Supporting Information

Palladium-Catalyzed Regioselective C−H Alkynylation of Indoles with Haloalkynes: Access to Functionalized 7-Alkynylindoles

Songjia Fang,‡ Guangbin Jiang,‡ Meng Li,‡ Zhenying Liu,‡ Huanfeng Jiang‡ and Wanqing Wu*,†,‡

† State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

‡ Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

E-mail: cewuwq@scut.edu.cn; Fax and Tel.: (+86) 20-87112906

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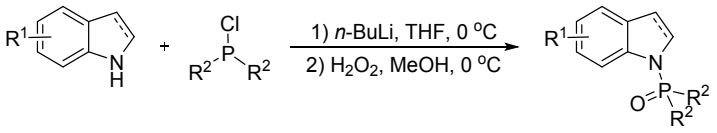
A. General Information

All purchased reagents and solvents were used without further purification unless otherwise noted. Analytical thin layer chromatography was performed by using commercially prepared 100-400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm. All the haloalkynes were prepared according to known procedures. ^1H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument.

B. General Procedure for the Synthesis of Starting Materials

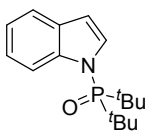
General Procedure for Synthesis of Starting Materials 1[1-3]



3 mmol 3.6 mmol 18~83%

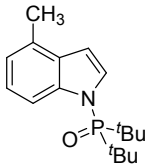
To a two-neck flask contained indole (3.0 mmol, 1.0 equiv) was added anhydrous THF (8 mL) under nitrogen. The reaction vessel was fitted with a rubber stopper and a three-way valve with nitrogen balloon, and was evacuated and back-filled with nitrogen. Subsequently, a solution of *n*-BuLi (solution in hexanes, 3.6 mmol, 1.2 equiv) was added dropwise. After stirring for 15 min, chloro-dialkyl phosphine (3.6 mmol, 1.2 equiv) was added dropwise. The mixture was allowed to stir and warm to room temperature until complete by TLC analysis. Then, 1.2 mL of MeOH was added and most of the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of MeOH (some DCM could be added to help dissolve) and cooled to 0 °C. Slow addition of excess H_2O_2 (0.6 mL of 30% solution, approx. 6 mmol) caused the completion of oxidation process. After adding 4.8 mL of Na_2SO_3 (2 M solution) dropwise, the solution was stirred for 2 h, allowed to warm to room temperature, treated with 7.2 mL of HCl (10% solution), and stirred for another hour. Most of MeOH was removed under reduced pressure, and the remaining residue was poured into 30 mL of H_2O and extracted with DCM (3 × 25 mL). The combined organics were dried over Na_2SO_4 and evaporated to give the crude product. Further purification was carried out by recrystallization or column chromatography (silica gel, petroleum ether /EtOAc /DCM).

Di-*tert*-butyl(1*H*-indol-1-yl)phosphine oxide (1a)[1]



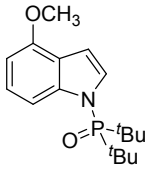
White solid (81%, 673.1 mg); Isolated by recrystallization; ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.24-7.15 (m, 3H), 6.68 (t, J = 2.2 Hz, 1H), 1.34 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 129.3 (d, J = 5.4 Hz), 126.4 (d, J = 5.0 Hz), 123.4, 121.5, 120.1, 116.2, 107.1 (d, J = 4.9 Hz), 38.6 (d, J = 68.8 Hz), 26.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.25-62.34 (m).

Di-*tert*-butyl(4-methyl-1*H*-indol-1-yl)phosphine oxide (1b)[2]



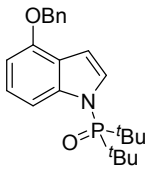
White solid (80%, 698.4 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 2.8 Hz, 1H), 7.15-7.11 (m, 1H), 6.97 (d, J = 7.8 Hz, 1H), 6.71 (s, 1H), 2.53 (s, 3H), 1.34 (d, J = 14.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 129.4, 129.0 (d, J = 5.4 Hz), 125.8 (d, J = 4.8 Hz), 123.5, 121.8, 113.8, 105.5 (d, J = 5.1 Hz), 38.6 (d, J = 68.9 Hz), 26.7, 18.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.00-62.09 (m).

Di-*tert*-butyl(4-methoxy-1*H*-indol-1-yl)phosphine oxide (1c)



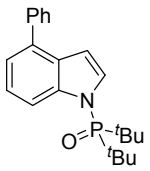
White solid (60%, 552.6 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 1H), 7.14 (t, J = 7.6 Hz, 2H), 6.81 (s, 1H), 6.59 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H), 1.32 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 142.8, 124.9 (d, J = 4.7 Hz), 124.0, 119.8 (d, J = 5.8 Hz), 109.4, 104.0 (d, J = 4.9 Hz), 101.3, 55.1, 38.5 (d, J = 68.8 Hz), 26.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.14-62.24 (m). HRMS (ESI) m/z: calcd for $C_{17}H_{27}NO_2P$ $[M+H]^+$, 308.1774; found 308.1775.

(4-(Benzyloxy)-1*H*-indol-1-yl)di-*tert*-butylphosphine oxide (1d)



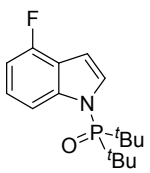
White solid (81%, 930.7 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.34-7.31 (m, 1H), 7.15-7.11 (m, 2H), 6.86 (s, 1H), 6.67 (d, J = 7.8 Hz, 1H), 5.19 (s, 2H), 1.34 (d, J = 14.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 143.0, 137.4, 128.4, 127.8, 127.4, 124.9 (d, J = 4.9 Hz), 124.1, 120.2 (d, J = 5.8 Hz), 109.7, 104.3 (d, J = 5.1 Hz), 102.8, 69.9, 38.5 (d, J = 68.8 Hz), 26.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.29-62.36 (m). HRMS (ESI) m/z: calcd for $C_{23}H_{31}NO_2P$ $[M+H]^+$, 384.2087; found 384.2093.

Di-*tert*-butyl(4-phenyl-1*H*-indol-1-yl)phosphine oxide (1e)



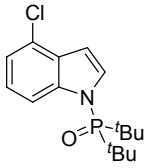
White solid (60%, 635.4 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 2H), 7.34-7.27 (m, 2H), 7.23 (s, 2H), 6.82 (s, 1H), 1.31 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.7, 133.8, 128.6, 128.2, 127.3 (d, J = 5.2 Hz), 126.7, 126.5 (d, J = 4.6 Hz), 123.4, 121.3, 115.1, 106.2 (d, J = 4.8 Hz), 38.4 (d, J = 68.7 Hz), 26.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.44-62.54 (m). HRMS (ESI) m/z: calcd for $C_{22}H_{29}NOP$ $[M+H]^+$, 354.1981; found 354.1987.

Di-*tert*-butyl(4-fluoro-1*H*-indol-1-yl)phosphine oxide (1f)[3]



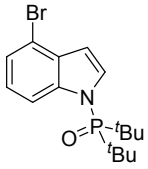
White solid (78%, 690.3 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 2.0 Hz, 1H), 7.14 (dd, J = 14.0, 7.6 Hz, 1H), 6.87-6.82 (m, 1H), 6.79 (s, 1H), 1.34 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7 (d, J = 245.1 Hz), 143.8 (d, J = 9.3 Hz), 126.2 (d, J = 4.7 Hz), 123.8 (d, J = 7.3 Hz), 118.4 (dd, J = 21.9, 5.7 Hz), 112.3 (d, J = 3.7 Hz), 106.3 (d, J = 18.0 Hz), 102.8 (d, J = 4.8 Hz), 38.6 (d, J = 68.4 Hz), 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.75 (dd, J = 9.7, 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.96-63.06 (m).

Di-*tert*-butyl(4-chloro-1*H*-indol-1-yl)phosphine oxide (1g)[2]



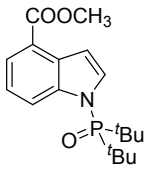
White solid (78%, 727.7 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.0 Hz, 1H), 7.27 (s, 1H), 7.19-7.12 (m, 2H), 6.81 (s, 1H), 1.33 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 128.1 (d, J = 5.3 Hz), 126.9 (d, J = 4.6 Hz), 125.3, 124.0, 121.3, 114.8, 105.4 (d, J = 4.7 Hz), 38.6 (d, J = 68.3 Hz), 26.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.22-63.31 (m).

(4-Bromo-1*H*-indol-1-yl)di-*tert*-butylphosphine oxide (1h)[3]



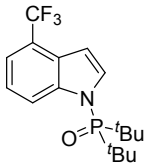
White solid (79%, 841.4 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 4.8 Hz, 1H), 7.09 (t, J = 8.0 Hz, 1H), 6.76 (s, 1H), 1.33 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 129.9 (d, J = 5.2 Hz), 126.9 (d, J = 4.5 Hz), 124.5, 124.4, 115.4, 113.8, 107.2 (d, J = 4.7 Hz), 38.6 (d, J = 68.1 Hz), 26.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.32-63.41 (m).

Methyl 1-(di-*tert*-butylphosphoryl)-1*H*-indole-4-carboxylate (1i)



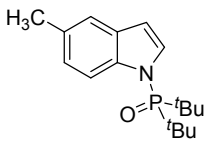
White solid (68%, 683.4 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.42 (s, 1H), 7.39 (s, 1H), 7.29 (d, J = 7.2 Hz, 1H), 3.97 (s, 3H), 1.34 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 142.2, 129.0 (d, J = 5.1 Hz), 128.2 (d, J = 4.4 Hz), 124.7, 122.7, 121.2, 121.1, 107.8 (d, J = 4.6 Hz), 51.7, 38.5 (d, J = 68.3 Hz), 26.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.29-63.37 (m). HRMS (ESI) m/z: calcd for $C_{18}H_{27}NO_3P$ $[M+H]^+$, 336.1723; found 336.1724.

Di-*tert*-butyl(4-(trifluoromethyl)-1*H*-indol-1-yl)phosphine oxide (1j)



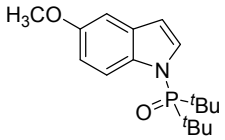
White solid (32%, 331.2 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.36 (s, 1H), 7.28 (s, 1H), 6.89 (s, 1H), 1.35 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 128.0 (d, J = 4.4 Hz), 125.6 (dd, J = 5.2, 2.0 Hz), 124.8 (q, J = 270.2 Hz), 122.6, 121.4 (q, J = 32.1 Hz), 119.9, 118.9 (q, J = 4.7 Hz), 105.5, 38.6 (d, J = 68.1 Hz), 26.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.18 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.75-63.83 (m). HRMS (ESI) m/z: calcd for $C_{17}H_{24}F_3NOP$ $[M+H]^+$, 346.1542; found 346.1545.

Di-*tert*-butyl(5-methyl-1*H*-indol-1-yl)phosphine oxide (1k)[2]



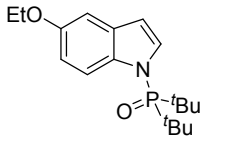
White solid (72%, 628.6 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.8 Hz, 1H), 7.36 (s, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.05 (d, J = 8.8 Hz, 1H), 6.60 (s, 1H), 2.42 (s, 3H), 1.33 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 130.8, 129.4 (d, J = 5.5 Hz), 126.3 (d, J = 4.8 Hz), 124.9, 119.8, 115.8, 106.7 (d, J = 5.0 Hz), 38.5 (d, J = 69.0 Hz), 26.6, 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.90-62.00 (m).

Di-*tert*-butyl(5-methoxy-1*H*-indol-1-yl)phosphine oxide (1l)[2]



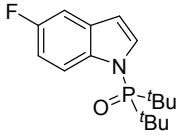
White solid (56%, 515.7 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 9.2 Hz, 1H), 7.21 (d, J = 3.2 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 6.87 (dd, J = 9.2, 2.4 Hz, 1H), 6.62-6.60 (m, 1H), 3.83 (s, 3H), 1.33 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 136.5, 129.8 (d, J = 5.5 Hz), 126.9 (d, J = 4.7 Hz), 116.9, 112.9, 106.9 (d, J = 4.9 Hz), 102.1, 55.6, 38.5 (d, J = 69.0 Hz), 26.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.00-62.10 (m).

Di-*tert*-butyl(5-ethoxy-1*H*-indol-1-yl)phosphine oxide (1m)



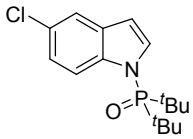
White solid (79%, 760.8 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 9.2 Hz, 1H), 7.19 (s, 1H), 7.01 (s, 1H), 6.86 (d, J = 9.2 Hz, 1H), 6.59 (s, 1H), 4.04 (q, J = 6.8 Hz, 2H), 1.41 (t, J = 6.8 Hz, 3H), 1.31 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 136.2, 129.7 (d, J = 5.6 Hz), 126.7 (d, J = 4.7 Hz), 116.7, 113.3, 106.8 (d, J = 5.0 Hz), 102.8, 63.6, 38.3 (d, J = 69.0 Hz), 26.4, 14.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.05-62.15 (m). HRMS (ESI) m/z: calcd for $C_{18}H_{29}NO_2P$ $[M+H]^+$, 322.1930; found 322.1935.

Di-*tert*-butyl(5-fluoro-1*H*-indol-1-yl)phosphine oxide (1n)[2]



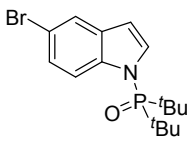
White solid (83%, 734.5 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, J = 9.2, 4.8 Hz, 1H), 7.27 (s, 1H), 7.20 (dd, J = 8.9, 1.8 Hz, 1H), 6.96 (td, J = 9.2, 2.4 Hz, 1H), 6.64 (s, 1H), 1.33 (d, J = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7 (d, J = 235.6 Hz), 137.9, 129.8 (dd, J = 10.0, 5.5 Hz), 127.9 (d, J = 4.4 Hz), 117.1 (d, J = 9.0 Hz), 111.5 (d, J = 24.8 Hz), 107.0 (t, J = 4.6 Hz), 105.0 (d, J = 23.4 Hz), 38.6 (d, J = 68.7 Hz), 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.85 (td, J = 9.1, 4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.73-62.82 (m).

Di-*tert*-butyl(5-chloro-1*H*-indol-1-yl)phosphine oxide (1o)



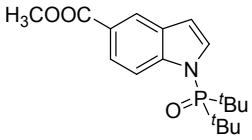
White solid (70%, 653.1 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.8 Hz, 1H), 7.54 (s, 1H), 7.26 (d, J = 4.4 Hz, 1H), 7.17 (d, J = 9.2 Hz, 1H), 6.63 (s, 1H), 1.33 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 130.4 (d, J = 4.9 Hz), 127.6 (d, J = 4.4 Hz), 127.2, 123.7, 119.6, 117.3, 106.6 (d, J = 4.9 Hz), 38.6 (d, J = 68.5 Hz), 26.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.08-63.17 (m). HRMS (ESI) m/z: calcd for $C_{16}H_{24}ClNOP$ $[M+H]^+$, 312.1279; found 312.1279.

(5-Bromo-1*H*-indol-1-yl)di-*tert*-butylphosphine oxide (1p)



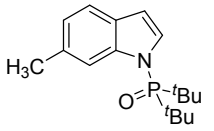
White solid (63%, 670.9 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.8 Hz, 1H), 7.70 (s, 1H), 7.30 (d, J = 9.2 Hz, 1H), 7.24 (s, 1H), 6.62 (s, 1H), 1.32 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 130.9 (d, J = 5.6 Hz), 127.4 (d, J = 4.5 Hz), 126.2, 122.7, 117.7, 114.9, 106.4 (d, J = 4.4 Hz), 38.5 (d, J = 68.4 Hz), 26.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.18-63.26 (m). HRMS (ESI) m/z: calcd for $C_{16}H_{24}BrNOP$ $[M+H]^+$, 356.0773; found 356.0771.

Methyl 1-(di-*tert*-utylphosphoryl)-1*H*-indole-5-carboxylate (1q)[2]



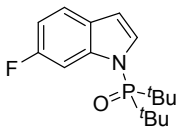
White solid (67%, 673.4 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 9.2 Hz, 1H), 8.33 (s, 1H), 7.92 (d, J = 9.2 Hz, 1H), 7.30 (s, 1H), 6.77 (s, 1H), 3.92 (s, 3H), 1.34 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 144.3, 128.9 (d, J = 5.4 Hz), 127.6 (d, J = 4.6 Hz), 124.5, 123.5, 122.8, 115.8, 107.9 (d, J = 4.5 Hz), 51.8, 38.5 (d, J = 68.1 Hz), 26.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.47-63.56 (m).

Di-*tert*-butyl(6-methyl-1*H*-indol-1-yl)phosphine oxide (1r)



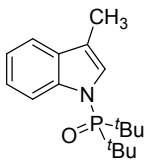
White solid (57%, 497.7 mg); Isolation by recrystallization; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 3.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.62 (t, J = 3.0 Hz, 1H), 2.45 (s, 3H), 1.33 (d, J = 15.0 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 133.2, 126.9 (d, J = 5.5 Hz), 125.7 (d, J = 4.8 Hz), 123.2, 119.6, 116.1, 106.9 (d, J = 5.1 Hz), 38.5 (d, J = 68.7 Hz), 26.9, 26.7, 21.9; ^{31}P NMR (202 MHz, $CDCl_3$) δ 62.93-62.21 (m). HRMS (ESI) m/z: calcd for $C_{17}H_{27}NOP$ $[M+H]^+$, 292.1825; found 292.1830.

Di-*tert*-butyl(6-fluoro-1*H*-indol-1-yl)phosphine oxide (1s)



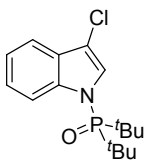
White solid (60%, 531.1 mg); Isolation by recrystallization; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (dd, J = 11.5, 2.5 Hz, 1H), 7.47 (dd, J = 8.5, 5.5 Hz, 1H), 7.24-7.18 (m, 1H), 6.93 (td, J = 9.0, 2.5 Hz, 1H), 6.65 (t, J = 2.5 Hz, 1H), 1.34 (d, J = 14.5 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2 (d, J = 237.0 Hz), 141.6 (d, J = 13.1 Hz), 126.7 (t, J = 4.1 Hz), 125.5 (d, J = 5.4 Hz), 120.5 (d, J = 10.0 Hz), 110.2 (d, J = 24.6 Hz), 107.0 (d, J = 4.8 Hz), 102.9 (d, J = 28.4 Hz), 38.6 (d, J = 68.5 Hz), 26.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.05 – -122.58 (m); ^{31}P NMR (202 MHz, $CDCl_3$) δ 63.90-63.17 (m). HRMS (ESI) m/z: calcd for $C_{16}H_{24}FNOP$ $[M+H]^+$, 296.1574; found 296.1580.

Di-*tert*-butyl(3-methyl-1*H*-indol-1-yl)phosphine oxide (1t)[2]



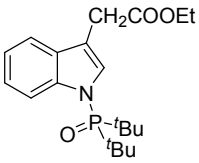
White solid (46%, 401.5 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.23-7.15 (m, 2H), 6.98 (s, 1H), 2.32 (s, 3H), 1.32 (d, J = 14.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 129.8 (d, J = 5.4 Hz), 123.3 (d, J = 4.5 Hz), 120.9, 118.1, 116.2, 115.9 (d, J = 4.9 Hz), 38.40 (d, J = 69.3 Hz), 26.6, 9.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.40-61.50 (m).

Di-*tert*-butyl(3-chloro-1*H*-indol-1-yl)phosphine oxide (1u)[3]



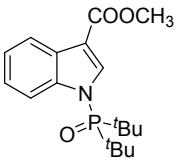
White solid (66%, 615.7 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.31-7.24 (m, 2H), 7.21 (s, 1H), 1.34 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 126.7 (d, J = 4.5 Hz), 124.6, 122.4 (d, J = 4.7 Hz), 122.1, 117.8, 116.5, 111.4 (d, J = 5.3 Hz), 38.6 (d, J = 68.0 Hz), 26.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.70-63.79 (m).

Ethyl 2-(1-(di-*tert*-utylphosphoryl)-1*H*-indol-3-yl)acetate (1v)



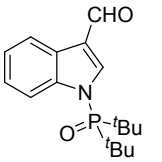
White solid (77%, 838.5 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.32 (s, 1H), 7.24-7.16 (m, 2H), 4.17 (q, J = 7.2 Hz, 2H), 3.76 (s, 2H), 1.33 (d, J = 14.8 Hz, 18H), 1.24 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 141.5, 128.6 (d, J = 5.1 Hz), 124.8 (d, J = 5.0 Hz), 123.4, 121.2, 117.9, 116.1, 112.6 (d, J = 5.1 Hz), 60.6, 38.3 (d, J = 68.7 Hz), 30.7, 26.4, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.49-62.58 (m). HRMS (ESI) m/z: calcd for $C_{20}H_{30}NNaO_3P$ $[M+H]^+$, 386.1856; found 386.1857.

Methyl 1-(di-*tert*-utylphosphoryl)-1*H*-indole-3-carboxylate (1w)[3]



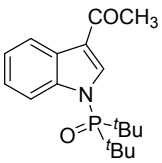
White solid (62%, 623.1 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 7.2 Hz, 1H), 8.16 (d, J = 6.8 Hz, 1H), 7.94 (s, 1H), 7.33-7.27 (m, 2H), 3.95 (s, 1H), 1.36 (d, J = 15.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 142.1, 132.5 (d, J = 4.7 Hz), 126.4 (d, J = 4.3 Hz), 124.4, 123.1, 120.8, 116.4, 112.5 (d, J = 4.6 Hz), 51.3, 38.6 (d, J = 66.9 Hz), 26.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 66.13-65.21 (m).

1-(Di-*tert*-butylphosphoryl)-1*H*-indole-3-carbaldehyde (1x)



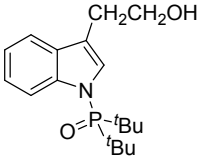
White solid (49%, 448.3 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.56-8.54 (m, 1H), 8.27-8.26 (m, 1H), 7.85 (s, 1H), 7.35-7.28 (m, 2H), 1.39 (d, J = 15.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 142.7, 136.5 (d, J = 4.1 Hz), 125.5, 125.2 (d, J = 4.2 Hz), 123.9, 122.2 (d, J = 4.1 Hz), 121.0, 116.6, 38.8 (d, J = 66.5 Hz), 26.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 66.41-65.67 (m). HRMS (ESI) m/z: calcd for $C_{17}H_{25}NO_2P$ $[M+H]^+$, 306.1617; found 306.1623.

1-(1-(Di-*tert*-butylphosphoryl)-1*H*-indol-3-yl)ethan-1-one (1y)



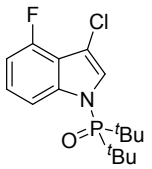
White solid (56%, 535.9 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 6.8 Hz, 1H), 8.30 (d, J = 6.8 Hz, 1H), 7.87 (s, 1H), 7.32-7.30 (m, 2H), 2.59 (s, 3H), 1.39 (d, J = 15.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 142.3, 132.6 (d, J = 4.3 Hz), 126.0 (d, J = 4.1 Hz), 124.7, 123.6, 121.5, 121.3 (d, J = 3.6 Hz), 116.3, 38.7 (d, J = 66.8 Hz), 28.0, 26.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 65.89-64.96 (m). HRMS (ESI) m/z: calcd for $C_{18}H_{27}NO_2P$ $[M+H]^+$, 320.1774; found 320.1771.

Di-*tert*-butyl(3-(2-hydroxyethyl)-1*H*-indol-1-yl)phosphine oxide (1z)



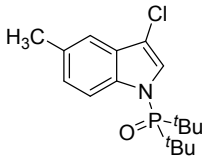
White solid (30%, 288.9 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.22-7.14 (m, 2H), 7.12 (s, 1H), 3.93 (t, J = 5.6 Hz, 2H), 3.02 (t, J = 6.0 Hz, 2H), 2.79 (s, 1H), 1.32 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 129.0 (d, J = 4.9 Hz), 124.2 (d, J = 4.7 Hz), 123.5, 121.2, 118.2, 117.1 (d, J = 4.9 Hz), 116.2, 62.1, 38.5 (d, J = 68.8 Hz), 28.5, 26.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.42-62.51 (m). HRMS (ESI) m/z: calcd for $C_{18}H_{29}NO_2P$ $[M+H]^+$, 322.1930; found 322.1933.

Di-*tert*-butyl(3-chloro-4-fluoro-1*H*-indol-1-yl)phosphine oxide (1aa)



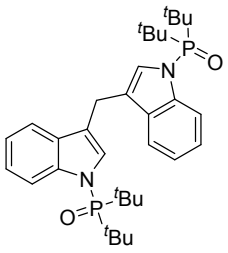
White solid (75%, 740.2 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.4 Hz, 1H), 7.20-7.15 (m, 2H), 6.87 (d, J = 9.2 Hz, 1H), 1.35 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5 (d, J = 238.1 Hz), 143.0 (d, J = 7.6 Hz), 125.0 (d, J = 7.5 Hz), 123.0 (d, J = 4.2 Hz), 115.6 (dd, J = 17.5, 4.7 Hz), 112.6 (d, J = 4.1 Hz), 108.5 (d, J = 4.2 Hz), 107.5 (d, J = 17.8 Hz), 38.7 (d, J = 67.5 Hz), 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.51 (dd, J = 10.6, 5.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 65.48-64.55 (m). HRMS (ESI) m/z: calcd for $C_{16}H_{23}ClFNOP$ $[M+H]^+$, 330.1184; found 330.1178.

Di-*tert*-butyl(3-chloro-5-methyl-1*H*-indol-1-yl)phosphine oxide (1ab)



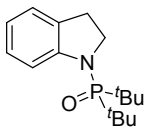
White solid (68%, 663.3 mg); Isolation by recrystallization; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.8 Hz, 1H), 7.36 (s, 1H), 7.17 (s, 1H), 7.11 (d, J = 8.8 Hz, 1H), 2.45 (s, 3H), 1.33 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 131.6, 126.7 (d, J = 4.4 Hz), 126.2, 122.4 (d, J = 4.6 Hz), 117.3, 116.1, 110.9 (d, J = 5.3 Hz), 38.5 (d, J = 68.1 Hz), 26.5, 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.26-63.35 (m). HRMS (ESI) m/z: calcd for $C_{17}H_{26}ClNOP$ $[M+H]^+$, 326.1435; found 326.1445.

Di-*tert*-butyl(indolin-1-yl)phosphine oxide (1ac)[3]



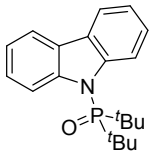
n-BuLi (7.2 mmol, 2.4 equiv), di-*tert*-butylchlorophosphane (3.6 mmol, 1.2 equiv) and H_2O_2 (1.2 mL of 30% solution, approx. 12 mmol). White solid (26%, 441.5 mg); Isolation by column chromatography (petroleum ether/EtOAc/DCM: 10/1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.86 (s, 1H), 4.22 (s, 1H), 1.23 (d, J = 14.8 Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 128.7 (d, J = 5.2 Hz), 124.1 (d, J = 4.4 Hz), 123.6, 121.1, 118.9 (d, J = 4.8 Hz), 118.5, 116.2, 38.3 (d, J = 69.4 Hz), 26.5, 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.80-61.90 (m). HRMS (ESI) m/z: calcd for $C_{33}H_{49}N_2O_2P_2$ $[M+H]^+$, 567.3264; found 567.3272.

Di-*tert*-butyl(indolin-1-yl)phosphine oxide (1ad)



White solid (50%, 418.5 mg); Isolation by column chromatography (petroleum ether/EtOAc/DCM: 10/1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H), 6.79 (t, J = 7.4 Hz, 1H), 3.86 (td, J = 8.4, 1.6 Hz, 2H), 3.07 (t, J = 8.2 Hz, 2H), 1.35 (d, J = 14.0 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 129.5 (d, J = 6.7 Hz), 127.5, 123.8, 120.3, 115.1, 50.1, 38.6 (d, J = 72.0 Hz), 30.3, 27.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.16-58.64 (m). HRMS (ESI) m/z: calcd for $C_{16}H_{27}NOP$ $[M+H]^+$, 280.1825; found 280.1832.

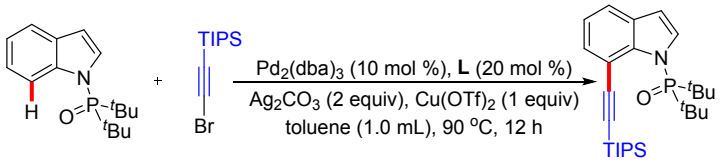
Di-*tert*-butyl(9*H*-carbazol-9-yl)phosphine oxide (1ae)



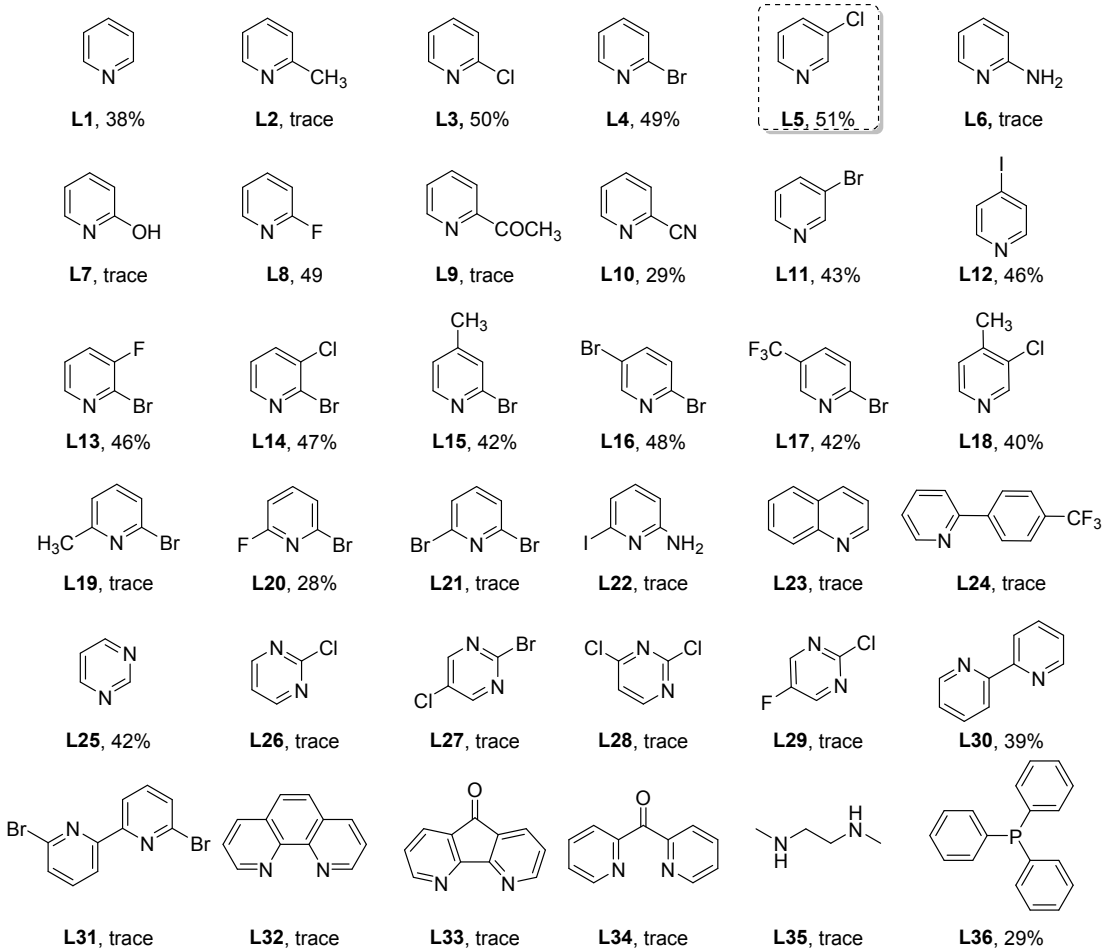
White solid (18%, 176.6 mg); Isolation by column chromatography (petroleum ether/EtOAc/DCM: 10/1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.38 (q, J = 7.2 Hz, 2H), 7.27 (t, J = 7.2 Hz, 2H), 1.42 (d, J = 15.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 140.2 (d, J = 3.3 Hz), 126.7 (d, J = 4.6 Hz), 126.5, 125.5 (d, J = 4.1 Hz), 124.9, 121.5, 121.2, 119.9, 118.8, 118.0, 114.8, 40.5 (d, J = 65.8 Hz), 27.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 69.66-68.73 (m). HRMS (ESI) m/z: calcd for $C_{20}H_{27}NOP$ $[M+H]^+$, 328.1825; found 328.1826.

C. Optimization of Reaction Conditions

(a) Screening of ligand[a]



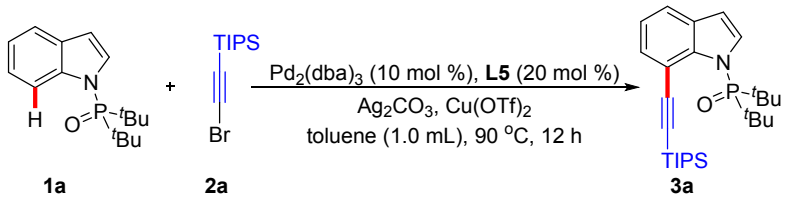
1a **2a** **3a**



[a] Conditions: unless otherwise noted, all reactions were performed with **1** (0.1 mmol), **2a** (2 equiv), $Pd_2(dba)_3$ (10 mol %), **L** (20 mol %), Ag_2CO_3 (2.0 equiv) and $Cu(OTf)_2$ (1.0 equiv) in toluene (1.5

mL) under air at 90 °C for 12 h.

(b) Optimization of additive amounts [a]

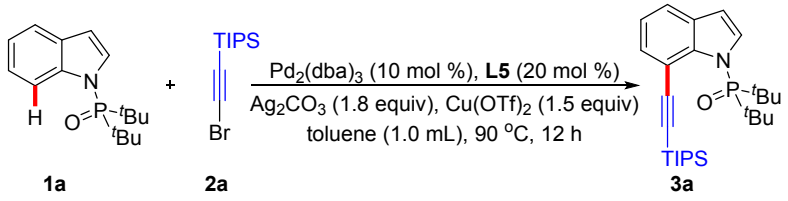


1a **2a** **3a**

entry	catalyst	Ag_2CO_3 (equiv)	$Cu(OTf)_2$ (equiv)	yield of **3a** (%)[b]
1	$Pd_2(dba)_3$	1.9	1.1	58
2	$Pd_2(dba)_3$	1.8	1.2	57
3	$Pd_2(dba)_3$	1.7	1.3	60
4	$Pd_2(dba)_3$	1.6	1.4	60
5	$Pd_2(dba)_3$	1.5	1.5	49
6	$Pd_2(dba)_3$	1.4	1.6	53
7	$Pd_2(dba)_3$	1.7	1.4	60
8	$Pd_2(dba)_3$	1.8	1.4	70
9	$Pd_2(dba)_3$	1.9	1.4	57
10	$Pd_2(dba)_3$	1.8	1.3	72
11	$Pd_2(dba)_3$	1.8	1.1	59
12	**$Pd_2(dba)_3$**	**1.8**	**1.5**	**74**
13	$Pd_2(dba)_3$	1.8	1.6	61

[a] Conditions: unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (2 equiv), $Pd_2(dba)_3$ (10 mol %), **L5** (20 mol %), Ag_2CO_3, $Cu(OTf)_2$ in solvent (1.0 mL) under air at 90 °C for 12 h. [b] Monitored by NMR using CH_2Br_2 as the internal standard.

(c) Optimization of substrate amounts[a]



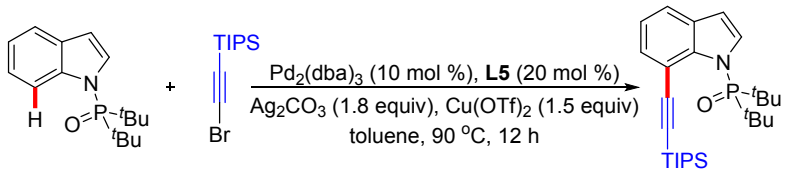
1a **2a** **3a**

entry	catalyst	additives	**2a** (equiv)	yield of **3a** (%)[b]
1	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	2.2	71

2	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	2.0	74
3	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	1.8	80
4	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	1.6	77
5	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	1.4	75

[a] Conditions: unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a**, $Pd_2(dba)_3$ (10 mol %), **L5** (20 mol %), Ag_2CO_3 (1.8 equiv), $Cu(OTf)_2$ (1.5 equiv) in solvent (1.0 mL) under air at 90 °C for 12 h. [b] Monitored by NMR using CH_2Br_2 as the internal standard.

(d) Optimization by varying toluene amounts[a]

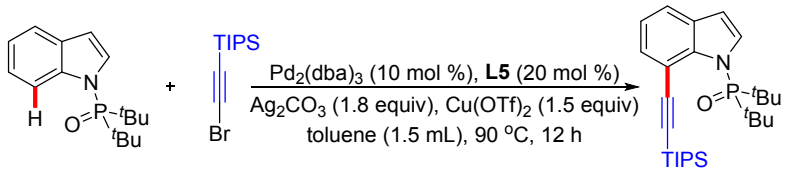


1a **2a** **3a**

entry	catalyst	additives	toluene (mL)	yield of **3a** (%)[b]
1	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	0.5	68
2	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	1.0	80
3	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	1.5	83
4	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	2.0	84
5	$Pd_2(dba)_3$	Ag_2CO_3/$Cu(OTf)_2$	2.5	80

[a] Conditions: unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (1.8 equiv), $Pd_2(dba)_3$ (10 mol %), **L5** (20 mol %), Ag_2CO_3 (1.8 equiv), $Cu(OTf)_2$ (1.5 equiv) in toluene under air at 90 °C for 12 h. [b] Monitored by NMR using CH_2Br_2 as the internal standard.

(e) Investigations of reaction atmosphere[a]



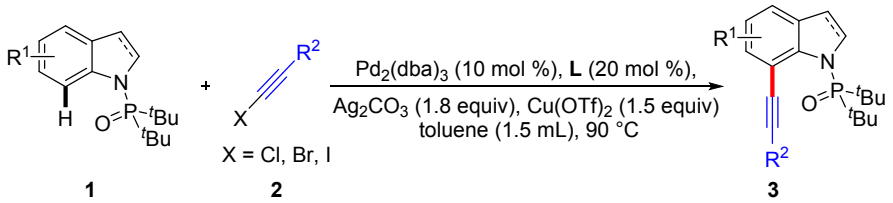
1a **2a** **3a**

entry	catalyst	atmosphere	toluene (mL)	yield of **3a** (%)[b]
1	$Pd_2(dba)_3$	N_2	1.5	56
2	$Pd_2(dba)_3$	O_2	1.5	76
3	$Pd_2(dba)_3$	air	1.5	83

[a] Conditions: unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (1.8 equiv),

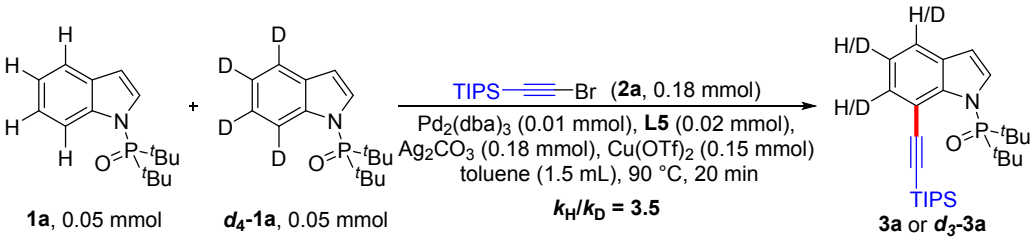
$Pd_2(dba)_3$ (10 mol %), **L5** (20 mol %), Ag_2CO_3 (1.8 equiv), $Cu(OTf)_2$ (1.5 equiv) in toluene (1.5 mL) at 90 °C for 12 h. [b] Monitored by NMR using CH_2Br_2 as the internal standard.

D. General Procedure for the Synthesis of 3

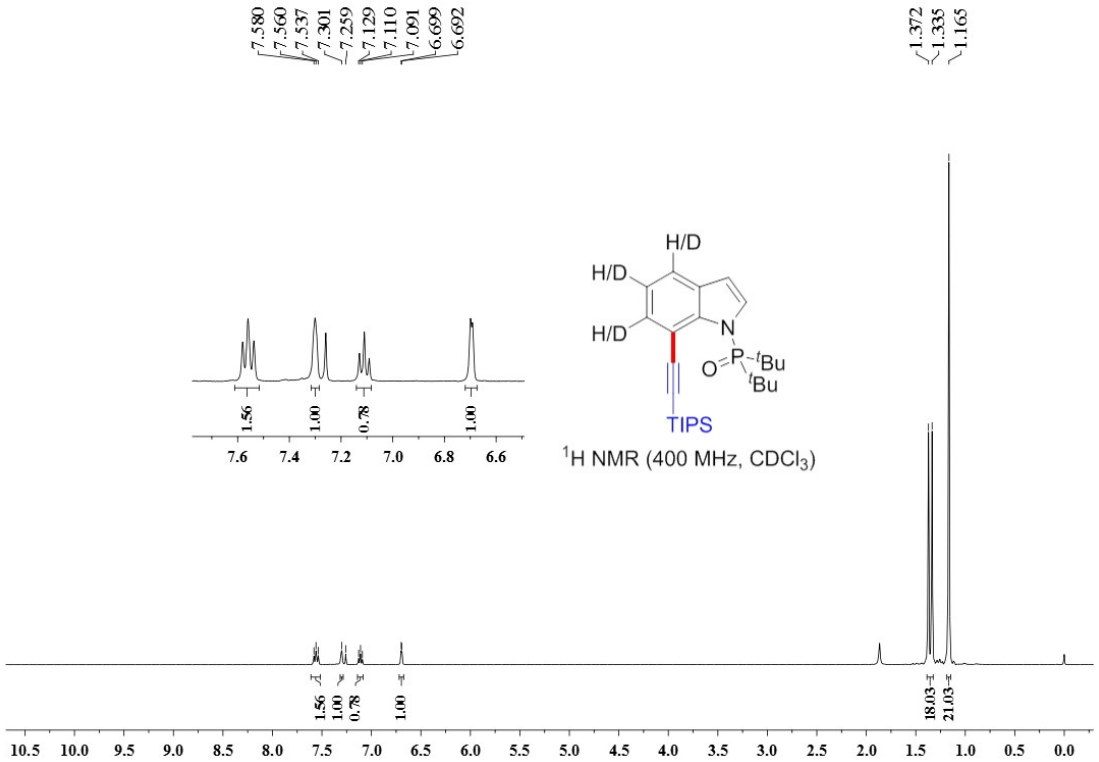


A mixture of substrate **1** (0.1 mmol), haloalkyne (**2**, 0.18 mmol), $Pd_2(dba)_3$ (10 mol %), $Cu(OTf)_2$ (1.5 equiv), Ag_2CO_3 (1.8 equiv), **L4** or **L5** (20 mol %) and 1.5 mL of toluene was added to a test tube equipped with a magnetic stirring bar. The mixture was then stirred at 90 °C under air for 2~12 h. After the reaction was completed (monitored by TLC), the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **3** was obtained in the corresponding yield after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

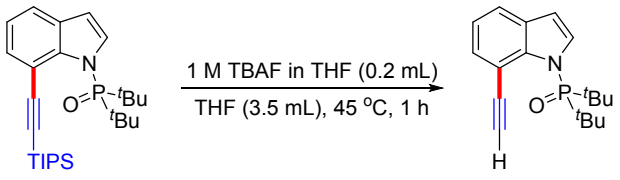
E. Mechanistic Studies



A mixture of di-*tert*-butyl(1*H*-indol-1-yl)phosphine oxide (**1a**, 0.05 mmol), di-*tert*-butyl(1*H*-indol-1-yl-4,5,6,7-d_4)phosphine oxide (***d*$_4$-1a**, 0.05 mmol), bromoalkyne (**2a**, 0.18 mmol), $Pd_2(dba)_3$ (10 mol %), Ag_2CO_3 (1.8 equiv), $Cu(OTf)_2$ (1.5 equiv), **L5** (20 mol %) and 1.5 mL of toluene was added to a test tube equipped with a magnetic stirring bar. The mixture was then stirred at 90 °C under air for 20 min. Then, the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product was obtained in 26% yield after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate (v/v = 30/1).

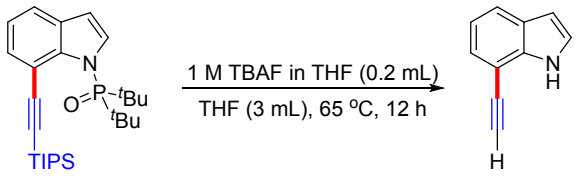


F. Futher Synthetic Applications



3a, 0.1 mmol **4a**, 86%

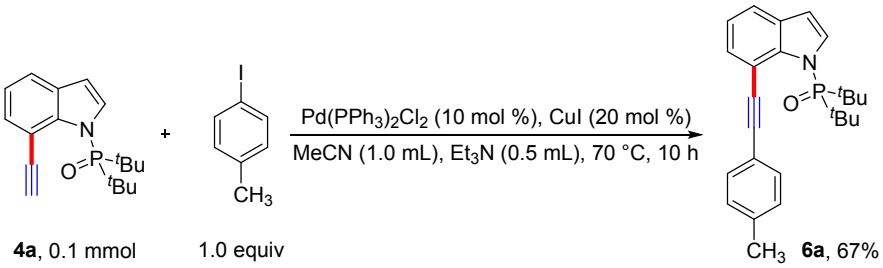
(a) Di-*tert*-butyl(7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (**3a**, 0.1 mmol), TBAF (1 M in THF, 0.2 mL) and THF (3.5 mL) were added in a test tube under air atmosphere. Then the mixture was stirred at 45 °C for 1 h. After the reaction was completed (monitored by TLC), the resulting mixture was extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **4a** was obtained in 86% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 5/1).



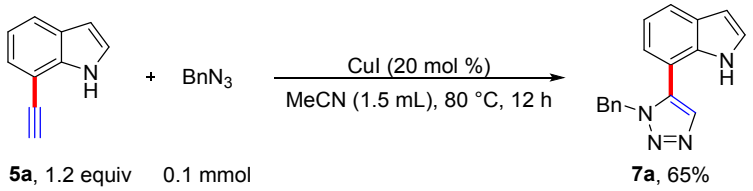
3a, 0.1 mmol **5a**, 93%

(b) Di-*tert*-butyl(7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (**3a**, 0.1 mmol), TBAF (1 M in THF, 0.2 mL) and THF (3.0 mL) were added in a test tube under air atmosphere. After this, the mixture was stirred at 65 °C for 12 h. After the reaction was completed (monitored

by TLC), the resulting mixture was extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **5a** was obtained in 93% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 30/1).



(c) To a resealable Schlenk tube or alternatively, a screw-cap pressure tube, were added **4a** (0.1 mmol), 1-iodo-4-methylbenzene (0.1 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (10 mol %), CuI (20 mol %), MeCN (1.0 mL), Et_3N (0.5 mL) and a stir bar. The reaction vessel was fitted with a rubber septum, and was evacuated and back-filled with nitrogen. The reaction tube was sealed and immersed in a preheated oil bath at 70 °C for 10 h and the solution was stirred with the aid of a magnetic stirrer. After the reaction was completed (monitored by TLC), the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **6a** was obtained in 67% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 20/1).



(d) 7-Ethynyl-1*H*-indole (**5a**, 0.12 mmol, 1.2 equiv), BnN_3 (0.1 mmol), CuI (20 mol %), MeCN (1.5 mL) were added in a test tube under air atmosphere and stirred at 80 °C for 12 h. Aftre the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **7a** was obtained in 65% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 5/1).

G. Reference

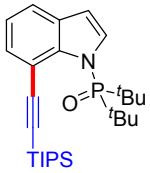
[1] C. G. Hartung, A. Fecher, B. Chapell and V. Snieckus, *Org. Lett.*, 2003, **5**, 1899.

[2] Y. Yang, X. Qiu, Y. Zhao, Y. Mu and Z. Shi, *J. Am. Chem. Soc.*, 2016, **138**, 495.

[3] Y. Yang, R. Li, Y. Zhao, D. Zhao and Z. Shi, *J. Am. Chem. Soc.*, 2016, **138**, 8734.

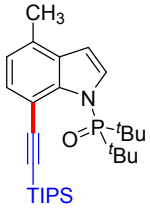
H. Characterization Data for All Products

Di-*tert*-butyl(7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3a)



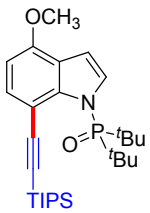
Brown solid (81%, 37.0 mg); mp: 83-84 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.29 (s, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 3.2 Hz, 1H), 1.35 (d, J = 14.4 Hz, 18H), 1.17 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 133.6, 131.5 (d, J = 4.1 Hz), 128.1 (d, J = 4.8 Hz), 121.6, 121.2, 112.4, 108.0 (d, J = 5.1 Hz), 107.5, 94.8, 39.2 (d, J = 67.3 Hz), 27.1, 18.8, 11.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.51-61.61 (m); IR: ν_{max}(KBr) = 2943, 2868, 2143, 1467, 1387, 1243, 1129, 993, 879, 738, 659, 474 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{45}NOPSi$ $[M+H]^+$, 458.3003; found 458.3008.

Di-*tert*-butyl(4-methyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3b)



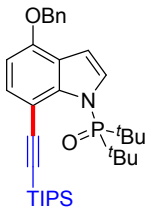
Brown solid (82%, 38.6 mg); mp: 105-106 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.6 Hz, 1H), 7.29 (s, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.71 (s, 1H), 2.50 (s, 3H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 133.6, 131.0 (d, J = 4.0 Hz), 130.7, 127.6 (d, J = 4.9 Hz), 122.2, 109.9, 107.8, 106.1 (d, J = 5.1 Hz), 93.8, 39.2 (d, J = 67.3 Hz), 27.1, 18.8, 11.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.17-61.28 (m); IR: ν_{max}(KBr) = 2945, 2867, 2141, 1471, 1355, 1242, 1122, 1003, 881, 813, 663, 474 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{28}H_{47}NOPSi$ $[M+H]^+$, 472.3159, found 472.3161.

Di-*tert*-butyl(4-methoxy-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3c)



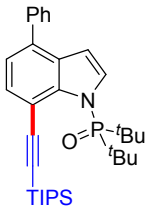
Brown oil (42%, 20.5 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 1H), 7.20 (s, 1H), 6.82 (d, J = 1.6 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 3.92 (s, 3H), 1.35 (d, J = 14.4 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 139.5, 134.9, 126.6 (d, J = 4.5 Hz), 121.7 (d, J = 4.6 Hz), 107.7, 105.5, 104.7 (d, J = 4.9 Hz), 102.2, 92.4, 55.3, 39.2 (d, J = 67.2 Hz), 27.1, 18.8, 11.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.47-61.57 (m); IR: ν_{max}(KBr) = 2941, 2864, 2139, 1482, 1364, 1272, 1119, 881, 756, 659, 476 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{28}H_{47}NO_2PSi$ $[M+H]^+$, 488.3108, found 488.3111.

(4-(Benzyloxy)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)di-*tert*-butylphosphine oxide (3d)



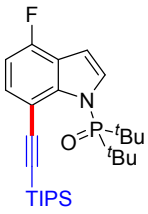
Brown solid (82%, 46.2 mg); mp: 115-116 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 3H), 7.38 (t, J = 7.3 Hz, 2H), 7.34-7.30 (m, 1H), 7.20 (s, 1H), 6.88 (s, 1H), 6.63 (d, J = 8.4 Hz, 1H), 5.18 (s, 2H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 139.6, 137.0, 134.9, 128.5, 127.9, 127.3, 126.6 (d, J = 4.7 Hz), 122.1 (d, J = 4.5 Hz), 107.6, 105.7, 104.9 (d, J = 5.1 Hz), 103.6, 92.6, 70.0, 39.2 (d, J = 67.2 Hz), 27.1, 18.8, 11.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.56-61.66 (m); IR: ν_{max}(KBr) = 2940, 2864, 2139, 1481, 1366, 1275, 1117, 1018, 881, 747, 657, 473 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{34}H_{51}NO_2PSi$ $[M+H]^+$, 564.3421, found 564.3429.

Di-*tert*-butyl(4-phenyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3e)



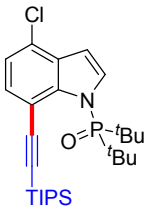
White solid (79%, 42.1 mg); mp: 175-176 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.37 (d, J = 7.0 Hz, 1H), 7.33 (s, 1H), 7.16 (d, J = 7.6 Hz, 1H), 6.85 (s, 1H), 1.37 (d, J = 14.4 Hz, 18H), 1.18 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 138.7, 135.0, 133.8, 129.8 (d, J = 3.8 Hz), 128.9, 128.5, 128.4, 127.2, 121.8, 111.4, 107.6, 107.3 (d, J = 5.0 Hz), 95.2, 39.4 (d, J = 67.1 Hz), 27.2, 18.8, 11.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.78-62.05 (m); IR: ν_{max}(KBr) = 3431, 2939, 2140, 1642, 1468, 1364, 1233, 1124, 1002, 891, 783, 663, 486 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{33}H_{48}NNaOPSi$ $[M+Na]^+$, 556.3135, found 556.3141.

Di-*tert*-butyl(4-fluoro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3f)



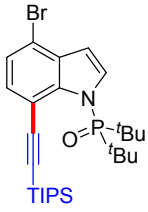
Brown solid (78%, 37.1 mg); mp: 96-97 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 1H), 7.27 (s, 1H), 6.83-6.79 (m, 2H), 1.36 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1 (d, J = 248.8 Hz), 140.5 (d, J = 9.4 Hz), 134.4 (d, J = 7.4 Hz), 128.0 (d, J = 4.6 Hz), 120.4 (dd, J = 22.2, 4.5 Hz), 108.7 (d, J = 4.0 Hz), 107.1 (d, J = 18.8 Hz), 106.7, 103.3 (d, J = 5.0 Hz), 94.2, 39.3 (d, J = 66.8 Hz), 27.1, 18.8, 11.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.43 (t, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.40-62.48 (m); IR: ν_{max}(KBr) = 2946, 2871, 2143, 1593, 1479, 1361, 1247, 1116, 1007, 882, 799, 662, 480 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{44}FNOPSi$ $[M+H]^+$, 476.2908, found 476.2910.

Di-*tert*-butyl(4-chloro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3g)



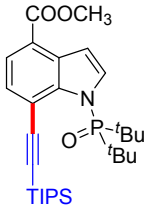
Brown solid (60%, 29.5mg); mp: 99-100 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 133.9, 130.2 (d, J = 4.1 Hz), 128.7 (d, J = 4.5 Hz), 126.3, 121.5, 111.2, 106.6, 106.2 (d, J = 4.8 Hz), 95.9, 39.3 (d, J = 66.6 Hz), 27.1, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.49-62.60 (m); IR: ν_{max}(KBr) = 2946, 2868, 2144, 1468, 1348, 1239, 1122, 998, 884, 812, 751, 657, 472 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{43}ClNNaOPSi$ $[M+Na]^+$, 514.2432, found 514.2438.

(4-Bromo-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)di-tert-butylphosphine oxide (3h)



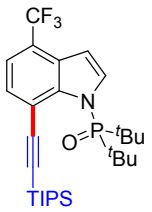
Brown solid (53%, 28.4 mg); mp: 100-101 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 1H), 7.34 (s, 1H), 7.28 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 134.0, 132.0 (d, J = 3.9 Hz), 128.6 (d, J = 4.6 Hz), 124.7, 115.0, 111.7, 108.1 (d, J = 4.6 Hz), 106.6, 96.1, 39.3 (d, J = 66.6 Hz), 27.1, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.60-62.70 (m); IR: ν_{max}(KBr) = 2942, 2866, 2142, 1466, 1342, 1238, 1123, 993, 878, 811, 744, 657, 473 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{43}BrNNaOPSi$ $[M+H]^+$, 558.1927, found 558.1931.

Methyl 1-(di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indole-4-carboxylate (3i)



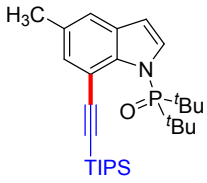
Brown solid (45%, 23.2 mg); mp: 153-154 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.44 (s, 1H), 3.95 (s, 3H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 139.1, 132.5, 131.8 (d, J = 3.9 Hz), 130.2 (d, J = 4.6 Hz), 124.3, 121.3, 117.2, 108.7 (d, J = 4.7 Hz), 106.8, 99.2, 51.8, 39.4 (d, J = 66.7 Hz), 27.1, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.61-62.72 (m); IR: ν_{max}(KBr) = 2940, 2142, 1710, 1570, 1462, 1361, 1248, 1102, 1007, 891, 806, 656, 522 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{29}H_{47}NO_3PSi$ $[M+H]^+$, 516.3057, found 516.3061.

Di-*tert*-butyl(4-(trifluoromethyl)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3j)



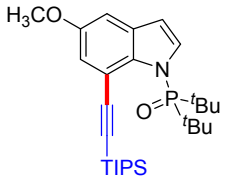
Brown solid (30%, 15.7 mg); mp: 71-72 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 1H), 7.43 (s, 1H), 7.39 (d, J = 7.6 Hz, 1H), 6.91 (s, 1H), 1.36 (d, J = 14.4 Hz, 18H), 1.17 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 132.6, 129.8 (d, J = 4.3 Hz), 128.3 (q, J = 19.3 Hz), 124.52 (q, J = 270.4 Hz), 121.6 (q, J = 32.5 Hz), 118.8 (q, J = 4.8 Hz), 116.3, 106.3, 106.2 (d, J = 2.7 Hz), 98.3, 39.4 (d, J = 66.4 Hz), 27.1, 18.8, 11.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.24 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.07-63.16 (m); IR: ν_{max}(KBr) = 2943, 2144, 1590, 1468, 1318, 1228, 1119, 1001, 896, 813, 655, 474 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{28}H_{43}F_3NNaOPSi$ $[M+Na]^+$, 548.2696, found 548.2697.

Di-*tert*-butyl(5-methyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3k)



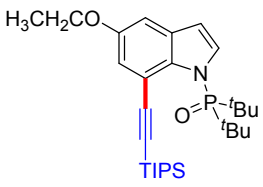
Brown solid (79%, 37.2 mg); mp: 116-117 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.33 (s, 1H), 7.25 (s, 1H), 6.61 (d, J = 2.0 Hz, 1H), 2.38 (s, 3H), 1.34 (d, J = 14.4 Hz, 18H), 1.17 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 134.6, 131.8 (d, J = 4.2 Hz), 130.9, 128.2 (d, J = 4.9 Hz), 121.3, 111.9, 107.6, 107.6 (d, J = 5.7 Hz), 94.2, 39.2 (d, J = 67.5 Hz), 27.1, 20.7, 18.8, 11.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.92-61.02 (m); IR: ν_{max}(KBr) = 2944, 2867, 2143, 1466, 1381, 1239, 1124, 991, 878, 753, 661, 608, 473 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{28}H_{47}NOPSi$ $[M+H]^+$, 472.3159, found 472.3163.

Di-*tert*-butyl(5-methoxy-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3l)



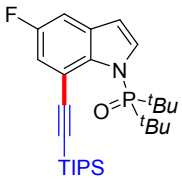
Brown oil (52%, 25.3 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 2.4 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.03 (d, J = 2.4 Hz, 1H), 6.61 (d, J = 3.2 Hz, 1H), 3.81 (s, 3H), 1.33 (d, J = 14.4 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 133.5, 132.4 (d, J = 4.2 Hz), 128.8, 121.8, 113.0, 107.8 (dd, J = 4.4, 3.3 Hz), 107.0, 104.0 (d, J = 1.4 Hz), 94.8, 55.6 (d, J = 5.8 Hz), 39.2 (d, J = 67.3 Hz), 27.1, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.13-61.21 (m); IR: ν_{max}(KBr) = 2945, 2870, 2145, 1679, 1595, 1467, 1387, 1228, 1047, 805, 660, 472 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{28}H_{47}NO_2PSi$ $[M+H]^+$, 488.3108, found 488.3111.

Di-*tert*-butyl(5-ethoxy-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3m)



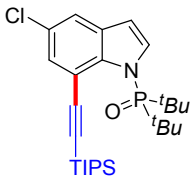
Brown solid (58%, 29.1 mg); mp: 93-94 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.19 (s, 1H), 7.03 (s, 1H), 6.61 (s, 1H), 4.05 (q, J = 6.9 Hz, 2H), 1.42 (t, J = 6.9 Hz, 3H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 133.5, 132.5 (d, J = 4.2 Hz), 128.8 (d, J = 4.7 Hz), 122.4, 113.0, 108.0 (d, J = 5.0 Hz), 107.1, 105.0, 94.8, 64.0, 39.3 (d, J = 67.3 Hz), 27.1, 18.9, 14.9, 11.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.38-61.49 (m); IR: ν_{max}(KBr) = 2943, 2145, 1604, 1468, 1381, 1231, 1156, 1004, 807, 660, 491 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{29}H_{49}NO_2PSi$ $[M+H]^+$, 502.3265, found 502.3271.

Di-*tert*-butyl(5-fluoro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3n)



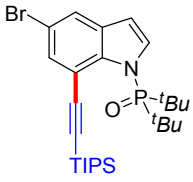
Brown solid (56%, 26.6 mg); mp: 117-118 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.28 (d, J = 9.6 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 6.65 (s, 1H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7 (d, J = 237.4 Hz), 135.1, 132.4 (dd, J = 10.3, 4.1 Hz), 129.7 (d, J = 4.6 Hz), 120.4 (d, J = 25.6 Hz), 113.3 (d, J = 10.2 Hz), 107.9 (t, J = 4.6 Hz), 106.7 (d, J = 22.9 Hz), 106.2 (d, J = 2.0 Hz), 96.3, 39.3 (d, J = 67.0 Hz), 27.1, 18.8, 11.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.43 (t, J = 9.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.90-62.00 (m); IR: ν_{max}(KBr) = 2945, 2870, 2147, 1581, 1467, 1381, 1234, 1138, 985, 871, 802, 662, 476 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{44}FNOPSi$ $[M+H]^+$, 476.2908, found 476.2913.

Di-*tert*-butyl(5-chloro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3o)



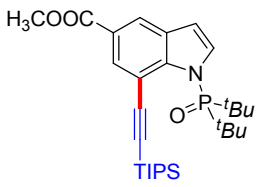
Brown solid (46%, 22.6 mg); mp: 140-141 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 132.8 (d, J = 3.9 Hz), 132.5, 129.4 (d, J = 4.7 Hz), 126.8, 120.6, 113.5, 107.4 (d, J = 4.9 Hz), 106.0, 96.5, 39.3 (d, J = 66.8 Hz), 27.1, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.25-62.40 (m); IR: ν_{max}(KBr) = 2939, 2868, 2146, 1459, 1371, 1235, 1132, 997, 879, 757, 671, 474 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{43}ClNNaOPSi$ $[M+Na]^+$, 514.2432, found 514.2435.

(5-Bromo-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)di-*tert*-butylphosphine oxide (3p)



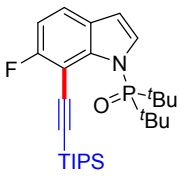
Brown solid (39%, 20.8 mg); mp: 141-142 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.61 (s, 1H), 7.30 (s, 1H), 6.63 (s, 1H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 135.0, 133.2 (d, J = 4.3 Hz), 129.3 (d, J = 4.7 Hz), 123.7, 114.2, 114.0, 107.3 (d, J = 4.9 Hz), 105.9, 96.6, 39.1 (d, J = 66.7 Hz), 27.1, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.17-62.45 (m); IR: ν_{max}(KBr) = 2937, 2145, 1719, 1456, 1368, 1233, 1115, 1006, 873, 669 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{44}BrNOPSi$ $[M+H]^+$, 536.2108, found 536.2110.

Methyl 1-(di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indole-5-carboxylate (3q)



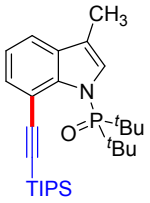
Brown solid (52%, 26.8 mg); mp: 132-133 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.22 (s, 1H), 7.4 (s, 1H), 6.8 (s, 1H), 3.93 (s, 3H), 1.35 (d, J = 14.8 Hz, 18H), 1.18 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 139.9, 133.3, 130.5 (d, J = 4.2 Hz), 128.3 (d, J = 4.8 Hz), 122.8, 122.0, 111.3, 107.6 (d, J = 4.5 Hz), 105.4, 94.8, 51.0, 38.3 (d, J = 66.6 Hz), 26.1, 17.8, 10.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.57-62.66 (m); IR: ν_{max}(KBr) = 2944, 2146, 1721, 1590, 1464, 1215, 1115, 998, 896, 664, 509 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{29}H_{47}NO_3PSi$ $[M+H]^+$, 516.3057, found 516.3059.

Di-*tert*-butyl(6-fluoro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3s)



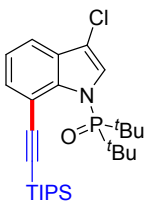
Brown oil (26%, 12.4 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.5, 5.5 Hz, 1H), 7.28 (dd, J = 3.4, 2.0 Hz, 1H), 6.99 (t, J = 9.0 Hz, 1H), 6.66 (dd, J = 3.5, 1.0 Hz, 1H), 1.35 (d, J = 14.5 Hz, 18H), 1.17 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0 (d, J = 242.9 Hz), 138.9, 128.4, 127.5, 121.1 (d, J = 10.1 Hz), 110.6, 110.4, 107.8 (d, J = 4.5 Hz), 101.8 (dd, J = 63.3, 14.4 Hz), 98.6, 39.3 (d, J = 66.9 Hz), 27.1, 18.7, 11.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.59 (dd, J = 9.3, 5.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 63.06-62.55 (m); IR: ν_{max}(KBr) = 2942, 2148, 1583, 1468, 1393, 1230, 1112, 1013, 918, 808, 729, 655 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{44}FNOPSi$ $[M+H]^+$, 476.2908, found 476.2914.

Di-*tert*-butyl(3-methyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3t)



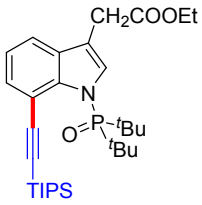
Brown solid (84%, 39.6 mg); mp: 104-105 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.04 (s, 1H), 2.29 (s, 3H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 133.5, 132.3 (d, J = 3.9 Hz), 125.2 (d, J = 2.5 Hz), 121.1, 119.1, 116.6 (d, J = 5.2 Hz), 112.4, 107.6, 94.6, 39.1 (d, J = 67.7 Hz), 27.1, 18.8, 11.5, 9.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.79-61.08 (m); IR: ν_{max}(KBr) = 2943, 2141, 1466, 1390, 1228, 1128, 1005, 908, 743, 660, 474 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{28}H_{47}NOPSi$ $[M+H]^+$, 472.3159, found 472.3161.

Di-*tert*-butyl(3-chloro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3u)



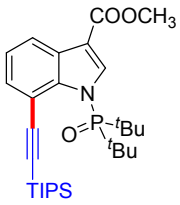
Brown solid (52%, 25.5 mg); mp: 102-103 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.26 (s, 1H), 7.20 (t, J = 7.6 Hz, 1H), 1.36 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 134.7, 129.0 (d, J = 3.1 Hz), 124.3 (d, J = 4.6 Hz), 122.1, 118.7, 112.9, 112.0 (d, J = 5.5 Hz), 106.7, 95.9, 39.3 (d, J = 66.4 Hz), 27.1, 18.8, 11.5.; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.97-63.07 (m); IR: ν_{max}(KBr) = 2944, 2145, 1467, 1388, 1247, 1123, 1069, 1002, 884, 739, 661, 518 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{43}ClNNaOPSi$ $[M+Na]^+$, 514.2432, found 514.2433.

Ethyl 2-(1-(di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-3-yl)acetate (3v)



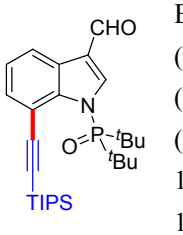
Brown solid (83%, 45.1 mg); mp: 116-117 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.38 (s, 1H), 7.14 (t, J = 7.5 Hz, 1H), 4.17 (q, J = 6.8 Hz, 2H), 3.73 (s, 2H), 1.35 (d, J = 14.4 Hz, 18H), 1.25 (t, J = 6.9 Hz, 3H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 138.7, 133.6, 131.1 (d, J = 3.5 Hz), 127.0 (d, J = 4.7 Hz), 121.5, 118.8, 113.4 (d, J = 5.1 Hz), 112.7, 107.3, 95.0, 60.9, 39.2 (d, J = 67.2 Hz), 30.8, 27.1, 18.8, 14.2, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.76-62.04 (m); IR: ν_{max}(KBr) = 2943, 2141, 1733, 1466, 1390, 1222, 1012, 899, 797, 651, 514 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{31}H_{51}NO_3PSi$ $[M+H]^+$, 544.3370, found 544.3376.

Methyl 1-(di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indole-3-carboxylate (3w)



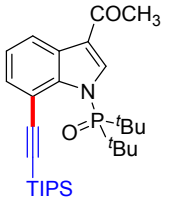
Brown solid (72%, 37.1 mg); mp: 85-86 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 1H), 8.00 (s, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 3.93 (s, 3H), 1.38 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 138.7, 134.6, 134.5 (d, J = 4.9 Hz), 128.6 (d, J = 3.5 Hz), 123.1, 121.8, 112.6 (d, J = 5.0 Hz), 106.8, 99.9, 95.9, 51.4, 39.4 (d, J = 65.4 Hz), 27.2, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 65.03-64.30 (m); IR: ν_{max}(KBr) = 2940, 2144, 1718, 1582, 1469, 1377, 1221, 1094, 998, 894, 794, 651, 502 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{29}H_{47}NO_3PSi$ $[M+H]^+$, 516.3057, found 516.3059.

1-(Di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indole-3-carbaldehyde (3x)



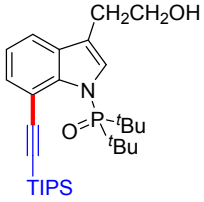
Brown solid (47%, 22.8 mg); mp: 172-173 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.31 (d, J = 7.6 Hz, 1H), 7.92 (s, 1H), 7.68 (d, J = 7.2 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 1.41 (d, J = 14.8 Hz, 18H), 1.17 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 139.2, 138.3 (d, J = 4.5 Hz), 135.5, 127.3 (d, J = 3.4 Hz), 123.8, 122.1 (d, J = 4.1 Hz), 121.9, 112.7, 106.5, 96.5, 39.5 (d, J = 64.9 Hz), 27.2, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 65.51-64.78 (m); IR: ν_{max}(KBr) = 2942, 2147, 1662, 1469, 1390, 1232, 1014, 906, 800, 663, 501 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{28}H_{45}NO_2PSi$ $[M+H]^+$, 486.2952, found 486.2955.

1-(1-(Di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-3-yl)ethan-1-one (3y)



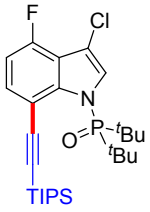
Brown solid (29%, 14.5 mg); mp: 111-112 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.6 Hz, 1H), 7.94 (s, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 6.6 Hz, 1H), 2.57 (s, 3H), 1.40 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 138.9, 134.9, 134.8 (d, J = 4.8 Hz), 128.3 (d, J = 3.3 Hz), 123.6, 122.6, 121.2 (d, J = 4.1 Hz), 112.5, 106.7, 96.0, 39.5 (d, J = 65.3 Hz), 27.9, 27.2, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.74-64.01 (m); IR: ν_{max}(KBr) = 2944, 2143, 1667, 1388, 1220, 1000, 888, 806, 651, 506 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{29}H_{46}NNaO_2PSi$ $[M+Na]^+$, 522.2928, found 522.2926.

Di-*tert*-butyl(3-(2-hydroxyethyl)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3z)



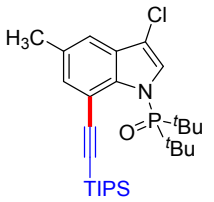
White solid (21%, 10.5 mg); mp: 138-139 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.18 (s, 1H), 7.11 (t, J = 7.4 Hz, 1H), 3.91 (t, J = 6.0 Hz, 2H), 2.97 (t, J = 5.6 Hz, 2H), 1.95 (s, 1H), 1.34 (d, J = 14.4 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 133.6, 131.4 (d, J = 3.8 Hz), 126.2 (d, J = 4.7 Hz), 121.3, 119.0, 117.7 (d, J = 5.1 Hz), 112.7, 107.4, 95.0, 62.1, 39.2 (d, J = 67.4 Hz), 28.2, 27.1, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.58-61.87 (m); IR: ν_{max}(KBr) = 3383, 2940, 2142, 1747, 1468, 1389, 1225, 1048, 899, 806, 653, 496 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{29}H_{49}NO_2PSi$ $[M+H]^+$, 502.3265, found 502.3271.

Di-*tert*-butyl(3-chloro-4-fluoro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3aa)



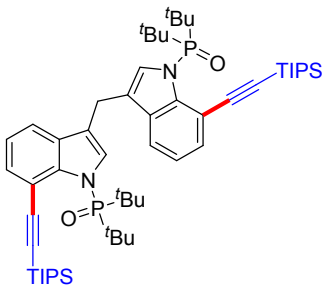
Brown oil (71%, 36.1 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 1H), 7.20 (s, 1H), 6.85 (t, J = 9.0 Hz, 1H), 1.36 (d, J = 14.8 Hz, 18H), 1.15 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0 (d, J = 252.6 Hz), 139.9 (d, J = 7.5 Hz), 135.4 (d, J = 7.6 Hz), 125.0 (d, J = 3.9 Hz), 117.5 (dd, J = 16.6, 3.2 Hz), 109.3 (d, J = 4.5 Hz), 109.2 (dd, J = 5.6, 1.9 Hz), 108.4 (d, J = 18.6 Hz), 105.9, 95.3, 39.4 (d, J = 65.8 Hz), 27.1, 18.8, 11.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.95 (dd, J = 9.6, 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 65.17-64.44 (m); IR: ν_{max}(KBr) = 2943, 2144, 1764, 1597, 1478, 1358, 1240, 1070, 895, 802, 669, 498 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{43}ClFNOPSi$ $[M+H]^+$, 510.2519, found 510.2514.

Di-*tert*-butyl(3-chloro-5-methyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3ab)



Brown solid (76%, 38.3 mg); mp: 81-82 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.35 (s, 1H), 7.23 (s, 1H), 2.42 (s, 3H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 135.8, 131.7, 129.2 (d, J = 3.3 Hz), 124.3 (d, J = 4.7 Hz), 118.8, 112.4, 111.5 (d, J = 5.7 Hz), 106.8, 95.2, 39.2 (d, J = 66.6 Hz), 27.1, 20.7, 18.8, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.43-62.71 (m); IR: ν_{max}(KBr) = 2942, 2145, 1762, 1654, 1466, 1376, 1244, 1010, 841, 655, 498 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{28}H_{46}ClNOPSi$ $[M+H]^+$, 506.2769, found 506.2772.

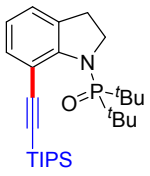
(Methylenebis(7-((triisopropylsilyl)ethynyl)-1*H*-indole-3,1-diyl))bis(di-*tert*-butylphosphine oxide (3ac)



Brown solid (48%, 44.3 mg); mp: 121-122 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.12 (t, J = 7.6 Hz, 2H), 6.89 (s, 2H), 4.13 (s, 2H), 1.22 (d, J = 14.8 Hz, 36H), 1.16 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 133.9, 131.0 (d, J = 4.2 Hz), 125.9 (d, J = 4.5 Hz), 121.3, 119.4, 118.9 (d, J = 4.9 Hz), 112.5, 107.5, 95.2, 39.0 (d, J = 67.4 Hz), 27.1, 21.0, 18.8,

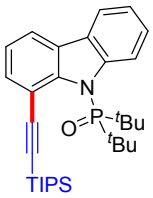
11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.15-61.44 (m); IR: ν_{max}(KBr) = 2942, 2142, 1742, 1595, 1468, 1387, 1230, 1126, 1010, 906, 807, 637, 497 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{55}H_{89}N_2O_2P_2Si_2$ $[M+H]^+$, 927.5932, found 927.5933.

Di-*tert*-butyl(7-((triisopropylsilyl)ethynyl)indolin-1-yl)phosphine oxide (3ad)



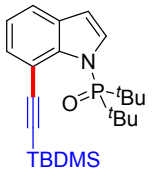
Brown oil (66%, 30.3 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.2 Hz, 1H), 7.09 (d, J = 6.8 Hz, 1H), 6.81 (t, J = 7.2 Hz, 1H), 3.83 (q, J = 7.2 Hz, 2H), 3.04 (t, J = 7.0 Hz, 2H), 1.36 (d, J = 14.0 Hz, 18H), 1.13 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 135.1, 134.0 (d, J = 3.5 Hz), 124.0, 121.8, 113.8, 107.3, 93.1, 50.1 (d, J = 1.5 Hz), 38.9 (d, J = 69.3 Hz), 30.9, 28.0, 18.8, 11.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.67-59.14 (m); IR: ν_{max}(KBr) = 2941, 2142, 1705, 1454, 1214, 1048, 893, 781, 661, 486 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{27}H_{47}NOPSi$ $[M+H]^+$, 460.3159, found 460.3162.

Di-*tert*-butyl(1-((triisopropylsilyl)ethynyl)-9*H*-carbazol-9-yl)phosphine oxide (3ae)



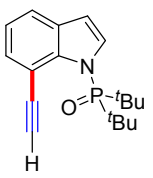
Brown solid (23%, 11.7 mg); mp: 131-132 ^{o}C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 6.4 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.37-7.30 (m, 2H), 7.26-7.21 (m, 1H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 141.7 (d, J = 2.4 Hz), 135.6, 128.7 (d, J = 2.6 Hz), 128.6 (d, J = 3.4 Hz), 125.2, 122.7, 122.2, 119.9, 119.4, 116.7, 115.4, 108.2, 94.5, 41.1 (d, J = 63.5 Hz), 28.3, 18.9, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 67.97-67.24 (m); IR: ν_{max}(KBr) = 2938, 2141, 1653, 1465, 1388, 1209, 999, 896, 757, 661, 501 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{31}H_{47}NOPSi$ $[M+H]^+$, 508.3159, found 508.3163.

Di-*tert*-butyl(7-((*tert*-butyldimethylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3af)



Brown oil (67%, 27.8 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 1.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.69 (s, 1H), 1.35 (d, J = 14.8 Hz, 18H), 0.99 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 133.0, 131.5 (d, J = 4.0 Hz), 128.2 (d, J = 4.8 Hz), 121.6, 121.3, 112.1, 108.1 (d, J = 5.0 Hz), 106.1, 96.2, 39.3 (d, J = 67.3 Hz), 27.1, 26.4, 17.0, -4.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.80-61.92 (m); IR: ν_{max}(KBr) = 2951, 2145, 1686, 1470, 1399, 1257, 1124, 988, 818, 739, 661, 598, 525 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{24}H_{39}NOPSi$ $[M+H]^+$, 416.2533, found 416.2531.

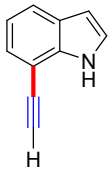
Di-*tert*-butyl(7-ethynyl-1*H*-indol-1-yl)phosphine oxide (4a)



White solid (86%, 25.9 mg); mp: 155-156 ^{o}C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, J = 7.2 Hz, 2H), 7.34 (s, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.72 (s, 1H), 3.37 (s, 1H), 1.37 (d, J = 14.4

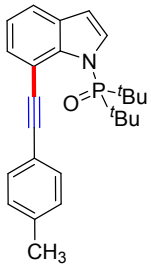
Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 132.9, 131.5 (d, J = 4.5 Hz), 128.2 (d, J = 5.4 Hz), 121.7, 121.6, 110.3, 107.8 (d, J = 5.1 Hz), 84.0, 81.0, 39.3 (d, J = 67.3 Hz), 27.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.24-62.51 (m); IR: ν_{max}(KBr) = 3186, 1466, 1246, 1119, 990, 736, 642, 527 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{18}H_{25}NOP$ $[M+H]^+$, 302.1668, found 302.1669.

7-Ethynyl-1*H*-indole (5a)



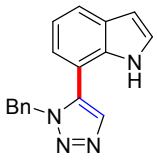
White solid (93%, 13.1 mg); mp: 86-87 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 6.8 Hz, 1H), 7.21 (s, 1H), 7.08 (t, J = 7.0 Hz, 1H), 6.57 (s, 1H), 3.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 127.4, 125.9, 124.4, 122.0, 119.6, 104.8, 103.3, 81.2, 80.3; IR: ν_{max}(KBr) = 3126, 2923, 1647, 1394, 1072, 793, 637 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{10}H_7NNa$ $[M+Na]^+$, 164.0471, found 164.0477.

Di-*tert*-butyl(7-(*p*-tolylethynyl)-1*H*-indol-1-yl)phosphine oxide (6a)



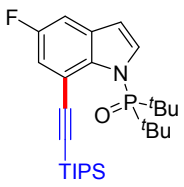
Brown oil (67%, 26.2 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.55 (m, 4H), 7.35 (s, 1H), 7.17-7.12 (m, 3H), 6.71 (s, 1H), 2.35 (s, 3H), 1.38 (d, J = 14.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.3, 131.5, 131.4 (d, J = 4.1 Hz), 128.8, 128.2 (d, J = 5.4 Hz), 121.9, 121.6, 120.9, 111.7, 107.8 (d, J = 5.1 Hz), 92.7, 90.3, 39.4 (d, J = 67.5 Hz), 27.1, 21.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.88-62.15 (m); IR: ν_{max}(KBr) = 2959, 1740, 1479, 1384, 1235, 1122, 983, 813, 726, 655, 513 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{25}H_{31}NOP$ $[M+H]^+$, 392.2138, found 392.2142.

7-(1-Benzyl-1*H*-1,2,3-triazol-5-yl)-1*H*-indole (7a)

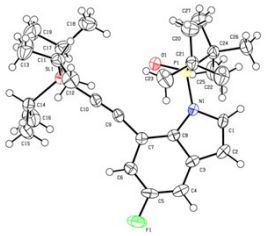


White solid (65%, 17.8 mg); mp: 112-113 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.69 (s, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.31 (s, 4H), 7.26-7.22 (m, 3H), 7.07 (t, J = 7.4 Hz, 1H), 6.57 (s, 1H), 5.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 134.5, 133.0, 129.0, 128.8, 128.7, 127.9, 125.0, 120.7, 119.3, 119.2, 118.1, 113.3, 102.0, 54.1; IR: ν_{max}(KBr) = 3401, 3130, 3047, 2934, 1610, 1436, 1335, 1213, 1062, 895, 799, 720, 542 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{17}H_{15}N_4$ $[M+H]^+$, 275.1291, found 275.1287.

I. X-ray Crystallographic Analysis



3n

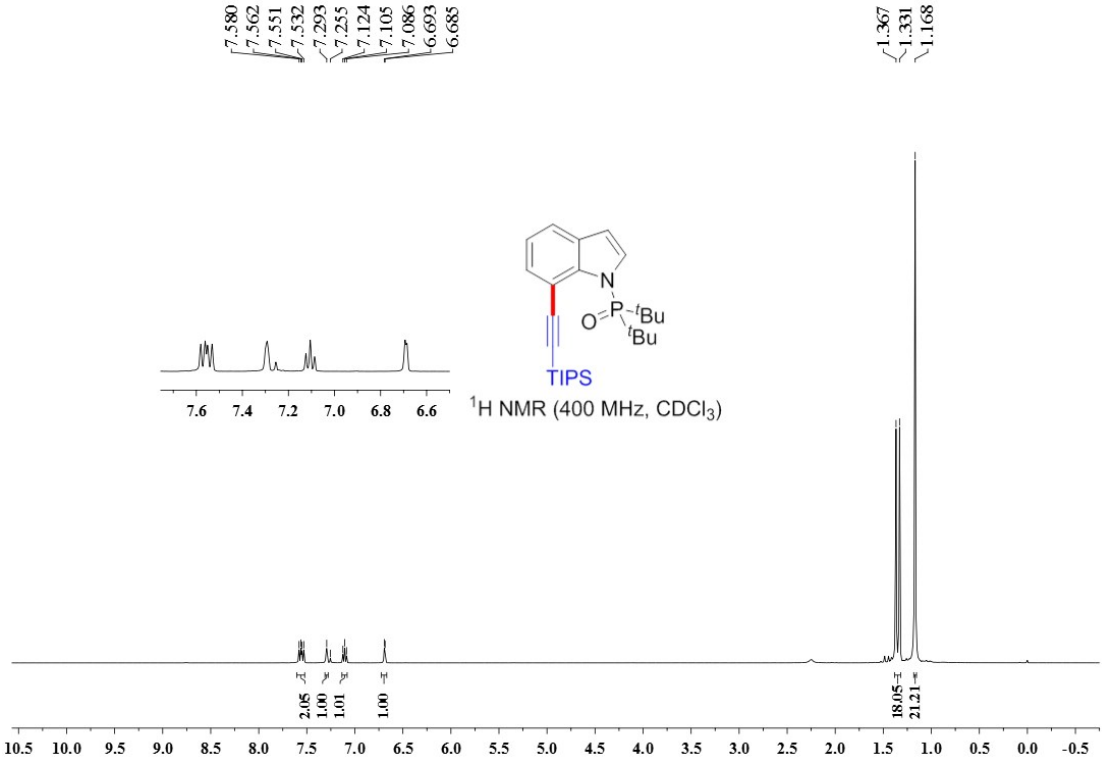


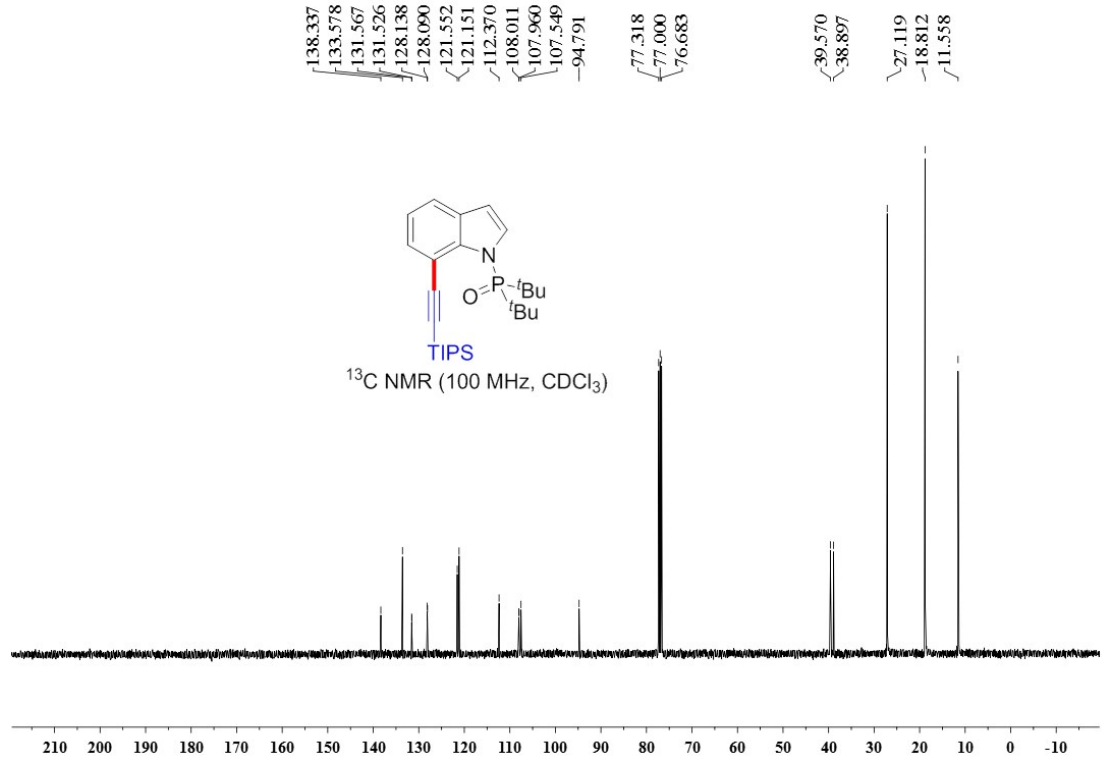
CCDC: 1915232

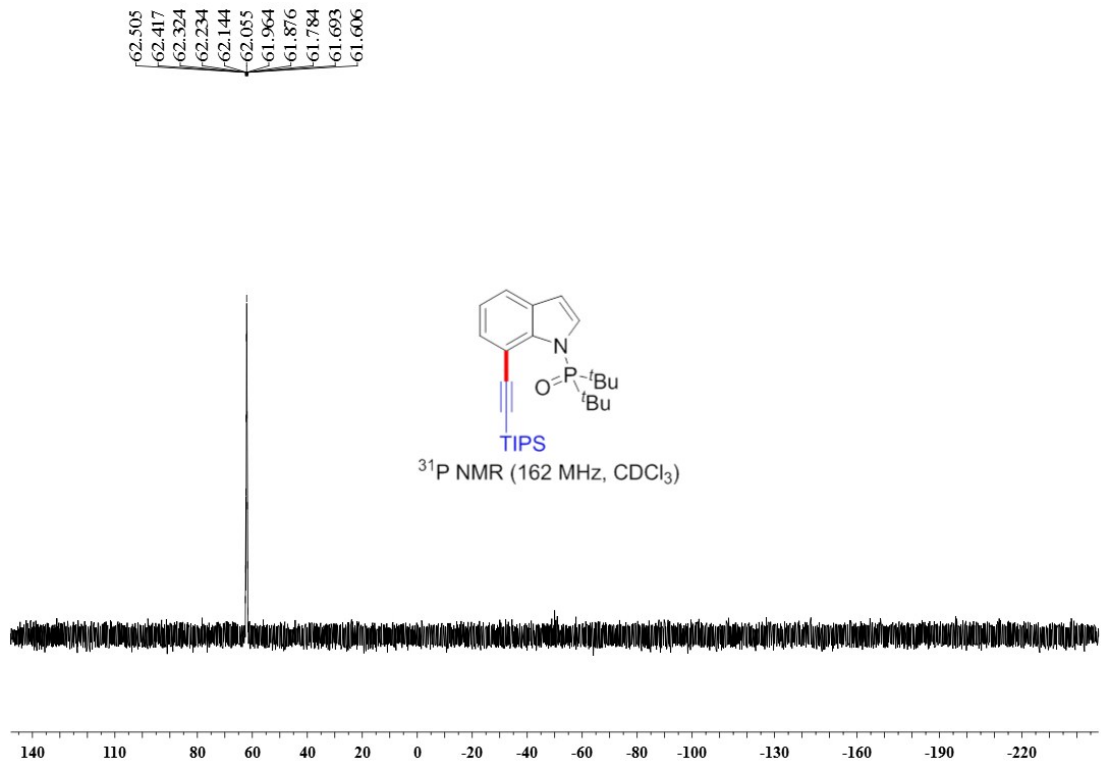
Empirical formula	$C_{27}H_{43}FNOPSi$
Formula weight	475.68
Temperature	220.0 K
Wavelength	0.71073 *Å*
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 11.936(3) *Å* alpha = 90 deg. b = 10.888(2) *Å* beta = 95.814(6) deg. c = 22.186(5) *Å* gamma = 90 deg.
Volume	2868.4(10) $Å^3$
Z, Calculated density	4, 1.102 g/cm^3
Absorption coefficient	0.162 mm^{-1}
F(000)	1032.0
Crystal size	0.19 × 0.15 × 0.12 mm^3
Theta range for data collection	3.43 to 50.014 deg.
Index ranges	$-14 \le h \le 14$, $-12 \le k \le 12$, $-18 \le l \le 26$
Reflections collected / unique	15016 / 5049 [R_{int} = 0.1142, R_{sigma} = 0.1418]
Completeness to theta = 25.007	0.998
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5049/0/301
Goodness-of-fit on F^2	0.903
Final R indices [I>2sigma(I)]	R_1 = 0.0633, wR_2 = 0.1297
R indices (all data)	R_1 = 0.1315, wR_2 = 0.1558

J. Copies of ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR Spectra

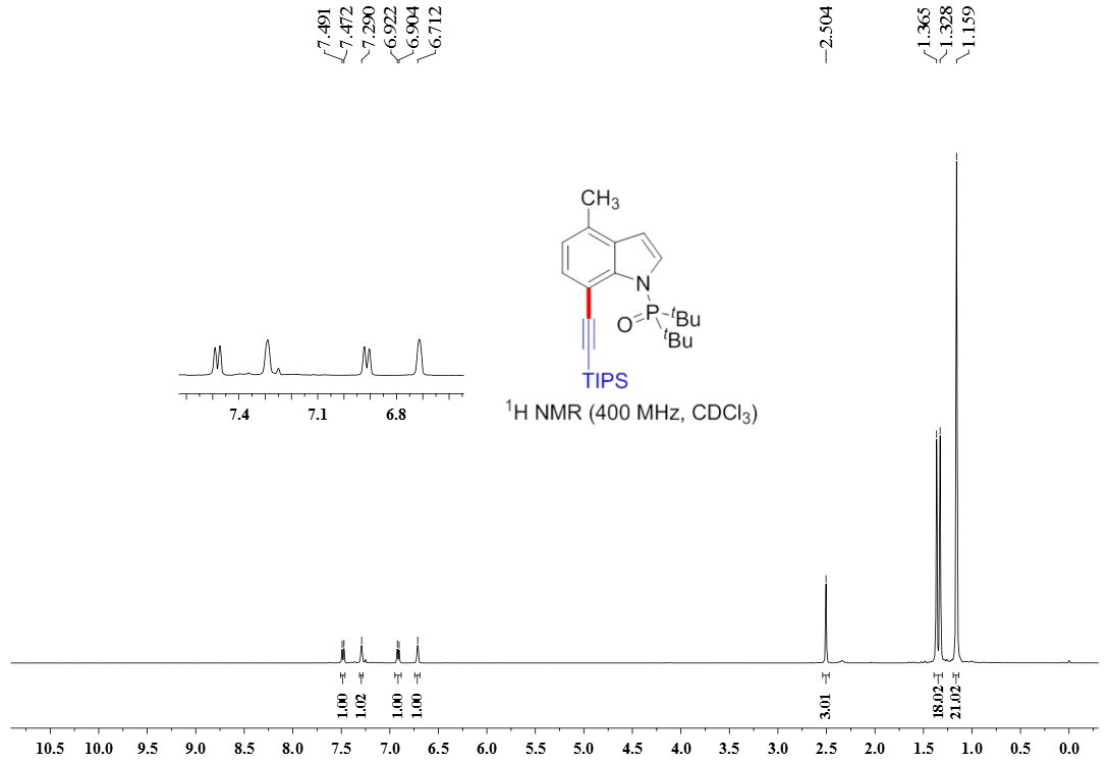
Di-*tert*-butyl(7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3a)

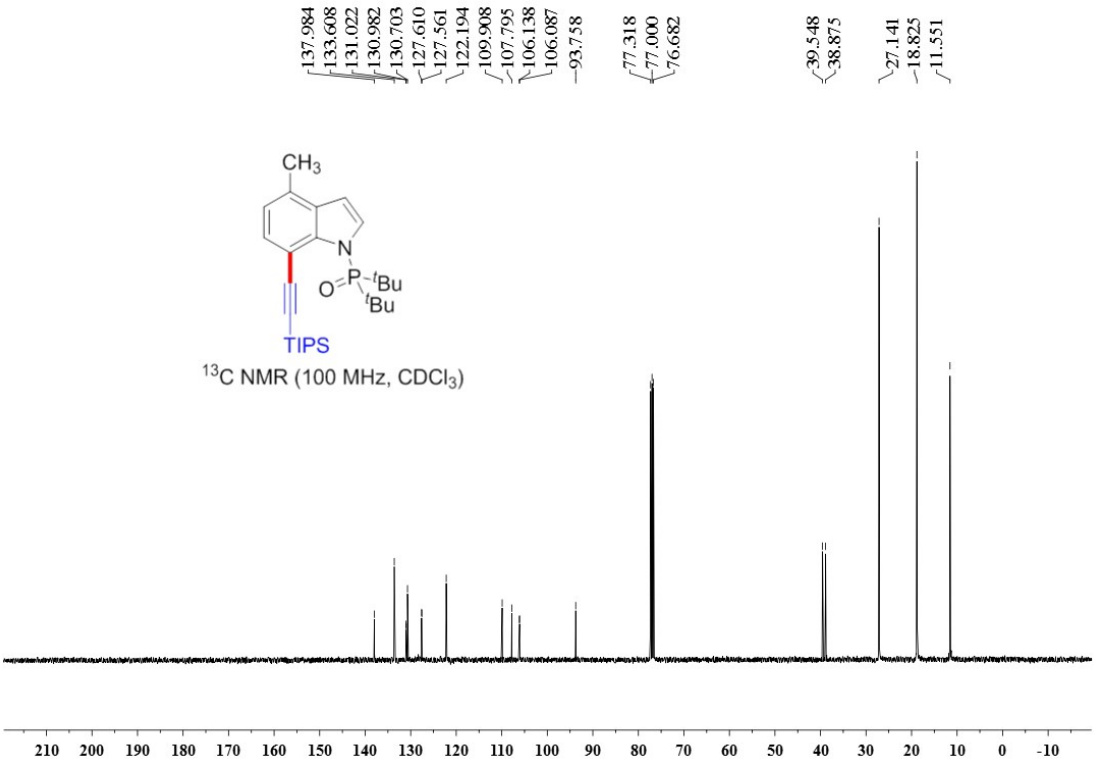




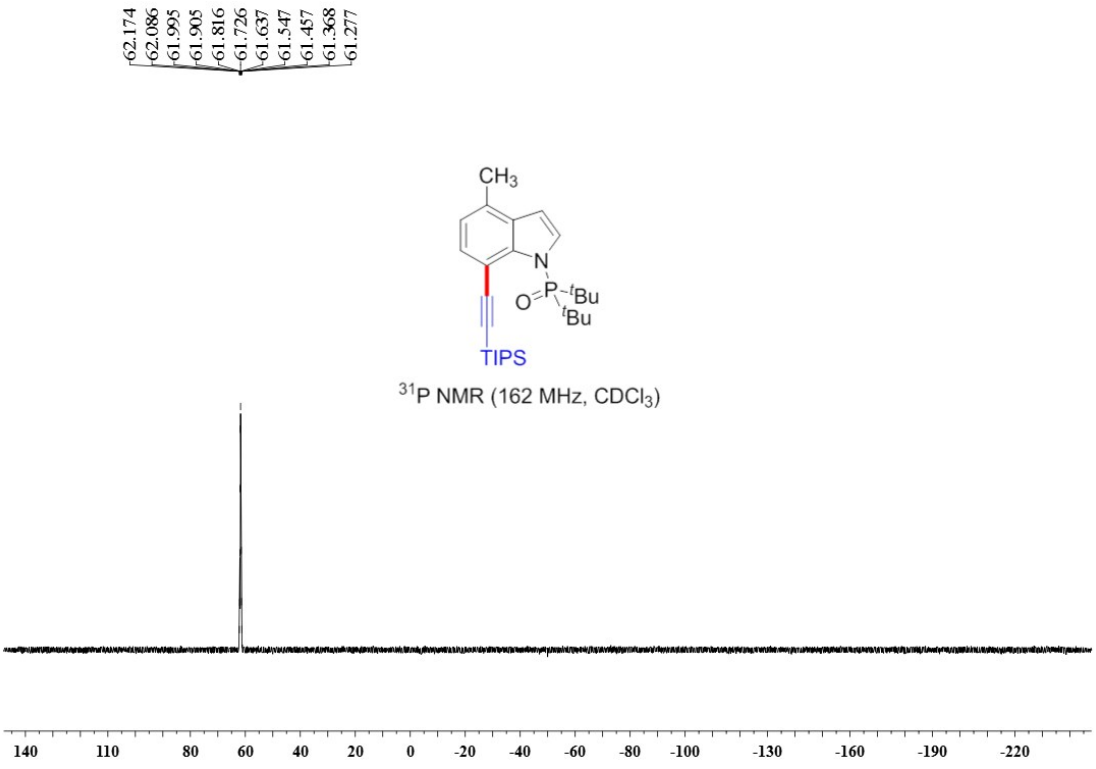


Di-*tert*-butyl(4-methyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3b)



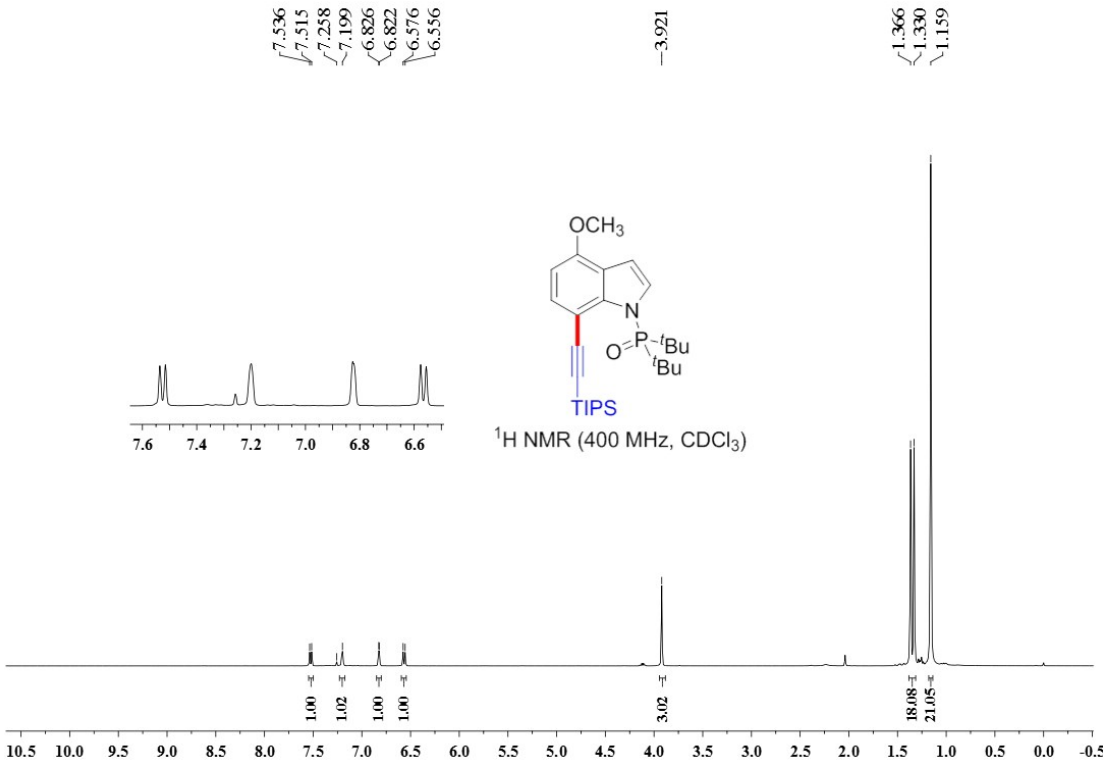


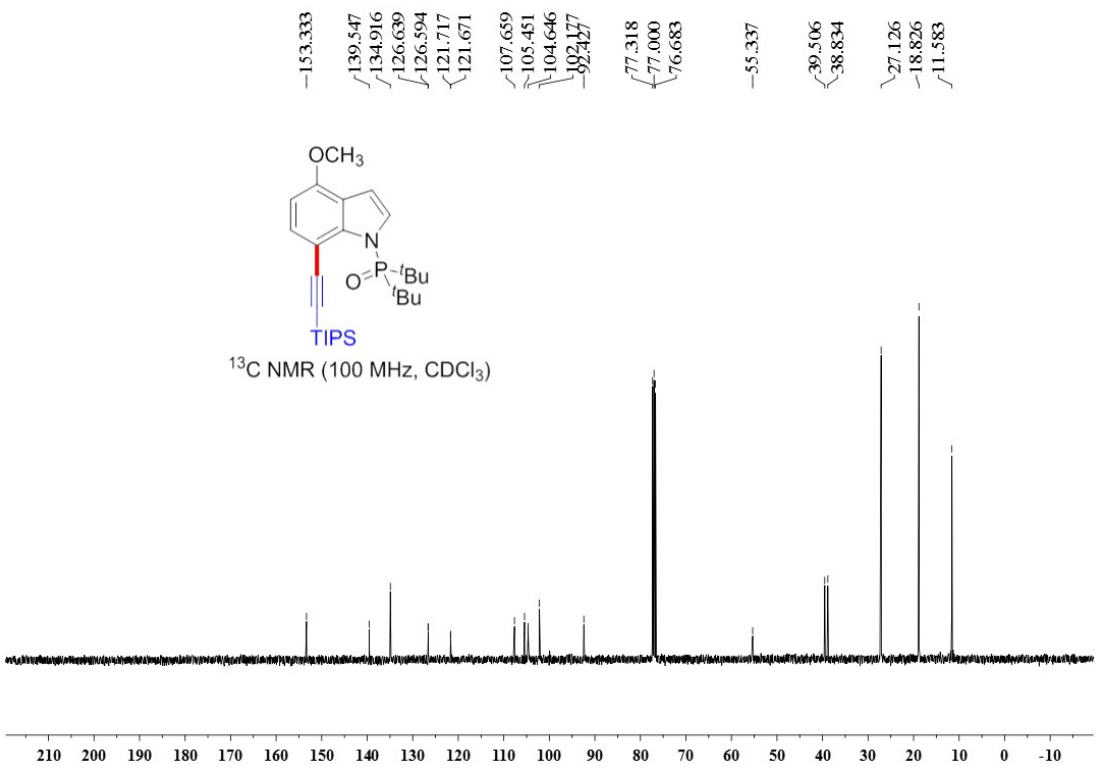
^{13}C NMR (100 MHz, $CDCl_3$)

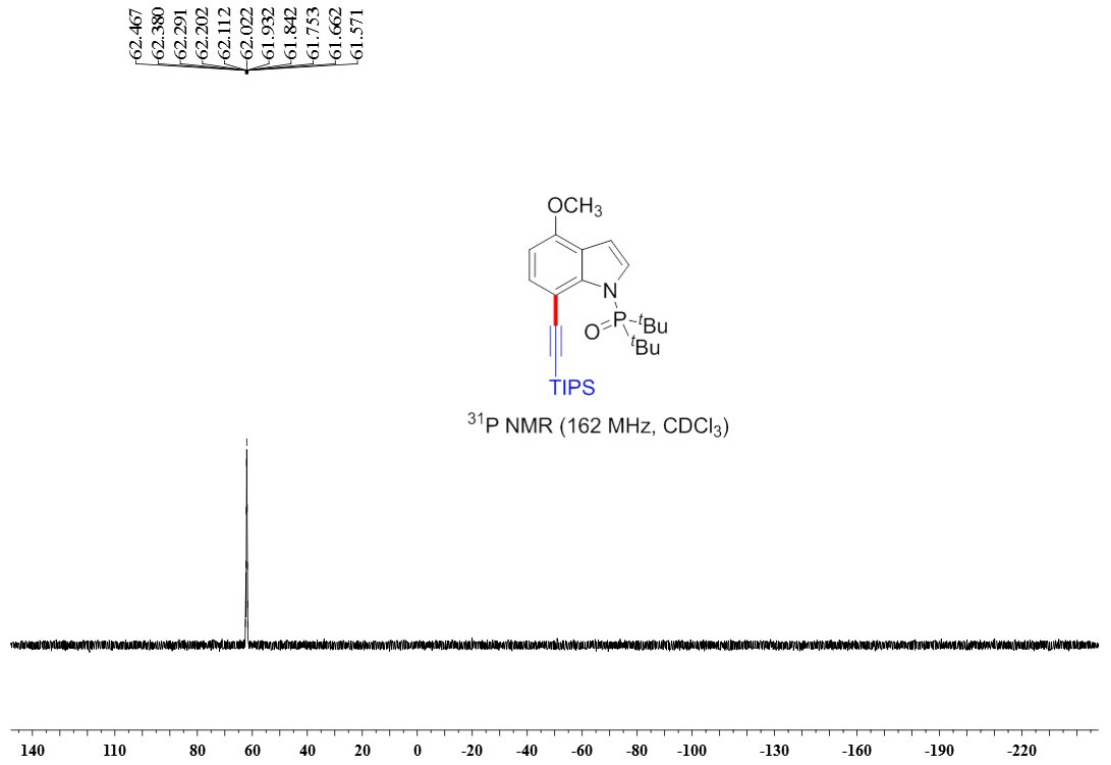


^{31}P NMR (162 MHz, $CDCl_3$)

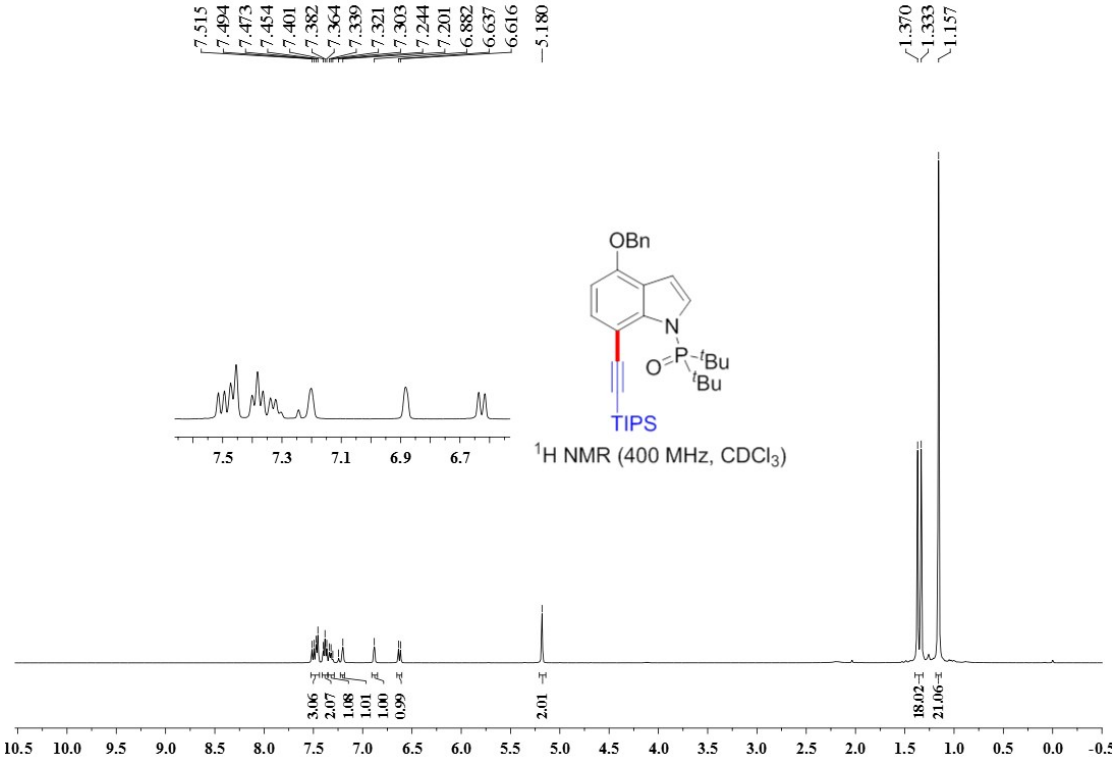
Di-*tert*-butyl(4-methoxy-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3c)

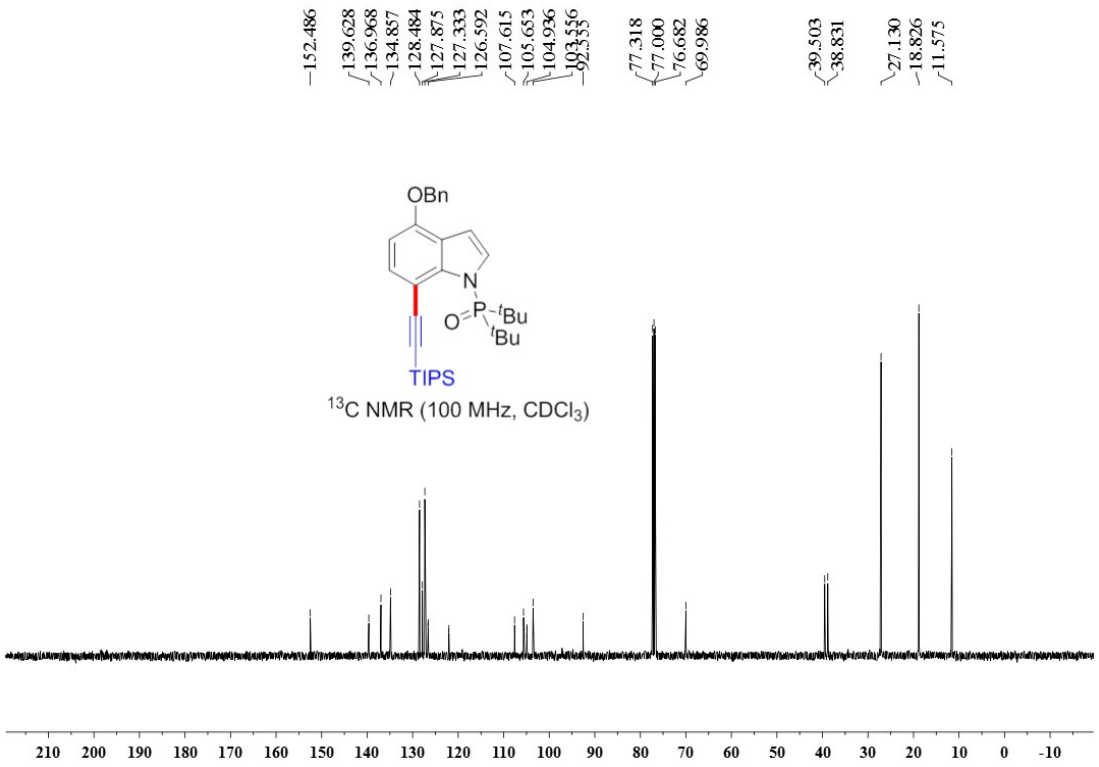


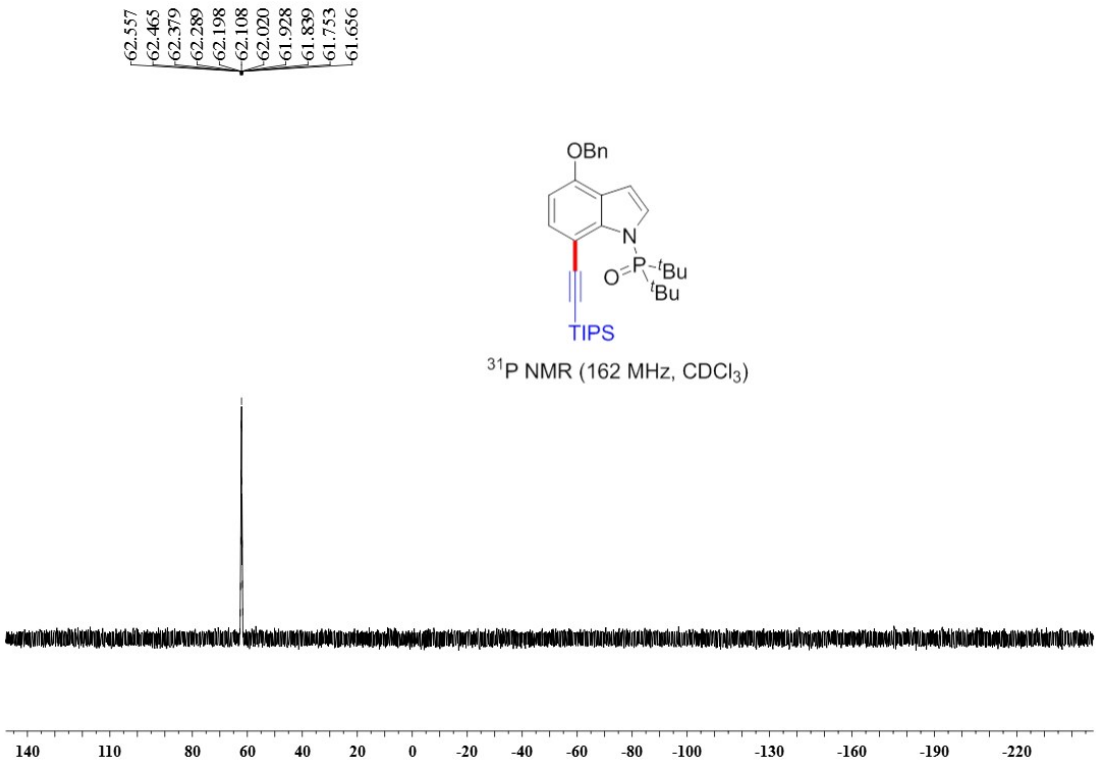




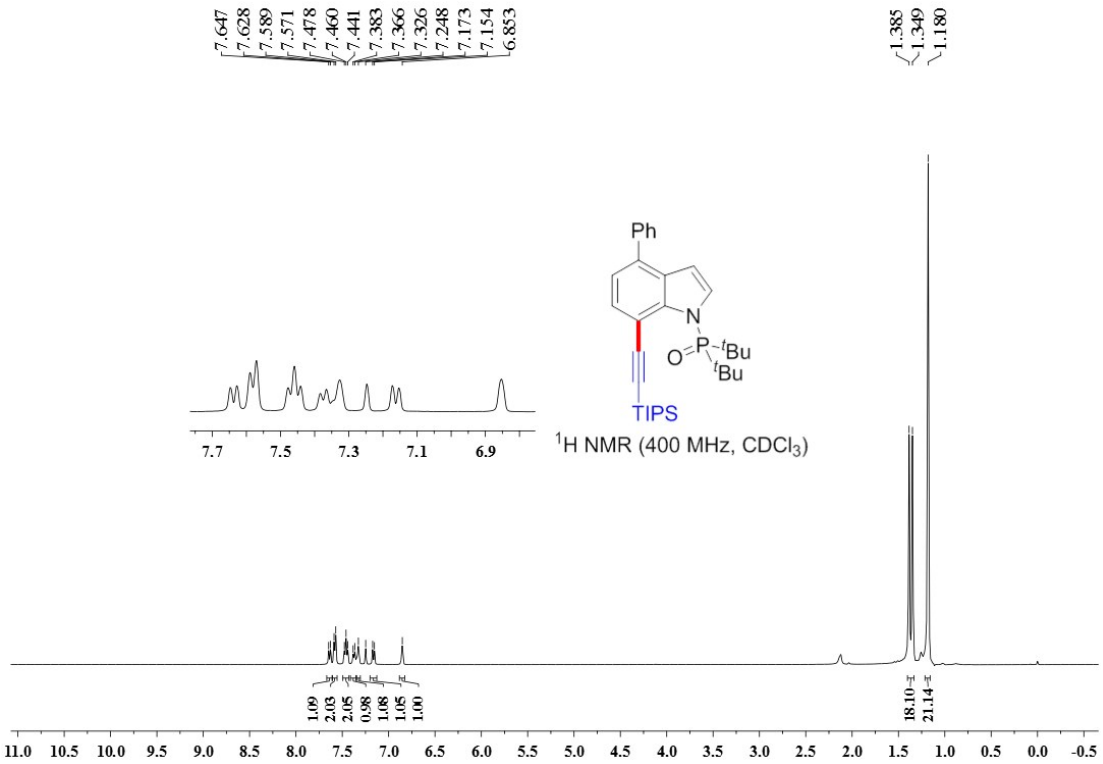
(4-(Benzyloxy)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)di-*tert*-butylphosphine oxide (3d)

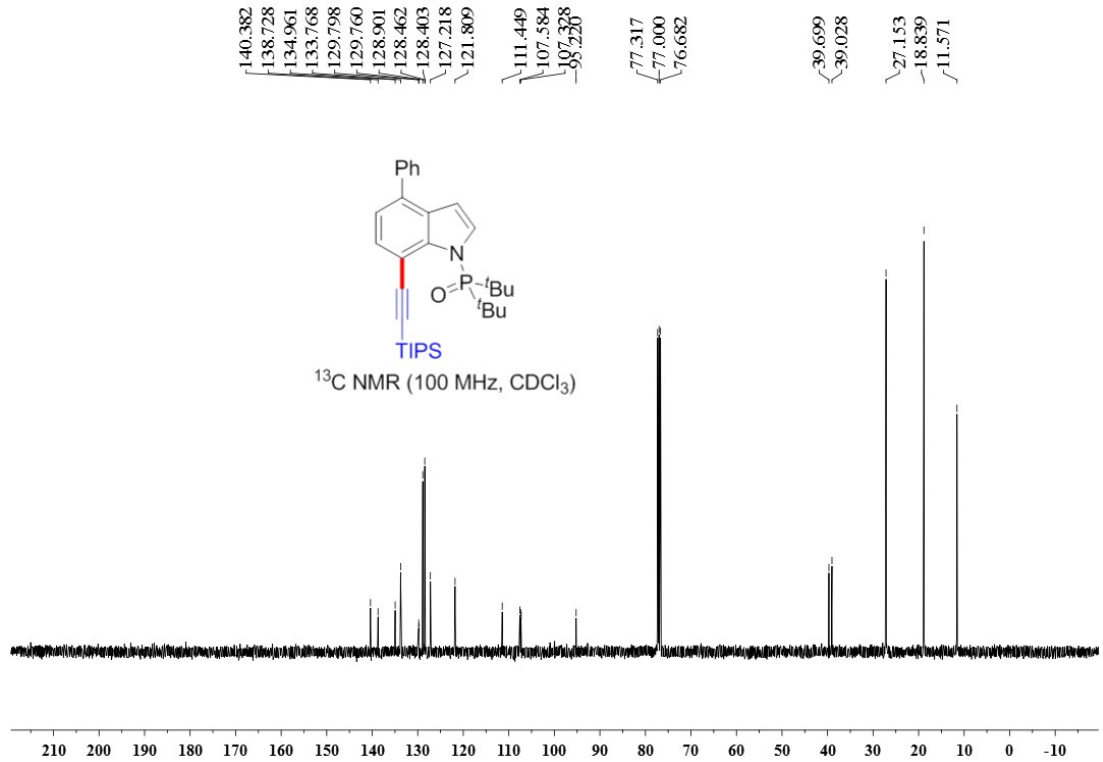


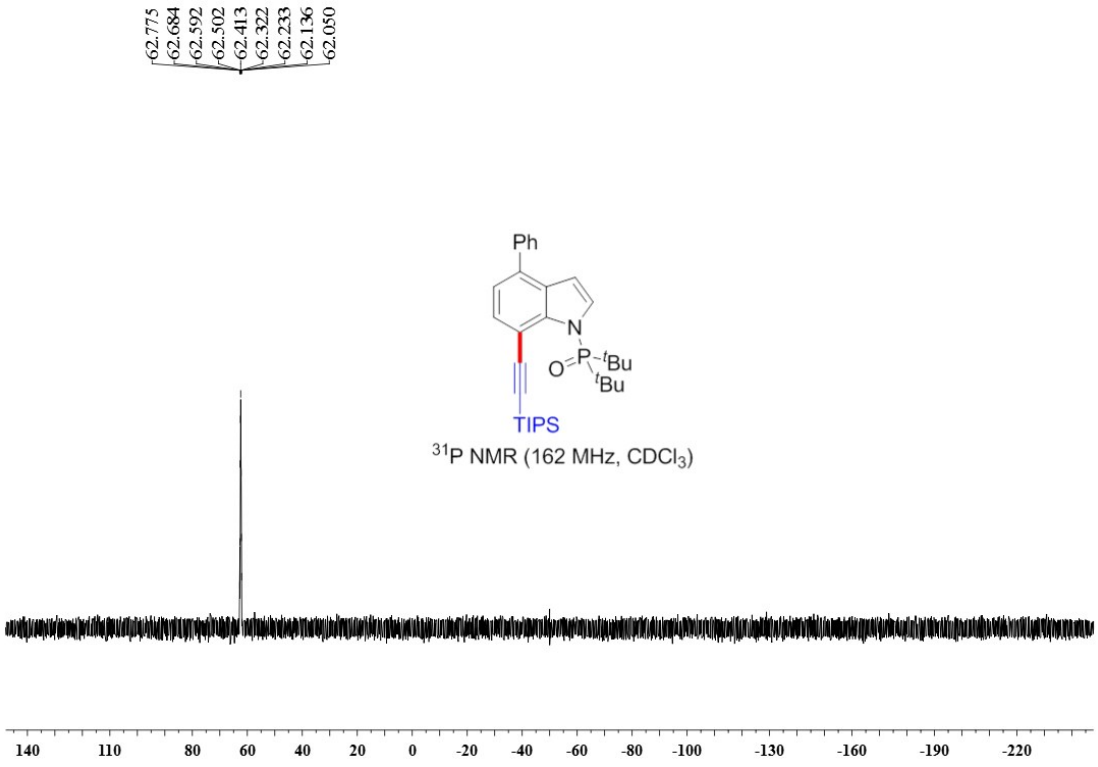

152.486
139.628
136.968
134.857
128.484
127.875
127.333
126.592
107.615
105.653
104.936
103.556
92.355
77.318
77.000
76.682
69.986
39.503
38.831
27.130
18.826
11.575
OBn
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


62.557
62.465
62.379
62.289
62.198
62.108
62.020
61.928
61.839
61.753
61.656
OBn
N
O
P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

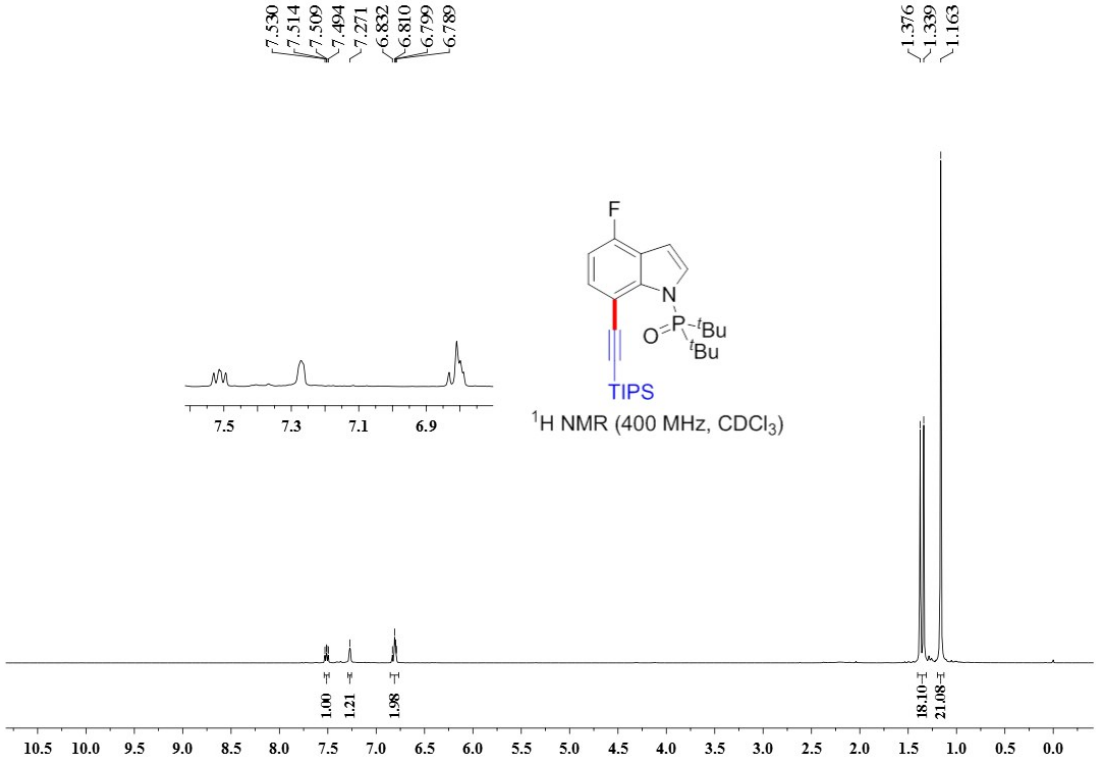
Di-*tert*-butyl(4-phenyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3e)

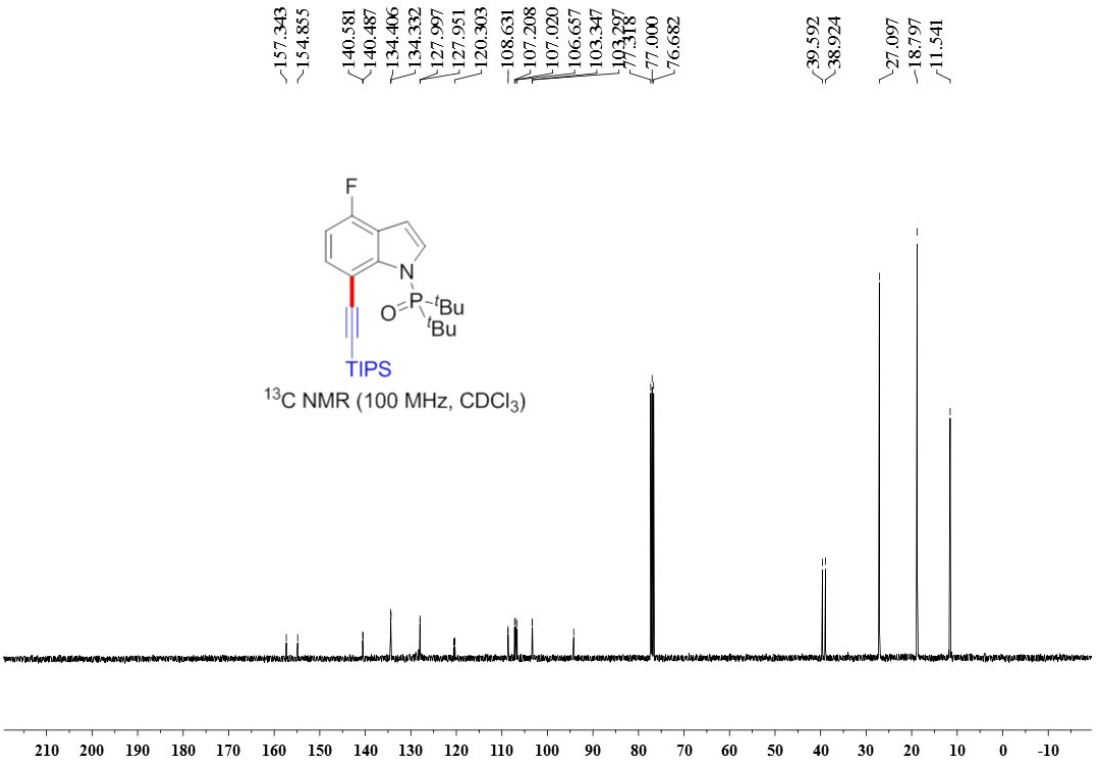


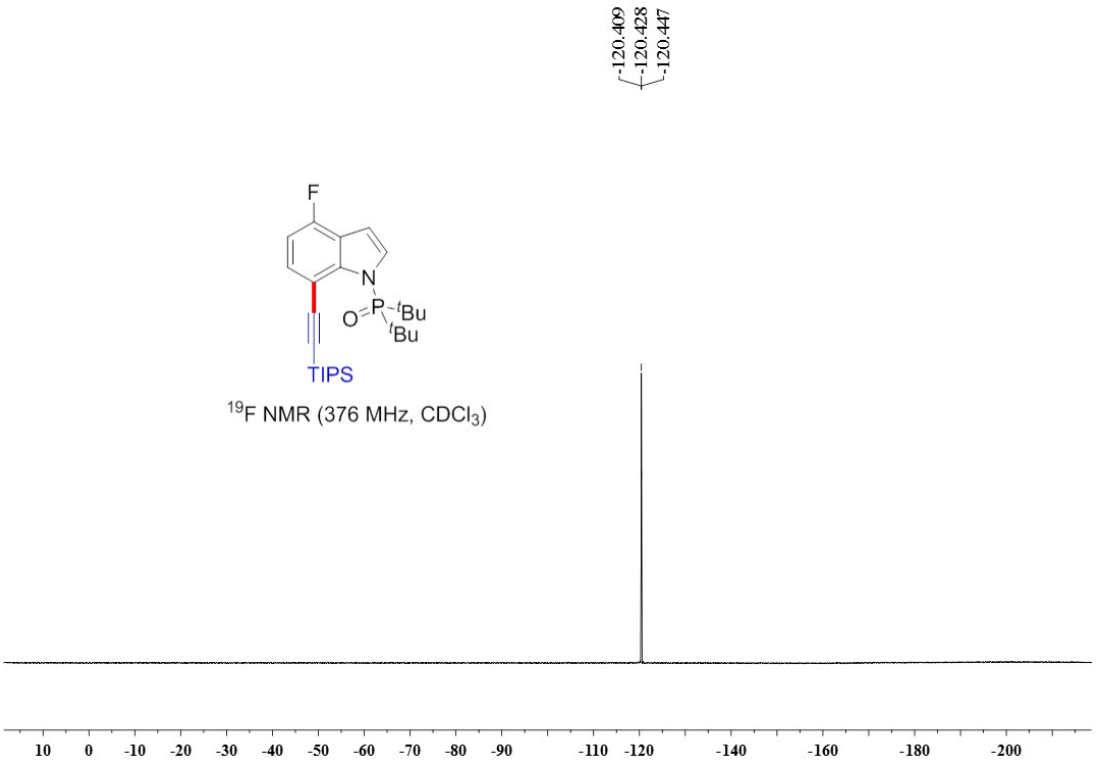


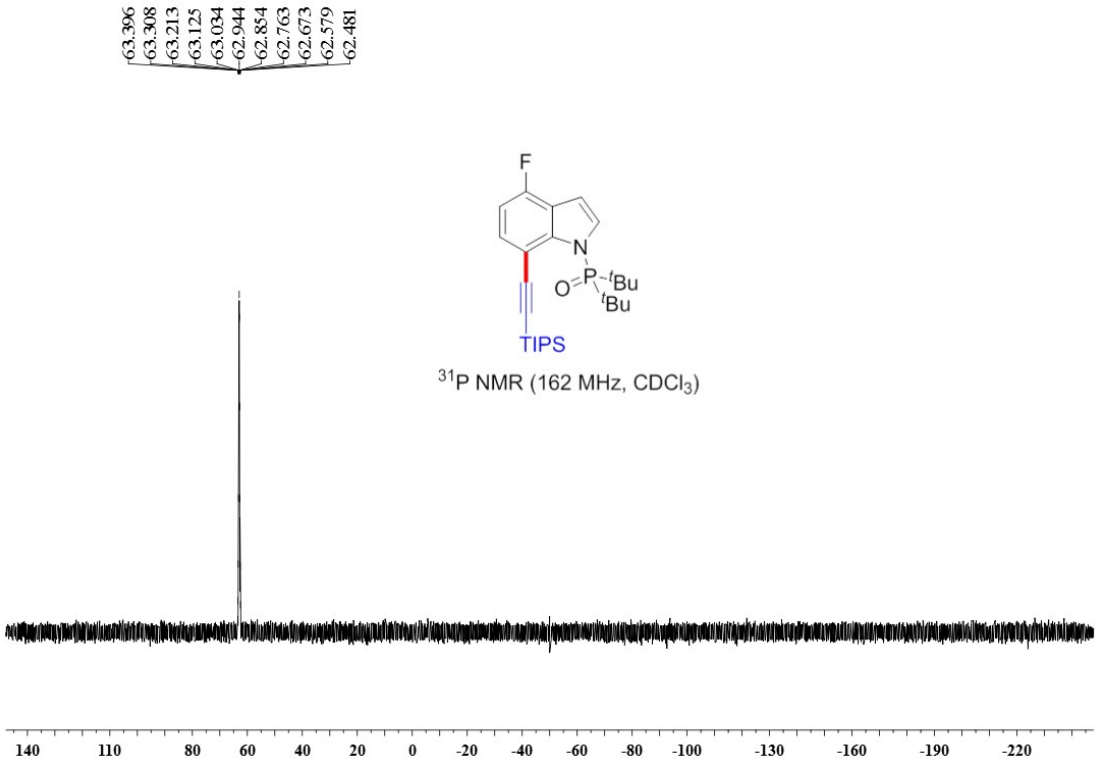


2-(4-Fluoro-2-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)aniline (3f)

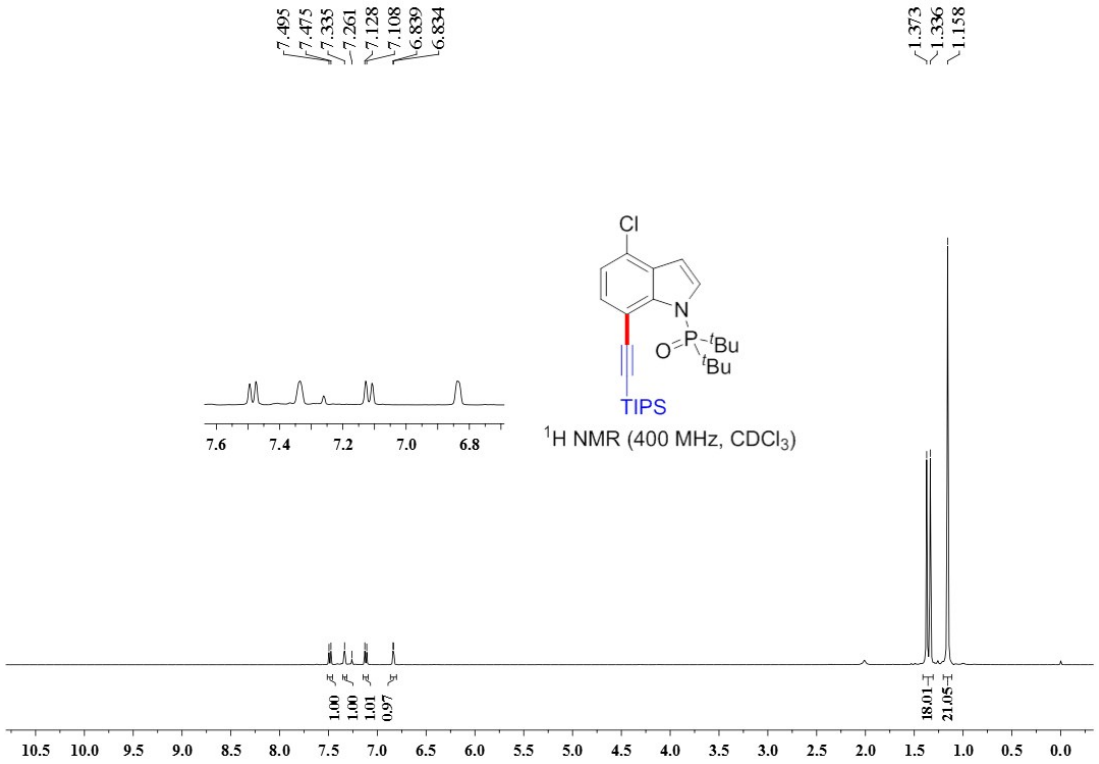


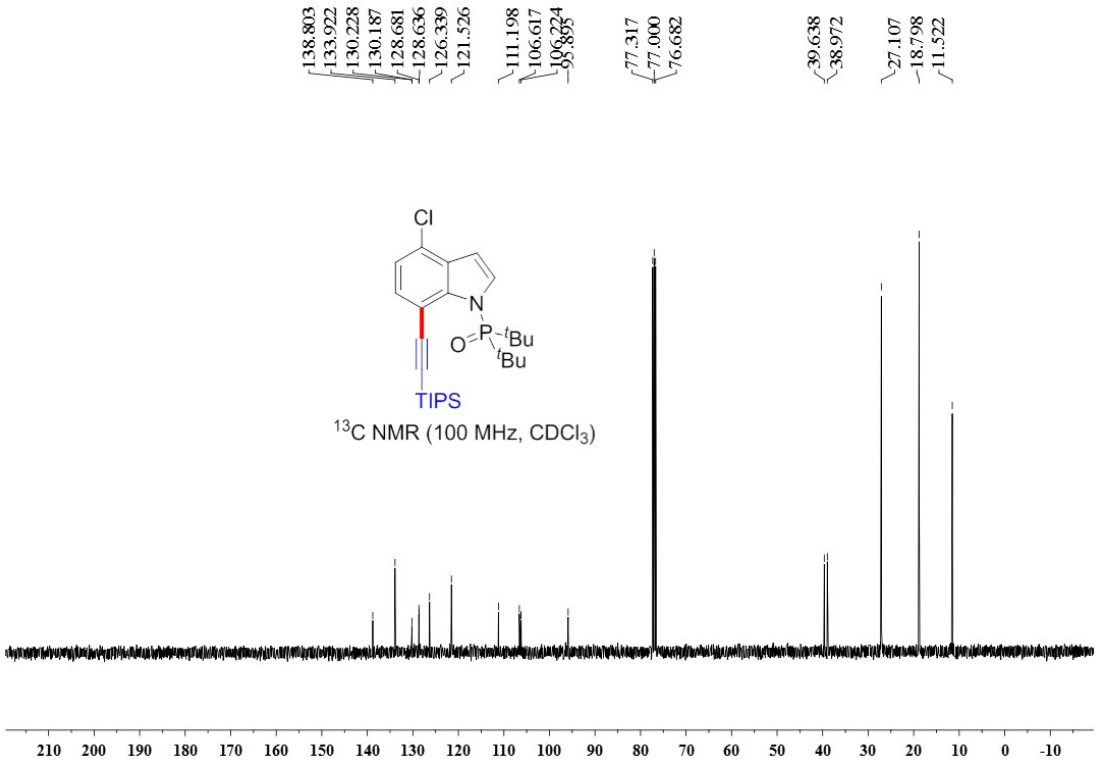

157.343
154.855
140.581
140.487
134.406
134.332
127.997
127.951
120.303
108.631
107.208
107.020
106.657
103.347
103.297
77.318
77.000
76.682
39.592
38.924
27.097
18.797
11.541
F
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


-120.409
-120.428
-120.447
F
N
O
P
tBu
tBu
TIPS
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -140 -160 -180 -200

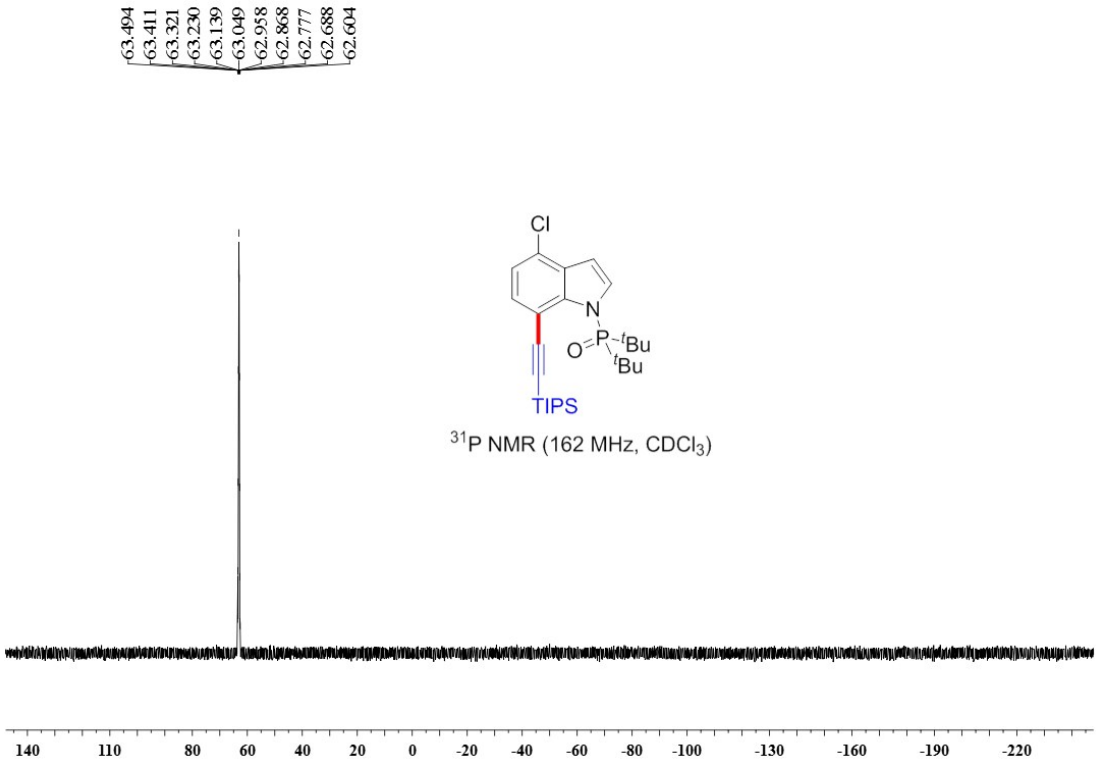


Di-*tert*-butyl(4-chloro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3g)



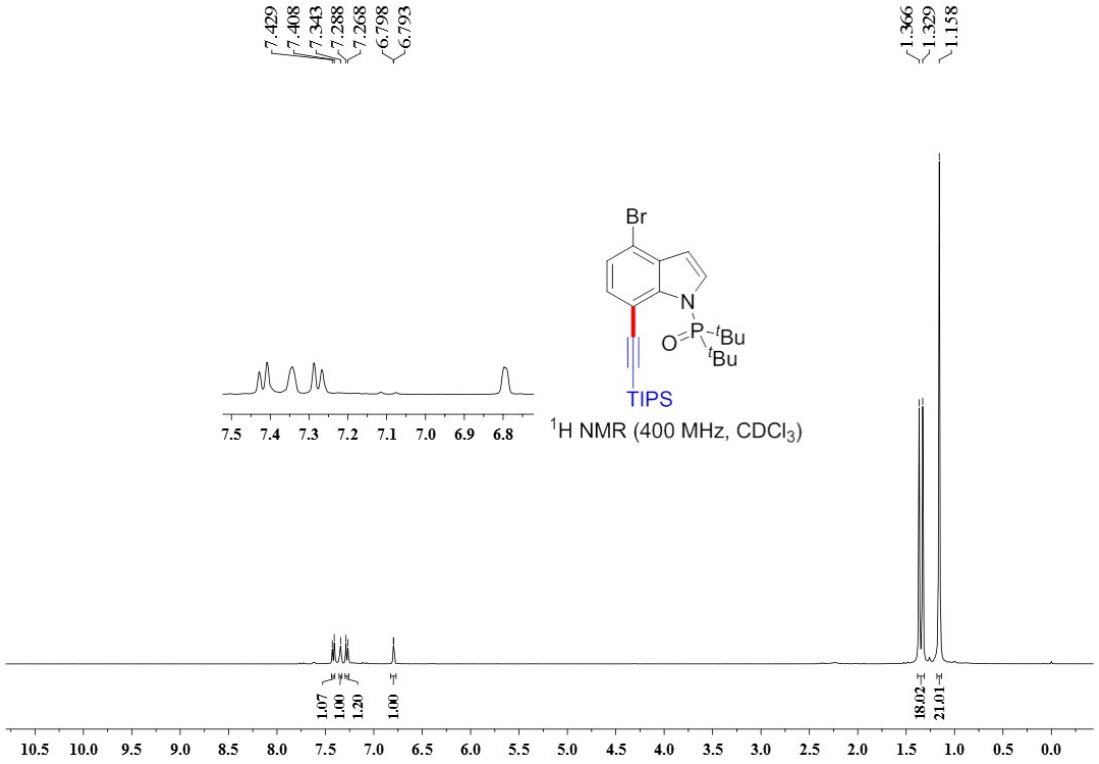


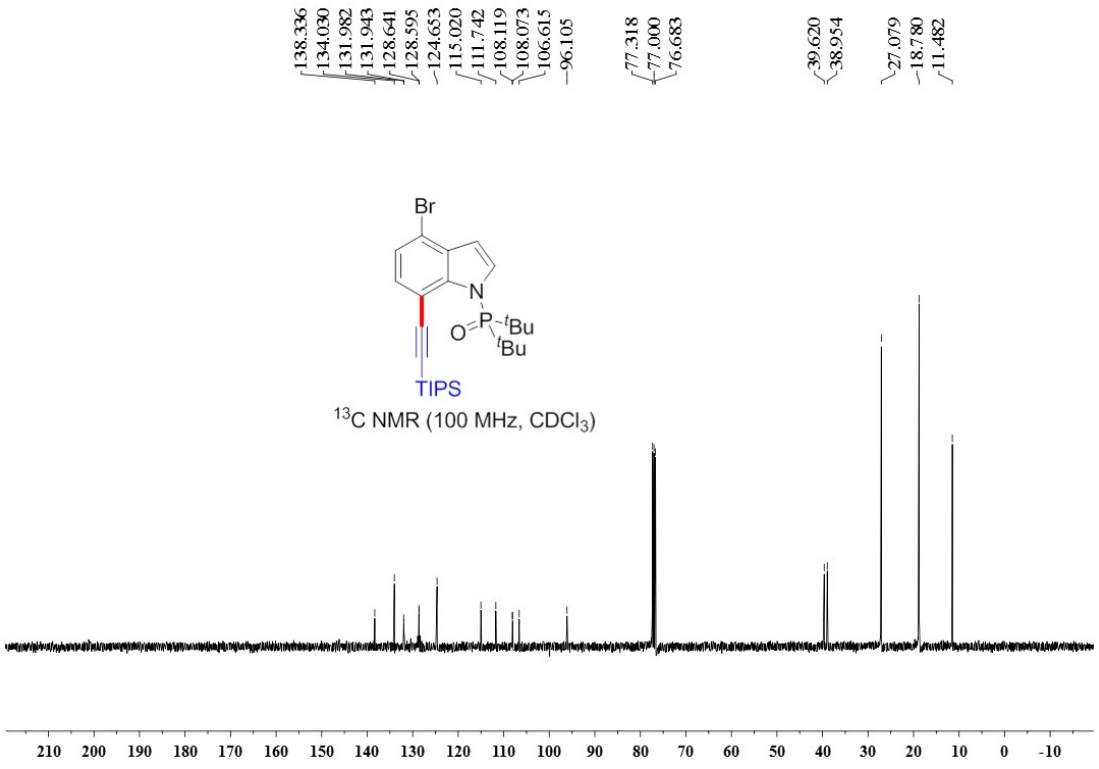
^{13}C NMR (100 MHz, $CDCl_3$)

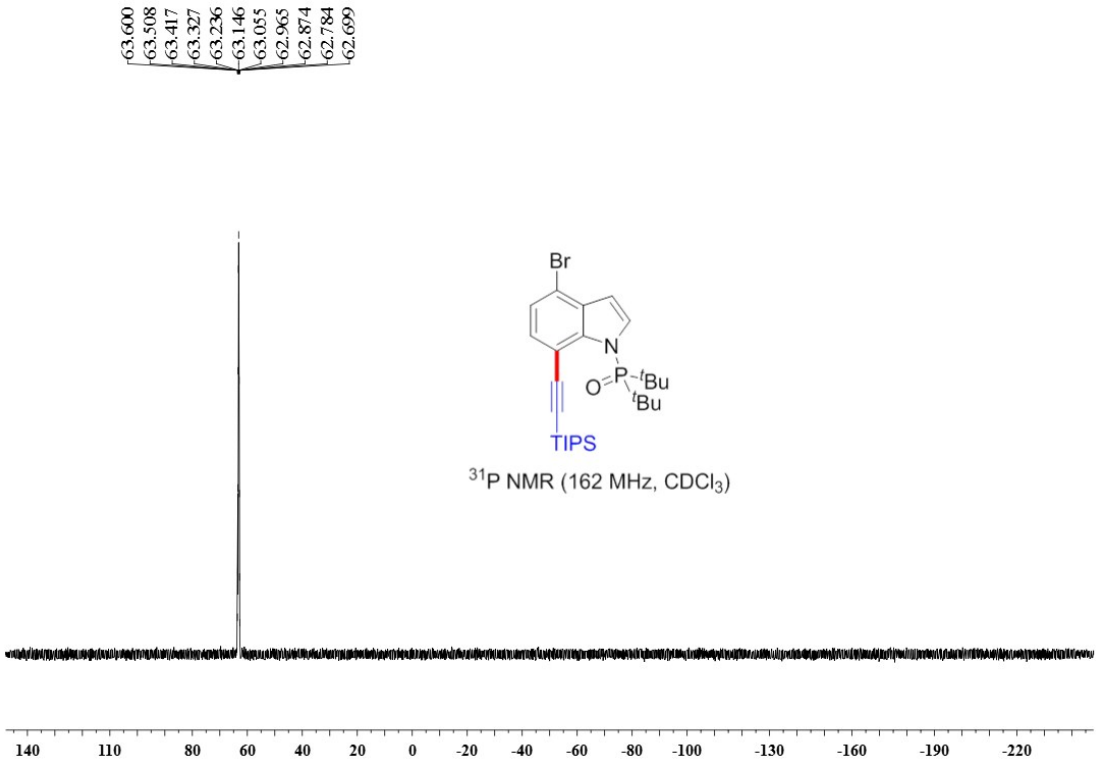


^{31}P NMR (162 MHz, $CDCl_3$)

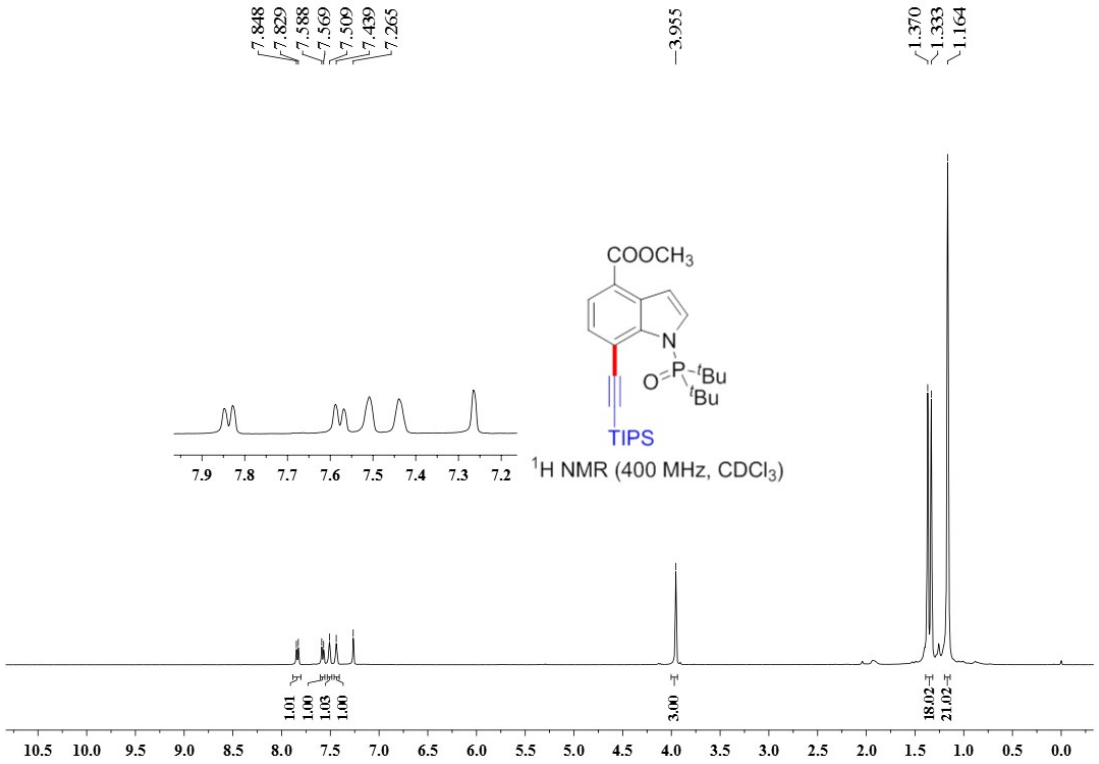
(4-Bromo-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)di-tert-butylphosphine oxide (3h)

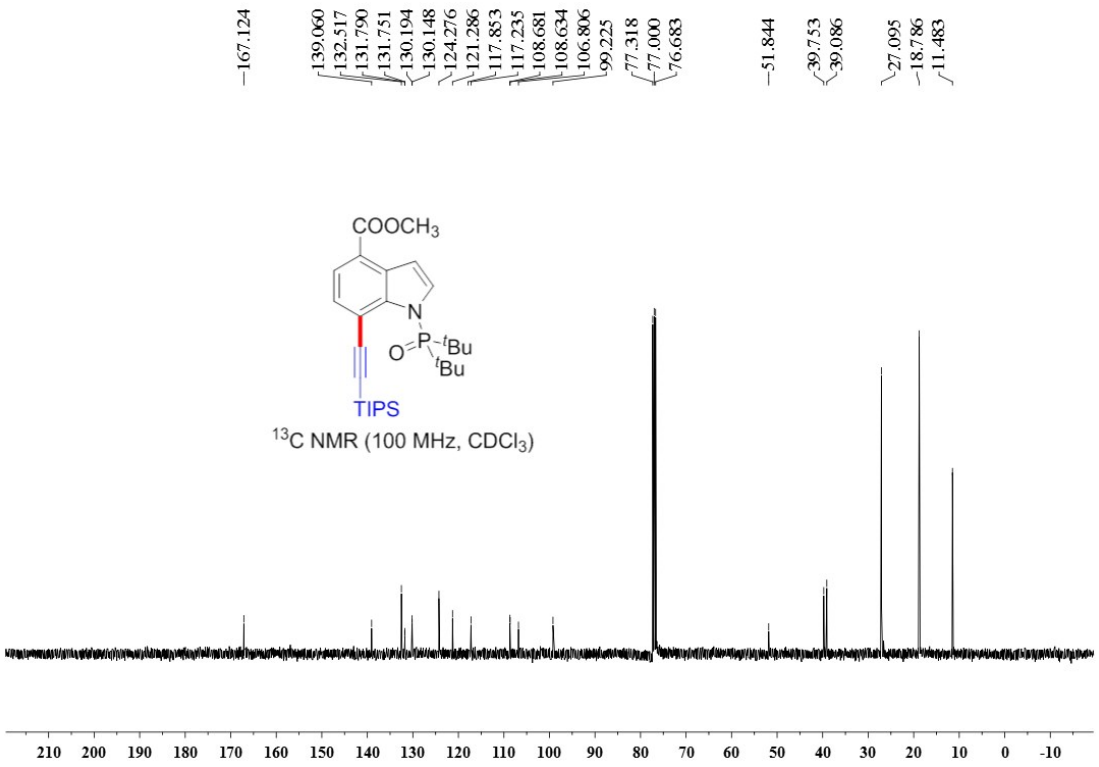


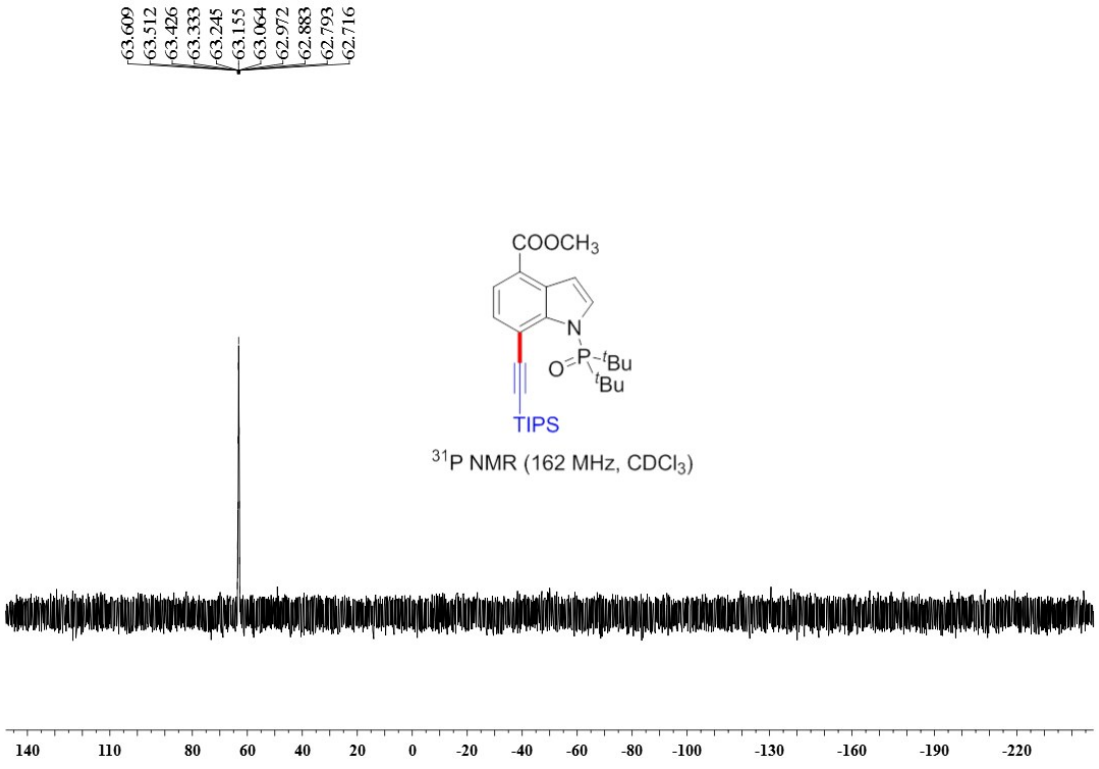




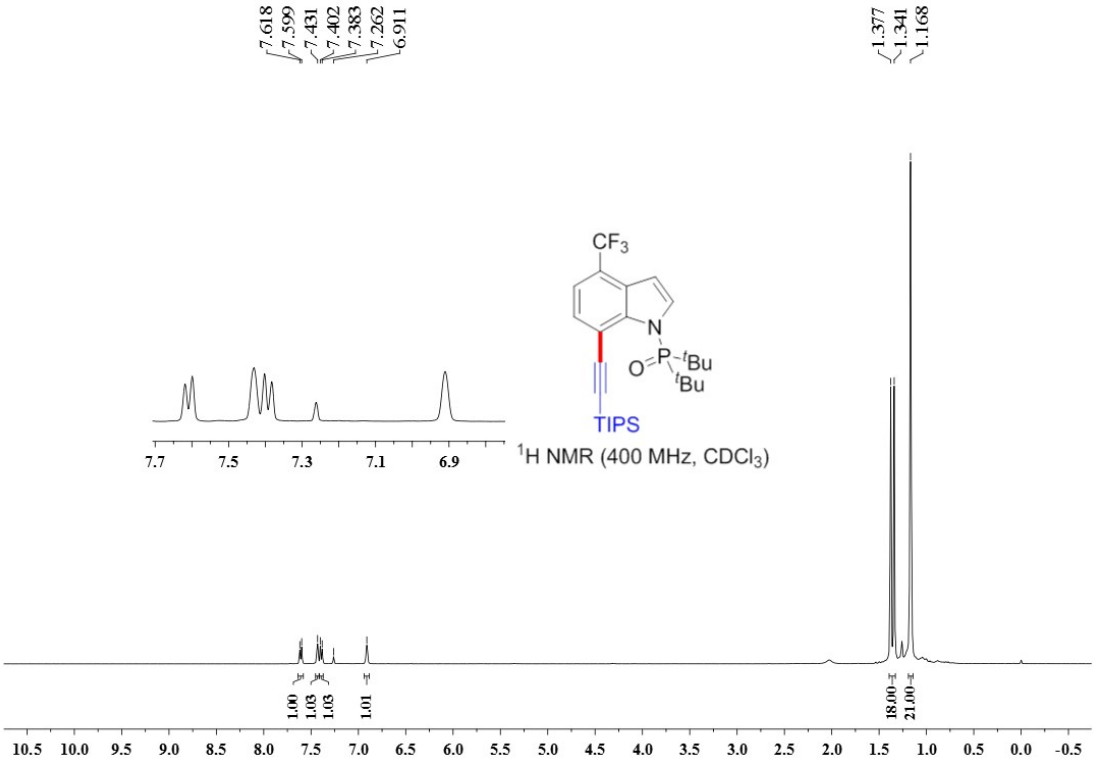
Methyl 1-(di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indole-4-carboxylate (3i)

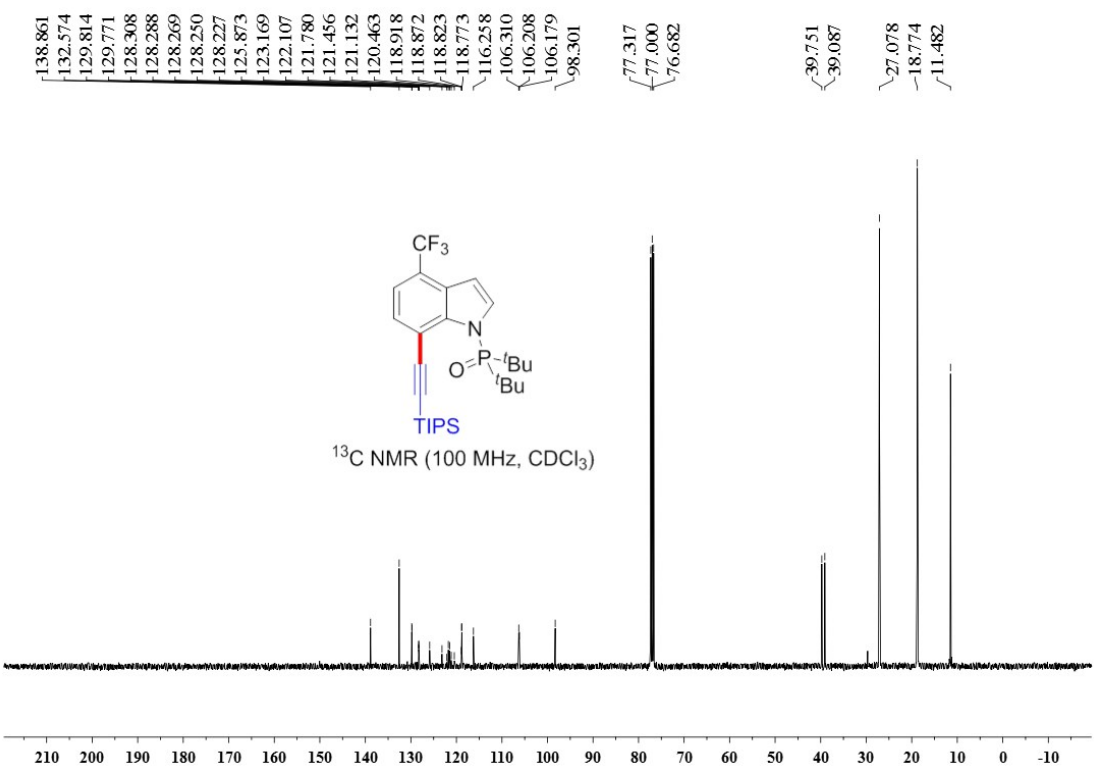


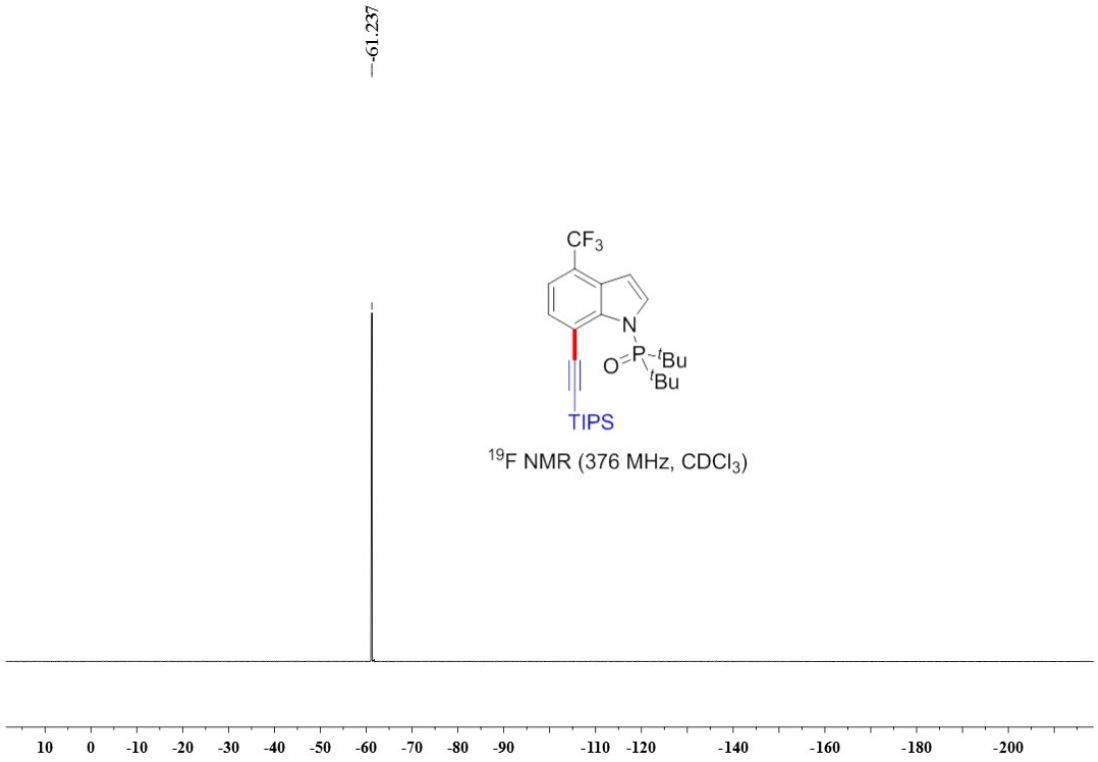

167.124
139.060
132.517
131.790
131.751
130.194
130.148
124.276
121.286
117.853
117.235
108.681
108.634
106.806
99.225
77.318
77.000
76.683
51.844
39.753
39.086
27.095
18.786
11.483
COOCH3
N
O=P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


63.609
63.512
63.426
63.333
63.245
63.155
63.064
62.972
62.883
62.793
62.716
COOCH3
N
O=P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

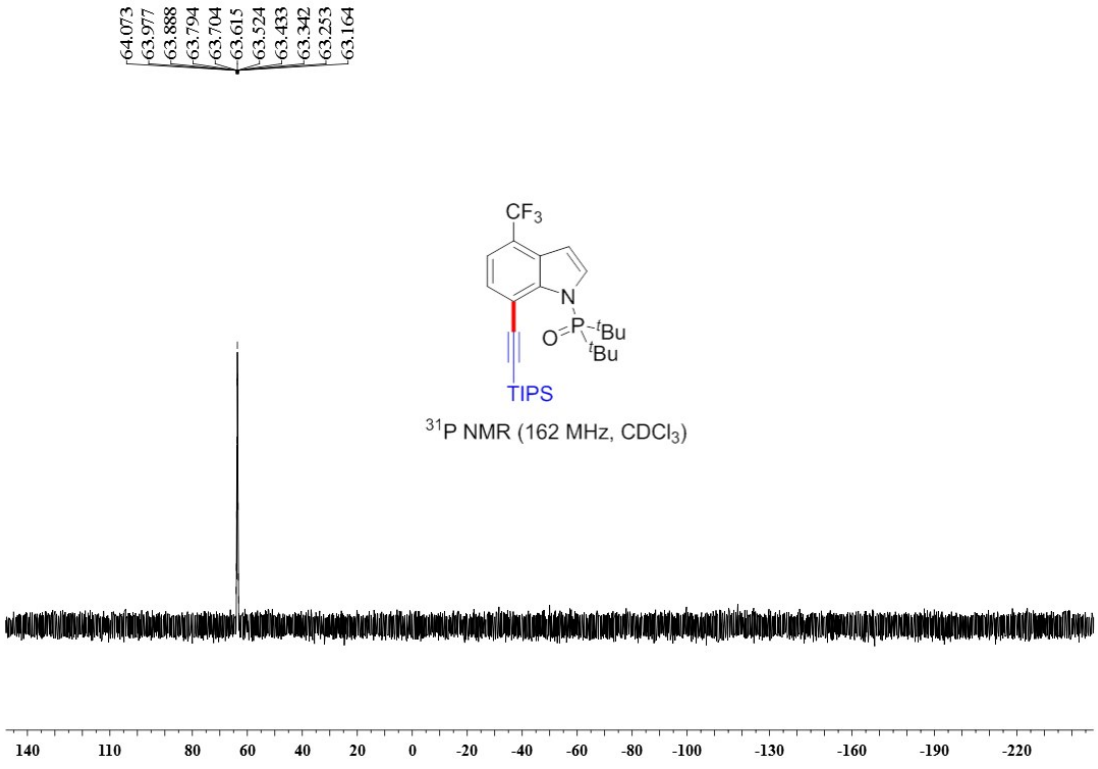
Di-*tert*-butyl(4-(trifluoromethyl)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3j)





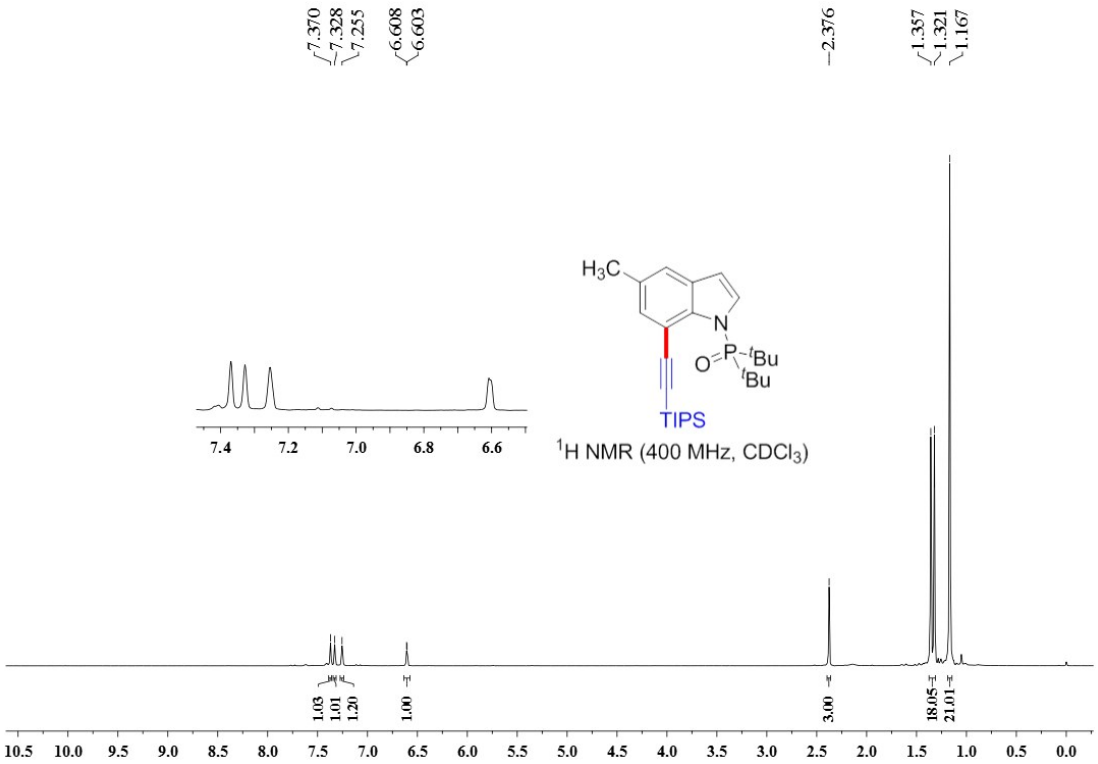


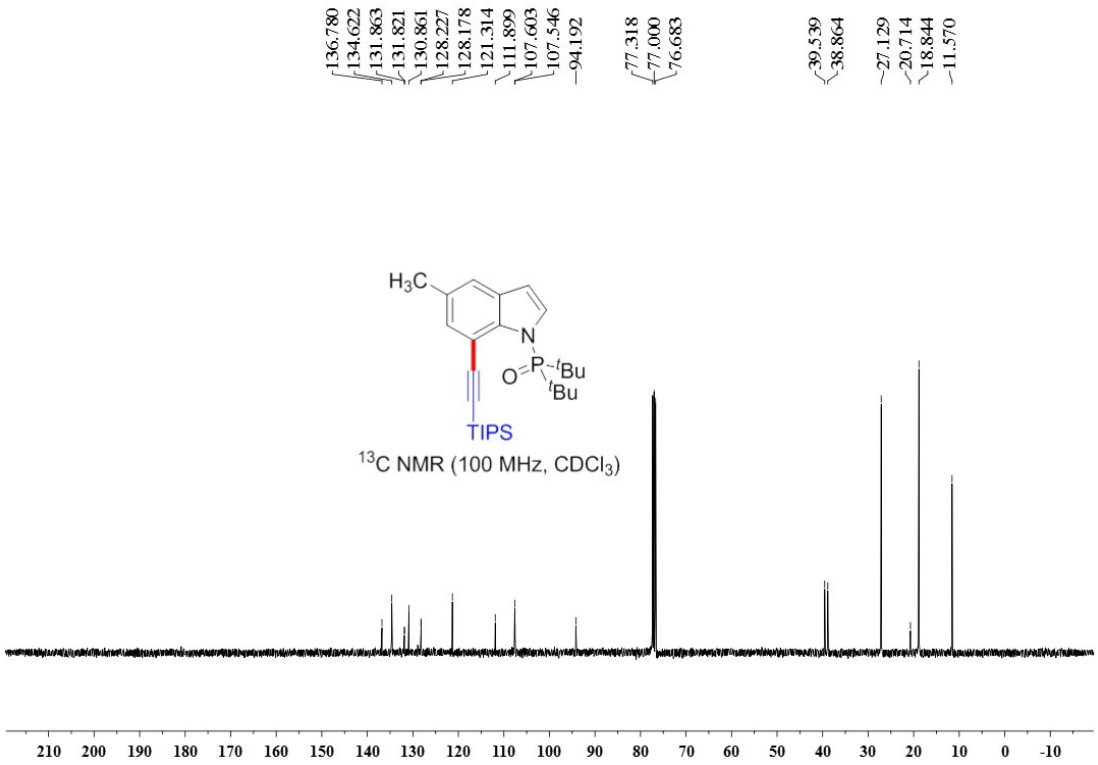
^{19}F NMR (376 MHz, $CDCl_3$)

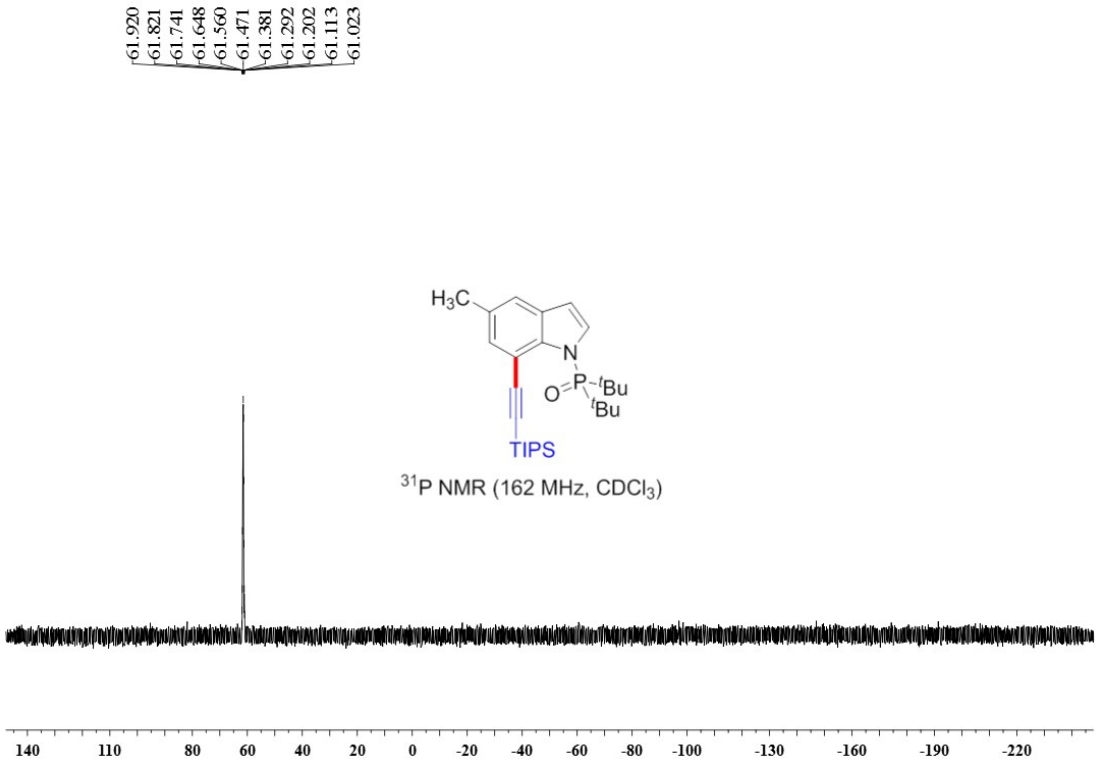


^{31}P NMR (162 MHz, $CDCl_3$)

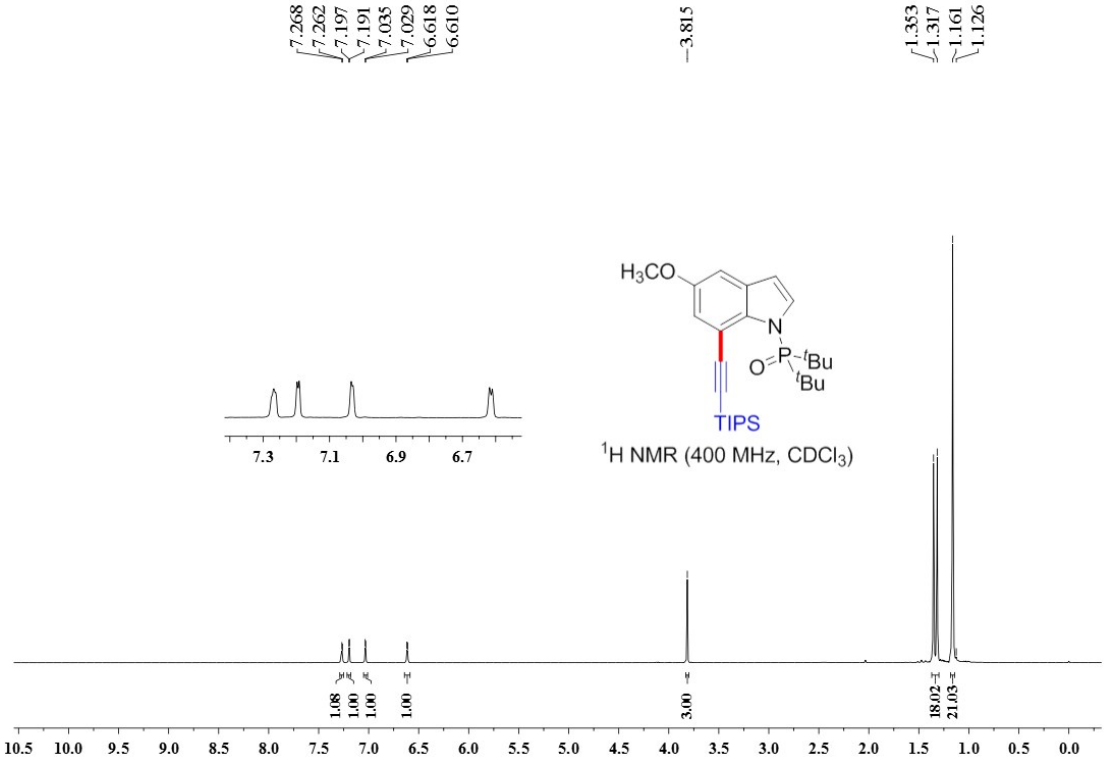
Di-*tert*-butyl(5-methyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3k)

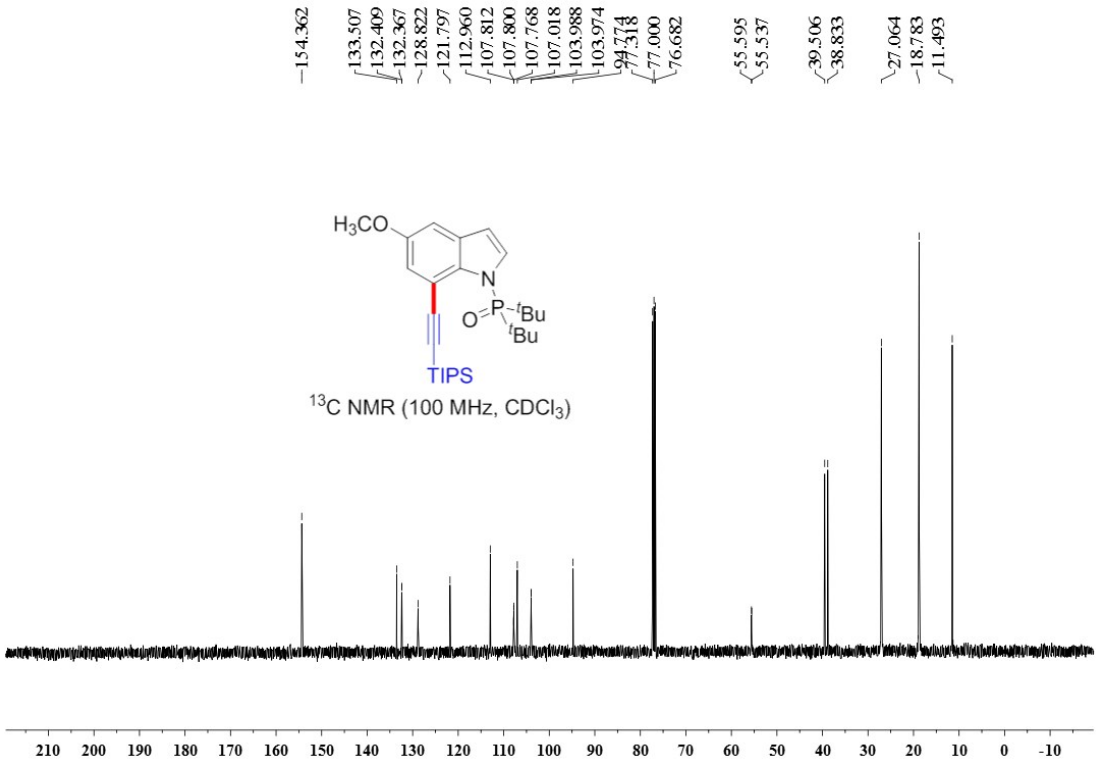


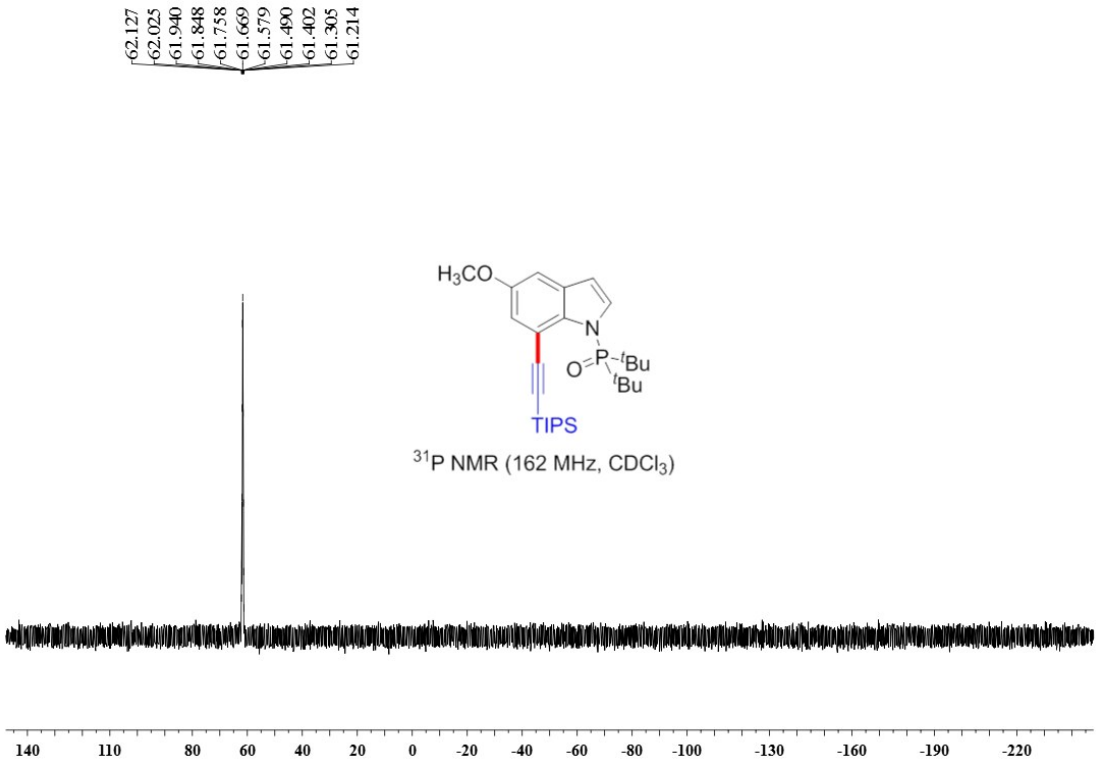




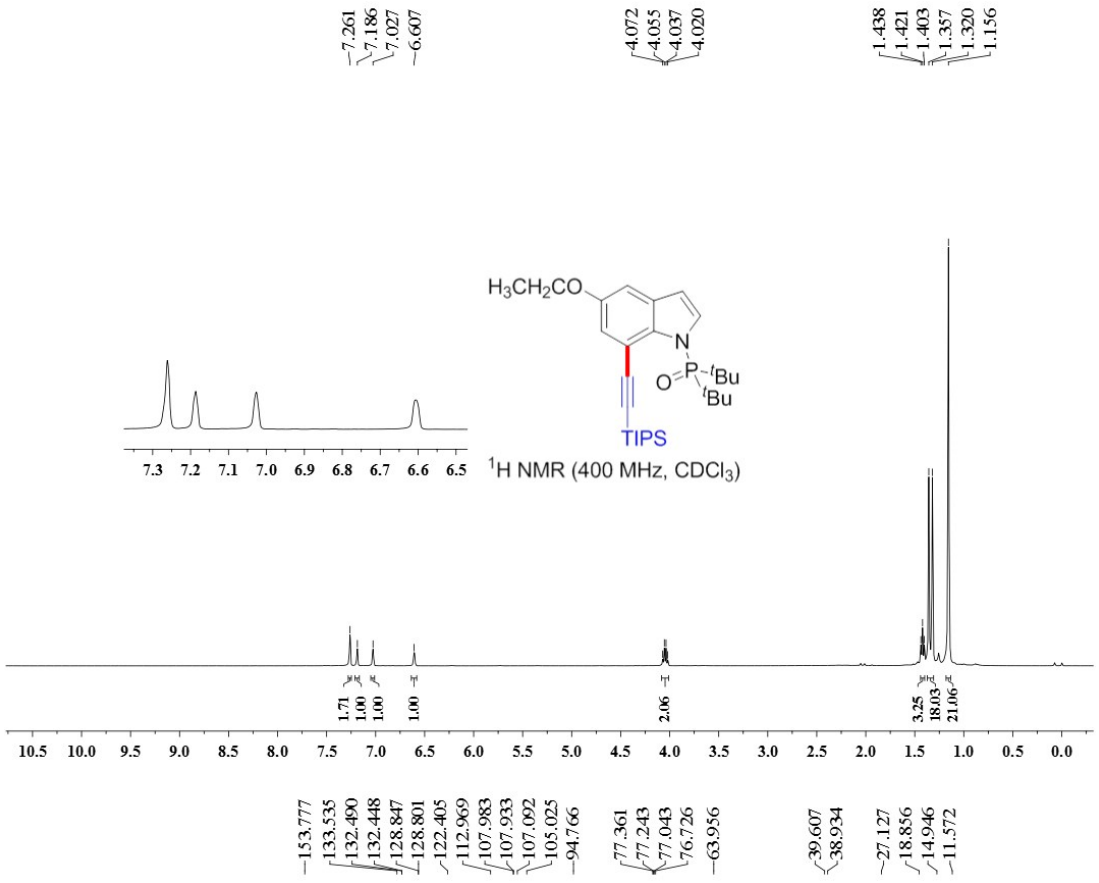
Di-*tert*-butyl(5-methoxy-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3l)

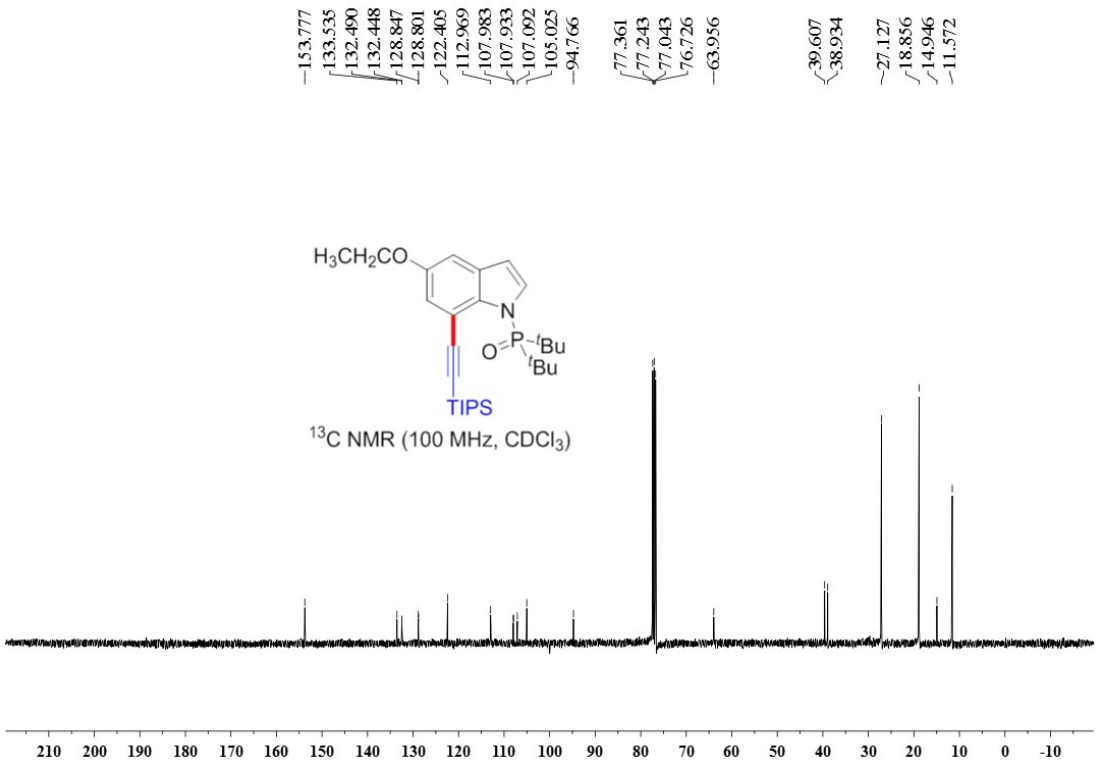


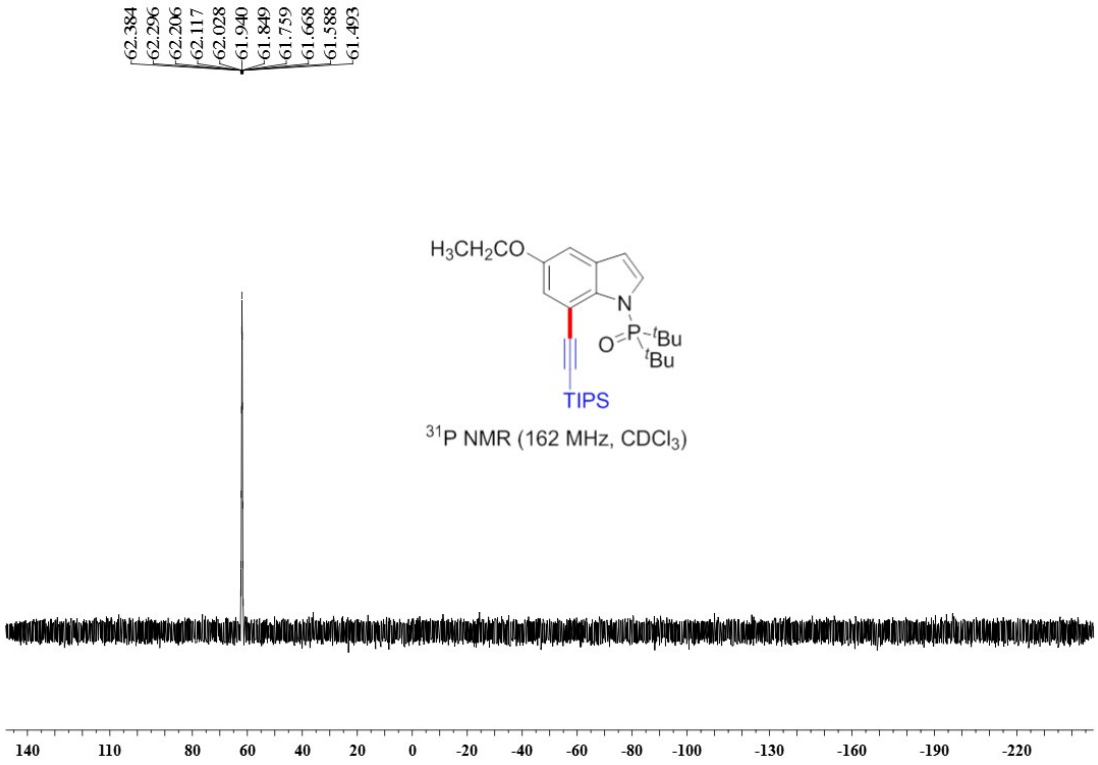

154.362
133.507
132.409
132.367
128.822
121.797
112.960
107.812
107.800
107.768
107.018
103.988
103.974
94.774
77.318
77.000
76.682
55.595
55.537
39.506
38.833
27.064
18.783
11.493
H3CO
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


62.127
62.025
61.940
61.848
61.758
61.669
61.579
61.490
61.402
61.305
61.214
H3CO
N
O
P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

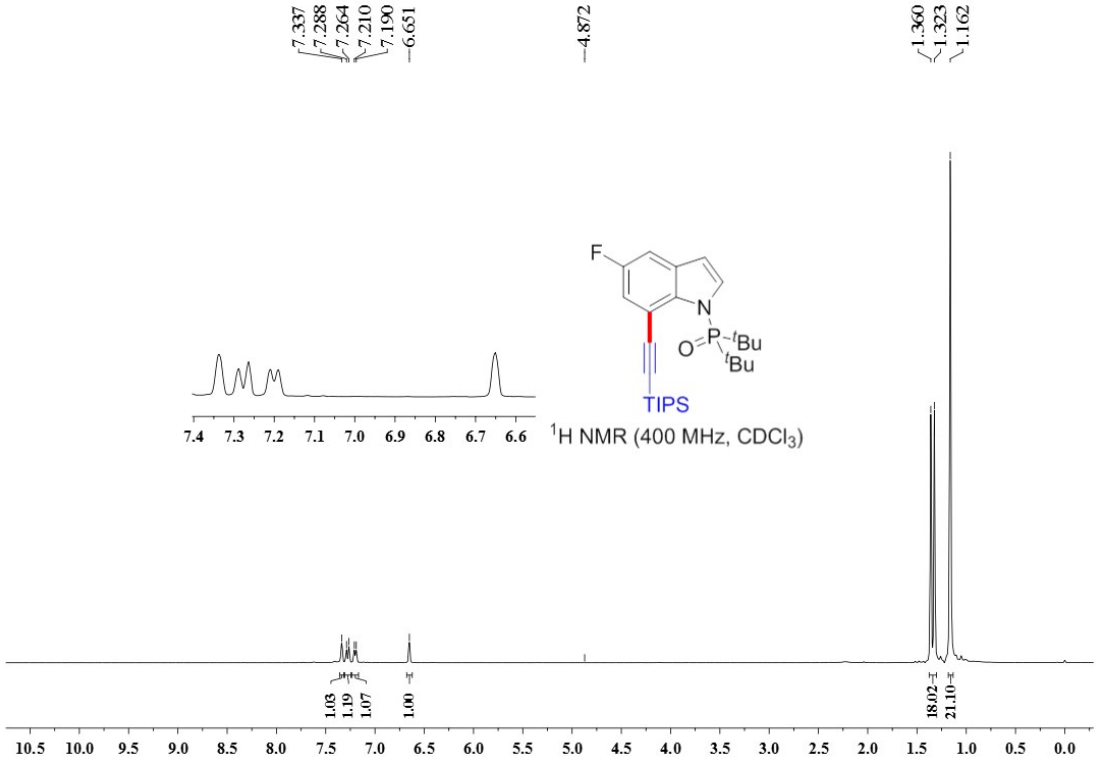
Di-*tert*-butyl(5-ethoxy-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3m)

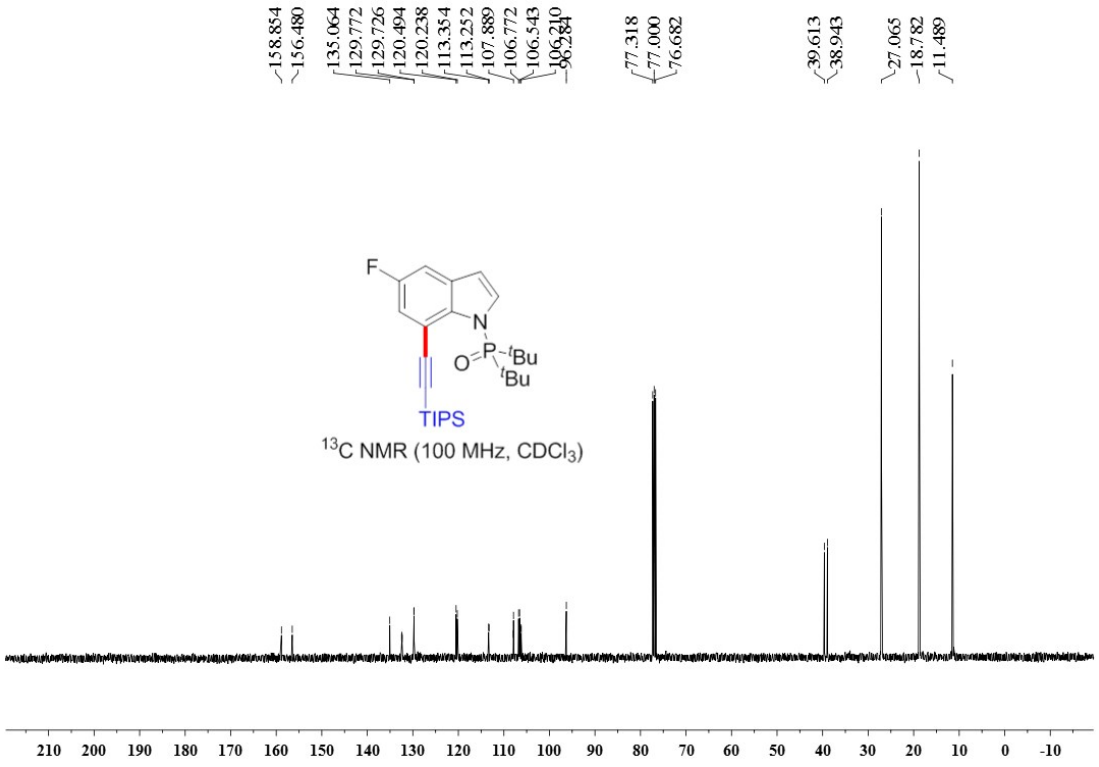


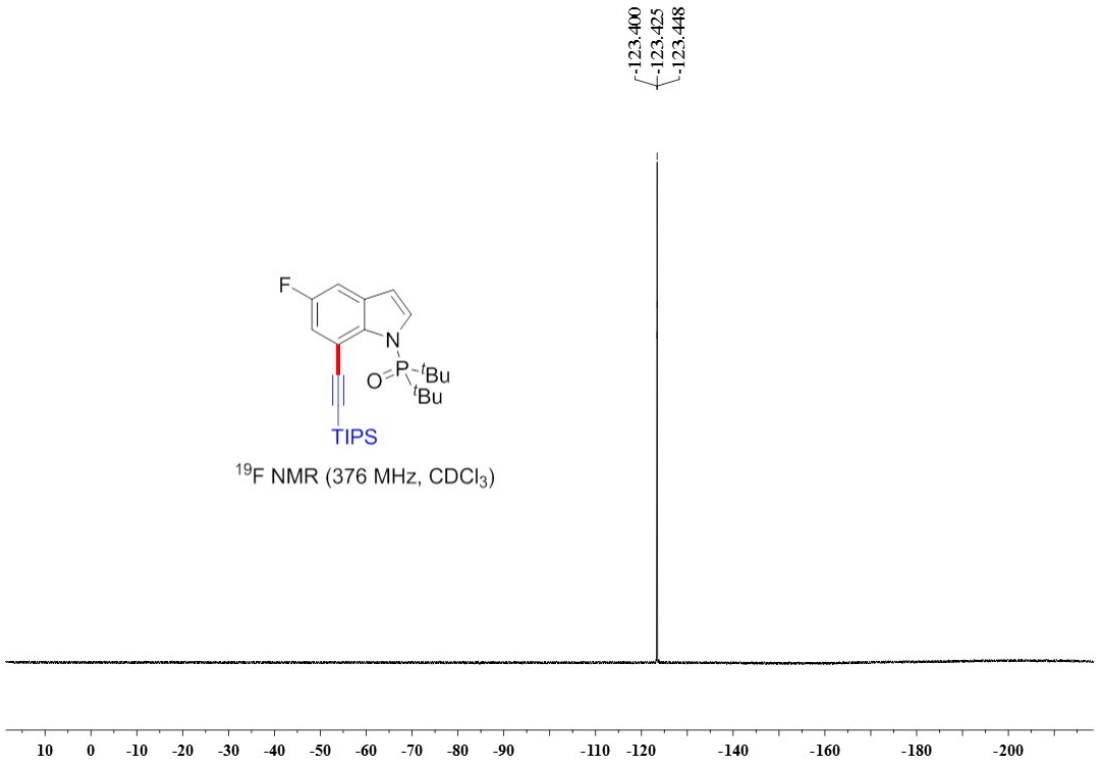


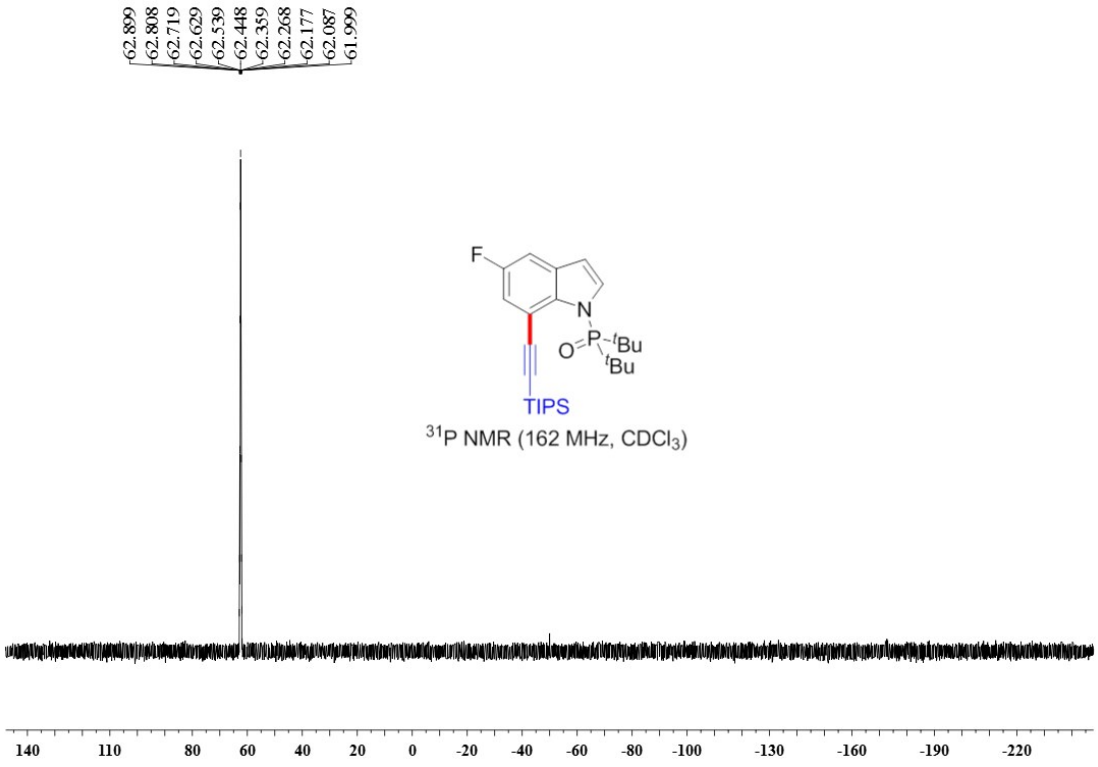


Di-*tert*-butyl(5-fluoro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3n)

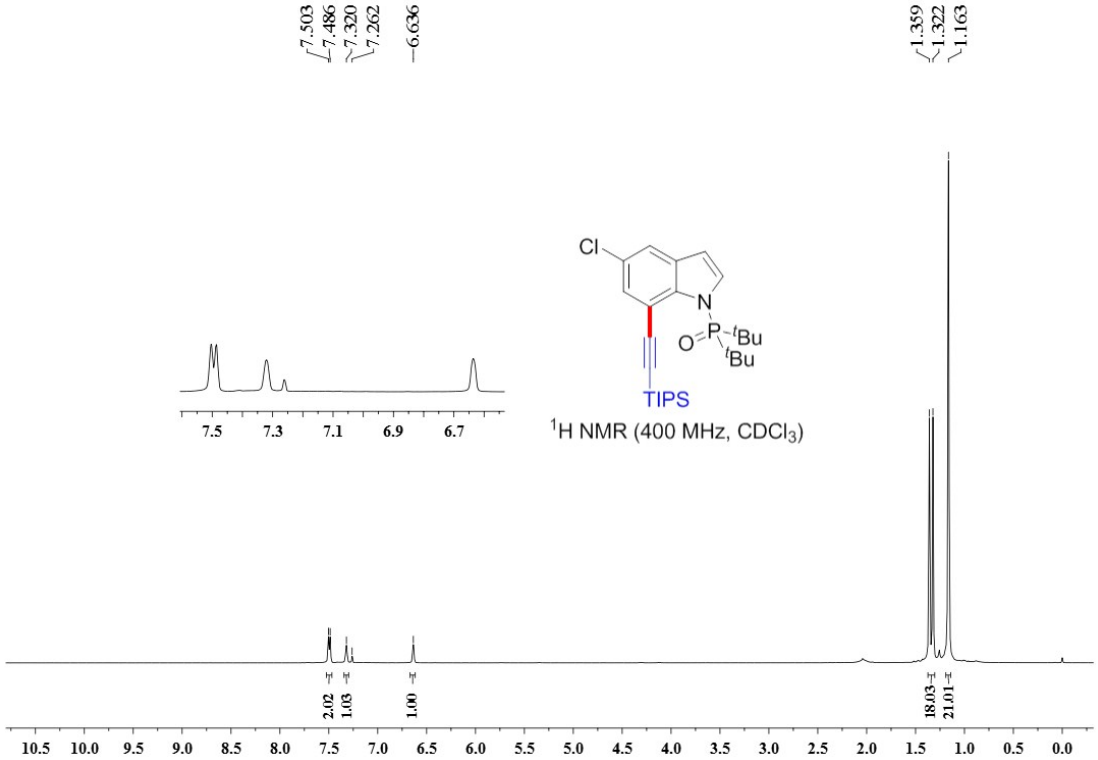


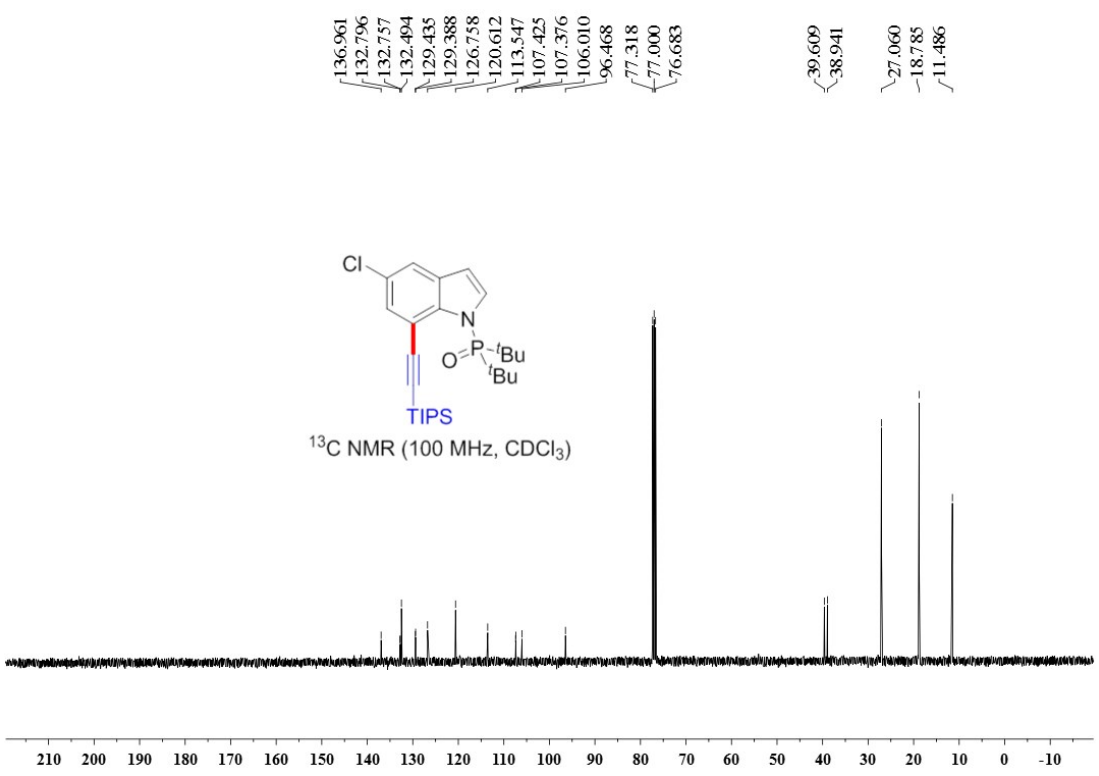

158.854
156.480
135.064
129.772
129.726
120.494
120.238
113.354
113.252
107.889
106.772
106.543
106.210
98.284
77.318
77.000
76.682
39.613
38.943
27.065
18.782
11.489
F
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

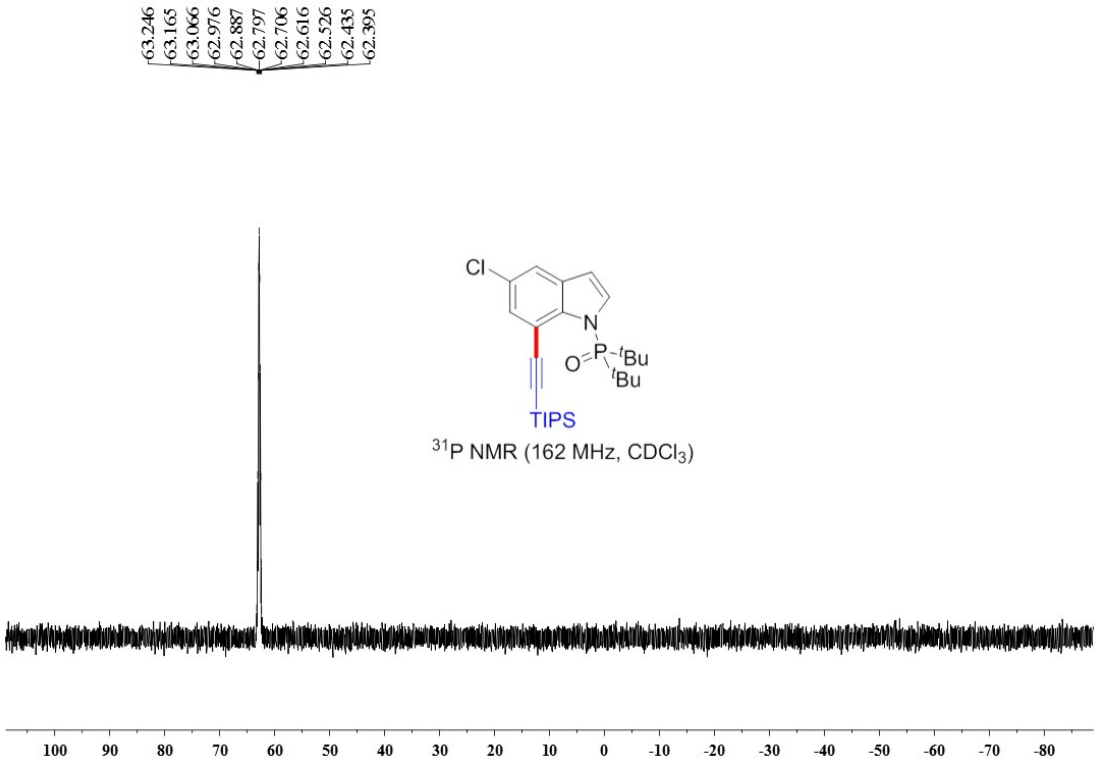

-123.400
-123.425
-123.448
F
N
O
P
tBu
tBu
TIPS
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -140 -160 -180 -200



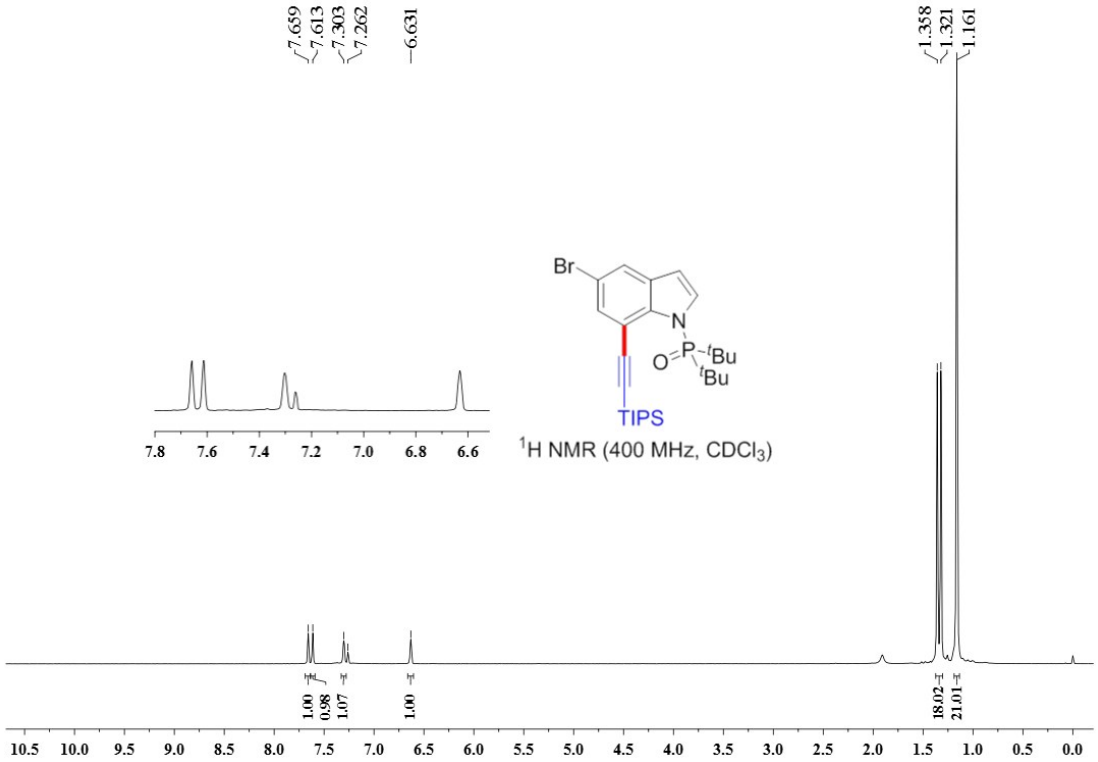
Di-*tert*-butyl(5-chloro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3o)

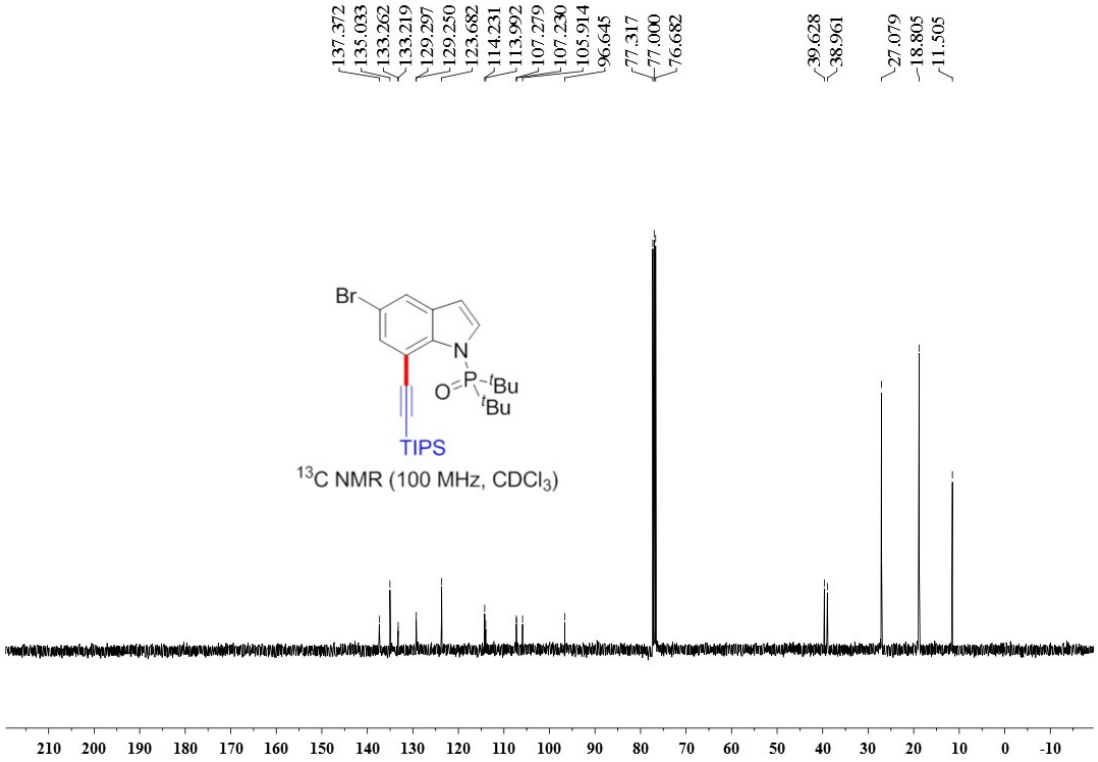


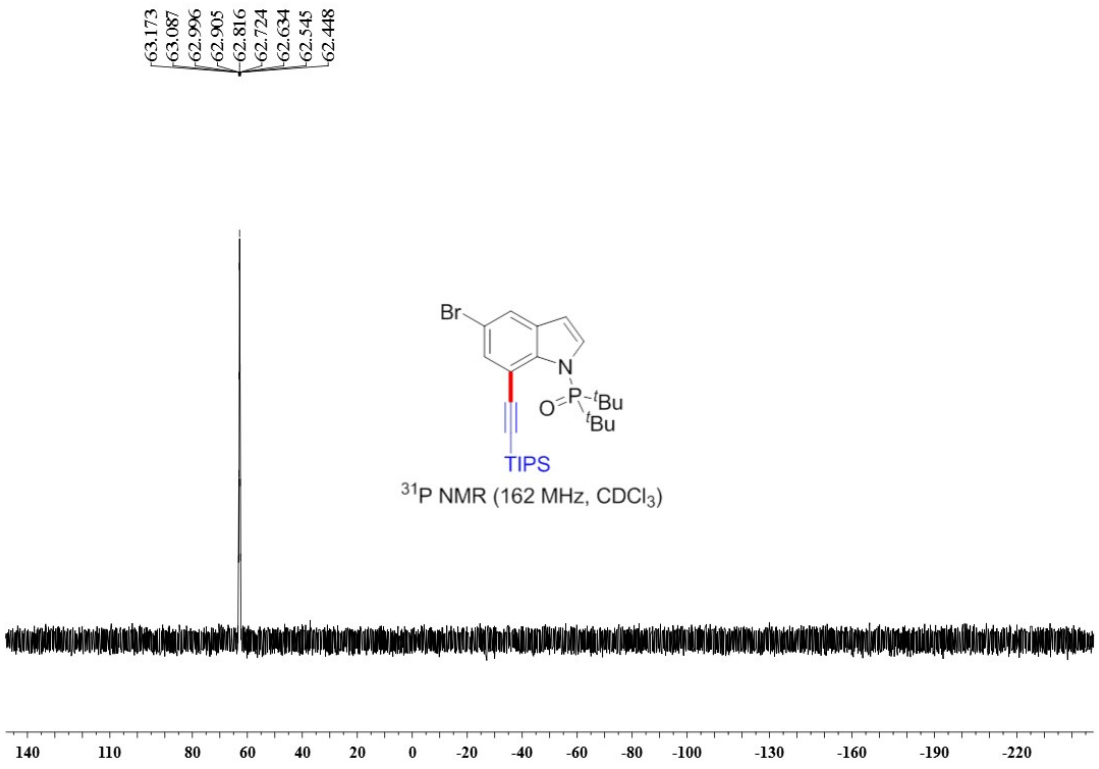

136.961
132.796
132.757
132.494
129.435
129.388
126.758
120.612
113.547
107.425
107.376
106.010
96.468
77.318
77.000
76.683
39.609
38.941
27.060
18.785
11.486
Cl
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


63.246
63.165
63.066
62.976
62.887
62.797
62.706
62.616
62.526
62.435
62.395
Cl
N
O
P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80

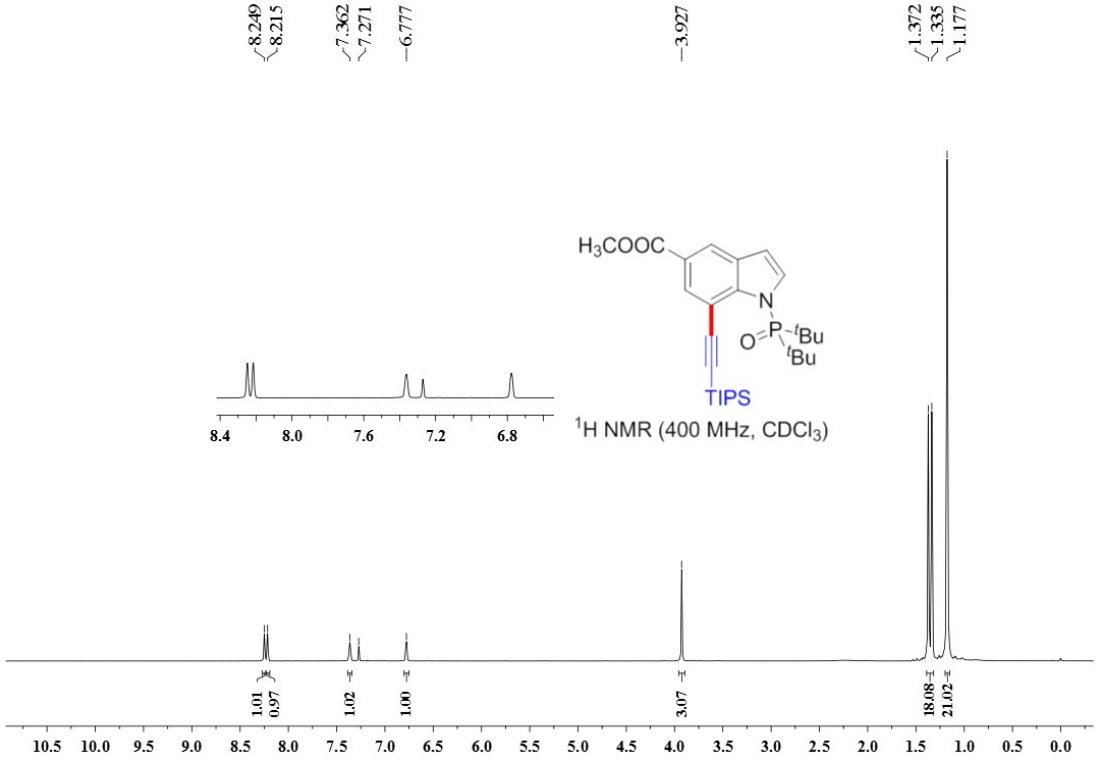
(5-Bromo-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)di-*tert*-butylphosphine oxide (3p)

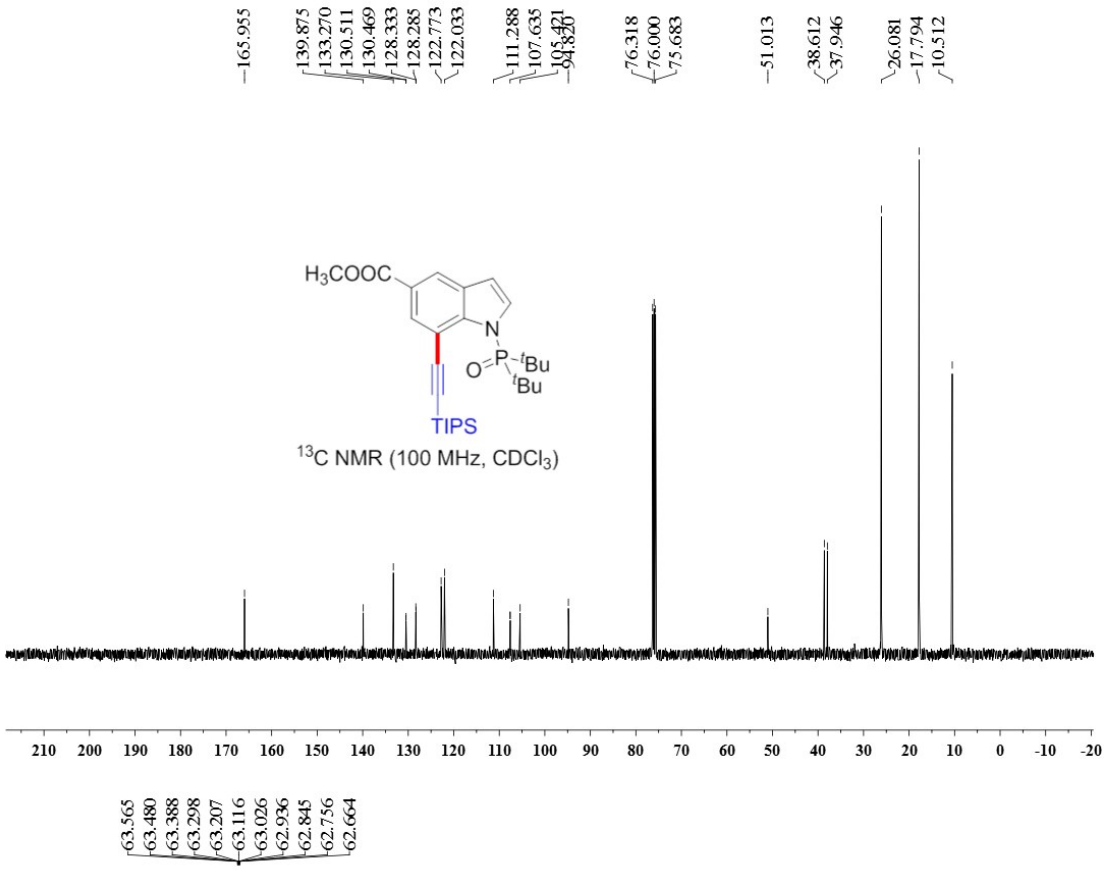


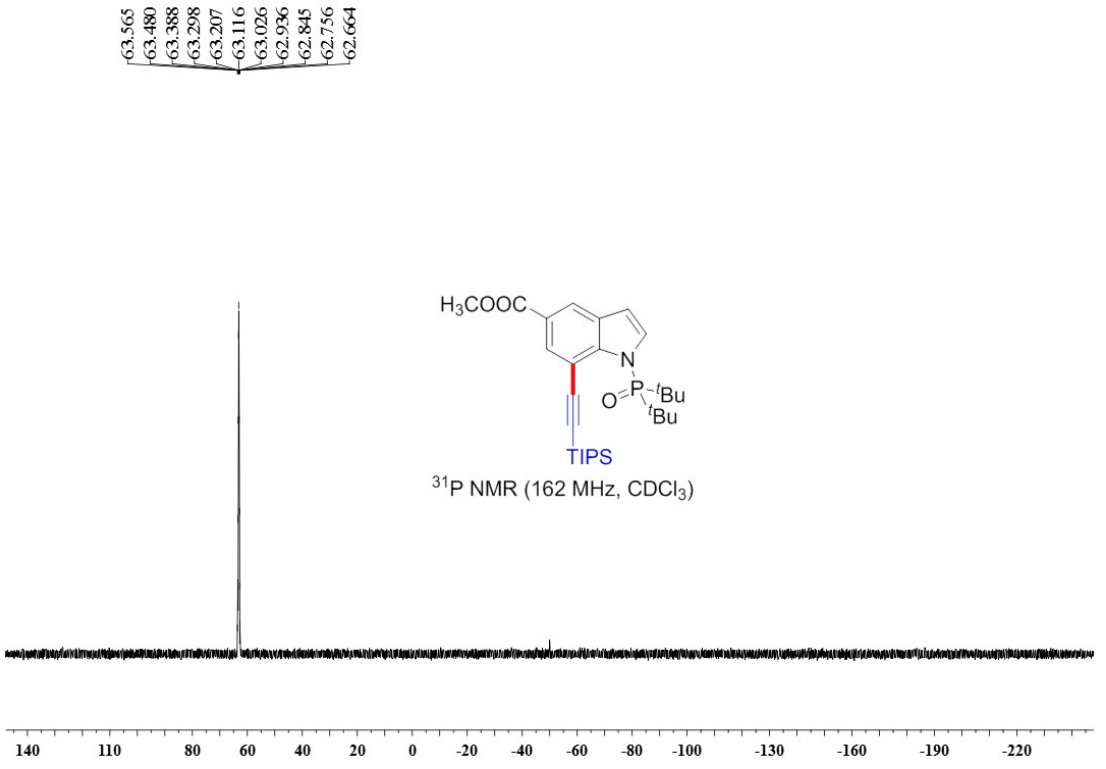




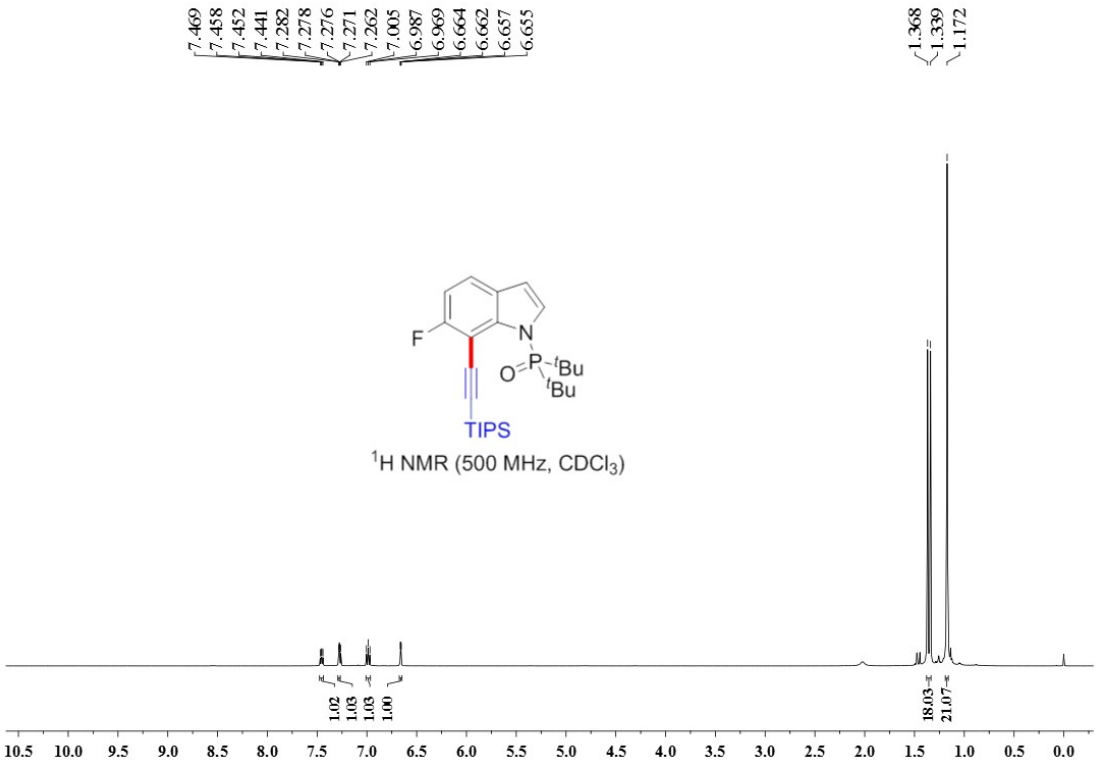
Methyl 1-(di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indole-5-carboxylate (3q)

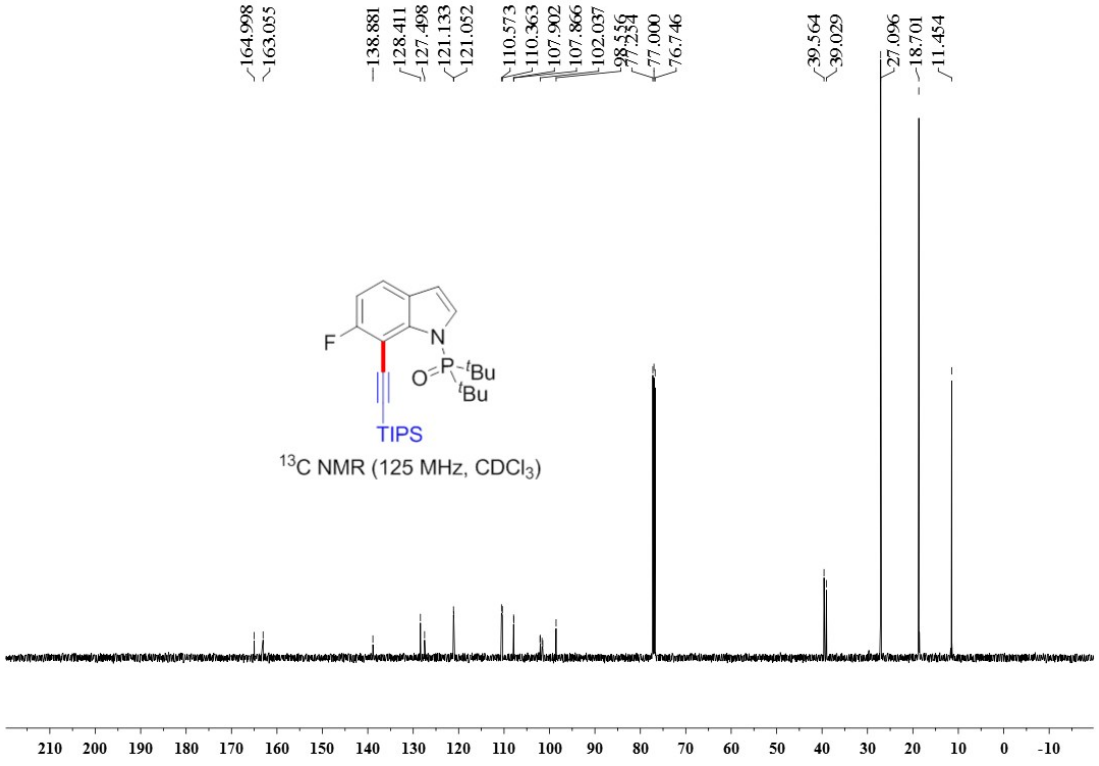


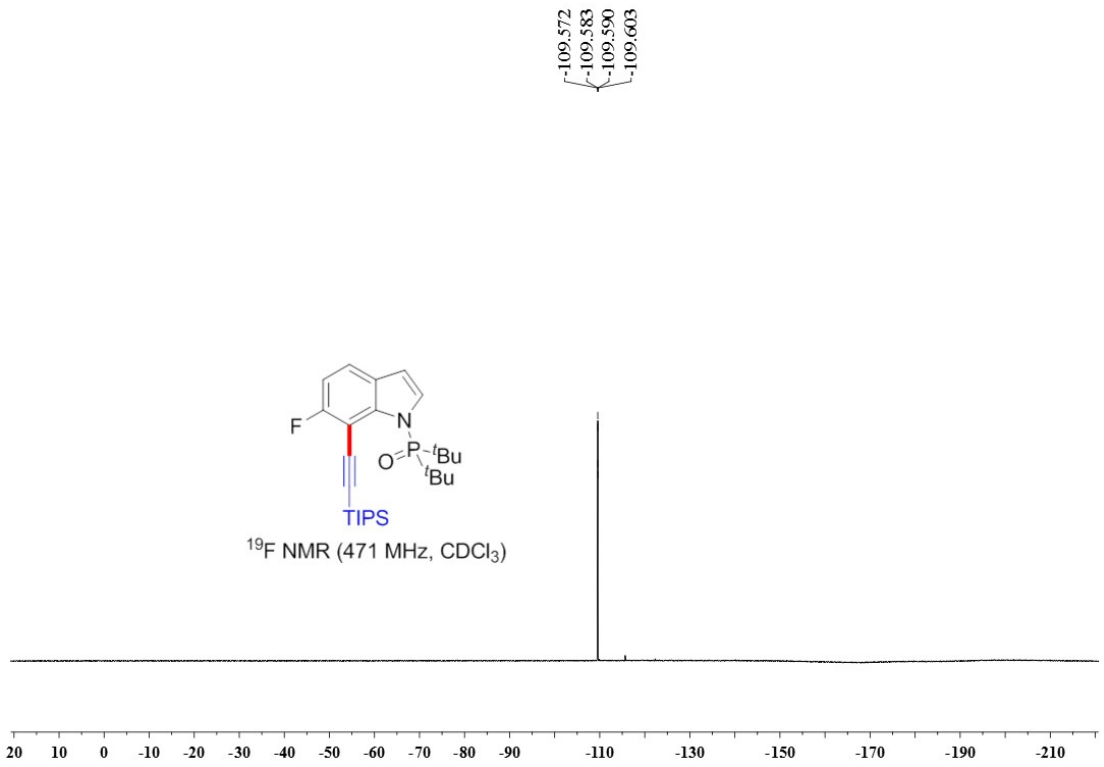

165.955
139.875
133.270
130.511
130.469
128.333
128.285
122.773
122.033
111.288
107.635
94.820
76.318
76.000
75.683
51.013
38.612
37.946
26.081
17.794
10.512
H3COOC
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

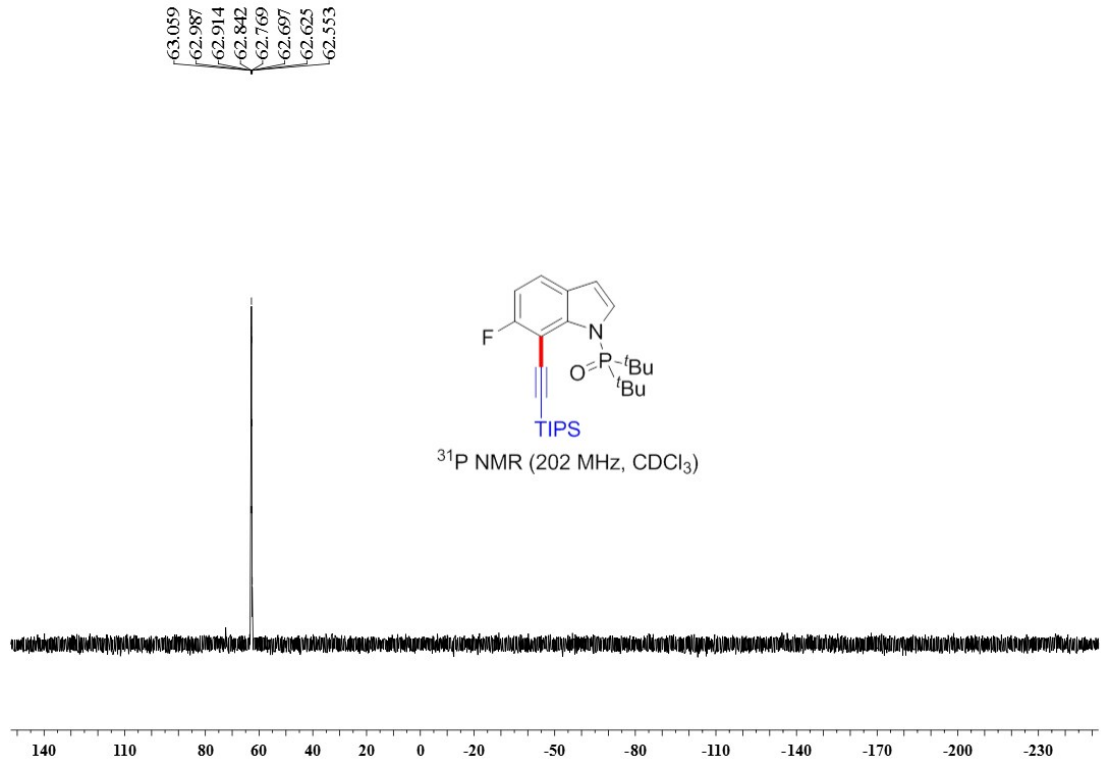

63.565
63.480
63.388
63.298
63.207
63.116
63.026
62.936
62.845
62.756
62.664
H3COOC
N
O
P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

Di-*tert*-butyl(6-fluoro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3s)

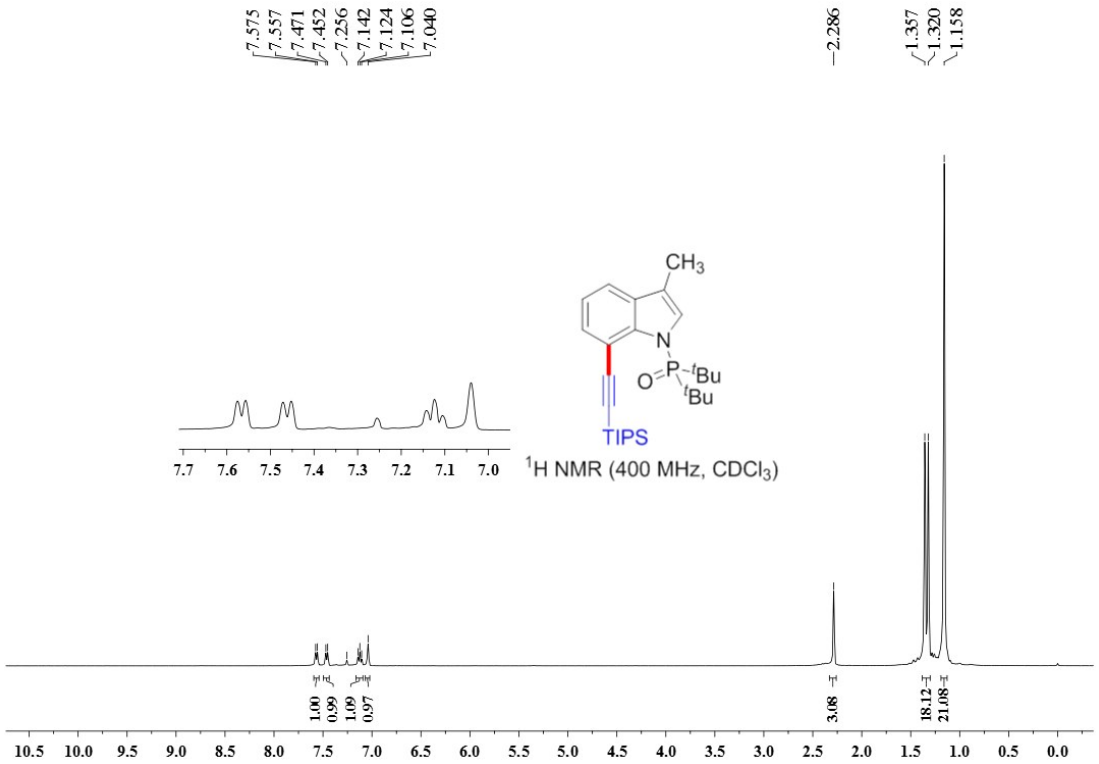


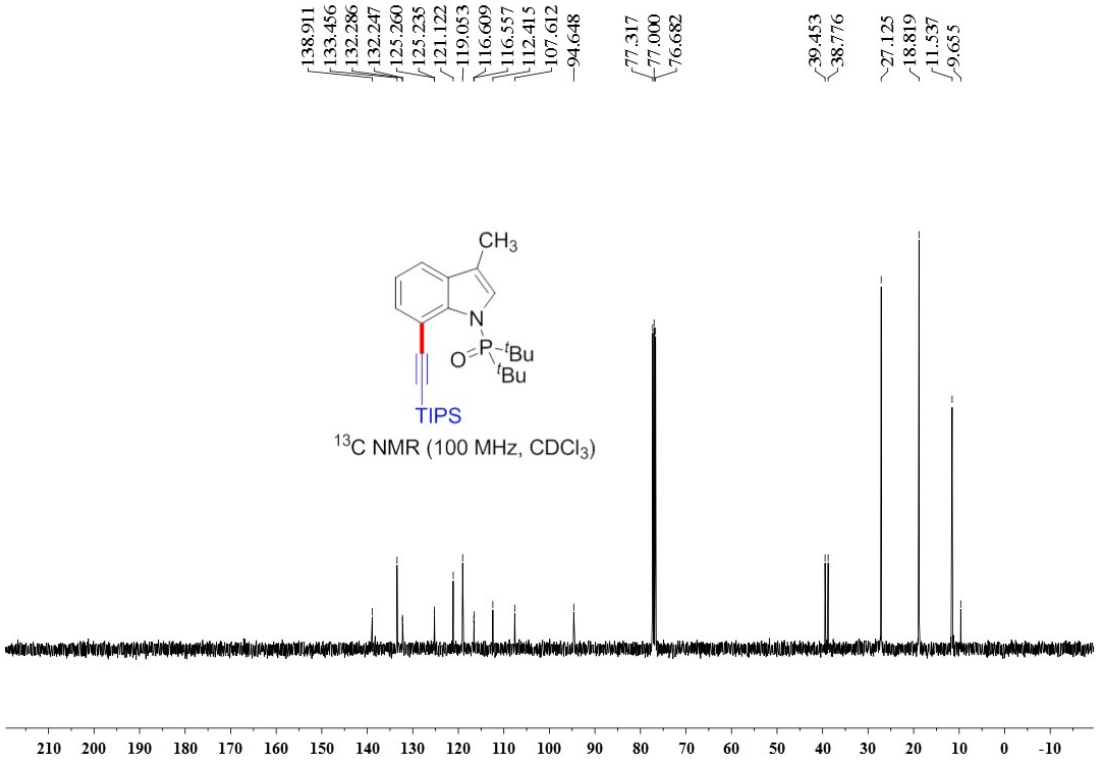


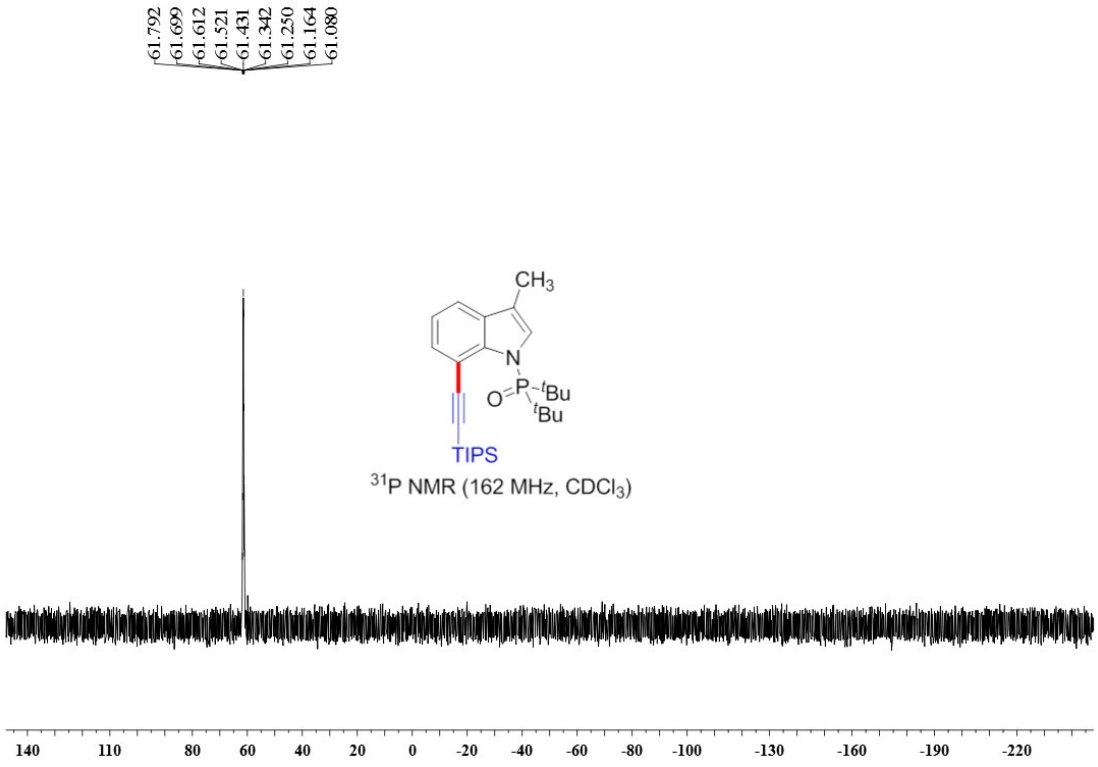

-109.572
-109.583
-109.590
-109.603
F
N
O
P
tBu
tBu
TIPS
19F NMR (471 MHz, CDCl3)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210


63.059
62.987
62.914
62.842
62.769
62.697
62.625
62.553
F
N
O
P
tBu
tBu
TIPS
31P NMR (202 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -50 -80 -110 -140 -170 -200 -230

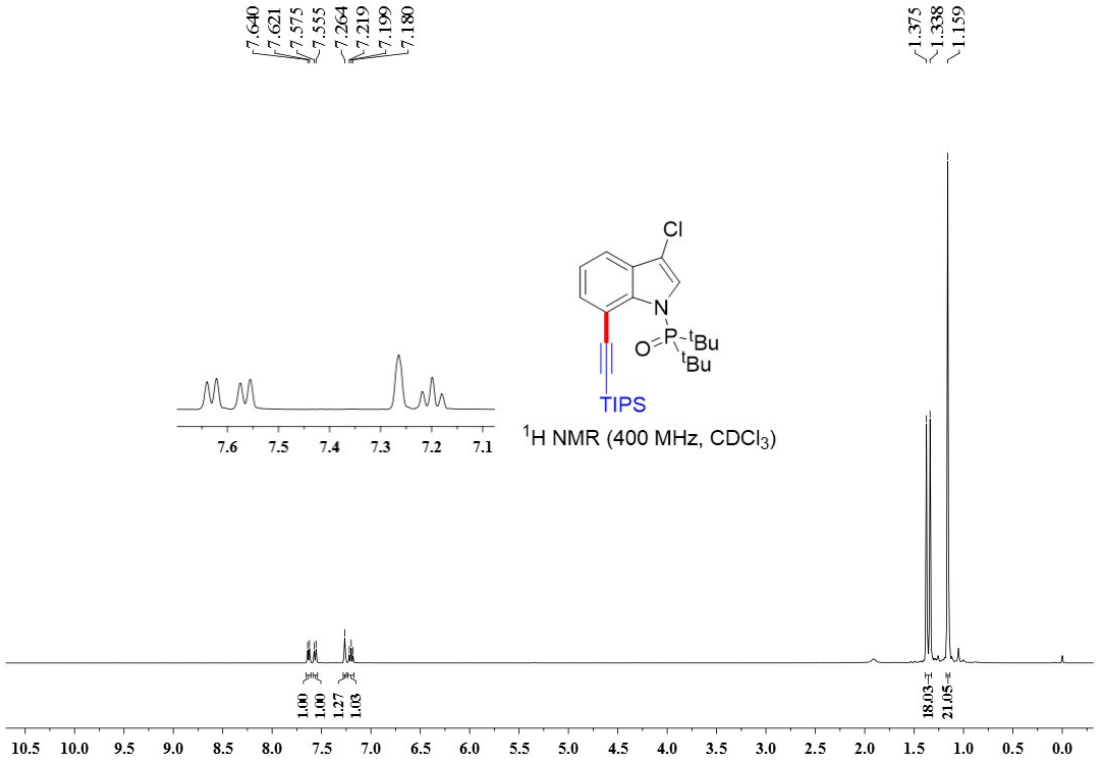
Di-*tert*-butyl(3-methyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3t)

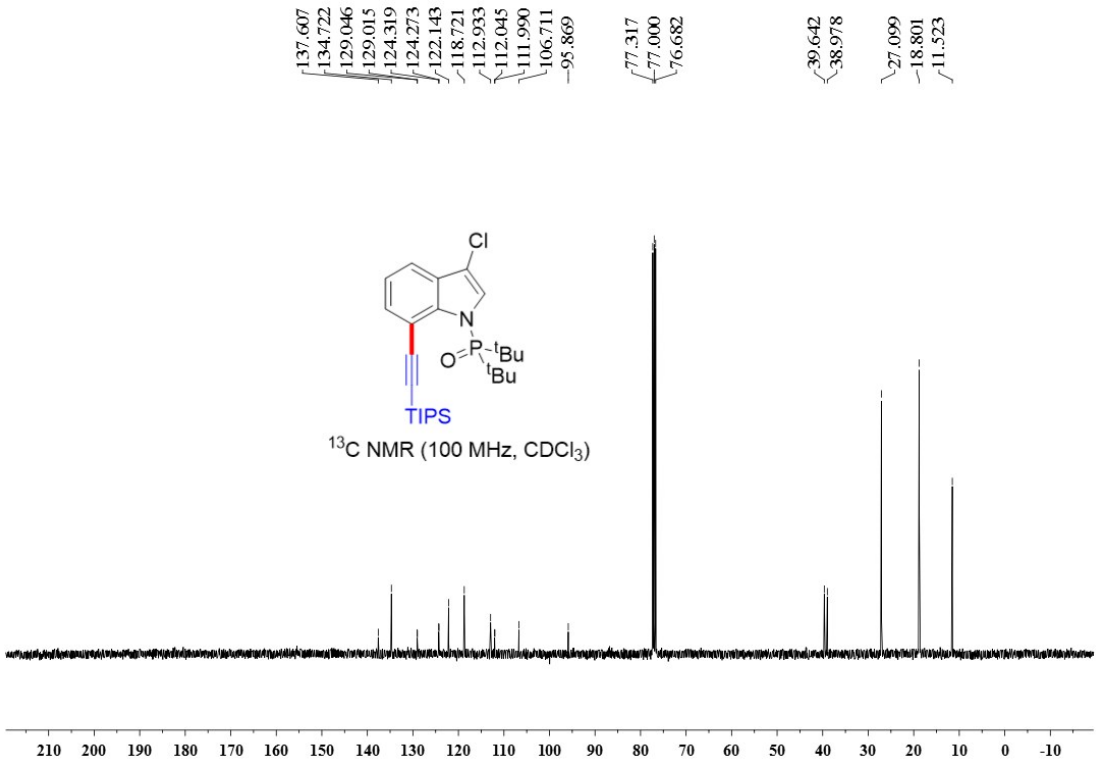


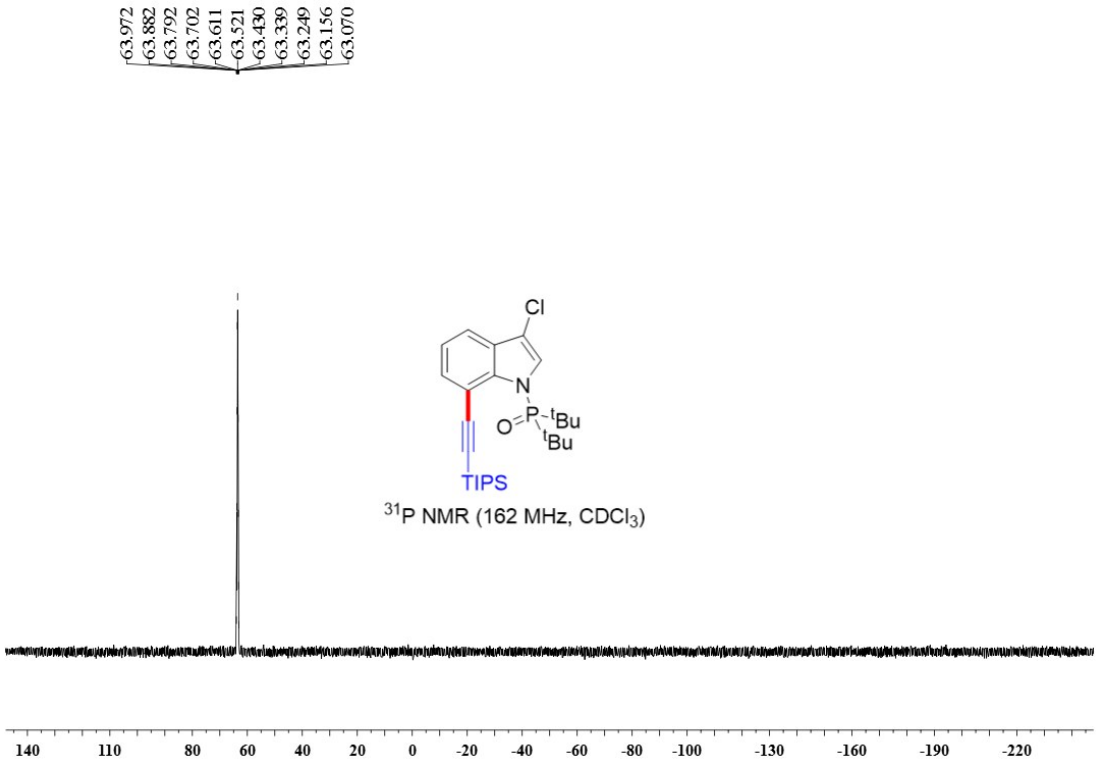




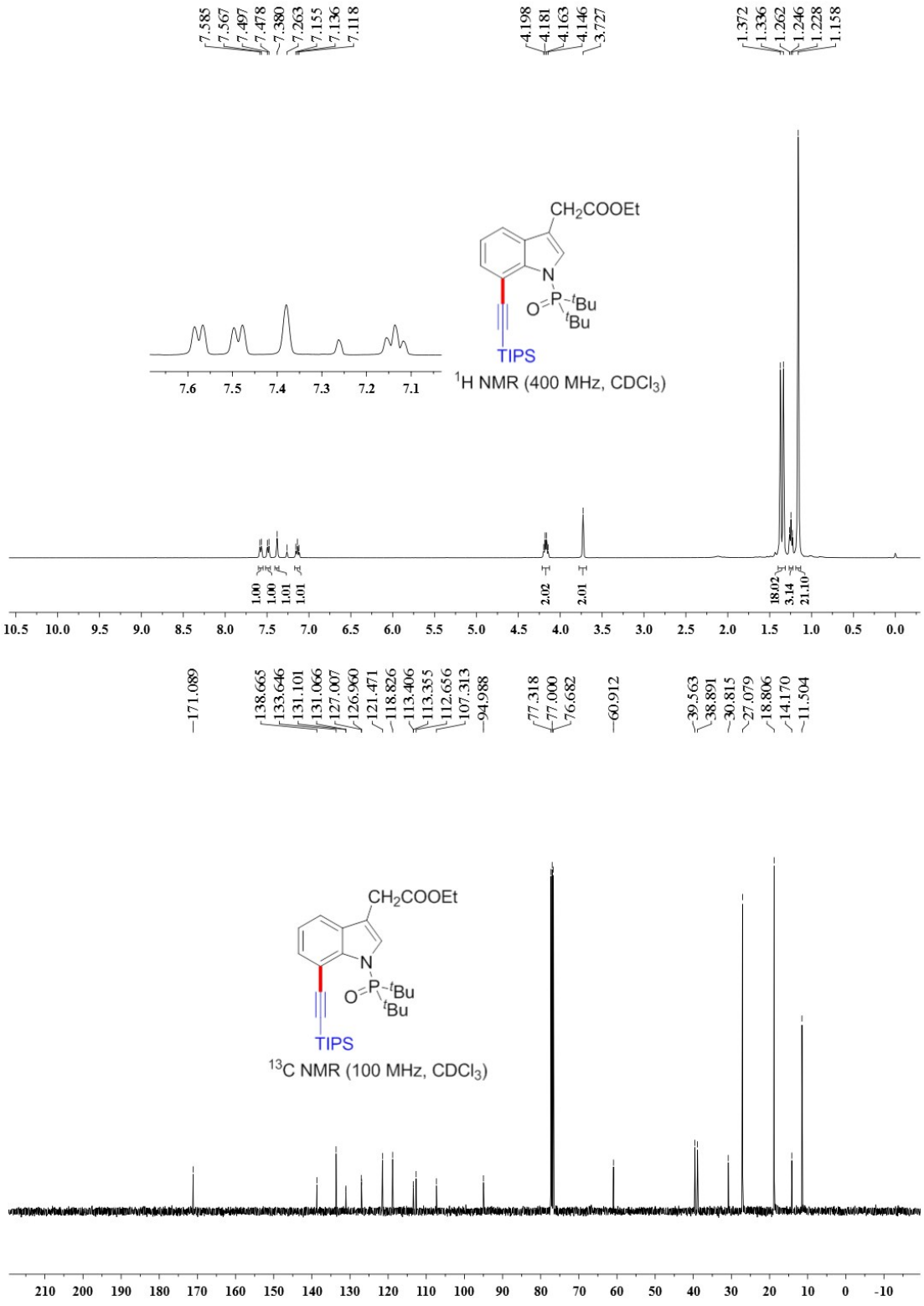
Di-*tert*-butyl(3-chloro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3u)

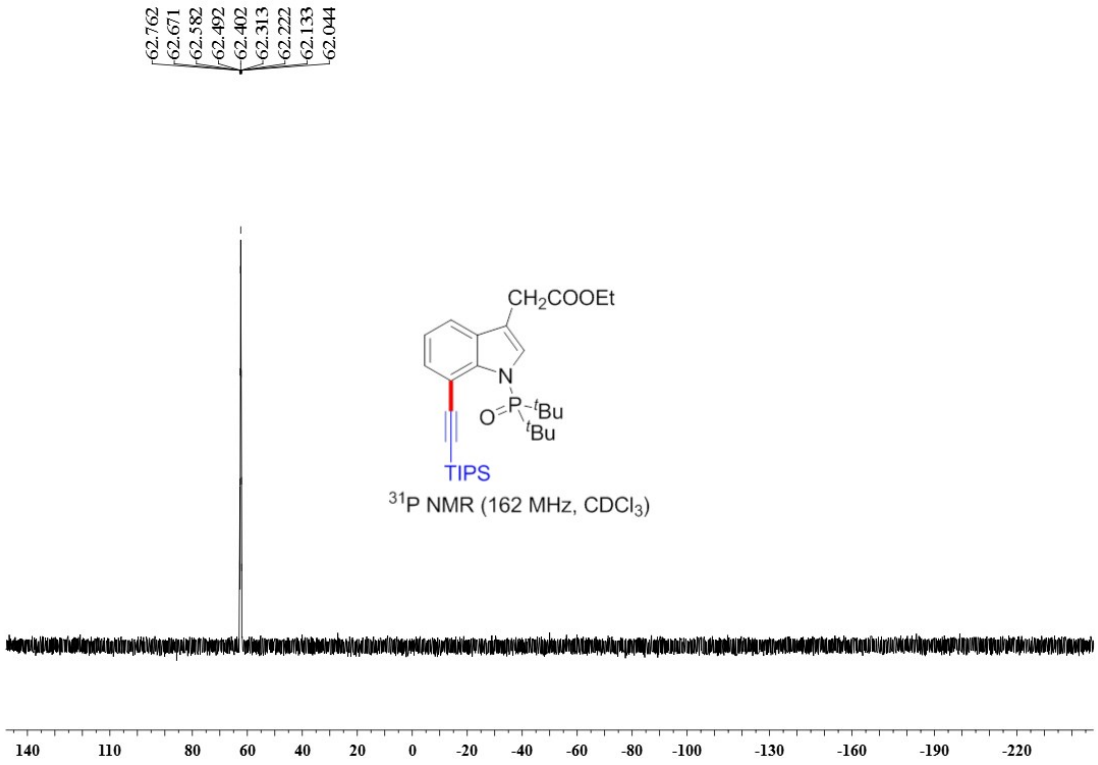



137.607
134.722
129.046
129.015
124.319
124.273
122.143
118.721
112.933
112.045
111.990
106.711
95.869
77.317
77.000
76.682
39.642
38.978
27.099
18.801
11.523
Cl
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

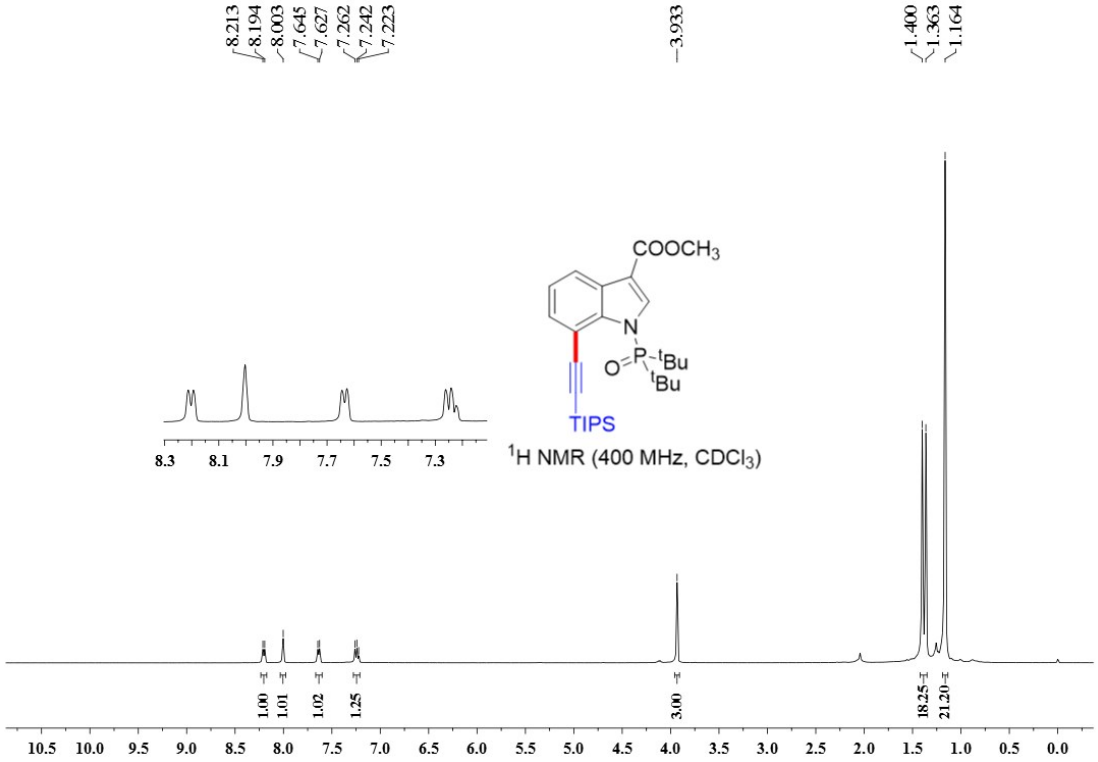

63.972
63.882
63.792
63.702
63.611
63.521
63.430
63.339
63.249
63.156
63.070
Cl
N
O
P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

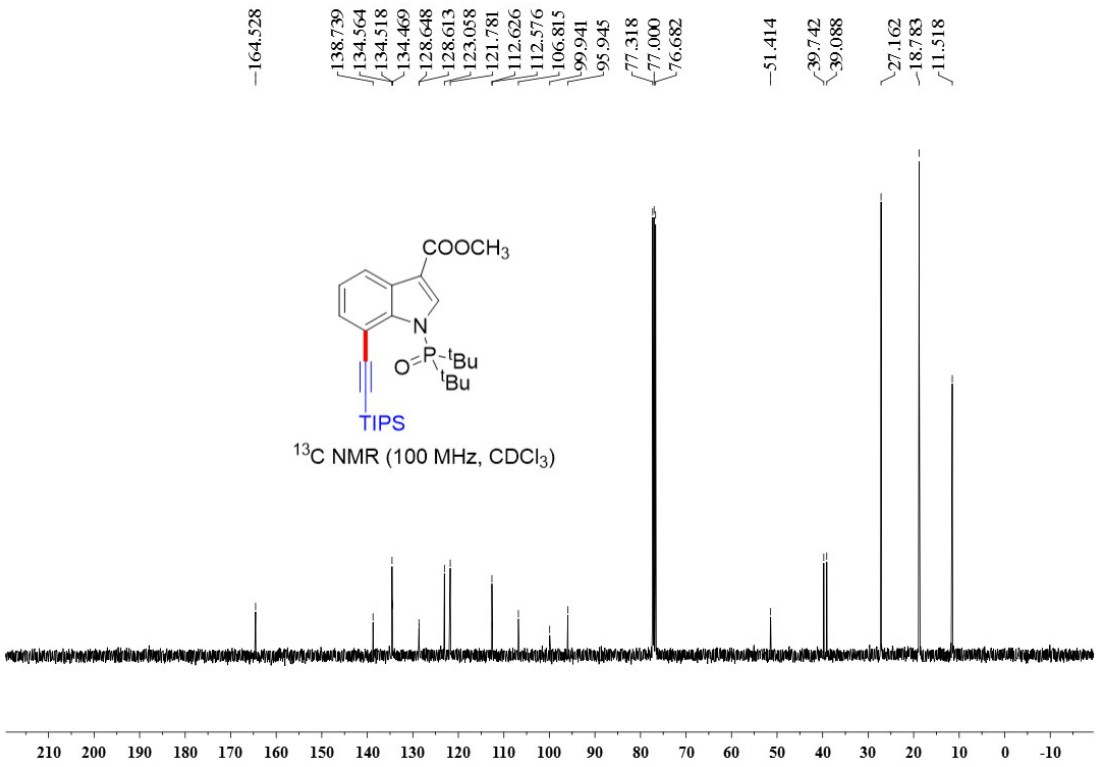
Ethyl 2-(1-(di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-3-yl)acetate (3v)

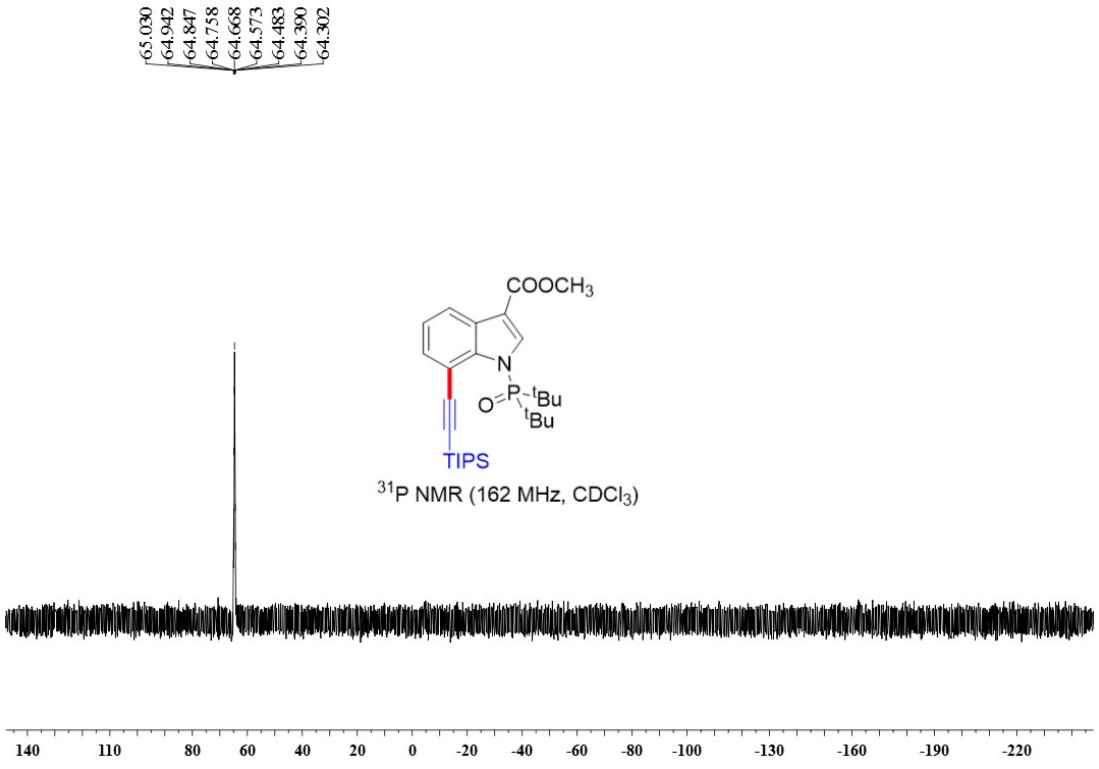




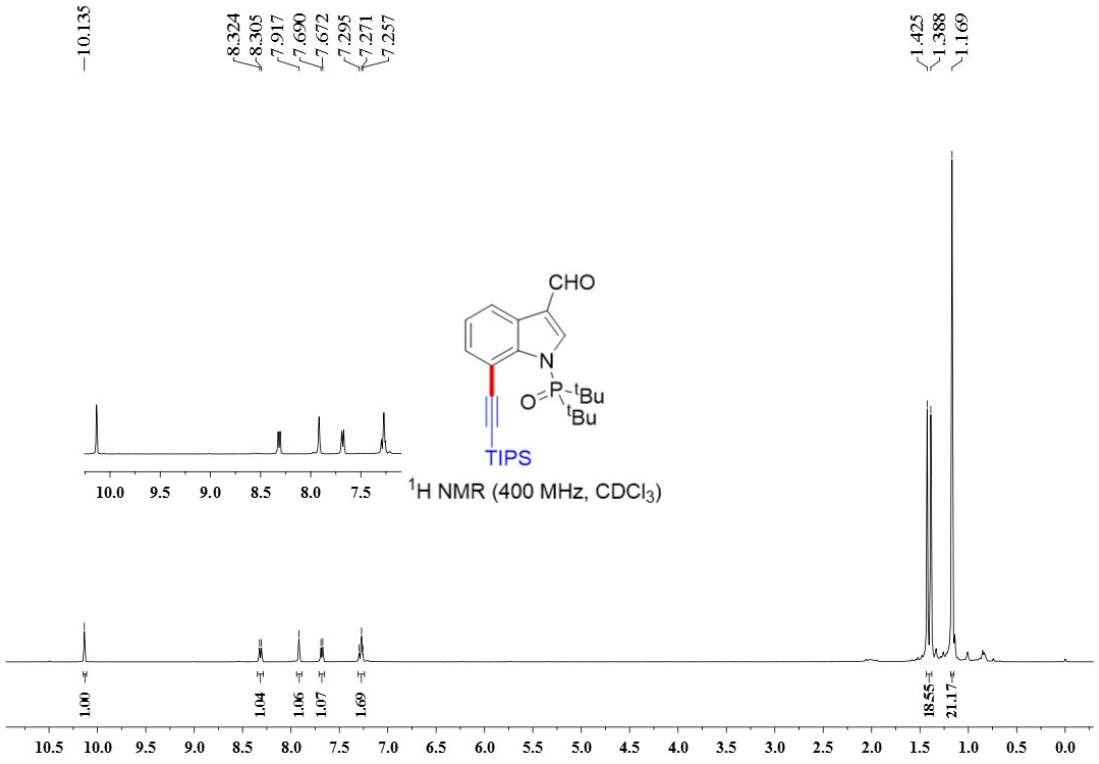
Methyl 1-(di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indole-3-carboxylate (3w)

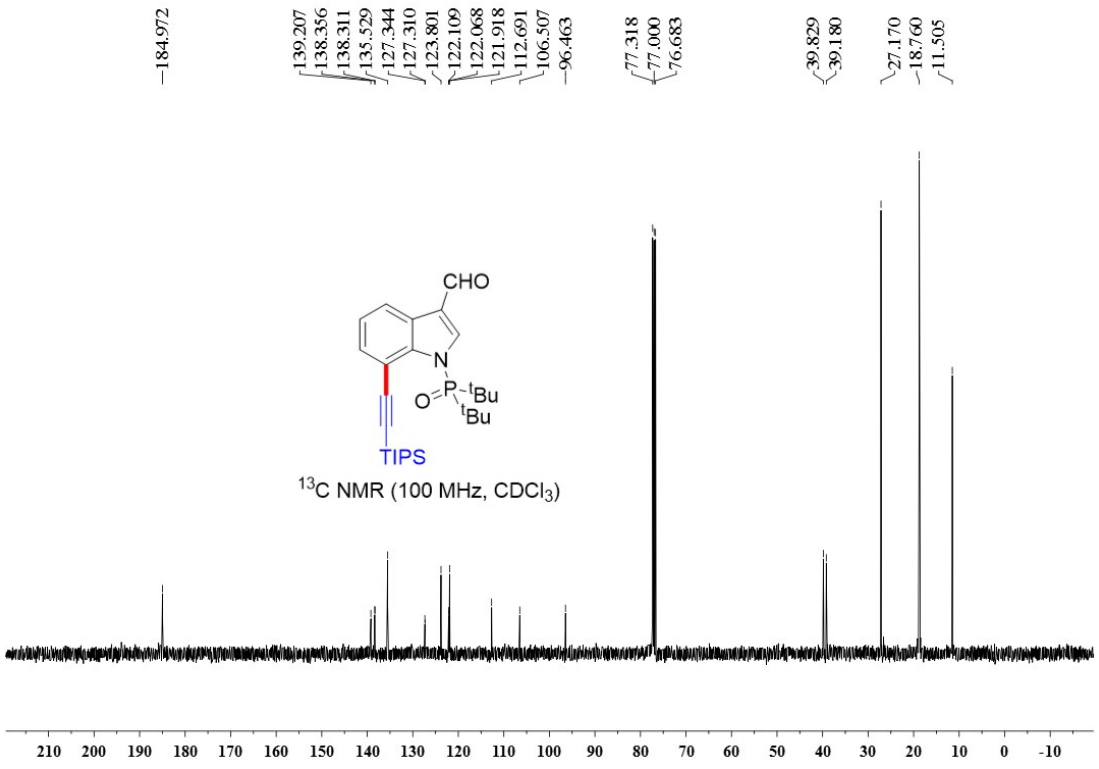


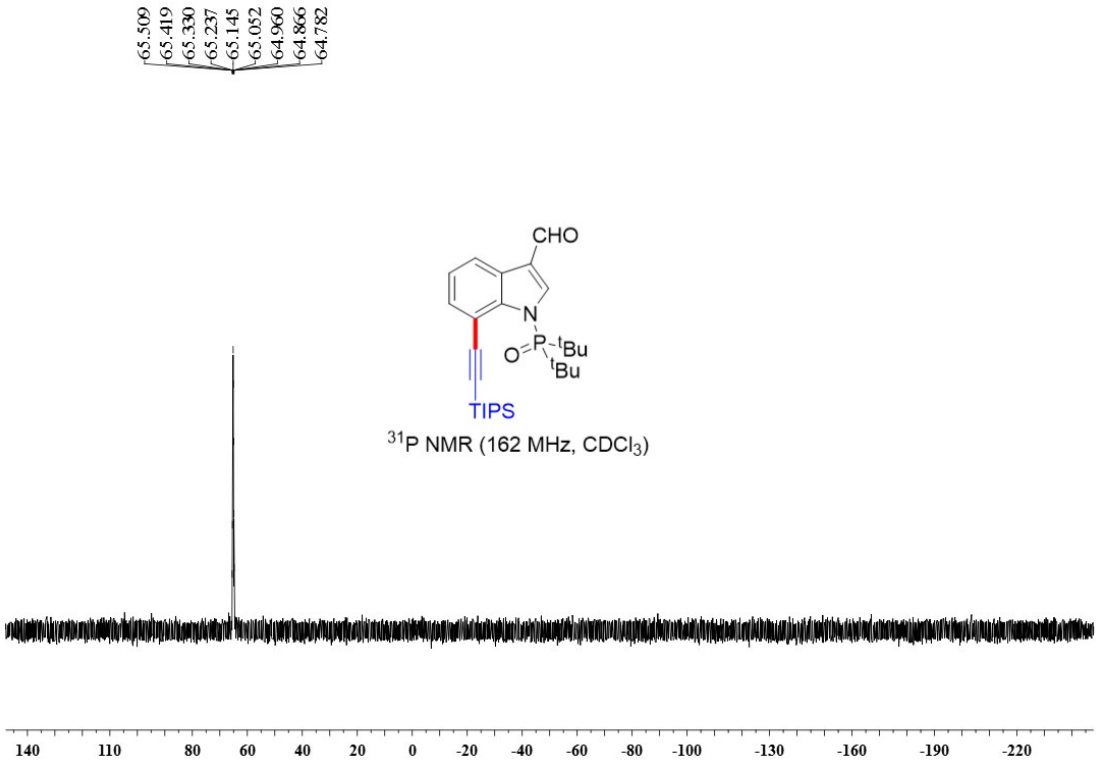

164.528
138.739
134.564
134.518
134.469
128.648
128.613
123.058
121.781
112.626
112.576
106.815
99.941
95.945
77.318
77.000
76.682
51.414
39.742
39.088
27.162
18.783
11.518
COOCH3
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


65.030
64.942
64.847
64.758
64.668
64.573
64.483
64.390
64.302
COOCH3
N
O
P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

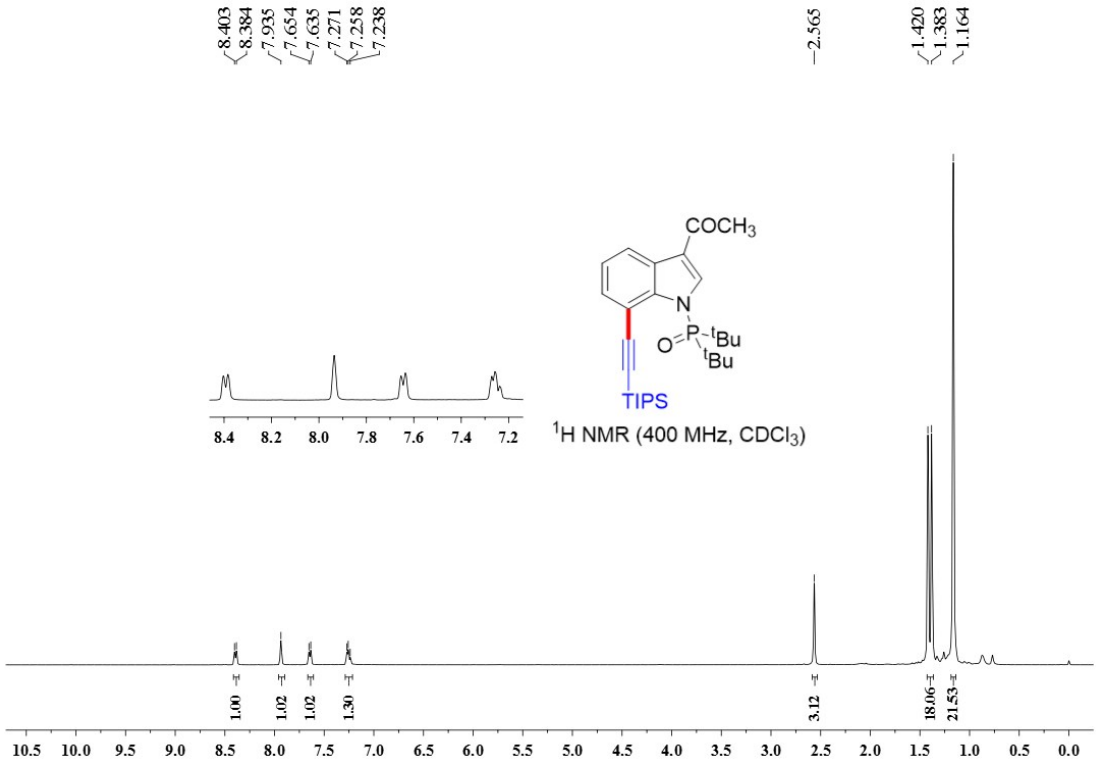
1-(Di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indole-3-carbaldehyde (3x)

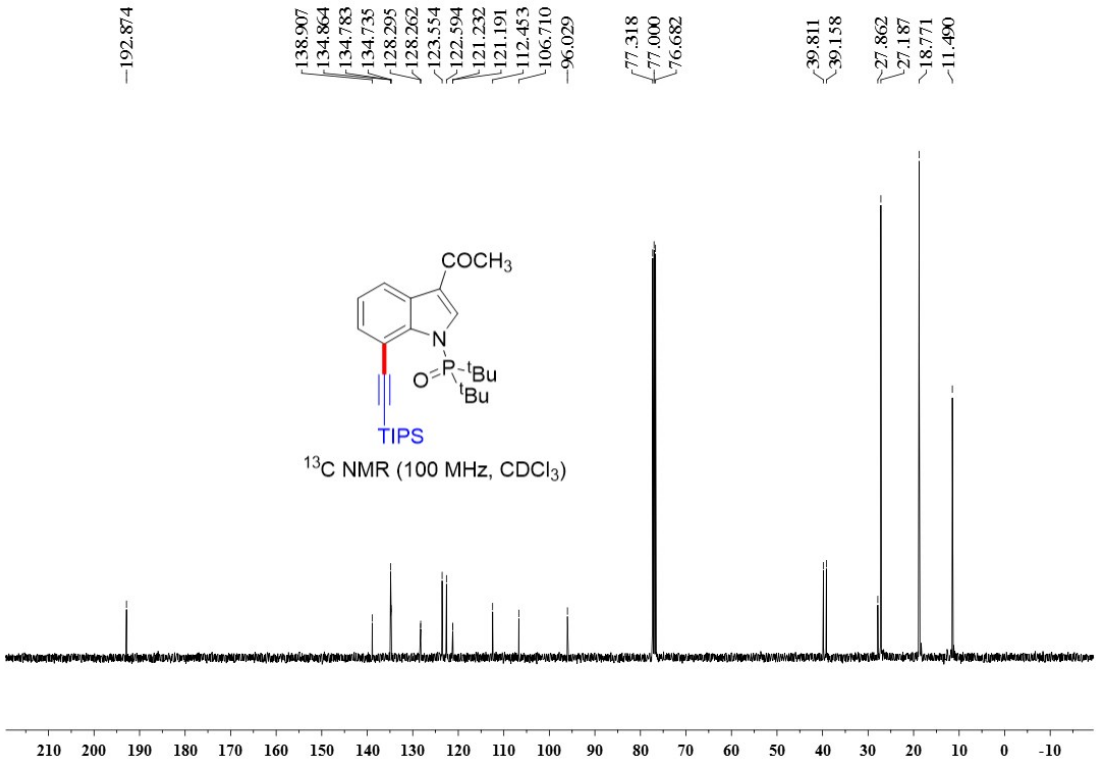


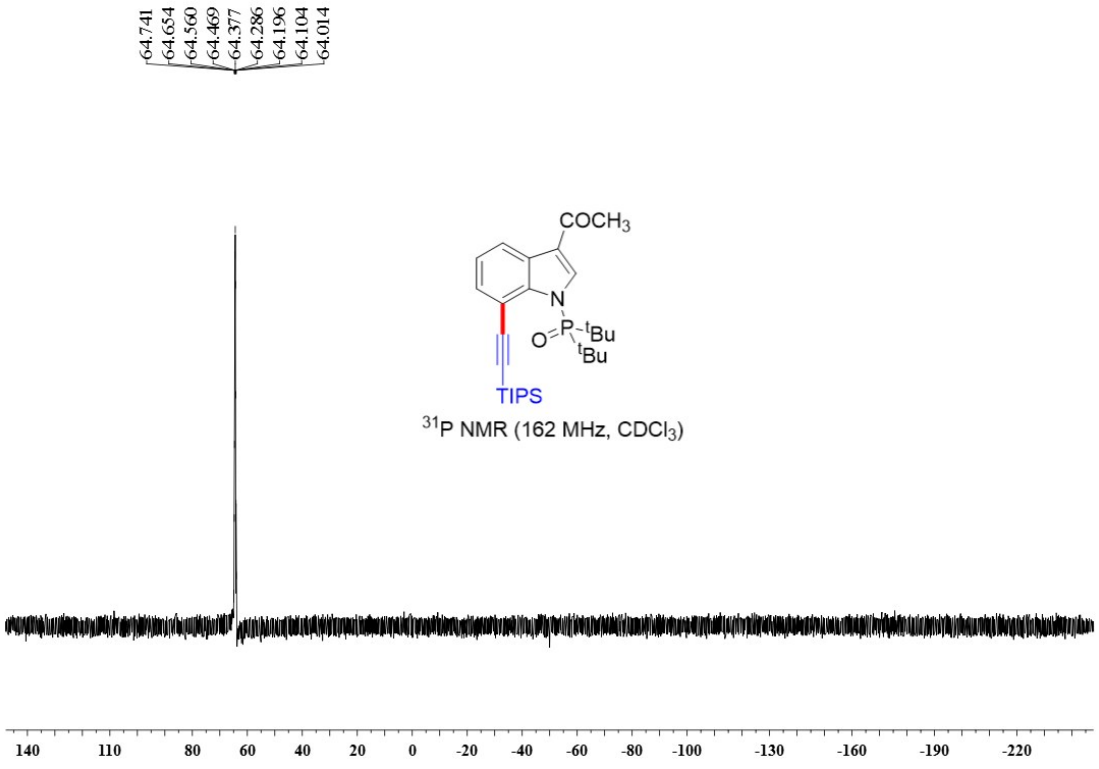




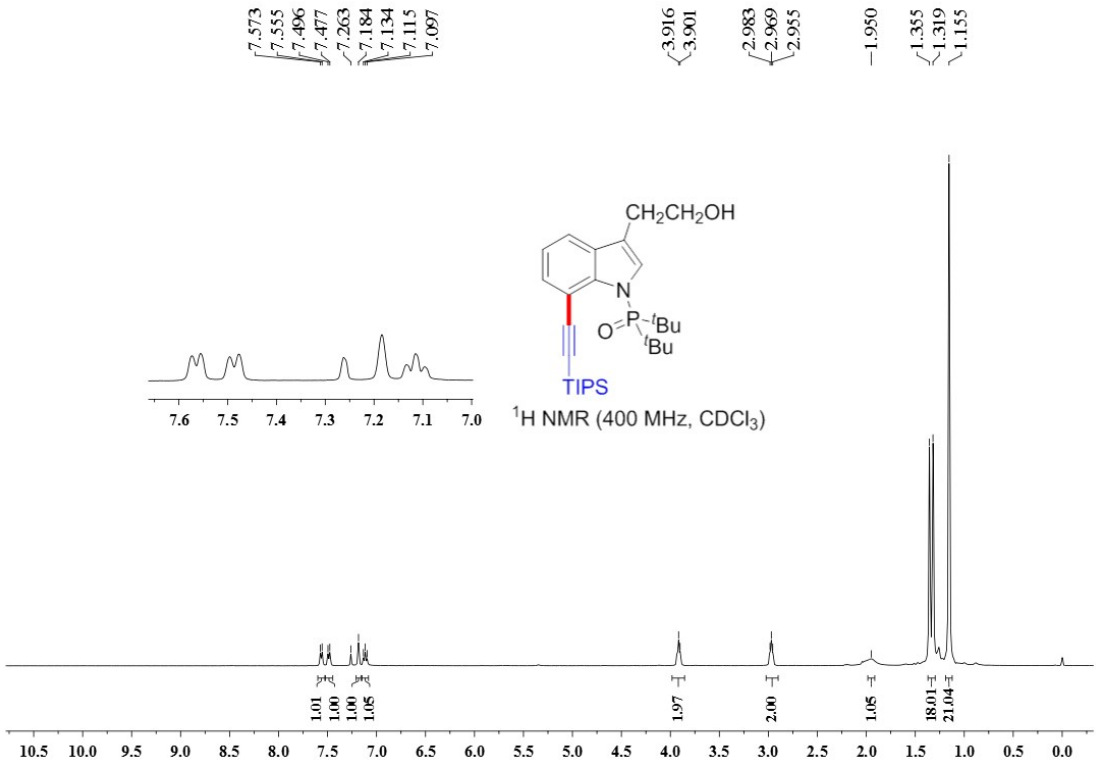
1-(1-(Di-*tert*-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-3-yl)ethan-1-one (3y)

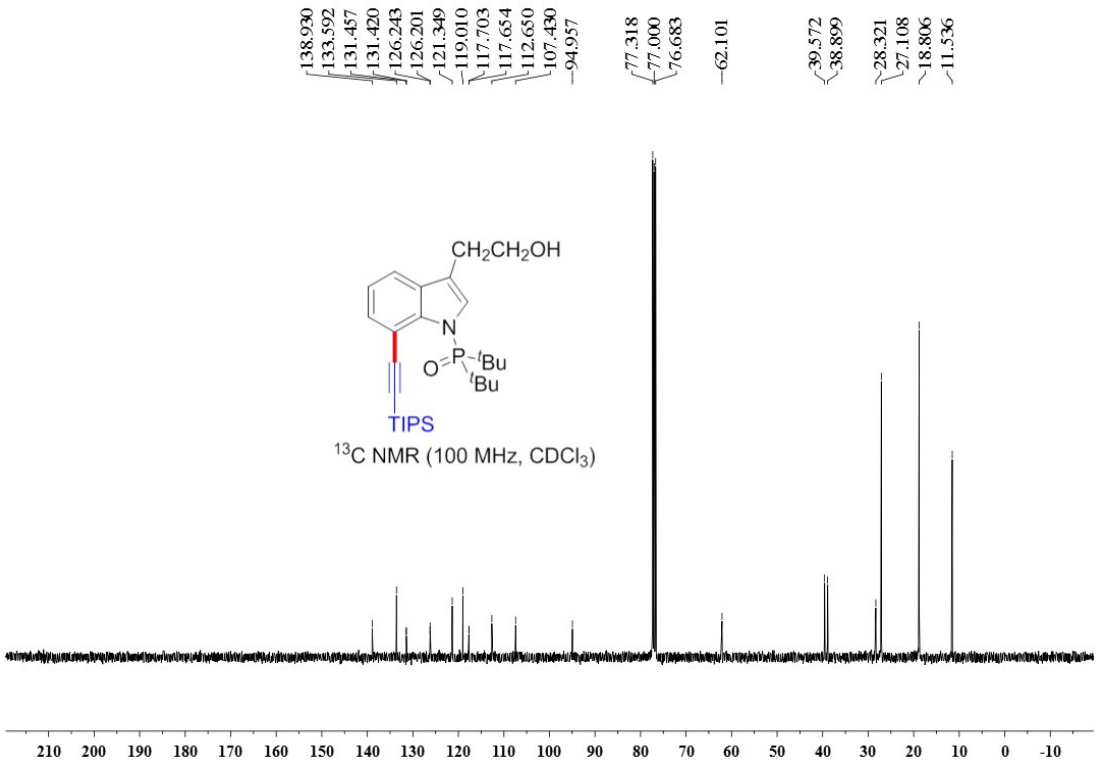


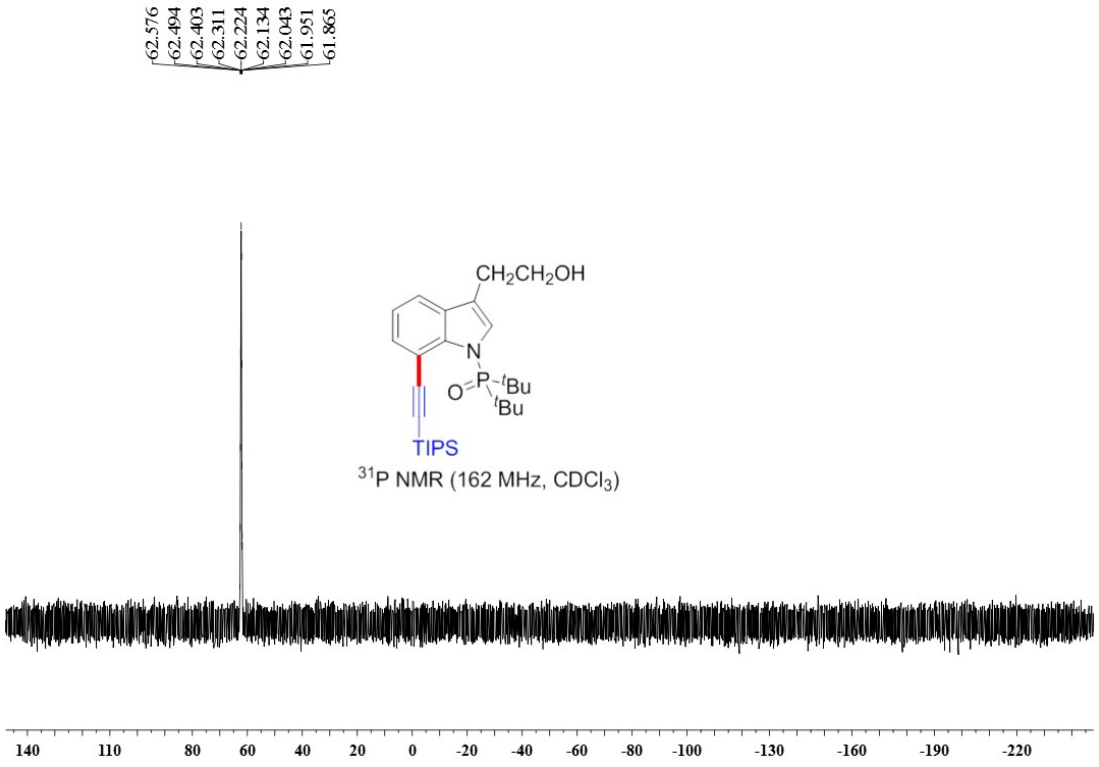

192.874
138.907
134.864
134.783
134.735
128.295
128.262
123.554
122.594
121.232
121.191
112.453
106.710
96.029
77.318
77.000
76.682
39.811
39.158
27.862
27.187
18.771
11.490
COCH3
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


64.741
64.654
64.560
64.469
64.377
64.286
64.196
64.104
64.014
COCH3
N
O
P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

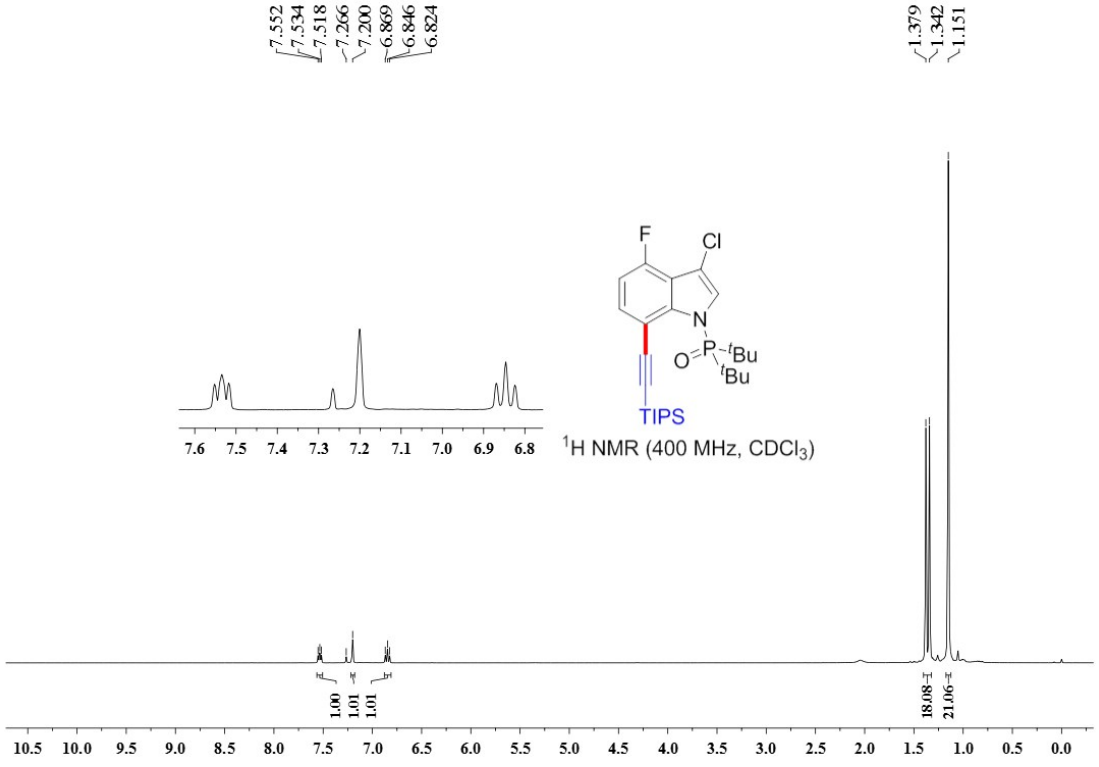
Di-*tert*-butyl(3-(2-hydroxyethyl)-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3z)

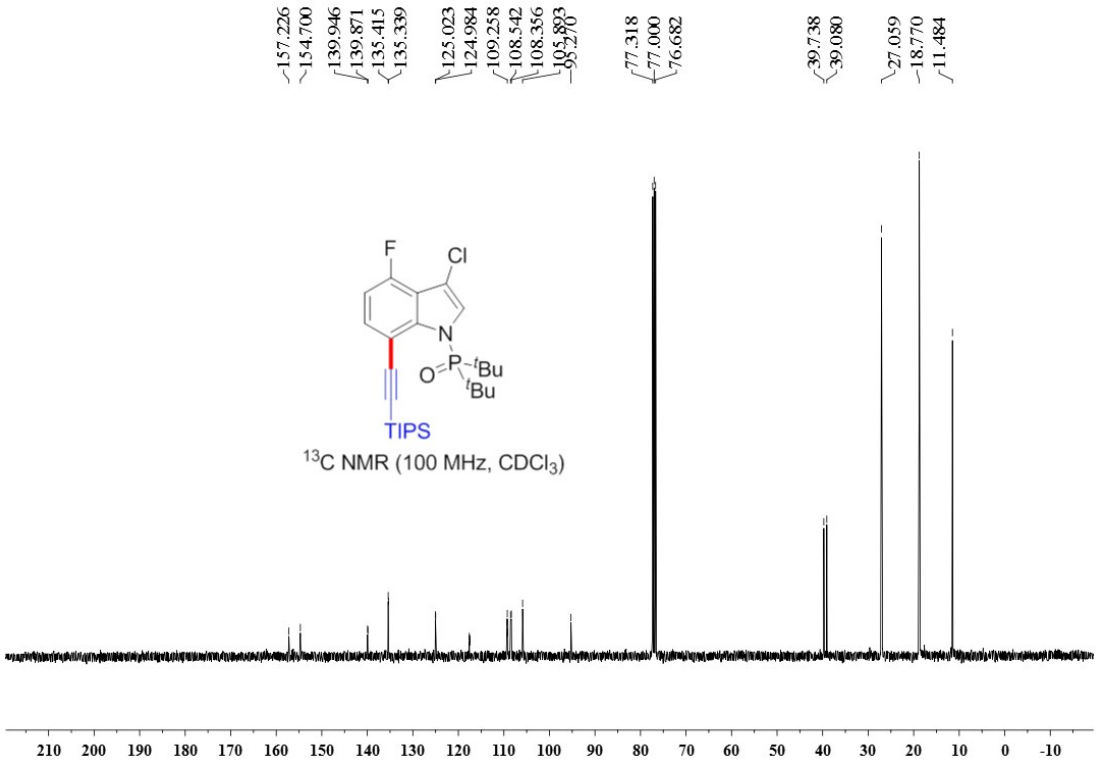


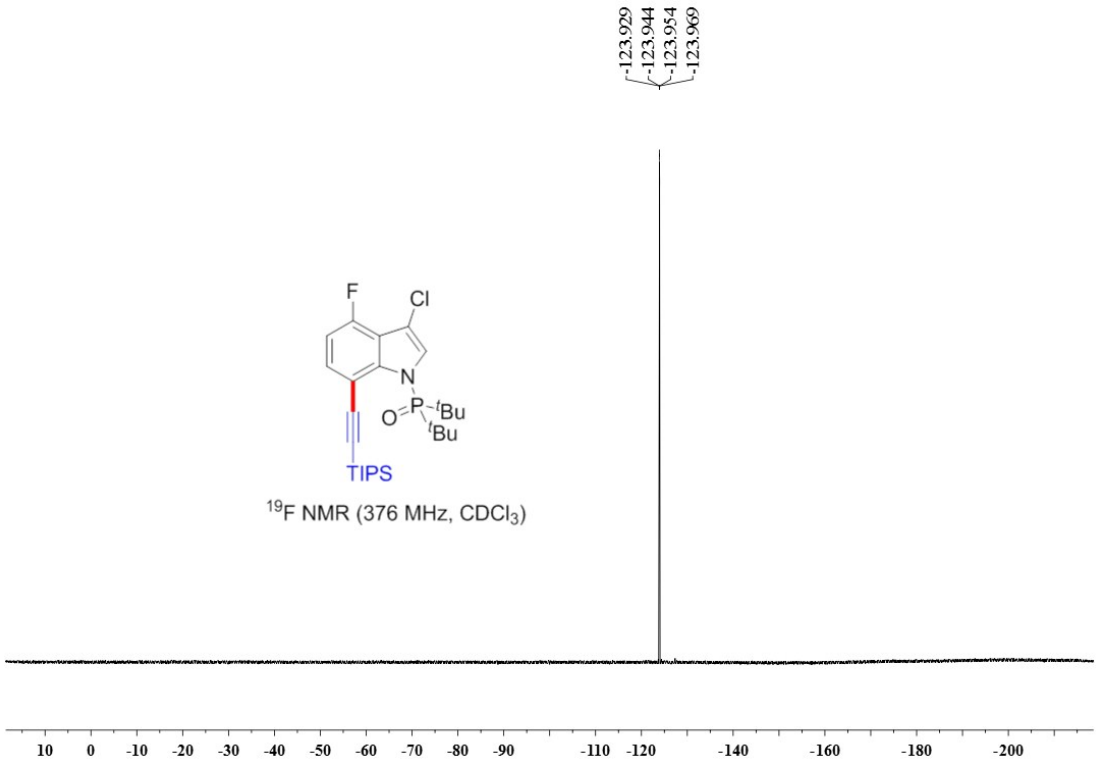


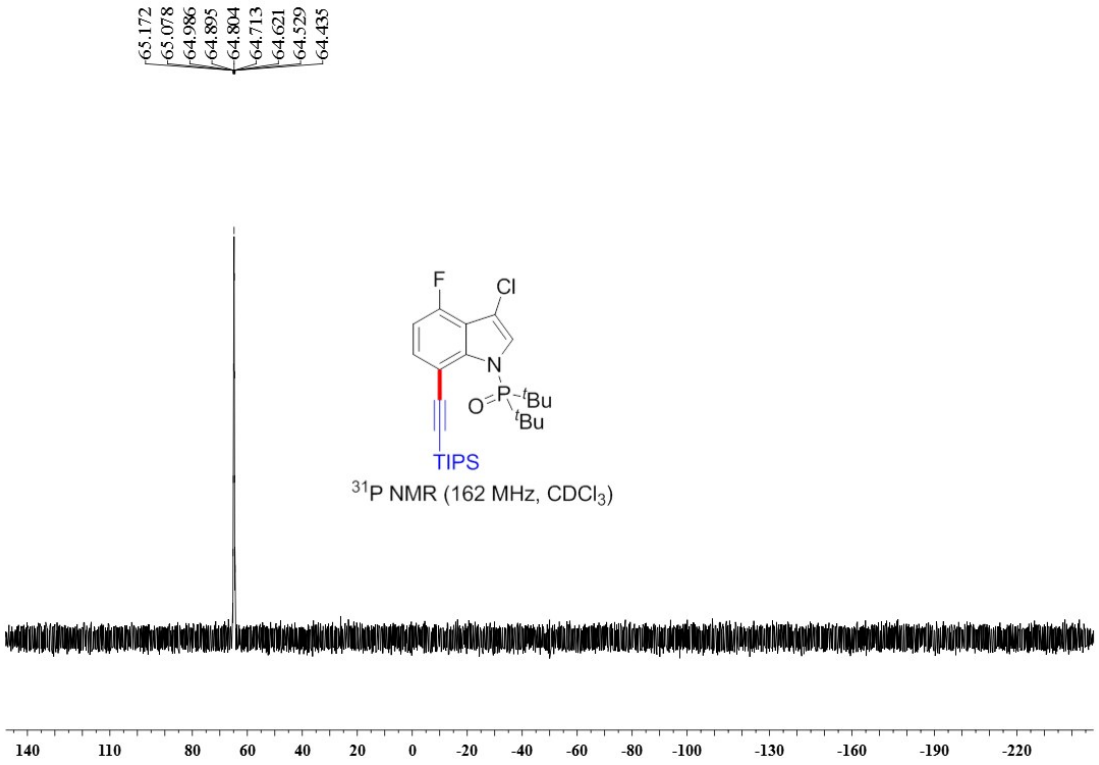


Di-*tert*-butyl(3-chloro-4-fluoro-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3aa)

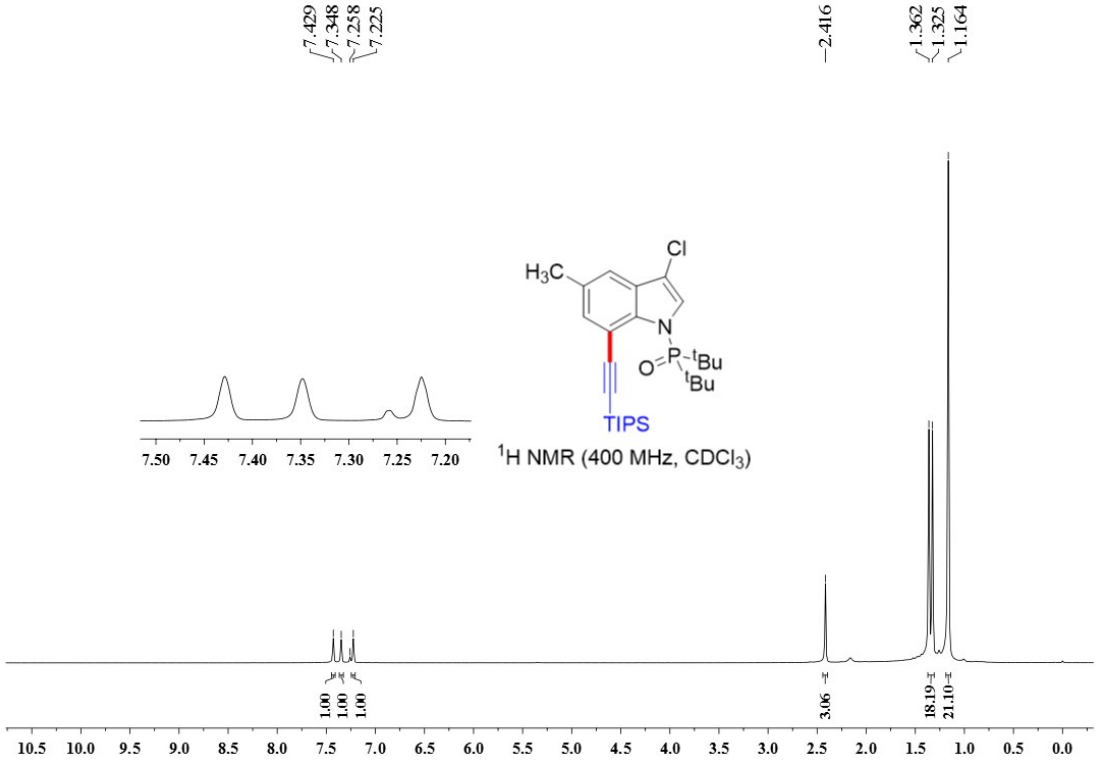


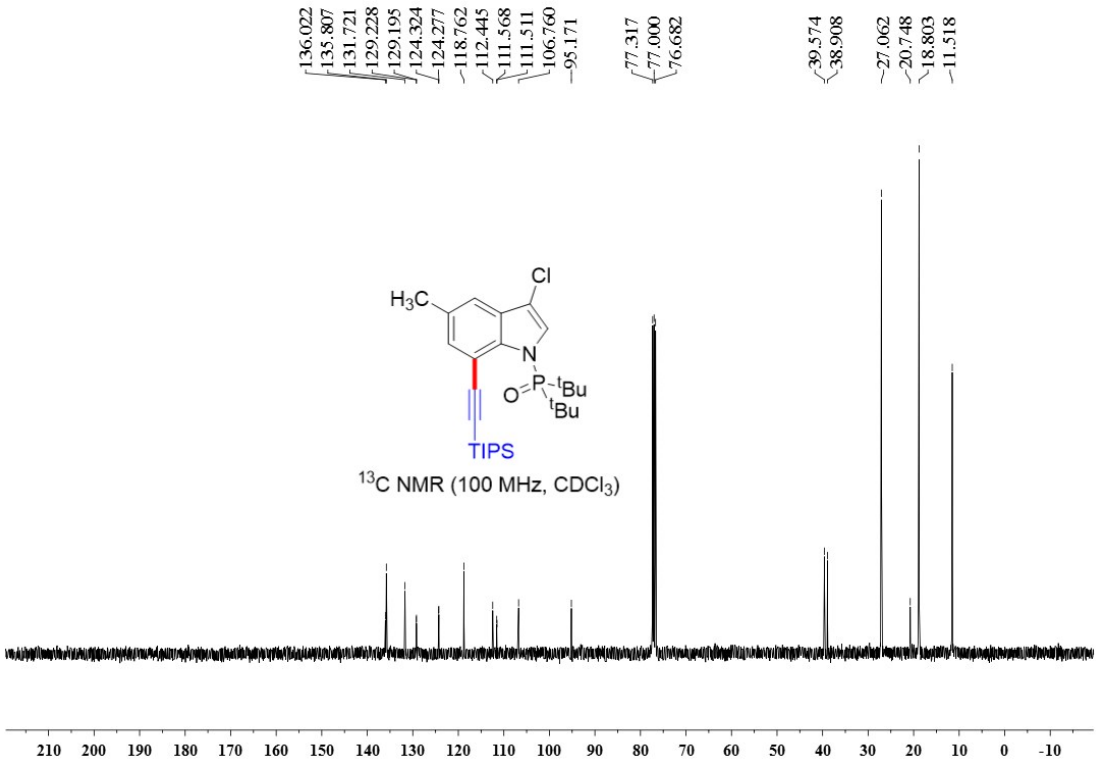

157.226
154.700
139.946
139.871
135.415
135.339
125.023
124.984
109.258
108.542
108.356
105.883
95.270
77.318
77.000
76.682
39.738
39.080
27.059
18.770
11.484
F
Cl
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

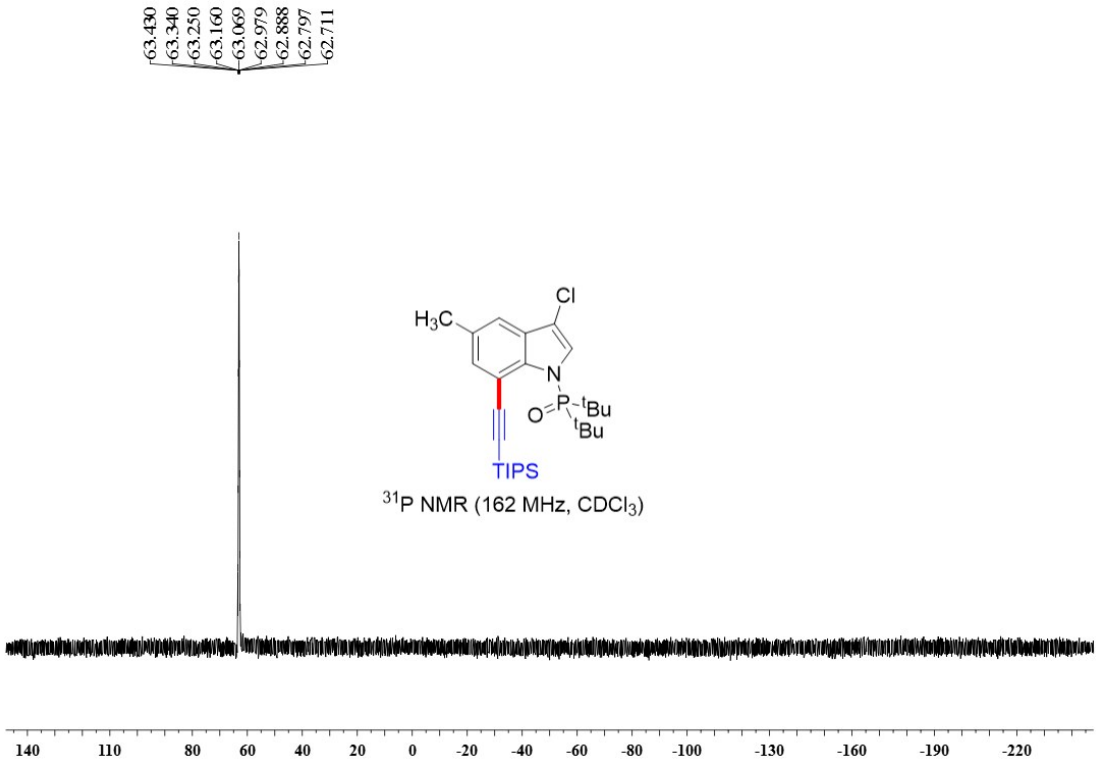

-123.929
-123.944
-123.954
-123.969
F
Cl
N
O
P
tBu
tBu
TIPS
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -140 -160 -180 -200



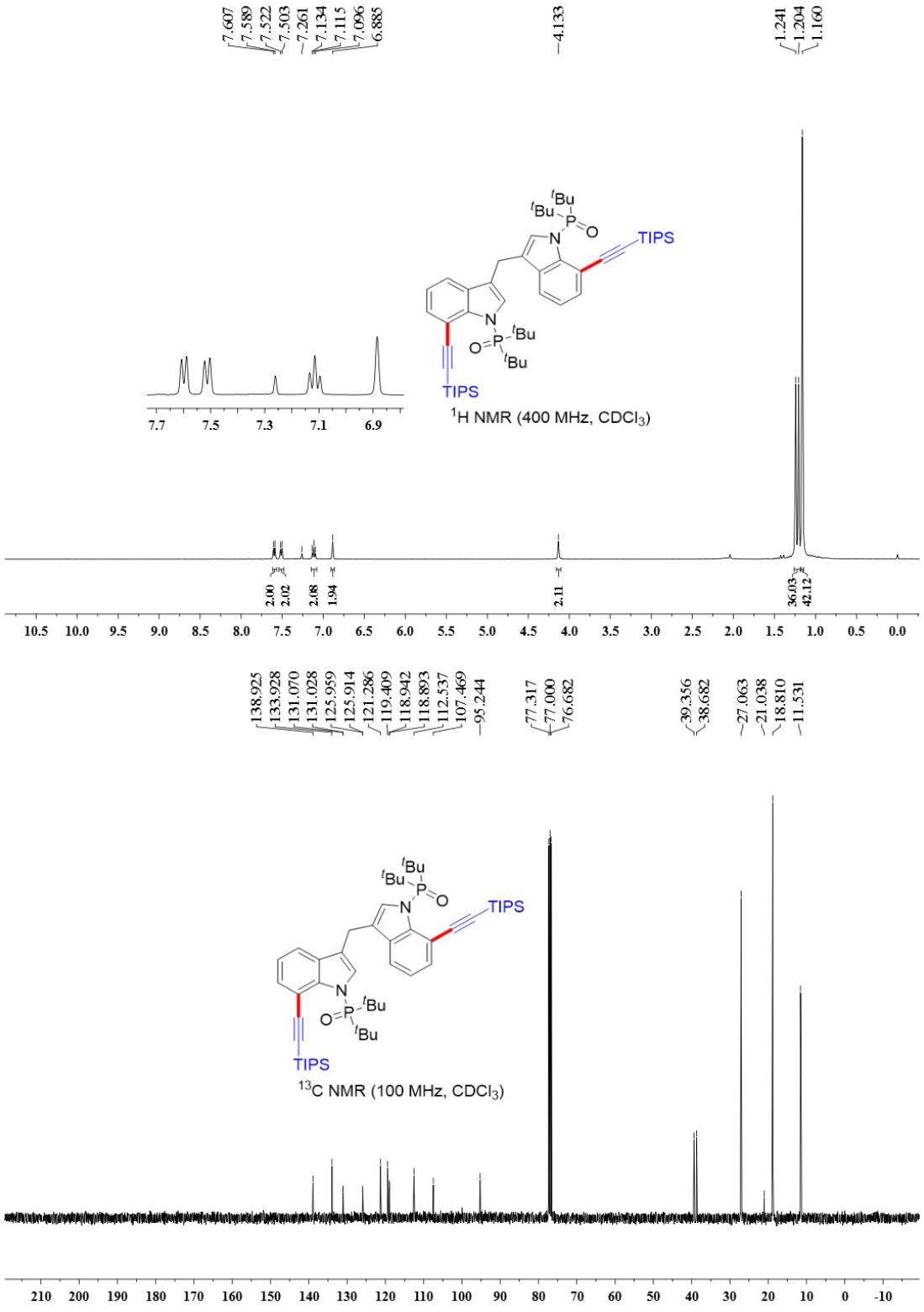
Di-*tert*-butyl(3-chloro-5-methyl-7-((triisopropylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3ab)

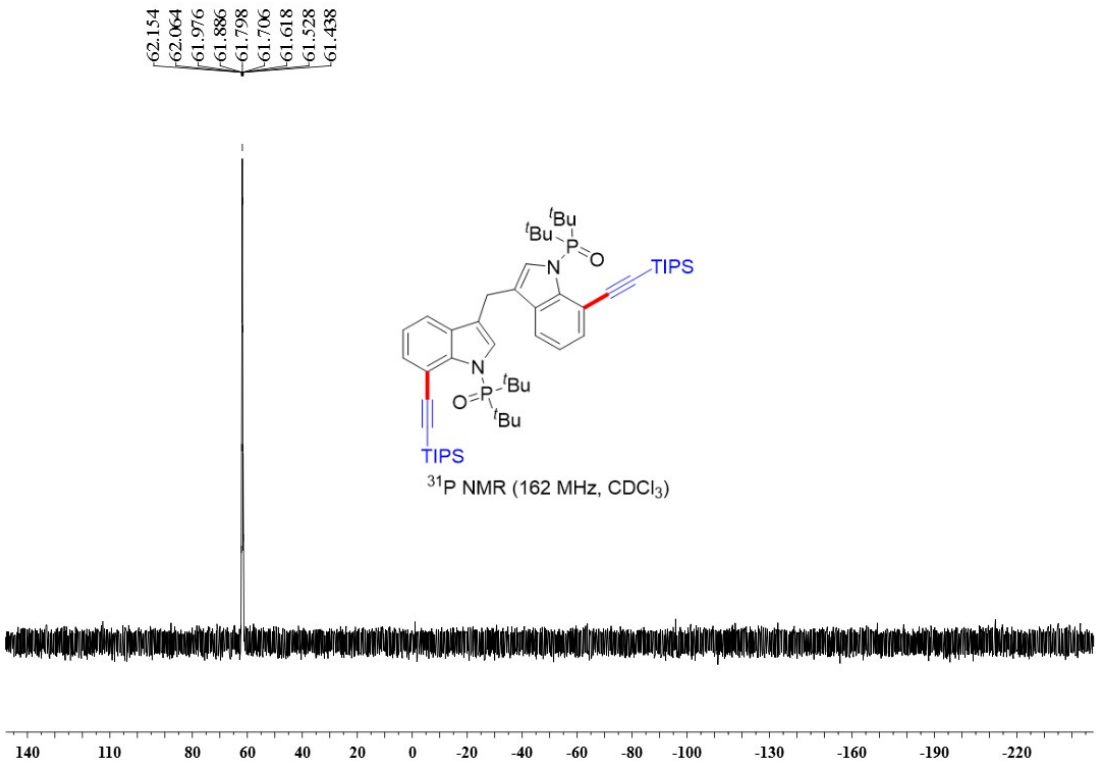



136.022
135.807
131.721
129.228
129.195
124.324
124.277
118.762
112.445
111.568
111.511
106.760
95.171
77.317
77.000
76.682
39.574
38.908
27.062
20.748
18.803
11.518
Cl
H3C
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

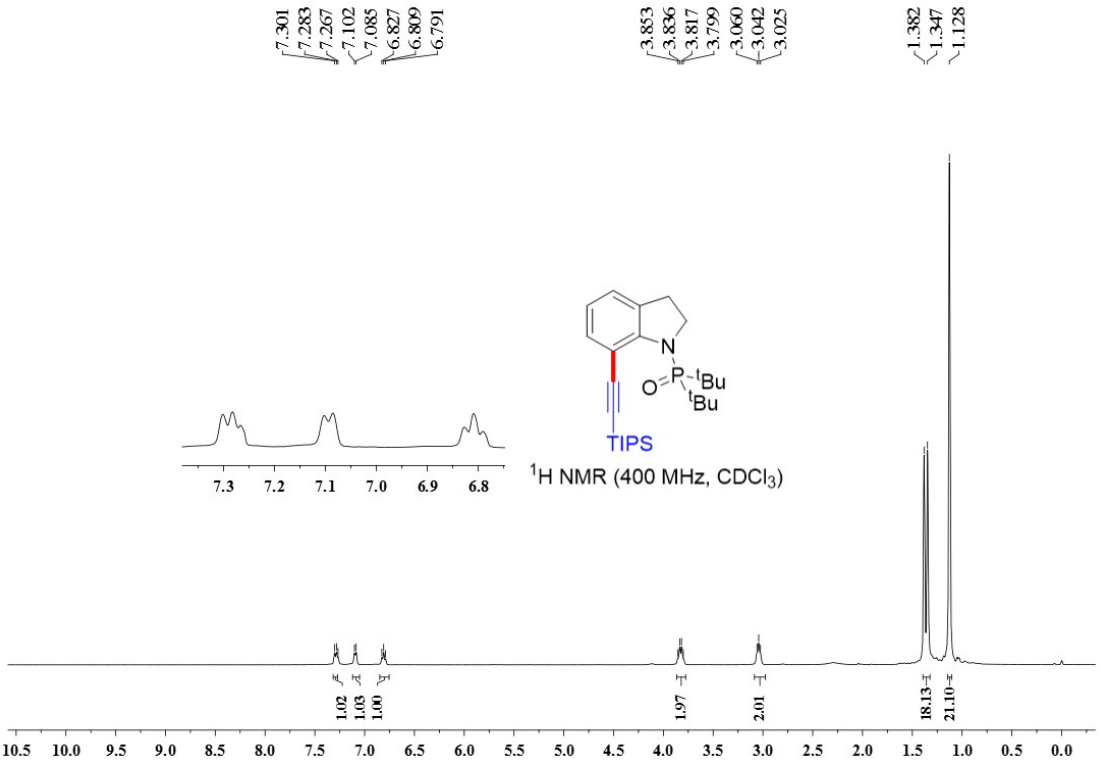

63.430
63.340
63.250
63.160
63.069
62.979
62.888
62.797
62.711
Cl
H3C
N
O
P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

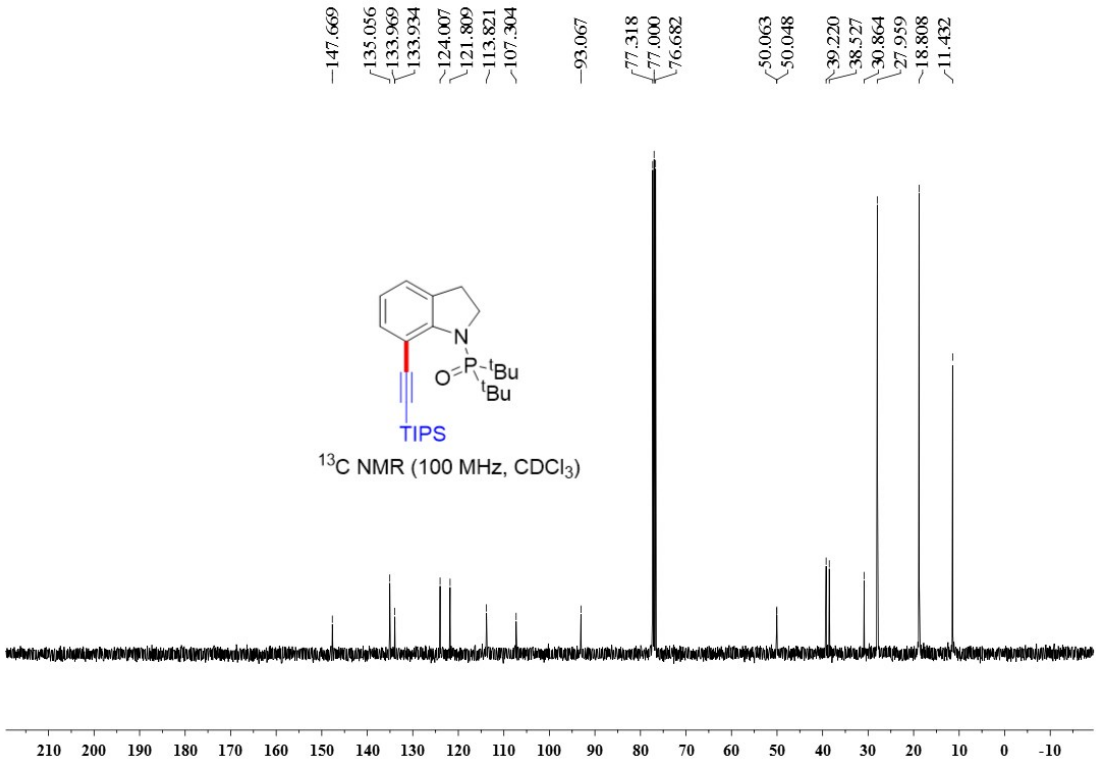
(Methylenebis(7-((triisopropylsilyl)ethynyl)-1*H*-indole-3,1-diyl))bis(di-*tert*-butylphosphine oxide) (3ac)

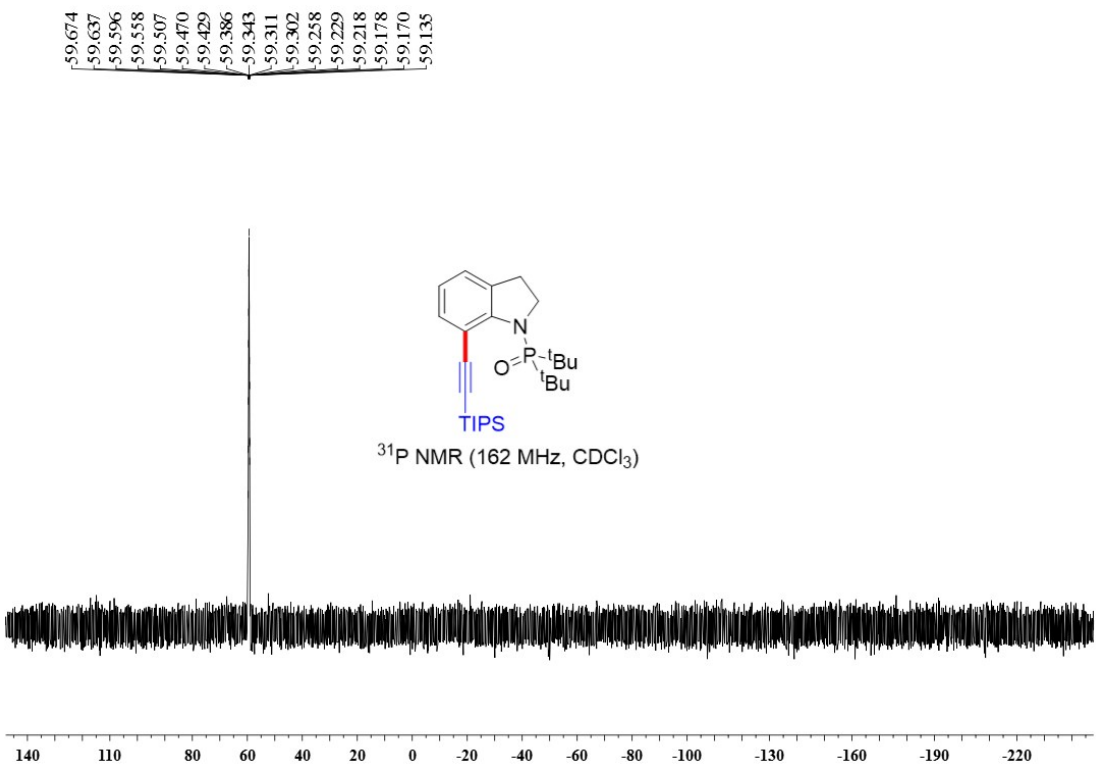




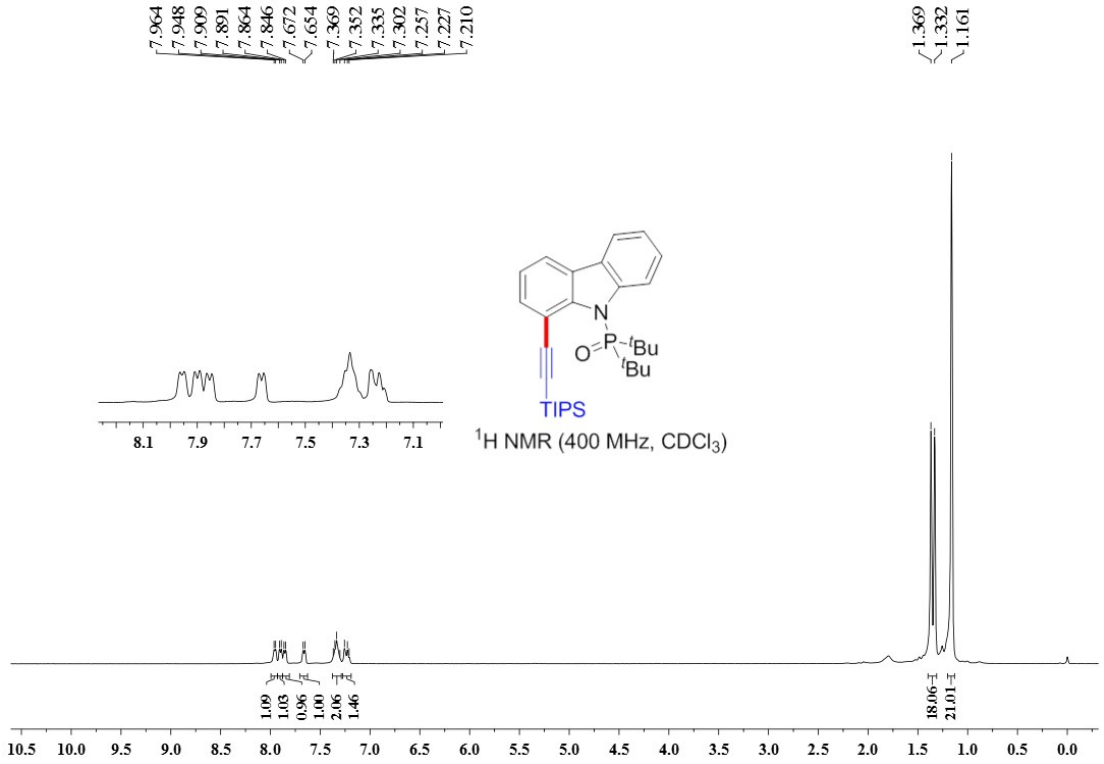
Di-*tert*-butyl(7-((triisopropylsilyl)ethynyl)indolin-1-yl)phosphine oxide (3ad)

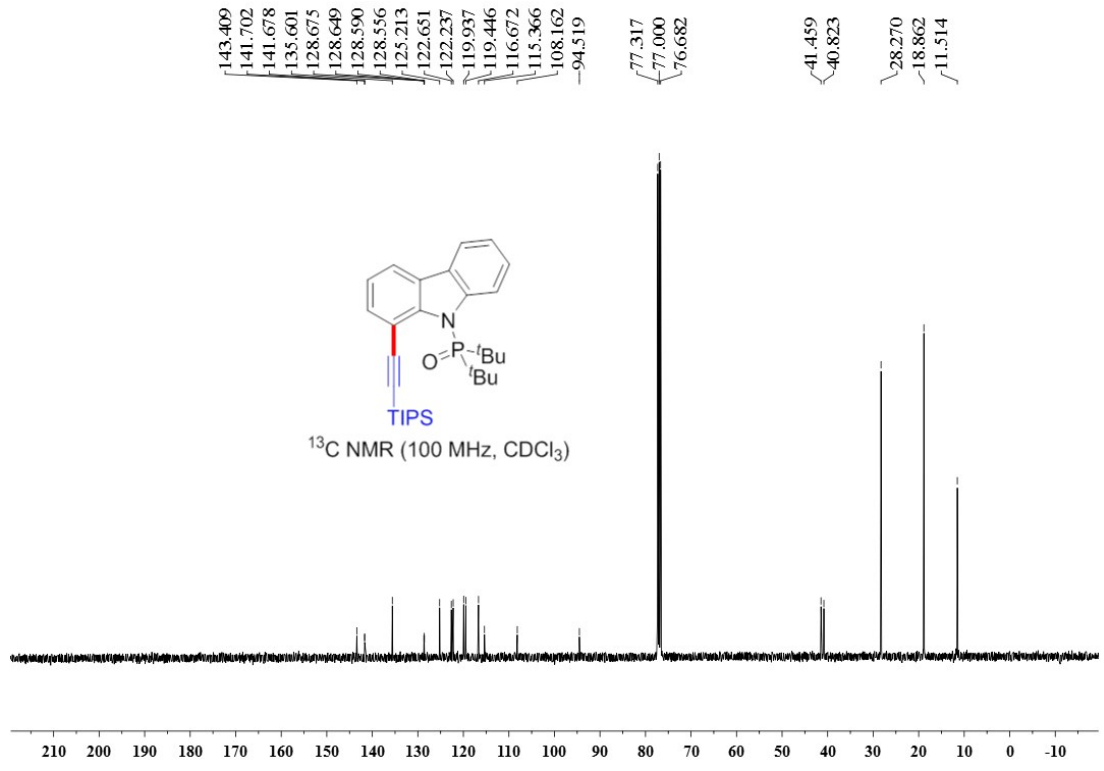


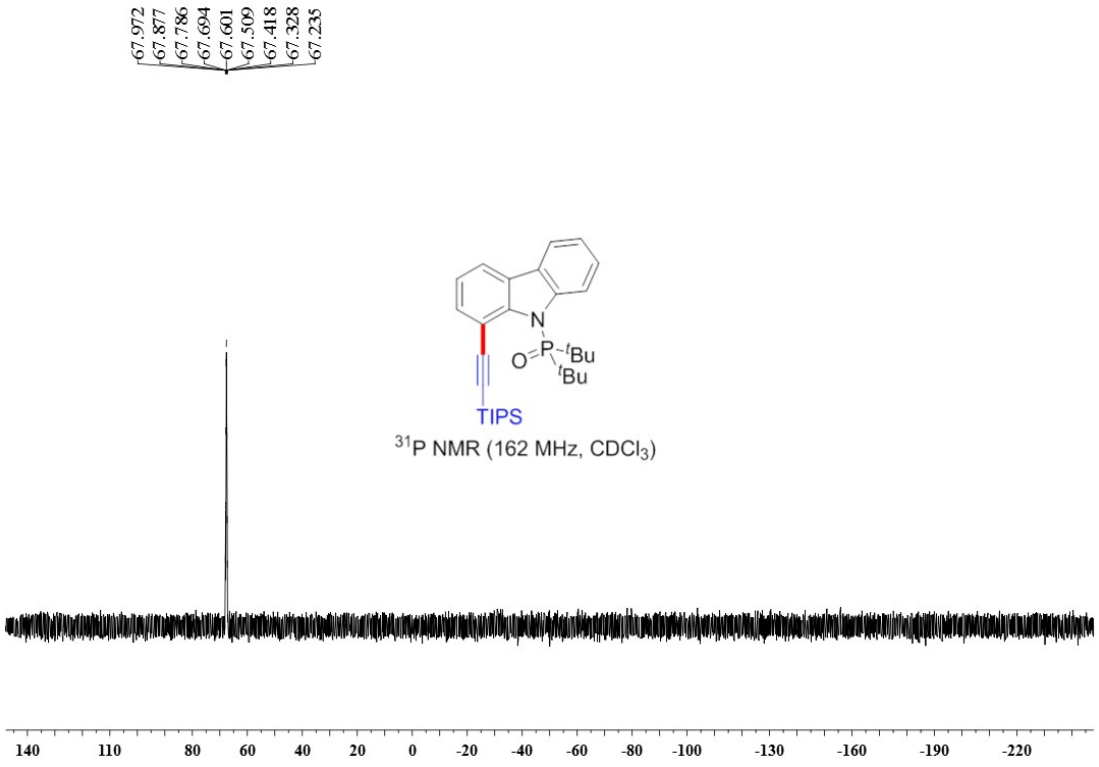

147.669
135.056
133.969
133.934
124.007
121.809
113.821
107.304
93.067
77.318
77.000
76.682
50.063
50.048
39.220
38.527
30.864
27.959
18.808
11.432
N
O
P
tBu
tBu
TIPS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


59.674
59.637
59.596
59.558
59.507
59.470
59.429
59.386
59.343
59.311
59.302
59.258
59.229
59.218
59.178
59.170
59.135
N
O
P
tBu
tBu
TIPS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

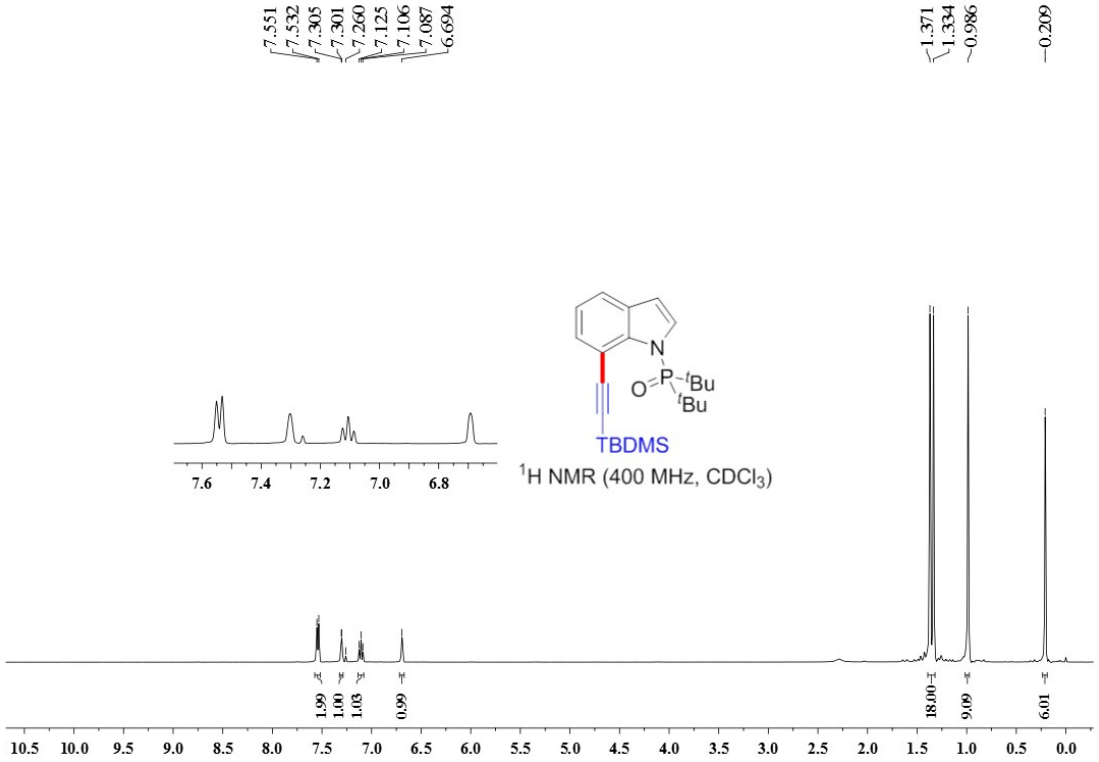
Di-*tert*-butyl(1-((triisopropylsilyl)ethynyl)-9*H*-carbazol-9-yl)phosphine oxide (3ae)

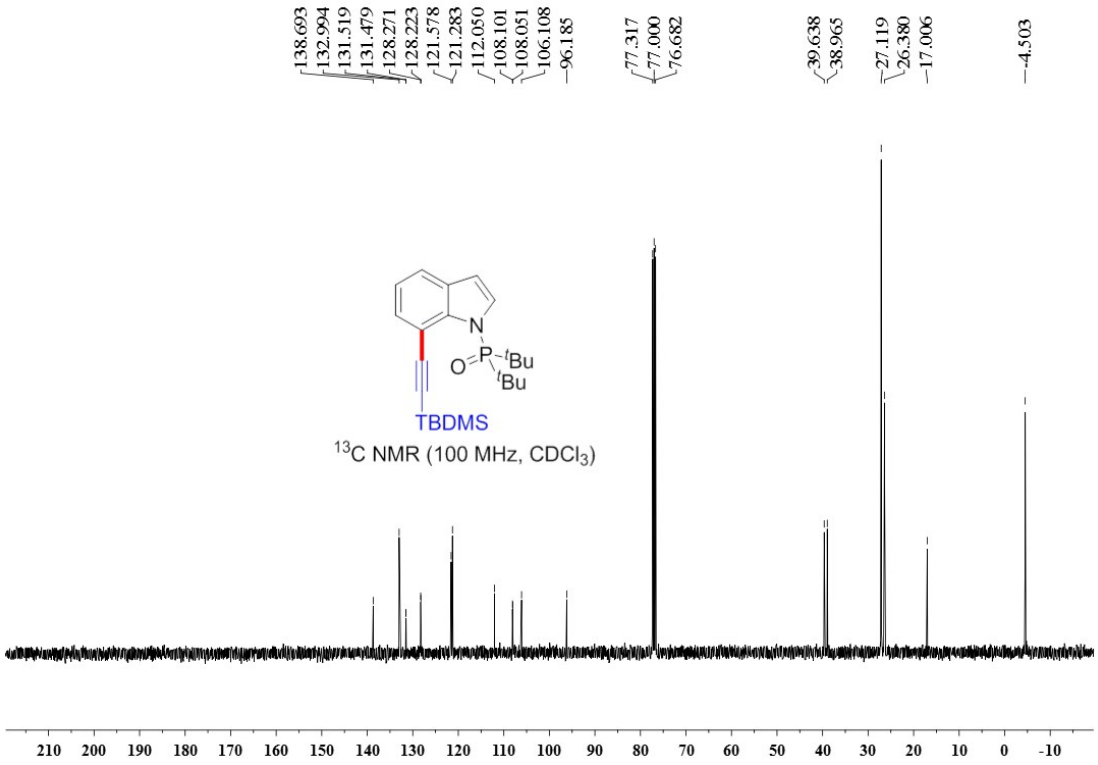


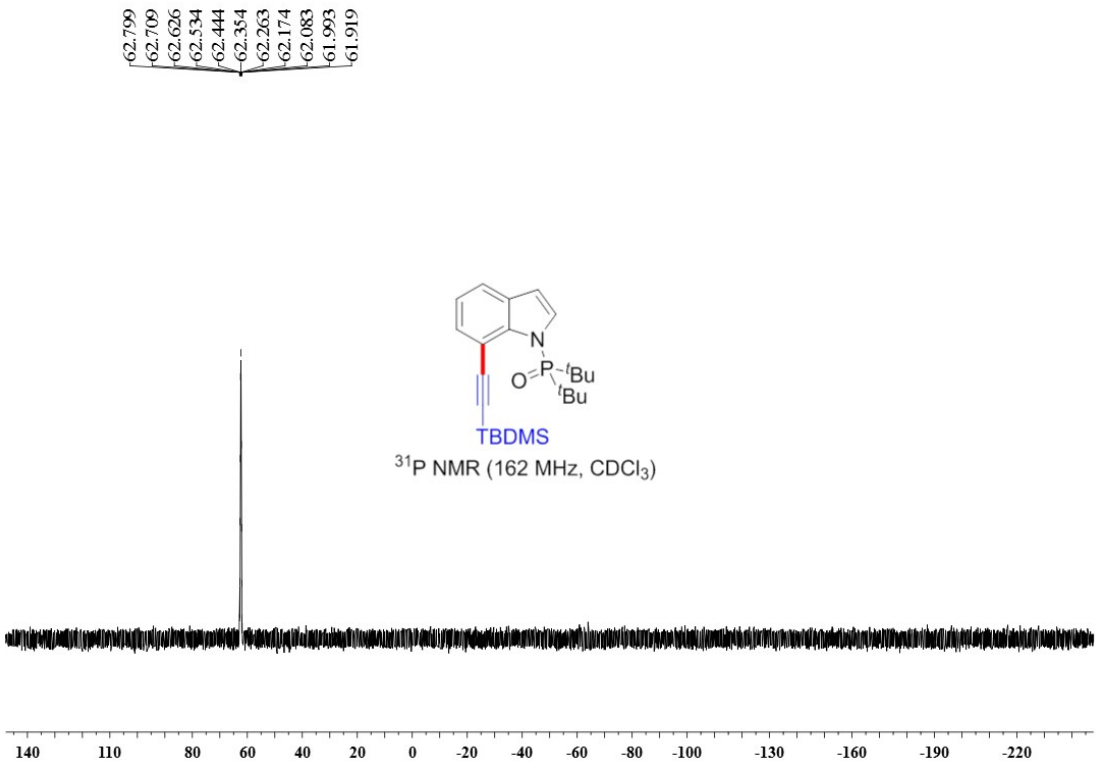




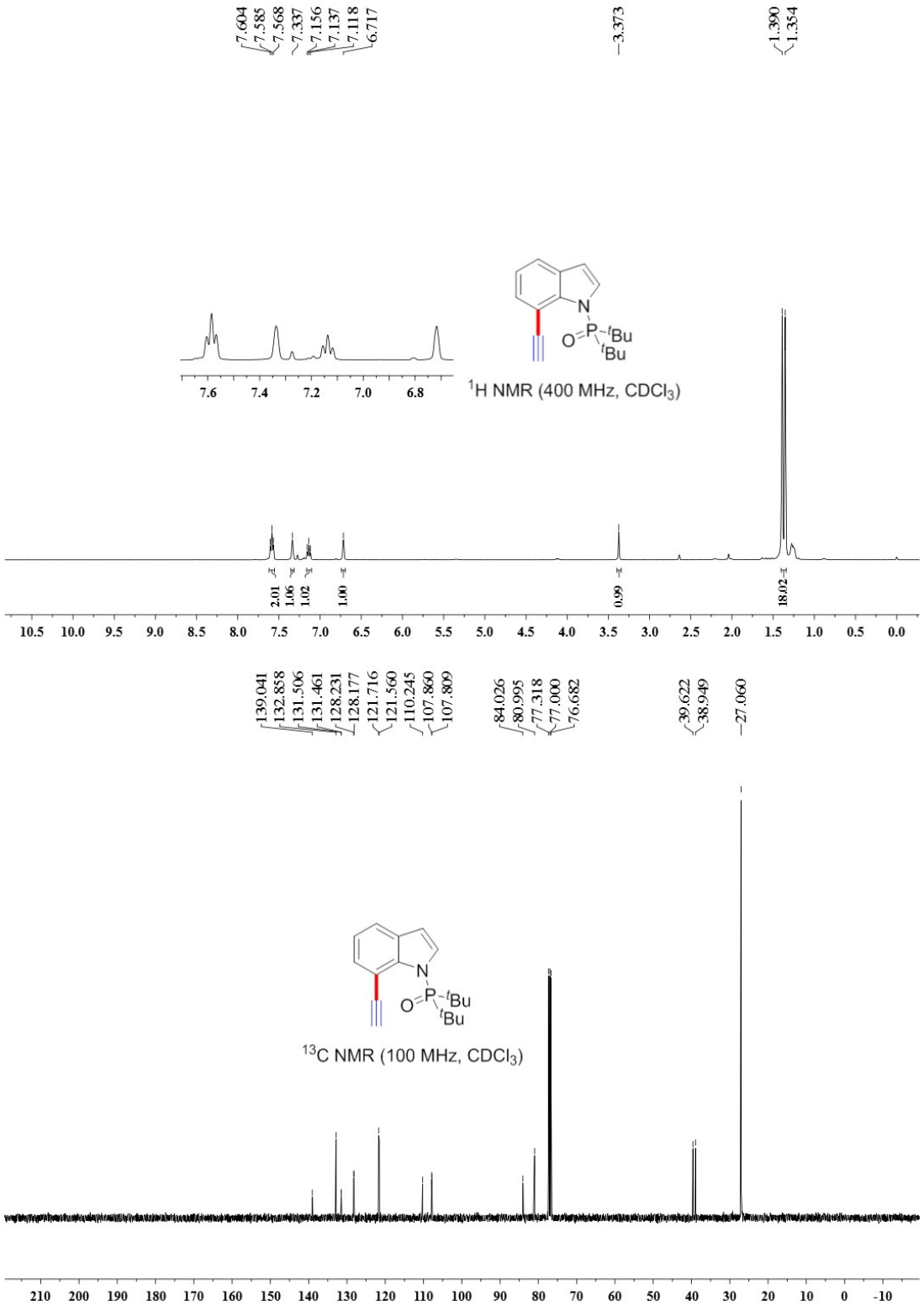
Di-*tert*-butyl(7-((*tert*-butyldimethylsilyl)ethynyl)-1*H*-indol-1-yl)phosphine oxide (3af)

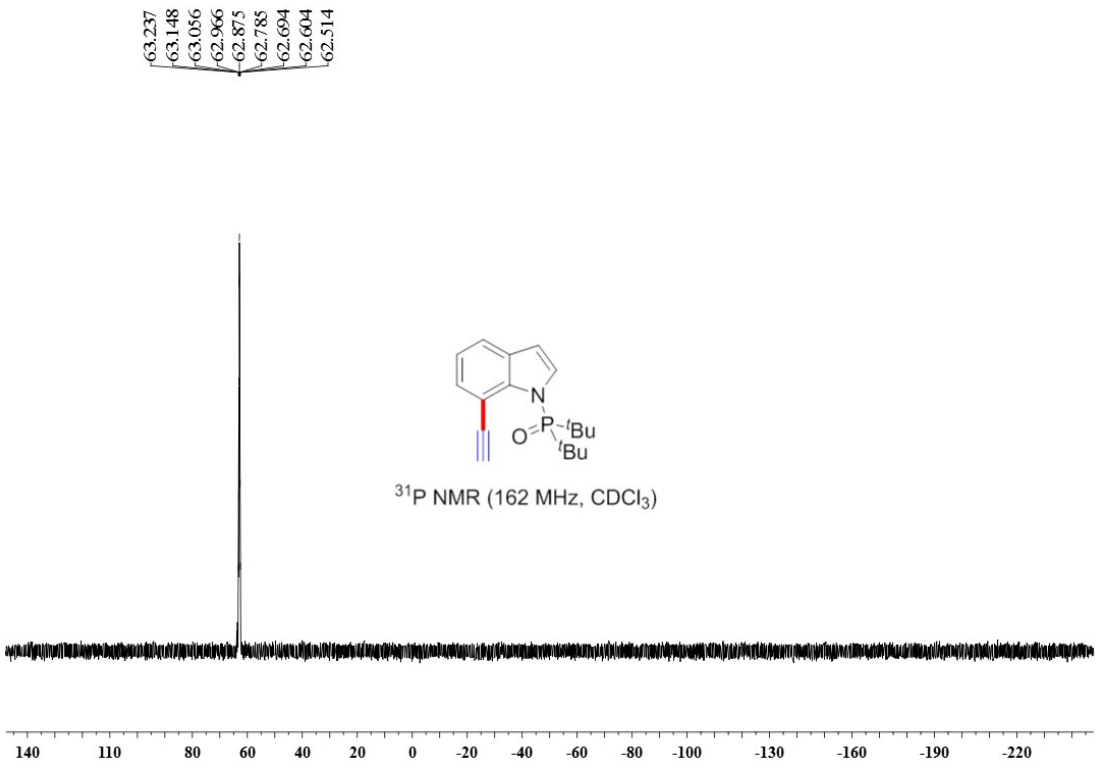



138.693
132.994
131.519
131.479
128.271
128.223
121.578
121.283
112.050
108.101
108.051
106.108
96.185
77.317
77.000
76.682
39.638
38.965
27.119
26.380
17.006
-4.503
N
O
P
tBu
tBu
TBDMS
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

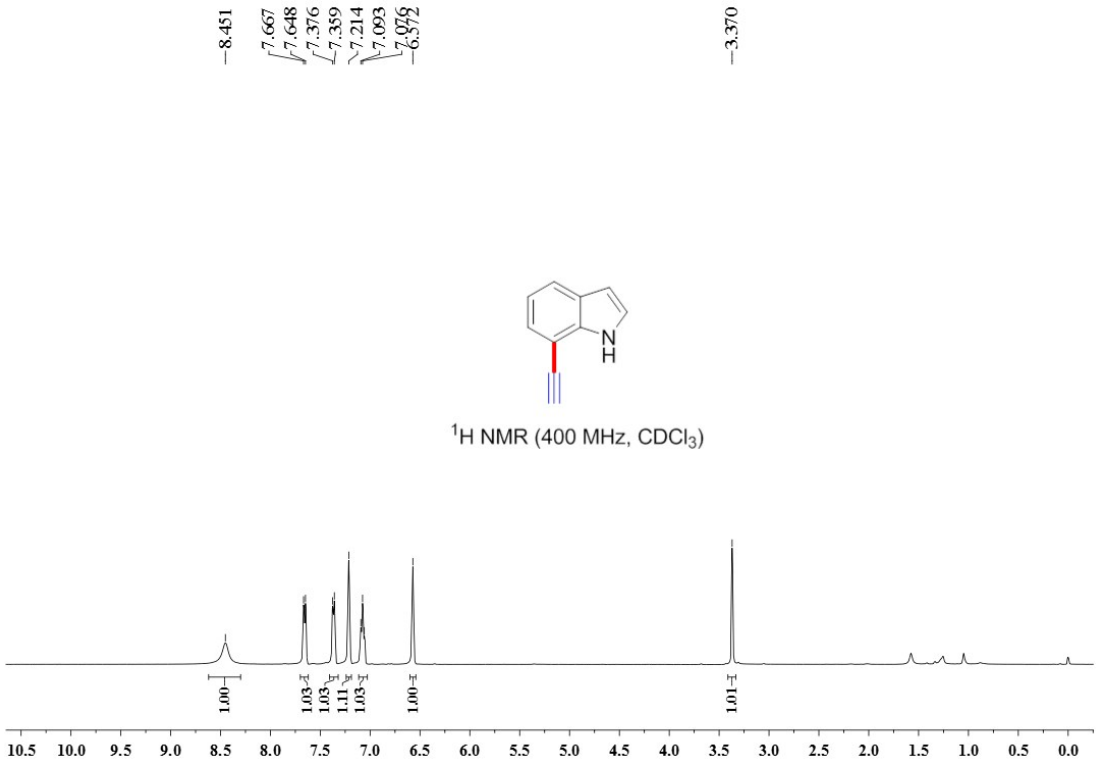

62.799
62.709
62.626
62.534
62.444
62.354
62.263
62.174
62.083
61.993
61.919
N
O
P
tBu
tBu
TBDMS
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

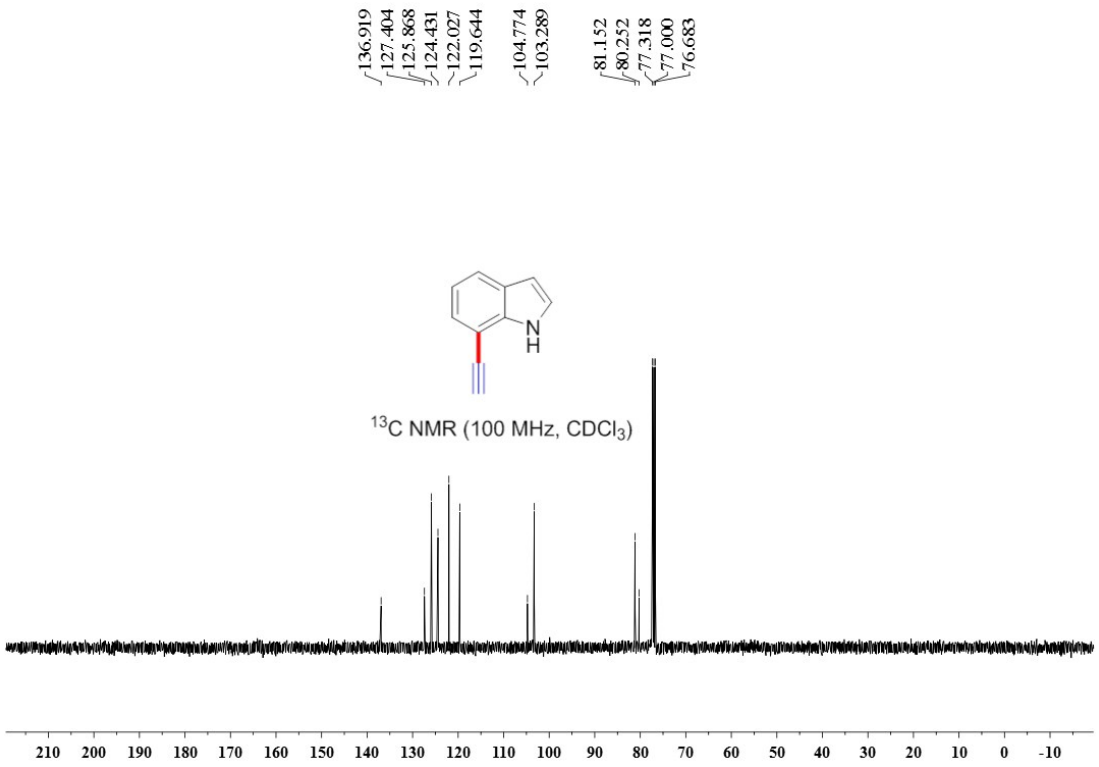
Di-*tert*-butyl(7-ethynyl-1*H*-indol-1-yl)phosphine oxide (4a)



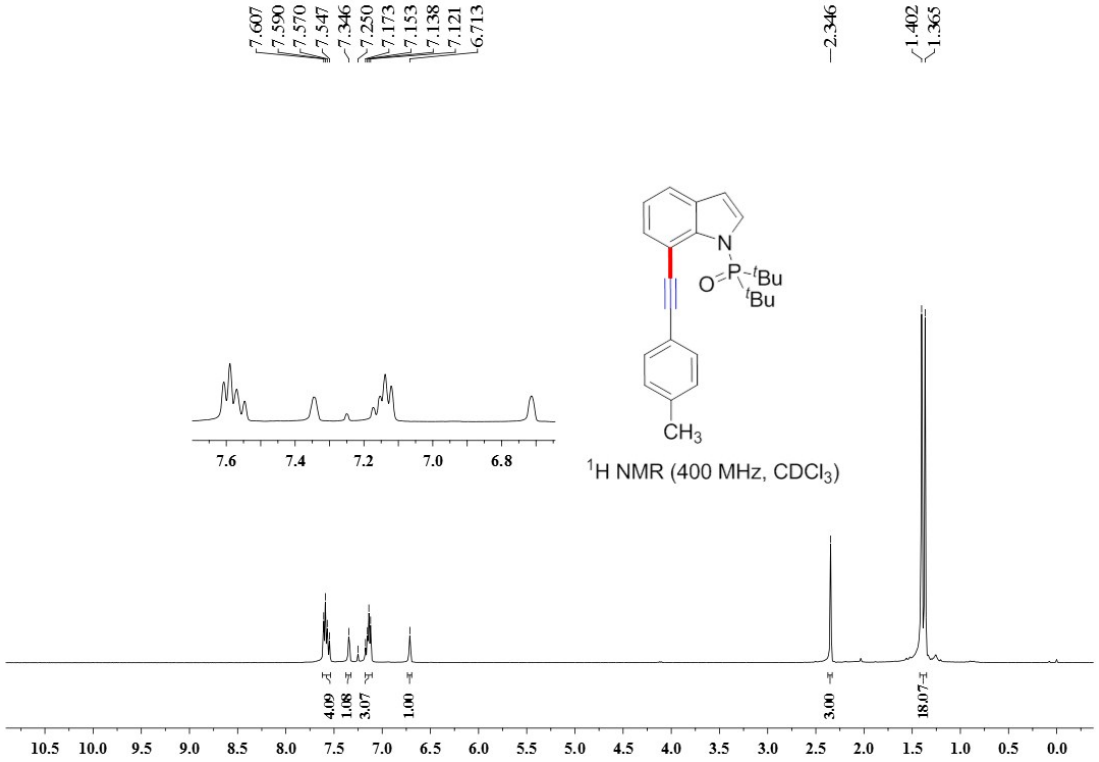


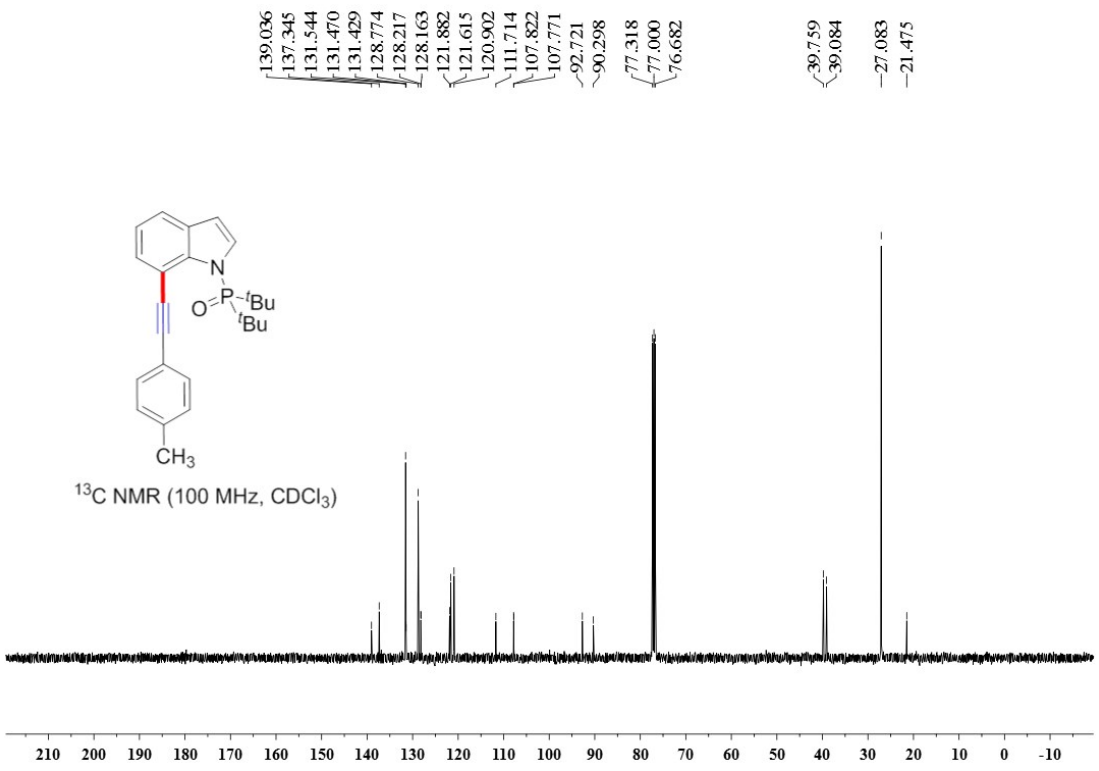
7-Ethynyl-1*H*-indole (5a)

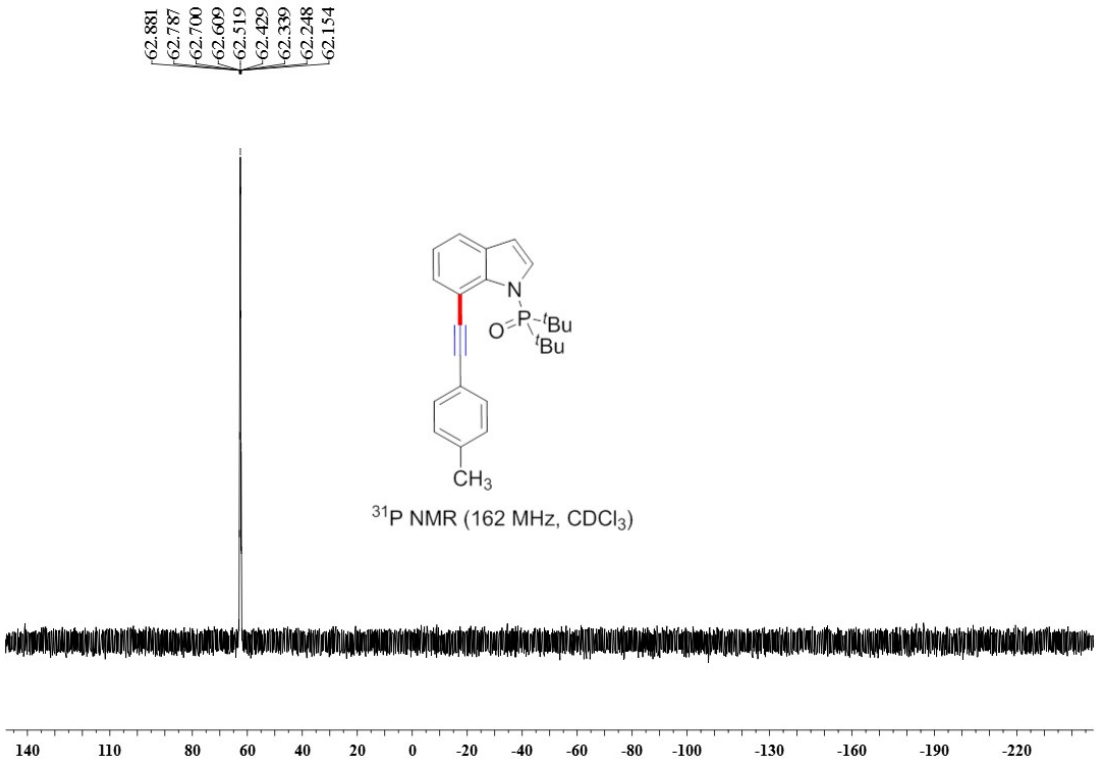




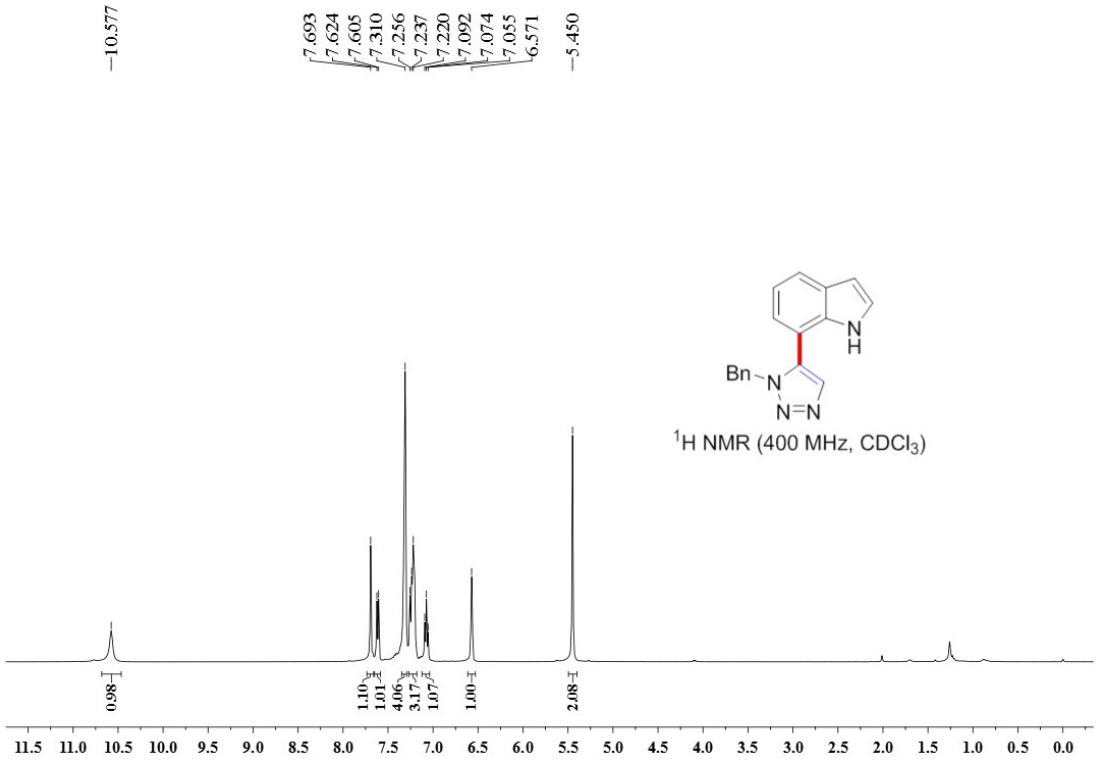
Di-*tert*-butyl(7-(*p*-tolylethynyl)-1*H*-indol-1-yl)phosphine oxide (6a)



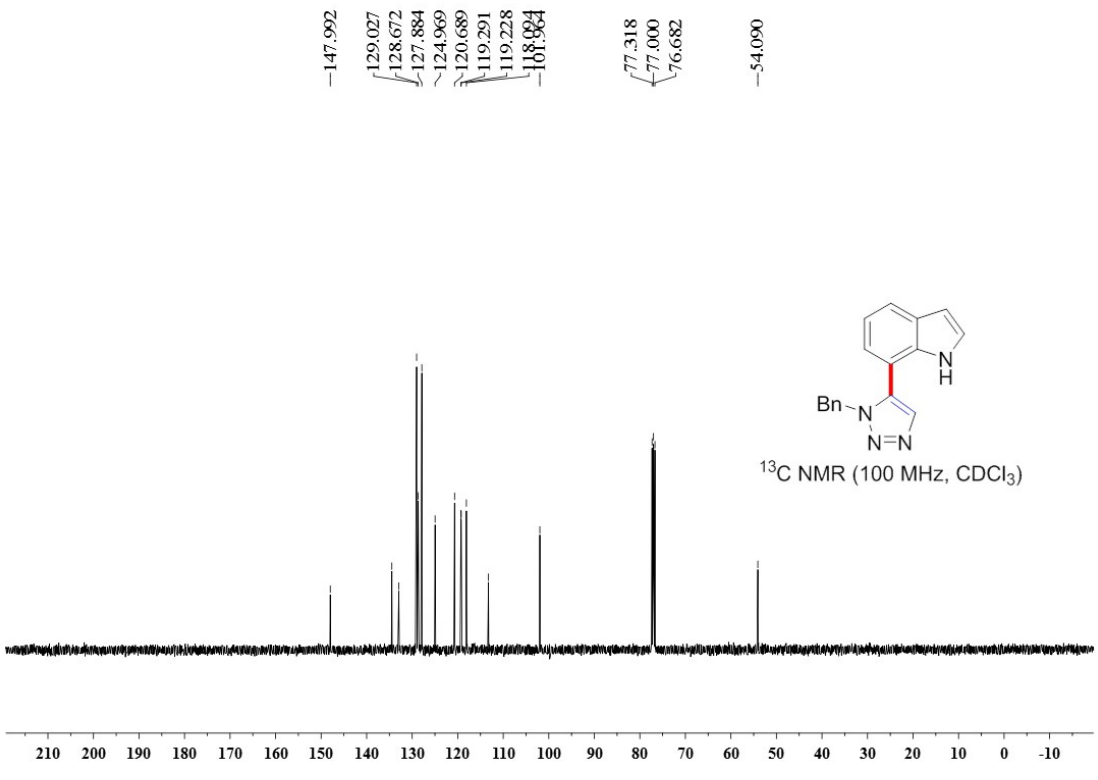

139.036
137.345
131.544
131.470
131.429
128.774
128.217
128.163
121.882
121.615
120.902
111.714
107.822
107.771
92.721
90.298
77.318
77.000
76.682
39.759
39.084
27.083
21.475
N
O
P
tBu
tBu
CH3
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


62.881
62.787
62.700
62.609
62.519
62.429
62.339
62.248
62.154
N
O
P
tBu
tBu
CH3
31P NMR (162 MHz, CDCl3)
140 110 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220

7-(1-Benzyl-1*H*-1,2,3-triazol-5-yl)-1*H*-indole (7a)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)