Electronic Supplementary Material (ESI) for Chemical Science.


# Tailored Trisubstituted Chiral $Cp^{x}Rh^{III}$ Catalysts for Kinetic Resolutions of Phosphinic Amides

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## Supplementary Information

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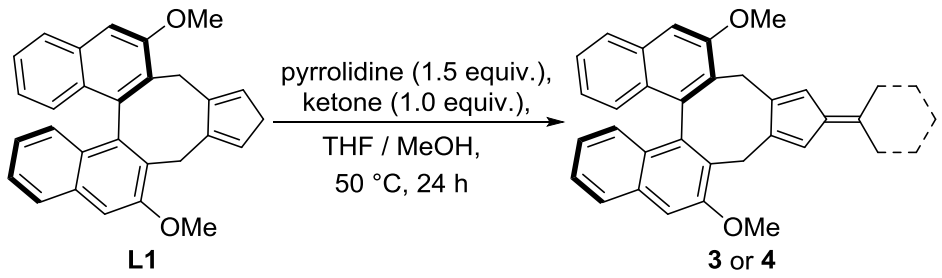
**General Methods:**

All reactions were carried out under nitrogen atmosphere in flame-dried glassware with magnetic stirring. Toluene, THF, diethyl ether and $CH_2Cl_2$ were purified by an Innovative Technology Solvent Delivery System. All other reagents were used as obtained from the suppliers. Flash Column Chromatography was performed with Fluka silica gel 60 (0.040-0.063 µm grade). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were visualized by UV-light at 254 nm and by dipping the plates in an ethanolic vanillin/sulfuric acid solution or an aqueous potassium permanganate solution followed by heating. Proton nuclear magnetic resonance ($^1$H NMR) data were acquired on a Bruker *AV400* (400 MHz), Bruker *AV500* (500 MHz), Bruker *AV600* (600 MHz) and Bruker *AV800* (800 MHz) spectrometers. Chemical shifts are reported in delta ($\delta$) units, in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm), residual methylene chloride (t, 5.32 ppm), residual dimethyl sulfoxide (quint, 2.50 ppm) or residual benzene (s, 7.16 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sept, septet; m, multiplet, br, broad. Coupling constants (*J*) are given in Hz. Proton decoupled Carbon-13 nuclear magnetic resonance ($^{13}$C NMR) data were acquired at 101 MHz on a Bruker *AV400*, at 125 MHz on a Bruker *AV500*, at 151 MHz on a Bruker *AV600* and at 201 MHz on a Bruker *AV800* spectrometers. Chemical shifts are reported in ppm relative to $CDCl_3$ (77.16 ppm), $CD_2Cl_2$ (53.84 ppm), DMSO-$D_6$ (39.52 ppm) or $C_6D_6$ (128.06 ppm). Proton decoupled Phosphorus-31 nuclear magnetic resonance ($^{31}$P NMR) data were acquired at 162 MHz on a Bruker *AV400* spectrometer or at 243 MHz on a Bruker *AV600* spectrometer. Proton decoupled Fluorine-19 nuclear magnetic resonance ($^{19}$F NMR) data were acquired at 376 MHz on a Bruker *AV400* spectrometer. Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters ($cm^{-1}$). HRMS measurements were performed by an Agilent LC-MS TOF. High resolution mass are given in *m/z*. Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter. X-ray analysis was performed by Dr. R. Scopelliti and Dr. F. FADAEI at the EPF Lausanne. The hydrogenation reactions were launched in Berghof high-pressure reactor BR100/200.

**Experimental Section**

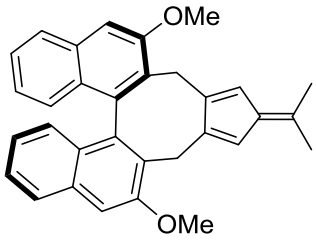
**Ligand synthesis:**

**Step 1: general procedure for synthesizing 3 & 4**




To a solution of mixture of **L1** (500 mg, 1.2 mmol) in anhydrous THF (10.0 mL) were added sequentially anhydrous MeOH (10.0 mL), corresponding ketone then freshly distilled pyrrolidine (152 µL, 1.9 mmol, 1.5 equiv.). The mixture was stirred at 50 °C for 24 hours then the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel, affording corresponding fulvene product **3** or **4** as bright yellow foam.

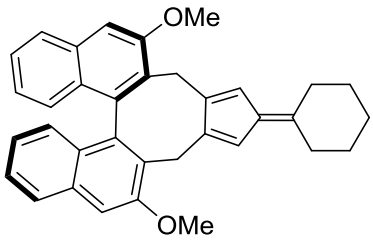
**5,16-Dimethoxy-2-(propan-2-ylidene)-4,17-dihydro-2*H*-cyclopenta[6,7]cycloocta[2,1-*a*:3,4-*a*']dinaphthalene (3):**




prepared from propan-2-one (91 µL, 1.2 mmol, 1.0 equiv.). **3** was obtained in 83% yield. **$^1$H NMR** (400 MHz, $C_6D_6$) δ = 7.75 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.30 (ddd, *J* = 7.5, 6.8, 1.3 Hz, 2H), 7.08 (s, 2H), 6.99 (ddd, *J* = 8.3, 6.7, 1.4 Hz, 2H), 6.39 (s, 2H), 4.40 (d, *J* = 14.0 Hz, 2H), 3.45 (s, 6H), 3.39 (d, *J* = 13.9 Hz, 2H), 1.74 (s, 6H) ppm; **$^{13}$C NMR** (101 MHz, $C_6D_6$) δ = 156.80, 143.23, 143.21, 141.36, 137.99, 134.24, 130.12, 128.42, 127.45, 127.21, 126.19, 124.28, 118.63, 105.75, 55.13, 29.33, 22.20 ppm; **IR (ATR)**: $\tilde{\nu}$ = 3061, 2997, 2956, 2934, 2903, 2849, 2828, 1643, 1618, 1595, 1572, 1502, 1449, 1424, 1408, 1389, 1370, 1357, 1338, 1328, 1310, 1298, 1286, 1262, 1241, 1226, 1194, 1173, 1148, 1114, 1089, 1074, 1021, 953, 907, 863, 827, 765 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{32}H_{29}O_2]^+$: 445.2162,

found: 445.2163; **$[\alpha]_D^{20}$** = +646.7 (c = 0.5, $CH_2Cl_2$); **eluent for flash column chromatography** (pentane:EtOAc, 20:1).

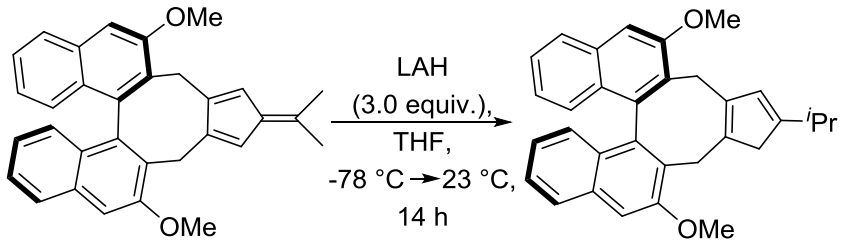
**2-Cyclohexylidene-5,16-dimethoxy-4,17-dihydro-2*H*-cyclopenta[6,7]cycloocta[2,1-*a*:3,4-*a*']dinaphthalene (4):**




prepared from cylcohexanone (128 µL, 1.2 mmol, 1.0 equiv.). **4** was obtained in 79% yield. **$^1$H NMR** (400 MHz, C6D6) δ = 7.75 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.29 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 2H) , 7.07 (s, 2H), 6.99 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 6.45 (d, *J* = 1.6 Hz, 2H), 4.42 (d, *J* = 13.9 Hz, 2H), 3.42 (s, 6H), 3.41 (d, *J* = 13.3 Hz, 2H), 2.29 (dd, *J* = 6.0 Hz, 4H), 1.48–1.34 (m, 4H), 1.34–1.23 (m, 2H) ppm; **$^{13}$C NMR** (101 MHz, $C_6D_6$) δ = 156.80, 151.46, 143.38, 138.37, 137.99, 134.24, 130.11, 128.43, 127.46, 127.20, 126.19, 124.27, 118.16, 105.72, 55.11, 33.22, 29.42, 28.77, 26.79 ppm; **IR (ATR)**: $\tilde{\nu}$ = 3060, 2999, 2928, 2853, 2831, 1634, 1619, 1595, 1572, 1502, 1448, 1424, 1408, 1389, 1360, 1345, 1328, 1311, 1297, 1287, 1262, 1239, 1225, 1194, 1175, 1168, 1148, 1114, 1088, 1074, 1020, 953, 936, 907, 864, 828, 786, 765, 744, 702 $cm^{-1}$; **HRMS (ESI)** calculated for $[C_{35}H_{33}O_2]^+$: 485.2475, found: 485.2479; **$[\alpha]_D^{20}$** = +540.4 (c = 1.0, $CH_2Cl_2$); **eluent for FCC** (pentane:EtOAc, 25:1).

**Step 2**

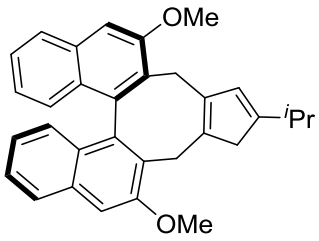
**Experimental procedure for synthesizing L6**




**3** **L6**

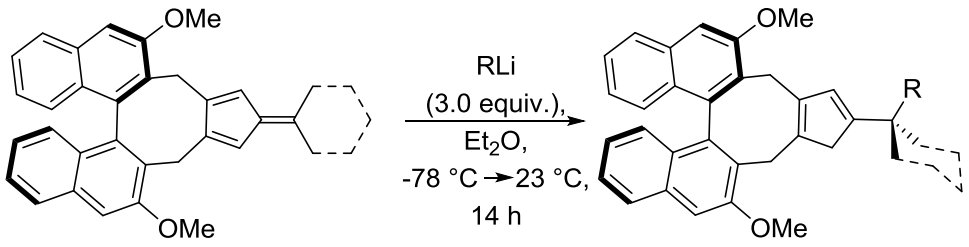
To a cold (-78 °C) solution of **3** (100.0 mg, 135 µmol) in anhydrous THF (4.0 mL) was added $LiAlH_4$ (281 µL, 0.7 mmol, 2.4 M in THF, 3.0 equiv.). The reaction mixture was allowed to warm up to 23 °C and stirred for 14 hours then quenched with aq. NaOH (25% w/w) at 0 °C. The mixture was diluted with water (10 mL) and extracted with EtOAc (3X30 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (pentane:EtOAc, 40:1) affording 89.0 mg (89% yield) of **L6** as white foam.

**2-Isopropyl-5,16-dimethoxy-4,17-dihydro-1*H*-cyclopenta[6,7]cycloocta[2,1-*a*:3,4-*a*']dinaphthalene (L6):**




**$^1$H NMR** (400 MHz, $C_6D_6$) δ = 7.76 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.30 (ddd, *J* = 8.1, 6.9 Hz, 1.3, 2H), 7.08 (d, *J* = 7.2 Hz, 2H), 7.01 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H), 6.13 (s, 1H), 4.21 (d, *J* = 14.4 Hz, 1H), 4.06 (d, *J* = 14.4 Hz, 1H), 3.40 (s, 3H), 3.39 (s, 3H), 3.16–2.97 (m, 3H), 2.82–2.70 (m, 1H), 2.56–2.44 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 6H) ppm; **$^{13}$C NMR** (101 MHz, $C_6D_6$) δ = 155.99, 155.84, 151.68, 138.08, 137.69, 137.34, 136.59, 133.76, 133.69, 130.49, 128.68, 128.66, 128.10, 127.59, 127.17, 126.03, 126.00, 124.32, 124.28, 106.08, 105.98, 55.08, 55.01, 46.69, 29.89, 26.90, 26.81, 23.22, 23.03 ppm; **IR (ATR)**: $\tilde{\nu}$ = 3057, 2999, 2956, 2934, 2868, 1620, 1595, 1572, 1502, 1449, 1421, 1409, 1391, 1376, 1339, 1327, 1293, 1259, 1234, 1218, 1197, 1162, 1149, 1111, 1073, 1021, 945, 861, 829, 763, 745 $cm^{-1}$; **HRMS (ESI)** calculated for $[C_{32}H_{31}O_2]^+$: 447.2319, found: 447.2321; **$[\alpha]_D^{20}$** = +329.0 (c = 0.5, $CH_2Cl_2$); **eluent for FCC** (pentane:EtOAc, 25:1).

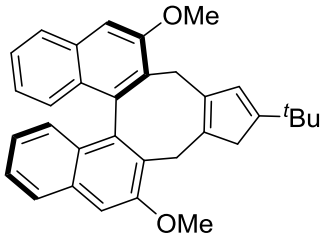
**General procedure for synthesizing L7-10**




**3** or **4** **L7-10**

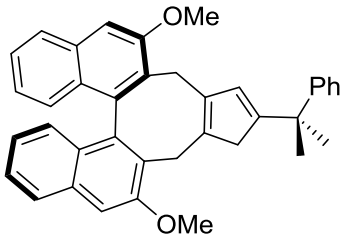
To a cold (-78 °C) solution of **3** or **4** (100.0 mg) in anhydrous $Et_2O$ (4.0 mL) was added corresponding organolithium reagent (3.0 equiv.). The reaction mixture was allowed to warm up to 23 °C slowly and stirred for 14 hours then quenched with sat. aq. $NH_4Cl$ at 0 °C. The mixture was diluted with water (10 mL) and extracted with EtOAc (3X30 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (pentane:EtOAc, 40:1) affording corresponding trisubstituted $Cp^X$ ligand **L7-10** as white foam.

**2-(*tert*-Butyl)-5,16-dimethoxy-4,17-dihydro-1*H*-cyclopenta[6,7]cycloocta[2,1-*a*:3,4-*a*']dinaphthalene (L7):**



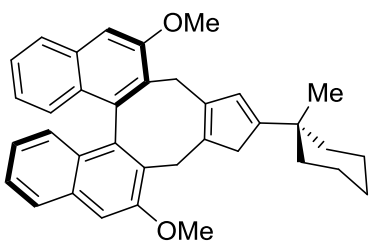

prepared from MeLi•LiBr complex solution (1.5 M in $Et_2O$) and **3**. **L7** was obtained in 77% yield. **$^1$H NMR** (400 MHz, $C_6D_6$) δ = 7.75 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.30 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.06 (d, *J* = 6.9 Hz, 2H), 7.00 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2H), 6.15 (s, 1H), 4.22 (d, *J* = 13.9 Hz, 1H), 4.07 (d, *J* = 14.3 Hz, 1H), 3.39 (s, 3H), 3.39 (s, 3H), 3.15–3.04 (m, 3H), 2.87–2.78 (m, 1H), 1.09 (s, 9H) ppm; **$^{13}$C NMR** (101 MHz, $C_6D_6$) δ = 156.00, 155.85, 154.81, 137.85, 137.72, 137.34, 136.59, 133.77, 133.69, 129.86, 128.68, 128.65, 128.12, 127.59, 127.58, 127.16, 126.03, 125.99, 124.32, 124.28, 106.15, 106.04, 55.09, 55.03, 45.46, 33.11, 31.05, 26.89, 26.82 ppm; **IR (ATR)**: $\tilde{\nu}$ = 3057, 2999, 2958, 2899, 2864, 2828, 1620, 1595, 1573, 1502, 1449, 1421, 1409, 1391, 1360, 1338, 1327, 1293, 1260, 1234, 1218, 1198, 1162, 1149, 1111, 1074, 1021, 945, 862, 829, 762, 745 $cm^{-1}$; **HRMS (ESI)** calculated for $[C_{33}H_{33}O_2]^+$: 461.2475, found: 461.2476; **$[\alpha]_D^{20}$** = +247.7 (c = 1.0, $CH_2Cl_2$); **eluent for FCC** (pentane:EtOAc, 40:1).

**5,16-Dimethoxy-2-(2-phenylpropan-2-yl)-4,17-dihydro-1*H*-cyclopenta[6,7]cycloocta[2,1-*a*:3,4-*a*']dinaphthalene (L8):**




prepared from PhLi solution (1.9 M in $Bu_2O$) and **3**. **L8** was obtained in 75% yield. **$^1$H NMR** (800 MHz, $C_6D_6$) δ = 7.87 (dd, *J* = 12.2, 8.3 Hz, 2H), 7.64 (ddd, *J* = 8.4, 6.2, 1.1 Hz, 2H), 7.42 (dddd, *J* = 8.0, 6.7, 2.8, 1.2 Hz, 2H), 7.40–7.36 (m, 2H), 7.31–7.26 (m, 3H), 7.22–7.17 (m, 1H), 7.16 (s, 1H), 7.14–7.11 (m, 2H), 6.40 (s, 1H), 4.36 (d, *J* = 14.6 Hz, 1H), 4.05 (d, *J* = 14.6 Hz, 1H), 3.57 (s, 3H), 3.48 (s, 3H), 3.20 (dd, *J* = 14.6, 3.5 Hz, 1H), 3.15 (dd, *J* = 14.6, 3.8 Hz, 1H), 3.08 (ddd, *J* = 23.1, 3.2, 1.1 Hz, 1H), 2.87 (dd, *J* = 23.1, 3.1 Hz, 1H), 1.58 (s, 3H), 1.55 (s, 3H) ppm; **$^{13}$C NMR** (201 MHz, $C_6D_6$) δ = 156.00, 155.82, 153.68, 150.41, 137.82, 137.76, 137.46, 137.24, 133.77, 133.68, 131.76, 128.65, 128.57, 128.12, 127.58, 127.54, 127.17, 127.16, 126.56, 126.04, 125.97, 125.79, 124.31, 124.28, 106.20, 106.14, 55.19, 55.00, 46.11, 40.84, 30.20, 30.04, 26.84, 26.81 ppm; **IR (ATR):** $\tilde{\nu}$ = 3057, 2999, 2962, 2935, 2829, 1620, 1596, 1573, 1494, 1449, 1421, 1410, 1391, 1376, 1361, 1338, 1327, 1293, 1259, 1234, 1219, 1198, 1162, 1150, 1111, 1074, 1021, 946, 880, 862, 830, 812, 785, 763, 746, 700 $cm^{-1}$; **HRMS (ESI)** calculated for $[C_{38}H_{35}O_2]^+$: 523.2632, found: 523.2623; **$[\alpha]_D^{20}$** = +266.7 (c = 1.0, $CH_2Cl_2$); **eluent for FCC** (pentane:EtOAc, 25:1).

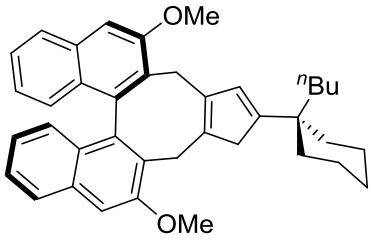
**5,16-Dimethoxy-2-(1-methylcyclohexyl)-4,17-dihydro-1*H*-cyclopenta[6,7]cycloocta[2,1-*a*:3,4-*a*']dinaphthalene (L9):**




prepared from MeLi•LiBr complex solution (1.5 M in $Et_2O$) and **4**. **L9** was obtained in 99% yield. **$^1$H NMR** (800 MHz, $C_6D_6$) δ = 7.74 (ddd, *J* = 8.2, 3.8, 1.2 Hz, 2H), 7.52 (ddd, *J* = 8.1, 6.5, 1.1 Hz, 2H),

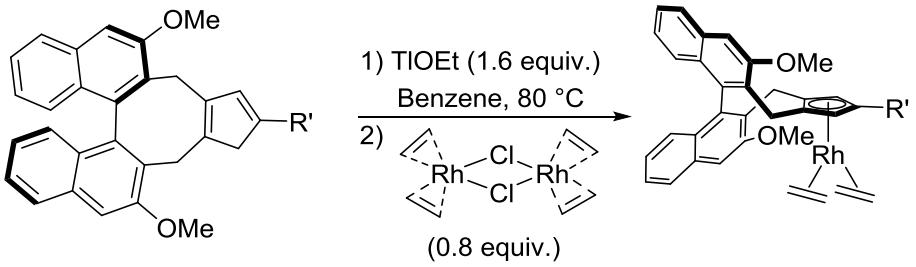
7.29 (ddt, *J* = 8.0, 6.8, 0.9 Hz, 2H), 7.06 (d, *J* = 3.1 Hz, 2H), 7.00 (dddd, *J* = 8.2, 6.8, 2.4, 1.3 Hz, 2H), 6.17 (s, 1H), 4.22 (d, *J* = 14.2 Hz, 1H), 4.09 (d, *J* = 14.5 Hz, 1H), 3.42 (s, 3H), 3.40 (s, 3H), 3.13 (dd, *J* = 14.5, 3.5 Hz, 1H), 3.11–3.04 (m, 2H), 2.85 (dd, *J* = 23.3, 3.7 Hz, 1H), 1.65 (ddd, *J* = 12.9, 7.7, 3.8 Hz, 2H), 1.51–1.27 (m, 8H), 1.04 (s, 3H) ppm; **$^{13}$C NMR** (201 MHz, $C_6D_6$) δ = 156.00, 155.87, 137.91, 137.68, 137.34, 136.42, 133.76, 133.69, 130.90, 128.70, 128.35, 128.12, 128.12, 127.58, 127.57, 127.17, 126.01, 125.98, 124.32, 124.27, 106.21, 106.12, 55.11, 55.07, 45.16, 38.46, 38.33, 36.54, 26.93, 26.86, 26.83, 23.07, 22.95 ppm; **IR (ATR):** $\tilde{\nu}$ = 3058, 2998, 2924, 2849, 1620, 1596, 1573, 1503, 1449, 1421, 1410, 1392, 1373, 1339, 1327, 1293, 1260, 1234, 1219, 1197, 1163, 1149, 1111, 1074, 1021, 945, 879, 861, 829, 763, 745 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{36}H_{37}O_2]^+$: 501.2788, found: 501.2788; **$[\alpha]_D^{20}$** = +299.3 (c = 0.5, $CH_2Cl_2$); **eluent for FCC** (pentane:EtOAc, 40:1).

**2-(1-Butylcyclohexyl)-5,16-dimethoxy-4,17-dihydro-1*H*-cyclopenta[6,7]cycloocta[2,1-*a*:3,4-*a*']dinaphthalene (L10):**



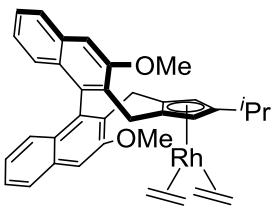

prepared from *n*-BuLi solution (2.5 M in hexanes) and **4**. **L10** was obtained in 82% yield. **$^1$H NMR** (400 MHz, $C_6D_6$) δ = 7.73 (dd, *J* = 8.3, 2.9 Hz, 2H), 7.51 (dd, *J* = 8.5, 4.4 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.06 (s, 2H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.14 (s, 1H), 4.18 (d, *J* = 13.9 Hz, 1H), 4.05 (d, *J* = 14.2 Hz, 1H), 3.45 (s, 3H), 3.44 (s, 3H), 3.14–2.95 (m, 3H), 2.83 (dd, *J* = 23.2, 3.5 Hz, 1H), 1.72 (t, *J* = 15.0 Hz, 2H), 1.59–1.28 (m, 10H), 1.27–1.04 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $C_6D_6$) δ = 156.04, 155.90, 151.19, 137.87, 137.63, 137.32, 136.64, 133.75, 133.69, 132.92, 128.83, 128.79, 128.14, 127.58, 127.18, 125.97, 125.95, 124.30, 124.25, 106.22, 55.19, 55.09, 45.41, 42.31, 39.99, 36.79, 36.66, 27.12, 26.96, 26.88, 26.42, 23.83, 22.97, 22.81, 14.44 ppm; **IR (ATR):** $\tilde{\nu}$ = 3057, 2999, 2956, 2934, 2868, 1620, 1595, 1572, 1502, 1449, 1421, 1409, 1391, 1376, 1339, 1327, 1293, 1259, 1234, 1218, 1197, 1162, 1149, 1111, 1073, 1021, 945, 861, 829, 763, 745 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{39}H_{43}O_2]^+$: 543.3258, found: 543.3258; **$[\alpha]_D^{20}$** = +219.7 (c = 0.5, $CH_2Cl_2$); **eluent for FCC** (pentane:EtOAc, 100:1).

**General procedure for synthesizing Rh(I)-complex:**




To a solution of the chiral $Cp^X$ ligand in degassed benzene (0.5 M) at 23 °C was added a solution of TlOEt (1.6 equiv.) in benzene (0.5 M). The mixture was stirred for 16 hours at 80 °C under protection from light. After cooling down to 23 °C, $[\{Rh(C_2H_4)_2Cl\}_2]$ (0.8 equiv.) was added into the reaction mixture and stirred for further 5 hours. The mixture was filtered through a pad of celite. The yellow filtrate was concentrated under reduced pressure. After a flash chromatography column with neutral aluminium oxide, the desired complex **RhX** was afforded as yellow foam.

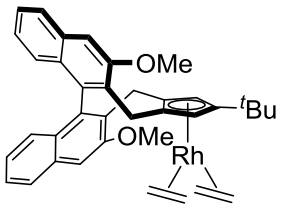
**Complex Rh6:**




obtained in 69% yield. **$^1$H NMR** (400 MHz, $C_6D_6$) δ = 7.77 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.29–7.23 (m, 2H), 7.20 (s, 1H), 6.98 (s, 1H), 6.97–6.89 (m, 2H), 5.28 (d, *J* = 2.0 Hz, 1H), 4.37 (d, *J* = 2.0 Hz, 1H), 4.25 (d, *J* = 14.2 Hz, 1H), 3.68 (s, 3H), 3.62 (d, *J* = 13.6 Hz, 1H), 3.42 (s, 3H), 3.08 (d, *J* = 14.4 Hz, 1H), 2.82–2.73 (m, 2H), 2.44 (d, *J* = 13.6 Hz, 1H), 2.15 (hept, *J* = 6.9 Hz, 1H), 1.75–1.67 (m, 2H), 1.44–1.35 (m, 2H), 1.12 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.97–0.91 (m, 2H) ppm; **$^{13}$C NMR** (125 MHz, $C_6D_6$) δ =

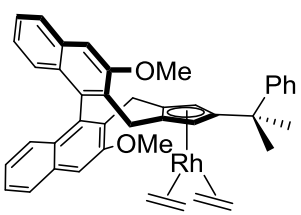
156.77, 155.86, 137.64, 137.19, 133.91, 133.86, 129.56, 129.26, 127.45, 127.30, 127.22, 127.13, 126.20, 126.15, 124.36, 124.25, 111.78 (d, $J_{Rh-C}$ = 4.2 Hz), 106.17, 105.51, 104.38 (d, $J_{Rh-C}$ = 4.7 Hz), 95.96 (d, $J_{Rh-C}$ = 4.0 Hz), 88.92 (d, $J_{Rh-C}$ = 4.0 Hz), 86.73 (d, $J_{Rh-C}$ = 3.9 Hz), 55.19, 55.13, 43.80 (d, $J_{Rh-C}$ = 13.8 Hz), 36.55 (d, $J_{Rh-C}$ = 13.2 Hz), 26.67, 26.10, 24.61, 23.86, 22.30 ppm; **IR (ATR):** $\tilde{\nu}$ = 3053, 2956, 2923, 2852, 1618, 1595, 1572, 1501, 1449, 1421, 1389, 1362, 1328, 1295, 1262, 1237, 1223, 1196, 1182, 1163, 1149, 1112, 1075, 1021, 946, 862, 829, 802, 768, 744 $cm^{-1}$; **HRMS (ESI)** calculated for $[M-2(C_2H_4)+H]^+$: 549.1295, found: 549.1301; **$[\alpha]_D^{20}$** = -185.0 (c = 0.1, $CH_2Cl_2$); **eluent for FCC** (pentane:$CH_2Cl_2$, 40:1).

**Complex Rh7:**



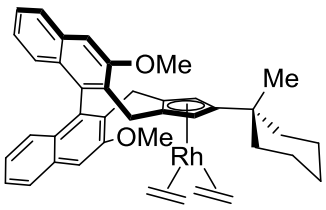

obtained in 82% yield. **$^1$H NMR** (800 MHz, $C_6D_6$) δ = 7.76 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.68 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.25 (dddd, *J* = 8.0, 6.7, 3.1, 1.2 Hz, 2H), 7.18 (s, 1H), 6.97 (s, 1H), 6.96–6.90 (m, 2H), 5.11 (d, *J* = 2.3 Hz, 1H), 4.46 (d, *J* = 2.3 Hz, 1H), 4.23 (d, *J* = 14.5 Hz, 1H), 3.67 (s, 3H), 3.59 (d, *J* = 13.7 Hz, 1H), 3.45 (s, 3H), 3.07 (d, *J* = 14.5 Hz, 1H), 2.85 (ddd, *J* = 11.8, 9.0, 2.0 Hz, 2H), 2.55 (d, *J* = 13.6 Hz, 1H), 2.05 (ddd, *J* = 11.5, 8.9, 2.1 Hz, 2H), 1.50–1.44 (m, 2H), 1.14 (s, 9H), 0.69 (dd, *J* = 12.4, 8.6 Hz, 2H) ppm; **$^{13}$C NMR** (201 MHz, $C_6D_6$) δ = 156.58, 155.85, 137.82, 137.09, 133.91, 133.89, 129.54, 129.37, 127.43, 127.32, 127.21, 127.17, 126.21, 126.09, 124.36, 124.25, 117.38 (d, $J_{Rh-C}$ = 4.7 Hz), 106.37, 105.54, 103.86 (d, $J_{Rh-C}$ = 4.6 Hz), 96.55 (d, $J_{Rh-C}$ = 4.1 Hz), 86.83 (d, $J_{Rh-C}$ = 3.5 Hz), 86.80 (d, $J_{Rh-C}$ = 4.2 Hz), 55.23, 55.06, 42.31 (d, $J_{Rh-C}$ = 13.7 Hz), 36.00 (d, $J_{Rh-C}$ = 12.8 Hz), 31.95, 29.56, 25.98, 24.17 ppm; **IR (ATR):** $\tilde{\nu}$ = 3056, 2989, 2955, 2924, 2869, 2827, 1618, 1595, 1573, 1501, 1450, 1421, 1389, 1361, 1338, 1327, 1294, 1261, 1224, 1196, 1162, 1149, 1112, 1075, 1022, 947, 904, 880, 860, 827, 802, 787, 767, 744 $cm^{-1}$; **HRMS (ESI)** calculated for $[M-2(C_2H_4)+H]^+$: 563.1452, found: 563.1451; **$[\alpha]_D^{20}$** = -254.4 (c = 0.5, $CH_2Cl_2$); **eluent for FCC** (pentane:$CH_2Cl_2$, 40:1).

**Complex Rh8:**




obtained in 67% yield. **$^{1}$H NMR** (600 MHz, $C_6D_6$) δ = 7.74 (dd, *J* = 13.0, 8.2 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.33–7.30 (m, 2H), 7.27 (tdd, *J* = 8.2, 5.5, 2.0 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 3H), 7.08 (s, 1H), 7.06–7.02 (m, 1H), 6.94 (ddt, *J* = 8.3, 6.8, 1.4 Hz, 2H), 4.97 (d, *J* = 2.3 Hz, 1H), 4.38 (d, *J* = 2.2 Hz, 1H), 4.09 (d, *J* = 14.8 Hz, 1H), 3.62 (s, 3H), 3.55 (d, *J* = 13.4 Hz, 1H), 3.48 (s, 3H), 2.94–2.85 (m, 3H), 2.67 (d, *J* = 13.4 Hz, 1H), 2.15 (dd, *J* = 11.8, 8.6 Hz, 2H), 1.69 (s, 3H), 1.48–1.41 (m, 2H), 1.39 (s, 3H), 0.81 (dd, *J* = 12.3, 8.6 Hz, 2H) ppm; **$^{13}$C NMR** (151 MHz, $C_6D_6$) δ = 156.43, 155.89, 151.28, 138.03, 136.92, 133.97, 133.88, 129.51, 129.28, 128.32, 128.10, 127.49, 127.39, 127.25, 127.20, 126.57, 126.26, 126.13, 125.81, 116.33 (d, $J_{Rh-C}$ = 4.6 Hz), 106.14, 105.50, 104.25 (d, $J_{Rh-C}$ = 4.5 Hz), 97.85 (d, $J_{Rh-C}$ = 3.7 Hz), 88.55 (d, $J_{Rh-C}$ = 3.6 Hz), 87.36 (d, $J_{Rh-C}$ = 3.6 Hz), 55.28, 54.93, 42.58 (d, $J_{Rh-C}$ = 13.7 Hz), 38.77, 36.70 (d, $J_{Rh-C}$ = 12.9 Hz), 32.20, 29.66, 25.75, 24.50 ppm; **IR (ATR):** $\tilde{\nu}$ = 3056, 2988, 2963, 2934, 2897, 2827, 1991, 1958, 1618, 1596, 1573, 1493, 1450, 1422, 1389, 1381, 1361, 1338, 1327, 1295, 1261, 1238, 1224, 1198, 1164, 1149, 1113, 1076, 1029, 1023, 947, 904, 862, 829, 803, 764, 746 $cm^{-1}$; **HRMS (ESI)** calculated for $[M-2(C_2H_4)+H]^+$: 625.1608, found: 625.1606; **$[\alpha]_D^{20}$** = -277.6 (c = 1.0, $CH_2Cl_2$); **eluent for FCC** (pentane:$CH_2Cl_2$, 10:1).

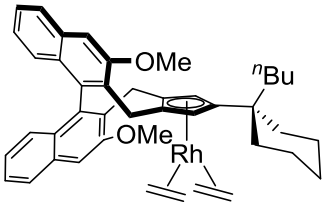
**Complex Rh9:**




obtained in 62% yield. **$^{1}$H NMR** (800 MHz, $C_6D_6$) δ = 7.76 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.35 (dd, *J* = 14.2, 8.4 Hz, 2H), 7.26 (tdd, *J* = 8.1, 3.5, 1.2 Hz, 2H), 7.19 (s, 1H), 6.99 (s, 1H), 6.94 (dtd, *J* = 8.0, 6.6, 1.3 Hz, 2H), 5.09 (d, *J* = 2.3 Hz, 1H), 4.47 (d, *J* = 2.3 Hz, 1H), 4.24 (d, *J* = 14.6 Hz, 1H), 3.67 (s, 3H), 3.60 (d, *J* = 13.6 Hz, 1H), 3.47 (s, 3H), 3.07 (d, *J* = 14.5 Hz, 1H), 2.92–2.84 (m, 2H), 2.60 (d, *J* = 13.6 Hz, 1H), 2.09 (t, *J* = 10.7 Hz, 2H), 1.61–1.44 (m, 9H), 1.44–1.33 (m, 3H), 1.15 (s, 3H), 0.71 (dd, *J* = 12.4, 8.6 Hz, 2H) ppm; **$^{13}$C NMR** (201 MHz, $C_6D_6$) δ = 156.55, 155.85, 137.84, 137.06, 133.91, 133.90, 129.56, 129.43, 128.36, 128.13, 127.44, 127.33, 127.22, 127.18, 126.20, 126.08, 124.35, 124.25, 119.27 (d, $J_{Rh-C}$ = 4.2 Hz), 106.35, 105.54, 103.62 (d, $J_{Rh-C}$ = 4.5 Hz), 96.49 (d, $J_{Rh-C}$ = 3.6 Hz), 86.85 (d, $J_{Rh-C}$ = 3.6 Hz), 86.47 (d, $J_{Rh-C}$ = 3.6 Hz), 55.27, 55.06, 42.36 (d, $J_{Rh-C}$ = 13.6 Hz), 39.81, 39.57, 36.00 (d, $J_{Rh-C}$ = 13.0 Hz), 33.82, 26.69, 25.98, 25.49,

24.27, 22.95, 22.78 ppm; **IR (ATR):** $\tilde{\nu}$ = 3057, 2987, 2924, 2852, 2278, 1991, 1960, 1618, 1596, 1573, 1501, 1449, 1422, 1390, 1374, 1361, 1328, 1295, 1260, 1238, 1225, 1197, 1183, 1164, 1149, 1113, 1076, 1022, 948, 925, 904, 862, 829, 812, 767, 746, 718 $cm^{-1}$; **HRMS (ESI)** calculated for $[M\text{-}2(C_2H_4)+H]^+$: 603.1765, found: 603.1756; $\mathbf{[\alpha]_D^{20}}$ = -186.2 (c = 1.0, $CH_2Cl_2$); **eluent for FCC** (pentane:$CH_2Cl_2$, 40:1).

**Complex Rh10:**

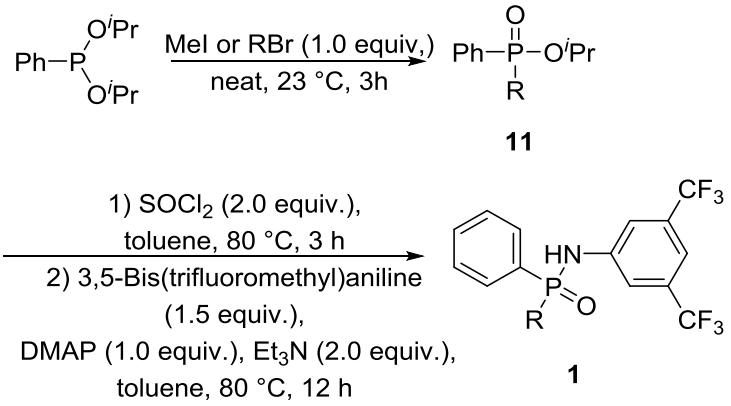



obtained in 72% yield. **$^1$H NMR** (800 MHz, $C_6D_6$) δ = 7.75 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.26 (ddd, *J* = 8.0, 6.7, 1.2 Hz, 2H), 7.18 (s, 1H), 7.08 (s, 1H), 6.93 (dtd, *J* = 8.2, 6.8, 1.2 Hz, 2H), 4.98 (d, *J* = 2.2 Hz, 1H), 4.43 (d, *J* = 2.2 Hz, 1H), 4.18 (d, *J* = 14.7 Hz, 1H), 3.66 (s, 3H), 3.58 (s, 3H), 3.56 (d, *J* = 13.4 Hz, 1H), 2.97 (d, *J* = 14.6 Hz, 1H), 2.89 (dd, *J* = 12.3, 9.0 Hz, 2H), 2.58 (d, *J* = 13.5 Hz, 1H), 2.14 (t, *J* = 10.6 Hz, 2H), 1.90–1.78 (m, 2H), 1.66–1.60 (m, 1H), 1.59–1.45 (m, 6H), 1.43–1.34 (m, 3H), 1.25–1.11 (m, 5H), 1.10–1.02 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.73 (dd, *J* = 12.4, 8.6 Hz, 2H) ppm; **$^{13}$C NMR** (201 MHz, $C_6D_6$) δ = 156.56, 155.86, 137.88, 137.00, 133.93, 133.88, 129.50, 128.35, 128.11, 127.48, 127.34, 127.21, 127.19, 126.20, 126.10, 124.35, 124.24, 117.96 (d, $J_{Rh\text{-}C}$ = 4.3 Hz), 105.86, 105.48, 103.19 (d, $J_{Rh\text{-}C}$ = 4.7 Hz), 96.27 (d, $J_{Rh\text{-}C}$ = 3.8 Hz), 87.39 (d, $J_{Rh\text{-}C}$ = 3.6 Hz), 86.54 (d, $J_{Rh\text{-}C}$ = 3.5 Hz), 55.21, 55.02, 42.86 (d, $J_{Rh\text{-}C}$ = 13.5 Hz), 38.19, 36.84, 36.19, 35.97 (d, $J_{Rh\text{-}C}$ = 12.8 Hz), 35.32, 26.81, 26.30, 25.93, 24.24, 23.71, 22.45, 22.27, 14.49 ppm; **IR (ATR):** $\tilde{\nu}$ = 3056, 2989, 2928, 2855, 1992, 1961, 1619, 1596, 1573, 1502, 1451, 1422, 1391, 1376, 1361, 1338, 1327, 1294, 1262, 1237, 1224, 1197, 1163, 1149, 1113, 1076, 1023, 948, 904, 880, 861, 829, 803, 766, 744, 704 $cm^{-1}$; **HRMS (ESI)** calculated for $[M\text{-}2(C_2H_4)+H]^+$: 645.2234, found: 645.2222; $\mathbf{[\alpha]_D^{20}}$ = -210.7 (c = 1.0, $CH_2Cl_2$); **eluent for FCC** (pentane:$CH_2Cl_2$, 50:1).

Other employed catalysts have been reported.[1]

**Substrates syntheses:**

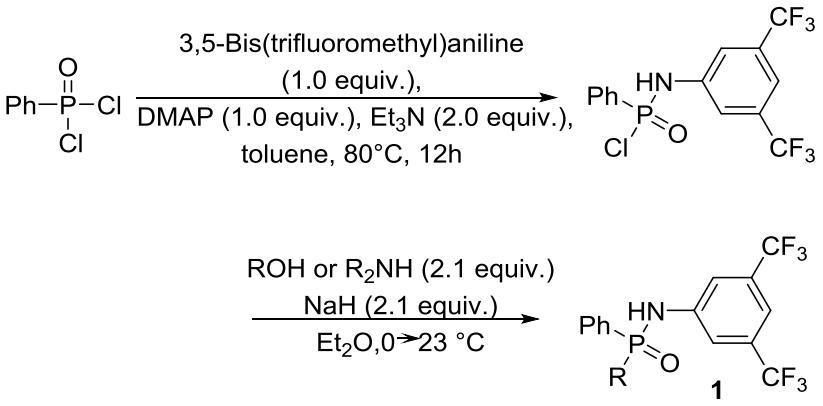
**General procedure for preparation of phosphinamide substrates A1**[2]




Methyl iodide or alkyl bromide (5.0 mmol, 1.0 equiv.) was placed in a frame-dried microwave tube equipped with magnetic stirring bar. Diisopropylphenylphosphinate (5.0 mmol, 1.0 equiv.) was added carefully dropwise at 23 °C under nitrogen atmosphere until an exothermic reaction was initiated. When the addition was complete, the mixture was stirred for further 3 hours. The volatile was removed under reduced pressure and the crude product **11** was employed in the next step without further purification.

To the solution of **11** in anhydrous toluene, thionyl chloride (2.0 equiv.) was added. The reaction mixture was stirred at 80 °C under nitrogen atmosphere for 3 hours. The volatile was removed by rotary evaporation and the residue was redissolved in anhydrous toluene. DMAP (1.0 equiv.), $Et_3N$ (2.0 equiv.) and 3,5-bis(trifluromethyl)aniline (1.0 equiv.) were added to the solution. The reaction mixture was stirred at 80 °C under nitrogen atmosphere for 12 hours. After cooling down to 23 °C, the volatile was removed by rotary evaporation and the residue was purified by flash column chromatography followed by recrystallization with $CH_2Cl_2$ affording **1** as white crystal.

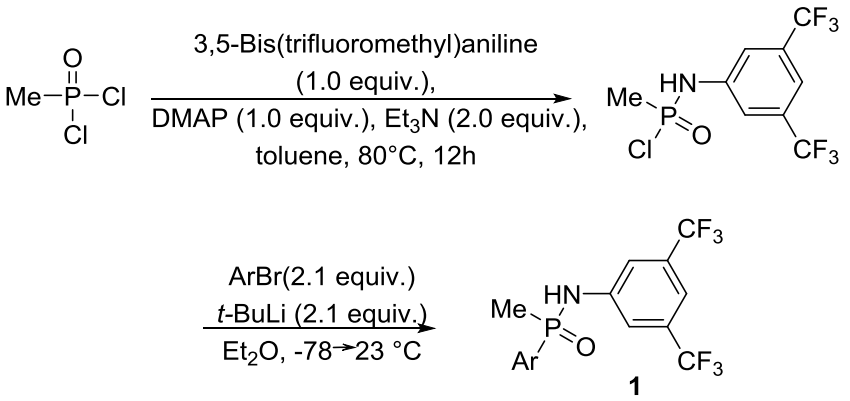
**General procedure for preparation of phosphinamide substrates A2**




To a solution of phenylphosphonic dichloride in anhydrous toluene, DMAP (1.0 equiv.), $Et_3N$ (2.0 equiv.) and 3,5-bis(trifluoromethyl)aniline (1.0 equiv.) were added. The reaction mixture was stirred at 80 °C under nitrogen atmosphere for 12 hours. After cooling down to 23 °C, the volatile was removed by rotary evaporation and the crude product was employed for next step without further purification.

To suspension of NaH (2.1 equiv.) in anhydrous $Et_2O$, phenol or the secondary amine (2.1 equiv.) solution in $Et_2O$ was added at 0 °C. The reaction mixture was allowed to warm up and stirred for further 1 hour at 23 °C. Then the solution of the crude product from last step in $Et_2O$ was added the reaction mixture at 0 °C. It was allowed to warm up and stirred for further 12 hours at 23 °C. Then sat. aq. $NH_4Cl$ was added at 0 °C. The aqueous phase was extracted with chloroform (3X50 mL). Combined the organic layers and dried over $Na_2SO_4$. The solvent removed by roatary evaporation and the residue was purified by flash column chromatography followed by recrystallization with $CH_2Cl_2$ affording **1** as white crystal.

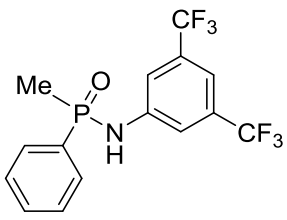
**General procedure for preparation of phosphinamide substrates A3**




To the solution of methylphosphonic dichloride in anhydrous toluene, DMAP (1.0 equiv.), $Et_3N$ (2.0 equiv.) and 3,5-bis(trifluoromethyl)aniline were added. The reaction mixture was stirred at 80 °C under nitrogen atmosphere for 12 hours. After cooling down to 23 °C, the volatile was removed by rotary evaporation and the crude product was employed for next step without further purification.

To the solution of aryl bromide (2.1 equiv.) in $Et_2O$, *t*-BuLi (2.1 equiv., 1.7 M in pentane) was added dropwise at -78 °C. The reaction mixture was stirred for further 1 hour. Then the solution of the crude product from last step in anhydrous $Et_2O$ was added dropwise to this prepared aryl lithium solution at -78 °C. The reaction mixture was allow to warm up slowly and stirred for further 12 hours at 23 °C. Then sat. aq. $NH_4Cl$ was added at 0 °C. The aqueous phase was extracted with chloroform (3X50 mL). Combined the organic layers and dried over $Na_2SO_4$. The solvent removed by rotary evaporation and the residue was purified by flash column chromatography followed by recrystallization with $CH_2Cl_2$ affording **1** as white crystal.

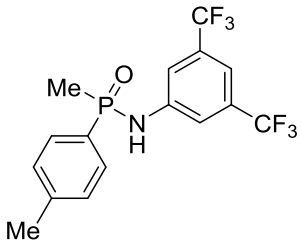
***N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-phenylphosphinic amide (1a)**



prepared from MeI according to **Procedure A1**. **1a** was obtained as a white crystal in 60% yield. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.86 (br, 1H), 7.79 (dd, *J* = 12.4, 6.4 Hz, 2H), 7.60–7.46 (m, 5H), 7.40 (s, 1H), 1.81

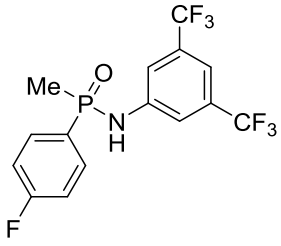
(d, $J$ = 14.3 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 144.61, 132.98 (d, $J_{C-P}$ = 119.8 Hz), 132.04 (d, $J_{C-P}$ = 2.7 Hz), 130.98 (d, $J_{C-P}$ = 10.4 Hz), 130.88 (q, $J_{C-F}$ = 32.6 Hz), 128.76 (d, $J_{C-P}$ = 12.5 Hz), 123.15 (q, $J_{C-F}$ = 272.7 Hz), 116.85, 112.75, 16.75 (d, $J_{C-P}$ = 91.0 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 26.30 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.93 ppm; **IR (ATR):** $\tilde{\nu}$ = 3157, 3120, 3078, 3012, 2900, 1621, 1518, 1473, 1421, 1412, 1381, 1275, 1173, 1128, 1000, 977, 910, 874, 851, 818, 779, 739, 728 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{15}H_{13}F_6NOP]^+$: 368.0633, found: 368.0641; **m.p.:** 200–201 °C; **eluent for FCC** ($CH_2Cl_2$:EtOAc, 1:1).

***N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-(*p*-tolyl)phosphinic amide (1b)**




prepared from 4-bromotoluene according to **Procedure A3**. **1b** was obtained as a white crystal in 42% yield. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.81 (d, $J$ = 11.6 Hz, 1H), 7.67 (dd, $J$ = 12.2, 8.0 Hz, 2H), 7.55 (s, 2H), 7.41 (s, 1H), 7.32 (dd, $J$ = 8.0, 2.9 Hz, 2H), 2.31 (s, 3H), 1.77 (d, $J$ = 14.3 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 144.69, 142.14 (d, $J_{C-P}$ = 2.8 Hz), 131.03 (d, $J_{C-P}$ = 10.7 Hz), 130.87 (q, $J_{C-F}$ = 32.5 Hz), 129.73 (d, $J_{C-P}$ = 122.3 Hz), 129.38 (d, $J_{C-P}$ = 12.9 Hz), 123.18 (q, $J_{C-F}$ = 272.7 Hz), 116.83, 112.72, 21.04, 16.88 (d, $J_{C-P}$ = 91.3 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 31.19 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -57.19 ppm; **IR (ATR):** $\tilde{\nu}$ = 3157, 3121, 3016, 2913, 2833, 1620, 1603, 1524, 1469, 1411, 1378, 1303, 1273, 1212, 1169, 1124, 1000, 974, 914, 876, 851, 806, 766, 741, 729, 701 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{16}H_{15}F_6NOP]^+$: 382.0790, found: 382.0803; **m.p.:** 171–173 °C; **eluent for FCC** (pure EtOAc).

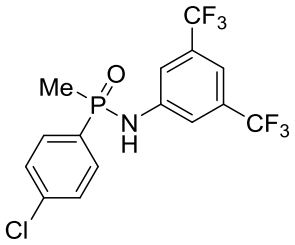
***N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-(4-fluorophenyl)-*P*-methylphosphinic amide (1c)**




prepared from 1-bromo-4-fluorobenzene according to **Procedure A3**. **1c** was obtained as a white crystal in 45% yield. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.86 (d, $J$ = 11.8 Hz, 1H), 7.92–7.79 (m, 2H), 7.54 (s, 2H), 7.43 (s, 1H), 7.36 (ddt, $J$ = 8.9, 6.6, 2.2 Hz, 2H), 1.81 (d, $J$ = 14.5 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 164.38 (dd, $J_{C-P}$ = 3.3 Hz, $J_{C-F}$ = 250.2 Hz), 144.43, 133.95 (dd, $J_{C-P}$ = 8.9 Hz, $J_{C-F}$ = 12.1 Hz), 130.92 (q, $J_{C-F}$ = 32.6 Hz), 129.31 (dd, $J_{C-P}$ =

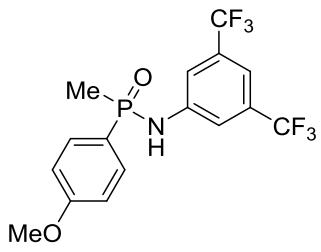
122.3Hz, $J_{C\text{-}F}$ = 3.1 Hz), 123.13 (q, $J_{C\text{-}F}$ = 272.8 Hz), 116.90, 116.01 (dd, $J_{C\text{-}P}$ = 13.6 Hz, $J_{C\text{-}F}$ = 21.3 Hz), 112.93 , 16.80 (d, $J_{C\text{-}P}$ = 91.7 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 25.59 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.99 (s, 6F) , -107.56 (s, 1F) ppm; **IR (ATR):** $\tilde{\nu}$ = 3160, 3122, 3016, 2912, 2831, 1621, 1593, 1523, 1500, 1470, 1412, 1379, 1306, 1274, 1239, 1173, 1116, 1015, 1000, 975, 915, 878, 834, 771, 740, 701 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{15}H_{12}F_7NOP]^+$: 386.0539, found: 386.0538; **m.p.:** 189–191 °C; **eluent for FCC** (pure EtOAc).

***N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-(4-chlorophenyl)-*P*-methylphosphinic amide (1d)**




prepared from 1-bromo-4-chlorobenzene according to **Procedure A3**. **1d** was obtained as a white crystal in 32% yield. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.90 (br, 1H), 7.79 (dd, *J* = 11.8, 8.4 Hz, 2H), 7.60 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.54 (d, *J* = 1.5 Hz, 2H), 7.45 (s, 1H), 1.82 (d, *J* = 14.5 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 144.37, 137.21 (d, $J_{C\text{-}P}$ = 3.6 Hz), 133.01 (d, $J_{C\text{-}P}$ = 11.2 Hz), 131.97 (d, $J_{C\text{-}P}$ = 120.0 Hz), 130.95 (q, $J_{C\text{-}F}$ = 32.7 Hz), 128.96 (d, $J_{C\text{-}P}$ = 13.2 Hz), 123.13 (q, $J_{C\text{-}F}$ = 272.7 Hz), 116.91, 113.05, 16.66 (d, $J_{C\text{-}P}$ = 92.2 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 25.74 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.92 ppm; **IR (ATR):** $\tilde{\nu}$ = 3383, 3184, 2924, 1648, 1618, 1585, 1523, 1470, 1422, 1409, 1379, 1308, 1273, 1171, 1128, 1109, 1095, 1082, 1048, 1023, 999, 983, 909, 883, 873, 850, 823, 777, 739, 728 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{15}H_{12}ClF_6NOP]^+$: 402.0244, found: 402.0244; **m.p.:** 196–198 °C; **eluent for FCC** (pure EtOAc).

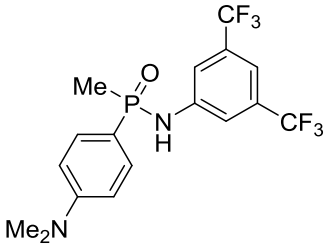
***N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-(4-methoxyphenyl)-*P*-methylphosphinic amide (1e)**




prepared from 4-bromoanisole according to **Procedure A3**. **1e** was obtained as a white crystal in 35% yield. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.76 (br, 1H), 7.71 (dd, *J* = 11.8, 8.7 Hz, 2H), 7.54 (s, 2H), 7.41 (s, 1H), 7.06 (dd, *J* = 8.8, 2.4 Hz, 2H), 3.78 (s, 3H), 1.76 (d, *J* = 14.3 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 162.13 (d, $J_{C\text{-}P}$ = 2.9 Hz), 144.72, 132.96 (d, $J_{C\text{-}P}$ = 11.7 Hz), 130.86 (q, $J_{C\text{-}F}$ = 32.6 Hz), 123.93 (d, $J_{C\text{-}P}$ = 126.2 Hz), 123.19 (q,

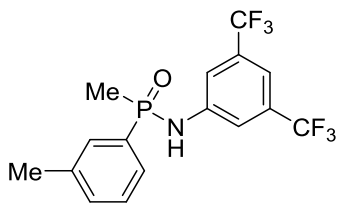
$J_{C\text{-}F}$ = 272.9 Hz), 116.83, 114.33 (d, $J_{C\text{-}P}$ = 13.6 Hz), 112.66, 55.33, 17.06 (d, $J_{C\text{-}P}$ = 91.8 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 26.22 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.93 ppm; **IR (ATR):** $\tilde{\nu}$ = 3167, 3132, 3097, 3072, 3024, 2923, 2845, 1621, 1601, 1571, 1533, 1507, 1443, 1431, 1409, 1306, 1295, 1274, 1166, 1118, 1106, 1026, 1000, 971, 912, 890, 875, 850, 821, 802, 770, 702 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{16}H_{15}F_6NO_2P]^+$: 398.0739, found: 398.0739; **m.p.:** 150–152 °C; **eluent for FCC (** pure EtOAc.

**_N_-(3,5-Bis(trifluoromethyl)phenyl)-_P_-(4-(dimethylamino)phenyl)-_P_-methylphosphinic amide (1f)**



prepared from 4-bromo-_N_,_N_-dimethylaniline according to **Procedure A3**. **1f** was obtained as a white crystal in 40% yield. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.65 (d, $J$ = 11.4 Hz, 1H), 7.59–7.47 (m, 4H), 7.40 (d, $J$ = 1.9 Hz, 1H), 6.75 (dd, $J$ = 9.0, 2.6 Hz, 2H), 2.94 (s, 6H), 1.70 (d, $J$ = 14.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 152.39, 145.03, 132.24 (d, $J_{C\text{-}P}$ = 11.8 Hz), 130.82 (q, $J_{C\text{-}F}$ = 32.3 Hz), 123.24 (q, $J_{C\text{-}F}$ = 272.7 Hz), 116.83 (d, $J_{C\text{-}P}$ = 132.1 Hz), 116.79, 112.31, 111.40 (d, $J_{C\text{-}P}$ = 13.3 Hz), 39.50, 17.29 (d, $J_{C\text{-}P}$ = 92.0 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 26.81 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.83 ppm; **IR (ATR):** $\tilde{\nu}$ = 3159, 3125, 3017, 2917, 2837, 1619, 1602, 1546, 1520, 1468, 1447, 1410, 1383, 1369, 1275, 1231, 1183, 1161, 1114, 1000, 974, 945, 917, 891, 873, 813, 783, 756, 729, 701 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{17}H_{18}F_6N_2OP]^+$: 411.1055, found: 411.1056; **m.p.:** 207–209 °C; **eluent for FCC** (pure EtOAc).

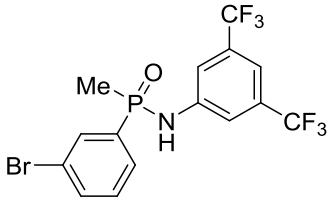
**_N_-(3,5-Bis(trifluoromethyl)phenyl)-_P_-methyl-_P_-(_m_-tolyl)phosphinic amide (1g)**



prepared from 3-bromotoluene according to **Procedure A3**. **1g** was obtained as a white crystal in 48% yield. **$^1$H NMR** (600 MHz, DMSO-$d_6$) δ = 8.80 (d, $J$ = 11.4 Hz, 1H), 7.62 (d, $J$ = 12.7 Hz, 1H), 7.59–7.54 (m, 3H), 7.42 (d, $J$ = 4.3 Hz, 1H), 7.42–7.35 (m, 2H), 2.33 (s, 3H), 1.79 (d, $J$ = 14.3 Hz, 3H) ppm; **$^{13}$C NMR** (151 MHz, DMSO-$d_6$) δ = 144.65, 138.14 (d, $J_{C\text{-}P}$ = 12.3 Hz),

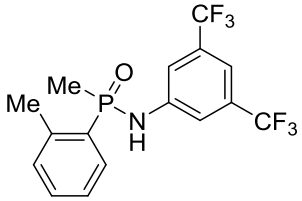
132.91 (d, $J_{C\text{-}P}$ = 119.4 Hz), 132.73 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.36 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.87 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.70 (d, $J_{C\text{-}P}$ = 13.1 Hz), 128.02 (d, $J_{C\text{-}P}$ = 10.2 Hz), 123.18 (q, $J_{C\text{-}F}$ = 272.7 Hz), 116.85, 112.77, 20.91, 16.72 (d, $J_{C\text{-}P}$ = 91.0 Hz) ppm; **$^{31}$P NMR** (243 MHz, DMSO-$d_6$) δ = 26.46 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.95 ppm; **IR (ATR):** $\tilde{\nu}$ = 3159, 3124, 3017, 2916, 2832, 1736, 1620, 1523, 1470, 1411, 1379, 1303, 1274, 1228, 1168, 1125, 1045, 1000, 975, 916, 876, 851, 817, 765, 739, 700 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{16}H_{15}F_6NOP]^+$: 382.0790, found: 382.0793; **m.p.:** 164–166 °C; **eluent for FCC** ($CHCl_3$:EtOAc, 1:1).

**_N_-(3,5-Bis(trifluoromethyl)phenyl)-_P_-(3-bromophenyl)-_P_-methylphosphinic amide (1h)**




prepared from 1,3-dibromobenzene according to **Procedure A3**. **1h** was obtained as a white crystal in 32% yield. **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ = 8.01 (dt, $J$ = 12.7, 1.8 Hz, 1H), 7.83–7.68 (m, 2H), 7.53–7.41 (m, 3H), 7.40 (s, 1H), 1.90 (d, $J$ = 14.6 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Methanol-$d_4$) δ = 144.62, 136.86 (d, $J_{C\text{-}P}$ = 2.5 Hz), 135.44 (d, $J_{C\text{-}P}$ = 122.1 Hz), 135.39 (d, $J_{C\text{-}P}$ = 11.5 Hz), 133.57 (q, $J_{C\text{-}F}$ = 33.3 Hz), 132.10 (d, $J_{C\text{-}P}$ = 13.8 Hz), 131.20 (d, $J_{C\text{-}P}$ = 10.3 Hz), 124.55 (q, $J_{C\text{-}F}$ = 271.8 Hz), 124.31 (d, $J_{C\text{-}P}$ = 16.7 Hz), 118.68, 115.27, 16.46 (d, $J_{C\text{-}P}$ = 93.1 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 27.98 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -64.85 ppm; **IR (ATR):** $\tilde{\nu}$ = 3149, 3117, 3075, 3012, 2910, 2803, 1620, 1560, 1523, 1468, 1411, 1380, 1306, 1276, 1176, 1128, 1071. 1000, 977, 917, 876, 851, 792, 777, 740, 729, 702 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{15}H_{12}{}^{79}BrF_6NOP]^+$: 445.9739, found: 445.9735; **m.p.:** 188–190 °C; **eluent for FCC** ($CHCl_3$:EtOAc, 1:1).

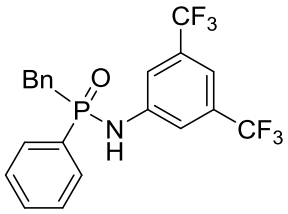
**_N_-(3,5-Bis(trifluoromethyl)phenyl)-_P_-methyl-_P_-(_o_-tolyl)phosphinic amide (1i)**




prepared from 2-bromotoluene according to **Procedure A3**. **1i** was obtained as a white crystal in 40% yield. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.88 (d, $J$ = 12.0 Hz, 1H), 7.86 (ddd, $J$ = 13.5, 7.7, 1.5 Hz, 1H), 7.60–7.52 (m, 2H), 7.49–7.39 (m, 2H), 7.38–7.28 (m, 1H), 7.27 (dd, $J$ = 7.6, 4.7 Hz, 1H), 2.52 (d, $J$ = 1.2 Hz, 3H), 1.84 (d, $J$ = 14.1 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$)

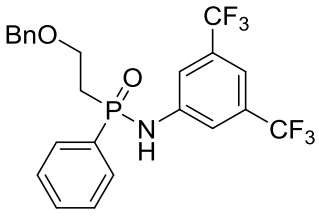
δ = 144.61, 140.72 (d, $J_{C-P}$ = 10.7 Hz), 133.00 (d, $J_{C-P}$ = 10.2 Hz), 132.18 (d, $J_{C-P}$ = 2.8 Hz), 131.72 (d, $J_{C-P}$ = 11.6 Hz), 130.90 (q, $J_{C-F}$ = 32.6 Hz), 130.74 (d, $J_{C-P}$ = 116.9 Hz), 125.85 (d, $J_{C-P}$ = 12.2 Hz), 123.15 (q, $J_{C-F}$ = 272.7 Hz), 116.65, 112.72, 20.65 (d, $J_{C-P}$ = 4.0 Hz), 16.83 (d, $J_{C-P}$ = 90.2 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 26.23 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.97 ppm; **IR (ATR):** $\tilde{\nu}$ = 3160, 3109, 3077, 3011, 2910, 2826, 1620, 1593, 1522, 1469, 1414, 1379, 1302, 1276, 1171, 1128, 1078, 999, 976, 912, 879, 848, 805, 775, 749, 726, 700 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{16}H_{15}F_6NOP]^+$: 382.0790, found: 382.0796; **m.p.:** 208–210 °C; **eluent for FCC** (pure EtOAc).

**_P_-Benzyl-_N_-(3,5-bis(trifluoromethyl)phenyl)-_P_-phenylphosphinic amide (1j)**



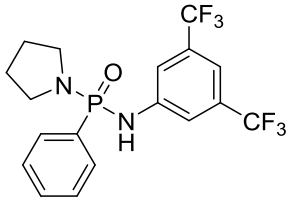

prepared from BnBr according to **Procedure A1**. **1j** was obtained as a white crystal in 66% yield. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.80 (s, 1H), 7.74 (dd, $J$ = 12.1, 7.4 Hz, 2H), 7.58 (s, 2H), 7.54 (d, $J$ = 7.2 Hz, 1H), 7.52–7.44 (m, 2H), 7.40 (s, 1H), 7.22–7.15 (m, 5H), 3.65–3.48 (m, 2H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 144.76 (d, $J_{C-P}$ = 1.2 Hz), 132.23 (d, $J_{C-P}$ = 2.8 Hz), 131.45 (d, $J_{C-P}$ = 118.7 Hz), 131.42 (d, $J_{C-P}$ = 10.1 Hz), 131.32 (d, $J_{C-P}$ = 9.0 Hz), 130.82 (q, $J_{C-F}$ = 32.3 Hz), 130.18 (d, $J_{C-P}$ = 5.6 Hz), 128.66 (d, $J_{C-P}$ = 12.4 Hz), 128.12 (d, $J_{C-P}$ = 2.9 Hz), 126.60 (d, $J_{C-P}$ = 3.3 Hz), 124.52 (q, $J_{C-F}$ = 273.5 Hz), 117.13, 112.92, 37.20 (d, $J_{C-P}$ = 84.2 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 26.41 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.94 ppm; **IR (ATR):** $\tilde{\nu}$ = 3157, 3111, 3013, 2902, 2837, 2806, 2766, 1622, 1532, 1469, 1424, 1381, 1282, 1230, 1180, 1133, 1108, 1065, 1000, 980, 908, 876, 838, 825, 780, 749, 732 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{21}H_{17}F_6NOP]^+$: 444.0946, found: 444.0959; **m.p.:** 212–214 °C; **eluent for FCC** ($CH_2Cl_2$:EtOAc, 4:1).

**_P_-(2-(Benzyloxy)ethyl)-_N_-(3,5-bis(trifluoromethyl)phenyl)-_P_-phenylphosphinic amide (1k)**



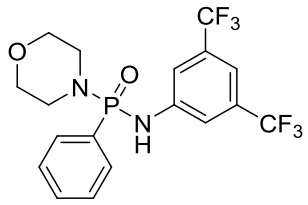
prepared from ((2-bromoethoxy)methyl)benzene according to **Procedure A1**. **1k** was obtained as a white crystal in 56% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.79 (ddd, *J* = 12.4, 8.3, 1.3 Hz, 2H), 7.59–7.50 (m, 1H), 7.50–7.35 (m, 7H), 7.28 (d, *J* = 7.9 Hz, 1H), 6.99 (s, 2H), 4.64 (d, *J* = 10.5 Hz, 1H), 4.53 (d, *J* = 10.5 Hz, 1H), 4.13 (dddd, *J* = 21.6, 9.5, 7.4, 4.5 Hz, 1H), 3.80 (dddd, *J* = 23.5, 9.4, 6.4, 4.4 Hz, 1H), 2.36–2.24 (m, 2H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 142.42 (d, $J_{C\text{-}P}$ = 1.8 Hz), 136.86, 132.81 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.39 (q, $J_{C\text{-}F}$ = 33.2 Hz), 132.03 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.37 (d, $J_{C\text{-}P}$ = 124.2 Hz), 129.19 (d, $J_{C\text{-}P}$ = 12.6 Hz), 129.04, 128.91, 128.45, 123.11 (q, $J_{C\text{-}F}$ = 272.2 Hz), 117.39, 114.4, 74.20, 64.39 (d, $J_{C\text{-}P}$ = 7.7 Hz), 31.85 (d, $J_{C\text{-}P}$ = 88.9 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 28.54 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.16 ppm; **IR (ATR):** $\tilde{\nu}$ = 3159, 3122, 3017, 2911, 1620, 1591, 1522, 1497, 1470, 1439, 1379, 1274, 1228, 1168, 1124, 1027, 999, 971, 873, 835, 795, 731 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{23}H_{21}F_6NO_2P]^+$: 488.1209, found: 488.1203; **m.p.:** 82–84 °C; **eluent for FCC** (hexane:EtOAc, 3:2).

***N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-phenyl-*P*-(pyrrolidin-1-yl)phosphinic amide (1l)**



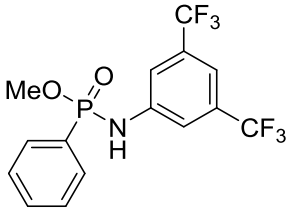

prepared from pyrrolidine according to **Procedure A2**. **1l** was obtained as a white crystal in 65% yield. **$^{1}$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.54 (d, *J* = 10.9 Hz, 1H), 7.85–7.72 (m, 4H), 7.64–7.48 (m, 3H), 7.44 (s, 1H), 3.19–2.96 (m, 4H), 1.84–1.62 (m, 4H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 144.78, 132.02 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.48 (d, $J_{C\text{-}P}$ = 154.4 Hz), 131.21 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.84 (q, $J_{C\text{-}F}$ = 32.3 Hz), 128.70 (d, $J_{C\text{-}P}$ = 13.5 Hz), 123.29 (q, $J_{C\text{-}F}$=272.6 Hz), 117.14, 112.72, 46.14 (d, $J_{C\text{-}P}$ = 4.3 Hz), 25.89 (d, $J_{C\text{-}P}$ = 8.0 Hz) ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 14.36 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.99 ppm; **IR (ATR):** $\tilde{\nu}$ = 3178, 3107, 3015, 2976, 2877, 1618, 1519, 1470, 1438, 1413, 1379, 1275, 1210, 1179, 1162, 1122, 1014, 999, 972, 874, 834, 747, 729, 715, 703 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{18}H_{16}F_6N_2OP]^+$: 423.1055, found: 423.1067; **m.p.:** 190–192 °C; **eluent for FCC** ($CH_2Cl_2$:EtOAc, 4:1).

***N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-morpholino-*P*-phenylphosphinic amide (1m)**



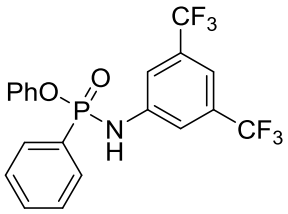
prepared from morpholin according to **Procedure A2**. **1m** was obtained as a white crystal in 55% yield. **$^{1}$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.55 (d, $J$ = 12.3 Hz, 1H), 7.82 (s, 2H), 7.87–7.73 (m, 2H), 7.70–7.61 (m, 1H), 7.61–7.54 (m, 2H), 7.54 (s, 1H), 3.55–3.37 (m, 4H), 3.15–2.97 (m, 4H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 144.28, 132.35 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.26 (d, $J_{C\text{-}P}$ = 10.1 Hz), 130.67 (q, $J_{C\text{-}F}$ = 32.6 Hz), 130.66 (d, $J_{C\text{-}P}$ = 154.2 Hz), 128.83 (d, $J_{C\text{-}P}$ = 13.5 Hz), 123.30 (q, $J_{C\text{-}F}$ = 272.6 Hz), 117.72, 113.24, 66.28 (d, $J_{C\text{-}P}$ = 5.8 Hz), 43.99 ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 15.89 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.83 ppm; **IR (ATR):** $\tilde{\nu}$ = 3153, 3123, 3012, 2965, 2901, 2855, 1619, 1517, 1470, 1438, 1410, 1379, 1276, 1260, 1184, 1116, 1086, 1000, 968, 915, 876, 835, 736 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{18}H_{18}F_6N_2O_2P]^+$: 439.1005, found: 439.1008; **m.p.:** 186–187 °C; **eluent for FCC** ($CH_2Cl_2$:EtOAc, 2:1).

**Methyl *N*-(3,5-bis(trifluoromethyl)phenyl)-*P*-phenylphosphonamidate (1n)**



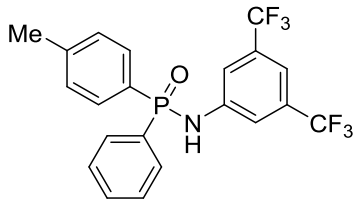
prepared from methanol according to **Procedure A2**. **1n** was obtained as a white crystal in 68% yield. **$^{1}$H NMR** (400 MHz, Chloroform-$d$) δ = 7.85 (dd, $J$ = 13.6, 7.0 Hz, 2H), 7.56 (tq, $J$ = 6.7, 1.4 Hz, 1H), 7.47 (ddd, $J$ = 8.5, 6.8, 4.2 Hz, 2H), 7.42 (d, $J$=5.6, 1H), 7.37 (s, 2H), 7.36 (s, 1H), 3.90 (d, $J$ = 11.4 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-$d$) δ = 142.35, 133.09 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.57 (q, $J_{C\text{-}F}$ = 33.2 Hz), 131.39 (d, $J_{C\text{-}P}$ = 10.4 Hz), 129.03 (d, $J_{C\text{-}P}$ = 15.0 Hz), 128.40 (d, $J_{C\text{-}P}$ = 178.4 Hz), 123.22 (q, $J_{C\text{-}F}$ = 272.8 Hz), 117.13, 114.69, 51.60 (d, $J_{C\text{-}P}$ = 6.4 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-$d$) δ = 18.39 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-$d$) δ = -63.23 ppm; **IR (ATR):** $\tilde{\nu}$ = 3170, 3136, 3074, 3025, 2962, 2923, 1620, 1593, 1523, 1468, 1443, 1419, 1377, 1275, 1206, 1181, 1166, 1120, 1037, 999, 977, 892, 878, 836, 808, 753, 716 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{15}H_{13}F_6NO_2P]^+$: 384.0583, found: 384.0575; **m.p.:** 117–119 °C; **eluent for FCC** (hexane:EtOAc, 1:2).

**Phenyl *N*-(3,5-bis(trifluoromethyl)phenyl)-*P*-phenylphosphonamidate (1o)**



prepared from phenol according to **Procedure A2**. **1o** was obtained as a white crystal in 48% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 8.06 (d, *J* = 5.7 Hz, 1H), 7.98–7.84 (m, 2H), 7.60 (td, *J* = 7.4, 1.5 Hz, 1H), 7.49 (td, *J* = 7.6, 4.3 Hz, 2H), 7.36 (s, 3H), 7.26–7.16 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 1H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 149.83 (d, $J_{C\text{-}P}$ = 8.7 Hz), 141.72, 133.44 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.54 (q, $J_{C\text{-}F}$ = 33.4 Hz), 131.60 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.05, 129.22 (d, $J_{C\text{-}P}$ = 15.3 Hz), 128.16 (d, $J_{C\text{-}P}$ = 180.1 Hz), 125.66, 123.17 (q, $J_{C\text{-}F}$ = 273.0 Hz), 120.63 (d, $J_{C\text{-}P}$ = 4.4 Hz), 117.57, 115.09 ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 15.03 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.15 ppm; **IR (ATR):** $\tilde{\nu}$ = 3086, 3043, 2996, 2916, 2849, 1618, 1592, 1497, 1467, 1440, 1414, 1375, 1274, 1182, 1123, 1107, 1001, 968, 903, 888, 871, 829, 753, 732 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{20}H_{15}F_6NO_2P]^+$: 446.0739, found: 446.0734; **m.p.:** 137–139 °C; **eluent for FCC** (hexane:EtOAc, 4:1).

***N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-phenyl-*P*-(*p*-tolyl)phosphinic amide (1p)**



prepared from 4-bromotolene (*t*-BuLi (1.7 M in pentane) instead of NaH) according to **Procedure A2**. **1p** was obtained as a white crystal in 52% yield. **$^{1}$H NMR** (400 MHz, DMSO-$d_6$) δ = 8.99 (s, 1H), 7.81 (ddt, *J* = 12.4, 6.9, 1.5 Hz, 2H), 7.75–7.68 (m, 2H), 7.65 (d, *J* = 1.6 Hz, 2H), 7.64–7.59 (m, 1H), 7.55 (ddd, *J* = 8.4, 6.4, 3.2 Hz, 2H), 7.47 (s, 1H), 7.37 (dd, *J* = 8.1, 3.0 Hz, 2H), 2.35 (s, 3H) ppm; **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ = 144.54 , 142.71 (d, $J_{C\text{-}P}$ = 3.1 Hz), 132.38 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.91 (d, $J_{C\text{-}P}$ = 126.3 Hz), 131.62 (d, $J_{C\text{-}P}$ = 10.7 Hz), 131.47 (d, $J_{C\text{-}P}$ = 10.1 Hz), 130.81 (q, $J_{C\text{-}F}$ = 32.4 Hz), 129.53 (d, $J_{C\text{-}P}$ = 13.1 Hz), 128.89 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.30 (d, $J_{C\text{-}P}$ = 129.7 Hz), 127.66, 123.15 (q, $J_{C\text{-}F}$ = 273.0Hz), 117.65, 113.18, 21.06 ppm; **$^{31}$P NMR** (162 MHz, DMSO-$d_6$) δ = 18.42 ppm; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ = -61.88 ppm; **IR (ATR):** $\tilde{\nu}$ = 3111, 3072, 3009, 2916, 2904, 2803, 1620, 1602, 1516, 1469, 1438, 1409, 1380, 1275, 1177, 1123, 1105, 1021, 1001, 976, 888, 877, 830, 811, 749, 732 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{21}H_{17}F_6NOP]^+$: 444.0946, found: 444.0946; **m.p.:** 198–200 °C; **eluent for FCC** ($CHCl_3$:EtOAc, 1:1).

Alkynes used in this work are described in literature and were prepared according to reported protocols.[3]

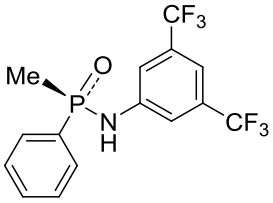
## Kinetic resolution

### *Representative procedure for the kinetic resolution*

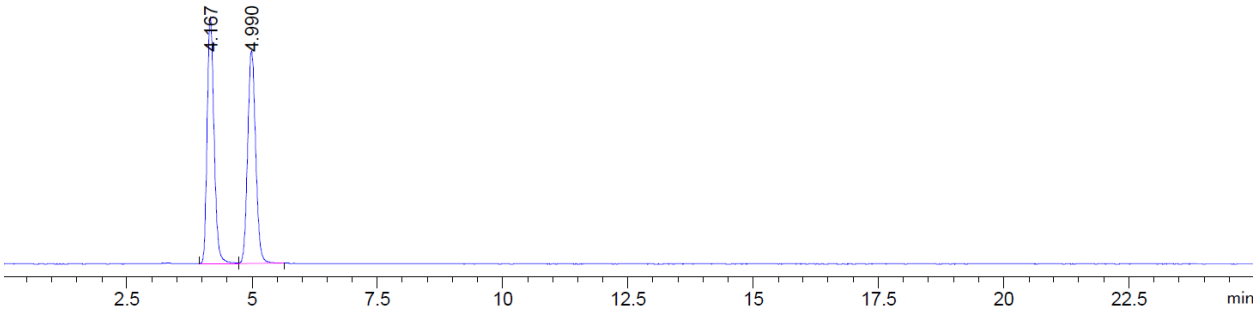
Without protection from oxygen or moisture, Rh-catalyst **Rh7** (6.2 mg, 10.0 µmol), and dibenzoylperoxide (2.4 mg, 10.0 µmol) were weighed into a microwave tube equipped with a magnetic stir bar. *t*BuOH (400 µL) was added and the mixture stirred at 23 °C for 15 min. To the solution were added **1a** (36.7 mg, 0.1 mmol, 1.0 equiv.), diphenylacetylene (26.7 mg, 0.2 mmol, 1.5 equiv.), $K_2CO_3$ (13.8 mg, 0.1 mmol, 1.0 equiv.), $Ag_2CO_3$ (55.1 mg, 0.2 mmol, 2.0 equiv.) and the tube sealed. The reaction mixture was stirred at the given temperature for the given reaction time. After cooling down to 23 °C, the mixture was filtered over a pad of celite (washing with EtOAc), the volatiles removed under reduced pressure and the crude purified by column chromatography on silica gel (hexane:EtOAc, 3:1), yielding 25.0 mg of **2a** with 93 : 7 *er*; ($CHCl_3$:EtOAc, 1:1), recovering 17.0 mg of *ent*-**1a** with 95 : 5 *er*.

### Recovered Starting Material

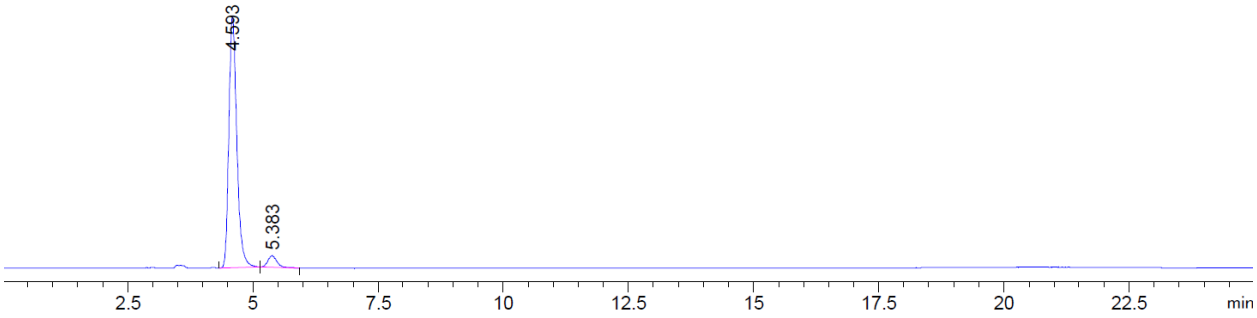
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-phenylphosphinic amide (1a)**




(at 90 °C, 8.5 hours) obtained as a white crystal in 46% yield; $[\alpha]_D^{20}$ = -6.3 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak AZH , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 4.6 min, $t_r$ (minor) = 5.4 min), 95 : 5 *er*. **S factor**: 42.



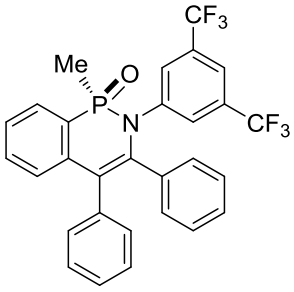
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.167 | BV | 0.1506 | 1252.89490 | 129.85233 | 49.9692 |
| 2 | 4.990 | VB | 0.1743 | 1254.44055 | 112.35071 | 50.0308 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.593 | BB | 0.1703 | 1946.94592 | 177.03801 | 95.0530 |
| 2 | 5.383 | BB | 0.1937 | 101.32866 | 8.11283 | 4.9470 |

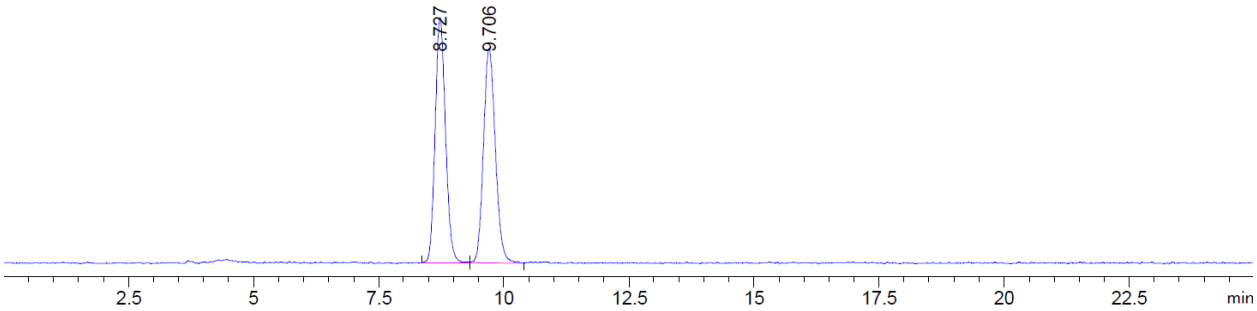
**Product**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-1-methyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2a)**

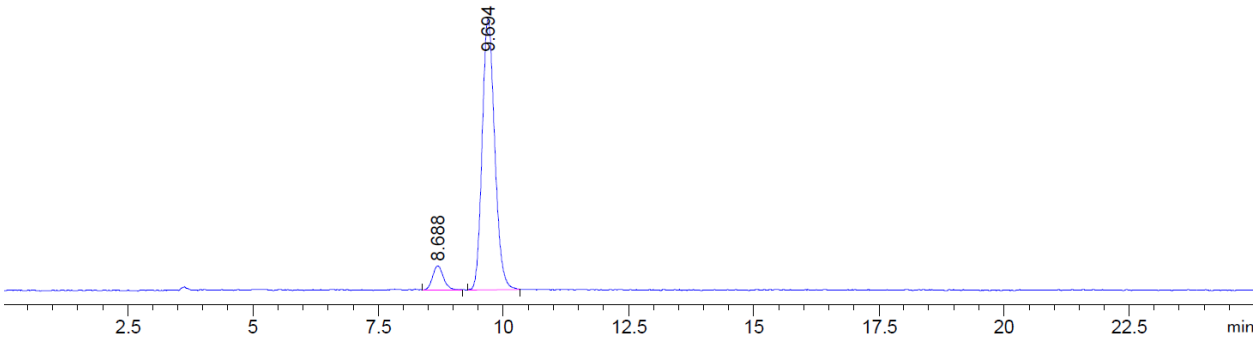



obtained as a white foam in 46% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.93 (dd, *J*=13.3, 7.0 Hz, 1H), 7.63 (s, 2H), 7.55–7.45 (m, 3H), 7.29–7.18 (m, 6H), 7.03 (dd, *J*=8.0, 1.7 Hz, 2H), 6.97–6.88 (m, 3H), 1.97 (d, *J*=13.7 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 141.34 (d, $J_{C\text{-}P}$ = 2.5 Hz), 139.02, 137.66 (d, $J_{C\text{-}P}$ = 6.2 Hz), 137.30, 135.29 (d, $J_{C\text{-}P}$ = 3.5 Hz), 132.42 (d, $J_{C\text{-}P}$ = 2.3 Hz), 131.86 (q, $J_{C\text{-}F}$ = 33.6 Hz), 131.71, 130.87, 128.70 (d, $J_{C\text{-}P}$ = 10.4 Hz), 128.26, 128.11, 127.96 (d, $J_{C\text{-}P}$ = 13.5 Hz), 127.95, 127.71, 127.44 (d, $J_{C\text{-}P}$ = 9.2 Hz), 127.30, 125.61 (d, $J_{C\text{-}P}$ = 7.8 Hz), 124.29 (d, $J_{C\text{-}P}$ = 121.8 Hz), 122.90 (q, $J_{C\text{-}F}$ = 272.9 Hz), 119.22, 16.47 (d, $J_{C\text{-}P}$ = 94.6 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 25.48

ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.05 ppm; **IR (ATR):** $\tilde{\nu}$ = 3058, 3027, 2981, 2920, 1735, 1602, 1588, 1551, 1489, 1465, 1443, 1370, 1274, 1241, 1221, 1171, 1127, 1096, 1013, 954, 915, 885, 845, 777, 761, 752, 736, 716 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{29}H_{21}F_6NOP]^+$: 544.1259, found: 544.1261; **$[\alpha]_D^{20}$** = +92.0 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 8.7 min, $t_r$ (major) = 9.7 min), 93 : 7 *er*.



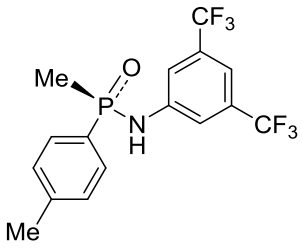

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.727 | BB | 0.2239 | 889.99371 | 61.82875 | 49.9565 |
| 2 | 9.706 | BB | 0.2563 | 891.54242 | 54.08825 | 50.0435 |



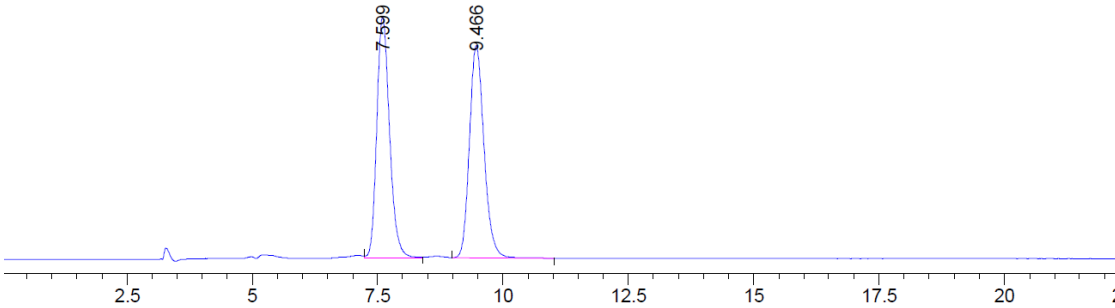

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.688 | BB | 0.2247 | 100.47264 | 6.63530 | 7.0676 |
| 2 | 9.694 | BB | 0.2695 | 1321.11304 | 75.72833 | 92.9324 |

**Recovered Starting Material**

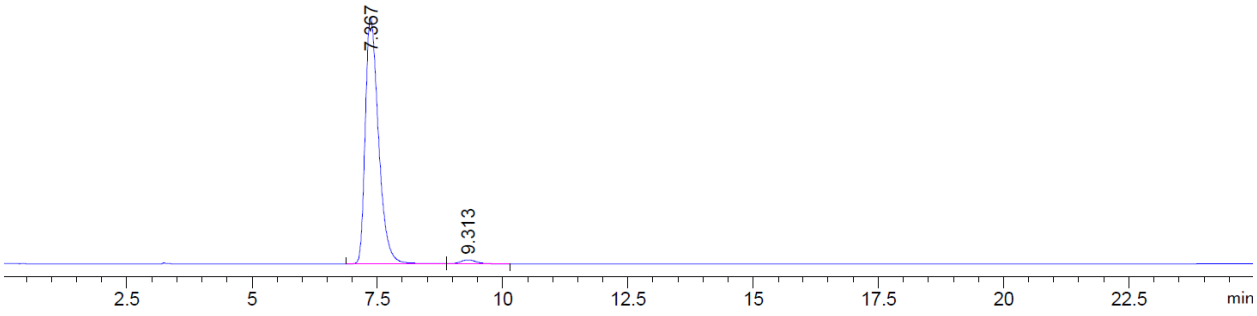
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-(*p*-tolyl)phosphinic amide (1b)**




(at 90 °C, 10.5 hours) obtained as a white crystal in 42% yield; $[\alpha]_D^{20}$ = +7.1 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IA , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 7.4 min, $t_r$ (minor) = 9.3 min), 98 : 2 *er*. **S factor**: 32.



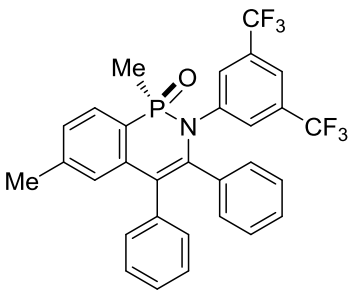

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.599 | VV | 0.2744 | 855.28906 | 48.33492 | 49.8149 |
| 2 | 9.466 | BB | 0.3143 | 861.64459 | 42.54821 | 50.1851 |



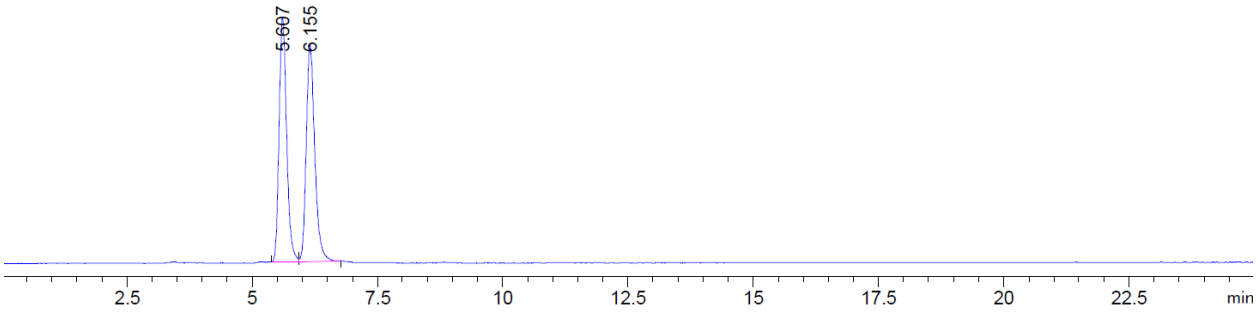

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.367 | VV | 0.2828 | 9279.43652 | 503.89807 | 98.0107 |
| 2 | 9.313 | VB | 0.3477 | 188.34021 | 8.46042 | 1.9893 |

**Product**

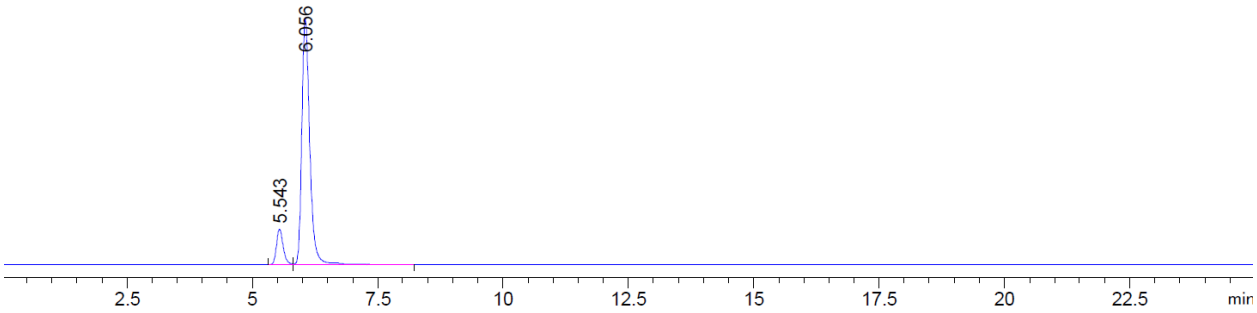
**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-1,6-dimethyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2b)**




obtained as a white foam in 50% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.82 (dd, *J* = 13.1, 7.7 Hz, 1H), 7.61 (s, 2H), 7.46 (s, 1H), 7.34–7.16 (m, 6H), 7.10–7.04 (m, 1H), 7.04–6.98 (m, 2H), 6.97–6.85 (m, 3H), 2.33 (s, 3H), 1.95 (d, *J* = 13.7 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 143.00 , 141.42 , 139.08 , 137.73 (d, $J_{C\text{-}P}$ = 6.6 Hz), 137.41 , 135.44 (d, $J_{C\text{-}P}$ = 3.6 Hz), 131.82 (q, $J_{C\text{-}F}$ = 33.8 Hz), 131.76 , 130.89 , 128.96 (d, $J_{C\text{-}P}$ = 13.8 Hz), 128.79 (d, $J_{C\text{-}P}$ = 10.9 Hz), 128.23 , 128.06 , 127.89 , 127.80 , 127.68 , 127.25 , 125.72 (d, $J_{C\text{-}P}$ = 7.8 Hz), 122.93 (q, $J_{C\text{-}F}$ = 272.8 Hz), 121.47 (d, $J_{C\text{-}P}$ = 124.2 Hz), 119.12 , 22.14 , 16.62 (d, $J_{C\text{-}P}$ = 94.5 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 26.04 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.04 ppm; **IR (ATR):** $\tilde{\nu}$ = 3055, 3029, 2998, 2980, 2922, 1601, 1549, 1465, 1444, 1372, 1277, 1226, 1208, 1175, 1134, 1102, 1082, 1020, 972, 904, 886, 847, 751, 736 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{30}H_{23}F_6NOP]^+$: 558.1416, found: 558.1423; **$[\alpha]_D^{20}$** = +113.9 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak ID , 4.6 x 250 mm; 20% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 5.5 min, $t_r$ (major) = 6.0 min), 89 : 11 *er*.



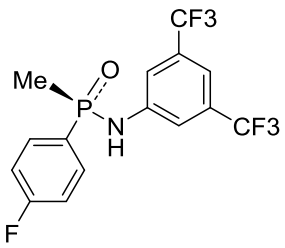

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.607 | BV | 0.1621 | 352.66534 | 33.68446 | 49.9274 |
| 2 | 6.155 | VB | 0.1821 | 353.69046 | 29.88302 | 50.0726 |



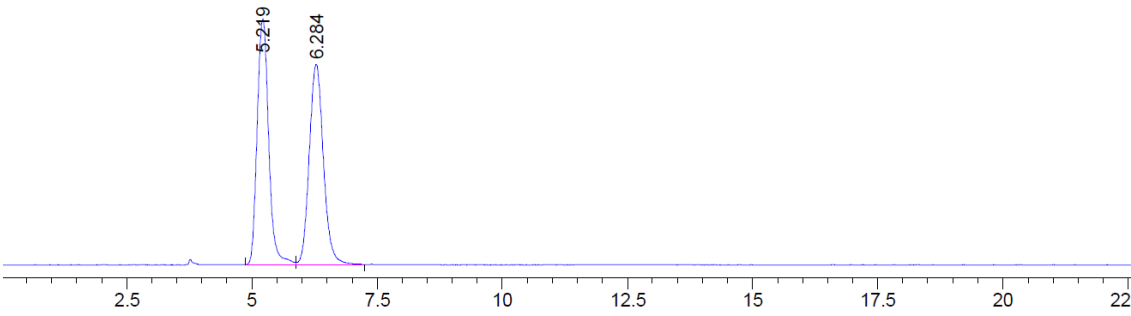

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.543 | VV | 0.1445 | 831.11206 | 89.32578 | 10.8904 |
| 2 | 6.056 | VB | 0.1683 | 6800.50635 | 618.62506 | 89.1096 |

**Recovered Starting Material**

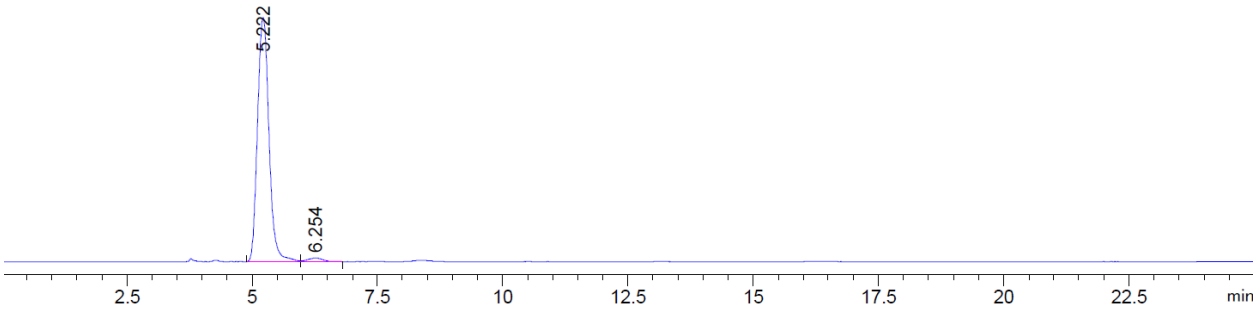
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-(4-fluorophenyl)-*P*-methylphosphinic amide (1c)**




(at 90 °C, 10.5 hours) obtained as a white crystal in 40% yield; $[\alpha]_D^{20}$ = -9.3 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak ID , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 5.2 min, $t_r$ (minor) = 6.2 min), 98 : 2 *er*. **S factor**: 32.



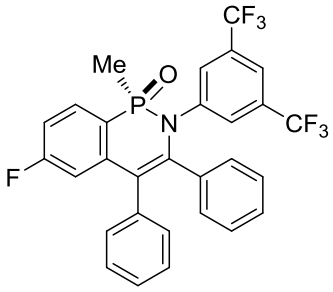

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.219 | BV | 0.2504 | 3526.02979 | 220.72365 | 49.9263 |
| 2 | 6.284 | VB | 0.3036 | 3536.44604 | 179.72728 | 50.0737 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.222 | BV | 0.2483 | 4459.46582 | 279.32181 | 97.9269 |
| 2 | 6.254 | VB | 0.2718 | 94.40646 | 4.30503 | 2.0731 |

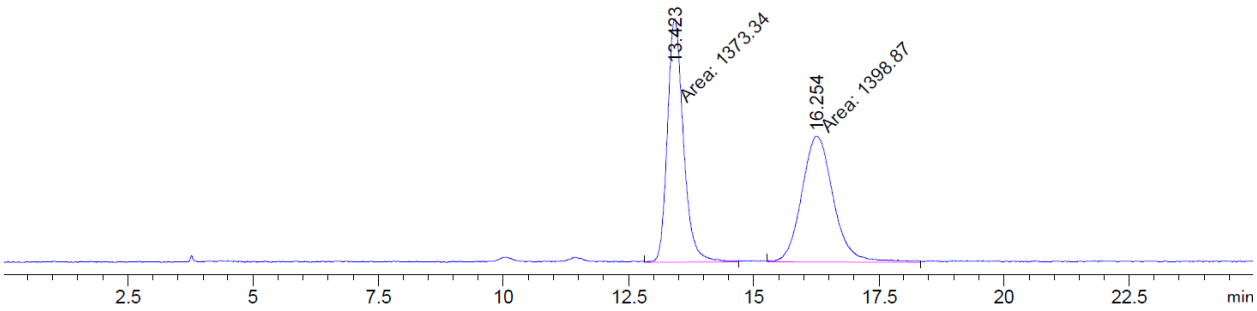
**Product**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-6-fluoro-1-methyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2c)**

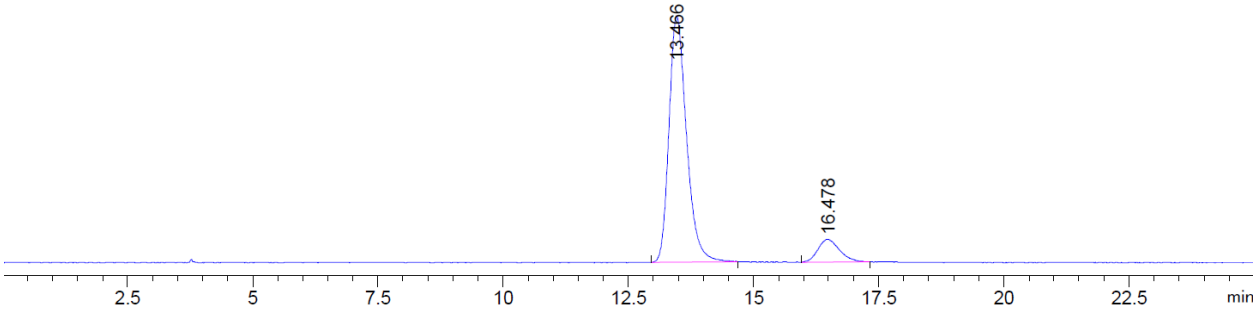



obtained as a white foam in 48% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.92 (ddd, *J* = 12.8, 8.4, 5.9 Hz, 1H), 7.62 (s, 2H), 7.49 (s, 1H), 7.34–7.13 (m, 4H), 7.00 (dd, *J* = 8.0, 1.8 Hz, 2H), 6.98–6.87 (m, 4H), 1.95 (d, *J* = 13.8 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 165.40 (dd, $J_{C\text{-}P}$ = 3.3 Hz, $J_{C\text{-}F}$ = 251.8 Hz), 141.11 (d, $J_{C\text{-}P}$ = 2.8 Hz), 140.80 (dd, $J_{C\text{-}P}$ = 7.4 Hz, $J_{C\text{-}F}$ = 8.6 Hz), 140.49, 136.82, 135.05 (d, $J_{C\text{-}P}$ = 3.7 Hz), 131.97 (q, $J_{C\text{-}F}$ = 33.8 Hz), 131.60, 131.46 (dd, $J_{C\text{-}P}$ = 9.4 Hz, $J_{C\text{-}F}$ = 12.0 Hz), 130.80, 128.48, 128.37, 128.15, 127.79, 127.57, 124.28 (d, $J_{C\text{-}P}$ = 2.5 Hz), 122.84 (q, $J_{C\text{-}F}$ = 273.0 Hz), 120.24 (dd, $J_{C\text{-}P}$ = 124.7, $J_{C\text{-}F}$ = 3.3 Hz), 119.56, 115.48 (dd, $J_{C\text{-}P}$ = 14.2 Hz, $J_{C\text{-}F}$ = 22.3 Hz), 114.14 (dd, $J_{C\text{-}P}$ = 10.3 Hz, $J_{C\text{-}F}$ = 23.8 Hz), 16.69 (d, $J_{C\text{-}P}$ = 95.4 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 25.08 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = - 63.07 (s, 6F) , -105.12 (s, 1F) ppm; **IR (ATR):** $\tilde{\nu}$ = 3164, 3060, 3029, 2988, 2919, 1587, 1467, 1444, 1402, 1371, 1335, 1276, 1208, 1176, 1133, 1100, 1077, 1019, 982, 912, 886, 876, 847, 808, 764, 751, 734 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{29}H_{20}F_7NOP]^+$: 562.1165, found: 562.1171; **$[\alpha]_D^{20}$** = +79.3 (c = 1.0, $CHCl_3$);

**eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak ID , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 13.5 min, $t_r$ (major) = 16.5 min), 90 : 10 *er*.



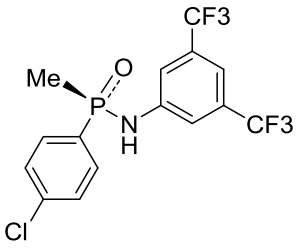

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.423 | MM | 0.3708 | 1373.33618 | 61.72043 | 49.5394 |
| 2 | 16.254 | MM | 0.7314 | 1398.87170 | 31.87466 | 50.4606 |



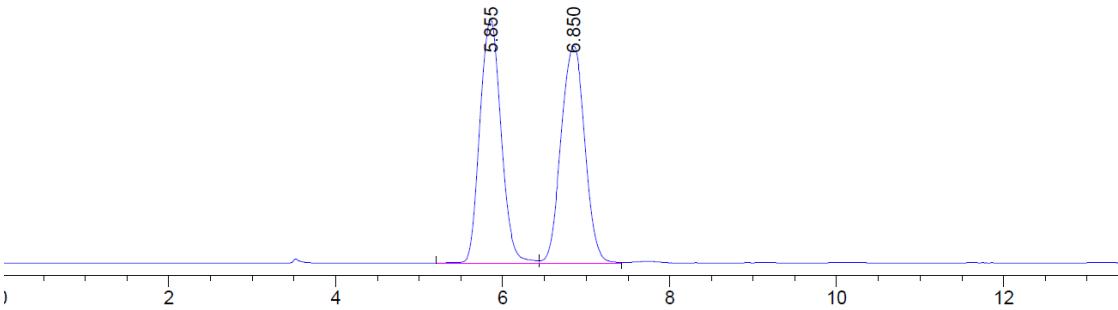

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.466 | BB | 0.3778 | 3150.00879 | 129.49130 | 89.7224 |
| 2 | 16.478 | BB | 0.3818 | 360.82932 | 11.96550 | 10.2776 |

**Recovered Starting Material**

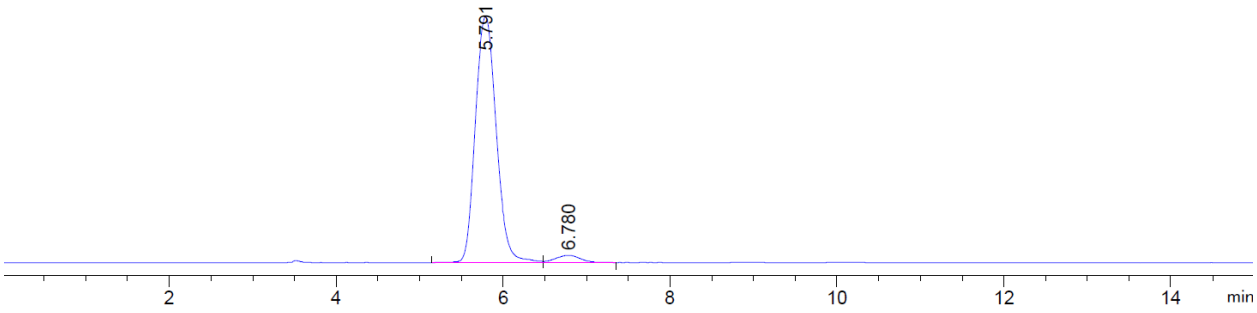
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-(4-chlorophenyl)-*P*-methylphosphinic amide (1d)**




(at 90 °C, 10.5 hours) obtained as a white crystal in 40% yield; $[\alpha]_D^{20}$ = -16.7 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IG , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 5.8 min, $t_r$ (minor) = 6.8 min), 97 : 3 *er*. **S factor**: 29.



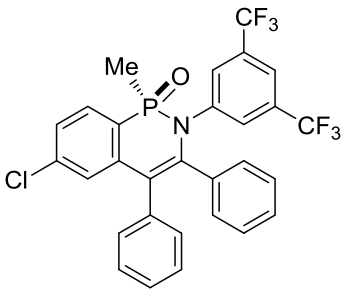

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.855 | VV | 0.2816 | 8678.91699 | 492.55948 | 50.1306 |
| 2 | 6.850 | VV | 0.3164 | 8633.67969 | 437.13086 | 49.8694 |



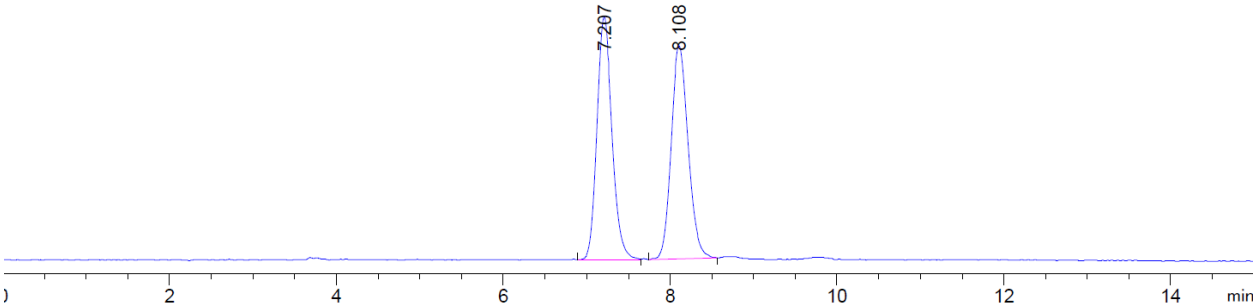

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.791 | BV | 0.2754 | 1.10749e4 | 635.15649 | 96.5282 |
| 2 | 6.780 | VB | 0.2669 | 398.32858 | 18.97264 | 3.4718 |

**Product**

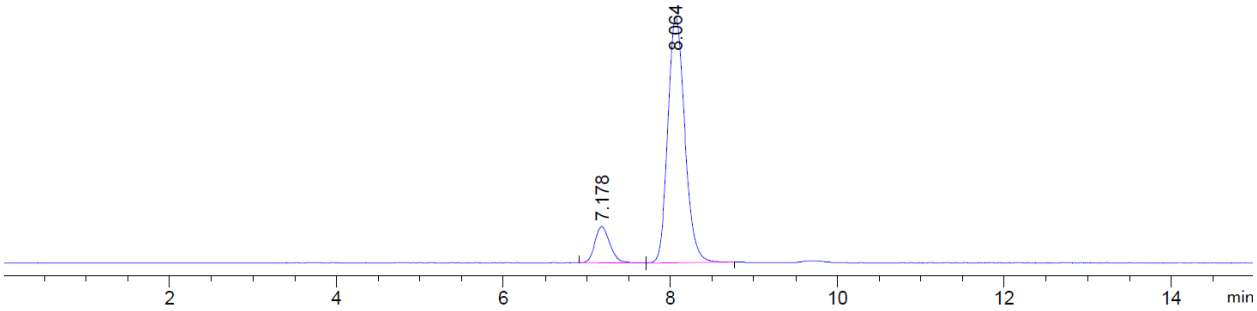
**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-6-chloro-1-methyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2d)**




obtained as a white foam in 45% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.85 (dd, *J* = 13.0, 8.1 Hz, 1H), 7.61 (s, 2H), 7.49 (s, 1H), 7.45 (dt, *J* = 8.1, 2.2 Hz, 1H), 7.31–7.16 (m, 6H), 7.03–6.98 (m, 2H), 6.97–6.87 (m, 3H), 1.96 (d, *J* = 13.8 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 141.04 (d, $J_{C\text{-}P}$ = 2.7 Hz), 140.56, 139.52 (d, $J_{C\text{-}P}$ = 7.0 Hz), 139.16 (d, $J_{C\text{-}P}$ = 3.5 Hz), 136.62, 135.02 (d, $J_{C\text{-}P}$ = 3.6 Hz), 132.00 (q, $J_{C\text{-}F}$ = 33.9 Hz), 131.63, 130.79, 130.26 (d, $J_{C\text{-}P}$ = 11.1 Hz), 128.51, 128.30, 128.18, 128.05, 127.80, 127.61, 127.24 (d, $J_{C\text{-}P}$ = 10.0 Hz), 124.32 (d, $J_{C\text{-}P}$ = 7.4 Hz), 122.84 (q, $J_{C\text{-}F}$ = 272.8 Hz), 122.41 (d, $J_{C\text{-}P}$ = 123.4 Hz), 119.57, 16.53 (d, $J_{C\text{-}P}$ = 95.7 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 25.02 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.06 ppm; **IR (ATR):** $\tilde{\nu}$ = 3059, 3027, 2924, 1603, 1578, 1541, 1488, 1460, 1444, 1370, 1332, 1274, 1219, 1173, 1130, 1101, 1075, 1016, 963, 908, 886, 875, 847, 820, 786, 764, 750, 732 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{29}H_{20}ClF_6NOP]^+$: 578.0870, found: 578.0869; **$[\alpha]_D^{20}$** = +59.5 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 7.2 min, $t_r$ (major) = 8.1 min), 89 : 11 *er*.



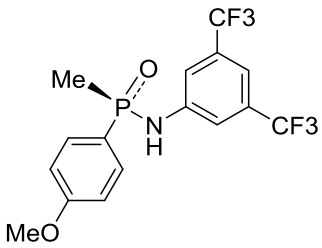

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.207 | BV | 0.1943 | 1028.12769 | 82.01434 | 50.2923 |
| 2 | 8.108 | BB | 0.2168 | 1016.17694 | 71.94894 | 49.7077 |



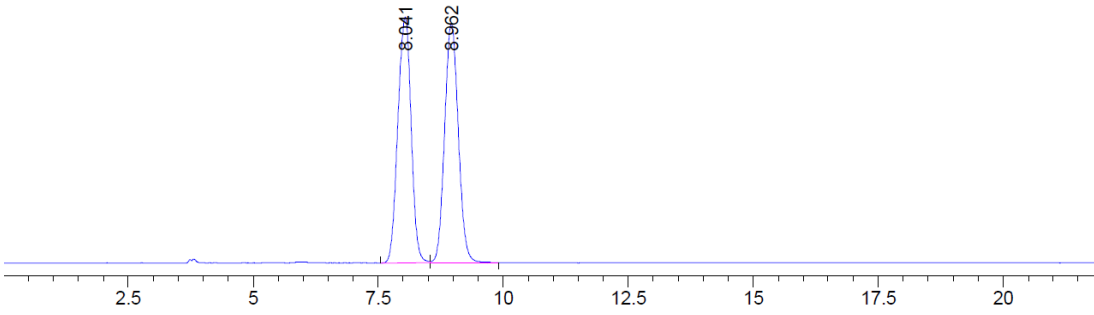

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.178 | BB | 0.1929 | 593.55261 | 47.78280 | 11.4875 |
| 2 | 8.064 | BB | 0.2181 | 4573.38721 | 325.10440 | 88.5125 |

**Recovered Starting Material**

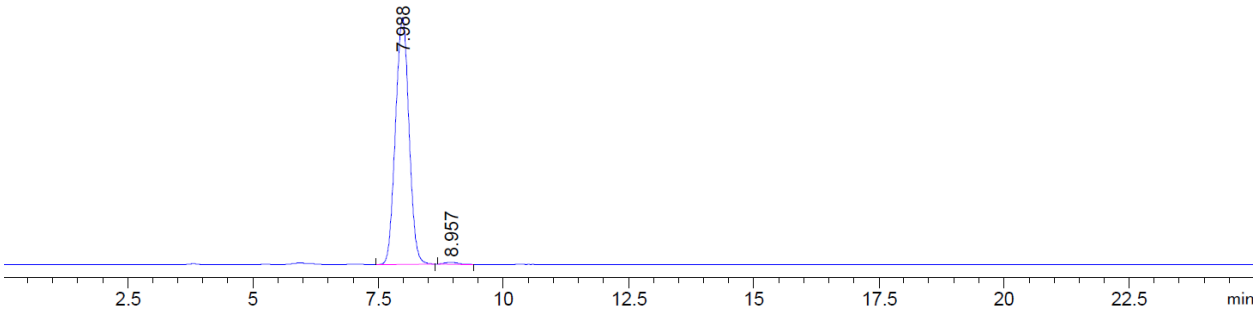
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-(4-methoxyphenyl)-*P*-methylphosphinic amide (1e)**




(at 90 °C, 8.5 hours) obtained as a white crystal in 42% yield; $[\alpha]_D^{20}$ = -12.3 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 8.0 min, $t_r$ (minor) = 9.0 min), 99 : 1 *er*. **S factor**: 50.



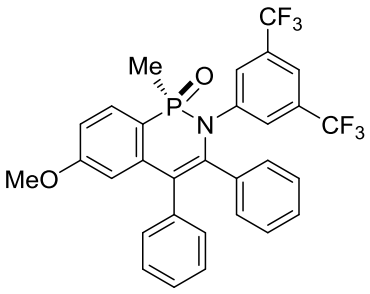

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.041 | BV | 0.2976 | 5036.11475 | 272.54730 | 49.9332 |
| 2 | 8.962 | VB | 0.3000 | 5049.58154 | 265.32434 | 50.0668 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.988 | BB | 0.2992 | 1.42786e4 | 760.10315 | 99.2991 |
| 2 | 8.957 | BB | 0.2391 | 100.78602 | 5.84594 | 0.7009 |

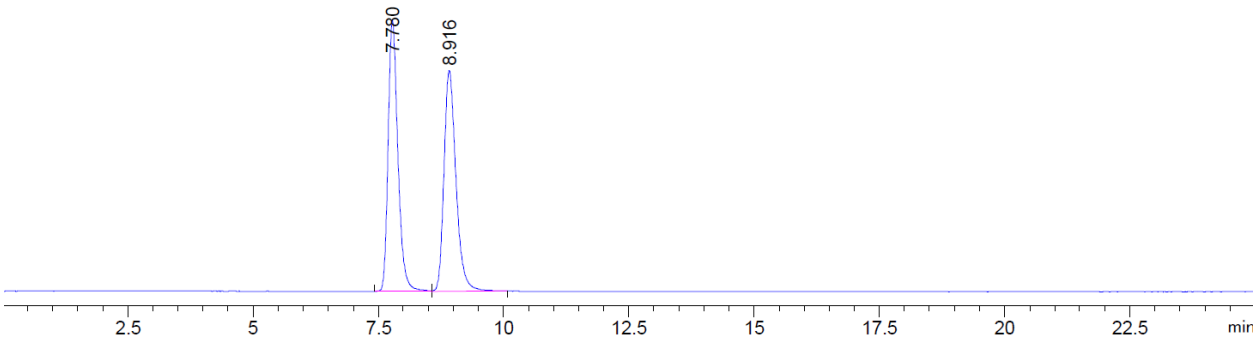
**Product**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-6-methoxy-1-methyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2e)**

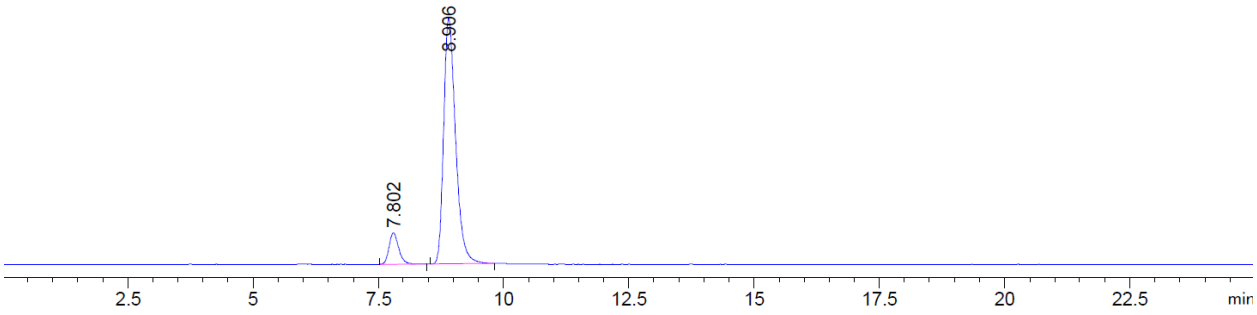



obtained as a white foam in 48% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.86 (dd, *J* = 12.9, 8.4 Hz, 1H), 7.62 (s, 2H), 7.46 (s, 1H), 7.29–7.15 (m, 5H), 7.04–6.97 (m, 3H), 6.97–6.85 (m, 3H), 6.75 (dd, *J* = 4.3, 2.4 Hz, 1H), 3.73 (s, 3H), 1.94 (d, *J* = 13.8 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 162.85 (d, $J_{C\text{-}P}$ = 3.0 Hz), 141.40 (d, $J_{C\text{-}P}$ = 2.5 Hz), 139.84 (d, $J_{C\text{-}P}$ = 7.4 Hz), 139.65, 137.34, 135.42 (d, $J_{C\text{-}P}$ = 3.7 Hz), 131.81 (q, $J_{C\text{-}F}$ = 33.9 Hz), 131.66, 130.86, 130.74, 128.28, 128.15, 127.91, 127.69, 127.30, 125.17 (d, $J_{C\text{-}P}$ = 7.4 Hz), 122.91 (q, $J_{C\text{-}F}$ = 272.9 Hz), 119.16, 116.47 (d, $J_{C\text{-}P}$ = 127.8 Hz), 113.66 (d, $J_{C\text{-}P}$ = 14.2 Hz), 112.95 (d, $J_{C\text{-}P}$ = 10.0 Hz), 55.40, 16.89 (d, $J_{C\text{-}P}$ = 95.5 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 26.15 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.04 ppm; **IR (ATR):** $\tilde{\nu}$ = 3445, 3058, 3026, 2974, 2940, 2917, 2840, 1590, 1553, 1465, 1443, 1410, 1371, 1336, 1275, 1220, 1172, 1130, 1104, 1078, 1014, 970, 885, 847, 801, 751, 737, 724 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{30}H_{23}F_6NO_2P]^+$: 574.1365, found: 574.1365; **$[\alpha]_D^{20}$** = +62.6 (c =

1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak ID , 4.6 x 250 mm; 20% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 7.8 min, $t_r$ (major) = 8.9 min), 91 : 9 *er*.



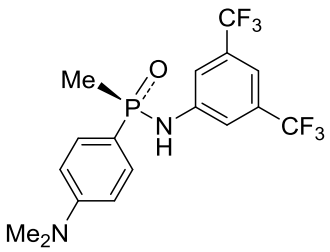

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.780 | BV | 0.2059 | 3726.73462 | 275.36026 | 50.0094 |
| 2 | 8.916 | VB | 0.2541 | 3725.33032 | 223.89194 | 49.9906 |



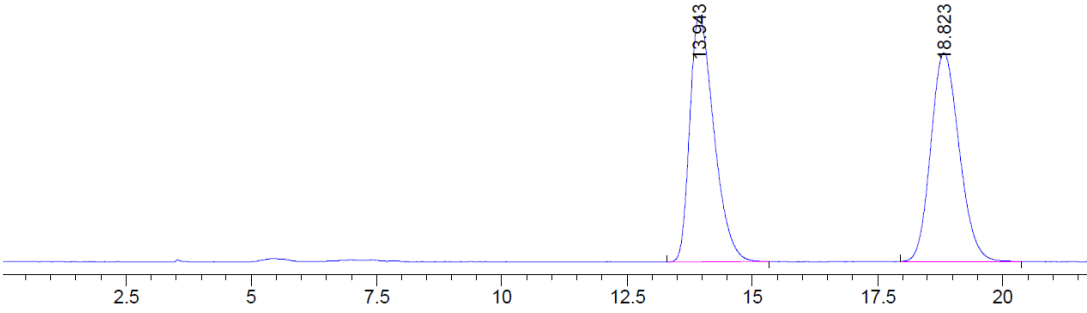

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.802 | BB | 0.2039 | 770.63818 | 57.68357 | 9.3468 |
| 2 | 8.906 | BB | 0.2526 | 7474.28174 | 452.68921 | 90.6532 |

**Recovered Starting Material**

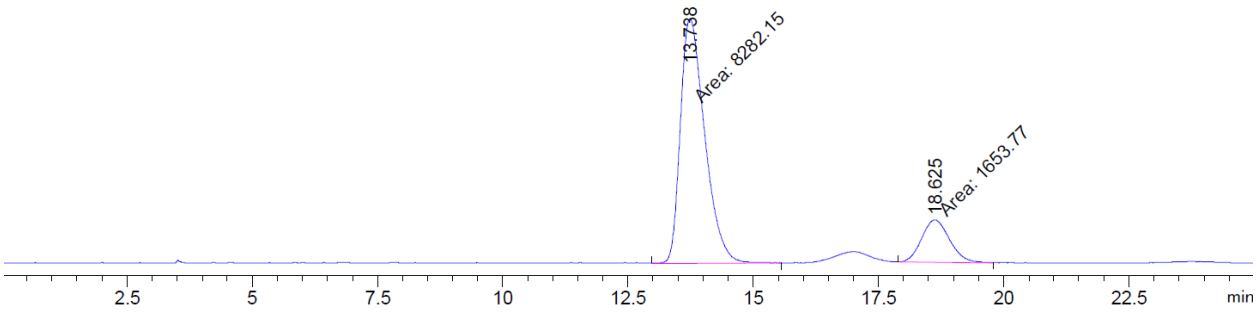
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-(4-(dimethylamino)phenyl)-*P*-methylphosphinic amide (1f)**




(at 90 °C, 9.5 hours) obtained as a white crystal in 50% yield; $[\alpha]_D^{20}$ = +13.9 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IG , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 13.7 min, $t_r$ (minor) = 18.6 min), 83 : 17 *er*. **S factor**: 43.



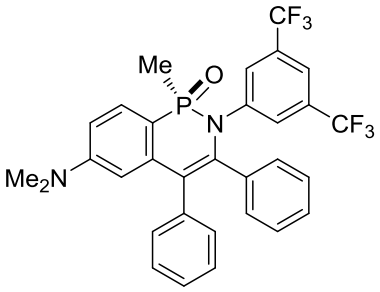

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.943 | BB | 0.5198 | 9820.55566 | 292.40640 | 50.0766 |
| 2 | 18.823 | BB | 0.5985 | 9790.50586 | 248.06030 | 49.9234 |



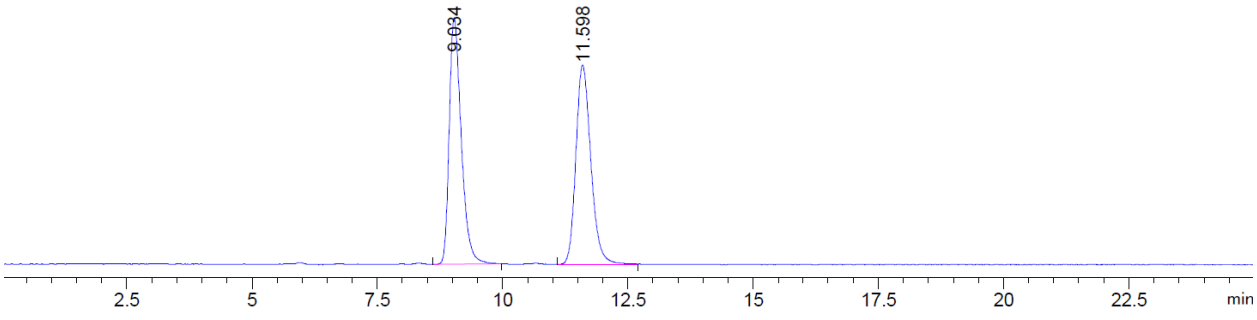

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.738 | MM | 0.5620 | 8282.14551 | 245.60762 | 83.3556 |
| 2 | 18.625 | MM | 0.6476 | 1653.77454 | 42.55993 | 16.6444 |

**Product**

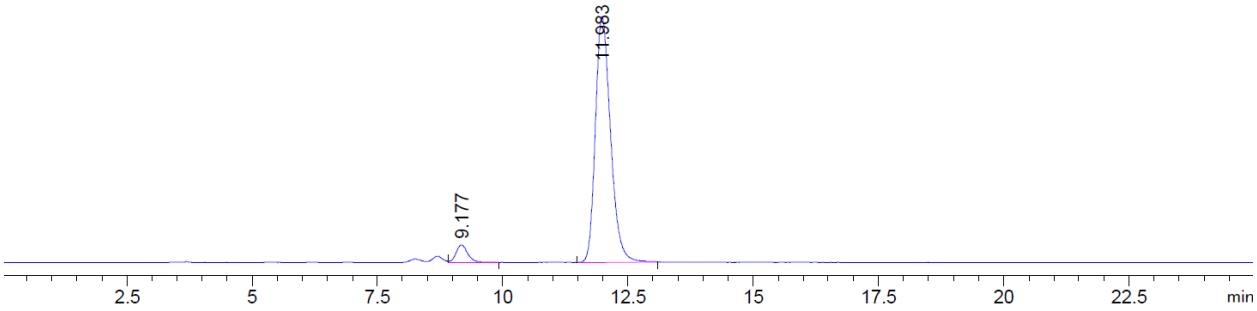
**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-6-(dimethylamino)-1-methyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2f)**




obtained as a white foam in 36% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.77 (dd, *J* = 12.7, 8.6 Hz, 1H), 7.64 (s, 2H), 7.45 (s, 1H), 7.31–7.15 (m, 5H), 7.07–7.00 (m, 2H), 6.98–6.85 (m, 3H), 6.79 (dt, *J* = 8.6, 2.3 Hz, 1H), 6.49 (dd, *J* = 4.5, 2.4 Hz, 1H), 2.90 (s, 6H), 1.95 (d, *J* = 13.8 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 152.73 (d, $J_{C\text{-}P}$ = 2.2 Hz), 141.61 (d, $J_{C\text{-}P}$ = 2.5 Hz), 139.01 (d, *J* = 7.5 Hz), 138.98, 137.78, 135.73 (d, $J_{C\text{-}P}$ = 3.6 Hz), 131.65, 131.56 (q, $J_{C\text{-}F}$ = 33.6 Hz), 130.86, 130.13 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.05, 127.81, 127.68, 127.58, 127.06, 126.12 (d, $J_{C\text{-}P}$ = 7.4 Hz), 122.94 (q, $J_{C\text{-}F}$ = 273.0 Hz), 118.69, 111.47 (d, $J_{C\text{-}P}$ = 14.0 Hz), 110.73 (d, $J_{C\text{-}P}$ = 133.4 Hz), 110.02 (d, $J_{C\text{-}P}$ = 9.6 Hz), 40.05, 17.13 (d, $J_{C\text{-}P}$ = 95.3 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 27.28 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -62.97 ppm; **IR (ATR):** $\tilde{\nu}$ = 3423, 3056, 3026, 2979, 2921, 1681, 1591, 1542, 1488, 1465, 1444, 1409, 1368, 1274, 1221, 1171, 1129, 1104, 1072, 1016, 982, 948, 915, 878, 847, 791, 752, 734, 723 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{31}H_{26}F_6N_2OP]^+$: 587.1681, found: 587.1682; **$[\alpha]_D^{20}$** = +50.9 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak IF , 4.6 x 250 mm; 20% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 9.2 min, $t_r$ (major) = 12.0 min), 95 : 5 *er*.



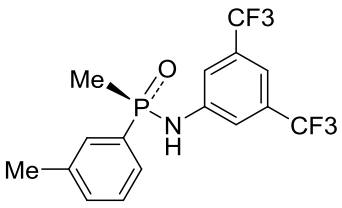
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.034 | BB | 0.2550 | 5267.87012 | 315.18973 | 49.8297 |
| 2 | 11.598 | VV | 0.3205 | 5303.88281 | 255.20135 | 50.1703 |



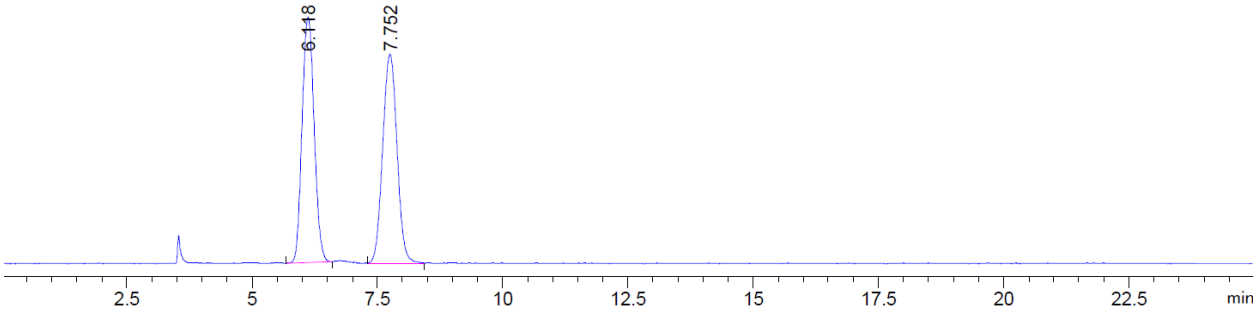

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.177 | VB | 0.2526 | 805.72748 | 49.30999 | 5.3191 |
| 2 | 11.983 | BB | 0.3253 | 1.43421e4 | 682.13293 | 94.6809 |

**Recovered Starting Material**

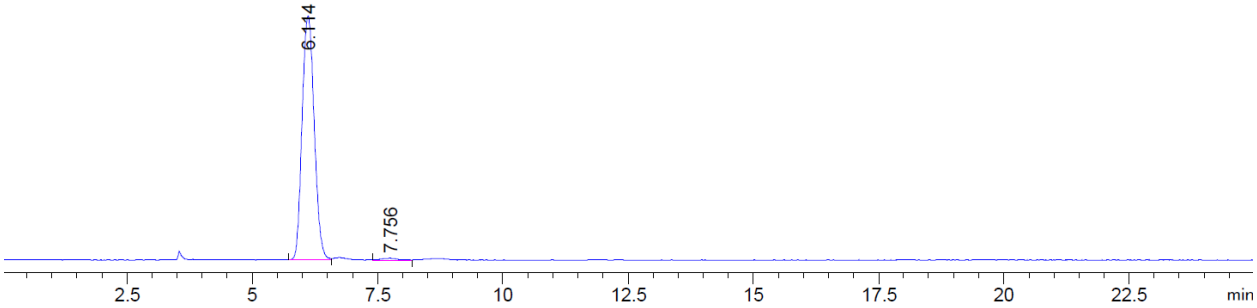
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-(*m*-tolyl)phosphinic amide (1g)**




(at 90 °C, 10.5 hours) obtained as a white crystal in 38% yield; $[\alpha]_D^{20}$ = -4.4 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IG , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 6.1 min, $t_r$ (minor) = 7.8 min), 99 : 1 *er*. **S factor**: 26.



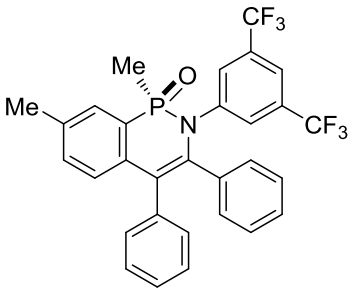
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.118 | BB | 0.2654 | 1649.15393 | 98.45816 | 49.7661 |
| 2 | 7.752 | BB | 0.3138 | 1664.65454 | 83.79720 | 50.2339 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.114 | BV | 0.2685 | 6028.13770 | 357.90753 | 99.1476 |
| 2 | 7.756 | VB | 0.2479 | 51.82730 | 2.58547 | 0.8524 |

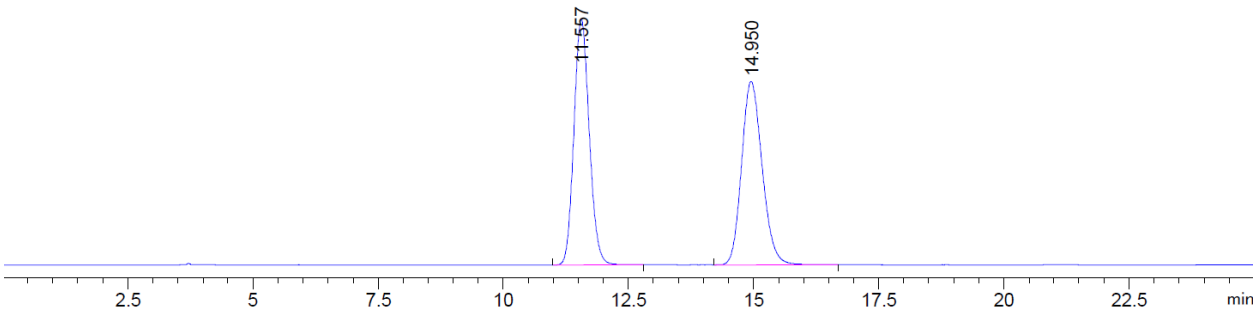
**Product**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-1,7-dimethyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2g)**

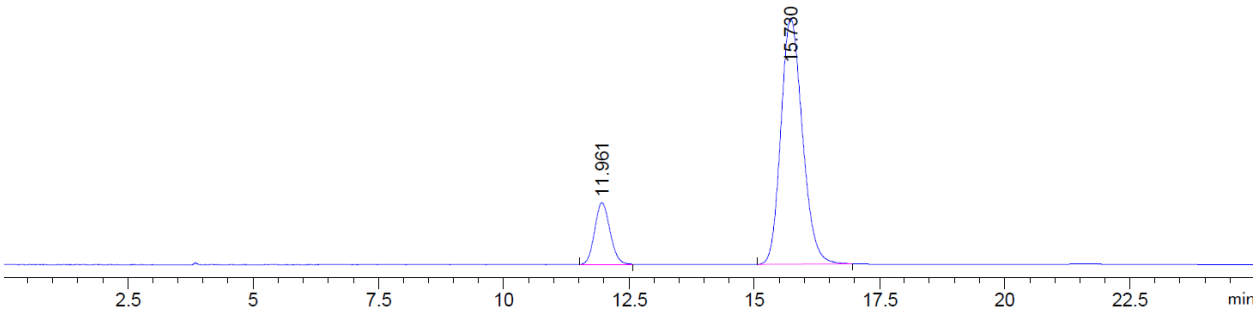



obtained as a white foam in 53% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.77 (dd, *J* = 13.8, 1.9 Hz, 1H), 7.66 (s, 2H), 7.50 (s, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.32–7.16 (m, 6H), 7.11–7.02 (m, 2H), 7.02–6.88 (m, 3H), 2.47 (s, 3H), 2.01 (d, *J* = 13.8 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 141.37 (d, $J_{C-P}$ = 2.6 Hz), 138.35 (d, $J_{C-P}$ = 13.2 Hz), 138.02, 137.43, 135.34 (d, $J_{C-P}$ = 3.6 Hz), 135.05 (d, $J_{C-P}$ = 6.3 Hz), 133.35 (d, $J_{C-P}$ = 2.5 Hz), 131.78 (q, $J_{C-F}$ = 34.2 Hz), 131.61, 130.87, 128.86 (d, $J_{C-P}$ = 10.6 Hz), 128.22, 127.91, 127.86, 127.68, 127.52 (d, $J_{C-P}$ = 10.1 Hz), 127.23, 126.08 (d, $J_{C-P}$ = 7.9 Hz), 124.21 (d, $J_{C-P}$ = 121.0 Hz), 122.92 (q, $J_{C-F}$ = 272.9 Hz), 119.03, 21.28, 16.49 (d, $J_{C-P}$ = 94.1 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 26.26 ppm; **$^{19}$F NMR** (376 MHz,

Chloroform-*d*) δ = -63.03 ppm; **IR (ATR):** $\tilde{\nu}$ = 3058, 3026, 2986, 2922, 2866, 2233, 1613, 1603, 1484, 1464, 1444, 1371, 1331, 1275, 1246, 1212, 1173, 1131, 1098, 1074, 1015, 955, 898, 872, 838, 764, 752, 731 $cm^{-1}$; **HRMS (ESI)** calculated for $[C_{30}H_{23}F_6NOP]^+$: 558.1416, found: 558.1418; **$[\alpha]_D^{20}$** = +94.7 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (minor) = 12.0 min, $t_r$ (major) = 15.7 min), 85 : 15 *er*.



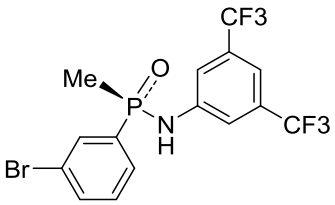

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.557 | BB | 0.3295 | 6208.52246 | 292.65939 | 49.9245 |
| 2 | 14.950 | BB | 0.4432 | 6227.30176 | 218.01648 | 50.0755 |



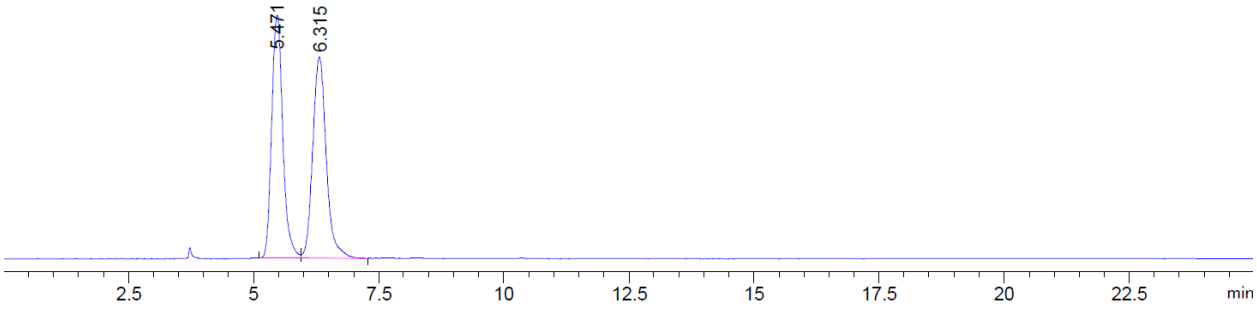

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.961 | BB | 0.3298 | 1078.44788 | 50.77315 | 15.0790 |
| 2 | 15.730 | BB | 0.4596 | 6073.54932 | 202.69971 | 84.9210 |

**Recovered Starting Material**

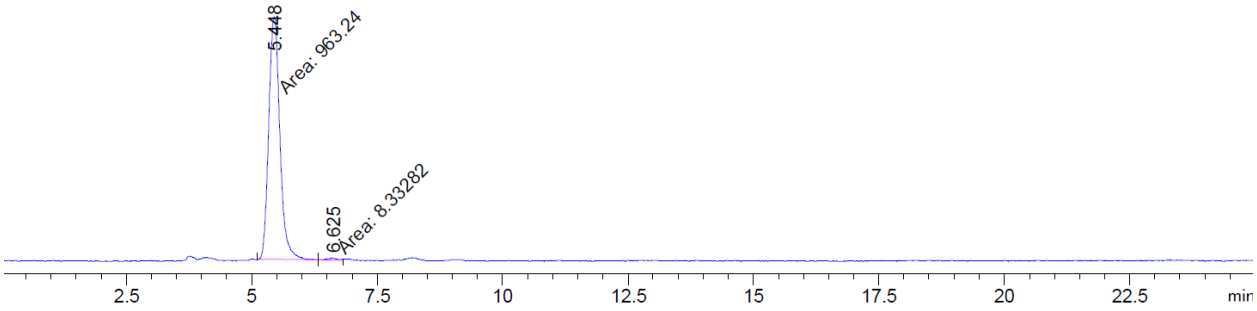
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-(3-bromophenyl)-*P*-methylphosphinic amide (1h)**




(at 90 °C, 14 hours) obtained as a white crystal in 38% yield; $[\alpha]_D^{20}$ = -6.1 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak ID , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 5.4 min, $t_r$ (minor) = 6.6 min), 99 : 1 *er*. **S factor**: 50.



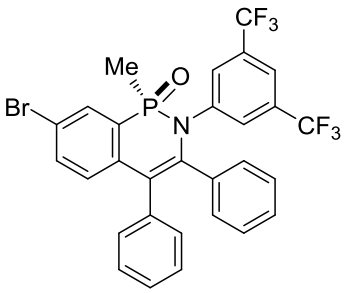

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.471 | BV | 0.2397 | 4016.32324 | 260.75629 | 49.6522 |
| 2 | 6.315 | VB | 0.2901 | 4072.58203 | 215.91635 | 50.3478 |



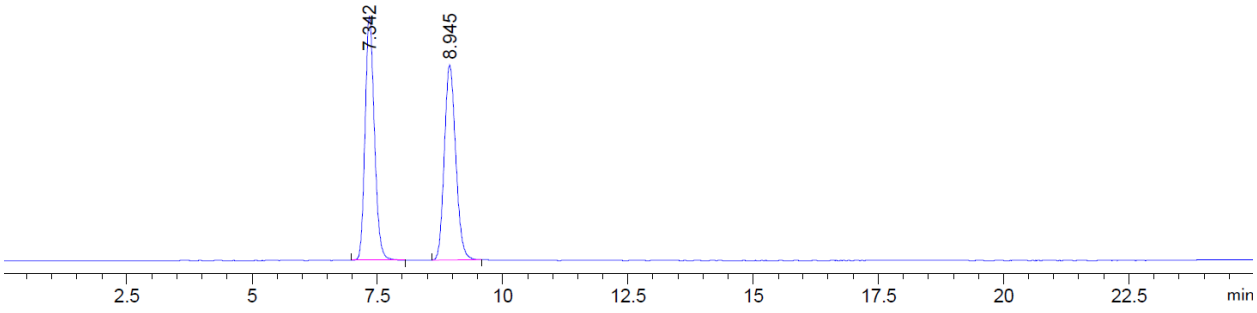

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.448 | MF | 0.2581 | 963.24011 | 62.20800 | 99.1423 |
| 2 | 6.625 | FM | 0.2536 | 8.33282 | 5.47712e-1 | 0.8577 |

**Product**

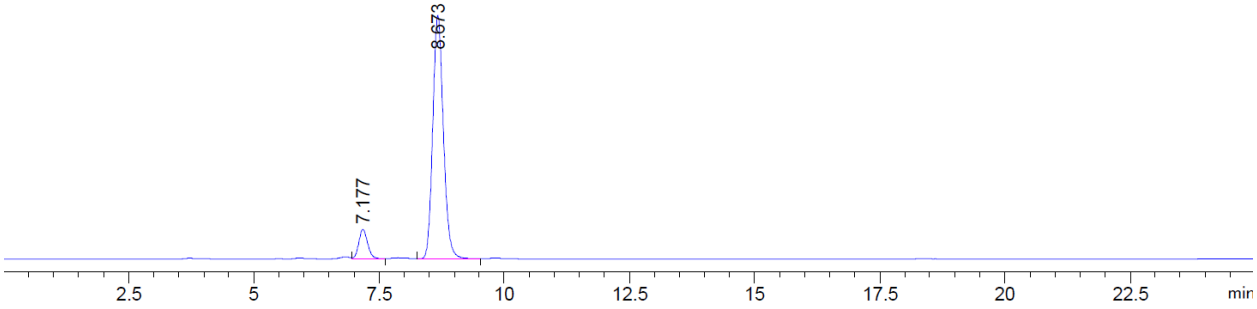
**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-7-bromo-1-methyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2h)**




obtained as a white foam in 42% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 8.02 (dd, *J* = 13.4, 2.1 Hz, 1H), 7.66–7.55 (m, 3H), 7.49 (s, 1H), 7.30–7.16 (m, 5H), 7.13 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.05–6.98 (m, 2H), 6.98–6.87 (m, 3H), 1.97 (d, *J* = 13.9 Hz, 3H) ppm; **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ = 141.01 , 139.50, 136.83, 136.40, 135.44, 134.99, 131.99 (q, $J_{C\text{-}F}$ = 33.6 Hz), 131.59, 131.32 (d, $J_{C\text{-}P}$ = 10.9 Hz), 130.77, 129.30 (d, $J_{C\text{-}P}$ = 10.2 Hz), 128.43, 128.20, 128.16, 127.80, 127.52, 126.08 (d, $J_{C\text{-}P}$ = 119.1 Hz), 124.93 (d, $J_{C\text{-}P}$ = 8.2 Hz), 122.83 (q, $J_{C\text{-}F}$ = 273.3 Hz), 121.98 (d, *J* = 16.6 Hz), 119.56, 16.35 (d, $J_{C\text{-}P}$ = 94.9 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 23.84 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.06 ppm; **IR (ATR):** $\tilde{\nu}$ = 3080, 3060, 3031, 2918, 1686, 1615, 1604, 1590, 1489, 1467, 1444, 1371, 1332, 1277, 1221, 1177, 1134, 1096, 1075, 1017, 954, 887, 847, 831, 792, 754, 724 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{29}H_{20}{}^{79}BrF_6NOP]^+$: 622.0365, found: 622.0362; **$[\alpha]_D^{20}$** = +90.8 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 7.2 min, $t_r$ (major) = 8.7 min), 91 : 9 *er*.



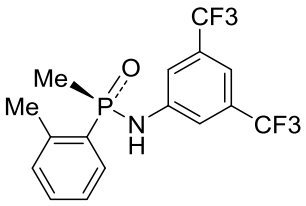
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.342 | BB | 0.1989 | 2684.66138 | 207.60201 | 50.5618 |
| 2 | 8.945 | BB | 0.2449 | 2625.00146 | 165.65732 | 49.4382 |



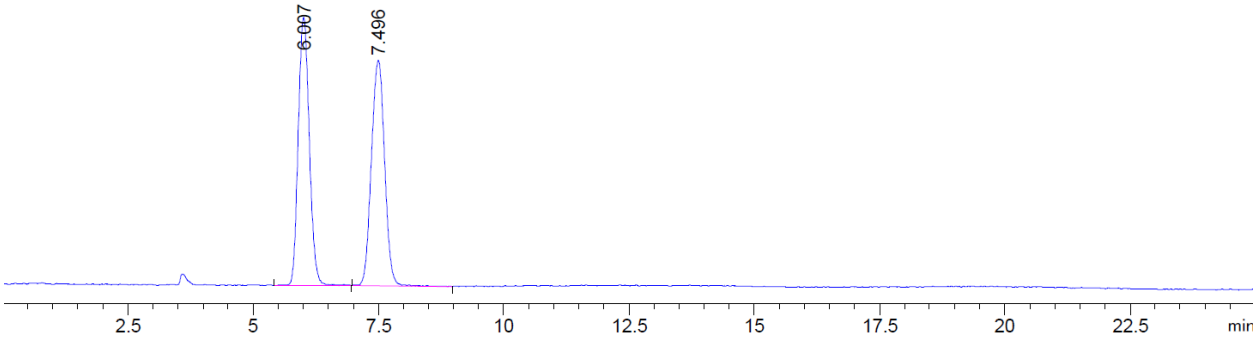

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.177 | VB | 0.1910 | 444.16437 | 36.24535 | 9.1555 |
| 2 | 8.673 | BB | 0.2273 | 4407.18457 | 300.09439 | 90.8445 |

**Recovered Starting Material**

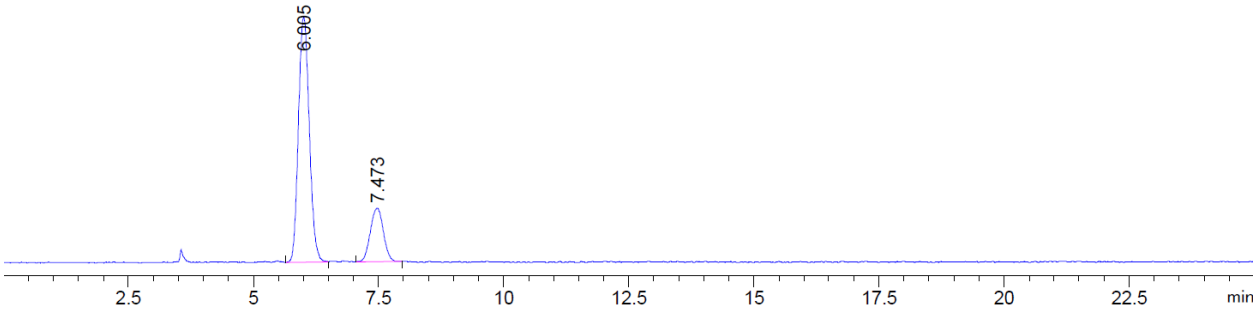
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-(*o*-tolyl)phosphinic amide (1i)**




(at 90 °C, 10 hours) obtained as a white crystal in 44% yield; $[\alpha]_D^{20}$ = -12.9 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IG , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 6.0 min, $t_r$ (minor) = 7.5 min), 79 : 21 *er*. **S factor**: 5.



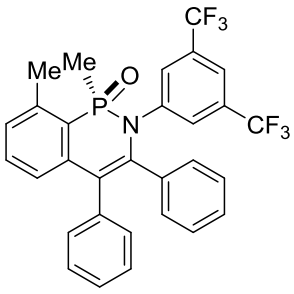
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.007 | BB | 0.2438 | 641.63037 | 41.62584 | 49.8183 |
| 2 | 7.496 | BB | 0.2950 | 646.31116 | 35.06307 | 50.1817 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.005 | BB | 0.2401 | 824.74060 | 54.63486 | 79.2592 |
| 2 | 7.473 | BB | 0.2872 | 215.82027 | 11.92446 | 20.7408 |

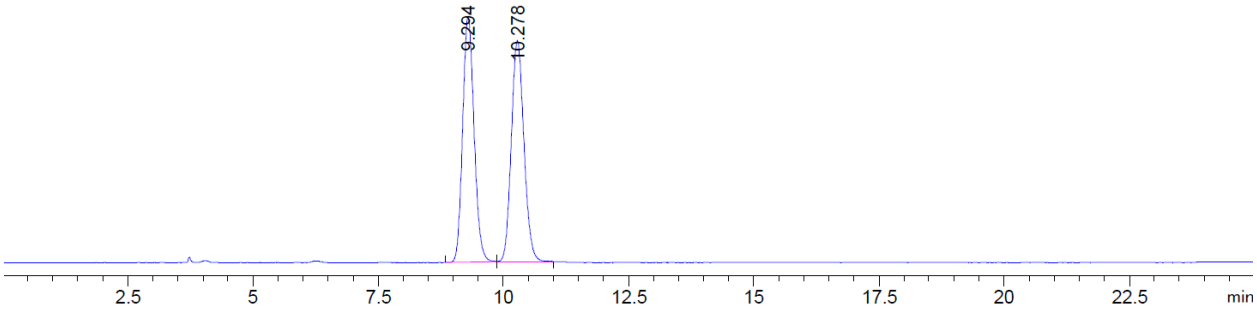
**Product**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-1,8-dimethyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2i)**

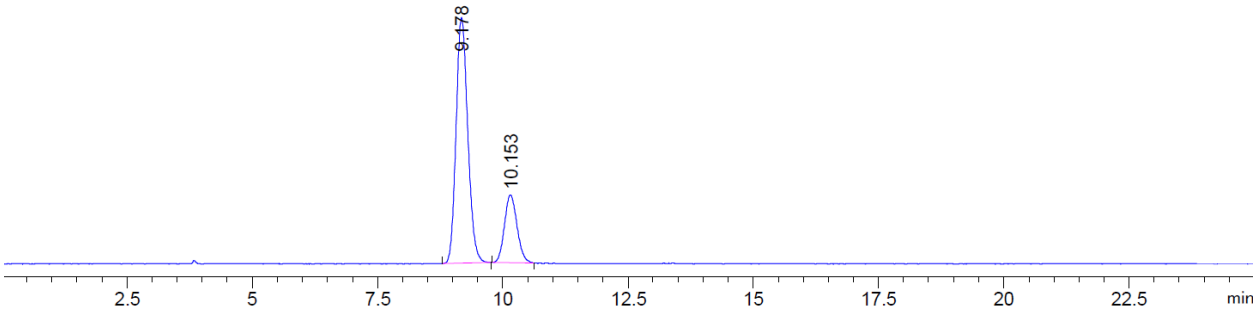



obtained as a white foam in 42% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.62 (s, 2H), 7.44 (s, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.29–7.17 (m, 6H), 7.11 (dd, *J* = 8.1, 4.9 Hz, 1H), 7.06–7.00 (m, 2H), 6.98–6.86 (m, 3H), 2.82 (d, *J* = 1.6 Hz, 3H), 2.04 (d, *J* = 13.6 Hz, 3H) ppm; **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ = 141.31 (d, $J_{C-P}$ = 9.9 Hz), 141.07 (d, $J_{C-P}$ = 2.4 Hz), 139.06 (d, $J_{C-P}$ = 7.3 Hz), 138.50, 137.81, 135.31 (d, $J_{C-P}$ = 3.6 Hz), 132.05 (d, $J_{C-P}$ = 2.2 Hz), 131.75, 131.57 (q, $J_{C-F}$ = 33.6 Hz), 130.99 (d, $J_{C-P}$ = 12.3 Hz), 130.63, 128.21, 128.19, 128.00, 127.71, 127.30, 127.19 (d, $J_{C-P}$ = 8.2 Hz), 125.95 (d, $J_{C-P}$ = 9.3 Hz), 123.12 (d, $J_{C-P}$ = 115.8 Hz), 123.01 (q, $J_{C-F}$ = 272.9 Hz), 118.92, 21.60 (d, $J_{C-P}$ = 4.0 Hz), 17.94 (d, $J_{C-P}$ = 91.2 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 29.69 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.00

ppm; **IR (ATR):** $\tilde{\nu}$ = 3056, 3027, 2980, 2930, 1701, 1684, 1606, 1594, 1579, 1560, 1489, 1463, 1454, 1407, 1370, 1274, 1225, 1170, 1126, 1103, 1074, 1013, 978, 917, 879, 846, 794, 763, 747, 735, 713 $cm^{-1}$; **HRMS (ESI)** calculated for $[C_{30}H_{23}F_6NOP]^+$: 558.1416, found: 558.1421; **$[\alpha]_D^{20}$** = +66.3 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 5:1); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 9.2 min, $t_r$ (major) = 10.2 min), 77 : 23 *er*.



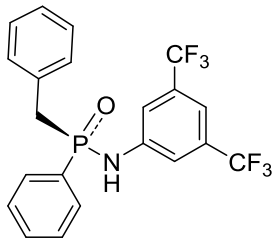

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.294 | BB | 0.2441 | 998.19250 | 63.24455 | 50.0237 |
| 2 | 10.278 | BB | 0.2720 | 997.24634 | 57.01938 | 49.9763 |



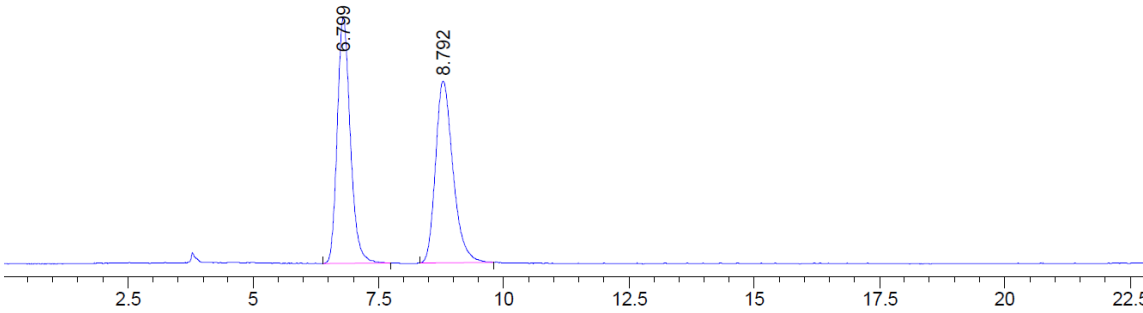

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.178 | BB | 0.2512 | 1978.88464 | 122.01922 | 77.0020 |
| 2 | 10.153 | BV | 0.2802 | 591.02887 | 33.77089 | 22.9980 |

**Recovered Starting Material**

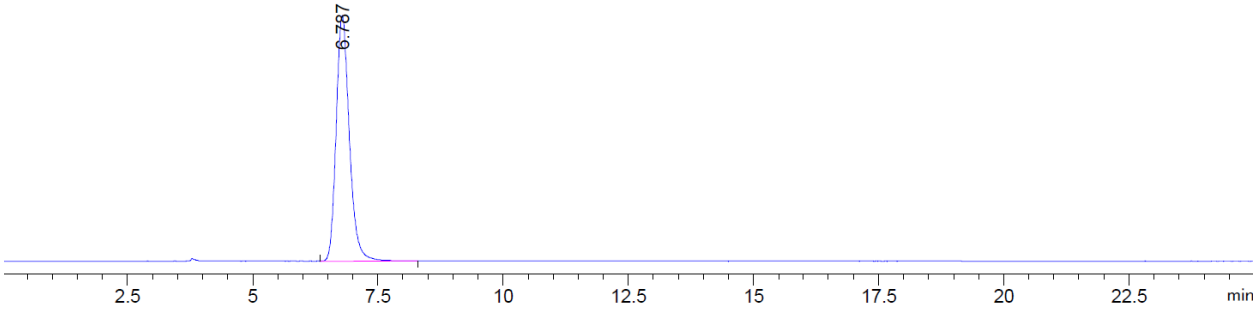
**(*S*)-*P*-Benzyl-*N*-(3,5-bis(trifluoromethyl)phenyl)-*P*-phenylphosphinic amide (1j)**




(at 90 °C, 4 hours) obtained as a white crystal in 37% yield; $[\alpha]_D^{20}$ = -4.5 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak ID , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 6.8 min, $t_r$ (minor) = 8.8 min), >99.5 : 0.5 *er*. **S factor**: 24.



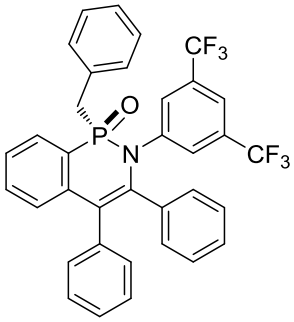

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.799 | BB | 0.2800 | 1740.90613 | 95.81599 | 50.3248 |
| 2 | 8.792 | BB | 0.3690 | 1718.43762 | 70.84932 | 49.6752 |



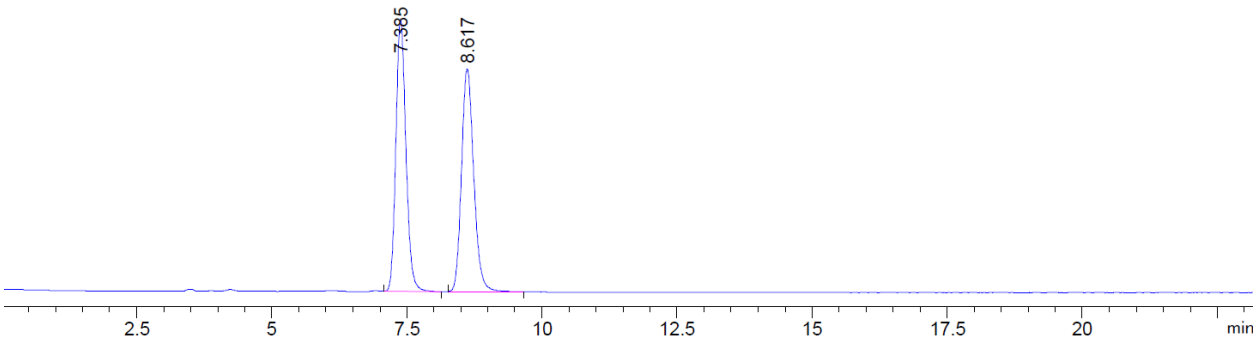
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.787 | BB | 0.2818 | 6477.77734 | 353.51324 | 100.0000 |

**Product**

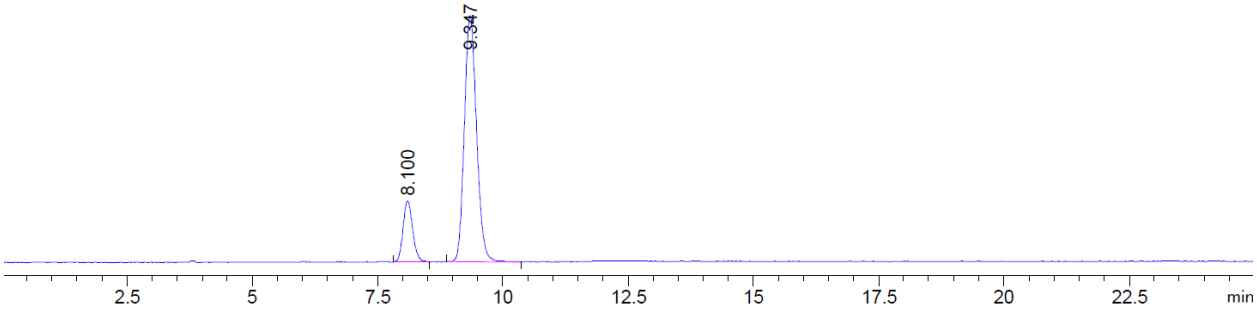
**(*R*)-1-Benzyl-2-(3,5-bis(trifluoromethyl)phenyl)-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2j)**




obtained as a white foam in 53% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.80 (ddd, *J*=12.5, 7.5, 1.4 Hz, 1H), 7.54 (t, *J*=7.7 Hz, 1H), 7.47–7.23 (m, 15H), 7.00–6.88 (m, 5H), 3.76–3.57 (m, 2H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 140.40 (d, $J_{C\text{-}P}$ = 1.6 Hz), 139.72, 138.29 (d, $J_{C\text{-}P}$ = 7.5 Hz), 137.41, 135.01 (d, $J_{C\text{-}P}$ = 4.0 Hz), 132.60 (d, $J_{C\text{-}P}$ = 2.3 Hz), 131.84, 131.34 (q, $J_{C\text{-}F}$ = 33.6 Hz), 131.17, 130.48 (d, $J_{C\text{-}P}$ = 8.2 Hz), 130.33 (d, $J_{C\text{-}P}$ = 6.2 Hz), 129.56 (d, $J_{C\text{-}P}$ = 8.5 Hz), 128.87 (d, $J_{C\text{-}P}$ = 2.9 Hz), 128.38, 128.31, 127.96, 127.87 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.67 (d, $J_{C\text{-}P}$ = 3.3 Hz), 127.59, 127.34, 127.00 (d, $J_{C\text{-}P}$ = 9.8 Hz), 125.96 (d, $J_{C\text{-}P}$ = 7.5 Hz), 122.91 (q, $J_{C\text{-}F}$ = 272.9 Hz), 122.72 (d, $J_{C\text{-}P}$ = 116.7 Hz), 118.84 , 37.90 (d, $J_{C\text{-}P}$ = 84.8 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 27.98 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.02 ppm; **IR (ATR):** $\tilde{\nu}$ = 3060, 3028, 2900, 1614, 1602, 1586, 1494, 1465, 1443, 1370, 1275, 1222, 1173, 1130, 1095, 1078, 1013, 953, 914, 887, 848, 777, 758, 738, 720 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{35}H_{25}F_6NOP]^+$: 620.1572, found: 620.1593; **$[\alpha]_D^{20}$** = +211.3 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 8.1 min, $t_r$ (major) = 9.3 min), 84 : 16 *er*.



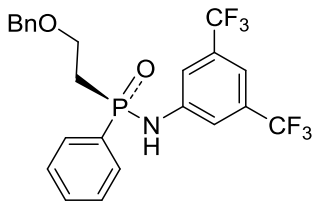
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.385 | BB | 0.2010 | 1871.89575 | 144.60474 | 50.0191 |
| 2 | 8.617 | BB | 0.2438 | 1870.46814 | 118.72016 | 49.9809 |



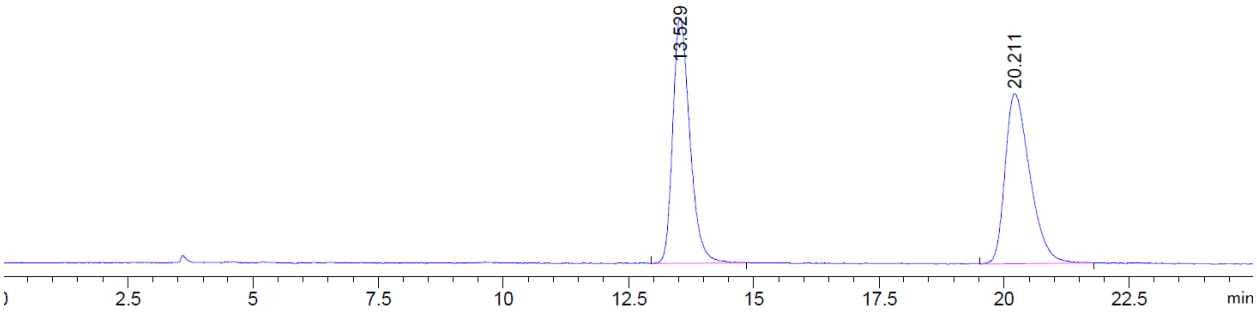

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.100 | BB | 0.2067 | 406.79999 | 30.67646 | 16.3259 |
| 2 | 9.347 | BB | 0.2630 | 2084.94946 | 123.49368 | 83.6741 |

**Recovered Starting Material**

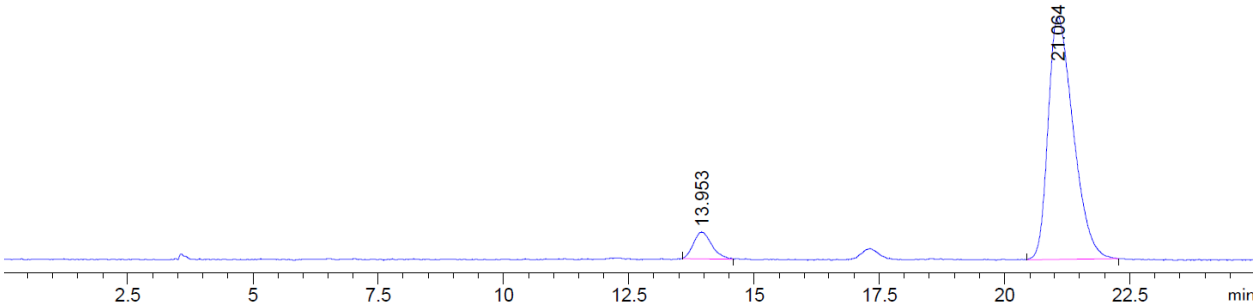
**(*S*)-*P*-(2-(Benzyloxy)ethyl)-*N*-(3,5-bis(trifluoromethyl)phenyl)-*P*-phenylphosphinic amide (1k)**




(at 90 °C, 6.5 hours) obtained as a white crystal in 44% yield; $[\alpha]_D^{20}$ = +33.3 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IF , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (minor) = 14.0 min, $t_r$ (major) = 21.0 min), 93 : 7 *er*. **S factor**: 29.



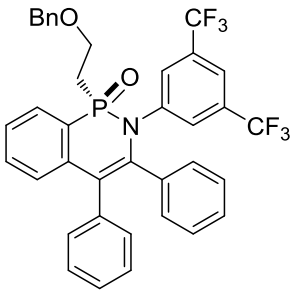
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.529 | BB | 0.3619 | 1123.16968 | 47.14782 | 49.9377 |
| 2 | 20.211 | BB | 0.5224 | 1125.97424 | 32.64282 | 50.0623 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.953 | BB | 0.3199 | 125.47073 | 4.98005 | 7.3557 |
| 2 | 21.064 | BB | 0.5222 | 1580.28516 | 45.38279 | 92.6443 |

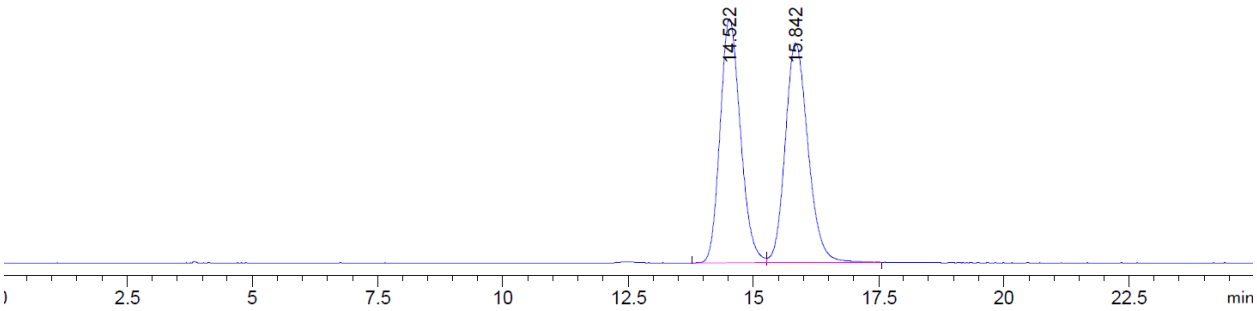
**Product**

**(*R*)-1-(2-(Benzyloxy)ethyl)-2-(3,5-bis(trifluoromethyl)phenyl)-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2k)**

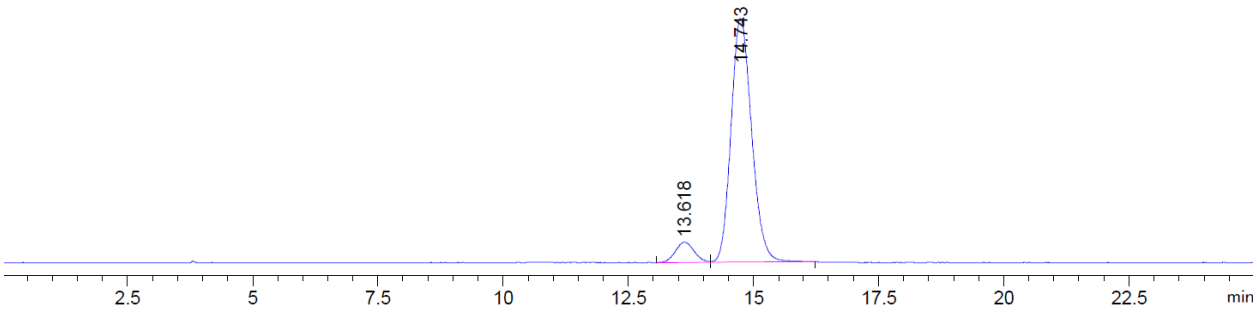



obtained as a white foam in 47% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.91 (ddd, *J* = 12.9, 7.4, 1.6 Hz, 1H), 7.64 (s, 2H), 7.55–7.41 (m, 3H), 7.38–7.17 (m, 11H), 7.11–7.02 (m, 2H), 6.91–6.76 (m, 3H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.18–4.03 (m, 1H), 3.83 (ddt, *J* = 19.9, 9.3, 6.0 Hz, 1H), 2.86 (dddd, *J* = 14.7, 12.6, 8.0, 6.3 Hz, 1H), 2.37 (ddt, *J* = 15.4, 11.8, 5.7 Hz, 1H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 140.76 (d, $J_{C\text{-}P}$ = 2.2 Hz), 139.16, 138.20 (d, $J_{C\text{-}P}$ = 7.0 Hz), 137.44 , 137.29 (d, $J_{C\text{-}P}$ = 1.1 Hz), 135.18 (d, $J_{C\text{-}P}$ = 3.9 Hz), 132.51 (d, $J_{C\text{-}P}$ = 2.2 Hz), 131.70, 131.38 (q, $J_{C\text{-}F}$ = 33.5 Hz), 131.13, 128.91 (d, $J_{C\text{-}P}$ = 9.2 Hz), 128.63, 128.21, 128.19, 128.19 (d, $J_{C\text{-}P}$ = 2.4 Hz), 128.05, 128.04, 127.87, 127.54, 127.27, 127.16 (d, $J_{C\text{-}P}$ = 9.6 Hz), 126.55 (d, $J_{C\text{-}P}$ = 7.7 Hz), 123.15 (d, $J_{C\text{-}P}$ = 118.1 Hz), 123.02 (q, $J_{C\text{-}F}$

= 272.9 Hz), 118.66, 73.82, 63.84 (d, $J_{C\text{-}P}$ = 3.7 Hz), 30.42 (d, $J_{C\text{-}P}$ = 90.3 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 29.12 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -62.91 ppm; **IR (ATR):** $\tilde{\nu}$ = 3059, 3030, 2864, 2798, 1614, 1601, 1586, 1550, 1489, 1444, 1371, 1326, 1275, 1220, 1172, 1129, 1093, 1077, 1013, 952, 914, 885, 847, 775, 759, 737, 719 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{37}H_{29}F_6NO_2P]^+$: 664.1835, found: 664.1834; **$[\alpha]_D^{20}$** = +146.7 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 2:1); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 13.6 min, $t_r$ (major) = 14.7 min), 93 : 7 *er*.



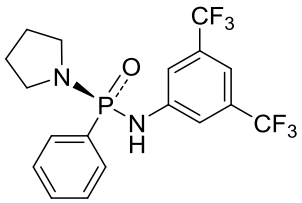

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.522 | BV | 0.4379 | 6007.08594 | 212.43524 | 49.7381 |
| 2 | 15.842 | VB | 0.4903 | 6070.33740 | 191.26746 | 50.2619 |



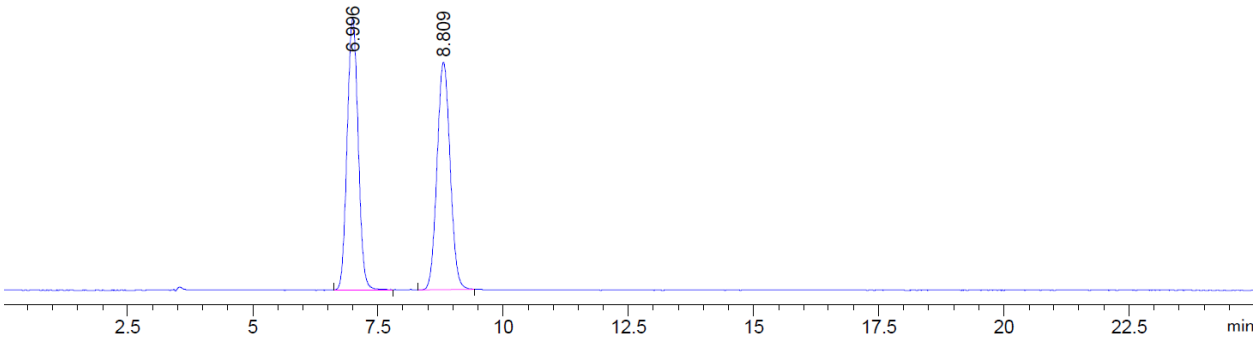

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.618 | BV | 0.3714 | 584.41644 | 22.47455 | 7.0211 |
| 2 | 14.743 | VB | 0.4423 | 7739.34424 | 270.05682 | 92.9789 |

**Recovered Starting Material**

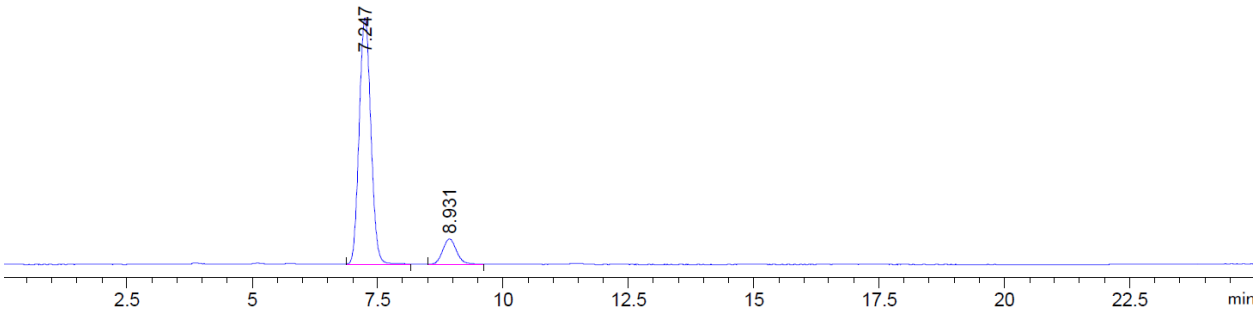
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-phenyl-*P*-(pyrrolidin-1-yl)phosphinic amide (1l)**




(at 90 °C, 5 hours) obtained as a white crystal in 40% yield; $[\alpha]_D^{20}$ = -43.9 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (major) = 7.2 min, $t_r$ (minor) = 8.9 min), 89 : 11 *er*. **S factor**: 9.



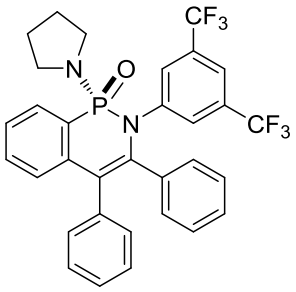

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.996 | BB | 0.2411 | 1061.24109 | 69.12734 | 50.1190 |
| 2 | 8.809 | BB | 0.2844 | 1056.19971 | 58.00835 | 49.8810 |



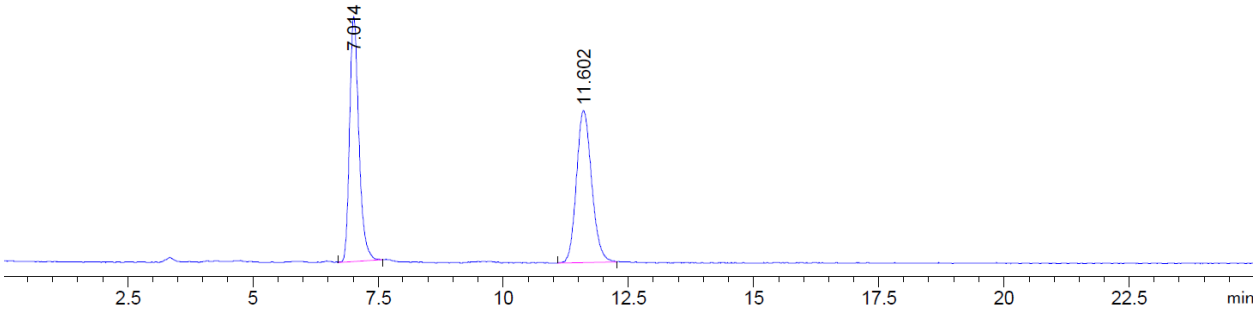
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.247 | BB | 0.2576 | 2900.53882 | 178.47655 | 89.2702 |
| 2 | 8.931 | BB | 0.3060 | 348.62766 | 18.32538 | 10.7298 |

**Product**

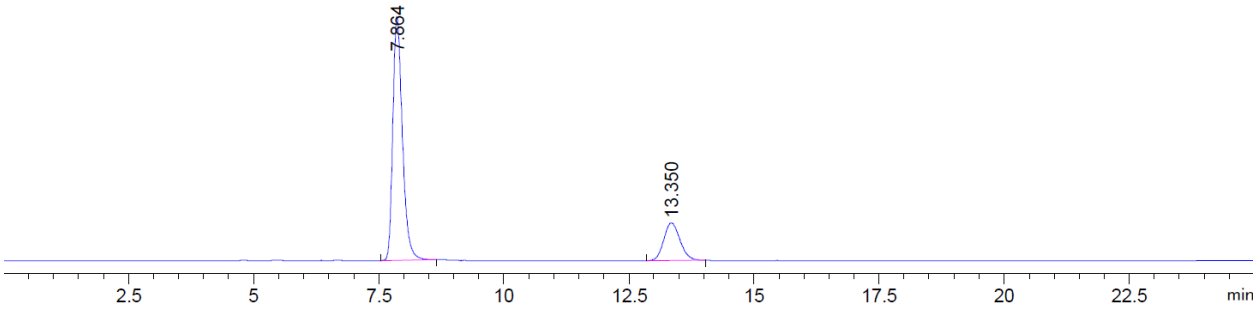
**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-3,4-diphenyl-1-(pyrrolidin-1-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2l)**




obtained as a white foam in 52% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.79 (ddd, *J*=14.3, 7.5, 1.5 Hz, 1H), 7.68 (s, 2H), 7.48–7.38 (m, 3H), 7.24–7.13 (m, 6H), 7.04–6.98 (m, 2H), 6.92–6.81 (m, 3H), 3.10–3.00 (m, 4H), 1.68–1.55 (m, 4H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 142.34 (d, $J_{C\text{-}P}$ = 2.0 Hz), 140.01 , 139.47 (d, $J_{C\text{-}P}$ = 6.7 Hz), 137.81 (d, $J_{C\text{-}P}$ = 1.4 Hz), 135.83 (d, $J_{C\text{-}P}$ = 3.7 Hz), 132.06 , 131.88 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.31 (q, $J_{C\text{-}F}$ = 33.7 Hz), 131.16 , 128.66 (d, $J_{C\text{-}P}$ = 9.2 Hz), 128.06 , 127.96 , 127.49 , 127.45 , 127.43 (d, $J_{C\text{-}P}$ = 11.0 Hz), 126.94 (d, $J_{C\text{-}P}$ = 14.3 Hz), 126.93 , 123.31 (d, $J_{C\text{-}P}$ = 158.9 Hz), 122.93 (q, $J_{C\text{-}F}$ = 272.9 Hz), 121.95 (d, $J_{C\text{-}P}$ = 8.0 Hz), 118.77 , 47.36 (d, $J_{C\text{-}P}$ = 5.1 Hz), 26.21 (d, $J_{C\text{-}P}$ = 8.4 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 11.14 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.02 ppm; **IR (ATR):** $\tilde{\nu}$ = 3057, 3027, 2974, 2870, 1604, 1589, 1549, 1489, 1465, 1443, 1371, 1335, 1274, 1225, 1172, 1129, 1088, 1010, 953, 913, 892, 847, 773, 755, 735, 720 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{32}H_{26}F_6N_2OP]^+$: 599.1681, found: 599.1697; **$[\alpha]_D^{20}$** = -146.0 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 5:1); HPLC separation (Chiralpak ID , 4.6 x 250 mm; 20% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (major) = 7.8 min, $t_r$ (minor) = 13.4 min), 79 : 21 *er*.



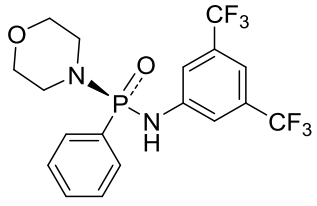

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.014 | BB | 0.1955 | 1642.23364 | 128.19145 | 49.5254 |
| 2 | 11.602 | BB | 0.3277 | 1673.71033 | 79.46290 | 50.4746 |



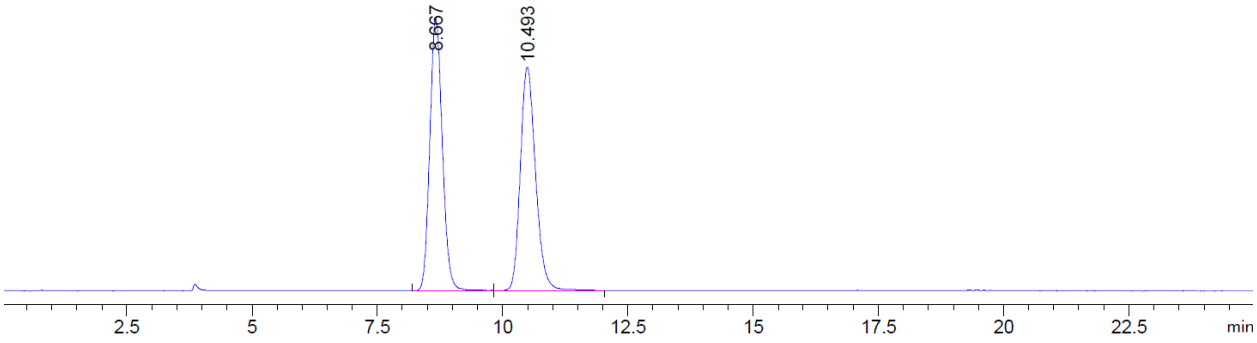

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.864 | BB | 0.2037 | 7014.93750 | 525.54474 | 79.2172 |
| 2 | 13.350 | BB | 0.3376 | 1840.38037 | 81.44162 | 20.7828 |

**Recovered Starting Material**

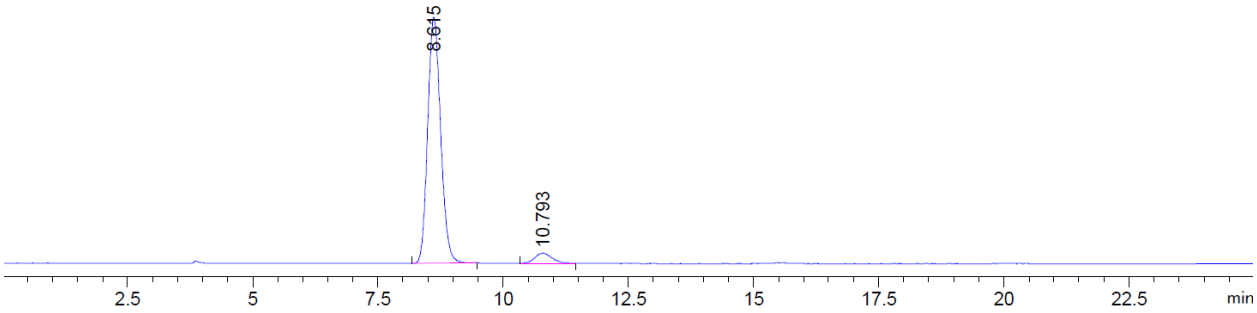
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-morpholino-*P*-phenylphosphinic amide (1m)**




(at 90 °C, 3.5 hours) obtained as a white crystal in 37% yield; $[\alpha]_D^{20}$ = -43.9 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 8.6 min, $t_r$ (minor) = 10.8 min), 95 : 5 *er*. **S factor**: 11.



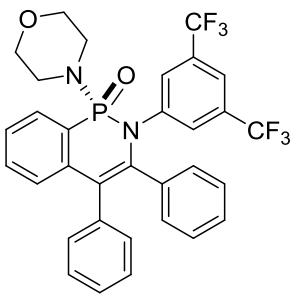

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.667 | BB | 0.2675 | 1771.95911 | 101.59856 | 50.0824 |
| 2 | 10.493 | BB | 0.3273 | 1766.12891 | 83.32843 | 49.9176 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.615 | BB | 0.2798 | 2929.69653 | 162.91325 | 94.8466 |
| 2 | 10.793 | BB | 0.3338 | 159.18332 | 6.68602 | 5.1534 |

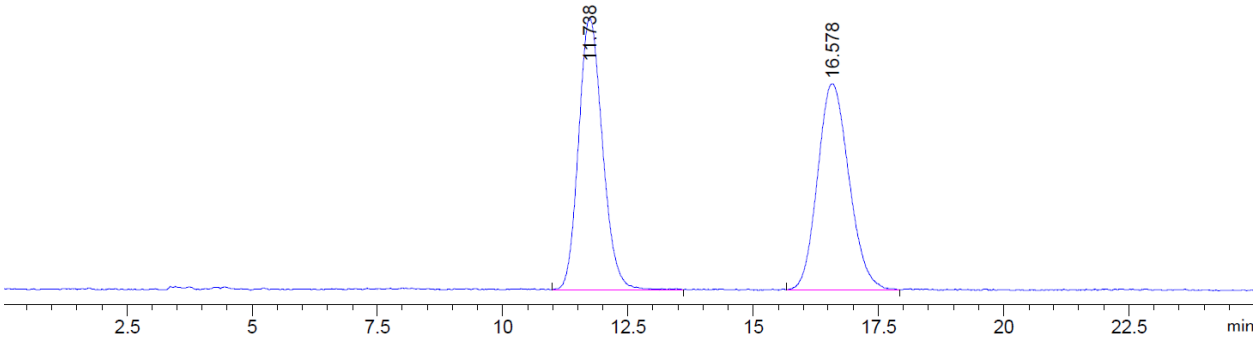
**Product**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-1-morpholino-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2m)**

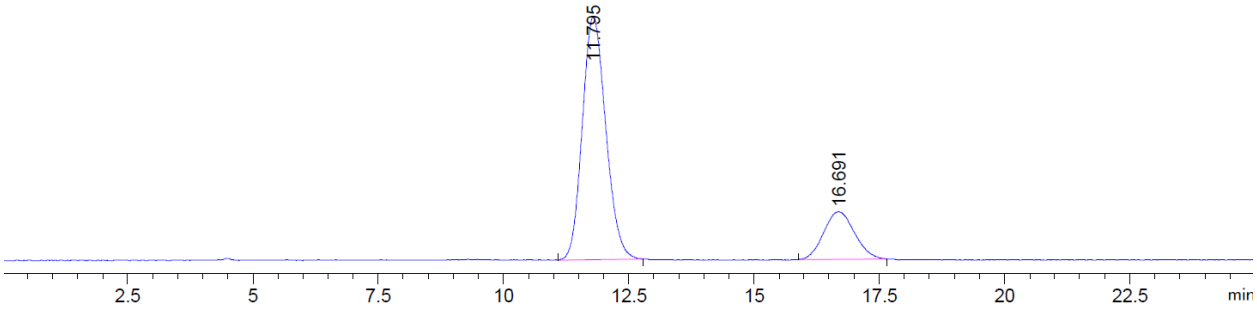



obtained as a white foam in 55% yield. **$^1$H NMR** (400 MHz, Chloroform-*d*) δ = 8.01–7.83 (m, 1H), 7.69 (s, 2H), 7.56–7.37 (m, 3H), 7.24–7.05 (m, 6H), 7.02–6.94 (m, 2H), 6.94–6.75 (m, 3H), 3.41 (dddd, *J* = 36.9, 11.0,

6.3, 2.9 Hz, 4H), 2.98 (ddtd, *J* = 52.3, 12.8, 6.2, 3.0 Hz, 4H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 142.11 (d, $J_{C-P}$ = 1.9 Hz), 140.10, 139.88 (d, $J_{C-P}$ = 6.9 Hz), 137.55, 135.55 (d, $J_{C-P}$ = 4.0 Hz), 132.25 (d, $J_{C-P}$ = 2.5 Hz), 131.98, 131.67 (q, $J_{C-F}$ = 33.7 Hz), 131.11, 128.82 (d, $J_{C-P}$ = 9.2 Hz), 128.46, 128.13, 127.57, 127.56, 127.47 (d, $J_{C-P}$ = 10.9 Hz), 127.03, 127.02 (d, $J_{C-P}$ = 14.5 Hz), 122.82 (q, $J_{C-F}$ = 273.1 Hz), 122.40 (d, $J_{C-P}$ = 160.4 Hz), 121.26 (d, $J_{C-P}$ = 7.8 Hz), 119.35, 66.66 (d, $J_{C-P}$ = 5.4 Hz), 44.34 ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 14.21 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -62.99 ppm; **IR (ATR):** $\tilde{\nu}$ = 3059, 3024, 2963, 2915, 2854, 2237, 1604, 1589, 1549, 1489, 1467, 1443, 1371, 1335, 1275, 1258, 1222, 1173, 1132, 1112, 1089, 1011, 970, 954, 909, 895, 847, 753, 729 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{32}H_{26}F_6N_2O_2P]^+$: 615.1631, found: 615.1652; **$[\alpha]_D^{20}$** = -260.0 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak IG , 4.6 x 250 mm; 20% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (major) = 11.8 min, $t_r$ (minor) = 16.7 min), 79 : 21 *er*.



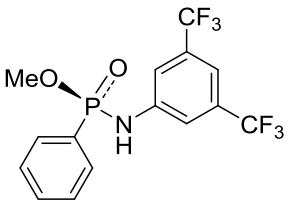

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.738 | BB | 0.5255 | 1236.10425 | 37.02210 | 50.1830 |
| 2 | 16.578 | BB | 0.6772 | 1227.09094 | 28.11479 | 49.8170 |



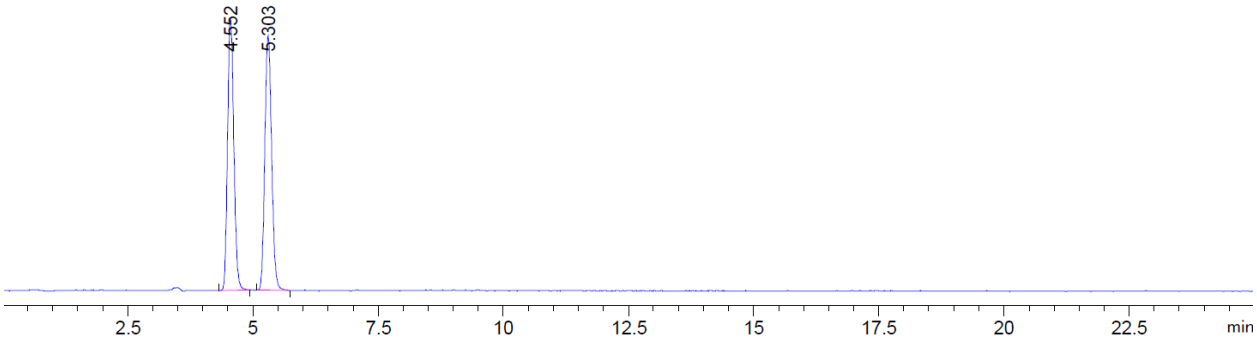
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.795 | BB | 0.4974 | 4127.69873 | 126.91244 | 79.4793 |
| 2 | 16.691 | BB | 0.5287 | 1065.72986 | 24.83311 | 20.5207 |

**Recovered Starting Material**

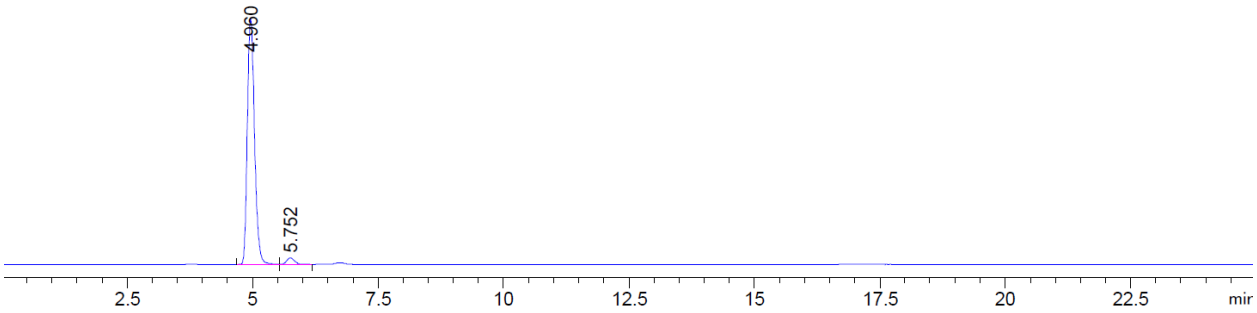
**Methyl (*S*)-*N*-(3,5-bis(trifluoromethyl)phenyl)-*P*-phenylphosphonamidate (1n)**




(at 70 °C, 24 hours) obtained as a white crystal in 37% yield; $[\alpha]_D^{20}$ = +22.5 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 5.0 min, $t_r$ (minor) = 5.8 min), 97 : 3 *er*. **S factor**: 15.



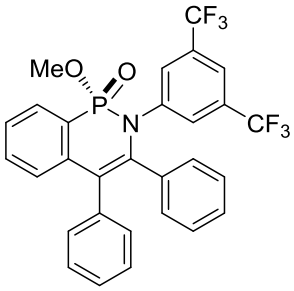

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.552 | BB | 0.1382 | 712.94788 | 81.37823 | 49.9649 |
| 2 | 5.303 | BB | 0.1474 | 713.94904 | 76.12270 | 50.0351 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.960 | BV | 0.1563 | 7105.57959 | 713.00745 | 97.1288 |
| 2 | 5.752 | VB | 0.1676 | 210.04977 | 19.20038 | 2.8712 |

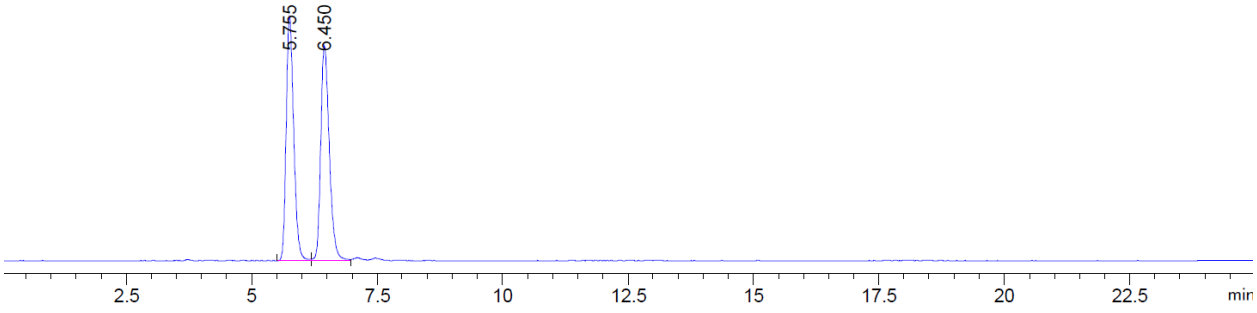
**Product**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-1-methoxy-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2n)**

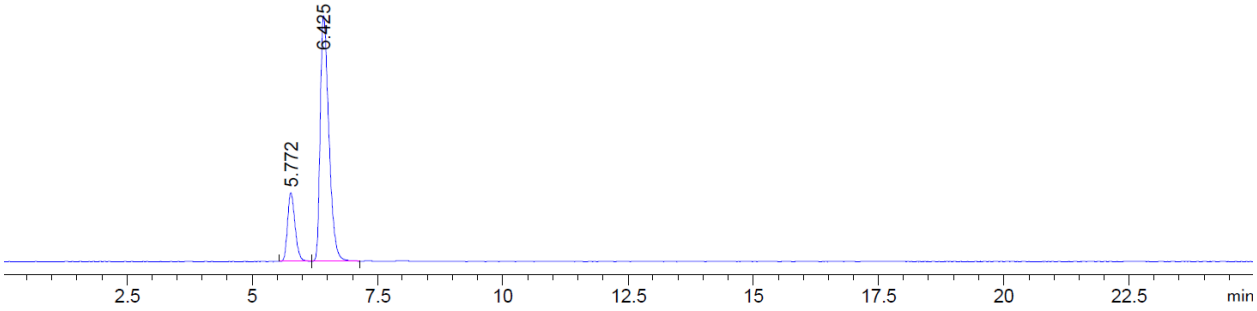



obtained as a white foam in 55% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 8.00 (ddd, *J* = 14.2, 7.4, 1.1 Hz, 1H), 7.60–7.53 (m, 3H), 7.52–7.44 (m, 2H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.31–7.19 (m, 5H), 7.12–7.06 (m, 2H), 7.01–6.90 (m, 3H), 3.90 (d, *J* = 11.7 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 140.67 (d, $J_{C-P}$ = 3.9 Hz), 139.35 , 139.15 (d, $J_{C-P}$ = 6.3 Hz), 137.22 (d, $J_{C-P}$ = 1.5 Hz), 135.26 (d, $J_{C-P}$ = 3.9 Hz), 132.71 (d, $J_{C-P}$ = 2.4 Hz), 131.68 , 131.58 (q, $J_{C-F}$ = 33.7 Hz), 130.96 , 129.10 (d, $J_{C-P}$ = 9.2 Hz), 128.21 , 128.02 , 127.95 (d, $J_{C-P}$ = 11.1 Hz), 127.69 , 127.59 (d, $J_{C-P}$ = 15.1 Hz), 127.36 , 127.35 , 126.91 (d, $J_{C-P}$ = 8.5 Hz), 122.98 (q, $J_{C-F}$ = 272.9 Hz), 121.75 (d, $J_{C-P}$ = 170.9 Hz), 118.91 , 52.34 (d, $J_{C-P}$ = 5.5 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 13.36 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.02 ppm; **IR (ATR):** $\tilde{\nu}$ = 3059, 3025, 2949, 2847, 1616, 1603, 1589, 1489, 1466, 1443, 1373, 1276, 1262, 1230, 1175, 1133, 1098, 1083, 1017, 956, 886, 798, 757, 738, 722 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{29}H_{21}F_6NO_2P]^+$: 560.1209, found: 560.1206; **$[\alpha]_D^{20}$** = +188.4 (c = 1.0, $CHCl_3$);

**eluent for FCC** (hexane:EtOAc, 6:1); HPLC separation (Chiralpak IB , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 5.8 min, $t_r$ (major) = 6.4 min), 81 : 19 *er*.



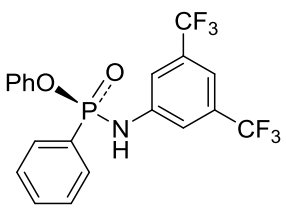

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.755 | BV | 0.1590 | 2400.15430 | 231.45363 | 49.7387 |
| 2 | 6.450 | VV | 0.1830 | 2425.37305 | 203.49959 | 50.2613 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.772 | BV | 0.1606 | 1117.00098 | 108.02933 | 19.3134 |
| 2 | 6.425 | VB | 0.1847 | 4666.56250 | 386.91238 | 80.6866 |

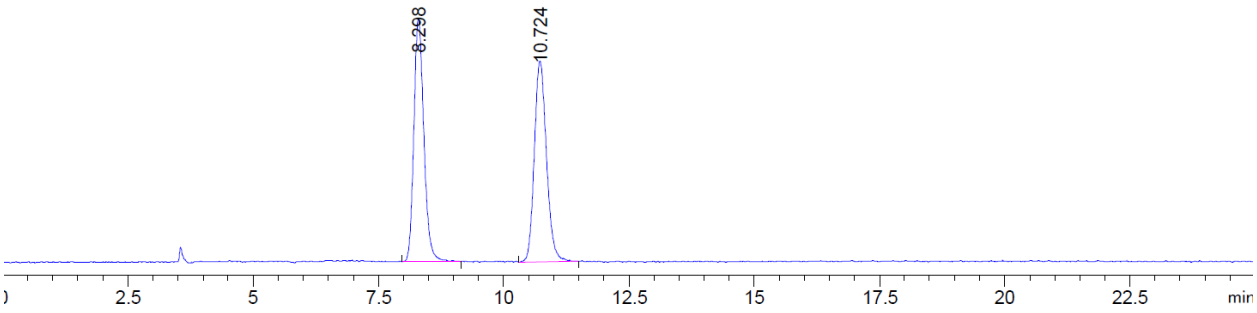
**Recovered Starting Material**

**Phenyl (*S*)-N-(3,5-bis(trifluoromethyl)phenyl)-*P*-phenylphosphonamidate (1o)**

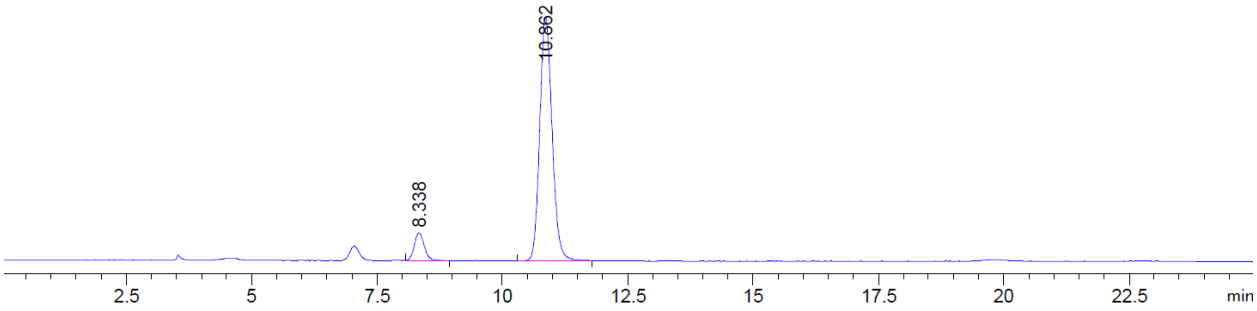



(at 70 °C, 14 hours) obtained as a white crystal in 44% yield; $[\alpha]_D^{20}$ = +43.3 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IF , 4.6 x 250 mm; 5%

*i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (minor) = 8.3 min, $t_r$ (major) = 10.9 min), 91 : 9 *er*. **S factor**: 16.



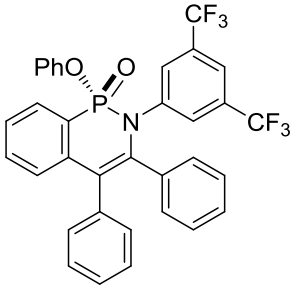

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.298 | BB | 0.2141 | 636.87823 | 45.82872 | 49.8868 |
| 2 | 10.724 | BB | 0.2610 | 639.76917 | 37.88813 | 50.1132 |



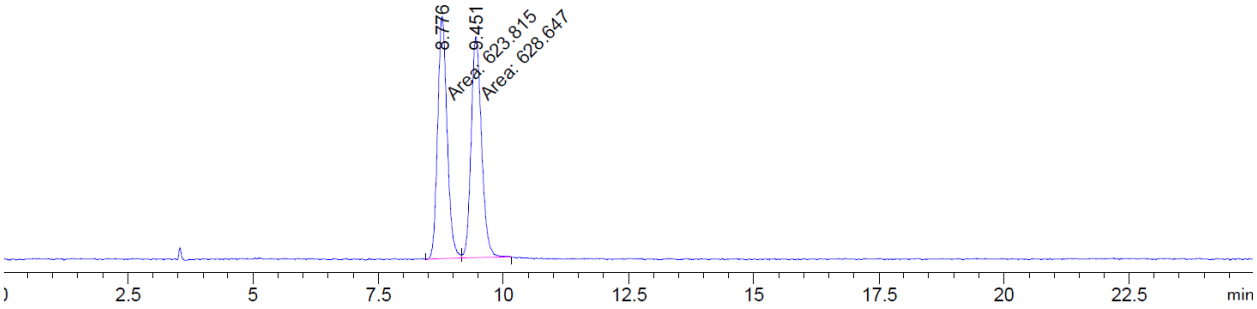

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.338 | VB | 0.2136 | 537.84375 | 38.36373 | 8.5690 |
| 2 | 10.862 | BB | 0.2659 | 5738.80469 | 334.98615 | 91.4310 |

**Product**

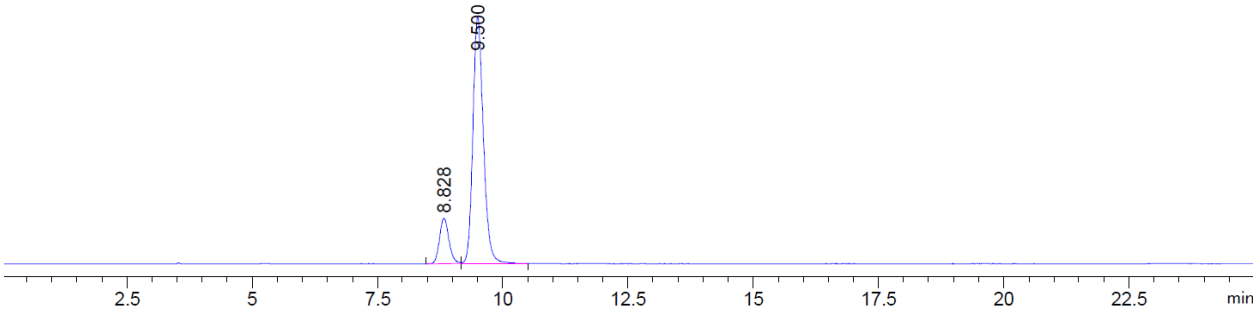
**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-1-phenoxy-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2o)**




obtained as a white foam in 48% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.95 (ddd, *J* = 14.6, 7.5, 1.4 Hz, 1H), 7.57 (ddt, *J* = 8.8, 7.7, 1.3 Hz, 1H), 7.49 (s, 2H), 7.47–7.35 (m, 5H), 7.34–7.21 (m, 8H), 6.97–6.85 (m, 5H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 149.96 (d, $J_{C-P}$ = 8.0 Hz), 140.34 (d, $J_{C-P}$ = 3.9 Hz), 139.67, 139.19 (d, $J_{C-P}$ = 6.5 Hz), 137.17, 134.91 (d, $J_{C-P}$ = 4.0 Hz), 132.99 (d, $J_{C-P}$ = 2.4 Hz), 131.78 , 131.74 (q, $J_{C-F}$ = 33.6 Hz), 131.08 , 130.09 , 129.51 (d, $J_{C-P}$ = 9.5 Hz), 128.32 , 128.05 , 127.87 (d, $J_{C-P}$ = 11.4 Hz), 127.76 , 127.64 , 127.59 (d, $J_{C-P}$ = 15.7 Hz), 127.46 , 126.90 (d, $J_{C-P}$ = 8.6 Hz), 125.77 (d, $J_{C-P}$ = 1.4 Hz), 122.92 (q, $J_{C-F}$ = 272.9 Hz), 121.63 (d, $J_{C-P}$ = 173.8 Hz), 121.13 (d, $J_{C-P}$ = 4.5 Hz), 119.25 ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 9.15 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.01 ppm; **IR (ATR):** $\tilde{\nu}$ = 3061, 3027, 2926, 2247, 1589, 1551, 1489, 1466, 1443, 1372, 1326, 1231, 1179, 1133, 1098, 1083, 1073, 1020, 956, 917, 891, 846, 760, 748, 724 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{34}H_{23}F_6NO_2P]^+$: 622.1365, found: 622.1361; **$[\alpha]_D^{20}$** = +231.2 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 20:1); HPLC separation (Chiralpak IF , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 8.8 min, $t_r$ (major) = 9.5 min), 86 : 14 *er*.



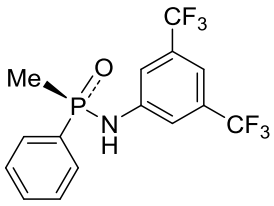

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.776 | MF | 0.2188 | 623.81549 | 47.50887 | 49.8071 |
| 2 | 9.451 | FM | 0.2414 | 628.64679 | 43.41082 | 50.1929 |



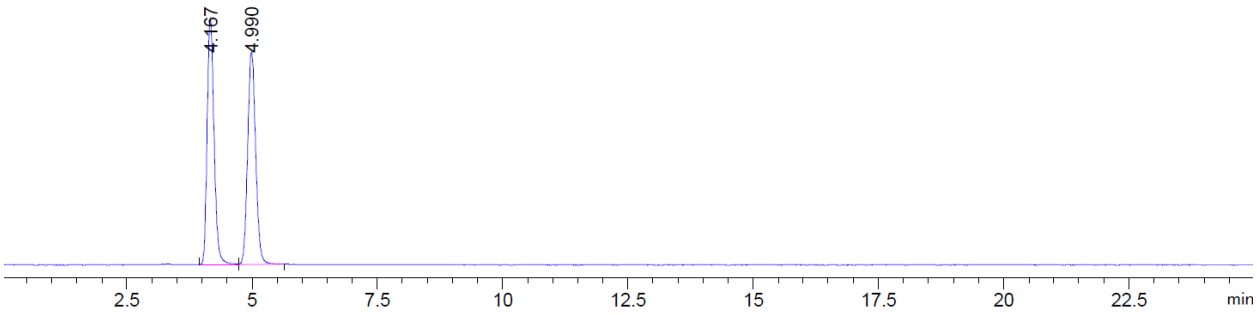

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.828 | BV | 0.2034 | 1069.08142 | 81.28844 | 14.2468 |
| 2 | 9.500 | VB | 0.2244 | 6434.94775 | 440.57608 | 85.7532 |

**Recovered Starting Material**

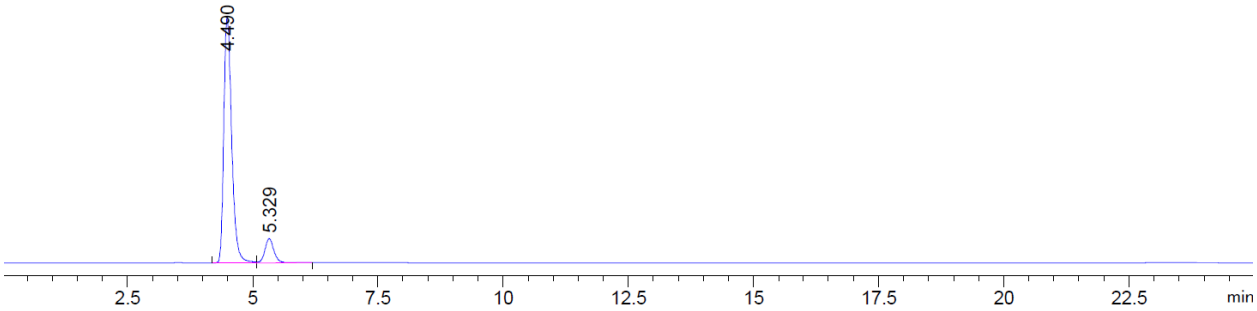
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-phenylphosphinic amide (1a)**




(at 90 °C, 9 hours) obtained as a white crystal in 46% yield; HPLC separation (Chiralpak AZH , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 4.5 min, $t_r$ (minor) = 5.3 min), 90 : 10 *er*. **S factor**: 18.



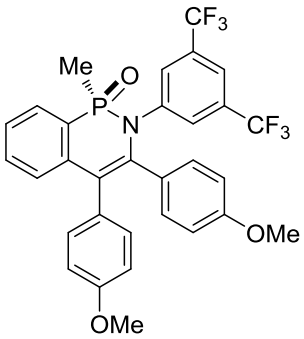
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.167 | BV | 0.1506 | 1252.89490 | 129.85233 | 49.9692 |
| 2 | 4.990 | VB | 0.1743 | 1254.44055 | 112.35071 | 50.0308 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.490 | BV | 0.1678 | 1.88140e4 | 1717.87927 | 89.9618 |
| 2 | 5.329 | VB | 0.1913 | 2099.31592 | 168.50969 | 10.0382 |

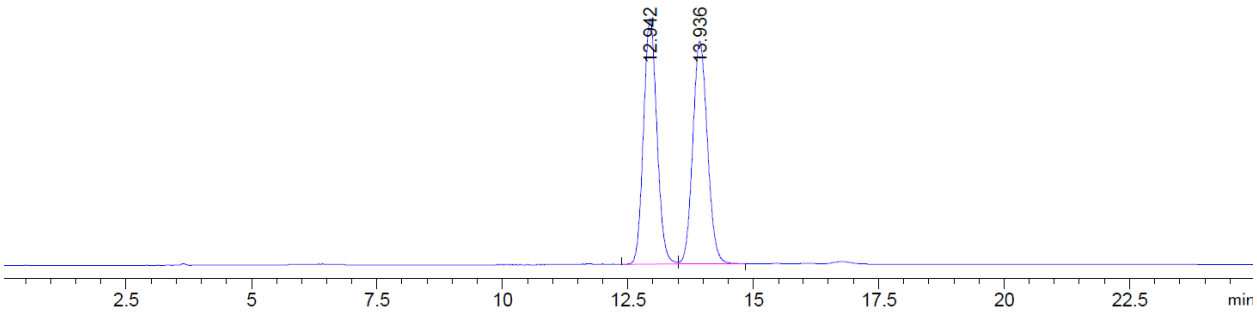
**Product**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-3,4-bis(4-methoxyphenyl)-1-methyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2ab)**

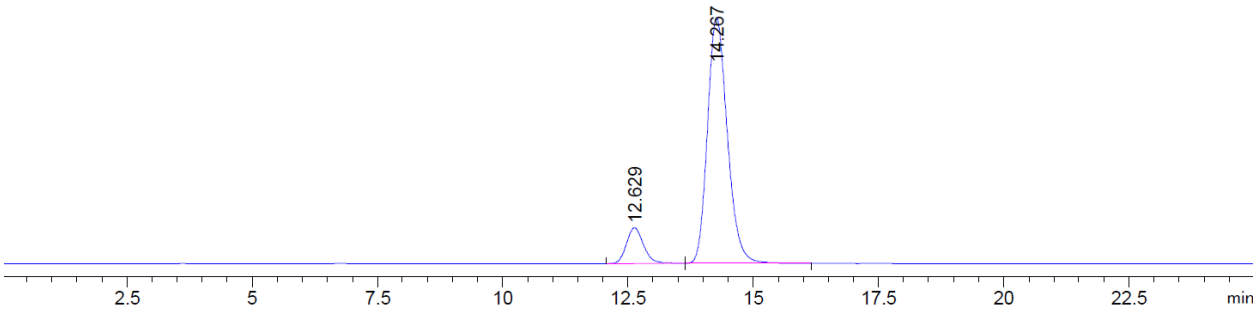



obtained as a white foam in 46% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.90 (ddd, *J* = 13.2, 7.3, 1.6 Hz, 1H), 7.60 (s, 2H), 7.55–7.40 (m, 3H), 7.33–7.24 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.48 (d, *J* = 8.7 Hz, 2H), 3.77 (s, 3H), 3.61 (s, 3H), 1.95 (d, *J* = 13.8 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 158.78, 158.57, 141.50 (d, $J_{C-P}$ = 2.5 Hz), 138.87, 138.23 (d, $J_{C-P}$ = 6.5 Hz), 132.65, 132.34 (d, $J_{C-P}$ = 2.4 Hz), 132.16, 131.74 (q, $J_{C-F}$ = 33.7 Hz), 129.63, 128.55 (d, $J_{C-P}$ = 10.4 Hz), 127.82 (d, $J_{C-P}$ = 3.7 Hz), 127.78 (d, $J_{C-P}$ = 13.3 Hz), 127.74, 127.41 (d, $J_{C-P}$ = 9.5 Hz), 125.52 (d, $J_{C-P}$ = 7.8 Hz), 124.37 (d, $J_{C-P}$ = 121.4 Hz), 122.95 (q, $J_{C-F}$ = 273.1

Hz), 118.91, 113.74, 113.16, 55.27, 55.10, 16.39 (d, $J_{C\text{-}P}$ = 94.0 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 26.18 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -62.97 ppm; **IR (ATR):** $\tilde{\nu}$ = 3056, 3035, 3003, 2959, 2936, 2911, 2838, 1608, 1588, 1507, 1464, 1441, 1410, 1371, 1275, 1245, 1222, 1172, 1130, 1095, 1030, 1016, 955, 886, 856, 815, 770, 735, 701 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{31}H_{25}F_6NO_3P]^+$: 604.1471, found: 604.1475; **$[\alpha]_D^{20}$** = +101.9 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:2); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 12.6 min, $t_r$ (major) = 14.3 min), 89 : 11 *er*.



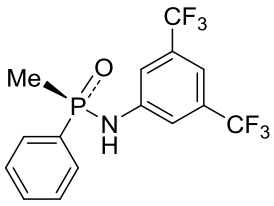

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.942 | BV | 0.2884 | 1837.37219 | 99.05038 | 50.0854 |
| 2 | 13.936 | VB | 0.3156 | 1831.10413 | 89.90022 | 49.9146 |



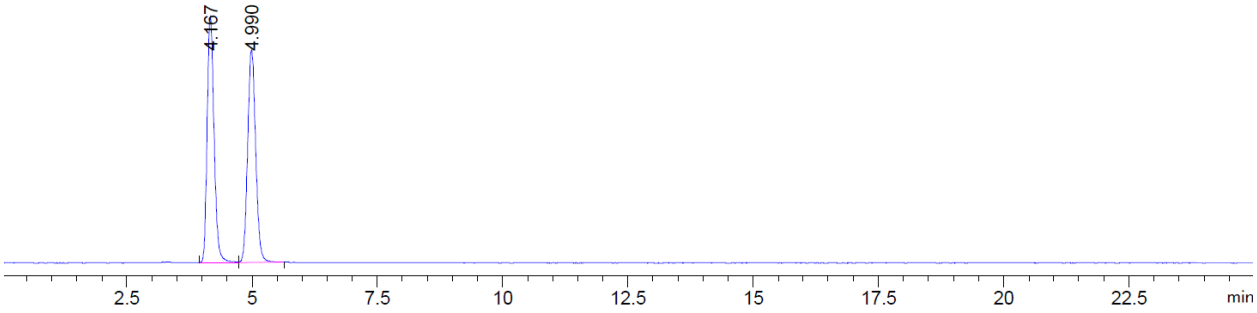

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.629 | BB | 0.3647 | 934.26202 | 39.39234 | 11.1079 |
| 2 | 14.267 | BB | 0.4261 | 7476.52539 | 270.78006 | 88.8921 |

**Recovered Starting Material**

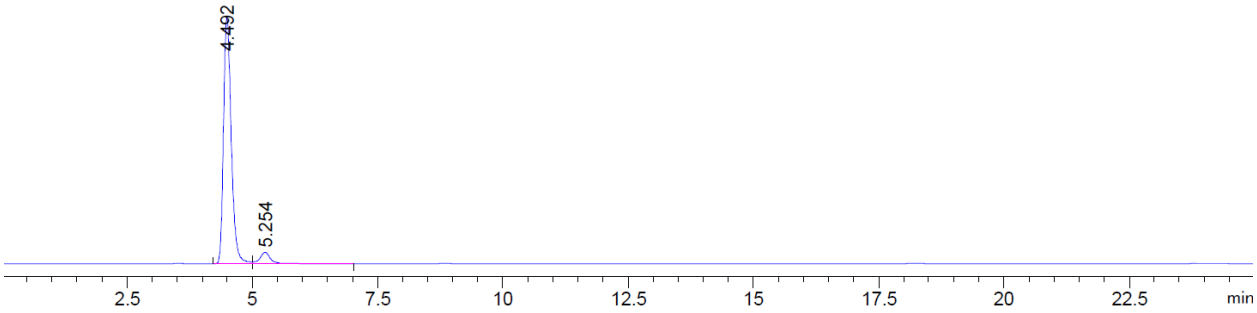
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-phenylphosphinic amide (1a)**




(at 90 °C, 8.8 hours) obtained as a white crystal in 46% yield; HPLC separation (Chiralpak AZH , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 4.5 min, $t_r$ (minor) = 5.3 min), 94 : 6 *er*. **S factor**: 45.



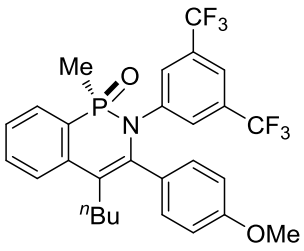

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.167 | BV | 0.1506 | 1252.89490 | 129.85233 | 49.9692 |
| 2 | 4.990 | VB | 0.1743 | 1254.44055 | 112.35071 | 50.0308 |



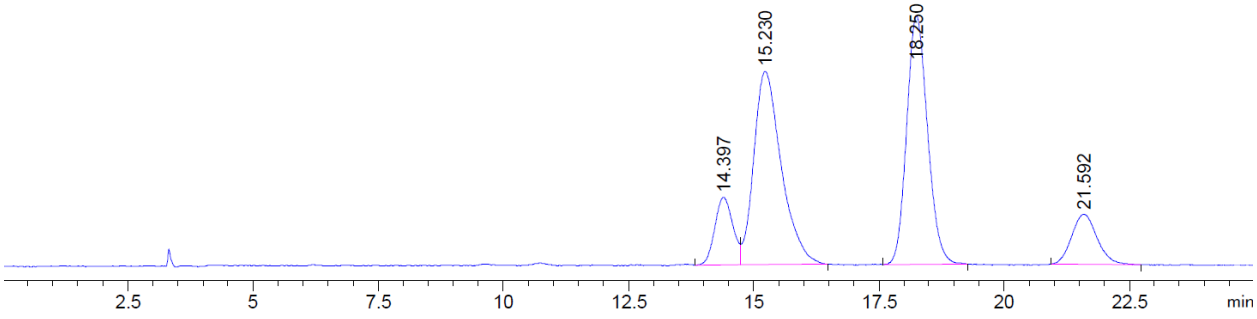

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.492 | BV | 0.1653 | 1.50179e4 | 1398.59326 | 93.8390 |
| 2 | 5.254 | VB | 0.2229 | 985.99384 | 65.04059 | 6.1610 |

**Product**

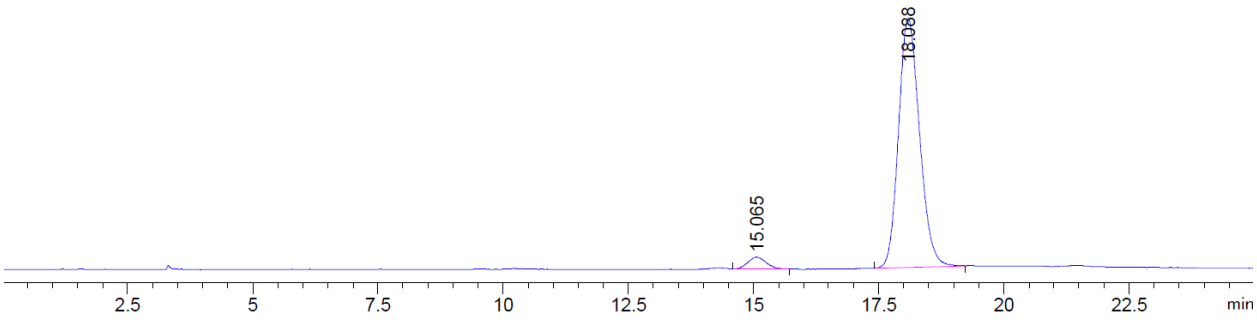
**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-4-butyl-3-(4-methoxyphenyl)-1-methyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2ac)**




obtained as a white foam in 46% yield with 18:1 regioselectivity. Major regioisomer was showed, and determined by ROESY. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.85 (ddt, *J* = 12.9, 7.4, 0.9 Hz, 1H), 7.75–7.60 (m, 2H), 7.50 (dddd, *J* = 7.5, 6.2, 3.0, 1.8 Hz, 1H), 7.43 (s, 2H), 7.40 (s, 1H), 7.23–7.13 (m, 2H), 6.83–6.73 (m, 2H), 3.75 (s, 3H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.88 (d, *J* = 13.9 Hz, 3H), 1.53–1.36 (m, 1H), 1.34–1.08 (m, 3H), 0.74 (t, *J* = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 159.59, 141.16, 137.81 (d, $J_{C\text{-}P}$ = 7.4 Hz), 136.38, 132.45 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.93, 131.51 (q, $J_{C\text{-}F}$ = 33.3 Hz), 128.61 (d, $J_{C\text{-}P}$ = 9.5 Hz), 128.17 (d, $J_{C\text{-}P}$ = 13.0 Hz), 127.60 (d, $J_{C\text{-}P}$ = 3.7 Hz), 127.05, 126.56 (d, $J_{C\text{-}P}$ = 119.3 Hz), 125.69 (d, *J* = 10.5 Hz), 125.67 (d, *J* = 6.9 Hz), 125.64, 123.08 (q, $J_{C\text{-}F}$ = 272.6 Hz), 118.31, 113.78, 55.34, 31.55, 29.26, 22.70, 15.82 (d, $J_{C\text{-}P}$ = 92.4 Hz), 13.83 ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 27.51 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -62.97 ppm; **IR (ATR):** $\tilde{\nu}$ = 3061, 2959, 2930, 2872, 1675, 1607, 1590, 1508, 1464, 1440, 1411, 1371, 1274, 1249, 1221, 1172, 1127, 1105, 1031, 1007, 927, 879, 844, 822, 772, 750, 732, 701 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{28}H_{27}F_6NO_2P]^+$: 554.1678, found: 554.1680; **$[\alpha]_D^{20}$** = +207.5 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak IF , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 15.1 min, $t_r$ (major) = 18.1 min), 95 : 5 *er*.



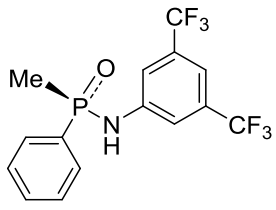
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.397 | BV | 0.3611 | 341.96017 | 13.61086 | 9.4215 |
| 2 | 15.230 | VB | 0.5720 | 1481.92578 | 38.76674 | 40.8292 |
| 3 | 18.250 | BB | 0.4469 | 1450.03992 | 49.91072 | 39.9507 |
| 4 | 21.592 | BB | 0.4401 | 355.64975 | 10.06940 | 9.7987 |



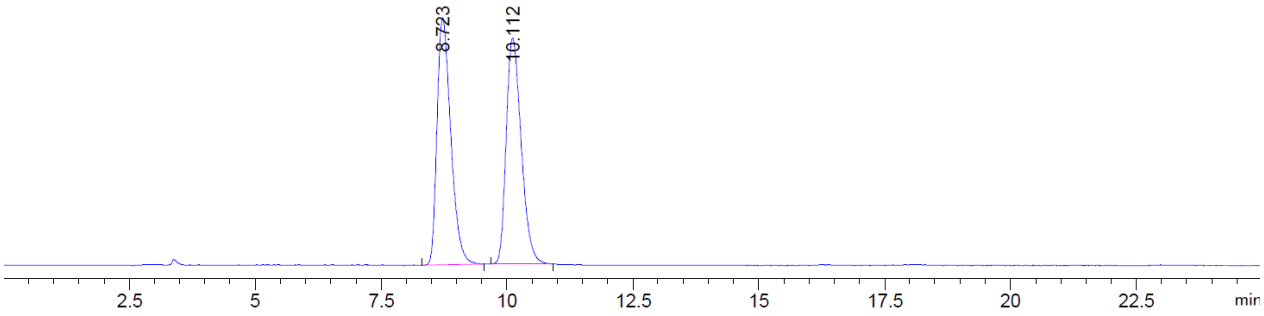

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.011 | BB | 0.4322 | 303.37228 | 10.40335 | 4.7056 |
| 2 | 17.564 | BB | 0.4012 | 6143.65869 | 236.37221 | 95.2944 |

**Recovered Starting Material**

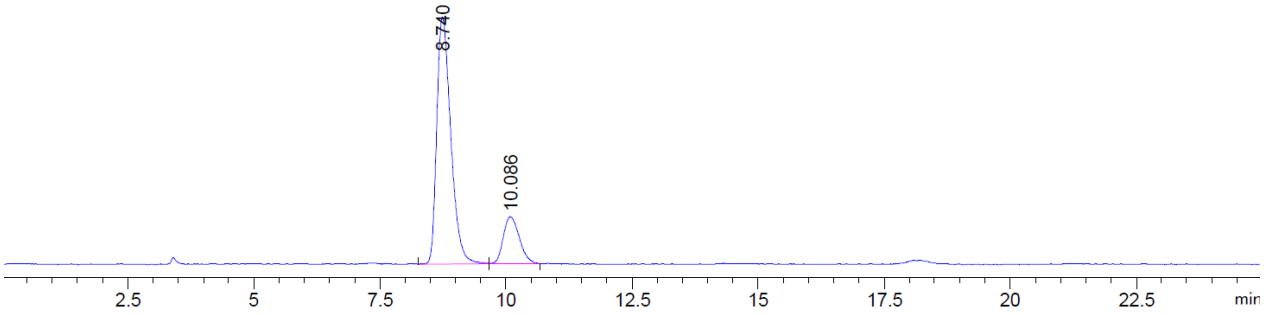
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-phenylphosphinic amide (1a)**




(at 90 °C, 8.8 hours) obtained as a white crystal in 52% yield; HPLC separation (Chiralpak IA , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 8.7 min, $t_r$ (minor) = 10.1 min), 82 : 18 *er*. **S factor**: 23.



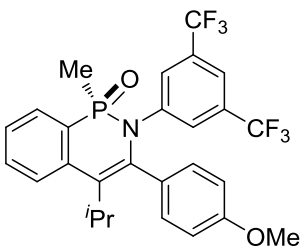

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.723 | BB | 0.2958 | 3025.00415 | 159.08710 | 50.0825 |
| 2 | 10.112 | BB | 0.3235 | 3015.03784 | 145.68352 | 49.9175 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.740 | BV | 0.2961 | 2907.48242 | 150.02908 | 82.0183 |
| 2 | 10.086 | VB | 0.3422 | 637.43573 | 28.57591 | 17.9817 |

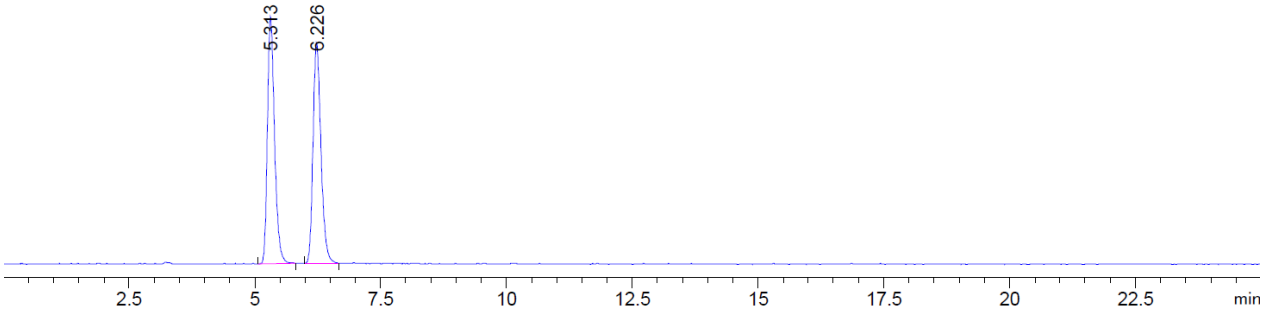
**Product**

**(*R*)-2-(3,5-bis(trifluoromethyl)phenyl)-4-isopropyl-3-(4-methoxyphenyl)-1-methyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2ad)**

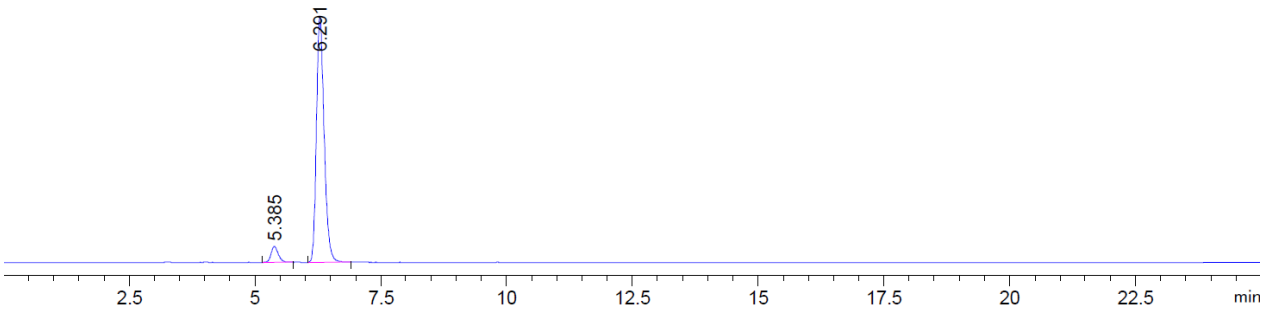



obtained as a white foam in 37% yield with >20:1 regioselectivity. Major regioisomer was showed, and determined by ROESY. **$^1$H NMR**

(400 MHz, Chloroform-*d*) δ = 7.91 (dd, *J* = 8.2, 5.2 Hz, 1H), 7.85 (ddd, *J* = 12.9, 7.5, 1.5 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.48 (td, *J* = 7.5, 2.8 Hz, 1H), 7.43 (s, 2H), 7.37 (s, 1H), 7.30 – 7.23 (m, 2H), 6.84 – 6.73 (m, 2H), 3.75 (s, 3H), 3.10 (hept, *J* = 7.3 Hz, 1H), 1.87 (d, *J* = 13.9 Hz, 3H), 1.64 (d, *J* = 7.3 Hz, 3H), 1.17 (d, *J* = 7.1 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 159.82 , 141.22 (d, $J_{C-P}$ = 2.8 Hz), 137.66 (d, $J_{C-P}$ = 7.5 Hz), 136.65 , 131.99 (d, $J_{C-P}$ = 8.0 Hz), 131.84 (d, $J_{C-P}$ = 2.4 Hz), 131.48 (q, $J_{C-F}$ = 33.4 Hz), 131.40 , 128.63 (d, $J_{C-P}$ = 9.4 Hz), 128.10 , 127.91 (d, $J_{C-P}$ = 12.8 Hz), 127.52 (d, $J_{C-P}$ = 123.2 Hz), 126.89 (d, $J_{C-P}$ = 10.0 Hz), 126.50 , 123.09 (q, $J_{C-F}$ = 273.0 Hz), 117.99 , 113.83 , 55.34 , 30.82 , 25.06 , 22.14 , 15.39 (d, $J_{C-P}$ = 91.8 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 28.12 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -62.95 ppm; **IR (ATR):** $\tilde{\nu}$ = 3059, 2963, 2931, 2876, 2840, 1607, 1588, 1507, 1464, 1441, 1411, 1371, 1274, 1249, 1220, 1171, 1128, 1091, 1023, 985, 881, 840, 811, 783, 768, 734, 700 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{27}H_{25}F_6NO_2P]^+$: 540.1522, found: 540.1523; **$[\alpha]_D^{20}$** = +269.2 (c = 1.0, $CH_2Cl_2$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak IA , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 5.4 min, $t_r$ (major) = 6.3 min), 94 : 6 *er*.



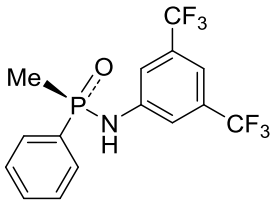

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.313 | BB | 0.1491 | 724.46979 | 73.44216 | 50.2521 |
| 2 | 6.226 | BB | 0.1656 | 717.20105 | 65.57968 | 49.7479 |



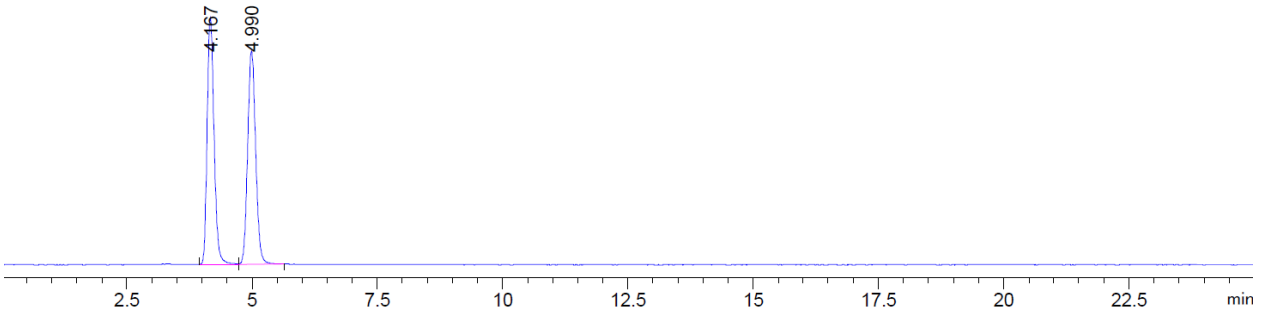

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.385 | BB | 0.1486 | 205.68738 | 20.93163 | 5.6677 |
| 2 | 6.291 | BB | 0.1620 | 3423.39795 | 322.08231 | 94.3323 |

**Recovered Starting Material**

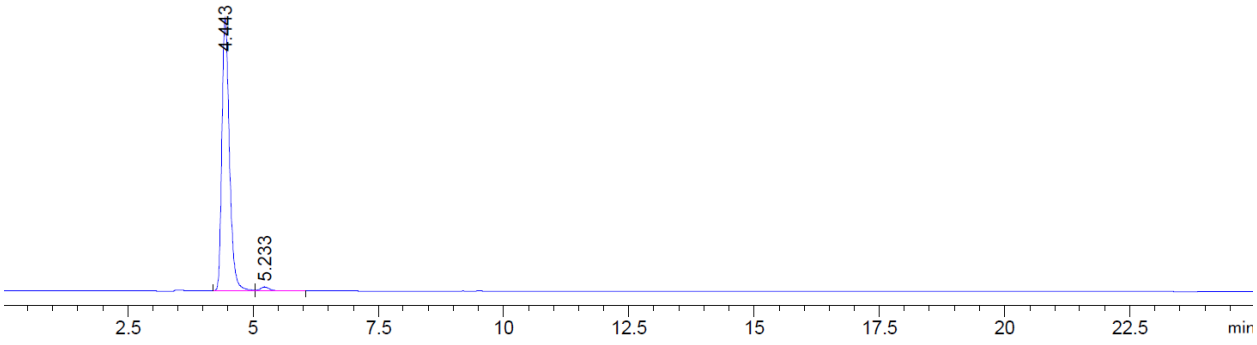
**(*S*)-*N*-(3,5-Bis(trifluoromethyl)phenyl)-*P*-methyl-*P*-phenylphosphinic amide (1a)**




(at 90 °C, 8.8 hours) obtained as a white crystal in 43% yield; HPLC separation (Chiralpak AZH , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 240 nm; $t_r$ (major) = 4.4 min, $t_r$ (minor) = 5.2 min), 98 : 2 *er*. **S factor**: 39.



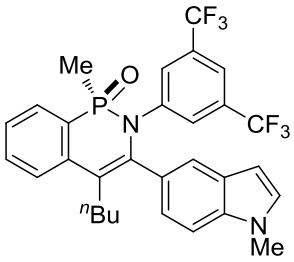

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.167 | BV | 0.1506 | 1252.89490 | 129.85233 | 49.9692 |
| 2 | 4.990 | VB | 0.1743 | 1254.44055 | 112.35071 | 50.0308 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 4.443 | VV | 0.1604 | 3697.91528 | 352.39493 | 98.0815 |
| 2 | 5.233 | VB | 0.2071 | 72.33054 | 5.17461 | 1.9185 |

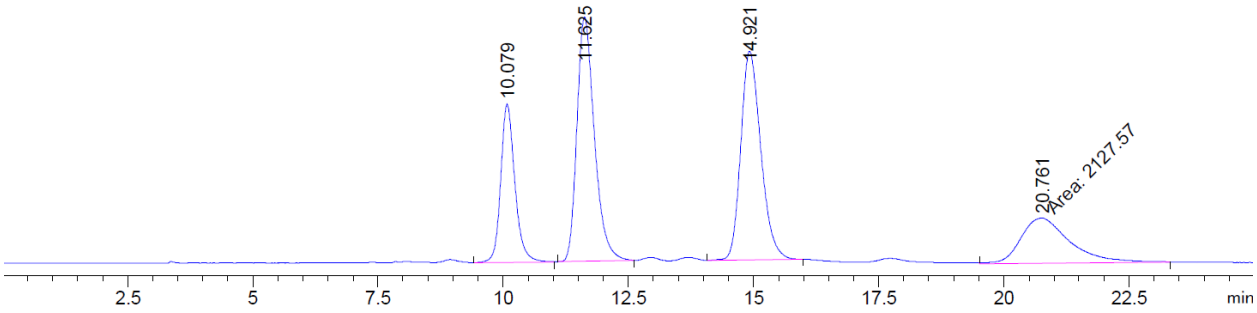
**Product**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-4-butyl-3-(4-methoxyphenyl)-1-methyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2ae)**

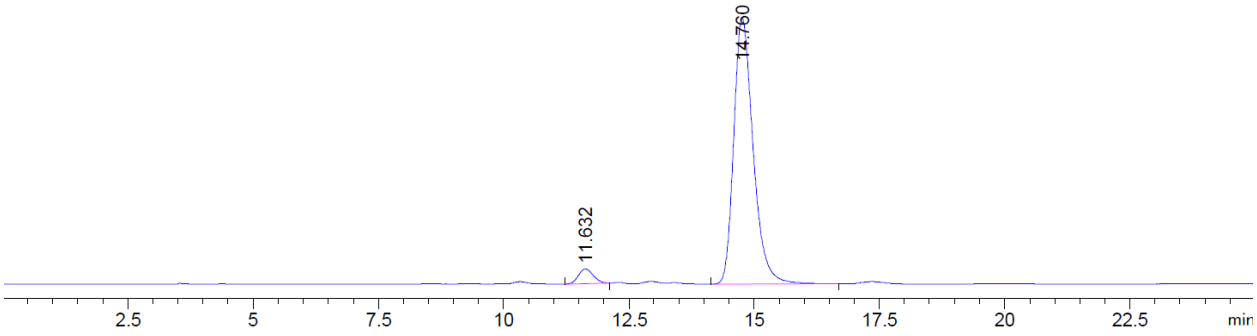



obtained as a white foam in 48% yield with >20:1 regioselectivity. Major regioisomer was showed, and determined by ROESY. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.86 (ddd, *J* = 12.8, 7.4, 1.4 Hz, 1H), 7.74–7.63 (m, 2H), 7.55–7.46 (m, 4H), 7.29 (s, 1H), 7.21–7.11 (m, 2H), 7.02 (d, *J* = 3.1 Hz, 1H), 6.43 (dd, *J* = 3.2, 0.8 Hz, 1H), 3.74 (s, 3H), 2.95–2.72 (m, 2H), 1.94 (d, *J* = 14.1 Hz, 3H), 1.48–1.35 (m, 1H), 1.34–1.18 (m, 1H), 1.19–1.07 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 141.24 (d, $J_{C\text{-}P}$ = 2.8 Hz), 138.18 (d, $J_{C\text{-}P}$ = 7.5 Hz), 137.88, 136.40, 132.37 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.20 (q, $J_{C\text{-}F}$ = 33.8 Hz), 129.82, 128.56 (d, $J_{C\text{-}P}$ = 9.9 Hz), 128.15, 127.97 (d, $J_{C\text{-}P}$ = 12.7 Hz), 127.05, 126.63 (d, $J_{C\text{-}P}$ = 119.2 Hz), 126.35 (d, $J_{C\text{-}P}$ = 3.4 Hz), 125.67 (d, $J_{C\text{-}P}$ = 10.2 Hz), 125.65 (d, $J_{C\text{-}P}$ = 7.6 Hz), 124.23, 123.56, 123.11 (d, $J_{C\text{-}F}$ = 272.8 Hz), 118.06, 109.07, 101.48, 33.04, 31.55, 29.43, 22.73, 15.86 (d, $J_{C\text{-}P}$ = 92.8 Hz), 13.89 ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 27.84 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -62.96 ppm; **IR (ATR):** $\tilde{\nu}$ = 3099, 3059, 2957, 2928, 2871, 2823, 1614, 1589, 1554, 1513, 1488, 1466, 1423, 1371, 1337, 1274, 1242, 1220, 1174, 1129, 1106, 1078, 1037, 1008, 926, 907, 885, 848,

800, 763, 729, 702 $cm^{-1}$; **HRMS (ESI)** calculated for $[C_{30}H_{28}F_6N_2OP]^+$: 577.1838, found: 577.1835; **$[\alpha]_D^{20}$** = +226.5 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 3:1); HPLC separation (Chiralpak ID , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 11.6 min, $t_r$ (major) = 14.8 min), 96 : 4 *er*; (racemic spectrum showed both regioisomers).




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.079 | BB | 0.2935 | 2175.56348 | 110.60922 | 17.3899 |
| 2 | 11.625 | BB | 0.3713 | 4146.94629 | 170.76372 | 33.1478 |
| 3 | 14.921 | BB | 0.4267 | 4060.39258 | 145.87300 | 32.4559 |
| 4 | 20.761 | MM | 1.1276 | 2127.57373 | 31.44658 | 17.0063 |

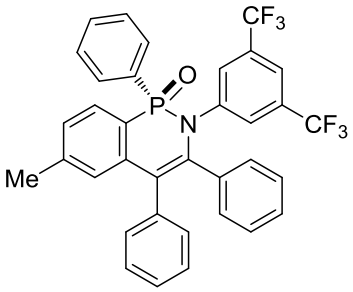



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.632 | BB | 0.3166 | 269.77045 | 13.19150 | 4.0361 |
| 2 | 14.760 | BB | 0.4116 | 6414.11719 | 238.58884 | 95.9639 |

**Parallel Resolution**

**Product 1**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-6-methyl-1,3,4-triphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2p')**

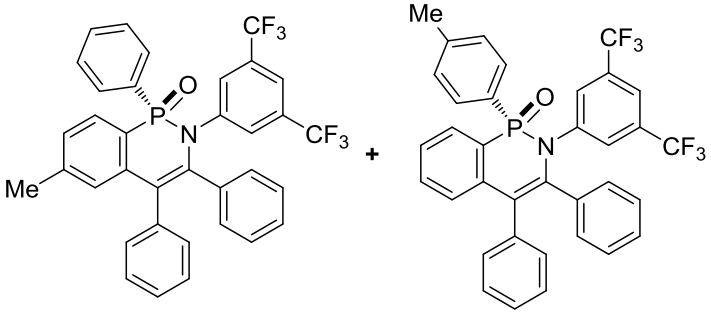


obtained as a white foam in 50% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.71 (ddd, *J* = 13.0, 8.3, 1.5 Hz, 2H), 7.49 (dd, *J* = 14.3, 7.8 Hz, 1H), 7.45–7.39 (m, 3H), 7.33 (ddd, *J* = 8.9, 6.8, 3.5 Hz, 2H), 7.26–7.15 (m, 7H), 7.06 (d, *J* = 4.7 Hz, 1H), 6.99–6.94 (m, 2H), 6.91–6.79 (m, 3H), 2.32 (s, 3H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 142.91 (d, $J_{C\text{-}P}$ = 2.6 Hz), 142.19 (d, $J_{C\text{-}P}$ = 3.2 Hz), 139.20, 138.54 (d, $J_{C\text{-}P}$ = 5.1 Hz), 137.70, 135.77 (d, $J_{C\text{-}P}$ = 3.3 Hz), 133.18 (d, $J_{C\text{-}P}$ = 10.3 Hz), 132.58 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.02, 131.20 (q, $J_{C\text{-}F}$ = 33.7 Hz), 131.12, 130.86 (d, $J_{C\text{-}P}$ = 12.8 Hz), 130.25 (d, $J_{C\text{-}P}$ = 132.4 Hz), 128.70, 128.41 (d, $J_{C\text{-}P}$ = 13.6 Hz), 128.36 (d, $J_{C\text{-}P}$ = 14.9 Hz), 128.15, 127.52, 127.37 (d, $J_{C\text{-}P}$ = 9.6 Hz), 127.05, 122.79 (d, $J_{C\text{-}P}$ = 7.3 Hz), 122.73 (q, $J_{C\text{-}F}$ = 273.0 Hz), 120.45 (d, $J_{C\text{-}P}$ = 131.4 Hz), 118.84, 22.19 ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 17.33 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.29 ppm; **IR (ATR):** $\tilde{\nu}$ = 3056, 3026, 2959, 2924, 2783, 1602, 1592, 1547, 1481, 1465, 1440, 1371, 1336, 1276, 1222, 1208, 1172, 1134, 1100, 1080, 1018, 972, 902, 848, 812, 745, 720 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{35}H_{25}F_6NOP]^+$: 620.1572, found: 620.1575; **$[\alpha]_D^{20}$** = -129.3 (c = 1.0, $CHCl_3$); **eluent for FCC** (hexane:EtOAc, 5:1).

**Product 1 & 2**

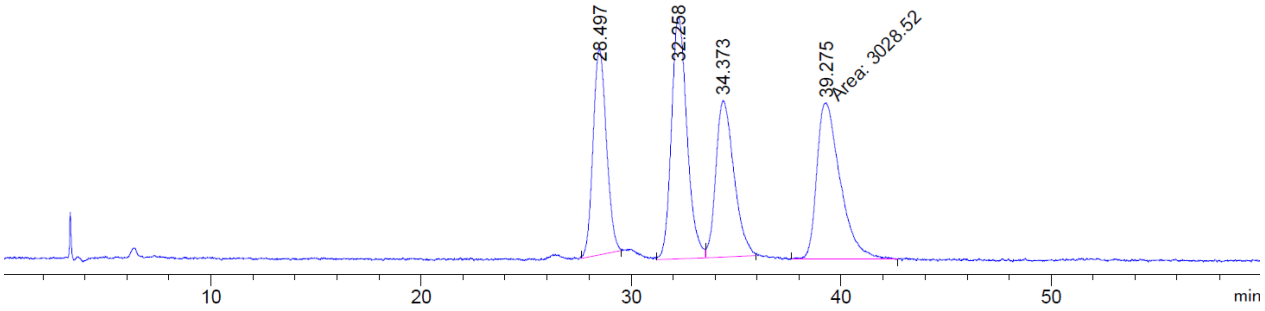
**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-6-methyl-1,3,4-triphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2p') &**

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-3,4-diphenyl-1-(*p*-tolyl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (2p)**

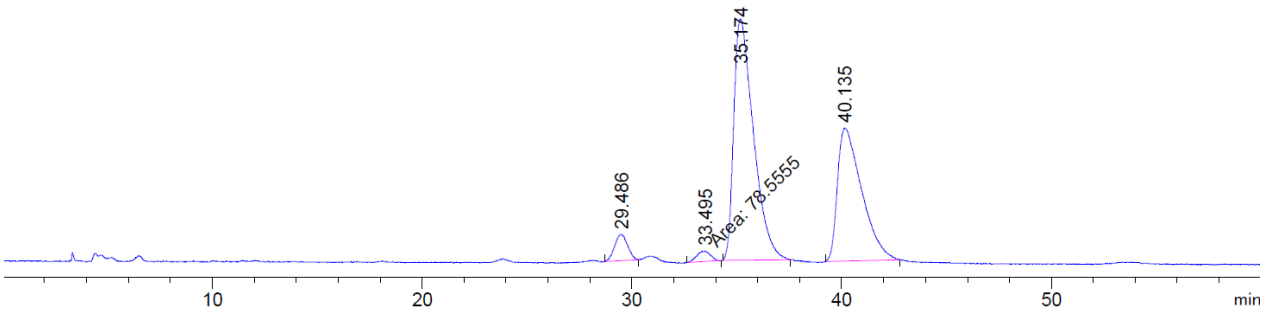


obtained the mixture as a white foam in 97% yield. **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.71 (ddd, *J* = 13.0,

8.3, 1.4 Hz, 2H), 7.64–7.57 (m, 2H), 7.57–7.46 (m, 3H), 7.45–7.39 (m, 5H), 7.37–7.30 (m, 3H), 7.28–7.12 (m, 17H), 7.06 (d, *J* = 4.8 Hz, 1H), 6.98 (tt, *J* = 7.9, 1.6 Hz, 4H), 6.92–6.79 (m, 6H), 2.32 (s, 6H) ppm; **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ = 143.49 (d, $J_{C-P}$ = 2.9 Hz), 142.90 (d, $J_{C-P}$ = 2.6 Hz), 142.26 (d, $J_{C-P}$ = 3.1 Hz), 142.19 (d, $J_{C-P}$ = 3.2 Hz), 139.21, 139.15, 138.55 (d, $J_{C-P}$ = 5.1 Hz), 138.37 (d, $J_{C-P}$ = 4.8 Hz), 137.70, 137.70 (d, $J_{C-P}$ = 3.1 Hz), 135.79, 135.75 (d, $J_{C-P}$ = 3.0 Hz), 133.32 (d, $J_{C-P}$ = 10.7 Hz), 133.17 (d, $J_{C-P}$ = 10.3 Hz), 132.57 (d, $J_{C-P}$ = 2.9 Hz), 132.21 (d, $J_{C-P}$ = 2.5 Hz), 132.02, 131.22 (q, $J_{C-F}$ = 33.8 Hz), 131.18 (q, $J_{C-F}$ = 33.8 Hz), 131.12, 130.86 (d, $J_{C-P}$ = 13.0 Hz), 130.73 (d, $J_{C-P}$ = 12.7 Hz), 130.30 (d, $J_{C-P}$ = 132.6 Hz), 129.23 (d, $J_{C-P}$ = 13.9 Hz), 128.72, 128.41 (d, $J_{C-P}$ = 13.5 Hz), 128.35 (d, $J_{C-P}$ = 14.9 Hz), 128.17, 128.15, 127.55, 127.53, 127.51, 127.38 (d, $J_{C-P}$ = 9.6 Hz), 127.15 (d, $J_{C-P}$ = 14.9 Hz), 127.08, 127.05, 127.05 (d, $J_{C-P}$ = 9.2 Hz), 127.04 (d, $J_{C-P}$ = 7.5 Hz), 126.34 (d, $J_{C-P}$ = 132.6 Hz), 123.80 (d, $J_{C-P}$ = 129.5 Hz), 122.79 (d, $J_{C-P}$ = 7.3 Hz), 122.75 (q, $J_{C-F}$ = 273.0 Hz), 122.74 (q, $J_{C-F}$ = 272.7 Hz), 120.47 (d, $J_{C-P}$ = 131.6 Hz), 118.83, 22.19, 21.70 (d, $J_{C-P}$ = 1.3 Hz) ppm; **$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ = 17.32, 17.12 ppm; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ = -63.28, 63.29 ppm; **eluent for FCC** (hexane:EtOAc, 5:1); HPLC separation (Chiralpak IF , 4.6 x 250 mm; 5% *i*-PrOH / hexane, 0.5 mL/min, 280 nm; product 1: $t_r$ (minor) = 29.5 min, $t_r$ (major) = 35.2 min), 93 : 7 *er*; product 2: $t_r$ (minor) = 33.5 min, $t_r$ (minor) = 40.1 min), 96 : 4 *er*.

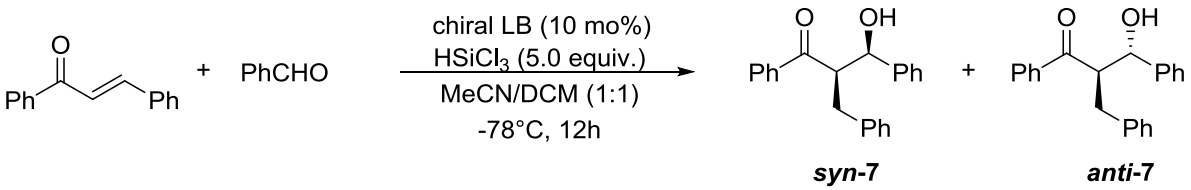



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 28.491 | BB | 0.5909 | 1840.33704 | 41.53518 | 20.9972 |
| 2 | 32.239 | BB | 0.5973 | 2583.97949 | 52.22110 | 29.4817 |
| 3 | 34.407 | BB | 0.6865 | 1743.39026 | 30.24462 | 19.8911 |
| 4 | 39.257 | MM | 1.2648 | 2596.98901 | 34.22166 | 29.6301 |



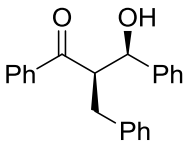

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 29.486 | BB | 0.5279 | 183.59442 | 4.28515 | 4.0483 |
| 2 | 33.495 | MM | 0.7822 | 78.55555 | 1.67380 | 1.7322 |
| 3 | 35.174 | BB | 0.8821 | 2551.15405 | 38.95083 | 56.2539 |
| 4 | 40.135 | BB | 0.9580 | 1721.76489 | 21.46156 | 37.9656 |

**Experimental procedure for the enantioselective reductive aldol reaction**[4,5]




To a solution of (*E*)-chalcone (31.2 mg, 0.15 mmol, 1.5 equiv.), benzaldehyde (10.2 µl, 0.1 mmol), and chiral Lewis base **2a** or **8** (10 mol %) in anhydrous acetonitrile/$CH_2Cl_2$ (ratio 1/1), trichlorosilane (50 µl, 0.5 mmol, 5.0 equiv.) was added at -78 °C. Upon the reaction was completed, sat. aq. $NaHCO_3$ was required to quench the reaction. The aqueous phase was extracted with $CH_2Cl_2$. Combined the organic layers and dried over $Na_2SO_4$. The solvent was removed by rotary evaporation and the residue was purified by flash column chromatography.

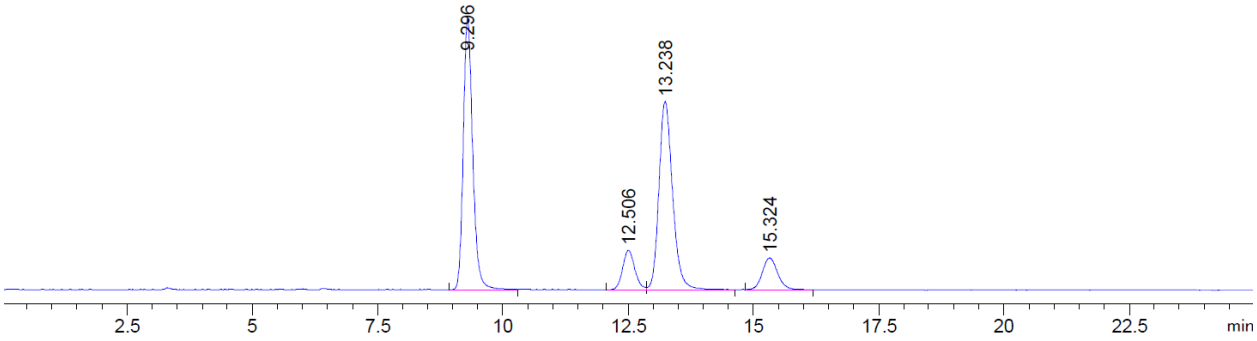
**(2*R*,3*R*)-2-Benzyl-3-hydroxy-1,3-diphenylpropan-1-one**



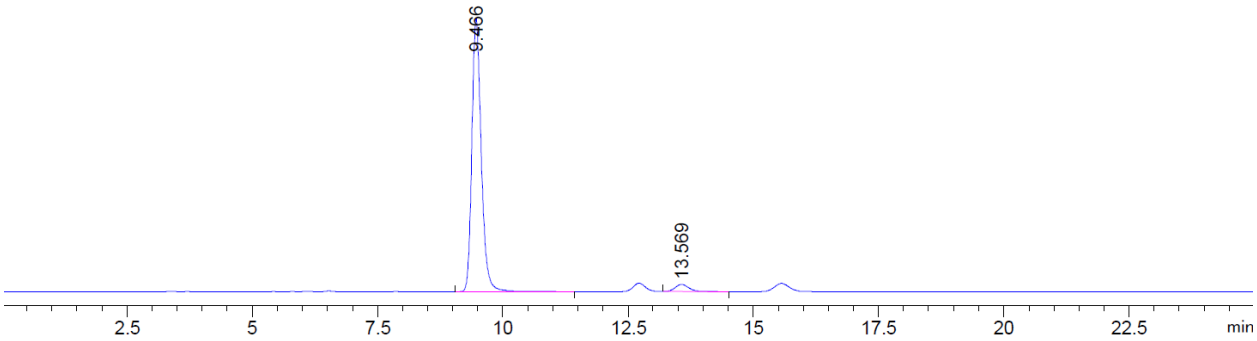

***syn***

prepared from **2a** as catalyst.obtained as a white foam in 95% yield (***syn***:***anti***, 10:1). **$^1$H NMR** (400 MHz, Chloroform-*d*) δ = 7.59–7.51 (m, 2H), 7.42 (tt, *J* = 7.4,

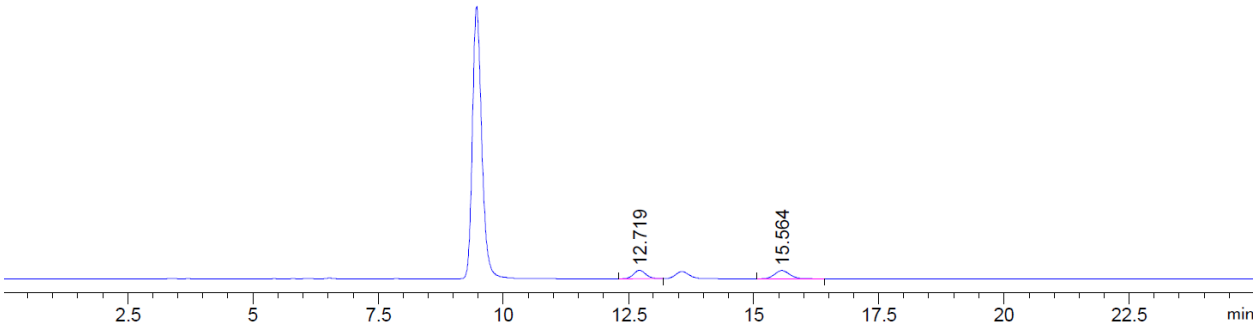
1.2 Hz, 3H), 7.36–7.30 (m, 2H), 7.29–7.22 (m, 3H), 7.13–7.00 (m, 3H), 6.98–6.92 (m, 2H), 5.12 (d, *J* = 4.4 Hz, 1H), 4.04 (ddd, *J* = 10.5, 4.5, 3.6 Hz, 1H), 3.20 (dd, *J* = 13.6, 10.5 Hz, 1H), 3.06 (dd, *J* = 13.6, 3.5 Hz, 1H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 205.10, 141.65, 139.39, 137.39, 133.24, 129.10, 128.53, 128.44, 128.43, 128.37, 127.77, 126.31, 126.26, 74.03, 55.64, 33.53 ppm; **$[\alpha]_D^{20}$** = +10.8 (c = 1.0, $CHCl_3$); **eluent for FCC** (pentane:EtOAc, 10:1); HPLC separation (Chiralpak IF , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 254 nm; $t_r$ (*syn*-major) = 9.5 min, $t_r$ (*syn*-minor) = 13.6 min), 96 : 4 *er*; HPLC separation (Chiralpak IF , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 254 nm; $t_r$ (*anti*-major) = 12.7 min, $t_r$ (*anti*-minor) = 15.6 min), 55 : 45 *er*; (racemic spectrum showed both diastereoisomers).




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.296 | BV | 0.2007 | 2306.11621 | 176.20003 | 41.9602 |
| 2 | 12.506 | BV | 0.2625 | 435.11584 | 25.56820 | 7.9170 |
| 3 | 13.238 | VB | 0.2893 | 2315.73169 | 122.10709 | 42.1351 |
| 4 | 15.324 | BB | 0.3269 | 439.00125 | 20.57627 | 7.9877 |

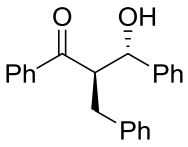


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.466 | BB | 0.2004 | 6983.66797 | 534.50903 | 96.3669 |
| 2 | 13.569 | BB | 0.2885 | 263.28754 | 13.92913 | 3.6331 |



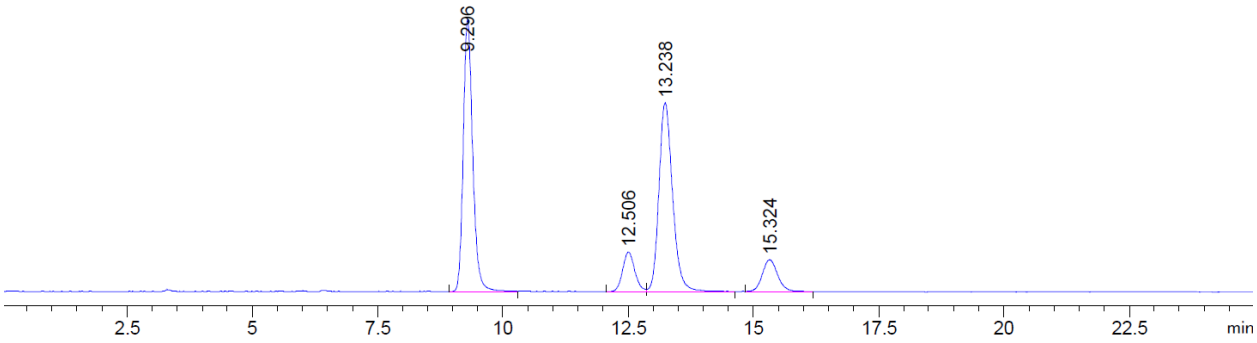

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.719 | BB | 0.2605 | 278.41135 | 16.52831 | 45.2332 |
| 2 | 15.564 | BB | 0.3223 | 337.09070 | 16.09870 | 54.7668 |

**2-Benzyl-3-hydroxy-1,3-diphenylpropan-1-one (*anti*)**

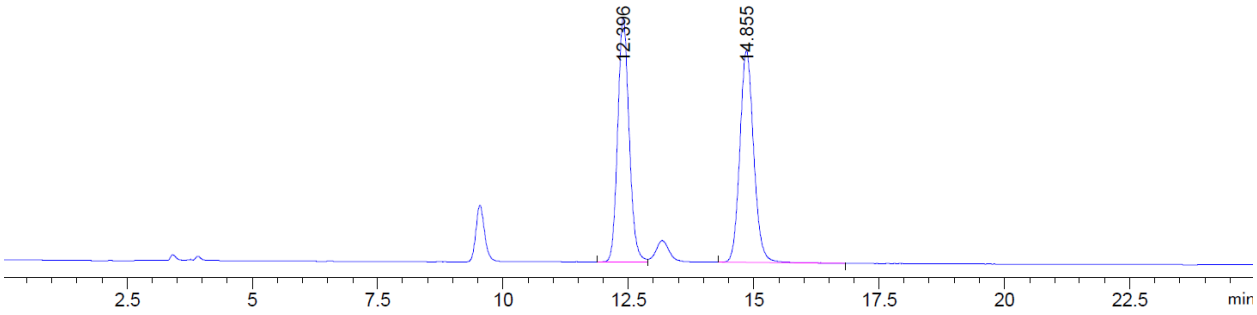



***anti***

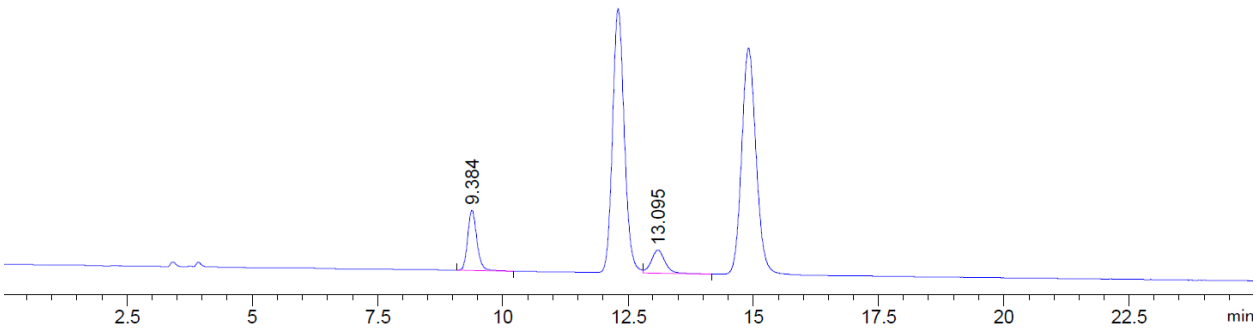
prepared from **8** as catalyst. obtained as a white foam in 89% yield (***anti*:*syn***, 5:1). **$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ = 7.70–7.63 (m, 2H), 7.49–7.40 (m, 1H), 7.39–7.27 (m, 6H), 7.27–7.15 (m, 3H), 7.15–7.00 (m, 3H), 4.97 (d, *J* = 6.0 Hz, 1H), 4.10 (dt, *J* = 8.5, 6.2 Hz, 1H), 3.05 (dd, *J* = 13.5, 8.6 Hz, 1H), 2.91 (dd, *J* = 13.4, 6.4 Hz, 1H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 205.74, 142.77, 138.68, 138.04, 133.23, 129.12, 128.61, 128.59, 128.48, 128.26, 127.85, 126.56, 126.26, 75.50, 54.82, 36.78 ppm; **eluent for FCC** (pentane:EtOAc, 10:1); HPLC separation (Chiralpak IF , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 254 nm; $t_r$ (*anti*-major) = 12.5 min, $t_r$ (*anti*-minor) = 14.9 min), 51 : 49 *er*; HPLC separation (Chiralpak IF , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 254 nm; $t_r$ (*syn*-major) = 9.4 min, $t_r$ (*syn*-minor) = 13.1 min), 63 : 37 *er*; (racemic spectrum showed both diastereoisomers).




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.296 | BV | 0.2007 | 2306.11621 | 176.20003 | 41.9602 |
| 2 | 12.506 | BV | 0.2625 | 435.11584 | 25.56820 | 7.9170 |
| 3 | 13.238 | VB | 0.2893 | 2315.73169 | 122.10709 | 42.1351 |
| 4 | 15.324 | BB | 0.3269 | 439.00125 | 20.57627 | 7.9877 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.396 | BV | 0.2452 | 1108.57520 | 69.83605 | 48.7433 |
| 2 | 14.855 | BB | 0.2966 | 1165.73633 | 60.55571 | 51.2567 |

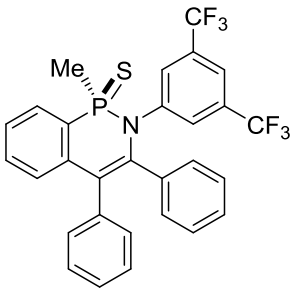


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.384 | BB | 0.1943 | 195.93544 | 15.41739 | 62.6346 |
| 2 | 13.095 | VB | 0.2906 | 116.88761 | 5.96637 | 37.3654 |

**Experimental procedure for synthesizing 9**[4]

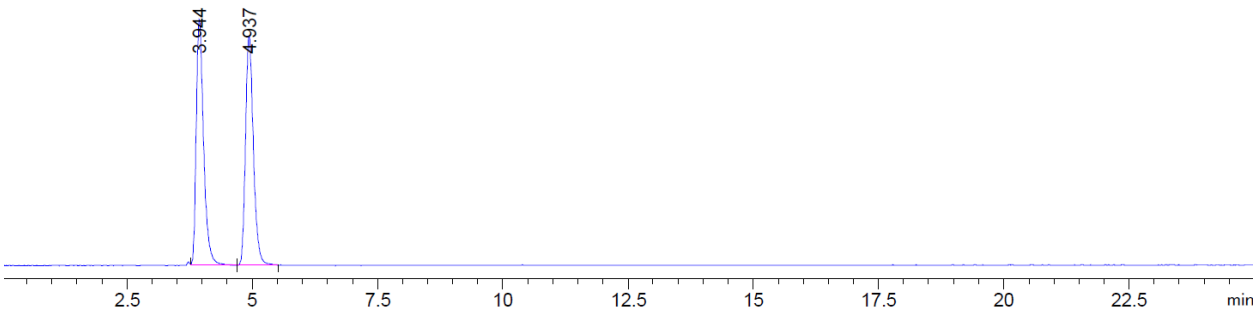
To a suspension of **2a** (109 mg, 0.2 mmol, >99% ee) in anhydrous toluene (5 mL) was added Lawesson's reagent (81 mg, 0.2 mmol). The reaction was stirred at 90 °C for 16 hours under nitrogen. After complete consumption of **2a** (indicated by TLC), the solvent was removed by rotary evaporation under reduced pressure. The residue was purified by flash column chromatography on silica gel (pentane:$CH_2Cl_2$, 3:1) to give **9** as a white form in 99% Yield.

**(*R*)-2-(3,5-Bis(trifluoromethyl)phenyl)-1-methyl-3,4-diphenyl-2*H*-benzo[*c*][1,2]azaphosphinine 1-sulfide (9)**

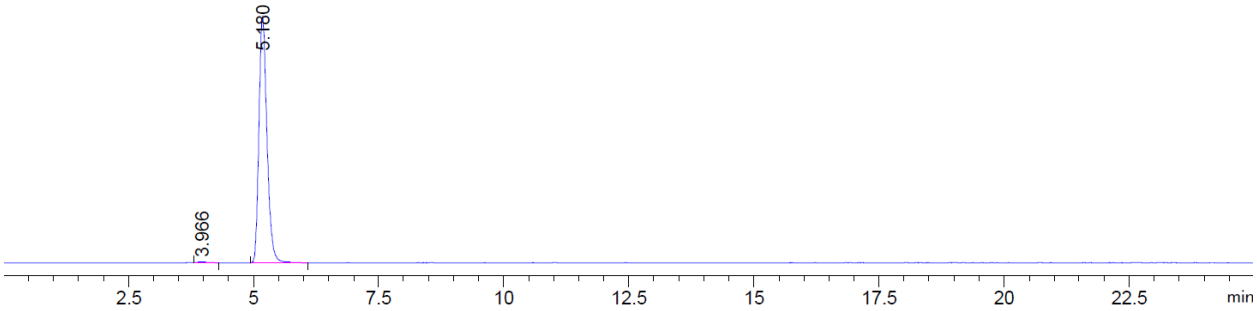



**$^1$H NMR** (400 MHz, $C_6D_6$) δ = 8.14 (ddd, *J* = 15.3, 7.3, 1.7 Hz, 1H), 7.77 (s, 2H), 7.28 (s, 1H), 7.23 (ddd, *J* = 6.4, 5.0, 1.3 Hz, 1H), 7.10–6.97 (m, 6H), 6.97–6.89 (m, 3H), 6.64 (t, *J* = 7.7 Hz, 2H), 6.55–6.45 (m, 1H), 1.79 (d, *J* = 13.0 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $C_6D_6$) δ = 142.04 (d, $J_{C\text{-}P}$ = 3.7 Hz), 139.96 (d, $J_{C\text{-}P}$ = 1.8 Hz), 137.59 , 136.87 (d, $J_{C\text{-}P}$ = 5.4 Hz), 136.20 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.12 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.79 , 131.23 (q, $J_{C\text{-}F}$ = 33.5 Hz), 130.71 , 130.08 (d, $J_{C\text{-}P}$ = 13.0 Hz), 129.65 , 128.84 (d, $J_{C\text{-}P}$ = 13.9 Hz), 128.25 , 128.08, 127.99, 127.80, 127.45 , 127.11 (d, $J_{C\text{-}P}$ = 8.9 Hz), 126.19 (d, $J_{C\text{-}P}$ = 96.8 Hz), 123.55 (q, $J_{C\text{-}F}$ = 272.9 Hz), 119.27 , 22.73 (d, $J_{C\text{-}P}$ = 72.5 Hz) ppm; **$^{31}$P NMR** (162 MHz, $C_6D_6$) δ = 55.02 ppm; **$^{19}$F NMR** (376 MHz, $C_6D_6$) δ = -62.79 ppm; **IR (ATR):** $\tilde{\nu}$ = 3058, 3026, 2983, 2913, 1602, 1585, 1551, 1488, 1462, 1443, 1404, 1370, 1324, 1274, 1173, 1130, 1093, 1076, 1013, 952, 914, 891, 845, 774, 758, 735, 717 cm$^{-1}$; **HRMS (ESI)** calculated for $[C_{29}H_{21}F_6NPS]^+$: 560.1031, found: 560.1036; **$[\alpha]_D^{20}$** = +427.2

(c = 1.0, $CH_2Cl_2$); HPLC separation (Chiralpak IC , 4.6 x 250 mm; 2% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (major) = 4.0 min, $t_r$ (minor) = 5.2 min), 99.5 : 0.5 *er*.




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 3.944 | VB | 0.1576 | 620.45221 | 60.51275 | 50.1545 |
| 2 | 4.937 | BB | 0.1674 | 616.63013 | 56.46541 | 49.8455 |



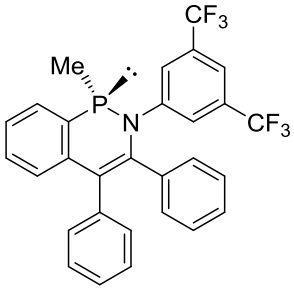

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 3.966 | VB | 0.1819 | 27.05594 | 2.22414 | 0.5294 |
| 2 | 5.180 | BB | 0.1731 | 5083.63281 | 452.43878 | 99.4706 |

**<u>Experimental procedure for synthesizing 10:</u>**

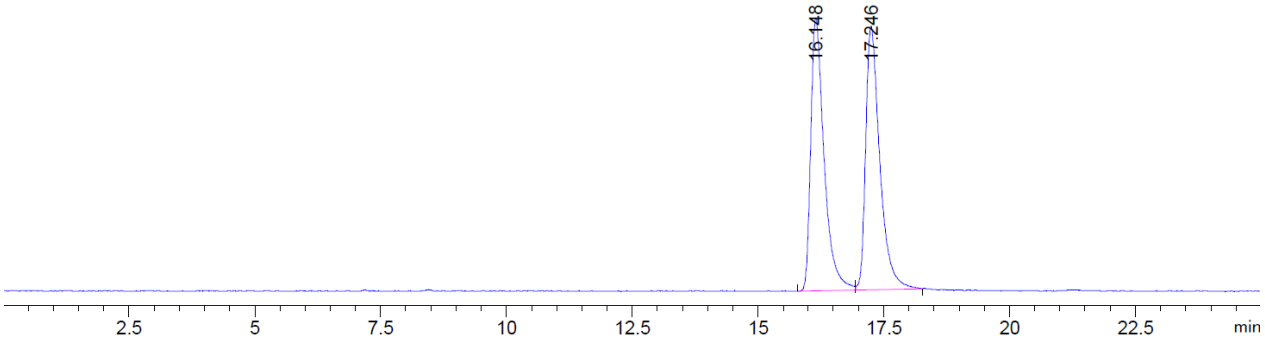
To a solution of **9** (56 mg, 0.1 mmol, 99.5 : 0.5 er) in anhydrous $CH_2Cl_2$ (2 mL), methyl trifluoromethanesulfonate (23 µL, 0.2 mmol) was added. The reaction mixture was stirred at 40 °C for 24 hours under nitrogen. After cooling down to 23 °C, *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethylphosphanetriamine (36 µL, 0.2 mmol) was added *via* micro-syringe. The reaction

mixture was then stirred at 40 °C for an additional hour. Then the volatiles were removed by rotary evaporation and the residue was purified by flash column chromatography on silica gel (pentane:$CH_2Cl_2$, 50:1) to give **10** as a white foam in 90% yield.

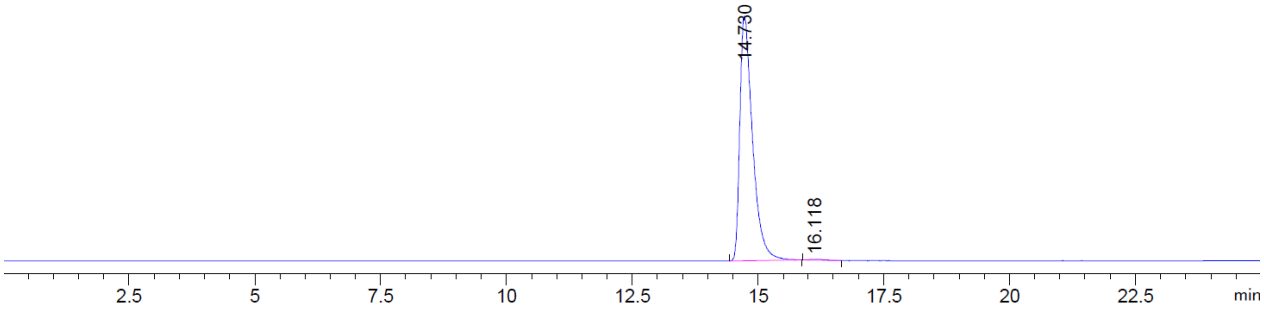
**(*S*)-2-(3,5-Bis(trifluoromethyl)phenyl)-1-methyl-3,4-diphenyl-1,2-dihydrobenzo[*c*][1,2]azaphosphinine (10)**




**$^1$H NMR** (600 MHz, $CD_2Cl_2$) δ = 7.62–7.50 (m, 3H), 7.43–7.25 (m, 9H), 7.19–7.12 (m, 2H), 7.06–6.94 (m, 3H), 1.62 (d, *J* = 6.2 Hz, 3H) ppm; **$^{13}$C NMR** (151 MHz, , $CD_2Cl_2$) δ = 149.06 (d, $J_{C\text{-}P}$ = 26.0 Hz), 138.77, 137.51, 136.39 (d, $J_{C\text{-}P}$ = 6.6 Hz), 135.47, 132.10, 132.03 (d, $J_{C\text{-}P}$ = 4.7 Hz), 131.48 (q, $J_{C\text{-}F}$ = 33.1 Hz), 131.26, 131.21, 130.64 (d, $J_{C\text{-}P}$ = 47.0 Hz), 130.24, 128.40, 127.75, 127.65, 127.47 (d, $J_{C\text{-}P}$ = 15.2 Hz), 127.31, 127.04 (d, $J_{C\text{-}P}$ = 2.0 Hz), 123.69 (q, $J_{C\text{-}F}$ = 272.7 Hz), 123.68–123.14 (m), 115.48, 14.85 (d, $J_{C\text{-}P}$ = 16.0 Hz) ppm; **$^{31}$P NMR** (243 MHz, $CD_2Cl_2$) δ = 20.46 ppm; **$^{19}$F NMR** (376 MHz $CD_2Cl_2$) δ = -62.76 ppm; **IR (ATR):** $\tilde{\nu}$ = 3056, 3026, 2965, 2927, 2901, 1613, 1585, 1548, 1488, 1463, 1443, 1413, 1373, 1323, 1275, 1227, 1173, 1131, 1092, 1074, 1027, 1004, 951, 914, 879, 845, 774, 754, 738, 712 $cm^{-1}$; **HRMS (ESI)** calculated for $[C_{29}H_{21}F_6NP]^+$: 528.1310, found: 528.1292; **$[\alpha]_D^{20}$** = +812.5 (c = 1.0, $CH_2Cl_2$); HPLC separation (Chiralpak IB, 4.6 x 500 mm (2 250 mm columns connected; hexane, 1.0 mL/min, 280 nm; $t_r$ (major) = 14.7 min, $t_r$ (minor) = 16.1 min), 99.5 : 0.5 *er*.



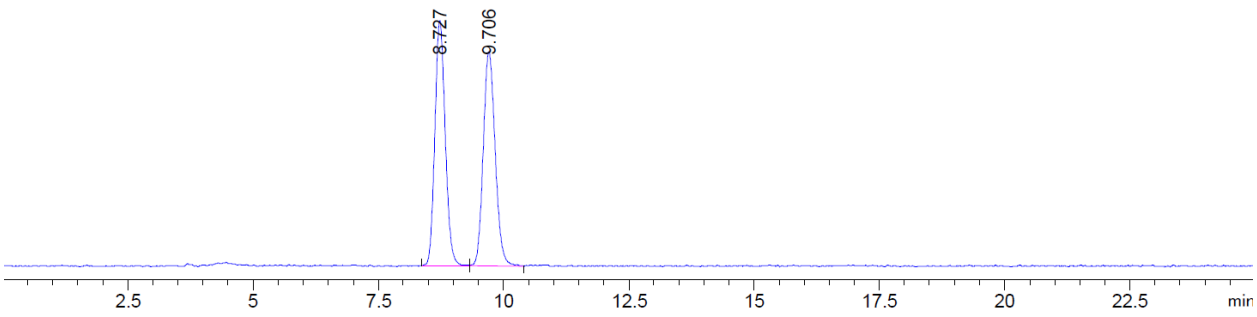
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.148 | BV | 0.2775 | 958.83167 | 51.92010 | 49.5481 |
| 2 | 17.246 | VB | 0.2931 | 976.32336 | 50.15775 | 50.4519 |



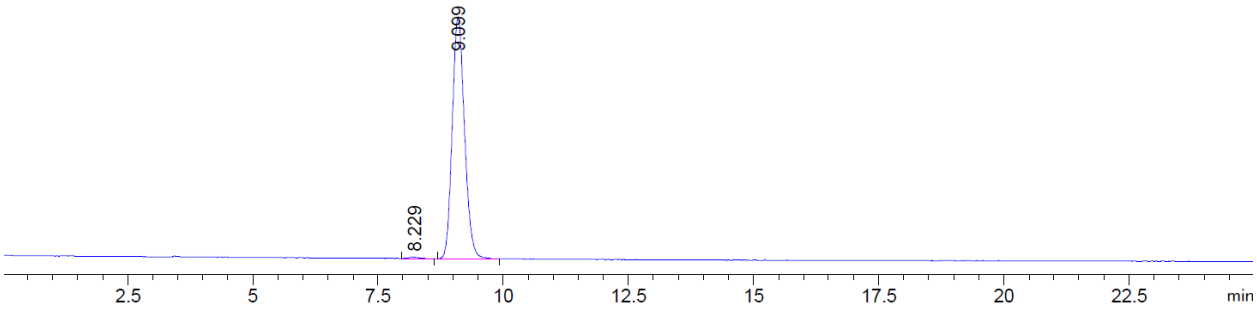

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.730 | BB | 0.2633 | 5348.95459 | 304.03867 | 99.5162 |
| 2 | 16.118 | BB | 0.2174 | 26.00479 | 1.49160 | 0.4838 |

**Experimental procedure for reoxidizing 10 to confirm the configuration:**

To a stirred solution of **10** (26.4 mg, 0.05 mmol, 99.5 : 0.5 er) in $CH_2Cl_2$ (2 mL), hydrogen peroxide solution (30% w/w in $H_2O$, 1 mL) was added dropwise at 23 °C, the reaction mixture was stirred for further 5 min. Then, organic layer was separated, dried over MgSO4 and filtrated. The volatiles were removed by rotary evaporation and **2a** was obtained in quant. yield without further purification. HPLC separation (Chiralpak IC , 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 280 nm; $t_r$ (minor) = 8.2 min, $t_r$ (major) = 9.1 min), 99.5 : 0.5 *er*.

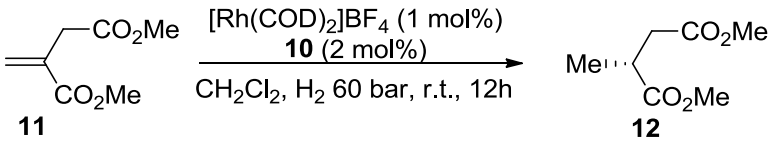


| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.727 | BB | 0.2239 | 889.99371 | 61.82875 | 49.9565 |
| 2 | 9.706 | BB | 0.2563 | 891.54242 | 54.08825 | 50.0435 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.229 | BB | 0.1931 | 16.16424 | 1.02969 | 0.5080 |
| 2 | 9.099 | BV | 0.2651 | 3165.67554 | 185.51180 | 99.4920 |

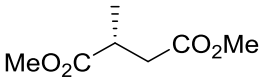
**Experimental procedure for hydrogenation with 10:**[5]



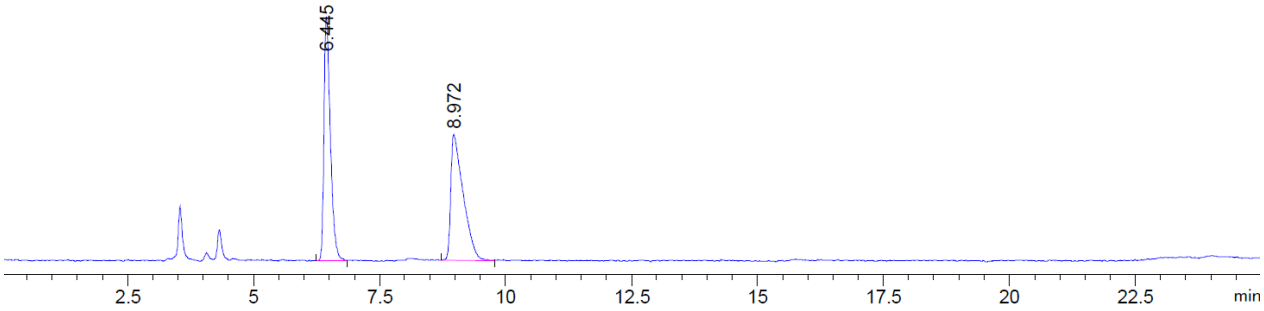

**11** **12**

To a test tube equipped with a septum and a stirring bar, $Rh(COD)_2BF_4$ (1.0 mg, 2.5 µmol, 0.01 equiv.) and ligand **10 (**2.6 mg, 5.0 µmol, 0.02 equiv.) were weighted. Then degassed dichloromethane (2.5 mL) was added under nitrogen atmosphere. The resulting yellow solution was stirred at room temperature for 40 min. Then it was transferred to another test tube containing substrate (0.25 mmol) under nitrogen atmosphere. The tube was placed in the autoclave. After applying 60 bar of hydrogen pressure the reaction mixture was stirred at room temperature for 12 hours. The reactors were opened and the samples were taken which were filtered over a short silica column and subjected to enantiomeric excess determination by GC or HPLC. Conversions were determined by measurement of $^1H$ NMR.

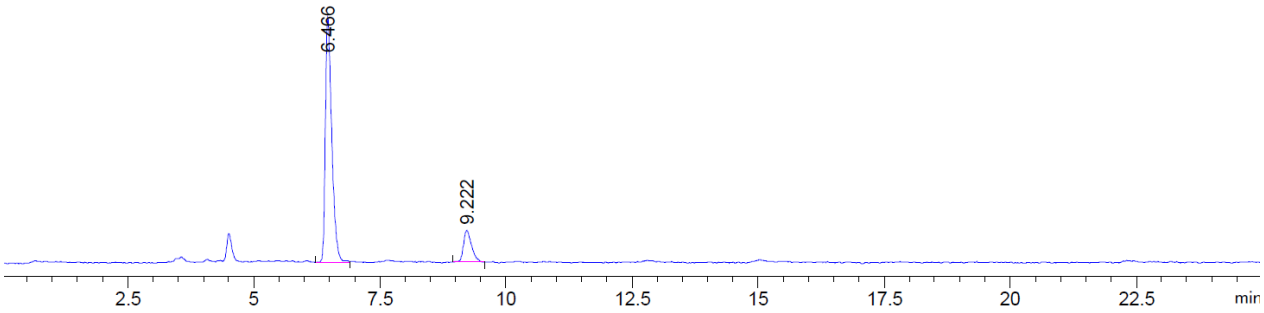
**Dimethyl (*R*)-2-methylsuccinate (12)**[5c]




**$^1$H NMR** (400 MHz, Chloroform-*d*) δ = 3.68 (d, *J* = 7.1 Hz, 6H), 2.97 – 2.83 (m, 1H), 2.73 (dd, *J* = 16.5, 8.2 Hz, 1H), 2.40 (dd, *J* = 16.6, 6.0 Hz, 1H), 1.21 (d, *J* = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 175.84, 172.42, 52.07, 51.86, 37.50, 35.80, 17.14 ppm; **$[\alpha]_D^{20}$** = +4.0 (c = 1.0, $CHCl_3$); HPLC separation (Chiralpak IB , 4.6 x 250 mm; 2% *i*-PrOH / hexane, 1.0 mL/min, 220 nm; $t_r$ (major) = 6.5 min, $t_r$ (minor) = 9.2 min), 86 : 14 *er*.




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.445 | BV | 0.1331 | 1421.39709 | 160.91280 | 50.0284 |
| 2 | 8.972 | BV | 0.2418 | 1419.78467 | 82.90094 | 49.9716 |




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.466 | BV | 0.1331 | 1333.09753 | 150.82167 | 85.7714 |
| 2 | 9.222 | BV | 0.1604 | 221.14685 | 19.48949 | 14.2286 |

**Experimental procedure in deuterium solvent for mechanism study:**

All the reagents were dried *in vacuo* overnight. The experiment was launched in glovebox. Rh-catalyst **Rh7** (6.2 mg, 10.0 µmol), and dibenzoylperoxide (2.4 mg, 10.0 µmol) were weighed into a oven-dried microwave tube equipped with a magnetic stir bar. *t*BuOD (400 µL) was added and the mixture stirred at 23 °C for 15 min. To the solution were added **1a** (36.7 mg, 0.1 mmol, 1.0 equiv.), diphenylacetylene (26.7 mg, 0.2 mmol, 1.5 equiv.), $K_2CO_3$ (13.8 mg, 0.1 mmol, 1.0 equiv.), $Ag_2CO_3$ (55.1 mg, 0.2 mmol, 2.0 equiv.), 50 mg 4Å molecular sieves (powder, actived, 325 mesh particle size) and the tube sealed. The reaction mixture was stirred at 90 °C for 8 hours. After cooling down to 23 °C, the mixture was filtered over a pad of celite (washing with EtOAc), the volatiles removed under reduced pressure and the crude purified by column chromatography on silica gel (hexane:EtOAc, 3:1), yielding 27.0 mg of **2a**; ($CHCl_3$:EtOAc, 1:1), recovering 15.0 mg of *ent*-**1a**.

0% D-incorporation was observed in both **2a** and recovered **1a.**

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[2] a) M. Oliana, F. King, P. N. Horton, M. B. Hursthouse, K. Kuok, M. Hii, C. London, L. Wcr, J. Matthey, P. O. Box, et al., *J. Org. Chem.* **2006**, *71*, 2472; b) Z.-J. Du, J. Guan, G.-J. Wu, P. Xu, L.-X. Gao, F.-S. Han, *J. Am. Chem. Soc.* **2015**, *137*, 632.

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[4] a) M. Sugiura, N. Sato, Y. Sonoda, S. Kotani, M. Nakajima, *Chem. Asian J.* **2010**, *5*, 478; b) T. Yamada, T. Nagata, K. D. Sugi, K. Yorozu, T. Ikeno, Y. Ohtsuka, D. Miyazaki, T. Mukaiyama, *Chem. Eur. J.* **2003**, *9*, 4485.

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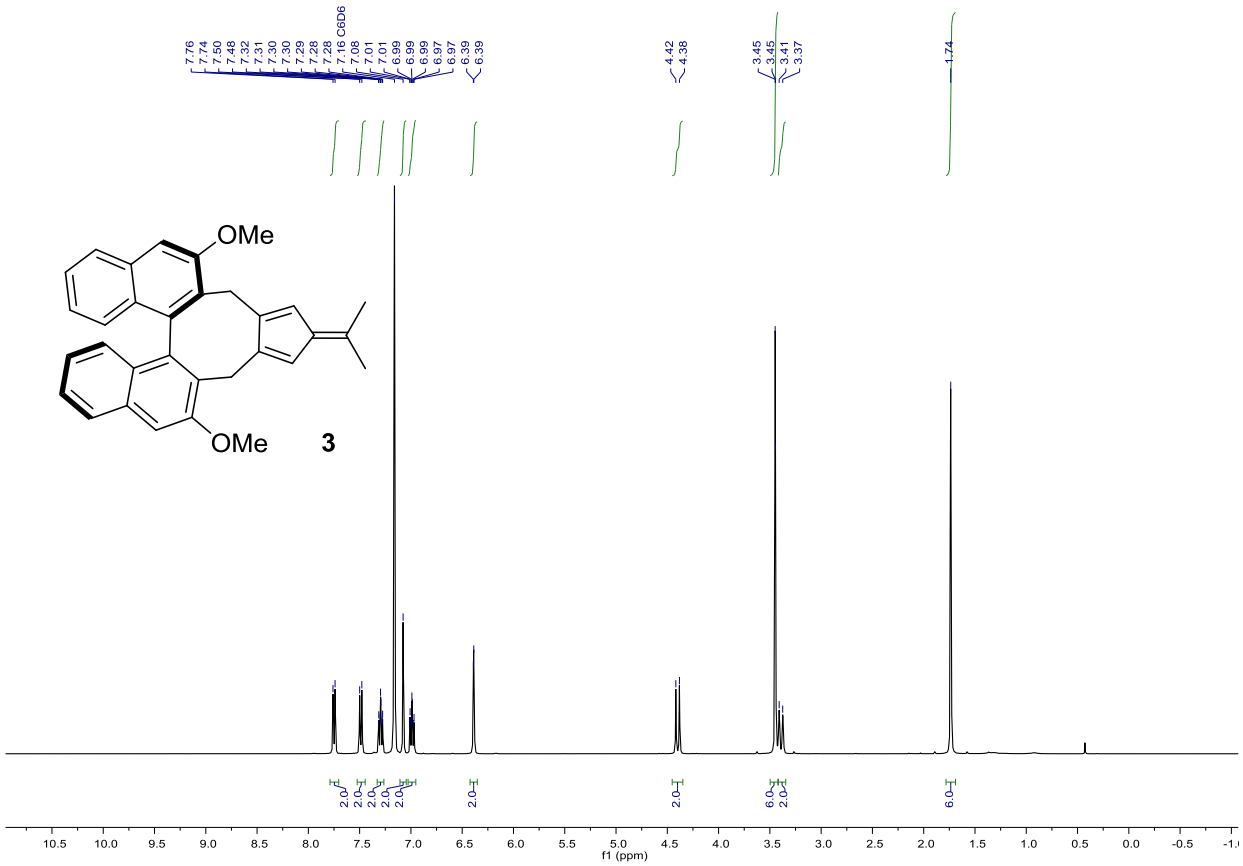
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7.74
7.50
7.48
7.32
7.31
7.30
7.30
7.29
7.28
7.16 C6D6
7.08
7.01
7.01
6.99
6.99
6.99
6.97
6.97
6.39
6.39
4.42
4.38
3.45
3.45
3.41
3.37
1.74
OMe
OMe
3
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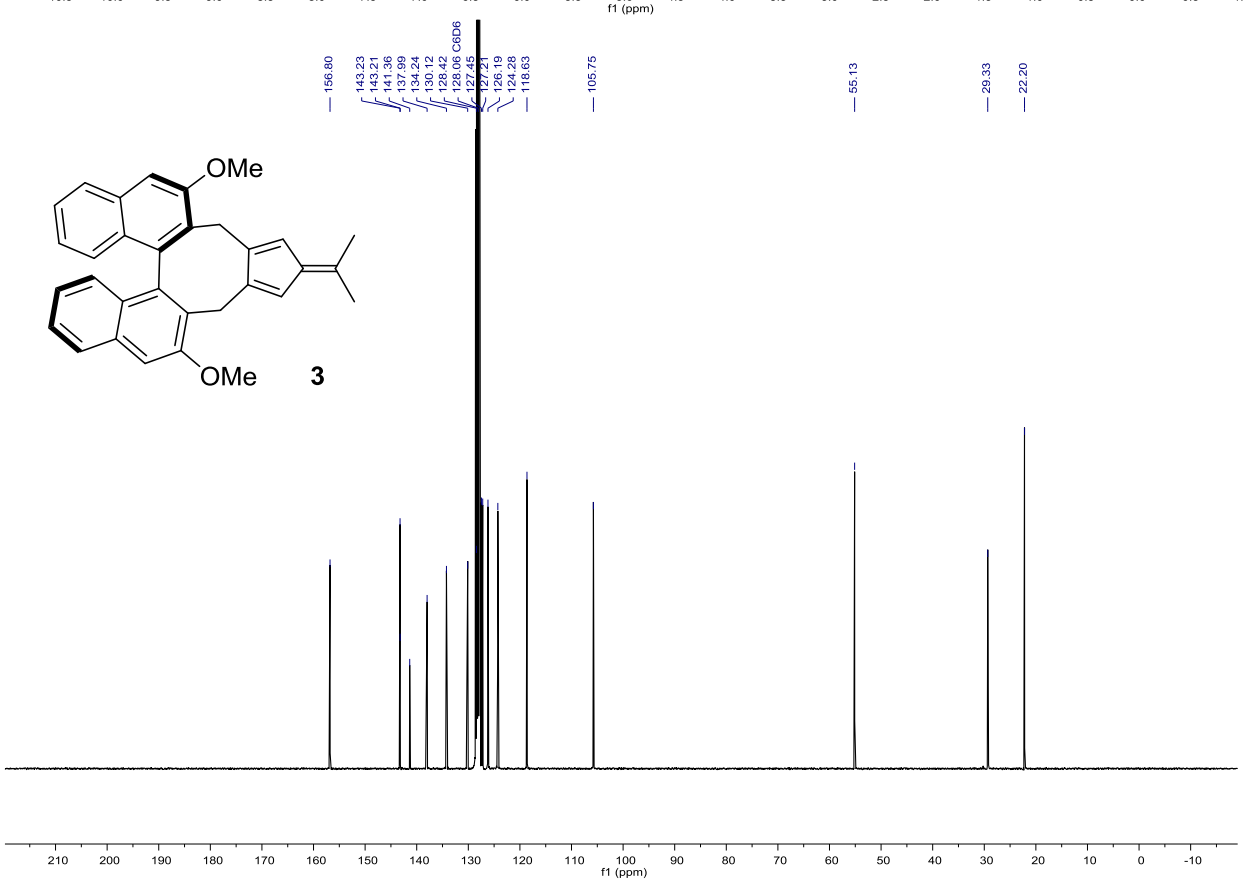
2.0
2.0
2.0
2.0
2.0
2.0
6.0
2.0
6.0
f1 (ppm)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137.99
134.24
130.12
128.42
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OMe
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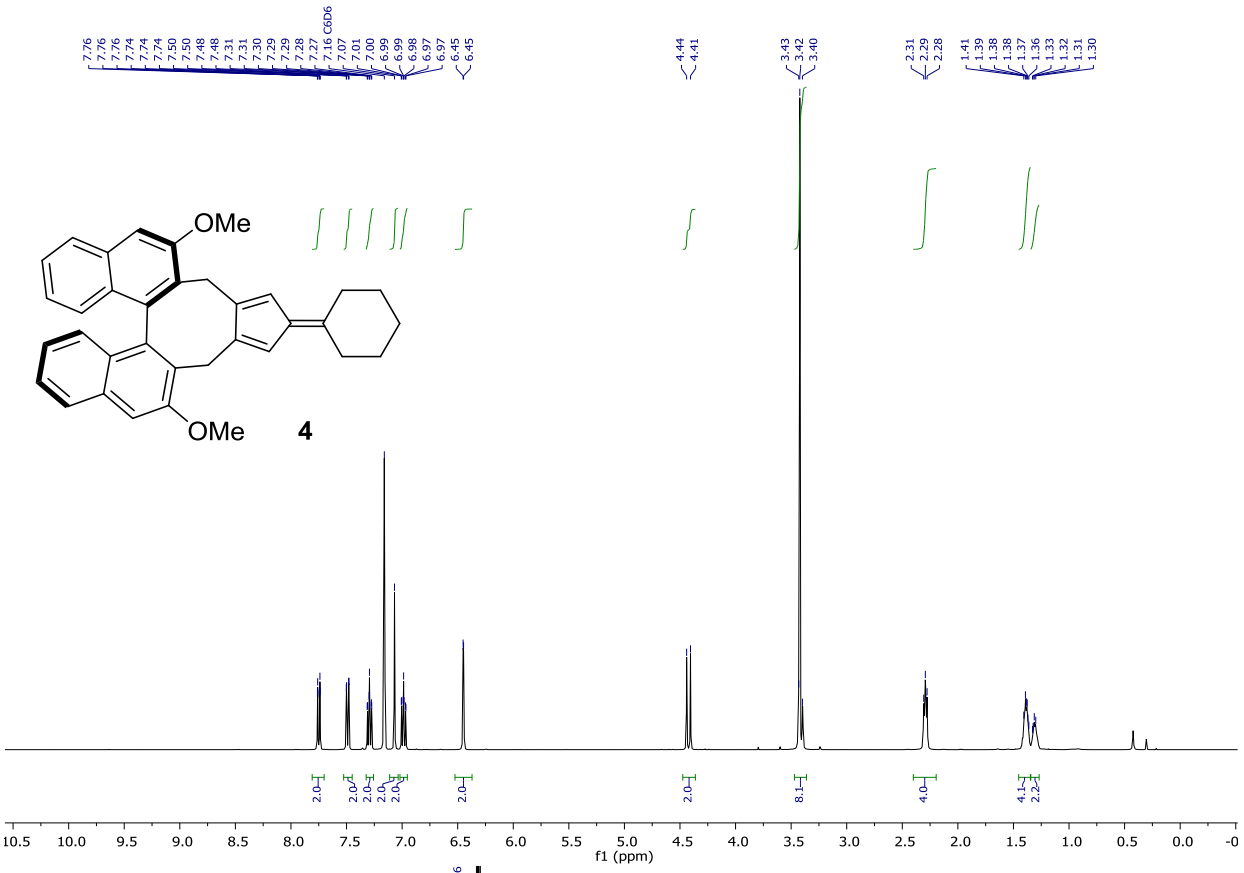
f1 (ppm)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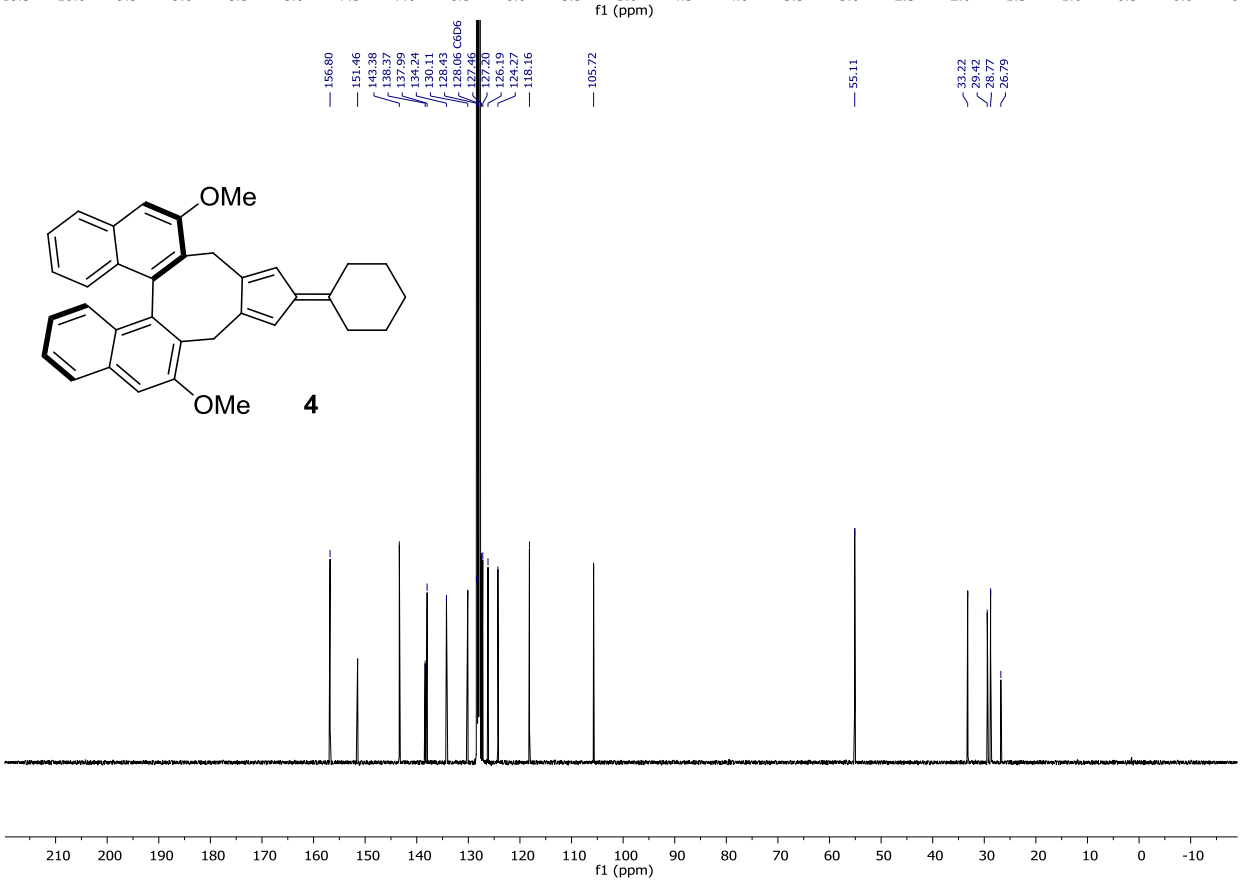
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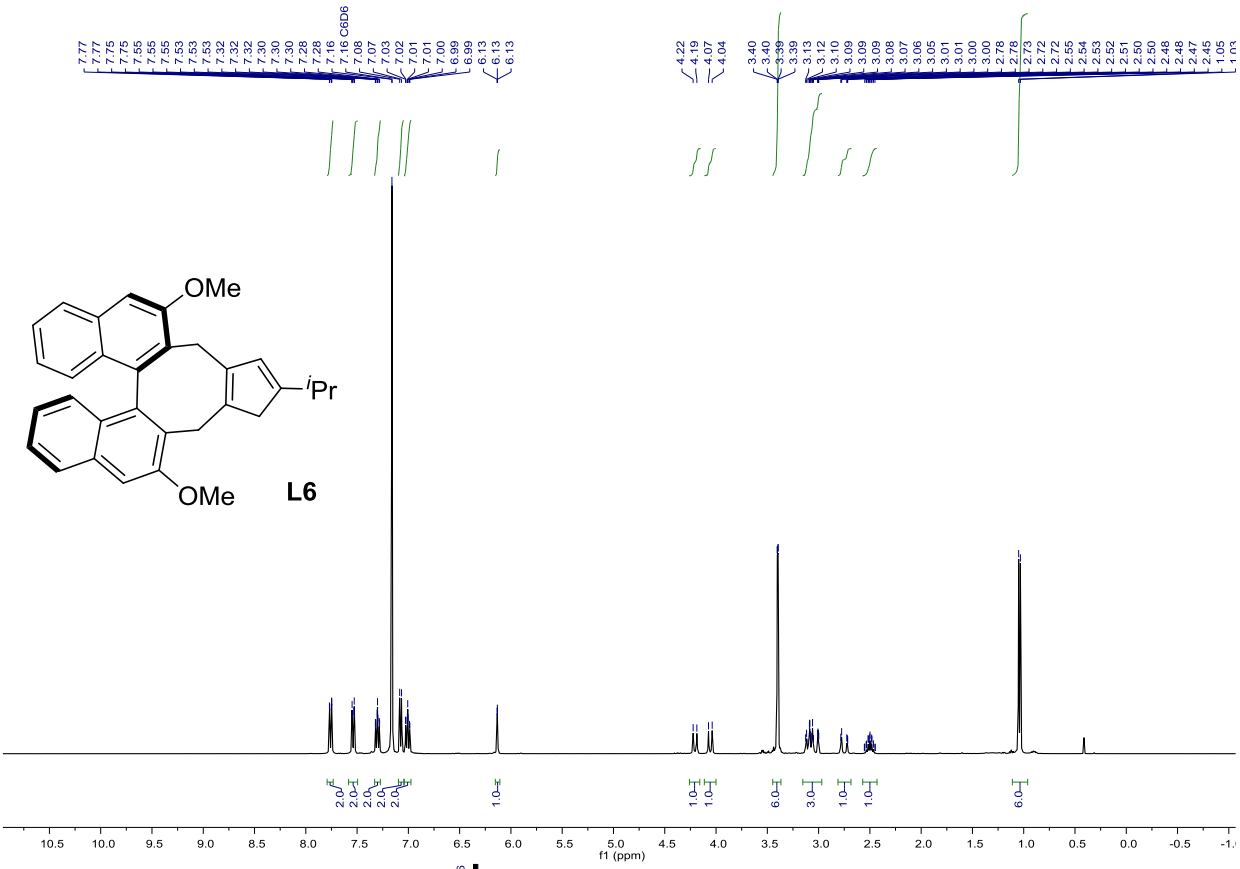
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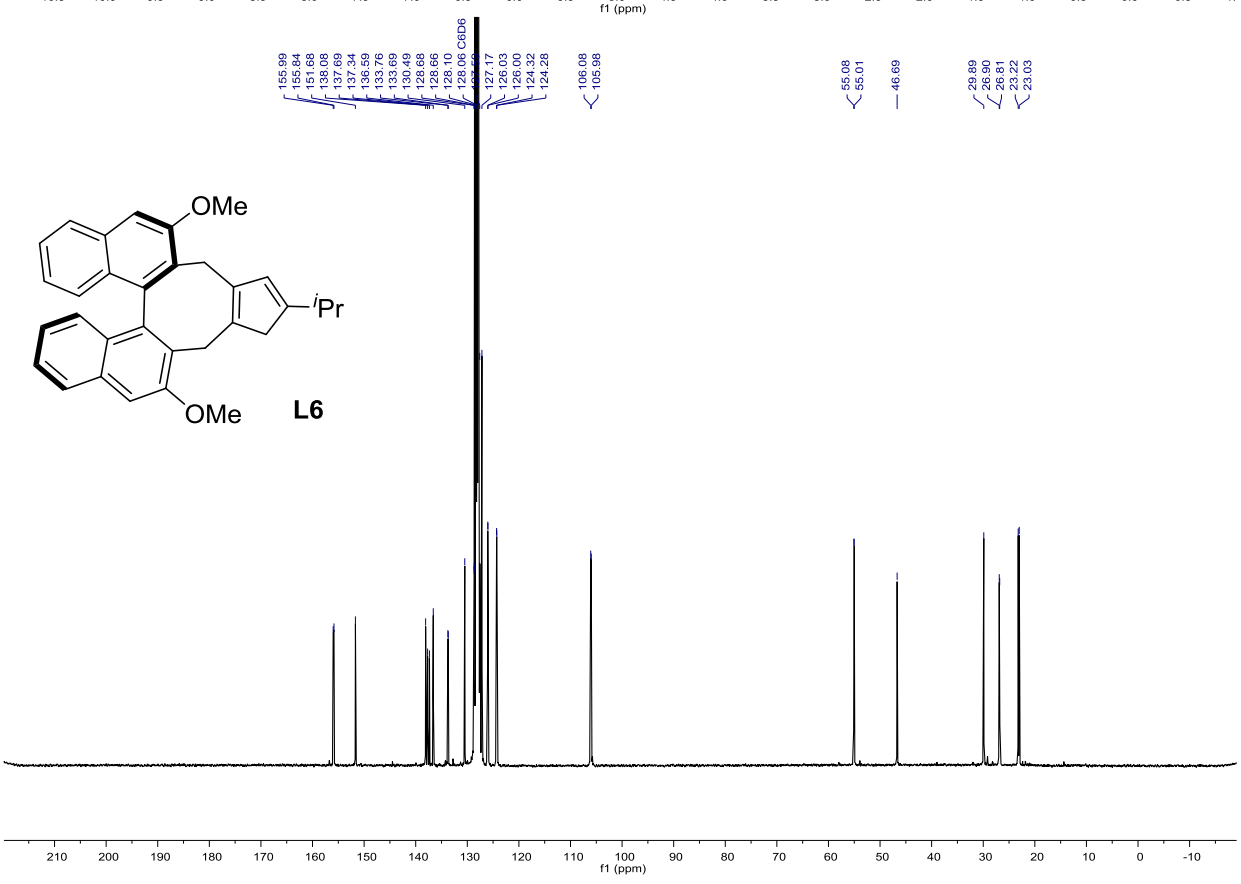
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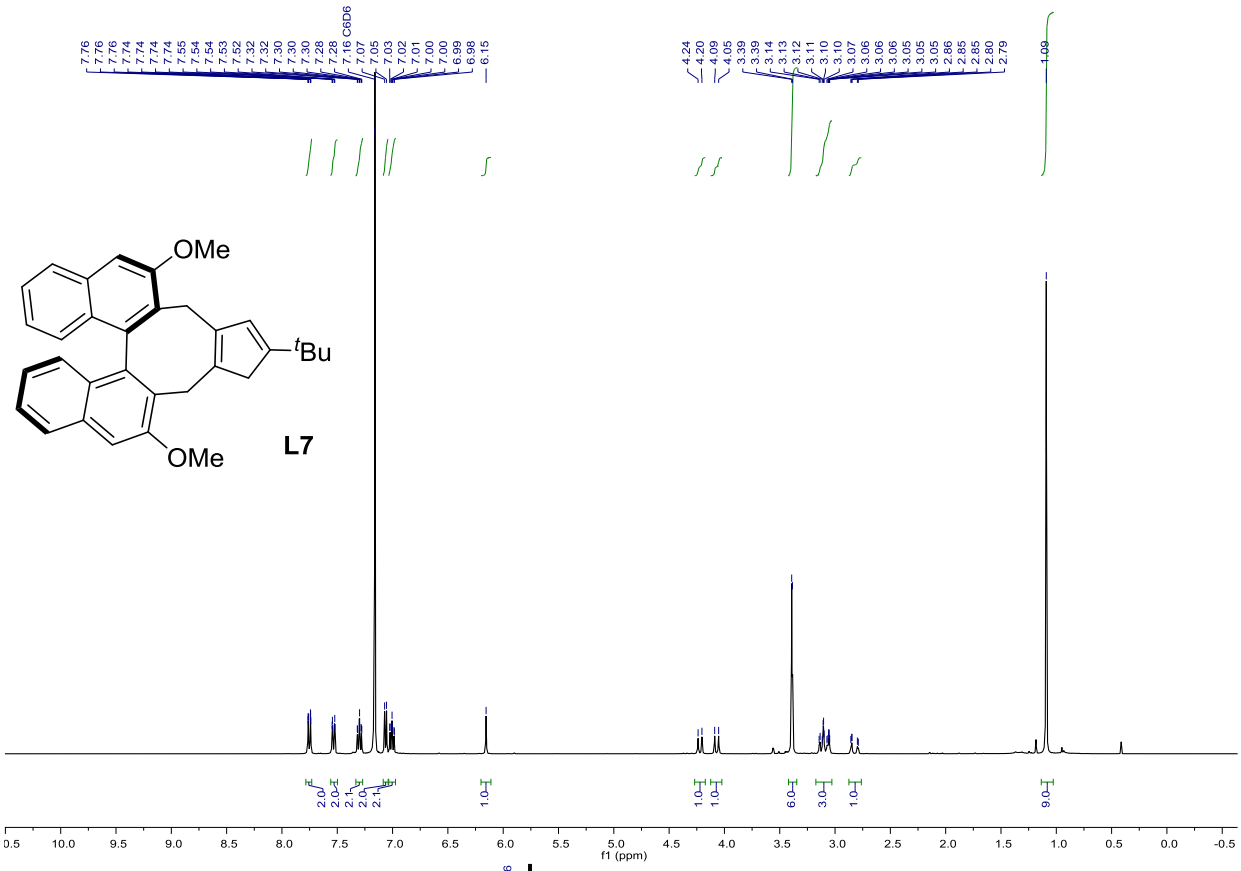
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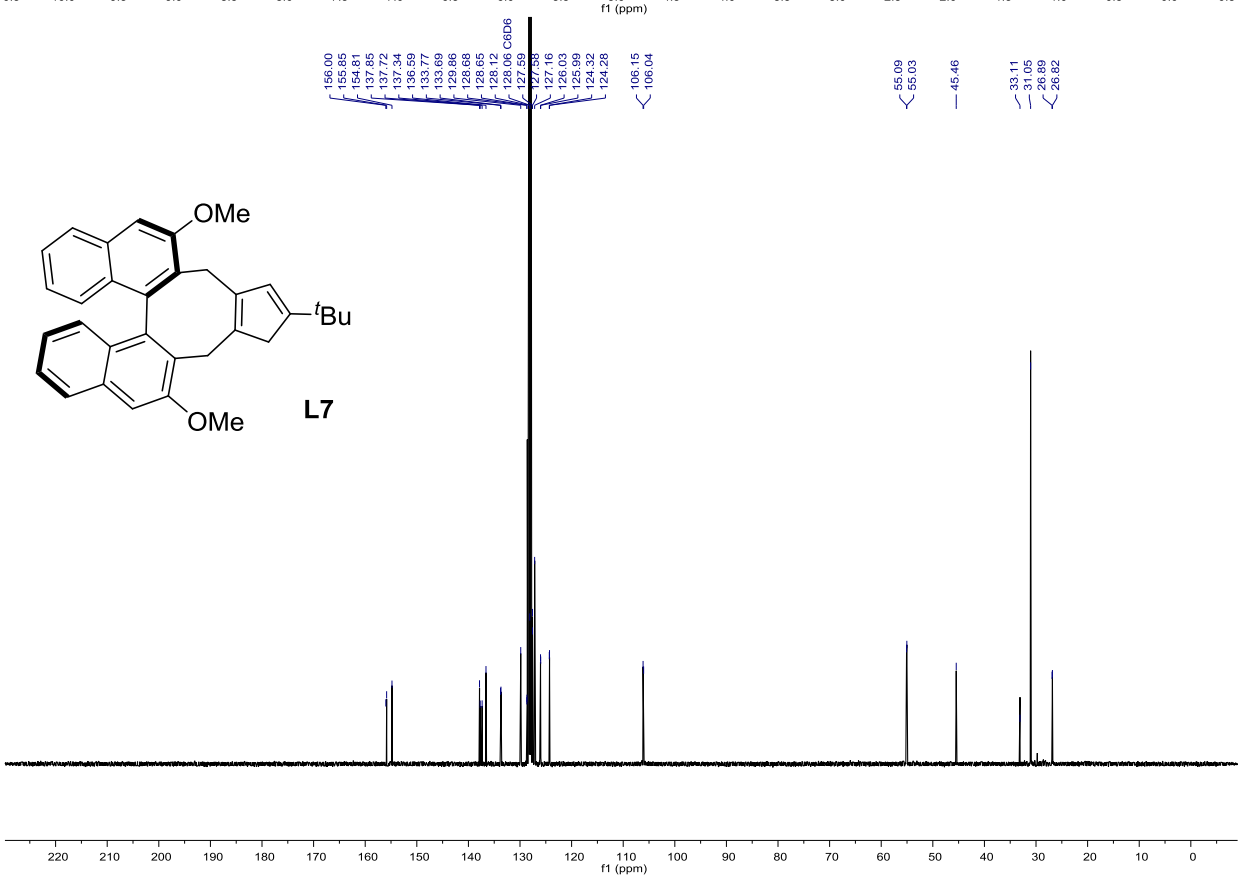
f1 (ppm)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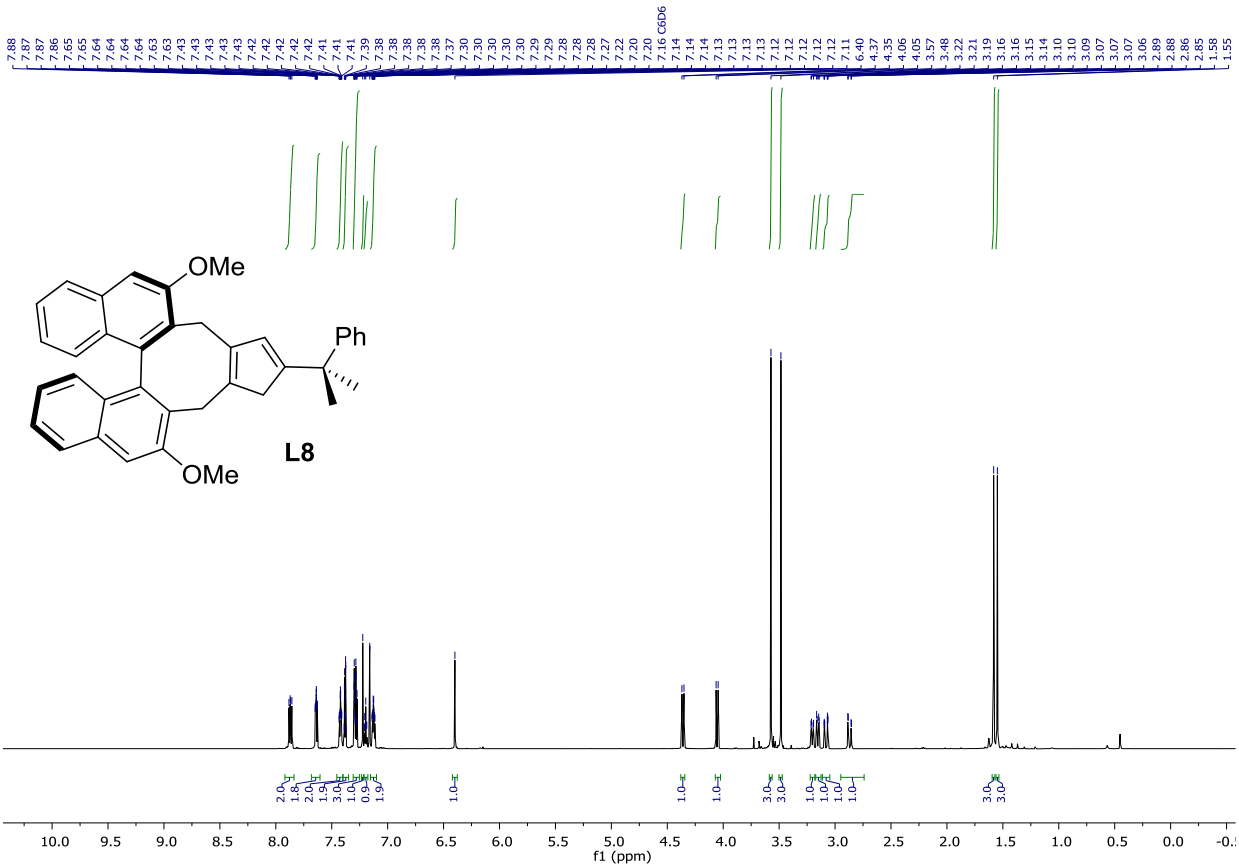
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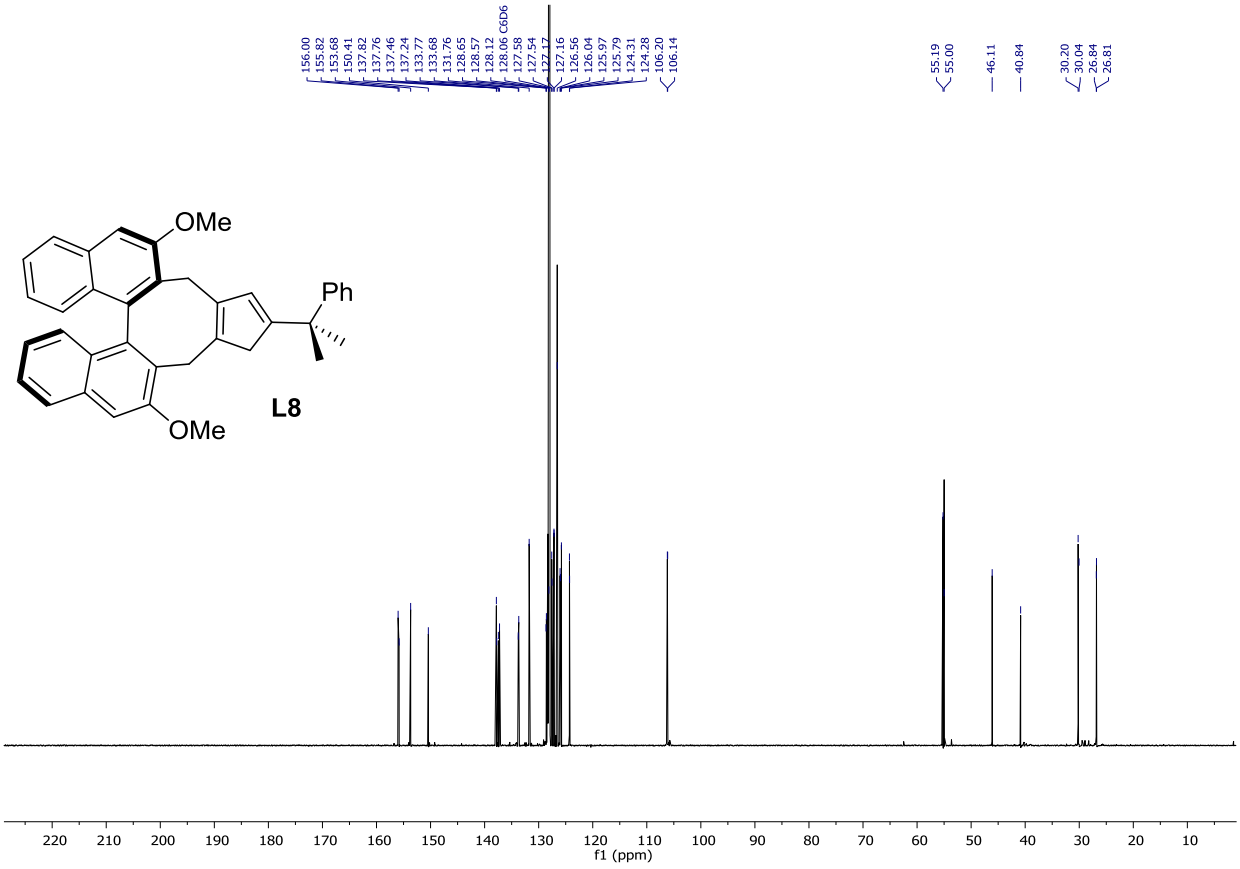
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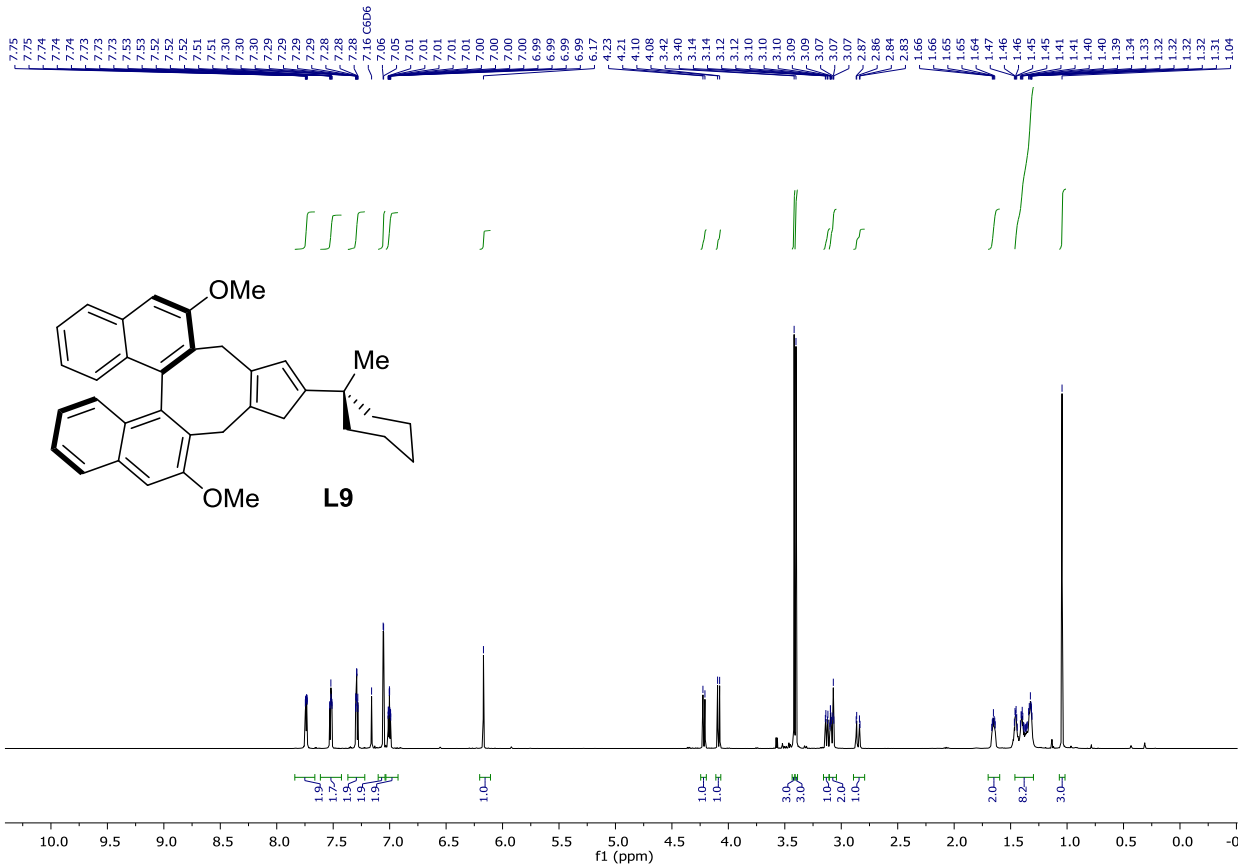
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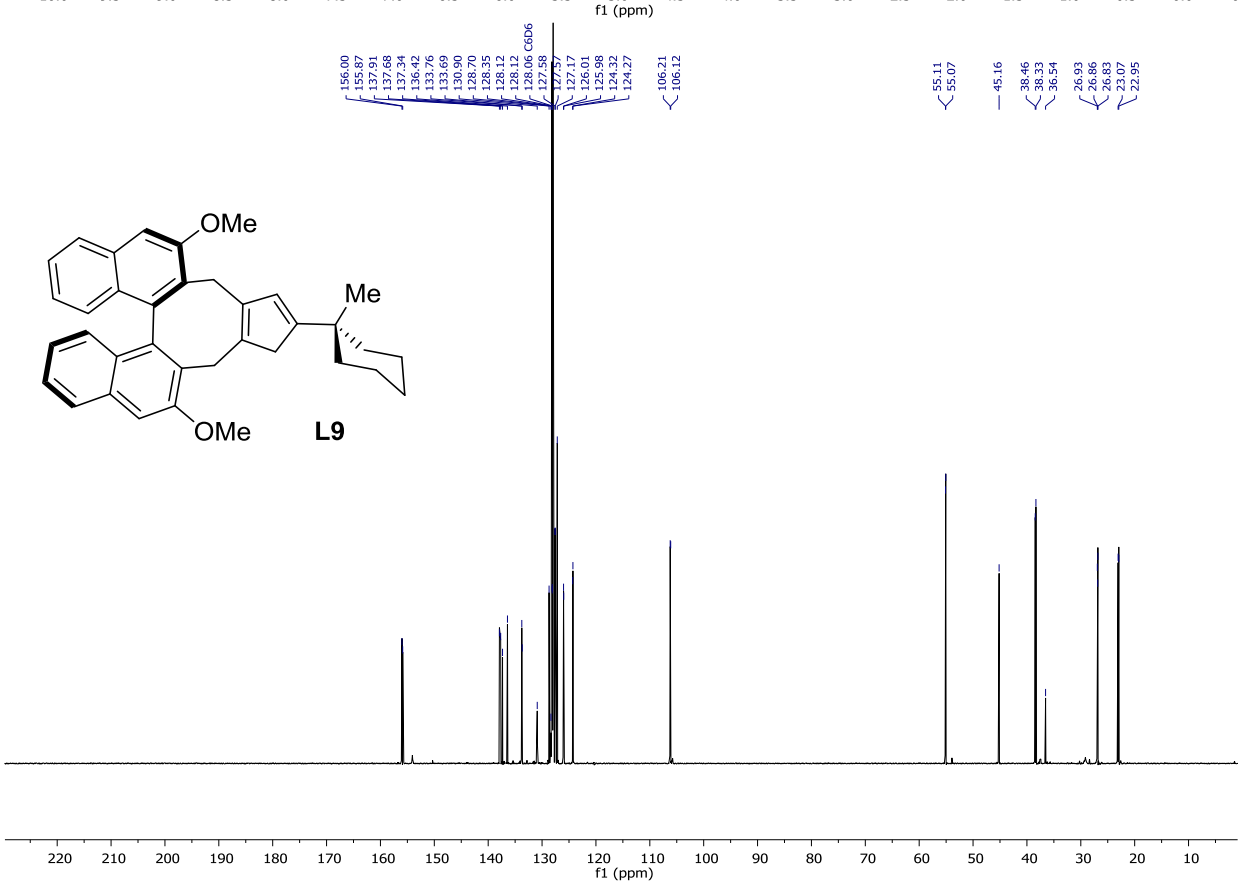
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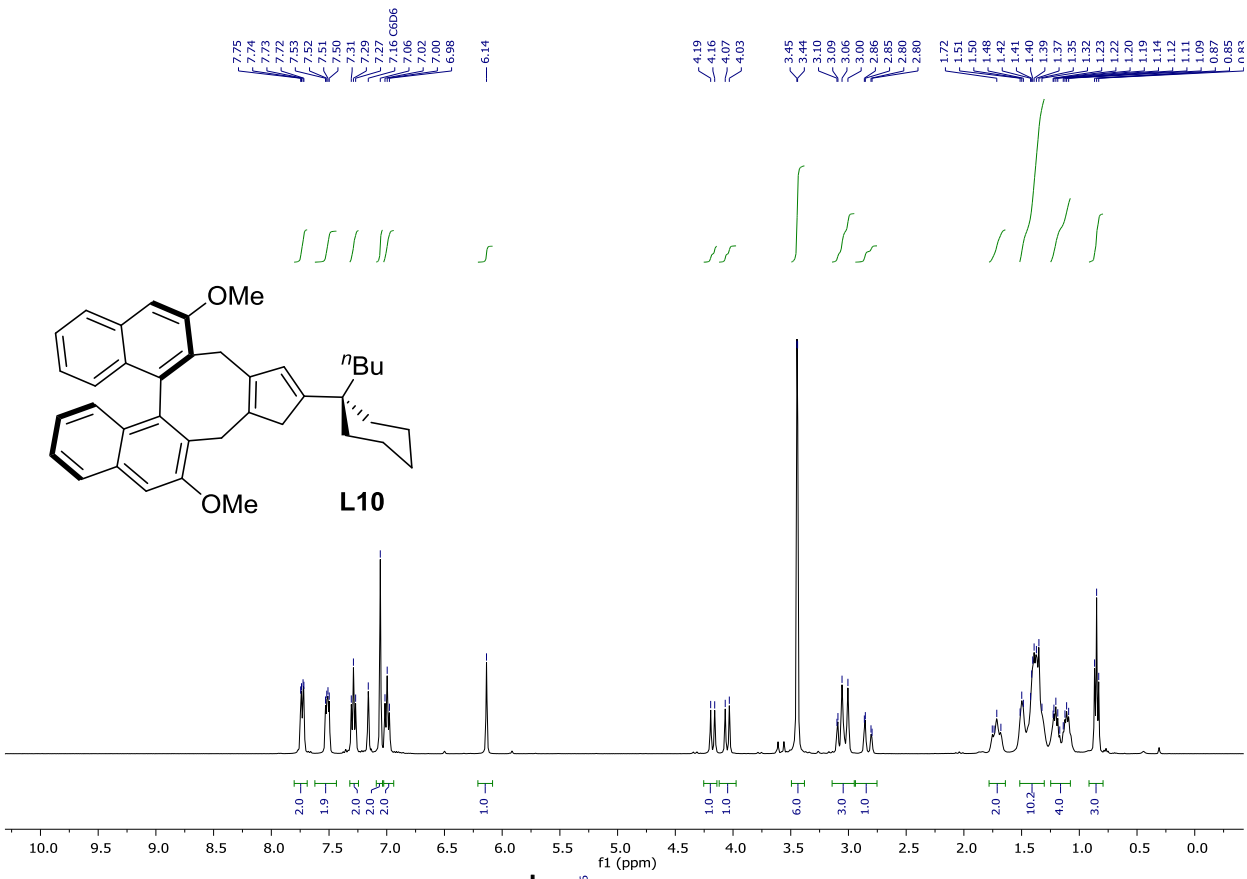
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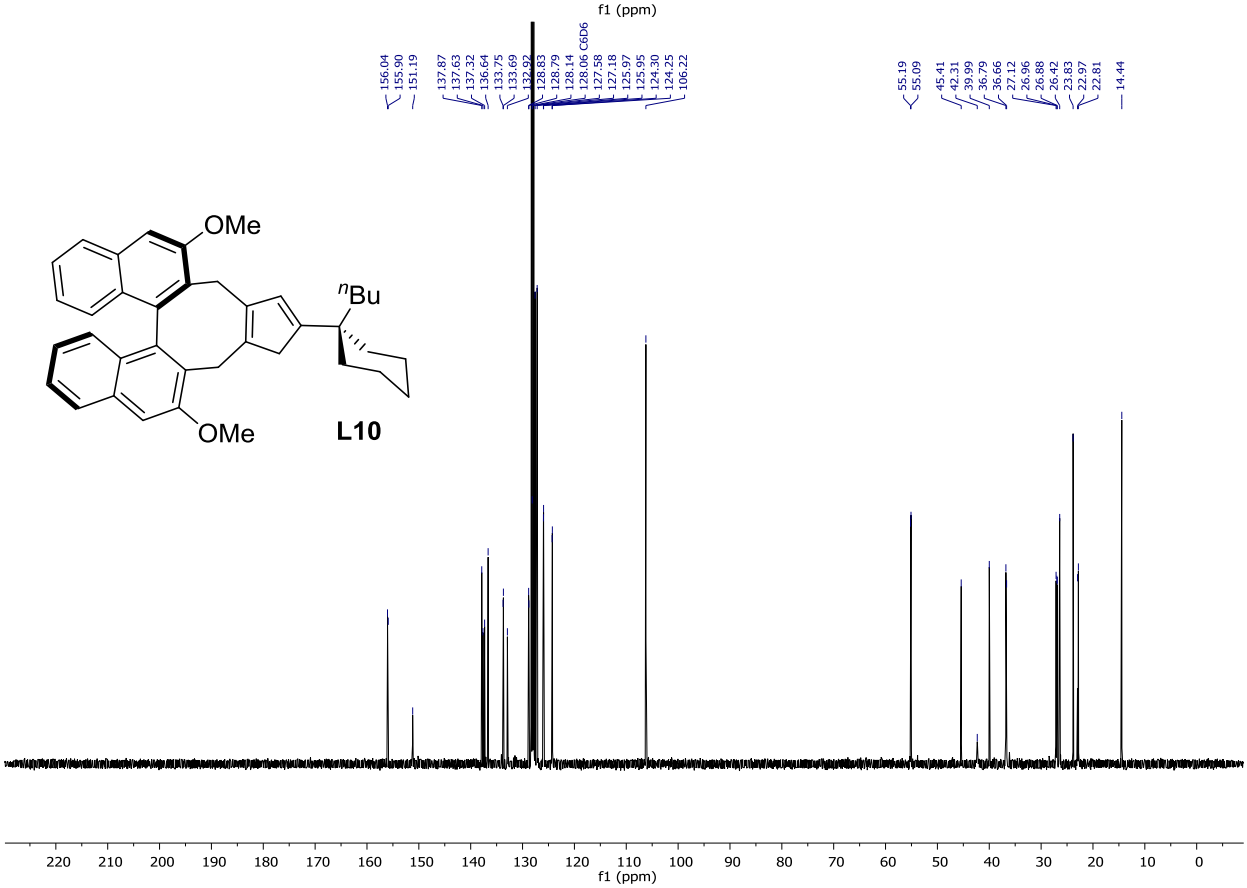
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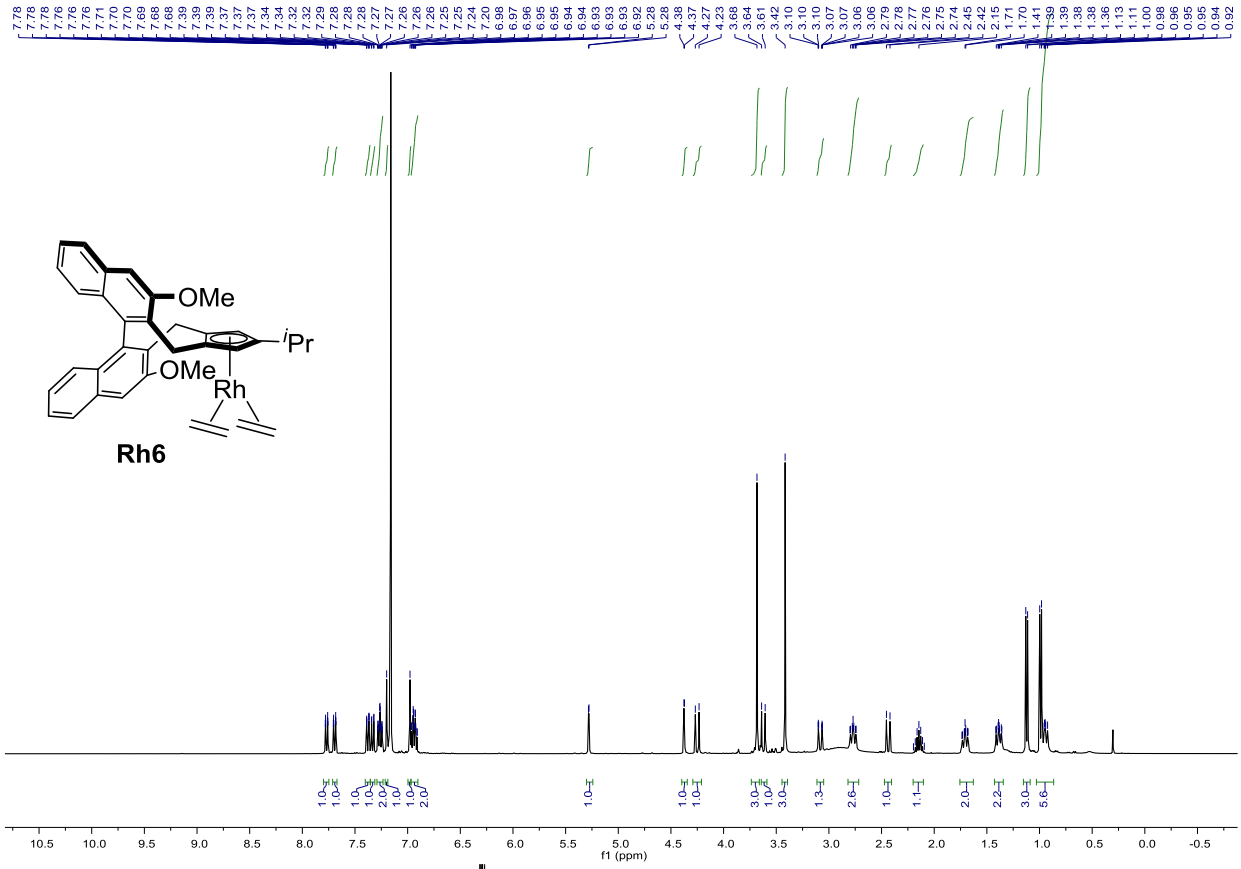


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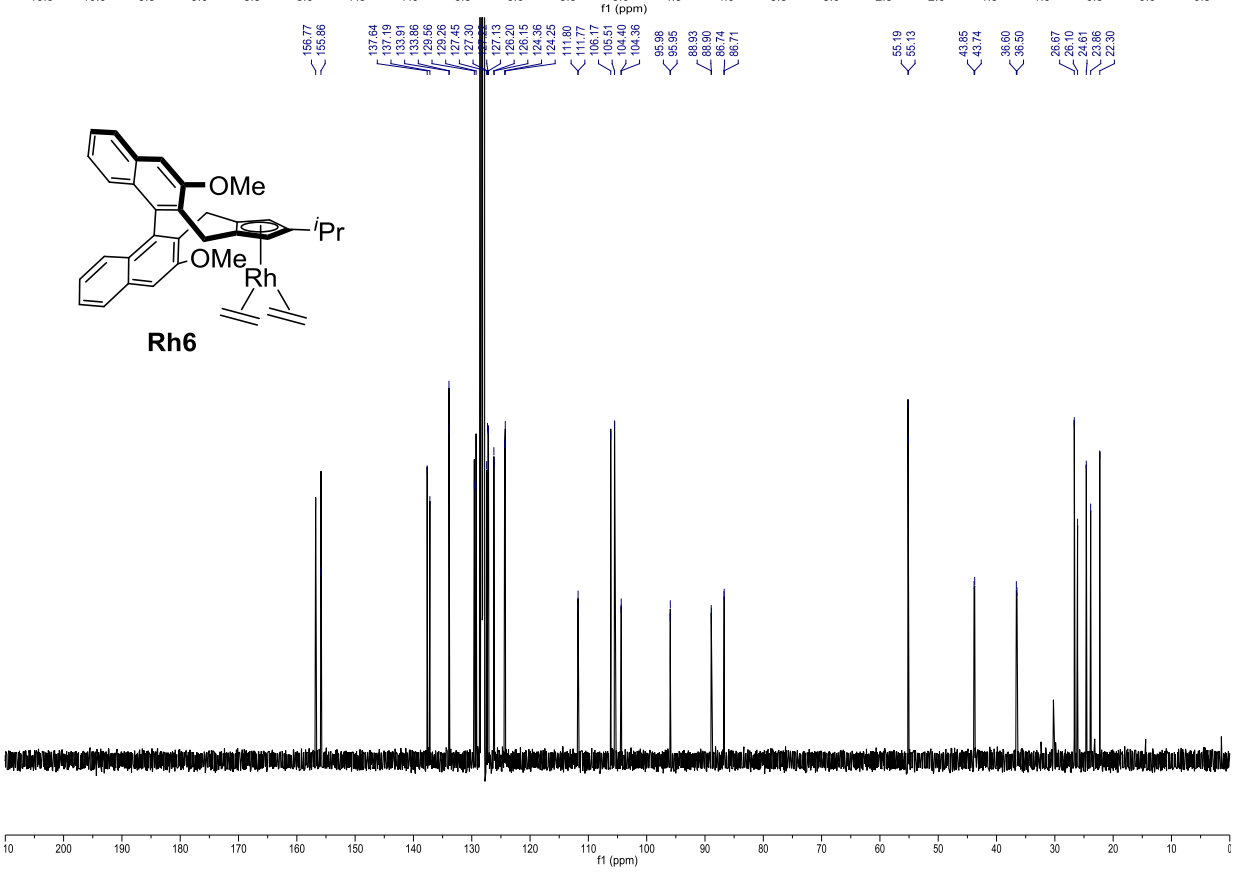


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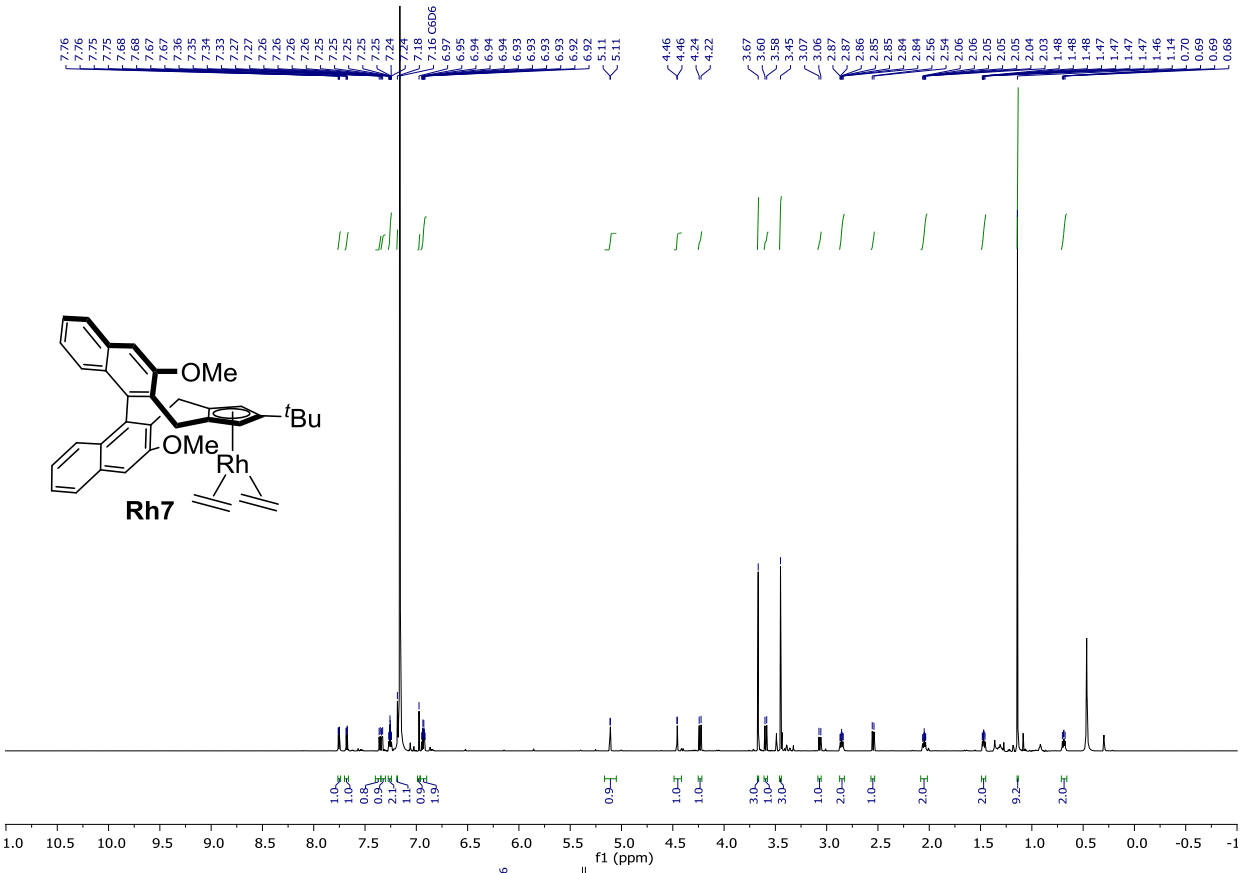
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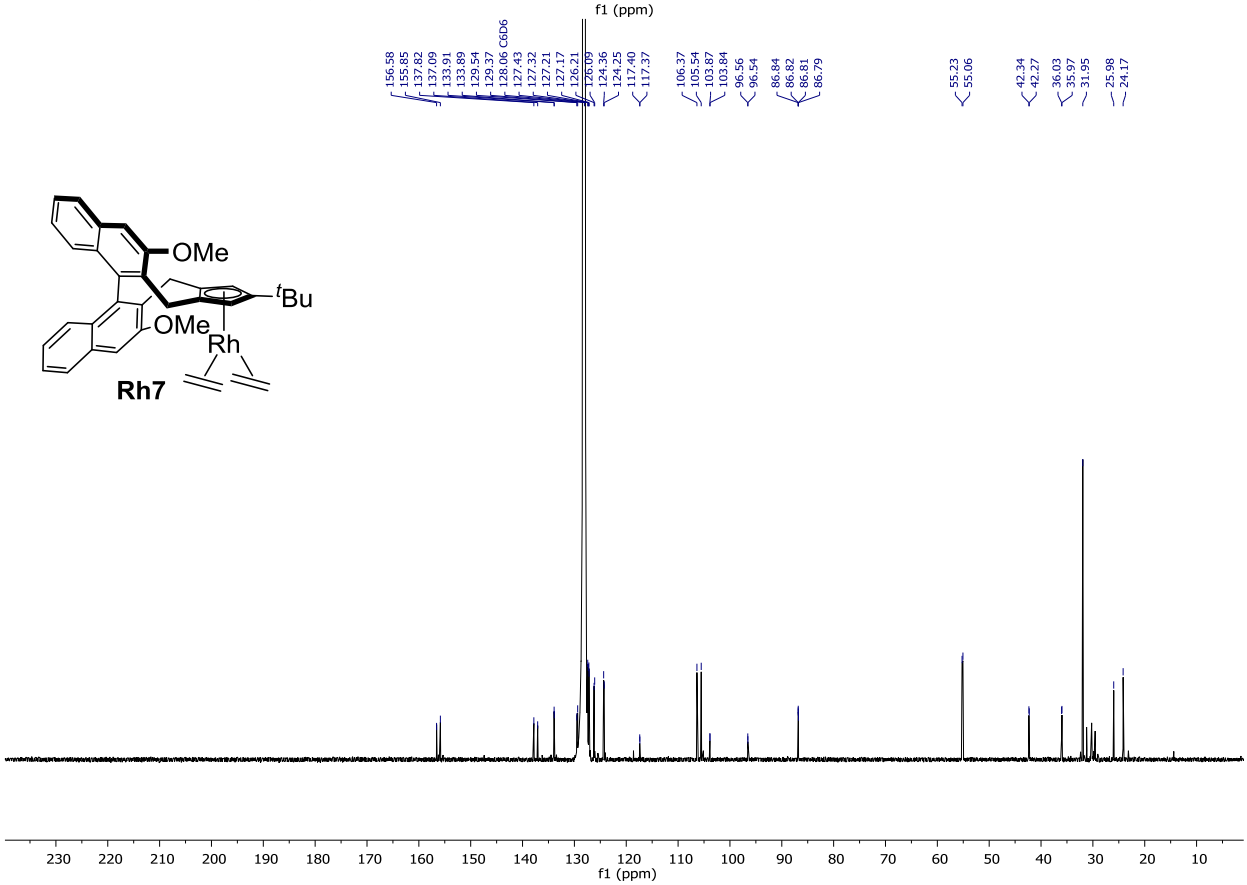
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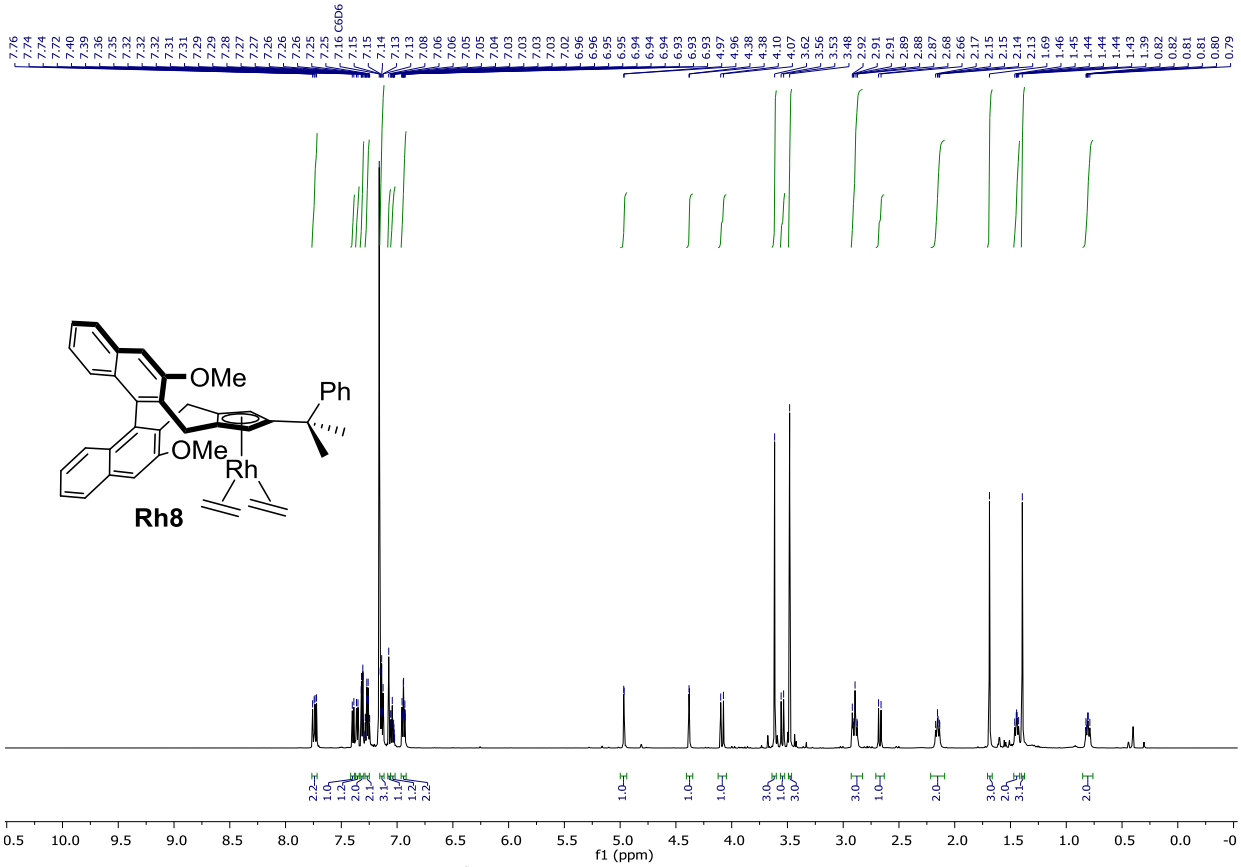
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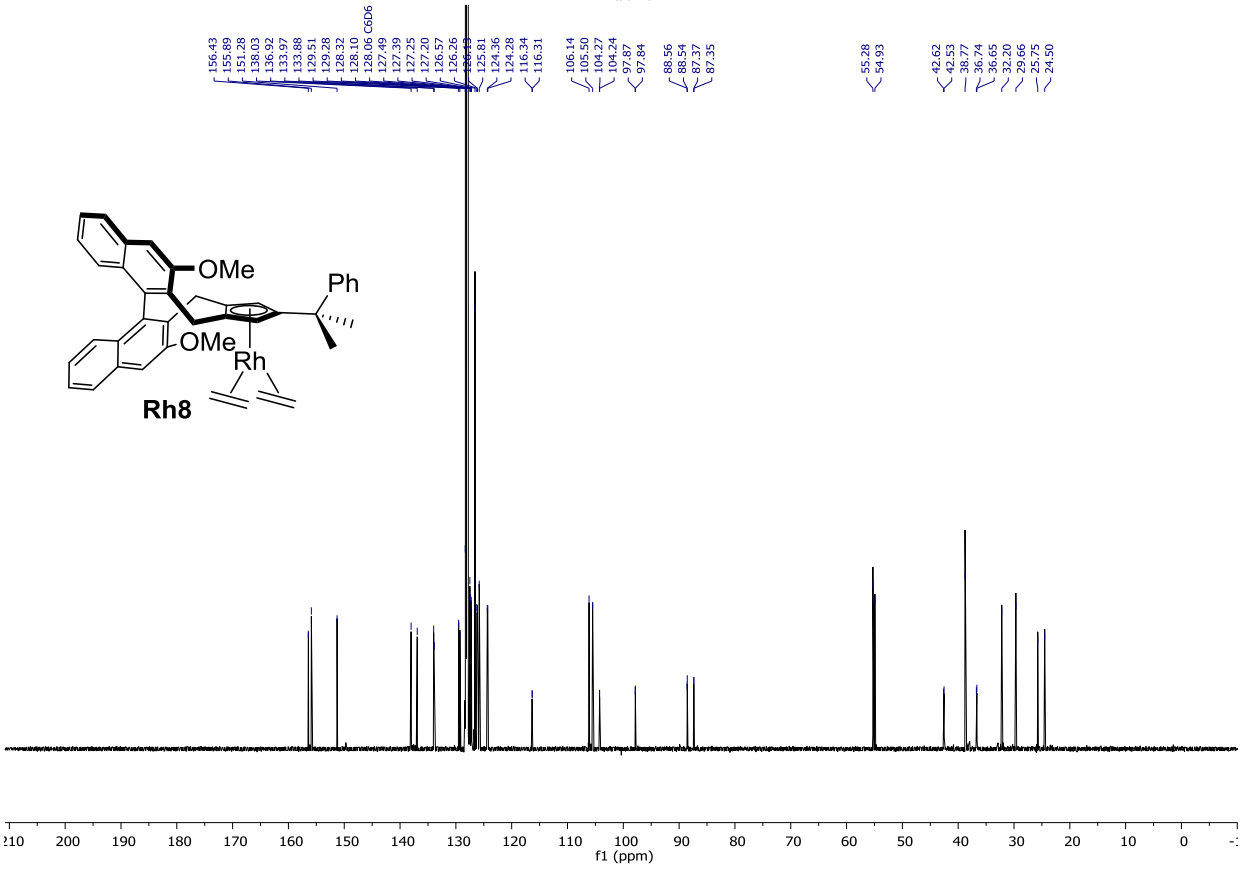
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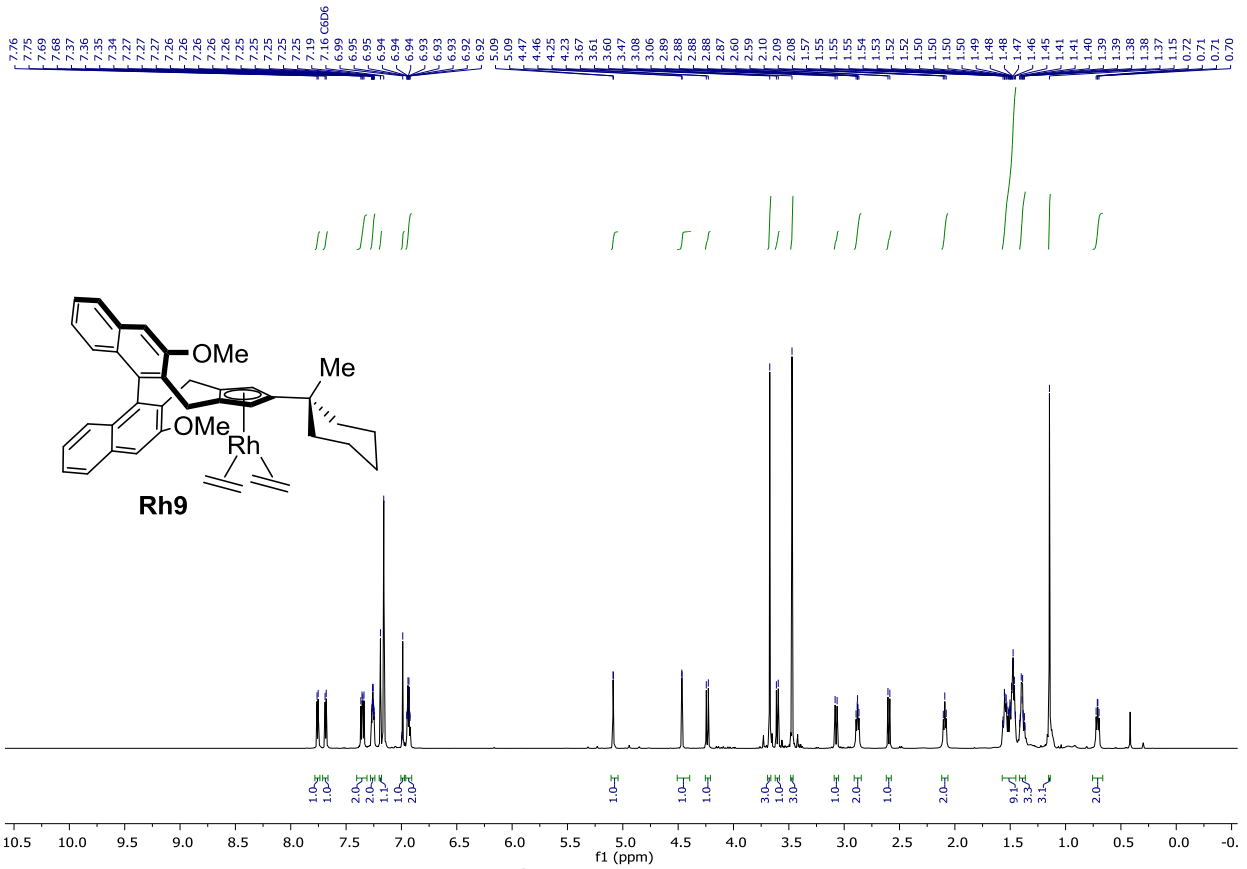
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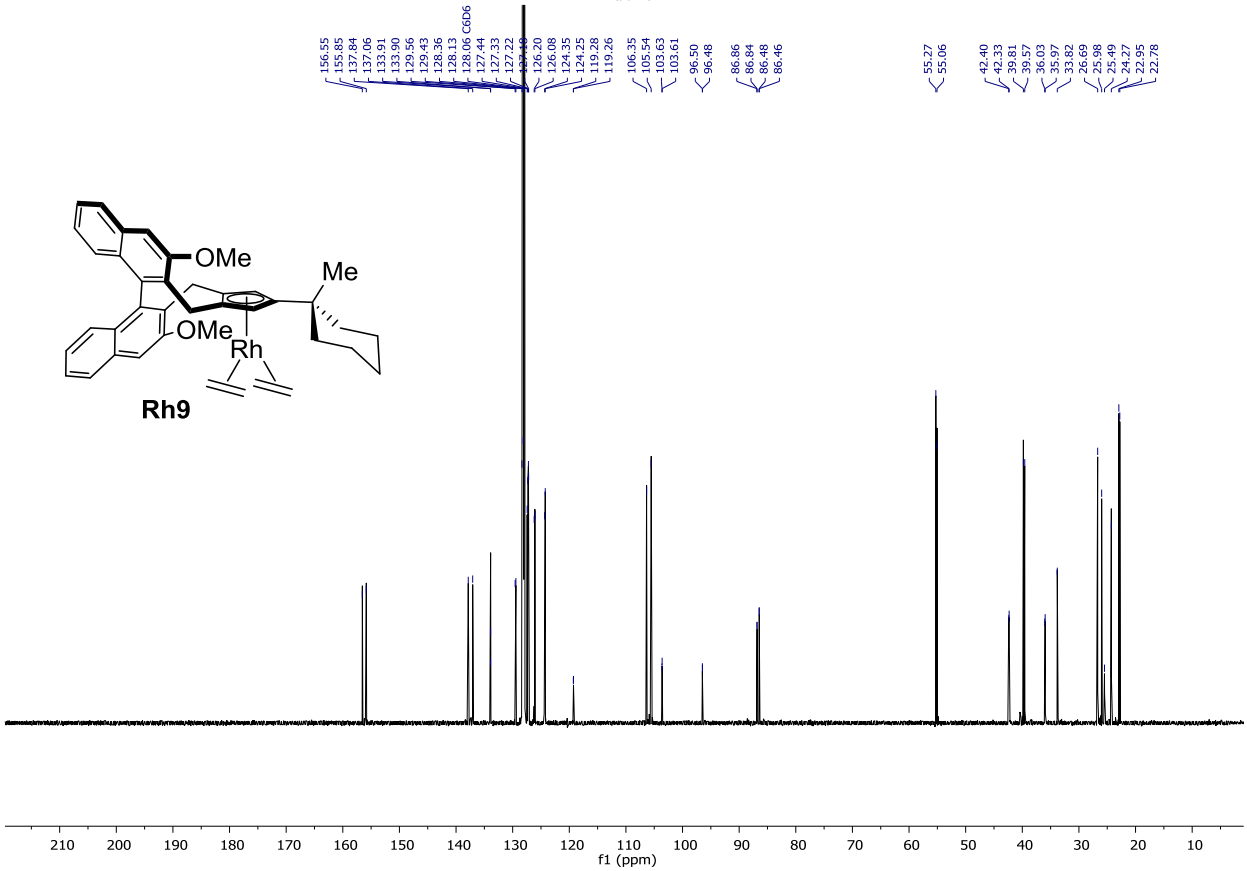
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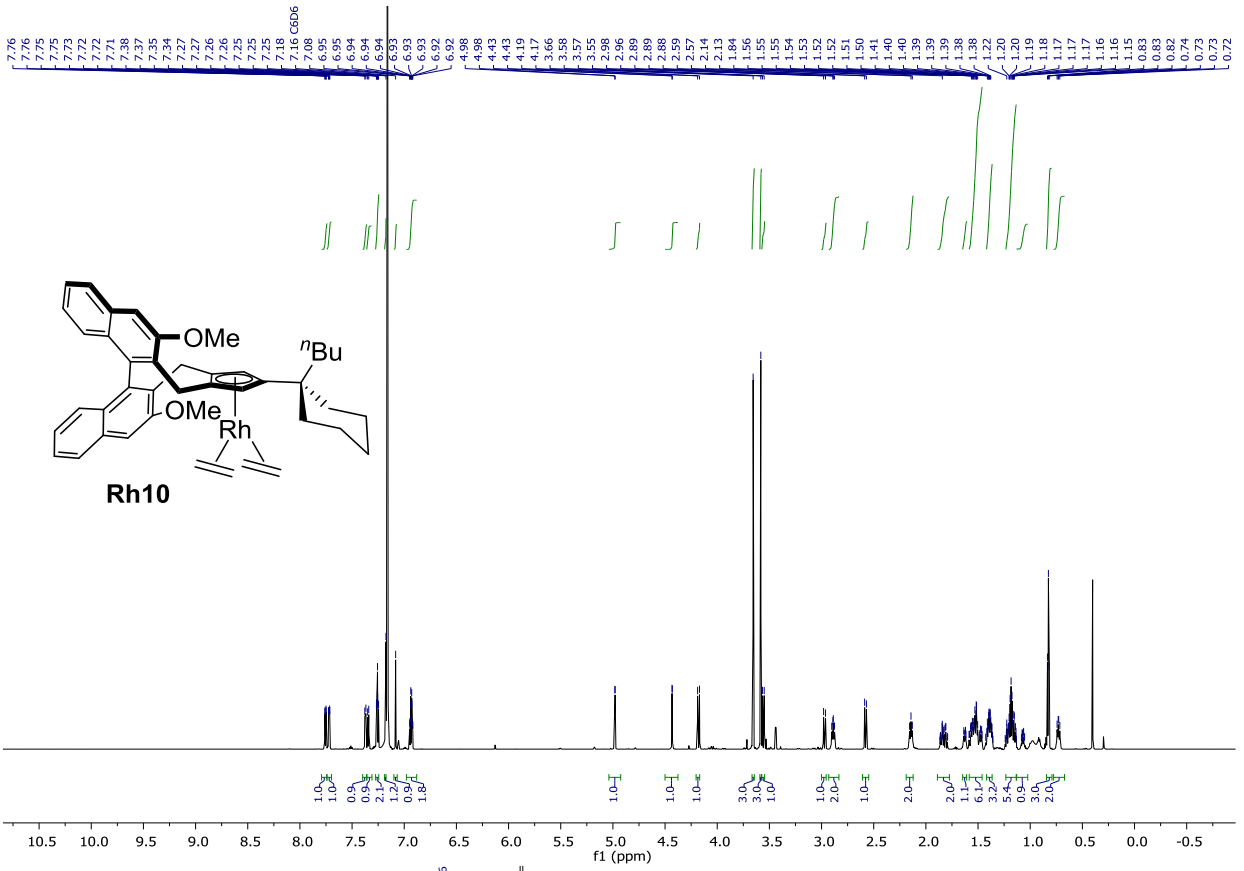


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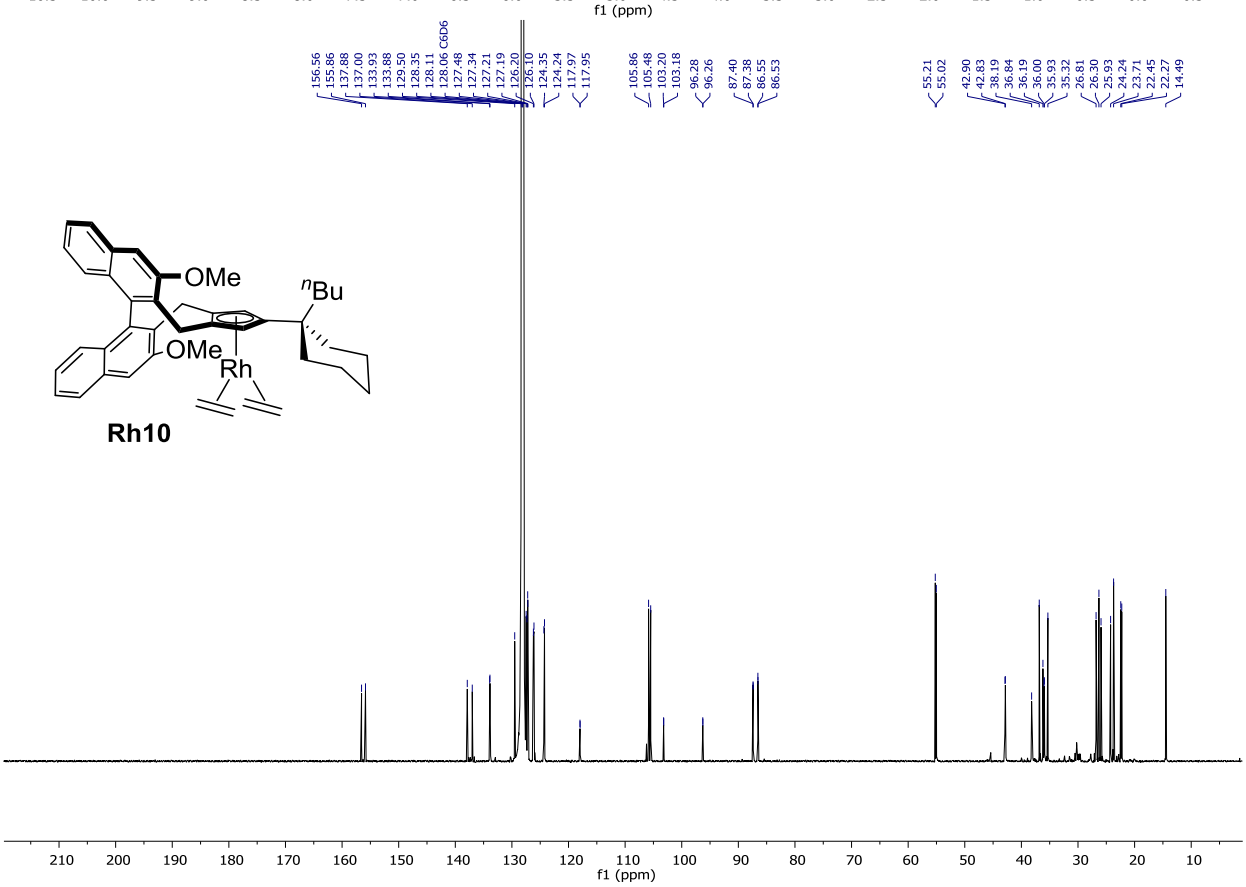
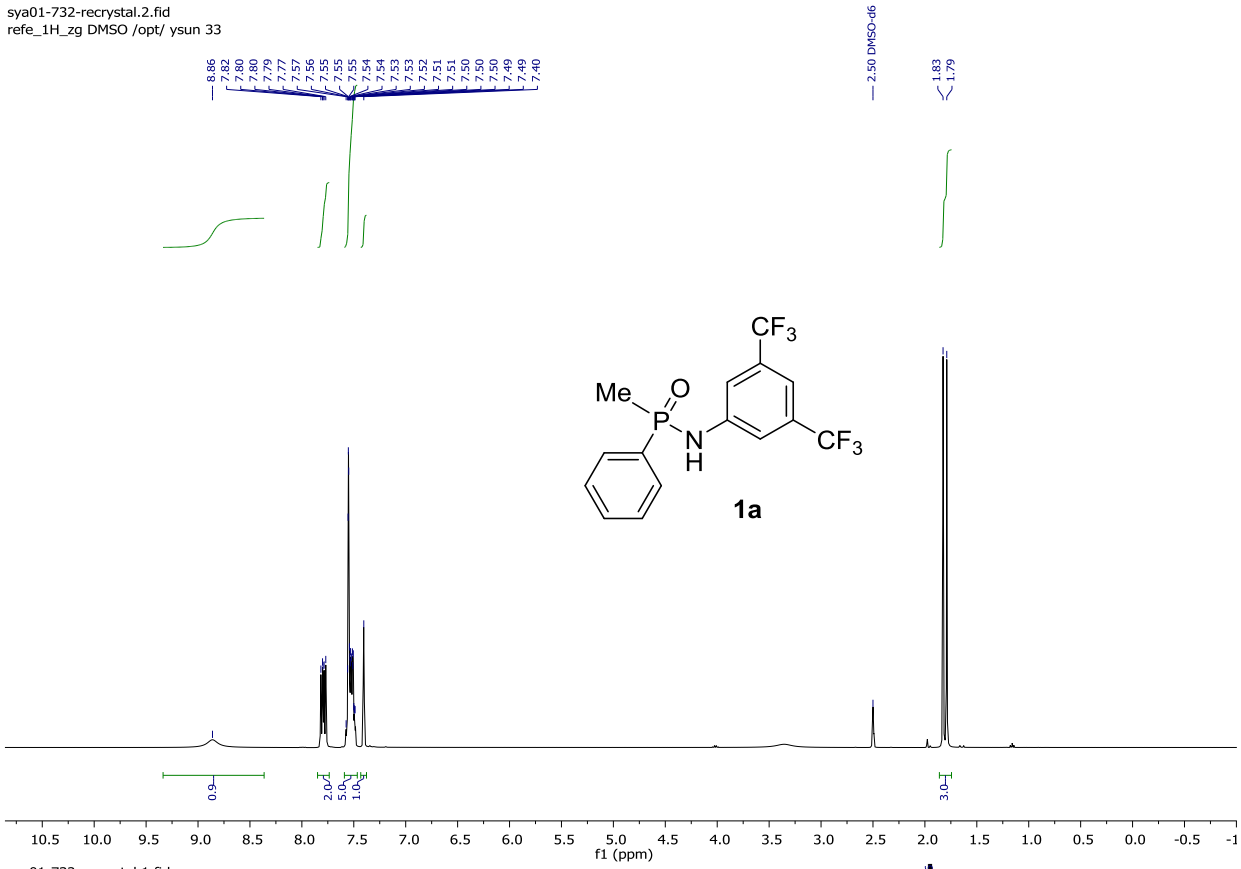
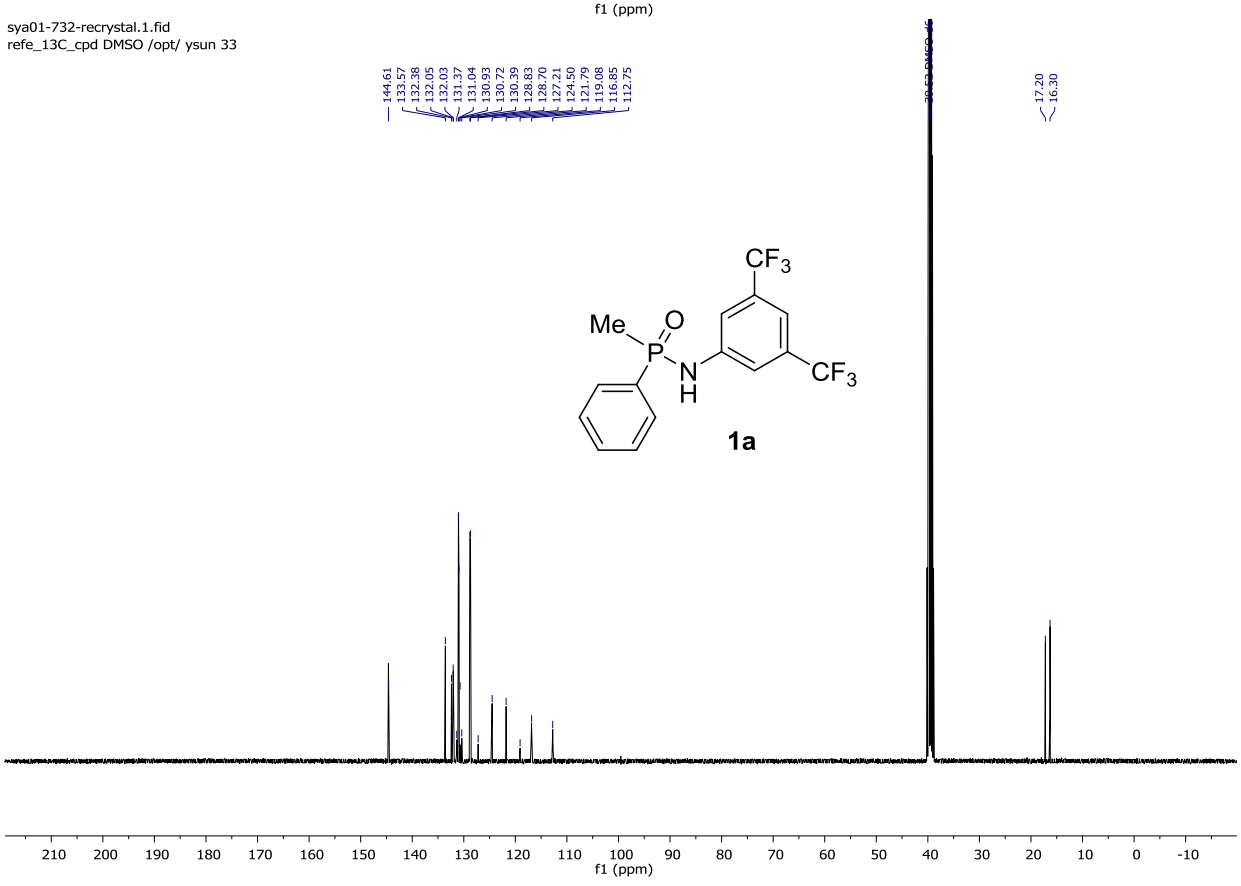


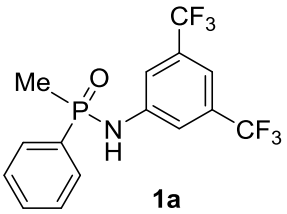

**Rh10**


sya01-732-recrystal.2.fid
refe_1H_zg DMSO /opt/ ysun 33
8.86
7.82
7.80
7.80
7.79
7.77
7.57
7.56
7.55
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.50
7.49
7.49
7.40
2.50 DMSO-d6
1.83
1.79
CF3
Me
O
P
N
H
CF3
1a
0.9
2.0
5.0
1.0
3.0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


sya01-732-recrystal.1.fid
refe_13C_cpd DMSO /opt/ ysun 33
144.61
133.57
132.38
132.05
132.03
131.37
131.04
130.93
130.72
130.39
128.83
128.70
127.21
124.50
121.79
119.08
116.85
112.75
39.51 DMSO-d6
17.20
16.30
CF3
Me
O
P
N
H
CF3
1a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

sya01-732-recrystal.3.fid
refe_31P_cpd DMSO /opt/ ysun 33

26.30

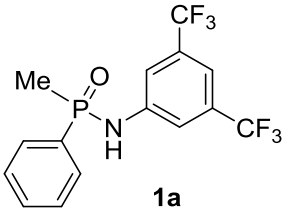



**1a**

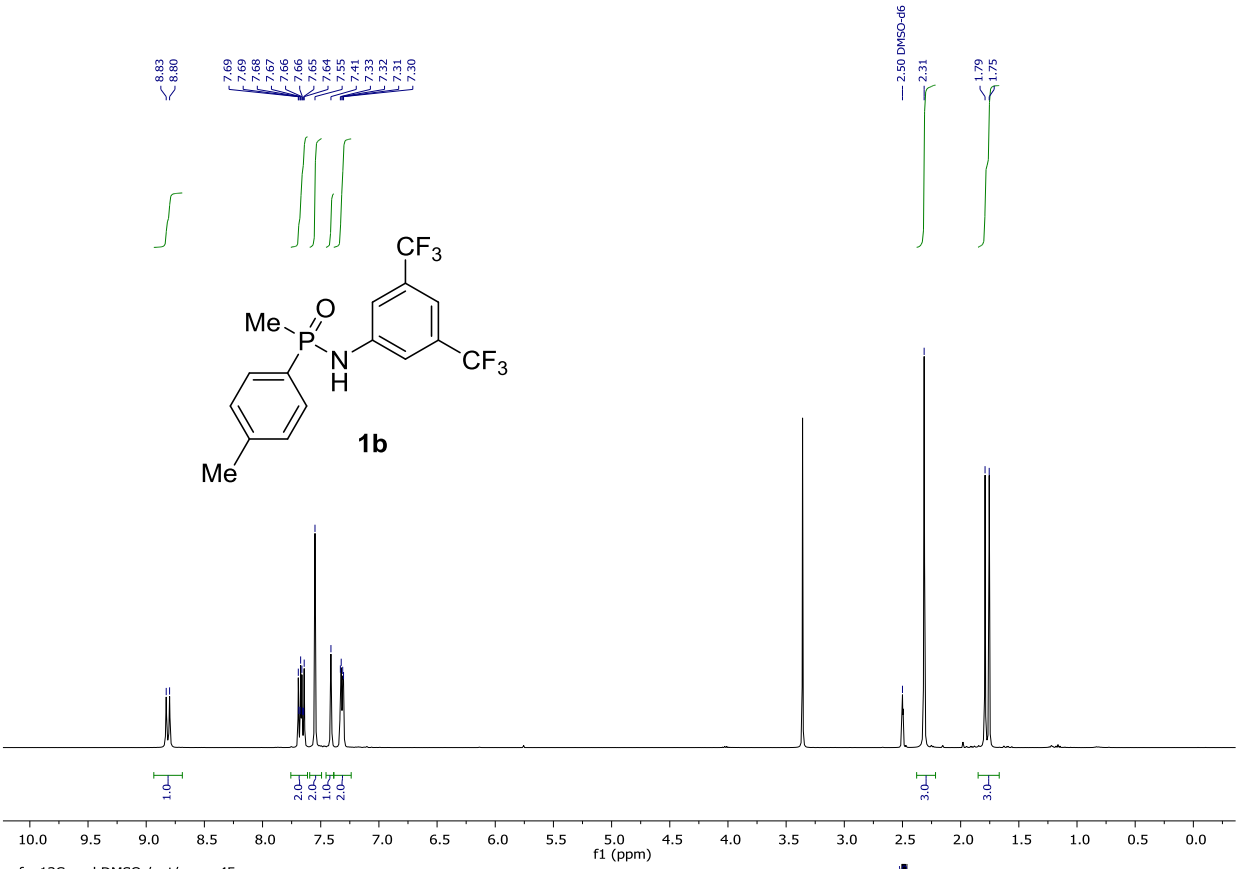



sya01-732-charact-19F/2
refe_F19cpd

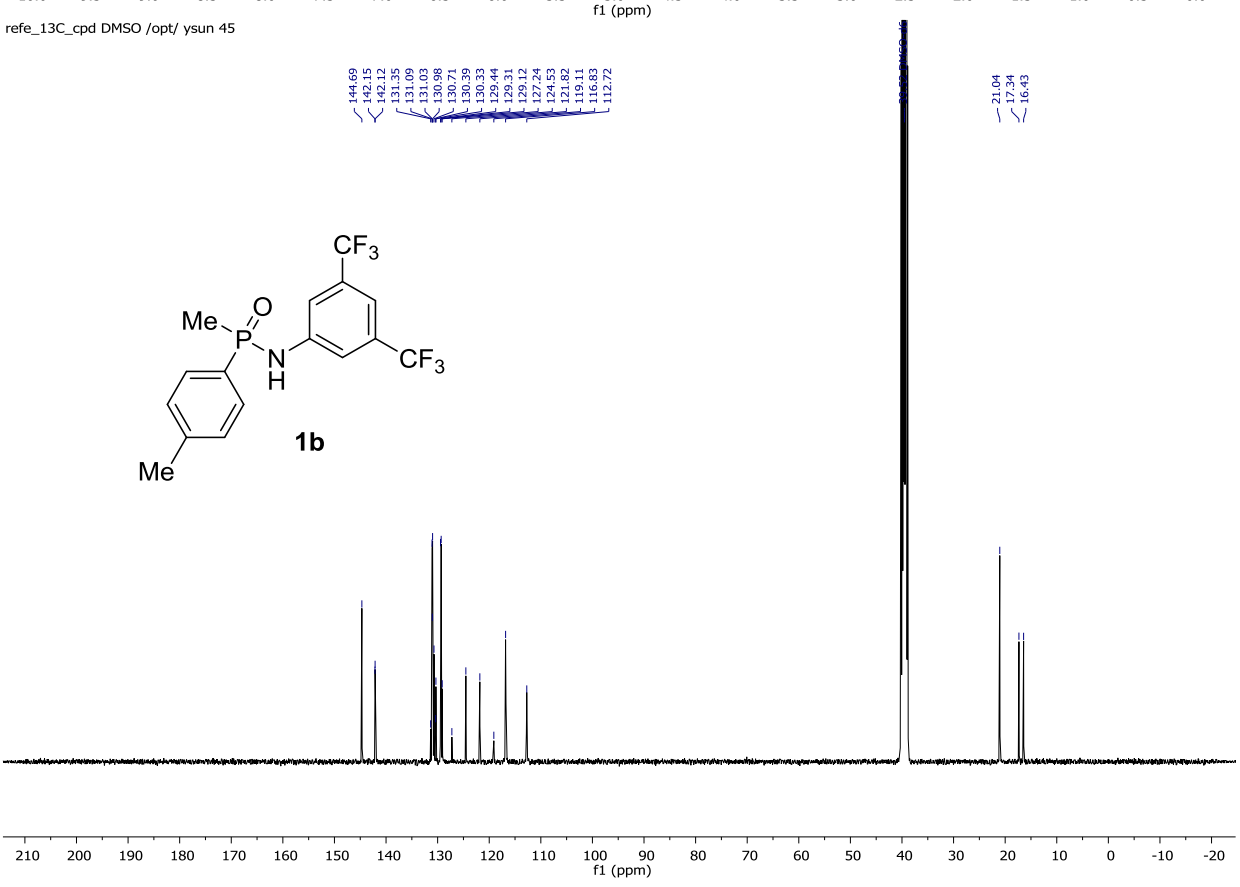
-61.93



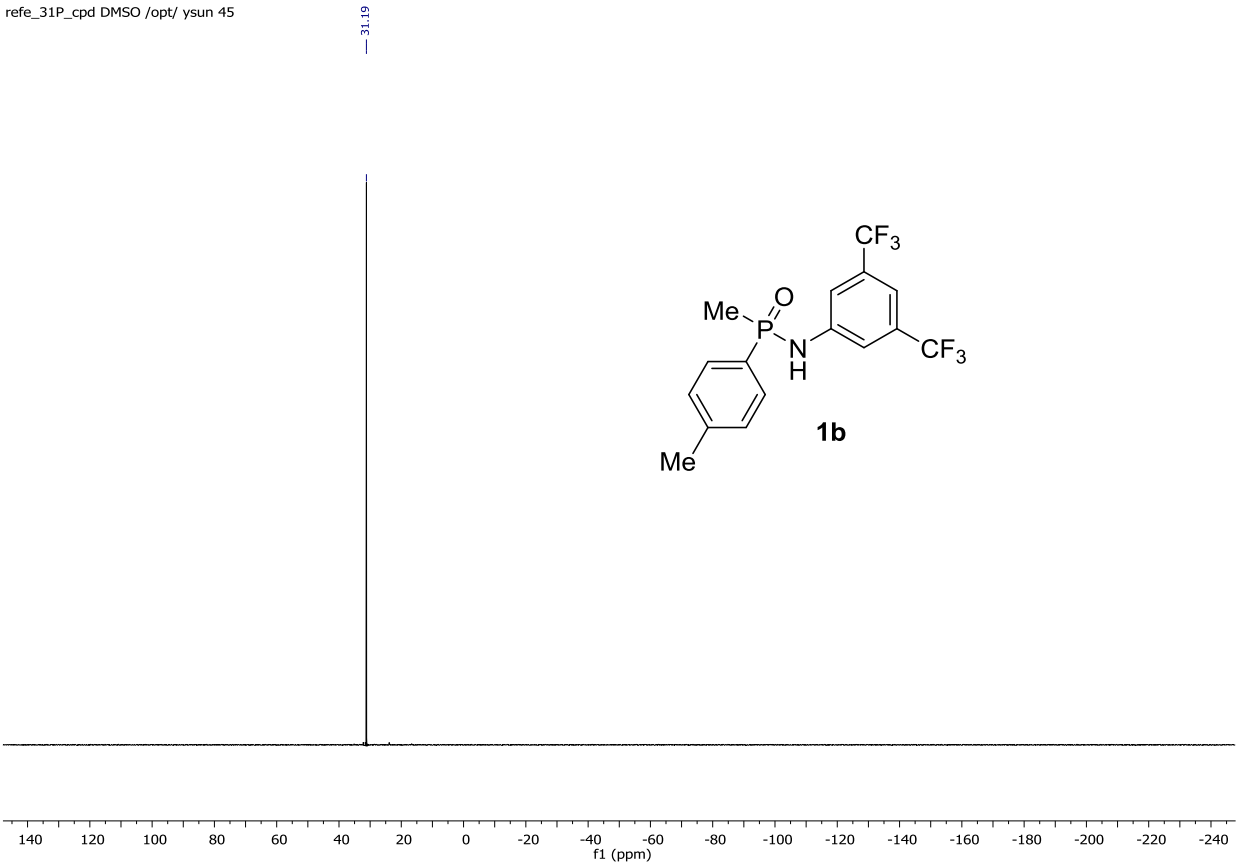

**1a**



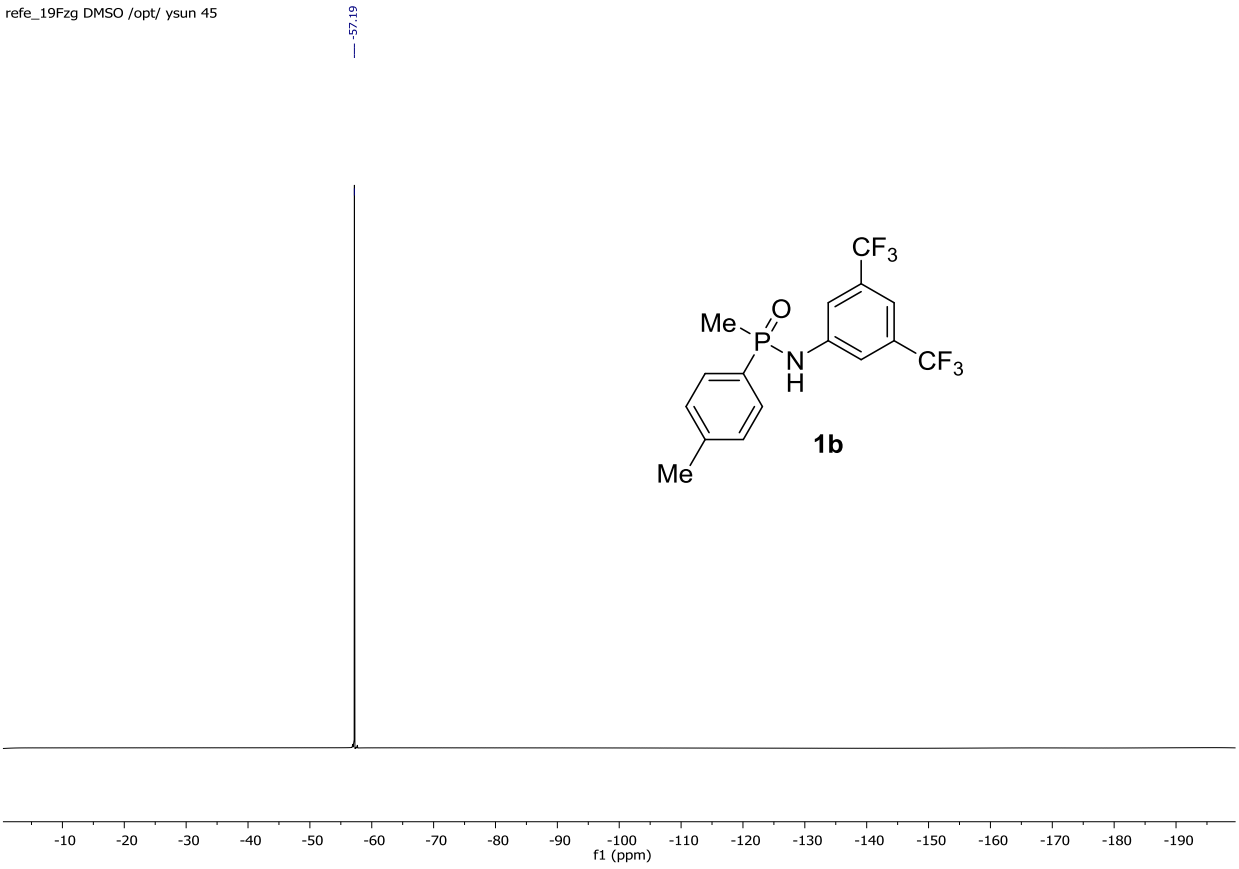

refe_13C_cpd DMSO /opt/ ysun 45

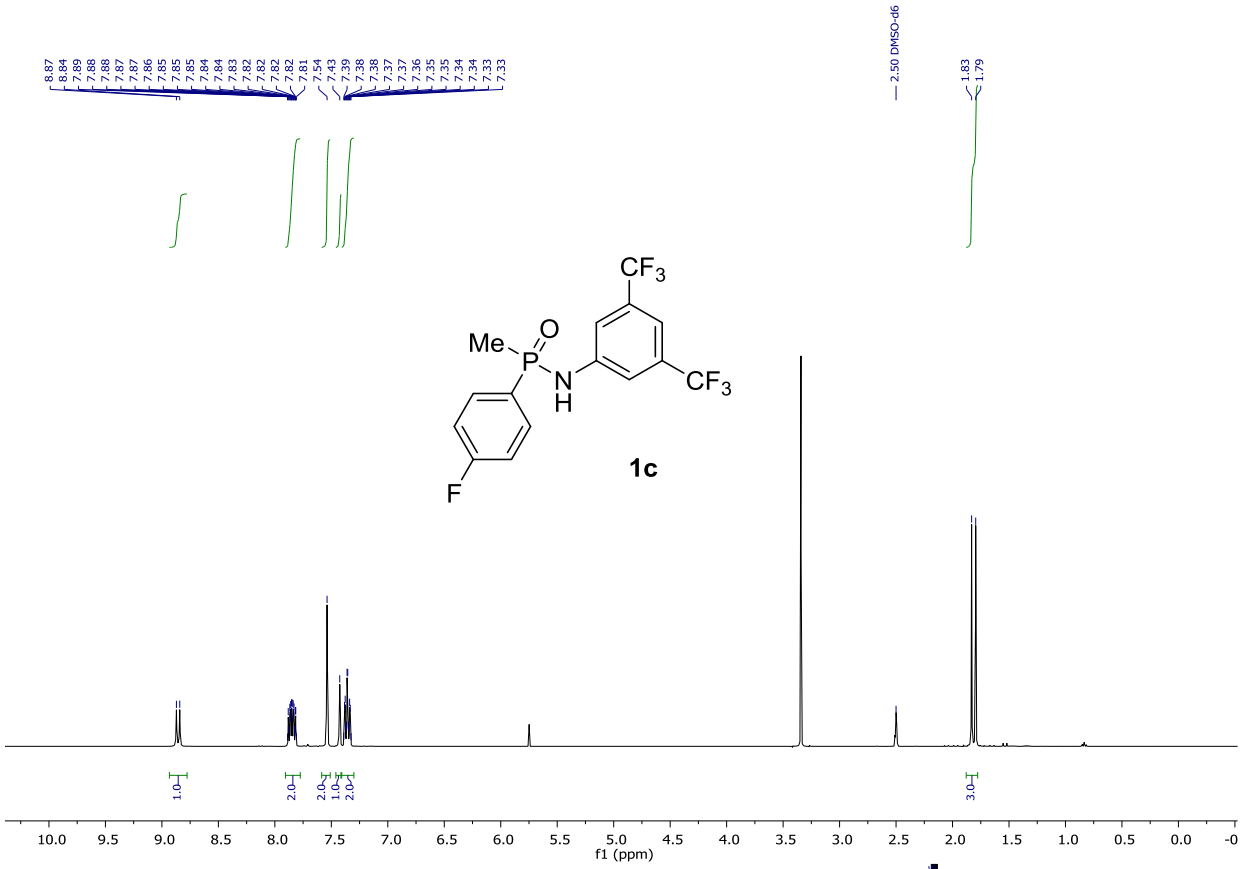


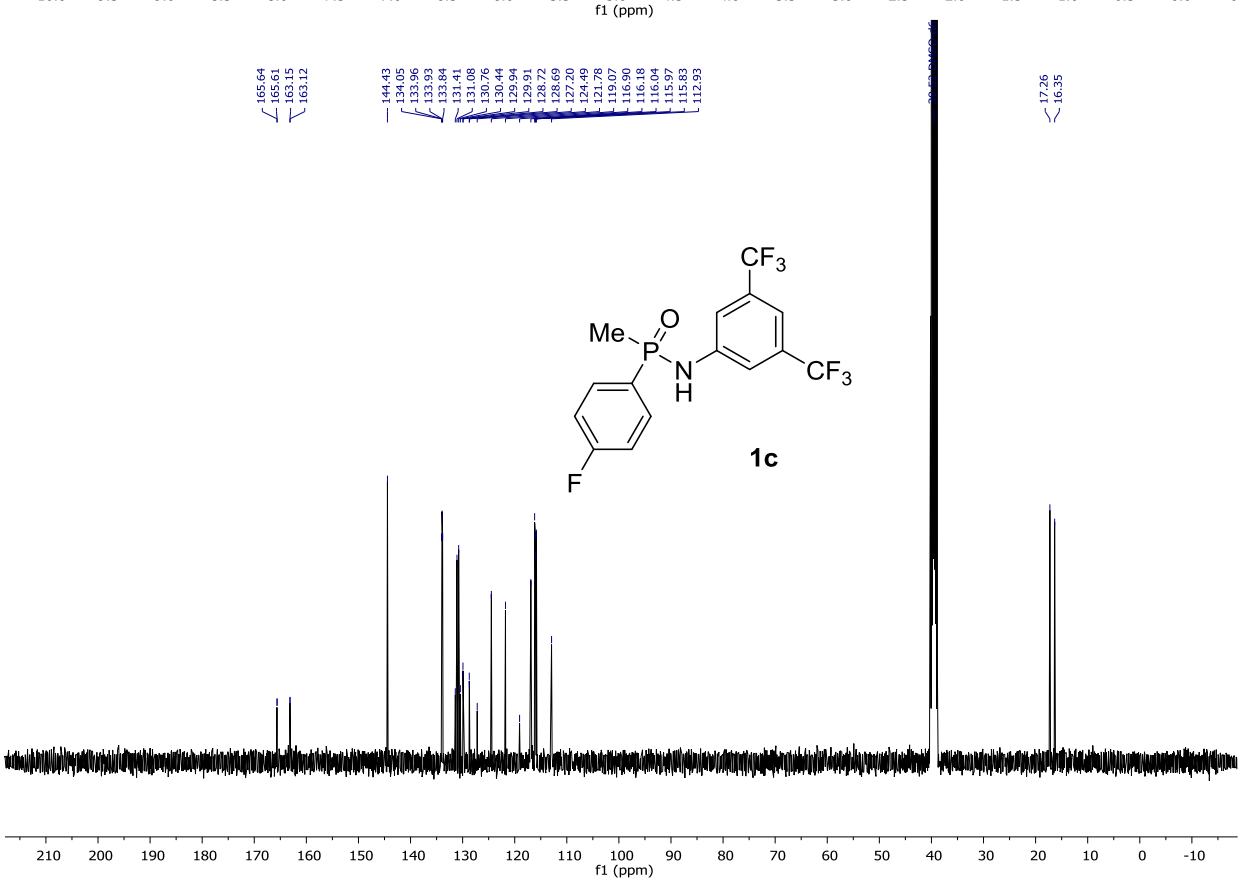
refe_31P_cpd DMSO /opt/ ysun 45



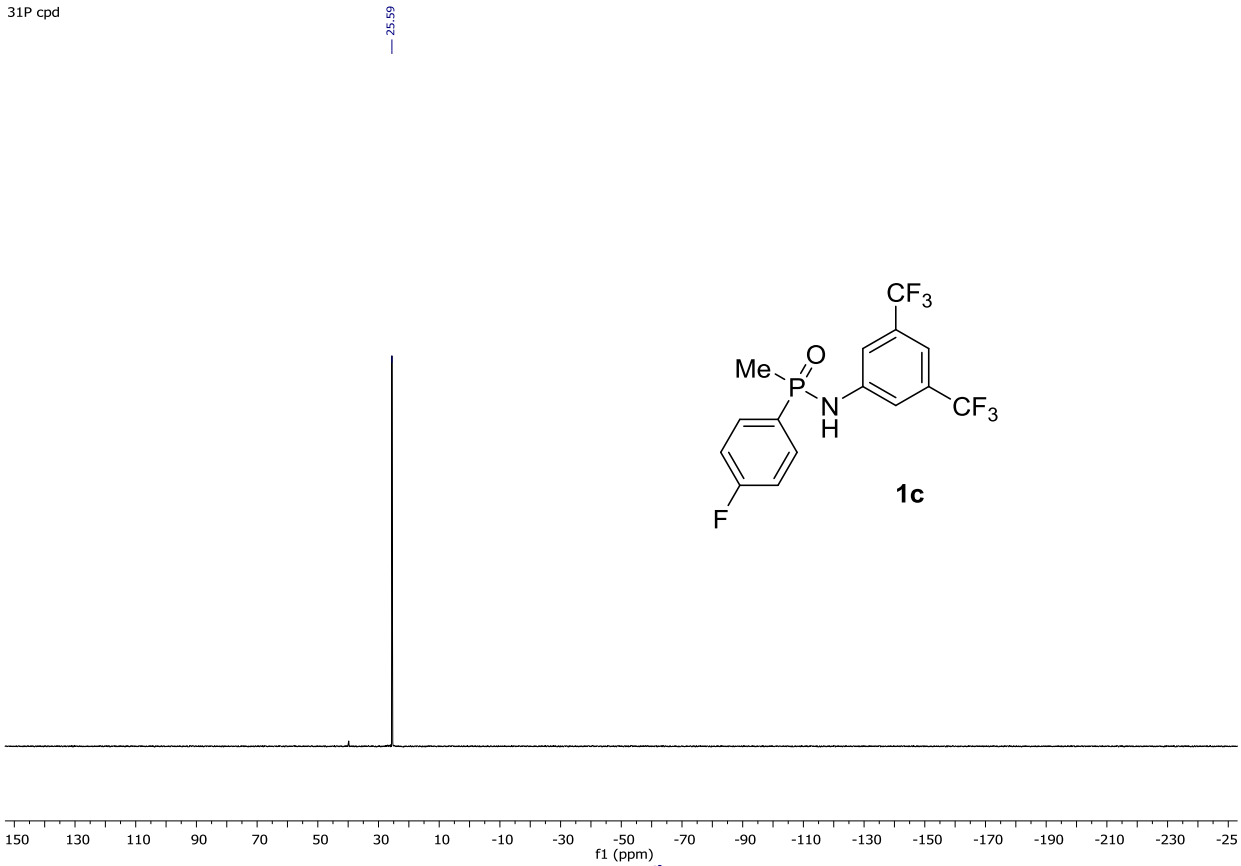

refe_19Fzg DMSO /opt/ ysun 45




8.87
8.84
7.89
7.88
7.88
7.87
7.87
7.86
7.85
7.85
7.85
7.84
7.84
7.83
7.82
7.82
7.82
7.82
7.81
7.54
7.43
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
2.50 DMSO-d6
1.83
1.79
CF3
Me
P
O
N
H
CF3
F
1c
1.0
2.0
2.0
1.0
2.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


165.64
165.61
163.15
163.12
144.43
134.05
133.96
133.93
133.84
131.41
131.08
130.76
130.44
129.94
129.91
128.72
128.69
127.20
124.49
121.78
119.07
116.90
116.18
116.04
115.97
115.83
112.93
17.26
16.35
CF3
Me
P
O
N
H
CF3
F
1c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

31P cpd

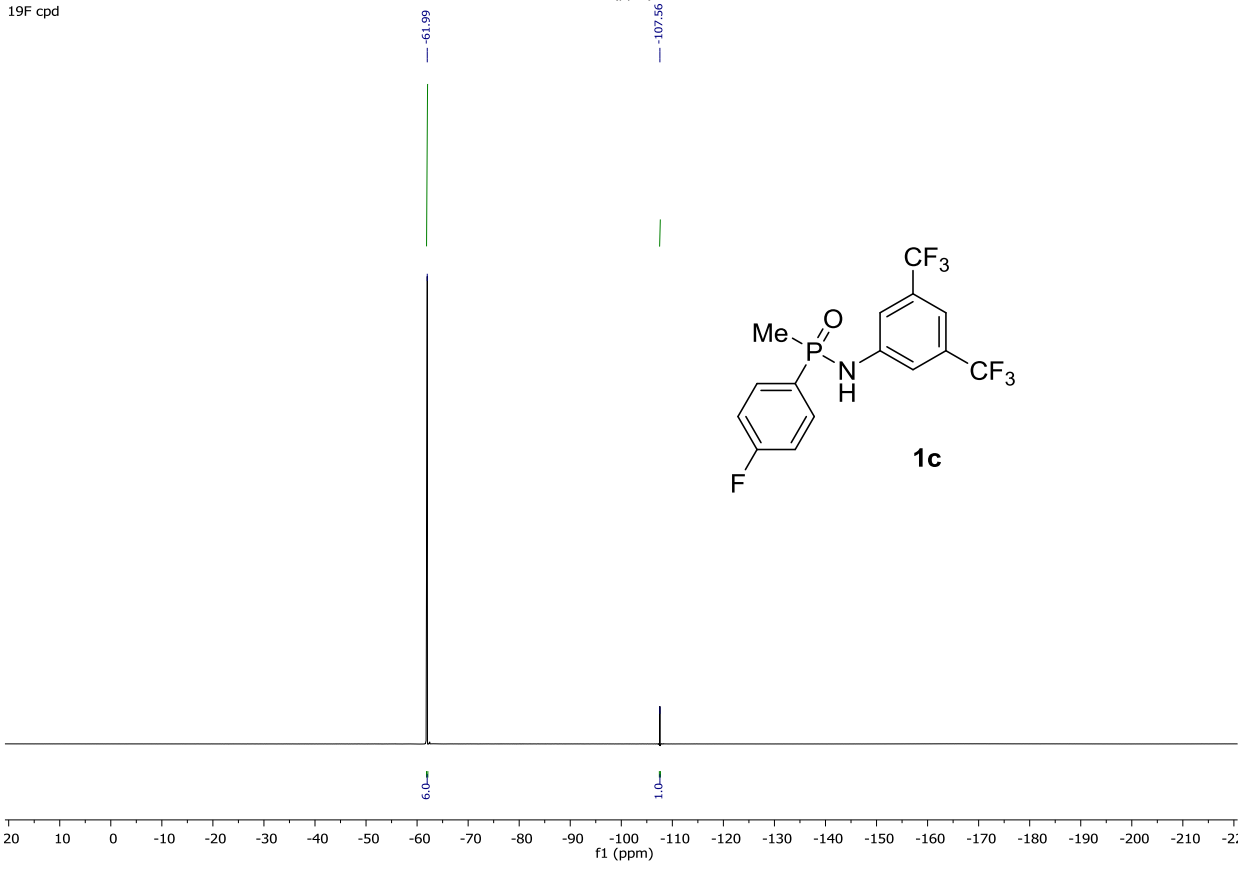






**1c**

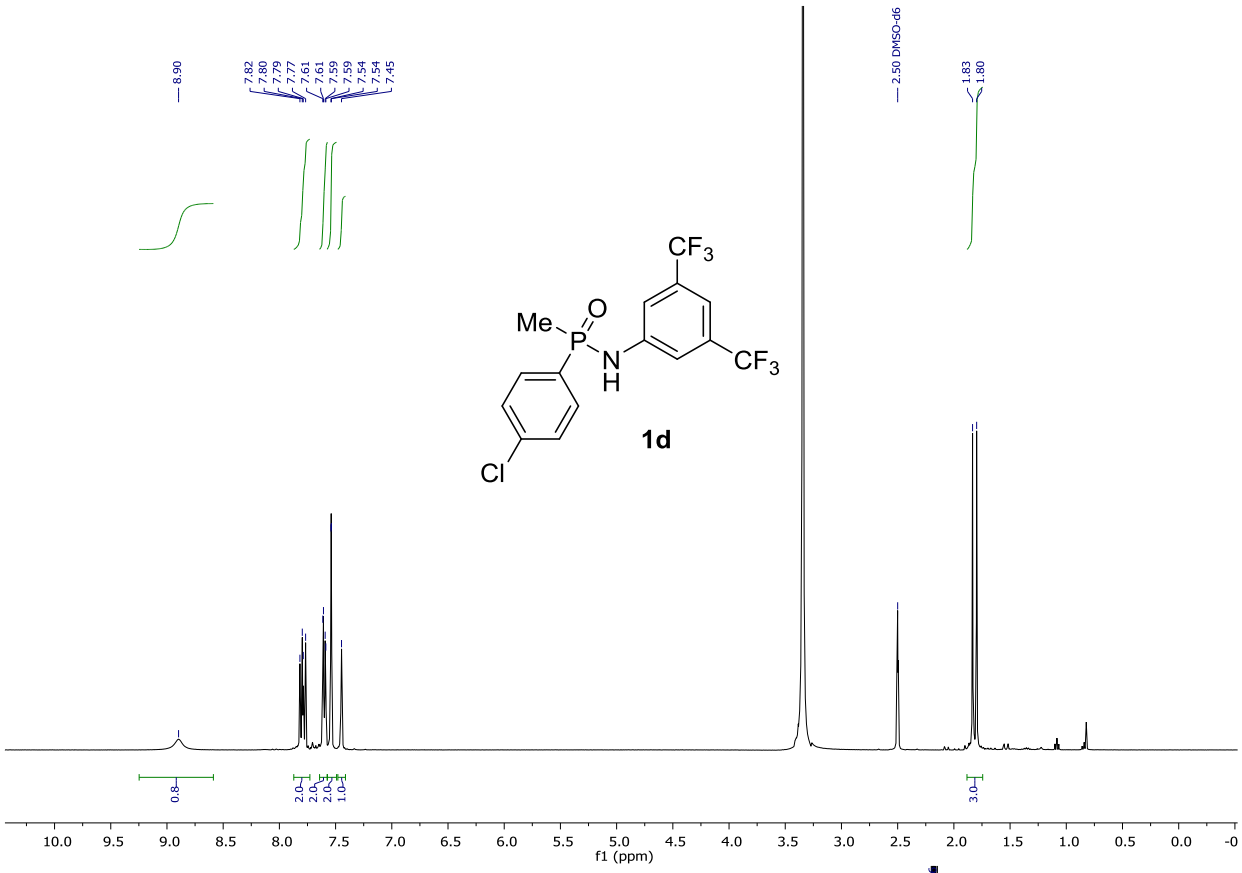
19F cpd

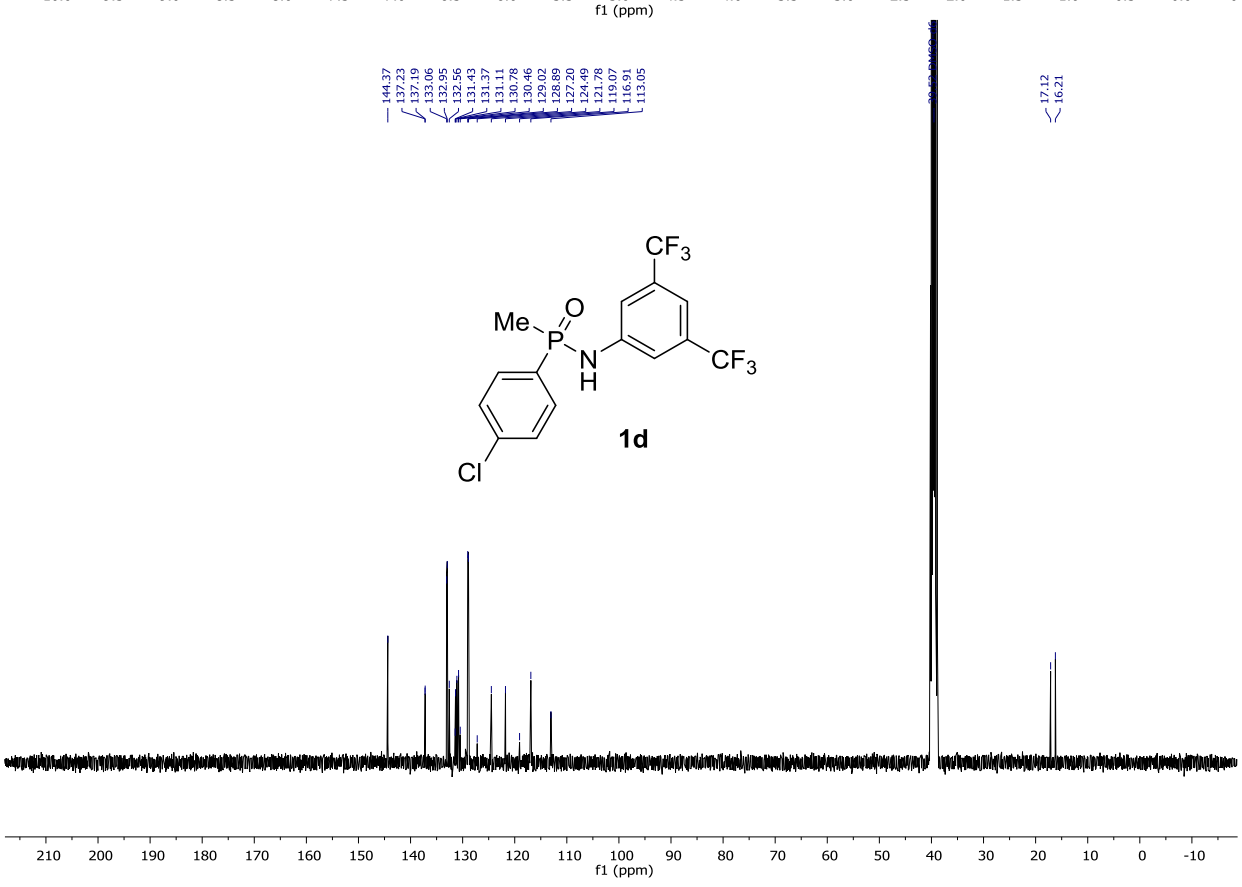




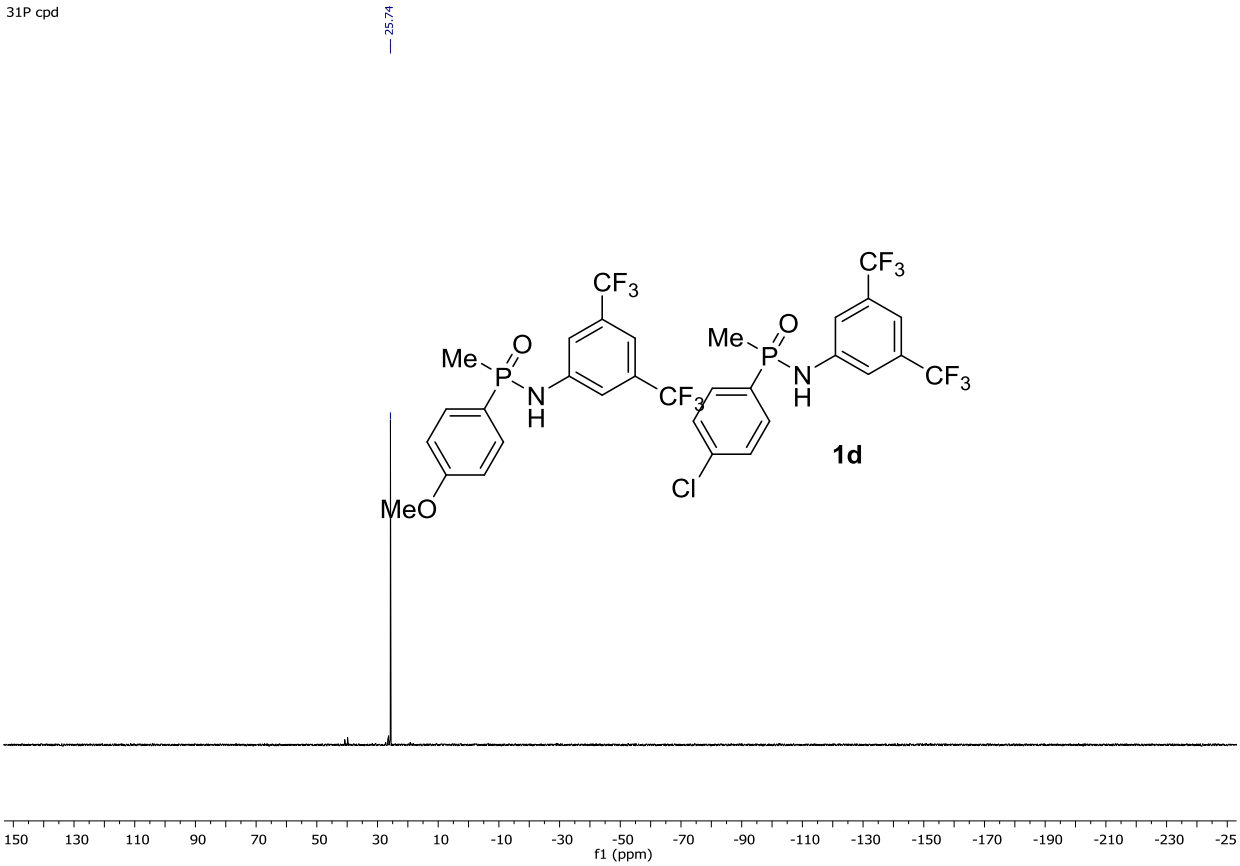


**1c**

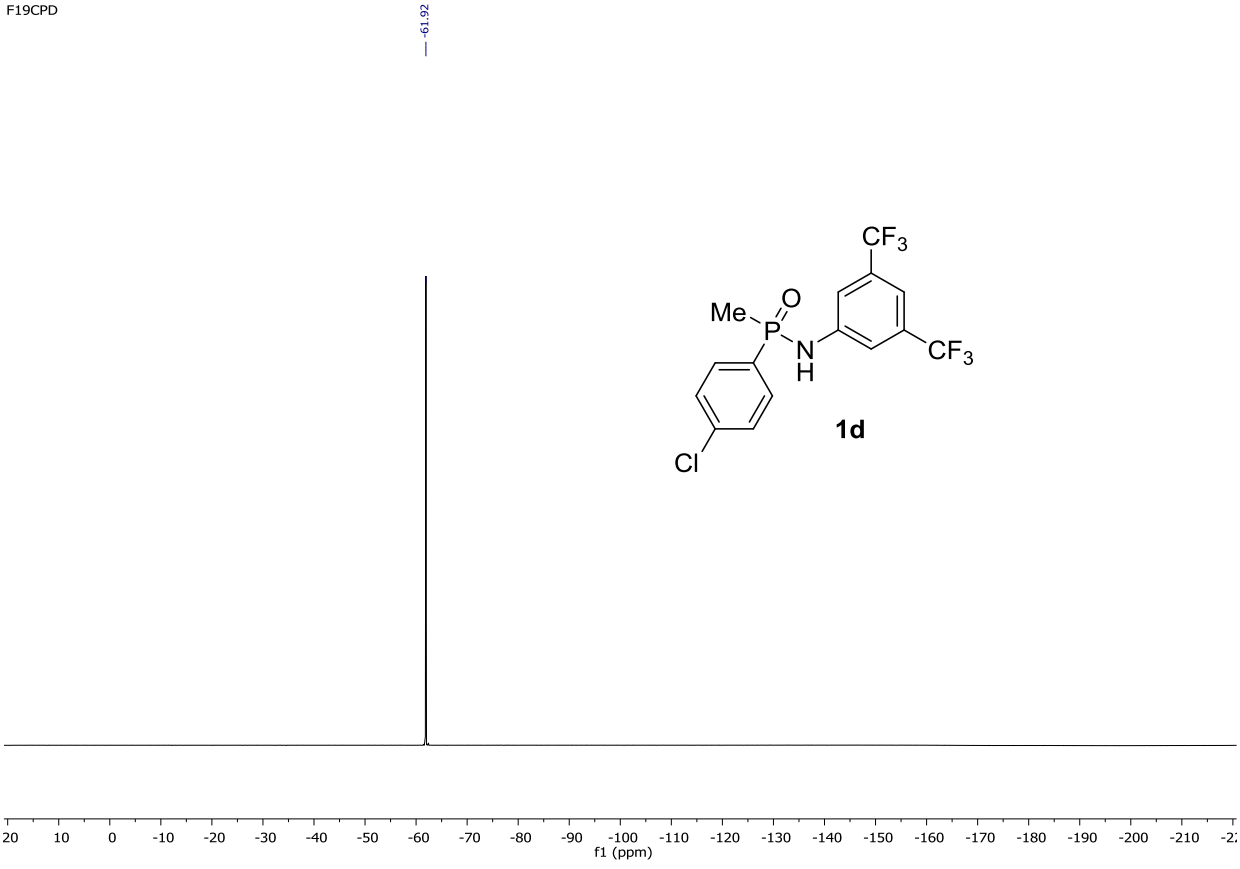

8.90
7.82
7.80
7.79
7.77
7.61
7.61
7.59
7.59
7.54
7.54
7.45
2.50 DMSO-d6
1.83
1.80
CF3
Me
P
O
N
H
CF3
Cl
1d
0.8
2.0
2.0
2.0
1.0
3.0
f1 (ppm)

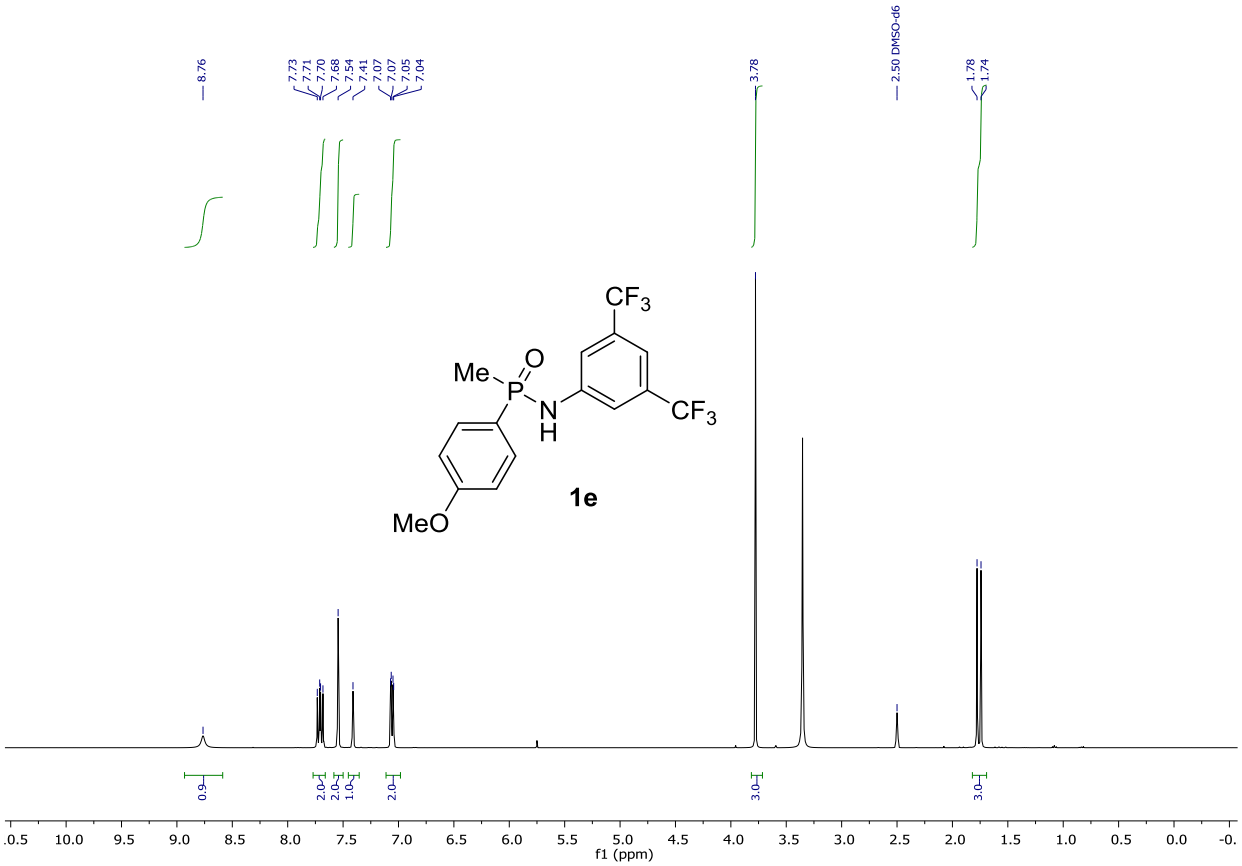

144.37
137.23
137.19
133.06
132.95
132.56
131.43
131.37
131.11
130.78
130.46
129.02
128.89
127.20
124.49
121.78
119.07
116.91
113.05
17.12
16.21
CF3
Me
P
O
N
H
CF3
Cl
1d
f1 (ppm)

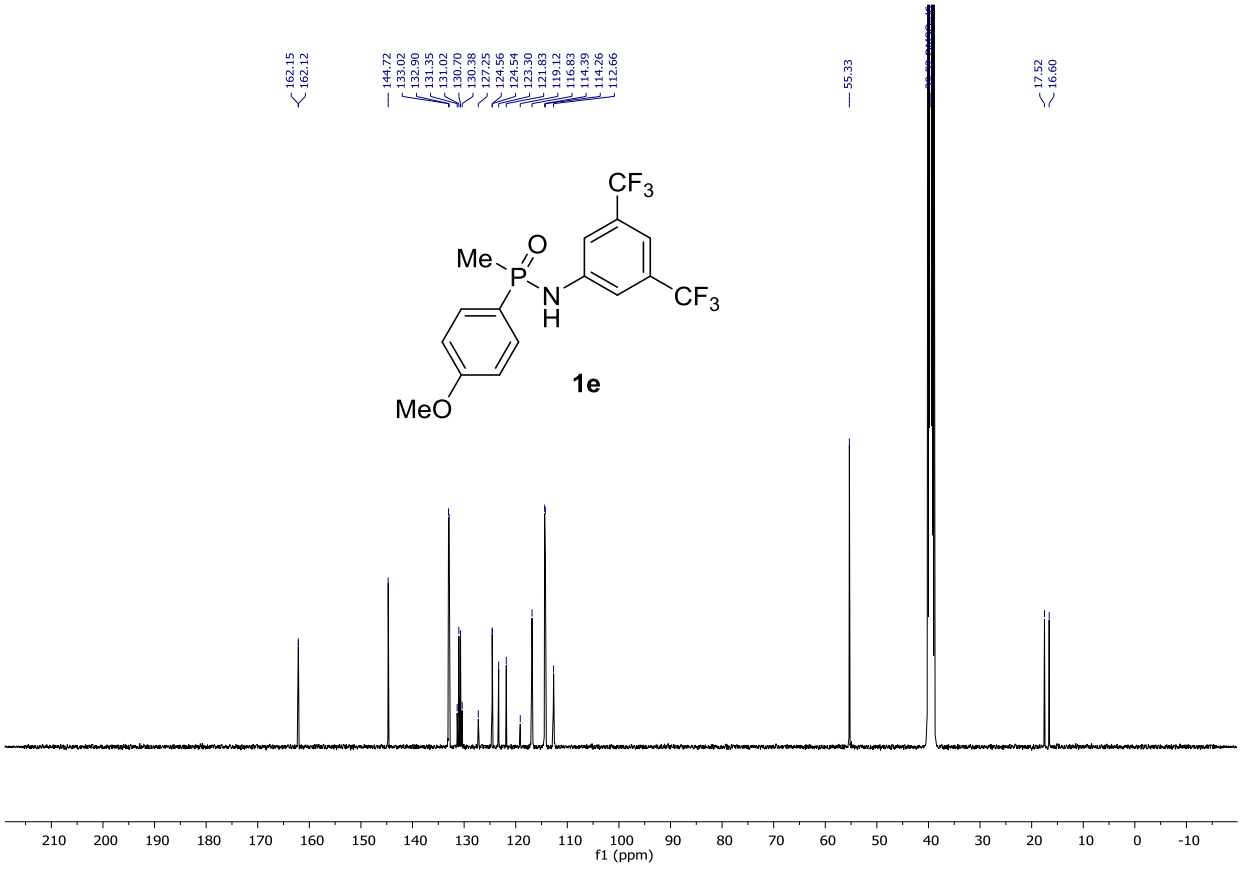
31P cpd



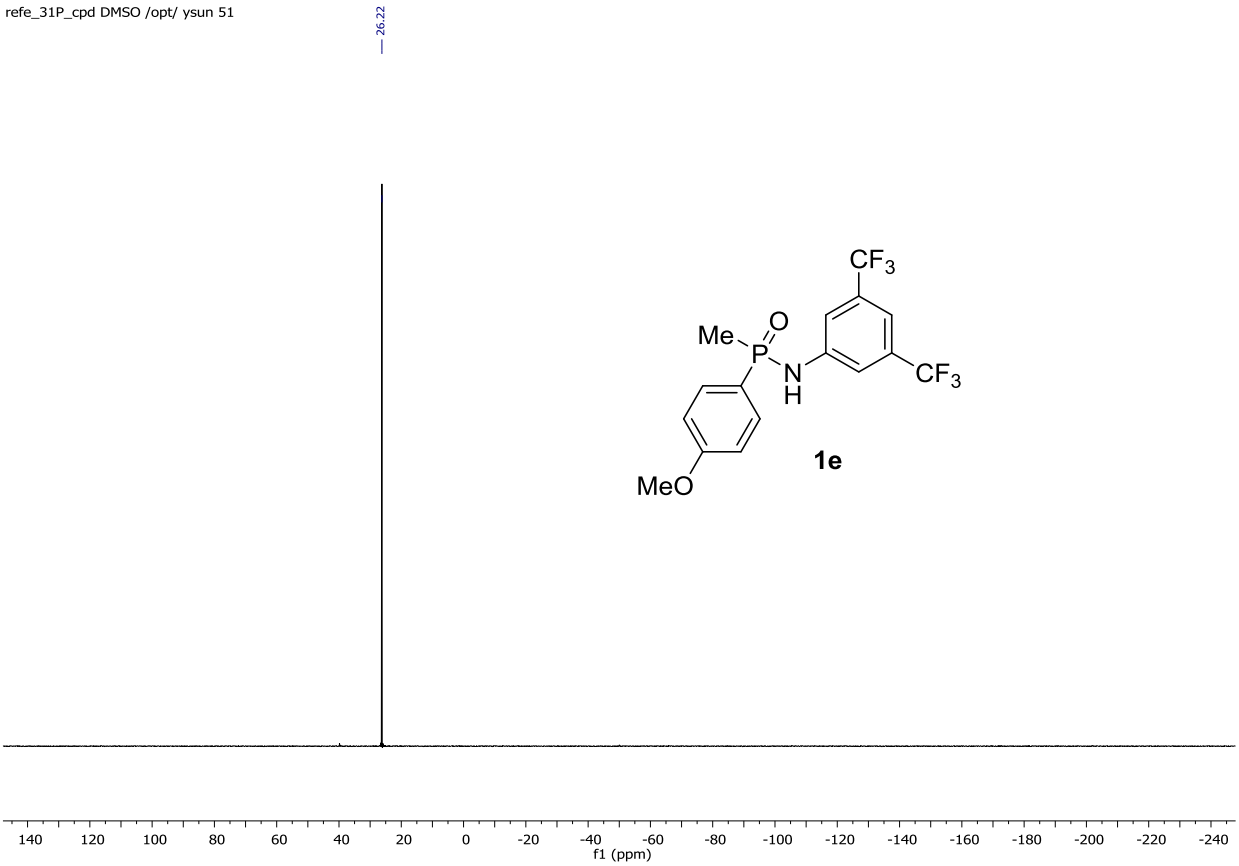

F19CPD



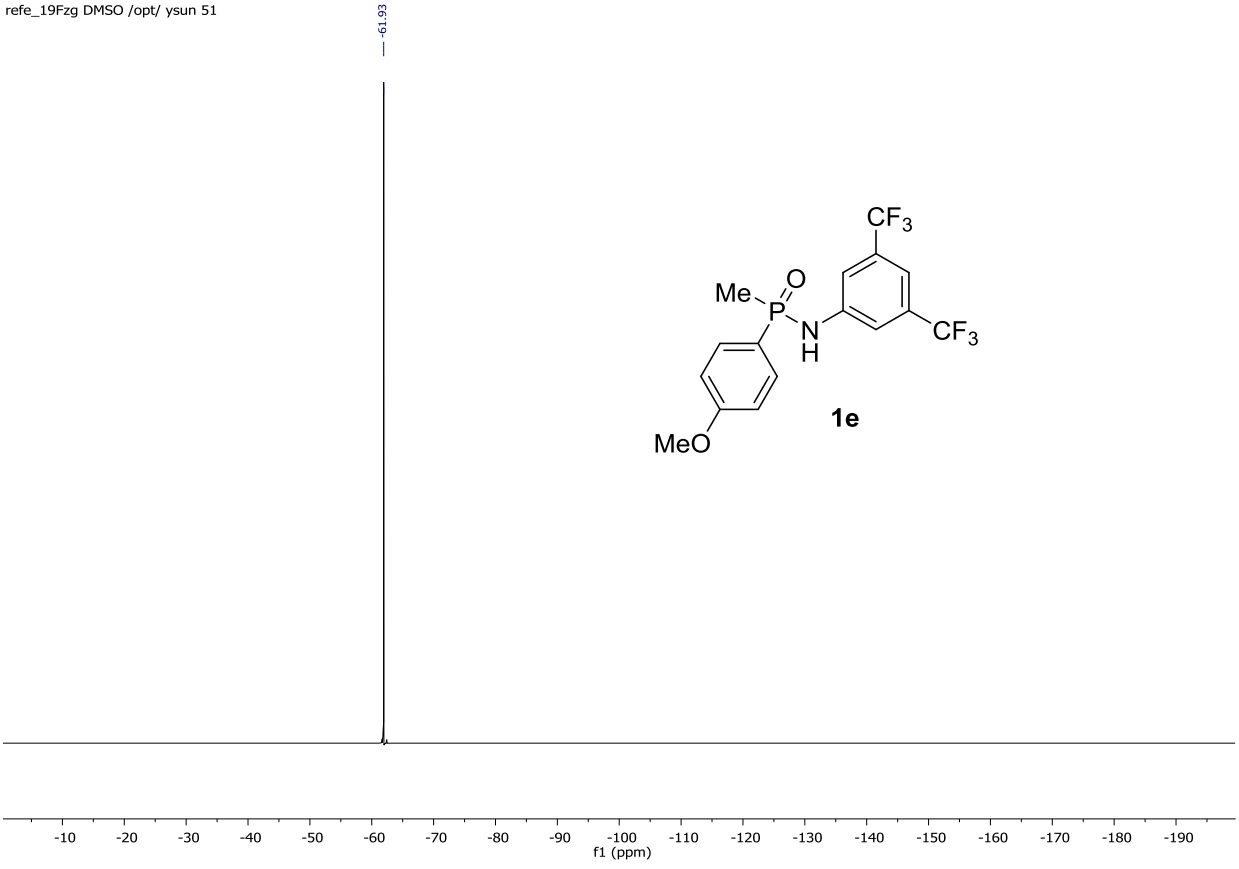

8.76
7.73
7.71
7.70
7.68
7.54
7.41
7.07
7.07
7.05
7.04
3.78
2.50 DMSO-d6
1.78
1.74
CF3
Me
O
P
N
H
CF3
MeO
1e
0.9
2.0
2.0
1.0
2.0
3.0
3.0
f1 (ppm)

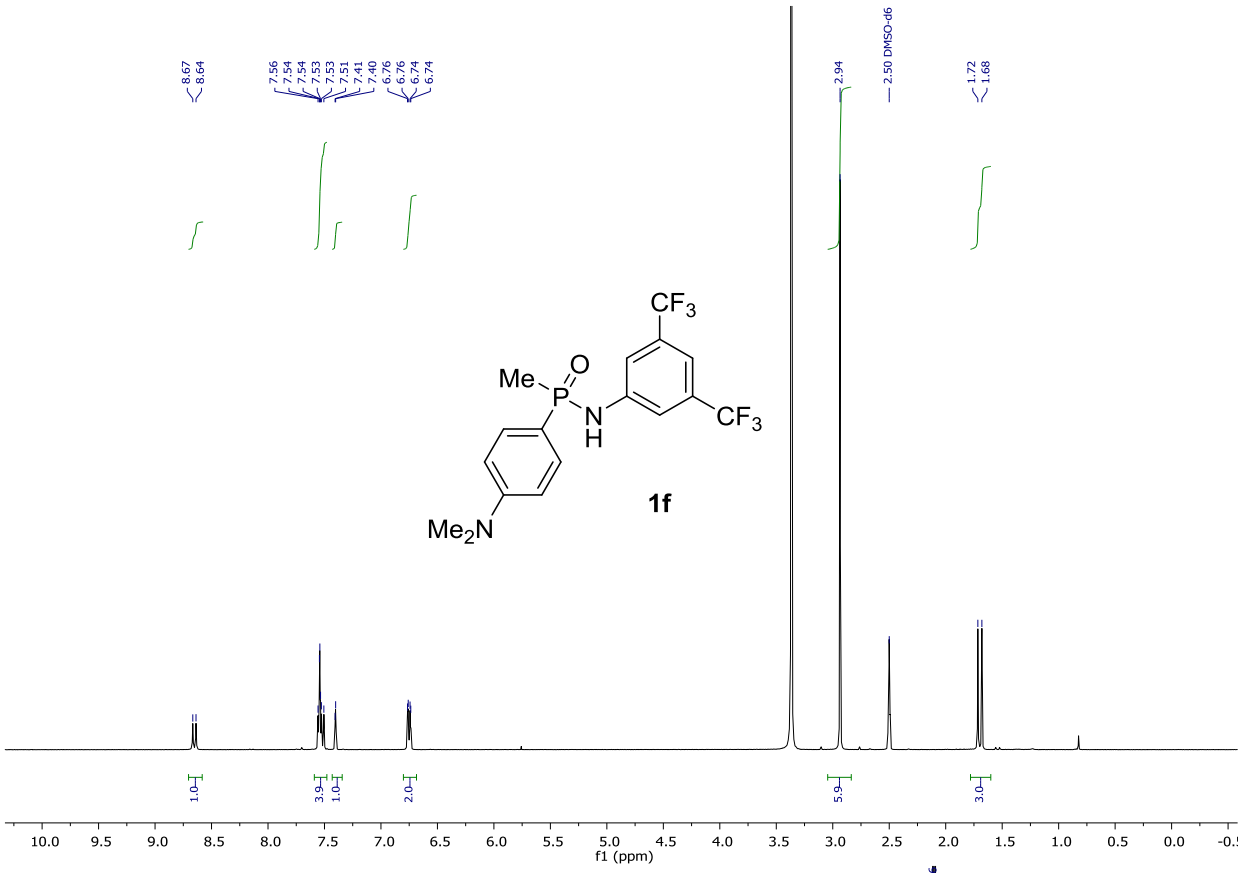

162.15
162.12
144.72
133.02
132.90
131.35
131.02
130.70
130.38
127.25
124.56
124.54
123.30
121.83
119.12
116.83
114.39
114.26
112.66
55.33
17.52
16.60
CF3
Me
O
P
N
H
CF3
MeO
1e
f1 (ppm)

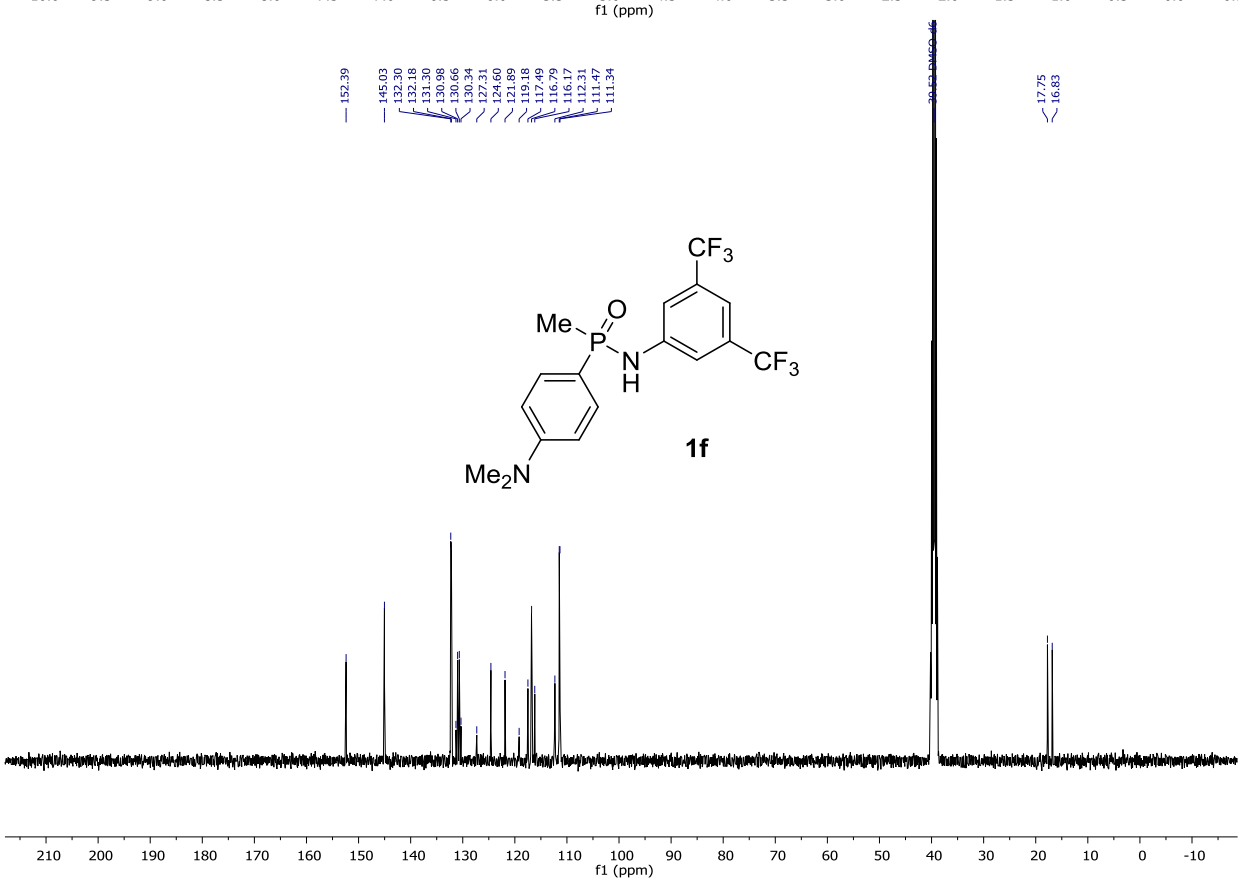
refe_31P_cpd DMSO /opt/ ysun 51



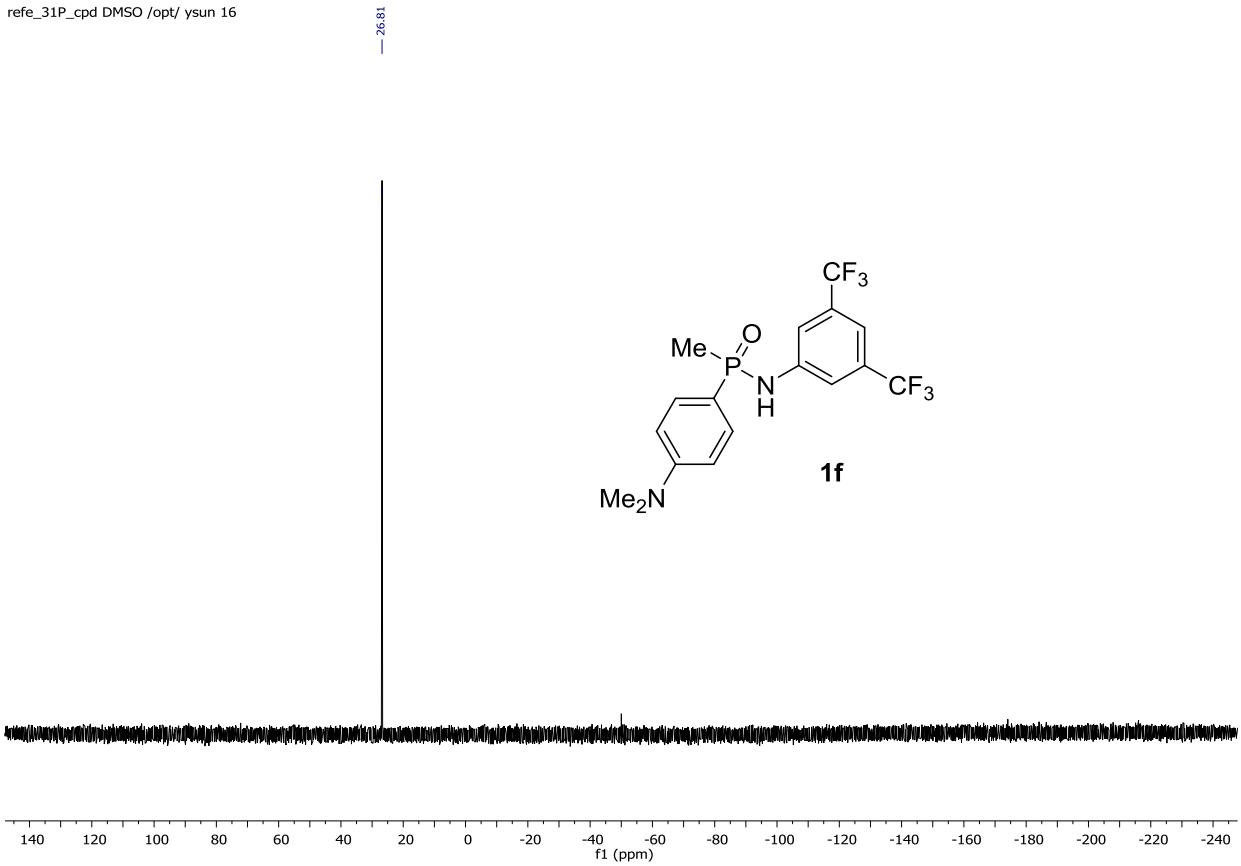

refe_19Fzg DMSO /opt/ ysun 51



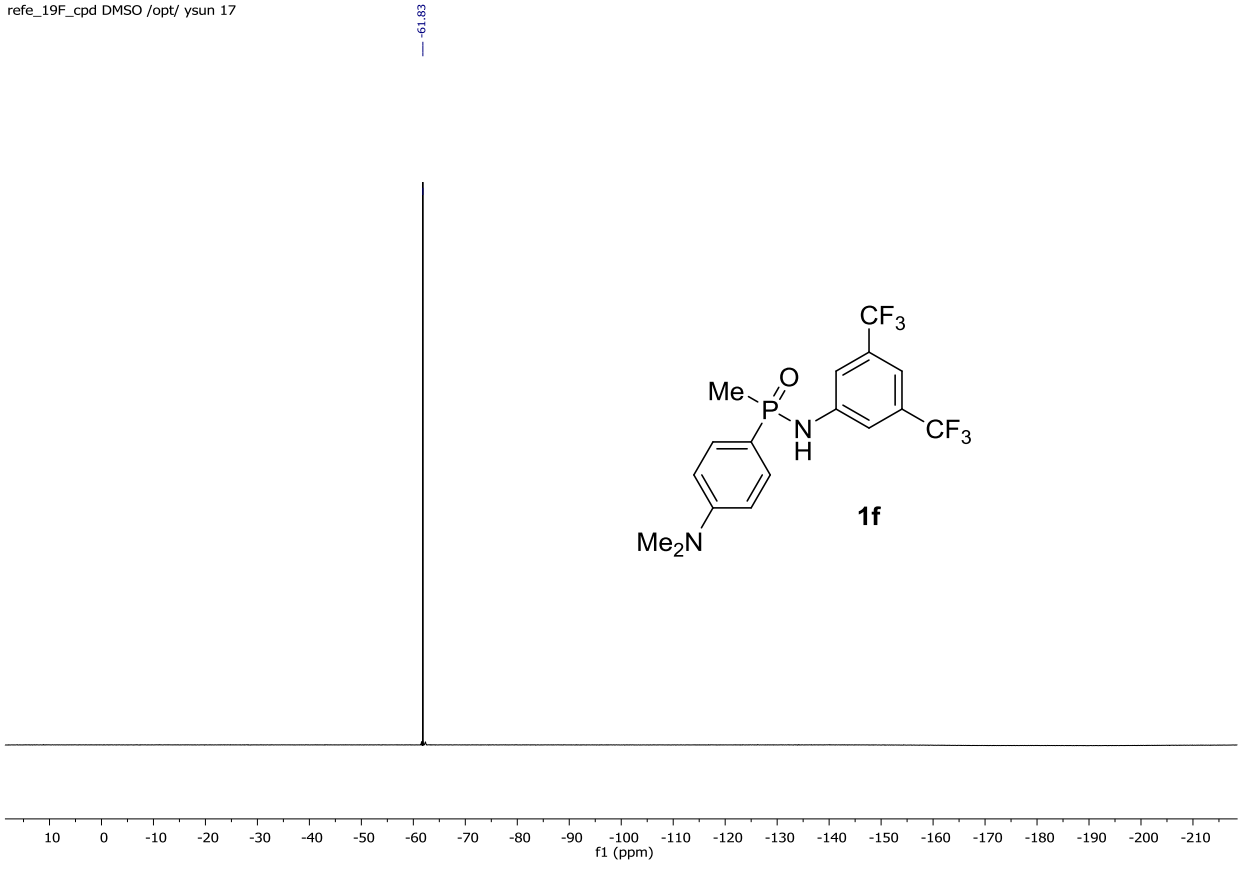

8.67
8.64
7.56
7.54
7.54
7.53
7.53
7.51
7.41
7.40
6.76
6.76
6.74
6.74
2.94
2.50 DMSO-d6
1.72
1.68
CF3
Me
O
P
N
H
CF3
Me2N
1f
1.0
3.9
1.0
2.0
5.9
3.0
f1 (ppm)

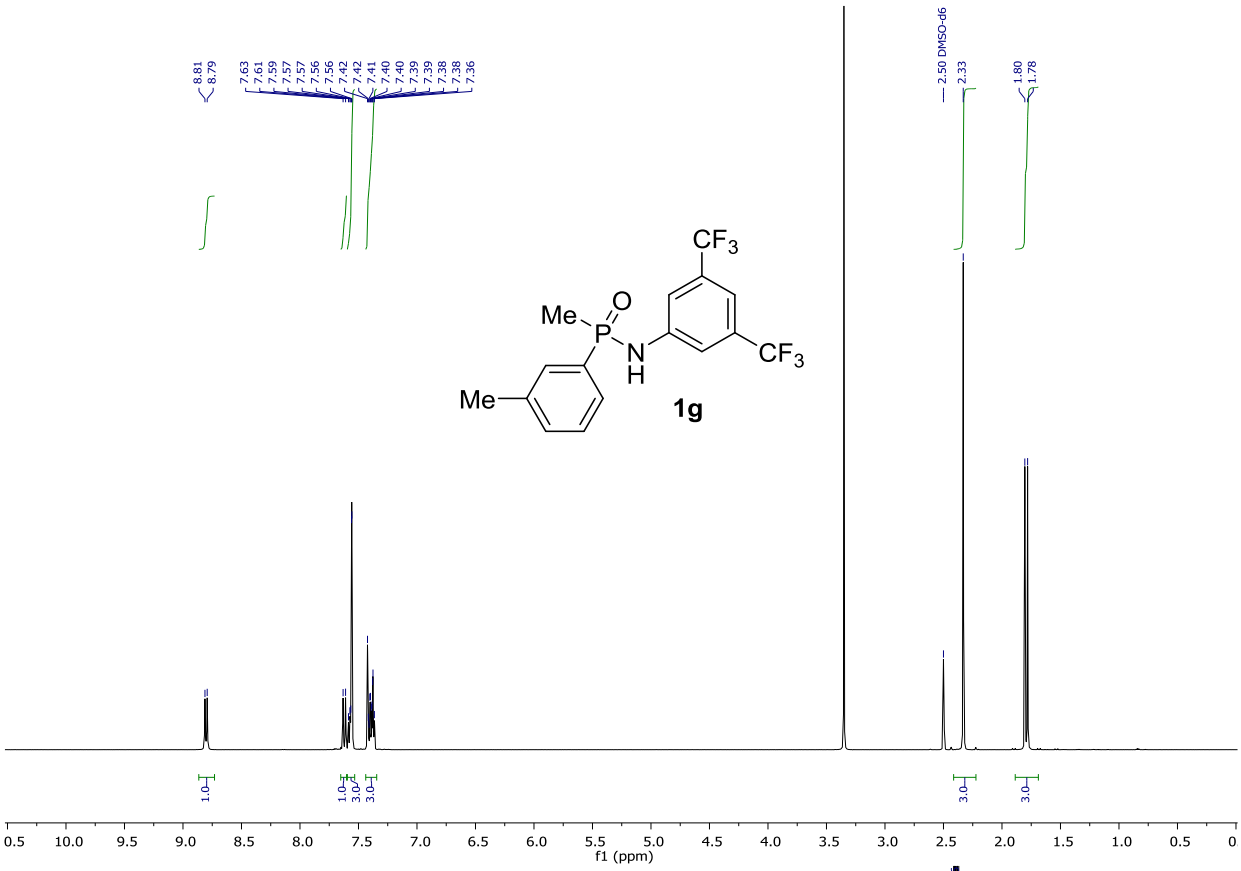

152.39
145.03
132.30
132.18
131.30
130.98
130.66
130.34
127.31
124.60
121.89
119.18
117.49
116.79
116.17
112.31
111.47
111.34
39.51 DMSO-d6
17.75
16.83
CF3
Me
O
P
N
H
CF3
Me2N
1f
f1 (ppm)

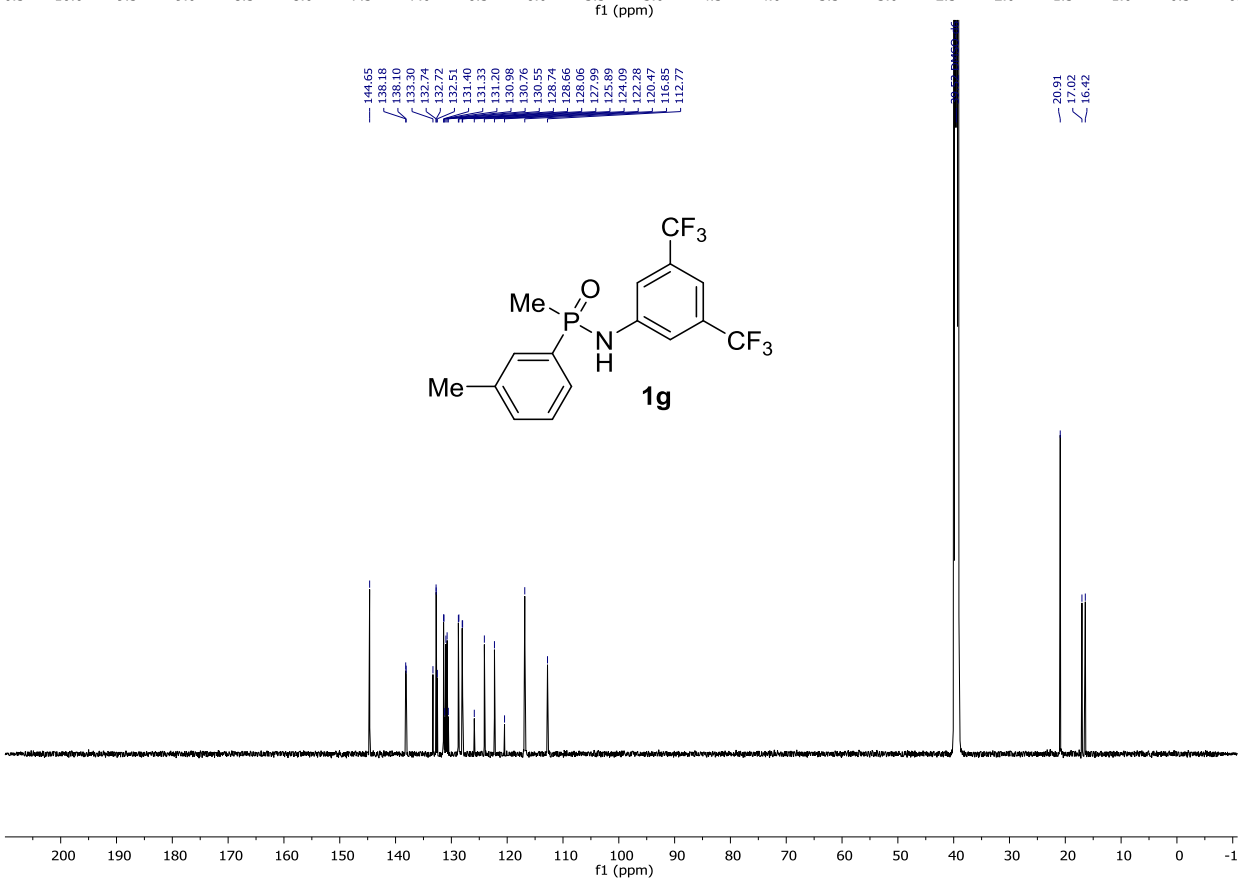
refe_31P_cpd DMSO /opt/ ysun 16



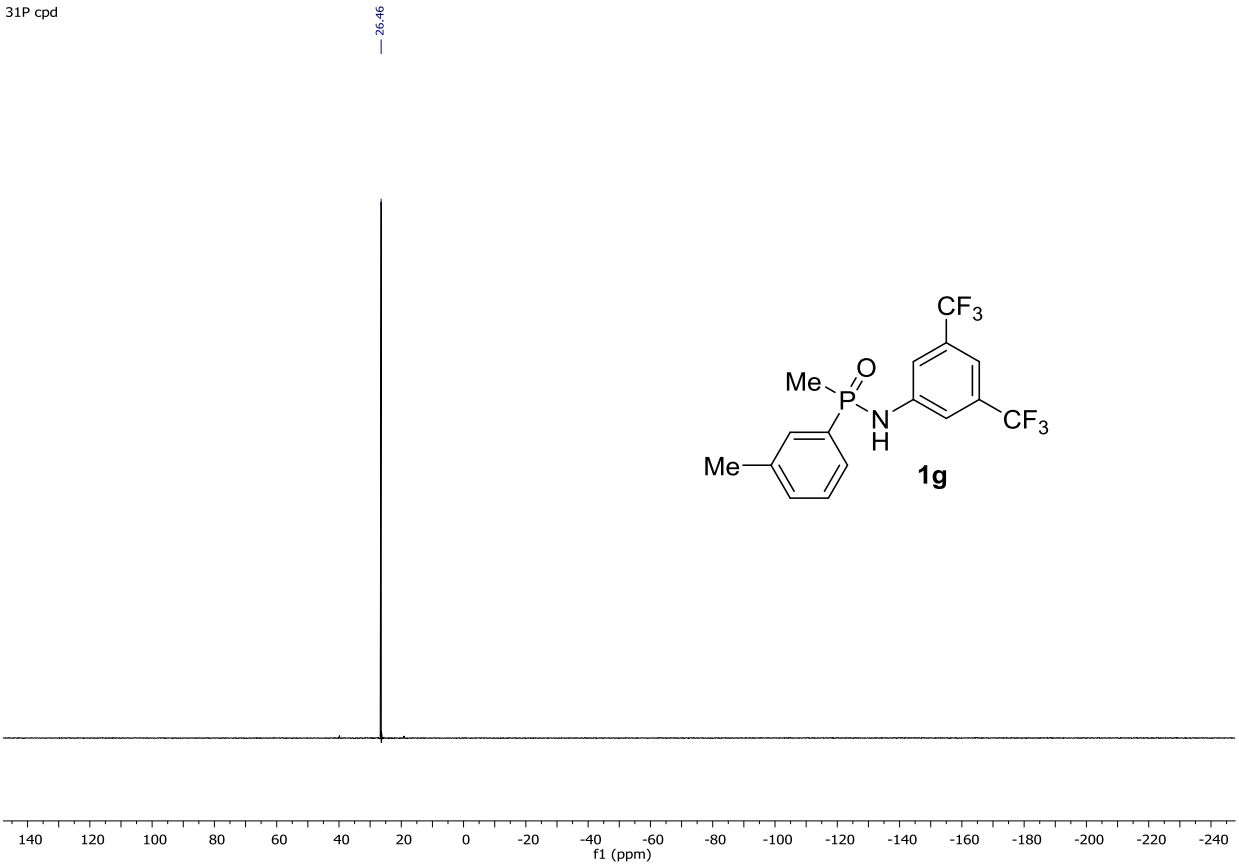

refe_19F_cpd DMSO /opt/ ysun 17



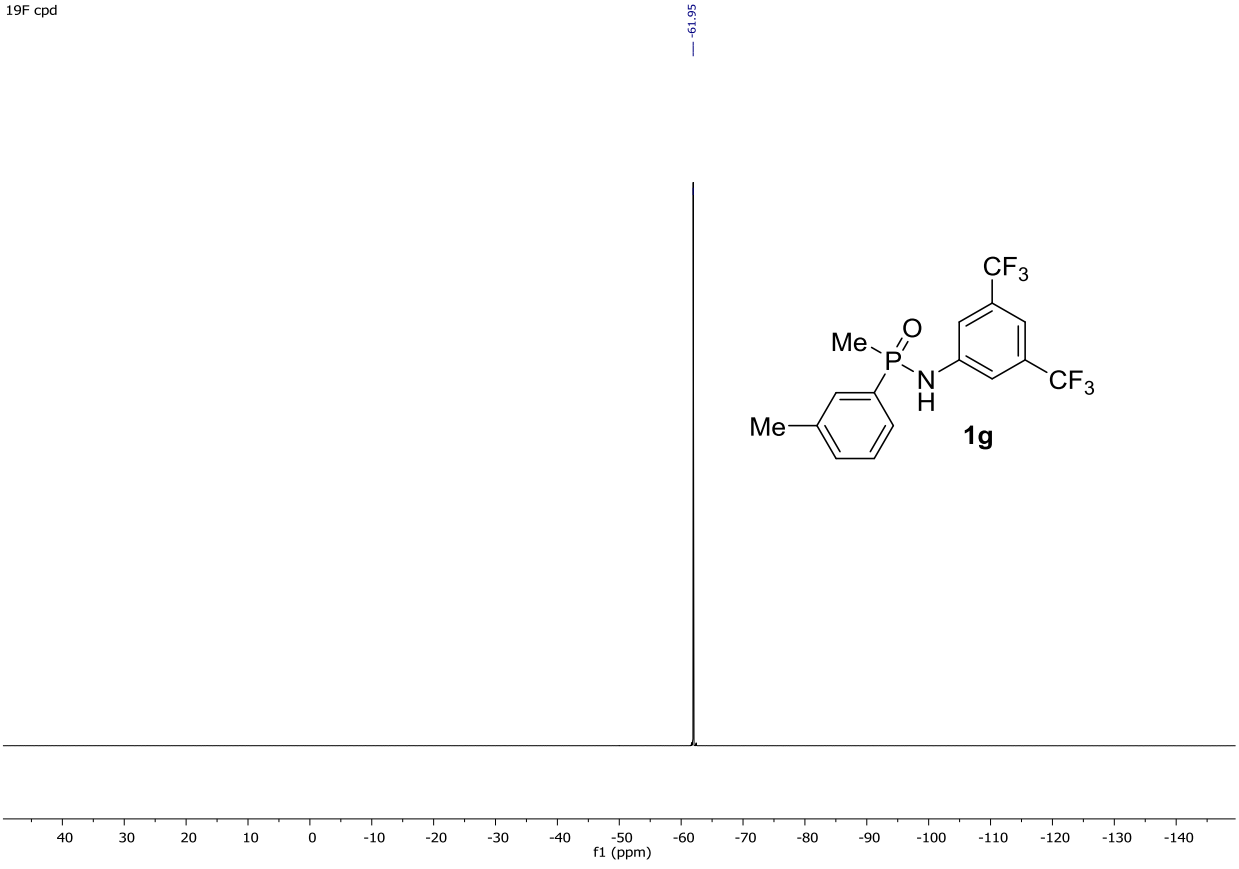

8.81
8.79
7.63
7.61
7.59
7.57
7.57
7.56
7.56
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.36
2.50 DMSO-d6
2.33
1.80
1.78
CF3
Me
P
O
N
H
CF3
Me
1g
1.0
1.0
3.0
3.0
3.0
3.0
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

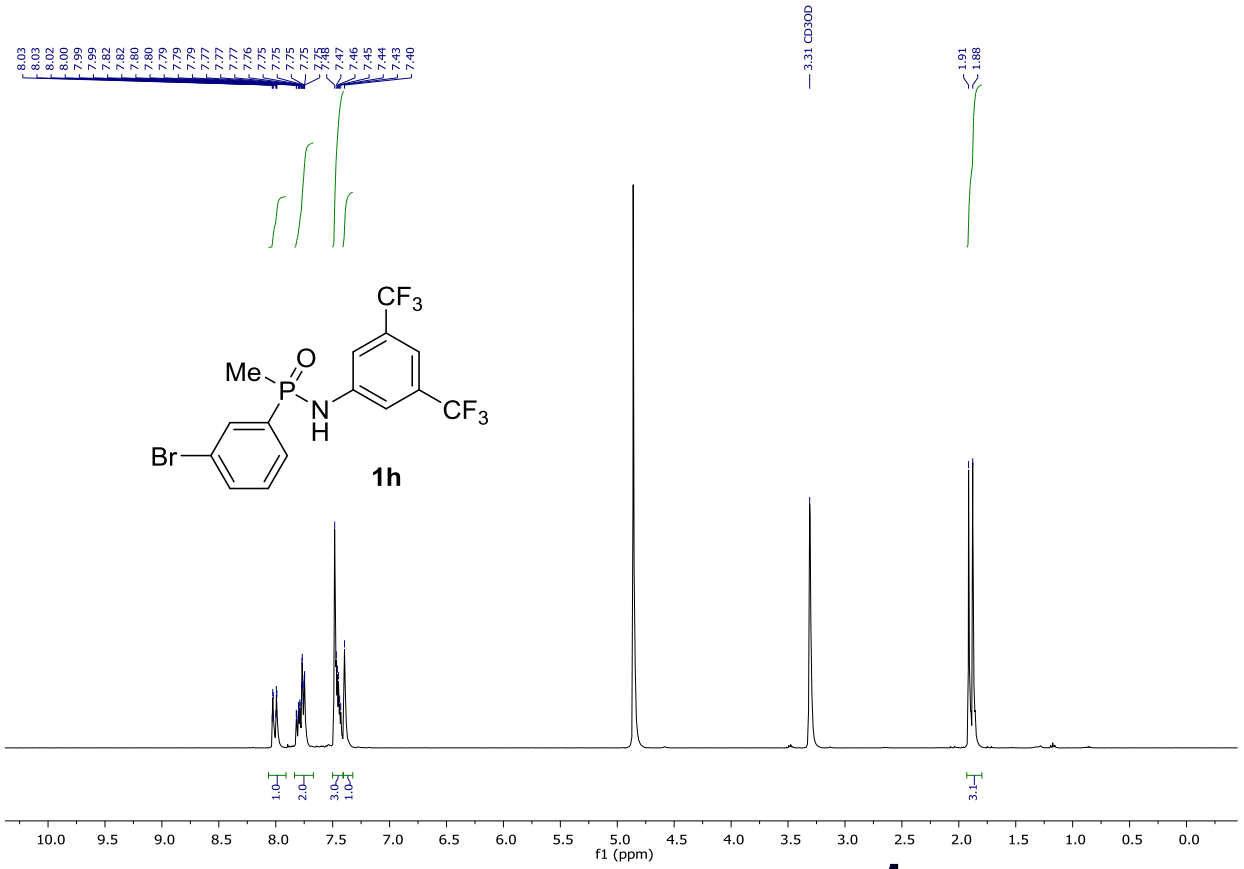

144.65
138.18
138.10
133.30
132.74
132.72
132.51
131.40
131.33
131.20
130.98
130.76
130.55
128.74
128.66
128.06
127.99
125.89
124.09
122.28
120.47
116.85
112.77
39.51 DMSO-d6
20.91
17.02
16.42
CF3
Me
P
O
N
H
CF3
Me
1g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

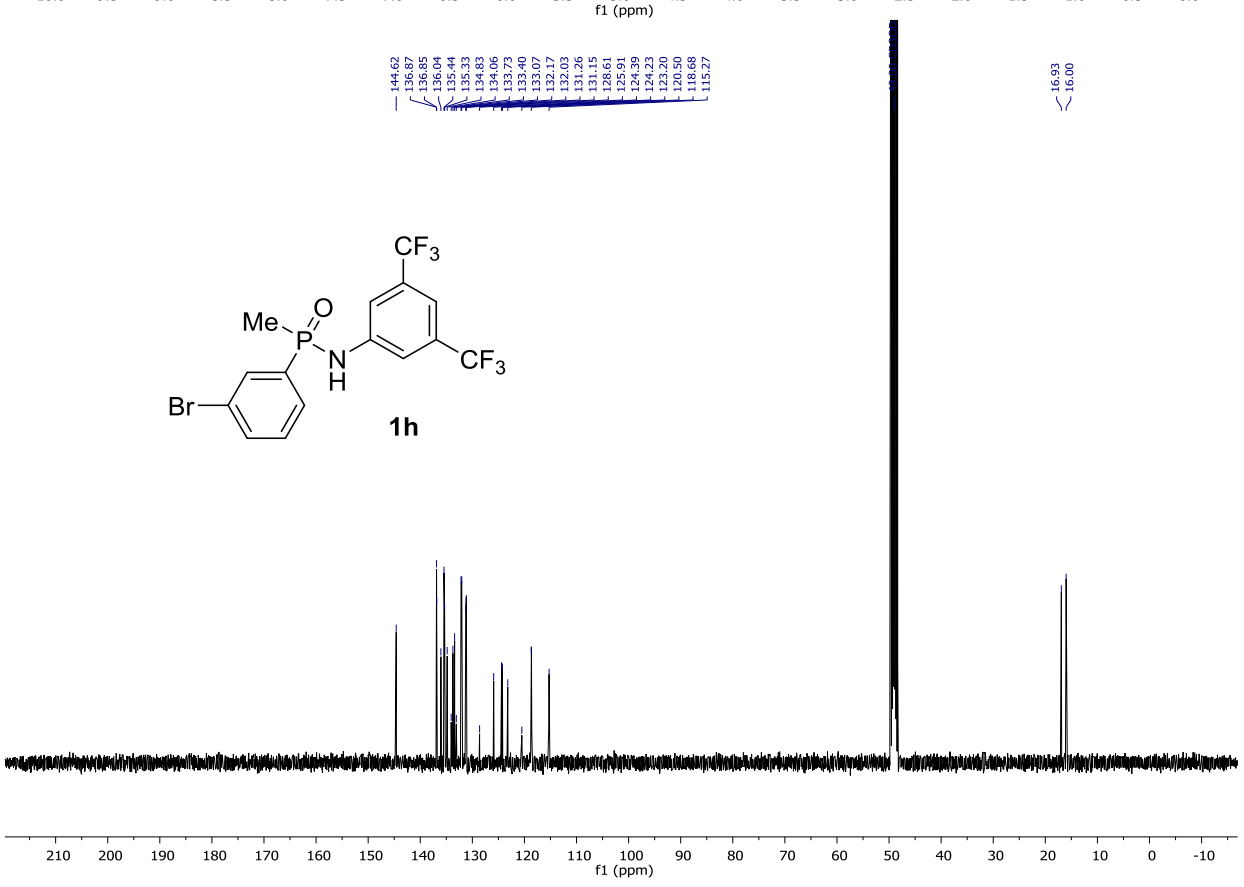
31P cpd




19F cpd

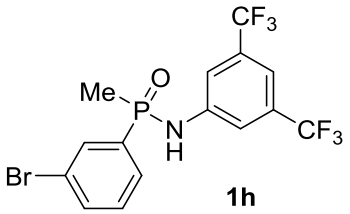



8.03
8.03
8.02
8.00
7.99
7.99
7.82
7.82
7.80
7.80
7.79
7.79
7.79
7.77
7.77
7.77
7.76
7.75
7.75
7.75
7.75
7.48
7.47
7.46
7.45
7.44
7.43
7.40
3.31 CD3OD
1.91
1.88
CF3
Me
O
P
N
H
CF3
Br
1h
1.0
2.0
3.0
1.0
3.1
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

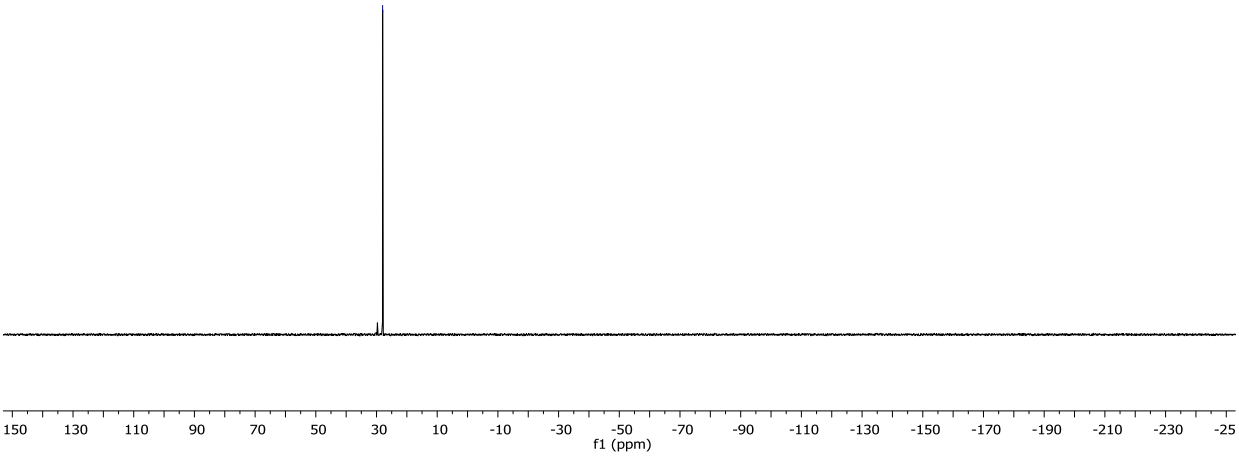

144.62
136.87
136.85
136.04
135.44
135.33
134.83
134.06
133.73
133.40
133.07
132.17
132.03
131.26
131.15
128.61
125.91
124.39
124.23
123.20
120.50
118.68
115.27
16.93
16.00
CF3
Me
O
P
N
H
CF3
Br
1h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

31P cpd

27.98

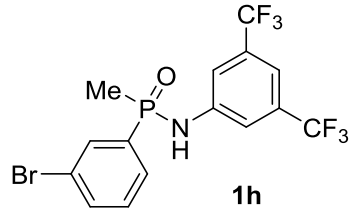



**1h**

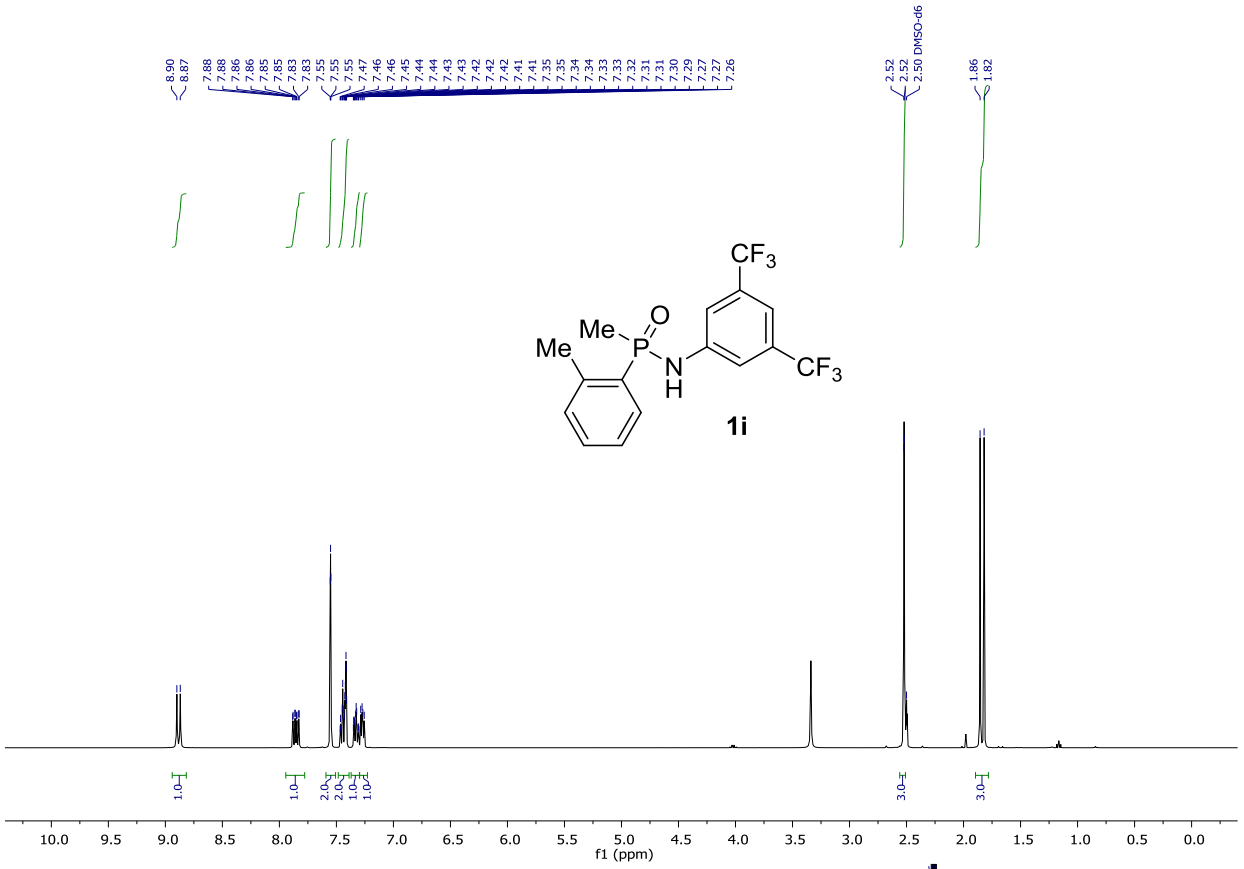


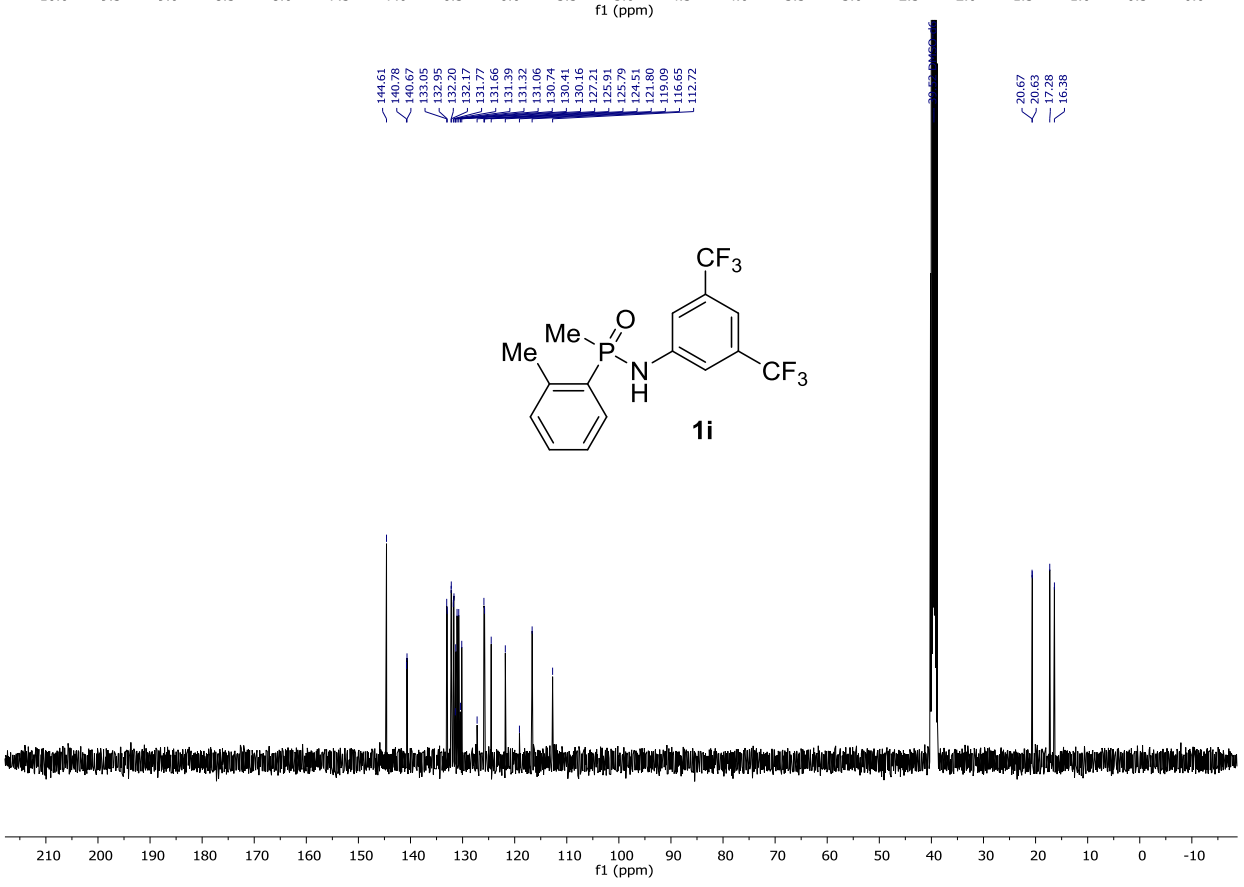

19F cpd

-64.85

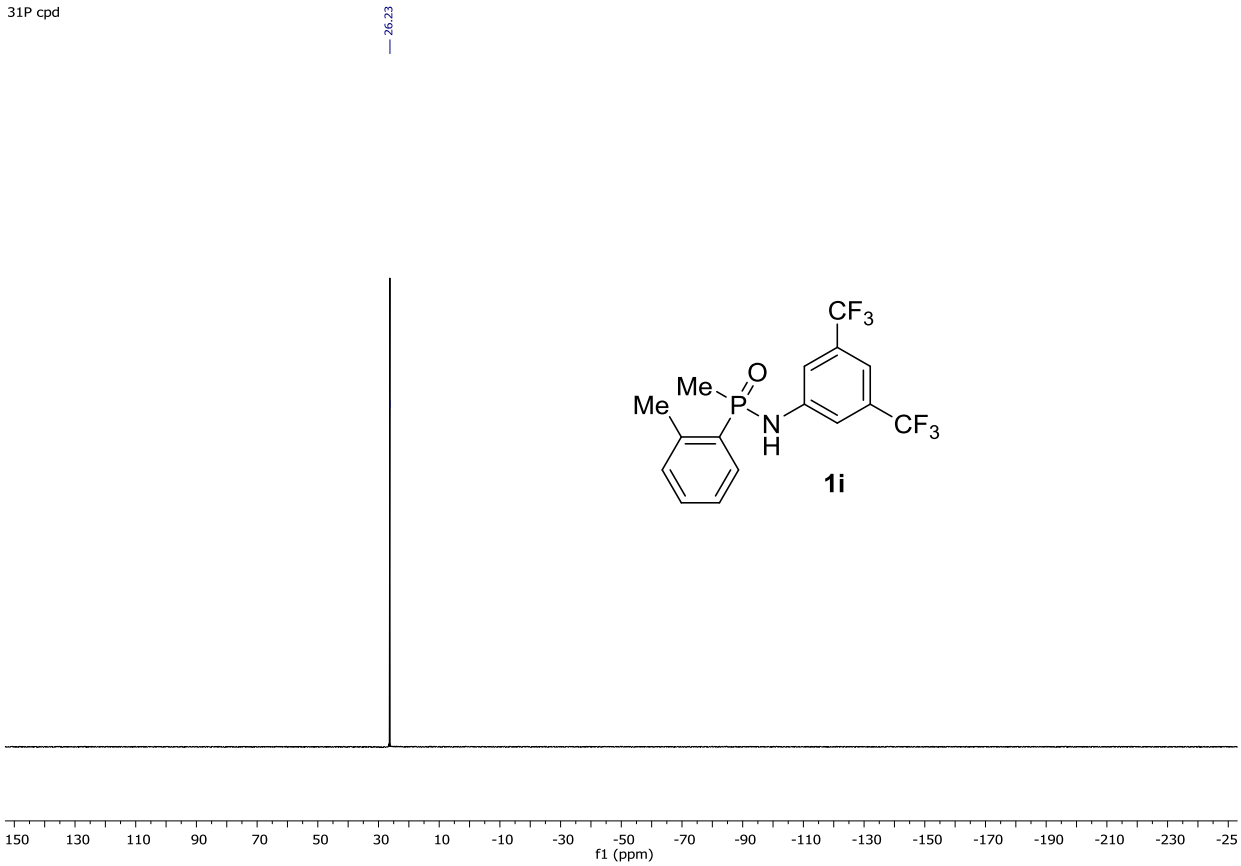



**1h**


8.90
8.87
7.88
7.88
7.86
7.86
7.86
7.85
7.85
7.83
7.83
7.55
7.55
7.55
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.27
7.27
7.26
2.52
2.52
2.50 DMSO-d6
1.86
1.82
CF3
Me
P
O
N
H
Me
CF3
1i
1.0
1.0
2.0
2.0
1.0
1.0
3.0
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.61
140.78
140.67
133.05
132.95
132.20
132.17
131.77
131.66
131.39
131.32
131.06
130.74
130.41
130.16
127.21
125.91
125.79
124.51
121.80
119.09
116.65
112.72
20.67
20.63
17.28
16.38
CF3
Me
P
O
N
H
Me
CF3
1i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

31P cpd

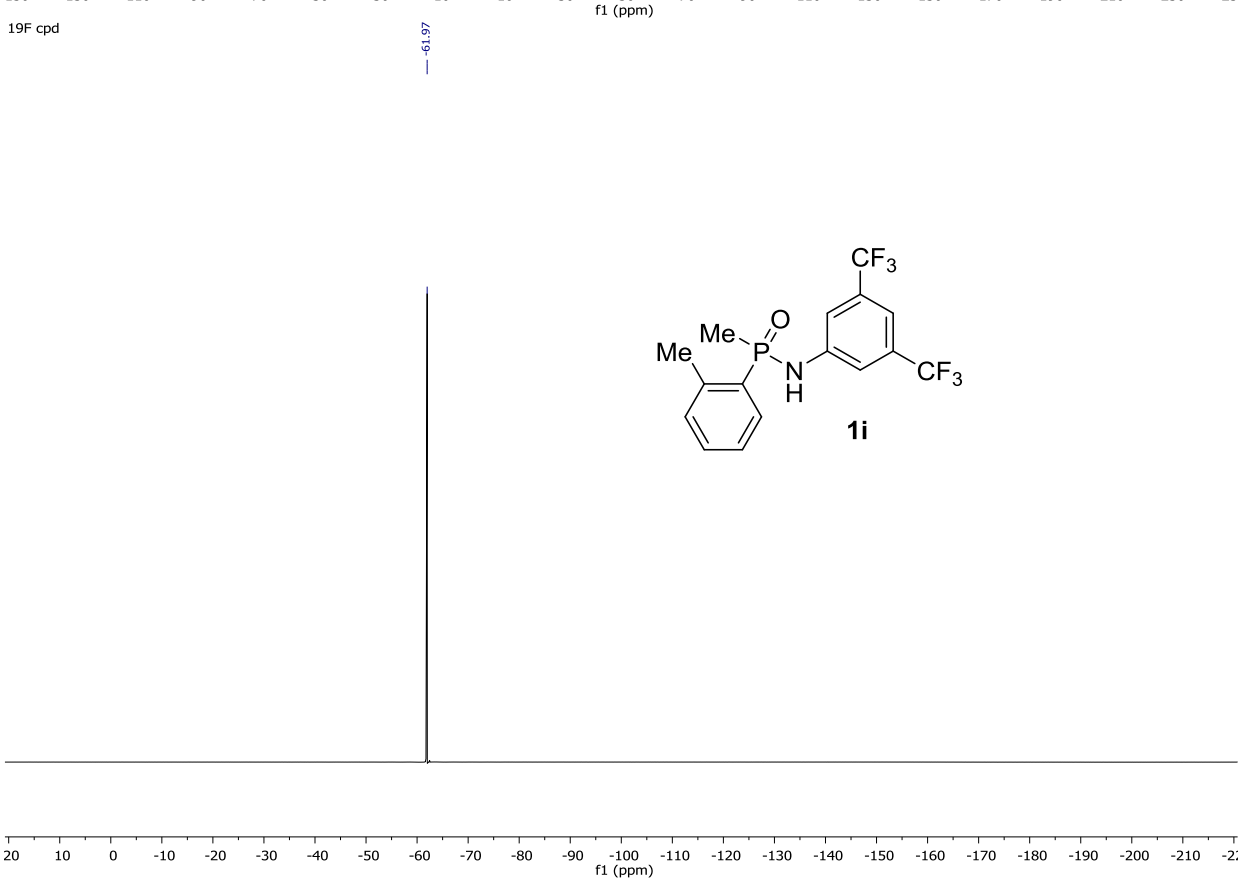






**1i**

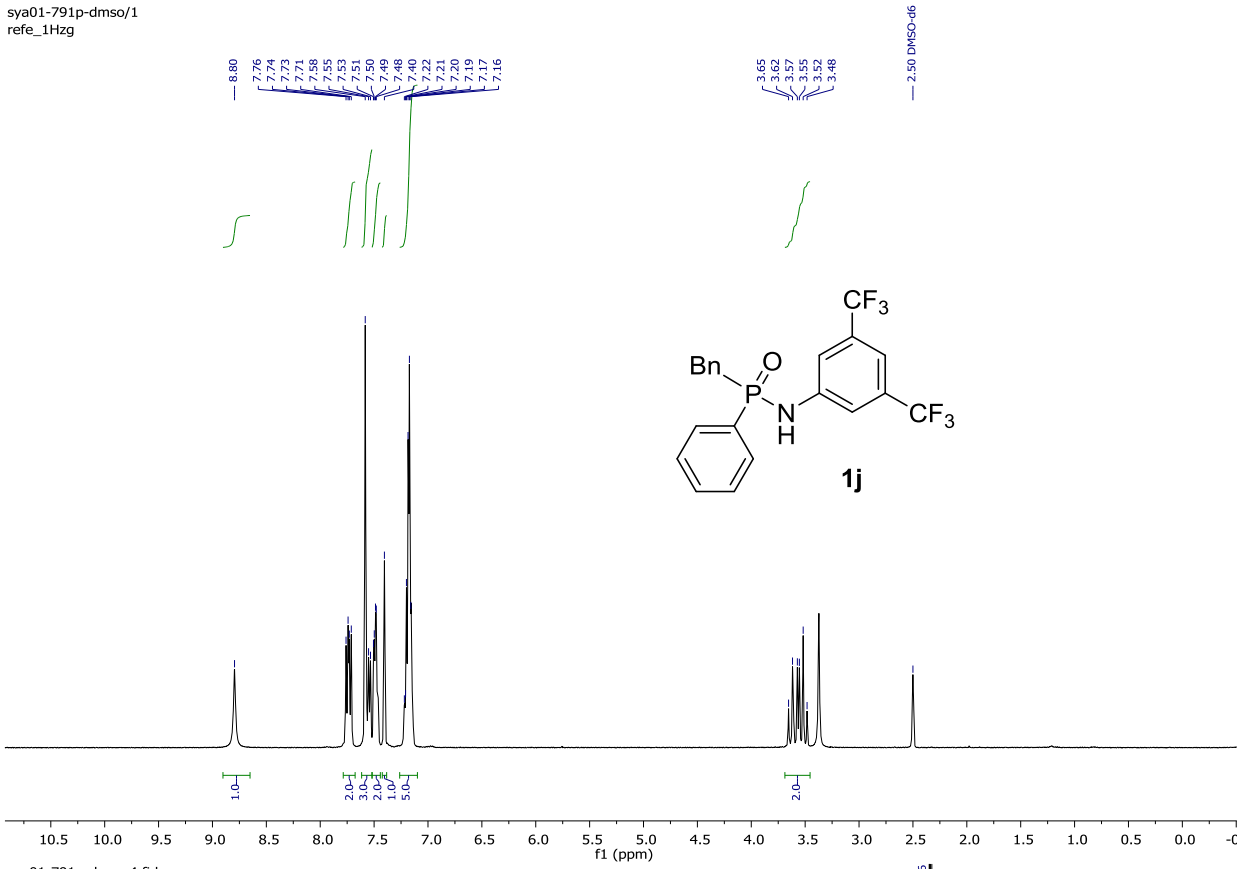
19F cpd

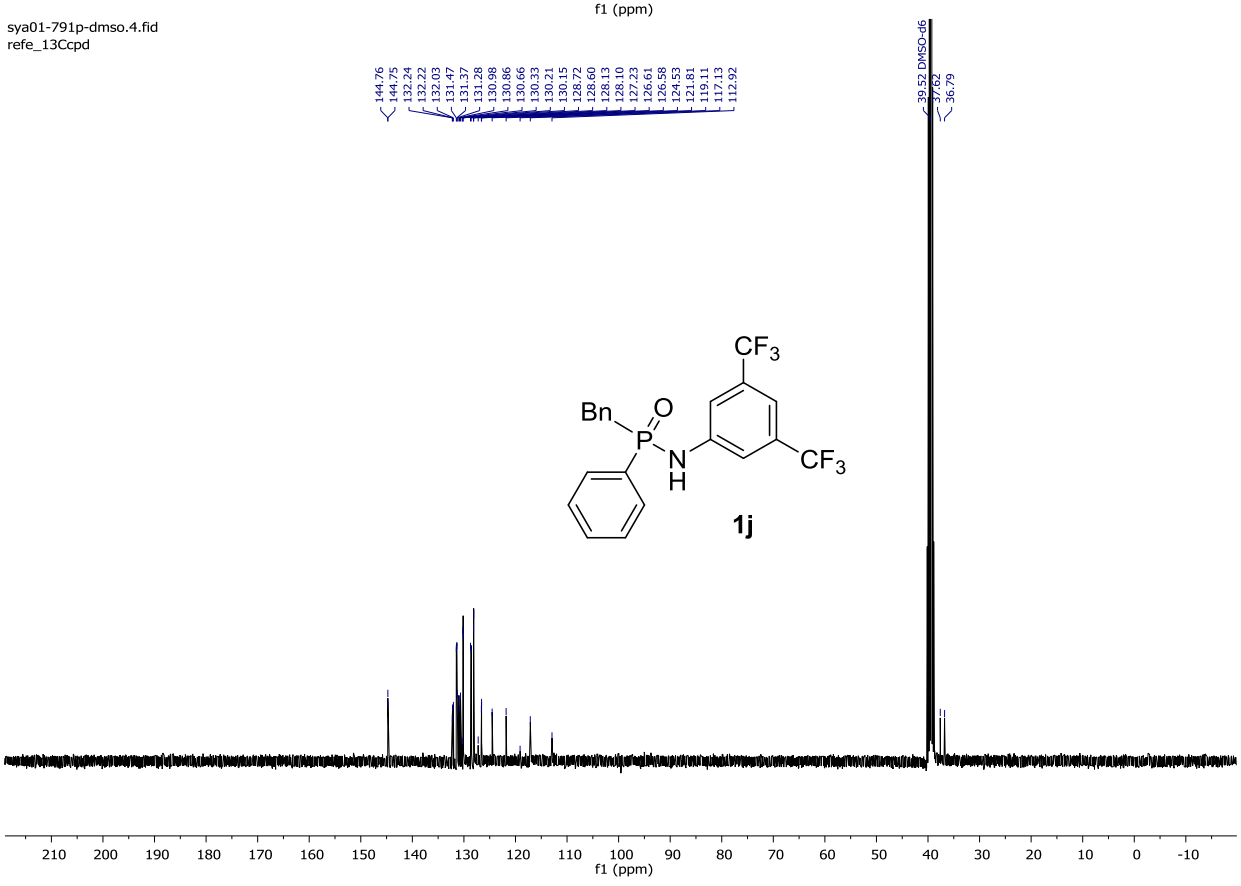




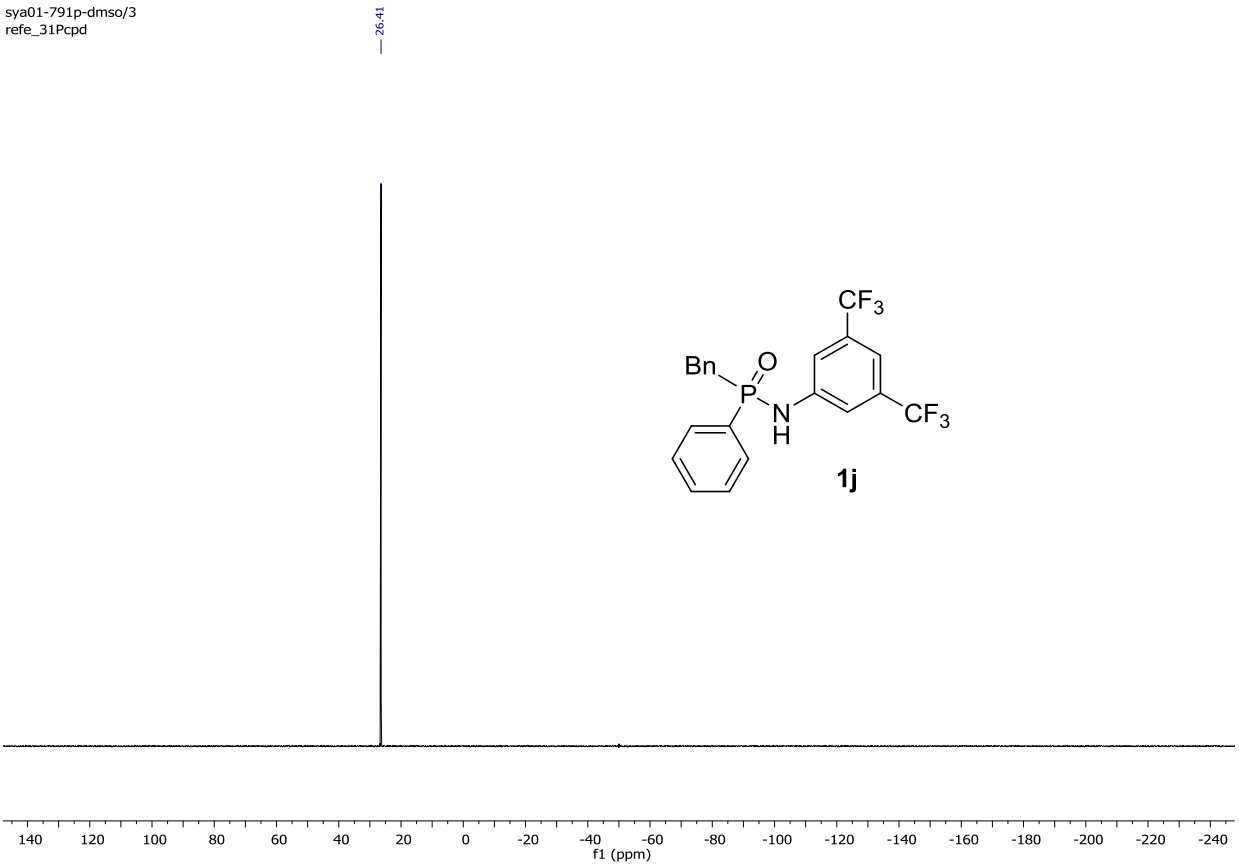


**1i**


sya01-791p-dmso/1
refe_1Hzg
8.80
7.76
7.74
7.73
7.71
7.58
7.55
7.53
7.51
7.50
7.49
7.48
7.40
7.22
7.21
7.20
7.19
7.17
7.16
3.65
3.62
3.57
3.55
3.52
3.48
2.50 DMSO-d6
Bn
O
P
N
H
CF3
CF3
1j
1.0
2.0
3.0
2.0
1.0
5.0
2.0
f1 (ppm)


sya01-791p-dmso.4.fid
refe_13Ccpd
144.76
144.75
132.24
132.22
132.03
131.47
131.37
131.28
130.98
130.86
130.66
130.33
130.21
130.15
128.72
128.60
128.13
128.10
127.23
126.61
126.58
124.53
121.81
119.11
117.13
112.92
39.52 DMSO-d6
37.62
36.79
Bn
O
P
N
H
CF3
CF3
1j
f1 (ppm)

sya01-791p-dmso/3
refe_31Pcpd

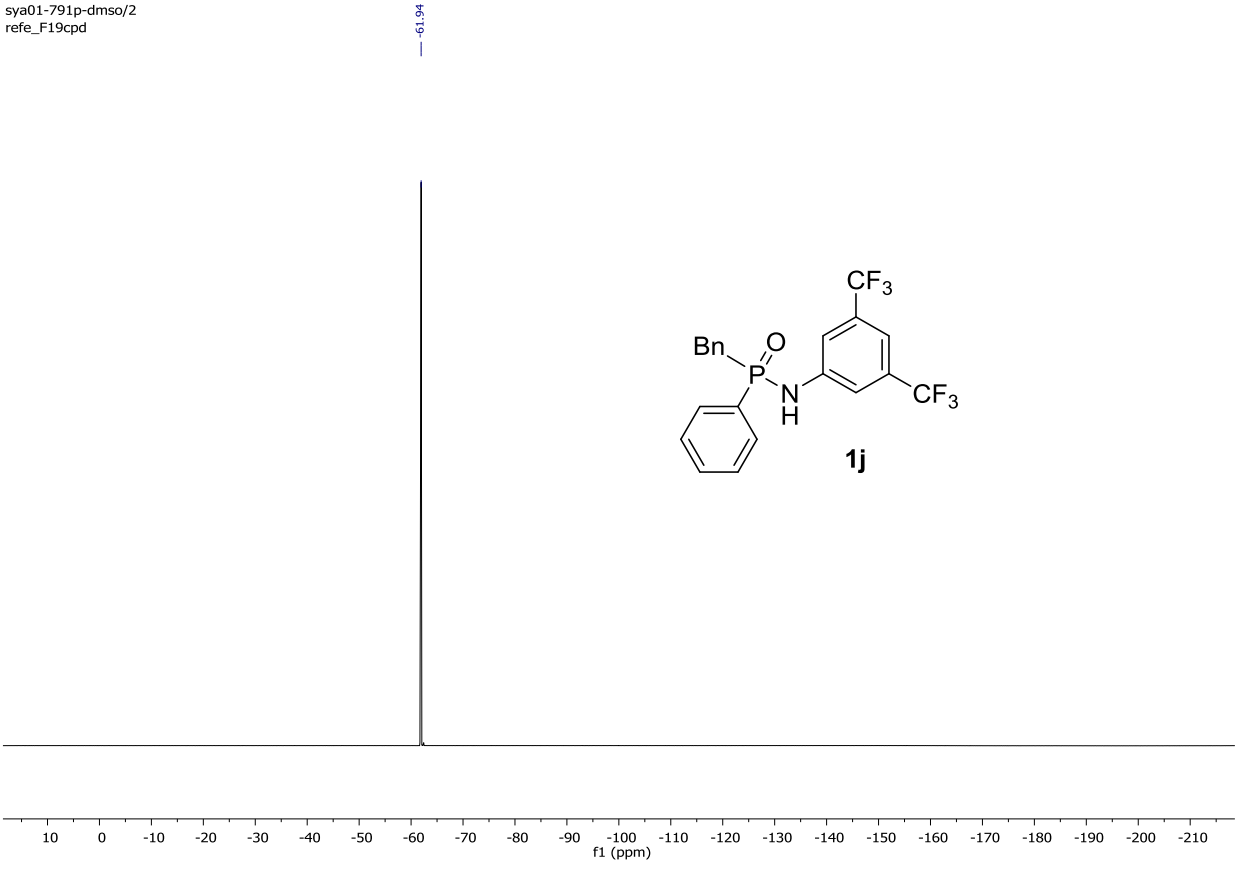






**1j**

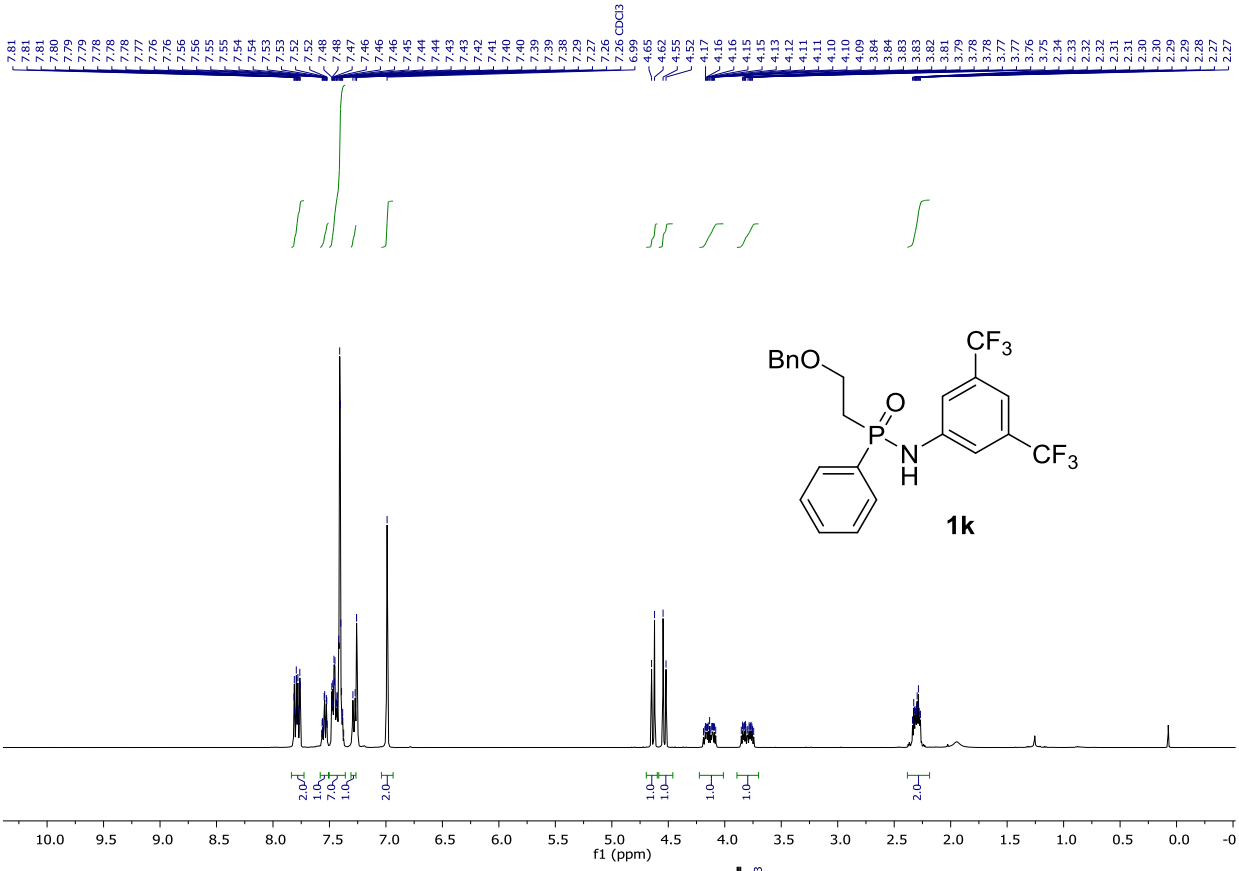
sya01-791p-dmso/2
refe_F19cpd

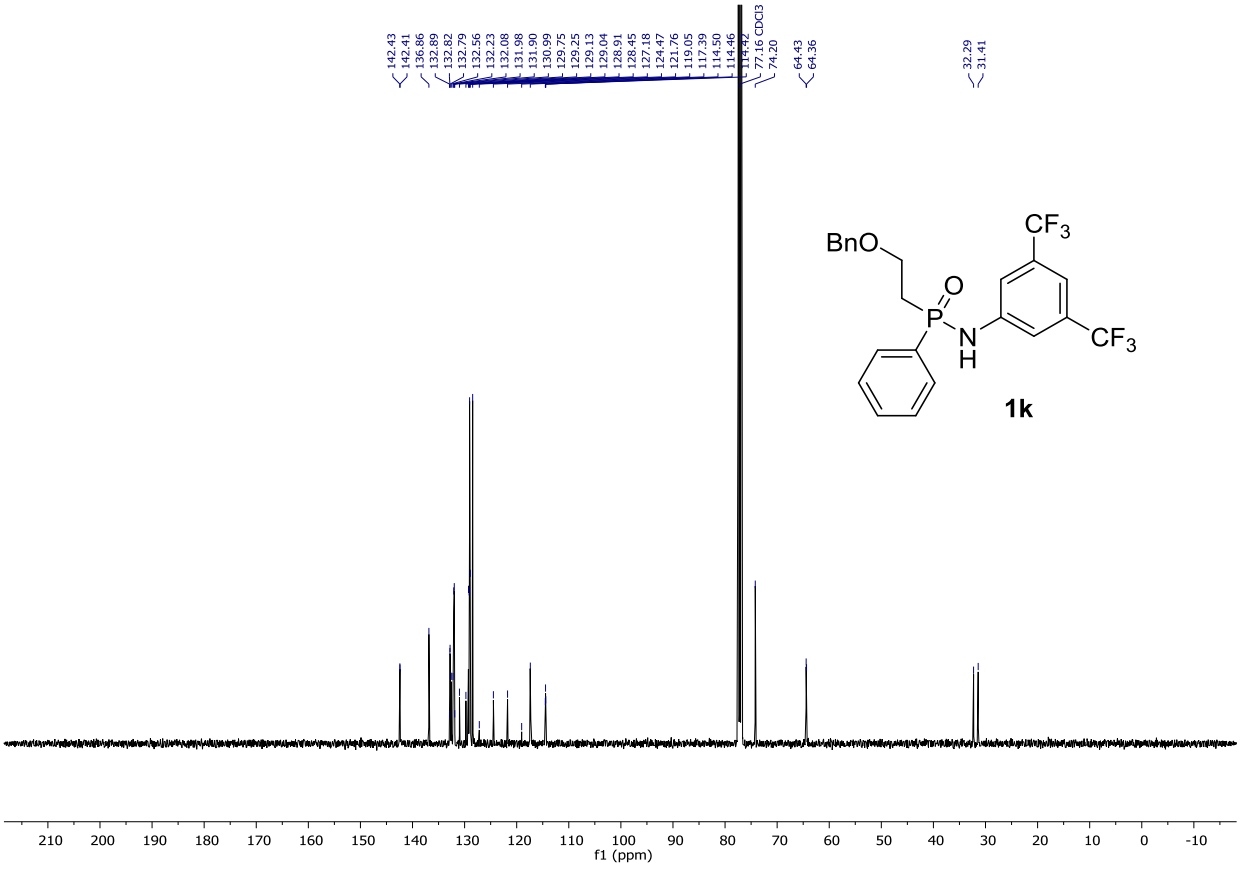






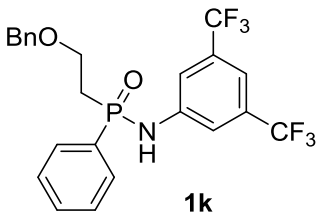
**1j**


BnO
CF3
O
P
N
H
CF3
1k
f1 (ppm)


BnO
CF3
O
P
N
H
CF3
1k
f1 (ppm)

31P cpd

28.54

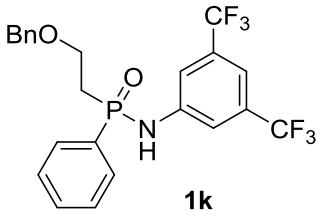



**1k**



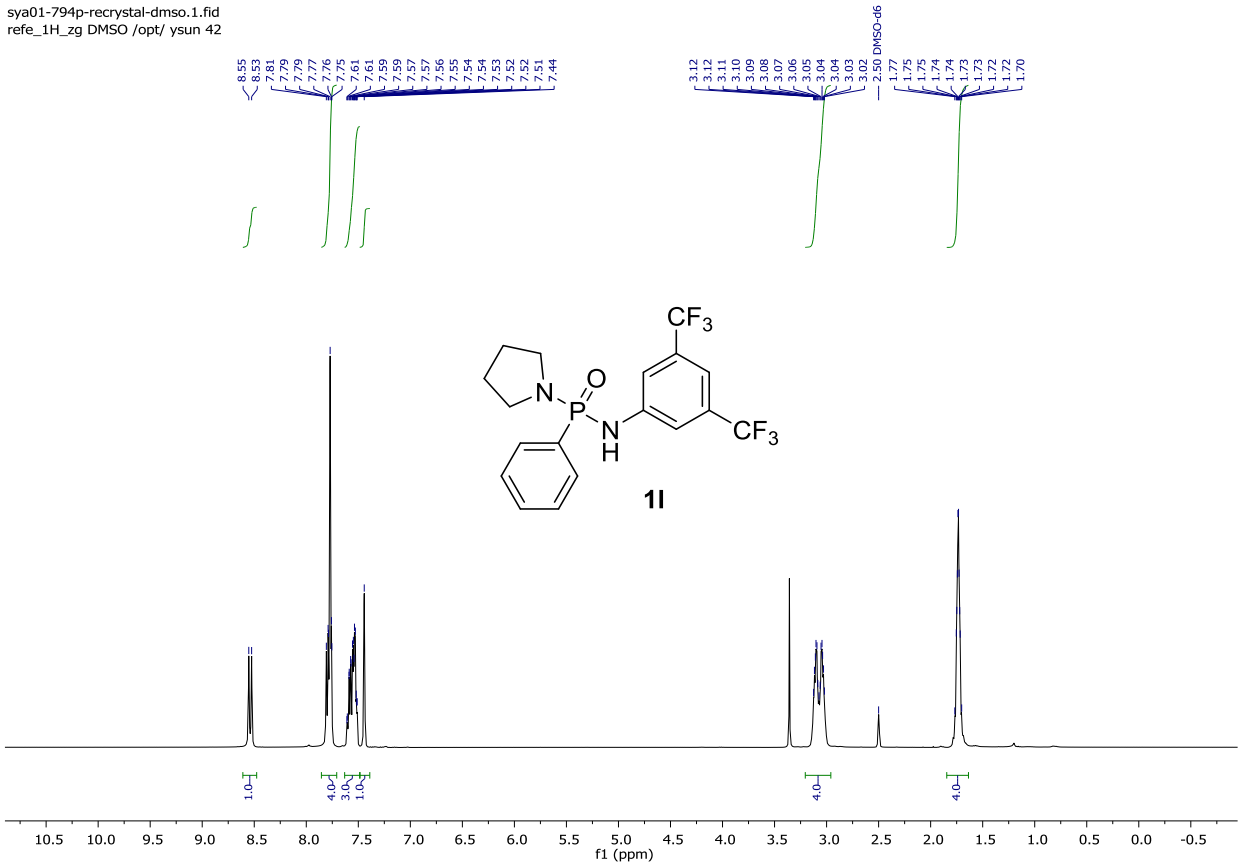

F19CPD

-63.16

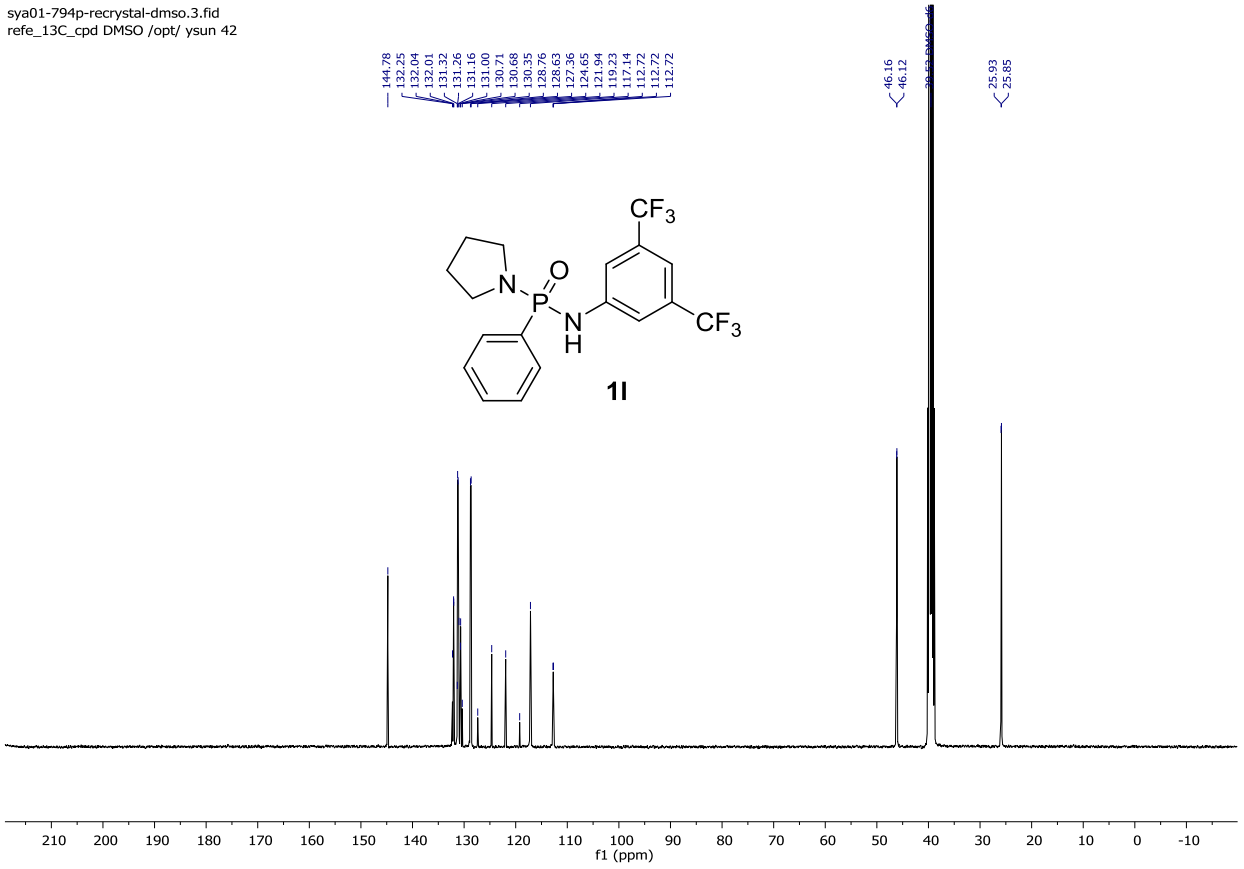



**1k**

sya01-794p-recrystal-dmso.1.fid
refe_1H_zg DMSO /opt/ ysun 42

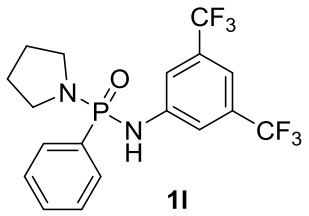



sya01-794p-recrystal-dmso.3.fid
refe_13C_cpd DMSO /opt/ ysun 42



sya01-794p-recrystal-dmso.2.fid
refe_31P_cpd DMSO /opt/ ysun 42

14.36

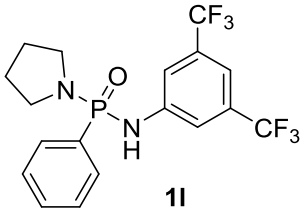



**1l**

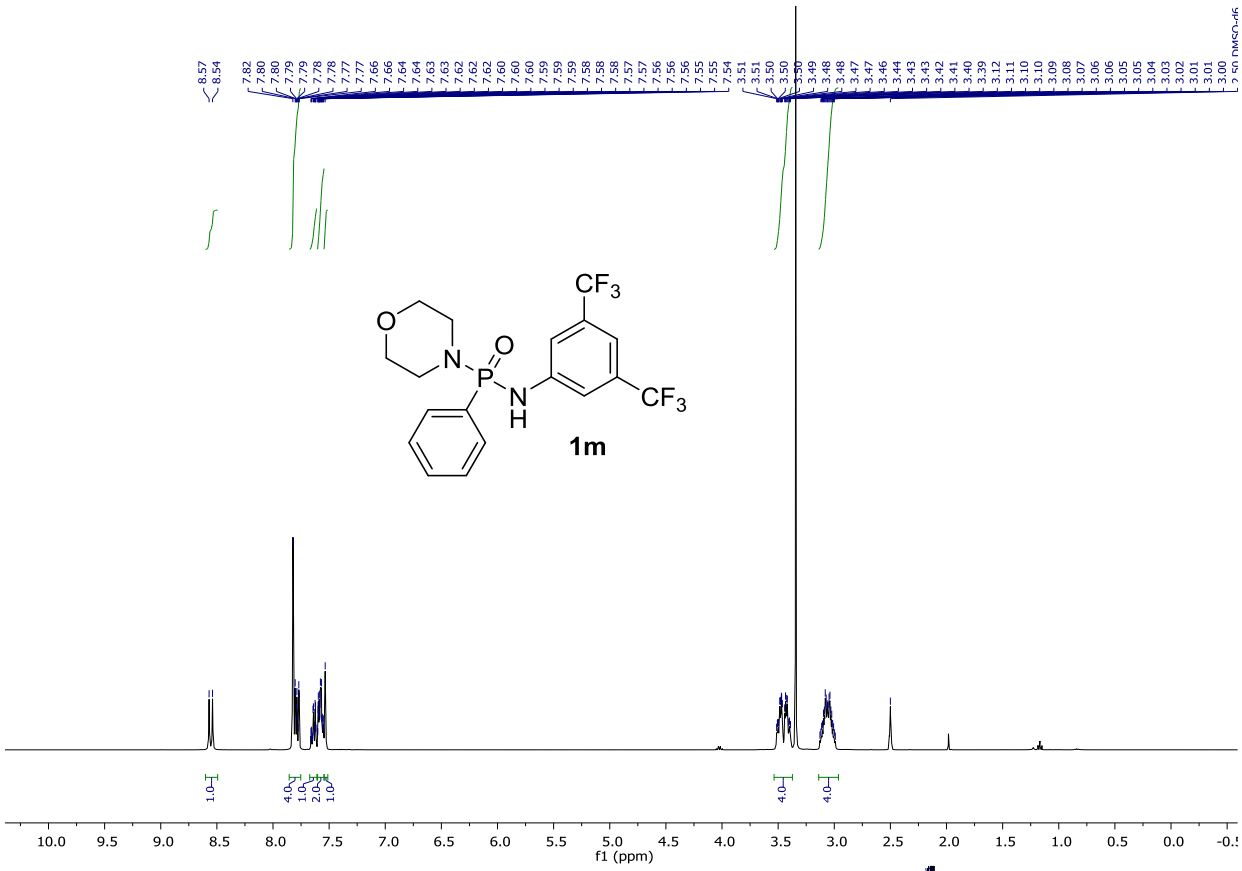


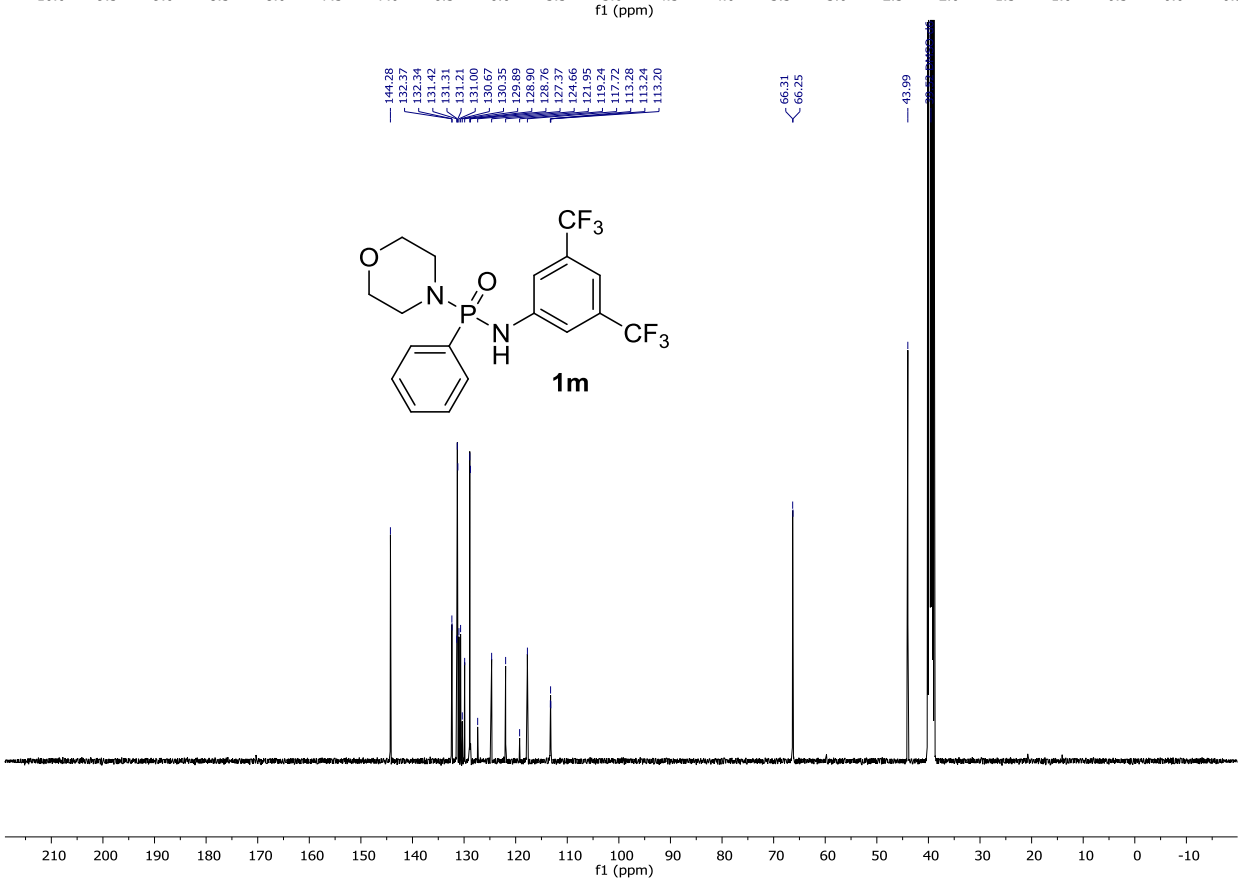

sya01-794p-recrystal-dmso.2.fid
refe_19F_cpd DMSO /opt/ ysun 16

-61.99



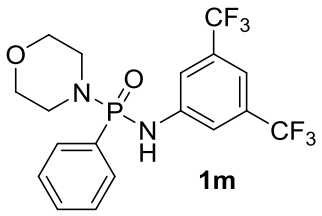

**1l**


CF3
O
N
P
O
N
H
CF3
1m
f1 (ppm)


CF3
O
N
P
O
N
H
CF3
1m
f1 (ppm)

refe_31P_cpd DMSO /opt/ ysun 36

15.89

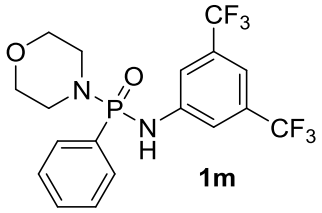



**1m**

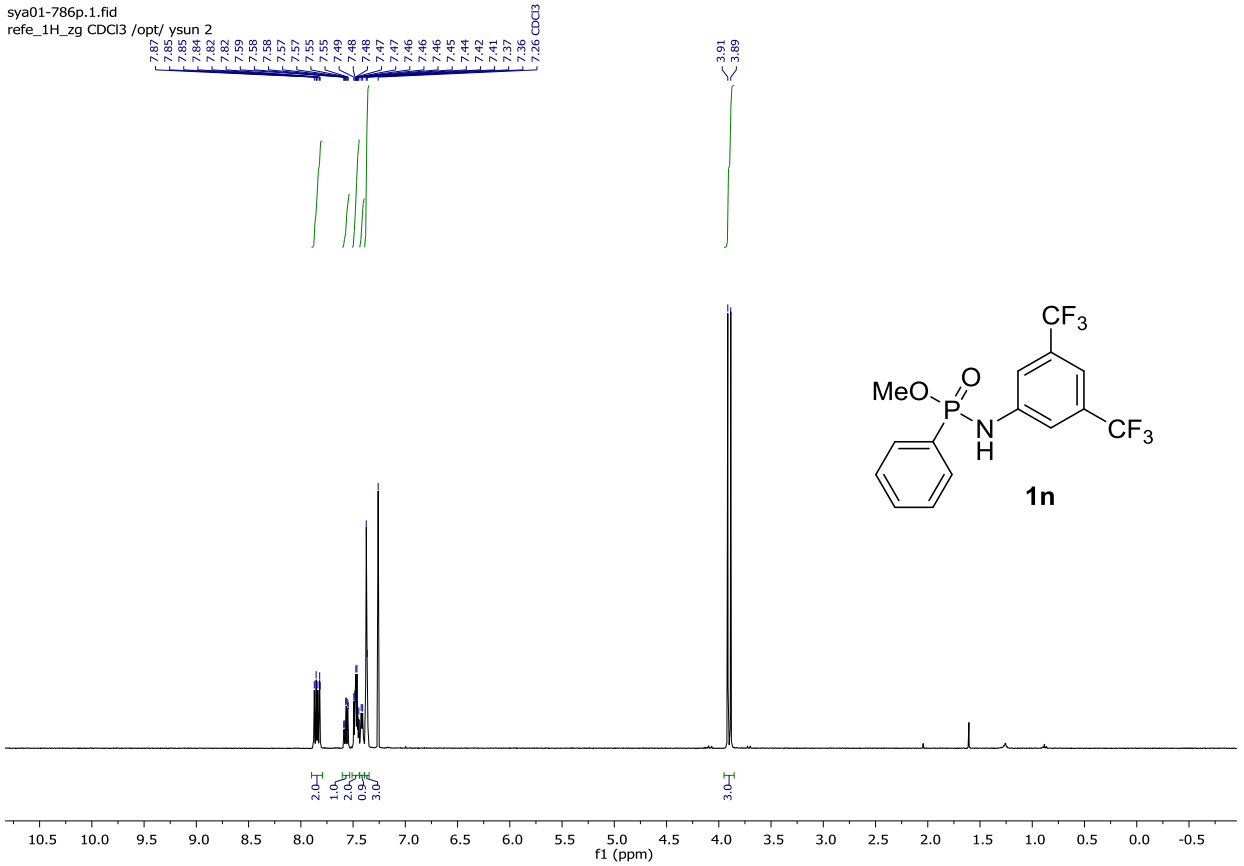


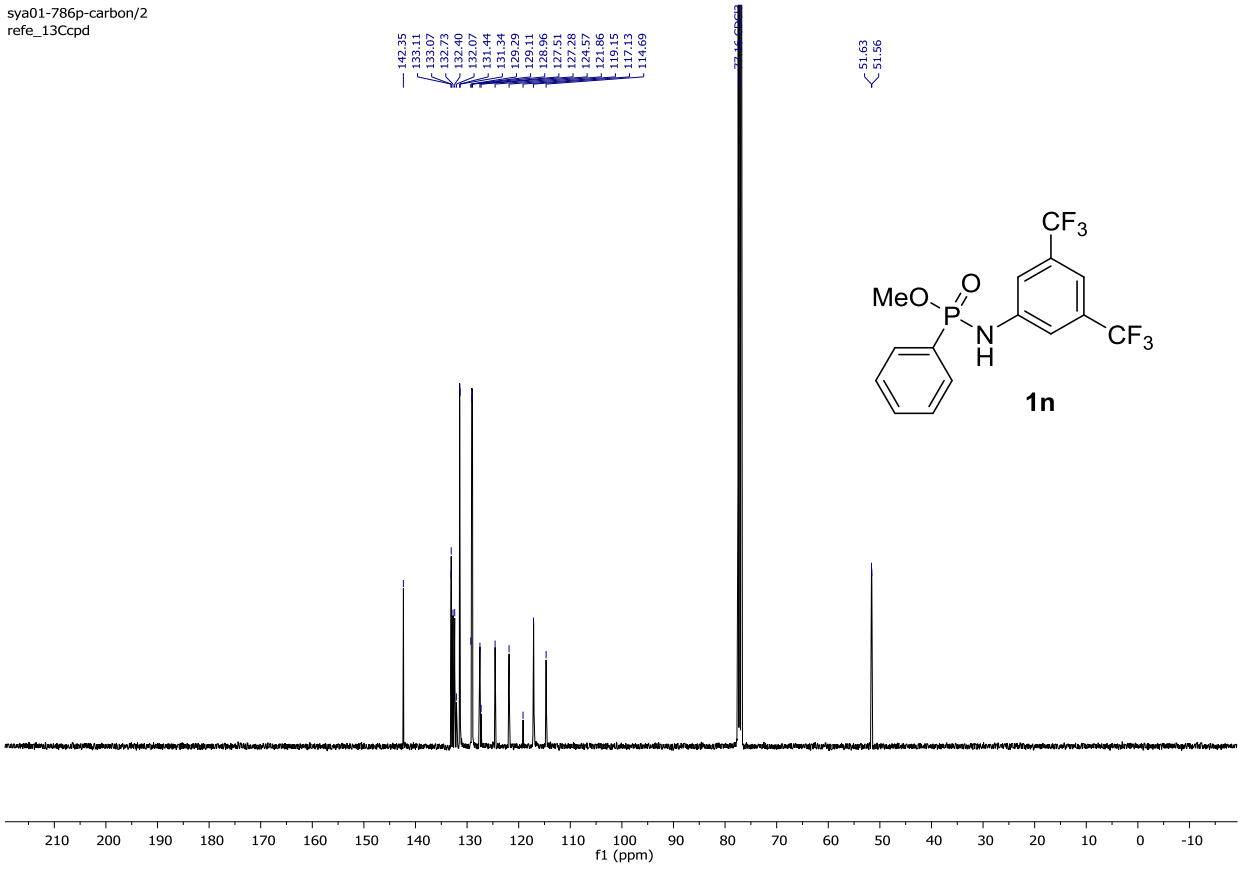

refe_19Fzg DMSO /opt/ ysun 36

-61.83



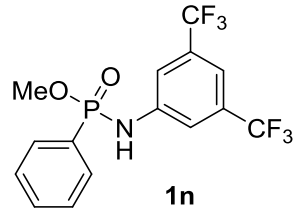

**1m**


sya01-786p.1.fid
refe_1H_zg CDCl3 /opt/ ysun 2
7.87
7.85
7.85
7.84
7.82
7.82
7.59
7.58
7.58
7.57
7.57
7.55
7.55
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.46
7.45
7.44
7.42
7.41
7.37
7.36
7.26 CDCl3
3.91
3.89
2.0
1.0
2.0
0.9
3.0
3.0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
CF3
MeO
O
P
N
H
CF3
1n


sya01-786p-carbon/2
refe_13Ccpd
142.35
133.11
133.07
132.73
132.40
132.07
131.44
131.34
129.29
129.11
128.96
127.51
127.28
124.57
121.86
119.15
117.13
114.69
77.16 CDCl3
51.63
51.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
CF3
MeO
O
P
N
H
CF3
1n

sya01-786p.2.fid
refe_31P_cpd CDCl3 /opt/ ysun 2

18.39

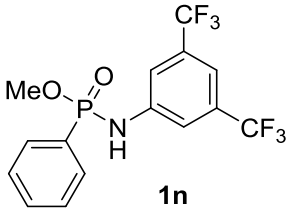



**1n**

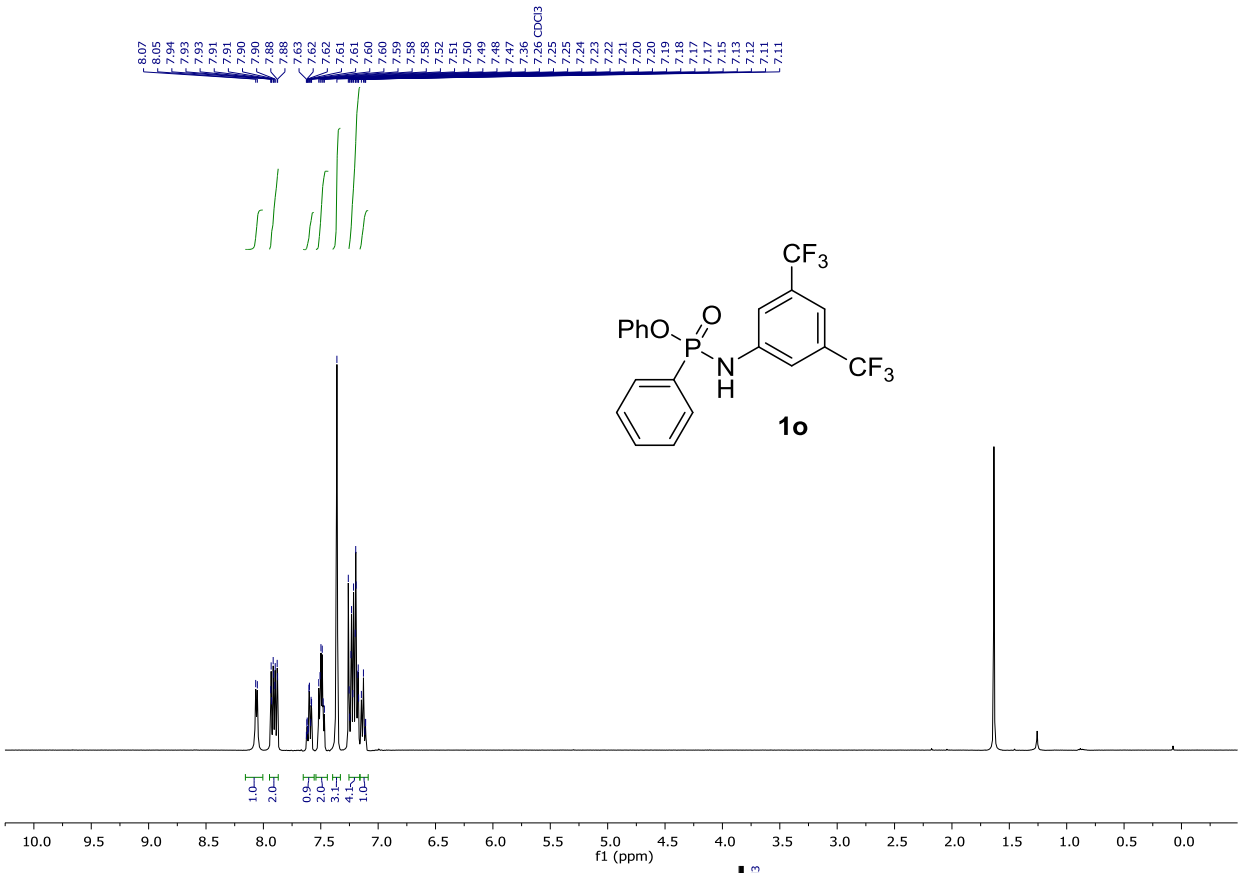


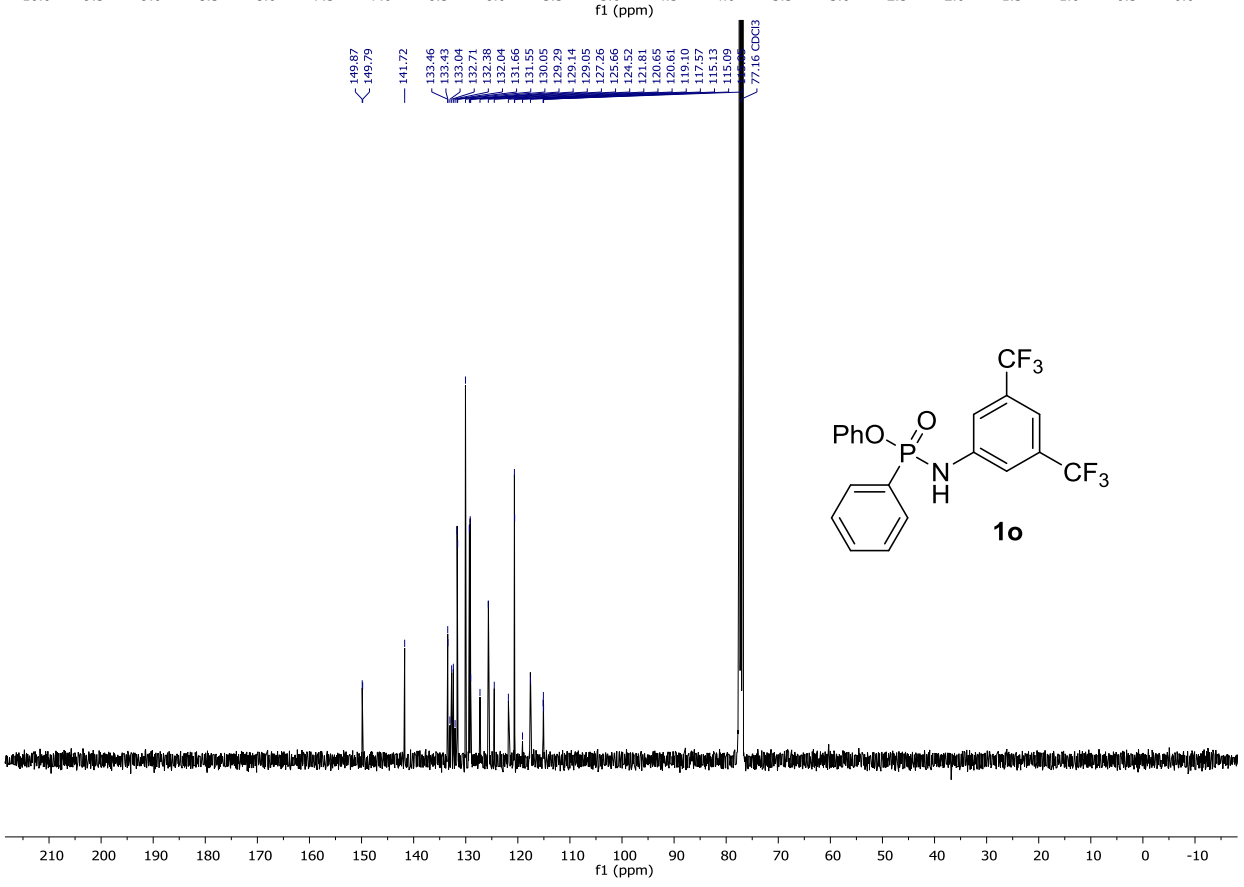

sya01-786p.3.fid
refe_19F_cpd CDCl3 /opt/ ysun 2

-63.23



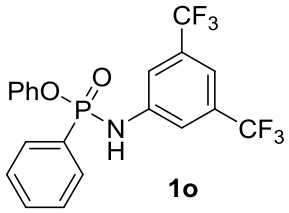

**1n**


8.07 8.05 7.94 7.93 7.93 7.91 7.91 7.90 7.90 7.88 7.88 7.63 7.62 7.62 7.61 7.61 7.60 7.60 7.59 7.58 7.58 7.52 7.51 7.50 7.49 7.48 7.47 7.36 CDCl3 7.26 7.25 7.25 7.24 7.23 7.22 7.21 7.20 7.20 7.19 7.18 7.17 7.17 7.15 7.13 7.12 7.11 7.11
CF3
PhO
O
P
N
H
CF3
1o
1.0 2.0 0.9 2.0 3.1 4.1 1.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.87 149.79 141.72 133.46 133.43 133.04 132.71 132.38 132.04 131.66 131.55 130.05 129.29 129.14 129.05 127.26 125.66 124.52 121.81 120.65 120.61 119.10 117.57 115.13 115.09 77.16 CDCl3
CF3
PhO
O
P
N
H
CF3
1o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

refe_31P_cpd CDCl3 /opt/ ysun 20

15.03

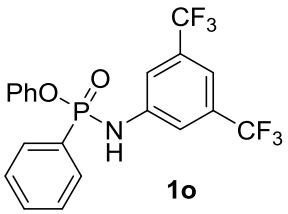



**1o**

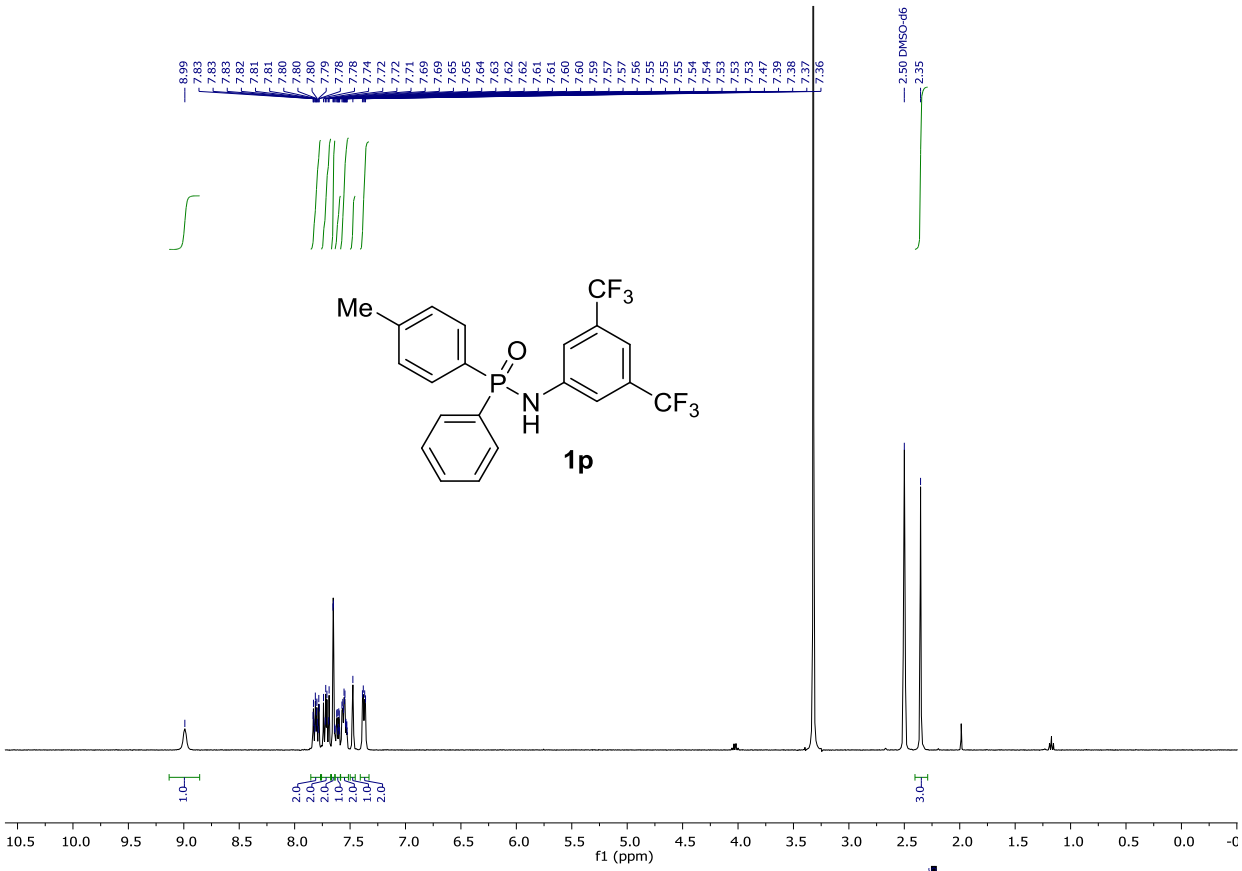


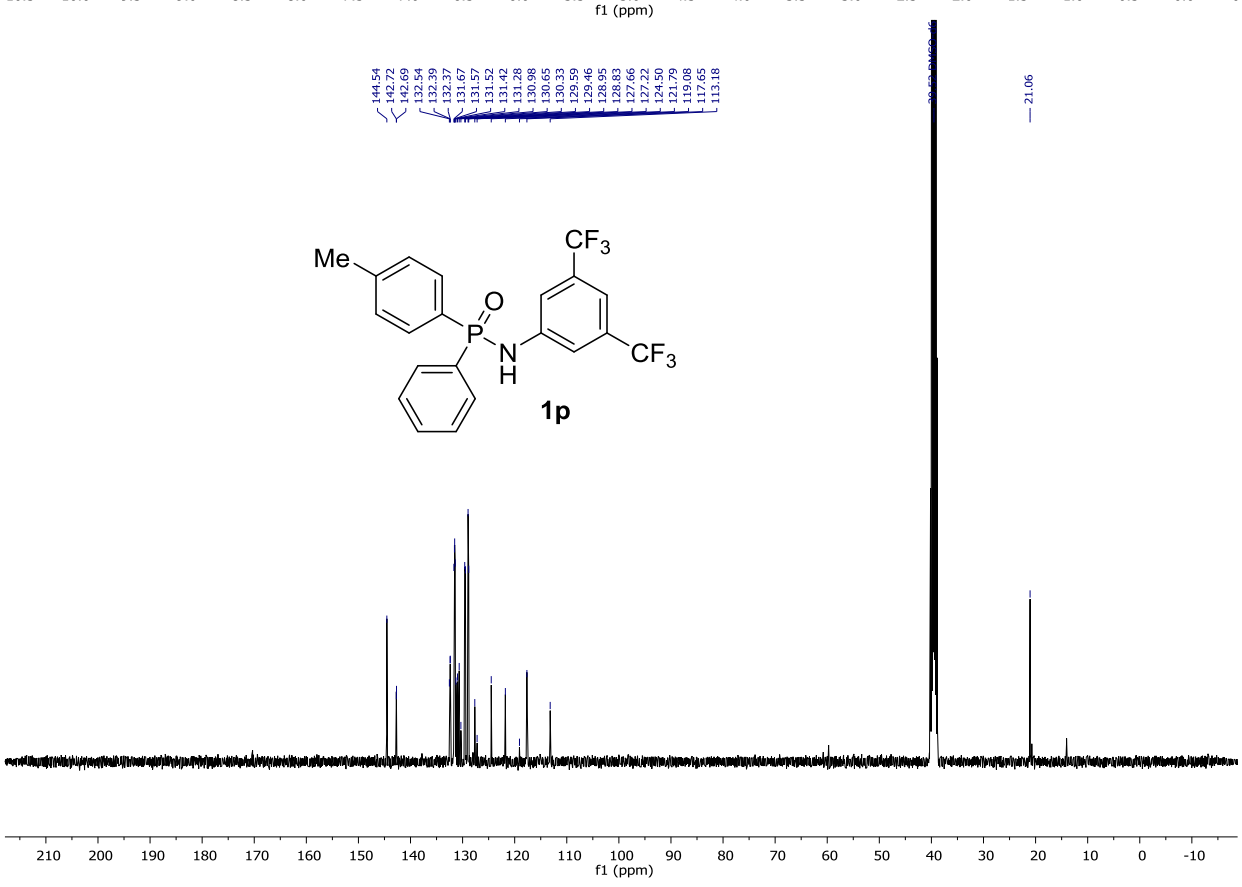

refe_19F_cpd CDCl3 /opt/ ysun 20

-63.15

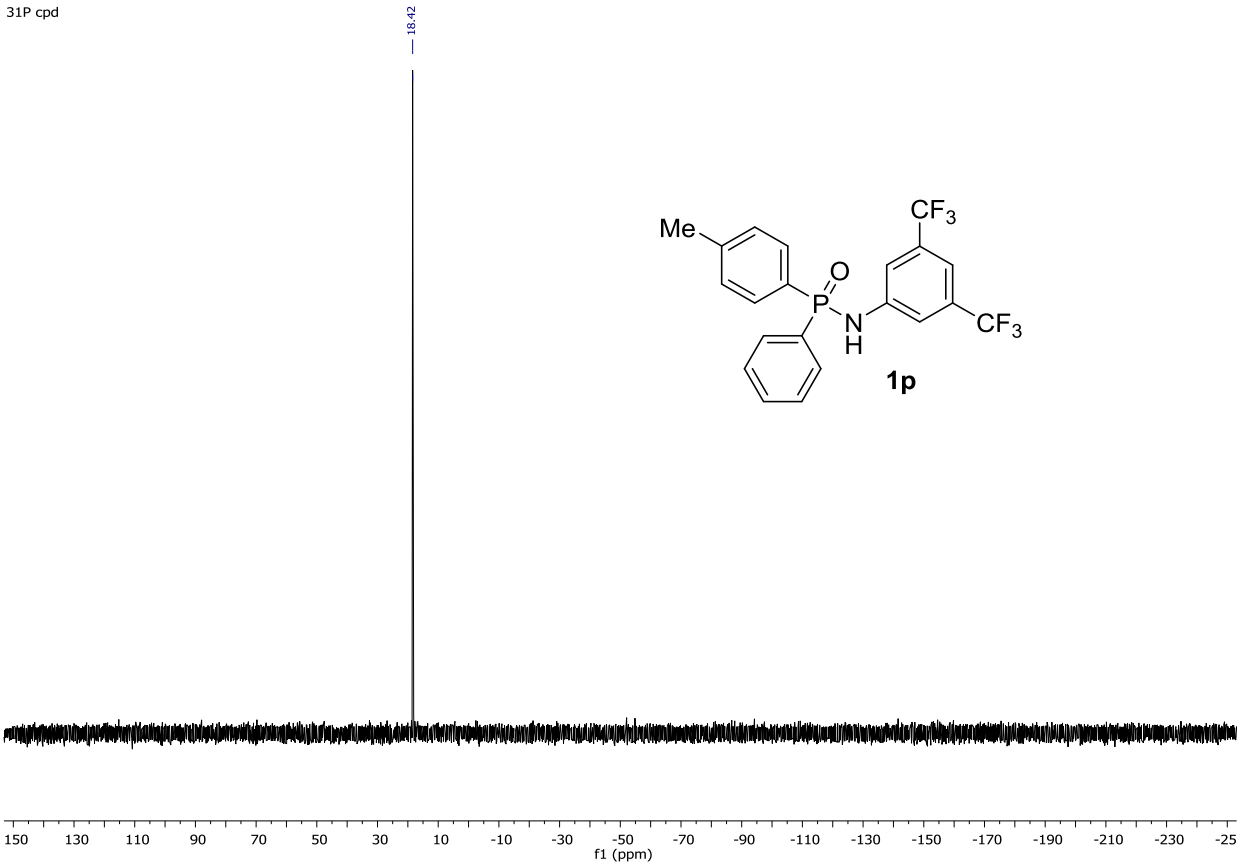



**1o**


8.99
7.83
7.83
7.83
7.82
7.81
7.81
7.80
7.80
7.80
7.79
7.78
7.78
7.74
7.72
7.72
7.71
7.69
7.69
7.65
7.65
7.64
7.63
7.62
7.62
7.61
7.61
7.60
7.60
7.59
7.57
7.57
7.56
7.55
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.47
7.39
7.38
7.37
7.36
2.50 DMSO-d6
2.35
Me
CF3
O
P
N
H
CF3
1p
1.0
2.0
2.0
2.0
1.0
2.0
1.0
2.0
3.0
f1 (ppm)


144.54
142.72
142.69
132.54
132.39
132.37
131.67
131.57
131.52
131.42
131.28
130.98
130.65
130.33
129.59
129.46
128.95
128.83
127.66
127.22
124.50
121.79
119.08
117.65
113.18
39.52 DMSO-d6
21.06
Me
CF3
O
P
N
H
CF3
1p
f1 (ppm)

31P cpd

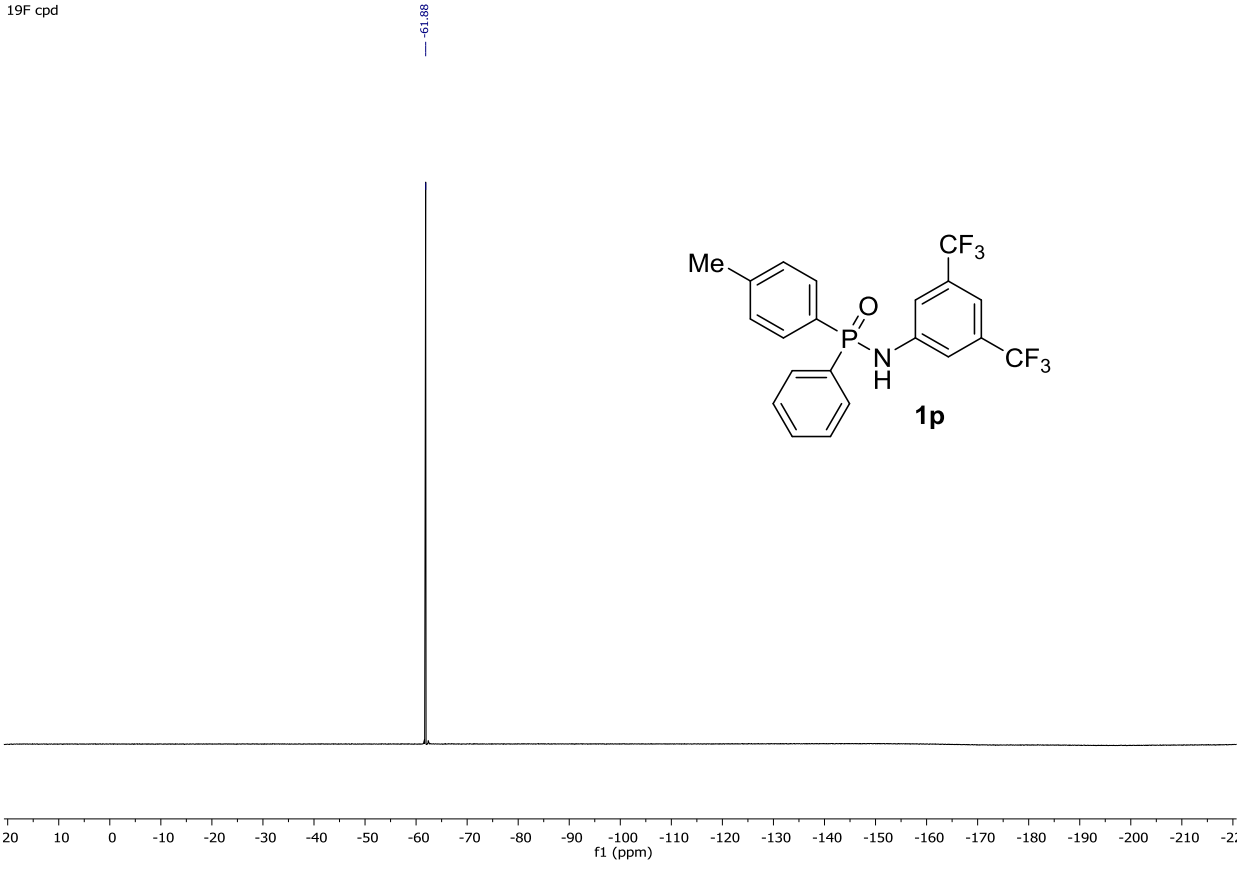






**1p**

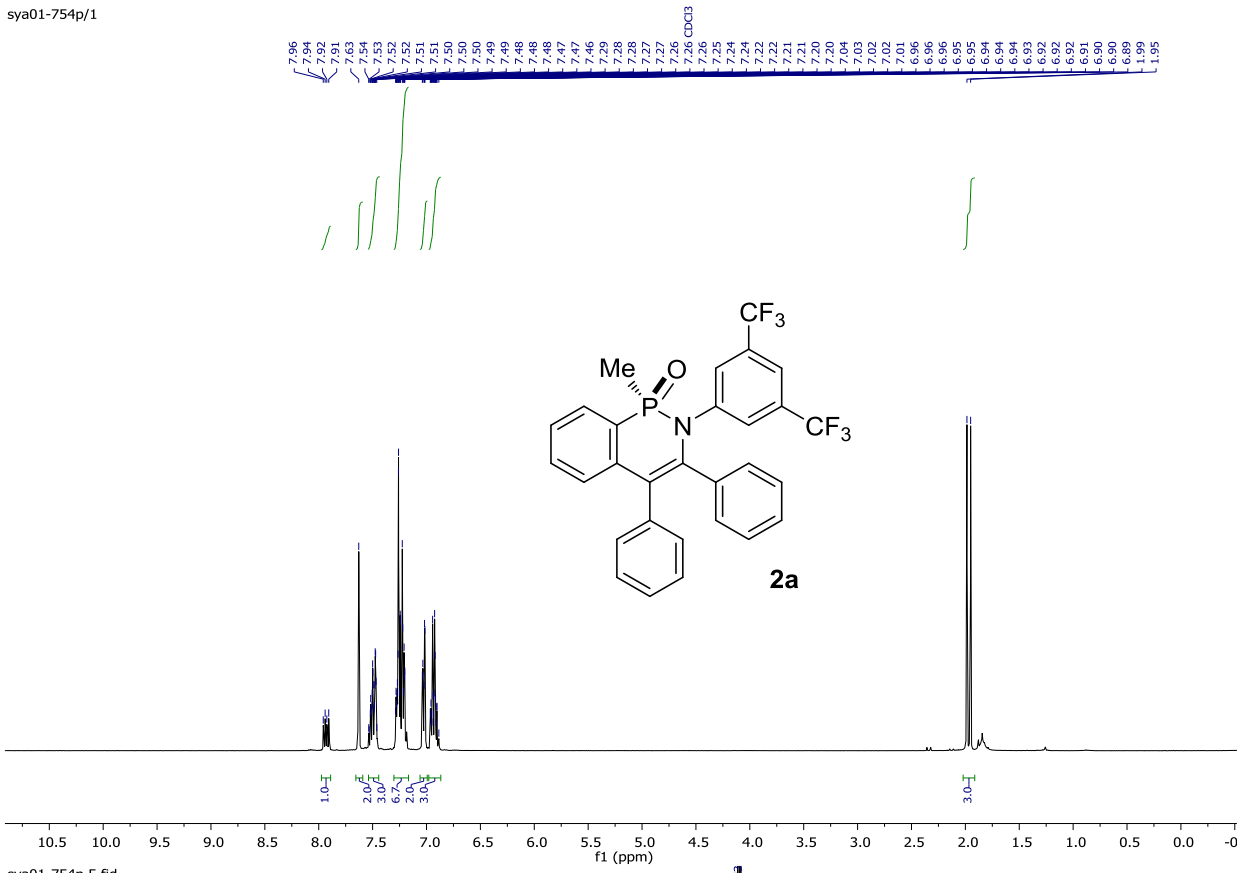
19F cpd

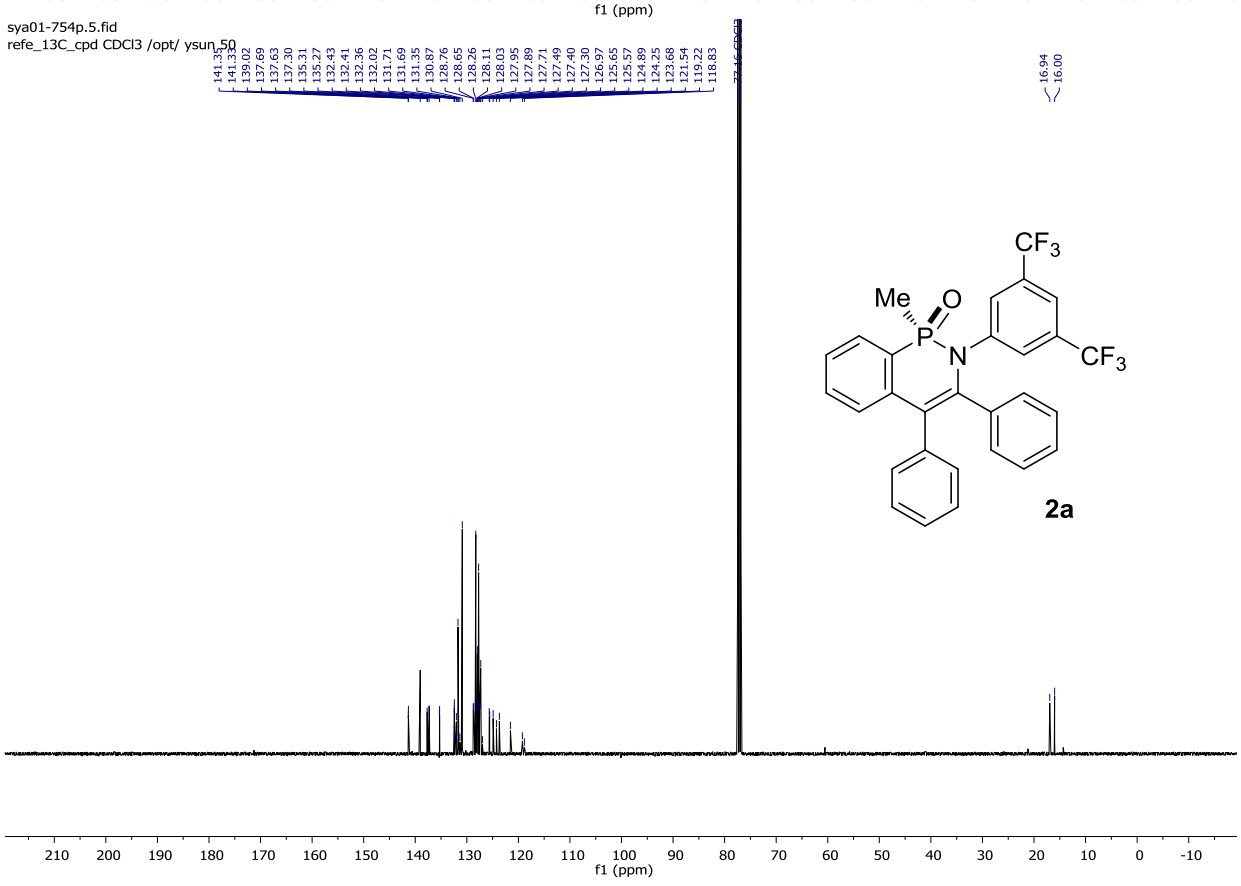






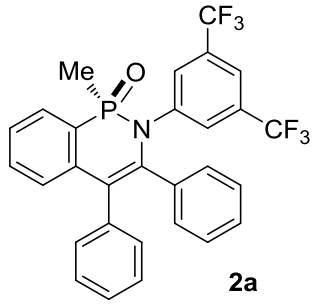
**1p**


sya01-754p/1
CF3
Me
O
P
N
CF3
2a
f1 (ppm)


sya01-754p.5.fid
refe_13C_cpd CDCl3 /opt/ ysun 50
CF3
Me
O
P
N
CF3
2a
f1 (ppm)

sya01-754p.4.fid
refe_31P_cpd CDCl3 /opt/ ysun 50

25.48

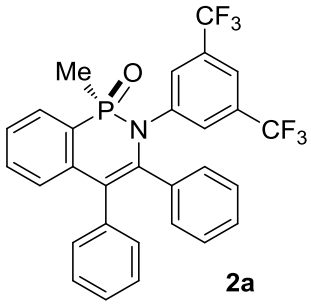



**2a**

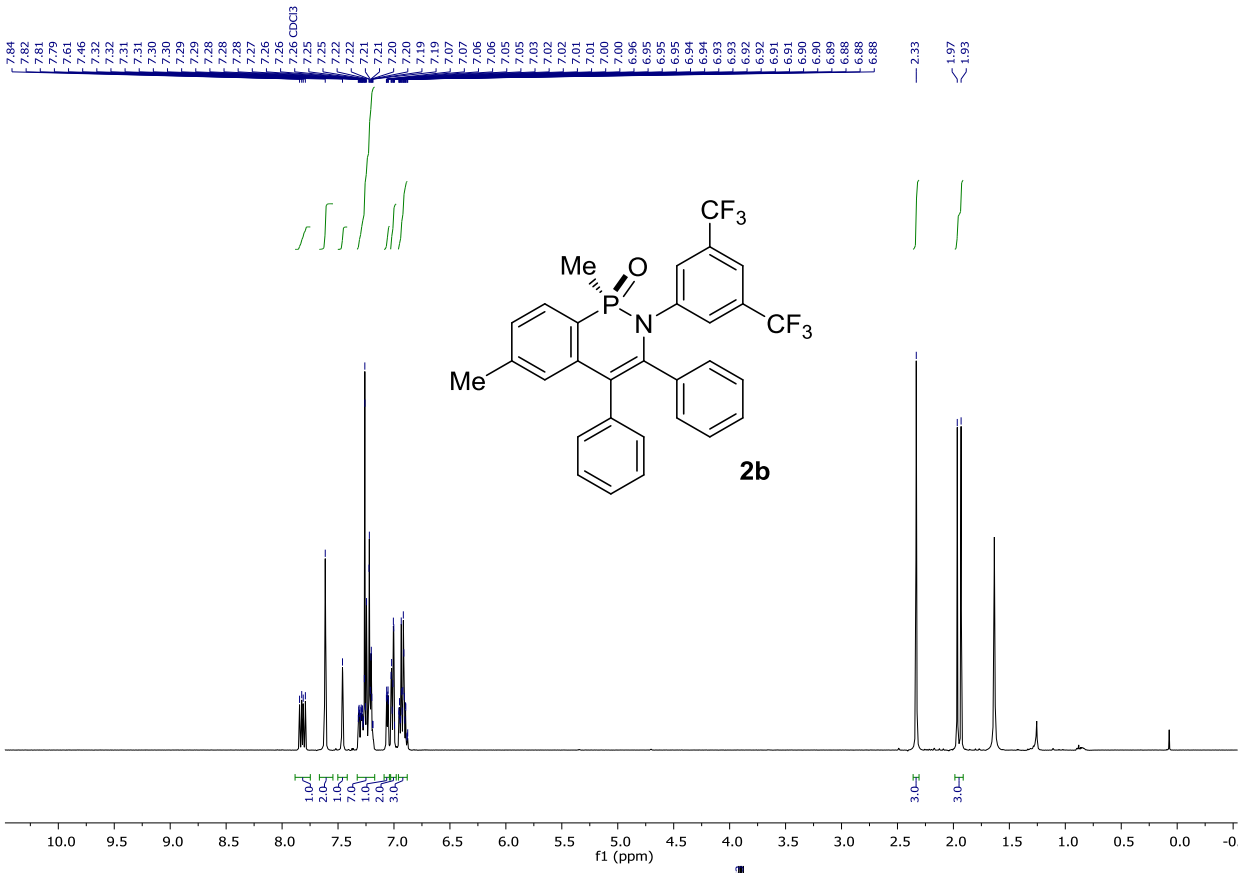


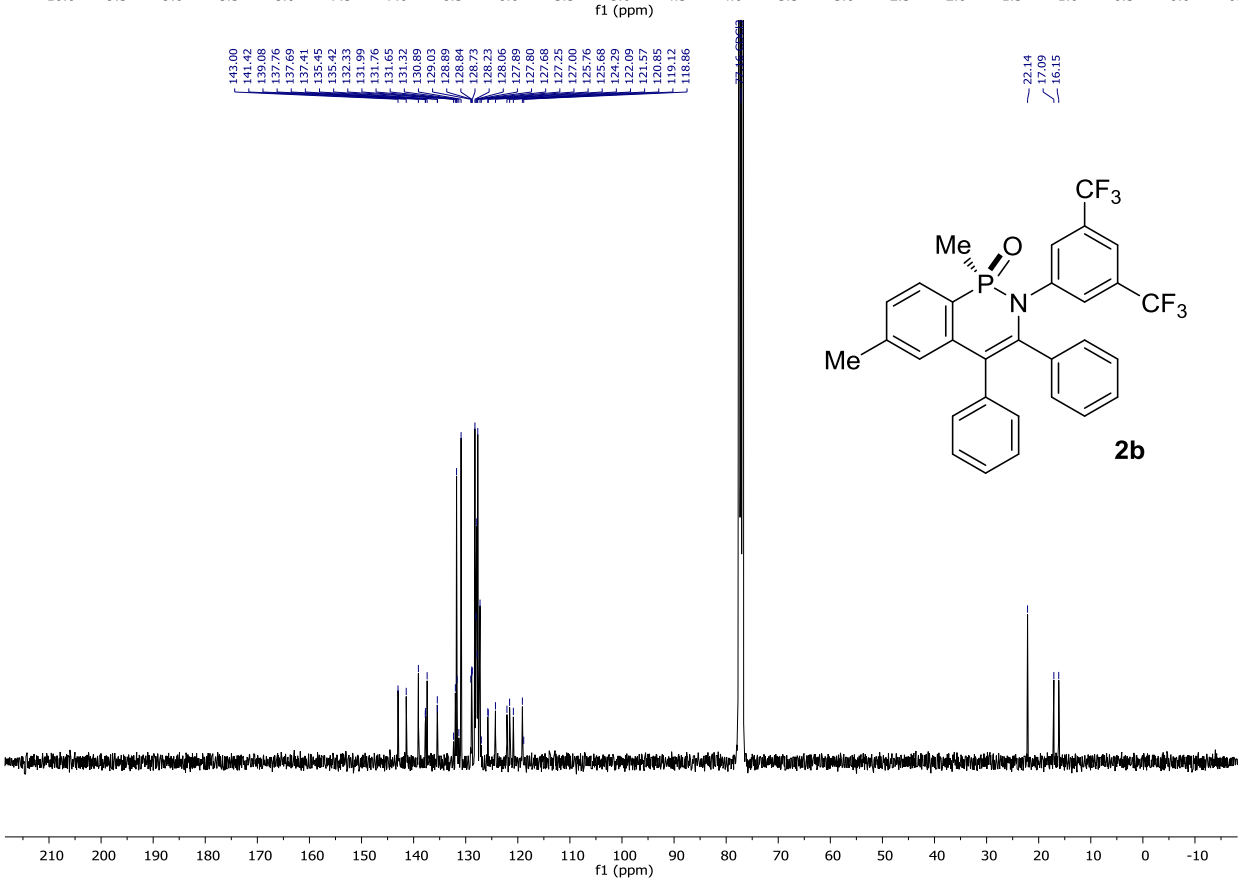

sya01-754p/2
refe_F19cpd

-63.05

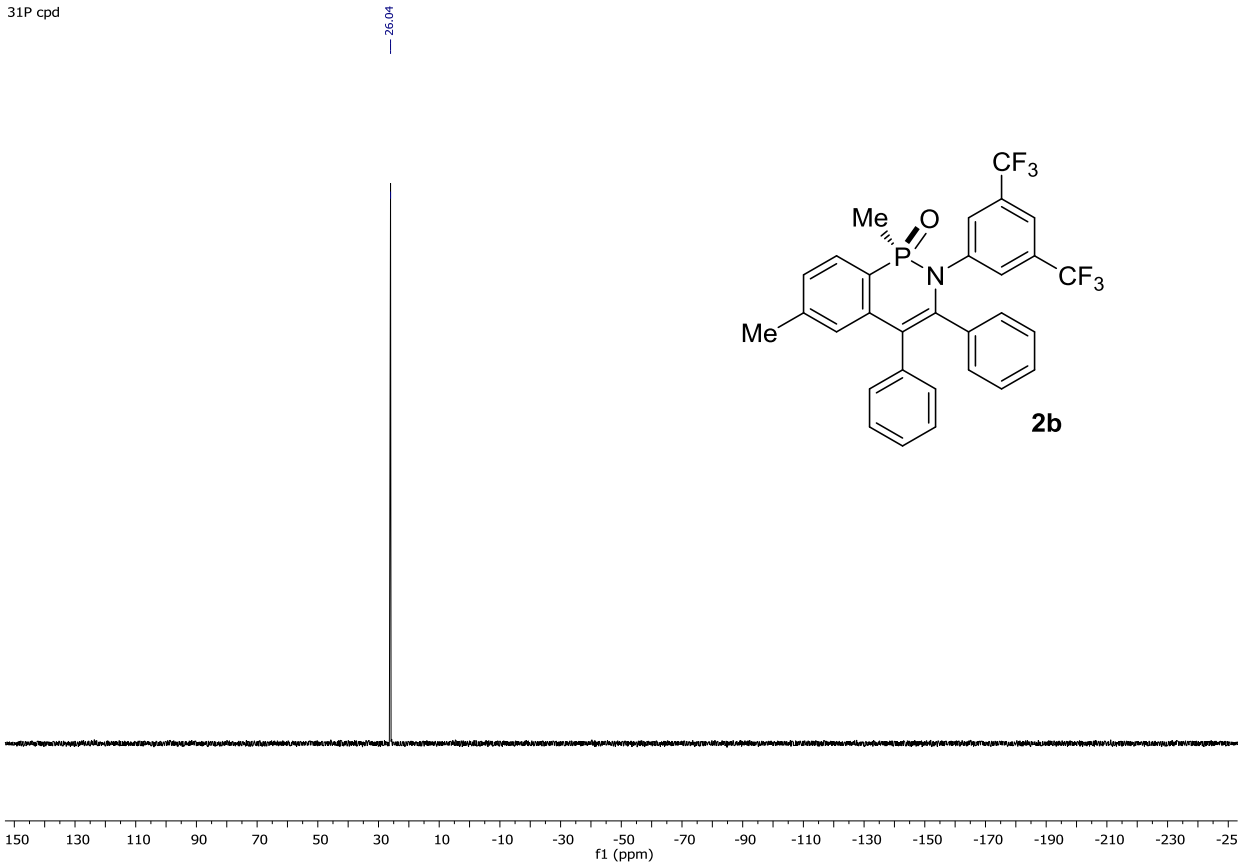



**2a**


CF3
Me
O
P
N
CF3
Me
2b
f1 (ppm)


CF3
Me
O
P
N
CF3
Me
2b
f1 (ppm)

31P cpd

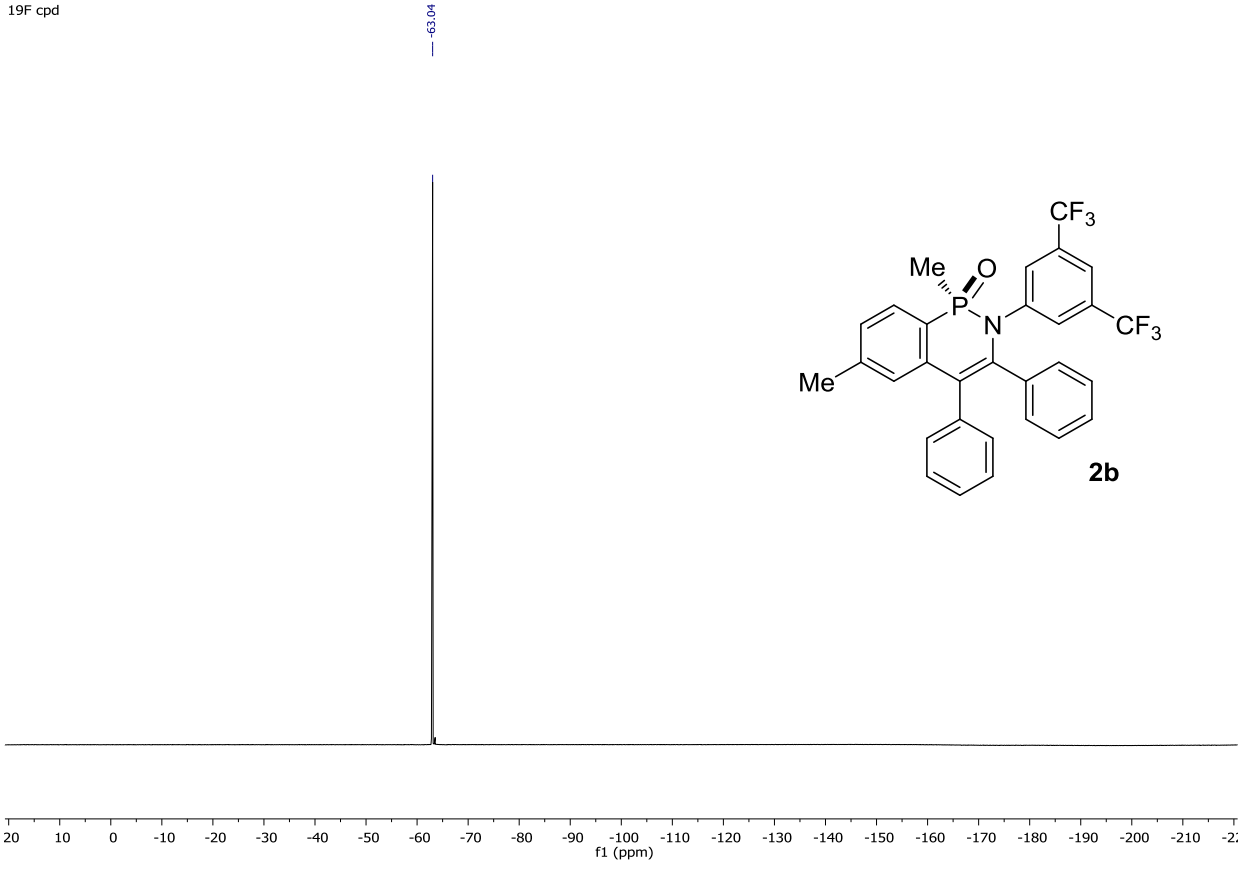






**2b**

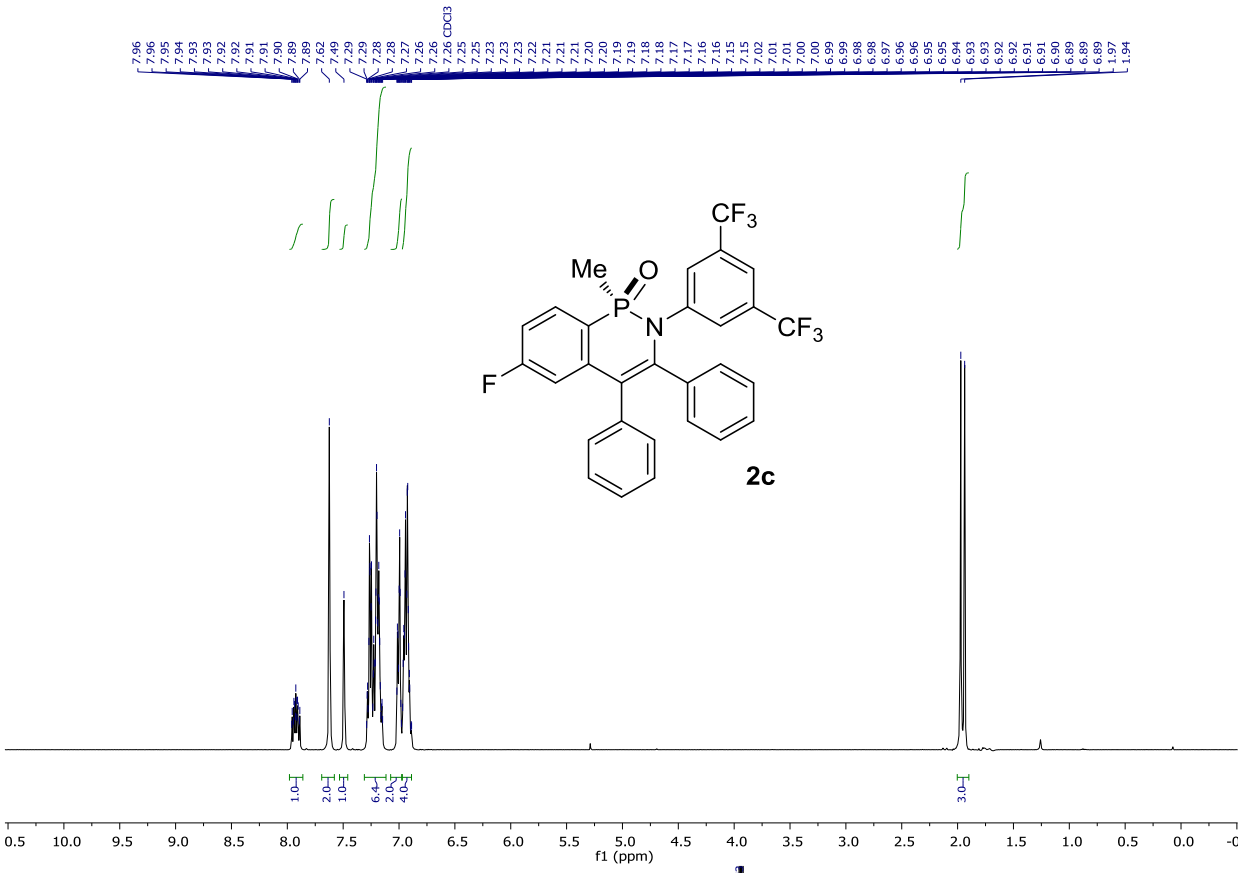
19F cpd

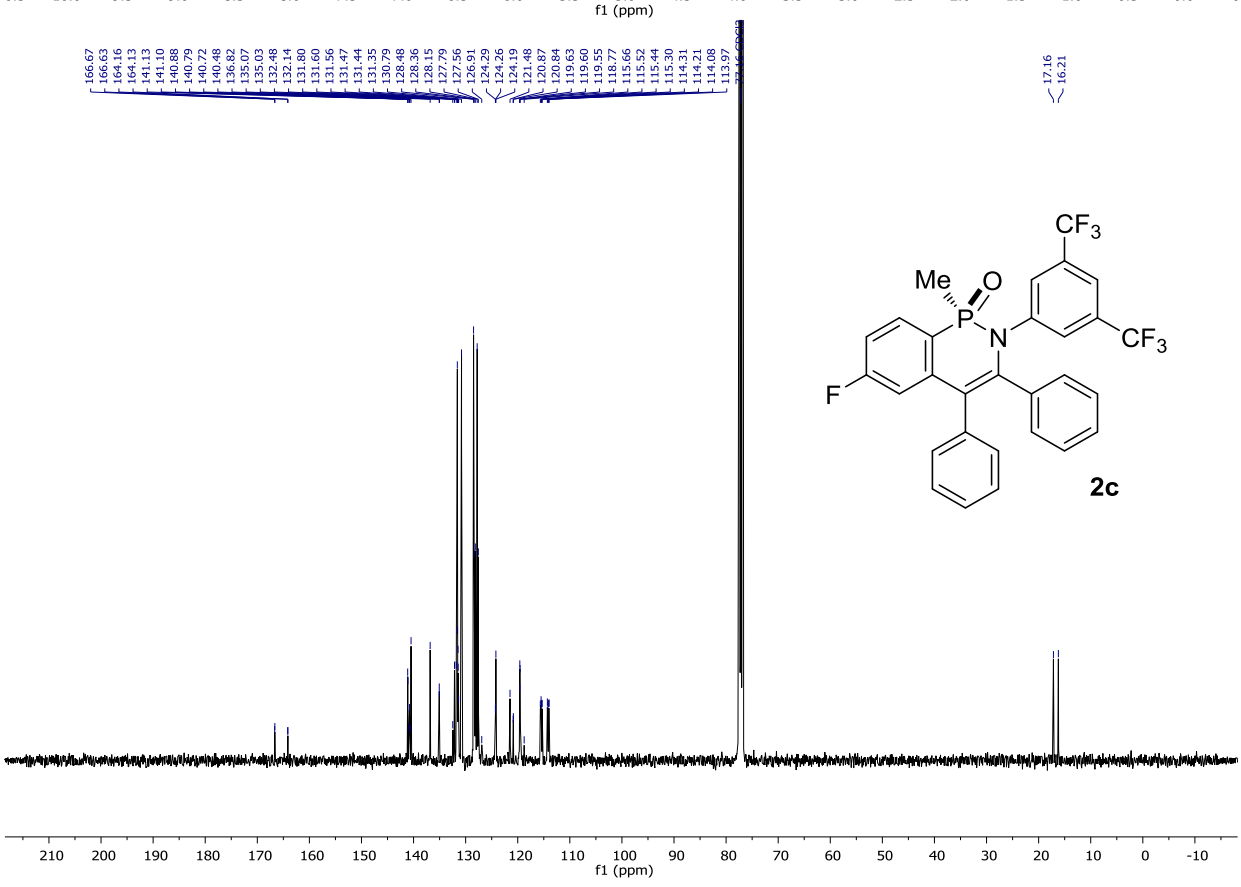




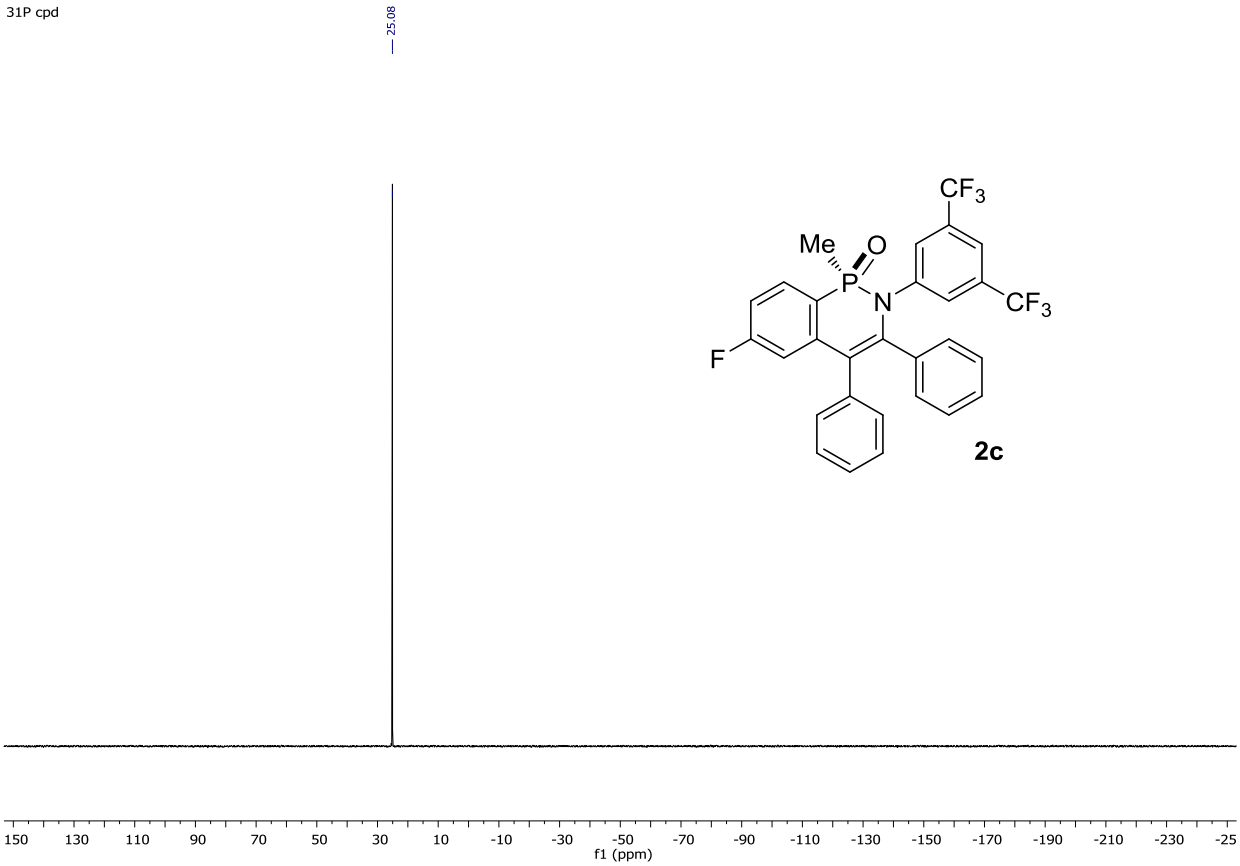


**2b**


CF3
Me
O
P
N
CF3
F
2c
f1 (ppm)


CF3
Me
O
P
N
CF3
F
2c
f1 (ppm)

31P cpd

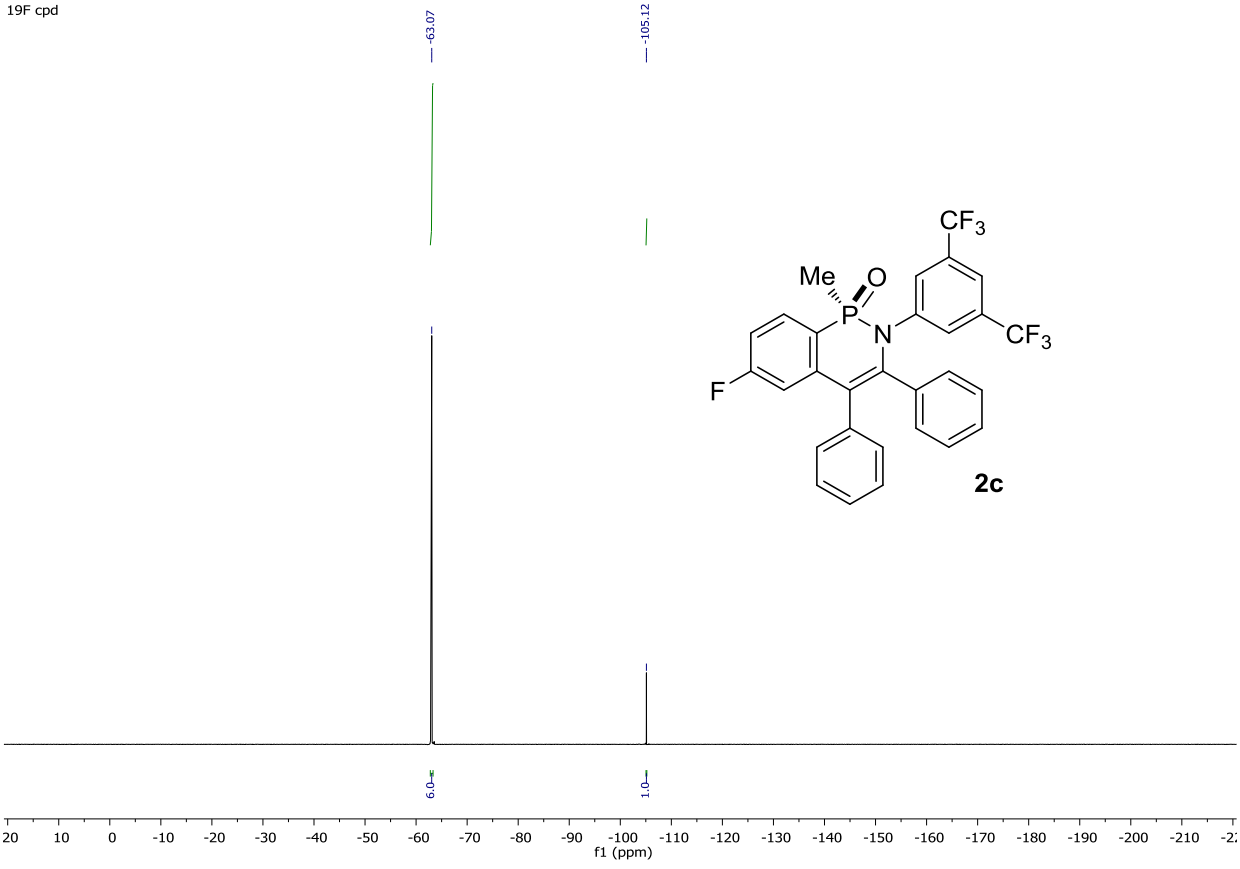






**2c**

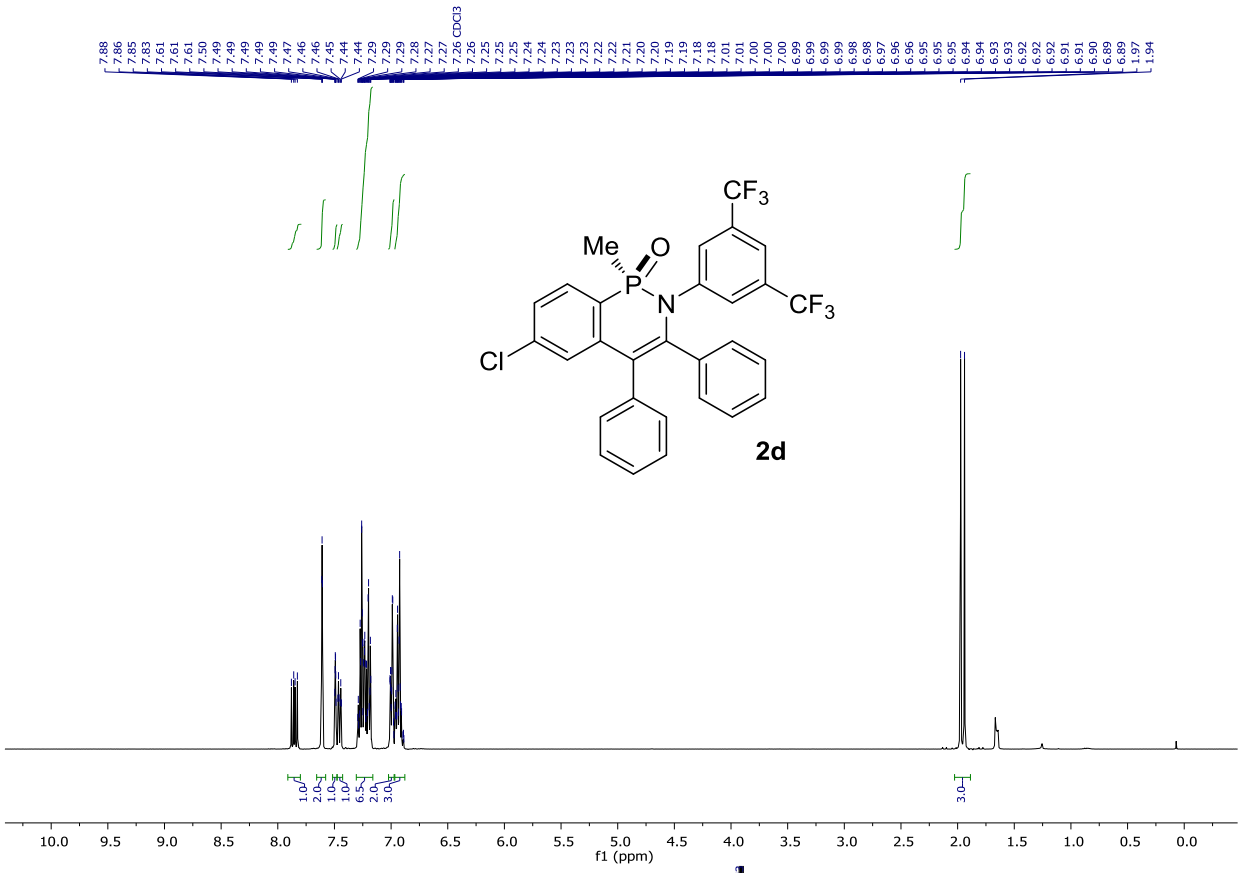
19F cpd

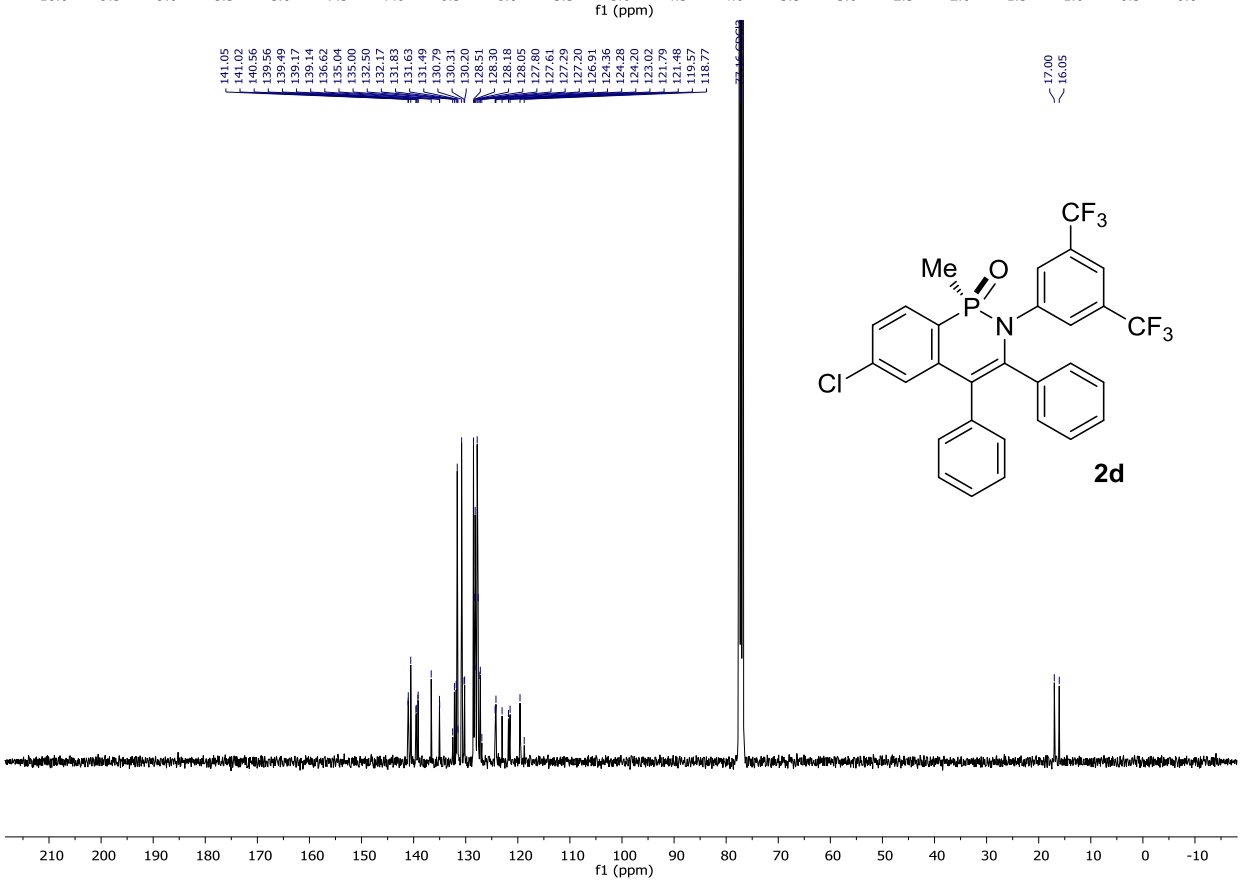




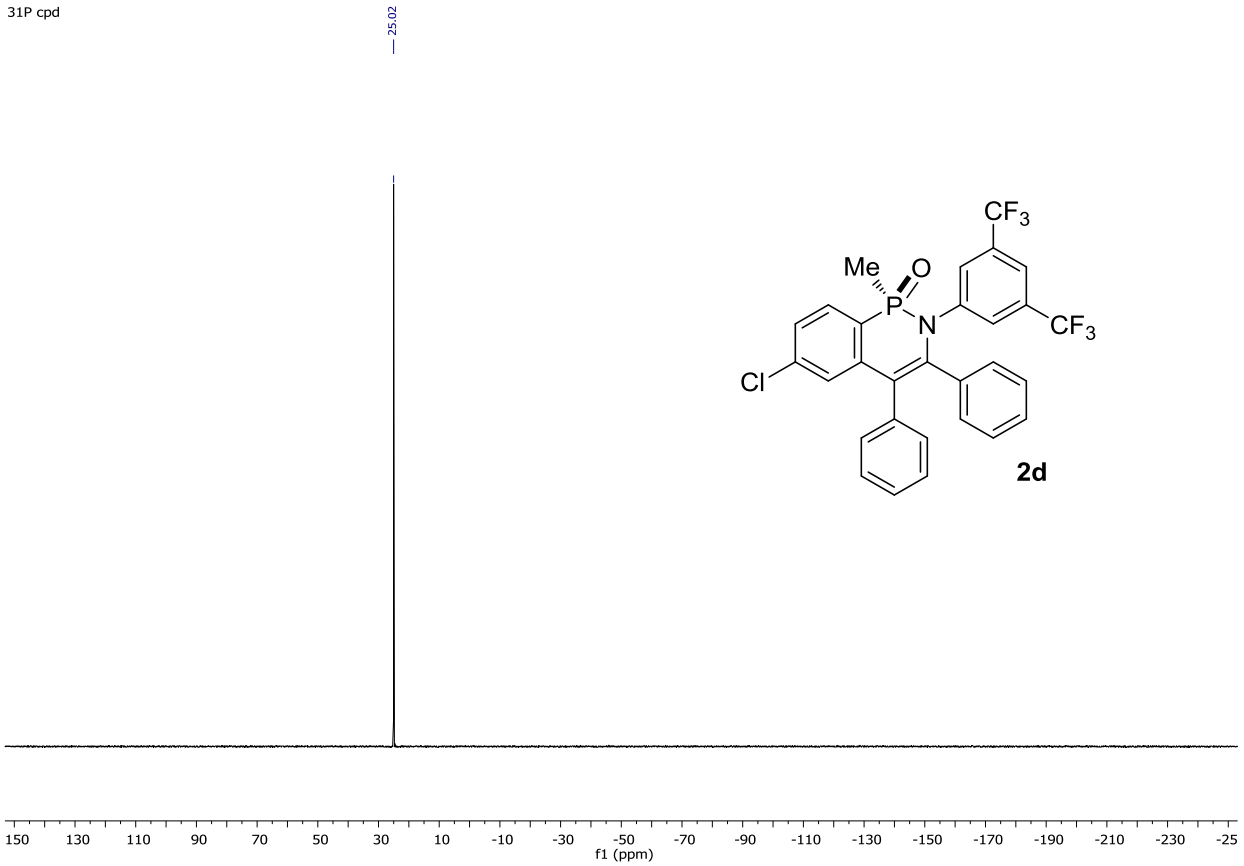


**2c**


CF3
Me
O
P
N
CF3
Cl
2d
f1 (ppm)


CF3
Me
O
P
N
CF3
Cl
2d
f1 (ppm)

31P cpd

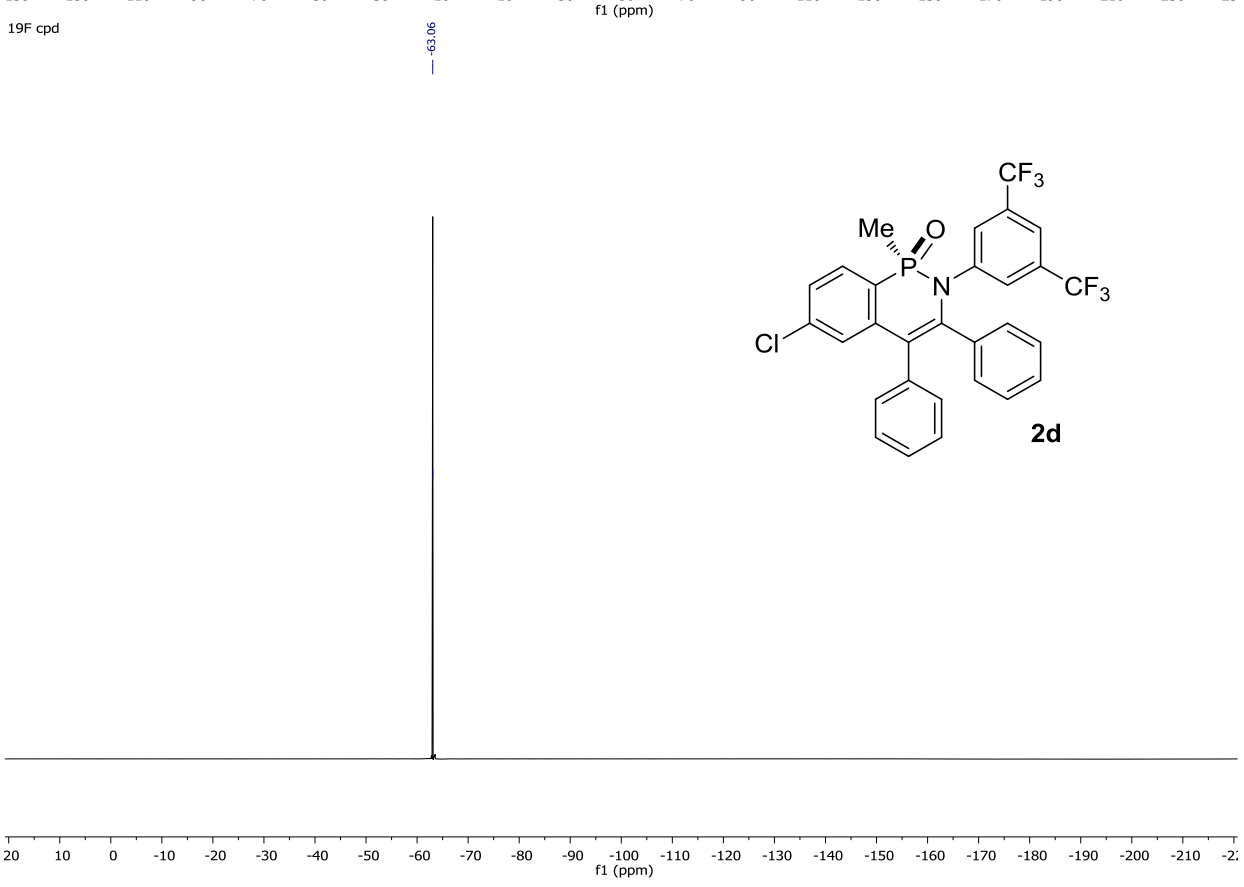






**2d**

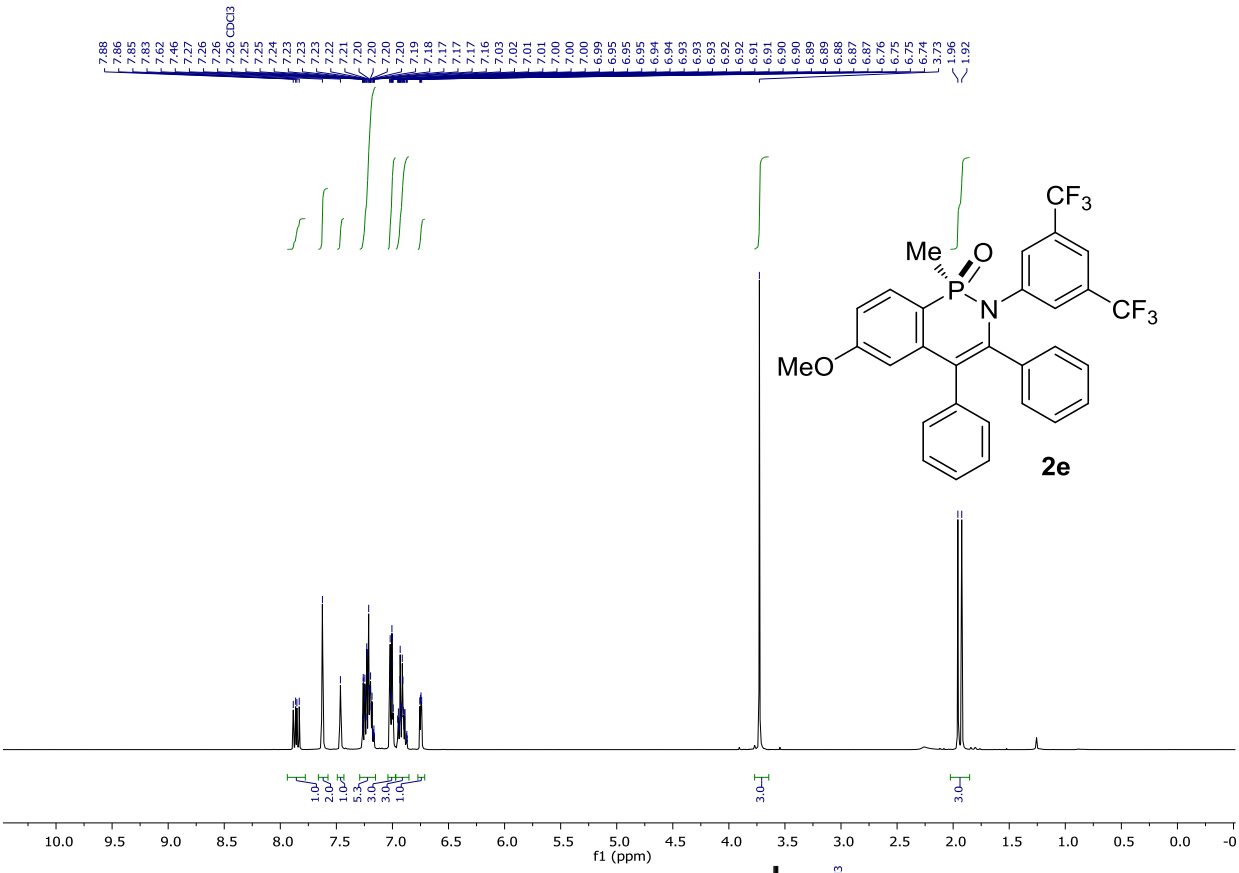
19F cpd

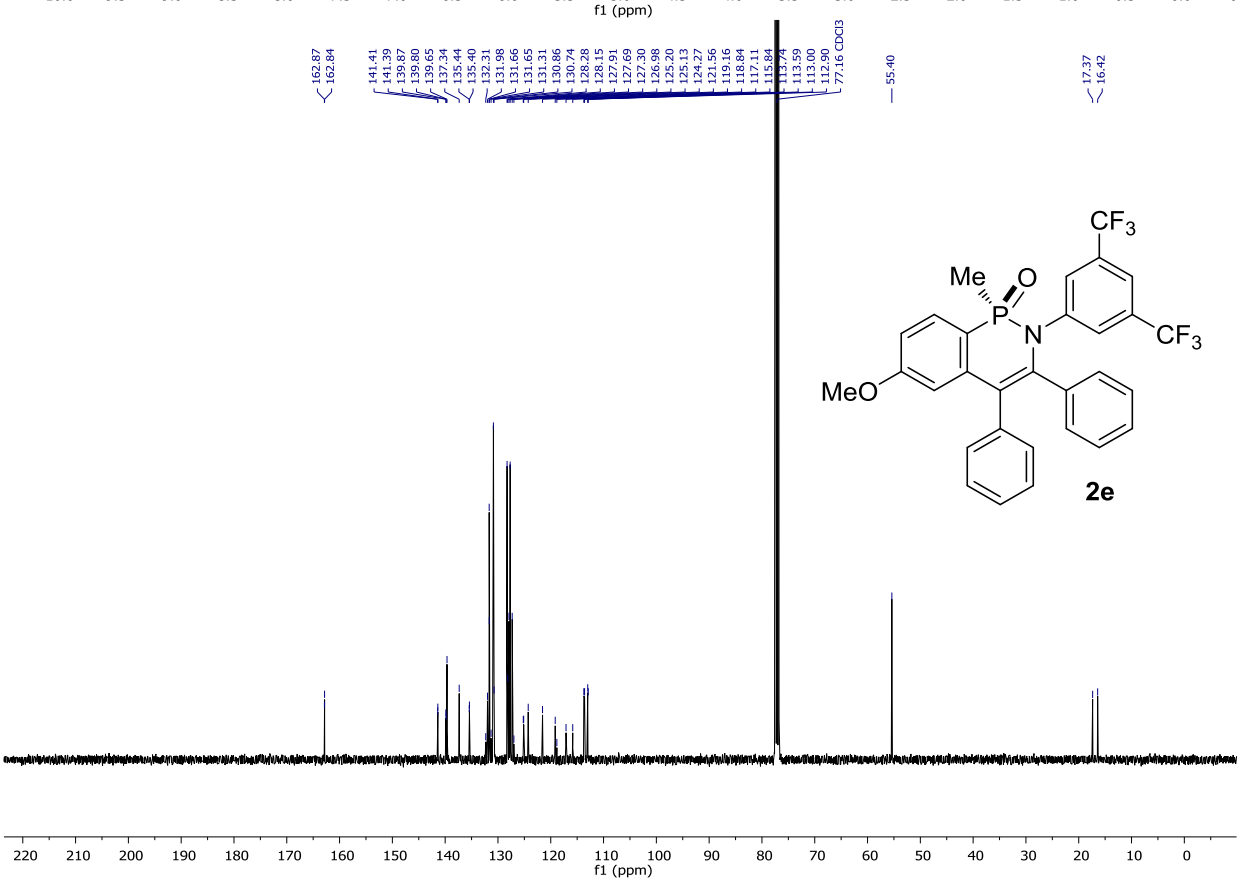




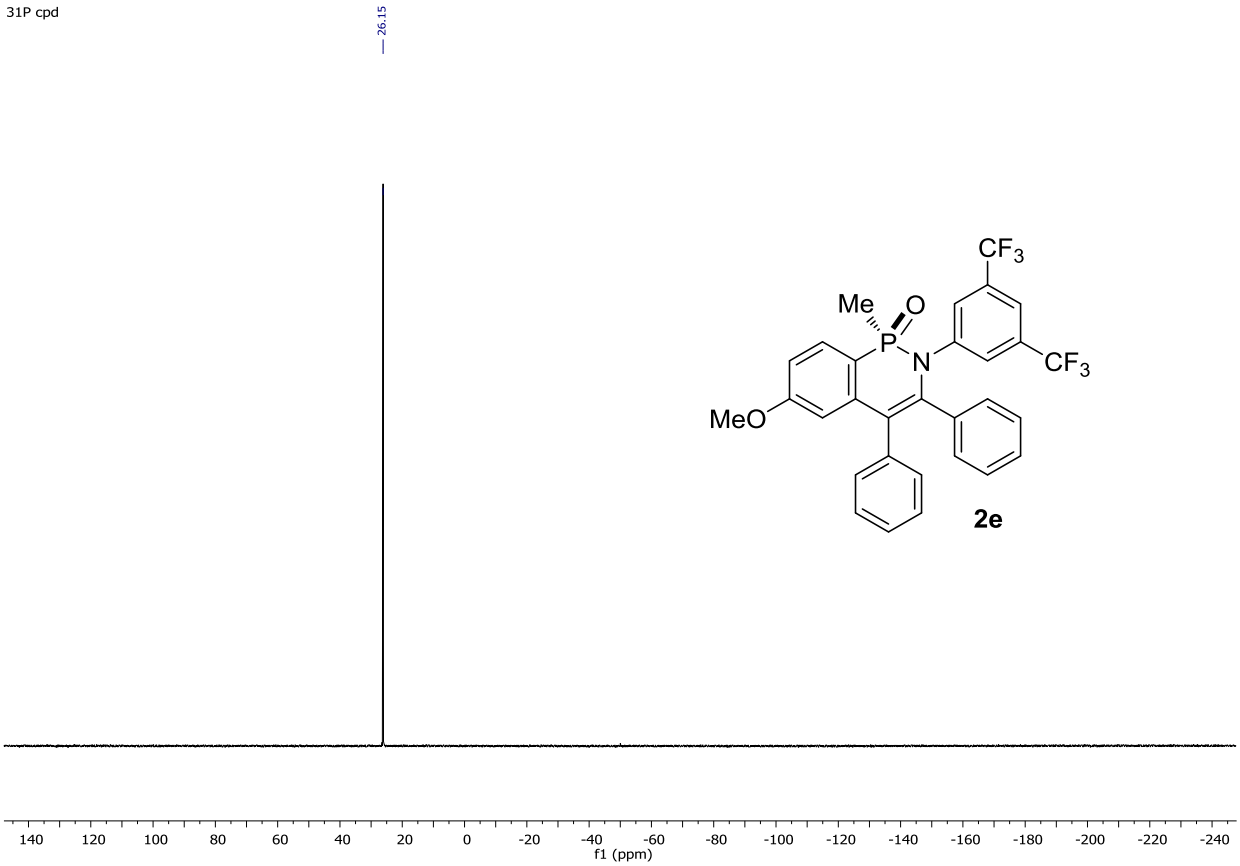


**2d**

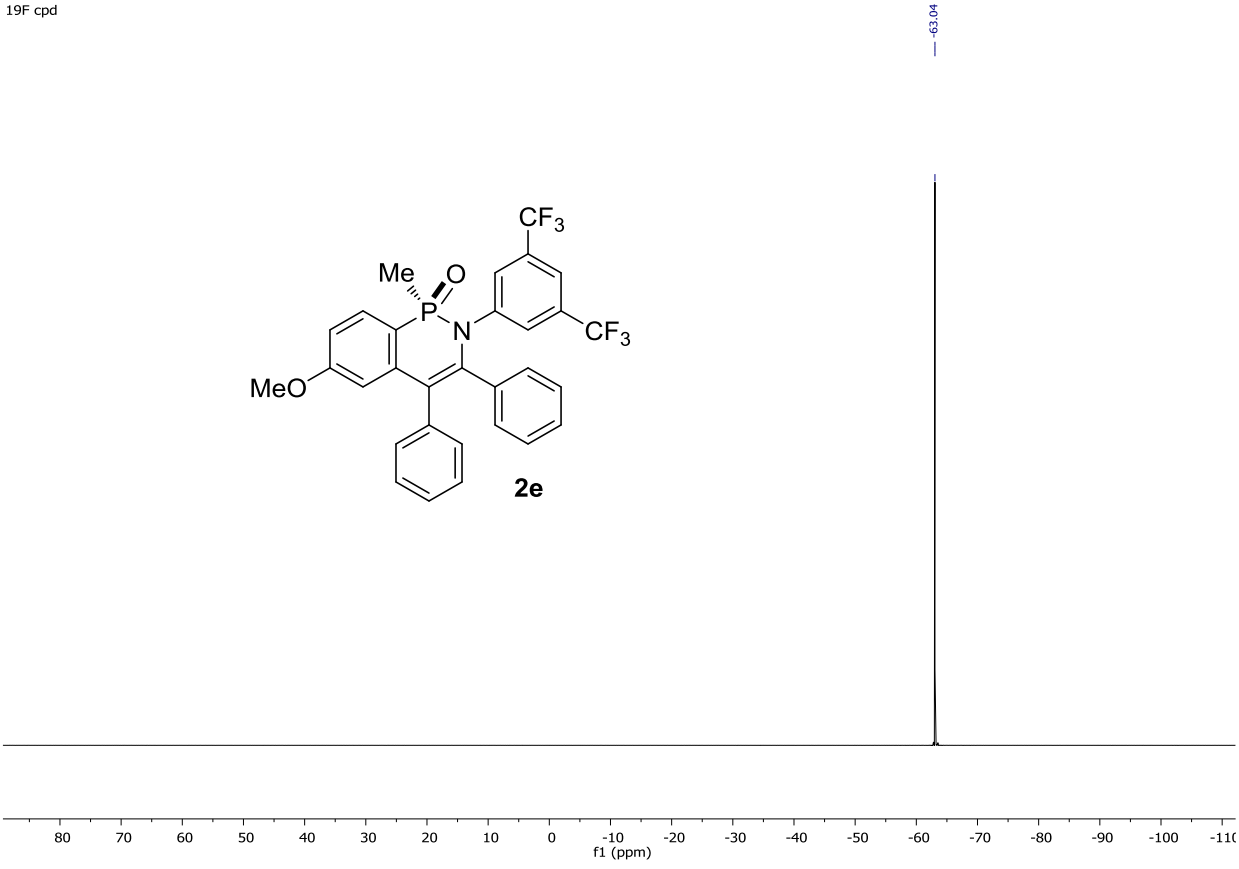

7.88 7.86 7.85 7.83 7.62 7.46 7.27 7.26 7.26 CDCl3 7.25 7.25 7.24 7.23 7.23 7.22 7.21 7.20 7.20 7.20 7.20 7.19 7.18 7.17 7.17 7.17 7.16 7.03 7.02 7.01 7.01 7.00 7.00 7.00 6.99 6.95 6.95 6.95 6.94 6.94 6.93 6.93 6.92 6.92 6.91 6.91 6.90 6.90 6.89 6.89 6.88 6.87 6.87 6.76 6.75 6.75 6.74 3.73 1.96 1.92
CF3
Me
O
P
N
CF3
MeO
2e
1.0 2.0 1.0 5.3 3.0 3.0 1.0 3.0 3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

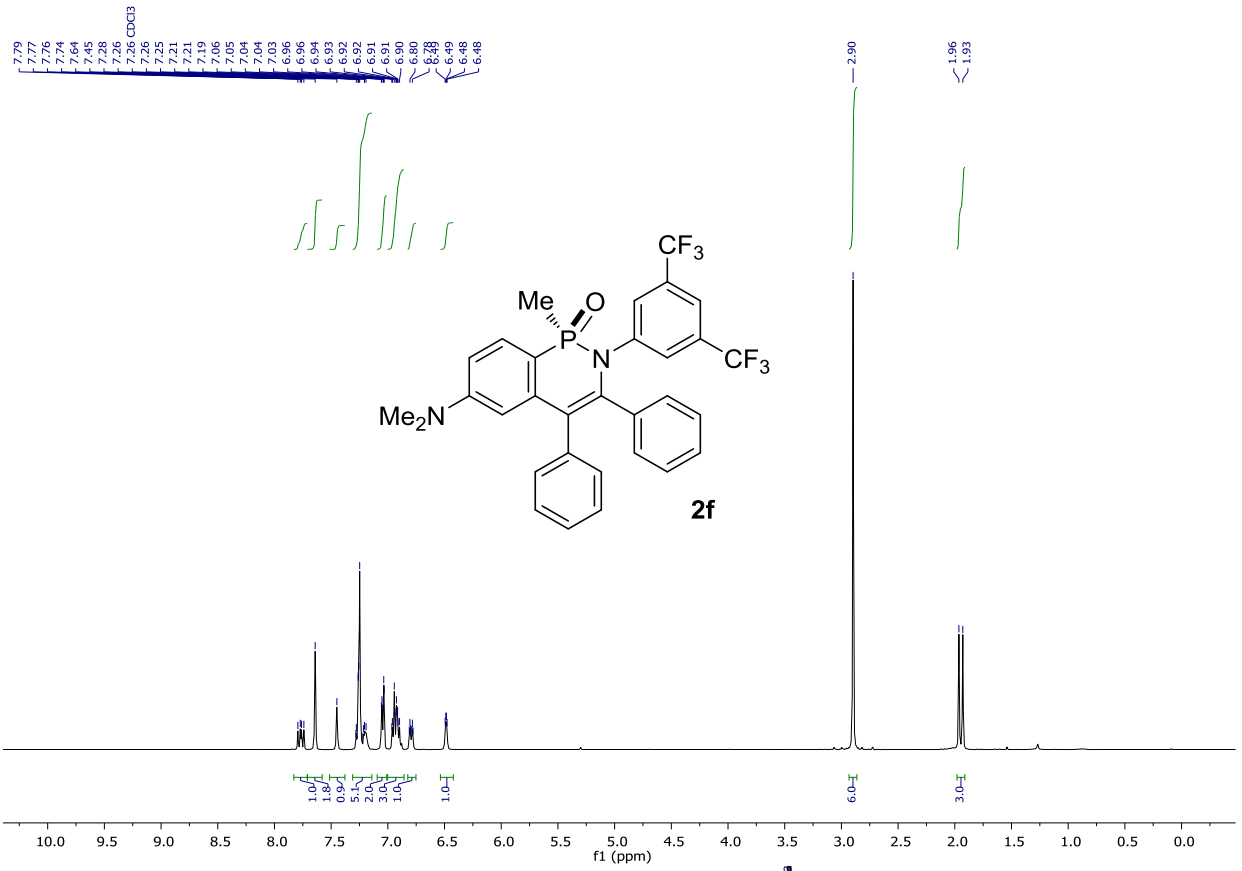

162.87 162.84 141.41 141.39 139.87 139.80 139.65 137.34 135.44 135.40 132.31 131.98 131.66 131.65 131.31 130.86 130.74 128.28 128.15 127.91 127.69 127.30 126.98 125.20 125.13 124.27 121.56 119.16 118.84 117.11 115.84 113.74 113.59 113.00 112.90 77.16 CDCl3 55.40 17.37 16.42
CF3
Me
O
P
N
CF3
MeO
2e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

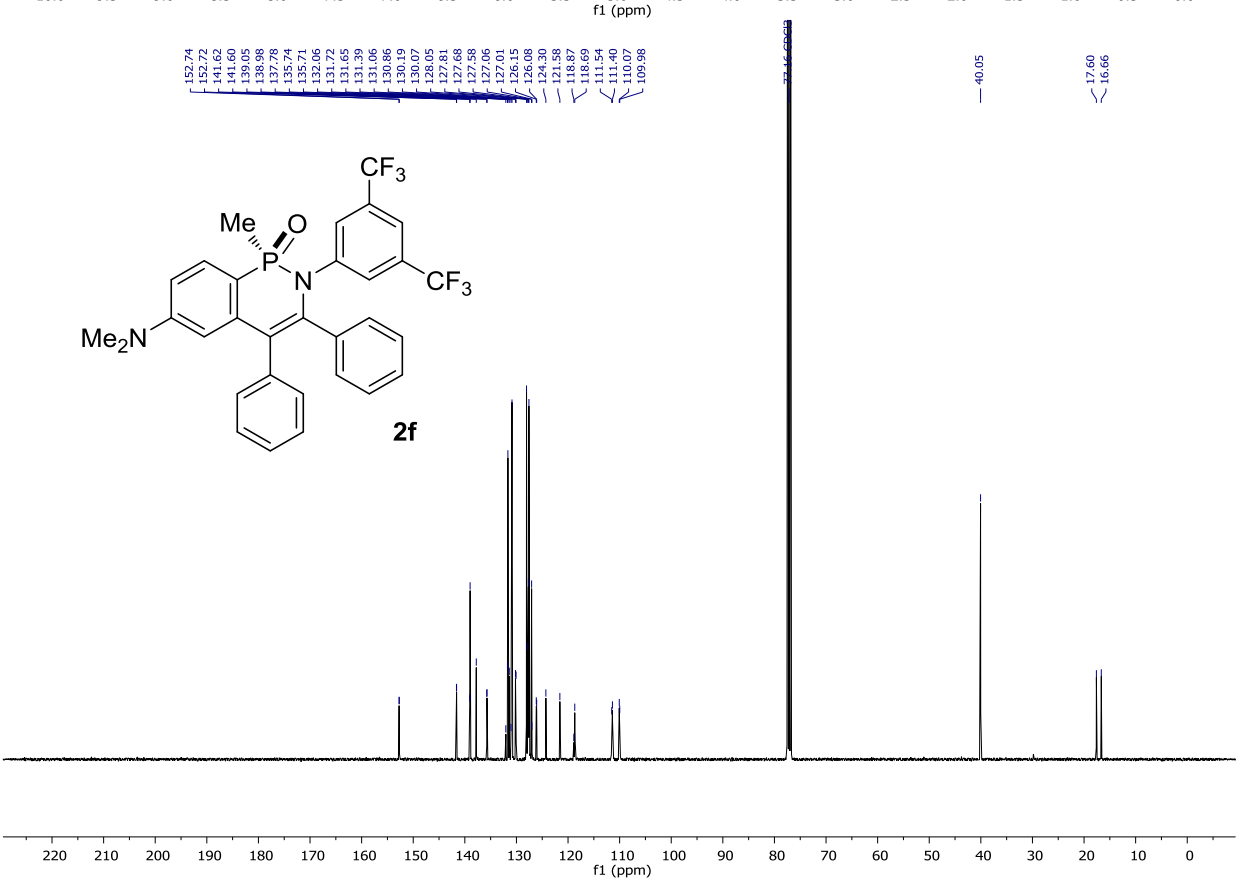
31P cpd




19F cpd

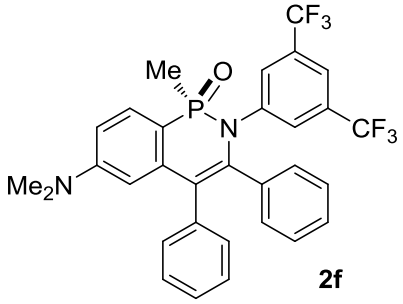



CF3
Me
O
P
N
CF3
Me2N
2f
f1 (ppm)

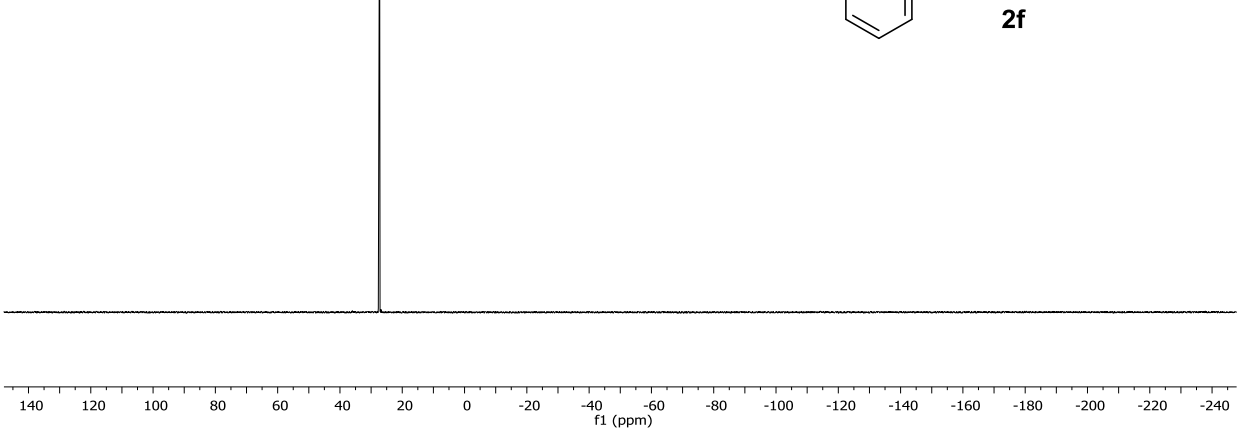

CF3
Me
O
P
N
CF3
Me2N
2f
f1 (ppm)

31P cpd

27.28

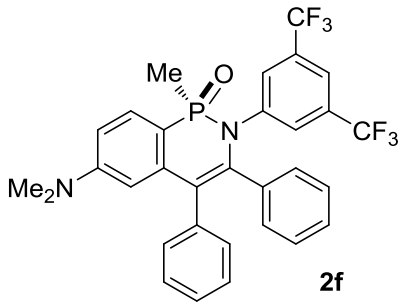



**2f**

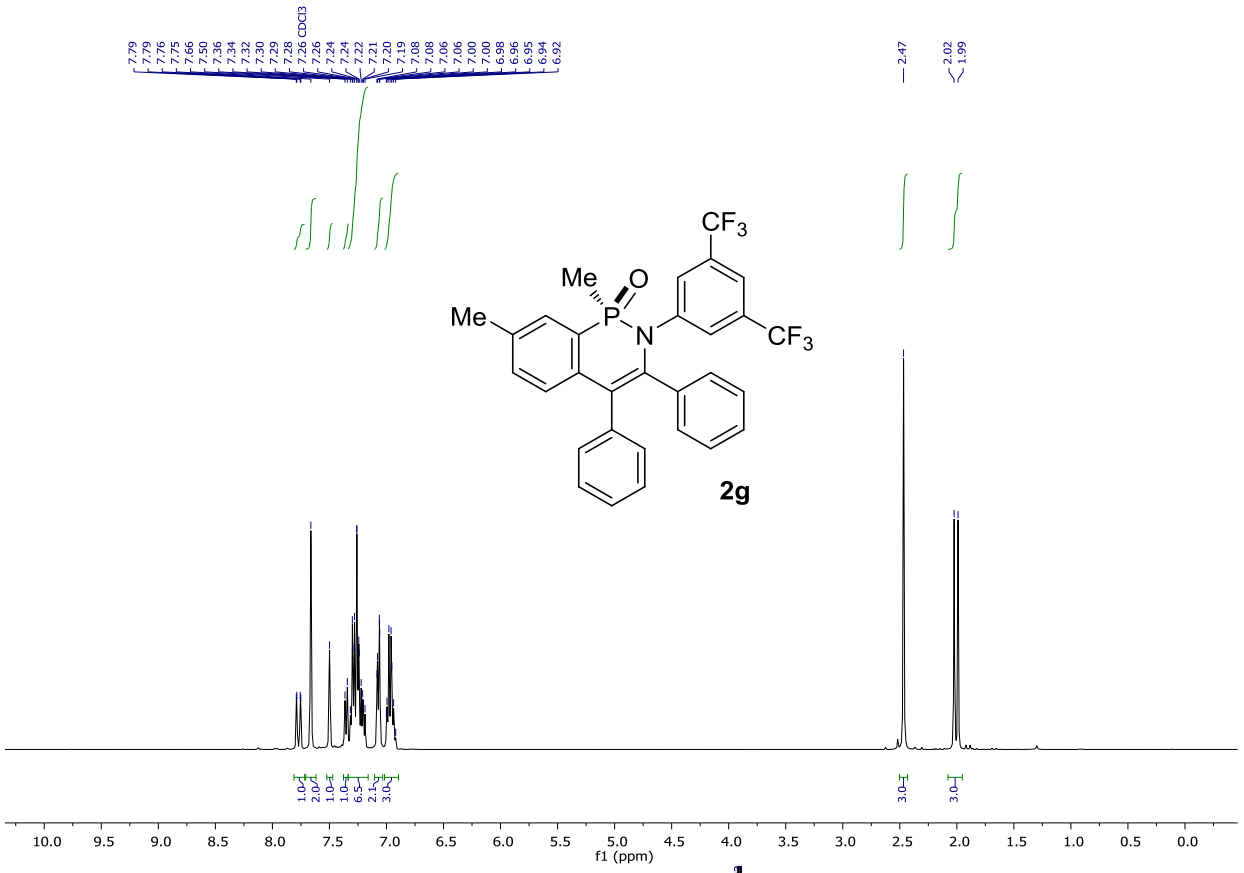


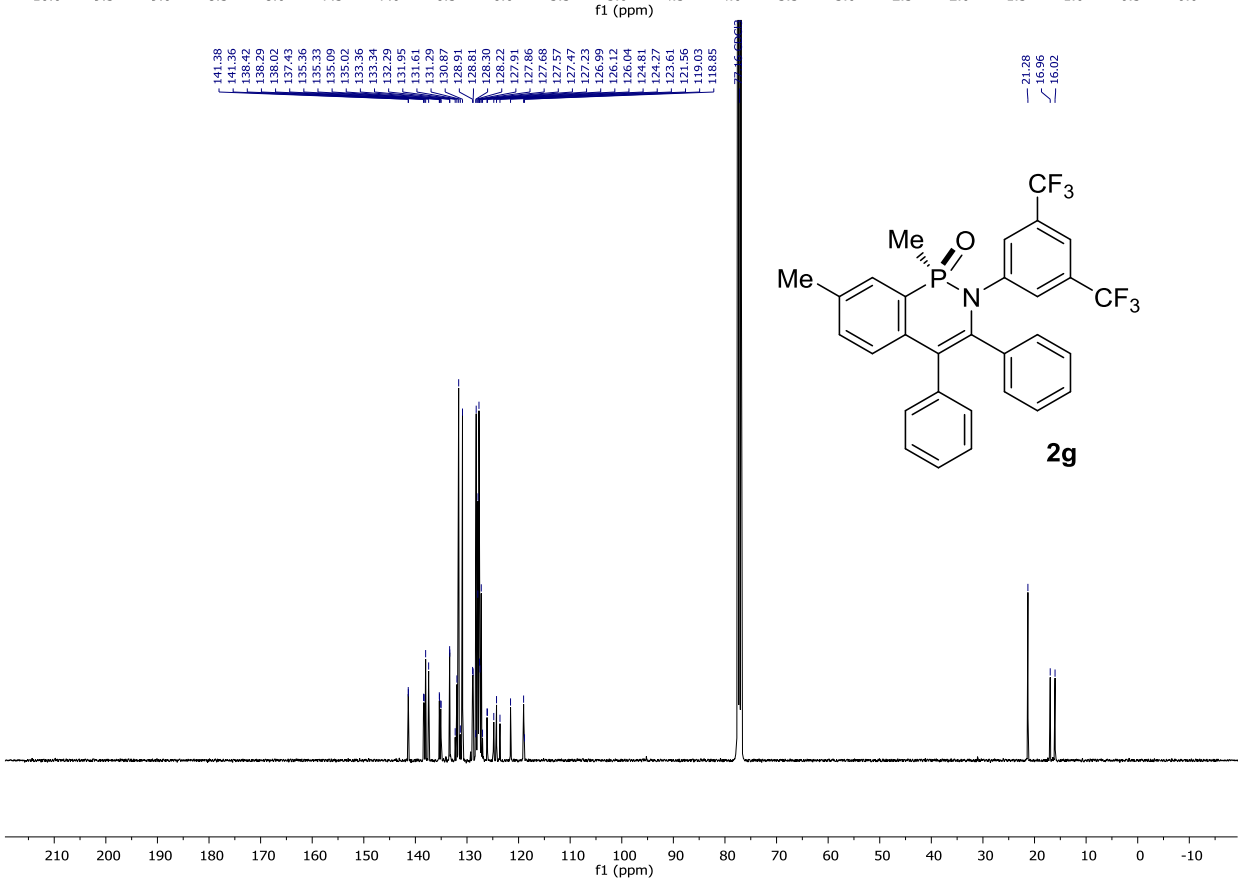

19F cpd

-62.97

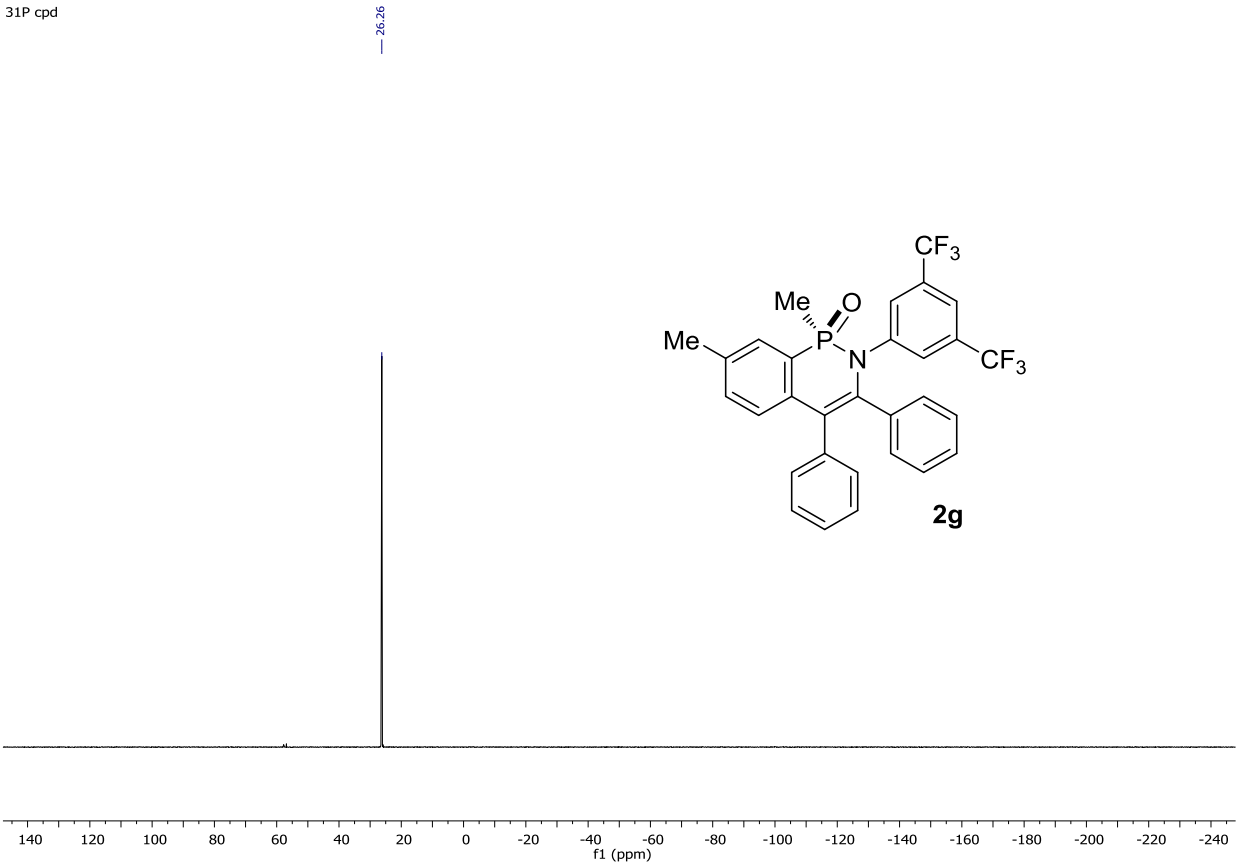



**2f**


7.79
7.79
7.76
7.75
7.66
7.50
7.36
7.34
7.32
7.30
7.29
7.28 CDCl3
7.26
7.24
7.24
7.22
7.21
7.20
7.19
7.08
7.08
7.06
7.06
7.00
7.00
6.98
6.96
6.95
6.94
6.92
2.47
2.02
1.99
CF3
Me
O
Me
P
N
CF3
2g
1.0
2.0
1.0
1.0
6.5
2.1
3.0
3.0
3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.38
141.36
138.42
138.29
138.02
137.43
135.36
135.33
135.09
135.02
133.36
133.34
132.29
131.95
131.61
131.29
130.87
128.91
128.81
128.30
128.22
127.91
127.86
127.68
127.57
127.47
127.23
126.99
126.12
126.04
124.81
124.27
123.61
121.56
119.03
118.85
77.46 CDCl3
21.28
16.96
16.02
CF3
Me
O
Me
P
N
CF3
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

31P cpd

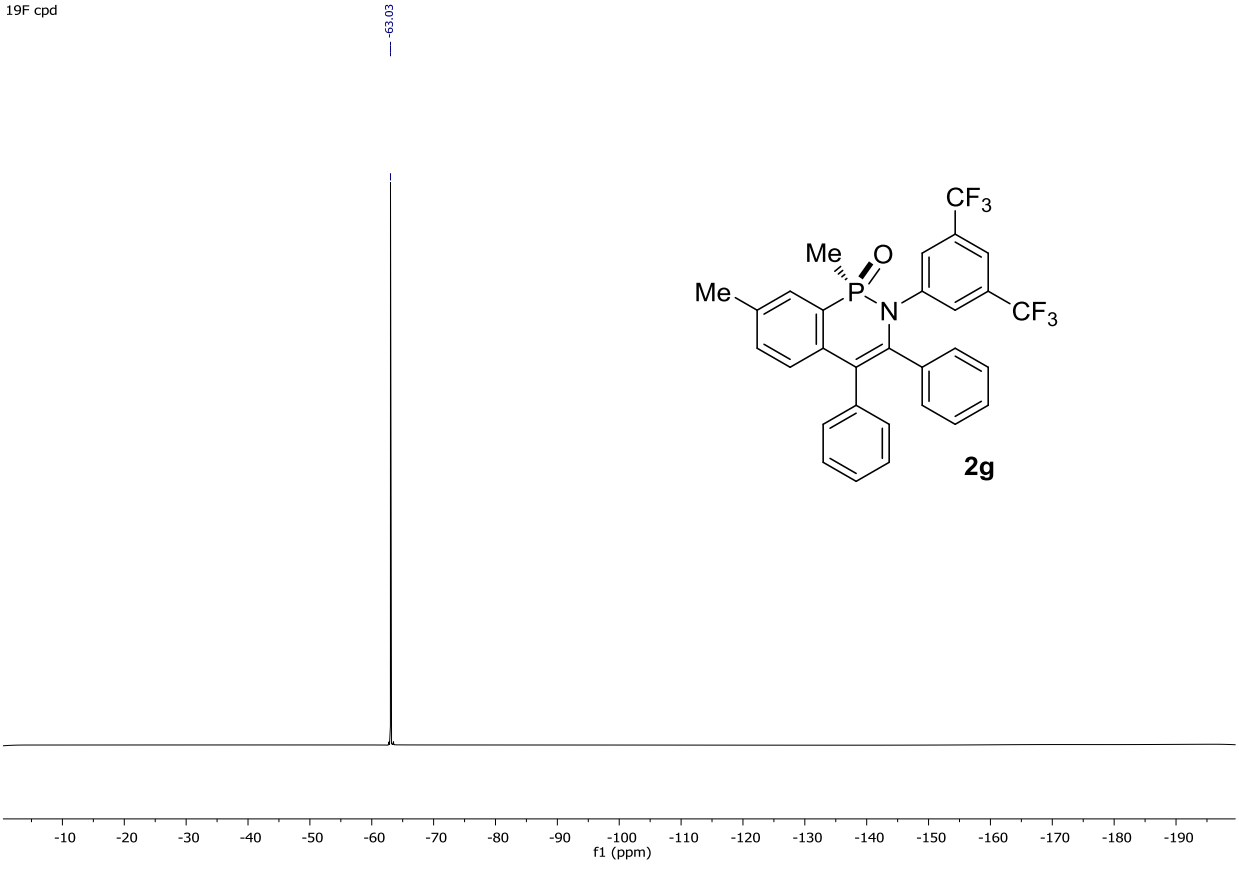






**2g**

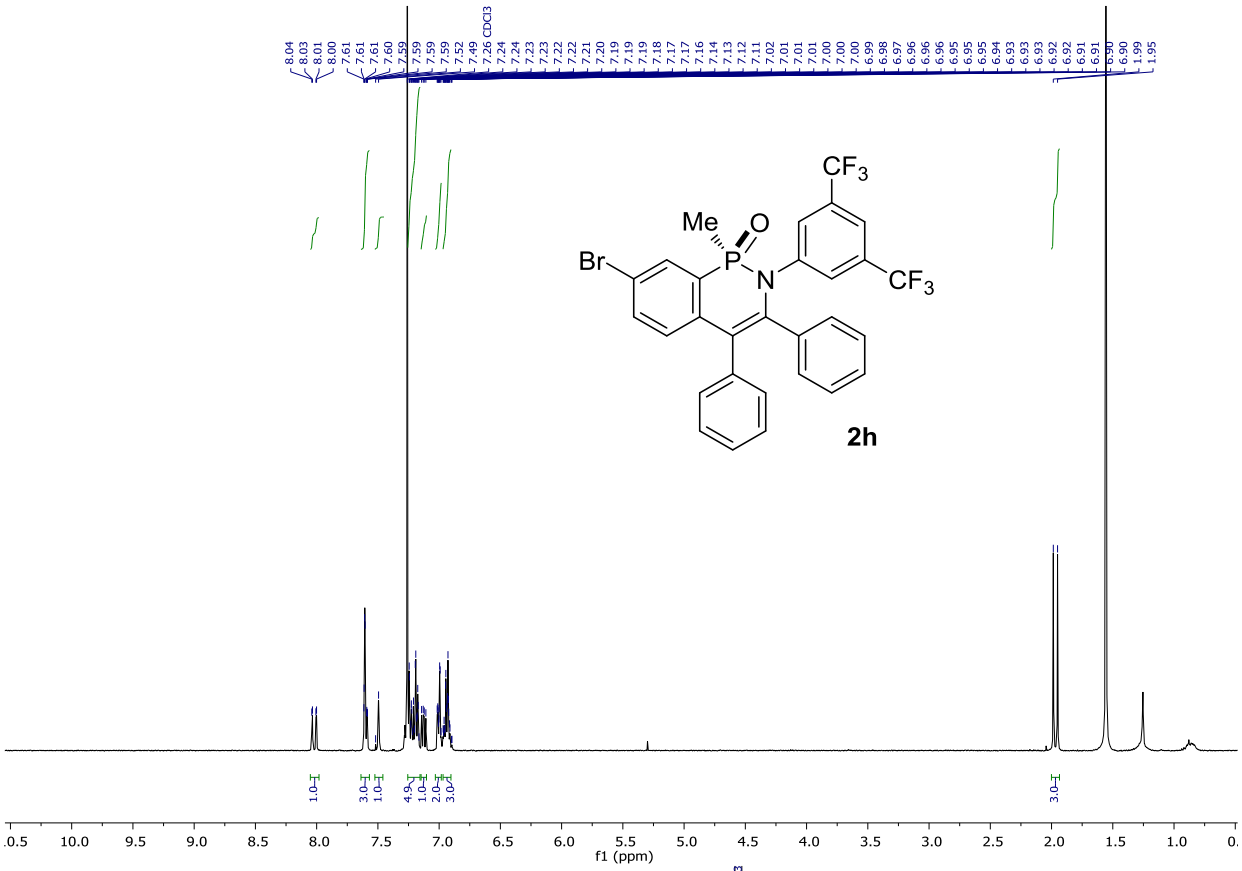
19F cpd

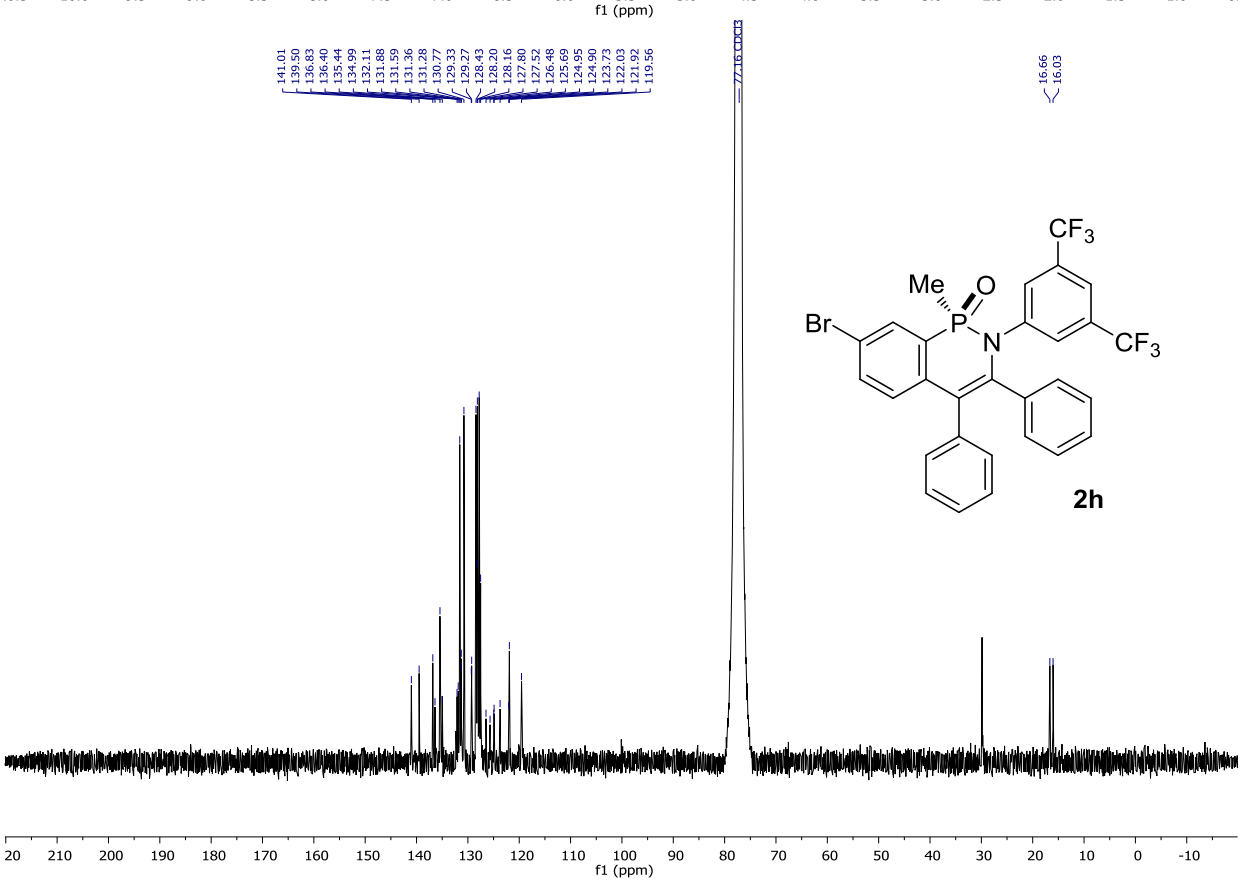




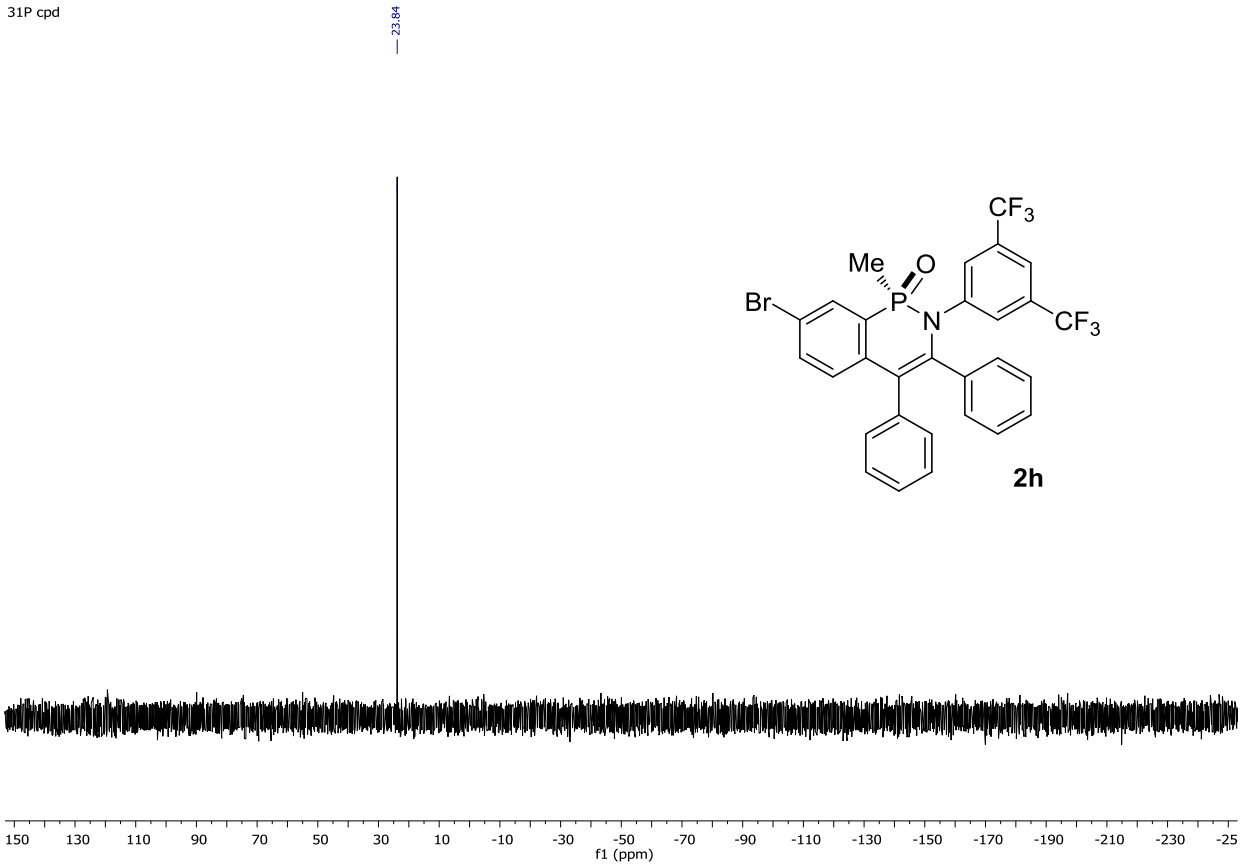


**2g**


CF3
Me
O
P
N
Br
CF3
2h
f1 (ppm)


CF3
Me
O
P
N
Br
CF3
2h
f1 (ppm)

31P cpd

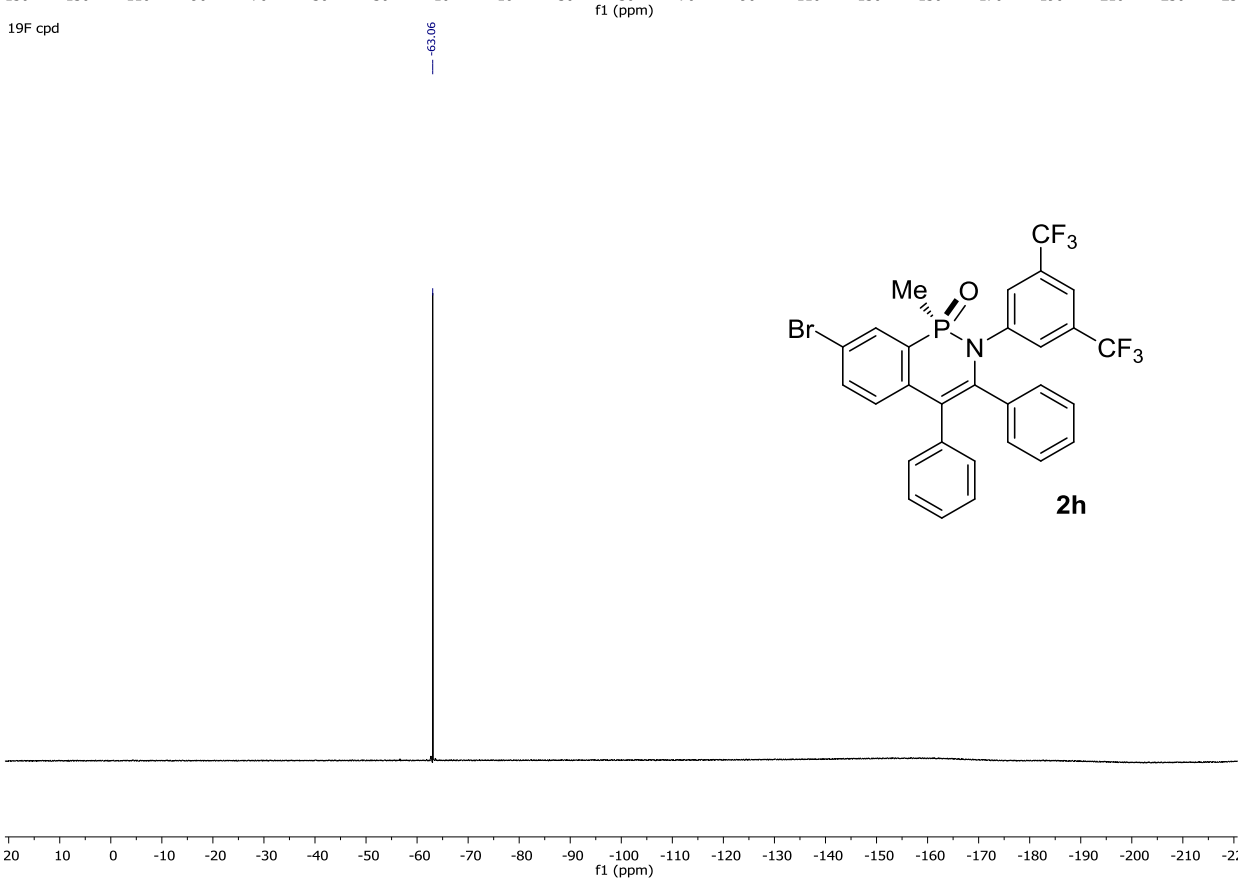






**2h**

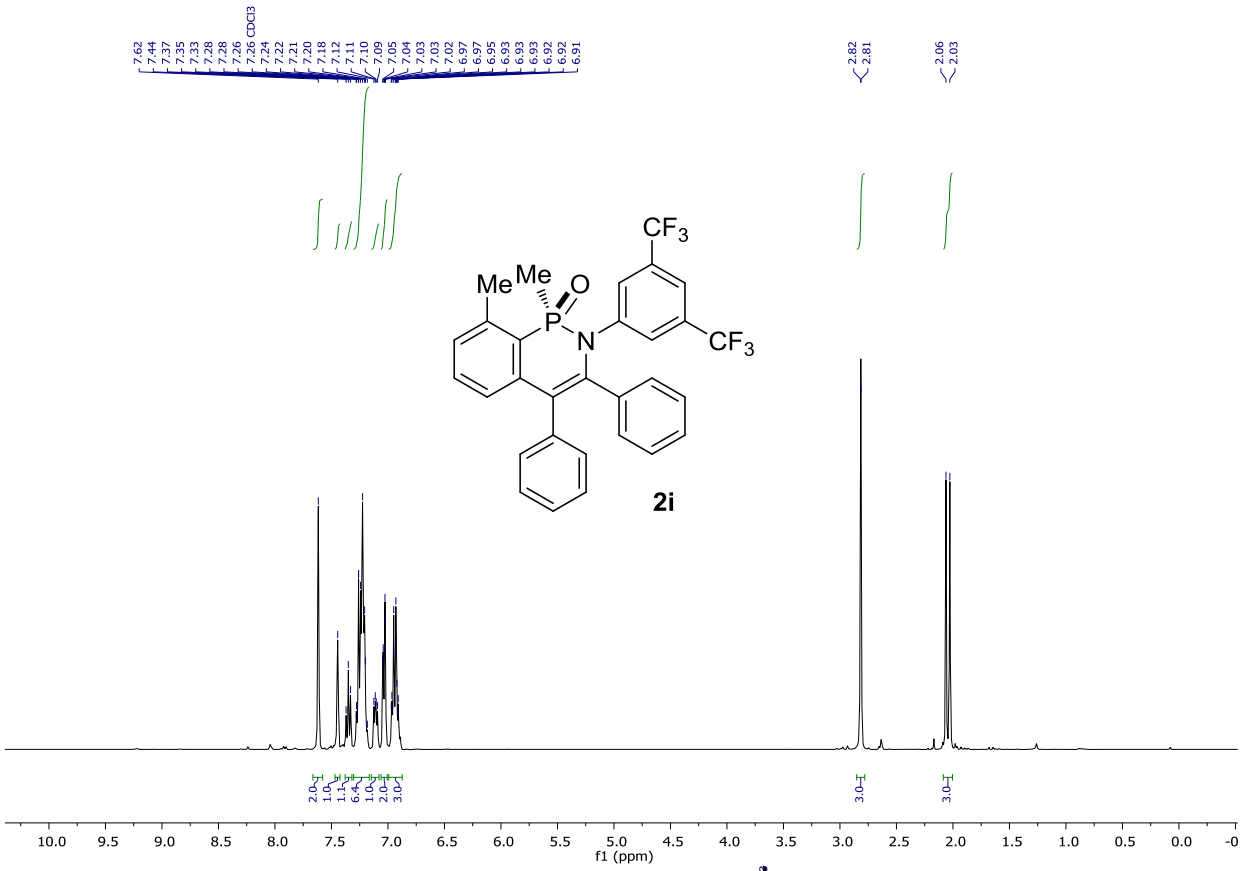
19F cpd

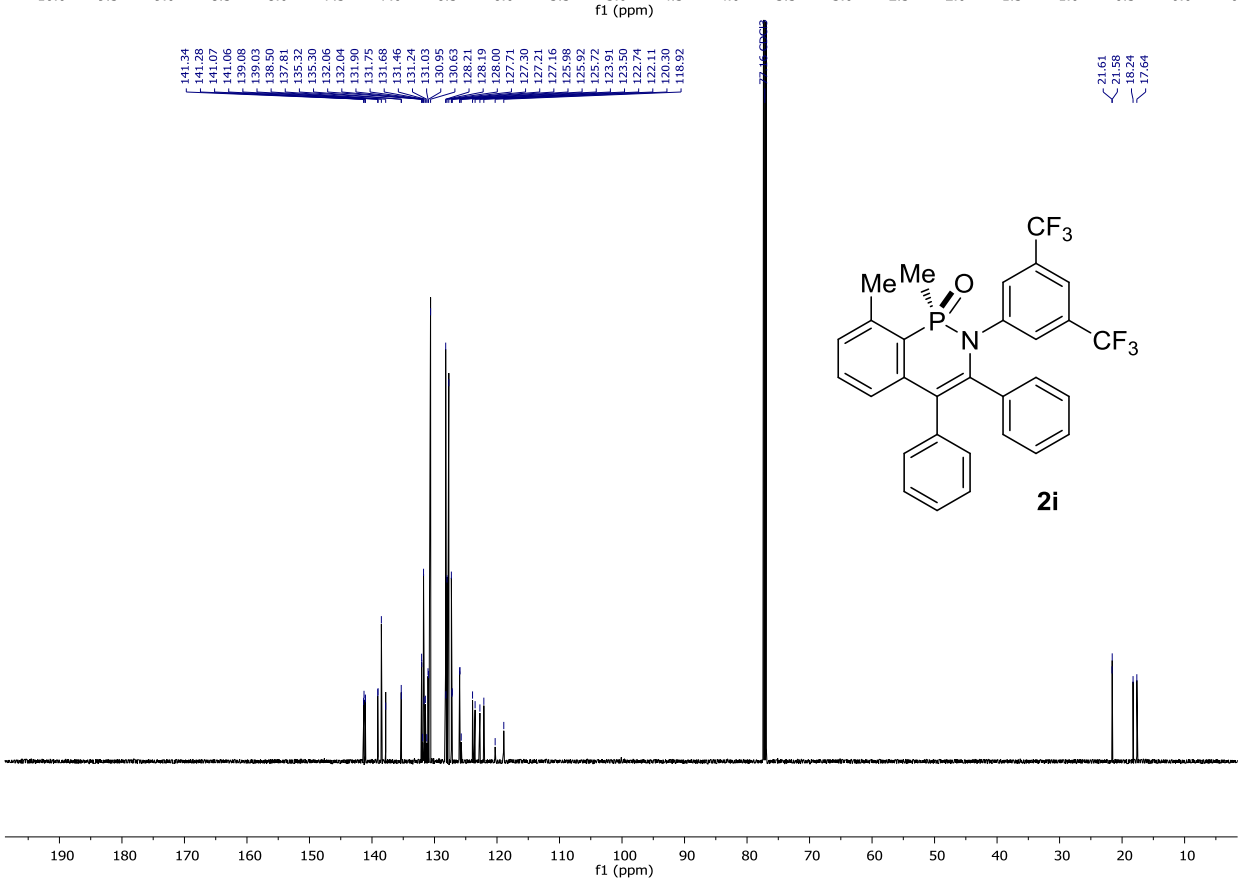




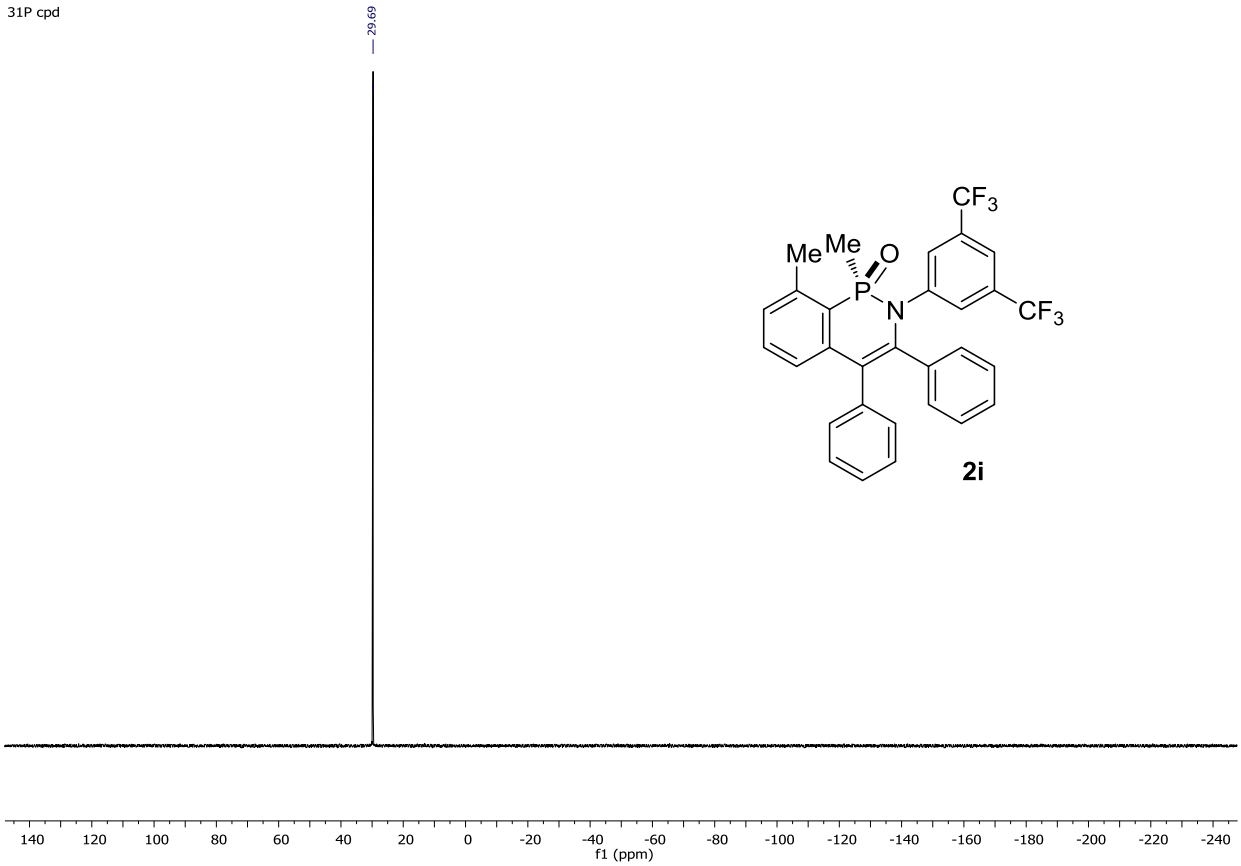


**2h**


7.62
7.44
7.37
7.35
7.33
7.28
7.28
7.26
7.26 CDCl3
7.24
7.22
7.21
7.20
7.18
7.12
7.11
7.10
7.09
7.05
7.04
7.03
7.03
7.02
6.97
6.97
6.95
6.93
6.93
6.93
6.92
6.92
6.91
2.82
2.81
2.06
2.03
CF3
Me
Me
O
P
N
CF3
2i
2.0
1.0
1.1
6.4
1.0
2.0
3.0
3.0
3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


141.34
141.28
141.07
141.06
139.08
139.03
138.50
137.81
135.32
135.30
132.06
132.04
131.90
131.75
131.68
131.46
131.24
131.03
130.95
130.63
128.21
128.19
128.00
127.71
127.30
127.21
127.16
125.98
125.92
125.72
123.91
123.50
122.74
122.11
120.30
118.92
77.16 CDCl3
21.61
21.58
18.24
17.64
CF3
Me
Me
O
P
N
CF3
2i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

31P cpd







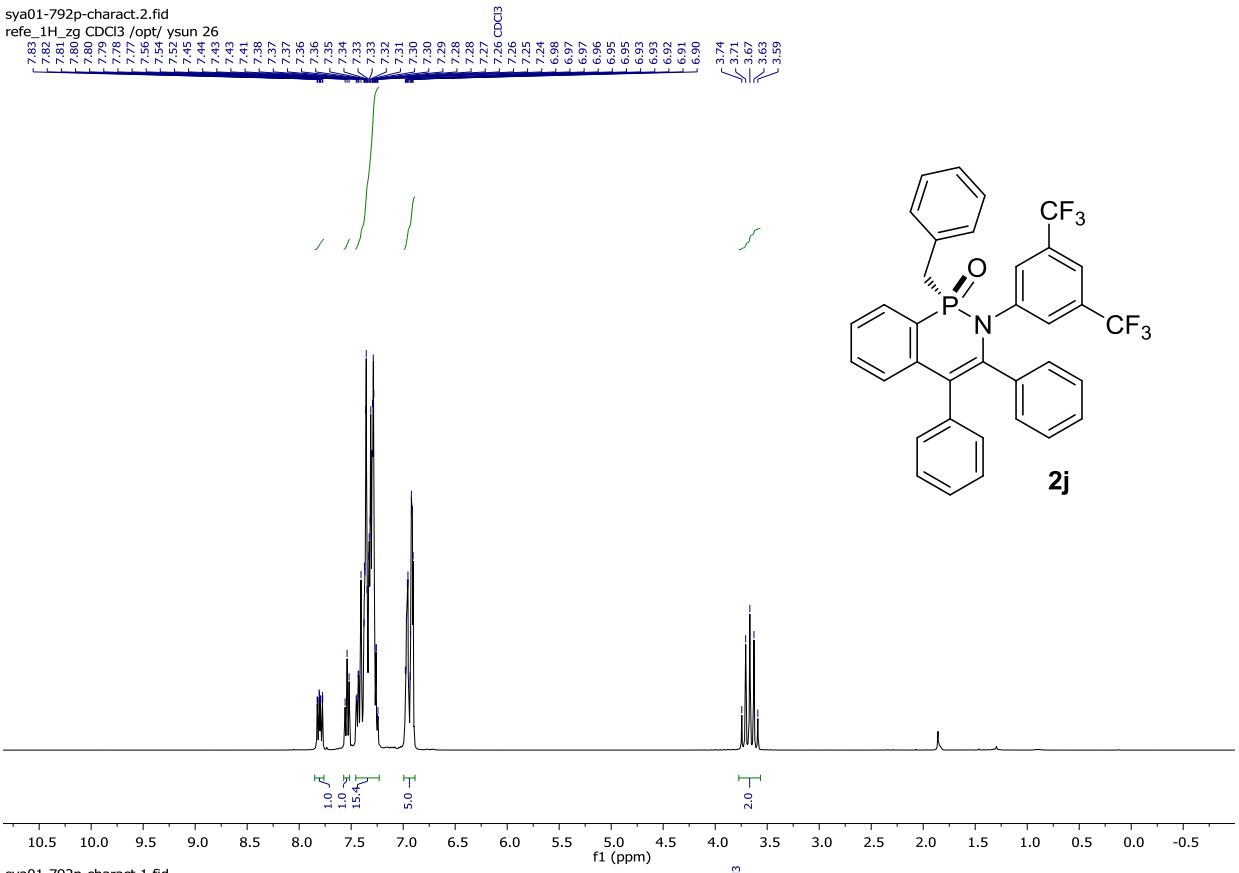
**2i**

19F cpd



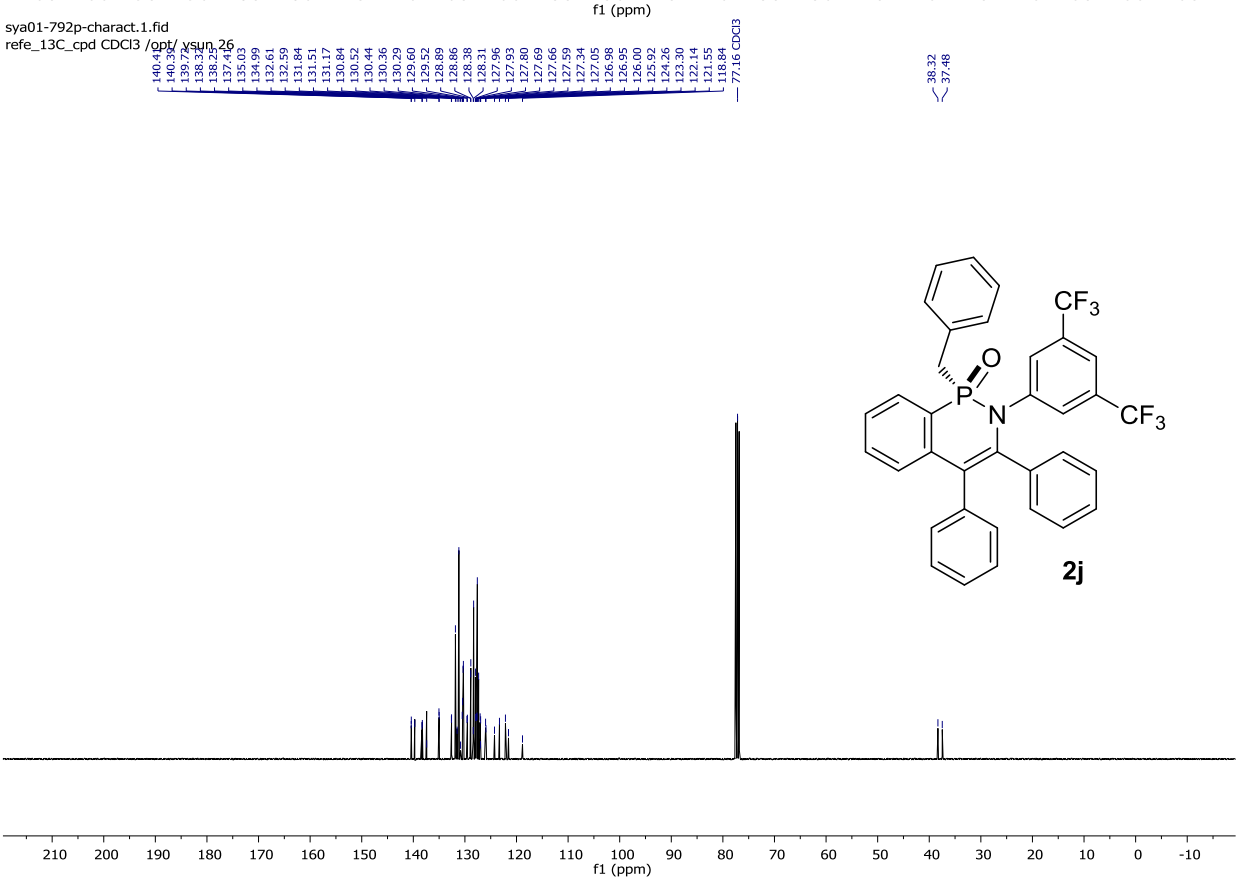


**2i**


sya01-792p-charact.2.fid
refe_1H_zg CDCl3 /opt/ ysun 26
CDCl3
f1 (ppm)


CF3
O
P
N
CF3

**2j**

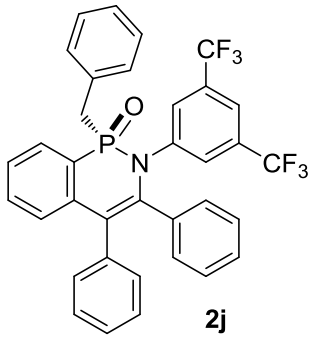

sya01-792p-charact.1.fid
refe_13C_cpd CDCl3 /opt/ ysun 26
77.16 CDCl3
f1 (ppm)


CF3
O
P
N
CF3

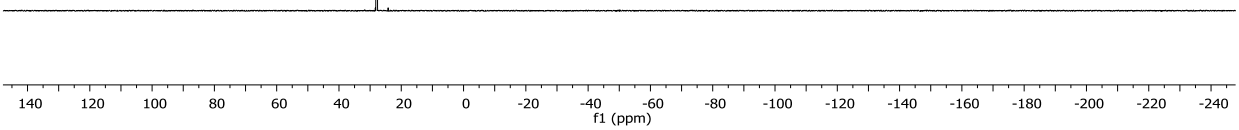
**2j**

sya01-792p-charact-19F-31P/3
refe_31Pcpd

27.98

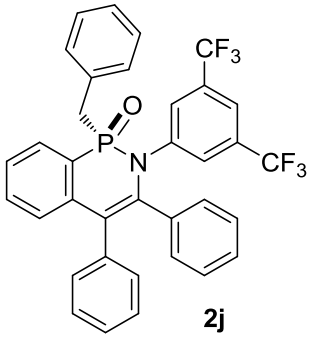



**2j**

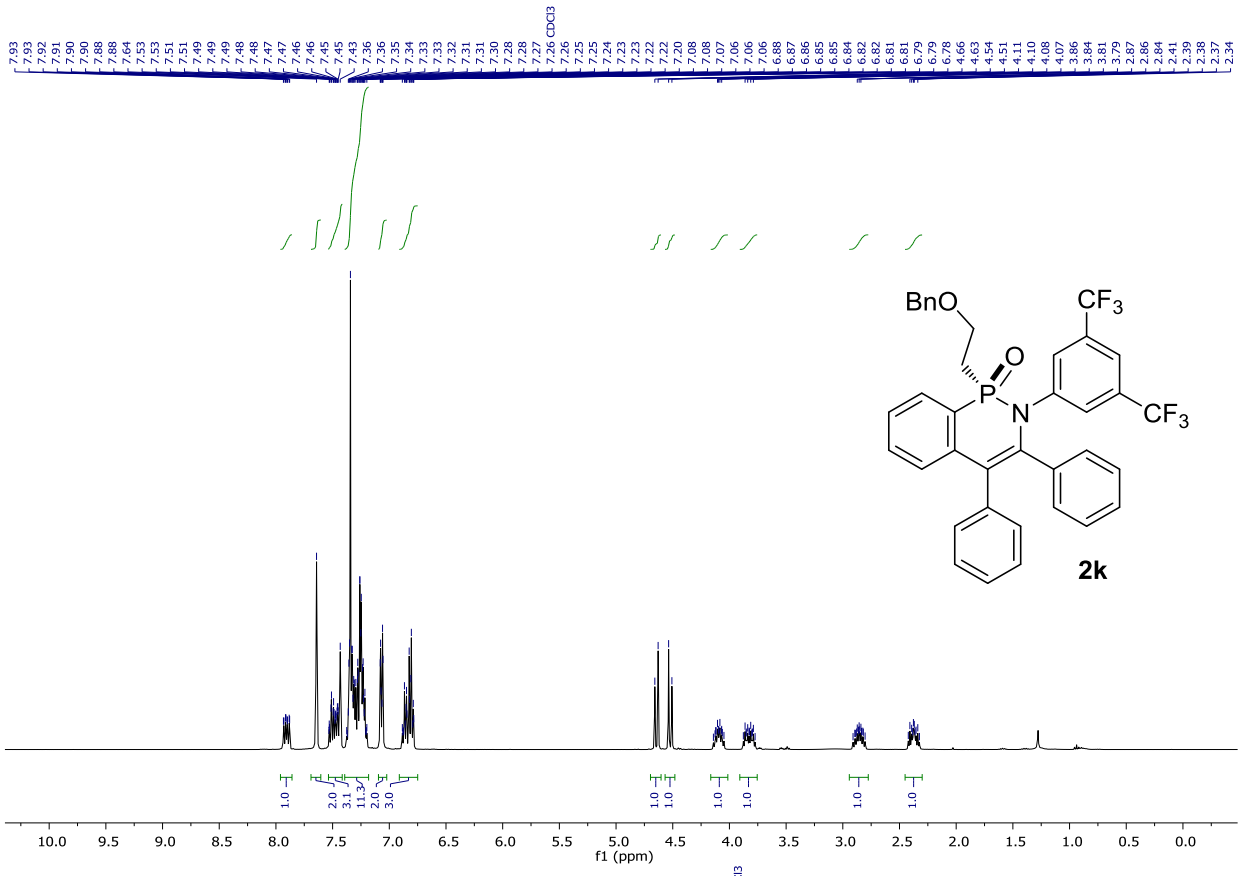


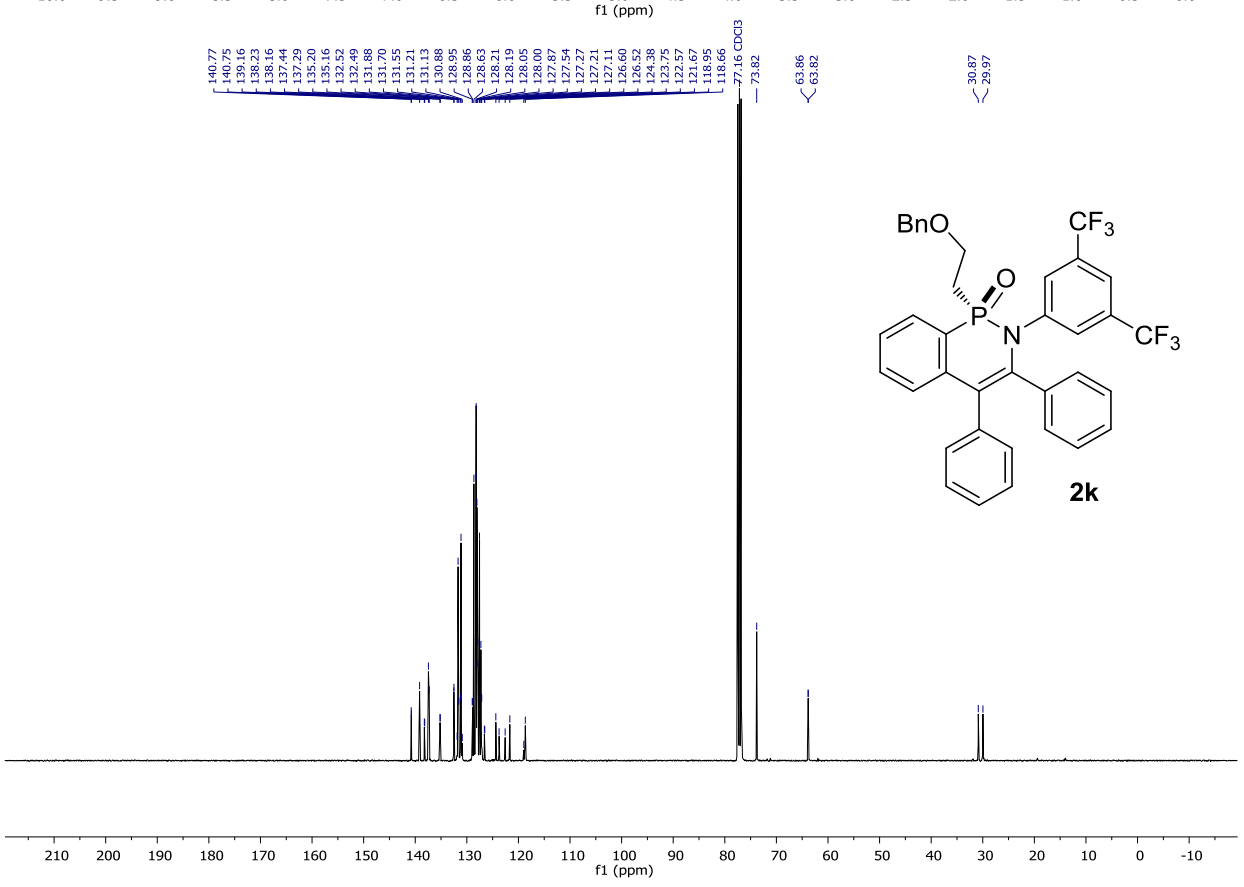

sya01-792p-charact-19F-31P/1
refe_F19cpd

-63.02

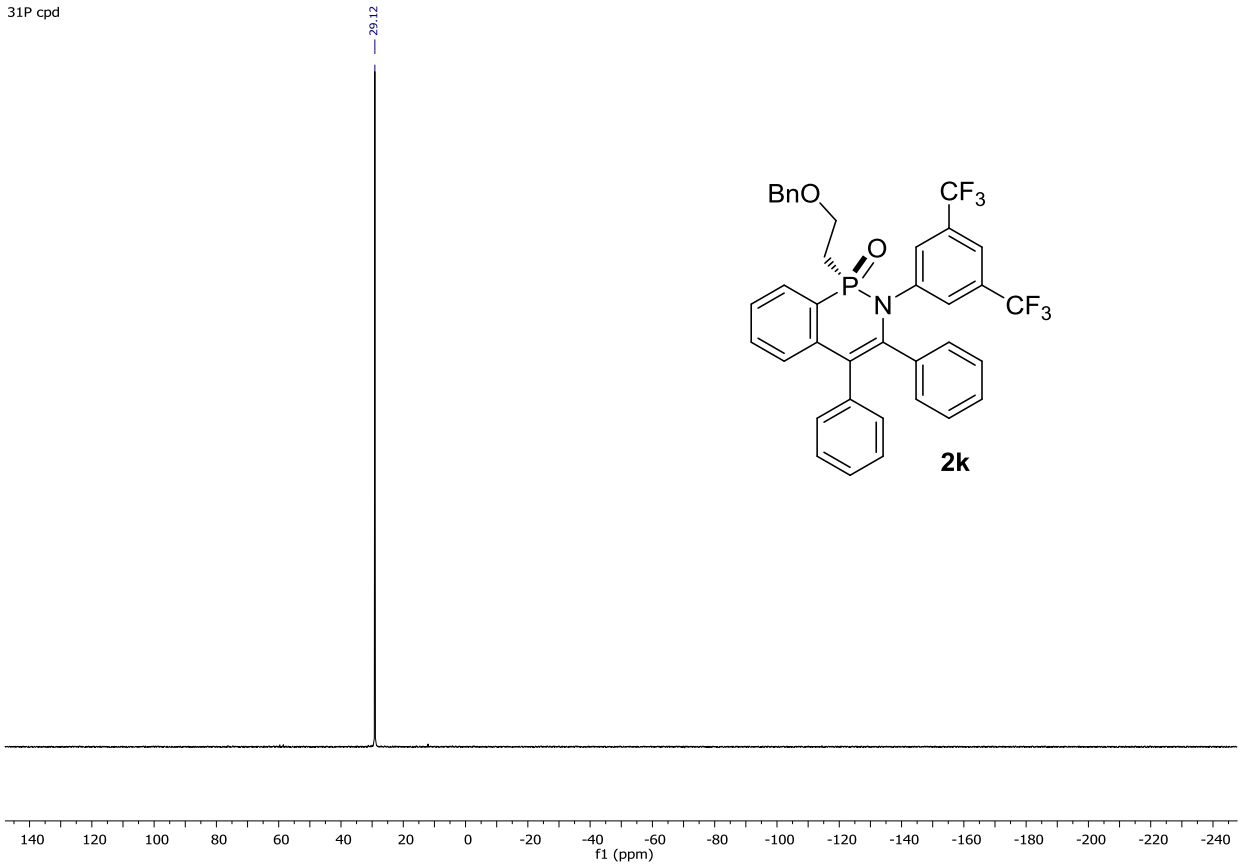



**2j**


BnO
CF3
O
P
N
CF3
2k
f1 (ppm)


BnO
CF3
O
P
N
CF3
2k
f1 (ppm)

31P cpd

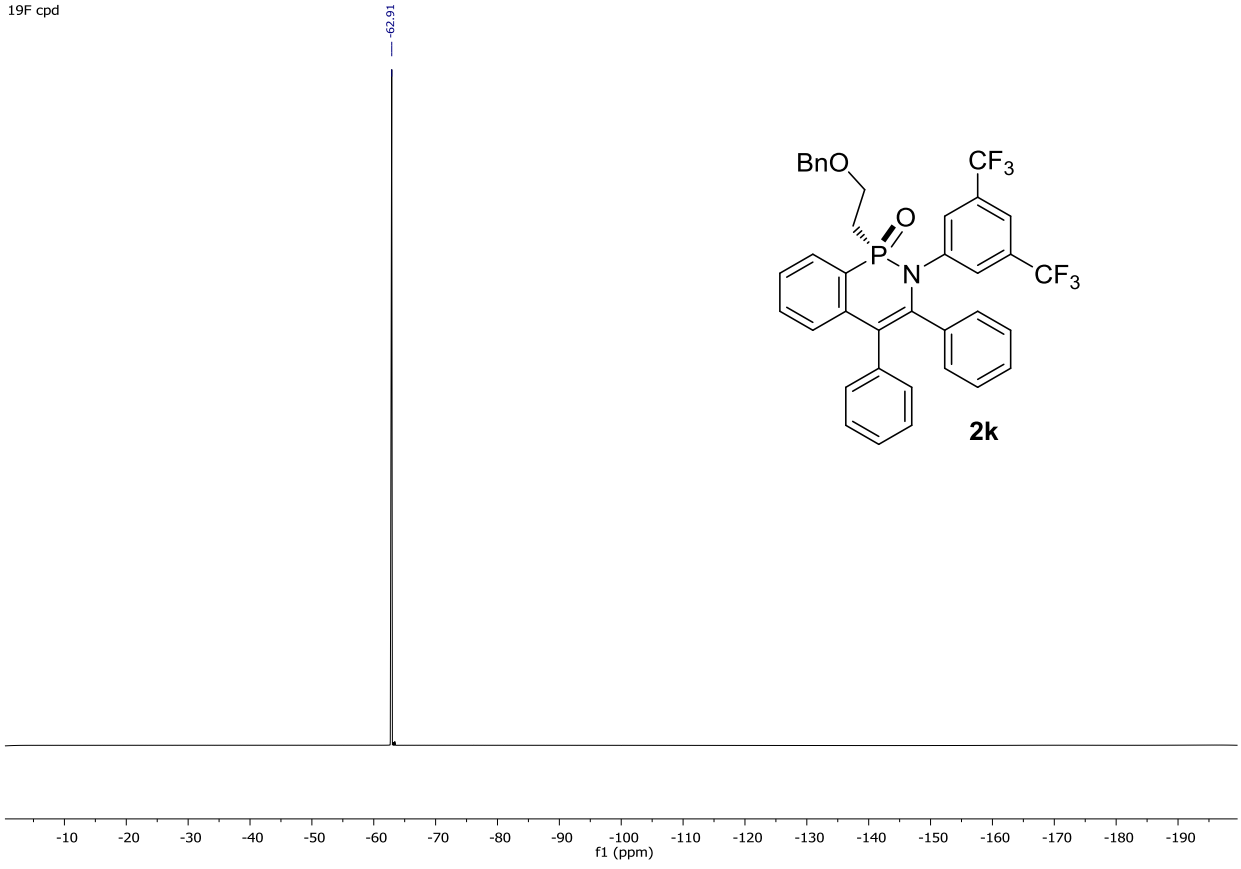






**2k**

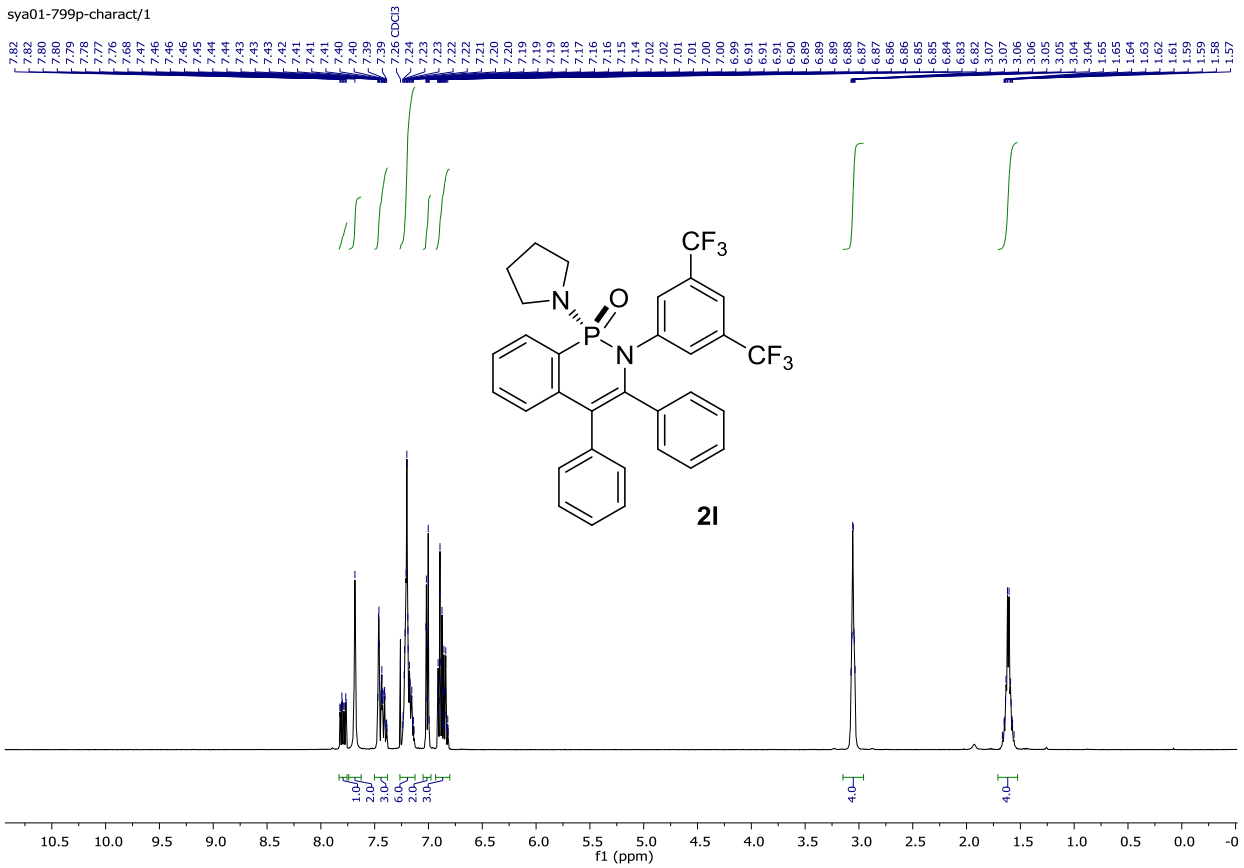
19F cpd

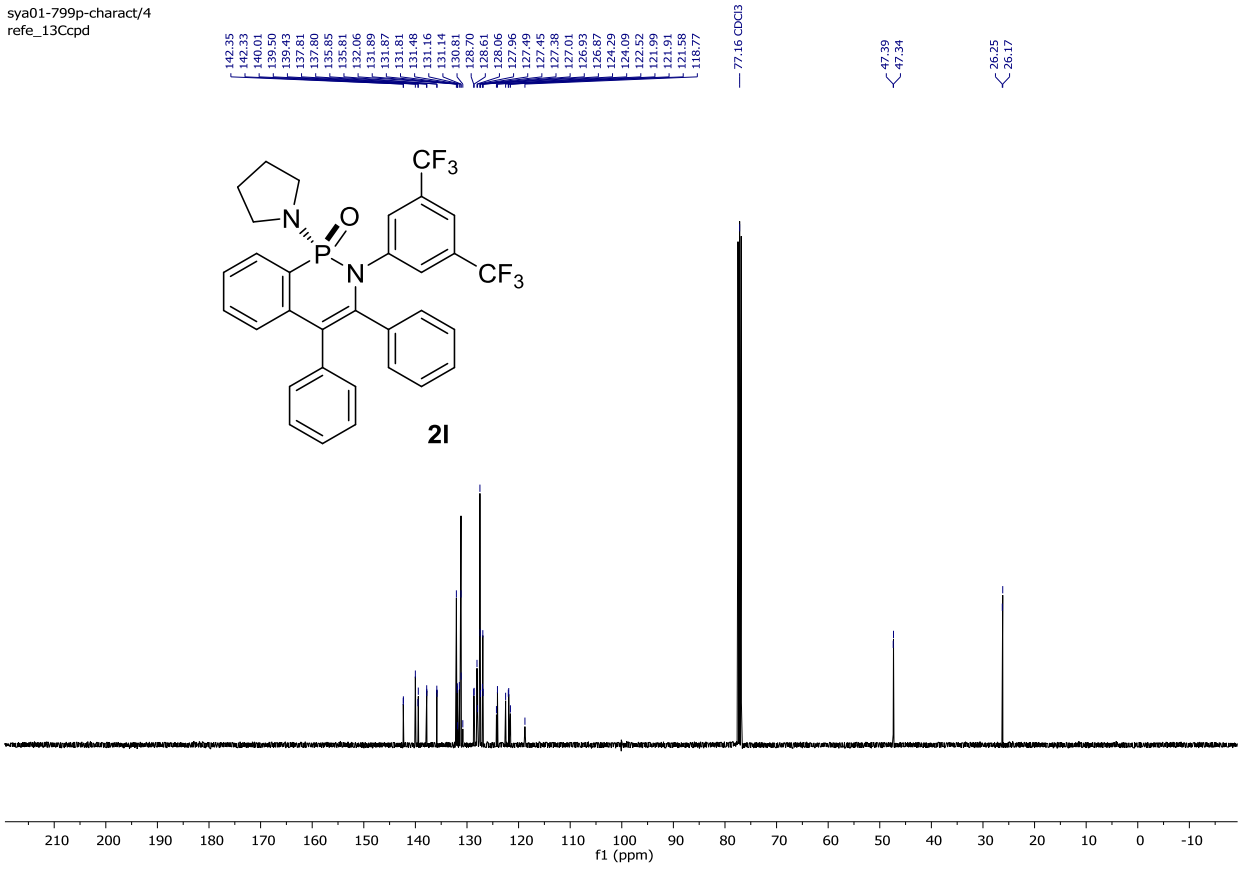






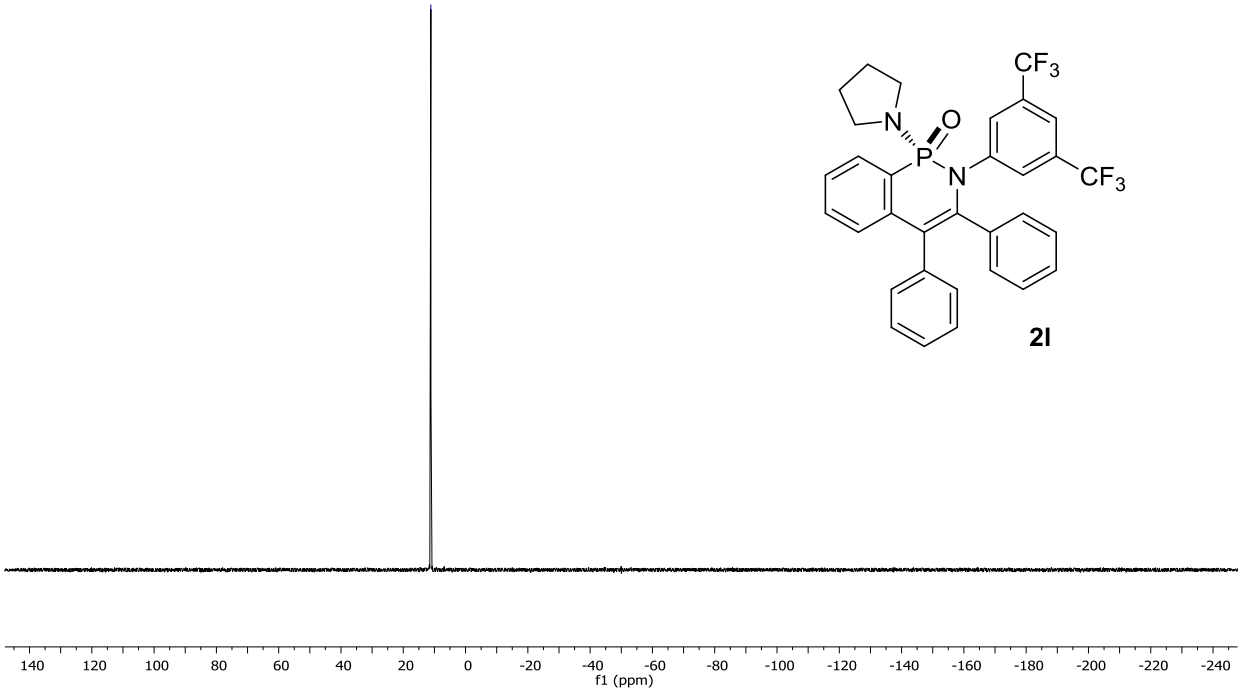
**2k**


sya01-799p-charact/1
CF3
CF3
2l
f1 (ppm)


sya01-799p-charact/4
refe_13Ccpd
77.16 CDCl3
47.39
47.34
26.25
26.17
CF3
CF3
2l
f1 (ppm)

sya01-799p-charact/3
refe_31Pcpd

11.14



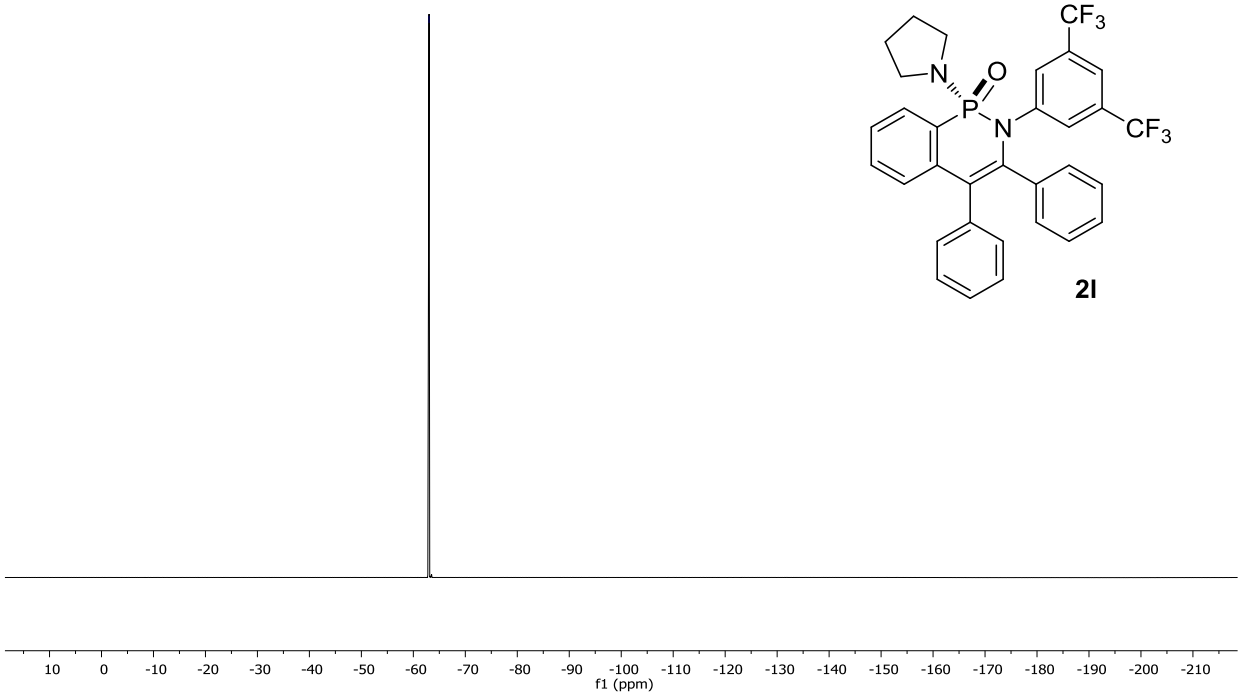




**2l**

sya01-799p-charact/2
refe_F19cpd

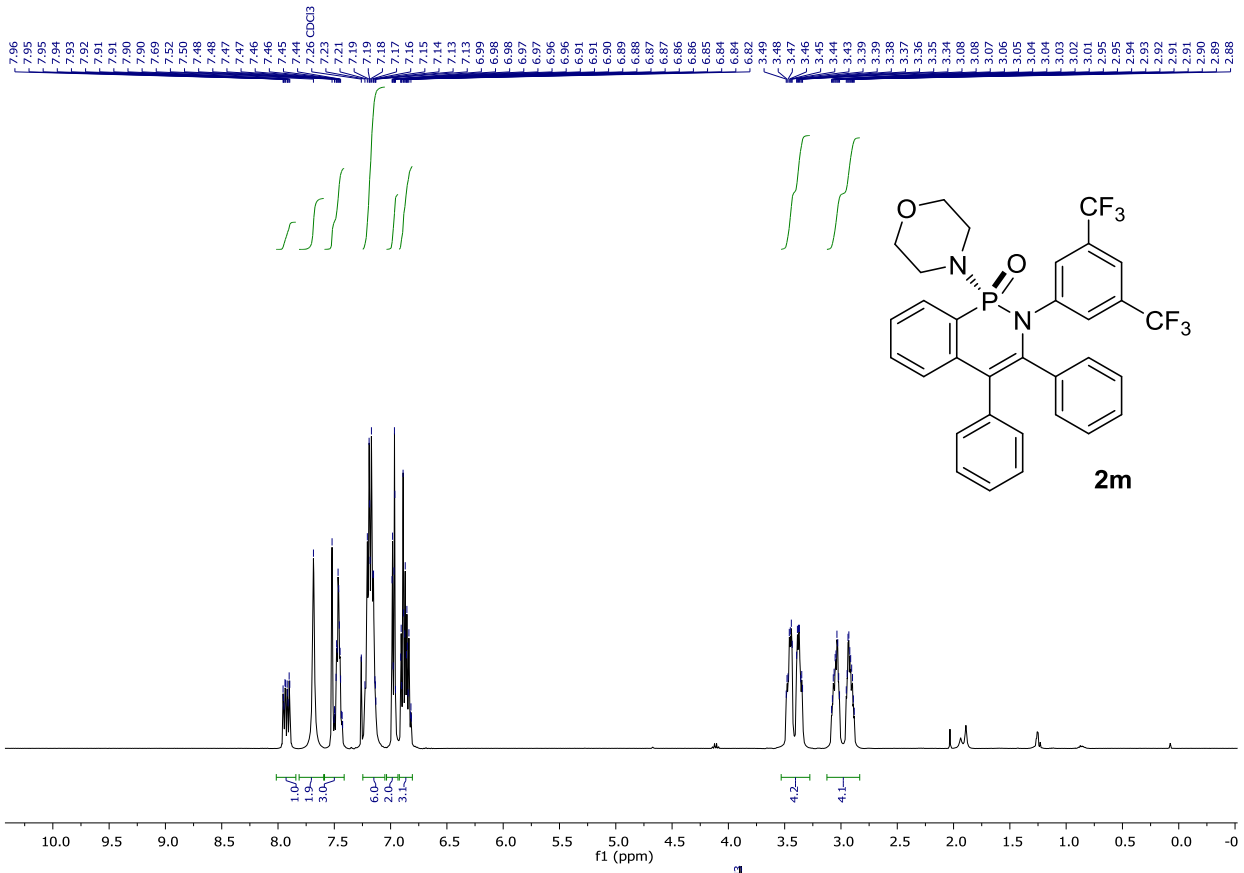
-63.02

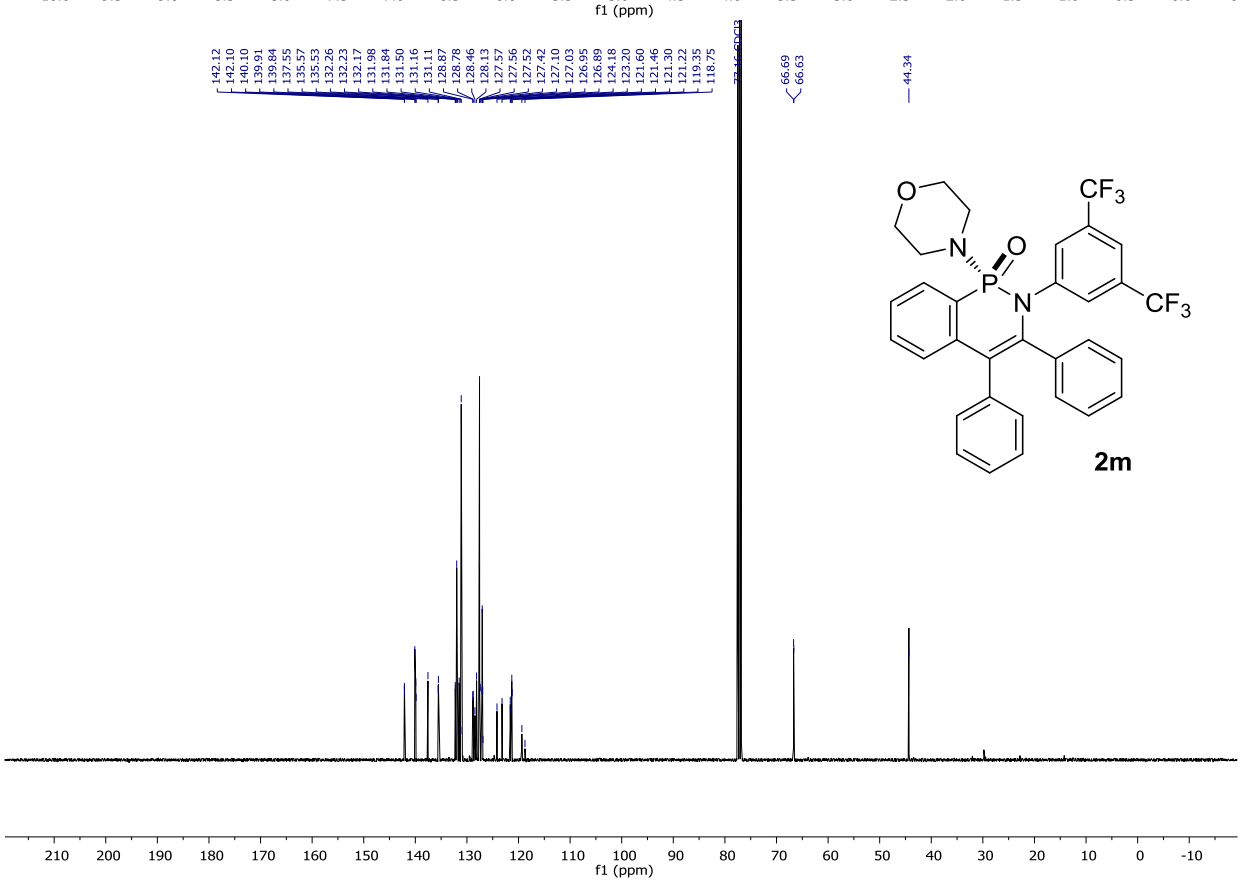




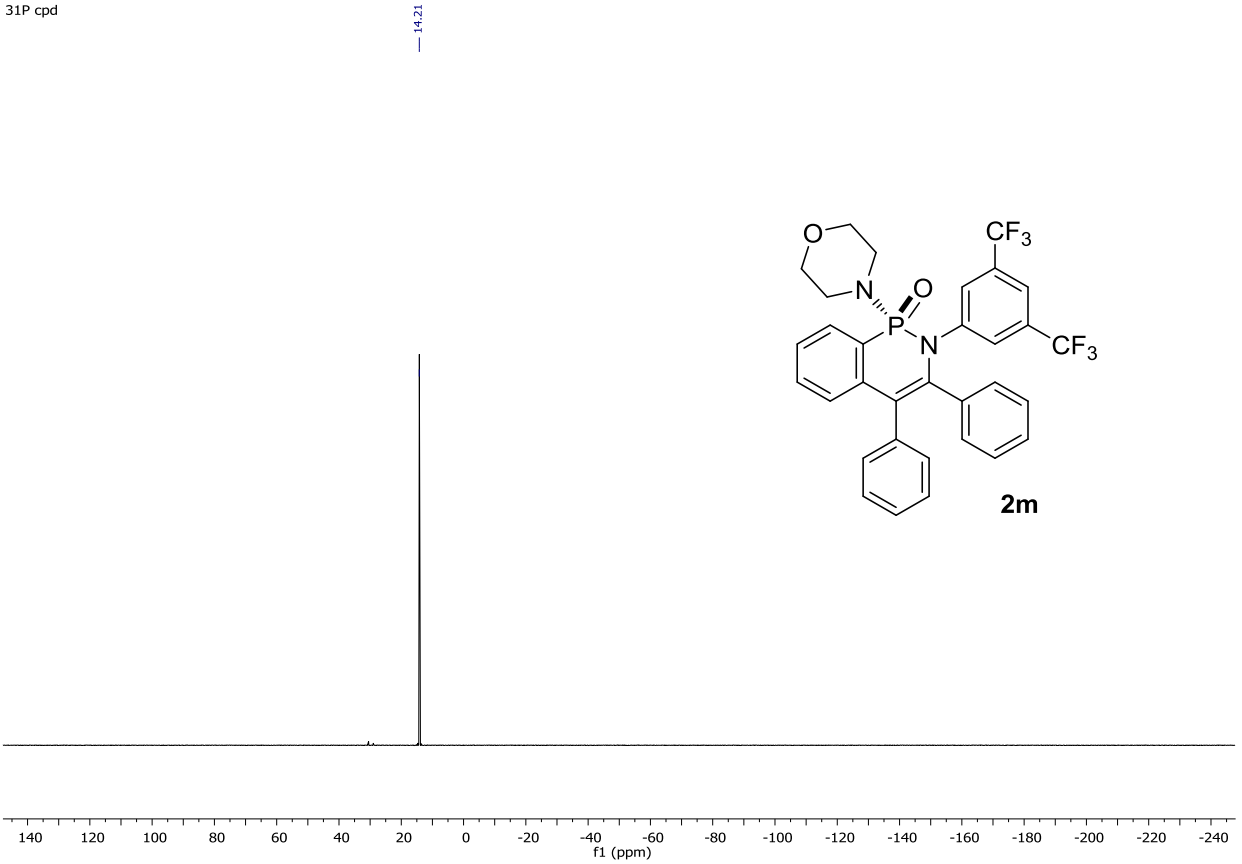


**2l**


7.96 7.95 7.95 7.94 7.93 7.92 7.91 7.91 7.90 7.90 7.90 7.69 7.52 7.50 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.44 7.26 CDCl3 7.23 7.21 7.19 7.19 7.18 7.17 7.16 7.15 7.14 7.13 7.13 6.99 6.98 6.98 6.97 6.97 6.96 6.96 6.91 6.91 6.90 6.89 6.88 6.87 6.87 6.86 6.86 6.85 6.84 6.84 6.82 3.49 3.48 3.47 3.46 3.45 3.44 3.43 3.39 3.39 3.38 3.37 3.36 3.35 3.34 3.08 3.08 3.07 3.06 3.05 3.04 3.04 3.03 3.02 3.01 2.95 2.95 2.94 2.93 2.92 2.91 2.91 2.90 2.89 2.88
O
N
P
O
N
CF3
CF3
2m
1.0 1.9 3.0 6.0 2.0 3.1 4.2 4.1
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


142.12 142.10 140.10 139.91 139.84 137.55 135.57 135.53 132.26 132.23 132.17 131.98 131.84 131.50 131.16 131.11 128.87 128.78 128.46 128.13 127.57 127.56 127.52 127.42 127.10 127.03 126.95 126.89 124.18 123.20 121.60 121.46 121.30 121.22 119.35 118.75 77.46 CDCl3 66.69 66.63 44.34
O
N
P
O
N
CF3
CF3
2m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

31P cpd

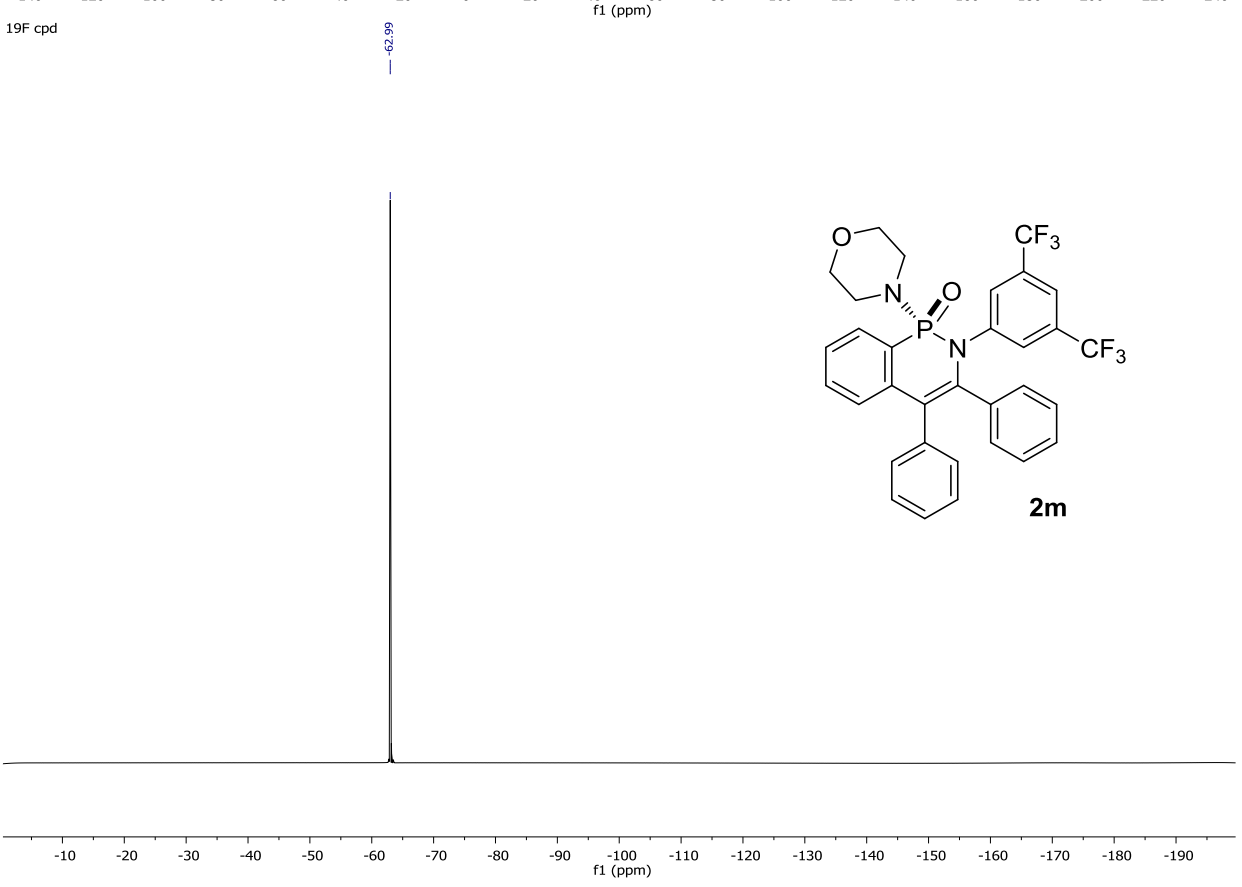






**2m**

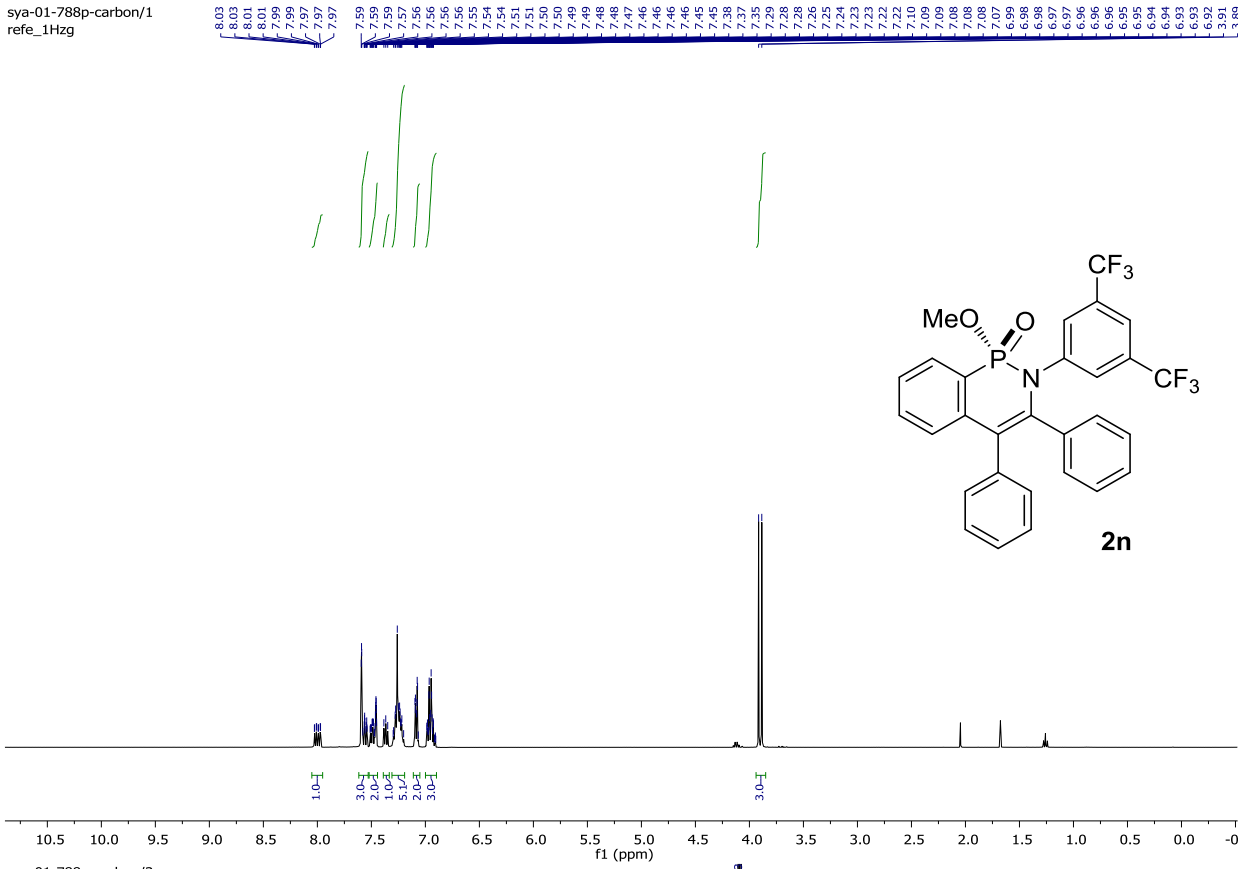
19F cpd

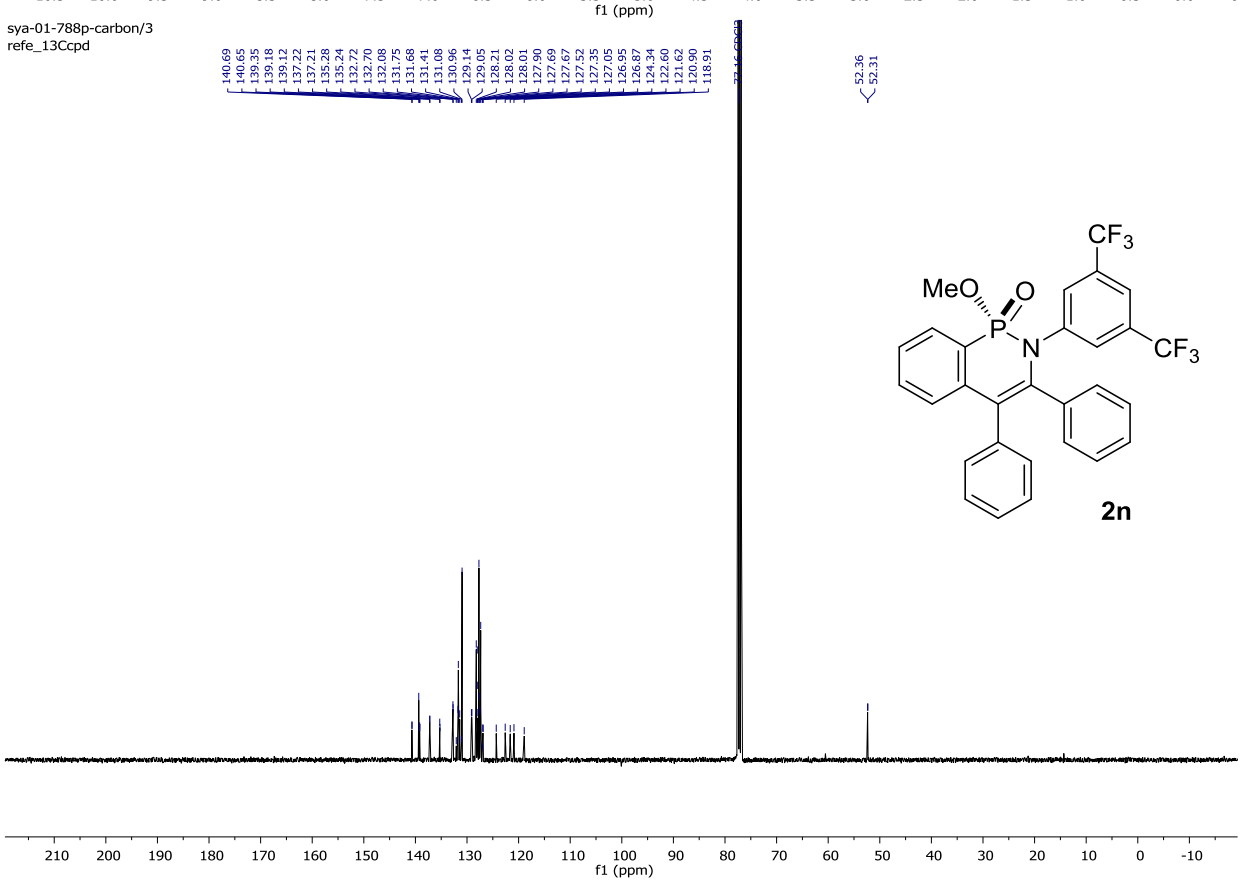






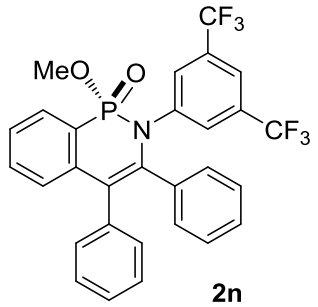
**2m**


sya-01-788p-carbon/1
refe_1Hzg
MeO
O
P
N
CF3
CF3
2n
f1 (ppm)


sya-01-788p-carbon/3
refe_13Ccpd
MeO
O
P
N
CF3
CF3
2n
f1 (ppm)

sya01-788p.2.fid
refe_31P_cpd CDCl3 /opt/ ysun 58

13.36

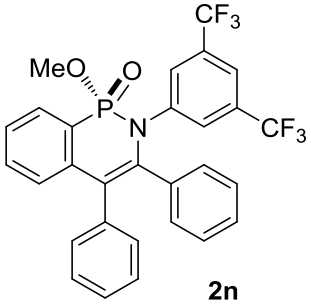



**2n**

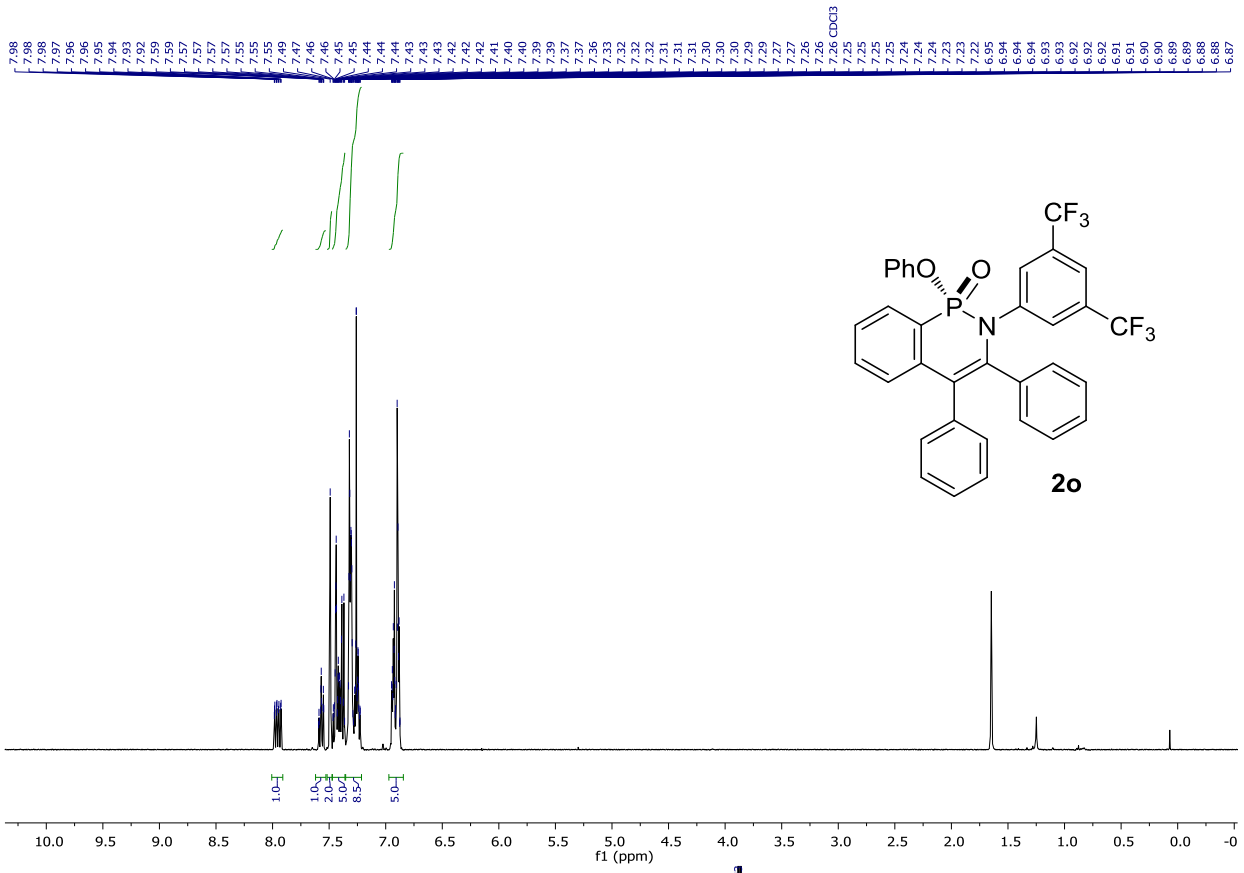


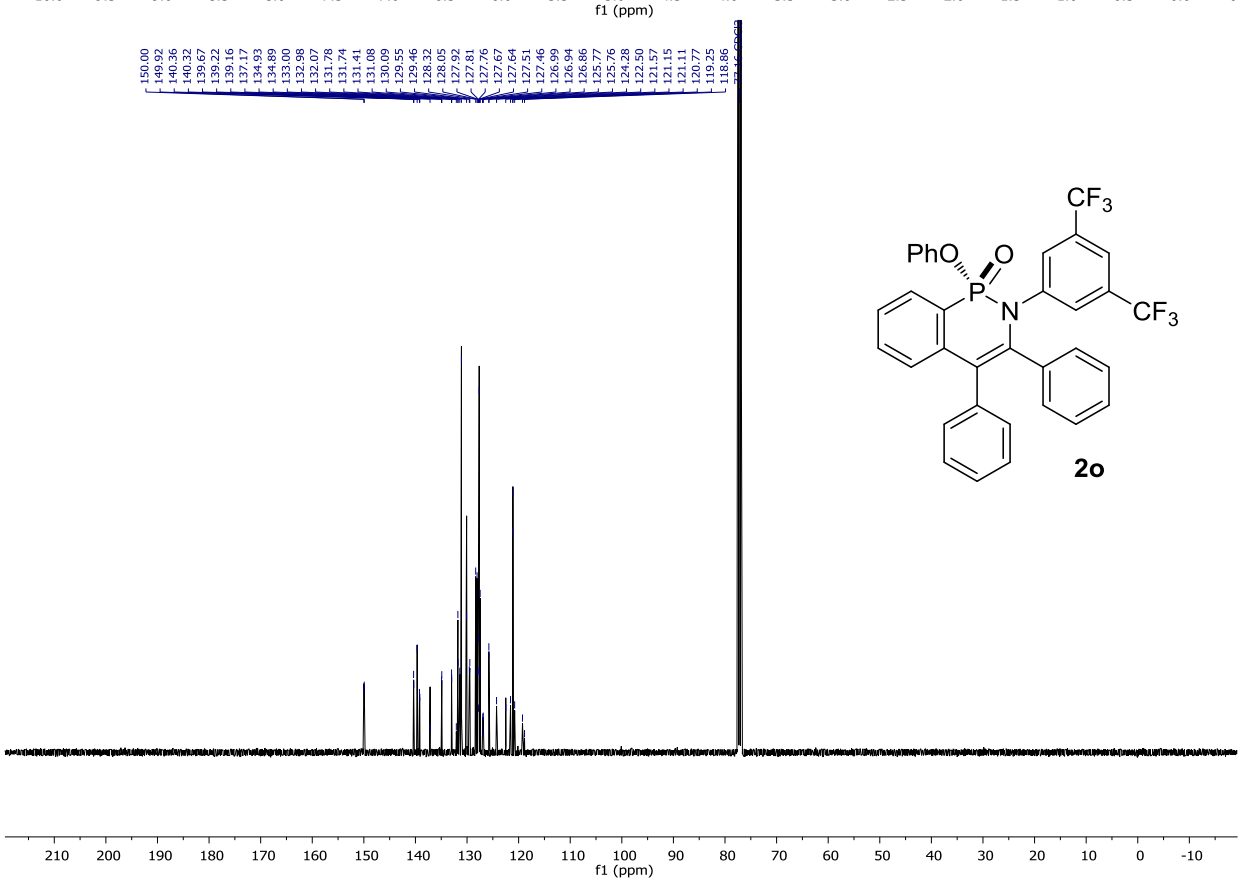

sya01-788p.3.fid
refe_19F_cpd CDCl3 /opt/ ysun 58

-63.02

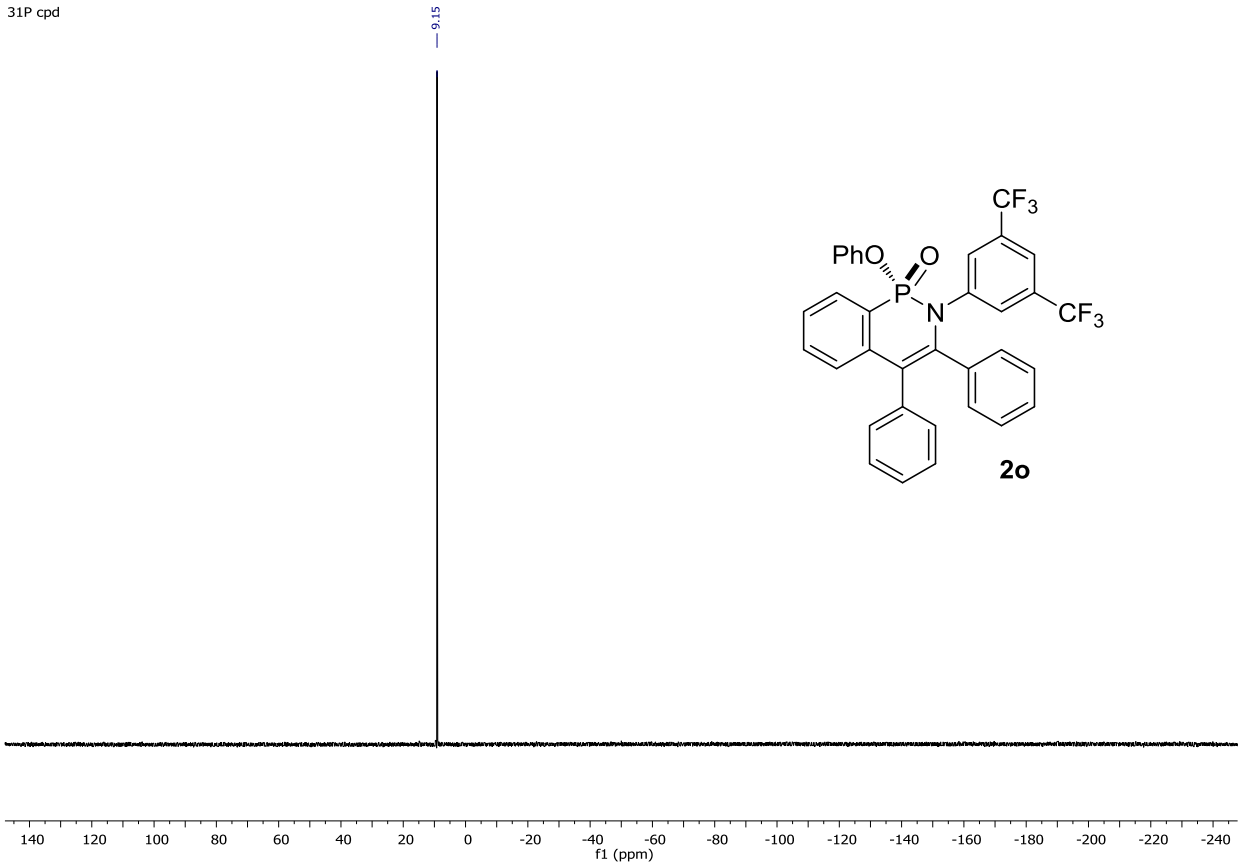



**2n**


CF3
PhO
O
P
N
CF3
2o
f1 (ppm)


CF3
PhO
O
P
N
CF3
2o
f1 (ppm)

31P cpd

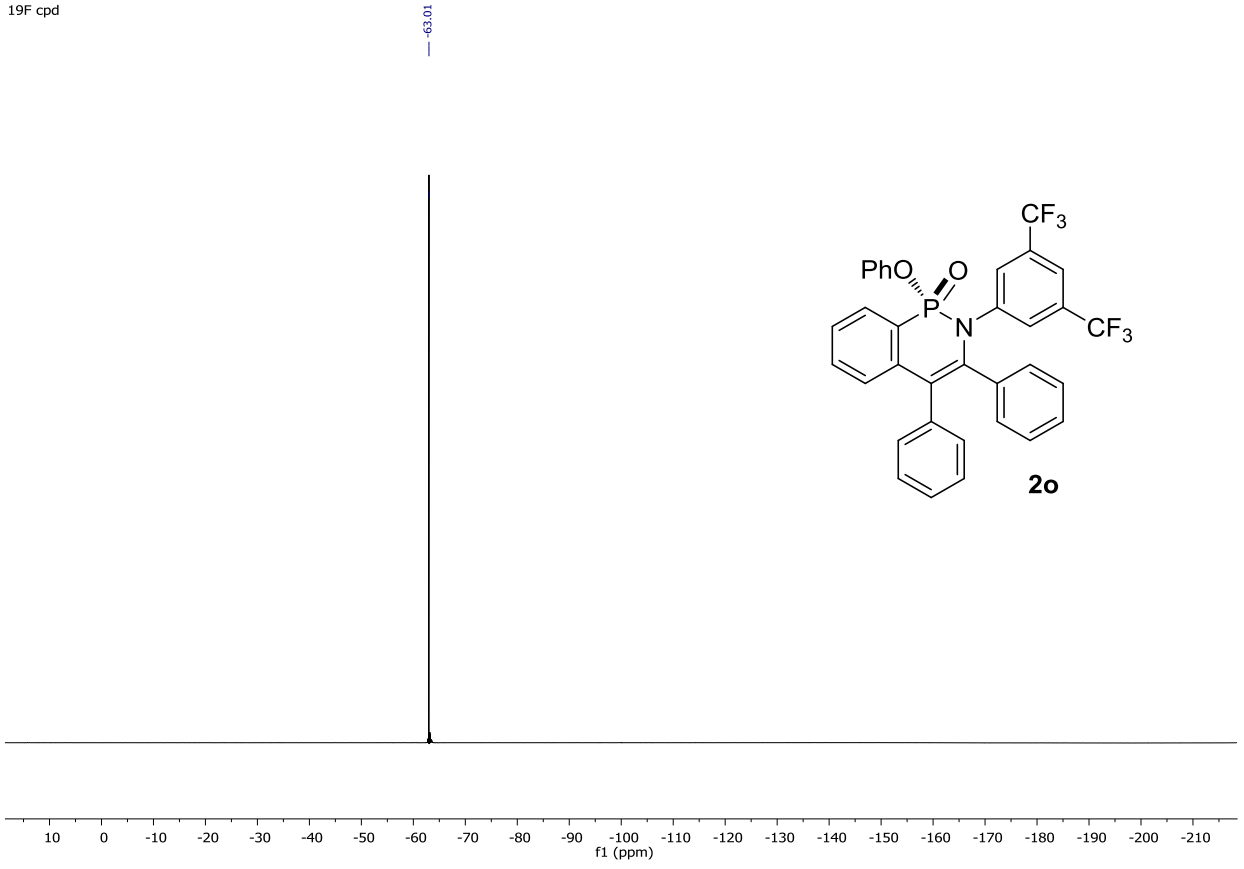






**2o**

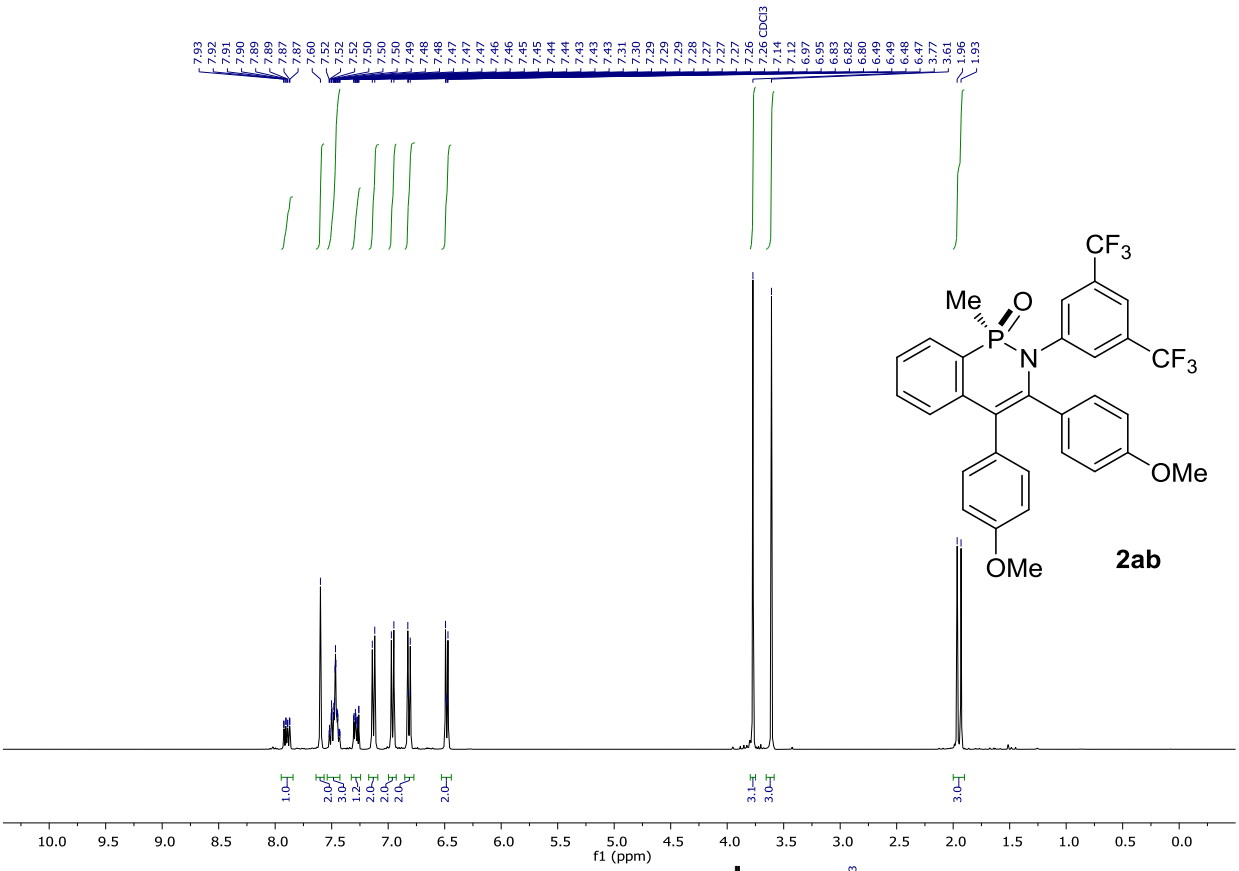
19F cpd

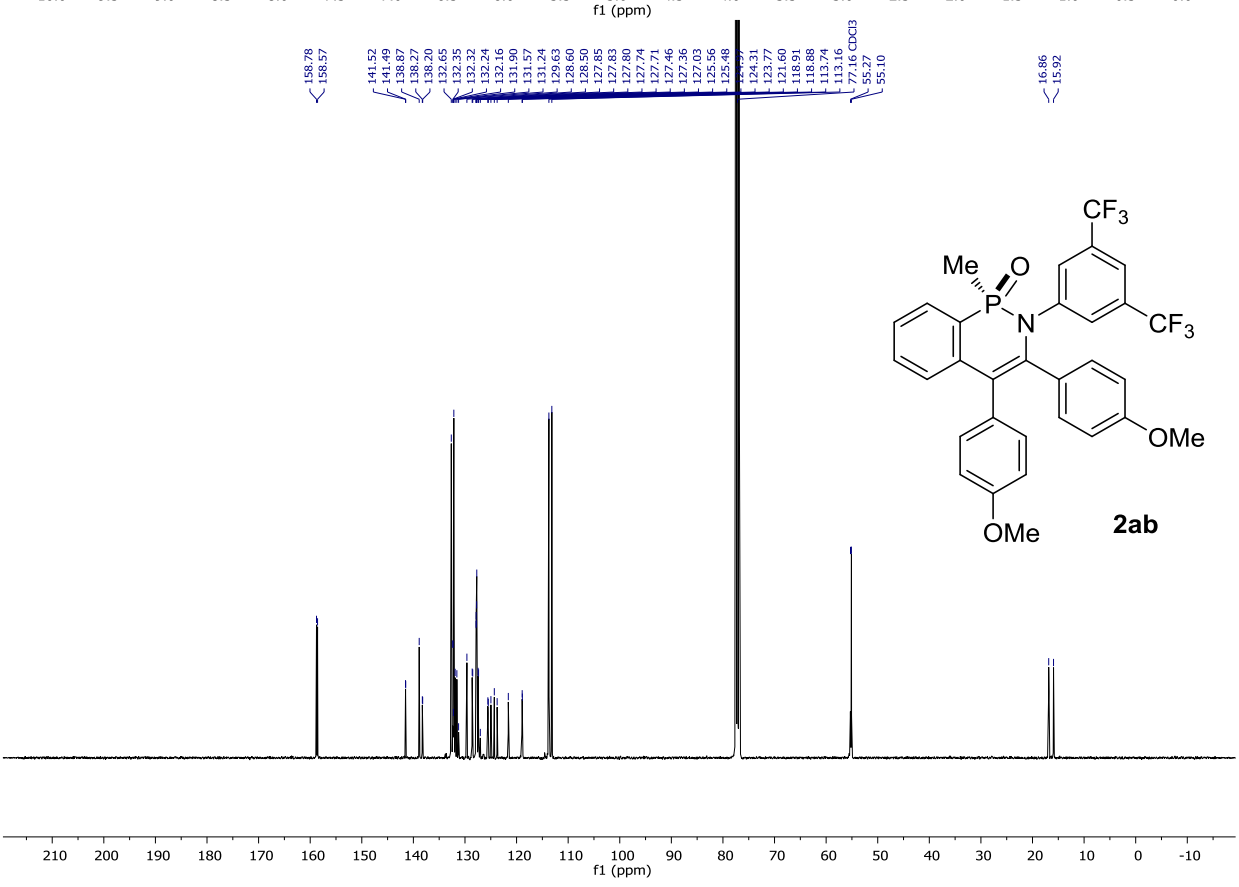




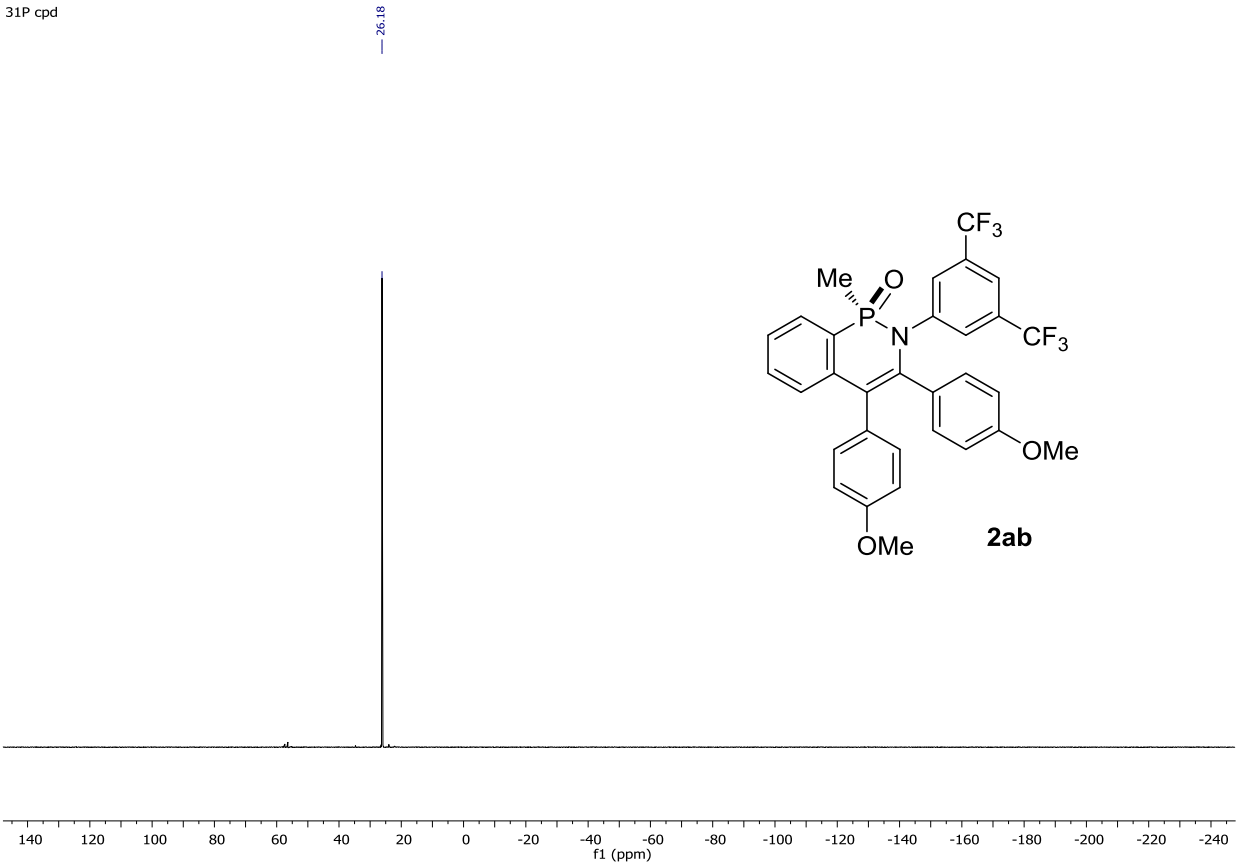


**2o**

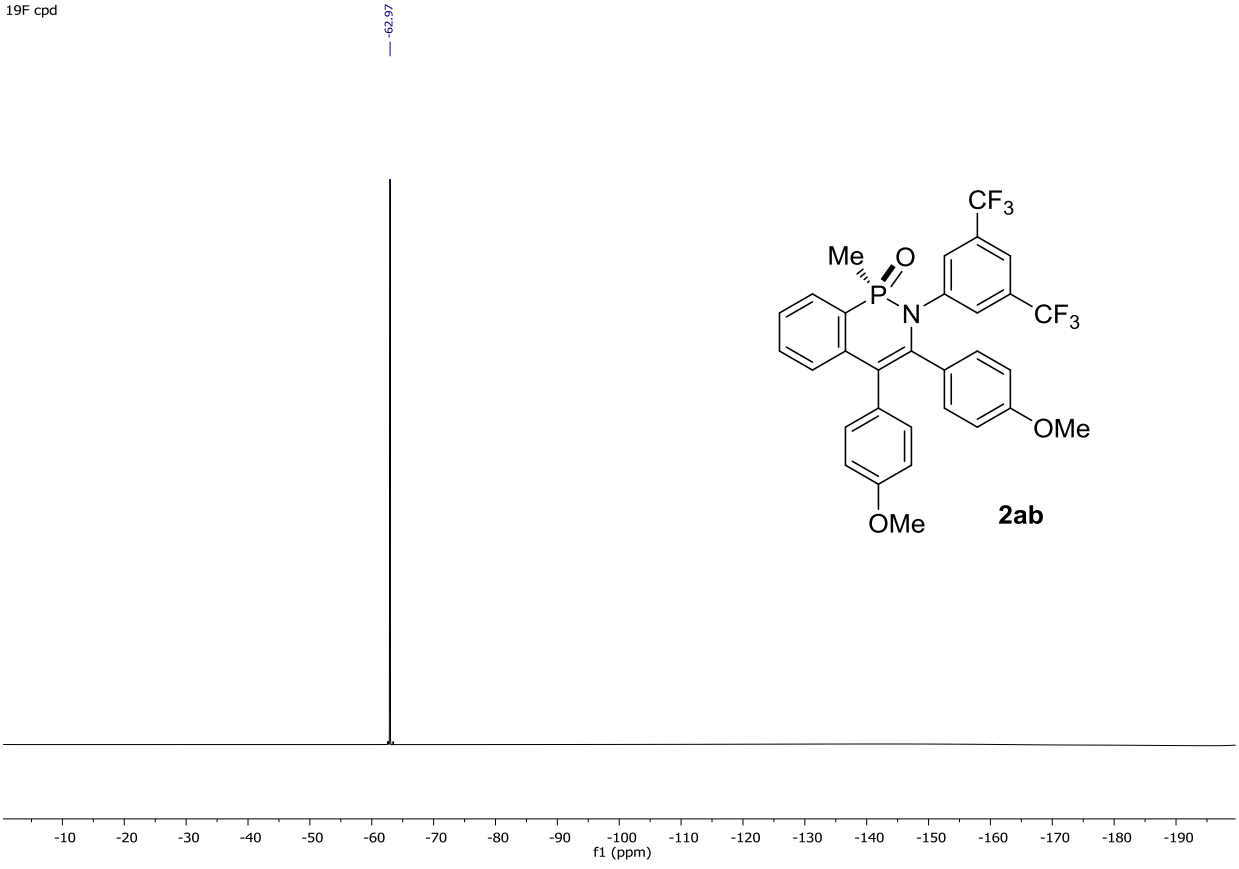

7.93 7.92 7.91 7.90 7.89 7.89 7.87 7.87 7.60 7.52 7.52 7.52 7.50 7.50 7.50 7.49 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.31 7.30 7.29 7.29 7.29 7.28 7.27 7.27 7.27 7.26 CDCl3 7.14 7.12 6.97 6.95 6.83 6.82 6.80 6.49 6.48 6.47 3.77 3.61 1.96 1.93
1.0 2.0 3.0 1.2 2.0 2.0 2.0 2.0 3.1 3.0 3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Me O P N CF3 CF3 OMe OMe
2ab

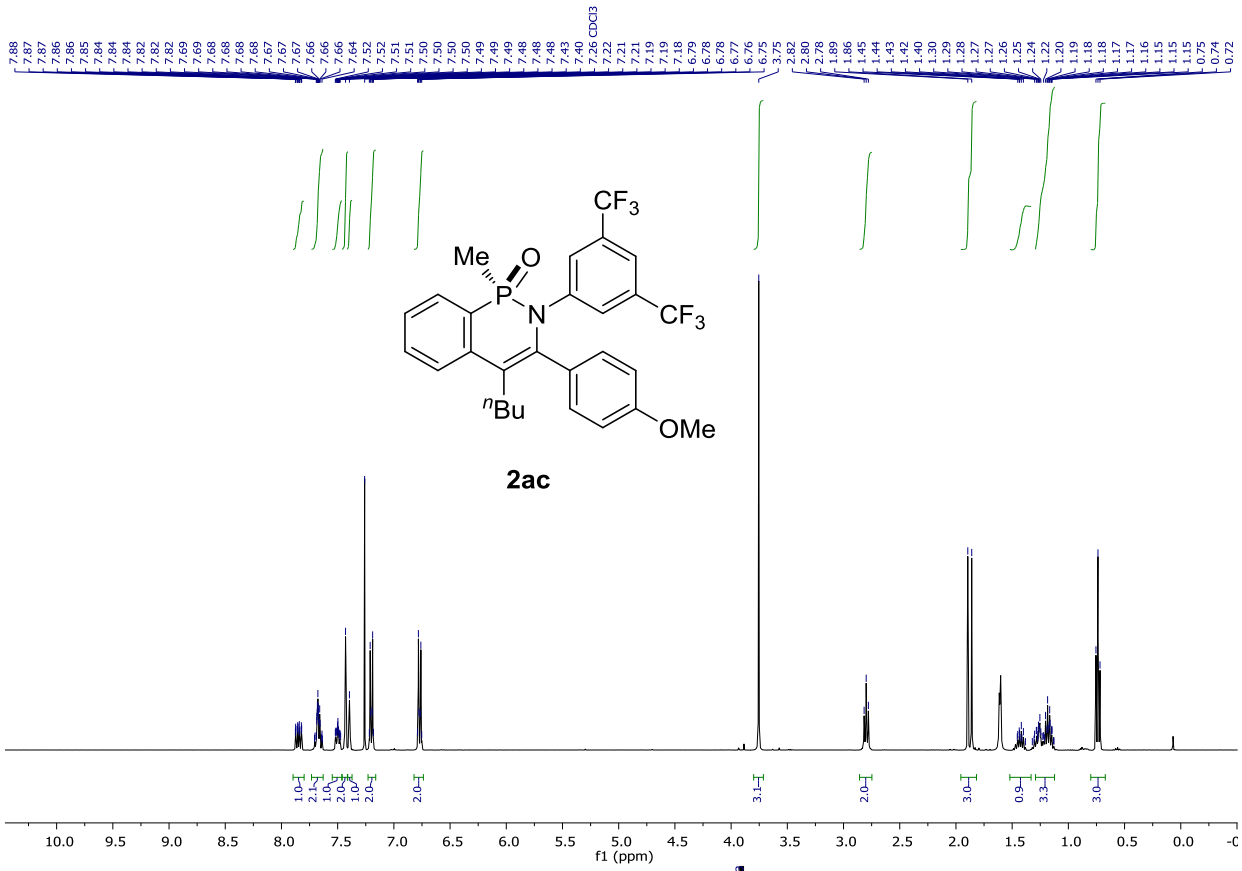

158.78 158.57 141.52 141.49 138.87 138.27 138.20 132.65 132.35 132.32 132.24 132.16 131.90 131.57 131.24 129.63 128.60 128.50 127.85 127.83 127.80 127.74 127.71 127.46 127.36 127.03 125.56 125.48 124.31 123.77 121.60 118.91 118.88 113.74 113.16 77.16 CDCl3 55.27 55.10 16.86 15.92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Me O P N CF3 CF3 OMe OMe
2ab

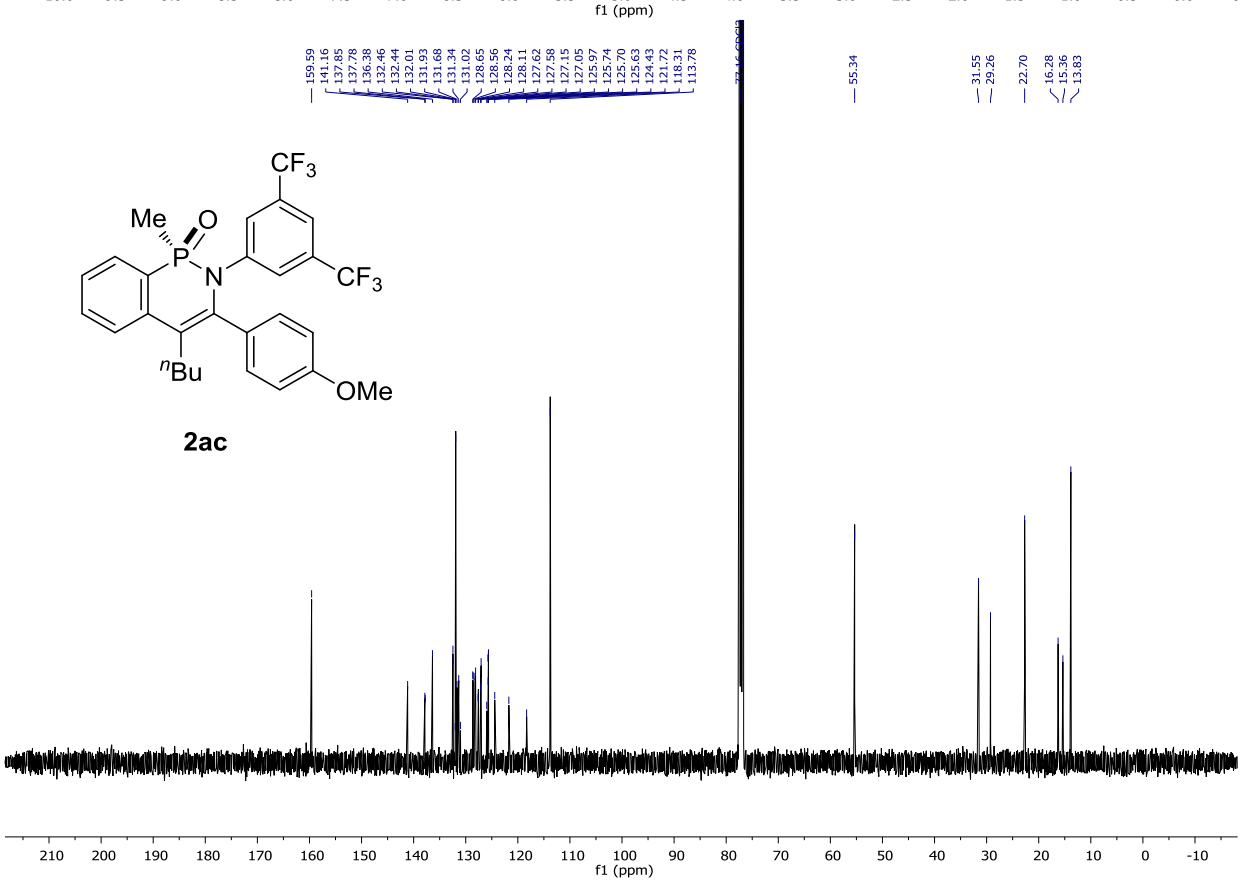
31P cpd




19F cpd

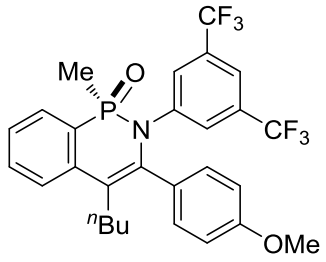



CF3
Me
O
P
N
CF3
nBu
OMe
2ac
f1 (ppm)


CF3
Me
O
P
N
CF3
nBu
OMe
2ac
f1 (ppm)

31P cpd

27.51

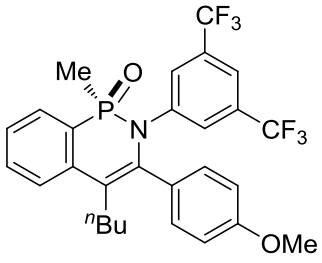



**2ac**

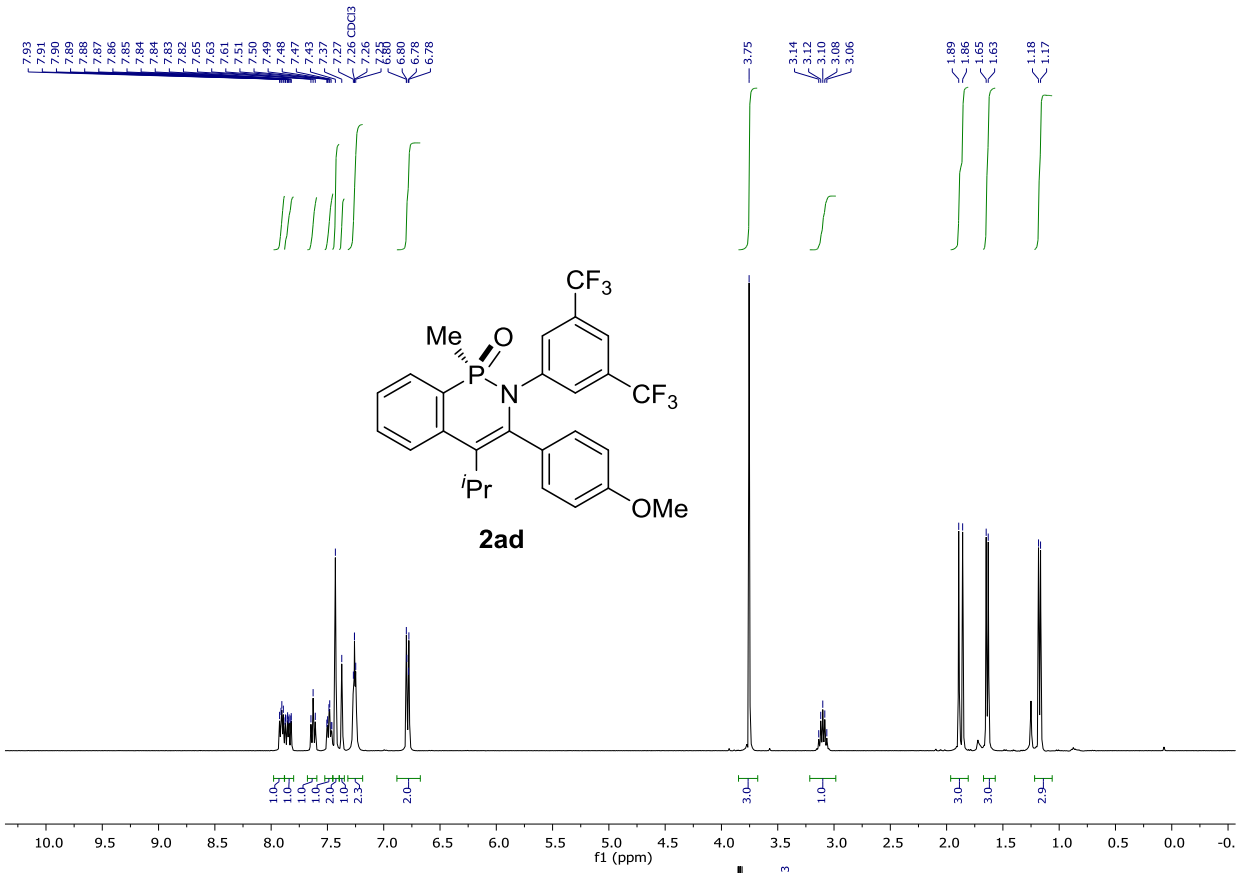


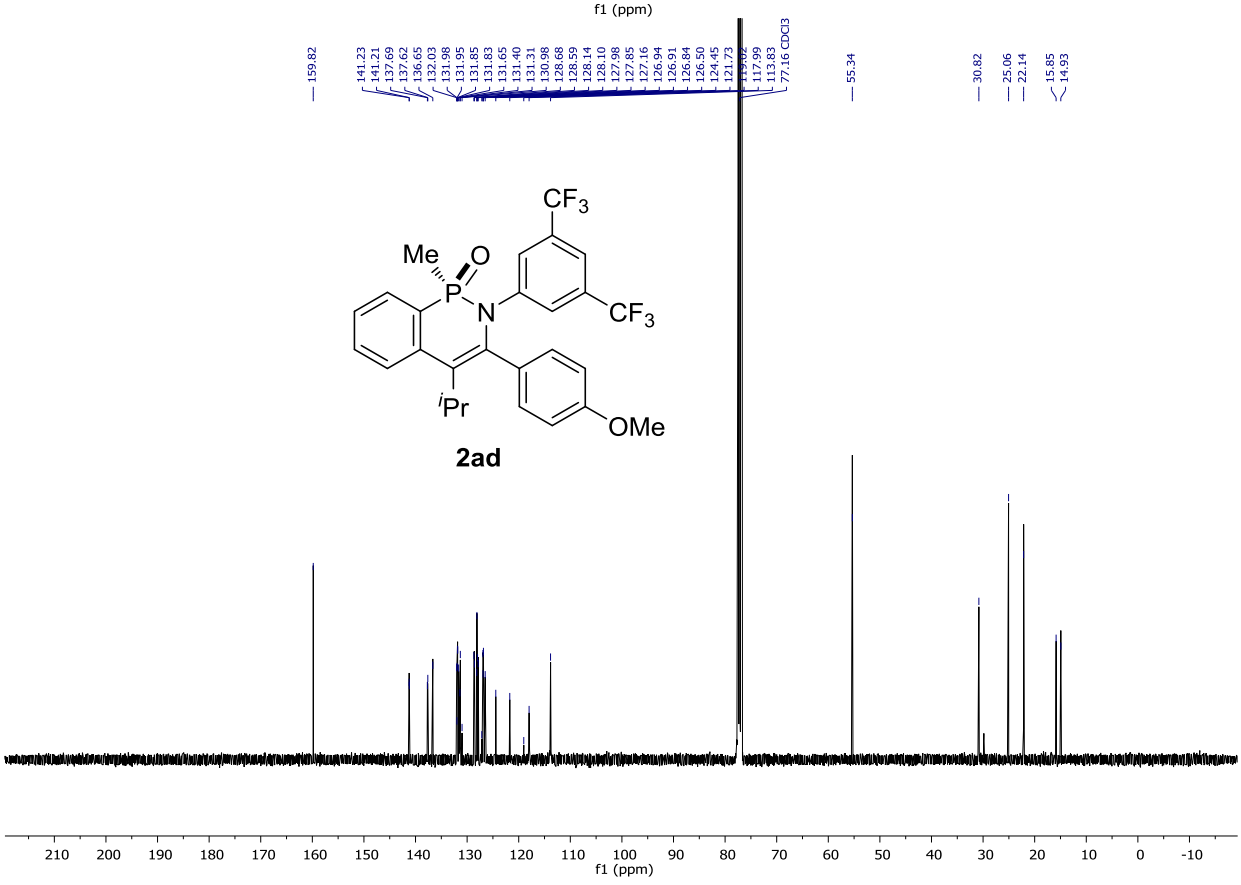

19F cpd

-62.97

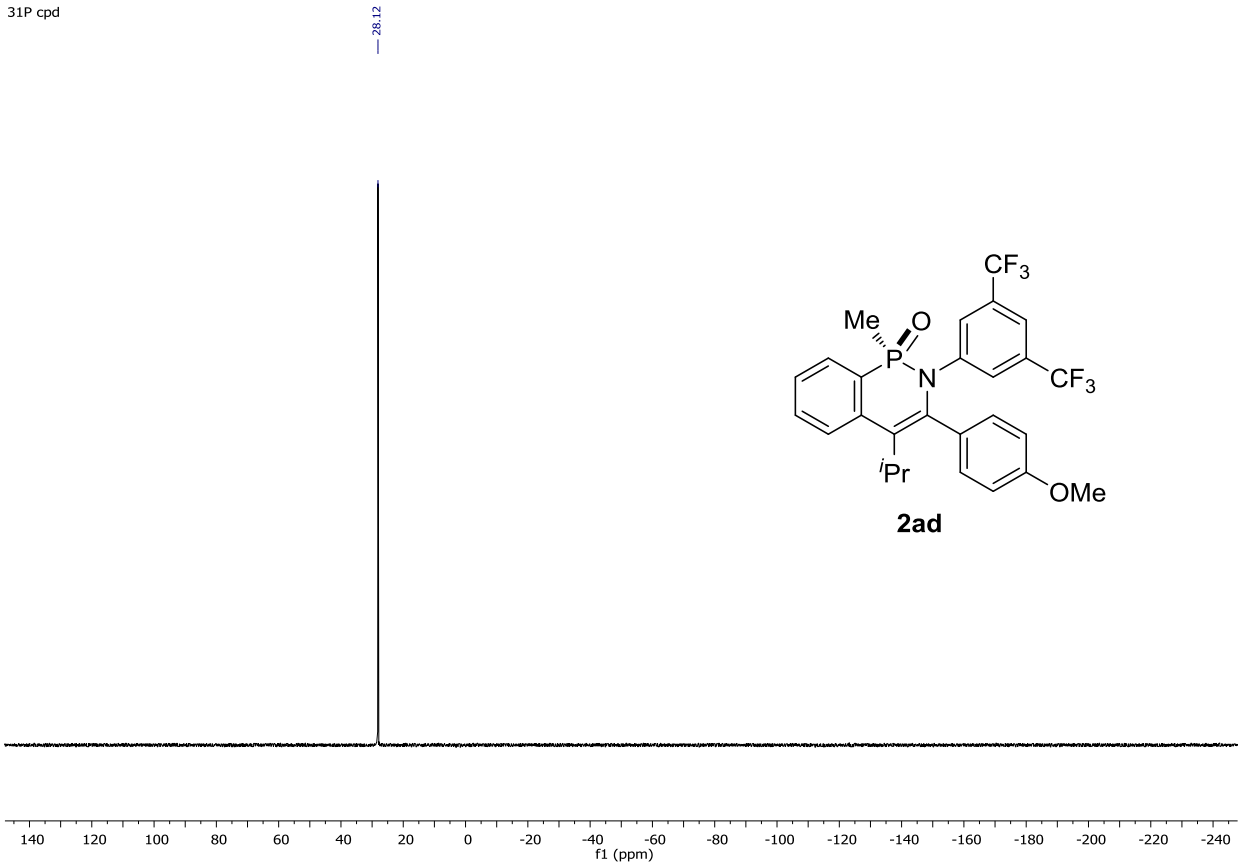



**2ac**


7.93
7.91
7.90
7.89
7.88
7.87
7.86
7.85
7.84
7.84
7.83
7.82
7.65
7.63
7.61
7.51
7.50
7.49
7.48
7.47
7.43
7.37
7.27
7.26 CDCl3
6.80
6.78
6.78
3.75
3.14
3.12
3.10
3.08
3.06
1.89
1.86
1.65
1.63
1.18
1.17
CF3
Me
O
P
N
CF3
iPr
OMe
2ad
f1 (ppm)

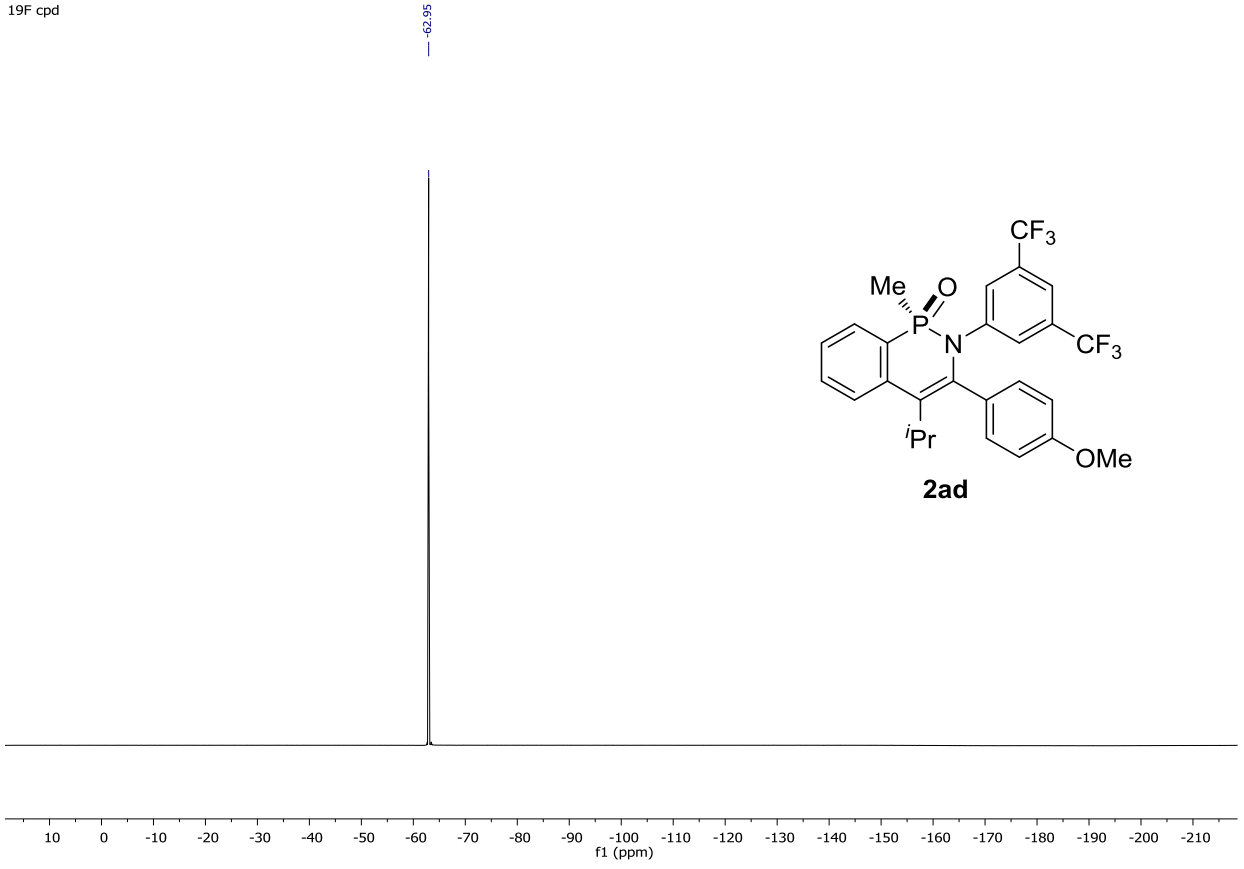

159.82
141.23
141.21
137.69
137.62
136.65
132.03
131.98
131.95
131.85
131.83
131.65
131.40
131.31
130.98
128.68
128.59
128.14
128.10
127.98
127.85
127.16
126.94
126.91
126.84
126.50
124.45
121.73
117.99
113.83
77.16 CDCl3
55.34
30.82
25.06
22.14
15.85
14.93
CF3
Me
O
P
N
CF3
iPr
OMe
2ad
f1 (ppm)

31P cpd

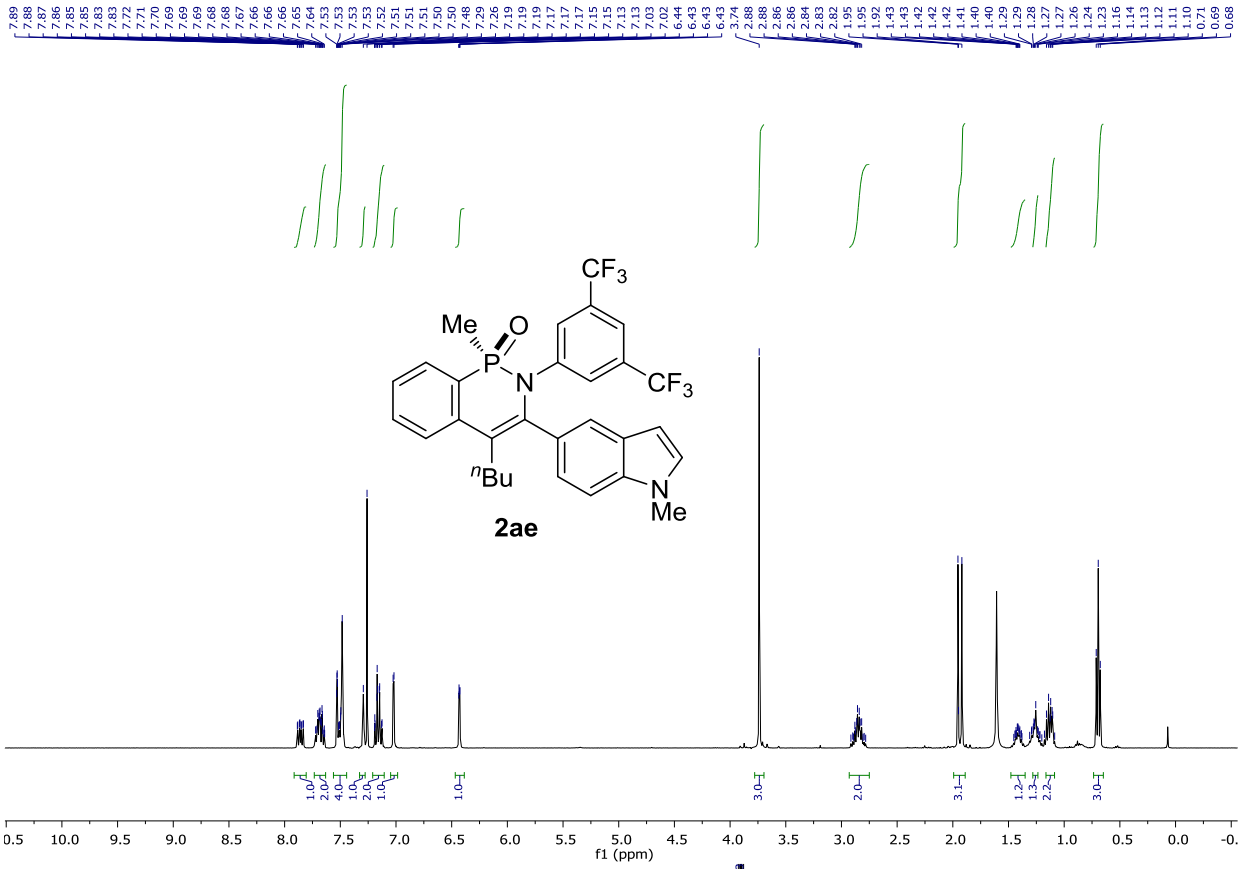


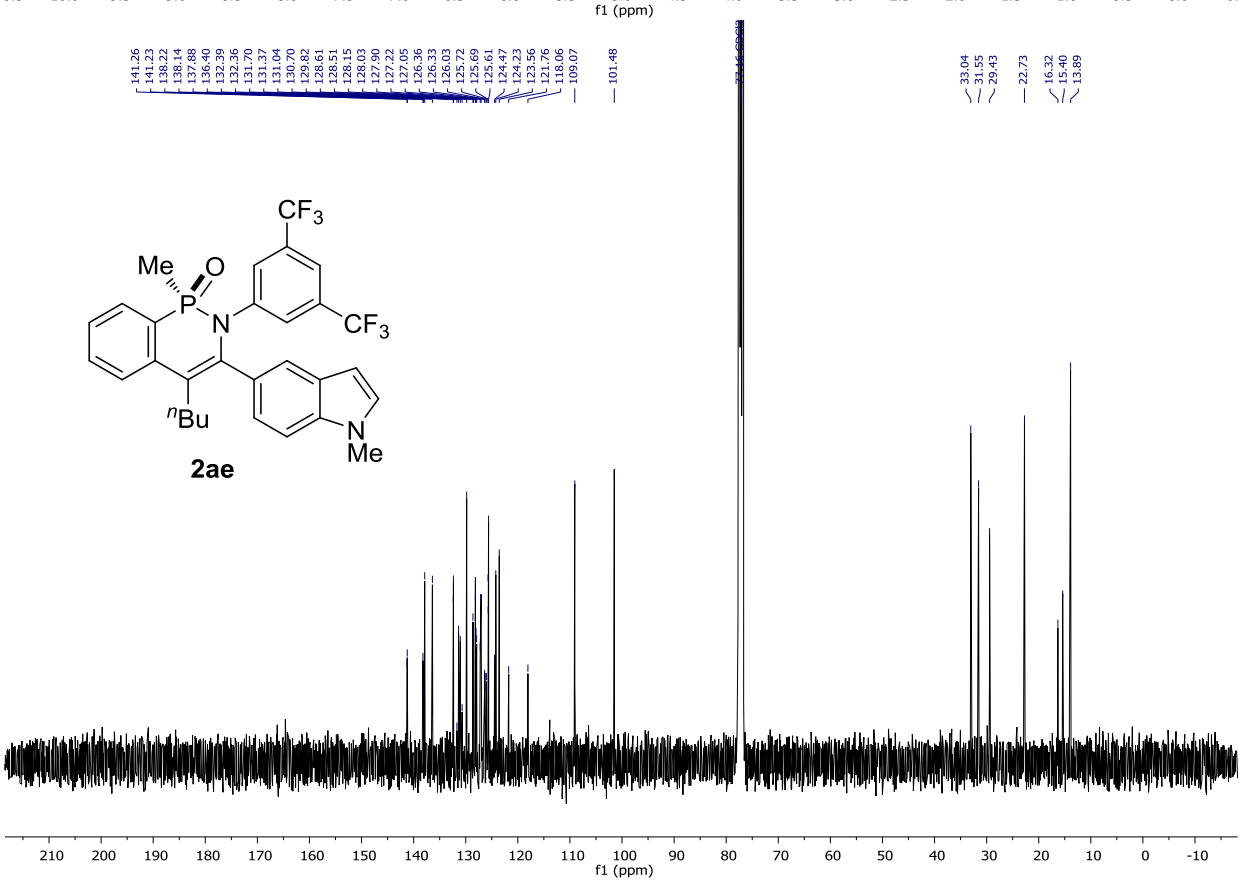

**2ad**

19F cpd



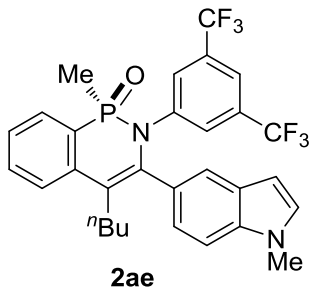

**2ad**


CF3
Me
O
P
N
CF3
nBu
N
Me
2ae
f1 (ppm)


CF3
Me
O
P
N
CF3
nBu
N
Me
2ae
f1 (ppm)

31P cpd

27.84

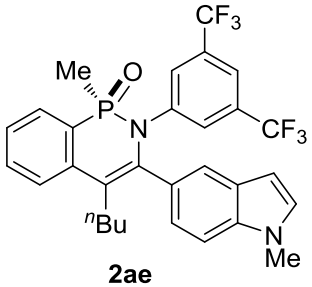



**2ae**

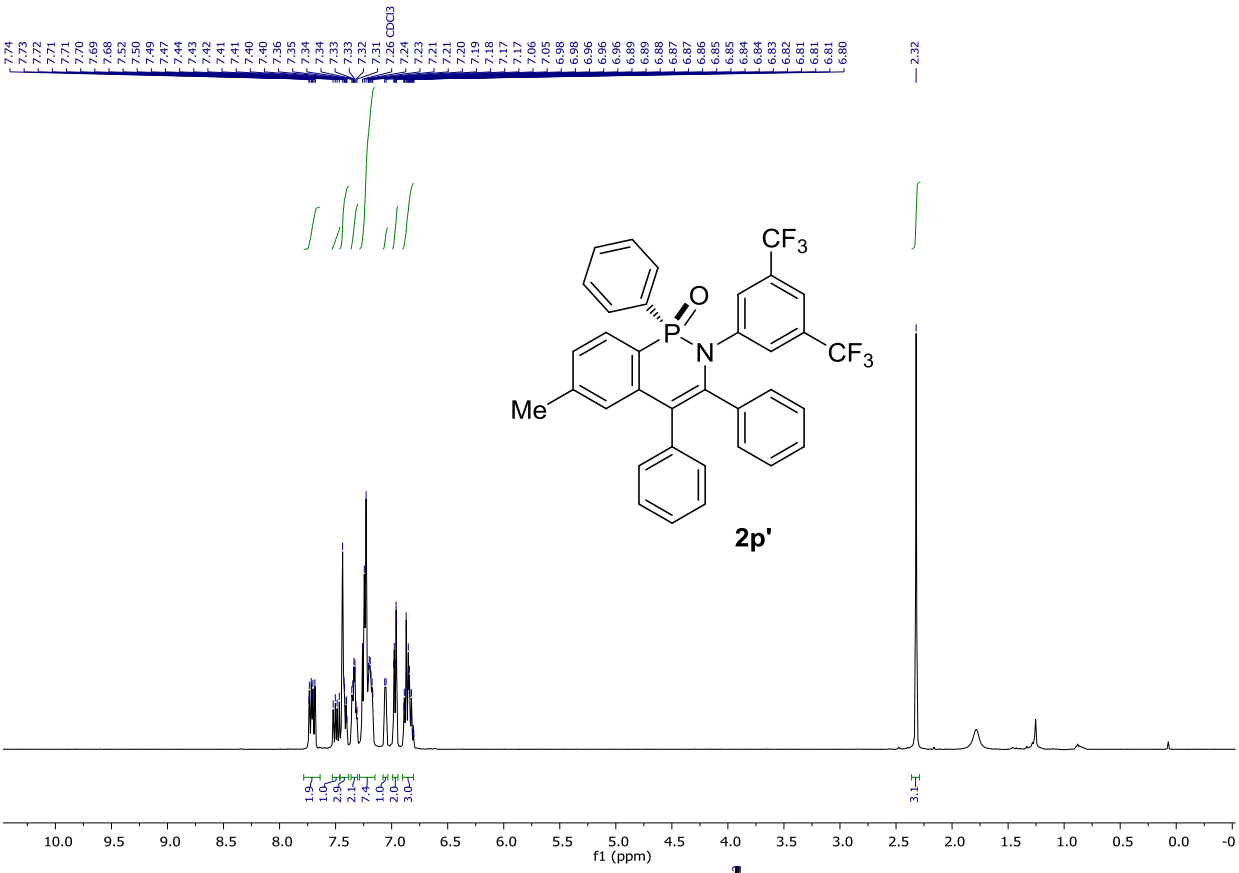


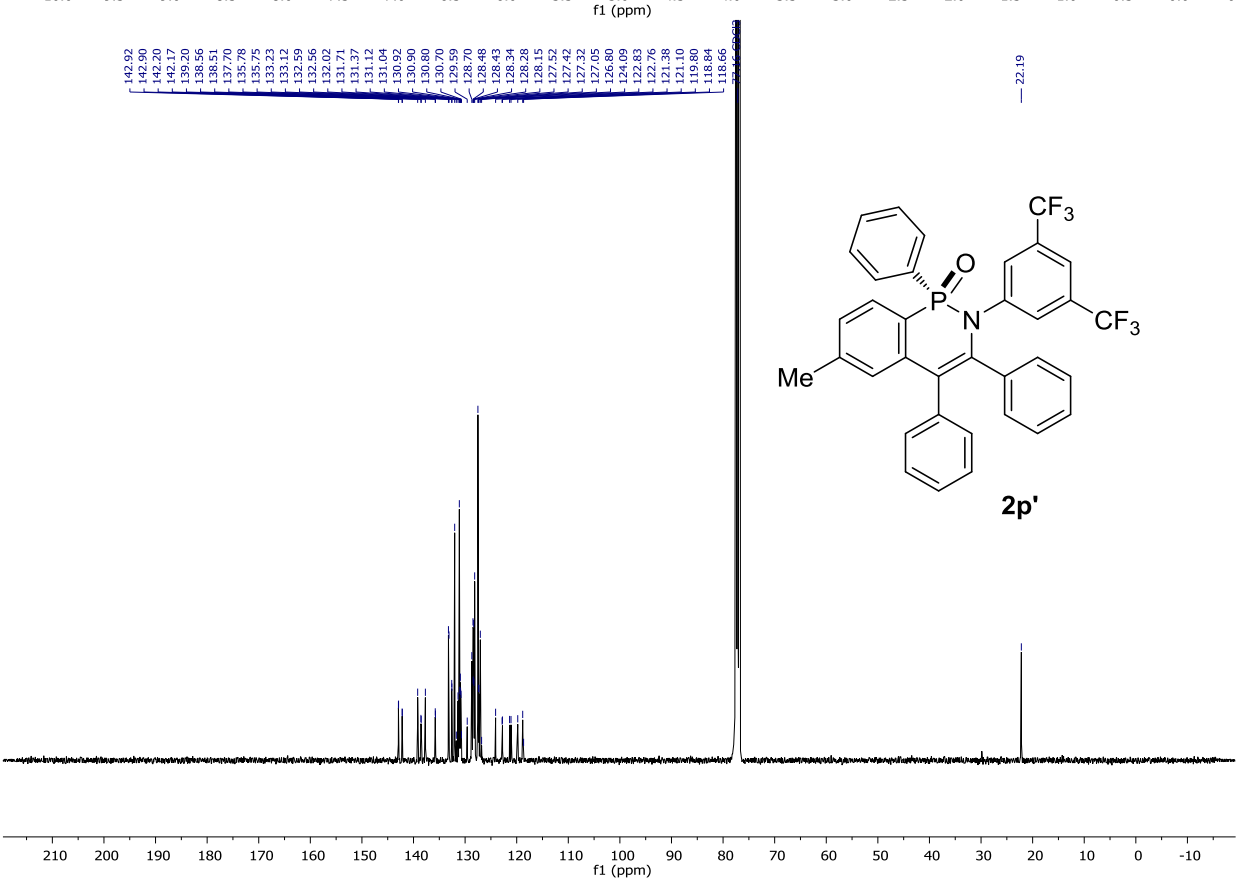

19F cpd

-62.96

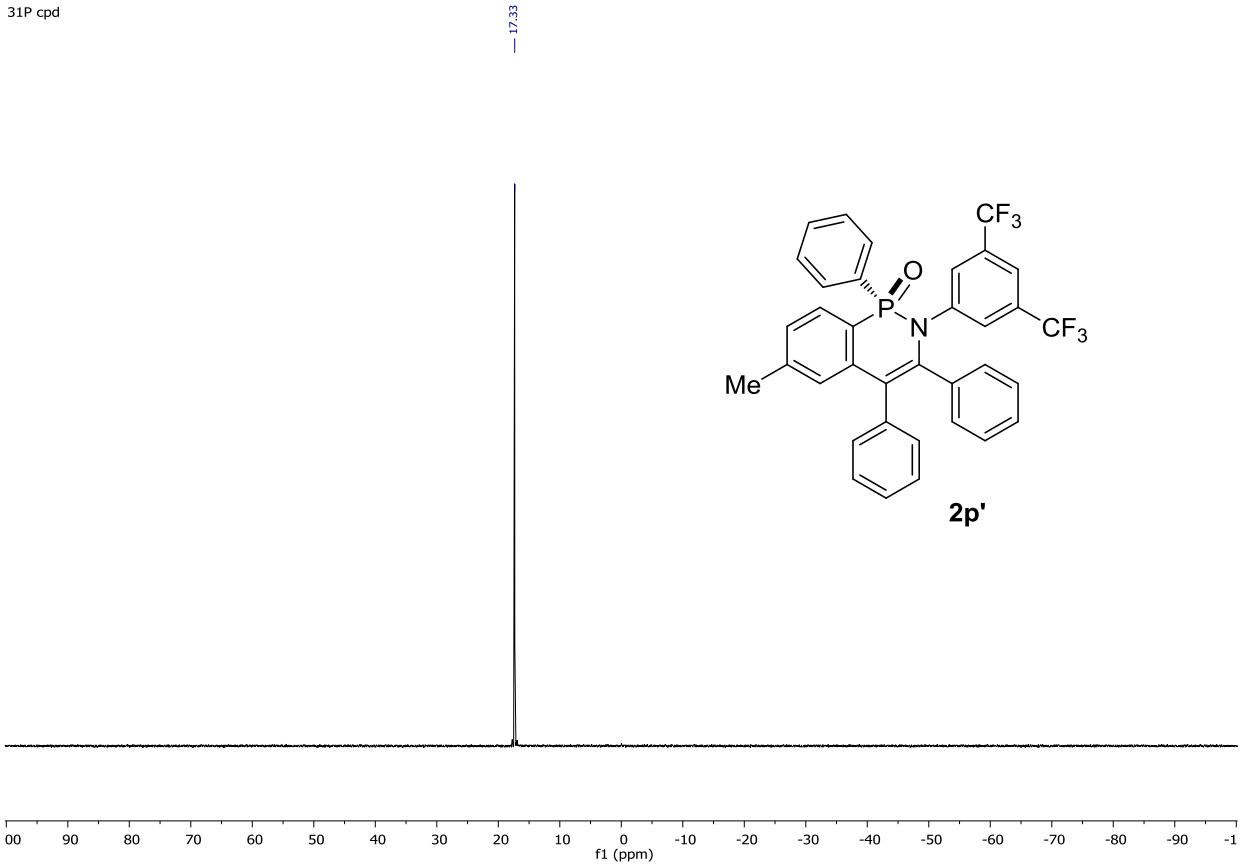



**2ae**


CF3
O
P
N
CF3
Me
2p'


CF3
O
P
N
CF3
Me
2p'
f1 (ppm)

31P cpd

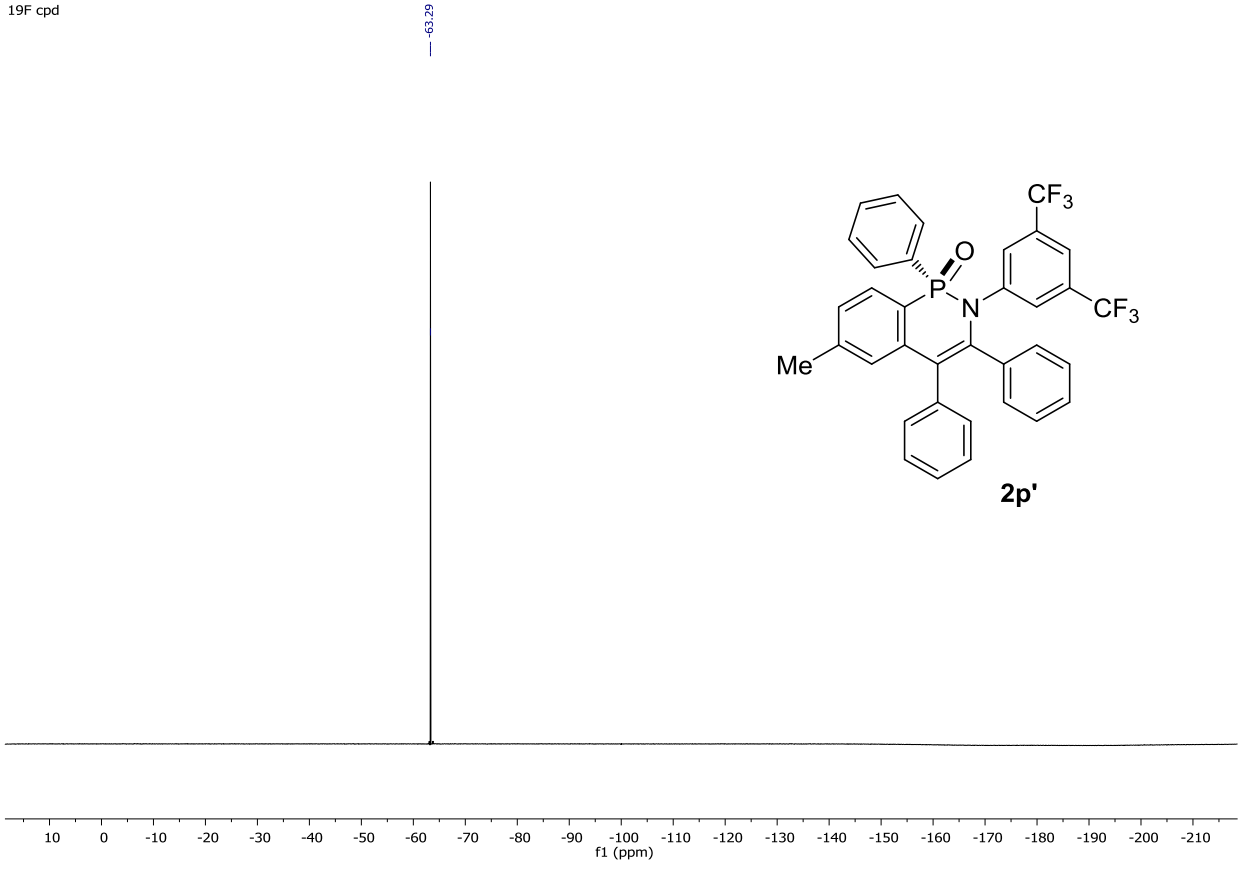






**2p'**

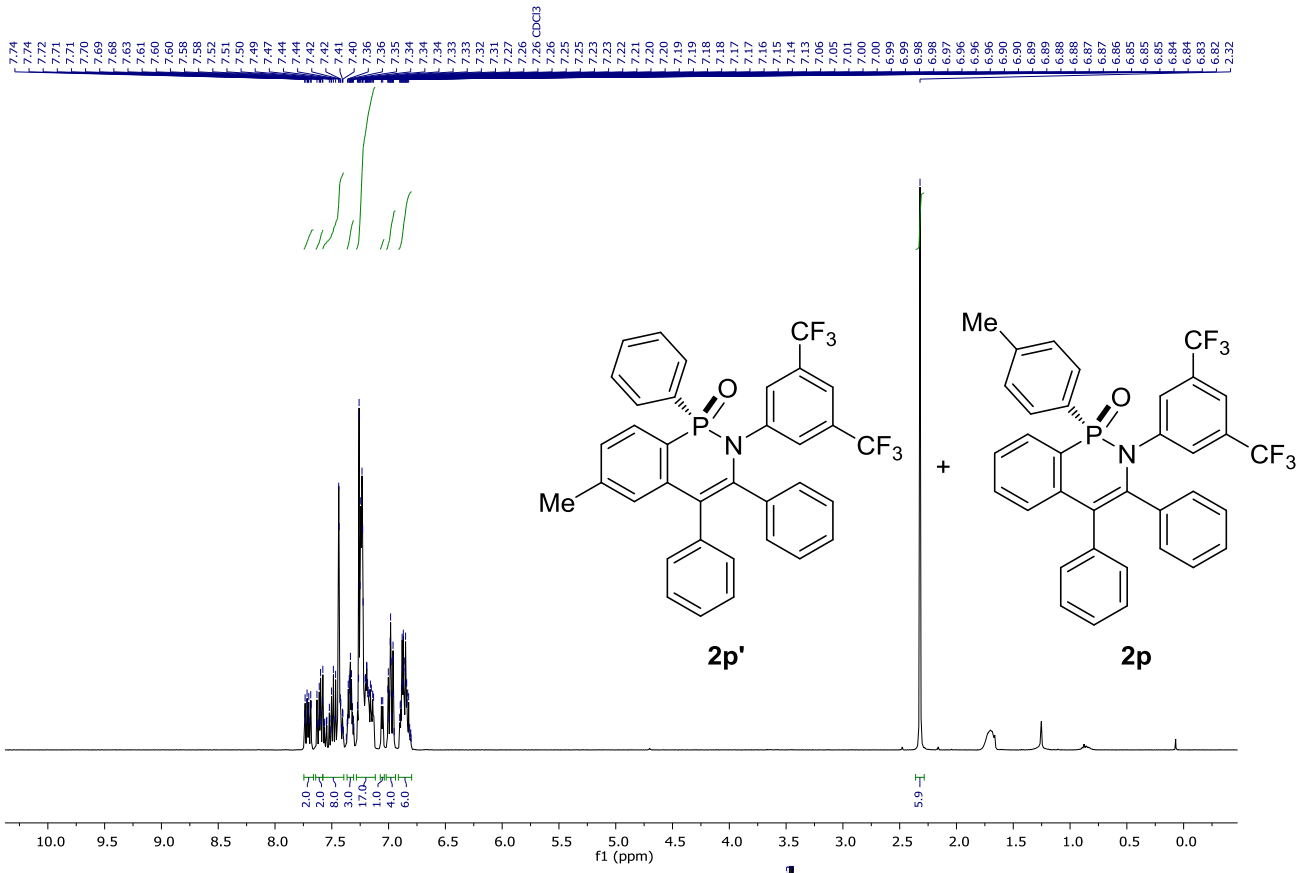
19F cpd

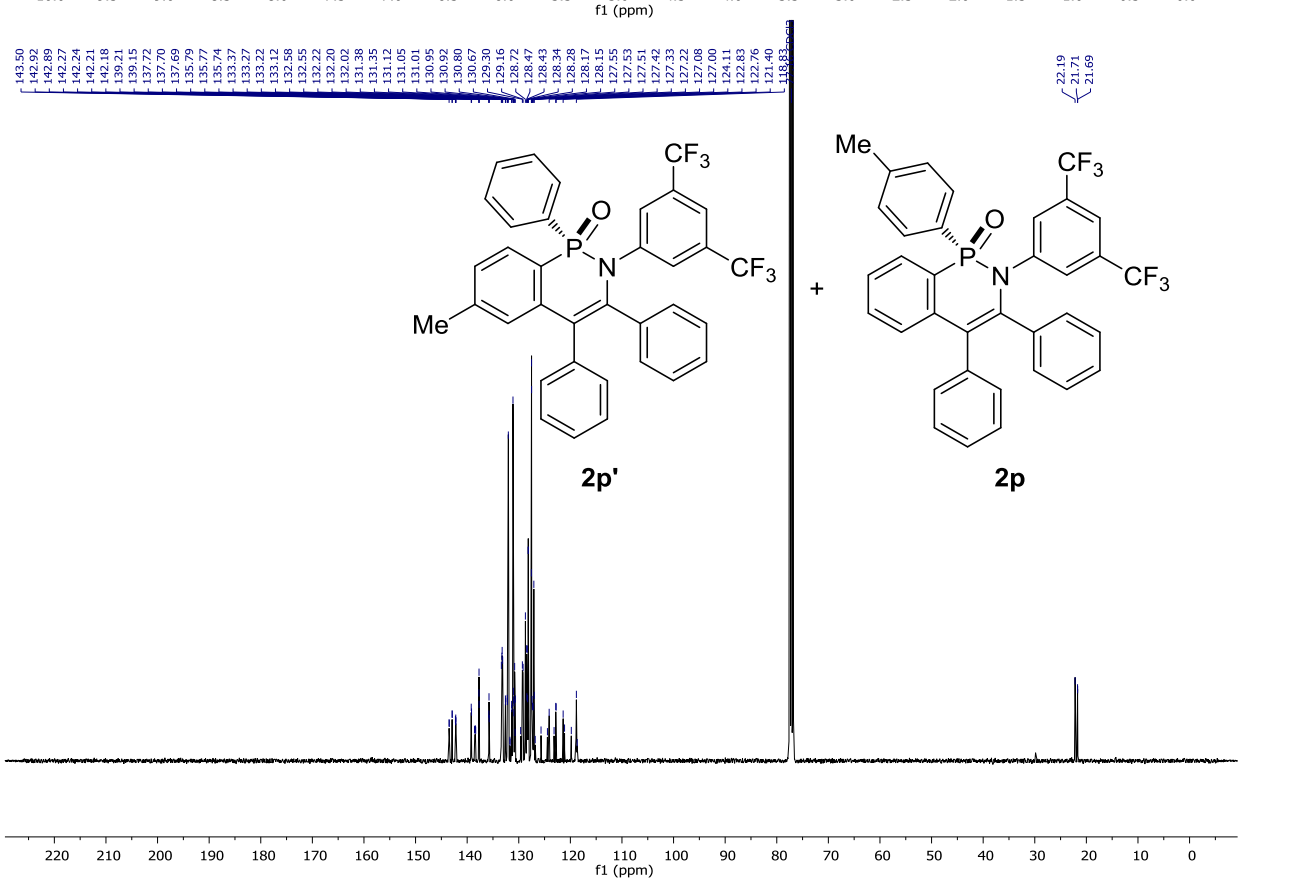






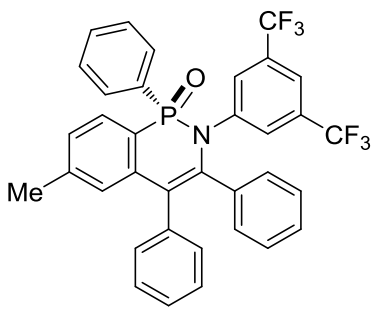
**2p'**


CF3
O
P
N
CF3
Me
2p'
+
Me
CF3
O
P
N
CF3
2p
f1 (ppm)


CF3
O
P
N
CF3
Me
2p'
+
Me
CF3
O
P
N
CF3
2p
f1 (ppm)

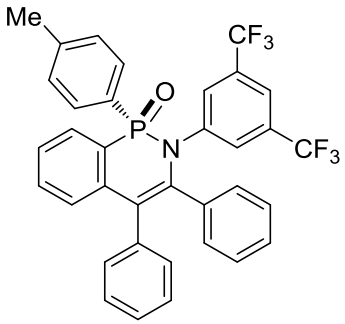
31P cpd

17.32
17.12




**2p'**

+

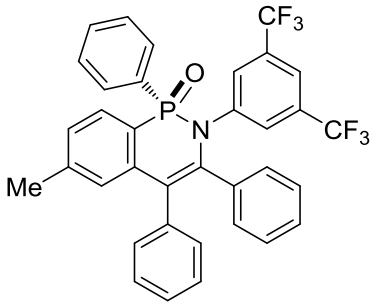



**2p**



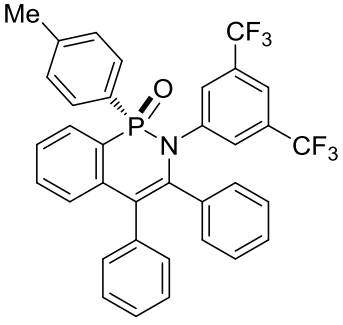

19F cpd

-63.28
-63.29

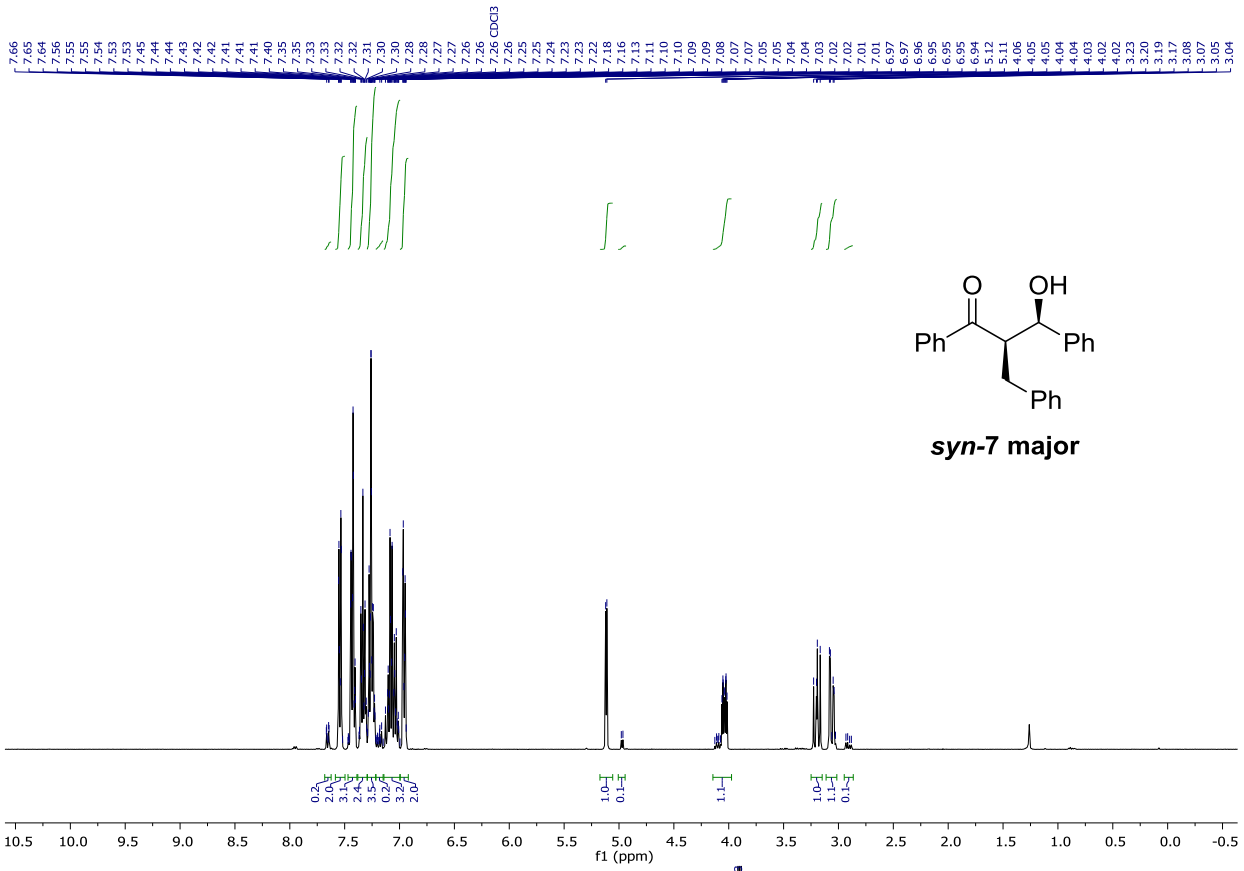



**2p'**

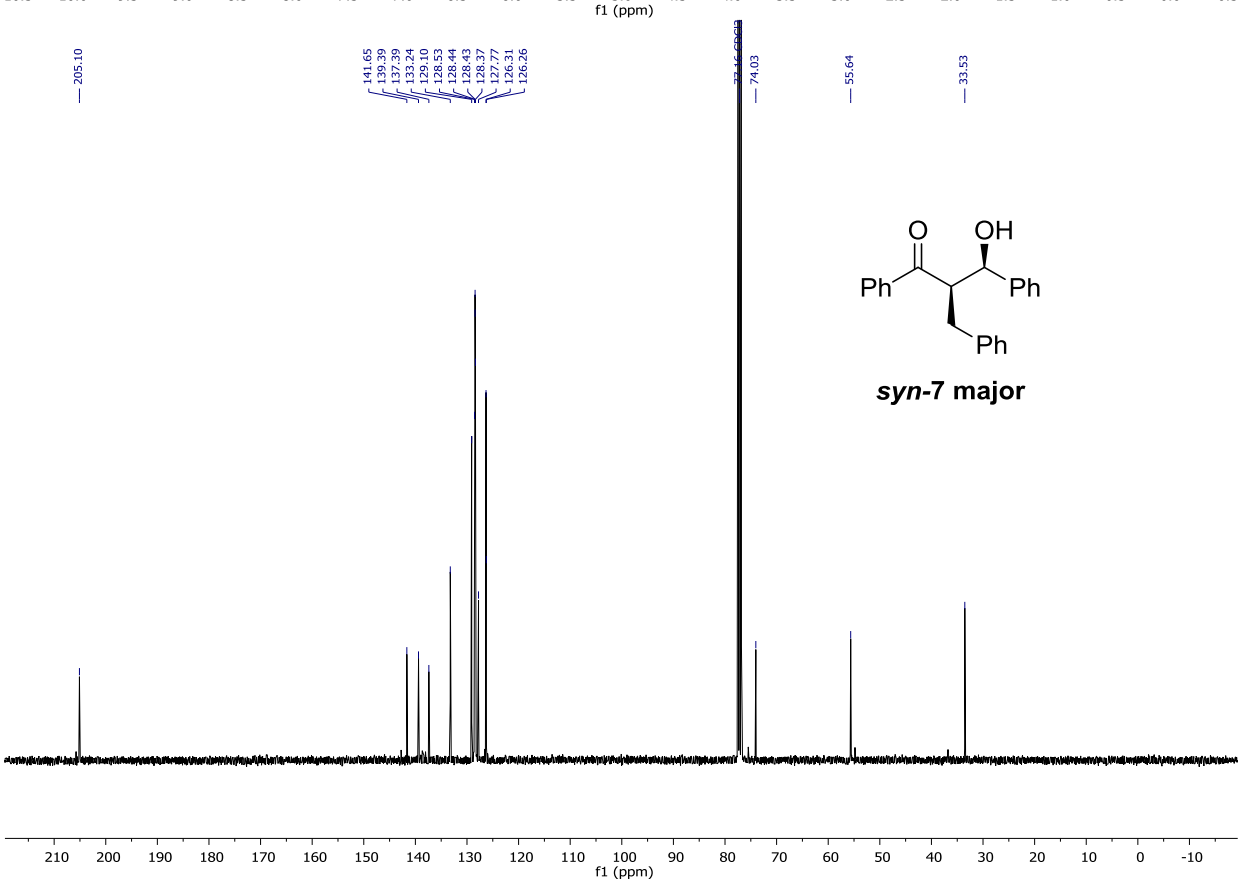
+



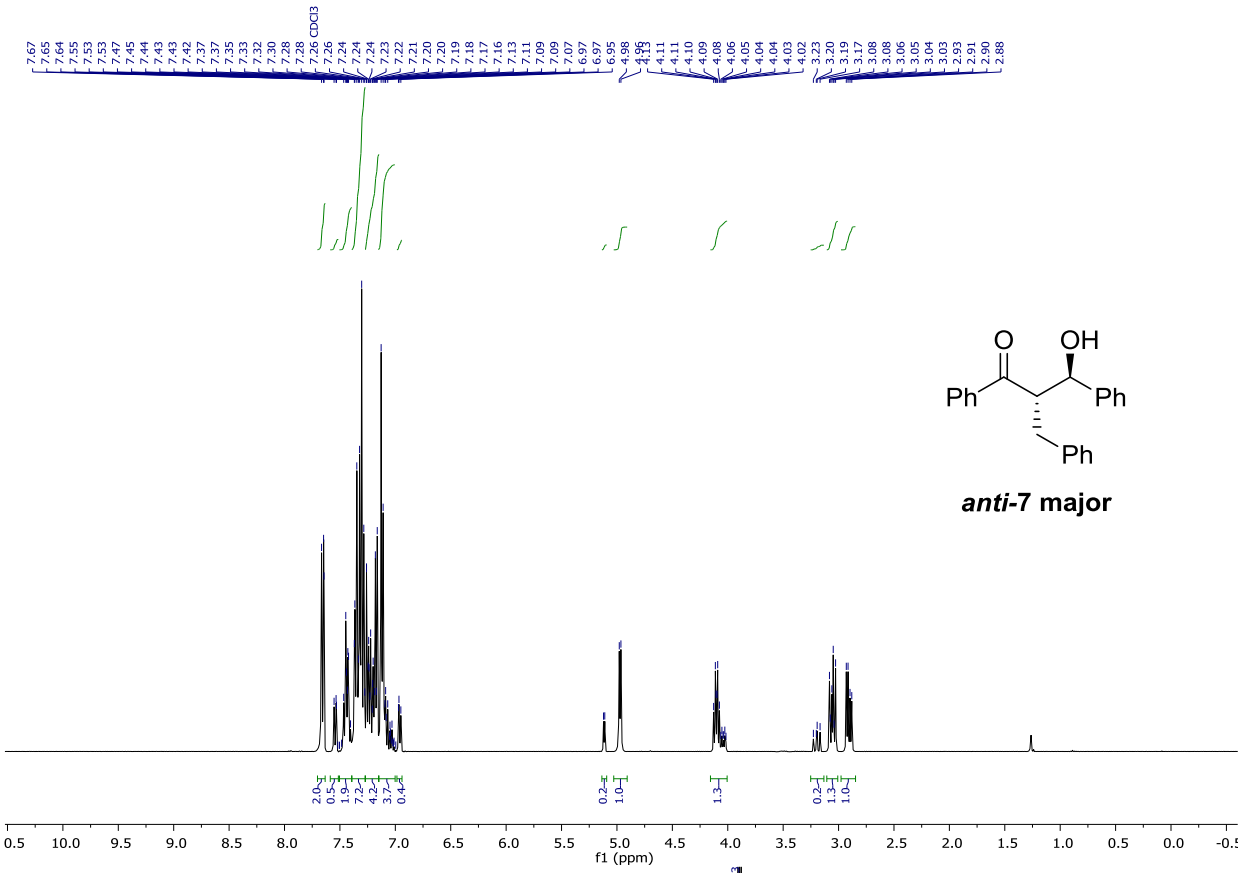

**2p**

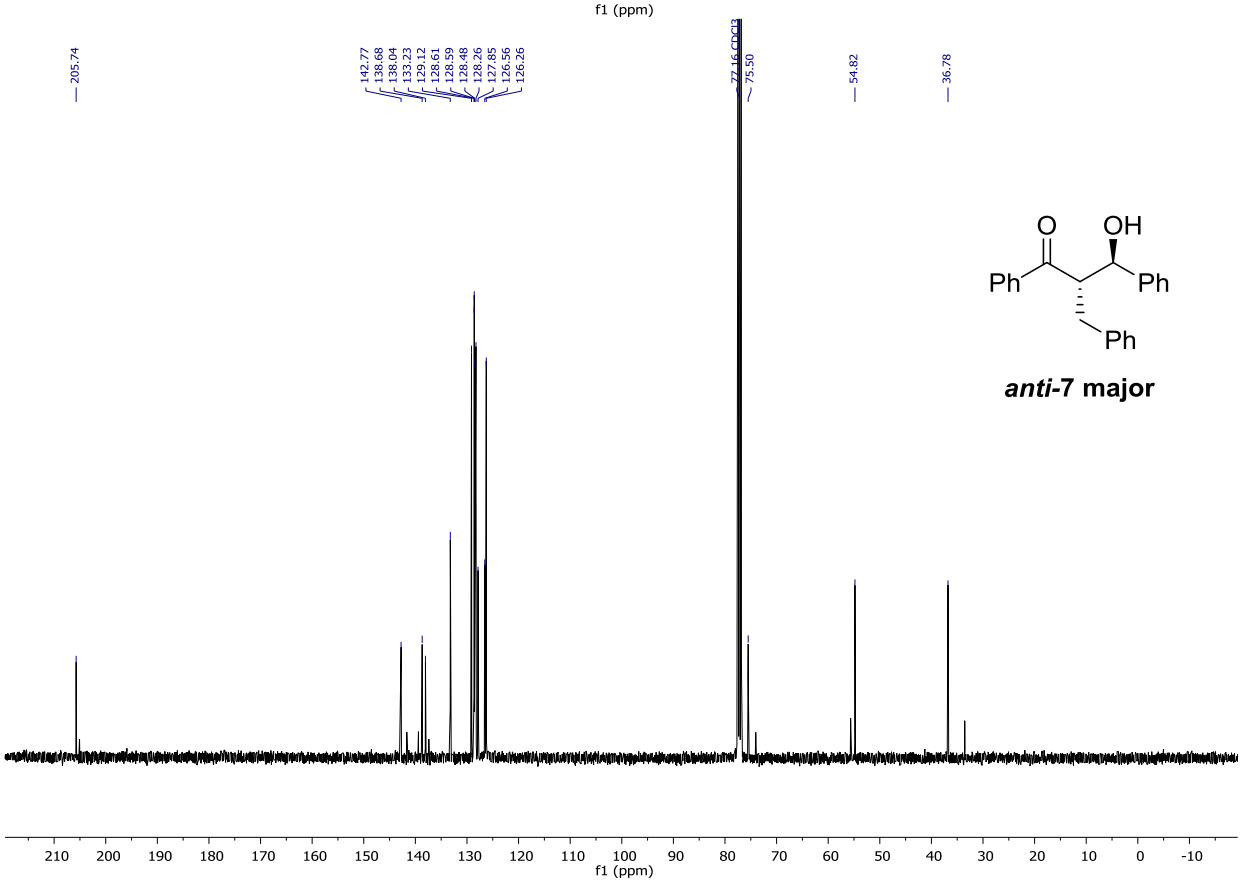


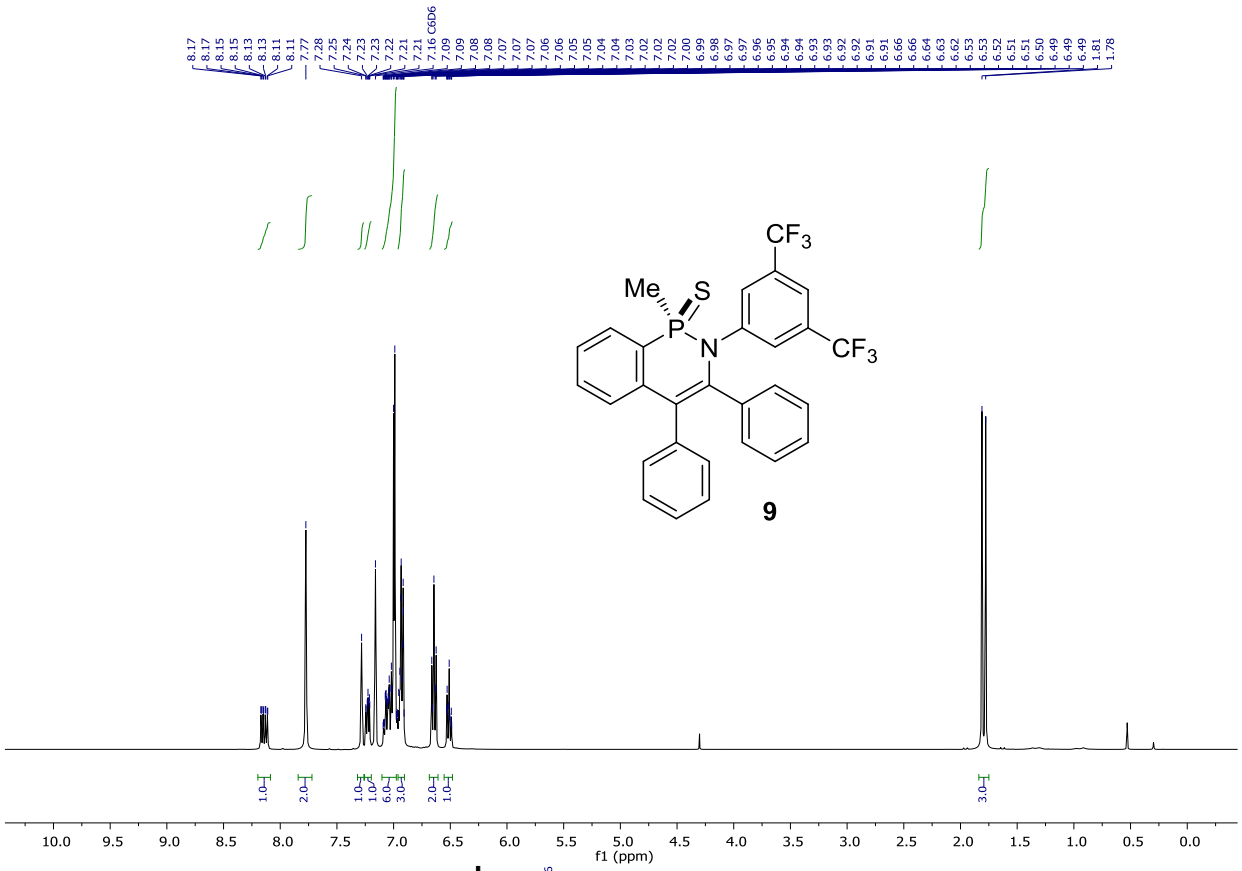

***syn*-7 major**

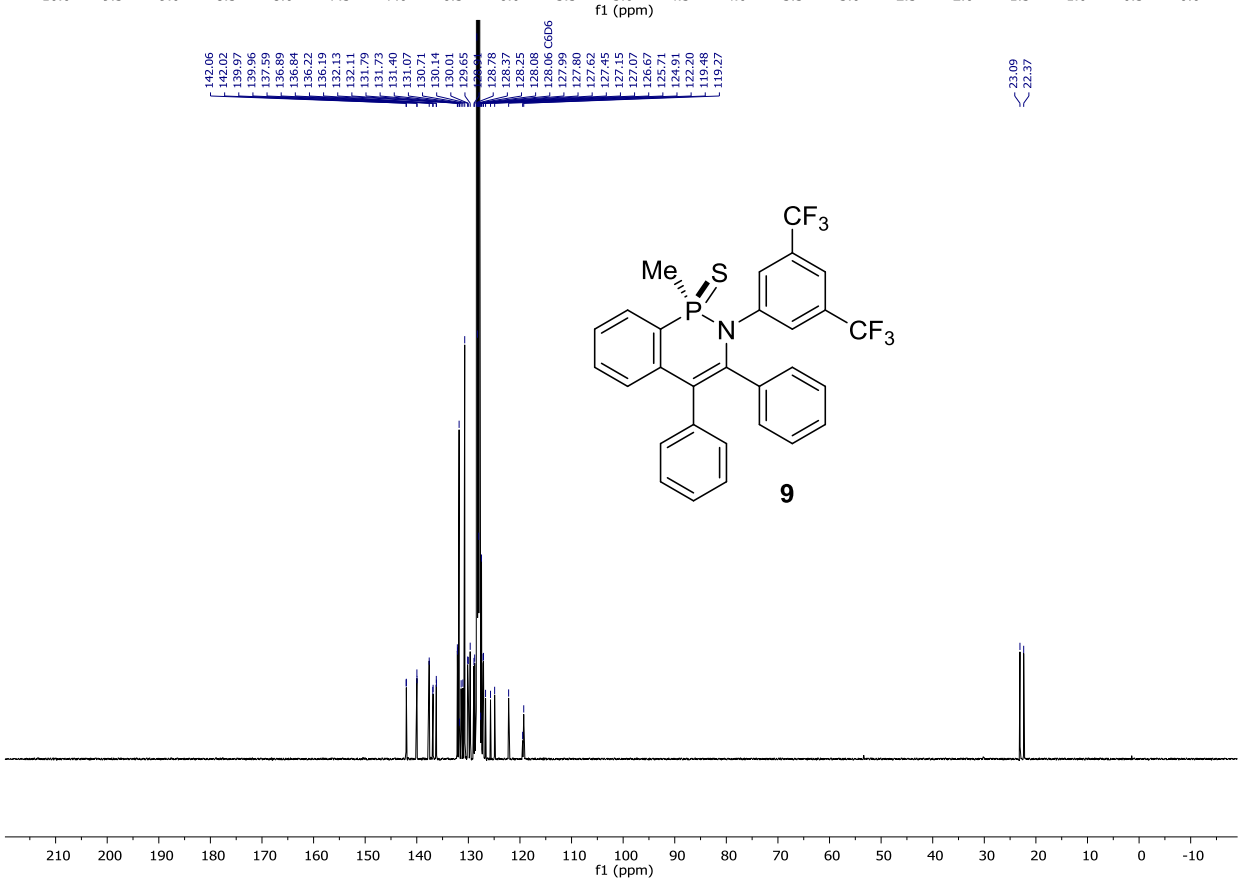



***syn*-7 major**


O
OH
Ph
Ph
Ph
anti-7 major
f1 (ppm)

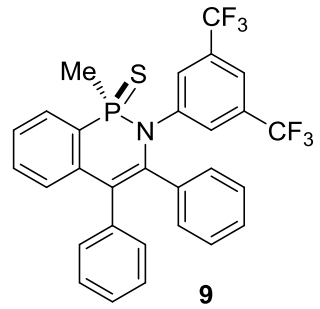

O
OH
Ph
Ph
Ph
anti-7 major
f1 (ppm)


8.17
8.17
8.15
8.15
8.13
8.13
8.11
8.11
7.77
7.28
7.25
7.24
7.23
7.23
7.22
7.21
7.16 C6D6
7.09
7.08
7.08
7.07
7.07
7.07
7.06
7.06
7.05
7.05
7.04
7.04
7.03
7.02
7.02
7.02
7.00
6.99
6.98
6.97
6.97
6.96
6.95
6.94
6.94
6.93
6.93
6.92
6.92
6.91
6.91
6.66
6.66
6.64
6.63
6.62
6.53
6.53
6.52
6.51
6.51
6.50
6.49
6.49
6.49
1.81
1.78
CF3
Me
S
P
N
CF3
9
1.0
2.0
1.0
1.0
6.0
3.0
2.0
1.0
3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.06
142.02
139.97
139.96
137.59
136.89
136.84
136.22
136.19
132.13
132.11
131.79
131.73
131.40
131.07
130.71
130.14
130.01
129.65
128.84
128.78
128.37
128.25
128.08
128.06 C6D6
127.99
127.80
127.62
127.45
127.15
127.07
126.67
125.71
124.91
122.20
119.48
119.27
23.09
22.37
CF3
Me
S
P
N
CF3
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

31P cpd

55.02

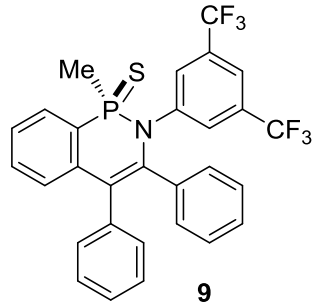



**9**

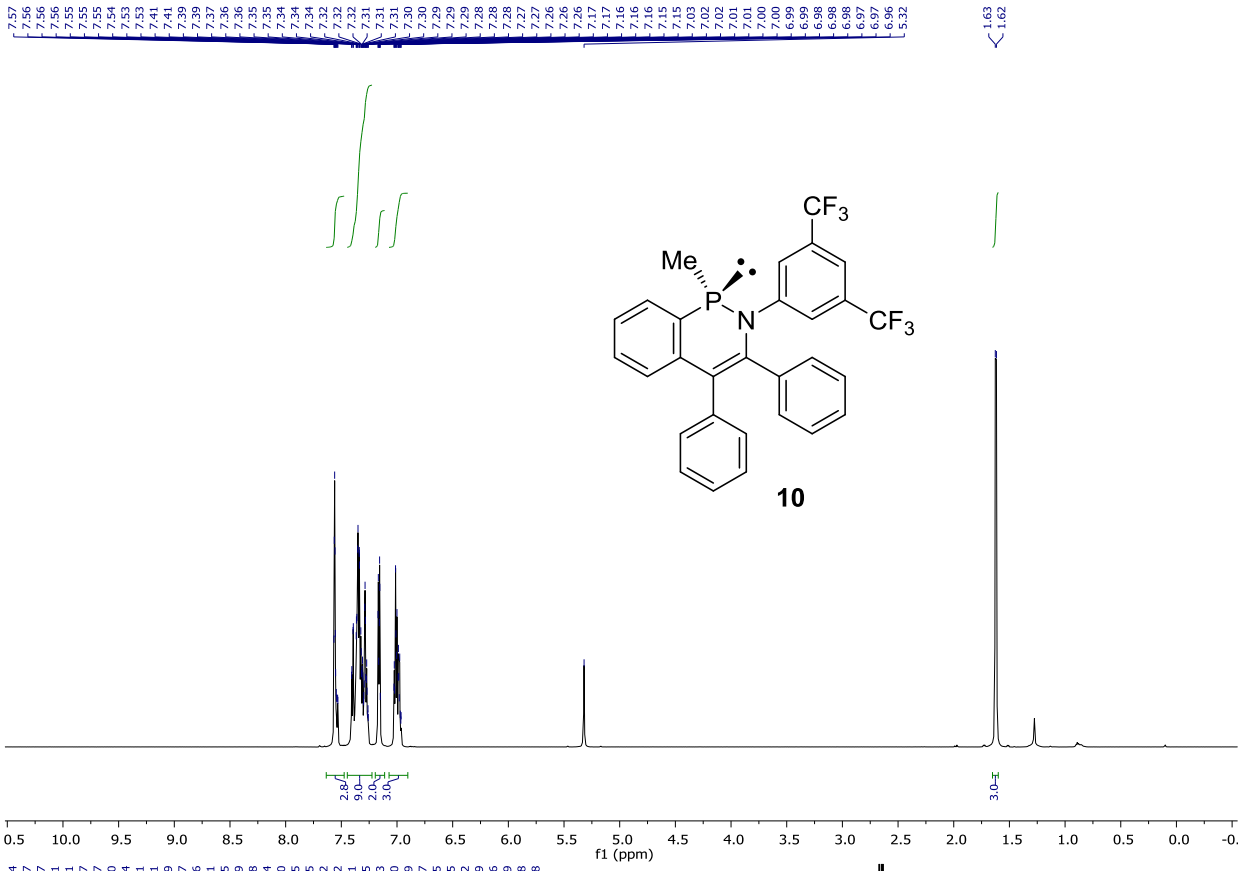


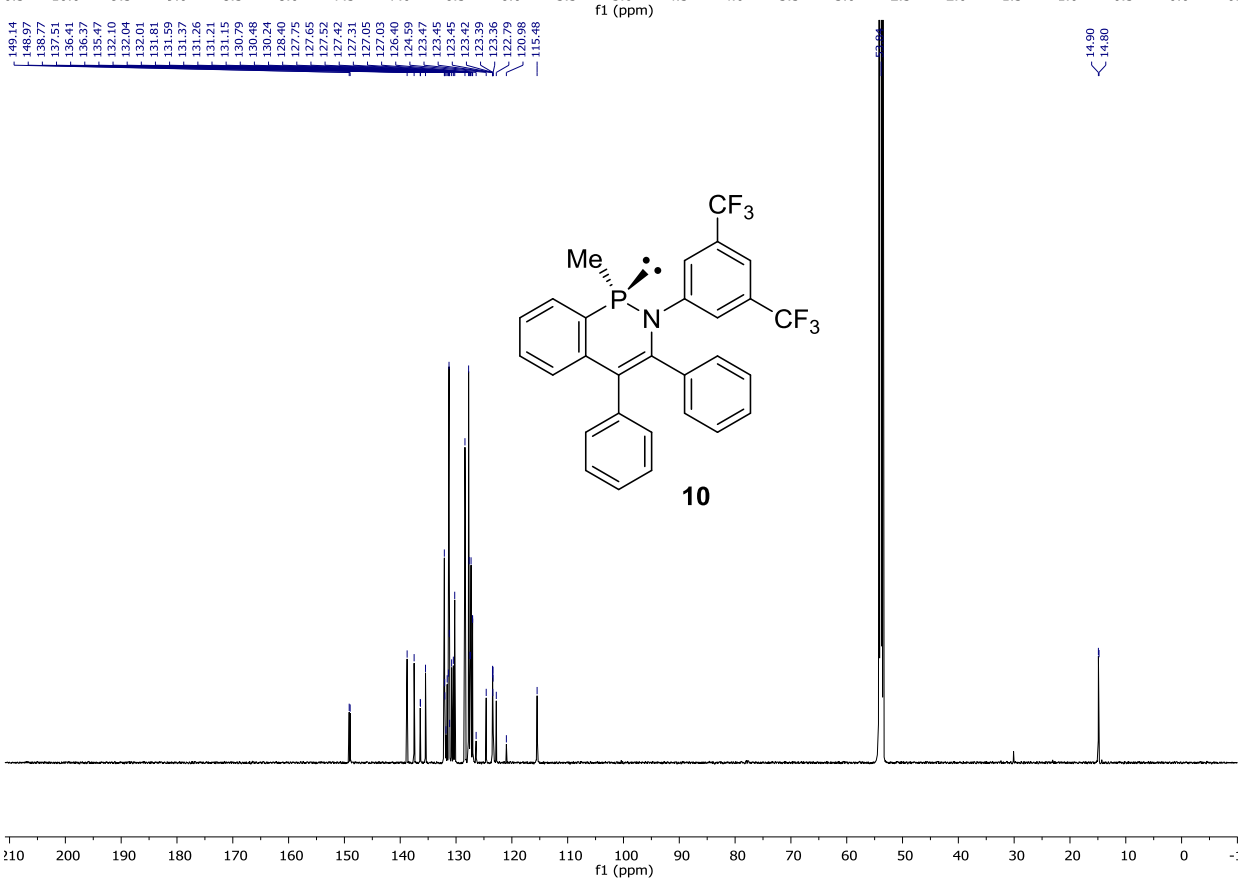

19F cpd

-62.79

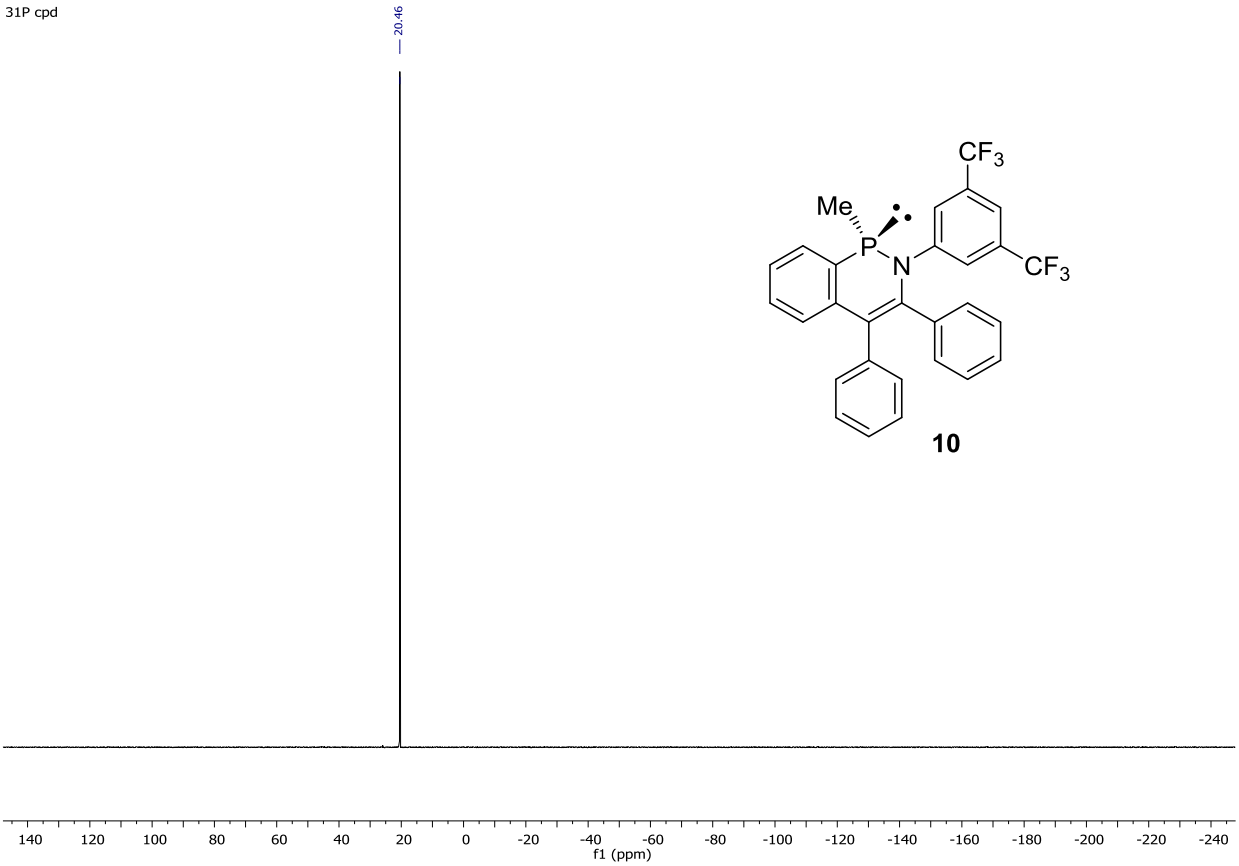



**9**


CF3
Me
P
N
CF3
10
f1 (ppm)


CF3
Me
P
N
CF3
10
f1 (ppm)

31P cpd

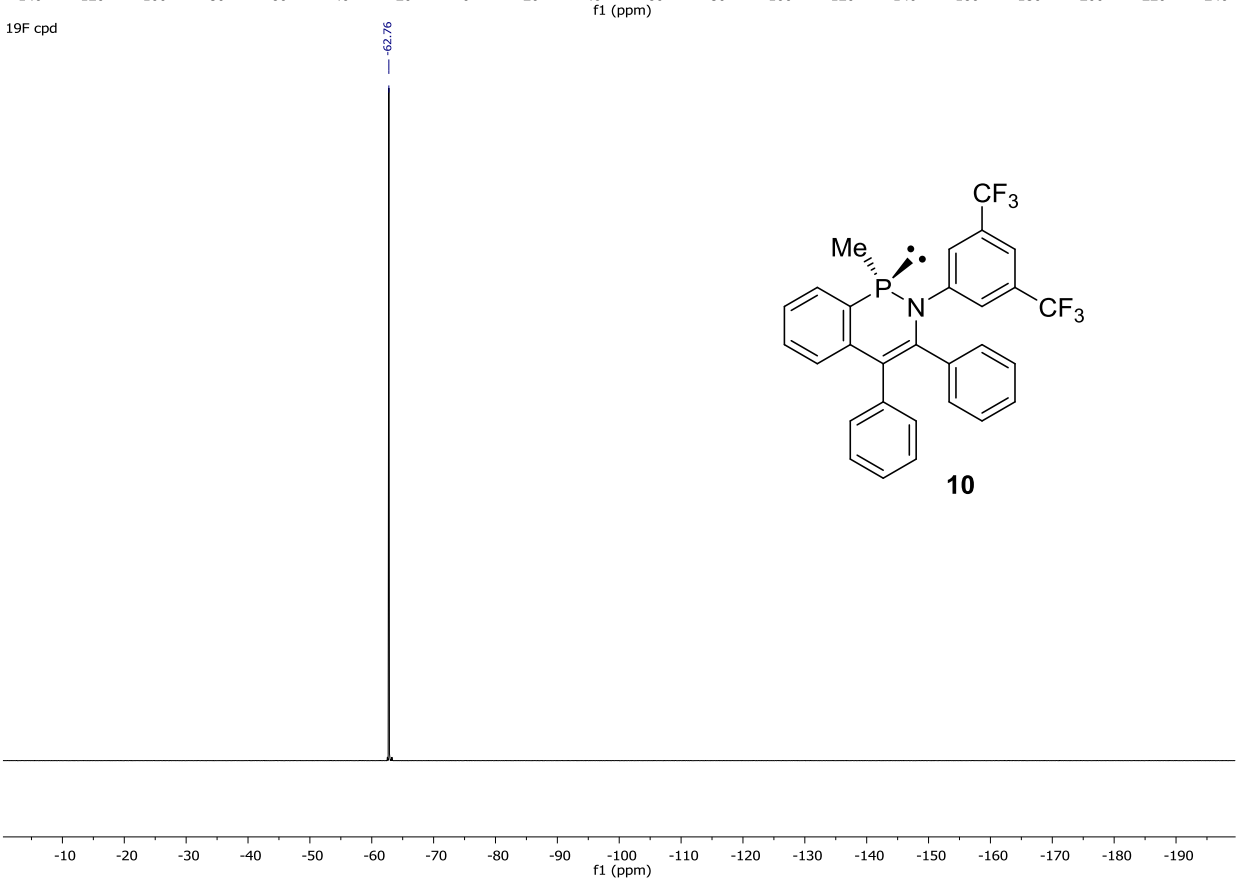






**10**

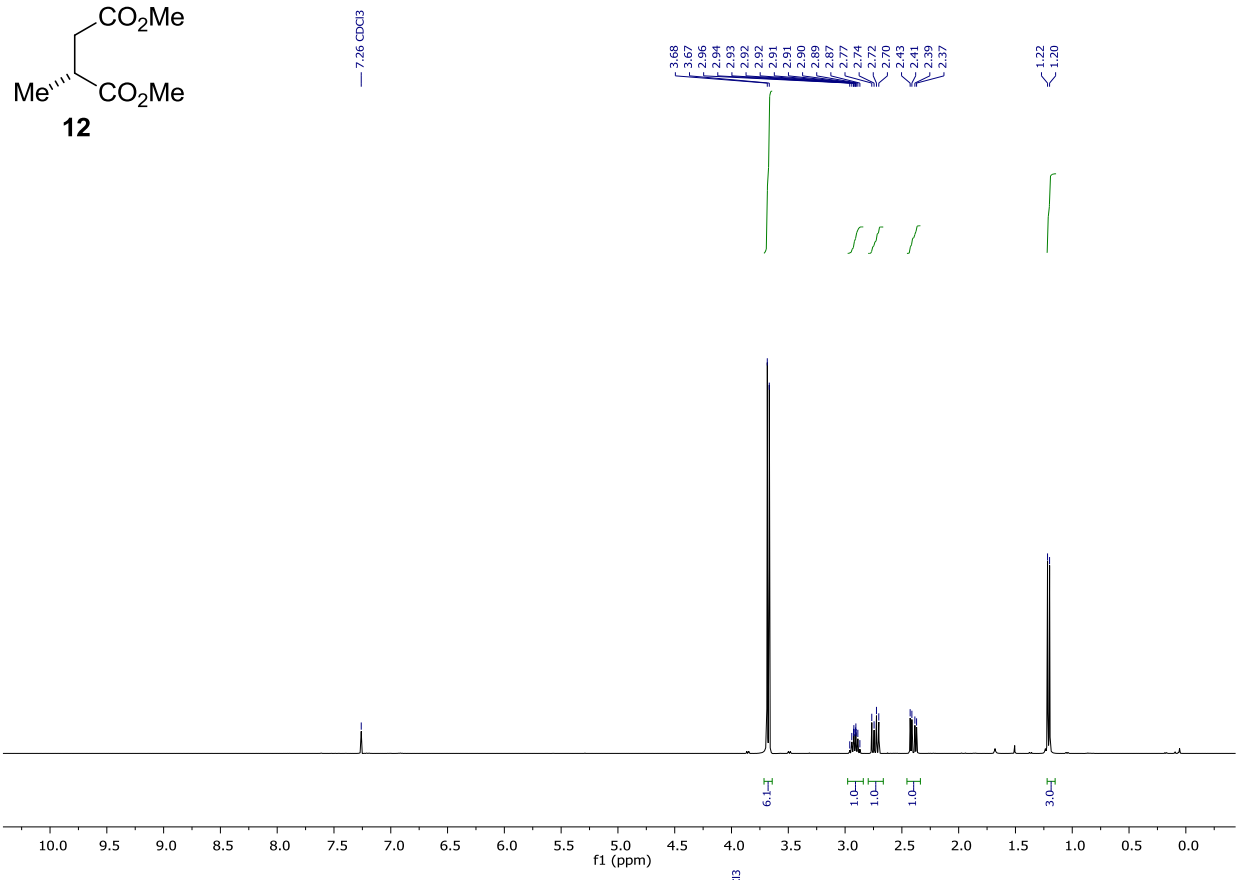
19F cpd

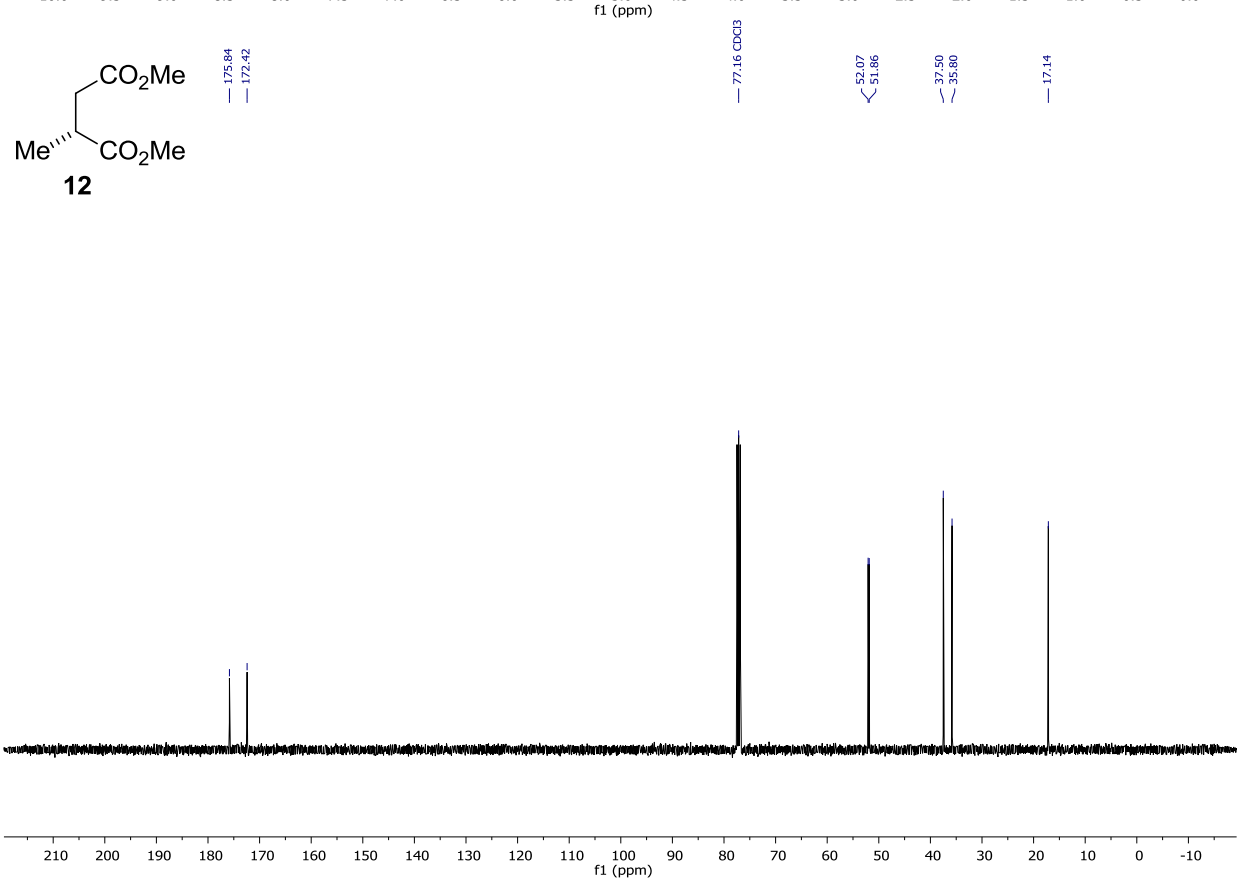






**10**


CO2Me
Me
CO2Me
12
7.26 CDCl3
3.68
3.67
2.96
2.94
2.93
2.92
2.92
2.91
2.91
2.90
2.89
2.87
2.77
2.74
2.72
2.70
2.43
2.41
2.39
2.37
1.22
1.20
6.1
1.0
1.0
1.0
3.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CO2Me
Me
CO2Me
12
175.84
172.42
77.16 CDCl3
52.07
51.86
37.50
35.80
17.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)