Supplementary Information

Pd-catalysed C–H alkynylation of benzophospholes

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Contents

Instrumentation and Chemicals

^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded at 400 MHz, 100 MHz, 376 MHz, and 162 MHz, respectively, for $CDCl_3$ solutions. HRMS data were obtained by APCI using TOF. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel $60F_{254}$. Silica gel (60 N, spherical neutral, Kanto Chemical Co.) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-20AR (pump, SHIMADZU, 7.5 mL/min $CHCl_3$) and SPD-20A (UV detector, SHIMADZU, 254 nm) with two in-line YMC-GPC T2000 (20 x 600 mm, particle size: 10 μm) (preparative columns, YMC). UV-vis spectra were acquired with JASCO V-750 spectrometer. Photoluminescence spectra and quantum yield measurements were conducted with JASCO FP-8500 spectrometer equipped with an integration sphere system. The crystal measurement was performed with XtaLAB Synergy-S/Cu or Mo (Rigaku). Cyclic voltammograms and differential pulse voltammograms were recorded on ALS Electrochemical Analyzer Model 600E equipped with SVC-3 Voltammetry cell. Counter and working electrodes were made of Pt, and the reference electrode was Ag/Ag^{+}. The working electrodes were polished on a cloth polishing pad in an alumina slurry and then washed in H_2O under sonication before use. The measurements were conducted in MeCN solvent (degassed by N_2 gas bubbling) containing tetrabutylammonium hexafluorophosphate as a supporting

electrolyte at an indicated scan rate. All the potentials were calibrated with the standard ferrocene/ferrocenium (Fc/Fc^+) redox couple measured in identical conditions.

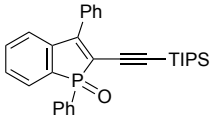
Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 1,4-Dioxane was dried on a Glass Contour Solvent dispensing system (Nikko Hansen & Co., Ltd.) prior to use. $Pd(OPiv)_2$ and NaOPiv were purchased from Sigma-Aldrich. The C2-H benzophospholes **1**[S1] and alkynyl bromides **2** [S2] were prepared according to the literature methods. Unless otherwise noted, all reactions were performed under nitrogen atmosphere.

Experimental Procedures and Characterization Data for Products

Pd-Catalysed C2-H Alkynylation of Benzophospholes (Scheme 2: general procedure A)

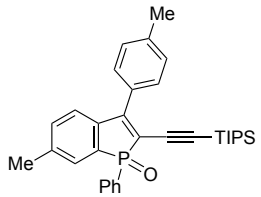
A 0.10 mmol scale synthesis of **3**: The benzophosphole oxide **1** (0.10 mmol), $Pd(OPiv)_2$ (3.1 mg, 0.010 mmol), and NaOPiv・xH_2O (25 mg, 0.20 mmol) were placed in a Schlenk tube, which was filled with N_2 by using the standard Schlenk technique. 1,4-Dioxane (1.5 mL) and the alkynyl bromide **2** (0.20 mmol) were finally added via syringe. The mixture was stirred at 60 ºC for 48 h (oil bath). The resulting mixture was cooled to room temperature and then quenched with water and brine. Extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate to give the corresponding C2–H alkynylated benzophosphole.

A 1.0 mmol scale synthesis of **3aa**: 1,3-Diphenylphosphindole 1-oxide (**1a**; 303 mg, 1.0 mmol), $Pd(OPiv)_2$ (31 mg, 0.10 mmol), NaOPiv・xH_2O (248 mg, 2.0 mmol), and 1,4-dioxane (15 mL) were placed in a Schlenk tube, which was filled with N_2 by using the standard Schlenk technique. 1,4-Dioxane (15 mL) and tri(isopropyl)silyl (TIPS)-substituted alkynyl bromide **2a** (523 mg, 2.0 mmol) were finally added via syringe. The mixture was stirred at 60 ºC for 48 h (oil bath). The resulting mixture was cooled to room temperature and then quenched with water and brine. Extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (2:1, v/v) then GPC ($CHCl_3$) to give 1,3-diphenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (**3aa**; 329 mg, 0.68 mmol) in 68% yield.

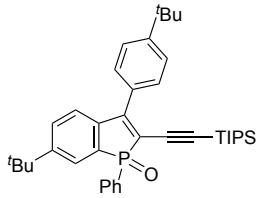


1,3-Diphenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (3aa): Synthesized from **1a** (31 mg, 0.10 mmol) and **2a** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v): 35 mg (72%, 0.10 mmol scale); Yellow solid; m.p. 111.1-111.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.78 (m, 2H), 7.73 (dd, J = 9.8, 7.2 Hz, 1H), 7.64-7.61 (m, 2H), 7.56-7.42 (m, 9H), 0.96-0.88 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ

157.1 (d, J = 20.7 Hz, 1C), 142.3 (d, J = 24.4 Hz, 1C), 133.2 (d, J = 13.2 Hz, 1C), 133.0 (d, J = 1.8 Hz, 1C), 132.5 (d, J = 2.8 Hz, 1C), 131.3 (1C), 131.2 (1C), 131.1 (d, J = 104.9 Hz, 1C), 129.9 (d, J = 10.8 Hz, 1C), 129.8 (d, J = 9.2 Hz, 1C), 129.5 (1C), 129.0 (d, J = 103.8, 1C), 128.9 (2C), 128.8 (1C), 128.7 (1C), 128.4 (2C), 124.6 (d, J = 10.3 Hz, 1C), 119.8 (d, J = 102.6 Hz, 1C), 104.8 (d, J = 5.8 Hz, 1C), 99.5 (d, J = 9.2 Hz, 1C), 18.5 (6C), 11.1 (3C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 36.30; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{31}H_{36}OPSi$: 483.2268, found: 483.2287.

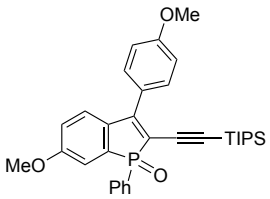


6-Methyl-1-phenyl-3-(*p*-tolyl)-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (3ba): Synthesized from **1b** (33 mg, 0.10 mmol) and **2a** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (1/1, v/v): 37 mg (72%, 0.10 mmol scale); Yellow solid; m.p. 135.8-136.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H), 7.56-7.51 (m, 4H), 7.46-7.41 (m, 2H), 7.34 (dd, J = 7.9, 3.3 Hz, 1H), 7.29-7.27 (m, 3H), 2.42 (s, 3H), 2.36 (s, 3H), 0.99-0.86 (m, 21H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.3 (dd, J = 20.7 Hz, 1C), 140.3 (d, J = 10.4 Hz, 1C), 139.7 (d J = 24.4 Hz, 1C), 139.6 (1C), 133.4 (d, J = 1.5 Hz, 1C), 132.3 (d, J = 2.8 Hz, 1C), 131.4 (d, J = 104.3 Hz, 1C), 131.3 (1C), 131.2 (1C), 130.52 (d, J = 9.3 Hz, 1C), 130.46 (d, J = 13.3 Hz, 1C), 129.3 (d, J = 103.3 Hz, 1C), 129.0 (2C), 128.8 (2C), 128.7 (1C), 128.6 (1C), 124.5 (d, J = 11.0 Hz, 1C), 117.9 (d, J = 103.7 Hz, 1C), 103.9 (d, J =5.8 Hz, 1C), 99.9 (d, J =9.4 Hz, 1C), 21.5 (1C), 21.3 (1C), 18.5 (6C), 11.2 (3C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 36.37; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{33}H_{40}OPSi$: 511.2581, found: 511.2585.

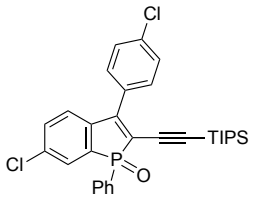


6-(*tert*-Butyl)-3-(4-(*tert*-butyl)phenyl)-1-phenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (3ca): Synthesized from **1c** (41 mg, 0.10 mmol) and **2a** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v) and GPC ($CHCl_3$): 50 mg (84%, 0.10 mmol scale); Yellow solid; m.p. 191.9-192.6 ℃; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.84-7.77 (m, 3H), 7.61-7.58 (m, 2H), 7.55-7.41 (m, 7H), 1.36 (s, 9H), 1.32 (s, 9H), 0.92-0.88 (m, 21H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.5 (dd, *J* = 20.9 Hz, 1C), 153.6 (d, *J* = 9.7 Hz, 1C), 152.6 (1C), 139.7 (d, *J* = 24.6 Hz, 1C), 132.3 (d, *J* = 2.8 Hz, 1C), 131.3 (1C), 131.2 (1C), 131.1 (d, *J* = 101.1 Hz, 1C), 130.5 (d, *J* = 9.9 Hz, 1C), 129.9 (d, *J* = 1.4 Hz, 1C), 129.4 (d, *J* = 103.2 Hz, 1C), 128.71 (1C), 128.67 (2C), 128.6 (1C), 126.9 (d, *J* = 9.7 Hz, 1C), 125.3 (2C), 124.4 (d, *J* = 11.0 Hz, 1C), 118.4 (d, *J* = 103.7 Hz, 1C), 103.4 (d, *J* = 5.8 Hz, 1C), 100.1 (d, *J* = 9.5 Hz, 1C), 35.1 (1C), 34.8 (1C), 31.25 (3C), 31.18 (3C), 18.5 (6C), 11.2 (3C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 36.64; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{39}H_{52}OPSi$: 595.3520, found: 595.3509.

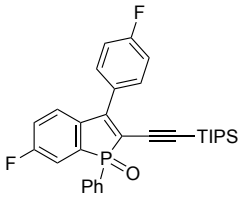


6-Methoxy-3-(4-methoxyphenyl)-1-phenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (3da): Synthesized from **1d** (36 mg, 0.10 mmol) and **2a** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (1/1, v/v): 52 mg (95%, 0.10 mmol scale); Orange solid; m.p. 165.2-165.9 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H), 7.66-7.63 (m, 2H), 7.59-7.55 (m, 1H), 7.44 (td, *J* = 7.7, 3.1 Hz, 2H), 7.40 (dd, *J* = 8.6, 3.8 Hz, 1H), 7.28 (dd, *J* = 11.1, 2.5 Hz, 1H), 7.01-6.96 (m, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 0.97-0.87 (m, 21H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.4 (d, *J* = 13.7 Hz, 1C), 160.5 (1C), 156.9 (d, *J* = 21.0 Hz, 1C), 134.7 (d, *J* = 24.3 Hz, 1C), 133.5 (d, *J* = 103.5 Hz, 1C), 132.4 (d, *J* = 2.8 Hz, 1C), 131.3 (1C), 131.2 (1C), 130.5 (2C), 129.3 (d, *J* = 103.7 Hz, 1C), 128.7 (1C), 128.6 (1C), 125.9 (d, *J* = 12.2 Hz, 1C), 125.8 (d, *J* = 12.6 Hz, 1C), 117.9 (1C), 115.7 (d, *J* = 105.6 Hz, 1C), 115.4 (d, *J* = 10.4 Hz, 1C), 113.8 (2C), 102.7 (d, *J* = 5.9 Hz, 1C), 100.1 (d, *J* = 9.5 Hz, 1C), 55.7 (1C), 55.4 (1C), 18.5 (6C), 11.2 (3C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 35.94; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{33}H_{40}O_3PSi$: 543.2479, found: 543.2469.

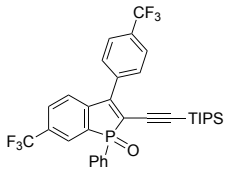


6-Chloro-3-(4-chlorophenyl)-1-phenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (3ea):

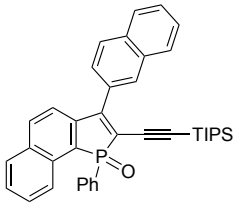
Synthesized from **1e** (37 mg, 0.10 mmol) and **2a** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v): 39 mg (71%, 0.10 mmol scale); Yellow solid; m.p. 138.5-139.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.76 (m, 2H), 7.69 (dd, *J* = 10.0, 1.96 Hz, 1H), 7.61-7.55 (m, 3H), 7.50-7.45 (m, 5H), 7.32 (dd, *J* = 8.3, 3.4 Hz, 1H), 1.00-0.86 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.8 (d, *J* = 20.3 Hz, 1C), 140.7 (d, *J* = 24.0 Hz, 1C), 136.7 (d, *J* = 14.0 Hz, 1C), 135.7 (1C), 133.2 (d, *J* = 102.3 Hz, 1C), 133.0 (d, *J* = 1.3 Hz, 1C), 132.9 (d, *J* = 2.9 Hz, 1C), 131.23 (d, *J* = 13.3 Hz, 1C), 131.21 (1C), 131.1 (1C), 130.2 (2C), 130.1 (d, *J* = 10.3, 1C), 129.0 (1C), 128.90 (2C), 128.88 (1C), 127.9 (d, *J* = 104.9 Hz, 1C), 125.3 (d, *J* = 11.2 Hz, 1C), 120.4 (d, *J* = 102.7 Hz, 1C), 106.6 (d, *J* = 5.9 Hz, 1C), 98.9 (d, *J* = 9.2 Hz, 1C), 18.4 (6C), 11.1 (3C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 35.10; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{31}H_{34}Cl_2OPSi$: 551.1488, found: 551.1480.



6-Fluoro-3-(4-fluorophenyl)-1-phenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (3fa): Synthesized from **1f** (34 mg, 0.10 mmol) and **2a** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v): 51 mg (97%, 0.10 mmol scale); Pale yellow solid; m.p. 107.8-108.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.76 (m, 2H), 7.64-7.56 (m, 3H), 7.49-7.35 (m, 4H), 7.21-7.16 (m, 3H), 0.99-0.87 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.1 (dd, *J* = 253.1, 15.3 Hz, 1C), 162.3 (d, *J* = 248.7 Hz, 1C), 154.1 (dd, *J* = 20.3, 1.8 Hz, 1C), 136.9 (dd, *J* = 23.8, 3.1 Hz, 1C), 133.0 (dd, *J* = 103.2, 6.7 Hz, 1C), 131.8 (d, *J* = 2.8 Hz, 1C), 130.1 (d, *J* = 10.9 Hz, 2C), 129.8 (d, *J* = 8.2 Hz, 2C), 128.0 (dd, *J* = 16.8, 3.4 Hz, 1C), 127.9 (1C), 127.8 (1C), 127.1 (d, *J* = 104.8 Hz, 1C), 125.0 (dd, *J* = 12.1, 7.8 Hz, 1C), 118.62 (dd, *J* = 22.5, 1.1 Hz, 1C), 118.58 (dd, *J* = 103.9, 4.0 Hz, 1C), 116.6 (dd, *J* = 23.9, 10.3 Hz, 1C), 114.7 (d, *J* = 21.7 Hz, 2C), 104.3 (d, *J* = 5.9 Hz, 1C), 98.0 (d, *J* = 9.3 Hz, 1C), 17.4 (6C), 10.1 (3C); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -109.6 (d, *J* = 4.8 Hz), -110.3; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 34.76 (d, *J* = 5.4 Hz); HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{31}H_{34}F_2OPSi$: 519.2079, found: 519.2080.

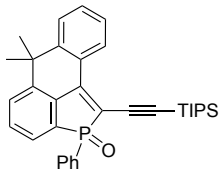


1-Phenyl-6-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (3ga): Synthesized from **1g** (44 mg, 0.10 mmol) and **2a** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v): 39 mg (63%, 0.10 mmol scale); Pale yellow solid; m.p. 148.5-149.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 10.0 Hz, 1H), 7.83-7.71 (m, 7H), 7.64-7.59 (m, 1H), 7.52-7.45 (m, 3H), 0.98-0.85 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.2 (d, *J* = 20.2 Hz, 1C), 145.0 (d, *J* = 24.0 Hz, 1C), 136.3 (d, *J* = 13.1 Hz, 1C), 133.2 (d, *J* = 2.9 Hz, 1C), 133.1 (1C), 132.7, 132.6, 132.5, 132.4, 132.3, 132.2, 132.1, 131.94, 131.88, 131.7, 131.61, 131.55, 131.50, 131.2 (1C), 130.5 (dd, *J* = 3.4, 2.2 Hz, 1C), 129.20 (2C), 129.16 (1C), 129.0 (1C), 127.8, 127.7, 127.5, 126.9, 126.83, 126.80, 126.76, 126.73, 126.67, 125.8 (dd, *J* = 7.2, 3.6 Hz, 1C), 125.1, 124.81, 124.79, 124.6, 124.2 (d, *J* = 10.1 Hz, 1C), 123.6, 122.4, 122.10, 122.08, 119.7, 119.4, 108.7 (d, *J* = 5.8 Hz, 1C), 98.4 (d, *J* = 9.0 Hz, 1C), 18.4 (6C), 11.0 (3C) (All observed signals cannot be completely assigned because of complexity associated with C–F and C–P couplings.); ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ -62.7, -62.9; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 34.96; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{33}H_{34}F_6OPSi$: 619.2015, found: 619.2018.

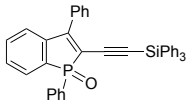


3-(Naphthalen-2-yl)-1-phenyl-2-((triisopropylsilyl)ethynyl)benzo[*g*]phosphindole 1-oxide (3ha): Synthesized from **1h** (40 mg, 0.10 mmol) and **2a** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v): 51 mg (88%, 0.10 mmol scale); Yellow solid; m.p. 105.8-106.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s,1H), 8.13-8.11 (m, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.93-7.83 (m, 5H), 7.77 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.65 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.59-7.48 (m, 5H), 7.46-7.41 (m, 2H), 0.97-0.84 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.4 (d, *J* = 22.3 Hz, 1C), 141.9 (d, *J* = 23.7 Hz, 1C), 133.93 (d, *J* = 10.0 Hz, 1C), 133.89 (1C), 133.7 (1C), 133.0 (1C), 132.5 (d, *J* = 2.8 Hz, 1C), 132.4 (d, *J*

= 8.6 Hz, 1C), 131.3 (1C), 131.2 (1C), 130.9 (d, *J* = 13.8 Hz, 1C), 129.3 (d, *J* = 100.2 Hz, 1C), 129.0 (1C), 128.9 (1C), 128.8 (1C), 128.75 (1C), 128.68 (1C), 128.5 (1C), 128.1 (1C), 127.8 (1C), 127.3 (1C), 127.1 (1C), 126.8 (d, *J* = 102.8 Hz, 1C), 126.5 (1C), 126.2 (1C), 126.1 (d, *J* = 4.6 Hz, 1C), 121.8 (d, *J* = 11.9 Hz, 1C), 120.8 (d, *J* = 102.8 Hz, 1C), 105.1 (d, *J* = 5.9 Hz, 1C), 99.9 (d, *J* = 9.8 Hz, 1C) 18.5 (6C), 11.3 (3C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 36.96; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{39}H_{40}OPSi$: 583.2581, found: 583.2562.

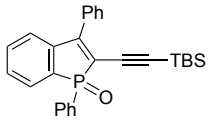


6,6-Dimethyl-2-phenyl-1-((triisopropylsilyl)ethynyl)-6*H*-naphtho[1,2,3-*cd*]phosphindole 2-oxide (3ia): Synthesized from **1i** (34 mg, 0.10 mmol) and **2a** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (1/1, v/v): 51 mg (97%, 0.10 mmol scale); Yellow solid; m.p. 176.6-177.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (dd, *J* = 2.0, 0.30 Hz, 1H), 7.79-7.73 (m, 2H), 7.71-7.67 (m, 2H), 7.63-7.59 (m, 1H), 7.55-7.47 (m, 3H), 7.42-7.38 (m, 2H), 7.34-7.30 (m, 1H), 1.74 (s, 3H), 1.69 (s, 3H), 1.17-1.00 (m, 21H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 146.5 (1C), 145.1 (d, *J* = 21.5 Hz, 1C), 142.3 (d, *J* = 11.0 Hz, 1C), 136.1 (d, *J* = 27.0 Hz, 1C), 132.2 (d, *J* = 2.8 Hz, 1C), 131.5 (1C), 131.4 (1C), 131.3 (1C), 130.9 (d, *J* = 13.8 Hz, 1C), 130.8 (d, *J* = 3.4 Hz, 1C), 130.5 (d, *J* = 11.4 Hz, 1C), 129.61 (d, *J* = 103.6 Hz, 1C), 129.60 (d, *J* = 104.6 Hz, 1C), 128.6 (1C), 128.5 (1C), 128.0 (1C), 127.7 (d, *J* = 9.2 Hz, 1C), 127.481 (1C), 127.479 (d, *J* = 14.7 Hz, 1C), 111.4 (d, *J* = 106.3 Hz, 1C), 109.2 (d, *J* = 6.4 Hz, 1C), 102.1 (d, *J* = 8.2 Hz, 1C), 38.7 (1C), 33.7 (1C), 32.7 (1C), 18.6 (6C), 11.3 (3C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 38.79; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{34}H_{40}OPSi$: 523.2581, found: 523.2588.

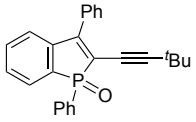


1,3-Diphenyl-2-((triphenylsilyl)ethynyl)phosphindole 1-oxide (3ab): Synthesized from **1a** (31 mg, 0.10 mmol) and **2b** (73 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v) and GPC ($CHCl_3$): 35 mg (59%, 0.10 mmol scale); Pale yellow solid; m.p. 228.6-229.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.75 (m, 3H), 7.66-7.64 (m, 2H), 7.61-7.57 (m, 1H), 7.55-7.42 (m, 14H), 7.39-7.34 (m, 3H), 7.28-7.24 (m, 6H);

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.0 (d, *J* = 20.4 Hz, 1C), 142.2 (d, *J* = 24.5 Hz, 1C), 135.5 (6C), 133.2 (d, *J* = 1.8 Hz, 1C), 133.1 (d, *J* = 12.9 Hz, 1C), 133.0 (3C), 132.7 (d, *J* = 2.8 Hz, 1C), 131.4 (1C), 131.3 (1C), 131.1 (d, *J* = 105.5 Hz, 1C), 130.3 (d, *J* = 10.8 Hz, 1C), 129.9 (d, *J* = 9.1 Hz, 1C), 129.84 (3C), 129.76 (1C), 129.0 (1C), 128.92 (2C), 128.88 (1C), 128.8 (d, *J* = 104.1 Hz, 1C), 128.6 (2C), 127.9 (6C), 125.0 (d, *J* = 10.3 Hz, 1C), 118.9 (d, *J* = 102.2 Hz, 1C), 102.1 (d, *J* = 9.5 Hz, 1C), 102.0 (d, *J* = 5.5 Hz, 1C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 36.48; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{40}H_{30}OPSi$: 585.1798, found: 585.1799.

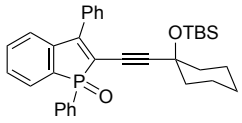


2-((*tert*-Butyldimethylsilyl)ethynyl)-1,3-diphenylphosphindole 1-oxide (3ac): Synthesized from **1a** (31 mg, 0.10 mmol) and **2c** (52 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v) and GPC ($CHCl_3$): 20 mg (46%, 0.10 mmol scale); Yellow solid; m.p. 145.2-145.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.78 (m, 2H), 7.77-7.72 (m, 1H), 7.63-7.60 (m, 2H), 7.59-7.54 (m, 1H), 7.53-7.42 (m, 8H), 0.77 (s, 9H), 0.015 (s, 3H), 0.00 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.4 (d, *J* = 20.7 Hz, 1C), 142.2 (d, *J* = 24.4 Hz, 1C), 133.1 (d, *J* = 13.2 Hz, 1C), 133.0 (d, *J* = 1.2 Hz, 1C), 132.5 (d, *J* = 2.8 Hz, 1C), 131.2 (1C), 131.1 (1C), 131.0 (d, *J* = 105.2 Hz, 1C), 129.9 (d, *J* = 10.7 Hz, 1C), 129.8 (d, *J* = 9.4 Hz, 1C), 129.5 (1C), 129.0 (d, *J* = 103.9 Hz, 1C), 128.8 (2C+1C), 128.7 (1C), 128.4 (2C), 124.7 (d, *J* = 10.3 Hz, 1C), 119.3 (d, *J* = 103.0 Hz, 1C), 106.6 (d, *J* = 5.6 Hz, 1C), 98.2 (d, *J* = 9.4 Hz, 1C), 25.9 (3C), 16.6 (1C), -4.94 (2C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 36.32; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{28}H_{30}OPSi$: 441.1798, found: 441.1798.



2-(3,3-Dimethylbut-1-yn-1-yl)-1,3-diphenylphosphindole 1-oxide (3ad): Synthesized from **1a** (31 mg, 0.10 mmol) and **2d** (32 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 12 mg (30%, 0.10 mmol scale); Pale yellow solid; m.p. 184.3-185.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H), 7.75-7.70 (m, 1H), 7.62-7.60 (m, 2H), 7.58-7.53 (m, 1H), 7.51-7.39 (m, 8H), 1.12 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz,

$CDCl_3$) δ 154.9 (d, *J* = 21.7 Hz, 1C), 142.5 (d, *J* = 24.9 Hz, 1C), 133.3 (d, *J* = 13.5 Hz, 1C), 132.9 (d, *J* = 1.9 Hz, 1C), 132.4 (d, *J* = 2.8 Hz, 1C), 131.2 (1C), 131.1 (1C), 130.9 (d, *J* = 105.0 Hz, 1C), 129.7 (d, *J* = 9.1 Hz, 1C), 129.39 (d, *J* = 10.7 Hz, 1C), 129.38 (d, *J* = 102.1 Hz, 1C), 129.3 (1C), 128.9 (2C), 128.8 (1C), 128.7 (1C), 128.2 (2C), 124.2 (d, *J* = 10.4 Hz, 1C), 119.8 (d, *J* = 104.9 Hz, 1C), 112.3 (d, *J* = 7.0 Hz, 1C), 72.6 (d, *J* = 9.6 Hz, 1C), 30.5 (3C), 28.6 (1C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 36.17; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{26}H_{24}OP$: 383.1559, found: 383.1559.

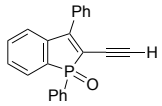


2-((1-((*tert*-Butyldimethylsilyl)oxy)cyclohexyl)ethynyl)-1,3-diphenylphosphindole 1-oxide (3ae): Synthesized from **1a** (31 mg, 0.10 mmol) and **2e** (63 mg, 0.20 mmol) according to the general procedure A, purified by silica gel column chromatography with hexane/ethyl acetate (2/1, v/v) and GPC ($CHCl_3$): 13 mg (25%, 0.10 mmol scale); White solid; m.p. 115.8-116.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 2H), 7.70-7.66 (m, 1H), 7.58-7.34 (m, 11H), 1.71-1.13 (m, 10H), 0.73 (s, 9H), -0.20 (s, 3H), -0.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.9 (d, *J* = 21.2 Hz, 1C), 142.4 (d, *J* = 24.2 Hz, 1C), 133.5 (d, *J* = 13.2 Hz, 1C), 133.0 (d, *J* = 1.8 Hz, 1C), 132.5 (d, *J* = 2.8 Hz, 1C), 131.5 (d, *J* = 105.0 Hz, 1C), 131.4 (1C), 131.3 (1C), 129.8 (d, *J* = 10.8 Hz, 1C), 129.6 (d, *J* = 9.5 Hz, 1C), 129.4 (1C), 128.9 (1C), 128.8 (1C), 128.71 (2C), 128.69 (d, *J* = 102.8 Hz, 1C), 128.5 (2C), 124.3 (d, *J* = 10.3 Hz, 1C), 119.3 (d, *J* = 103.9 Hz, 1C), 105.5 (d, *J* = 6.6 Hz, 1C), 78.4 (d, *J* = 11.4 Hz, 1C), 70.0 (1C), 40.9 (2C), 25.7 (3C), 25.1 (1C), 22.7 (2C), 17.9 (1C), -3.25 (1C), -3.35 (1C); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 36.02; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{34}H_{40}O_2PSi$: 539.2530, found: 539.2520.

Protodesilylation of 3aa (Scheme 3)

In a Schlenk tube, 1,3-diphenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (**3aa**; 48 mg, 1.0 mmol) was dissolved in THF (1.0 mL), and MeOH (0.10 mmol, 4.1 μL) was added under N_2. The tube was cooled to 0 ºC with an ice bath, and tetrabutylammmonium fluoride (TBAF, 1 mol/L in THF, 0.105 mmol, 0.105 mL) was slowly added. The mixture was stirred at 0 °C for 30 min. After quenching with water, extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was purified by silica gel

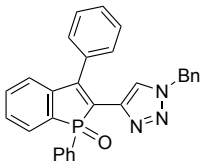
column chromatography with hexane/EtOAc (1:2, v/v) to give 2-ethynyl-1,3-diphenylphosphindole 1-oxide (**4;** 83%, 27.5 mg).



2-Ethynyl-1,3-diphenylphosphindole 1-oxide (4): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 28 mg (83%, 0.10 mmol scale); Brown solid; m.p. 228.3-229.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.78 (m, 2H), 7.75-7.71 (m, 1H), 7.63-7.41 (m, 11H), 3.36 (d, *J* = 4.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.7 (d, *J* = 20.3 Hz, 1C), 141.9 (d, *J* = 24.6 Hz, 1C), 133.2 (1C), 132.9 (d, *J* = 13.1 Hz, 1C), 132.7 (d, *J* = 2.8 Hz, 1C), 131.24 (d, *J* = 105.5 Hz, 1C), 131.21 (1C), 131.1 (1C), 130.2 (d, *J* = 10.8 Hz, 1C), 129.8 (1C), 129.7 (d, *J* = 9.5 Hz, 1C), 129.0 (1C), 128.9 (1C), 128.6 (2C+2C), 128.4 (d, *J* = 102.0 Hz, 1C), 124.9 (d, *J* = 10.4 Hz, 1C), 118.1 (d, *J* = 103.8 Hz, 1C), 89.1 (d, *J* = 6.7 Hz, 1C), 76.6 (d, *J* = 9.9 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 36.90; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{22}H_{16}OP$: 327.0933, found: 327.0914.

Protodesilylation/Cu-Catalysed Azide-Alkyne Cycloaddition of 3aa (Scheme 3)

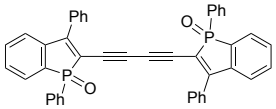
In a Schlenk tube, 1,3-diphenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (**3aa**; 48 mg, 0.10 mmol) was dissolved in THF (1.0 mL), and MeOH (0.10 mmol, 4.1 μL) was added under N_2. The tube was cooled to 0 ºC with an ice bath, and tetrabutylammmonium fluoride (TBAF, 1 mol/L in THF, 0.105 mmol, 0.105 mL) was slowly added. The mixture was stirred at 0 °C for 30 min. After quenching with water, extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was directly transferred to another Schlenk tube. CuI (3.8 mg, 0.020 mmol), THF (1.0 mL), DIPEA (3.5 μL, 0.20 mmol), and benzyl azide (13 mg, 0.10 mmol) were added under N_2. The mixture was stirred at room temperature for 28 h. After quenching with water, extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was purified by column chromatography on silica gel with ethyl acetate then GPC ($CHCl_3$) to give 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-1,3-diphenylphosphindole 1-oxide (**5**; 37.5 mg, 0.082 mmol) in 81% yield.



2-(1-Benzyl-1H-1,2,3-triazol-4-yl)-1,3-diphenylphosphindole 1-oxide (5): Purified by silica gel column chromatography with ethyl acetate and GPC ($CHCl_3$): 38 mg (81%, 0.10 mmol scale); White solid; m.p. 208.6-209.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 2H), 7.73 (dd, *J* = 9.2, 7.2 Hz, 1H), 7.67-7.25 (m, 13H), 7.12-7.03 (m, 3H), 6.80 (s, 1H), 5.33 (d, *J* = 14.9 Hz, 1H) 5.26 (d, *J* = 14.9 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.4 (d, *J* = 18.9 Hz, 1C), 143.9 (d, *J* = 25.7 Hz, 1C), 141.0 (d, *J* = 11.1 Hz, 1C), 134.4 (d, *J* = 14.3 Hz, 1C), 134.3 (1C), 133.0 (d, *J* = 1.8 Hz, 1C), 132.2 (d, *J* = 2.8 Hz, 1C), 131.8 (d, *J* = 106.4 Hz, 1C), 131.4 (1C), 131.3 (1C), 129.9 (d, *J* = 102.2 Hz, 1C), 129.3 (d, *J* = 2.8 Hz, 1C), 129.24 (2C), 129.22 (d, *J* = 4.2 Hz, 1C), 129.0 (1C), 128.9 (2C), 128.8 (1C), 128.64 (1C), 128.60 (1C), 128.2 (2C), 128.0 (2C), 125.6 (d, *J* = 98.1 Hz, 1C), 124.0 (d, *J* = 10.6 Hz, 1C), 122.4 (d, *J* = 6.8 Hz, 1C), 53.9 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 38.63; HRMS (APCI) m/z ([M+H]$^+$) calcd for $C_{29}H_{23}N_3OP$: 460.1573, found: 460.1566.

Protodesilylation/Cu-Catalysed Glaser Coupling of 3aa (Scheme 3)

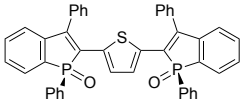
In a Schlenk tube, 1,3-diphenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (**3aa**; 48 mg, 0.10 mmol) was dissolved in THF (1.0 mL), and MeOH (0.10 mmol, 4.1 μL) was added under N_2. The tube was cooled to 0 ºC with an ice bath, and tetrabutylammmonium fluoride (TBAF, 1 mol/L in THF, 0.105 mmol, 0.105 mL) was slowly added. The mixture was stirred at 0 °C for 30 min. After quenching with water, extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was directly transferred to another Schlenk tube. In a vial, CuCl (2.0 mg, 0.020 mmol) and TMEDA (2.0 μL, 0.013 mmol) were dissolved in acetone (0.050 mL) under N_2. The mixture was stirred at room temperature for 15 minutes. The mixture was transferred to the Schlenk tube with acetone (0.050 mL). The mixture was stirred at room temperature for 1 h under O_2 (1 atm, balloon). After quenching with water, extraction with $CHCl_3$ three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was purified by column chromatography on silica gel with ethyl acetate to give 2,2'-(buta-1,3-diyne-1,4-diyl)bis(1,3-diphenylphosphindole 1-oxide) (**6**; 31.9 mg, 0.049 mmol) in 97% yield.



2,2'-(Buta-1,3-diyne-1,4-diyl)bis(1,3-diphenylphosphindole 1-oxide) (6, 1:1 diastereomixture): Purified by silica gel column chromatography with ethyl acetate: 32 mg (97%, 0.050 mmol scale); Yellow solid; m.p. 128.4-129.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76-7.67 (m, 6H), 7.59-7.42 (m, 22H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4 (d, *J* = 20.8 Hz, 2C), 160.2 (d, *J* = 20.7 Hz, 2C), 141.7 (d, *J* = 23.9 Hz, 4C), 133.3 (4C), 132.85 (d, *J* = 2.6 Hz, 4C), 132.81 (d, *J* = 11.0 Hz, 4C), 131.4 (d, *J* = 105.1 Hz, 4C), 131.2 (4C), 131.1 (4C), 130.5 (d, *J* = 10.8 Hz, 4C), 130.1 (4C), 129.8 (d, *J* = 9.4 Hz, 4C), 129.1 (4C), 129.0 (4C), 128.8 (4C), 128.6 (8C), 128.3 (d, *J* = 103.7 Hz, 2C), 128.2 (d, *J* = 103.3 Hz, 2C), 125.1 (d, *J* = 10.1 Hz, 4C), 117.8 (d, *J* = 101.9 Hz, 4C), 85.4 (dd, *J* = 6.6, 5.1 Hz, 2C), 85.3 (dd, *J* = 6.5, 5.1 Hz, 2C), 78.94 (d, *J* = 8.7 Hz, 2C), 78.85 (d, *J* = 8.4 Hz, 2C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 36.46, 36.42; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{44}H_{29}O_2P_2$: 651.1637, found: 651.1610.

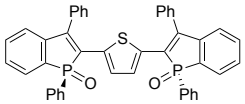
Cyclization of 1,3-Diyne 4 with TIPS-SH (Scheme 3)

2,2'-(Buta-1,3-diyne-1,4-diyl)bis(1,3-diphenylphosphindole 1-oxide) (**6**; 33 mg, 0.050 mmol) and CsF (36 mg, 0.20 mmol) were placed in a Schlenk tube, which was filled with N_2 by using the standard Schlenk technique. DMF (2.0 mL) and triisopropylsilanethiol (19 mg, 0.10 mmol) were finally added via syringe. The mixture was stirred at room temperature for 4 h. After quenching with water, extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was purified by preparative thin-layer chromatography with ethyl acetate and GPC ($CHCl_3$) to give (1*R*',1'*S*')-2,2'-(Thiophene-2,5-diyl)bis(1,3-diphenylphosphindole 1-oxide) (***syn*-7**; 5.9 mg, 0.0086 mmol) in 17% yield and (1*R*',1'*R*')-2,2'-(thiophene-2,5-diyl)bis(1,3-diphenylphosphindole 1-oxide) (***anti*-7**; 6.7 mg, 0.0098 mmol) in 19% yield.



(1*R'*,1*'S'*)-2,2'-(Thiophene-2,5-diyl)bis(1,3-diphenylphosphindole 1-oxide) (*syn*-7): Purified by preparative thin-layer chromatography with ethyl acetate and GPC ($CHCl_3$): 5.9 mg (17%, 0.050 mmol scale); Orange solid; m.p. 139.1-139.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.66 (m, 4H), 7.58 (dd,

J = 9.8, 7.1 Hz, 2H), 7.51-7.47 (m, 4H), 7.44-7.34 (m, 10H), 7.30-7.25 (m, 2H), 7.19-7.17 (m, 4H), 7.02 (s, 2H), 6.87 (dd, *J* = 7.6, 2.9 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 147.0 (d, *J* = 20.4 Hz, 2C), 144.4 (d, *J* = 25.7 Hz, 2C), 137.1 (d, *J* = 14.1 Hz, 2C), 133.6 (d, *J* = 14.3 Hz, 2C), 133.1 (d, *J* = 1.9 Hz, 2C), 132.2 (d, *J* = 2.8 Hz, 2C), 131.3 (d, *J* = 106.8 Hz, 2C), 131.0 (2C), 130.9 (2C), 130.0 (d, *J* = 99.2 Hz, 2C), 129.44 (4C), 129.39 (2C), 129.2 (2C), 129.0 (2C), 128.9 (2C), 128.816 (d, *J* = 21.0 Hz, 2C), 128.812 (2C), 128.6 (4C), 128.4 (d, *J* = 95.2 Hz, 2C), 123.8 (d, *J* = 10.6 Hz, 2C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 38.34; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{44}H_{31}O_2P_2S$: 685.1515, found: 685.1520.

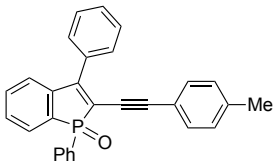


(1*R′*,1*′R′*)-2,2'-(Thiophene-2,5-diyl)bis(1,3-diphenylphosphindole 1-oxide) (*anti*-7): Purified by preparative thin-layer chromatography with ethyl acetate and GPC ($CHCl_3$): 6.7 mg (19%, 0.050 mmol scale); Orange solid; m.p. 143.8-144.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.70 (m, 4H), 7.58 (dd, *J* = 10.0, 7.5 Hz, 2H), 7.54-7.47 (m, 4H), 7.44-7.33 (m, 10H), 7.29-7.24 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 4H), 7.11 (s, 2H), 6.83 (dd, *J* = 7.6, 2.9 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 146.6 (d, *J* = 20.3 Hz, 2C), 144.5 (d, *J* = 25.9 Hz, 2C), 137.3 (d, *J* = 15.1 Hz, 2C), 133.4 (d, *J* = 14.2 Hz, 2C), 133.1 (d, *J* = 2.3 Hz, 2C), 132.4 (d, *J* = 2.8 Hz, 2C), 131.1 (d, *J* = 106.9 Hz, 2C), 130.9 (2C), 130.8 (2C), 130.0 (d, *J* = 99.2 Hz, 2C), 129.8 (d, *J* = 5.0 Hz, 2C), 129.4 (4C), 129.3 (2C), 129.1 (2C), 129.0 (2C), 128.9 (d, *J* = 5.5 Hz, 2C), 128.8 (d, *J* = 6.4 Hz, 2C), 128.6 (4C), 128.3 (d, *J* = 93.3 Hz, 2C), 123.8 (d, *J* = 10.9 Hz, 2C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ 38.76; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{44}H_{31}O_2P_2S$: 685.1515, found: 685.1524.

Desilylative Sonogashira Coupling of 3aa with Aryl Iodides (Scheme 3, 3ag)

In a Schlenk tube, 1,3-diphenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (**3aa**; 48 mg, 0.10 mmol), 4-iodotoluene (44 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (7.1 mg, 0.010 mmol), CuI (3.8 mg, 0.020 mmol) were dissolved in THF (1.0 mL), and Et_3N (0.18 mL, 1.3 mmol) was added under N_2. The tube was cooled to 0 ºC with an ice bath, and tetrabutylammmonium fluoride (TBAF, 1 mol/L in THF, 0.105 mmol, 0.105 mL) was slowly added. The mixture was stirred at 0 °C for 30 min and then heated at 50 °C for 16.5 h (oil bath). The resulting mixture was cooled to room temperature. After quenching with water, extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was purified by column

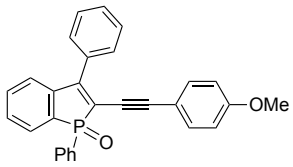
chromatography on silica gel with hexane/ethyl acetate (1:2, v/v) to give 1,3-diphenyl-2-(*p*-tolylethynyl)phosphindole 1-oxide (**3ag**; 31.7 mg, 0.076 mmol) in 76% yield.



1,3-Diphenyl-2-(*p*-tolylethynyl)phosphindole 1-oxide (3ag): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 32 mg (76%, 0.10 mmol scale); Yellow solid; m.p. 157.8-158.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.83 (m, 2H), 7.76-7.69 (m, 3H), 7.58-7.41 (m, 9H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9 (d, *J* = 21.2 Hz, 1C), 142.4 (d, *J* = 24.3 Hz, 1C), 139.0 (1C), 133.4 (d, *J* = 13.2 Hz, 1C), 133.1 (d, *J* = 1.4 Hz, 1C), 132.6 (d, *J* = 2.8 Hz, 1C), 131.78 (1C), 131.76 (1C), 131.3 (d, *J* = 105.1 Hz, 1C), 131.2 (1C), 131.1 (1C), 129.8 (1C), 129.7 (d, *J* = 2.0 Hz, 1C), 129.6 (1C), 129.0 (d, *J* = 103.6 Hz, 1C), 129.0 (3C), 128.94 (2C), 128.86 (1C), 128.5 (2C), 124.5 (d, *J* = 10.4 Hz, 1C), 119.8 (d, *J* = 2.2 Hz, 1C), 119.1 (d, *J* = 103.9 Hz, 1C), 101.5 (d, *J* = 6.6 Hz, 1C), 82.8 (d, *J* = 9.6 Hz, 1C), 21.6 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 36.34; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{29}H_{22}OP$: 417.1403, found: 417.1390.

Desilylative Sonogashira Coupling of 3aa with Aryl Iodides (Scheme 3, 3ah)

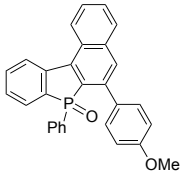
In a Schlenk tube, 1,3-Diphenyl-2-((triisopropylsilyl)ethynyl)phosphindole 1-oxide (**3aa**; 483 mg, 1.0 mmol), 4-iodoanisole (468 mg, 2.0 mmol), $PdCl_2(PPh_3)_2$ (72 mg, 0.10 mmol), CuI (38 mg, 0.20 mmol) were dissolved in THF (1.0 mL), and Et_3N (1.8 mL , 13 mmol) was added under N_2. The tube was cooled to 0 ºC with an ice bath, and tetrabutylammmonium fluoride (TBAF, 1 mol/L in THF, 1.05 mmol, 1.05 mL) was slowly added. The mixture was stirred at 0 °C for 30 min and then heated at 50 °C for 16.5 h (oil bath). The resulting mixture was cooled to room temperature. After quenching with water, extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1:2, v/v) to give 2-((4-methoxyphenyl)ethynyl)-1,3-diphenylphosphindole 1-oxide (**3ah**; 326 mg, 0.75 mmol) in 75% yield.



2-((4-Methoxyphenyl)ethynyl)-1,3-diphenylphosphindole 1-oxide (3ah): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 326 mg (75%, 1.0 mmol scale); Yellow solid; m.p. 167.8-168.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.83 (m, 2H), 7.76-7.68 (m, 3H), 7.58-7.40 (m, 9H), 7.26-7.21 (m, 2H), 6.79-6.75 (m, 2H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0 (1C), 155.3 (d, *J* = 21.2 Hz, 1C), 142.5 (d, *J* = 24.6 Hz, 1C), 133.4 (d, *J* = 13.1 Hz, 1C), 133.45 (1C), 133.43 (1C), 133.1 (d, *J* = 1.6 Hz, 1C), 132.6 (d, *J* = 2.8 Hz, 1C), 131.3 (d, *J* = 105.3 Hz, 1C), 131.2 (1C), 131.1 (1C), 129.7 (d, *J* = 9.0 Hz, 1C), 129.6 (d, *J* = 10.4 Hz, 1C), 129.5 (1C), 129.1 (d, *J* = 103.3 Hz, 1C), 129.0 (1C), 128.9 (2C), 128.8 (1C), 128.5 (2C), 124.3 (d, *J* = 10.3 Hz, 1C), 119.2 (d, *J* = 103.8 Hz, 1C), 115.0 (d, *J* = 2.4 Hz, 1C), 113.9 (2C), 101.5 (d, *J* = 6.6 Hz, 1C), 82.2 (d, *J* = 9.5 Hz, 1C), 55.3 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 36.34; HRMS (APCI) m/z ([M+H]$^{+}$) calcd for $C_{29}H_{22}O_2P$: 433.1352, found: 433.1338.

Pt-Catalysed Cycloisomerization of 3ah (Scheme 3)

In a Schlenk tube, 2-((4-methoxyphenyl)ethynyl)-1,3-diphenylphosphindole 1-oxide (**3ah**; 22 mg, 0.050 mmol) and $PtCl_2$ (2.7 mg, 0.010 mmol) were dissolved in TCE (1.0 mL) under N_2. The mixture was refluxed at 150 ºC for 20 h (oil bath). The resulting mixture was cooled to room temperature. After quenching with water, extraction with ethyl acetate three times, filtration through a short pad of Na_2SO_4 and cerite, and evaporation under reduced pressure formed a crude material. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1:2, v/v) to give 6-(4-methoxyphenyl)-7-phenyldibenzo[*b,e*]phosphindole 7-oxide (**8**; 18 mg, 0.042 mmol) in 83% yield.



6-(4-Methoxyphenyl)-7-phenyldibenzo[*b,e*]phosphindole 7-oxide (8): Purified by silica gel column chromatography with hexane/ethyl acetate (1/2, v/v): 18 mg (83%, 0.050 mmol scale); Yellow solid;

m.p. 189.9-190.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.5 Hz, 1H), 8.54 (dd, *J* = 8.0, 3.3 Hz, 1H), 7.93 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.77-7.61 (m, 5H), 7.46-7.38 (m, 3H), 7.32-7.28 (m, 1H), 7.19-7.09 (m, 4H), 6.88-6.85 (m, 2H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3 (1C), 142.9 (d, *J* = 21.6 Hz, 1C), 141.1 (d, *J* = 8.8 Hz, 1C), 139.8 (d, *J* = 21.5 Hz, 1C), 137.0 (d, *J* = 1.4 Hz, 1C), 134.3 (d, *J* = 106.4 Hz, 1C), 133.0 (d, *J* = 1.6 Hz, 1C), 132.4 (d, *J* = 101.4 Hz, 1C), 131.6 (d, *J* = 3.1 Hz, 1C), 131.5 (d, *J* = 2.7 Hz, 1C), 131.2 (2C), 130.9 (1C), 130.8 (1C), 130.5 (d, *J* = 9.1 Hz, 1C), 130.2 (d, *J* = 9.6 Hz, 1C), 130.0 (d, *J* = 105.9 Hz, 1C), 129.5 (1C), 128.9 (d, *J* = 11.2 Hz, 1C), 128.3 (d, *J* = 11.0 Hz, 1C), 128.0 (1C), 127.9 (2C), 127.4 (1C), 125.4 (d, *J* = 10.4 Hz, 1C), 124.7 (1C), 113.2 (2C), 55.3 (1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 33.20; HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{29}H_{22}O_2P$: 433.1352, found: 433.1364.

X-Ray Analysis

The single X-ray quality crystals of **3ac** were grown from pentane/$CHCl_3$ by slow evaporation at room temperature. The structure was refined by full-matrix least-squares method using SHELXL-2017/1.

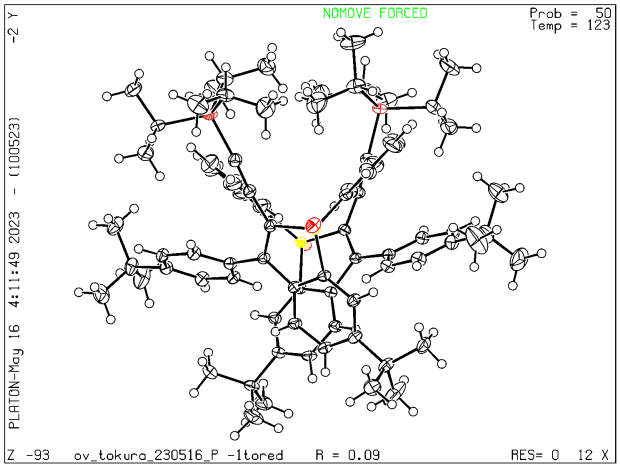


Figure S1. ORTEP drawing of **3ac** (CCDC 2279968, 50% thermal probability).

Table S1. Crystal data for **3ac**

Crystal system	triclinic
Space group IT number	2
Space group name H-M alt	P -1
Space group name Hall	-P 1
Cell length a	14.1352(4)
Cell length b	15.4491(5)
Cell length c	19.4502(6)
Cell angle alpha	85.750(2)
Cell angle beta	69.641(2)
Cell angle gamma	64.337(3)
Cell volume	3574.6(2)
Cell formula units Z	2
Refine ls R factor all	0.1073
Refine ls R factor gt	0.0916
Refine ls wR factor gt	0.2915
Refine ls wR factor ref	0.3000
Refine ls goodness of fit ref	1.095

The single X-ray quality crystals of **5** were grown from pentane/EtOAc by slow evaporation at room temperature. The structure was refined by full-matrix least-squares method using SHELXL-2017/1.

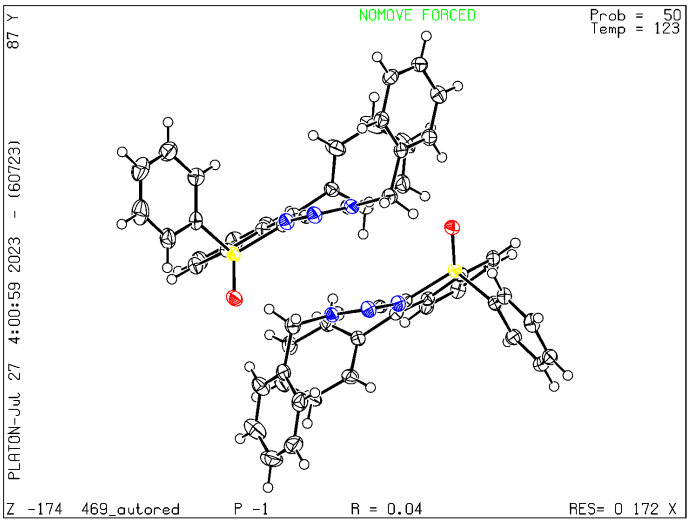


Figure S2. ORTEP drawing of **5** (CCDC 2285491, 50% thermal probability).

Table S2. Crystal data for **5**

Crystal system	triclinic
Space group IT number	2
Space group name H-M alt	P -1
Space group name Hall	-P 1
Cell length a	9.9714(2)
Cell length b	10.8463(2)
Cell length c	22.5248(4)
Cell angle alpha	77.043(2)
Cell angle beta	86.915(2)
Cell angle gamma	82.273(2)
Cell volume	2351.83(8)
Cell formula units Z	2
Refine ls R factor all	0.0464
Refine ls R factor gt	0.0417
Refine ls wR factor gt	0.1109
Refine ls wR factor ref	0.1152
Refine ls goodness of fit ref	1.054

The single X-ray quality crystals of **7** were grown from pentane/$CHCl_3$ by slow evaporation at room temperature. The structure was refined by full-matrix least-squares method using SHELXL-2017/1.

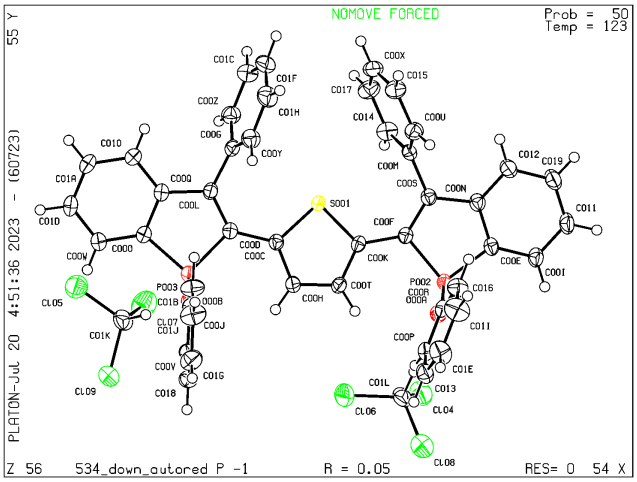


Figure S3. ORTEP drawing of **7** (CCDC 2283132, 50% thermal probability).

Table S3. Crystal data for **7**

Crystal system	triclinic
Space group IT number	2
Space group name H-M alt	P -1
Space group name Hall	-P 1
Cell length a	14.0465(2)
Cell length b	14.1358(2)
Cell length c	14.4268(2)
Cell angle alpha	118.189(2)
Cell angle beta	92.5060(10)
Cell angle gamma	114.771(2)
Cell volume	2185.49(7)
Cell formula units Z	2
Refine ls R factor all	0.0496
Refine ls R factor gt	0.0450
Refine ls wR factor gt	0.1195
Refine ls wR factor ref	0.1234
Refine ls goodness of fit ref	1.068

The single X-ray quality crystals of **8** were grown from pentane/EtOAc by slow evaporation at room temperature. The structure was refined by full-matrix least-squares method using SHELXL-2017/1.

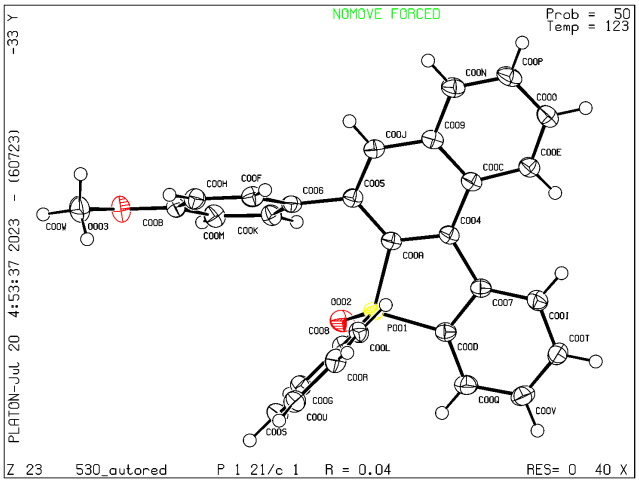


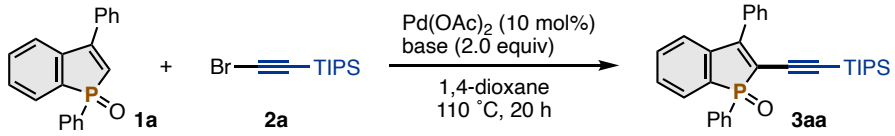
Figure S4. ORTEP drawing of **8** (CCDC 2283133, 50% thermal probability).

Table S4. Crystal data for **8**

Crystal system	monoclinic
Space group IT number	14
Space group name H-M alt	P 1 21/c 1
Space group name Hall	-P 2ybc
Cell length a	9.4750(2)
Cell length b	18.8265(3)
Cell length c	12.4890(2)
Cell angle alpha	90
Cell angle beta	109.249(2)
Cell angle gamma	90
Cell volume	2103.25(7)
Cell formula units Z	4
Refine ls R factor all	0.0421
Refine ls R factor gt	0.0377
Refine ls wR factor gt	0.1013
Refine ls wR factor ref	0.1052
Refine ls goodness of fit ref	1.060

Detailed Optimisation Studies

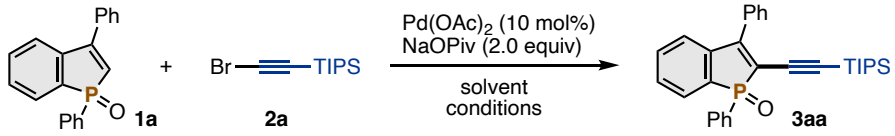
Table S5. Pd-Catalysed C2–H Alkynylation of **1a** with **2a**: Screening of Bases.[a]



entry	base	yield (%)[b]	entry	base	yield (%)[b]
1	CsOPiv	7	***9***	***NaOPiv***	***38***
2	CsOAc	2	10	NaOAc	20
3	Cs_2CO_3	2	11	Na_2CO_3	11
4	KOPiv	8	12	$NaHCO_3$	0
5	KOAc	10	13	NaTFA	1
6	K_2CO_3	5	14	LiOAc	7
7	$KHCO_3$	9	15	Li_2CO_3	0
8	K_3PO_4	6	16	none	0

[a] Reaction conditions: $Pd(OAc)_2$ (0.010 mmol), base (0.20 mmol), **1a** (0.10 mmol), **2a** (0.20 mmol), 1,4-dioxane (1.0 mL), 110 ˚C, 20 h, N_2. [b] Estimated by $^{31}P\{^1H\}$ NMR with $P(O)(OEt)_3$ as the internal standard.

Table S6. Pd-Catalysed C2–H Alkynylation of **1a** with **2a**: Screening of Solvents and Temperature.[a]

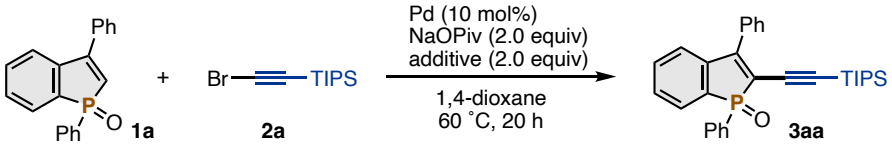


entry	solvent, conditions	yield (%)[b]
1	1,4-dioxane (1.0 mL), 110 ˚C	38
2	DMSO (1.0 mL), 110 ˚C	0
3	toluene (1.0 mL), 110 ˚C	41
4	***1,4-dioxane (1.0 mL), 60 ˚C***	***60***
5	THF (1.0 mL), 60 ˚C	54
6	MeCN (1.0 mL), 60 ˚C	5
7	toluene (1.0 mL), 60 ˚C	33
8	CPME (1.0 mL), 60 ˚C	57
9	MTBE (1.0 mL), 60 ˚C	17

10	2-MeTHF (1.0 mL), 60 ˚C	41
11	*i*-Pr_2O (1.0 mL), 60 ˚C	5
12	hexane (1.0 mL), 60 ˚C	4
13	cyclohexane (1.0 mL), 60 ˚C	15
14	1,4-dioxane (1.0 mL)/H_2O (0.20 mL), 60 ˚C	0
15	1,4-dioxane (1.0 mL), 80 ˚C	52
16	1,4-dioxane (1.0 mL), 40 ˚C	28
17	1,4-dioxane (1.0 mL), rt	7

[a] Reaction conditions: $Pd(OAc)_2$ (0.010 mmol), NaOPiv (0.20 mmol), **1a** (0.10 mmol), **2a** (0.20 mmol), solvent, 20 h, N_2. [b] Estimated by $^{31}P\{^1H\}$ NMR with $P(O)(OEt)_3$ as the internal standard.

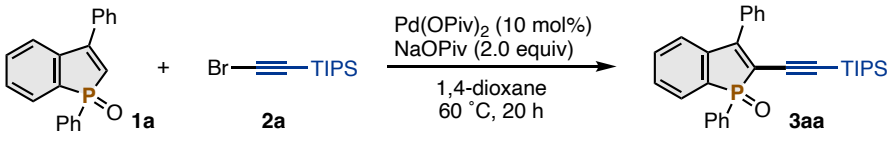
Table S7. Pd-Catalysed C2–H Alkynylation of **1a** with **2a**: Screening of Pd sources and additives.[a]



entry	Pd	additive	yield (%)[b]
1	$Pd(OAc)_2$	none	60
2	$Pd(OAc)_2$	AcOH	5
3	$Pd(OAc)_2$	AgTFA	0
4	***$Pd(OPiv)_2$***	***none***	***73***
5	$Pd(TFA)_2$	none	65
6	$PdCl_2$	none	64
7	$Pd_2(dba)_3$	none	64

[a] Reaction conditions: Pd (0.010 mmol), NaOPiv (0.20 mmol), **1a** (0.10 mmol), **2a** (0.20 mmol), 1,4-dioxane (1.0 mL), 60 ˚C, 20 h, N_2. [b] Estimated by $^{31}P\{^1H\}$ NMR with $P(O)(OEt)_3$ as the internal standard.

Table S8. Pd-Catalysed C2–H Alkynylation of **1a** with **2a**: Concentration Effect.[a]

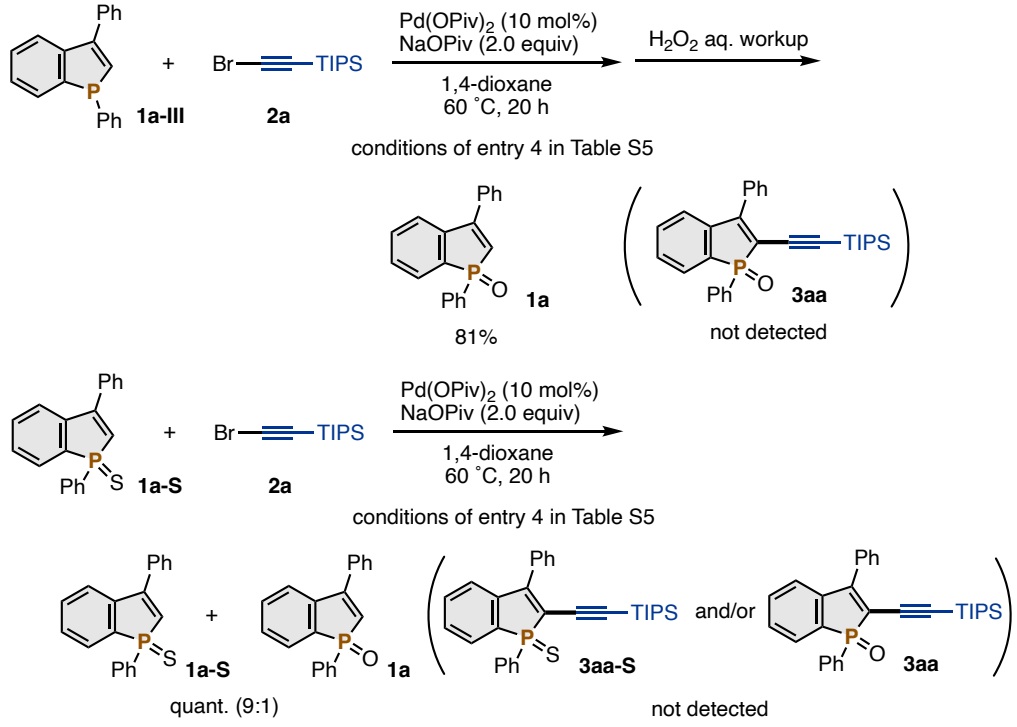


entry	solvent amount (mL)	yield (%)[b]	entry	solvent amount (mL)	yield (%)[b]
1	1.0	73	***4[c]***	***1.5***	***84 (72)***

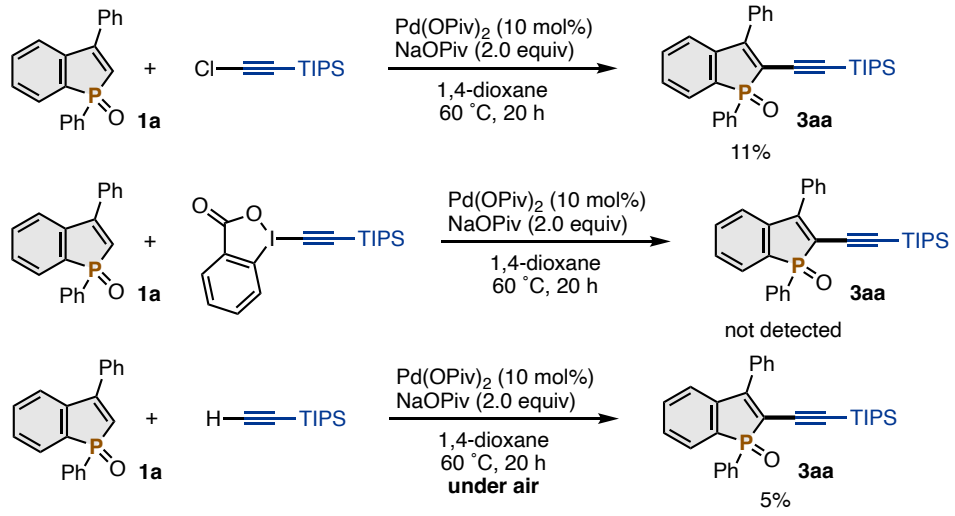
2	0.5	6	5[c,d]	1.5	40[e]
3	1.5	68			

[a] Reaction conditions: $Pd(OPiv)_2$ (0.010 mmol), NaOPiv (0.20 mmol), **1a** (0.10 mmol), **2a** (0.20 mmol), 1,4-dioxane, 60 ˚C, 20 h, N_2. [b] Estimated by $^{31}P\{^1H\}$ NMR with $P(O)(OEt)_3$ as the internal standard. Isolated yield is in parentheses. [c] For 48 h. [d] With 5 mol% $Pd(OPiv)_2$ (0.0050 mmol). [e] The unreacted **1a** was recovered in 44% yield.

Scheme S1. Effect of Phosphorus Moiety.

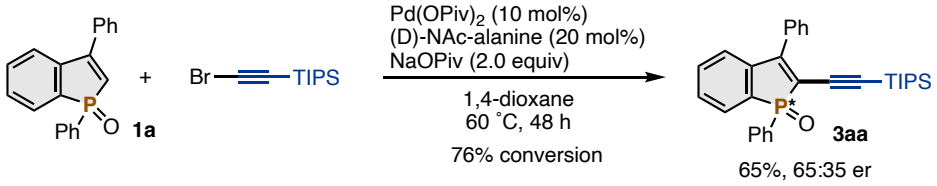


Scheme S2. Effect of Alkynyl Sources.

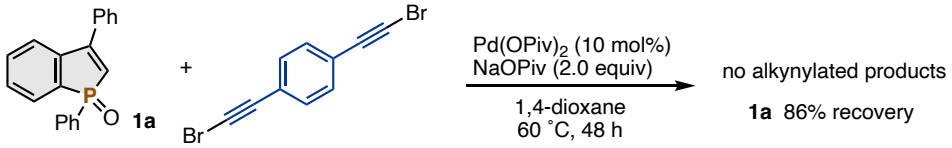


Scheme S3. Other Attempts.

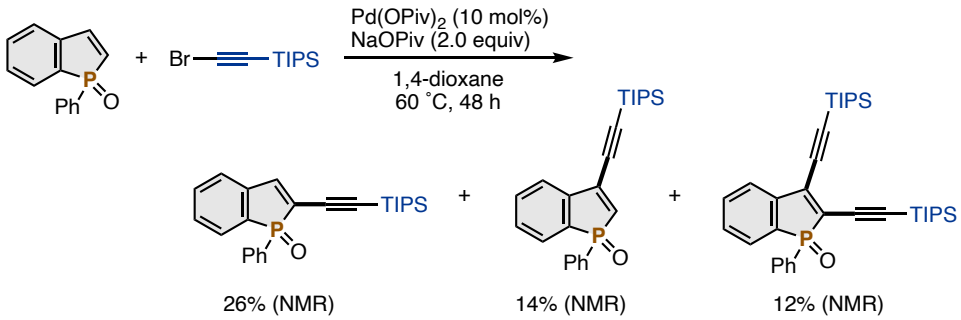
a) attempt to apply asymmteric catalysis



b) attempt to apply double C–H alkynylation



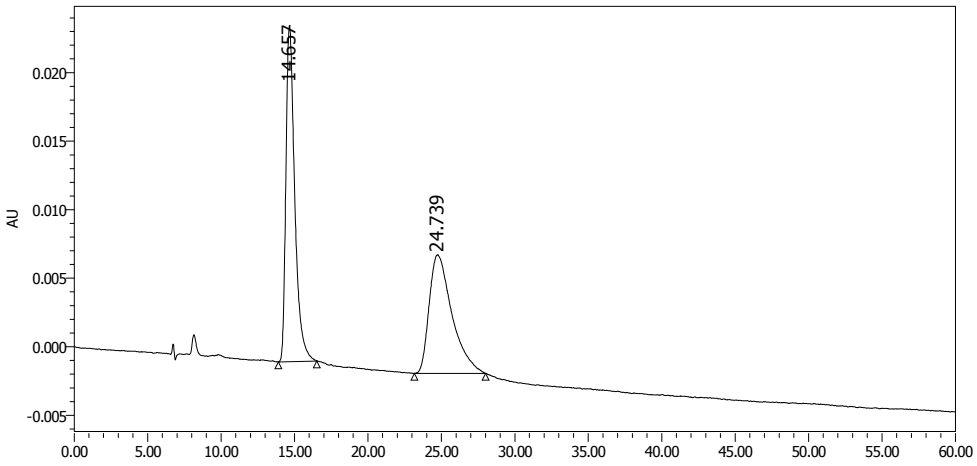
c) attempt to apply C2,C3-free benzophosphole



Chiral HPLC Charts

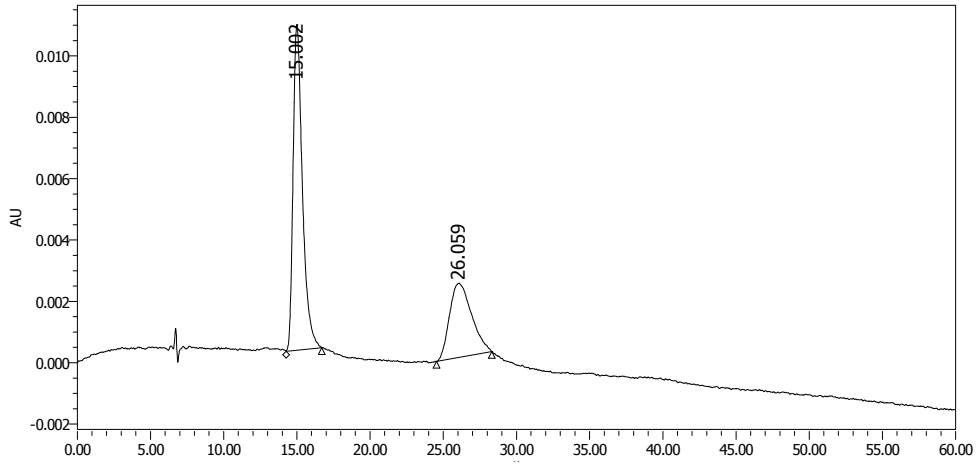
3aa: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AS-H column, 95/5 hexane/isopropyl alcohol, 0.5 mL/min, t_R = 15.0, 26.1 min, UV detection at 258 nm, 30 ºC).

3aa synthesized under nonenantioselective conditions



Peak #	Ret. Time	Area	Area %
1	14.657	1026332	52.37
2	24.739	933579	47.63

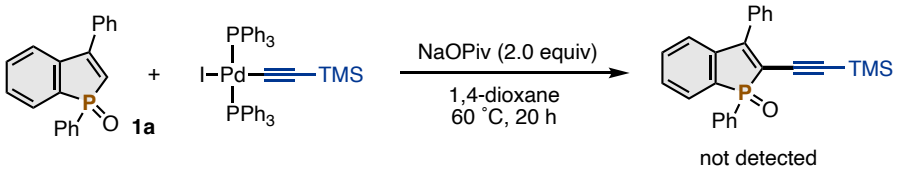
3aa synthesized under enantioselective conditions using (D)-*N*-Ac-alanine



Peak #	Ret. Time	Area	Area %
1	15.002	470011	65.01
2	26.059	252973	34.99

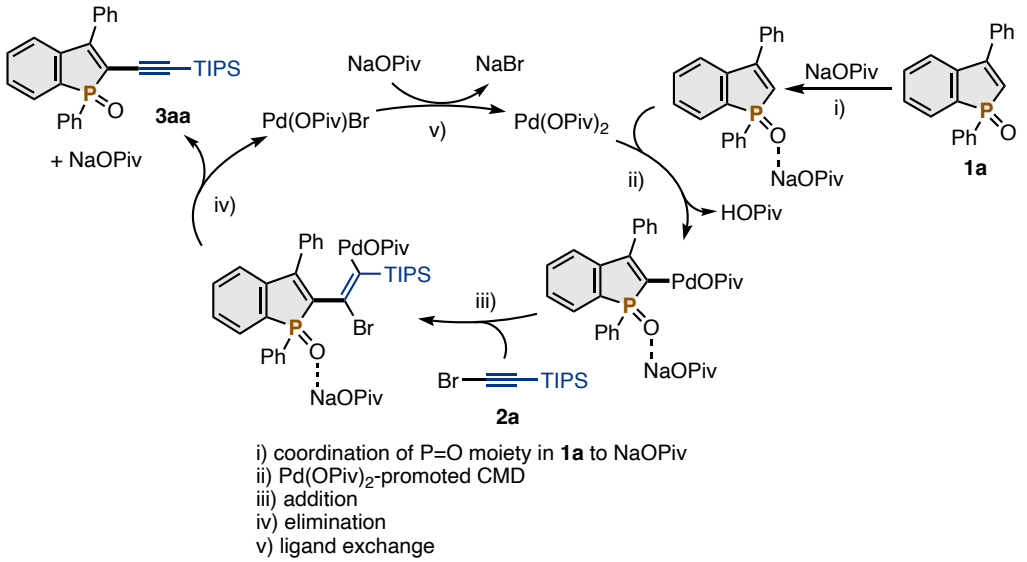
Control Experiments

Scheme S4. Stoichiometric Reaction with Isolated Pd(II)-Alkynyl Complex.[S3]



Plausible Reaction Mechanism

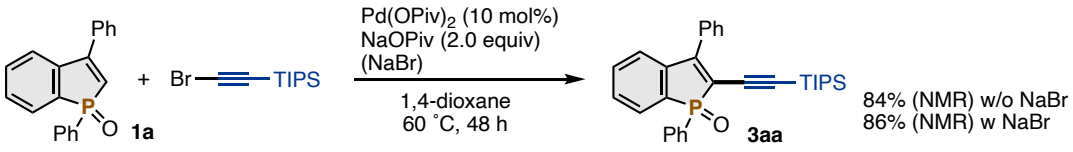
Scheme S5. Plausible Catalytic Cycle.



Notably, a trans elimination process similar to the step iv) was proposed in the Rh-catalysed C-H alkynylation reaction with the alkynyl bromide, where the effective abstraction with the Ag cation was observed in the calculated transition state.[S4] Thus, the related abstraction with Na cation might be involved also in the present Pd-catalysed reaction.

In addition, we also investigated the effect of additional NaBr under otherwise identical conditions (see below). However, the almost same result was obtained (86% NMR yield w/ NaBr vs 84%NMR yield w/o NaBr), thus suggesting the negligible role of NaBr in the catalytic reaction.

Scheme S6. Effects of NaBr.



Photoluminescence Properties

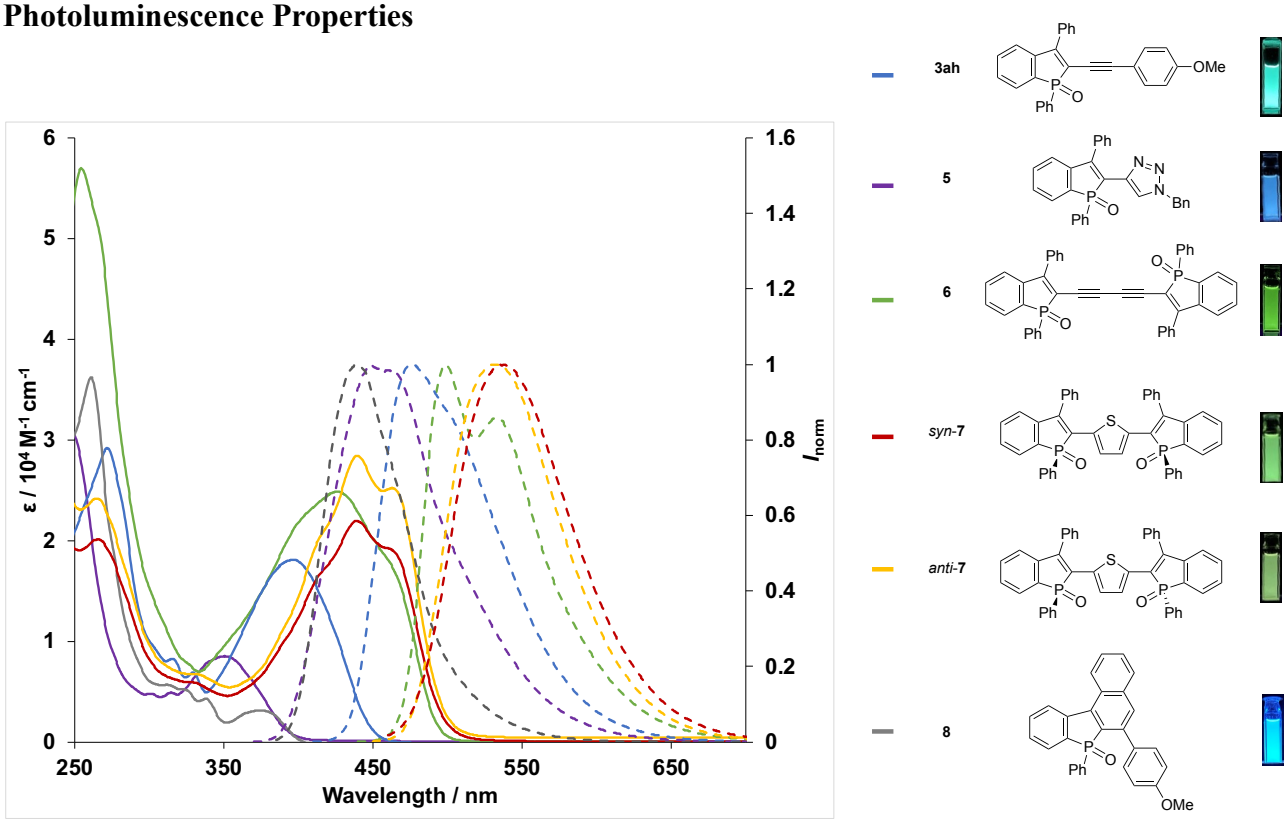


Figure S1. UV-vis absorption spectra (solid line), emission (dotted line) spectra, and fluorescence images of **3ah**, **5**, **6**, *syn*-**7**, *anti*-**7**, and **8** (1.0×10^{-5} M in $CHCl_3$). Excited at the absorption maxima for the emission spectrum.

Table S10. Photoluminescence properties of selected compounds in $CHCl_3$ (1.0×10^{-5} M).

compd	λ_{abs} (nm) (ε (10^4 M^{-1} cm^{-1}))	λ_{em}[a] (nm)	Φ_F[b]	$\Delta\nu$ (cm^{-1})[c]
3ah	273 (2.91), 396 (1.81)	475	0.74	4200
5	350 (0.85)	450, 461	0.15	6349
6	256 (5.67), 426 (2.49)	500, 534	0.11	3474
***syn*-7**	266 (2.01), 440 (2.20), 463 (1.91)	537	0.16	2976
***anti*-7**	265 (2.41), 440 (2.84), 465 (2.51)	532	0.19	2708
8	262 (3.60), 373 (0.31)	439	0.51	4031

[a] Excited at 396 nm (**3ah**), 350 nm (**5**), 426 nm (**6**), 463 nm (*syn*-**7**), 465 nm (*anti*-**7**), and 373 nm (**8**). [b] Absolute fluorescence quantum yields. [c] Stokes shifts.

Cyclic Voltammetry and Differential Pulse Voltammetry

The IUPAC convention was used to report the CV and DPV data. The CV and DPV of the indicated compounds were recorded in MeCN (0.01 M, degassed by N_2 gas bubbling) containing 0.1 M n-Bu_4NPF_6 with a Pt working electrode, a Pt counter electrode, and a Ag/Ag+ reference electrode. The measurements were performed at room temperature.

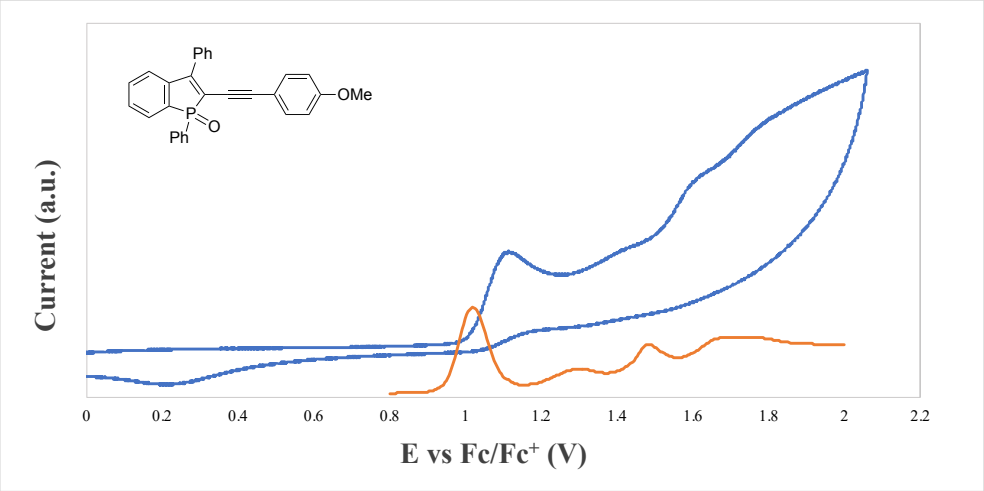


Figure S2. Cyclic voltammograms (blue line, from 0 V to 2.0 V then back to 0 V) and differential pulse voltammograms (orange line) of **3ah** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

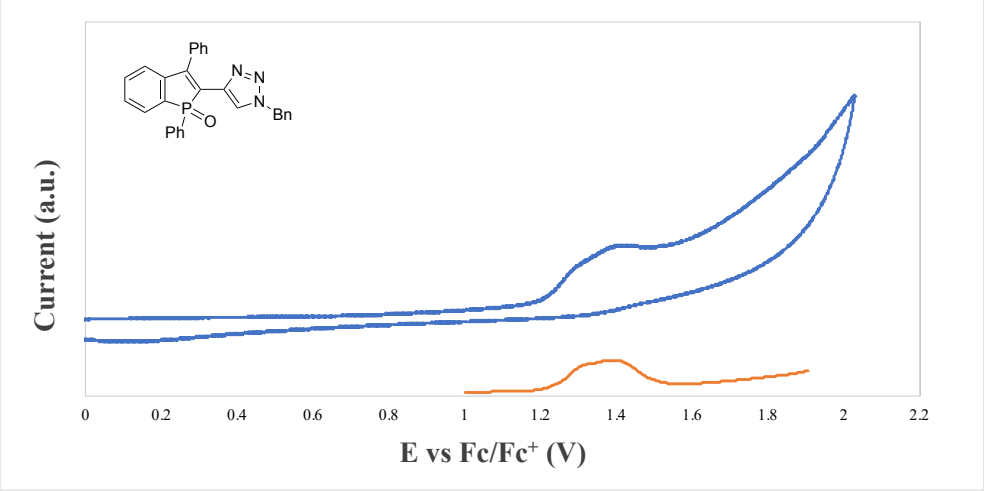


Figure S3. Cyclic voltammograms (blue line, from 0 V to 2.0 V then back to 0 V) and differential pulse voltammograms (orange line) of **5** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

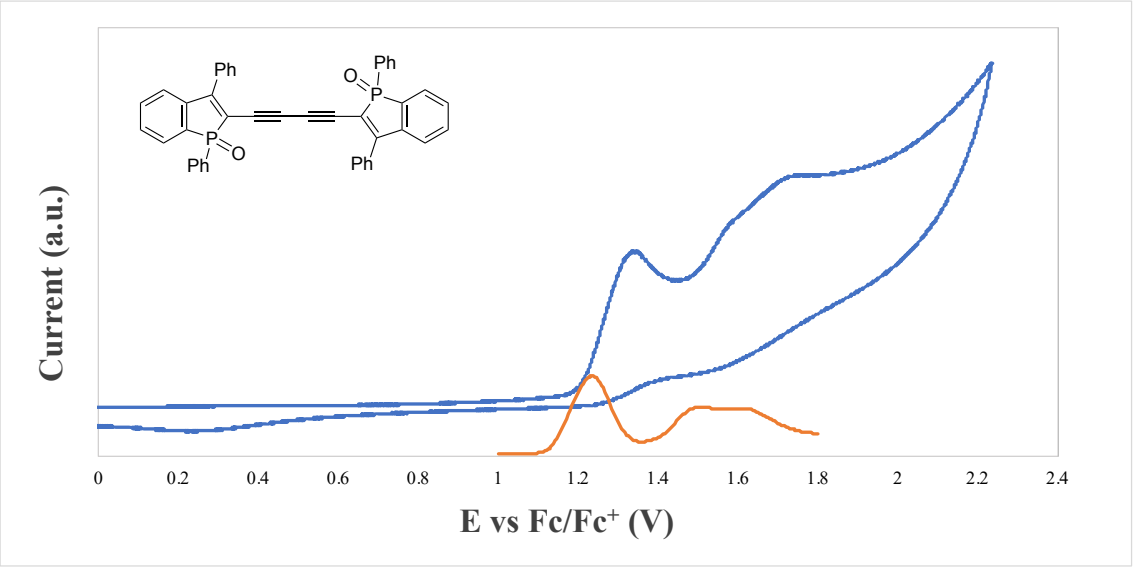


Figure S4. Cyclic voltammograms (blue line, from 0 V to 2.2 V then back to 0 V) and differential pulse voltammograms (orange line) of **6** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

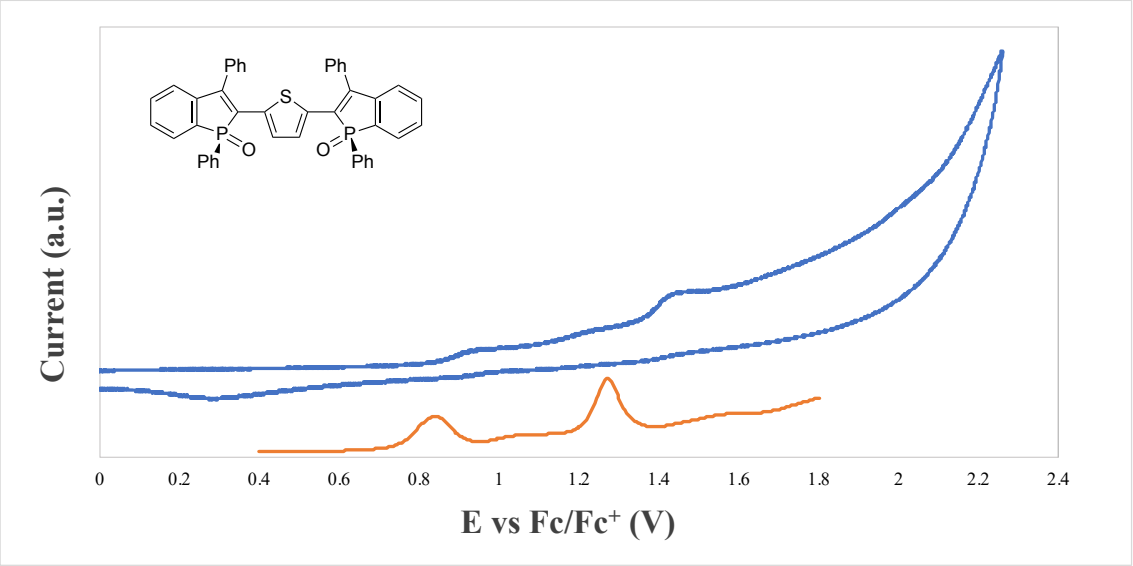


Figure S5. Cyclic voltammograms (blue line, from 0 V to 2.2 V then back to 0 V) and differential pulse voltammograms (orange line) of ***syn*-7** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

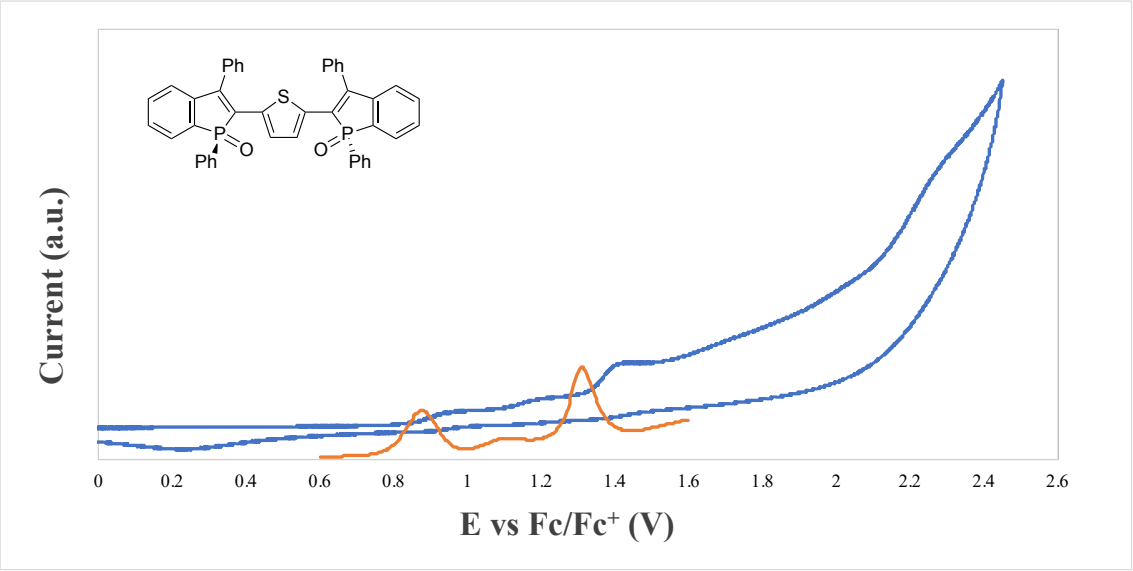


Figure S6. Cyclic voltammograms (blue line, from 0 V to 2.4 V then back to 0 V) and differential pulse voltammograms (orange line) of ***anti*-7** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

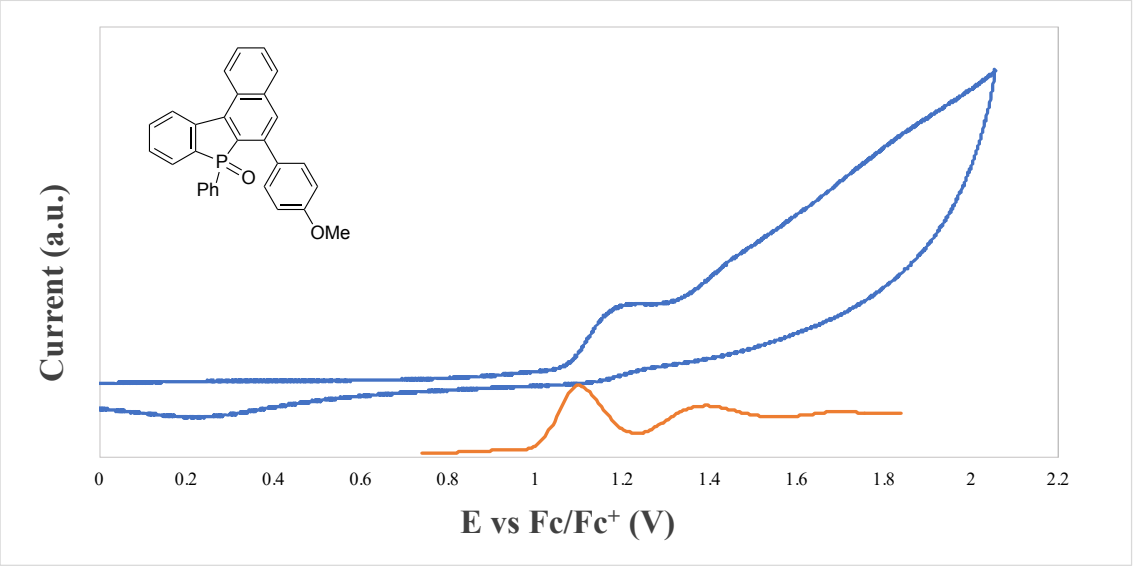


Figure S7. Cyclic voltammograms (blue line, from 0 V to 2.0 V then back to 0 V) and differential pulse voltammograms (orange line) of **8** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

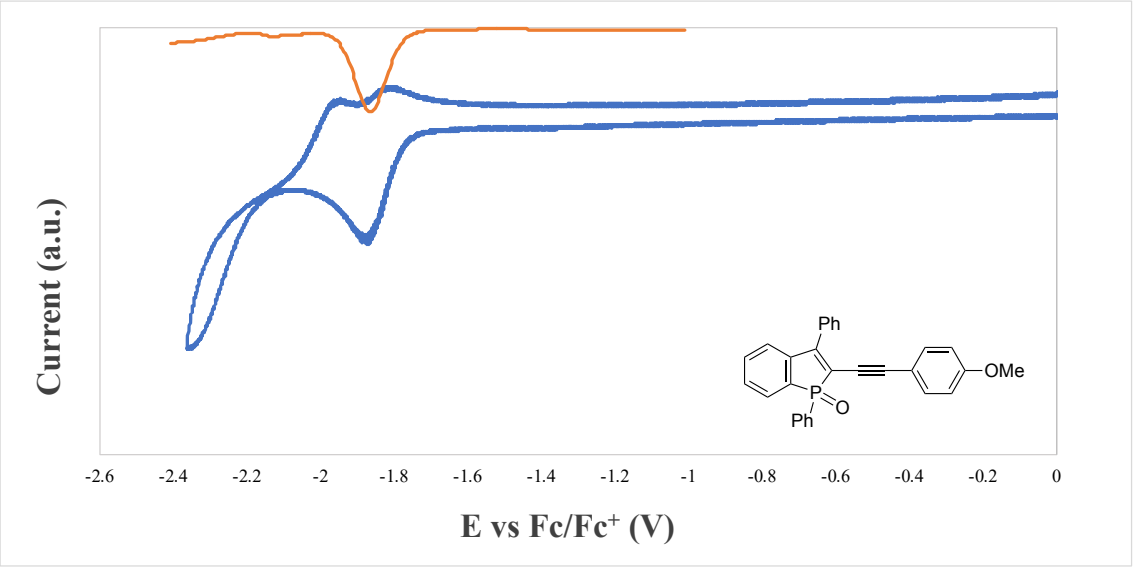


Figure S8. Cyclic voltammograms (blue line, from 0 V to –2.4 V then back to 0 V) and differential pulse voltammograms (orange line) of **3ah** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scale rate of 0.10 V/s.

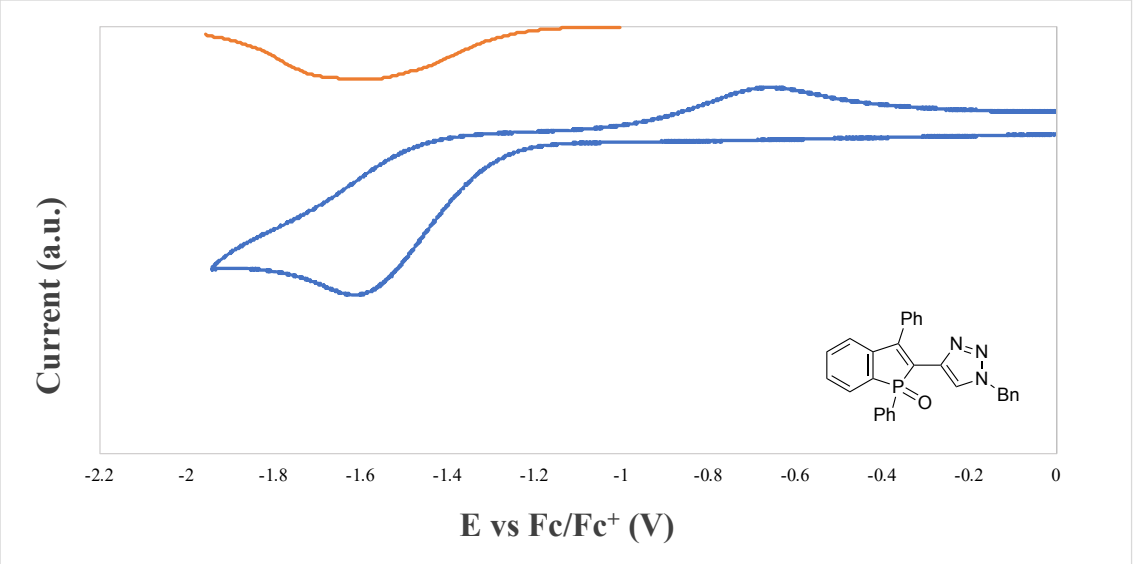


Figure S9. Cyclic voltammograms (blue line, from 0 V to –2.0 V then back to 0 V) and differential pulse voltammograms (orange line) of **5** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scale rate of 0.10 V/s.

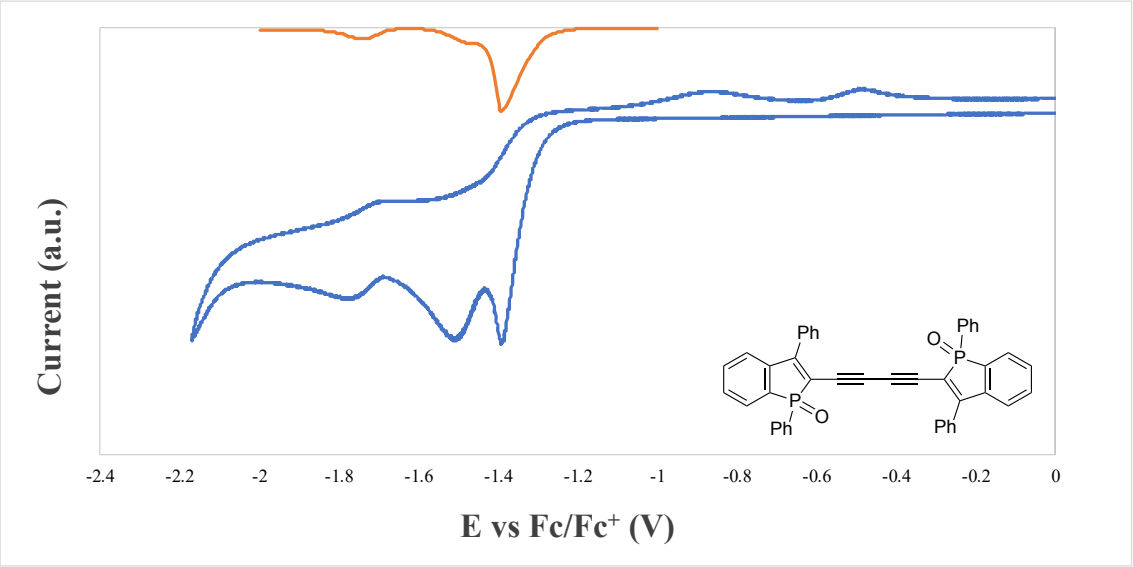


Figure S10. Cyclic voltammograms (blue line, from 0 V to –2.2 V then back to 0 V) and differential pulse voltammograms (orange line) of **6** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

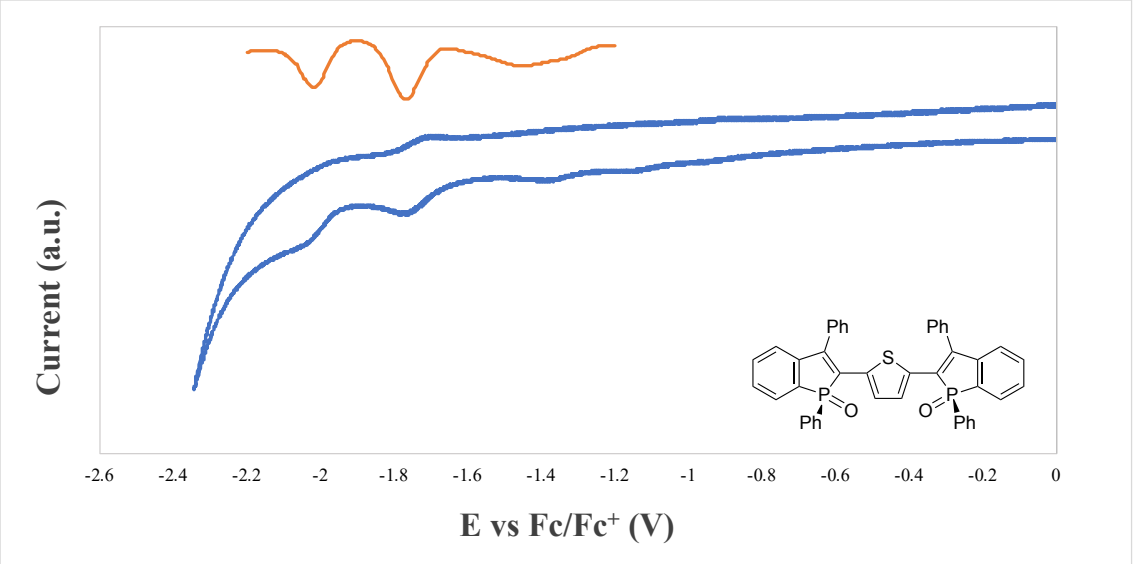


Figure S11. Cyclic voltammograms (blue line, from 0 V to –2.4 V then back to 0 V) and differential pulse voltammograms (orange line) of ***syn*-7** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

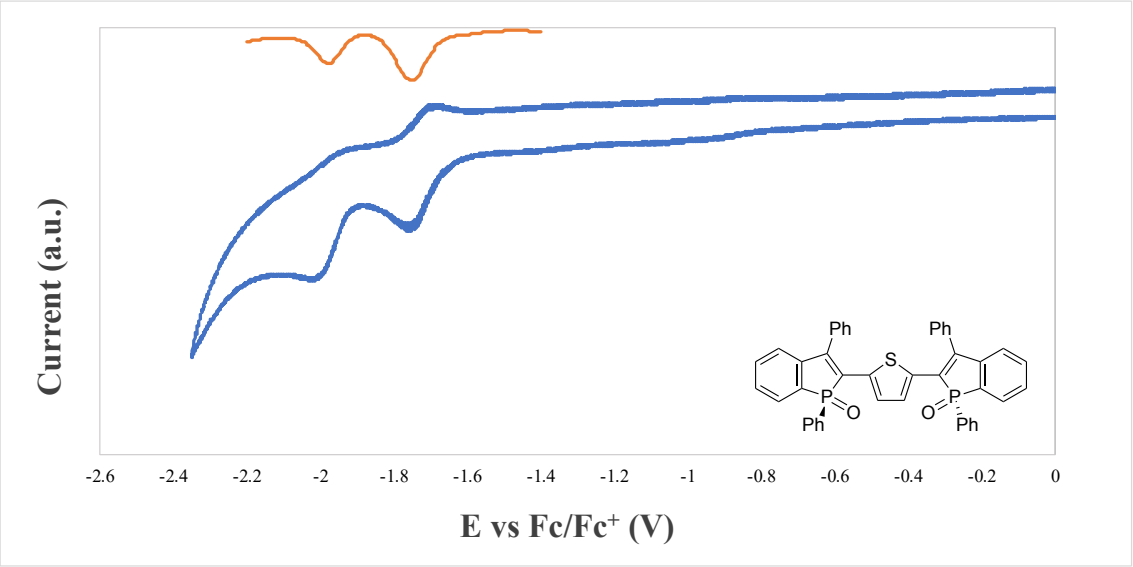


Figure S12. Cyclic voltammograms (blue line, from 0 V to –2.4 V then back to 0 V) and differential pulse voltammograms (orange line) of ***anti*-7** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

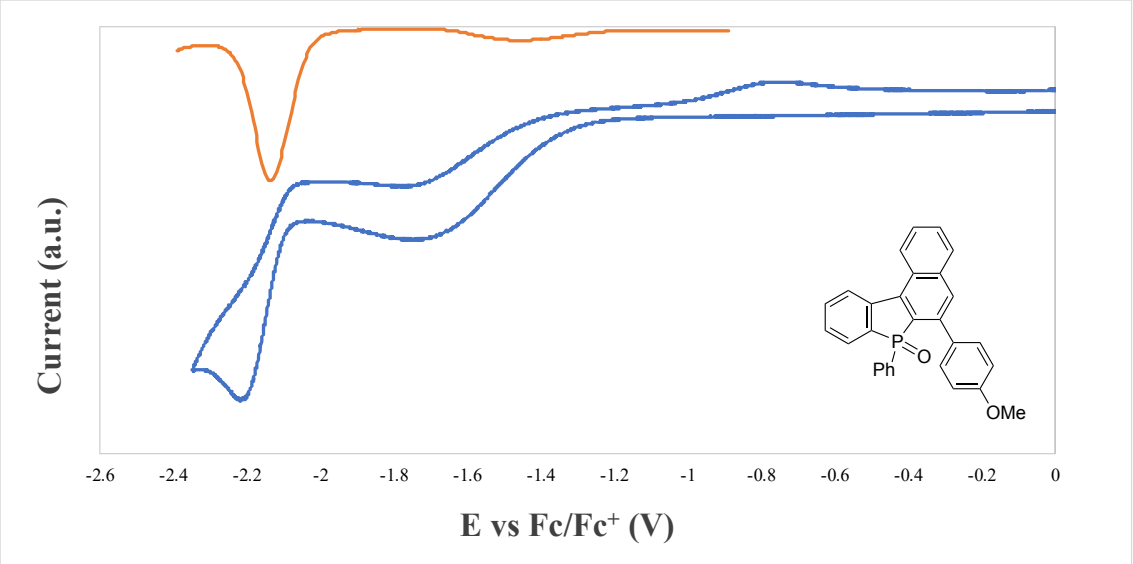


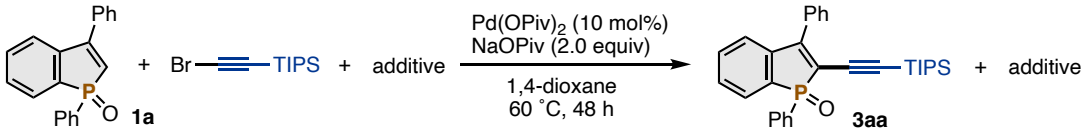
Figure S13. Cyclic voltammograms (blue line, from 0 V to –2.4 V then back to 0 V) and differential pulse voltammograms (orange line) of **8** in MeCN containing 0.1 M n-Bu_4NPF_6 at a scan rate of 0.10 V/s.

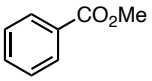
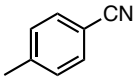
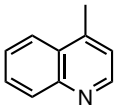
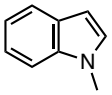
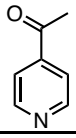
Table S11. Absorption wavelengths, HOMO-LUMO energy gaps, and cyclic (differential pulse) voltammogram data of selected compounds.

compd	λ_{onset}^{abs} (nm)[a]	E_g^{opt} (eV)[b]	E_{ox} (V)[c]	E_{HOMO} (eV)[d]	E_{red} (V)[c]	E_{LUMO} (eV)[d]	E_{LUMO} (eV)[e]
3ah	448	2.77	1.02	-5.82	-1.86	-2.94	-3.05
5	400	3.10	1.41	-6.21	-1.60	-3.21	-3.11
6	524	2.37	1.24	-6.04	-1.39	-3.41	-3.67
***syn*-7**	496	2.50	0.84	-5.64	-1.77	-3.03	-3.14
***anti*-7**	496	2.50	0.88	-5.68	-1.76	-3.04	-3.18
8	395	3.14	1.10	-5.90	-2.14	-2.66	-2.76

[a] Measured in CH_3Cl. [b] Determined from the onset of the absorption spectra. [c] Performed in MeCN in the presence of Bu_4NPF_6. v = 0.10 V/s. Values determined by DPV, versus Fc/Fc^+. [d] The approximation for Fc/Fc^+ level is -4.8 eV versus vacuum: E_{HOMO} = -4.8 - E_{ox}. E_{LUMO} = -4.8 - E_{red}. [e] Estimated from E_{HOMO} and E_g^{opt}. $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

Robustness Screen

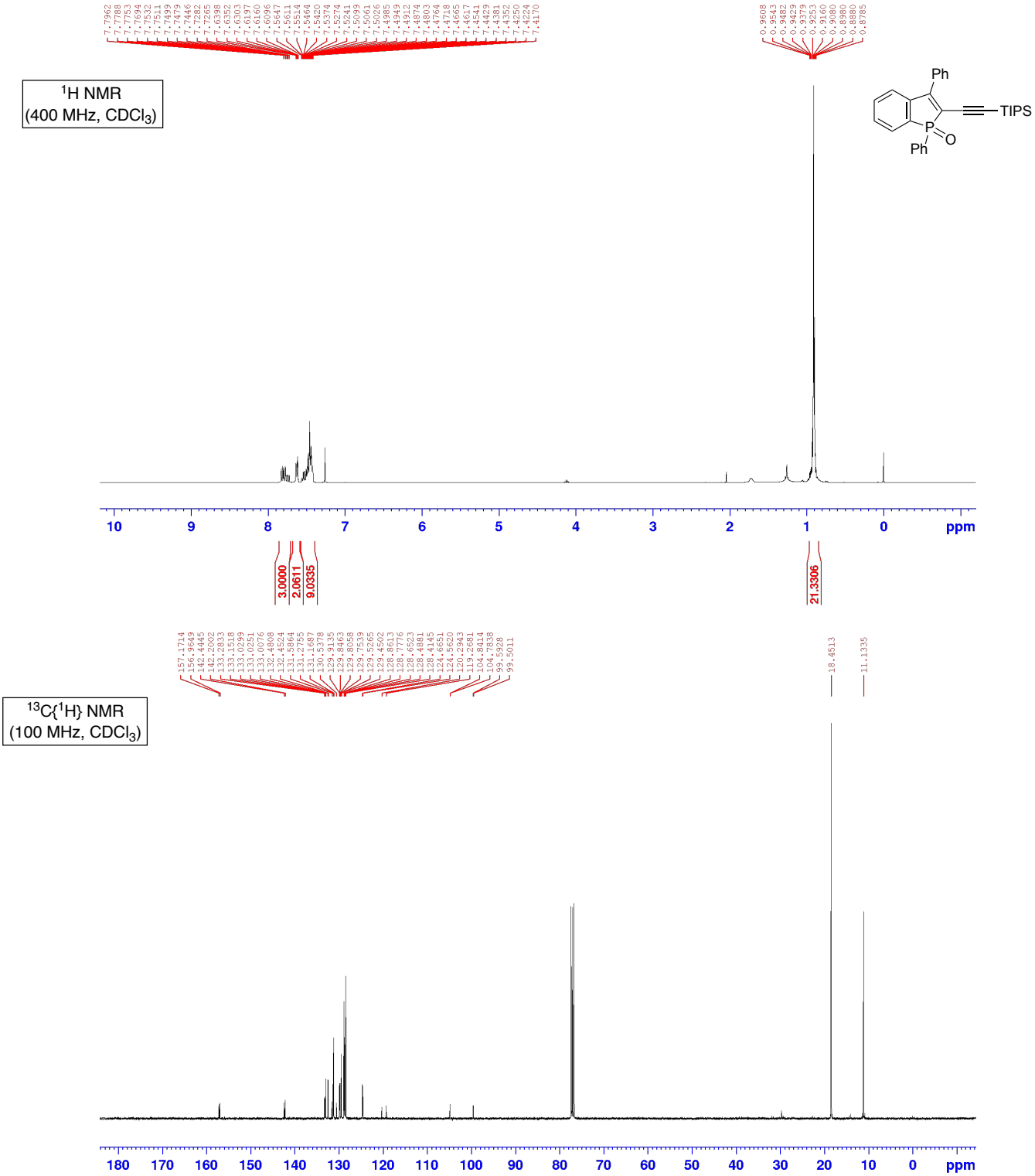


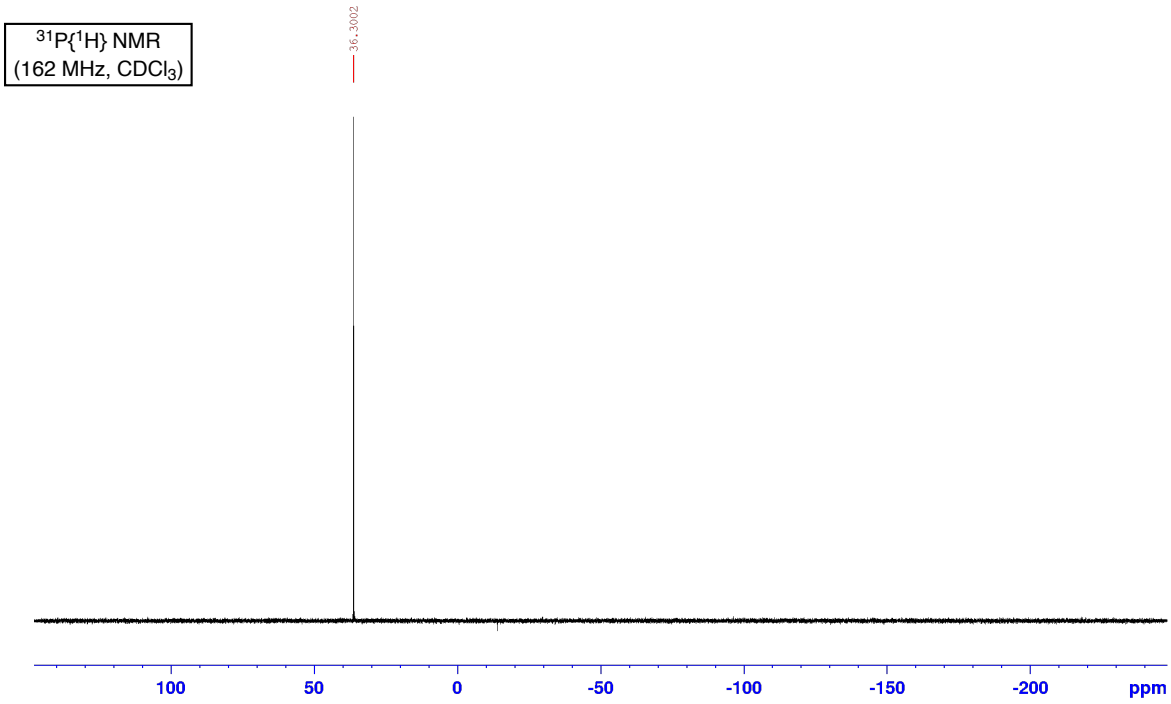
entry	additive	yield of **3aa** (%)	yield of recovered **1a** (%)	yield of recovered additive (%)
1		88 ✔	12	72 ✔
2		86 ✔	0	74 ✔
3		26 ×	31	0 ×
4		0 ×	quant.	quant. ✔
5		46 –	49	32 ×
6		0 ×	quant.	quant. ✔

Reaction conditions: $Pd(OPiv)_2$ (0.010 mmol), NaOPiv (0.20 mmol), **1a** (0.10 mmol), **2a** (0.20 mmol), additive (0.010 mmol), 1,4-dioxane (1.5 mL), 60 ˚C, 48 h, N_2. Yields were estimated by $^{31}P\{^1H\}$ and/or ^1H NMR with $P(O)(OEt)_3$ as the internal standard.

Copies of NMR Spectra

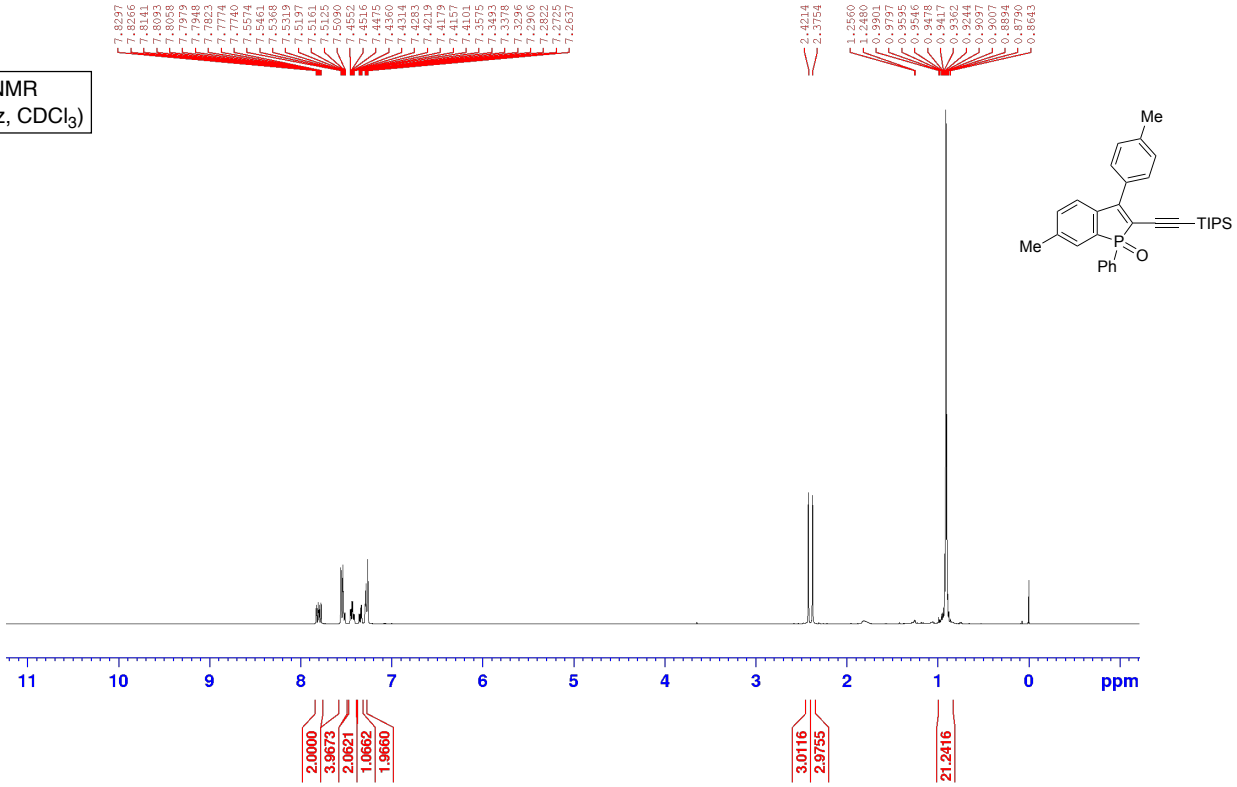
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3aa**]



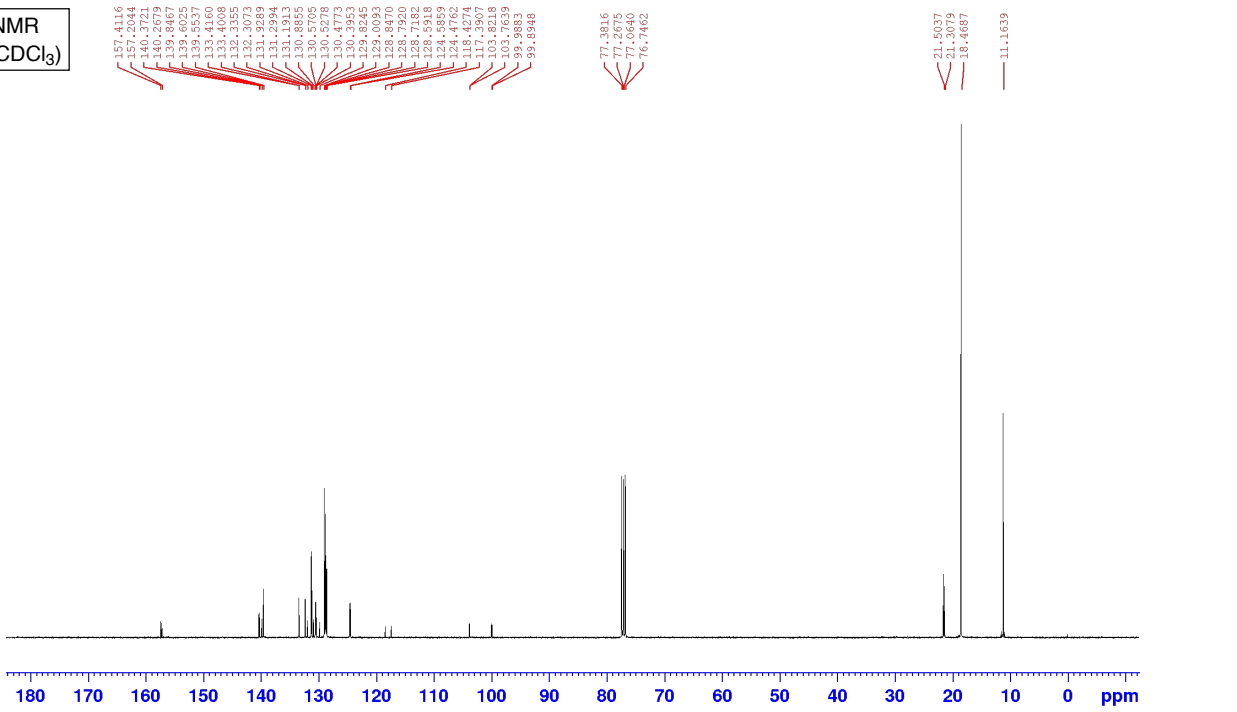

31P{1H} NMR
(162 MHz, CDCl3)
36.3002
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ba**]

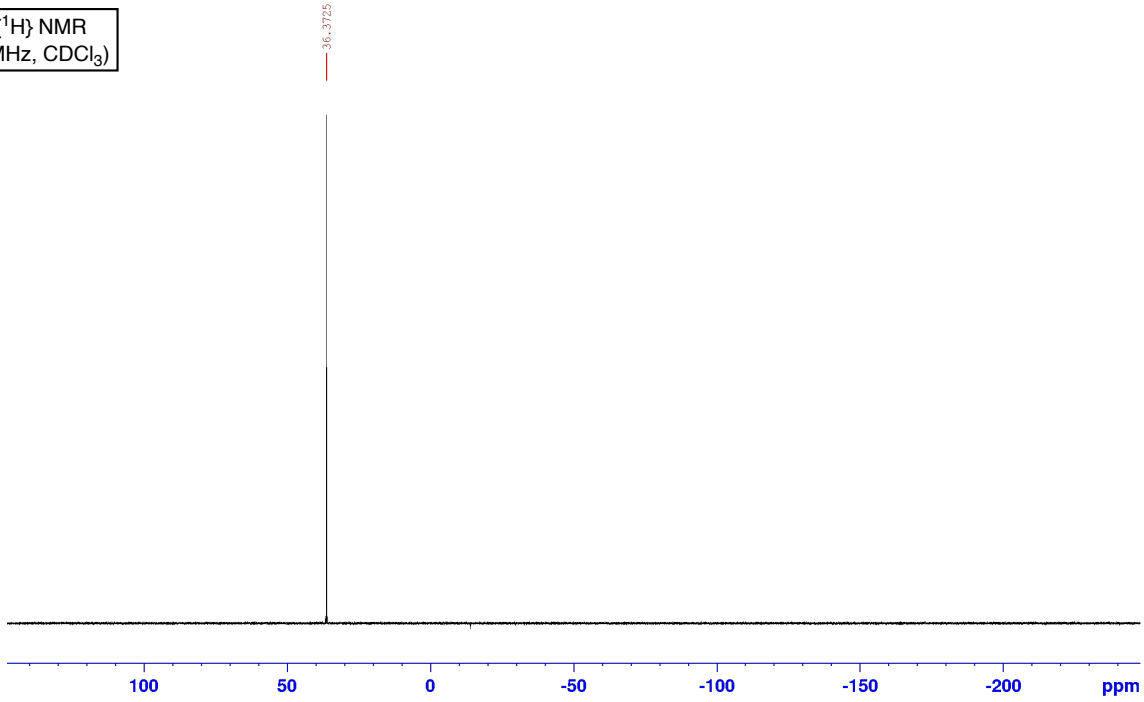
^{1}H NMR
(400 MHz, $CDCl_3$)



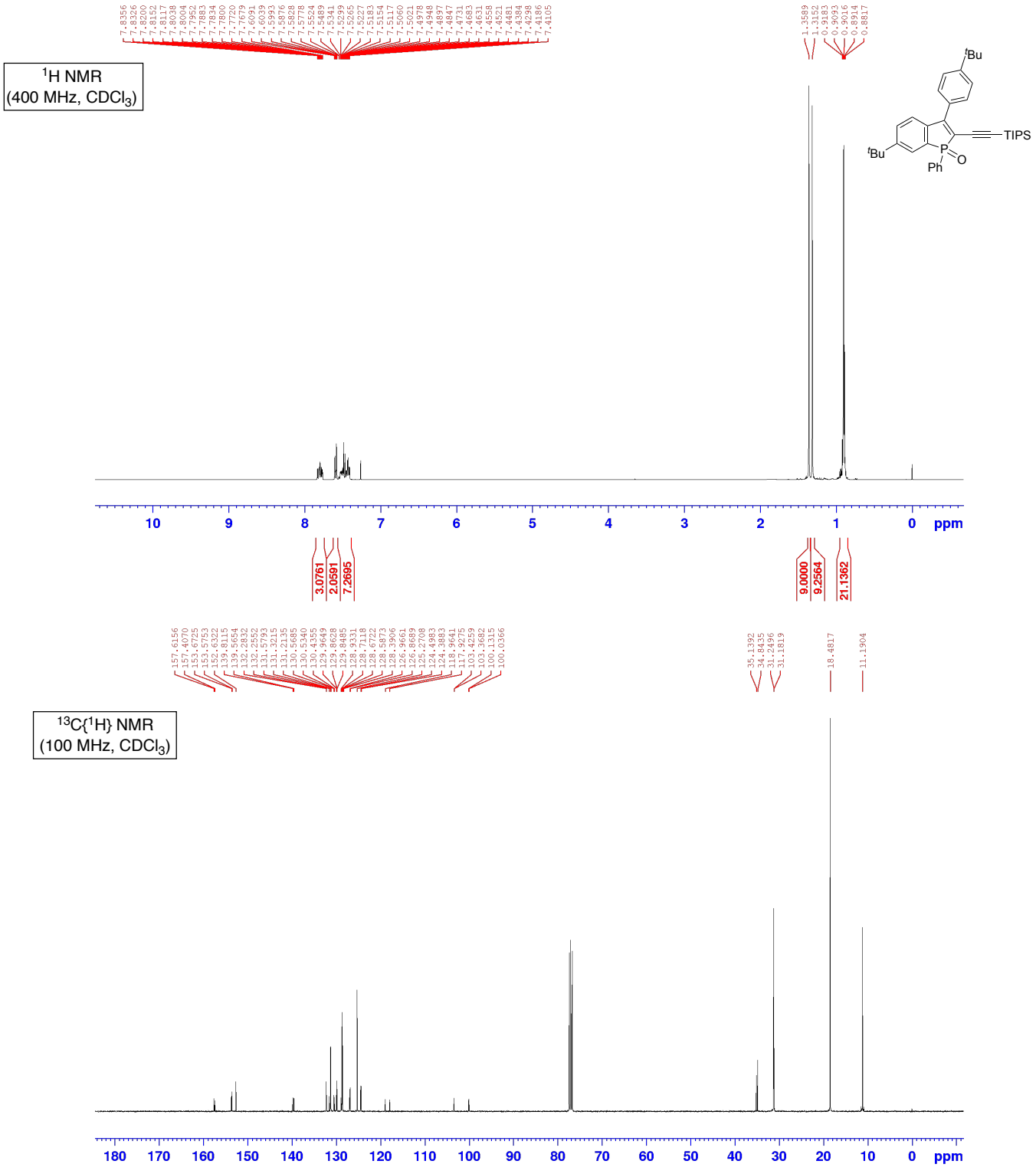
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



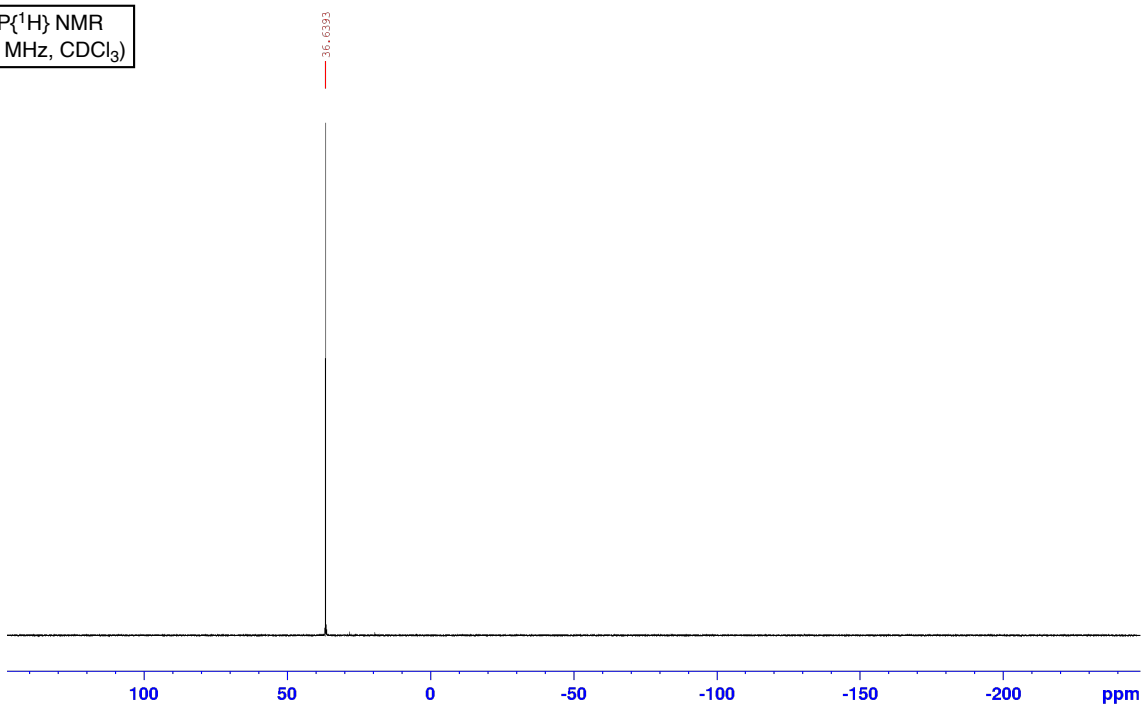
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



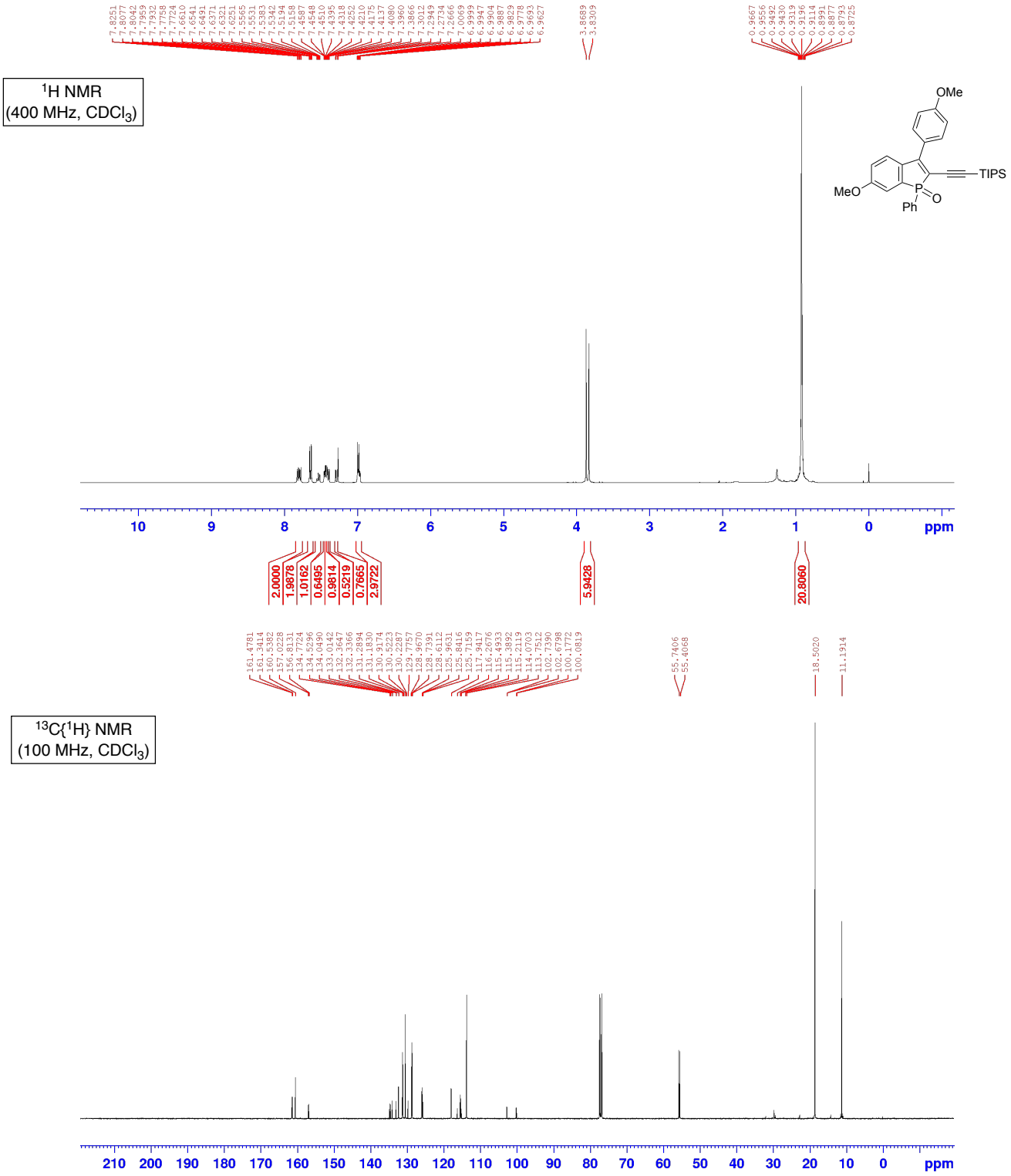
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ca**]



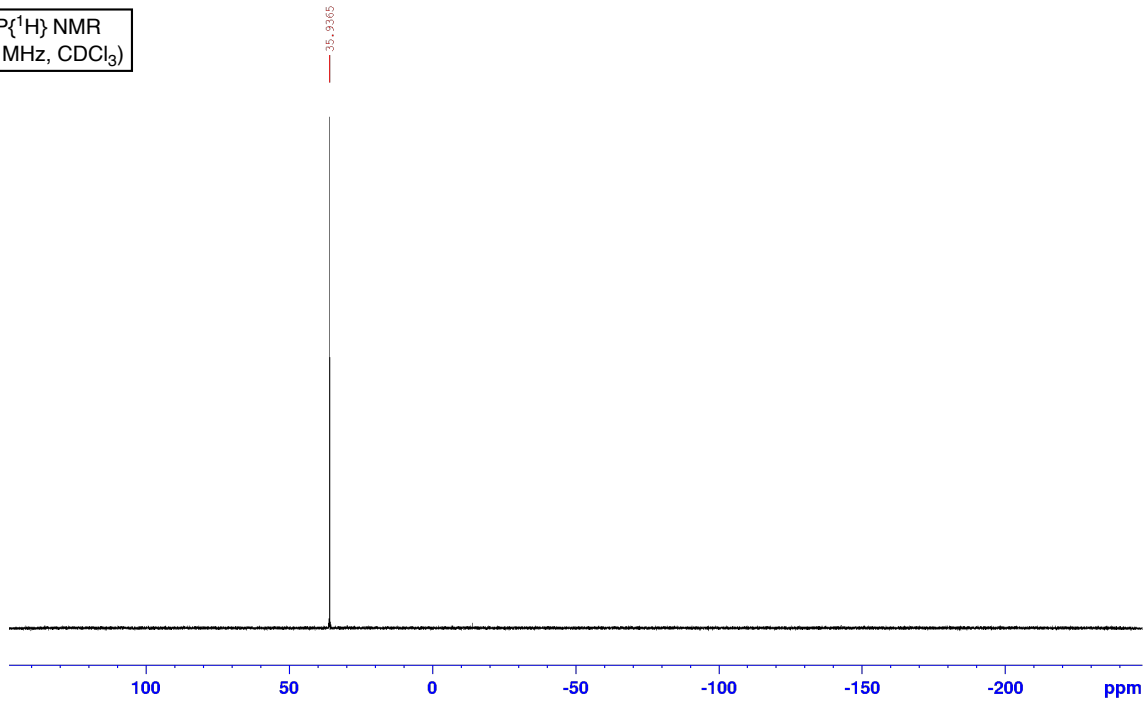
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



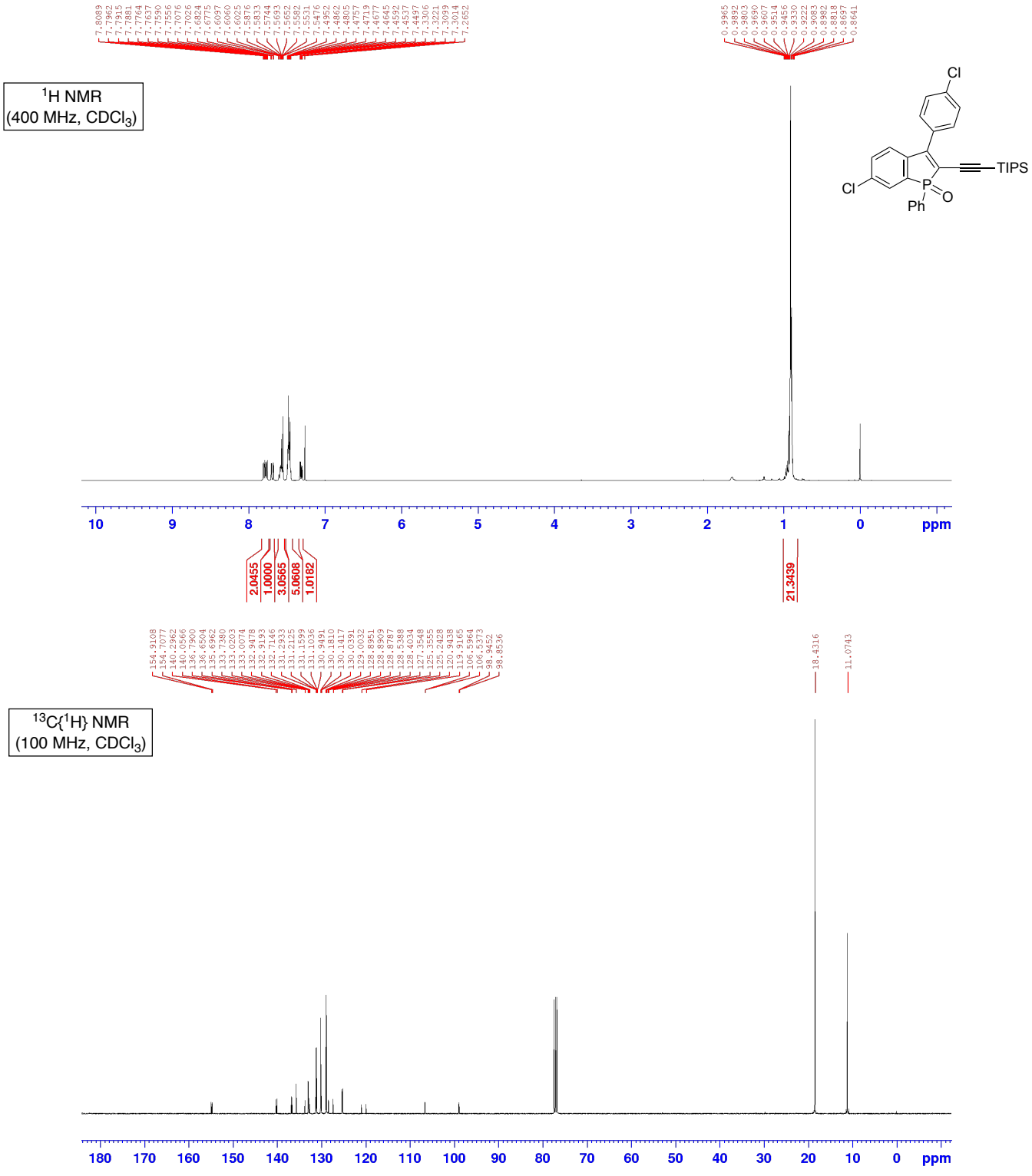
[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3da**]

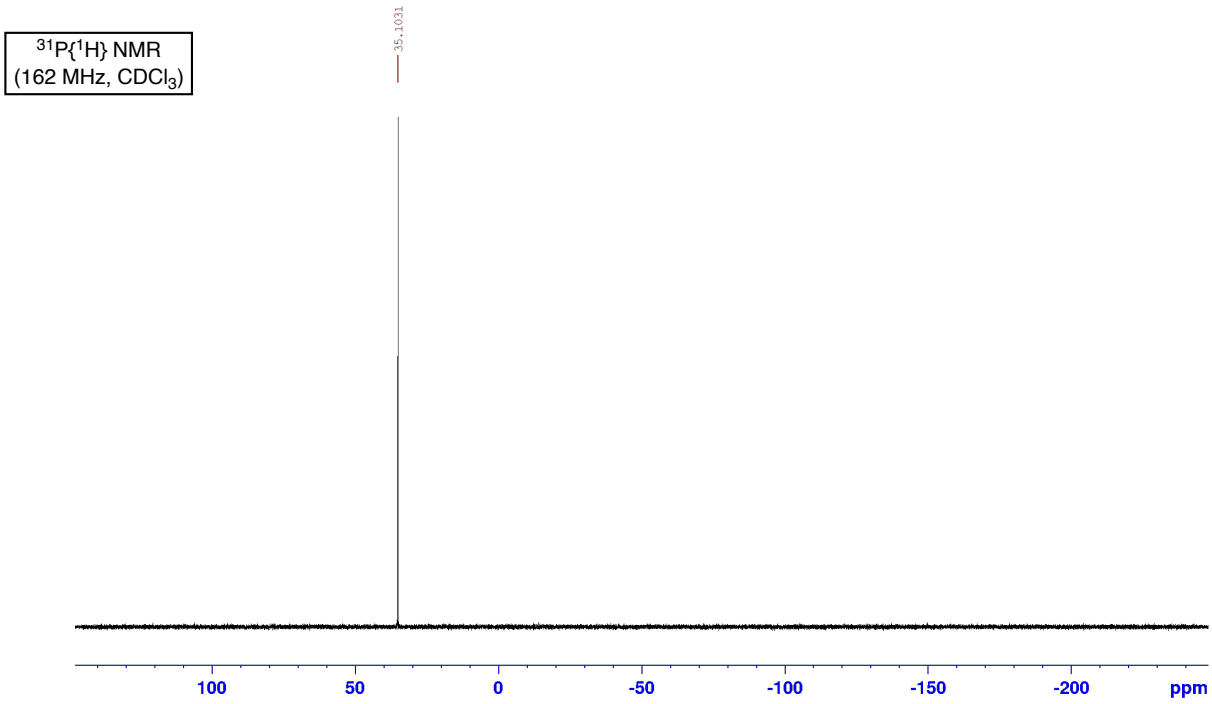


$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

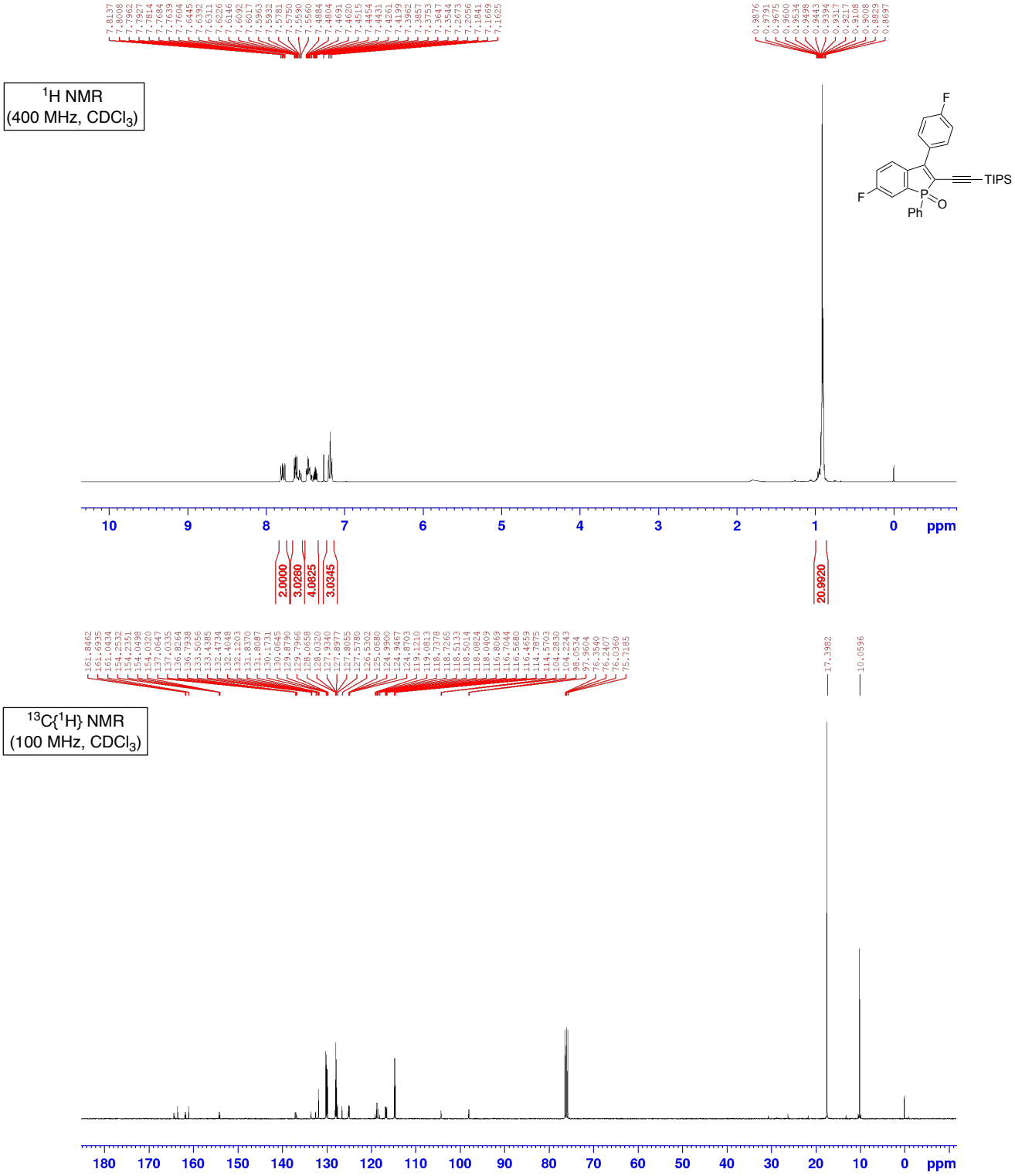


[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ea**]

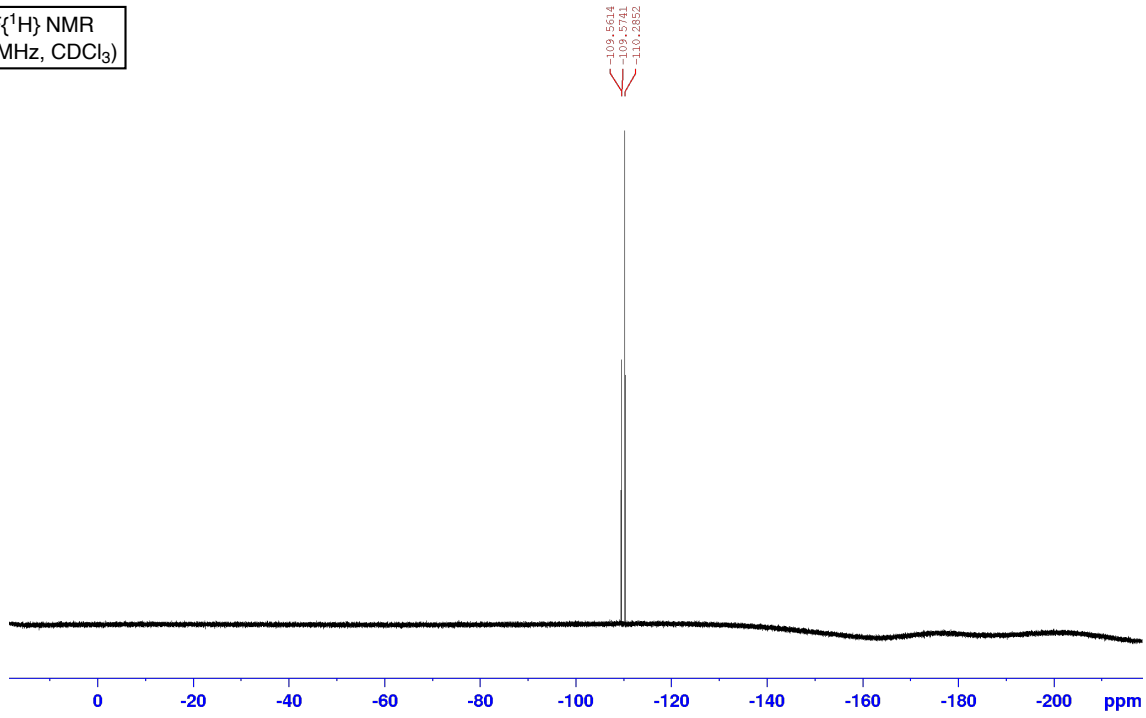



31P{1H} NMR
(162 MHz, CDCl3)
35.1031
100
50
0
-50
-100
-150
-200
ppm

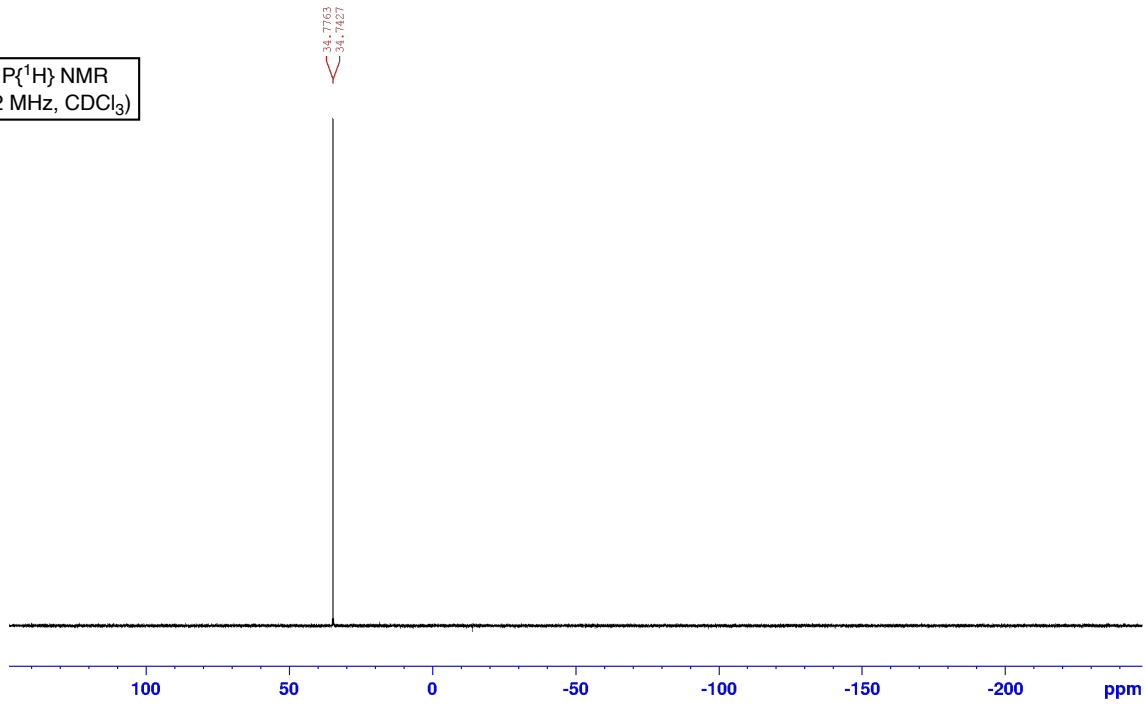
[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3fa**]



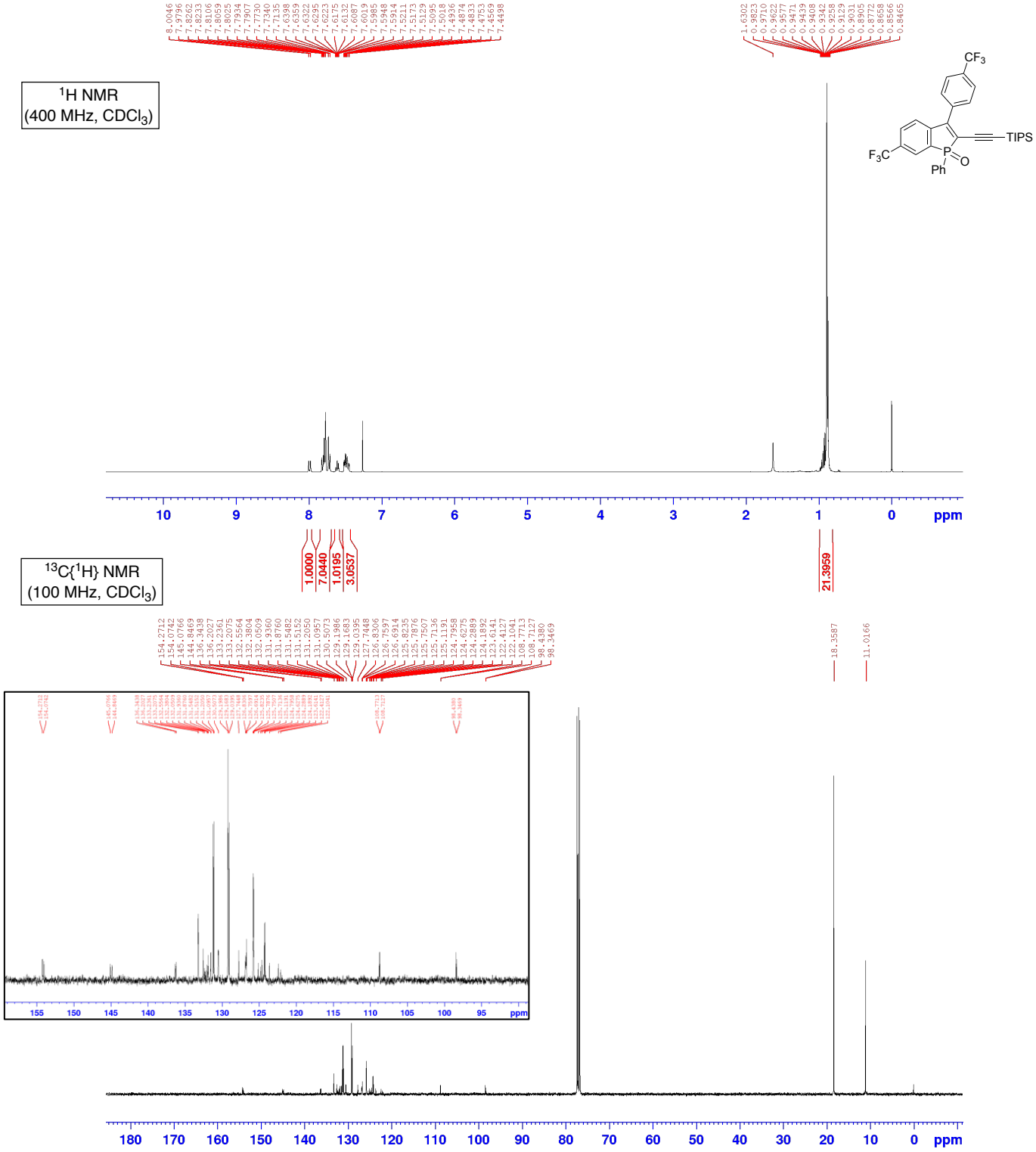
$^{19}F\{^{1}H\}$ NMR
(376 MHz, $CDCl_3$)



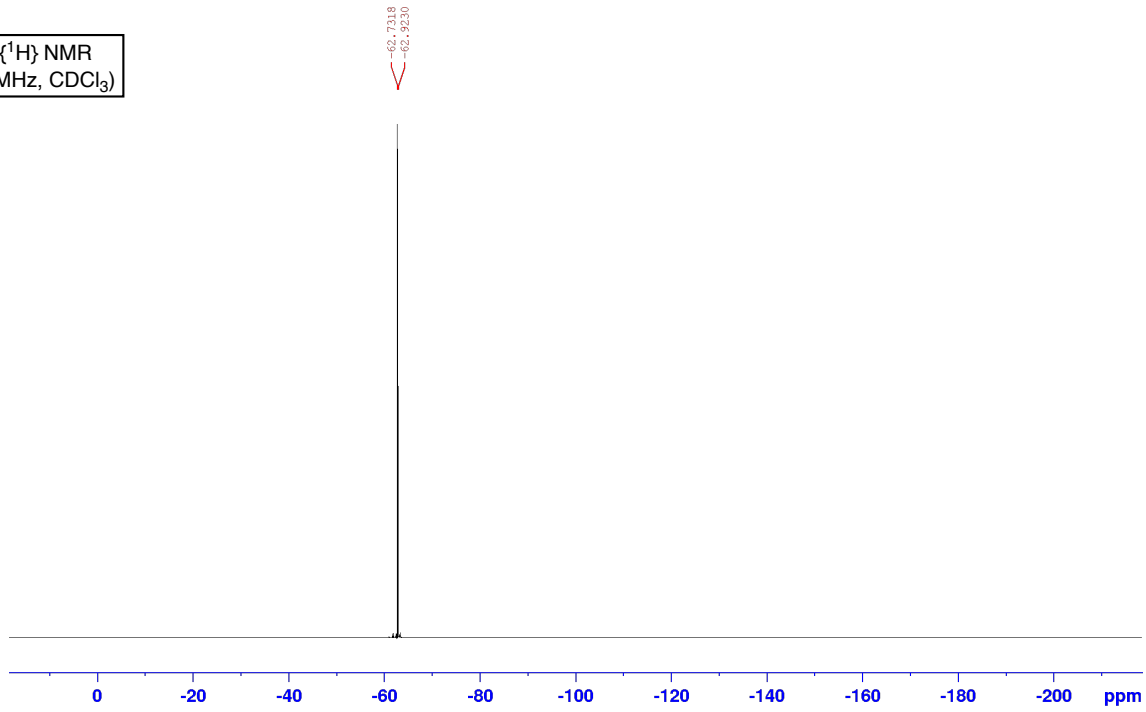
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



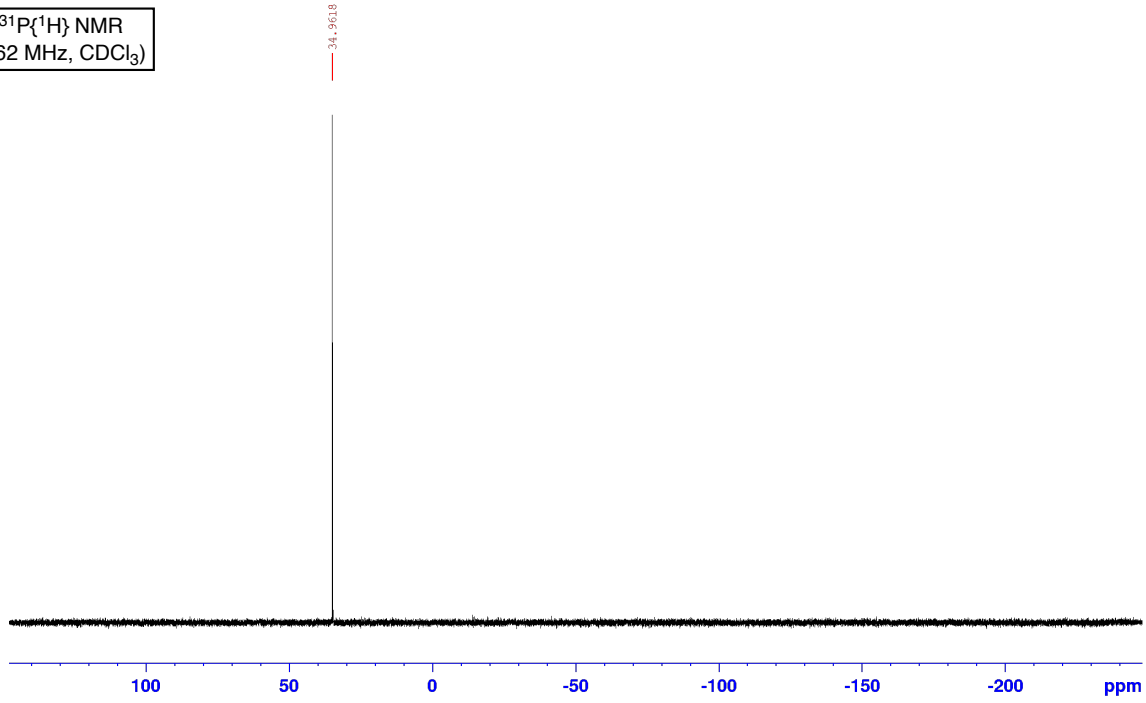
[^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ga**]



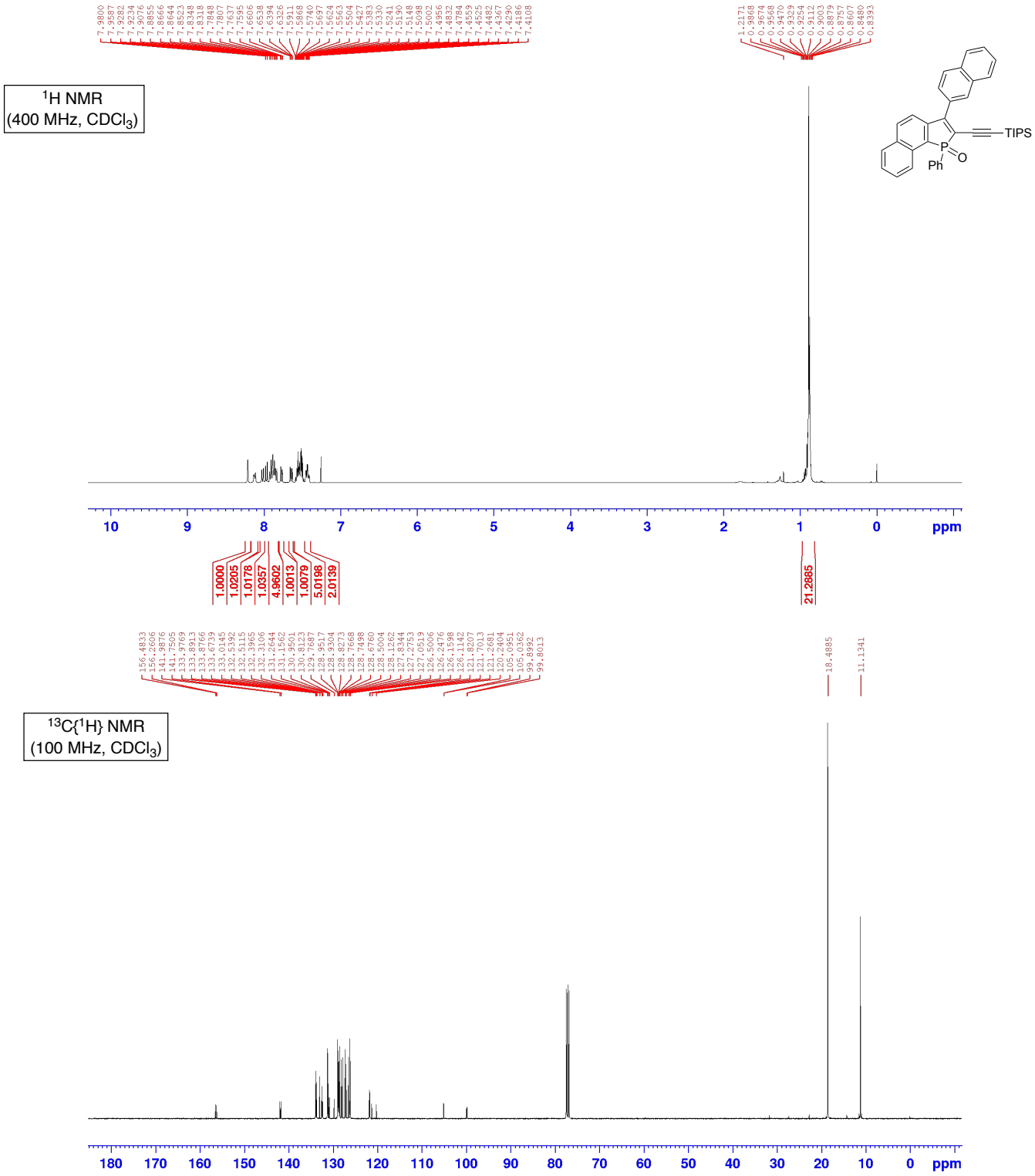
$^{19}F\{^{1}H\}$ NMR
(376 MHz, $CDCl_3$)



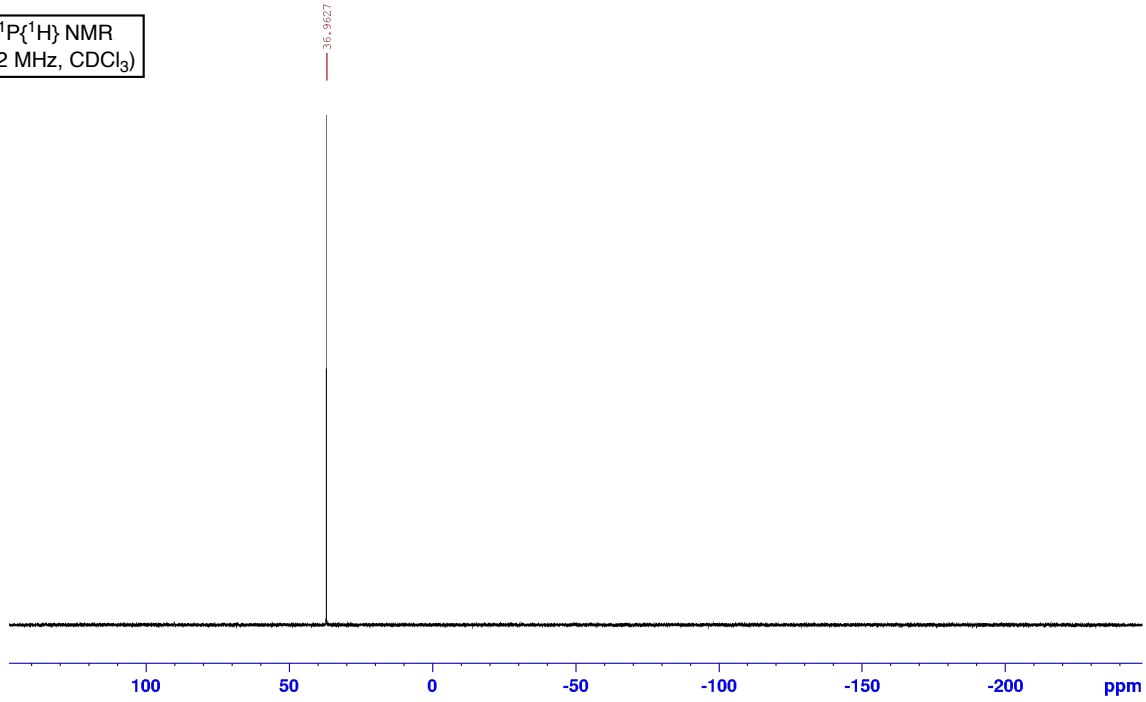
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



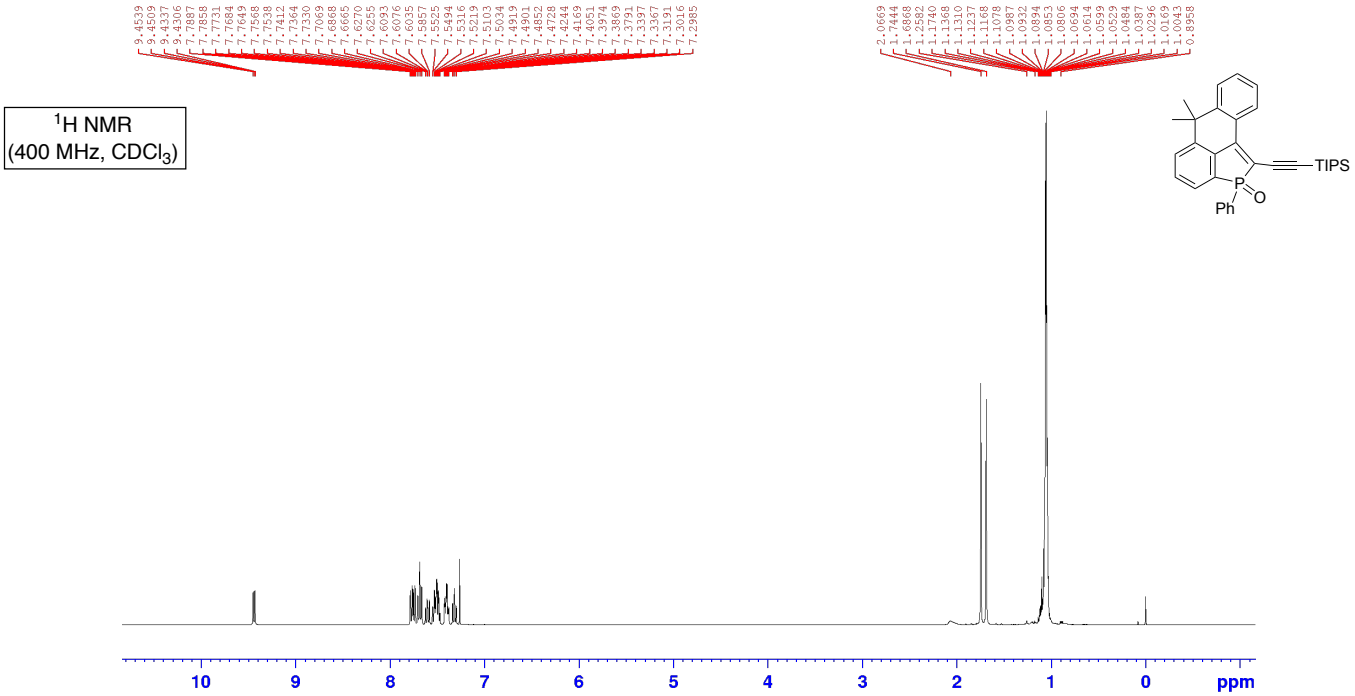
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ha**]

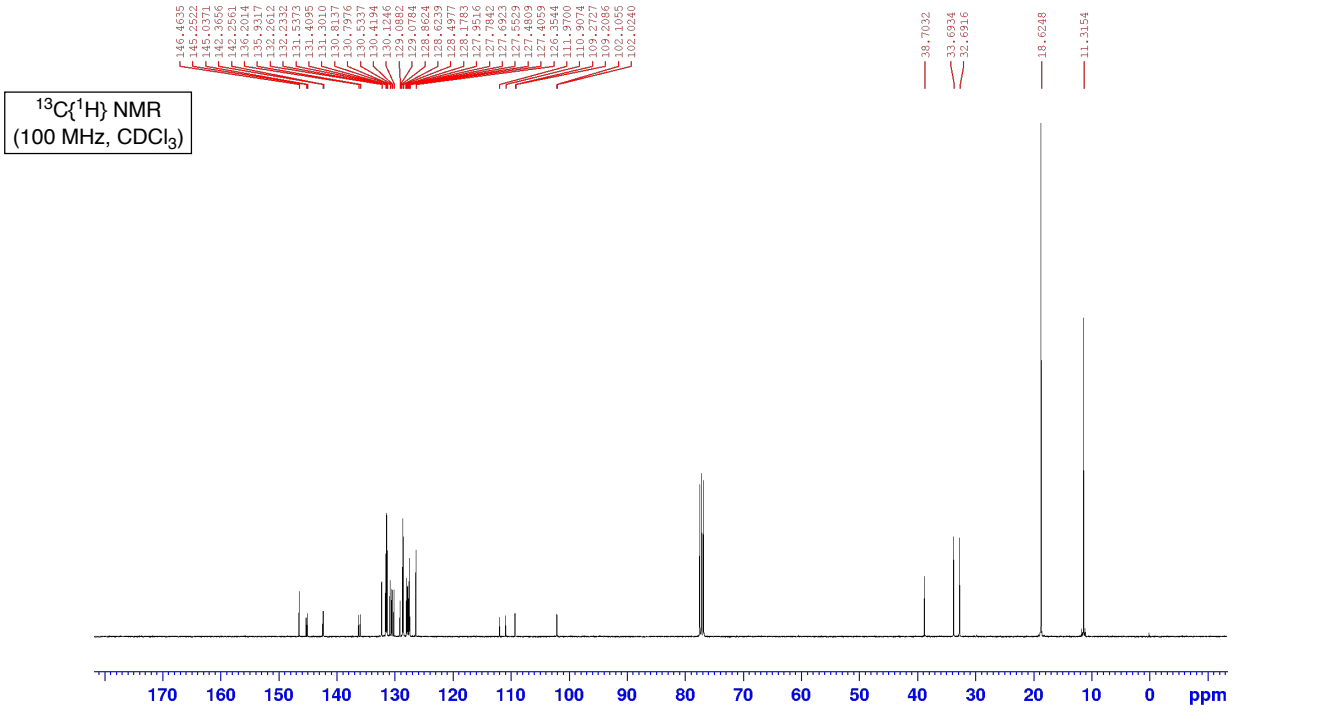


$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

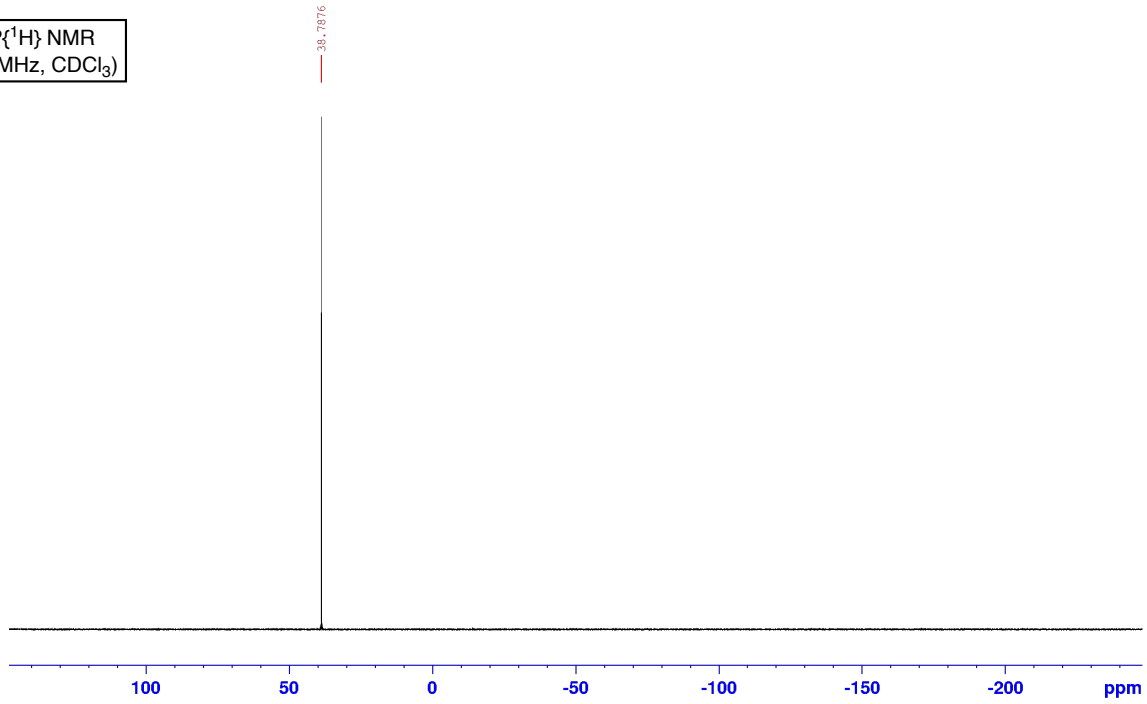


[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ia**]

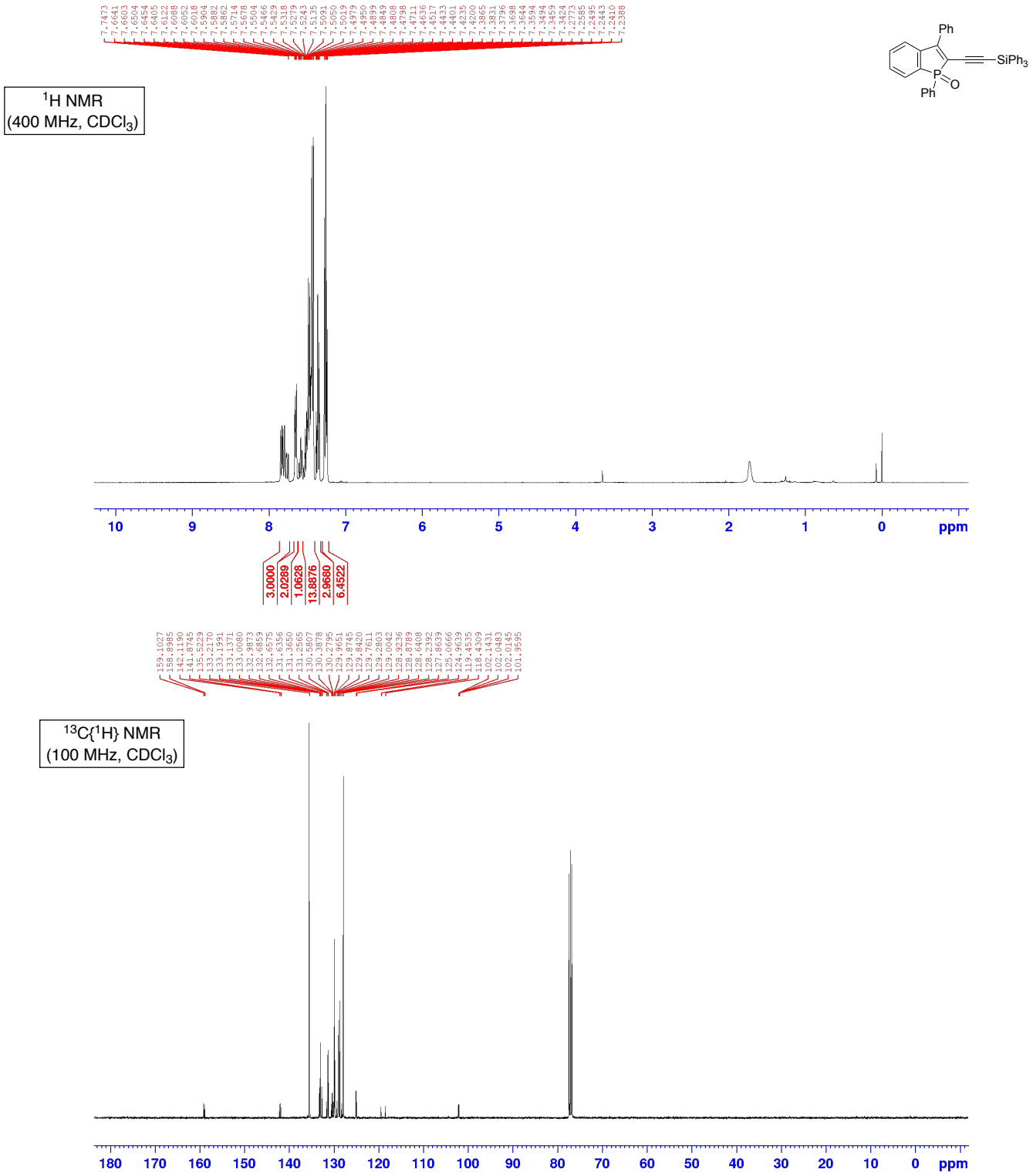


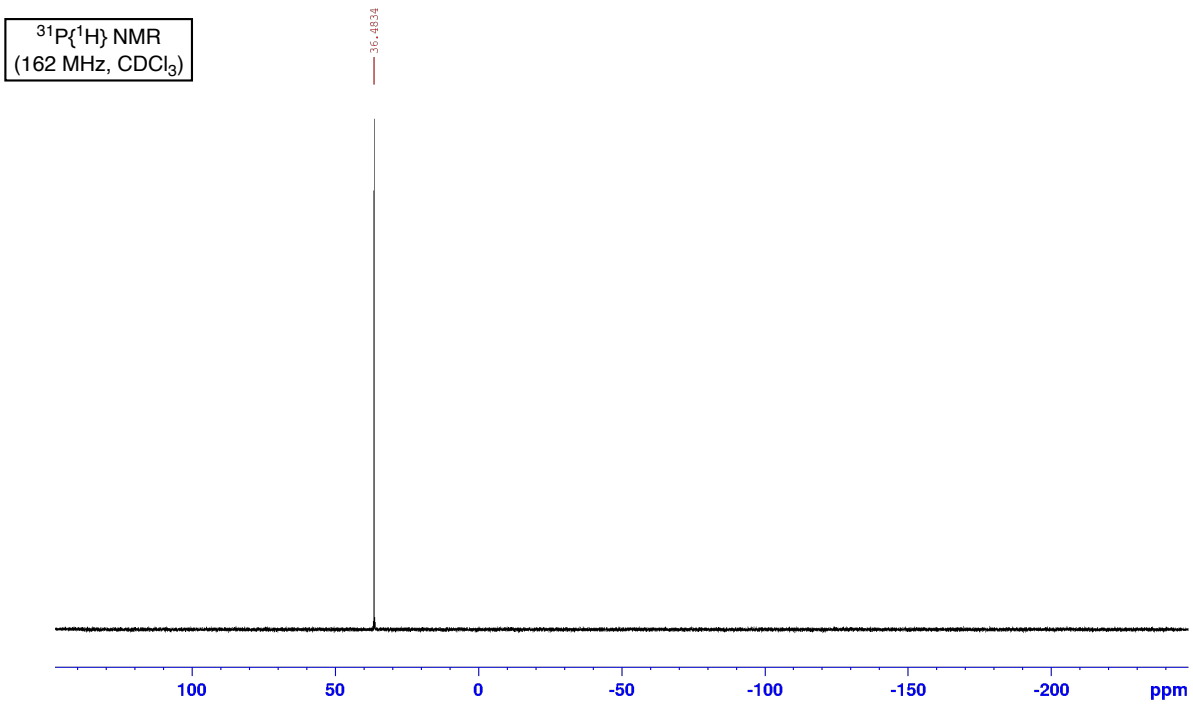


$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

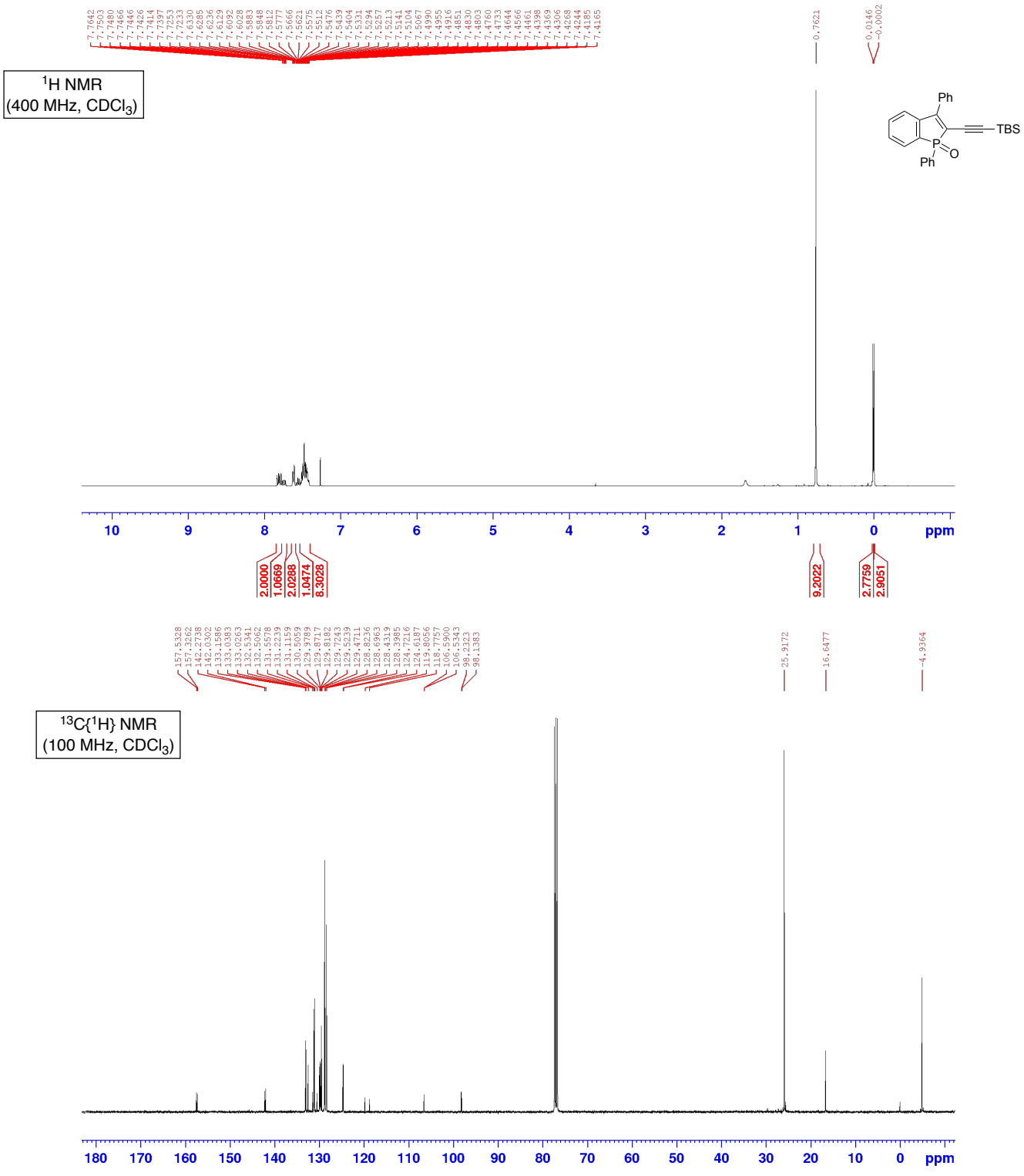


[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ab**]

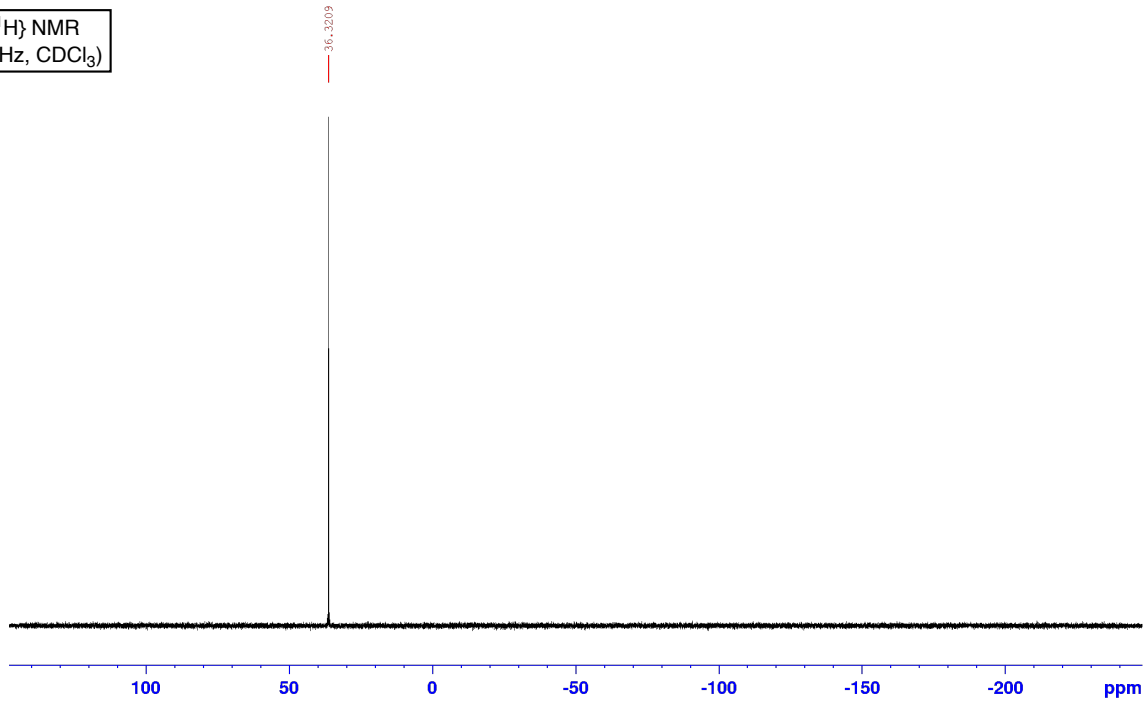



31P{1H} NMR
(162 MHz, CDCl3)
36.4834
100
50
0
-50
-100
-150
-200
ppm

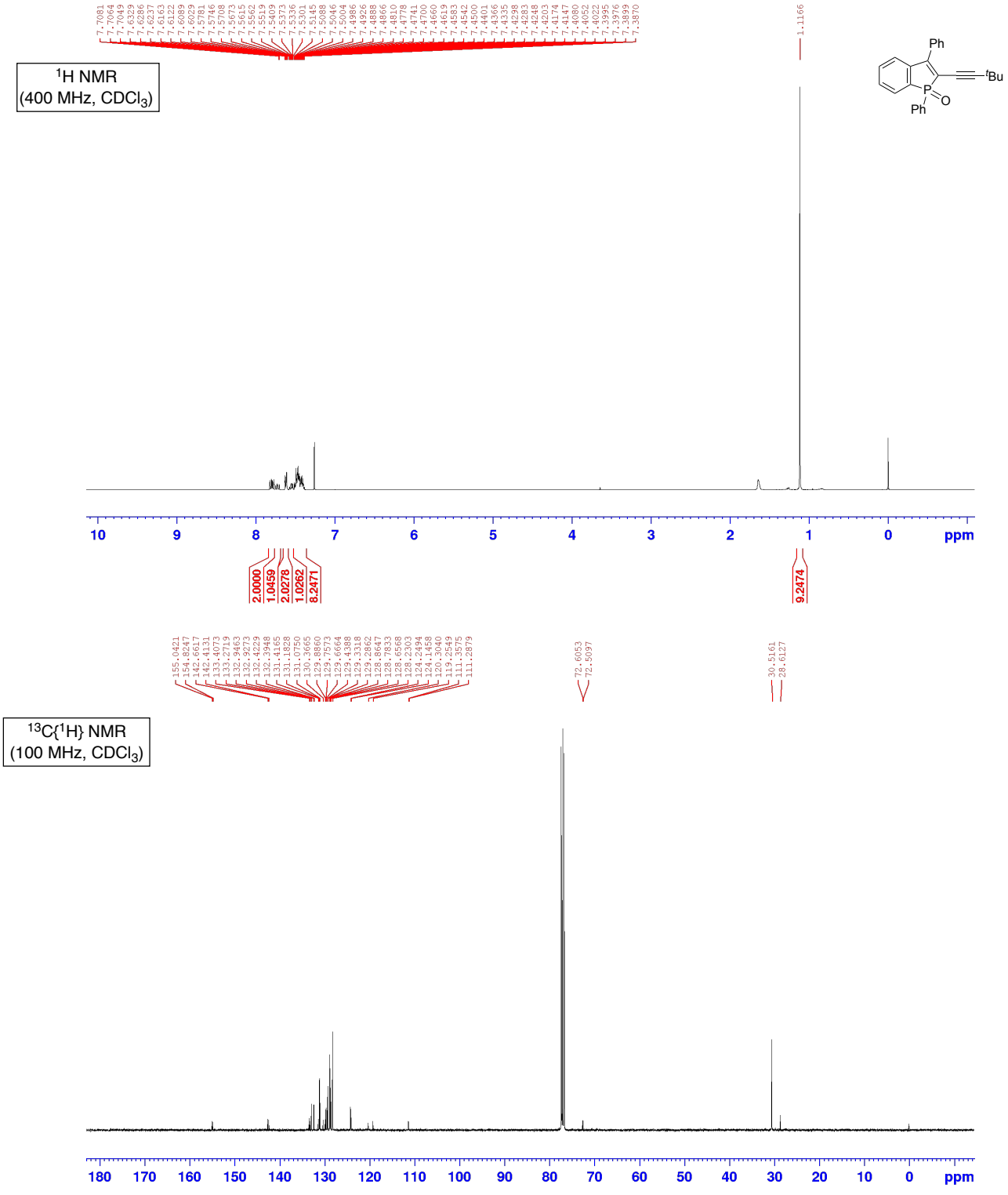
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ac**]



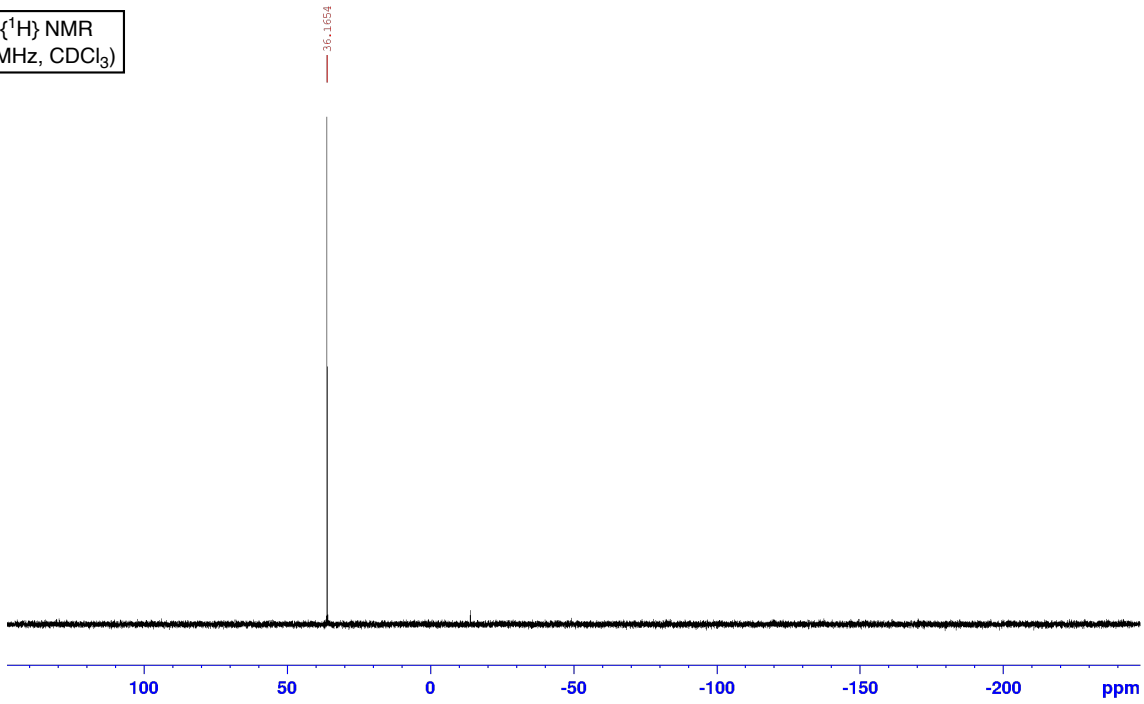
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



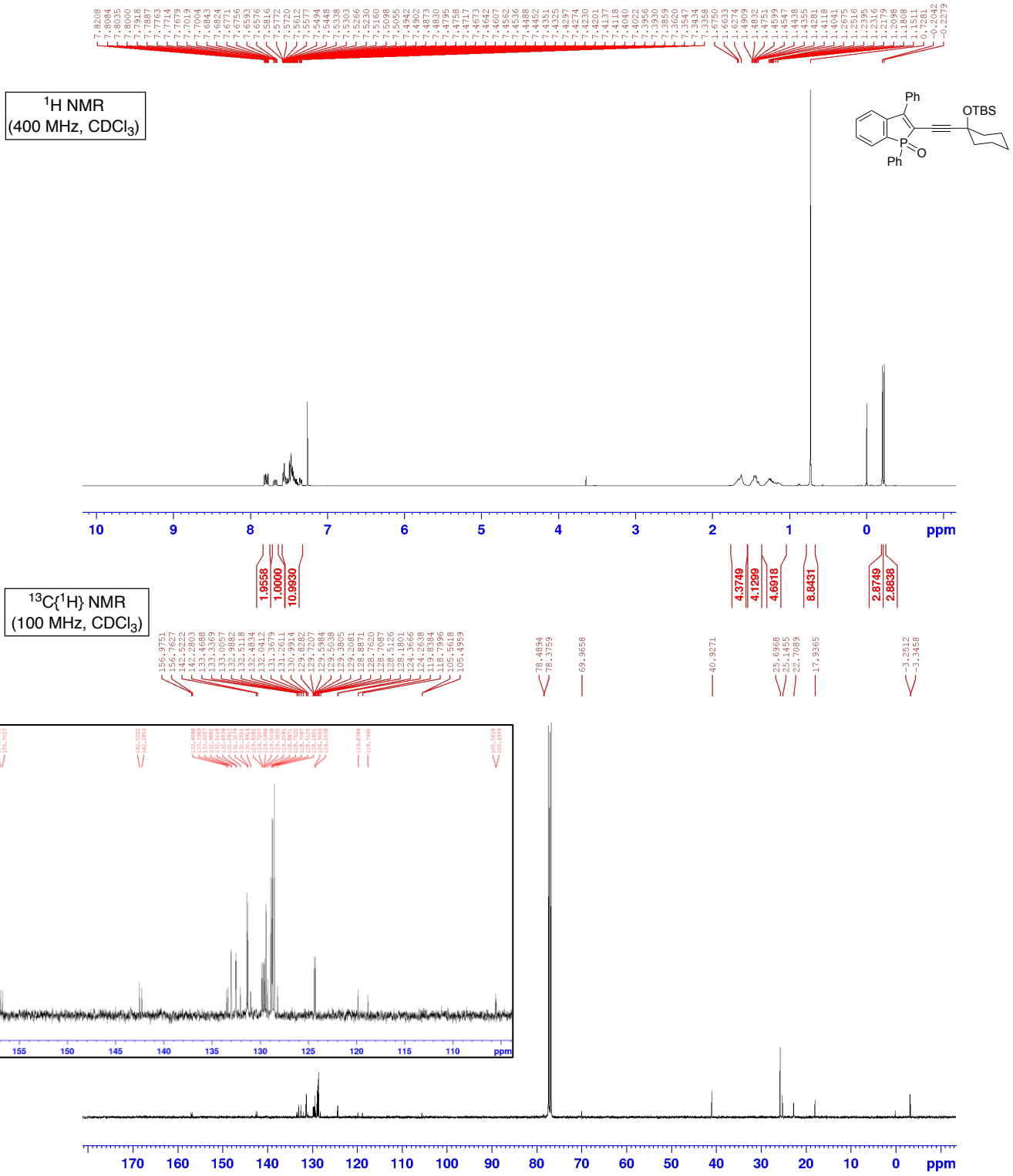
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ad**]

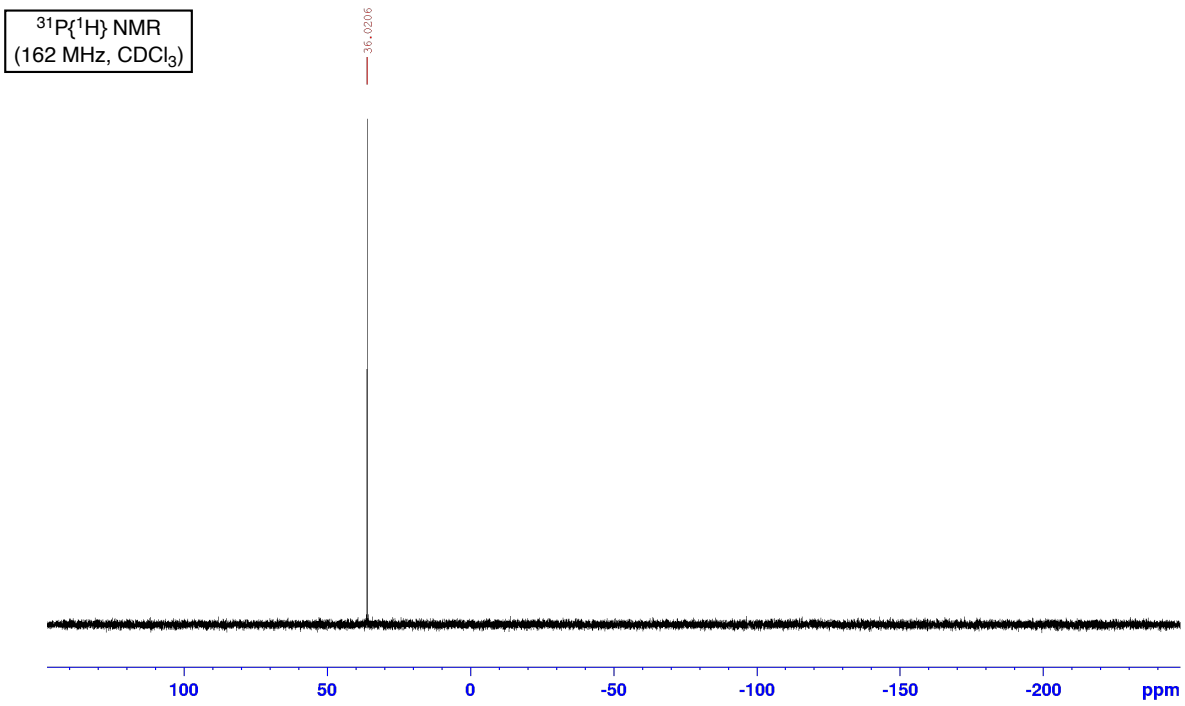


$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)

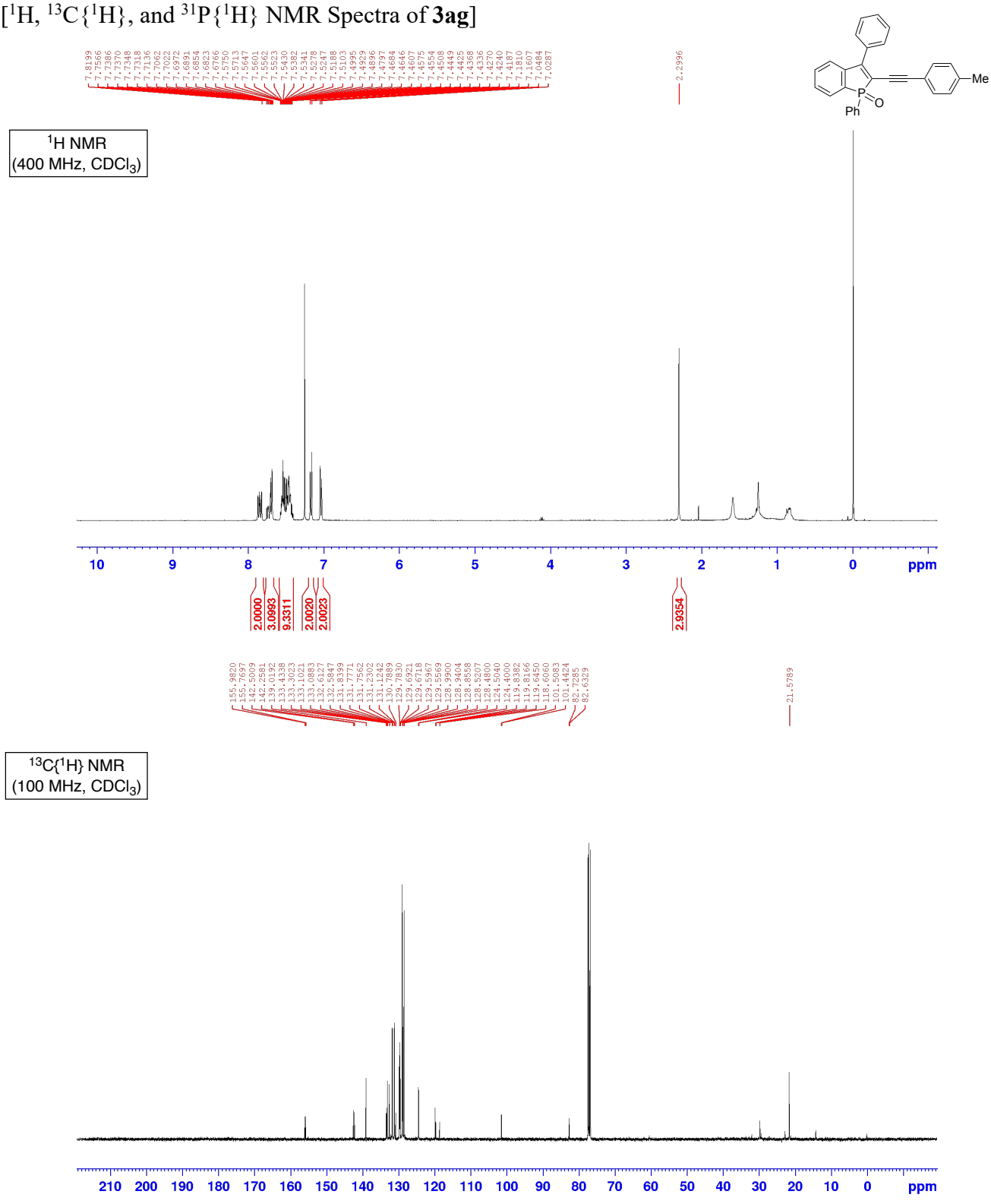


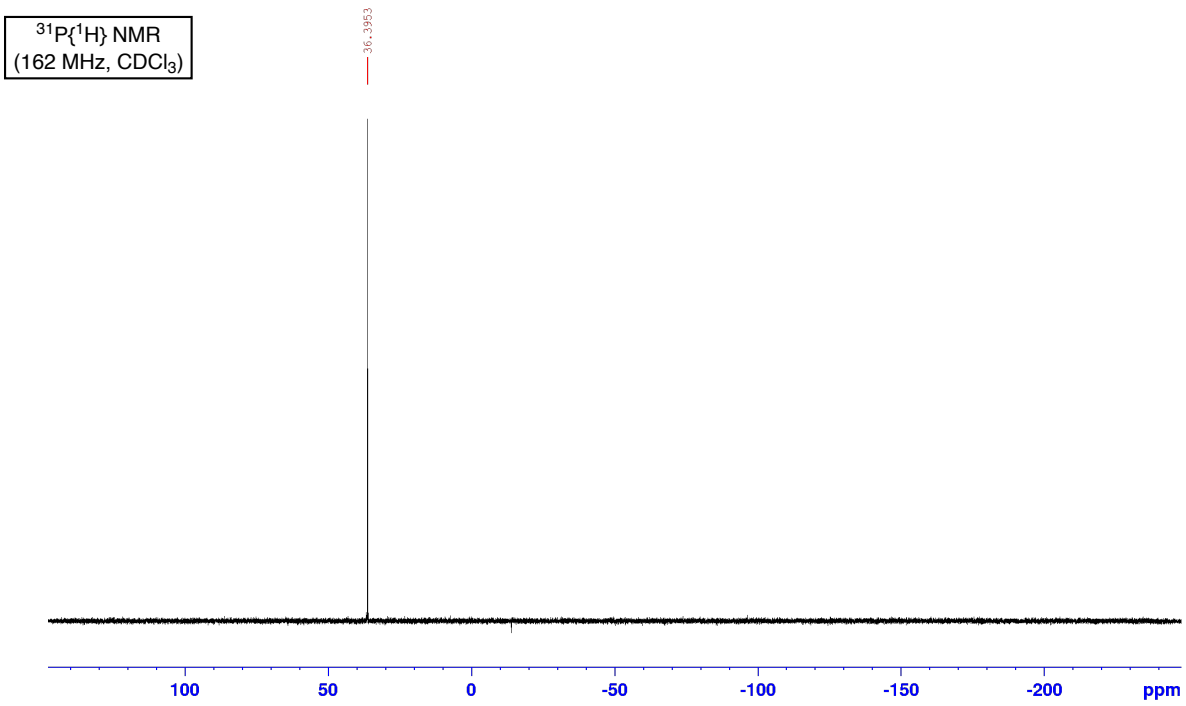
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ae**]



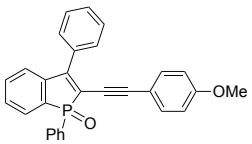

$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)
36.0206
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ag**]

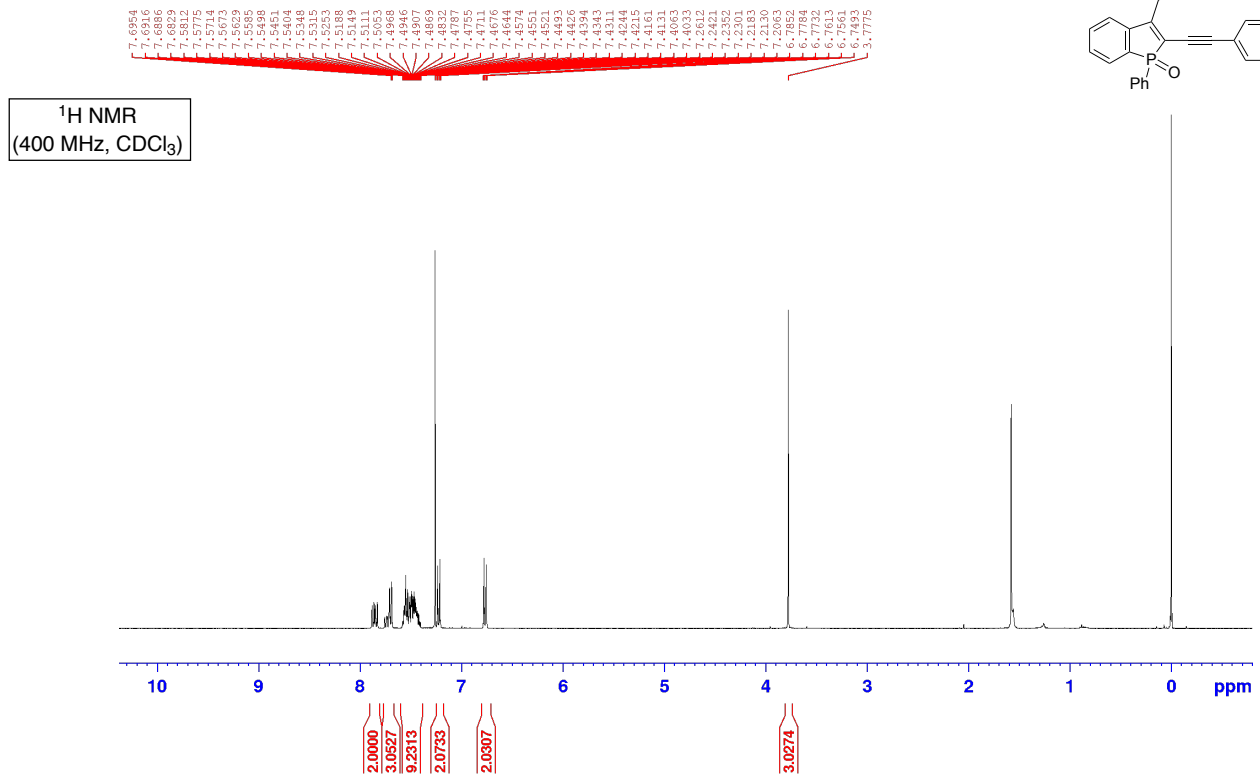



$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)
36.3953
100
50
0
-50
-100
-150
-200
ppm

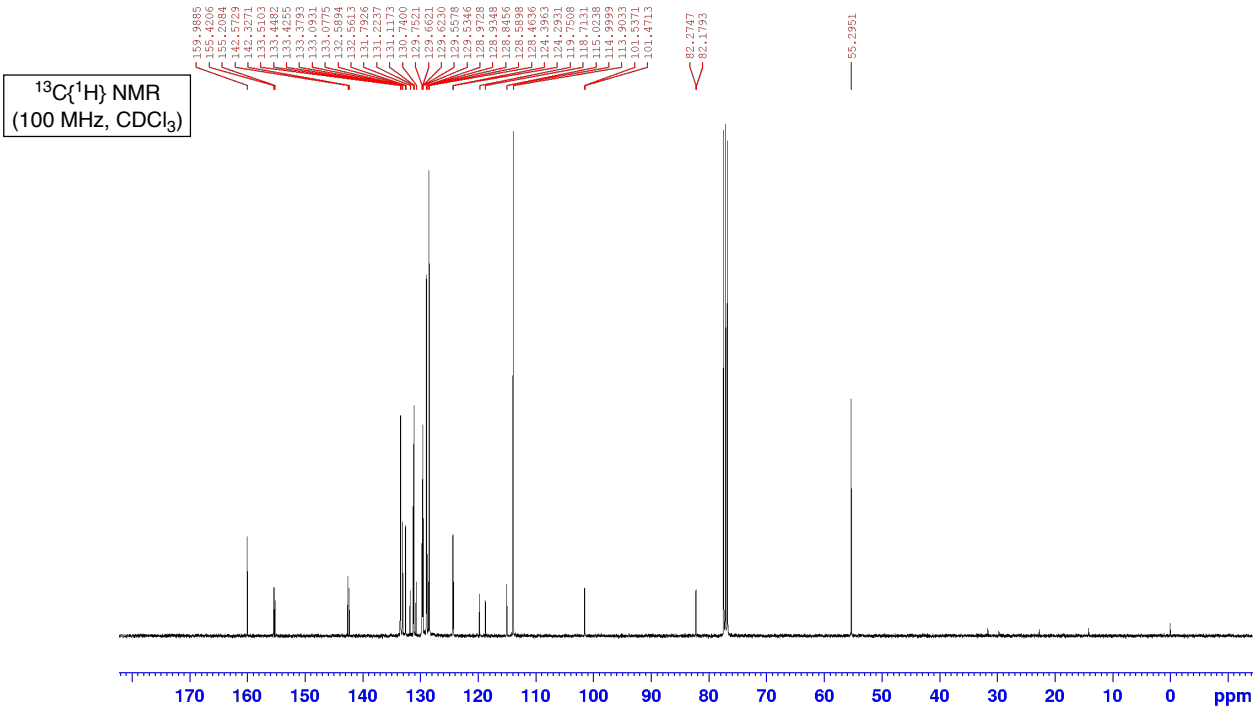
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **3ah**]

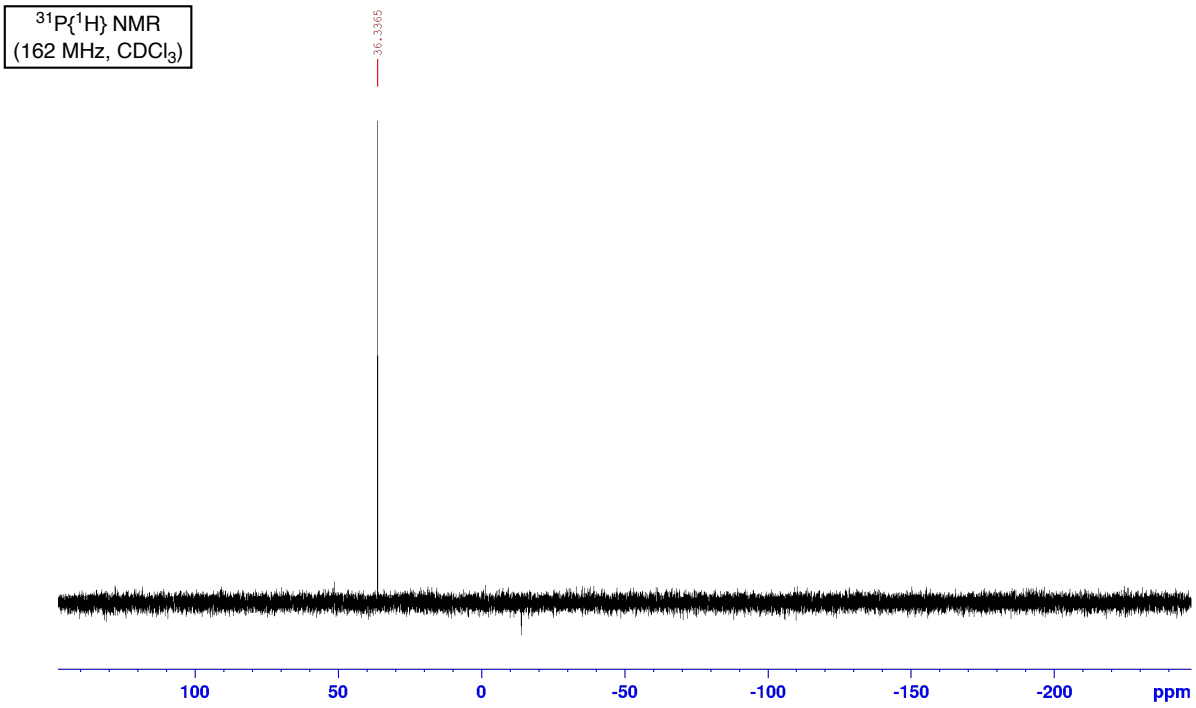


^{1}H NMR
(400 MHz, $CDCl_3$)

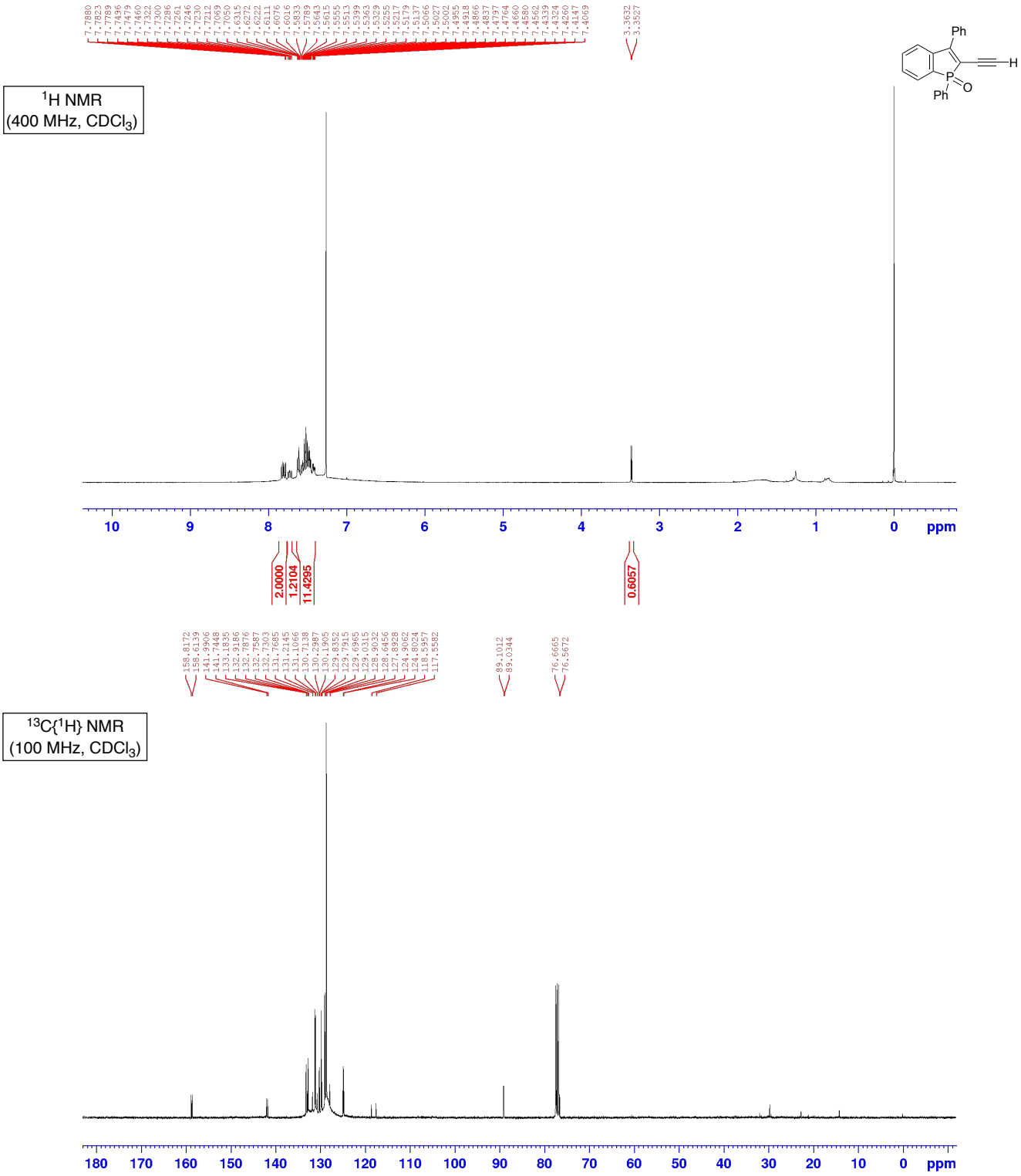


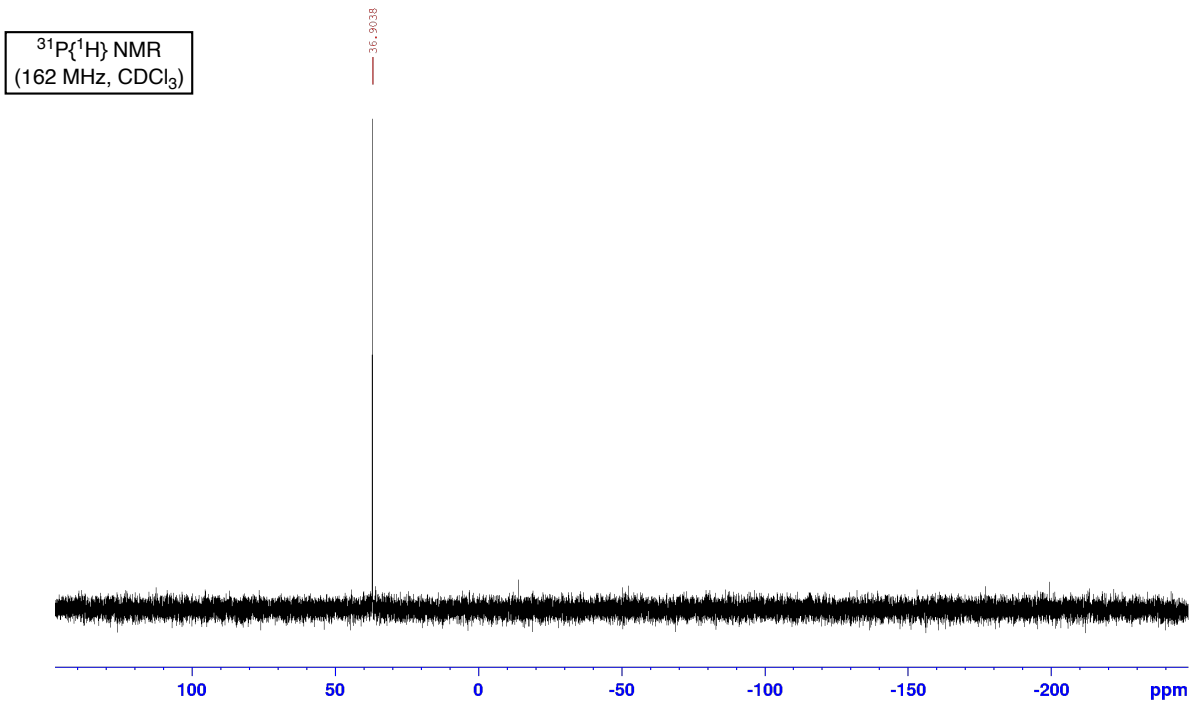
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



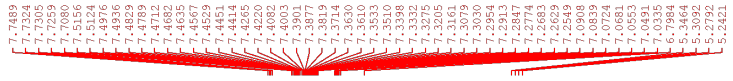

$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)
36.3365
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **4**]

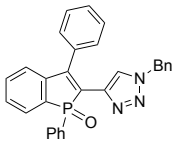


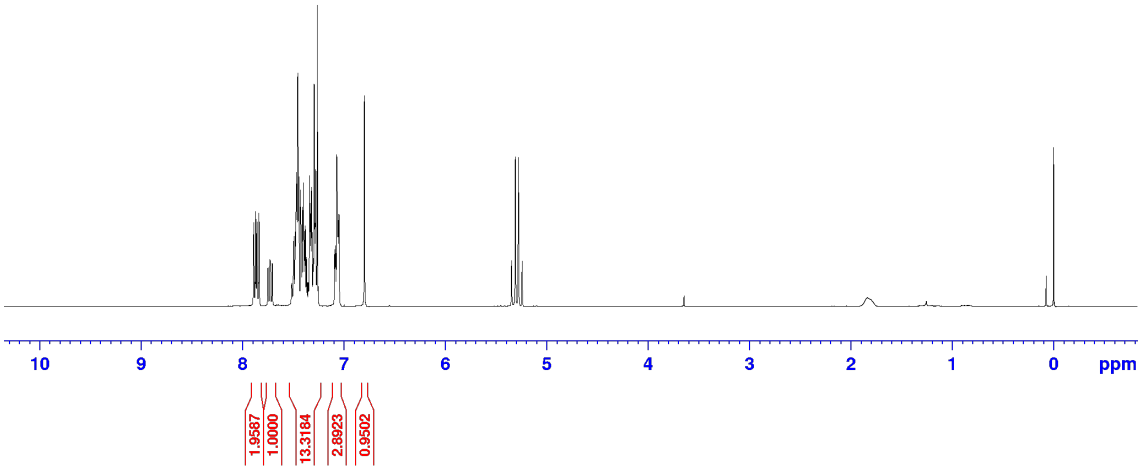

$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)
36.9038
100
50
0
-50
-100
-150
-200
ppm

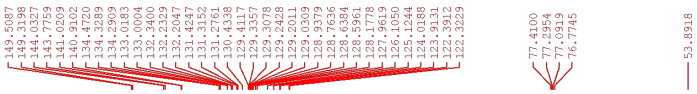
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **5**]



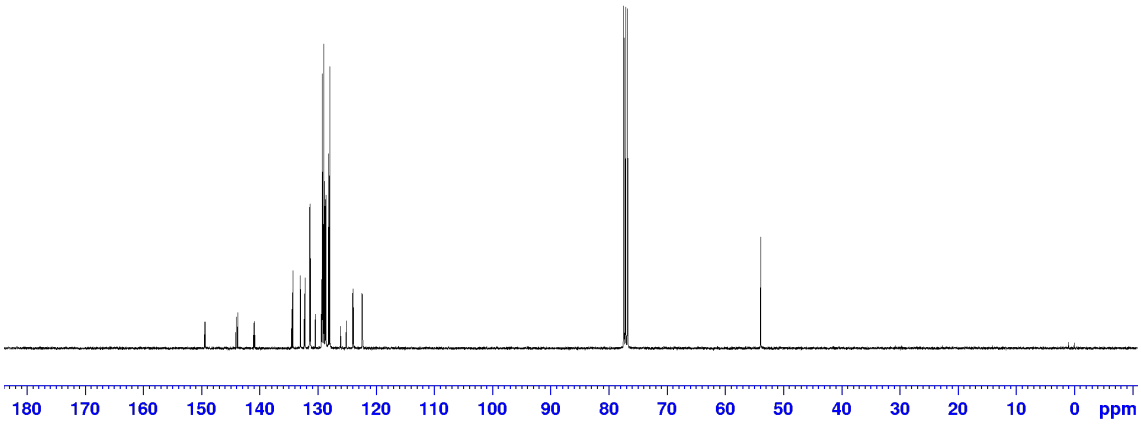
^{1}H NMR
(400 MHz, $CDCl_3$)

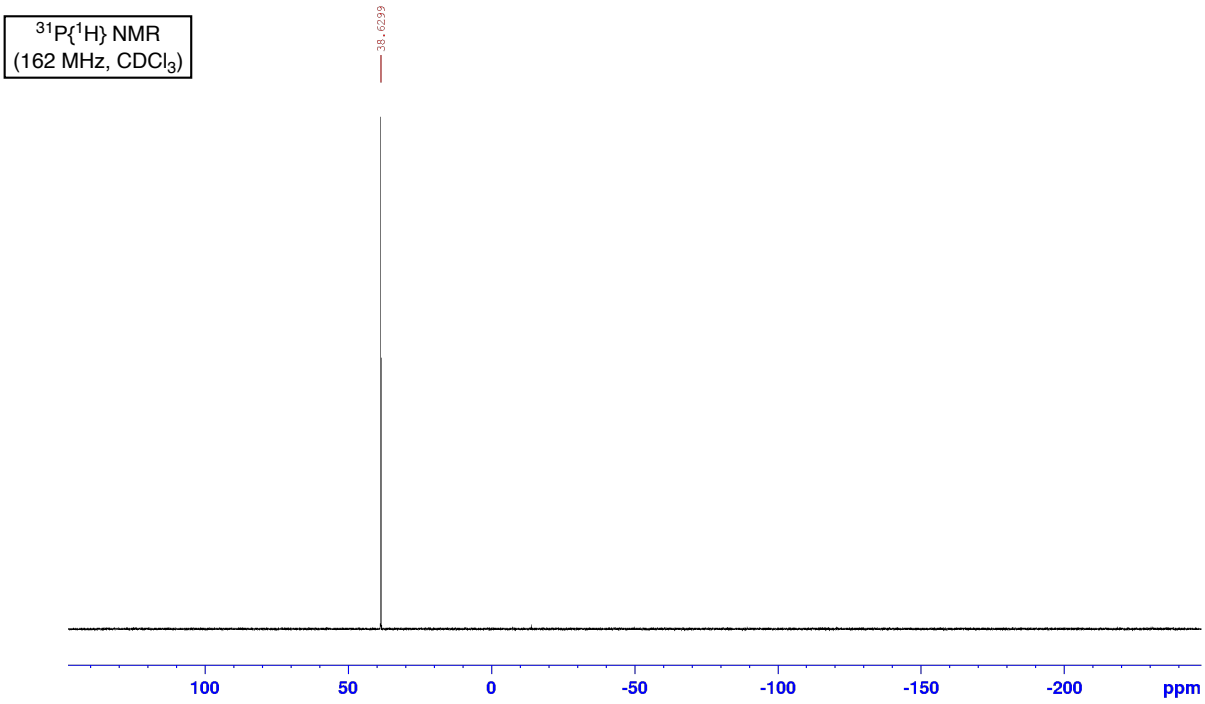




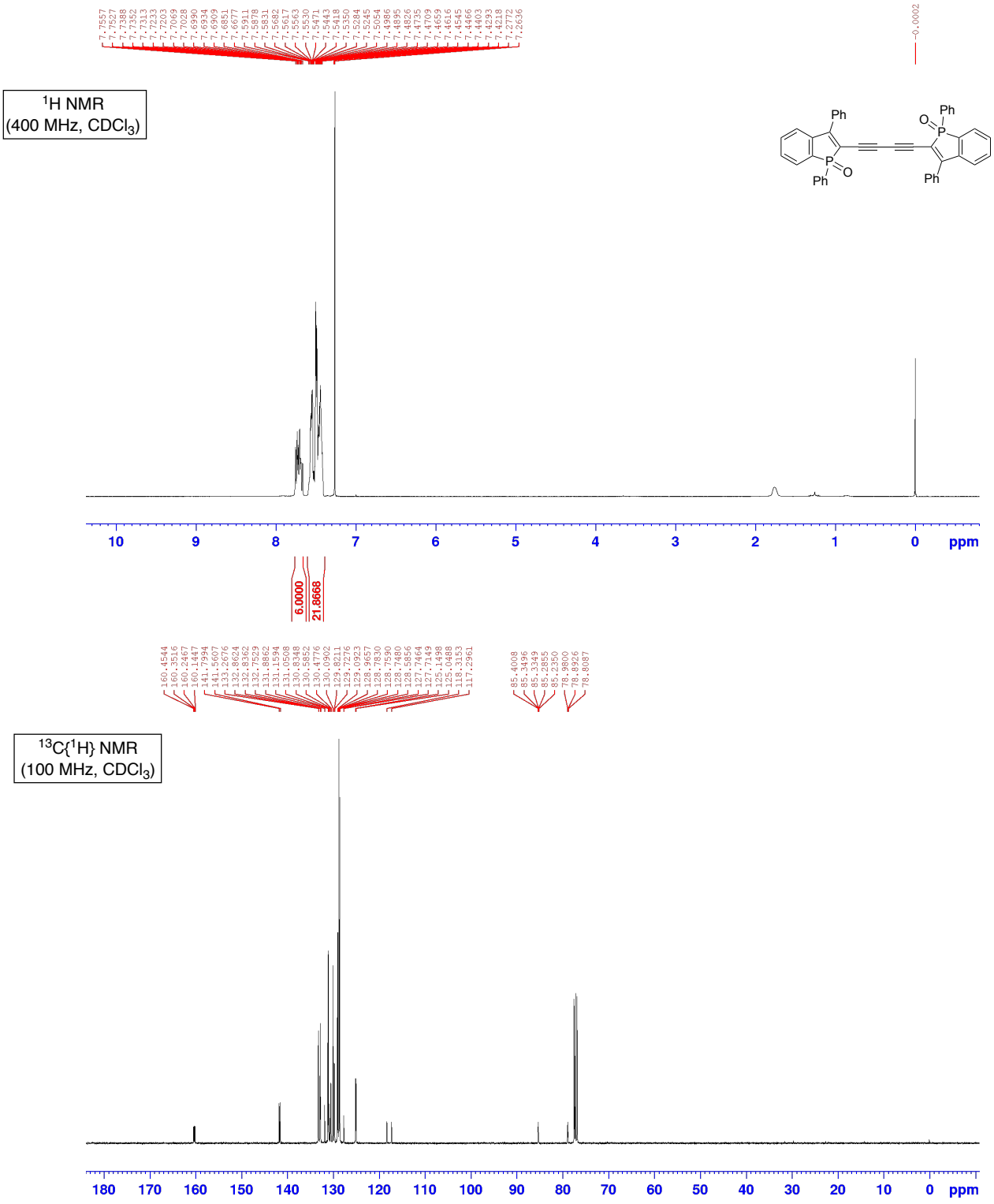


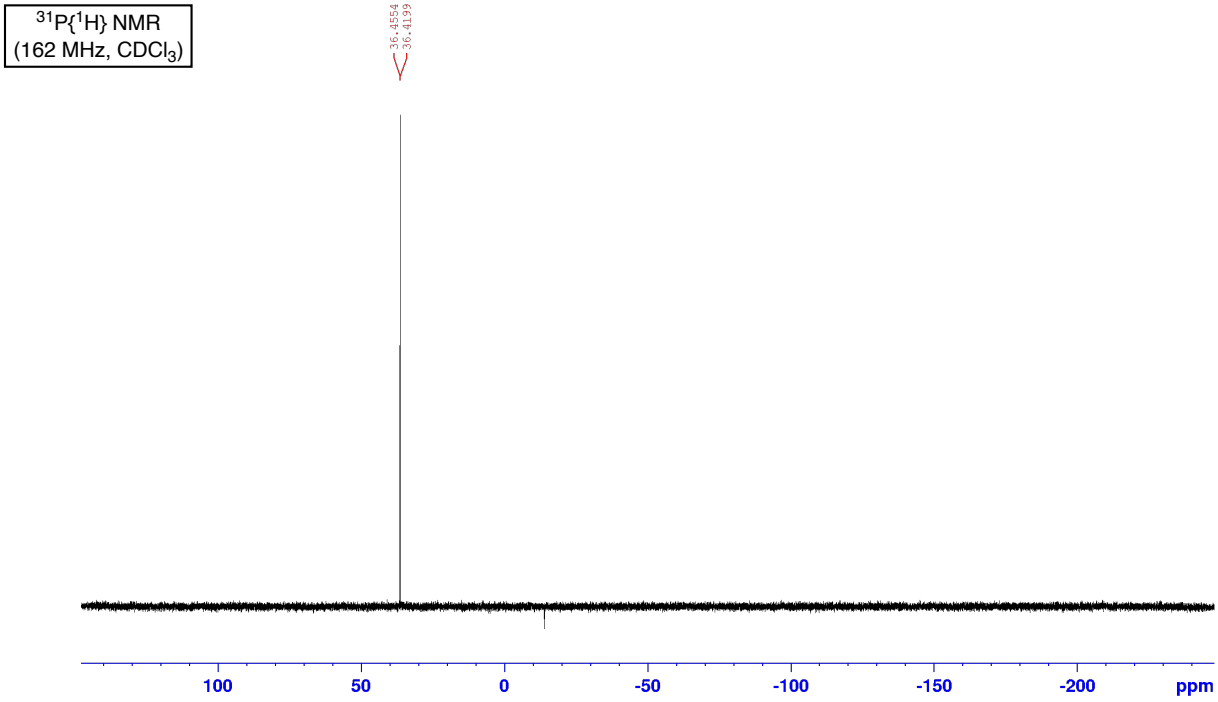
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



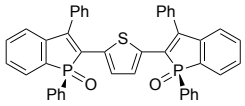

31P{1H} NMR
(162 MHz, CDCl3)
38.6299
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **6**]

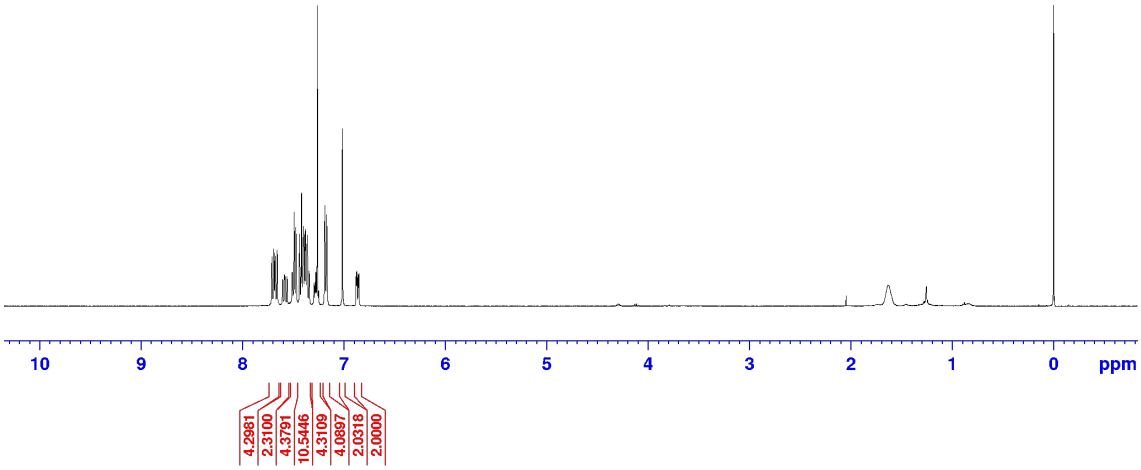



$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)
36.4554
36.4199
100
50
0
-50
-100
-150
-200
ppm

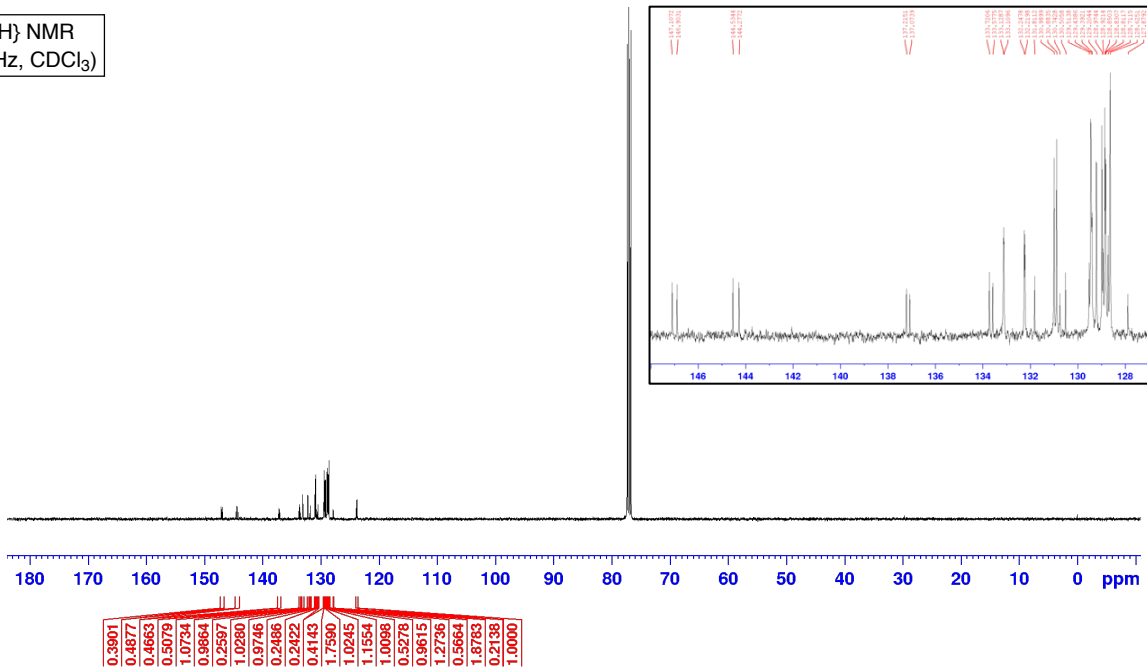
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of *syn*-**7**]



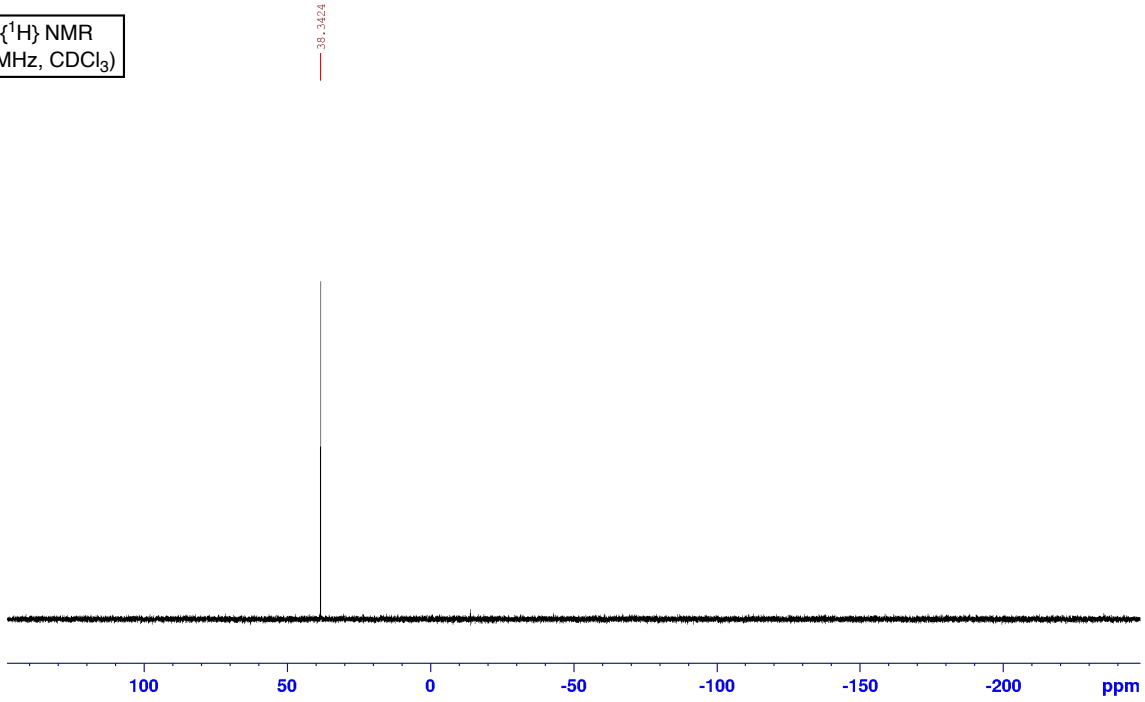
^{1}H NMR
(400 MHz, $CDCl_3$)



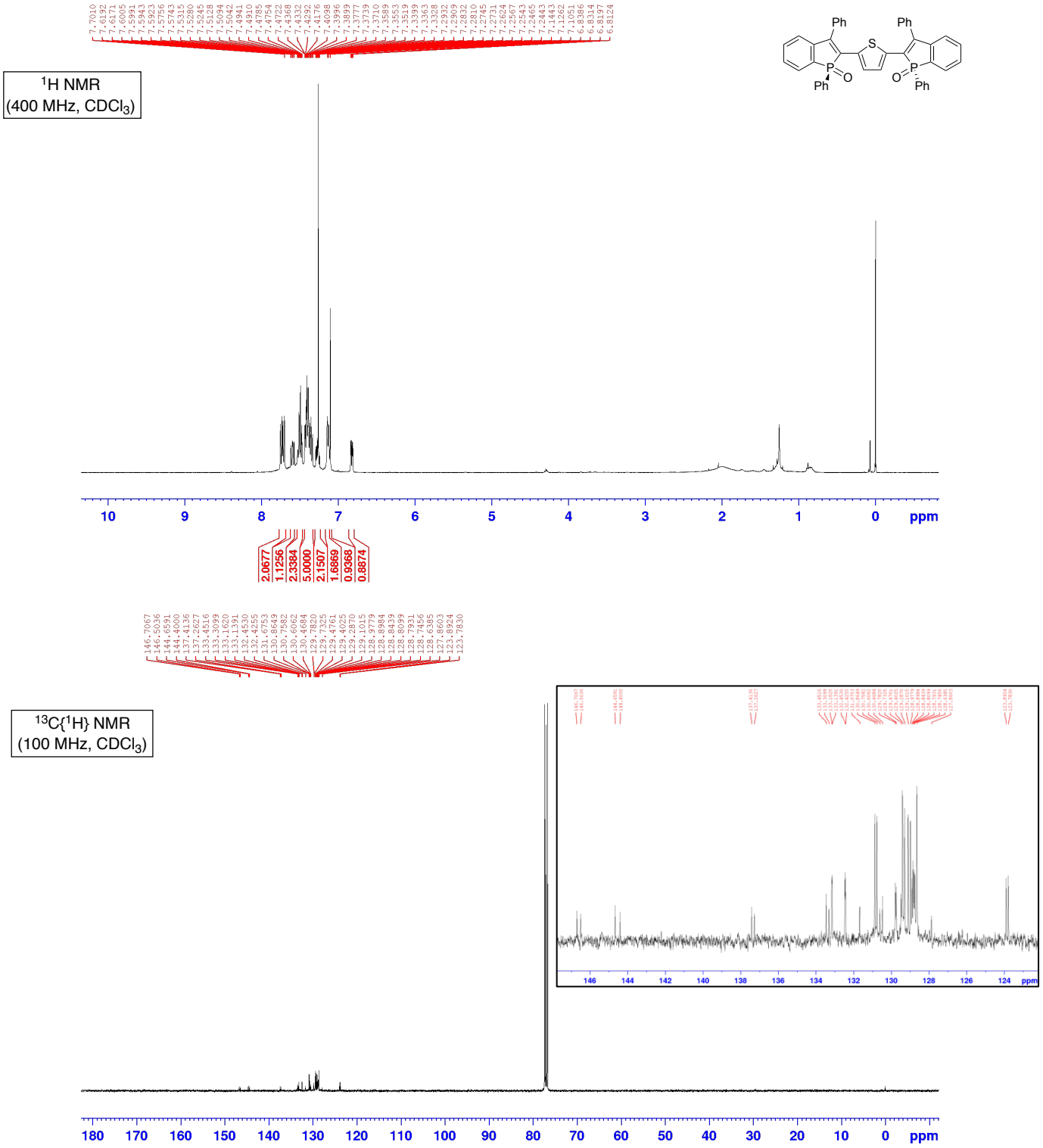
^{13}C{^{1}H} NMR
(100 MHz, $CDCl_3$)



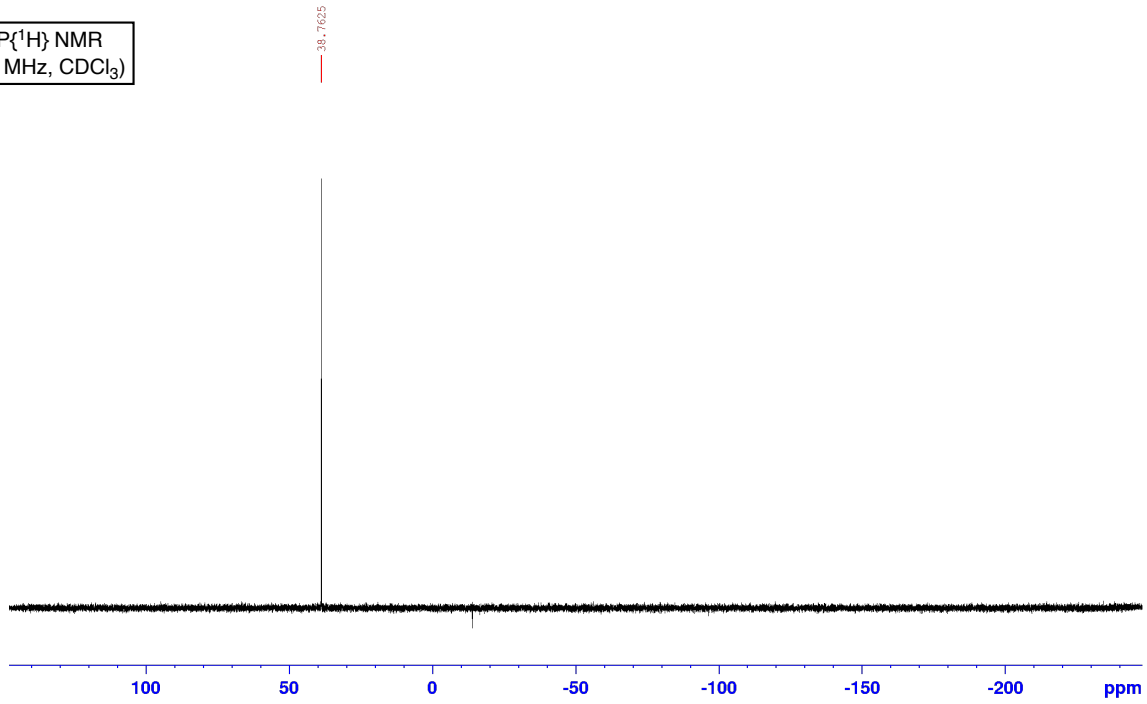
$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



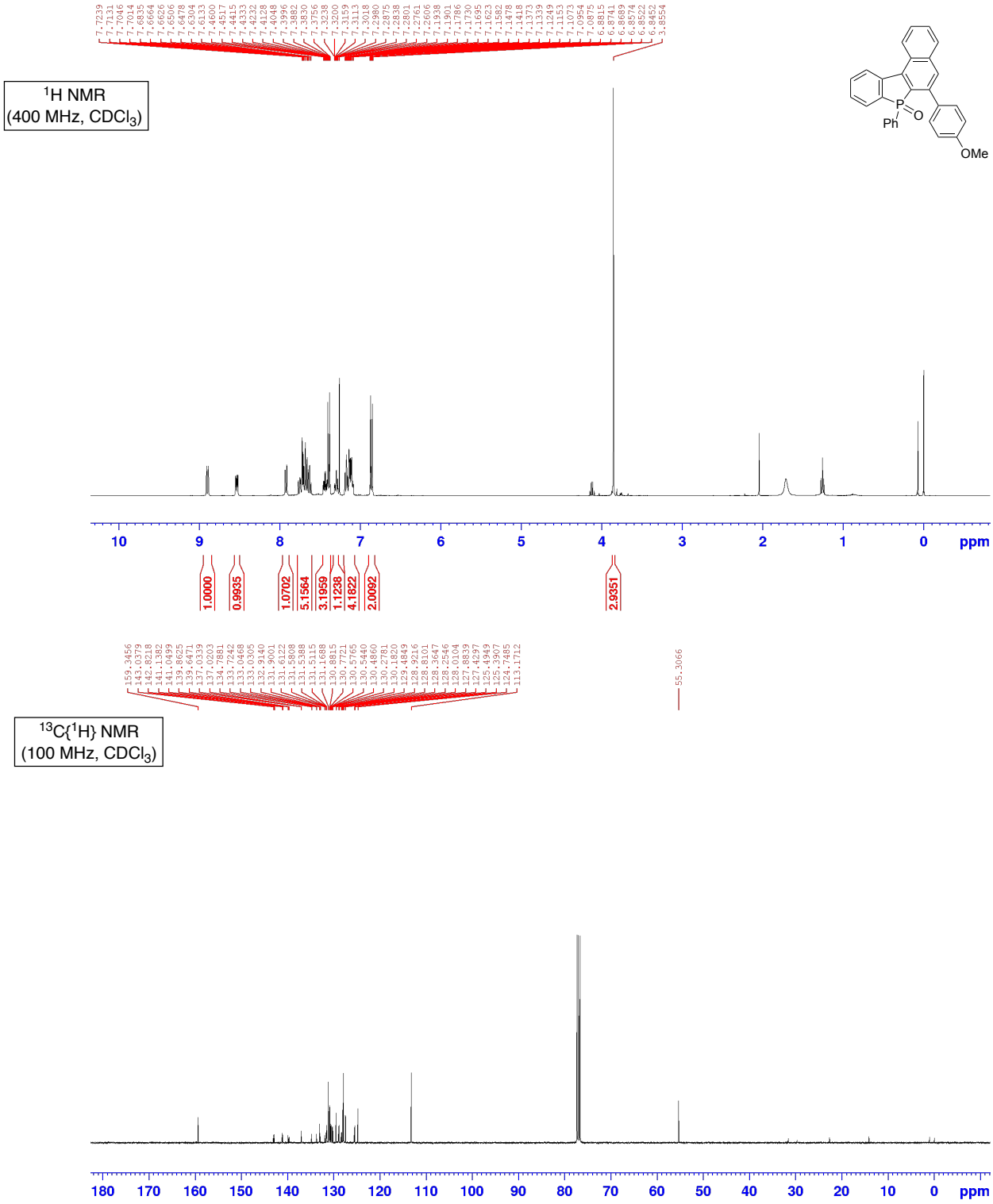
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of *anti*-**7**]

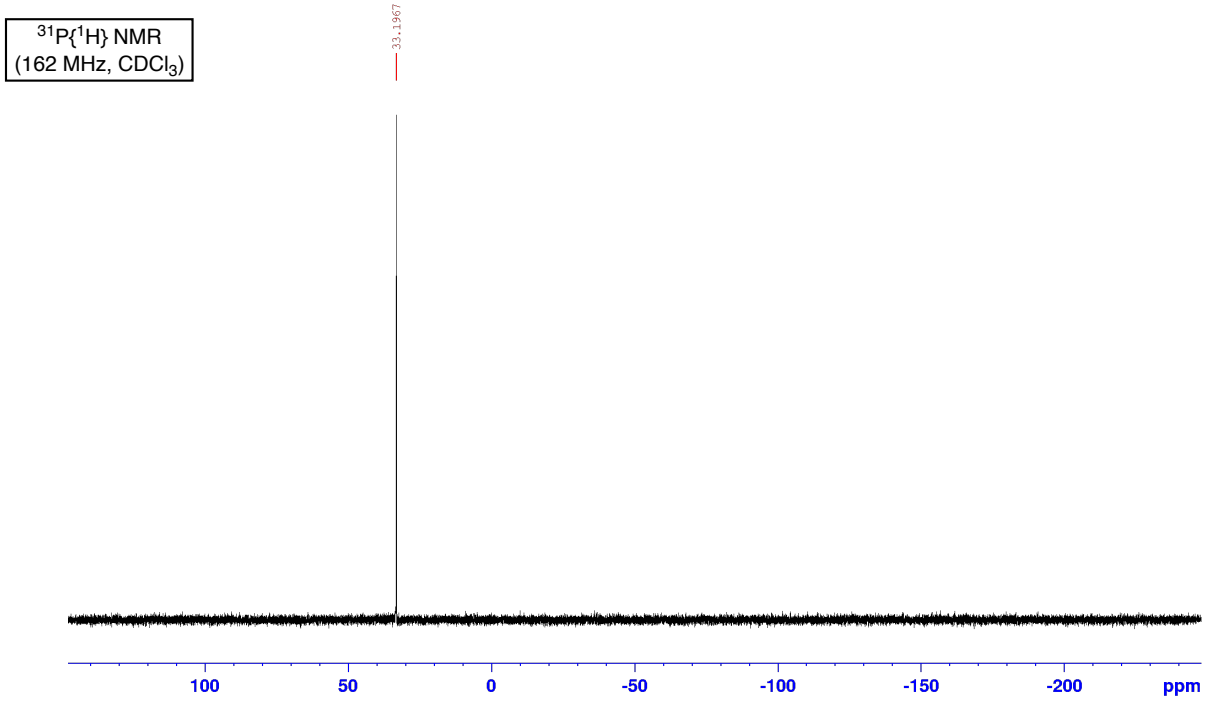


$^{31}P\{^{1}H\}$ NMR
(162 MHz, $CDCl_3$)



[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **8**]




31P{1H} NMR
(162 MHz, CDCl3)
33.1967
100
50
0
-50
-100
-150
-200
ppm

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(S3) H. K. Klein, B. Zettel, U. Flöker and H.-J. Haupt, *Chem. Ber.,* 1992, **125**, 9.

(S4) U. Dutta, G. Prakash, K. Devi, K. Borah, X. Zhang and D. Maiti, *Chem. Sci.,* 2023, **14**, 11381.