

SUPPORTING INFORMATION

Brønsted Acid-mediated Tandem Cyclization of Triarylphosphines and *in situ* generated *ortho*-Alkynyl Quinone Methides: Access to Heterocyclic Quaternary Phosponium Salts

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Materials, Methods, and General Remarks:

All moisture or oxygen-sensitive reactions were carried out under an argon atmosphere in oven flasks. Commercially obtained reagents such as trifluoromethanesulfonic acid (TfOH), PPh₃, aldehyde and phenylacetylene derivatives were used as received. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: THF (Na), CH₂Cl₂ (CaH₂), toluene (Na), ClCH₂CH₂Cl (CaH₂). Thin-layer chromatography was performed using silica gel 60 F-254 precoated plates (0.25 mm) and was visualized by UV irradiation. The products were purified by flash column chromatography on silica gel (200-300 meshes) from the Anhui Liangchen Silicon Material Company in China. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a Varian 500 MHz instrument. ³¹P and ¹⁹F operation frequencies were 202 and 471 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent (CDCl₃) signal ($\delta = 7.26$ for ¹H NMR and $\delta = 77.0$ for ¹³C NMR), Data for ¹H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and the number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), brs (broad singlet). The MS data were obtained with ESI technique, and the relative intensity (%) is given in brackets. High-Resolution Mass Spectrometry (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique. The IR spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer. The X-ray single-crystal determination was performed on a Bruker Smart 1000 CCD X-ray single crystal diffractometer. Compound **1** was prepared according to the reported literature.¹

1. Typical Procedure and Characterization for Phosphonium Salt.

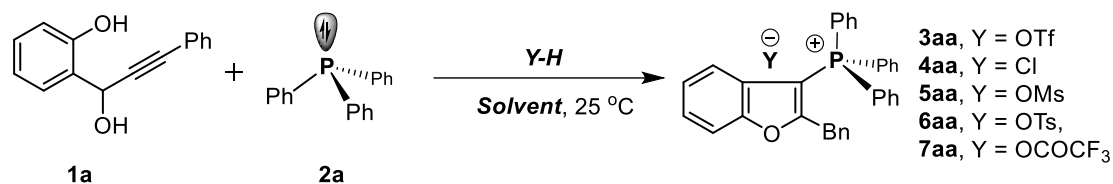


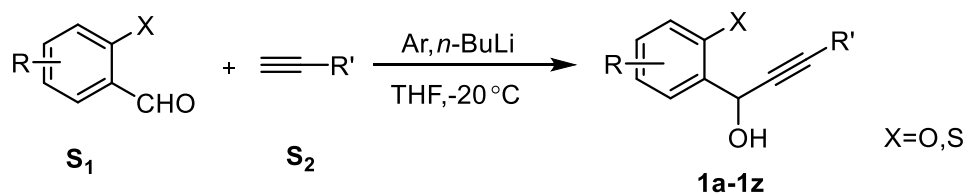
Table 1. Optimization of the Reaction Conditions

entry	solvent	Y-H	yield (%) ^a
1	DCE	TfOH	85
2	DMF	TfOH	53
3	MeCN	TfOH	77
4	THF	TfOH	90
5	CHCl ₃	TfOH	97
6	acetone	TfOH	99
7	acetone	HCl ^b	98
8	acetone	MsOH	98
9	acetone	TsOH	90
10	acetone	CF ₃ COOH	81

Reaction conditions: A mixture of **2a** (0.11 mmol; 1.1 equiv.), solvent (1 mL), and **Y-H** (0.11 mmol; 1.1 equiv.) was prepared at 25 °C. The reaction mixture was stirred for 3 minutes, then charged with **1a** (0.10 mmol; 1.0 equiv.), and stirred for 4 h. ^a Yields determined after purification of the compounds are reported. ^b HCl (0.33 mmol; 3.3 equiv.) was used.

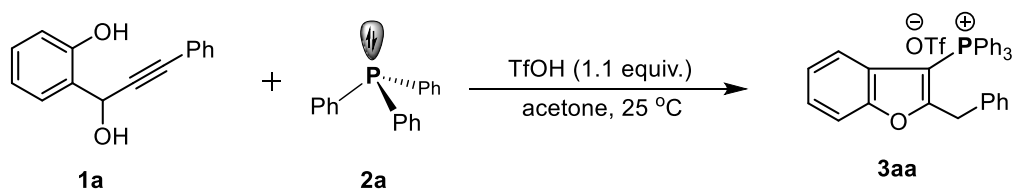
2. General Procedure for the Synthesis of *o*-hydroxyl-benzyl alcohol (*o*-HBAs)

Compounds *o*-hydroxyl-benzyl alcohol (*o*-HBAs) **1a-1x** were prepared according to the reported literature.¹ Compounds **1y** and **1z** were prepared according to ref. 1i.



To the solution of S_2 (2.2 mmol) in dry THF (10 mL) was slowly added $n\text{-BuLi}$ (2.1 mmol, 2.5 M in THF) at -20°C under argon. The reaction mixture was stirred at this temperature for 1 h, then a solution of the corresponding salicylaldehyde S_1 (1 mmol in 4 mL of THF) was added dropwise via cannula slowly. The reaction mixture was stirred at -20°C for another 0.5 h until the disappearance of the starting material. Then the reaction mixture was quenched by the addition of saturated NH_4Cl . The aqueous phase was extracted with EtOAc. Combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. Crude products **1a-1z** were purified by column chromatography [gradient eluent: petroleum ether/EtOAc].

3. General Procedure for the Synthesis of Heterocyclic Phosphonium Salts and the Spectral Data of the Compounds.



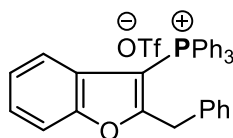
For 0.1 mmol Scale:

A dry and nitrogen-flushed 15 mL screw-capped vial equipped with a magnetic stir bar and septum was sequentially charged with phosphine PPh_3 (0.11 mmol; 1.1 equiv.), acetone (1 mL) and TfOH (0.11 mmol; 1.1 equiv.). The reaction mixture was stirred for 3 minutes; then, it was charged *o*-hydroxyl-benzyl alcohol (*o*-HBAs) (0.1 mmol; 1.0 equiv.) at 25°C . Next, the septum was removed, and the vial was fitted with a Teflon cap. The reaction mixture was allowed to stir for 4 h at room temperature. The reaction mixture without aqueous workup was directly purified by flash column chromatography

on silica gel [gradient eluent: MeOH/CH₂Cl₂ = 1/50 to 1/20] to obtain pure phosphonium salts (61.7 mg) in 99 % yield.

For 3.0 g Scale:

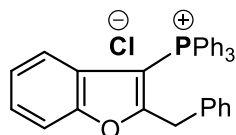
A mixture of **2a** (3.8 g, 14.7 mmol) and TfOH (1.3 mL, 14.7 mmol) was dissolved in acetone (40.0 mL), The reaction mixture was stirred for 30 minutes; then, it was charged **1a** (13.4 mmol, 3.0 g) at 25 °C and stirred for 30 h. The reaction mixture without aqueous workup was directly purified by flash column chromatography on silica gel [gradient eluent: MeOH/CH₂Cl₂ = 1/50 to 1/20] to obtain pure phosphonium salts **3aa** (7.4 g) in 90 % yield.



3aa

Compound 3aa: (99% yield, *R_f* = 0.25 [20:1 CH₂Cl₂/CH₃OH], white crystal, mp. = 191-192°C):

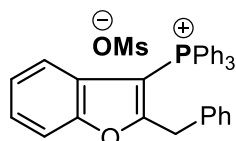
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.91 – 7.83 (m, 3H), 7.78 – 7.69 (m, 12H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.41 (s, 1H), 7.22 – 7.15 (m, 3H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.49 (d, *J* = 8.0 Hz, 1H), 3.64 ppm (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ = 169.4 (d, *J* = 20.4 Hz), 154.4 (d, *J* = 12.8 Hz), 135.8 (d, *J* = 3.0 Hz), 134.5, 134.1 (d, *J* = 10.9 Hz), 130.8 (d, *J* = 13.2 Hz), 128.7, 127.9, 127.3, 127.0 (d, *J* = 9.7 Hz), 126.5, 125.1, 120.8 (q, *J* = 319.1 Hz), 120.4, 117.3 (d, *J* = 92.0 Hz), 112.4, 92.8 (d, *J* = 112.2 Hz), 33.8 ppm; ³¹P NMR (202 MHz, CDCl₃): δ = 10.7 ppm; ¹⁹F NMR (471 MHz, CDCl₃): δ = -78.1 ppm; HRMS (ESI): *m/z* calcd for [M]⁺ = C₃₃H₂₆OP: 469.1721; found: 469.1823; ATR-FTIR (cm⁻¹): $\bar{\nu}$ = 3215, 3060, 2864, 1439, 1239, 750, 515 cm⁻¹.



4aa

Compound 4aa: (98% yield, $R_f = 0.30$ [10:1 CH₂Cl₂/CH₃OH], white crystal, mp. = 192-193 °C):

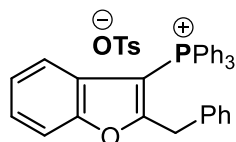
¹H NMR (500 MHz, Chloroform-*d*) $\delta = 7.96 - 7.89$ (m, 3H), 7.77 (dq, $J = 16.4, 8.1$ Hz, 12H), 7.68 (d, $J = 8.3$ Hz, 1H), 7.44 (t, $J = 7.9$ Hz, 1H), 7.22 - 7.18 (m, 3H), 7.14 (t, $J = 7.7$ Hz, 1H), 6.80 - 6.72 (m, 2H), 6.49 (d, $J = 8.0$ Hz, 1H), 3.67 ppm (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) $\delta = 169.2$ (d, $J = 20.4$ Hz), 154.4 (d, $J = 12.7$ Hz), 136.1 (d, $J = 3.1$ Hz), 134.4, 134.1 (d, $J = 10.9$ Hz), 131.0 (d, $J = 13.2$ Hz), 128.8, 127.9, 127.4, 126.9 (d, $J = 9.7$ Hz), 126.7, 125.2, 120.5, 117.2 (d, $J = 92.1$ Hz), 112.5, 92.9 (d, $J = 112.0$ Hz), 34.0 ppm; **³¹P NMR** (202 MHz, CDCl₃) $\delta = 10.7$ ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₃H₂₆OP: 469.1721 found: 469.1725; **ATR-FTIR** (cm⁻¹): $\bar{\nu} = 3054, 2921, 1437, 1118, 721, 541$ cm⁻¹.



5aa

Compound 5aa: (98% yield, $R_f = 0.27$ [10:1 CH₂Cl₂/CH₃OH], white crystal, mp. = 204-206 °C):

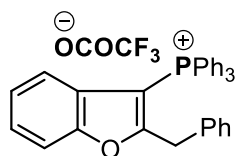
¹H NMR (500 MHz, Chloroform-*d*) $\delta = 7.90$ (dtd, $J = 8.8, 4.3, 2.1$ Hz, 3H), 7.81 - 7.73 (m, 12H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.44 - 7.39 (m, 1H), 7.19 (dd, $J = 4.9, 1.8$ Hz, 3H), 7.14 - 7.08 (m, 1H), 6.76 (dd, $J = 6.3, 2.6$ Hz, 2H), 6.48 (d, $J = 8.0$ Hz, 1H), 3.65 (s, 2H), 2.71 ppm (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) $\delta = 169.2$ (d, $J = 20.3$ Hz), 154.3 (d, $J = 12.8$ Hz), 135.9 (d, $J = 3.2$ Hz), 134.3, 134.0 (d, $J = 11.0$ Hz), 130.8 (d, $J = 13.2$ Hz), 128.6, 127.8, 127.2, 126.9 (d, $J = 9.7$ Hz), 126.5, 125.0, 120.4, 117.1 (d, $J = 92.0$ Hz), 112.4, 92.8 (d, $J = 112.1$ Hz), 39.2, 33.8 ppm; **³¹P NMR** (202 MHz, CDCl₃) $\delta = 10.6$ ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₃H₂₆OP: 469.1721; found: 469.1718; **ATR-FTIR** (cm⁻¹): $\bar{\nu} = 3063, 2922, 1436, 1204, 756, 544$ cm⁻¹.



6aa

Compound 6aa: (90% yield, $R_f = 0.35$ [10:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 197-199 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.86$ (t, $J = 7.0$ Hz, 3H), 7.80 – 7.69 (m, 14H), 7.64 (d, $J = 8.4$ Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.20 – 7.15 (m, 3H), 7.10 (t, $J = 7.7$ Hz, 1H), 7.01 (d, $J = 7.8$ Hz, 2H), 6.74 (d, $J = 4.8$ Hz, 2H), 6.46 (d, $J = 8.0$ Hz, 1H), 3.63 (s, 2H), 2.26 ppm (s, 3H); $^{13}\text{C NMR}$ (126 MHz, Chloroform- d) $\delta = 169.4$ (d, $J = 20.3$ Hz), 154.4 (d, $J = 12.8$ Hz), 144.5, 138.2, 135.9 (d, $J = 3.2$ Hz), 134.6, 134.1 (d, $J = 11.0$ Hz), 130.9 (d, $J = 13.3$ Hz), 128.7, 128.0 (d, $J = 11.9$ Hz), 127.3, 127.1 (d, $J = 10.0$ Hz), 126.5, 126.1, 125.0, 120.5, 117.2 (d, $J = 92.0$ Hz), 112.4, 92.9 (d, $J = 112.2$ Hz), 33.9, 21.2 ppm; $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = 10.6$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{26}\text{OP}$: 469.1721 found: 469.1722; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3057$, 2916, 1435, 1212, 678, 545 cm^{-1} .

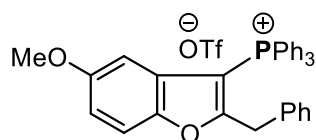


7aa

Compound 7aa: (81% yield, $R_f = 0.30$ [10:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 164-166 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.87$ (dq, $J = 8.7, 4.7$ Hz, 3H), 7.76 – 7.69 (m, 12H), 7.67 – 7.64 (m, 1H), 7.44 – 7.39 (m, 1H), 7.19 (dd, $J = 4.9, 1.8$ Hz, 3H), 7.14 – 7.09 (m, 1H), 6.75 (dd, $J = 6.4, 2.9$ Hz, 2H), 6.49 (d, $J = 7.9$ Hz, 1H), 3.63 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform- d) $\delta = 169.3$ (d, $J = 20.2$ Hz), 154.5 (d, $J = 12.8$ Hz), 136.0 (d, $J = 3.1$ Hz), 134.5, 134.1 (d, $J = 11.0$ Hz), 130.9 (d, $J = 13.3$ Hz), 128.8, 127.9, 127.4, 127.0 (d, $J = 9.8$ Hz), 126.8, 125.2, 120.5, 117.3 (d, $J = 92.0$ Hz), 112.5, 93.0 (d,

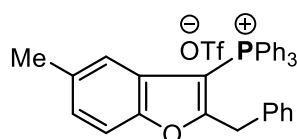
$J = 111.8$ Hz), 33.8 ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.7$ ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -75.1$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{26}\text{OP}$: 469.1721; found: 469.1721; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3065, 2921, 1685, 1439, 1207, 722, 542$ cm^{-1} .



3ba

Compound 3ba: (99% yield, $R_f = 0.25$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 192-193 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.88$ (dd, $J = 8.4, 5.0$ Hz, 3H), 7.80 – 7.71 (m, 12H), 7.57 – 7.51 (m, 1H), 7.18 (dt, $J = 3.4, 1.7$ Hz, 3H), 7.00 – 6.95 (m, 1H), 6.77 – 6.70 (m, 2H), 5.77 (d, $J = 2.0$ Hz, 1H), 3.62 (s, 2H), 3.41 ppm (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 169.7$ (d, $J = 20.4$ Hz), 157.1, 149.3 (d, $J = 12.7$ Hz), 135.8 (d, $J = 3.1$ Hz), 134.5, 134.1 (d, $J = 10.9$ Hz), 130.9 (d, $J = 13.2$ Hz), 128.7, 128.0, 127.7 (d, $J = 9.4$ Hz), 127.3, 120.9 (q, $J = 319.0$ Hz), 117.2 (d, $J = 92.0$ Hz), 114.9, 113.0, 103.0, 92.4 (d, $J = 112.1$ Hz), 55.6, 34.0 ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.7$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{34}\text{H}_{28}\text{O}_2\text{P}$: 499.1827; found: 499.1826; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3068, 2916, 1474, 1265, 1154, 723, 516$ cm^{-1} .

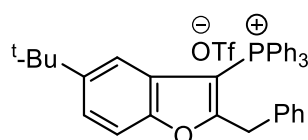


3ca

Compound 3ca: (99% yield, $R_f = 0.23$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 160-161 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.91 - 7.87$ (m, 3H), 7.78 – 7.70 (m, 12H), 7.52 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.23 – 7.20 (m, 1H), 7.19 – 7.15 (m, 3H), 6.78 – 6.71 (m, 2H), 6.21 (s, 1H), 3.60 (s, 2H), 2.17 ppm (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 169.2$ (d, $J = 20.5$ Hz), 152.9 (d, $J = 12.8$ Hz), 135.8 (d, $J = 3.0$ Hz), 135.0, 134.6,

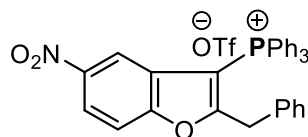
134.1 (d, $J = 10.9$ Hz), 130.8 (d, $J = 13.2$ Hz), 128.7, 127.9, 127.8, 127.3, 127.1 (d, $J = 9.6$ Hz), 120.9 (q, $J = 319.1$ Hz), 120.1, 117.4 (d, $J = 92.1$ Hz), 111.9, 92.3 (d, $J = 112.2$ Hz), 33.8, 21.3 ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.0$ ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.7$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{34}\text{H}_{28}\text{OP}$: 483.1878; found: 483.1873; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3064, 2920, 1442, 1265, 721, 544$ cm^{-1} .



3da

Compound 3da: (99% yield, $R_f = 0.25$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 194-196 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.81$ (td, $J = 6.3, 5.9, 2.7$ Hz, 3H), 7.71 – 7.64 (m, 12H), 7.47 (s, 1H), 7.36 (dd, $J = 8.8, 1.7$ Hz, 1H), 7.11 – 7.06 (m, 3H), 6.69 – 6.63 (m, 2H), 6.26 – 6.23 (m, 1H), 3.57 (s, 2H), 0.93 ppm (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 169.1$ (d, $J = 20.6$ Hz), 152.7 (d, $J = 12.8$ Hz), 148.3, 135.8 (d, $J = 3.0$ Hz), 134.4, 134.1 (d, $J = 10.9$ Hz), 130.8 (d, $J = 13.2$ Hz), 128.7, 127.9, 127.2, 126.7 (d, $J = 9.7$ Hz), 124.2, 120.8 (q, $J = 319.3$ Hz), 117.3 (d, $J = 92.0$ Hz), 116.7, 111.6, 92.6 (d, $J = 111.9$ Hz), 34.6, 34.0, 31.2 ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.8$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{37}\text{H}_{34}\text{OP}$: 525.2347; found: 525.2341; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3063, 2954, 1436, 1265, 726, 545$ cm^{-1} .

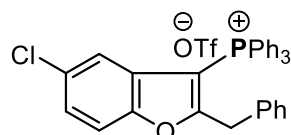


3ea

Compound 3ea: (99% yield, $R_f = 0.21$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 173-175 $^\circ\text{C}$)

^1H NMR (500 MHz, Chloroform- d) $\delta = 8.27 - 8.19$ (m, 1H), 7.91 – 7.80 (m, 9H), 7.79 – 7.69 (m, 7H), 7.21 – 7.13 (m, 3H), 7.11 (s, 1H), 6.82 – 6.71 (m, 2H), 3.76 ppm (s, 2H); ^{13}C NMR (126 MHz, Chloroform- d) $\delta = 173.2$ (d, $J = 19.5$ Hz), 157.4 (d, $J =$

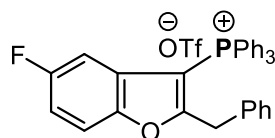
12.4 Hz), 145.0, 136.2 (d, $J = 3.3$ Hz), 134.4 (d, $J = 11.1$ Hz), 133.9, 131.1 (d, $J = 13.4$ Hz), 128.9, 128.4, 128.0 (d, $J = 9.8$ Hz), 127.6, 122.0, 117.1, 116.3 (d, $J = 2.8$ Hz), 120.9 (t, $J = 318.8$ Hz), 113.4, 94.0 (d, $J = 112.2$ Hz), 34.6 ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.6$ ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.2$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{25}\text{NO}_3\text{P}$: 514.1572; found: 514.1570; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3061, 2923, 1529, 1261, 638, 514$ cm^{-1} .



3fa

Compound 3fa: (99% yield, $R_f = 0.26$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 192-193 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.89$ (ddd, $J = 7.5, 4.4, 1.9$ Hz, 3H), 7.80 – 7.74 (m, 12H), 7.59 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.35 (dd, $J = 8.9, 2.0$ Hz, 1H), 7.19 (q, $J = 3.7$ Hz, 3H), 6.75 (dd, $J = 6.4, 2.8$ Hz, 2H), 6.31 (d, $J = 1.9$ Hz, 1H), 3.66 ppm (s, 2H); ^{13}C NMR (126 MHz, Chloroform- d) $\delta = 171.1$ (d, $J = 20.0$ Hz), 152.9 (d, $J = 12.5$ Hz), 136.0 (d, $J = 3.1$ Hz), 134.2 (d, $J = 11.0$ Hz), 131.0 (d, $J = 13.3$ Hz), 130.7, 128.8, 128.5 (d, $J = 9.6$ Hz), 128.1, 127.4, 126.9, 120.9 (q, $J = 319.1$ Hz), 119.8, 117.0 (d, $J = 92.0$ Hz), 113.6, 92.5 (d, $J = 112.3$ Hz), 34.1 ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.5$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{25}\text{ClOP}$: 503.1331; found: 503.1330; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3084, 2921, 1443, 1265, 725, 541$ cm^{-1} .

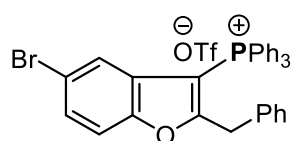


3ga

Compound 3ga: (99% yield, $R_f = 0.25$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 164 -165 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.91 - 7.86$ (m, 3H), 7.80 – 7.73 (m, 12H),

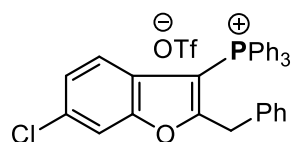
7.62 (ddd, $J = 8.9, 3.9, 1.6$ Hz, 1H), 7.23 – 7.16 (m, 3H), 7.12 (td, $J = 9.0, 2.5$ Hz, 1H), 6.79 – 6.72 (m, 2H), 6.04 (dd, $J = 8.3, 2.4$ Hz, 1H), 3.65 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform- d) $\delta = 171.3$ (d, $J = 20.1$ Hz), 159.7 (d, $J = 243.6$ Hz), 150.7 (d, $J = 12.5$ Hz), 135.9 (d, $J = 3.2$ Hz), 134.3, 134.1 (d, $J = 11.0$ Hz), 128.8, 128.1, 127.4, 120.9 (q, $J = 318.8$ Hz), 116.9 (d, $J = 92.2$ Hz), 114.5 (d, $J = 26.2$ Hz), 113.7 (d, $J = 9.6$ Hz), 106.3 (d, $J = 27.0$ Hz), 92.9 (dd, $J = 112.4, 3.6$ Hz), 34.1 ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -78.1, -115.4$ ppm; $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = 10.6$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{25}\text{FOP}$: 487.1627; found: 487.1625; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3063, 2899, 1440, 1266, 1143, 752, 514$ cm^{-1} .



3ha

Compound 3ha: (99% yield, $R_f = 0.25$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 177-178 $^\circ\text{C}$):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.93 - 7.86$ (m, 3H), 7.82 – 7.73 (m, 12H), 7.54 (dd, $J = 8.8, 1.5$ Hz, 1H), 7.49 (d, $J = 1.8$ Hz, 1H), 7.22 – 7.16 (m, 3H), 6.79 – 6.72 (m, 2H), 6.44 (d, $J = 1.6$ Hz, 1H), 3.66 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform- d) $\delta = 170.8$ (d, $J = 19.9$ Hz), 153.2 (d, $J = 12.4$ Hz), 135.9 (d, $J = 3.2$ Hz), 134.1 (d, $J = 10.9$ Hz), 130.9 (d, $J = 13.3$ Hz), 129.5, 129.0 (d, $J = 9.5$ Hz), 128.7, 128.0, 127.3, 122.7, 120.9 (q, $J = 320.0$ Hz), 118.0, 116.8 (d, $J = 92.1$ Hz), 114.0, 92.4 (d, $J = 112.2$ Hz), 34.0 ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -78.1$ ppm; $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = 10.5$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{25}\text{BrOP}$: 547.0826; found: 547.0825; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3085, 2922, 1541, 1444, 1262, 722, 568$ cm^{-1} .

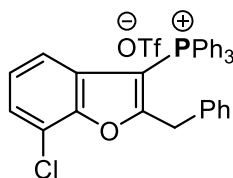


3ia

Compound 3ia: (99% yield, $R_f = 0.22$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. =

207-208 °C):

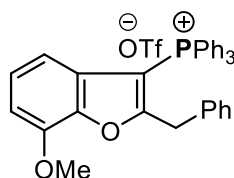
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.84 – 7.75 (m, 3H), 7.73 – 7.61 (m, 12H), 7.56 (s, 1H), 7.14 – 7.06 (m, 3H), 7.00 (dd, J = 8.6, 1.8 Hz, 1H), 6.70 – 6.63 (m, 2H), 6.29 (d, J = 8.6 Hz, 1H), 3.56 ppm (s, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ = 170.3 (d, J = 20.1 Hz), 154.5 (d, J = 12.6 Hz), 135.9 (d, J = 3.0 Hz), 134.3, 134.1 (d, J = 11.0 Hz), 132.5, 130.9 (d, J = 13.3 Hz), 128.8, 128.0, 127.4, 125.7 (d, J = 9.5 Hz), 125.7, 120.8 (q, J = 319.1 Hz), 120.9, 117.0 (d, J = 92.0 Hz), 113.0, 93.1 (d, J = 112.2 Hz), 33.8 ppm; **¹⁹F NMR** (471 MHz, CDCl₃) δ = -78.1, -78.1 ppm; **³¹P NMR** (202 MHz, CDCl₃) δ = 10.6 ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₃H₂₅ClOP: 503.1332; found: 503.1331; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3063, 2915, 1437, 1265, 721, 514 cm⁻¹.



3ja

Compound 3ja: (99% yield, R_f = 0.22 [20:1 CH₂Cl₂/CH₃OH], white crystal, mp. = 220 -221°C):

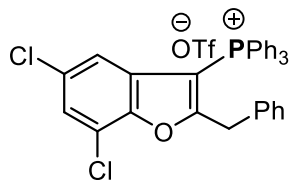
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.88 (dq, J = 6.1, 3.3 Hz, 3H), 7.78 – 7.69 (m, 12H), 7.41 (d, J = 7.8 Hz, 1H), 7.21 – 7.16 (m, 3H), 7.07 (t, J = 8.0 Hz, 1H), 6.78 – 6.71 (m, 2H), 6.37 (d, J = 8.0 Hz, 1H), 3.69 ppm (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ = 170.0 (d, J = 20.1 Hz), 150.5 (d, J = 12.4 Hz), 136.0 (d, J = 3.1 Hz), 134.2, 134.1 (d, J = 11.0 Hz), 130.9 (d, J = 13.3 Hz), 128.7, 128.5 (d, J = 9.9 Hz), 127.9, 127.4, 126.7, 126.0, 120.8 (q, J = 320.0 Hz), 118.9, 118.1, 116.8 (d, J = 92.0 Hz), 94.0 (d, J = 111.2 Hz), 33.8 ppm; **³¹P NMR** (202 MHz, CDCl₃) δ = 10.7 ppm; **¹⁹F NMR** (471 MHz, CDCl₃) δ = -78.1 ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₃H₂₅ClOP: 503.1331; found: 503.1327; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3064, 2919, 1537, 1438, 1273, 723, 514 cm⁻¹.



3ka

Compound 3ka: (85% yield, $R_f = 0.25$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 169-171 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) $\delta = 7.91 - 7.82$ (m, 3H), 7.75 – 7.67 (m, 12H), 7.17 (dd, $J = 4.9, 1.6$ Hz, 3H), 7.05 (t, $J = 8.1$ Hz, 1H), 6.92 (d, $J = 8.1$ Hz, 1H), 6.75 – 6.68 (m, 2H), 6.07 (d, $J = 8.0$ Hz, 1H), 4.03 (s, 3H), 3.65 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) $\delta = 169.0$ (d, $J = 20.3$ Hz), 145.8, 144.1 (d, $J = 12.8$ Hz), 135.8 (d, $J = 3.2$ Hz), 134.6, 134.1 (d, $J = 11.0$ Hz), 130.8 (d, $J = 13.3$ Hz), 128.7, 128.6 (d, $J = 9.8$ Hz), 127.7, 127.3, 126.2, 120.9 (q, $J = 320.0$ Hz), 117.2 (d, $J = 92.2$ Hz), 112.2, 108.7, 93.3 (d, $J = 111.7$ Hz), 56.3, 33.7 ppm; $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = 10.9$ ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -78.1$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{34}\text{H}_{28}\text{O}_2\text{P}$: 499.1827; found:499.1825; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3059, 2922, 1492, 1262, 730, 515 \text{ cm}^{-1}$.

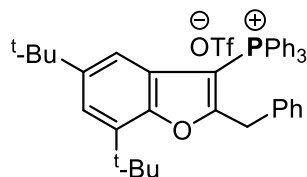


3la

Compound 3la: (99% yield, $R_f = 0.25$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 190-191 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) $\delta = 7.92 - 7.87$ (m, 3H), 7.79 – 7.73 (m, 12H), 7.38 (d, $J = 1.8$ Hz, 1H), 7.19 (q, $J = 3.7$ Hz, 3H), 6.74 (dd, $J = 6.4, 2.7$ Hz, 2H), 6.19 (d, $J = 1.8$ Hz, 1H), 3.71 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) $\delta = 171.5$ (d, $J = 19.6$ Hz), 149.3 (d, $J = 12.0$ Hz), 136.1 (d, $J = 3.2$ Hz), 134.2 (d, $J = 11.0$ Hz), 133.9, 131.0 (d, $J = 13.3$ Hz), 129.4 (d, $J = 9.6$ Hz), 128.8, 128.0, 127.4, 126.7, 120.9 (q, $J = 318.8$ Hz), 118.9, 118.3, 116.5 (d, $J = 91.9$ Hz), 93.7 (d, $J = 111.3$ Hz), 34.0

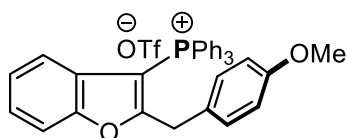
ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.5$ ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{24}\text{Cl}_2\text{OP}$: 537.042; found: 537.0938; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3075, 2922, 1577, 1439, 1270, 726, 514$ cm^{-1} .



3ma

Compound 3ma: (78% yield, $R_f = 0.35$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 112-115 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.88$ (d, $J = 7.1$ Hz, 3H), 7.77 (h, $J = 7.4$ Hz, 12H), 7.32 (d, $J = 1.7$ Hz, 1H), 7.21 – 7.14 (m, 3H), 6.77 (dd, $J = 6.6, 2.8$ Hz, 2H), 6.20 (d, $J = 1.7$ Hz, 1H), 3.65 (s, 2H), 1.48 (s, 9H), 1.01 ppm (s, 9H); ^{13}C NMR (126 MHz, Chloroform- d) $\delta = 169.3$ (d, $J = 20.6$ Hz), 160.7 (d, $J = 16.7$ Hz), 154.4 (d, $J = 12.8$ Hz), 134.7, 132.3 (d, $J = 15.7$ Hz), 128.8, 127.8, 127.3, 127.0 (d, $J = 9.7$ Hz), 126.6, 126.0 (d, $J = 10.5$ Hz), 125.1, 120.9 (d, $J = 3.1$ Hz), 120.9 (q, $J = 318.8$ Hz), 120.6, 119.7 (d, $J = 12.6$ Hz), 118.3 (d, $J = 91.7$ Hz), 112.5, 92.9 (d, $J = 112.2$ Hz), 55.8, 33.8 ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.8$ ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{41}\text{H}_{42}\text{OP}$: 581.2968; found: 581.2972; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3066, 2938, 1592, 1262, 1030, 636, 498$ cm^{-1} .

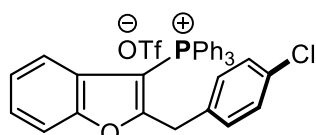


3na

Compound 3na: (99% yield, $R_f = 0.30$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 92-94 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.89$ (dq, $J = 8.7, 4.4, 4.0$ Hz, 4H), 7.81 – 7.72 (m, 12H), 7.58 (dd, $J = 8.8, 1.5$ Hz, 1H), 7.34 (dd, $J = 8.8, 1.5$ Hz, 1H), 6.99 (d, $J = 7.9$ Hz, 2H), 6.64 (d, $J = 7.9$ Hz, 2H), 6.30 (d, $J = 1.8$ Hz, 1H), 3.59 (s, 2H), 2.26 ppm (s,

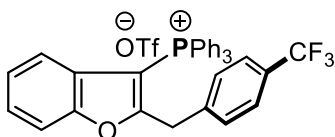
3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ = 171.3 (d, J = 20.2 Hz), 152.9 (d, J = 12.4 Hz), 137.1, 135.9 (d, J = 3.2 Hz), 134.1 (d, J = 10.9 Hz), 131.0, 130.9 (d, J = 13.3 Hz), 130.6, 129.4, 128.5 (d, J = 9.5 Hz), 128.0, 126.8, 120.8 (q, J = 320.0 Hz), 119.7, 116.9 (d, J = 92.0 Hz), 113.6, 92.3 (d, J = 112.3 Hz), 33.6, 20.9 ppm; ^{31}P NMR (202 MHz, CDCl_3) δ = 10.6 ppm; ^{19}F NMR (471 MHz, CDCl_3) δ = -78.1 ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{28}\text{O}_2\text{P}$: 487.1827; found: 487.1914; ATR-FTIR (cm^{-1}): $\bar{\nu}$ = 3059, 2920, 1441, 1268, 637, 541 cm^{-1} .



30a

Compound 30a: (99% yield, R_f = 0.26 [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 160-162 $^\circ\text{C}$):

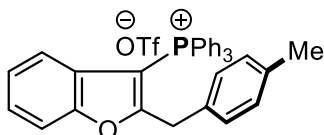
^1H NMR (500 MHz, Chloroform-*d*) δ = 7.91 – 7.85 (m, 3H), 7.75 (h, J = 8.2, 7.7 Hz, 12H), 7.64 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.11 (t, J = 7.7 Hz, 1H), 6.74 (d, J = 8.3 Hz, 2H), 6.48 (d, J = 8.0 Hz, 1H), 3.62 ppm (s, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ = 168.9 (d, J = 20.3 Hz), 154.5 (d, J = 12.8 Hz), 135.9 (d, J = 3.2 Hz), 134.2 (d, J = 11.0 Hz), 133.2 (d, J = 12.0 Hz), 130.9 (d, J = 13.2 Hz), 129.5, 128.8, 127.0 (d, J = 9.7 Hz), 126.6, 125.1, 120.9 (q, J = 320.0 Hz), 120.5, 117.3 (d, J = 92.0 Hz), 112.5, 93.0 (d, J = 112.1 Hz), 33.2 ppm; ^{19}F NMR (471 MHz, CDCl_3) δ = -78.1 ppm; ^{31}P NMR (202 MHz, CDCl_3) δ = 10.7 ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{25}\text{ClOP}$: 503.1331; found: 503.1328; ATR-FTIR (cm^{-1}): $\bar{\nu}$ = 3063, 2923, 2247, 1552, 1262, 725, 572 cm^{-1} .



3pa

Compound 3pa: (43% yield, R_f = 0.22 [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 105-106 $^\circ\text{C}$):

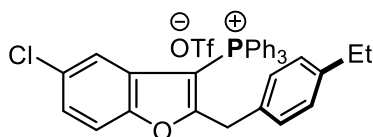
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.87 (t, J = 7.2 Hz, 3H), 7.81 – 7.71 (m, 13H), 7.64 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 7.7 Hz, 1H), 6.96 (d, J = 8.0 Hz, 2H), 6.49 (d, J = 8.0 Hz, 1H), 3.73 ppm (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ = 168.3 (d, J = 20.2 Hz), 154.5 (d, J = 12.6 Hz), 138.7, 135.9 (d, J = 3.2 Hz), 134.1 (d, J = 10.9 Hz), 130.9 (d, J = 13.3 Hz), 129.5 (q, J = 32.7 Hz), 128.6, 126.9 (d, J = 9.6 Hz), 126.7, 125.6 (d, J = 3.8 Hz), 125.2, 124.9, 122.7, 120.8 (q, J = 318.8 Hz), 120.5, 117.2 (d, J = 91.9 Hz), 112.5, 93.3 (d, J = 111.9 Hz), 33.6 ppm; **³¹P NMR** (202 MHz, CDCl₃) δ = 10.7 ppm; **¹⁹F NMR** (471 MHz, CDCl₃) δ = -62.6, -78.2 ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₄H₂₅F₃OP: 537.1595; found: 537.1591; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3012, 2924, 1555, 1439, 1108, 751, 526 cm⁻¹.



3qa

Compound 3qa: (97% yield, R_f = 0.25 [20:1 CH₂Cl₂/CH₃OH], white crystal, mp. = 204-205 °C):

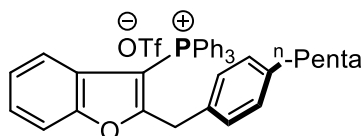
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.91 – 7.85 (m, 3H), 7.80 – 7.71 (m, 12H), 7.65 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.6 Hz, 2H), 6.65 (d, J = 7.7 Hz, 2H), 6.48 (d, J = 8.0 Hz, 1H), 3.57 (s, 2H), 2.27 ppm (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ = 169.7 (d, J = 20.4 Hz), 154.4 (d, J = 12.8 Hz), 137.1, 135.9 (d, J = 3.2 Hz), 134.1 (d, J = 10.9 Hz), 131.4, 130.8 (d, J = 13.3 Hz), 129.4, 127.9, 127.0 (d, J = 9.7 Hz), 126.5, 125.1, 120.9 (q, J = 318.8 Hz), 120.5, 117.3 (d, J = 92.1 Hz), 112.4, 92.6 (d, J = 112.2 Hz), 33.4, 20.9 ppm; **³¹P NMR** (202 MHz, CDCl₃) δ = 10.8 ppm; **¹⁹F NMR** (471 MHz, CDCl₃) δ = -78.1 ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₄H₂₈OP: 483.1878; found: 483.1874; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3059, 2920, 1438, 1273, 725, 636 cm⁻¹.



3ra

Compound 3ra: (99% yield, $R_f = 0.33$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 80-82 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.89$ (t, $J = 6.0$ Hz, 3H), 7.83 – 7.70 (m, 13H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.38 – 7.31 (m, 1H), 7.01 (d, $J = 7.8$ Hz, 2H), 6.68 (d, $J = 7.8$ Hz, 2H), 6.33 – 6.25 (m, 1H), 3.60 (s, 2H), 2.57 (q, $J = 7.5$ Hz, 2H), 1.18 ppm (t, $J = 7.6$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, Chloroform- d) $\delta = 171.5$ (d, $J = 20.2$ Hz), 152.9 (d, $J = 12.4$ Hz), 143.6, 136.0 (d, $J = 3.2$ Hz), 134.3 (d, $J = 10.9$ Hz), 131.4, 131.0 (d, $J = 13.3$ Hz), 130.7, 128.6 (d, $J = 9.6$ Hz), 128.2 (d, $J = 15.3$ Hz), 126.8, 120.8 (q, $J = 318.8$ Hz), 119.8, 117.1 (d, $J = 92.0$ Hz), 113.6, 92.4 (d, $J = 112.6$ Hz), 33.8, 28.3, 15.5 ppm; $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = 10.6$ ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -78.1$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{29}\text{ClOP}$: 507.1645; found: 507.1823; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3063, 2922, 1440, 1265, 637, 517$ cm^{-1} .

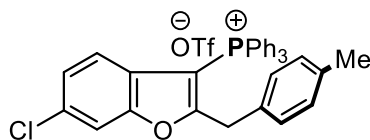


3sa

Compound 3sa: (95% yield, $R_f = 0.27$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 97-98 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.91 - 7.84$ (m, 3H), 7.79 – 7.69 (m, 12H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.11 (t, $J = 7.7$ Hz, 1H), 7.00 (d, $J = 7.9$ Hz, 2H), 6.67 (d, $J = 7.9$ Hz, 2H), 6.48 (d, $J = 8.0$ Hz, 1H), 3.58 (s, 2H), 2.55 – 2.49 (m, 2H), 1.57 – 1.50 (m, 2H), 1.36 – 1.26 (m, 4H), 0.87 ppm (t, $J = 7.0$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, Chloroform- d) $\delta = 169.7$ (d, $J = 20.5$ Hz), 154.4 (d, $J = 12.8$ Hz), 142.2, 135.9 (d, $J = 3.2$ Hz), 134.1 (d, $J = 10.8$ Hz), 131.6, 130.8 (d, $J = 13.3$ Hz), 128.7, 127.9, 127.0 (d, $J = 9.9$ Hz), 126.5, 125.1, 120.8 (t, $J = 318.8$ Hz), 120.5, 117.3 (d, $J = 92.2$ Hz), 112.5, 92.6 (d, $J = 112.2$ Hz), 35.3, 33.5, 31.3, 31.0, 22.4, 13.9 ppm; $^{19}\text{F NMR}$

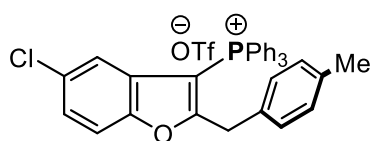
(471 MHz, CDCl₃) $\delta = -78.1$ ppm; ³¹P NMR (202 MHz, CDCl₃) $\delta = 10.8$ ppm; HRMS (ESI): m/z calcd for [M]⁺ = C₃₈H₃₆OP: 539.2504; found: 539.2484; ATR-FTIR (cm⁻¹): $\bar{\nu} = 3061, 2925, 1438, 1266, 1030, 636, 542$ cm⁻¹.



3ta

Compound 3ta: (99.5% yield, $R_f = 0.28$ [20:1 CH₂Cl₂/CH₃OH]), yellow crystal, mp. = 172-174 °C)

¹H NMR (500 MHz, Chloroform-*d*) $\delta = 7.91 - 7.84$ (m, 3H), 7.77 – 7.71 (m, 1H), 7.65 (d, $J = 8.5$ Hz, 1H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.11 (t, $J = 7.7$ Hz, 1H), 6.73 (d, $J = 8.7$ Hz, 2H), 6.68 (d, $J = 8.7$ Hz, 2H), 6.47 (d, $J = 8.0$ Hz, 1H), 3.74 (s, 3H), 3.55 ppm (s, 2H); ¹³C NMR (126 MHz, Chloroform-*d*) $\delta = 169.9$ (d, $J = 20.6$ Hz), 158.8, 154.4 (d, $J = 12.8$ Hz), 135.9 (d, $J = 3.1$ Hz), 134.1 (d, $J = 10.9$ Hz), 130.9 (d, $J = 13.1$ Hz), 129.1, 127.0 (d, $J = 10.0$ Hz), 126.5, 126.3, 125.1, 120.9 (q, $J = 320.0$ Hz), 120.4, 117.3 (d, $J = 92.1$ Hz), 114.1, 112.4, 92.4 (d, $J = 112.3$ Hz), 55.3, 33.0 ppm; ³¹P NMR (202 MHz, CDCl₃) $\delta = 10.8$ ppm; ¹⁹F NMR (471 MHz, CDCl₃) $\delta = -78.1$ ppm; HRMS (ESI): m/z calcd for [M]⁺ = C₃₄H₂₈OP: 483.1878; found: 483.1872; ATR-FTIR (cm⁻¹): $\bar{\nu} = 3061, 2956, 1511, 1262, 725, 515$ cm⁻¹.

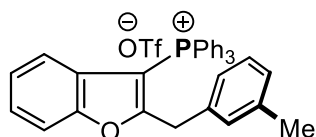


3ua

Compound 3ua: (99% yield, $R_f = 0.28$ [20:1 CH₂Cl₂/CH₃OH]), white crystal, mp. = 154-156 °C):

¹H NMR (500 MHz, Chloroform-*d*) $\delta = 7.89$ (td, $J = 6.3, 5.7, 2.7$ Hz, 3H), 7.82 – 7.72 (m, 12H), 7.58 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.35 (dd, $J = 8.9, 2.0$ Hz, 1H), 6.99 (d, $J = 7.8$ Hz, 2H), 6.64 (d, $J = 7.9$ Hz, 2H), 6.30 (d, $J = 1.9$ Hz, 1H), 3.59 (s, 2H), 2.27 ppm (s, 3H) ppm; ¹³C NMR (126 MHz, Chloroform-*d*) $\delta = 171.4$ (d, $J = 20.1$ Hz), 152.9 (d, $J = 12.6$ Hz), 137.2, 136.0 (d, $J = 3.1$ Hz), 134.2 (d, $J = 11.0$ Hz), 131.1, 131.0 (d, $J =$

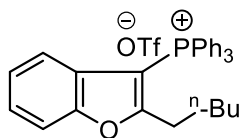
13.2 Hz), 130.7, 129.5, 128.5 (d, $J = 9.7$ Hz), 128.0, 126.8, 120.9 (q, $J = 318.8$ Hz), 119.8, 117.0 (d, $J = 92.0$ Hz), 113.6, 92.4 (d, $J = 112.6$ Hz), 33.7, 20.9 ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.6$ ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{34}\text{H}_{27}\text{ClOP}$: 517.148; found: 517.149; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3063, 2921, 1440, 1265, 635, 516$ cm^{-1} .



3va

Compound 3va: (86% yield, $R_f = 0.27$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 161-162 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.91 - 7.85$ (m, 3H), 7.74 (q, $J = 6.1, 4.1$ Hz, 12H), 7.67 (d, $J = 8.3$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 1H), 7.12 (t, $J = 7.7$ Hz, 1H), 7.07 (t, $J = 7.6$ Hz, 1H), 7.00 (d, $J = 7.4$ Hz, 1H), 6.56 (d, $J = 7.4$ Hz, 2H), 6.49 (d, $J = 12.1$ Hz, 2H), 3.61 (s, 0H), 2.21 ppm (s, 3H); ^{13}C NMR (126 MHz, Chloroform- d) $\delta = 169.5$ (d, $J = 20.3$ Hz), 154.4 (d, $J = 12.8$ Hz), 138.4, 135.8 (d, $J = 3.0$ Hz), 134.4, 134.1 (d, $J = 10.9$ Hz), 130.8 (d, $J = 13.2$ Hz), 128.7 (d, $J = 12.1$ Hz), 128.0, 127.0 (d, $J = 9.9$ Hz), 126.5, 125.0 (d, $J = 22.9$ Hz), 120.9 (q, $J = 318.8$ Hz), 120.4, 117.3 (d, $J = 92.1$ Hz), 112.5, 92.7 (d, $J = 112.2$ Hz), 33.8, 21.2 ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.7$ ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.0$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{34}\text{H}_{28}\text{OP}$: 483.1878; found: 483.1872; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3066, 2921, 1546, 1453, 1262, 751, 542$ cm^{-1} .

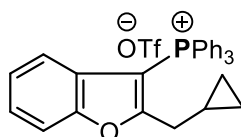


3wa

Compound 3wa: (99% yield, $R_f = 0.30$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 154-155 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.96 - 7.89$ (m, 3H), 7.84 - 7.72 (m, 12H), 7.68 - 7.62 (m, 1H), 7.44 - 7.37 (m, 1H), 7.14 - 7.07 (m, 1H), 6.44 (d, $J = 7.9$ Hz, 1H),

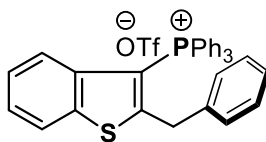
2.17 – 2.08 (m, 2H), 1.47 (p, $J = 7.8$ Hz, 2H), 1.12 (h, $J = 7.2$ Hz, 2H), 0.95 (p, $J = 7.5$ Hz, 2H), 0.78 ppm (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) $\delta = 172.4$ (d, $J = 21.0$ Hz), 154.2 (d, $J = 12.9$ Hz), 135.9 (d, $J = 3.0$ Hz), 134.0 (d, $J = 10.9$ Hz), 130.8 (d, $J = 13.2$ Hz), 126.9 (d, $J = 9.9$ Hz), 126.3, 125.0, 120.8 (q, $J = 318.8$ Hz), 120.2, 117.5 (d, $J = 92.1$ Hz), 112.2, 91.4 (d, $J = 113.3$ Hz), 31.2, 28.2, 28.0, 21.9, 13.6 ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.7$; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{31}\text{H}_{30}\text{OP}$: 449.2034; found: 449.2036; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3059, 2928, 1549, 1439, 1263, 723, 515$ cm^{-1} .



3xa

Compound 3xa: (98% yield, $R_f = 0.35$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 197-199 $^\circ\text{C}$):

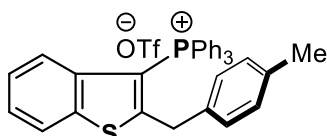
^1H NMR (500 MHz, Chloroform-*d*) $\delta = 7.91$ (td, $J = 5.8, 3.1$ Hz, 3H), 7.81 – 7.74 (m, 12H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.42 (t, $J = 7.7$ Hz, 1H), 7.11 (t, $J = 7.7$ Hz, 1H), 6.46 (d, $J = 8.0$ Hz, 1H), 2.04 (d, $J = 6.9$ Hz, 2H), 1.83 (s, 1H), 0.82 (ddt, $J = 12.4, 7.5, 3.7$ Hz, 1H), 0.43 (q, $J = 5.6$ Hz, 2H), -0.08 ppm (q, $J = 5.1$ Hz, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) $\delta = 171.8$ (d, $J = 20.8$ Hz), 154.4 (d, $J = 12.8$ Hz), 135.9 (d, $J = 3.1$ Hz), 134.1 (d, $J = 10.9$ Hz), 130.9 (d, $J = 13.2$ Hz), 127.0 (d, $J = 10.0$ Hz), 126.4, 125.0, 120.9 (q, $J = 318.8$ Hz), 120.4, 117.5 (d, $J = 92.2$ Hz), 112.4, 91.7 (d, $J = 113.1$ Hz), 32.4, 9.3, 4.7 ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.8$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{30}\text{H}_{26}\text{OP}$: 433.1721 found: 433.1731; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3065, 3007, 1556, 1441, 1265, 721, 513$ cm^{-1} .



3ya

Compound 3ya: (50% yield, $R_f = 0.30$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 229-231 $^\circ\text{C}$):

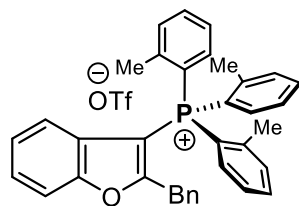
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.88 (d, J = 8.2 Hz, 1H), 7.84 (t, J = 7.2 Hz, 3H), 7.76 – 7.68 (m, 12H), 7.38 (t, J = 7.7 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.12 (t, J = 7.8 Hz, 1H), 6.91 – 6.87 (m, 2H), 6.78 (d, J = 8.4 Hz, 1H), 3.66 ppm (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ = 166.6 (d, J = 13.3 Hz), 139.6 (d, J = 14.2 Hz), 138.6 (d, J = 14.2 Hz), 137.2, 135.7 (d, J = 3.2 Hz), 134.4 (d, J = 10.9 Hz), 130.8 (d, J = 13.0 Hz), 128.8, 128.6, 127.7, 125.8 (d, J = 10.3 Hz), 123.8 (d, J = 1.7 Hz), 122.9, 120.9 (q, J = 318.8 Hz), 118.4 (d, J = 89.4 Hz), 104.3 (d, J = 94.8 Hz), 35.6 ppm (d, J = 3.0 Hz); **³¹P NMR** (202 MHz, CDCl₃) δ = 10.8 ppm; **¹⁹F NMR** (471 MHz, CDCl₃) δ = -78.1 ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₃H₂₆PS: 485.1487 found: 485.1482; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3063, 2922, 1436, 1204, 756, 544 cm⁻¹.



3za

Compound 3za: (51% yield, R_f = 0.30 [20:1 CH₂Cl₂/CH₃OH], white crystal, mp. = 212-214 °C):

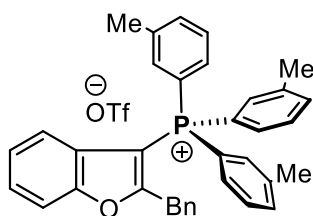
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.89 – 7.82 (m, 4H), 7.75 (d, J = 7.5 Hz, 3H), 7.72 (q, J = 4.7 Hz, 9H), 7.38 (t, J = 7.7 Hz, 1H), 7.11 (t, J = 7.8 Hz, 1H), 7.04 (d, J = 7.7 Hz, 2H), 6.78 (dd, J = 11.6, 8.1 Hz, 3H), 3.58 (s, 2H), 2.30 ppm (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ = 167.2 (d, J = 13.5 Hz), 139.6 (d, J = 14.2 Hz), 138.5 (d, J = 14.2 Hz), 137.6, 135.7 (d, J = 3.2 Hz), 134.3 (d, J = 10.6 Hz), 134.1, 130.8 (d, J = 13.0 Hz), 129.5, 128.5, 125.8 (d, J = 12.8 Hz), 123.7, 122.8, 120.9 (q, J = 318.8 Hz), 118.4 (d, J = 89.3 Hz), 104.1 (d, J = 95.1 Hz), 35.3 (d, J = 2.9 Hz), 21.0 ppm; **³¹P NMR** (202 MHz, CDCl₃) δ = 10.8 ppm; **¹⁹F NMR** (471 MHz, CDCl₃) δ = -78.0 ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₄H₂₈PS: 499.1644 found: 499.1649; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3059, 2923, 1455, 1263, 725, 513 cm⁻¹.



3ab

Compound 3ab: (84% yield, $R_f = 0.30$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 218-219 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 8.02 - 7.90$ (m, 1H), 7.89 – 7.77 (m, 2H), 7.76 – 7.54 (m, 9H), 7.49 – 7.34 (m, 3H), 7.24 – 7.04 (m, 4H), 6.73 (dd, $J = 16.7, 7.0$ Hz, 1H), 6.55 (d, $J = 7.4$ Hz, 1H), 4.16 (d, $J = 15.8$ Hz, 1H), 3.87 (d, $J = 15.7$ Hz, 0.5H), 3.61 (d, $J = 16.0$ Hz, 0.5H), 2.03 (d, $J = 10.9$ Hz, 3H), 1.93 (s, 1H), 1.88 (s, 3H), 1.78 (s, 1H), 1.67 ppm (s, 1H); $^{13}\text{C NMR}$ (126 MHz, Chloroform- d) $\delta = 167.0$ (dd, $J = 18.8, 21.3$ Hz), 154.7 (d, $J = 13.0$ Hz), 144.2 (d, $J = 17.1$ Hz), 143.8 (d, $J = 6.4$ Hz), 143.3 (dd, $J = 1.25, 1.25$ Hz), 136.3 (d, $J = 17.9$ Hz), 135.7, 135.1 (d, $J = 11.4$ Hz), 134.2 (dd, $J = 18.1, 10.1$ Hz), 132.6 (d, $J = 11.5$ Hz), 128.6 (d, $J = 24.0$ Hz), 128.3 (d, $J = 11.7$ Hz), 128.1 (d, $J = 14.6$ Hz), 127.4 (d, $J = 31.2$ Hz), 126.5 (d, $J = 34.3$ Hz), 125.3 (d, $J = 46.5$ Hz), 122.1, 120.7 (q, $J = 318.8$ Hz), 120.3, 112.4 (d, $J = 45.6$ Hz), 92.9 (d, $J = 110.9$ Hz), 41.8, 34.8 (d, $J = 286.5$ Hz), 26.8, 24.1 (d, $J = 167.6$ Hz), 22.5 ppm (t, $J = 21.3$ Hz); $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = 11.2, 10.4$ ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -78.0$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{36}\text{H}_{32}\text{OP}$: 511.2186; found: 511.2187; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3006, 2924, 1450, 1266, 1156, 752$ cm^{-1}

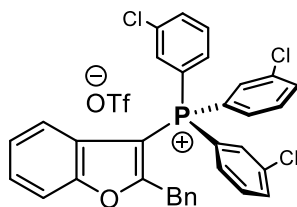


3ac

Compound 3ac: (99% yield, $R_f = 0.35$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 92-94 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.70 - 7.66$ (m, 5H), 7.66 – 7.63 (m, 2H), 7.52

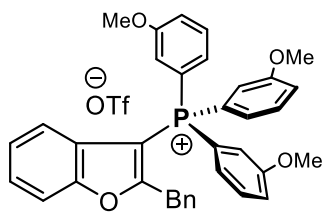
(ddt, $J = 13.5, 7.6, 1.7$ Hz, 3H), 7.44 – 7.39 (m, 4H), 7.21 (dd, $J = 5.1, 1.9$ Hz, 3H), 7.17 – 7.12 (m, 1H), 6.80 – 6.73 (m, 2H), 6.51 (d, $J = 8.0$ Hz, 1H), 3.64 (s, 2H), 2.38 ppm (s, 9H); ^{13}C NMR (126 MHz, Chloroform-*d*) $\delta = 168.8$ (d, $J = 20.2$ Hz), 154.3 (d, $J = 12.6$ Hz), 141.1 (d, $J = 13.0$ Hz), 136.6 (d, $J = 3.2$ Hz), 134.6, 133.8 (d, $J = 10.9$ Hz), 131.3 (d, $J = 10.7$ Hz), 130.6 (d, $J = 14.1$ Hz), 120.8 (q, $J = 318.8$ Hz), 128.6, 127.7, 127.2, 126.9 (d, $J = 9.7$ Hz), 126.4, 124.9, 120.8 (t, $J = 320.0$ Hz), 120.4, 117.2 (d, $J = 91.4$ Hz), 112.3, 93.3 (d, $J = 111.6$ Hz), 33.7, 21.4 ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.6$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{36}\text{H}_{32}\text{OP}$: 511.2191; found: 511.2189; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3060, 2923, 1453, 1265, 1147, 752, 560$ cm^{-1} .



3ad

Compound 3ad: (88% yield, $R_f = 0.35$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 154-156 °C):

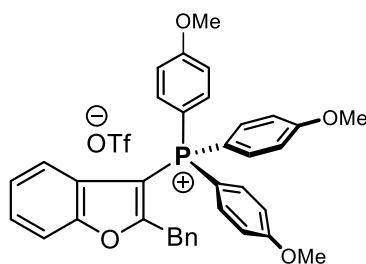
^1H NMR (500 MHz, Chloroform-*d*) $\delta = 7.90 - 7.79$ (m, 9H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.53 – 7.43 (m, 4H), 7.25 – 7.15 (m, 4H), 6.78 – 6.70 (m, 2H), 6.52 (d, $J = 7.9$ Hz, 1H), 3.79 ppm (s, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) $\delta = 170.8$ (d, $J = 21.2$ Hz), 154.5 (d, $J = 13.3$ Hz), 137.2 (d, $J = 17.6$ Hz), 136.5 (d, $J = 3.0$ Hz), 134.5, 133.1, 133.1 (d, $J = 20$ Hz), 133.0 (d, $J = 4.2$ Hz), 132.9 (d, $J = 3.6$ Hz), 132.9 (d, $J = 3.6$ Hz), 129.0, 127.7, 127.5, 127.0, 126.5 (d, $J = 10.1$ Hz), 125.5, 120.7 (q, $J = 318.8$ Hz), 120.0, 118.6 (d, $J = 92.1$ Hz), 112.9, 90.7 (d, $J = 114.5$ Hz), 34.2 ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 10.5$ ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.2$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{33}\text{H}_{23}\text{Cl}_3\text{OP}$: 571.0552; found: 571.0551; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3061, 2921, 1467, 1262, 1150, 753, 562$ cm^{-1} .



3ae

Compound 3ae: (99% yield, $R_f = 0.30$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 207-209 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) $\delta = 7.68$ (td, $J = 8.1, 4.7$ Hz, 4H), 7.43 (ddd, $J = 8.4, 7.4, 1.2$ Hz, 1H), 7.39 (ddt, $J = 8.5, 2.4, 1.1$ Hz, 3H), 7.29 (dddd, $J = 13.2, 7.6, 1.7, 0.8$ Hz, 3H), 7.22 – 7.19 (m, 3H), 7.19 – 7.15 (m, 1H), 7.11 (dt, $J = 15.1, 2.0$ Hz, 3H), 6.80 – 6.75 (m, 2H), 6.62 – 6.57 (m, 1H), 3.76 (s, 9H), 3.69 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) $\delta = 169.3$ (d, $J = 20.4$ Hz), 160.7 (d, $J = 17.0$ Hz), 154.4 (d, $J = 12.5$ Hz), 134.7, 132.3 (d, $J = 15.6$ Hz), 128.8, 127.8, 127.3, 127.0 (d, $J = 9.7$ Hz), 126.6, 126.0 (d, $J = 10.6$ Hz), 125.1, 120.9 (d, $J = 3.1$ Hz), 120.9 (t, $J = 318.8$ Hz), 120.6, 119.7 (d, $J = 12.6$ Hz), 118.3 (d, $J = 91.9$ Hz), 112.5, 92.9 (d, $J = 112.3$ Hz), 55.8, 33.8 ppm; $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = 11.4$ ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -78.1$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{36}\text{H}_{32}\text{O}_4\text{P}$: 559.2038; found: 559.2054L; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3061, 2963, 1439, 1262, 1152, 726, 517$ cm^{-1}

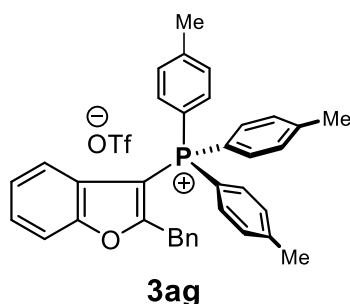


3af

Compound 3af: (69.2% yield, $R_f = 0.25$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 151-152 °C):

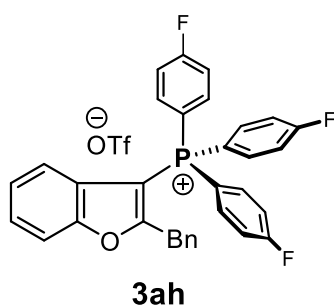
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) $\delta = 7.60$ (dt, $J = 12.8, 7.8$ Hz, 7H), 7.40 (t, $J = 7.9$ Hz, 1H), 7.24 – 7.10 (m, 10H), 6.81 (dd, $J = 6.6, 2.8$ Hz, 2H), 6.57 (d, $J = 8.0$ Hz, 1H), 3.92 (s, 9H), 3.66 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) $\delta = 168.4$ (d, $J =$

20.2 Hz), 165.0 (d, $J = 3.0$ Hz), 154.3 (d, $J = 12.5$ Hz), 135.8 (d, $J = 12.6$ Hz), 134.8, 128.6, 127.9, 127.2 (d, $J = 8.8$ Hz), 127.2, 126.3, 124.9, 120.7, 120.8 (q, $J = 318.8$ Hz), 116.4 (d, $J = 14.4$ Hz), 112.2, 108.1 (d, $J = 100.8$ Hz), 94.8 (d, $J = 112.2$ Hz), 55.9, 33.6 ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 8.6$ ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{36}\text{H}_{32}\text{O}_4\text{P}$: 559.2038; found: 559.2037; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3095, 2942, 1592, 1269, 1104, 1029, 545$ cm^{-1} .



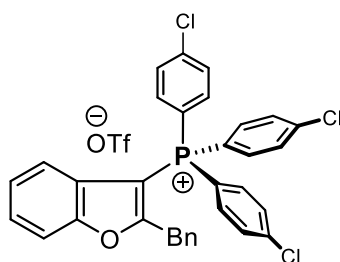
Compound 3ag: (96% yield, $R_f = 0.30$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 167-169 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.64$ (d, $J = 8.4$ Hz, 1H), 7.57 (dd, $J = 13.2, 8.2$ Hz, 6H), 7.49 (dd, $J = 8.1, 3.3$ Hz, 6H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.23 – 7.18 (m, 3H), 7.13 (t, $J = 7.7$ Hz, 1H), 6.83 – 6.74 (m, 2H), 6.52 (d, $J = 8.0$ Hz, 1H), 3.64 (s, 2H), 2.50 ppm (s, 9H); ^{13}C NMR (126 MHz, Chloroform- d) $\delta = 168.8$ (d, $J = 20.2$ Hz), 154.4 (d, $J = 12.7$ Hz), 147.3 (d, $J = 3.1$ Hz), 134.7, 133.9 (d, $J = 11.4$ Hz), 131.4 (d, $J = 13.6$ Hz), 128.7, 128.0, 127.3, 127.1 (d, $J = 9.6$ Hz), 126.4, 125.0, 120.9 (q, $J = 318.8$ Hz), 120.6, 114.2 (d, $J = 94.9$ Hz), 112.3, 93.7 (d, $J = 112.0$ Hz), 33.7, 21.8 ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.1$ ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 9.9$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{36}\text{H}_{32}\text{OP}$: 511.2191; found: 511.2191; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3030, 2922, 1597, 1266, 1107, 637, 535$ cm^{-1} .



Compound 3ah: (89% yield, $R_f = 0.25$ [20:1 CH₂Cl₂/CH₃OH], white crystal, mp. = 176-178 °C):

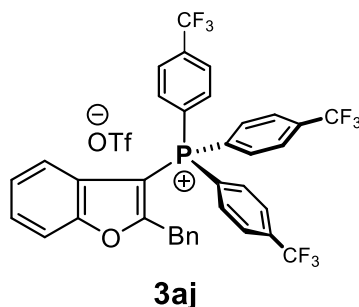
¹H NMR (500 MHz, Chloroform-*d*) $\delta = 7.81$ (ddd, $J = 12.7, 8.2, 4.8$ Hz, 6H), 7.66 (d, $J = 8.3$ Hz, 1H), 7.41 (dt, $J = 15.8, 7.8$ Hz, 7H), 7.23 – 7.17 (m, 3H), 7.15 (t, $J = 7.7$ Hz, 1H), 6.76 (s, 2H), 6.50 (d, $J = 7.9$ Hz, 1H), 3.71 ppm (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) $\delta = 169.9$ (d, $J = 20.8$ Hz), 168.1 (d, $J = 3.5$ Hz), 166.0 (d, $J = 3.3$ Hz), 154.5 (d, $J = 12.9$ Hz), 137.2 (dd, $J = 13.1, 9.8$ Hz), 134.7, 128.8, 127.8, 127.4, 126.8 (d, $J = 10.1$ Hz), 126.7, 125.2, 120.7 (q, $J = 318.8$ Hz), 120.2, 118.7 (dd, $J = 22.3, 14.9$ Hz), 113.4 (d, $J = 3.5$ Hz), 112.7, 112.6 (d, $J = 3.4$ Hz), 92.5 (d, $J = 114.3$ Hz), 33.9 ppm; **³¹P NMR** (202 MHz, CDCl₃) $\delta = 9.8$ ppm; **¹⁹F NMR** (471 MHz, CDCl₃) $\delta = -78.3, -98.1, -98.1$ ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₃H₂₃F₃OP: 523.1439; found: 23.1436; **ATR-FTIR** (cm⁻¹): $\bar{\nu} = 3065, 2975, 1592, 1274, 1155, 835, 540$ cm⁻¹.



3ai

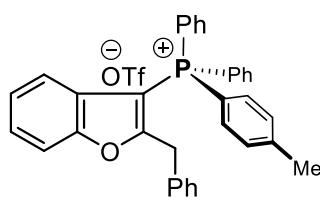
Compound 3ai: (99% yield, $R_f = 0.30$ [20:1 CH₂Cl₂/CH₃OH], white crystal, mp. = 84-86 °C):

¹H NMR (500 MHz, Chloroform-*d*) $\delta = 7.78 - 7.64$ (m, 13H), 7.59 (d, $J = 7.5$ Hz, 1H), 7.43 (t, $J = 7.9$ Hz, 1H), 7.19 (dd, $J = 4.6, 2.5$ Hz, 3H), 6.80 – 6.70 (m, 2H), 6.51 (d, $J = 8.0$ Hz, 1H), 3.76 ppm (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) $\delta = 170.4$ (d, $J = 21.1$ Hz), 154.5 (d, $J = 13.1$ Hz), 143.3 (d, $J = 3.7$ Hz), 135.6 (d, $J = 12.4$ Hz), 134.9, 131.4 (d, $J = 14.3$ Hz), 128.8, 127.8, 127.4, 126.8, 126.7, 125.3, 120.7 (q, $J = 318.8$ Hz), 120.2, 115.2 (d, $J = 95.6$ Hz), 112.8, 91.6 (d, $J = 114.5$ Hz), 34.1 ppm; **³¹P NMR** (202 MHz, CDCl₃) $\delta = 10.5$ ppm; **¹⁹F NMR** (471 MHz, CDCl₃) $\delta = -78.2$ ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₃H₂₃Cl₃OP: 571.0552; found: 571.0549; **ATR-FTIR** (cm⁻¹): $\bar{\nu} = 3086, 2923, 1577, 1262, 760, 559$ cm⁻¹



Compound 3aj: (98% yield, $R_f = 0.25$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 95-96 °C)

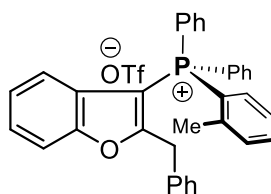
$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 8.03 - 7.88$ (m, 12H), 7.70 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.46 (t, $J = 7.9$ Hz, 1H), 7.21 - 7.09 (m, 4H), 6.63 (d, $J = 7.2$ Hz, 2H), 6.51 (d, $J = 8.0$ Hz, 1H), 3.83 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform- d) $\delta = 171.3$ (d, $J = 21.5$ Hz), 154.6 (d, $J = 13.2$ Hz), 137.4 (q, $J = 33.8$ Hz), 135.3 (d, $J = 11.9$ Hz), 134.9, 128.9, 127.7 (dd, $J = 14.0, 3.8$ Hz), 127.5, 127.4, 127.0, 126.6 (d, $J = 10.1$ Hz), 125.6, 123.7, 121.5, 120.6 (q, $J = 318.8$ Hz), 120.7 (d, $J = 91.6$ Hz), 120.0, 113.0, 90.0 (d, $J = 114.6$ Hz), 34.3 ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -63.8, -78.5$ ppm; $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = 10.9$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{36}\text{H}_{23}\text{F}_9\text{OP}$: 673.1343; found: 673.1339; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3100, 2922, 1545, 1262, 1135, 714, 546$ cm^{-1} .



Compound 3ak: (98% yield, $R_f = 0.30$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 167 -168°C):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.86$ (td, $J = 6.1, 5.6, 2.6$ Hz, 2H), 7.80 - 7.69 (m, 8H), 7.67 - 7.59 (m, 3H), 7.51 (dd, $J = 8.2, 3.5$ Hz, 2H), 7.44 - 7.38 (m, 1H), 7.23 - 7.16 (m, 3H), 7.12 (t, $J = 7.7$ Hz, 1H), 6.82 - 6.73 (m, 2H), 6.50 (d, $J = 8.0$ Hz, 1H),

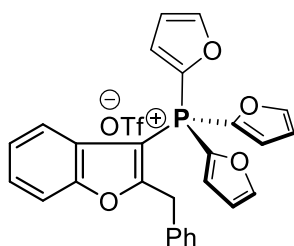
3.64 (s, 2H), 2.51 ppm (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ = 169.2(d, J = 20.3 Hz), 154.4 (d, J = 12.8 Hz), 147.5 (d, J = 3.1 Hz), 135.7 (d, J = 3.1 Hz), 134.6, 134.0 (dd, J = 11.2, 3.8 Hz), 131.5 (d, J = 13.6 Hz), 130.7 (d, J = 13.1 Hz), 128.7, 127.9, 127.3, 127.0 (d, J = 9.7 Hz), 126.5, 125.0, 120.8 (q, J = 318.8Hz), 120.5, 117.6 (d, J = 92.2 Hz), 113.4 (d, J = 94.5 Hz), 112.4, 93.1 (d, J = 112.1 Hz), 33.7, 21.8 ppm; ^{31}P NMR (202 MHz, CDCl_3) δ = 10.5 ppm; ^{19}F NMR (471 MHz, CDCl_3) δ = -78.1; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{34}\text{H}_{28}\text{OP}$: 483.1878; found: 483.1880; ATR-FTIR (cm^{-1}): $\bar{\nu}$ = 3063, 2923, 1439, 1273, 1107, 753, 543 cm^{-1} .



3al

Compound 3al: (99% yield, R_f = 0.30 [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 206-208 $^\circ\text{C}$):

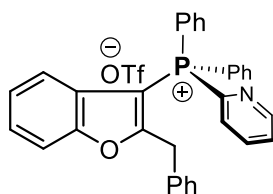
^1H NMR (500 MHz, Chloroform-*d*) δ = 7.89 – 7.81 (m, 3H), 7.77 – 7.71 (m, 8H), 7.65 (d, J = 8.5 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.49 (dt, J = 7.6, 3.8 Hz, 1H), 7.42 (dt, J = 15.9, 7.7 Hz, 2H), 7.22 – 7.17 (m, 3H), 7.10 (t, J = 7.7 Hz, 1H), 6.74 (dd, J = 6.3, 2.5 Hz, 2H), 6.50 (d, J = 8.0 Hz, 1H), 3.77 (s, 2H), 2.06 ppm (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ = 168.4 (d, J = 20.4 Hz), 154.4 (d, J = 12.8 Hz), 143.8 (d, J = 9.6 Hz), 136.3 (d, J = 3.0 Hz), 135.8, 135.6 (d, J = 3.2 Hz), 134.3 (d, J = 6.1 Hz), 134.1, 133.8 (d, J = 10.9 Hz), 131.0 (d, J = 13.3 Hz), 128.8, 128.2 (d, J = 13.5 Hz), 127.4, 126.8 (d, J = 9.8 Hz), 126.6, 125.1, 120.9 (q, J = 318.8 Hz), 120.2, 117.7 (d, J = 91.4 Hz), 115.5 (d, J = 90.5 Hz), 112.4, 93.3 (d, J = 110.9 Hz), 34.0, 23.1 ppm (d, J = 5.4 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ = -78.0 ppm; ^{31}P NMR (202 MHz, CDCl_3) δ = 10.8 ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{34}\text{H}_{28}\text{OP}$: 483.1878; found: 483.1873; ATR-FTIR (cm^{-1}): $\bar{\nu}$ = 3063, 2966, 1450, , 1270, 1149, 753, 545 cm^{-1} .



3am

Compound 3am: (58% yield, $R_f = 0.50$ [10:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 111-113 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) $\delta = 8.12 - 8.10$ (m, 2H), 7.65 (dt, $J = 3.7, 2.0$ Hz, 4H), 7.46 – 7.42 (m, 1H), 7.30 – 7.24 (m, 3H), 7.03 – 6.97 (m, 2H), 6.90 (dt, $J = 3.7, 1.8$ Hz, 3H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.81 – 6.78 (m, 1H), 6.41 (dt, $J = 3.3, 1.7$ Hz, 1H), 3.82 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) $\delta = 170.4$ (d, $J = 24.3$ Hz), 154.7 (d, $J = 14.7$ Hz), 154.4 (d, $J = 9.4$ Hz), 134.1, 132.0 (d, $J = 24.3$ Hz), 130.5, 129.3, 128.9, 128.3, 127.6, 126.8, 125.9 (d, $J = 12.4$ Hz), 125.5, 120.9 (q, $J = 318.8$ Hz), 119.7, 114.0 (d, $J = 10.5$ Hz), 112.5, 90.0 (d, $J = 130.7$ Hz), 34.0 ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -78.2$ ppm; $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = -29.7$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{27}\text{H}_{20}\text{O}_4\text{P}$: 439.1099; found: 439.1096; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3118, 2992, 1452, 1271, 1033, 765 \text{ cm}^{-1}$.

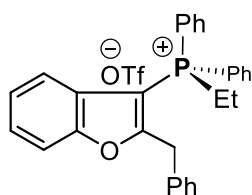


3an

Compound 3an: (93% yield, $R_f = 0.40$ [10:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], red crystal, mp. = 222-224 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) $\delta = 9.23$ (d, $J = 6.4$ Hz, 1H), 8.00 (t, $J = 7.6$ Hz, 1H), 7.91 – 7.85 (m, 2H), 7.71 (dd, $J = 16.0, 7.5$ Hz, 4H), 7.56 – 7.51 (m, 3H), 7.48 (dt, $J = 12.3, 6.1$ Hz, 5H), 7.44 – 7.36 (m, 4H), 7.36 – 7.30 (m, 1H), 6.96 (t, $J = 7.6$ Hz, 1H), 6.82 (d, $J = 8.2$ Hz, 1H), 5.22 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) $\delta = 164.0$ (d, $J = 10.9$ Hz), 158.4 (d, $J = 2.3$ Hz), 144.5, 143.2, 137.1, 134.2, 132.8 (d,

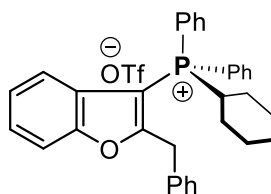
$J = 2.2$ Hz), 132.1 (d, $J = 3.6$ Hz), 130.3 (d, $J = 11.4$ Hz), 129.8(t, $J = 17.5$ Hz), 129.2 (d, $J = 3.4$ Hz), 129.1, 128.3, 128.0, 127.7, 123.5 (d, $J = 16.8$ Hz), 122.0 (d, $J = 7.8$ Hz), 120.9, 120.9 (q, $J = 318.8$ Hz), 120.7, 116.7 (d, $J = 22.1$ Hz), 113.9 (d, $J = 3.7$ Hz), 32.3 ppm (d, $J = 13.3$ Hz); ^{31}P NMR (202 MHz, CDCl_3) $\delta = -59.2$ ppm; ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.2$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{32}\text{H}_{25}\text{NOP}$: 470.1674; found: 470.1672; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3057, 2920, 1600, 1461, 1262, 738, 540$ cm^{-1} .



3ao

Compound 3ao: (63% yield, $R_f = 0.40$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 142-144 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform- d) $\delta = 7.85 - 7.74$ (m, 6H), 7.65 (ddd, $J = 8.4, 7.0, 3.1$ Hz, 5H), 7.41 (ddd, $J = 8.4, 7.3, 1.2$ Hz, 1H), 7.25 - 7.17 (m, 4H), 6.88 - 6.77 (m, 3H), 3.91 (s, 2H), 3.51 - 3.41 (m, 2H), 1.34 ppm (dt, $J = 21.0, 7.5$ Hz, 3H); ^{13}C NMR (126 MHz, Chloroform- d) $\delta = 168.4$ (d, $J = 19.4$ Hz), 154.5 (d, $J = 12.4$ Hz), 135.3 (d, $J = 3.1$ Hz), 134.7, 132.9 (d, $J = 10.4$ Hz), 130.7 (d, $J = 12.8$ Hz), 128.9, 128.1, 127.4, 126.8 (d, $J = 9.7$ Hz), 126.4, 124.9, 120.8 (q, $J = 318.8$ Hz), 120.5, 117.9 (d, $J = 88.2$ Hz), 112.4, 92.7 (d, $J = 105.7$ Hz), 34.5, 16.9 (d, $J = 54.8$ Hz), 7.0 ppm (d, $J = 5.4$ Hz); ^{19}F NMR (471 MHz, CDCl_3) $\delta = -78.2$ ppm; ^{31}P NMR (202 MHz, CDCl_3) $\delta = 16.1$ ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{29}\text{H}_{26}\text{OP}$: 421.1721; found: 421.1718; ATR-FTIR (cm^{-1}): $\bar{\nu} = 3062, 2920, 1439, 1263, 1030, 753, 637$ cm^{-1} .

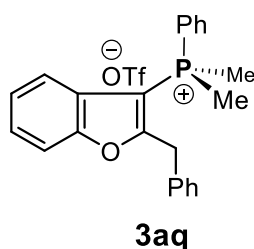


3ap

Compound 3ap: (80% yield, $R_f = 0.40$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. =

147-149 °C):

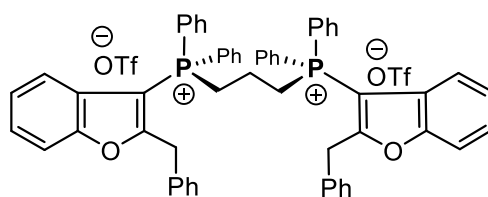
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.90 (dd, J = 12.5, 7.5 Hz, 4H), 7.75 – 7.69 (m, 2H), 7.63 (td, J = 7.6, 3.5 Hz, 5H), 7.43 (t, J = 7.5 Hz, 1H), 7.31 – 7.21 (m, 4H), 6.98 (d, J = 8.0 Hz, 1H), 6.95 – 6.90 (m, 2H), 4.22 (q, J = 12.0 Hz, 1H); 3.97 (s, 2H), 2.16 (s, 2H), 1.89 – 1.73 (m, 6H), 1.21 – 1.11 ppm (m, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ = 167.9 (d, J = 18.3 Hz), 154.7 (d, J = 12.3 Hz), 134.9 (d, J = 3.0 Hz), 134.4, 133.0 (d, J = 9.8 Hz), 130.7 (d, J = 12.5 Hz), 128.9, 128.3, 127.5, 126.9 (d, J = 9.3 Hz), 126.4, 124.9, 121.3, 120.9 (q, J = 318.8 Hz), 117.7 (d, J = 85.4 Hz), 112.3, 92.1 (d, J = 101.6 Hz), 35.17, 30.8 (d, J = 49.0 Hz), 27.0 (d, J = 3.3 Hz), 25.2 (d, J = 15.0 Hz), 25.2 ppm (d, J = 1.8 Hz); **¹⁹F NMR** (471 MHz, CDCl₃) δ = -78.1 ppm; **³¹P NMR** (202 MHz, CDCl₃) δ = 18.0 ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₃₃H₃₂OP: 475.2191; found: 475.2191; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 3061, 2935, 1454, 1262, 1031, 637, 517 cm⁻¹.



Compound 3aq: (97% yield, R_f = 0.50 [20:1 CH₂Cl₂/CH₃OH], white crystal, mp. = 117-119 °C):

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.81 – 7.73 (m, 2H), 7.71 – 7.65 (m, 1H), 7.61 – 7.55 (m, 3H), 7.38 (t, J = 7.8 Hz, 1H), 7.29 (t, J = 7.2 Hz, 2H), 7.24 (td, J = 7.6, 2.7 Hz, 2H), 7.10 (dd, J = 16.8, 7.6 Hz, 3H), 4.32 (s, 2H), 2.58 ppm (d, J = 14.2 Hz, 6H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ = 167.1 (d, J = 20.2 Hz), 154.4 (d, J = 12.7 Hz), 135.4, 134.9 (d, J = 3.1 Hz), 131.6 (d, J = 11.4 Hz), 130.3 (d, J = 13.2 Hz), 129.1, 128.1, 127.5, 126.5 (d, J = 10.1 Hz), 126.2, 124.9, 120.3 (d, J = 90.6 Hz), 120.7 (q, J = 318.8 Hz), 119.8, 112.3, 94.6 (d, J = 106.6 Hz), 34.4, 10.5 ppm (d, J = 58.1 Hz); **³¹P NMR** (202 MHz, CDCl₃) δ = 12.6 ppm; **¹⁹F NMR** (471 MHz, CDCl₃) δ = -78.3 ppm; **HRMS** (ESI): m/z calcd for [M]⁺ = C₂₃H₂₂OP: 345.1408; found: 345.1412; **ATR-FTIR** (cm⁻¹):

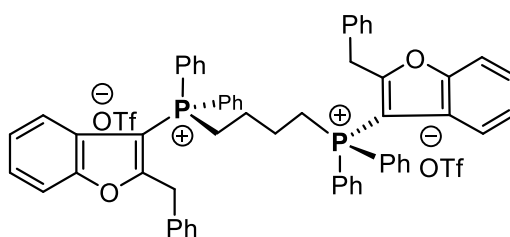
$\bar{\nu} = 3061, 2915, 1547, 1262, 750, 637 \text{ cm}^{-1}$.



3ar

Compound 3ar: (94% yield, $R_f = 0.25$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 197-199 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.73$ (dd, $J = 12.5, 7.9$ Hz, 8H), 7.67 (t, $J = 7.4$ Hz, 4H), 7.56 – 7.47 (m, 10H), 7.29 (d, $J = 7.8$ Hz, 2H), 7.16 – 7.07 (m, 6H), 6.95 (t, $J = 7.7$ Hz, 2H), 6.78 – 6.70 (m, 4H), 6.61 (d, $J = 8.0$ Hz, 2H), 4.04 (t, $J = 13.8$ Hz, 4H), 3.81 (s, 4H), 2.00 ppm (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform- d) $\delta = 169.2$ (t, $J = 10$ Hz), 154.4 (t, $J = 6.25$ Hz), 135.2, 135.0, 133.3 (p, $J = 6.7$ Hz), 130.6 (p, $J = 6.3$ Hz), 128.7, 128.3, 127.1, 126.9 (t, $J = 5$ Hz), 125.9, 124.5, 120.7 (q, $J = 318.8$ Hz), 120.5, 120.4, 117.2 (d, $J = 89.7$ Hz), 112.3, 92.5 (d, $J = 108.2$ Hz), 34.4, 29.5 (d, $J = 47.5$ Hz), 23.1 (m, $J = 18.8$ Hz), 18.3 ppm; $^{19}\text{F NMR}$ (471 MHz, CDCl_3) $\delta = -78.3$ ppm; $^{31}\text{P NMR}$ (202 MHz, CDCl_3) $\delta = 13.2$ ppm; **HRMS** (ESI): m/z calcd for $[\text{M}]^+ = \text{C}_{57}\text{H}_{48}\text{O}_2\text{P}_2$: 826.3130 found: 826.3135; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3065, 2916, 1541, 1439, 1273, 732 \text{ cm}^{-1}$.

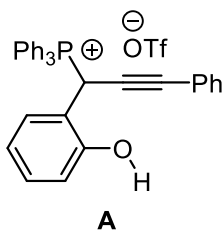


3as

Compound 3as: (62% yield, $R_f = 0.30$ [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 197-199 °C):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.84 - 7.77$ (m, 8H), 7.74 – 7.71 (m, 4H), 7.64 (td, $J = 7.7, 3.5$ Hz, 8H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.37 – 7.32 (m, 2H), 7.16 – 7.08 (m, 8H), 6.83 – 6.76 (m, 6H), 3.91 (s, 4H), 3.45 (t, $J = 13.9$ Hz, 4H), 2.10 – 1.98 ppm (m,

4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ = 168.7 (d, J = 20.0 Hz), 154.5 (d, J = 12.8 Hz), 135.2 (d, J = 2.8 Hz), 135.1, 133.4 (d, J = 10.8 Hz), 130.7 (d, J = 13.3 Hz), 128.5 (d, J = 50.0 Hz), 127.2, 127.0 (d, J = 10.1 Hz), 126.1, 124.8, 120.8 (q, J = 318.8 Hz), 120.7, 117.7 (d, J = 88.6 Hz), 112.3, 93.0 (d, J = 106.7 Hz), 34.4, 23.6 (dd, J = 20.3, 3.7 Hz), 22.7 ppm (d, J = 54.6 Hz); ^{19}F NMR (471 MHz, CDCl_3) δ = -78.2, -78.2 ppm; ^{31}P NMR (202 MHz, CDCl_3) δ = 13.5 ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+$ = $\text{C}_{58}\text{H}_{50}\text{O}_2\text{P}_2$: 840.3286 found: 840.3299; ATR-FTIR (cm^{-1}): $\bar{\nu}$ = 3062, 2917, 1439, 1259, 748, 516 cm^{-1} .



Compound A: (99% yield, R_f = 0.25 [20:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$], white crystal, mp. = 160-162 $^\circ\text{C}$):

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.86 (dq, J = 6.3, 3.6, 2.8 Hz, 3H), 7.71 – 7.65 (m, 11H), 7.37 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 7.6 Hz, 3H), 7.10 (d, J = 8.2 Hz, 1H), 6.93 – 6.88 (m, 1H), 6.71 (t, J = 7.5 Hz, 1H), 6.47 (d, J = 18.1 Hz, 1H), 1.74 ppm (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ = 154.9 (d, J = 5.5 Hz), 135.7 (d, J = 3.1 Hz), 134.3 (d, J = 9.0 Hz), 131.5 (d, J = 3.0 Hz), 131.4 (d, J = 3.5 Hz), 130.1 (d, J = 12.4 Hz), 129.6, 129.5 (d, J = 4.1 Hz), 128.6, 120.5 (q, J = 318.8 Hz), 120.3 (dd, J = 94.1, 3.4 Hz), 116.9 (d, J = 2.8 Hz), 116.7 (d, J = 83.7 Hz), 114.4 (d, J = 5.9 Hz), 89.5 (d, J = 9.6 Hz), 81.5 (d, J = 9.6 Hz), 41.9, 30.5 (d, J = 50.2 Hz), 25.9 ppm (d, J = 260.9 Hz); ^{31}P NMR (202 MHz, CDCl_3) δ = 23.0 ppm; ^{19}F NMR (471 MHz, CDCl_3) δ = -78.2 ppm; HRMS (ESI): m/z calcd for $[\text{M}]^+$ = $\text{C}_{33}\text{H}_{26}\text{OP}$: 469.1721 found: 469.1716; ATR-FTIR (cm^{-1}): $\bar{\nu}$ = 3059, 2864, 1439, 1238, 1025, 749, 516 cm^{-1} .

4. Relative Configuration Assignment of A and 3aa by X-Ray

Crystallographic Analysis:

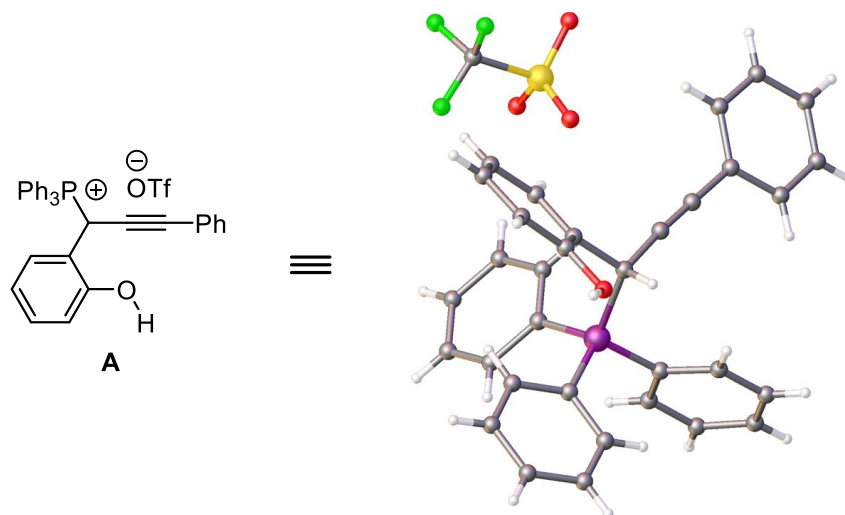


Table 2 Crystal data and structure refinement for A.

Identification code	A
CCDC	2218943
Empirical formula	C ₃₄ H ₂₆ F ₃ O ₄ PS
Formula weight	618.58
Temperature/K	298(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.3536(8)
b/Å	11.2590(9)
c/Å	14.7083(12)
α/°	91.052(1)
β/°	92.132(3)
γ/°	90.8130(10)
Volume/Å ³	1547.5(2)

Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.328
μ/mm^{-1}	0.211
F(000)	640.0
Crystal size/ mm^3	$0.45 \times 0.41 \times 0.4$
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	4.358 to 50.036
Index ranges	$-11 \leq h \leq 11, -12 \leq k \leq 13, -14 \leq l \leq 17$
Reflections collected	7806
Independent reflections	5365 [$R_{\text{int}} = 0.0298, R_{\text{sigma}} = 0.0409$]
Data/restraints/parameters	5365/0/389
Goodness-of-fit on F^2	1.036
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0574, wR_2 = 0.1531$
Final R indexes [all data]	$R_1 = 0.0798, wR_2 = 0.1679$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.41/-0.48

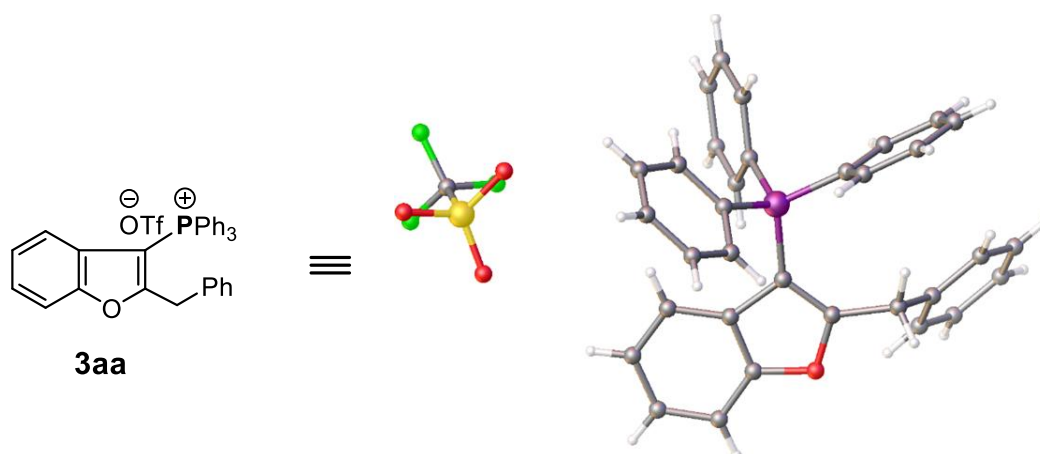
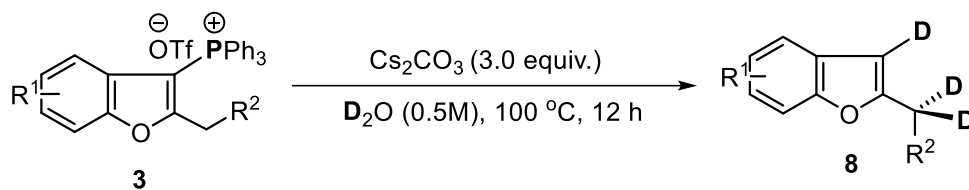


Table 3 Crystal data and structure refinement for 3aa.

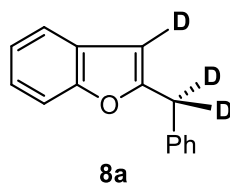
Identification code	3aa
CCDC	2218944
Empirical formula	$\text{C}_{34}\text{H}_{26}\text{F}_3\text{O}_4\text{PS}$
Formula weight	618.58

Temperature/K	298 (2)
Crystal system	triclinic
Space group	P-1
a/Å	9.7924(8)
b/Å	10.8723(9)
c/Å	16.3126(14)
α /°	98.275(2)
β /°	97.020(2)
γ /°	116.223(4)
Volume/Å ³	1507.6(2)
Z	2
ρ_{calc} /cm ³	1.367
μ /mm ⁻¹	0.217
F(000)	640.0
Crystal size/mm ³	0.41 × 0.21 × 0.1
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.28 to 50.04
Index ranges	-11 ≤ h ≤ 11, -8 ≤ k ≤ 12, -19 ≤ l ≤ 16
Reflections collected	7386
Independent reflections	5199 [R_{int} = 0.0373, R_{sigma} = 0.0741]
Data/restraints/parameters	5199/0/388
Goodness-of-fit on F ²	0.974
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0708, wR_2 = 0.1739
Final R indexes [all data]	R_1 = 0.1108, wR_2 = 0.1939
Largest diff. peak/hole / e Å ⁻³	0.49/-0.55

5. Deuteration of 2-benzofuranyl phosphonium salts

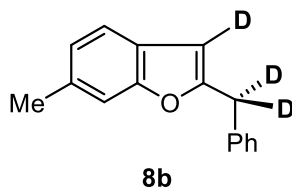


The reactions were performed in a sealed tube with **3** (1.0 equiv.), Cs₂CO₃ (3.0 equiv.) in D₂O (0.2 M) at 100 °C for 12 h under N₂. The reaction mixture was then washed with aqueous 1N HCl (10.0 mL) and extracted with ethyl acetate (2 × 10 mL). The combined organic phases were washed with water (10.0 mL), brine solution (10 mL) and dried over anhydrous sodium sulfate, and evaporated. The residue was purified by chromatography to give **8** (65%-97%).



Compound 8a: (80% yield, *R_f* = 0.60 [petroleum ether], colourless oil):

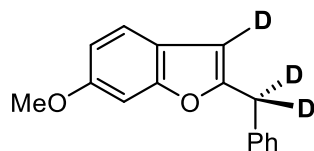
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.46 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.35 – 7.28 (m, 4H), 7.27 – 7.23 (m, 1H), 7.18 (dtd, *J* = 18.0, 7.3, 1.4 Hz, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ = 157.7, 155.0, 137.2, 128.9, 128.6, 126.8, 123.4, 122.5, 120.4, 110.9, 103.2 (t, *J* = 27.5 Hz), 34.4 ppm (m, *J* = 21.2 Hz); **HRMS** (ESI): *m/z* calcd for C₁₅H₉D₃ONa: 234.0974; found: 234.0945 [*M* + Na]⁺; **ATR-FTIR** (cm⁻¹): $\bar{\nu}$ = 2922, 2853, 1617, 1105, 804, 473 cm⁻¹.



Compound 8b: (80% yield, *R_f* = 0.60 [petroleum ether], colourless oil):

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.32 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.28 (m, 3H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.26 (d, *J* = 4.5 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.00 (dd, *J* =

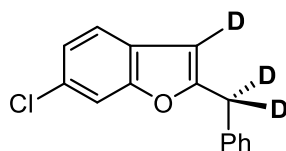
8.4, 1.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ = 157.8, 153.4, 137.3, 131.9, 128.9, 128.9, 128.6, 126.7, 124.6, 120.3, 110.4, 102.9 (t, J = 27.5 Hz), 34.4 ppm (m, J = 20.0 Hz); **HRMS** (ESI): m/z calcd for $\text{C}_{16}\text{H}_{12}\text{D}_3\text{O}$: 226.1306; found: 226.1342 $[M + \text{H}]^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu}$ = 3026, 2922, 1469, 1261, 799, 704 cm^{-1} .



8c

Compound 8c: (85% yield, R_f = 0.60 [petroleum ether], brown oil):

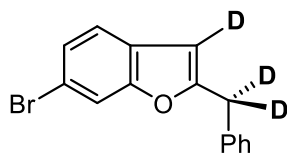
^1H NMR (500 MHz, Chloroform- d) δ = 7.34 – 7.31 (m, 1H), 7.31 – 7.28 (m, 3H), 7.27 (dd, J = 3.2, 1.3 Hz, 1H), 7.26 – 7.22 (m, 1H), 6.93 (d, J = 2.6 Hz, 1H), 6.80 (dd, J = 8.8, 2.6 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ = 158.5, 155.8, 149.9, 137.2, 129.3, 128.8, 128.6, 126.7, 111.8, 111.2, 103.3, 103.3 (t, J = 26.9 Hz), 55.9, 34.4 ppm (m, J = 18.8 Hz); **HRMS** (ESI): m/z calcd for $\text{C}_{16}\text{H}_{11}\text{D}_3\text{O}_2\text{Na}$: 264.1075; found: 264.1008 $[M + \text{Na}]^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu}$ = 3024, 2956, 1473, 1200, 1028, 807, 707 cm^{-1} .



8d

Compound 8d: (97% yield, R_f = 0.50 [petroleum ether], white crystal, mp. = 43-45°C):

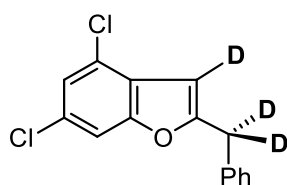
^1H NMR (500 MHz, Chloroform- d) δ = 7.40 (d, J = 1.8 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.30 – 7.25 (m, 3H), 7.14 ppm (dd, J = 8.2, 1.8 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ = 158.6, 155.0, 136.8, 129.1, 128.9, 128.6, 127.4, 126.9, 123.2, 120.8, 111.5, 102.9 (t, J = 27.5 Hz), 33.3 ppm (m, J = 20.0 Hz); **HRMS** (ESI): m/z calcd for $\text{C}_{15}\text{H}_8\text{D}_3\text{ClONa}$: 268.0579; found: 268.0575 $[M + \text{Na}]^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu}$ = 2923, 2853, 1654, 1466, 1056, 705 cm^{-1} .



8e

Compound 8e: (80% yield, $R_f = 0.50$ [petroleum ether], colourless oil):

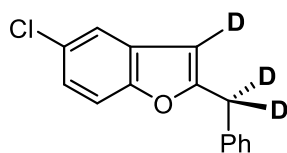
$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.57$ (d, $J = 2.0$ Hz, 1H), 7.32 (dd, $J = 8.0, 6.7$ Hz, 2H), 7.28 (td, $J = 4.5, 2.1$ Hz, 3H), 7.25 ppm (d, $J = 8.4$ Hz, 2H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 159.2, 153.7, 136.7, 130.7, 128.9, 128.7, 126.9, 126.2, 123.0, 115.6, 112.3, 102.7$ (t, $J = 26.3$ Hz), 34.3 ppm (m, $J = 20.0$ Hz); **HRMS** (ESI): m/z calcd for $\text{C}_{15}\text{H}_9\text{D}_3\text{BrO}$: 290.0255; found: 290.0247 [$M + \text{H}$] $^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3026, 2923, 1448, 1258, 704$ cm^{-1} .



8f

Compound 8f: (74% yield, $R_f = 0.60$ [petroleum ether], colourless oil):

$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.34$ (dd, $J = 8.1, 6.8$ Hz, 2H), 7.30 (d, $J = 1.7$ Hz, 2H), 7.29 (d, $J = 1.4$ Hz, 1H), 7.27 (d, $J = 7.1$ Hz, 1H), 7.21 ppm (d, $J = 2.0$ Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 160.6, 149.4, 136.2, 131.1, 129.0, 128.8, 128.3, 127.1, 123.6, 118.7, 116.8, 103.5$ (t, $J = 26.3$ Hz), 34.3 ppm (m, $J = 18.8$ Hz); **HRMS** (ESI): m/z calcd for $\text{C}_{15}\text{H}_8\text{D}_3\text{Cl}_2\text{O}$: 280.0370; found: 280.0435 [$M + \text{H}$] $^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3084, 2924, 1444, 1169, 857, 700$ cm^{-1} .

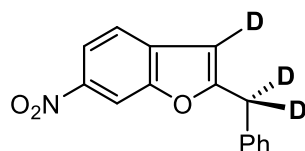


8g

Compound 8g: (88% yield, $R_f = 0.50$ [petroleum ether], colourless oil):

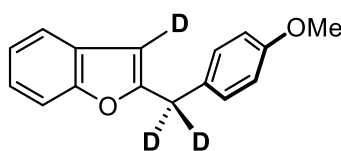
$^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.42$ (d, $J = 2.2$ Hz, 1H), 7.35 – 7.30 (m, 3H),

7.29 (d, $J = 1.7$ Hz, 2H), 7.25 (d, $J = 10.2$ Hz, 1H), 7.15 ppm (dd, $J = 8.7, 2.2$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 159.4, 153.4, 136.7, 130.1, 128.9, 128.7, 128.1, 126.9, 123.5, 112.0, 111.8, 102.8$ (t, $J = 26.2$ Hz), 34.4 ppm (m, $J = 20.0$ Hz); **HRMS** (ESI): m/z calcd for $\text{C}_{15}\text{H}_8\text{D}_3\text{ClOK}$: 284.0319; found: 284.0271 [$M + \text{K}$] $^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3027, 2923, 1450, 1255, 705$ cm^{-1} .



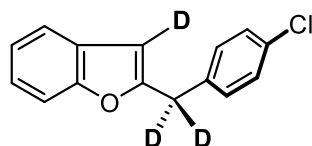
8h

Compound 8h: (76% yield, $R_f = 0.40$ [petroleum ether], white crystal, mp. = 92-94°C): ^1H NMR (500 MHz, Chloroform- d) $\delta = 8.31$ (d, $J = 2.4$ Hz, 1H), 8.07 (dd, $J = 9.0, 2.4$ Hz, 1H), 7.38 (d, $J = 9.0$ Hz, 1H), 7.28 (dd, $J = 8.1, 6.8$ Hz, 2H), 7.23 ppm (dt, $J = 8.2, 2.5$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 160.4, 156.8, 143.1, 135.0, 128.1, 127.9, 127.8, 126.2, 118.5, 115.9, 110.2, 102.9$ (t, $J = 27.5$ Hz), 33.4 ppm (m, $J = 17.5$ Hz); **HRMS** (ESI): m/z calcd for $\text{C}_{15}\text{H}_9\text{D}_3\text{NO}_3$: 257.1000; found: 257.0978 [$M + \text{H}$] $^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3087, 2921, 1519, 1339, 1057, 708$ cm^{-1} .



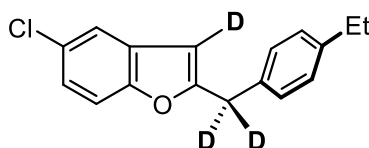
8i

Compound 8i: (65% yield, $R_f = 0.50$ [petroleum ether], white crystal, mp. = 57-58°C): ^1H NMR (500 MHz, Chloroform- d) $\delta = 7.45$ (dt, $J = 7.3, 1.0$ Hz, 1H), 7.41 – 7.37 (m, 1H), 7.25 – 7.19 (m, 3H), 7.19 – 7.13 (m, 1H), 6.88 – 6.84 (m, 2H), 3.79 ppm (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 158.5, 155.0, 129.9, 129.2, 128.8, 123.3, 122.5, 120.3, 114.0, 110.9, 102.9$ (t, $J = 27.0$ Hz), 55.3, 33.5 ppm (m, $J = 18.8$ Hz); **HRMS** (ESI): m/z calcd for $\text{C}_{16}\text{H}_{11}\text{D}_3\text{O}_2\text{Na}$: 264.1075; found: 264.1061 [$M + \text{Na}$] $^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 2922, 1617, 1247, 729, 492$ cm^{-1} .



8j

Compound 8j: (88% yield, $R_f = 0.50$ [petroleum ether], yellow crystal, mp. = 59-60°C): $^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.47$ (dd, $J = 7.4, 1.6$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.24 – 7.19 (m, 3H), 7.18 ppm (dd, $J = 7.5, 1.3$ Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 157.0, 155.0, 135.7, 132.7, 130.3, 128.8, 128.6, 123.6, 122.6, 120.5, 111.0, 103.3$ (t, $J = 26.2$ Hz), 34.8 ppm (m, $J = 20.0$ Hz); **HRMS** (ESI): m/z calcd for $\text{C}_{15}\text{H}_8\text{D}_3\text{ClONa}$: 268.0579; found: 268.0541 [$M + \text{Na}$] $^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3057, 2922, 1489, 1248, 935, 751$ cm^{-1} .



8k

Compound 8k: (92% yield, $R_f = 0.40$ [petroleum ether], brown oil): $^1\text{H NMR}$ (500 MHz, Chloroform- d) $\delta = 7.41$ (d, $J = 2.2$ Hz, 1H), 7.29 (d, $J = 8.7$ Hz, 1H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.17 – 7.12 (m, 3H), 2.63 (q, $J = 7.6$ Hz, 2H), 1.23 (t, $J = 7.6$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 159.7, 153.3, 142.9, 133.9, 130.1, 128.8, 128.2, 128.0, 123.5, 119.9, 111.8, 102.7$ (t, $J = 26.2$ Hz), 34.0 (m, $J = 18.8$ Hz); 28.5, 15.6 ppm; **HRMS** (ESI): m/z calcd for $\text{C}_{17}\text{H}_{12}\text{D}_3\text{ClONa}$: 296.0892; found: 296.0793 [$M + \text{Na}$] $^+$; **ATR-FTIR** (cm^{-1}): $\bar{\nu} = 3021, 2964, 1451, 1256, 800$ cm^{-1} .

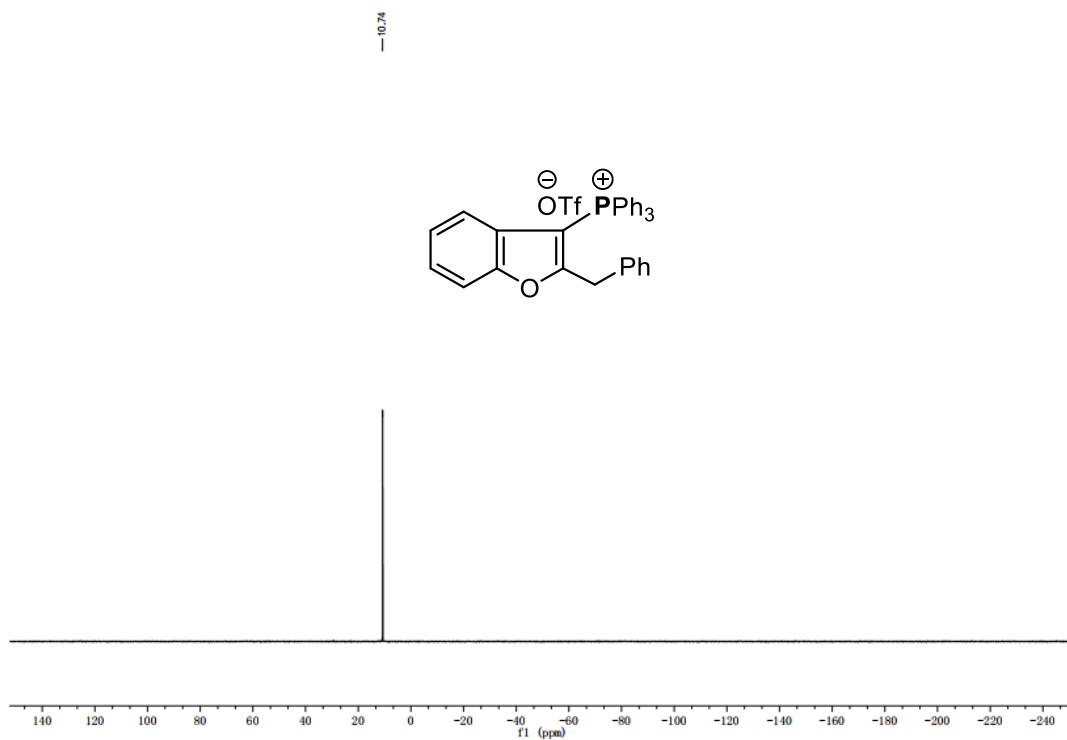
6. Reference

1. a) Saha S.; Schneider C. *Org. Lett.* **2015**, *17*, 648. b) Rajesh M.; Thirupathi N.; Reddy T. J.; Kanojiya, S.; Reddy M. S. *J. Org. Chem.* **2014**, *80*, 12311. c) Kumar G. R.; Kumar, Y. K.; Kant R.; Reddy M. S. *Org. Biomol. Chem.* **2016**, *14*, 4077. d) Harkat,

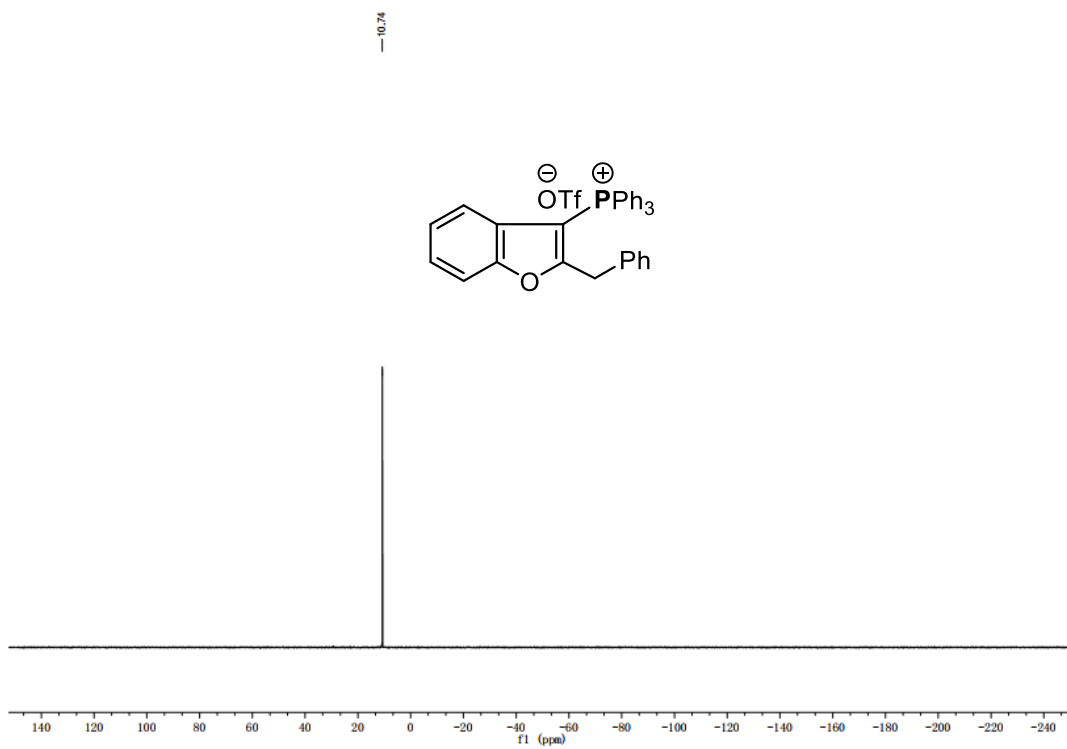
H.; Blanc, A.; Weibel, J.-M.; Pale, P *J. Org. Chem.* **2008**, *73*, 1620. e) Yoshida, M.; Fujino, Y.; Doi, T. *Org. Lett.* **2011**, *13*, 4526. f) Tian, T.; Li, L.; Xue, J.; Zhang, J.; Li, Y. *J. Org. Chem.* **2015**, *80*, 4189. g) Du, J.-Y.; Ma, Y.-H.; Meng, F.-X. Meng; B.-L. Chen; Zhang, S.-L. ; Li, Q.-L. ; Gong, S.-W.; Wang, D.-Q. and Ma, C.-L.. *Org. Lett.* **2018**, *20*, 4371. h) Du, J.Y., Ma, Y.-H., Yuan, R.-Q., Xin, N., Nie, S.-Z., Ma, C.-L., Li, C.-Z., Zhao, C.-Q. *Org. Lett.* **2018**, *20*, 477. i) Gabriele, B., Mancuso, R., Lupinaci, E., Veltri, L., Salerno, G., Carfagna, C. *J. Org. Chem.* **2011**, *76*, 8277.

7. Copies of NMR Spectra

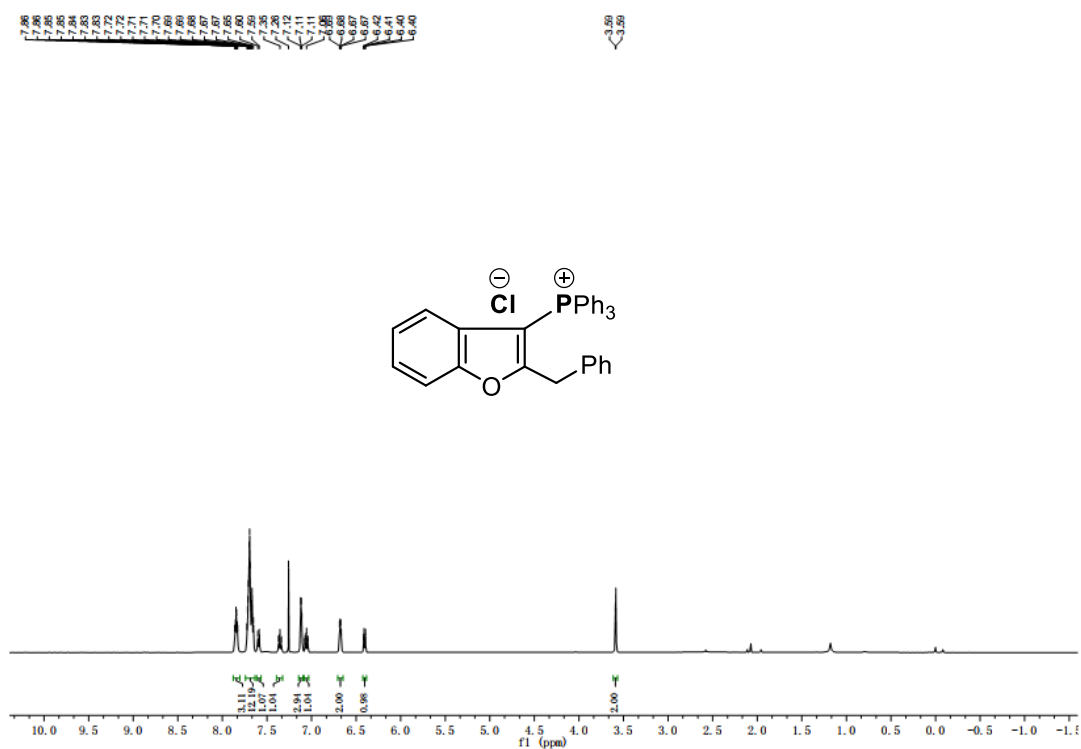
^{19}F NMR (471 MHz, CDCl_3) of compound **3aa**



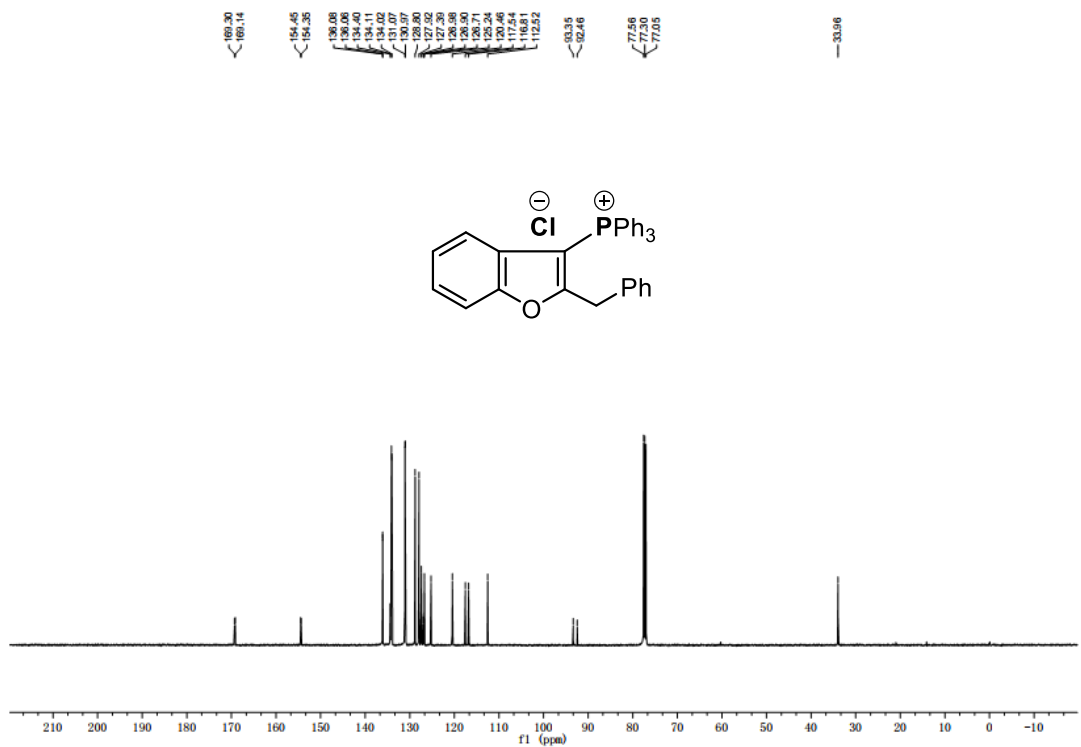
^{31}P NMR (202 MHz, CDCl_3) of compound **3aa**



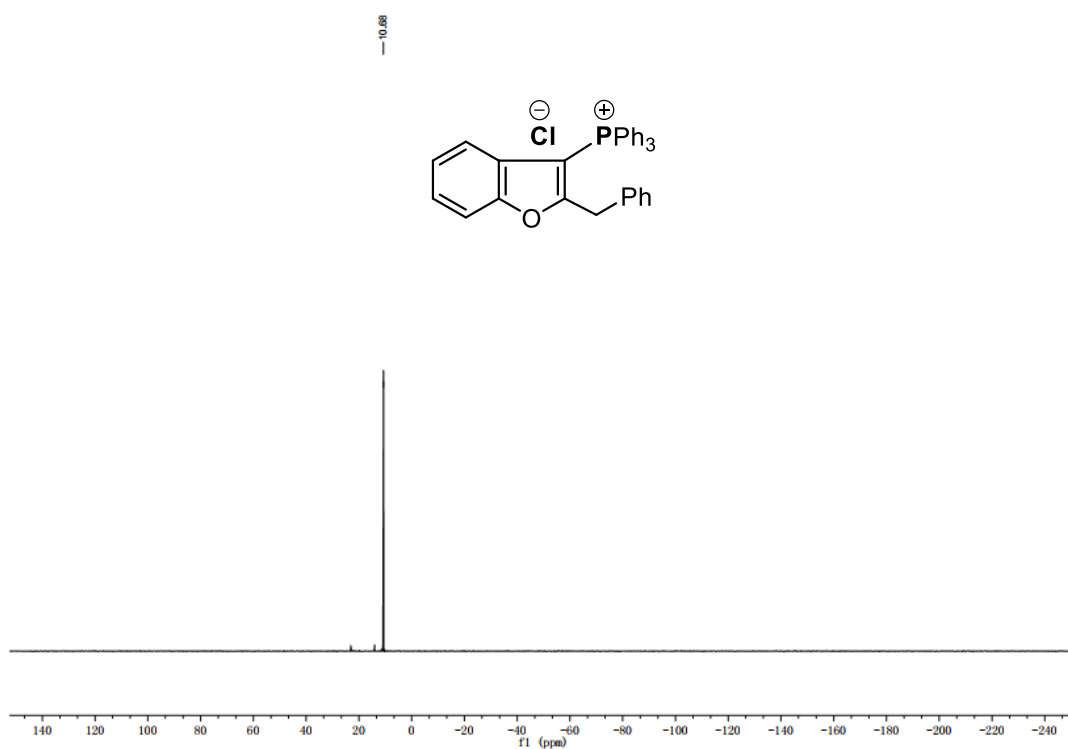
¹H NMR (500 MHz, CDCl₃) of compound **4aa**



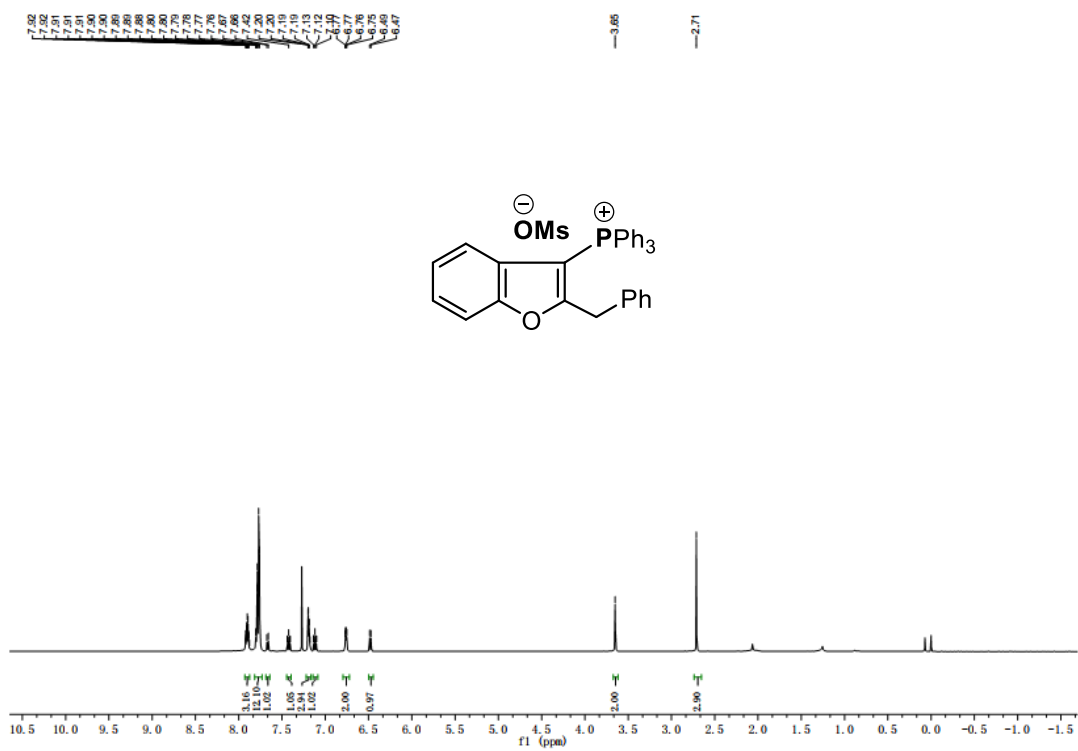
¹³C NMR (126 MHz, CDCl₃) of compound **4aa**



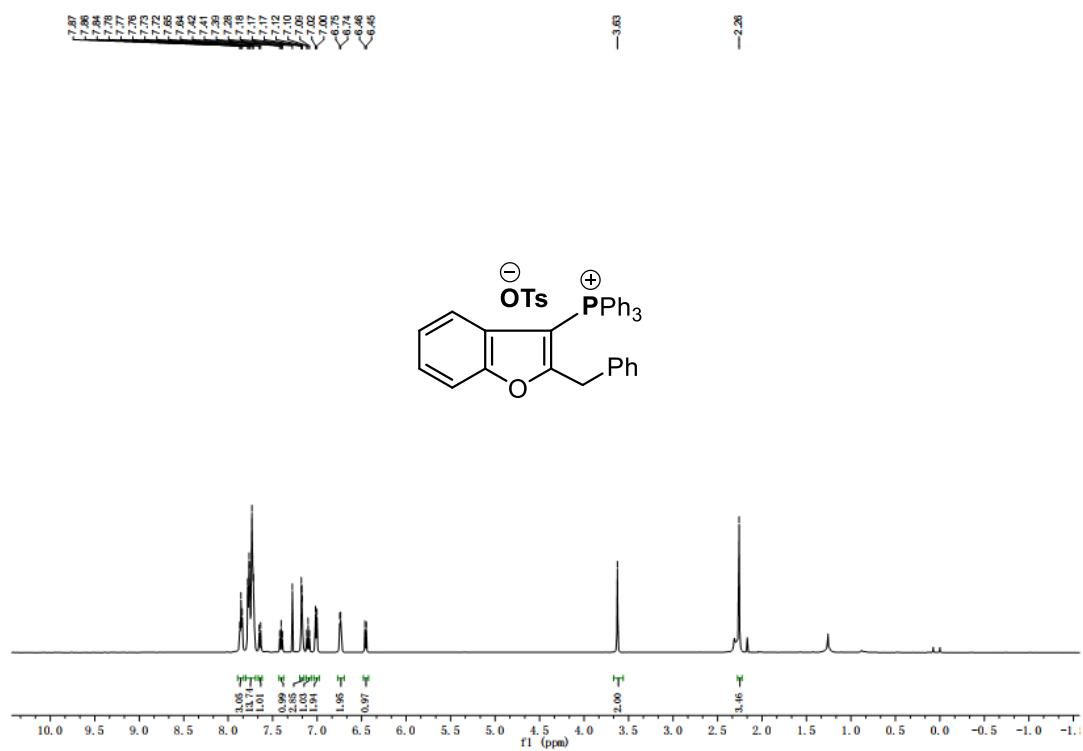
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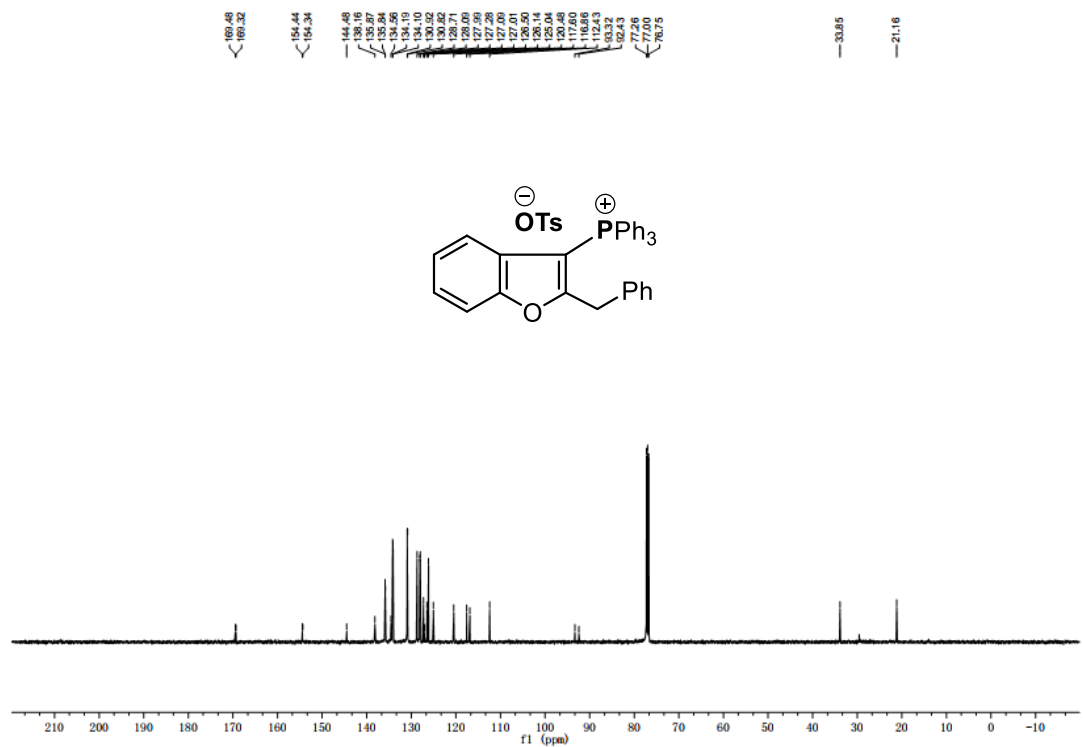
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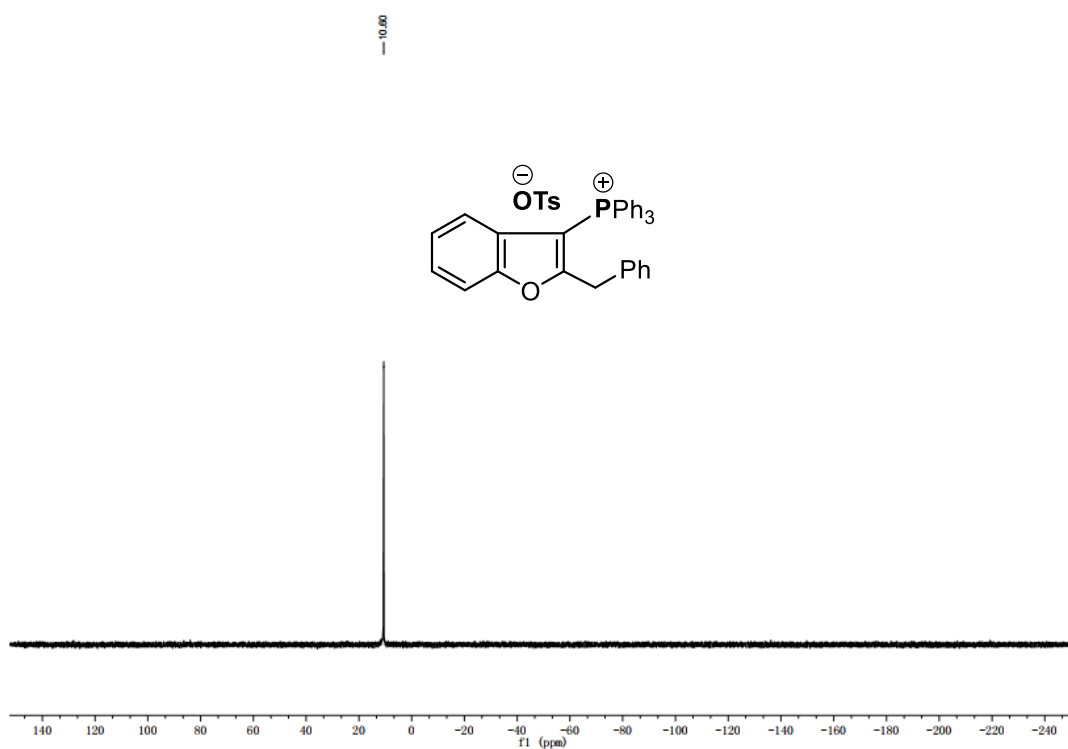
¹H NMR (500 MHz, CDCl₃) of compound **6aa**



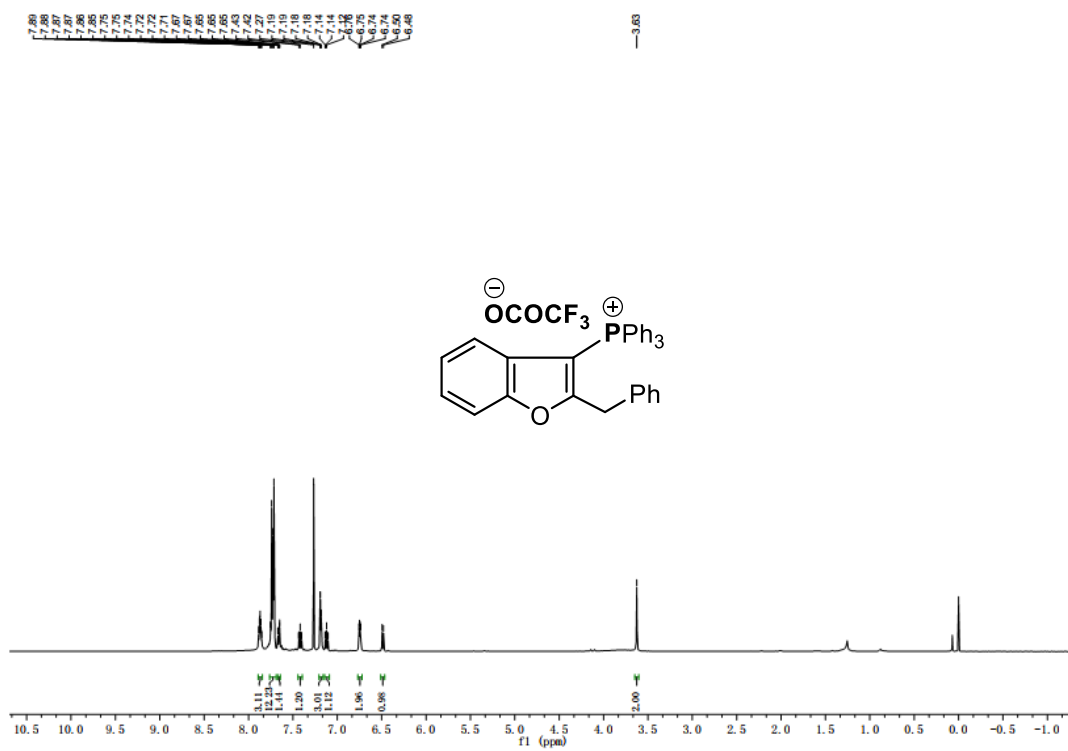
¹³C NMR (126 MHz, CDCl₃) of compound **6aa**



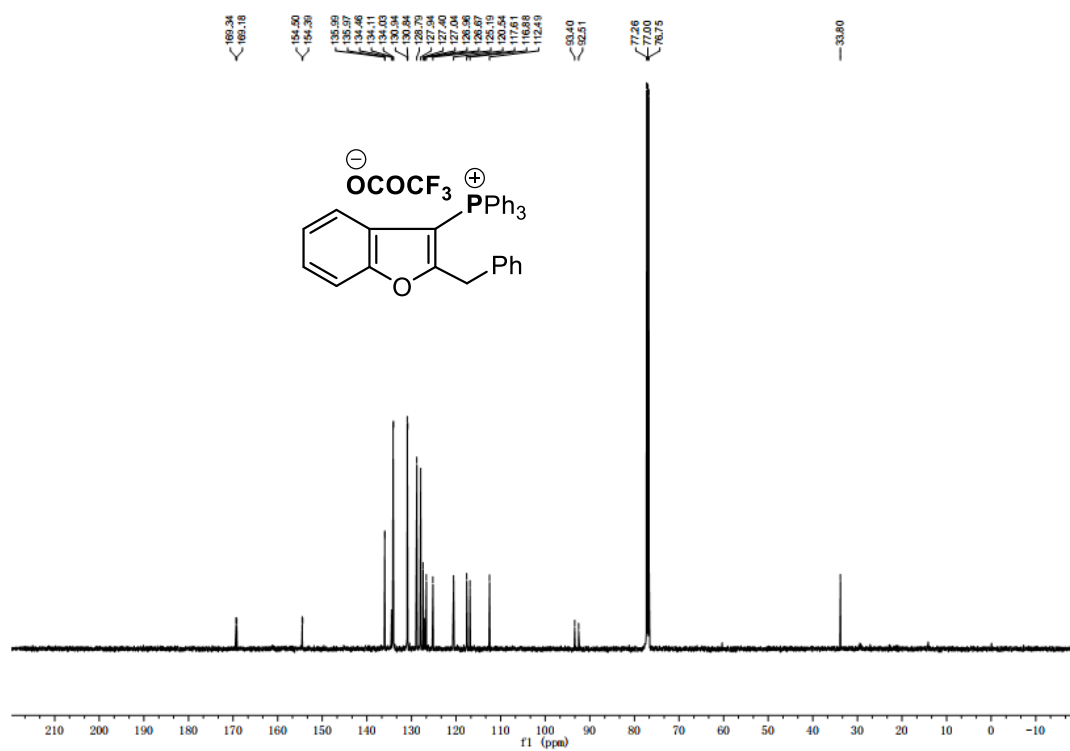
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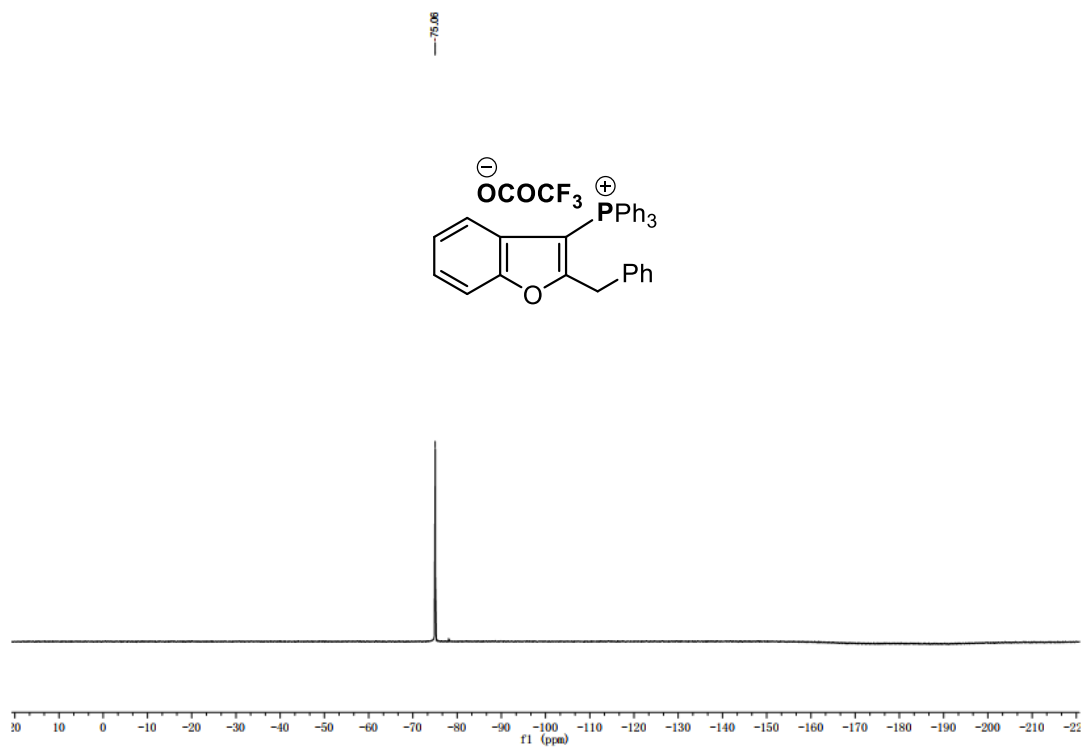
^1H NMR (500 MHz, CDCl_3) of compound **7aa**



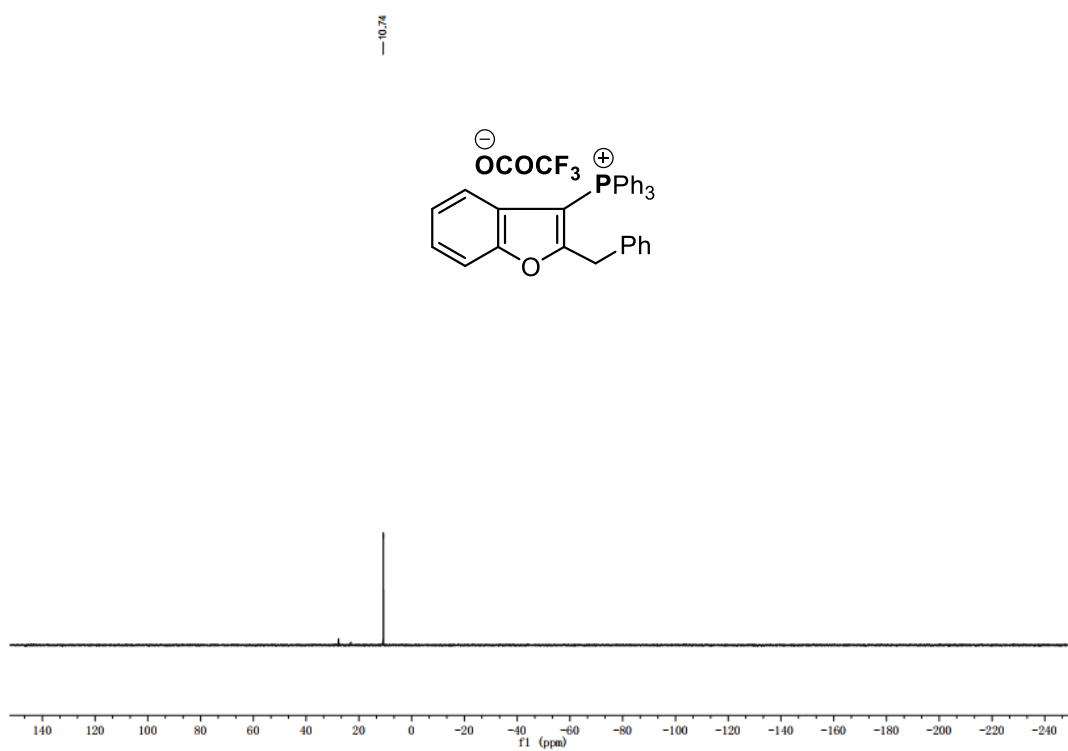
^{13}C NMR (126 MHz, CDCl_3) of compound **7aa**



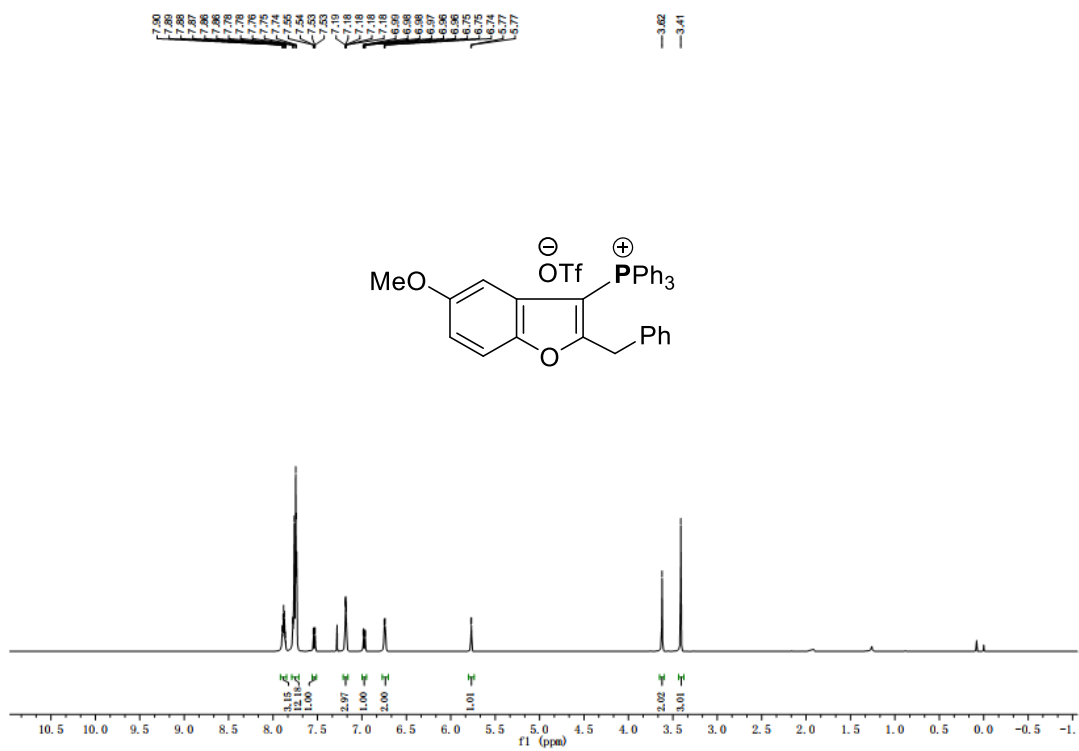
^{19}F NMR (471 MHz, CDCl_3) of compound **7aa**



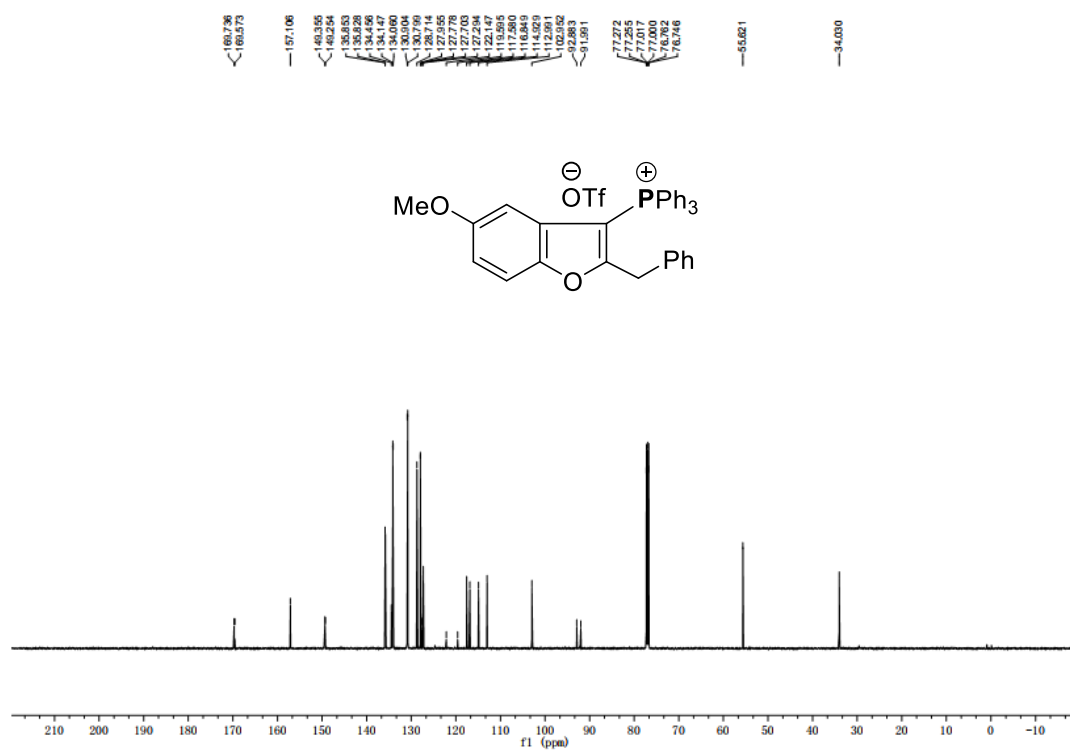
^{31}P NMR (202 MHz, CDCl_3) of compound **7aa**



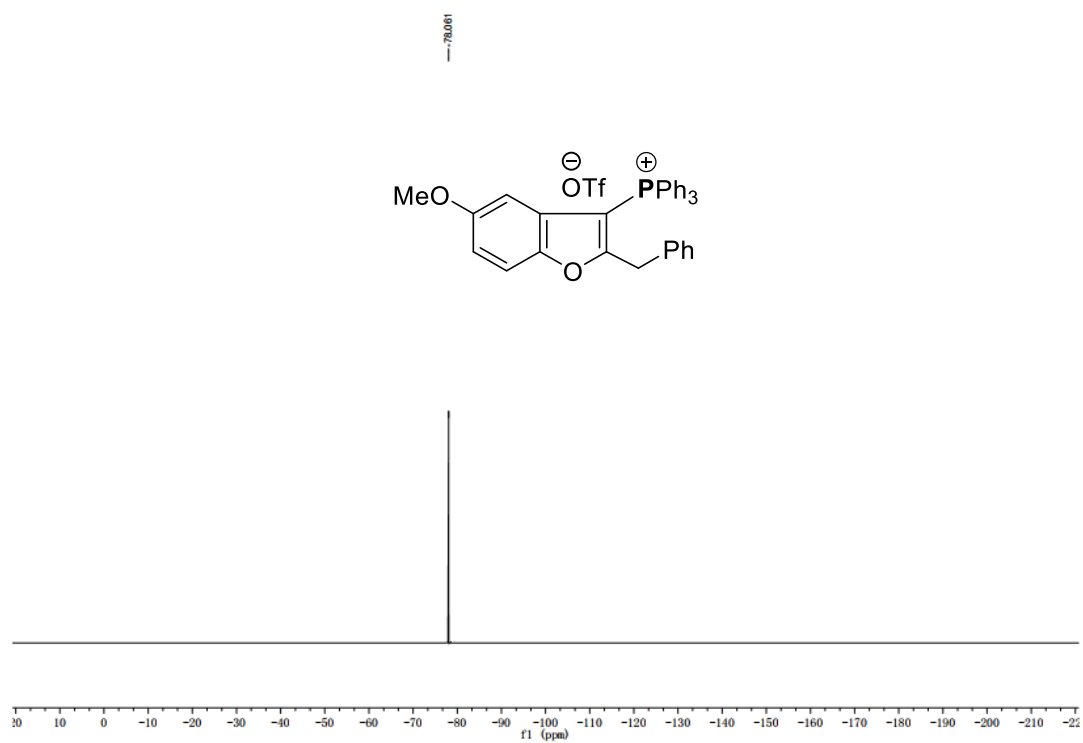
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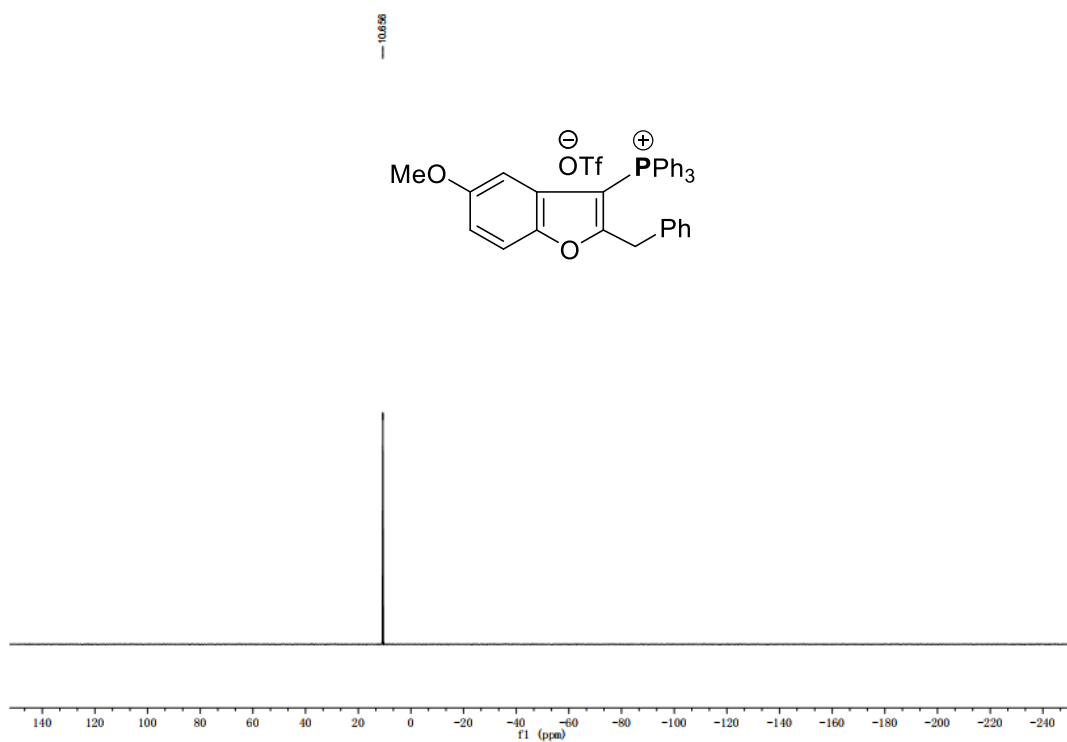
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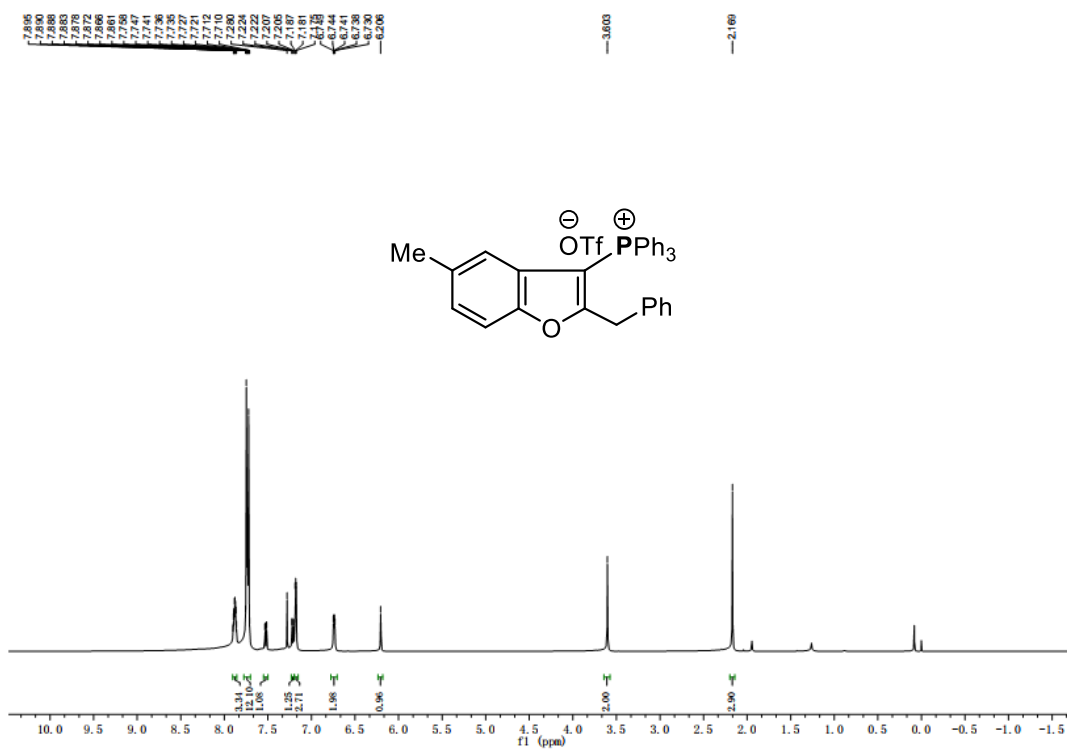
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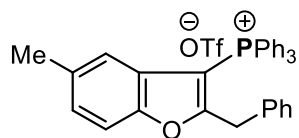
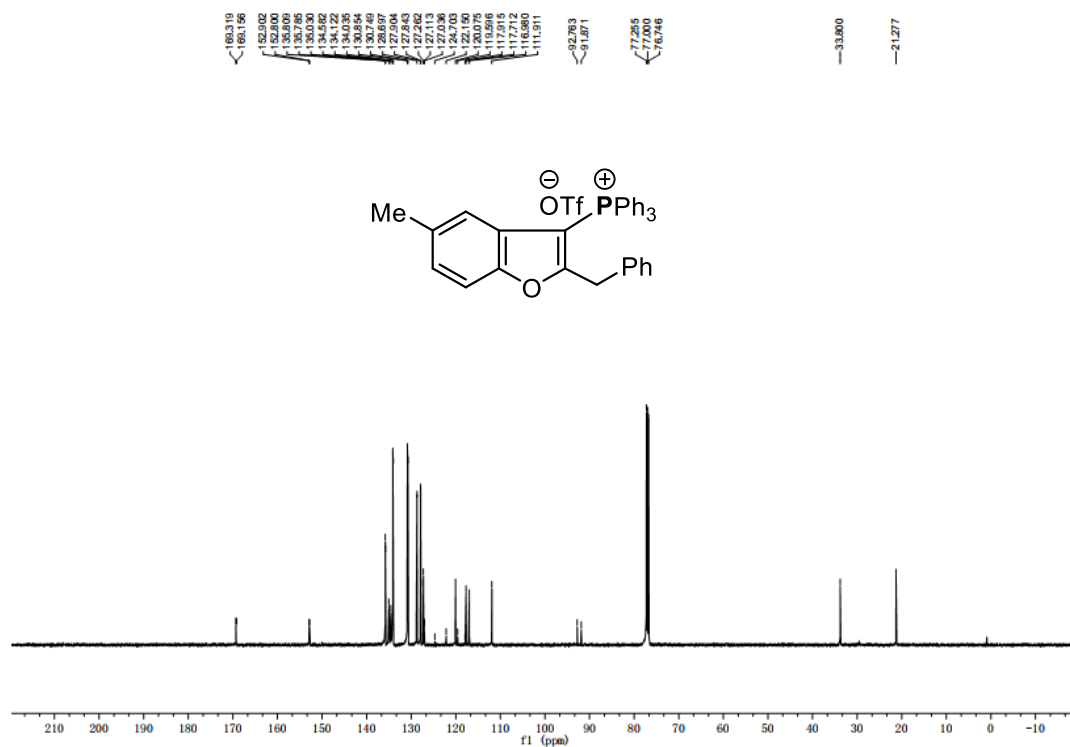
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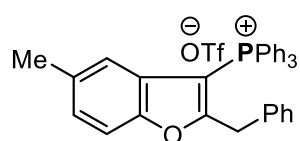
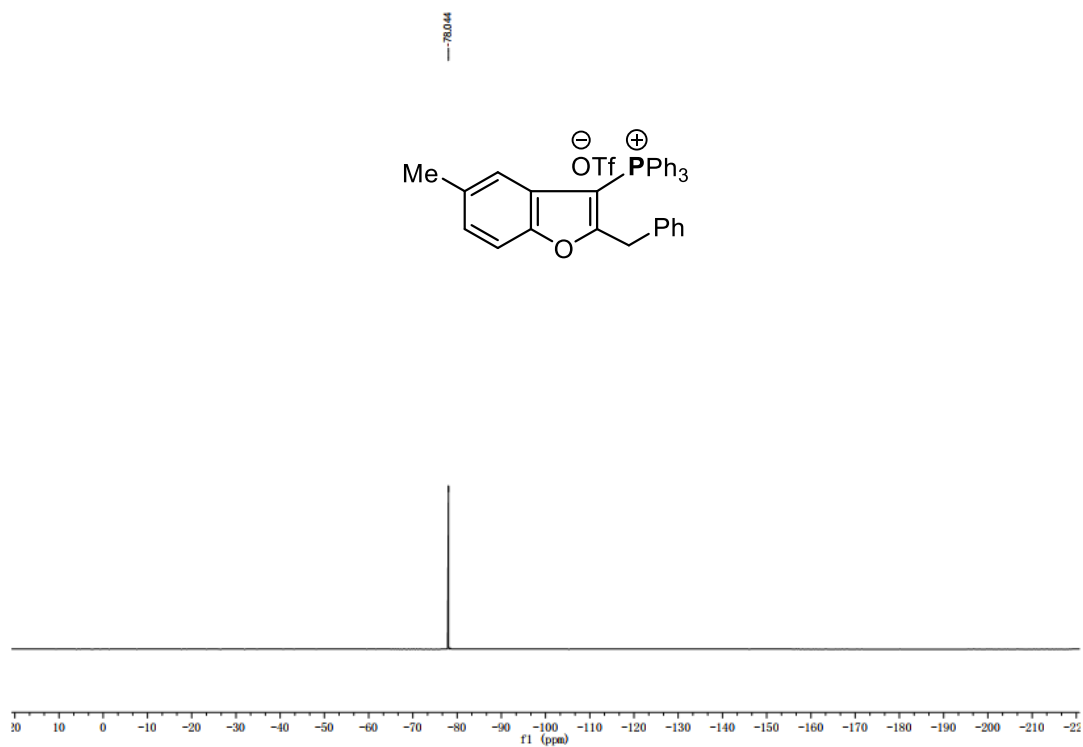
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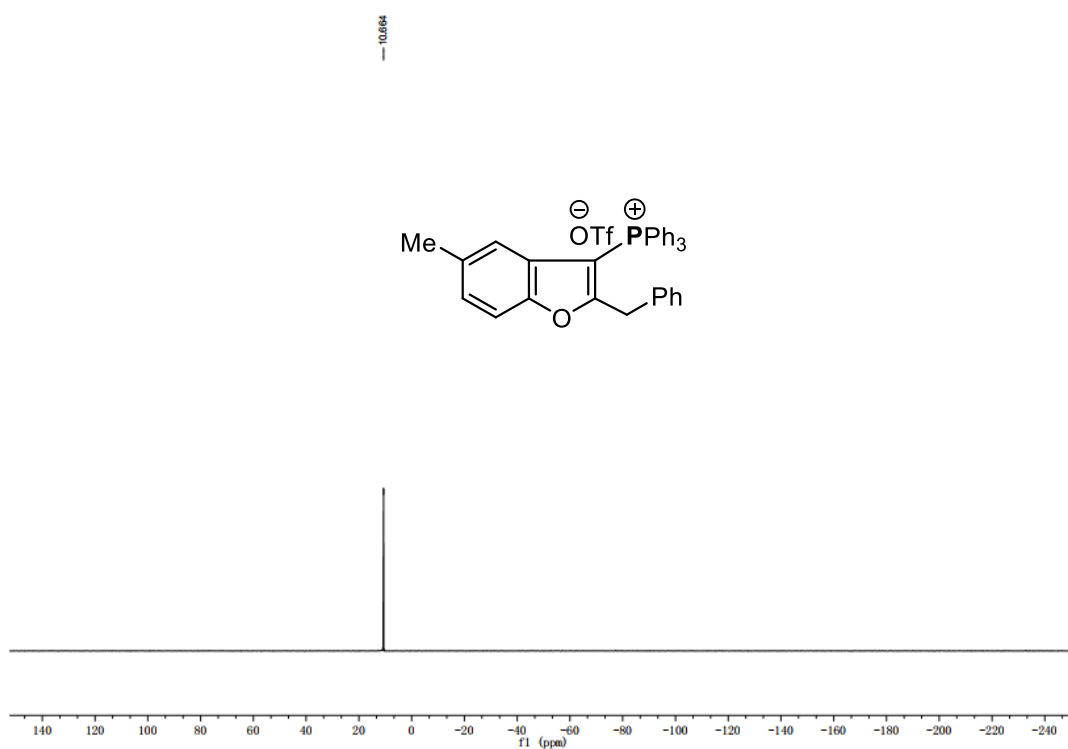
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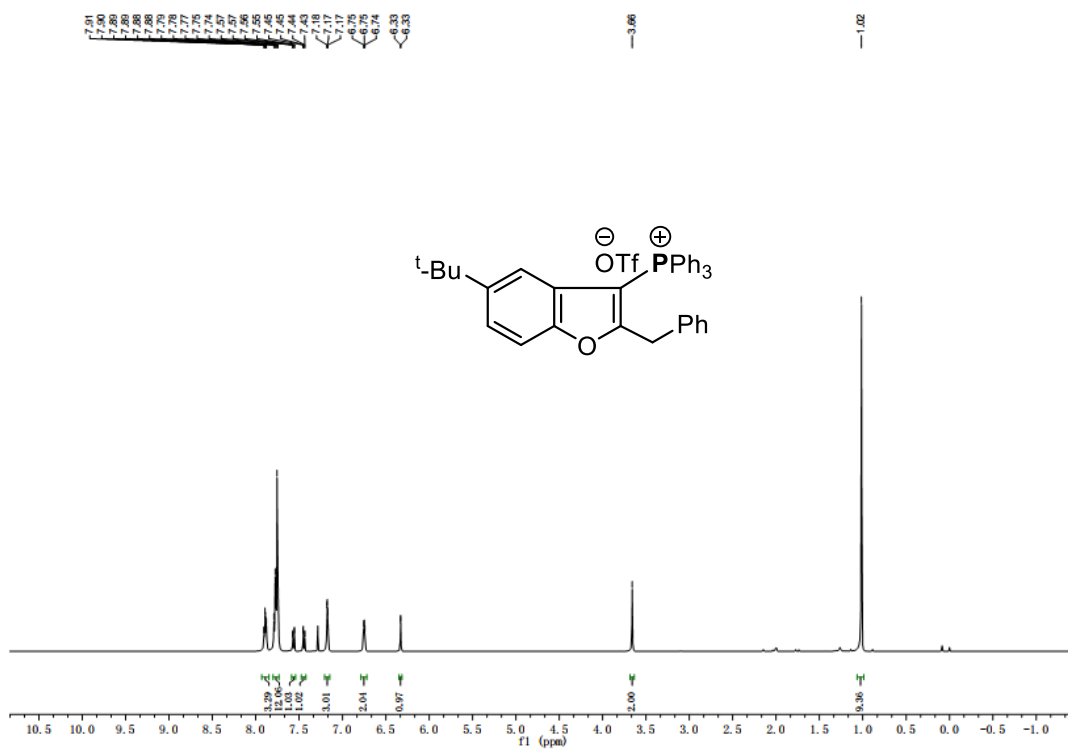
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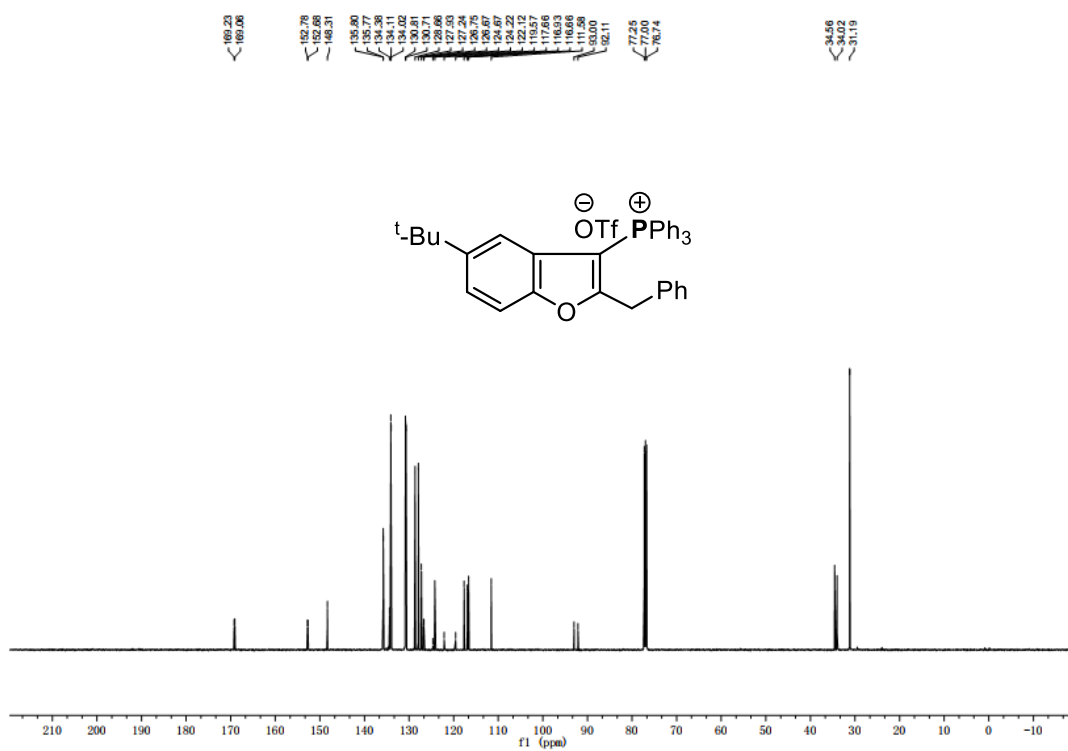
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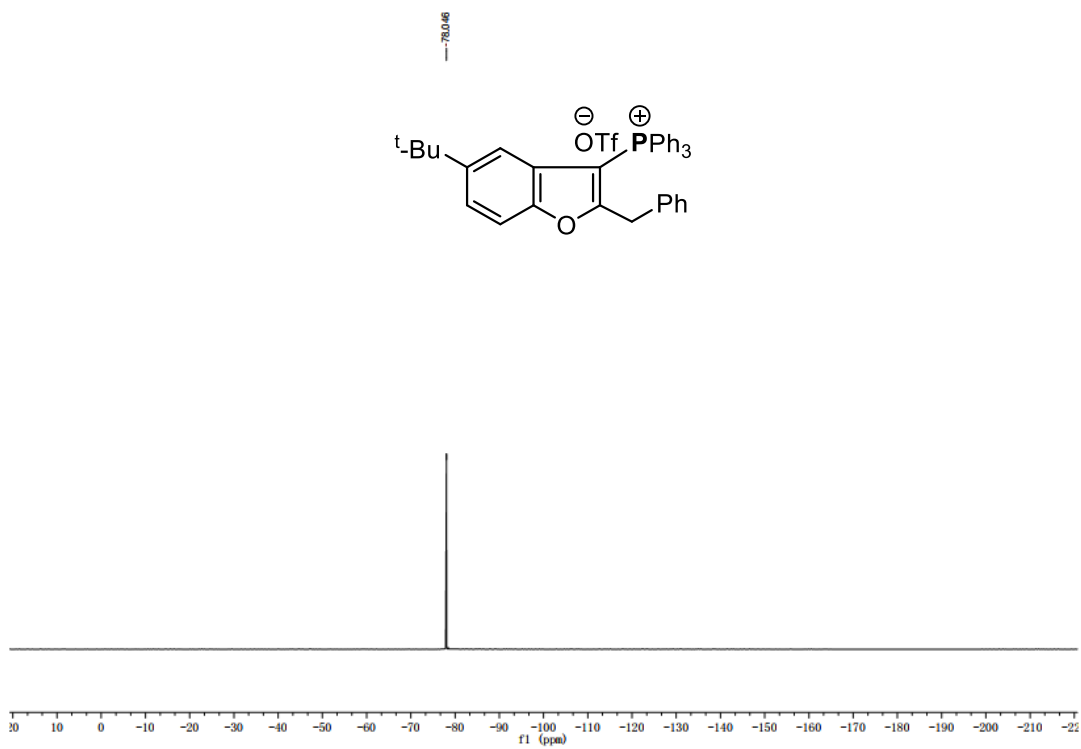
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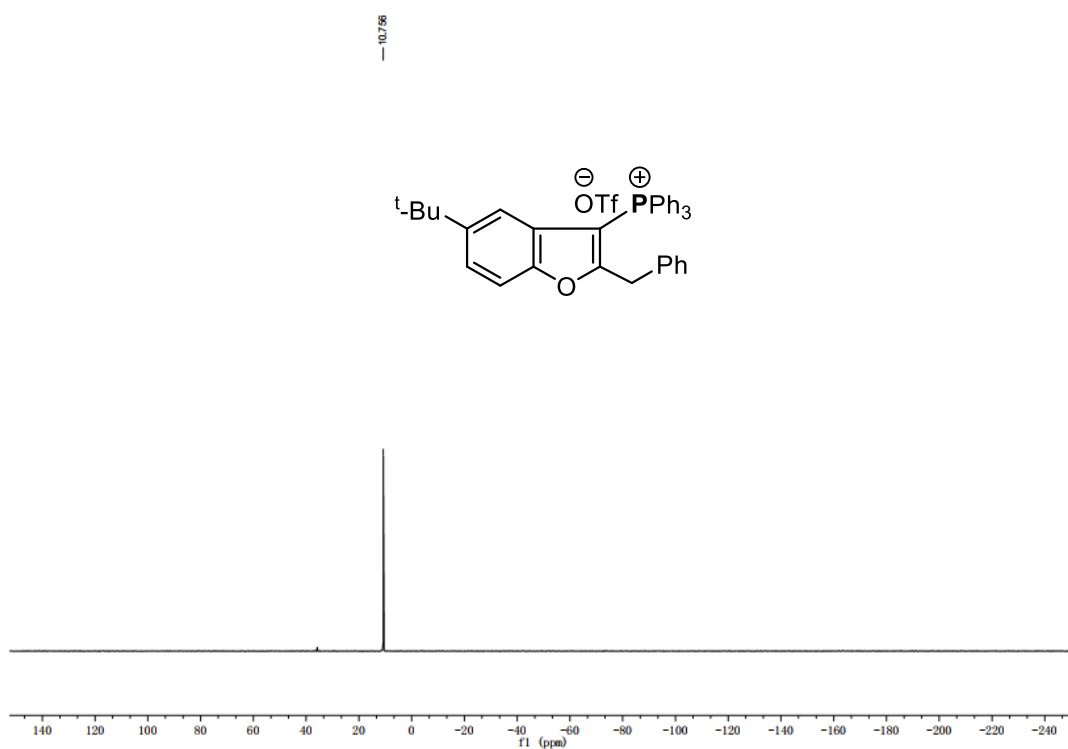
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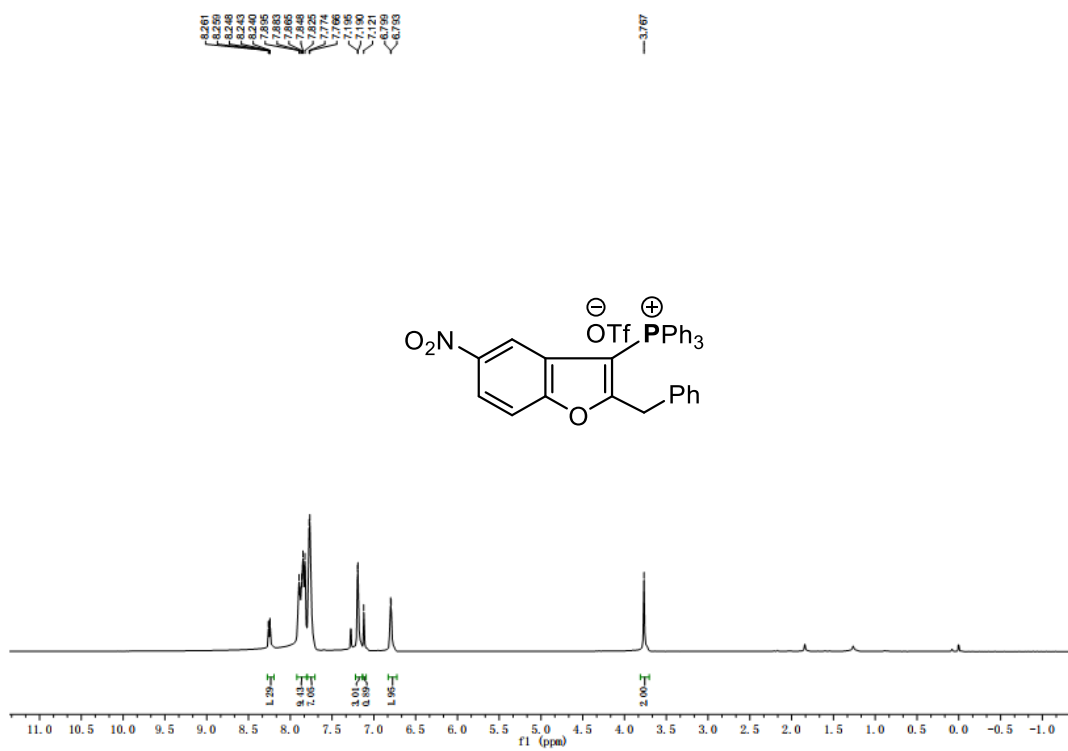
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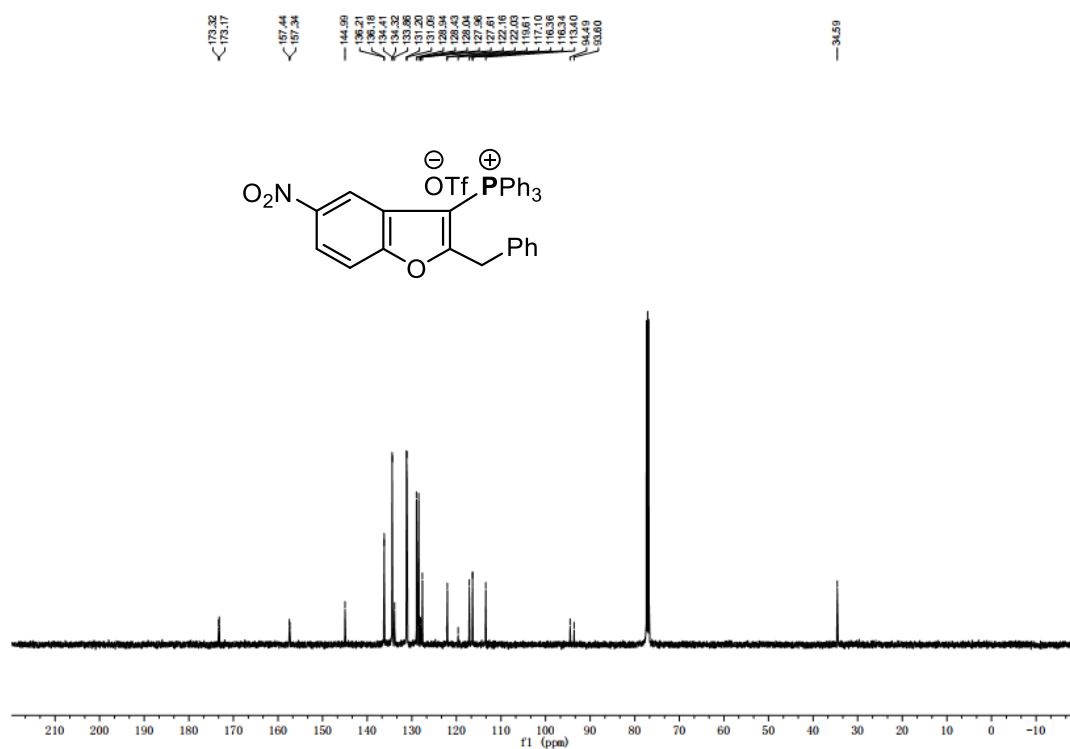
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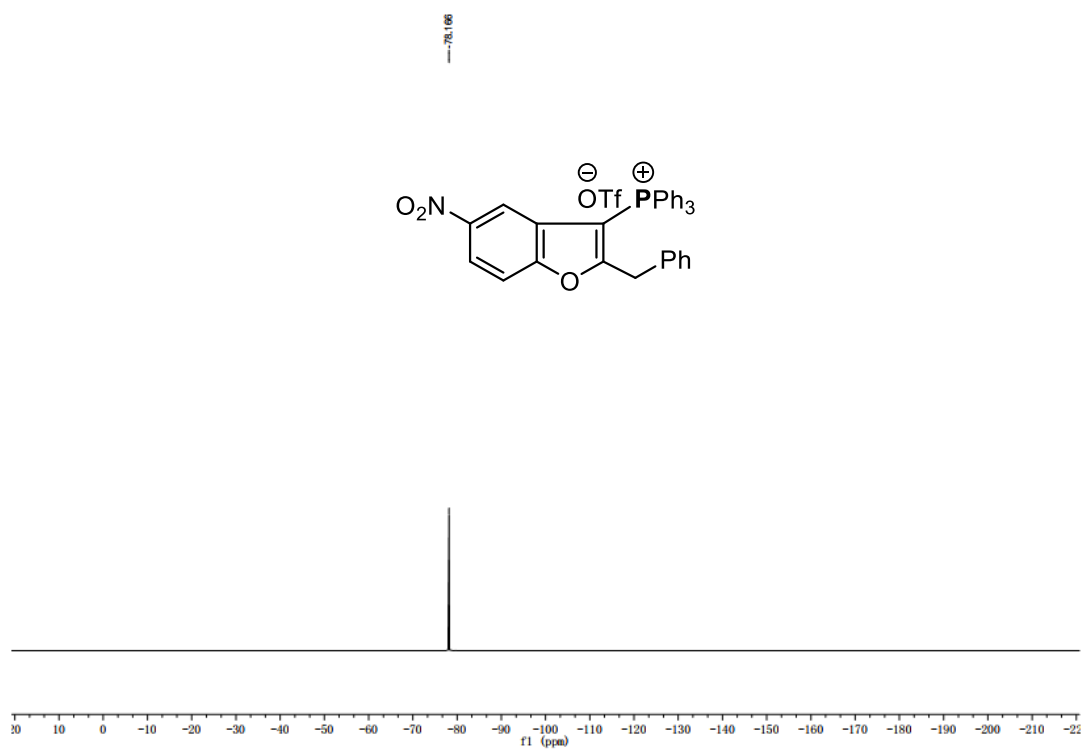
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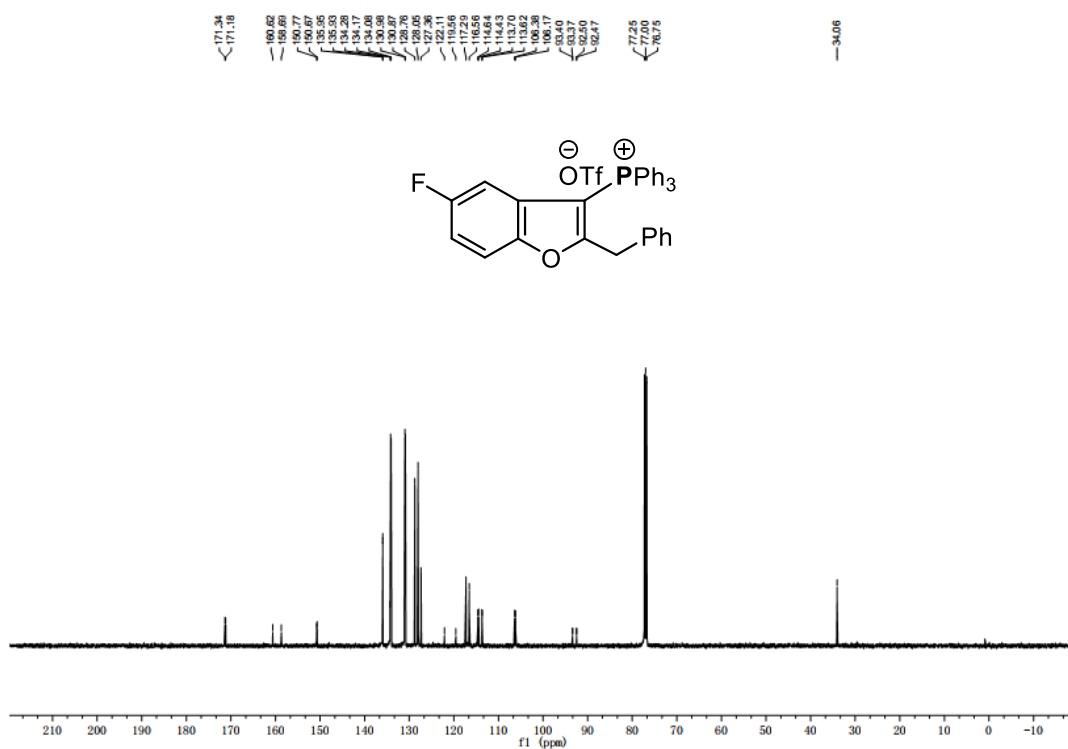
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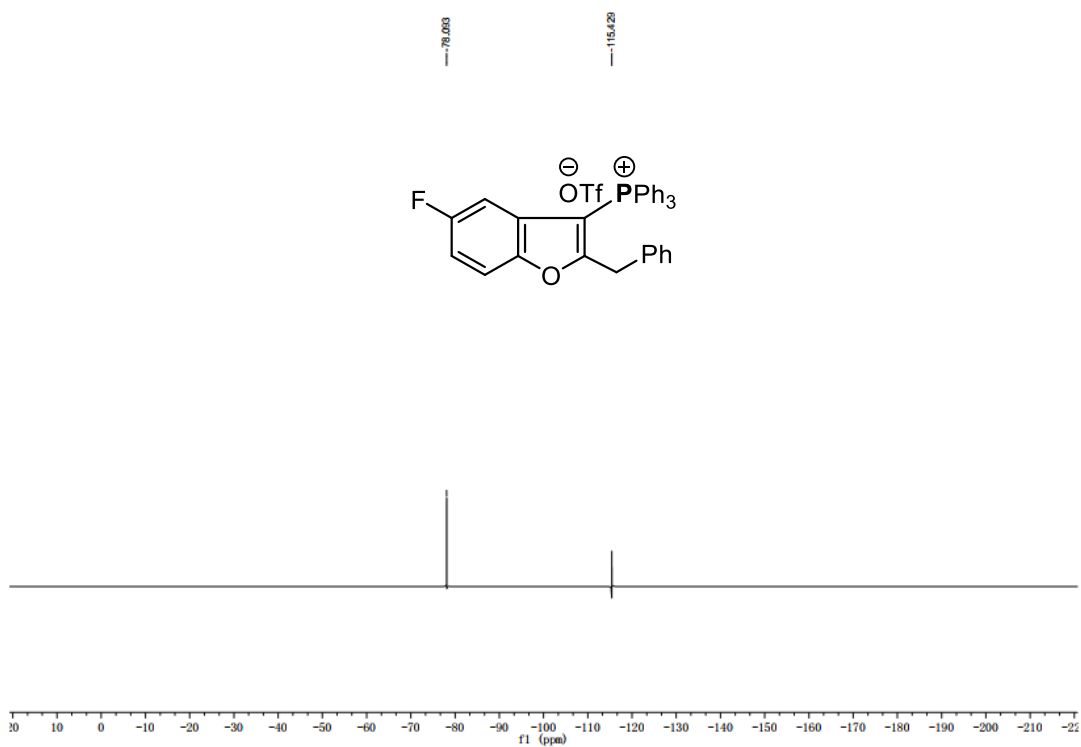
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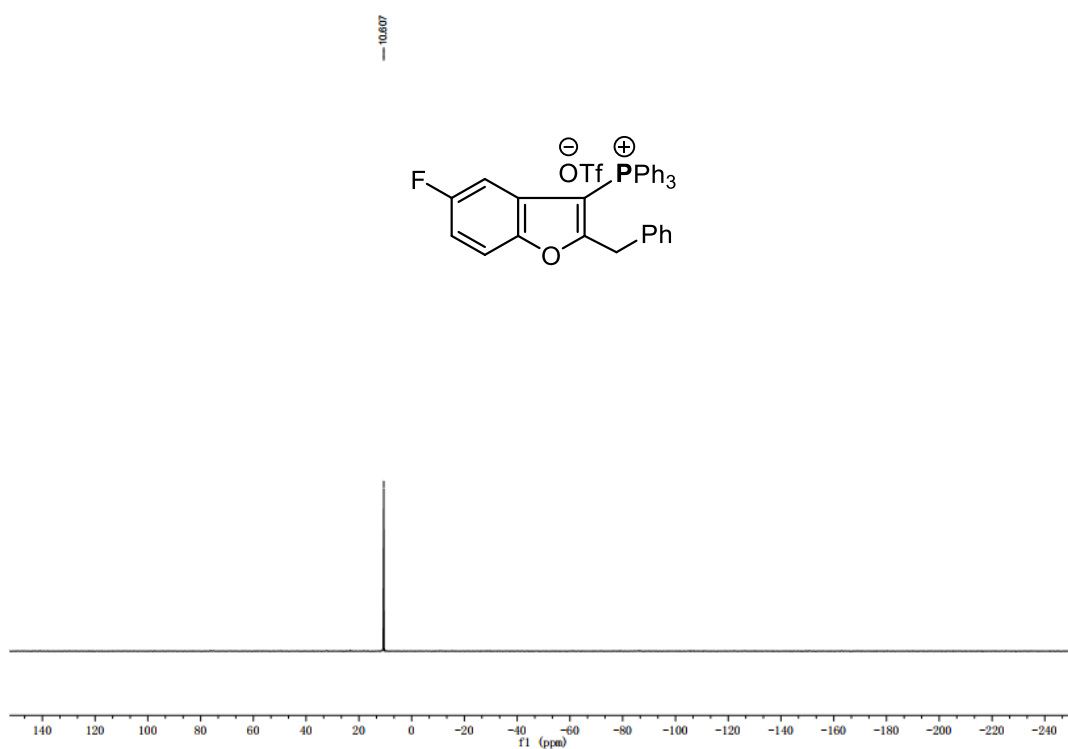
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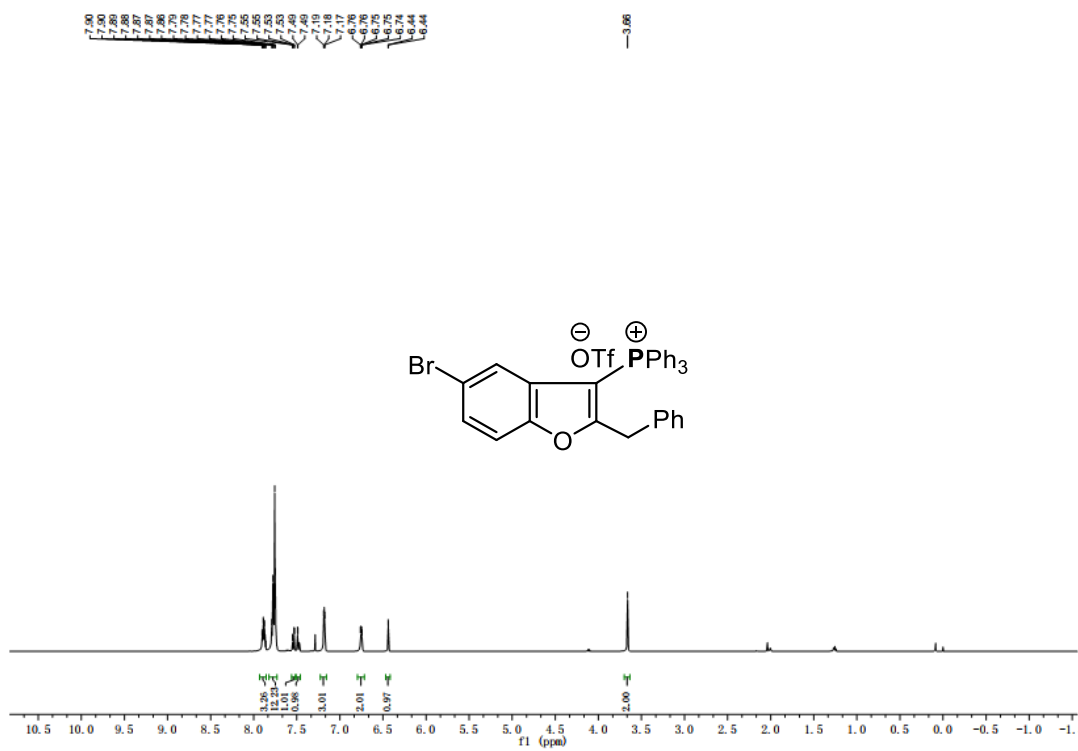
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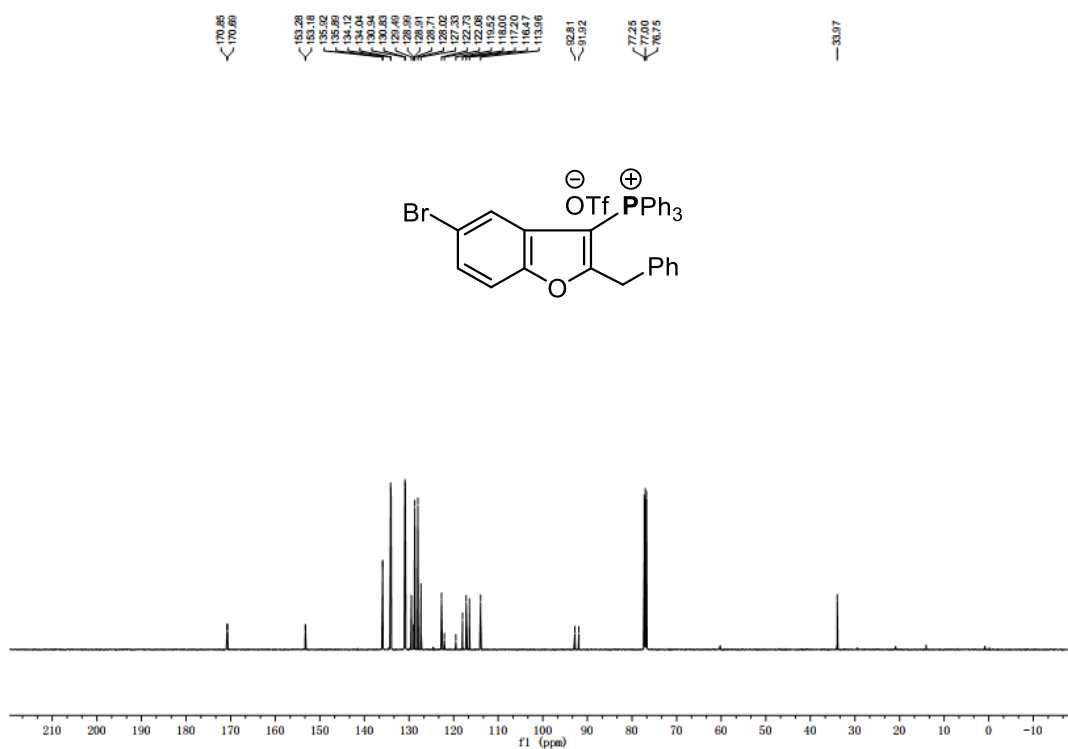
^{31}P NMR (202 MHz, CDCl_3) of compound **3ga**



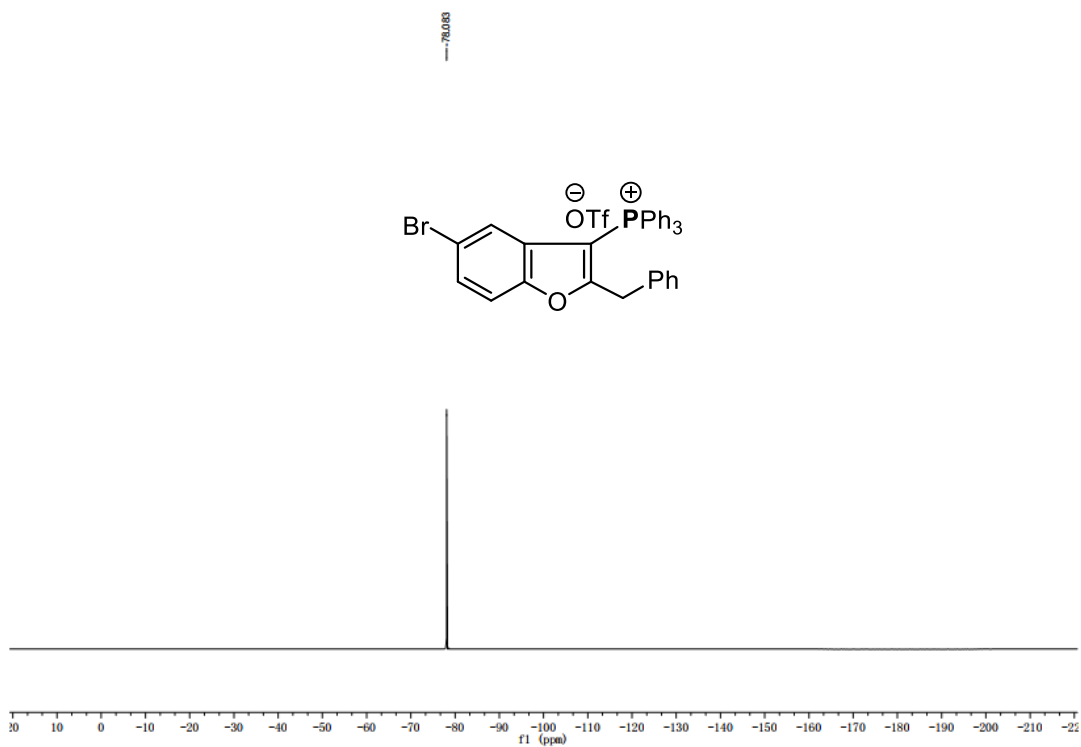
^1H NMR (500 MHz, CDCl_3) of compound **3ha**



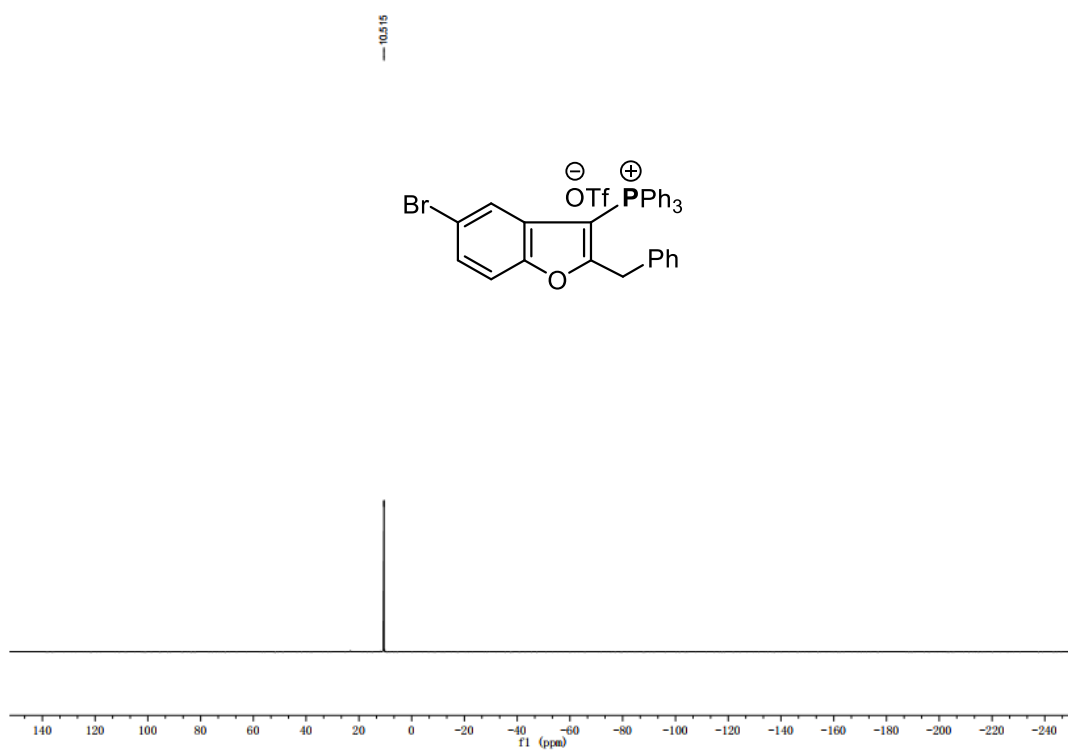
^{13}C NMR (126 MHz, CDCl_3) of compound **3ha**



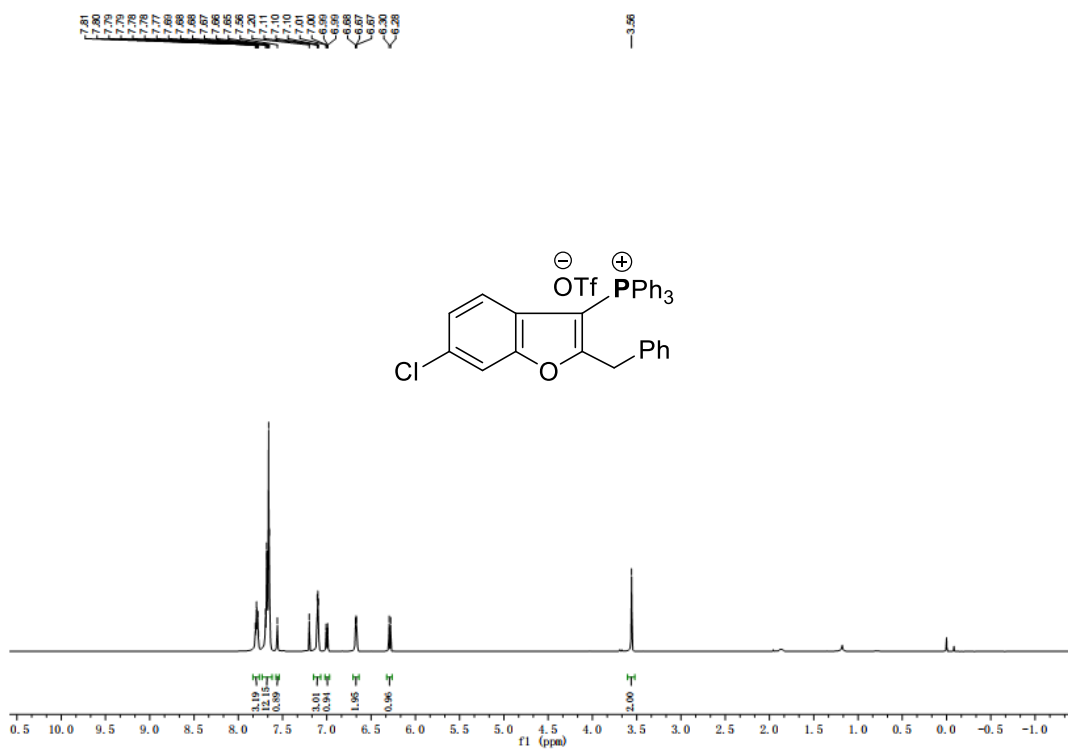
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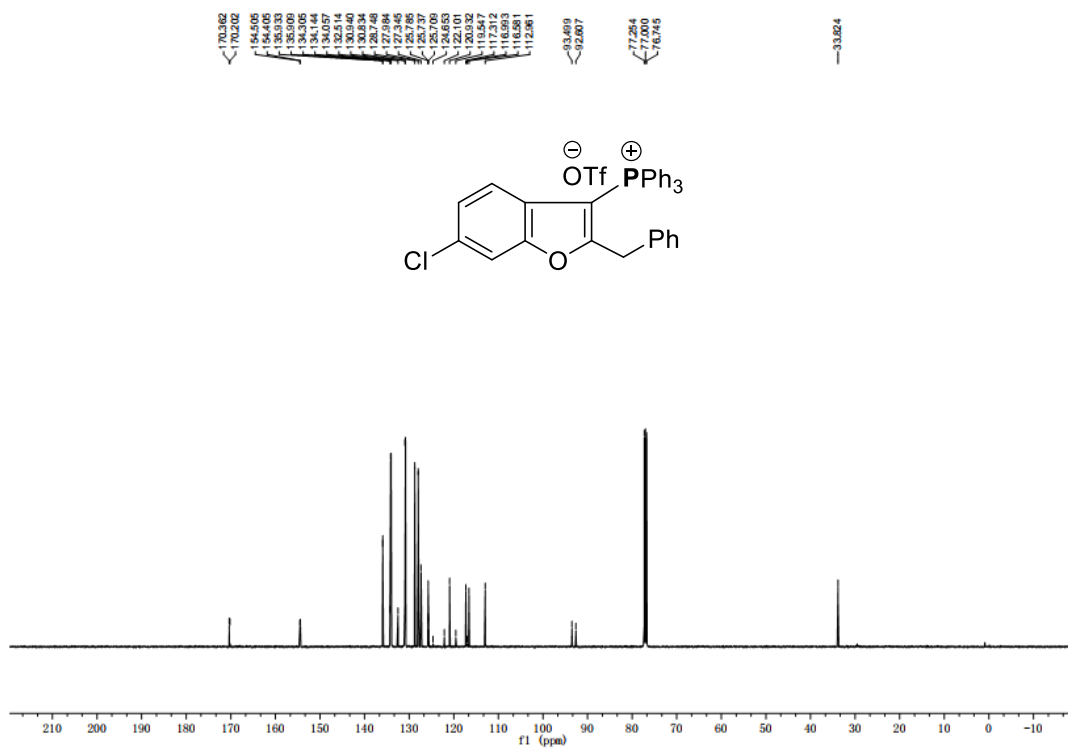
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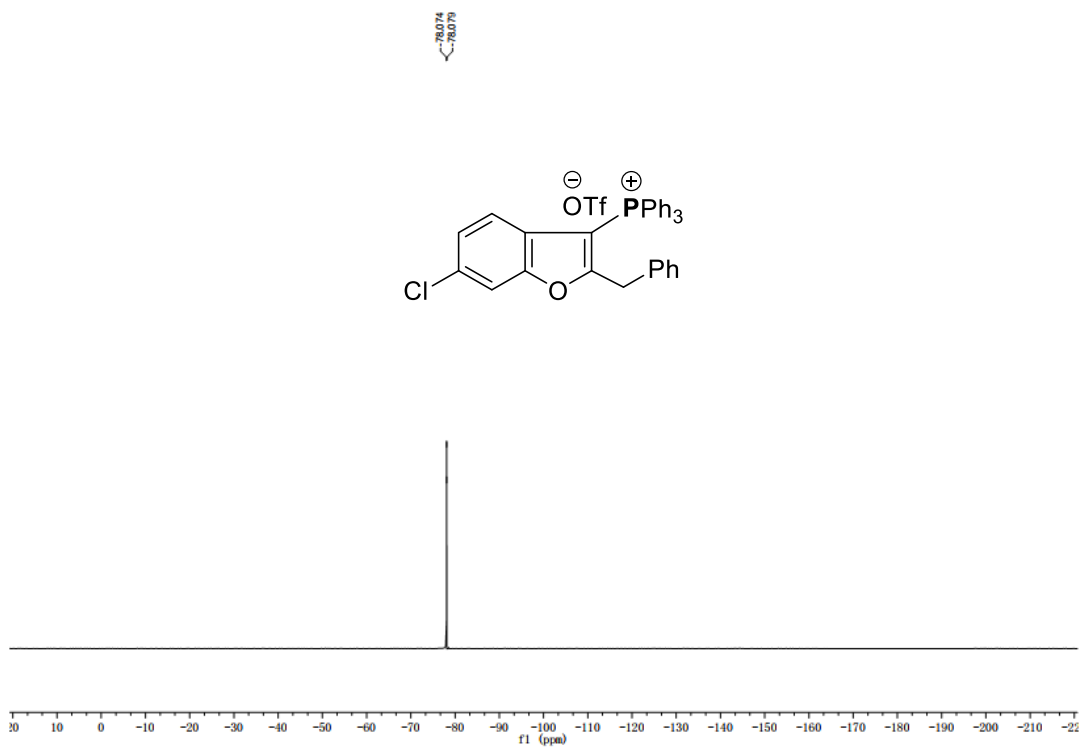
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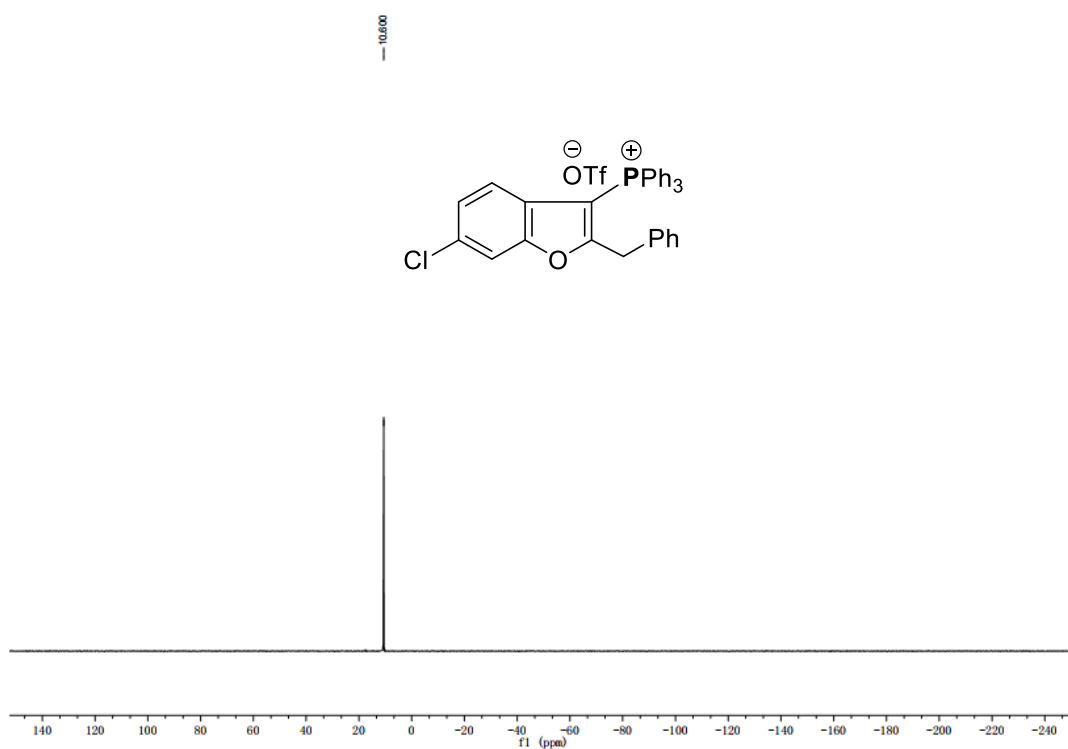
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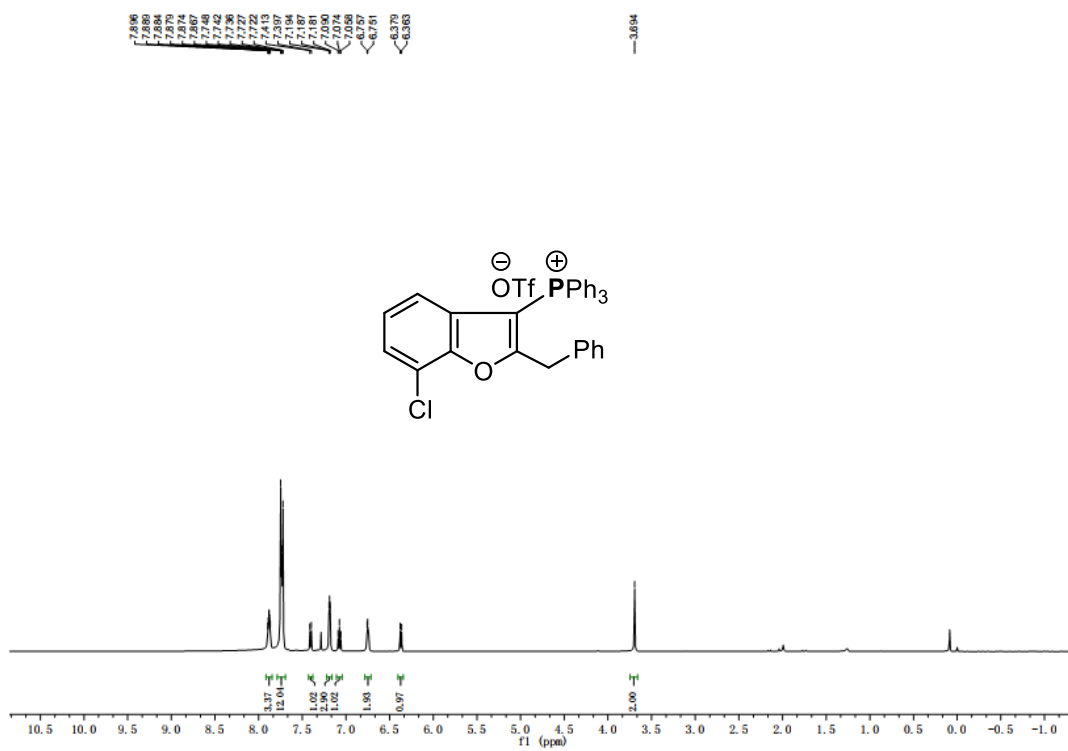
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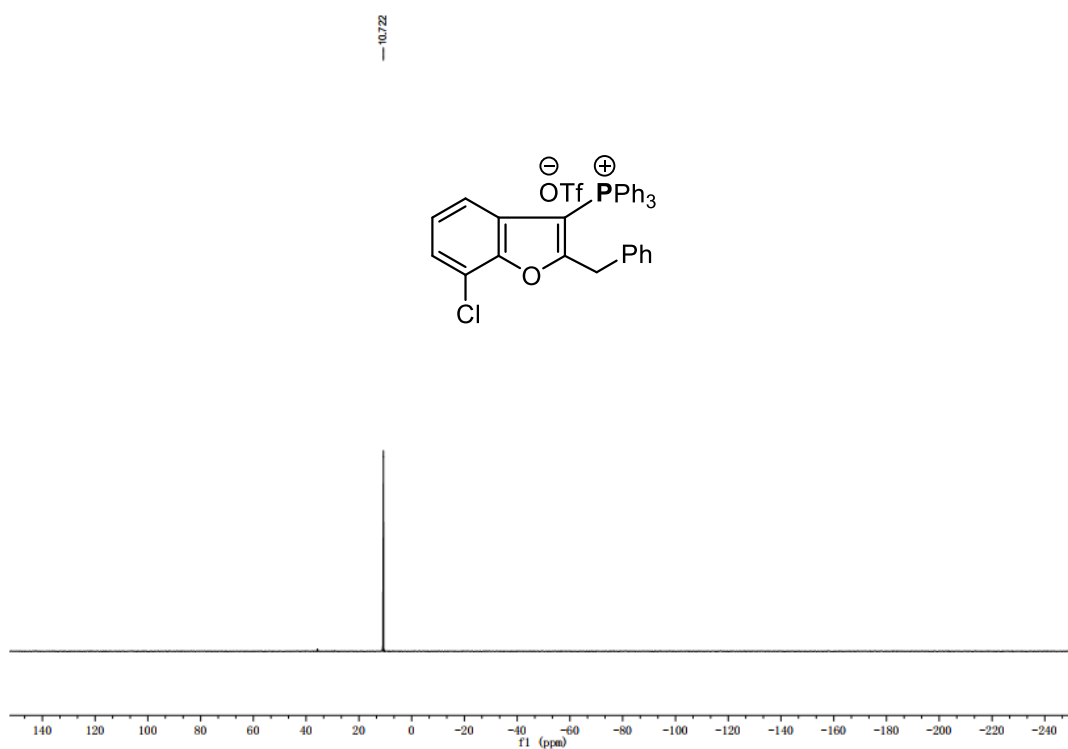
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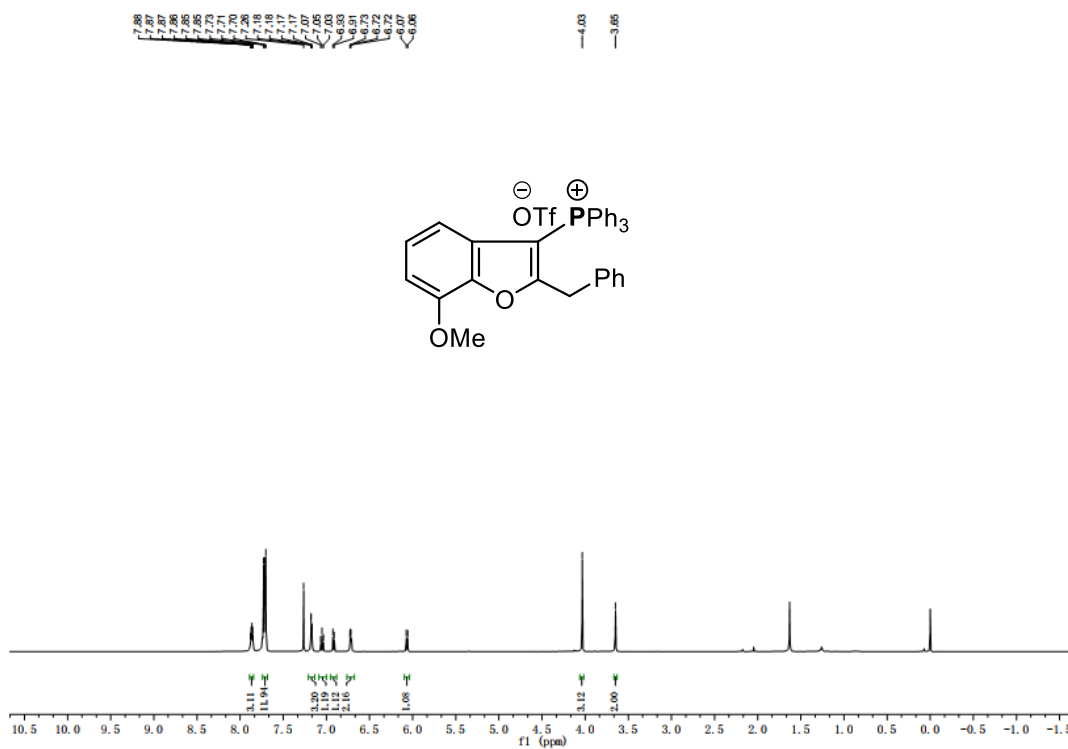
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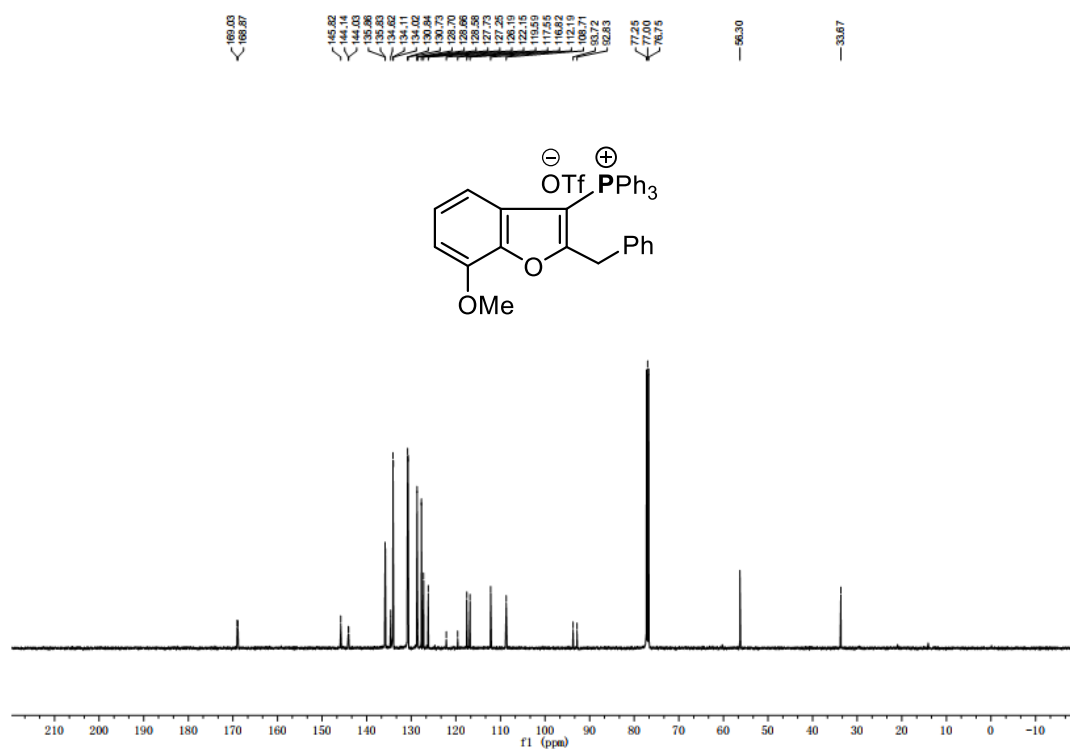
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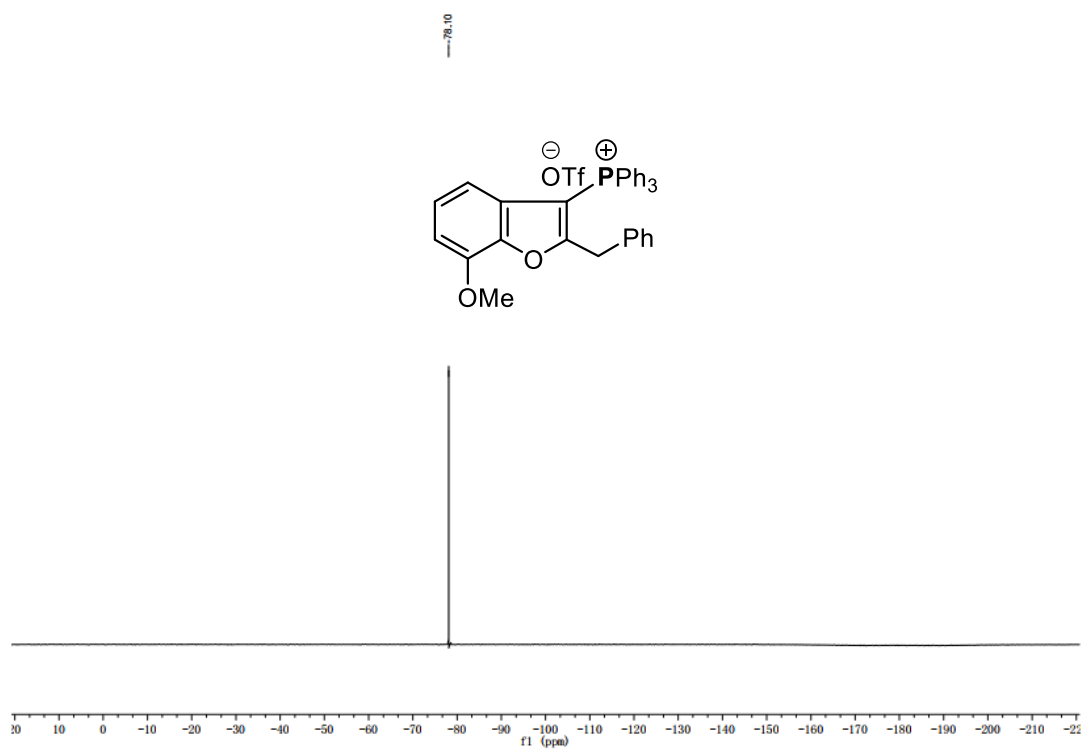
^1H NMR (500 MHz, CDCl_3) of compound **3ka**



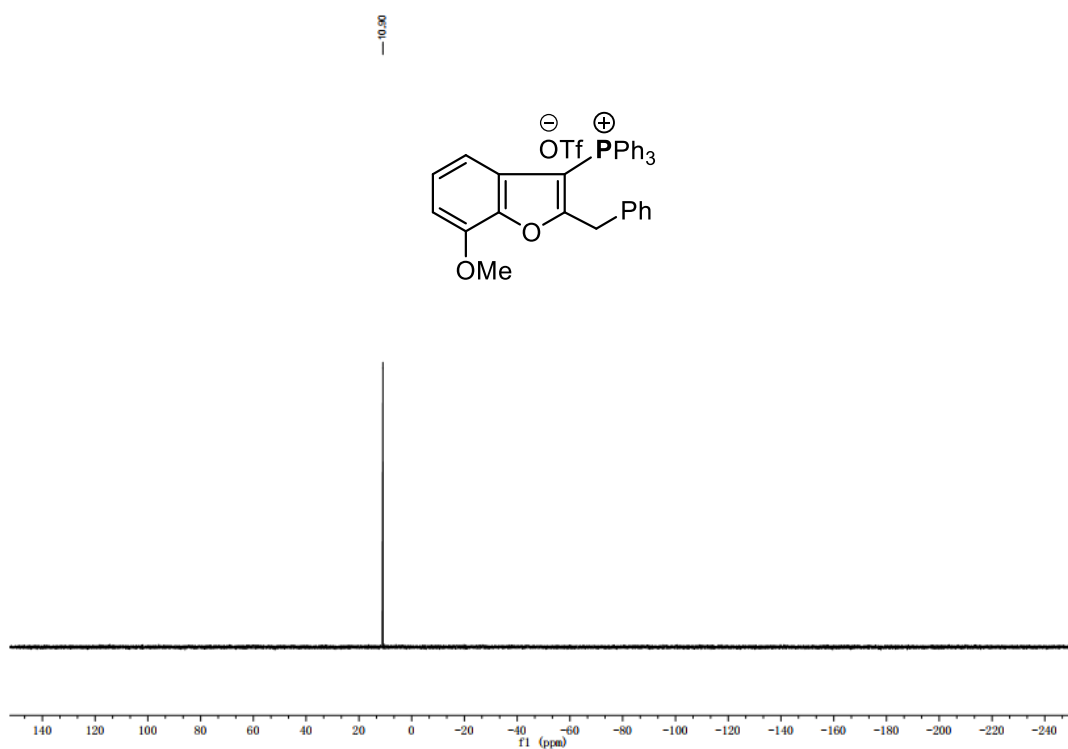
^{13}C NMR (126 MHz, CDCl_3) of compound **3ka**



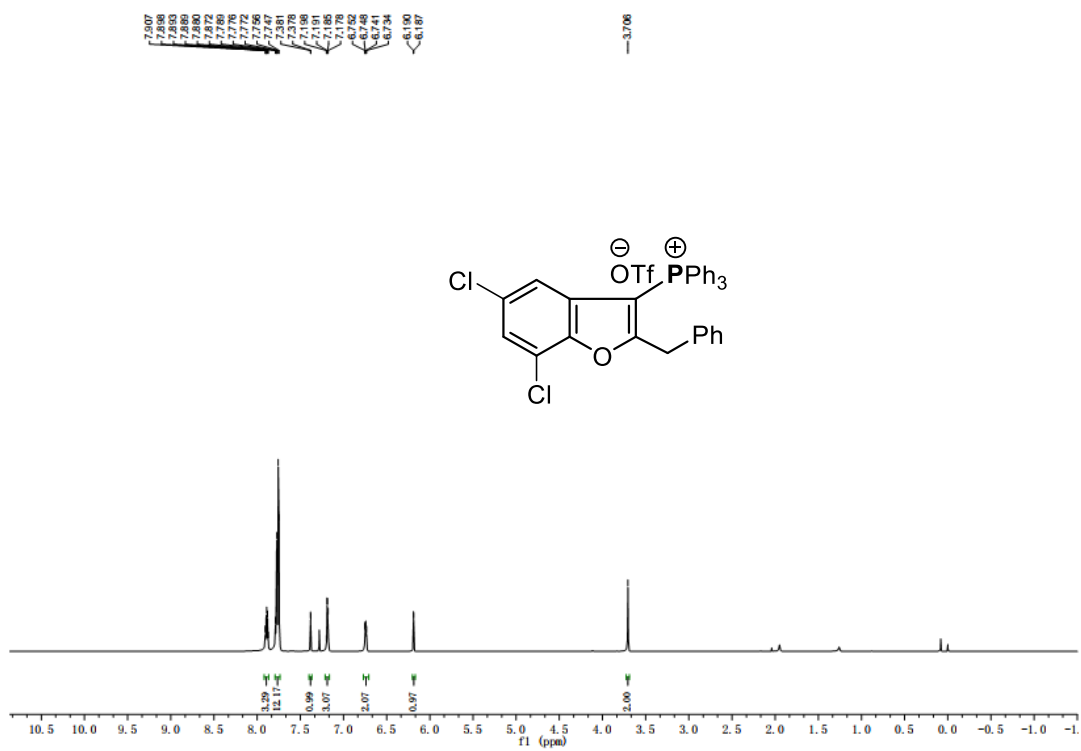
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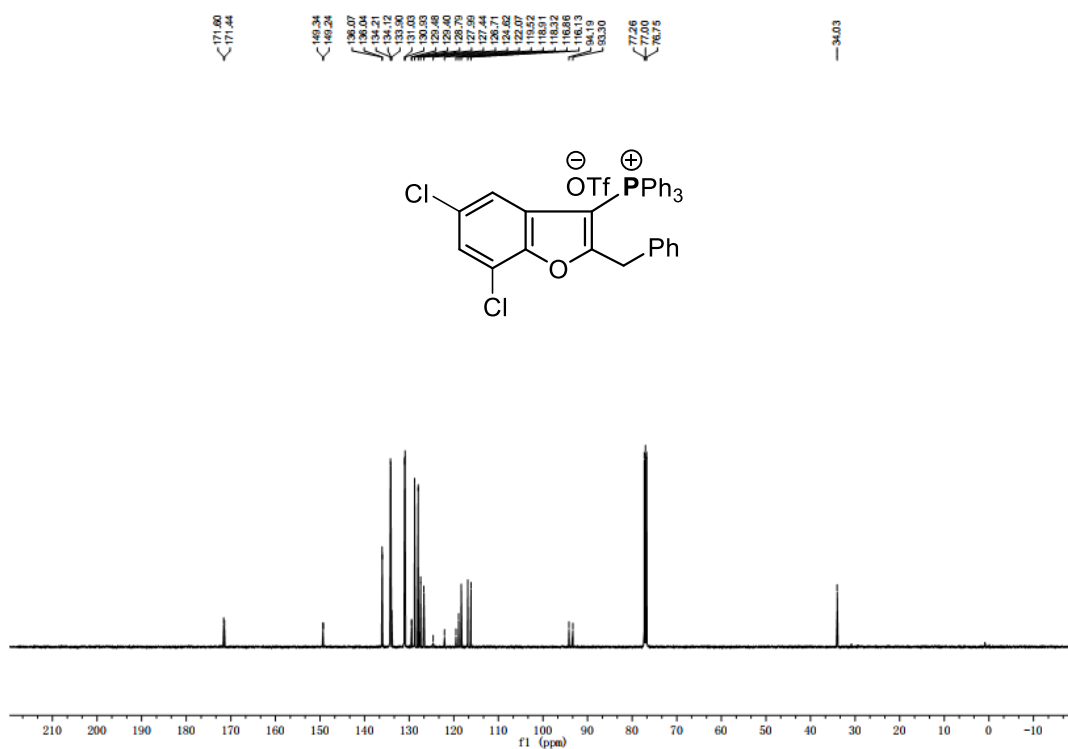
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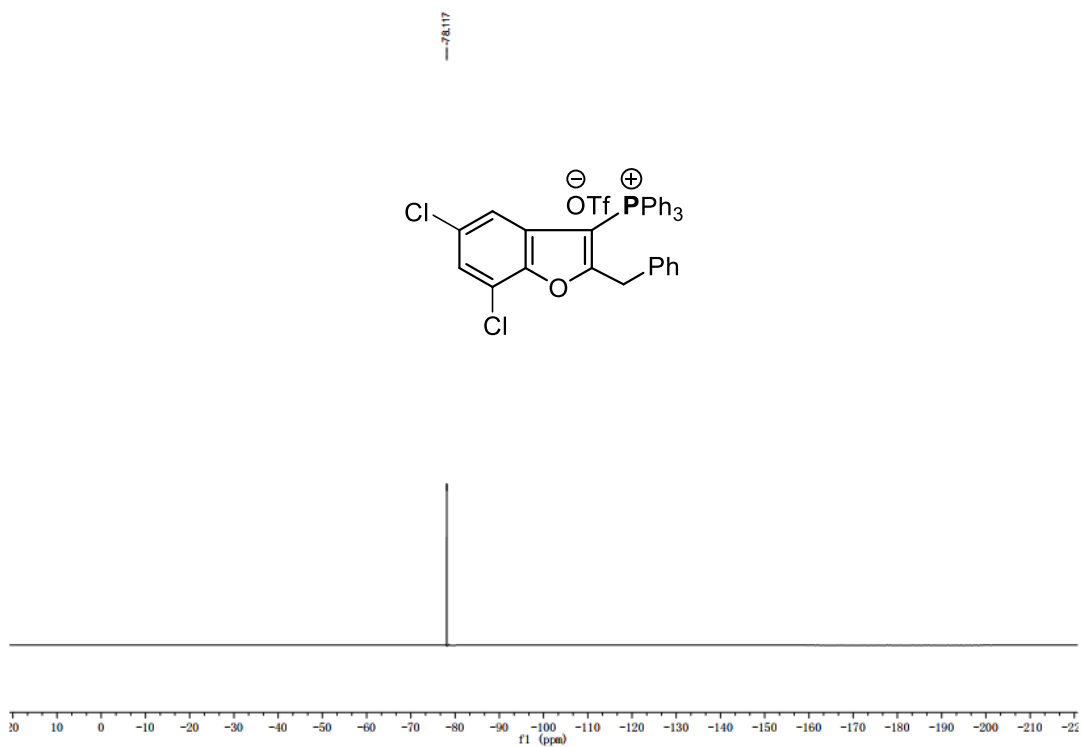
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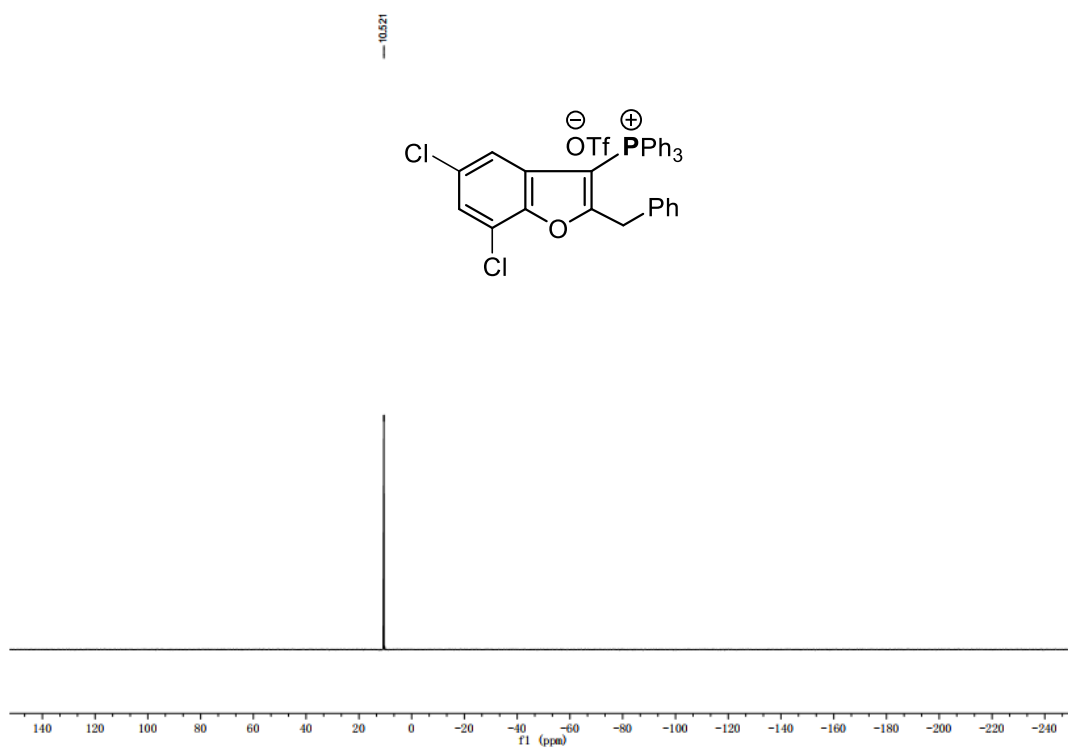
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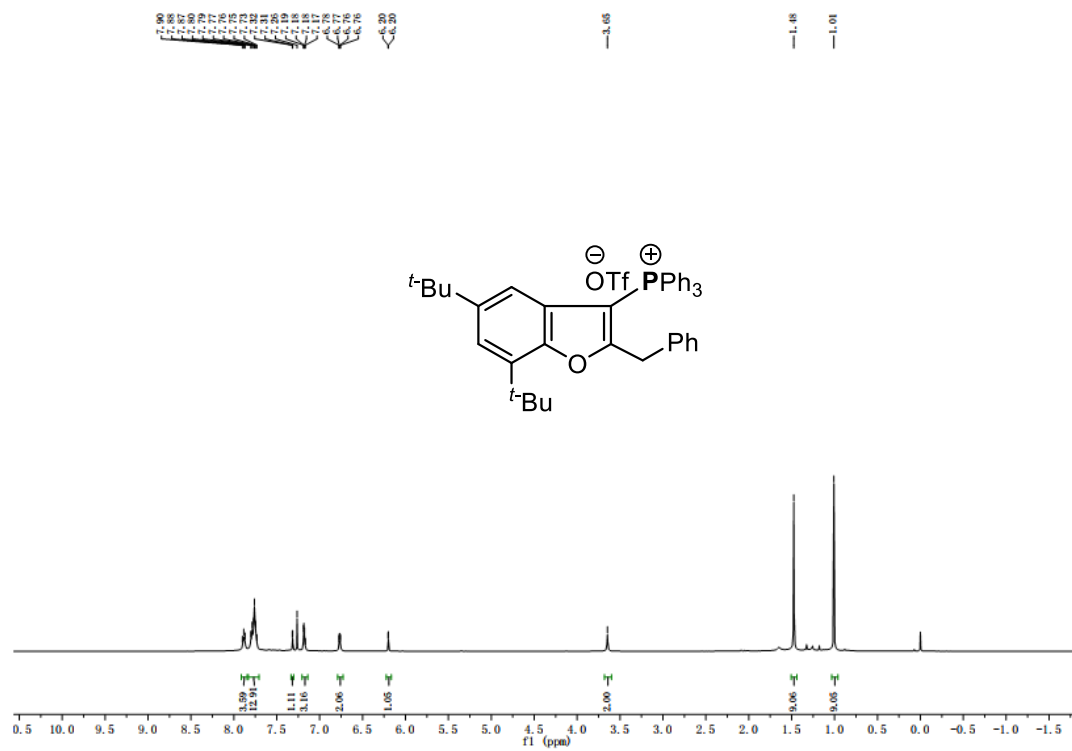
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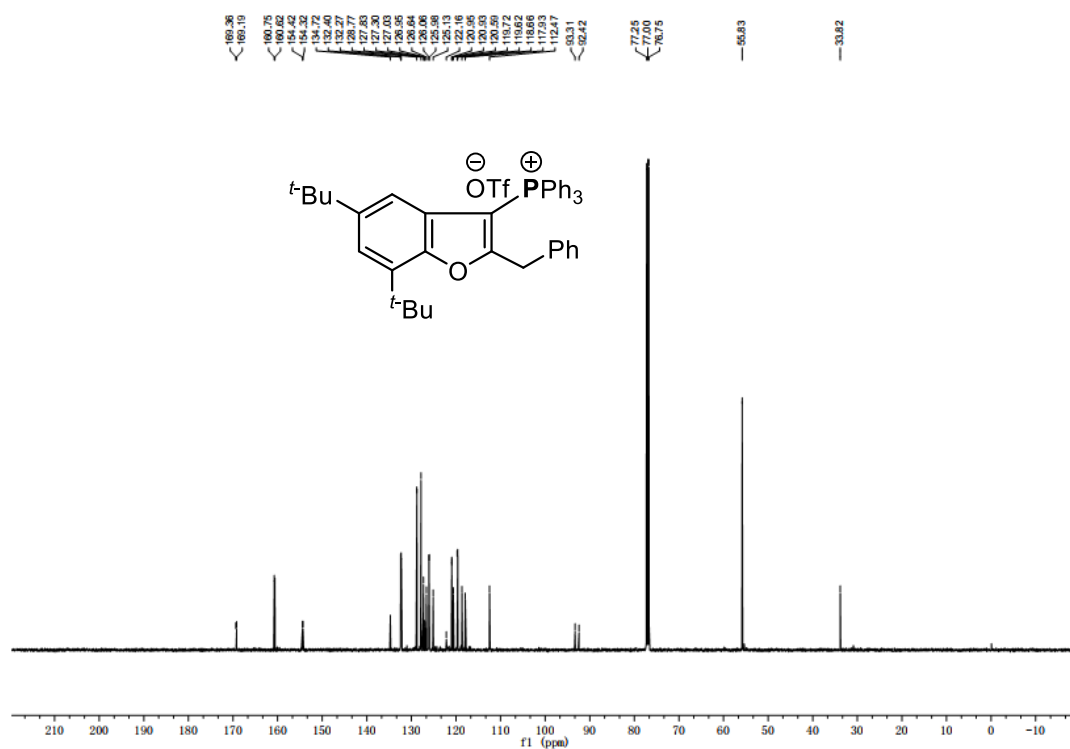
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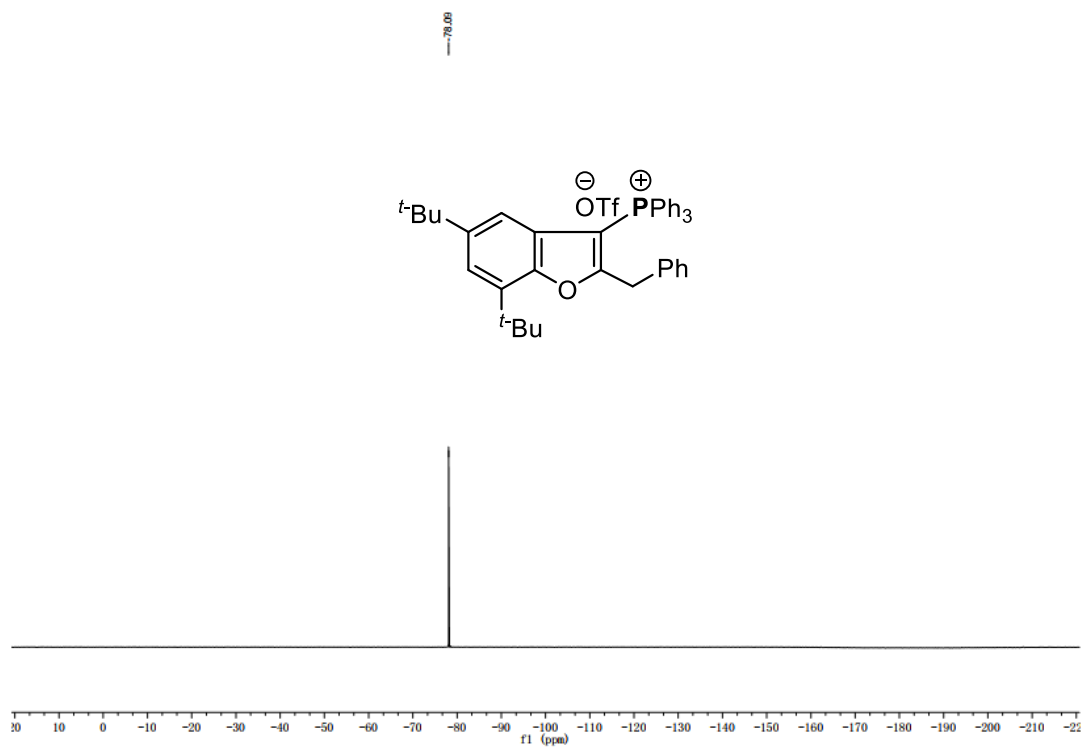
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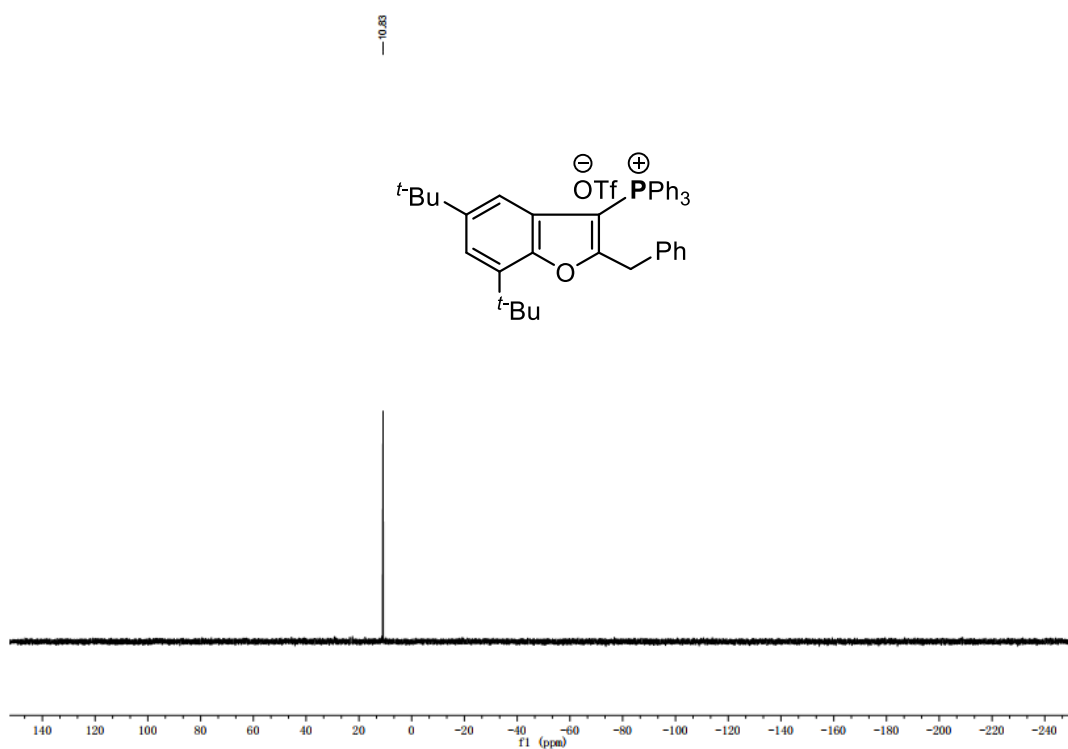
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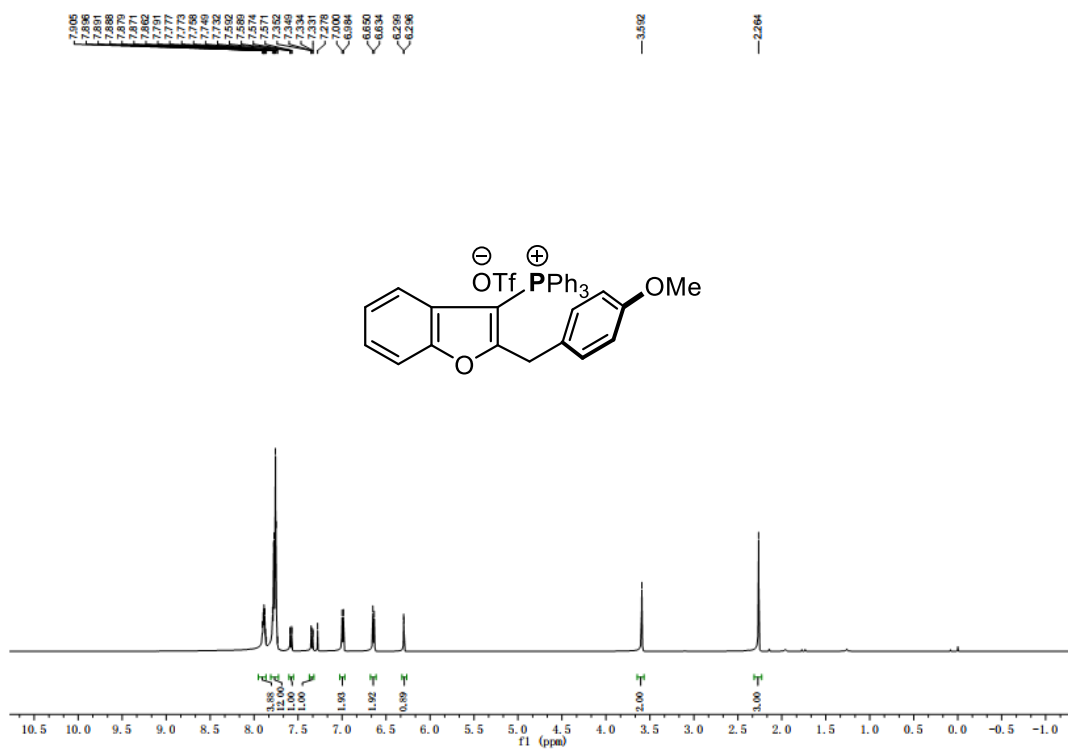
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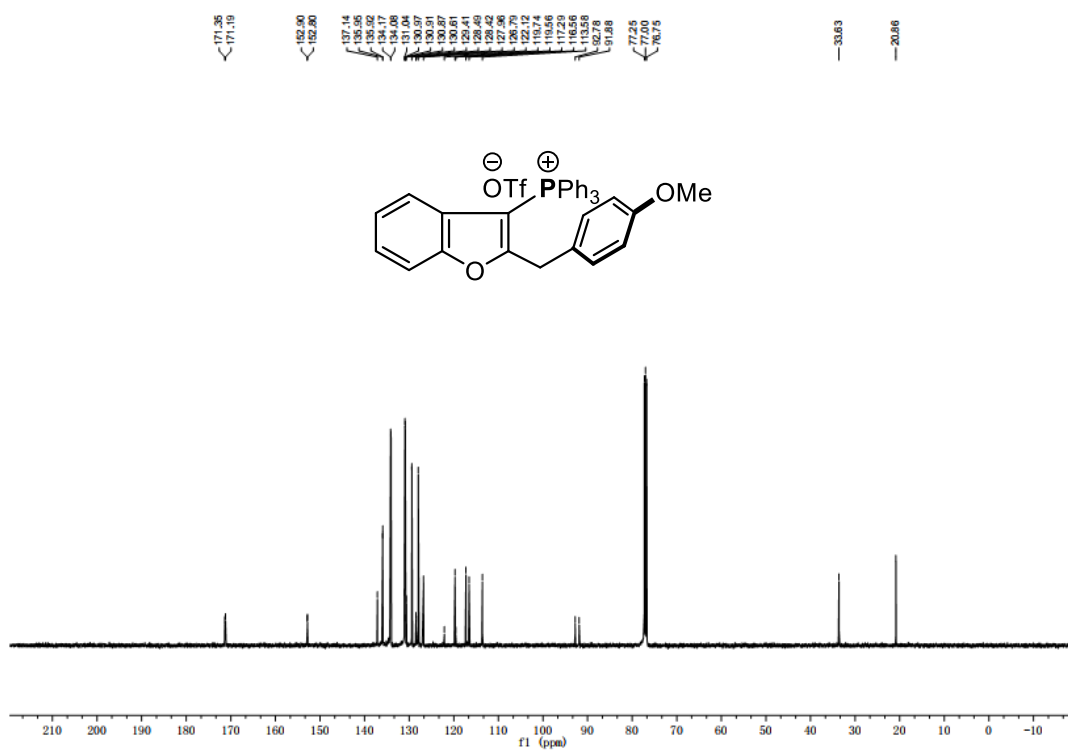
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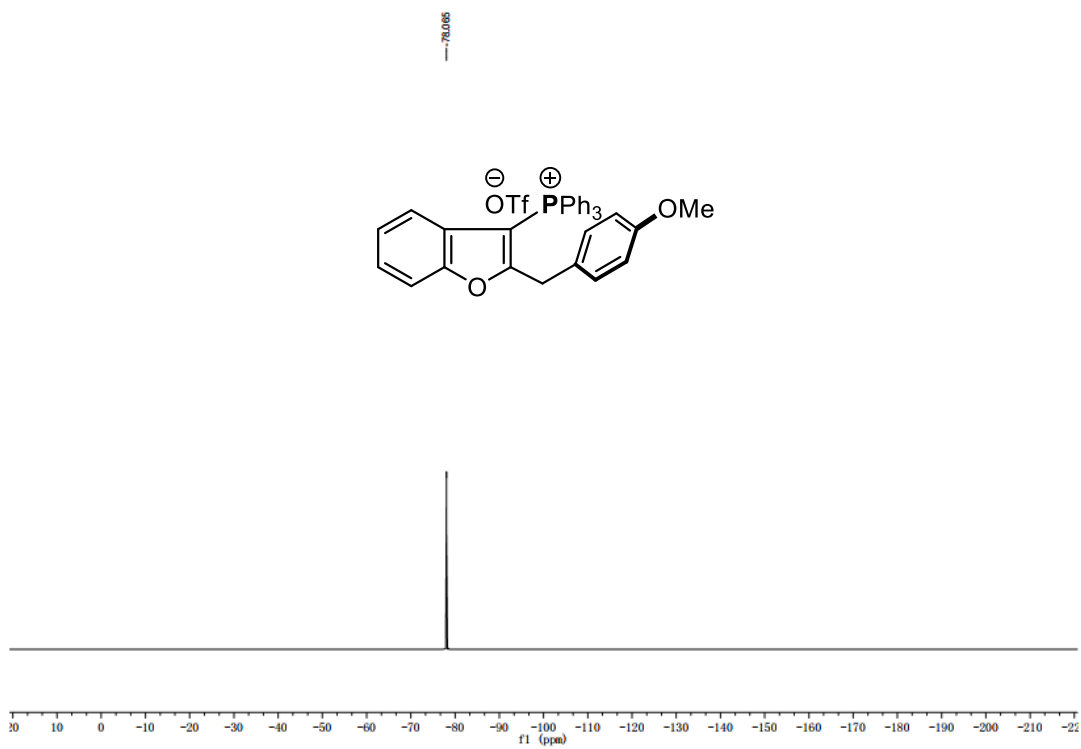
^1H NMR (500 MHz, CDCl_3) of compound **3na**



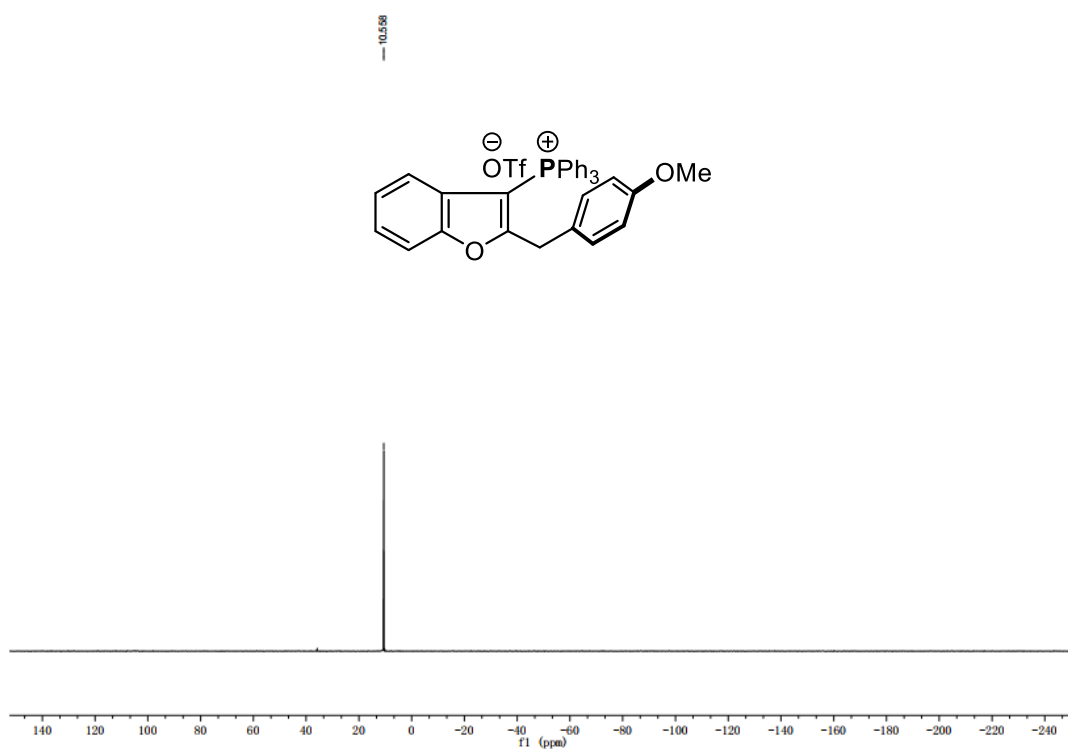
^{13}C NMR (126 MHz, CDCl_3) of compound **3na**



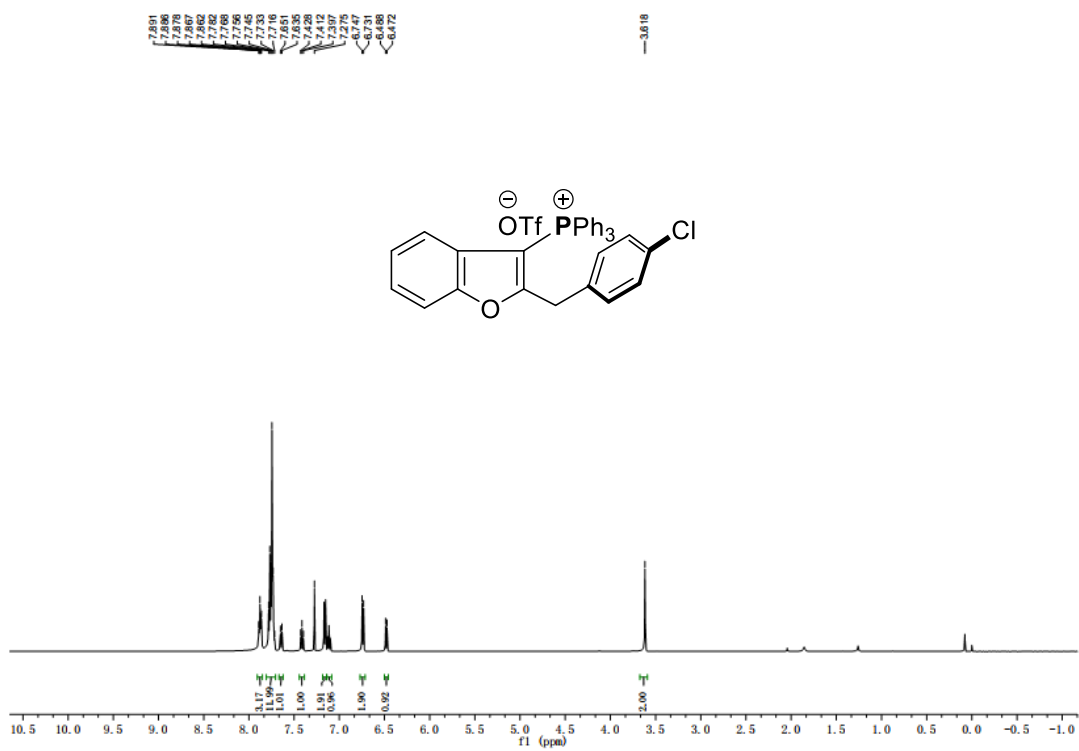
^{19}F NMR (471 MHz, CDCl_3) of compound **3na**



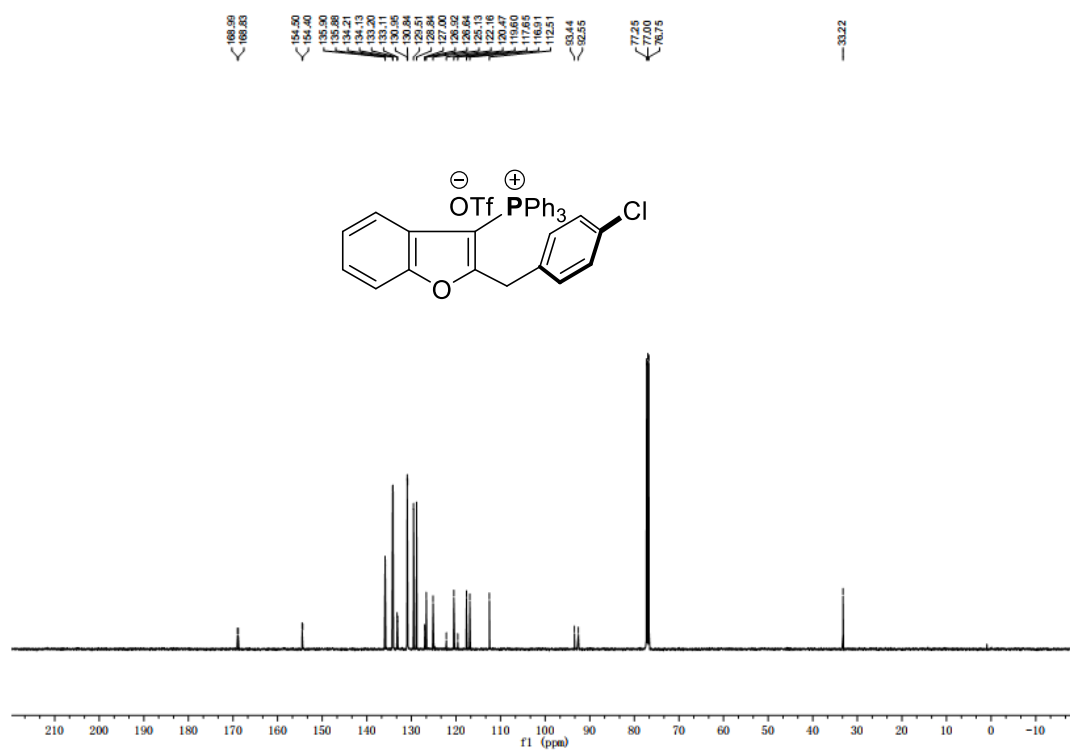
^{31}P NMR (202 MHz, CDCl_3) of compound **3na**



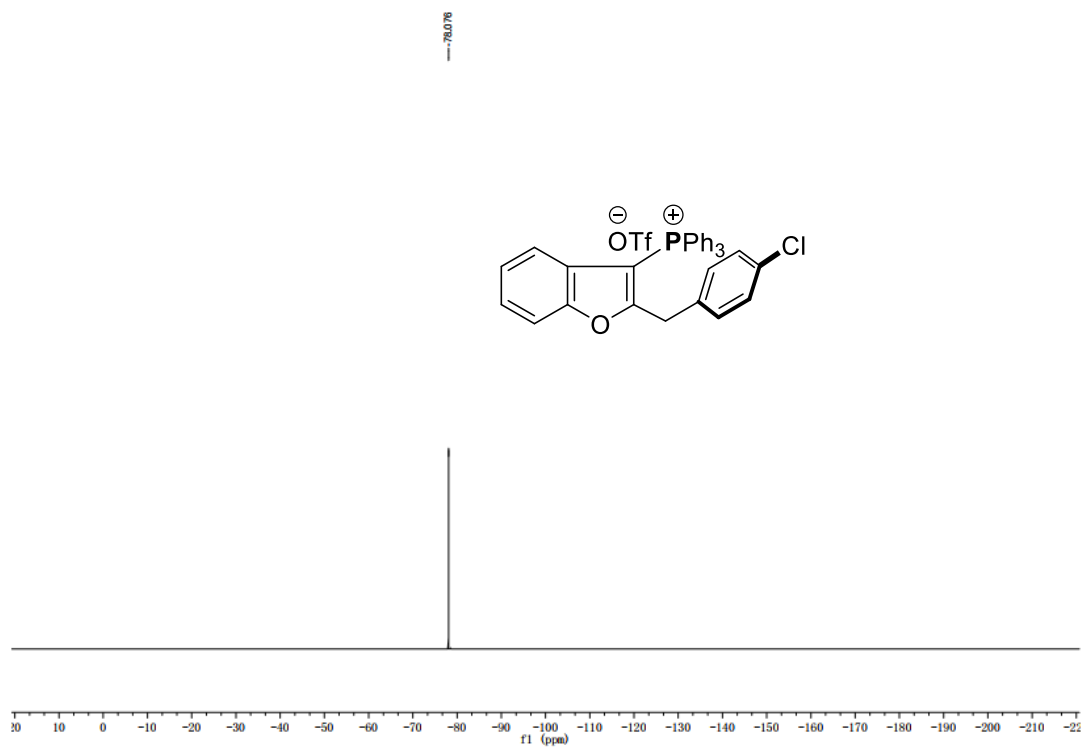
^1H NMR (500 MHz, CDCl_3) of compound **3oa**



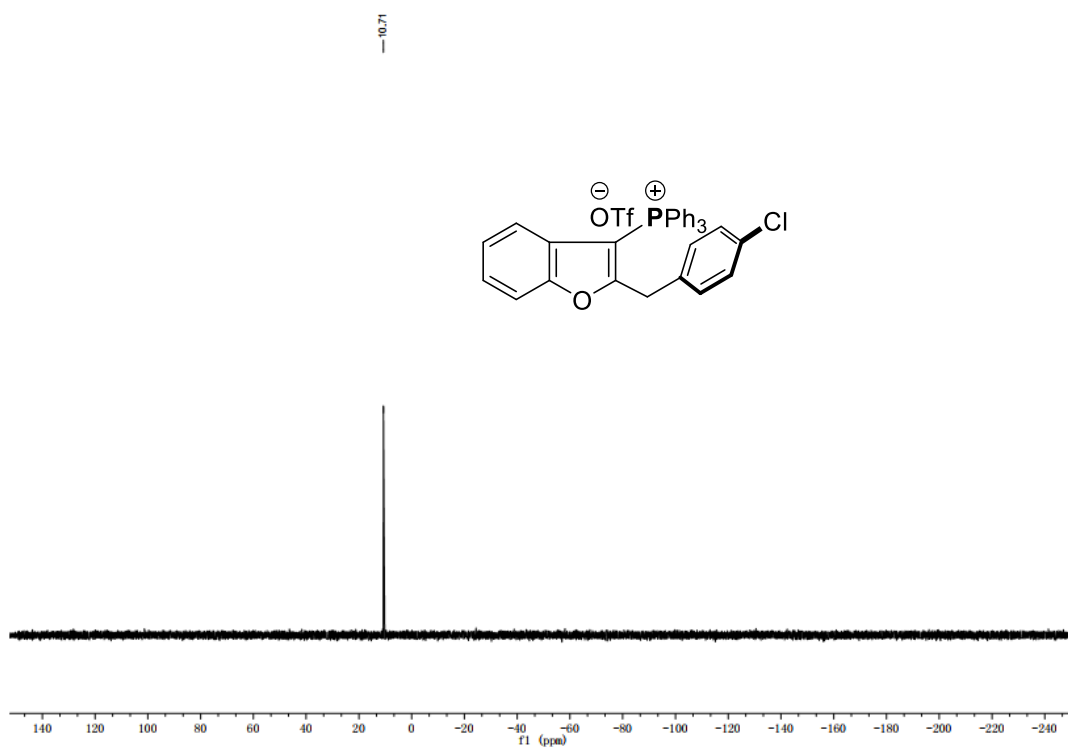
^{13}C NMR (126 MHz, CDCl_3) of compound **30a**



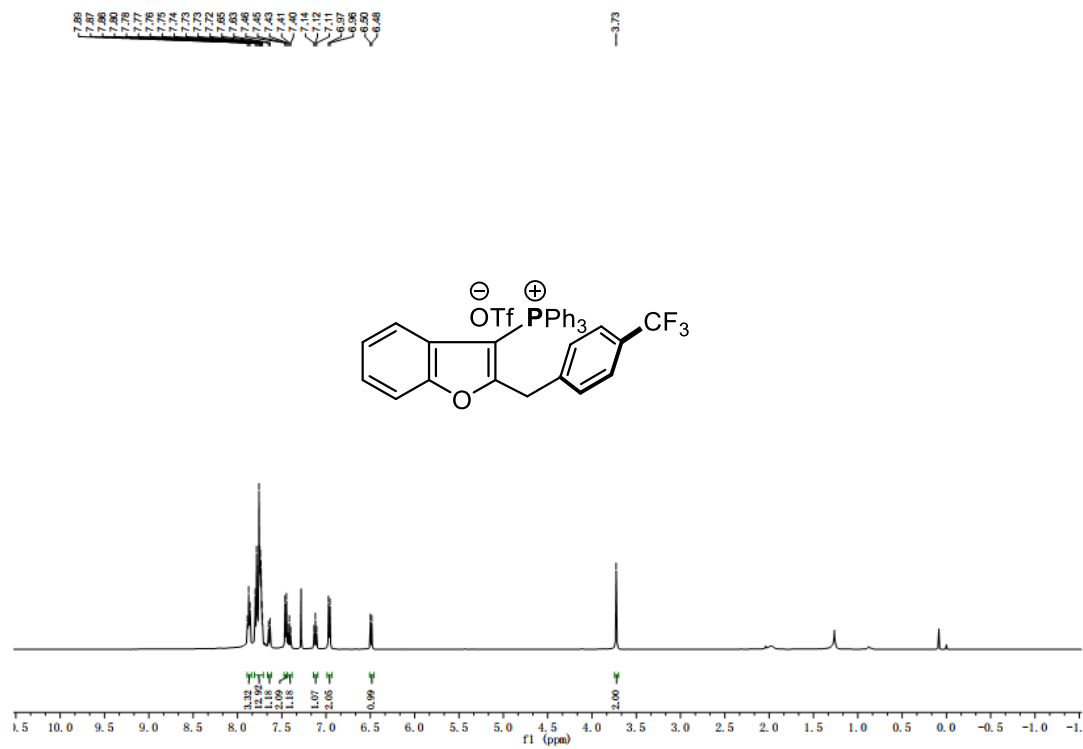
^{19}F NMR (471 MHz, CDCl_3) of compound **30a**



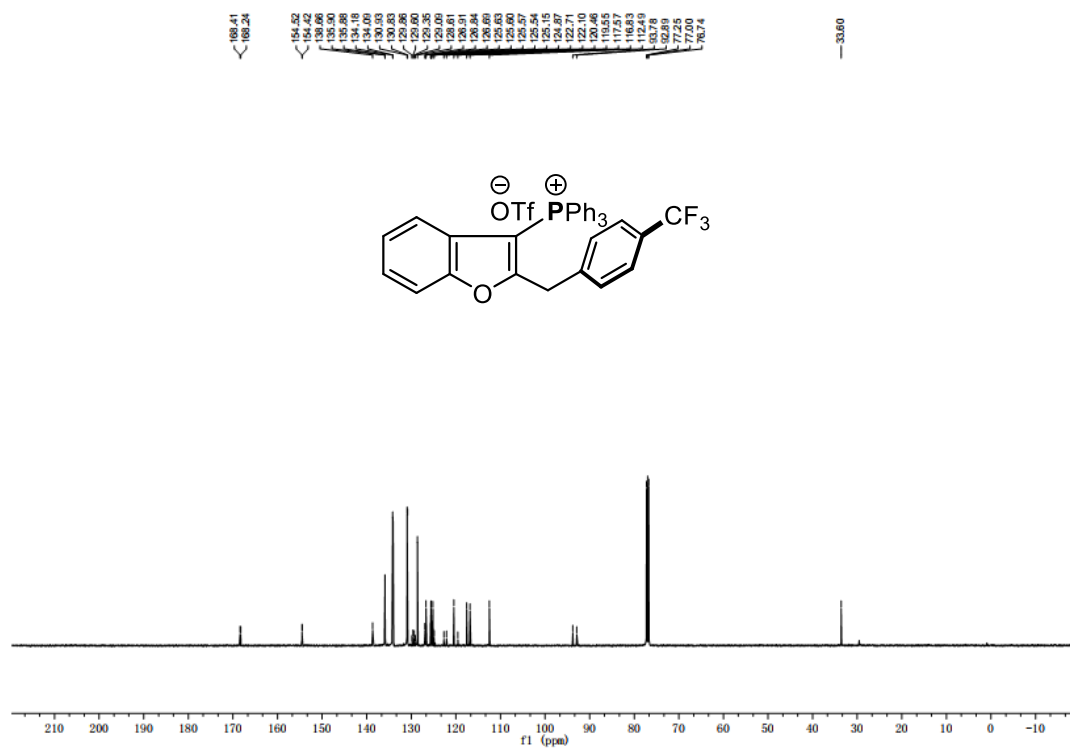
^{31}P NMR (202 MHz, CDCl_3) of compound **30a**



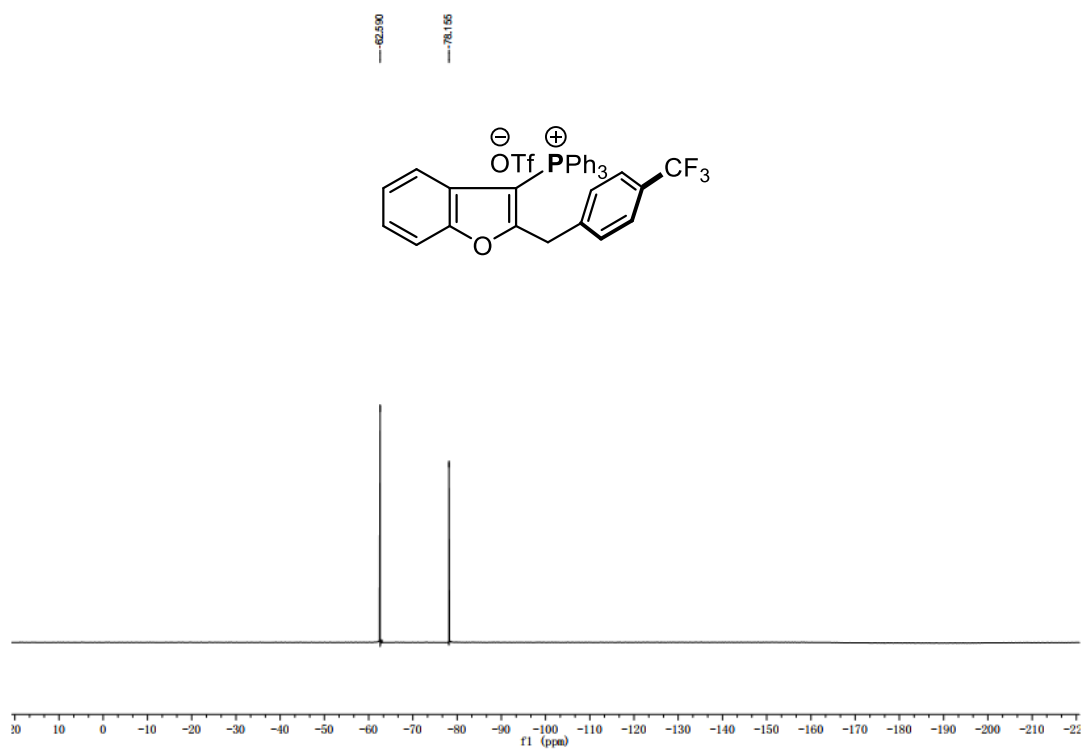
^1H NMR (500 MHz, CDCl_3) of compound **3pa**



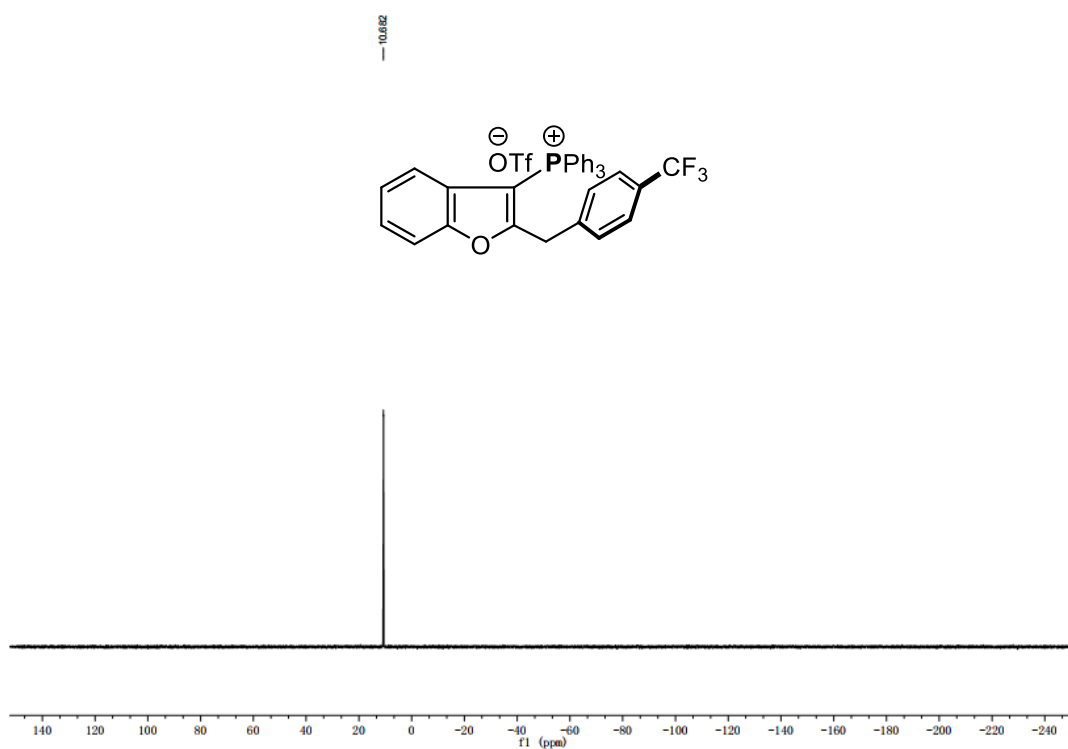
^{13}C NMR (126 MHz, CDCl_3) of compound **3pa**



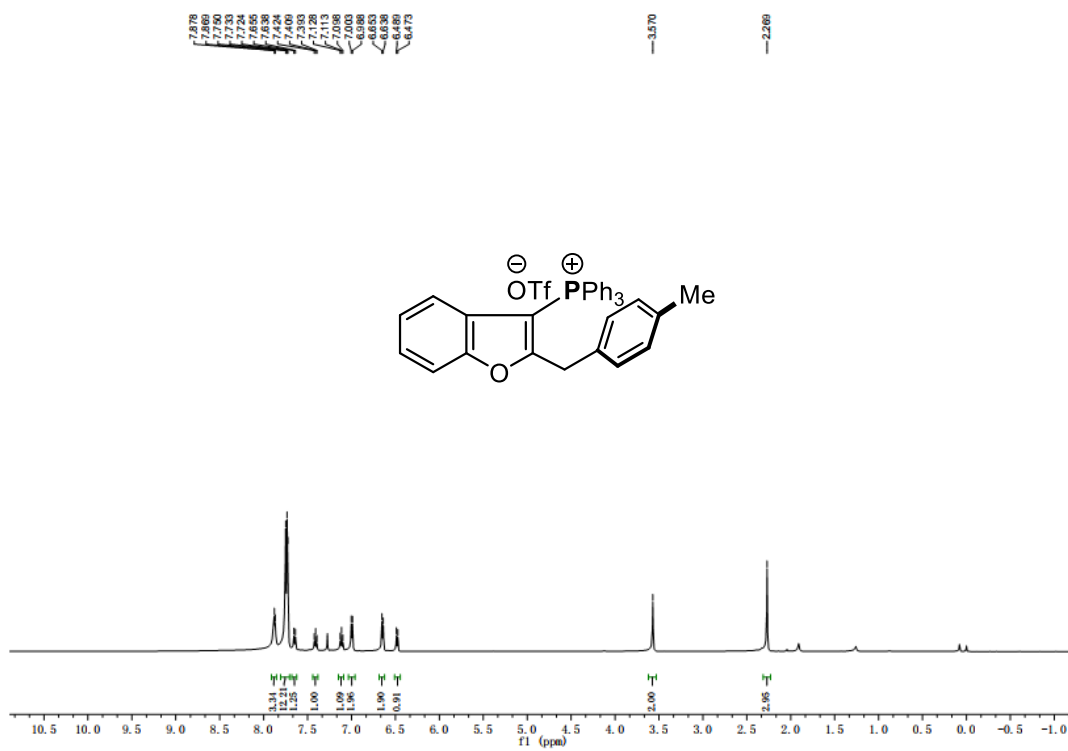
^{19}F NMR (471 MHz, CDCl_3) of compound **3pa**



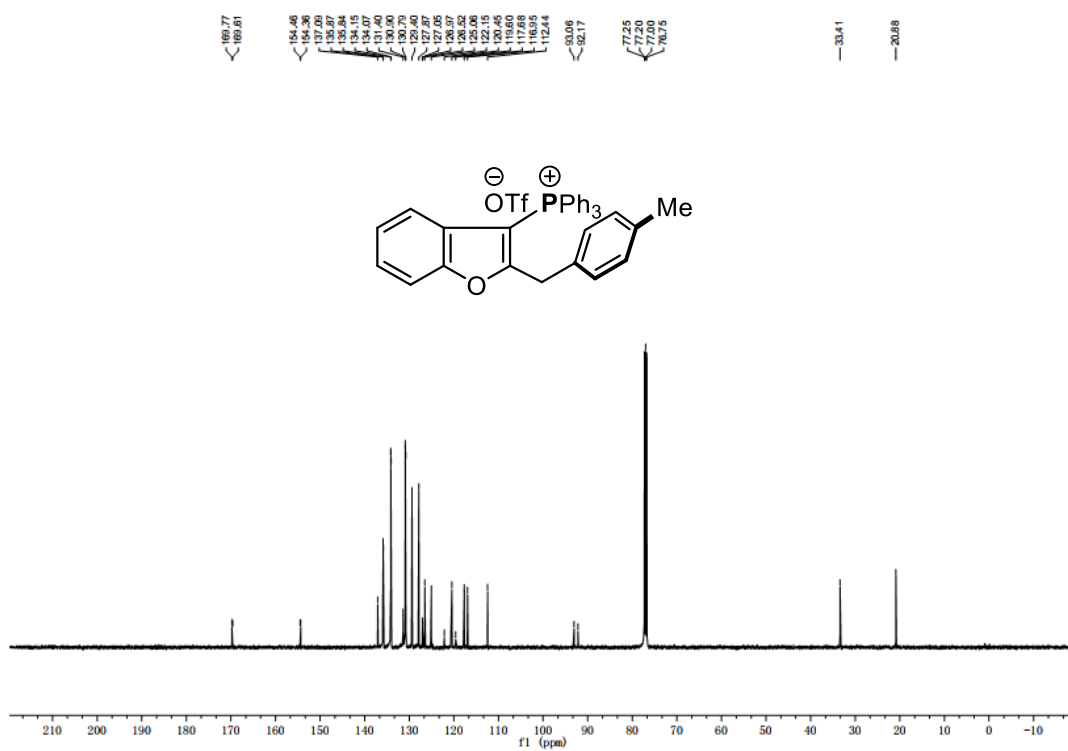
^{31}P NMR (202 MHz, CDCl_3) of compound **3pa**



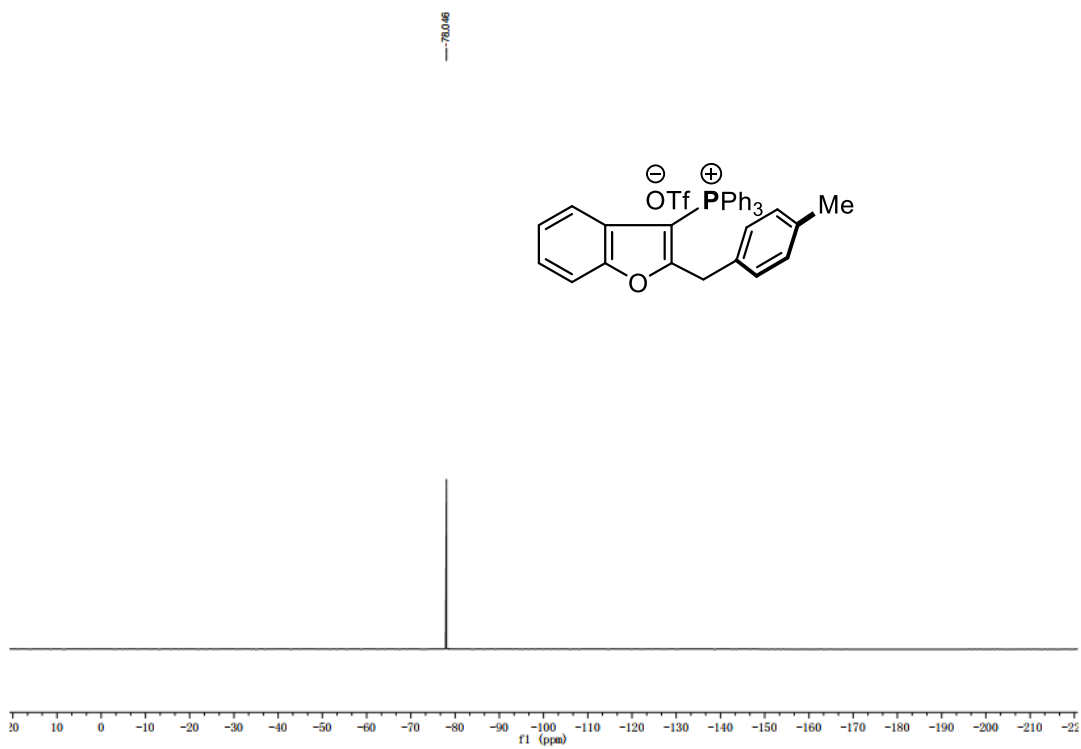
^1H NMR (500 MHz, CDCl_3) of compound **3qa**



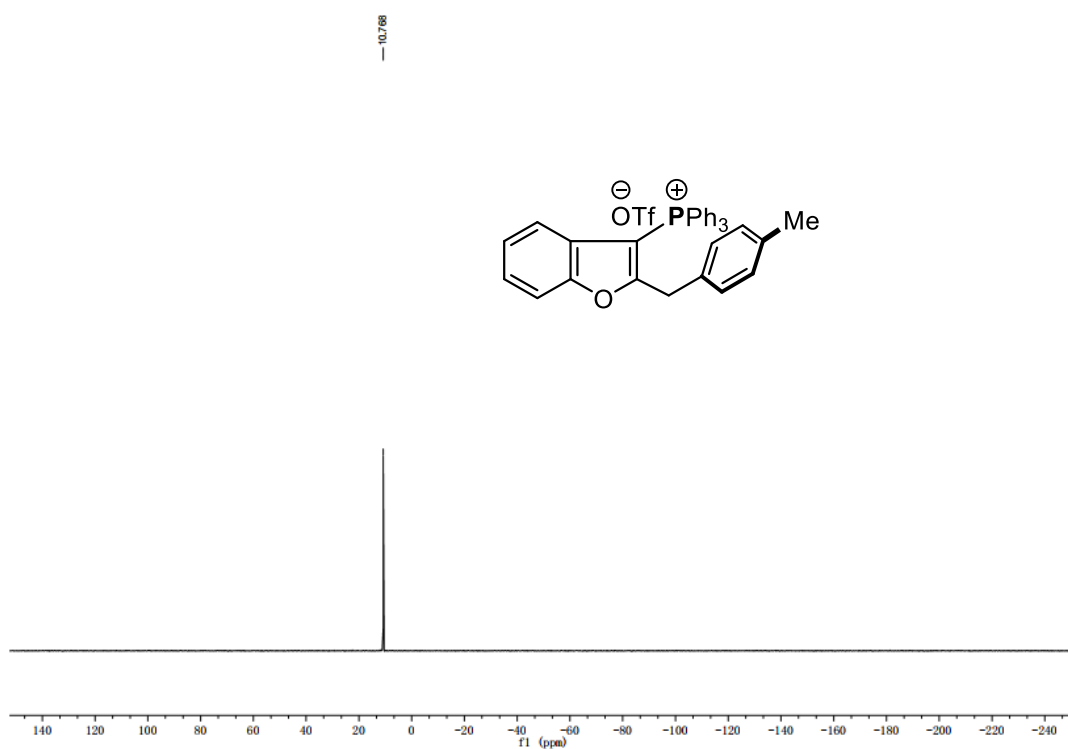
^{13}C NMR (126 MHz, CDCl_3) of compound **3qa**



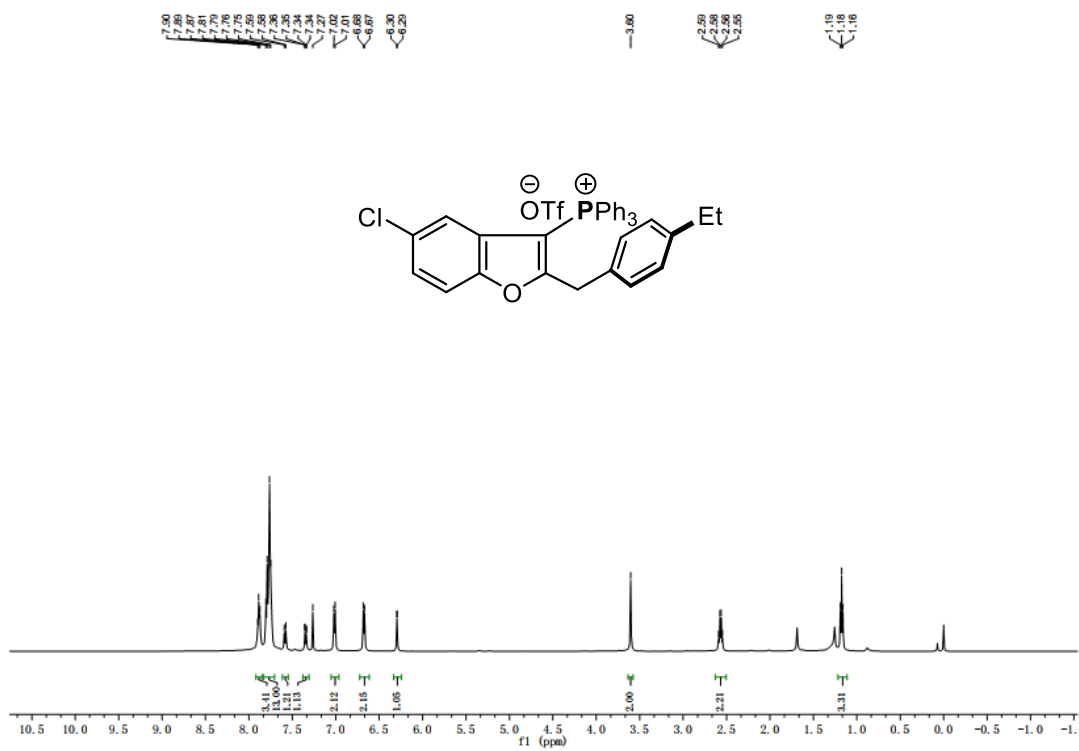
^{19}F NMR (471 MHz, CDCl_3) of compound **3qa**



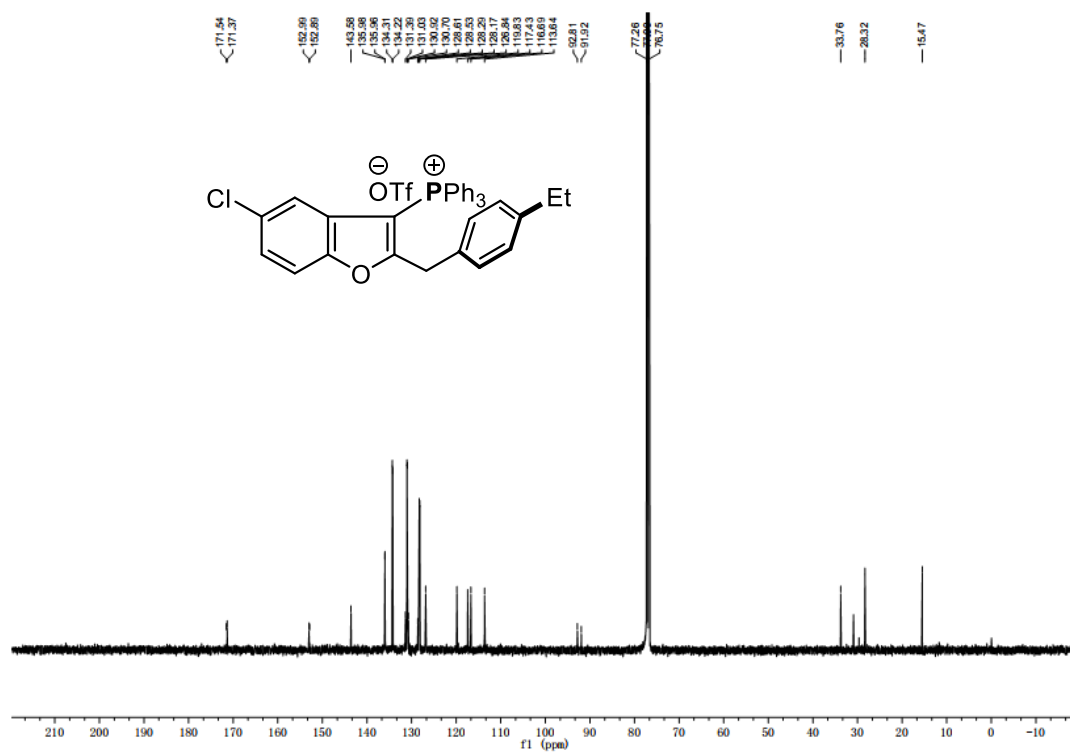
^{31}P NMR (202 MHz, CDCl_3) of compound **3qa**



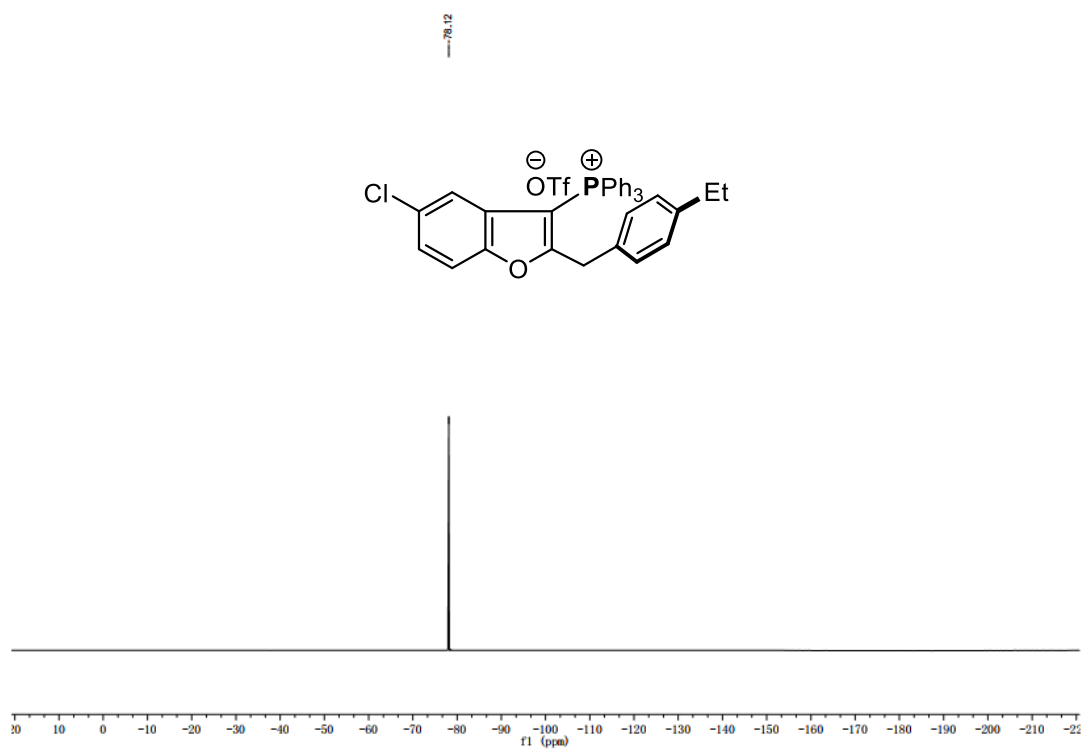
^1H NMR (500 MHz, CDCl_3) of compound **3ra**



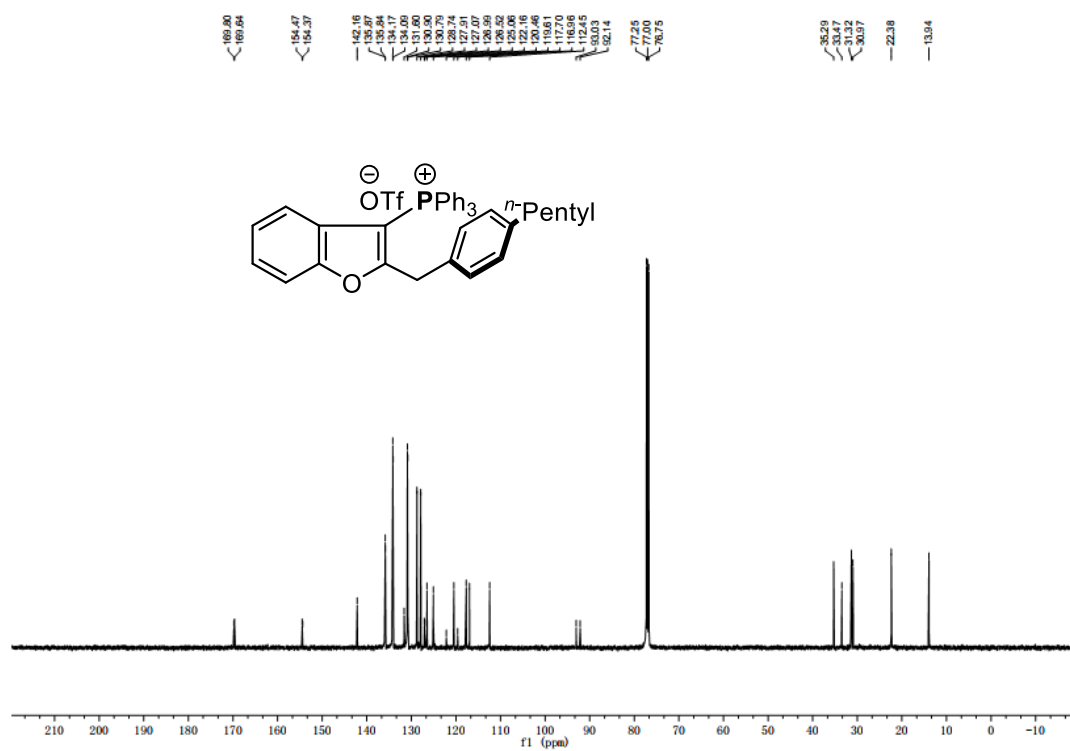
^{13}C NMR (126 MHz, CDCl_3) of compound **3ra**



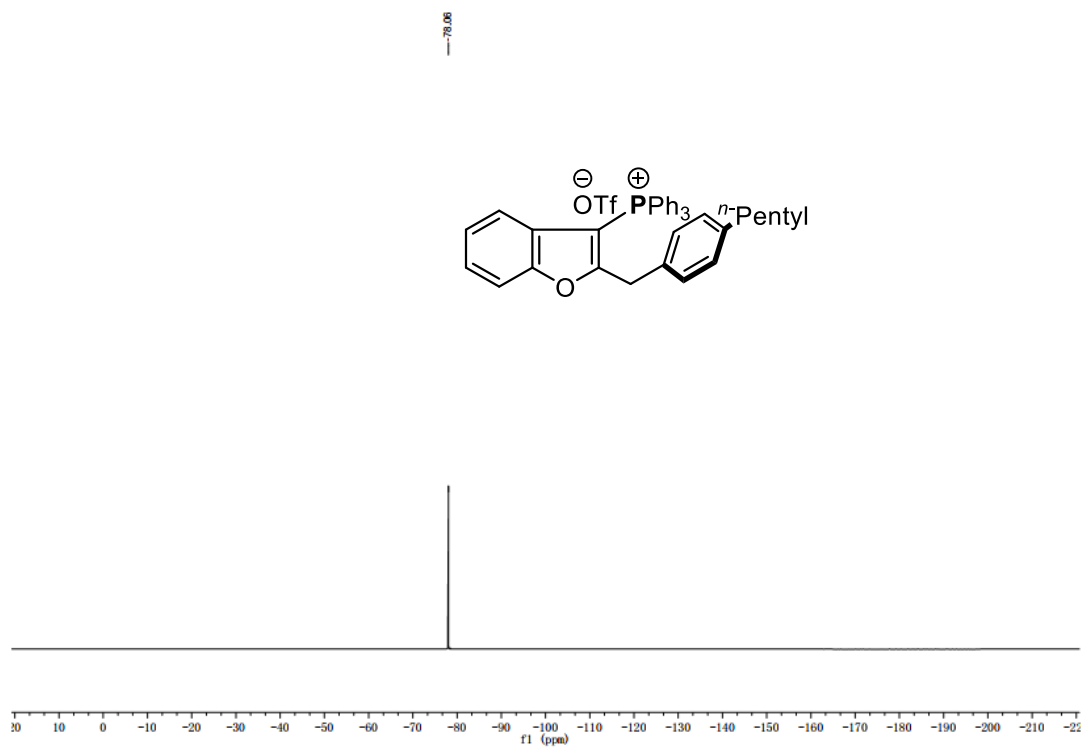
^{19}F NMR (471 MHz, CDCl_3) of compound **3ra**



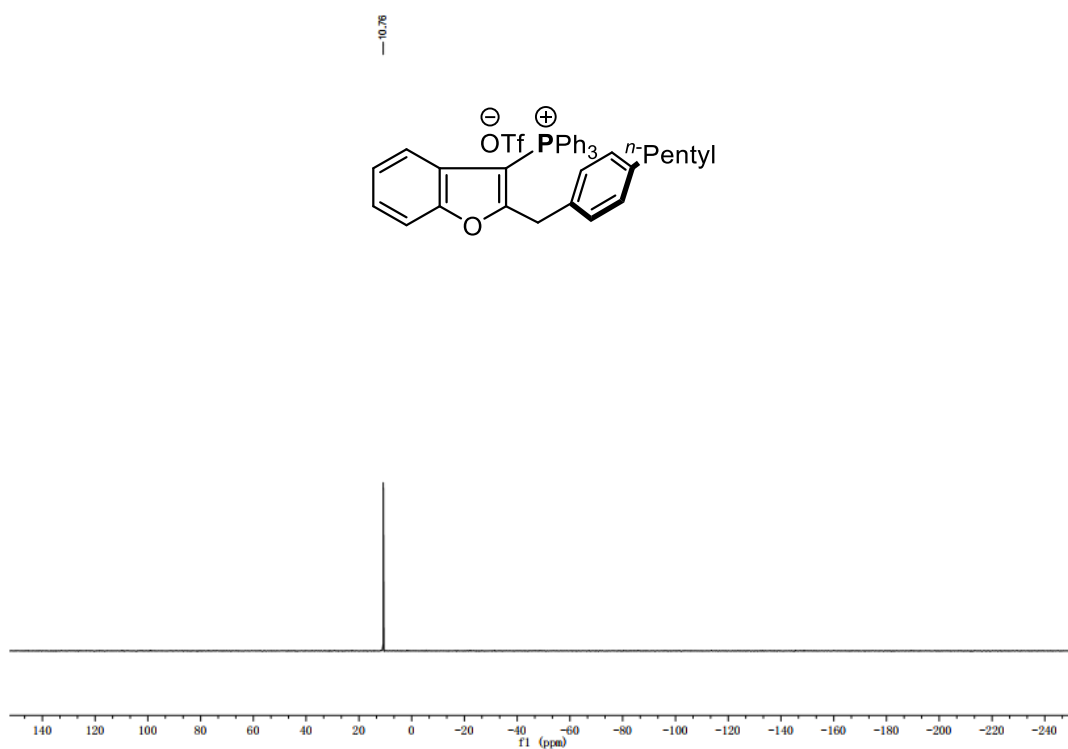
^{13}C NMR (126 MHz, CDCl_3) of compound **3sa**



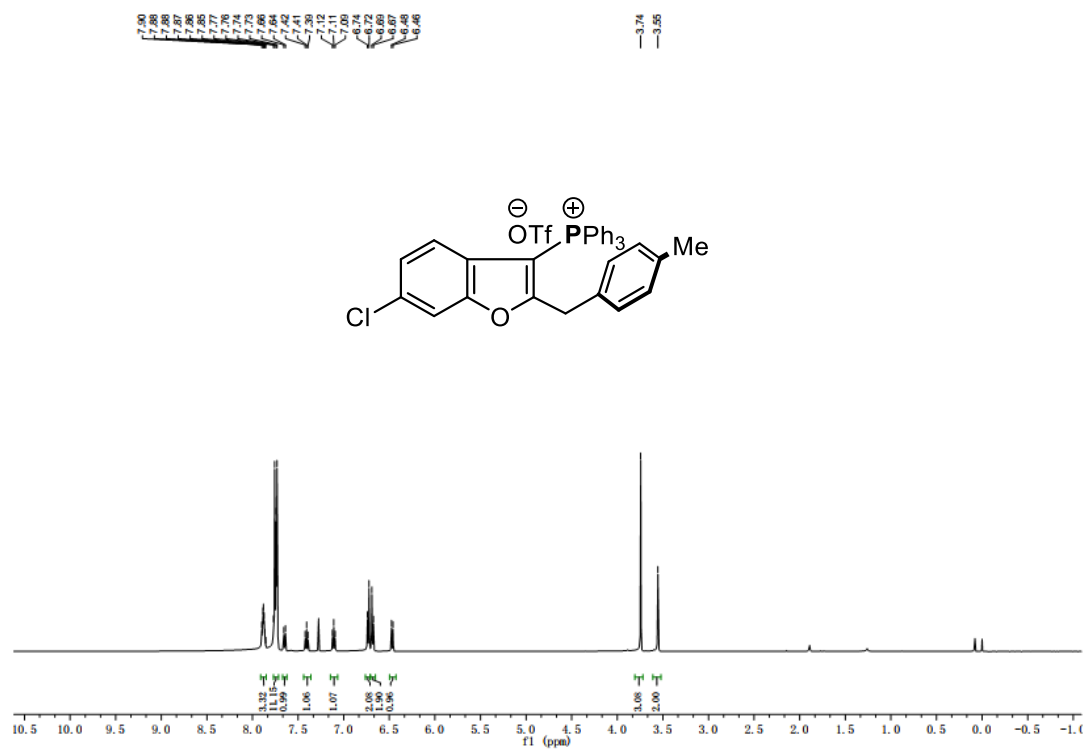
^{19}F NMR (471 MHz, CDCl_3) of compound **3sa**



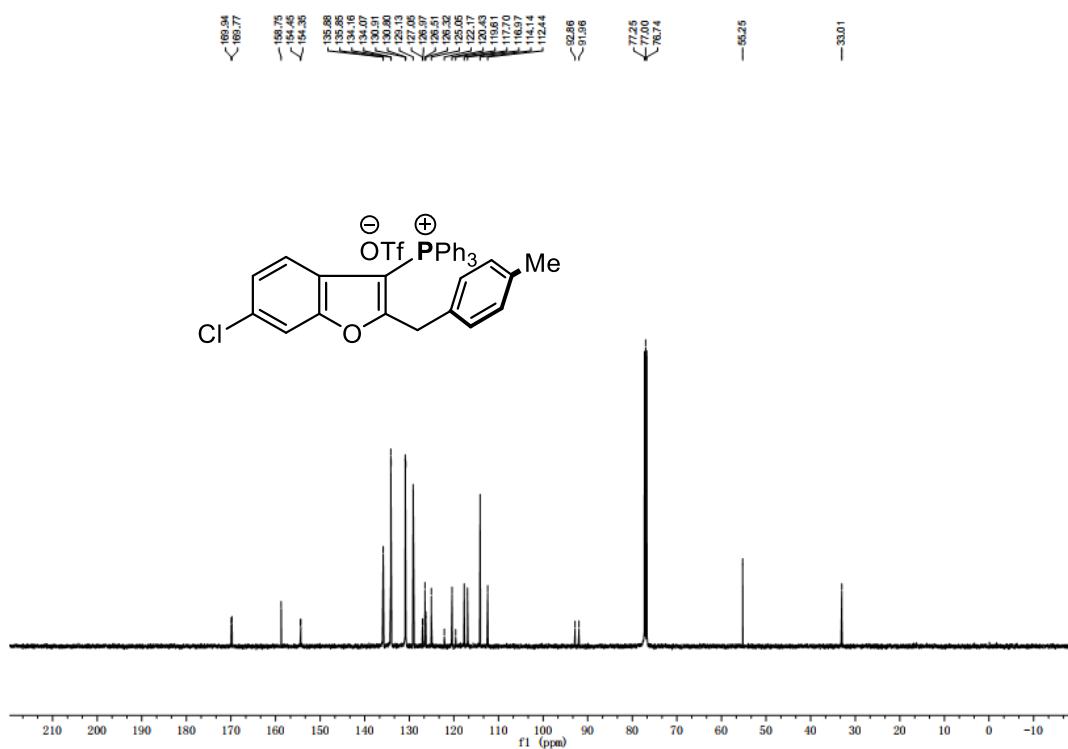
^{31}P NMR (202 MHz, CDCl_3) of compound **3sa**



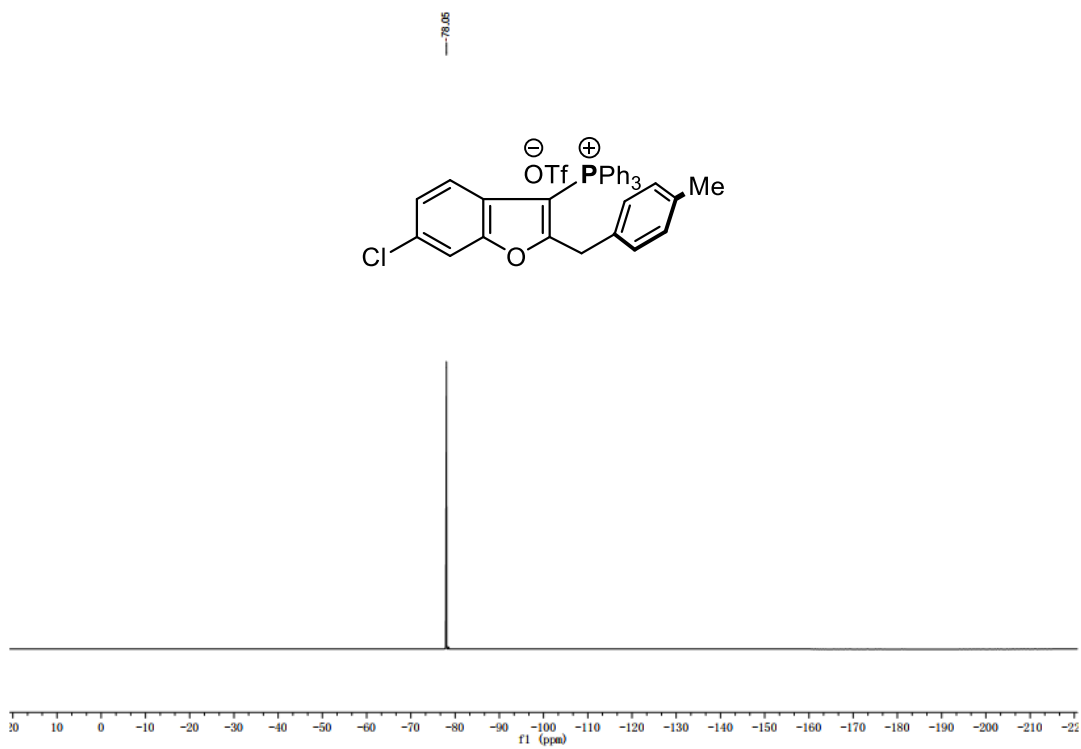
^1H NMR (500 MHz, CDCl_3) of compound **3ta**



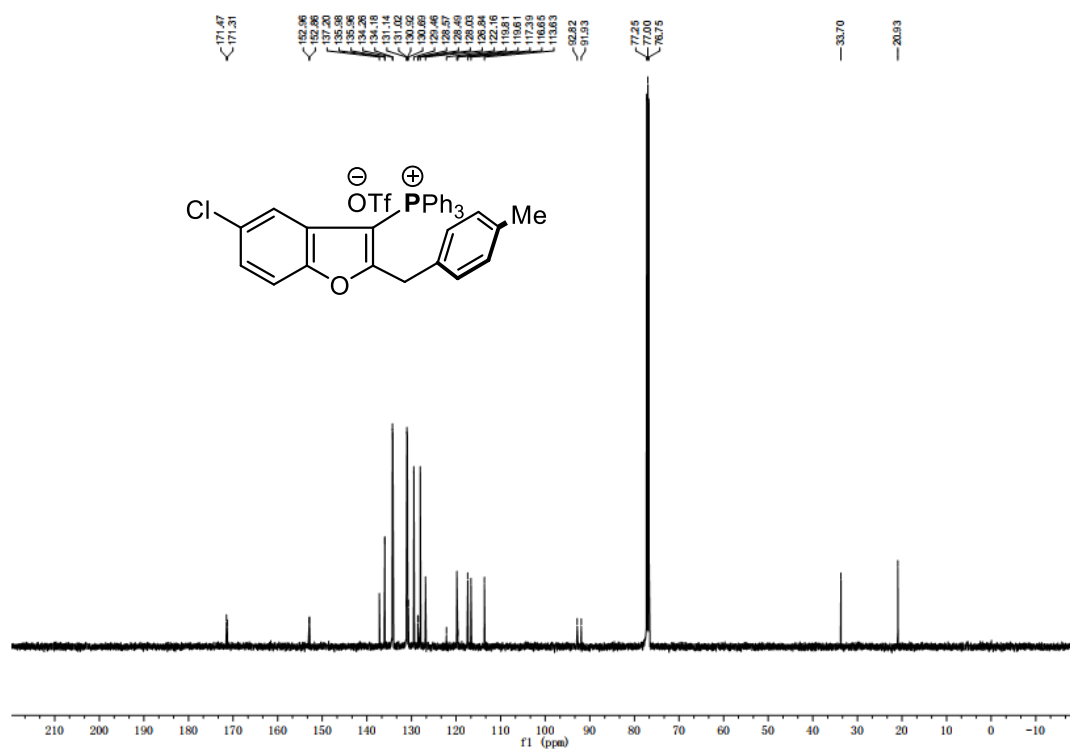
^{13}C NMR (126 MHz, CDCl_3) of compound **3ta**



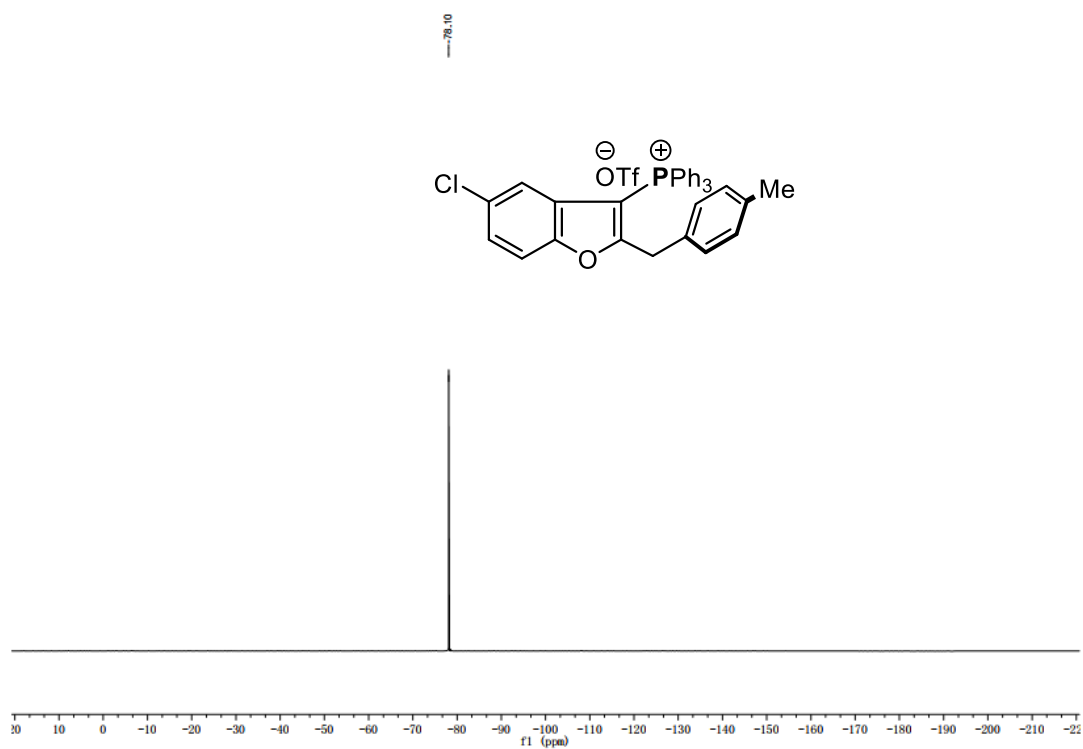
^{19}F NMR (471 MHz, CDCl_3) of compound **3ta**



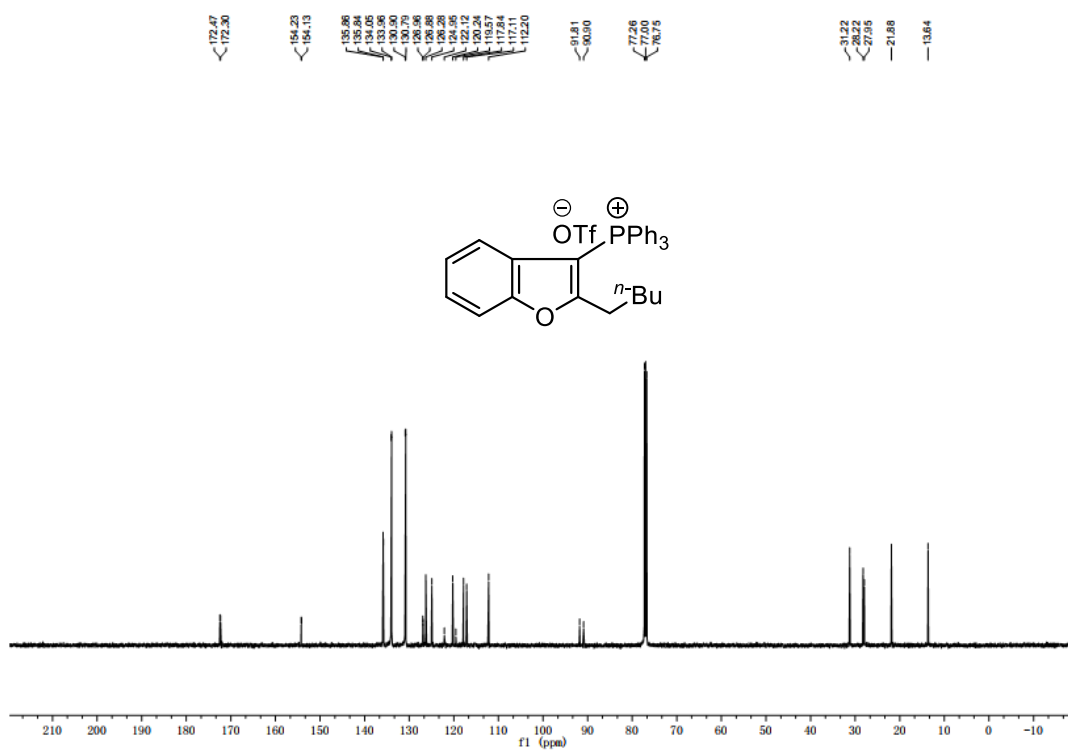
^{13}C NMR (126 MHz, CDCl_3) of compound **3ua**



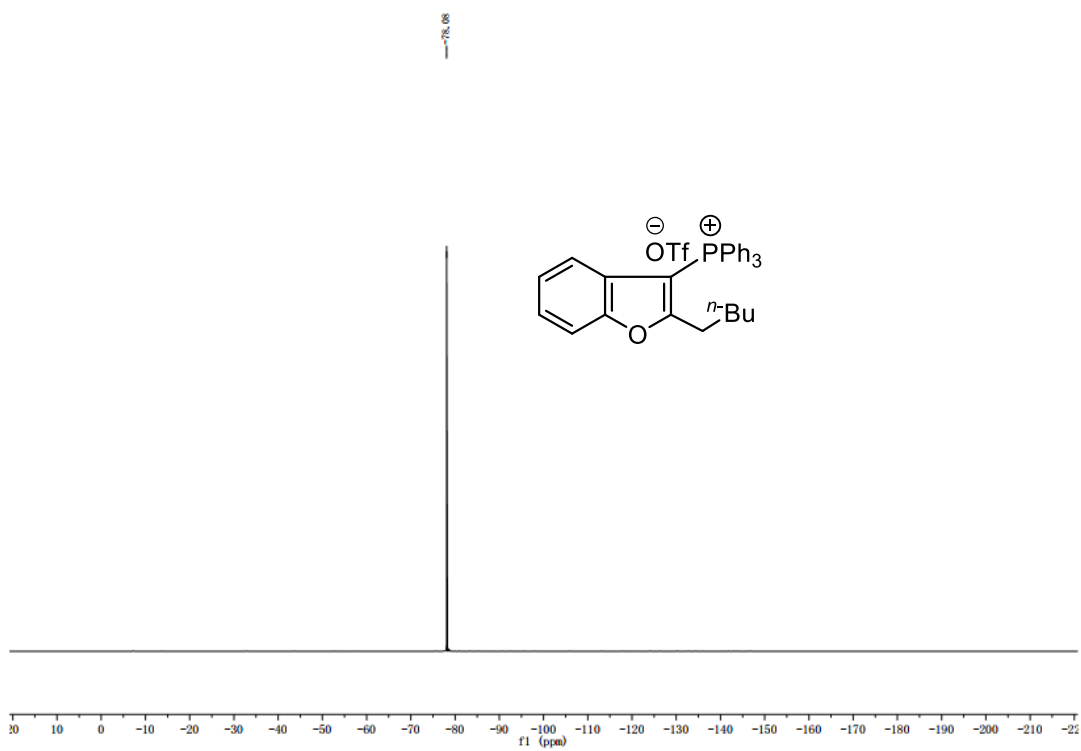
^{19}F NMR (471 MHz, CDCl_3) of compound **3ua**



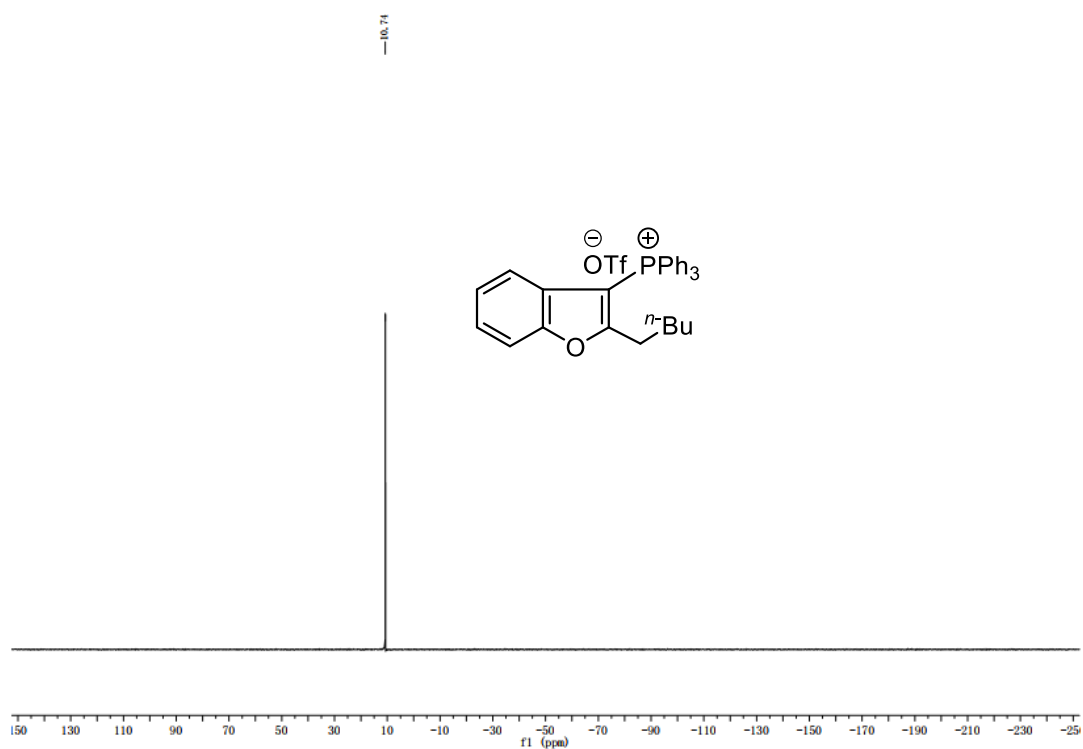
^{13}C NMR (126 MHz, CDCl_3) of compound **3wa**



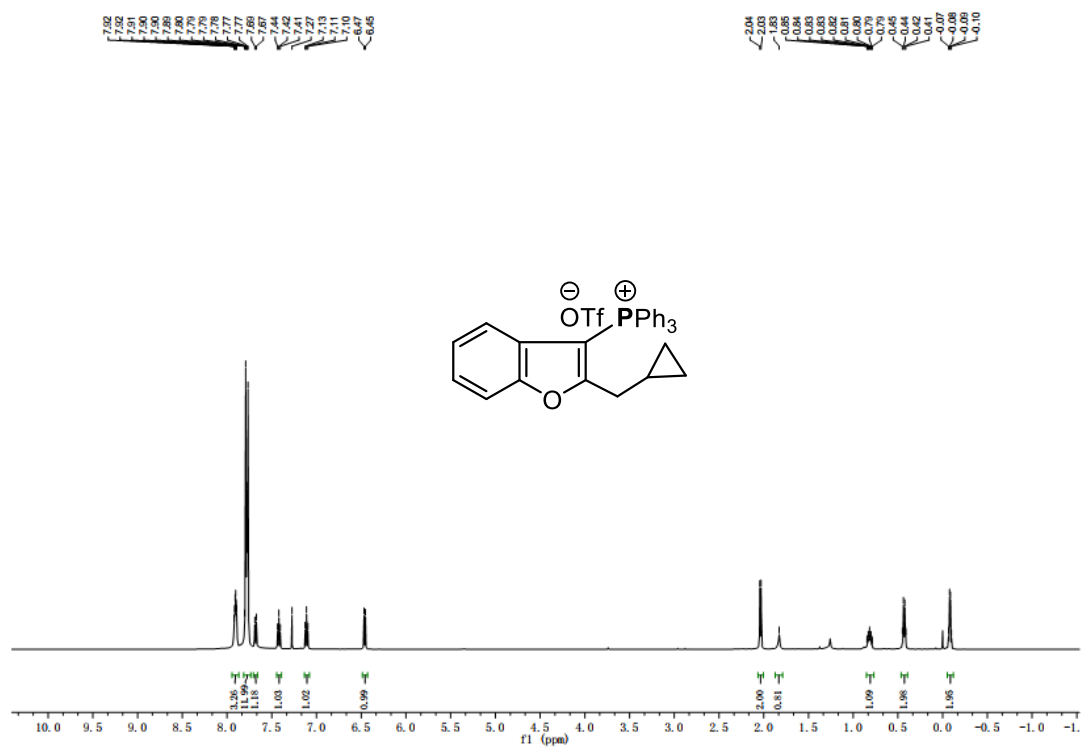
^{19}F NMR (471 MHz, CDCl_3) of compound **3wa**



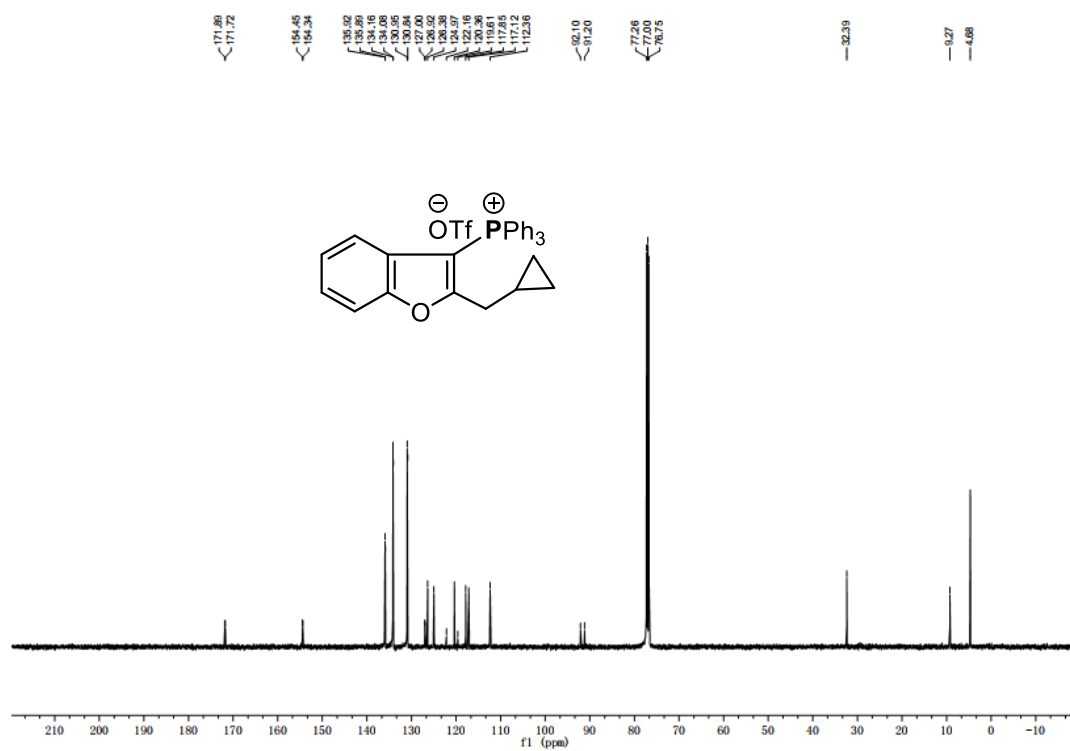
^{31}P NMR (202 MHz, CDCl_3) of compound **3wa**



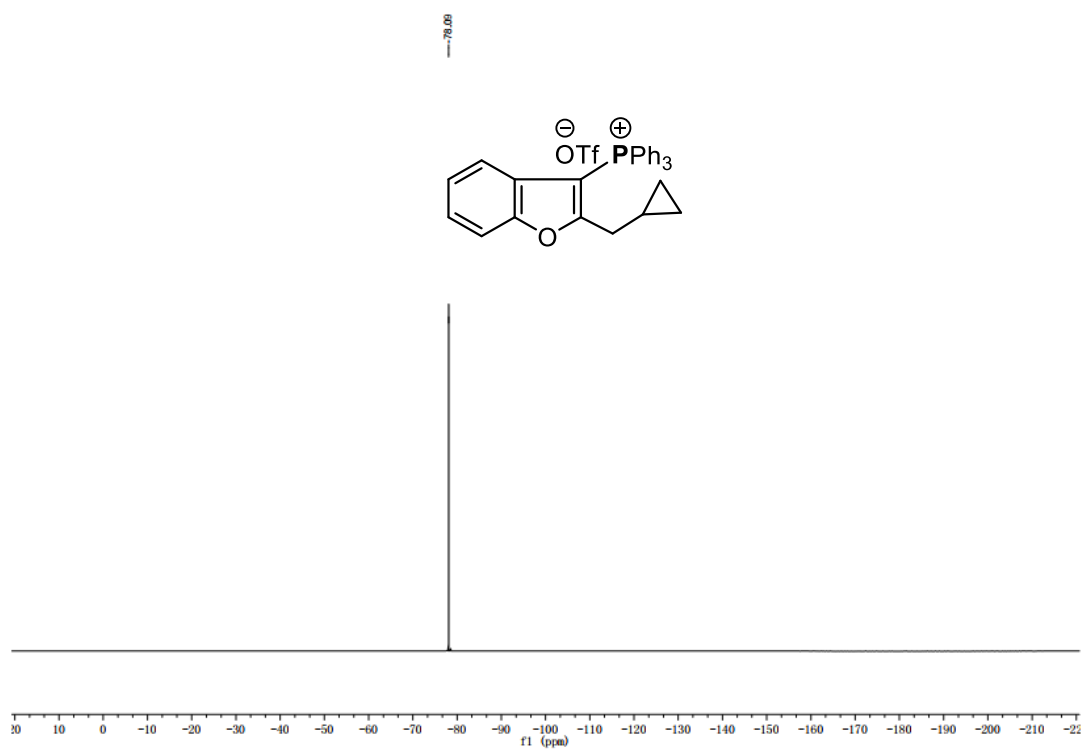
^1H NMR (500 MHz, CDCl_3) of compound **3xa**



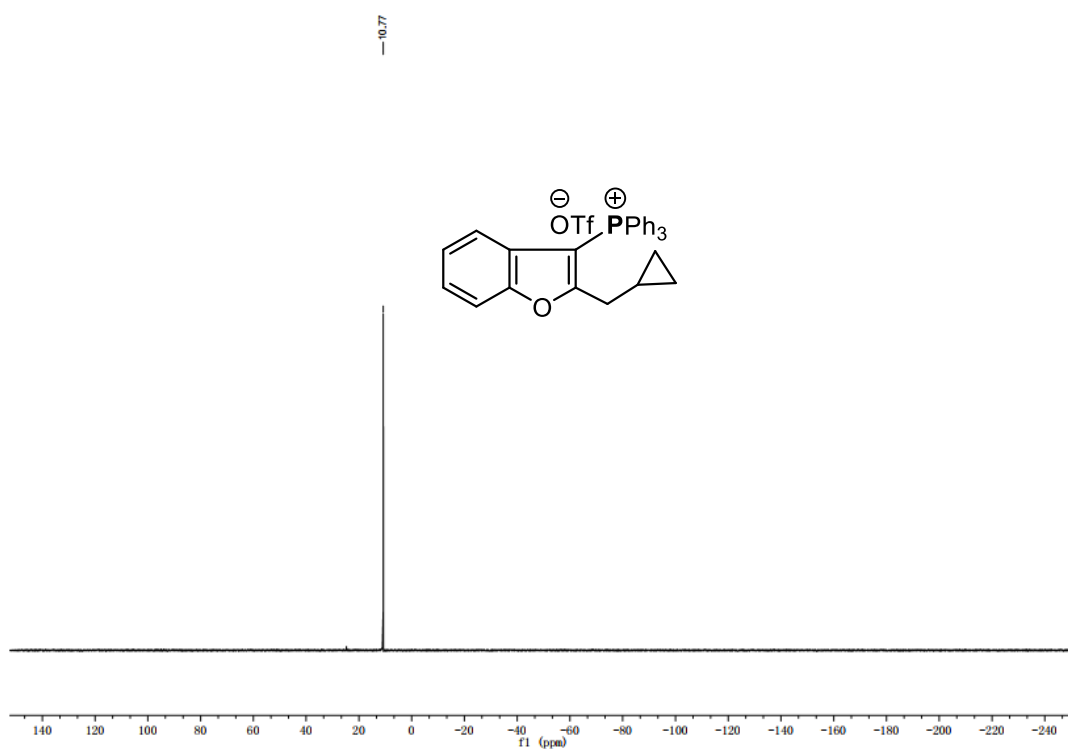
^{13}C NMR (126 MHz, CDCl_3) of compound **3xa**



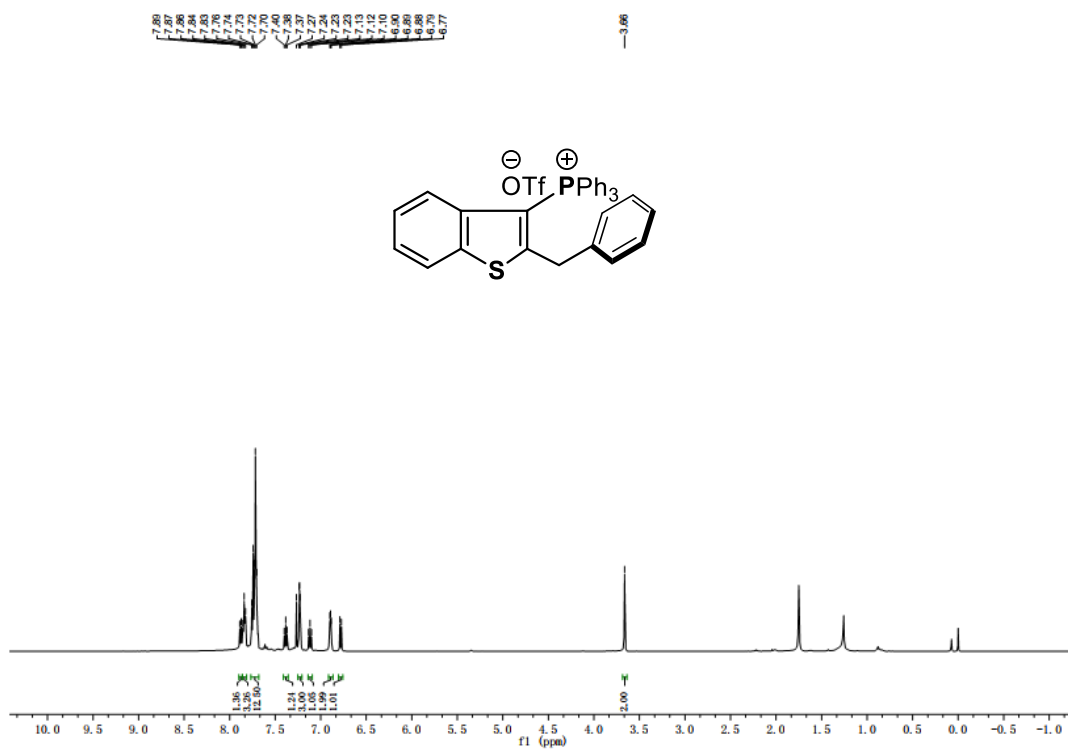
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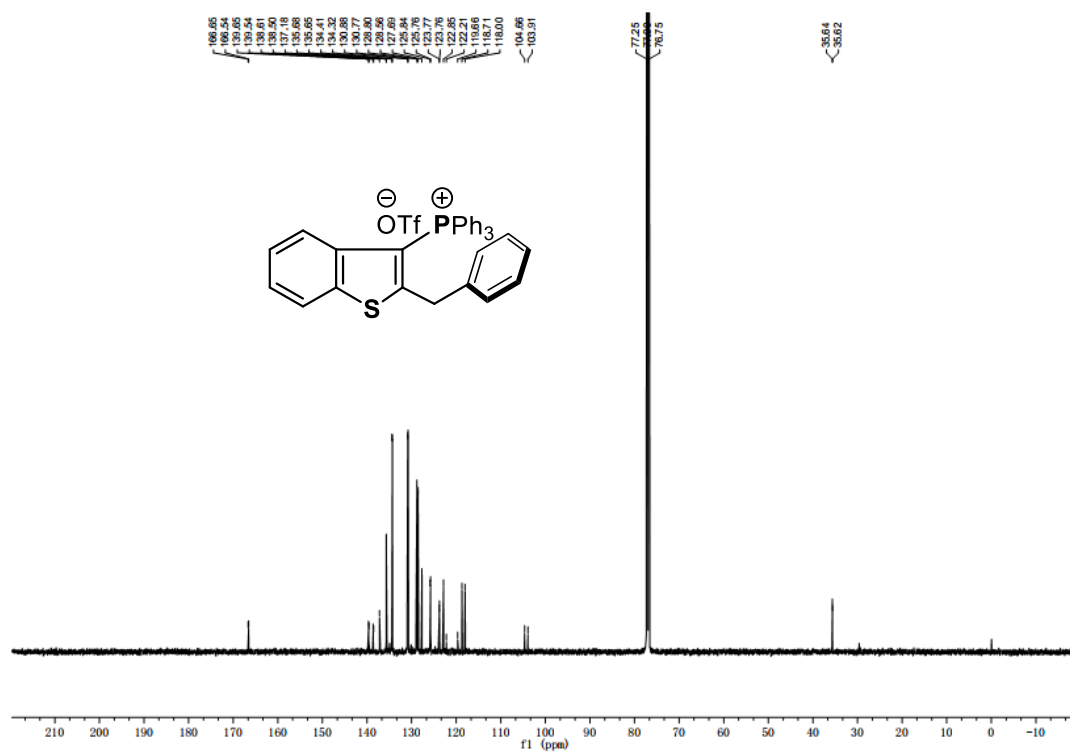
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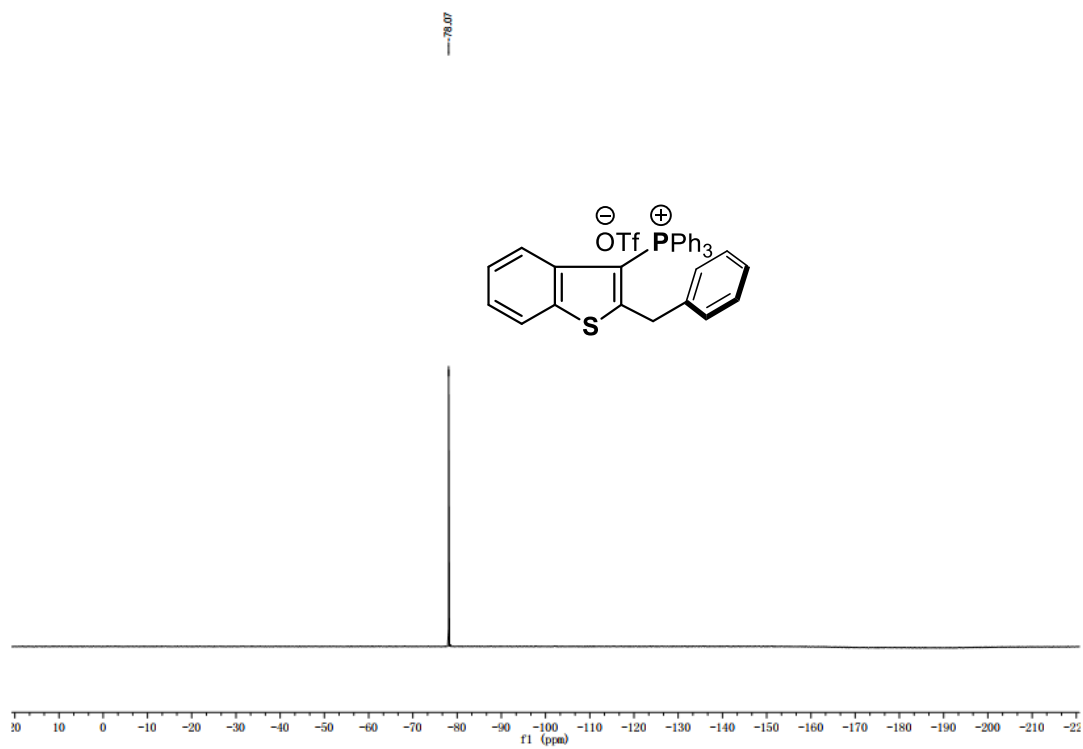
^1H NMR (500 MHz, CDCl_3) of compound **3ya**



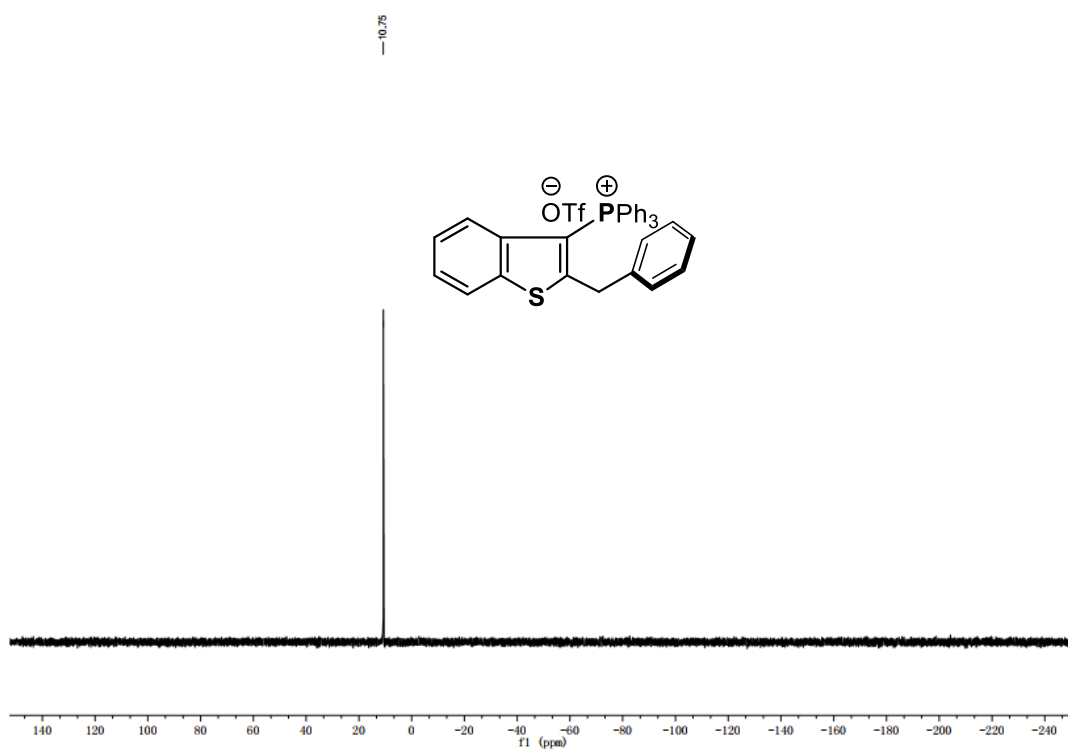
^{13}C NMR (126 MHz, CDCl_3) of compound **3ya**



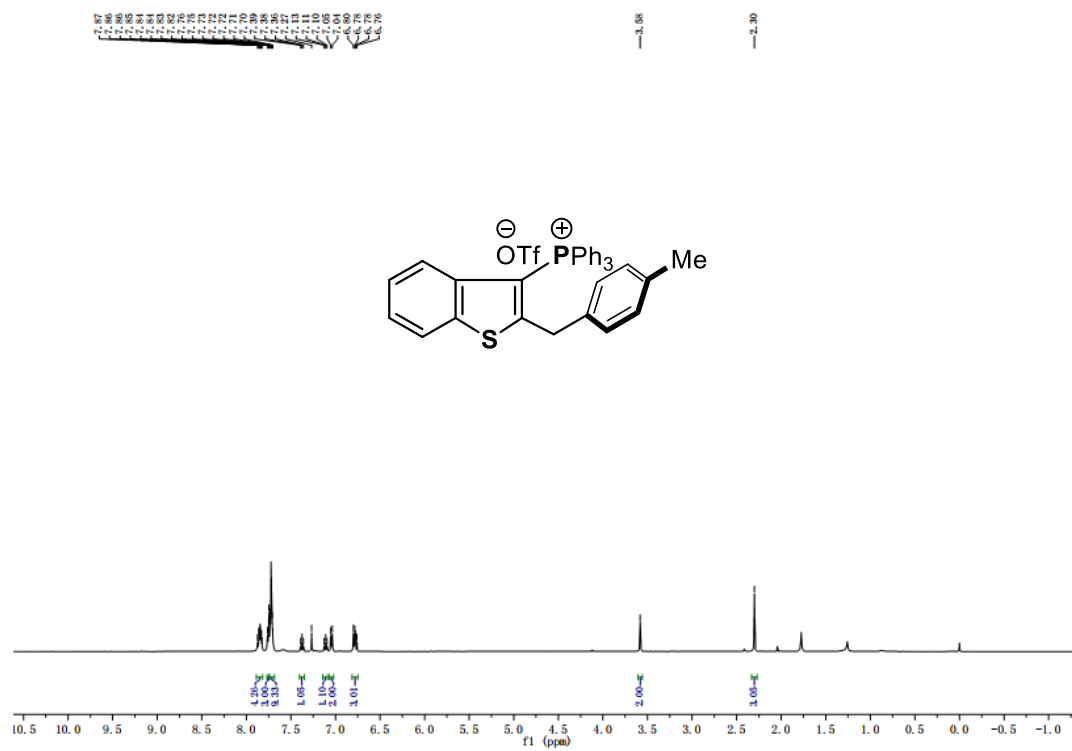
^{19}F NMR (471 MHz, CDCl_3) of compound **3ya**



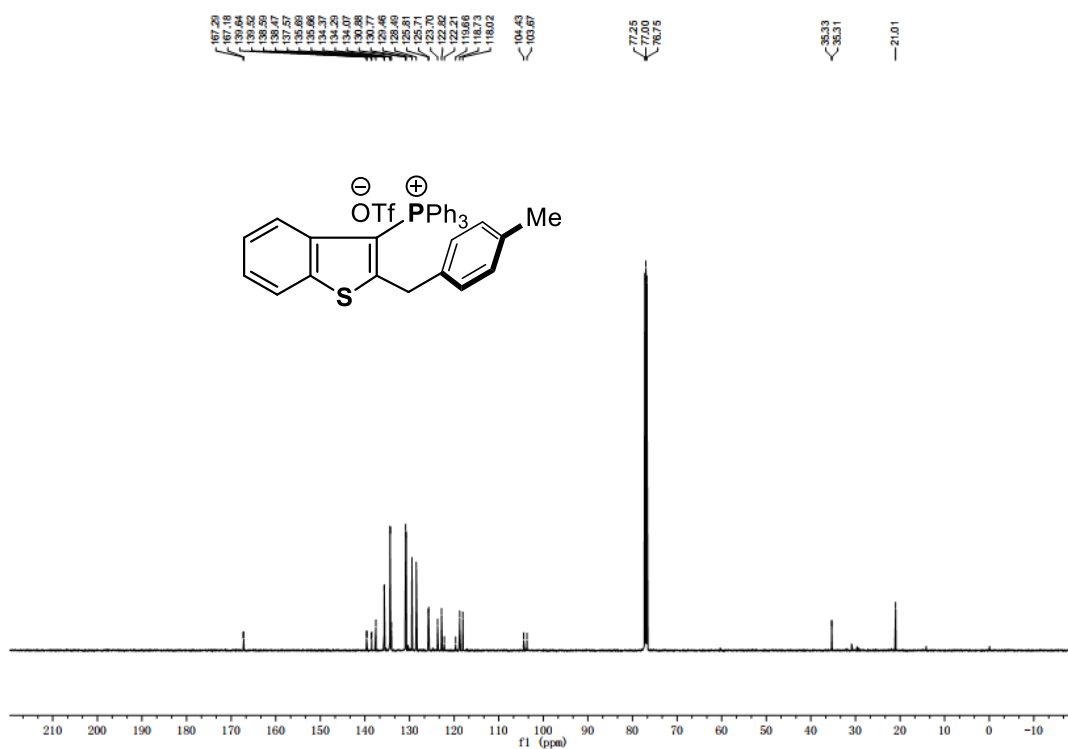
^{31}P NMR (202 MHz, CDCl_3) of compound **3ya**



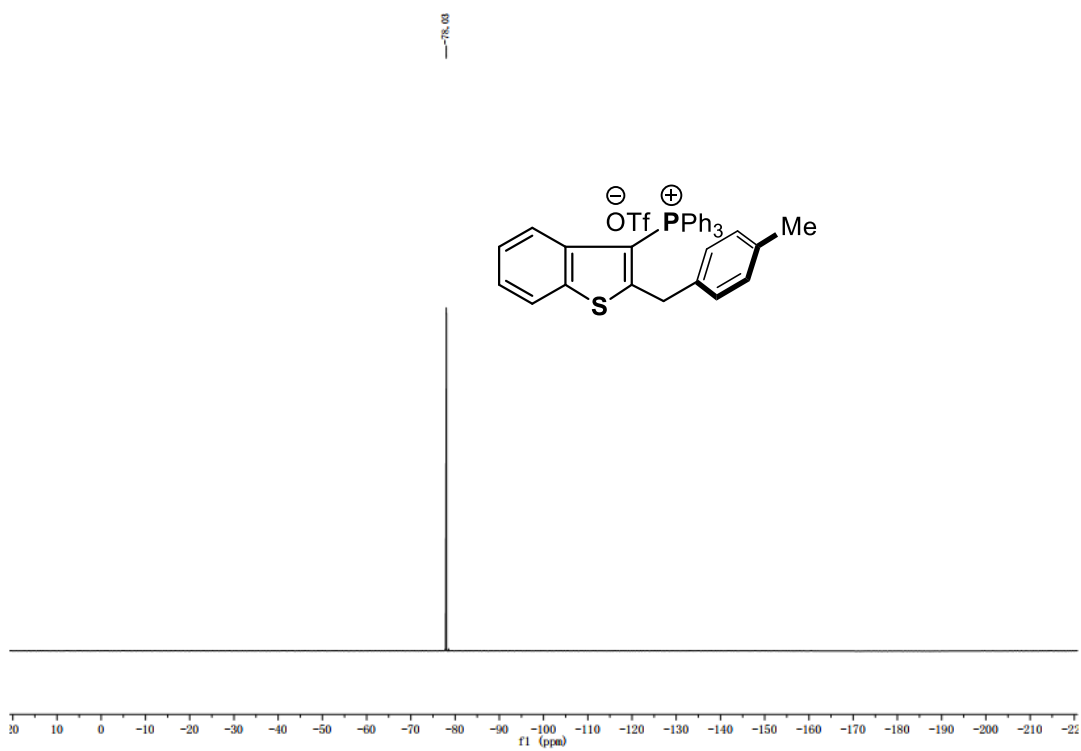
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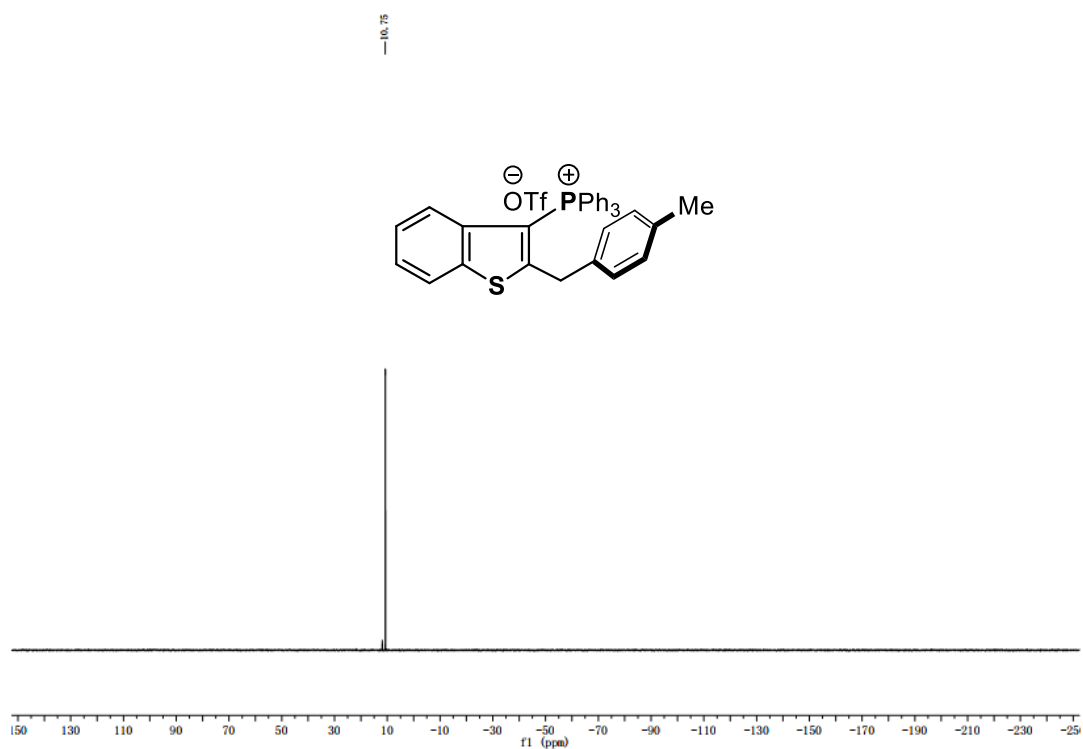
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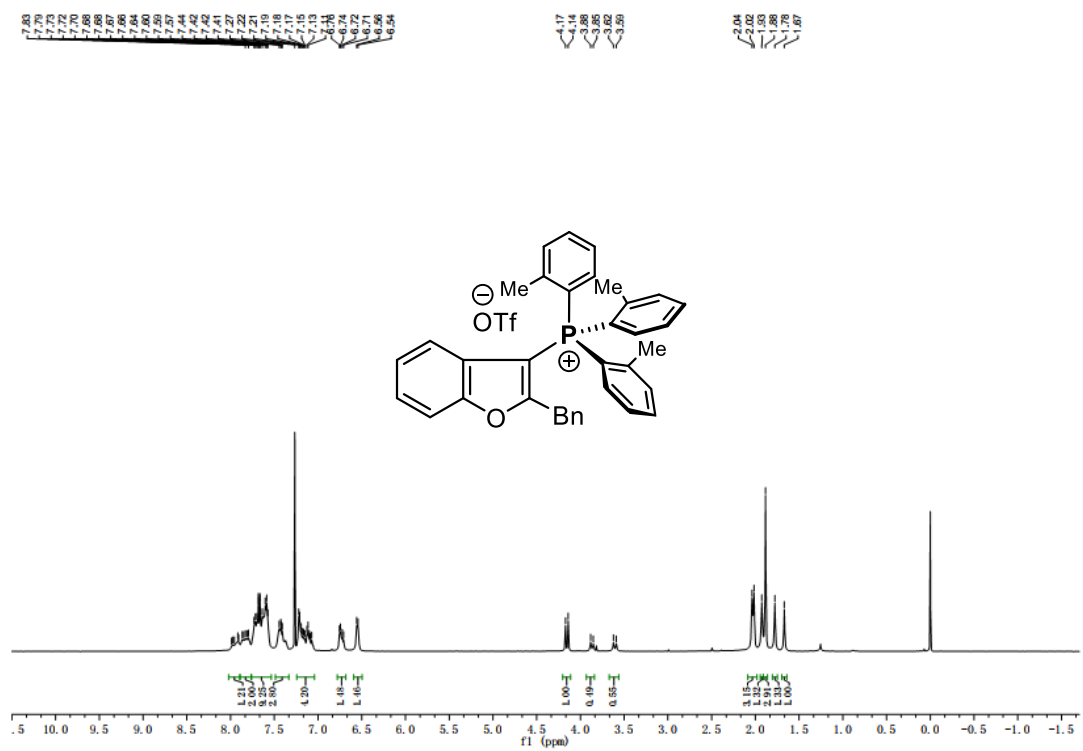
^{19}F NMR (471 MHz, CDCl_3) of compound **3za**



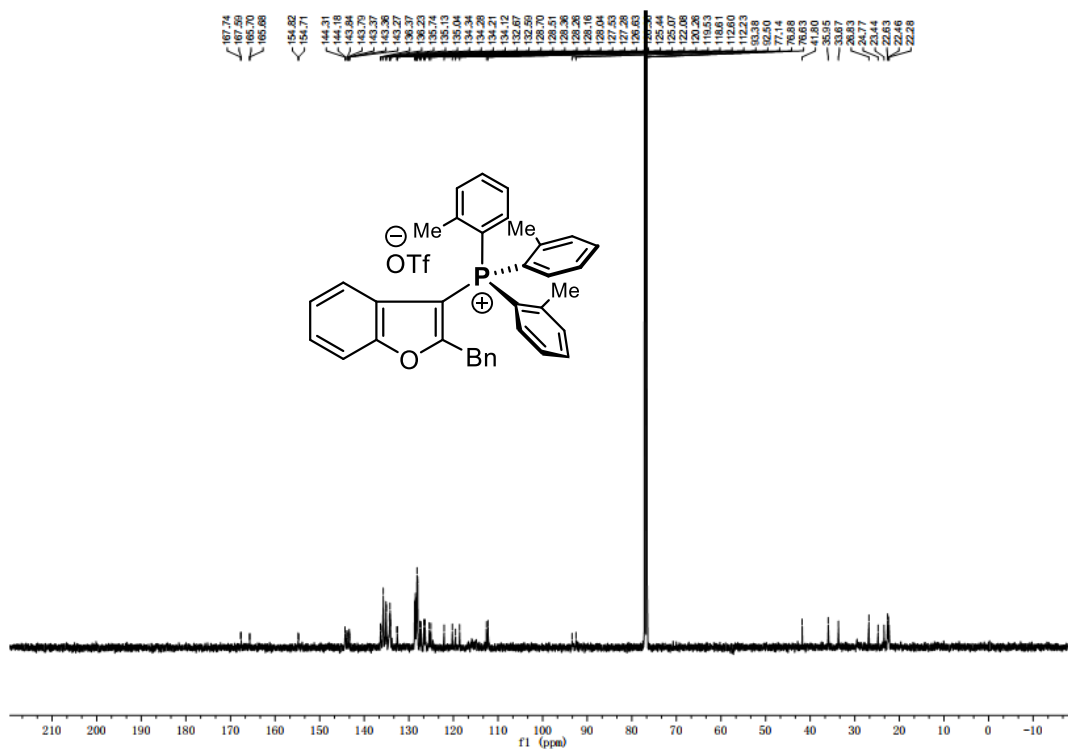
^{31}P NMR (202 MHz, CDCl_3) of compound **3za**



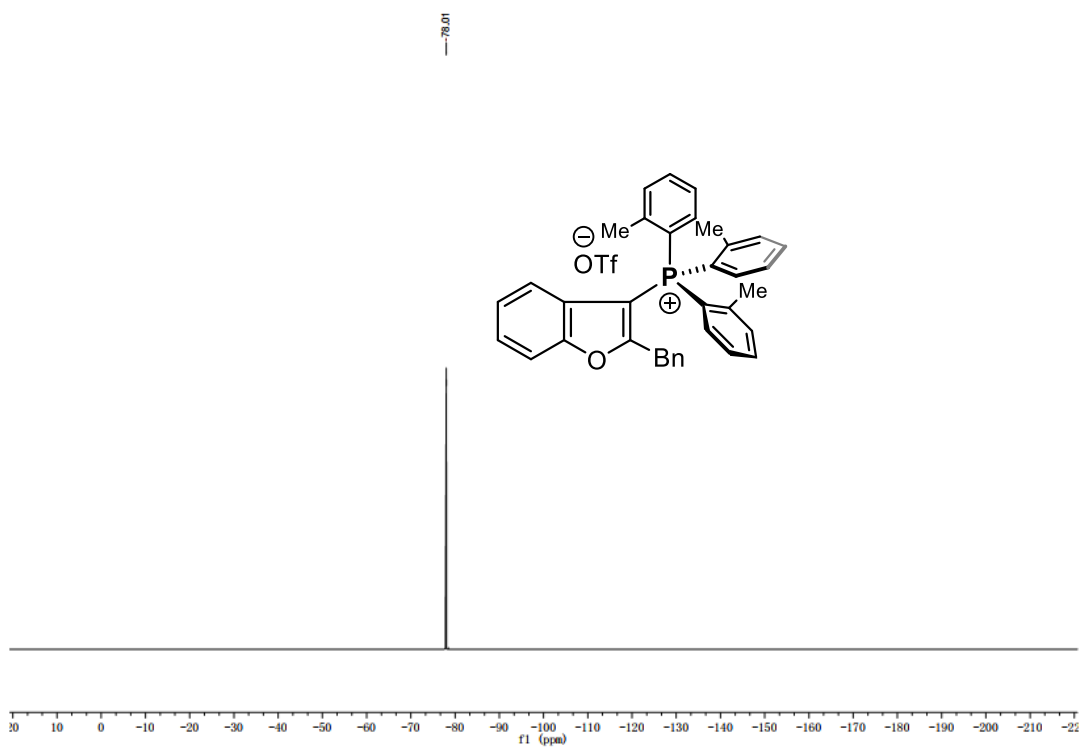
^1H NMR (500 MHz, CDCl_3) of compound **3ab**



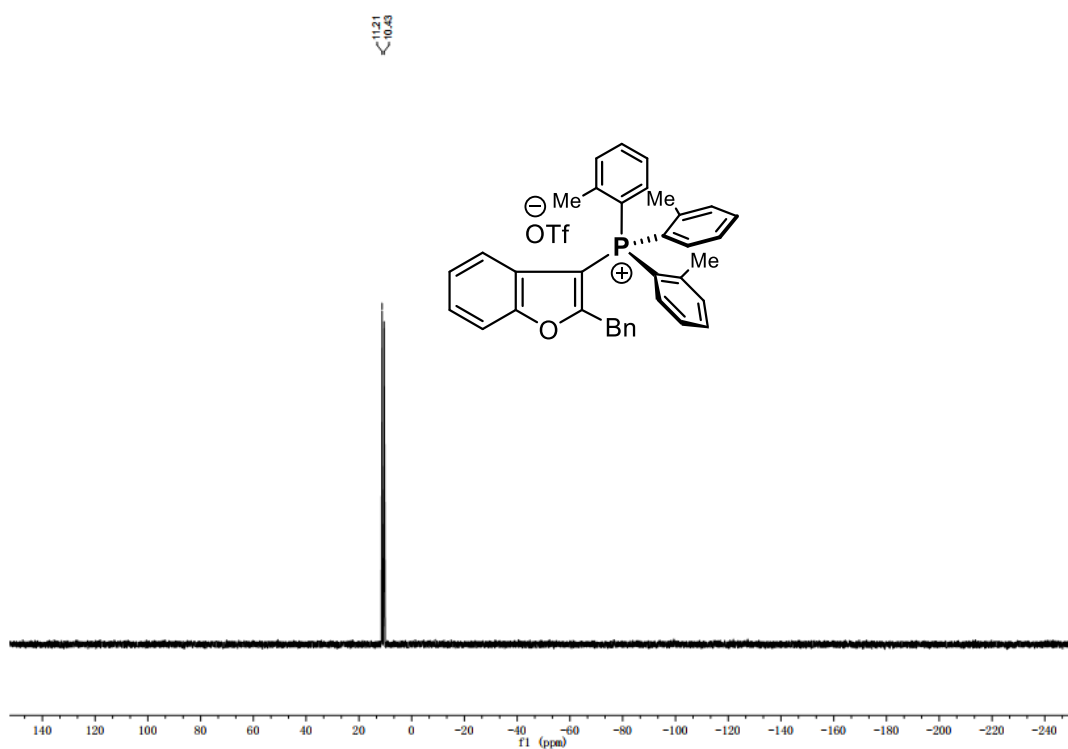
^{13}C NMR (126 MHz, CDCl_3) of compound **3ab**



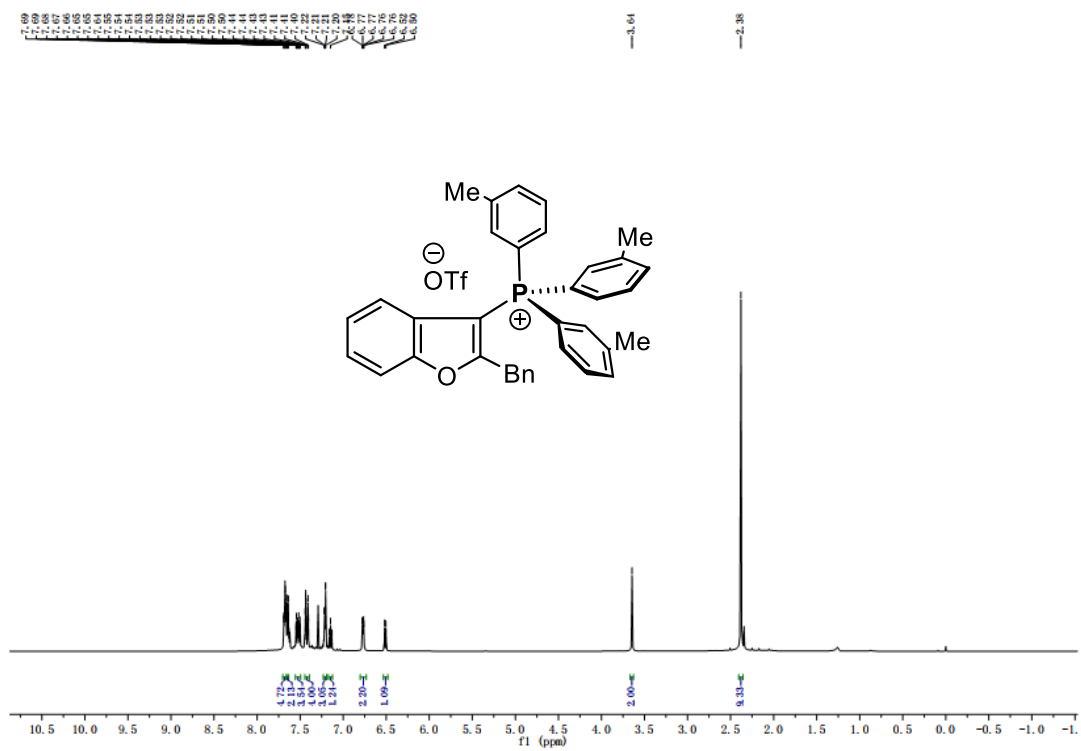
^{19}F NMR (471 MHz, CDCl_3) of compound **3ab**



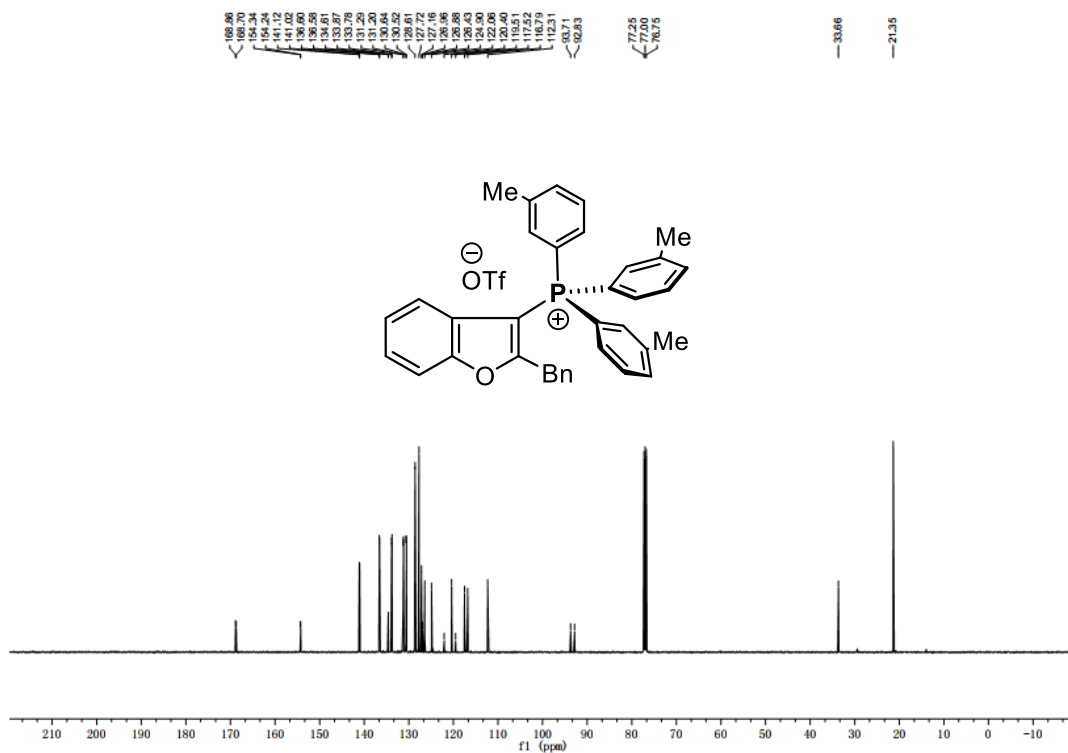
^{31}P NMR (202 MHz, CDCl_3) of compound **3ab**



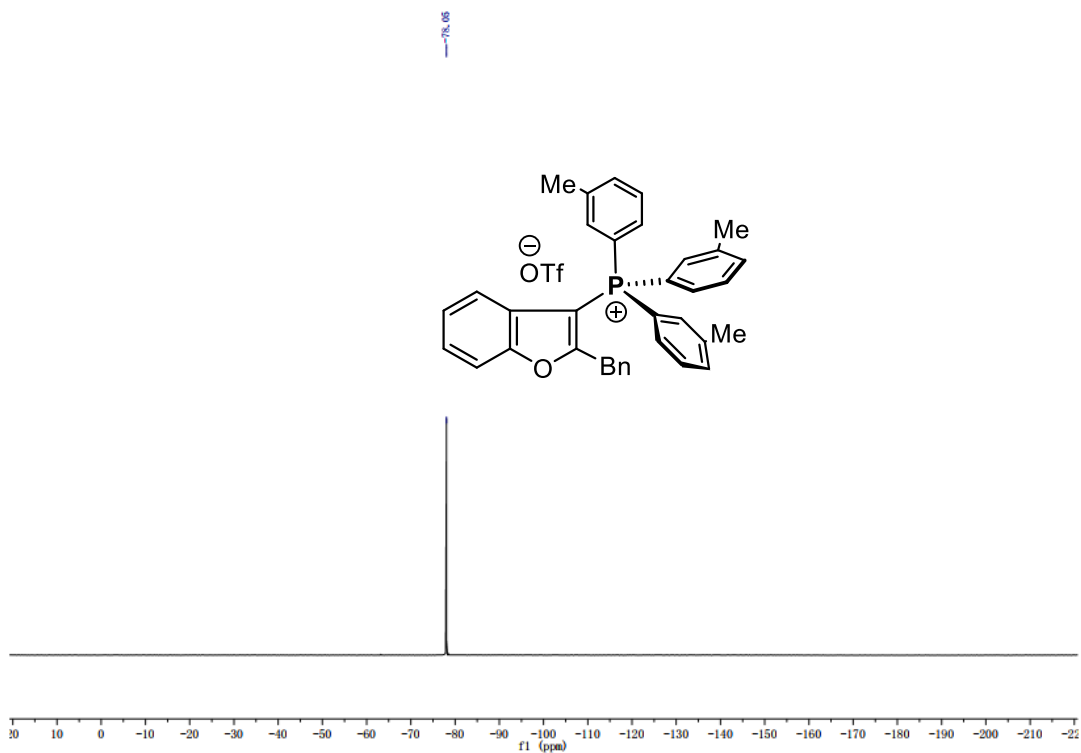
^1H NMR (500 MHz, CDCl_3) of compound **3ac**



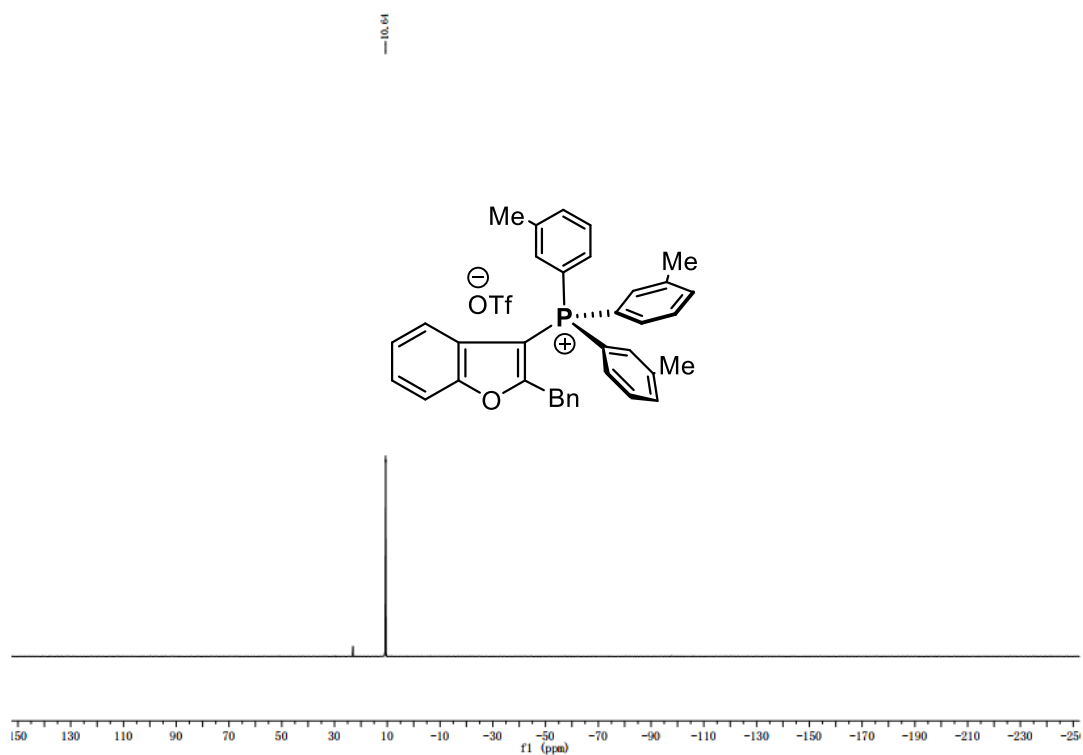
^{13}C NMR (126 MHz, CDCl_3) of compound **3ac**



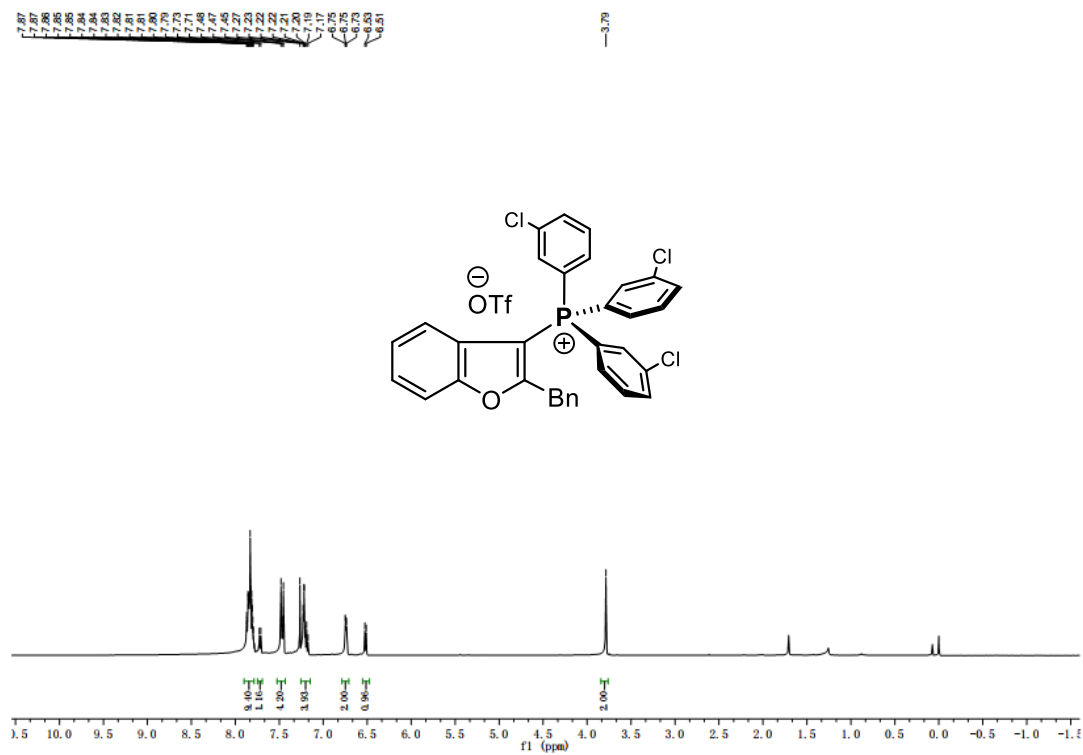
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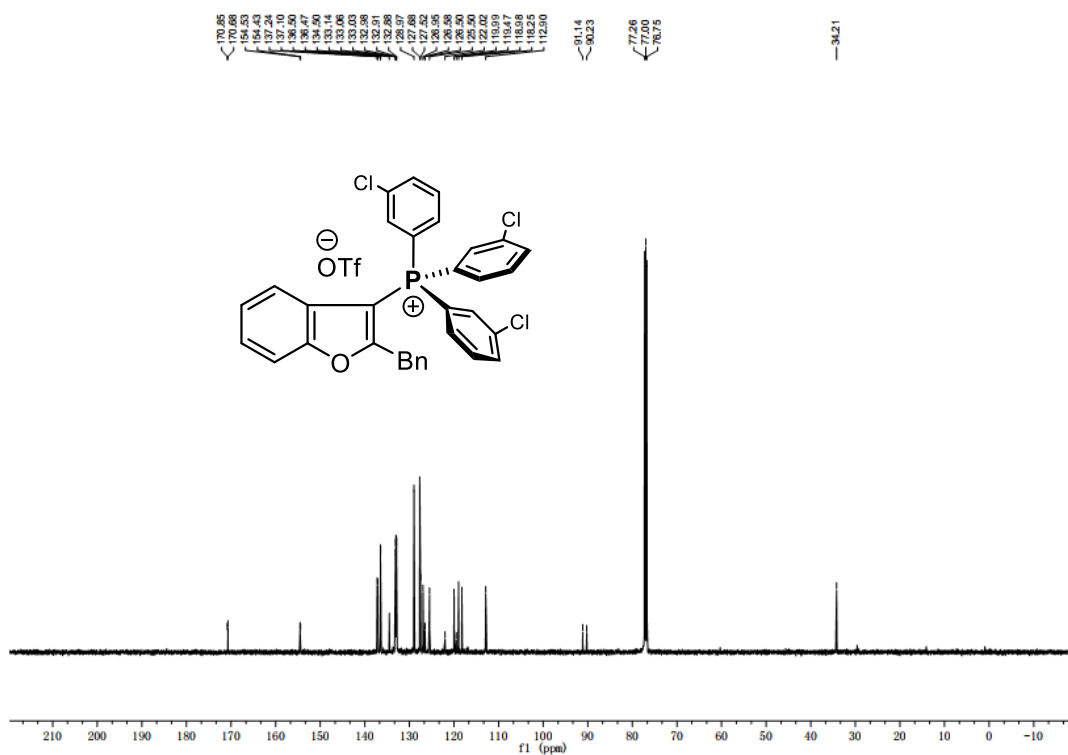
^{31}P NMR (202 MHz, CDCl_3) of compound **3ac**



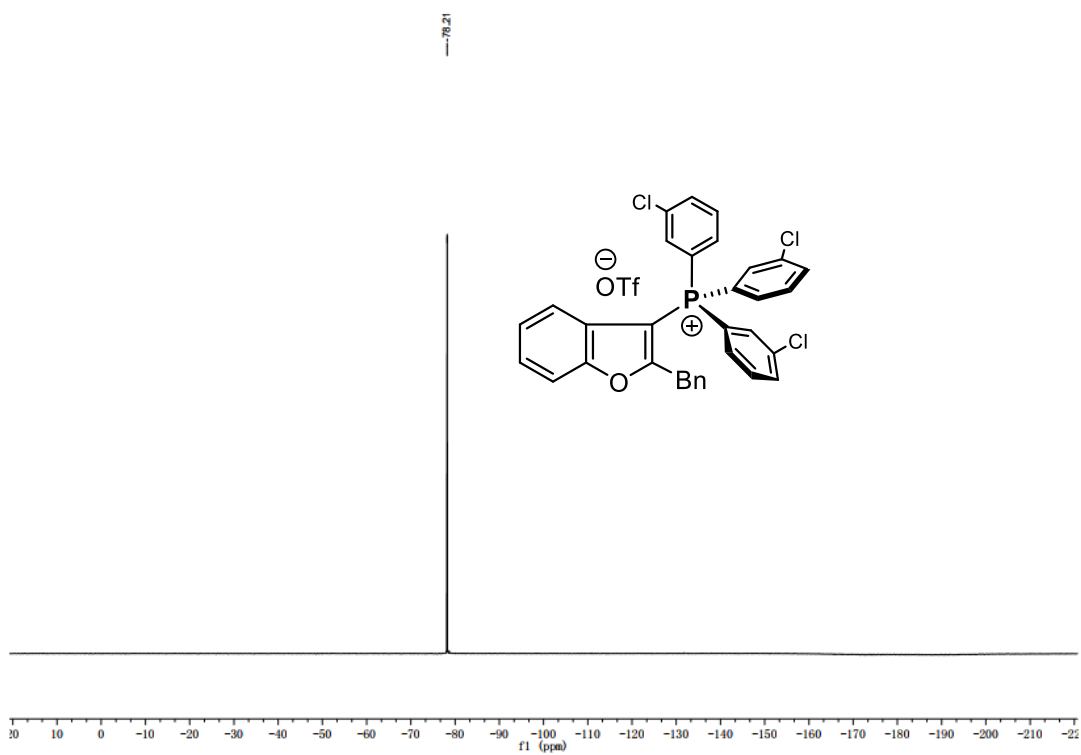
^1H NMR (500 MHz, CDCl_3) of compound **3ad**



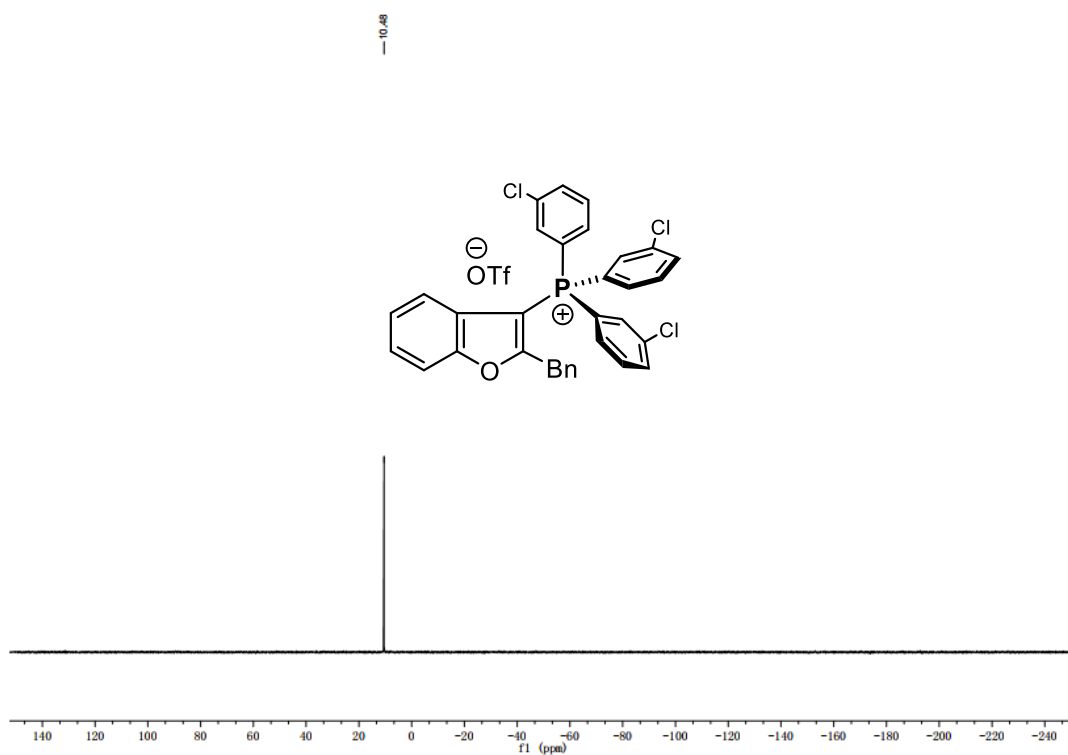
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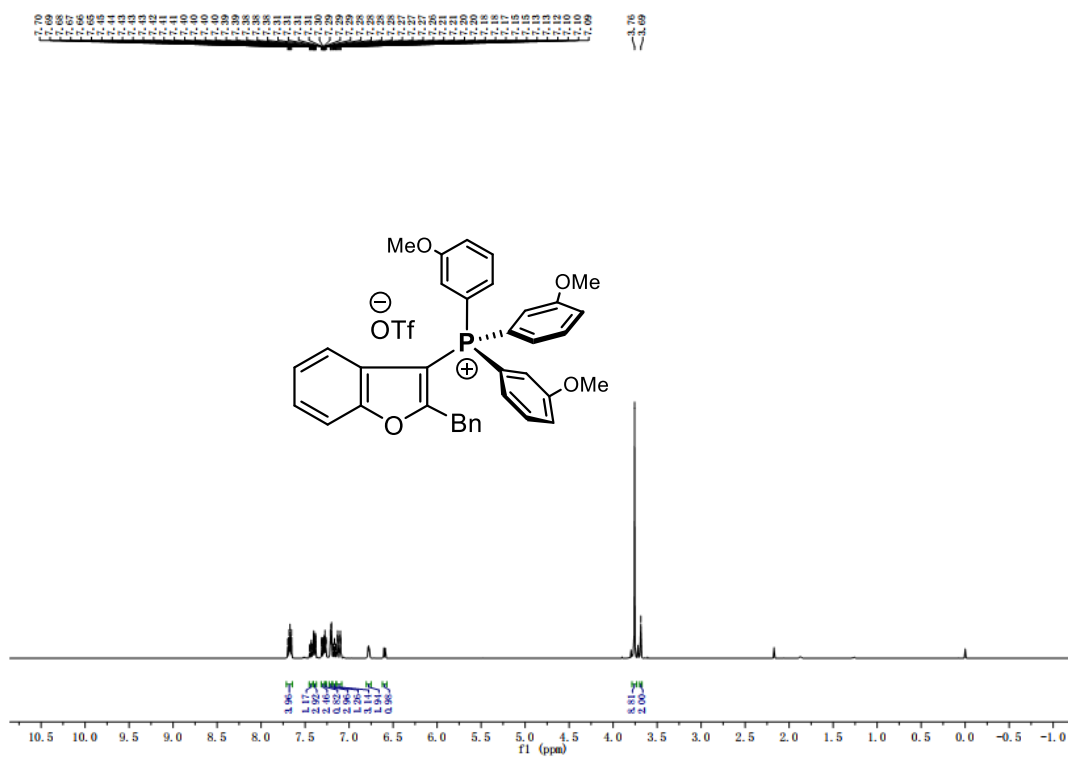
^{19}F NMR (471 MHz, CDCl_3) of compound **3ad**



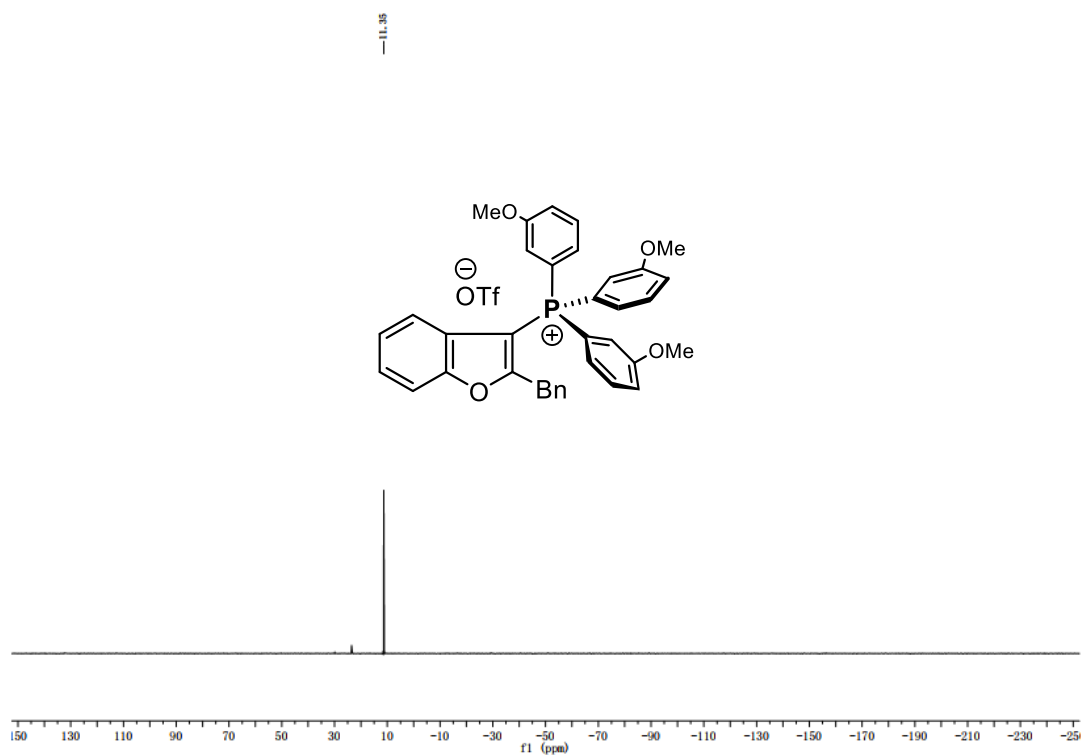
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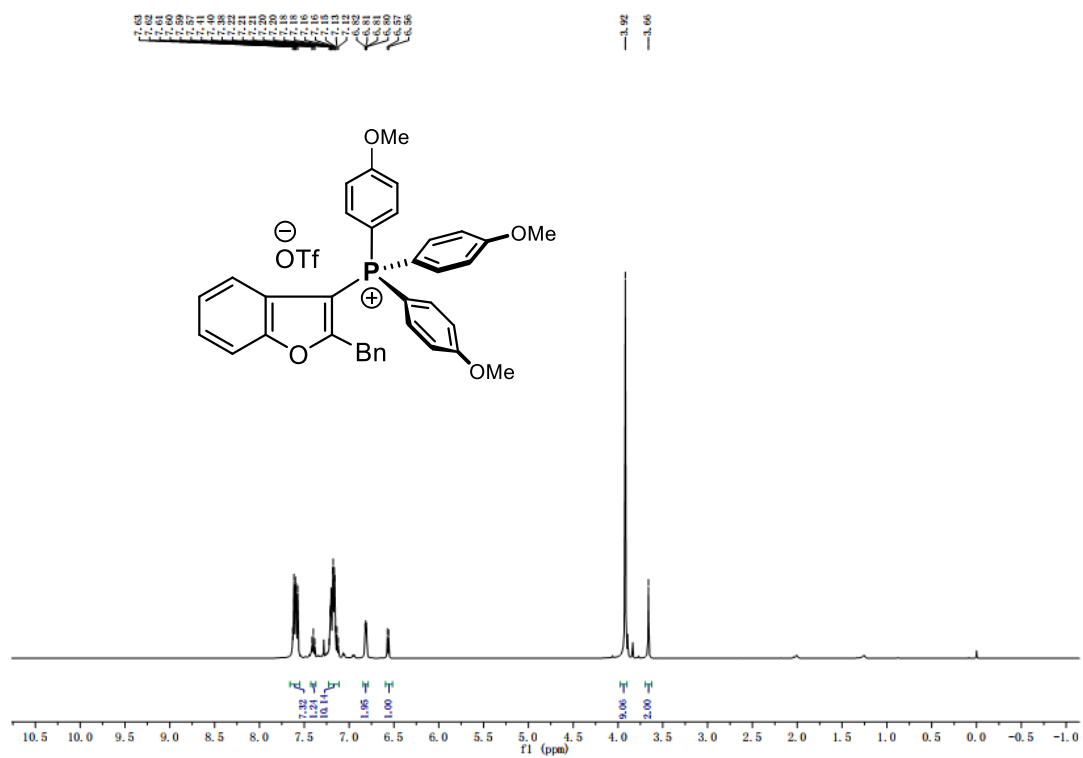
^1H NMR (500 MHz, CDCl_3) of compound **3ae**



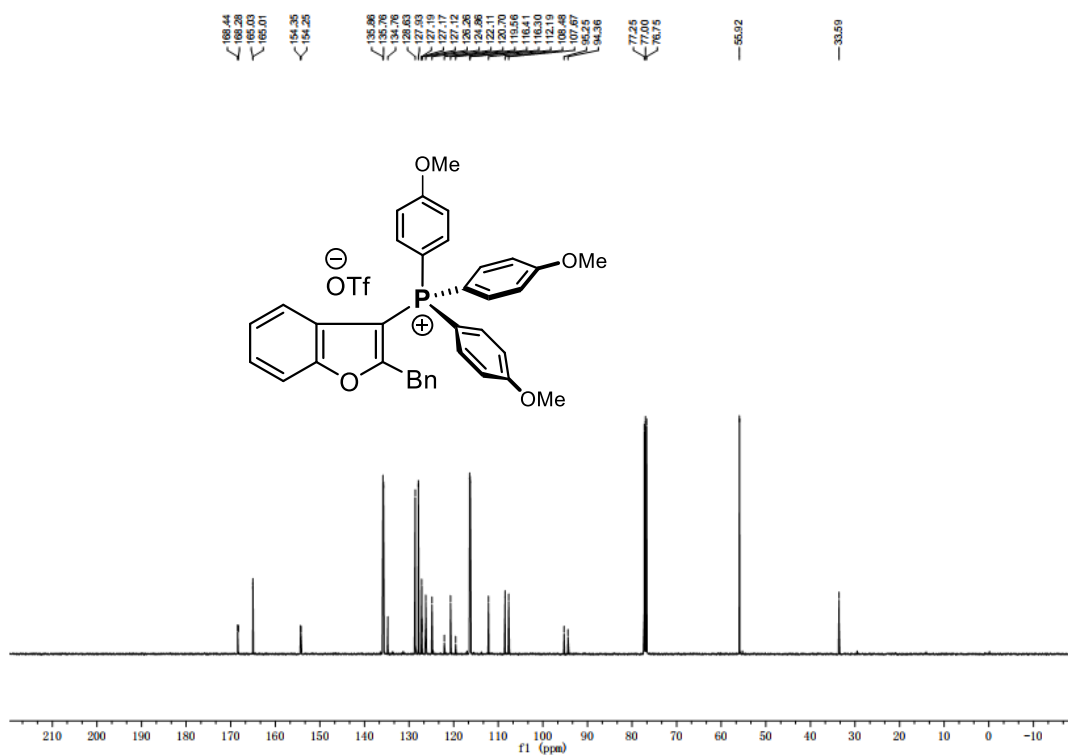
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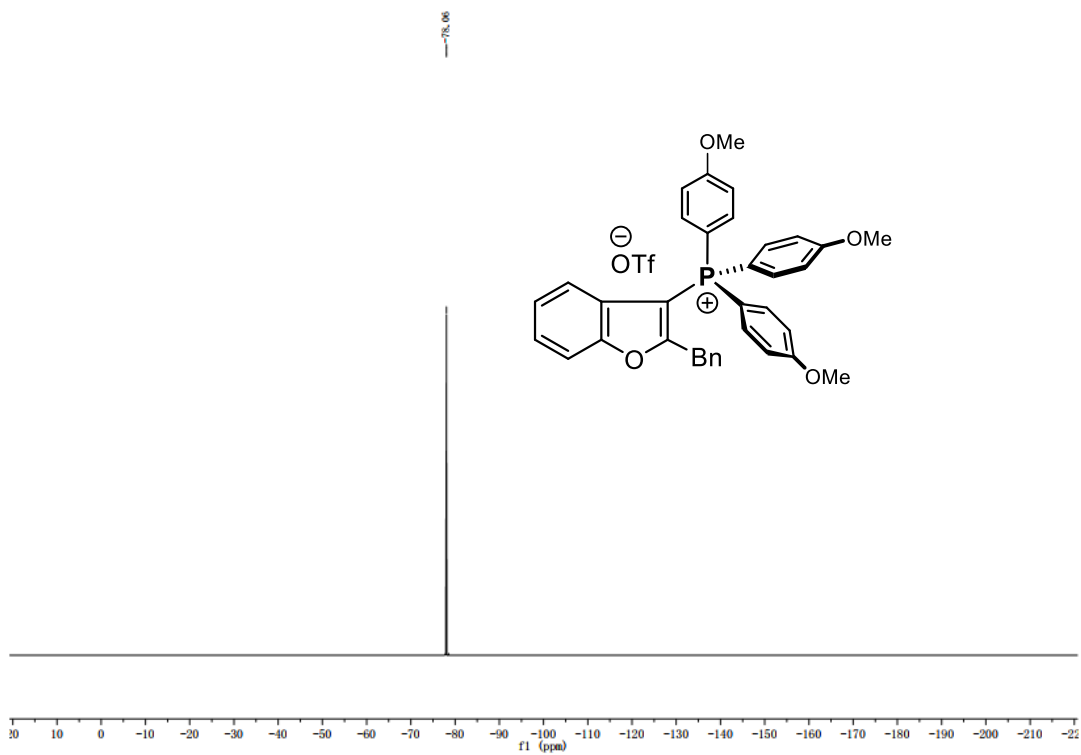
^1H NMR (500 MHz, CDCl_3) of compound **3af**



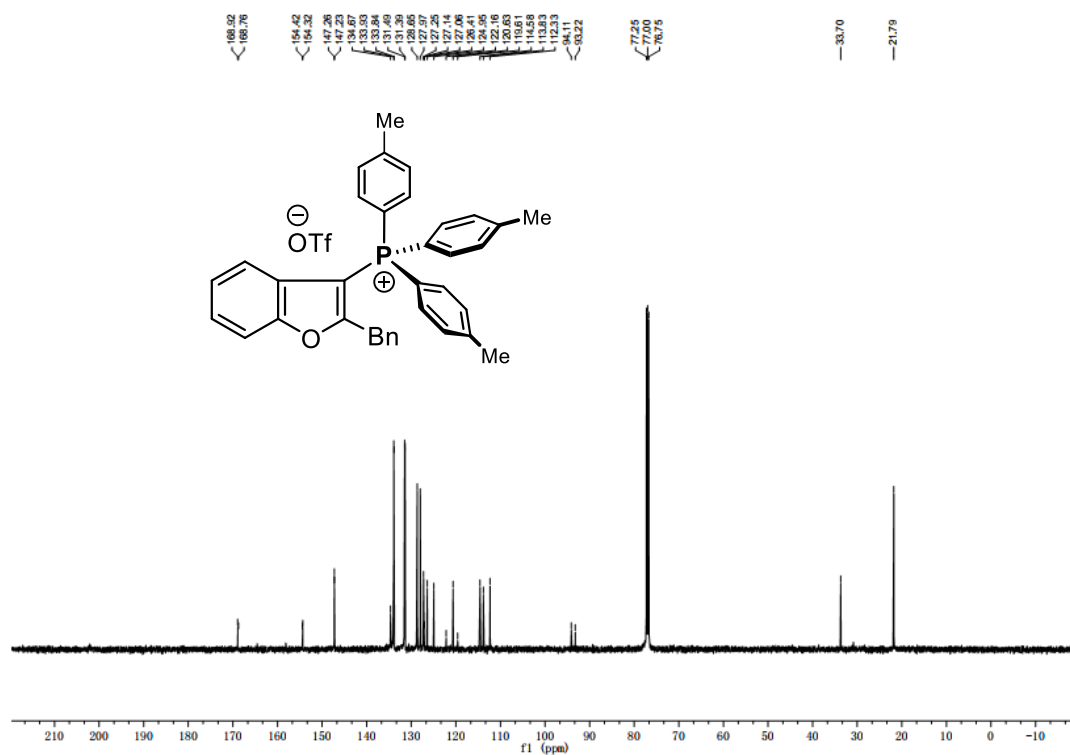
^{13}C NMR (126 MHz, CDCl_3) of compound **3af**



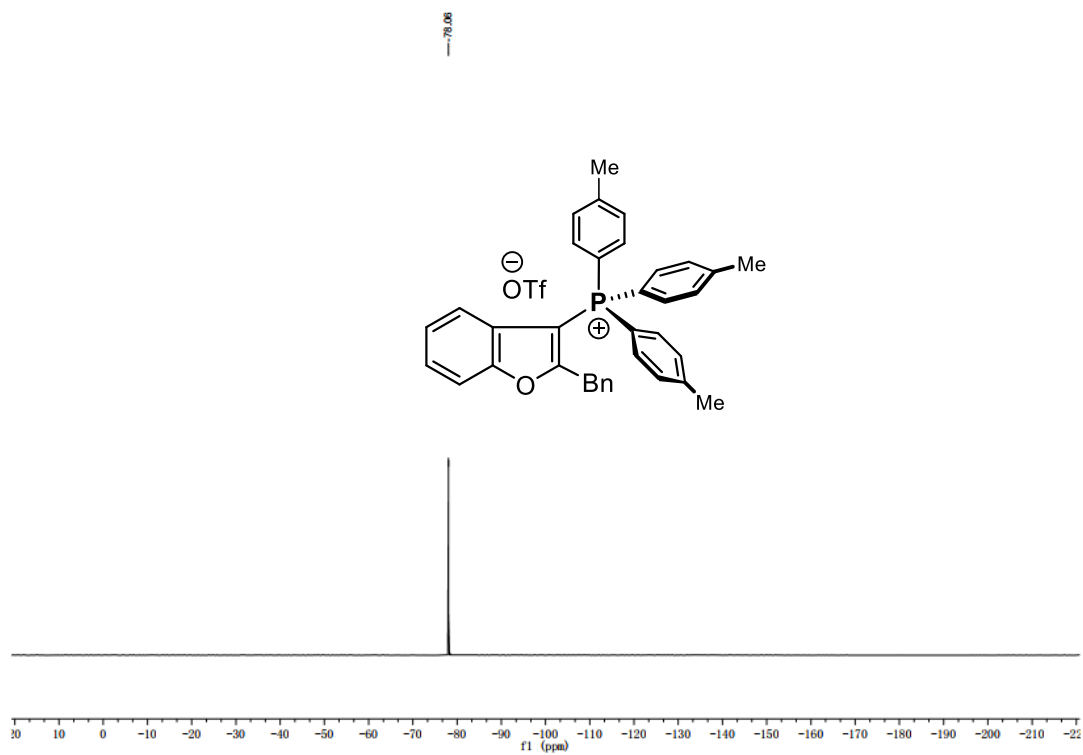
^{19}F NMR (471 MHz, CDCl_3) of compound **3af**



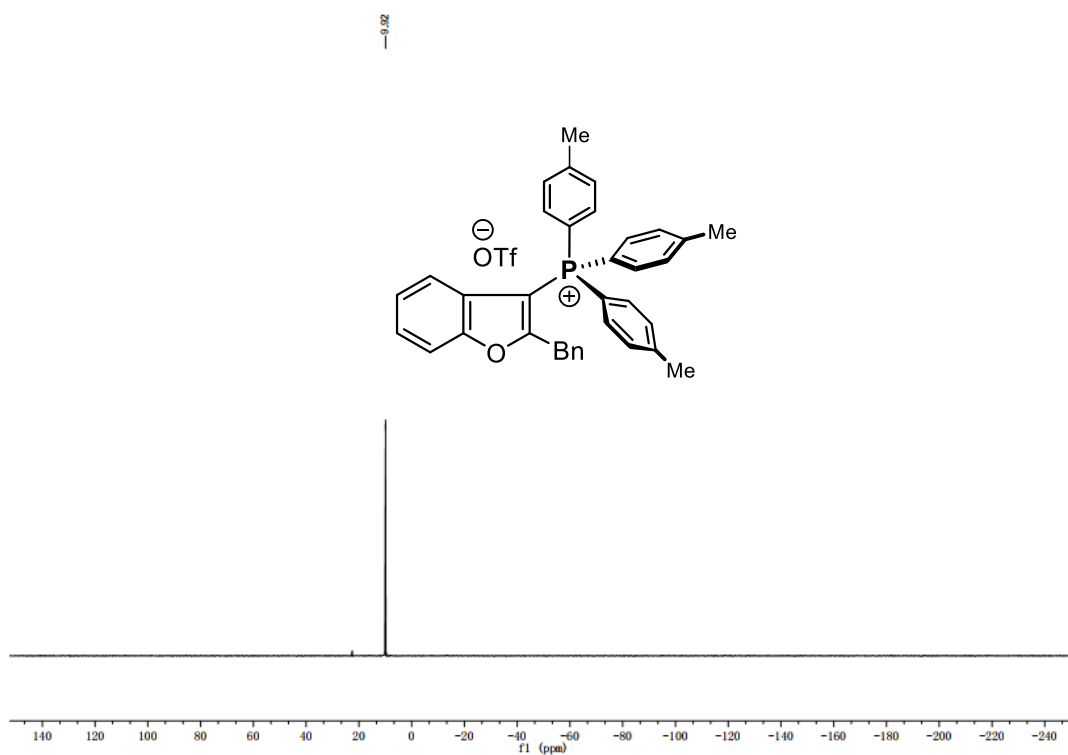
^{13}C NMR (126 MHz, CDCl_3) of compound **3ag**



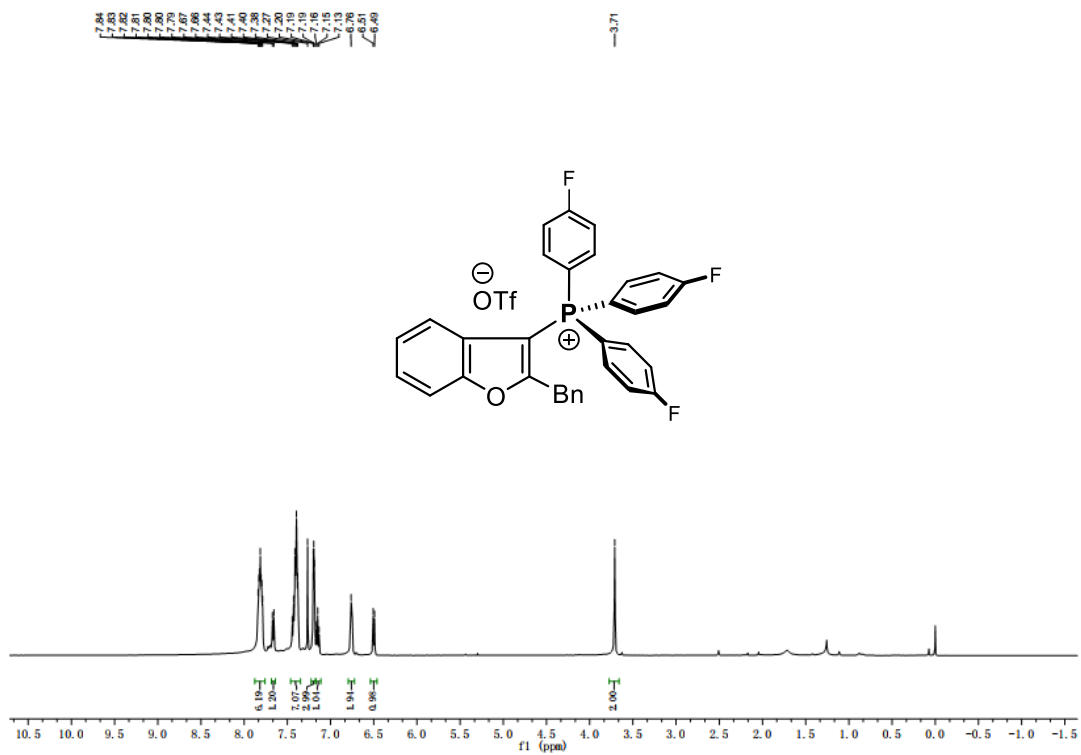
^{19}F NMR (471 MHz, CDCl_3) of compound **3ag**



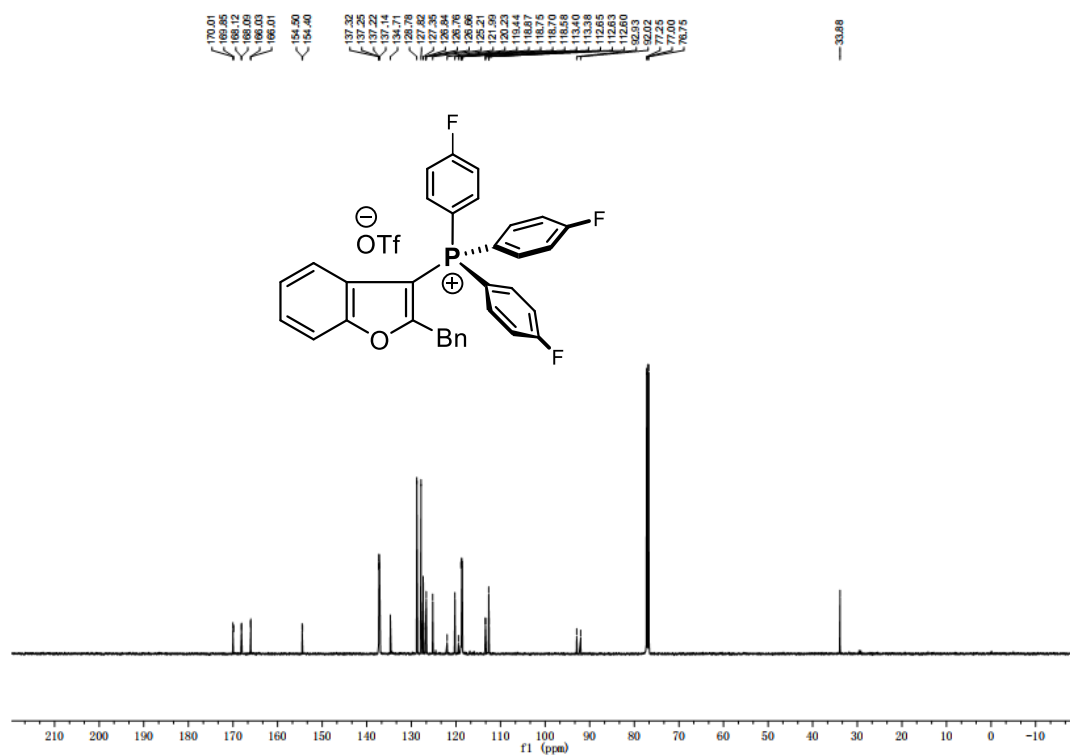
^{31}P NMR (202 MHz, CDCl_3) of compound **3ag**



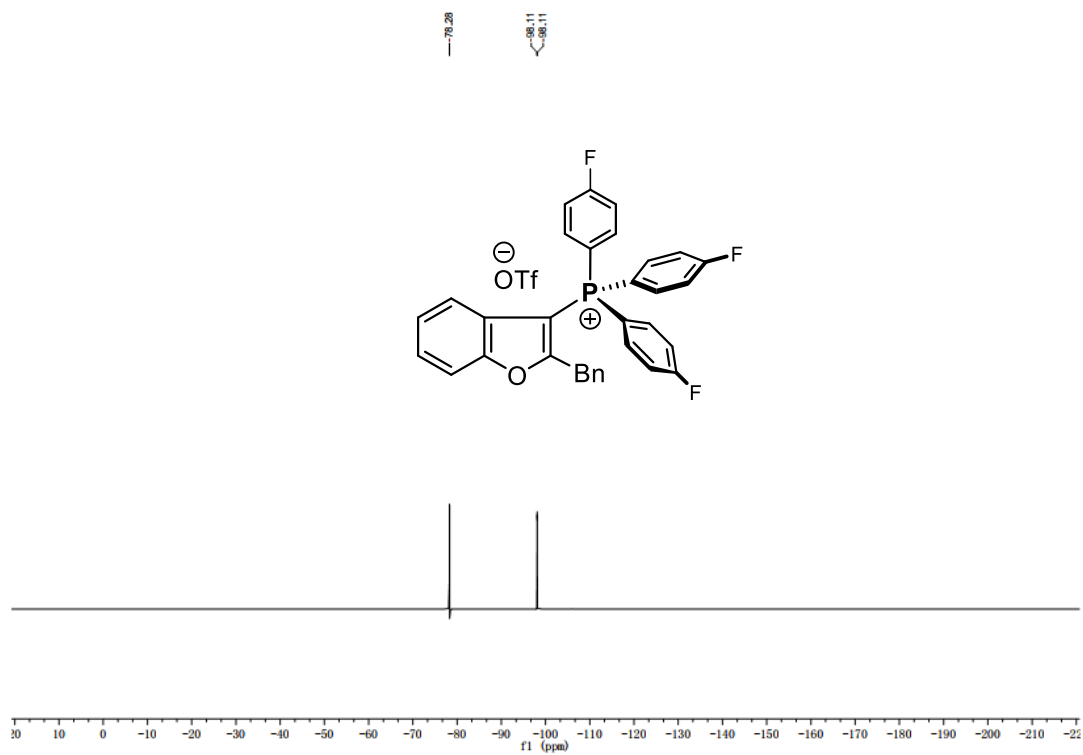
^1H NMR (500 MHz, CDCl_3) of compound **3ah**



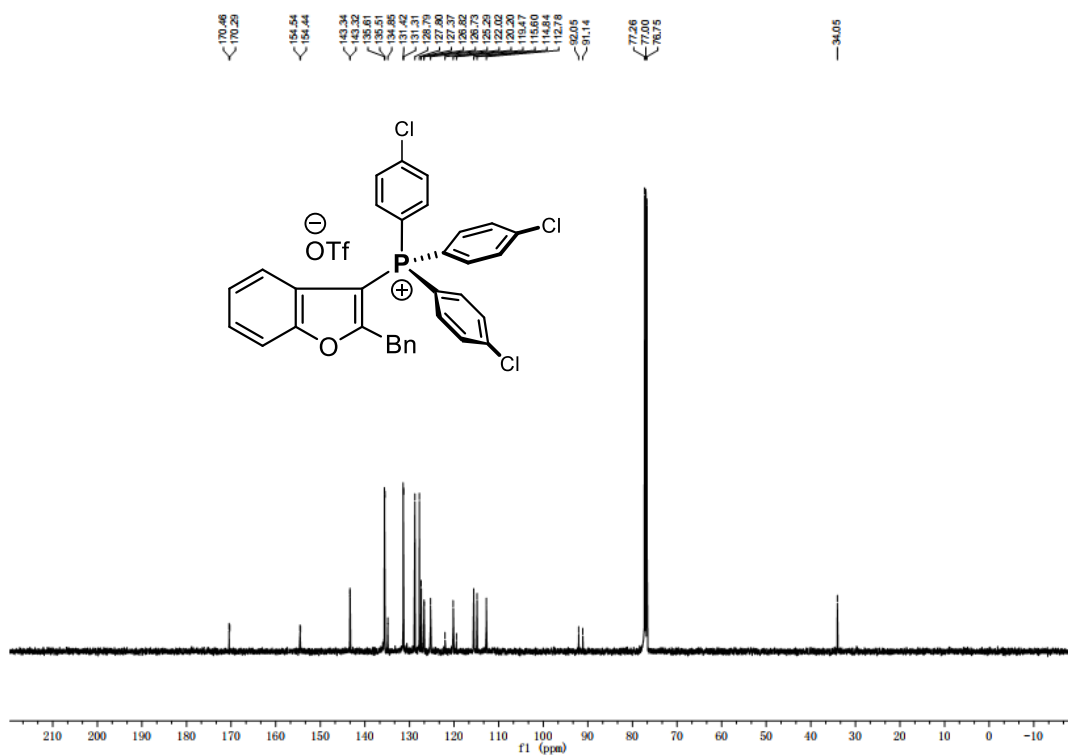
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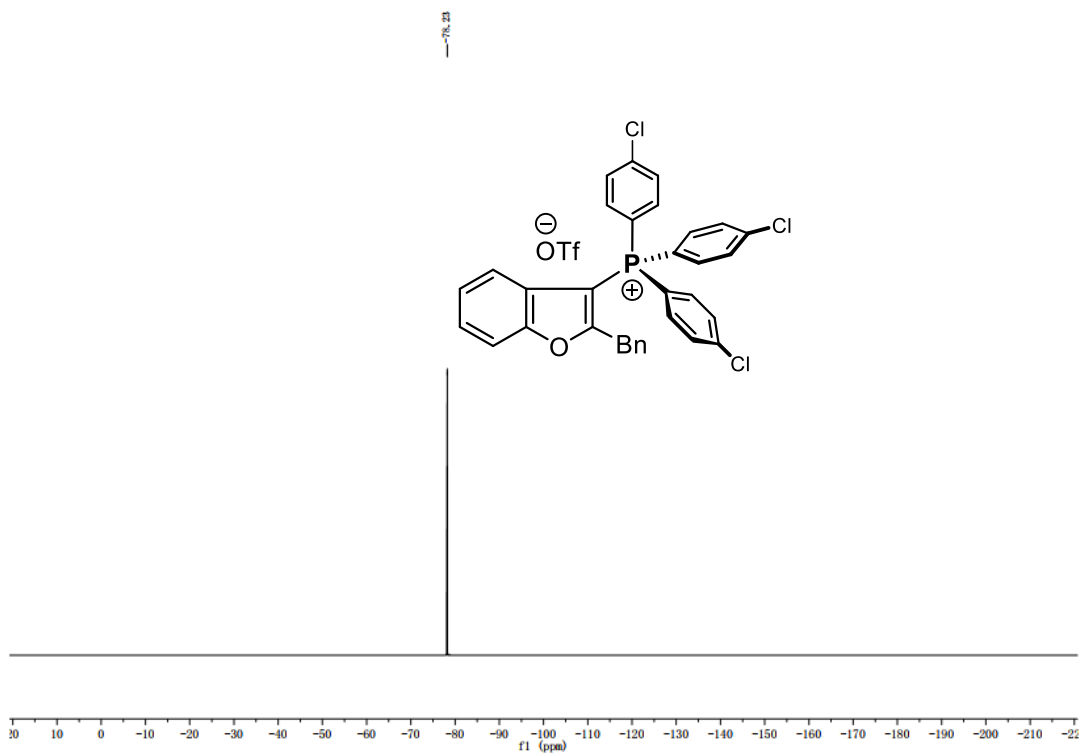
^{19}F NMR (471 MHz, CDCl_3) of compound **3ah**



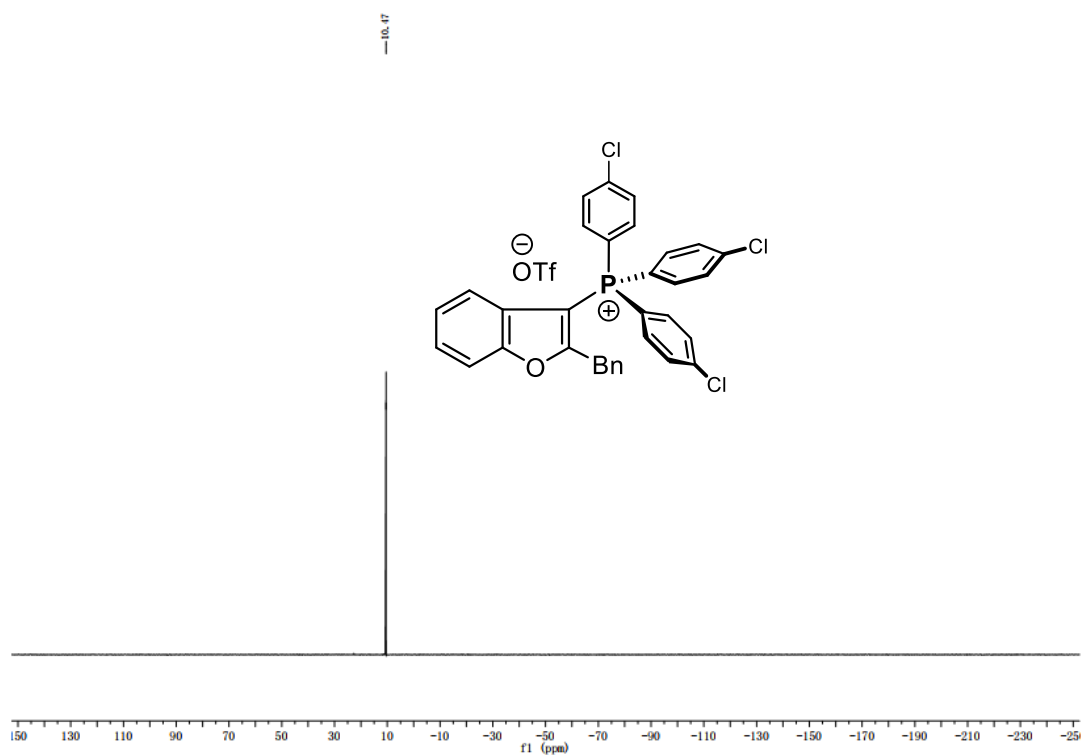
^{13}C NMR (126 MHz, CDCl_3) of compound **3ai**



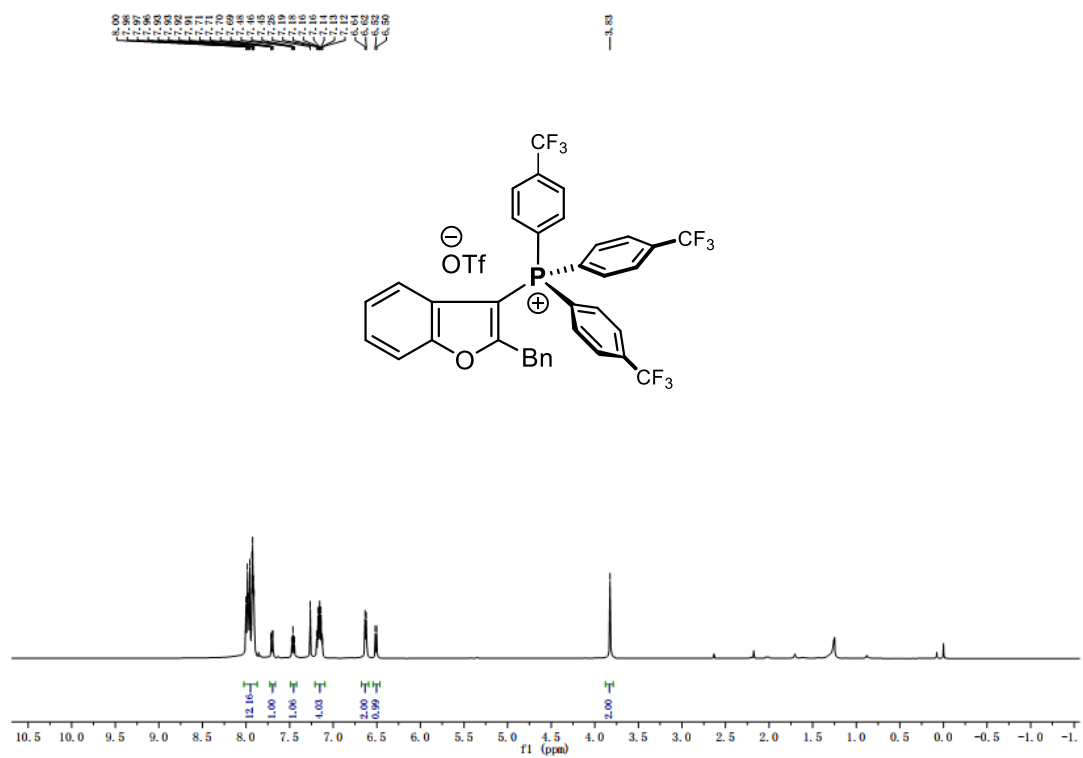
^{19}F NMR (471 MHz, CDCl_3) of compound **3ai**



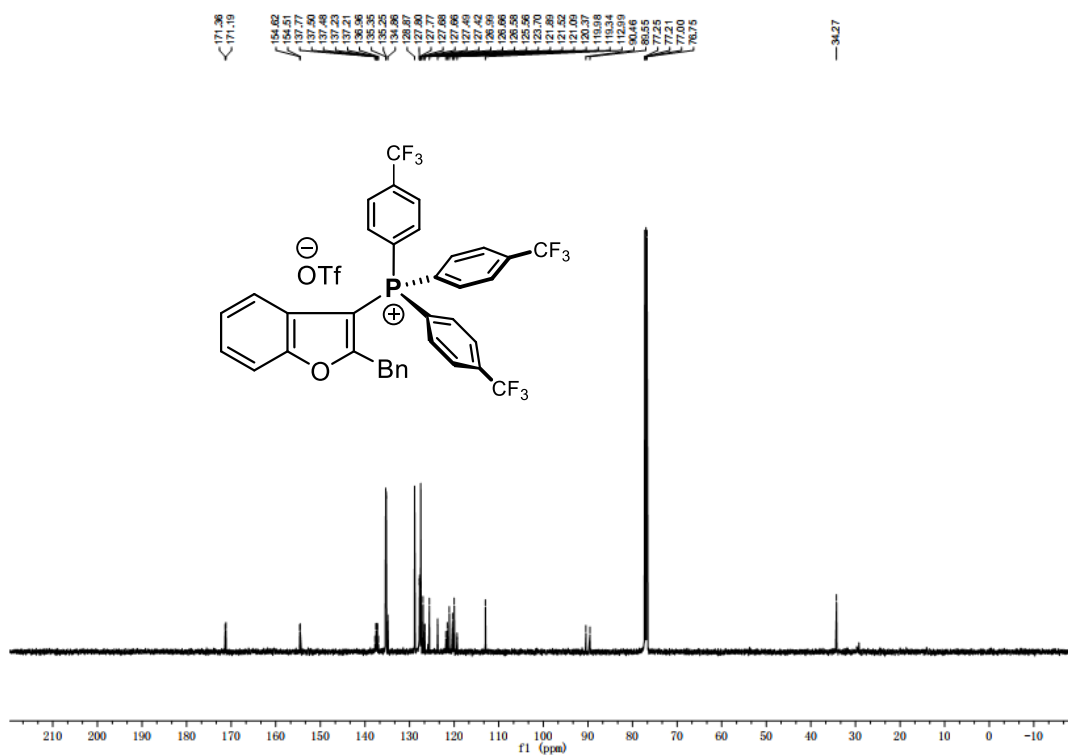
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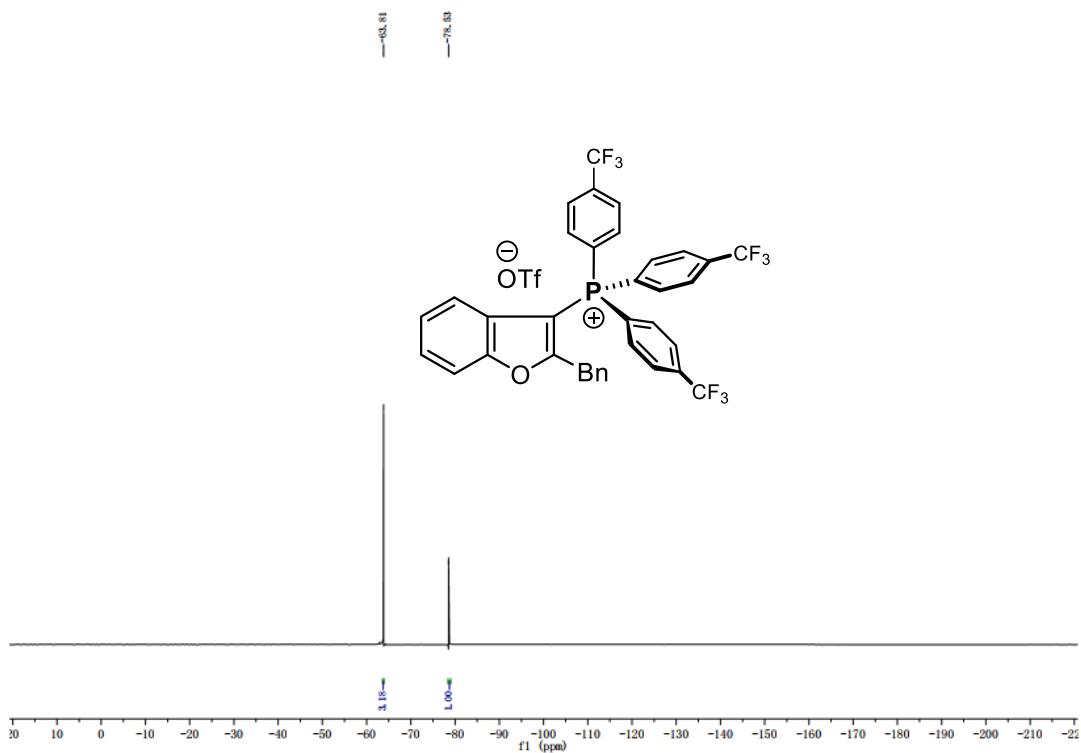
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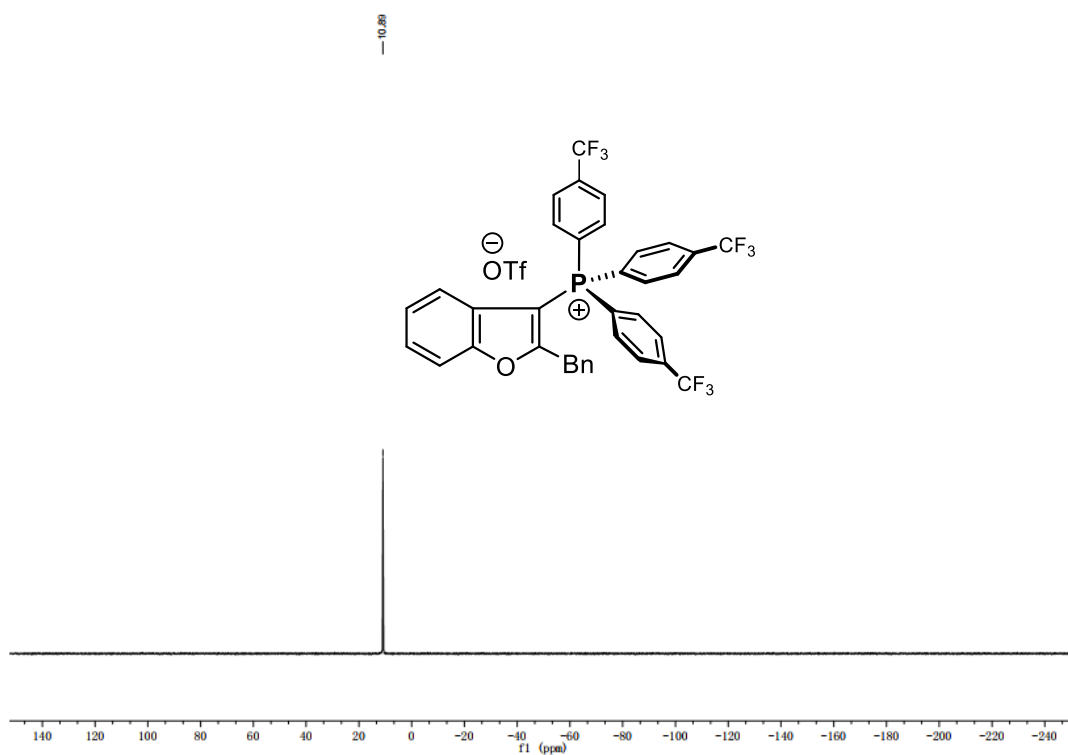
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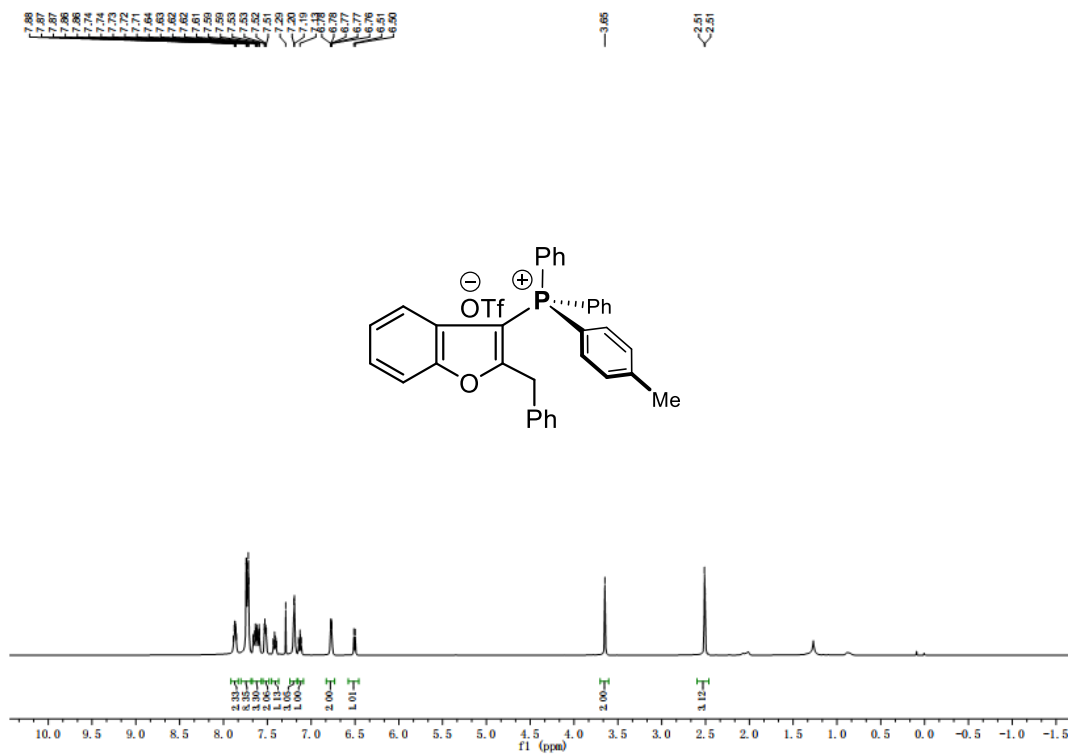
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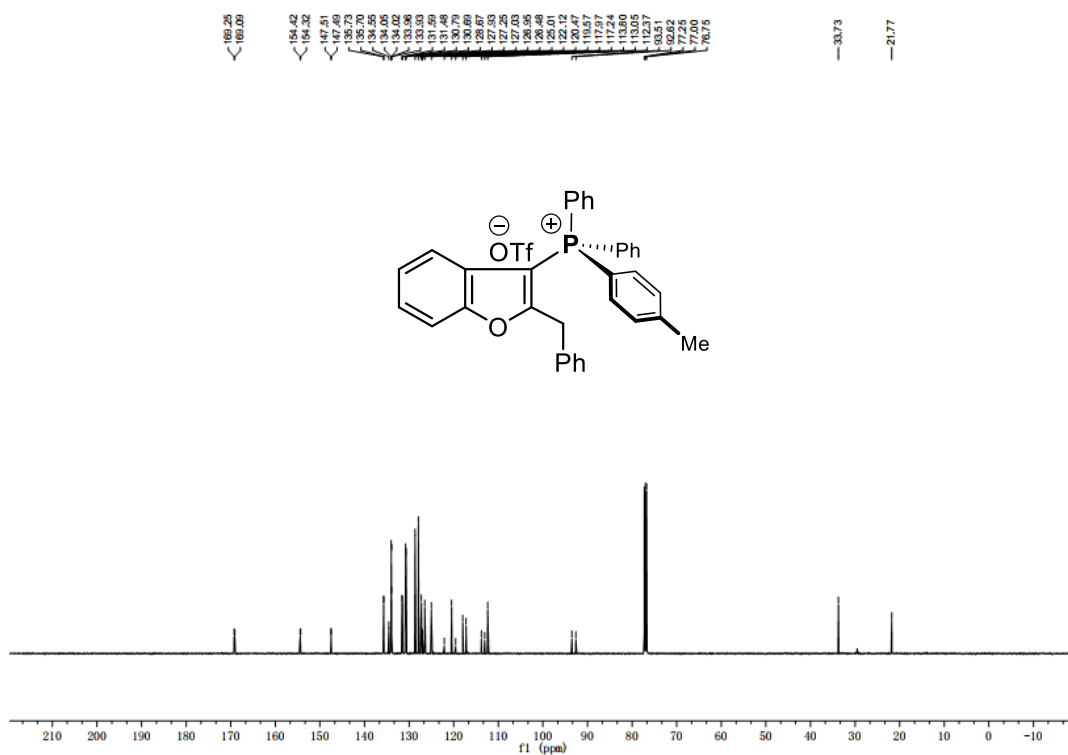
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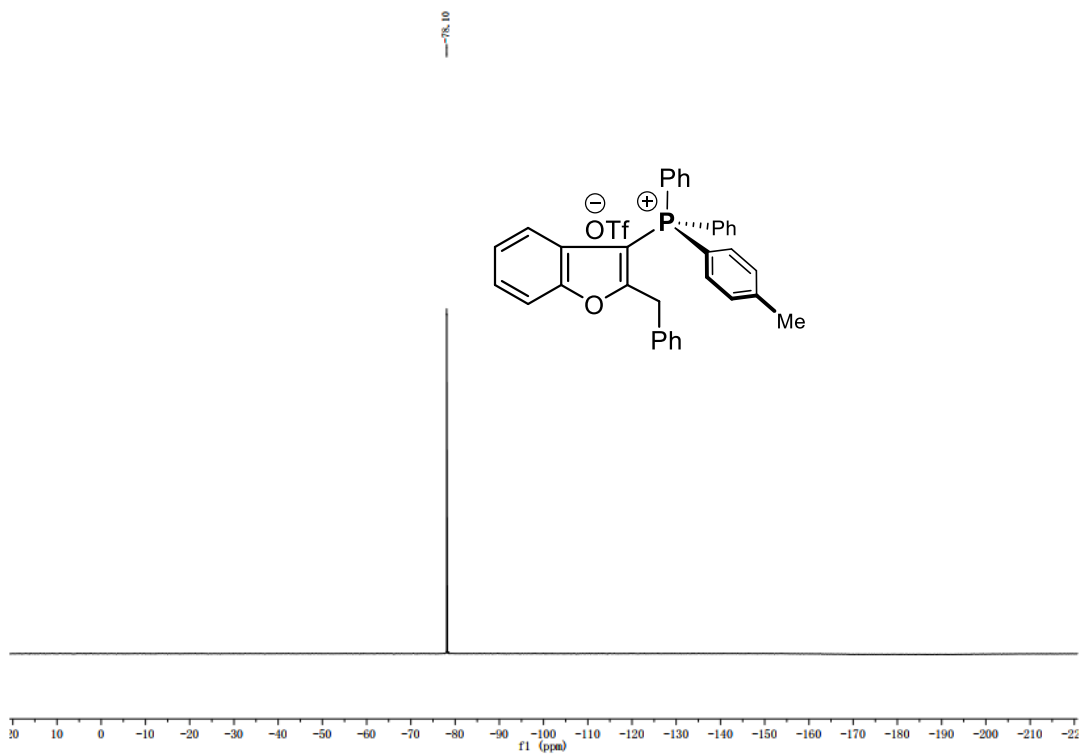
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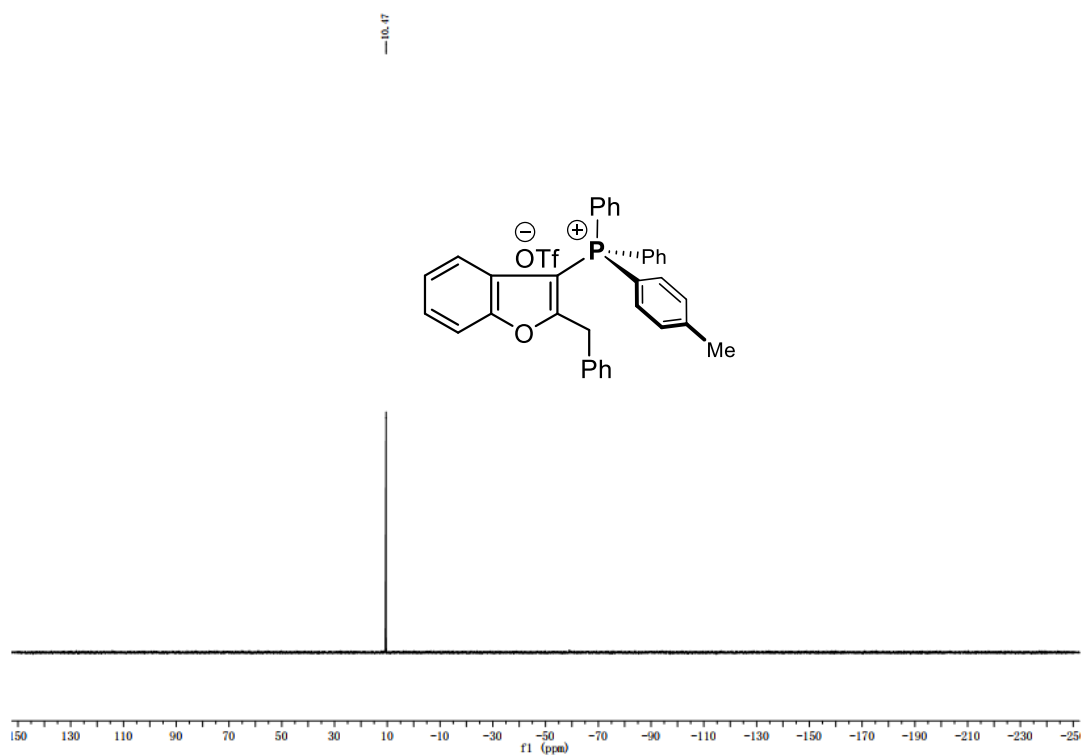
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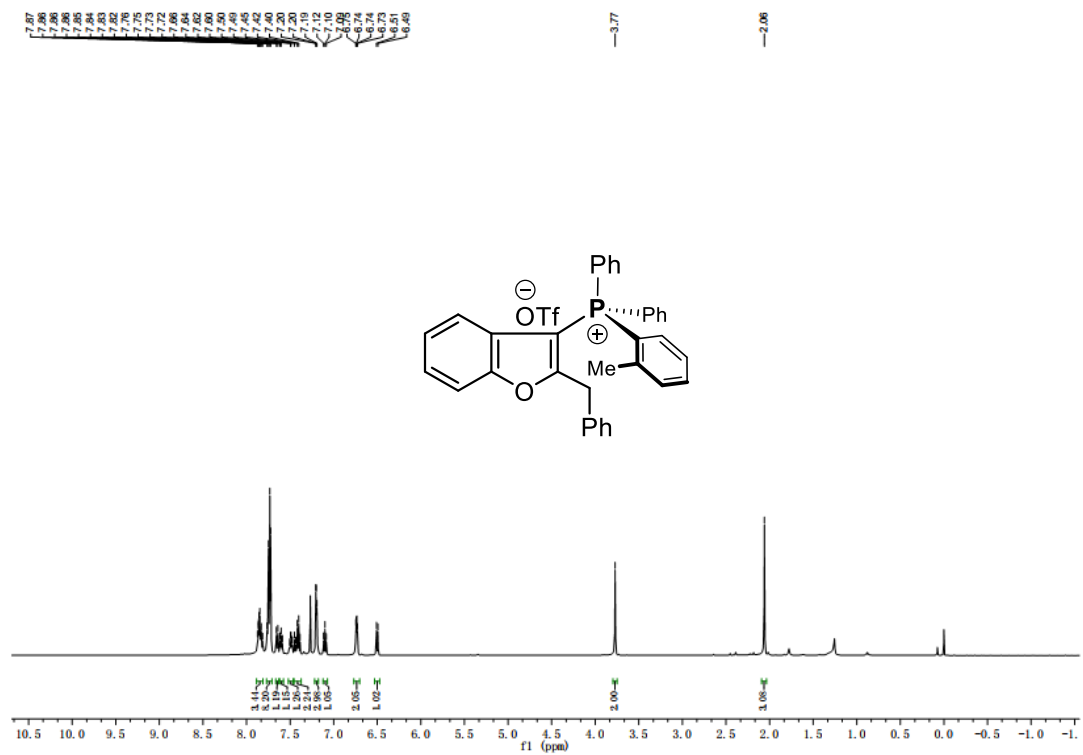
^{19}F NMR (471 MHz, CDCl_3) of compound **3ak**



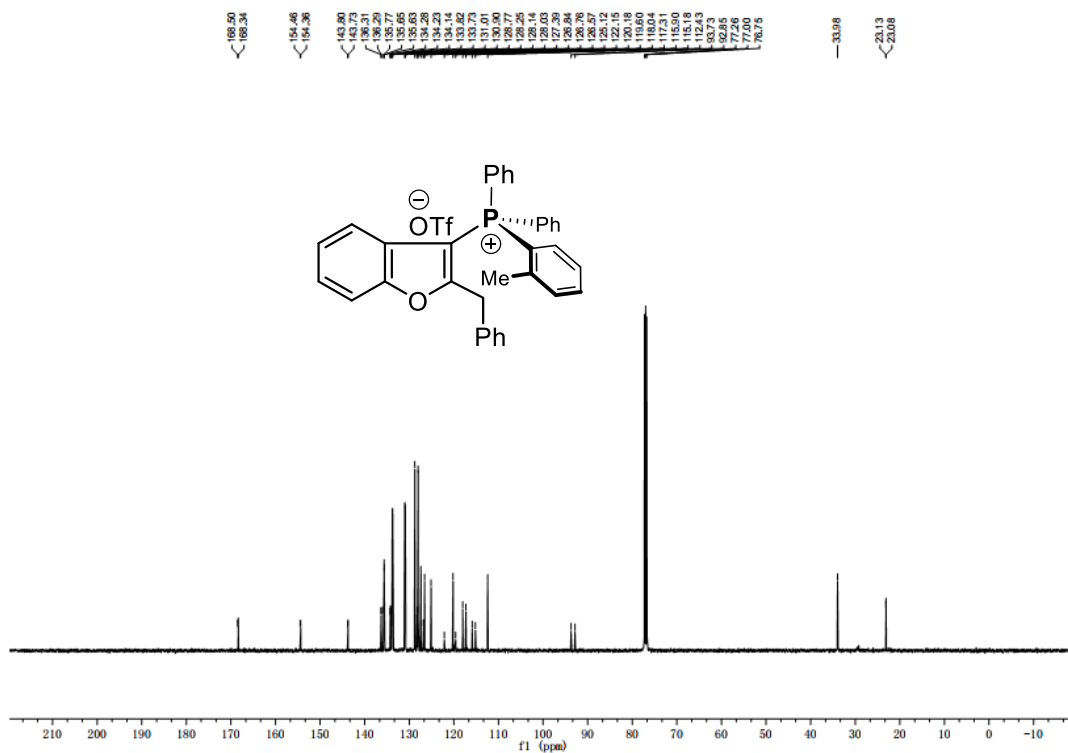
^{31}P NMR (202 MHz, CDCl_3) of compound **3ak**



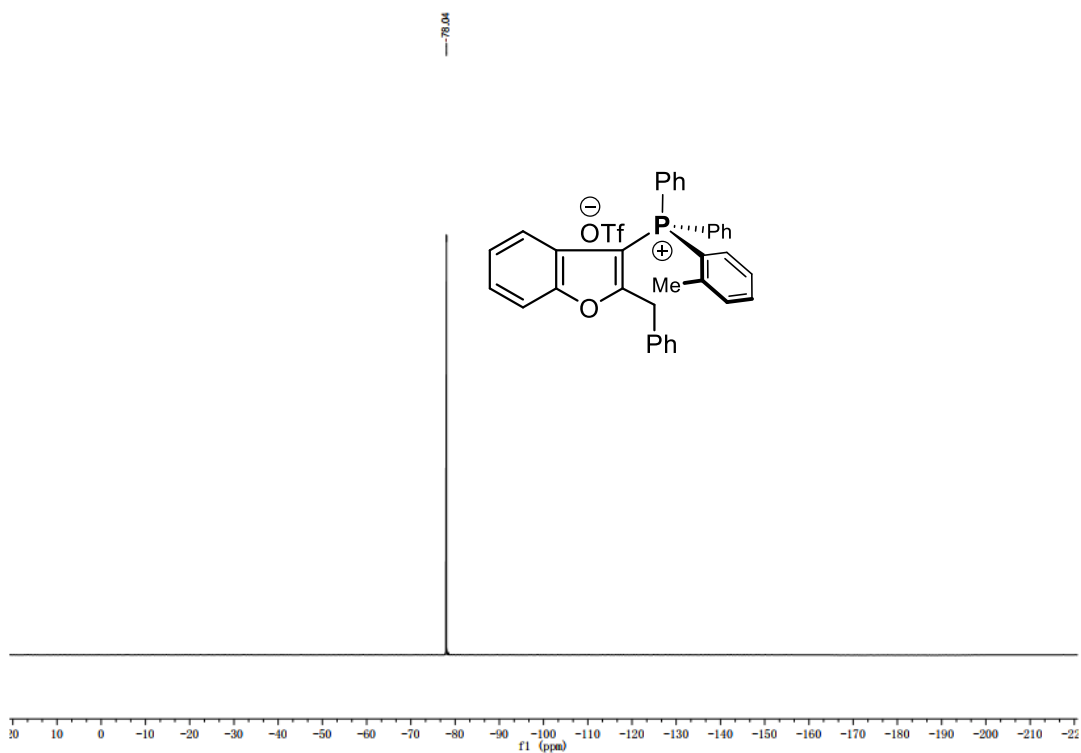
^1H NMR (500 MHz, CDCl_3) of compound **3al**



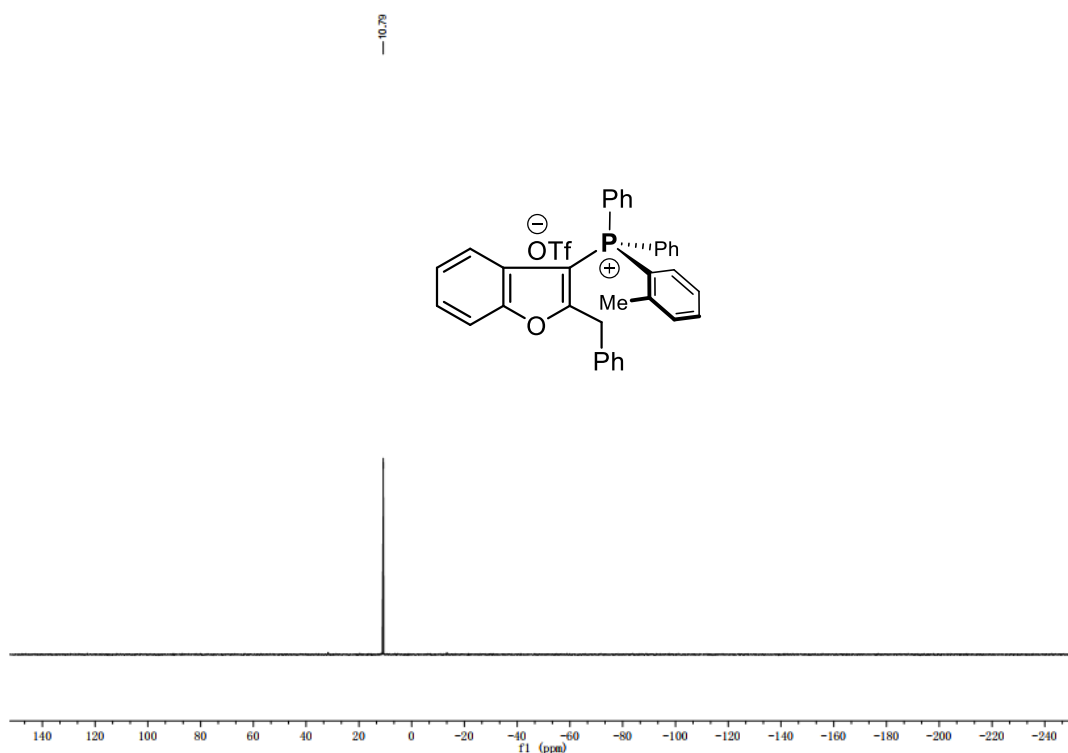
^{13}C NMR (126 MHz, CDCl_3) of compound **3al**



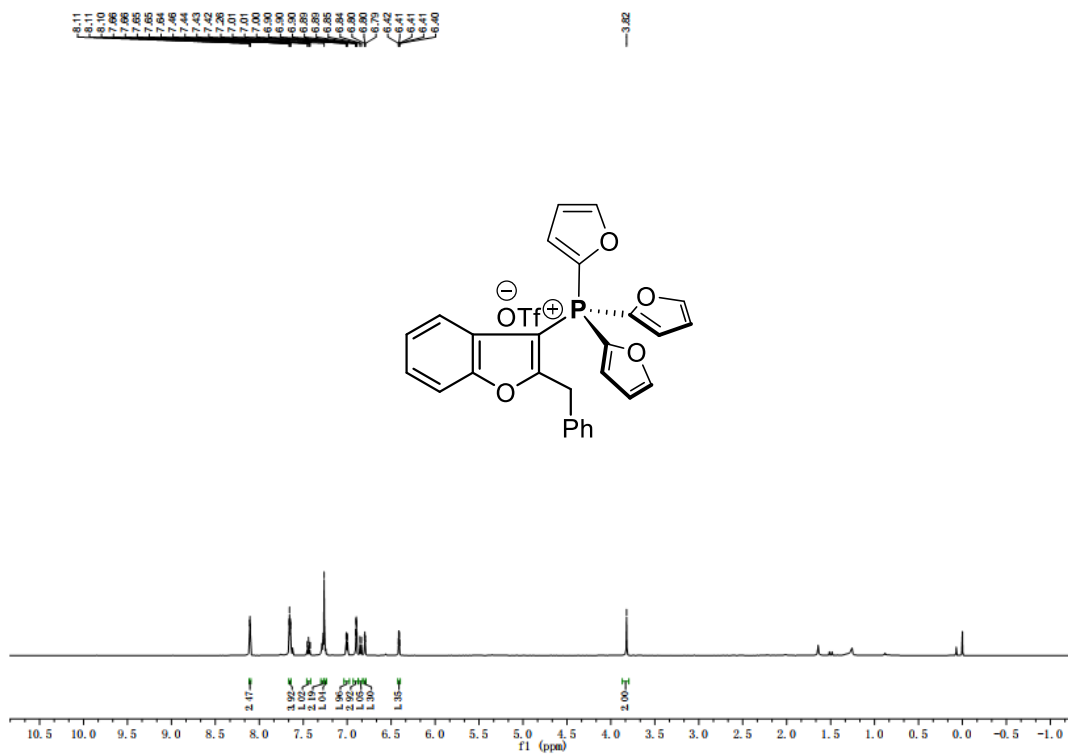
^{19}F NMR (471 MHz, CDCl_3) of compound **3al**



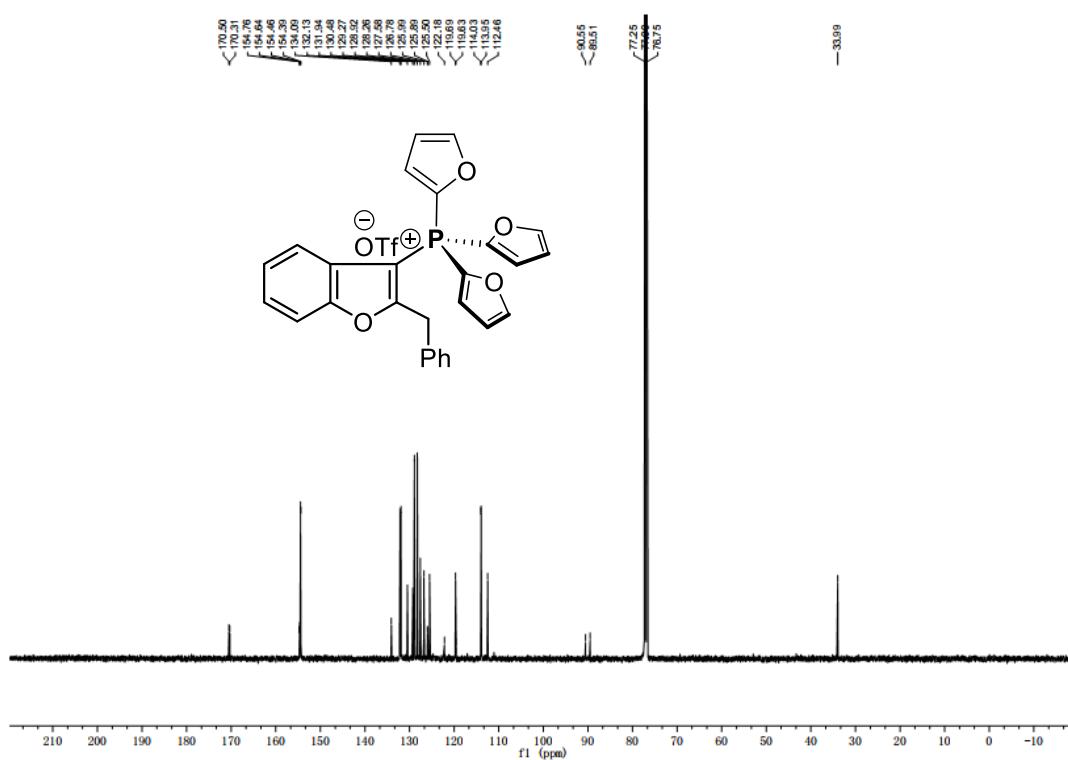
^{31}P NMR (202 MHz, CDCl_3) of compound **3al**



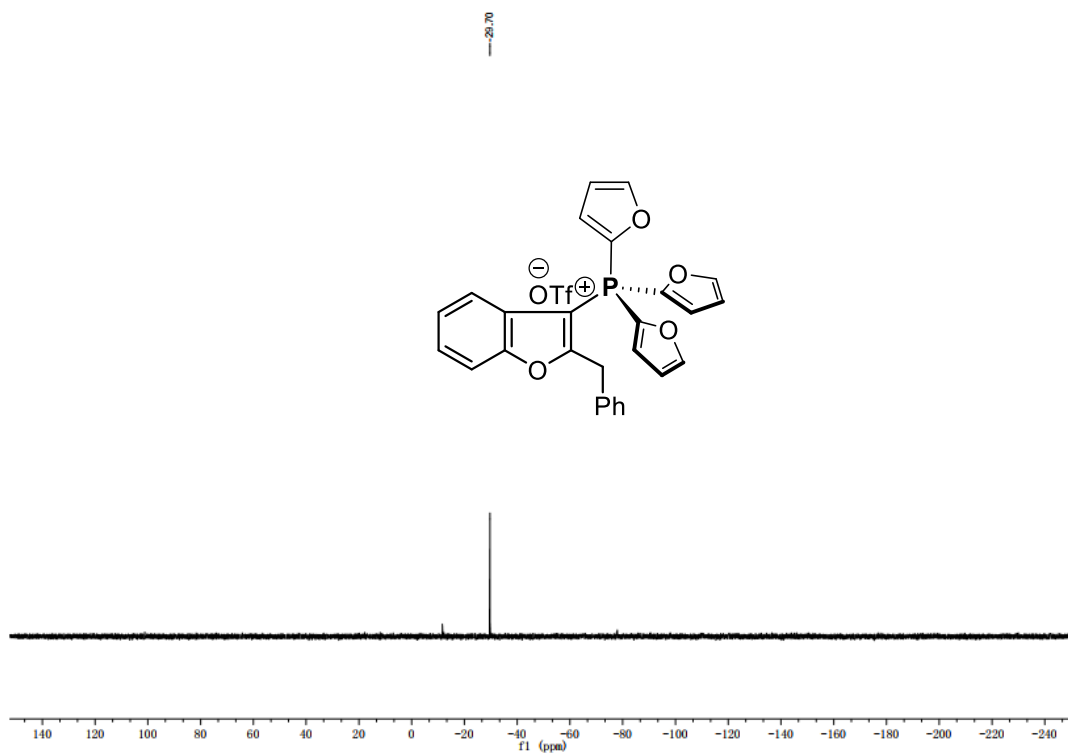
^1H NMR (500 MHz, CDCl_3) of compound **3am**



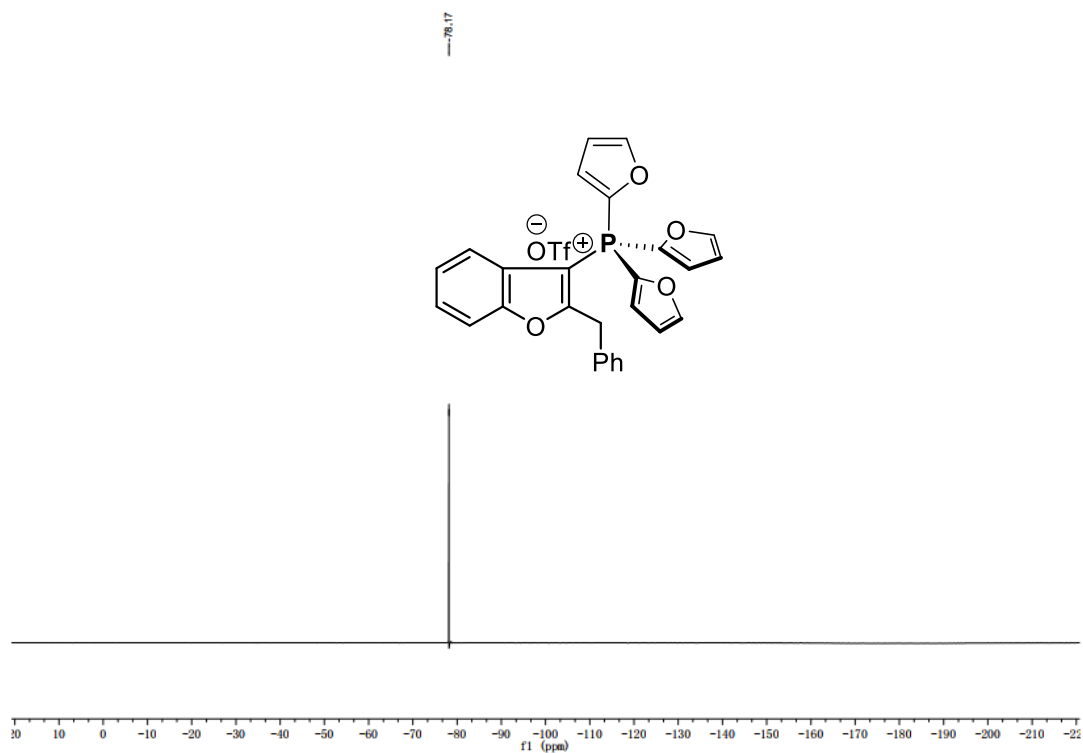
^{13}C NMR (126 MHz, CDCl_3) of compound **3am**



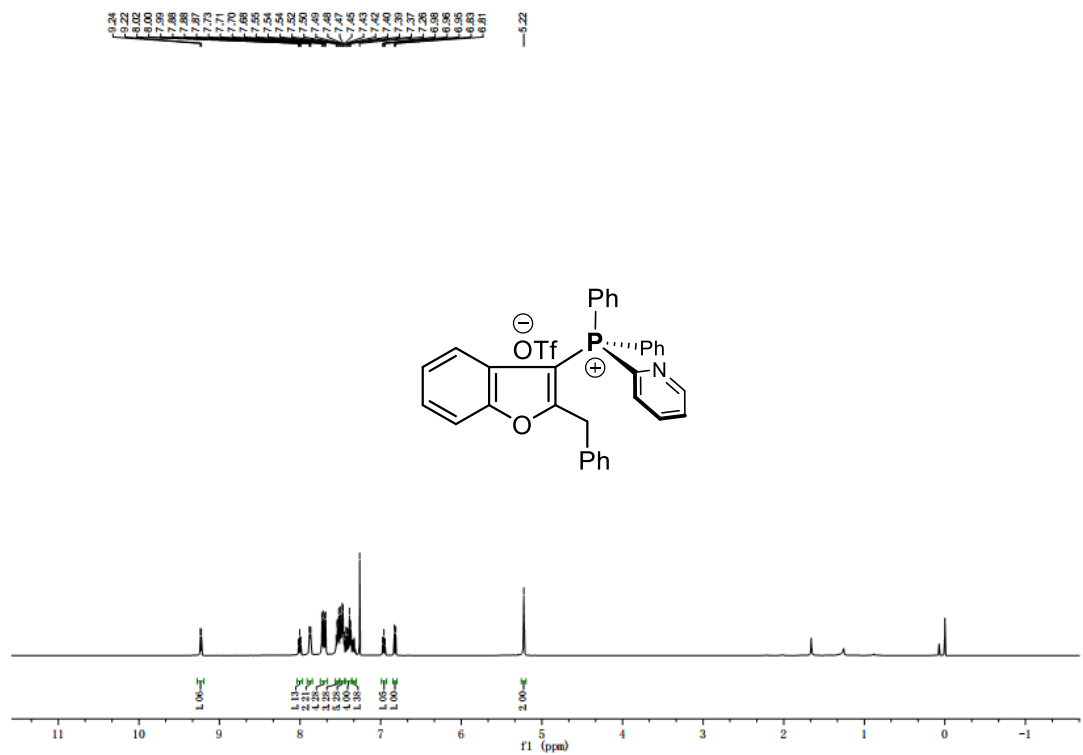
^{31}P NMR (202 MHz, CDCl_3) of compound **3am**



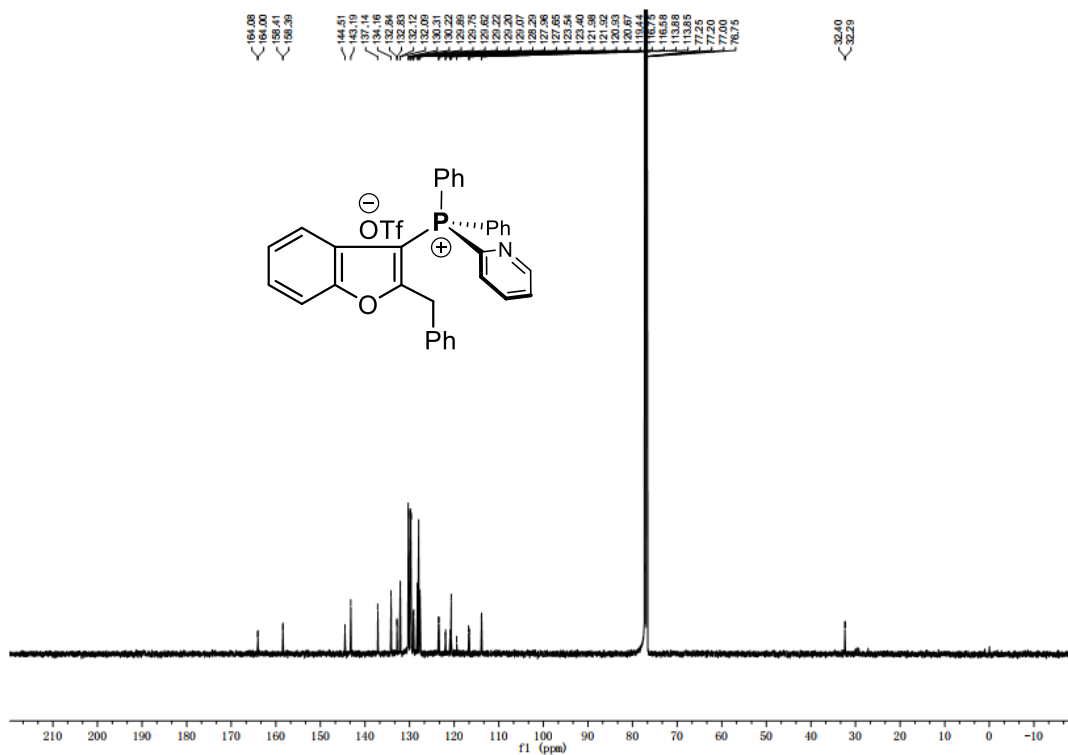
^{19}F NMR (471 MHz, CDCl_3) of compound **3am**



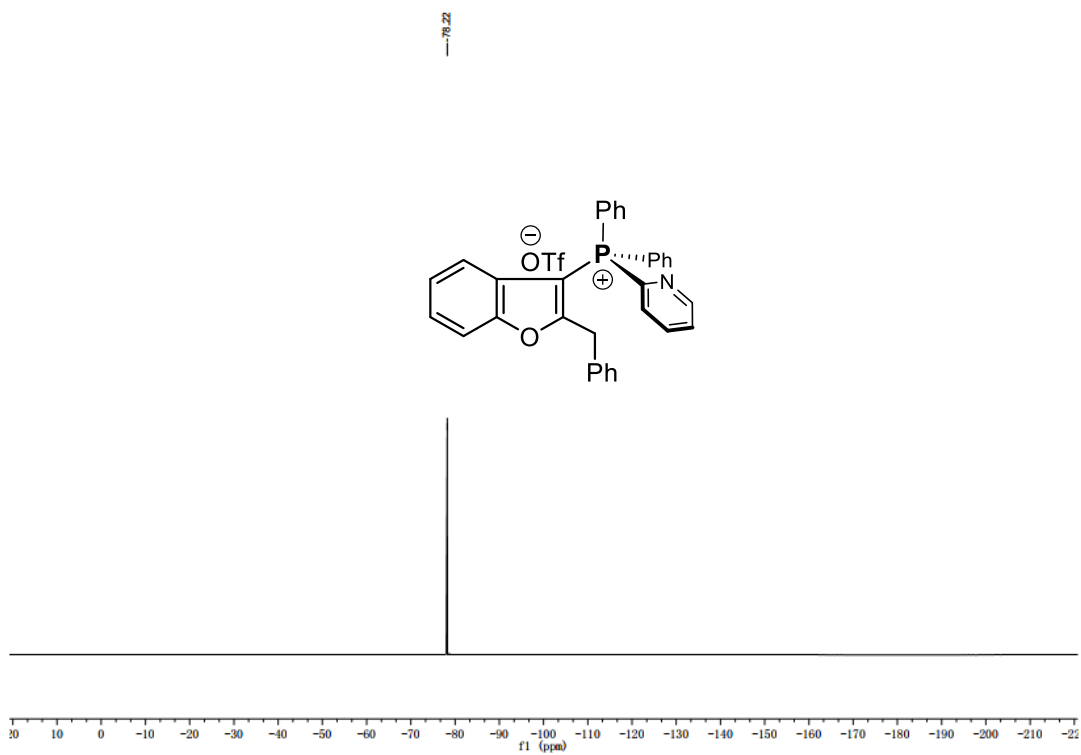
^1H NMR (500 MHz, CDCl_3) of compound **3an**



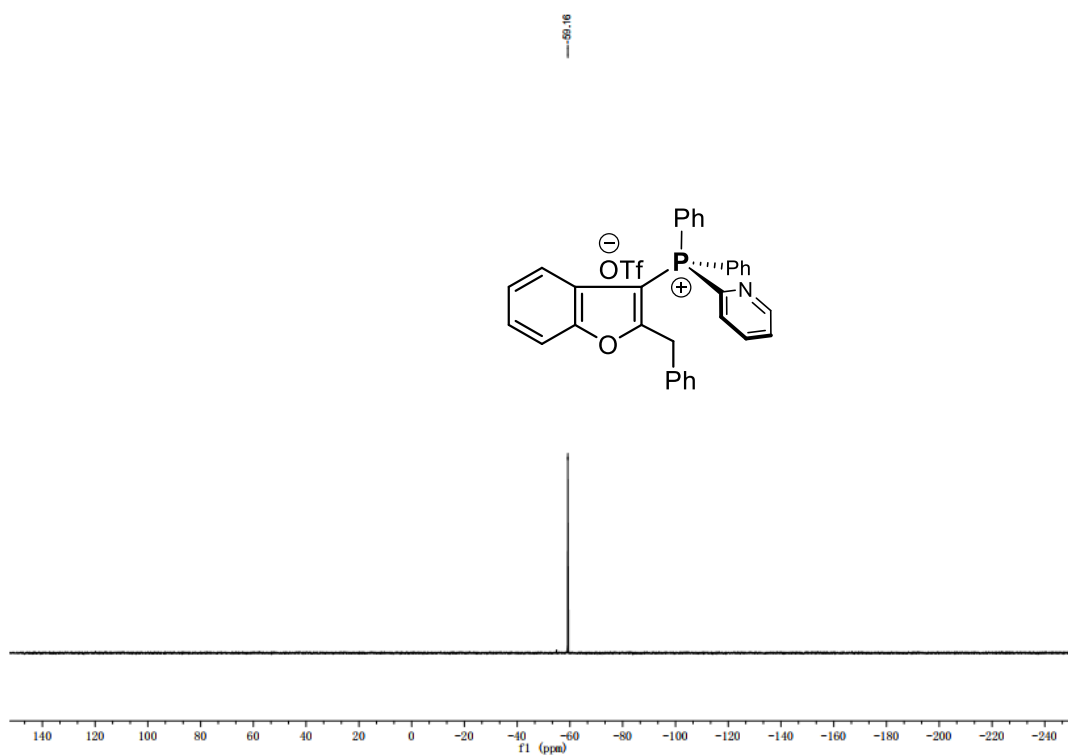
^{13}C NMR (126 MHz, CDCl_3) of compound **3an**



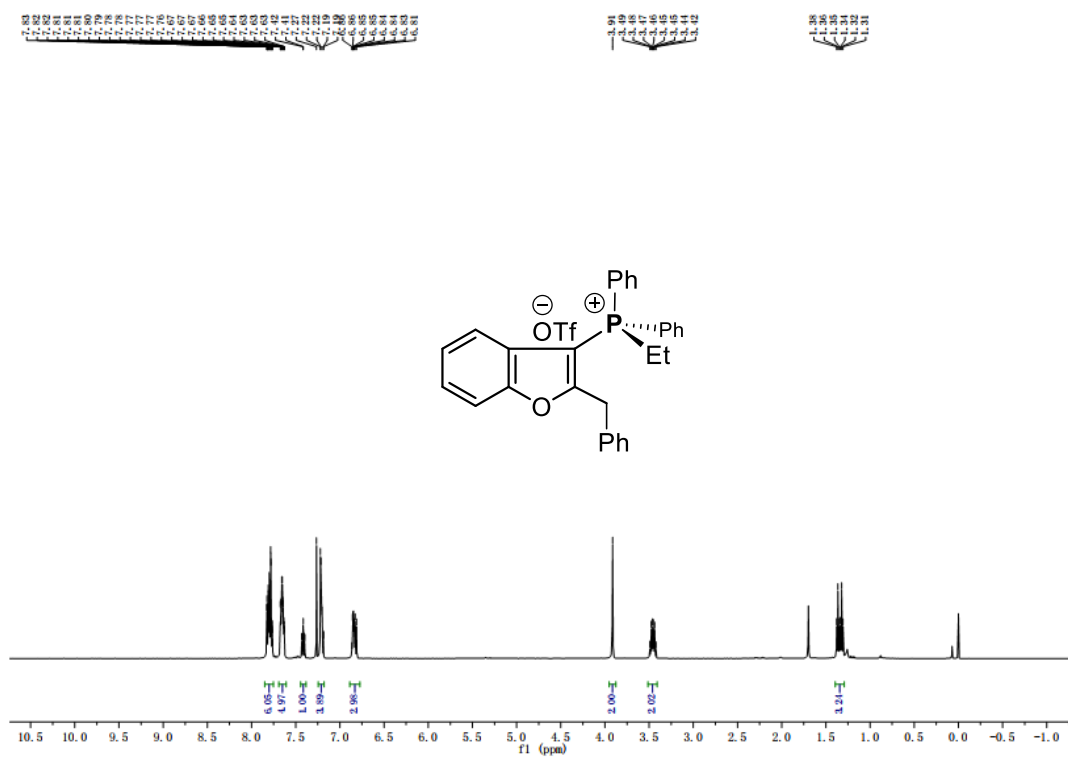
^{19}F NMR (471 MHz, CDCl_3) of compound **3an**



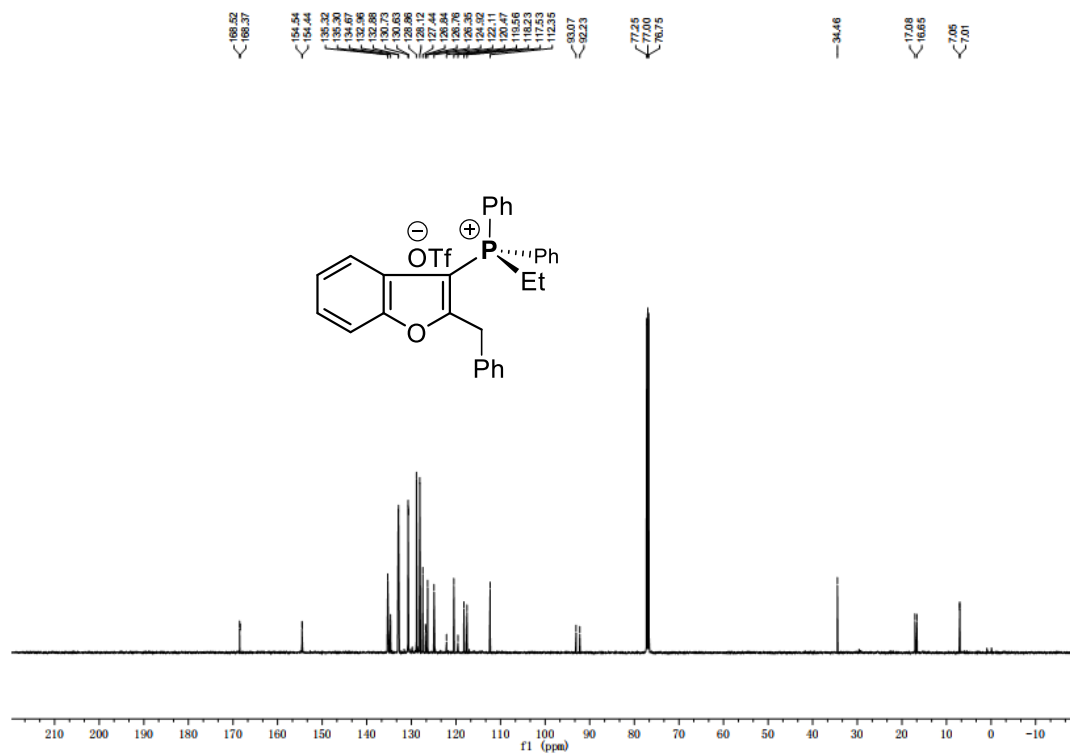
^{31}P NMR (202 MHz, CDCl_3) of compound **3an**



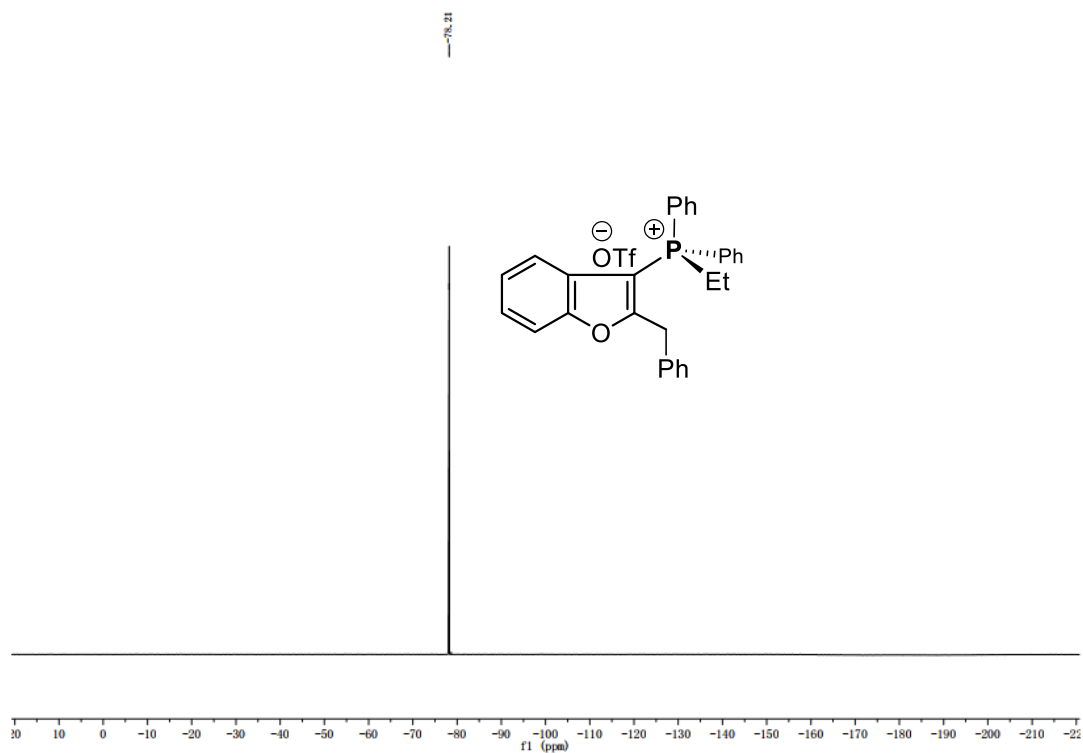
^1H NMR (500 MHz, CDCl_3) of compound **3ao**



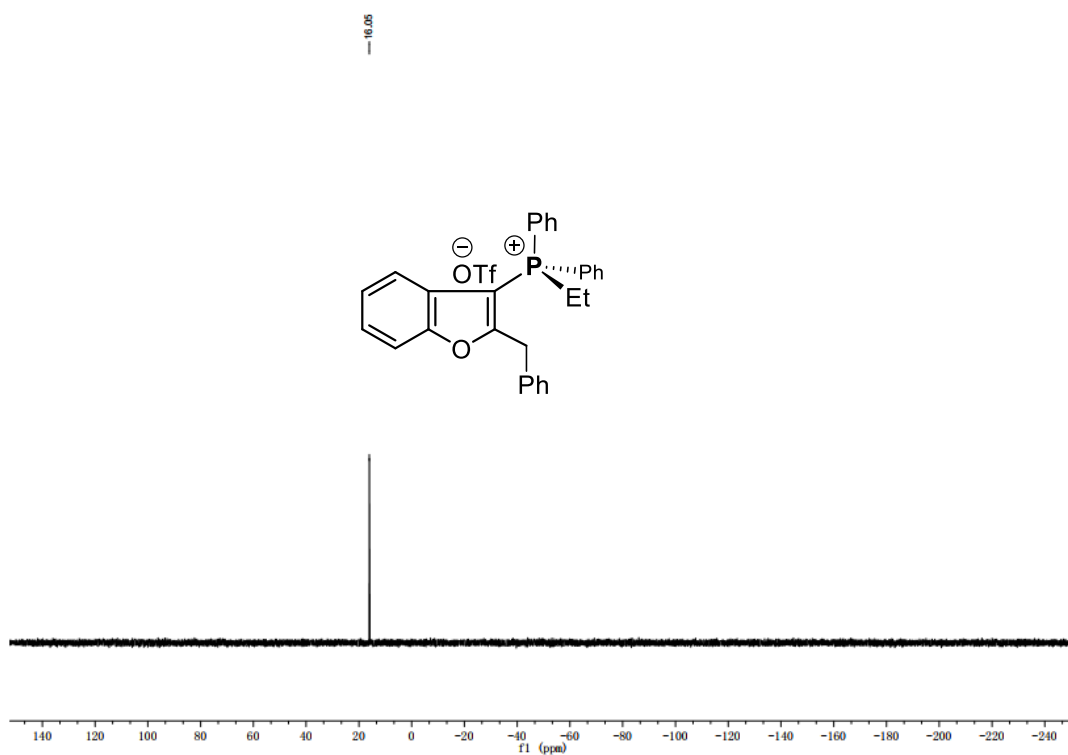
^{13}C NMR (126 MHz, CDCl_3) of compound **3ao**



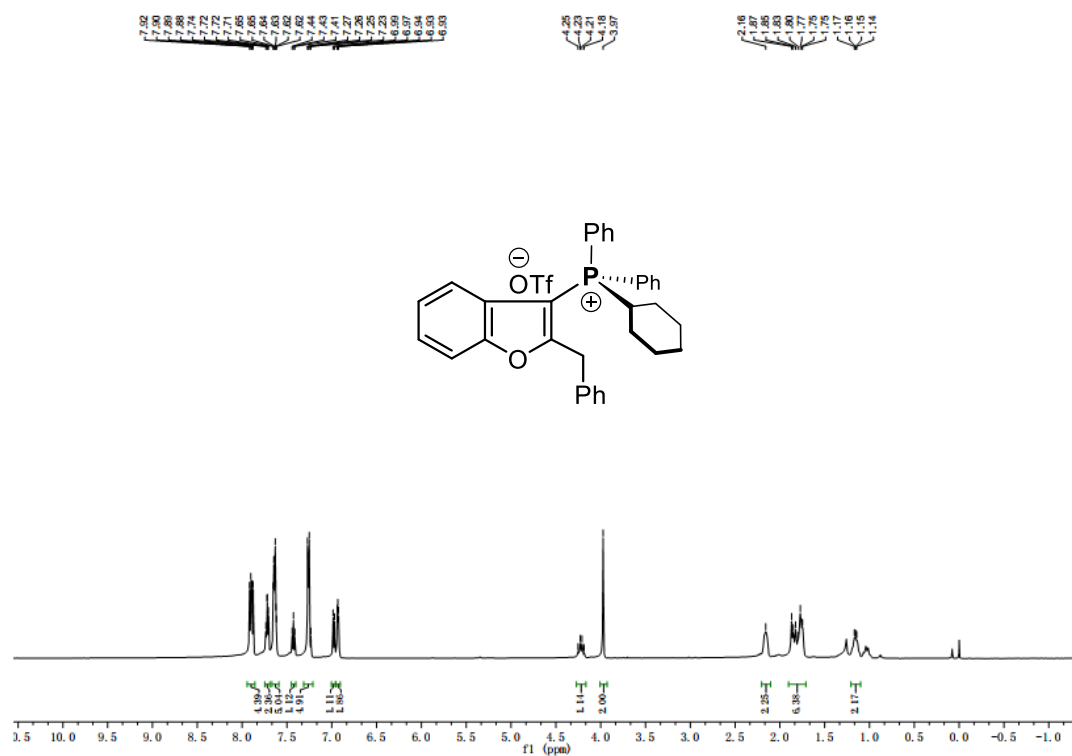
^{19}F NMR (471 MHz, CDCl_3) of compound **3ao**



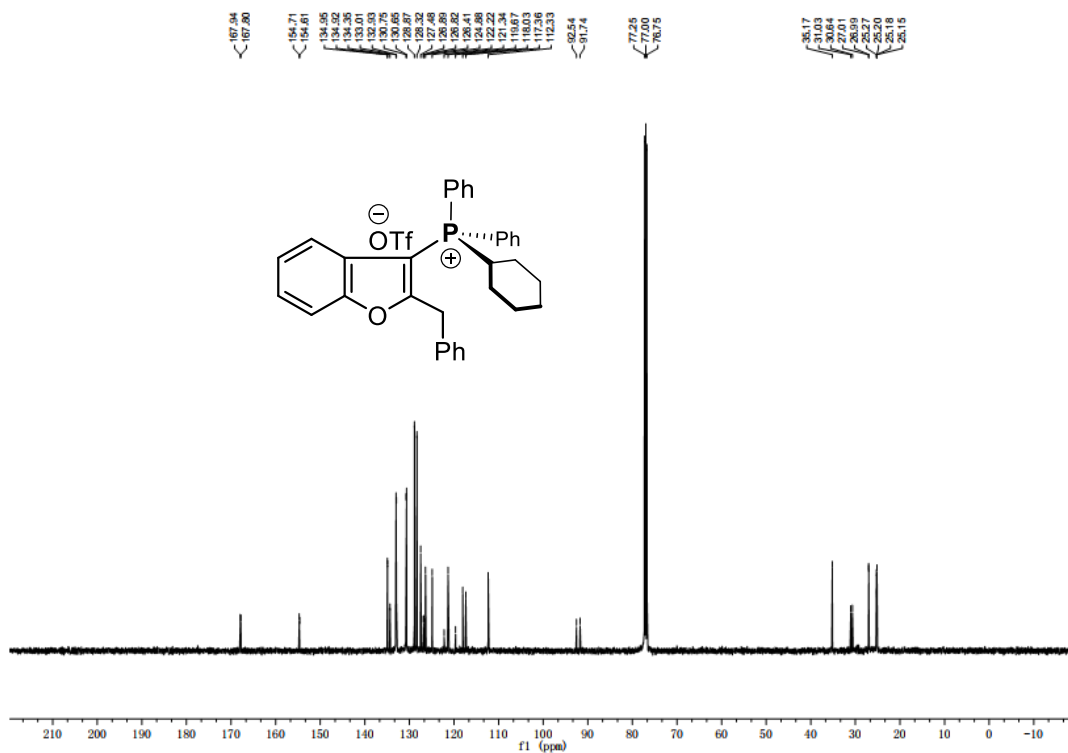
^{31}P NMR (202 MHz, CDCl_3) of compound **3ao**



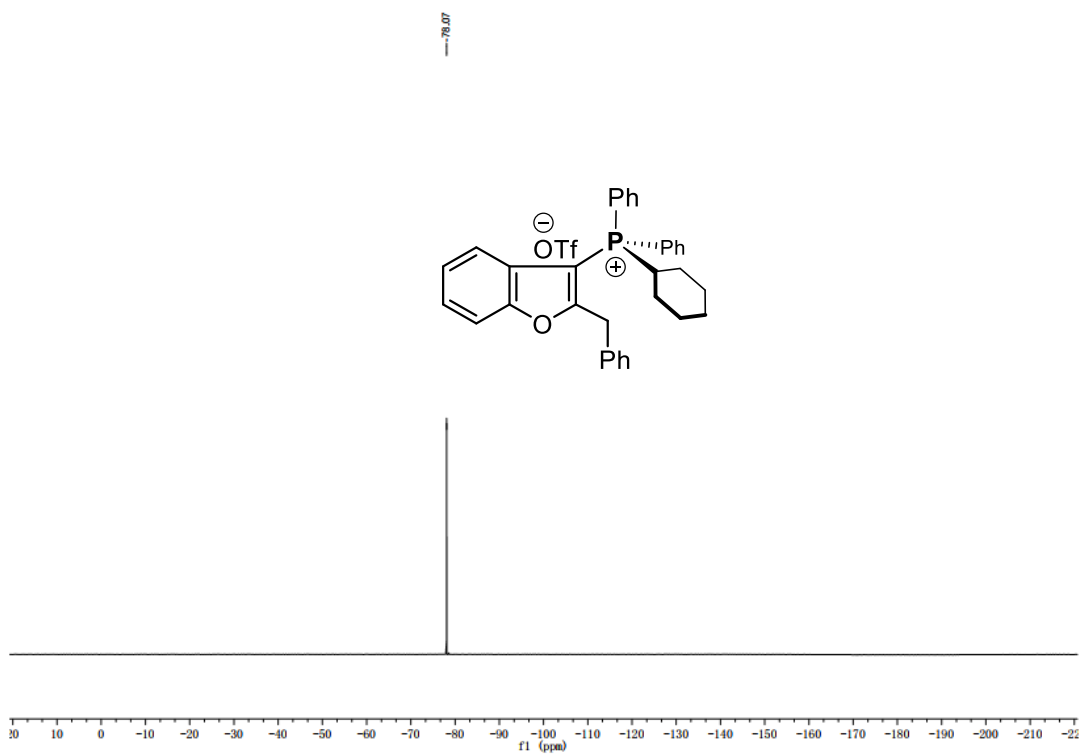
^1H NMR (500 MHz, CDCl_3) of compound **3ap**



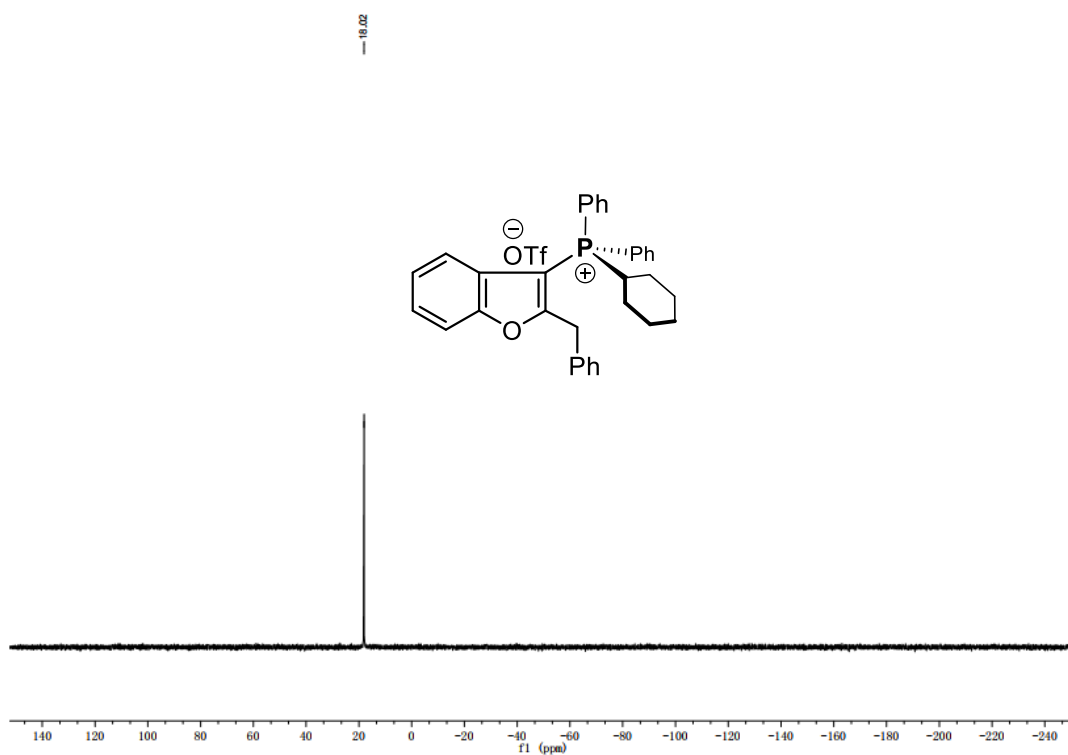
^{13}C NMR (126 MHz, CDCl_3) of compound **3ap**



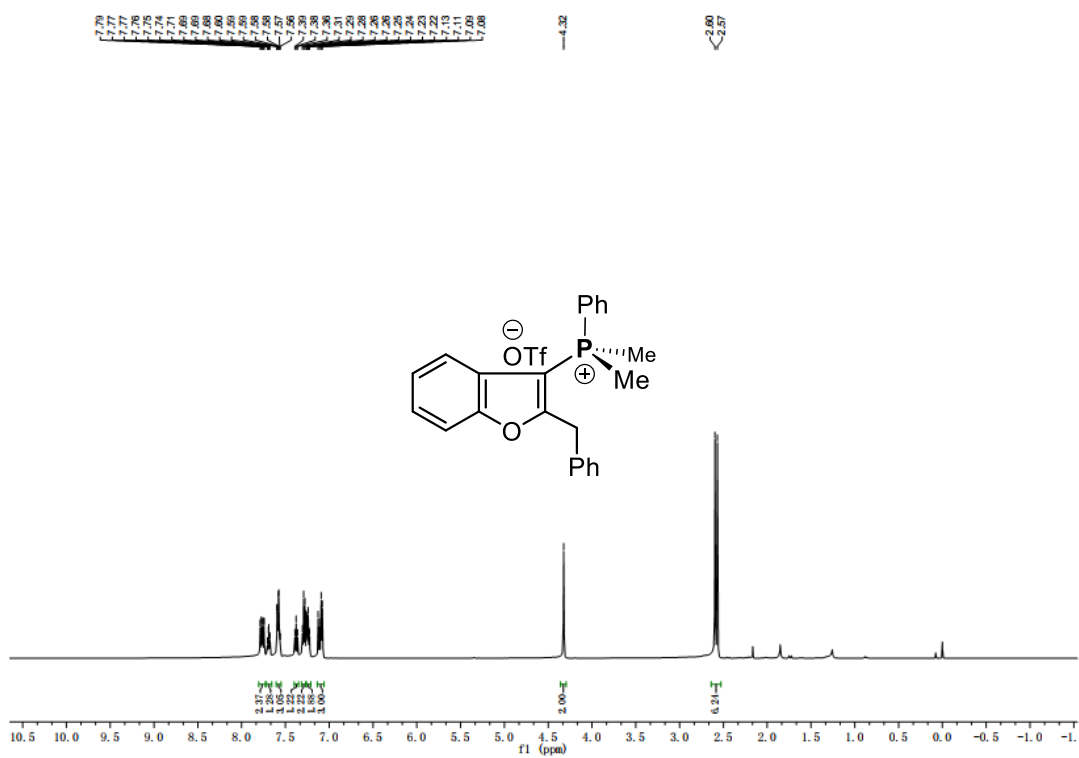
^{19}F NMR (471 MHz, CDCl_3) of compound **3ap**



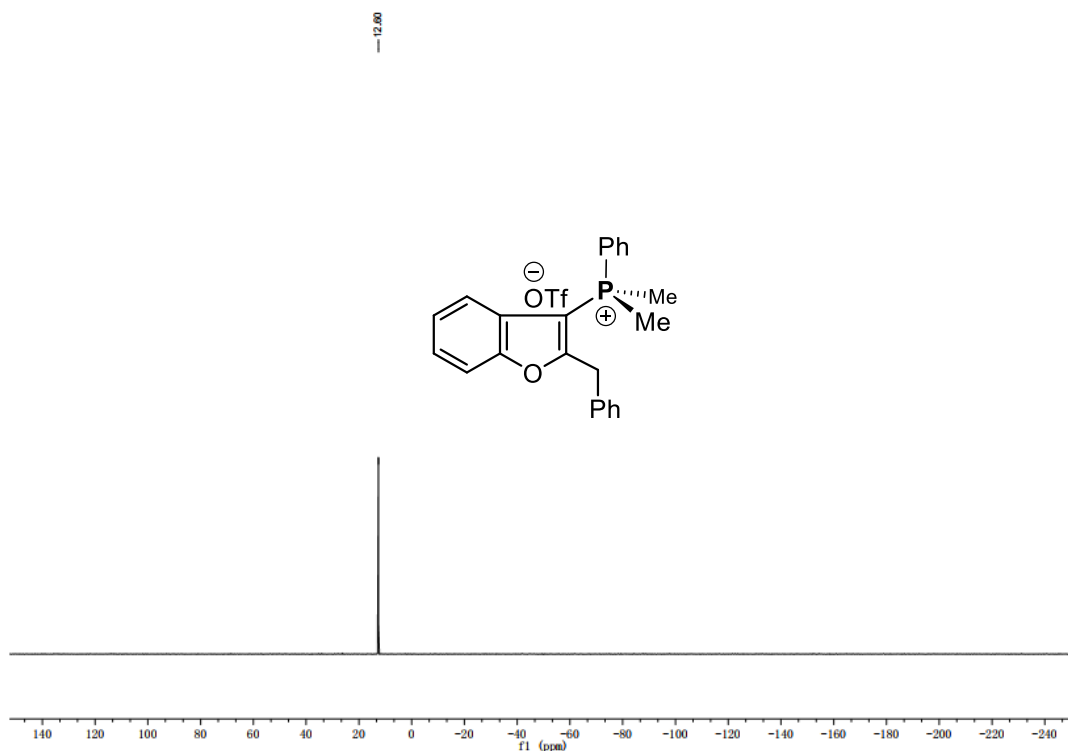
^{31}P NMR (202 MHz, CDCl_3) of compound **3ap**



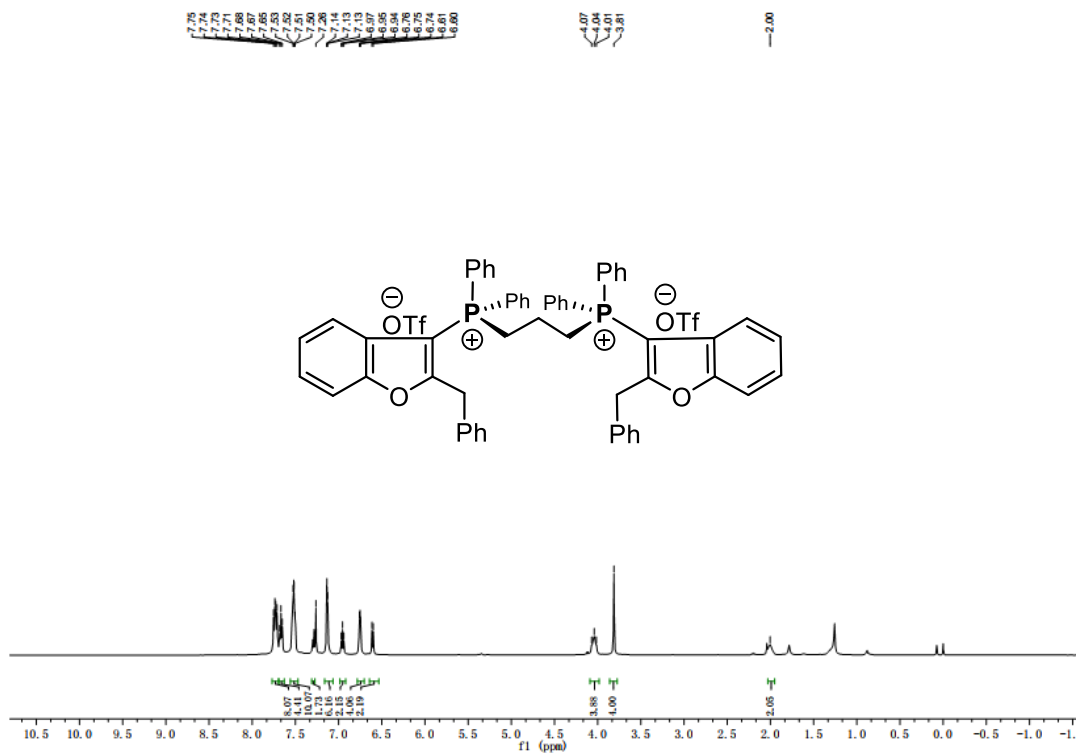
^1H NMR (500 MHz, CDCl_3) of compound **3aq**



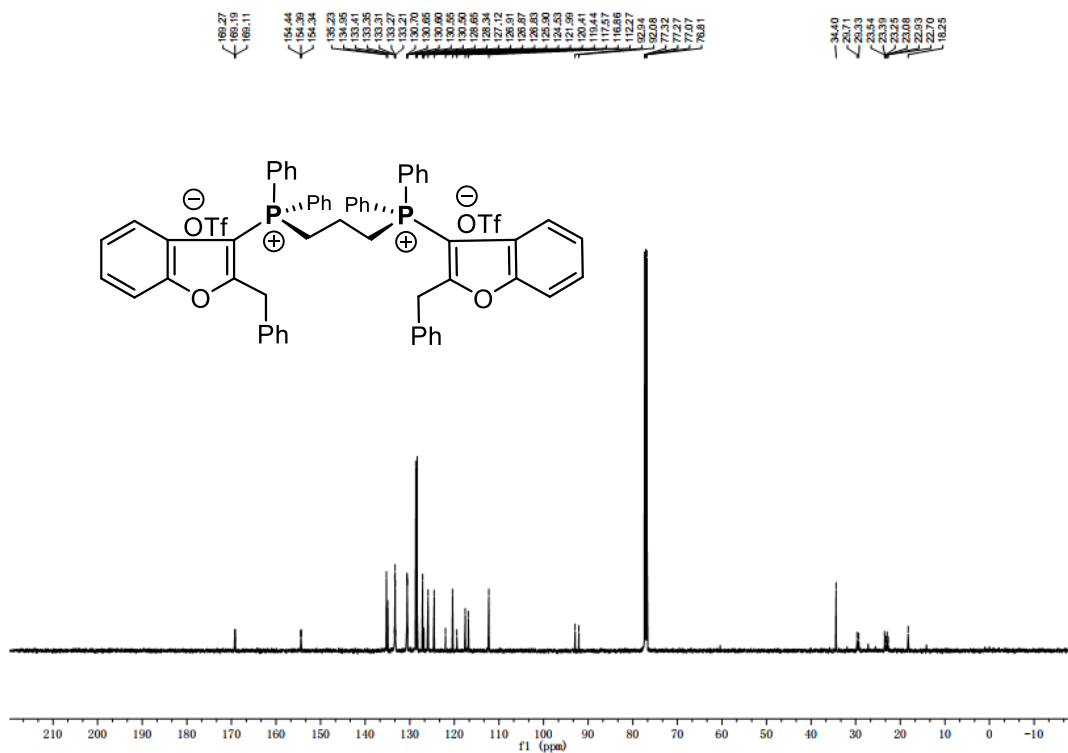
^{31}P NMR (202 MHz, CDCl_3) of compound **3aq**



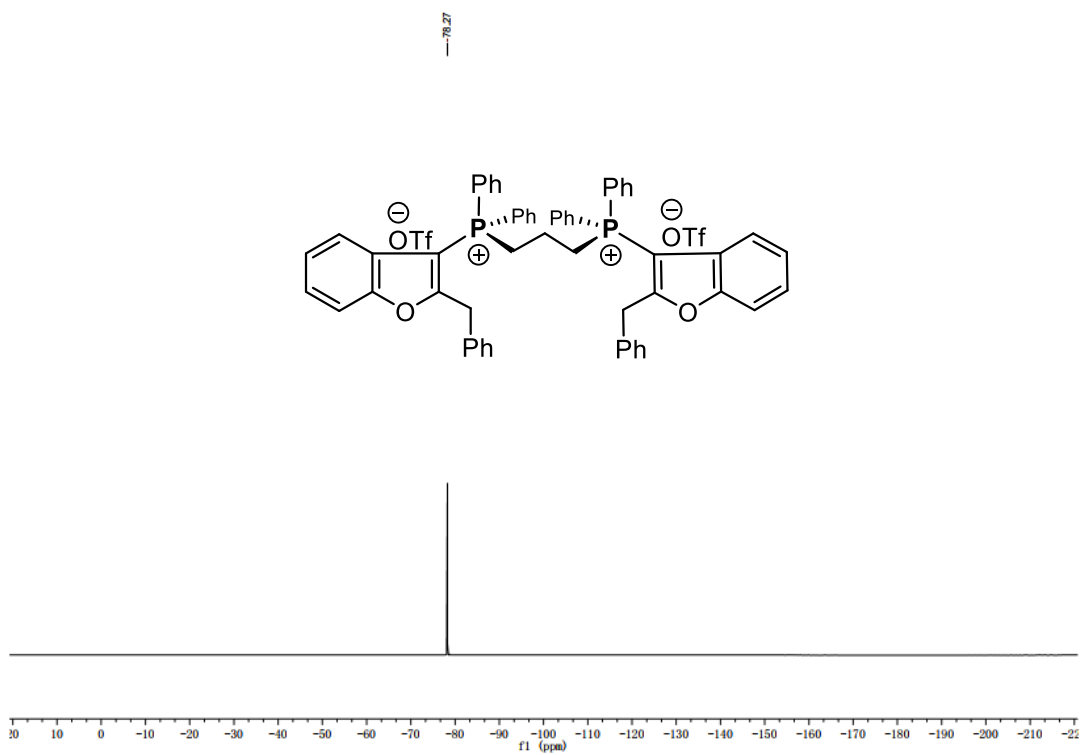
^1H NMR (500 MHz, CDCl_3) of compound **3ar**



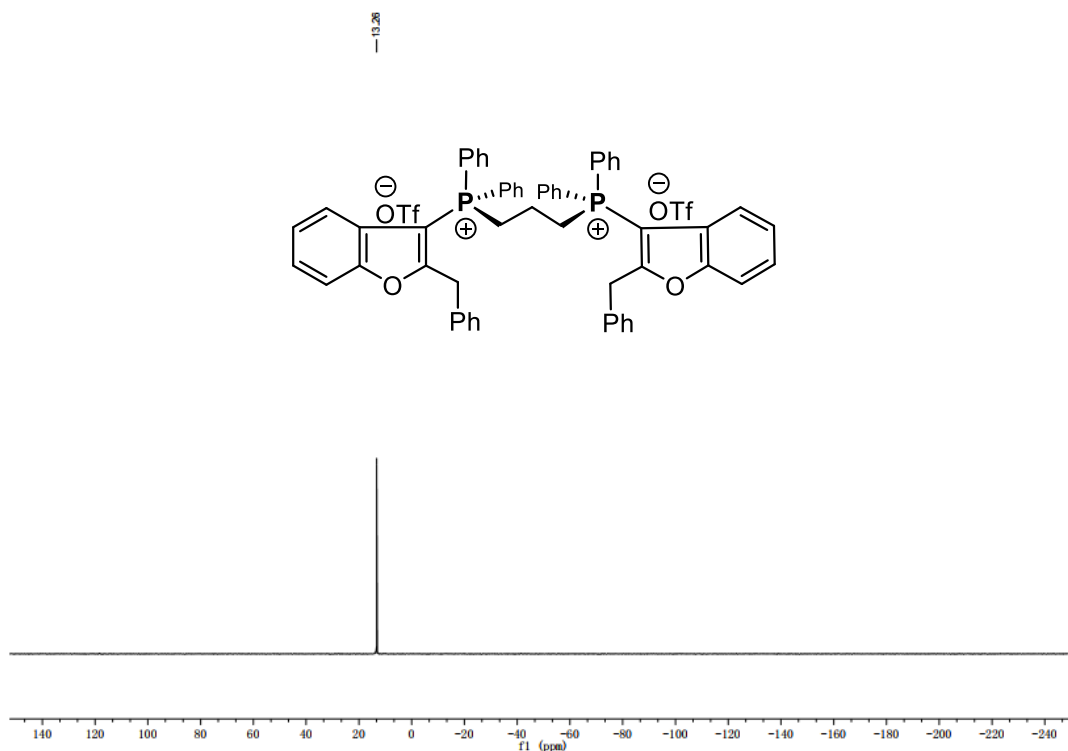
¹³C NMR (126 MHz, CDCl₃) of compound **3ar**



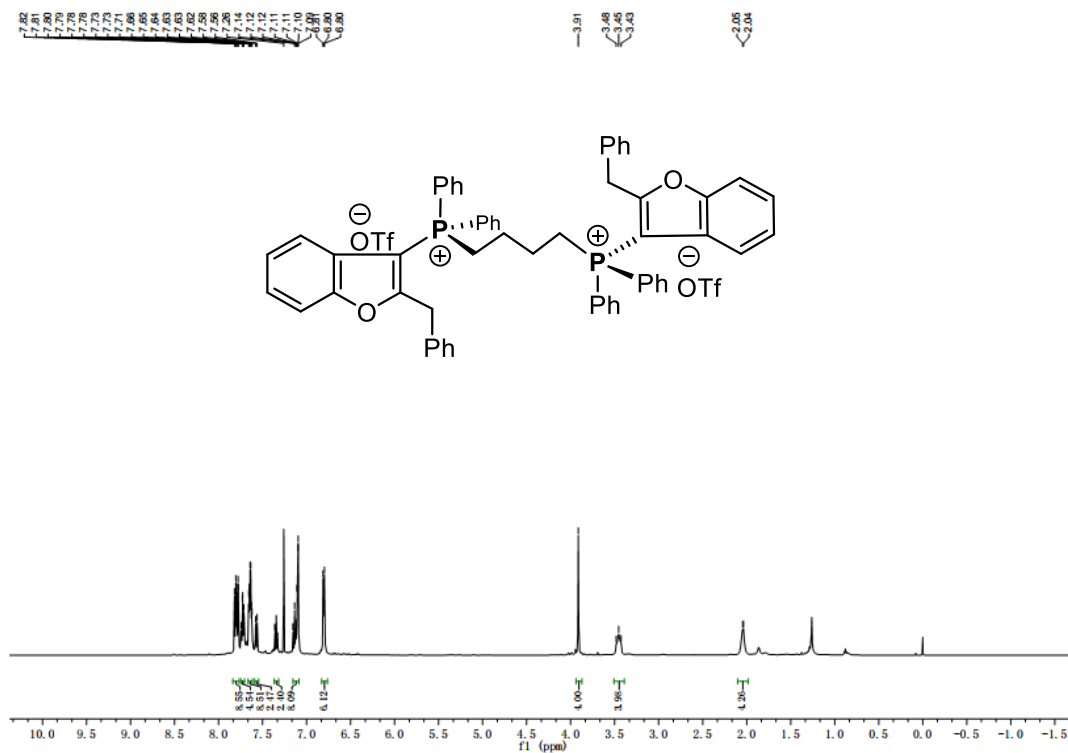
¹⁹F NMR (471 MHz, CDCl₃) of compound **3ar**



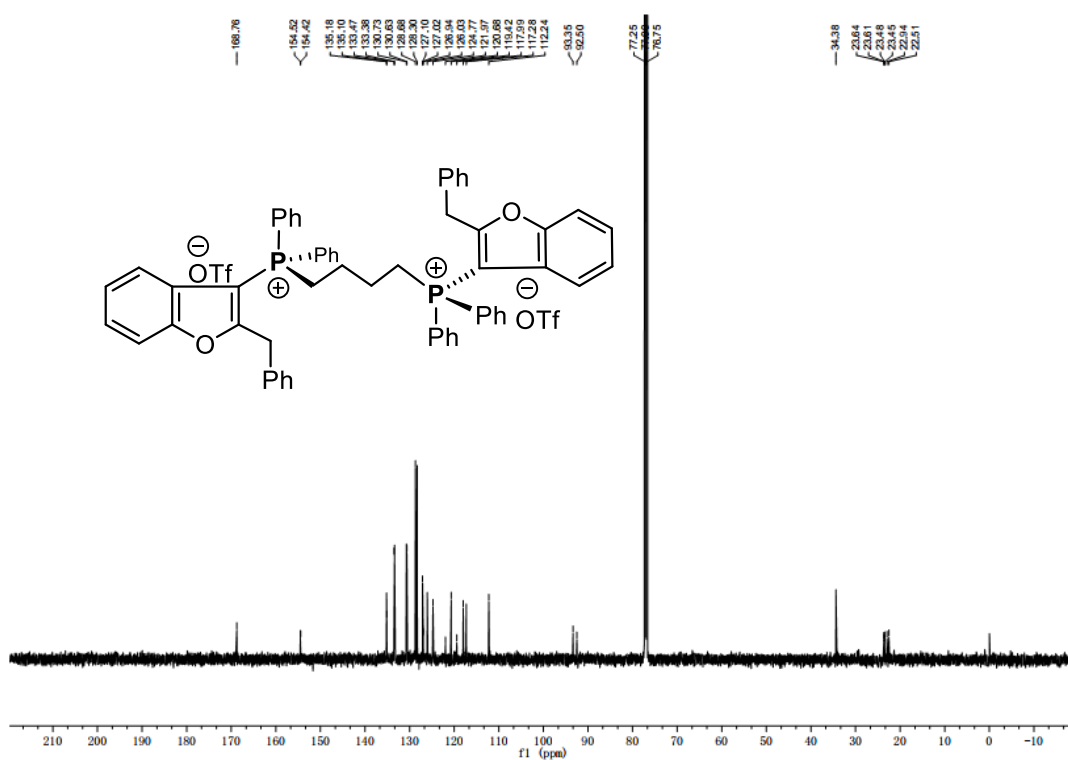
^{31}P NMR (202 MHz, CDCl_3) of compound **3ar**



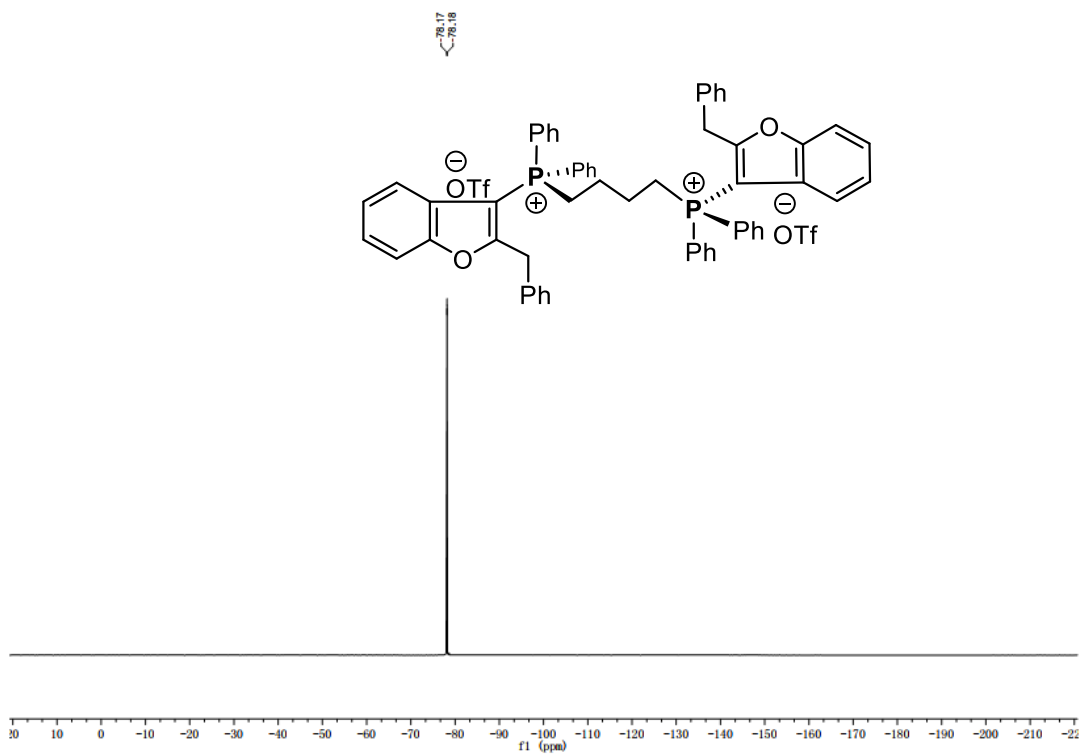
^1H NMR (500 MHz, CDCl_3) of compound **3as**



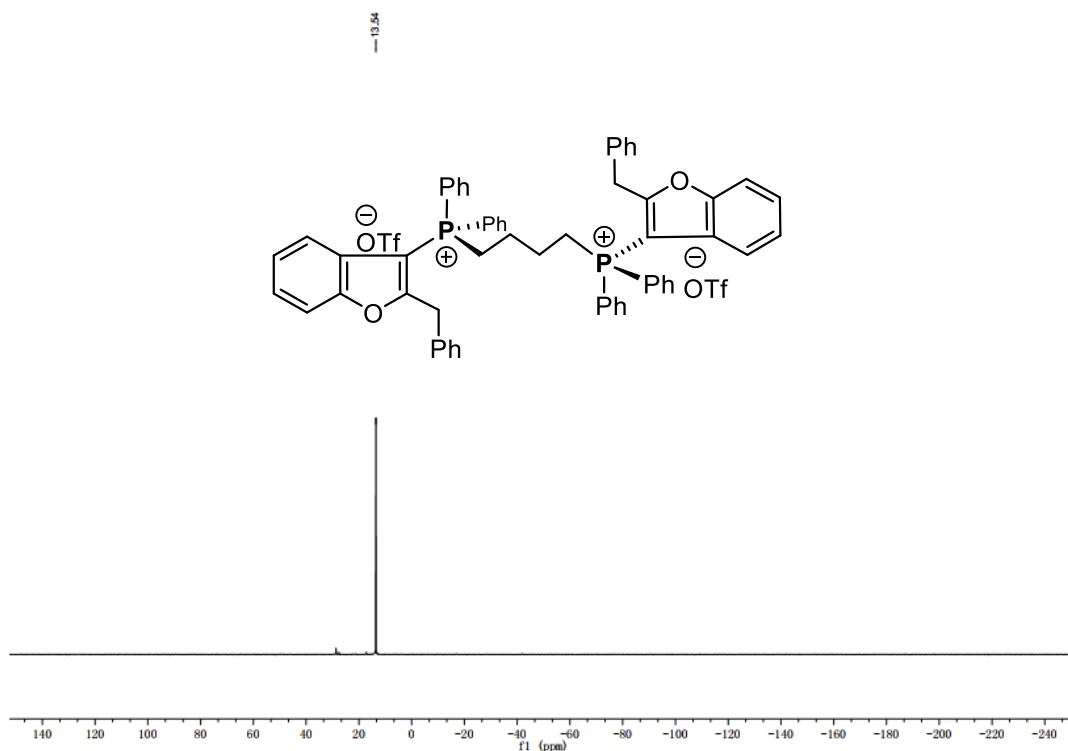
^{13}C NMR (126 MHz, CDCl_3) of compound **3as**



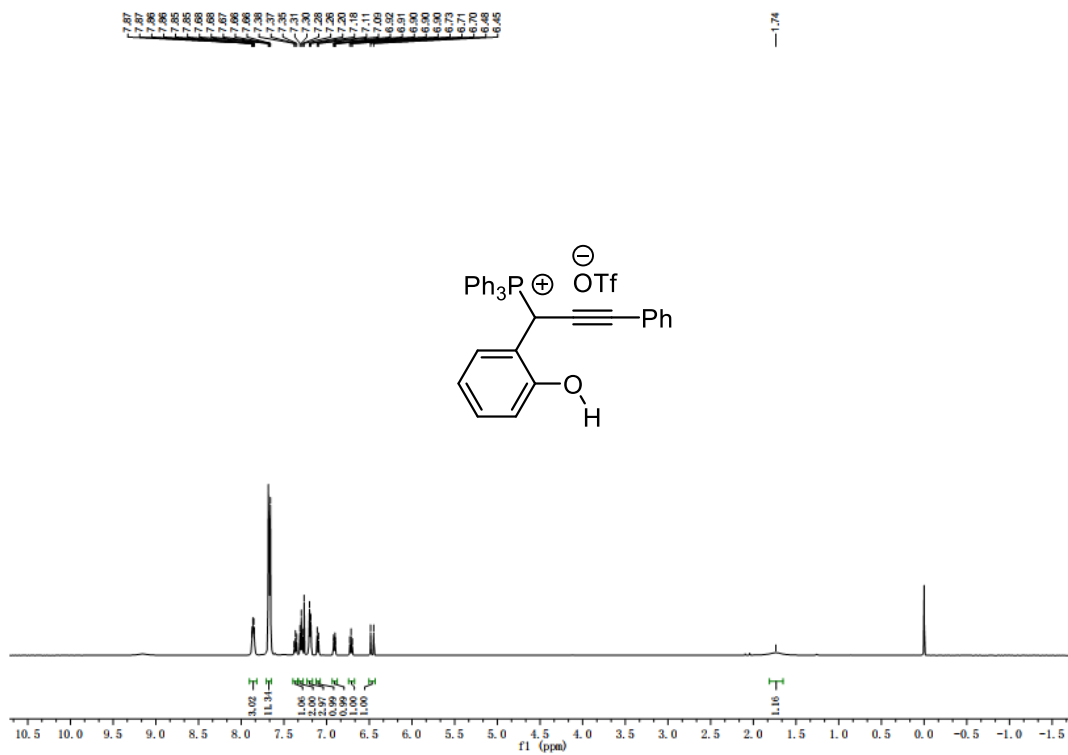
^{19}F NMR (471 MHz, CDCl_3) of compound **3as**



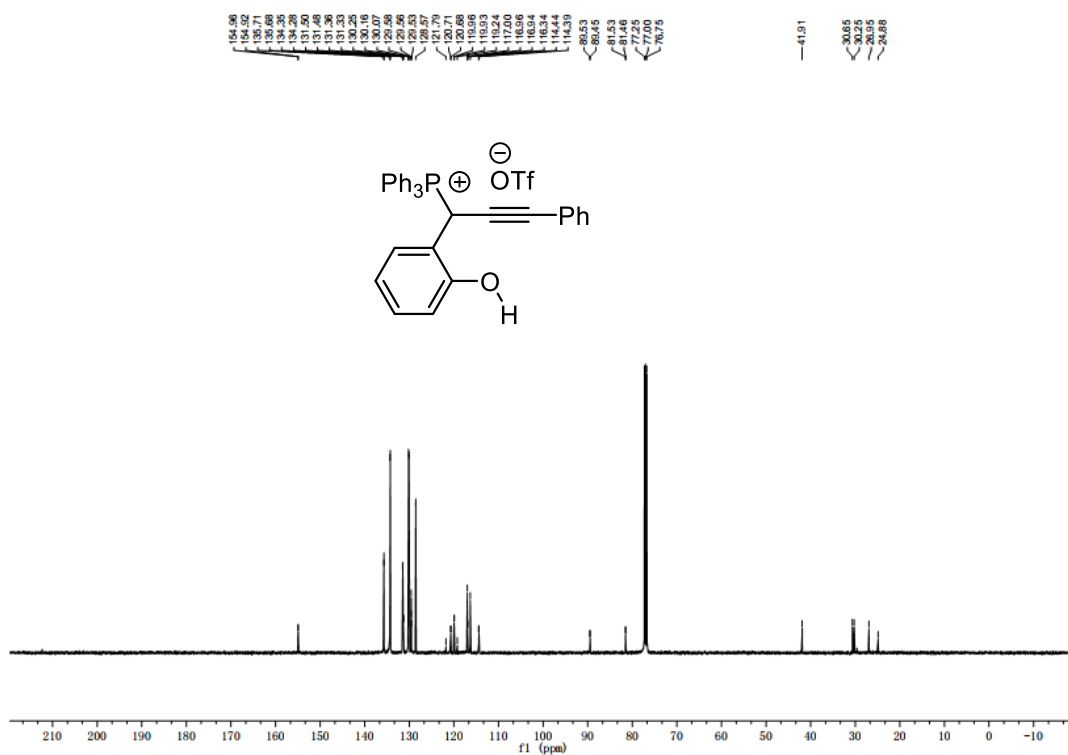
^{31}P NMR (202 MHz, CDCl_3) of compound **3as**



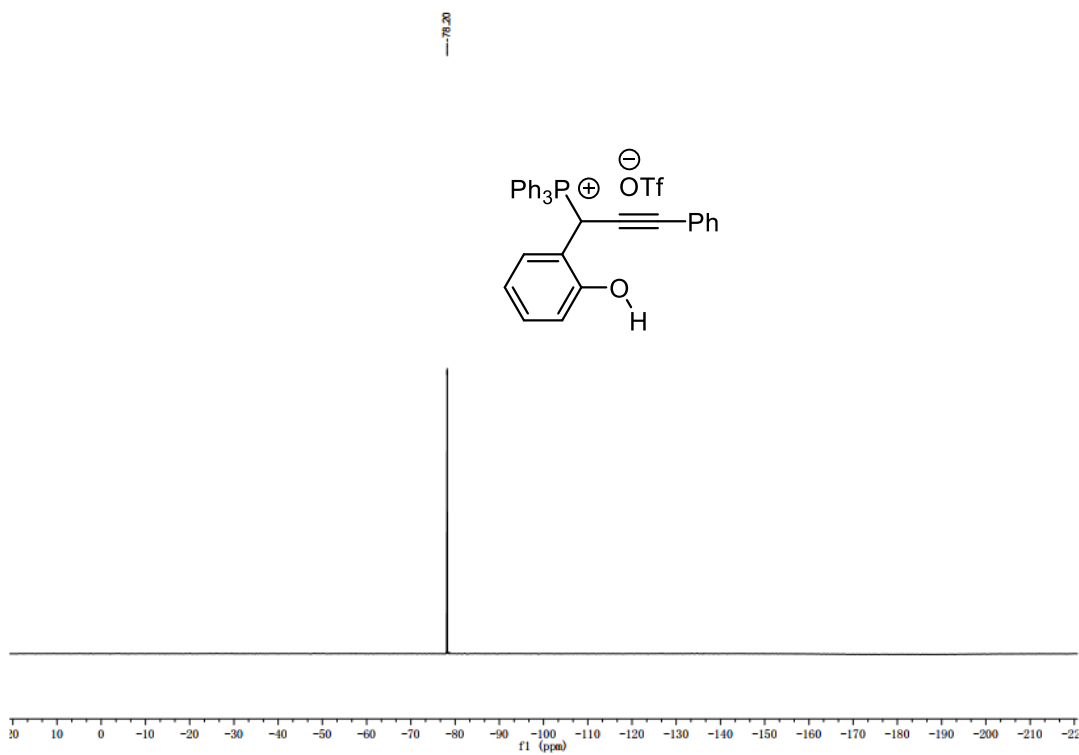
^1H NMR (500 MHz, CDCl_3) of compound **A**



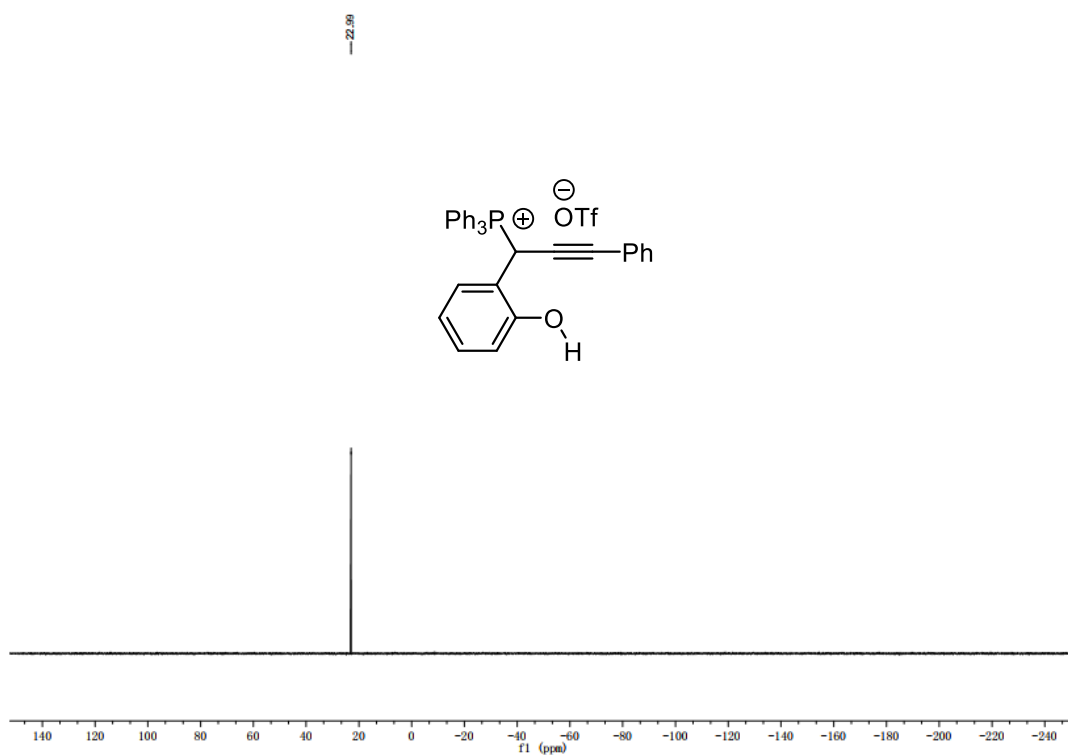
¹³C NMR (126 MHz, CDCl₃) of compound A



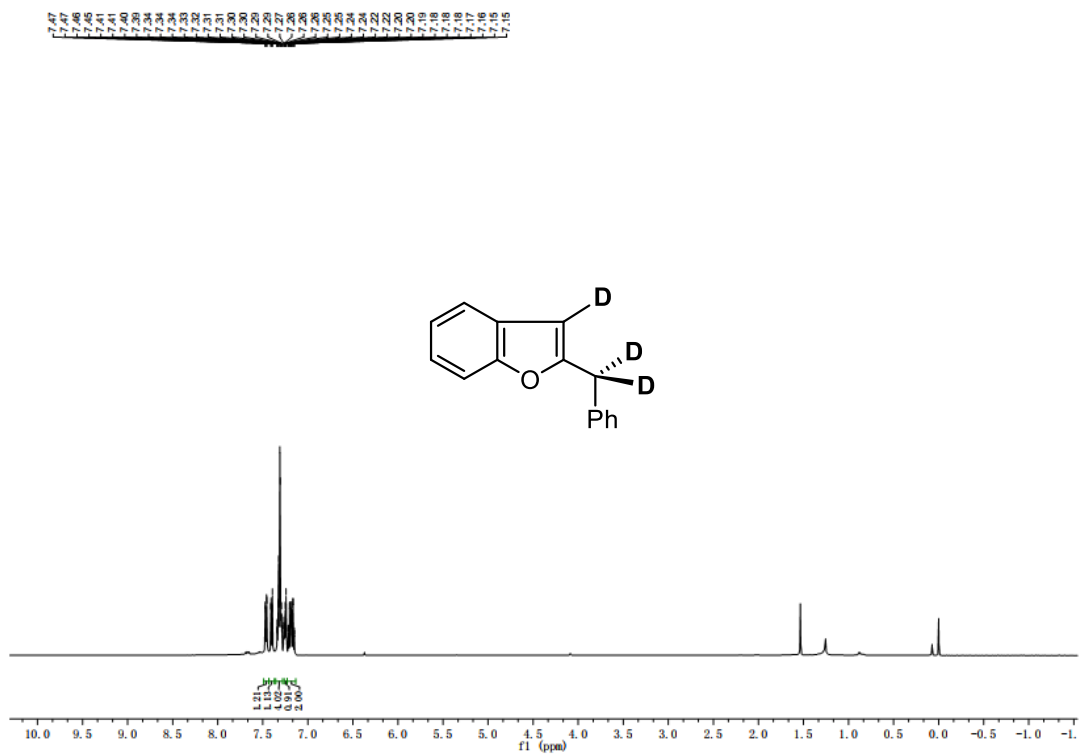
¹⁹F NMR (471 MHz, CDCl₃) of compound A



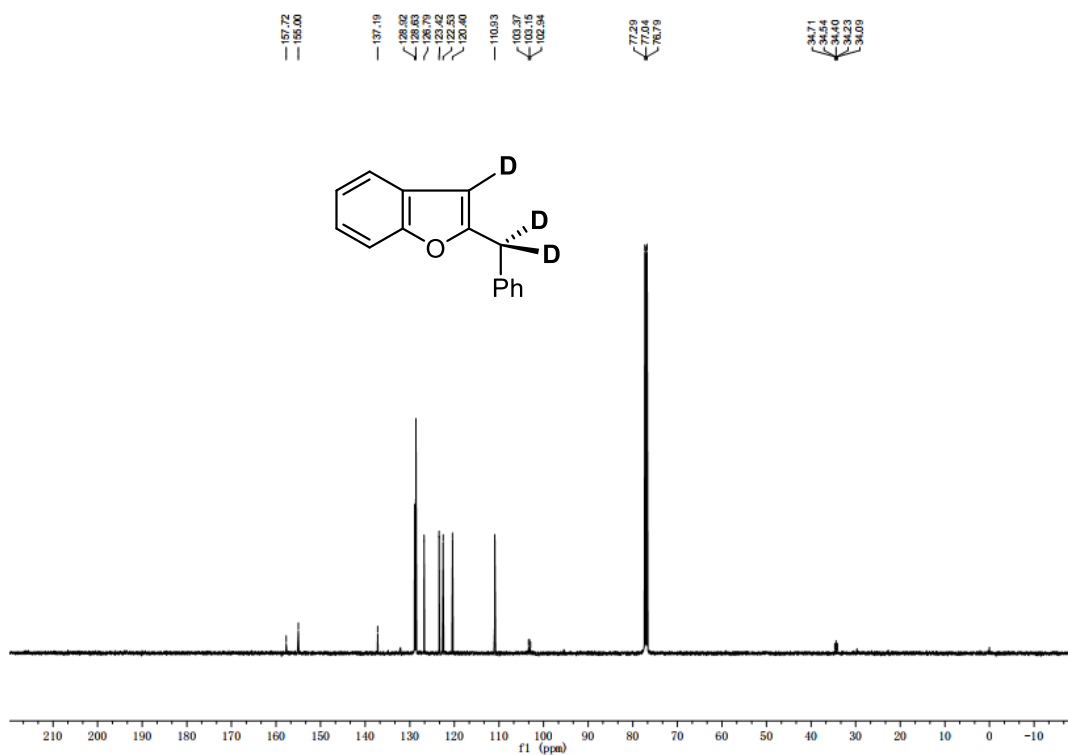
^{31}P NMR (202 MHz, CDCl_3) of compound **A**



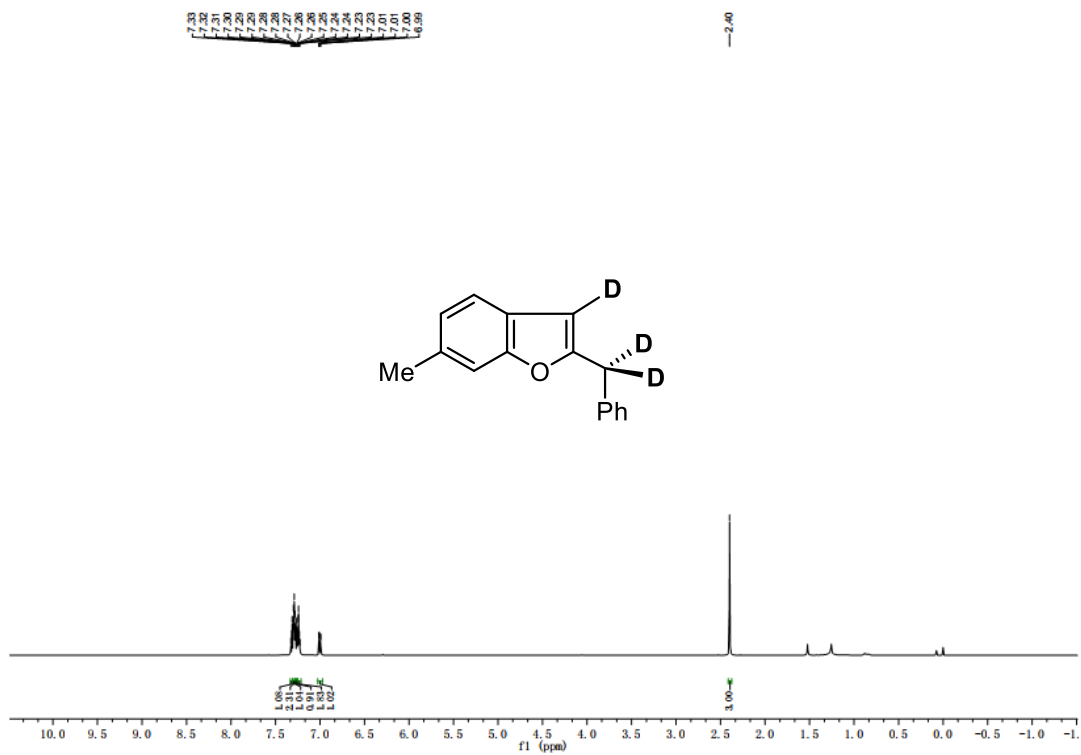
^1H NMR (500 MHz, CDCl_3) of compound **8a**



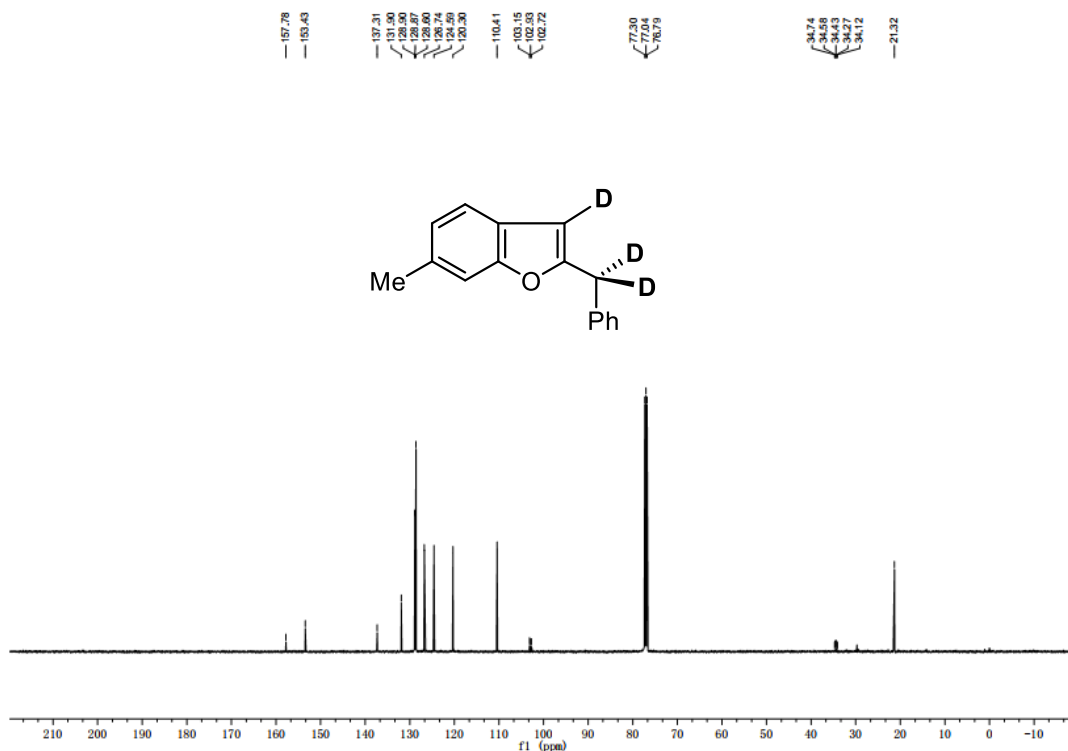
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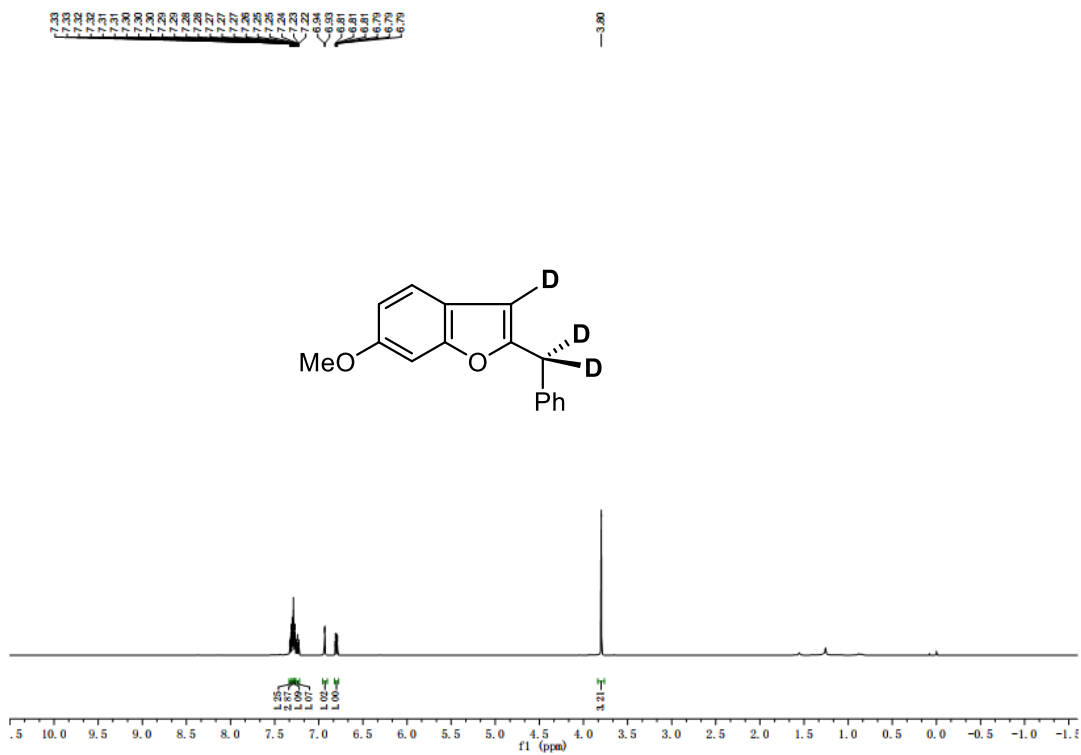
^1H NMR (500 MHz, CDCl_3) of compound **8b**



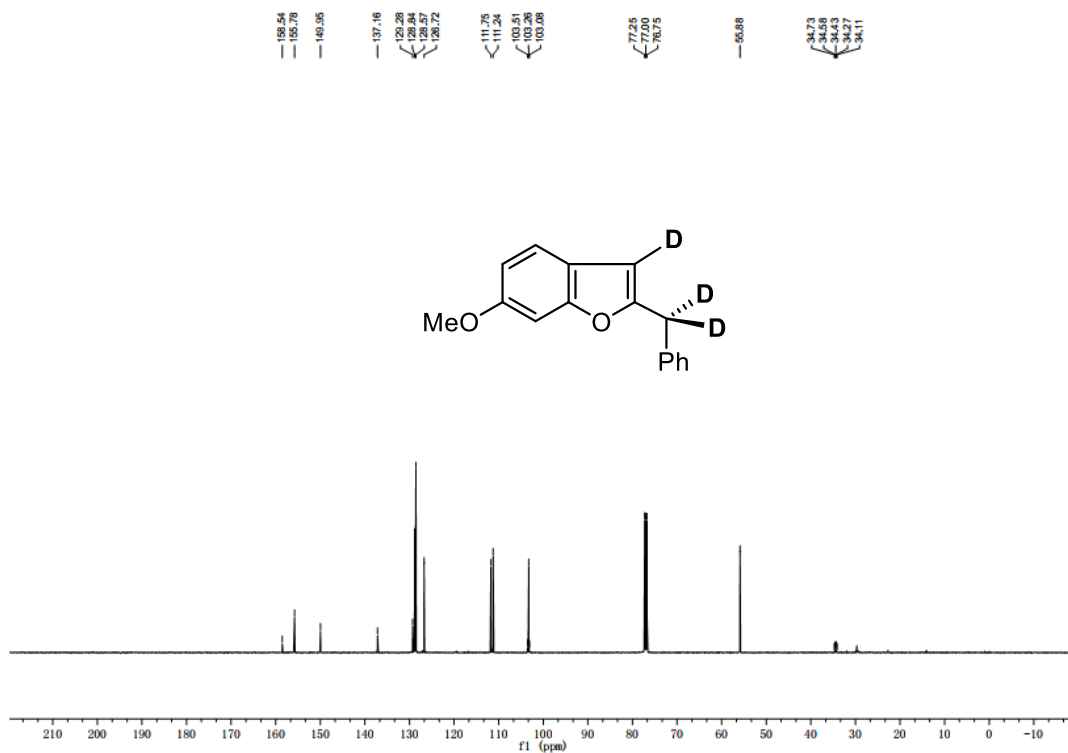
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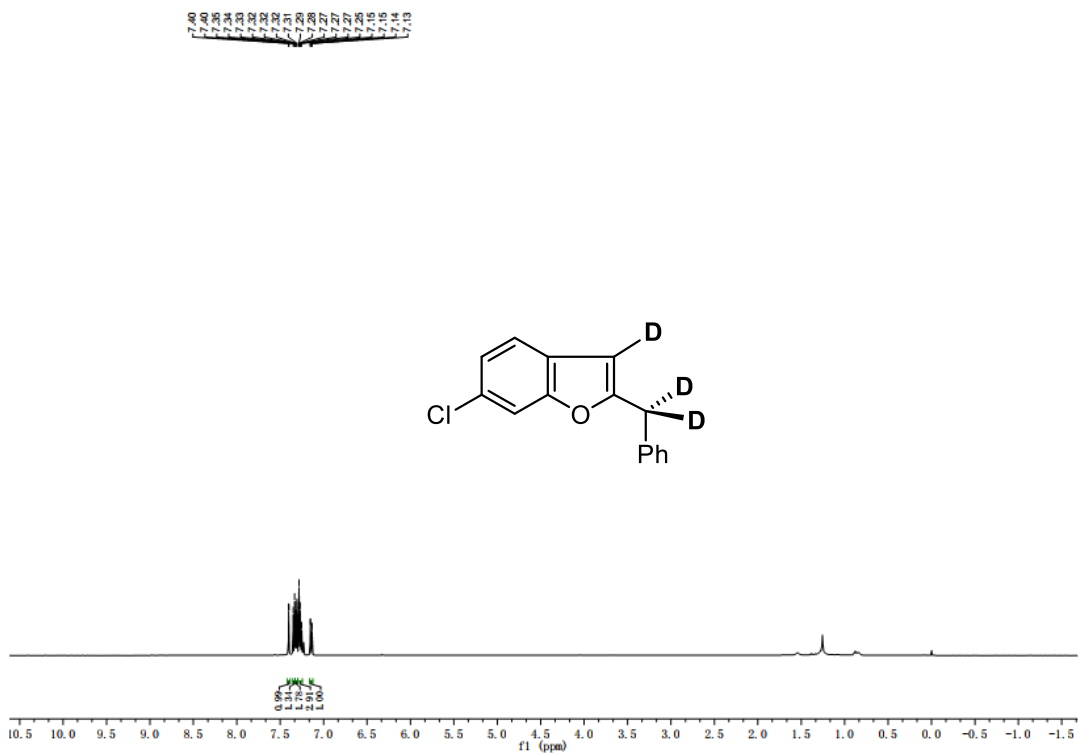
^1H NMR (500 MHz, CDCl_3) of compound **8c**



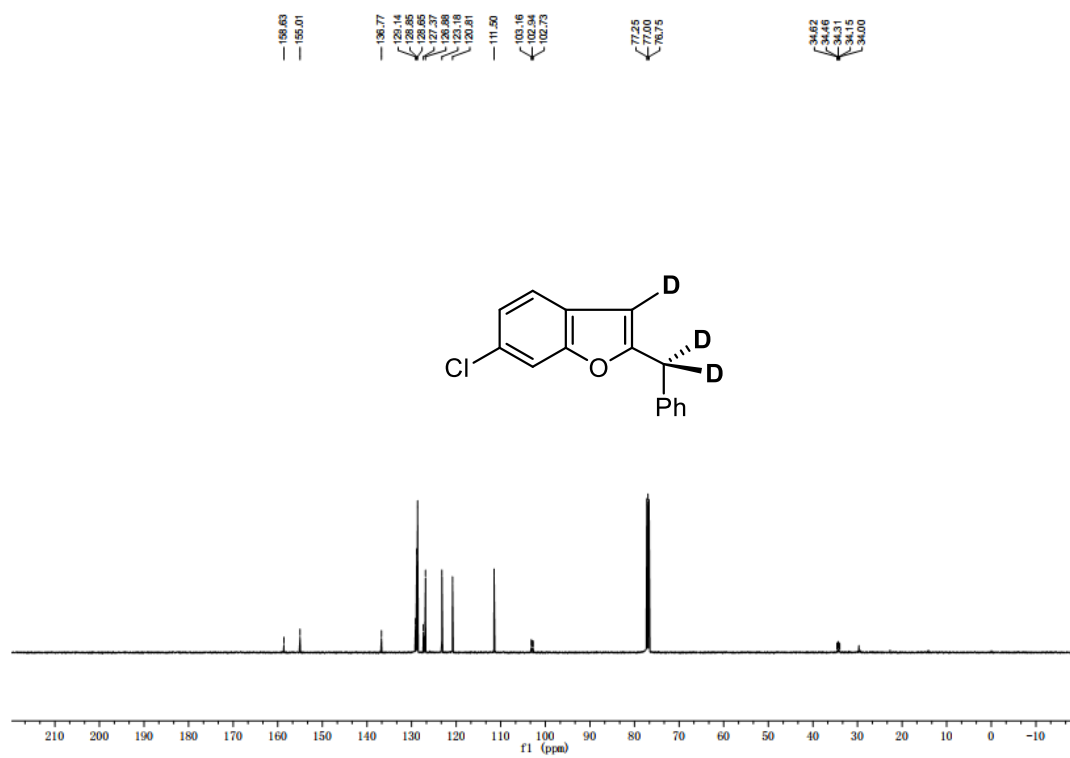
^{13}C NMR (126 MHz, CDCl_3) of compound **8c**



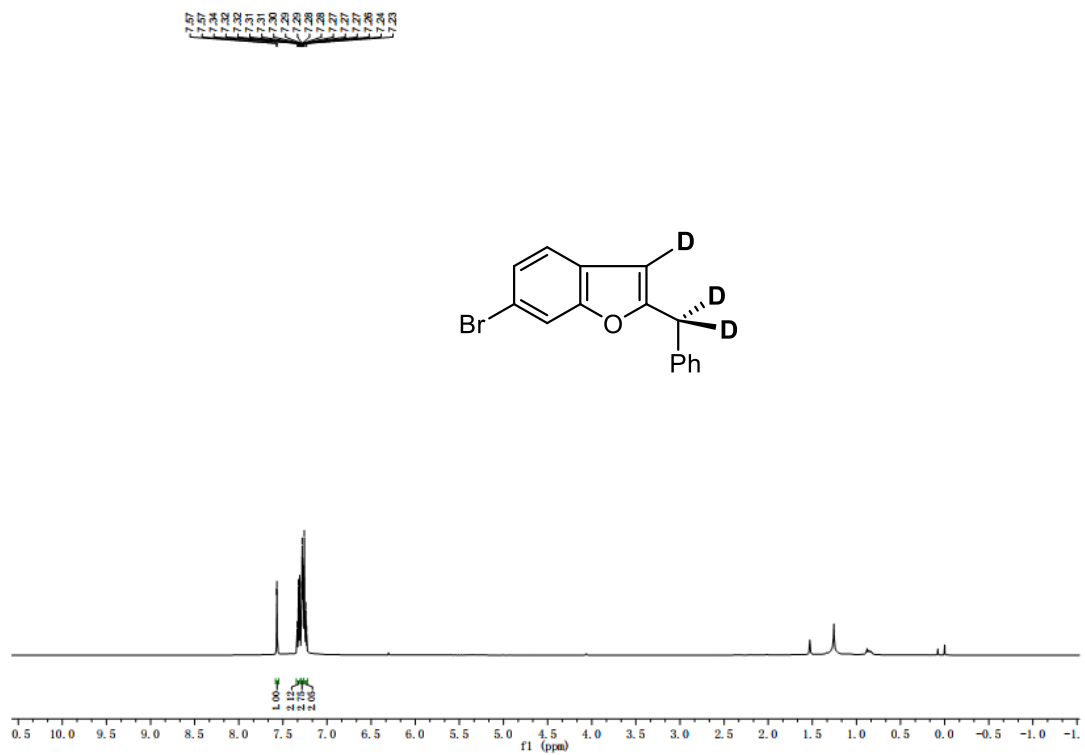
^1H NMR (500 MHz, CDCl_3) of compound **8d**



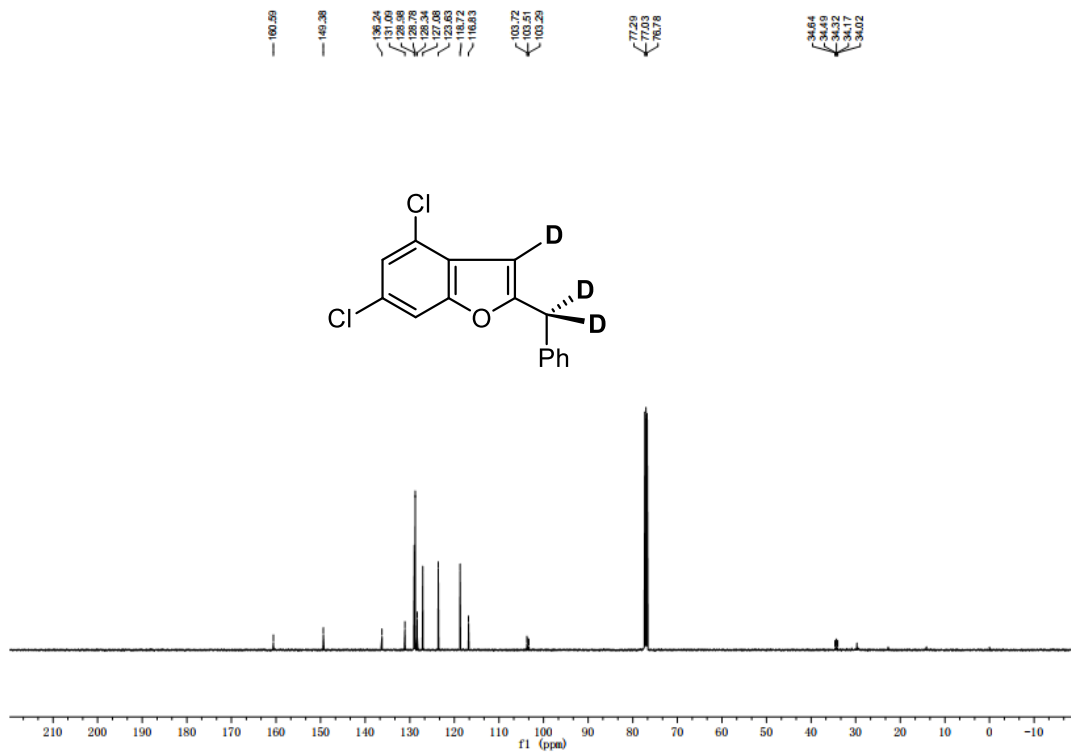
^{13}C NMR (126 MHz, CDCl_3) of compound **8d**



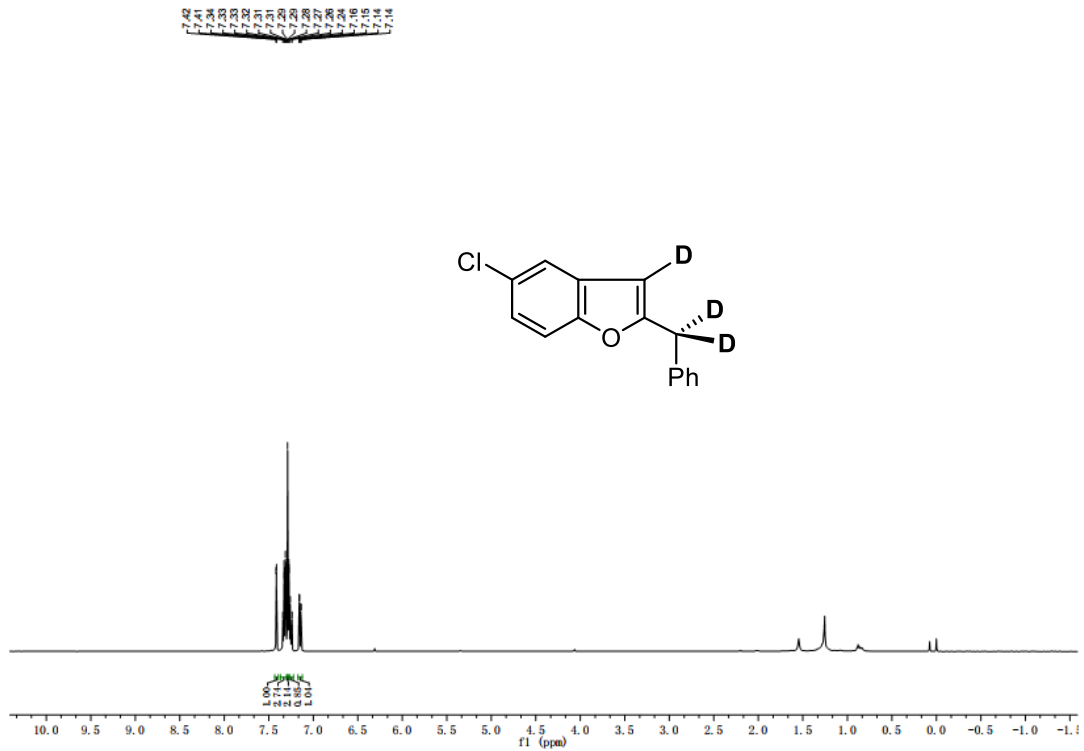
^1H NMR (500 MHz, CDCl_3) of compound **8e**



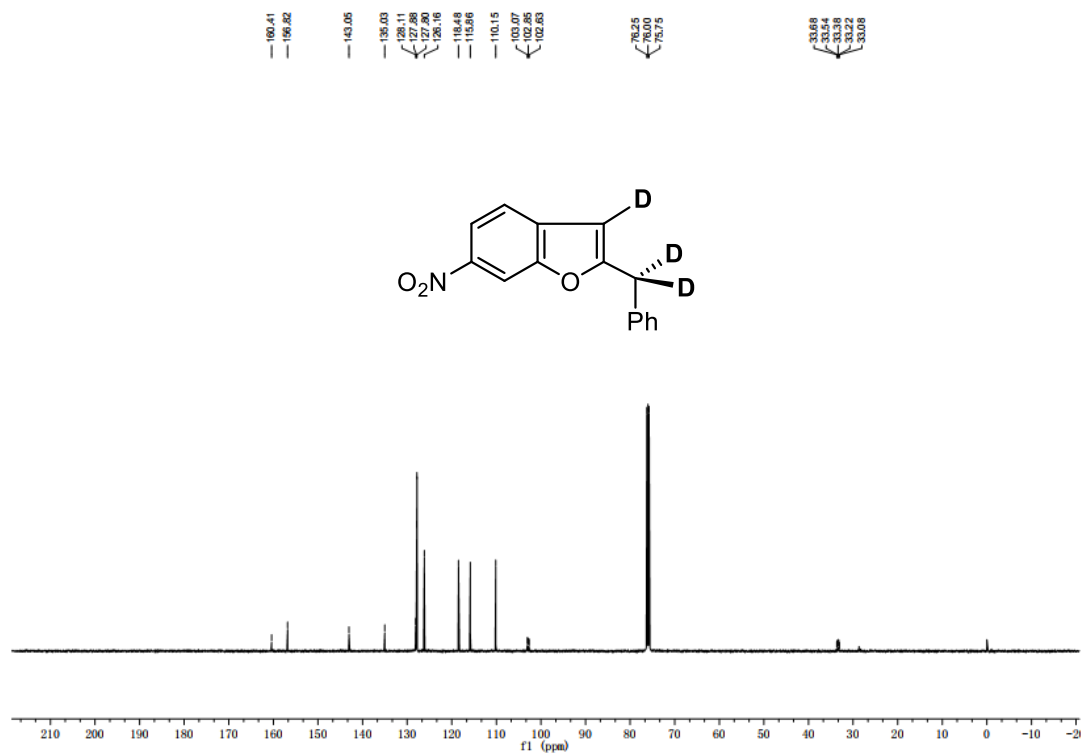
^{13}C NMR (126 MHz, CDCl_3) of compound **8f**



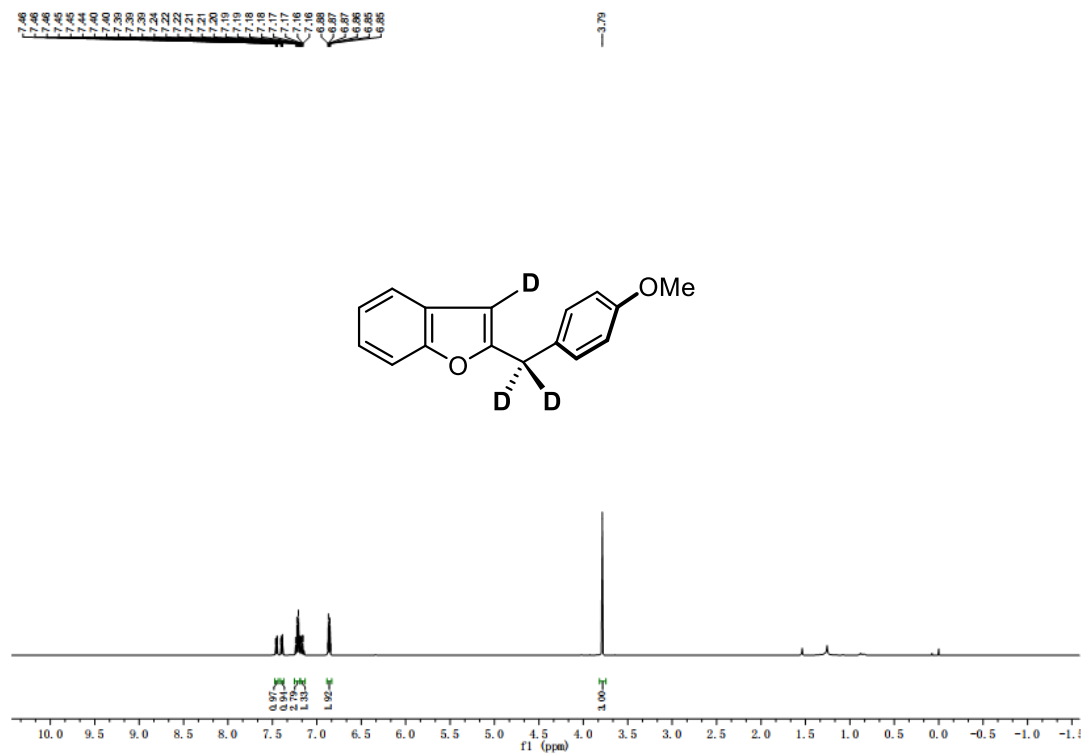
^1H NMR (500 MHz, CDCl_3) of compound **8g**



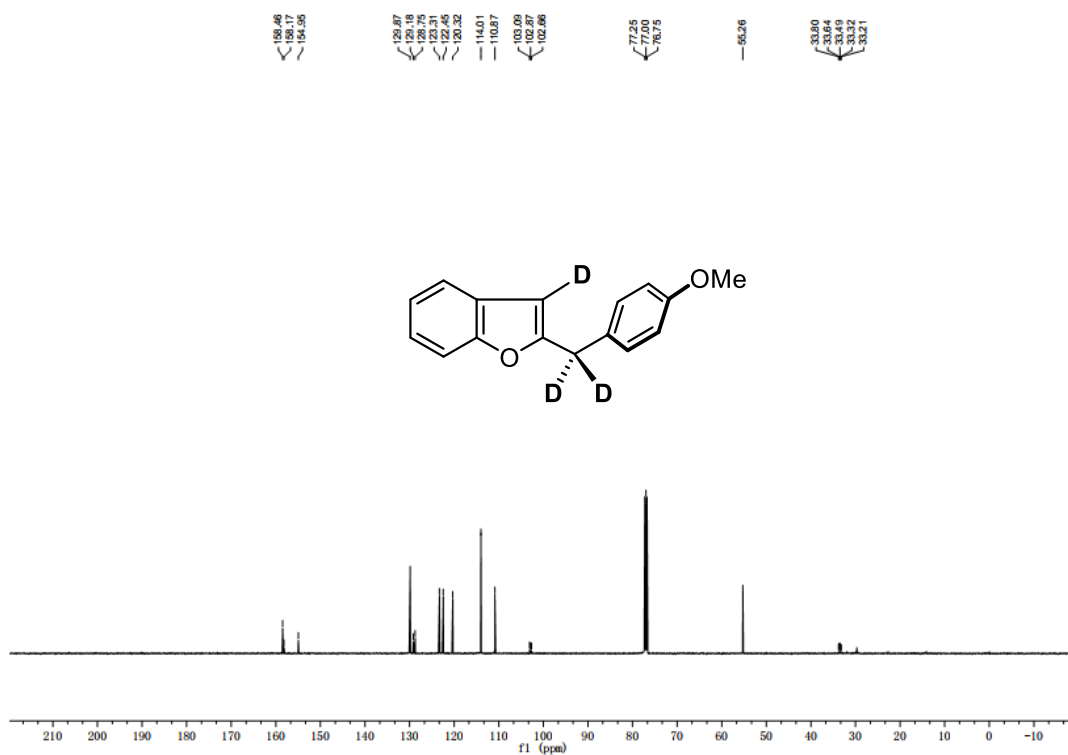
^{13}C NMR (126 MHz, CDCl_3) of compound **8h**



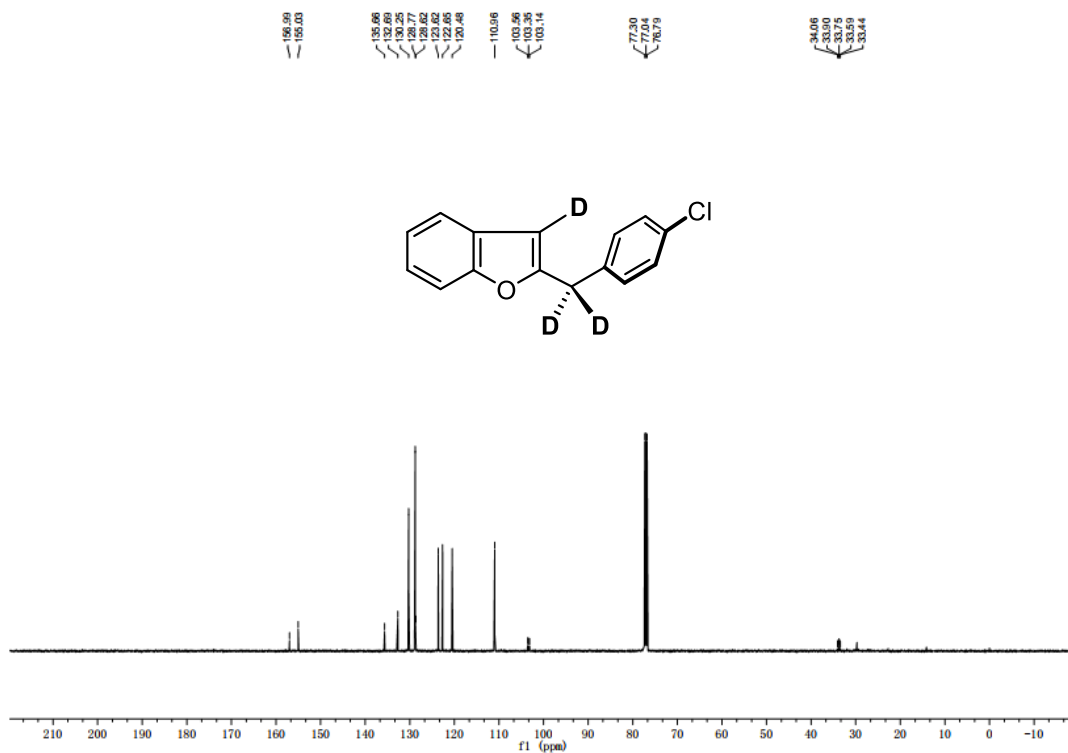
^1H NMR (500 MHz, CDCl_3) of compound **8i**



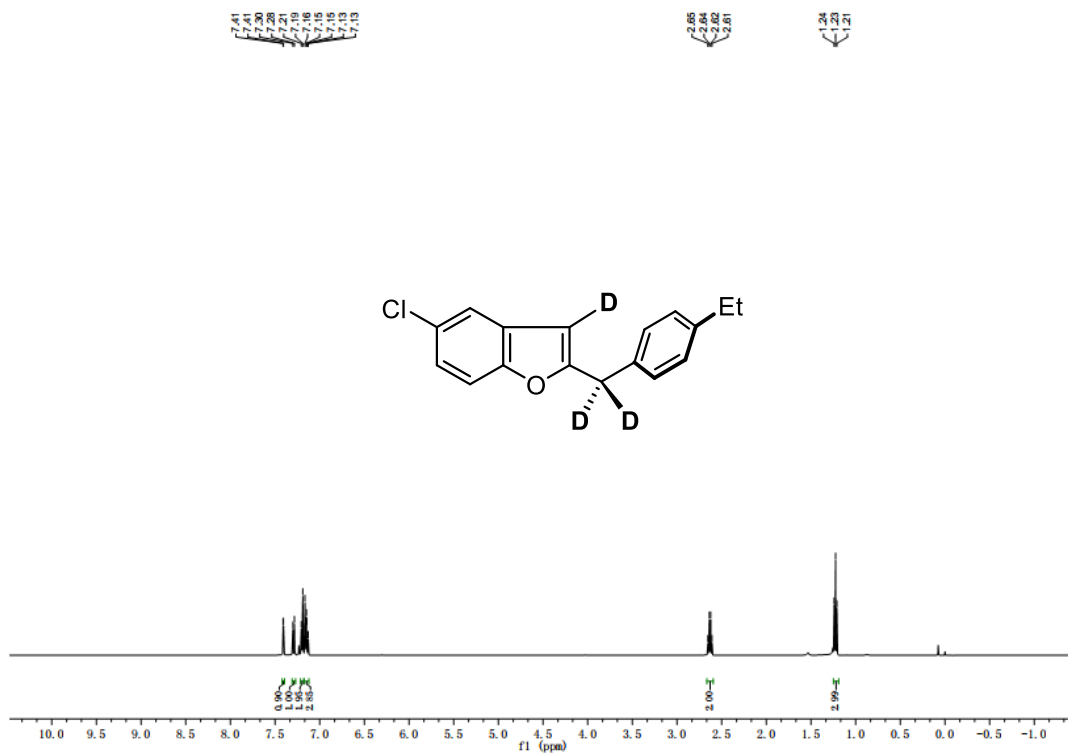
^{13}C NMR (126 MHz, CDCl_3) of compound **8i**



^{13}C NMR (126 MHz, CDCl_3) of compound **8j**



^1H NMR (500 MHz, CDCl_3) of compound **8k**



^{13}C NMR (126 MHz, CDCl_3) of compound **8k**

