Supporting Information

TBAI-Catalyzed Oxidative C-H Functionalization: A New Route to Benzo[*b*]phosphole Oxides

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General Information:

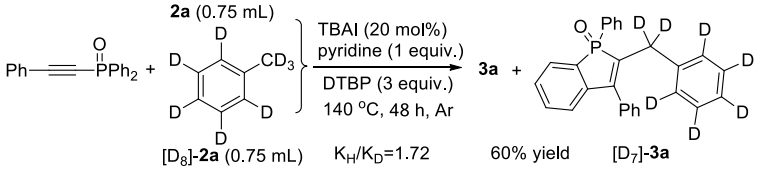
1a-**1y** substrates were prepared according to the known references: (a) *J. Org. Chem*. 2013, **78**, 12802; (b) *J. Org. Chem*. 2014, **79**, 3678. Other reagents were purchased from commercial sources and used without further purification. Spectroscopy data of the known compounds matches with the data reported in the corresponding references. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Av400 spectrometer using tetramethylsilane (TMS) in $CDCl_3$ as the internal standard for ^{1}H, and ^{13}C NMR (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm) and 85% H_3PO_4 as external standard for ^{31}P NMR. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. ESI mass spectra was aquired on a Bruker Dalton Esquire3000 Plus mass spectrometer. HRMS spectra of new compounds were recorded on a Waters Micromass LCT Premier TOF-MS apparatus. Infrared spectra were recorded on a Nicollet Avatar 330 spectrometer. Melting points were recorded on a WRS-1B Digital Melting-Point apparatus. The products were purified by Column chromatography on silica gel 300-400 mesh.

Experimental section:

General procedure for the synthesis of 3: To a sealed tube equipped with a magnetic stir bar were added under argon TBAI (23 mg, 0.06 mmol), pyridine (23.7 mg, 0.3 mmol) and diaryl(arylethynyl)phosphine oxides (0.3 mmol). Under argon, toluene derivatives (1.5 mL, except for solid **2i** (2.52 g) and **2m** (1.53g)) and DTBP (di-*tert*-butyl peroxide, 0.9 mmol) were added. The resulting reaction mixture was kept stirring at 140 ℃ for 30 h. After required reaction time, the mixture was cooled down to room temperature and purified by flash chromatography (petroleum ether/ethyl acetate) afforded the corresponding product.

Competing Kinetic Isotope Effect (KIE) Experiment:

A mixture of diphenyl(phenylethynyl)phosphine oxide (91 mg, 0.3 mmol), TBAI (23 mg, 0.06 mmol), pyridine (23.7 mg, 0.3 mmol) and DTBP (0.9 mmol) in toluene (0.75 mL) and toluene-D_8 (0.75 mL) under argon in a sealed tube was stirred at 140 ℃ for 30 h. After cooling to room temperature, the mixture was concentrated under vacuum. The residue was purified by silica gel preparative thin layer chromatography with petroleum ether/ethyl acetate = 2/1 to afford the product.



Scheme S1. The kinetic deuterium isotope effect for reactions between toluene and **3a**

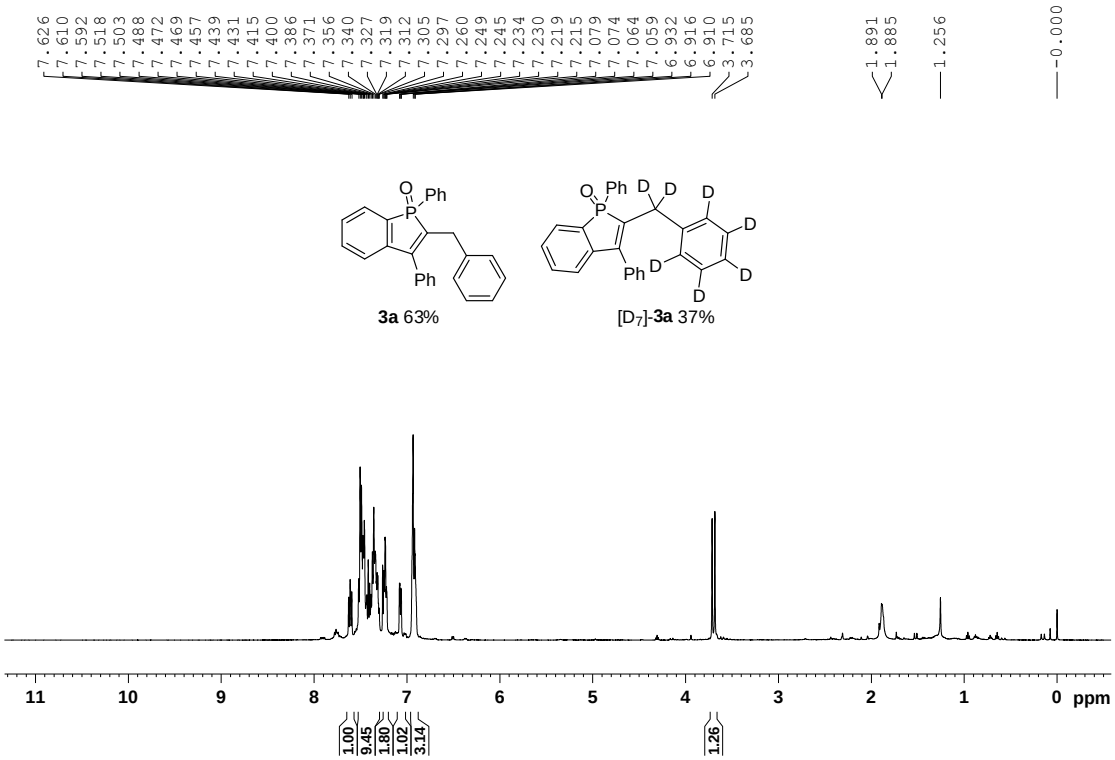
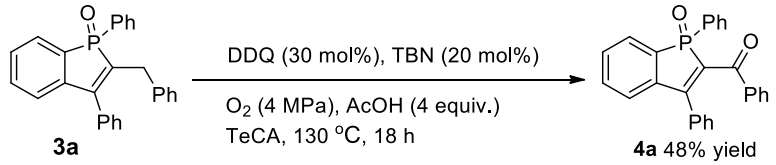


Figure S1. ^{1}H NMR spectra of the mixture of compound **3a** and [D_7]-**3a**.

Note: The value of k_H/k_D was calculated from the ^{1}H NMR spectra above which should be the mixture of compound **3a** and [D_7]-**3a** (Scheme ***S1***). The sum of the integral of **3a** and [D_7]-**3a** at chemical shift 7.62-7.59 was integrated as 1.00. Compound **3a** has 2 hydrogen atoms at chemical shift 3.71-3.68, while [D_7]-**3a** has no H atoms. The amount of **3a** could be defined as 0.63 (1.26/2=0.63), on the other hand, the sum of **3a** and [D_7]-**3a** is 1.00, so the amount of [D_7]-**3a**

is 0.37 (1.00-0.63 = 0.37). As a result, k_H/k_D = 0.63/0.37 = 1.72.

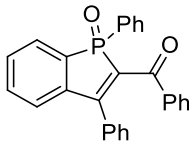
Derivatization Reaction:



Scheme S2. Derivatization of **3a**

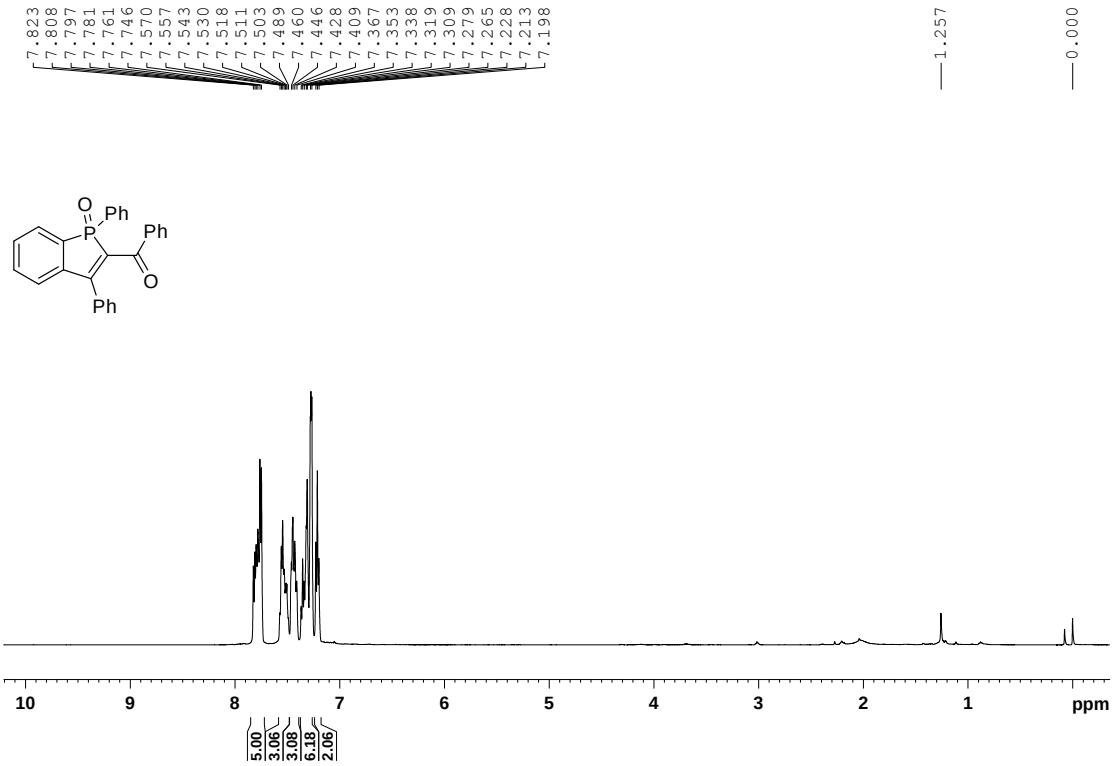
A Teflon-lines 316 L stainless steel autoclave (300 mL) equipped with magnetic stirring bar was charged with **3a** (196 mg, 0.5 mmol), DDQ (1,2-dichloro-4,5-dicyanobenzoquinone, 34.1 mg, 0.15 mmol, 30 mol%), TBN (*tert*-butyl nitrite, 10.3 mg, 0.1 mmol, 20 mol%), acetic acid (120 mg, 2 mmol) and 5 mL TeCA (1,1,2,2-tetrachlorethane). The autoclave was closed and charged with oxygen to 4 MPa. Then the autoclave was placed in an oil bath, which was preheated to 130 ℃. After 18 h, the autoclave was taken out from the oil bath, cooled to room temperature and carefully depressurized. The mixture was concentrated under reduced pressure and purified by column chromatography.

Spectral data:

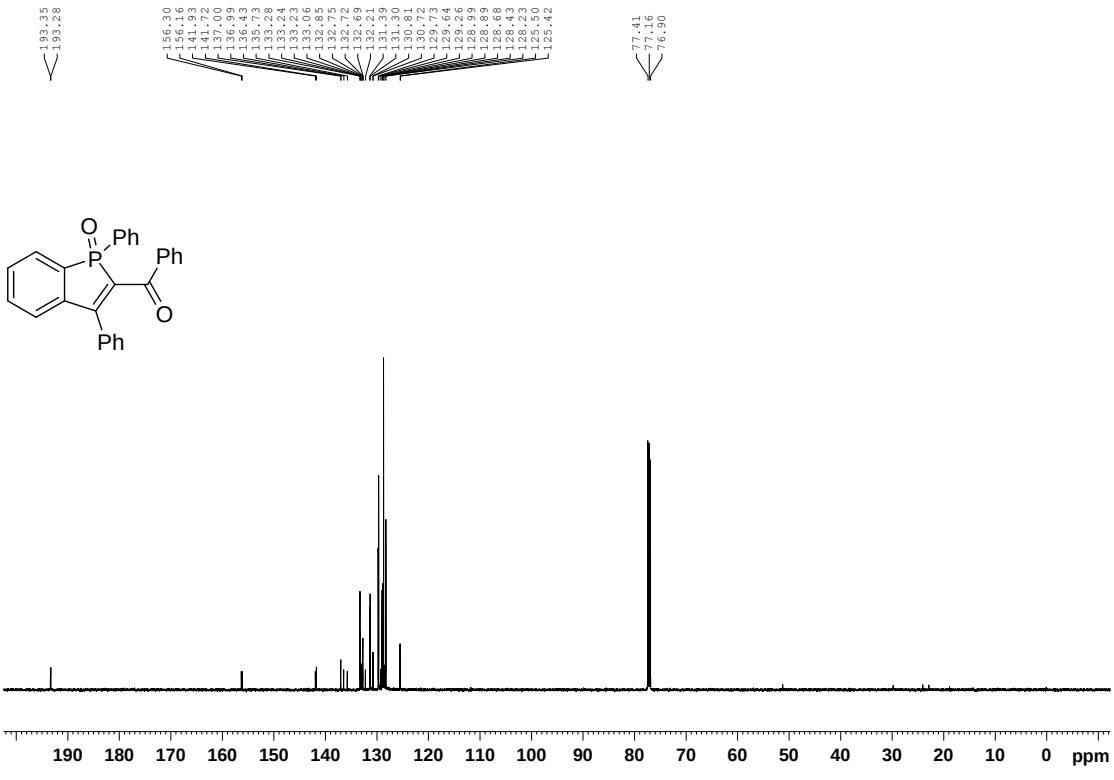


(1-oxido-1,3-diphenyl-1*H*-phosphindol-2-yl)(phenyl)methanone, yellow solid; m.p.: 96.6-97.3 ℃;^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.40 (m, 5 H), 7.55-7.49 (m, 3 H), 7.46-7.39 (m, 3 H), 7.36-7.26 (m, 6 H), 7.23-7.19 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.3 (d, J_{C-P} = 8.8 Hz), 156.2 (d, J_{C-P} = 1.6 Hz), 141.8 (d, J_{C-P} = 26.1 Hz), 137.0 (d, J_{C-P} = 1.8 Hz), 136.1 (d, J_{C-P} = 88.1 Hz), 133.3, 133.2 (d, J_{C-P} = 1.6 Hz), 133.1, 132.8 (d, J_{C-P} = 13.7 Hz), 132.7 (d, J_{C-P} = 2.8 Hz), 132.2, 131.3 (d, J_{C-P} = 11.4 Hz), 130.8 (d, J_{C-P} = 10.9 Hz), 129.7, 129.6, 129.3, 128.9 (d, J_{C-P} = 12.8 Hz), 128.7, 128.4, 128.2, 125.5 (d, J_{C-P} = 11.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 38.2; IR (film) υ_{max}: 3057, 1646, 1558, 1521, 1196 (P=O), 1131, 1077 cm^{-1}; HRMS: $[M+Na]^+$ m/z calcd for $C_{17}H_{21}OPNa^+$: 429.1015, found: 429.1015.

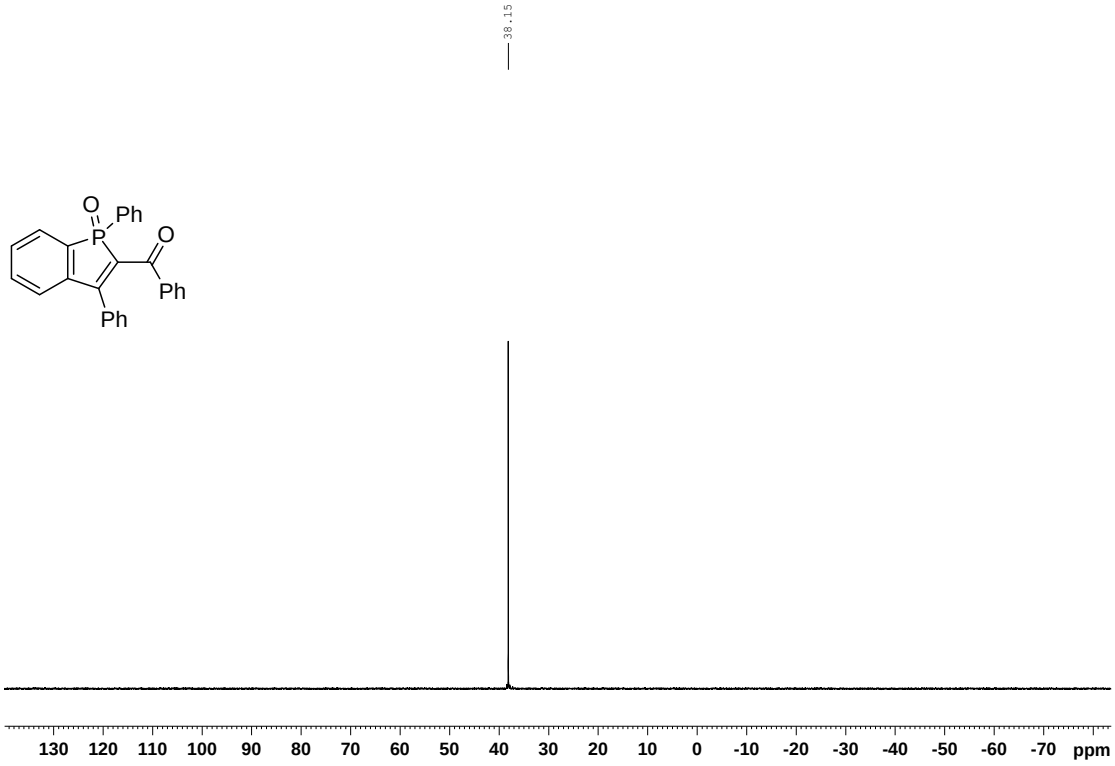
^{1}H NMR of **4a**



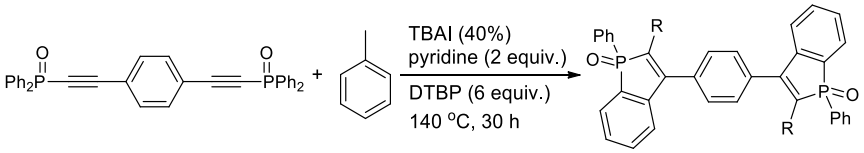
^{13}C NMR of **4a**



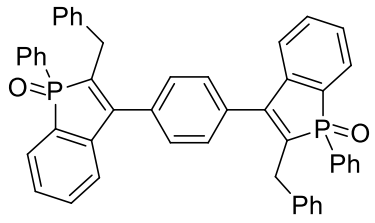
^{31}P NMR of **4a**



Application for the Synthesis of Bis(benzo[*b*]phosphole oxides) 3w.



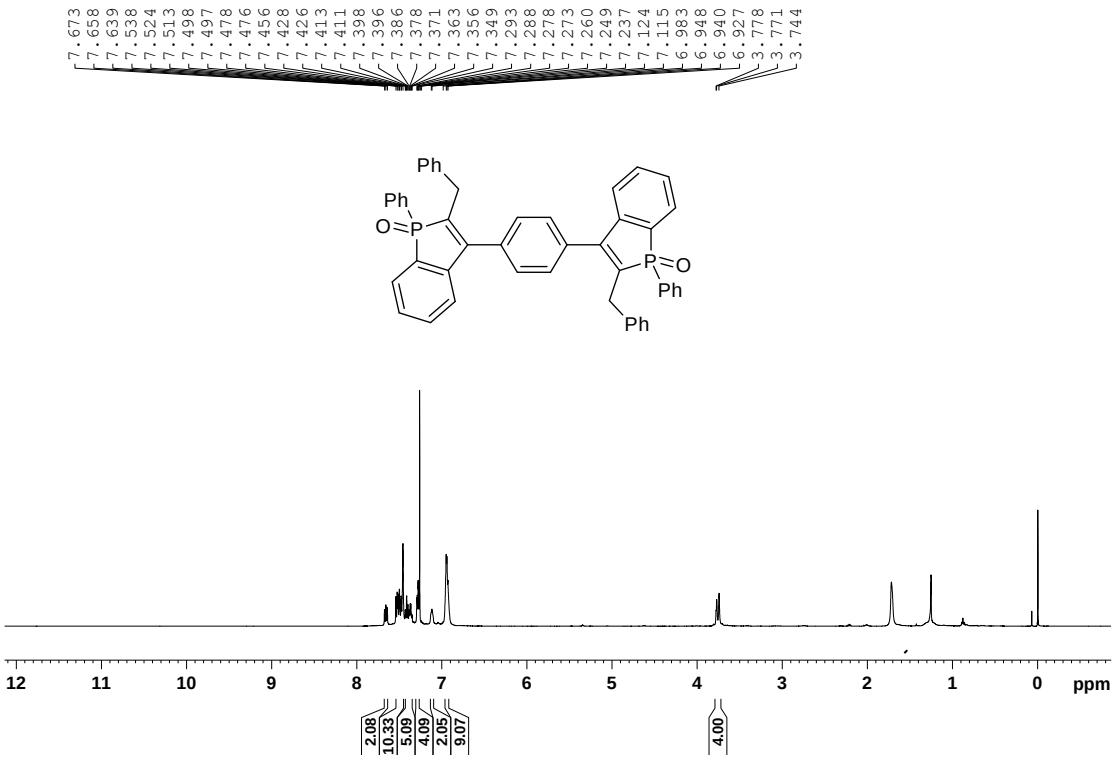
A mixture of **1x** (211 mg, 0.40 mmol), TBAI (59 mg, 0.16 mmol), pyridine (0.8 mmol) and DTBP (2.4 mmol) in toluene (4.0 mL) under argon in a sealed tube was stirred at 140 ^{o}C for 30 h. After cooling to room temperature, the mixture was concentrated under vacuum. The residue was purified by silica gel preparative thin layer chromatography with CH_2Cl_2/MeOH = 60/1 to afford the desired product **3x**.



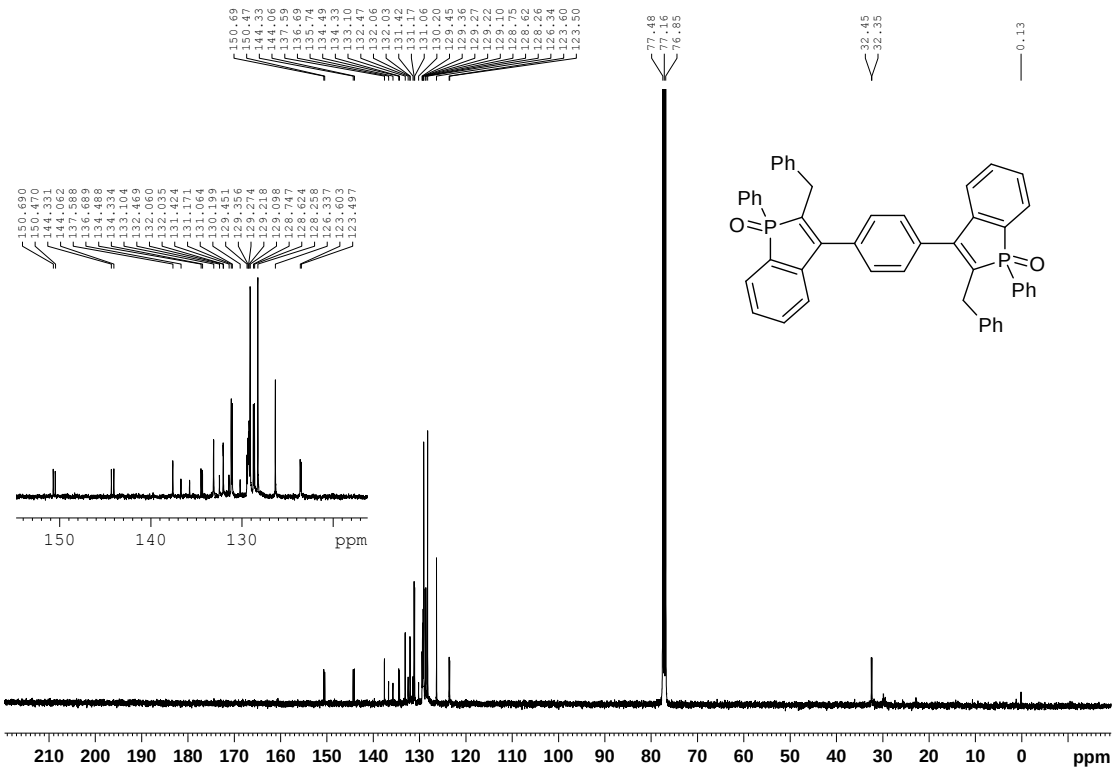
3,3'-(1,4-phenylene)bis(2-benzyl-1-phenyl-1*H*-phosphindole 1-oxide) (**3x, new compound**),

white solid, m.p.: 102.9-104.2 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67-7.64 (m, 2 H), 7.54-7.46 (m, 10 H), 7.43-7.35 (m, 5 H), 7.29-7.27 (m, 4 H), 7.12-7.11 (m, 2 H), 6.95-6.93 (m, 9 H), 3.78-3.74 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.6 (d, $J_{C\text{-}P}$ = 22.2 Hz), 144.2 (d, $J_{C\text{-}P}$ = 27.1 Hz), 137.6, 136.2 (d, $J_{C\text{-}P}$ = 95.1 Hz), 134.4 (d, $J_{C\text{-}P}$ = 15.5 Hz), 133.1, 131.9 (d, $J_{C\text{-}P}$ = 105.0 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.8 Hz), 130.2 (d, $J_{C\text{-}P}$ = 96.0 Hz, overlapped), 129.4 (d, $J_{C\text{-}P}$ = 9.5 Hz), 129.3 (2C, overlapped),129.2, 129.1, 128.7 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.3, 126.3, 123.6 (d, $J_{C\text{-}P}$ = 10.7 Hz), 32.4 (d, $J_{C\text{-}P}$ = 10.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.6; IR (film) υ_{max}: 3648, 1683, 1652, 1558, 1506, 1456 (P=O), 1437 (P=O), 1131 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{48}H_{36}O_2P_2H^+$: 707.2263, found: 707.2309.

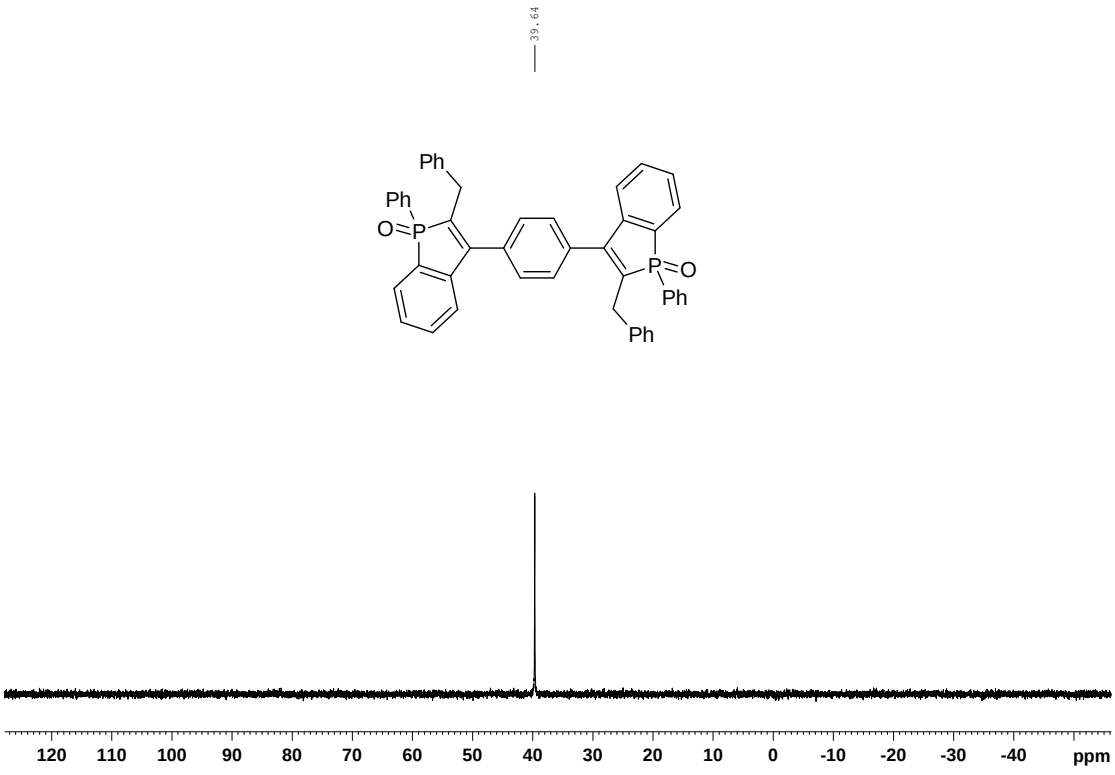
^{1}H NMR of **3x**



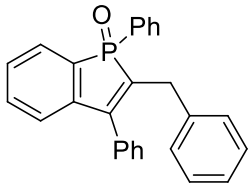
^{13}C NMR of **3x**



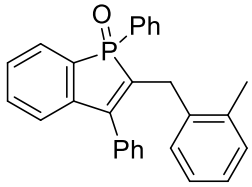
^{31}P NMR of **3x**



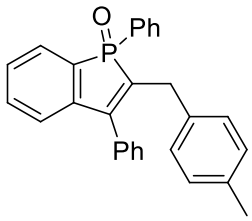
NMR Spectral Data of 3a-3w:



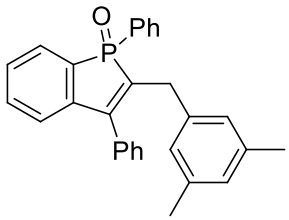
2-benzyl-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3a, new compound**), wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (dd, *J* = 7.2, 9.5 Hz, 1 H), 7.52-7.30 (m, 10 H), 7.25-7.21 (m, 2 H), 7.07 (dd, *J* = 2.9, 7.7 Hz, 1 H), 6.95-6.90 (m, 5 H), 3.70 (d, *J* = 15.01 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.3 (d, $J_{C\text{-}P}$ = 22.2 Hz), 144.4 (d, $J_{C\text{-}P}$ = 27.2 Hz), 137.6 (d, $J_{C\text{-}P}$ = 1.5 Hz), 135.3 (d, $J_{C\text{-}P}$ = 95.5 Hz), 133.8 (d, $J_{C\text{-}P}$ = 2.2 Hz), 133.0 (d, $J_{C\text{-}P}$ = 1.6 Hz), 132.0 (d, $J_{C\text{-}P}$ = 104.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.8 Hz), 129.8 (d, $J_{C\text{-}P}$ = 99.3 Hz), 129.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 129.1, 129.0 (2C, overlapped), 128.9 (d, $J_{C\text{-}P}$ = 10.8 Hz), 128.8, 128.5 (d, $J_{C\text{-}P}$ = 12.2 Hz), 128.1, 123.7 (d, $J_{C\text{-}P}$ = 10.9 Hz), 126.2, 32.4 (d, $J_{C\text{-}P}$ = 10.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 38.8; IR (film) υ_{max}: 3057, 1601, 1493, 1437, 1196 (P=O), 1131, 1113, 699 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{17}H_{21}OPH^+$: 393.1402, found: 393.1425.



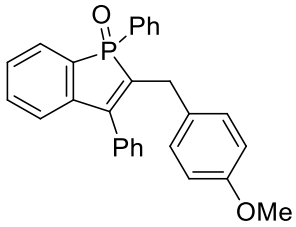
2-(2-methylbenzyl)-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3b, new compound**), yellow solid; m.p.: 116.3-117.1 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.56 (m, 1 H), 7.51-7.28 (m, 10 H), 7.21-7.16 (m, 2 H), 6.89-6.82 (m, 2 H), 6.70-6.68 (m, 1 H), 3.80-3.58 (m, 2 H), 1.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.8 (d, $J_{C\text{-}P}$ = 21.9 Hz), 144.3 (d, $J_{C\text{-}P}$ = 27.1 Hz), 136.3, 135.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 135.2 (d, $J_{C\text{-}P}$ = 95.9 Hz), 133.9 (d, $J_{C\text{-}P}$ = 15.4 Hz), 132.9 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.1 (d, $J_{C\text{-}P}$ = 105.1 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 129.6 (d, $J_{C\text{-}P}$ = 99.3 Hz), 130.0, 129.7, 129.1 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.9, 128.8 (d, $J_{C\text{-}P}$ = 10.8 Hz), 128.7, 128.3, 128.2, 126.7, 125.8, 123.5 (d, $J_{C\text{-}P}$ = 10.8 Hz), 30.6 (d, $J_{C\text{-}P}$ = 10.1 Hz), 19.6; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.7; IR (film) υ_{max}: 3056, 1587, 1490, 1437, 1196 (P=O), 1125, 1106, 749, 716 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{28}H_{23}OPH^+$: 407.1559, found: 407.1562.



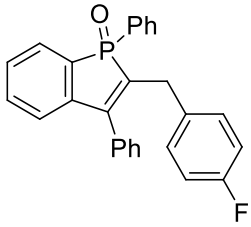
2-(4-methylbenzyl)-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3c, new compound**), white solid; m.p.: 113.4-114.2 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.58 (m, 1 H), 7.52-7.35 (m, 9 H), 7.32-7.28 (m, 1 H), 7.24-7.20 (m, 2 H), 7.10-7.05 (m, 1 H), 6.80-6.72 (m, 4 H), 3.67-3.64 (m, 2 H), 2.14 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.9 (d, $J_{C\text{-}P}$ = 22.2 Hz), 144.4 (d, $J_{C\text{-}P}$ = 27.3 Hz), 135.7 (d, $J_{C\text{-}P}$ = 95.5 Hz), 135.5, 134.4 (d, $J_{C\text{-}P}$ = 1.5 Hz), 133.8 (d, $J_{C\text{-}P}$ = 15.4 Hz), 132.9 (d, $J_{C\text{-}P}$ = 1.6 Hz), 132.0 (d, $J_{C\text{-}P}$ = 104.7 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.6 Hz), 129.9 (d, $J_{C\text{-}P}$ = 99.5 Hz), 129.1 (d, $J_{C\text{-}P}$ = 9.7 Hz), 129.0, 128.9, 128.9, 128.8, 128.7, 128.6 (2C, overlapped), 128.4 (d, $J_{C\text{-}P}$ = 12.5 Hz), 123.6 (d, $J_{C\text{-}P}$ = 10.9 Hz), 32.0 (d, $J_{C\text{-}P}$ = 10.1 Hz), 21.0; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.7; IR (film) υ_{max}: 3056, 1510, 1490, 1437, 1247, 1193 (P=O), 1033, 728, 703 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{28}H_{23}OPH^+$: 407.1559, found: 407.1554.



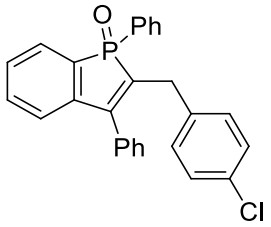
2-(3,5-dimethylbenzyl)-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3d, new compound**), wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.57 (m, 1 H), 7.52-7.50 (m, 2 H), 7.48-7.40 (m, 4 H), 7.36-7.29 (m, 4 H), 7.25-7.21 (m, 2 H), 7.07 (dd, *J* = 2.8, 7.7 Hz, 1 H), 6.53-6.44 (m, 3 H), 3.66-3.63 (m, 2 H), 2.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.9 (d, $J_{C\text{-}P}$ = 22.2 Hz), 144.5 (d, $J_{C\text{-}P}$ = 27.3 Hz), 137.5, 137.2, 135.5 (d, $J_{C\text{-}P}$ = 95.6 Hz), 133.9 (d, $J_{C\text{-}P}$ = 15.4 Hz), 132.9, 132.0 (d, $J_{C\text{-}P}$ = 104.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.8 Hz), 130.0 (d, $J_{C\text{-}P}$ = 99.3 Hz), 129.1 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.9 (2C, overlapped), 128.8 (d, $J_{C\text{-}P}$ = 10.8 Hz), 128.7, 128.2 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.8, 127.0, 123.6 (d, $J_{C\text{-}P}$ = 10.9 Hz), 32.2 (d, $J_{C\text{-}P}$ = 10.4 Hz), 21.1; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.7; IR (film) υ_{max}: 3057, 1605, 1491, 1437, 1195 (P=O), 1111, 1066, 750, 720 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{29}H_{25}OPH^+$: 421.1715, found: 421.1715.



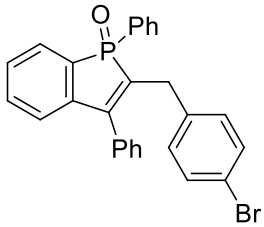
2-(4-methoxybenzyl)-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3e, new compound**), wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.58 (m, 1 H), 7.52-7.30 (m, 10 H), 7.25-7.22 (m, 2 H), 7.06 (dd, *J* = 2.6, 7.6 Hz, 1 H), 6.81 (d, *J* = 8.5 Hz, 2 H), 6.46 (d, *J* = 8.5 Hz, 2 H), 3.67 (s, 3 H), 3.64 d, *J* = 15.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.0, 150.8 (d, $J_{C\text{-}P}$ = 22.4 Hz), 144.4 (d, $J_{C\text{-}P}$ = 27.2 Hz), 135.9 (d, $J_{C\text{-}P}$ = 95.4 Hz), 133.9 (d, $J_{C\text{-}P}$ = 15.3 Hz), 133.0, 132.0 (d, $J_{C\text{-}P}$ = 104.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.9 Hz), 130.1, 129.9 (d, $J_{C\text{-}P}$ = 99.4 Hz), 129.7, 129.1 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.0 (2C, overlapped), 128.9 (d, $J_{C\text{-}P}$ = 10.3 Hz), 128.8, 128.5 (d, $J_{C\text{-}P}$ = 12.6 Hz), 123.7 (d, $J_{C\text{-}P}$ = 10.9 Hz), 113.6, 55.2, 31.6 (d, $J_{C\text{-}P}$ = 10.1 Hz); ^{31}P NMR (CDCl3, 162 MHz): δ 39.7; IR (film) υ_{max}: 3056, 1510, 1491, 1437, 1246, 1194 (P=O), 1107, 1033, 728, 703 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{28}H_{23}O_2PH^+$: 423.1508, found: 423.1511.



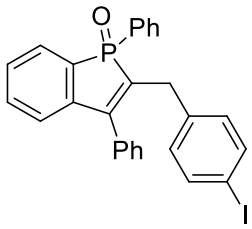
2-(4-fluorobenzyl)-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3f, new compound**), wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.58 (m, 1 H), 7.52-7.49 (m, 2 H), 7.48-7.45 (m, 5 H), 7.34-7.30 (m, 3 H), 7.27-7.24 (m, 2 H), 7.06 (dd, *J* = 2.9, 7.6 Hz, 1 H), 6.88-6.86 (m, 2 H), 6.82-6.80 (m, 2 H), 3.66 (d, *J* = 14.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.3, 160.4, 151.3 (d, $J_{C\text{-}P}$ = 21.9 Hz), 144.3 (d, $J_{C\text{-}P}$ = 27.2 Hz), 135.2 (d, $J_{C\text{-}P}$ = 95.6 Hz), 133.7 (d, $J_{C\text{-}P}$ = 15.3 Hz), 133.3 (d, $J_{C\text{-}P}$ = 2.0 Hz), 133.0 (d, $J_{C\text{-}P}$ = 1.6 Hz), 131.8 (d, $J_{C\text{-}P}$ = 105.2 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.7 Hz), 130.5 (d, $J_{C\text{-}P}$ = 7.8 Hz), 129.7 (d, $J_{C\text{-}P}$ = 99.5 Hz), 129.1 (d, $J_{C\text{-}P}$ = 10.2 Hz), 129.0 (d, $J_{C\text{-}P}$ = 10.4 Hz), 128.9, 128.6, 128.5, 123.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 114.8 (d, $J_{C\text{-}P}$ = 21.4 Hz), 31.6 (d, $J_{C\text{-}P}$ = 10.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.5; IR (film) υ_{max}: 3057, 1588, 1510, 1437, 1220, 1196 (P=O), 1114, 715, 702 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{27}H_{20}FOPH^+$: 411.1308, found: 411.1313.



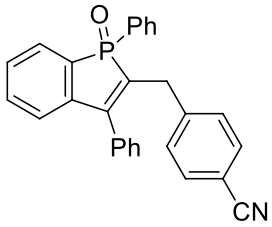
2-(4-chlorobenzyl)-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3g, new compound**), wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.59 (m, 1 H), 7.52-7.40 (m, 7 H), 7.32-7.24 (m, 5 H), 7.07-7.06 (m, 1 H), 6.88-6.81 (m, 4 H), 3.65 (d, J = 14.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.4 (d, $J_{C\text{-}P}$ = 22.0 Hz), 144.2 (d, $J_{C\text{-}P}$ = 27.1 Hz), 136.1, 135.0 (d, $J_{C\text{-}P}$ = 95.6 Hz), 133.6 (d, $J_{C\text{-}P}$ = 15.3 Hz), 133.1, 132.0, 131.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.7 (d, $J_{C\text{-}P}$ = 105.1 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.8 Hz), 130.4, 129.6 (d, $J_{C\text{-}P}$ = 99.4 Hz), 129.2 (d, $J_{C\text{-}P}$ = 21.3 Hz), 129.1 (2C, overlapped), 129.0 (d, $J_{C\text{-}P}$ = 23.5 Hz), 128.9, 128.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.2, 123.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 31.7 (d, $J_{C\text{-}P}$ = 10.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.4; IR (film) υ_{max}: 3056, 1588, 1490, 1437, 1198 (P=O), 1091, 1015, 720, 706 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{27}H_{20}ClOPH^+$: 427.1013, found: 427.1013.



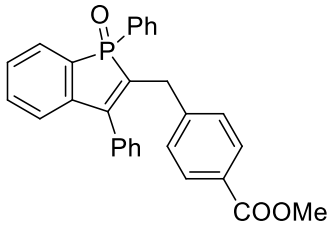
2-(4-bromobenzyl)-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3h, new compound**), yellow solid; m.p.: 155.8-157.2 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.60 (m, 1 H), 7.53-7.41 (m, 7 H), 7.35-7.31 (m, 3 H), 7.28-7.24 (m, 2 H), 7.08-7.01 (m, 3 H), 6.76 (d, J = 8.4 Hz, 2 H), 3.64 (d, J = 14.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.4 (d, $J_{C\text{-}P}$ = 22.2 Hz), 144.2 (d, $J_{C\text{-}P}$ = 27.1 Hz), 136.6 (d, $J_{C\text{-}P}$ = 1.7 Hz), 135.0 (d, $J_{C\text{-}P}$ = 95.5 Hz), 133.6 (d, $J_{C\text{-}P}$ = 15.2 Hz), 133.1, 131.8 (d, $J_{C\text{-}P}$ = 105.3 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.1, 131.0 (d, $J_{C\text{-}P}$ = 10.7 Hz), 130.8, 130.0 (d, $J_{C\text{-}P}$ = 106.5 Hz, overlapped), 129.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.1, 129.0 (2C, overlapped), 128.9, 128.7 (d, $J_{C\text{-}P}$ = 12.2 Hz), 123.8 (d, $J_{C\text{-}P}$ = 10.6 Hz), 120.2, 31.8 (d, $J_{C\text{-}P}$ = 10.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.3; IR (film) υ_{max}: 3056, 1558, 148, 1437, 1196 (P=O), 1070, 1011, 719, 704 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{27}H_{20}BrOPH^+$: 471.0507, found: 471.0511.



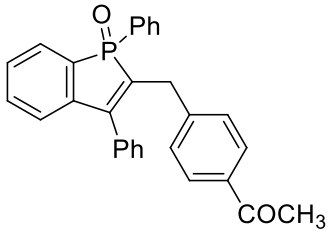
2-(4-iodobenzyl)-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3i, new compound**), yellow solid; m.p.: 166.5-167.8 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.59 (m, 1 H), 7.53-7.41 (m, 7 H), 7.33-7.32 (m, 3 H), 7.27-7.21 (m, 4 H), 7.07-7.06 (m, 1 H), 6.64 (d, *J* = 7.9 Hz, 2 H), 3.65-3.62 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.4 (d, $J_{C\text{-}P}$ = 21.9 Hz), 144.2 (d, $J_{C\text{-}P}$ = 27.1 Hz), 137.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 137.1, 134.9 (d, $J_{C\text{-}P}$ = 95.8 Hz), 133.6 (d, $J_{C\text{-}P}$ = 15.0 Hz), 133.1, 131.7 (d, $J_{C\text{-}P}$ = 105.3 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.3, 130.9 (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.9 (d, $J_{C\text{-}P}$ = 99.5 Hz, overlapped), 129.2, 129.1 (2C, overlapped), 129.0, 128.9, 128.7 (d, $J_{C\text{-}P}$ = 12.2 Hz), 123.8 (d, $J_{C\text{-}P}$ = 10.9 Hz), 91.9, 31.9 (d, $J_{C\text{-}P}$ = 10.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.5; IR (film) υ_{max}: 3055, 1587, 1483, 1436, 1197 (P=O), 1131, 1006, 718, 704 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{27}H_{20}IOPH^+$: 519.0369, found: 519.0371.



4-((1-oxido-1,3-diphenyl-1*H*-phosphindol-2-yl)methyl)benzonitrile (**3j, new compound**), yellow solid; m.p.: 50.8-51.7 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.61 (m, 1 H), 7.53-7.43 (m, 7 H), 7.37-7.22 (m, 7 H), 7.08 (d, *J* = 6.9 Hz, 1 H), 7.01 (d, *J* = 7.8 Hz, 2 H), 3.73 (d, *J* = 14.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.3 (d, $J_{C\text{-}P}$ = 21.9 Hz), 144.0 (d, $J_{C\text{-}P}$ = 26.7 Hz), 143.4 (d, $J_{C\text{-}P}$ = 1.6 Hz), 133.8 (d, $J_{C\text{-}P}$ = 85.5 Hz), 133.4 (d, $J_{C\text{-}P}$ = 4.8 Hz), 133.2 (d, $J_{C\text{-}P}$ = 1.6 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.9, 131.6 (d, $J_{C\text{-}P}$ = 105.4 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.8 Hz), 129.8, 129.4 (d, $J_{C\text{-}P}$ = 99.2 Hz), 129.4, 129.2 (d, $J_{C\text{-}P}$ = 9.7 Hz), 129.1, 128.8 (d, *J* = 12.5 Hz,), 128.5 (2C, overlapped), 123.9 (d, $J_{C\text{-}P}$ = 10.8 Hz), 119.0, 110.1, 32.4 (d, $J_{C\text{-}P}$ = 10.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.1; IR (film) υ_{max}: 3056, 1606, 1505, 1437, 1195 (P=O), 1109, 1066, 725, 701 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{28}H_{20}NOPH^+$: 418.1355, found: 418.1360.

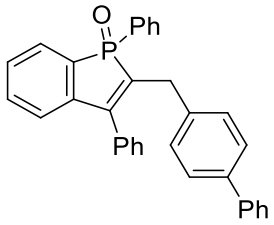


Methyl 4-((1-oxido-1,3-diphenyl-1*H*-phosphindol-2-yl)methyl)benzoate (**3k, new compound**), wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.61 (m, 3 H), 7.52-7.45 (m, 5 H), 7.43-7.37 (m, 2 H), 7.36-7.31 (m, 3 H), 7.26-7.23 (m, 2 H), 7.08 (dd, *J* = 2.8, 7.6 Hz, 1 H), 6.96 (d, *J* = 8.3 Hz, 2 H), 3.86 (s, 3 H), 3.73 (d, *J* = 14.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.0, 151.9 (d, $J_{C\text{-}P}$ = 21.9 Hz), 144.2 (d, $J_{C\text{-}P}$ = 27.0 Hz), 143.2, 134.4 (d, $J_{C\text{-}P}$ = 95.9 Hz), 133.6 (d, $J_{C\text{-}P}$ = 15.2 Hz), 133.1, 131.7 (d, $J_{C\text{-}P}$ = 105.4 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 129.9 (d, $J_{C\text{-}P}$ = 95.0 Hz, overlapped), 129.5, 129.2 (d, $J_{C\text{-}P}$ = 10.2 Hz), 129.1 (d, $J_{C\text{-}P}$ = 9.3 Hz), 129.0 (d, $J_{C\text{-}P}$ = 13.7 Hz), 129.0, 128.8 (2C, overlapped), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.1, 123.8 (d, $J_{C\text{-}P}$ = 10.8 Hz), 52.1, 32.3 (d, $J_{C\text{-}P}$ = 10.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.5; IR (film) υ_{max}: 3057, 1715, 1609, 1436, 1285, 1195 (P=O), 1108, 719, 704 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{29}H_{23}O_3PH^+$: 451.1457, found: 451.1461.

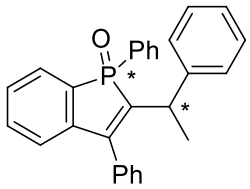


1-(4-((1-oxido-1,3-diphenyl-1*H*-phosphindol-2-yl)methyl)phenyl)ethanone (**3l, new compound**), wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.59 (m, 1 H), 7.54-7.42 (m, 8 H), 7.39-7.31 (m, 4 H), 7.24-7.21 (m, 2 H), 7.07 (dd, *J* = 2.6, 7.5 Hz, 1 H), 6.99 (d, *J* = 8.1 Hz, 2 H), 3.74-3.71 (m, 2 H), 2.46 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.8, 152.0 (d, $J_{C\text{-}P}$ = 21.9 Hz), 144.2 (d, $J_{C\text{-}P}$ = 27.1 Hz), 143.4 (d, $J_{C\text{-}P}$ = 1.4 Hz), 135.2, 134.3 (d, $J_{C\text{-}P}$ = 95.8 Hz), 133.6 (d, $J_{C\text{-}P}$ = 15.3 Hz), 133.1 (d, $J_{C\text{-}P}$ = 1.4 Hz), 131.7 (d, $J_{C\text{-}P}$ = 105.4 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.7 Hz), 129.6 (d, $J_{C\text{-}P}$ = 100.4 Hz), 129.3, 129.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 129.1 (2C, overlapped), 129.0 (d, $J_{C\text{-}P}$ = 13.9 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.2 Hz), 128.3, 123.8 (d, $J_{C\text{-}P}$ = 10.7 Hz), 32.3 (d, $J_{C\text{-}P}$ = 10.2 Hz), 26.6; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.6; IR (film) υ_{max}: 3056, 1681, 1605, 1437, 1267 (P=O), 1110, 723, 694 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{29}H_{23}O_2PH^+$:

435.1508, found: 435.1513

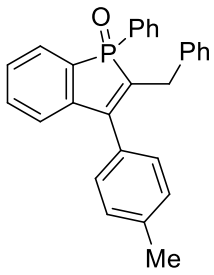


2-([1,1'-biphenyl]-4-ylmethyl)-1,3-diphenyl-1*H*-phosphindole 1-oxide (**3m, new compound**), yellow solid; m.p.: 62.5-63.4 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.60 (m, 1 H), 7.55-7.52 (m, 2 H), 7.49-7.46 (m, 3 H), 7.44-7.38 (m, 7 H), 7.35-7.29 (m, 3 H), 7.21-7.18 (m, 2 H.), 7.13 (d, J = 7.7 Hz, 2 H), 7.09 (dd, J = 7.5 Hz, 1 H), 6.97 (d, J = 7.8 Hz, 2 H), 3.78-3.74 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.1 (d, $J_{C\text{-}P}$ = 22.1 Hz), 144.4 (d, $J_{C\text{-}P}$ = 27.2 Hz), 141.1, 139.0, 136.7 (d, $J_{C\text{-}P}$ = 1.3 Hz), 135.4 (d, $J_{C\text{-}P}$ = 95.6 Hz), 133.8 (d, $J_{C\text{-}P}$ = 15.4 Hz), 133.0 (d, $J_{C\text{-}P}$ = 1.5 Hz), 131.9 (d, $J_{C\text{-}P}$ = 104.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1, 131.0 (d, $J_{C\text{-}P}$ = 10.8 Hz), 130.8, 129.8 (d, $J_{C\text{-}P}$ = 99.6 Hz), 129.5, 129.1 (d, $J_{C\text{-}P}$ = 9.5 Hz), 129.0, 128.9 (d, $J_{C\text{-}P}$ = 10.7 Hz), 128.8, 128.7, 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.1, 126.9 (d, $J_{C\text{-}P}$ = 17.2 Hz), 123.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 32.1 (d, $J_{C\text{-}P}$ = 10.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.6; IR (film) υ_{max}: 3055, 2917, 2849, 1487, 1437, 1195 (P=O), 1132, 1108, 725, 699 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{33}H_{25}OPH^+$: 469.1715, found: 469.1718.

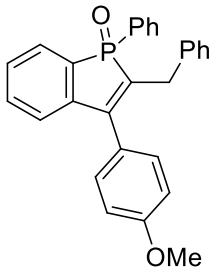


1,3-diphenyl-2-(1-phenylethyl)-1*H*-phosphindole 1-oxide (**3n, new compound**), one diastereoisomer **3n'**: yellow solid; m.p.: 44.5-45.8 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84-7.80 (m, 2 H), 7.59-7.51 (m, 2 H), 7.48-7.44 (m, 3 H), 7.42-7.39 (m, 1 H), 7.37-7.33 (m, 2 H), 7.30-7.27 (m, 1 H), 7.18-7.14 (m, 4 H), 7.11-7.08 (m, 1 H), 6.91-6.86 (m, 2 H), 3.95-3.90 (m, 1 H), 1.23 (d, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.9 (d, $J_{C\text{-}P}$ = 22.0 Hz), 145.4, 144.2 (d, $J_{C\text{-}P}$ = 27.2 Hz), 140.1 (d, $J_{C\text{-}P}$ = 92.1 Hz), 134.4 (d, $J_{C\text{-}P}$ = 15.6 Hz), 132.9, 132.3 (d, $J_{C\text{-}P}$ = 106.0 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 97.9 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.1 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.8, 128.7 (d, $J_{C\text{-}P}$ = 10.2 Hz), 128.5, 128.1, 127.8, 126.2, 123.4 (d, $J_{C\text{-}P}$ = 10.7

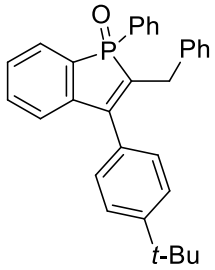
Hz), 40.0 (d, $J_{C\text{-}P}$ = 9.1 Hz), 21.6 (d, $J_{C\text{-}P}$ = 4.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 38.4; IR (film) υ_{max}: 3057, 1587, 1493, 1437, 1193 (P=O), 1104, 1020, 718, 699 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{28}H_{22}OPH^+$: 407.1559, found: 407.1580; another diastereoisomer **3n"**: yellow solid; m.p.: 147.8-148.5 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.53 (m, 2 H), 7.51-7.46 (m, 2 H), 7.37-7.34 (m, 3 H), 7.30-7.29 (m, 1 H), 7.28-7.27 (m, 1 H), 7.26-7.23 (m, 1 H), 7.18-7.14 (m, 2 H), 6.93-6.91 (m, 3 H), 6.85-6.80 (m, 3 H), 4.10-4.04 (m, 1 H), 1.69 (d, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.2 (d, $J_{C\text{-}P}$ = 22.6 Hz), 144.1 (d, $J_{C\text{-}P}$ = 26.9 Hz), 141.5 (d, $J_{C\text{-}P}$ = 2.3 Hz), 140.6 (d, $J_{C\text{-}P}$ = 92.8 Hz), 134.4 (d, $J_{C\text{-}P}$ = 15.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 105.1 Hz), 132.8 (d, $J_{C\text{-}P}$ = 1.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.7 (d, $J_{C\text{-}P}$ = 10.6 Hz), 130.3 (d, $J_{C\text{-}P}$ = 99.1 Hz), 129.3, 128.9, 128.7 (d, $J_{C\text{-}P}$ = 100.5 Hz), 128.6, 128.5, 128.3, 128.1 (d, $J_{C\text{-}P}$ = 12.3 Hz), 127.9 (d, $J_{C\text{-}P}$ = 14.6 Hz), 126.3, 123.5 (d, $J_{C\text{-}P}$ = 10.3 Hz), 38.6 (d, $J_{C\text{-}P}$ = 9.5 Hz), 19.2 (d, $J_{C\text{-}P}$ = 1.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.6; IR (film) υ_{max}: 3057, 1587, 1491, 1437, 1206 (P=O), 1106, 1022, 720, 700 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{28}H_{22}OPH^+$: 407.1559, found: 407.1542.



2-benzyl-1-phenyl-3-(*p-tolyl*)-1*H*-phosphindole 1-oxide (**3o, new compound**), yellow solid; m.p.: 129.1-130.0 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57-7.54 (m, 1 H), 7.44-7.30 (m, 4 H), 7.28-7.25 (m, 3 H), 7.22-7.16 (m, 4 H), 7.06 (dd, J = 2.8, 7.6 Hz, 1 H), 6.90-6.88 (m, 5 H), 3.66 (d, J = 15.2 Hz, 2 H), 2.39 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.4 (d, $J_{C\text{-}P}$ = 22.1 Hz), 144.5 (d, $J_{C\text{-}P}$ = 27.2 Hz), 138.7, 137.7, 134.9 (d, $J_{C\text{-}P}$ = 95.7 Hz), 132.9 (d, $J_{C\text{-}P}$ = 1.4 Hz), 132.0 (d, $J_{C\text{-}P}$ = 105.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 15.3 Hz), 129.8 (d, $J_{C\text{-}P}$ = 99.3 Hz), 129.6, 129.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.1, 128.8 (d, $J_{C\text{-}P}$ = 10.3 Hz), 128.6, 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.1, 126.1, 123.7 (d, $J_{C\text{-}P}$ = 10.9 Hz), 32.4 (d, $J_{C\text{-}P}$ = 10.4 Hz), 21.4; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.7; IR (film) υ_{max}: 2916, 2849, 1437, 1195 (P=O), 1113, 731, 695 cm^{-1}; HRMS: $[M+Na]^+$ m/z calcd for $C_{28}H_{23}OPNa^+$: 429.1378, found: 429.1381.

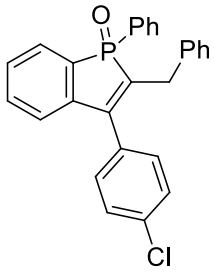


2-benzyl-3-(4-methoxyphenyl)-1-phenyl-1*H*-phosphindole 1-oxide (**3p, new compound**), yellow solid; m.p.: 138.5-139.4 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.58 (m, 1 H), 7.49-7.41 (m, 3 H), 7.38-7.35 (m, 1 H), 7.33-7.28 (m, 3 H), 7.25-7.21 (m, 2 H), 7.12 (dd, *J* = 2.8, 7.6 Hz, 1 H), 7.02 (d, *J* = 8.8 Hz, 2 H), 6.97-6.92 (m, 5 H), 3.88 (s, 3 H), 3.71 (d, *J* = 15.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.0, 151.2 (d, $J_{C\text{-}P}$ = 22.0 Hz), 144.6 (d, $J_{C\text{-}P}$ = 27.0 Hz), 137.8, 134.8 (d, $J_{C\text{-}P}$ = 96.1 Hz), 132.9 (d, $J_{C\text{-}P}$ = 1.4 Hz), 132.0 (d, $J_{C\text{-}P}$ = 104.6 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.6 Hz), 130.1, 129.9 (d, $J_{C\text{-}P}$ = 99.3 Hz), 129.1, 129.0, 128.9 (d, $J_{C\text{-}P}$ = 10.4 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.2 Hz), 128.2, 126.2, 125.8 (d, $J_{C\text{-}P}$ = 15.5 Hz), 123.7 (d, $J_{C\text{-}P}$ = 10.9 Hz), 114.4, 55.5, 32.4 (d, $J_{C\text{-}P}$ = 10.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.6; IR (film) υ_{max}: 3058, 2962, 1588, 1494, 1437, 1200 (P=O), 1118, 724, 695 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{28}H_{23}O_2PH^+$: 423.1508, found: 423.1532.

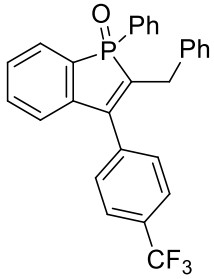


2-benzyl-3-(4-(*tert*-butyl)phenyl)-1-phenyl-1*H*-phosphindole 1-oxide (**3q, new compound**), yellow solid; m.p.: 138.5-139.4 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.58 (m, 1 H), 7.51-7.46 (m, 4 H), 7.43-7.40 (m, 1 H), 7.36-7.34 (m, 1 H), 7.33-7.28 (m, 3 H), 7.24-7.21 (m, 2 H), 7.14 (dd, *J* = 2.6, 7.6 Hz, 2 H), 6.94-6.92 (m, 5 H), 3.74-3.71 (m, 2 H), 1.38 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.9, 151.4 (d, $J_{C\text{-}P}$ = 22.0 Hz), 144.5 (d, $J_{C\text{-}P}$ = 27.2 Hz), 137.7 (d, $J_{C\text{-}P}$ = 1.3 Hz), 134.9 (d, $J_{C\text{-}P}$ = 96.0 Hz), 132.9 (d, $J_{C\text{-}P}$ = 1.4 Hz), 132.0 (d, $J_{C\text{-}P}$ = 104.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 10.8 Hz), 130.7 (d, $J_{C\text{-}P}$ = 15.4 Hz), 129.9 (d, $J_{C\text{-}P}$ = 99.3 Hz), 129.1, 129.0, 128.8 (d, $J_{C\text{-}P}$ = 10.7 Hz), 128.5, 128.4, 128.1, 126.1, 125.8, 123.8 (d, $J_{C\text{-}P}$ = 10.9 Hz), 34.9, 32.4 (d, $J_{C\text{-}P}$ = 10.3 Hz), 31.4; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.7; IR (film) υ_{max}: 3058, 2962, 1588, 1494,

1437, 1200 (P=O), 1118, 724, 695 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{31}H_{29}OPH^+$: 449.2028, found: 449.2034.

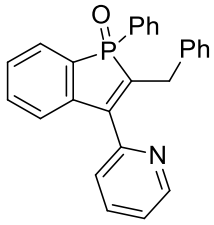


2-benzyl-3-(4-chlorophenyl)-1-phenyl-1*H*-phosphindole 1-oxide (**3r, new compound**), yellow solid; m.p.: 141.8-143.0 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.60 (m, 1 H), 7.49-7.33 (m, 7 H), 7.28-7.23 (m, 4 H), 7.04-7.03 (m, 1 H), 6.95-6.90 (m, 5 H), 3.67 (d, J = 14.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.1 (d, J_{C-P} = 22.6 Hz), 144.0 (d, J_{C-P} = 27.1 Hz), 137.4, 136.1 (d, J_{C-P} = 95.1 Hz), 134.9, 133.1 (d, J_{C-P} = 1.6 Hz), 132.2 (d, J_{C-P} = 8.6 Hz), 132.0 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 98.1 Hz), 131.0 (d, J_{C-P} = 10.8 Hz), 130.2, 129.5 (d, J_{C-P} = 99.5 Hz), 129.3, 129.2, 129.1 (d, J_{C-P} = 10.3 Hz), 129.0, 128.6 (d, J_{C-P} = 12.6 Hz), 128.2, 126.3, 123.5 (d, J_{C-P} = 10.7 Hz), 32.3 (d, J_{C-P} = 10.1 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.4; IR (film) υ_{max}: 3058, 1601, 1487, 1437, 1196 (P=O), 1088, 1014, 732, 695 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{27}H_{20}ClOPH^+$: 427.1013, found: 427.1017.

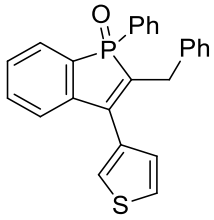


2-benzyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)-1*H*-phosphindole 1-oxide (**3s, new compound**), yellow wax like solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, J = 8.2 Hz, 2 H), 7.66-7.62 (m, 1 H), 7.51-7.33 (m, 7 H), 7.28-7.25 (m, 2 H), 7.00-6.86 (m, 6 H), 3.69-3.62 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.7 (d, J_{C-P} = 22.6 Hz), 143.8 (d, J_{C-P} = 27.1 Hz), 137.7 (d, J_{C-P} = 15.5 Hz), 137.2 (d, J_{C-P} = 1.6 Hz), 136.8 (d, J_{C-P} = 94.5 Hz), 133.2 (d, J_{C-P} = 1.3 Hz), 132.1 (d, J_{C-P} = 2.6 Hz), 131.0 (q, J_{C-F} = 32.5 Hz), 131.7 (d, J_{C-P} = 105.0 Hz), 131.0 (d, J_{C-P} = 10.8 Hz), 129.8 (d, J_{C-P} = 98.6 Hz, overlapped), 129.4 (d, J_{C-P} = 9.5 Hz), 129.3 (d, J_{C-P} = 10.3 Hz), 129.0, 128.7 (d, J_{C-P} = 12.5 Hz), 127.3, 126.4, 126.0 (2C, overlapped), 124.0 (q, J_{C-F} = 272.4 Hz), 123.4 (d, J_{C-P} =

10.8 Hz), 32.3 (d, $J_{C\text{-}P}$ = 10.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.4; IR (film) υ_{max}: 3060, 1437, 1324, 1121 (P=O), 1065, 1018, 743, 696 cm^{-1}; HRMS: $[M+Na]^+$ m/z calcd for $C_{28}H_{20}F_3OPNa^+$:483.1096, found: 483.1110.

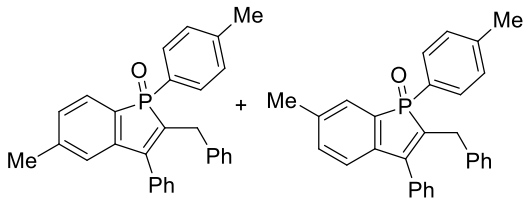


2-benzyl-1-phenyl-3-(pyridin-2-yl)-1*H*-phosphindole 1-oxide (**3t, new compound**), wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.81 (d, *J* = 4.6 Hz, 1 H), 7.78 (t, *J* = 7.6 Hz, 1 H), 7.62-7.58 (m, 1 H), 7.50 (dd, *J* = 7.6, 12.6 Hz, 2 H), 7.43-7.40 (m, 1 H), 7.36-7.29 (m, 4 H), 7.21-7.16 (m, 3 H), 6.97-6.91 (m, 5 H), 3.81-3.69 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.4 (d, $J_{C\text{-}P}$ = 17.3 Hz), 150.3, 149.1 (d, $J_{C\text{-}P}$ = 21.9 Hz), 143.5 (d, $J_{C\text{-}P}$ = 27.2 Hz), 137.0 (d, $J_{C\text{-}P}$ = 94.0 Hz), 137.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 136.9, 133.1 (d, $J_{C\text{-}P}$ = 1.5 Hz),e 131.8 (d, $J_{C\text{-}P}$ = 105.5 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.4 (d, $J_{C\text{-}P}$ = 99.6 Hz), 129.3 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.1, 129.0 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.6 Hz), 128.2, 126.3, 124.7, 123.8 (d, $J_{C\text{-}P}$ = 10.9 Hz), 123.5, 32.1 (d, $J_{C\text{-}P}$ = 9.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 40.2; IR (film) υ_{max}: 3862, 3648, 2959, 1652, 1558, 1506, 1456, 1195 (P=O) cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{26}H_{20}NOPH^+$: 394.1355, found: 394.1359.

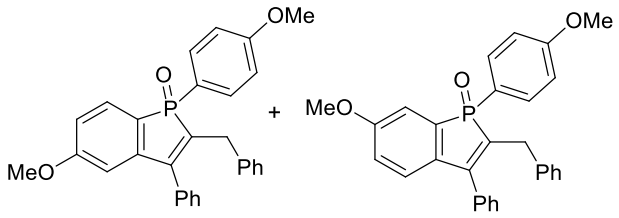


2-benzyl-1-phenyl-3-(thiophen-3-yl)-1*H*-phosphindole 1-oxide (**3u, new compound**), wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.61 (m, 1 H), 7.50-7.45 (m, 4 H), 7.39-7.32 (m, 3 H), 7.24-7.23 (m, 2 H), 7.46-7.42 (m, 1 H), 7.16 (d, *J* = 4.6 Hz, 1 H), 6.97-6.95 (m, 5 H), 3.82-3.71 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.6 (d, $J_{C\text{-}P}$ = 23.4 Hz), 144.2 (d, $J_{C\text{-}P}$ = 27.0 Hz), 137.8 (d, $J_{C\text{-}P}$ = 1.9 Hz), 135.6 (d, $J_{C\text{-}P}$ = 95.5 Hz), 133.7 (d, $J_{C\text{-}P}$ = 15.9 Hz), 133.1, 131.8 (d, $J_{C\text{-}P}$ = 105.1 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.8 Hz), 129.7 (d, $J_{C\text{-}P}$ = 102.8 Hz, overlapped), 129.2 (d, $J_{C\text{-}P}$ = 9.3 Hz), 129.0 (d, $J_{C\text{-}P}$ = 10.7 Hz), 128.9, 128.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.3, 128.0, 126.7,

126.2, 125.3, 123.6 (d, $J_{C\text{-}P}$ = 10.8 Hz), 32.5 (d, $J_{C\text{-}P}$ = 10.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.4; IR (film) υ_{max}: 3059, 1588, 1494, 1437, 1195 (P=O), 1111, 730, 694 cm^{-1}; HRMS: $[M+H]^+$ m/z calcd for $C_{25}H_{19}OPSH^+$: 399.0967, found: 399.0962.



2-(di-p-tolylphosphoryl)-5-methyl-3-phenyl-1-(p-tolyl)-1H-phosphindole 1-oxide and 2-(di-p-tolylphosphoryl)-6-methyl-3-phenyl-1-(p-tolyl)-1H-phosphindole 1-oxide (**3v, New Compound**); wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51-7.32 (m, 10 H), 7.13-7.11 (m, 1 H), 7.07-7.03 (m, 2.5 H), 6.95-6.88 (m, 6.4 H), 6.84 (m, 1 H), 3.66 (d, J = 15.0 Hz, 2.5 H), 2.31-2.30 (m, 7.6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.0 (d, $J_{C\text{-}P}$ = 21.8 Hz), 144.7 (d, $J_{C\text{-}P}$ = 27.5 Hz), 143.5, 142.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 141.7 (d, $J_{C\text{-}P}$ = 27.2 Hz), 139.1 (d, $J_{C\text{-}P}$ = 10.7 Hz), 138.0, 137.9, 135.8 (d, $J_{C\text{-}P}$ = 95.4 Hz), 134.3 (d, $J_{C\text{-}P}$ = 96.1 Hz), 134.1(d, $J_{C\text{-}P}$ = 15.4 Hz), 134.0 (d, $J_{C\text{-}P}$ = 15.3 Hz), 132.3, 132.2 (d, $J_{C\text{-}P}$ = 104.5 Hz), 131.1 (d, $J_{C\text{-}P}$ = 11.0 Hz), 129.8 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.4-129.2 (m), 128.9, 128.6, 128.4, 128.1 , 126.6 (d, $J_{C\text{-}P}$ = 101.8 Hz), 125.9, 124.5 (d, $J_{C\text{-}P}$ = 11.1 Hz), 123.4 (d, $J_{C\text{-}P}$ = 104.5 Hz), 32.3 (d, $J_{C\text{-}P}$ = 10.2 Hz), 22.0, 21.7; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.5, 39.9; IR (film) υ_{max}: 3056, 2921, 1600, 1494, 1442, 1195 (P=O), 1109, 756, 700 cm^{-1}; HRMS: $[M+Na]^+$ m/z calcd for $C_{36}H_{32}O_2P_2Na^+$: 421.1715, found: 421.1719.

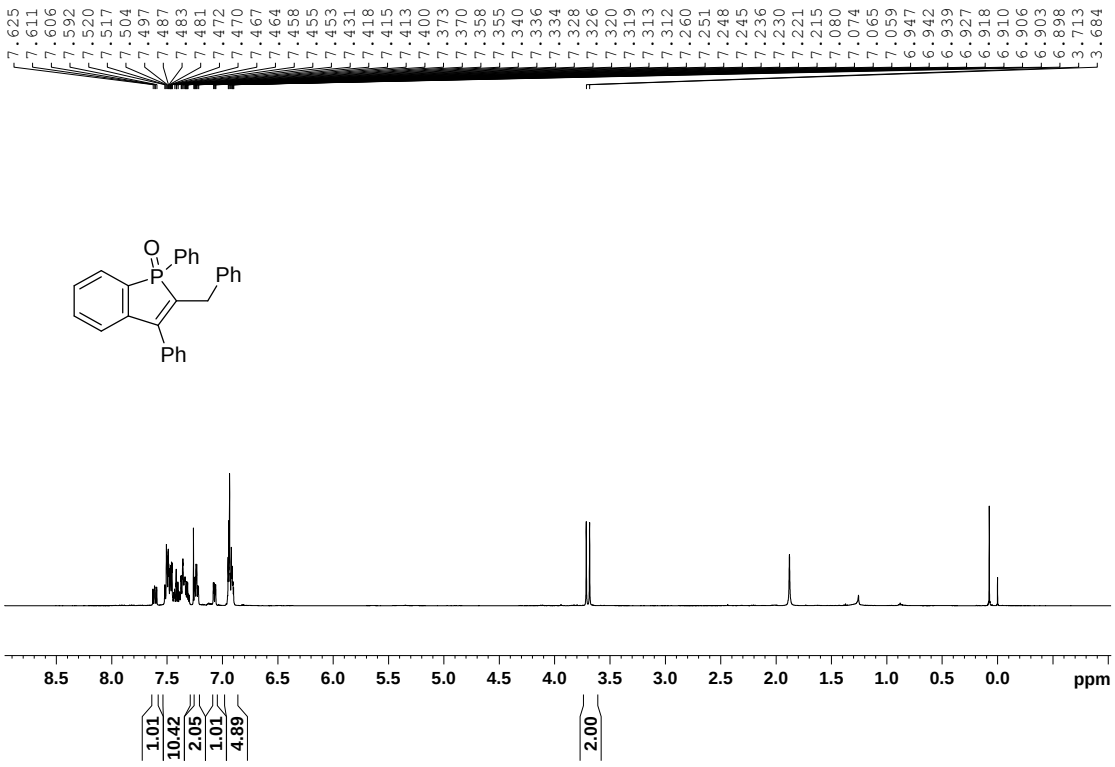


2-benzyl-5-methoxy-1-(4-methoxyphenyl)-3-phenyl-1H-phosphindole 1-oxide and 2-benzyl-6-methoxy-1-(4-methoxyphenyl)-3-phenyl-1H-phosphindole 1-oxide (**3w, New Compound**); wax; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.37 (m, 8 H), 7.32-7.30 (m, 2 H), 6.97-6.87 (m, 7 H), 6.81-6.73 (m, 3 H), 6.59-6.58 (m, 1 H), 3.79-3.76 (m, 7.36 H), 3.67-3.63 (m, 2.46 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 162.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 160.5 (d, $J_{C\text{-}P}$ = 13.0 Hz), 150.1 (d, $J_{C\text{-}P}$ = 21.4 Hz), 138.2, 137.8, 137.1 (d, $J_{C\text{-}P}$ = 95.6 Hz), 133.8 (d, $J_{C\text{-}P}$ = 14.9 Hz), 133.0 (d, $J_{C\text{-}P}$ = 12.3 Hz), 129.0-128.7 (m), 128.1, 124.7 (d, $J_{C\text{-}P}$ = 12.6 Hz), 122.9 (d, $J_{C\text{-}P}$

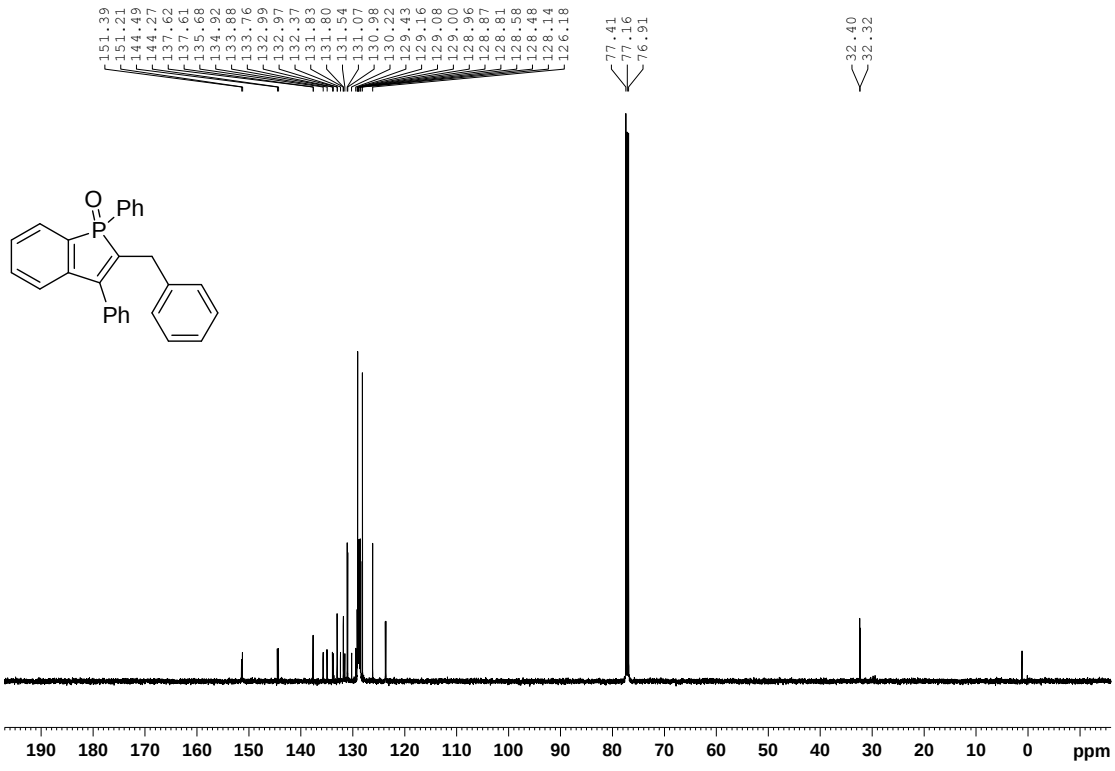
= 111.2 Hz), 121.0 (d, $J_{C\text{-}P}$ = 106.7 Hz), 120.1, 117.9, 114.7 (d, $J_{C\text{-}P}$ = 11.0 Hz), 114.3, 114.2 (d, $J_{C\text{-}P}$ = 13.4 Hz), 112.4 (d, $J_{C\text{-}P}$ = 11.7 Hz), 111.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 55.6, 55.4, 32.4 (d, $J_{C\text{-}P}$ = 10.1 Hz), 32.2 (d, $J_{C\text{-}P}$ = 10.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 38.5, 39.7; IR (film) υ_{max}: 3056, 1596, 1500, 1453, 1254 (P=O), 1176, 1113, 1027, 829, 701 cm^{-1}; HRMS: $[M+Na]^+$ m/z calcd for $C_{36}H_{32}O_2P_2Na^+$: 453.1614, found: 453.1612.

NMR Spectra of 3a-3w:

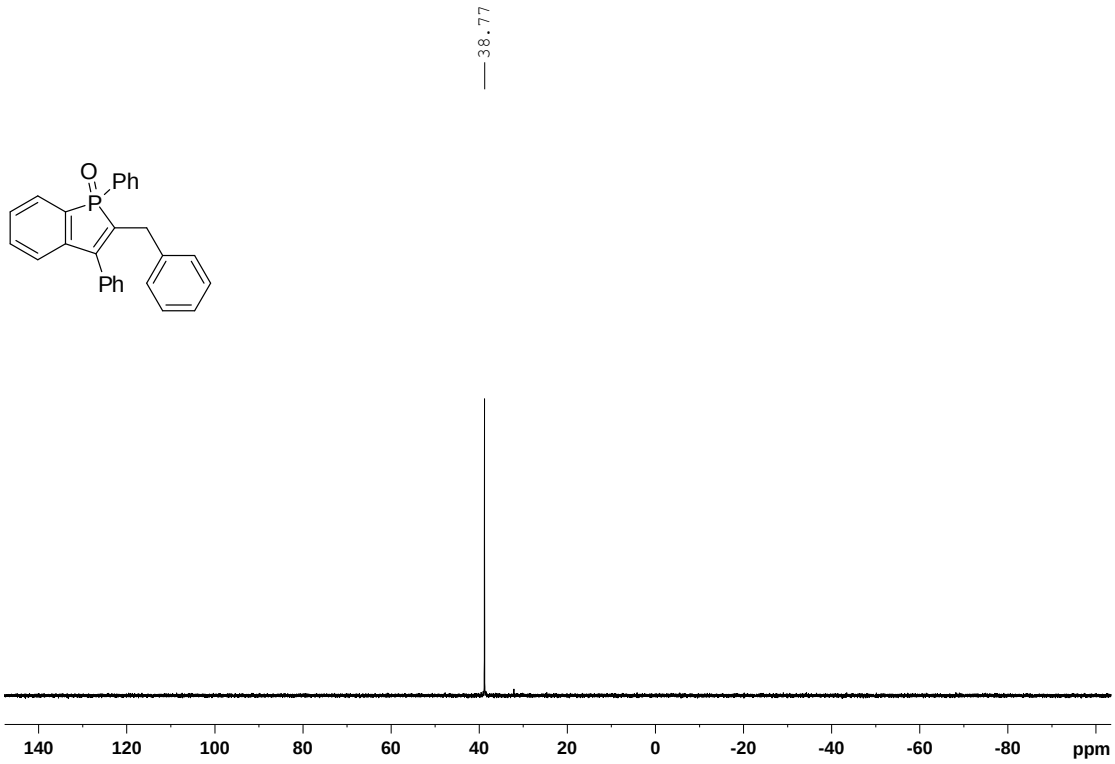
^{1}H NMR of **3a**



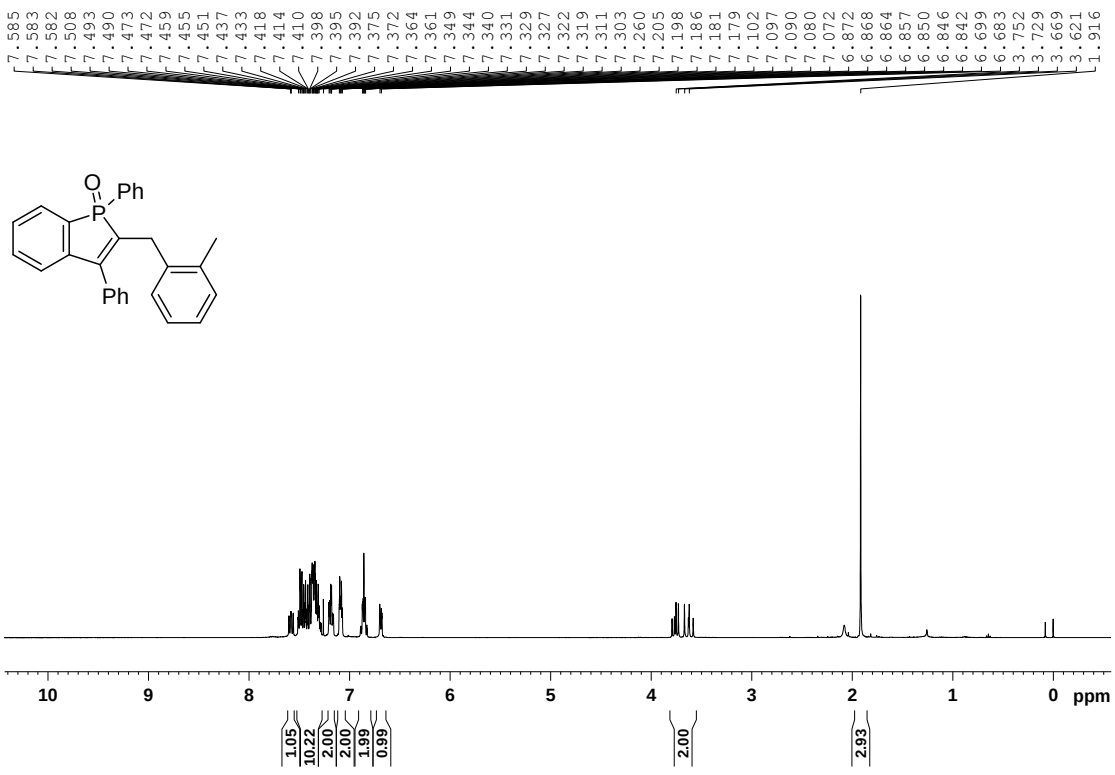
^{13}C NMR of **3a**



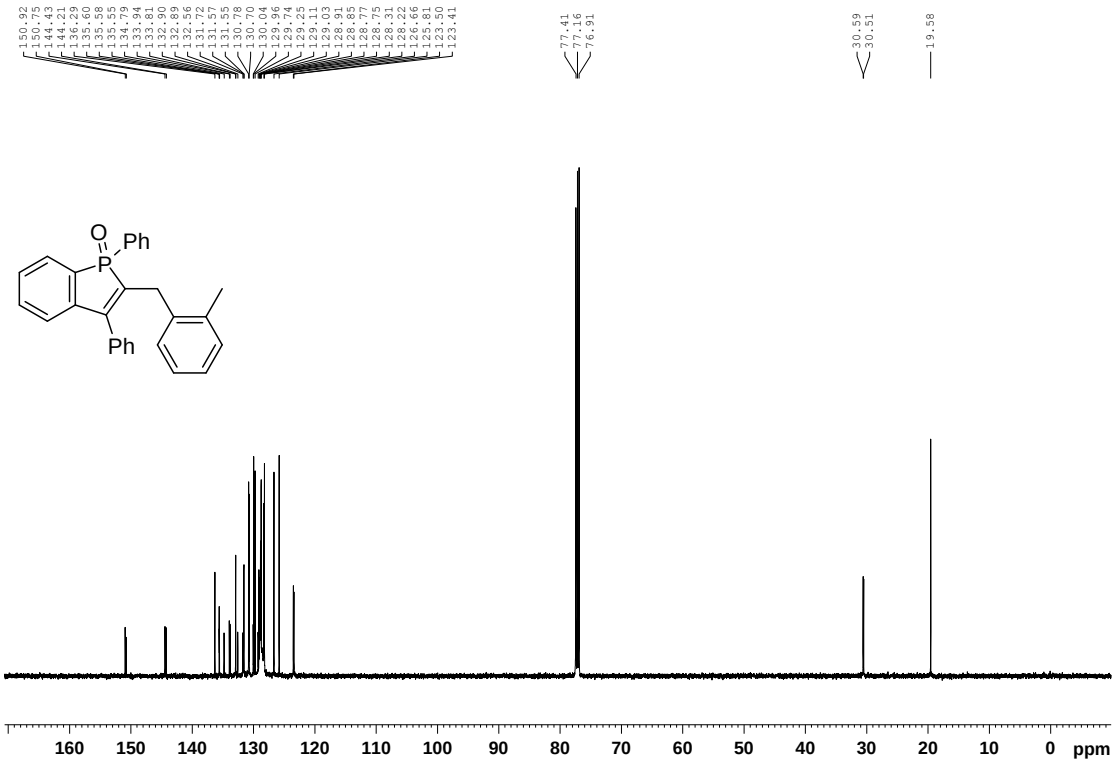
^{31}P NMR of **3a**



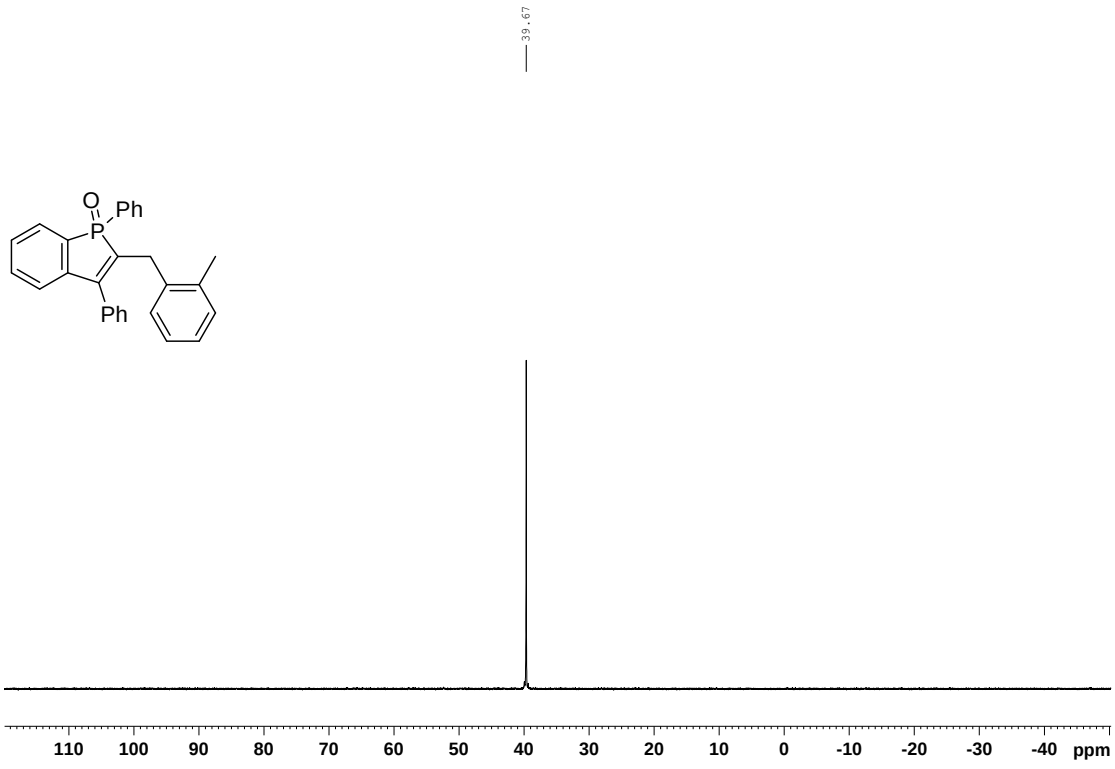
^{1}H NMR of **3b**



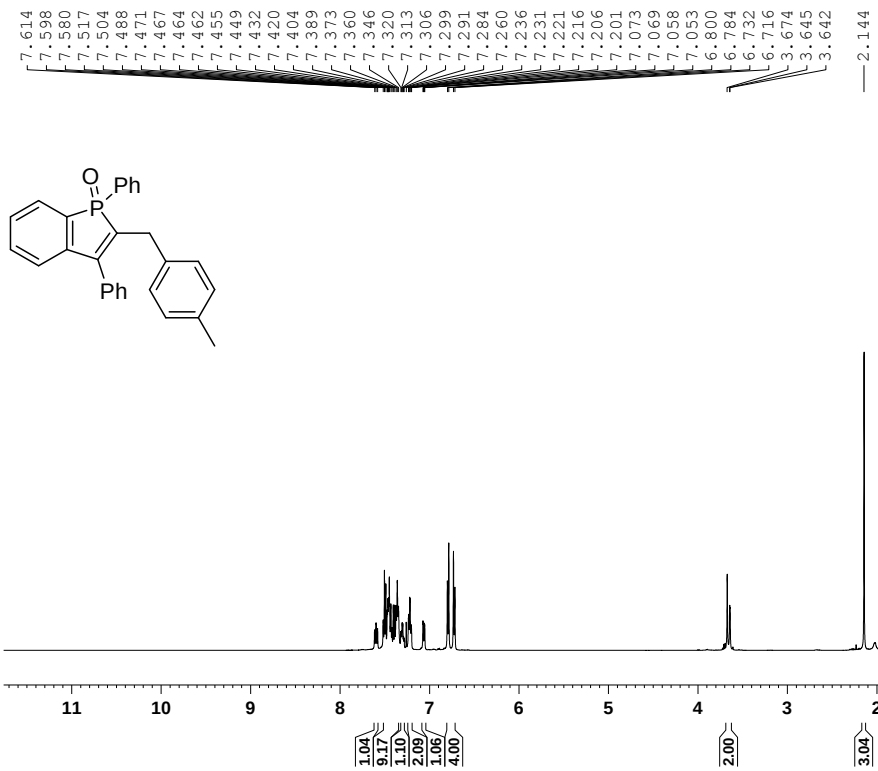
^{13}C NMR of **3b**



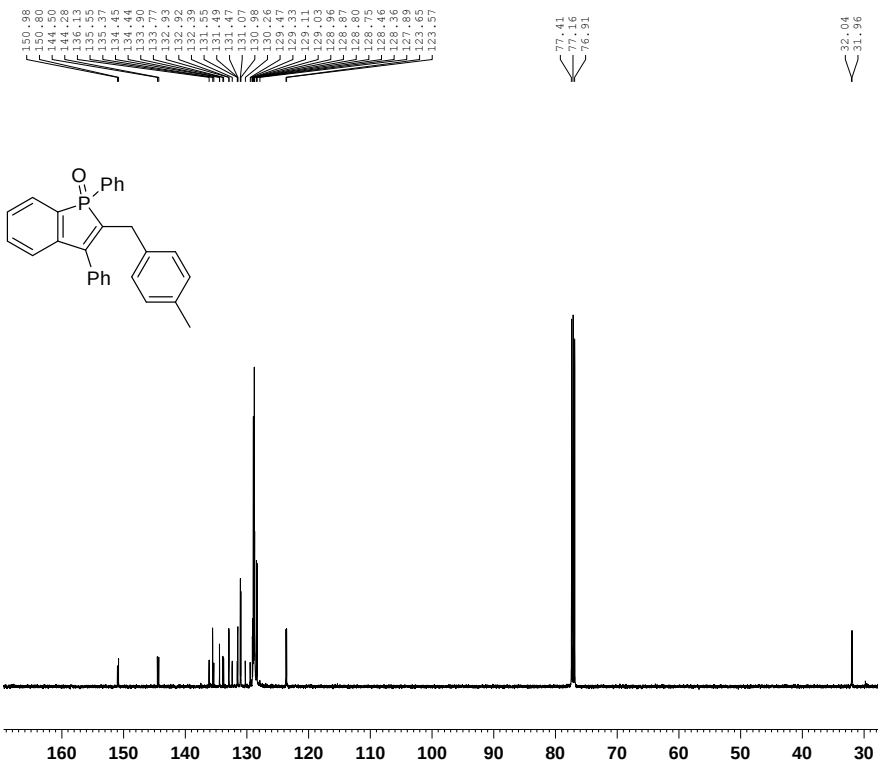
^{31}P NMR of **3b**



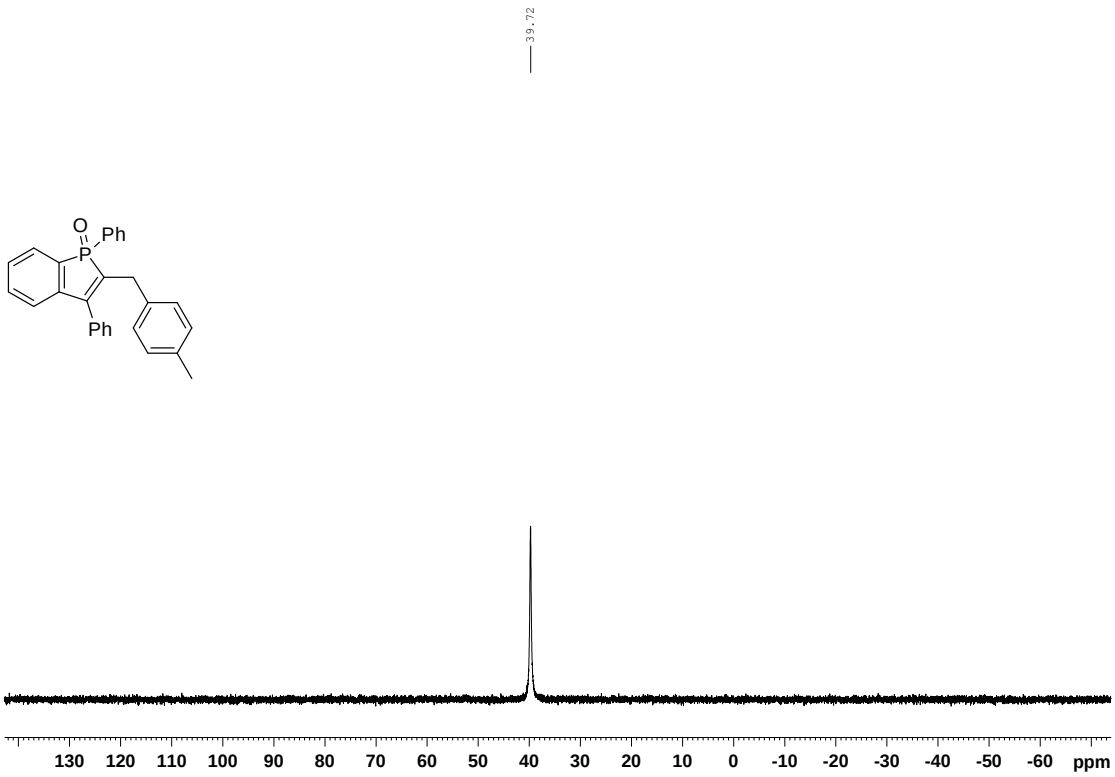
^{1}H NMR of **3c**



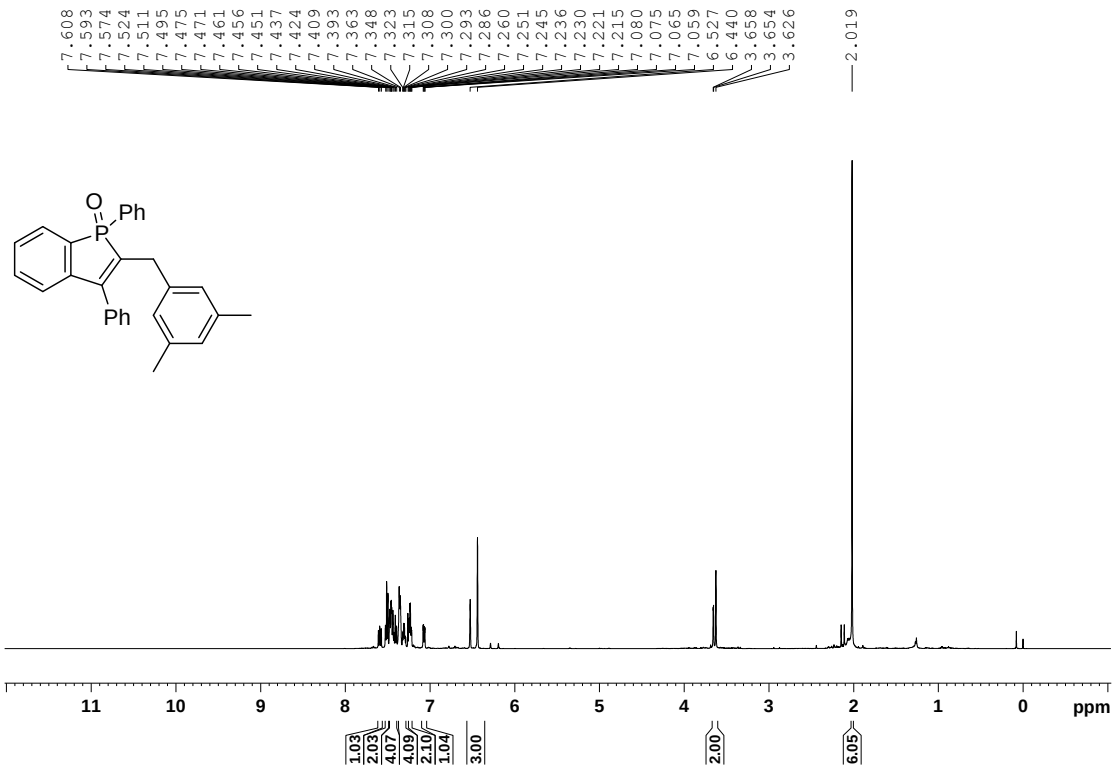
^{13}C NMR of **3c**



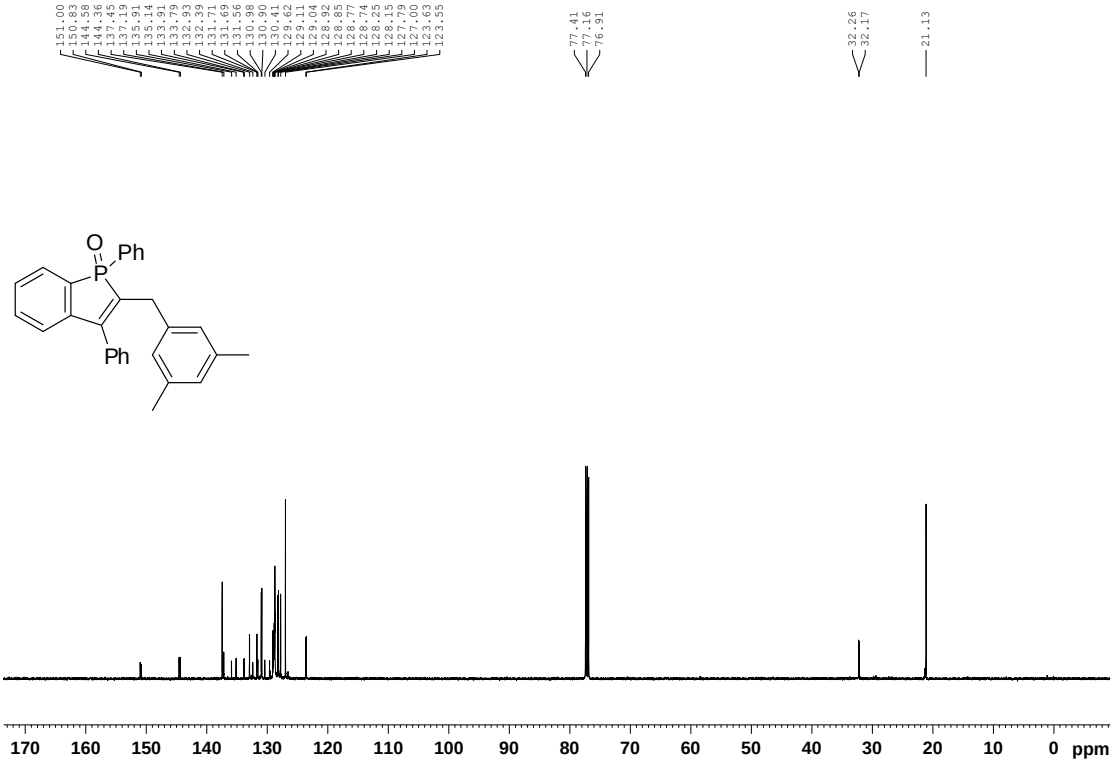
^{31}P NMR of **3c**



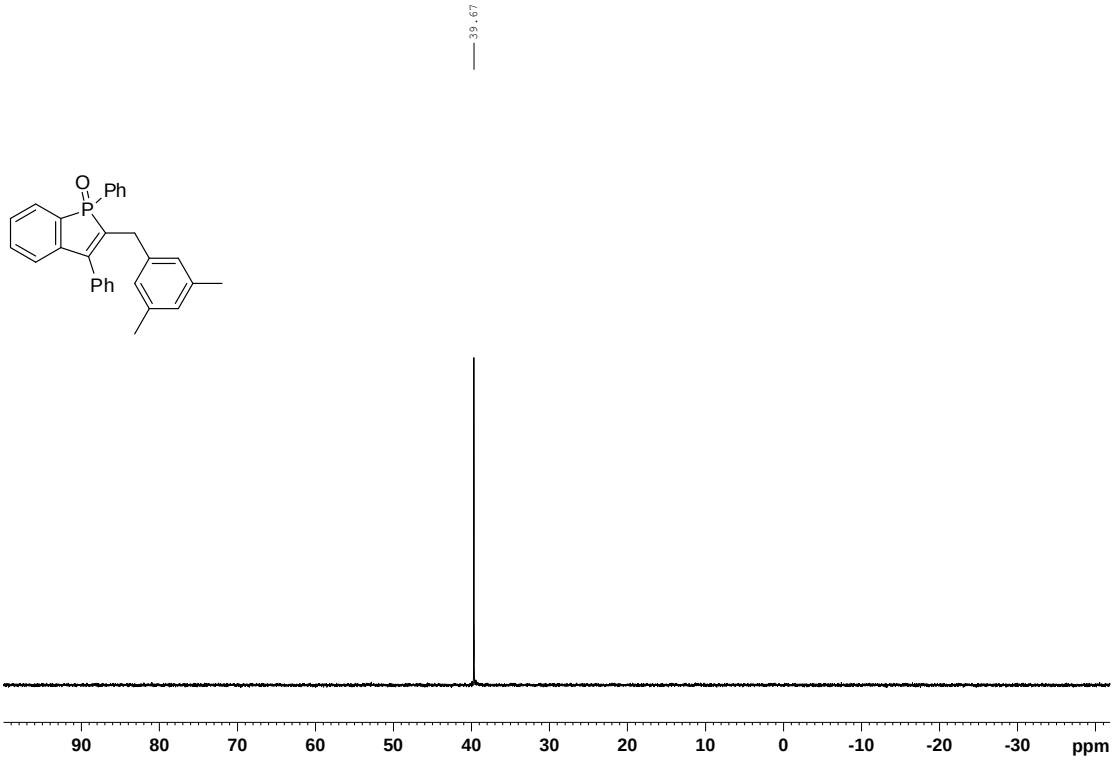
^{1}H NMR of **3d**



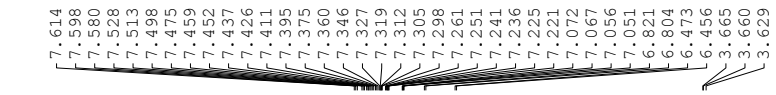
^{13}C NMR of **3d**

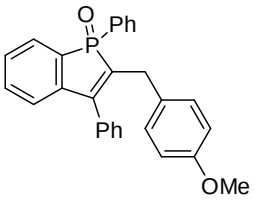


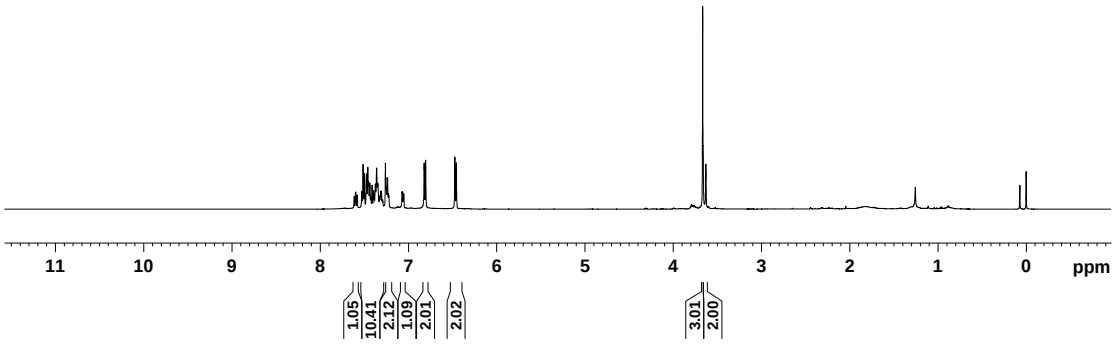
^{31}P NMR of **3d**



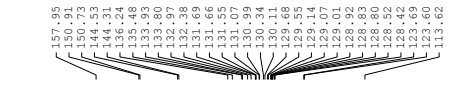
^{1}H NMR of **3e**

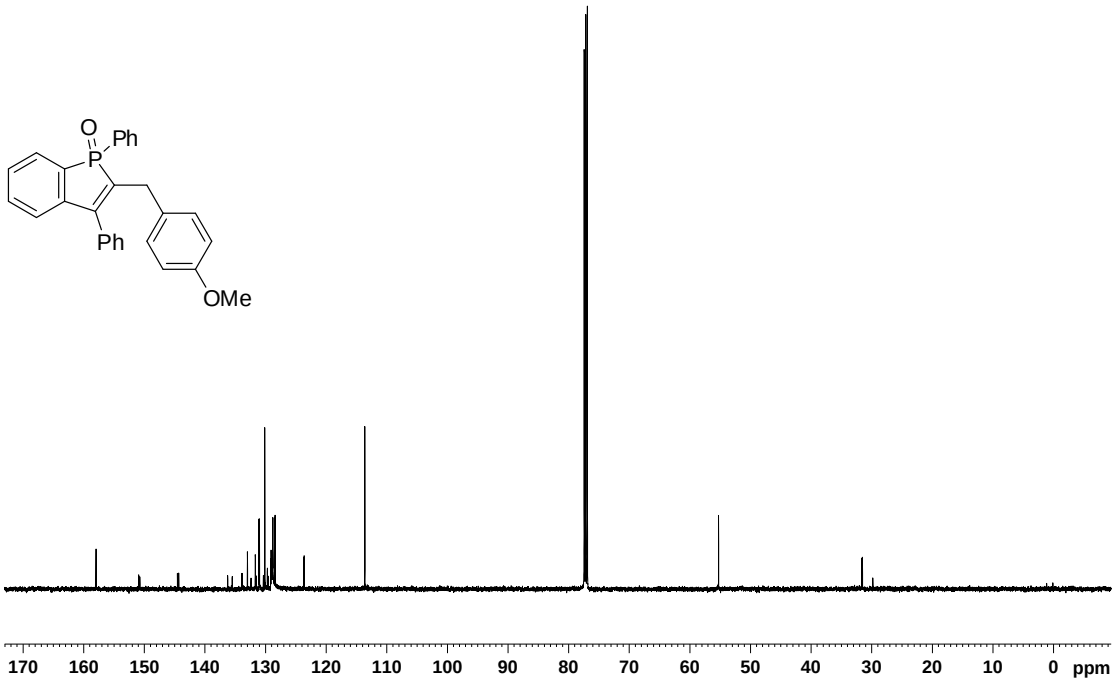




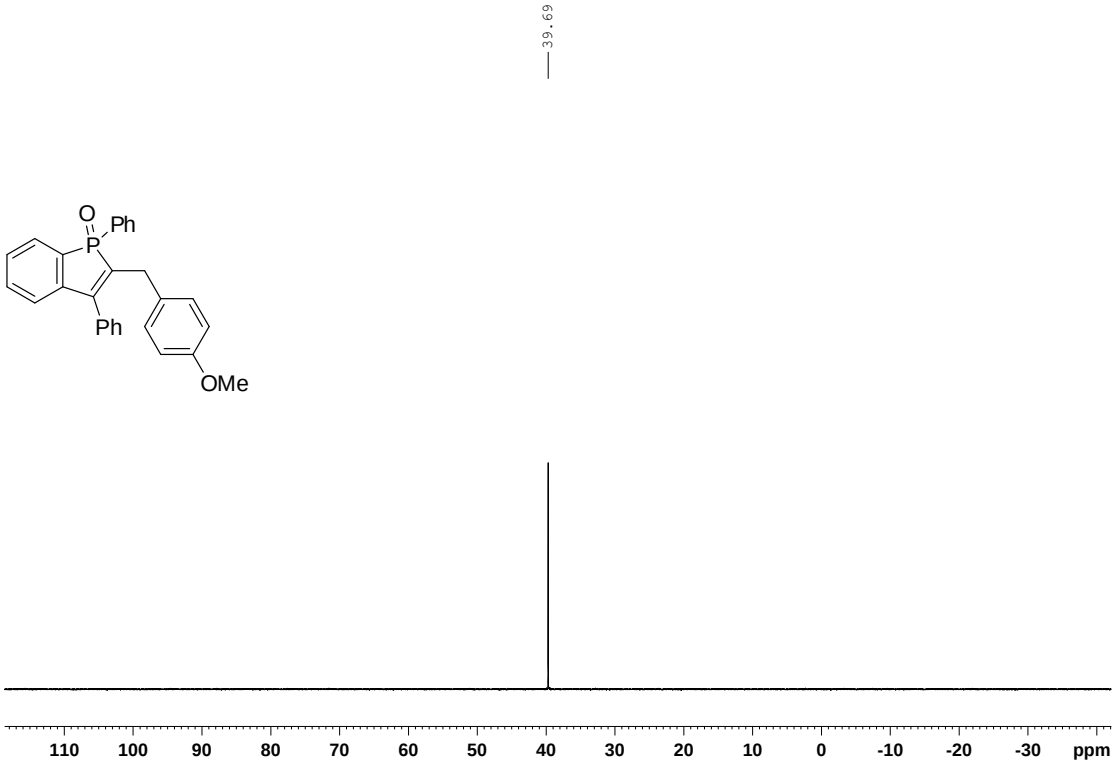


^{13}C NMR of **3e**

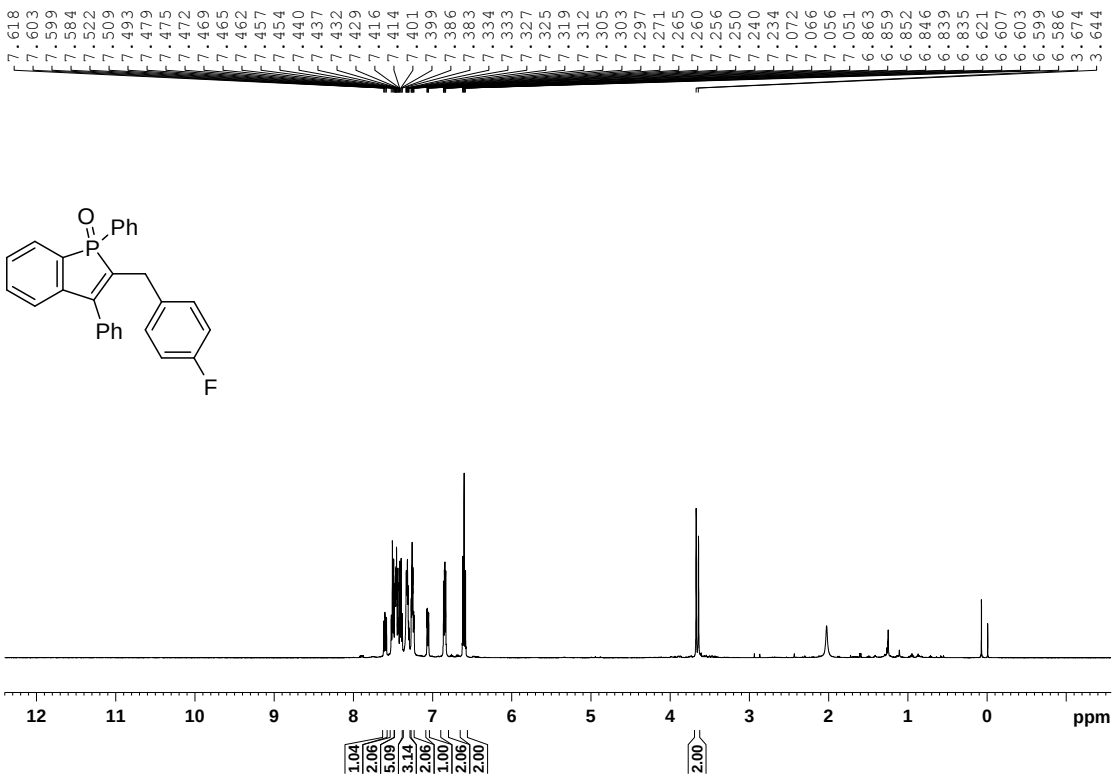




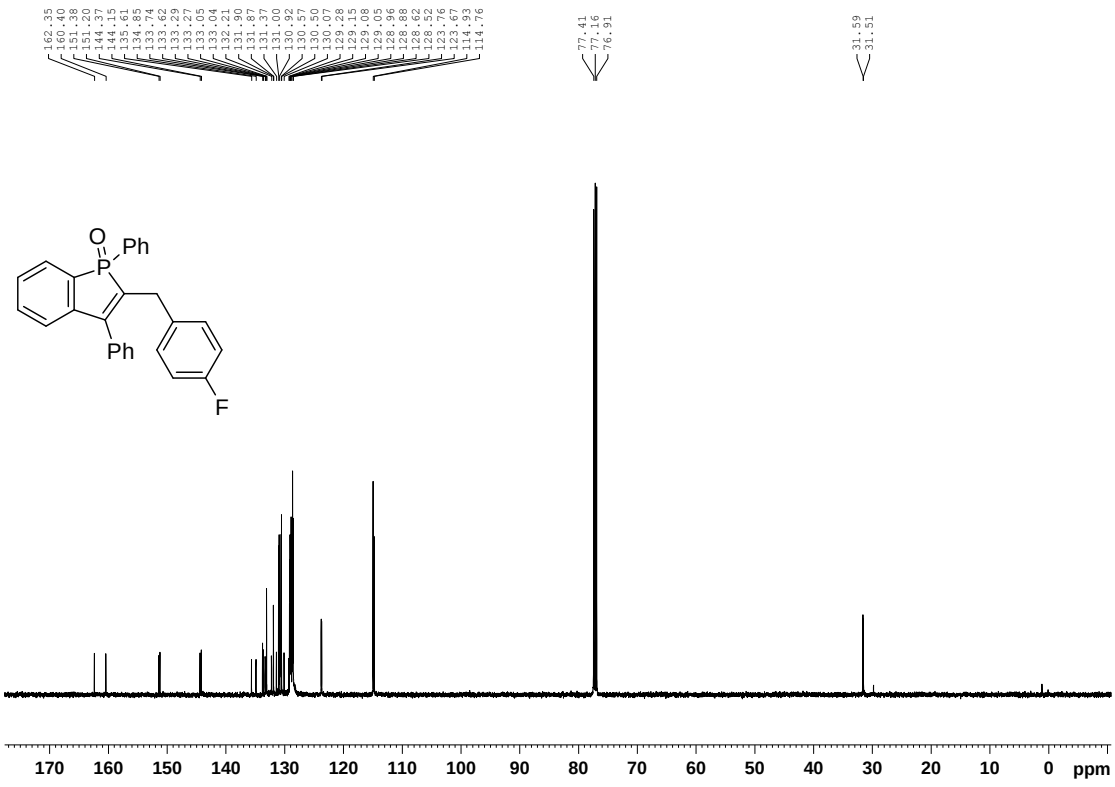
^{31}P NMR of **3e**



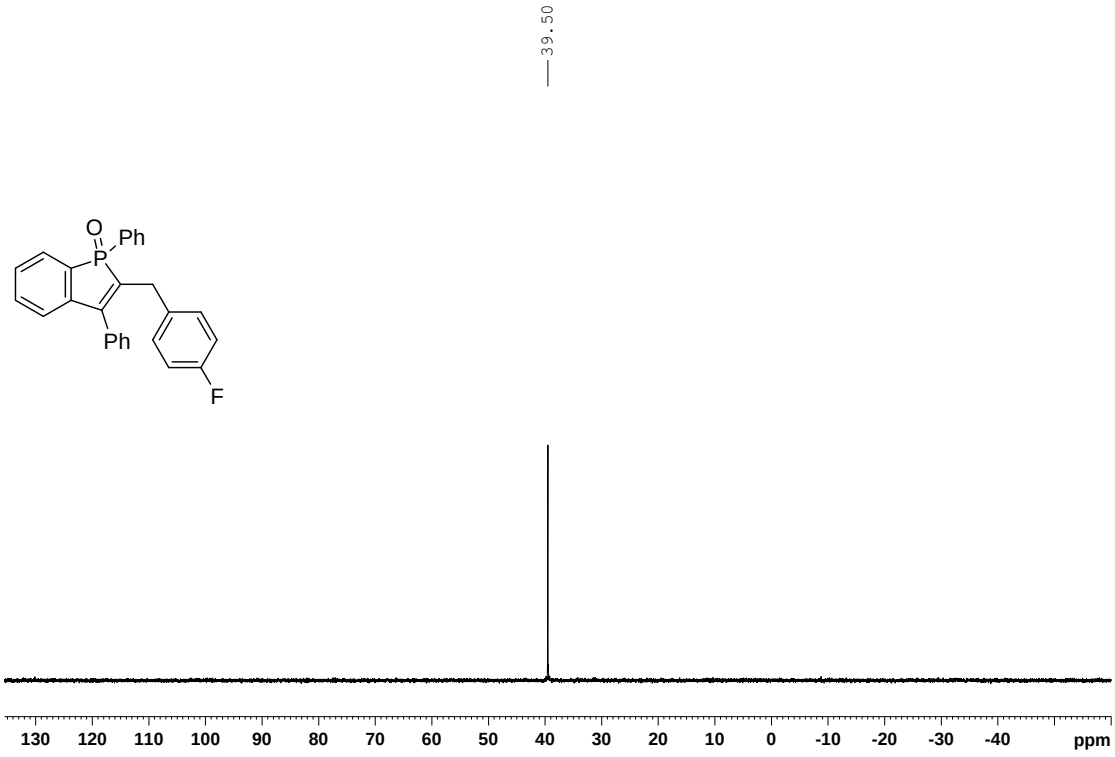
^{1}H NMR of **3f**



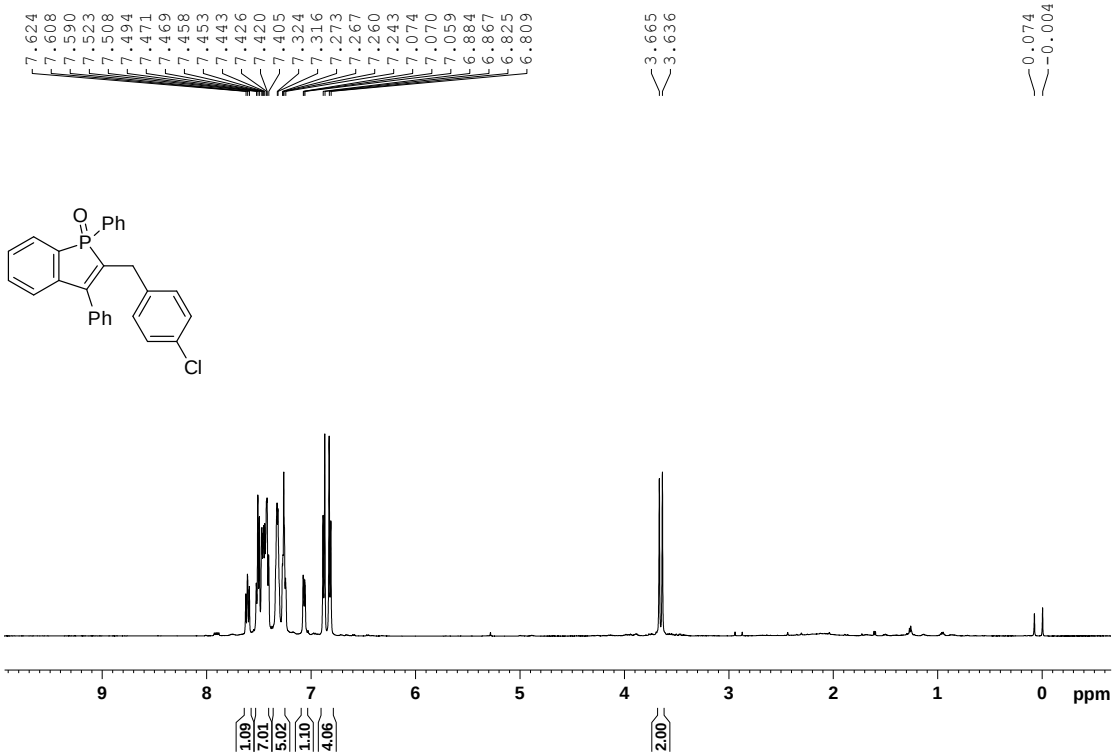
^{13}C NMR of **3f**



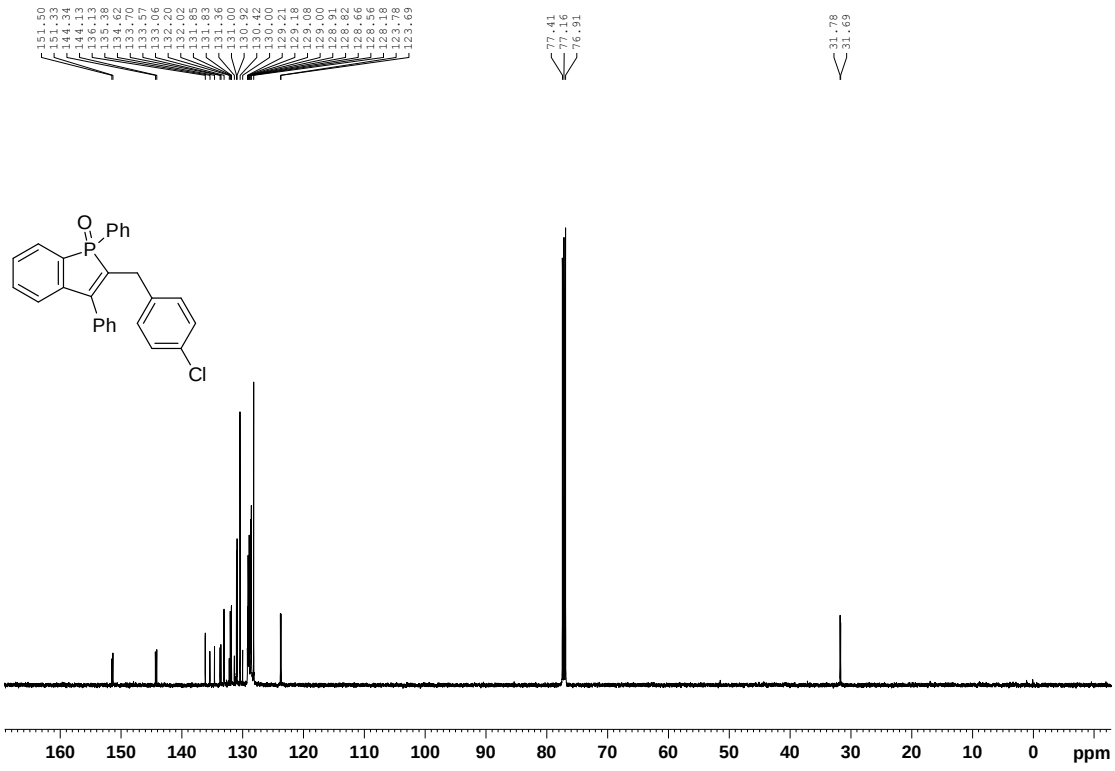
^{31}P NMR of **3f**



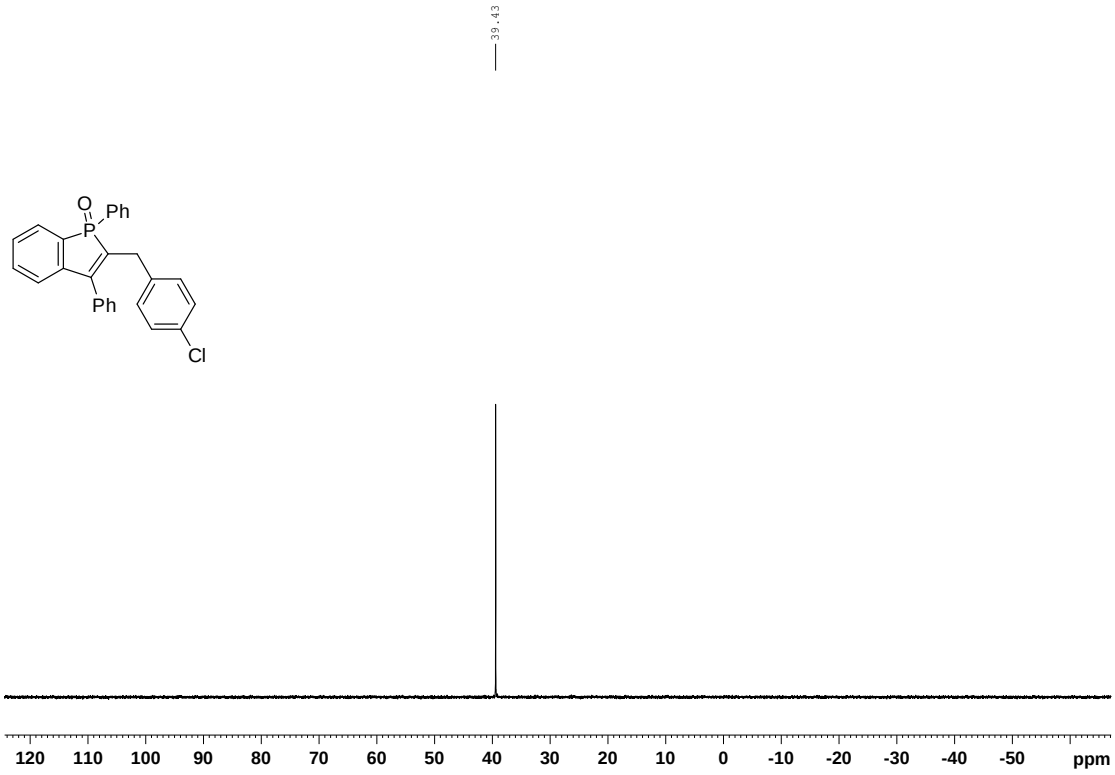
^{1}H NMR of **3g**



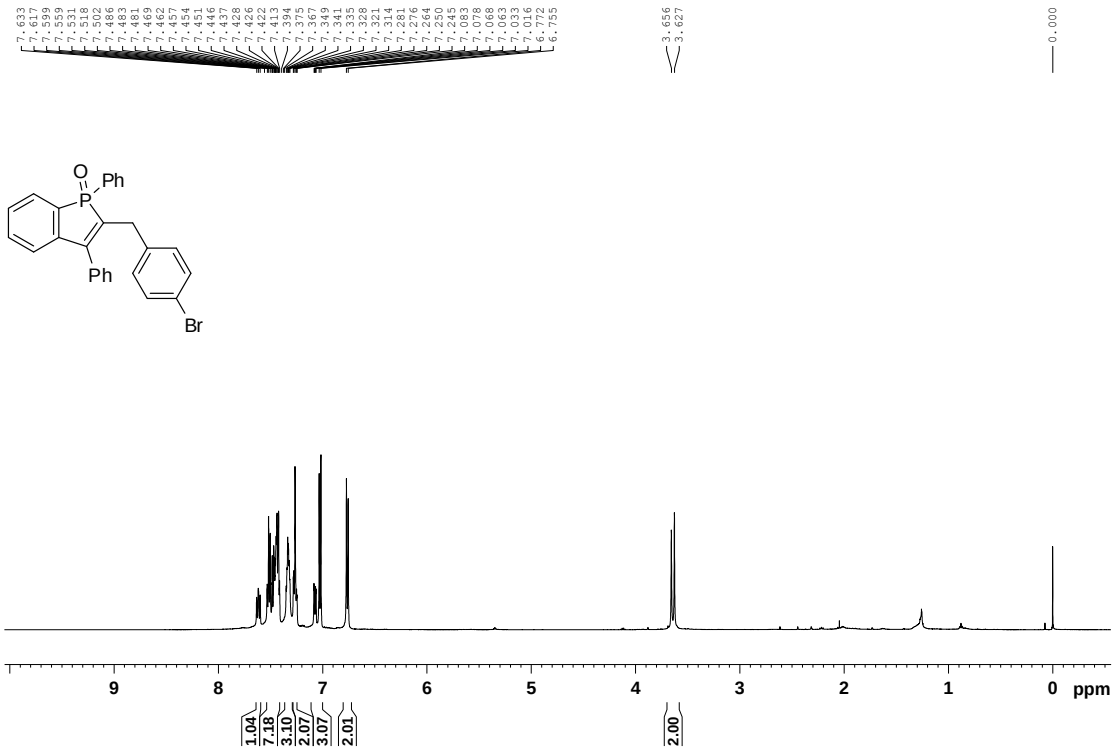
^{13}C NMR of **3g**



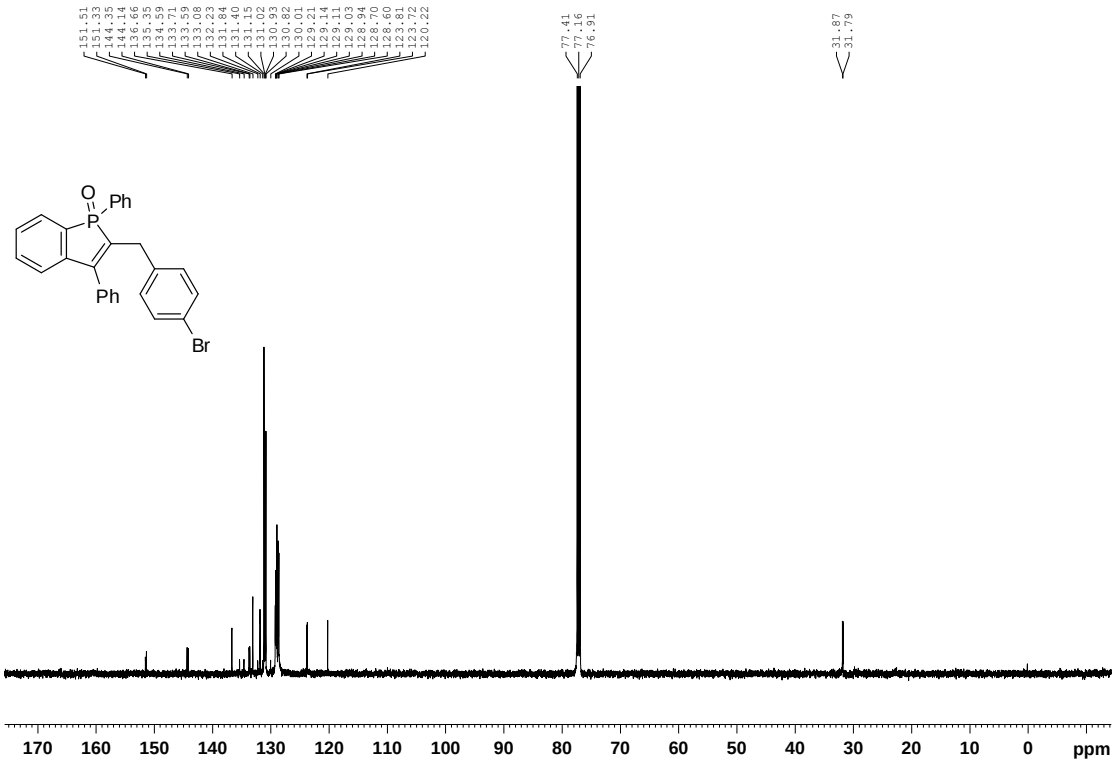
^{31}P NMR of **3g**



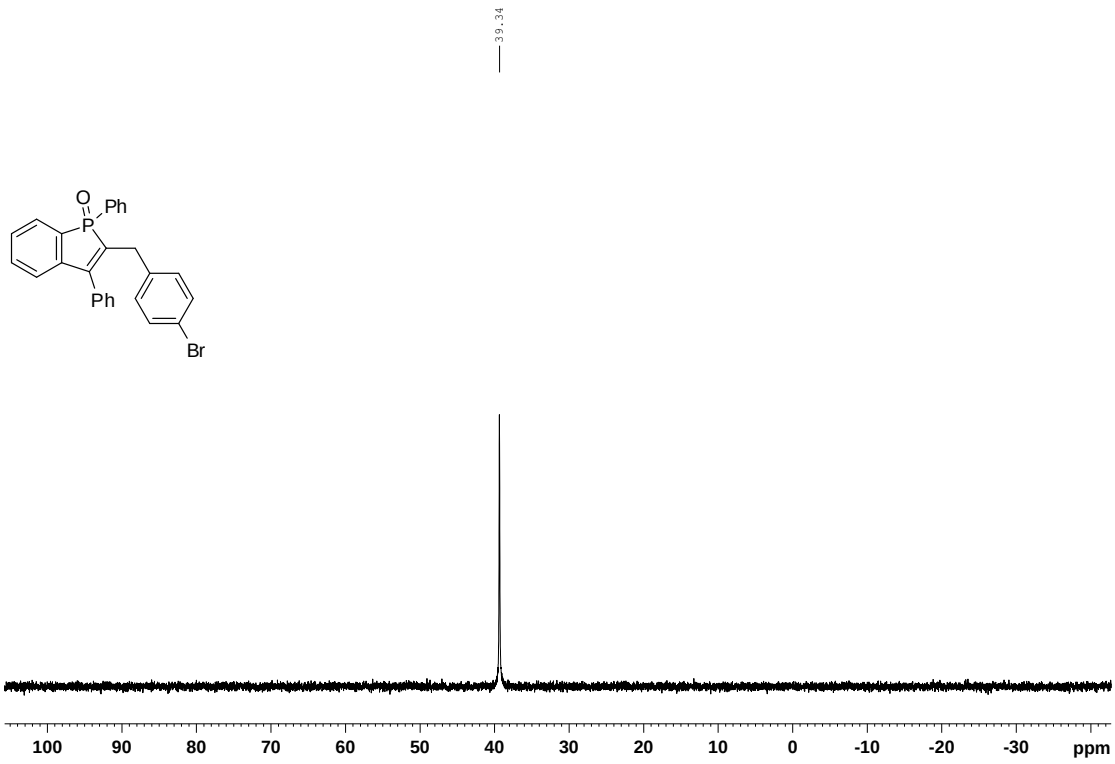
^{1}H NMR of **3h**



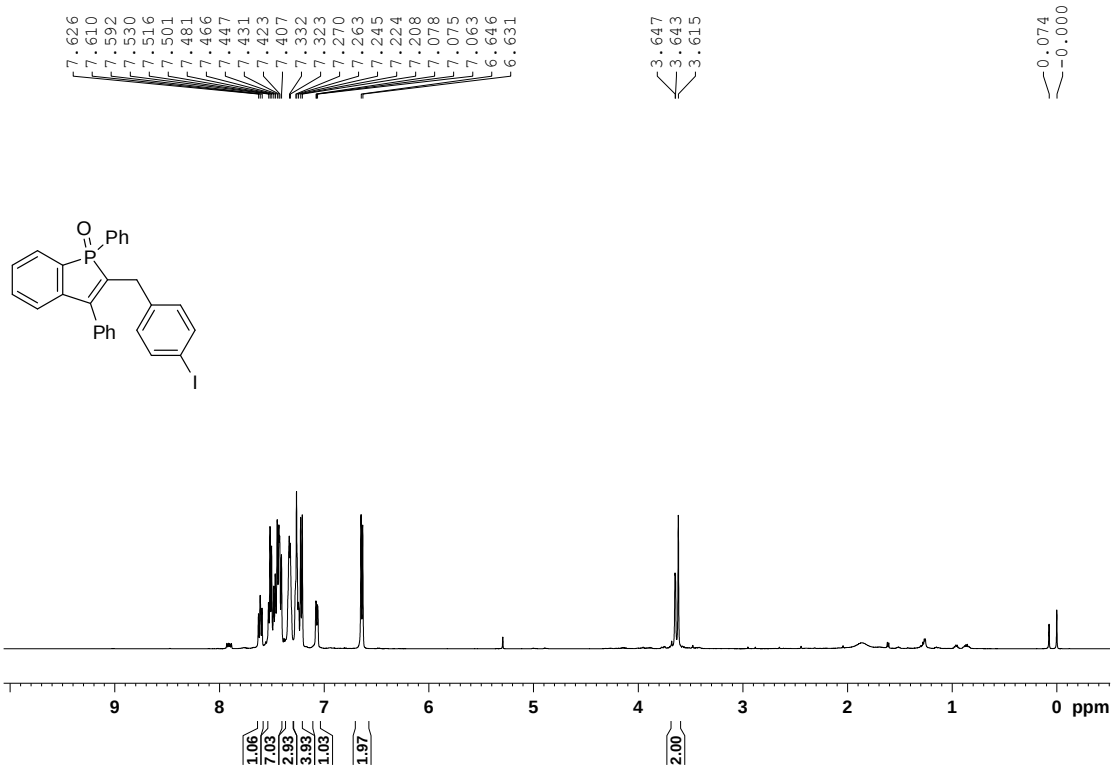
^{13}C NMR of **3h**



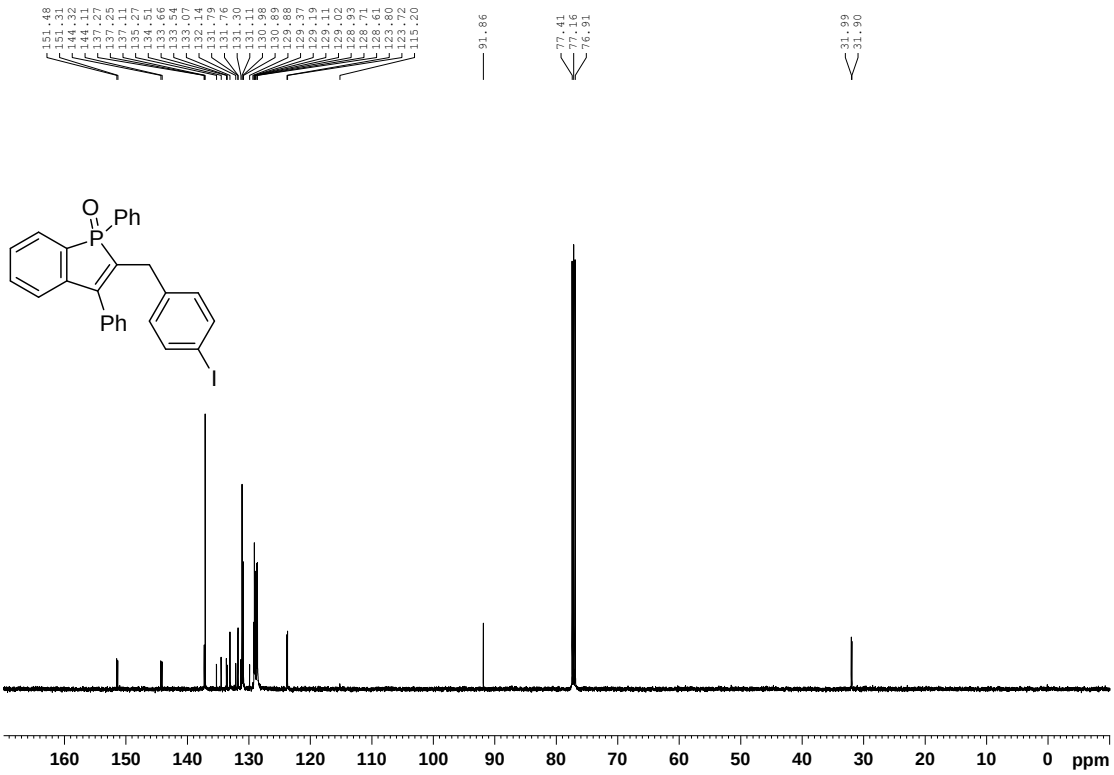
^{31}P NMR of **3h**



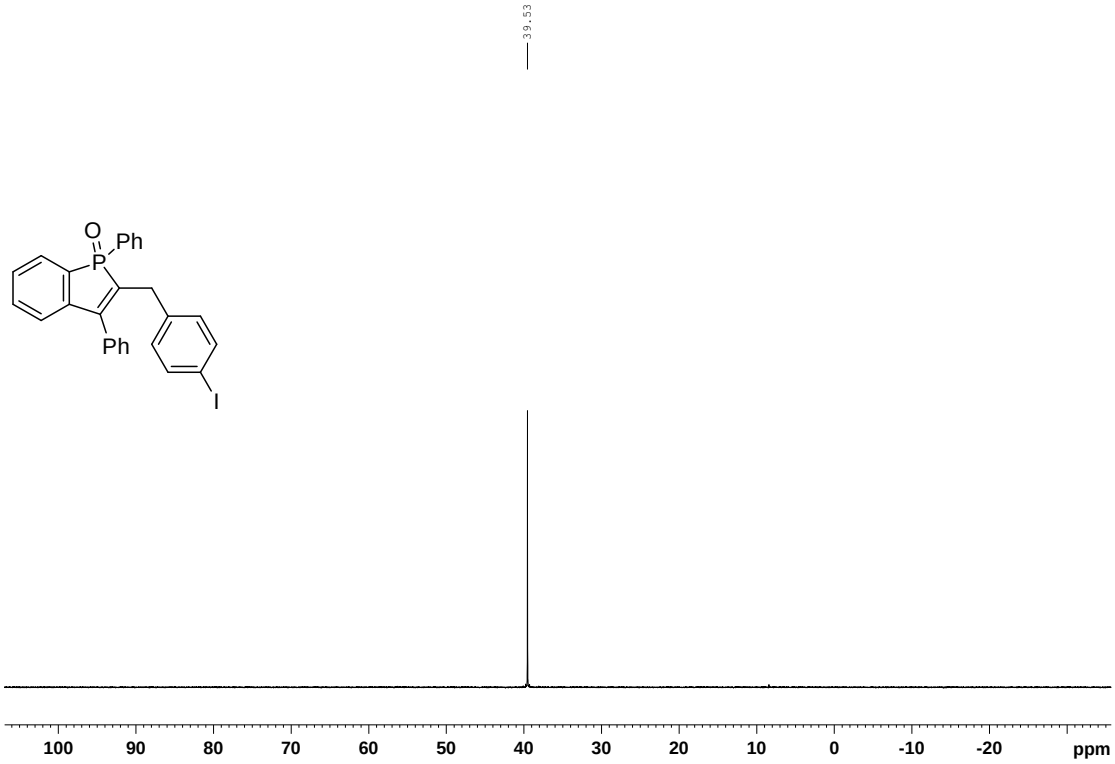
^{1}H NMR of **3i**



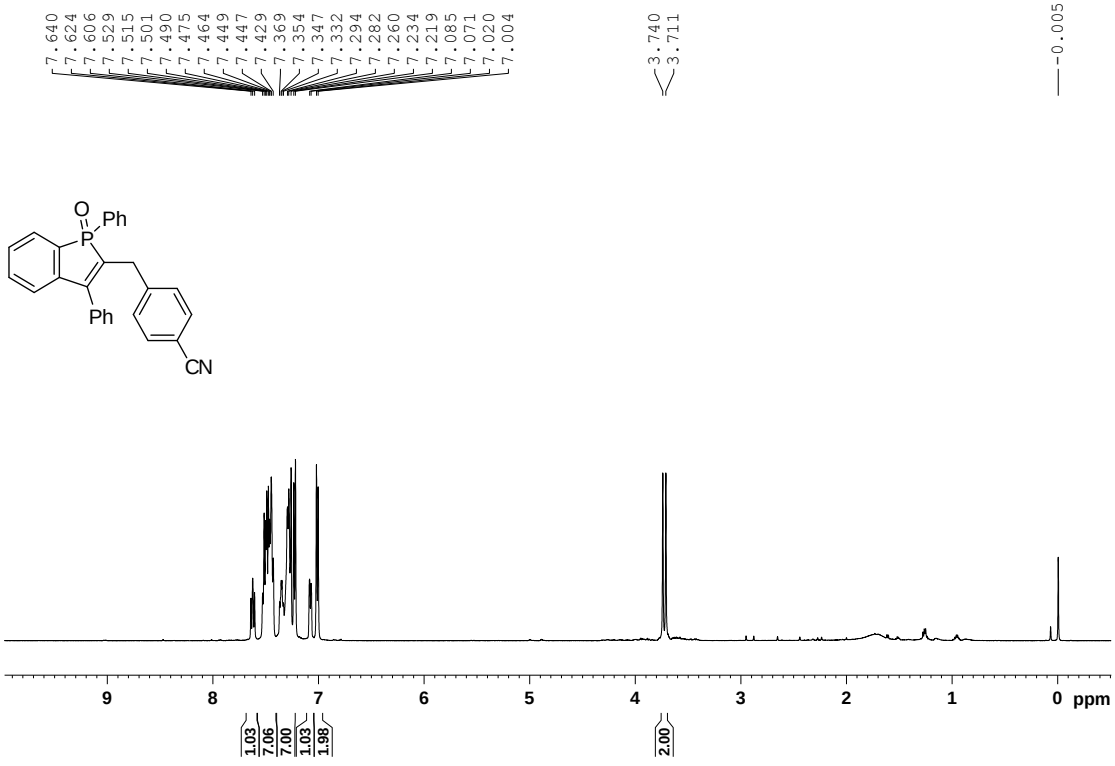
^{13}C NMR of **3i**



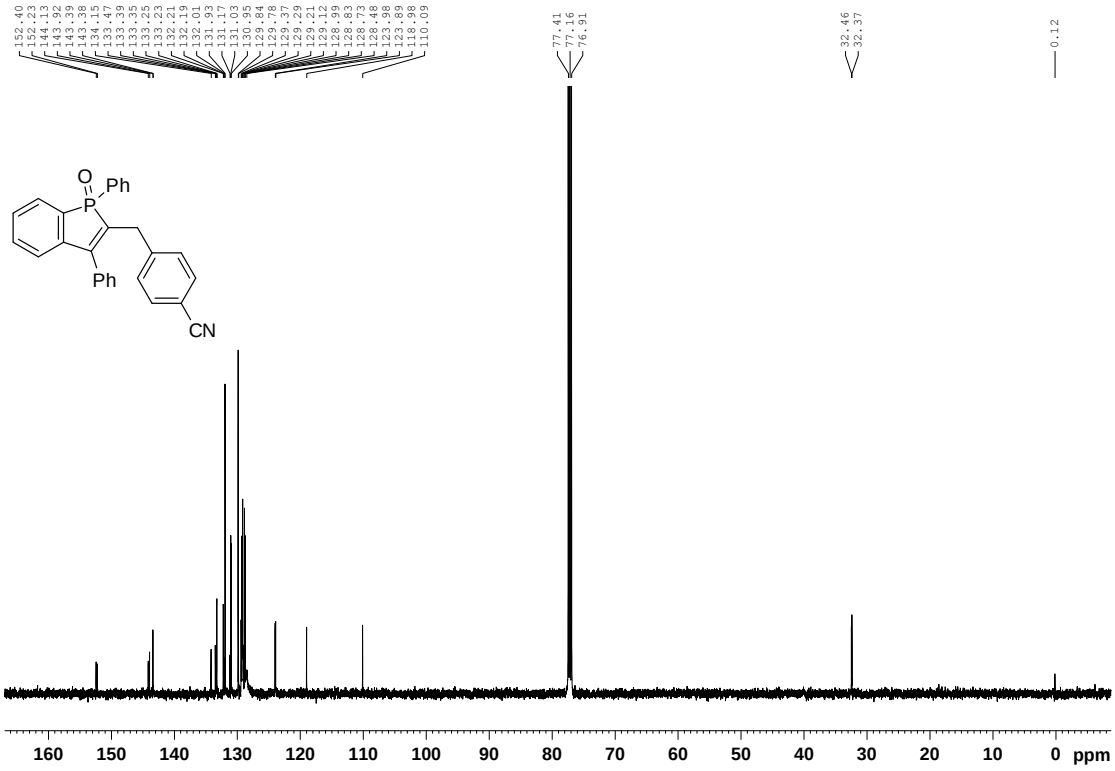
^{31}P NMR of **3i**



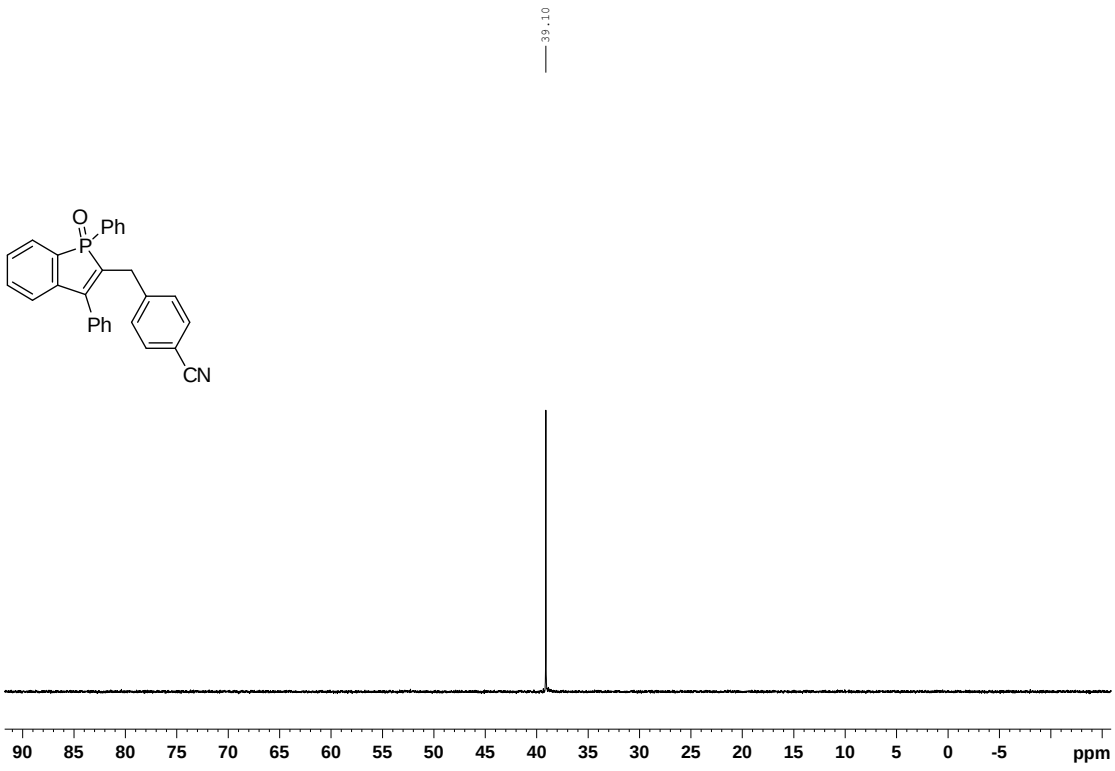
^{1}H NMR of **3j**



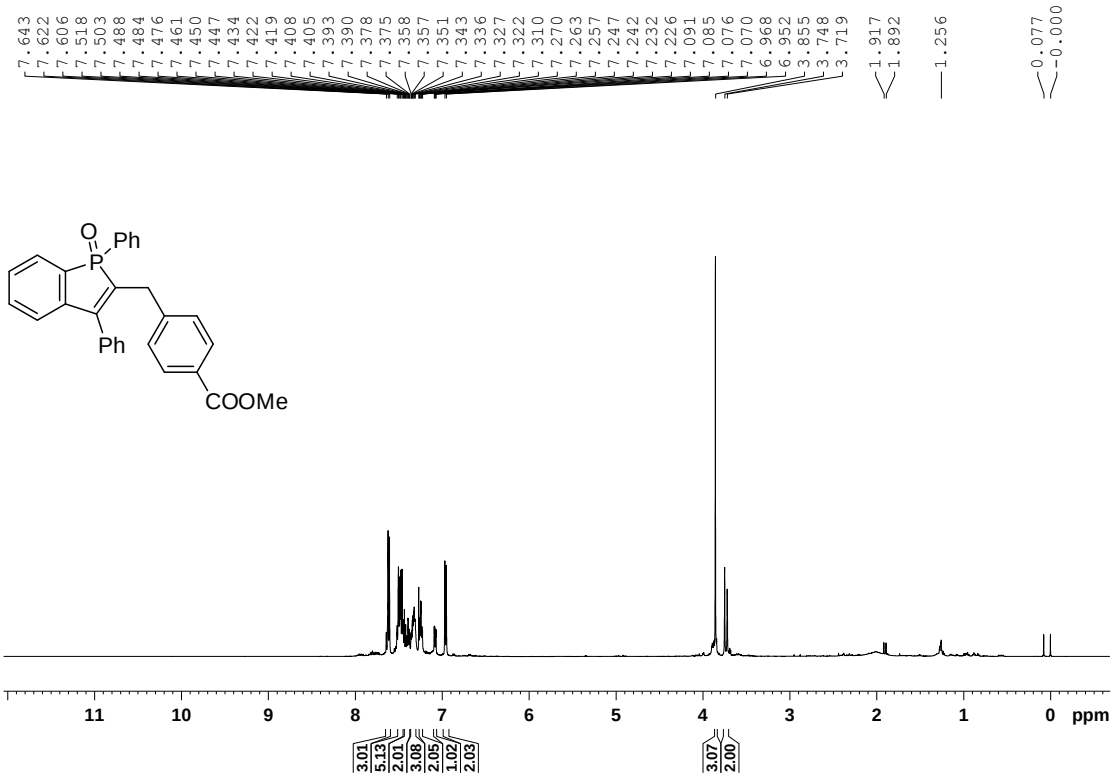
^{13}C NMR of **3j**



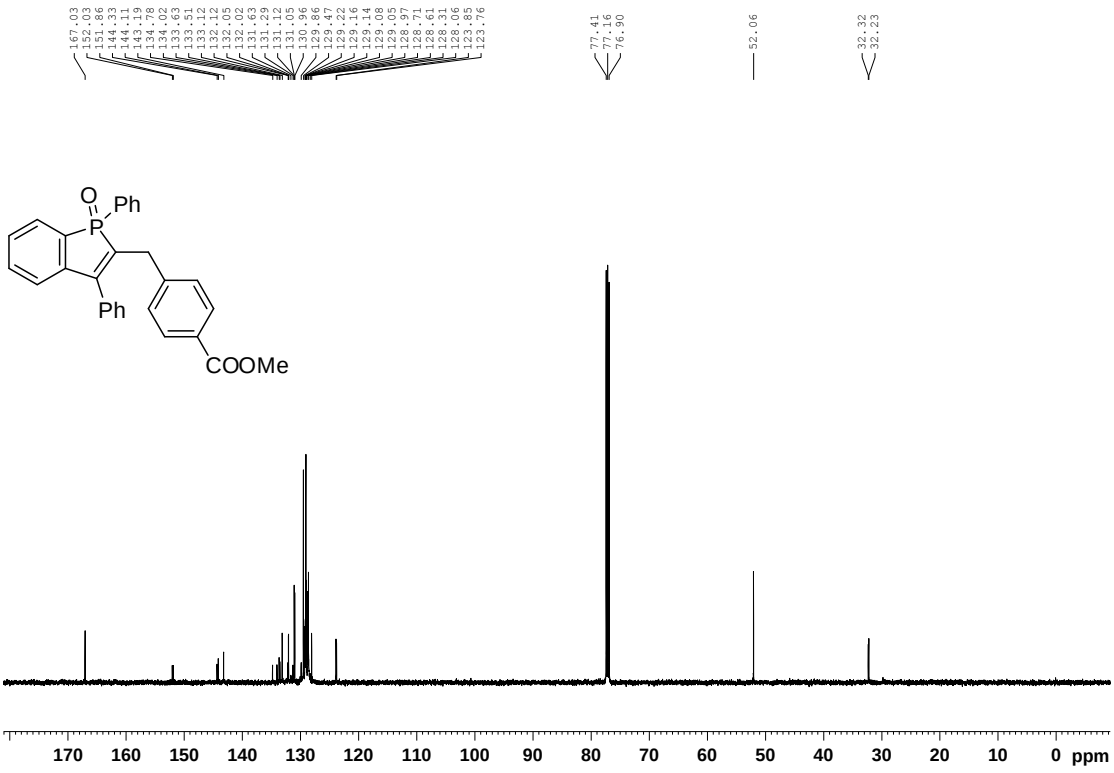
^{31}P NMR of **3j**



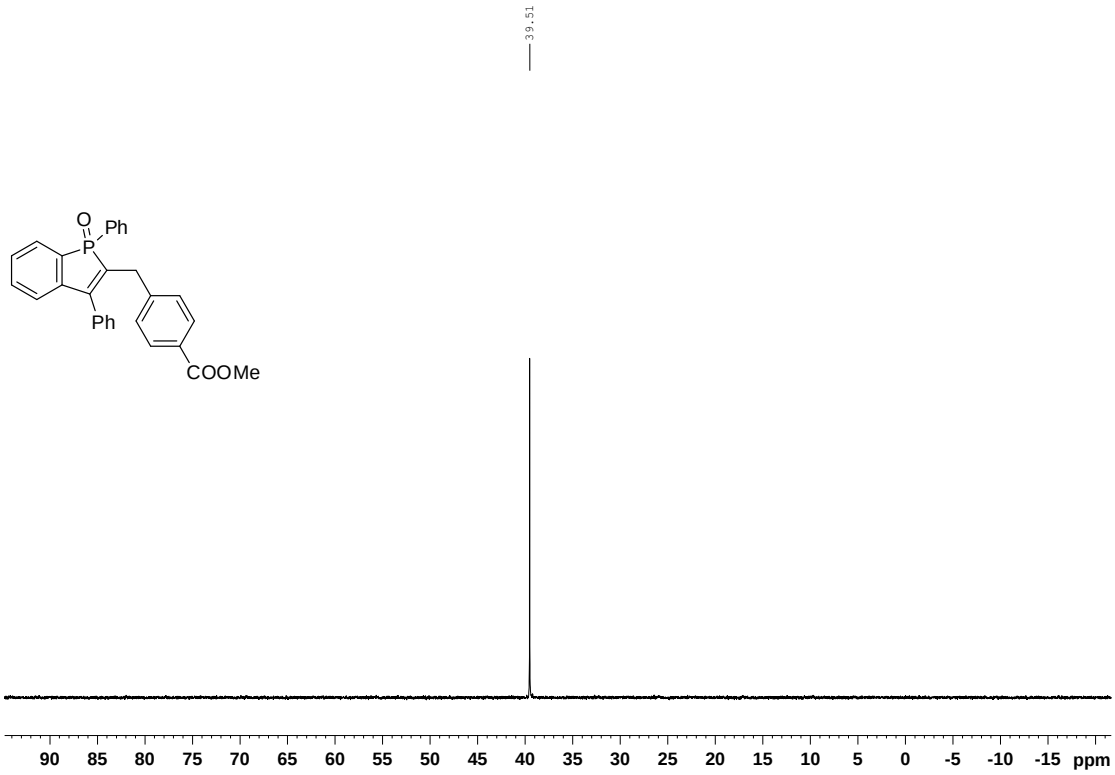
^{1}H NMR of **3k**



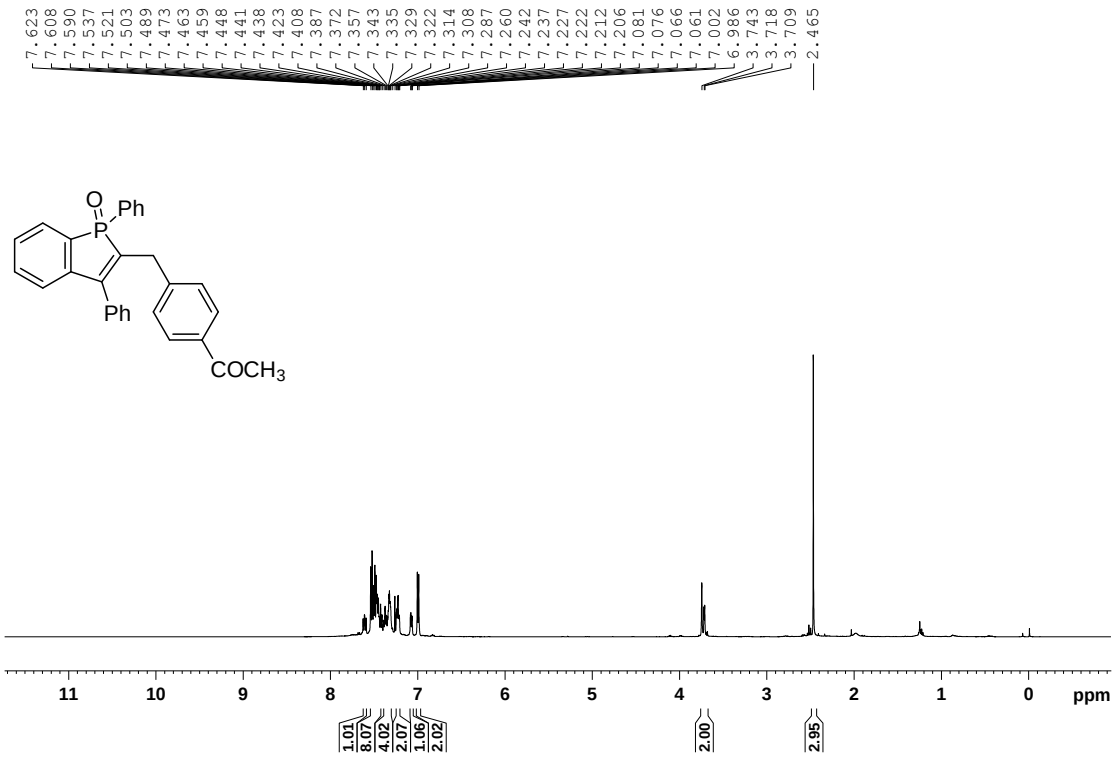
^{13}C NMR of **3l**



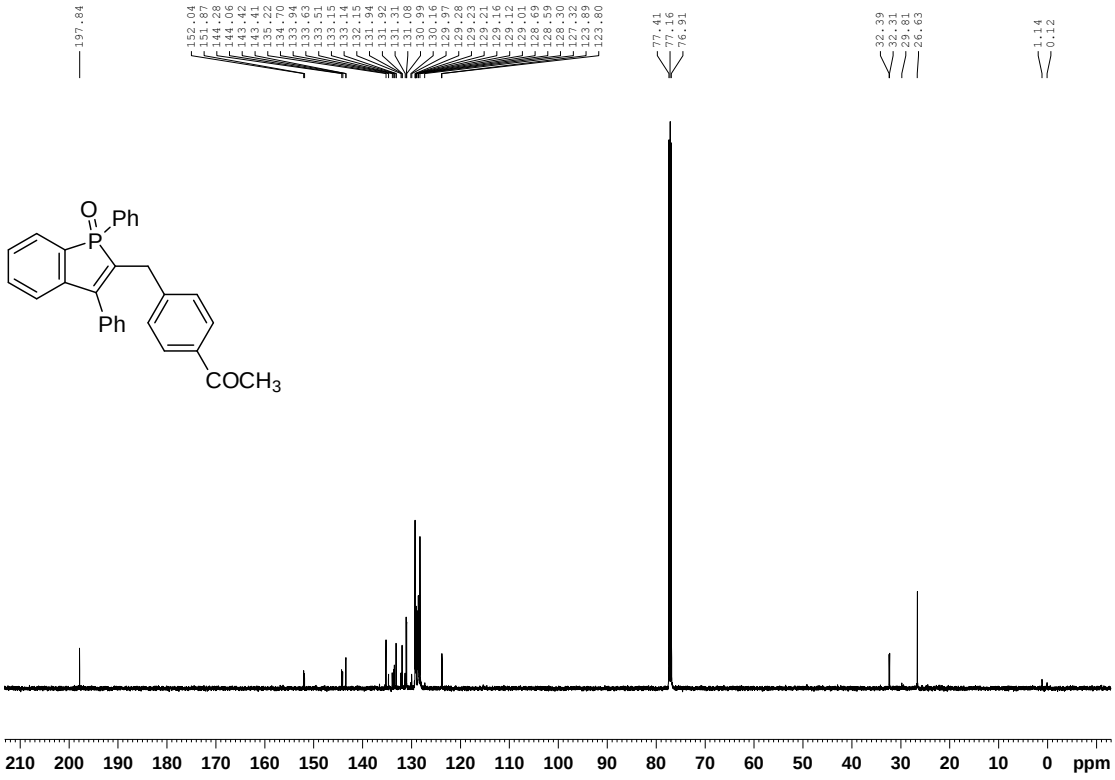
^{31}P NMR of **3k**



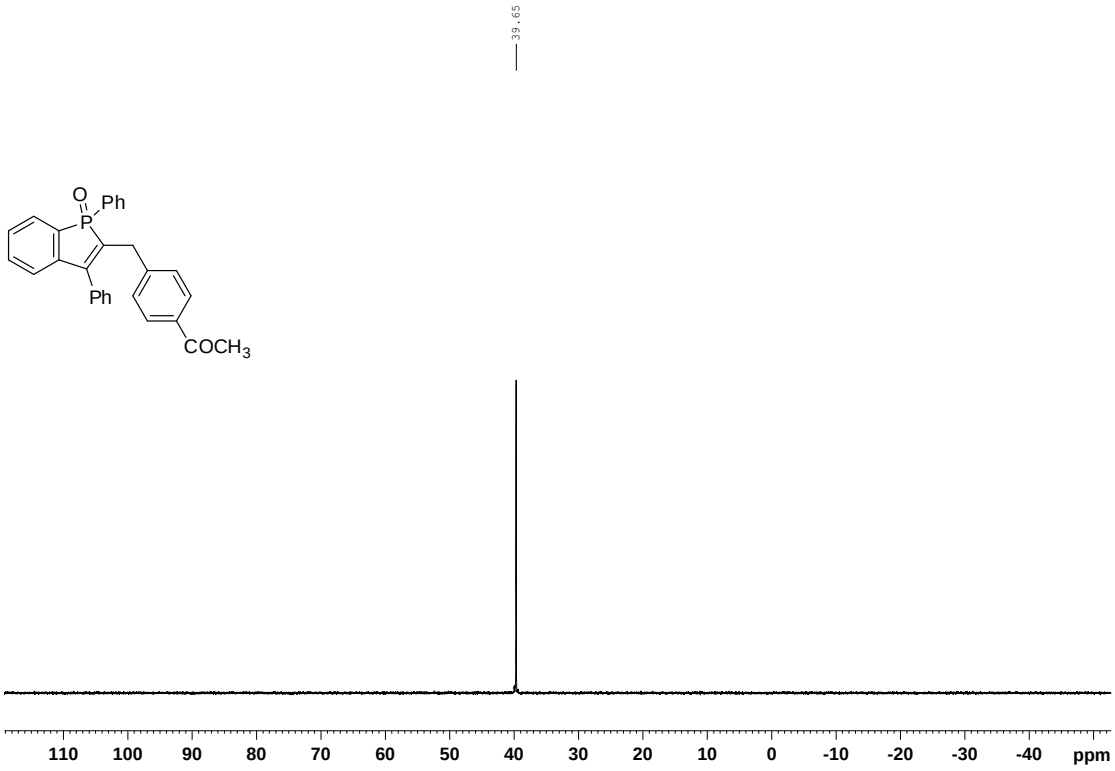
^{1}H NMR of **3l**



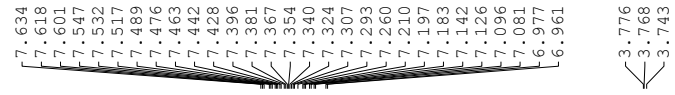
^{13}C NMR of **3l**

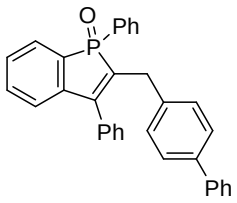


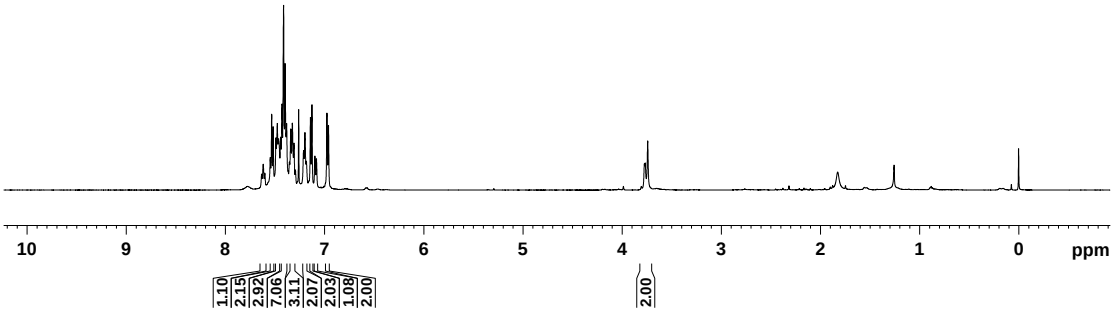
^{31}P NMR of **3l**



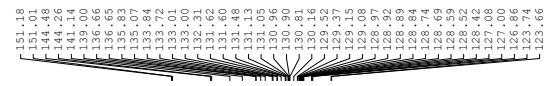
^{1}H NMR of **3m**

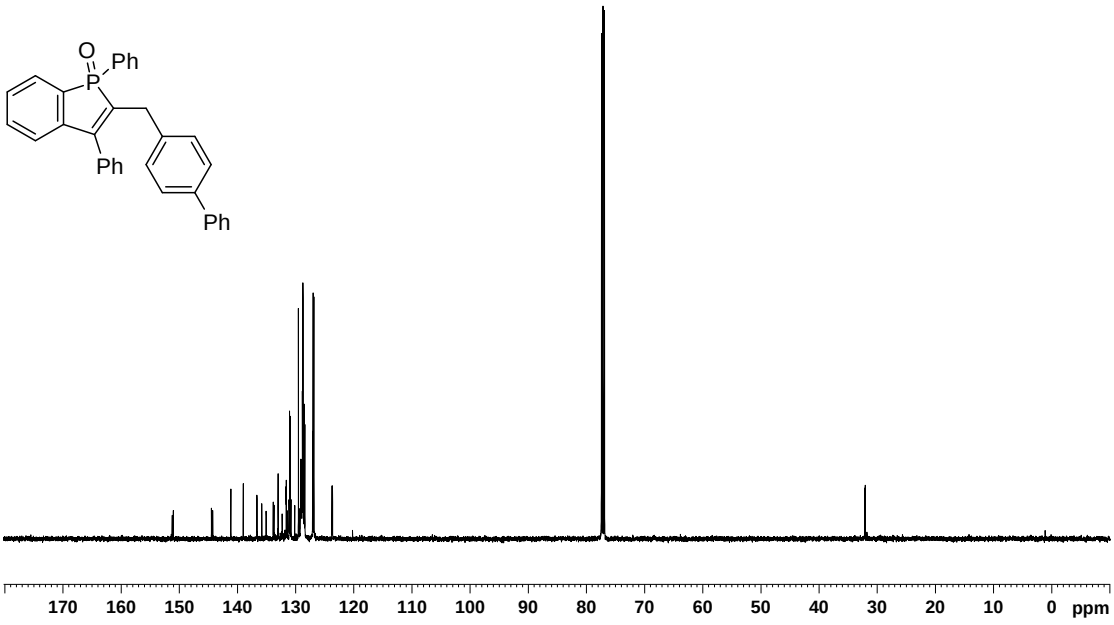




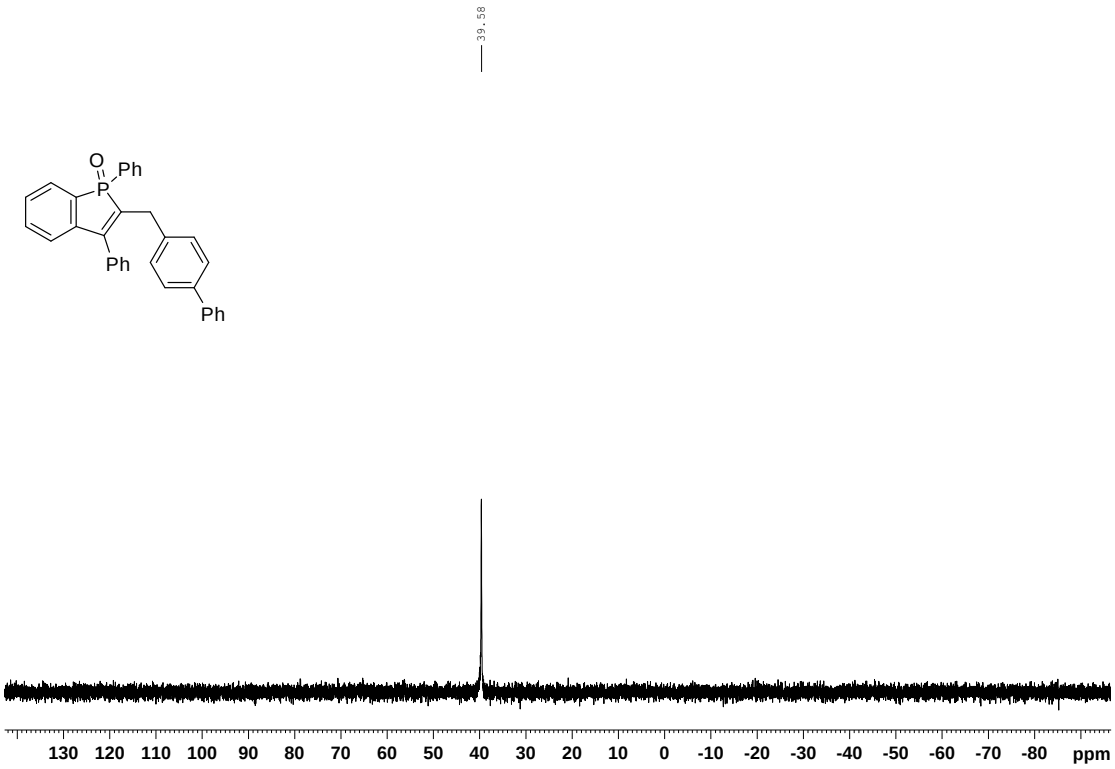


^{13}C NMR of **3m**

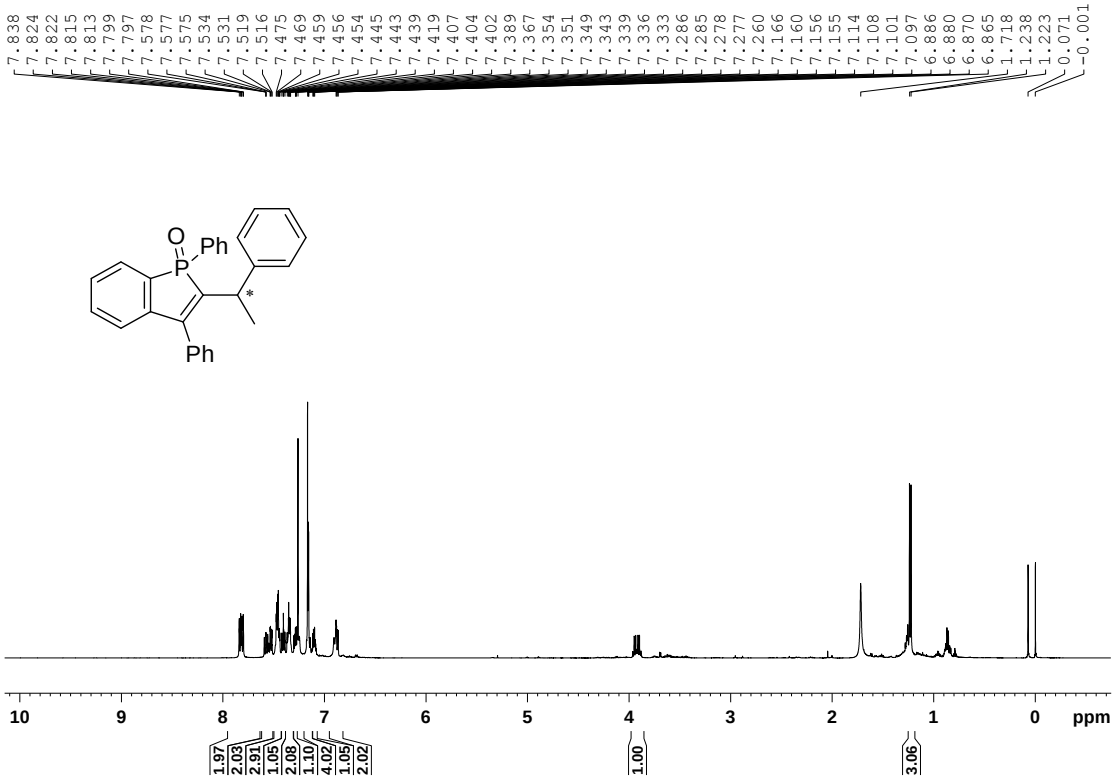




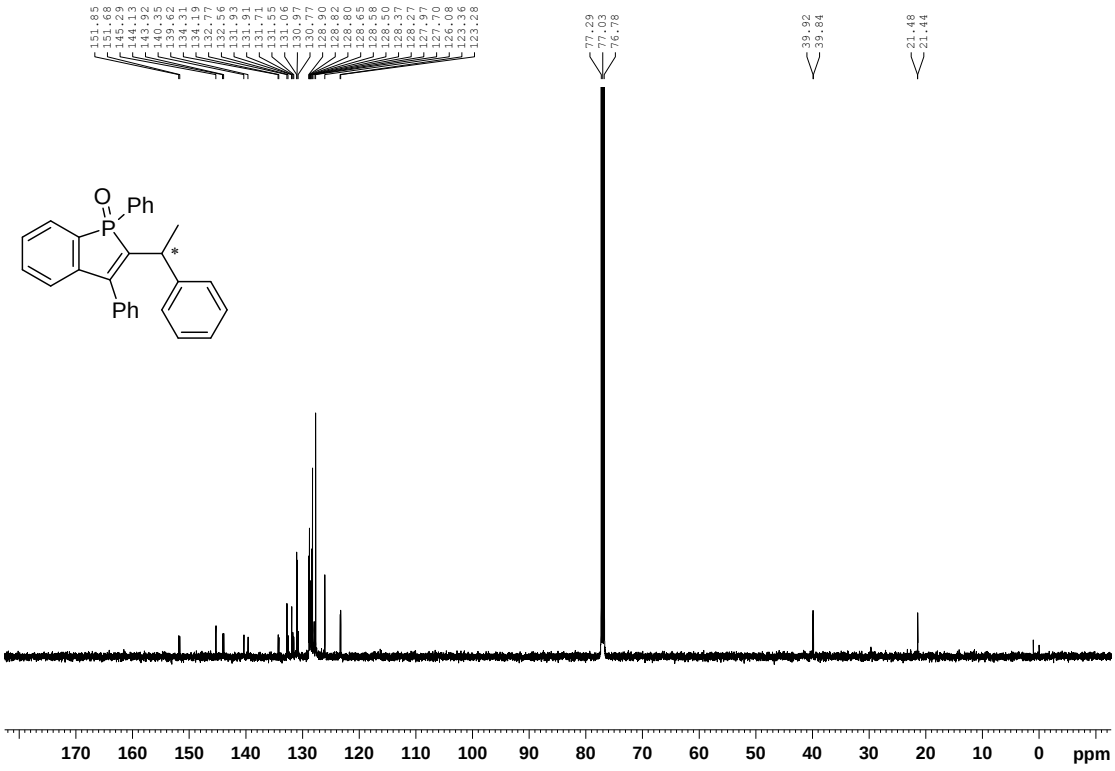
^{31}P NMR of **3m**



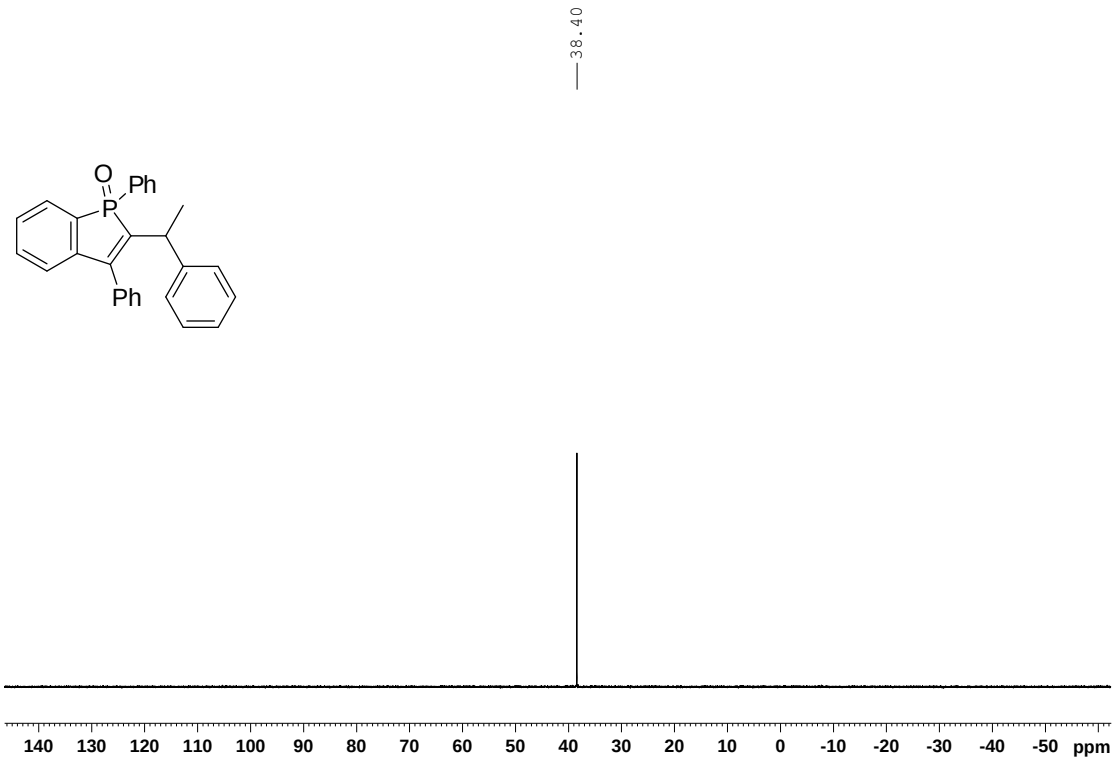
^{1}H NMR of **3n'** in **3n**



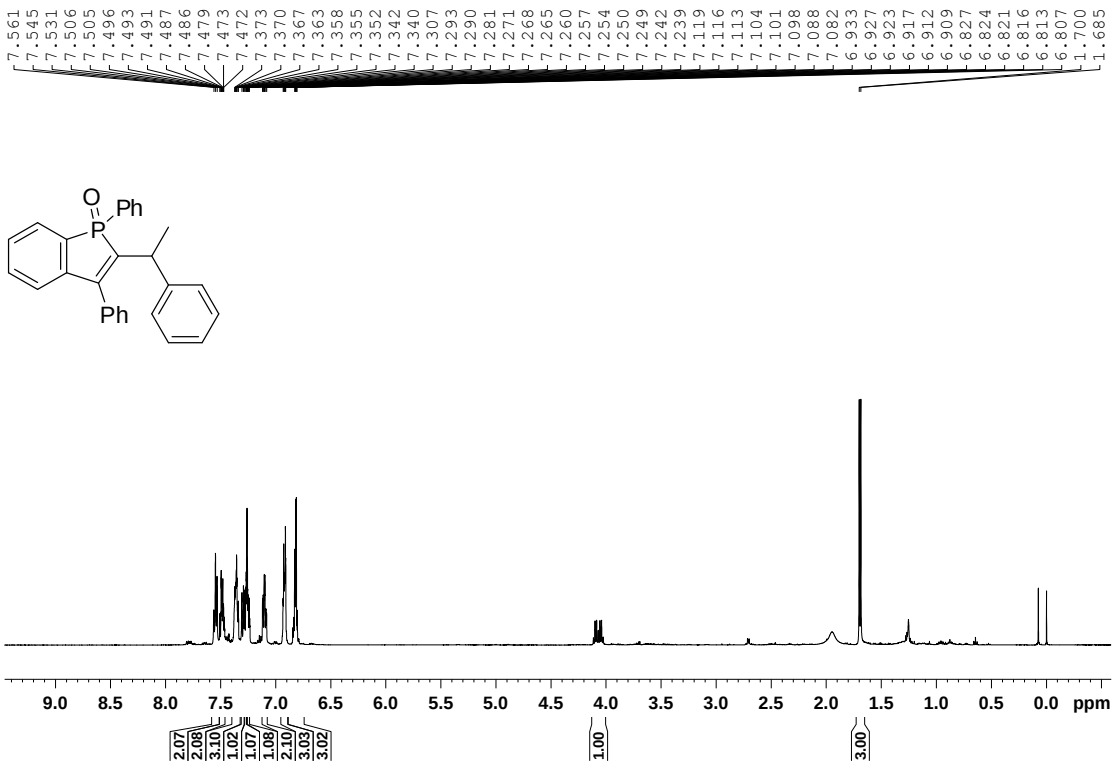
^{13}C NMR of **3n'** in **3n**



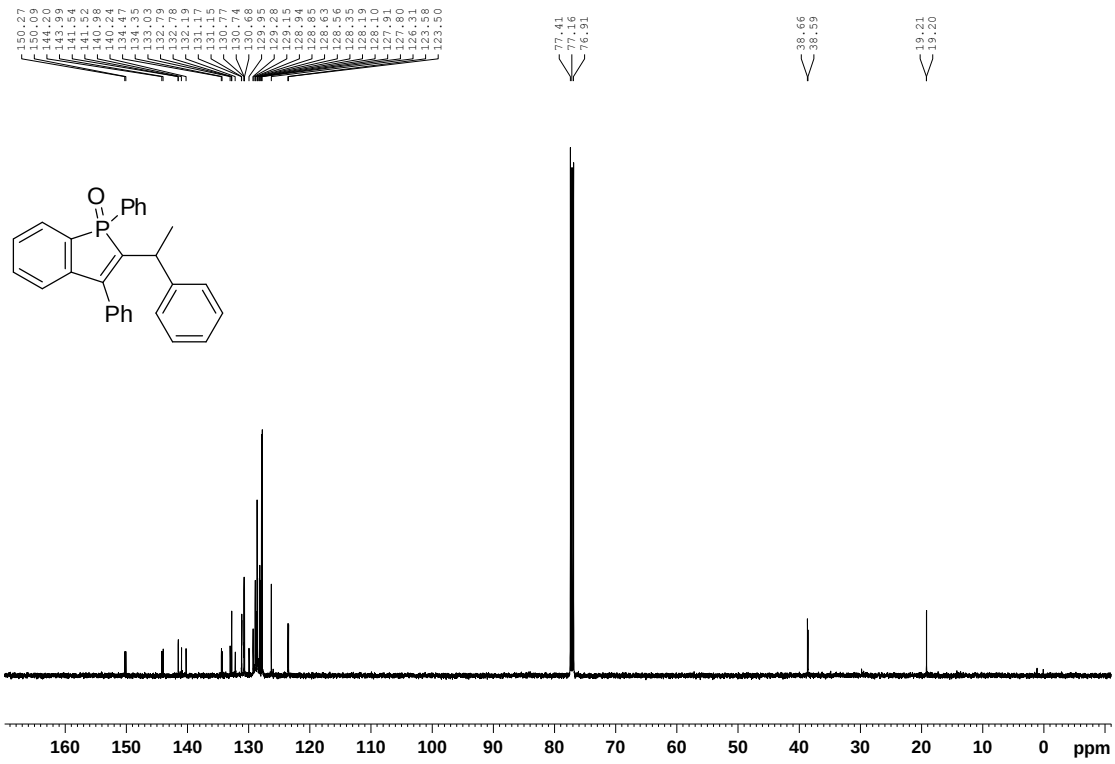
^{31}P NMR of **3n'** in **3n**



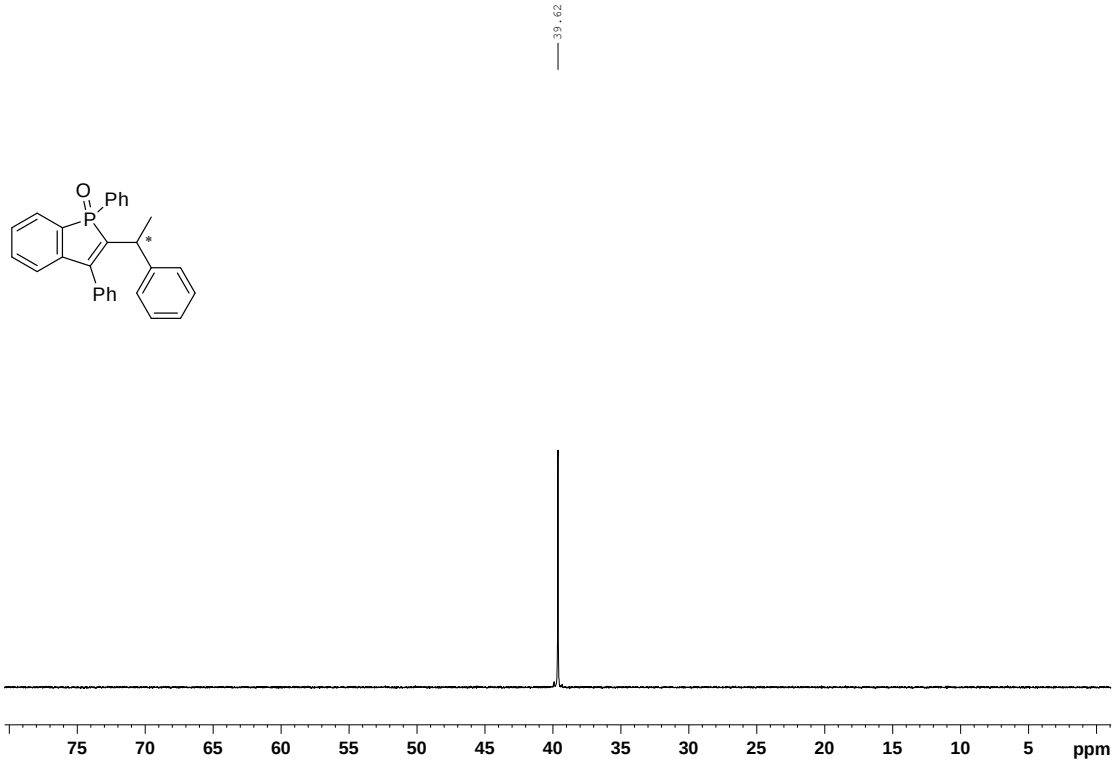
^{1}H NMR of **3n''** in **3n**



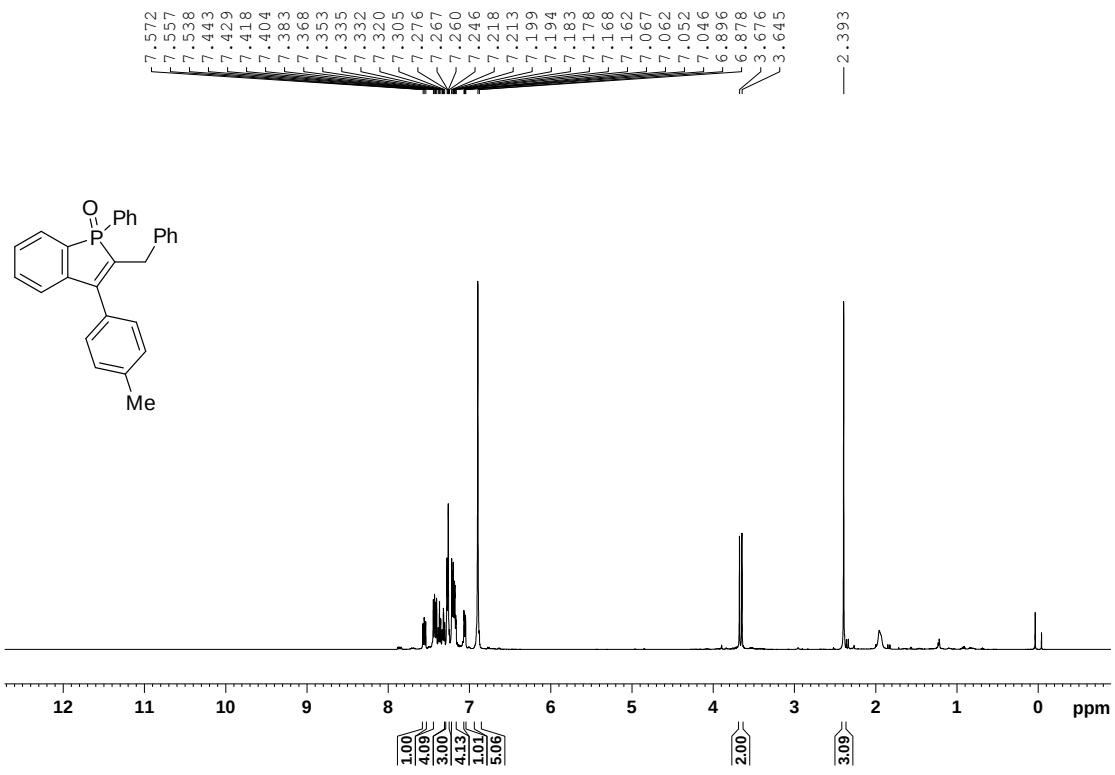
^{13}C NMR of **3n''** in **3n**



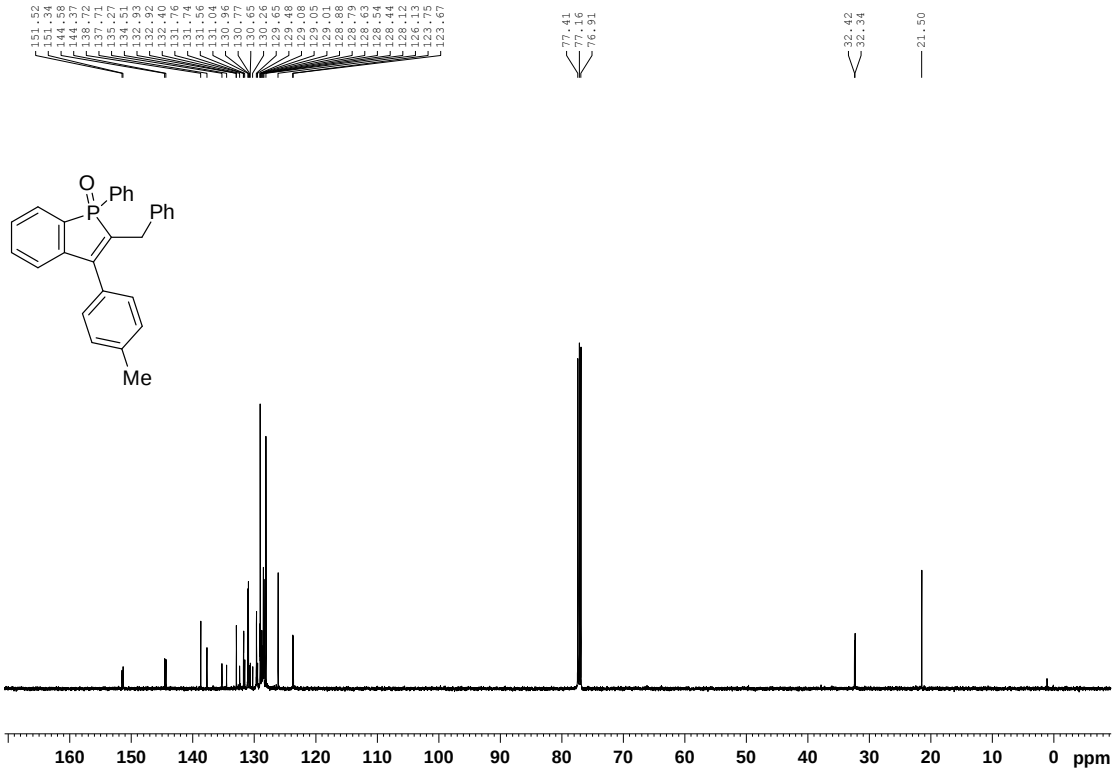
^{31}P NMR of **3n''** in **3n**



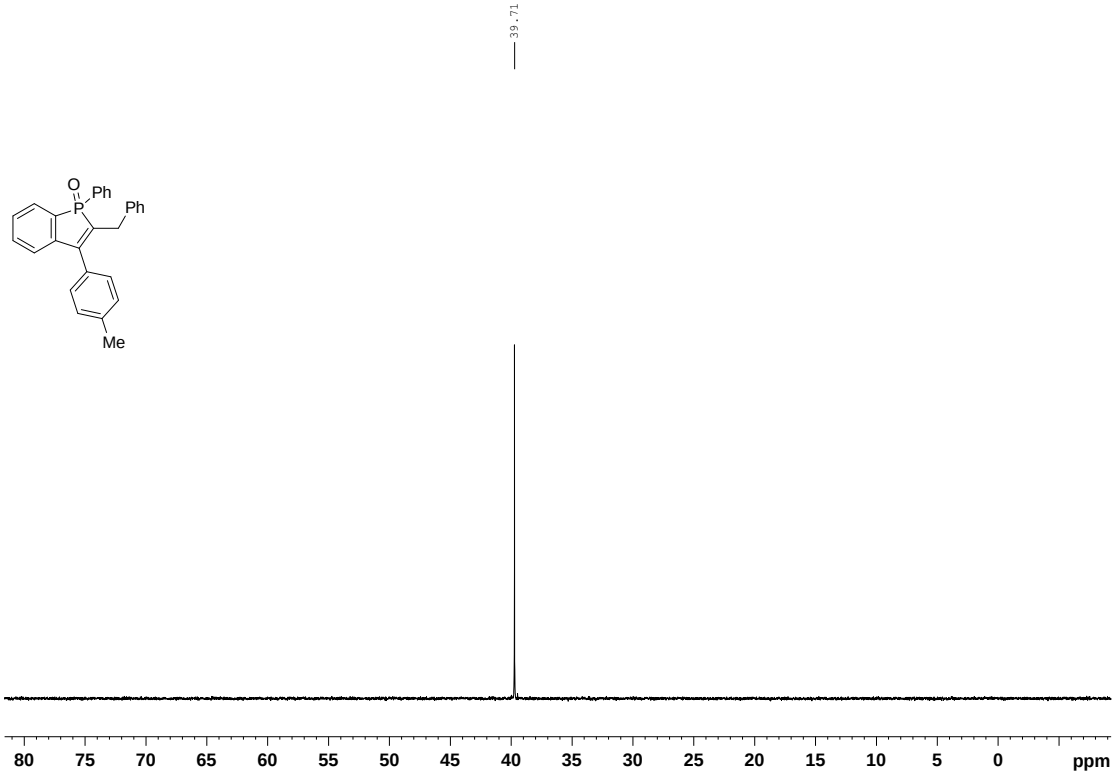
^{1}H NMR of **3o**



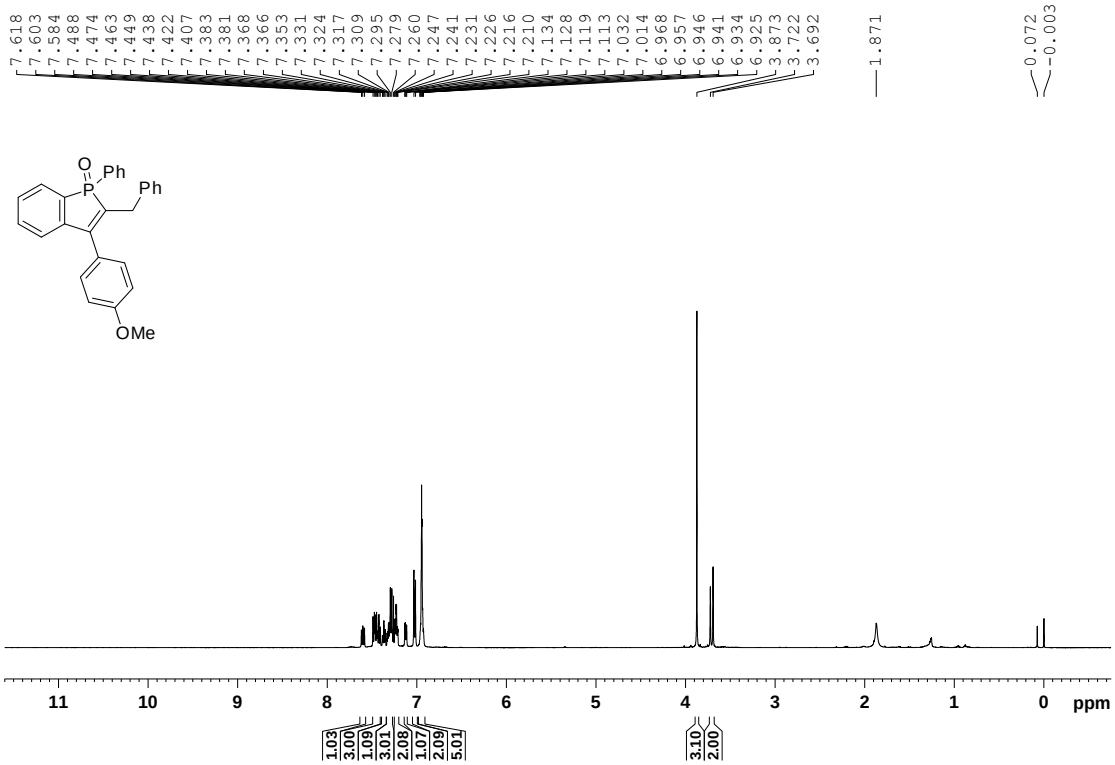
^{13}C NMR of **3o**



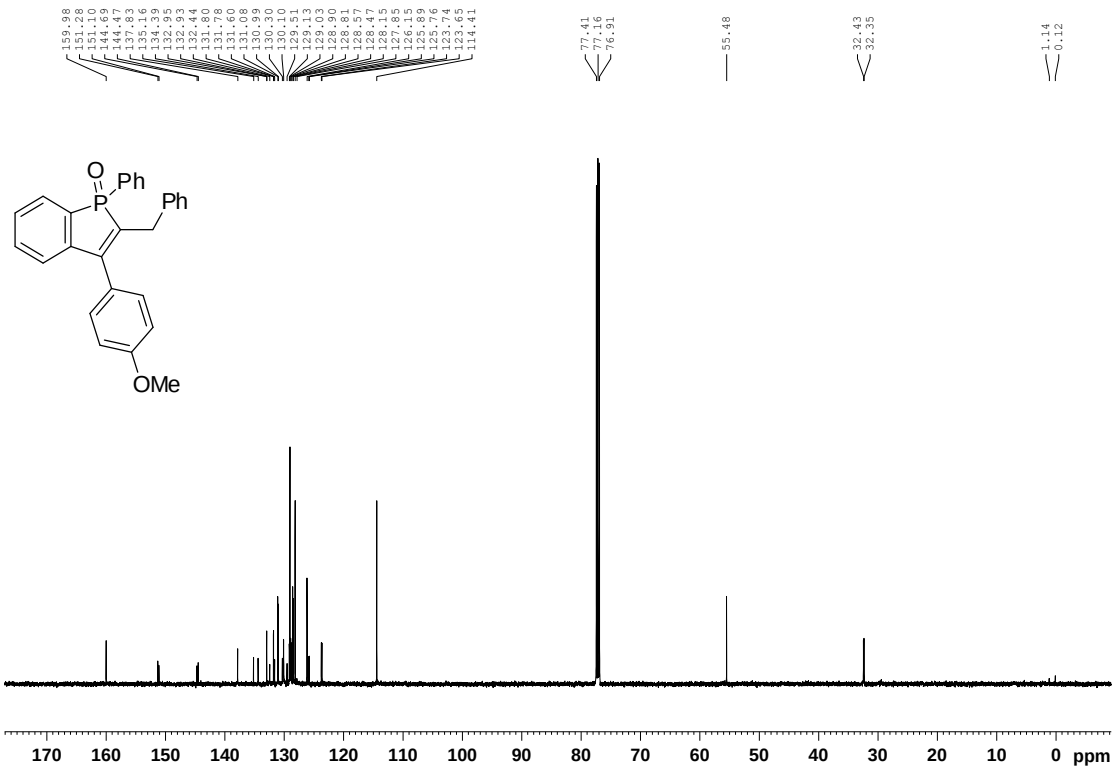
^{31}P NMR of **3o**



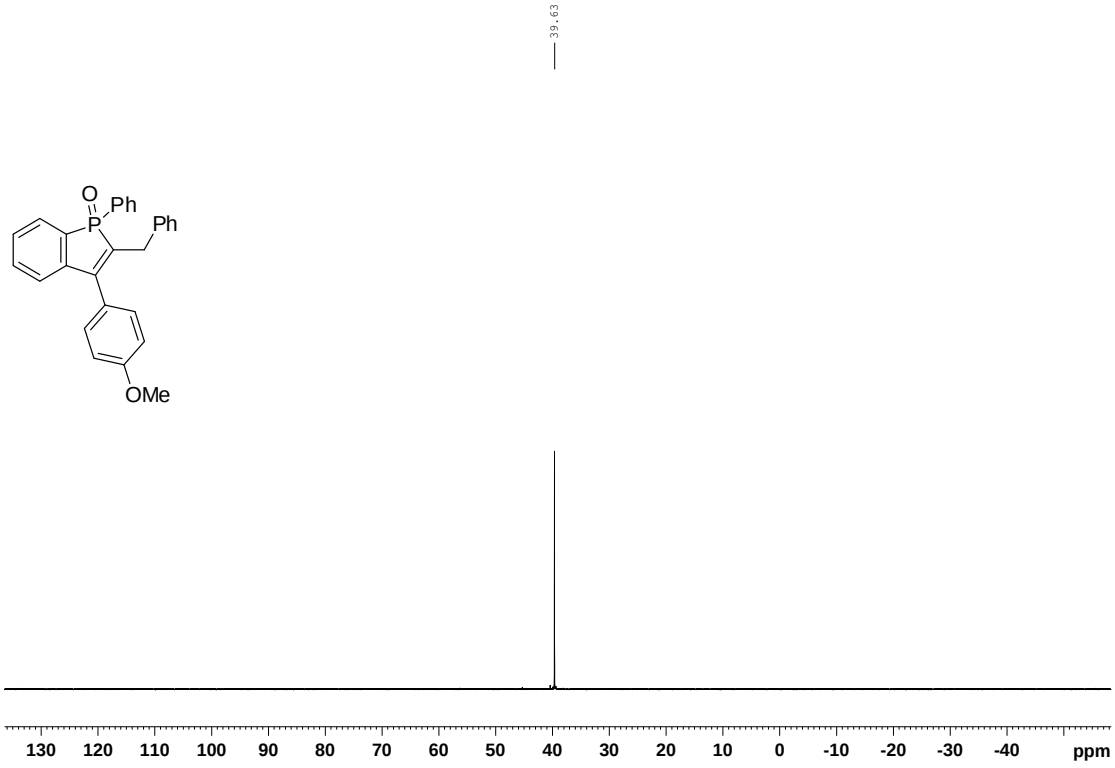
^{1}H NMR of **3p**



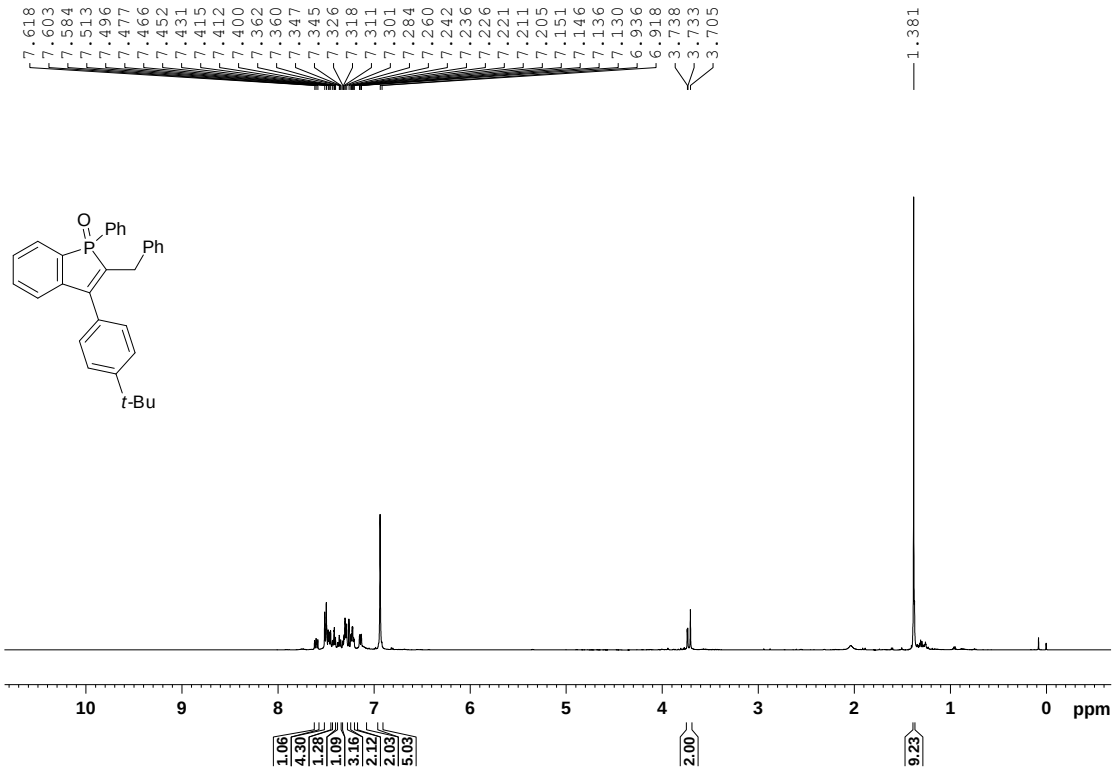
^{13}C NMR of **3p**



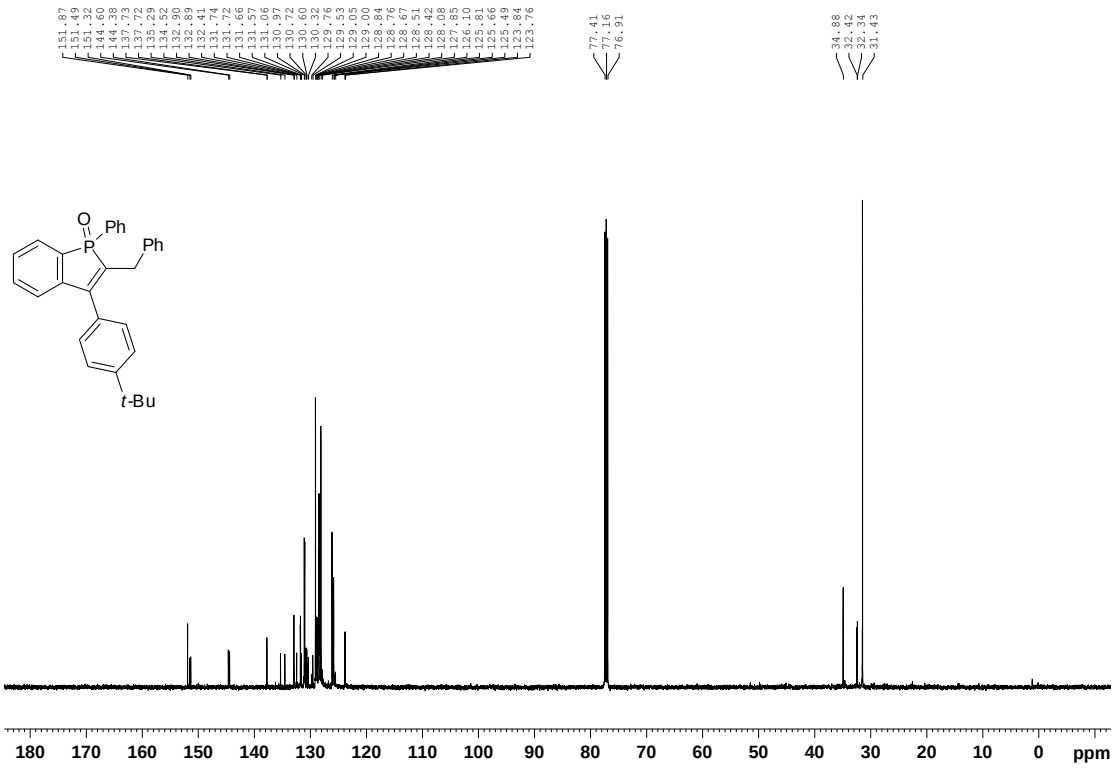
^{31}P NMR of **3p**



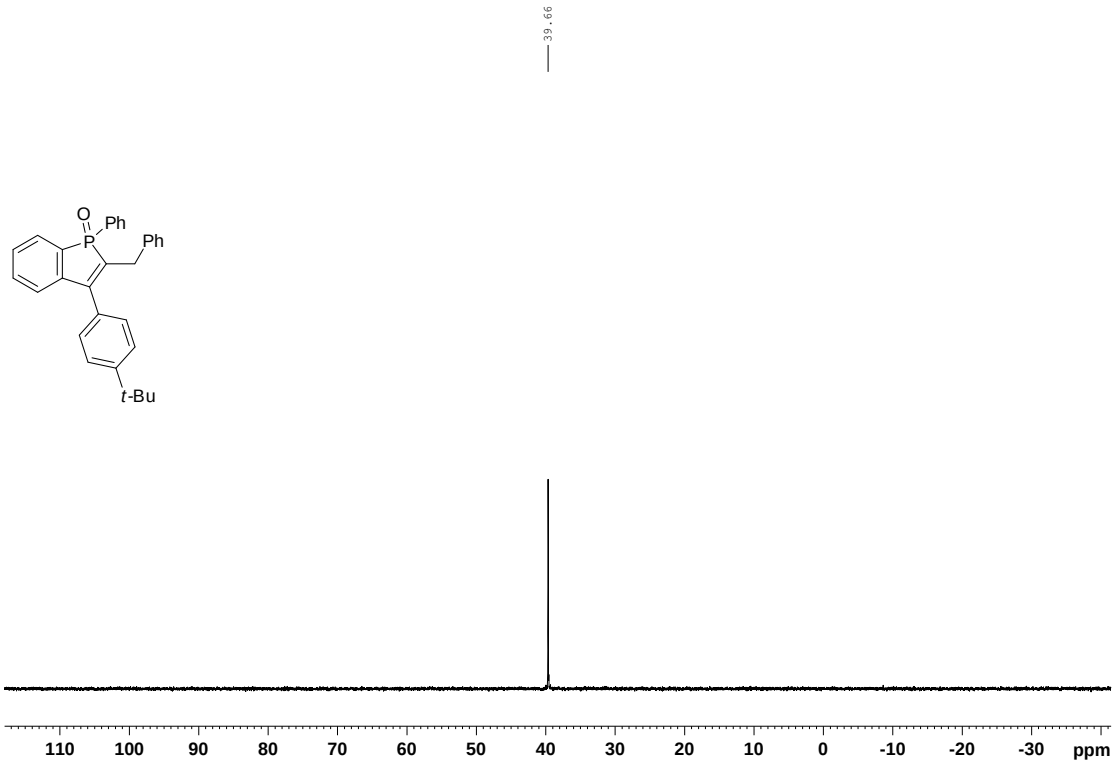
^{1}H NMR of **3q**



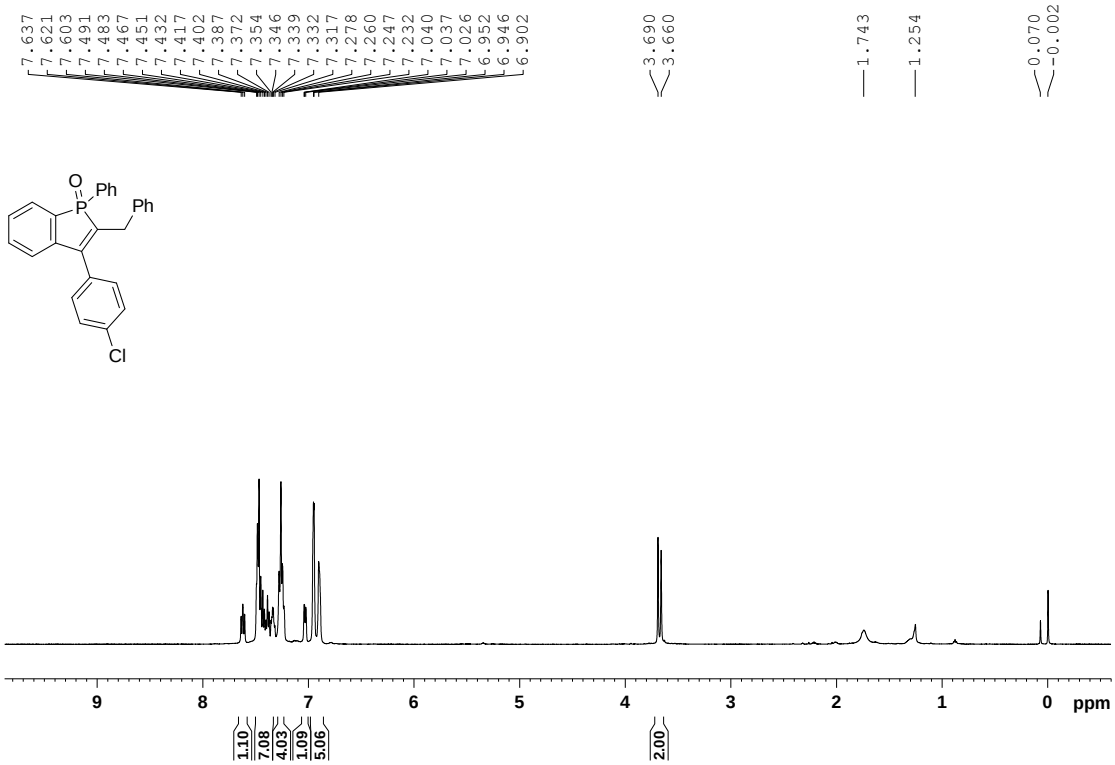
^{13}C NMR of **3q**



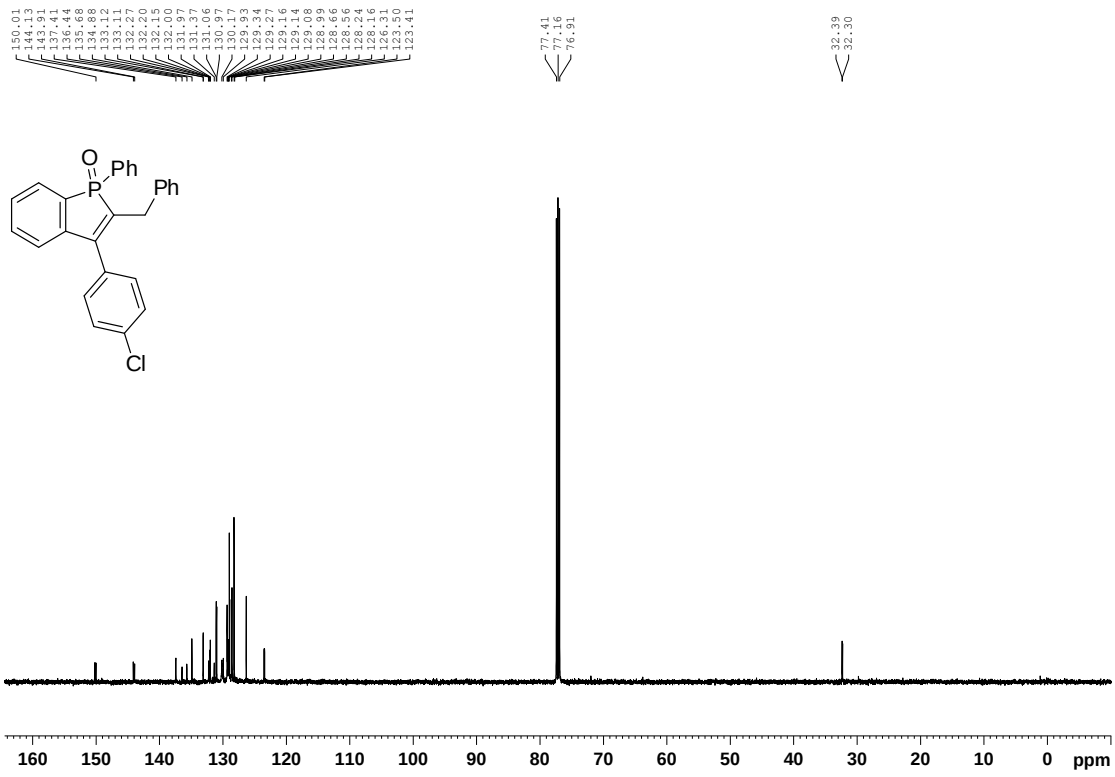
^{31}P NMR of **3q**



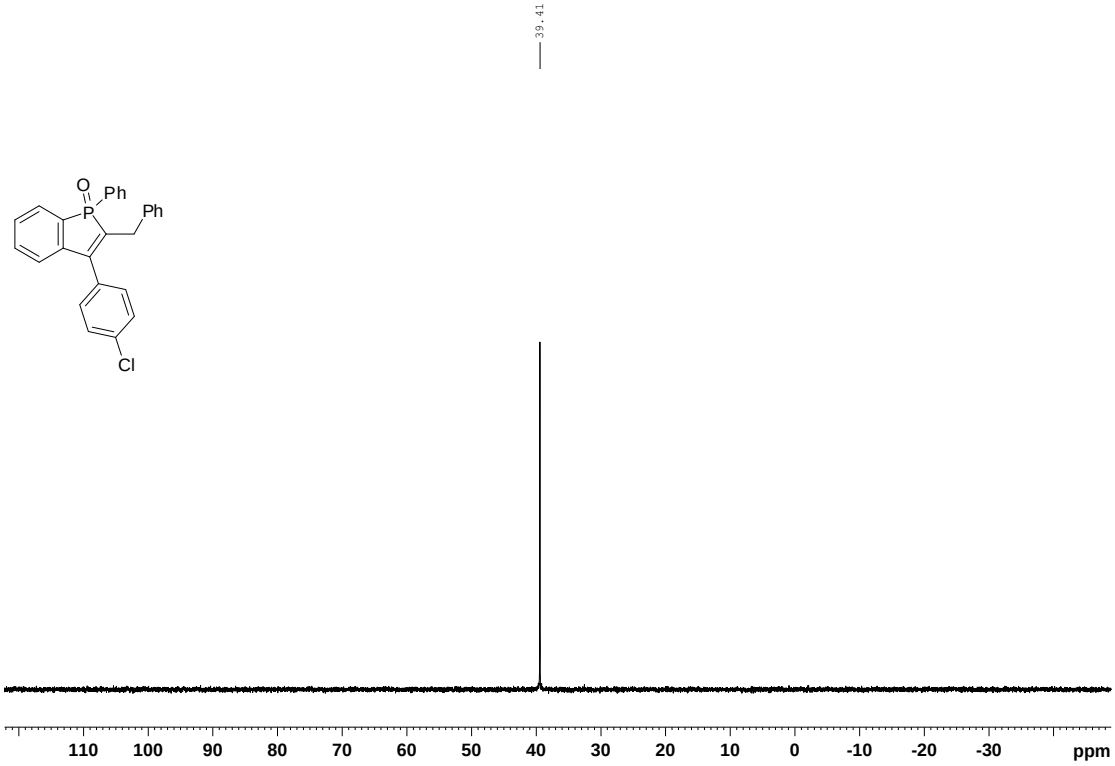
^{1}H NMR of **3r**



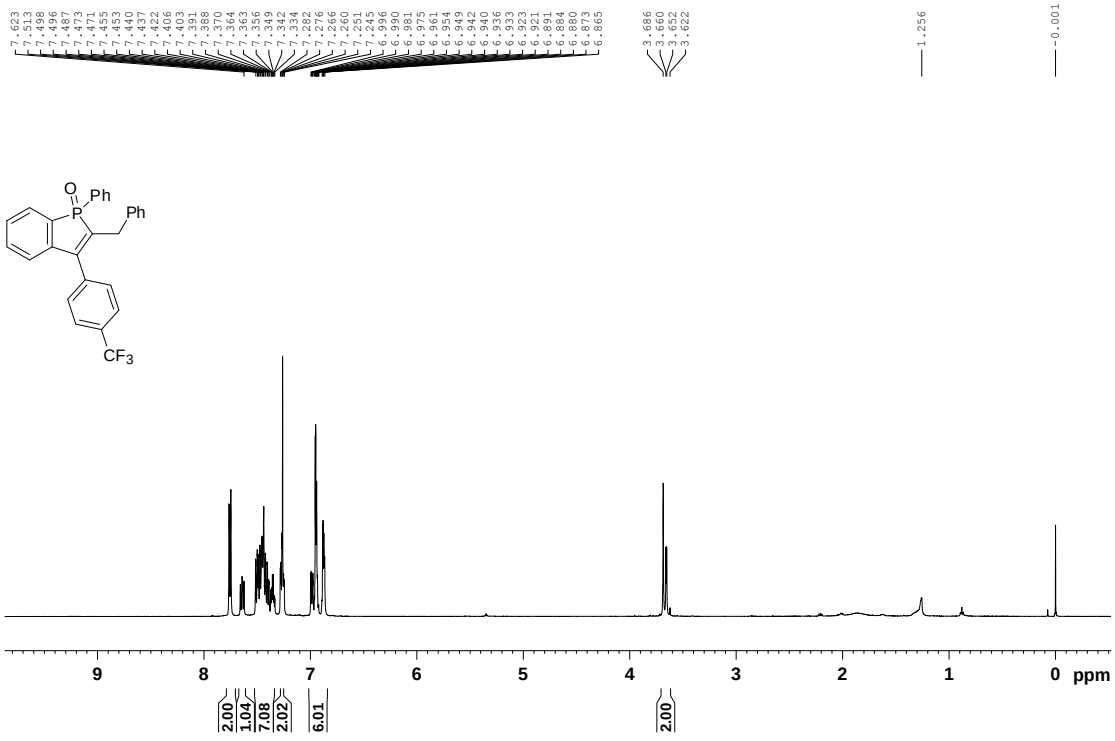
^{13}C NMR of **3r**



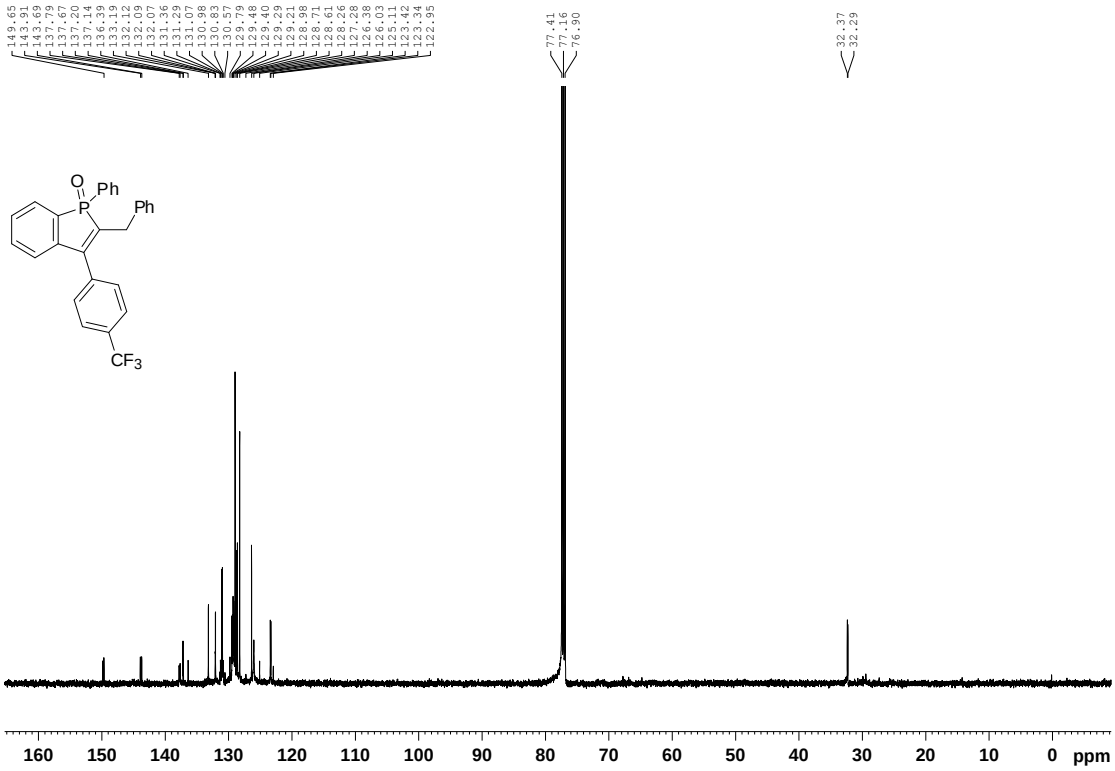
^{31}P NMR of **3r**



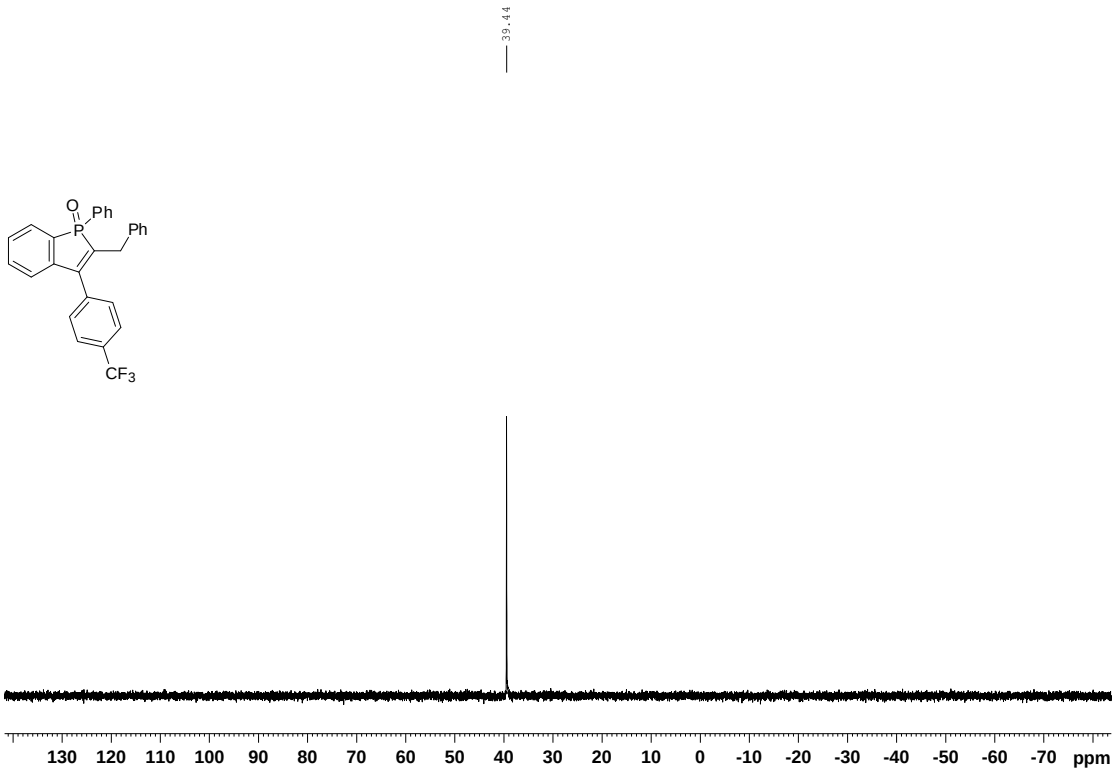
^{1}H NMR of **3s**



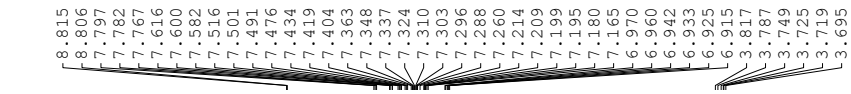
^{13}C NMR of **3s**

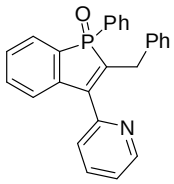


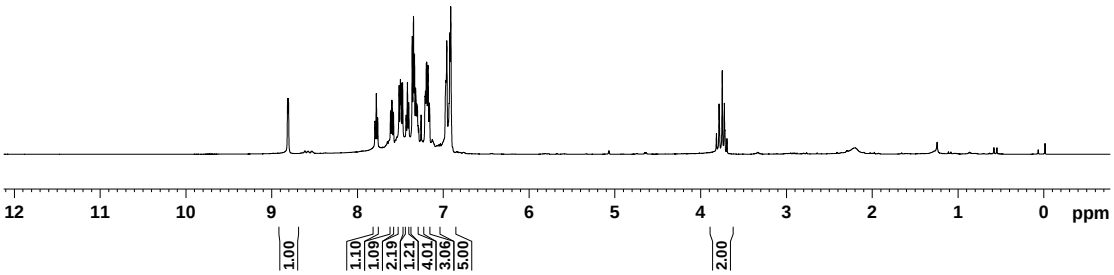
^{31}P NMR of **3s**



^{1}H NMR of **3t**







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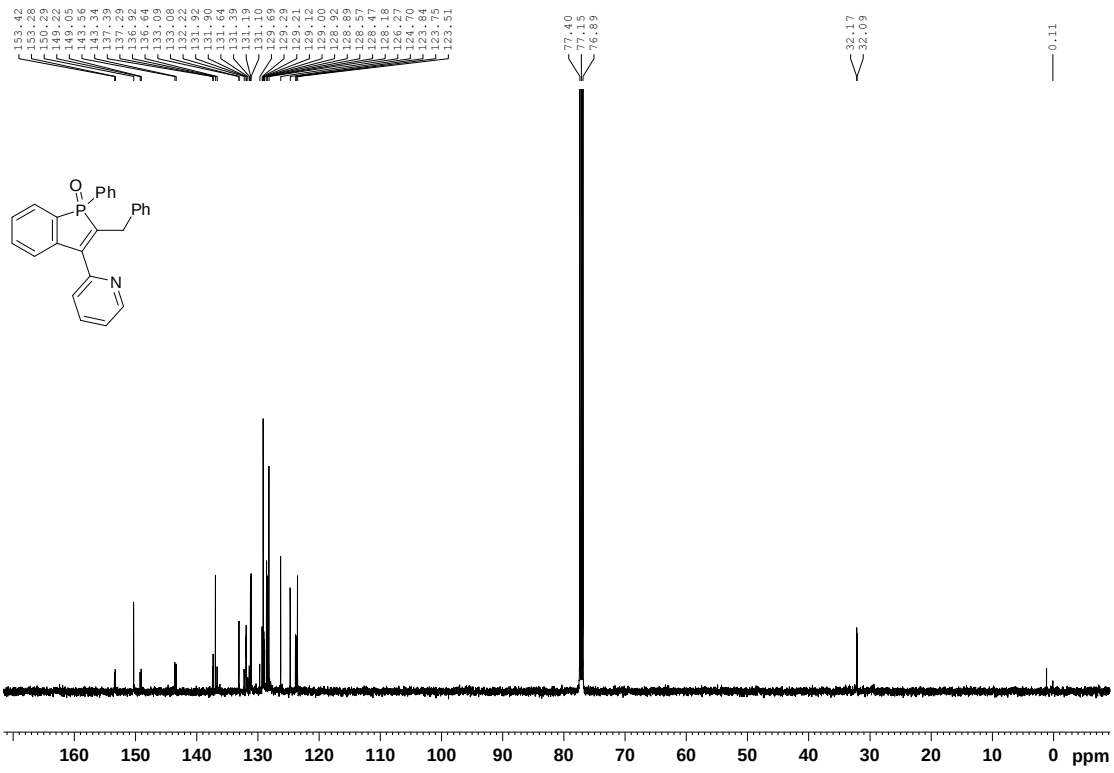
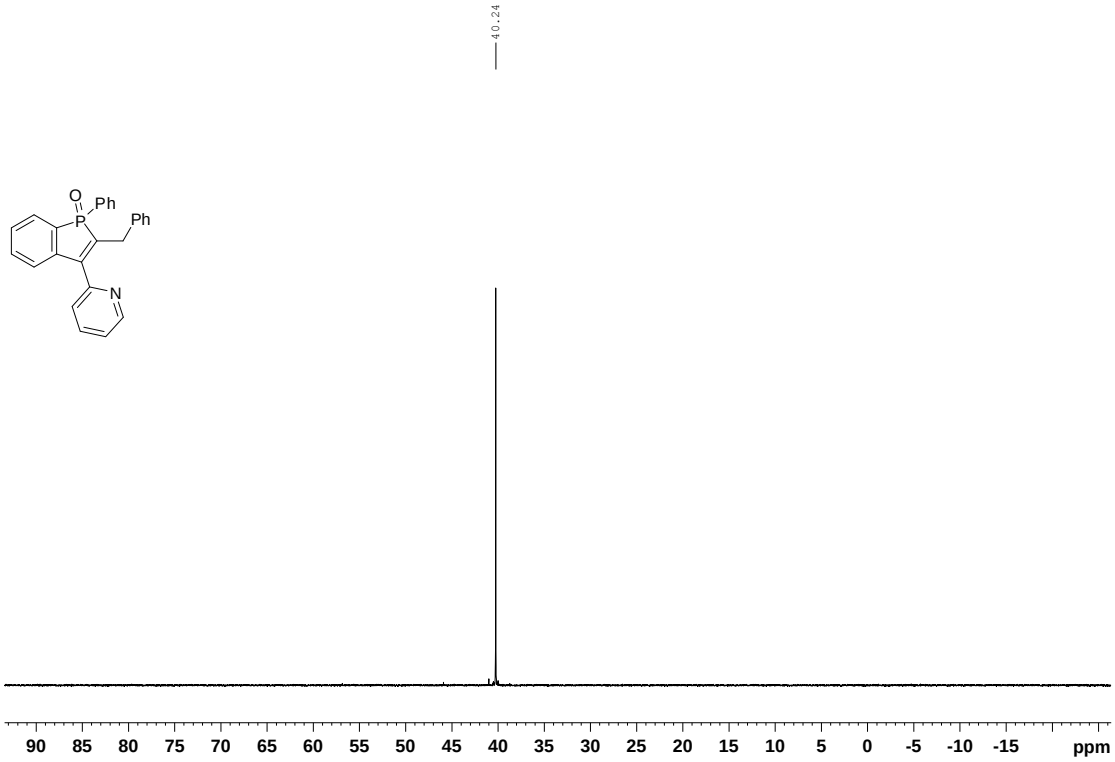
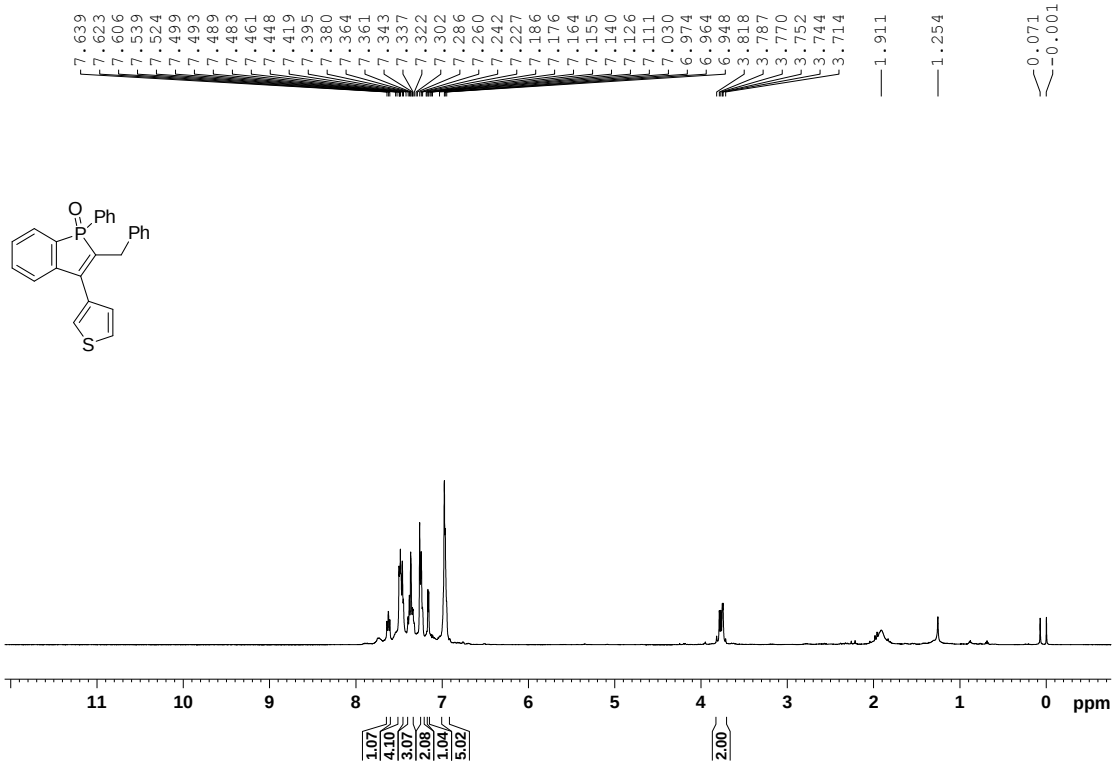


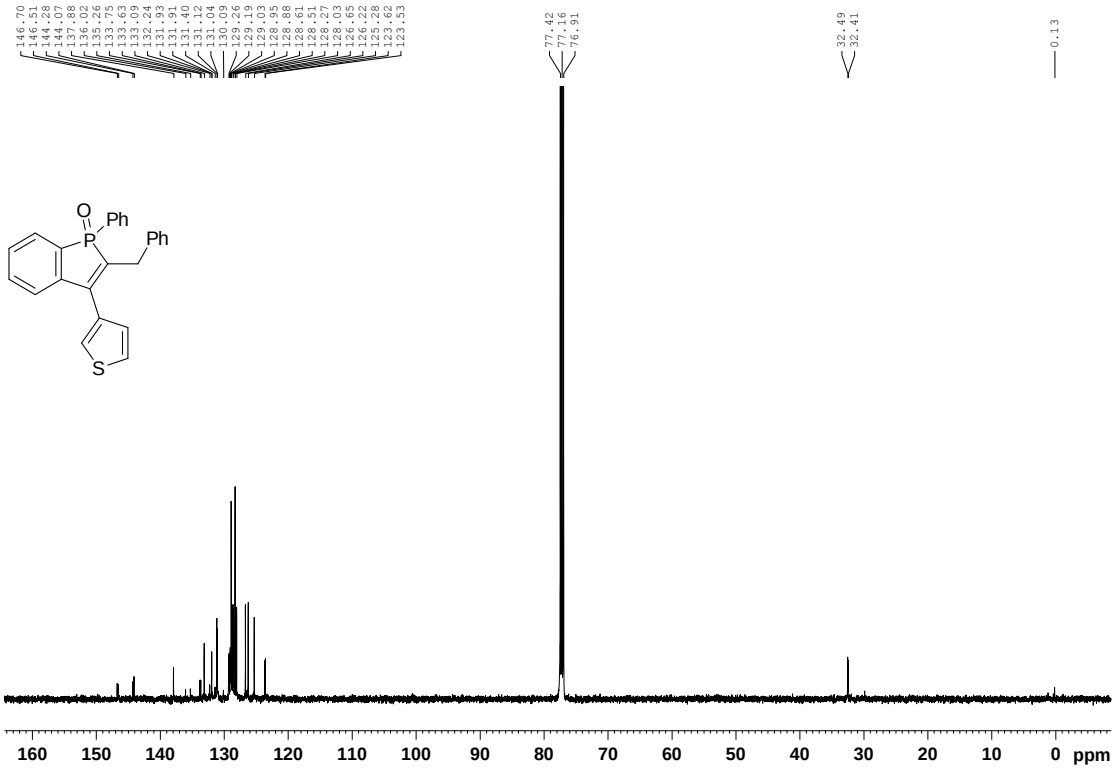
^{31}P NMR of **3t**



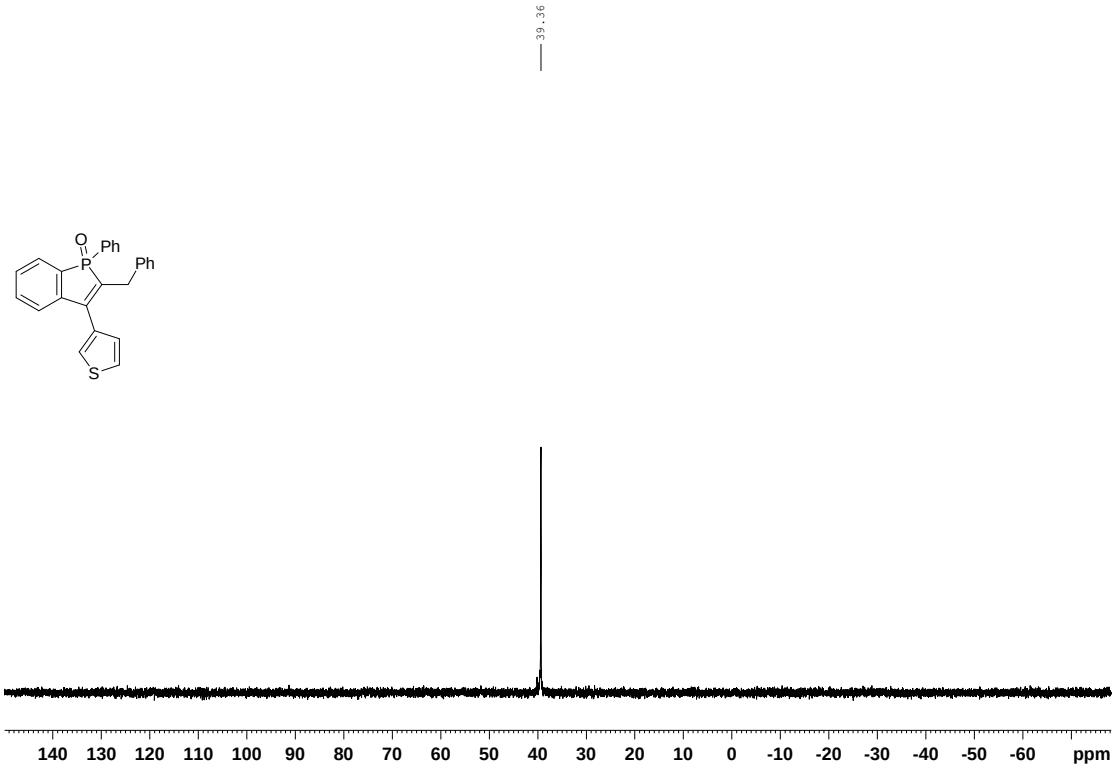
^{1}H NMR of **3u**



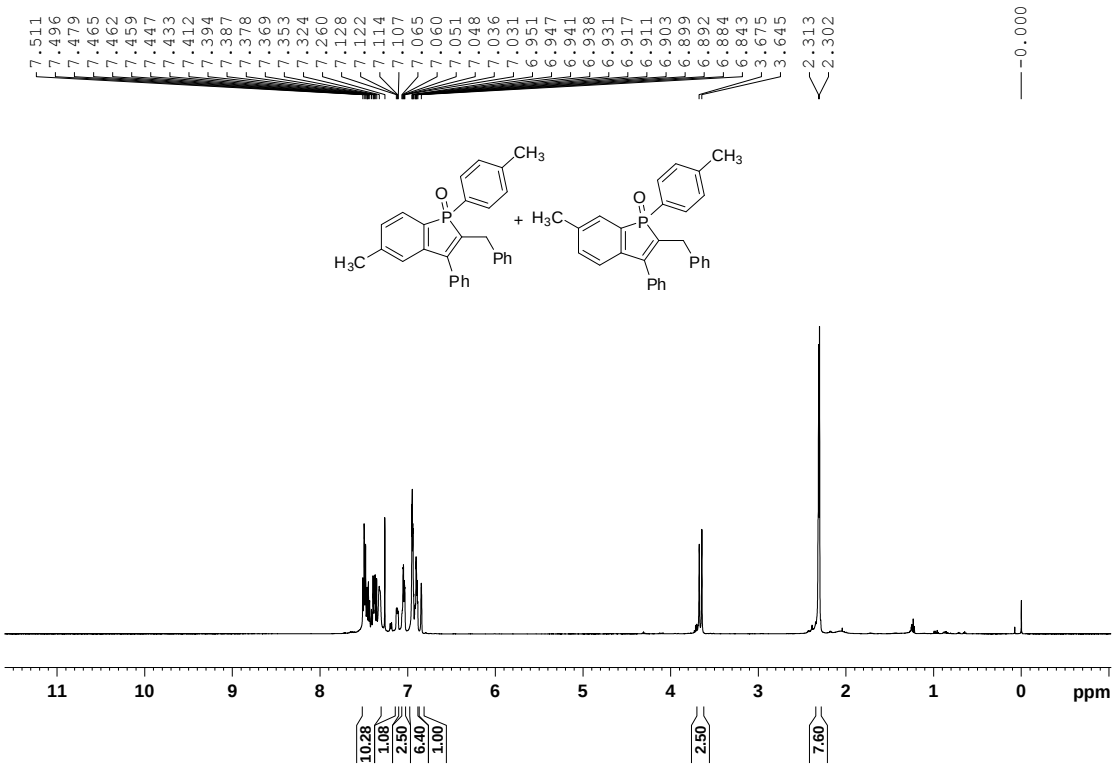
^{13}C NMR of **3u**



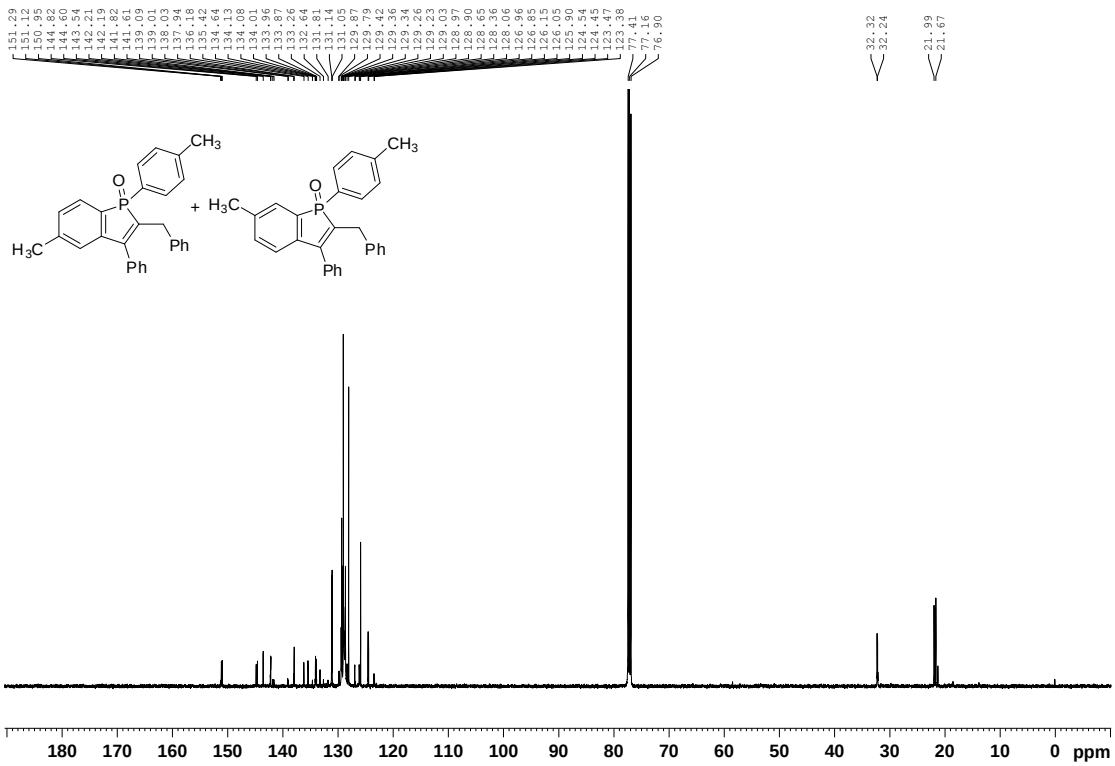
^{31}P NMR of **3u**



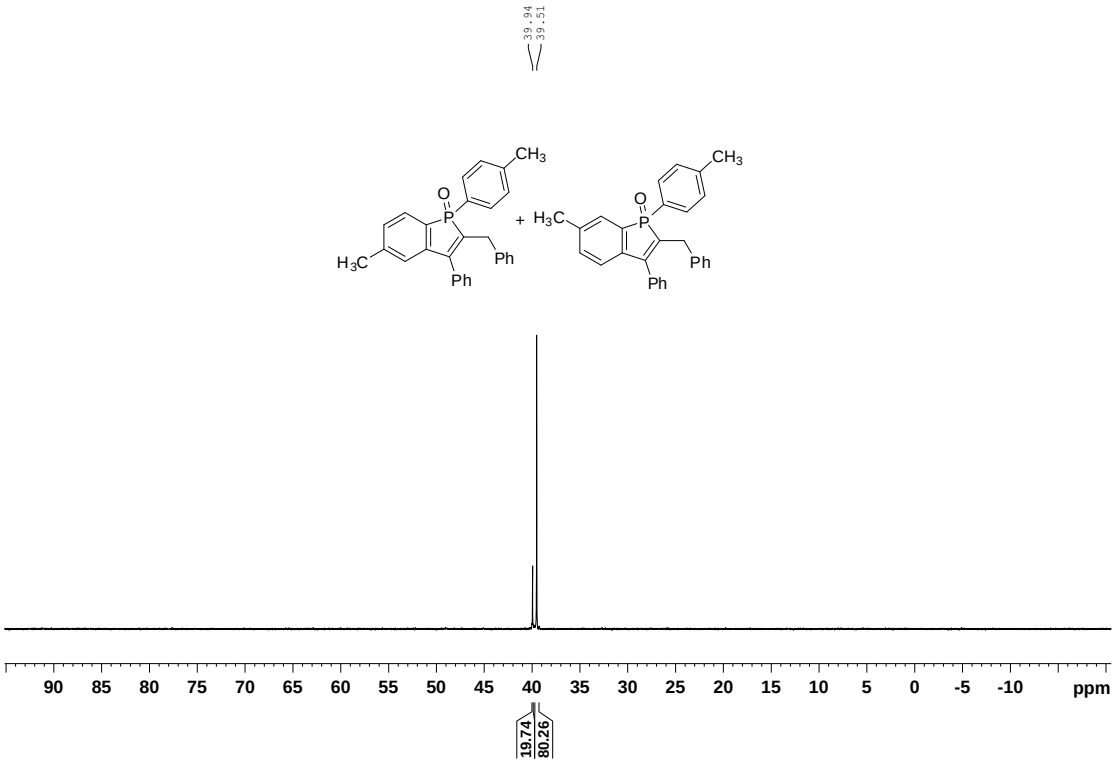
^{1}H NMR of **3v**



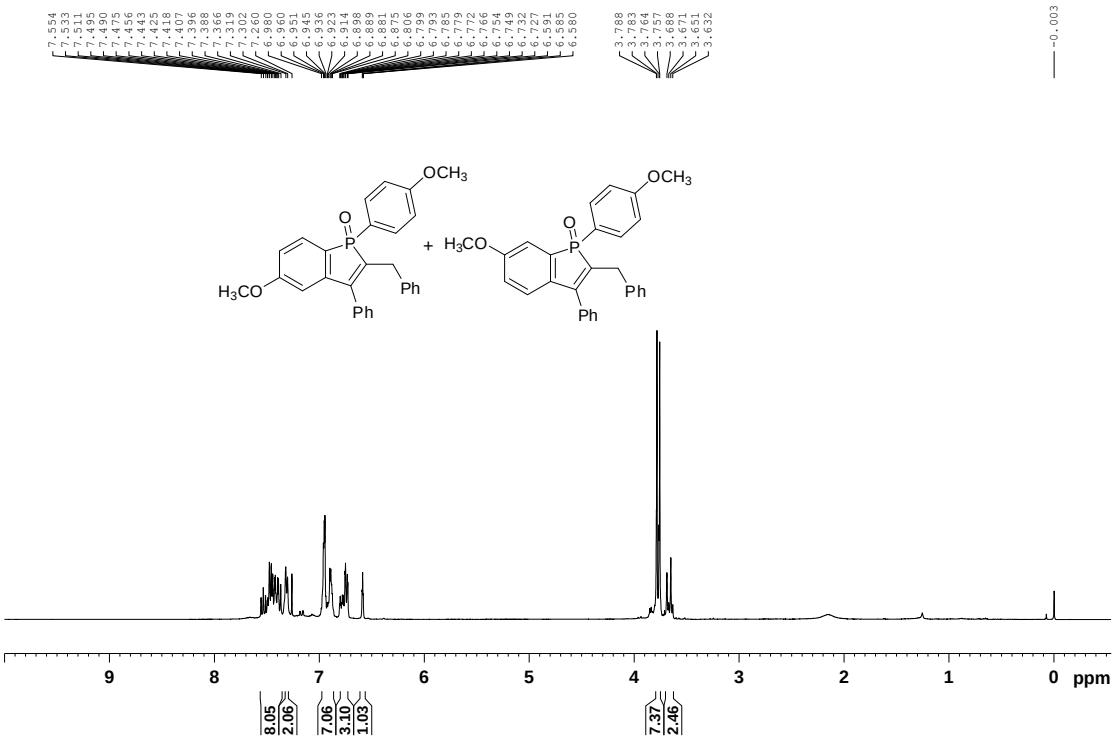
^{13}C NMR of **3v**



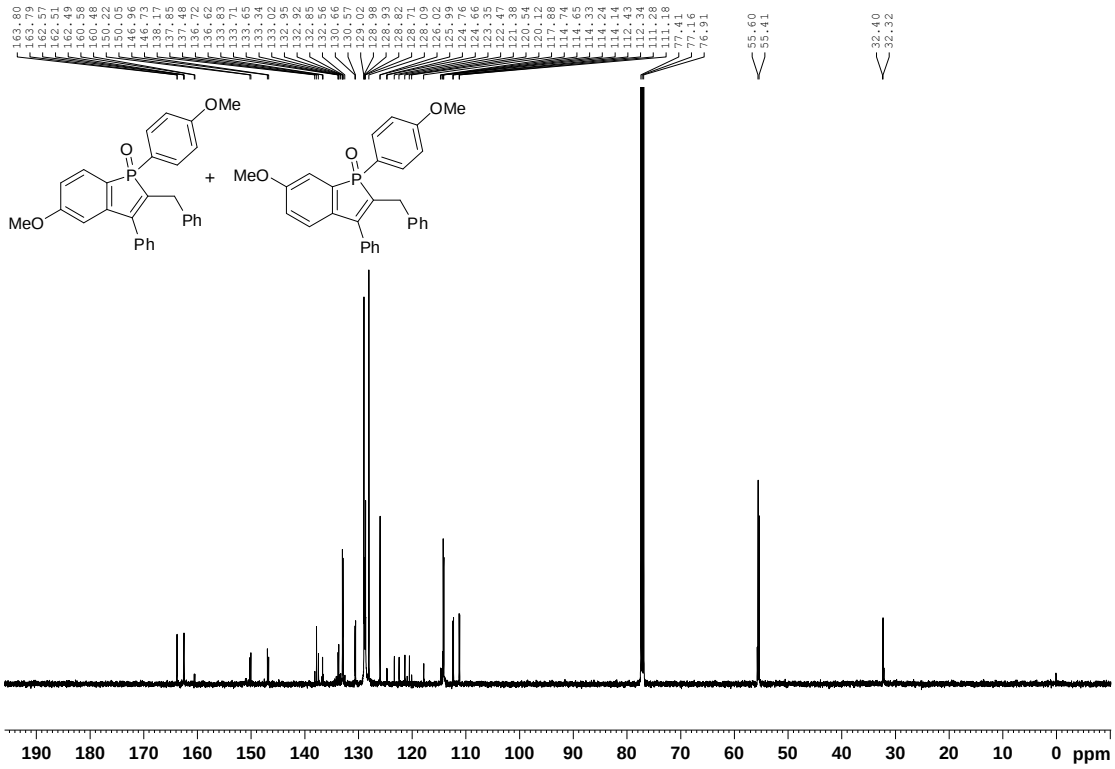
^{31}P NMR of **3v**



^{1}H NMR of **3w**



^{13}C NMR of **3w**



^{31}P NMR of **3w**