Supplementary Information (SI) for Chemical Science.

Non-Innocent P-Centers in Nonbenzenoid Polycyclic Aromatic Molecules with Tunable Structure and Property

Can Li,[a]‡ Wei Zhou,[a]‡ Zhaoxin Liu,[a]‡ Rong Gao,[a] Qixi, Mi,[a] Zhijun Ning,*[a] and Yi Ren*[a]

[a] School of Physical Science and Technology, ShanghaiTech University, Shanghai, 201210, China
‡ These authors contributed equally to this work.

Materials and Experiments General.

All manipulations were carried out under a dry nitrogen atmosphere employing standard Schlenk techniques. Solvents and Reagents were purchased from Shanghai Titan Scientific Co. Ltd. (Adamas-beta® regents), Bide Pharmatech Ltd, Energy Chemical, J&K Scientific, Sinopharm Chemical Reagent and TCI Shanghai, and were, unless otherwise noted, used as-received. Solvents were dried using an MBRAUN Solvent Purification System. NMR solvents were purchased from Cambridge Isotope Laboratories and J&K Scientific. Formamidinium iodide (FAI, > 99.99%) was purchased from Greatcell Solar. Lead (II) iodide (PbI2, 99.99%) was purchased from TCI. CsI (> 99.0%), Al2O3 (nanoparticles, 20 wt. % in isopropanol), 2-Propanol (IPA, anhydrous, 99.5%), N,N-Dimethylformamide (DMF, 99.8%), Dimethyl sulfoxide (DMSO, > 99.9%) and chlorobenzene (anhydrous, CB, 99.8%) were purchased from Sigma-Aldrich. Anisole (Super Dry, water ≤ 20 ppm, 99.7%) was purchased from J&KSeal. C_{60}, bathocuproine (BCP) and Ethylenediamine Dihydroiodide (EDADI2) were purchased from Xi'an Yuri Solar Co., Ltd. All the materials were used as received without any purification. F-doped Tin Oxide (FTO) was purchased from Suzhou SUNYO solar energy technology Co., Ltd. ^{1}H NMR, ^{13}C {^{1}H} NMR, and ^{31}P {^{1}H} NMR were recorded on Bruker AVANCE NEO 400 and AVANCE III HD 500 MHz spectrometers. High-resolution mass experiments were collected on the Thermo Scientific ultimate 3000-Q Exactive Focus LC-MS spectrometer in atmospheric press chemical ionization (APCI) mode. The crystal structures of **1CO** (CCDC 2379333), **PC3O** (CCDC 2379334), **PN3O** (CCDC 2379335), and **PN1S** (CCDC 2379336) were obtained in the X-ray Crystallography Facility at the ShanghaiTech University. UV-vis experiments were carried out on the Agilent Cary 100 spectrophotometer. The fluorescence measurements were performed using a HORIBA Fluorolog-3 fluorescence spectrophotometer. Absolute quantum yields were obtained with a pre-calibrated Quanta-φ integrating sphere attached to a Fluorolog-3 instrument. Lifetime experiments were carried out on a HORIBA DeltaFlex-011x time-resolved fluorescence spectrometer with DD-375L laser for excitation and MCP-PMT detector. This set-up allows the time resolution is ~25 ps. Cyclic voltammetry (CV) were recorded using a CHI650E from CH_2Cl_2 solutions using tetrabutylammonium hexafluorophosphate as electrolyte, Pt electrode as a working electrode, Pt wire as a counter electrode, and Ag wire as a pseudoreference electrode, using ferrocene/ferrocenium (Fc/Fc^{+}) as internal standard. The scan rate was 50 mV s^{-1}. Theoretical calculations were carried out using the GAUSSIAN 09 suite of programs.[S1]

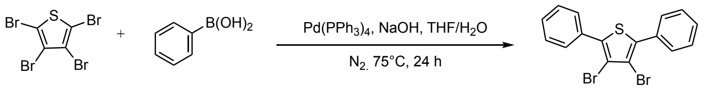
Device Fabrication: The pre-patterned FTO substrates were cleaned by an ultrasonic instrument using sequentially washing with DI water bath with 2% Triton X-100 v/v, DI water, and IPA for 30 min each. The substrates were further cleaned with UV ozone treatment for 20 min before used. The E/G molecules were dissolved in chlorobenzene with concentration of 2mg/ml and spin-coated on the FTO substrate at 6000 rpm for 30 s, following annealed on a hotplate at 20 °C for 10 min. Al_2O_3 nanoplate dispersions with concentration of 0.5 wt% in isopropanol were spin-coated on HTL at 4000 rpm for 30 s, followed by thermal annealing at 100 °C for 10 min.

1.5 M $Cs_{0.03}FA_{0.97}PbI_3$ perovskite precursors were prepared by dissolving CsI, FAI, and PbI_2 in mixed solution (DMSO:DMF =1:4 v/v), 2% CsSCN was added to improve the quality of perovskite films. The precursor solutions were stirred at 60 °C for 1 h and then filtered using a 0.22 polytetrafluoroethylene membrane before use. Then the perovskite solutions were spin-coated at 2000 r.p.m for 15 s (acceleration rate 1000 r.p.m./s) and 6000 r.p.m. for 25 s (acceleration rate 6000 r.p.m./s), respectively. At the last 10 s of the second step, 150 μL anisole was dropped as antisolvent. The films were then annealed at 100 °C for 10 min.

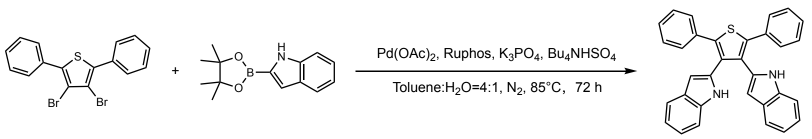
For the post-treatment, 0.5 mg EDADI was dissolved in 1 mL isopropanol solvent and filtered before use, 50 μL solution was spin-coated on the perovskite films at 4000 r.p.m for 25 s, followed by annealing at 100 °C for 10 min. After cooling down to room temperature, the substrates were transferred to the evaporation system and a 23 nm C_{60} film was subsequently deposited on top by thermal evaporation at a rate of 0.2 A s^{-1}, after finishing the C_{60} deposition, an 8 nm BCP layers was deposited at a ret of 0.08 A s^{-1}. Finally, 100nm Ag electrode was evaporated by thermal evaporation.

Device characterizations: Keithley 2400 source unit was employed to obtain J-V curves under simulated AM1.5G solar illumination at 100 mW cm^{-2} (1 sun). For the J-V curves measurement, the active area of all the devices was masked using a metal mask with an area of 0.04522. The calibration of light was enabled by a KG-5 Si diode with a solar simulator (Enli Tech, Taiwan). The devices are measured in reverse scan (1.15 V to 0 V, step 0.01 V) and forward scan (0 V to 1.15 V, step 0.01 V) with a delay time of 30 ms at room temperature in a glovebox.

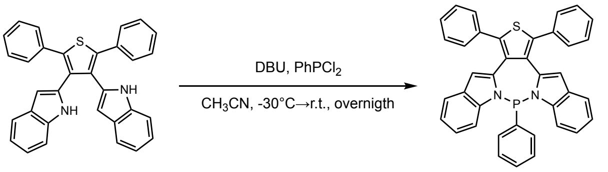
Synthesis of target molecules



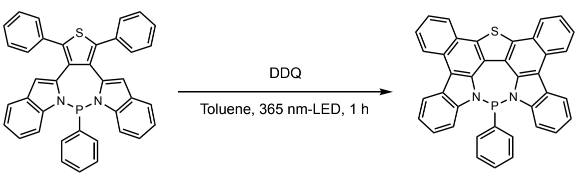
2a: Tetrabromothiophene (500 mg, 1.25 mmol, 1.0 equiv), phenylboronic acid (320.3 mg. 2.63 mmol, 2.1 equiv), $Pd(PPh_3)_4$ (72.3 mg, 0.063 mmol, 0.05 equiv) and NaOH (200 mg, 5 mmol, 4.0 equiv) were added to a mixture of degassed THF (20 mL) and H_2O (5 mL). The mixture was degassed for 10 min, heated at 75 °C under N_2 for 12 hours before being cooled to room temperature, after which it was poured into 10 mL of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (petroleum ether). Isolated yield: 83%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.69 – 7.64 (m, 4H), 7.50 – 7.39 (m, 6H) ppm. The NMR spectra is consistent with previous reported NMR spectra.[s1]



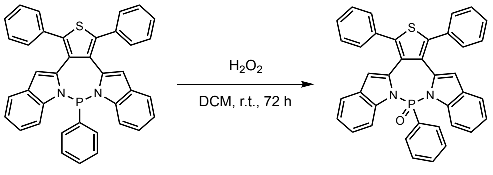
3a: 2a (200 mg, 0.5 mmol, 1.0 equiv) 2-(pinacolatebory)indole (296 mg, 1.22 mmol, 2.4 equiv), palladium(II) acetate (9.1 mg 0.04 mmol, 0.08 equiv), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (37.9 mg, 0.08 mmol, 0.16 equiv), K_3PO_4 (323 mg, 1.52 mmol, 3.0 equiv) and tetrabutylammonium hydrogen sulfate (17.3 mg, 0.05 mmol, 0.1 equiv) were added to a mixture of degassed Toluene (20 mL) and H_2O (5 mL). The mixture was degassed for 15 min, heated at 85°C under N_2 for 72 hours before being cooled to room temperature and filtered. And the residue was washed with petroleum ether and dried it in ambient condition to a yield off-white solid. Isolated yield: 80%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.83 (s, 2H), 7.47 (d, J = 7.8 Hz, 2H), 7.38 – 7.33 (m, 4H), 7.32 – 7.28 (m, 6H), 7.15 – 7.08 (m, 4H), 7.08 – 6.02 (m, 2H), 6.27 (dd, J = 2.2, 0.8 Hz, 2H) ppm. ^{13}C NMR (DMSO-d_6, 101 MHz, 298 K) δ: 140.2, 136.1, 133.3, 132.3, 131.8, 128.9, 128.2, 128.0, 127.8, 121.1, 120.0, 119.0, 111.3, 102.7 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{32}H_{23}N_2S^+$ 467.1577; Found 467.1583.



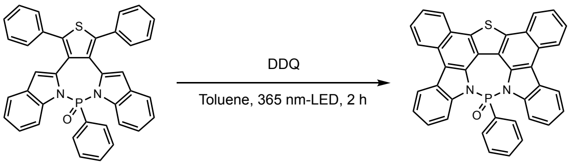
4a: In a 1-necked 100 mL Schlenk flask, **3a** (80 mg, 0.17 mmol, 1.0 equiv) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) (0.08 ml, 0.53 mmol, 3.0 equiv) were added to 50 mL dry MeCN under N_2 atmosphere. The solution was cooled to -30 °C for 30 min, then the dichlorophenylphosphine (0.3 mL, 0.22 mmol, 1.3 equiv, 10 % in dry toluene, V:V) was slowly injected. The mixture was allowed up to room tempetature slowly and stirred for 12 hours before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 3:17, V:V). Isolated yield: 90%. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) δ: 8.05 (dd, J = 8.0, 1.8 Hz 2H), 7.43 (td, J = 7.3, 1.7 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.35 – 7.30 (m, 11H), 7.29 – 7.27 (m, 2H), 7.25 – 7.24 (m, 1H), 7.17 – 7.11 (m, 3H), 6.25 (s, 2H). ^{13}C NMR (CDCl$_3$, 101 MHz, 298 K) δ: 142.1 (d, J = 26.4 Hz), 140.1, 137.4, 136.6 (d, J = 7.0 Hz), 134.3, 129.6, 129.5 (d, J = 9.0 Hz), 129.4, 129.1, 128.7, 128.3 (d, J = 4.8 Hz), 128.1, 123.0, 121.5, 120.9, 111.9 (d, J = 20.3 Hz), 111.5 ppm. ^{31}P {^{1}H} NMR (CDCl$_3$, 162 MHz, 298 K) δ: 37.7 ppm. HRMS (APCI-TOF) m/z: [M+H]$^+$ Calcd. for $C_{38}H_{26}N_2PS^+$ 573.1549; Found 573.1548.



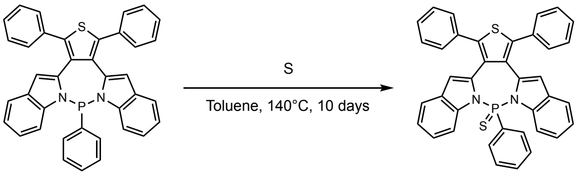
PN1: In a 100 mL Schlenk tube, **4a** (72.6 mg, 0.13 mmol, 1.0 equiv), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (72 mg, 0.32 mmol, 2.5 equiv) were dissolved in 25 mL anhydrous toluene under N_2 atmosphere. The solution was stirred for 1 hour under the irradiation of a 365 nm LED lamp (10 W) at room temperature before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 1:1, V:V). Isolated yield: 96%. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) δ: 8.86 (d, J = 8.3 Hz, 2H), 8.61 (d, J = 7.9 Hz, 2H), 8.39 (d, J = 8.2 Hz, 2H), 8.24 (d, J = 8.1 Hz, 2H), 7.73 (t, J = 7.5 Hz, 2H), 7.66 (d, J = 7.6 Hz, 2H), 7.59 (q, J = 8.2, 4H), 6.78 (t, J = 7.2 Hz, 1H), 6.60 (t, J = 7.7 Hz, 2H), 5.73 (t, J = 7.5 Hz, 2H) ppm. ^{31}P {^{1}H} NMR (CDCl$_3$, 162 MHz, 298 K) δ: 54.7 ppm. HRMS (APCI-TOF) m/z: [M+H]$^+$ Calcd. for $C_{38}H_{22}N_2PS^+$ 569.1236; Found 569.1226. ^{13}C NMR spectrum was obtained due to its insufficient solubility in CDCl$_3$, THF-d$_6$, acetone-d$_6$, and acetonitrile-d$_3$.



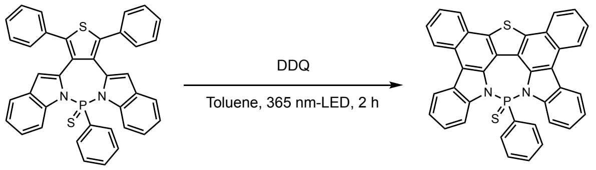
4aO: To a dichloromethane (8 mL) solution of **4a** (30.3 mg, 0.05 mmol), and H_2O_2 (30% in H_2O) was added. The solution was stirred for 3 days under dark at room temperature. Then, the mixture was quenched with H_2O (30 mL). The aqueous phase was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 2:3, V:V). Isolated yield: 81%. ^{1}H NMR (CDCl$_3$, 500 MHz, 298 K) δ: 8.70 (d, J =8.5 Hz, 2H), 7.80 (dd, J = 15.1, 7.5 Hz, 2H), 7.42 – 7.30 (m, 17H), 7.18 (t, J = 7.5 Hz 2H), 6.26 (d, J = 2.1 Hz, 2H) ppm. ^{13}C NMR (CDCl$_3$, 101 MHz, 298 K) δ: 140.9, 140.6 (d, J = 3.7 Hz), 133.6, 133.2 (d, J = 5.7 Hz), 132.8, 131.1, 130.8 (d, J = 11.9 Hz), 130.1 (d, J = 8.5 Hz), 129.3, 128.9, 128.6, 128.5, 128.4, 124.3, 122.7, 120.8, 115.8, 112.2 (d, *J* = 6.6 Hz) ppm. ^{31}P {^{1}H} NMR (CDCl$_3$, 202 MHz) δ: 15.5 ppm. HRMS (APCI-TOF) m/z: [M+H]$^+$ Calcd. for $C_{38}H_{26}N_2OPS^+$ 589.1498; Found 589.1487.



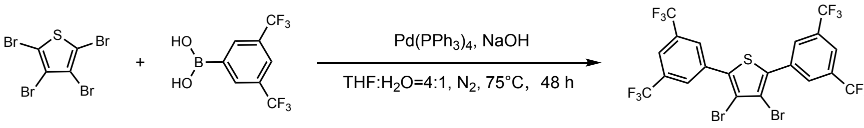
PN1O: In a 100 mL Schlenk tube, **4aO** (52.5 mg, 0.09 mmol, 1.0 equiv) and DDQ (50.2 mg, 0.22 mmol, 2.4 equiv) were dissolved in 19 mL anhydrous toluene under N_2 atmosphere. The solution was stirred for 2 hours under the irradiation of a 365 nm LED lamp (10 W) at room temperature, after which it was poured into 50 mL of saturated sodium bicarbonate solution. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. And the residue was washed with methanol and dried it in ambient condition to yield a white solid. Yield: 95%. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) δ: 9.14 – 9.12 (m, 2H), 8.94 (d, *J* = 8.4 Hz, 2H), 8.65 (d, *J* = 7.3 Hz, 2H), 8.29 (d, *J* = 8.1 Hz, 2H), 7.79 (t, *J* = 7.9 Hz, 2H), 7.68 – 7.62 (m, 6H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.81 – 6.76 (m, 2H), 6.32 – 6.28 (m, 2H) ppm. ^{31}P {^{1}H} NMR (CDCl3, 162 MHz, 298 K) δ: 14.3 ppm. HRMS (APCI-TOF) m/z: [M+H]$^+$ Calcd. for $C_{38}H_{22}N_2OPS^+$ 585.1185; Found 585.1191. ^{13}C NMR spectrum was not obtained due to its insufficient solubility in CDCl$_3$, THF-d$_6$, acetone-d$_6$, and acetonitrile-d$_3$.



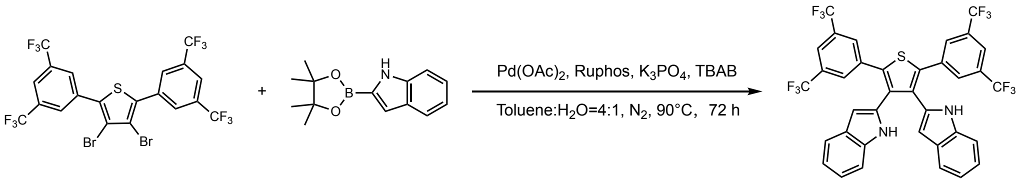
4aS: Under N_2 atmosphere, **4a** (45.8 mg, 0.08 mmol, 1.0 equiv) and sublimed sulfur powder (25.6 mg, 0.8 mmol, 10.0 equiv) were added to 5 mL anhydrous toluene. The solution was stirred for 10 days under dark at 140 °C. After cooling to room temperature, the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 1:4, V:V). Isolated yield: 96%. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) δ: 9.34 (d, *J* = 8.6 Hz, 2H), 7.77 (dd, *J* = 15.8, 7.6 Hz, 2H), 7.38 – 7.27 (m, 17H), 7.18 (t, *J* = 7.4 Hz 2H), 6.27 (d, *J* = 1.6 Hz, 2H) ppm. ^{13}C NMR (CDCl$_3$, 101 MHz, 298 K) δ: 141.4 (d, *J* = 4.1 Hz), 140.0, 139.3, 138.0, 135.1, 133.6, 132.0 (d, *J* = 2.5 Hz), 130.7 (d, *J* = 8.2 Hz), 129.2, 128.9, 128.7 (d, *J* = 12.2 Hz), 128.5 (d, *J* = 15.9 Hz), 128.3, 123.8, 122.7, 120.9, 116.5, 112.3 (d, *J* = 5.8 Hz) ppm. ^{31}P {^{1}H} NMR (CDCl$_3$, 162 MHz, 298 K) δ: 47.1 ppm. HRMS (APCI-TOF) m/z: [M+H]$^+$ Calcd. for $C_{38}H_{26}N_2PS_2^+$ 605.1270; Found 605.1261.



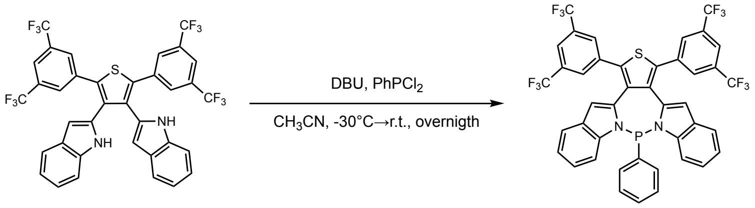
PN1S: In a 100 mL Schlenk tube, **4aS** (54.1 mg, 0.09 mmol, 1.0 equiv), and DDQ (50.8 mg, 0.22 mmol, 2.4 equiv) were dissolved in 22 mL anhydrous toluene under N_2 atmosphere. The solution was stirred for 3 hours under the irradiation of a 365 nm LED lamp (10 W) at room temperature before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 3:7, V:V). Isolated yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 9.29 – 9.26 (m, 2H), 8.86 (d, *J* = 8.8 Hz, 2H), 8.60 – 8.58 (m, 2H), 8.15 (d, *J* = 8.1 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.73 – 7.55 (m, 6H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.69 – 6.64 (m, 2H), 6.14 – 6.08 (m, 2H) ppm. ^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: 49.5 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{38}H_{22}N_2PS_2^+$ 601.0957; Found 601.0955. ^{13}C NMR spectrum was not obtained due to its insufficient solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3.



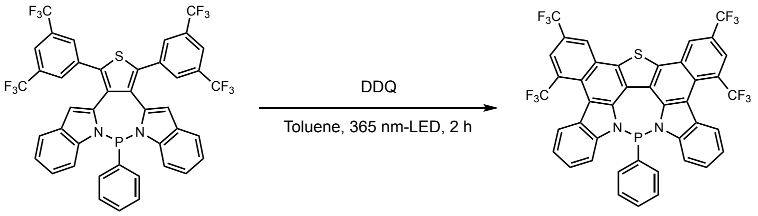
2b: Tetrabromothiophene (100 mg, 0.25 mmol, 1.0 equiv), 3,5-bis(trifluoromethyl)benzeneboronic acid (142 mg. 0.55 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (14.5 mg, 0.013 mmol, 0.05 equiv) and NaOH (40 mg, 1.0 mmol, 4.0 equiv) were added to a mixture of degassed THF (8 mL) and H_2O (2 mL). The mixture was degassed for 10 min, heated at 75 °C under N_2 for 48 hours before being cooled to room temperature, after which it was poured into 10 mL of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (petroleum). Isolated yield: 65%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.12 (s, 4H), 7.96 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 136.2, 134.4, 132.6 (q, *J* = 33.6 Hz), 129.3, 123.1 (q, *J* = 275.4 Hz), 123.0, 115.3 ppm. ^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz, 298 K) δ: -63.0 ppm.



3b: **2b** (100 mg, 0.15 mmol, 1.0 equiv), 2-(pinacolatebory)indole (87.6 mg, 0.36 mmol, 2.4 equiv), palladium(II) acetate (2.7 mg 0.012 mmol, 0.08 equiv), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (11.2 mg, 0.024 mmol, 0.16 equiv), K_3PO_4 (95.6 mg, 0.45 mmol, 3.0 equiv) and tetrabutylammonium bromide (4.84 mg, 0.015 mmol, 0.1 equiv) were added to a mixture of degassed Toluene (8 mL) and H_2O (2 mL). The mixture was degassed for 15 min, heated at 90 °C under N_2 for 72 hours before being cooled to room temperature, after which it was poured into 10 mL of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 3:7, V:V). Isolated yield: 51%. ^1H NMR ($CDCl_3$, 500 MHz, 298 K) δ: 7.83 (s, 2H), 7.81 (s, 2H), 7.77 (s, 4H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.14 – 7.13 (m, 4H), 7.11 – 7.06 (m, 2H), 6.36 (d, *J* = 2.1 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 138.6, 136.3, 135.3, 132.4, 132.2 (q, *J* = 34.2 Hz), 129.4, 129.1, 128.0, 123.2, 123.0 (q, *J* = 272.7 Hz), 122.2, 121.0, 120.6, 111.2, 105.6 ppm, ^{19}F {^1H} NMR ($CDCl_3$, 376 MHz, 298 K) δ: -63.2 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{36}H_{19}F_{12}N_2S^+$ 739.1072; Found 739.1074.

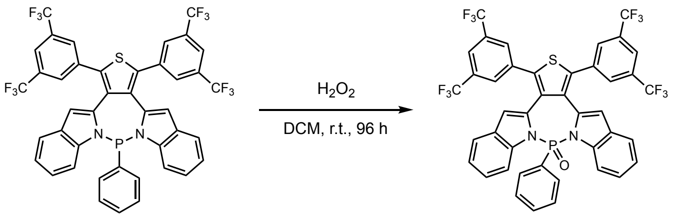


4b: In a 1-necked 100 mL Schlenk flask, **3b** (96.4 mg, 0.13 mmol, 1.0 equiv) and DBU (0.06 mL, 0.39 mmol, 3.0 equiv) were added to 30 mL dry CH_3CN under N_2 atmosphere. The solution was cooled to -30 °C for 30 min, then the dichlorophenylphosphine (0.23 mL, 0.17 mmol, 1.3 equiv, 10% in dry toluene, V:V) was slowly injected in one portion. The mixture was allowed up to room temperature slowly and stirred for 12 hours before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 1:9, V:V). Isolated yield: 83%. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.05 (d, *J* = 8.2 Hz, 2H), 7.86 (s, 2H), 7.79 (s, 4H), 7.42 (d, *J* = 7.8, 2H), 7.36 – 7.31 (m, 4H), 7.29 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.23 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, 298 K) δ: 142.3 (d, *J* = 26.2 Hz), 137.6, 137.0, 136.1, 134.5 (d, *J* = 7.0 Hz), 132.3 (q, *J* = 32.8 Hz), 132.0, 130.1, 129.6, 129.1 (d, *J* = 4.6 Hz), 129.0, 128.9, 128.5 (d, *J* = 4.6 Hz), 124.0, 123.1 (q, *J* = 272.9 Hz), 122.1, 121.2, 112.5, 111.9 (d, *J* = 20.1 Hz) ppm. ^{31}P {^1H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: 38.2 ppm. ^{19}F {^1H} NMR ($CDCl_3$, 376 MHz, 298 K) δ: -62.9 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{42}H_{22}F_{12}N_2PS^+$ 845.1045; Found 845.1052.

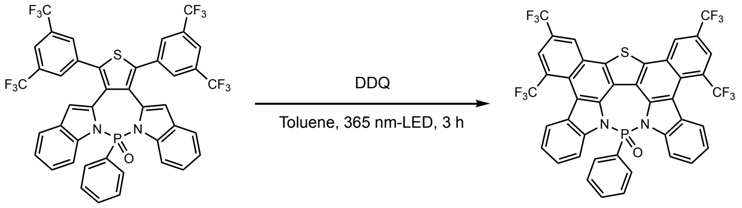


PN2: In a 1-necked 350 mL Schlenk flask, **4b** (60.3 mg, 0.07 mmol, 1.0 equiv) and DDQ (50 mg, 0.2 mmol, 2.9 equiv) were dissolved in 100 mL anhydrous toluene under N_2 atmosphere. The solution was stirred for 4 hours under the irradiation of a 365 nm LED lamp (10 W) at room temperature before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 2:3, V:V). Isolated yield: 93%. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.54 – 8.52 (m, 4H), 8.38 (d, *J* = 8.2 Hz, 2H), 8.24 (s, 2H), 7.71 (t, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.7, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.75

– 6.73 (m, 2H), 5.97 (t, *J* = 8.0 Hz, 2H) ppm. ^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: 53.4 ppm.^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz, 298 K) δ: -52.5, -61.9 ppm. HRMS (MALDI-TOF) m/z: [M] Calcd. for $C_{42}H_{17}F_{12}N_2PS$ 840.0664; Found 840.0664. ^{13}C NMR spectrum was not obtained due to its insufficient solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3.

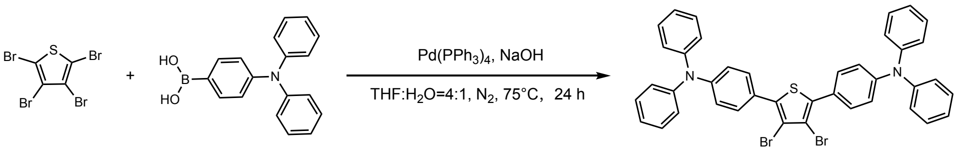


4bO: To a dichloromethane (6 mL) solution of **4b** (68.8 mg, 0.08 mmol), 5 mL H_2O_2 (30% in H_2O) was added. The solution was stirred for 4 days under dark at room temperature. Then, the mixture was quenched with H_2O (30 mL), and the aqueous phase was extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 1:1, V:V). Isolated yield: 93%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.69 (d, *J* = 8.5 Hz, 2H), 7.88 (s, 2H), 7.75 (s, 4H), 7.72 – 7.69 (m, 2H), 7.52 – 7.49 (m, 1H), 7.44 – 7.41 (m, 4H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 6.26 (d, *J* = 2.6 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, 298 K) δ: 140.9 (d, *J* = 3.5 Hz), 137.7, 135.4, 134.3, 132.7, 132.5 (q, *J* = 33.5 Hz), 131.1 (d, *J* = 5.6 Hz), 130.8, 130.6 (d, *J* = 11.9 Hz), 129.5, 129.4, 128.9 (d, *J* = 15.4 Hz), 125.3, 123.3, 123.0 (q, *J* = 274.2 Hz), 122.5, 121.0, 115.9, 113.3 (d, *J* = 6.8 Hz) ppm. ^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: 14.3 ppm. ^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz, 298 K) δ: -63.0 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{42}H_{22}F_{12}N_2OPS^+$ 861.0994; Found 861.1002.

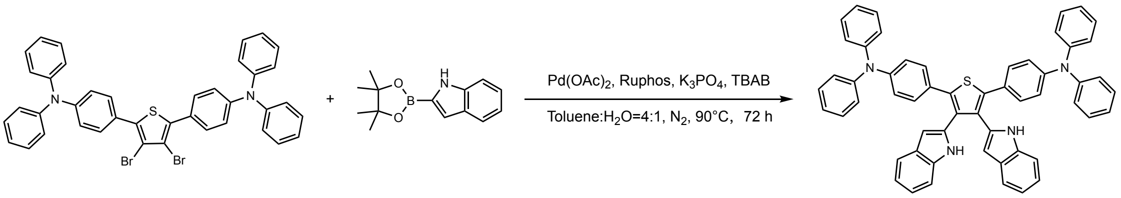


PN2O: In a 1-necked 350 mL Schlenk flask, **4bO** (65.5 mg, 0.076 mmol, 1.0 equiv) and DDQ (52 mg, 0.23 mmol, 3.0 equiv) were dissolved in 150 mLanhydrous toluene under N_2 atmosphere. The solution was stirred for 3 hours under the irradiation of a 365 nm LED lamp (10 W) at room temperature before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 2:3, V:V). Isolated yield: 99%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.99 (d, *J* = 7.6 Hz, 2H), 8.47 (s, 1H), 8.24 (s, 3H), 8.23 (s, 2H), 7.72 – 7.63 (m, 4H), 7.12 – 7.08 (m, 1H), 6.85 (td, *J* = 7.7, 4.4 Hz, 2H), 6.43 – 6.37 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 140.8 (d, *J* = 4.0 Hz), 136.8, 135.1 (d, *J* = 4.9 Hz), 133.7 (d, *J* = 3.3 Hz), 131.3, 129.8, 129.2 (d, *J* = 15.8 Hz), 128.5 (d, *J* = 11.7 Hz), 128.0 (q, *J* = 32.8 Hz), 127.5, 127.2, 126.8 (q, *J* = 33.9 Hz), 125.7, 125.5, 124.6, 124.3 (q, *J* = 275.7 Hz), 124.1 (d, J = 8.0 Hz), 123.6 (d, J = 7.0 Hz), 123.4 (q, *J* = 273.7 Hz), 121.5, 117.9 (d, *J* = 6.0 Hz), 117.2 ppm. ^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz, 298

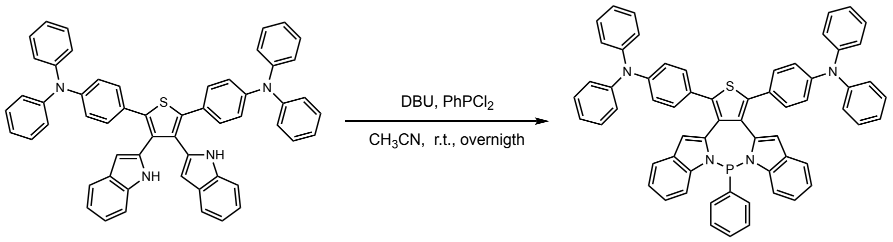
K) δ: 13.3 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{42}H_{18}F_{12}N_2OPS^+$ 857.0681; Found 857.0684.



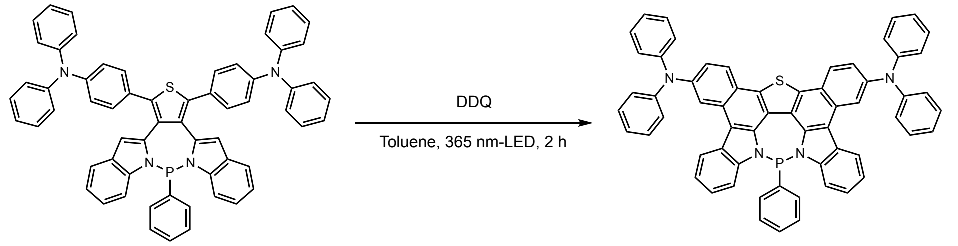
2c: Tetrabromothiophene (500 mg, 1.25 mmol, 1.0 equiv), 4-(diphenylamino)phenylboronic acid (759.5 mg. 2.63 mmol, 2.1 equiv), $Pd(PPh_3)_4$ (72.3 mg, 0.063 mmol, 0.05 equiv) and NaOH (200 mg, 5 mmol, 4 equiv) were added to a mixture of degassed THF (20 mL) and H_2O (5 mL). The mixture was degassed for 10 min, heated at 75 °C under N_2 for 24 hours before being cooled to room temperature, after which it was poured into 10 mL of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 1 : 19, V:V). Isolated yield: 84%. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.54 – 7.48 (m, 2H), 7.33 – 7.27 (m, 4H), 7.19 – 7.12 (m, 4H), 7.12 – 7.04 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 148.4, 147.4, 137.4, 129.7, 129.6, 126.1, 125.3, 123.8, 122.2, 111.5 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{40}H_{29}Br_2N_2S^+$ 729.0393; Found 729.0394.



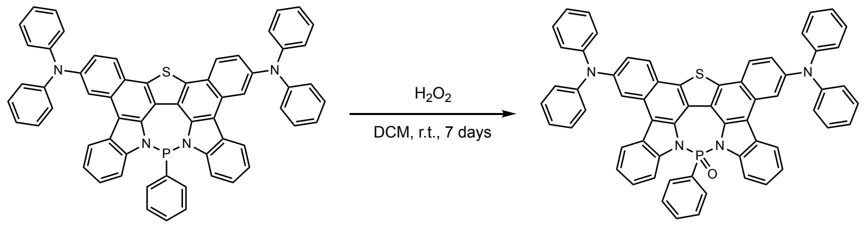
3c: **2c** (400 mg, 0.54 mmol, 1.0 equiv) 2-(pinacolatebory)indole (320.4 mg, 1.32 mmol, 2.4 equiv), palladium(II) acetate (12.3 mg 0.054 mmol, 0.1 equiv), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (51.2 mg, 0.011 mmol, 0.2 equiv), K_3PO_4 (349.6 mg, 1.62 mmol, 3.0 equiv) and tetrabutylammonium bromide (17.7 mg, 0.054 mmol, 0.1 equiv) were added to a mixture of degassed toluene (32 mL) and H_2O (8 mL). The mixture was degassed for 15 min, heated at 95 °C under N_2 for 72 hours before being cooled to room temperature, after which it was poured into 20 mL of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane : petroleum ether = 2 : 3, V:V). Isolated yield: 55%. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.80 (s, 2H), 7.46 (d, $J = 7.6$ Hz, 2H), 7.27 – 7.22 (m, 6H), 7.15 (d, $J = 8.9$ Hz 7H), 7.08 (d, $J = 8.8$ Hz, 11H), 7.04 – 7.00 (m, 6H), 6.90 (d, $J = 8.8$, 4H), 6.27 (d, $J = 2.1$ Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 147.9, 147.3, 140.3, 136.0, 132.1, 129.6, 129.5, 129.3, 128.4, 126.9, 125.1, 123.6, 122.5, 122.1, 120.8, 119.9, 110.9, 104.2 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{56}H_{41}N_4S^+$ 801.3047; Found 801.3029.



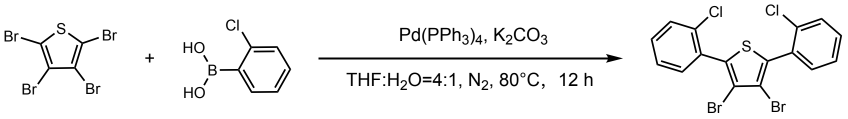
4c: In a 1-necked 200 mL Schlenk flask, **3c** (210.8 mg, 0.26 mmol, 1.0 equiv) and DBU (0.12 mL, 0.79 mmol, 3.0 equiv) were added to 140 mL dry CH_3CN under N_2 atmosphere. The solution was stirred at room temperature for 5 min, then a toluene solution of dichlorophenylphosphine (0.47 mL, 0.34 mmol, 1.3 equiv, 10% in dry toluene, V:V) was slowly injected in one portion. The mixture stirred for 12 hours before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 1:4, V:V). Isolated yield: 85%. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.03 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.2, 3H), 7.30 – 7.28 (m, 8H), 7.21 (td, *J* = 7.2, 2.5 Hz, 3H), 7.17 – 7.12 (m, 15H), 7.05 (tt, *J* = 7.0, 1.2 Hz, 4H), 6.99 – 6.96 (m, 4H), 6.34 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 147.7, 147.5, 142.5 (d, *J* = 26.5 Hz), 139.6, 137.4, 136.9 (d, *J* =6.8 Hz), 130.2, 129.7 (d, *J* = 4.6 Hz), 129.5, 129.4, 129.2 (d, *J* = 3.0 Hz), 129.0, 128.2 (d, *J* = 2.0 Hz), 127.6, 125.1, 123.5, 122.9, 122.5, 121.5, 120.7, 111.9 (d, *J* = 20.1 Hz), 111.3 ppm. ^{31}P {^1H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: 37.6 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{62}H_{44}N_4PS^+$ 907.3019; Found 907.2997.



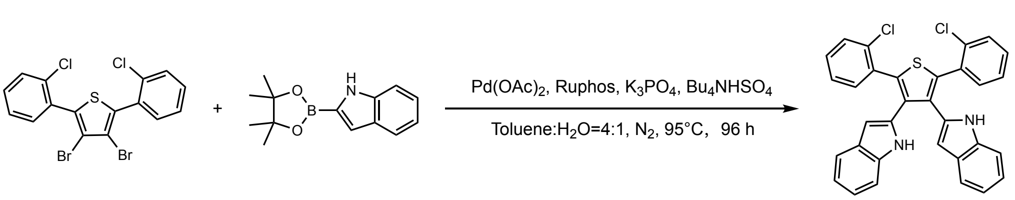
PN3: In a 1-necked 500 mL Schlenk flask, **4c** (77.7 mg, 0.086 mmol, 1.0 equiv) and DDQ (44 mg, 0.19 mmol, 2.2 equiv) were dissolved in 220 mL anhydrous toluene under N_2 atmosphere. The solution was stirred for 2 hours under the irradiation of a 365 nm LED lamp (10 W) at room temperature before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 3:2, V:V). Isolated yield: 83%. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.49 (d, *J* = 2.3 Hz, 2H), 8.37 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.31 (m, 20H), 7.18 – 7.14 (m, 4H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.71 (td, *J* = 7.7, 2.4 Hz, 2H), 5.85 (t, *J* = 7.1 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 147.7, 146.9, 143.5 (d, *J* = 26.6 Hz), 138.9 (d, *J* = 8.7 Hz), 138.6 (d, *J* = 16.2 Hz), 136.2, 129.7, 129.2, 129.0, 128.7 (d, *J* = 4.6 Hz), 127.6 (d, *J* = 17.0 Hz), 126.3 (d, *J* = 3.9 Hz), 125.9, 125.2, 124.6, 123.8, 122.3, 122.2, 121.6, 121.5, 121.4, 117.7, 116.4, 113.3 (d, *J* = 21.5 Hz) ppm. ^{31}P {^1H} NMR (CDCl3, 162 MHz, 298 K) δ: 54.7 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{62}H_{40}N_4PS^+$ 903.2706; Found 903.2679.



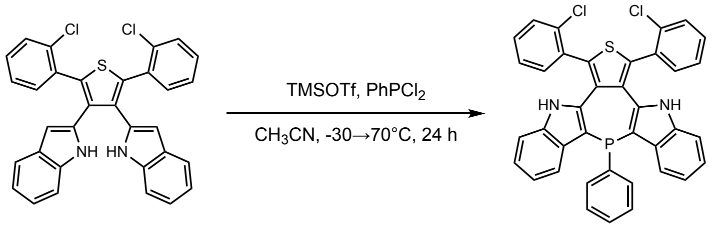
4cO: To a dichloromethane (22 mL) solution of **4c** (48.2 mg, 0.053 mmol) , 6 mL H_2O_2 (30% in H_2O) was added. The solution was stirred for 7 days under dark at room temperature. Then, the mixture was quenched with H_2O (30 mL), and the aqueous phase was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 3:2, V:V). Isolated yield: 82%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 9.08 (d, J = 8.4 Hz, 2H), 8.51 (d, J = 2.1 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 7.8 Hz, 2H), 7.45 – 7.38 (m, 12H), 7.34 – 7.32 (m, 8H), 7.18 (t, J = 7.2 Hz, 4H), 7.1 (t, J = 7.6 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.40 (dd, J = 14.9, 7.7 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 147.6, 147.2, 141.9 (d, J = 4.7 Hz), 136.3, 133.1 (d, J = 4.1 Hz), 132.8, 132.1, 130.5, 129.8, 128.9, 128.8, 127.2 (d, J = 6.8 Hz), 125.7, 125.6, 125.5, 124.1, 123.9, 121.6, 121.4, 121.0, 119.9, 117.5, 117.2 (d, J = 7.0 Hz), 115.7 ppm. ^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: 14.2 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{62}H_{40}N_4PS^+$ 919.2655; Found 919.2660.



2d: Tetrabromothiophene (1000 mg, 2.50 mmol, 1.0 equiv), 2-chlorophenylboronic acid (860.6 mg. 5.50 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (144.6 mg, 0.125 mmol, 0.05 equiv) and K_2CO_3 (2074.6 mg, 15.0 mmol, 6.0 equiv) were added to a mixture of degassed THF (32 mL) and H_2O (16 mL). The mixture was degassed for 10 min, heated at 75 °C under N_2 for 24 hours before being cooled to room temperature, after which it was poured into 10 mL of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 1:19, V:V). The target compound was obtained as a white powder solid. Isolated yield: 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.53 (dd, J = 7.7, 1.6 Hz, 2H), 7.47 (dd, J = 7.4, 1.9 Hz, 2H), 7.43 – 7.33 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 136.1, 134.6, 132.8, 131.6, 130.8, 130.0, 126.8, 114.5 ppm.

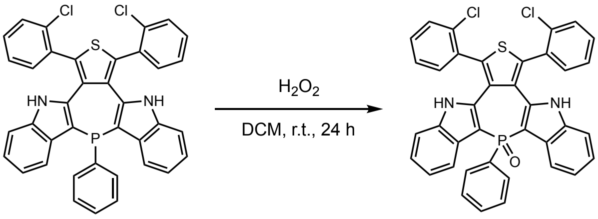


3d: **2d** (200 mg, 0.43 mmol, 1.0 equiv), 2-(pinacolatebory)indole (252 mg, 1.04 mmol, 2.4 equiv), palladium(II) acetate (10 mg, 0.043 mmol, 0.1 equiv), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (40.3 mg, 0.086 mmol, 0.2 equiv), K_3PO_4 (275 mg, 1.29 mmol, 3.0 equiv) and tetrabutylammonium hydrogen sulfate (14.7 mg, 0.043 mmol, 1.0 equiv) were added to a mixture of degassed Toluene (16 mL) and H_2O (4 mL). The mixture was degassed for 15 min, heated at 95 °C under N_2 for 96 hours before being cooled to room temperature and filtered. And the residue was washed with petroleum ether and dried it in ambient condition to yield a white powder solid. Yield: 58%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.82 (s, 2H), 7.50 – 7.40 (m, 6H), 7.32 (td, *J* = 7.7, 1.9 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.09 – 7.04 (m, 4H), 7.03 – 6.99 (m, 2H), 6.19 (d, *J* = 2.1 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 138.2, 136.0, 134.9, 133.0, 132.6, 131.5, 130.8, 130.2, 130.0, 128.2, 126.9, 122.2, 120.7, 119.9, 111.0, 104.2 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{32}H_{21}Cl_2N_2S^+$ 535.0797; Found 535.0801.

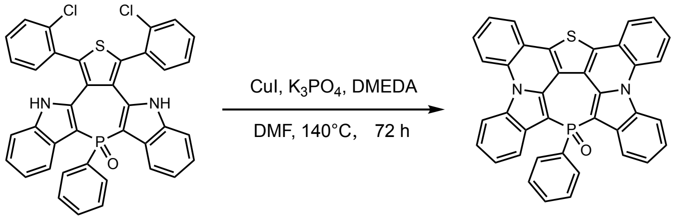


5d: In a 1-necked 25 mL Schlenk flask, trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.09 mL, 0.47 mmol, 2.3 equiv) was added to an acetonitrile solution (2 mL) of $PhPCl_2$ (0.38 mL, 0.27 mmol, 1.3 equiv 10% in dry toluene) at room temperature. The mixture was stirred for 1 hour at this temperature. Then the mixture was added to an acetonitrile solution (58 mL) of **3Cla** (109.2 mg, 0.20 mmol, 1.0 equiv) at -30 °C. The resulting mixture was stirred at 70 °C for 24 hours. All volatile was removed under vacuum. The crude product was purified by flash chromatography (dichloromethane:petroleum ether = 1:1, V:V). The target compound was obtained as a white powder solid. Isolated yield: 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.19 (d, *J* = 7.8 Hz, 2H), 7.93 (s, 2H), 7.52 (s, 2H), 7.39 (t, *J* = 6.7 Hz, 3H), 7.35 – 7.26 (m, 2H), 7.23 – 7.13 (m, 7H), 7.09 – 7.01 (m, 5H). ^{13}C NMR ($CDCl_3$, 126 MHz, 298 K) δ: 141.2, 136.6, 136.2, 136.2, 136.0, 134.7, 133.0, 132.8, 132.7, 132.5, 130.7, 130.5, 130.3, 127.5, 127.3 (d, *J* = 5.1 Hz), 126.5, 122.8, 120.7, 120.6, 110.6 ppm. ^{31}P {1H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: -82.5 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{38}H_{24}Cl_2N_2PS^+$ 641.0770; Found 641.0759.

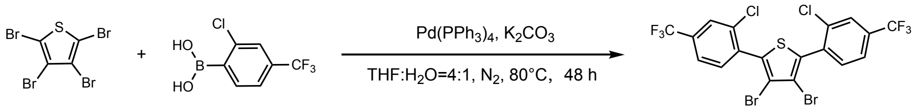
PC1: A 50 mL Schlenk tube was charged with **5a** (69.6 mg, 0.11 mmol, 1.0 equiv). The Schlenk tube was evacuated and filled with N_2 (this procedure was repeated three times), and then CuI (2.06 mg, 0.011 mmol, 0.1 equiv), K_3PO_4 (184 mg, 0.87 mmol, 8.0 equiv), DMF (2.0 mL) and DMEDA (0.024 ml, 0.22 mmol, 2.0 equiv) were added under N_2. The resulting mixture was stirred at 140 °C for 48 hours. Cooling to room temperature before the solvent was removed under vacuum. The crude product purified by washing with dichloromethane and methyl alcohol to yield the desired product as a yellow powder solid. Isolated yield: 92% yield. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.17 (dbr, J = 8.6 Hz, 2H), 8.11 (dbr, J = 8.1 Hz, 2H), 7.92 (sbr, 2H), 7.76 (dbr, J = 8.6 Hz, 2H), 7.71 (dbr, J = 7.6 Hz, 2H), 7.58 (tbr, J = 6.6 Hz, 2H), 7.48 (tbr, J = 7.5 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.97 (sbr, 2H), 6.81 (dbr, J = 8.0 Hz, 3H) ppm. ^{13}C NMR spectrum was not obtained due to its insufficient solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. ^{31}P {1H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: -46.2 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{38}H_{22}N_2PS^+$ 569.1236; Found 569.1230.



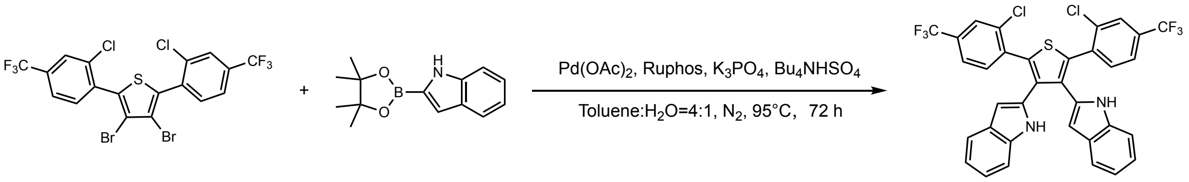
5dO: To a dichloromethane (7 mL) solution of **5d** (115.2 mg, 0.18 mmol), 1 mL H_2O_2 (30% in H_2O) was added. The solution was stirred for 24 hours under dark at room temperature. Then the mixture was quenched with H_2O and the aqueous phase was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:ethyl acetate = 7 : 3, V:V). The target compound was obtained as a white powder solid. Isolated yield: 93%. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.67 (d, *J* = 7.5 Hz, 2H), 7.92 (s, 2H), 7.69 (s, 3H), 7.44 (s, 6H), 7.35 – 7.33 (m, 2H), 7.25 – 7.16 (m, 5H), 7.05 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6, 101 MHz, 298 K) δ: 138.3, 138.1, 137.0 (d, J = 11.4 Hz), 133.9 (d, J = 20.3 Hz), 133.1, 131.3, 130.9, 130.7, 130.44, 130.0, 129.8 (d, J = 4.4 Hz), 129.1, 128.2 (d, J = 12.3 Hz), 127.5, 122.8, 121.5, 120.6, 112.0, 107.3, 106.0 ppm. ^{31}P {^1H} NMR (DMSO-d_6, 162 MHz, 298 K) δ: 18.5 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{38}H_{24}Cl_2N_2OPS^+$ 657.0719; Found 657.0705.



PC1O: A 50 mL Schlenk tube was charged with **5dO** (100.0 mg, 0.15 mmol, 1.0 equiv). The Schlenk tube was evacuated and filled with N_2 (this procedure was repeated three times), and then CuI (2.90 mg, 0.015 mmol, 0.1 equiv), K_3PO_4 (258.0 mg, 1.22 mmol, 8.0 equiv), DMF (2.0 mL) and DMEDA (0.032 ml, 0.30 mmol, 2.0 equiv) were added under N_2. The resulting mixture was stirred at 140 °C for 96 h. Cooling to room temperature before the solvent was removed under vacuum. The crude product purified by washing with dichloromethane and methyl alcohol to yield the desired product as a yellow powder solid. Isolated yield: 84% yield. ^1H NMR ($C_2Cl_4D_2$, 500 MHz, 298 K) δ: 8.56 (t, 4H), 8.41 (d, J=8.3 Hz, 2H), 7.87 (dd, J = 13.3, 7.2 Hz, 2H), 7.81 (d, J = 7.81 Hz, 2H), 7.58 – 7.45 (m, 6H), 7.27 (t, J = 7.6 Hz, 2H) ppm. ^{31}P {1H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: 10.3 ppm. ^{13}C NMR spectrum was obtained due to its insufficient solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{38}H_{22}N_2OPS^+$ 585.1185; Found 585.1184.

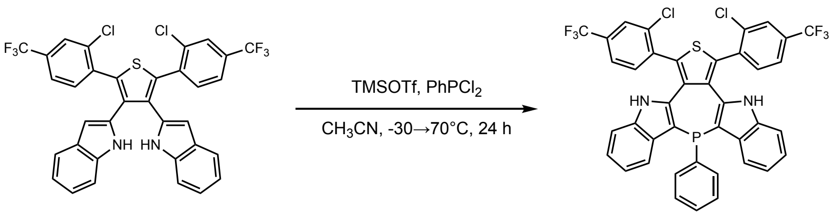


2e: Tetrabromothiophene (200 mg, 0.5 mmol, 1.0 equiv), 2-chloro-4-(trifluoromethyl)phenylboronic acid (269.4 mg. 1.20 mmol, 2.4 equiv), $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol, 0.05 equiv) and K_2CO_3 (414.9 mg, 3.0 mmol, 6.0 equiv) were added to a mixture of degassed THF (8 mL) and H_2O (2 mL). The mixture was degassed for 10 min, heated at 75°C under N_2 for 48 h before being cooled to room temperature, after which it was poured into 10 ml of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (petroleum ether). The target compound was obtained as a white solid. Isolated yield: 64%. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.81 (s, 2H), 7.67 – 7.59 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 135.5, 135.2, 135.1, 133.3, 133.1 (q, *J* = 33.4 Hz), 127.3 (d, *J* = 3.8 Hz), 123.8 (d, *J* = 3.8 Hz), 123.1 (q, *J* = 272.2 Hz), 115.5 ppm. ^{19}F {^1H} NMR ($CDCl_3$, 376 MHz, 298 K) δ: -62.9 ppm.

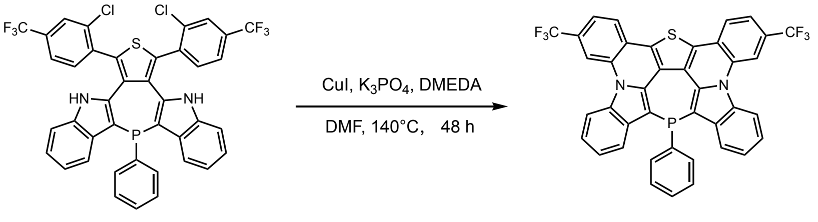


3e: **2e** (100 mg, 0.17 mmol 1.0 equiv), 2-(pinacolatebory)indole (104.8 mg, 0.43 mmol, 2.5 equiv), palladium(II) acetate (3.87 mg, 0.017 mmol, 0.1 equiv), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (16.1 mg, 0.034 mmol, 0.2 equiv), K_3PO_4 (109.8 mg, 0.52 mmol, 3.0

equiv) and tetrabutylammonium hydrogen sulfate (5.56 mg, 0.017 mmol, 0.1 equiv) were added to a 4 : 1 mixture of degassed Toluene (8 mL) and H_2O (2 mL). To complete the reaction, the mixture was degassed for 15 min, heated at 95 °C under N_2 for 72 h before being cooled to room temperature. Then it was poured into 10 ml of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 7 : 13, V:V). The target compound was obtained as a yellow solid. Yield: 29%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.80 (s, 2H), 7.73 (s, 2H), 7.57 – 7.50 (m, 4H), 7.47 (d, J = 7.5 Hz, 2H), 7.14 – 6.99 (m, 6H), 6.20 (d, J = 2.2 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 137.2, 136.2, 136.1, 133.5, 132.4 (q, J = 33.4 Hz), 131.6, 130.5, 128.0, 127.2(4), 127.2(0), 123.2 (q, J = 273.7 Hz), 123.9 (d, J = 3.0 Hz), 122.7, 120.8, 120.2, 111.2, 104.7 ppm. ^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz, 298 K) δ: -62.9 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{34}H_{19}Cl_2F_6N_2S^+$ 671.0545; Found 671.0544.

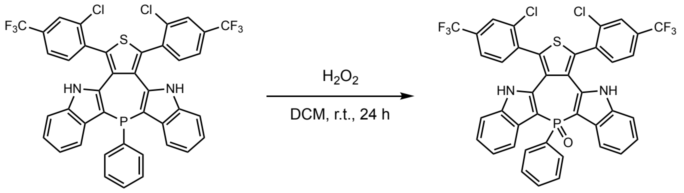


5e: In a 1-necked 25mL Schlenk flask, trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.072 ml, 0.40 mmol, 2.3 equiv) was added to an acetonitrile solution (2 mL) of $PhPCl_2$ (0.30 ml, 0.22 mmol, 1.3 equiv 10% in dry toluene, V:V) at room temperature. The mixture was stirred for 1 hours at this temperature. Then the mixture was added to an acetonitrile solution (58 mL) of **3e** (116.1 mg, 0.17 mmol, 1.0 equiv) at -30 °C. The resulting mixture was stirred at 70 °C for 24 h. All volatile was removed under vacuum. The crude product was purified by flash chromatography (dichloromethane:petroleum ether = 1 : 1, V:V). The target compound was obtained as a faint yellow powder solid. Isolated yield: 81%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.20 (d, J = 7.7 Hz, 2H), 7.82 (s, 4H), 7.57 (s, 2H), 7.25 – 7.01 (m, 13H), 7.23 – 7.18 (m, 5H), 7.15 (td, J = 7.5, 1.3 Hz, 3H), 7.11 – 7.00 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, 298 K) δ: 140.94, 136.34, 136.27, 135.50, 135.37, 135.09 (d, J=7.93 Hz), 133.51, 132.83 (q, J=34.0 Hz), 132.77, 132.48, 131.58, 130.47, 130.34, 127.40 (d, J=5.0 Hz), 126.75, 124.32, 123.28, 123.03 (q, J=272.9 Hz), 120.98, 120.75 (d, J=9.4 Hz), 110.81 ppm. ^{31}P {1H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: -82.16 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{40}H_{22}Cl_2F_6N_2PS^+$ 777.0518; Found 777.0568.



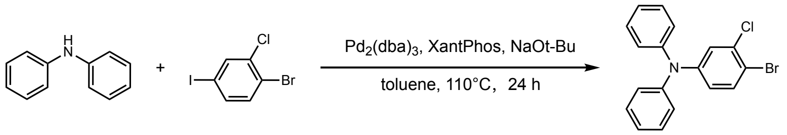
PC2: A 50 mL Schlenk tube was charged with **5b** (50 mg, 0.064 mmol, 1.0 equiv). The Schlenk tube was evacuated and filled with N_2 (this procedure was repeated three times), and

then CuI (12.2 mg, 0.064 mmol, 1.0 equiv), K_3PO_4 (109.2 mg, 0.51 mmol, 8.0 equiv), DMF (2.0 mL) and DMEDA (0.014 ml, 0.13 mmol, 2.0 equiv) were added under N_2. The resulting mixture was stirred at 140 °C for 72 h. Cooling to room temperature before the solvent was removed under vacuum. The crude product purified by washing with dichloromethane and methyl alcohol to yield the desired product as a orange powder solid. Isolated yield: 85%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.48 (sbr, 2H), 8.08 (d, J = 8.5 Hz, 2H), 7.84 (mbro, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.73 – 7.52 (m, 2H), 7.15 (t, J = 8.0 Hz, 2H), 7.03 – 7.01 (m, 3H), 6.89 (t, J = 8.0 Hz, 2H) ppm. ^{31}P {1H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: -46.1 ppm. ^{13}C NMR spectrum was obtained due to its insufficient solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. HRMS (MALDI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{40}H_{22}Cl_2F_6N_2OPS^+$ 705.0984; Found 705.0981.

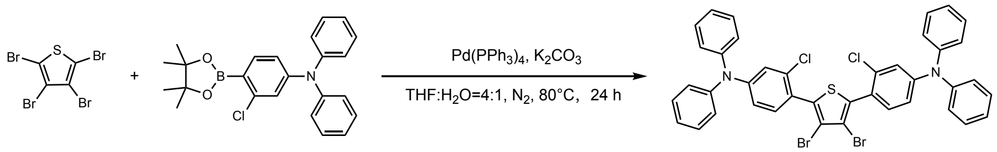


5eO: To a dichloromethane (5 mL) solution of **5e** (252.5 mg, 0.32 mmol), 2 ml H_2O_2 (30% in H_2O) was added. The solution was stirred for 24 h under dark at room temperature. Then the mixture was separated and the aqueous phase was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:ethyl acetate = 4:1, V:V). The target compound was obtained as a faint yellow powder solid. Isolated yield: 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 8.63 (d, J = 5.7 Hz, 2H), 7.94 – 7.59 (m, 8H), 7.37 (t, J = 7.4 Hz,1H), 7.31 – 7.17 (m, 8H), 7.11 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 137.35, 136.68, 136.39, 136.28, 135.48, 133.19, 133.10 (q, J = 33.2 Hz), 132.86, 132.65, 131.49, 130.28 (d, J = 11.7Hz), 129.89 (d, J = 4.4 Hz), 129.80, 128.01 (d, J = 12.7 Hz), 127.55, 124.38, 123.97, 122.88, 122.84 (q, J = 273.7 Hz), 121.75, 110.65 ppm. ^{19}F {^{1}H} NMR ($CDCl_3$, 376 MHz, 298 K) δ: -62.9 ppm. ^{31}P {1H} NMR ($CDCl_3$, 162 MHz, 298 K) δ: 18.06 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{40}H_{22}Cl_2F_6N_2OPS^+$ 793.0467; Found 793.0427.

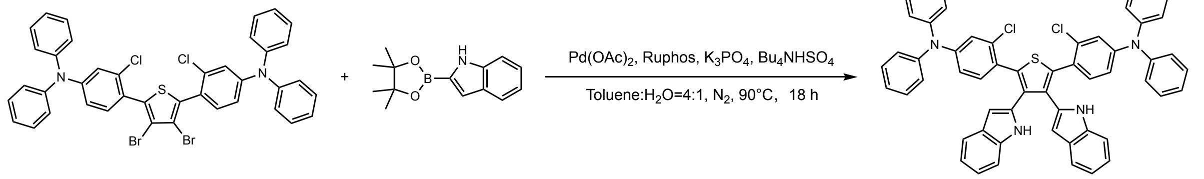
PC2O: A 50 mL Schlenk tube was charged with **5eO** (100.0 mg, 0.13 mmol, 1.0 equiv). The Schlenk tube was evacuated and filled with N_2 (this procedure was repeated three times), and then CuI (24.0 mg, 0.13 mmol, 1.0 equiv), K_3PO_4 (214 mg, 1.00 mmol, 8.0 equiv), DMF (2.0 mL) and DMEDA (0.027 ml, 0.25 mmol, 2.0 equiv) were added under N_2. The resulting mixture was stirred at 140 °C for 96 h. Cooling to room temperature before the solvent was removed under vacuum. The crude product purified by washing with dichloromethane and methyl alcohol to yield the desired product as a yellow powder solid. Isolated yield: 82%. Found 721.0920. ^{13}C NMR spectrum was obtained due to its insufficient solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. ^{1}H NMR ($C_2Cl_4D_2$, 500 MHz, 373 K) δ: 9.00 (sbr, 2H), 8.70 (d, J = 8.2 Hz, 2H), 8.43 (d, J = 8.6 Hz, 2H), 8.18 (d, J = 8.0 Hz, 2H), 7.96 – 7.82 (mbr, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.64 (sbr, 2H), 7.55 (sbr, 2H), 7.37 – 7.16 (m, 2H) ppm. ^{31}P {1H} NMR ($CDCl_3$, 162 MHz, 373 K) δ: 9.4 ppm. ^{13}C NMR spectrum was obtained due to its insufficient solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. HRMS (MALDI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{40}H_{22}Cl_2F_6N_2OPS^+$ 721.0933.



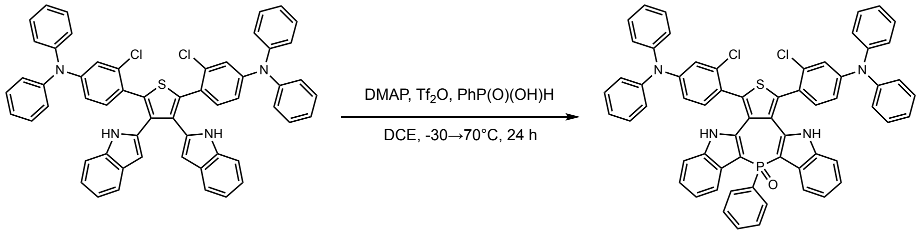
NBzCl-Br: Under an argon atmosphere, l-bromo-2-chloro-4-iodobenzene (2.0 g, 6.30 mmol, 1.0 equiv), diphenylamine (1.1 g, 6.30 mmol, 1.0 equiv), tris(dibenzylideneacetone)dipalladium(0)($Pd_2(dba)_3$), 115.0 mg, 0.13 mmol, 0.02 equiv), 4,5'-bis(diphenylphosphino)-9,9'-dimethylxanthene (XantPhos, 145.9 mg, 0.25 mmol, 0.04 equiv), and NaO^{t}Bu (605.6 mg, 6.3 mmol, 1.0 equiv) were refluxed in toluene (60 mL) for 24 hours. After completion of the reaction, thereaction solution was subjected to celite filtration, followed by concentration. The resulting mixture was purified by silica gel column chromatography to obtain a white solid. Isolated yield: 73% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.39 (d, J = 8.76 Hz, 2H), 7.40 – 7.38 (m, 4H), 7.12(d, J = 2.67 Hz, 1H), 7.10 – 7.06 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 148.3, 146.9, 134.9, 133.9, 129.7, 125.0, 124.1, 123.9, 122.2, 113.9 ppm.



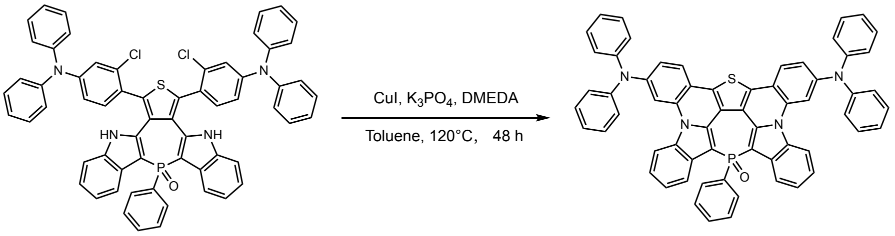
2f: tetrabromothiophene (579 mg, 1.45 mmol, 1.0 equiv), **NBzCl-Bpin** (1234.3 mg. 3.04 mmol, 2.1 equiv), $Pd(PPh_3)_4$ (83.7 mg, 0.072 mmol, 0.05 equiv) and K_2CO_3 (800.8 mg, 5.79 mmol, 4.0 equiv) were added to a mixture of degassed THF (20 mL) and H_2O (10 mL). The mixture was degassed for 10 min, heated at 80 °C under N_2 for 24 h before being cooled to room temperature, after which it was poured into 10 mL of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 1:9, V:V). The target compound was obtained as a yellowish-green powder solid. Isolated yield: 79%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.33 (dd, *J* = 8.5, 7.28 Hz, 8H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.10 (m, 14H), 6.94 (dd, *J* = 8.5, 2.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 148.8, 145.6, 136.2, 134.9, 133.0, 129.8, 125.7, 124.5, 123.6, 121.7, 119.2, 114.3 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{40}H_{27}Br_2Cl_2N_2S^+$ 796.9613; Found 796.9611.



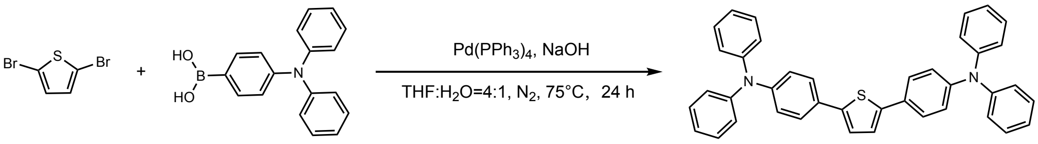
3f: **2f** (500 mg, 0.63 mmol, 1.0 equiv), 2-(pinacolatebory)indole (365.8 mg, 1.50 mmol, 2.4 equiv), palladium(II) acetate (9.9 mg, 0.044 mmol, 0.07 equiv), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (41.0 mg, 0.088 mmol, 0.14 equiv), K_3PO_4 (399.3 mg, 1.88 mmol, 3.0 equiv) and tetrabutylammonium hydrogen sulfate (21.3 mg, 0.044 mmol, 0.1 equiv) were added to a mixture of degassed toluene (36 mL) and H_2O (9 mL). The mixture was degassed for 15 min, heated at 95 °C under N_2 for 18 h before being cooled to room temperature. Then it was poured into 10 mL of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 3 : 7, V:V). The target compound was obtained as a yellow powder solid. Yield: 62%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.87 (s, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.29 (dd, J = 8.5, 7.2 Hz, 8H), 7.17 (d, J=8.5 Hz, 2H), 7.13 – 7.05 (m, 20H), 6.84 (dd, J = 8.5, 2.4 Hz, 2H), 6.35 (d, J = 2.1 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 149.4, 146.8, 138.2, 136.0, 135.3, 133.2, 131.9, 130.7, 129.7, 128.3, 125.5, 124.8, 124.3, 122.1, 122.1, 120.7, 119.9, 119.8, 111.0, 104.0 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{56}H_{39}Cl_2N_4S^+$ 869.2267; Found 869.2261.



5fO: In a 50 mL Schlenk tube, **3f** (50 mg, 0.06 mmol, 1.0 equiv), phenylphosphinic acid (16.3 mg, 0.12 mmol, 2.0 eqv) and DMAP (33.7 mg, 0.29 mmol, 4.8 equiv) were placed under N_2. Chlorobenzene (1.0 mL) was subsequently added by a syringe. The resulting mixture was stirred until it became homogeneous solution. Tf_2O (0.05 ml, 0.29 mmol, 4.8 equiv) was then added by a syringe. The reaction mixture was heated at 90 ˚C in an oil bath for 24 h. After cooling, $NaHCO_3$ aq was added. The resulting mixture was extracted three times with dichloromethane (10 mL x 3). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (dichloromethane:ethyl acetate = 4 : 1, V:V). The target compound was obtained as a yellow powder solid. Isolated yield: 31%. ^{1}H NMR (DMSO-d_6, 400 MHz, 298 K) δ: 10.89 (s, 2H), 8.42 (d, J = 8.03, 2H), 7.65 – 7.50 (m, 3H), 7.48 – 7.17 (m, 17H), 7.12 (dd, J = 7.9, 5.5 Hz, 14H), 6.86 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6, 101 MHz, 298 K) δ: 149.0, 146.2, 145.4, 138.40 (d, J = 25.3 Hz), 137.8, 137.0 (d, J = 12.7 Hz), 134.0, 133.7, 130.7 (d, J = 87.2 Hz), 129.9, 129.7 (d, J = 11.2 Hz), 128.8, 128.1 (d, J = 12.4 Hz), 126.0, 125.0, 124.5, 123.5, 122.8, 122.2 (d, J = 50 Hz), 121.4, 120.5, 111.9, 107.1, 105.8 ppm. ^{31}P {^{1}H} NMR (DMSO-d_6, 162 MHz, 298 K) δ: 16.9 ppm. HRMS (APCI-TOF) m/z: [M+H]$^+$ Calcd. for $C_{62}H_{42}Cl_2N_4OPS^+$ 991.2189; Found 991.2170.



PC3O: A 50 mL Schlenk tube was charged with **5O** (86.0 mg, 0.087 mmol, 1.0 equiv). The Schlenk tube was evacuated and filled with N_2 (this procedure was repeated three times), and then CuI (8.2 mg, 0.043 mmol, 0.5 equiv), K_3PO_4 (85.6 mg, 0.35 mmol, 4.0 equiv), DMF (1.0 mL) and DMEDA (0.01 ml, 0.087 mmol, 1.0 equiv) were added under N_2. The resulting mixture was stirred at 140 °C for 96 h. After cooling to room temperature, the reaction mixture was extracted with DCM (20 mL×3). The organic extracts were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by column chromatography (dichloromethane:ethyl acetate = 1 : 1, V:V) to yield the desired product as a orange solid. Isolated yield: 80%. ^{1}H NMR (CDCl3, 400 MHz, 298 K) δ: 8.47 (d, J = 8.0 Hz, 2H), 8.23 (s, 2H), 7.88 – 7.83 (m, 4H), 7.68 (d, J = 8.6 Hz, 2H), 7.41 (t, J = 7.7 Hz, 8H), 7.32 – 7.28 (m, 10H), 7.23 – 7.12 (m, 11H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 149.8, 146.9, 138.7, 137.8 (d, J = 51.8Hz), 135.0 (d, J = 14.0 Hz), 134.7 (d, J = 20.7 Hz), 134.0 (d, J = 9.5 Hz), 131.4 (d, J = 7.8 Hz), 130.8 (d, J = 10.7 Hz), 130.5, 129.9, 128.1(d, J = 12.7 Hz), 124.8, 123.3, 123.0, 122.8, 117.5, 113.9, 113.7, 108.8, 98.2 (d, J = 128.9 Hz) ppm. 31P {1H} NMR (DMSO-d6, 162 MHz, 298 K) δ: 10.81 ppm.HRMS (APCI-TOF) m/z: [M+H]+ Calcd. for C62H40N4OPS+ 919.2655; Found 919.2630.



ThN: 2.5-dibromothiophene (226.7 mg, 0.94 mmol, 1.0 equiv), 4-(diphenylamino)phenylboronic acid (569 mg. 1.97 mmol, 2.1 equiv), $Pd(PPh_3)_4$ (54 mg, 0.047 mmol, 0.05 equiv) and NaOH (150 mg, 3.75 mmol, 4.0 equiv) were added to a mixture of degassed THF (24 mL) and H_2O (6 mL). To complete the reaction, the mixture was degassed for 10 min, heated at 75 °C under N_2 for 24 h before being cooled to room temperature, after which it was poured into 10 mL of water. The organic layer was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 before the solvent was removed under vacuum. The crude product was purified by column chromatography (dichloromethane:petroleum ether = 1:4, V:V). The target compound was obtained as a yellow powder solid. Isolated yield: 82%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.48 (d, J = 8.8 Hz 2H), 7.30 – 7.23 (m, 8H), 7.18 (s, 2H), 7.14 – 7.10 (m, 8H), 7.09 – 7.01 (m, 8H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 147.6, 147.2, 142.7, 129.4, 128.6, 126.4, 124.5, 123.9, 123.3, 123.2 ppm. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{40}H_{31}N_2S^+$ 571.2203; Found 571.2204.

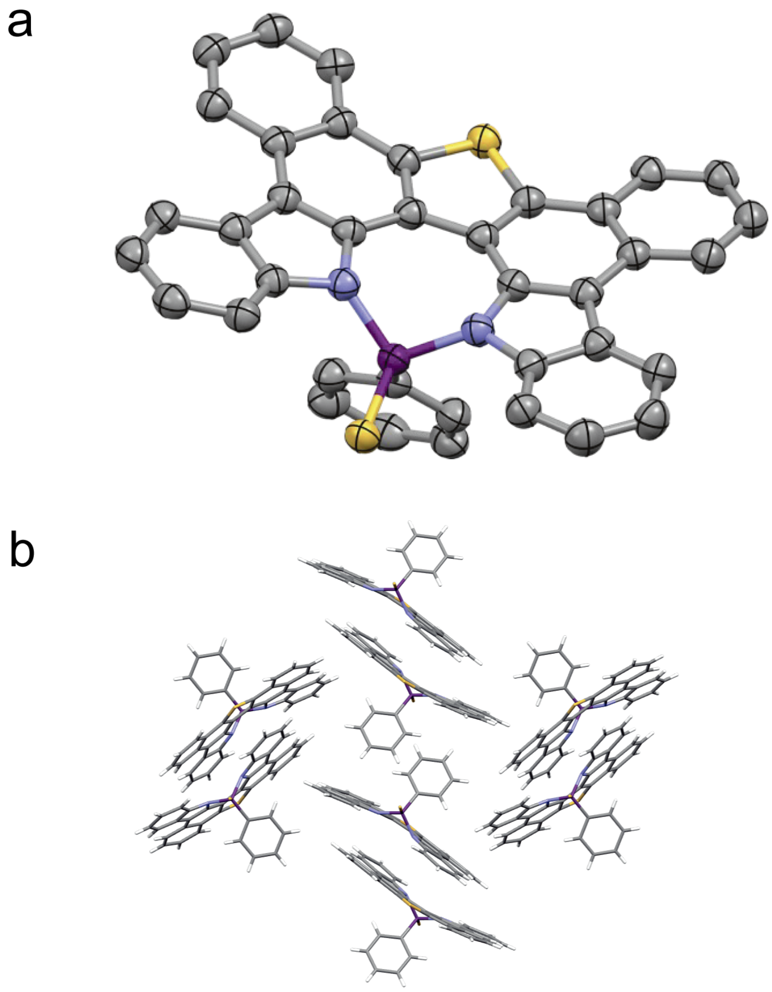


Figure S1. Single crystal structures of **PN1S** at 50% probability level.

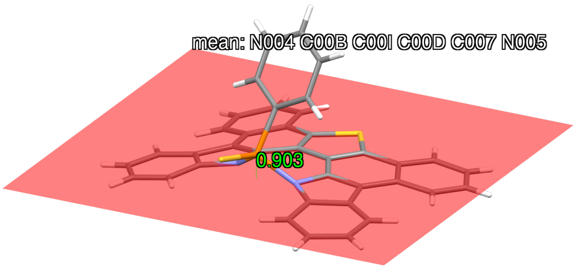


Figure S2. Distances between the P-center and the central heteropine plane in **PN1S**, which is calculated by Mercury software.

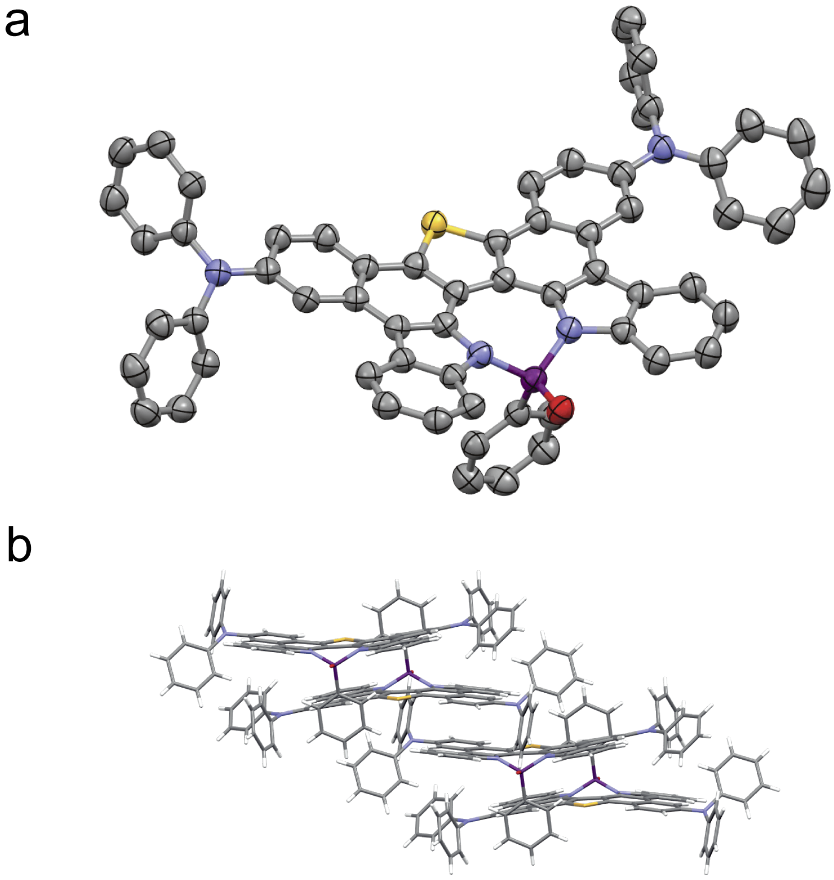


Figure S3. Single crystal structures of **PN3O** at 50% probability level.

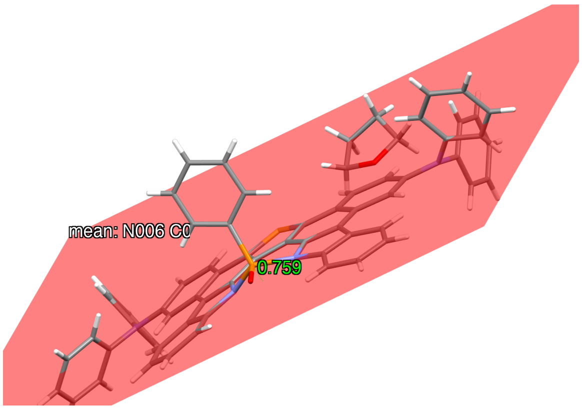


Figure S4. Distances between the P-center and the central heteropine plane in **PN3O**, which is calculated by Mercury software.

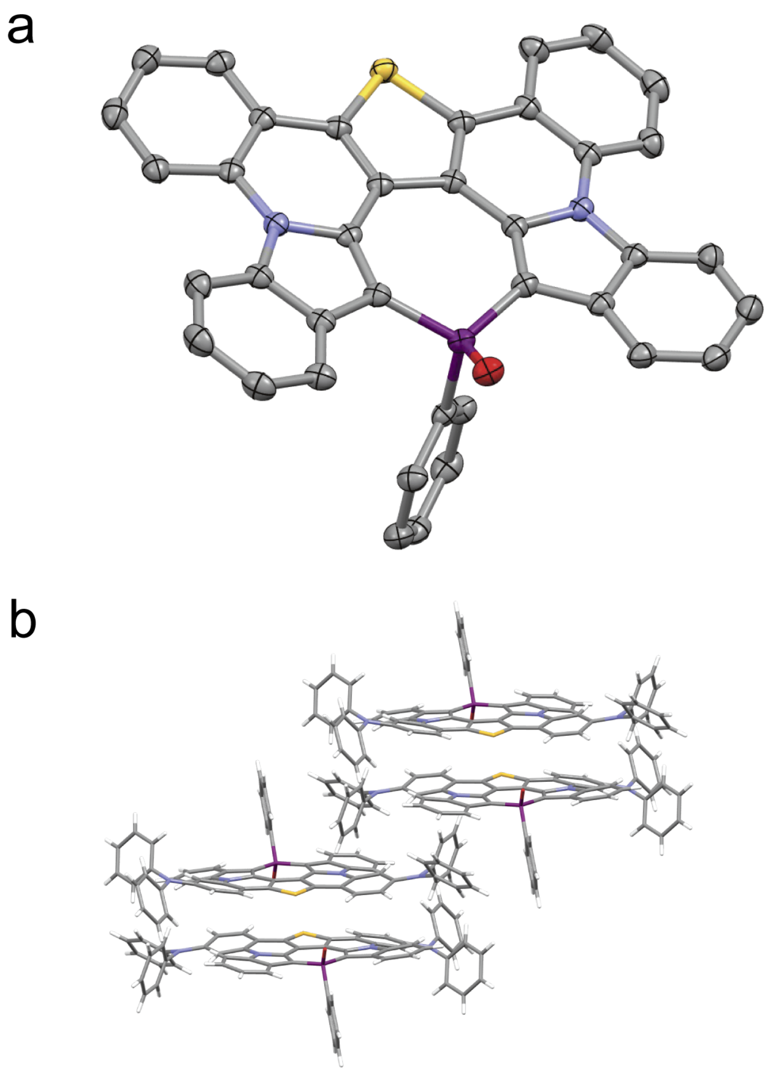


Figure S5. Single crystal structures of **PC1O** at 50% probability level.

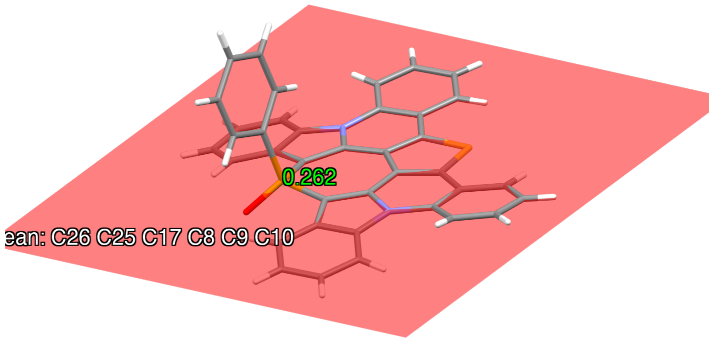


Figure S6. Distances between the P-center and the central heteropine plane in **PC1O**, which is calculated by Mercury software.

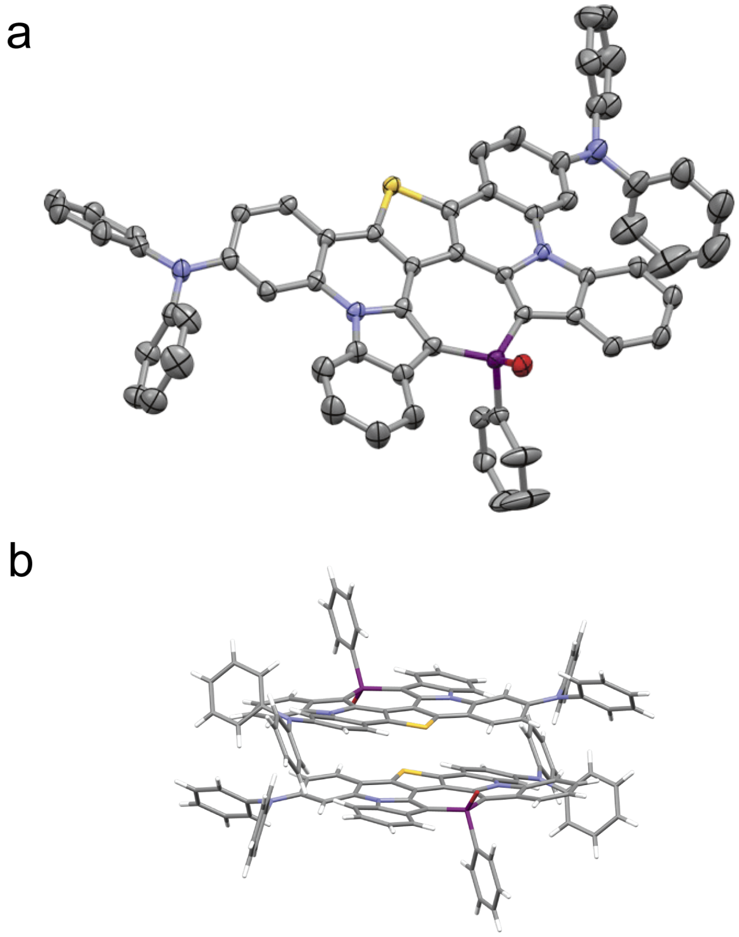


Figure S7. Single crystal structures of **PC3O** at 50% probability level.

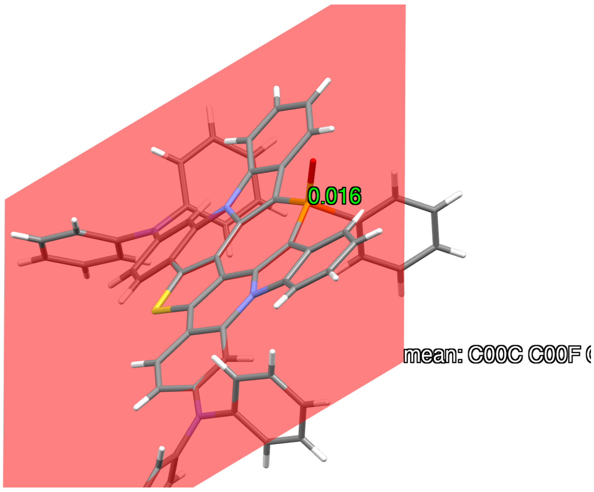


Figure S8. Distances between the P-center and the central heteropine plane in **PC3O**, which is calculated by Mercury software.

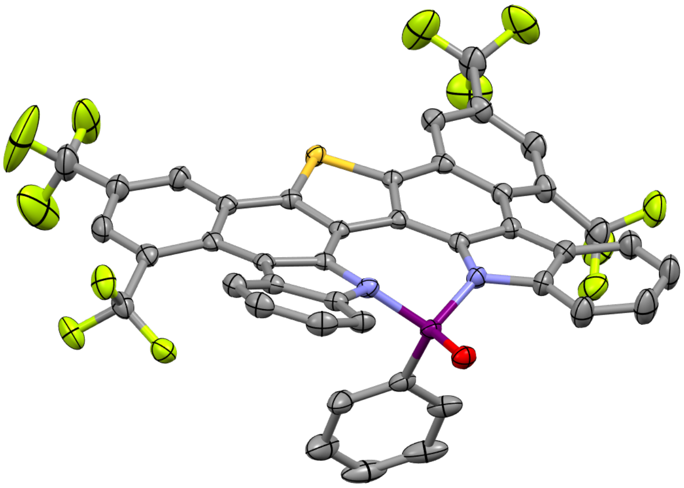


Figure S9. Single crystal structures of **PN2O** at 50% probability level. Single crystal structure of **PN2O** contained a disordered solvent that results in a overall low quality of the crystal data.

Table S1. Crystal data and structure refinement for **PH-PAHs**.

Compound	**PN1S**	**PN3O**	**PC1O**	**PC3O**
Empirical Formula	$C_{62}H_{39}N_4OPS$	$C3_8H_{21}N_2PS_2$	$C_{62}H_{39}N_4OPS$	$C_{38}H_{21}N_2OPS$
Formula Wright	991.10	600.66	919.00	584.60
Temperature / K	150K	150.0	150.00	150.00
Crystal system	triclinic	orthorhombic	triclinic	monoclinic
Space group	P-1	Pbca	P-1	P21/c
a/Å	11.4860(3)	20.9037(14)	13.6771(8)	8.0774(2)
b/Å	14.0112(4)	14.1564(9	14.4294(9)	18.4805(5)
c/Å	15.5461(5)	21.8058(15)	14.6848(9)	17.7635(5)
α/ °	79.869(1)	90	60.57	90
β/ °	84.017(1)	90	84.003(2)	99.2710(10)
γ/ °	87.229(1)	90	77.723(2)	90
Volume / Å^3	2448.30(12)	6452.8(7)	2466.5(3)	2617.00(12)
Z	2	8	2	4
ρ_{calc} g/cm^3	1.344	1.237	1.237	1.484
μ / mm^{-1}	1.316	2.181	1.252	1.292
F(000)	1036.0	2480.0	956.0	1208.0
Crystal size / mm^3	0.2 × 0.15 × 0.1	0.2 × 0.15 × 0.1	0.2 × 0.15 × 0.1	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	GaKα (λ = 1.34138)
2θ range for data collection / °	6.41 to 149.064	8.564 to 148.936	8.798 to 151.79	8.324 to 114.012
Index ranges	-13 ≤ h ≤ 14, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	-23 ≤ h ≤ 26, -16 ≤ k ≤ 17, -26 ≤ l ≤ 26	-14 ≤ h ≤ 17, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18	-8 ≤ h ≤ 10, -23 ≤ k ≤ 23, -22 ≤ l ≤ 22
Reflections collected	43411	34064	25959	32351
Independent reflections	9970 [Rint = 0.0377, Rsigma = 0.0357]	6576 [Rint = 0.0301, Rsigma = 0.0242]	9816 [Rint = 0.0588, Rsigma = 0.0661]	5338 [Rint = 0.0515, Rsigma = 0.0325]
Data/restraints/parameters	9970/0/667	6576/0/388	9816/2/622	5338/2/405
Goodness-of-fit on F^2	1.079	1.064	1.049	1.032
Final R indexes [I>=2σ (I)]	R1 = 0.0696, wR2 = 0.1918	R1 = 0.0628, wR2 = 0.1739	R1 = 0.0707, wR2 = 0.1898	R1 = 0.0336, wR2 = 0.0851
Final R indexes [all data]	R1 = 0.0739, wR2 = 0.1988	R1 = 0.0636, wR2 = 0.1754	R1 = 0.0759, wR2 = 0.1949	R1 = 0.0402, wR2 = 0.0880

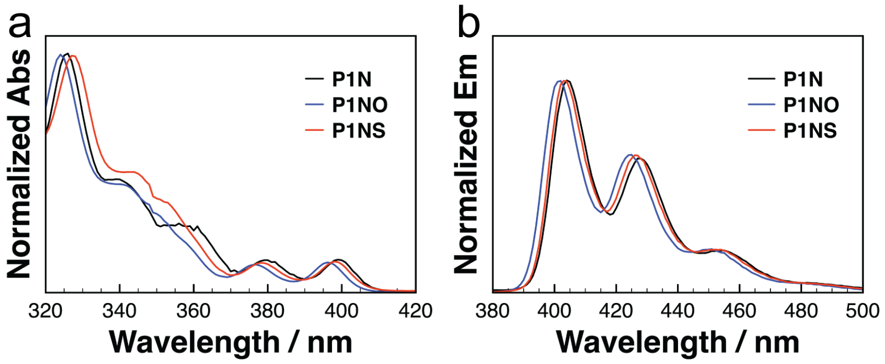


Figure S10. (a) Absorption spectra and (b) emission spectra of **PN1** series in DCM.

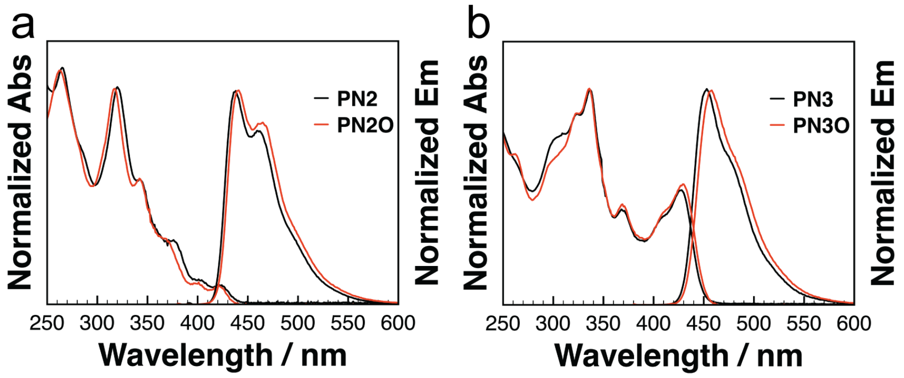


Figure S11. Absorption spectra and emission spectra of (a) **PN2** series and (b) **PN3** series in DCM.

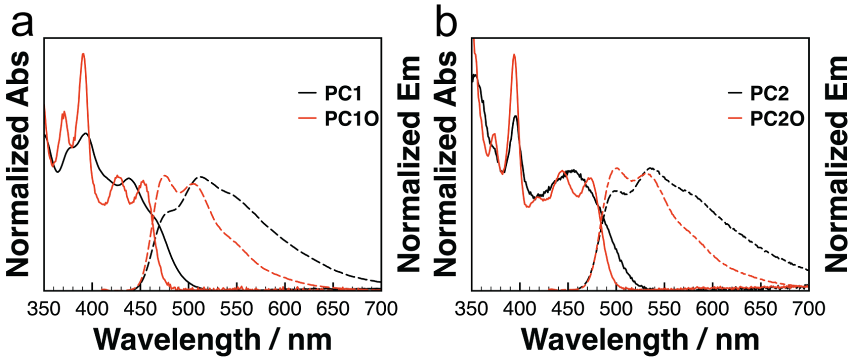


Figure S12. Absorption spectra and emission spectra of (a) **PC1** series and (b) **PC2** series in DCM.

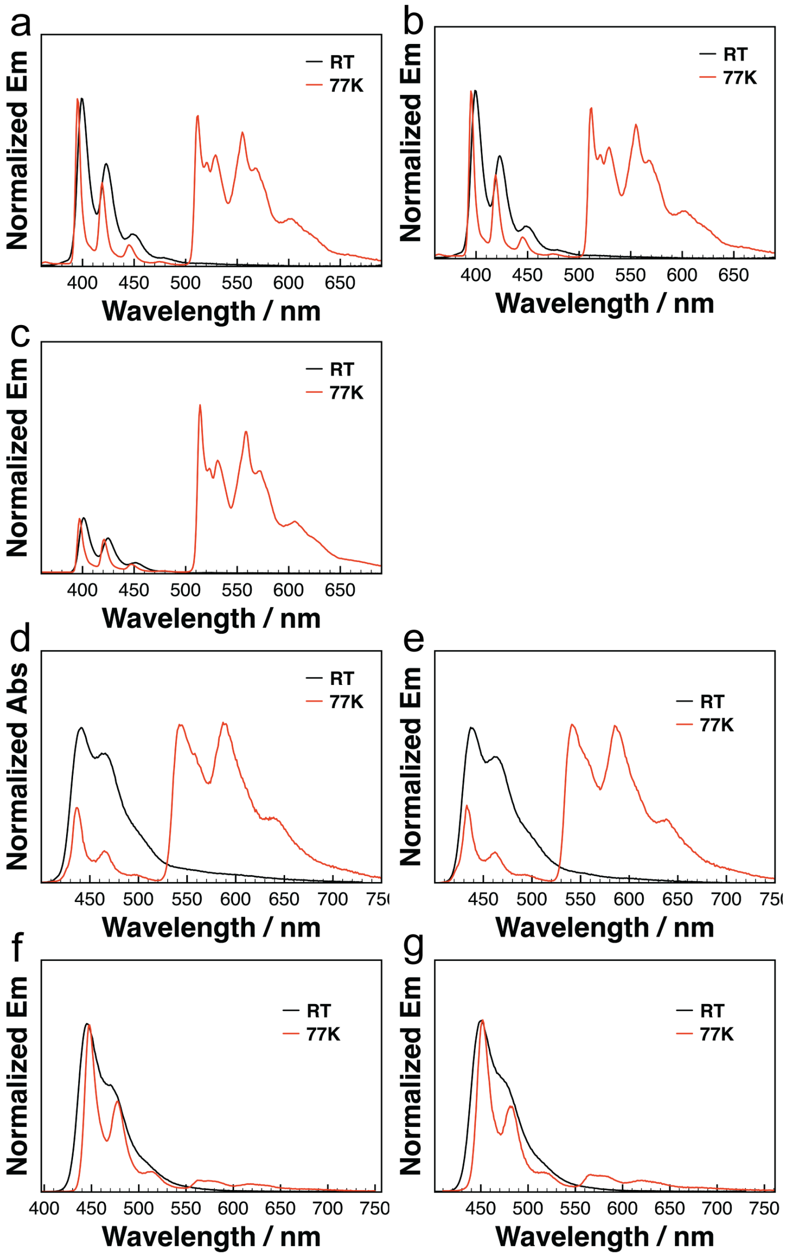


Figure S13. Low-temperature emission spectra of (a) **PN1**, (b) **PN1O**, (c) **PN1S**, (d) **PN2**, (e) **PN2O**, (f) **PN3**, and (g) **PN3O** in 2Me-THF.

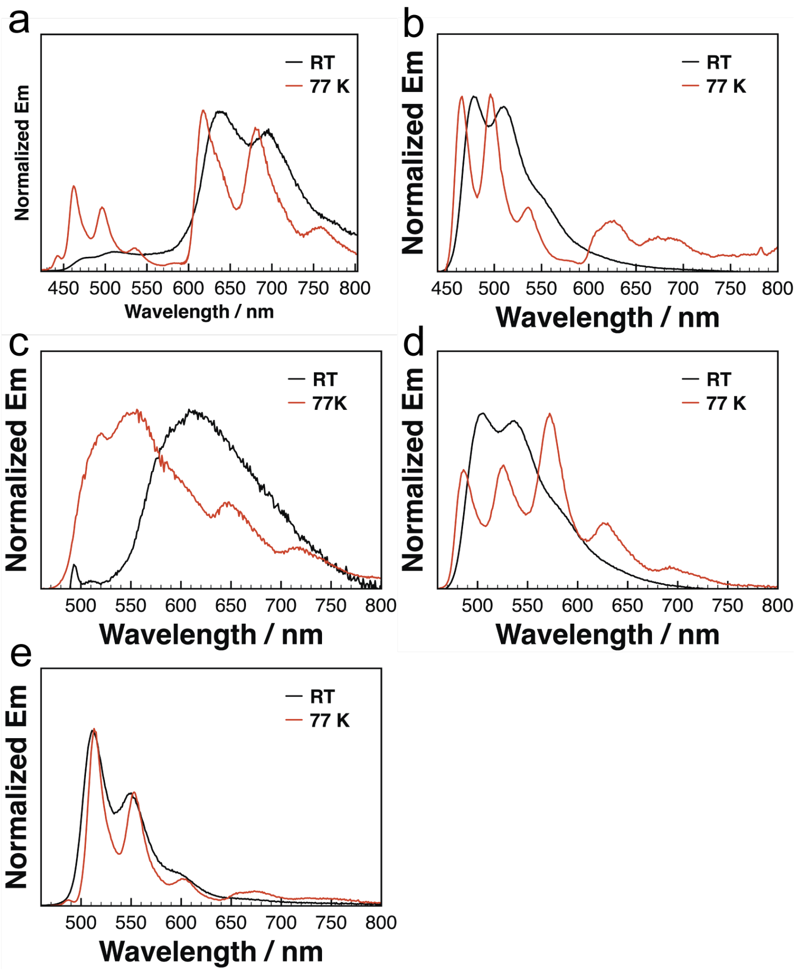


Figure S14. Low-temperature emission spectra of (a) **PC1**, (b) **PC1O**, (c) **PC2**, (d) **PC2O**, and (e) **PC3O** in 2Me-THF.

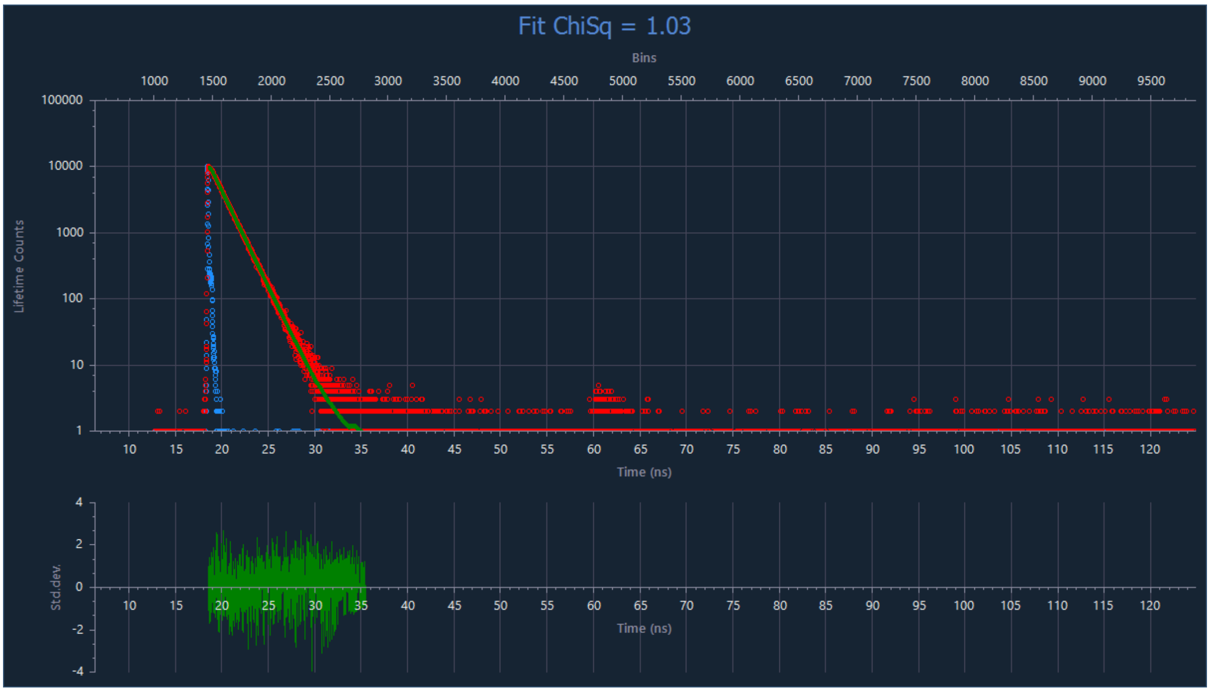


Figure S15. Emission decay of PN1@ 404 nm in DCM.

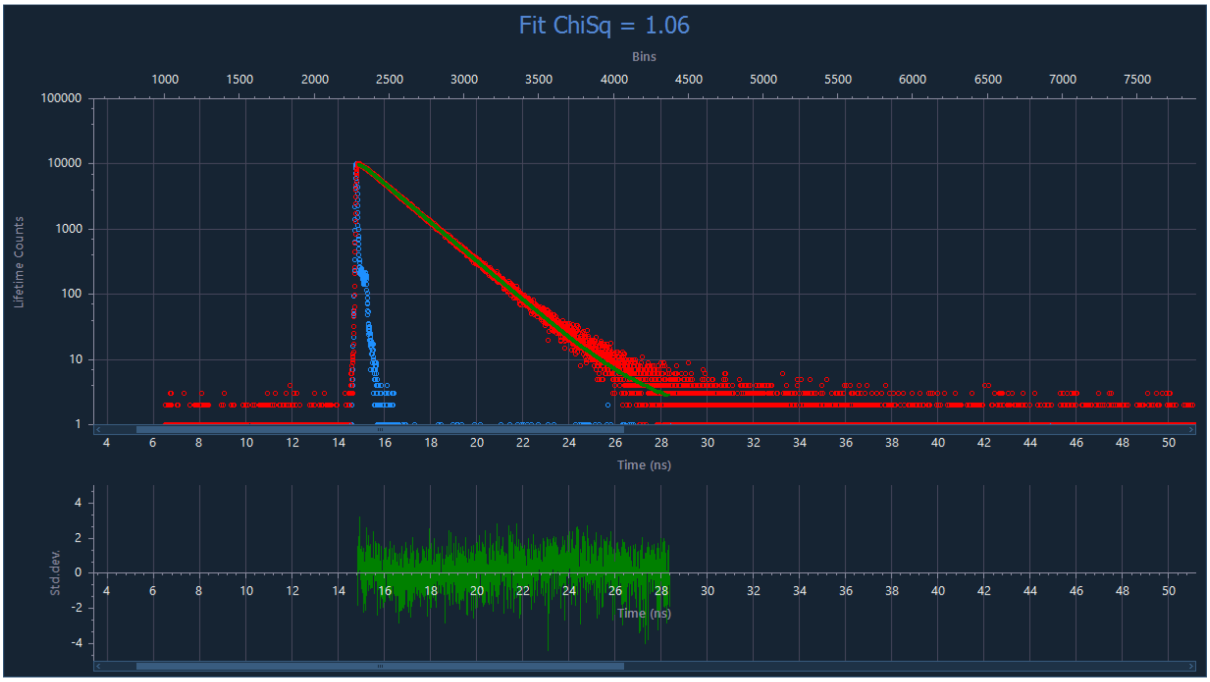


Figure S16. Emission decay of **PN1O**@ 425 nm in DCM.

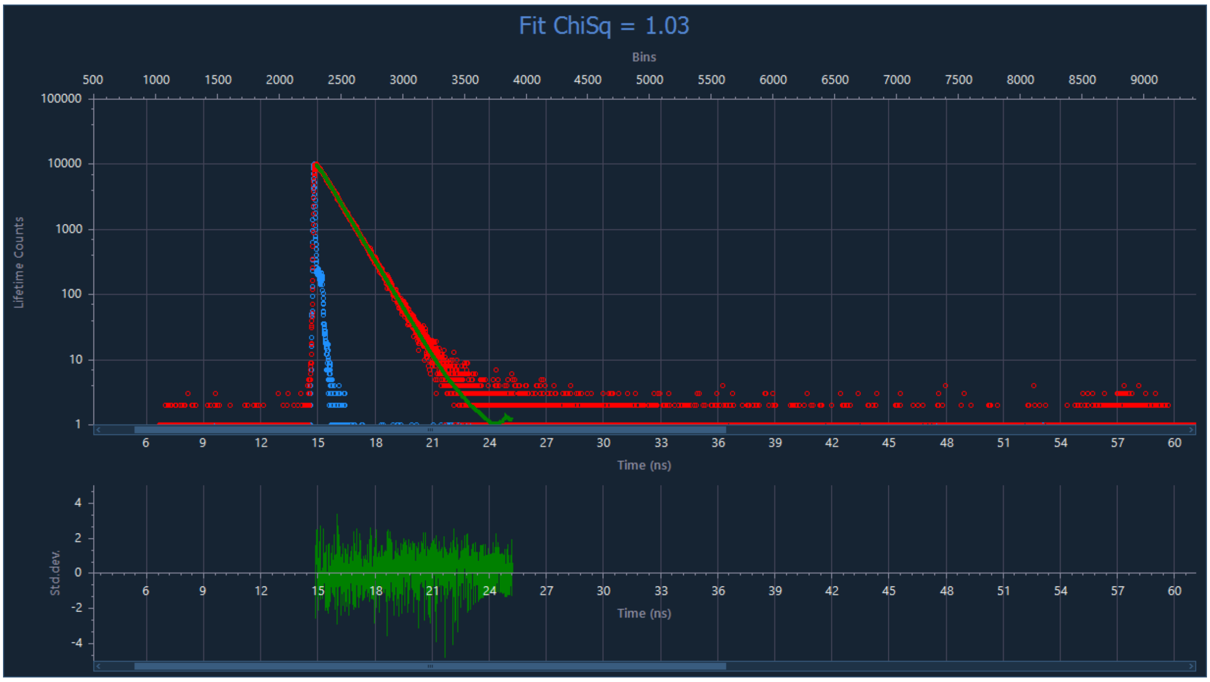


Figure S17. Emission decay of **PN1S** @ 425 nm in DCM.

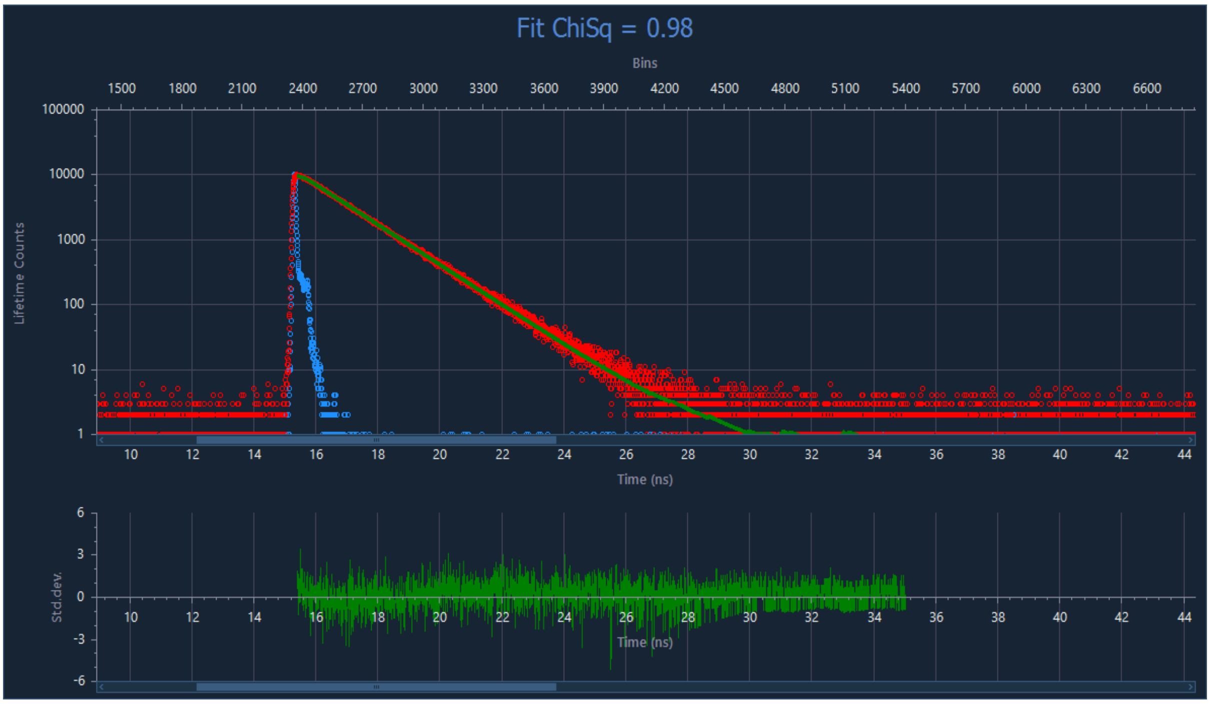


Figure S18. Emission decay of **PN2** @ 440 nm in DCM.

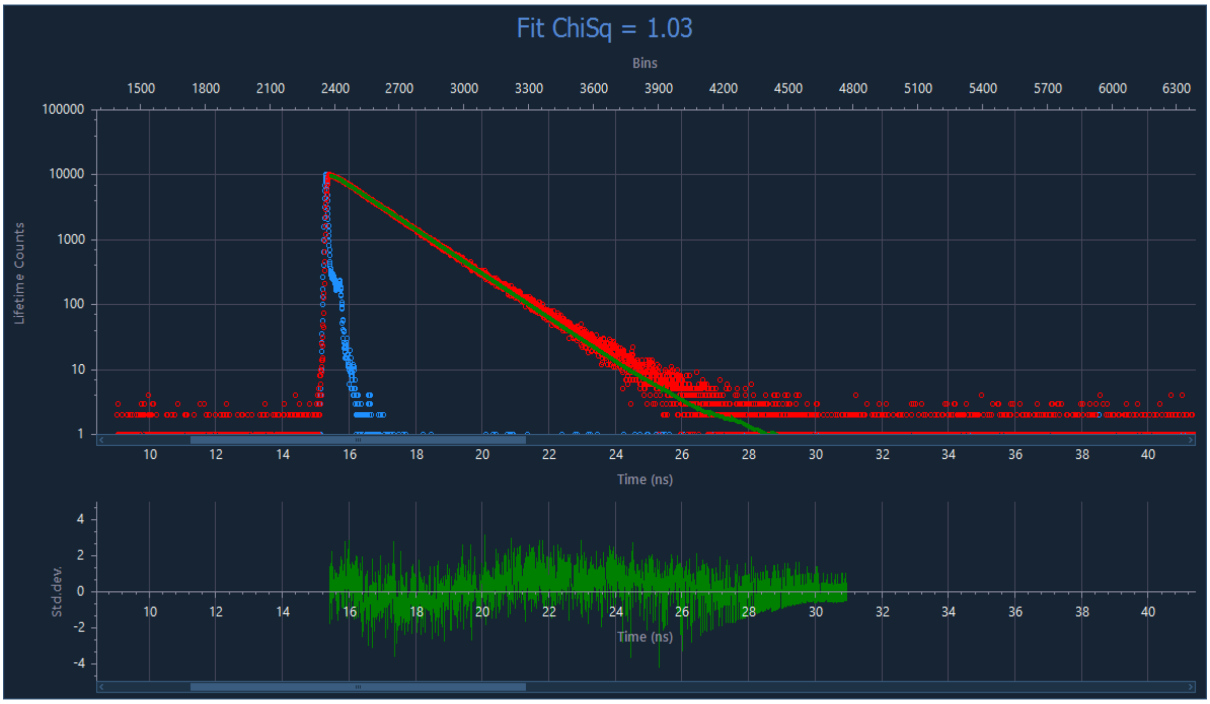


Figure S19. Emission decay of **PN2O** @ 460 nm in DCM.

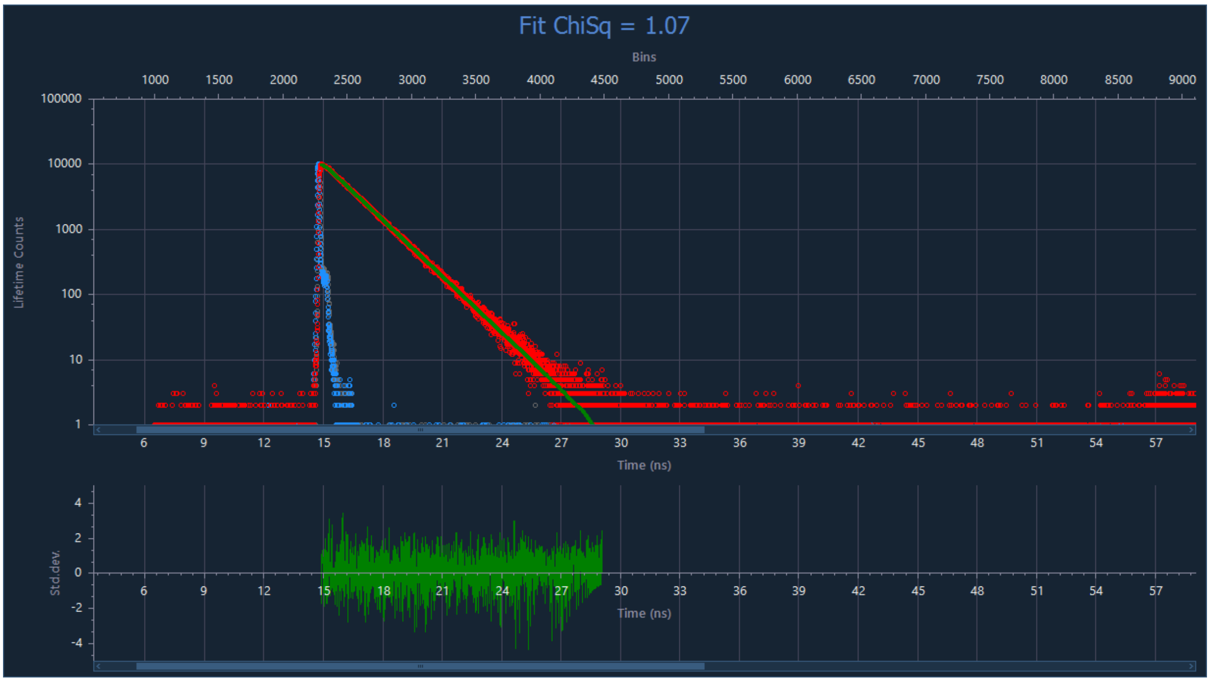


Figure S20. Emission decay of **PN3** @ 450 nm in DCM.

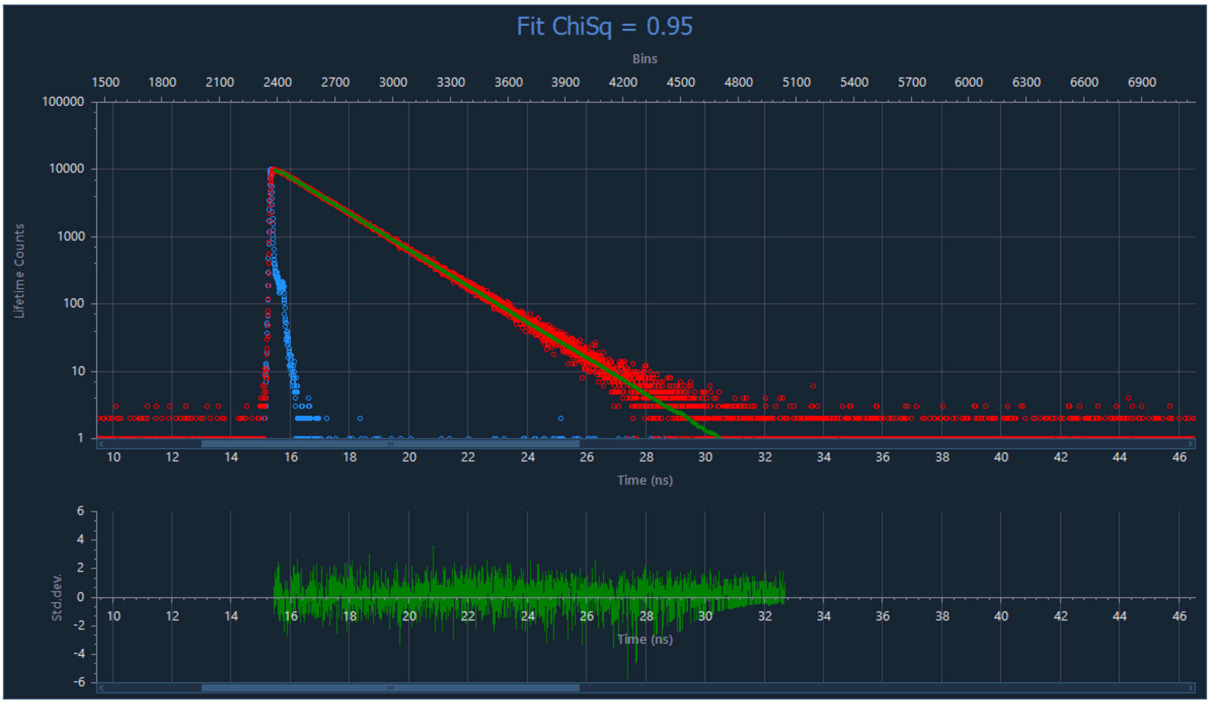


Figure S21. Emission decay of **PN3O** @ 507 nm in DCM.

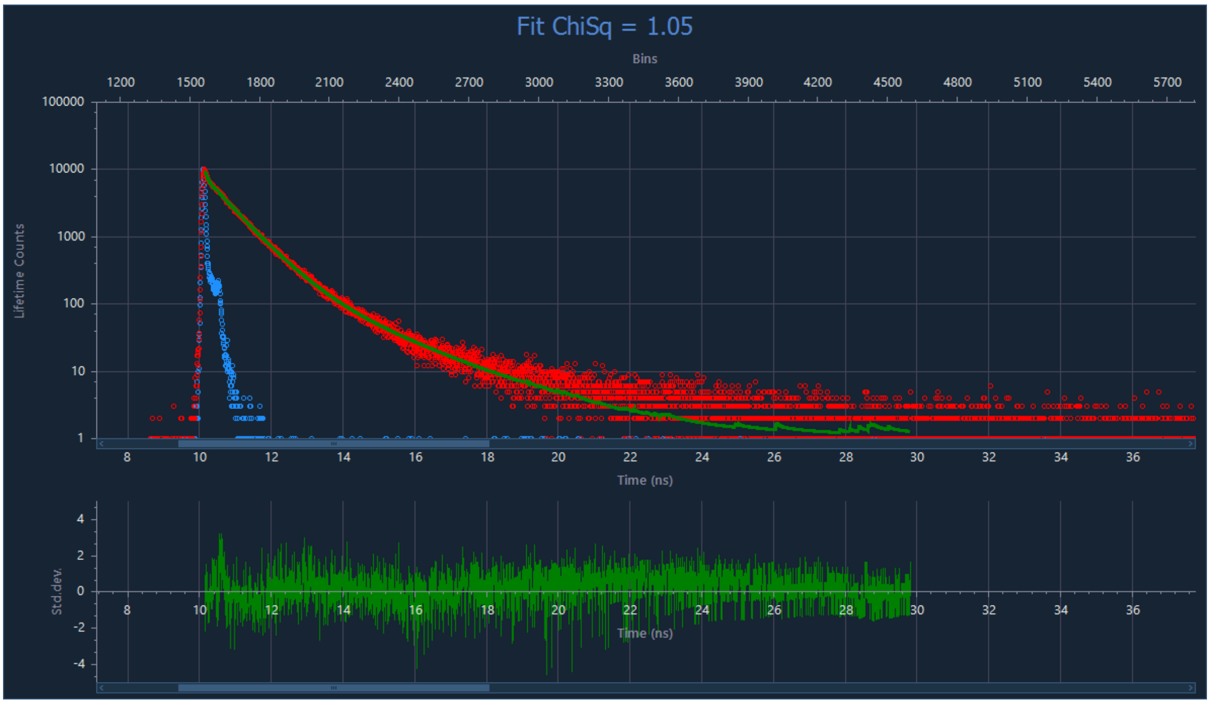


Figure S22. Emission decay of **PC1** @ 521 nm in DCM.

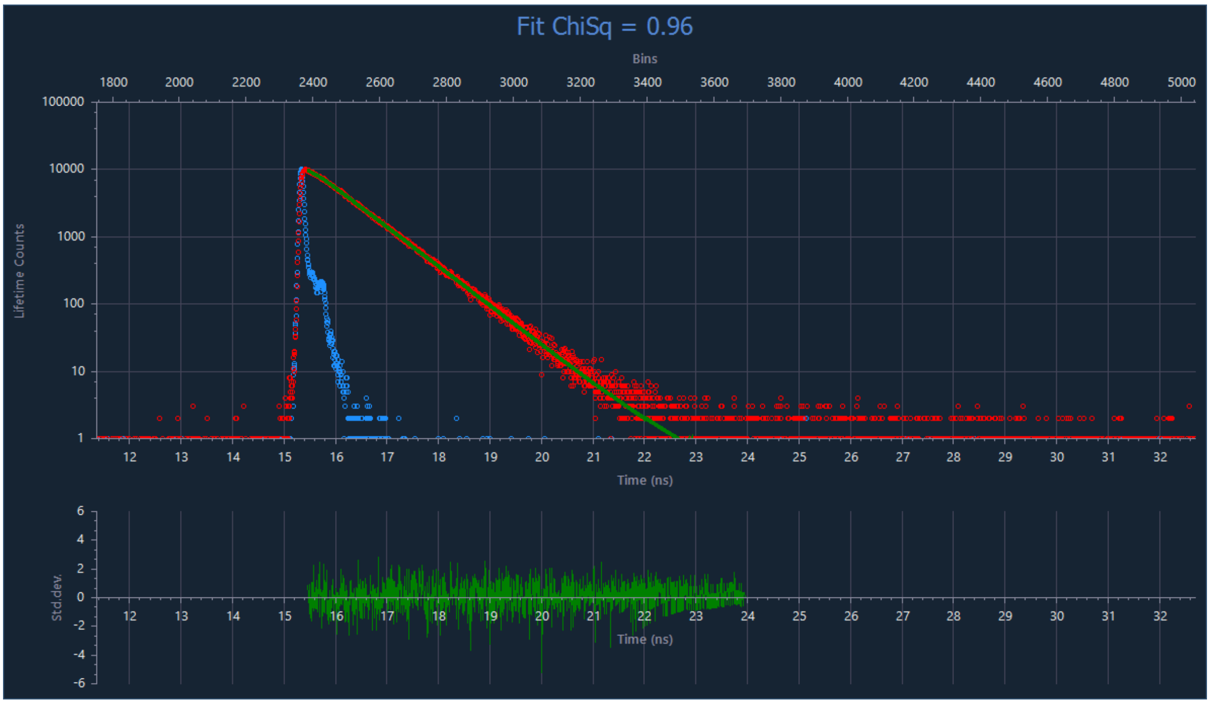


Figure S23. Emission decay of **PC1O** @ 505 nm in DCM.

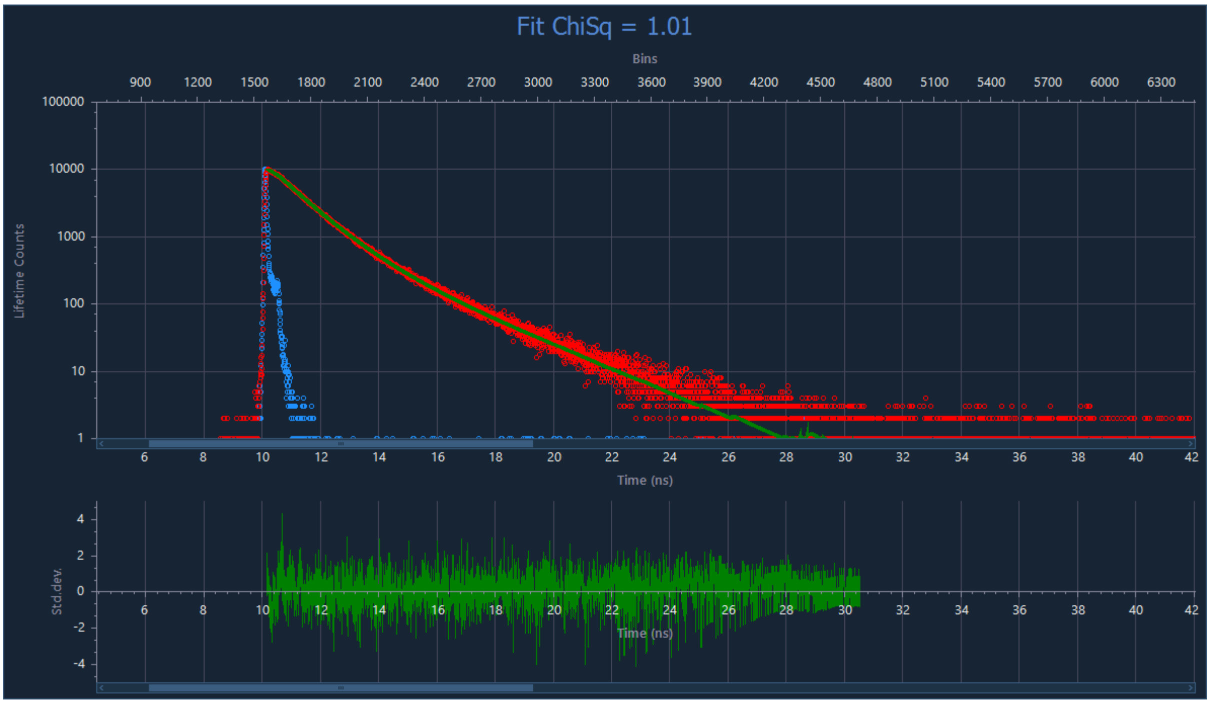


Figure S24. Emission decay of **PC2** @ 537 nm in DCM.

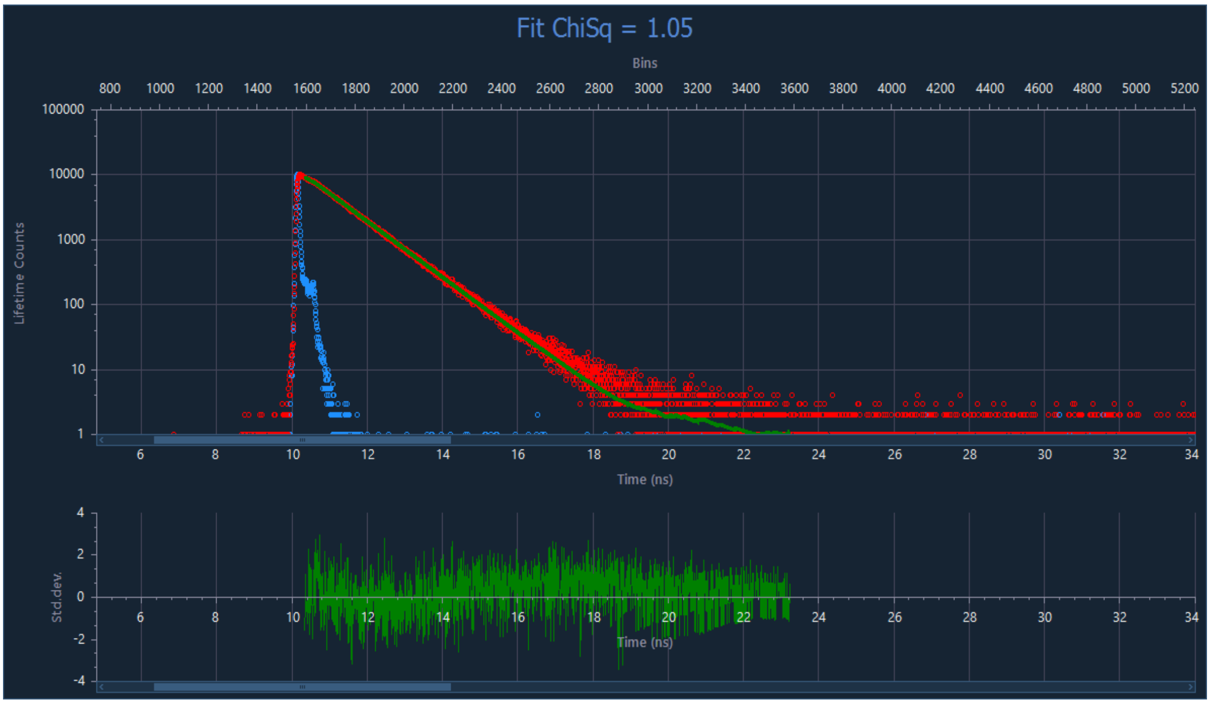


Figure S25. Emission decay of **PC2O** @ 502 nm in DCM.

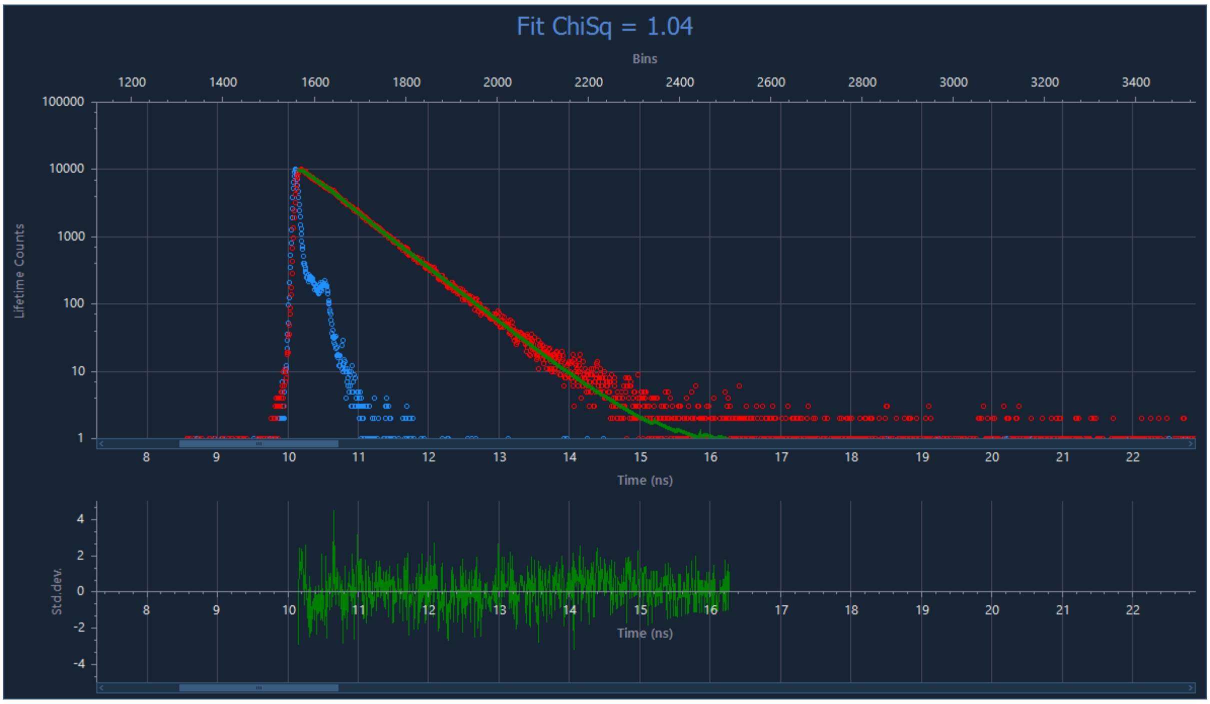


Figure S26. Emission decay of **PC3O** @ 548 nm in DCM.

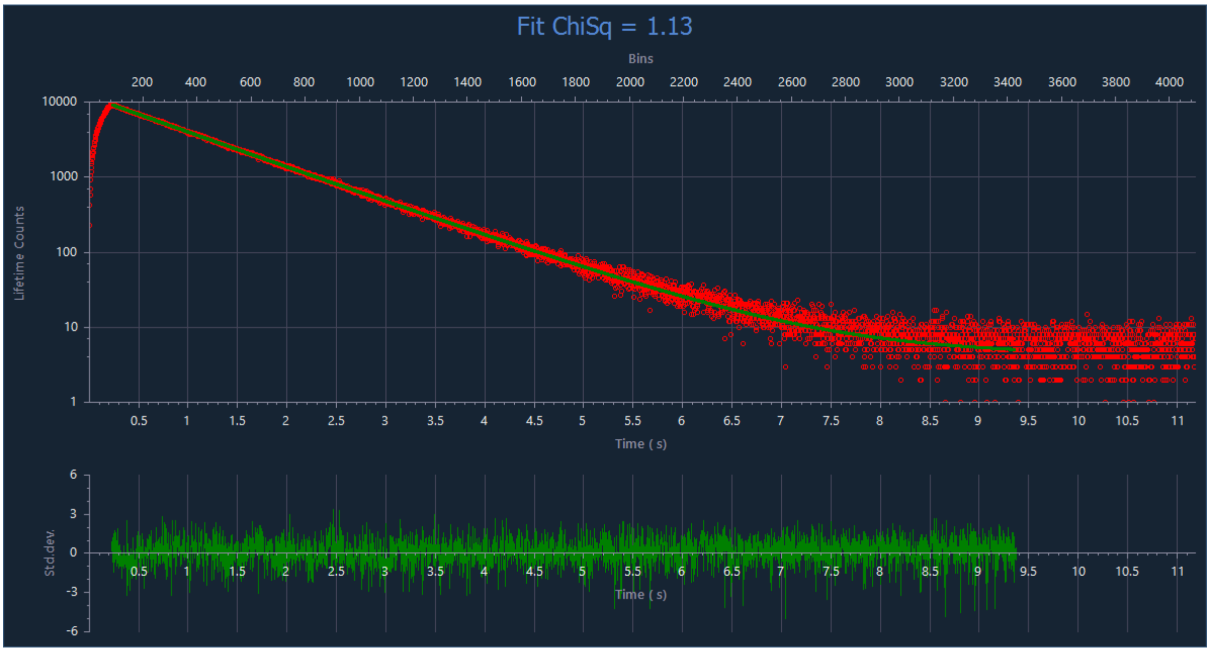


Figure S27. Emission decay of **PN1** @ 555 nm, 77 K in 2Me-THF.

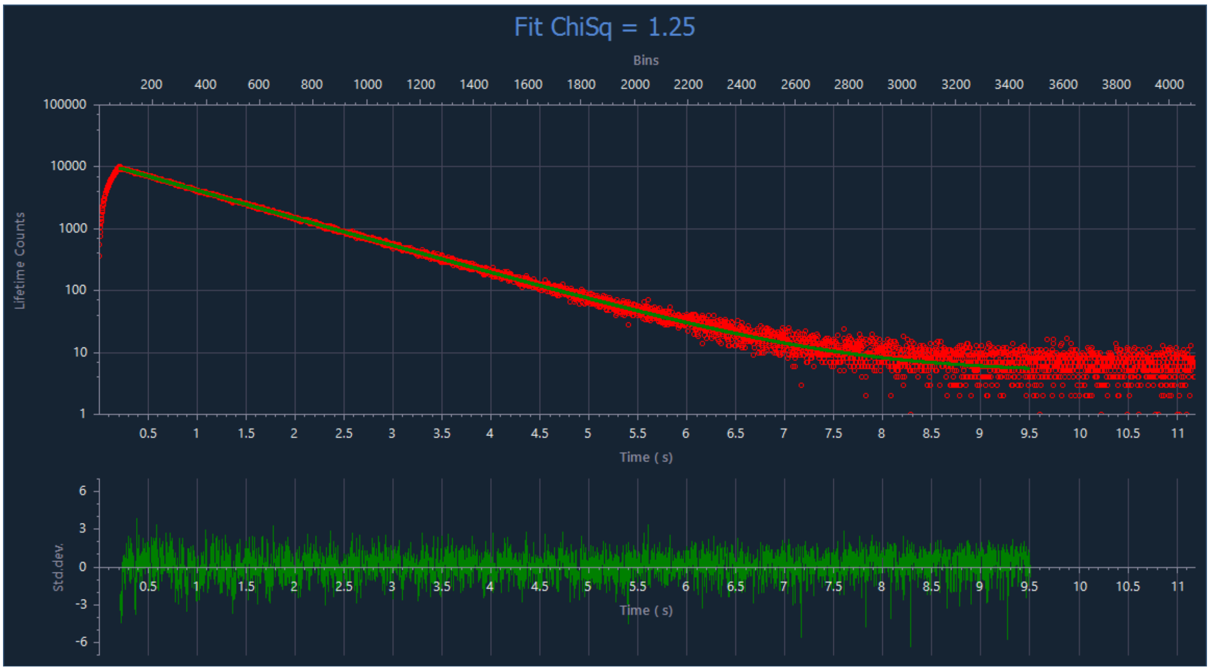


Figure S28. Emission decay of **PN1S** @ 555 nm, 77 K in 2Me-THF.

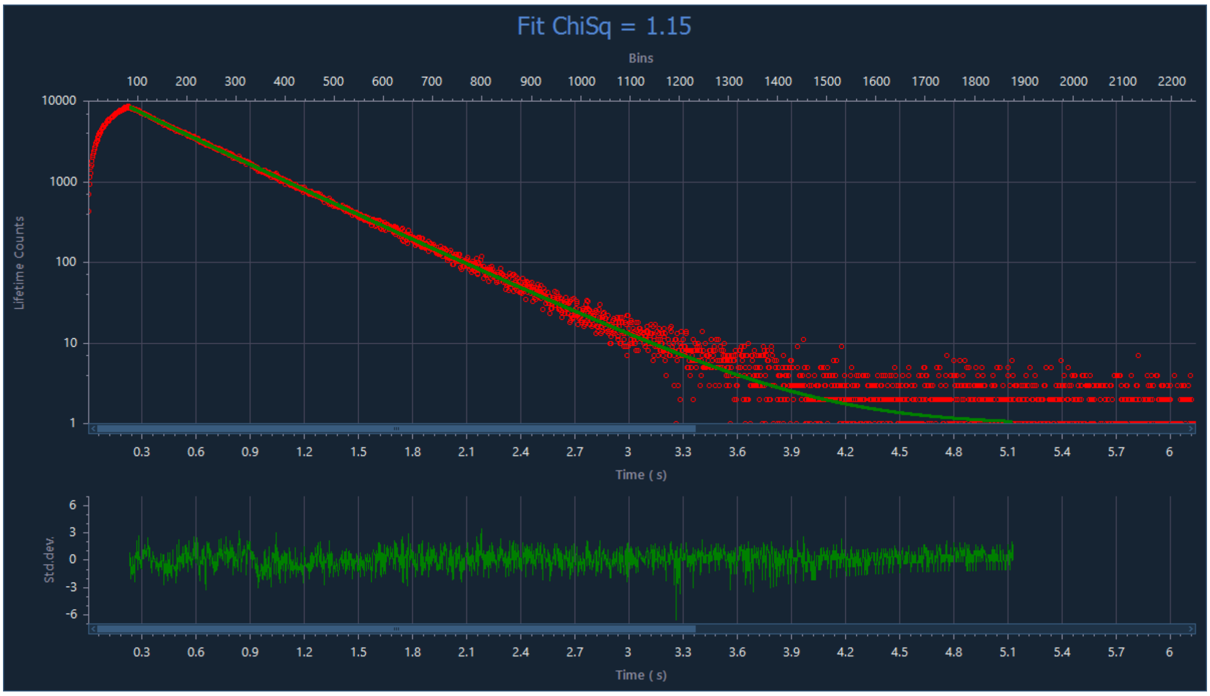


Figure S29. Emission decay of **PN2** @ 544 nm, 77 K in 2Me-THF.

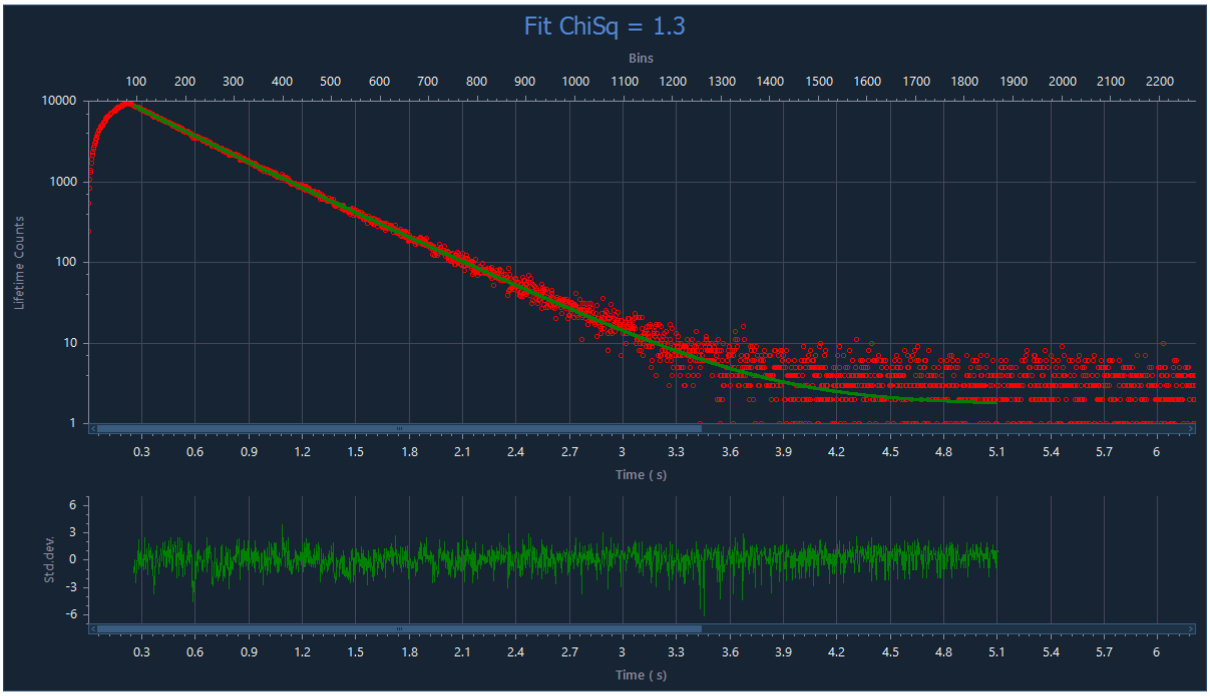


Figure S30. Emission decay of **PN2O** @ 540 nm, 77 K in 2Me-THF.

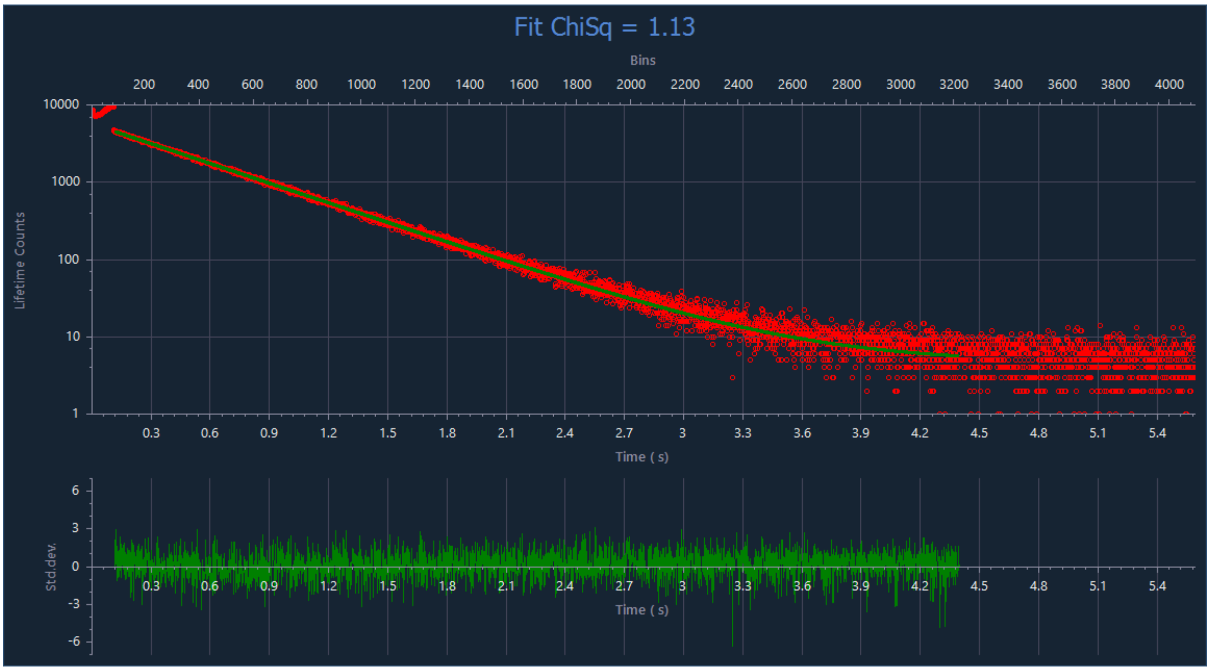


Figure S31. Emission decay of **PN3** @ 564 nm, 77 K in 2Me-THF.

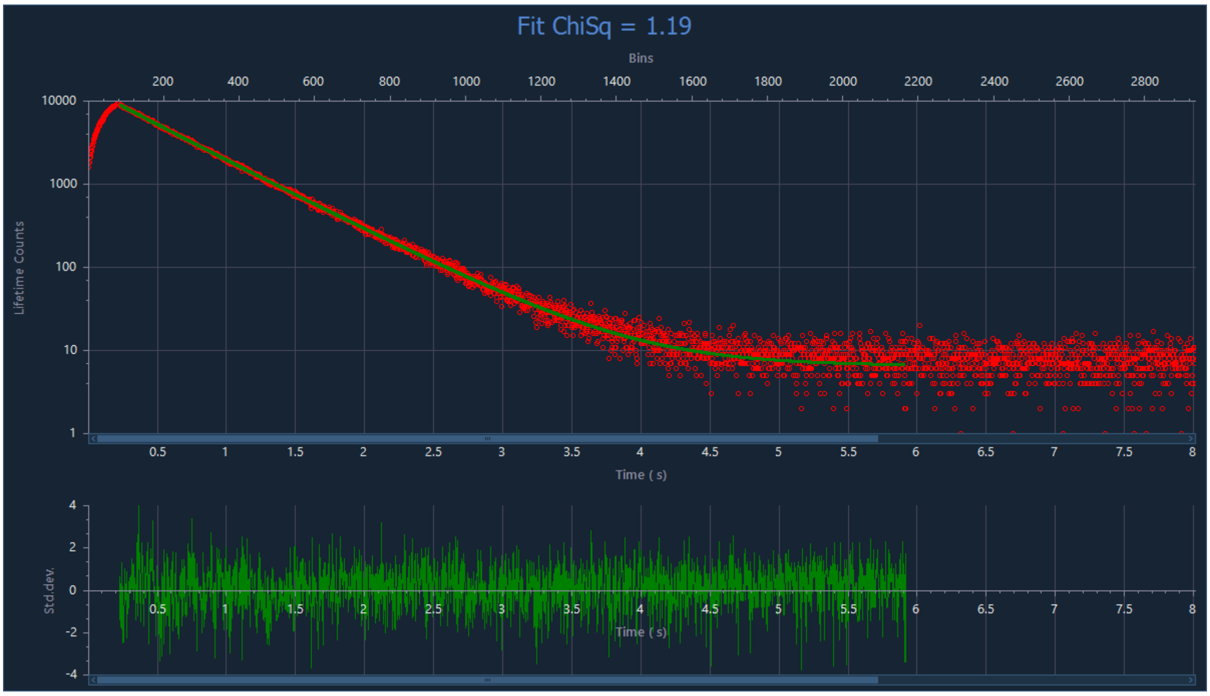


Figure S32. Emission decay of **PN3O** @ 619 nm, 77 K in 2Me-THF.

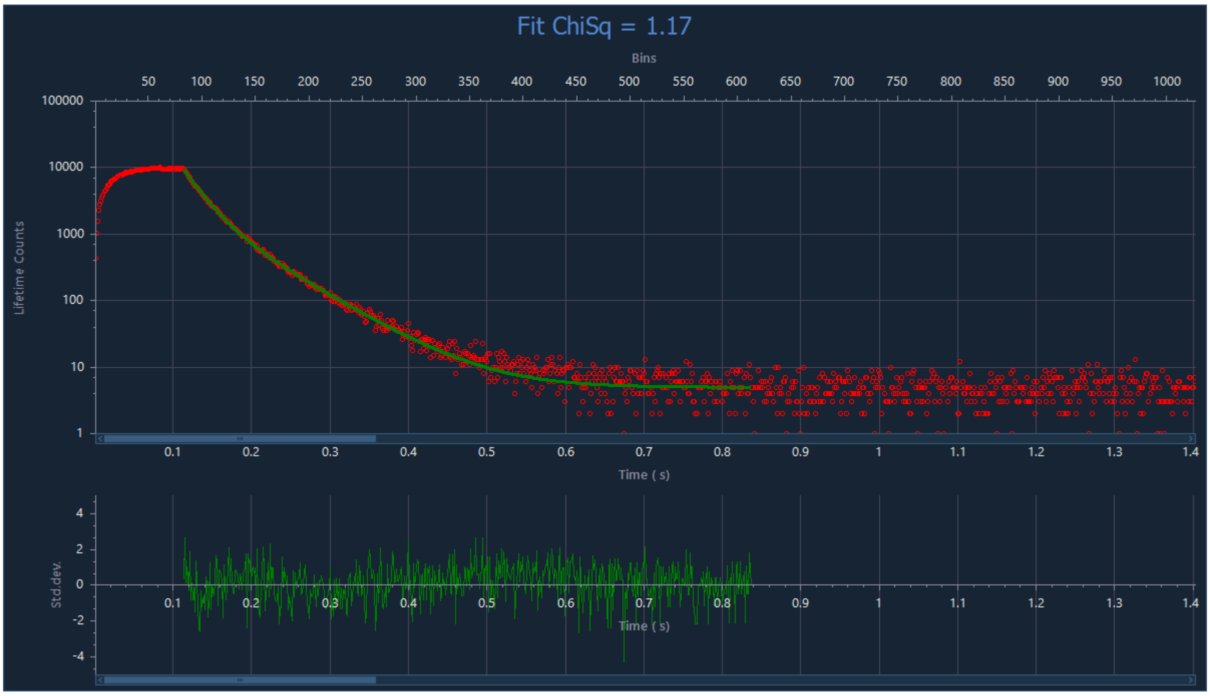


Figure S33. Emission decay of **PC1** @ 690 nm, 77 K in 2Me-THF.

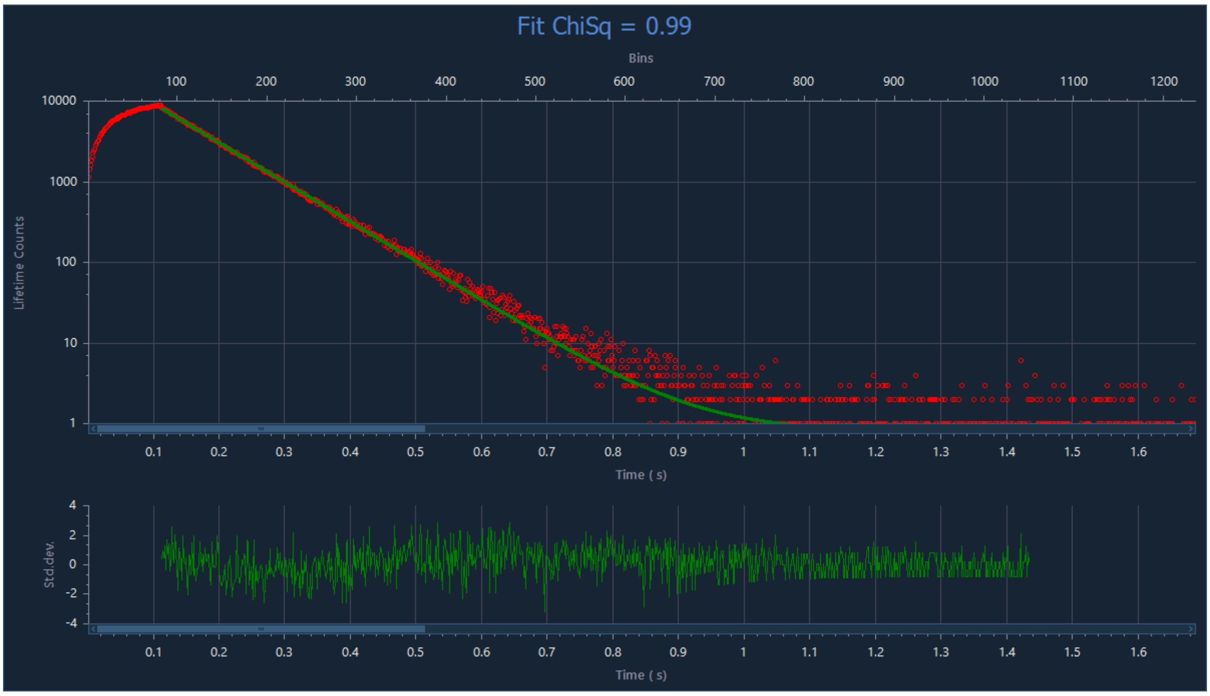


Figure S34. Emission decay of **PC1O** @ 626 nm, 77 K in 2Me-THF.

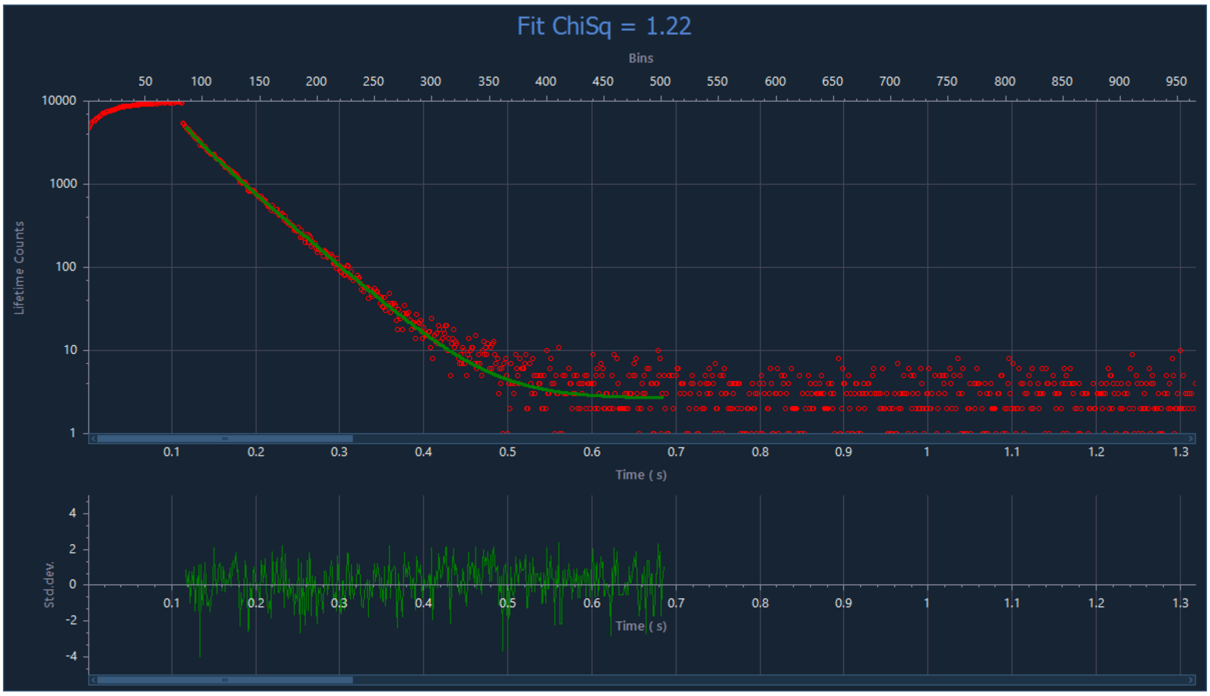


Figure S35. Emission decay of **PC2** @ 648 nm, 77 K in 2Me-THF.

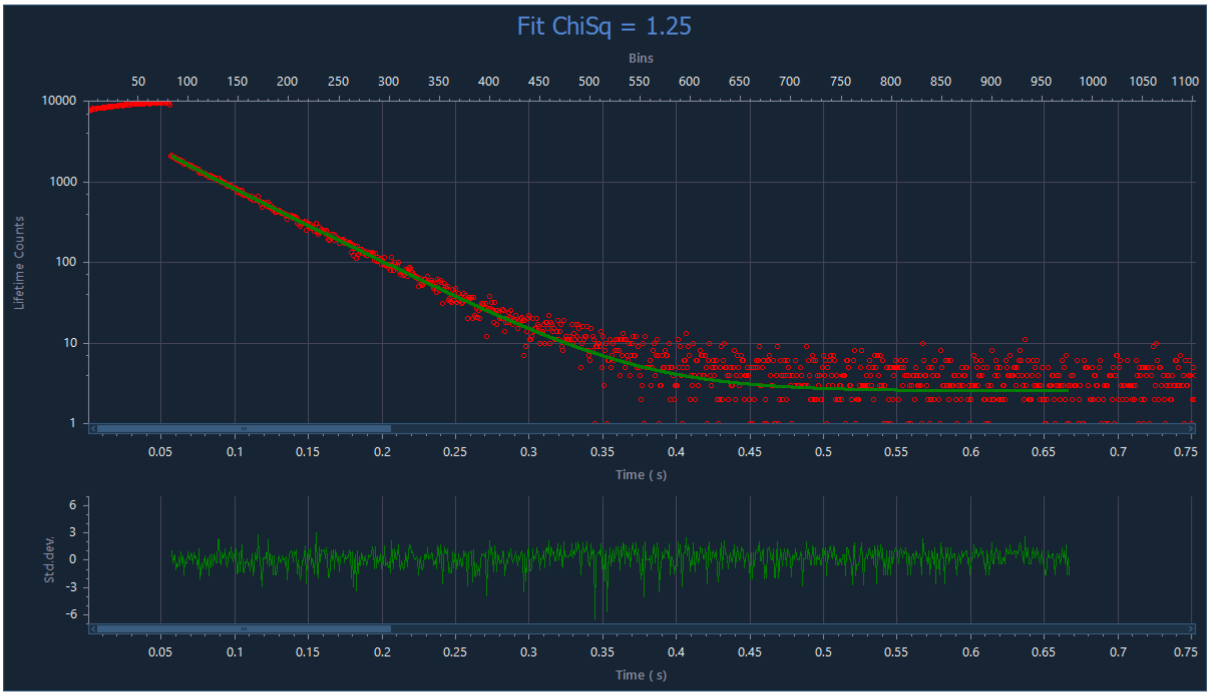


Figure S36. Emission decay of **PC2O** @ 693 nm, 77 K in 2Me-THF.

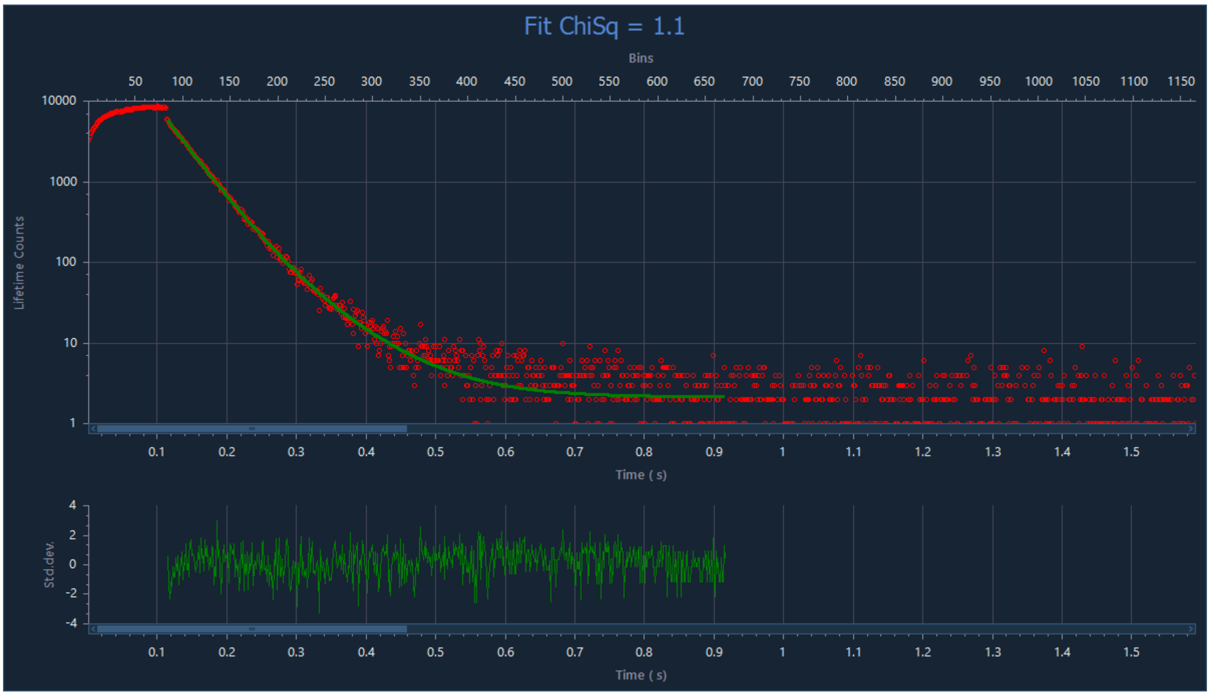


Figure S37. Emission decay of **PC2O** @ 677 nm, 77 K in 2Me-THF.

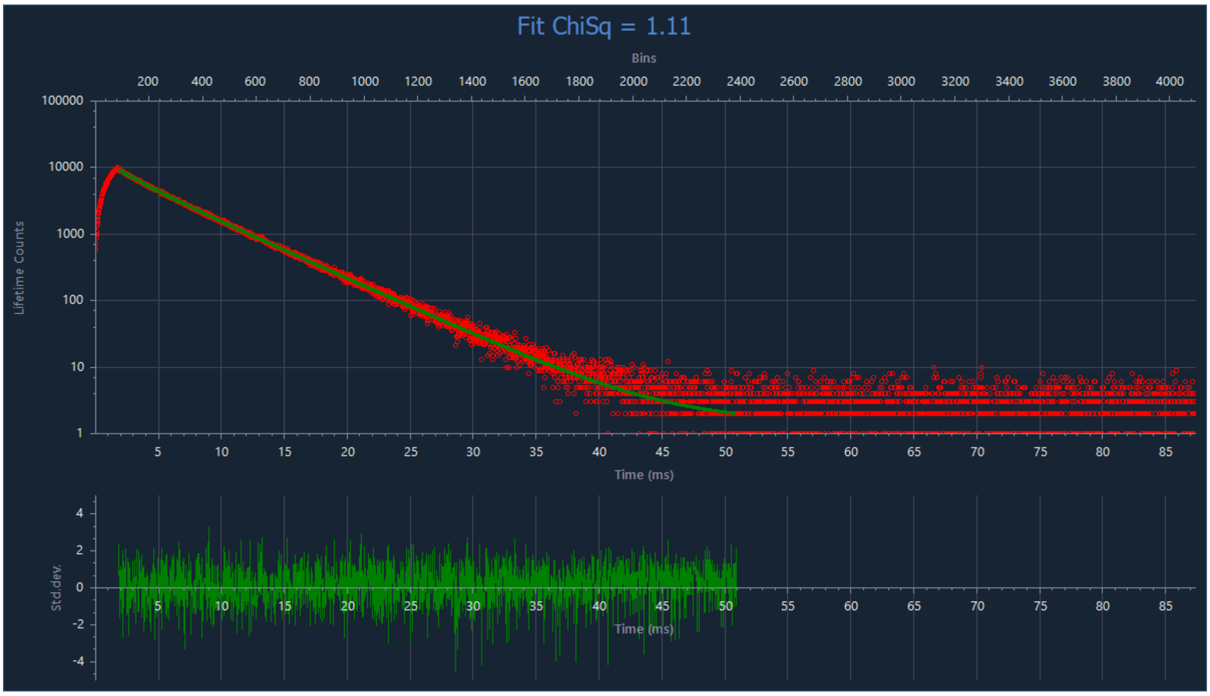


Figure S38. Emission decay of **PC1** @ 690 nm, 298 K in 2Me-THF.

Theoretical calculation

For models molecules, all the calculations were performed using Gaussian09 Packages[S2] by supercomputer cluster supported by HPC Platform of ShanghaiTech University. Geometry optimizations were carried out with B3LYP/G-311+(d,p) level in vacuum. Single point calculations at TD-B3LYP/G-311+(d,p) level in vacuum were performed to reevaluate the energy of optimized structures. For monocations and dications, geometry optimizations were carried out with UB3LYP/G-311+(d,p) level in vacuum. For monocations, single point calculations at TD-UCAM-B3LYP/G-311+(d,p) level in vacuum were performed to reevaluate the energy of optimized structures. For dications, single point calculations at TD-B3LYP/G-311+(d,p) level in vacuum were performed to reevaluate the energy of optimized structures. NICS values were obtained in the S_0 and T_1 states through calculations using the GIAO method in Gaussian 09 Revision E.01 at B3LYP/6-311G(d,p) level. Use the LQA (Local quadratic approximation) method to calculate the intrinsic reaction coordinate (IRC) in Gaussian 16 Revision C.02 at B3LYP/6-311G(d,p) level.[S3]

Table S2. TD-DFT data of P-OCMs at the level of TD-DFT B3LYP/6-311+G (d,p).

Compound	LUMO [eV]	HOMO [eV]	HOMO-LUMO gap (eV)	S_0-S_1 Wavelength (nm) Energy gap (eV)	S_0-S_1 Oscillator strength
PN1	-1.92	-5.59	3.67	388 (3.19)	0.05
PN1O	-2.03	-5.69	3.65	390 (3.17)	0.05
PN2	-2.81	-6.22	3.42	422 (2.94)	0.04
PN2O	-2.92	-6.30	3.38	427 (2.90)	0.04
PN3	-1.83	-5.06	3.23	441 (2.81)	0.66
PN3O	-1.92	-5.12	3.21	444 (2.79)	0.64
PC1	-2.22	-5.29	3.08	469 (2.64)	0.15
PC1O	-2.37	-5.42	3.05	473 (2.62)	0.15
PC2O	-2.94	-5.84	2.89	503 (2.46)	0.16
PC3O	-2.18	-5.01	2.83	510 (2.43)	0.64

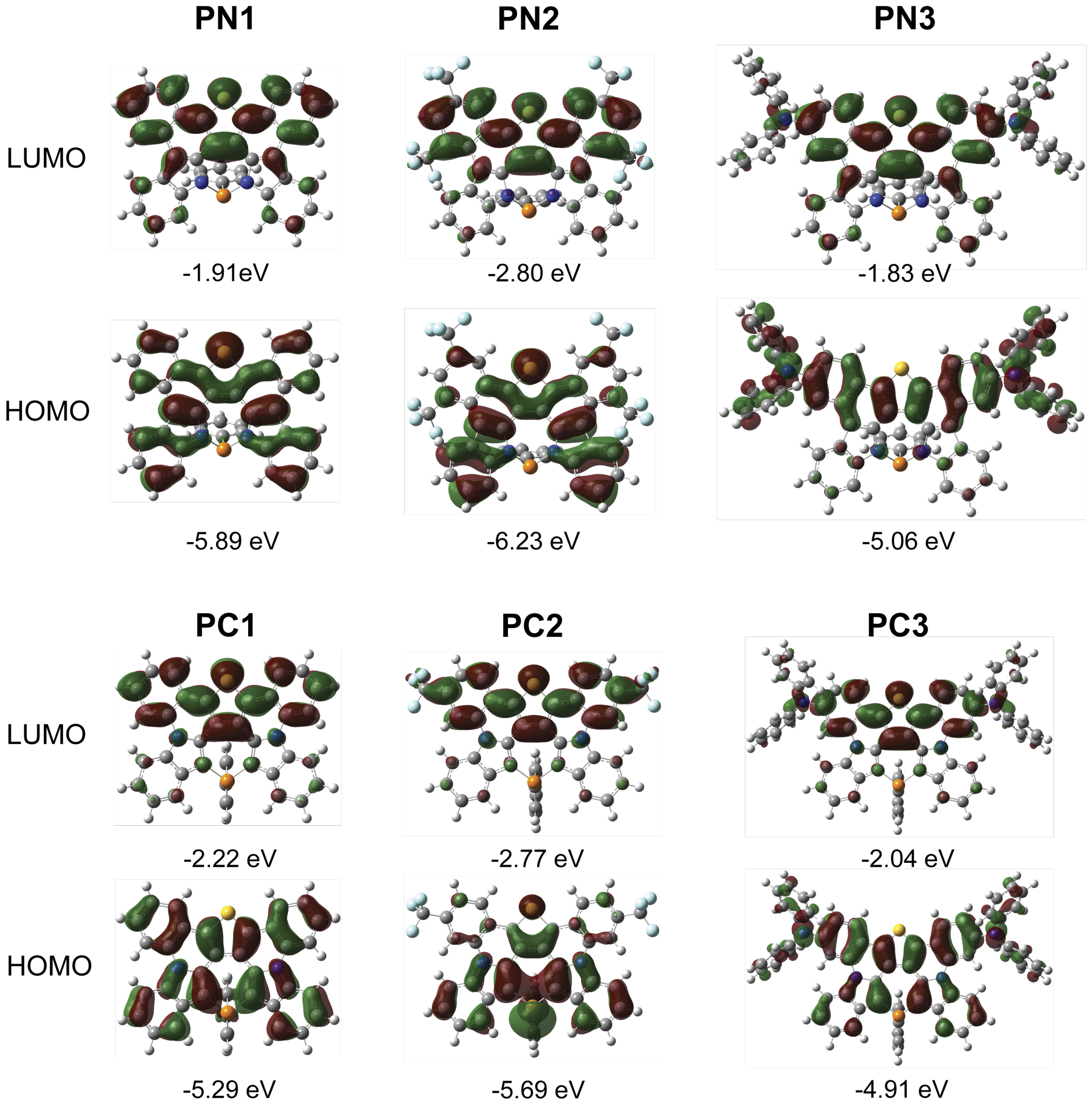


Figure S39. FMOs of **PN** and **PC** series with P(III) centers.

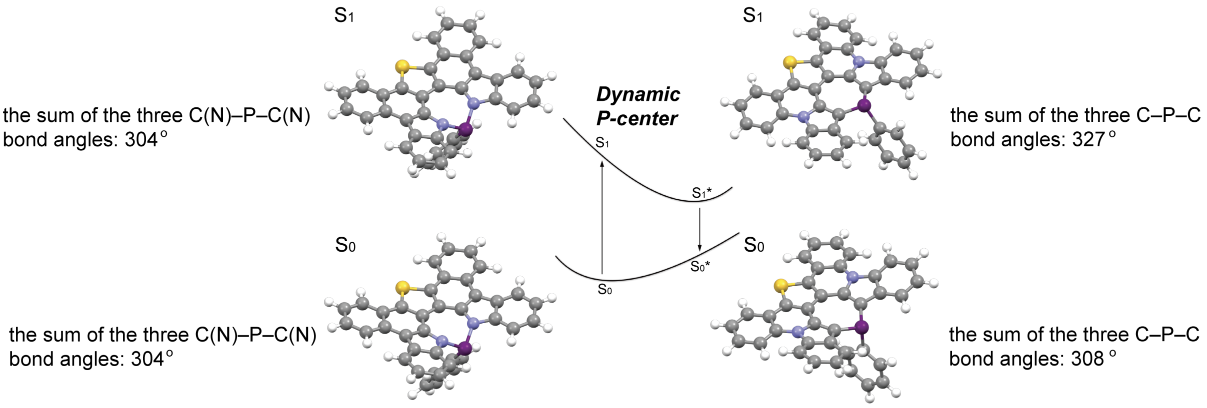


Figure S40. Optimized structures and FMOs of **PN1** and **PC1** in S_0 and in S_1.

Table S3. TD-DFT data of **PN3O** radical monocation the level of TD-DFT CAM-UB3LYP/6-311+G (d,p) in vacuum.

Excited State	Energy gap (nm)	Energy gap (eV)	Oscillator strength
1	2283	0.54	0.65
2	1506	0.82	0.19
3	954	1.30	0.004
4	784	1.58	0.08
5	639	1.94	0.0002
6	520	2.38	0.01
7	495	2.50	0.19
8	474	2.61	0.0002
9	463	2.67	0.011
10	460	2.69	0.04

Table S4. TD-DFT data of **PN3O** neutral dication at the level of TD-DFT RB3LYP/6-311+G (d,p) in vacuum.

Excited State	Energy gap (nm)	Energy gap (eV)	Oscillator strength
1	2080	0.59	0.02
2	1370	0.90	0.003
3	1036	1.19	0.23
4	968	1.39	1.27
5	887	1.40	0.14
6	692	1.79	0.004
7	669	1.85	0.002
8	667	1.86	0.009
9	649	1.91	0.0002
10	625	1.98	0.002

Table S5. TD-DFT data of **PC3O** radical monocation at the level of TD-DFT CAM-UB3LYP/6-311+G (d,p) in vacuum.

Excited State	Energy gap (nm)	Energy gap (eV)	Oscillator strength
1	1538	0.80	0.36
2	867	1.43	0.26
3	849	1.46	0.11
4	693	1.79	0.002
5	618	2.01	0.01
6	547	2.26	0.43
7	489	2.53	0.01
8	456	2.72	0.10
9	437	2.84	0.008
10	431	2.87	0.00

Table S6. TD-DFT data of **PC3O** neutral dication at the level of TD-DFT RB3LYP/6-311+G (d,p) in vacuum.

Excited State	Energy gap (nm)	Energy gap (eV)	Oscillator strength
1	1055	1.17	0.24
2	974	1.27	0.17
3	942	1.00	0.001
4	867	1.43	0.14
5	773	1.60	0.0002
6	748	1.66	0.03
7	702	1.76	0.02
8	637	1.94	0.01
9	633	1.95	0.02
10	596	2.08	0.02]09

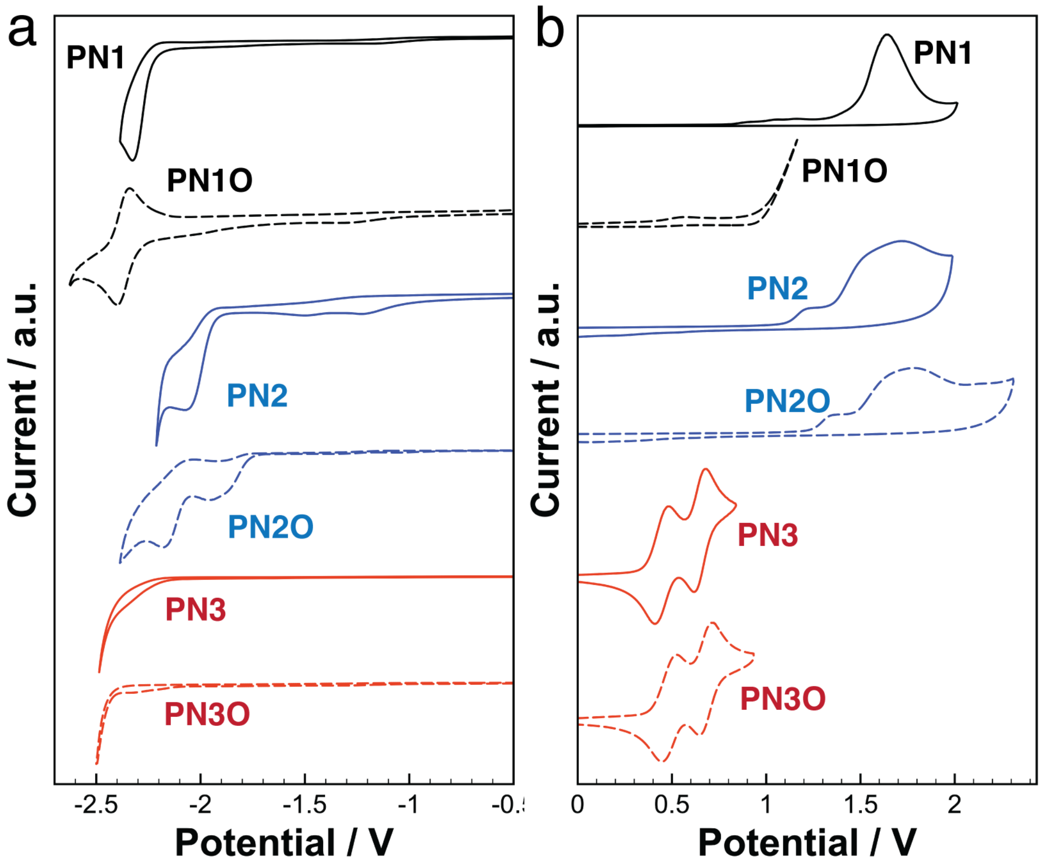


Figure S41. Electrochemical measurements of **PN** and **PC** sereis molecules.

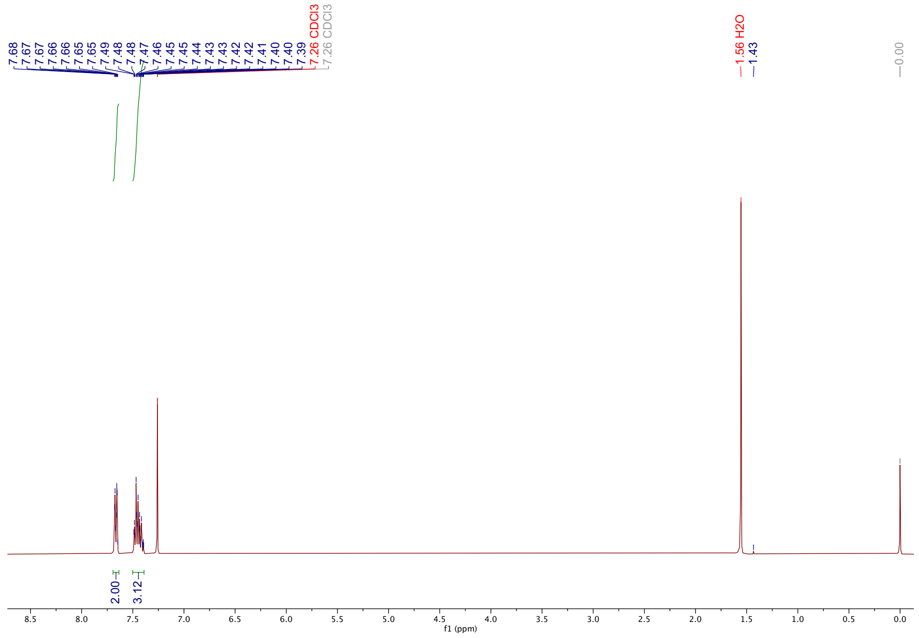


Figure S42. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) of **2a**.

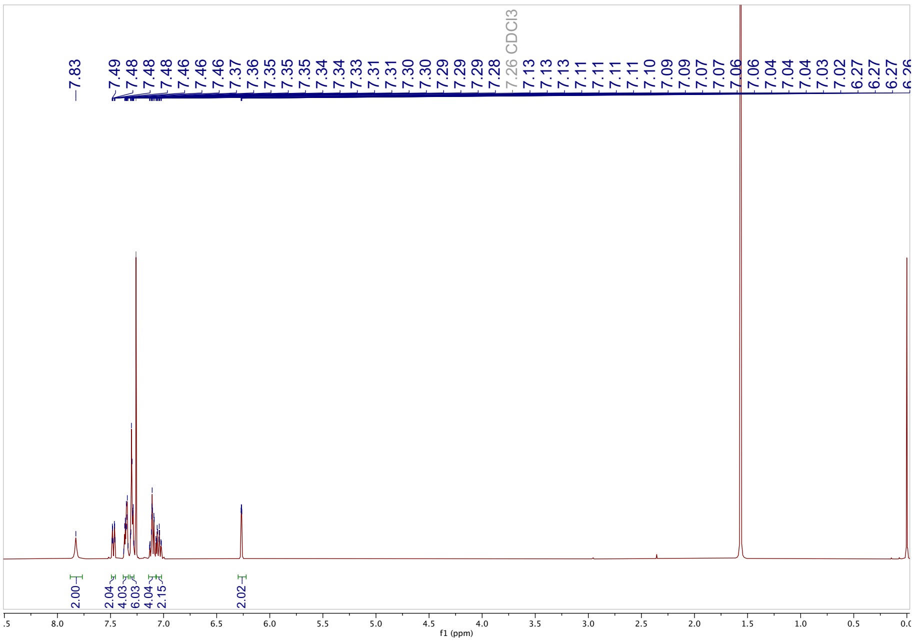


Figure S43. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **3a**.

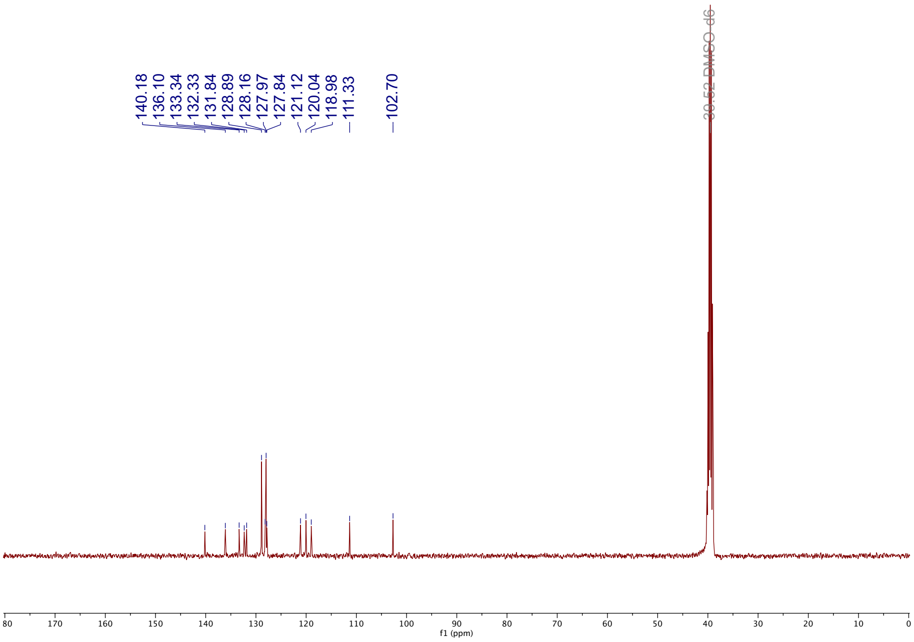


Figure S44. ^{13}C {H} NMR (DMSO-d$_6$, 101 MHz, 298 K) of **3a**.

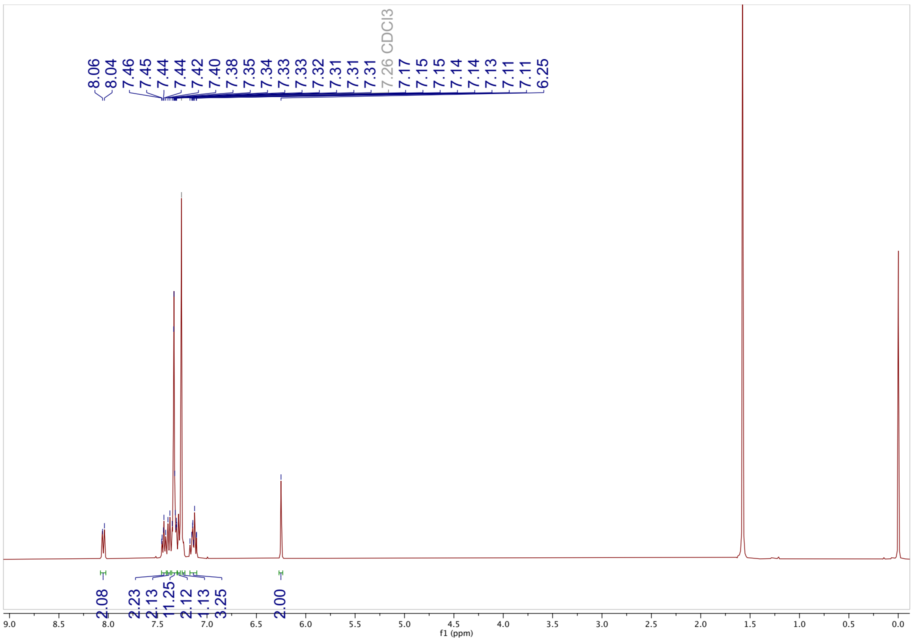


Figure S45. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **4a**.

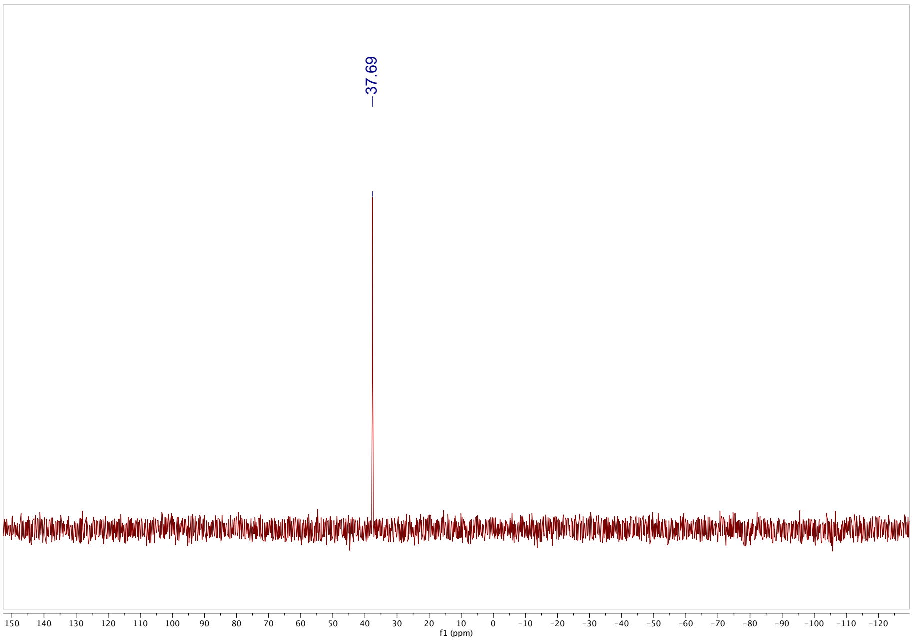


Figure S46. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **4a**.

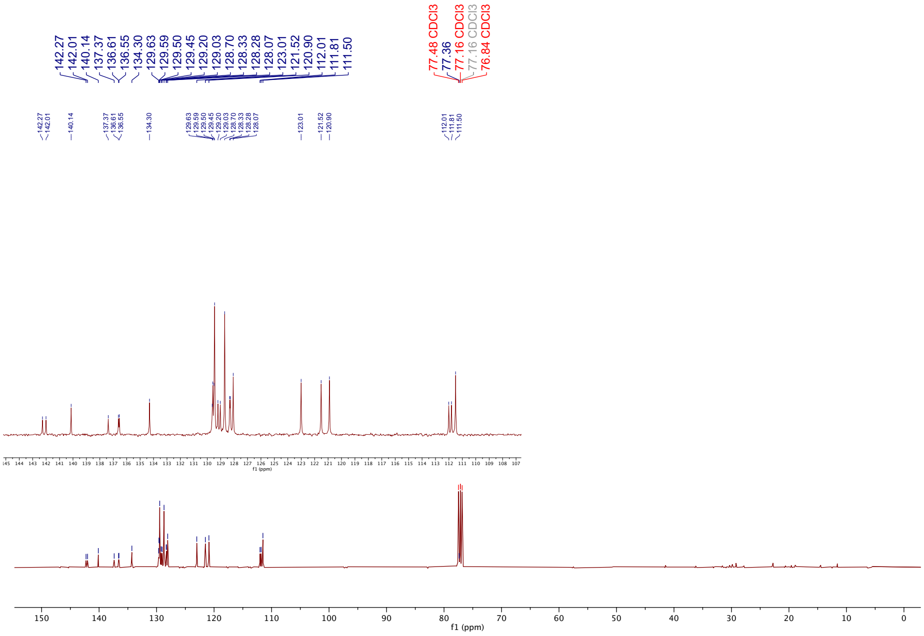


Figure S47. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **4a**.

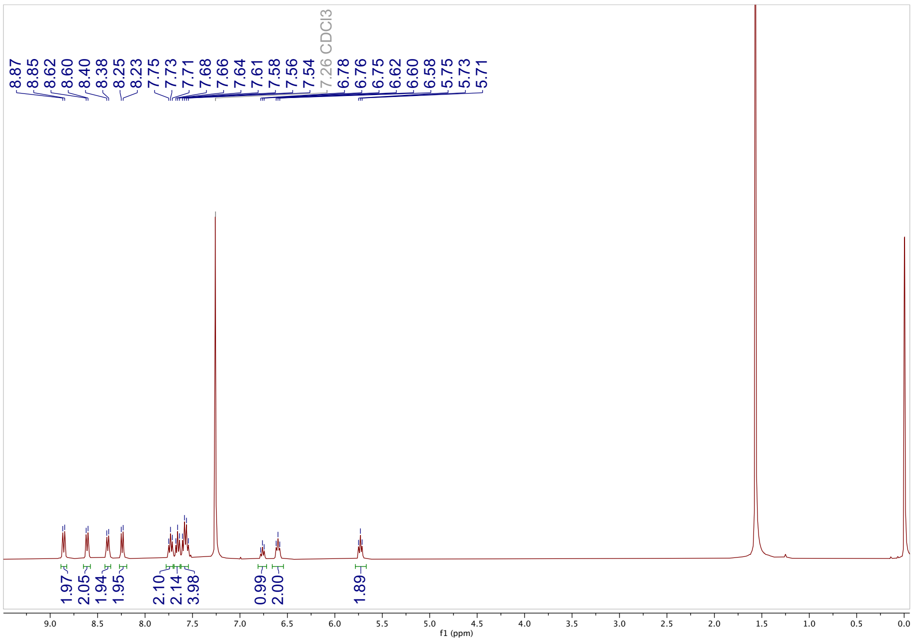


Figure S48. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **PN1**.

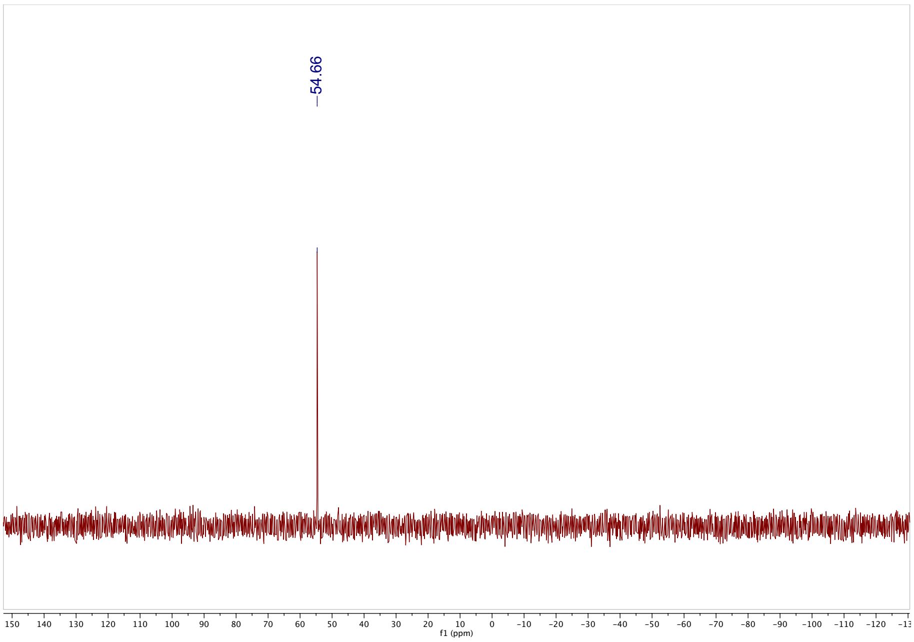


Figure S49. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **PN1**.

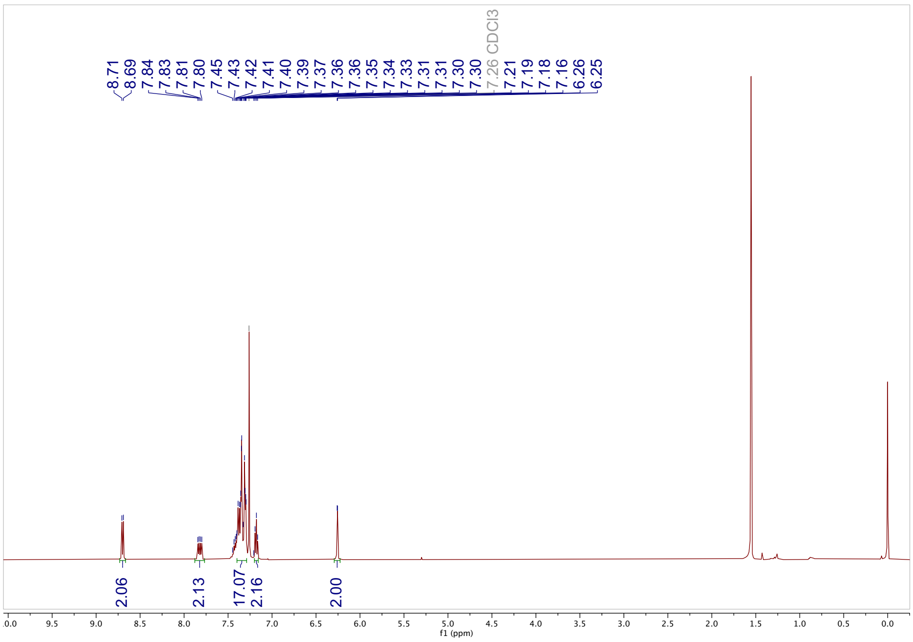


Figure S50. ^{1}H NMR (CDCl$_3$, 500 MHz, 298 K) of **4aO**.

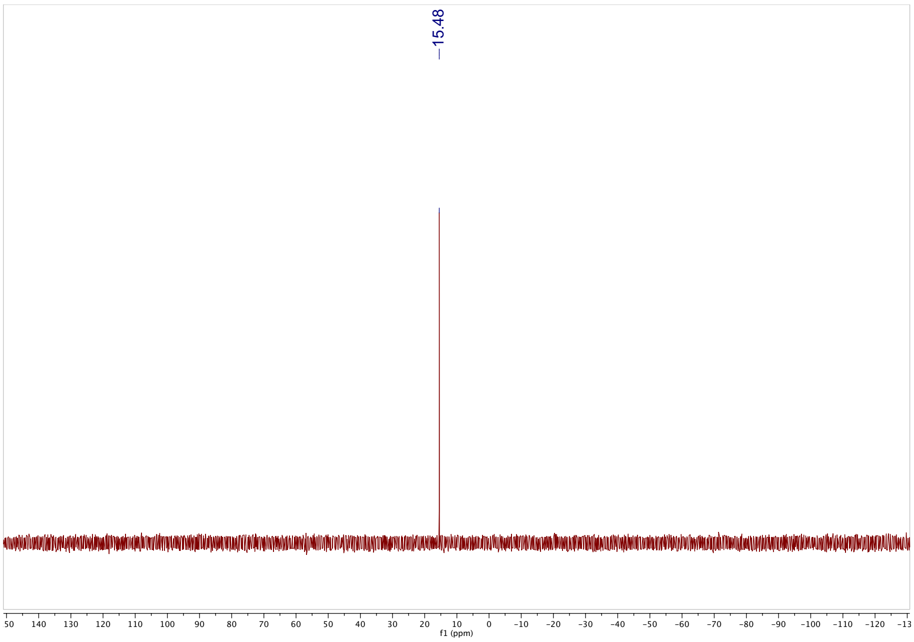


Figure S51. ^{31}P {H} NMR ($CDCl_3$, 202 MHz, 298 K) of **4aO**.

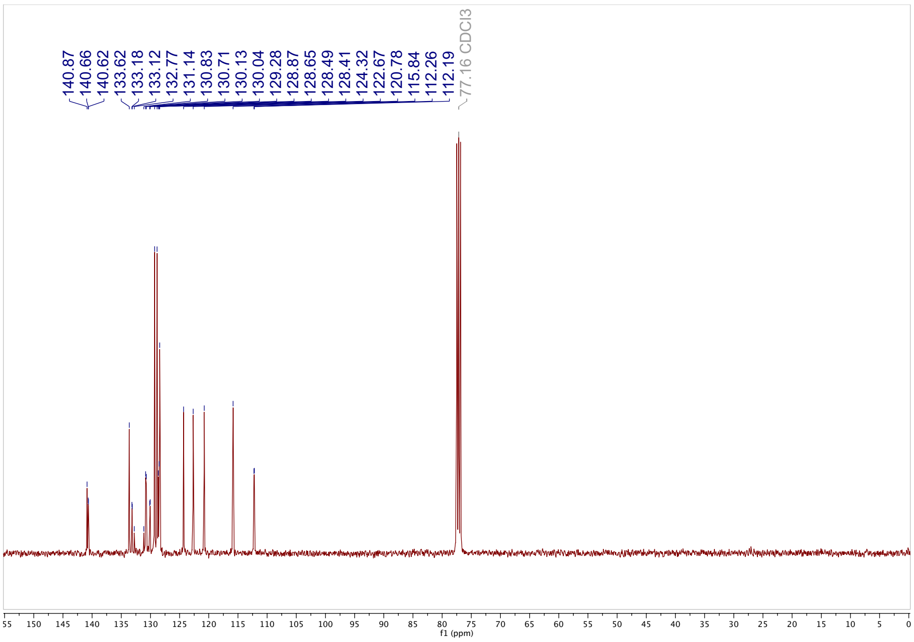


Figure S52. ^{13}C {H} NMR ($CDCl_3$, 101 MHz, 298 K) of **4aO**.

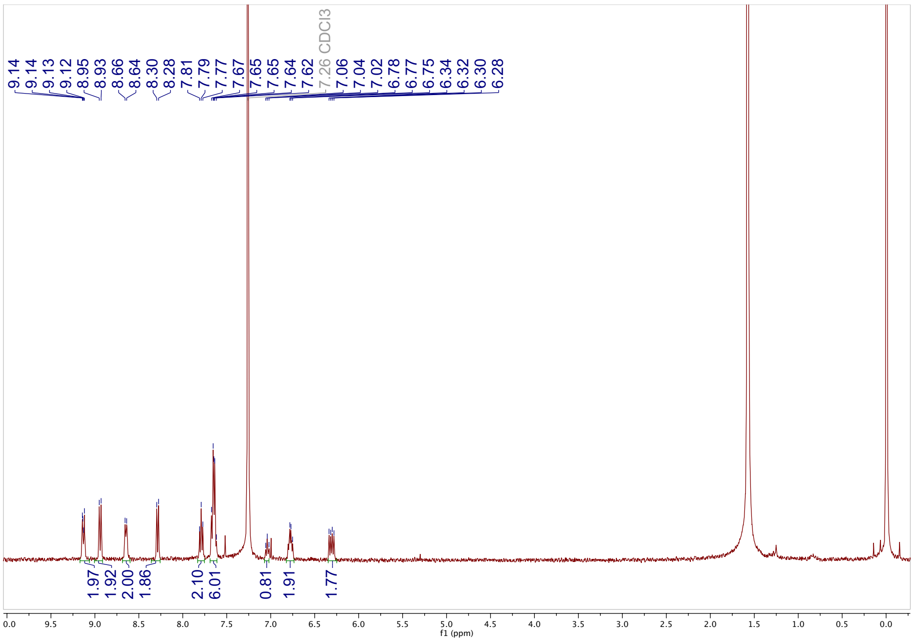


Figure S53. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **PN1O**.

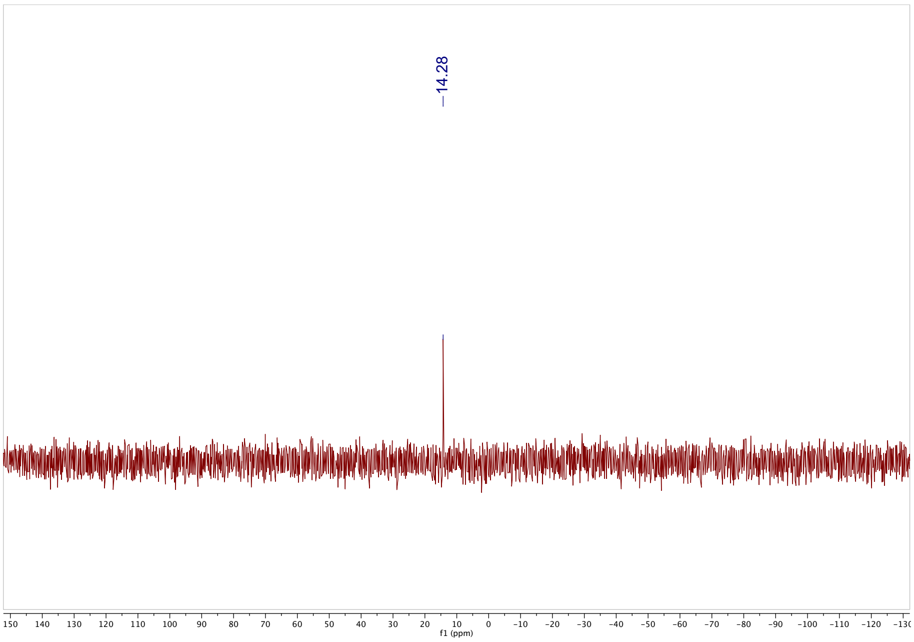


Figure S54. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **PN1O**.

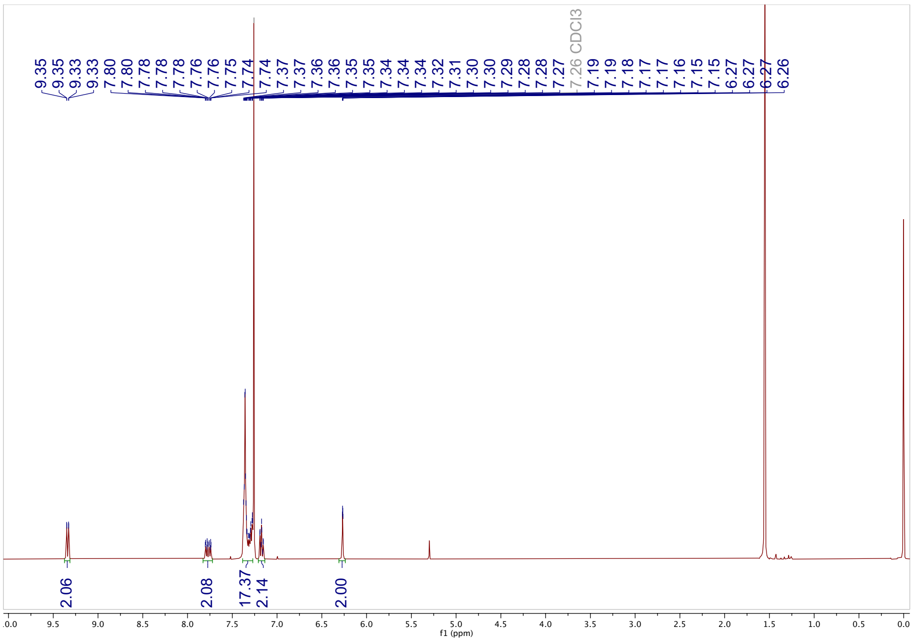


Figure S55. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **4aS**.

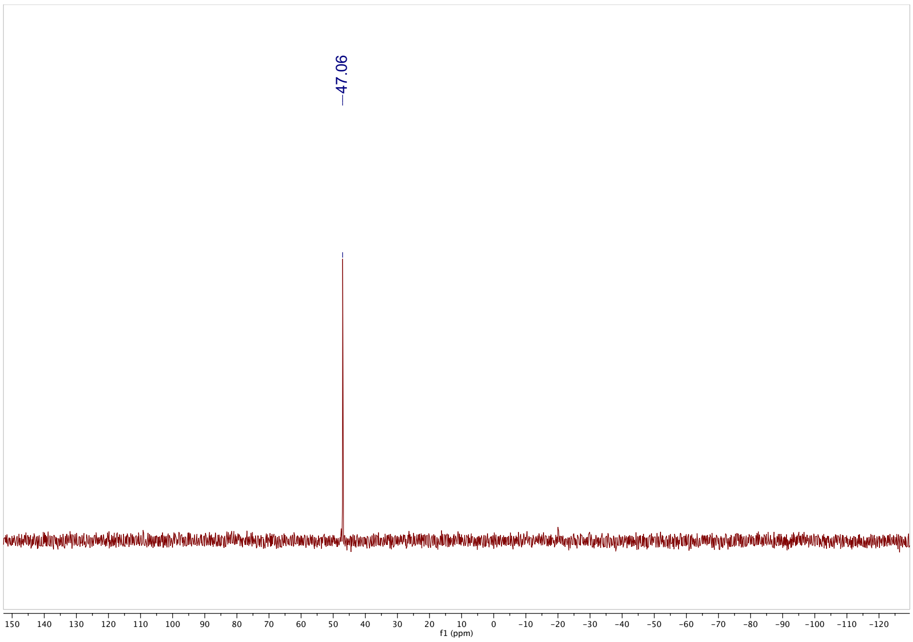


Figure S56. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **4aS**.

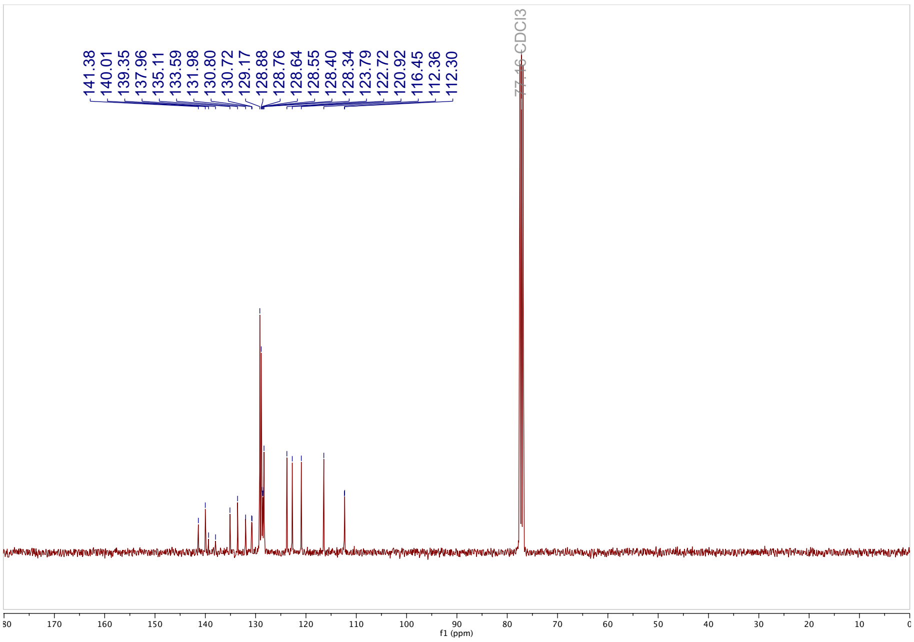


Figure S57. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **4aS**.

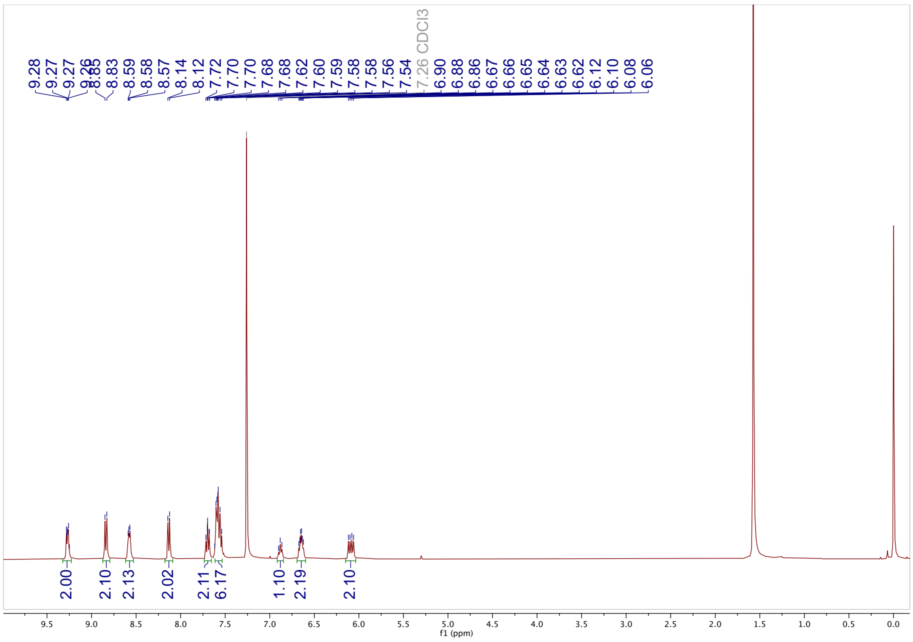


Figure S58. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **PN1S**.

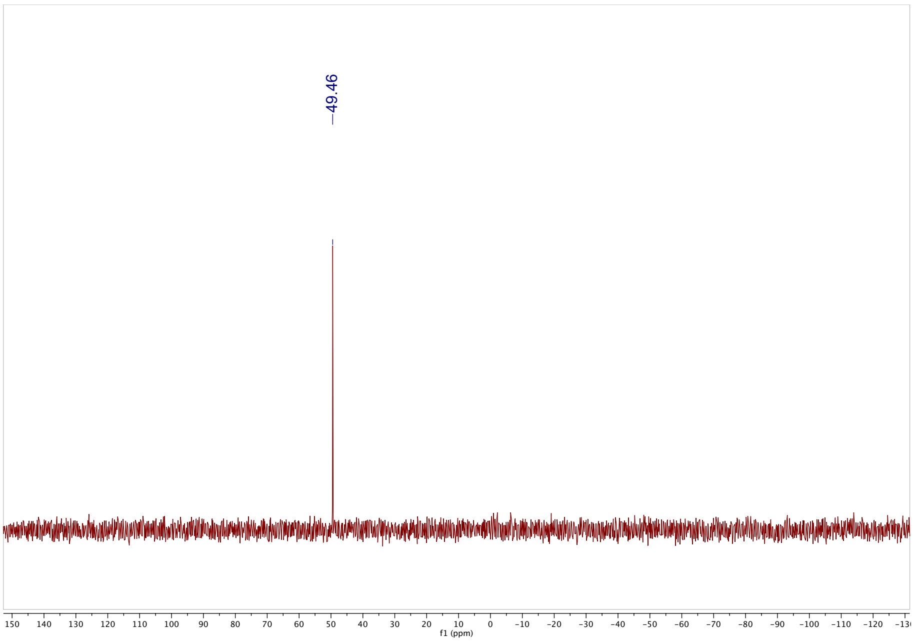


Figure S59. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **PN1S**.

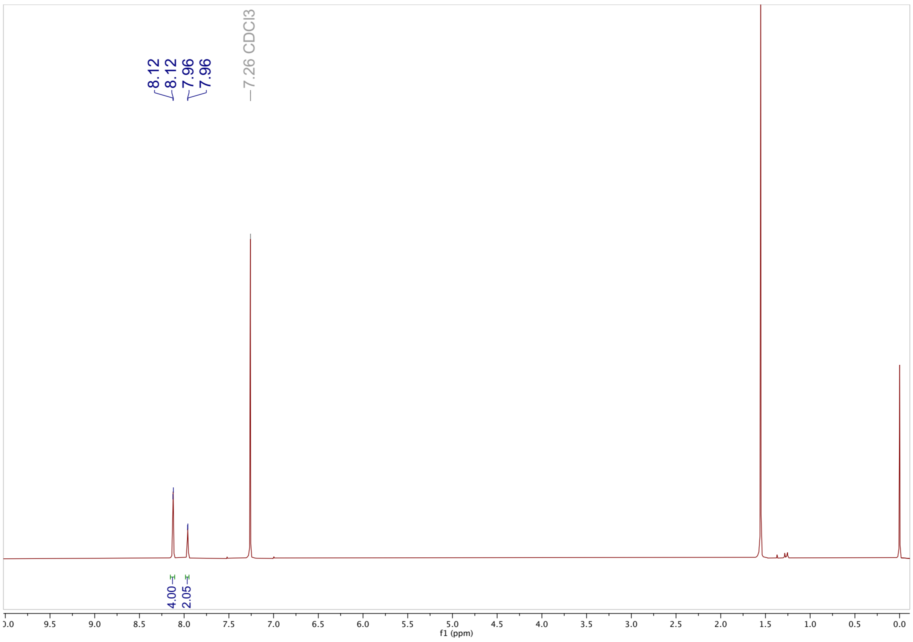


Figure S60. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **2b**.

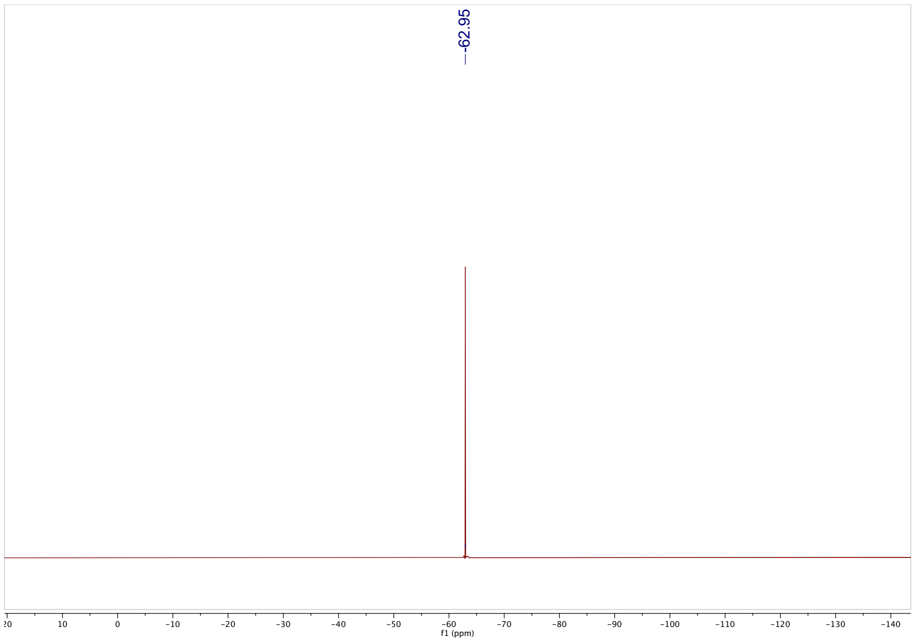


Figure S61. ^{19}F {H} NMR (CDCl$_3$, 376 MHz, 298 K) of **2b**.

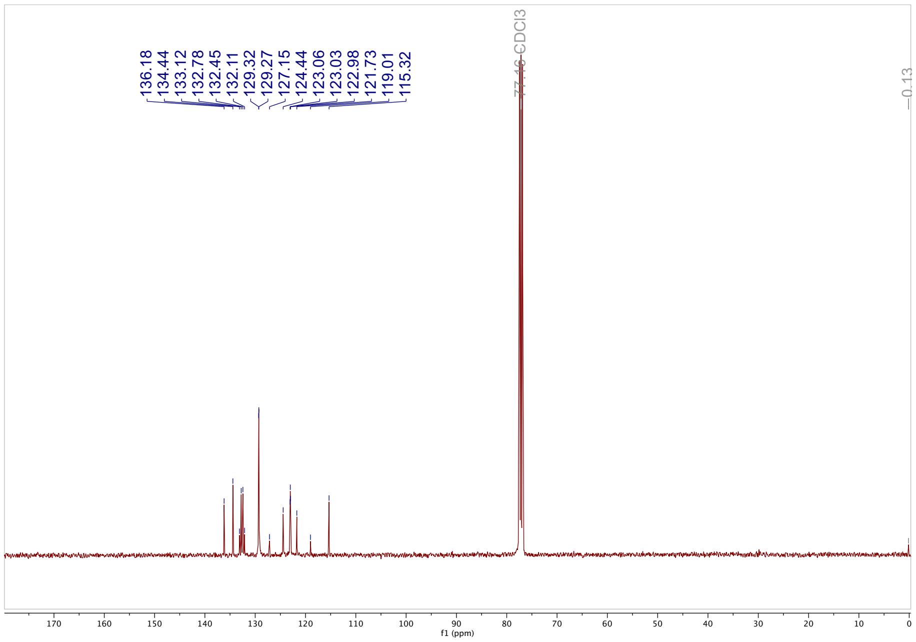


Figure S62. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **2b**.

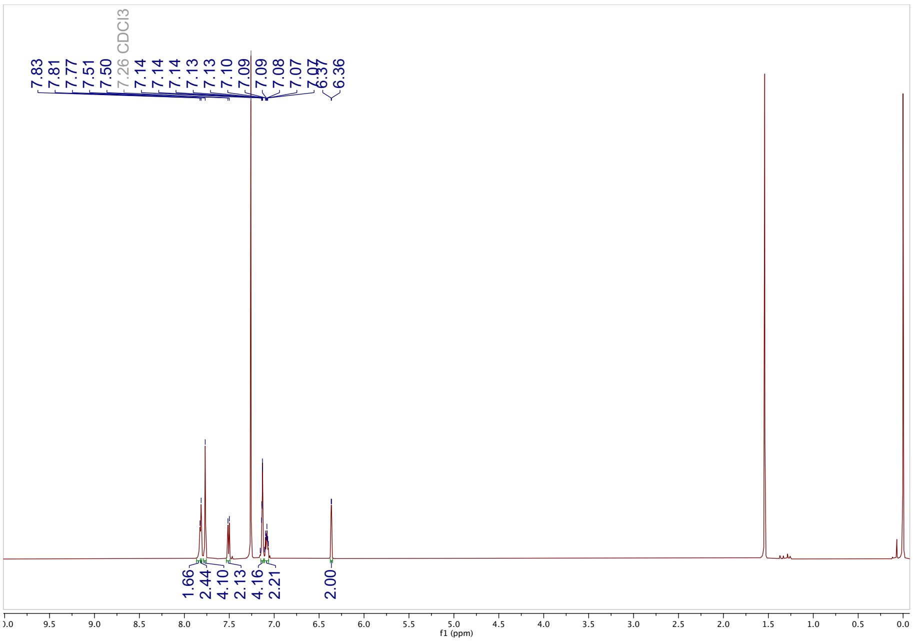


Figure S63. ^{1}H NMR (CDCl$_3$, 500 MHz, 298 K) of **3b**.

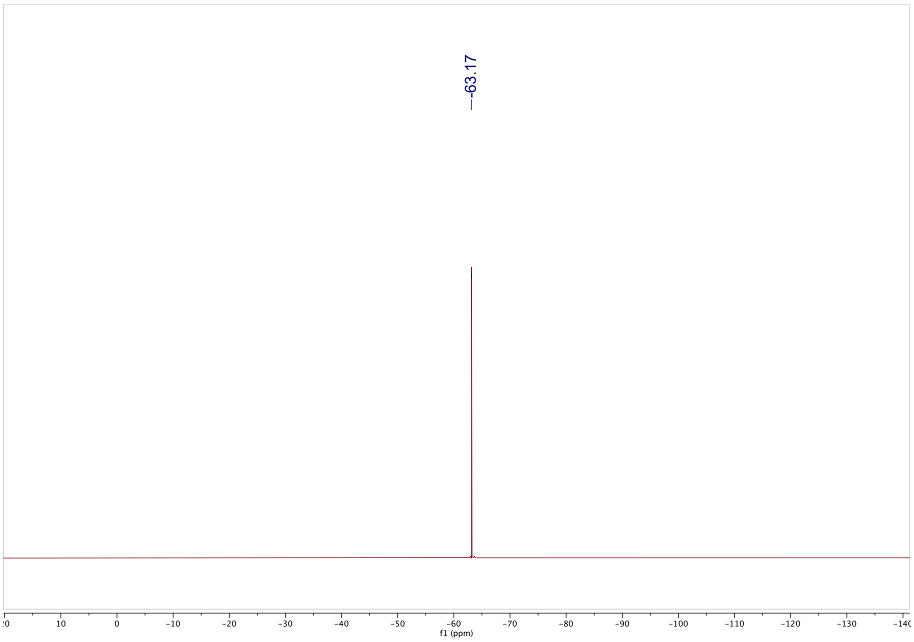


Figure S64. ^{19}F {H} NMR (CDCl$_3$, 376 MHz, 298 K) of **3b**.

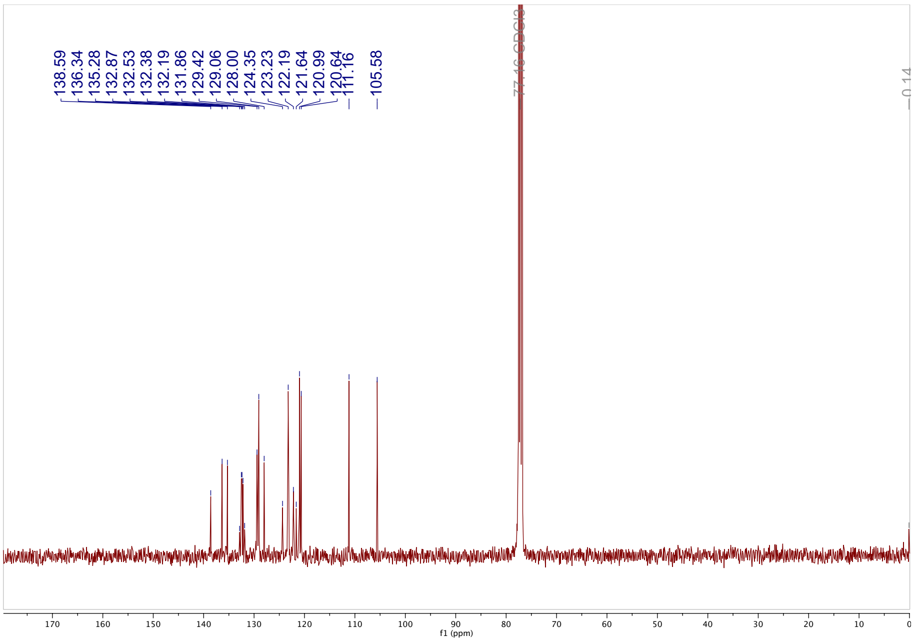


Figure S65. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **3b**.

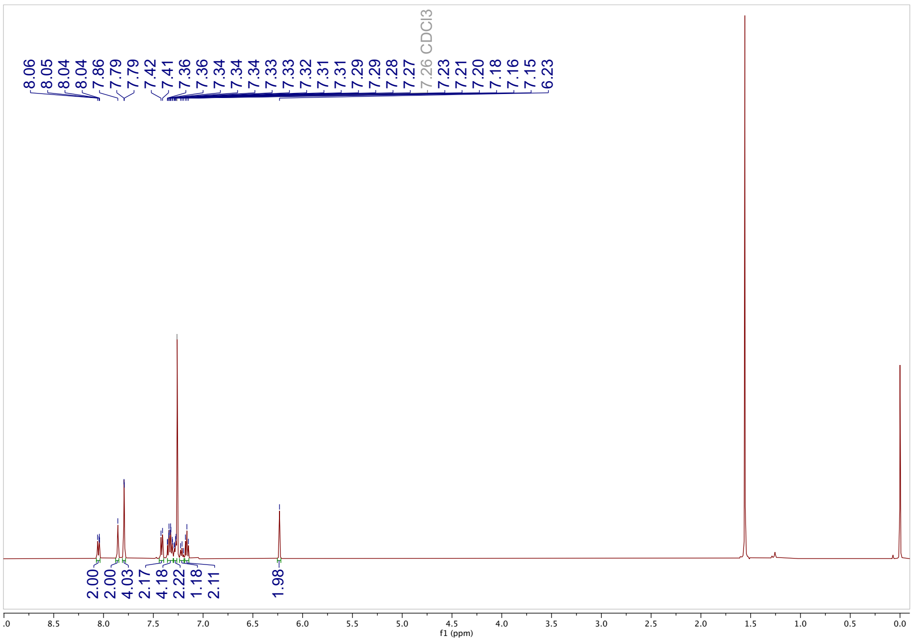


Figure S66. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **4b**.

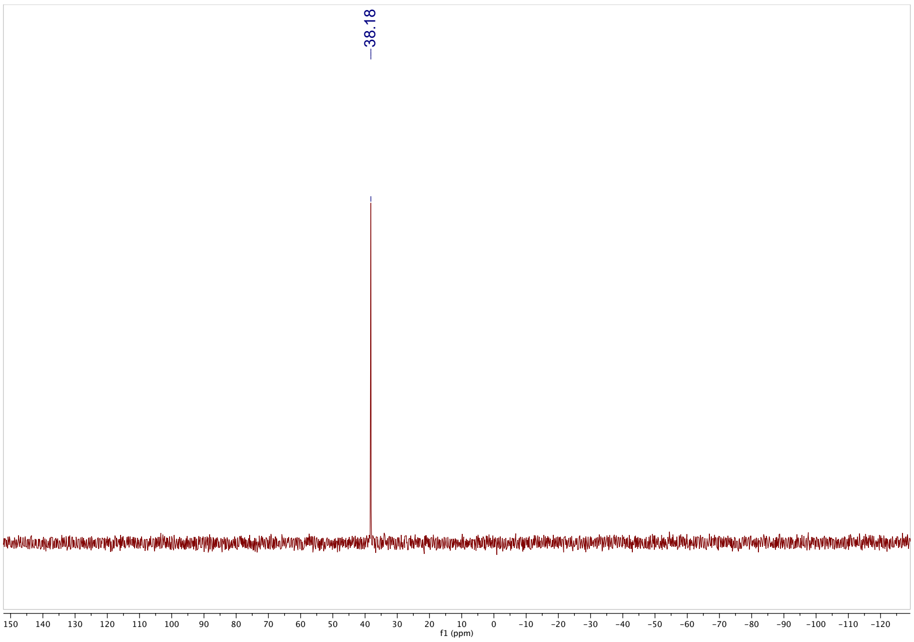


Figure S67. ^{31}P {H} NMR ($CDCl_3$, 162 MHz, 298 K) of **4b**.

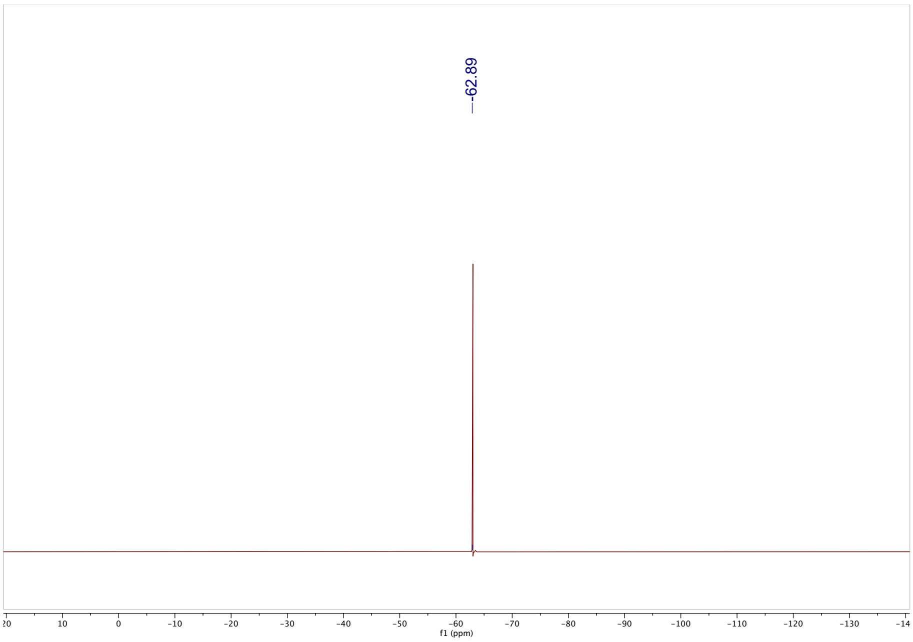


Figure S68. ^{19}F {H} NMR ($CDCl_3$, 376 MHz, 298 K) of **4b**.

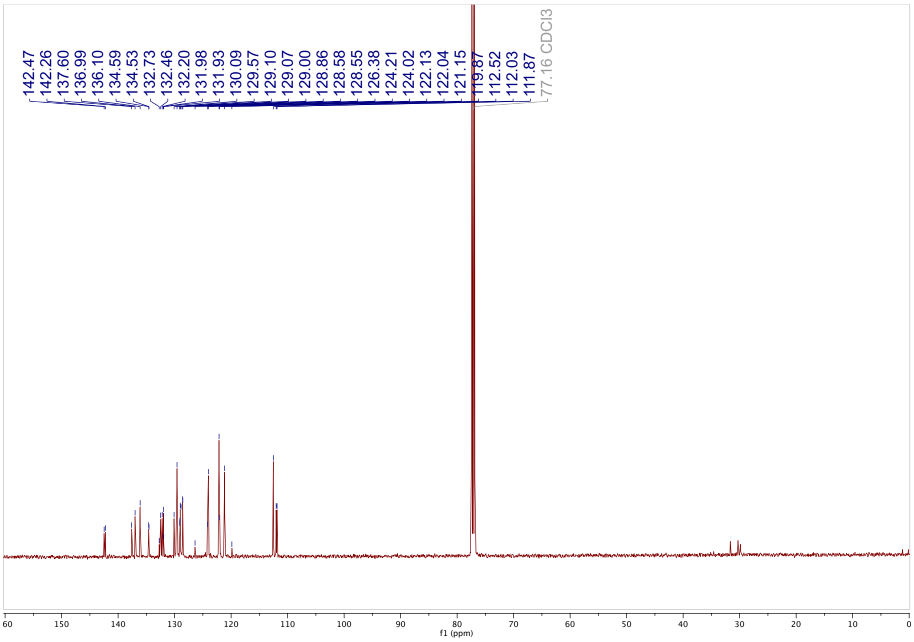


Figure S69. ^{13}C {H} NMR ($CDCl_3$, 126 MHz, 298 K) of **4b**.

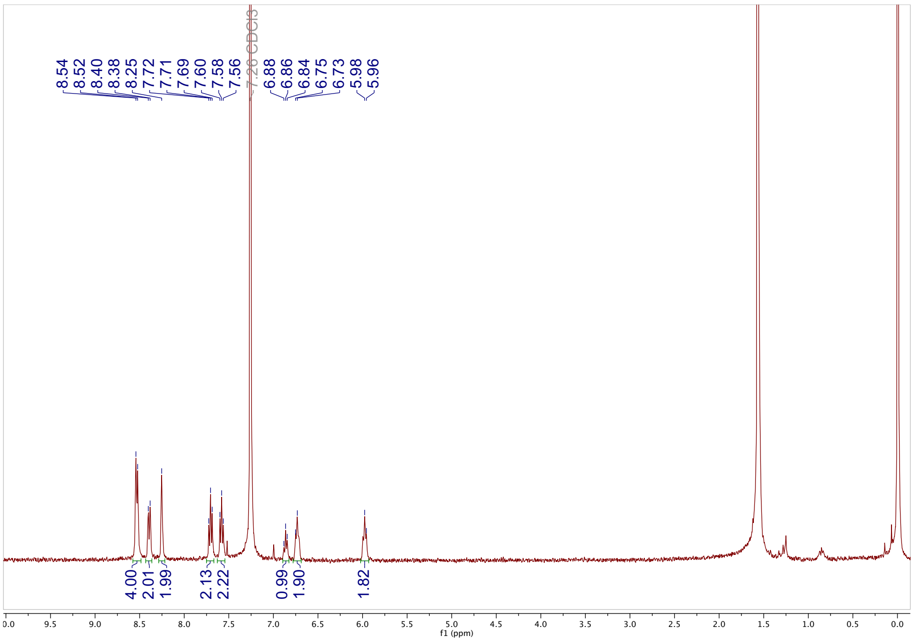


Figure S70. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) of **PN2**.

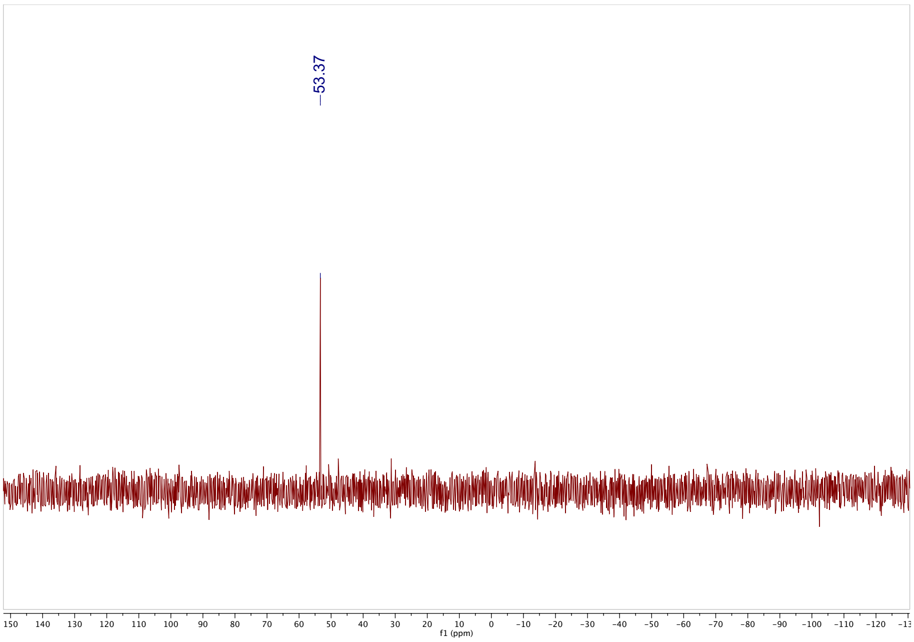


Figure S71. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **PN2**.

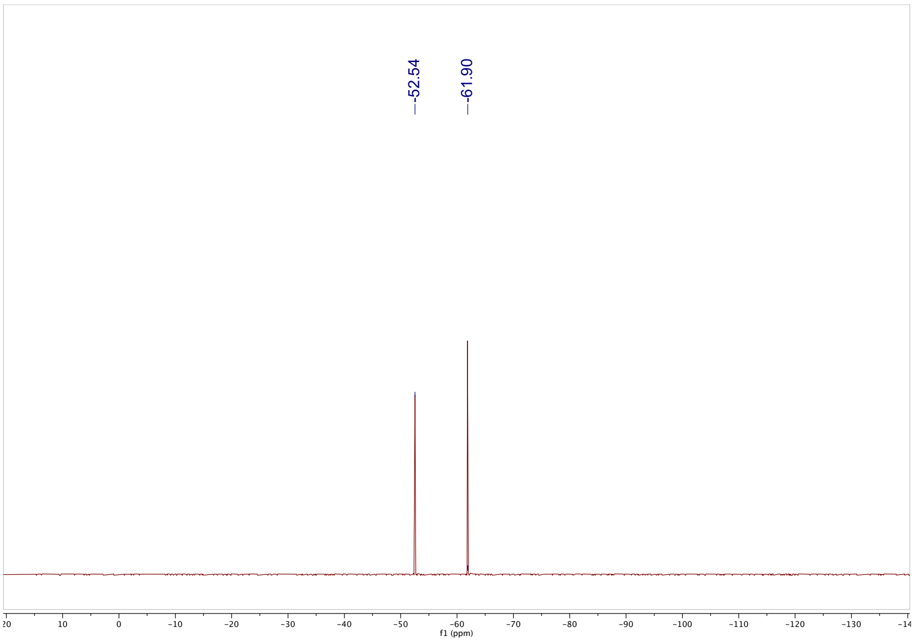


Figure S72. ^{19}F {H} NMR (CDCl$_3$, 376 MHz, 298 K) of **PN2**.

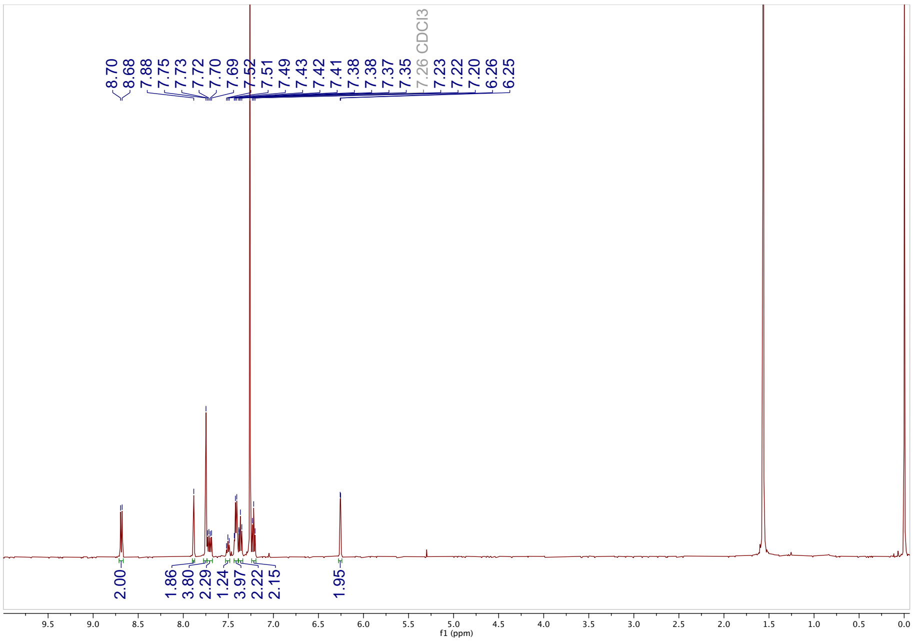


Figure S73. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) of **4bO**.

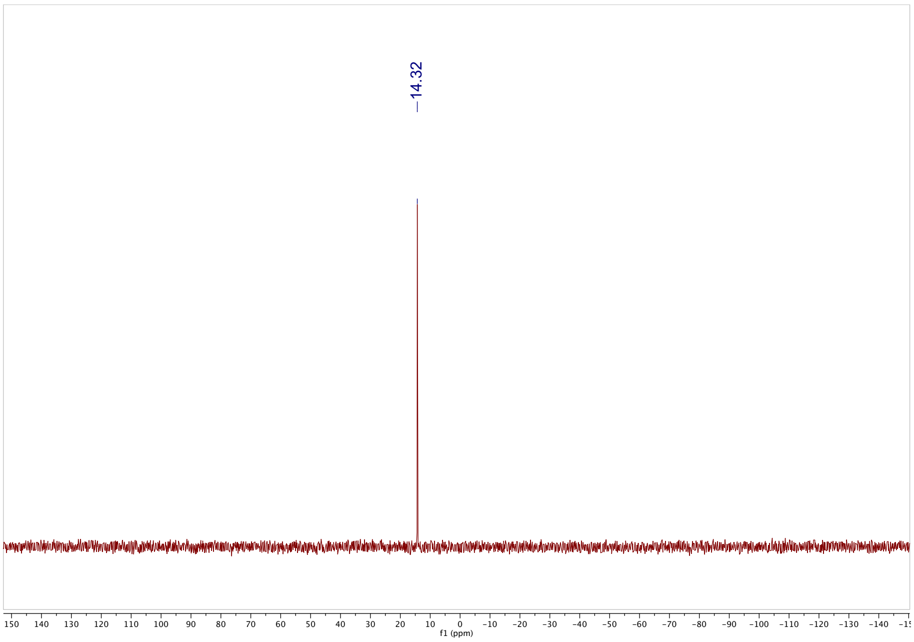


Figure S74. ^{31}P {H} NMR ($CDCl_3$, 162 MHz, 298 K) of **4bO**.

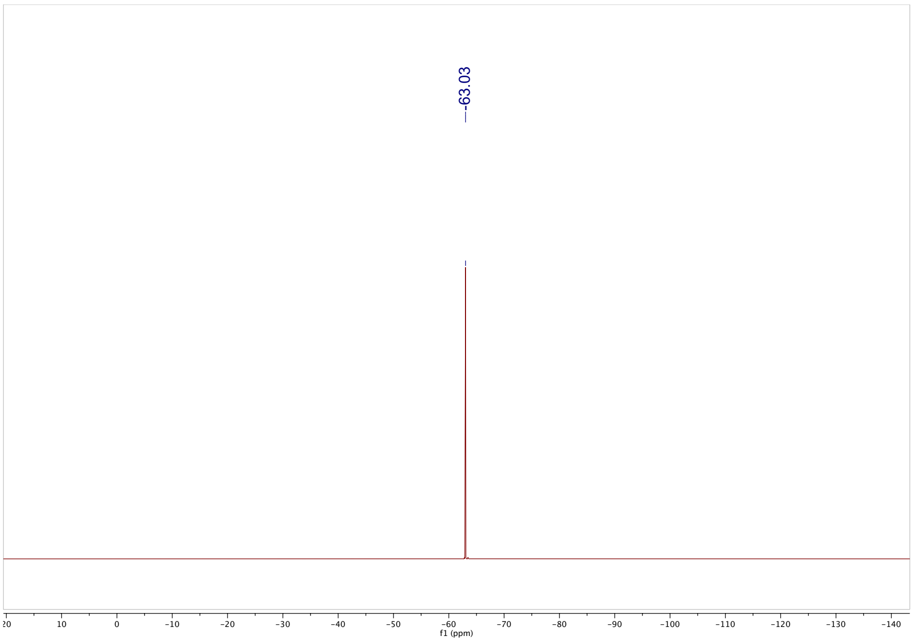


Figure S75. ^{19}F {H} NMR (CDCl$_3$, 376 MHz, 298 K) of **4bO**.

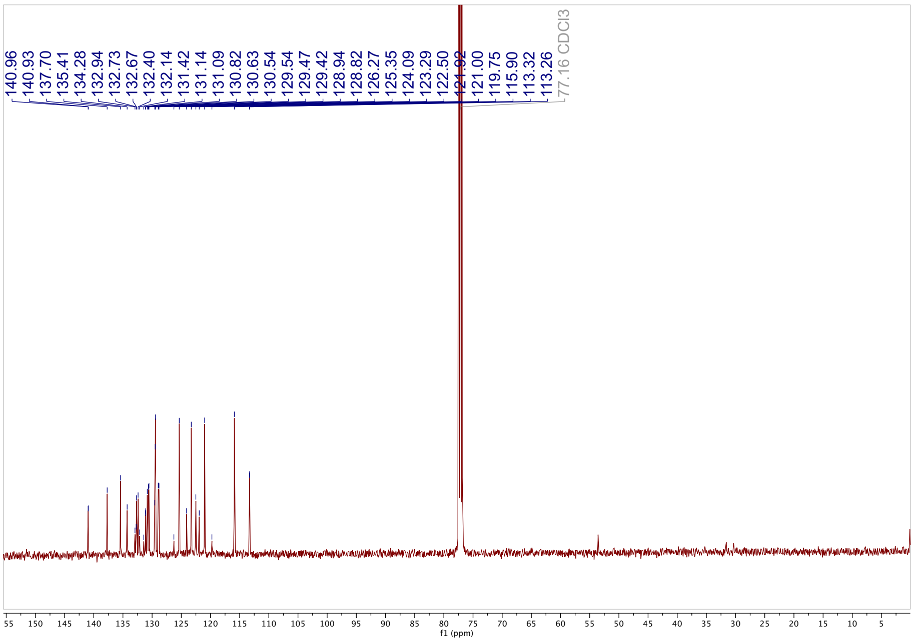


Figure S76. ^{13}C {H} NMR (CDCl$_3$, 126 MHz, 298 K) of **4bO**.

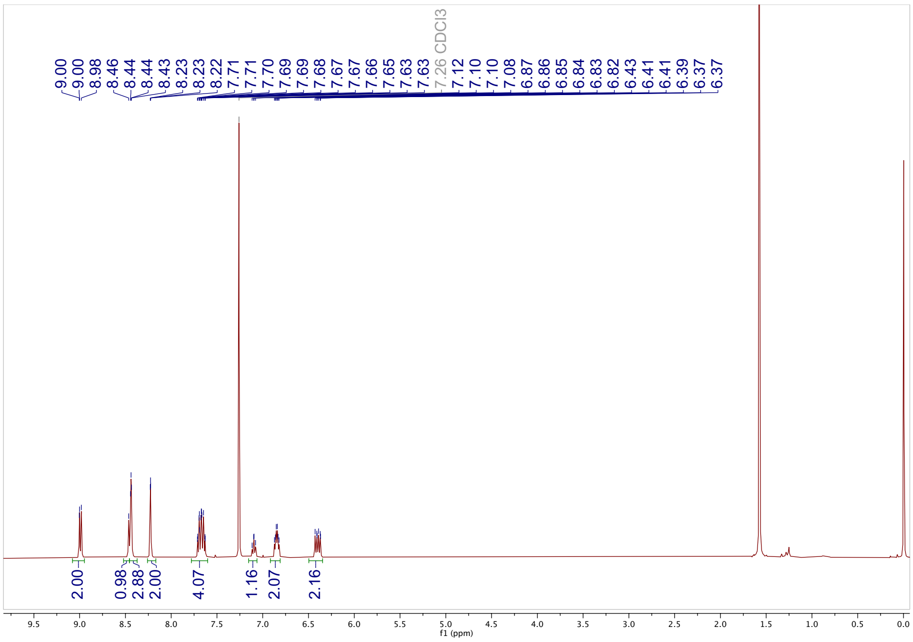


Figure S77. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) of **PN2O**.

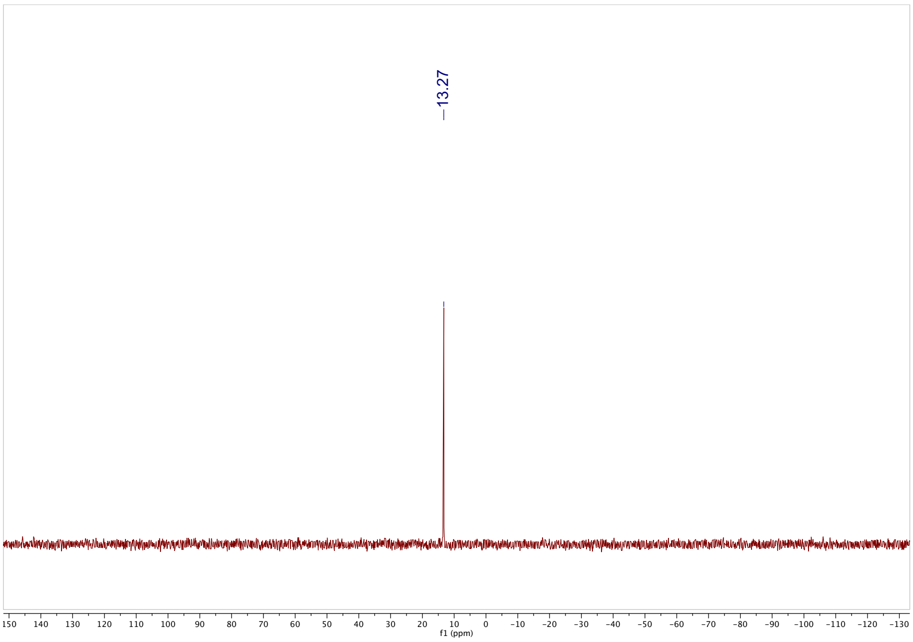


Figure S78. ^{31}P {H} NMR ($CDCl_3$, 162 MHz, 298 K) of **PN2O**.

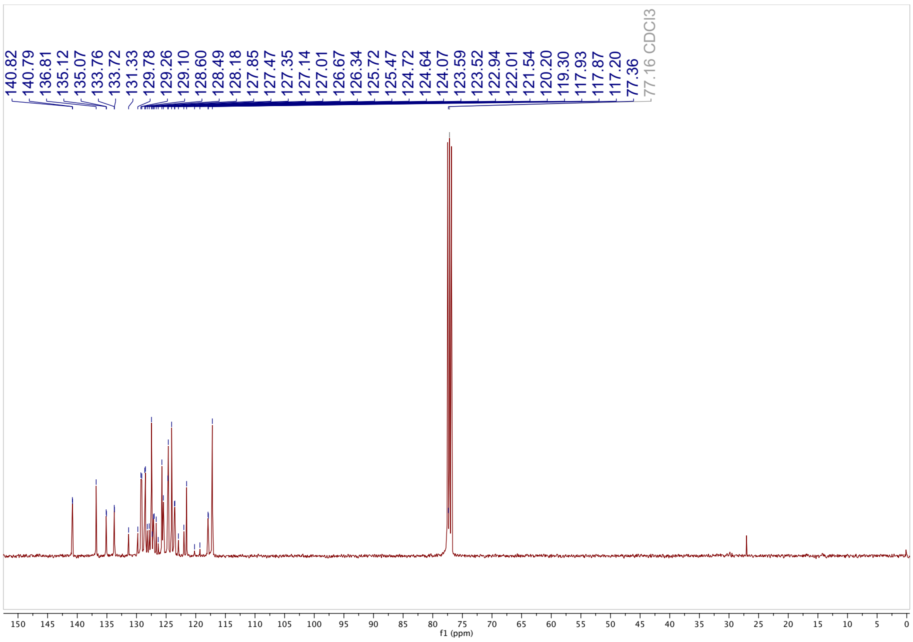


Figure S79. ^{13}C {H} NMR ($CDCl_3$, 101 MHz, 298 K) of **PN2O**.

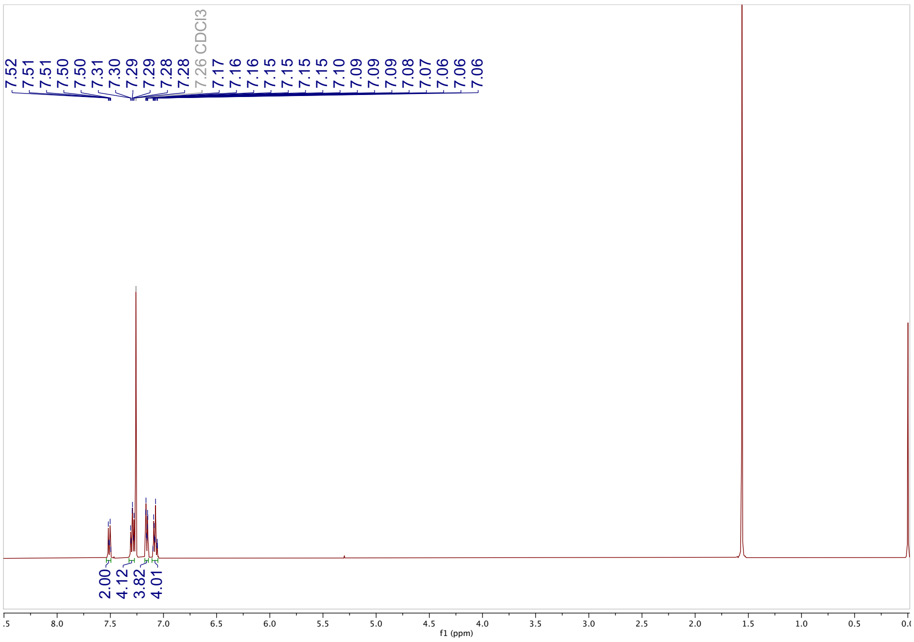


Figure S80. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) of **2c**.

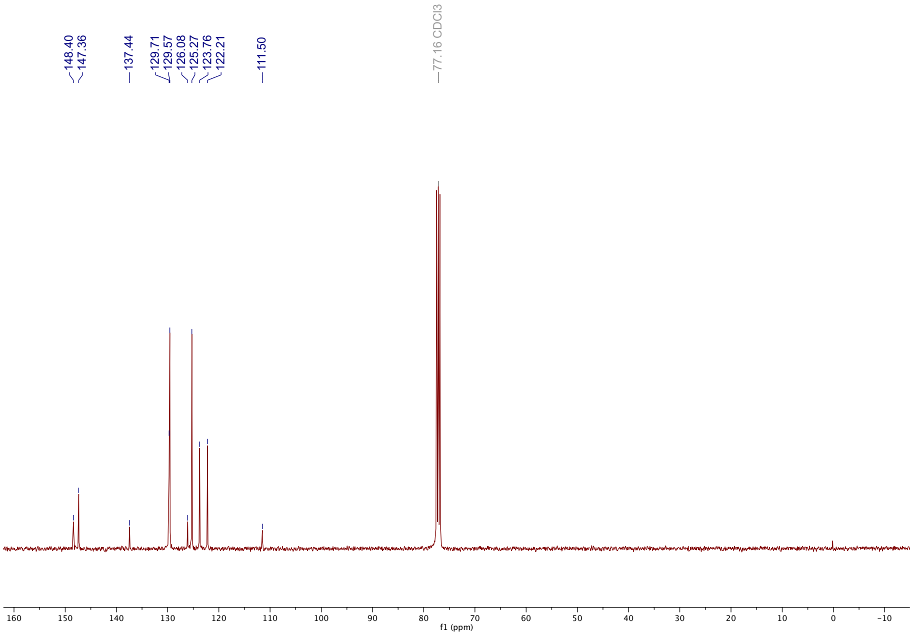


Figure S81. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **2c**.

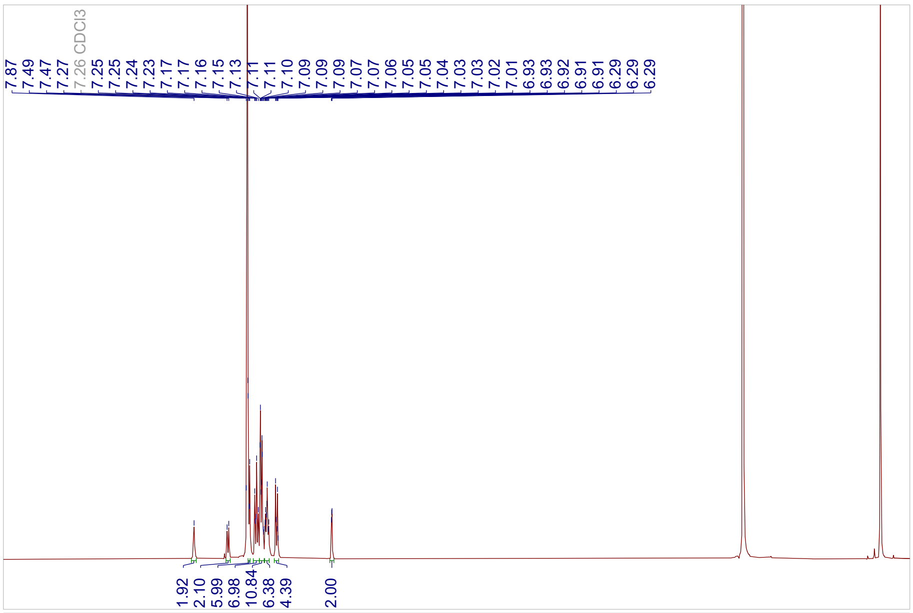


Figure S82. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **3c**.

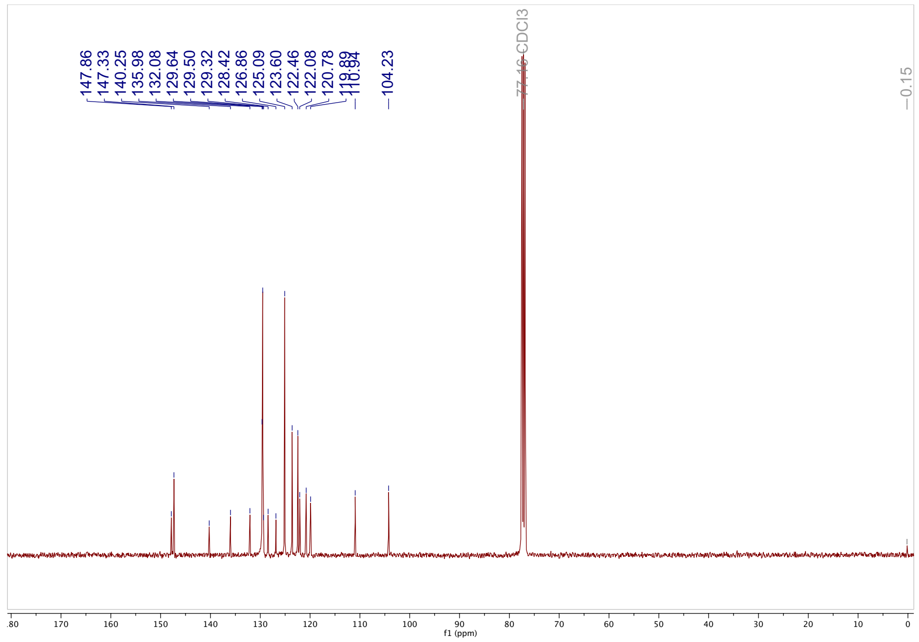


Figure S83. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **3c**.

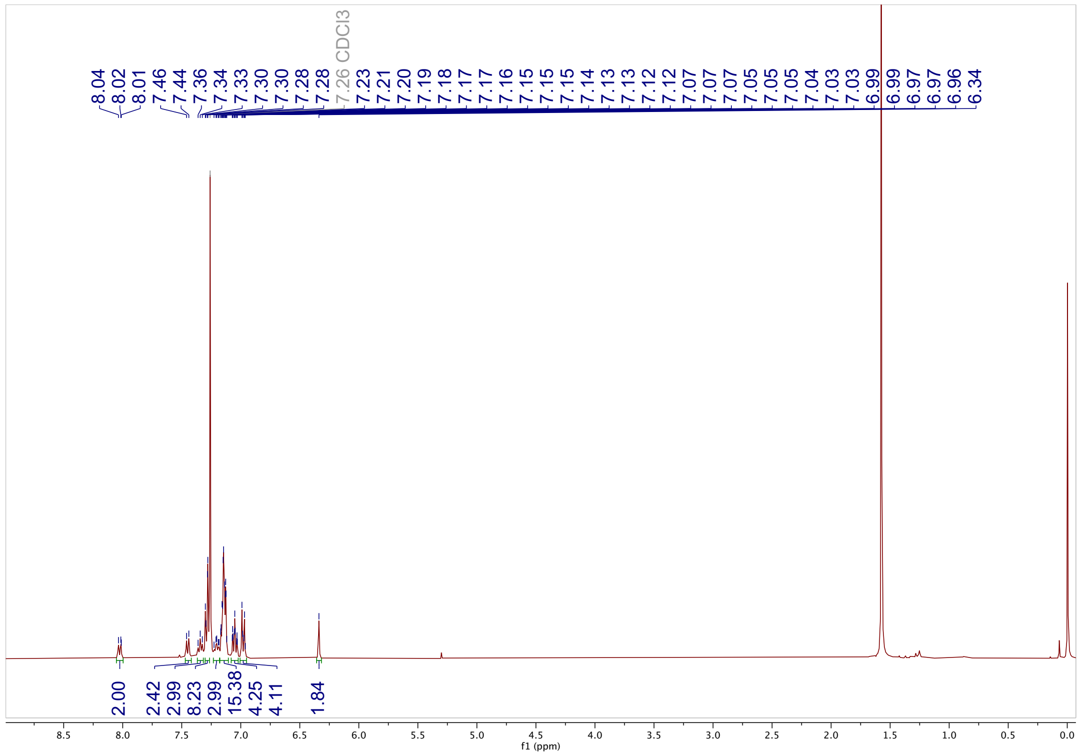


Figure S84. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **4c**.

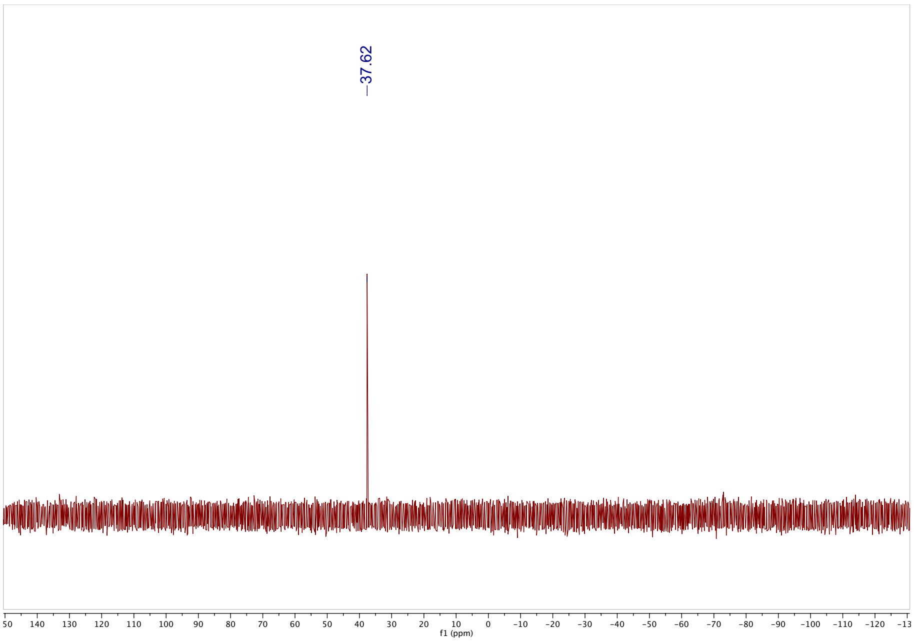


Figure S85. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **4c**.

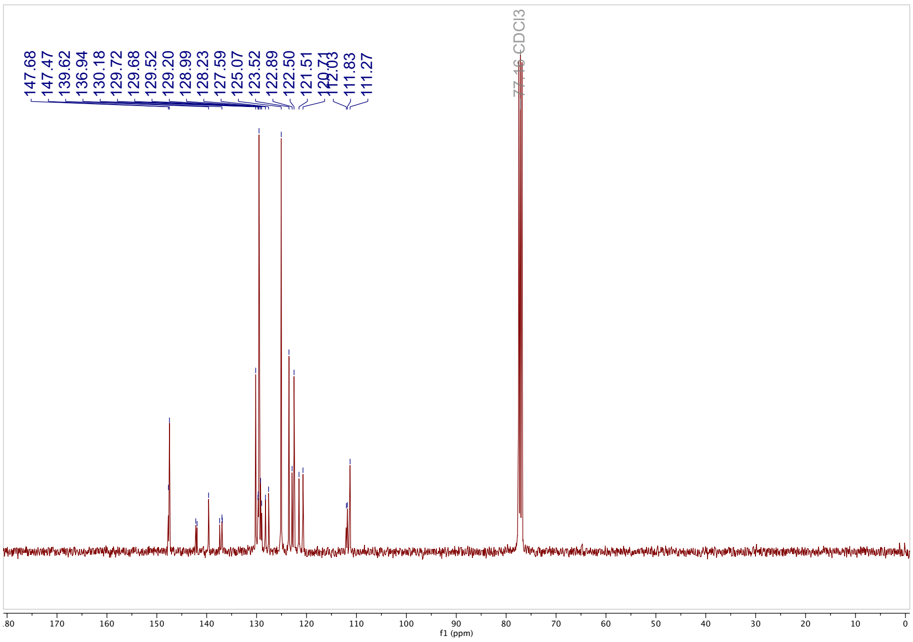


Figure S86. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **4c**.

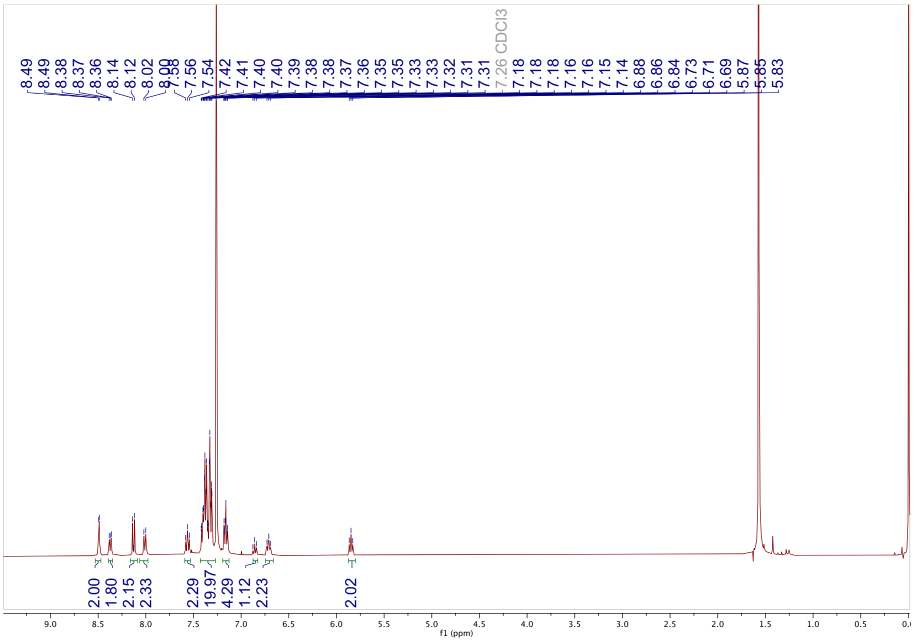


Figure S87. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) of **PN3**.

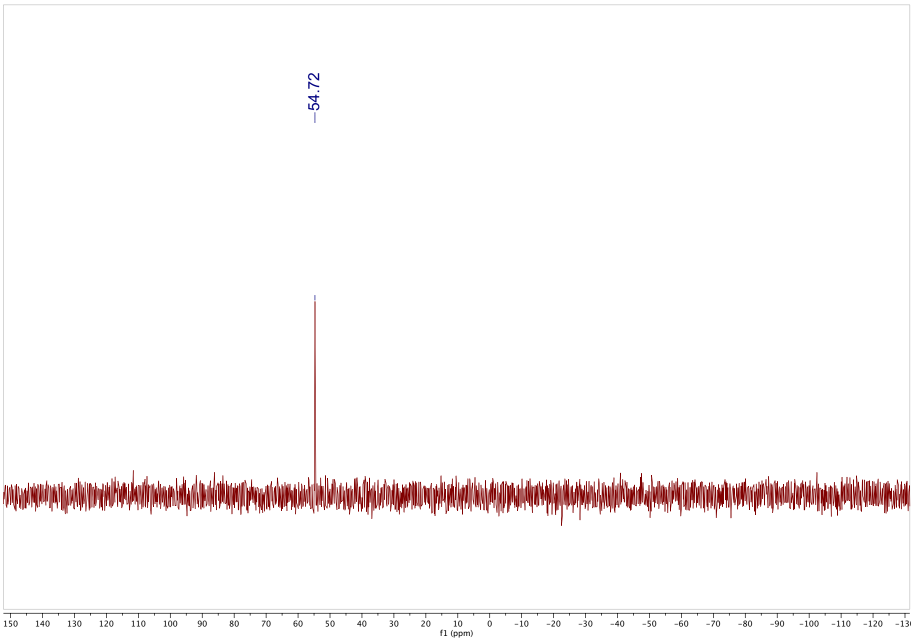


Figure S88. ^{31}P {H} NMR ($CDCl_3$, 162 MHz, 298 K) of **PN3**.

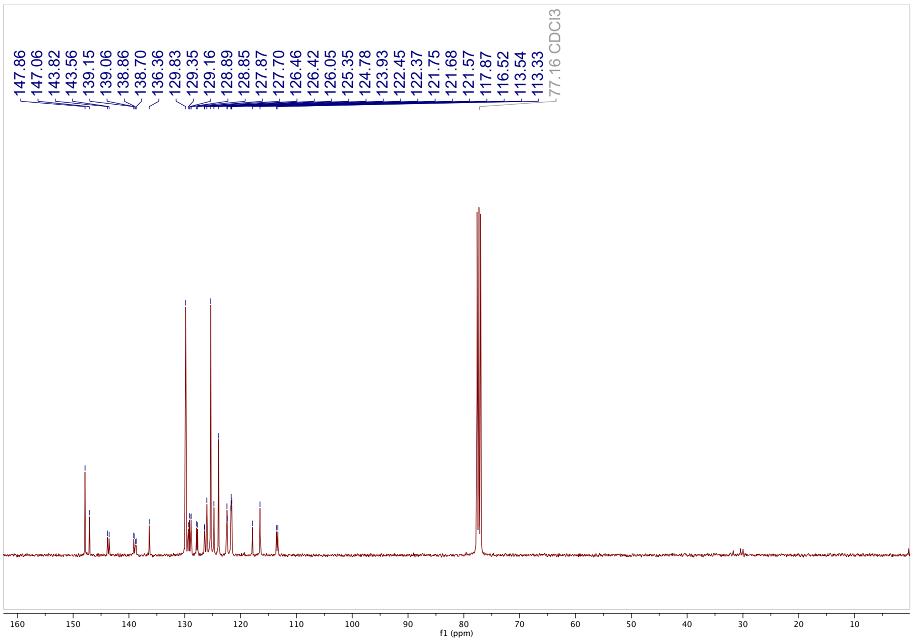


Figure S89. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **PN3**.

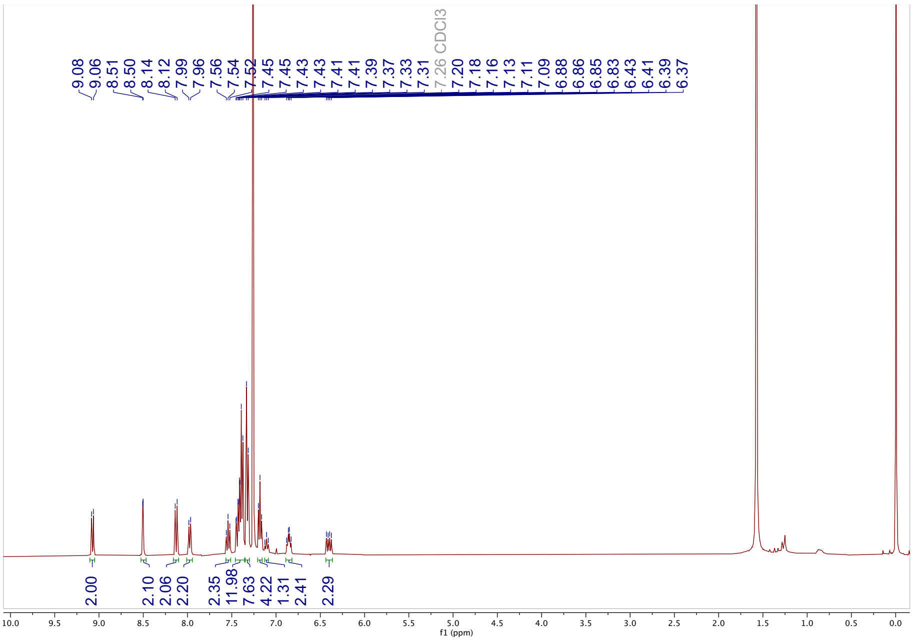


Figure S90. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **4cO**.

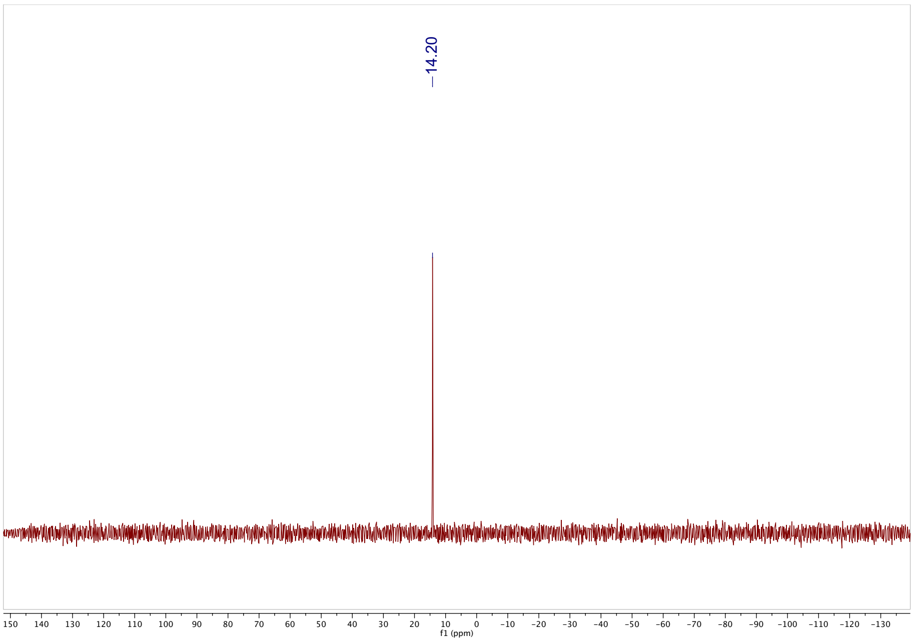


Figure S91. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **4cO**.

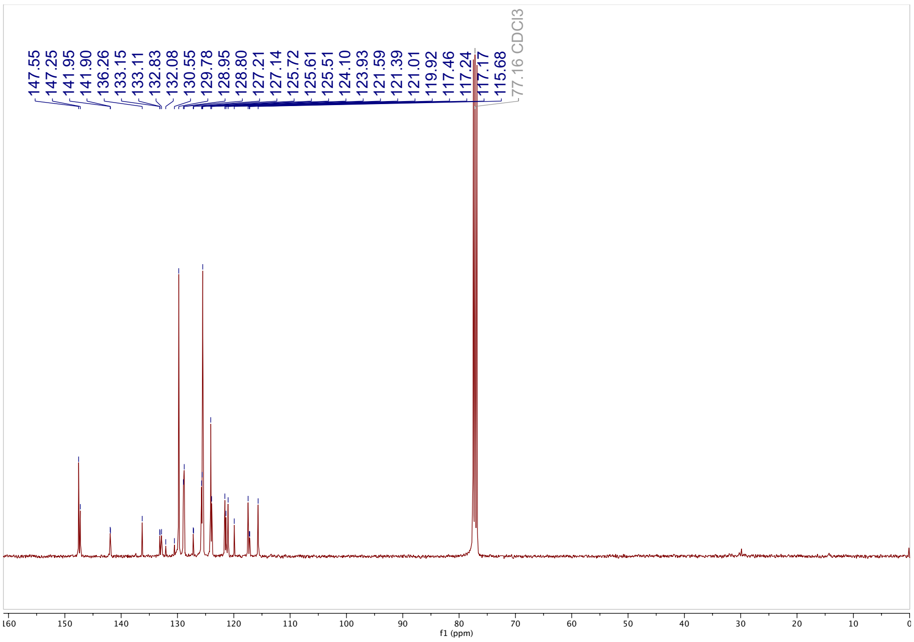


Figure S92. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **4cO**.

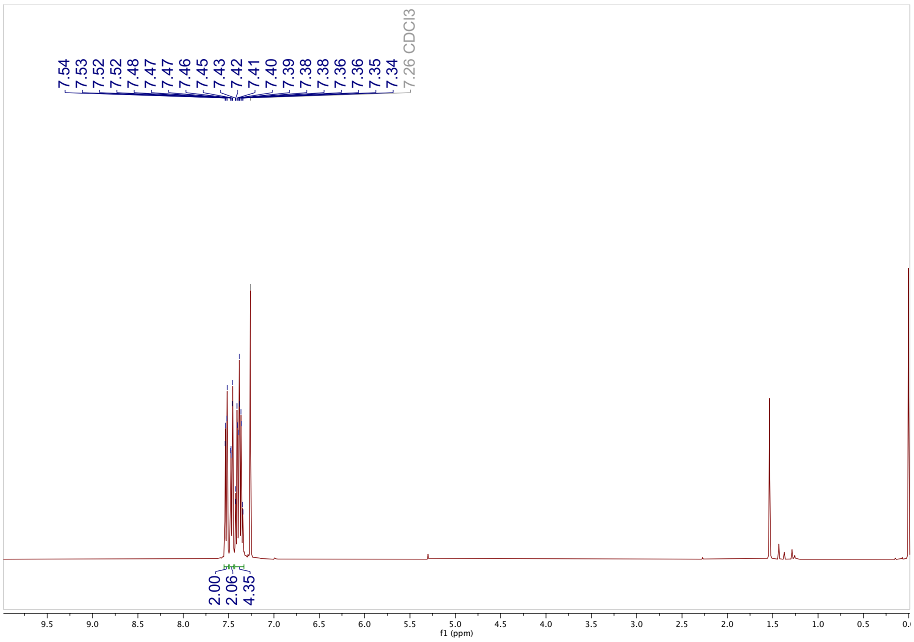


Figure S93. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **2d**.

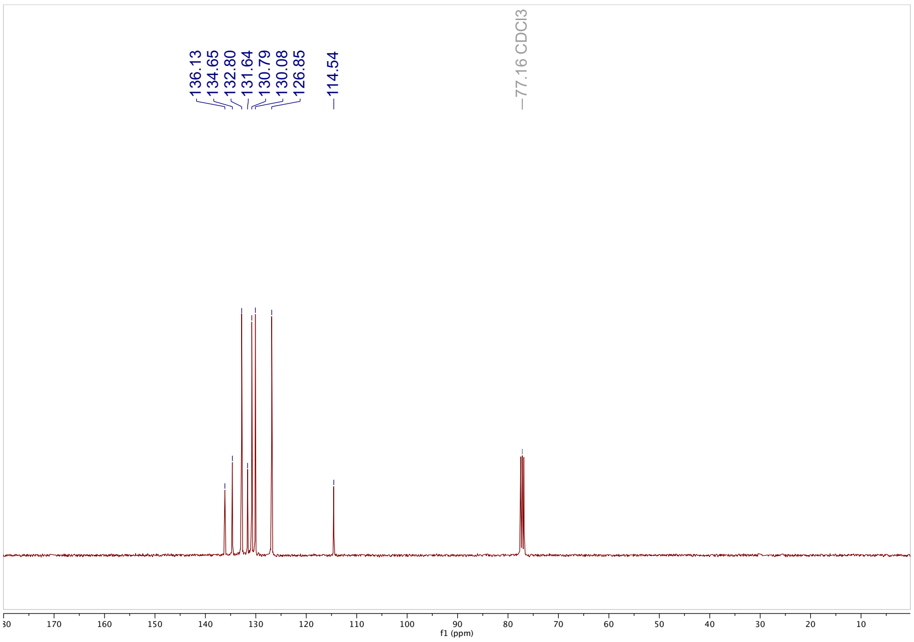


Figure S94. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **2d**.

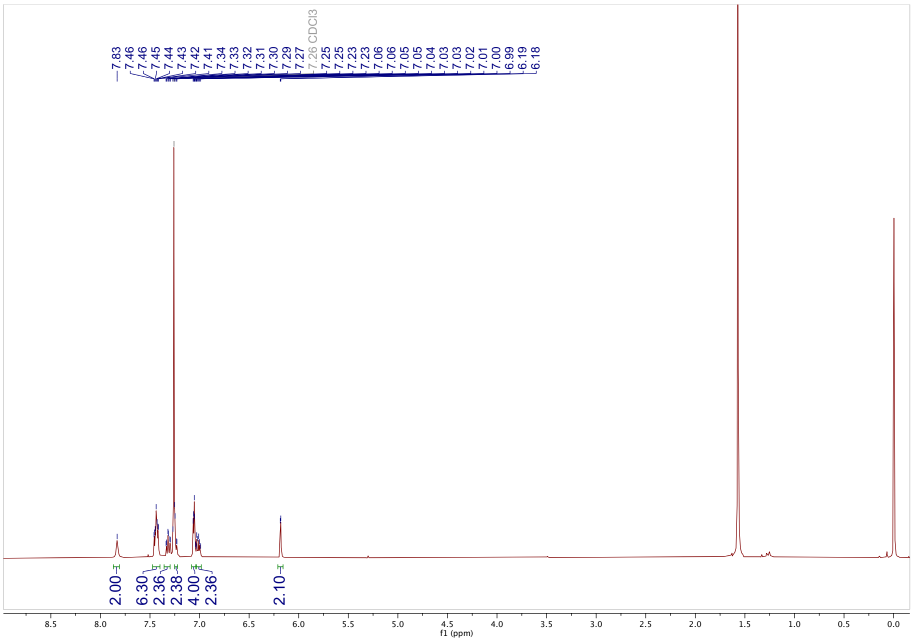


Figure S95. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **3d**.

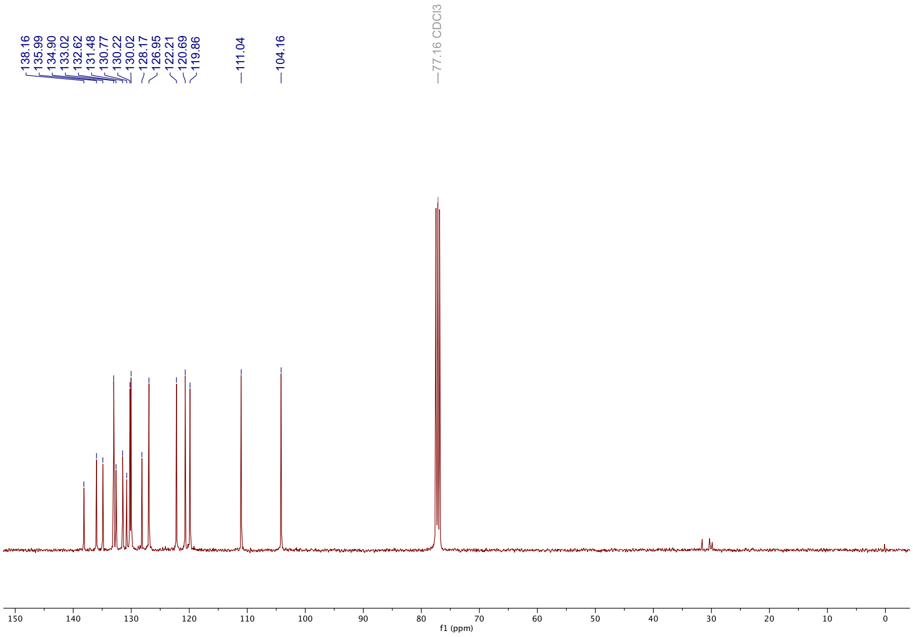


Figure S96. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **3d**.

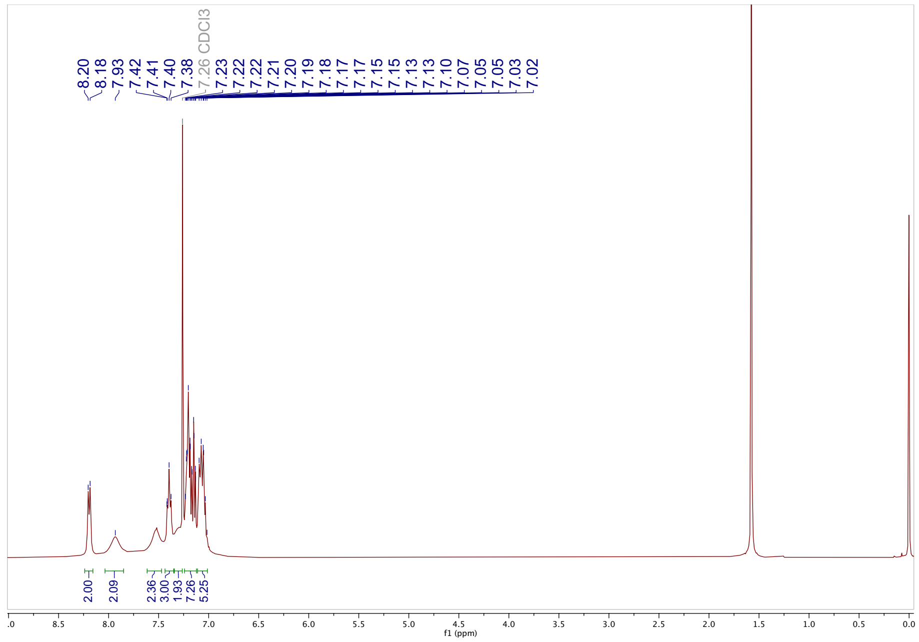


Figure S97. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **5d**.

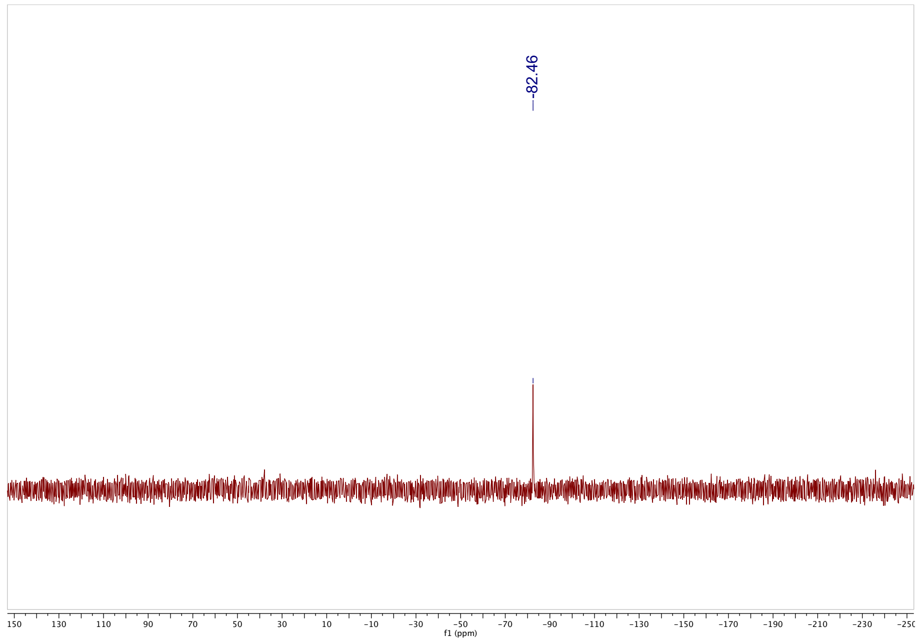


Figure S98. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **5d**.

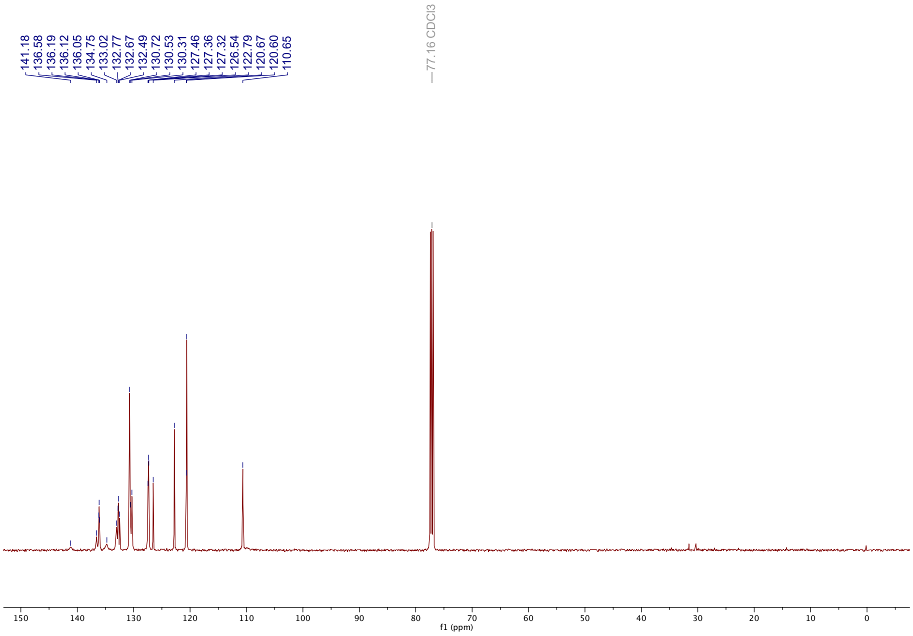


Figure S99. ^{13}C {H} NMR ($CDCl_3$, 126 MHz, 298 K) of **5d**.

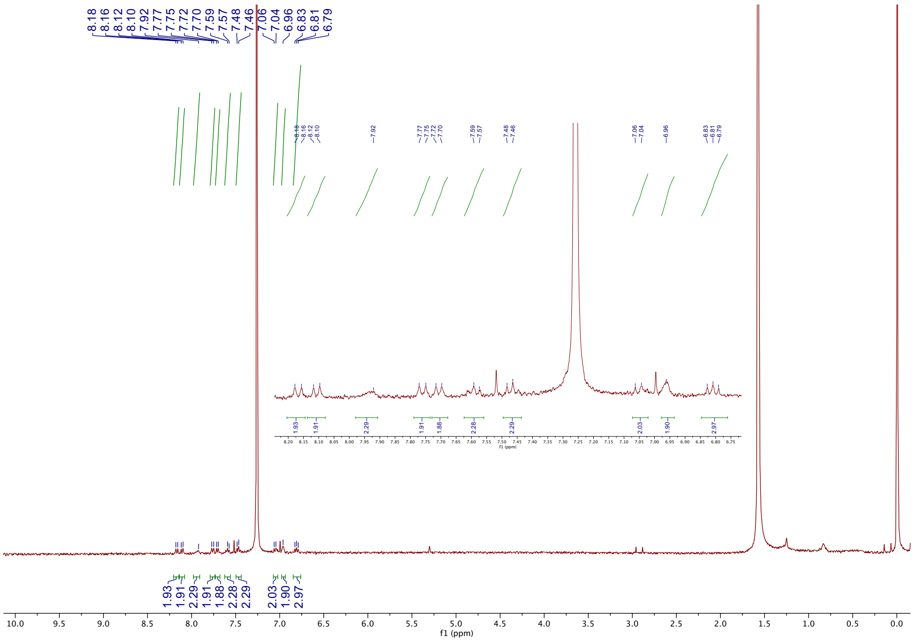


Figure S100. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) of **PC1**.

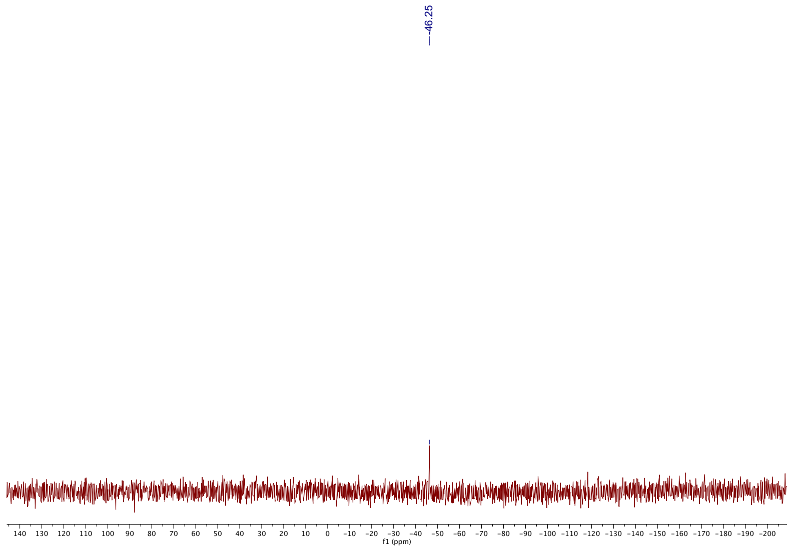


Figure S101. ^{31}P {H} NMR ($CDCl_3$, 162 MHz, 298 K) of **PC1**.

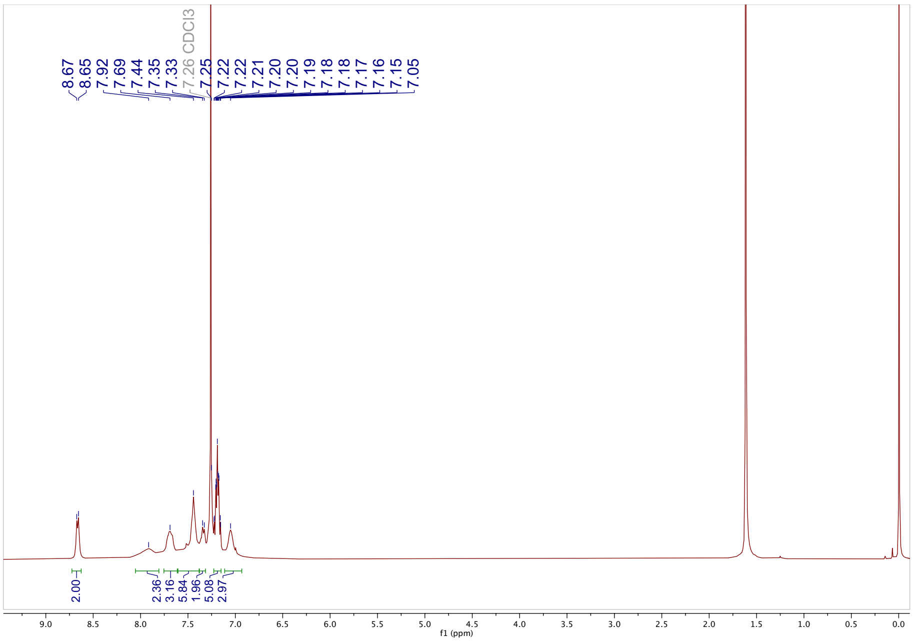


Figure S102. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) of **5dO**.

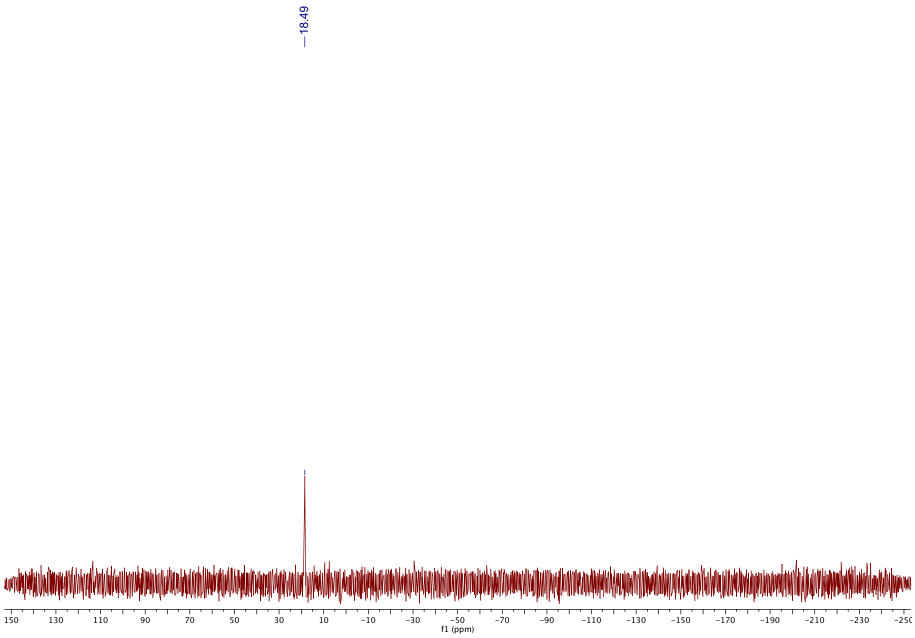


Figure S103. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **5dO**.

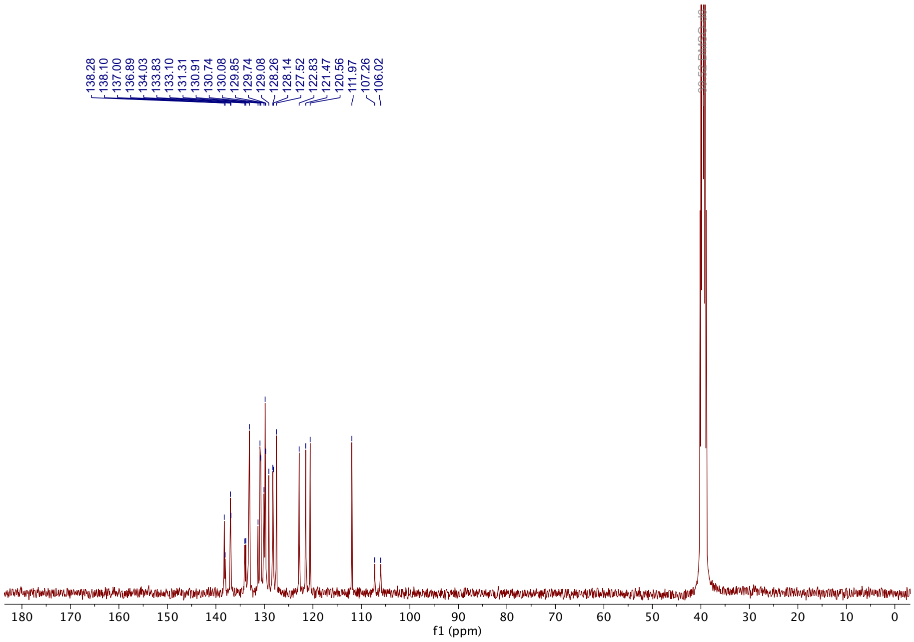


Figure S104. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **5dO**.

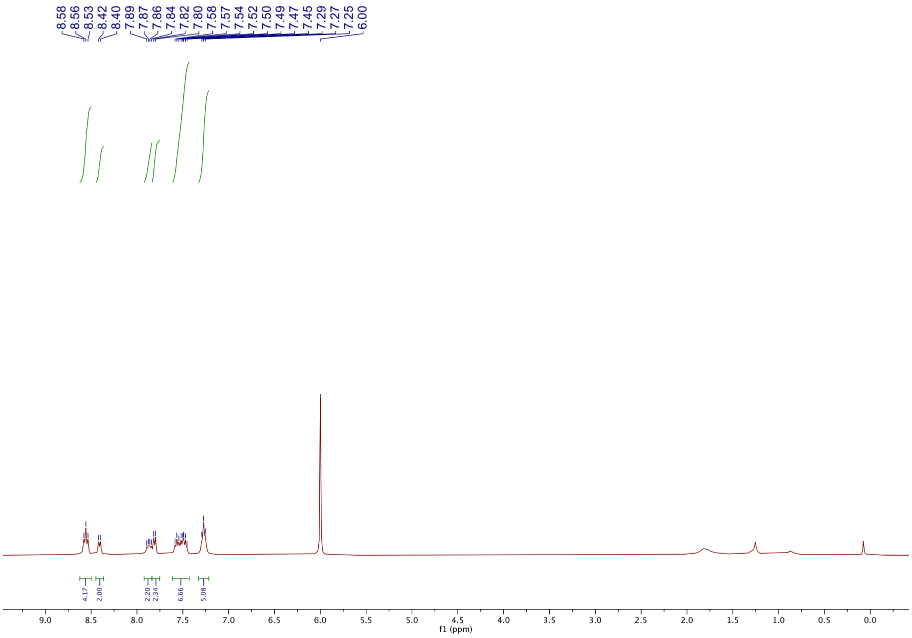


Figure S105. ^{1}H NMR ($C_2Cl_4D_2$, 500 MHz, 373 K) of **PC1O**.

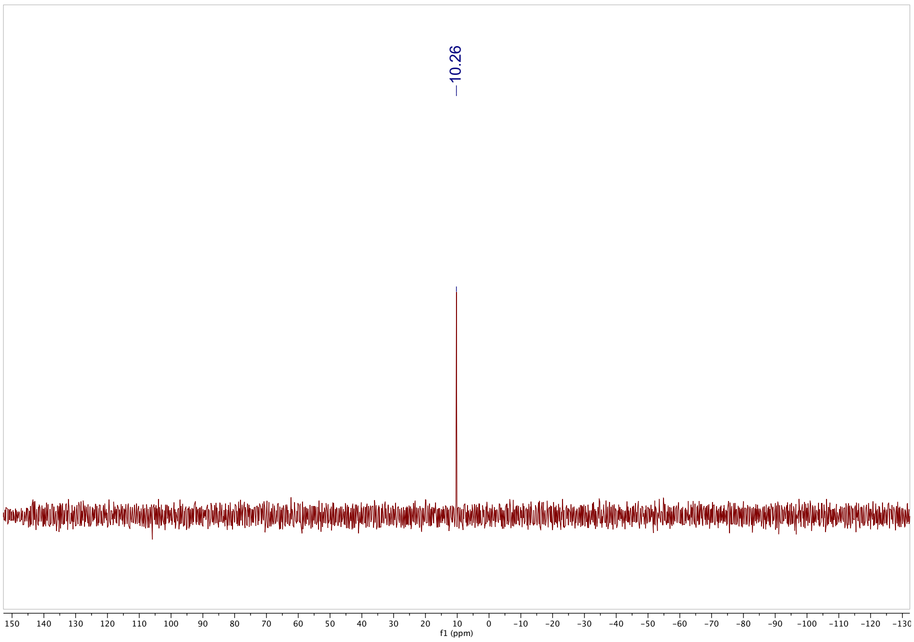


Figure S106. ^{31}P {H} NMR ($C_2Cl_4D_2$, 162 MHz, 373 K) of **PC1O**.

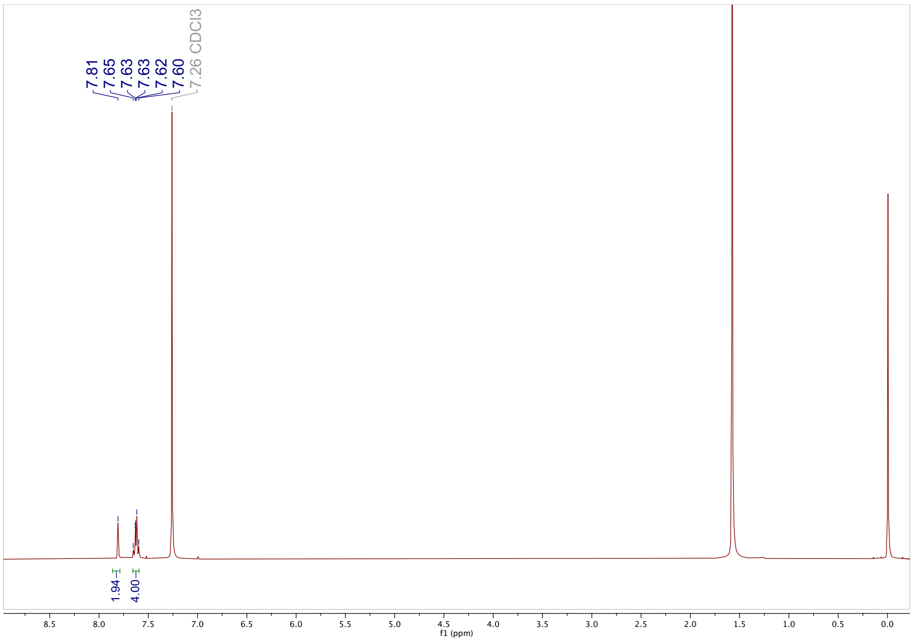


Figure S107. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **2e**.

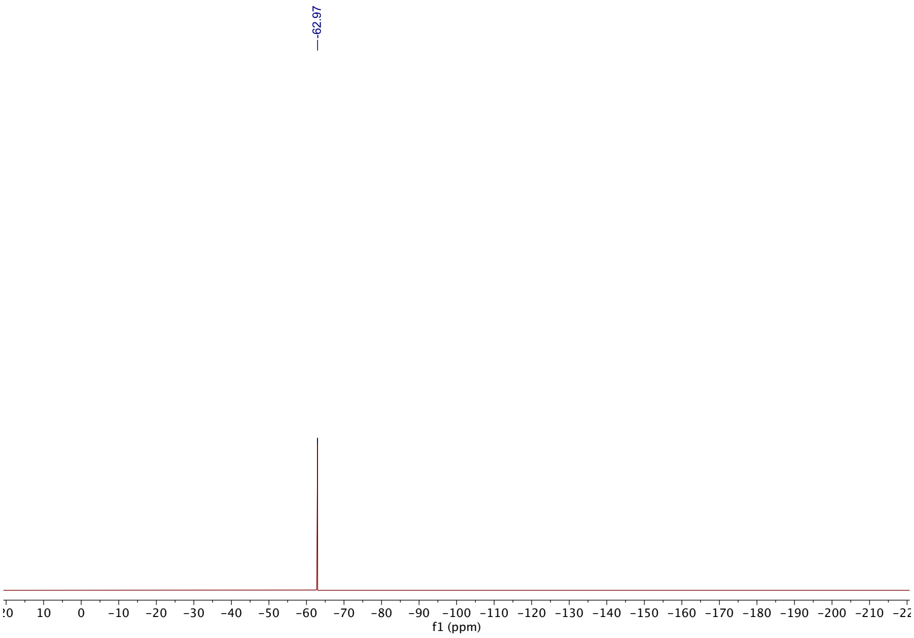


Figure S108. ^{19}F {H} NMR (CDCl$_3$, 376 MHz, 298 K) of **2e**.

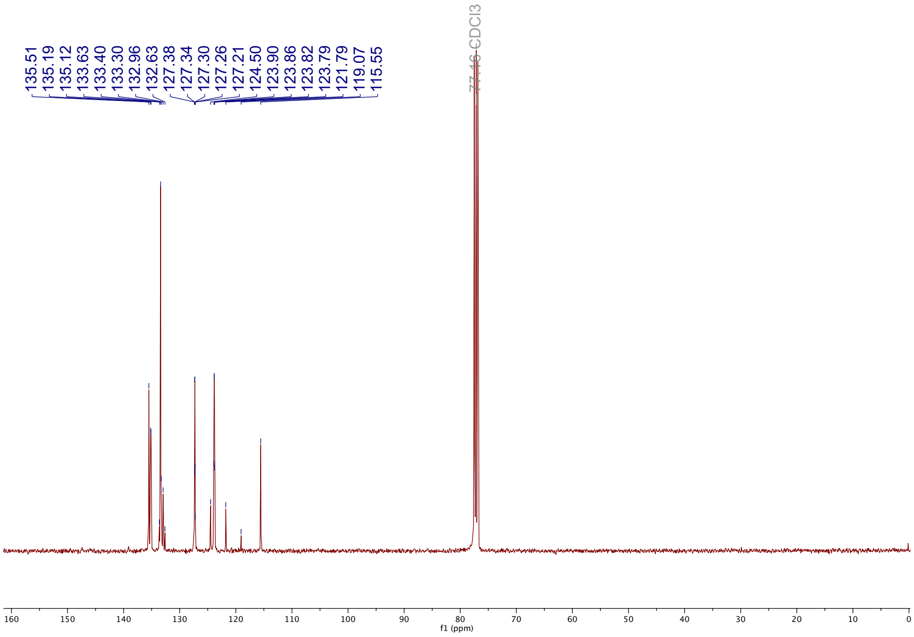


Figure S109. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **2e**.

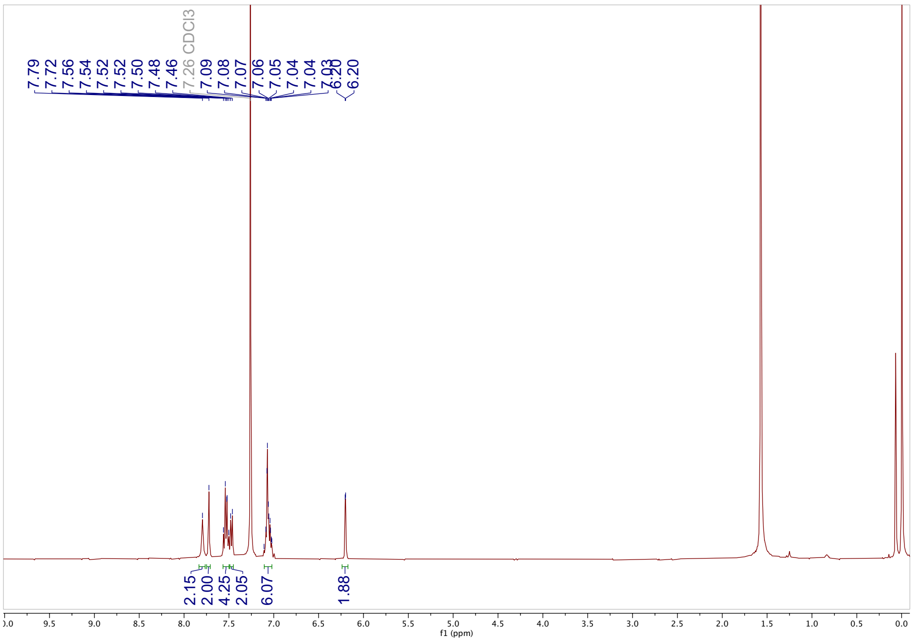


Figure S110. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **3e**.

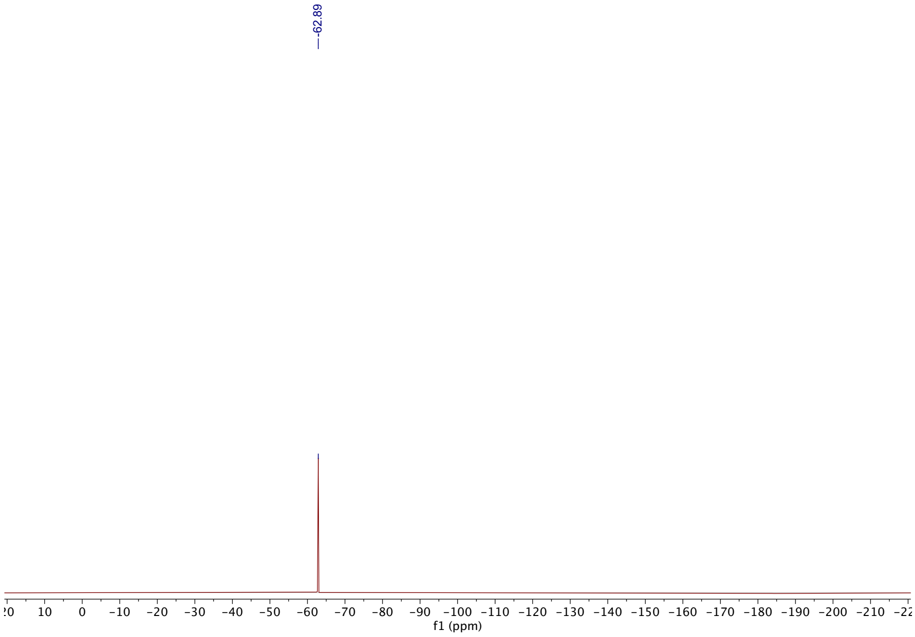


Figure S111. ^{19}F {H} NMR (CDCl$_3$, 376 MHz, 298 K) of **3e**.

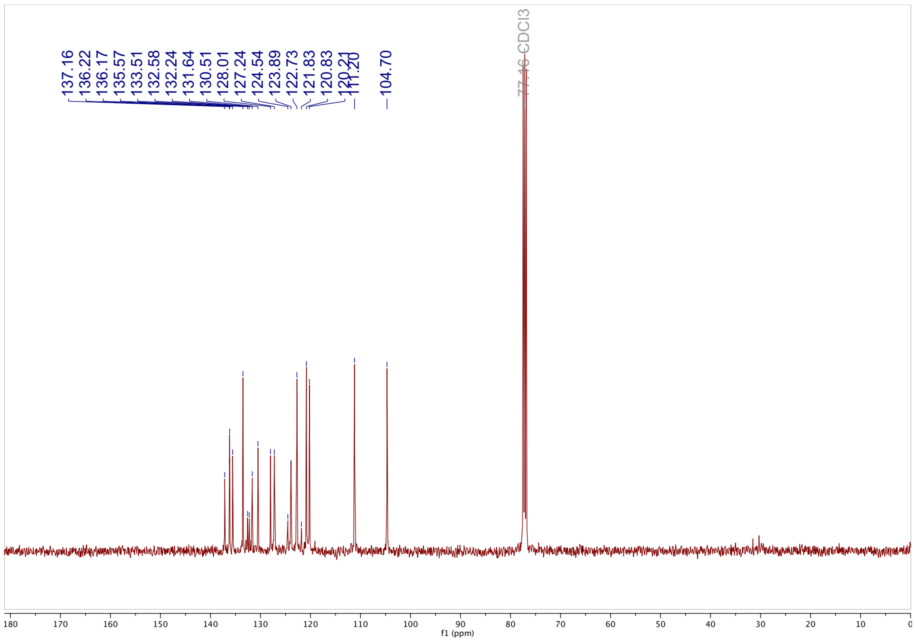


Figure S112. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **3e**.

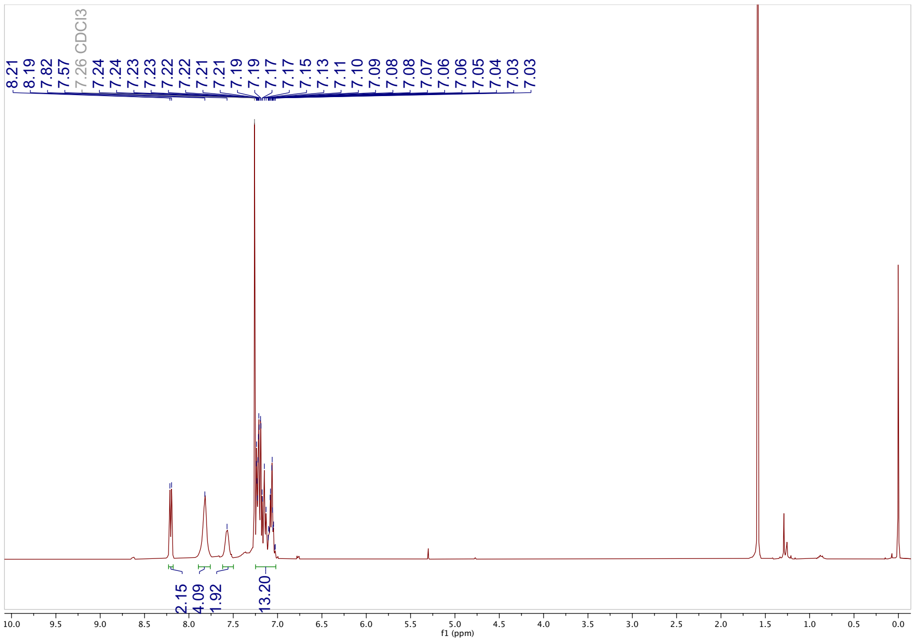


Figure S113. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) of **5e**.

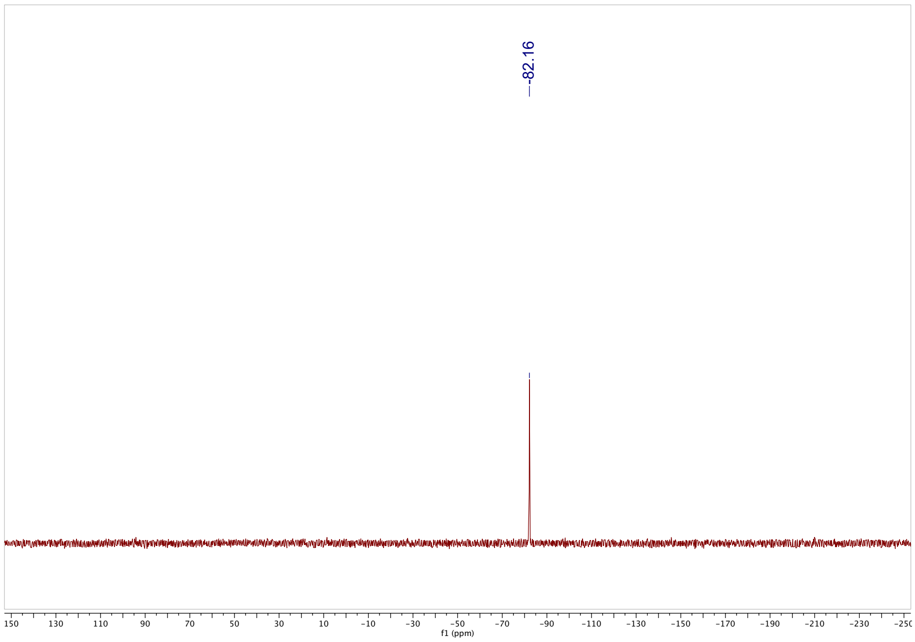


Figure S114. ^{31}P {H} NMR ($CDCl_3$, 162 MHz, 298 K) of **5e**.

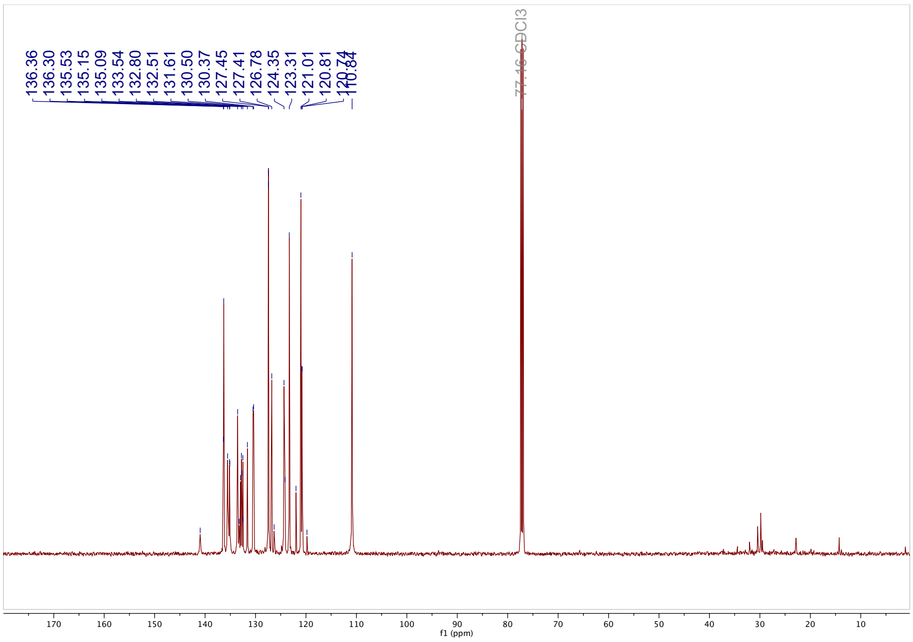


Figure S115. ^{13}C {H} NMR (CDCl$_3$, 126 MHz, 298 K) of **5e**.

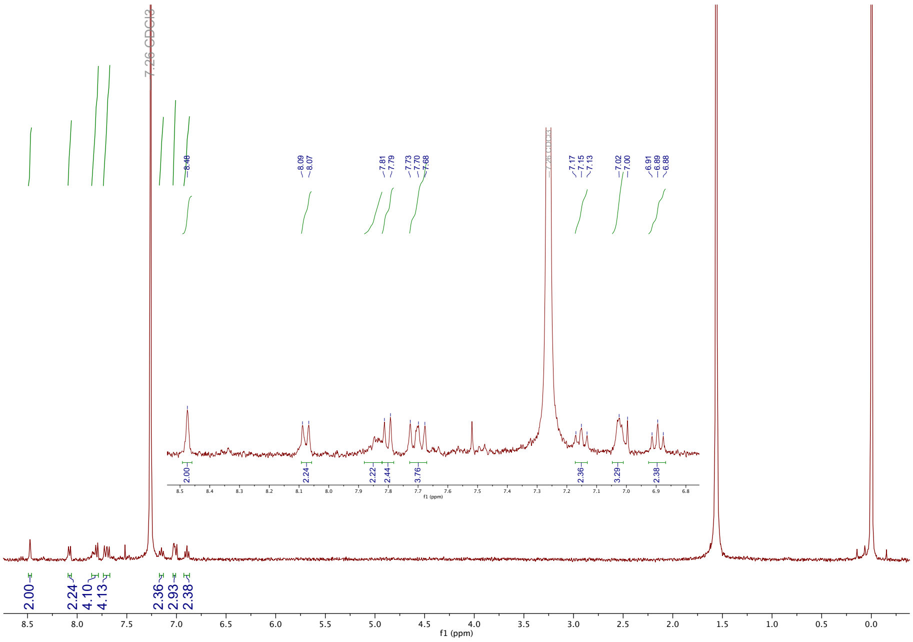


Figure S116. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **PC2**.

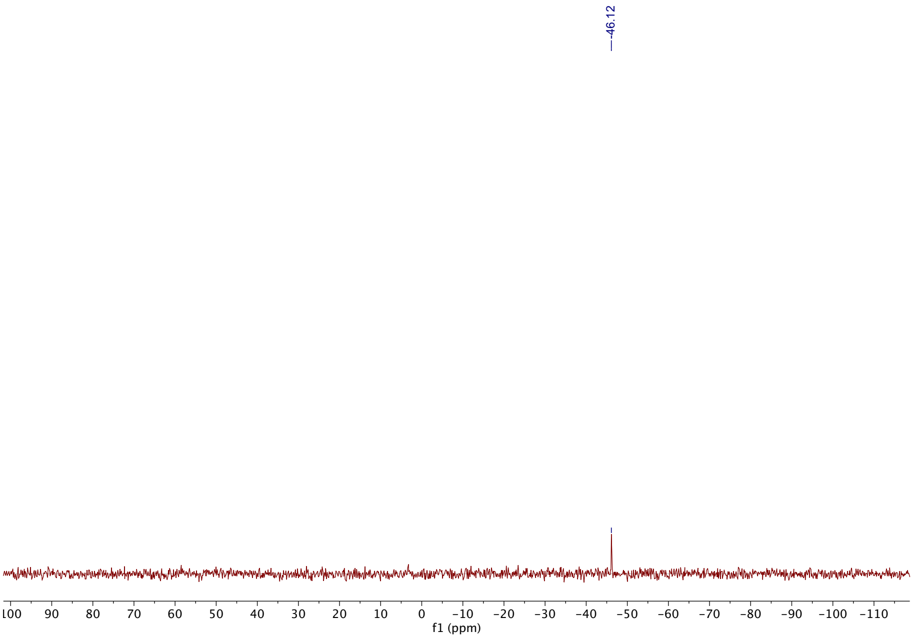


Figure S117. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **PC2**.

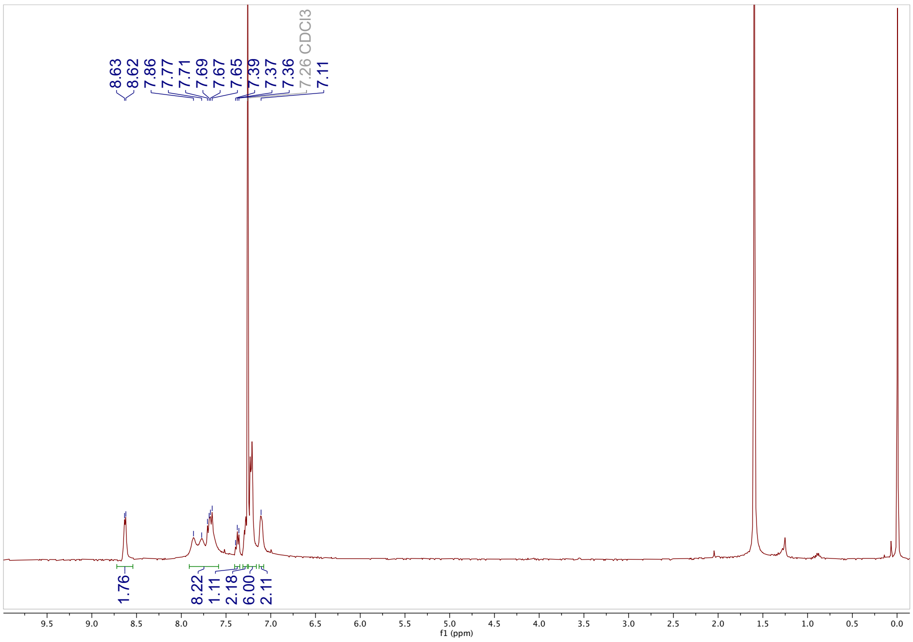


Figure S118. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **5eO**.

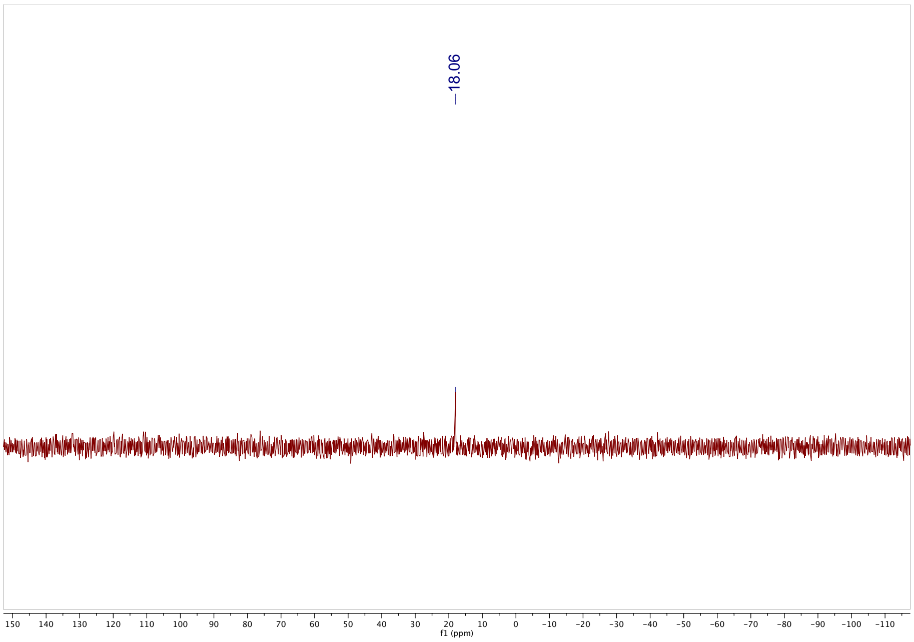


Figure S119. ^{31}P {H} NMR ($CDCl_3$, 162 MHz, 298 K) of **5eO**.

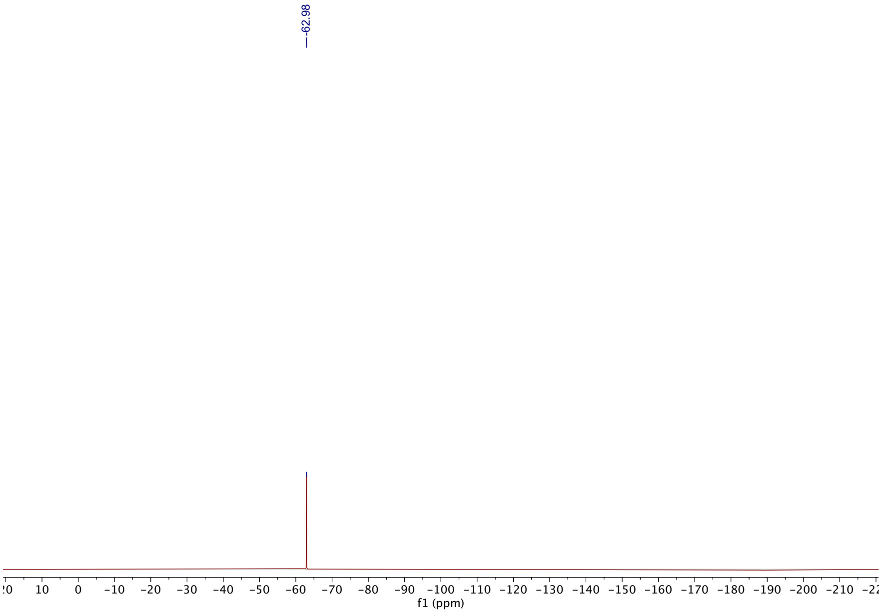


Figure S120. ^{19}F {H} NMR ($CDCl_3$, 376 MHz, 298 K) of **5eO**.

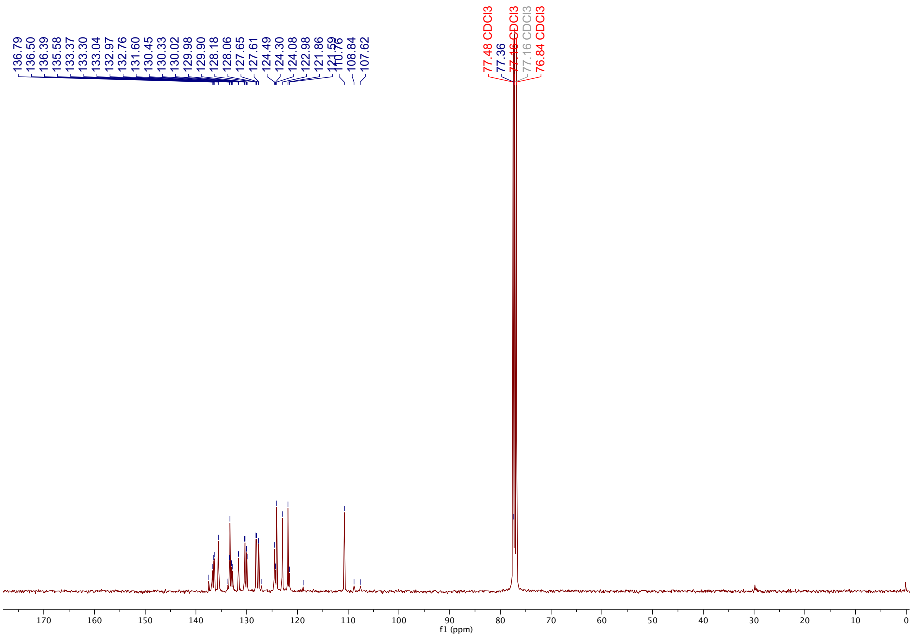


Figure S121. ^{13}C {H} NMR ($CDCl_3$, 101 MHz, 298 K) of **5eO**.

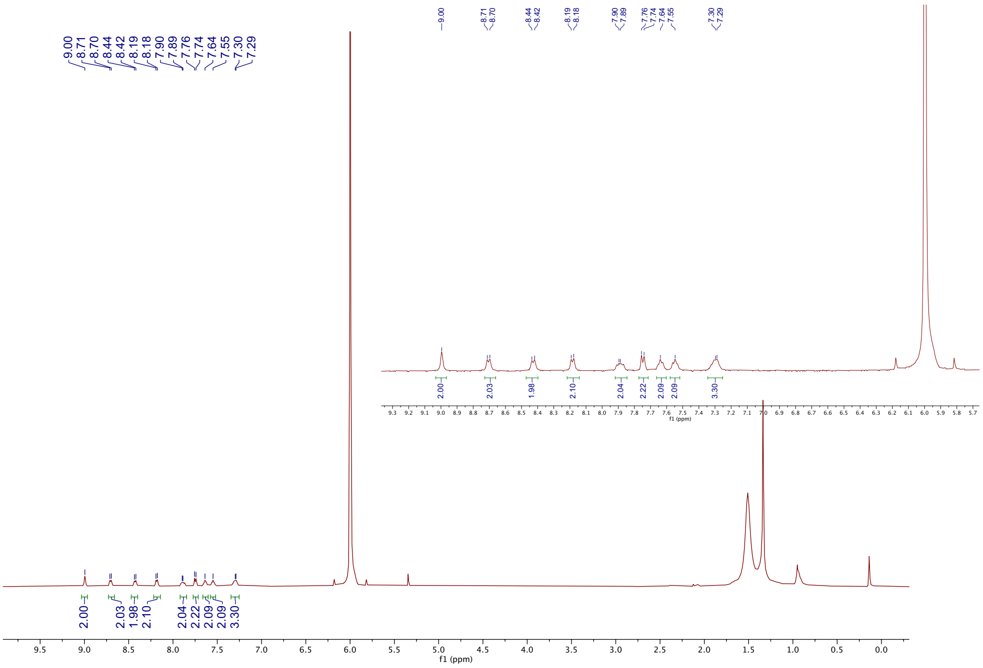


Figure S122. ^{1}H NMR ($C_2Cl_4D_2$, 400 MHz, 373 K) of **PC2O**.

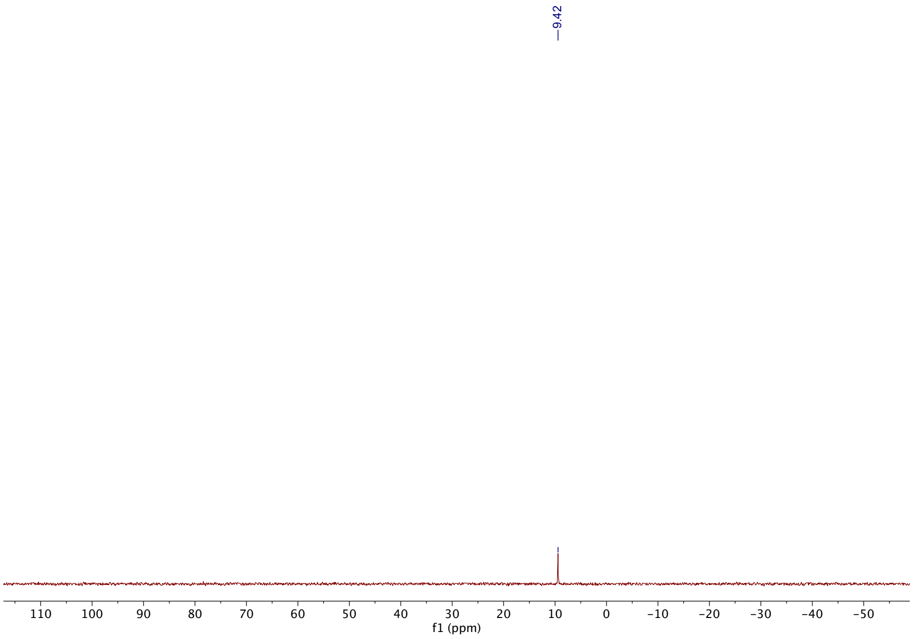


Figure S123. ^{31}P {H} NMR ($C_2Cl_4D_2$, 162 MHz, 373 K) of **PC2O** .

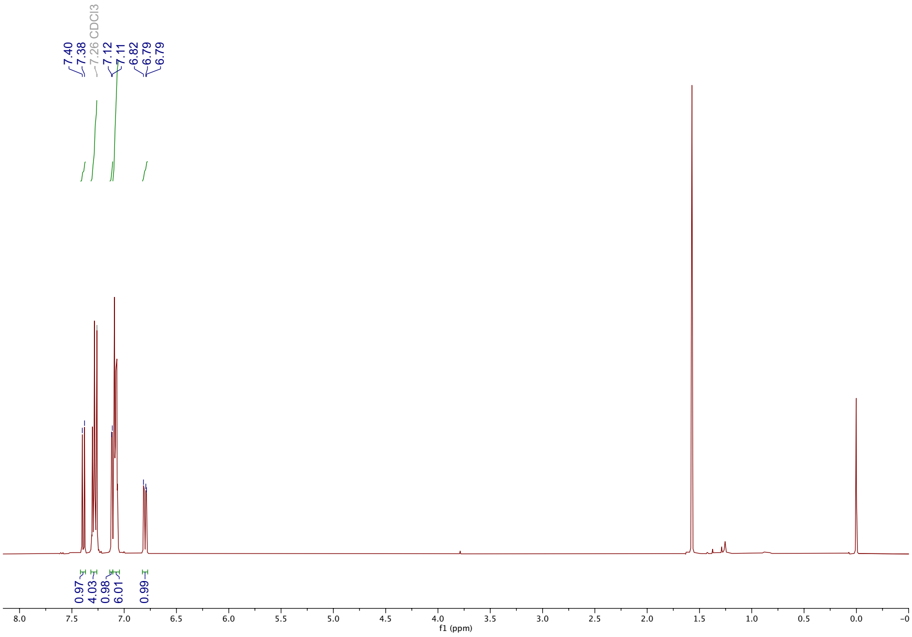


Figure S124. ^1H NMR ($CDCl_3$, 400 MHz, 298 K) of **NBzCl-Br**.

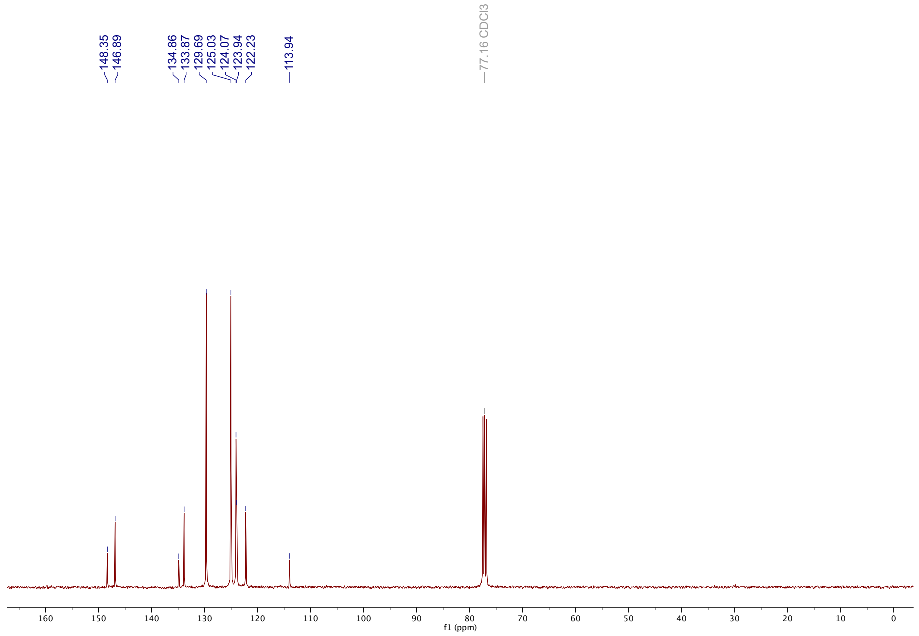


Figure S125. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **NBzCl-Br**.

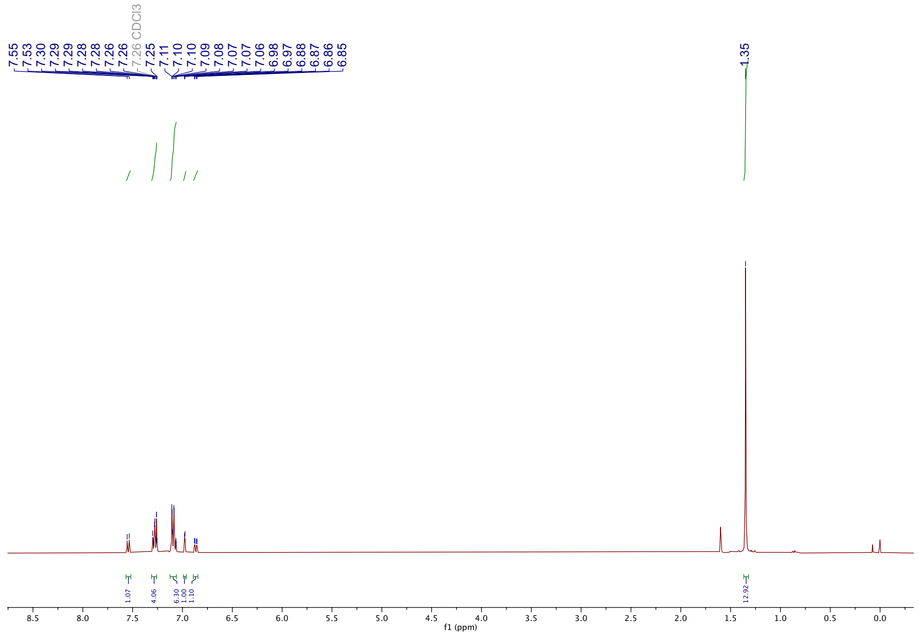


Figure S126. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **NBzCl-Bpin**.

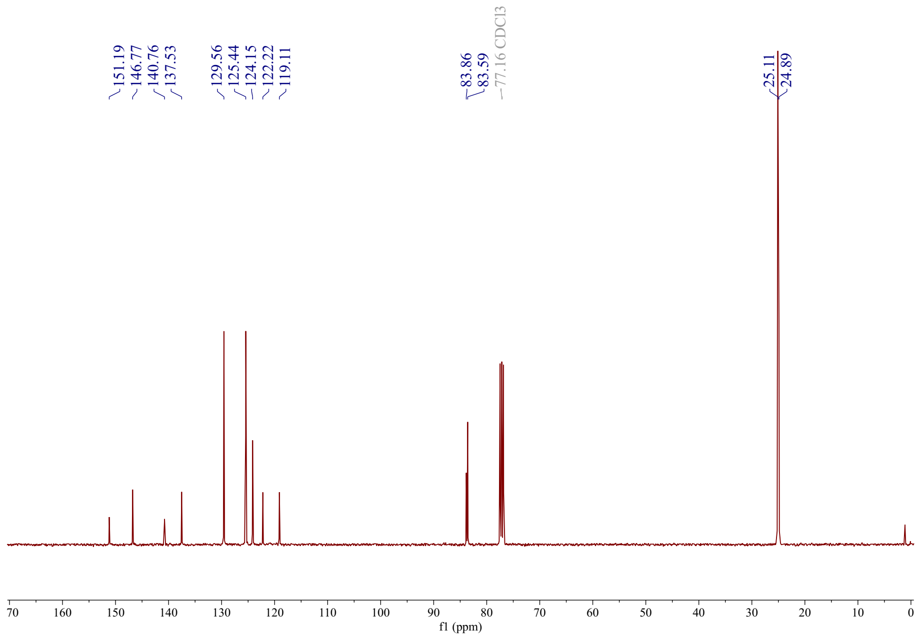


Figure S127. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **NBzCl-Bpin**.

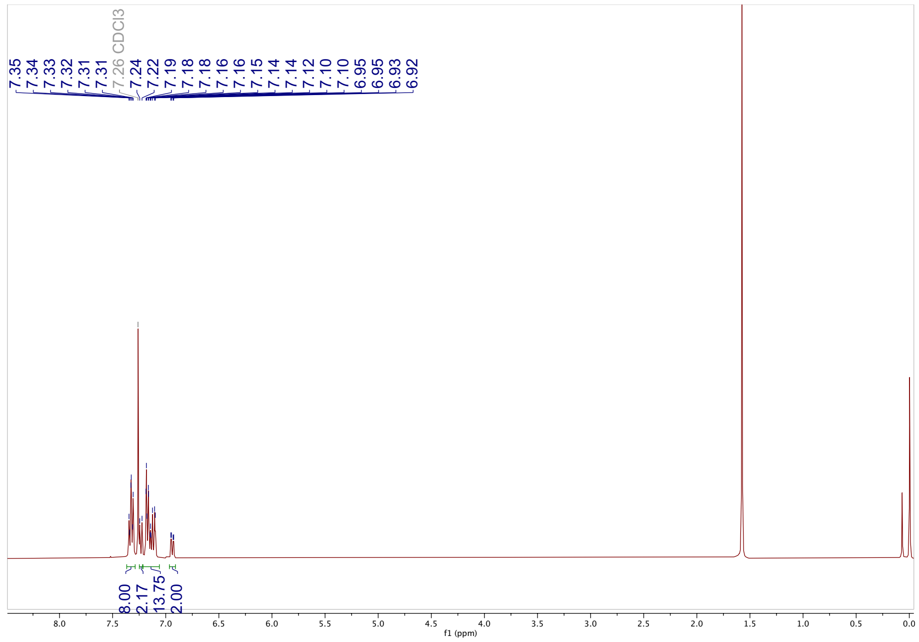


Figure S128. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **2f**.

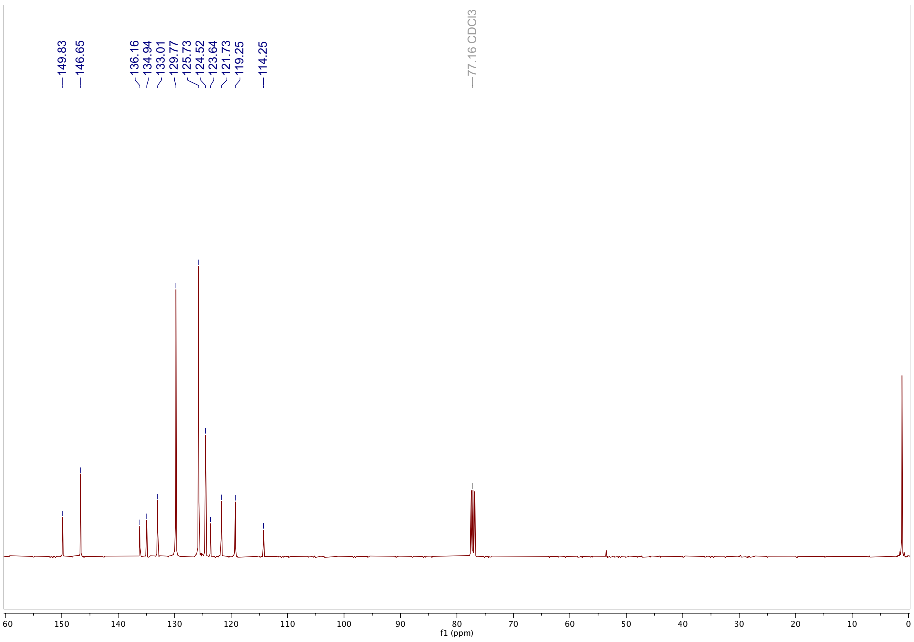


Figure S129. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **2f**.

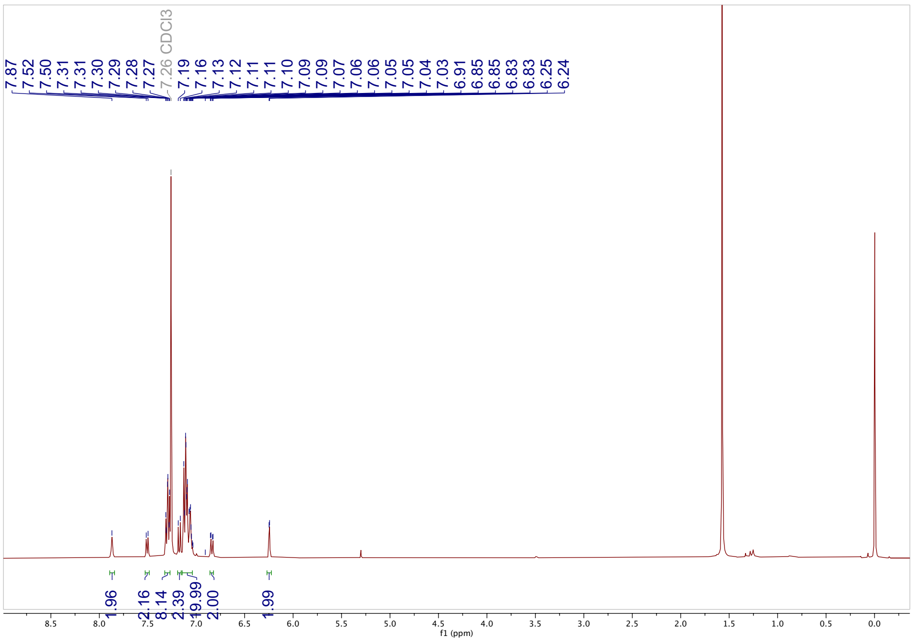


Figure S130. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **3f**.

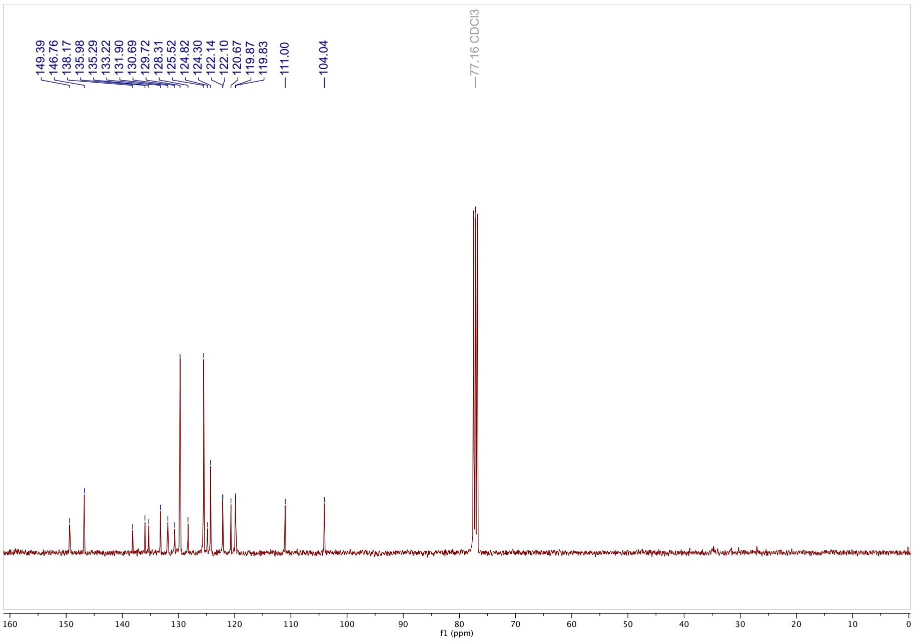


Figure S131. ^{13}C {H} NMR ($CDCl_3$, 101 MHz, 298 K) of **3f**.

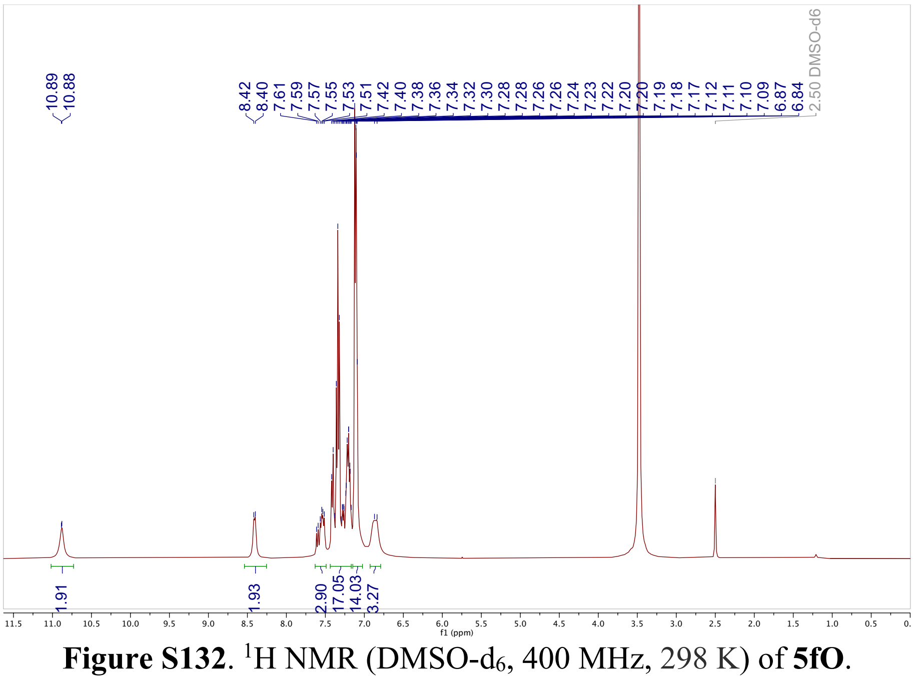


Figure S132. ^{1}H NMR (DMSO-d_6, 400 MHz, 298 K) of **5fO**.

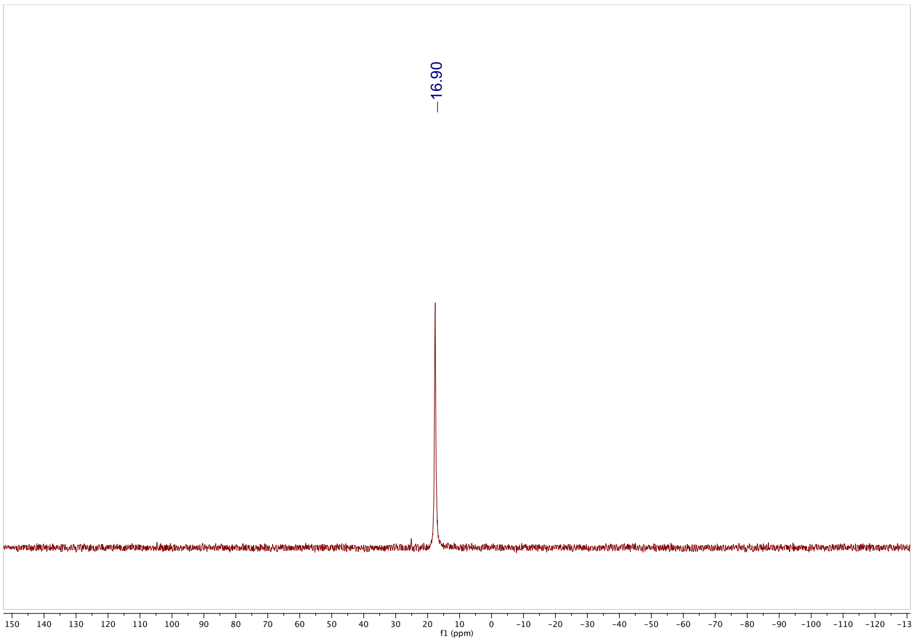


Figure S133. ^{31}P {H} NMR (DMSO-d_6, 162 MHz, 298 K) of **5fO**.

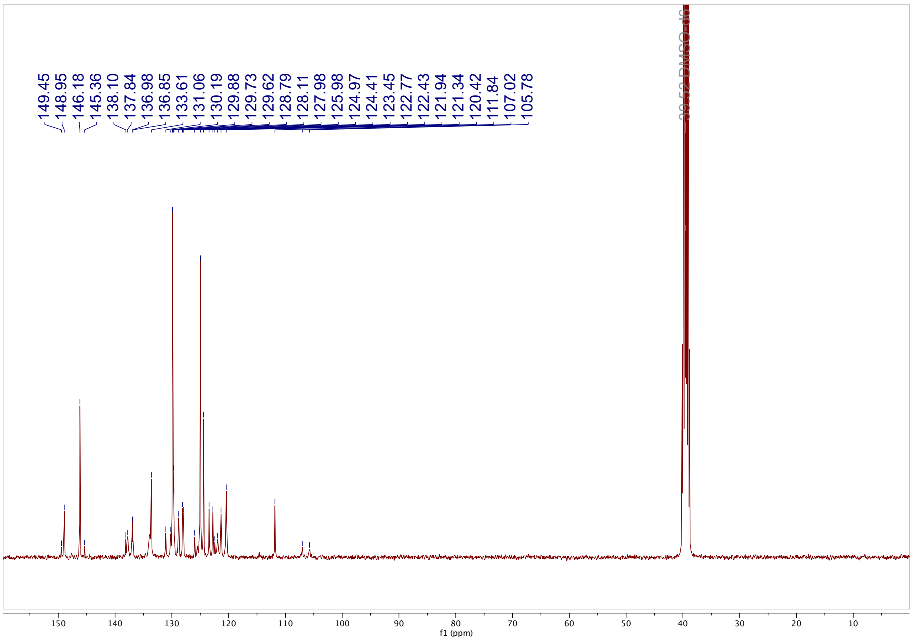


Figure S134. ^{13}C {H} NMR (DMSO-d_6, 101 MHz, 298 K) of **5cO**.

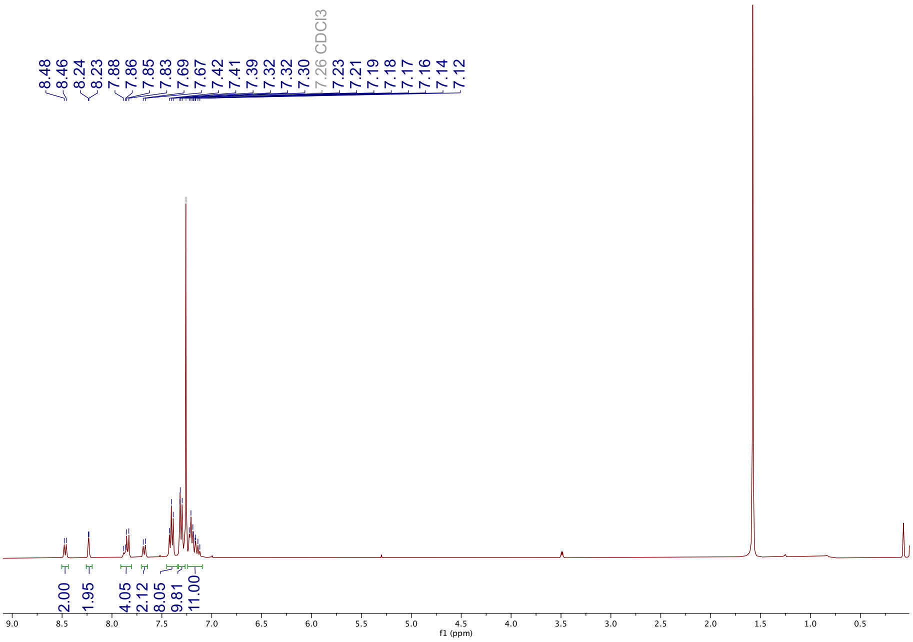


Figure S135. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **PC3O**.

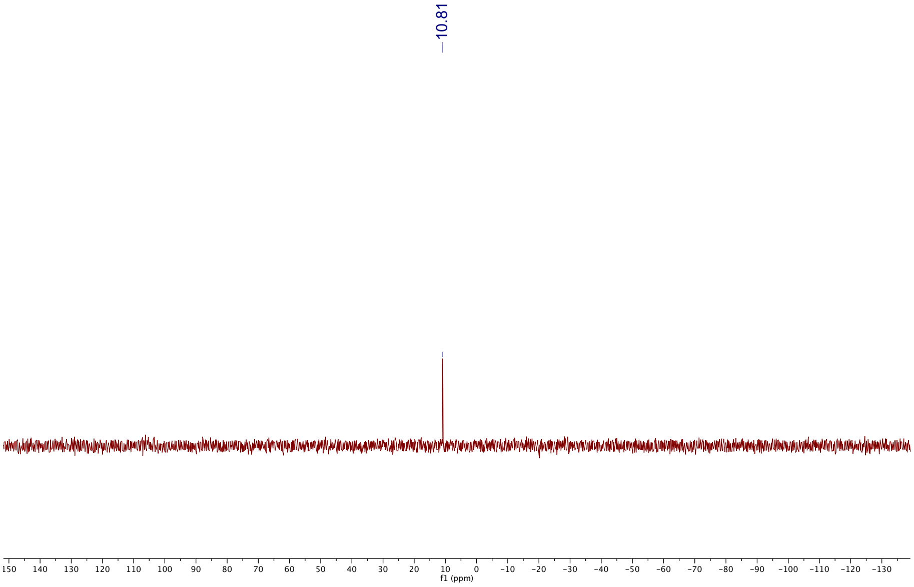


Figure S136. ^{31}P {H} NMR (CDCl$_3$, 162 MHz, 298 K) of **PC3O**.

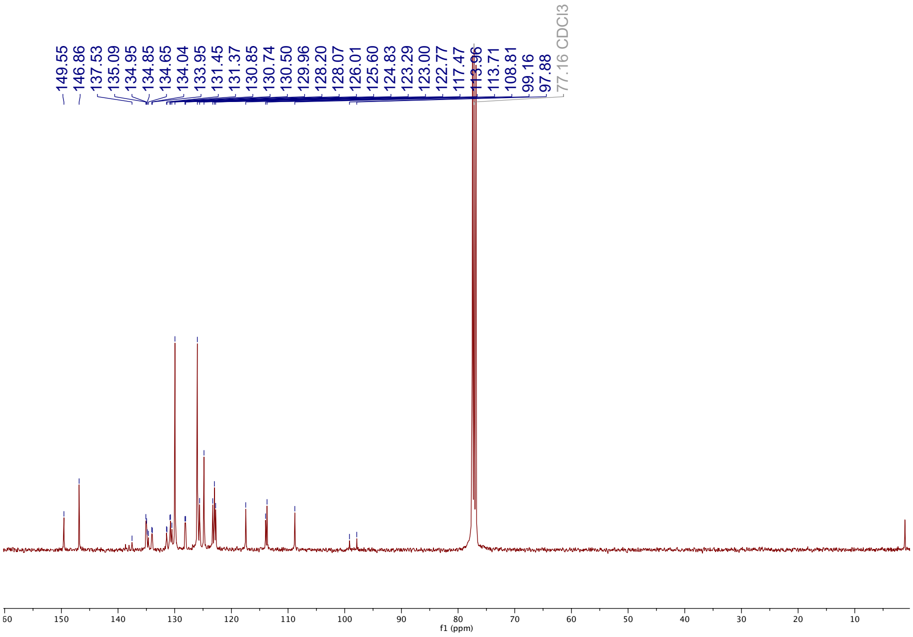


Figure S137. ^{13}C {H} NMR (CDCl$_3$, 101 MHz, 298 K) of **PC3O**.

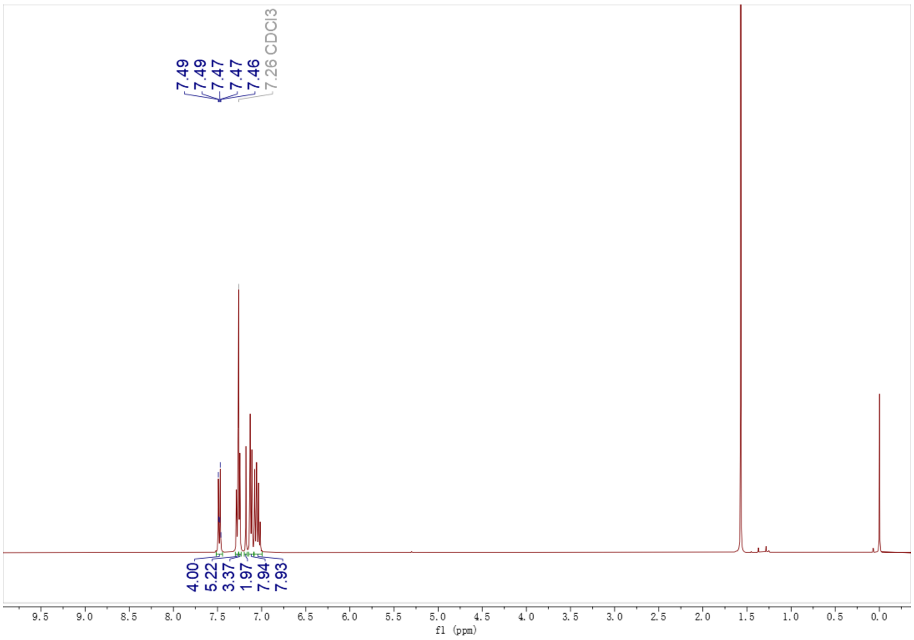


Figure S138. ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) of **ThN**.

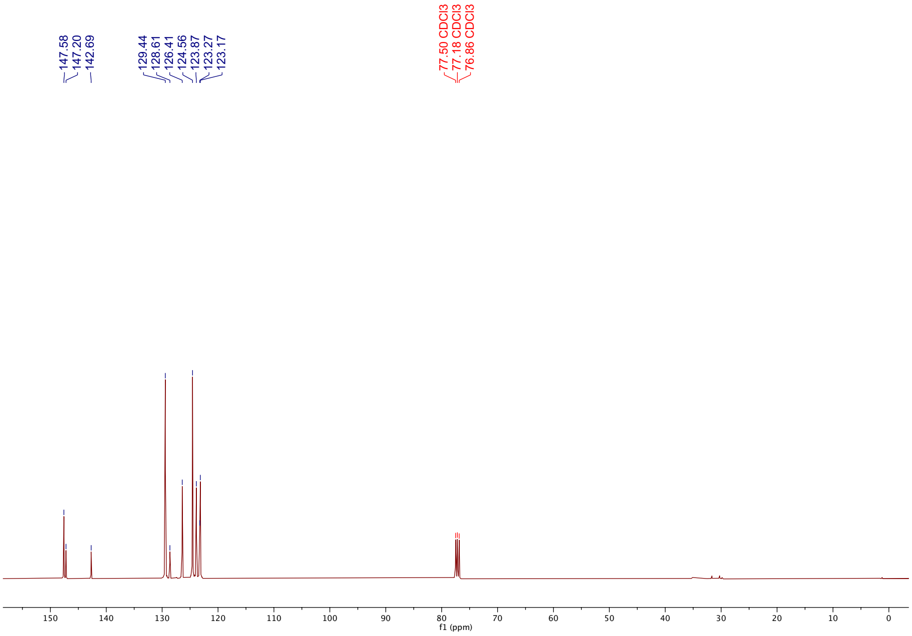


Figure S139. ^{13}C {H} NMR ($CDCl_3$, 101 MHz, 298 K) of **ThN**.

References:

S1.Maddala, S.; Kollimalaian, K.; Samal, A.; Parthasarathy, *Tetrahedron*, **2024**, *151*, 133807.
S2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez C.; Pople, J. A. *Gaussian 03, Revision E.01*, *Gaussian Inc.,* Wallingford, CT, **2007**.
S3. Gaussian 16, Revision C.01 , Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.