Supporting Information

Diastereoselective dearomative bifunctionalization of isoquinolinium salts to access bridged tetrahydroisoquinolines

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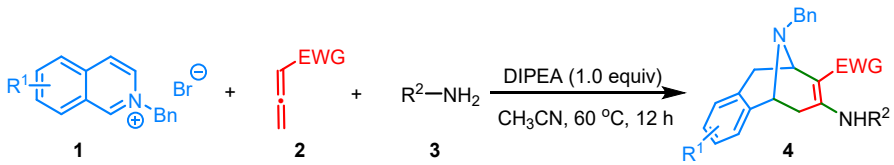
Table of Contents

1. General methods

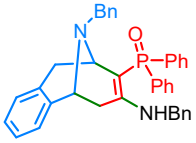
NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. IR spectra were recorded on a Thermo Fisher Nicolet Avatar 360 FTIR spectrometer on a KBr beam splitter. All the solvents were used directly without any purification.

2. Experimental data for the formation of 4



1 2 3 4

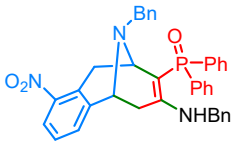
General procedure： To a solution of *N*-benzyl isoquinolinium salts **1** (0.22 mmol, 1.1 equiv), allenes **2** (0.20 mmol) in 1.0 mL of CH_3CN were successively added primary amines **3** (0.40 mmol) and DIPEA (33.7 μL, 0.20 mmol). The resulting mixture was stirred at 60 °C for 12 h. Then, the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding products **4a-w**.



(11-Benzyl-7-(benzylamino)-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4a**)

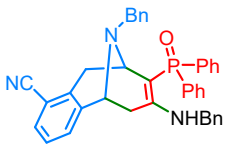
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 54.3 mg, 48% yield, >20:1 dr; reaction time = 12 h; mp 88.3-90.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (t, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.50-7.41 (m, 6H), 7.37-7.34 (m, 2H), 7.20-7.11 (m, 10H), 7.07-7.05 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.29-

4.17 (m, 2H), 4.00 (d, J = 4.0 Hz, 1H), 3.59 (s, 2H), 3.21-3.18 (m, 1H), 2.82 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 2.67 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 2.03 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 140.0, 138.6 (d, J = 40.0 Hz, 1C), 133.9 (d, J = 51.0 Hz, 1C), 132.9 (d, J = 51.0 Hz, 1C), 132.8, 132.1 (d, J = 10.0 Hz, 1C), 131.9 (d, J = 10.0 Hz, 1C), 131.5 (t, J = 3.0 Hz, 1C), 129.6, 128.7, 128.4, 128.3 (d, J = 3.0 Hz, 1C), 128.2 (d, J = 2.0 Hz, 1C), 128.1, 126.9, 126.7, 126.4, 125.9, 85.8 (d, J = 103.0 Hz, 1C), 56.6, 54.1, 51.2 (d, J = 15.0 Hz, 1C), 46.0, 33.2, 31.2 (d, J = 9.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.33. IR (KBr) ν 3057, 1588, 1410, 733 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{36}N_2OP$ $[M+H]^+$: 567.2565, found: 567.2567.



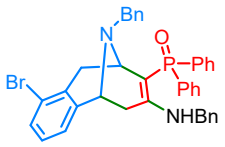
(11-Benzyl-7-(benzylamino)-1-nitro-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4b**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 82.0 mg, 67% yield, >20:1 dr; reaction time = 12 h; mp 126.7-128.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.68 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.51 (t, J = 8.0 Hz, 2H), 7.45-7.35 (m, 6H), 7.24-7.13 (m, 10H), 7.05 (d, J = 4.0 Hz, 1H), 7.04 (s, 1H), 4.27-4.16 (m, 2H), 4.06 (d, J = 8.0 Hz, 1H), 3.58 (s, 2H), 3.24 (t, J = 8.0 Hz, 1H), 2.87-2.77 (m, 2H), 2.21 (d, J = 16.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 149.8, 141.7, 139.9, 137.7, 133.3 (d, J = 44.0 Hz, 1C), 132.3 (d, J = 44.0 Hz, 1C), 132.0, 131.8 (d, J = 10.0 Hz, 1C), 131.5 (d, J = 10.0 Hz, 1C), 129.2, 128.6 (d, J = 12.0 Hz, 1C), 128.5 (d, J = 7.0 Hz, 1C), 128.4 (d, J = 12.0 Hz, 1C), 128.3, 127.0 (d, J = 36.0 Hz, 1C), 126.4, 126.3, 123.4, 85.7 (d, J = 102.0 Hz, 1C), 56.4, 54.2, 50.4 (d, J = 15.0 Hz, 1C), 46.0, 31.2, 30.9 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.16. IR (KBr) ν 3060, 2915, 1577, 1524, 742 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{35}N_3O_3P$ $[M+H]^+$: 612.2416, found: 612.2414.



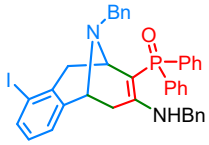
11-Benzyl-7-(benzylamino)-8-(diphenylphosphoryl)-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulene-1-carbonitrile (**4c**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 86.3 mg, 73% yield, >20:1 dr; reaction time = 12 h; mp 74.3-75.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.75 (t, J = 8.0 Hz, 2H), 7.54-7.42 (m, 10H), 7.26-7.06 (m, 11H), 4.23 (s, 2H), 4.00 (d, J = 4.0 Hz, 1H), 3.58 (s, 2H), 3.30 (t, J = 8.0 Hz, 1H), 2.83 (d, J = 12.0 Hz, 1H), 2.63 (d, J = 12.0 Hz, 1H), 2.22 (d, J = 16.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 140.2, 139.8, 137.7, 137.3, 133.4, 132.4, 132.0 (d, J = 2.0 Hz, 1C), 131.8 (d, J = 10.0 Hz, 1C), 131.7 (d, J = 10.0 Hz, 1C), 131.3, 128.6 (d, J = 12.0 Hz, 1C), 128.5 (d, J = 14.0 Hz, 1C), 128.4 (d, J = 12.0 Hz, 1C), 128.3, 127.2, 126.8, 126.3, 117.1, 113.3, 86.0 (d, J = 103.0 Hz, 1C), 56.6, 53.8, 50.6 (d, J = 15.0 Hz, 1C), 46.0, 31.9, 31.0 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.74. IR (KBr) ν 3059, 2924, 1596, 1148, 1116, 736 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{35}N_3OP$ $[M+H]^+$: 592.2518, found: 592.2520.



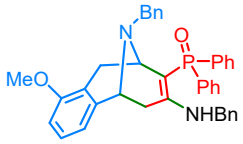
(11-Benzyl-7-(benzylamino)-1-bromo-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4d**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 90.5 mg, 70% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, J = 8.0 Hz, 1H), 7.72 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.52-7.38 (m, 9H), 7.23-7.19 (m, 8H), 7.08-7.06 (m, 2H), 7.00 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 4.29-4.17 (m, 2H), 3.98 (d, J = 8.0 Hz, 1H), 3.58 (s, 2H), 3.27 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.84 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.40 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 2.16 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5 (d, J = 2.0 Hz, 1C), 141.2, 139.9, 138.1, 133.6 (d, J = 22.0 Hz, 1C), 132.8, 132.7 (d, J = 22.0 Hz, 1C), 131.9 (d, J = 10.0 Hz, 1C), 131.8 (d, J = 10.0 Hz, 1C), 131.5 (t, J = 2.0 Hz, 1C), 130.7, 128.6, 128.4 (d, J = 21.0 Hz, 1C), 128.3, 128.2, 127.1 (d, J = 21.0 Hz, 1C), 126.7, 126.3, 126.0 (d, J = 14.0 Hz, 1C), 86.2 (d, J = 104.0 Hz, 1C), 56.4, 54.2, 51.2 (d, J = 14.0 Hz, 1C), 45.9, 34.0, 31.5 (d, J = 9.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.15. IR (KBr) ν 3266, 3058, 2916, 1490, 1108, 733 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{35}N_2OBrP$ $[M+H]^+$: 645.1670, found: 645.1672.



(11-Benzyl-7-(benzylamino)-1-iodo-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4e**)

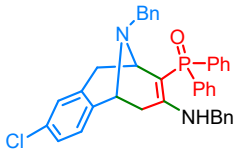
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 109.1 mg, 79% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, J = 8.0 Hz, 1H), 7.73 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 3H), 7.52-7.42 (m, 8H), 7.22-7.19 (m, 8H), 7.07-7.05 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 6.85 (t, J = 8.0 Hz, 1H), 4.28-4.17 (m, 2H), 3.94 (d, J = 8.0 Hz, 1H), 3.57 (s, 2H), 3.25 (t, J = 8.0 Hz, 1H), 2.84 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 2.36 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 2.27 (d, J = 16.0 Hz, 1H), 2.02 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 141.0, 139.9, 138.1, 137.4, 135.8, 133.6 (d, J = 13.0 Hz, 1C), 132.6 (d, J = 13.0 Hz, 1C), 131.9 (dd, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1C), 131.5 (d, J = 2.0 Hz, 1C), 128.7 (d, J = 12.0 Hz, 1C), 128.6, 128.3 (d, J = 24.0 Hz, 1C), 128.3, 127.7, 127.0 (d, J = 4.0 Hz, 1C), 126.7, 126.3, 103.4, 86.3 (d, J = 104.0 Hz, 1C), 56.4, 54.4, 51.7 (d, J = 15.0 Hz, 1C), 45.9, 39.2, 31.6 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.00. IR (KBr) ν 3057, 2922, 1597, 1442, 1145, 732 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{35}N_2OIP$ $[M+H]^+$: 693.1532, found: 693.1534.



(11-Benzyl-7-(benzylamino)-1-methoxy-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4f**)

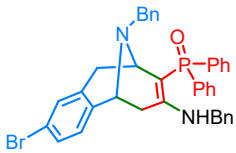
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 52.8 mg, 44% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.70 (m, 3H), 7.50-7.44 (m, 6H), 7.32 (t, J = 8.0 Hz, 2H), 7.19-7.07 (m, 11H), 6.71 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 4.28-4.17 (m, 2H), 3.98 (d, J = 8.0 Hz, 1H), 3.72 (s, 3H), 3.57 (s, 2H), 3.21 (t, J = 4.0 Hz, 1H), 2.80 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.34-2.27 (m, 2H), 2.21 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 156.8 (d, J = 2.0 Hz, 1C), 140.0, 139.8, 138.4, 133.9 (d, J = 57.0 Hz, 1C), 132.9 (d, J = 58.0 Hz, 1C), 131.9 (dd, J_1 = 14.0 Hz, J_2 = 10.0 Hz, 1C), 131.3 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 1C), 128.5 (d, J = 29.0 Hz, 1C), 128.3, 128.1 (d, J = 3.0 Hz, 1C), 128.0, 126.7 (d, J = 20.0 Hz, 1C), 126.4, 126.3, 121.5, 119.1, 107.6, 86.2 (d, J = 103.0 Hz, 1C), 56.5, 55.0, 53.9, 50.8 (d, J = 14.0 Hz, 1C), 45.9, 31.3 (d, J = 8.0 Hz, 1C), 27.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.64. IR (KBr) ν 3282, 2923, 1594, 1465, 1086, 733 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{38}N_2O_2P$ $[M+H]^+$:

597.2671, found: 597.2672.



(11-Benzyl-7-(benzylamino)-2-chloro-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4g**)

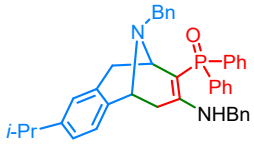
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 52.1 mg, 43% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, J = 8.0 Hz, 1H), 7.72 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1H, 2H), 7.54-7.37 (m, 8H), 7.22-7.16 (m, 8H), 7.10-7.04 (m, 3H), 6.88 (s, 1H), 6.84 (d, J = 8.0 Hz, 1H), 4.28-4.16 (m, 2H), 3.96 (d, J = 4.0 Hz, 1H), 3.58 (s, 2H), 3.21 (t, J = 8.0 Hz, 1H), 2.81 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.61 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.20 (d, J = 16.0 Hz, 1H), 1.95 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (d, J = 3.0 Hz, 1C), 139.9, 138.1, 137.2, 135.0, 133.8 (d, J = 40.0 Hz, 1C), 132.8 (d, J = 40.0 Hz, 1C), 132.0 (d, J = 10.0 Hz, 1C), 131.8 (d, J = 10.0 Hz, 1C), 131.5 (dd, J_1 = 12.0 Hz, J_2 = 2.0 Hz, 1C), 129.3, 128.6, 128.4, 128.3 (dd, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1C), 128.2, 127.0, 126.7, 126.3, 126.1, 85.8 (d, J = 103.0 Hz, 1C), 56.6, 53.6, 50.8 (d, J = 15.0 Hz, 1C), 46.0, 33.1, 31.2 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.93. IR (KBr) ν 3058, 2923, 1596, 1146, 1106, 732 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{35}N_2OPCl$ $[M+H]^+$: 601.2176, found: 601.2171.



(11-Benzyl-7-(benzylamino)-2-bromo-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4h**)

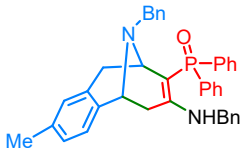
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 59.4 mg, 46% yield, >20:1 dr; reaction time = 12 h; mp 168.6-169.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, J = 8.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 2H), 7.52-7.39 (m, 8H), 7.24-7.17 (m, 9H), 7.03 (s, 3H), 6.78 (d, J = 8.0 Hz, 1H), 4.23-4.16 (m, 2H), 3.94 (d, J = 4.0 Hz, 1H), 3.57 (s, 2H), 3.19 (s, 1H), 2.80 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.61 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.20 (d, J = 16.0 Hz, 1H), 1.94 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 139.9, 137.9 (d, J = 40.0 Hz, 1C), 135.5, 133.8 (d, J = 40.0 Hz, 1C), 132.8 (d, J = 40.0 Hz, 1C), 132.3, 132.0 (d, J = 10.0 Hz, 1C),

131.9 (d, J = 10.0 Hz, 1C), 131.6 (dd, J_1 = 14.0 Hz, J_2 = 2.0 Hz, 1C), 129.1, 128.6, 128.6, 128.4, 128.3, 128.2, 126.9 (d, J = 27.0 Hz, 1C), 126.4, 120.0, 85.8 (d, J = 103.0 Hz, 1C), 56.6, 53.7, 50.9 (d, J = 15.0 Hz, 1C), 46.0, 33.0, 31.2 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.92. IR (KBr) ν 3273, 2920, 1590, 1392, 1087, 728 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{35}N_2OPBr$ $[M+H]^+$: 645.1670, found: 645.1669.



(11-Benzyl-7-(benzylamino)-2-isopropyl-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4i**)

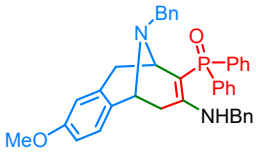
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 29.2 mg, 24% yield, >20:1 dr; reaction time = 12 h; mp 180.5-181.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.60 (m, 3H), 7.44-7.32 (m, 6H), 7.28-7.24 (m, 2H), 7.14-7.10 (m, 8H), 6.99-6.97 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.68 (s, 1H), 4.21-4.09 (m, 2H), 3.89 (d, J = 8.0 Hz, 1H), 3.50 (s, 2H), 3.07 (t, J = 8.0 Hz, 1H), 2.83-2.76 (m, 1H), 2.71 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.58 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.16 (d, J = 16.0 Hz, 1H), 1.98 (d, J = 16.0 Hz, 1H), 1.20 (t, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0 (d, J = 3.0 Hz, 1C), 147.2, 140.1, 138.5, 136.4, 133.9 (d, J = 61.0 Hz, 1C), 132.8 (d, J = 61.0 Hz, 1C), 132.5, 132.1 (d, J = 10.0 Hz, 1C), 131.9 (d, J = 10.0 Hz, 1C), 131.5 (dd, J_1 = 5.0 Hz, J_2 = 3.0 Hz, 1C), 128.5 (d, J = 32.0 Hz, 1C), 128.2 (dd, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1C), 128.1, 127.3, 126.9, 126.7 (d, J = 8.0 Hz, 1C), 126.4, 124.2, 85.8 (d, J = 102.0 Hz, 1C), 56.6, 53.8, 51.4 (d, J = 14.0 Hz, 1C), 45.9, 33.9, 33.7, 30.9 (d, J = 8.0 Hz, 1C), 24.1 (d, J = 9.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.62. IR (KBr) ν 2958, 1589, 1153, 1108, 732 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{42}N_2OP$ $[M+H]^+$: 609.3035, found: 609.3028.



(11-Benzyl-7-(benzylamino)-2-methyl-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4j**)

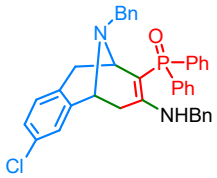
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 33.9 mg, 29%

yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.69 (m, 3H), 7.50-7.35 (m, 8H), 7.19 (s, 8H), 7.06 (s, 2H), 6.95 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.70 (s, 1H), 4.27-4.16 (m, 2H), 3.96 (d, J = 4.0 Hz, 1H), 3.58 (s, 2H), 3.19 (t, J = 8.0 Hz, 1H), 2.79 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.61 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.32 (s, 3H), 2.24 (d, J = 16.0 Hz, 1H), 1.94 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 140.0, 138.5, 136.1, 135.7, 134.0 (d, J = 35.0 Hz, 1C), 133.0 (d, J = 36.0 Hz, 1C), 132.6, 132.1 (d, J = 10.0 Hz, 1C), 131.8 (d, J = 10.0 Hz, 1C), 131.4 (t, J = 3.0 Hz, 1C), 130.0, 128.6, 128.4, 128.2 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1C), 128.1, 126.8 (d, J = 8.0 Hz, 1C), 126.7, 126.4, 86.0 (d, J = 103.0 Hz, 1C), 56.7, 53.8, 51.2 (d, J = 15.0 Hz, 1C), 46.0, 32.9, 31.5 (d, J = 8.0 Hz, 1C), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.15. IR (KBr) ν 3056, 2925, 1588, 1406, 1153, 733 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{38}N_2OP$ $[M+H]^+$: 581.2722, found: 587.2723.



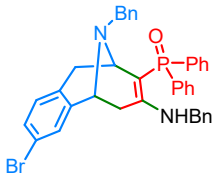
(1-Benzyl-7-(benzylamino)-2-methoxy-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4k**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 25.4 mg, 21% yield, >20:1 dr; reaction time = 12 h; mp 154.8-155.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, J = 8.0 Hz, 1H), 7.71 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 2H), 7.52-7.47 (m, 4H), 7.44-7.41 (m, 2H), 7.38-7.35 (m, 2H), 7.19-7.18 (m, 8H), 7.07 (d, J = 8.0 Hz, 1H), 7.05 (s, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.71 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.42 (d, J = 4.0 Hz, 1H), 4.28-4.17 (m, 2H), 3.95 (d, J = 4.0 Hz, 1H), 3.79 (s, 3H), 3.58 (s, 2H), 3.17 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.79 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.64 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 2.22 (d, J = 16.0 Hz, 1H), 1.99 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 157.0, 140.0, 138.5, 134.1, 134.0 (d, J = 50.0 Hz, 1C), 133.0 (d, J = 50.0 Hz, 1C), 132.1 (d, J = 10.0 Hz, 1C), 131.8 (d, J = 10.0 Hz, 1C), 131.5-131.4 (m, 1C), 131.1, 128.5 (d, J = 27.0 Hz, 1C), 128.2 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1C), 128.1, 127.9, 126.8 (d, J = 21.0 Hz, 1C), 126.4, 113.8, 112.6, 85.8 (d, J = 102.0 Hz, 1C), 56.7, 55.3, 53.5, 51.0 (d, J = 15.0 Hz, 1C), 46.0, 33.6, 31.4 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.21. IR (KBr) ν 3053, 2939, 2897, 1597, 1148, 743 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{38}N_2O_2P$ $[M+H]^+$: 597.2671, found: 597.2672.



(11-Benzyl-7-(benzylamino)-3-chloro-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4l**)

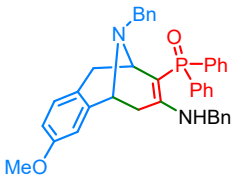
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 65.1 mg, 54% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, J = 8.0 Hz, 1H), 7.73-7.68 (m, 2H), 7.54-7.41 (m, 6H), 7.38-7.34 (m, 2H), 7.24-7.13 (m, 9H), 7.07-7.05 (m, 2H), 6.90 (d, J = 4.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.24-4.22 (m, 2H), 3.94 (d, J = 8.0 Hz, 1H), 3.57 (s, 2H), 3.21 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.81 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.59 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 2.25 (d, J = 16.0 Hz, 1H), 1.96 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 (d, J = 4.0 Hz, 1C), 140.1 (d, J = 72.0 Hz, 1C), 138.1, 133.8 (d, J = 51.0 Hz, 1C), 132.8 (d, J = 53.0 Hz, 1C), 132.0 (d, J = 10.0 Hz, 1C), 131.8 (d, J = 10.0 Hz, 1C), 131.5 (t, J = 3.0 Hz, 1C), 131.3 (d, J = 7.0 Hz, 1C), 130.9, 128.6, 128.4, 128.3 (d, J = 3.0 Hz, 1C), 128.2 (d, J = 3.0 Hz, 1C), 128.2, 127.0, 126.8 (d, J = 4.0 Hz, 1C), 126.8, 126.4, 85.9 (d, J = 103.0 Hz, 1C), 56.6, 53.9, 51.0 (d, J = 14.0 Hz, 1C), 46.0, 32.4, 31.3 (d, J = 7.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.98. IR (KBr) ν 3436, 1638, 732, 698 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{35}N_2OClP$ $[M+H]^+$: 601.2176, found: 601.2177.



(11-Benzyl-7-(benzylamino)-3-bromo-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4m**)

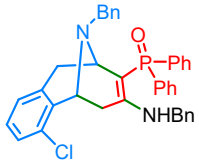
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 55.5 mg, 43% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (t, J = 8.0 Hz, 1H), 7.73-7.68 (m, 2H), 7.52-7.43 (m, 6H), 7.36 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.20-7.17 (m, 8H), 7.05 (s, 3H), 6.75 (d, J = 8.0 Hz, 1H), 4.28-4.18 (m, 2H), 3.94 (d, J = 4.0 Hz, 1H), 3.56 (s, 2H), 3.21 (t, J = 4.0 Hz, 1H), 2.80 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.56 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.25 (d, J = 16.0 Hz, 1H), 1.94 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6

(d, J = 3.0 Hz, 1C), 140.9, 139.8, 138.1, 133.8 (d, J = 51.0 Hz, 1C), 132.8 (d, J = 52.0 Hz, 1C), 131.9 (d, J = 10.0 Hz, 1C), 131.8 (d, J = 10.0 Hz, 1C), 131.5 (t, J = 3.0 Hz, 1C), 131.3, 129.7 (d, J = 3.0 Hz, 1C), 128.6, 128.4, 128.3 (dd, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1C), 128.2, 127.0, 126.8, 126.4, 119.3, 85.9 (d, J = 102.0 Hz, 1C), 56.6, 53.8, 51.0 (d, J = 15.0 Hz, 1C), 46.0, 32.5, 31.3 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.95. IR (KBr) ν 3057, 2922, 1596, 1146, 1108, 732 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{35}N_2OPBr$ $[M+H]^+$: 645.1670, found: 645.1670.



(11-Benzyl-7-(benzylamino)-3-methoxy-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4n**)

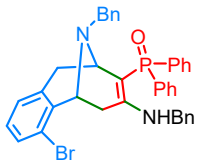
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 25.6 mg, 22% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.52-7.40 (m, 6H), 7.38-7.33 (m, 2H), 7.19-7.18 (m, 8H), 7.07-7.05 (m, 2H), 6.81-6.75 (m, 2H), 6.42 (d, J = 4.0 Hz, 1H), 4.29-4.17 (m, 2H), 3.93 (d, J = 4.0 Hz, 1H), 3.72 (s, 3H), 3.58 (s, 2H), 3.17 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.81 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.59 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 1.96 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 156.9, 139.9 (d, J = 31.0 Hz, 1C), 138.5, 134.3 (d, J = 59.0 Hz, 1C), 133.0 (d, J = 60.0 Hz, 1C), 132.1 (d, J = 10.0 Hz, 1C), 131.9 (d, J = 10.0 Hz, 1C), 131.4 (t, J = 3.0 Hz, 1C), 130.5, 128.5 (d, J = 31.0 Hz, 1C), 128.3 (d, J = 2.0 Hz, 1C), 128.2 (d, J = 2.0 Hz, 1C), 128.1, 126.8 (d, J = 23.0 Hz, 1C), 126.4, 124.7, 113.3, 111.5, 85.9 (d, J = 103.0 Hz, 1C), 56.7, 55.2, 54.3, 51.5 (d, J = 15.0 Hz, 1C), 46.0, 32.2, 31.4 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.50. IR (KBr) ν 3336, 2974, 2925, 1089, 1049, 882 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{38}N_2O_2P$ $[M+H]^+$: 597.2671, found: 597.2668.



(11-Benzyl-7-(benzylamino)-4-chloro-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4o**)

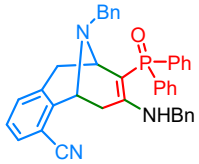
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 76.4 mg, 64%

yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 8.0 Hz, 1H), 7.73-7.68 (m, 2H), 7.53-7.40 (m, 6H), 7.37-7.33 (m, 2H), 7.22-7.17 (m, 9H), 7.13-7.08 (m, 3H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.34 (d, *J* = 4.0 Hz, 1H), 4.25 (d, *J* = 8.0 Hz, 2H), 3.65-3.57 (m, 2H), 3.21 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.81 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 2.61 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 2.49 (d, *J* = 16.0 Hz, 1H), 1.99 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3 (d, *J* = 3.0 Hz, 1C), 139.8, 138.1, 135.6 (d, *J* = 37.0 Hz, 1C), 133.9 (d, *J* = 48.0 Hz, 1C), 132.9 (d, *J* = 48.0 Hz, 1C), 132.2, 132.0 (d, *J* = 10.0 Hz, 1C), 131.8 (d, *J* = 10.0 Hz, 1C), 131.4 (t, *J* = 2.0 Hz, 1C), 128.6, 128.3, 128.2 (d, *J* = 3.0 Hz, 1C), 128.2 (d, *J* = 4.0 Hz, 1C), 128.1, 127.4, 126.9 (d, *J* = 4.0 Hz, 1C), 126.7, 126.4, 85.5 (d, *J* = 104.0 Hz, 1C), 56.6, 52.2, 50.2 (d, *J* = 15.0 Hz, 1C), 46.0, 33.0, 28.7 (d, *J* = 9.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.80. IR (KBr) ν 3059, 2925, 1597, 1442, 731, 698 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{35}N_2OClP$ $[M+H]^+$: 601.2176, found: 601.2178.



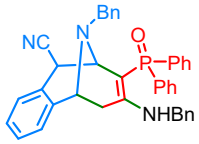
(11-Benzyl-7-(benzylamino)-4-bromo-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4p**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 67.6 mg, 52% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 8.0 Hz, 1H), 7.71 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.51-7.34 (m, 9H), 7.20 (d, *J* = 8.0 Hz, 8H), 7.10-7.02 (m, 3H), 6.83 (d, *J* = 4.0 Hz, 1H), 4.30 (d, *J* = 8.0 Hz, 1H), 4.25 (d, *J* = 4.0 Hz, 2H), 3.64-3.56 (m, 2H), 3.20 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.79 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 2.62 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.53 (d, *J* = 16.0 Hz, 1H), 1.97 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2 (d, *J* = 2.0 Hz, 1C), 139.7, 138.0, 137.2, 135.8, 133.8 (d, *J* = 50.0 Hz, 1C), 132.8 (d, *J* = 50.0 Hz, 1C), 132.0 (d, *J* = 10.0 Hz, 1C), 131.8 (d, *J* = 10.0 Hz, 1C), 131.4 (t, *J* = 3.0 Hz, 1C), 130.3, 128.7 (d, *J* = 19.0 Hz, 1C), 128.3, 128.2 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1C), 128.1, 127.9, 126.8 (d, *J* = 28.0 Hz, 1C), 126.4, 123.0, 85.4 (d, *J* = 104.0 Hz, 1C), 56.6, 54.5, 50.2 (d, *J* = 15.0 Hz, 1C), 46.0, 33.2, 28.9 (d, *J* = 9.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.74. IR (KBr) ν 3274, 3058, 2926, 1490, 1441, 1147, 731 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{35}N_2OBrP$ $[M+H]^+$: 645.1670, found: 645.1667.



11-Benzyl-7-(benzylamino)-8-(diphenylphosphoryl)-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulene-4-carbonitrile (**4q**)

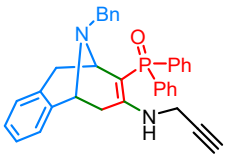
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 72.5 mg, 61% yield, >20:1 dr; reaction time = 12 h; mp 153.3-154.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, J = 8.0 Hz, 1H), 7.68 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.51 (q, J = 8.0 Hz, 2H), 7.46-7.40 (m, 5H), 7.35-7.33 (m, 2H), 7.24-7.15 (m, 9H), 7.09-7.05 (m, 3H), 4.37 (d, J = 4.0 Hz, 1H), 4.24 (d, J = 8.0 Hz, 2H), 3.66-3.57 (m, 2H), 3.23 (t, J = 8.0 Hz, 1H), 2.97 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 2.58 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1H), 2.45 (d, J = 16.0 Hz, 1H), 1.95 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5 (d, J = 2.0 Hz, 1C), 142.1, 139.5, 137.7, 134.9, 134.4, 133.7 (d, J = 41.0 Hz, 1C), 132.7 (d, J = 42.0 Hz, 1C), 131.9 (d, J = 10.0 Hz, 1C), 131.7 (d, J = 10.0 Hz, 1C), 131.6, 130.7, 128.5 (d, J = 14.0 Hz, 1C), 128.3 (d, J = 4.0 Hz, 1C), 128.2, 127.2, 126.8 (d, J = 19.0 Hz, 1C), 126.5, 117.4, 110.3, 85.7 (d, J = 103.0 Hz, 1C), 56.6, 53.5, 49.8 (d, J = 15.0 Hz, 1C), 46.1, 32.8, 30.0 (d, J = 9.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.08. IR (KBr) ν 3279, 1592, 1429, 1108, 735 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{35}N_3OP$ $[M+H]^+$: 592.2518, found: 592.2521.



11-Benzyl-7-(benzylamino)-8-(diphenylphosphoryl)-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulene-10-carbonitrile (**4r**)

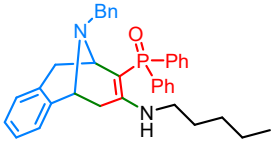
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 75.4 mg, 64% yield, 8:1 dr; reaction time = 12 h; mp 167.1-167.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.68 (m, 4H), 7.54-7.37 (m, 7H), 7.34-7.30 (m, 7H), 7.25-7.23 (m, 2H), 7.10-7.03 (m, 3H), 6.87 (d, J = 8.0 Hz, 1H), 6.84 (s, 1H), 5.15 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 4.96 (d, J = 16.0 Hz, 1H), 4.42 (d, J = 4.0 Hz, 1H), 4.38 (d, J = 4.0 Hz, 1H), 3.99 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 3.87 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1H), 3.67 (s, 1H), 3.36 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1H), 2.60 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2 (d, J = 11.0 Hz, 1C), 146.2, 137.5, 136.5, 136.2, 131.0, 131.0 (d, J = 2.0 Hz, 1C), 130.8 (d, J = 2.0 Hz, 1C), 130.6 (d, J = 10.0 Hz, 1C),

128.8, 128.7, 128.5, 128.4 (d, J = 4.0 Hz, 1C), 128.3 (d, J = 3.0 Hz, 1C), 127.9, 127.8 (d, J = 8.0 Hz, 1C), 126.1 (d, J = 10.0 Hz, 1C), 125.9, 121.2, 119.7, 80.4, 79.5, 79.2, 60.4, 57.4, 48.3, 37.7 (d, J = 4.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.35. IR (KBr) ν 3029, 2197, 1605, 1563, 1151, 748 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{34}N_3OPNa$ $[M+Na]^+$: 614.2337, found: 614.2332.



(11-Benzyl-7-(prop-2-yn-1-ylamino)-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4s**)

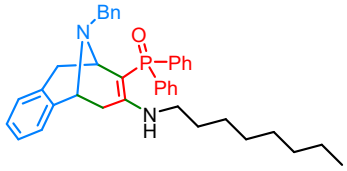
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 15.9 mg, 15% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H), 7.55-7.17 (m, 16H), 7.07 (s, 1H), 6.84 (s, 1H), 4.12 (s, 1H), 3.73-3.67 (m, 4H), 3.14 (d, J = 20.0 Hz, 2H), 2.64 (d, J = 12.0 Hz, 1H), 2.40 (d, J = 16.0 Hz, 1H), 2.11 (s, 1H), 1.97 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 138.8, 138.4, 134.0, 132.7, 132.1 (d, J = 10.0 Hz, 1C), 131.9 (d, J = 10.0 Hz, 1C), 131.5 (t, J = 3.0 Hz, 1C), 129.6, 128.7, 128.3 (d, J = 11.0 Hz, 1C), 128.1, 126.9 (d, J = 5.0 Hz, 1C), 126.7, 125.9, 88.4 (d, J = 103.0 Hz, 1C), 81.0, 71.3, 56.7, 54.2, 51.1 (d, J = 15.0 Hz, 1C), 32.9, 31.9, 31.1 (d, J = 8.0 Hz, 1C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.62. IR (KBr) ν 3056, 2924, 2855, 1732, 1597, 1119, 733 cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{32}N_2OP$ $[M+H]^+$: 515.2252, found: 515.2255.



(11-Benzyl-7-(pentylamino)-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4t**)

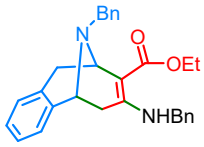
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 26.6 mg, 24% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.49-7.38 (m, 6H), 7.35-7.31 (m, 2H), 7.27-7.21 (m, 5H), 7.19-7.14 (m, 2H), 7.09-7.03 (m, 2H), 6.87 (t, J = 4.0 Hz, 1H), 4.09 (d, J = 8.0 Hz, 1H), 3.72-3.64 (m, 2H), 3.21-3.18 (m, 1H), 2.95 (q, J = 8.0 Hz, 3H), 2.64 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.29 (d, J = 16.0 Hz, 1H), 1.99 (d, J = 16.0 Hz, 1H), 1.37-1.28 (m, 2H), 1.21-1.08 (m, 4H), 0.77 (t, J = 8.0 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 156.3 (d, J = 3.0 Hz, 1C), 138.8 (d, J = 32.0 Hz, 1C), 134.1 (d, J = 52.0 Hz, 1C), 133.1 (d, J = 52.0 Hz, 1C), 133.0, 132.0 (d, J = 10.0 Hz, 1C), 131.8 (d, J = 10.0 Hz, 1C), 131.3, 129.7, 128.7, 128.2 (dd, J_1 = 11.0 Hz, J_2 = 2.0 Hz, 1C), 128.1, 126.9 (d, J = 2.0 Hz, 1C), 126.7, 125.9, 83.9 (d, J = 105.0 Hz, 1C), 56.7, 54.3, 51.0 (d, J = 15.0 Hz, 1C), 42.4, 33.0, 31.8 (d, J = 9.0 Hz, 1C), 30.1, 28.9, 22.3, 13.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.14. IR (KBr) ν 3057, 2928, 1428, 1116, 733 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{40}N_2OP$ $[M+H]^+$: 547.2878, found: 547.2881.



(11-Benzyl-7-(octylamino)-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-8-yl)diphenylphosphine oxide (**4u**)

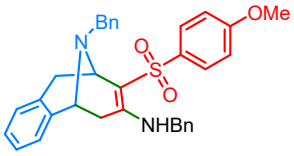
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 41.6 mg, 35% yield, >20:1 dr; reaction time = 12 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.65 (m, 2H), 7.52-7.32 (m, 8H), 7.25-7.15 (m, 7H), 7.05-6.98 (m, 2H), 6.88 (d, J = 4.0 Hz, 1H), 4.09 (d, J = 4.0 Hz, 1H), 3.72-3.58 (m, 2H), 3.21-3.18 (m, 1H), 2.94 (t, J = 8.0 Hz, 3H), 2.64 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.29 (d, J = 16.0 Hz, 1H), 1.99 (d, J = 16.0 Hz, 1H), 1.34-1.28 (m, 8H), 0.87-0.84 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 138.8 (d, J = 32.0 Hz, 1C), 134.1 (d, J = 53.0 Hz, 1C), 133.1 (d, J = 54.0 Hz, 1C), 133.0, 132.0 (d, J = 10.0 Hz, 1C), 131.7 (d, J = 10.0 Hz, 1C), 131.3, 129.7, 128.6, 128.1 (dd, J_1 = 12.0 Hz, J_2 = 2.0 Hz, 1C), 128.1, 126.8 (d, J = 2.0 Hz, 1C), 126.7, 125.9, 83.9 (d, J = 105.0 Hz, 1C), 56.7, 54.3, 51.0 (d, J = 15.0 Hz, 1C), 42.4, 33.0, 31.8 (d, J = 9.0 Hz, 1C), 31.7, 30.4, 29.7, 29.1 (d, J = 14.0 Hz, 1C), 26.7, 22.6, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.14. IR (KBr) ν 3057, 2926, 1599, 1118, 733 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{46}N_2OP$ $[M+H]^+$: 589.3348, found: 589.3353.



Ethyl 11-benzyl-7-(benzylamino)-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulene-8-carboxylate (**4v**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 25:1); 34.0 mg, 39% yield, >20:1 dr; reaction time = 16 h; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (t, J = 8.0 Hz, 1H),

7.29 (t, J = 8.0 Hz, 3H), 7.24-7.18 (m, 5H), 7.14-7.05 (m, 5H), 6.85 (d, J = 5.0 Hz, 1H), 4.25 (d, J = 5.0 Hz, 2H), 4.17-4.08 (m, 3H), 3.89 (d, J = 5.0 Hz, 1H), 3.74 (d, J = 10.0 Hz, 1H), 3.65 (d, J = 10.0 Hz, 1H), 3.22 (dd, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 2.79 (dd, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 2.74 (d, J = 15.0 Hz, 1H), 2.25 (d, J = 20.0 Hz, 1H), 1.25 (t, J = 10.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 156.8, 138.8, 138.7, 137.7, 134.0, 129.7, 128.7, 128.6, 128.2, 127.1, 127.0, 126.9, 126.6, 126.6, 125.7, 92.3, 58.7, 56.7, 52.9, 50.9, 45.9, 32.4, 31.9, 14.6. IR (KBr) ν 2927, 1648, 1595, 1225, 1070, 792 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{31}N_2O_2$ $[M+H]^+$: 439.2386, found: 439.2387.



N,11-dibenzyl-8-((4-methoxyphenyl)sulfonyl)-5,6,9,10-tetrahydro-5,9-epiminobenzo[8]annulen-7-amine (**4w**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1); 26.1 mg, 24% yield, >20:1 dr; reaction time = 12 h; mp 142.9-143.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.67 (m, 3H), 7.27 (t, J = 10.0 Hz, 3H), 7.19-7.15 (m, 4H), 7.09 (d, J = 5.0 Hz, 4H), 7.03 (d, J = 5.0 Hz, 2H), 6.88 (d, J = 10.0 Hz, 3H), 4.27 (d, J = 10.0 Hz, 2H), 3.96 (d, J = 5.0 Hz, 1H), 3.88 (s, 3H), 3.75 (d, J = 5.0 Hz, 1H), 3.49 (d, J = 10.0 Hz, 1H), 3.34 (d, J = 10.0 Hz, 1H), 3.22 (dd, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 3.07 (d, J = 10.0 Hz, 1H), 2.76 (dd, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 2.25 (d, J = 15.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 151.3, 138.6, 138.2, 138.0, 135.1, 133.3, 129.8, 128.7, 128.4, 128.1, 127.3, 127.0, 126.9, 126.5, 126.4, 125.7, 113.9, 98.1, 56.3, 55.5, 54.5, 50.8, 46.1, 34.8, 30.6, one carbon missing in the aromatic region. IR (KBr) ν 3349, 1595, 1259, 1123, 739 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{33}N_2O_3S$ $[M+H]^+$: 537.2212, found: 537.2211.

3. Crystal structure of 4i

Preparation of the single crystals of **4i**: 20.0 mg of pure compound **4i** was dissolved in 2.0 mL of dichloromethane at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After about one day, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **4i**. The data were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 294(2) K during data collection.

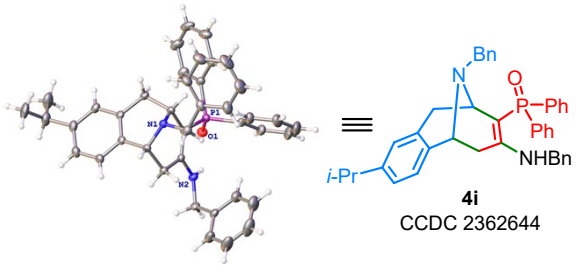


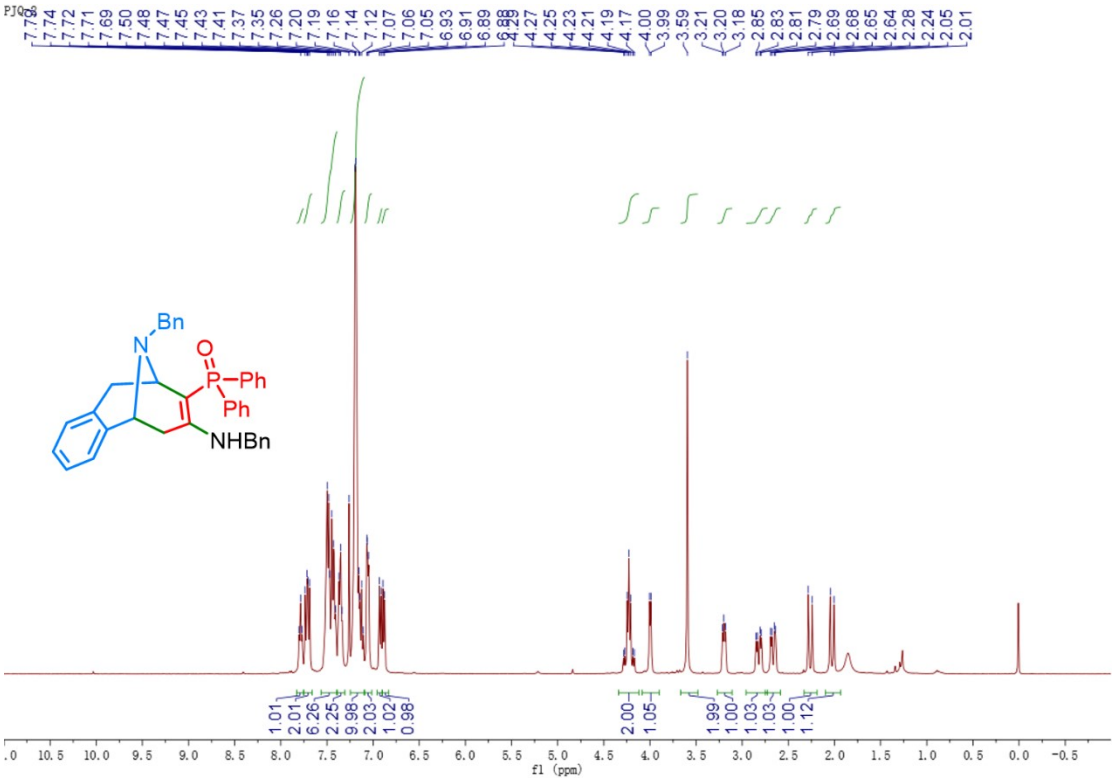
Table S1 Crystal data and structure refinement for 4i.

Identification code	**4i**
Empirical formula	$C_{41}H_{41}N_2OP$
Formula weight	608.73
Temperature/K	294(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.0596(7)
b/Å	11.2945(8)
c/Å	15.3318(9)
α/°	111.600(6)
β/°	93.776(5)
γ/°	104.186(6)
Volume/Å^3	1700.3(2)
Z	2
ρ_{calc}g/cm^3	1.189
μ/mm^{-1}	0.970
F(000)	648.0
Crystal size/mm^3	0.16 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.296 to 148.436
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	11982

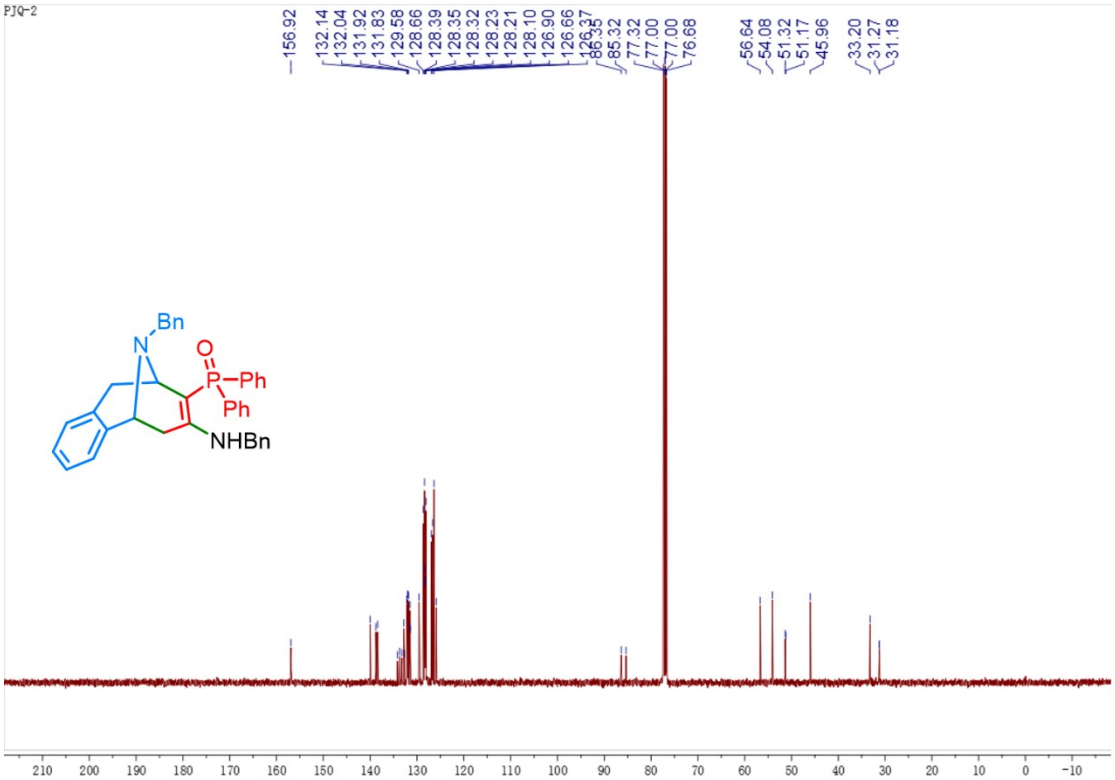
Independent reflections	6613 [R_{int} = 0.0443, R_{sigma} = 0.0618]
Data/restraints/parameters	6613/0/413
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0655, wR_2 = 0.1714
Final R indexes [all data]	R_1 = 0.0858, wR_2 = 0.1980
Largest diff. peak/hole / e $Å^{-3}$	0.40/-0.36

4. NMR spectra

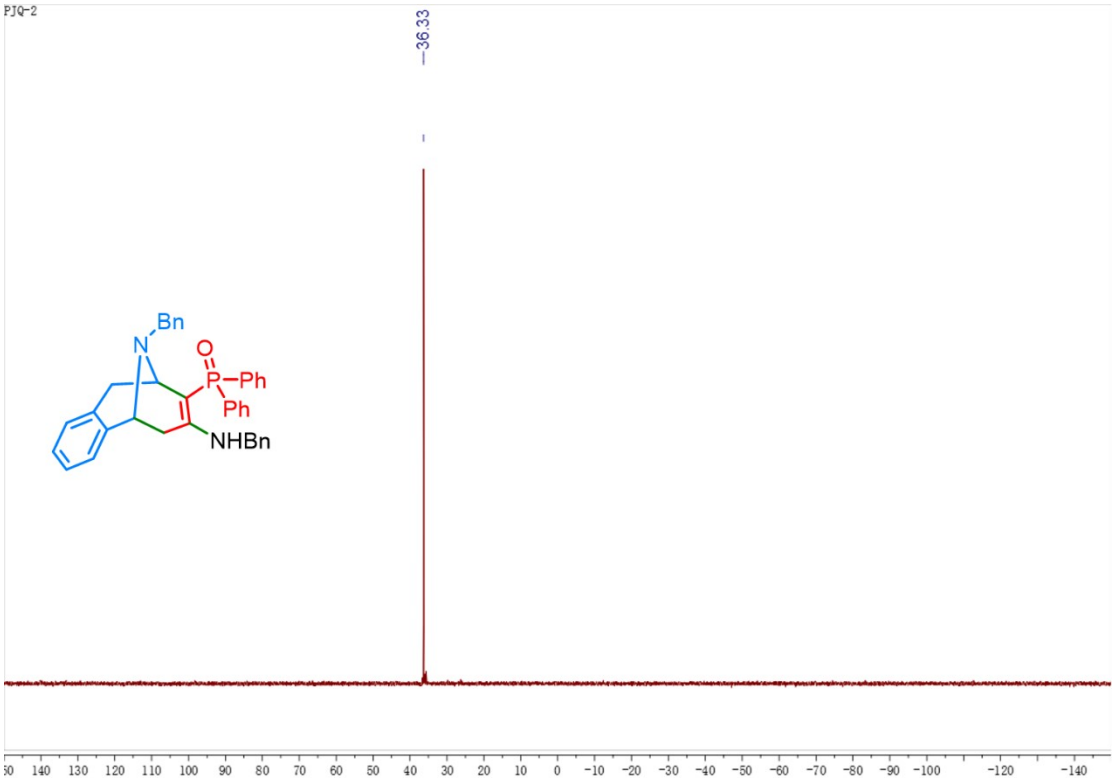
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



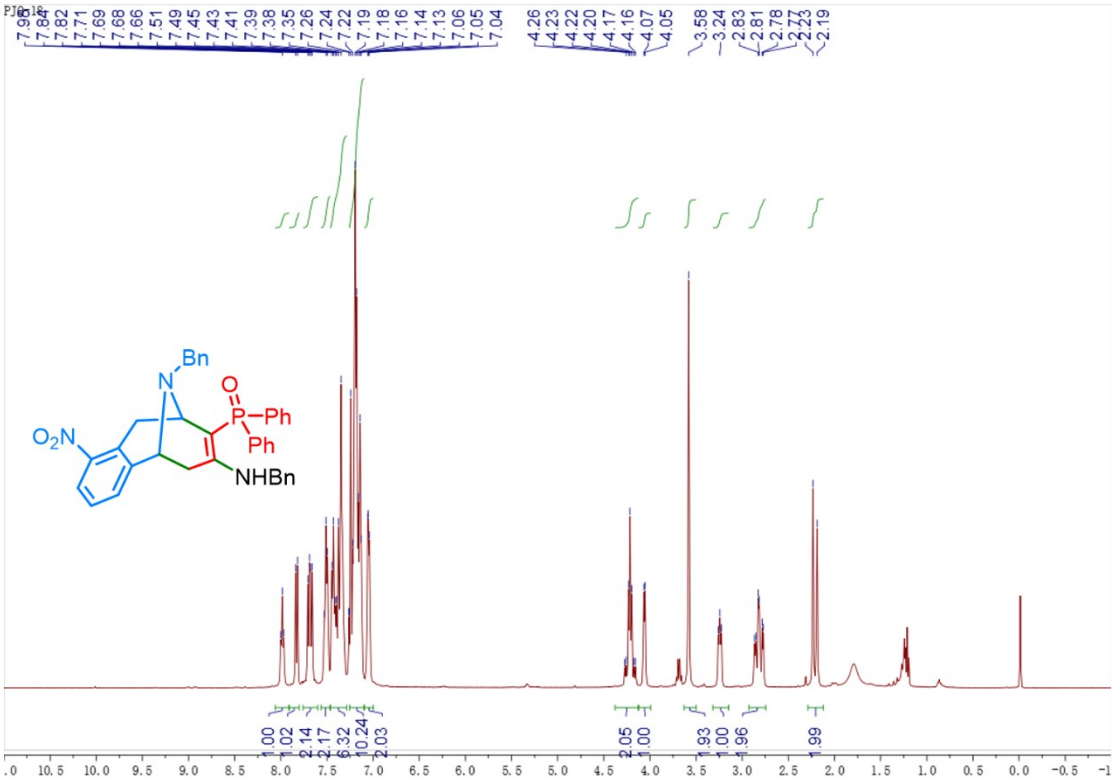
^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



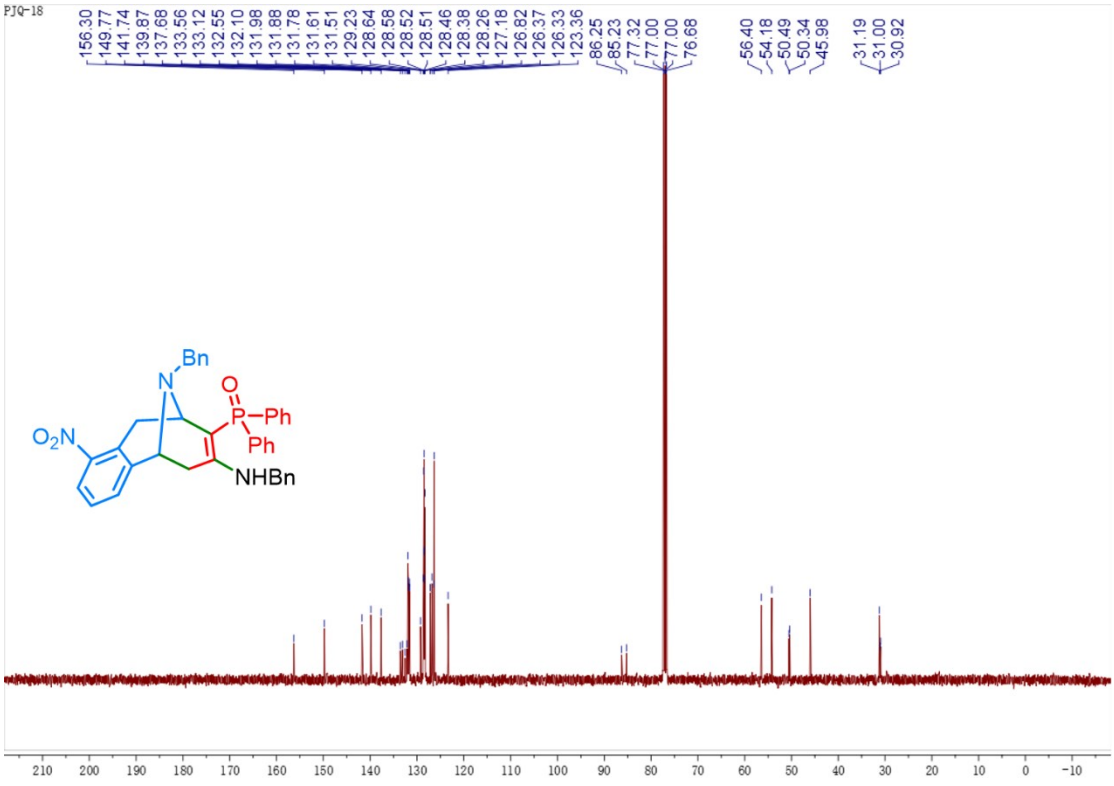
^{31}P NMR spectrum of **4a** (162 MHz, $CDCl_3$)



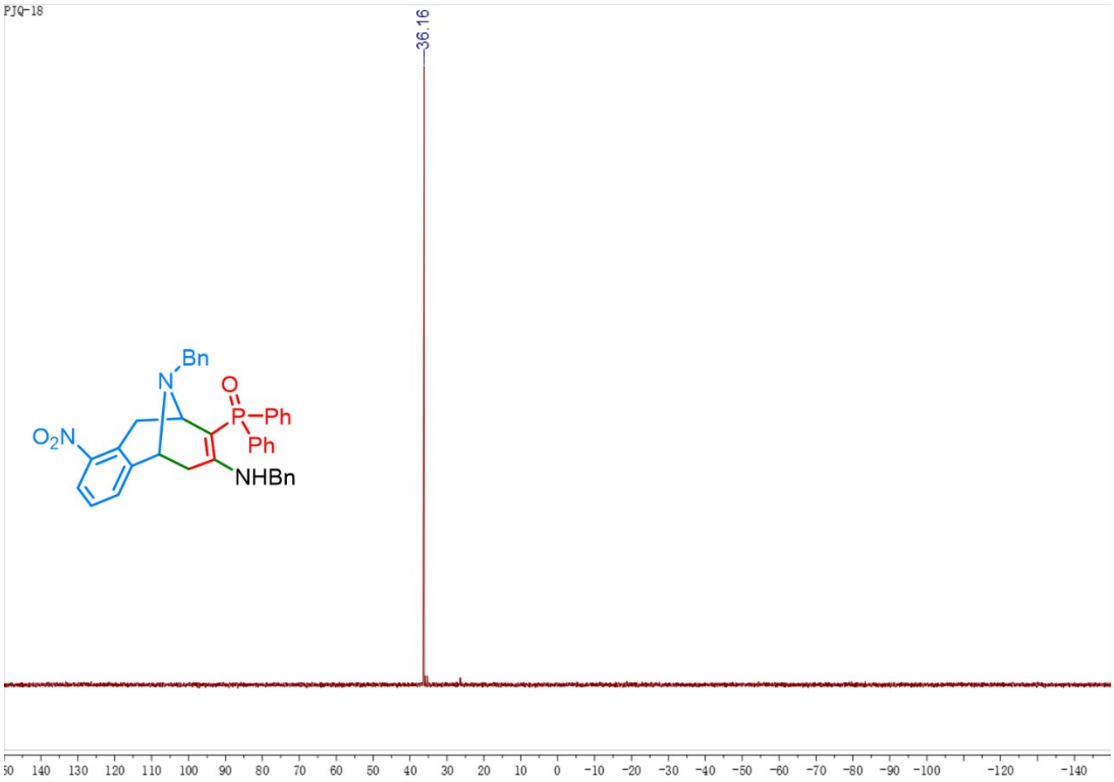
^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$)



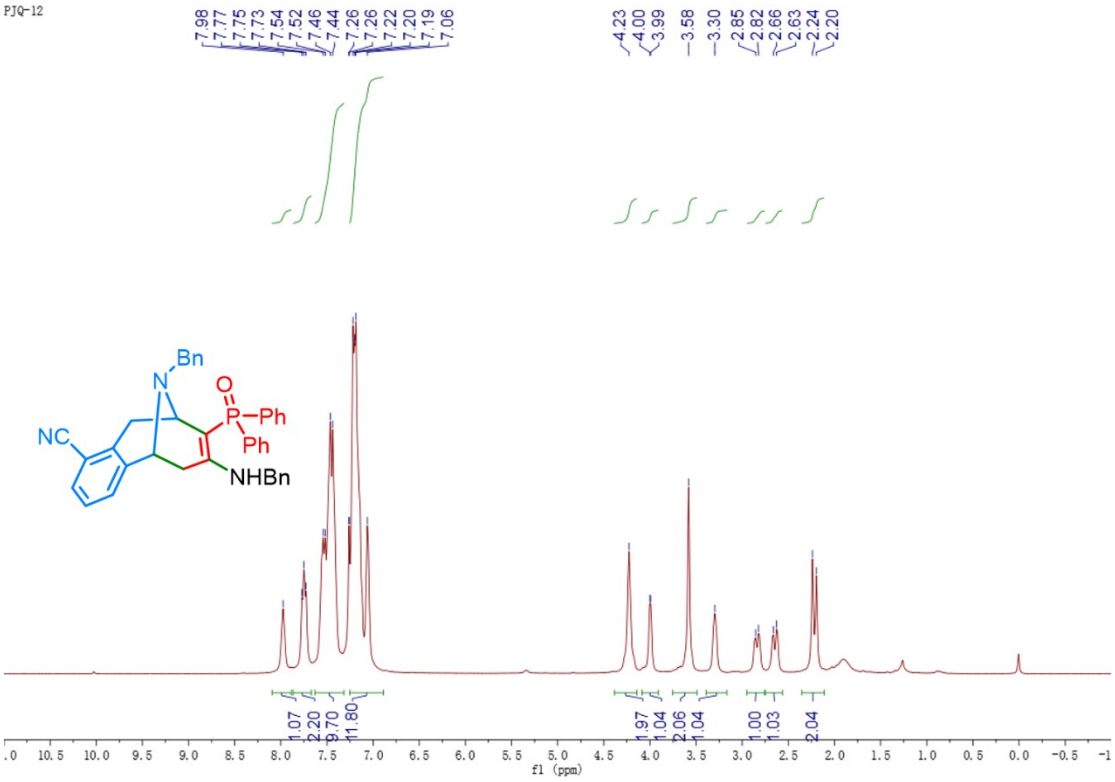
^{13}C NMR spectrum of **4b** (100 MHz, $CDCl_3$)



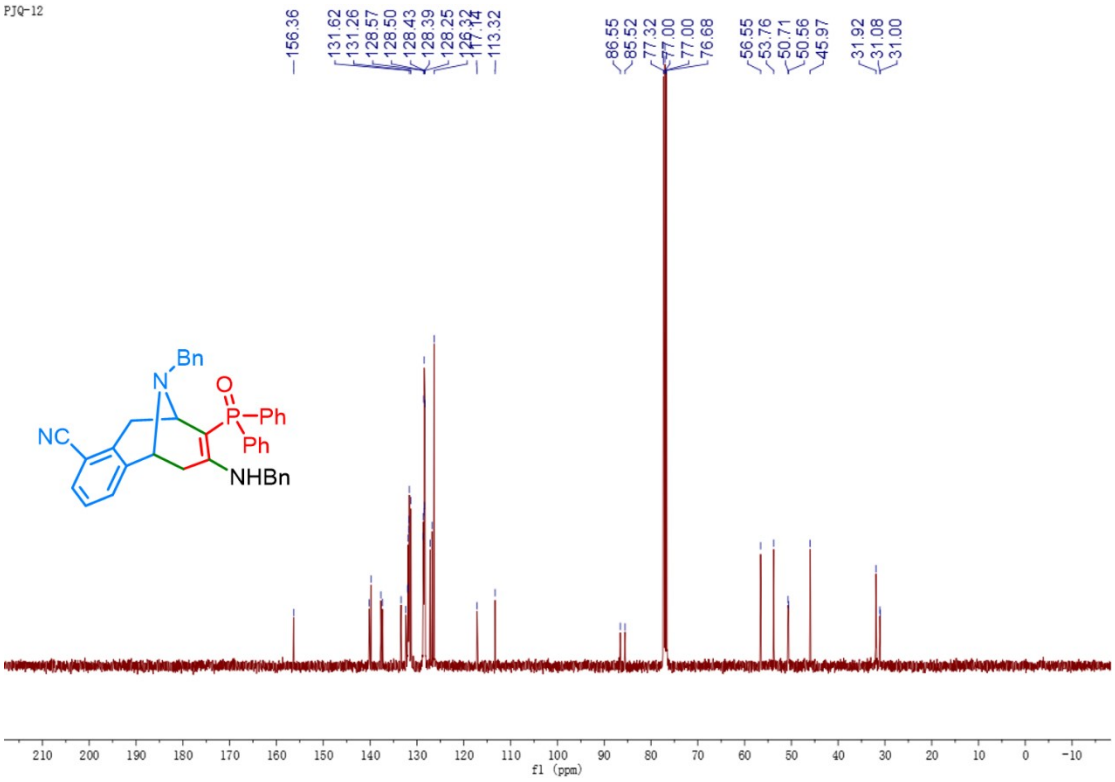
^{31}P NMR spectrum of **4b** (162 MHz, $CDCl_3$)



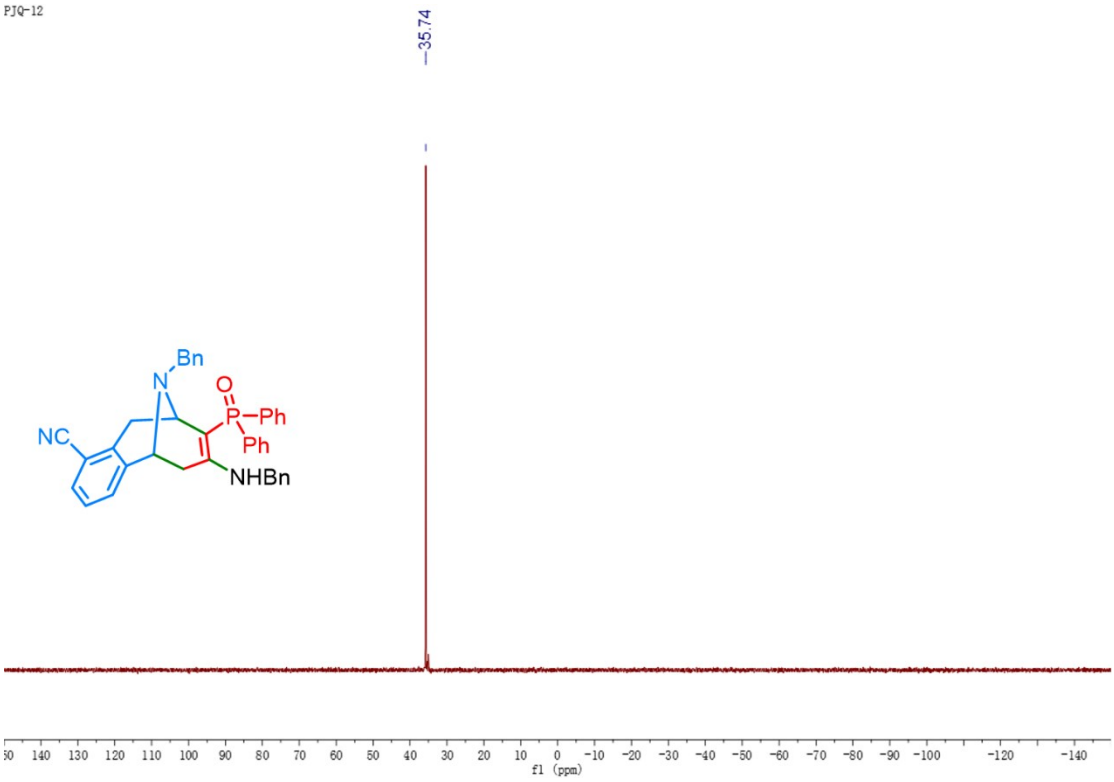
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)



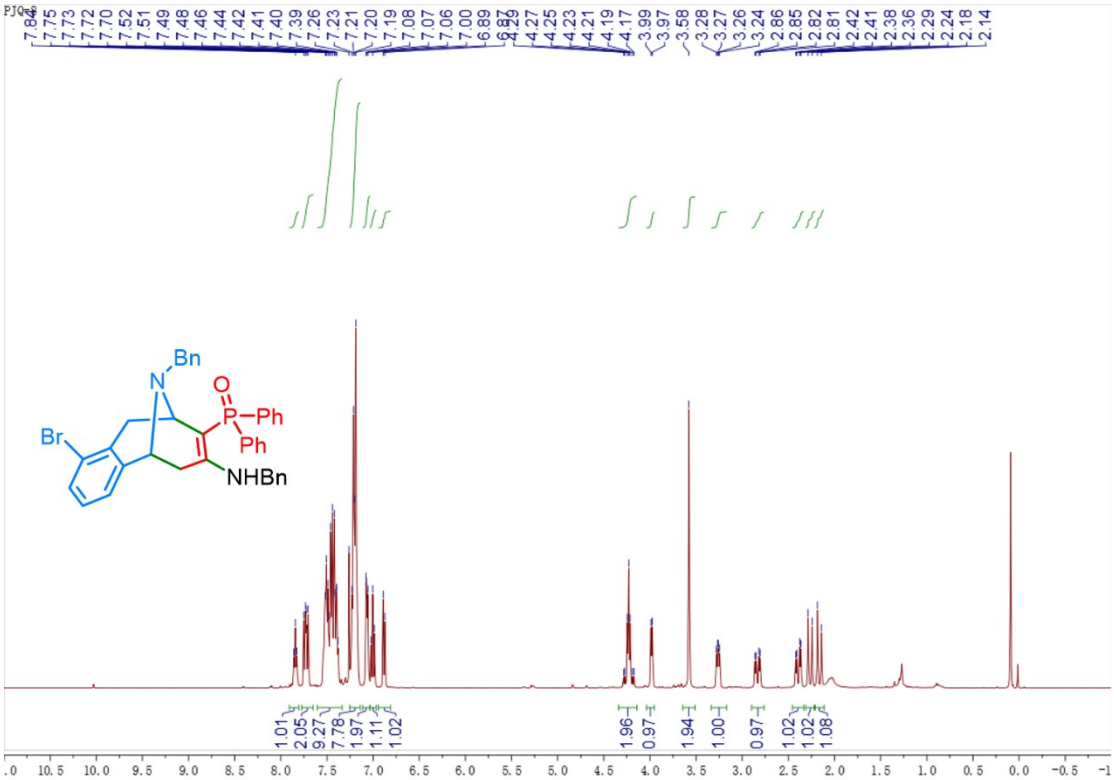
^{13}C NMR spectrum of **4c** (100 MHz, $CDCl_3$)



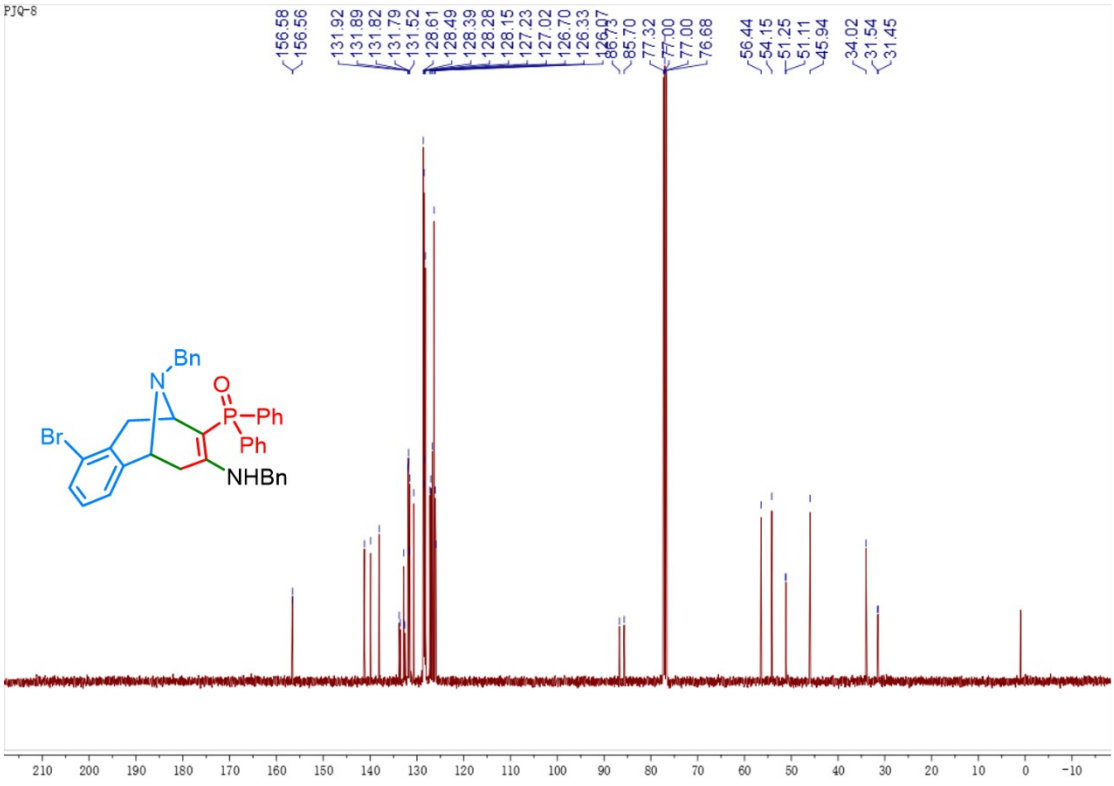
^{31}P NMR spectrum of **4c** (162 MHz, $CDCl_3$)



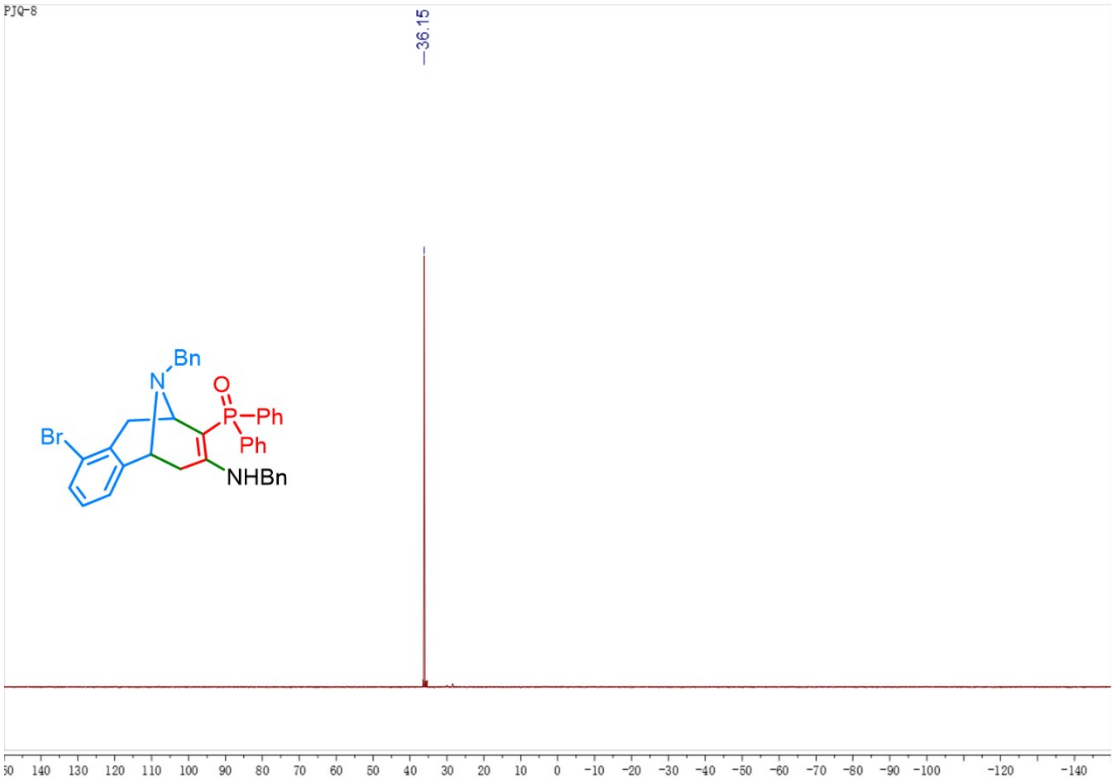
^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$)



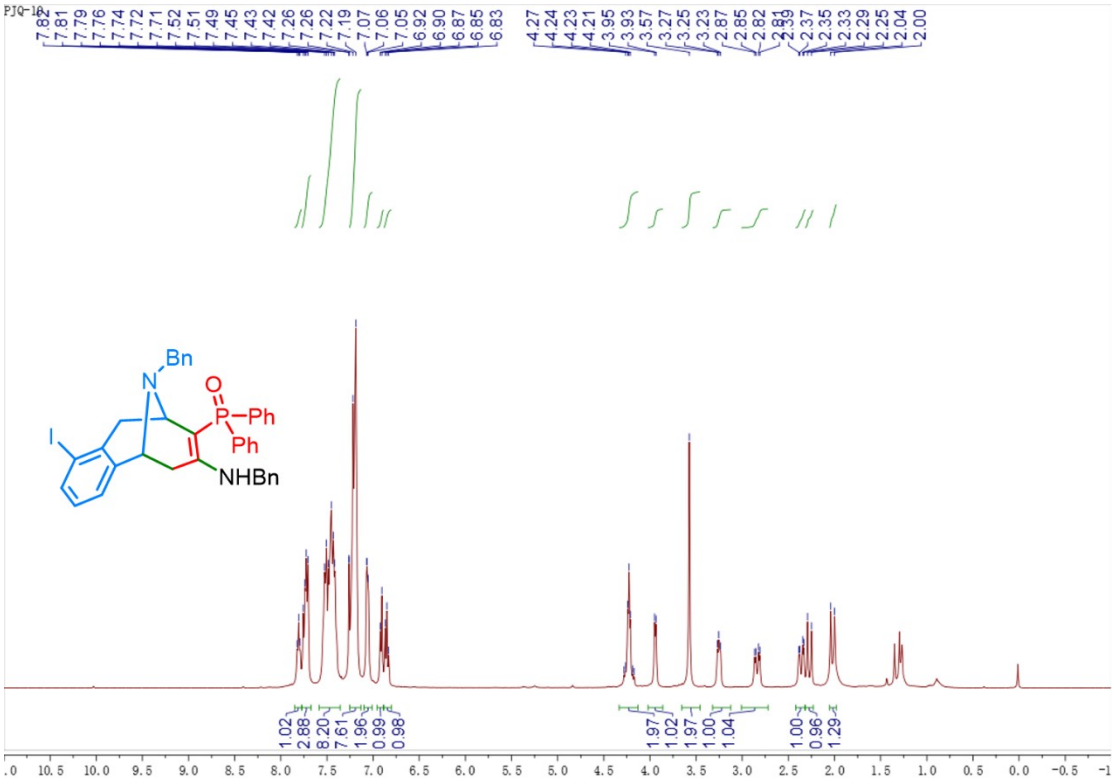
^{13}C NMR spectrum of **4d** (100 MHz, $CDCl_3$)



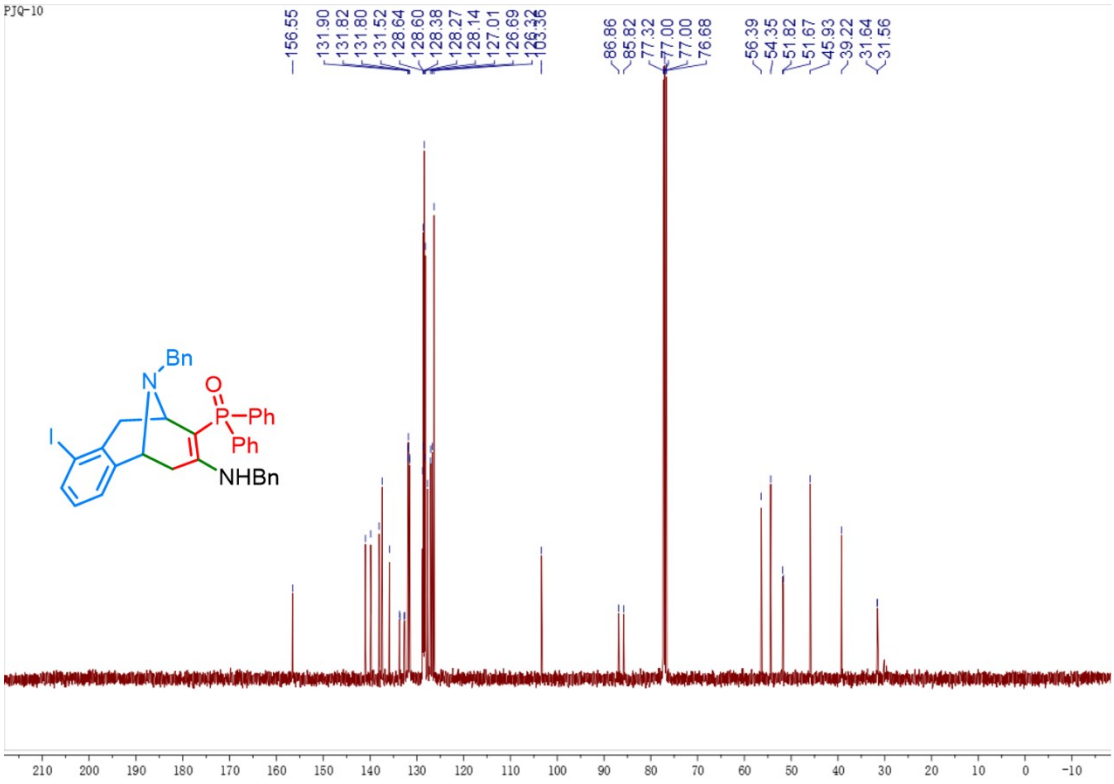
^{31}P NMR spectrum of **4d** (162 MHz, $CDCl_3$)



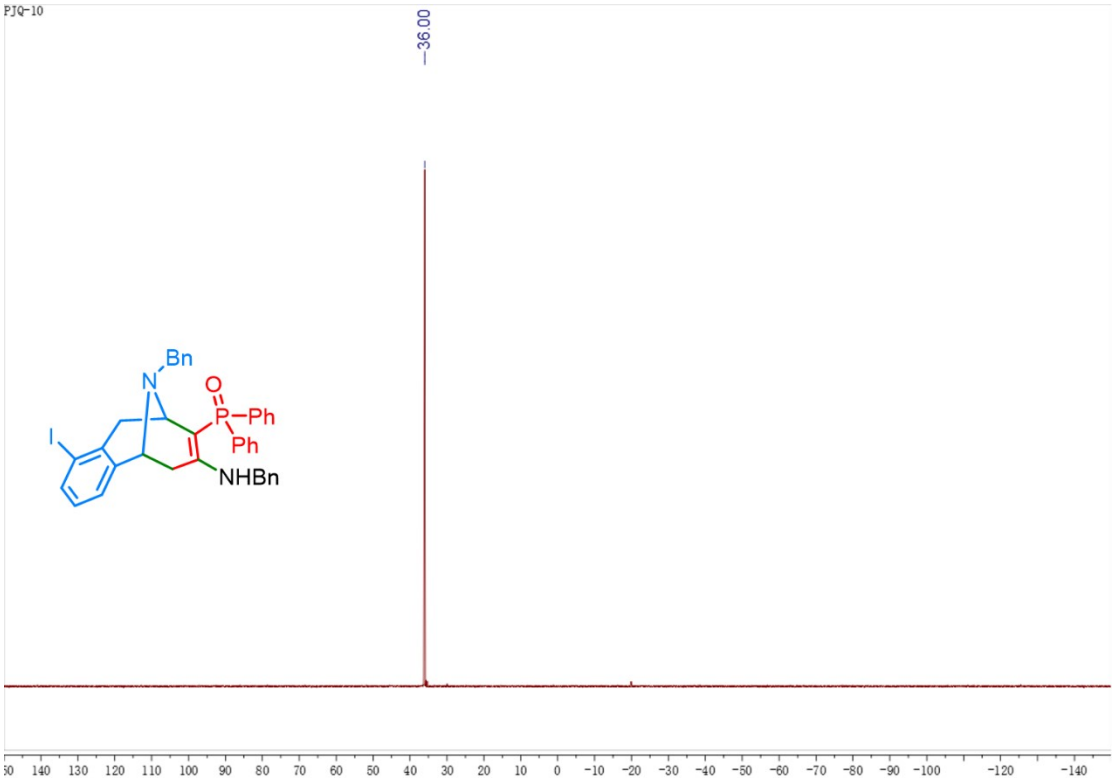
^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$)



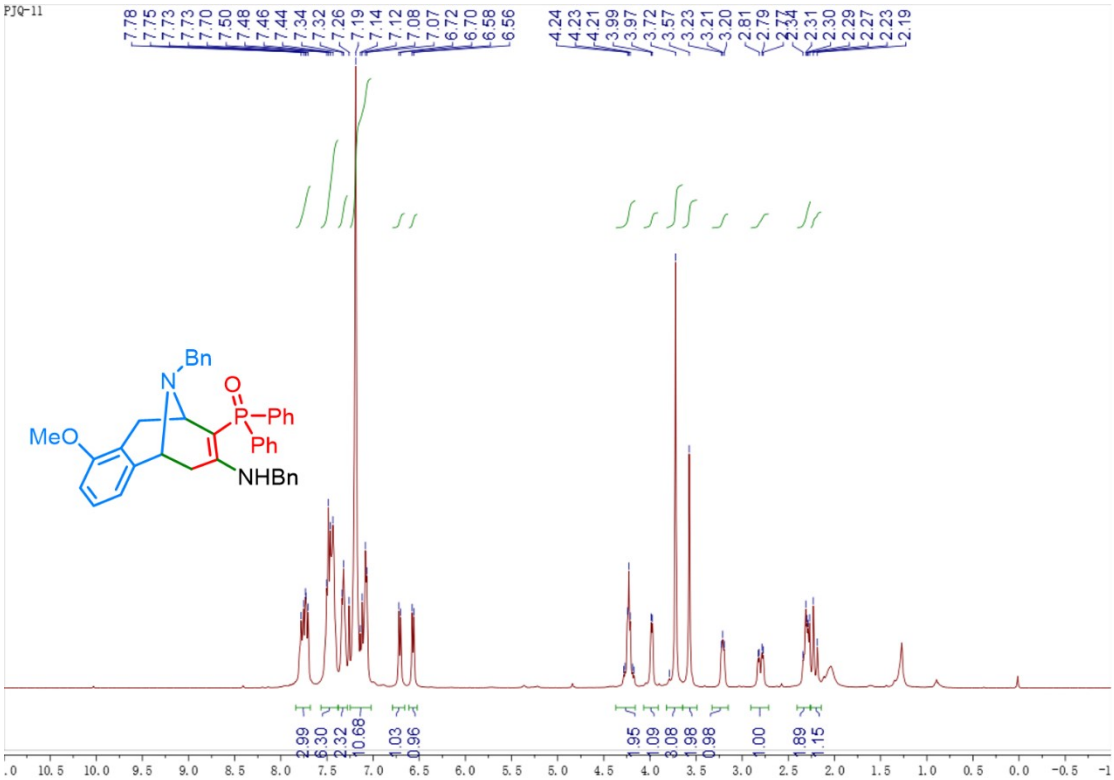
^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$)



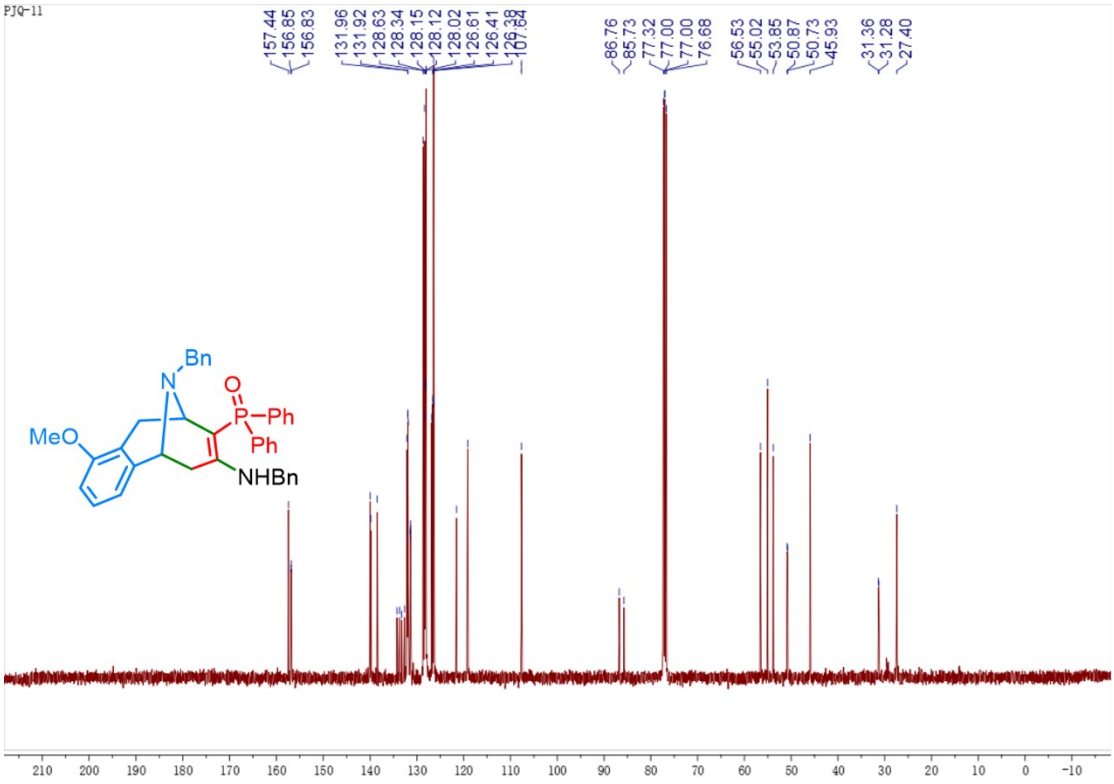
^{31}P NMR spectrum of **4e** (162 MHz, $CDCl_3$)



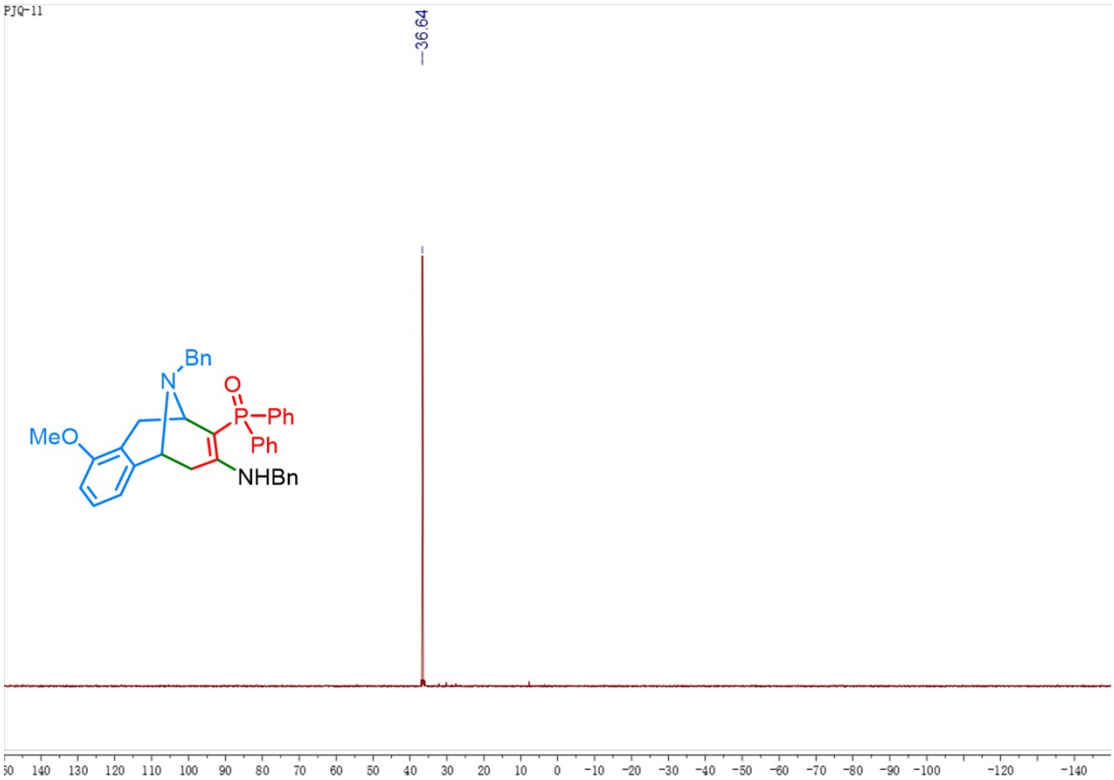
^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$)



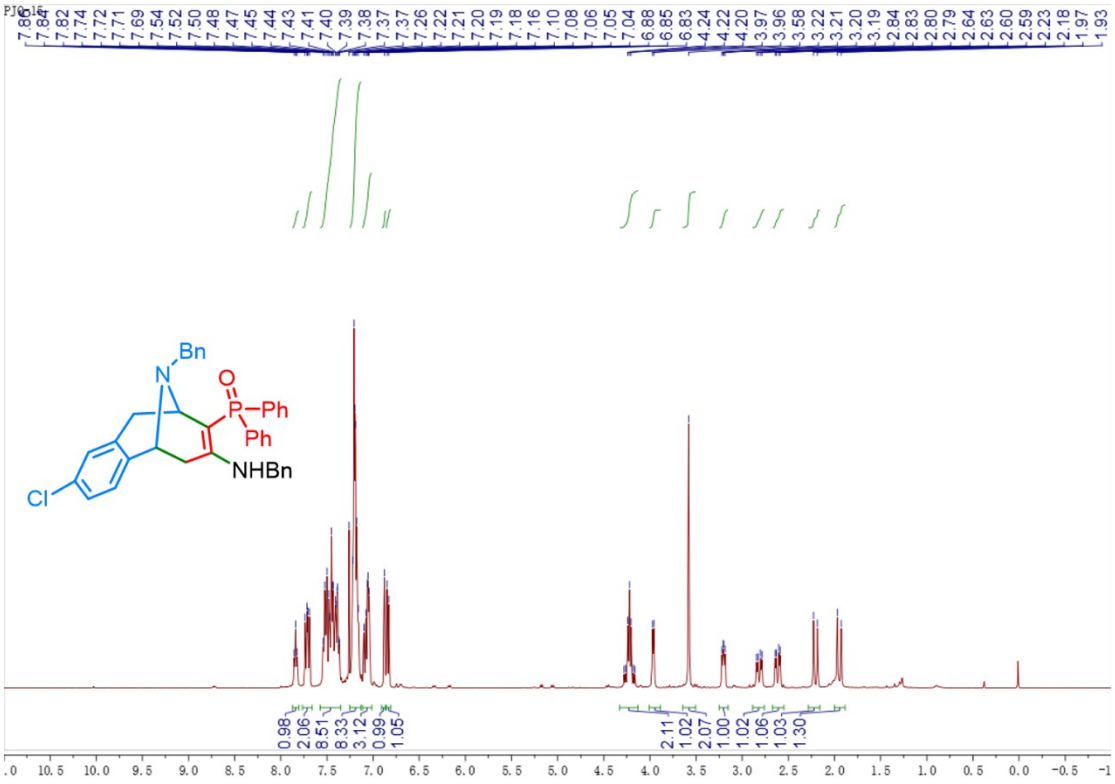
^{13}C NMR spectrum of **4f** (100 MHz, $CDCl_3$)



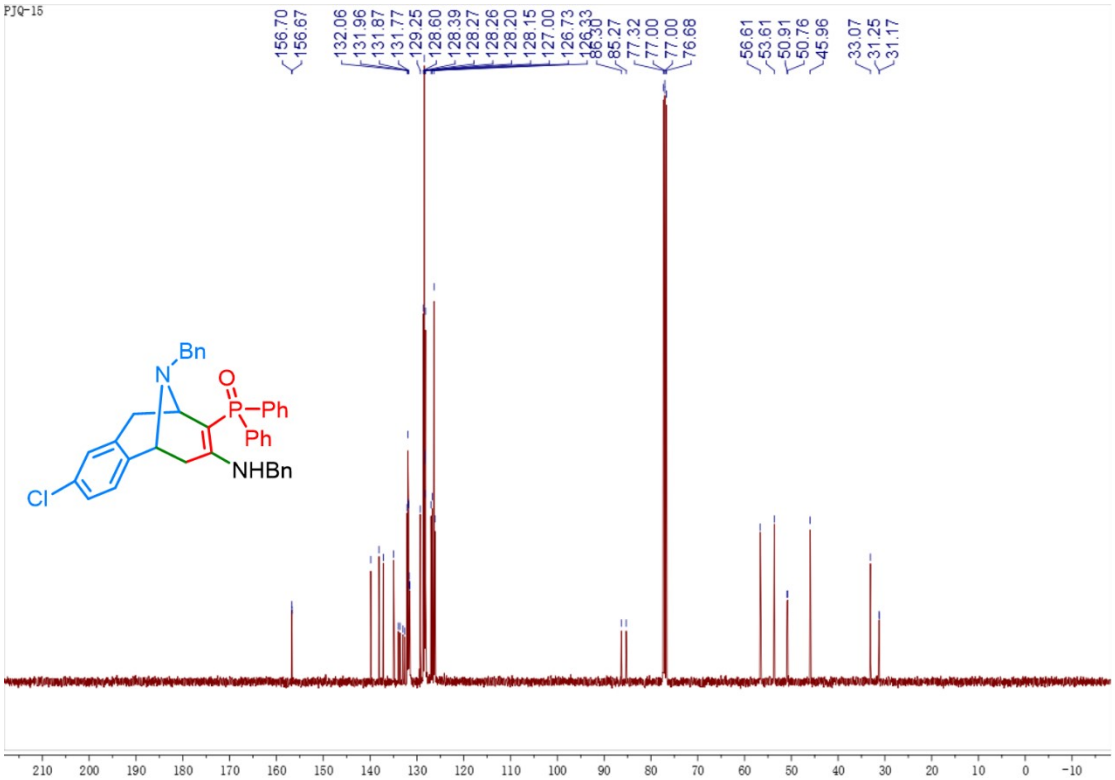
^{31}P NMR spectrum of **4f** (162 MHz, $CDCl_3$)



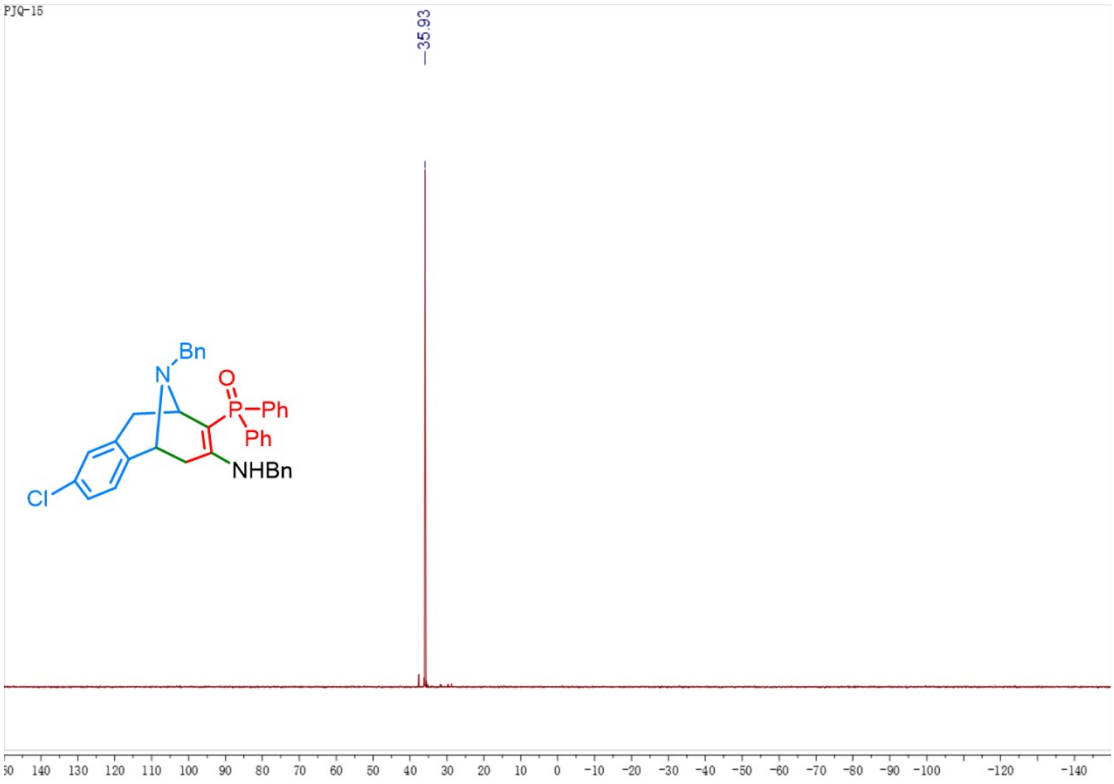
^{1}H NMR spectrum of **4g** (400 MHz, $CDCl_3$)



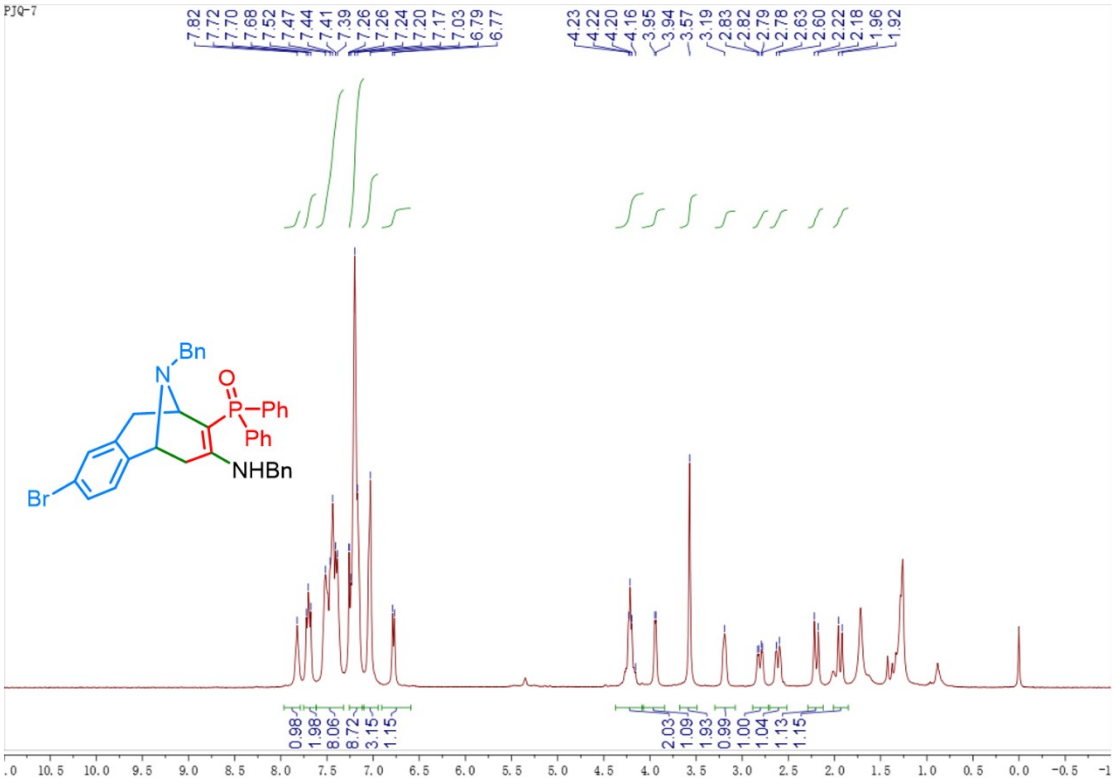
^{13}C NMR spectrum of **4g** (100 MHz, $CDCl_3$)



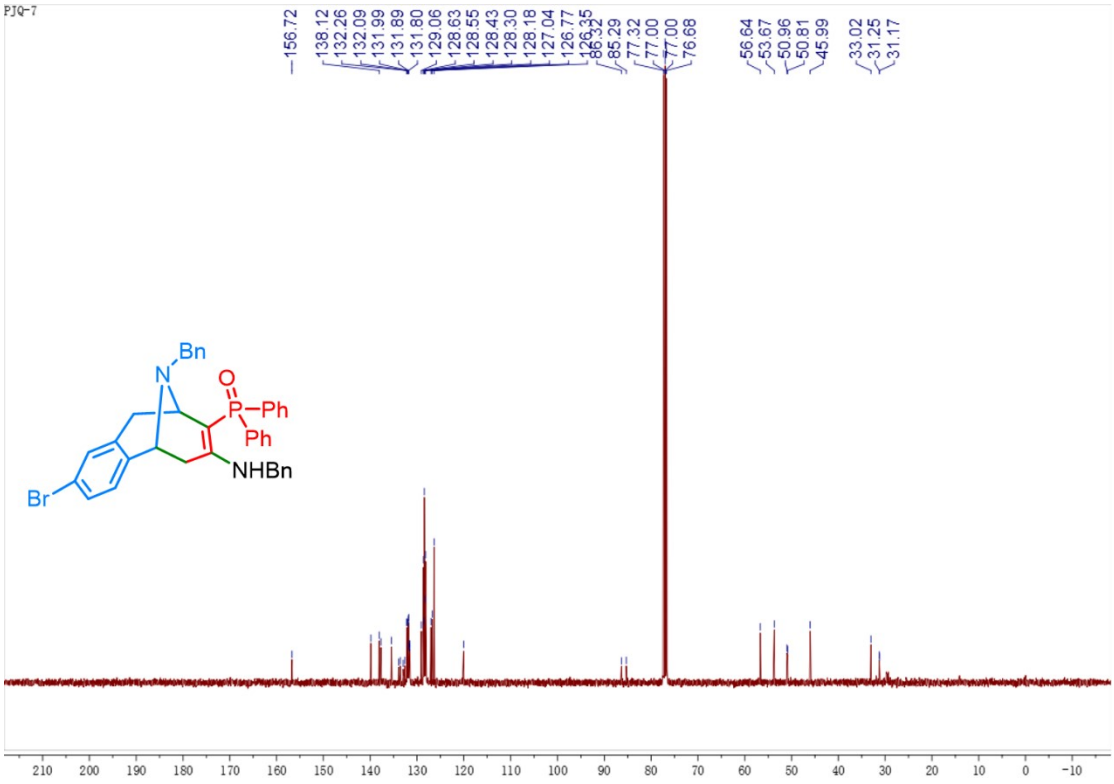
^{31}P NMR spectrum of **4g** (162 MHz, $CDCl_3$)



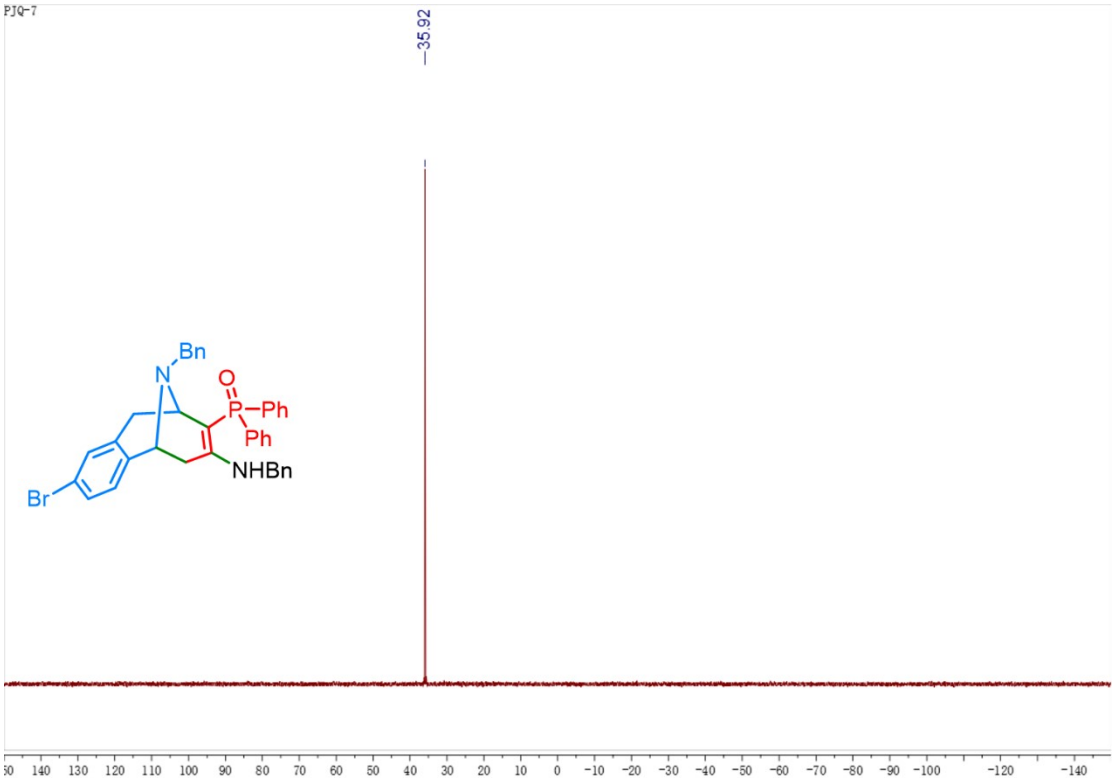
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$)



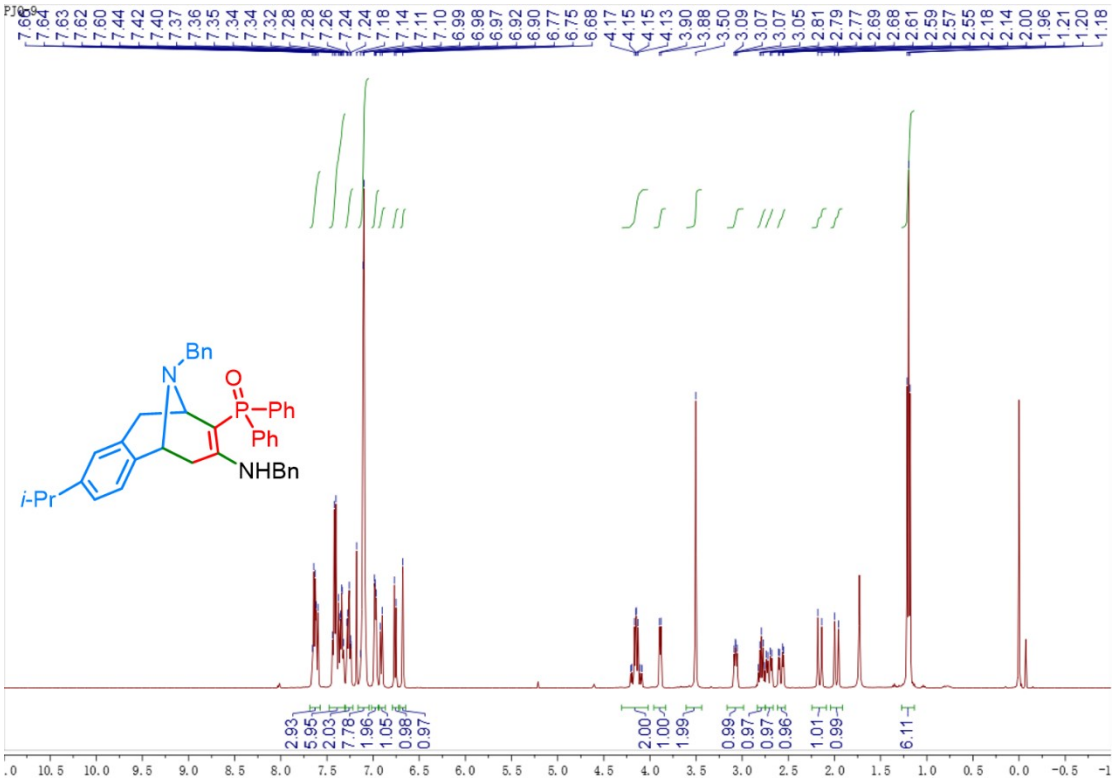
^{13}C NMR spectrum of **4h** (100 MHz, $CDCl_3$)



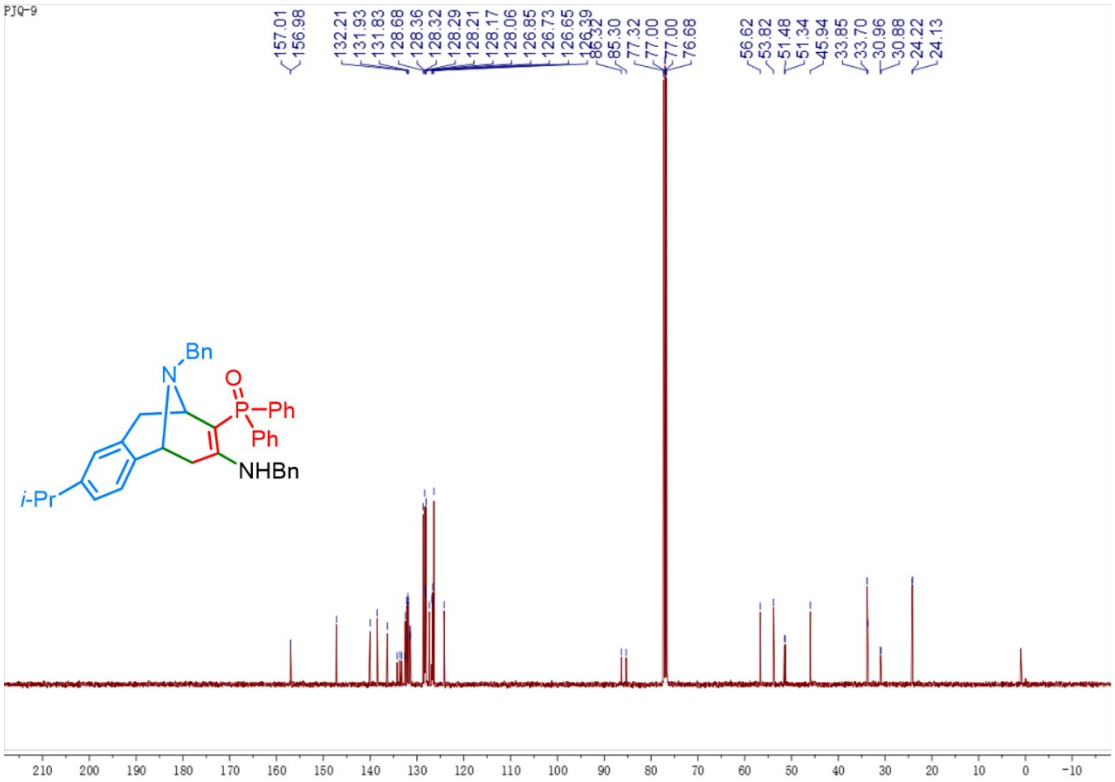
^{31}P NMR spectrum of **4h** (162 MHz, $CDCl_3$)



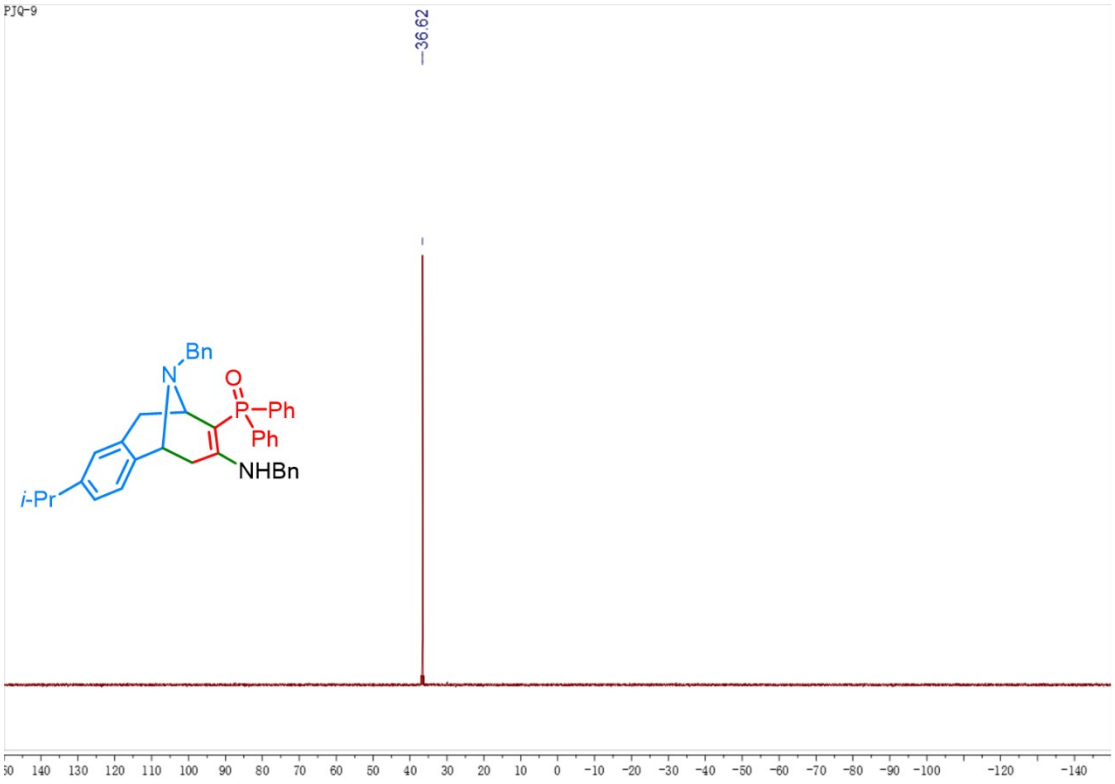
^{1}H NMR spectrum of **4i** (400 MHz, $CDCl_3$)



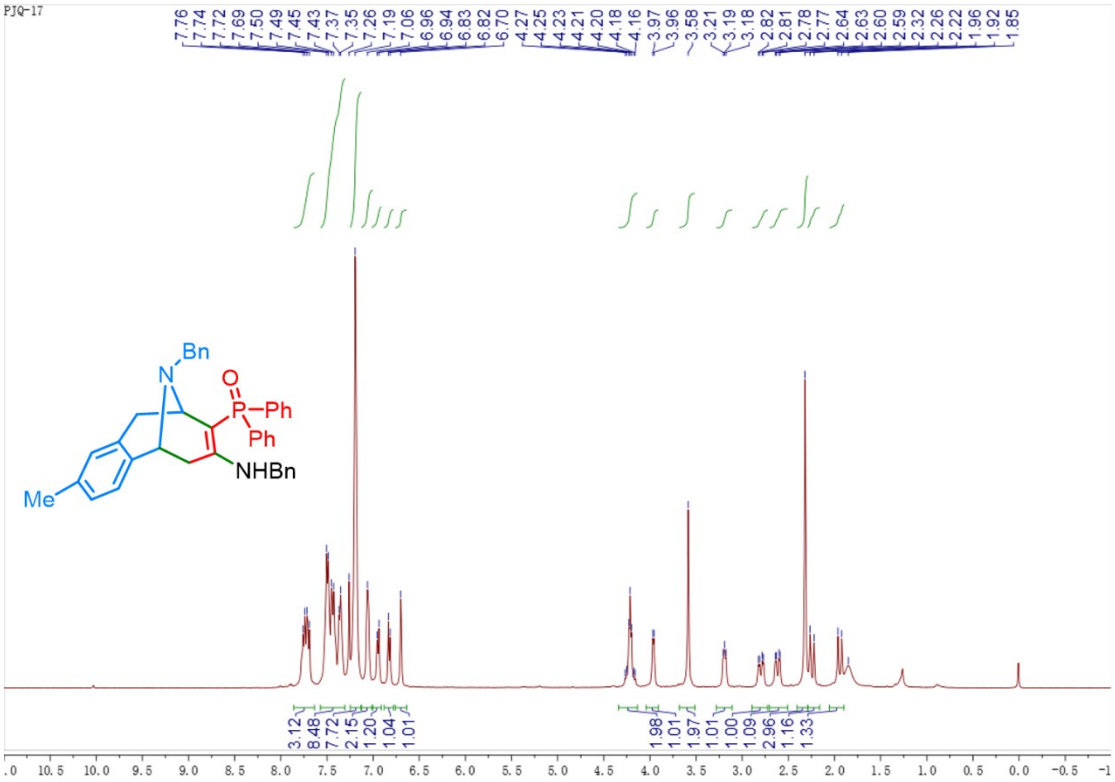
^{13}C NMR spectrum of **4i** (100 MHz, $CDCl_3$)



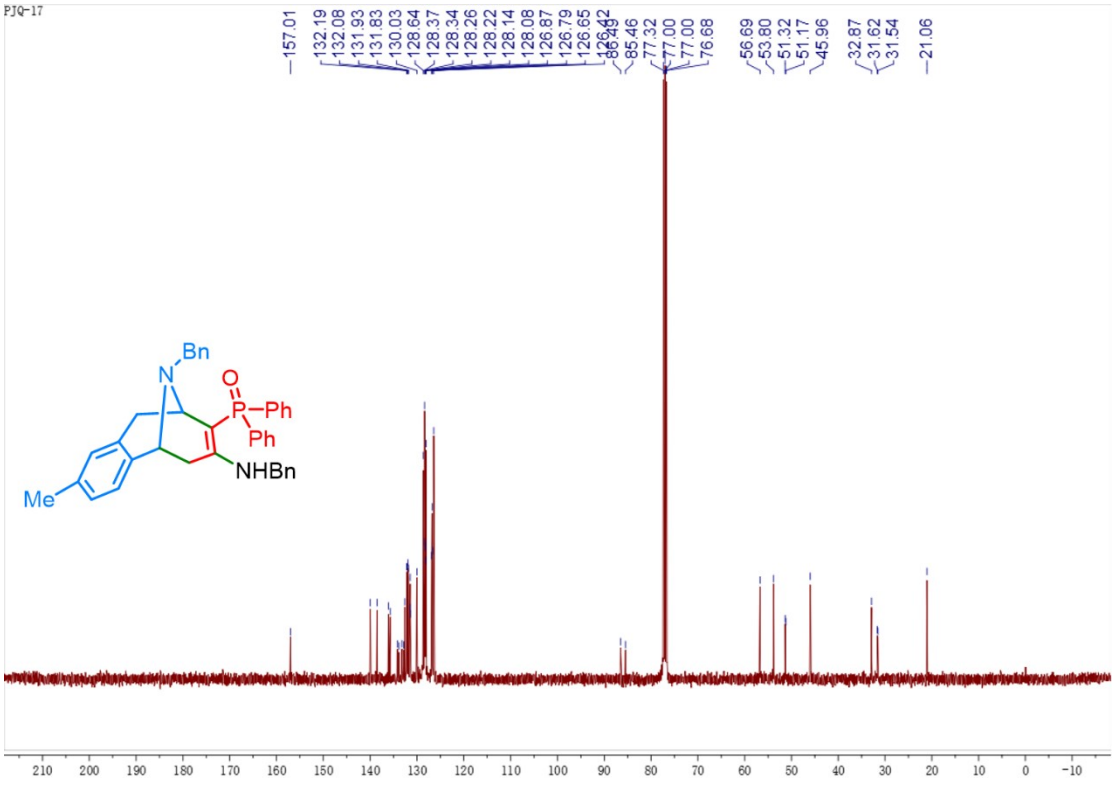
^{31}P NMR spectrum of **4i** (162 MHz, $CDCl_3$)



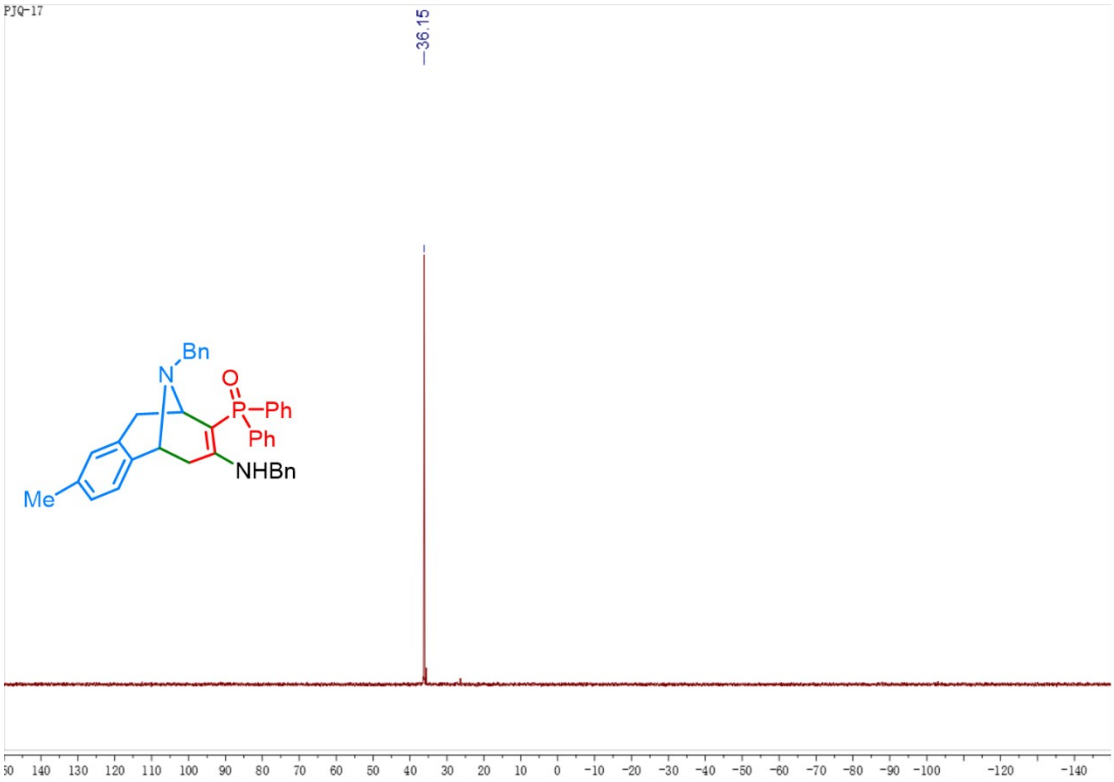
^{1}H NMR spectrum of **4j** (400 MHz, $CDCl_3$)



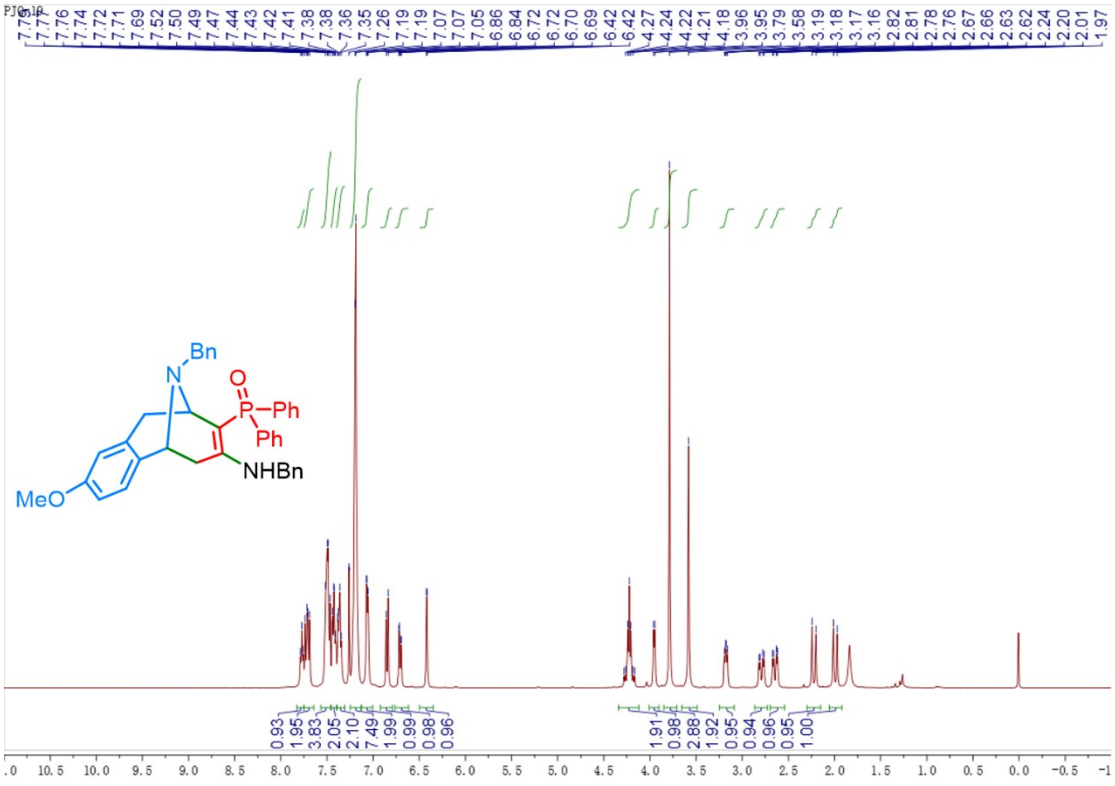
^{13}C NMR spectrum of **4j** (100 MHz, $CDCl_3$)



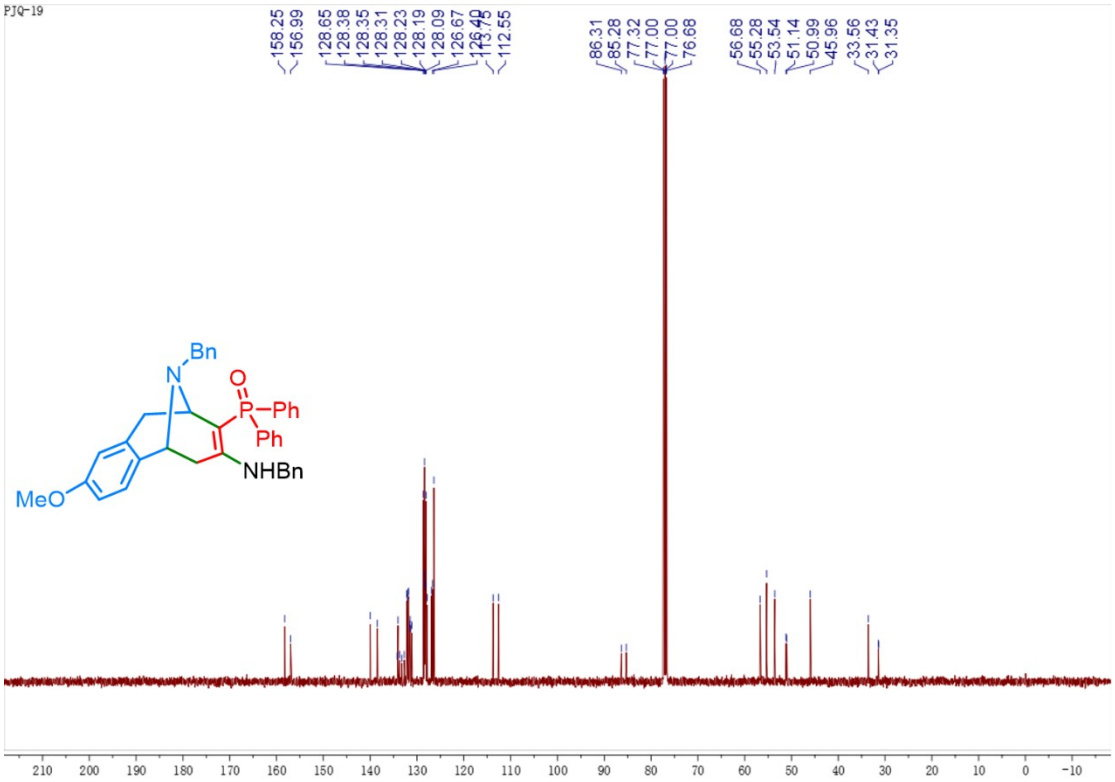
^{31}P NMR spectrum of **4j** (162 MHz, $CDCl_3$)



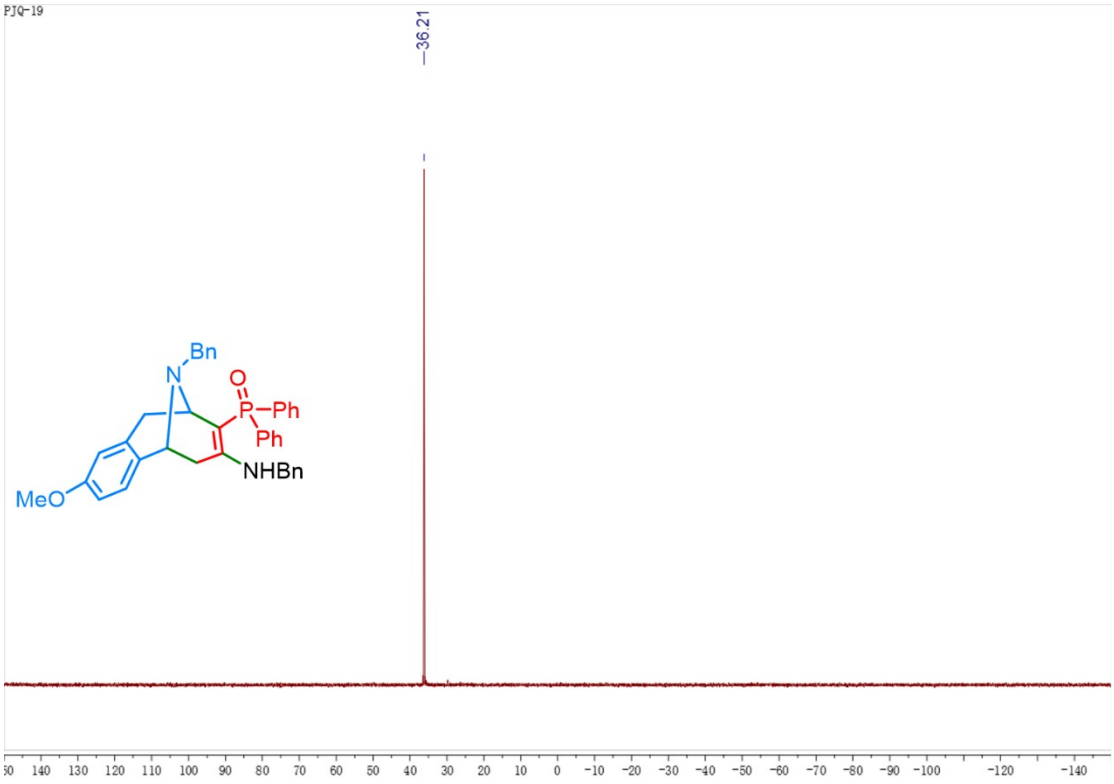
^{1}H NMR spectrum of **4k** (400 MHz, $CDCl_3$)



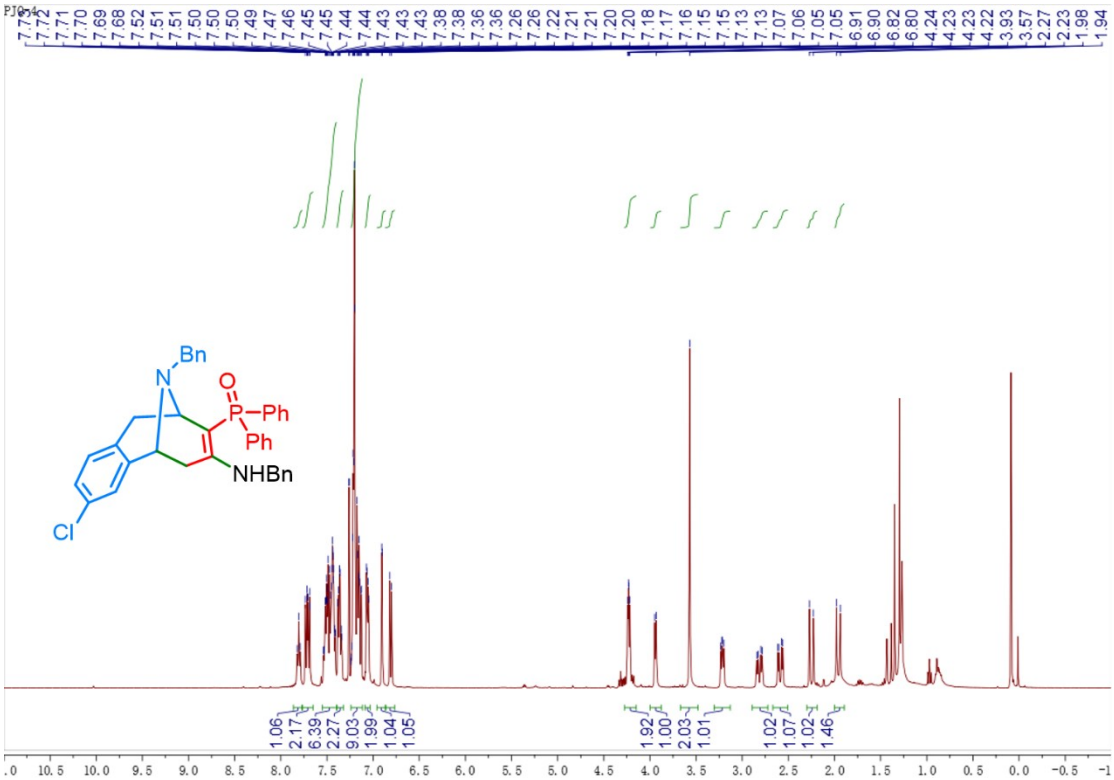
^{13}C NMR spectrum of **4k** (100 MHz, $CDCl_3$)



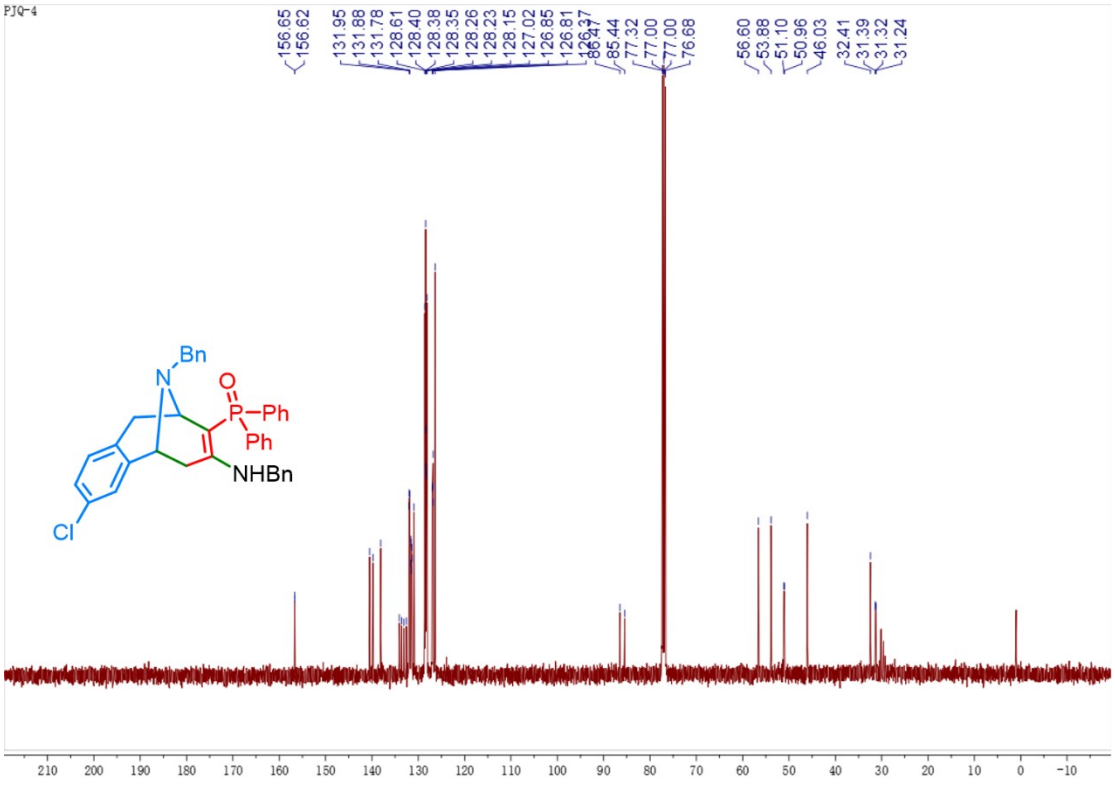
^{31}P NMR spectrum of **4k** (162 MHz, $CDCl_3$)



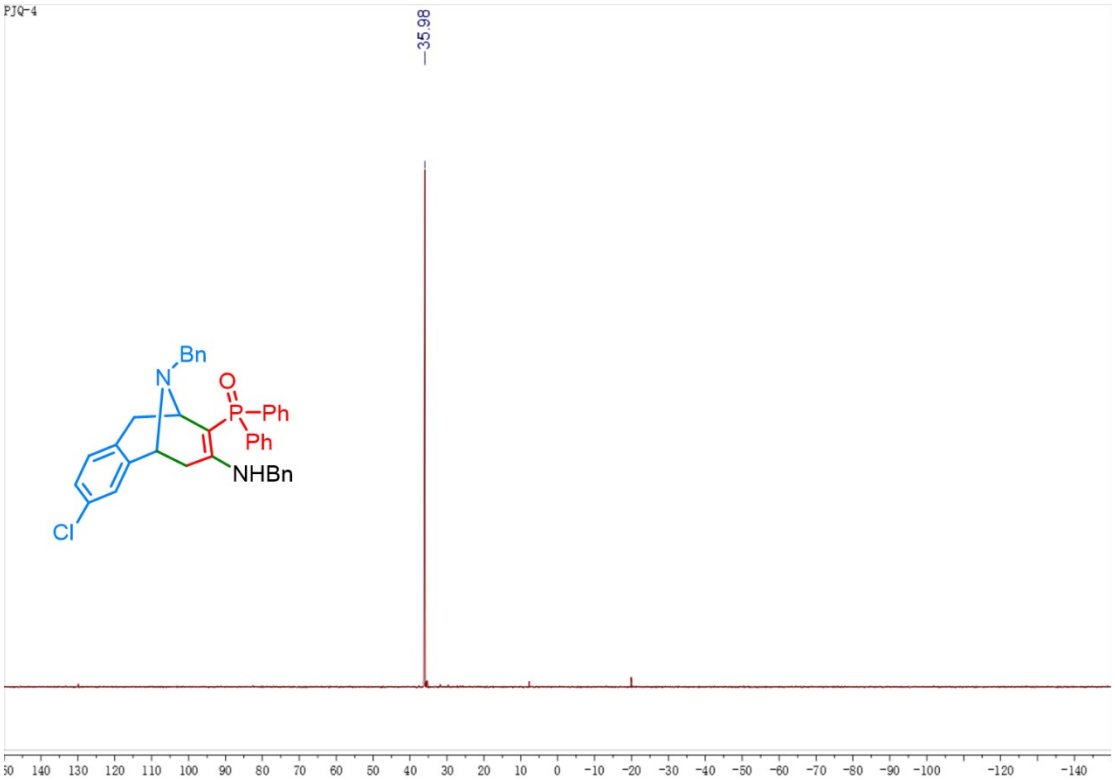
^{1}H NMR spectrum of **4l** (400 MHz, $CDCl_3$)



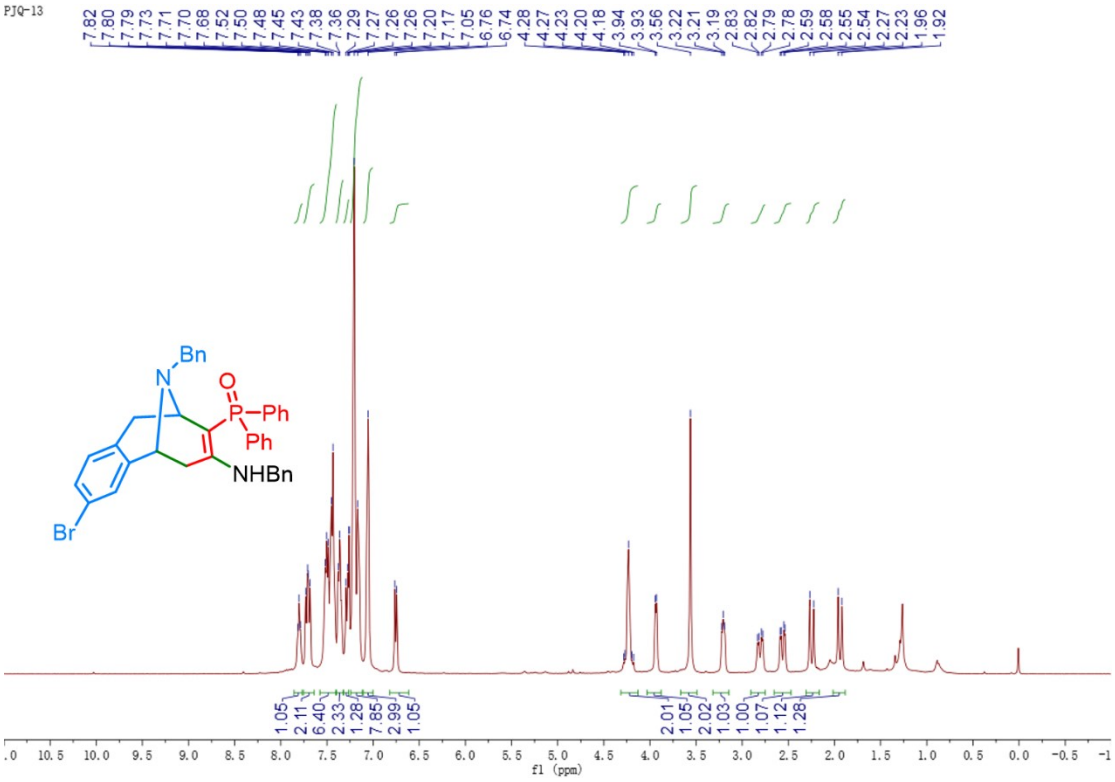
^{13}C NMR spectrum of **4l** (100 MHz, $CDCl_3$)



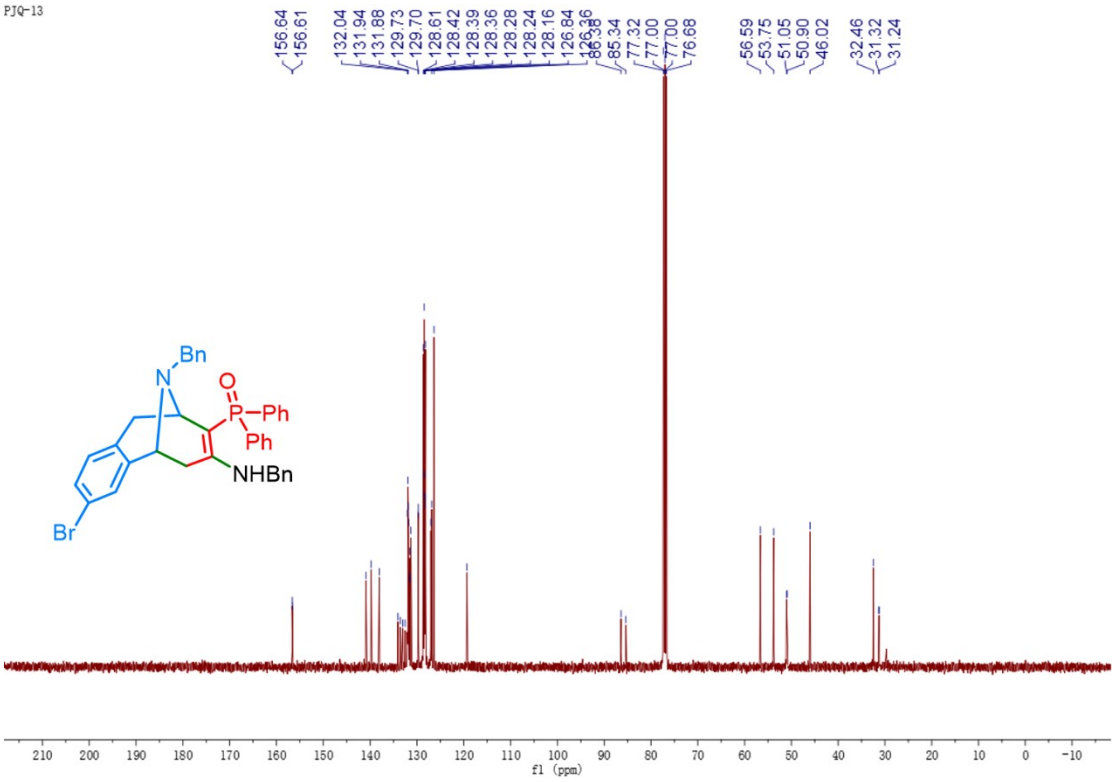
^{31}P NMR spectrum of **4l** (162 MHz, $CDCl_3$)



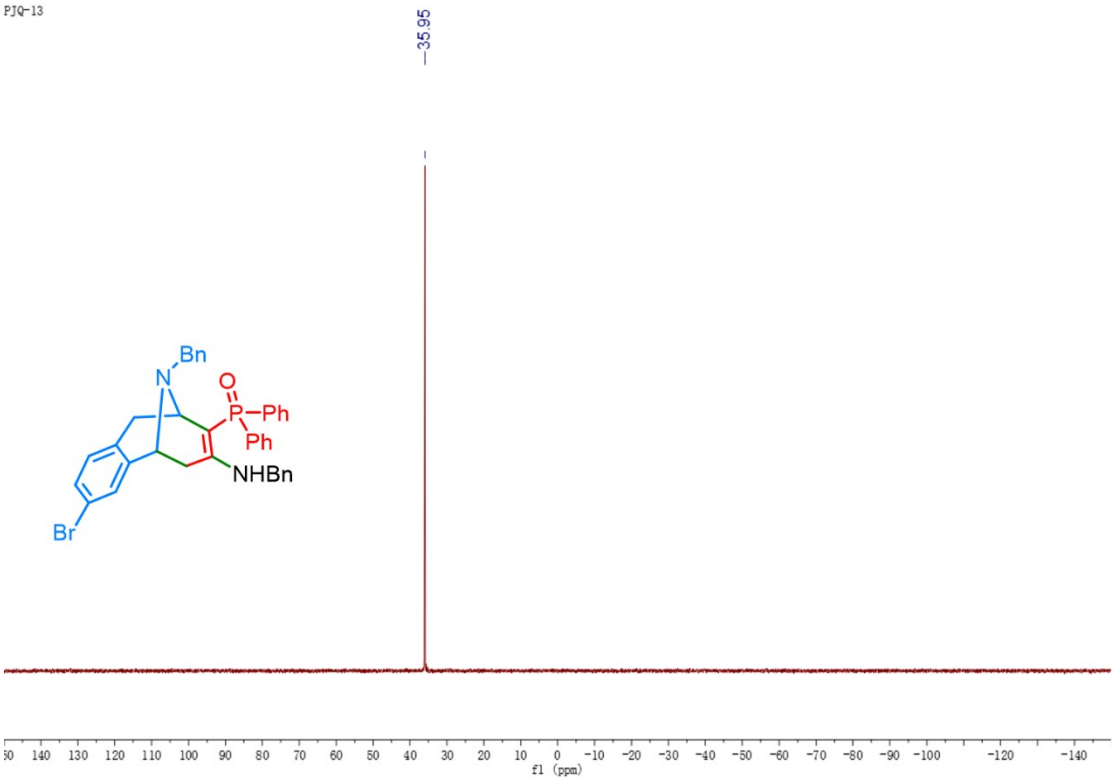
^{1}H NMR spectrum of **4m** (400 MHz, $CDCl_3$)



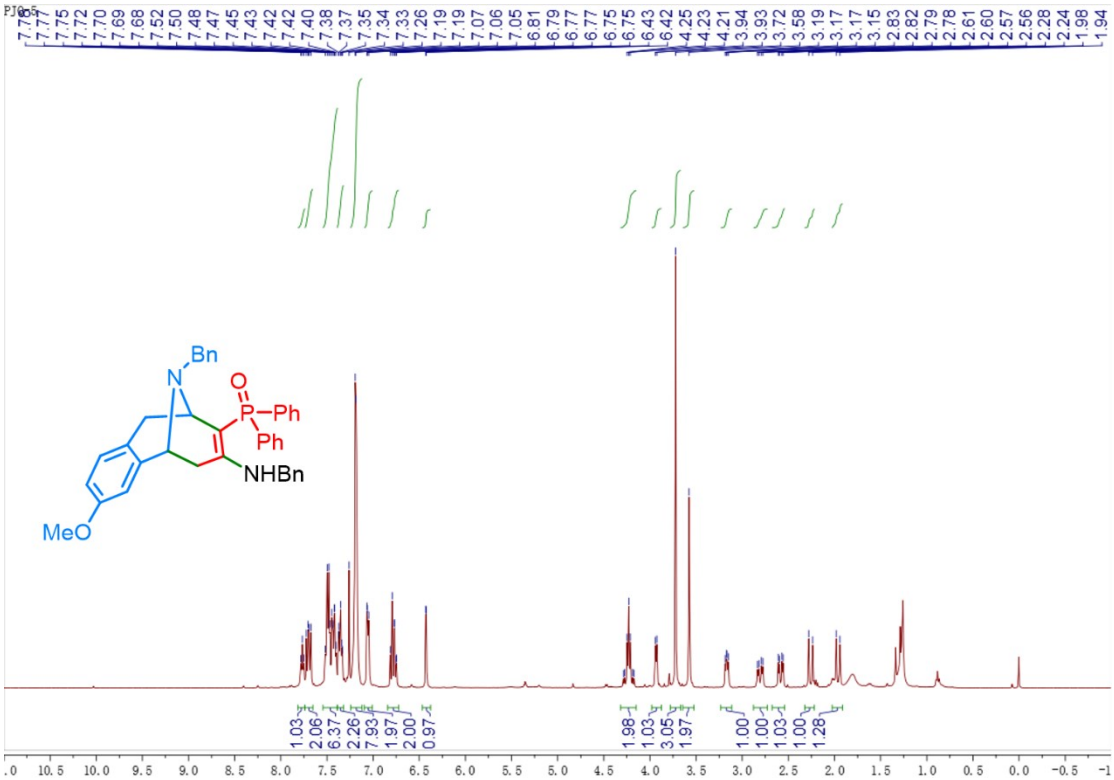
^{13}C NMR spectrum of **4m** (100 MHz, $CDCl_3$)



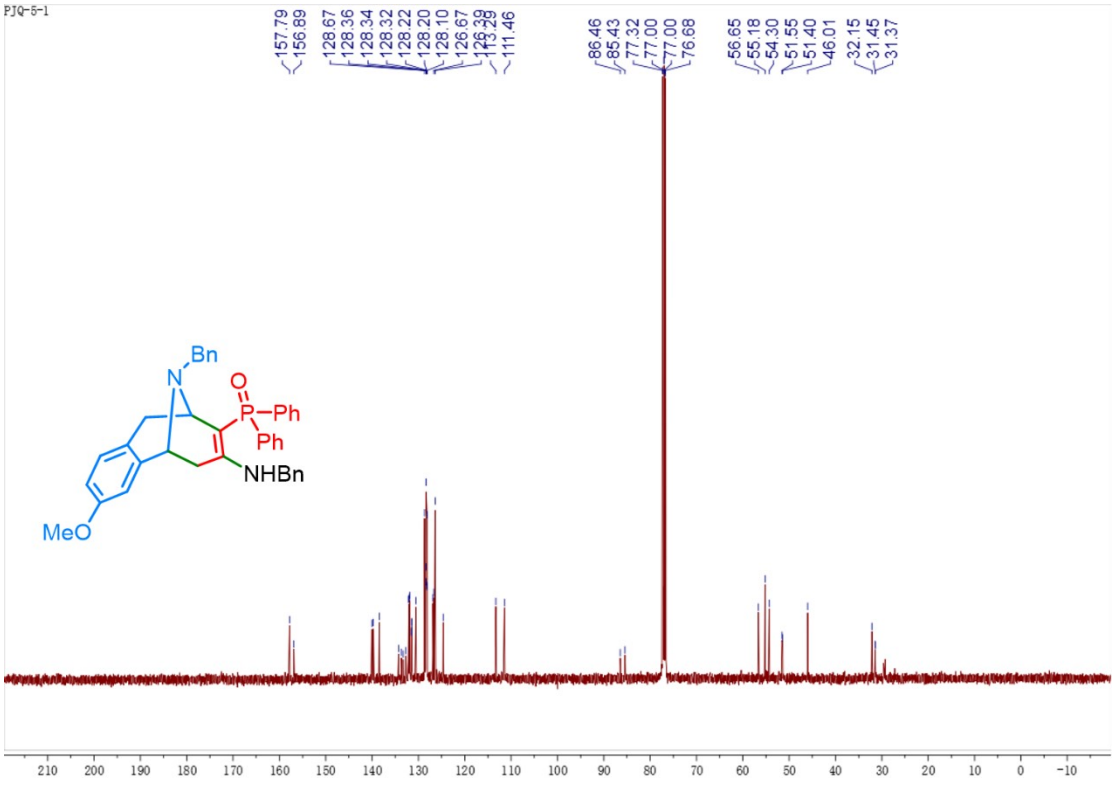
^{31}P NMR spectrum of **4m** (162 MHz, $CDCl_3$)



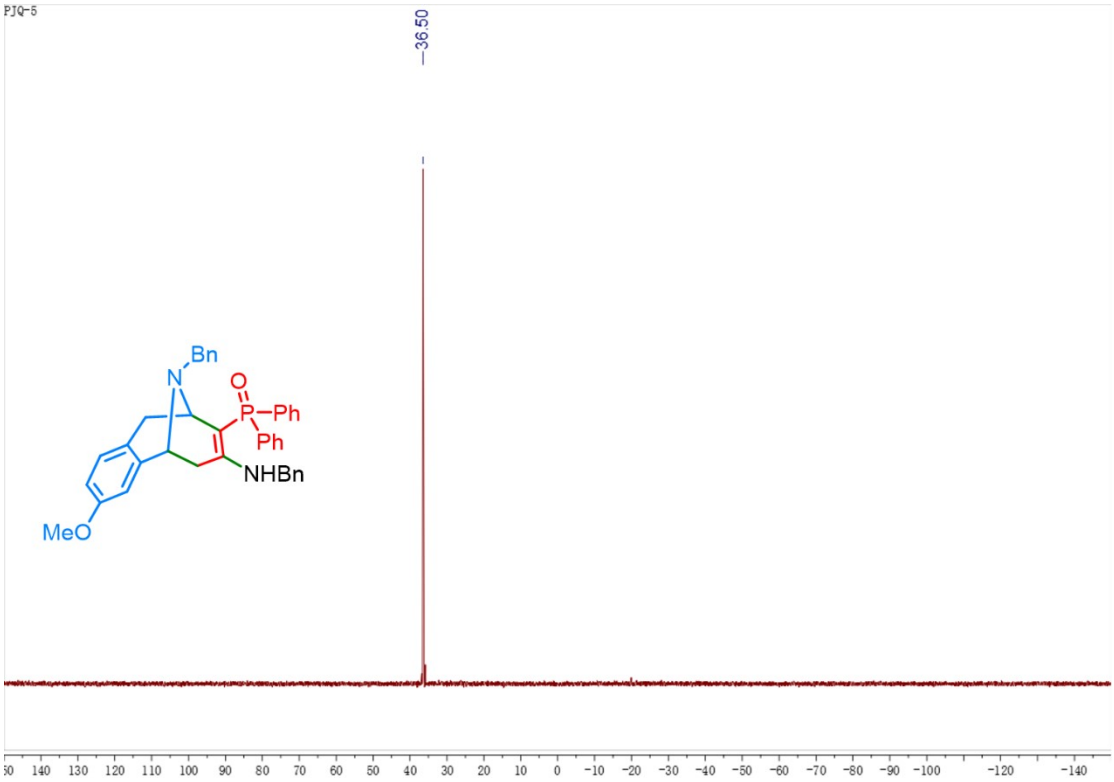
^{1}H NMR spectrum of **4n** (400 MHz, $CDCl_3$)



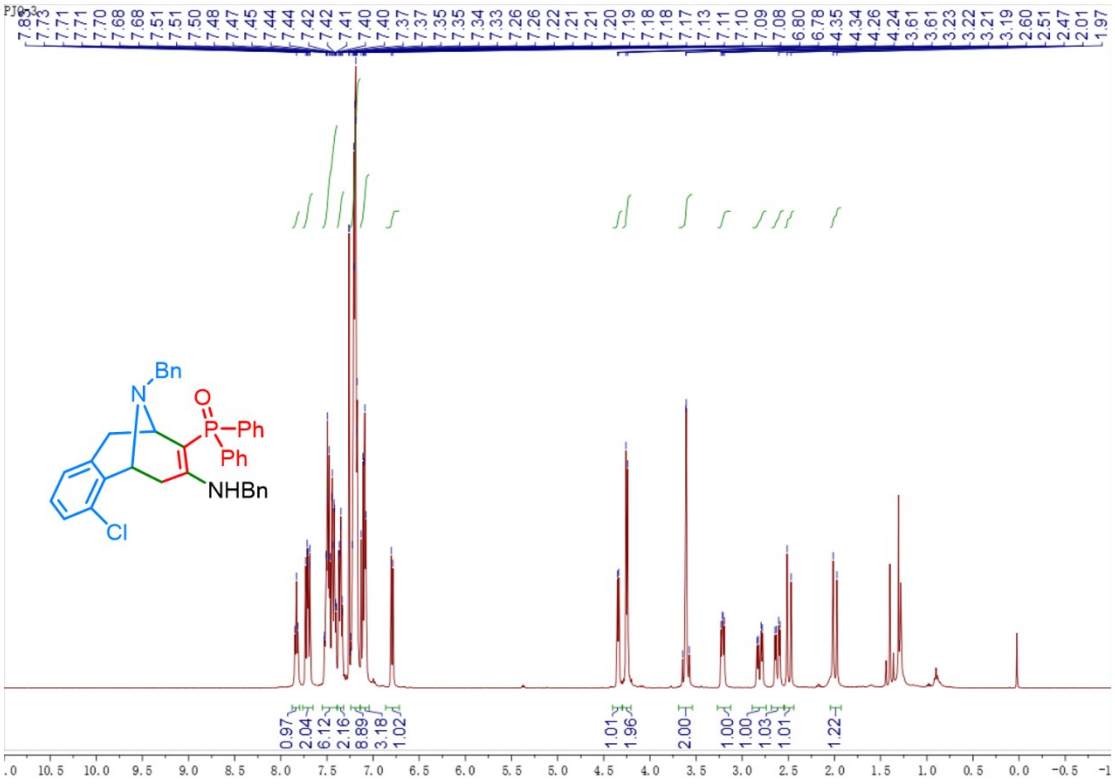
^{13}C NMR spectrum of **4n** (100 MHz, $CDCl_3$)



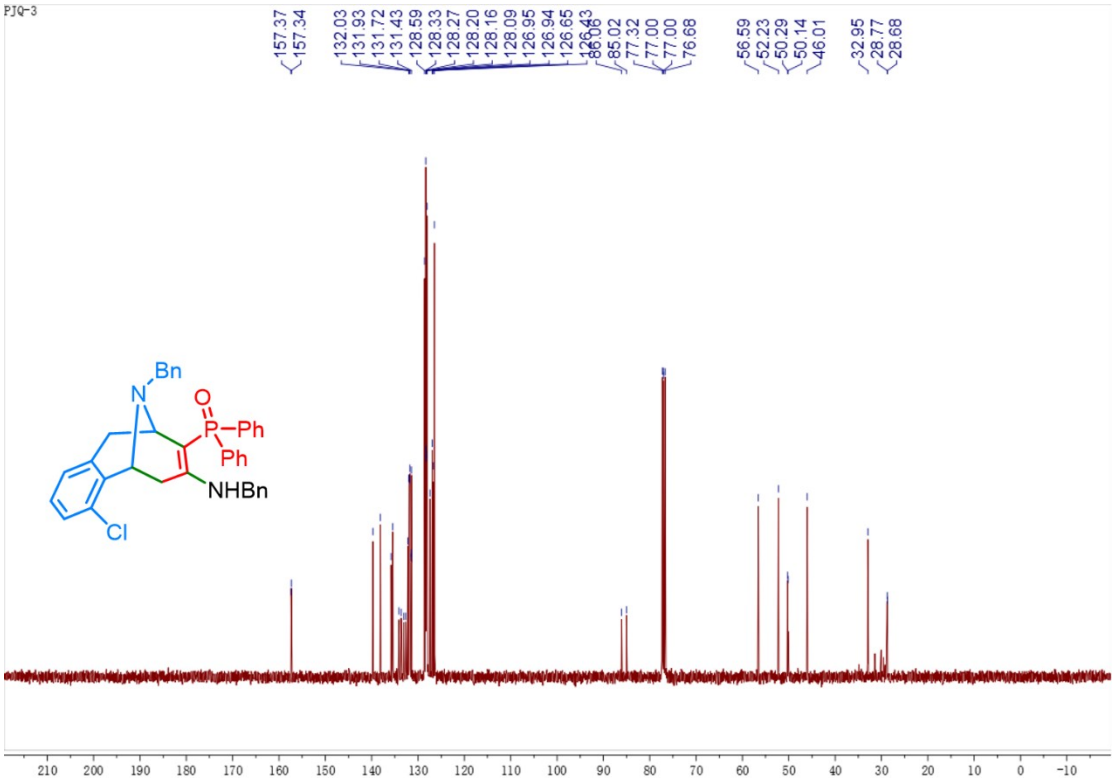
^{31}P NMR spectrum of **4n** (162 MHz, $CDCl_3$)



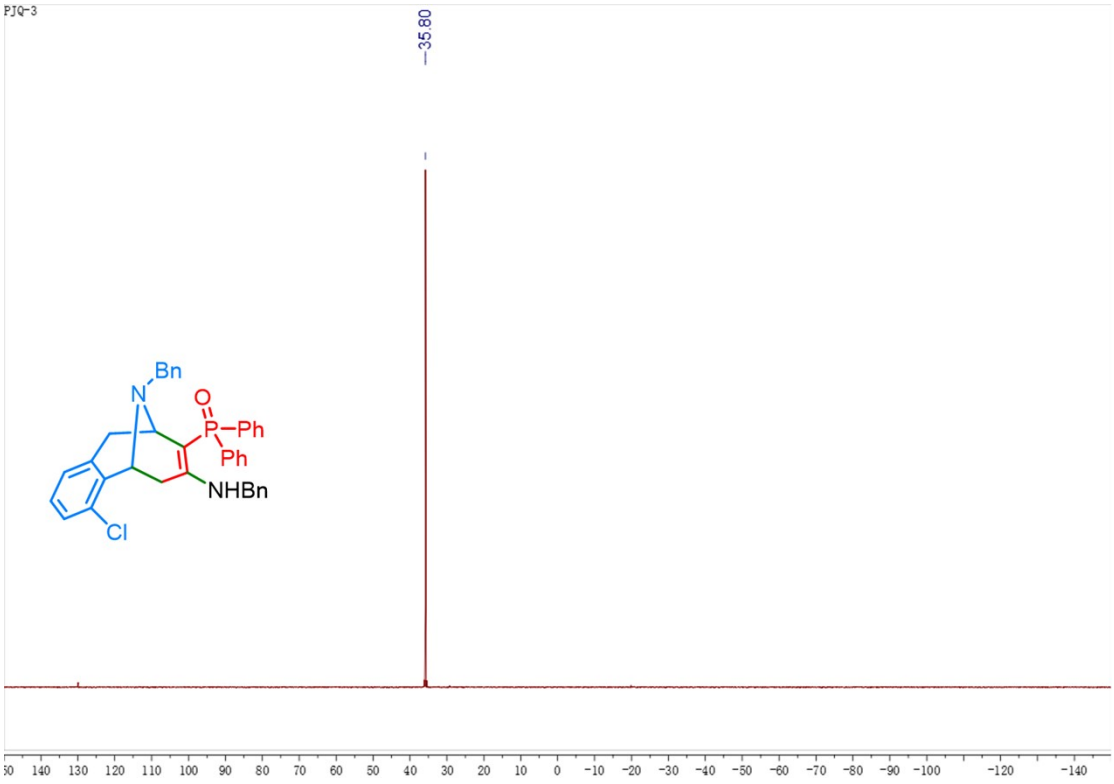
^{1}H NMR spectrum of **4o** (400 MHz, $CDCl_3$)



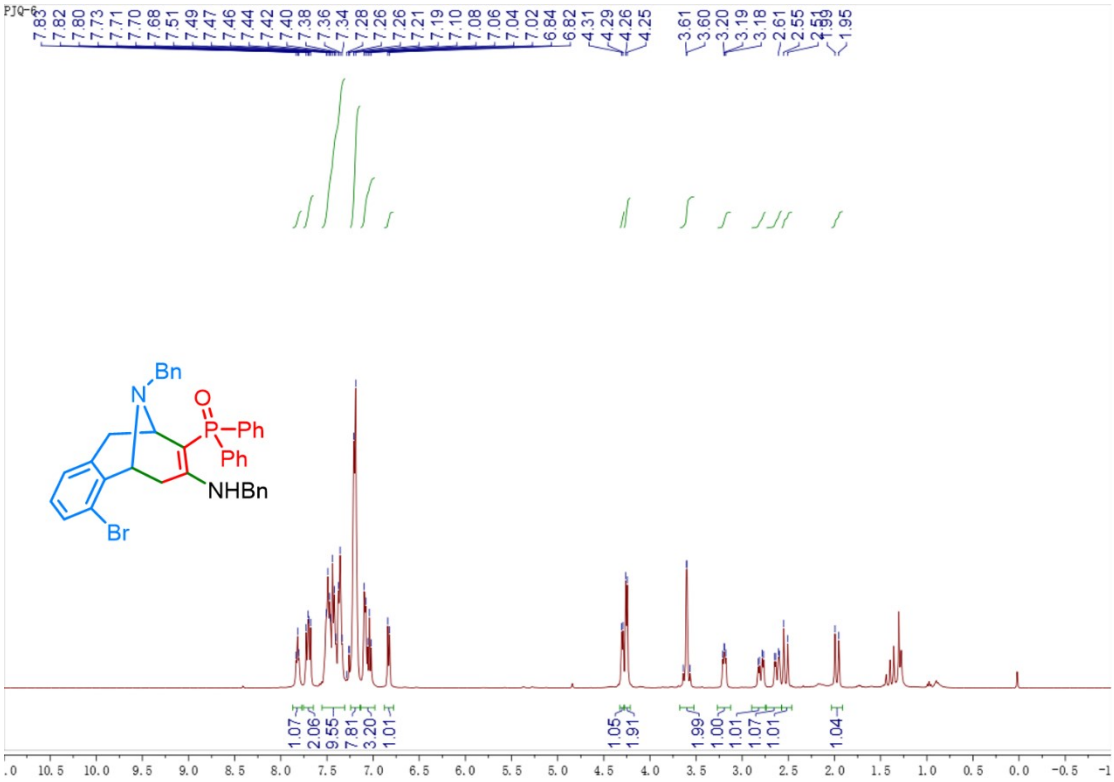
^{13}C NMR spectrum of **4o** (100 MHz, $CDCl_3$)



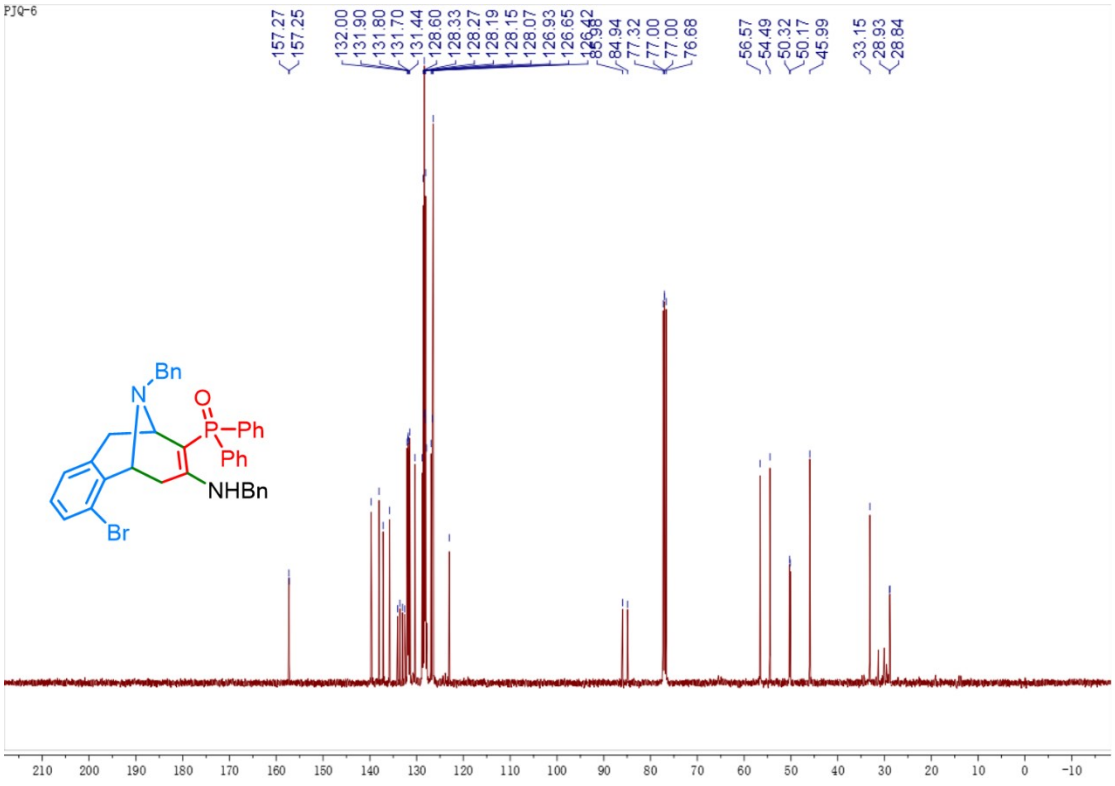
^{31}P NMR spectrum of **4o** (162 MHz, $CDCl_3$)



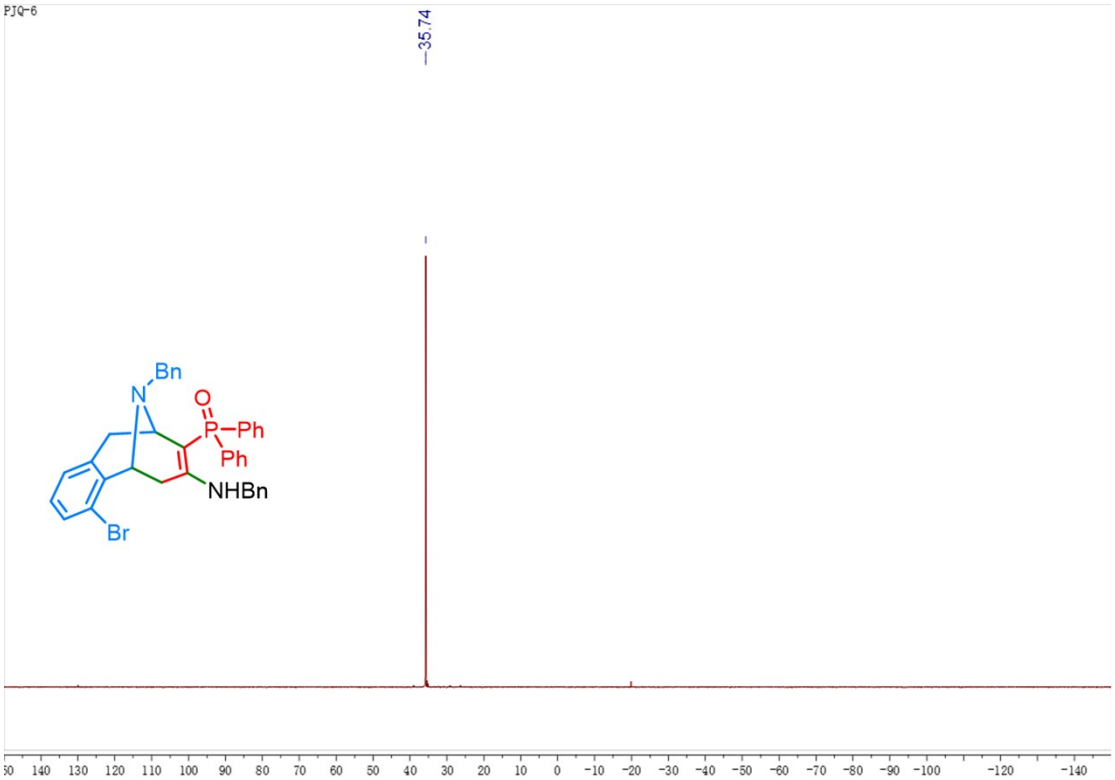
^{1}H NMR spectrum of **4p** (400 MHz, $CDCl_3$)



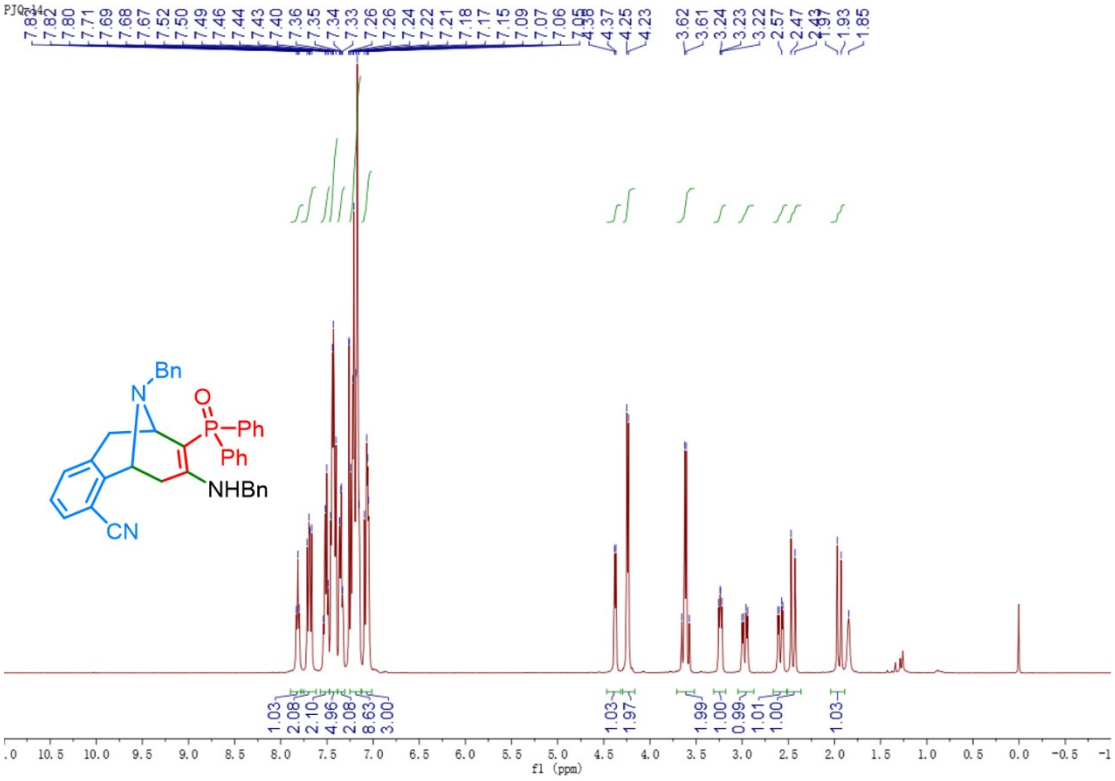
^{13}C NMR spectrum of **4p** (100 MHz, $CDCl_3$)



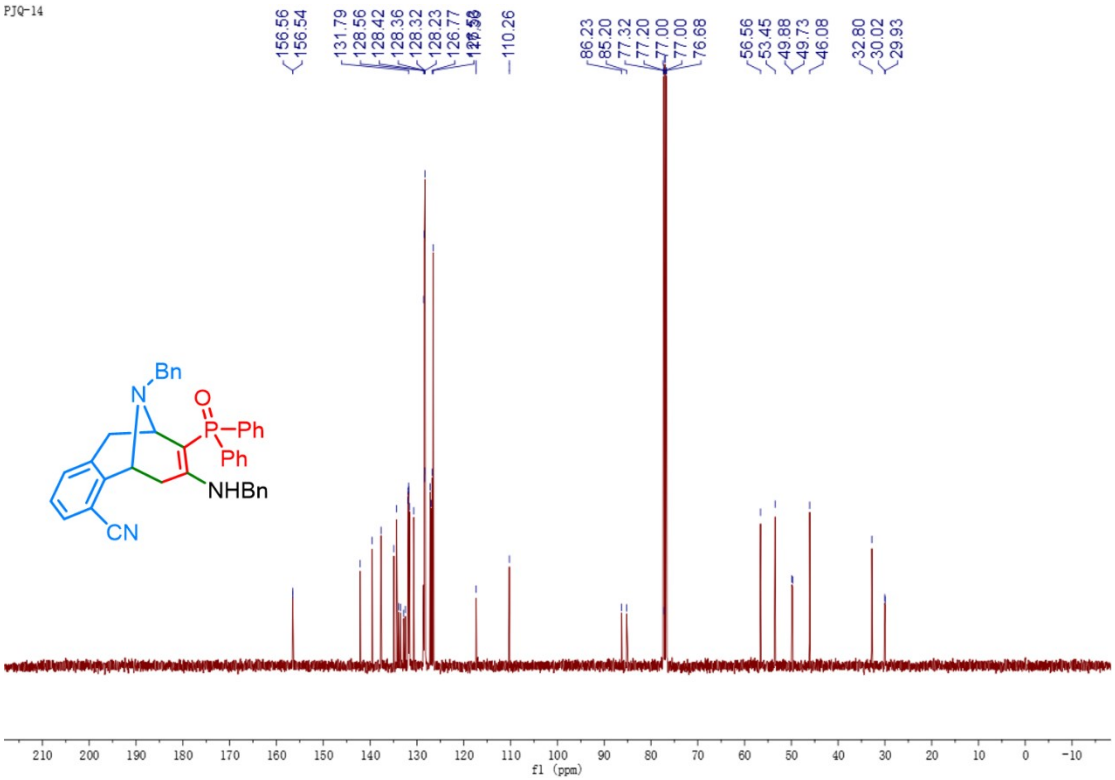
^{31}P NMR spectrum of **4p** (162 MHz, $CDCl_3$)



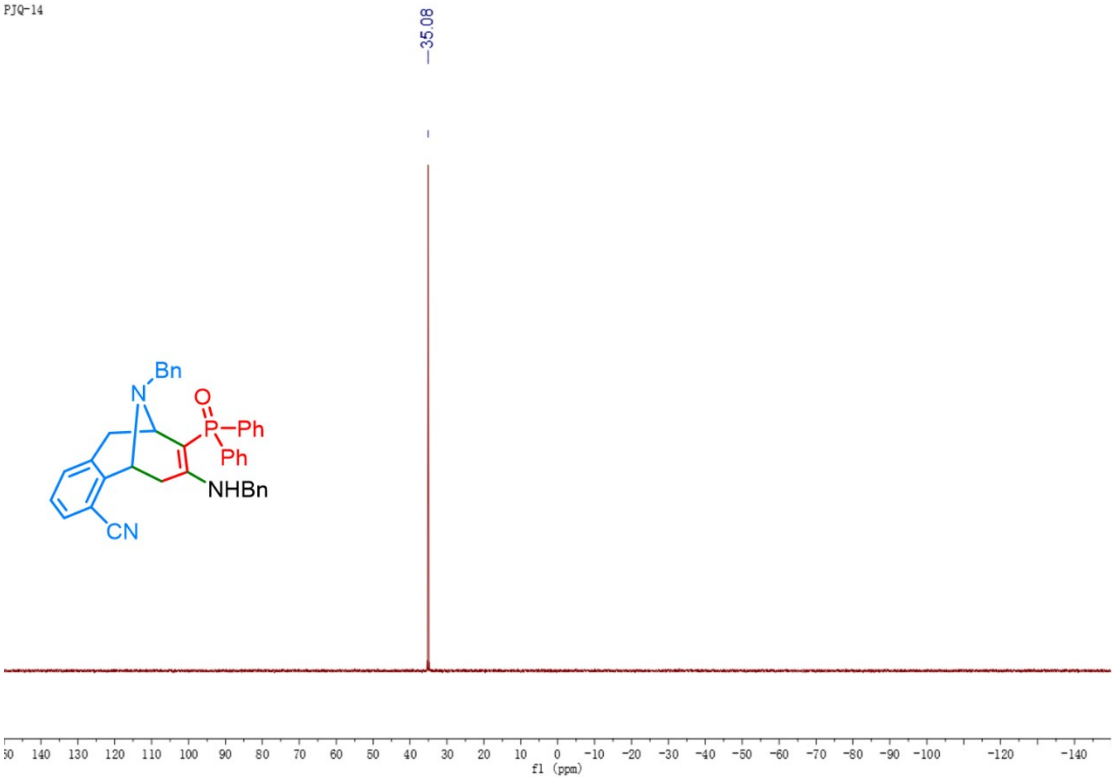
^{1}H NMR spectrum of **4q** (400 MHz, $CDCl_3$)



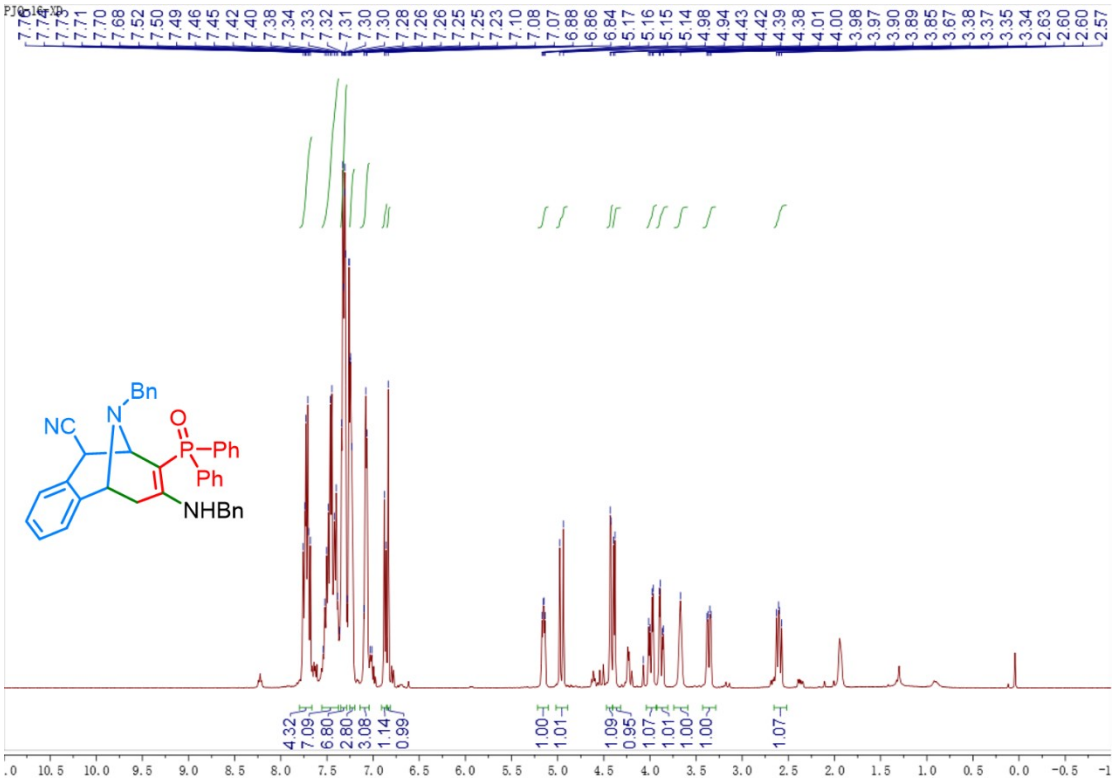
^{13}C NMR spectrum of **4q** (100 MHz, $CDCl_3$)



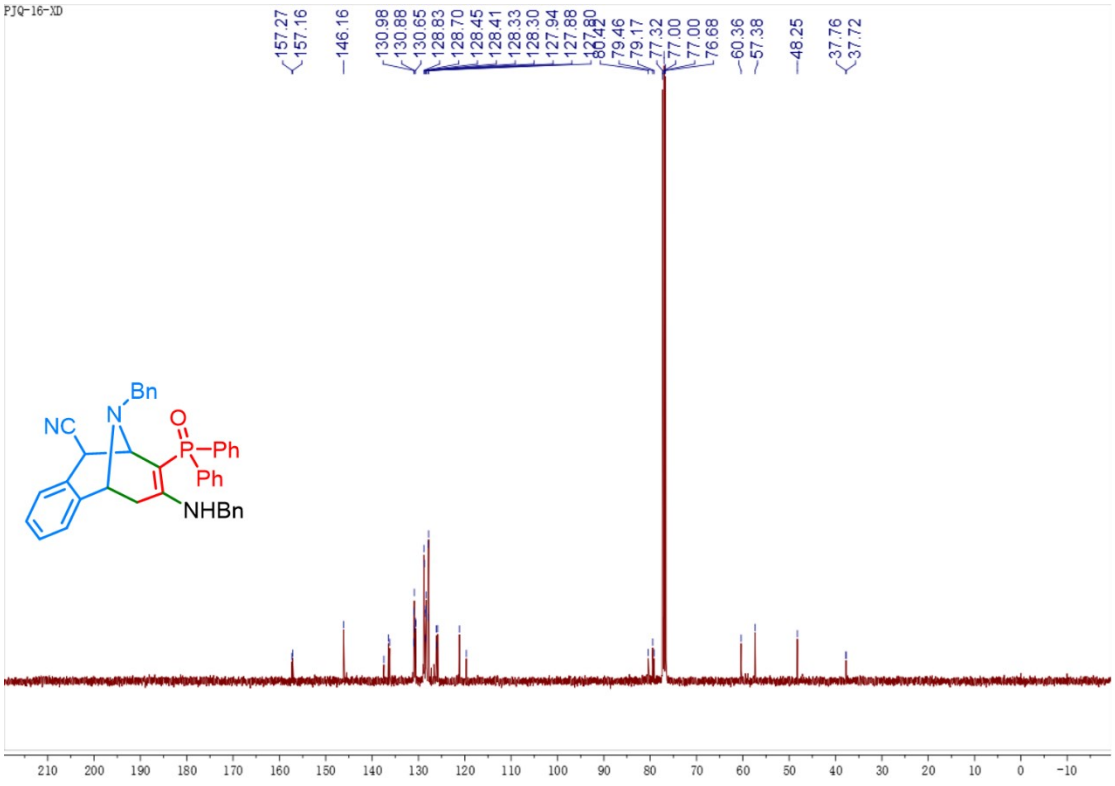
^{31}P NMR spectrum of **4q** (162 MHz, $CDCl_3$)



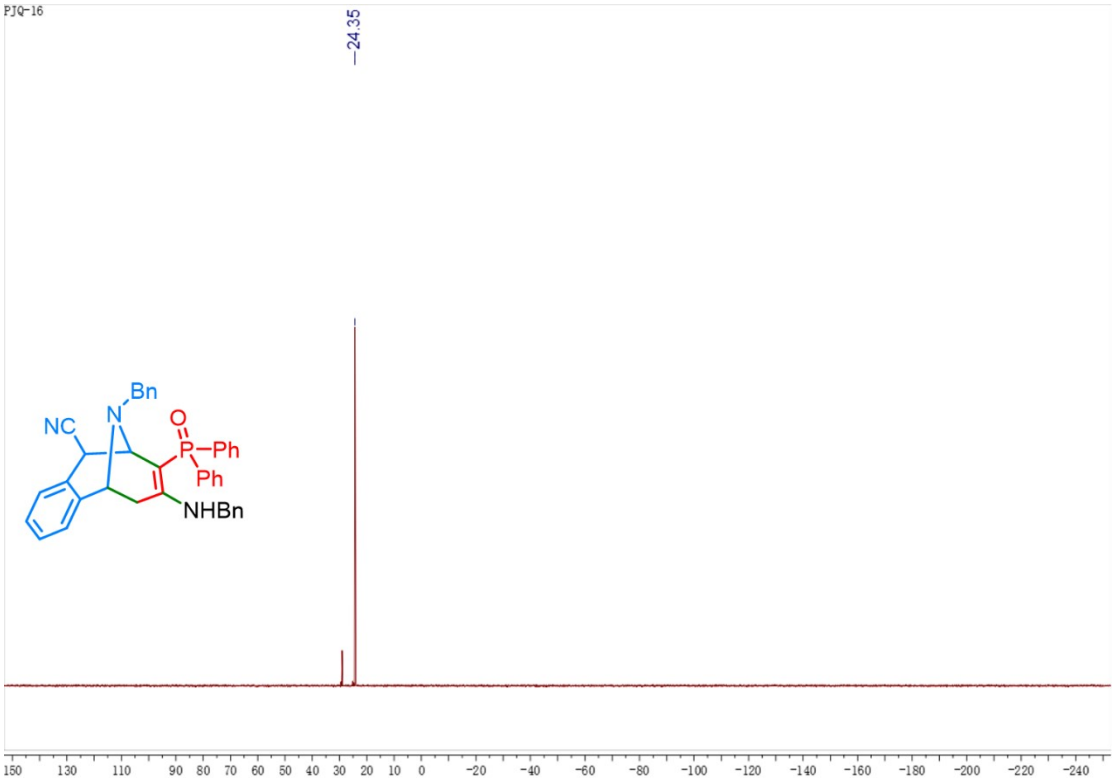
^{1}H NMR spectrum of **4r** (400 MHz, $CDCl_3$)



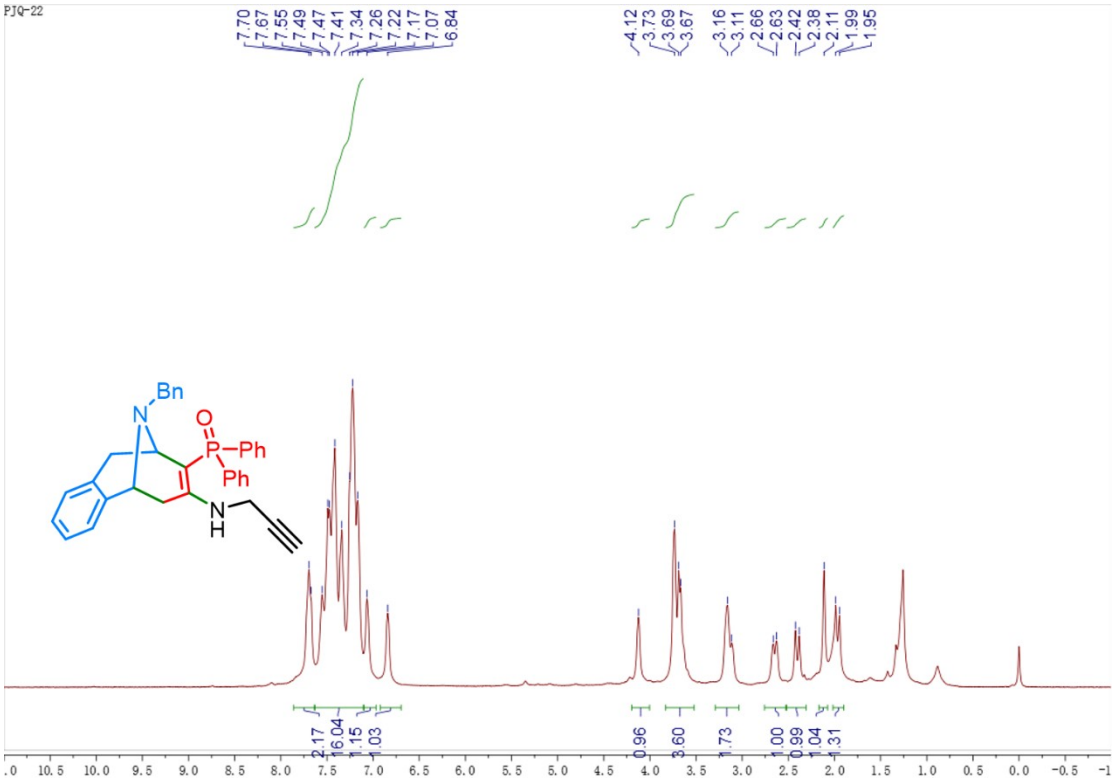
^{13}C NMR spectrum of **4r** (100 MHz, $CDCl_3$)



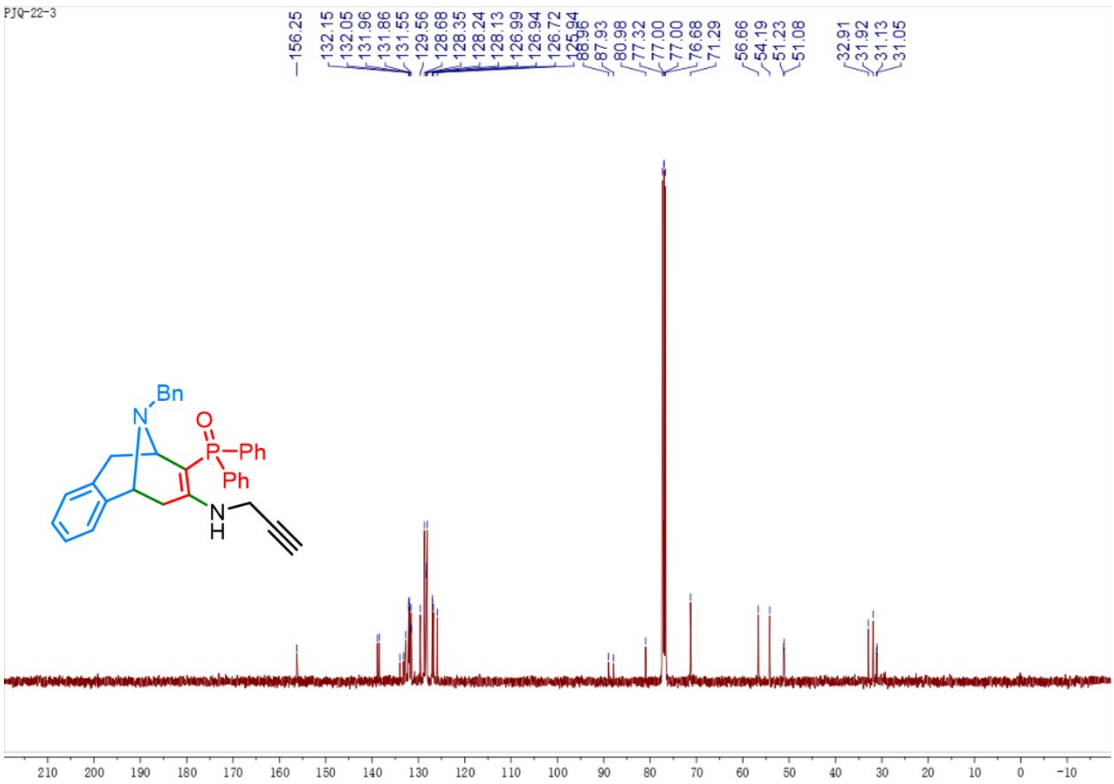
^{31}P NMR spectrum of **4r** (162 MHz, $CDCl_3$)



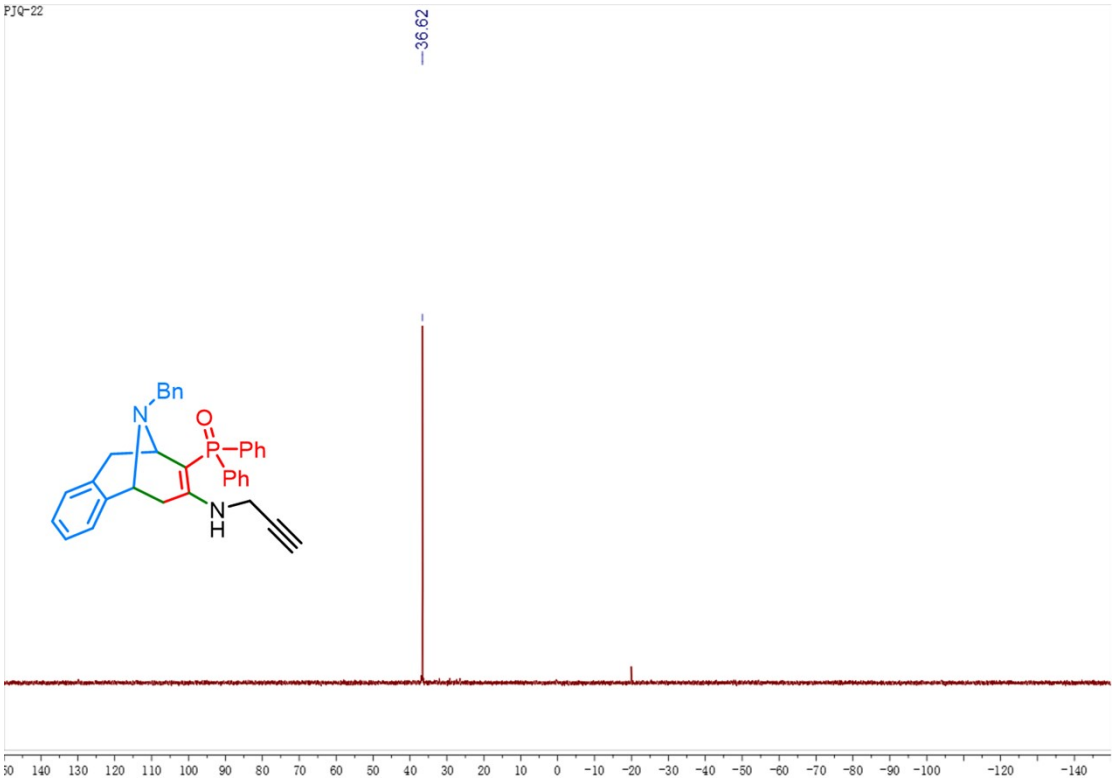
^{1}H NMR spectrum of **4s** (400 MHz, $CDCl_3$)



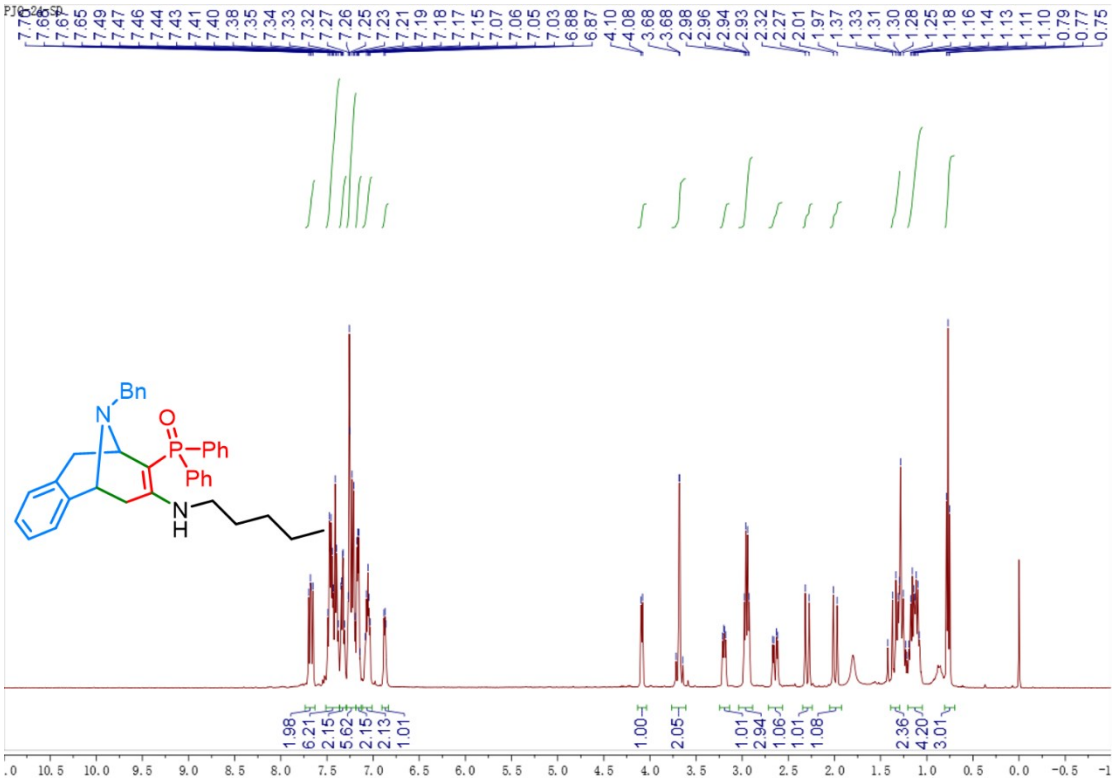
^{13}C NMR spectrum of **4s** (100 MHz, $CDCl_3$)



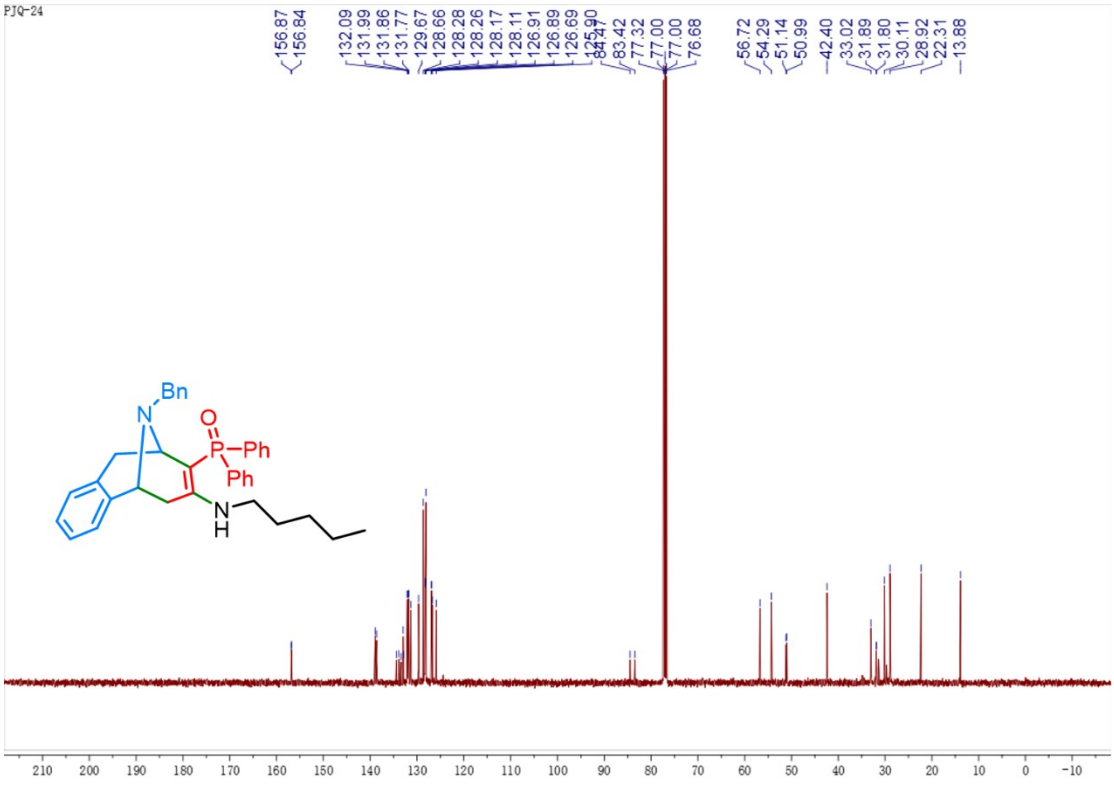
^{31}P NMR spectrum of **4s** (162 MHz, $CDCl_3$)



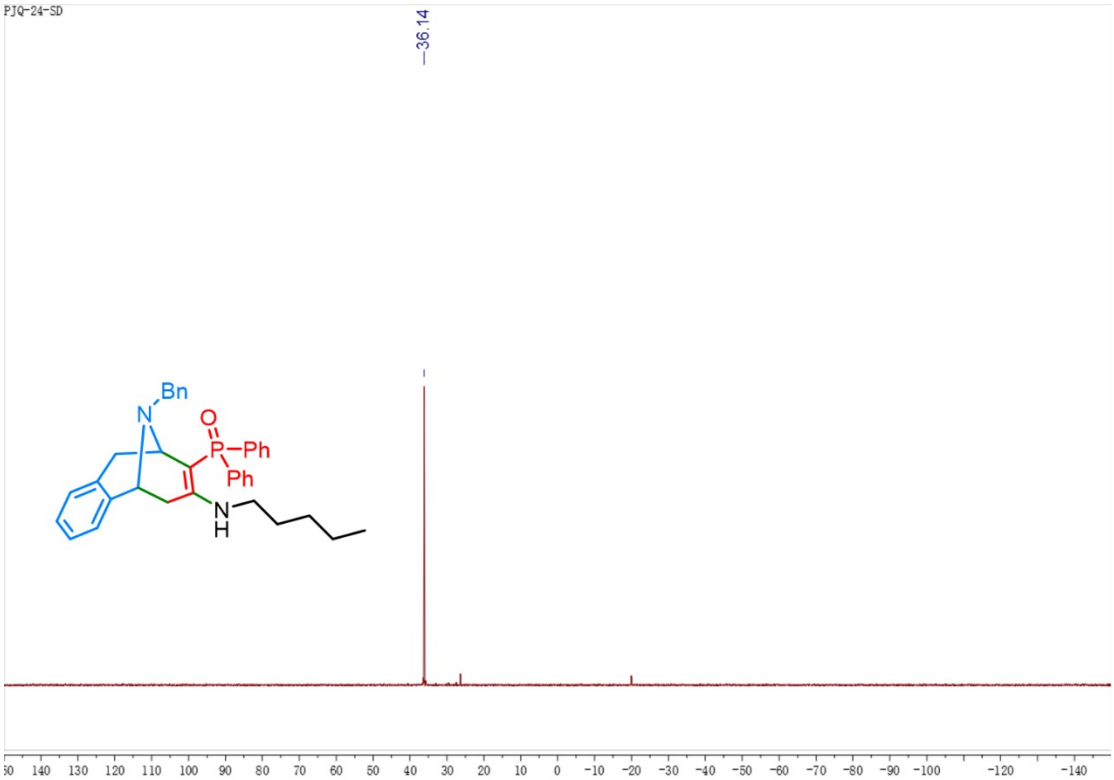
^{1}H NMR spectrum of **4t** (400 MHz, $CDCl_3$)



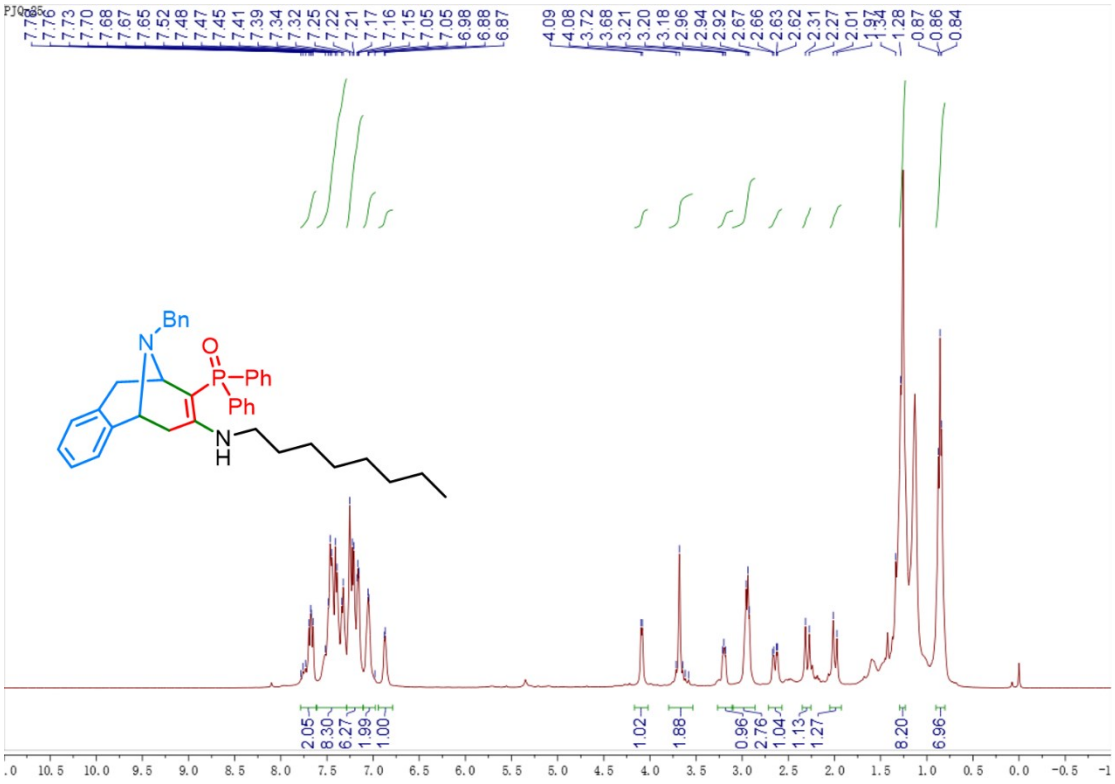
^{13}C NMR spectrum of **4t** (100 MHz, $CDCl_3$)



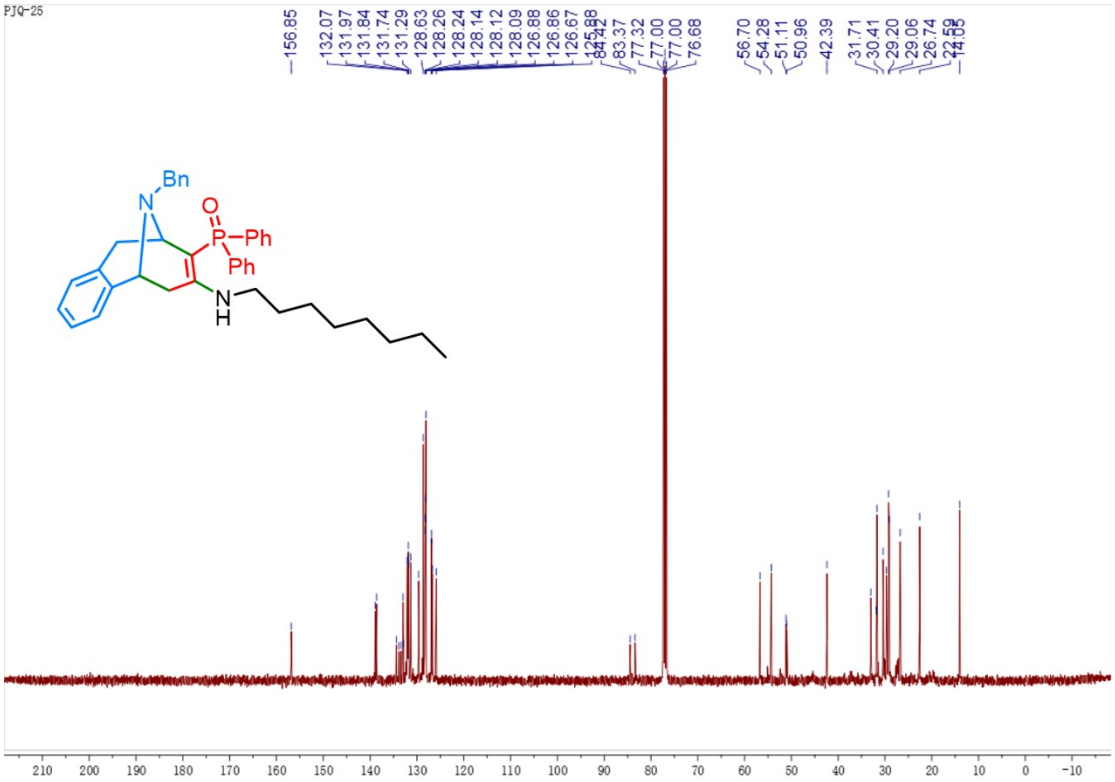
^{31}P NMR spectrum of **4t** (162 MHz, $CDCl_3$)



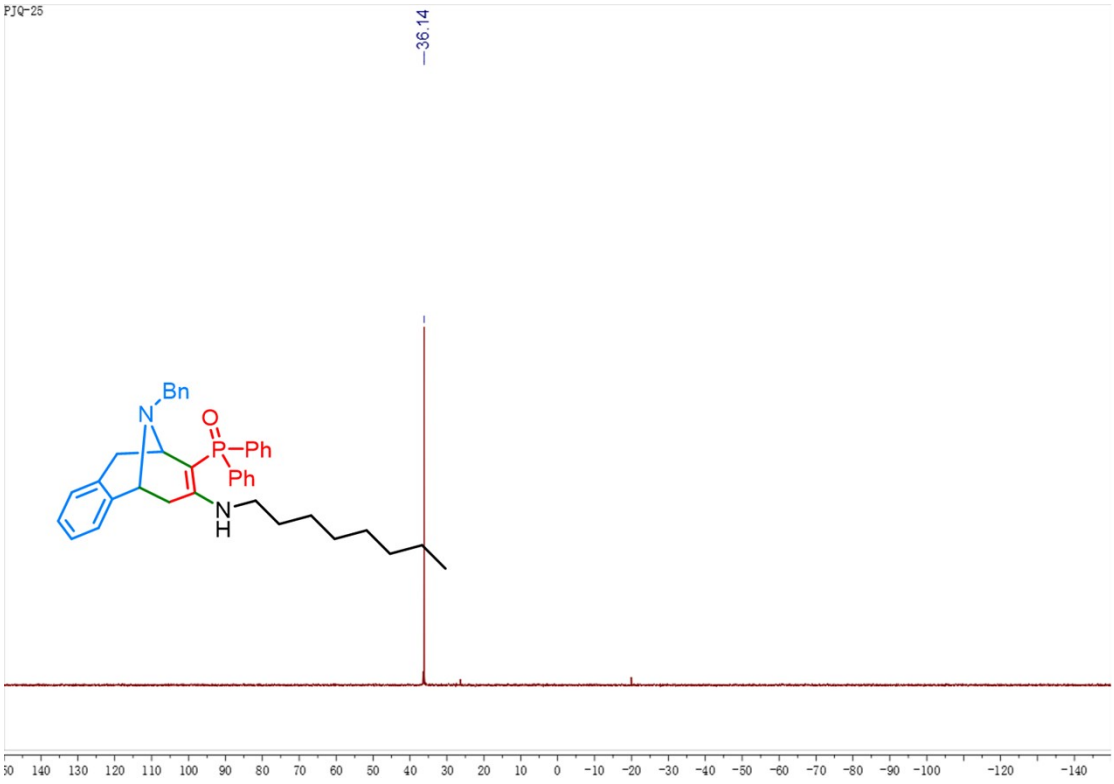
^{1}H NMR spectrum of **4u** (400 MHz, $CDCl_3$)



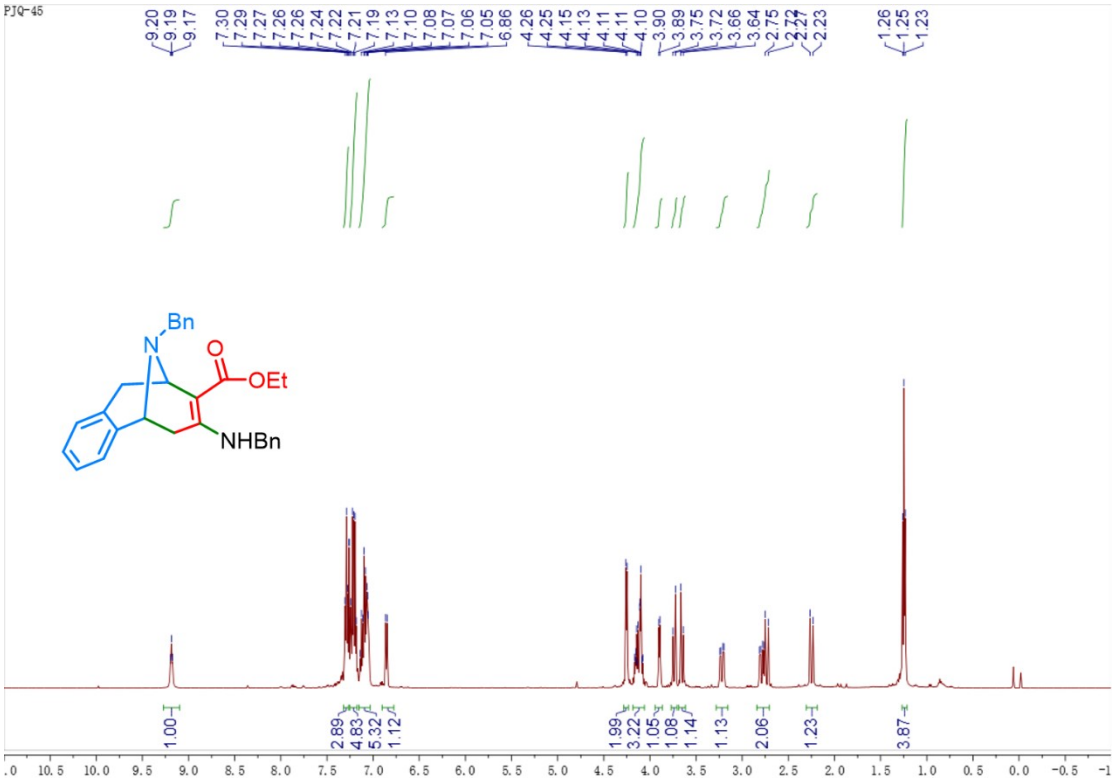
^{13}C NMR spectrum of **4u** (100 MHz, $CDCl_3$)



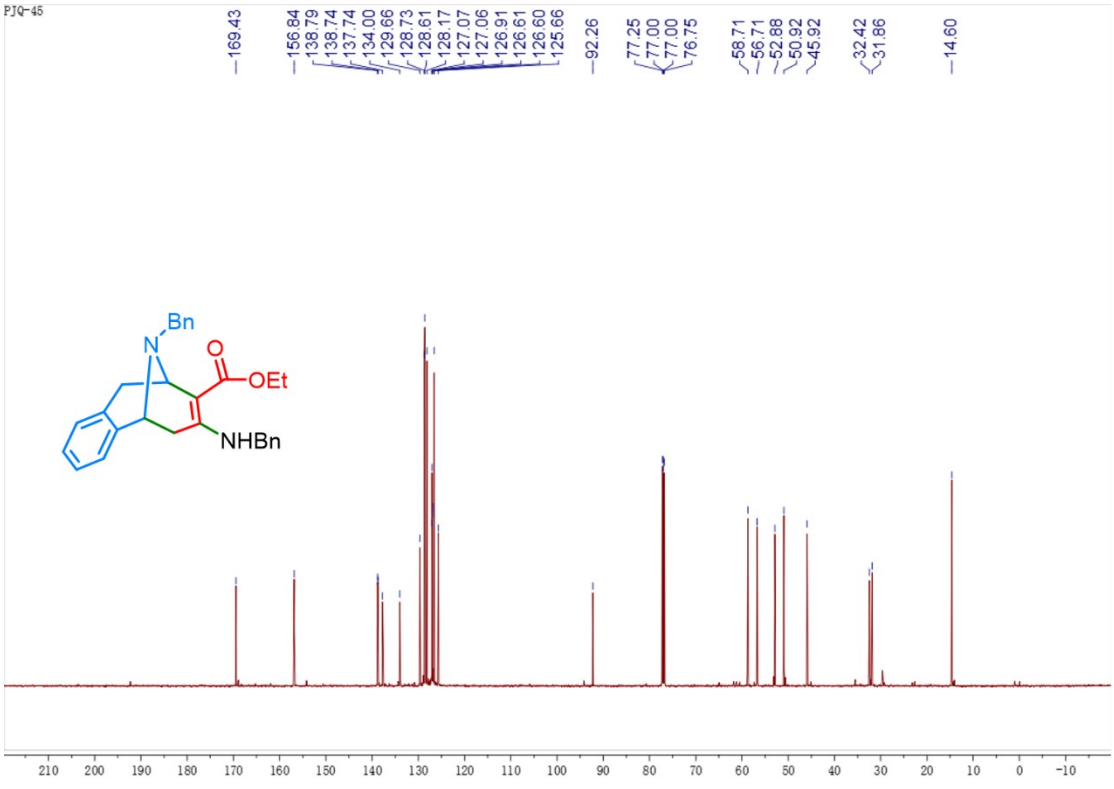
^{31}P NMR spectrum of **4u** (162 MHz, $CDCl_3$)



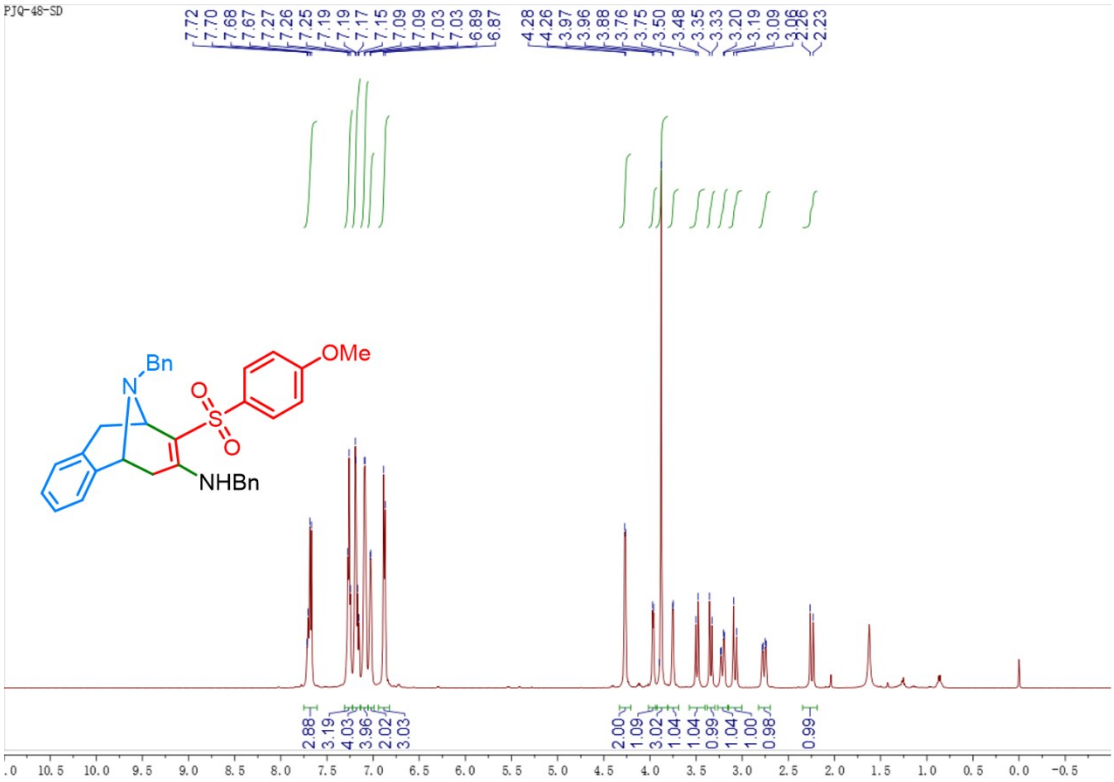
^{1}H NMR spectrum of **4v** (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of **4v** (125 MHz, $CDCl_3$)



^{1}H NMR spectrum of **4w** (500 MHz, $CDCl_3$)



^{13}C NMR spectrum of **4w** (125 MHz, $CDCl_3$)