Supporting Information

PN-Doped tetraphenylnaphthalene: a straightforward synthetic strategy analogous BN-annulation

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1. General Information and Procedures

A. General. All chemicals were purchased from Combi-Blocks, TCI, Daejung Chemicals, or Samchun Chemical. All chemicals and solvents were used without further purification, unless otherwise noted. Solvents such as acetonitrile, dichloromethane, 1,2,4-trichlorobenzene (TCB), triethylamine, and toluene were dried with 3 Å molecular sieves. The glassware was oven dried at 150°C overnight. All reactions were performed under dry argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on silica gel coated glass sheets with F254 indicator. Flash chromatography was performed using Isolera Spektra System (Biotage) according to the manufacturer's recommended protocols. All yields given refer to isolated yields. Chemical names were provided using ChemDraw Professional 20.0.

B. Product Characterization Procedures. The intermediates and products were all routinely characterized via ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy with a combination of ^{31}P NMR spectroscopy, as well as mass spectrometry. The ^{1}H, ^{13}C, and ^{31}P spectra were recorded on a Bruker AVANCE III HD (400 MHz) spectrophotometer. The chemical shifts for the NMR data were referenced as follows: 1) for samples in $CDCl_3$, the ^{1}H NMR was referenced to tetramethylsilane (TMS) at 0.00 ppm, and the ^{13}C NMR was referenced to the solvent peak at 77.16 ppm; 2) the ^{31}P NMR was externally referenced to triphenyl phosphate at -17.57 ppm. Data were reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, t = triplet, m = multiplet), coupling constants *J* (Hz), and integration values. Accurate mass measurements were obtained via electrospray ionization (ESI) high resolution mass spectrometry (HRMS) at UNIST Central Research Facilities on a JEOL AccuTOF4G+DART time-of-flight (TOF) instrument. UV-Vis spectra were recorded on a Jasco V-760 spectrophotometer with a quartz cuvette (path length, 1 cm). Spectroscopic grade dichloromethane was used to measure the absorption spectroscopy. FTIR spectra were recorded on a Varian 670-IR spectrometer using potassium bromide pellets.

2. Detailed Experimental Protocols

The compound **2** was prepared by modifying previously reported methods.[1]

Standard procedure for Table 1

4-Chloro-2,3-diphenyl-1*H*-benzo[*e*][1,2]azaphosphinine 2-oxide (1).

To a 100 mL Schlenk flask were added 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), 1,2,4-trichlorobenzene (8.0 mL), and DBU (0.07 mL, 0.5 mmol) under argon atmosphere, sequentially. Then, phenylphosphonic dichloride (0.21 mL, 1.5 mmol) was added dropwise to the Schlenk flask. The reaction mixture was stirred at 220 ℃ for 24 h. After cooled to room temperature, the reaction mixture was quenched with a saturated aqueous sodium bicarbonate solution (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and removed *in vacuo* to afford the crude product. The residue was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.2541 g, 72% yield). ^{1}H NMR (ppm, 400 MHz, 298 K, $CDCl_3$) δ 8.32 (s, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.46–7.41 (m, 2H), 7.36–7.28 (m, 2H), 7.22–7.04 (m, 9H); ^{13}C NMR (ppm, 101 MHz, 298 K, $CDCl_3$) δ 141.4 (d, J = 14.7 Hz), 139.2 (d, J = 3.2 Hz), 134.3 (d, J = 7.3 Hz), 132.8 (d, J = 10.5 Hz), 132.3, 132.2 (d, J = 3.0 Hz), 131.3, 130.9, 130.1 (d, J = 4.4 Hz), 128.3, 128.2, 128.1 (d, J = 11.9 Hz), 127.3, 126.2 , 121.0, 118.1 (d, J = 8.7 Hz); ^{31}P NMR (ppm, 162 MHz, 298 K, $CDCl_3$) δ 12.22; HRMS *m/z* calcd for $C_{20}H_{15}ClNNaOP$ $[M + Na]^+$ 374.0472, found 374.0469 (Δ = 0.8 ppm).

Entry 1. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), and 1,2,4-trichlorobenzene (8.0 mL). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.1910 g, 54% yield).

Entry 2. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and triethylamine (0.07 mL, 0.5 mmol). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.2281 g, 65% yield).

Entry 3. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and triethylamine (0.14 mL, 1.0 mmol). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.2213 g, 63% yield).

Entry 4. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and triethylamine (0.21 mL, 1.5 mmol). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.2042 g, 58% yield).

Entry 5. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and triethylamine (0.28 mL, 2.0 mmol). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.2079 g, 59% yield).

Entry 6. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and diisopropylamine (0.07 mL, 0.5 mmol). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.2120 g, 60% yield).

Entry 7. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and 2,2,6,6-tetramethylpiperidine (0.09 mL, 0.5 mmol). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.1901 g, 54% yield).

Entry 8. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and 1,8-bis(dimethylamino)naphthalene (0.11 g, 0.5 mmol).

The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.2144 g, 61% yield).

Entry 9. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and pyridine (0.04 mL, 0.5 mmol). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.1522 g, 43% yield).

Entry 10. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and 2,6-lutidine (0.06 mL, 0.5 mmol). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.1582 g, 45% yield).

Entry 11. The product was prepared according to the standard procedure as above from 2-(phenylethynyl)aniline (0.19 g, 1.0 mmol), phenylphosphonic dichloride (0.21 mL, 1.5 mmol), 1,2,4-trichlorobenzene (8.0 mL), and 4-dimethylaminopyridine (0.06 g, 0.5 mmol). The crude product was purified by flash column chromatography (eluent: 100/0 to 20/80 hexanes/ethyl acetate) over silica gel to give **1** as a white solid (0.1839 g, 52% yield).

***N*-Phenyl-2-(phenylethynyl)aniline (2).**

To a mixture of 2-(phenylethynyl)aniline (1.93 g, 10.0 mmol), phenylboronic acid (1.83 g, 15.0 mmol), $Cu(OAc)_2 \bullet H_2O$ (2.20 g, 11.0 mmol), and molecular sieves (3 Å, 15.0 g) in dichloromethane (80 mL) was added triethylamine (2.79 mL, 20.0 mmol) under air. Then, the reaction mixture was stirred at room temperature for 24 h. After finishing the reaction, the reaction mixture was filtered through a pad of Celite with ethyl acetate (25 mL) and concentrated. The residue was diluted with ethyl acetate (50 mL), and sequentially washed with aqueous sodium bicarbonate solution (50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (eluent: 100/0 to 90/10 hexanes/dichloromethane) over silica gel to give **2** as a yellow oil (1.6 g, 61% yield).

4-Chloro-1,2,3-triphenyl-1*H*-benzo[*e*][1,2]azaphosphinine 2-oxide (3).

To a mixture of **1** (0.35 g, 1.0 mmol), phenylboronic acid (1.45 g, 6.00 mmol), $Cu(OAc)_2•H_2O$ (0.60 g, 3.0 mmol) and molecular sieves (3 Å, 2.0 g) in MeCN (20 mL) was added triethylamine (2.80 mL, 20.0 mmol) in air. Then, the reaction mixture was stirred at 80 °C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with ethyl acetate (25 mL), and the filtrate was concentrated *in vacuo*. The residue was diluted with ethyl acetate (50 mL), and sequentially washed with aqueous sodium bicarbonate solution (50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (eluent: 100/0 to 75/25 hexanes/ethyl acetate) over silica gel to give **3** as a white solid (0.18 g, 42% yield). ^{1}H NMR (ppm, 400 MHz, 298 K, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.52 (dd, *J* = 13.3, 7.5 Hz, 2H), 7.34–7.11 (m, 15H), 6.60 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (ppm, 101 MHz, 298 K, $CDCl_3$) δ 142.4 (d, *J* = 1.2 Hz), 140.9 (d, *J* = 13.6 Hz), 138.3 (d, *J* = 1.6 Hz), 134.8 (d, *J* = 7.8 Hz), 133.1 (d, *J* = 10.0 Hz), 131.9 (d, *J* = 3.0 Hz), 131.1, 130.6, 130.26 (d, *J* = 4.9 Hz), 129.8, 128.7 (d, *J* = 1.0 Hz), 128.10 (d, *J* = 1.2 Hz), 128.06, 128.0 (d, *J* = 1.8 Hz), 127.97 (d, *J* = 230.3 Hz), 127.96, 127.8 (d, *J* = 14.0 Hz), 121.4, 119.7 (d, *J* = 7.6 Hz), 117.7 (d, *J* = 4.5 Hz); ^{31}P NMR (ppm, 162 MHz, 298 K, $CDCl_3$) δ 12.82; HRMS *m/z* calcd for $C_{26}H_{19}ClNNaOP$ $[M + Na]^+$ 450.0785, found 450.0782 (Δ = 0.7 ppm).

3-(Chloro(phenyl)methylene)-1,2-diphenyl-1,3-dihydrobenzo[*d*][1,2]azaphosphole 2-oxide (4).

To a 100 mL Schlenk flask were added **2** (0.269 g, 1.0 mmol) and DBU (0.074 mL, 0.5 mmol) in 1,2,4-trichlorobenzene (8.0 mL) under argon atmosphere. Subsequently, phenylphosphonic dichloride (0.21 mL, 1.5 mmol) was added dropwise to the flask. The reaction mixture was heated at 220 ℃ for 12 h. After cooled down to room temperature, the reaction mixture was quenched with a saturated aqueous sodium bicarbonate solution (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered. After the filtrate was concentrated *in vacuo*, the residue was purified by flash column chromatography (eluent: 100/0 to 75/25 hexanes/ethyl acetate) over silica gel to give **4** as a white solid (0.1541 g, 36% yield). ^{1}H NMR (ppm, 400 MHz, 298 K, $CDCl_3$) δ 7.84 (ddd, *J* = 15.3, 8.3, 1.2 Hz, 2H), 7.60 (dt, *J* = 8.2, 1.3 Hz, 1H), 7.49–7.40 (m, 6H), 7.37–7.30 (m, 4H), 7.27–7.22 (m, 5H), 7.13–7.09 (m, 1H); ^{13}C NMR (ppm, 101 MHz, 298 K, $CDCl_3$) δ 142.5 (d, *J* = 3.2 Hz), 142.2 (d, *J* = 3.8 Hz), 133.8, 133.0 (d, *J* = 3.4 Hz), 132.2 (d, *J* = 11.1 Hz), 132.1, 131.7, 131.1 (d, *J* = 3.1 Hz), 130.4, 129.4, 129.1, 128.6, 128.4 (d, *J* = 72.7 Hz),

128.2, 126.1 (d, J = 4.4 Hz), 125.9, 125.3 (d, J = 4.5 Hz), 123.0, 94.6, 87.1; ^{31}P NMR (ppm, 162 MHz, 298 K, $CDCl_3$) δ 30.75; HRMS *m/z* calcd for $C_{26}H_{19}ClNNaOP$ $[M + Na]^+$ 450.0785, found 450.0785 (Δ = 0 ppm).

3-(Diphenylmethylene)-1,2-diphenyl-1,3-dihydrobenzo[*d*][1,2]azaphosphole 2-oxide (5). Compound **4** (0.051 g, 0.12 mmol), phenylboronic acid (0.029 g, 0.24 mmol), $Pd(PPh_3)_4$ (7 mg, 0.006 mmol) and K_3PO_4 (0.051 g, 0.24 mmol) were added to degassed toluene (6.0 mL) and water (1.0 mL) under argon atmosphere. Then, the reaction mixture was heated to reflux for 24 h. After cooled down to room temperature, the reaction mixture was filtered through a pad of Celite and washed with ethyl acetate (25 mL), and the filtrate was concentrated *in vacuo*. The residue was diluted with ethyl acetate (25 mL), and sequentially washed with water (25 mL) and brine (25 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (eluent: 100/0 to 50/50 hexanes/ethyl acetate) over silica gel to give **5** as a yellow solid (0.020 g, 36% yield). ^{1}H NMR (ppm, 400 MHz, 298 K, $CDCl_3$) δ 7.48–7.32 (m, 8H), 7.27 (t, J = 8.0 Hz, 2H), 7.20–7.01 (m, 11H), 6.66–6.63 (m, 2H), 6.58 (t, J = 7.6 Hz, 1H); ^{13}C NMR (ppm, 101 MHz, 298 K, $CDCl_3$) δ 154.3 (d, J = 12.5 Hz), 147.7 (d, J = 15.3 Hz), 141.3 (d, J = 16.6 Hz), 140.7 (d, J = 8.2 Hz), 137.2 (d, J = 2.3 Hz), 132.3 (d, J = 10.7 Hz), 131.4 (d, J = 3.0 Hz), 130.8 (d, J = 1.5 Hz), 130.6 (d, J = 87.9 Hz), 129.67 (d, J = 49.5 Hz), 129.65, 129.4 (d, J = 103.0 Hz), 129.3, 128.8 (d, J = 2.2 Hz), 128.6 (d, J = 11.1 Hz), 127.8 (d, J = 3.3 Hz), 127.6, 127.5, 127.4, 126.8, 126.0 (d, J = 9.6 Hz), 123.8 (d, J = 17.1 Hz), 120.0, 110.9 (d, J = 5.2 Hz); ^{31}P NMR (ppm, 162 MHz, 298 K, $CDCl_3$) δ 32.38; HRMS *m/z* calcd for $C_{32}H_{24}NNaOP$ $[M + Na]^+$ 492.1488, found 492.1487 (Δ = 0.2 ppm).

1,2,3,4-Tetraphenyl-1*H*-benzo[*e*][1,2]azaphosphinine 2-oxide (6). Compound **3** (0.50 g, 1.2 mmol), phenylboronic acid (0.28 g, 2.3 mmol), $Pd(PPh_3)_4$ (0.07 g, 0.06 mmol), and K_3PO_4 (0.50 g, 2.3 mmol) were added to degassed toluene (25 mL) and water (0.5 mL) under argon atmosphere. Then, the reaction mixture was heated to reflux for 24 h. After cooled down to room temperature, the reaction mixture was filtered through a pad of Celite and washed with ethyl acetate (50 mL), and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluent: 100/0 to 50/50 hexanes/ethyl acetate) over silica gel to give **6** as a white solid (0.42 g, 75% yield). ^{1}H NMR (ppm, 400 MHz, 298 K, $CDCl_3$) δ 7.56 (ddd, J = 12.9, 8.1, 1.3 Hz, 2H), 7.37–7.34 (m, 3H), 7.29–7.04 (m, 14H), 6.92–6.84 (m, 4H), 6.63 (d, J = 8.4 Hz, 1H); ^{13}C NMR (ppm, 101 MHz,

298 K, $CDCl_3$) δ 149.4 (d, *J* = 4.2 Hz), 142.6, 139.1 (d, *J* = 1.0 Hz), 138.3 (d, *J* = 13.2 Hz), 135.9 (d, *J* = 10.9 Hz), 133.1 (d, *J* = 9.7 Hz), 131.3 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 5.5 Hz), 130.7, 130.64, 130.55 (d, *J* = 1.8 Hz), 130.5 (d, *J* = 140.2 Hz), 130.0, 129.6, 128.4, 128.0, 127.7, 127.6, 127.5 (d, *J* = 2.2 Hz), 126.8, 126.6 (d, *J* = 1.8 Hz), 122.8 (d, *J* = 10.3 Hz), 120.6, 117.7 (d, *J* = 4.1 Hz); ^{31}P NMR (ppm, 162 MHz, 298 K, $CDCl_3$) δ 12.06; HRMS *m/z* calcd for $C_{32}H_{25}NOP$ $[M + H]^+$ 470.1668, found 470.1672 (Δ = 0.9 ppm).

1,2,3,4-Tetraphenyl-1*H*-benzo[*e*][1,2]azaphosphinine 2-sulfide (7).

To a solution of compound **6** (0.94 g, 2.0 mmol) in toluene (45 mL) was added Lawesson's reagent (1.62 g, 4.00 mmol) under argon atmosphere. Then, the reaction mixture was heated at 90 °C for 24 h. After the reaction mixture was cooled down to room temperature, the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (eluent: 100/0 to 90/10 hexanes/ethyl acetate) over silica gel to give **7** as a white solid (0.82 g, 85% yield). ^{1}H NMR (ppm, 400 MHz, 298 K, $CDCl_3$) δ 7.87 (dd, *J* = 14.3, 7.4 Hz, 2H), 7.29–7.04 (m, 17H), 6.89–6.85 (m, 4H), 6.54 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (ppm, 101 MHz, 298 K, $CDCl_3$) δ 147.3 (d, *J* = 3.8 Hz), 142.4, 139.6 (d, *J* = 1.6 Hz), 138.4 (d, *J* = 13.2 Hz), 135.6 (d, *J* = 12.0 Hz), 133.4 (d, *J* = 11.3 Hz), 131.7, 131.6 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 5.4 Hz), 130.7 (d, *J* = 39.4 Hz), 130.62 (d, *J* = 1.8 Hz), 130.58, 130.1, 129.4, 127.9 (d, *J* = 54.5 Hz), 127.7, 127.6, 127.5 (d, *J* = 6.3 Hz), 127.3, 127.2 (d, *J* = 1.1 Hz), 126.8 (d, *J* = 2.2 Hz), 124.1 (d, *J* = 10.2 Hz), 120.9, 118.7 (d, *J* = 3.7 Hz); ^{31}P NMR (ppm, 162 MHz, 298 K, $CDCl_3$) δ 52.04; HRMS *m/z* calcd for $C_{32}H_{24}NNaPS$ $[M + Na]^+$ 508.1259, found 508.1261 (Δ = 0.4 ppm).

1,2,3,4-Tetraphenyl-1,2-dihydrobenzo[*e*][1,2]azaphosphinine (PN-TPN).

To a 100 mL Schlenk flask were added **7** (0.801 g, 1.65 mmol) in anhydrous dichloromethane (50 mL) under argon atmosphere and the reaction mixture was subjected to degas and backfill with argon for three times. Subsequently, MeOTf (0.36 mL, 3.3 mmol) was added to the flask under argon atmosphere. Then, the reaction mixture was heated at 40 °C for 16 h. After the reaction mixture was cooled down to room temperature, $P(NMe_2)_3$ (0.60 mL, 3.3 mmol) was added via syringe. The reaction mixture was heated at 40 °C for 2 h. Then, the solvent was removed *in vacuo* and the crude product was purified by flash column chromatography (eluent: 100/0 to 90/10 hexanes/ethyl acetate) over silica gel to give **PN-TPN** as a yellow solid (0.50 g, 67% yield). ^{1}H NMR (ppm, 400 MHz, 298 K, $CDCl_3$) δ 7.59–7.55 (m, 2H), 7.43 (dt, *J* = 8.4, 1.4 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.29–7.20 (m, 8H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.07–6.95 (m, 8H), 6.79–6.75 (m, 1H); ^{13}C NMR (ppm, 101 MHz, 298 K, $CDCl_3$) δ 148.7, 148.4, 143.0,

124.2 (d, J = 5.9 Hz), 140.8, 140.5, 139.8 (d, J = 3.0 Hz), 139.5, 139.3, 133.2 (d, J = 10.8 Hz), 131.2 (d, J = 19.7 Hz), 131.0 (d, J = 34.9 Hz), 129.7 (d, J = 9.0 Hz), 129.4 (d, J = 10.6 Hz), 129.2, 128.6, 128.5 (d, J = 5.5 Hz), 128.0 (d, J = 19.2 Hz), 127.2, 126.4 (d, J = 2.3 Hz), 125.0 (d, J = 10.7 Hz), 124.0 (d, J = 1.0 Hz), 122.3, 121.3; ^{31}P NMR (ppm, 162 MHz, 298 K, $CDCl_3$) δ 19.79; HRMS *m/z* calcd for $C_{32}H_{25}NP$ $[M + H]^+$ 454.1719, found 454.1721 (Δ = 0.4 ppm).

3. UV-Vis Spectra

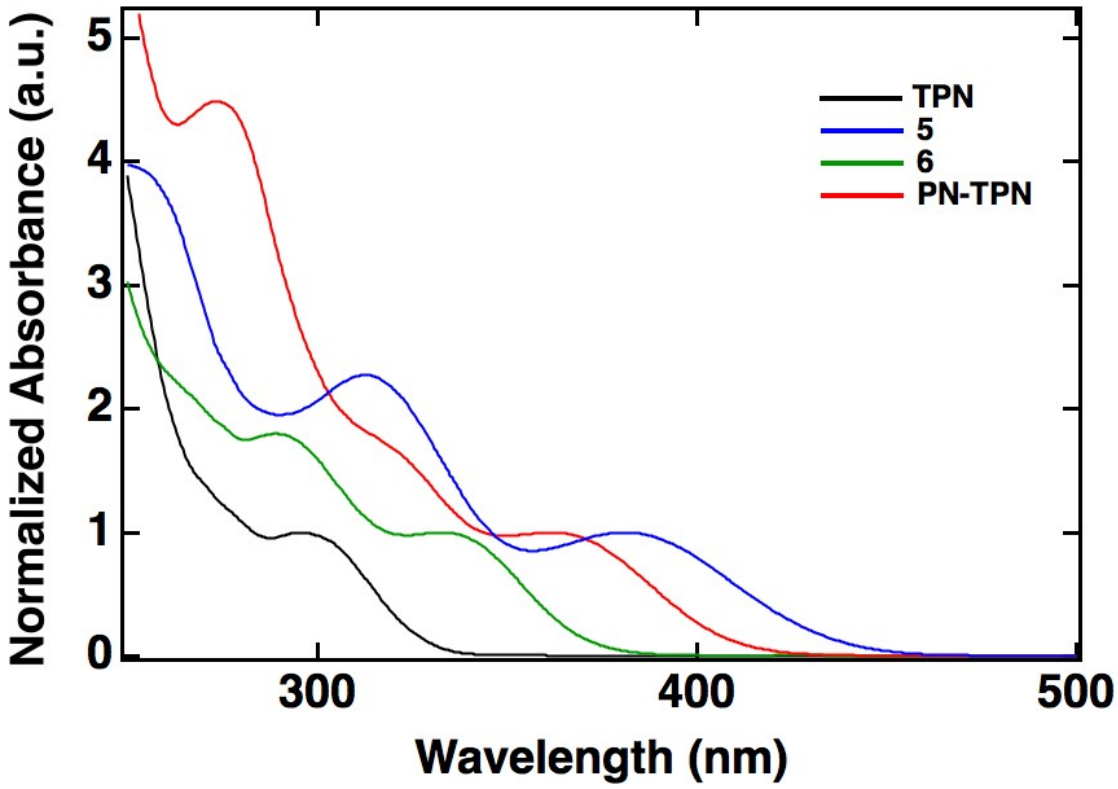


Figure S1. UV-Vis absorbance spectra obtained for **TPN**, **5**, **6**, and **PN-TPN** in dichloromethane.

4. Cyclic Voltammograms

Cyclic voltammetry was carried out with a VersaSTAT3-200 (Princeton Applied Research) using a one-compartment electrolysis cell consisting of a glassy carbon working electrode, a platinum wire counter electrode, and non-aqueous Ag/Ag^+ reference electrode bought from Neoscience (Cat. No. A-012171). Specifically, the electrode was made by placing a silver wire into an electrolyte containing silver ion. The electrode also consists of a porous glass on the one end, which will allow contact between the field environments with the silver ion electrolyte. The silver ion electrolyte in the reference electrode was 0.1 M tetrabutylammonium perchlorate in acetonitrile with 0.01 M $AgNO_3$ and in this condition the electrode's reference potential was known to be +0.542 V at 25 °C (vs NHE). The measurements were performed in 1.0 mM acetonitrile solution with 0.025 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, Aldrich, Electrochemical grade) as supporting electrolyte at a scan rate of 100 mV/s. The redox potential was calibrated after each experiment against the Fc/Fc^+ couple (0.11 V vs. Ag/Ag^+), which allowed conversion of all potentials vs. Fc/Fc^+. The working solution was degassed with N_2 for more than 15 min before measurement to remove the dissolved oxygen and then kept under a positive N_2 pressure during the measurement.

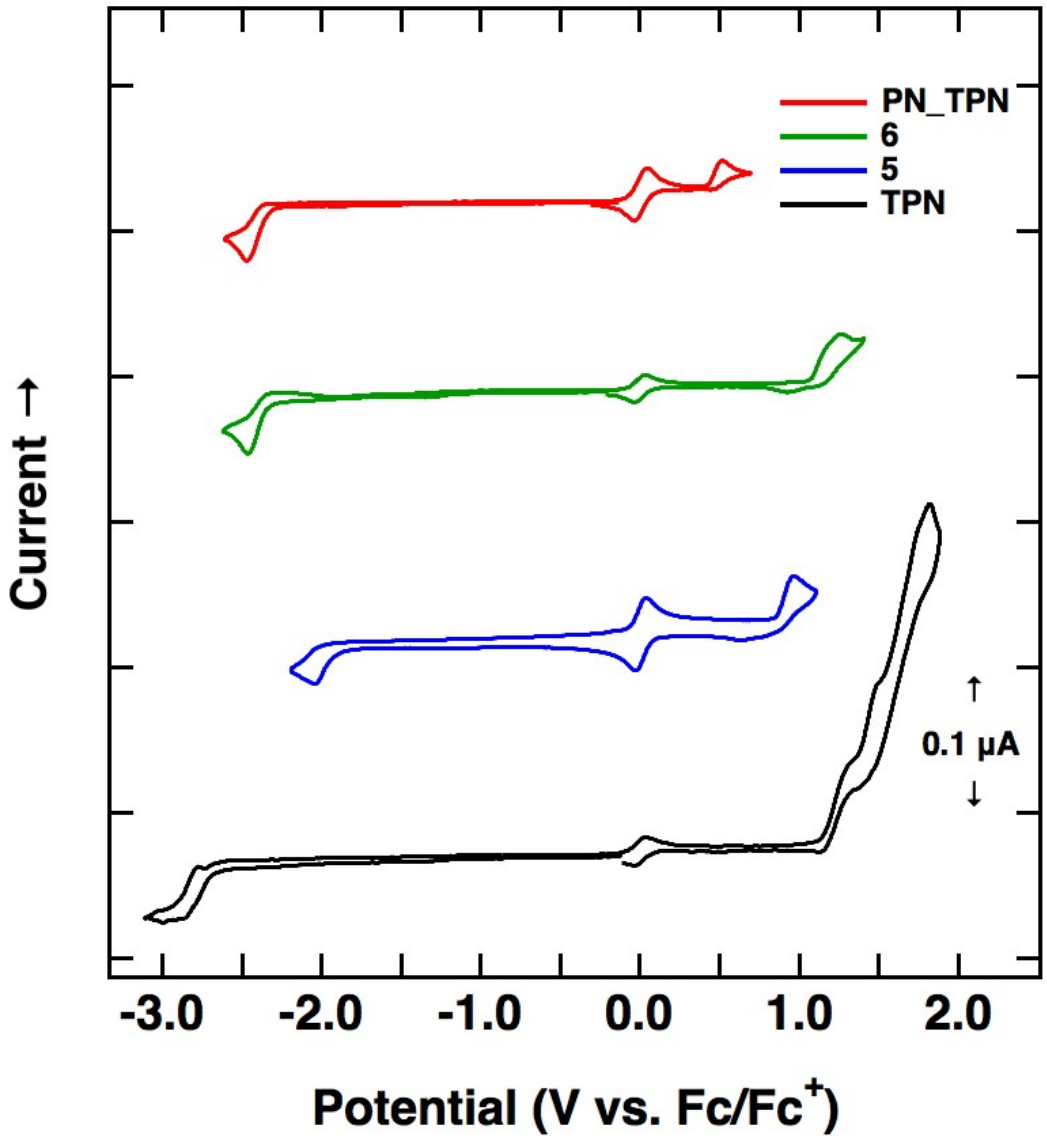


Figure S2. Cyclic voltammograms obtained for **TPN**, **5**, **6**, and **PN-TPN** in acetonitrile. Ferrocene was added as an internal standard.

5. Compiled NMR Characterization Data

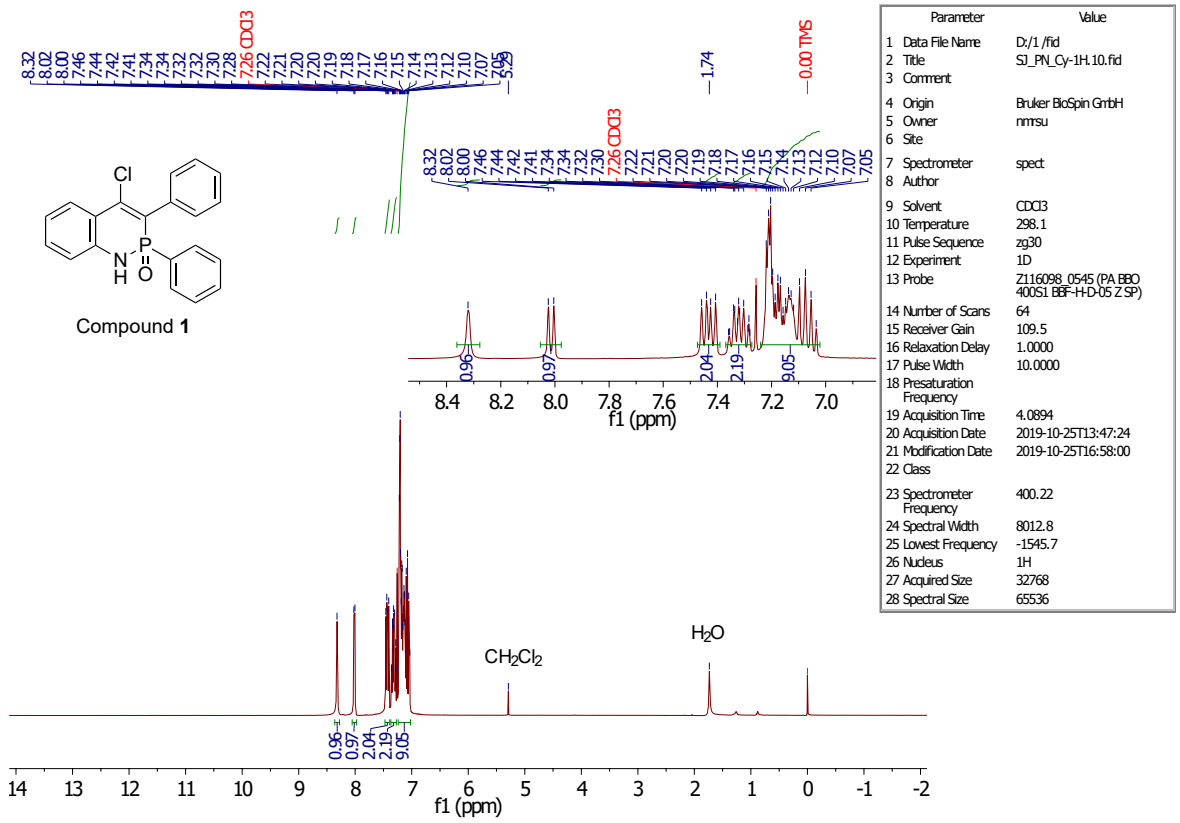


Figure S3. The ^{1}H NMR spectrum obtained for compound **1**.

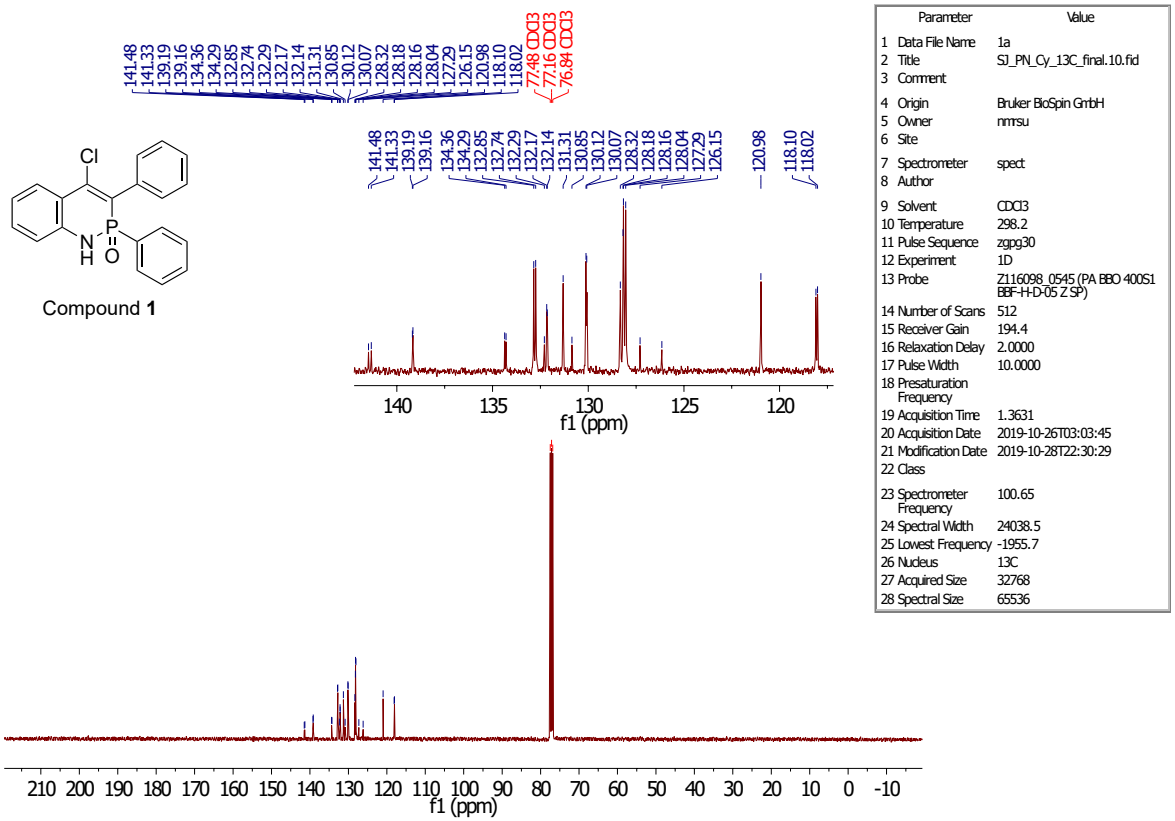


Figure S4. The ^{13}C NMR spectrum obtained for compound **1**.

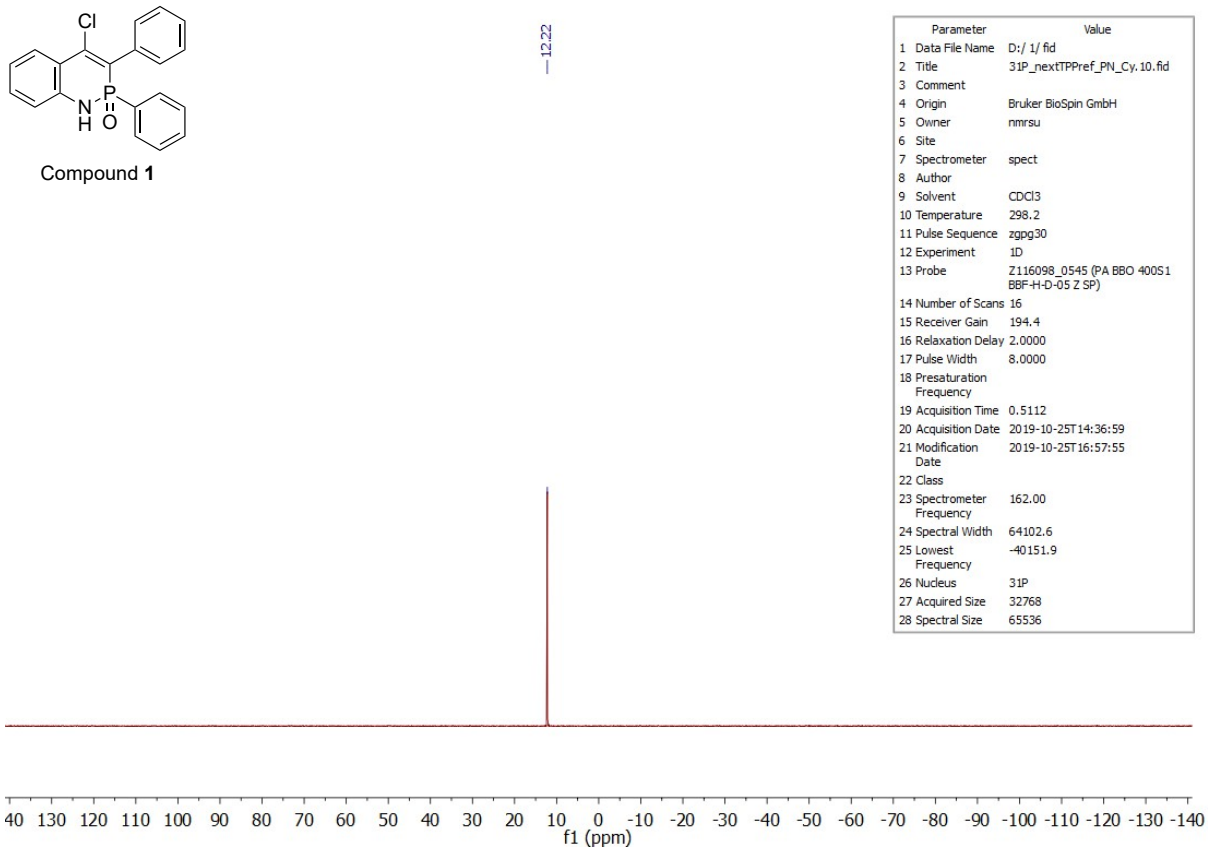


Figure S5. The ^{31}P NMR spectrum obtained for compound **1**.

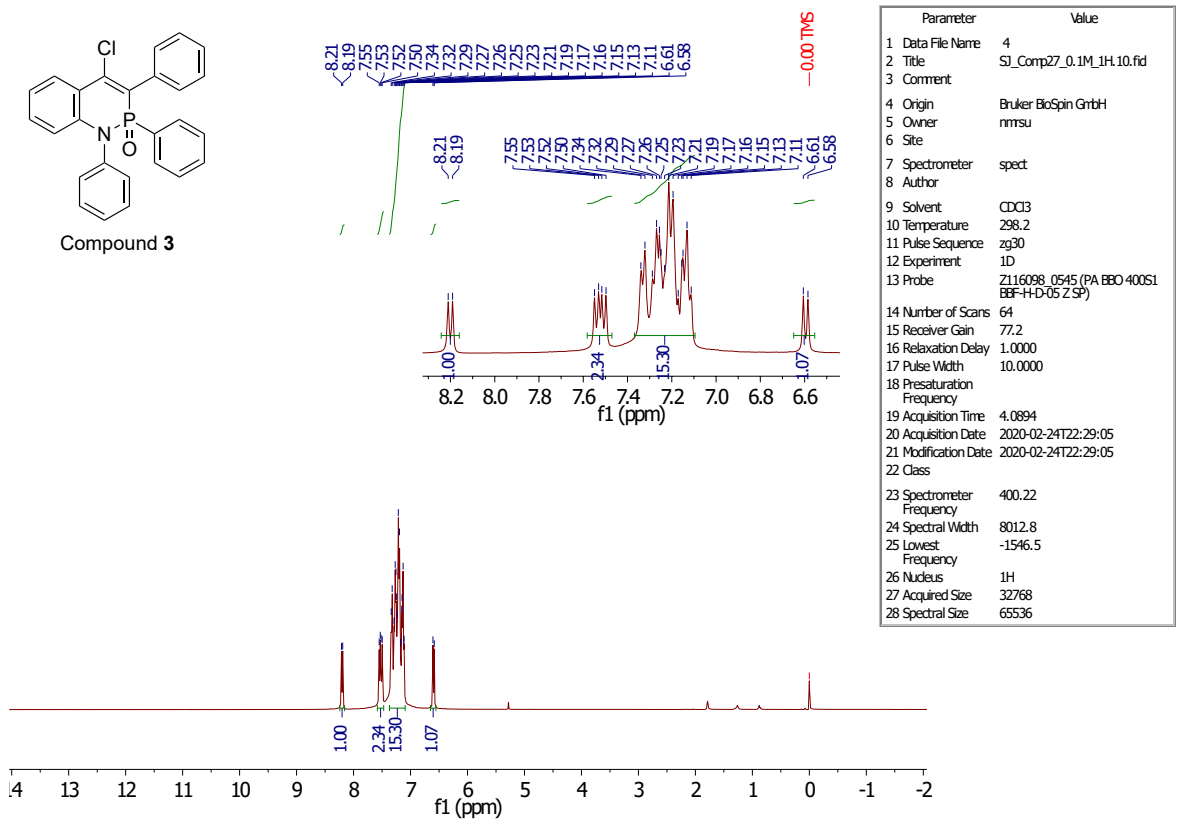
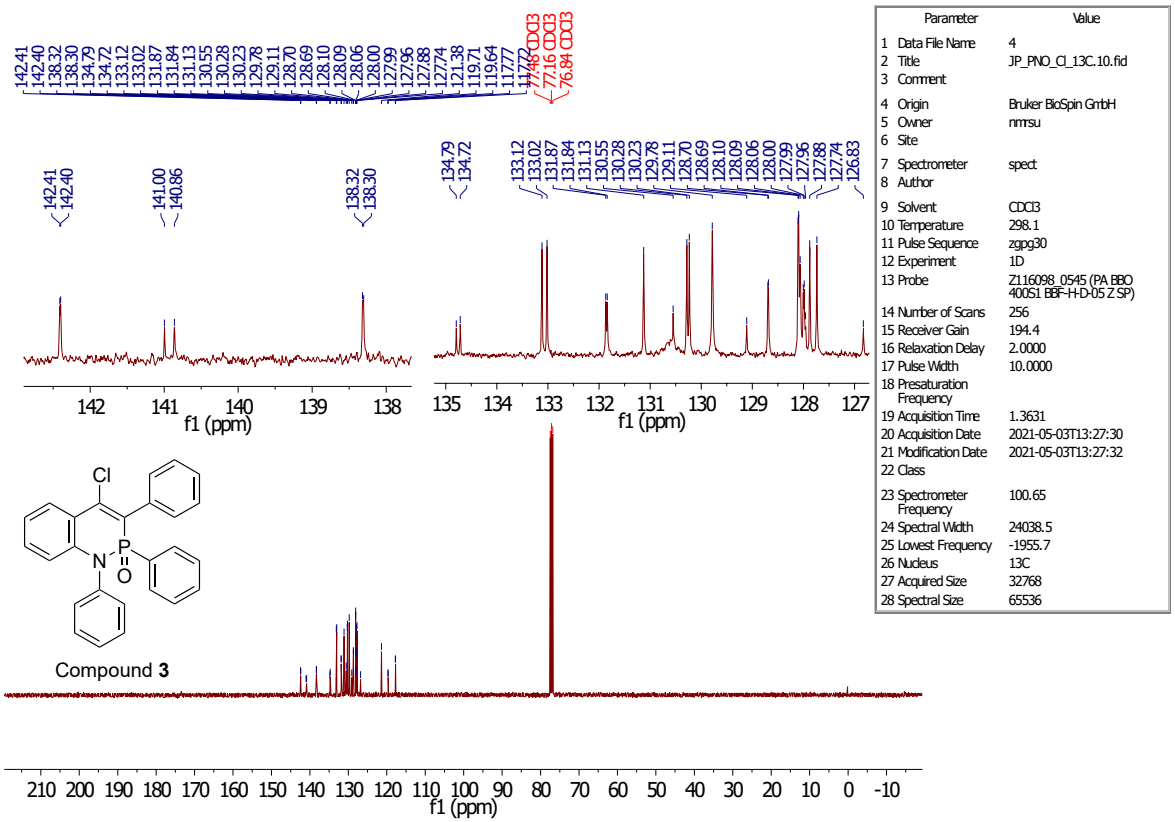


Figure S6. The ^{1}H NMR spectrum obtained for compound **3**.



Parameter	Value
1 Data File Name	4
2 Title	JP_PNO_Cl_13C.10.fid
3 Comment	
4 Origin	Bruker BioSpin GmbH
5 Owner	nmrsu
6 Site	
7 Spectrometer	spect
8 Author	
9 Solvent	CDCl3
10 Temperature	298.1
11 Pulse Sequence	zgpg30
12 Experiment	1D
13 Probe	Z116098_0545 (PA BBO 400S1 BBF-H-D-05 Z SP)
14 Number of Scans	256
15 Receiver Gain	194.4
16 Relaxation Delay	2.0000
17 Pulse Width	10.0000
18 Presaturation Frequency	
19 Acquisition Time	1.3631
20 Acquisition Date	2021-05-03T13:27:30
21 Modification Date	2021-05-03T13:27:32
22 Class	
23 Spectrometer Frequency	100.65
24 Spectral Width	24038.5
25 Lowest Frequency	-1955.7
26 Nucleus	13C
27 Acquired Size	32768
28 Spectral Size	65536

Figure S7. The ^{13}C NMR spectrum obtained for compound **3**.

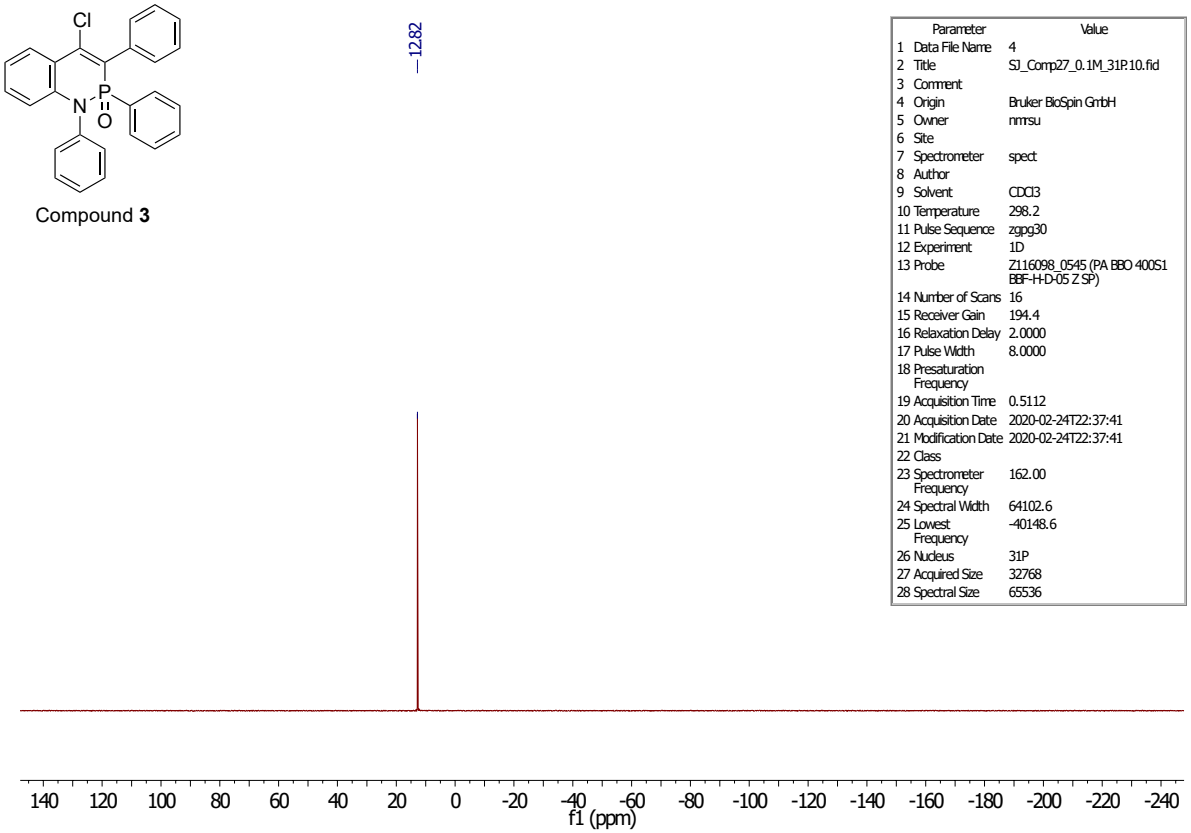


Figure S8. The ^{31}P NMR spectrum obtained for compound **3**.

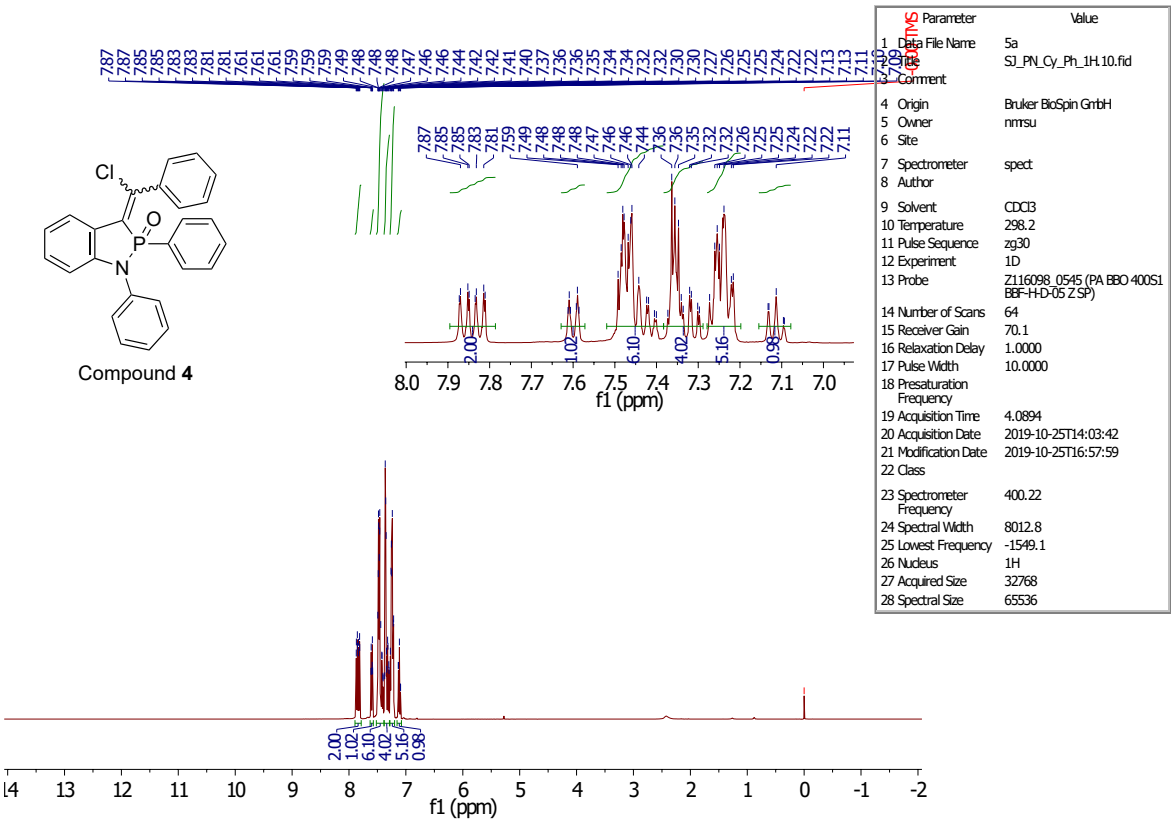
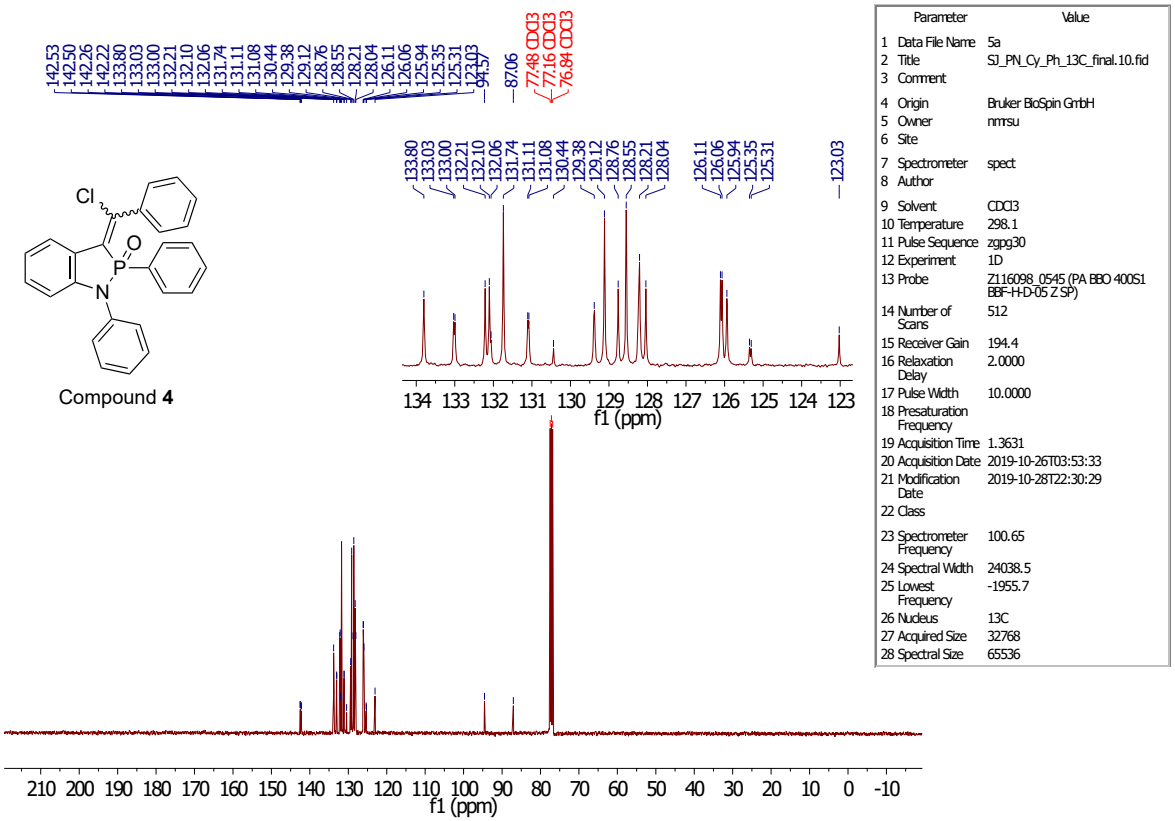


Figure S9. The ^{1}H NMR spectrum obtained for compound **4**.



	Parameter	Value
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3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.1
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Probe	Z116098_0545 (PA BBO 400S1 BBF-H-D-05 Z SP)
14	Number of Scans	512
15	Receiver Gain	194.4
16	Relaxation Delay	2.0000
17	Pulse Width	10.0000
18	Presaturation Frequency	
19	Acquisition Time	1.3631
20	Acquisition Date	2019-10-26T03:53:33
21	Modification Date	2019-10-28T22:30:29
22	Class	
23	Spectrometer Frequency	100.65
24	Spectral Width	24038.5
25	Lowest Frequency	-1955.7
26	Nucleus	13C
27	Acquired Size	32768
28	Spectral Size	65536

Figure S10. The ^{13}C NMR spectrum obtained for compound **4**.

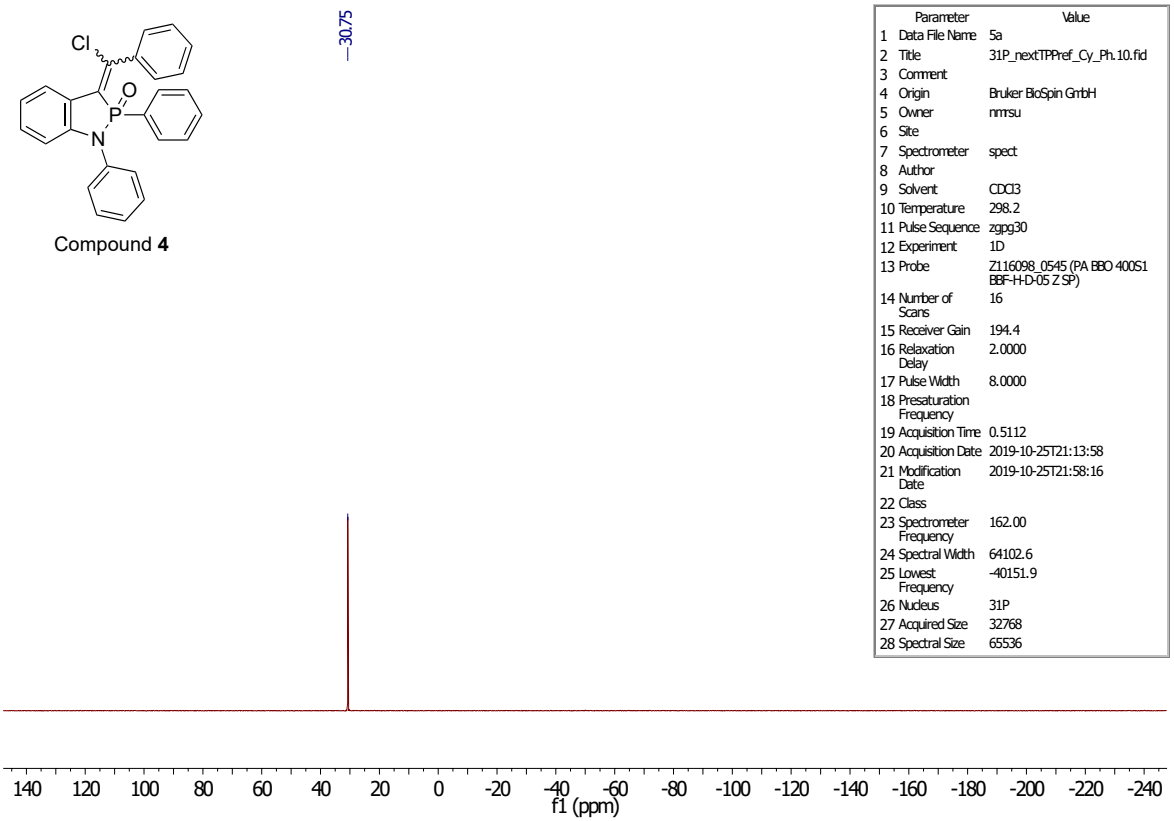


Figure S11. The ^{31}P NMR spectrum obtained for compound **4**.

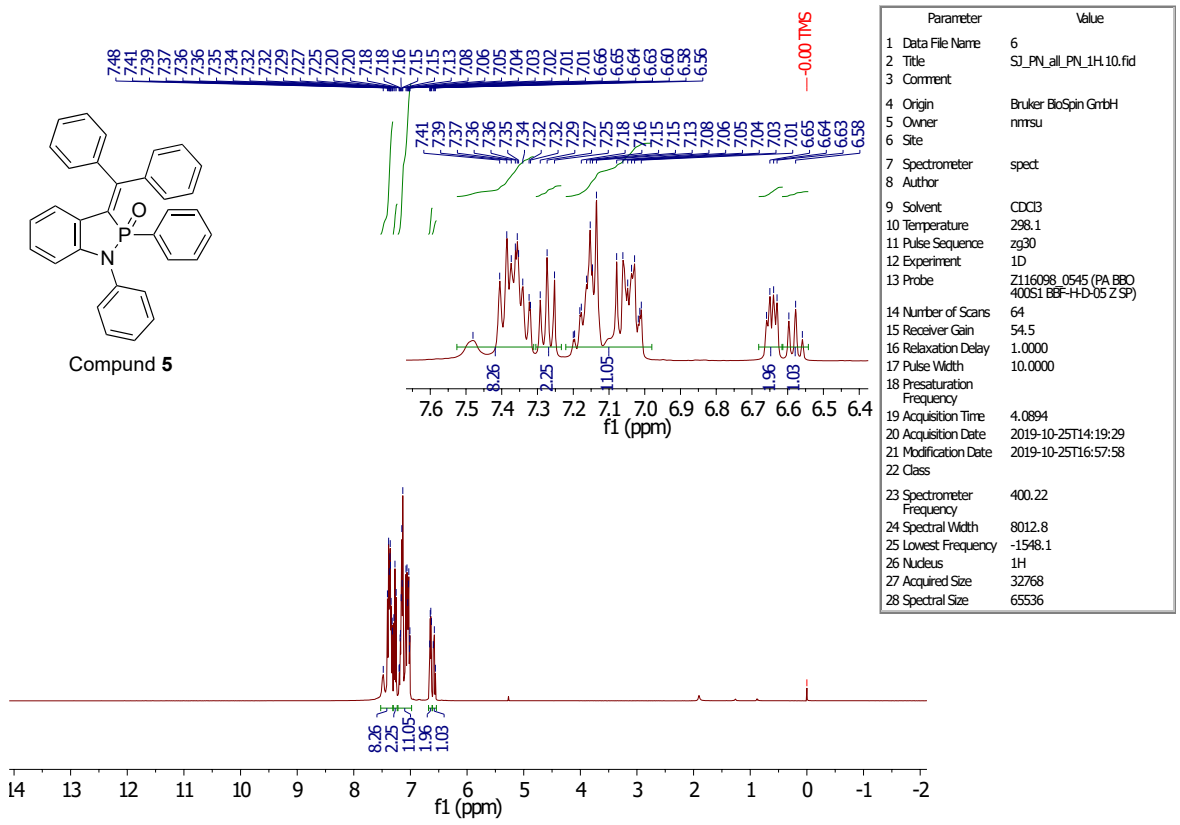
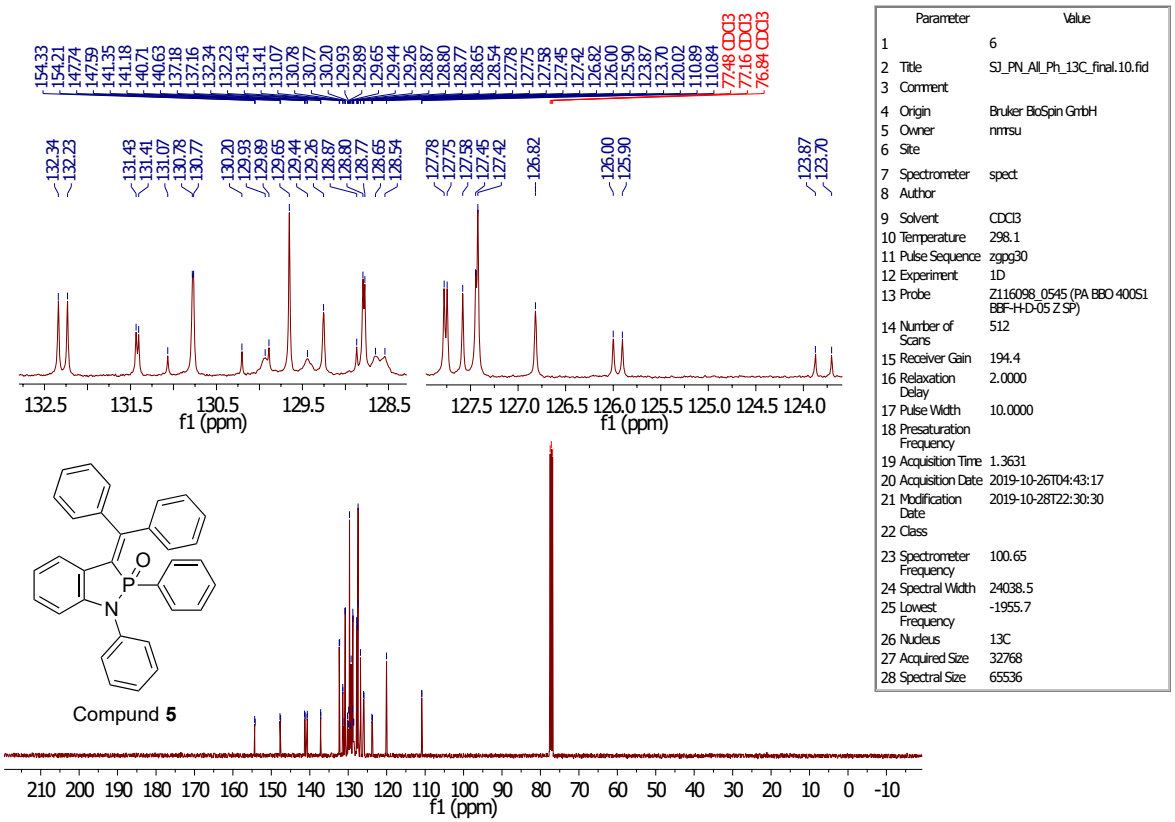


Figure S12. The ^{1}H NMR spectrum obtained for compound **5**.



	Parameter	Value
1		6
2	Title	SJ_PN_All_Ph_13C_final.10.fid
3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.1
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Probe	Z116098_0545 (PA BBO 400S1 BBF-H-D-05 Z SP)
14	Number of Scans	512
15	Receiver Gain	194.4
16	Relaxation Delay	2.0000
17	Pulse Width	10.0000
18	Presaturation Frequency	
19	Acquisition Time	1.3631
20	Acquisition Date	2019-10-26T04:43:17
21	Modification Date	2019-10-28T22:30:30
22	Class	
23	Spectrometer Frequency	100.65
24	Spectral Width	24038.5
25	Lowest Frequency	-1955.7
26	Nucleus	13C
27	Acquired Size	32768
28	Spectral Size	65536

Figure S13. The ^{13}C NMR spectrum obtained for compound **5**.

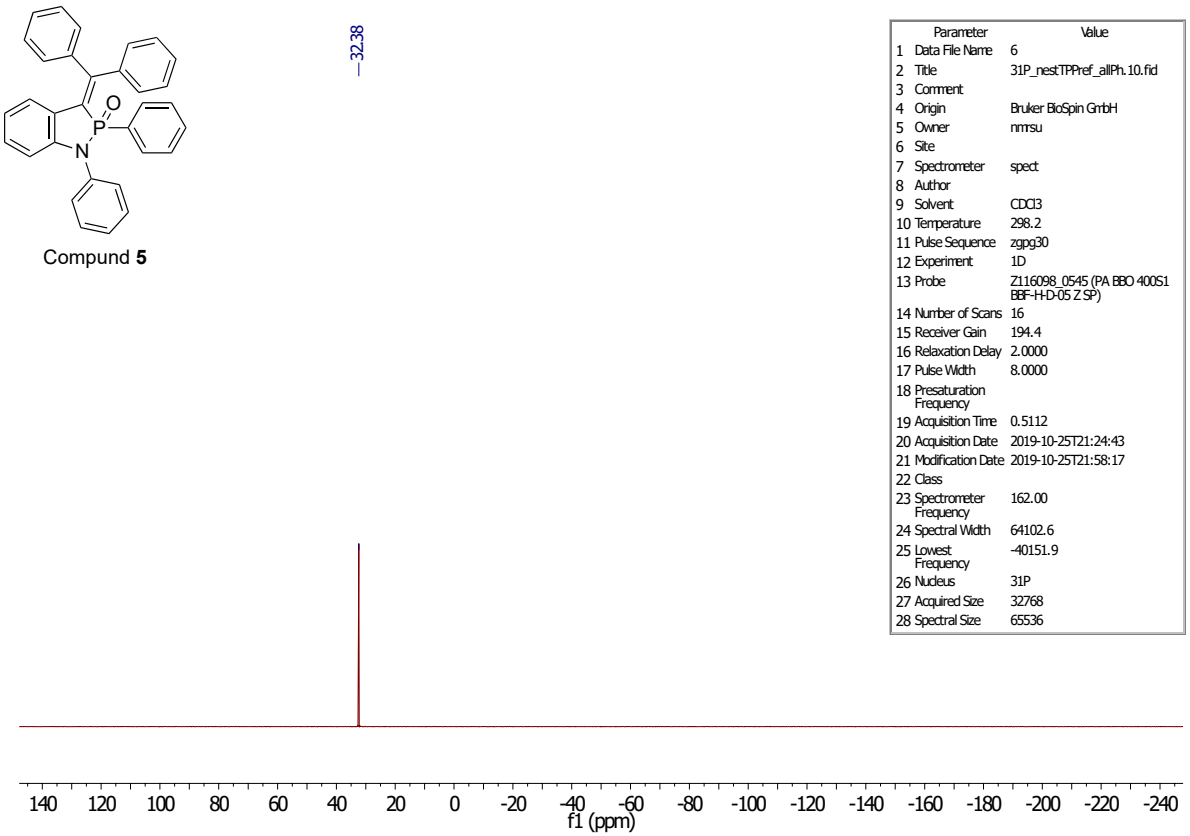


Figure S14. The ^{31}P NMR spectrum obtained for compound **5**.

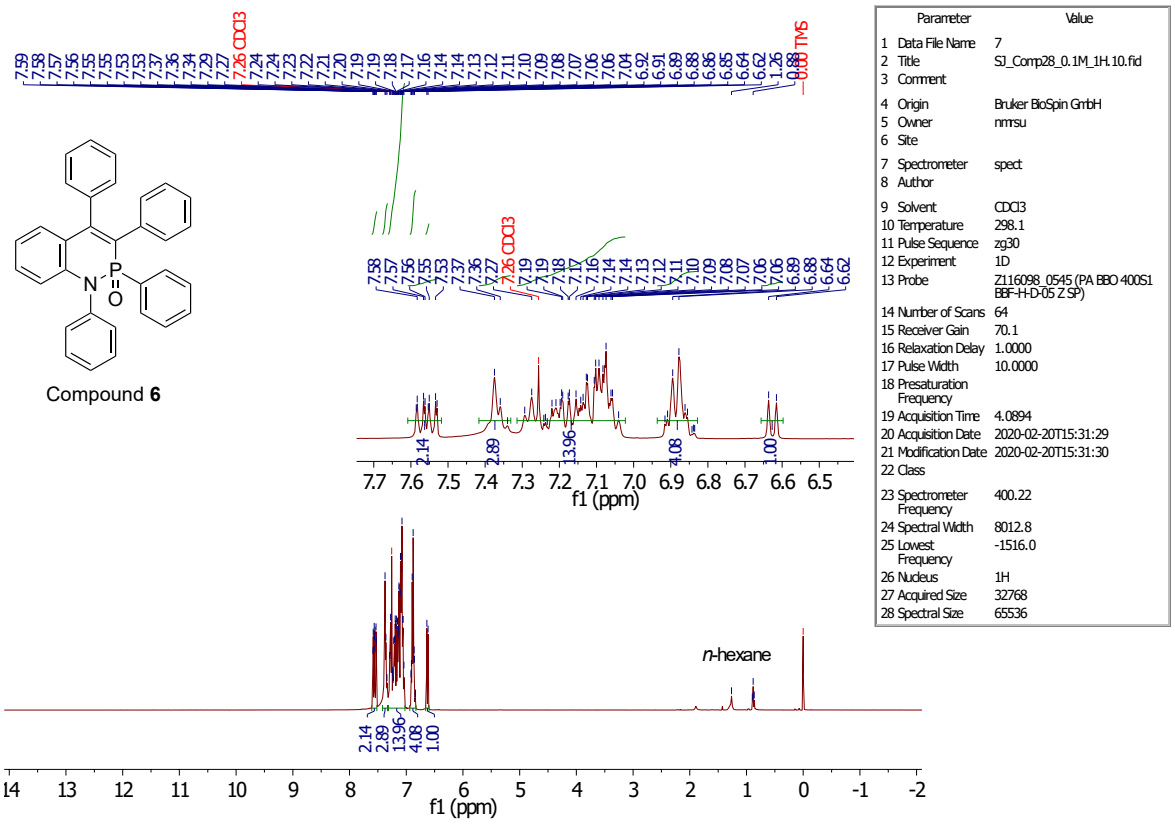


Figure S15. The ^{1}H NMR spectrum obtained for compound **6**.

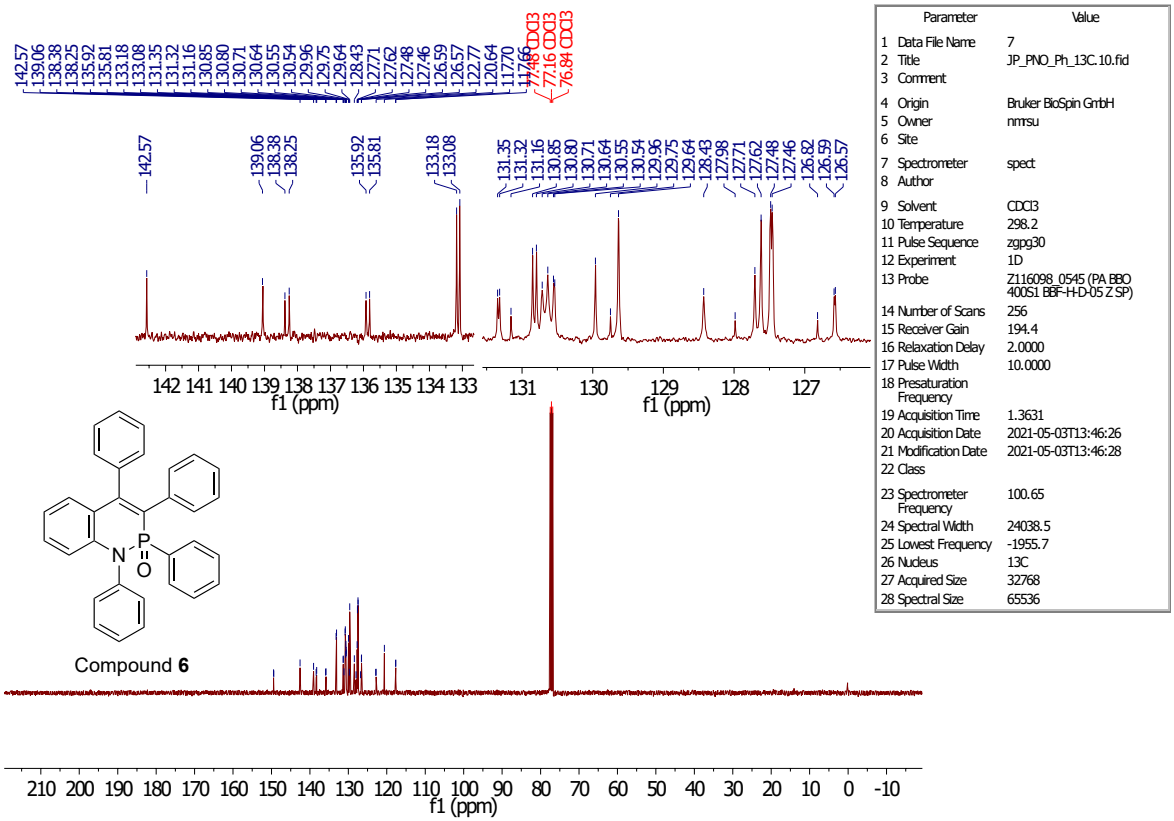


Figure S16. The ^{13}C NMR spectrum obtained for compound **6**.

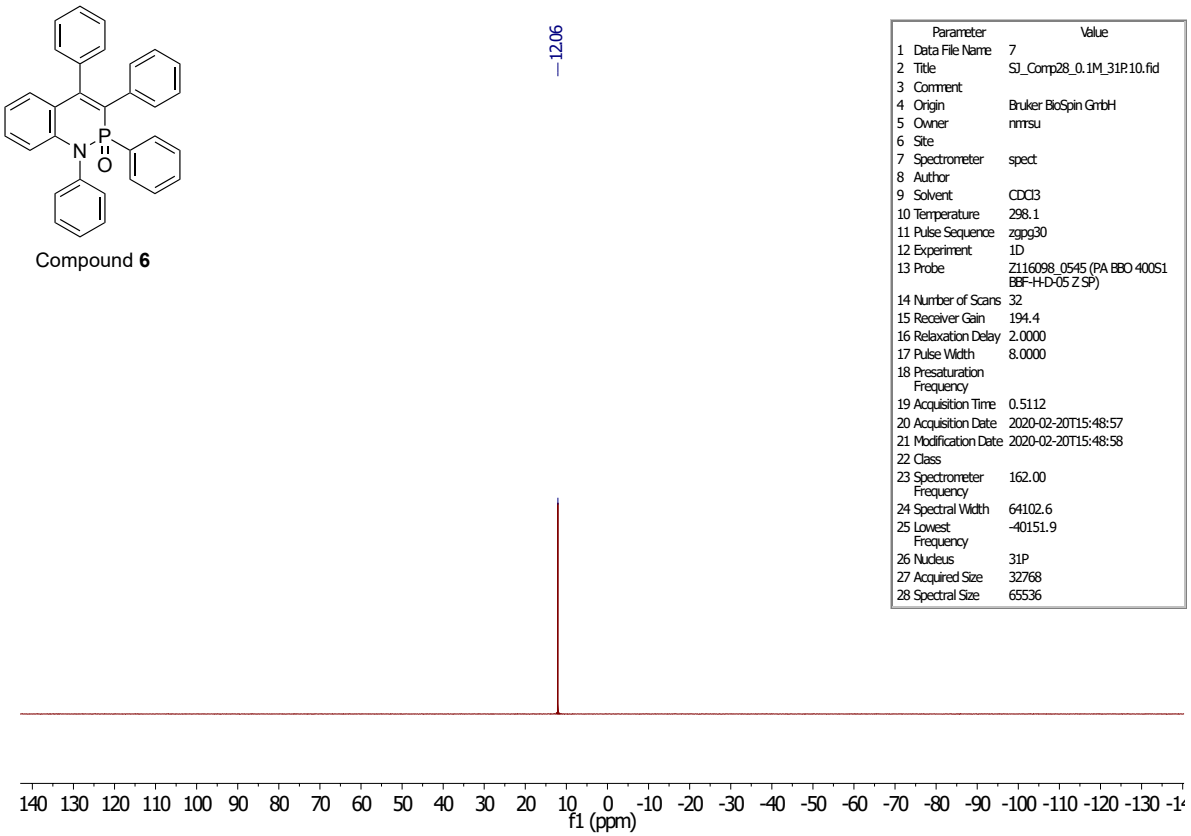


Figure S17. The ^{31}P NMR spectrum obtained for compound **6**.

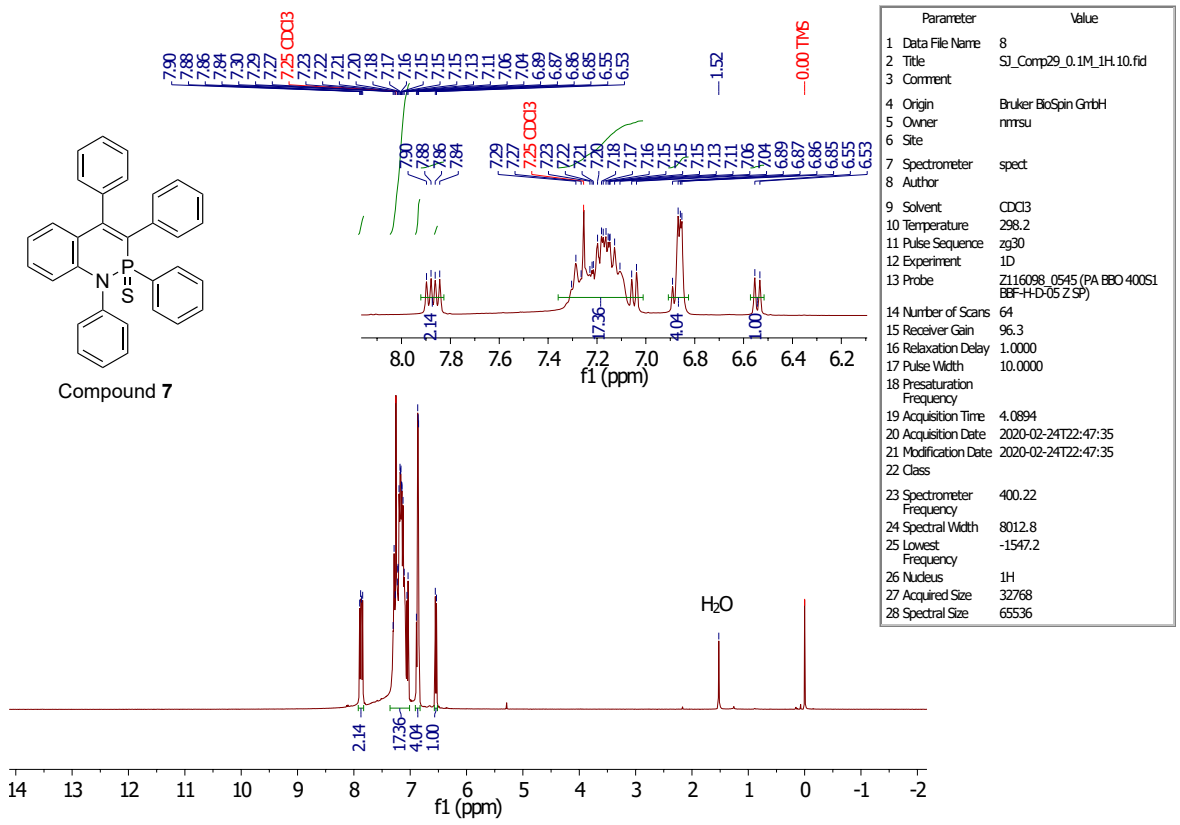


Figure S18. The ^{1}H NMR spectrum obtained for compound **7**.

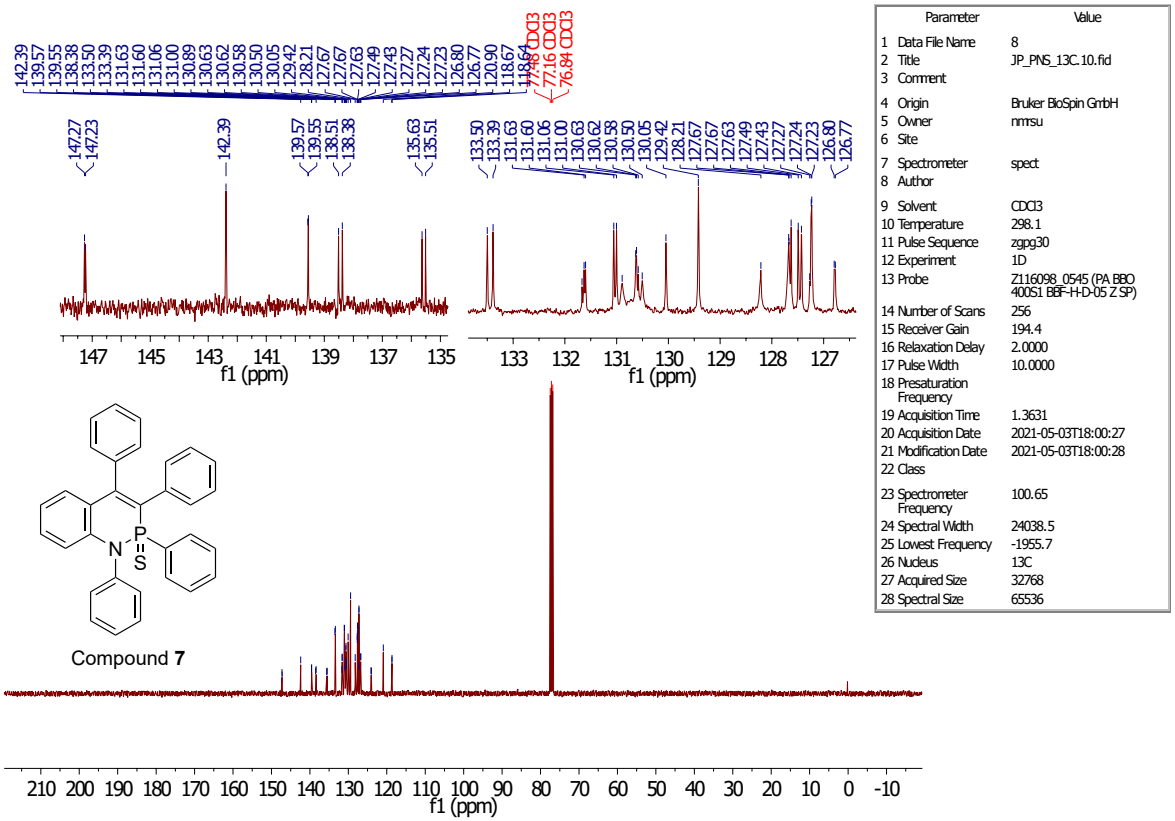


Figure S19. The ^{13}C NMR spectrum obtained for compound **7**.

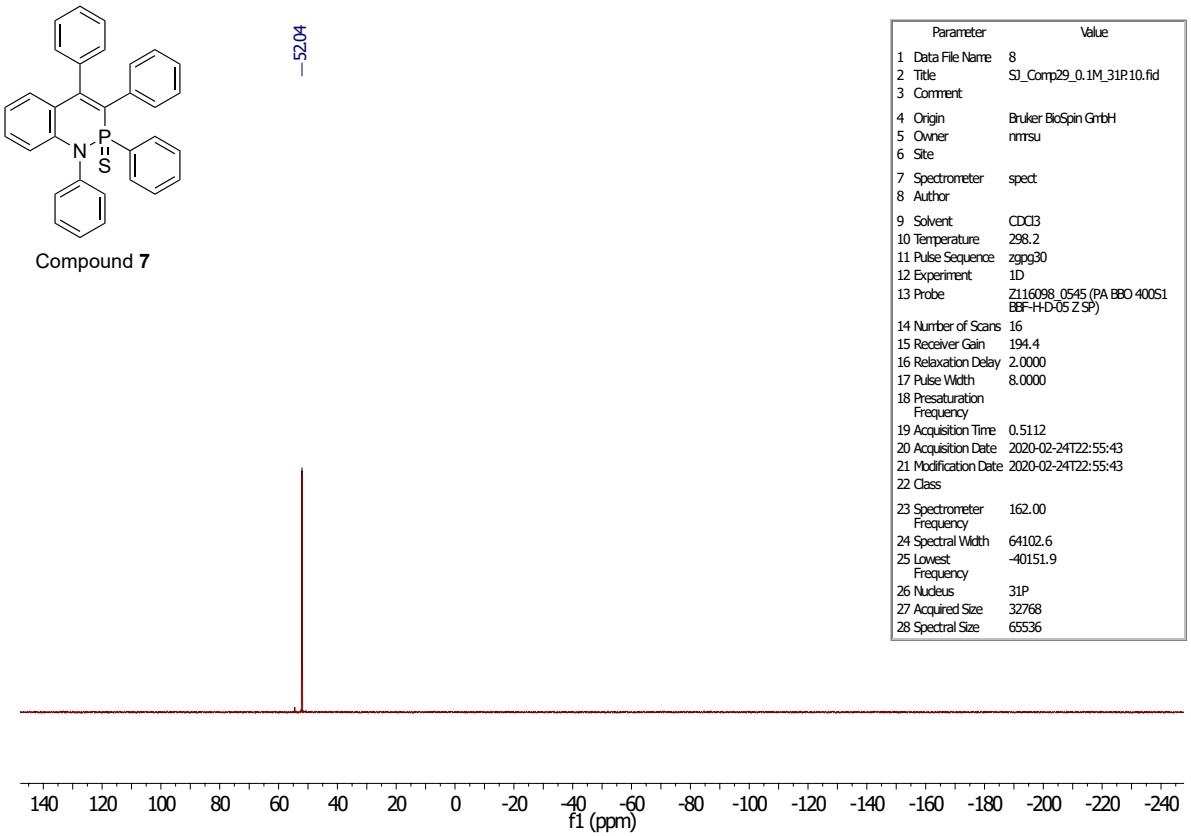


Figure S20. The ^{31}P NMR spectrum obtained for compound **7**.

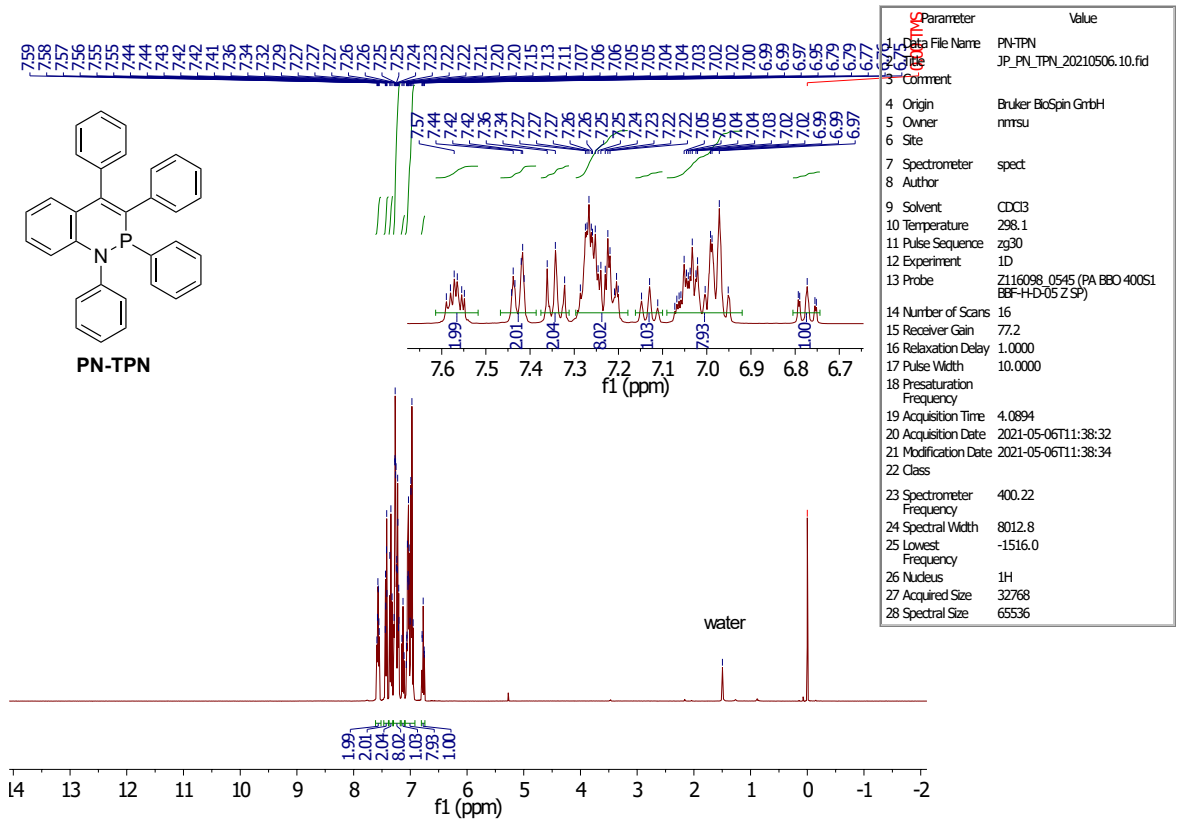


Figure S21. The ^{1}H NMR spectrum obtained for compound **PN-TPN**.

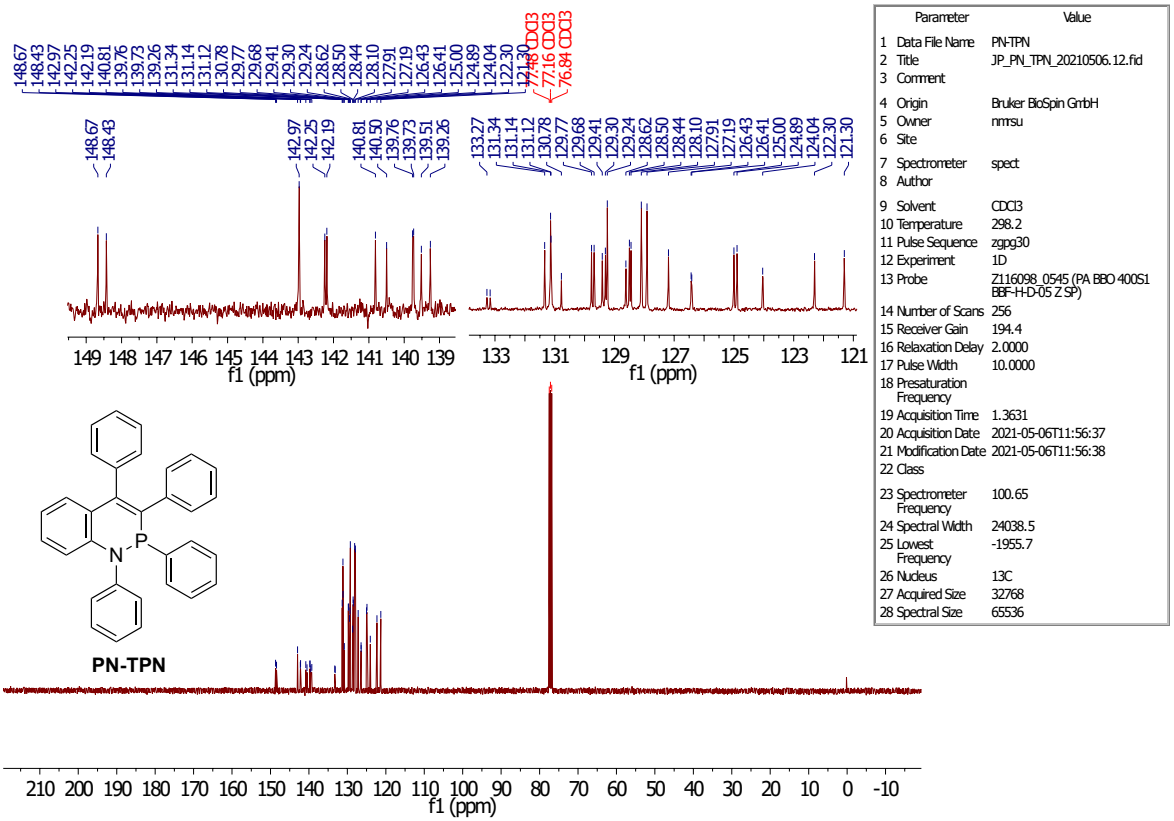


Figure S22. The ^{13}C NMR spectrum obtained for compound **PN-TPN**.

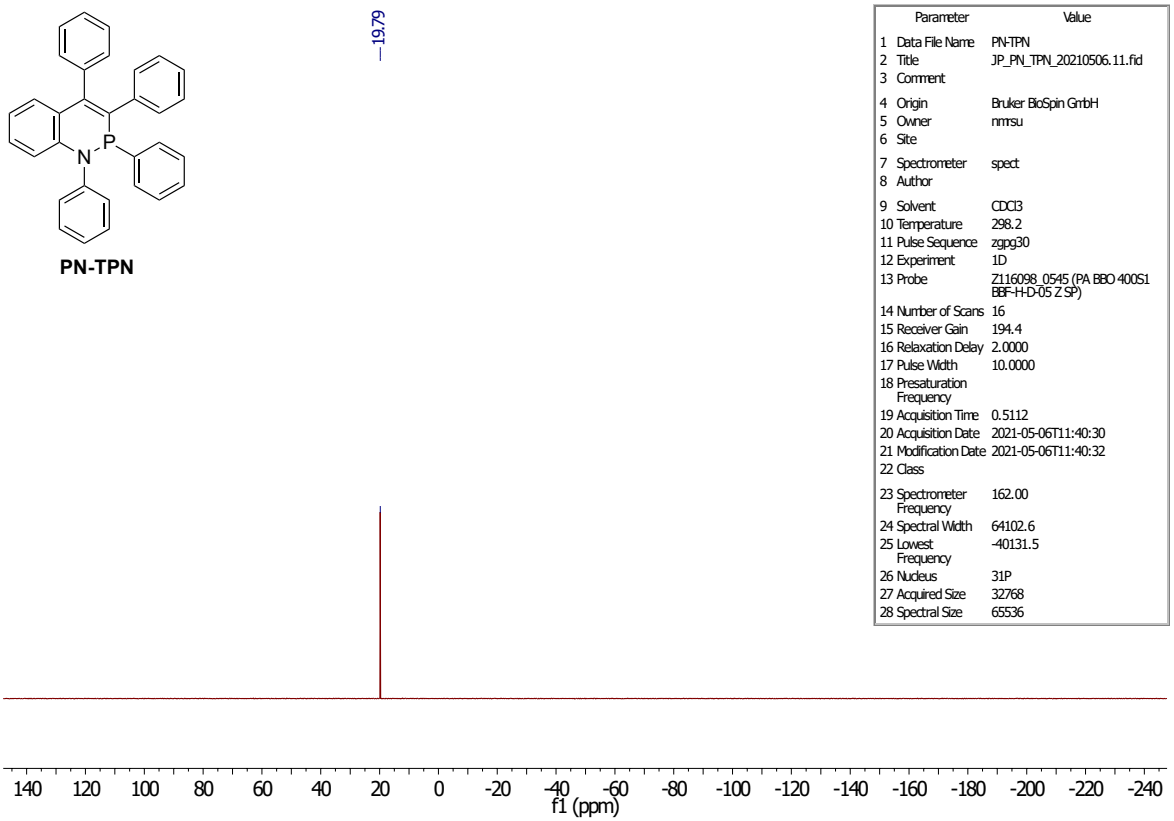


Figure S23. The ^{31}P NMR spectrum obtained for compound **PN-TPN**.

6. Crystallographic Data Collection and Structure Refinement of Compounds

A crystal of the compound was coated with paratone-*N* oil and the single-crystal diffraction data was collected at 173 K with Mo Kα radiation (λ = 0.71073 Å) using a Rigaku R-Axis Rapid II with a graphite crystal incident beam monochromator. Data collection and processing were performed using Rapid Auto software.[2] The structure of the compound was solved by the direct method and refined by full-matrix least-squares calculations using the SHELXL program.[3] Crystallographic Information File (CIF) of the compound was included in Supporting Information.

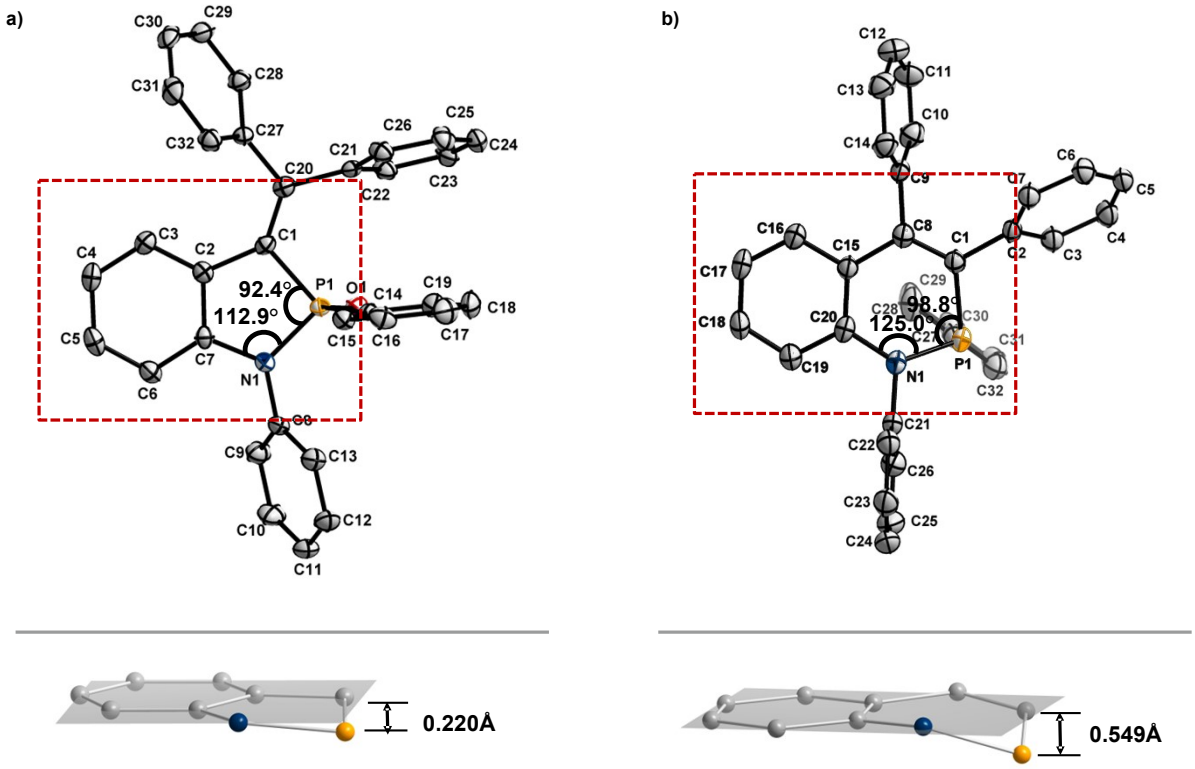


Figure S24. Top view (upper) and side view (lower) of inner core structures in a) **5** and b) **PN-TPN**.

Table S1. Crystallographic Data for PN-TPN

Complex	**PN-TPN**
Empirical formula	$C_{32}H_{24}NP$
Formula weight	453.49
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P-1*
a (Å)	9.4530(19)
b (Å)	10.884(2)
c (Å)	13.043(3)
α (°)	104.06(3)
β (°)	110.34(3)
γ (°)	96.4993)
V (Å^3)	1191.4(5)
Z	2
ρ_{calc} (Mg/m^3)	1.264
μ (mm^{-1})	0.136
Goodness-of-fit on F^2	1.014
R1, I>2σ(I)	0.0621
wR2, I>2σ(I)	0.1180
R1, all data	0.0959
wR2, all data	

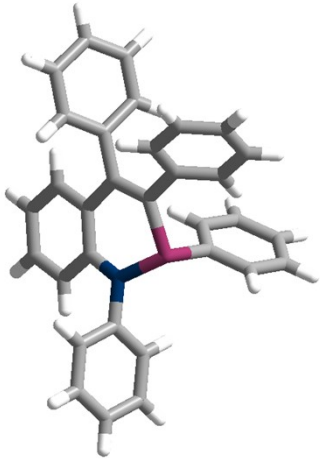
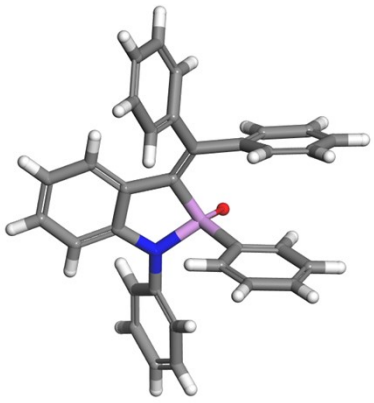


Table S2. Crystallographic Data for Compound 5

Complex	**Compound 5**
Empirical formula	$C_{32}H_{24}NOP$
Formula weight	469.49
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P-1*
a (Å)	10.347(2)
b (Å)	11.030(2)
c (Å)	11.987(2)
α (°)	69.43(3)
β (°)	86.51(3)
γ (°)	71.10(3)
V (Å^3)	1209.6(5)
Z	2
ρ_{calc} (Mg/m^3)	1.289
μ (mm^{-1})	0.140
Goodness-of-fit on F^2	1.040
R1, I>2σ(I)	0.0477
wR2, I>2σ(I)	0.0924
R1, all data	0.0704
wR2, all data	0.1009



7. Compiled FTIR Characterization Data

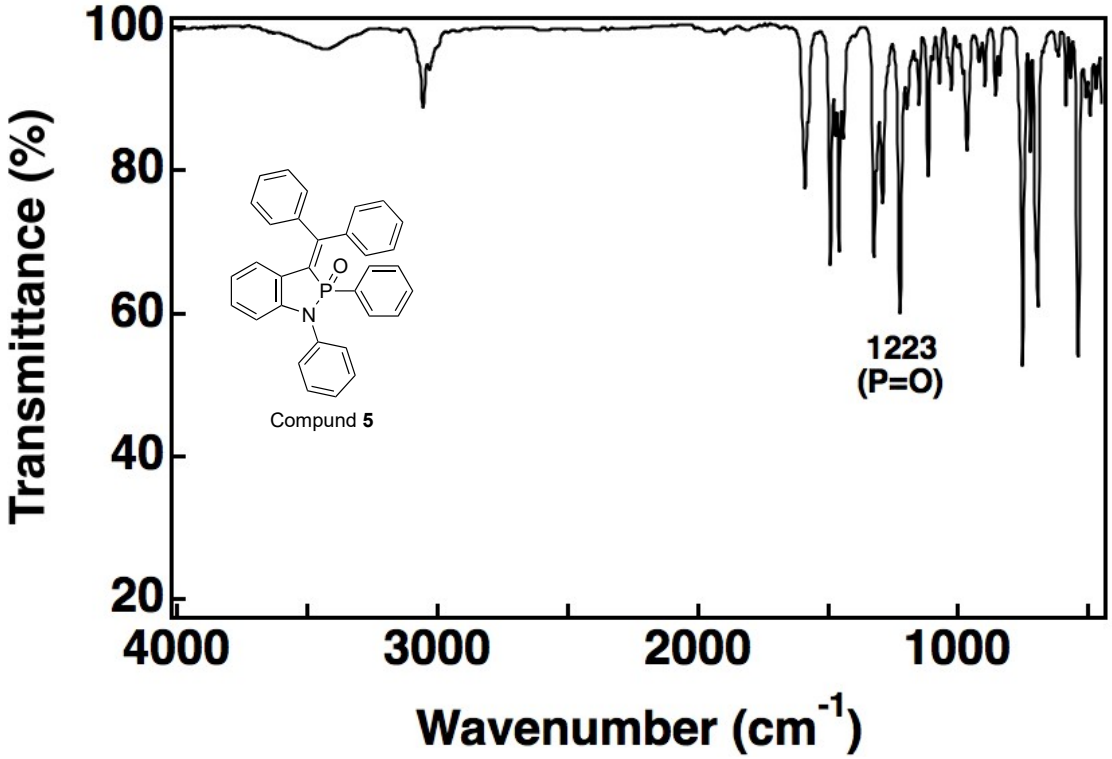


Figure S25. The FTIR spectrum obtained for **5** in KBr pellet.

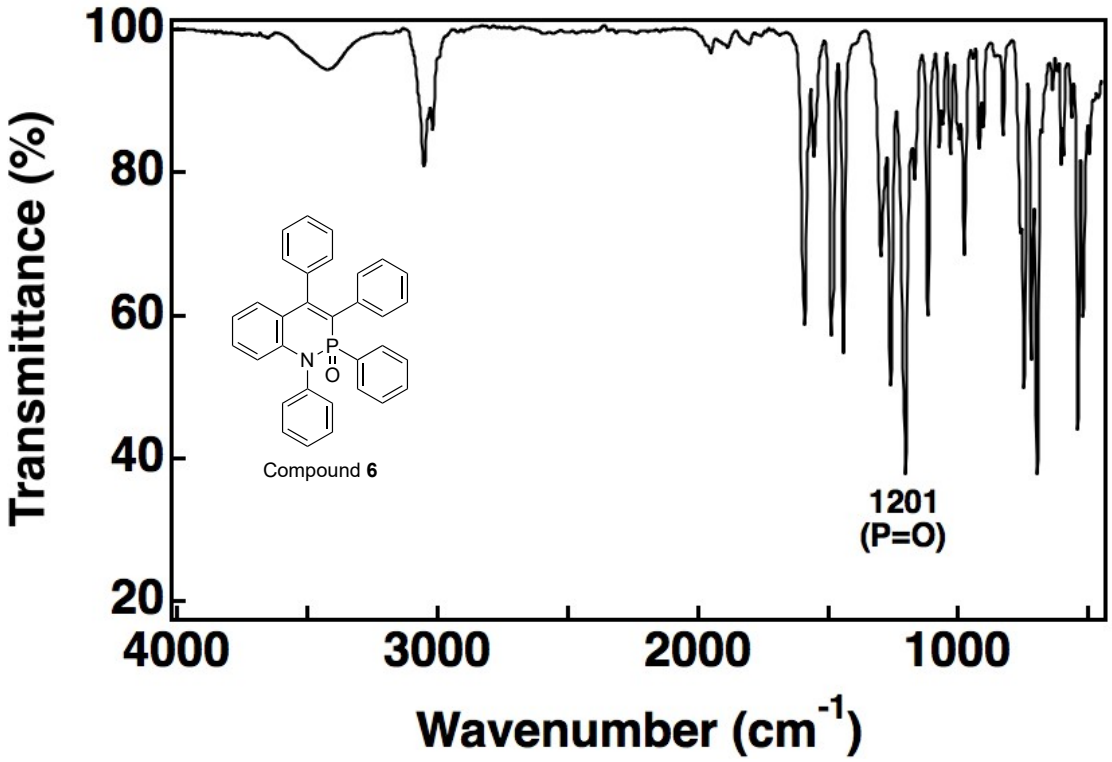


Figure S26. The FTIR spectrum obtained for **6** in KBr pellet.

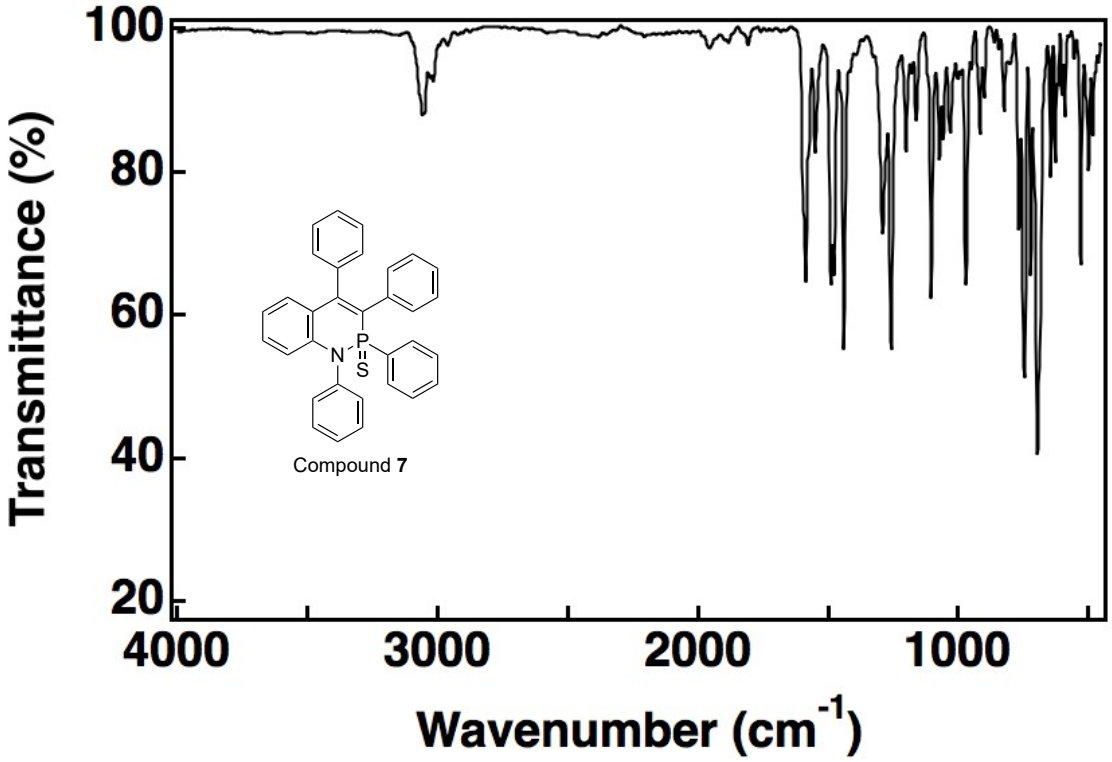


Figure S27. The FTIR spectrum obtained for **7** in KBr pellet.

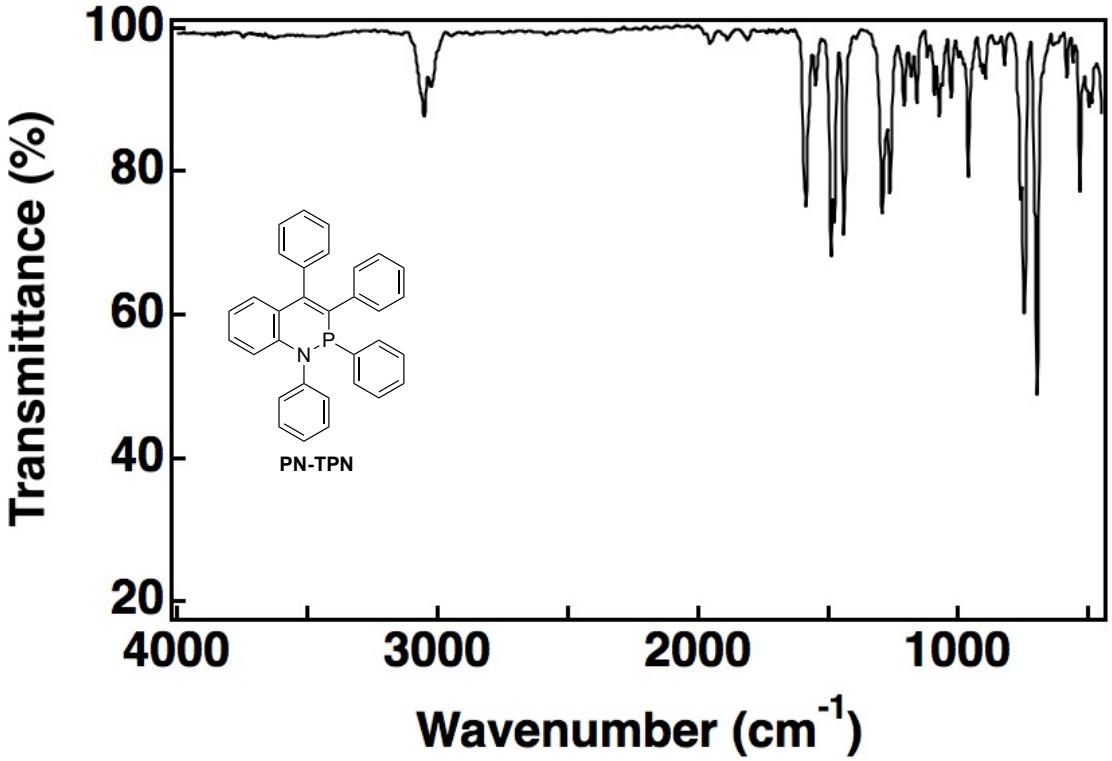


Figure S28. The FTIR spectrum obtained for **PN-TPN** in KBr pellet.

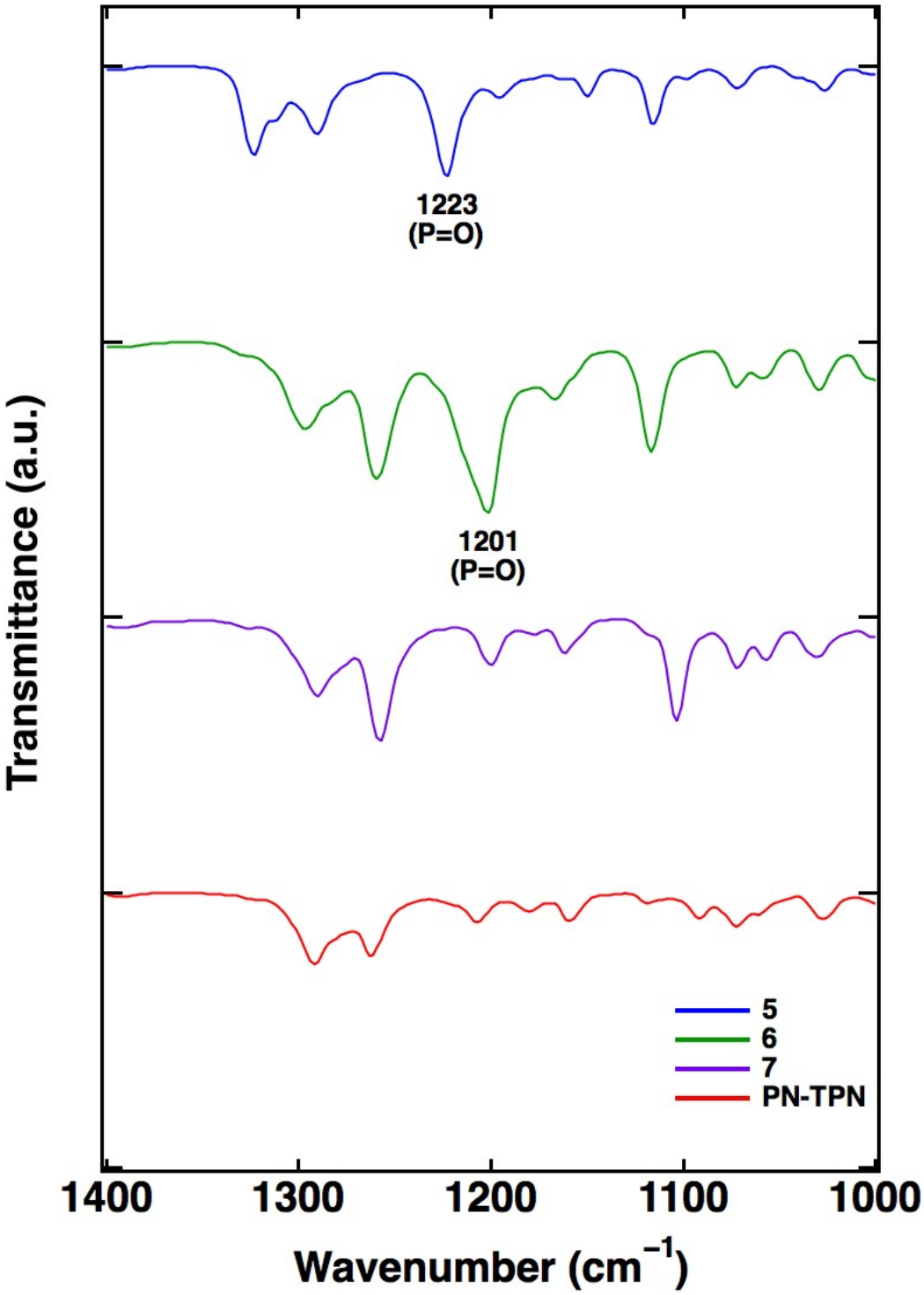


Figure S29. The FTIR spectra of **5**, **6**, **7**, and **PN-TPN** in the range of 1400-1000 cm^{-1}.

7. References

(1) J. Gao, Y. Shao, J. Zhu, J. Zhu, H. Mao, X. Wang and X. Lv, *J. Org. Chem*., 2014, **79**, 9000–9008.

(2) Rapid Auto software, R-Axis series, Cat. No. 9220B101, Rigaku Corporation.

(3) G. M. Sheldrick, *Acta Crystallogr., Sect C: Struct. Chem.,* 2015, **C71**, 3–8.