Supplementary Information

A direct method for phosphorus atom insertion via phosphorous acid for synthesizing P-doped curved polycyclic π-systems

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1. Experimental Section

Instrumentation and Materials.

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Silica-gel column chromatography was performed with UltraPure Silica Gel (230-400 mesh, SiliCycle) unless otherwise noted. Thin-layer chromatography (TLC) was performed with Silica gel 60 F_{254} (Merck). Recycling preparative HPLC was conducted using JAI LaboAce LC-5060. Microwave-assisted reactions were performed in sealed tubes using a CEM Discover microwave reactor, with the maximum power output set to 100 W. UV/Vis absorption spectra were measured with a Shimadzu UV3600-i Plus spectrometer. Steady-state emission spectra were obtained by a HORIBA Nanolog spectrometer. Emission lifetimes were determined by a HORIBA Nanolog spectrometer equipped with NanoLED light sources or a Hamamatsu Photonics Quantaurus-Tau C11367-01 fluorescence lifetime measurement system. An absolute fluorescence quantum yield was obtained by Hamamatsu Photonics Quantaurus-QY spectrometer. For emission measurements, ca. 10 μM solutions in toluene or 2-MeTHF were prepared using spectrochemical analysis-grade solvents. ^{1}H, ^{13}C{^{1}H}, ^{19}F, and ^{31}P{^{1}H} NMR spectra were recorded with a JEOL EX-400 spectrometer (operating at 399.65 MHz for ^{1}H, 100.40 MHz for ^{13}C, 376.17 MHz for ^{19}F, and 161.7 MHz for ^{31}P) by using the residual solvent as the internal reference for ^{1}H ($CDCl_3$: $\delta = 7.26$ ppm and CD_2Cl_2: $\delta = 5.32$ ppm) and ^{13}C ($CDCl_3$: $\delta = 77.16$ ppm), or hexafluorobenzene for ^{19}F ($\delta = -162.0$ ppm) and trimethylphosphite for ^{31}P ($\delta = 140.0$ ppm) as the external references. FT-IR spectra were recorded on a NICOLET iS50 spectrometer. High-resolution mass spectra (HRMS) were measured on a Thermo Fischer Scientific EXACTIVE Fourier-transform orbitrap mass spectrometer (APCI and ESI). Electrochemical measurements were made using an ALS electrochemical analyzer model 601E with DPV technique.

X-Ray Crystallographic details

Single-crystal X-ray diffraction analysis data for compounds **1PO**, **1(PO)$_2$**, **4PO**, and **5PO** were collected at –120 °C on a Rigaku Saturn724+ CCD diffractometer with graphite-monochromated MoK_α radiation (0.71075 Å). Data integration and scaling were performed with CrystalClear-SM Expert 2.1 b46 (Rigaku, 2016) for **4PO** and **5PO**, and with CrysAlisPro 1.171.39.46e (Rigaku OD, 2018) for **1PO** and **1(PO)$_2$**. The crystal structures were solved by direct methods using SHELXS-2014 and refined by full-matrix least-squares methods using SHELXL-2014 on Yadokari-XG. Owing to severe disorder of solvent molecules occupying in large voids in the crystal lattice of **1(PO)$_2$**, the PLATON SQUEEZE procedure was applied in the final refinement. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model.

Density Functional Theory (DFT) Calculations.

All calculations were carried out using the *Gaussian 09* program.[S1] All structures were fully optimized without any symmetry restriction. The optimization were performed using the density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional) level,[S2,S3] employing a basis set 6-31G(d,p) for C, H, N, O, and P. Excitation energies and oscillator strengths on the optimized structures were calculated using the TD-SCF method at the B3LYP/6-31G(d,p) level.

2. Synthesis

1,3,5-Tris{di(*p*-tolyl)amino}benzene **1** was synthesized according to literature.[S4]

General Procedure for the microwave-assisted reaction of arylamines with H_3PO_3.

To a mixture of arylamine (ca. 50 mg, 1 equiv), DMAP (15 equiv), and H_3PO_3 (5 equiv) in 1,2-dichloroethane was added Tf_2O (15 equiv). The resulting mixture was then heated in a sealed tube using a microwave reactor (maximum power output: 100 W) under an argon atmosphere. After cooling to room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography.

Compound 1PO:

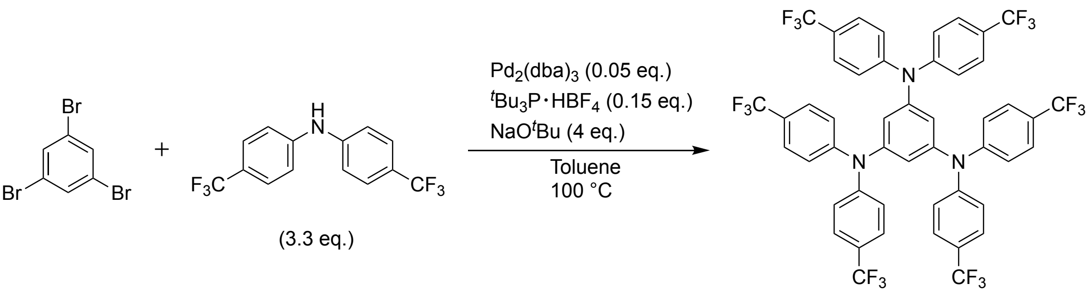
The reaction was performed according to the General Procedure at 110 °C for 20 min using **1** (51.1 mg, 0.077 mmol), DMAP (138.9 mg, 1.14 mmol), H_3PO_3 (31.5 mg, 0.38 mmol), and Tf_2O (0.185 mL, 1.13 mmol) in 1,2-dichloroethane (0.5 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **1PO** as a white solid (26.1 mg, 0.037 mmol, 48%).

1PO: ^{1}H NMR (399.78 MHz, $CDCl_3$, 25 °C): δ = 8.10 (d, J = 12.0 Hz, 2H, Ar-H), 7.20 (d, J = 8.0 Hz, 4H, Ar-H), 7.07 (m, 6H, Ar-H), 6.88 (d, J = 8.4 Hz, 4H, Ar-H), 6.76 (d, J = 8.8 Hz, 4H, Ar-H), 6.55 (dd, J = 8.8 Hz, J = 6.0 Hz, 2H, Ar-H), 5.46 (d, J = 4.0 Hz, 2H, Ar-H), 2.42 (s, 6H, $-CH_3$), 2.35 (s, 6H, $-CH_3$), and 2.26 (s, 6H, $-CH_3$) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 151.3, 146.8, 143.7, 143.30, 143.27, 138.7, 138.1, 133.4, 132.2, 131.1, 130.3 (d, J_{PC} = 7.7 Hz), 129.5, 126.0, 118.3 (d, J_{PC} = 7.7 Hz), 117.2 (d, J_{PC} = 115 Hz), 99.93, 99.88, 91.6 (d, J_{PC} = 104 Hz), 21.2, 20.90, and 20.87 ppm; ^{31}P NMR (161.8 MHz, $CDCl_3$, 25 °C): δ = –23.3 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 303 (43000), and 364 (15000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 388 nm (Φ_F = 0.11). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 423 nm. FT-IR (ATR): ν = 1196 (P=O) and 1117 (N–C) cm^{-1}. HRMS (ESI, positive) calcd. for $C_{48}H_{42}N_3O_1P_1Na_1$ $[M+Na]^+$ 730.2958; found 730.2953. m.p.: >300 °C.

Compound 1(PO)₂:

The reaction was performed according to the General Procedure at 150 °C for 15 min using **1** (51.8 mg, 0.078 mmol), DMAP (139.9 mg, 1.15 mmol), H_3PO_3 (31.4 mg, 0.38 mmol) and Tf_2O (0.190 mL, 1.16 mmol) in 1,2-dichloroethane (0.5 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **1(PO)₂** as a white solid (8.1 mg, 0.011 mmol, 14%).

1(PO)$_2$: ^{1}H NMR (399.78 MHz, CD_2Cl_2, 25 °C): δ = 8.24 (d, J = 12.4 Hz, 2H, Ar-H), 7.93 (d, J = 11.6 Hz, 2H, Ar-H), 7.53 (dd, J = 8.2 Hz, J = 5.4 Hz, 2H, Ar-H), 7.31 (d, J = 7.6 Hz, 2H, Ar-H), 7.21 (m, 6H, Ar-H), 6.90 (d, J = 8.4 Hz, 4H, Ar-H), 6.52 (dd, J = 9.0 Hz, J = 6.6 Hz, 2H, Ar-H), 5.07 (t, J = 4.0 Hz, 1H, Ar-H), 2.50 (s, 6H, -CH_3), 2.48 (s, 6H, -CH_3), and 2.44 (s, 6H, -CH_3); ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 148.1, 147.4, 143.5, 142.7, 138.6, 138.0, 134.6, 134.5, 133.6, 131.7 (d, J_{PC} = 5.8 Hz), 131.5, 131.3, 129.7, 127.4 (d, J_{PC} = 5.8 Hz), 125.9 (d, J_{PC} = 116 Hz), 124.8 (d, J_{PC} = 7.7 Hz), 118.8 (d, J_{PC} = 7.7 Hz), 113.4 (d, J_{PC} = 113 Hz), 98.8, 96.3 (d, J_{PC} = 100 Hz), 21.4, 21.3, and 20.8 ppm; ^{31}P NMR (161.7 MHz, $CDCl_3$, 25 °C): δ = –21.2 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 303 (44000), 327 (36000), and 364 (21000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 374 nm (Φ_F = 0.09). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 408 nm. FT-IR (ATR): ν = 1175 (P=O) and 1107 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{48}H_{40}N_3O_2P_2$ [M+H]$^+$ 752.2590; found 752.2564. m.p.: >300 °C.



2

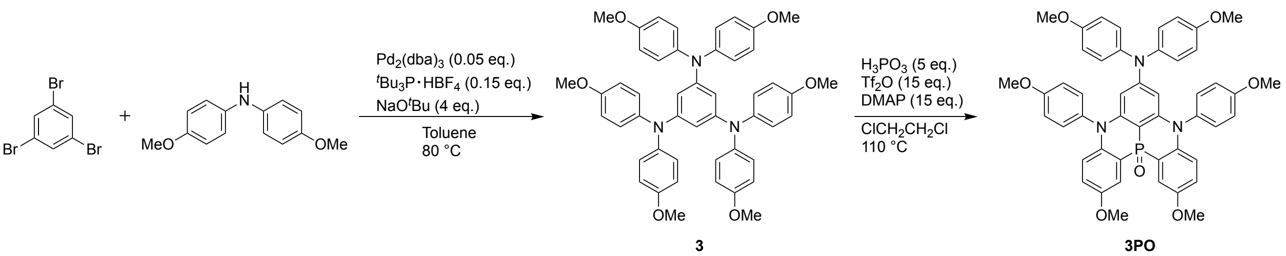
Scheme S1. Synthesis of **2**.

1,3,5-Tris{di(*p*-trifluoromethylphenyl)amino}benzene (2):

A mixture of 1,3,5-tribromobenzene (402.3 mg, 1.28 mmol), di(*p*-trifluoromethylphenyl)amine (1.300 g, 4.26 mmol), $Pd_2(dba)_3$ (59.3 mg, 0.065 mmol), ^{t}Bu$_3$P·HBF$_4$ (57.8 mg, 0.20 mmol), and NaO^{t}Bu (491.1 mg, 5.11 mmol) in toluene (10 mL) was heated at 100 °C for 18 h under an argon atmosphere. After cooling to room temperature, the product was extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [hexane/ethyl acetate (20:1)] to afford **2** as a white solid (302.3 mg, 0.31 mmol, 24%).

2: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.47 (d, J = 8.7 Hz, 12H, Ar-H), 7.11 (d, J = 8.5 Hz, 12H, Ar-H), and 6.47 (s, 3H, Ar-H) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 149.2, 148.8, 126.9, 125.8 (q, J_{CF} = 32.8 Hz), 124.1 (q, J_{CF} = 271.7 Hz), 123.7, and 116.8 ppm; ^{19}F NMR (376.17 MHz, $CDCl_3$, 25 °C): δ = –62.7 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 307 (71000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 377 nm (Φ_F = 0.07). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 430 nm.

FT-IR (ATR): ν = 1162 (F–C) and 1101 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{48}H_{28}F_{18}N_3$ $[M+H]^+$ 988.1990; found 988.1997. m.p.: 208-209 °C.



Scheme S2. Synthesis of **3PO**.

1,3,5-Tris{di(*p*-methoxyphenyl)amino}benzene (3):

A mixture of 1,3,5-tribromobenzene (503.1 mg, 1.60 mmol), di(*p*-methoxyphenyl)amine (1.236 g, 5.39 mmol), $Pd_2(dba)_3$ (73.5 mg, 0.080 mmol), ^{t}Bu$_3$P·HBF$_4$ (71.8 mg, 0.25 mmol), and NaO^{t}Bu (613.7 mg, 6.39 mmol) in toluene (13 mL) was heated at 80 °C for 16 h under an argon atmosphere. After cooling to room temperature, the product was extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [hexane/CH_2Cl_2 (1:1)] to afford **3** as a white solid (1.021 g, 1.34 mmol, 84%).

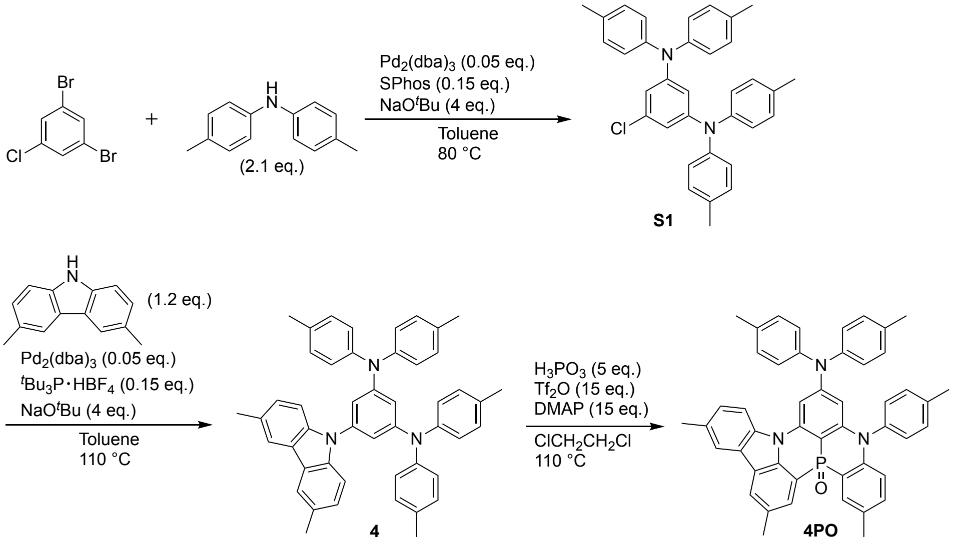
3[S5]**:** ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 6.93 (d, J = 9.2 Hz, 12H, Ar-H), 6.70 (d, J = 9.2 Hz, 12H, Ar-H), 6.05 (s, 3H, Ar-H), and 3.74 (s, 18H, -OCH_3) ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 305 (71000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 406 nm (Φ_F = 0.07). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 450 nm.

Compound 3PO:

The reaction was performed according to the General Procedure at 110 °C for 20 min using **3** (50.8 mg, 0.067 mmol), DMAP (122.3 mg, 1.00 mmol), H_3PO_3 (28.2 mg, 0.34 mmol), and Tf_2O (0.165 mL, 0.98 mmol) in 1,2-dichloroethane (0.5 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (1:1)] to afford **3PO** as a white solid (3.5 mg, 0.0044 mmol, 6%).

3PO: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.81 (d, J = 12.4 Hz, 2H, Ar-H), 7.13 (d, J = 9.2 Hz, 4H, Ar-H), 6.91 (d, J = 9.2 Hz, 4H, Ar-H), 6.86 (m, 2H, Ar-H), 6.84 (d, J = 9.2 Hz, 4H, Ar-H), 6.65 (d, J = 9.2 Hz, 4H, Ar-H), 6.63 (m, 2H, Ar-H), 5.37 (d, J = 4.1 Hz, 2H, Ar-H), 3.89 (s, 6H, -OCH_3), 3.82 (s, 6H, -OCH_3), and 3.76 (s, 6H, -OCH_3) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 159.3, 156.6, 153.7 (d, J_{PC} = 12.5 Hz), 152.2, 147.1, 140.0, 139.2, 134.0, 131.7, 127.8, 120.0 (d, J_{PC} = 7.7 Hz), 118.9, 117.5 (d, J_{PC} = 116 Hz), 115.7, 114.4, 112.4, 99.3 (d, J_{PC} = 107 Hz), 98.2, 55.9, 55.6, and 55.5 ppm; ^{31}P NMR (161.8 MHz, $CDCl_3$, 25 °C): δ = –22.4 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 308 (40000), and 376 (15000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 393 nm (Φ_F = 0.13). Phosphorescence (2-MeTHF, –190 °C,

λ_{ex} = 340 nm): λ_{max} = 433 nm. FT-IR (ATR): ν = 1150 (P=O) 1106 (N–C) and 1029 (C–O–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{48}H_{43}N_3O_7P_1$ [*M*+H]$^+$ 804.2833; found 804.2833. m.p.: 259-260 °C.



Scheme S3. Synthesis of **4PO**.

1-Chloro-3,5-bis{di-(*p*-tolyl)amino}benzene (S1):

A mixture of 1,3-dibromo-5-chlorobenzene (410.3 mg, 1.52 mmol), di(*p*-tolyl)amine (629.2 mg, 3.19 mmol), $Pd_2(dba)_3$ (70.1 mg, 0.077 mmol), S-Phos (94.9 mg, 0.23 mmol), and NaO^{t}Bu (585.7 mg, 6.09 mmol) in toluene (20 mL) was heated at 80 °C for 17 h under an argon atmosphere. After cooling to room temperature, the product was extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [hexane/CH_2Cl_2 (8:1)] to afford **S1** as a white solid (540.5 mg, 1.07 mmol, 71%).

S1: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.02 (d, *J* = 8.4 Hz, 8H, Ar-H), 6.93 (d, *J* = 8.4 Hz, 8H, Ar-H), 6.51 (t, *J* = 2.0 Hz, 1H, Ar-H), 6.45 (d, *J* = 2.4 Hz, 2H, Ar-H), and 2.28 (s, 12H, -CH_3) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 149.7, 144.7, 135.0, 133.0, 130.0, 124.9, 115.0, 114.1, and 20.9 ppm. FT-IR (ATR): ν = 1098 (N–C) and 682 (Cl–C) cm^{-1}. HRMS (ESI, positive) calcd. for $C_{34}H_{32}Cl_1N_2$ [*M*+H]$^+$ 503.2249; found 503.2248. m.p.: 153–155 °C.

1-(3,6-Dimethylcarbazolyl)-3,5-bis{di-(*p*-tolyl)amino}benzene (4):

A mixture of **S1** (540.5 mg, 1.07 mmol), 3,6-dimethylcarbazole (251.5 mg, 1.29 mmol), $Pd_2(dba)_3$ (50.1 mg, 0.055 mmol), ^{t}Bu$_3$P·HBF$_4$ (47.2 mg, 0.16 mmol), and NaO^{t}Bu (415.6 mg, 4.32 mmol) in toluene (15 mL) was heated at 110 °C for 16 h under an argon atmosphere. After cooling to room temperature, the product was extracted with dichloromethane. The combined organic extracts were dried over

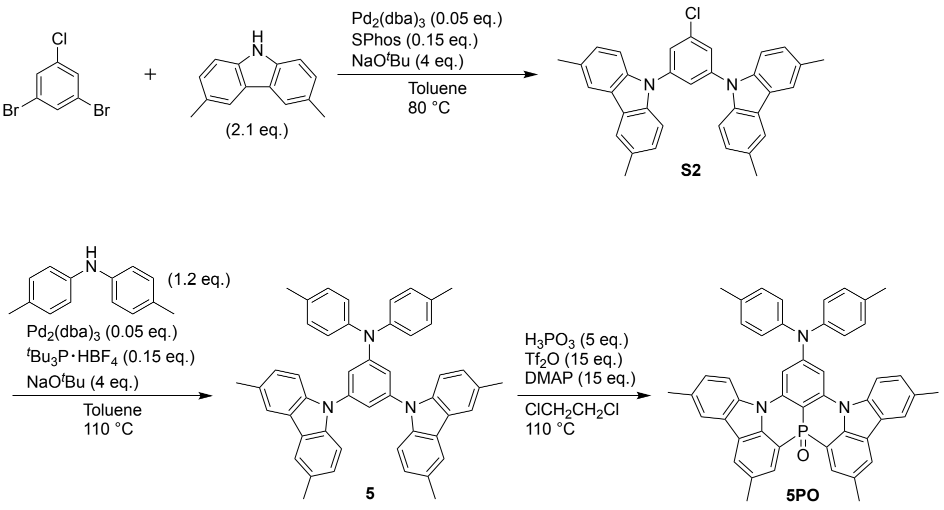
Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [hexane/CH_2Cl_2 (1:1)] to afford **4** as a white solid (687.8 mg, 1.04 mmol, 97%).

4: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.80 (s, 2H, Ar-H), 7.28 (d, J = 8.4 Hz, 2H, Ar-H), 7.15 (dd, J = 8.2 Hz, J = 1.4 Hz, 2H, Ar-H), 7.03 (16H, Ar-H), 6.72 (t, J = 2.0 Hz, 1H, Ar-H), 6.65 (d, J = 2.4 Hz, 2H, Ar-H), 2.49 (s, 6H, -CH_3), and 2.27 (s, 12H, -CH_3) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 149.9, 144.9, 139.2, 138.9, 132.8, 130.0, 128.9, 126.9, 124.8, 123.4, 120.1, 114.2, 113.2, 109.9, 21.5, and 20.9 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 351 (11000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 391 nm (Φ_F = 0.07). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 432 nm. FT-IR (ATR): ν = 1111 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{48}H_{44}N_3$ [M+H]$^+$ 662.3530; found 662.3527. m.p.: 220-222 °C.

Compound 4PO:

The reaction was performed according to the General Procedure at 110 °C for 20 min using **4** (50.8 mg, 0.077 mmol), DMAP (139.9 mg, 1.15 mmol), H_3PO_3 (31.5 mg, 0.38 mmol), and Tf_2O (0.190 mL, 1.15 mmol) in 1,2-dichloroethane (0.5 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **4PO** as a white solid (19.5 mg, 0.028 mmol, 36%).

4PO: ^{1}H NMR (399.78 MHz, $CDCl_3$, 25 °C): δ = 8.22 (dd, J = 12.4 Hz, J = 1.6 Hz, 1H, Ar-H), 8.08 (d, J = 11.2 Hz, 1H, Ar-H), 7.96 (s, 1H, Ar-H), 7.83 (s, 1H, Ar-H), 7.40 (d, J = 8.8 Hz, 1H, Ar-H), 7.37 (m, 1H, Ar-H), 7.22 (d, J = 8.0 Hz, 2H, Ar-H), 6.99–7.12 (m, 12H, Ar-H), 6.50 (dd, J = 8.8 Hz, J = 6.4 Hz, 1H, Ar-H), 5.69 (dd, J = 4.0 Hz, J = 2.0 Hz, 1H, Ar-H), 2.67 (s, 3H, -CH_3), 2.49 (s, 3H, -CH_3), 2.46 (s, 3H, -CH_3), 2.38 (s, 3H, -CH_3), and 2.37 (s, 6H, -CH_3) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 151.9, 147.8, 143.9, 143.34, 143.31, 142.0, 139.1, 138.5 (d, J_{PC} = 10.6 Hz), 137.8, 134.1, 133.0, 132.3 (d, J_{PC} = 10.6 Hz), 131.6, 130.8 (d, J_{PC} = 117 Hz), 130.7 (d, J_{PC} = 10.6 Hz), 130.0, 128.0, 126.4, 126.3, 126.2 (d, J_{PC} = 8.6 Hz), 125.2 (d, J_{PC} = 6.7 Hz), 123.2, 121.0, 118.1 (d, J_{PC} = 7.7 Hz), 116.6 (d, J_{PC} = 115 Hz), 115.7, 114.7 (d, J_{PC} = 8.7 Hz), 102.44, 102.39, 100.07, 100.02, 94.8 (d, J_{PC} = 106 Hz), 22.0, 21.3, 21.3, 21.0, and 20.8 ppm; ^{31}P NMR (161.8 MHz, $CDCl_3$, 25 °C): δ = –20.8 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 382 (16000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 398 nm (Φ_F = 0.19). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 436 nm. FT-IR (ATR): ν = 1154 (P=O) and 1102 (N–C) cm^{-1}. HRMS (ESI, positive) calcd. for $C_{48}H_{40}N_3O_1P_1Na_1$ [M+Na]$^+$ 728.2801; found 728.2794. m.p.: >300 °C.



Scheme S4. Synthesis of **5PO**.

1-Chloro-3,5-bis(3,6-dimethylcarbazolyl)benzene (S2):

A mixture of 1,3-dibromo-5-chlorobenzene (162.0 mg, 0.60 mmol), 3,6-dimethylcarbazole (248.1 mg, 1.27 mmol), $Pd_2(dba)_3$ (28.7 mg, 0.031 mmol), S-Phos (37.9 mg, 0.92 mmol), and NaO^{t}Bu (232.5 mg, 2.42 mmol) in toluene (8 mL) was heated at 80 °C for 16 h under an argon atmosphere. After cooling to room temperature, the product was extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [silica, hexane/CH_2Cl_2 (8:1)] to afford **S2** as a white solid (221.3 mg, 0.44 mmol, 74%).

S2: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.89 (s, 4H, Ar-H), 7.70 (t, *J* = 1.8 Hz, 1H, Ar-H), 7.64 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.43 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.24 (dd, *J* = 8.6 Hz, *J* = 1.8 Hz, 4H, Ar-H), and 2.54 (s, 12H, -CH_3) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 140.8, 138.8, 136.5, 130.1, 127.5, 125.0, 124.0, 122.7, 120.5, 109.5, and 21.5 ppm. FT-IR (ATR): ν = 1112 (N–C) and 700 (Cl–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{34}H_{28}Cl_1N_2$ [*M*+H]$^+$ 499.1936; found 499.1917. m.p.: 215-217 °C.

1,3-Bis(3,6-dimethylcarbazolyl)-5-{di-(*p*-tolyl)amino}benzene (5):

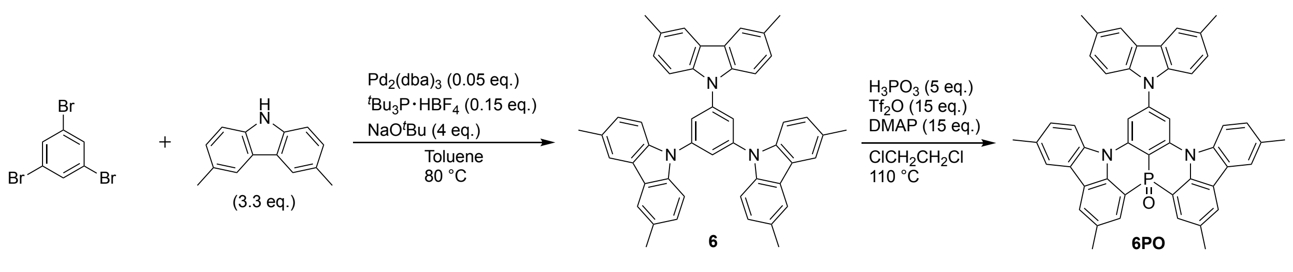
A mixture of **S2** (215.7 mg, 0.43 mmol), di-(*p*-tolyl)amine (180.2 mg, 0.91 mmol), $Pd_2(dba)_3$ (20.5 mg, 0.022 mmol), ^{t}Bu$_3$P·HBF$_4$ (19.9 mg, 0.69 mmol), and NaO^{t}Bu (170.2 mg, 1.77 mmol) in toluene (6 mL) was heated at 110 °C for 17 h under an argon atmosphere. After cooling to room temperature, the product was extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [silica, hexane/CH_2Cl_2 (1:1)] to afford **5** as a white solid (283.2 mg, 0.43 mmol, 99%).

5: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.85 (s, 4H, Ar-H), 7.40 (d, J = 8.4 Hz, 4H, Ar-H), 7.25 (t, J = 1.8 Hz, 1H, Ar-H), 7.20 (d, J = 8.4 Hz, 8H, Ar-H), 7.16 (d, J = 2.0 Hz, 2H, Ar-H), 7.13 (d, J = 8.0 Hz, 4H, Ar-H), 2.52 (s, 12H, $-CH_3$), and 2.31 (s, 6H, $-CH_3$) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 151.0, 144.5, 140.0, 138.9, 134.1, 130.4, 129.4, 127.2, 125.6, 123.6, 120.3, 116.8, 115.8, 109.8, 21.5, and 21.0 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 335 (15000), and 351 (15000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 369 nm (Φ_F = 0.08). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 426 nm. FT-IR (ATR): ν = 1106 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{48}H_{42}N_3$ $[M+H]^+$ 660.3373; found 660.3370. m.p.: 227-229 °C.

Compound 5PO:

The reaction was performed according to the General Procedure at 110 °C for 20 min using **5** (50.4 mg, 0.076 mmol), DMAP (135.8 mg, 1.11 mmol), H_3PO_3 (31.5 mg, 0.38 mmol), and Tf_2O (0.190 mL, 1.15 mmol) in 1,2-dichloroethane (0.5 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] and preparative TLC [silica, Toluene/MeOH (10:1)] to afford **5PO** as a white solid (10.4 mg, 0.015 mmol, 19%).

5PO: ^{1}H NMR (399.78 MHz, $CDCl_3$, 25 °C): δ = 8.18 (d, J = 11.6 Hz, 2H, Ar-H), 8.01 (s, 2H, Ar-H), 7.86 (s, 2H, Ar-H), 7.63 (d, J = 3.6 Hz, 2H, Ar-H), 7.51 (d, J = 8.8 Hz, 2H, Ar-H), 7.22 (d, J = 3.2 Hz, 8H, Ar-H), 7.09 (dd, J = 8.8 Hz, J = 1.2 Hz, 2H, Ar-H), 2.71 (s, 6H, $-CH_3$), 2.51 (s, 6H, $-CH_3$), and 2.42 (s, 6H, $-CH_3$) ppm; ^{13}C NMR (100.53 MHz, $CDCl_3$, 25 °C): δ = 152.7, 143.8, 143.4, 139.3, 137.8, 135.1, 132.7 (d, J_{PC} = 11.6 Hz), 131.9, 130.6, 128.1, 126.8 (d, J_{PC} = 4.8 Hz), 126.7, 126.2, 125.0 (d, J_{PC} = 5.8 Hz), 123.8, 121.2, 114.71 (d, J_{PC} = 114 Hz), 114.68, 101.8 (d, J_{PC} = 5.8 Hz), 99.0 (d, J_{PC} = 107 Hz), 22.0, 21.4, and 21.2 ppm; ^{31}P NMR (161.8 MHz, $CDCl_3$, 25 °C): δ = –18.5 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 351 (13000) and 387 (22000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 396 nm (Φ_F = 0.25). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 437 nm. FT-IR (ATR): ν = 1156 (P=O) and 1096 (N–C) cm^{-1}. HRMS (ESI, positive) calcd. for $C_{48}H_{38}N_3O_1P_1Na_1$ $[M+Na]^+$ 726.2645; found 726.2639. m.p.: >300 °C.



Scheme S5. Synthesis of **6PO**.

1,3,5-Tris(3,6-dimethylcarbazolyl)benzene (6):

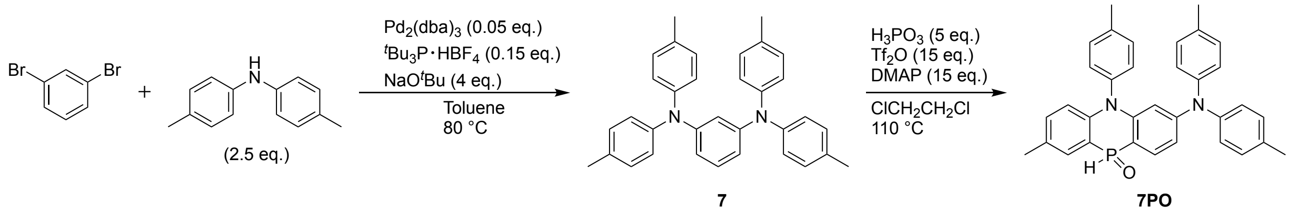
A mixture of 1,3,5-tribromobenzene (191 mg, 0.61 mmol), 3,6-dimethylcarbazole (395 mg, 2.02 mmol), $Pd_2(dba)_3$ (27.5 mg, 0.03 mmol), $^{t}Bu_3P\cdot HBF_4$ (26.8 mg, 0.09 mmol), and NaO^{t}Bu (235 mg, 2.43 mmol) in toluene (5 mL) was heated at 80 °C for 17 h under an argon atmosphere. After cooling to room temperature, the product was extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [silica, hexane/CH_2Cl_2 (2:1)] to afford **6** as a white solid (346.6 mg, 0.53 mmol, 87%).

6: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.91 (s, 6H, Ar-H), 7.86 (s, 3H, Ar-H), 7.54 (d, J = 8.2 Hz, 6H, Ar-H), 7.25 (dd, J = 8.2 Hz, J = 1.4 Hz, 6H, Ar-H) and 2.54 (s, 18H, $-CH_3$) ppm; ^{13}C NMR (100.53 MHz, $CDCl_3$, 25 °C): δ = 141.1, 138.9, 130.0, 127.5, 124.0, 122.5, 120.6, 109.6, and 21.5 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 333 (15000), and 349 (14000) nm. Fluorescence (Toluene, λ_{ex} = 320 nm): λ_{max} = 355 nm (Φ_F = 0.20). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 417 nm. FT-IR (ATR): ν = 1145 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{48}H_{40}N_3$ $[M+H]^+$ 658.3217; found 658.3216. m.p.: >300 °C.

Compound 6PO:

The reaction was performed according to the General Procedure at 110 °C for 20 min using **6** (50.5 mg, 0.077 mmol), DMAP (141.0 mg, 1.15 mmol), H_3PO_3 (31.9 mg, 0.39 mmol), and Tf_2O (0.195 mL, 1.19 mmol) in 1,2-dichloroethane (0.5 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **6PO** as a white solid (2.3 mg, 0.0033 mmol, 4%).

6PO: ^{1}H NMR (399.78 MHz, $CDCl_3$, 25 °C): δ = 8.38 (d, J = 4.0 Hz, 2H, Ar-H), 8.28 (d, J = 10.8 Hz, 2H, Ar-H), 8.11 (s, 2H, Ar-H), 7.97 (d, J = 8.8 Hz, 2H, Ar-H), 7.94 (d, J = 4.4 Hz, 4H, Ar-H), 7.49 (d, J = 8.4 Hz, 2H, Ar-H), 7.30 (dd, J = 8.2 Hz, J = 1.4 Hz, 2H, Ar-H), 7.28 (m, 2H, Ar-H), 2.77 (s, 6H, $-CH_3$), 2.57 (s, 6H, $-CH_3$), and 2.53 (s, 6H, $-CH_3$) ppm; ^{13}C NMR (100.53 MHz, $CDCl_3$, 25 °C): δ = 144.2, 142.4, 139.4, 139.0, 137.8, 133.5 (d, J_{PC} = 10.6 Hz), 132.8, 130.2, 129.0, 127.8, 127.0 (d, J_{PC} = 5.8 Hz), 126.4, 125.5 (d, J_{PC} = 6.7 Hz), 124.3, 124.1, 121.5, 120.6, 114.9, 114.3 (d, J_{PC} = 117 Hz), 109.5, 108.8 (d, J_{PC} = 5.8 Hz), 105.8 (d, J_{PC} = 103 Hz), 22.0, 21.6, and 21.4 ppm; ^{31}P NMR (161.8 MHz, $CDCl_3$, 25 °C): δ = –18.4 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 349 (12000) and 387 (22000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 394 nm (Φ_F = 0.27). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 440 nm. FT-IR (ATR): ν = 1163 (P=O) and 1148 (N–C) cm^{-1}. HRMS (ESI, positive) calcd. for $C_{48}H_{36}N_3O_1P_1Na_1$ $[M+Na]^+$ 724.2488; found 724.2492. m.p.: >300 °C.



Scheme S6. Synthesis of **7PO**.

1,3-Bis{di(*p*-tolyl)amino}benzene (7):

A mixture of 1,3-dibromobenzene (0.380 mL, 3.14 mmol), di(*p*-tolyl)amine (1.55 g, 7.85 mmol), $Pd_2(dba)_3$ (147.1 mg, 0.16 mmol), ^{t}Bu$_3$P·HBF$_4$ (138.3 mg, 0.48 mmol), and NaO^{t}Bu (1.27 g, 13.2 mmol) in toluene (22 mL) was heated at 80 °C for 16 h under an argon atmosphere. After cooling to room temperature, the product was extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [hexane/CH_2Cl_2 (3:1)] to afford **7** as a white solid (1.45 g, 3.09 mmol, 99%).

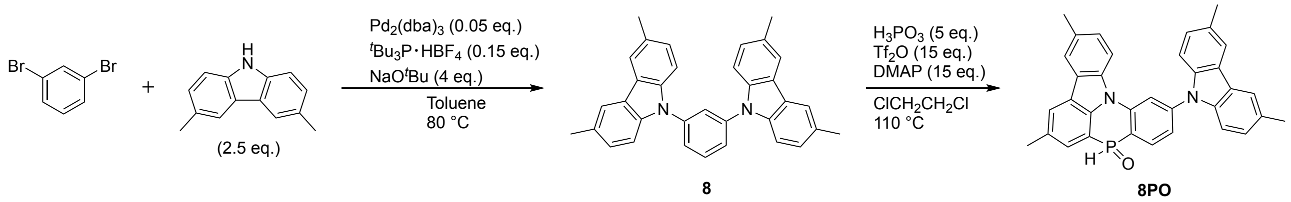
7: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.03 (d, *J* = 8.2 Hz, 9H, Ar-H), 6.98 (d, *J* = 8.2 Hz, 8H, Ar-H), 6.79 (t, *J* = 2.3 Hz, 1H, Ar-H), 6.58 (dd, *J* = 8.2 Hz, *J* = 2.3 Hz, 2H, Ar-H), and 2.30 (s, 12H, -CH_3) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 148.9, 145.3, 132.1, 129.8, 129.5, 124.3, 118.1, 116.9, and 20.9 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 304 (49000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 388 nm (Φ_F = 0.06). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 431 nm. FT-IR (ATR): ν = 1145 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{34}H_{33}N_2$ [*M*+H]$^+$ 469.2638; found 469.2633. m.p.: 100-101 °C.

Compound 7PO:

The reaction was performed according to the General Procedure at 110 °C for 20 min using **7** (50.1 mg, 0.11 mmol), DMAP (197.3 mg, 1.61 mmol), H_3PO_3 (44.8 mg, 0.55 mmol), and Tf_2O (0.270 mL, 1.60 mmol) in 1,2-dichloroethane (0.7 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **7PO** as a white solid (24.8 mg, 0.048 mmol, 45%).

7PO: ^{1}H NMR (399.78 MHz, $CDCl_3$, 25 °C): δ = 8.77 (d, *J* = 509 Hz, 1H, P-H), 7.77 (d, *J* = 14.6 Hz, 1H, Ar-H), 7.71 (dd, *J* = 14.2 Hz, *J* = 8.7 Hz, 1H, Ar-H), 7.19 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.10 (dd, *J* = 8.7 Hz, *J* = 1.8 Hz, 1H, Ar-H), 7.00 (d, *J* = 7.8 Hz, 4H, Ar-H), 6.93 (d, *J* = 8.2 Hz, 2H, Ar-H), 6.89 (d, *J* = 8.7 Hz, 4H, Ar-H), 6.71 (d, *J* = 9.2 Hz, 1H, Ar-H), 6.39 (dd, *J* = 8.7 Hz, *J* = 6.4 Hz, 1H, Ar-H), 5.70 (dd, *J* = 5.5 Hz, *J* = 1.8 Hz, 1H, Ar-H), 2.36 (s, 3H, -CH_3), 2.34 (s, 3H, -CH_3), and 2.30 (s, 6H, -CH_3) ppm; ^{13}C NMR (100.52 MHz, $CDCl_3$, 25 °C): δ = 152.4, 146.3, 143.5, 142.9, 138.5, 138.2, 134.3, 134.0, 133.3, 132.5, 131.4, 130.4, 130.04, 129.98, 126.3, 117.4 (d, J_{PC} = 6.7 Hz), 112.8 (d, J_{PC} = 11.6 Hz), 111.9 (d, J_{PC} = 99.2 Hz), 106.6

(d, J_{PC} = 7.7 Hz), 102.5 (d, J_{PC} = 107.9 Hz), 21.2, 21.0, and 20.4 ppm; ^{31}P NMR (161.8 MHz, $CDCl_3$, 25 °C): δ = –9.04 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 349 (13000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 400 nm (Φ_F = 0.28). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 443 nm. FT-IR (ATR): ν = 2316 (P–H), 1185 (P=O), and 1148 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{34}H_{32}N_2O_1P_1$ $[M+H]^+$ 515.2247; found 515.2246. m.p.: 121-122 °C.



Scheme S7. Synthesis of **8PO**.

1,3-Bis(3,6-dimethylcarbazolyl)benzene (8):

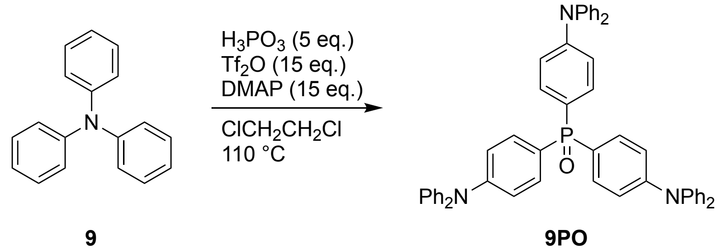
A mixture of 1,3-dibromobenzene (0.100 mL, 0.83 mmol), 3,6-dimethylcarbazole (407.3 mg, 2.09 mmol), $Pd_2(dba)_3$ (39.1 mg, 0.043 mmol), $^tBu_3P\cdot HBF_4$ (37.8 mg, 0.13 mmol), and NaO^tBu (323.5 mg, 3.37 mmol) in toluene (7 mL) was heated at 80 °C for 16 h under an argon atmosphere. After cooling to room temperature, and the product was extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [hexane/CH_2Cl_2 (4:1)] to afford **8** as a white solid (205.2 mg, 0.44 mmol, 53%).

8: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.92 (s, 4H, Ar-H), 7.78-7.82 (m, 2H, Ar-H), 7.65 (dd, J = 7.8 Hz, J = 1.8 Hz, 2H, Ar-H), 7.44 (d, J = 8.7 Hz, 4H, Ar-H), 7.25 (dd, J = 8.2 Hz, J = 0.9 Hz, 4H, Ar-H), and 2.56 (s, 12H, $-CH_3$) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 139.8, 139.2, 131.1, 129.6, 127.4, 125.2, 124.7, 123.8, 120.4, 109.5, and 21.5 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 336 (13000) and 350 (14000) nm. Fluorescence (Toluene, λ_{ex} = 320 nm): λ_{max} = 353 nm (Φ_F = 0.20). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 417 nm. FT-IR (ATR): ν = 1141 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{34}H_{29}N_2$ $[M+H]^+$ 465.2325; found 465.2323. m.p.: 105-106 °C.

Compound 8PO:

The reaction was performed according to the General Procedure at 110 °C for 20 min using **8** (50.0 mg, 0.11 mmol), DMAP (198.1 mg, 1.62 mmol), H_3PO_3 (44.6 mg, 0.54 mmol), and Tf_2O (0.270 mL, 1.60 mmol) in 1,2-dichloroethane (0.7 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **8PO** as a white solid (5.0 mg, 0.010 mmol, 9%).

8PO: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 8.95 (d, J = 516 Hz, 1H, P-H), 8.49 (dd, J = 5.5 Hz, J = 1.8 Hz 1H, Ar-H), 8.41 (dd, J = 14.2 Hz, J = 8.2 Hz 1H, Ar-H), 8.10 (s 1H, Ar-H), 7.98 (d, J = 13.7 Hz, 1H, Ar-H), 7.94 (s 2H, Ar-H), 7.91 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.63 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.49 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.28 (m, 3H, Ar-H), 2.66 (s, 3H, $-CH_3$), 2.57 (s, 6H, $-CH_3$), and 2.51 (s, 3H, $-CH_3$) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 143.3, 141.9, 138.8, 138.0, 137.3, 135.9, 133.4 (d, J_{PC} = 11.6 Hz), 132.8, 130.3, 129.8, 129.1, 127.7, 126.0, 125.2, 124.9, 124.2, 121.5, 121.3 (d, J_{PC} = 11.6 Hz), 120.6, 114.4 (d, J_{PC} = 98.3 Hz), 113.9, 113.7 (d, J_{PC} = 6.7 Hz), 110.5 (d, J_{PC} = 102 Hz), 109.5, 21.60, 21.55, and 21.3 ppm; ^{31}P NMR (161.8 MHz, $CDCl_3$, 25 °C): δ = –9.72 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 338 (17000), 348 (17000), and 365 (9000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 377 nm (Φ_F = 0.31). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 440 nm. FT-IR (ATR): ν = 2314 (P–H), 1176 (P=O), and 1157 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{34}H_{28}N_2O_1P_1$ [*M*+H]$^+$ 511.1934; found 511.1932. m.p.: 197-198 °C.

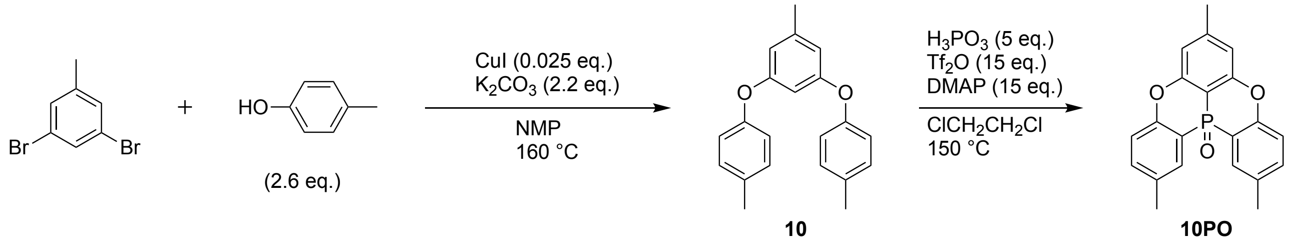


Scheme S8. Synthesis of **9PO**.

Compound 9PO:

The reaction was performed according to the General Procedure at 110 °C for 20 min using **9** (50.9 mg, 0.21 mmol), DMAP (381.7 mg, 3.12 mmol), H_3PO_3 (86.0 mg, 1.05 mmol), and Tf_2O (0.520 mL, 3.07 mmol) in 1,2-dichloroethane (1.4 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **9PO** as a white solid (16.4 mg, 0.021 mmol, 30%).

9PO[S6]**:** ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): δ = 7.46 (dd, *J* = 11.4 Hz, *J* = 8.7 Hz, 6H, Ar-H), 7.29 (dd, *J* = 8.2 Hz, *J* = 7.3 Hz, 12H, Ar-H), 7.13 (dd, *J* = 8.7 Hz, *J* = 0.9 Hz, 12H, Ar-H), 7.08 (dd, *J* = 9.2 Hz, *J* = 2.3 Hz, 6H, Ar-H), and 7.02 (dd, *J* = 9.2 Hz, *J* = 2.3 Hz, 6H, Ar-H) ppm; ^{31}P NMR (161.8 MHz, $CDCl_3$, 25 °C): δ = 30.0 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 329 (42000) nm. Fluorescence (Toluene, λ_{ex} = 340 nm): λ_{max} = 374 nm (Φ_F = 0.40). Phosphorescence (2-MeTHF, –190 °C, λ_{ex} = 340 nm): λ_{max} = 431 nm. FT-IR (ATR): ν = 1175 (P=O), and 1112 (N–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{54}H_{43}N_3O_1P_1$ [*M*+H]$^+$ 780.3138; found 780.3147. m.p.: 131-132 °C.



Scheme S9. Synthesis of **10PO**.

3,5-Bis(4-methylphonoxy)toluene (10):

A mixture of 3,5-dibromotoluene (500.7 mg, 2.00 mmol), *p*-cresol (564.8 mg, 5.22 mmol), CuI (9.9 mg, 0.052 mmol), and K_2CO_3 (610.1 mg, 4.41 mmol) in *N*-methyl-2-pyrrolidone (1.3 mL) was heated at 160 °C for 17 h under an argon atmosphere. After cooling to room temperature, the mixture was filtered through Celite and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [hexane/CH_2Cl_2 (8:1)] to afford **10** as a white solid (461.1 mg, 1.51 mmol, 73%).

10: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): $\delta = 7.14$ (d, $J = 8.7$ Hz, 4H, Ar-H), 6.93 (d, $J = 8.7$ Hz, 4H, Ar-H), 6.49 (d, $J = 1.4$ Hz, 2H, Ar-H), 6.46 (t, $J = 2.3$ Hz, 1H, Ar-H), 2.34 (s, 6H, -CH_3), and 2.26 (s, 3H, -CH_3) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 159.0, 154.5, 140.9, 133.2, 130.4, 119.4, 113.3, 105.8, 21.7, and 20.9 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 282 (2700) nm. Fluorescence (Toluene, λ_{ex} = 270 nm): λ_{max} = 303 nm. FT-IR (ATR): ν = 1122 (N–C) and 1104 (C–O–C) cm^{-1}. HRMS (APCI, positive) calcd. for $C_{21}H_{21}O_2$ [*M*+H]$^+$ 305.1536; found 305.1530. m.p.: 81-83 °C.

Compound 10PO:

The reaction was performed according to the General Procedure at 150 °C for 5 min using **10** (48.1 mg, 0.16 mmol), DMAP (280.0 mg, 2.29 mmol), H_3PO_3 (63.2 mg, 0.77 mmol), and Tf_2O (0.380 mL, 2.32 mmol) in 1,2-dichloroethane (1.0 mL). The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **10PO** as a white solid (2.9 mg, 0.0083 mmol, 5%).

10PO: ^{1}H NMR (399.38 MHz, $CDCl_3$, 25 °C): $\delta = 7.93$ (d, $J = 12.4$ Hz, 2H, Ar-H), 7.39 (dd, $J = 8.7$ Hz, $J = 1.8$ Hz 2H, Ar-H), 7.27 (dd, $J = 8.7$ Hz, $J = 6.4$ Hz, 2H, Ar-H), 6.94 (d, $J = 4.1$ Hz, 2H, Ar-H), 2.48 (s, 6H, -CH_3), and 2.46 (s, 3H, -CH_3) ppm; ^{13}C NMR (100.42 MHz, $CDCl_3$, 25 °C): δ = 156.8, 155.6, 145.6, 134.4, 134.2 (d, J_{PC} = 10.6 Hz), 129.2, 119.8 (d, J_{PC} = 6.7 Hz), 117.6 (d, J_{PC} = 115.6 Hz), 112.6, 100.9 (d, J_{PC} = 100.2 Hz), 22.3, and 21.1 ppm; ^{31}P NMR (161.8 MHz, $CDCl_3$, 25 °C): δ = –30.0 ppm. UV/Vis (Toluene): λ (ε, M^{-1} cm^{-1}) = 289 (4000), and 315 (10000) nm. Fluorescence (Toluene, λ_{ex} = 300 nm): λ_{max} = 332 nm. FT-IR (ATR): ν = 1191 (P=O), 1131 (N–C) and 1115 (C–O–C) cm^{-1}. HRMS (ESI, positive) calcd. for $C_{21}H_{18}O_3P_1$ [*M*+H]$^+$ 349.0988; found 349.0985. m.p.: 260-262 °C.

3. Evaluation of Reaction Conditions

Procedures for $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR Experiments

In an NMR tube, $\mathrm{Tf_2O}$ (1-3 equiv) was added to a mixture of $\mathrm{H_3PO_3}$ (10.3 mg, 1 equiv) and DMAP (1-3 equiv) in $\mathrm{CD_3CN}$ (0.5 mL). The sample tube was immediately transferred to the NMR spectrometer and the $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum was recorded at room temperature.

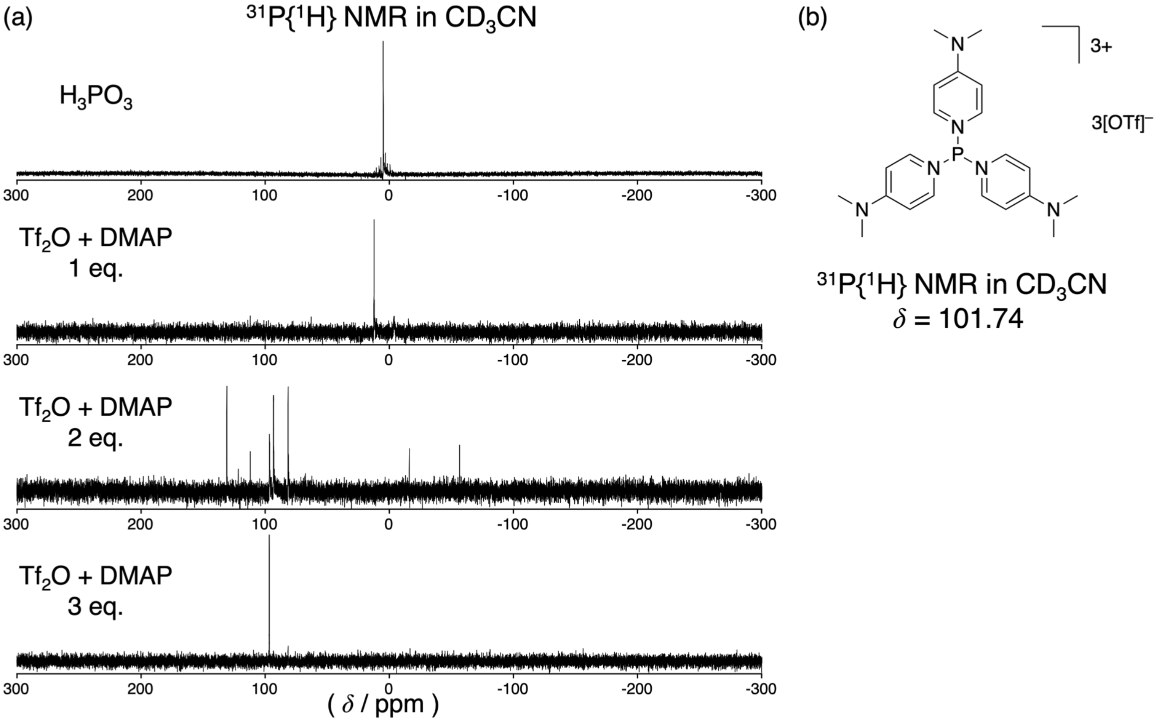
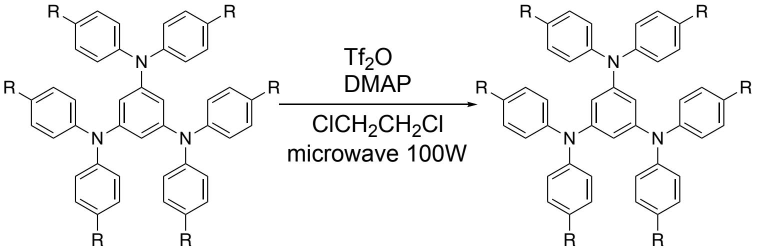


Figure S1. (a) $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectra of $\mathrm{H_3PO_3}$ with $\mathrm{Tf_2O}$ and DMAP in $\mathrm{CD_3CN}$. (b) Structure and chemical shift of $[\mathrm{P(DMAP)_3}][\mathrm{OTf}]_3$.[S7] Upon the addition of 3 equivalents of $\mathrm{Tf_2O}$ and DMAP, the distinct signal was observed at δ = 96.7 ppm, supporting the formation of $[\mathrm{P(DMAP)_3}][\mathrm{OTf}]_3$. Although the same signal at δ = 96.7 ppm was observed upon the addition of 2 equivalents of $\mathrm{Tf_2O}$ and DMAP, no signal corresponding to $[\mathrm{P(DMAP)_3}][\mathrm{OTf}]_3$ was observed in the spectrum with 1 equivalent of $\mathrm{Tf_2O}$ and DMAP.

Table S1. Evaluation of stabilities of amines in the presence of Tf_2O.

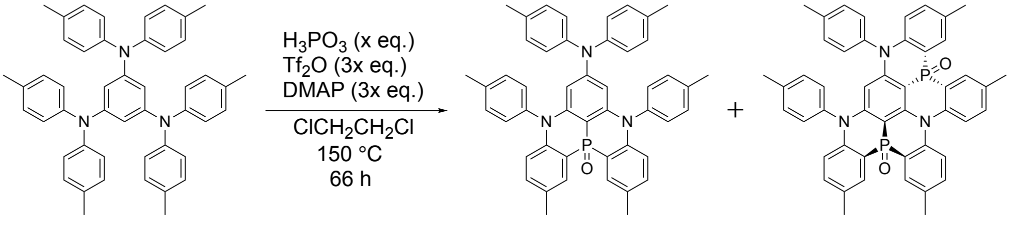


1 (R = Me)
2 (R = CF_3)
3 (R = OMe)

entry	amine	Tf_2O [eq.]	DMAP [eq.]	temp. [°C]	time [min]	recovery of amine [%][a]
1	**1**	0	15	150	5	95
2	**1**	15	15	150	5	49
3	**1**	15	15	110	20	63
4	**1**	30	30	150	15	20
5	**2**	15	15	110	20	93
6	**3**	15	15	110	20	15

[a] Determined by ^1H NMR using CH_2Br_2 as an internal standard.

Table S2. Reaction of **1** with H_3PO_3 using a conventional oil-bath heating.



1 **1PO** **1(PO)₂**

entry	x [eq.]	[**1**] [M]	**1PO** [%][a]	**1(PO)**$_2$ [%][a]
1	5	0.075	10	0.3[b]
2	10	0.075	23	1.5[b]
3	5	0.15	0	12

[a] Isolated yield. [b] NMR yield calculated by using CH_2Br_2 as an internal standard.

Procedure for the oil-bath heating reaction of 1 with H_3PO_3.

1PO (entry 2)

A pressure tube (15 mL ACE pressure tube) was charged with **1** (108.7 mg, 0.164 mmol), DMAP (553.1 mg, 4.53 mmol), and H_3PO_3 (125.8 mg, 1.53 mmol) in 1,2-dichloroethane (2.0 mL), and Tf_2O (0.740 mL, 4.52 mmol) was added. The tube was purged with argon, sealed, and heated at 150 °C in an oil bath for 66 h. After cooling to room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **1PO** as a white solid (26.5 mg, 0.037 mmol, 23%).

1(PO)$_2$ (entry 3)

A pressure tube (15 mL ACE pressure tube) was charged with **1** (102.5 mg, 0.154 mmol), DMAP (290.4 mg, 2.38 mmol), and H_3PO_3 (67.0 mg, 0.82 mmol) in 1,2-dichloroethane (1.0 mL), and Tf_2O (0.370 mL, 2.26 mmol) was added. The tube was purged with argon, sealed, and heated at 150 °C in an oil bath for 66 h. After cooling to room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography [$CHCl_3$/ethyl acetate (5:1)] to afford **1(PO)$_2$** as a white solid (14.1 mg, 0.019 mmol, 12%).

4. X-Ray Crystallographic Details

Table S3. Crystal data of **1PO**, **1(PO)$_2$**, **4PO**, and **5PO**.

	1PO	**1(PO)$_2$**	**4PO**	**5PO**
formula	$C_{48}H_{42}N_3OP\cdot C_6H_{14}\cdot CHCl_3$	$2(C_{48}H_{39}N_3O_2P_2)\cdot$ solvent	$C_{48}H_{40}N_3OP$	$C_{48}H_{38}N_3OP\cdot CH_2Cl_2$
M_r	913.35	1503.52	705.80	788.71
T [K]	143(2)	153(2)	143(2)	143(2)
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	*P*-1 (No.2)	$P2_1/a$ (No.14)	$P2_1/a$ (No.14)	*P*-1 (No.2)
a [Å]	12.1068(3)	31.8252(13)	11.369(4)	9.206(3)
b [Å]	13.6178(3)	10.1657(5)	23.274(7)	15.011(4)
c [Å]	15.8744(4)	35.5011(11)	15.200(7)	15.431(4)
α [°]	84.506(2)	90	90	66.258(6)
β [°]	71.614(2)	90.257(3)	111.820(4)	85.7172(10)
γ [°]	85.016(2)	90	90	85.8719(10)
V [Å^3]	2467.72(11)	11485.4(8)	3734(2)	1944.5(10)
Z	2	4	4	2
ρ_{calcd} [g cm^{-3}]	1.229	0.870	1.256	1.347
F [000]	964	3152	1488	824
crystal size [mm^3]	0.50×0.20×0.10	0.40×0.05×0.05	0.30×0.30×0.30	0.30×0.20×0.20
$2\theta_{max}$ [°]	53.99	52.00	54.94	55.06
reflections collected	19982	76024	29962	15869
independent reflections	10476	22593	8511	8512
parameters	605	1003	484	511
R_1 [$I > 2\sigma(I)$]	0.0656	0.0962	0.0467	0.0401
wR_2 [all data]	0.1978	0.3215	0.1274	0.1019
GOF	1.029	1.016	1.013	1.028
CCDC number	2361474	2361475	2361473	2361472

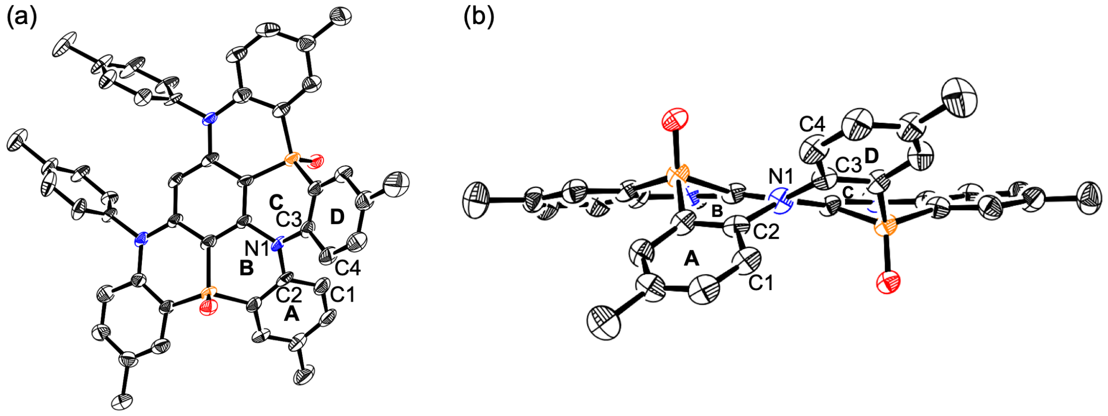


Figure S2. X-Ray crystal structure of **1(PO)**$_2$: (a) top view and (b) side view. Thermal ellipsoids represent 50% probability. One of the two independent molecules in the unsymmetric unit cell is shown. In (b), *p*-tolyl groups are omitted for clarity. Large solvent-accessible voids containing severely disordered solvent molecules were present in the crystal structure. The contribution of the disordered solvent was removed using the PLATON SQUEEZE procedure.

5. Optical Properties

Table S4. Photophysical properties of amines and the P-doped products.

	λ_{abs}[a] [nm] (ε [M^{-1} cm^{-1}])	λ_{fl}[b] [nm] (Φ_{F}[c])	$\Delta\nu$[h] [cm^{-1}]	τ_{F}[i] [ns]	k_{r} [10^{8} s^{-1}]	k_{nr} [10^{8} s^{-1}]	λ_{phos}[j] [nm]	ΔE_{ST}[k] [eV]
1	304 (73000)	391 (0.06)	7300	1.4	0.4	6.7	434	0.31
1PO	364 (15000)	388 (0.11)	1700	0.7	1.6	12.7	423	0.27
1(PO)$_2$	364 (21000)	374 (0.09)	700	0.5	1.8	18.2	408	0.28
2	307 (71000)	377 (0.07)	6000	1.3	0.5	7.2	430	0.41
3	305 (71000)	406 (0.07)	8200	1.7	0.4	5.5	450	0.30
3PO	376 (15000)	393 (0.13)	1200	0.8	1.6	10.9	433	0.29
4	351 (11000)	391 (0.07)	2900	1.6	0.4	5.8	432	0.30
4PO	382 (16000)	398 (0.19)	1100	1.7	1.1	4.8	436	0.27
5	351 (15000)	369 (0.08)	1400	1.9	0.4	4.8	426	0.44
5PO	387 (22000)	396 (0.25)	600	1.6	1.6	4.7	437	0.29
6	349 (14000)	355[d] (0.20)	500	5.6	0.4	1.4	417	0.52
6PO	387 (22000)	394 (0.27)	460	1.4	1.9	5.2	440	0.33
7	304 (49000)	388 (0.06)	7100	1.7	0.4	5.5	431	0.32
7PO	349 (13000)	400 (0.28)	3700	1.4	2.0	5.1	443	0.30
8	350 (14000)	353[d] (0.20)	200	5.7	0.4	1.4	417	0.54
8PO	365 (9000)	377 (0.31)	900	1.9	1.6	3.6	440	0.47
9	301 (23000)	358[d] (0.12)	5300	2.0	0.6	4.4	409	0.43
9PO	329 (42000)	374 (0.40)	3700	1.0	4.0	6.0	431	0.44
10	282 (2700)	303[e] (n.d.[f])	2500	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]
10PO	315 (10000)	332[g] (n.d. [f])	1600	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]

[a] Absorption maxima at the longest wavelength. [b] Fluorescence maxima upon excitation at λ = 340 nm. [c] Absolute fluorescence quantum yields upon excitation at λ = 355 nm. [d] Excited at λ = 320 nm. [e] Excited at λ = 270 nm. [f] Not determined. [g] Excited at λ = 300 nm. [h] Stokes shifts. [i] Fluorescence lifetimes determined by the time-correlated single-photon counting (TCSPC) technique upon excitation at λ = 378 nm. [j] Phosphorescence maxima in 2-MeTHF at –190 °C upon excitation at λ = 340 nm. [k] Energy difference between the S_1 and T_1 states calculated from the fluorescence and phosphorescence maxima.

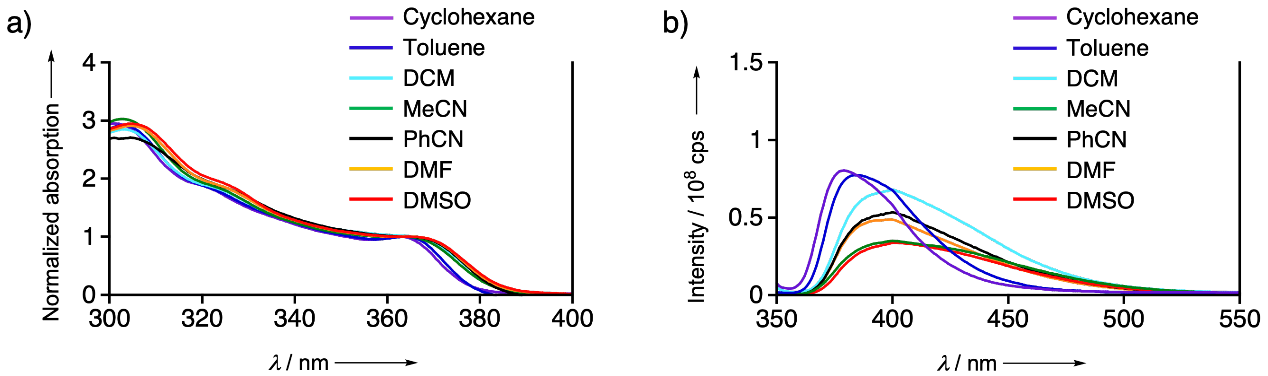


Figure S3. a) UV/Vis absorption and b) fluorescence spectra of **1PO** in various solvents at room temperature. For the fluorescence measurements, the absorbances at 340 nm were adjusted to be identical (0.10) and the samples were excited at λ = 340 nm under the same excitation condition for accurate intensity comparison.

Table S5. Absorption and fluorescence maxima of **1PO** in various solvents.

	cyclohexane	toluene	DCM	MeCN	PhCN	DMF	DMSO
λ_{abs} [nm]	362	364	365	365	365	366	367
λ_{fl} [nm]	379	388	400	400	400	401	405

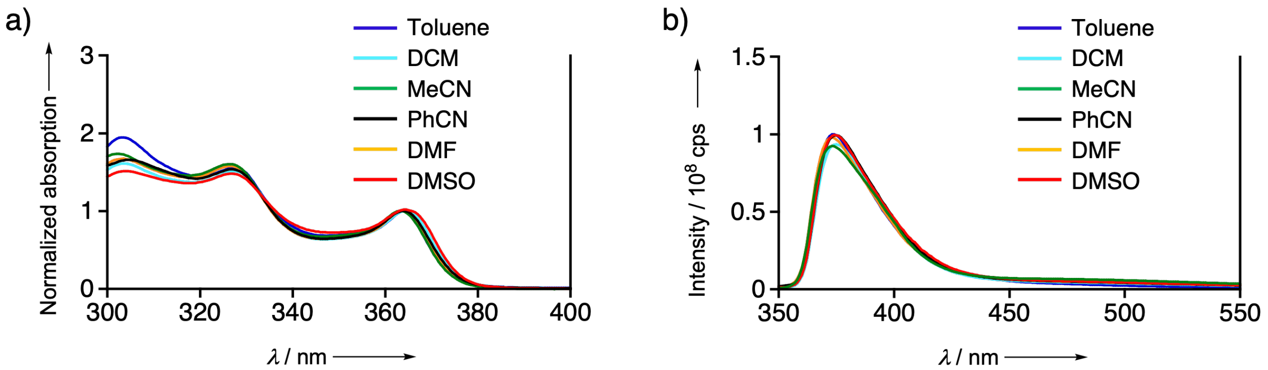


Figure S4. a) UV/Vis absorption and b) fluorescence spectra of **1(PO)₂** in various solvents at room temperature. For the fluorescence measurements, the absorbances at 340 nm were adjusted to be identical (0.10) and the samples were excited at λ = 340 nm under the same excitation condition for accurate intensity comparison.

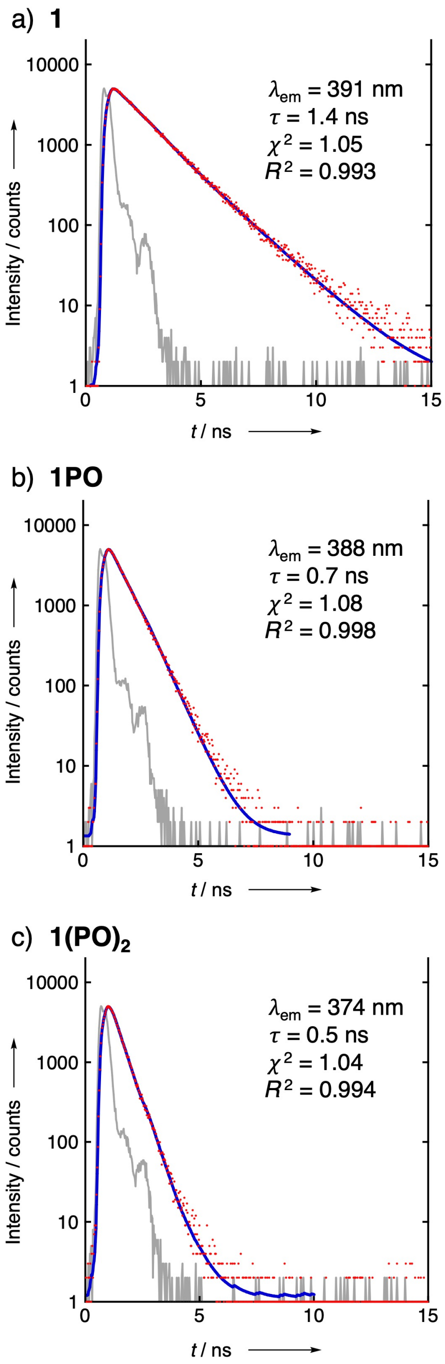


Figure S5. Fluorescence decays of a) **1**, b) **1PO**, and c) **1(PO)$_2$** in toluene. The samples were excited at 378 nm. The solid lines present decay fittings and the gray lines show the instrumental response function (IRF). The monitoring wavelengths (λ_{em}), fluorescence lifetimes (τ), χ-squared values (χ^2), and R-squared values (R^2) are given in the figures.

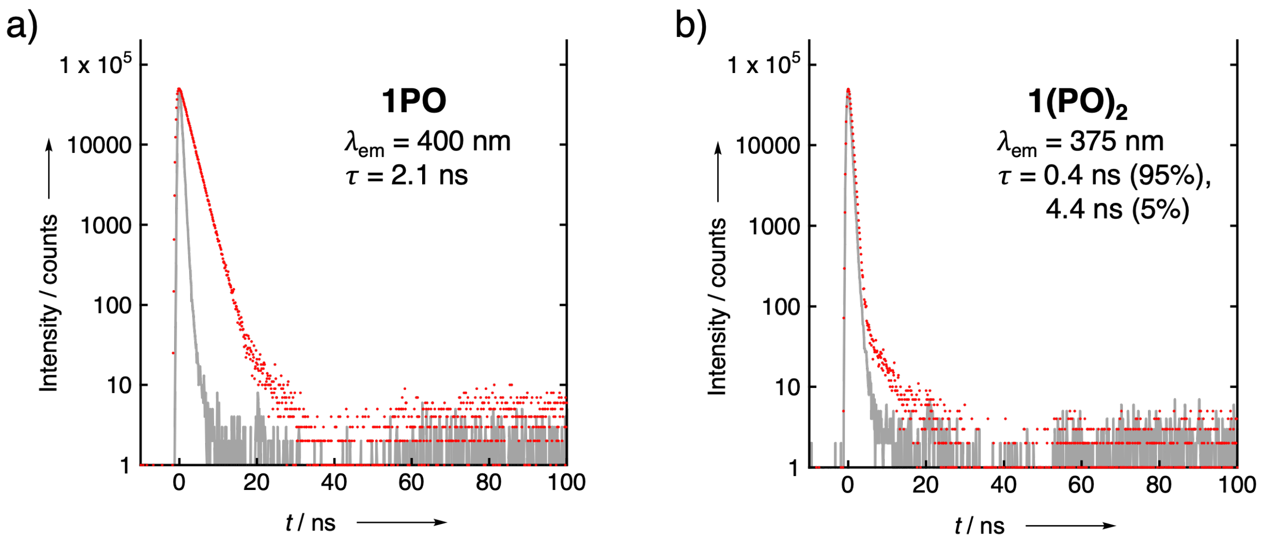


Figure S6. Fluorescence decays of a) **1PO**, and b) **$1(PO)_2$** in acetonitrile. The samples were excited at 340 nm. The gray lines show the IRF. The monitoring wavelengths (λ_{em}) and fluorescence lifetimes (τ) are given in the figures. The slow component for **$1(PO)_2$** can be attributed to the aggregated state (See also Figure S23).

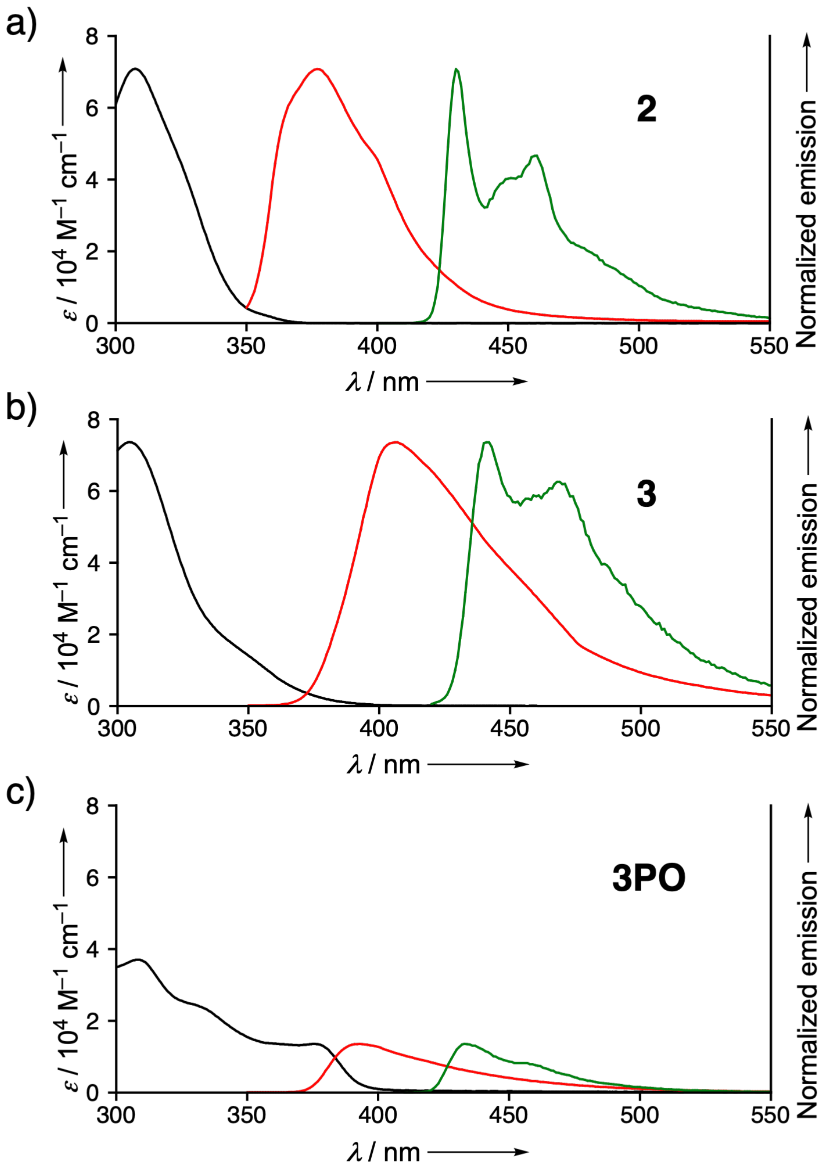


Figure S7. UV/Vis absorption (black) and normalized fluorescence (red) spectra in toluene at room temperature, and normalized phosphorescence spectra (green) in 2-MeTHF at –190 °C (delay time: 0.05 ms) of a) **2**, b) **3**, and c) **3PO**. The samples were excited at λ = 340 nm for both fluorescence and phosphorescence measurements.

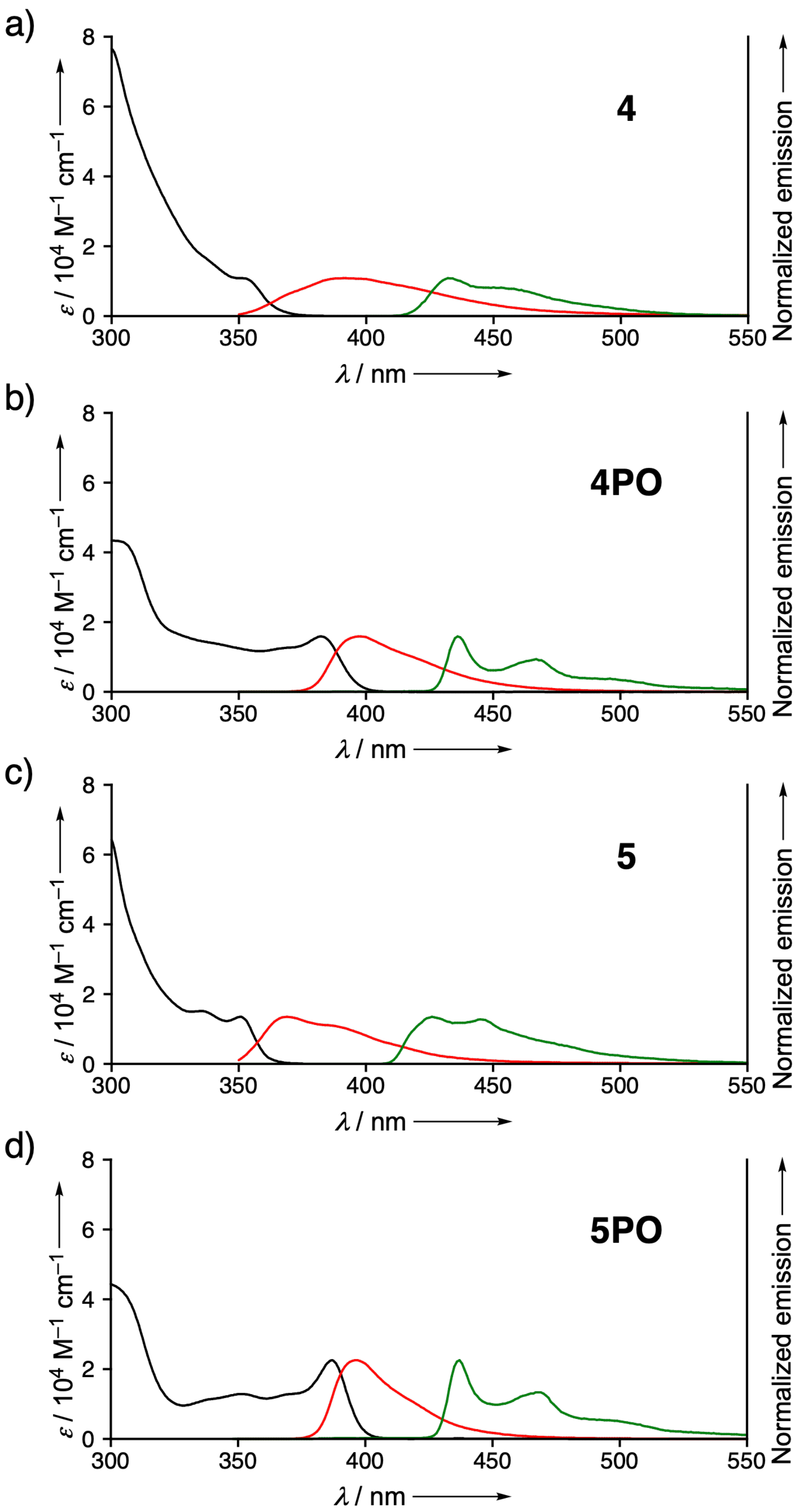


Figure S8. UV/Vis absorption (black) and normalized fluorescence (red) spectra in toluene at room temperature, and normalized phosphorescence spectra (green) in 2-MeTHF at –190 °C (delay time: 0.05 ms) of a) **4**, b) **4PO**, c) **5**, and d) **5PO**. The samples were excited at λ = 340 nm for both fluorescence and phosphorescence measurements.

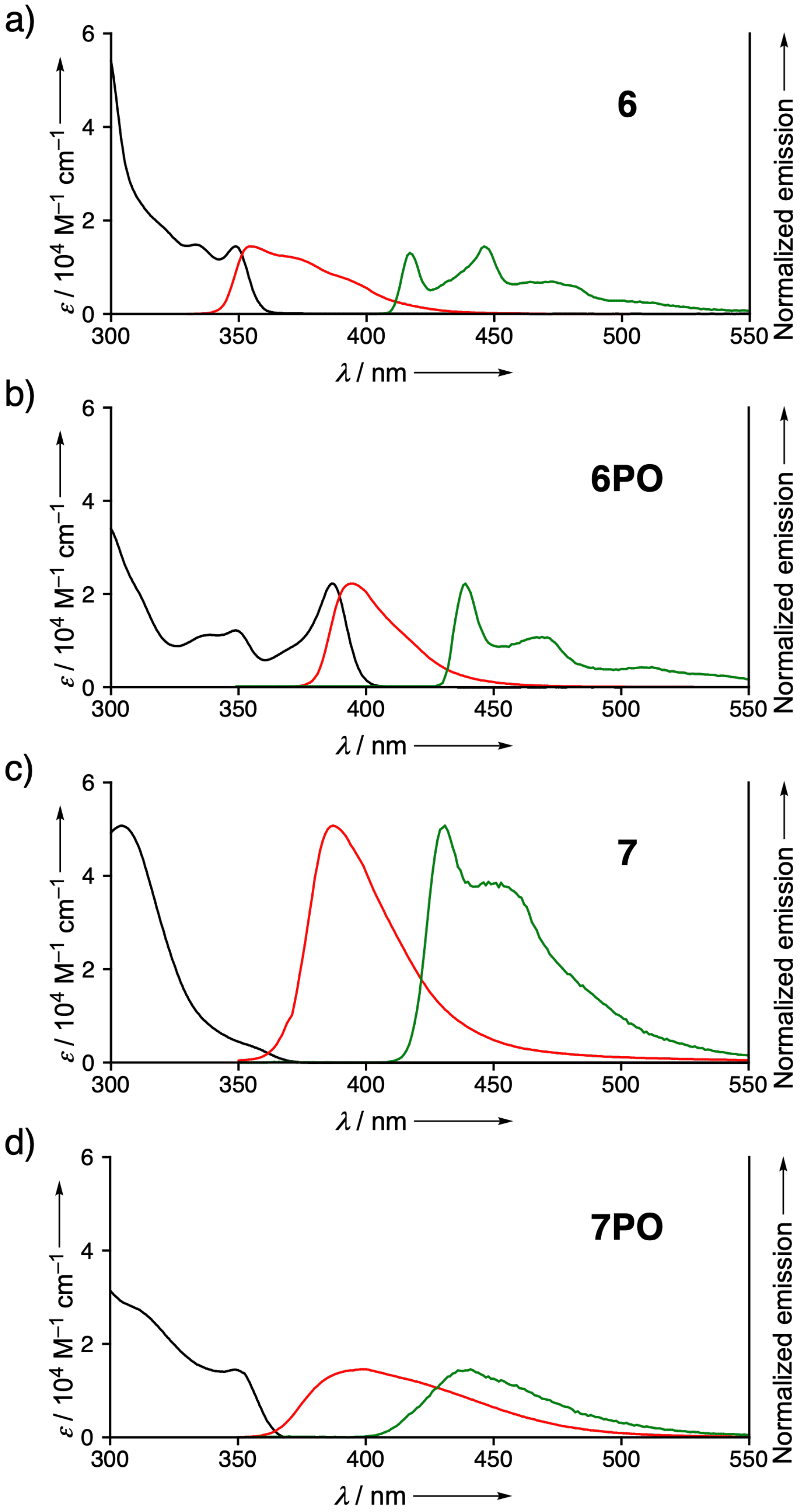


Figure S9. UV/Vis absorption (black) and normalized fluorescence (red) spectra in toluene at room temperature, and normalized phosphorescence spectra (green) in 2-MeTHF at –190 °C (delay time: 0.05 ms) of a) **6**, b) **6PO**, c) **7**, and d) **7PO**. The samples were excited at λ = 340 nm for both fluorescence and phosphorescence measurements.

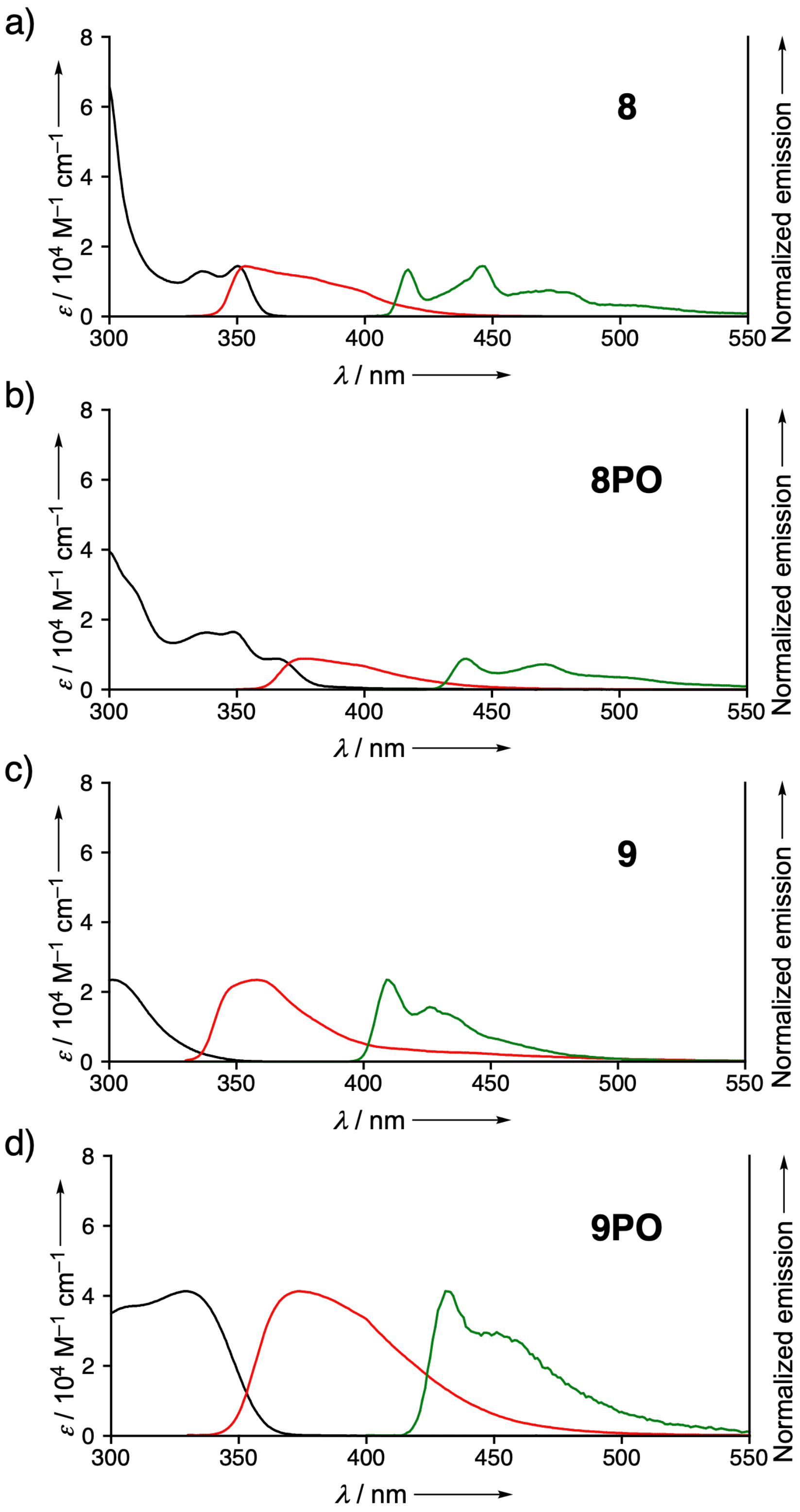


Figure S10. UV/Vis absorption (black) and normalized fluorescence (red) spectra in toluene at room temperature, and normalized phosphorescence spectra (green) in 2-MeTHF at –190 °C (delay time: 0.05 ms) of a) **8**, b) **8PO**, c) **9,** and d) **9PO**. The excitation wavelengths used for fluorescence and phosphorescence measurements were at λ = 320 nm for **8**, and λ = 340 nm for **8PO**, **9**, and **9PO**.

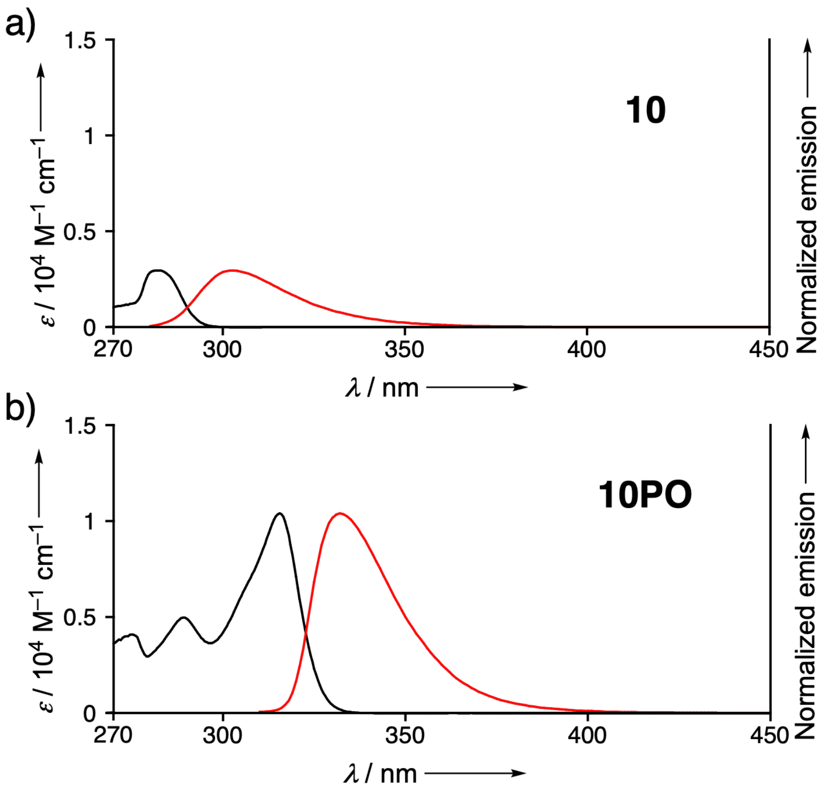


Figure S11. UV/Vis absorption (black) and normalized fluorescence (red) spectra in toluene at room temperature of a) **10**, b) **10PO**. The excitation wavelengths were at λ = 270 nm for **10** and λ = 300 nm for **10PO**.

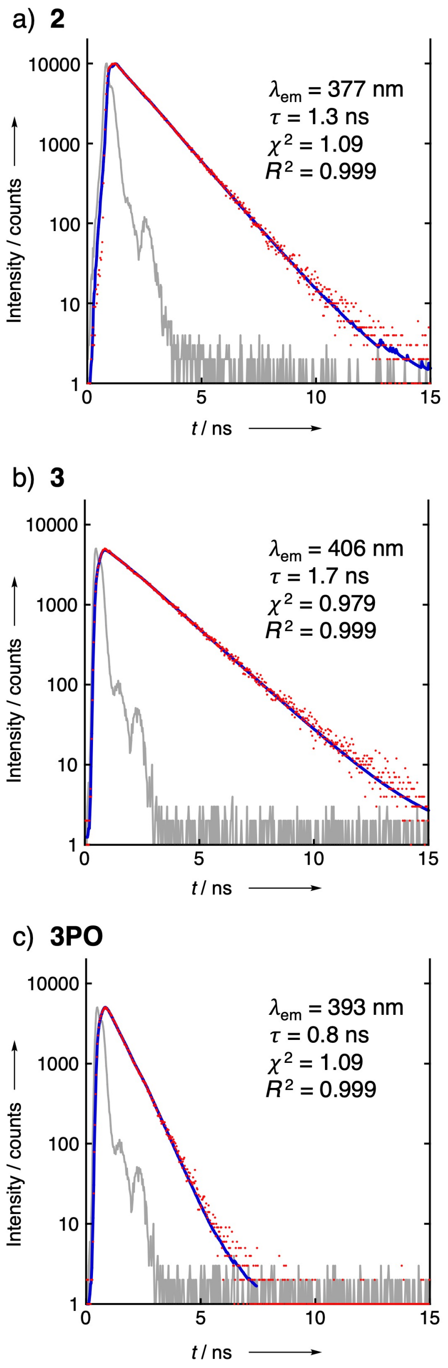


Figure S12. Fluorescence decays of a) **2**, b) **3**, and c) **3PO** in toluene. The samples were excited at 378 nm. The solid lines present decay fittings and the gray lines show the IRF. The monitoring wavelengths (λ_{em}), fluorescence lifetimes (τ), χ-squared values (χ^2), and R-squared values (R^2) are given in the figures.

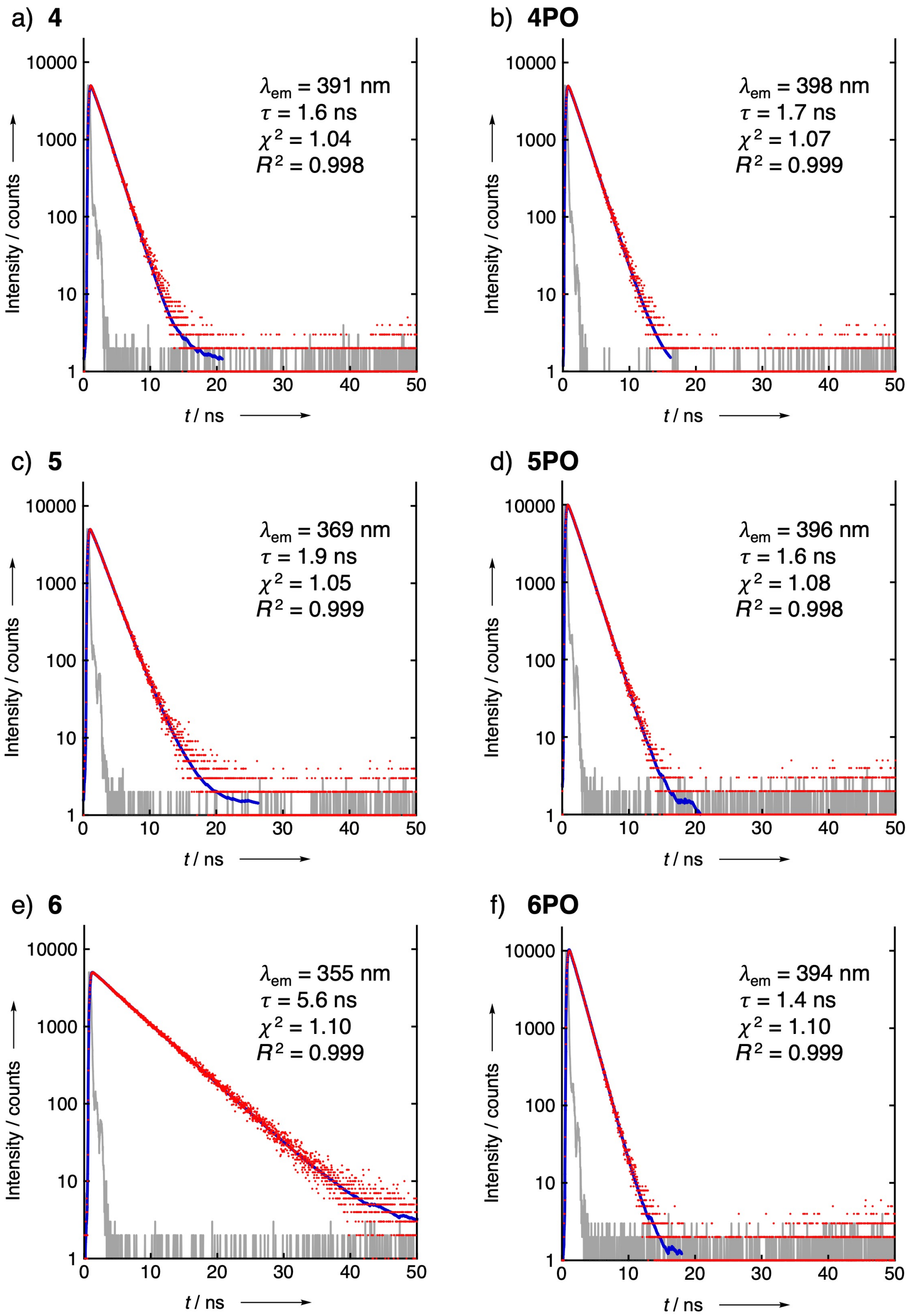


Figure S13. Fluorescence decays of a) **4**, b) **4PO**, c) **5**, d) **5PO**, e) **6**, and f) **6PO** in toluene. The samples were excited at 378 nm. The solid lines present decay fittings and the gray lines show the IRF. The monitoring wavelengths (λ_{em}), fluorescence lifetimes (τ), χ-squared values (χ^2), and R-squared values (R^2) are given in the figures.

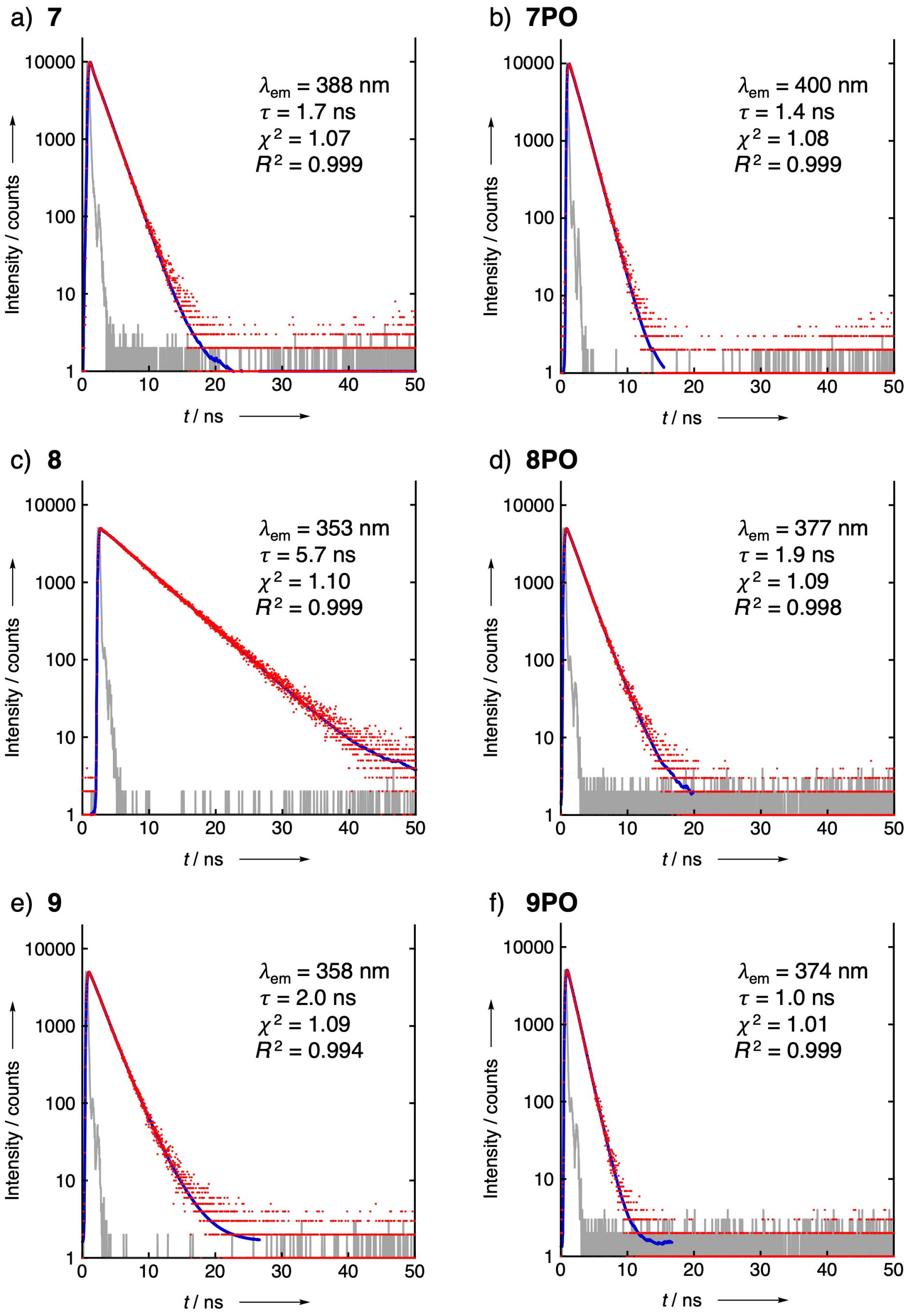


Figure S14. Fluorescence decays of a) **7**, b) **7PO**, c) **8**, d) **8PO**, e) **9**, and f) **9PO** in toluene. The samples were excited at 378 nm. The solid lines present decay fittings and the gray lines show the IRF. The monitoring wavelengths (λ_{em}), fluorescence lifetimes (τ), χ-squared values (χ^2), and R-squared values (R^2) are given in the figures.

6. Electrochemical Properties

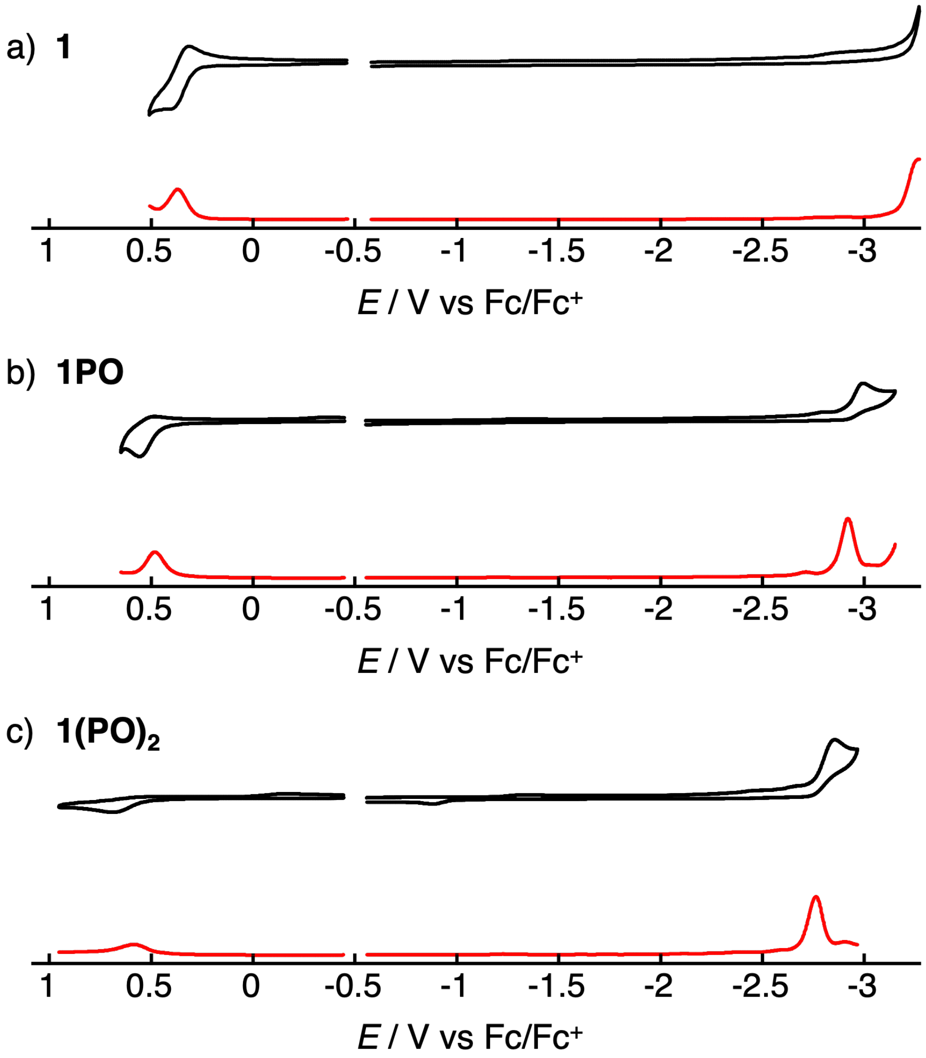


Figure S15. Cyclic voltammograms (black) and differential pulse voltammetry (DPV) curves (red) of a) **1**, b) **1PO**, and c) **1(PO)**$_2$ in acetonitrile (oxidation) and DMF (reduction). scan rate: 0.10 V s^{-1}; working electrode: glassy carbon; reference electrode: Ag/AgCl; electrolyte: 0.1 M *n*-Bu_4NPF_6.

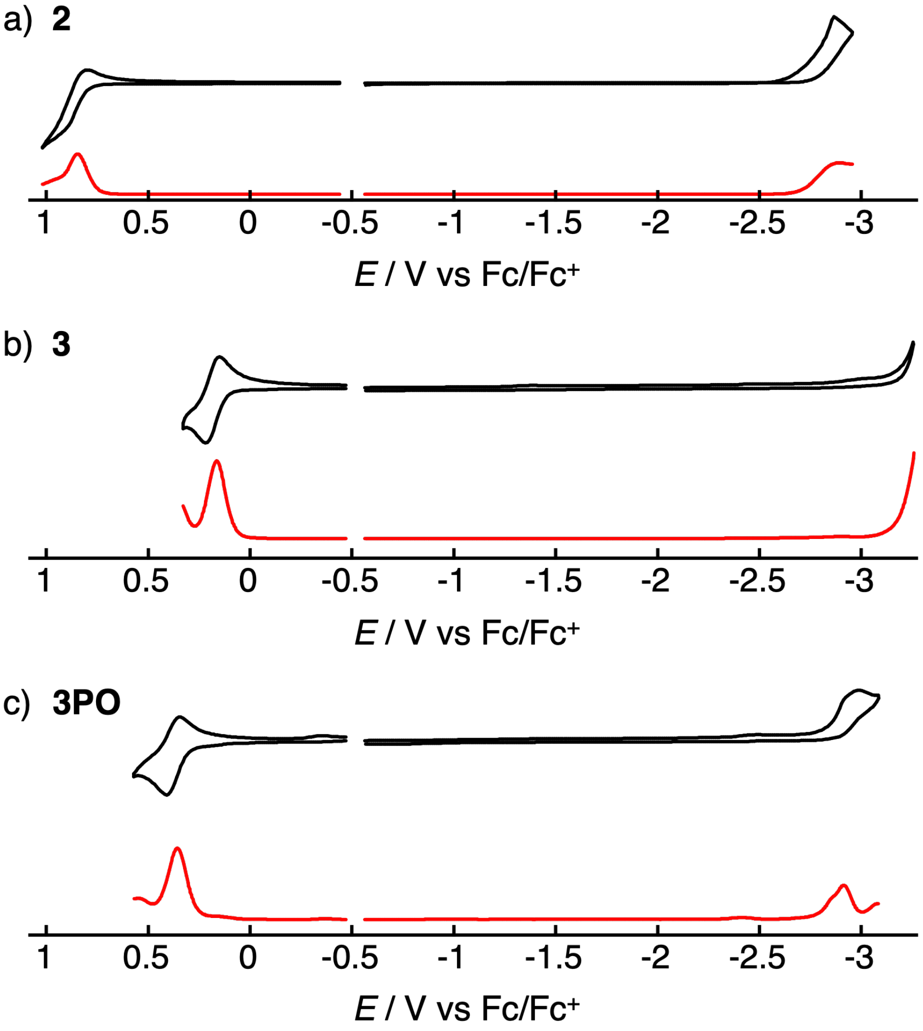


Figure S16. Cyclic voltammograms (black) and differential pulse voltammetry (DPV) curves (red) of a) **2**, b) **3**, and c) **3PO** in acetonitrile (oxidation) and DMF (reduction). scan rate: 0.10 V s^{-1}; working electrode: glassy carbon; reference electrode: Ag/AgCl; electrolyte: 0.1 M *n*-Bu_4NPF_6.

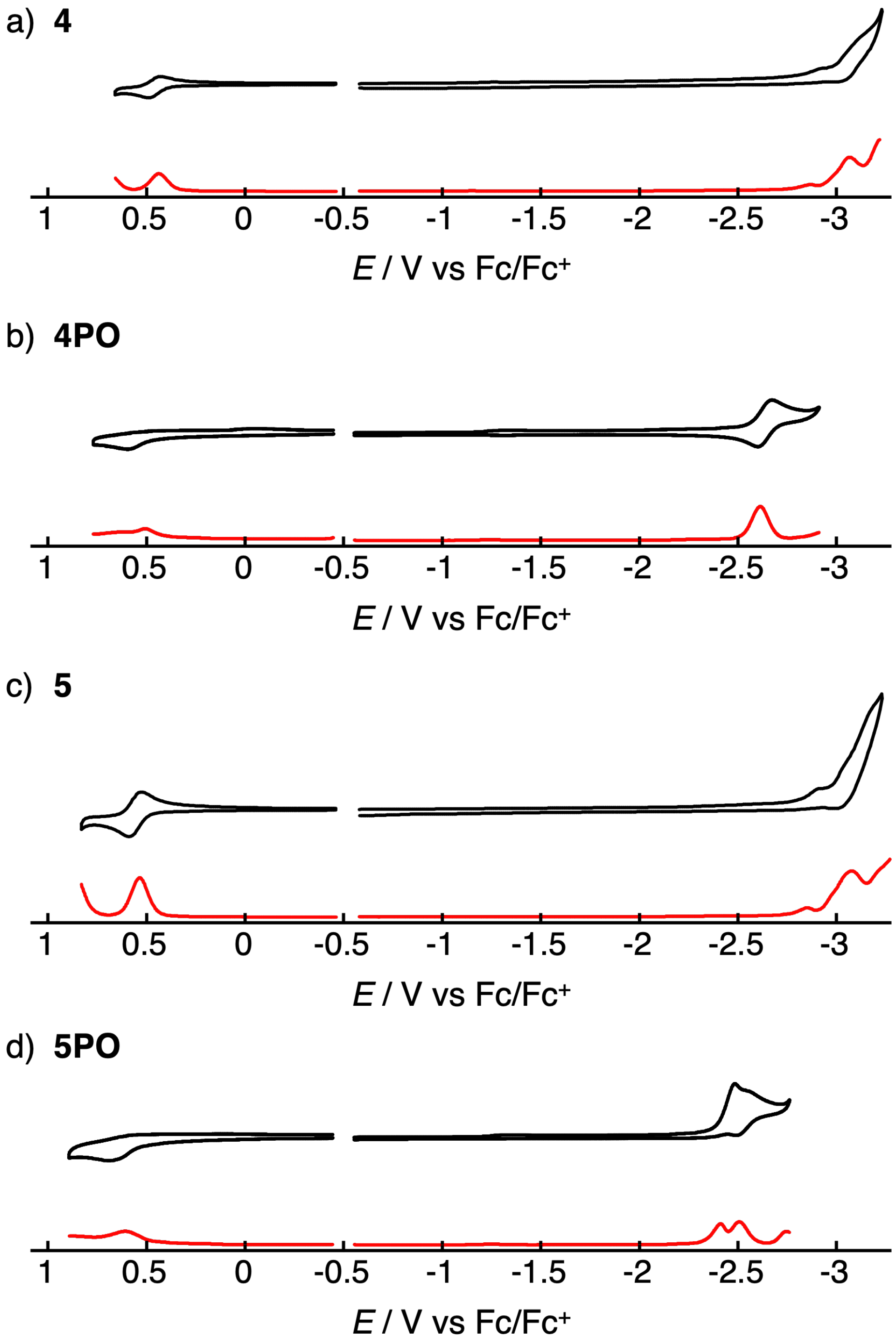


Figure S17. Cyclic voltammograms (black) and differential pulse voltammetry (DPV) curves (red) of a) **4**, b) **4PO**, c) **5**, and d) **5PO** in acetonitrile (oxidation) and DMF (reduction). scan rate: 0.10 V s^{-1}; working electrode: glassy carbon; reference electrode: Ag/AgCl; electrolyte: 0.1 M *n*-Bu_4NPF_6.

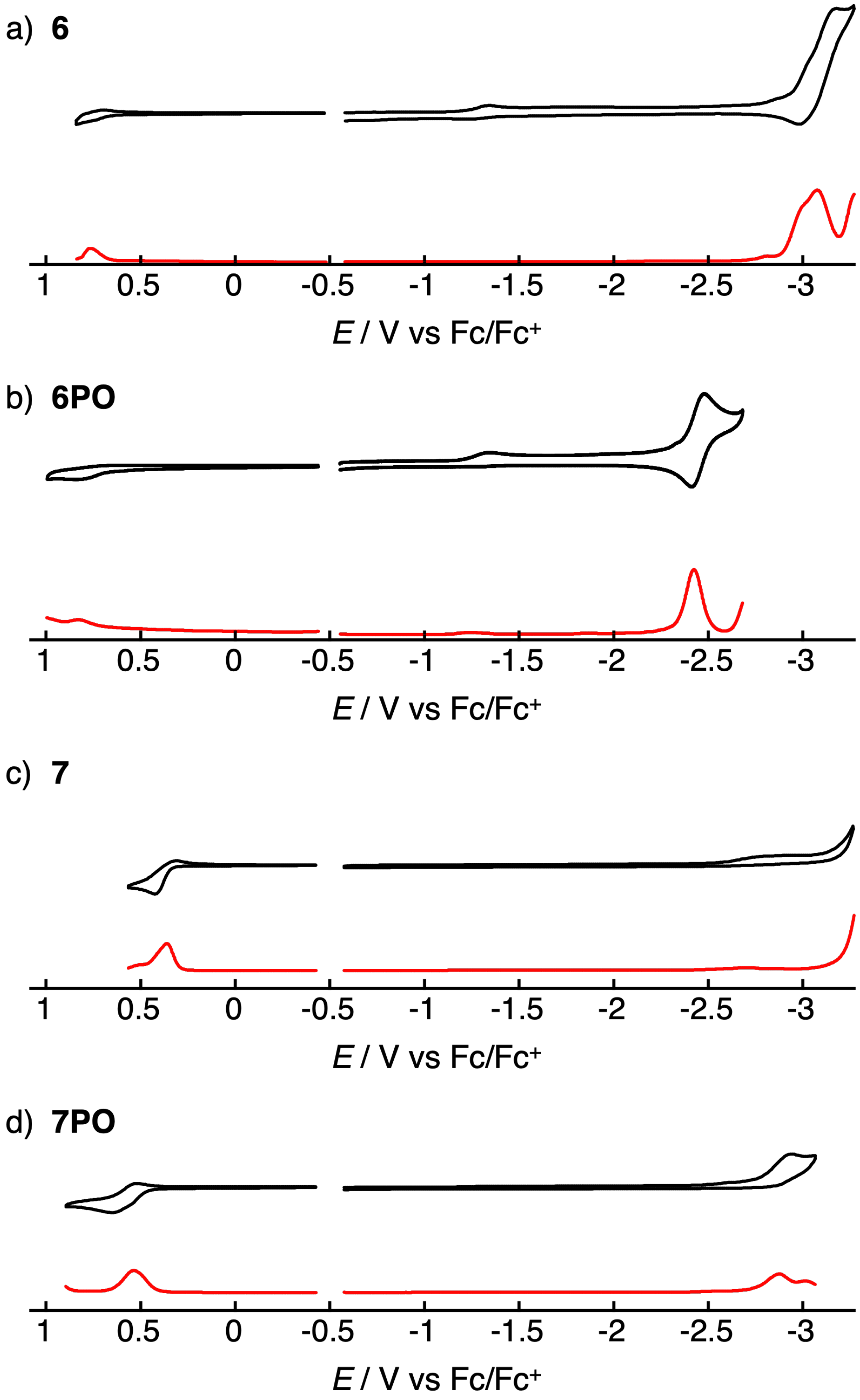


Figure S18. Cyclic voltammograms (black) and differential pulse voltammetry (DPV) curves (red) of a) **6**, b) **6PO**, c) **7**, and d) **7PO** in acetonitrile (oxidation) and DMF (reduction). scan rate: 0.10 V s^{-1}; working electrode: glassy carbon; reference electrode: Ag/AgCl; electrolyte: 0.1 M *n*-Bu_4NPF_6.

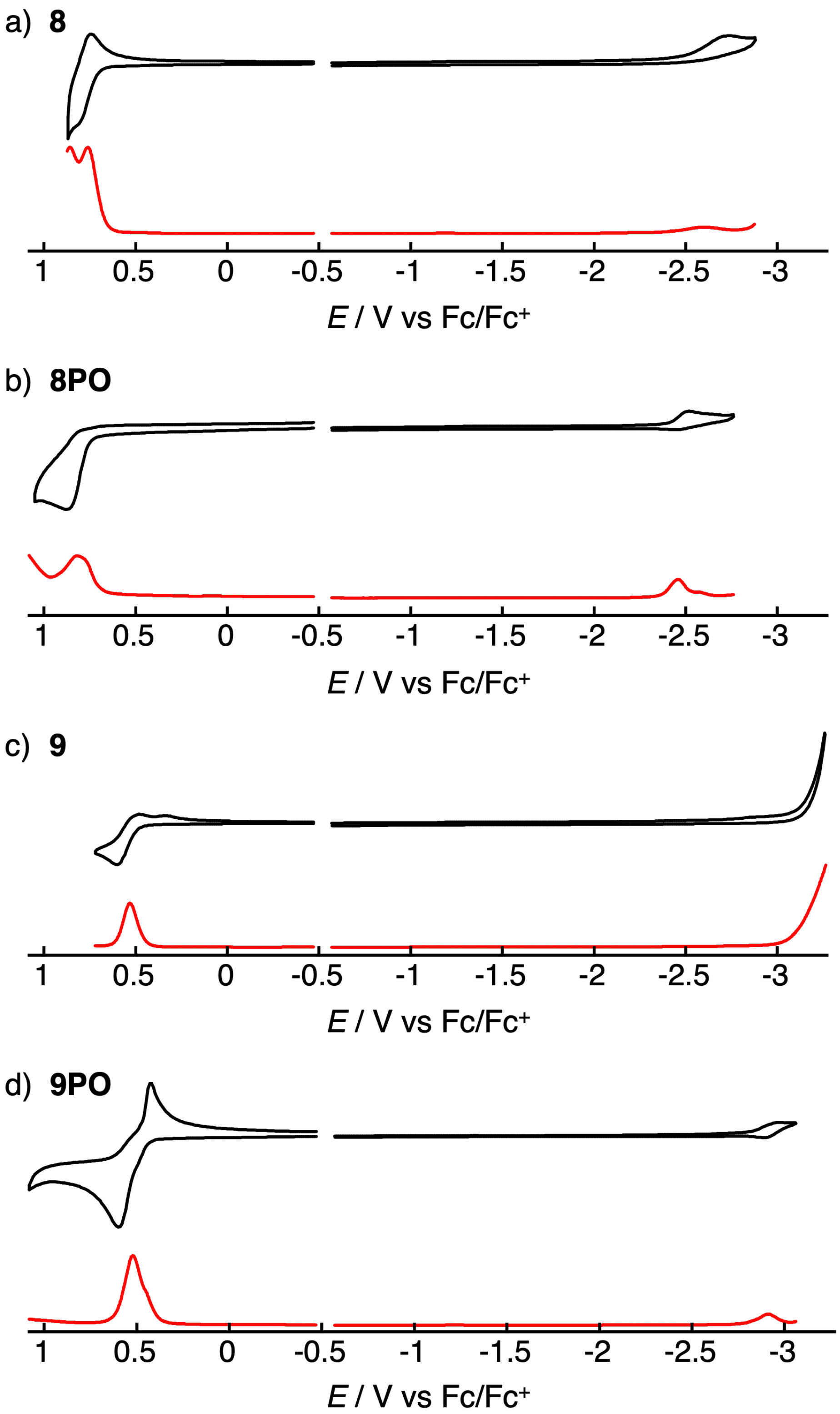


Figure S19. Cyclic voltammograms (black) and differential pulse voltammetry (DPV) curves (red) of a) **8**, b) **8PO**, c) **9**, and d) **9PO** in acetonitrile (oxidation) and DMF (reduction). scan rate: 0.10 V s^{-1}; working electrode: glassy carbon; reference electrode: Ag/AgCl; electrolyte: 0.1 M *n*-Bu_4NPF_6.

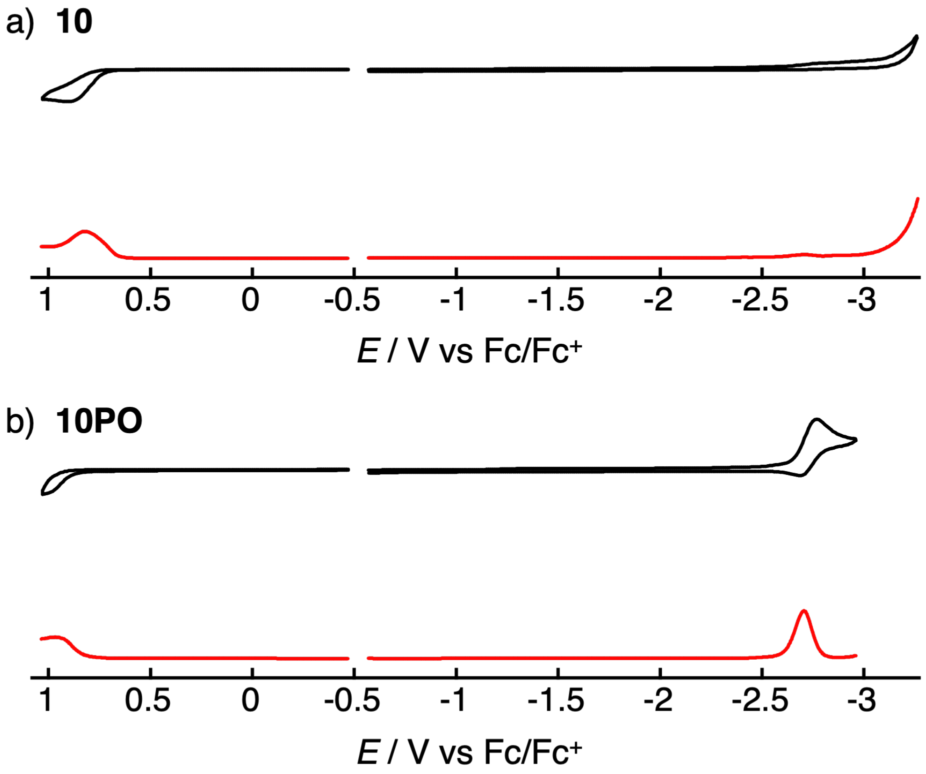


Figure S20. Cyclic voltammograms (black) and differential pulse voltammetry (DPV) curves (red) of a) **10** and b) **10PO** in acetonitrile (oxidation) and DMF (reduction). scan rate: 0.10 V s^{-1}; working electrode: glassy carbon; reference electrode: Ag/AgCl; electrolyte: 0.1 M *n*-Bu_4NPF_6.

Table S6. Electrochemical properties of amines and the P-doped products.

	E_{ox}[a] [V]	E_{red}[b] [V]
1	0.37	n.d.[c]
1PO	0.48	–2.92
1(PO)$_2$	0.59	–2.77
2	0.85	–2.89
3	0.17	n.d.[c]
3PO	0.36	–2.91
4	0.44	–3.07
4PO	0.51	–2.61
5	0.54	–3.08
5PO	0.61	–2.41
6	0.77	–3.08
6PO	0.82	–2.42
7	0.36	n.d.[c]
7PO	0.54	–2.88
8	0.76	–2.60
8PO	0.82	–2.46
9	0.53	n.d.[c]
9PO	0.54	–2.91
10	0.82	n.d.[c]
10PO	0.90	–2.71

[a] Oxidation potentials versus ferrocene/ferrocenium couple (Fc/Fc$^+$) in acetonitrile. [b] Reduction potentials versus Fc/Fc$^+$ in DMF. [c] Not determined.

7. DFT Calculations

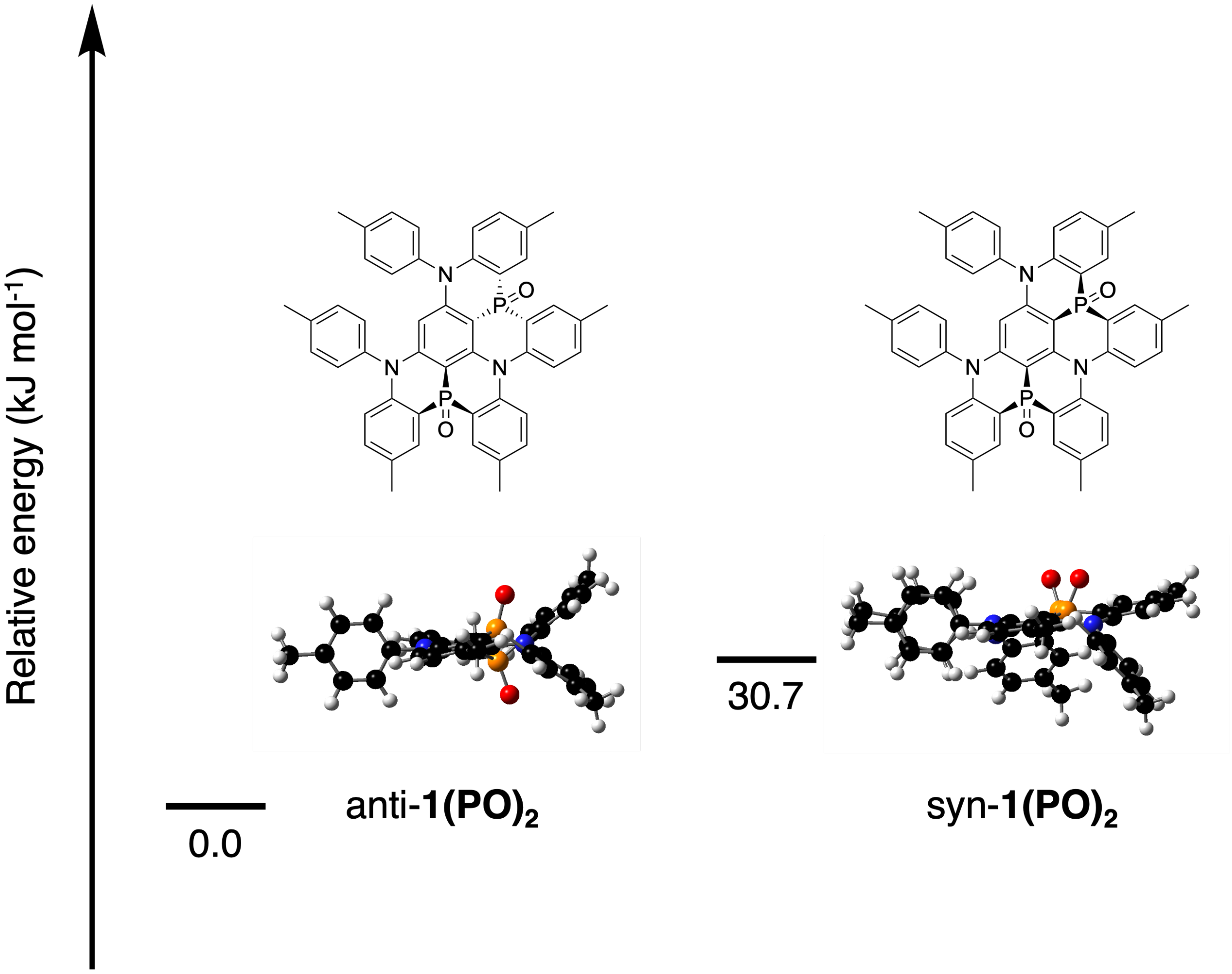


Figure S21. Optimized structures and relative energies of *anti*-**1(PO)**$_2$ and *syn*-**1(PO)**$_2$.

Table S7. Selected excitation energies and oscillator strength of P-doped products calculated by the TD-DFT method.

	state	excitation energy [eV]	excitation energy [nm]	oscillator strength (*f*)	excitation			weight [%]
1PO	1	3.6650	338	0.1149	HOMO–1	→	LUMO	74
					HOMO	→	LUMO	4
	2	3.6714	338	0.3074	HOMO	→	LUMO	76
					HOMO	→	LUMO+1	17
1(PO)$_2$	1	3.6111	343	0.1633	HOMO	→	LUMO	83
					HOMO–1	→	LUMO+1	11
	2	3.7407	332	0.0183	HOMO	→	LUMO+1	86
					HOMO–1	→	LUMO	11

Table S8. The calculated wavelengths for the lowest excited state of **1PO** by the TD-DFT method on the optimized geometry with the polarizable continuum model (PCM) using various solvents.

	cyclohexane	toluene	DCM	MeCN	PhCN	DMF	DMSO
λ [nm]	344	345	349	350	350	350	350

8. Chiroptical Properties

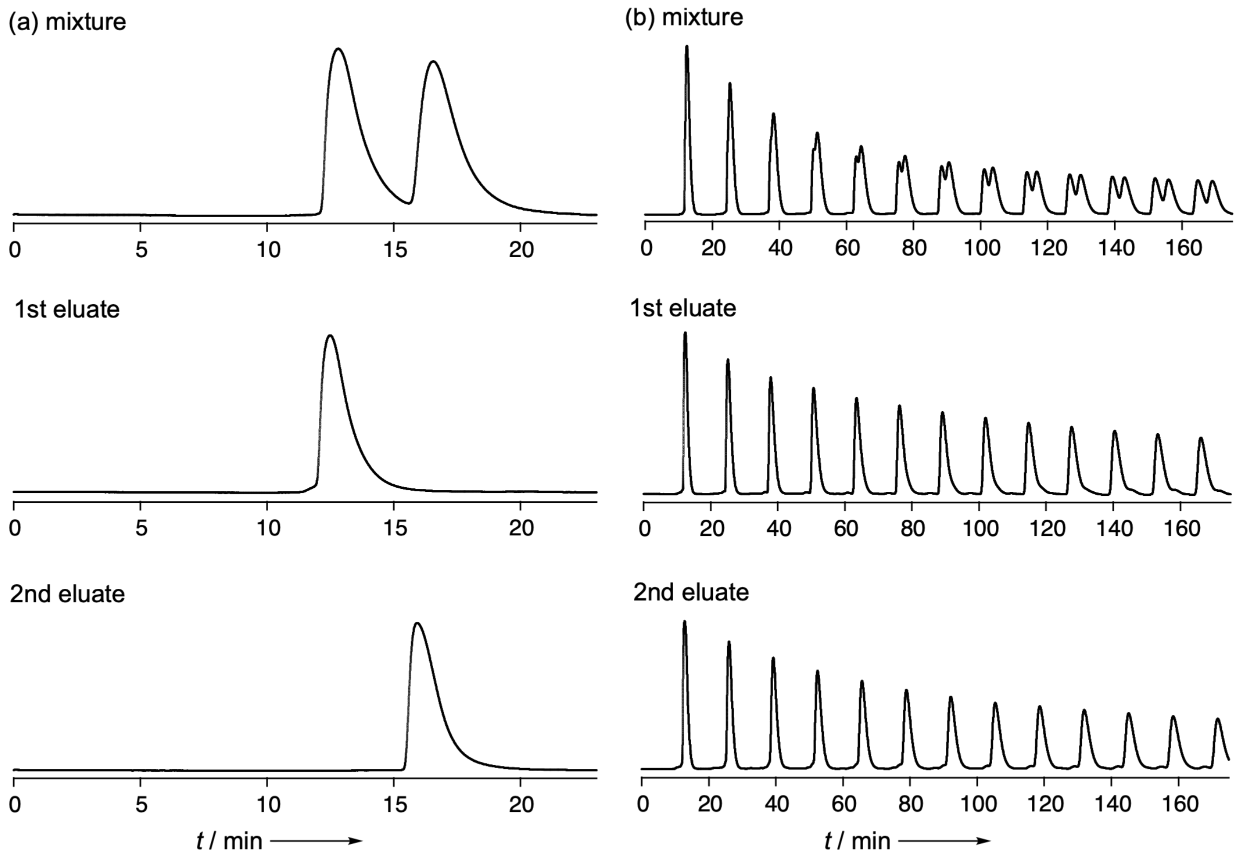


Figure S22. Chiral HPLC chromatographic charts of a) **1(PO)$_2$** and b) **4PO** using CHCl$_3$. Column: CHIRALPAK IA (φ 30 mm × 25 cm); Flow rate: 5 mL min^{-1}.

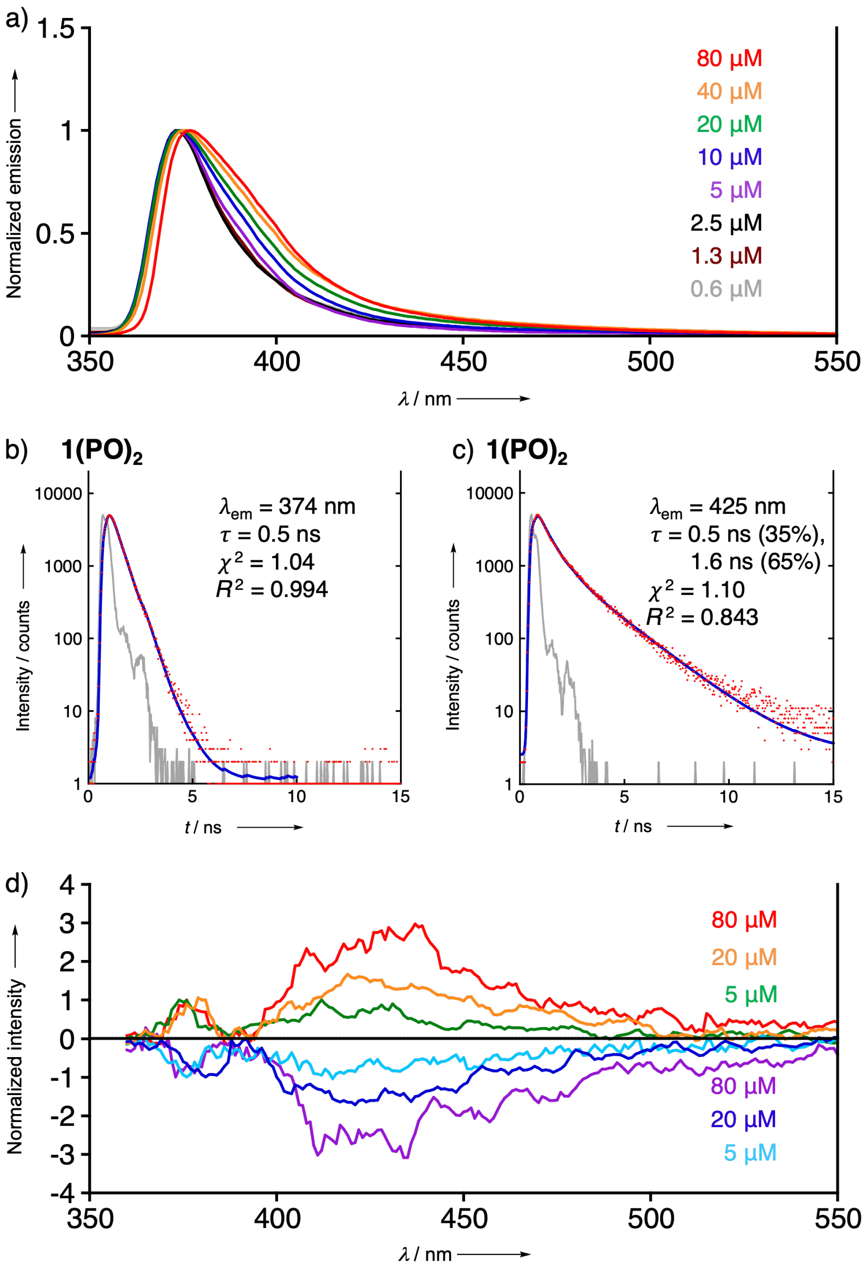


Figure S23. a) Concentration-dependent fluorescence spectra of **1(PO)**$_2$ in toluene (λ_{ex} = 340 nm). b) and c) Fluorescence decays of **1(PO)**$_2$ at 10 μM in toluene. The samples were excited at 378 nm. The solid lines present decay fittings and the gray lines show the IRF. The monitoring wavelengths (λ_{em}), fluorescence lifetimes (τ), χ-squared values (χ^2), and R-squared values (R^2) are given in the figures. d) Concentration-dependent CPL spectra of **1(PO)**$_2$ in toluene (λ_{ex} = 320 nm). With increasing concentration, the relative emission intensity at 400-425 nm increased, which is attributed to the emission from the aggregated state. In addition, the decay profile at 425 nm was fitted well with a biexponential model, in which the longer lifetime component is originated from the aggregated-state emission. Indeed, the relative CPL intensity (ΔI) at 425 nm increases compared to that at 375 nm at higher concentrations, thus the peak at 425 nm in the CPL spectra is ascribed to the emission from the aggregated state.

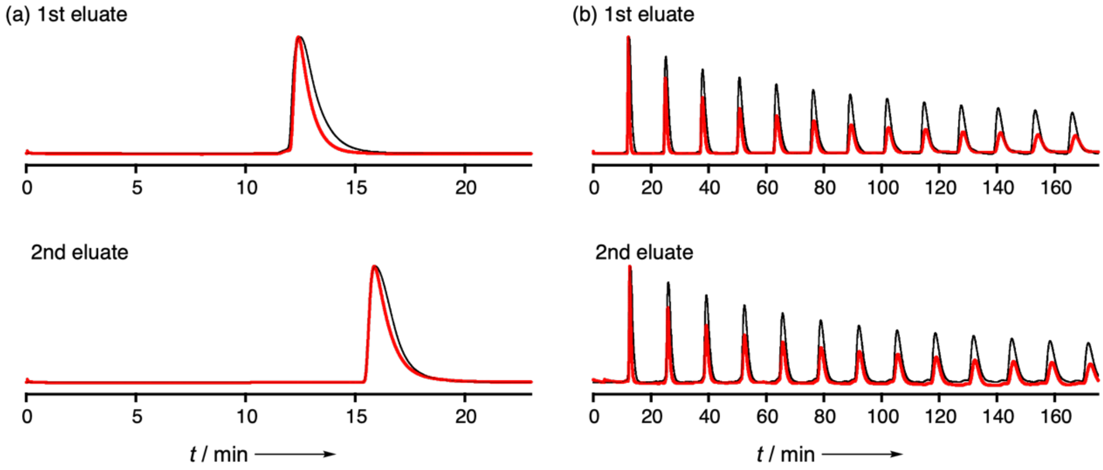


Figure S24. Normalized chiral HPLC chromatographic charts of the enantiomers of (a) **1(PO)$_2$** and (b) **4PO** before heating (black) and after refluxing in toluene for 20 h (red) using $CHCl_3$. Column: CHIRALPAK IA (φ 30 mm × 25 cm); Flow rate: 5 mL min^{-1}. The charts show no significant change in the enantiomeric ratio, indicating negligible racemization under these conditions.

9. High-Resolution Mass Spectra

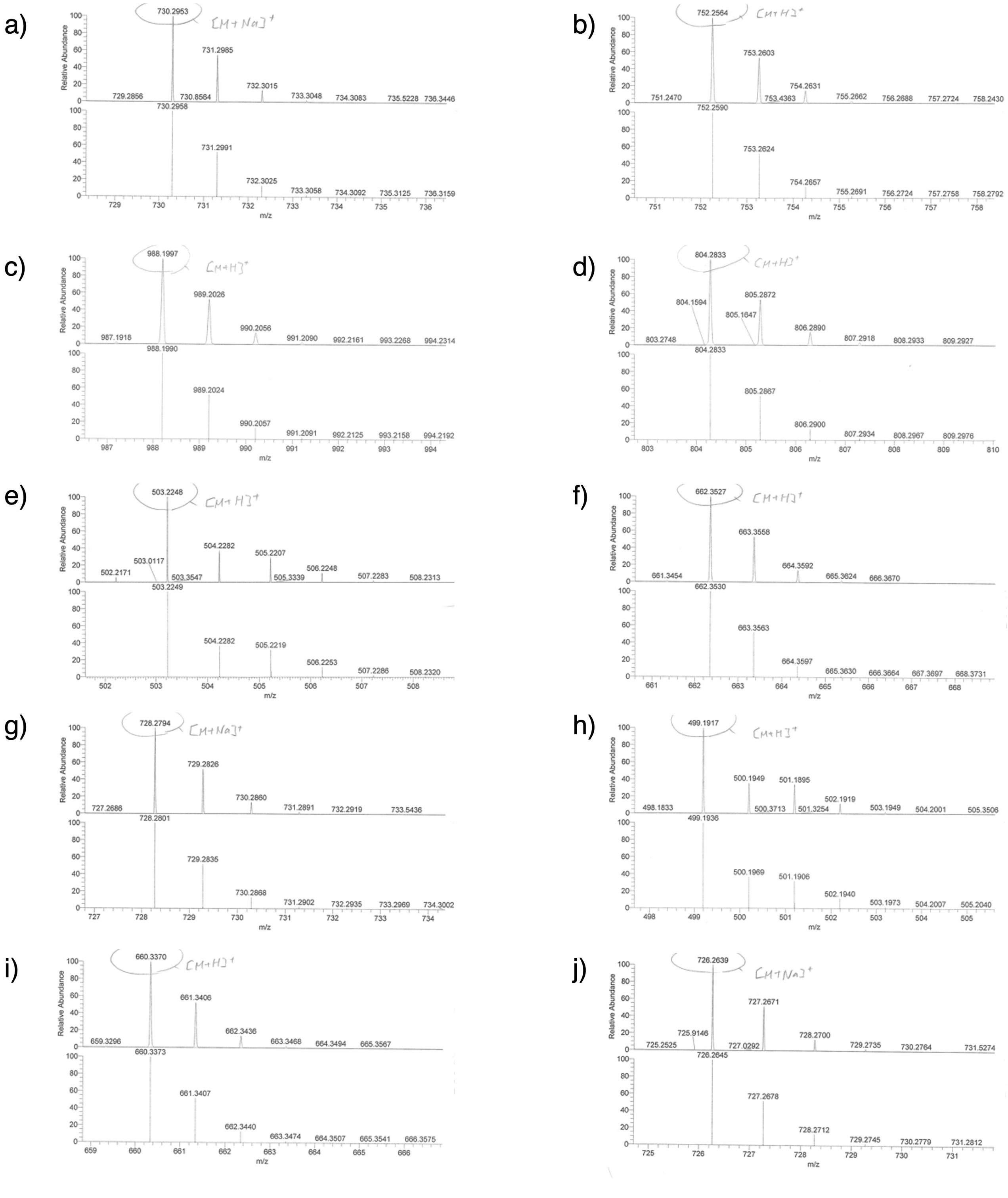


Figure S25. Observed (top) and simulated (bottom) high-resolution mass spectra of a) **1PO**, b) **1(PO)$_2$**, c) **2**, d) **3PO**, e) **S1**, f) **4**, g) **4PO**, h) **S2**, i) **5**, and j) **5PO**.

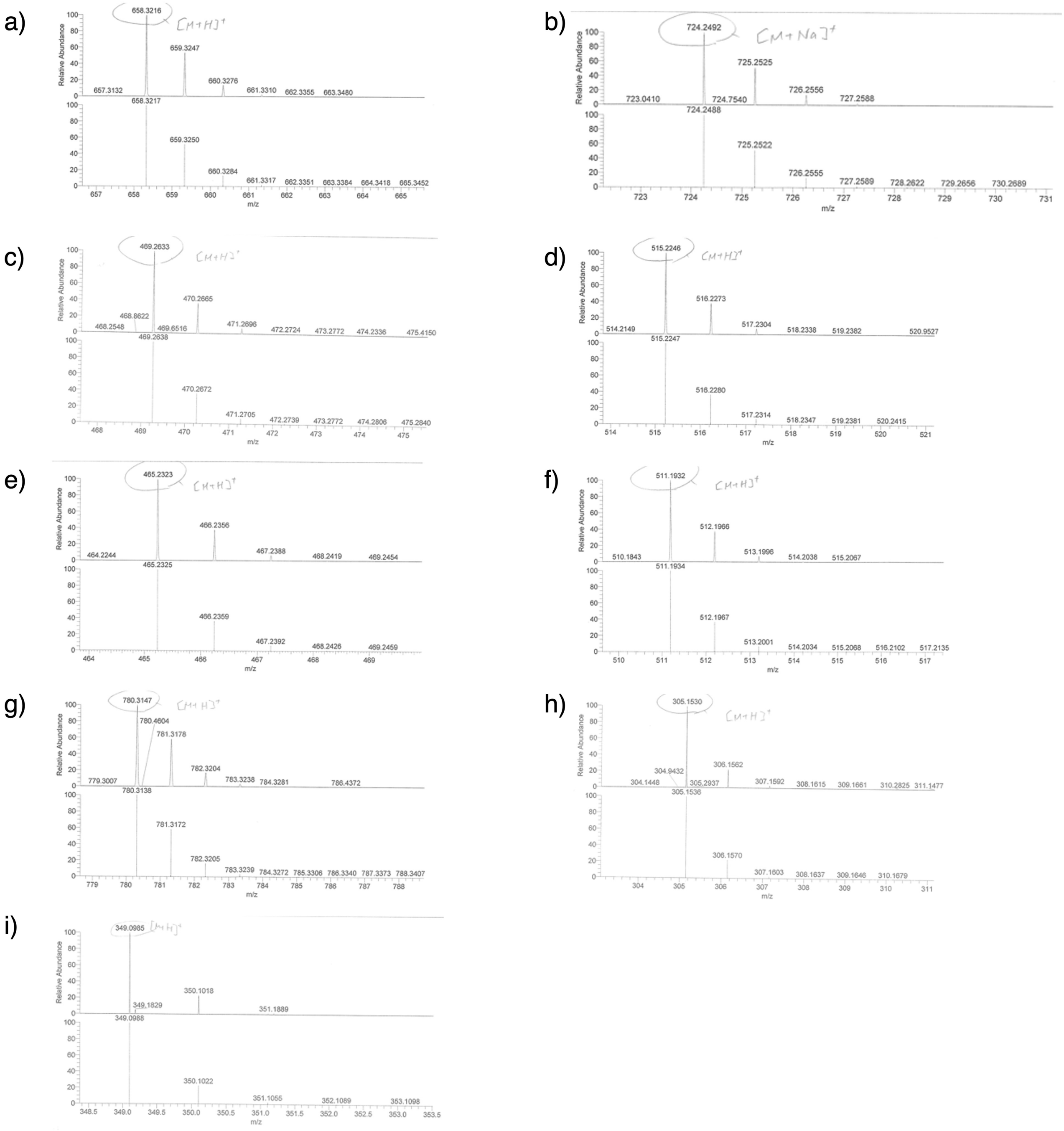


Figure S26. Observed (top) and simulated (bottom) high-resolution mass spectra of a) **6**, b) **6PO**, c) **7**, d) **7PO**, e) **8**, f) **8PO**, g) **9PO**, h) **10,** and i) **10PO.**

9. NMR Spectra

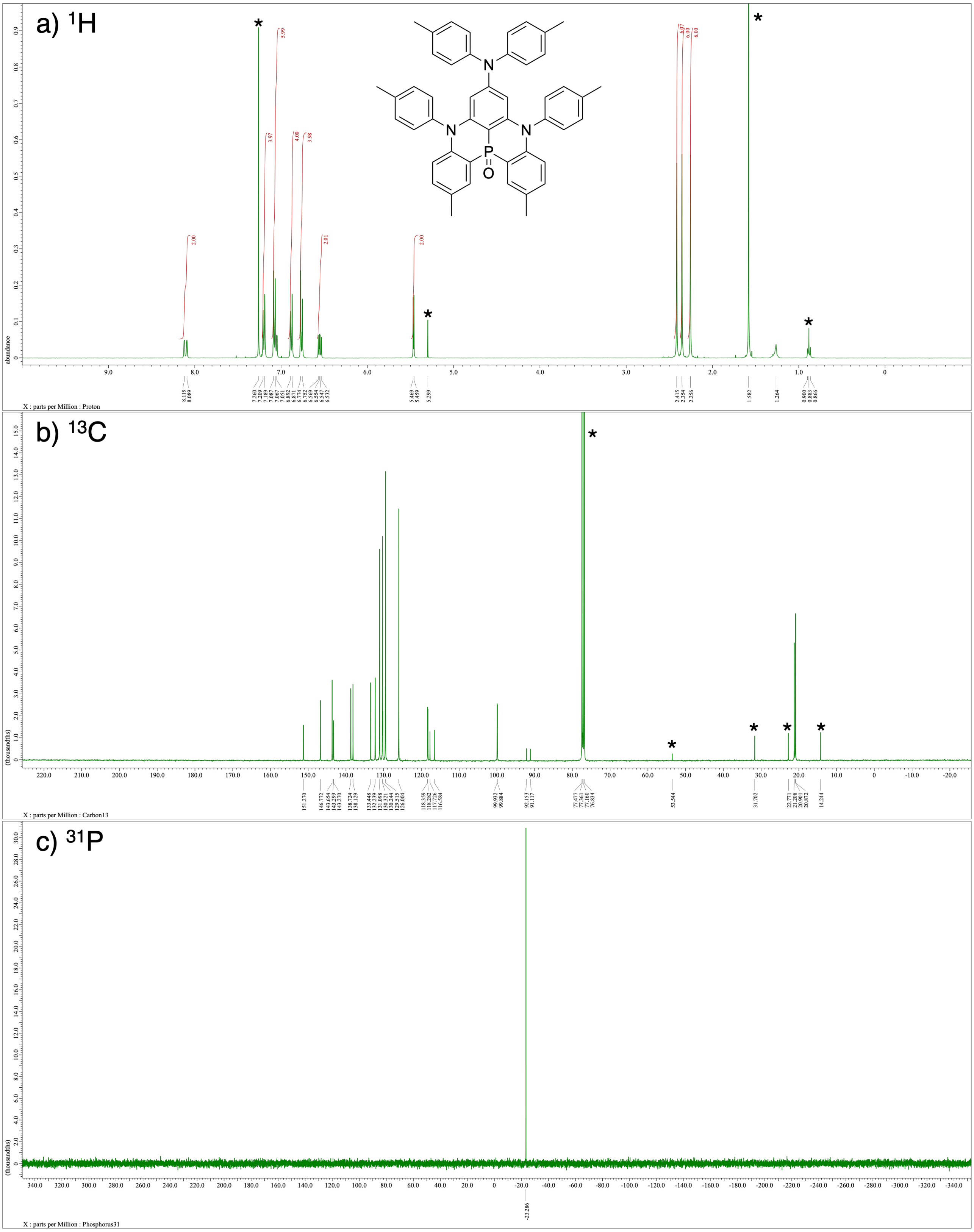


Figure S27. (a) ¹H (399.78 MHz), (b) ¹³C (100.42 MHz), and (c) ³¹P NMR (161.8 MHz) spectra of **1PO** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.

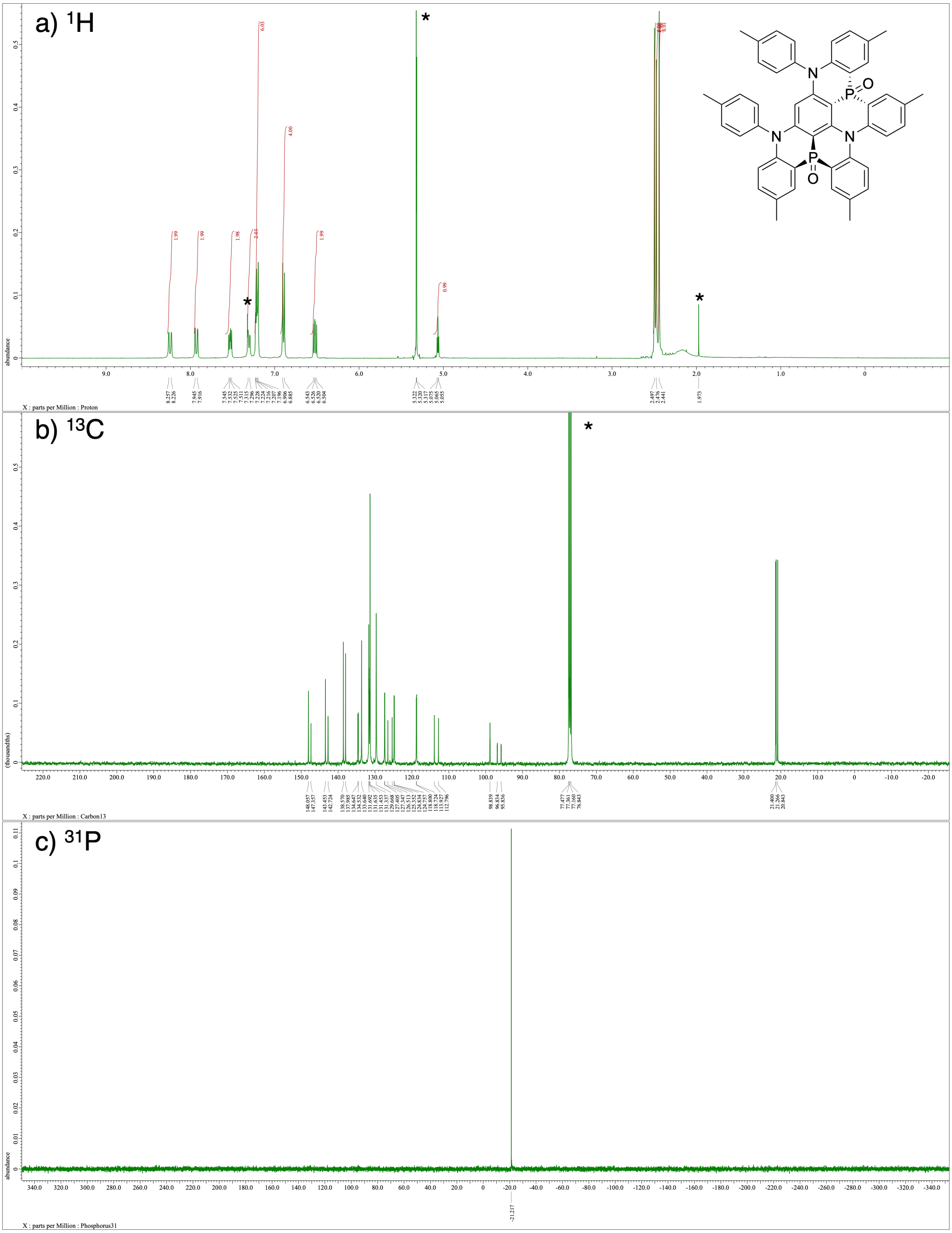


Figure S28. (a) ^{1}H (399.78 MHz) spectra in CD_2Cl_2, and (b) ^{13}C (100.42 MHz) and (c) ^{31}P NMR (161.7 MHz) spectra of **1(PO)$_2$** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.

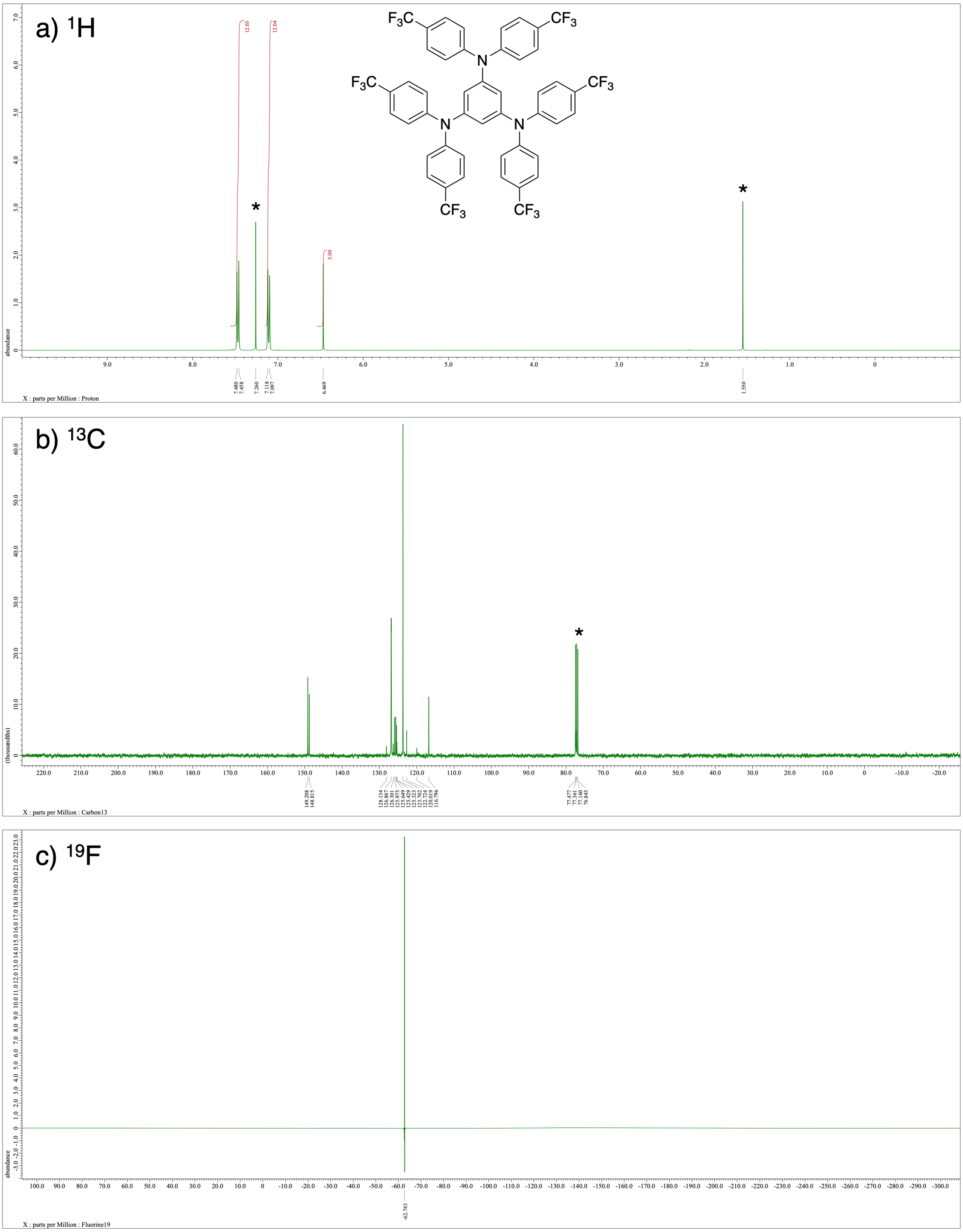


Figure S29. (a) ^{1}H (399.38 MHz), (b) ^{13}C (100.42 MHz), and (c) ^{19}F NMR (376.17 MHz) spectra of **2** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.

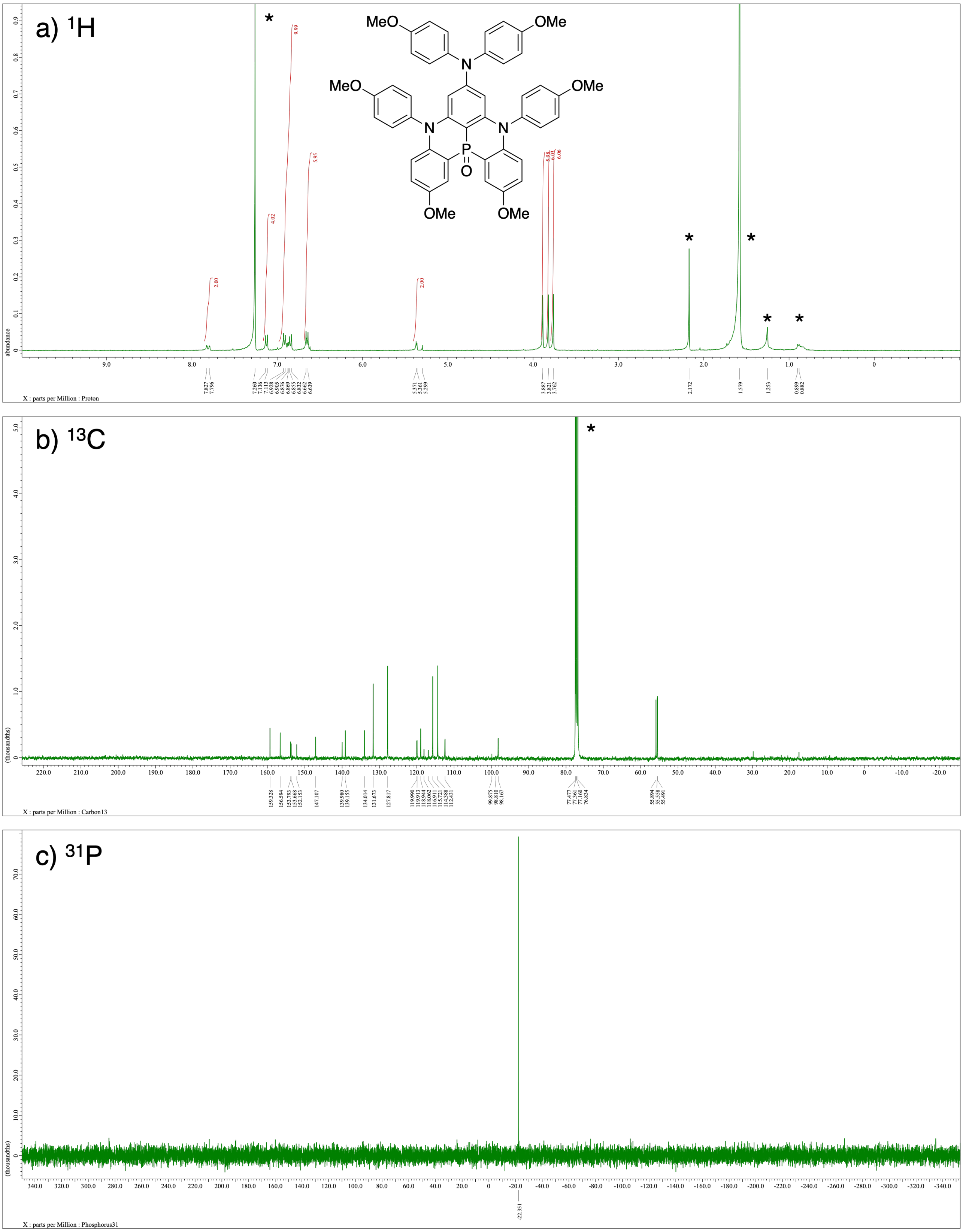
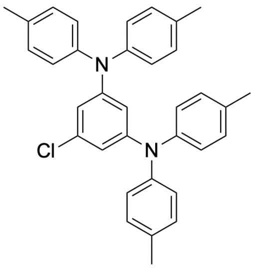


Figure S30. (a) ¹H (399.38 MHz), (b) ¹³C (100.42 MHz), and (c) ³¹P NMR (161.8 MHz) spectra of **3PO** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.



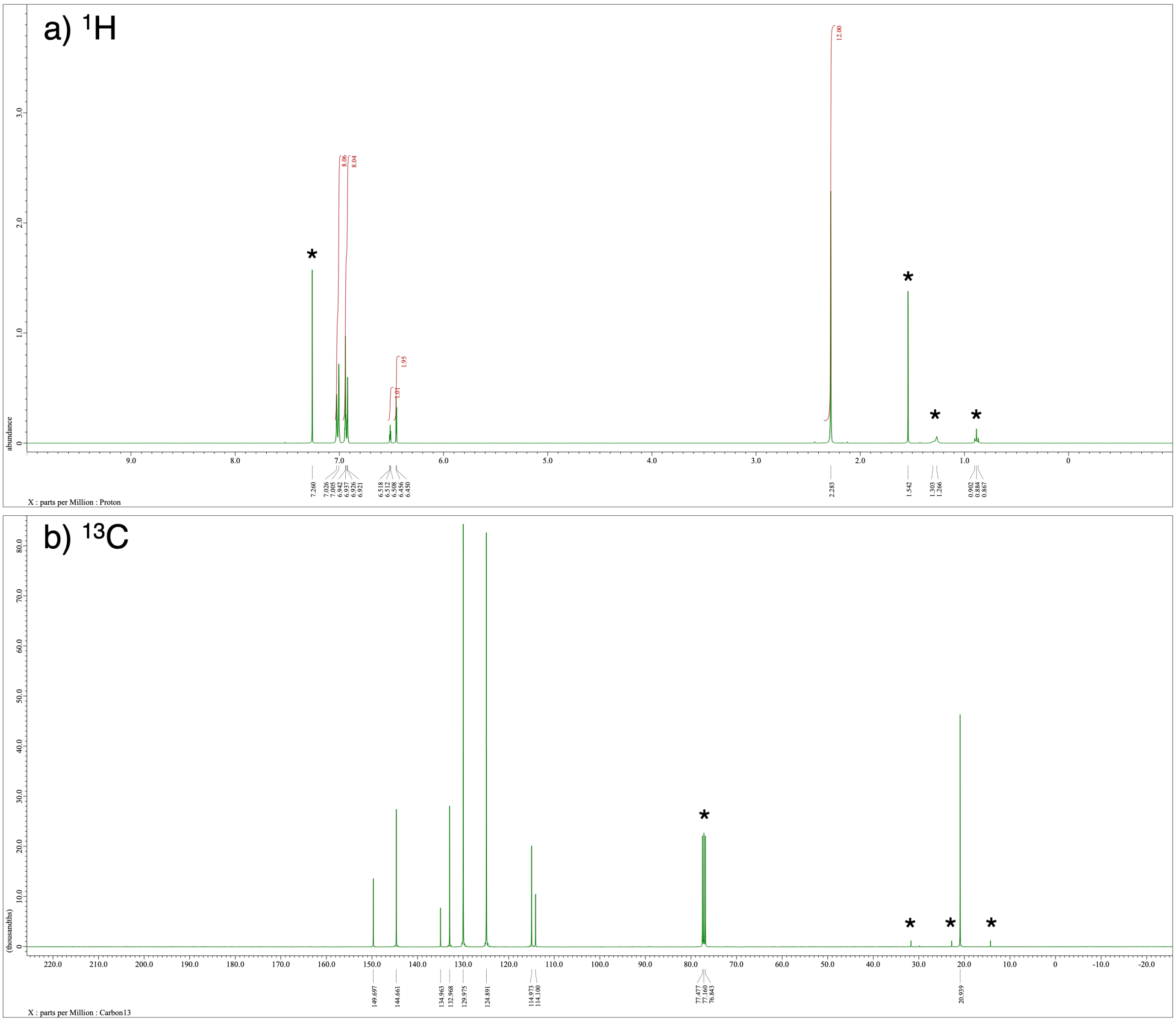
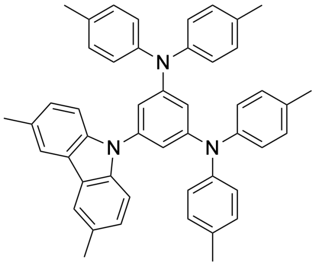


Figure S31. (a) ^{1}H (399.38 MHz) and (b) ^{13}C (100.42 MHz) spectra of **S1** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.



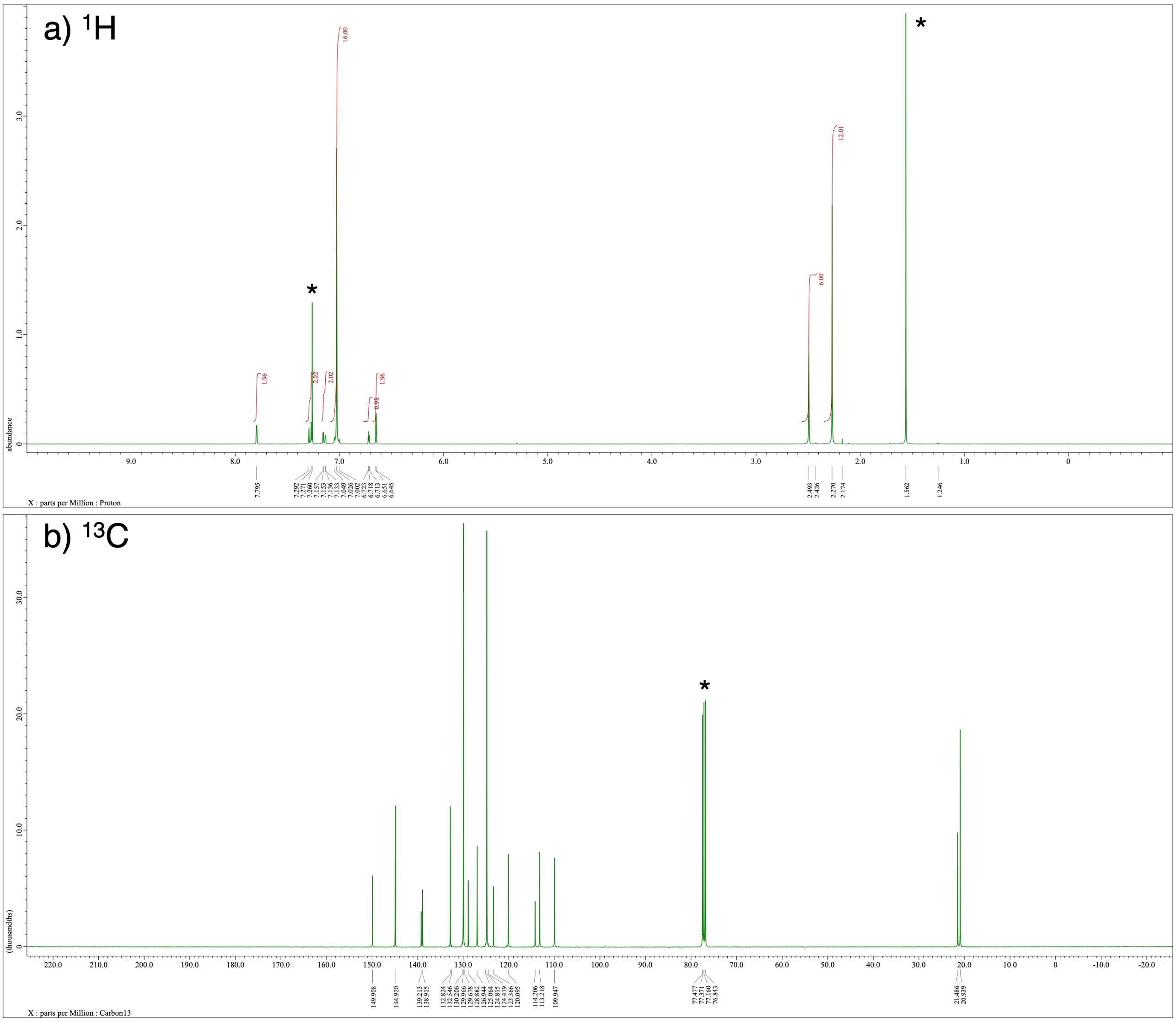


Figure S32. (a) ^{1}H (399.38 MHz) and (b) ^{13}C (100.42 MHz) spectra of **4** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.

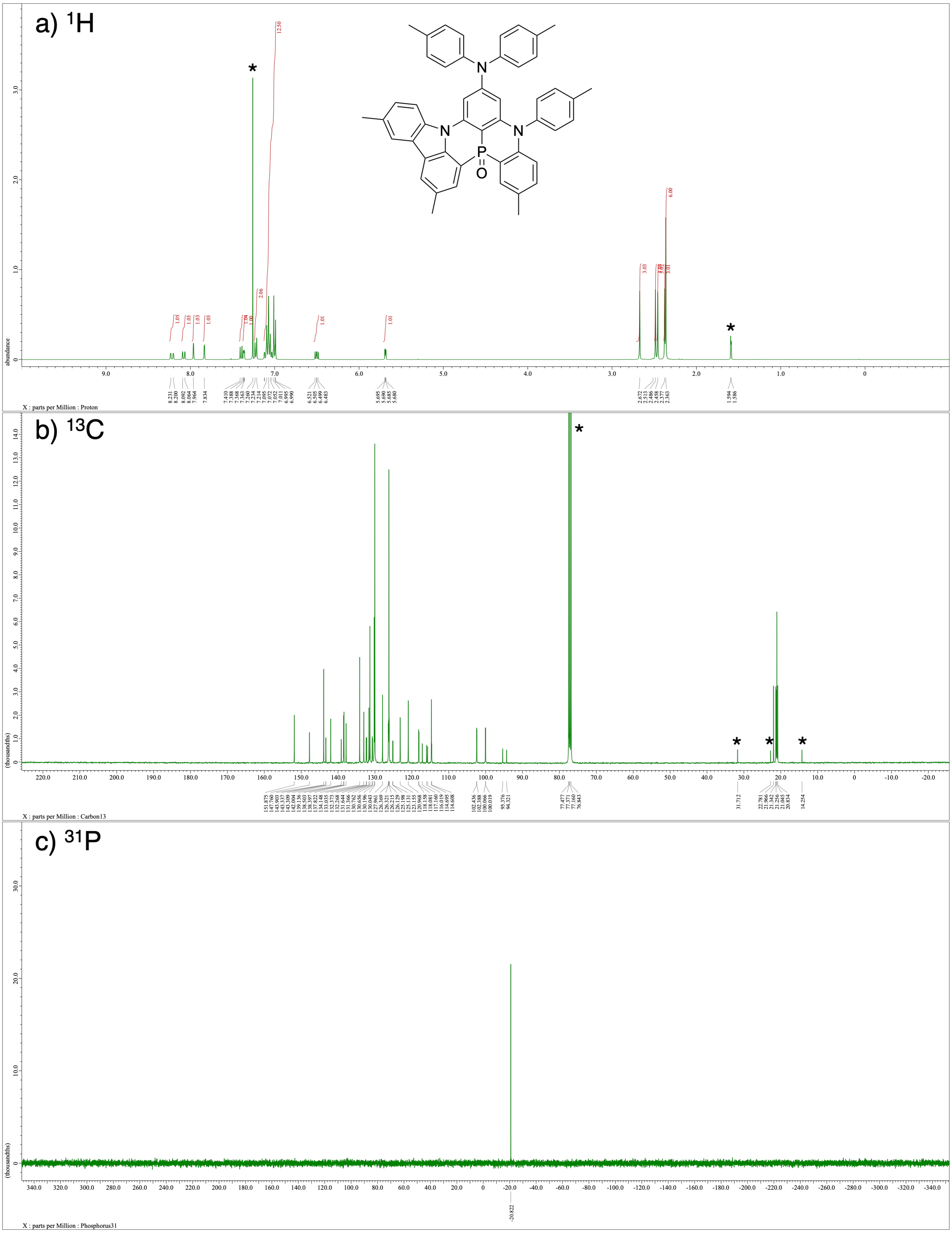
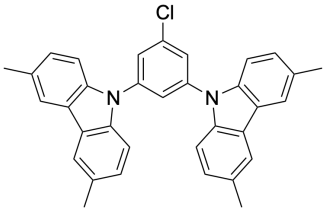


Figure S33. (a) ¹H (399.78 MHz), (b) ¹³C (100.42 MHz), and (c) ³¹P NMR (161.8 MHz) spectra of **4PO** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.



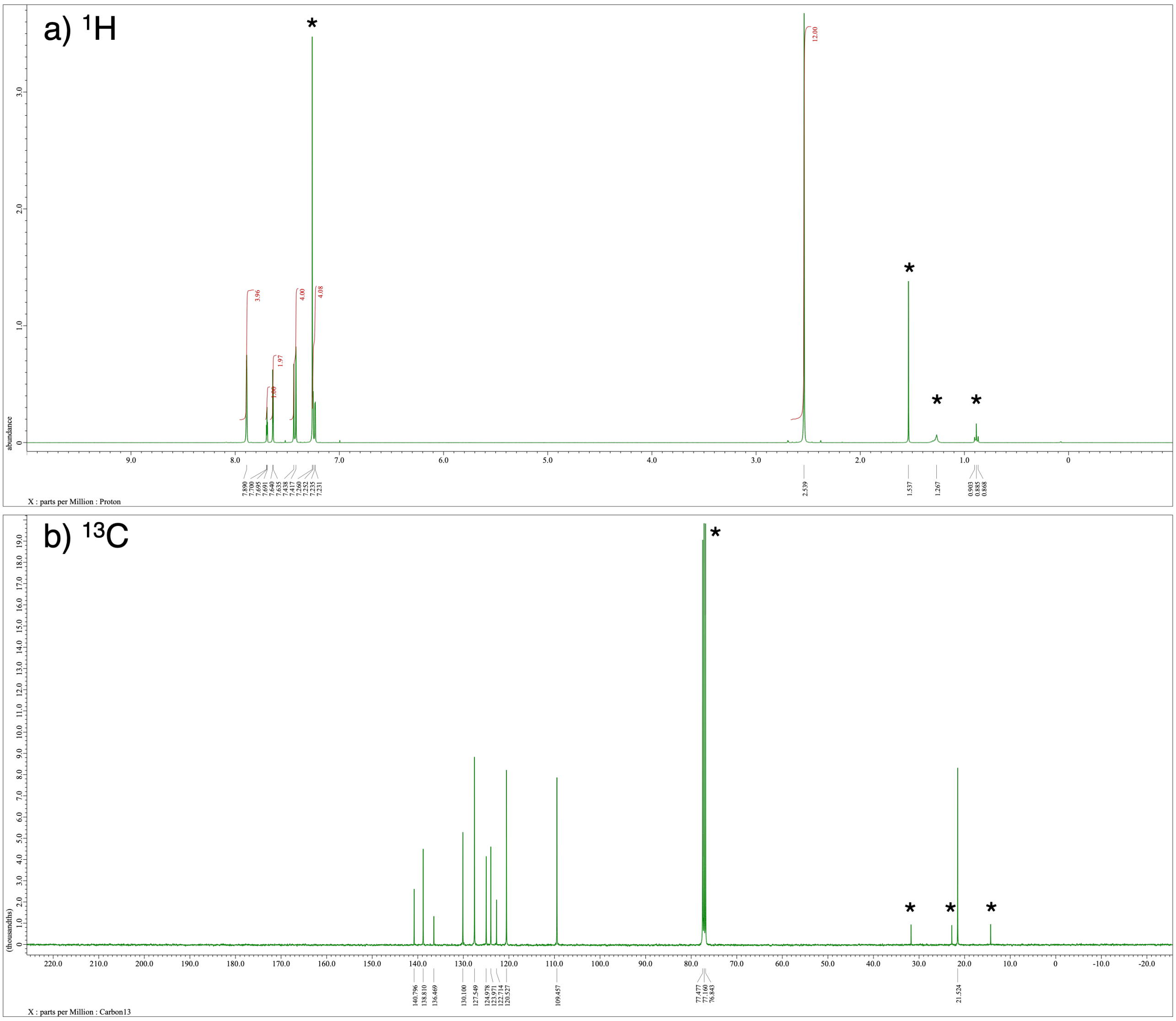


Figure S34. (a) ^{1}H (399.38 MHz) and (b) ^{13}C (100.42 MHz) spectra of **S2** in CDCl$_3$ at 25 °C. Peaks marked with * arise from residual solvents.

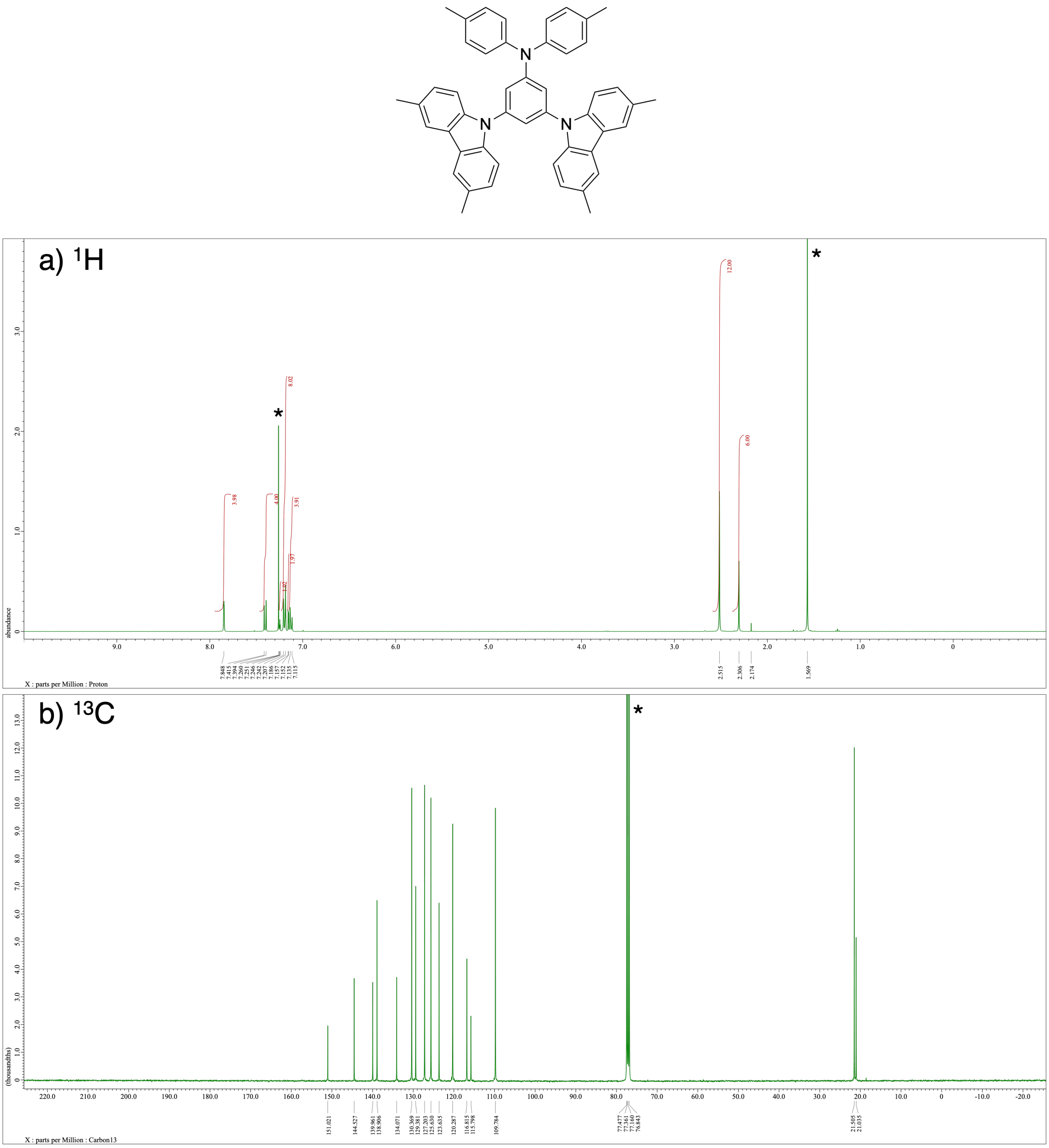


Figure S35. (a) ^{1}H (399.38 MHz) and (b) ^{13}C (100.42 MHz) spectra of **5** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.

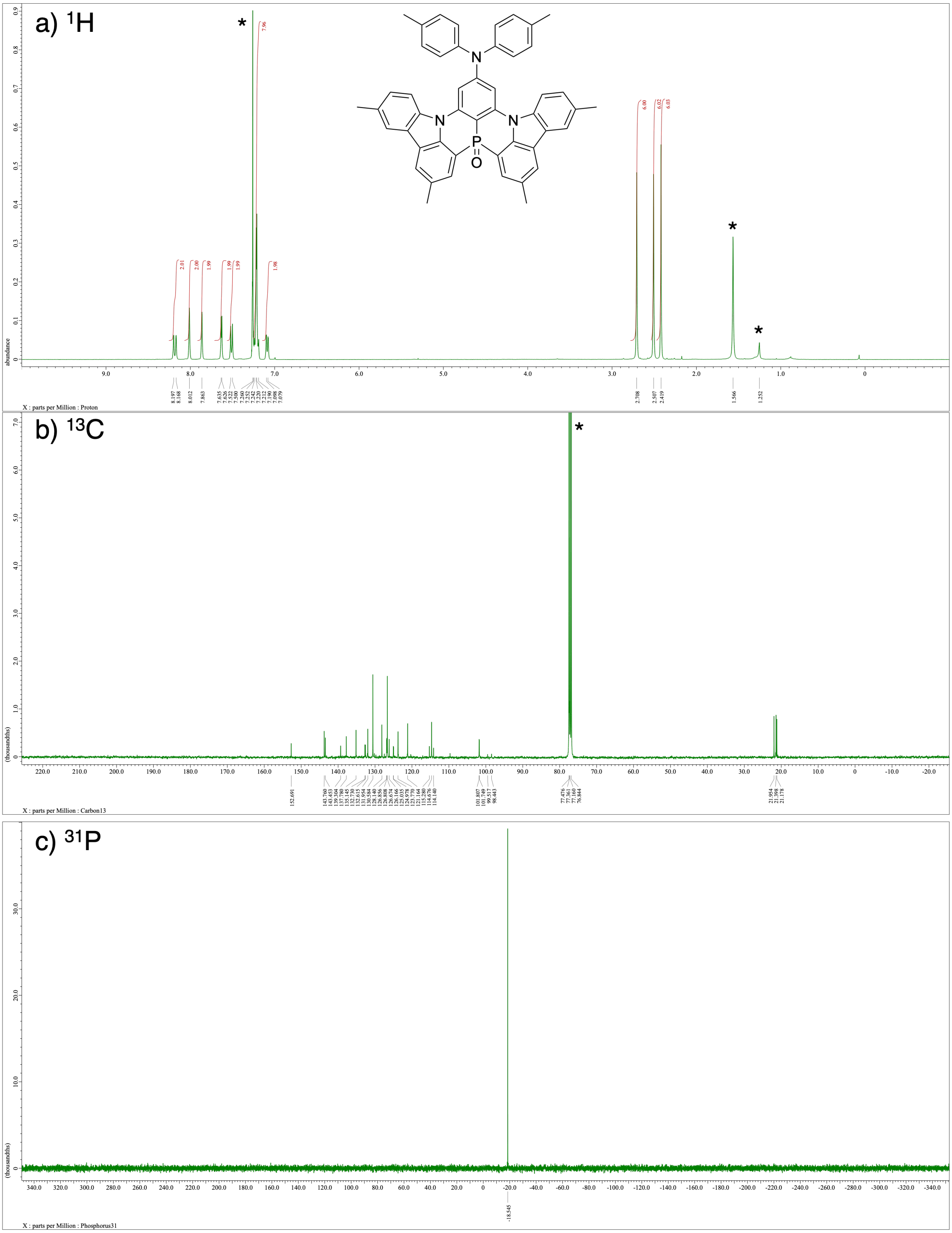


Figure S36. (a) ¹H (399.78 MHz), (b) ¹³C (100.53 MHz), and (c) ³¹P NMR (161.8 MHz) spectra of **5PO** in $CDCl_3$. Peaks marked with * arise from residual solvents.

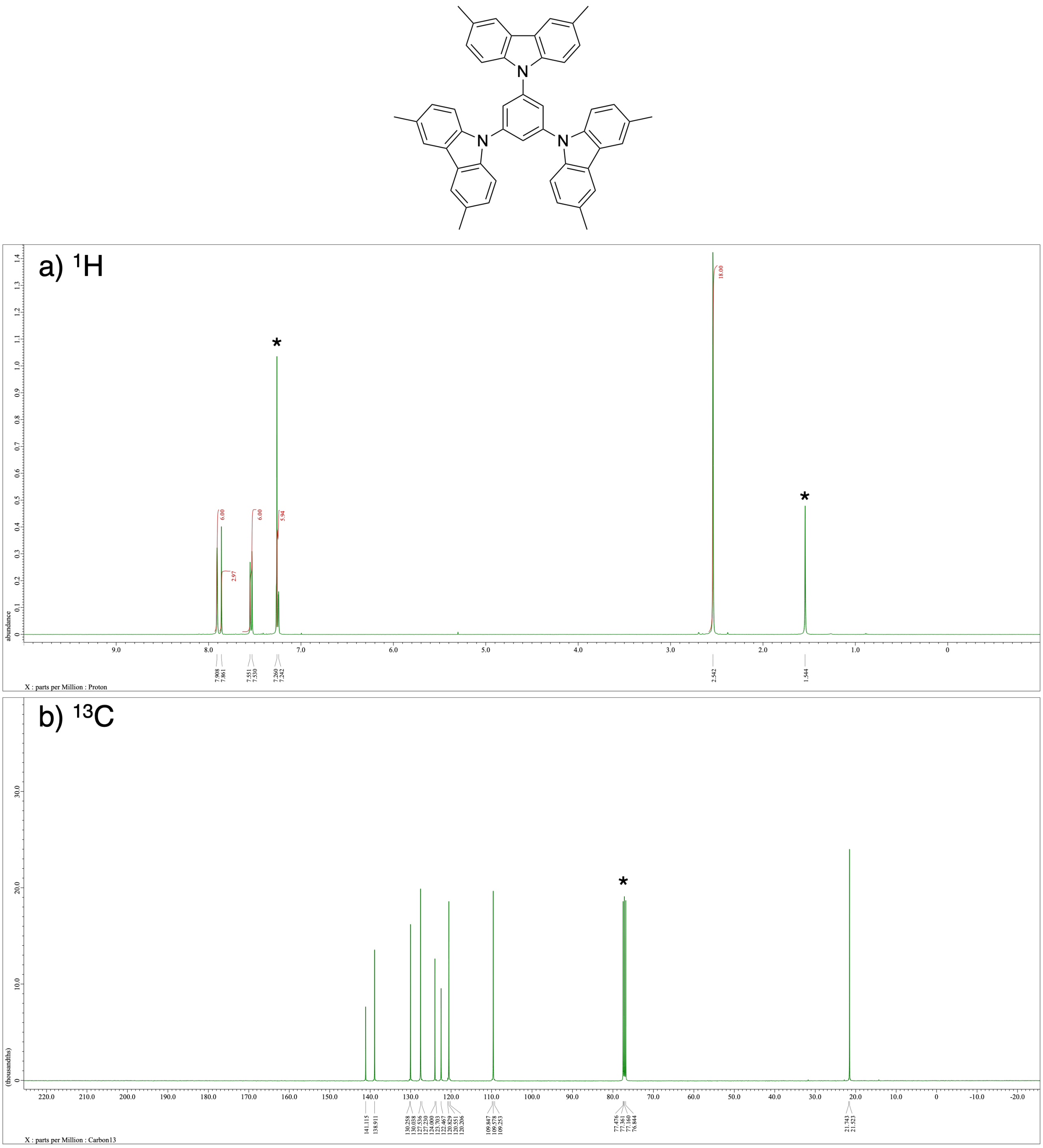


Figure S37. (a) ^{1}H (399.38 MHz) and (b) ^{13}C (100.53 MHz) spectra of **6** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.

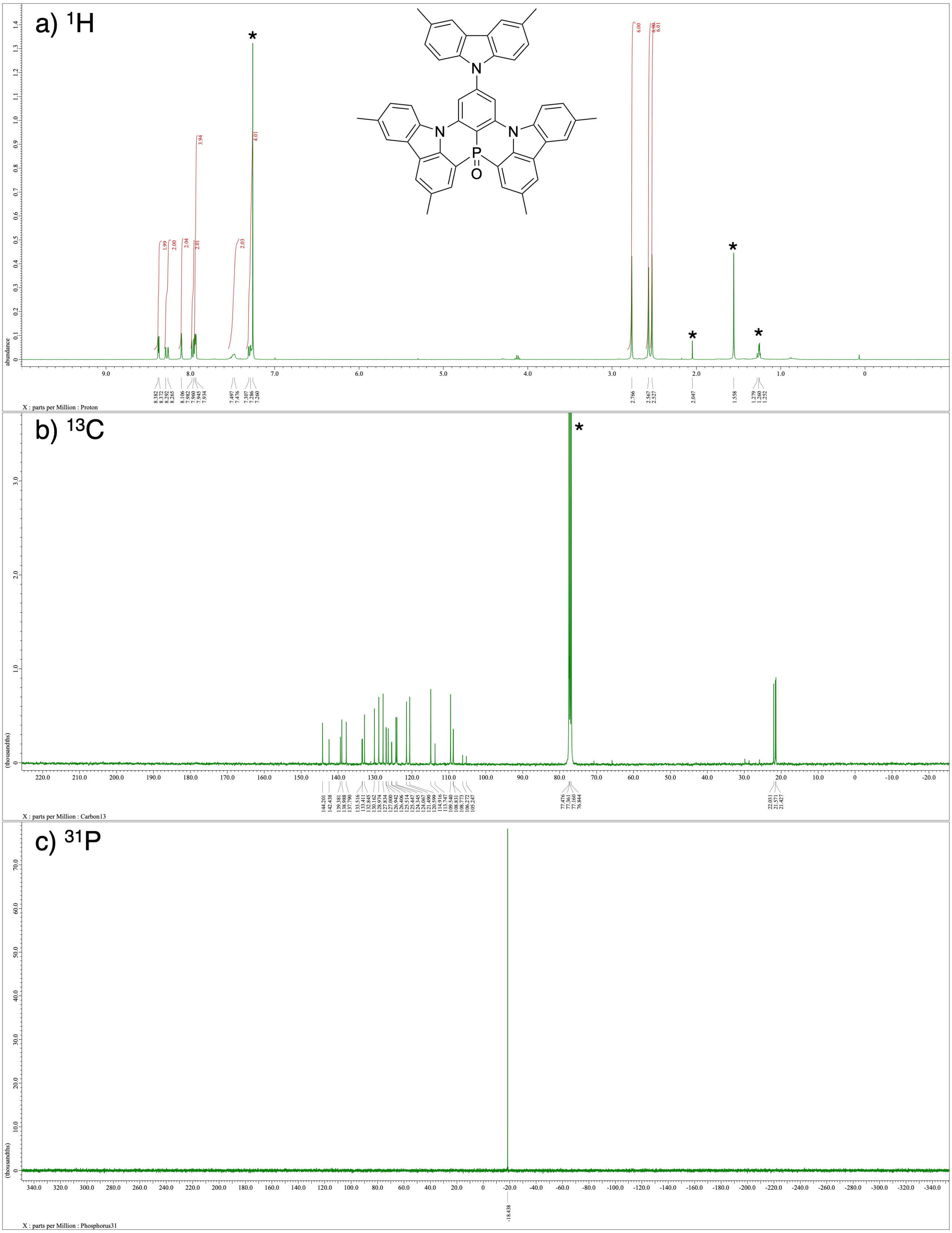
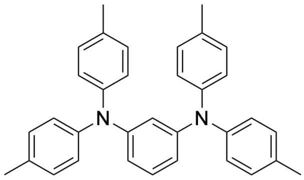


Figure S38. (a) ^{1}H (399.78 MHz), (b) ^{13}C (100.53 MHz), and (c) ^{31}P NMR (161.8 MHz) spectra of **6PO** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.



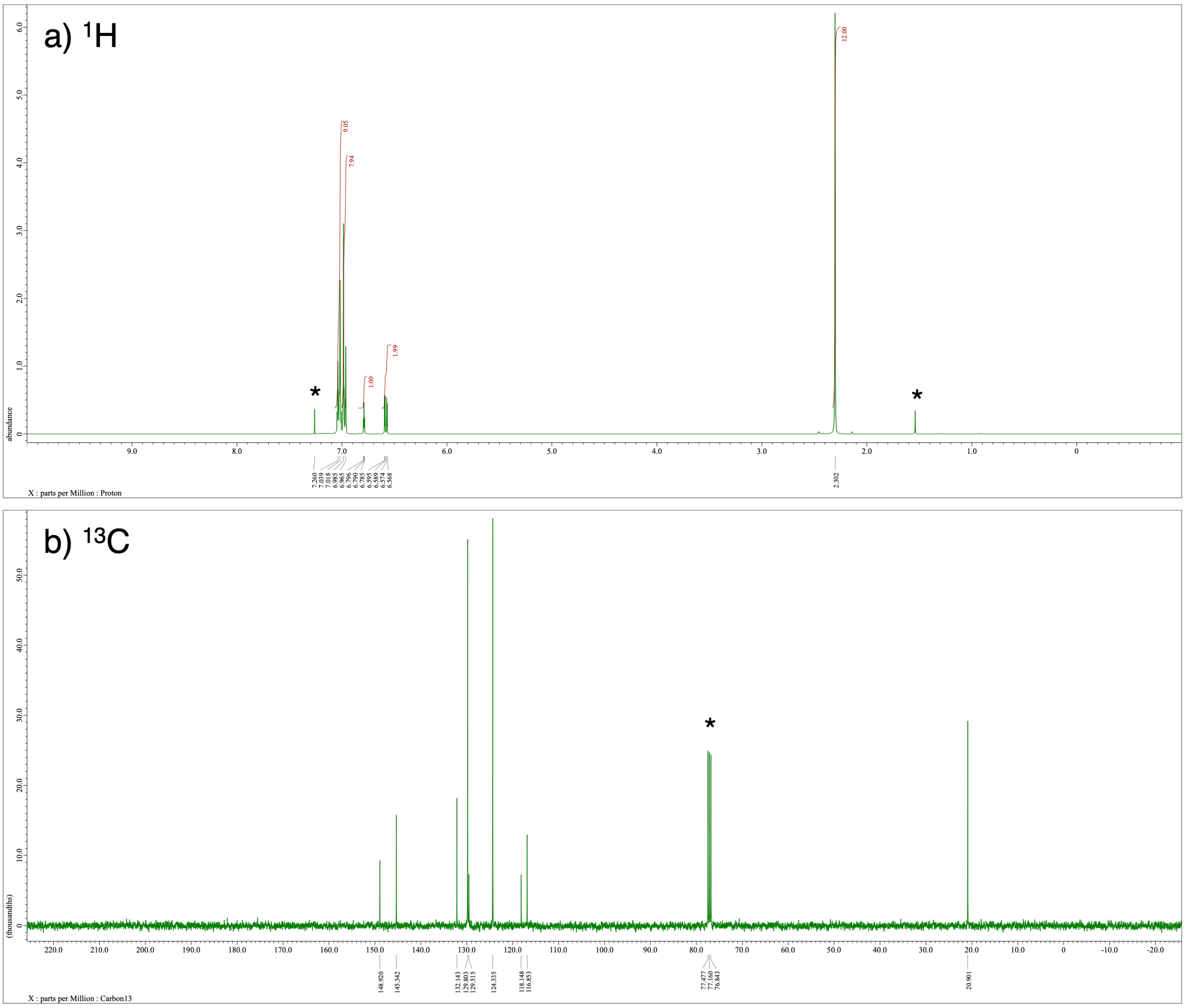


Figure S39. (a) ^{1}H (399.38 MHz) and (b) ^{13}C (100.42 MHz) spectra of **7** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.

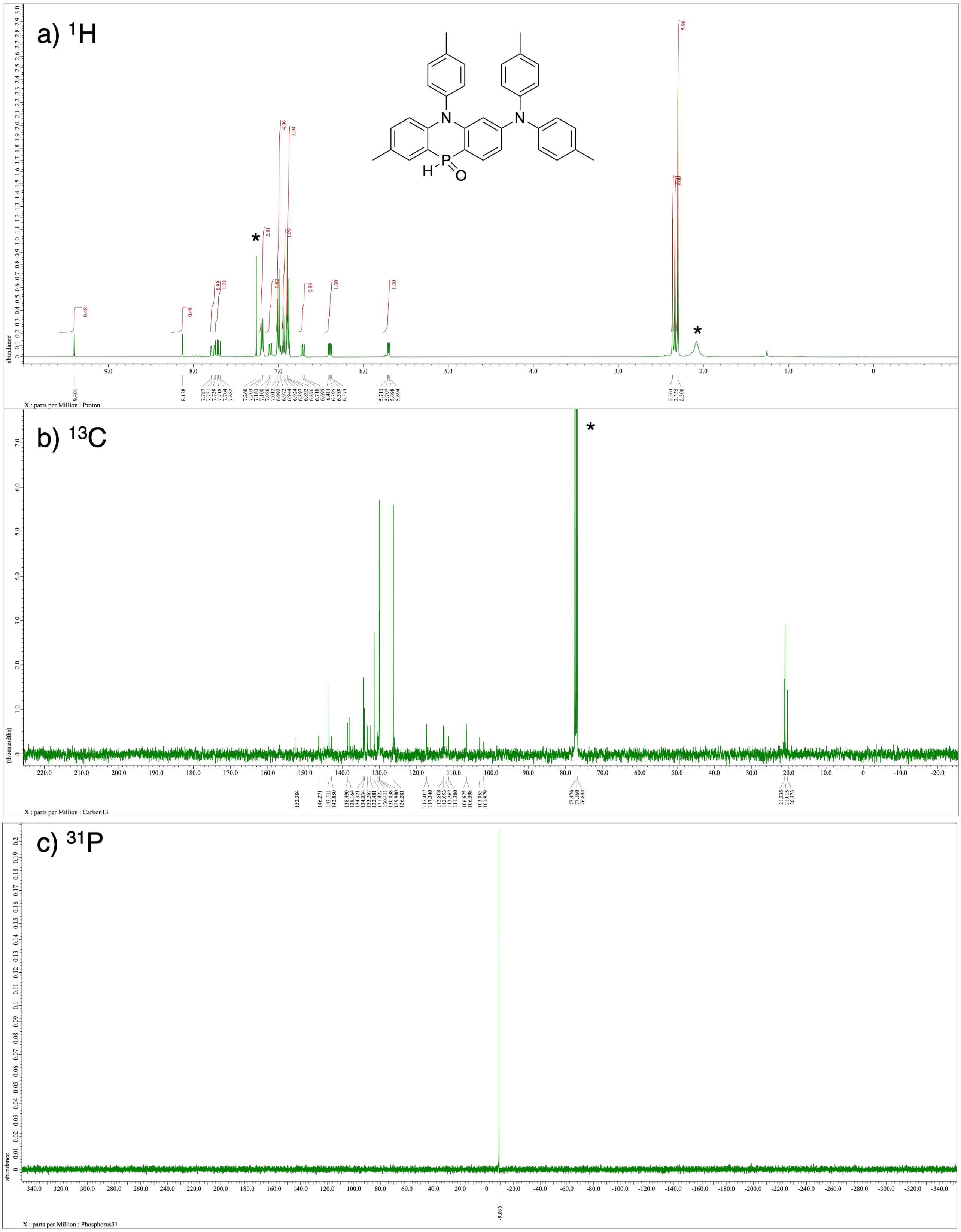
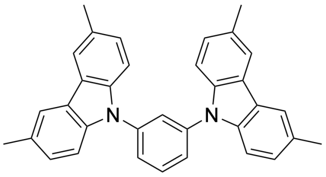


Figure S40. (a) ¹H (399.78 MHz), (b) ¹³C (100.52 MHz), and (c) ³¹P NMR (161.8 MHz) spectra of **7PO** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.



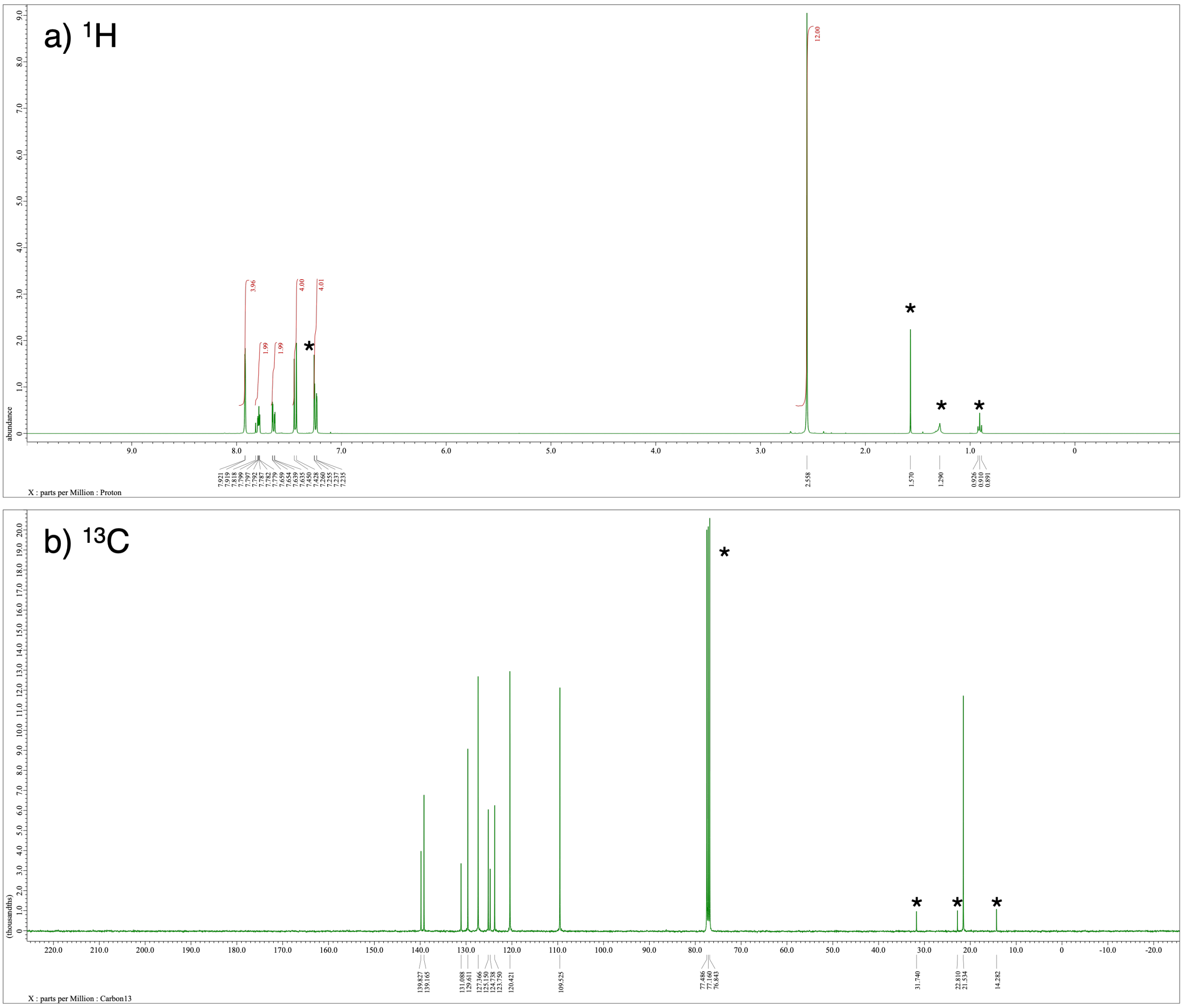


Figure S41. (a) ¹H (399.38 MHz) and (b) ¹³C (100.42 MHz) spectra of **8** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.

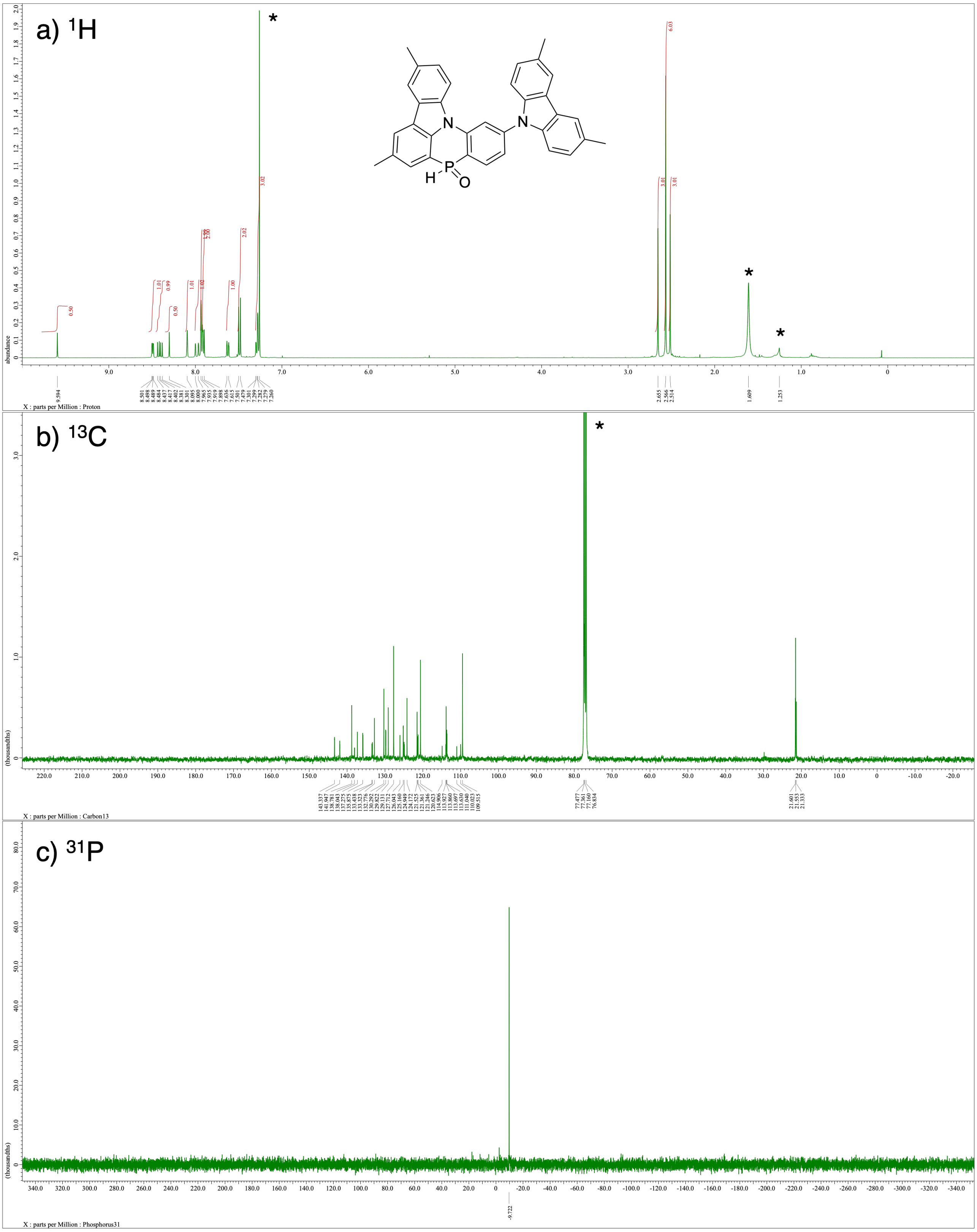
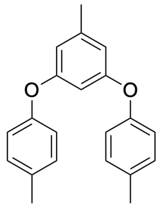


Figure S42. (a) ¹H (399.38 MHz), (b) ¹³C (100.42 MHz), and (c) ³¹P NMR (161.8 MHz) spectra of **8PO** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.



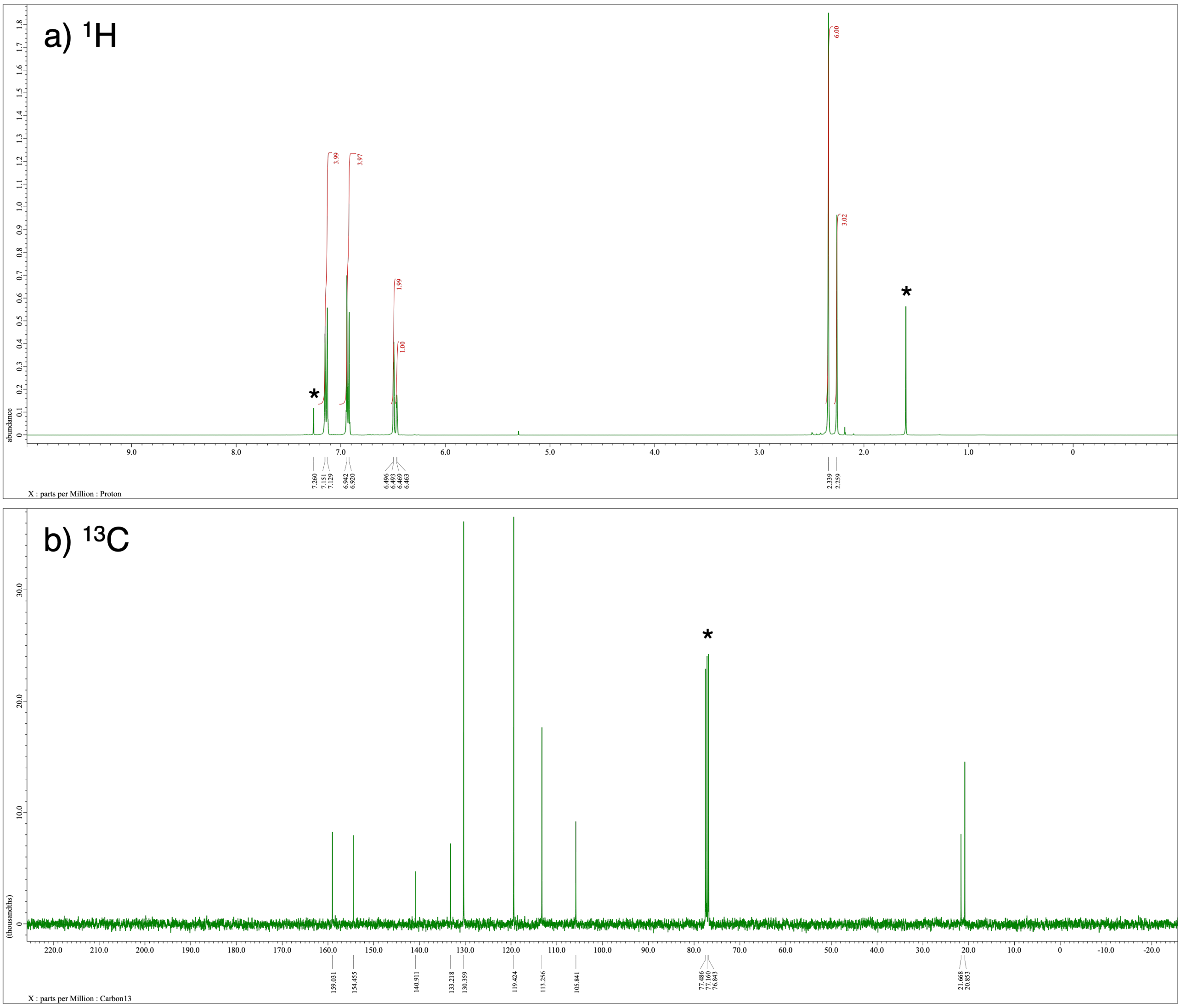


Figure S43. (a) ^{1}H (399.38 MHz) and (b) ^{13}C (100.42 MHz) spectra of **10** in CDCl$_3$ at 25 °C. Peaks marked with * arise from residual solvents.

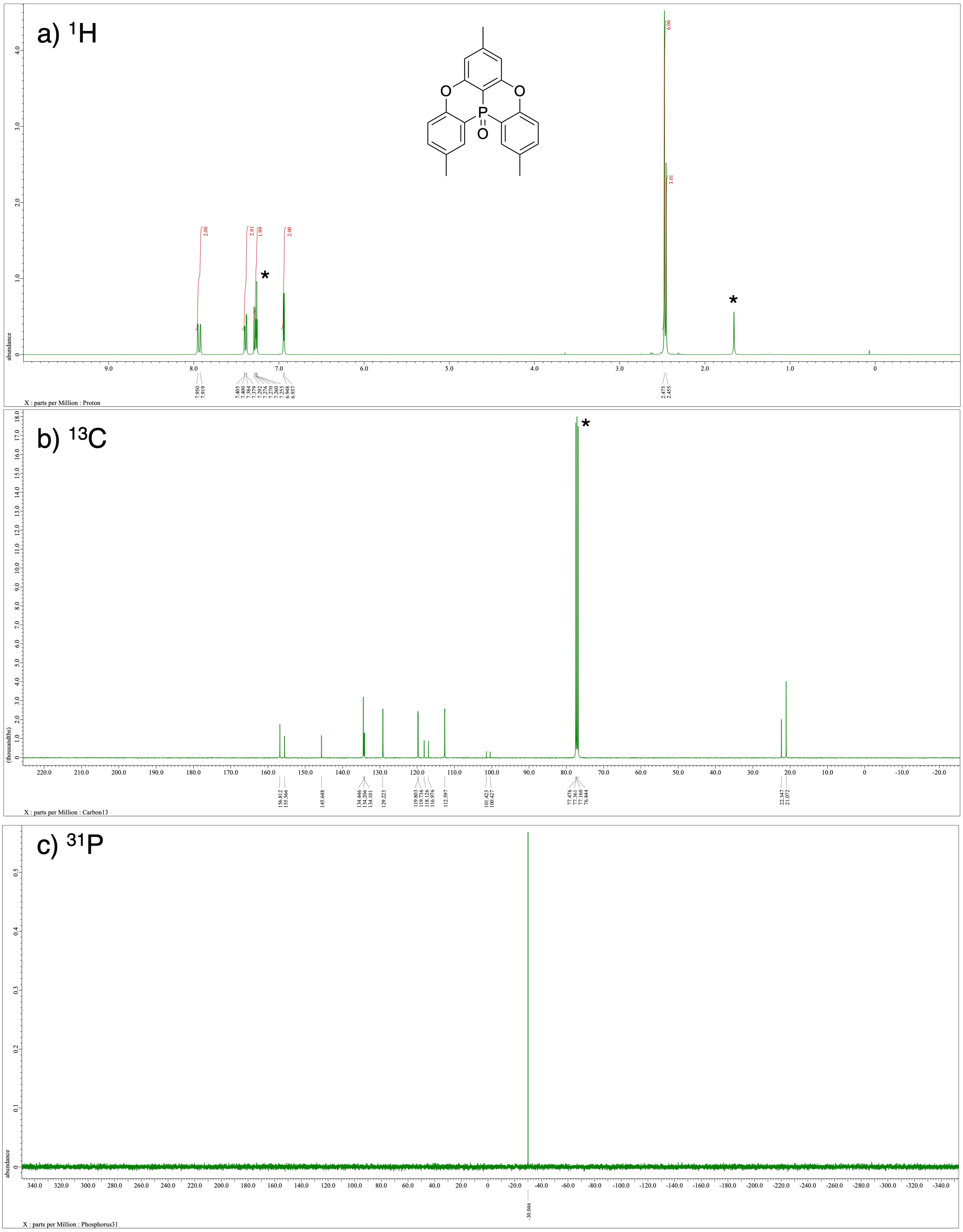


Figure S44. (a) ^{1}H (399.38 MHz), (b) ^{13}C (100.42 MHz), and (c) ^{31}P NMR (161.8 MHz) spectra of **10PO** in $CDCl_3$ at 25 °C. Peaks marked with * arise from residual solvents.

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