30)	119.8(4)
C(32)-C(31)-H(31A)	118(2)
C(30)-C(31)-H(31A)	122(2)
C(33)-C(32)-C(31)	120.9(4)
C(33)-C(32)-H(32A)	120(2)
C(31)-C(32)-H(32A)	119(2)
C(32)-C(33)-C(34)	119.8(4)
C(32)-C(33)-H(33A)	124(2)
C(34)-C(33)-H(33A)	116(2)
C(29)-C(34)-C(33)	120.6(4)
C(29)-C(34)-H(34A)	120.0(19)
C(33)-C(34)-H(34A)	119.0(19)
C(45)-Rh(2)-C(35)	103.41(16)
C(45)-Rh(2)-C(38)	104.75(17)
C(35)-Rh(2)-C(38)	63.06(18)
C(45)-Rh(2)-C(39)	85.08(16)
C(35)-Rh(2)-C(39)	37.67(17)
C(38)-Rh(2)-C(39)	37.39(19)
C(45)-Rh(2)-C(37)	142.63(17)
C(35)-Rh(2)-C(37)	62.03(17)
C(38)-Rh(2)-C(37)	38.02(17)
C(39)-Rh(2)-C(37)	62.24(18)
C(45)-Rh(2)-C(36)	140.93(16)
C(35)-Rh(2)-C(36)	37.56(16)

C(38)-Rh(2)-C(36)	61.85(16)
C(39)-Rh(2)-C(36)	61.93(16)
C(37)-Rh(2)-C(36)	35.61(16)
C(45)-Rh(2)-P(2)	92.74(11)
C(35)-Rh(2)-P(2)	108.79(13)
C(38)-Rh(2)-P(2)	161.90(12)
C(39)-Rh(2)-P(2)	143.23(14)
C(37)-Rh(2)-P(2)	124.13(13)
C(36)-Rh(2)-P(2)	101.47(12)
C(45)-Rh(2)-Cl(2)	91.90(11)
C(35)-Rh(2)-Cl(2)	153.83(13)
C(38)-Rh(2)-Cl(2)	92.77(14)
C(39)-Rh(2)-Cl(2)	125.47(14)
C(37)-Rh(2)-Cl(2)	92.99(13)
C(36)-Rh(2)-Cl(2)	123.54(12)
P(2)-Rh(2)-Cl(2)	91.26(4)
C(57)-P(2)-C(63)	102.21(19)
C(57)-P(2)-C(51)	102.38(19)
C(63)-P(2)-C(51)	102.83(18)
C(57)-P(2)-Rh(2)	115.51(14)
C(63)-P(2)-Rh(2)	120.00(14)
C(51)-P(2)-Rh(2)	111.73(14)
C(39)-C(35)-C(36)	108.0(4)
C(39)-C(35)-C(40)	124.2(4)
C(36)-C(35)-C(40)	126.0(4)
C(39)-C(35)-Rh(2)	72.4(2)
C(36)-C(35)-Rh(2)	74.9(2)
C(40)-C(35)-Rh(2)	130.3(3)
C(37)-C(36)-C(35)	108.0(4)
C(37)-C(36)-C(41)	126.2(4)
C(35)-C(36)-C(41)	125.3(4)
C(37)-C(36)-Rh(2)	71.2(2)
C(35)-C(36)-Rh(2)	67.6(2)
C(41)-C(36)-Rh(2)	132.7(3)
C(36)-C(37)-C(38)	108.3(4)
C(36)-C(37)-C(42)	126.5(4)
C(38)-C(37)-C(42)	125.0(5)
C(36)-C(37)-Rh(2)	73.2(2)

C(38)-C(37)-Rh(2)	68.7(2)
C(42)-C(37)-Rh(2)	127.0(3)
C(39)-C(38)-C(37)	107.6(4)
C(39)-C(38)-C(43)	126.6(5)
C(37)-C(38)-C(43)	125.5(5)
C(39)-C(38)-Rh(2)	72.2(3)
C(37)-C(38)-Rh(2)	73.2(3)
C(43)-C(38)-Rh(2)	125.4(3)
C(38)-C(39)-C(35)	107.7(4)
C(38)-C(39)-C(44)	127.1(5)
C(35)-C(39)-C(44)	125.1(5)
C(38)-C(39)-Rh(2)	70.5(3)
C(35)-C(39)-Rh(2)	69.9(2)
C(44)-C(39)-Rh(2)	127.2(3)
C(35)-C(40)-H(40A)	109.5
C(35)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(35)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(36)-C(41)-H(41A)	109.5
C(36)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(36)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(37)-C(42)-H(42A)	109.5
C(37)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(37)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(38)-C(43)-H(43A)	109.5
C(38)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
C(38)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5

C(39)-C(44)-H(44A)	109.5
C(39)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(39)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(50)-C(45)-C(46)	116.1(4)
C(50)-C(45)-Rh(2)	124.2(3)
C(46)-C(45)-Rh(2)	118.6(3)
C(47)-C(46)-C(45)	121.9(4)
C(47)-C(46)-H(46A)	119(2)
C(45)-C(46)-H(46A)	119(2)
C(48)-C(47)-C(46)	120.4(4)
C(48)-C(47)-H(47A)	119.8
C(46)-C(47)-H(47A)	119.8
C(47)-C(48)-C(49)	119.5(4)
C(47)-C(48)-H(48A)	120.2
C(49)-C(48)-H(48A)	120.2
C(48)-C(49)-C(50)	120.4(5)
C(48)-C(49)-H(49A)	119.8
C(50)-C(49)-H(49A)	119.8
C(49)-C(50)-C(45)	121.7(4)
C(49)-C(50)-H(50A)	119.2
C(45)-C(50)-H(50A)	119.2
C(56)-C(51)-C(52)	118.4(4)
C(56)-C(51)-P(2)	118.9(3)
C(52)-C(51)-P(2)	122.7(4)
C(53)-C(52)-C(51)	121.1(5)
C(53)-C(52)-H(52A)	119.5
C(51)-C(52)-H(52A)	119.5
C(54)-C(53)-C(52)	119.0(5)
C(54)-C(53)-H(53A)	120.5
C(52)-C(53)-H(53A)	120.5
C(55)-C(54)-C(53)	120.3(5)
C(55)-C(54)-H(54A)	125(3)
C(53)-C(54)-H(54A)	114(3)
C(54)-C(55)-C(56)	121.0(5)
C(54)-C(55)-H(55A)	119.5

C(56)-C(55)-H(55A)	119.5
C(55)-C(56)-C(51)	120.2(5)
C(55)-C(56)-H(56A)	119.9
C(51)-C(56)-H(56A)	119.9
C(58)-C(57)-C(62)	117.4(4)
C(58)-C(57)-P(2)	122.3(3)
C(62)-C(57)-P(2)	120.2(3)
C(59)-C(58)-C(57)	120.0(4)
C(59)-C(58)-H(58A)	120(2)
C(57)-C(58)-H(58A)	120(2)
C(60)-C(59)-C(58)	121.2(4)
C(60)-C(59)-H(59A)	119.4
C(58)-C(59)-H(59A)	119.4
C(59)-C(60)-C(61)	120.1(5)
C(59)-C(60)-H(60A)	119.9
C(61)-C(60)-H(60A)	119.9
C(60)-C(61)-C(62)	119.9(4)
C(60)-C(61)-H(61A)	120.1
C(62)-C(61)-H(61A)	120.1
C(61)-C(62)-C(57)	121.4(4)
C(61)-C(62)-H(62A)	114(2)
C(57)-C(62)-H(62A)	124(2)
C(64)-C(63)-C(68)	117.9(4)
C(64)-C(63)-P(2)	122.4(3)
C(68)-C(63)-P(2)	119.6(3)
C(63)-C(64)-C(65)	120.7(4)
C(63)-C(64)-H(64A)	119.7
C(65)-C(64)-H(64A)	119.7
C(66)-C(65)-C(64)	120.4(5)
C(66)-C(65)-H(65A)	119.8
C(64)-C(65)-H(65A)	119.8
C(67)-C(66)-C(65)	120.6(4)
C(67)-C(66)-H(66A)	123(3)
C(65)-C(66)-H(66A)	116(3)
C(66)-C(67)-C(68)	120.5(5)
C(66)-C(67)-H(67A)	119.7
C(68)-C(67)-H(67A)	119.7
C(67)-C(68)-C(63)	119.9(4)

C(67)-C(68)-H(68A)	120.0
C(63)-C(68)-H(68A)	120.0

Symmetry transformations used to generate equivalent atoms:

Figure S3. Molecular structure of Rhodium, dichloro-(1,2,3,4,5-pentamethylcyclopentadienyl)(triphenylphosphine) complex
(CCDC number 1455770)

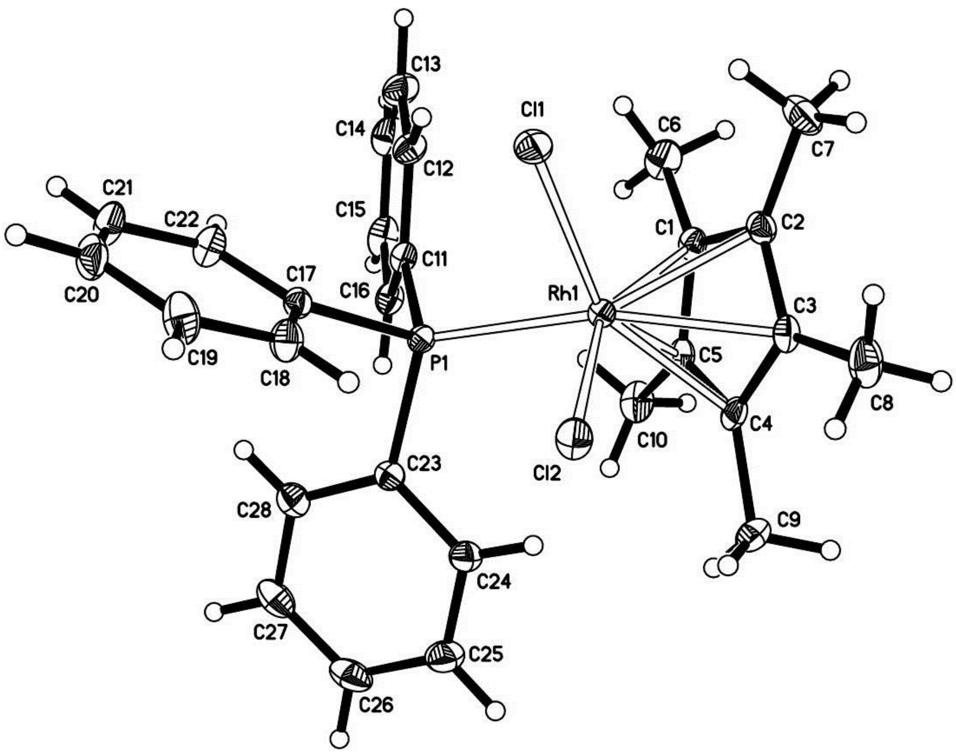


Table S9. Crystal data and structure refinement for Rhodium, dichloro-(1,2,3,4,5-pentamethylcyclopentadienyl)(triphenylphosphine) complex

CCDC number	1455770	
Identification code	lyf6	
Empirical formula	$C_{29} H_{32} Cl_4 P Rh$	
Formula weight	656.23	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.5942(2) Å	α= 90°.
	b = 16.8880(4) Å	β= 91.8090(10)°.
	c = 19.6492(4) Å	γ = 90°.
Volume	2850.44(11) Å^3	
Z	4	
Density (calculated)	1.529 Mg/m^3	
Absorption coefficient	1.048 mm^{-1}	
F(000)	1336	
Crystal size	0.38 x 0.14 x 0.10 mm^3	
Theta range for data collection	1.59 to 27.60°.	
Index ranges	-11<=h<=11, -21<=k<=21, -25<=l<=24	
Reflections collected	48750	
Independent reflections	6594 [R(int) = 0.0615]	
Completeness to theta = 27.60°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6497	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6594 / 0 / 376	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0657	
R indices (all data)	R1 = 0.0559, wR2 = 0.0750	
Largest diff. peak and hole	0.851 and -0.711 e.Å^{-3}	

Table S10. Bond lengths [Å] and angles [°] for Rhodium, dichloro-(1,2,3,4,5-pentamethylcyclopentadienyl)(triphenylphosphine) complex

Rh(1)-C(1)	2.1699(19)
Rh(1)-C(4)	2.1786(19)
Rh(1)-C(5)	2.1877(19)
Rh(1)-C(3)	2.213(2)
Rh(1)-C(2)	2.229(2)
Rh(1)-P(1)	2.3439(5)
Rh(1)-Cl(1)	2.3997(6)
Rh(1)-Cl(2)	2.4152(5)
P(1)-C(23)	1.828(2)
P(1)-C(11)	1.829(2)
P(1)-C(17)	1.833(2)
C(1)-C(5)	1.432(3)
C(1)-C(2)	1.442(3)
C(1)-C(6)	1.491(3)
C(2)-C(3)	1.407(3)
C(2)-C(7)	1.493(3)
C(3)-C(4)	1.441(3)
C(3)-C(8)	1.493(3)
C(4)-C(5)	1.416(3)
C(4)-C(9)	1.500(3)
C(5)-C(10)	1.499(3)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10C)	0.94(3)
C(10)-H(10B)	0.96(3)

C(10)-H(10A)	0.91(3)
C(11)-C(16)	1.383(3)
C(11)-C(12)	1.393(3)
C(12)-C(13)	1.378(3)
C(12)-H(12A)	0.91(2)
C(13)-C(14)	1.374(4)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.371(4)
C(14)-H(14A)	0.93(2)
C(15)-C(16)	1.394(3)
C(15)-H(15A)	0.88(2)
C(16)-H(16A)	0.898(18)
C(17)-C(18)	1.386(3)
C(17)-C(22)	1.386(3)
C(18)-C(19)	1.385(3)
C(18)-H(18A)	0.9300
C(19)-C(20)	1.361(4)
C(19)-H(19A)	0.89(2)
C(20)-C(21)	1.370(4)
C(20)-H(20A)	0.96(3)
C(21)-C(22)	1.384(3)
C(21)-H(21A)	0.91(2)
C(22)-H(22A)	0.9300
C(23)-C(24)	1.383(3)
C(23)-C(28)	1.388(3)
C(24)-C(25)	1.389(3)
C(24)-H(24A)	0.93(2)
C(25)-C(26)	1.367(4)
C(25)-H(25A)	0.93(2)
C(26)-C(27)	1.374(4)
C(26)-H(26A)	0.9300
C(27)-C(28)	1.381(3)
C(27)-H(27A)	0.9300
C(28)-H(28A)	0.89(3)
C(29)-Cl(3)	1.726(3)
C(29)-Cl(4)	1.741(3)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700

C(1)-Rh(1)-C(4)	64.09(8)
C(1)-Rh(1)-C(5)	38.38(8)
C(4)-Rh(1)-C(5)	37.84(7)
C(1)-Rh(1)-C(3)	63.59(7)
C(4)-Rh(1)-C(3)	38.30(8)
C(5)-Rh(1)-C(3)	63.37(8)
C(1)-Rh(1)-C(2)	38.23(8)
C(4)-Rh(1)-C(2)	63.03(8)
C(5)-Rh(1)-C(2)	63.18(8)
C(3)-Rh(1)-C(2)	36.92(7)
C(1)-Rh(1)-P(1)	108.39(6)
C(4)-Rh(1)-P(1)	120.99(6)
C(5)-Rh(1)-P(1)	97.99(5)
C(3)-Rh(1)-P(1)	159.11(6)
C(2)-Rh(1)-P(1)	144.64(6)
C(1)-Rh(1)-Cl(1)	103.18(6)
C(4)-Rh(1)-Cl(1)	151.16(6)
C(5)-Rh(1)-Cl(1)	140.84(6)
C(3)-Rh(1)-Cl(1)	113.16(6)
C(2)-Rh(1)-Cl(1)	90.67(6)
P(1)-Rh(1)-Cl(1)	87.130(19)
C(1)-Rh(1)-Cl(2)	154.62(6)
C(4)-Rh(1)-Cl(2)	93.26(5)
C(5)-Rh(1)-Cl(2)	126.74(6)
C(3)-Rh(1)-Cl(2)	91.69(5)
C(2)-Rh(1)-Cl(2)	122.59(6)
P(1)-Rh(1)-Cl(2)	92.749(19)
Cl(1)-Rh(1)-Cl(2)	91.46(2)
C(23)-P(1)-C(11)	105.30(9)
C(23)-P(1)-C(17)	101.86(9)
C(11)-P(1)-C(17)	102.52(9)
C(23)-P(1)-Rh(1)	115.34(7)
C(11)-P(1)-Rh(1)	109.97(7)
C(17)-P(1)-Rh(1)	120.18(7)
C(5)-C(1)-C(2)	107.26(17)
C(5)-C(1)-C(6)	127.3(2)
C(2)-C(1)-C(6)	124.3(2)

C(5)-C(1)-Rh(1)	71.48(11)
C(2)-C(1)-Rh(1)	73.11(11)
C(6)-C(1)-Rh(1)	130.39(15)
C(3)-C(2)-C(1)	108.37(18)
C(3)-C(2)-C(7)	127.4(2)
C(1)-C(2)-C(7)	124.2(2)
C(3)-C(2)-Rh(1)	70.93(11)
C(1)-C(2)-Rh(1)	68.66(11)
C(7)-C(2)-Rh(1)	127.01(15)
C(2)-C(3)-C(4)	108.01(18)
C(2)-C(3)-C(8)	127.0(2)
C(4)-C(3)-C(8)	124.8(2)
C(2)-C(3)-Rh(1)	72.15(12)
C(4)-C(3)-Rh(1)	69.54(11)
C(8)-C(3)-Rh(1)	127.38(15)
C(5)-C(4)-C(3)	108.02(18)
C(5)-C(4)-C(9)	128.0(2)
C(3)-C(4)-C(9)	123.37(19)
C(5)-C(4)-Rh(1)	71.43(11)
C(3)-C(4)-Rh(1)	72.15(11)
C(9)-C(4)-Rh(1)	129.01(15)
C(4)-C(5)-C(1)	108.19(18)
C(4)-C(5)-C(10)	126.3(2)
C(1)-C(5)-C(10)	125.09(19)
C(4)-C(5)-Rh(1)	70.73(11)
C(1)-C(5)-Rh(1)	70.14(11)
C(10)-C(5)-Rh(1)	130.34(15)
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5

H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5
C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10C)	114.3(16)
C(5)-C(10)-H(10B)	112.2(16)
H(10C)-C(10)-H(10B)	109(2)
C(5)-C(10)-H(10A)	108.5(16)
H(10C)-C(10)-H(10A)	109(2)
H(10B)-C(10)-H(10A)	103(2)
C(16)-C(11)-C(12)	118.75(19)
C(16)-C(11)-P(1)	123.95(16)
C(12)-C(11)-P(1)	117.25(15)
C(13)-C(12)-C(11)	120.4(2)
C(13)-C(12)-H(12A)	121.3(14)
C(11)-C(12)-H(12A)	118.3(14)
C(14)-C(13)-C(12)	120.3(2)
C(14)-C(13)-H(13A)	119.9
C(12)-C(13)-H(13A)	119.9
C(15)-C(14)-C(13)	120.4(2)
C(15)-C(14)-H(14A)	118.0(14)
C(13)-C(14)-H(14A)	121.5(14)
C(14)-C(15)-C(16)	119.7(2)
C(14)-C(15)-H(15A)	122.1(16)
C(16)-C(15)-H(15A)	118.2(16)
C(11)-C(16)-C(15)	120.6(2)
C(11)-C(16)-H(16A)	120.9(12)
C(15)-C(16)-H(16A)	118.5(12)
C(18)-C(17)-C(22)	118.38(19)

C(18)-C(17)-P(1)	119.18(16)
C(22)-C(17)-P(1)	122.32(16)
C(19)-C(18)-C(17)	120.1(2)
C(19)-C(18)-H(18A)	119.9
C(17)-C(18)-H(18A)	119.9
C(20)-C(19)-C(18)	121.1(2)
C(20)-C(19)-H(19A)	121.6(17)
C(18)-C(19)-H(19A)	117.3(17)
C(19)-C(20)-C(21)	119.3(2)
C(19)-C(20)-H(20A)	123.4(16)
C(21)-C(20)-H(20A)	117.3(16)
C(20)-C(21)-C(22)	120.6(2)
C(20)-C(21)-H(21A)	124.2(15)
C(22)-C(21)-H(21A)	115.1(15)
C(21)-C(22)-C(17)	120.4(2)
C(21)-C(22)-H(22A)	119.8
C(17)-C(22)-H(22A)	119.8
C(24)-C(23)-C(28)	118.6(2)
C(24)-C(23)-P(1)	119.13(16)
C(28)-C(23)-P(1)	122.27(17)
C(23)-C(24)-C(25)	120.2(2)
C(23)-C(24)-H(24A)	121.9(14)
C(25)-C(24)-H(24A)	117.8(14)
C(26)-C(25)-C(24)	120.5(2)
C(26)-C(25)-H(25A)	120.4(15)
C(24)-C(25)-H(25A)	119.0(15)
C(25)-C(26)-C(27)	119.7(2)
C(25)-C(26)-H(26A)	120.1
C(27)-C(26)-H(26A)	120.1
C(26)-C(27)-C(28)	120.2(2)
C(26)-C(27)-H(27A)	119.9
C(28)-C(27)-H(27A)	119.9
C(27)-C(28)-C(23)	120.6(2)
C(27)-C(28)-H(28A)	122.4(17)
C(23)-C(28)-H(28A)	116.8(17)
Cl(3)-C(29)-Cl(4)	112.18(15)
Cl(3)-C(29)-H(29A)	109.2
Cl(4)-C(29)-H(29A)	109.2

Cl(3)-C(29)-H(29B)	109.2
Cl(4)-C(29)-H(29B)	109.2
H(29A)-C(29)-H(29B)	107.9

Symmetry transformations used to generate equivalent atoms:

6. ¹H and ¹³C Spectra

Figure S4. ¹H NMR spectrum of **3a**

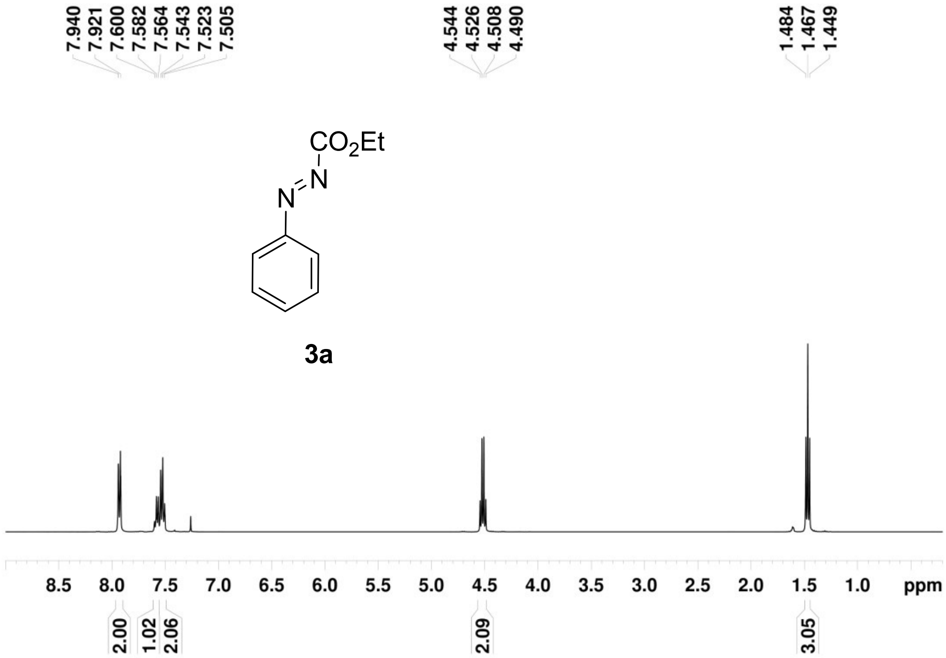


Figure S5. ¹³C NMR spectrum of **3a**

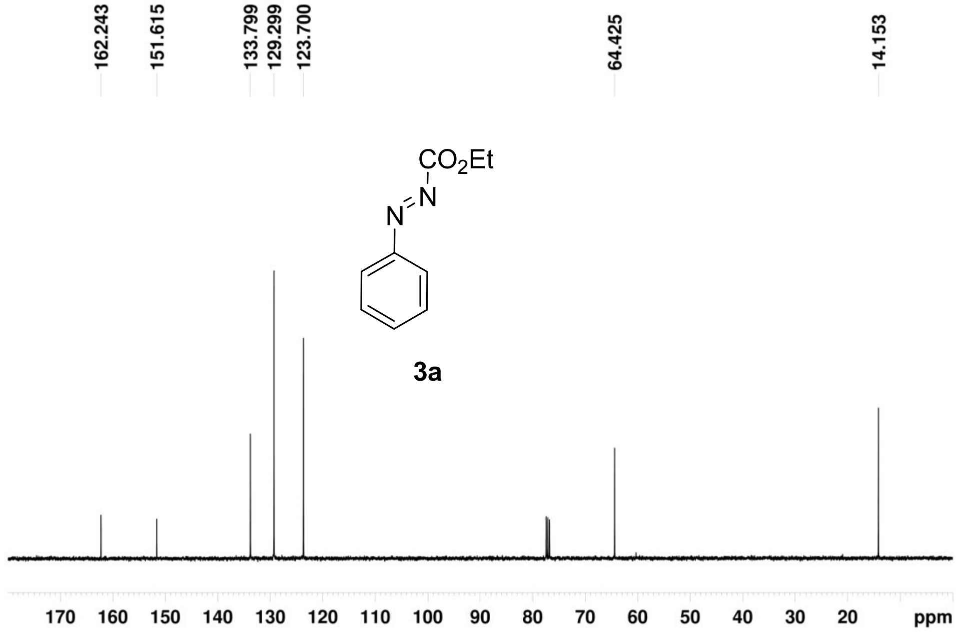


Figure S6. ^{1}H NMR spectrum of **3b**

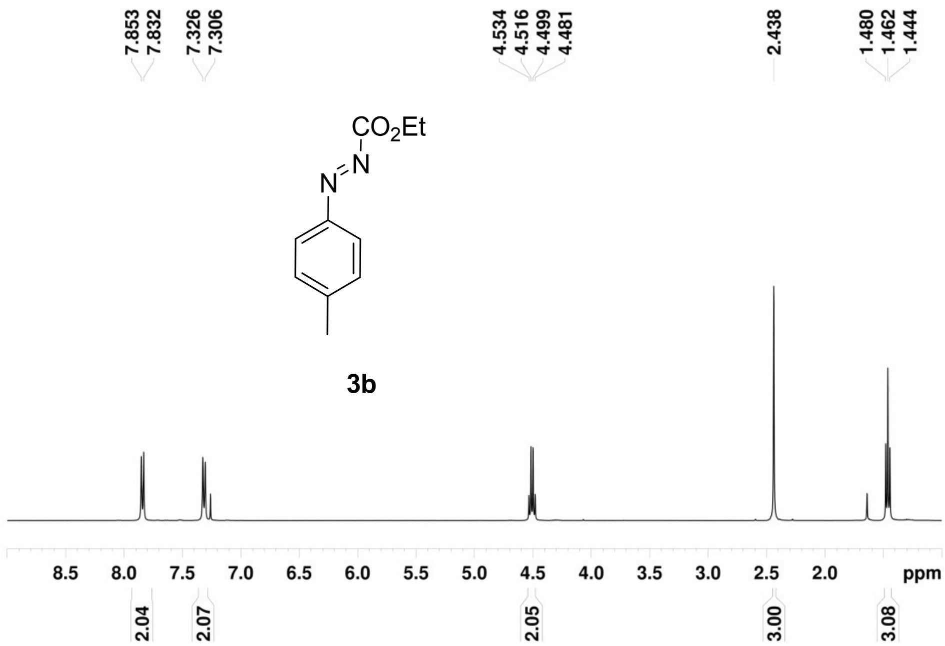


Figure S7. ^{13}C NMR spectrum of **3b**

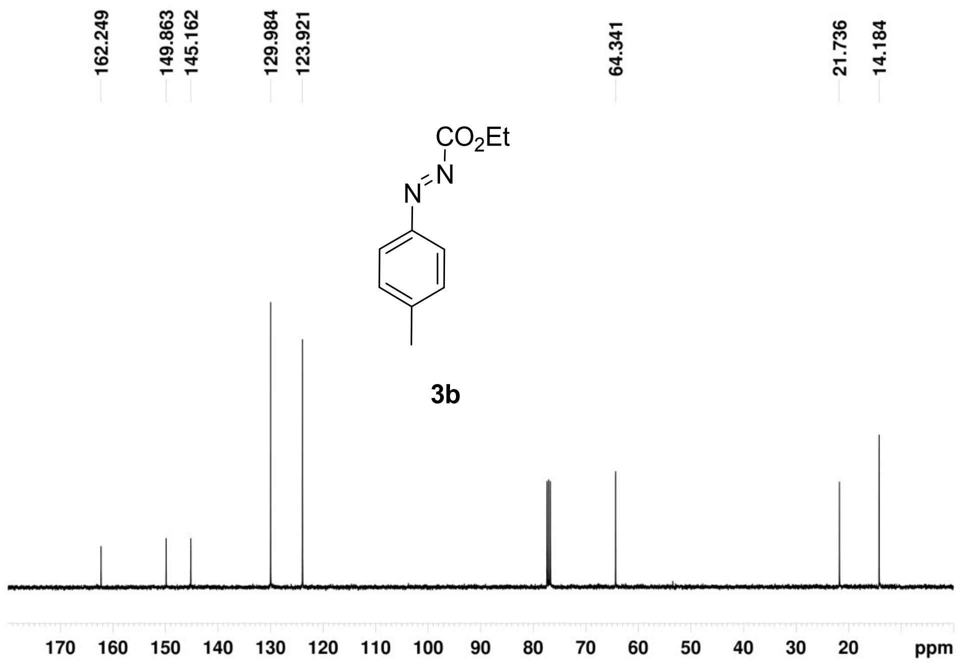


Figure S8. ^{1}H NMR spectrum of **3c**

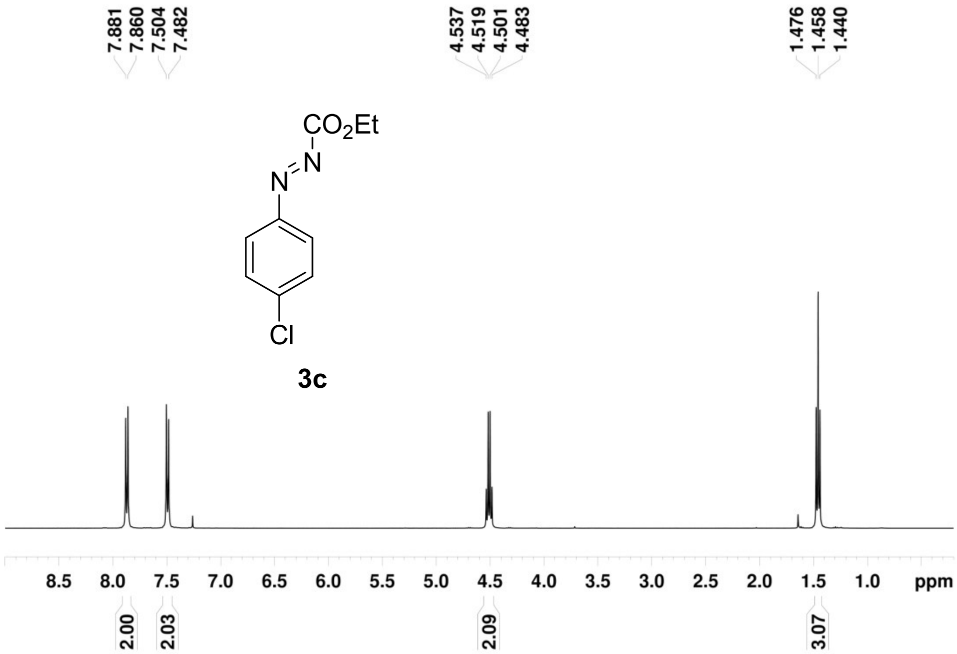


Figure S9. ^{13}C NMR spectrum of **3c**

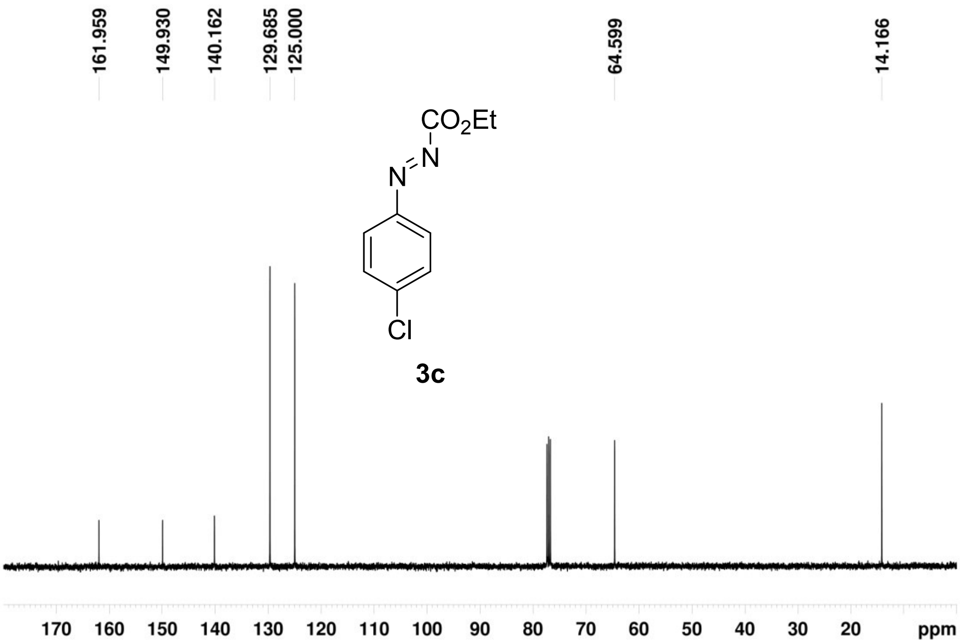


Figure S10. ^{1}H NMR spectrum of **3d**

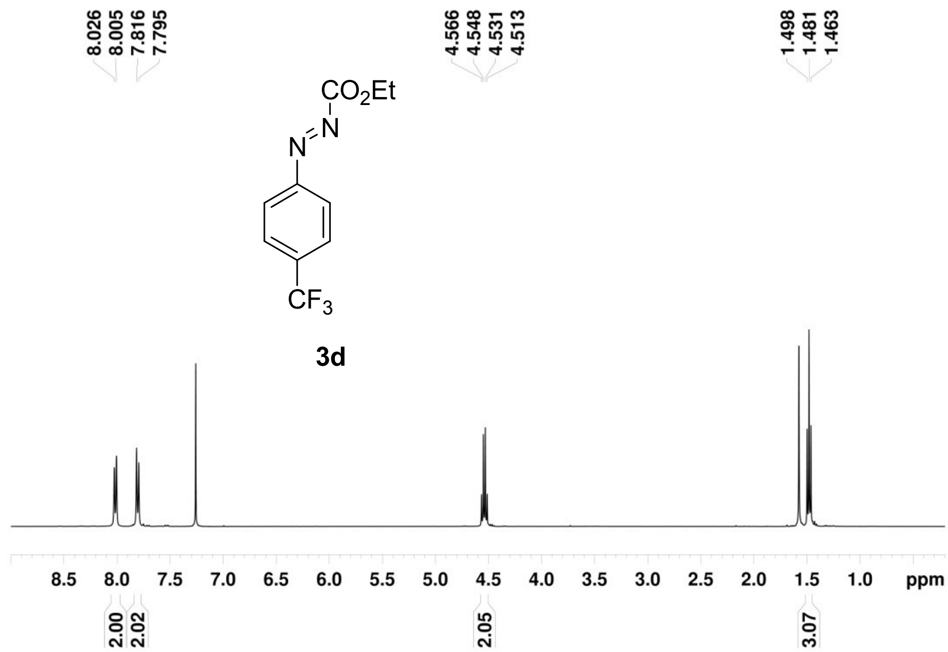


Figure S11. ^{13}C NMR spectrum of **3d**

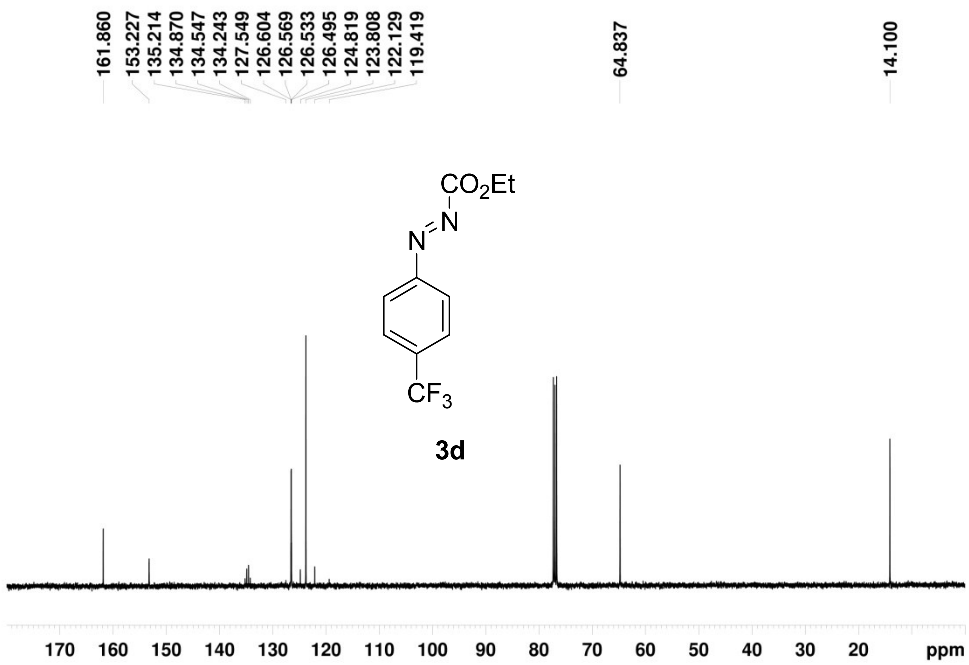
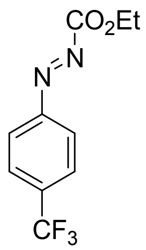


Figure S12. ^{19}F NMR spectrum of **3d**



3d

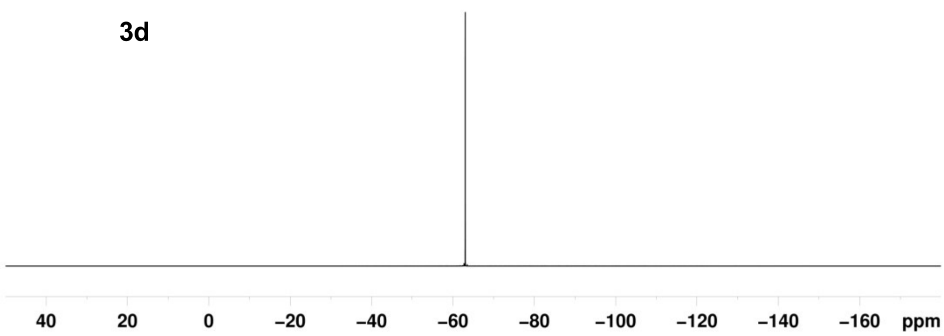


Figure S13. ^{1}H NMR spectrum of **3e**

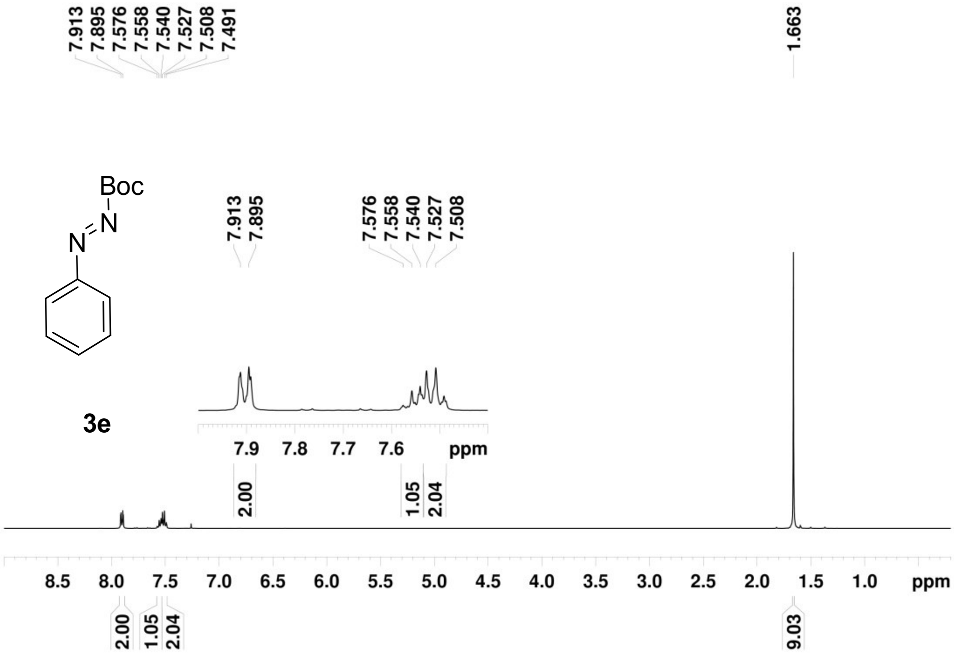


Figure S14. ^{13}C NMR spectrum of **3e**

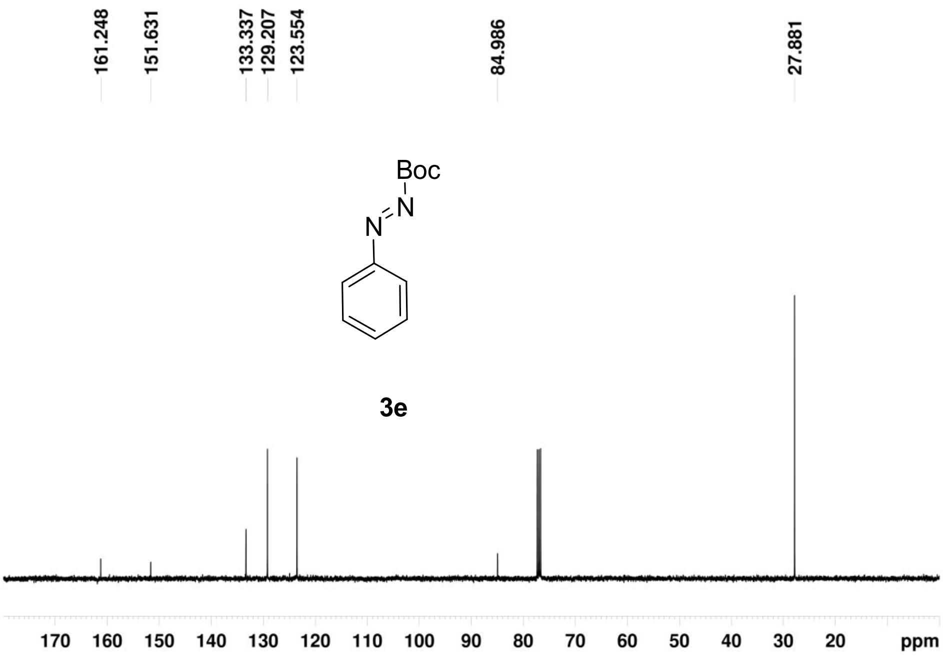


Figure S15. ^{1}H NMR spectrum of **2a**

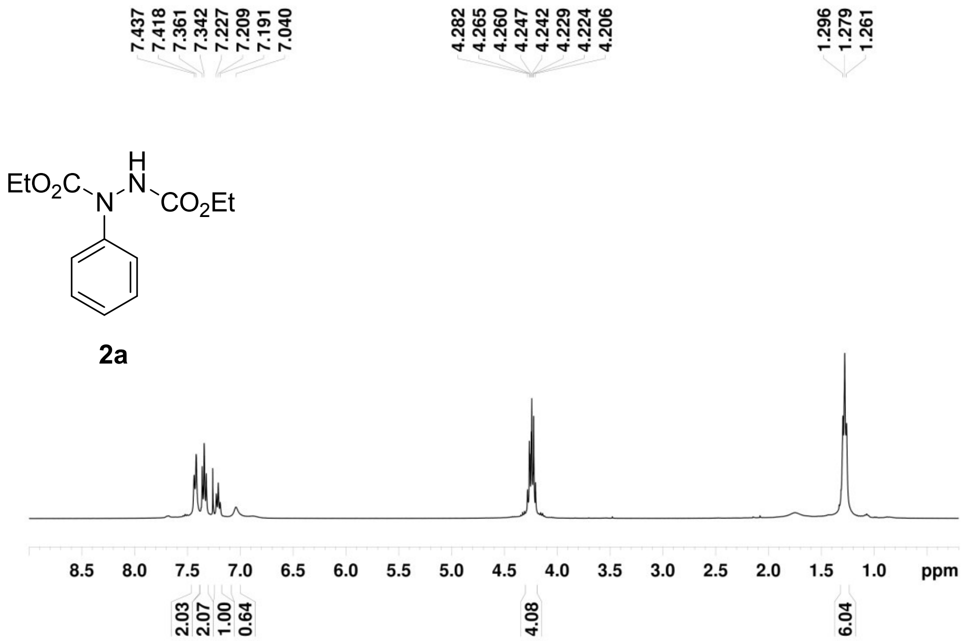


Figure S16. ^{13}C NMR spectrum of **2a**

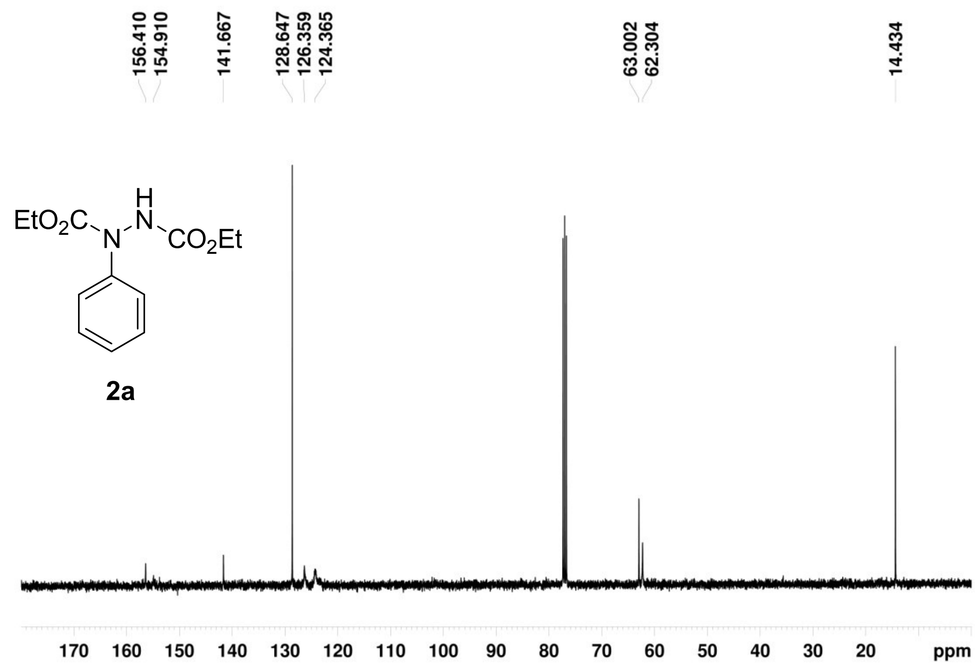


Figure S17. ^{1}H NMR spectrum of **2b**

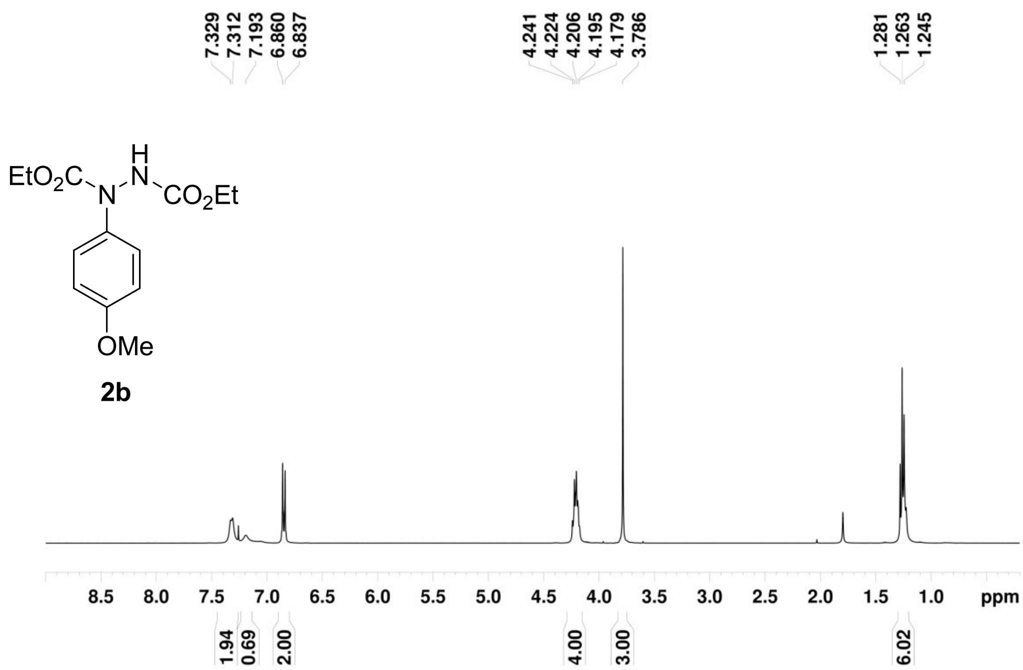


Figure S18. ^{13}C NMR spectrum of **2b**

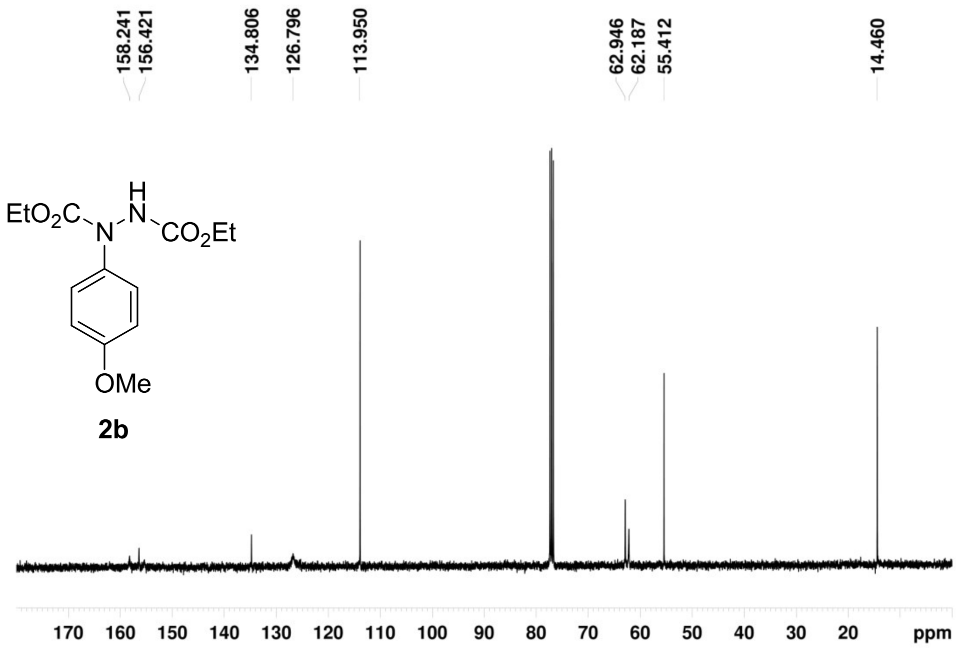


Figure S19. ^1H NMR spectrum of **2c**

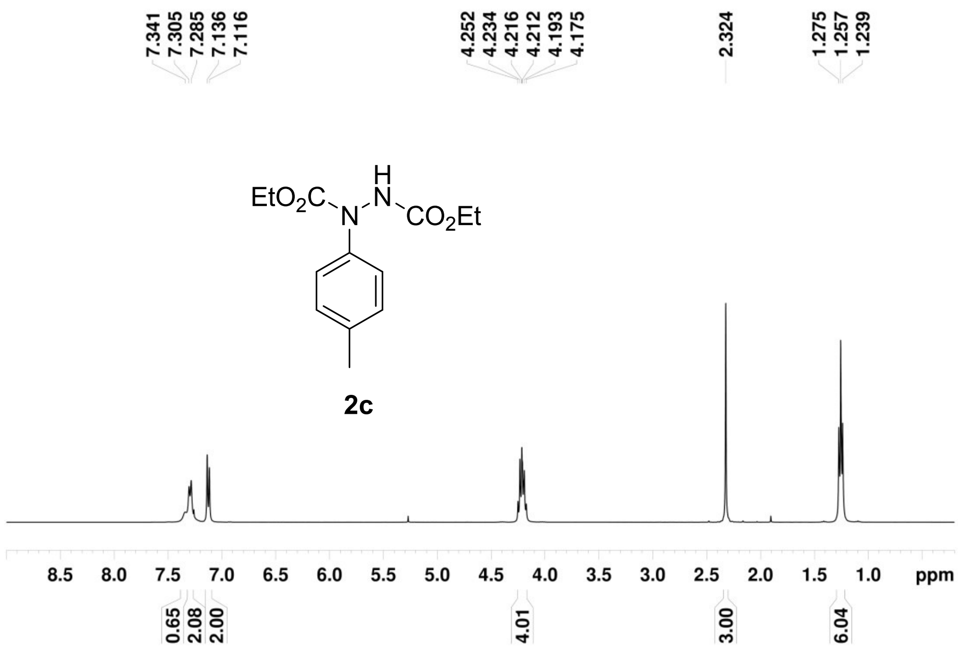


Figure S20. ^{13}C NMR spectrum of **2c**

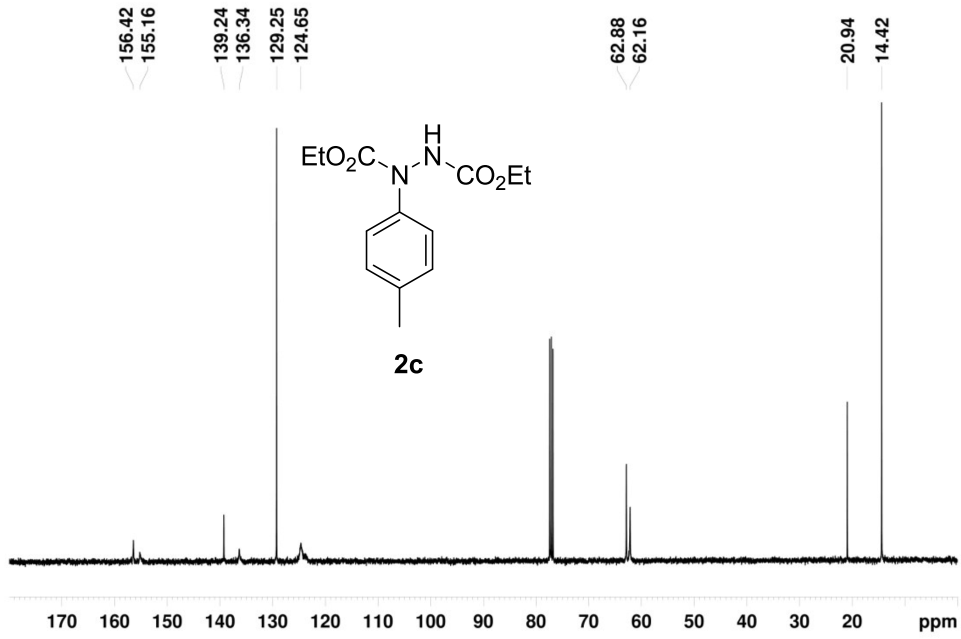


Figure S21. ^{1}H NMR spectrum of **2d**

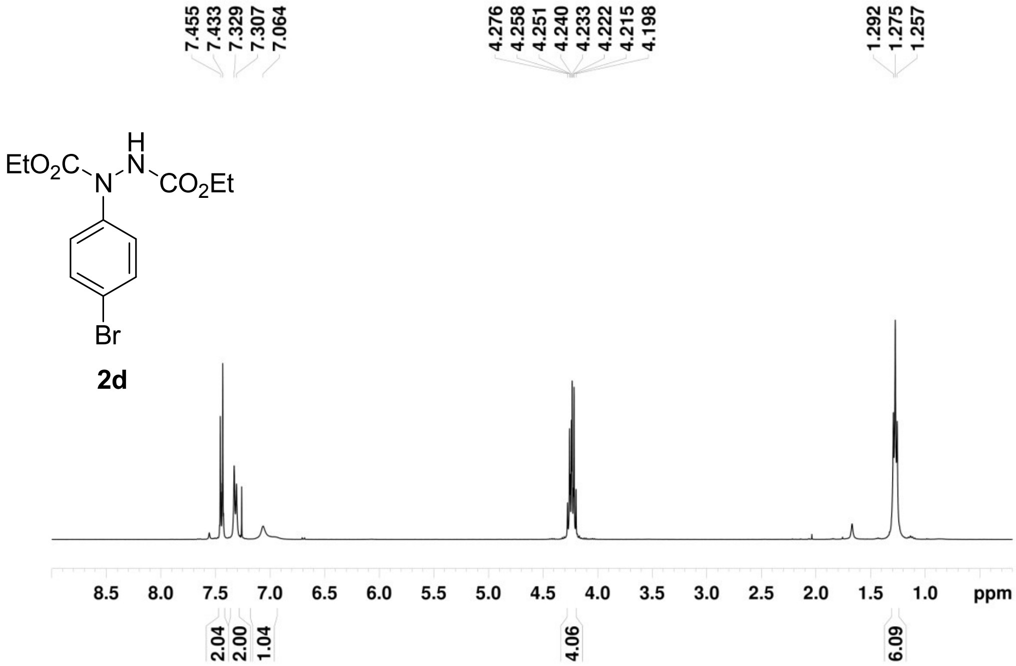


Figure S22. ^{13}C NMR spectrum of **2d**

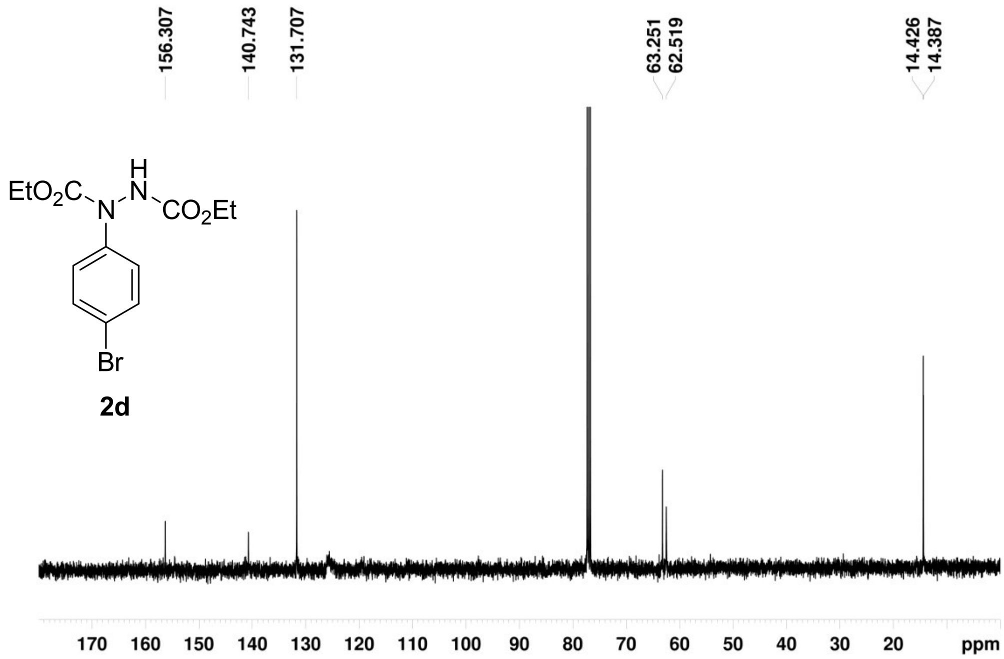


Figure S23. ^{1}H NMR spectrum of **2e**

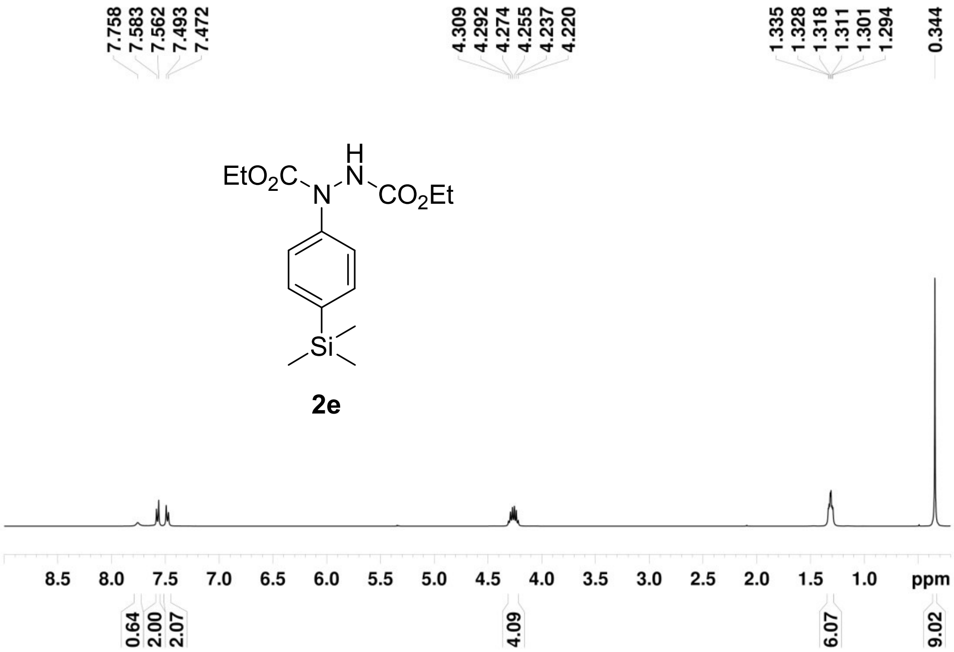


Figure S24. ^{13}C NMR spectrum of **2e**

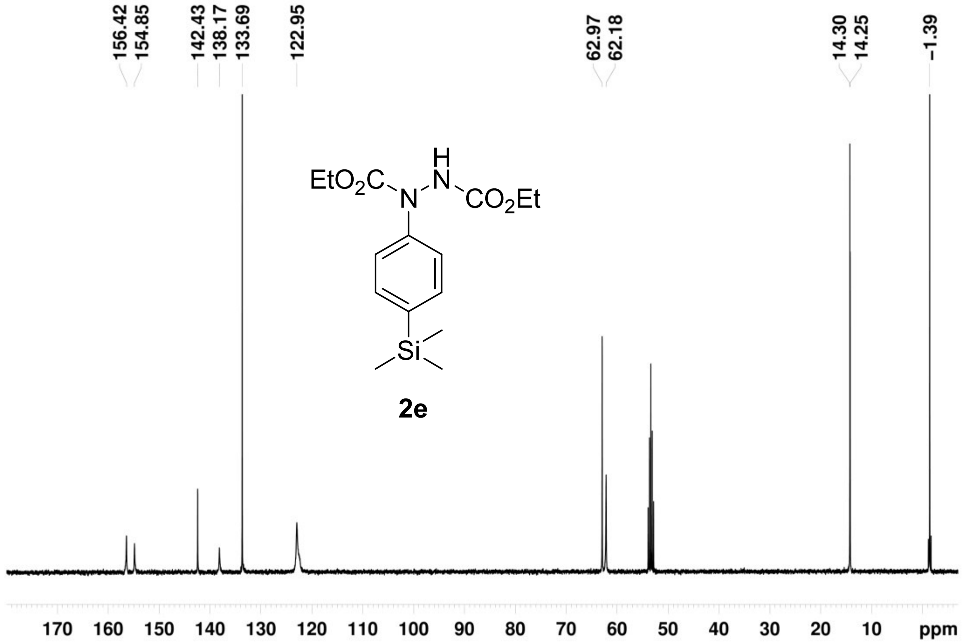


Figure S25. ^{1}H NMR spectrum of **2f**

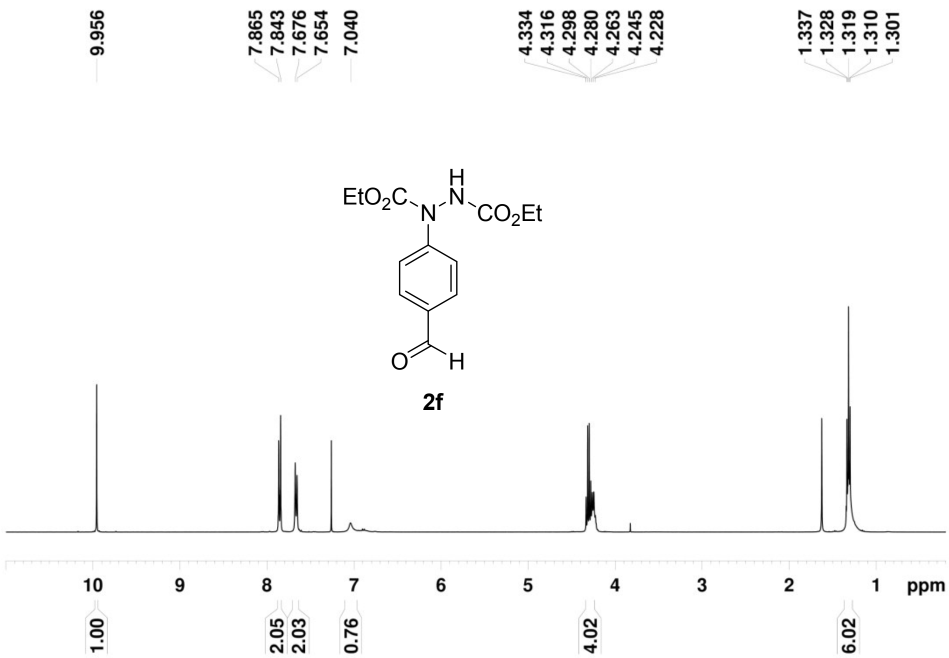


Figure S26. ^{13}C NMR spectrum of **2f**

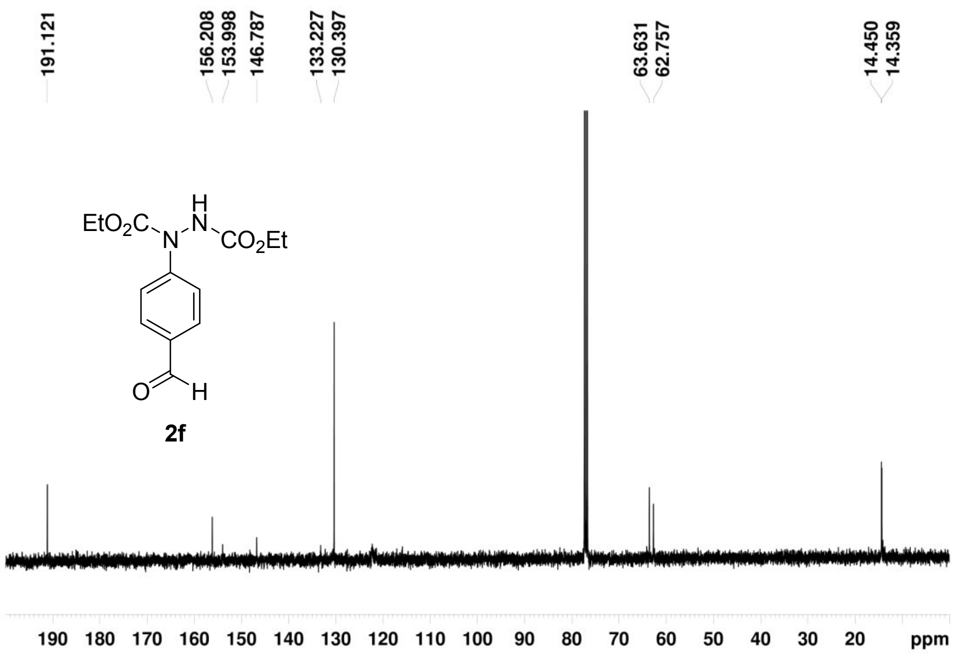


Figure S27. ^{1}H NMR spectrum of **2g**

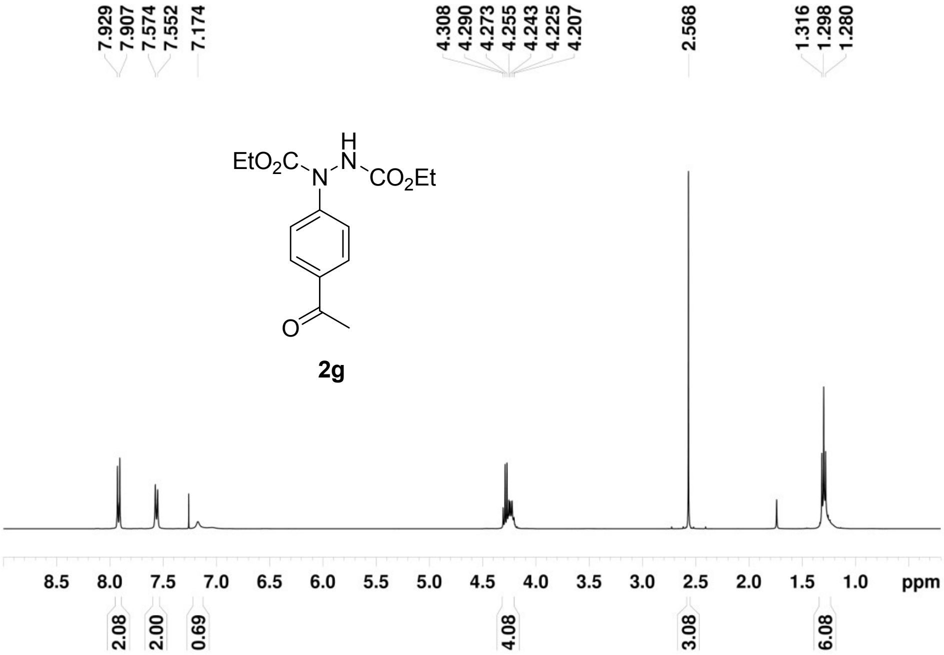


Figure S28. ^{13}C NMR spectrum of **2g**

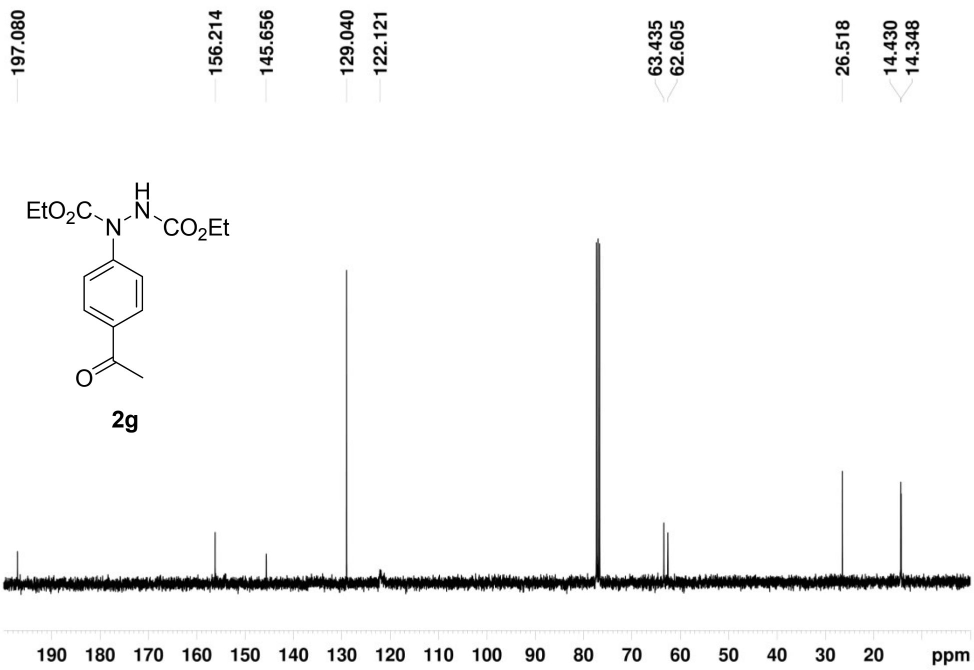


Figure S29. ^{1}H NMR spectrum of **2h**

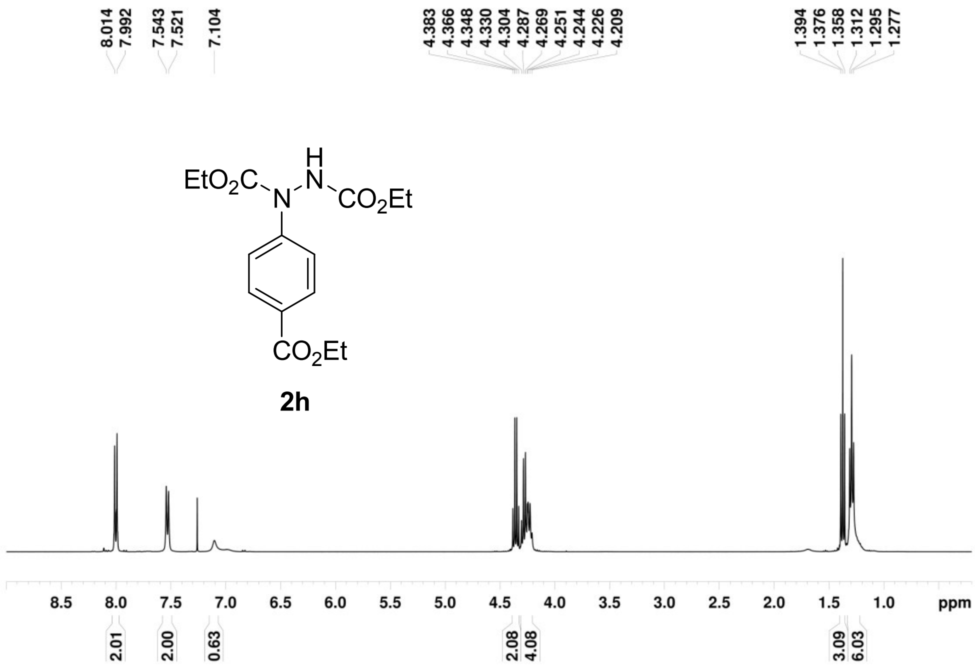


Figure S30. ^{13}C NMR spectrum of **2h**

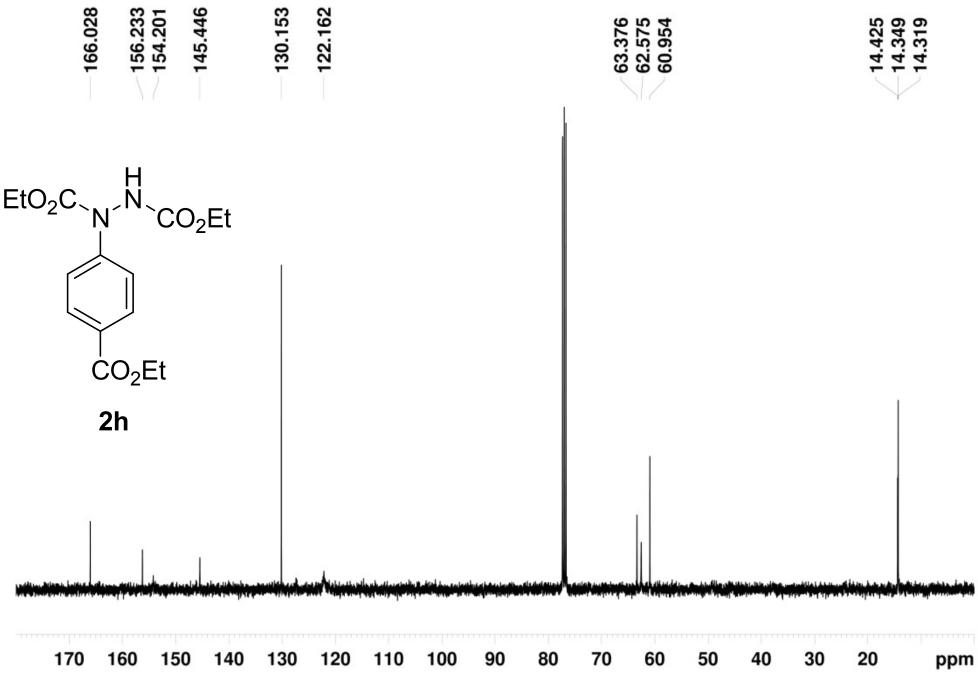


Figure S31. ^{1}H NMR spectrum of **2i**

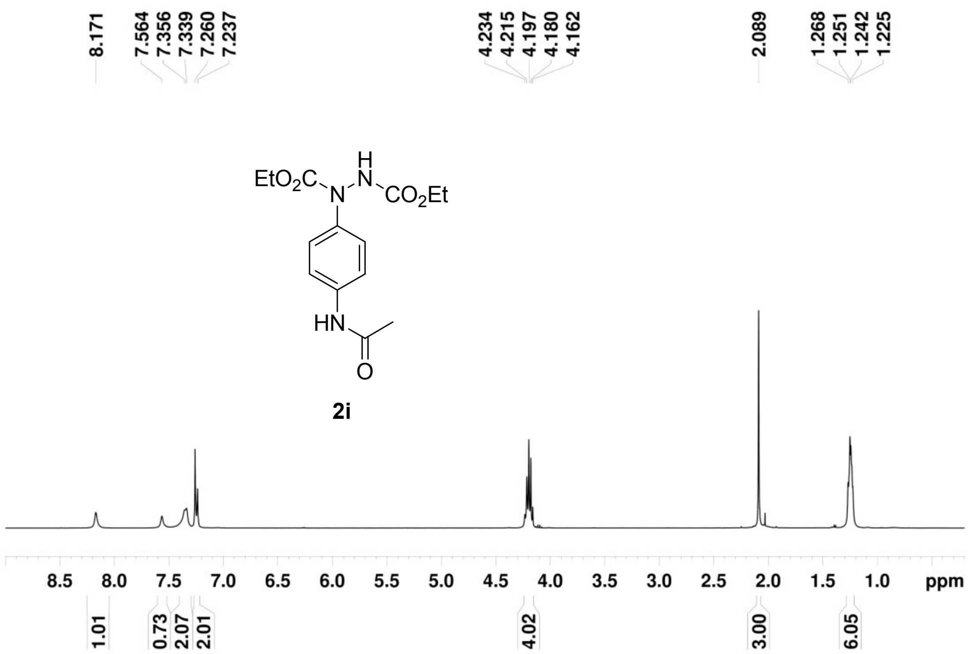


Figure S32. ^{13}C NMR spectrum of **2i**

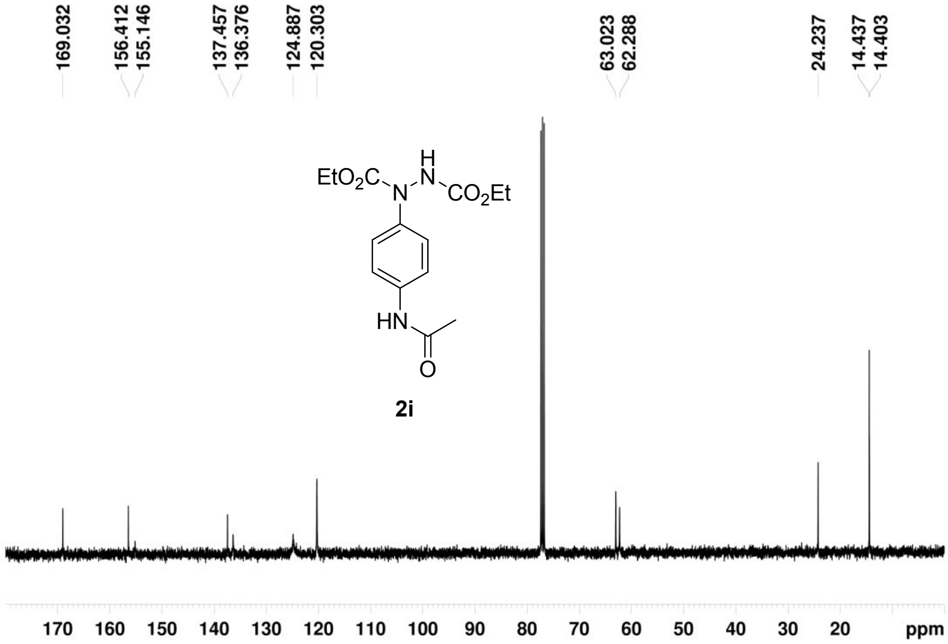


Figure S33. ^{1}H NMR spectrum of **2j**

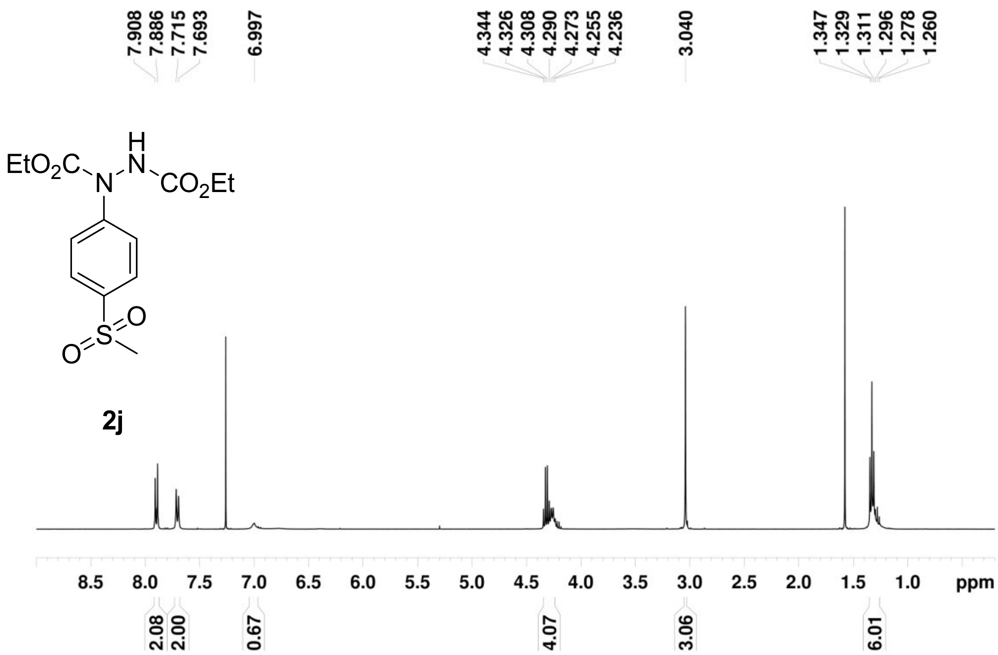


Figure S34. ^{13}C NMR spectrum of **2j**

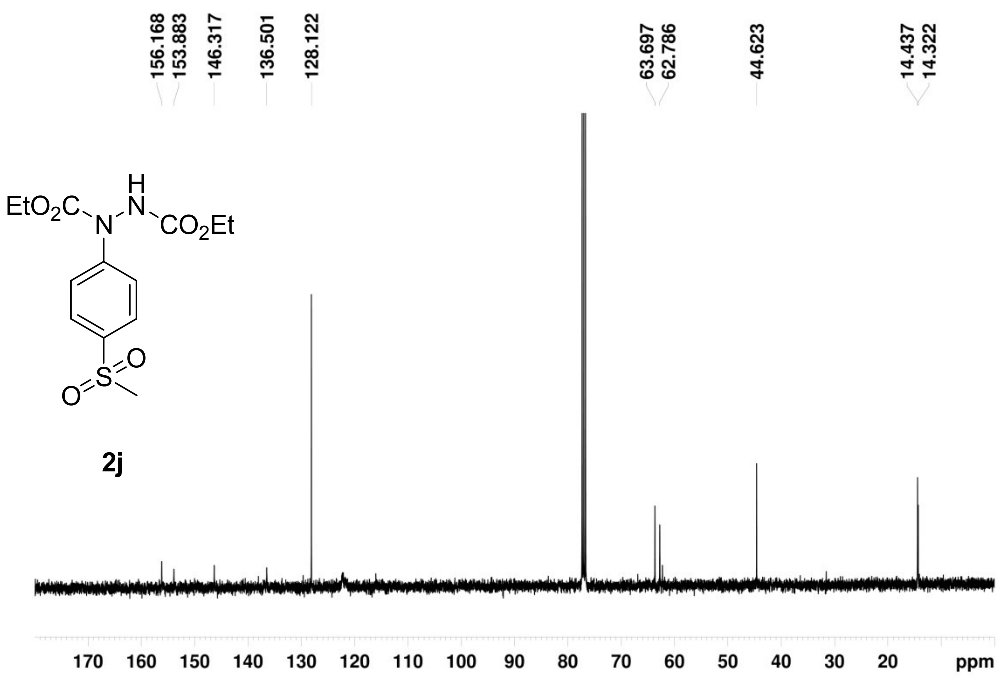


Figure S35. ^{1}H NMR spectrum of **2k**

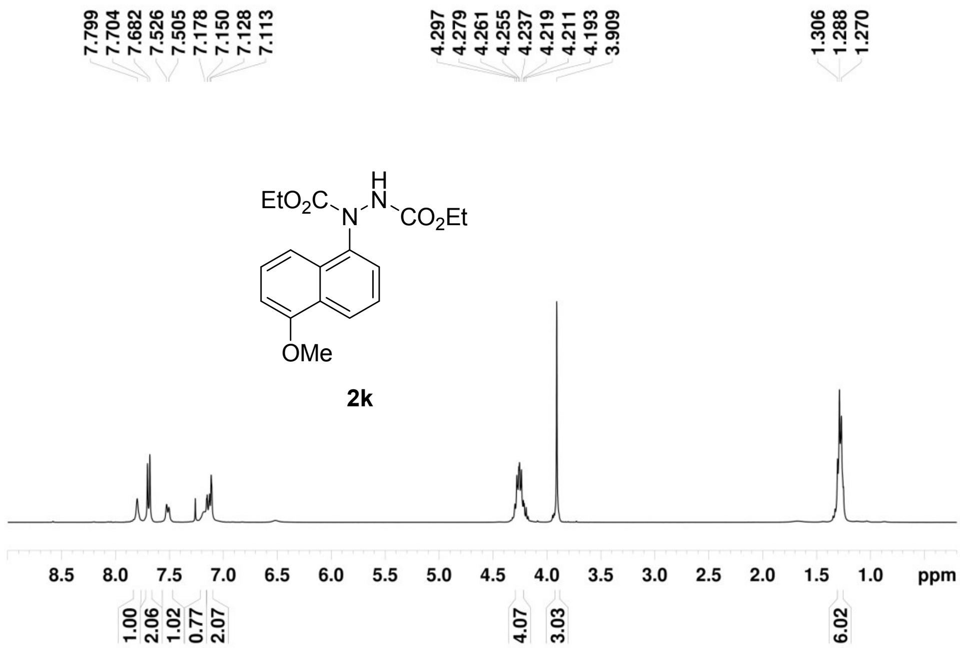


Figure S36. ^{13}C NMR spectrum of **2k**

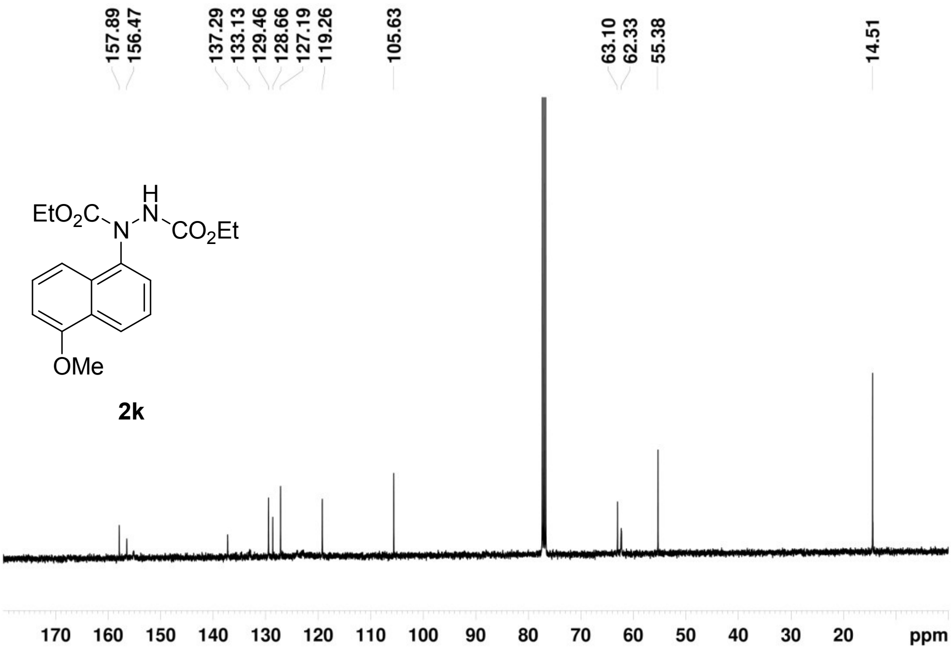


Figure S37. ^{1}H NMR spectrum of **2l**

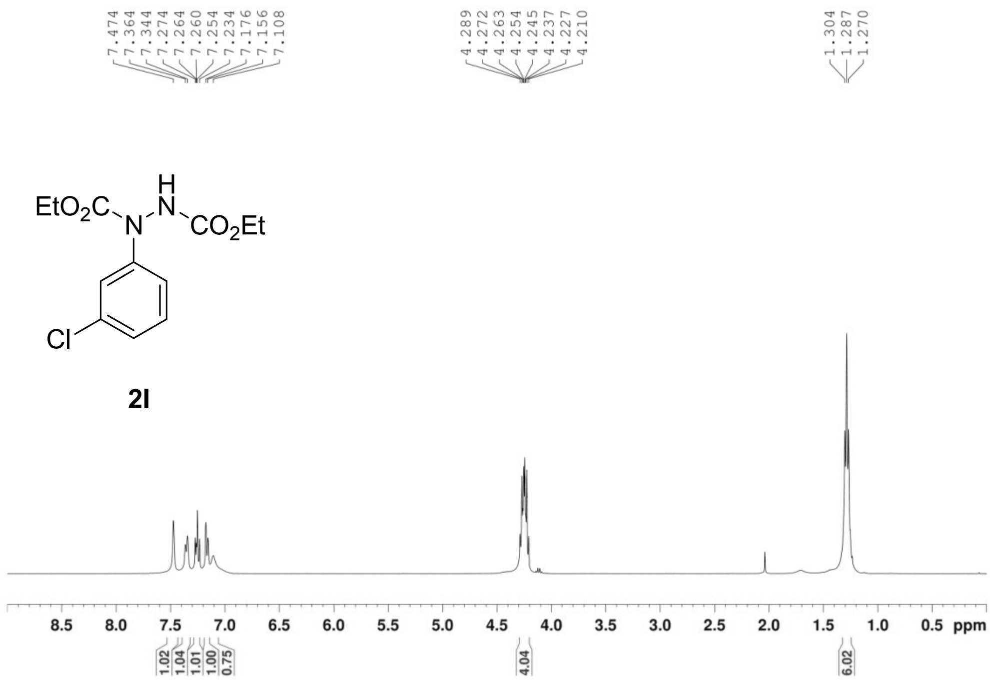


Figure S38. ^{13}C NMR spectrum of **2l**

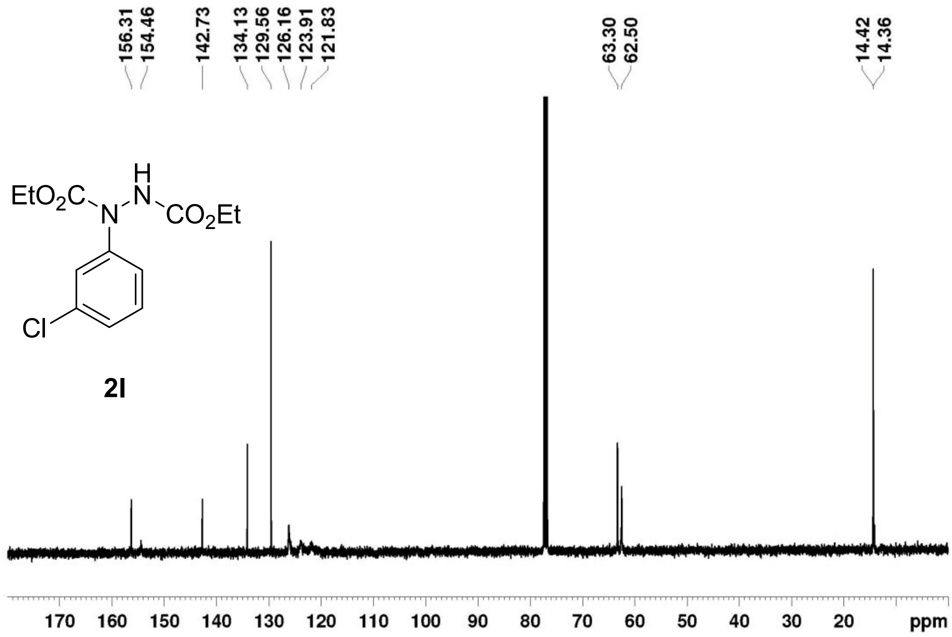


Figure S39. ^{1}H NMR spectrum of **2m**

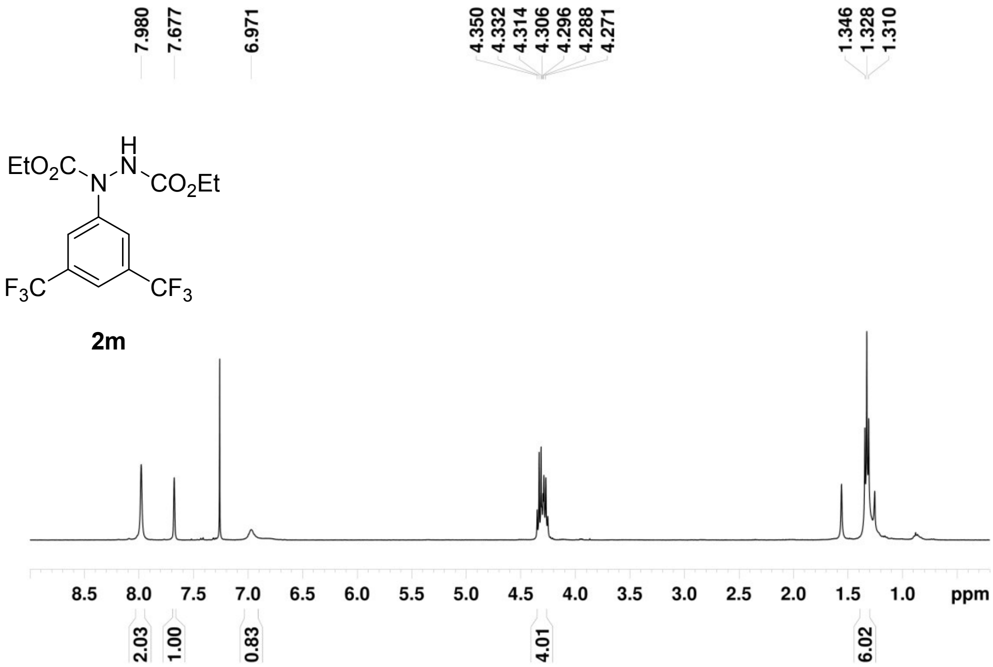


Figure S40. ^{13}C NMR spectrum of **2m**

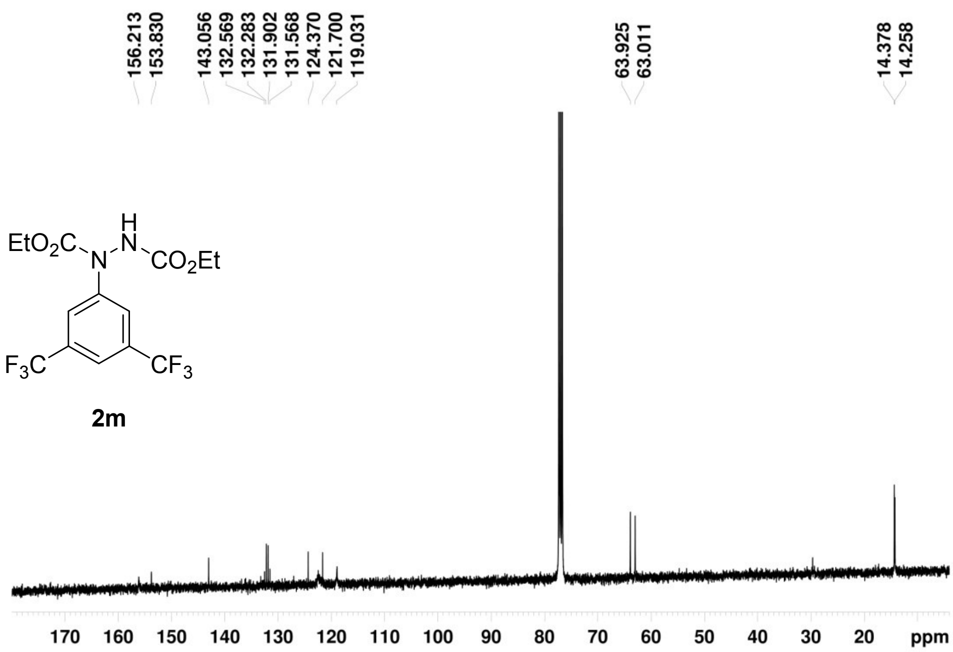
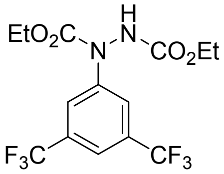


Figure S41. ^{19}F NMR spectrum of **2m**



2m

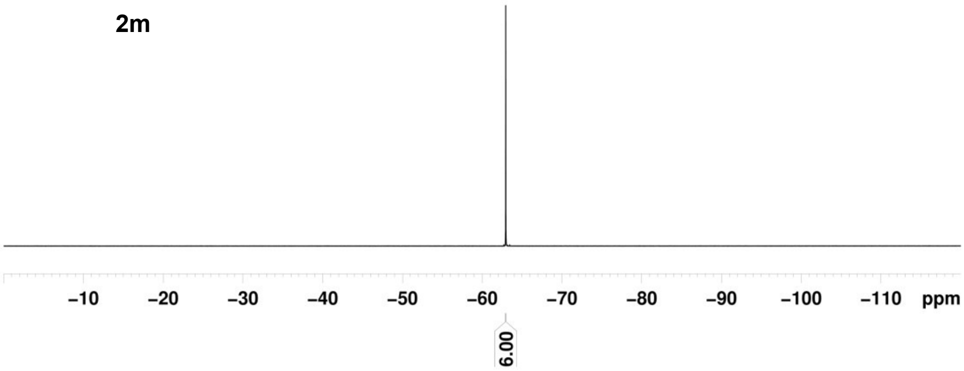


Figure S42. ^{1}H NMR spectrum of **2n**

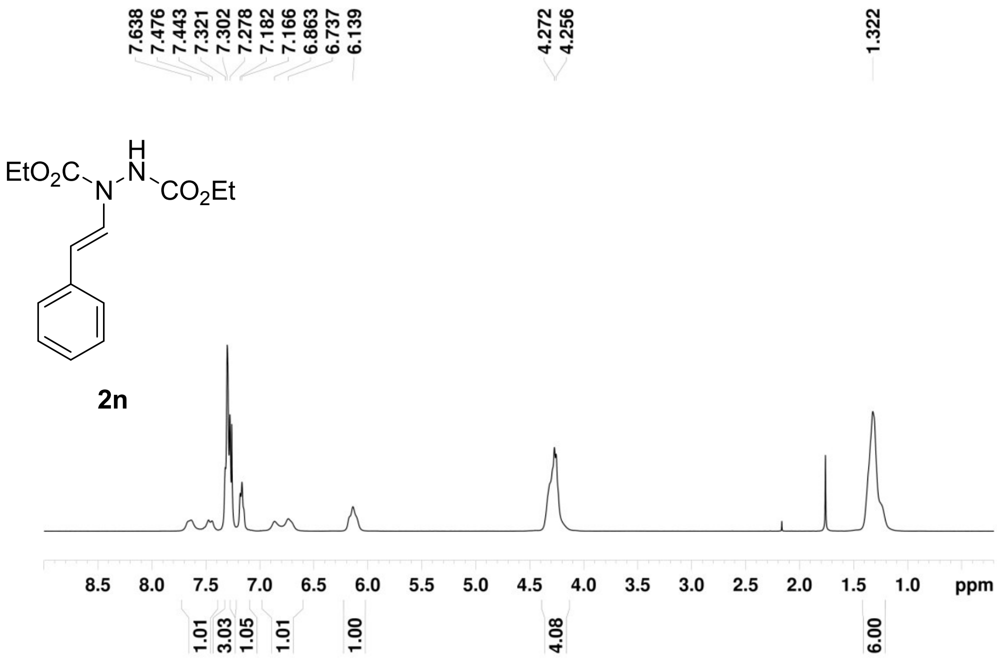


Figure S43. ^{13}C NMR spectrum of **2n**

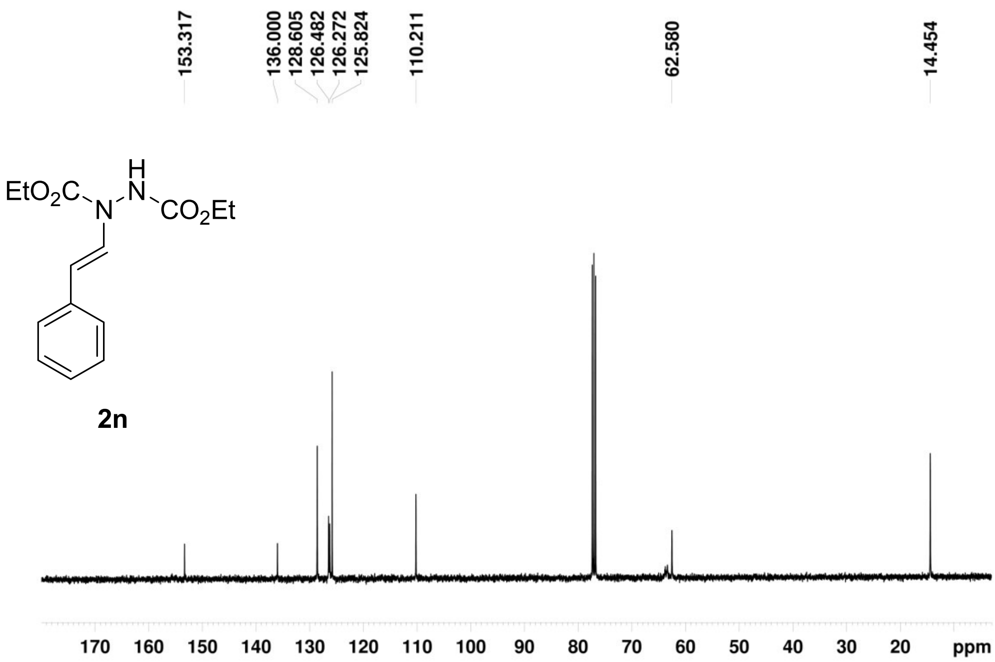


Figure S44. ^{1}H NMR spectrum of **2o**

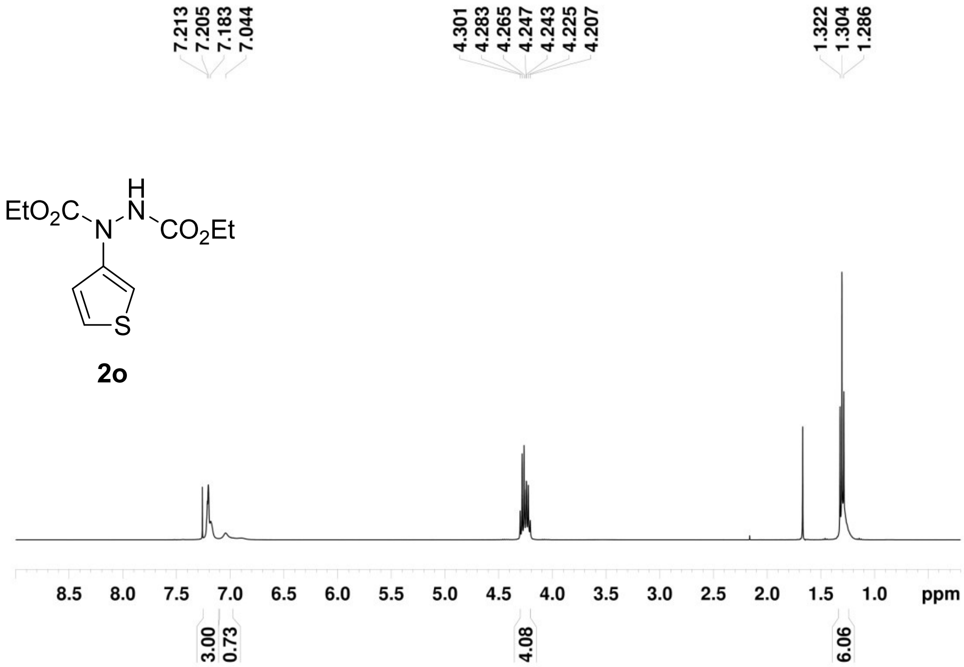


Figure S45. ^{13}C NMR spectrum of **2o**

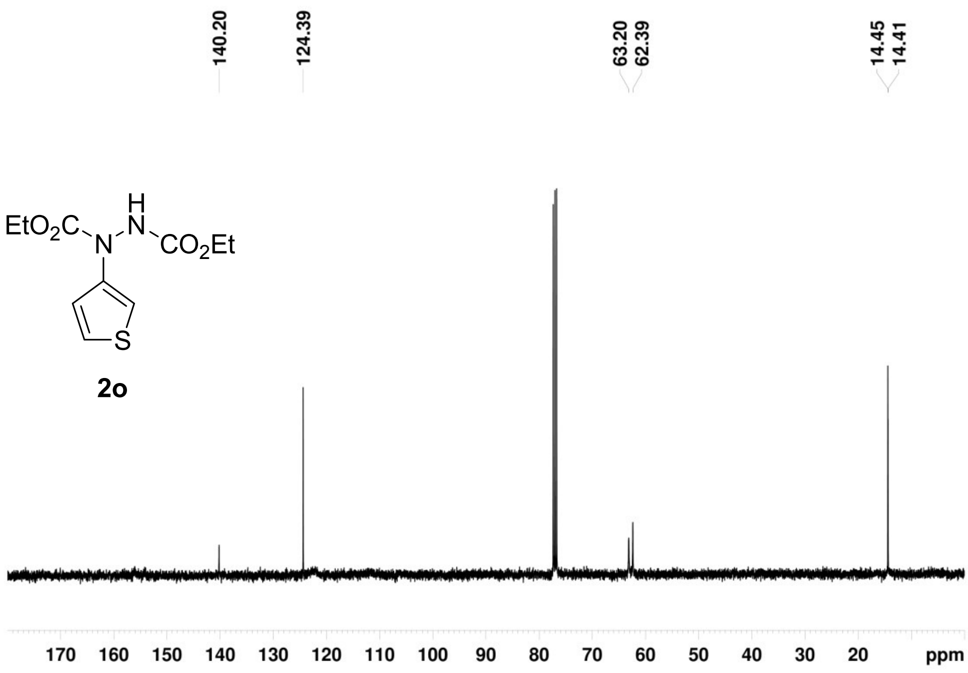


Figure S46. ^{1}H NMR spectrum of **2p**

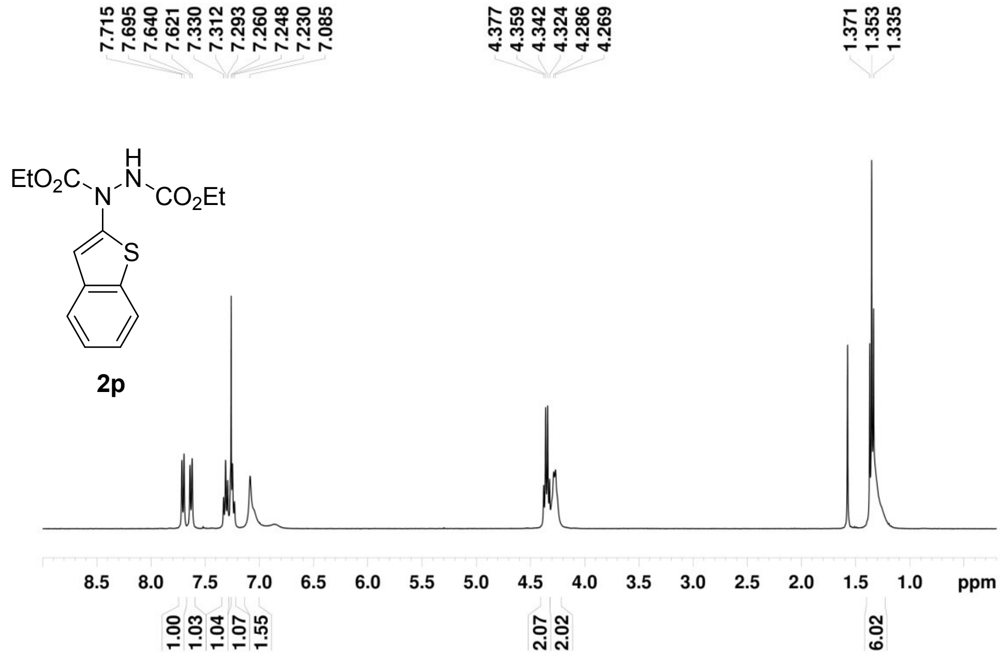


Figure S47. ^{13}C NMR spectrum of **2p**

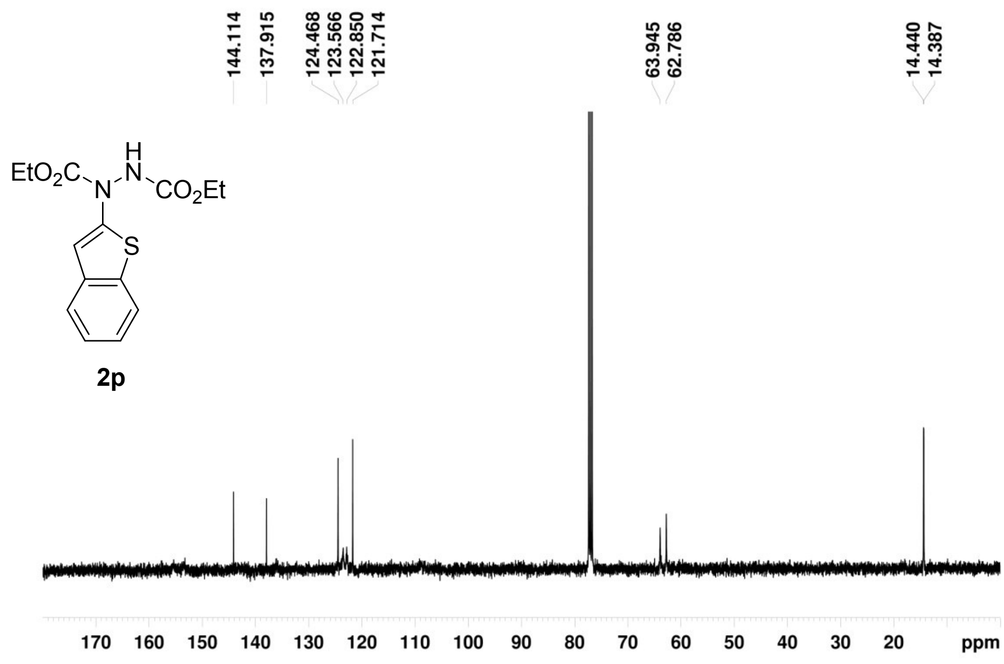


Figure S48. ^{1}H NMR spectrum of **2q**

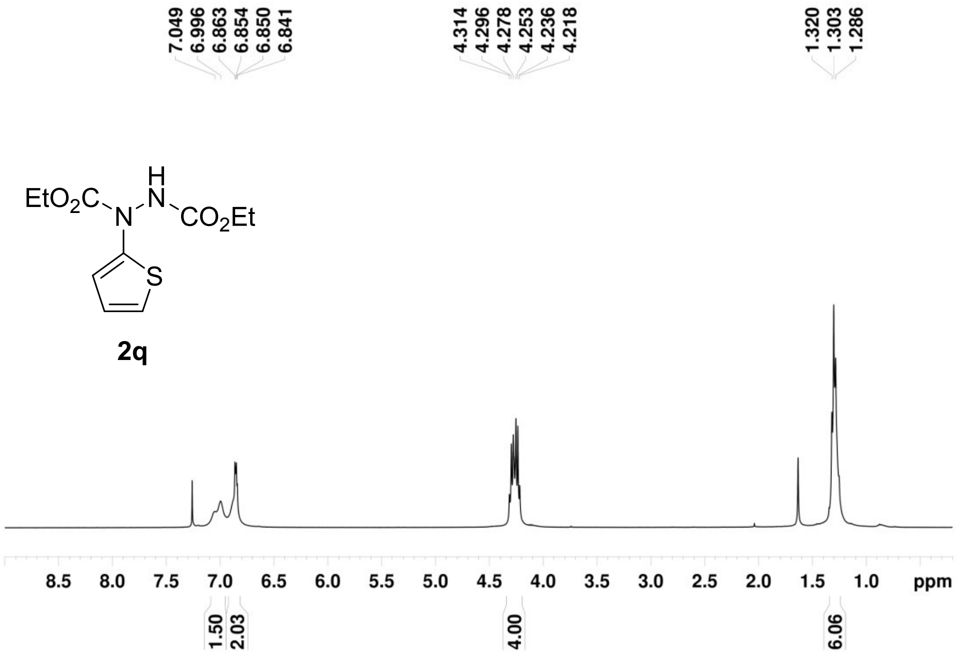


Figure S49. ^{13}C NMR spectrum of **2q**

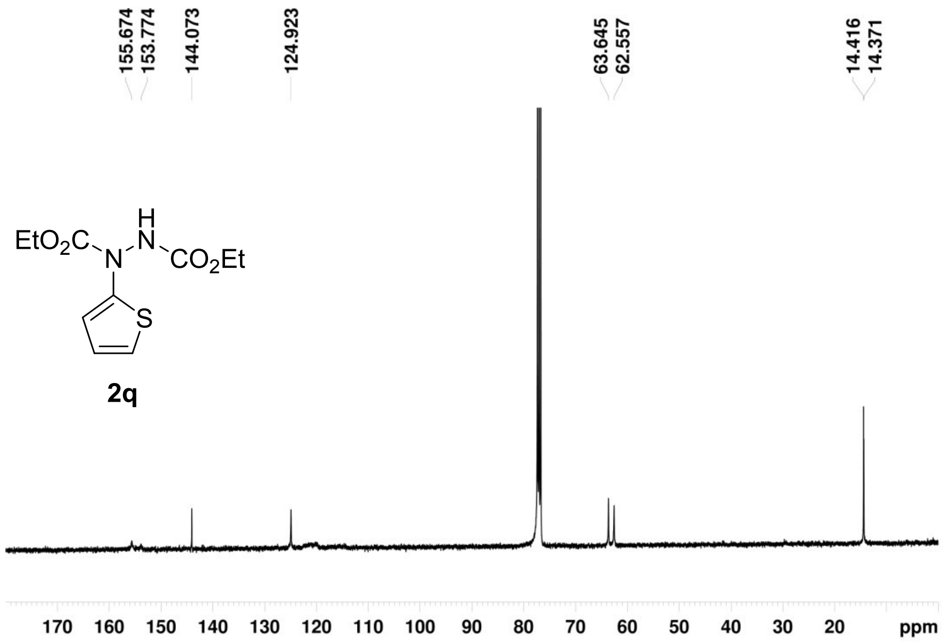


Figure S50. ^{1}H NMR spectrum of **4aa**

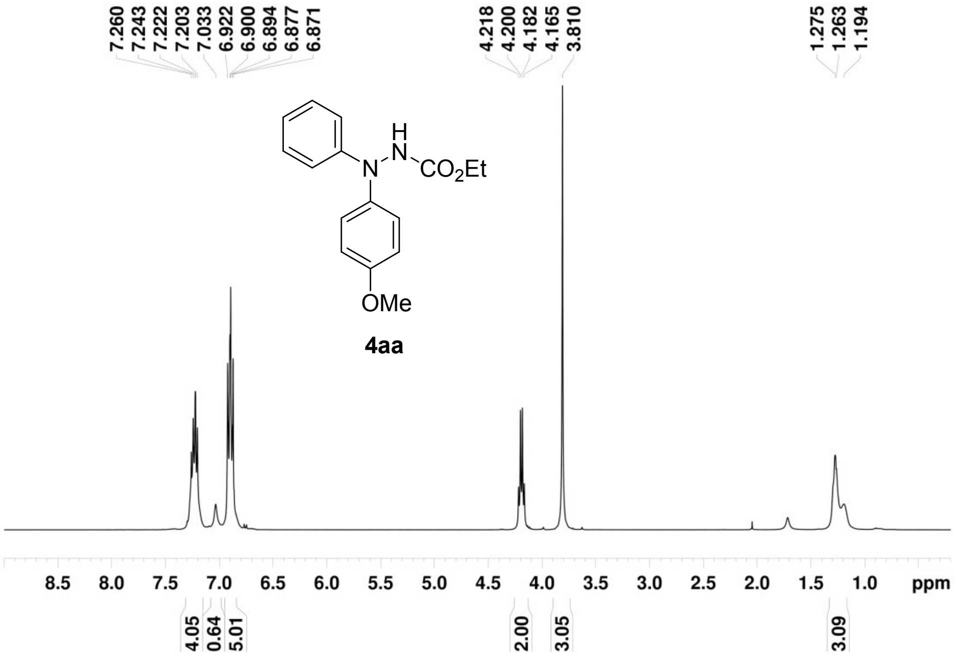


Figure S51. ^{13}C NMR spectrum of **4aa**

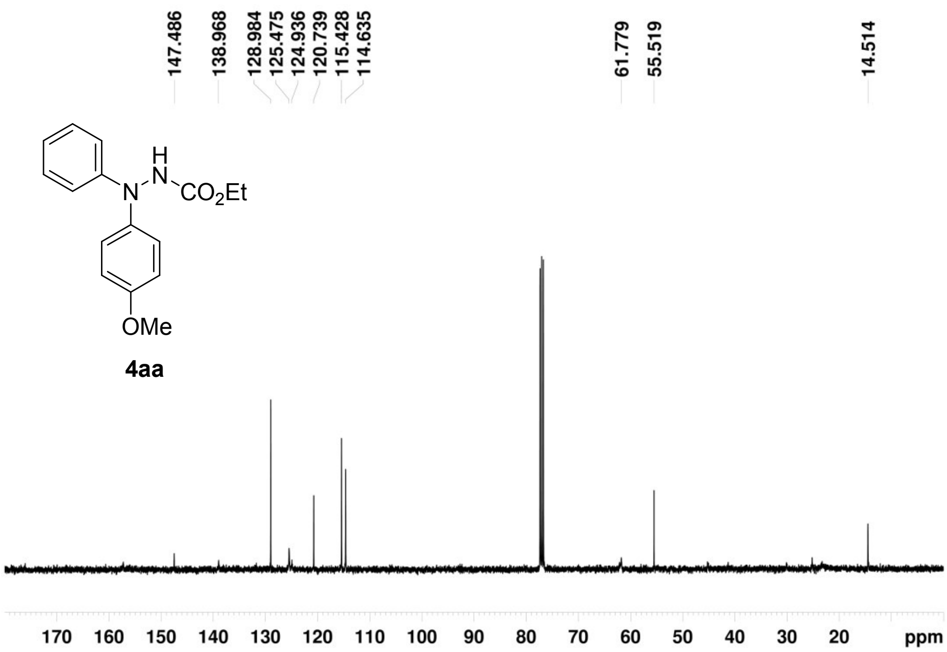


Figure S52. ^{1}H NMR spectrum of **4ba**

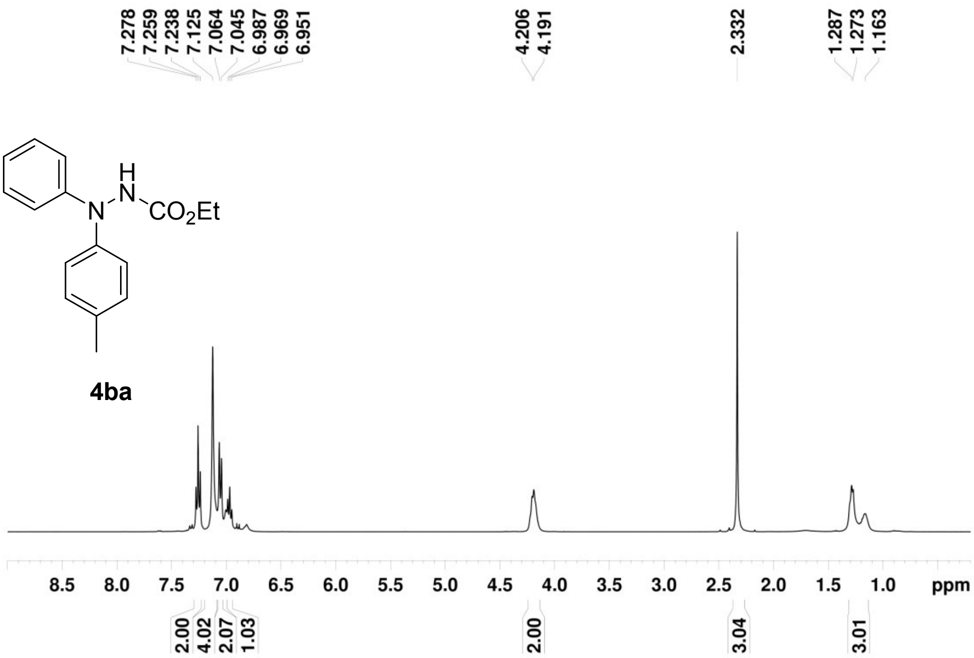


Figure S53. ^{13}C NMR spectrum of **4ba**

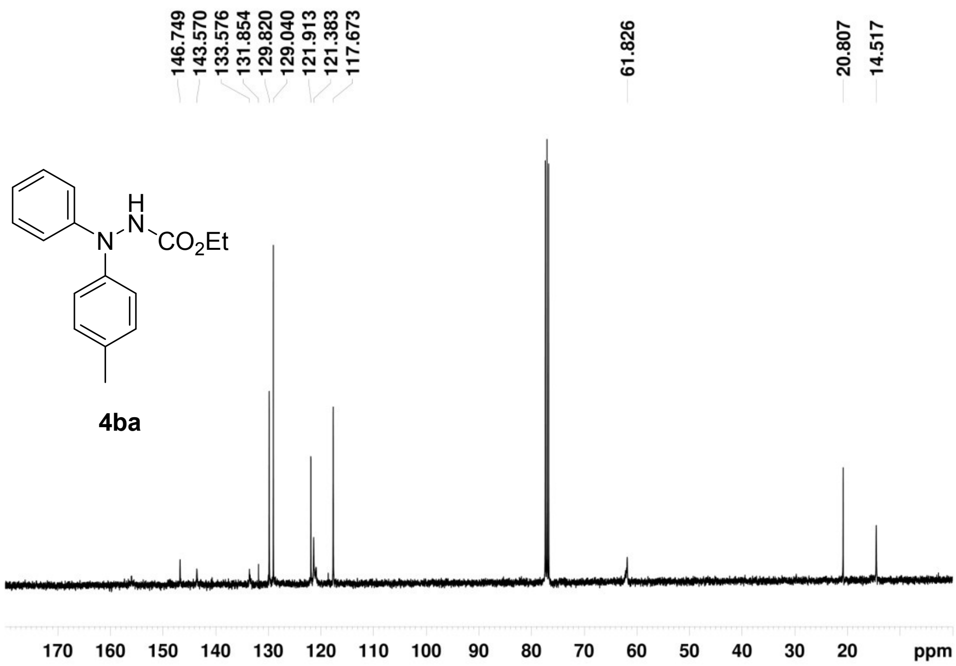


Figure S54. ^{1}H NMR spectrum of **4ca**

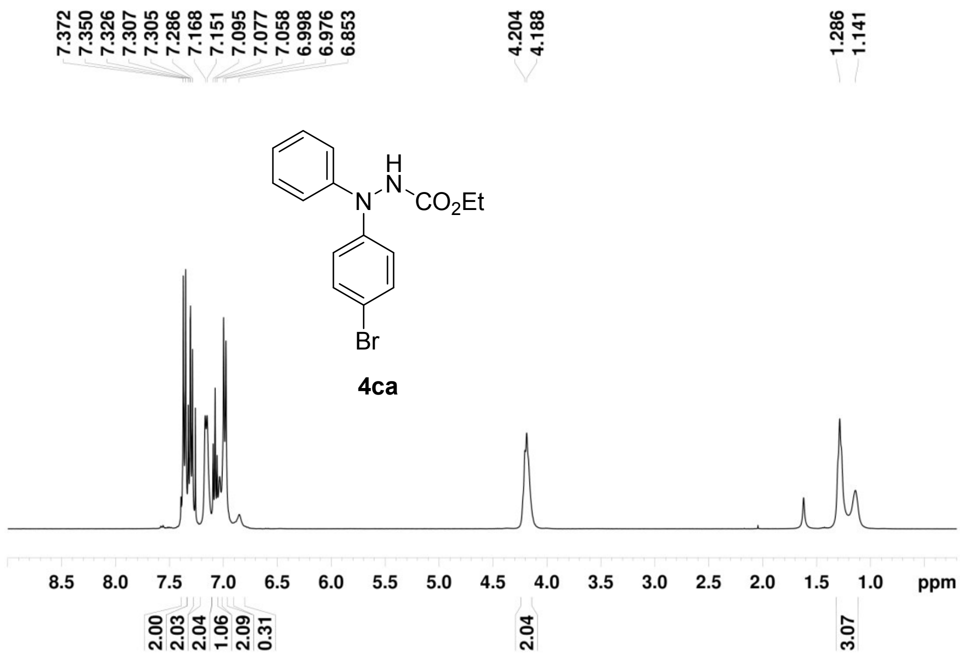


Figure S55. ^{13}C NMR spectrum of **4ca**

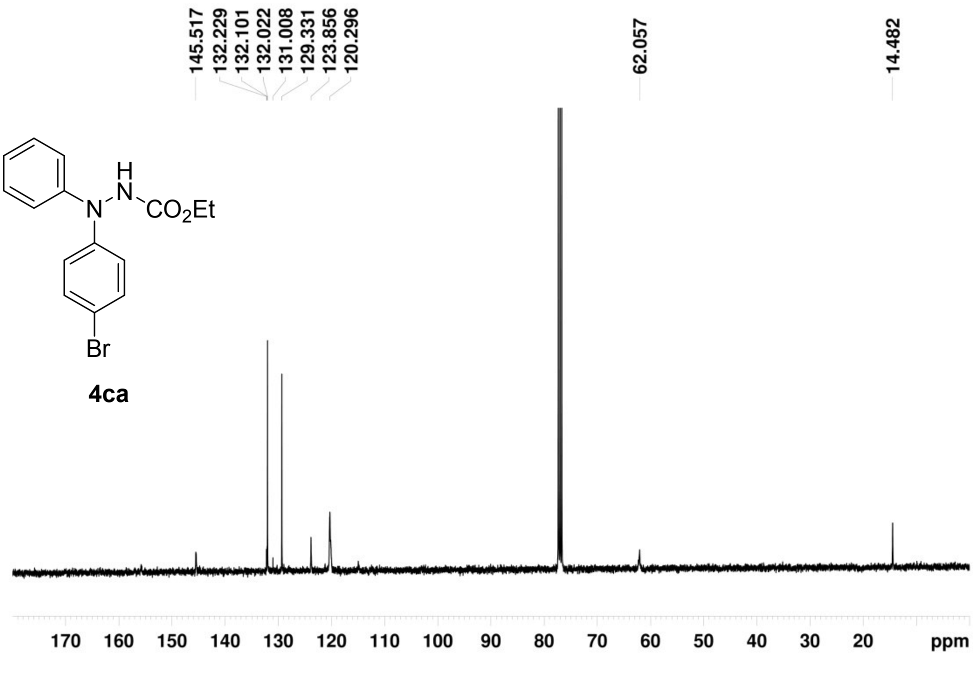


Figure S56. ^{1}H NMR spectrum of **4da**

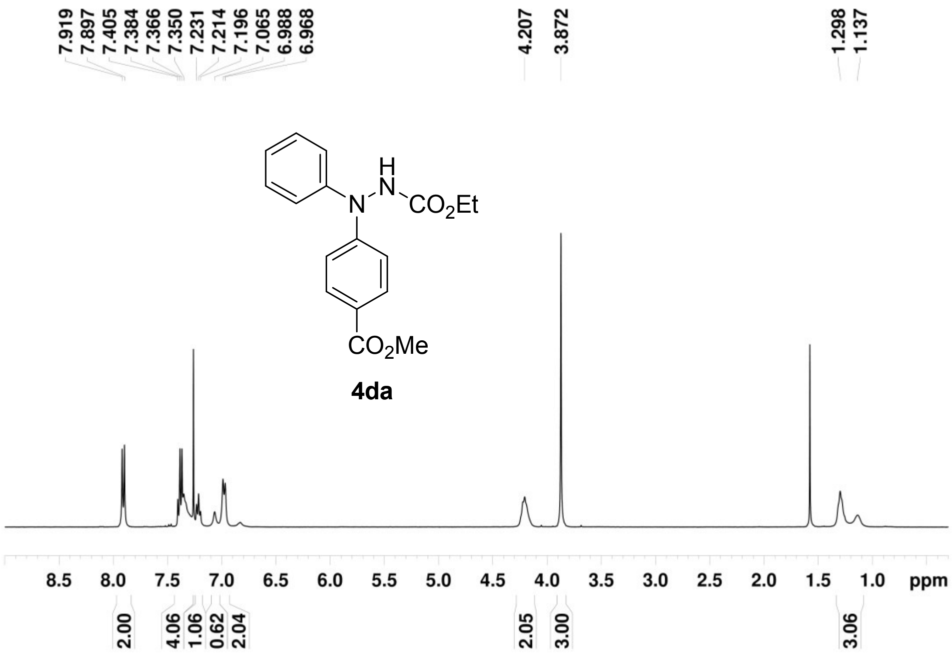


Figure S57. ^{13}C NMR spectrum of **4da**

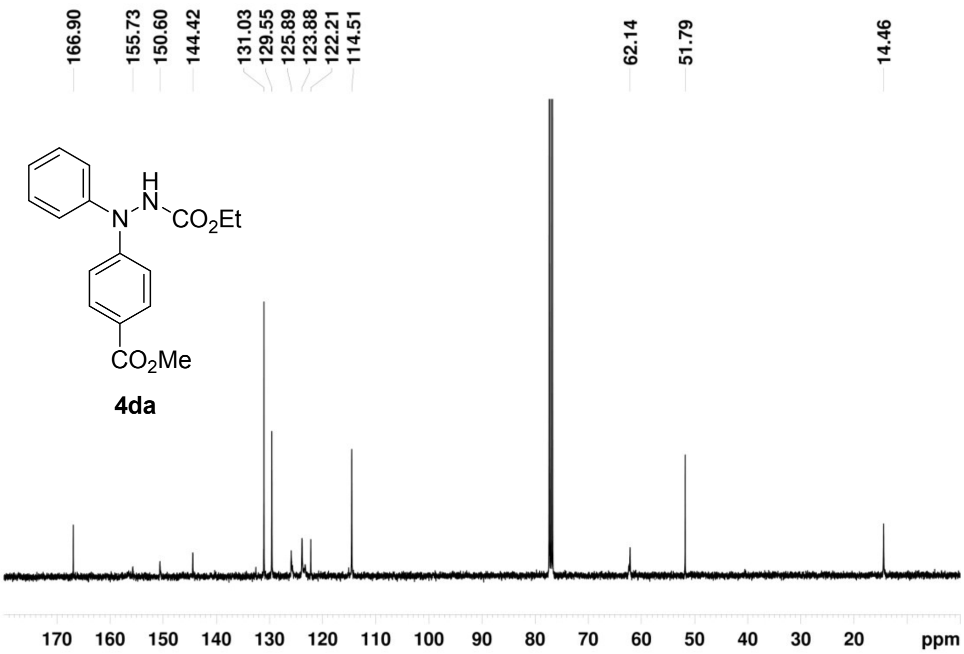


Figure S58. ^{1}H NMR spectrum of **4ea**

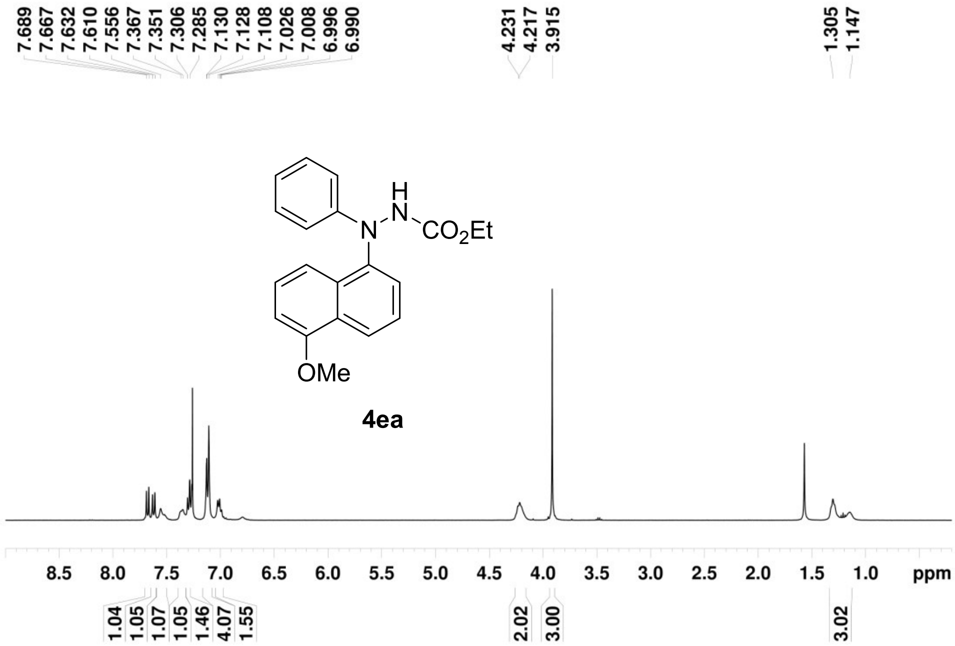


Figure S59. ^{13}C NMR spectrum of **4ea**

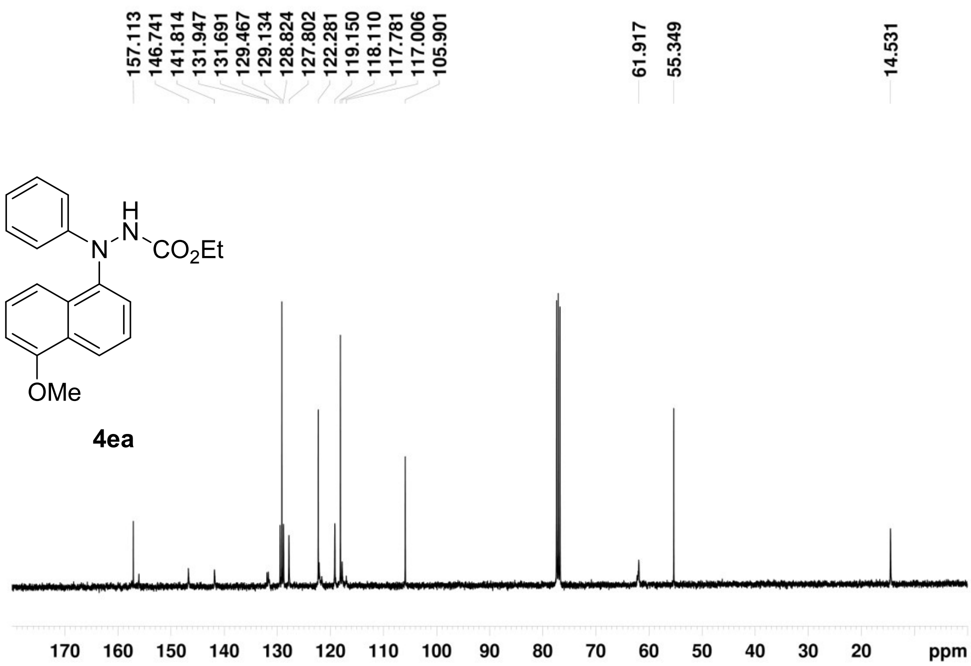


Figure S60. ^{1}H NMR spectrum of **4fa**

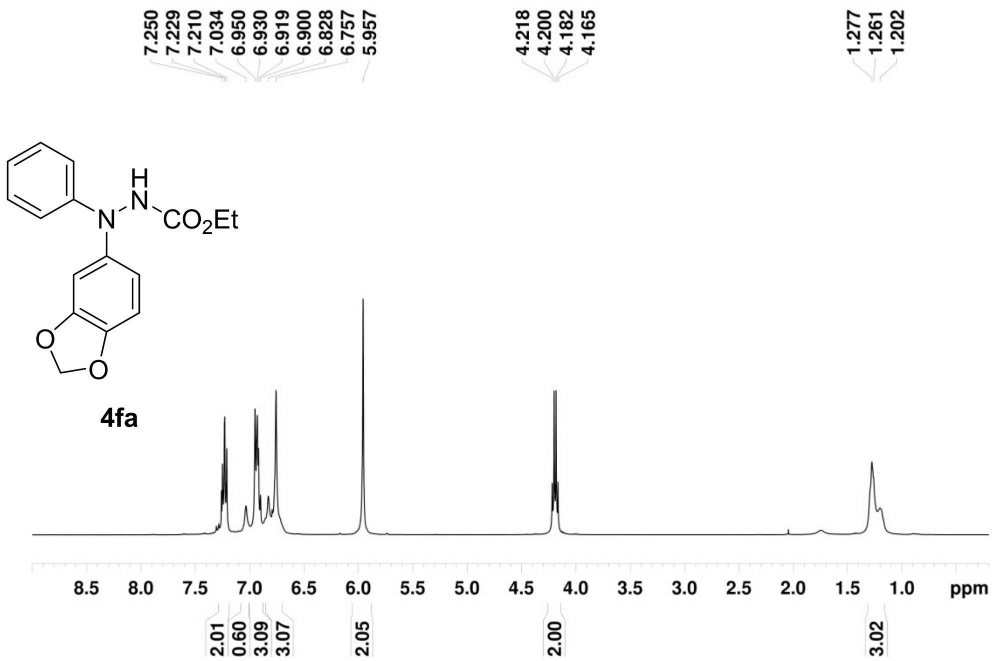


Figure S61. ^{13}C NMR spectrum of **4fa**

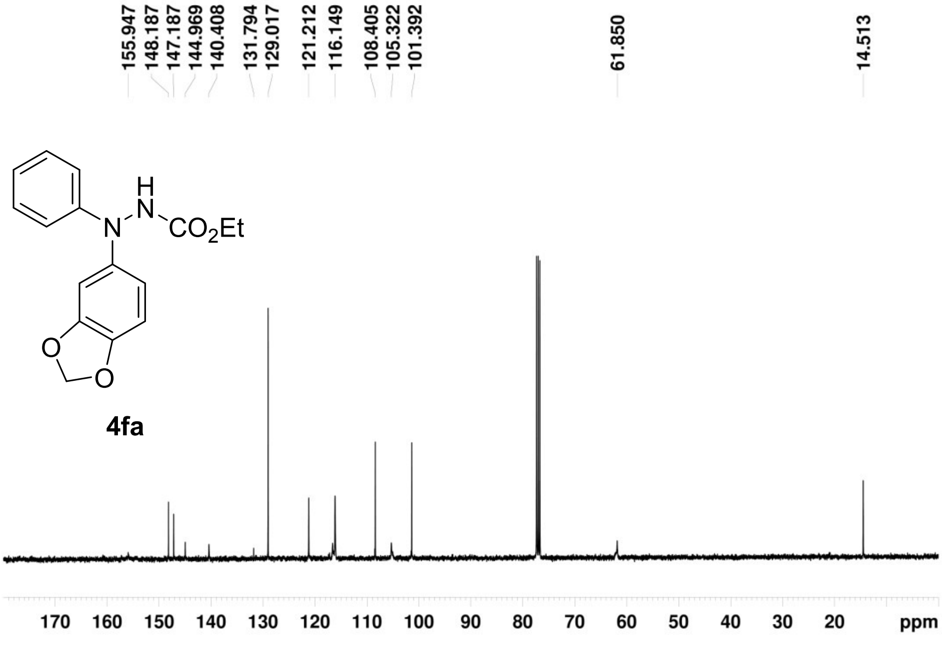


Figure S62. ^{1}H NMR spectrum of **4ga**

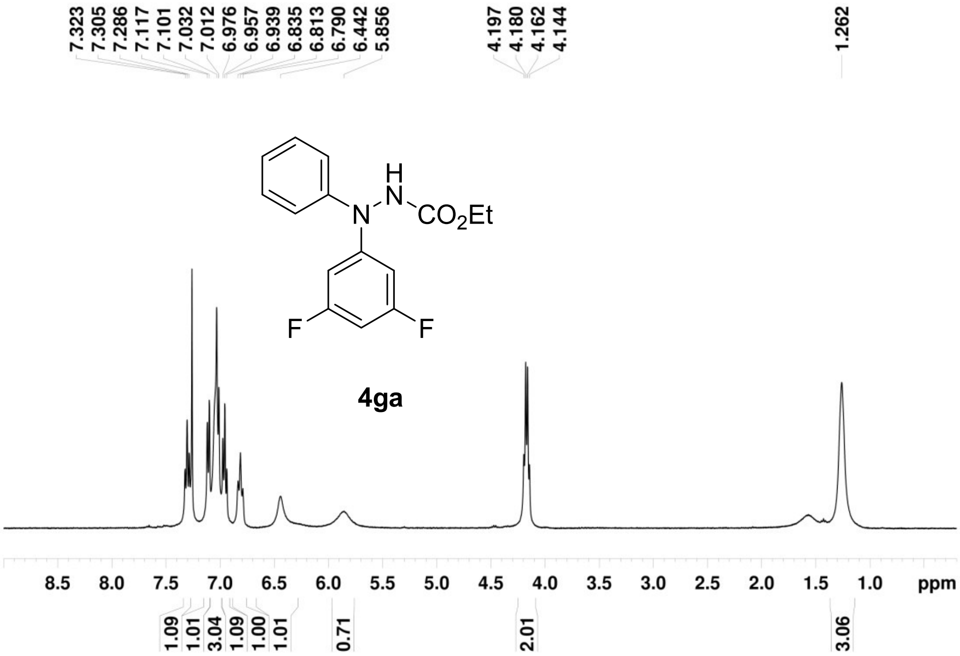


Figure S63. ^{13}C NMR spectrum of **4ga**

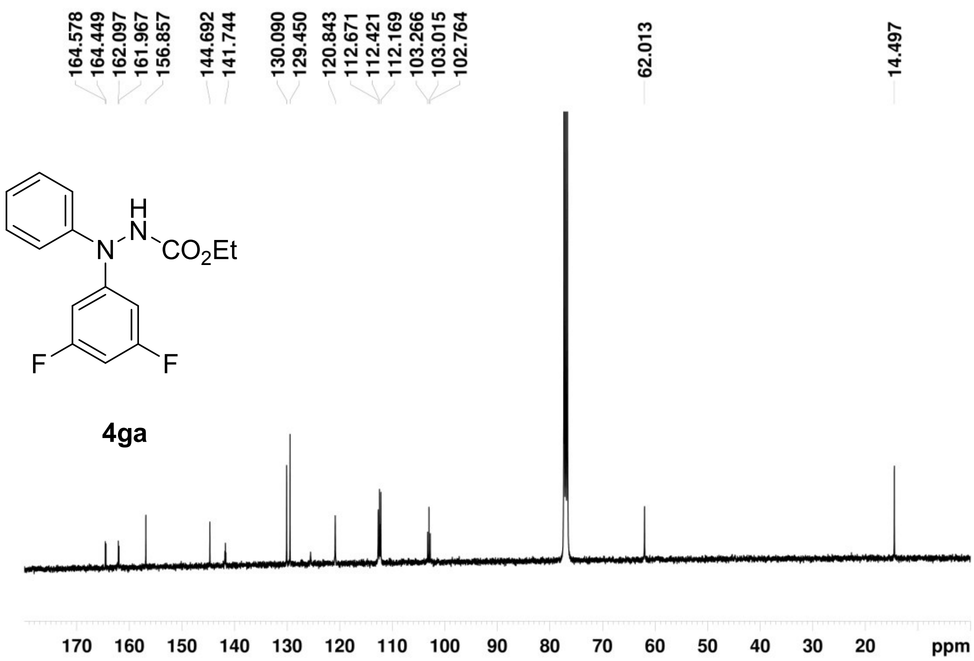


Figure S64. ^{19}F NMR spectrum of **4ga**

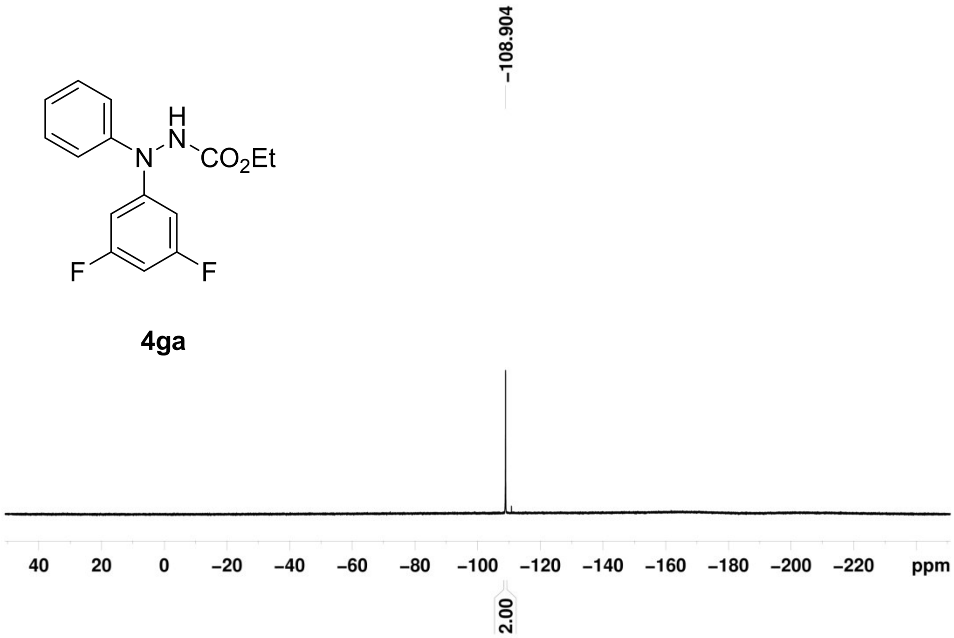


Figure S65. ^{1}H NMR spectrum of **4ab**

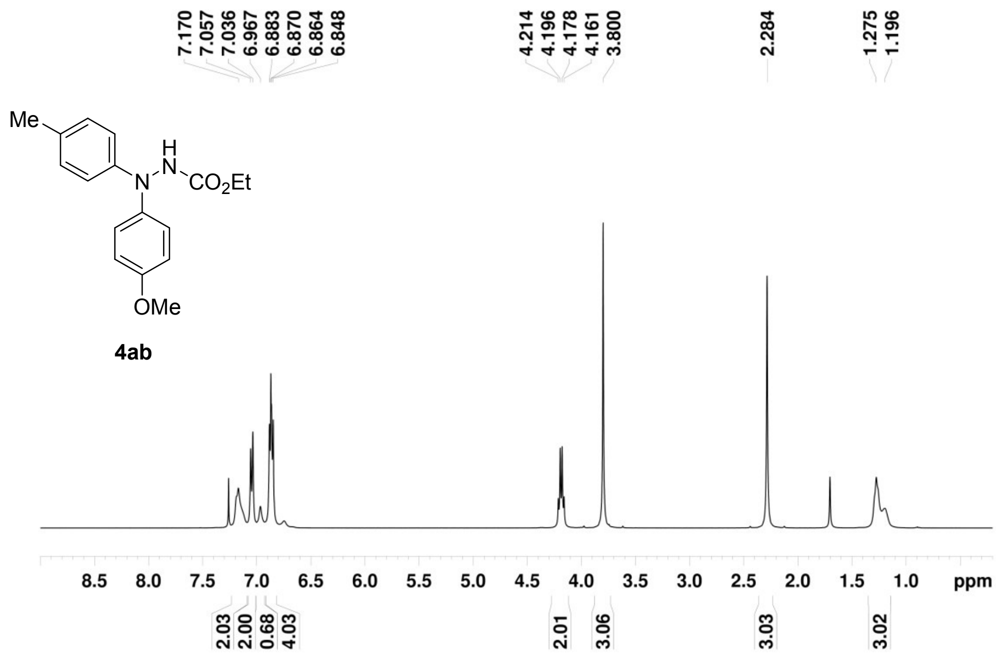


Figure S66. ^{13}C NMR spectrum of **4ab**

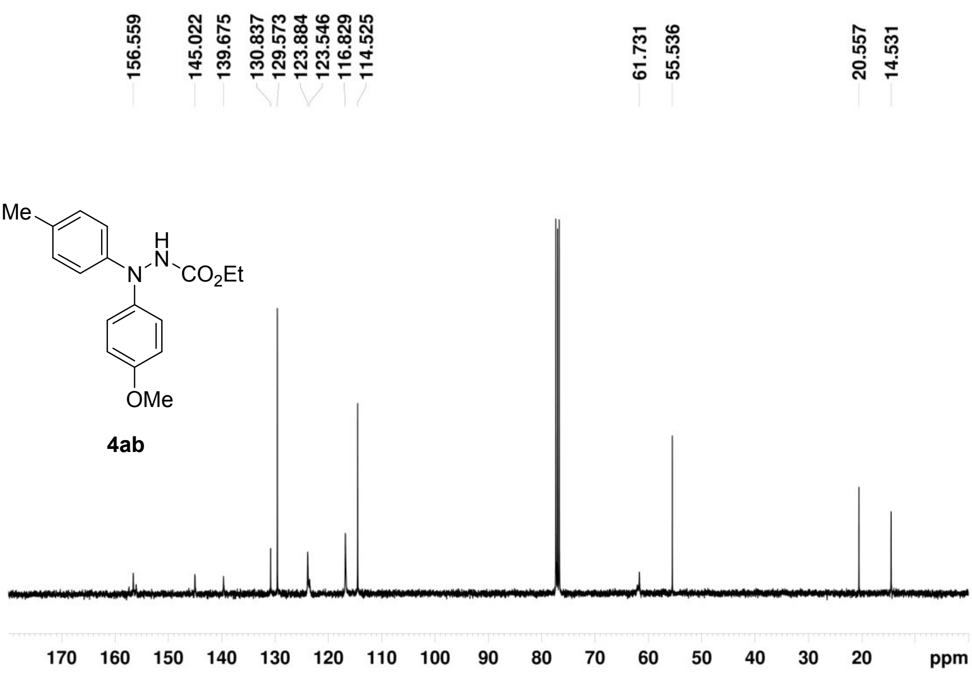


Figure S67. ^{1}H NMR spectrum of **4ac**

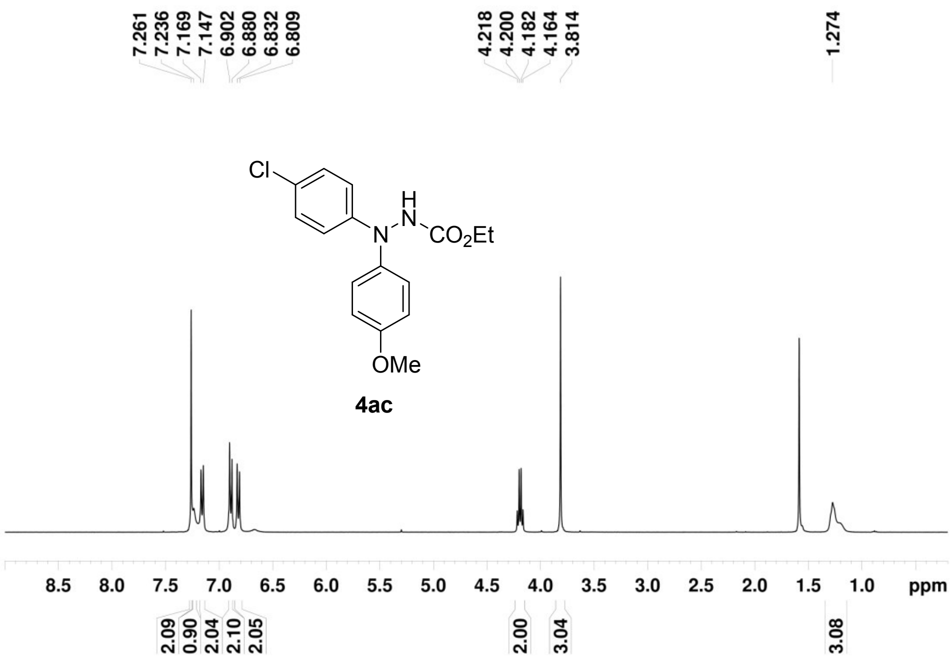


Figure S68. ^{13}C NMR spectrum of **4ac**

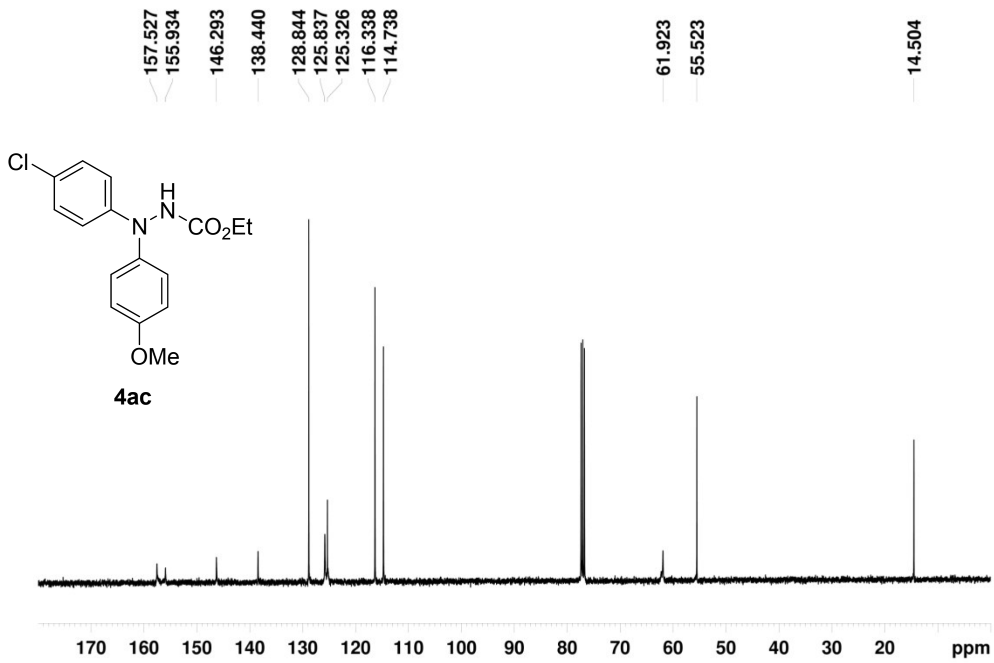


Figure S69. ^{1}H NMR spectrum of **4ad**

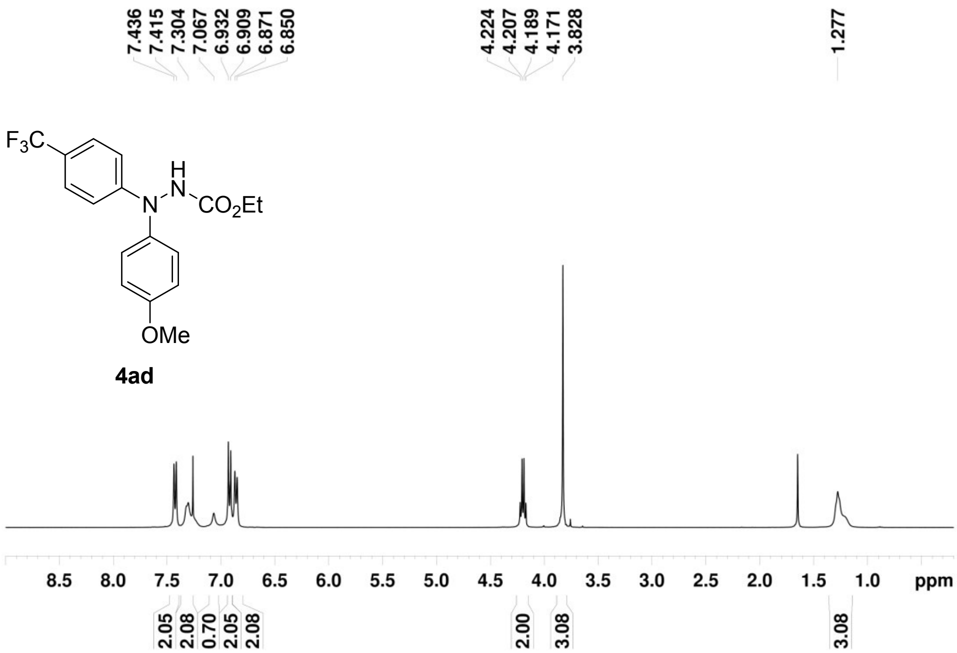


Figure S70. ^{13}C NMR spectrum of **4ad**

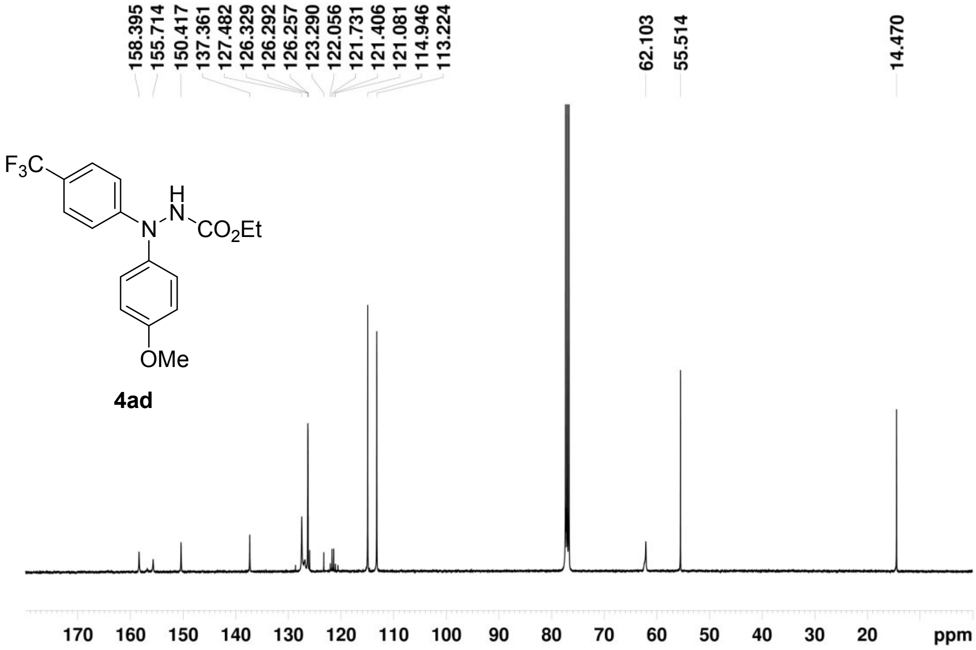


Figure S71. ^{19}F NMR spectrum of **4ad**

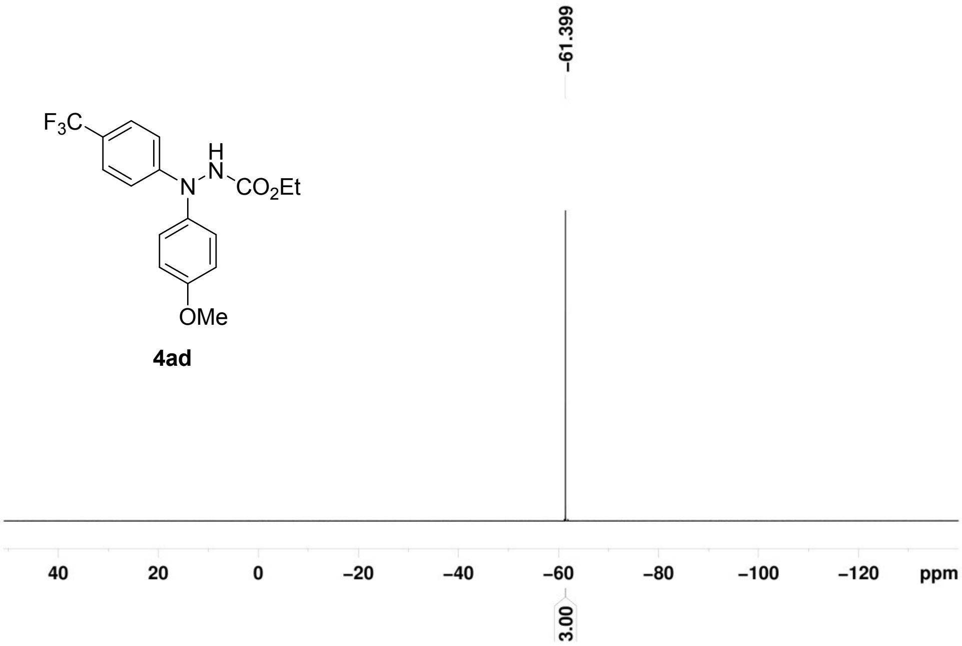


Figure S72. ^{1}H NMR spectrum of **4ae**

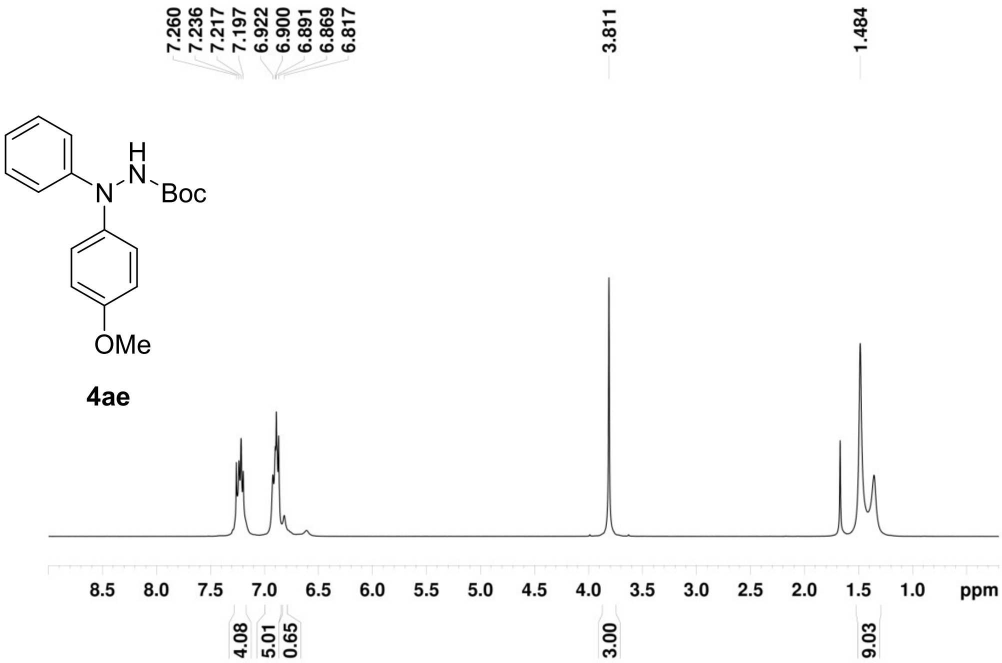


Figure S73. ^{13}C NMR spectrum of **4ae**

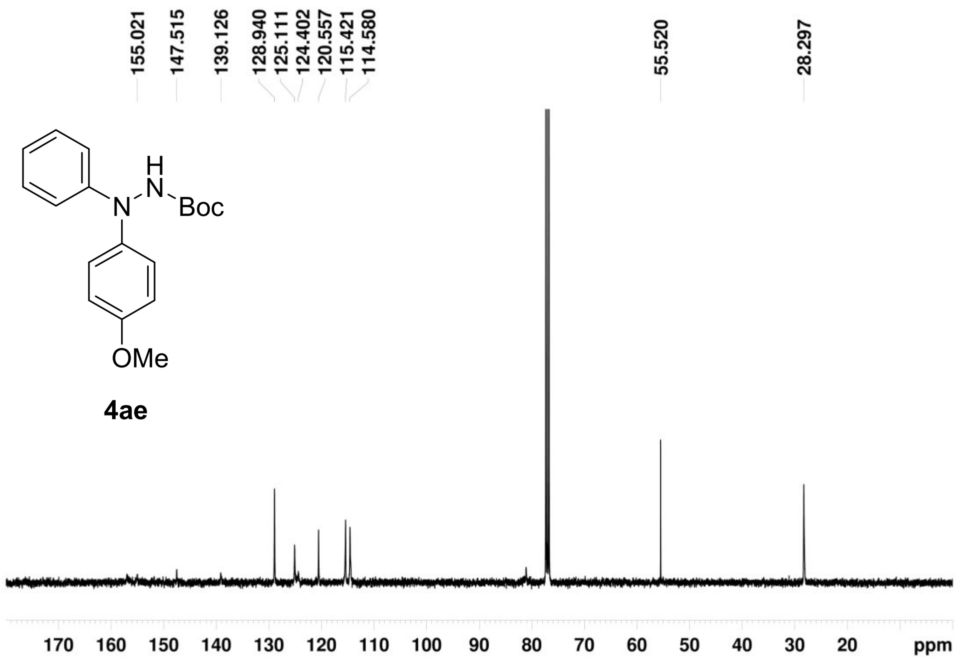


Figure S74. ^{1}H NMR spectrum of [Cp*RhCl$_2$(PPh$_3$)]

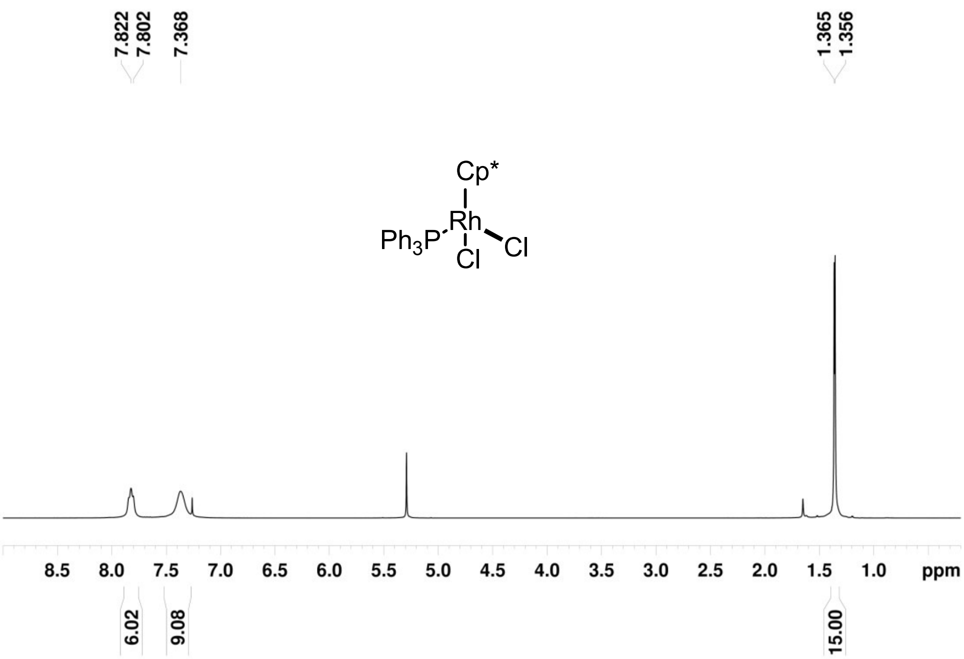


Figure S75. ^{13}C NMR spectrum of [Cp*RhCl$_2$(PPh$_3$)]

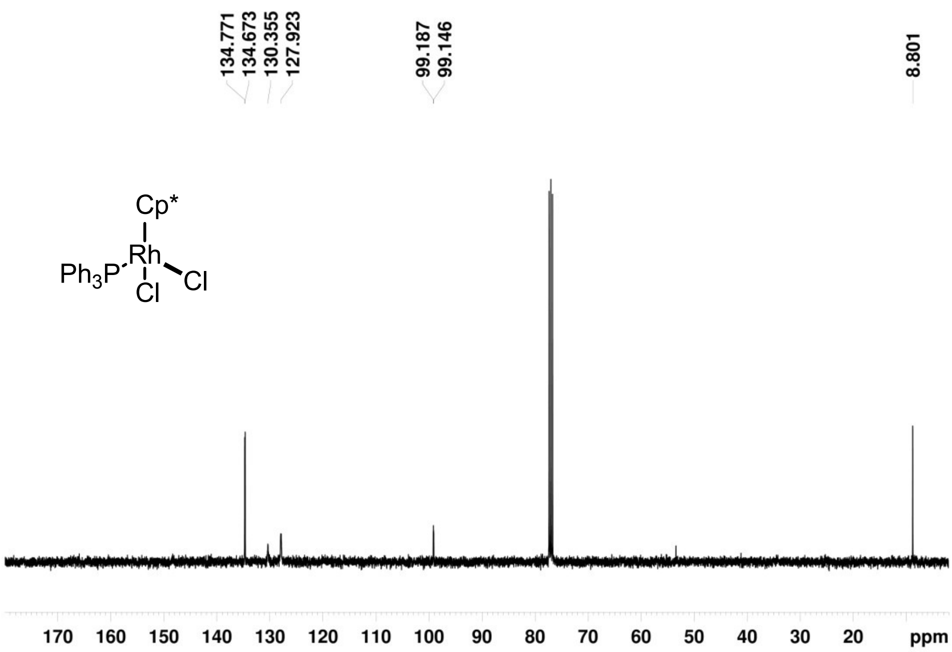


Figure S76. ^{31}P NMR spectrum of $[Cp^*RhCl_2(PPh_3)]$

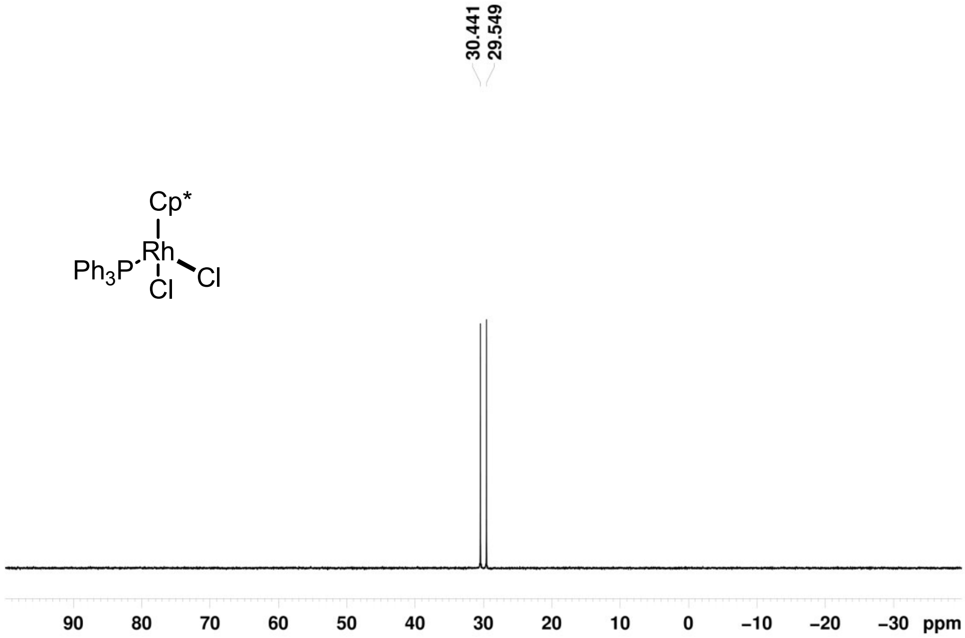


Figure S77. ^{1}H NMR spectrum of **5a**

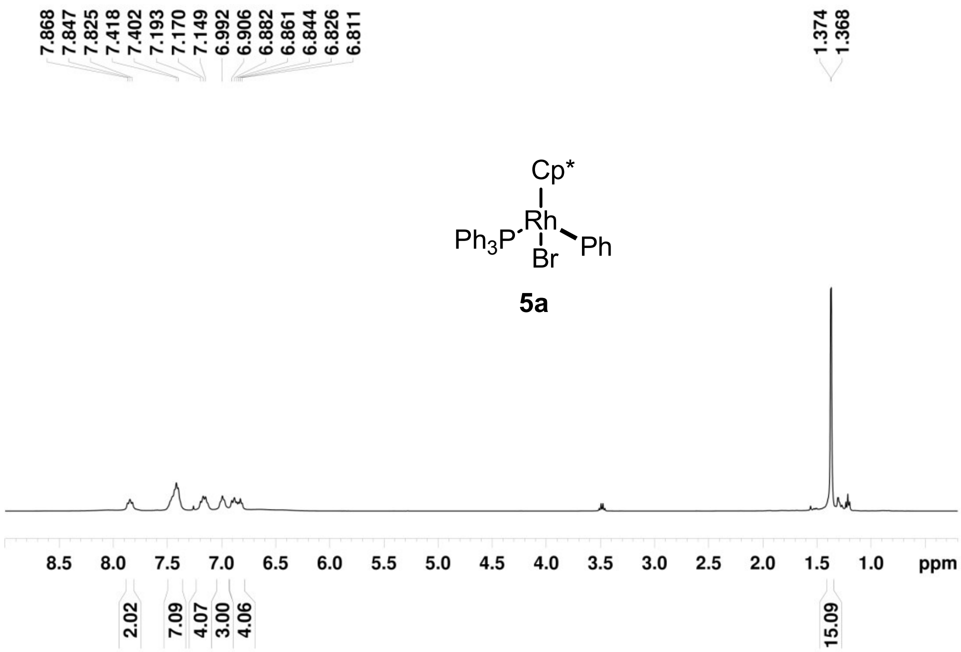


Figure S78. ^{13}C NMR spectrum of **5a**

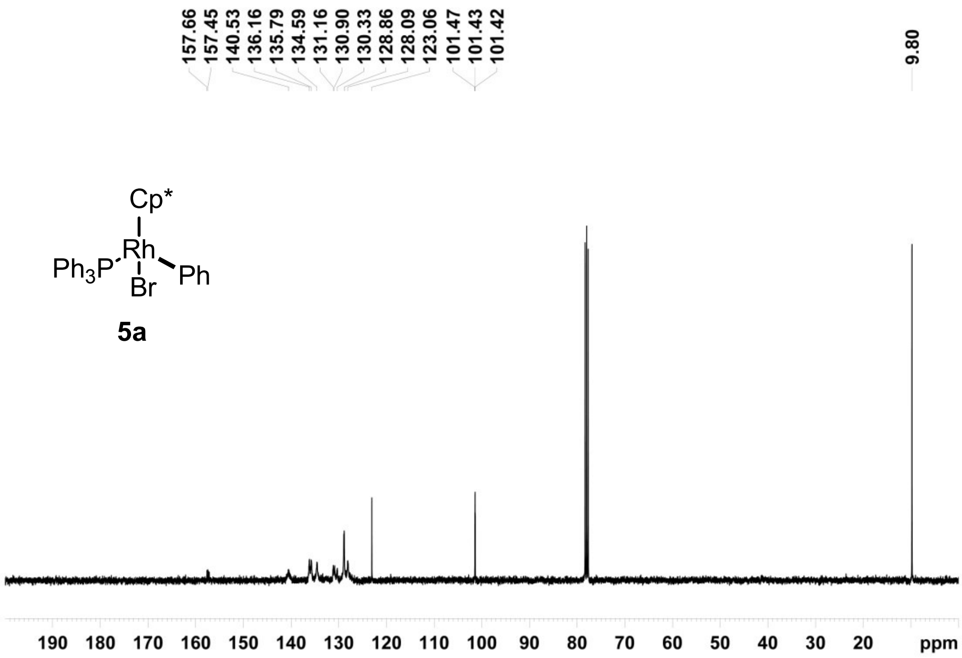


Figure S79. ^{31}P NMR spectrum of **5a**

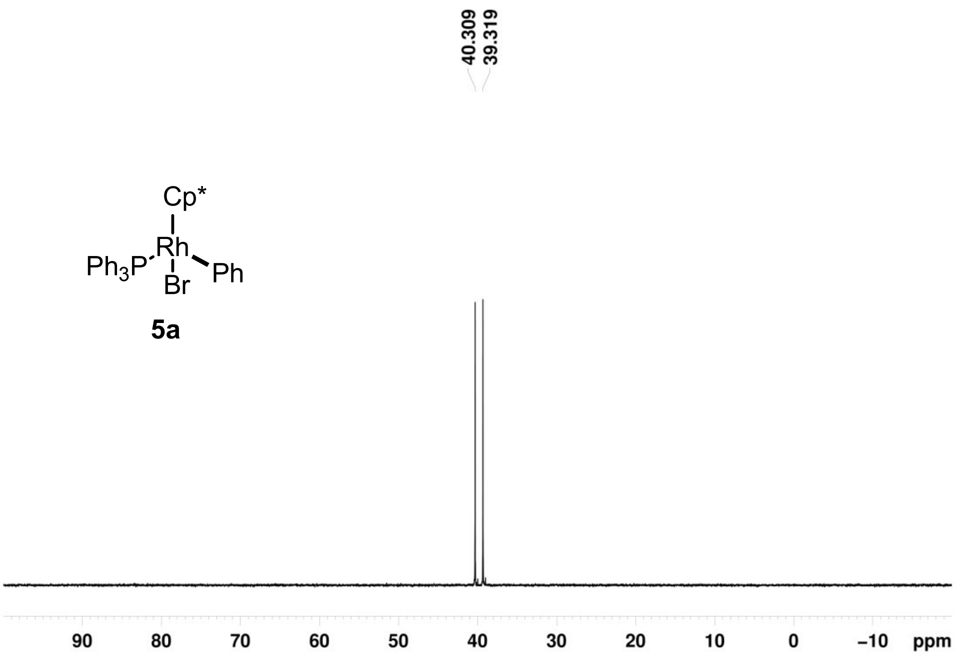


Figure S80. ^{1}H NMR spectrum of **5b**

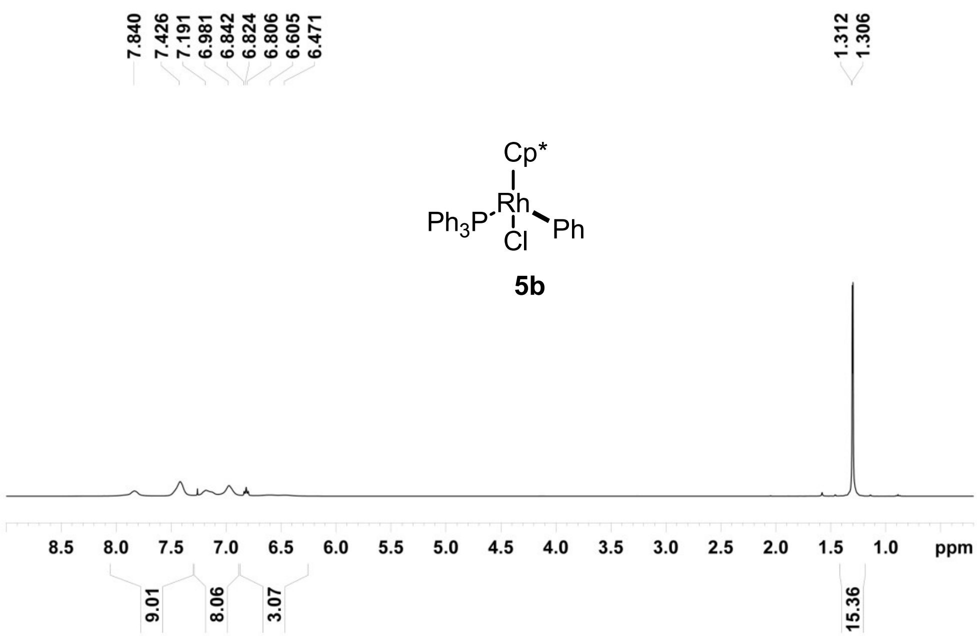


Figure S81. ^{13}C NMR spectrum of **5b**

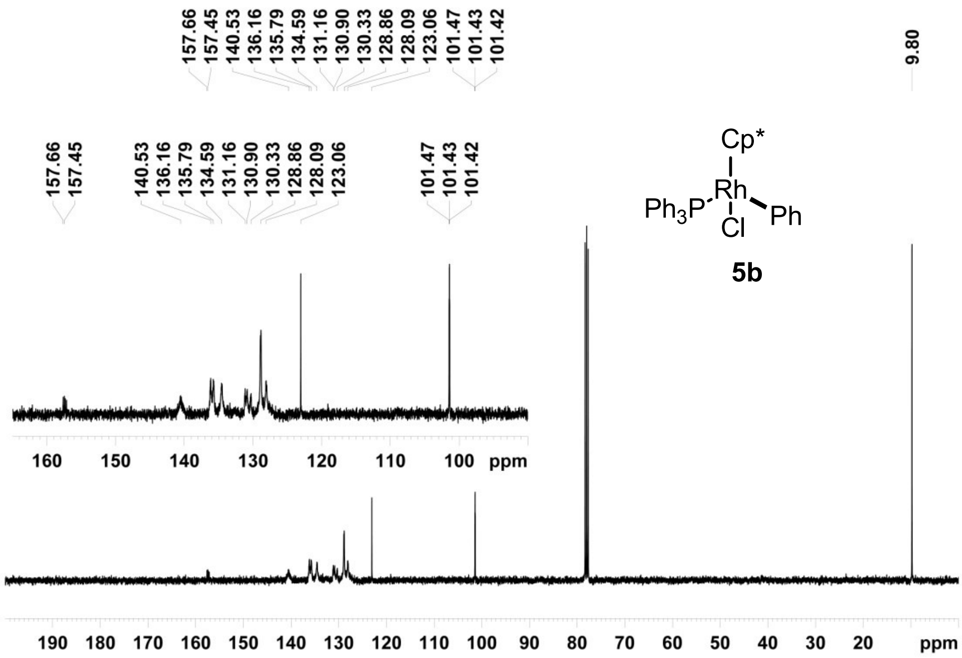
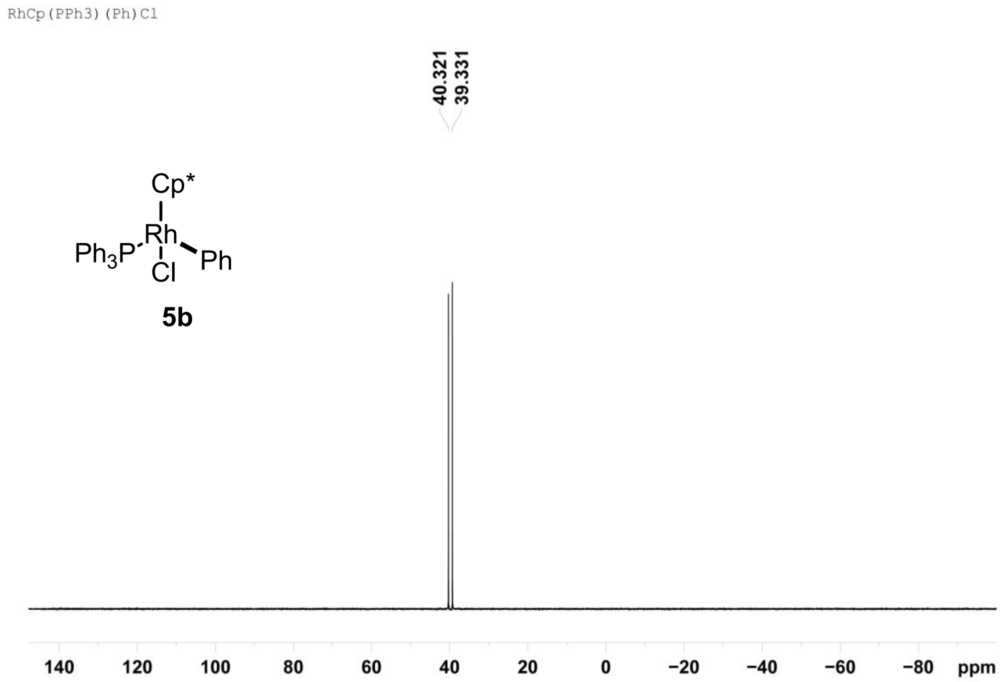


Figure S82. ^{31}P NMR spectrum of **5b**



7. References

1 W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Butterworth Heinemann [a division of Reed Educational & Professional Publishers], Oxford, 1997.

2 (a) C. White, A. Yates, P. M. Maitlis and D. M. Heinekey, *Inorganic Synthesis*, Grimes, R. N., Eds, Inorganic Synthesis, Inc., 1992, **29**, 228-232; (b) G. Giordano, R. H. Crabtree, R. M. Heintz, D. Forster and D. E. Morris, *Inorganic Synthesis,* Angelici, R. J., Eds, Inorganic Synthesis, Inc., 1989, **28**, 88-90; (c) P. M. Boyer, C. P. Roy, J. M. Bielski and J. S. Merola, *Inorg. Chim. Acta.*, 1996, **245,** 7-15.