Electronic Supplementary Material (ESI) for Dalton Transactions.

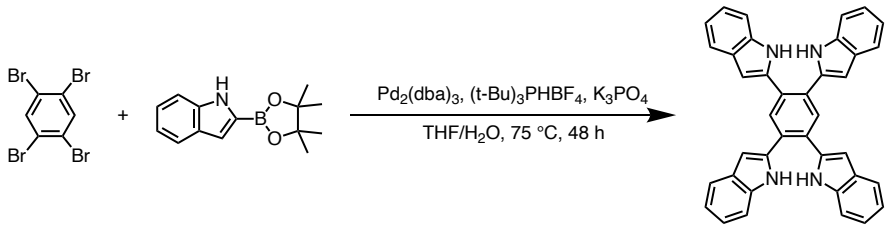
Synthesis, Post-Functionalization, and Photoluminescence of Contorted Diazaphosphepine-Based Polycyclic Aromatic Heterocycles

Can Li,[a]+ Kai Yang,[a]+ Xinyu Li,[a] Shuya Wen,[a] Na Yu,[a] Yi Ren[a]*

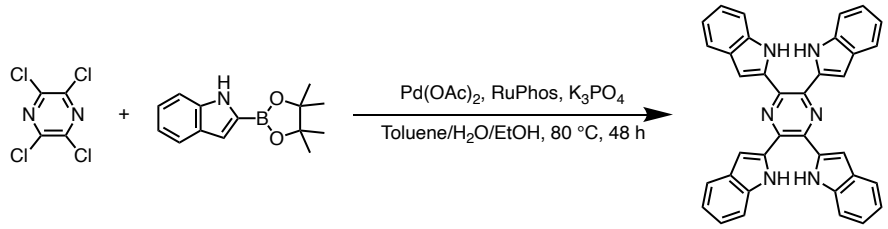
[a] School of Physical Science and Technology, ShanghaiTech University, 201210 Shanghai, People's Republic of China

Materials and Experiments

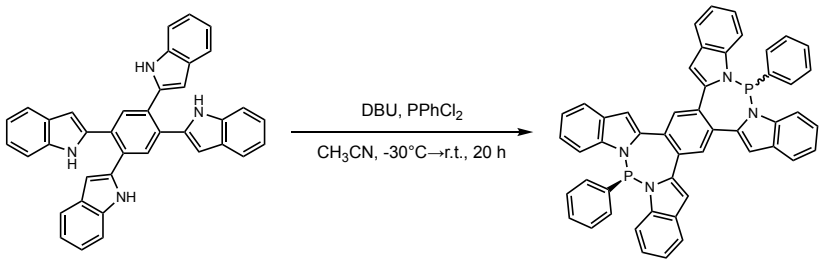
All manipulations were carried out under a dry nitrogen atmosphere employing standard Schlenk techniques. Reagents were purchased from Shanghai Titan Scientific, Energy Chemical, J&K Scientific, Sinopharm Chemical Reagent and TCI Shanghai, and were, unless otherwise noted, used as-received. Solvents were dried using an MBRAUN Solvent Purification System. NMR solvents were purchased from Cambridge Isotope Laboratories and J&K Scientific. ^{1}H NMR, ^{13}C {^{1}H} NMR, and ^{31}P {^{1}H} NMR were recorded on Bruker AVANCE NEO 400 and AVANCE III HD500 MHz spectrometers. High-resolution mass spectra were carried out on the Thermo HPLC-Q Exactive Focus in atmospheric press chemical ionization (APCI). The crystal structures of **2c** (CCDC2251030), **2Ot** (CCDC2251032), **2St** (CCDC2251027), **2Sc (**CCDC 2251028), **3Oc (**CCDC2251840), **3St (**CCDC 2251029), and **3Sc** (CCDC2251031) were obtained by Dr. Na Yu of the X-ray Crystallography Facility at the ShanghaiTech University. Single-crystal X-ray diffraction was performed on a Bruker D8 VENTURE diffractometer and Bruker APEX-II CCD diffractometer. The crystals were kept at a steady T = 150K during the data collection. 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-375 laser for excitation and MCP-PMT detector. This set-up allows the time resolution is ~25 ps. Theoretical calculations were carried out using the GAUSSIAN 09 suite of programs.[S1]



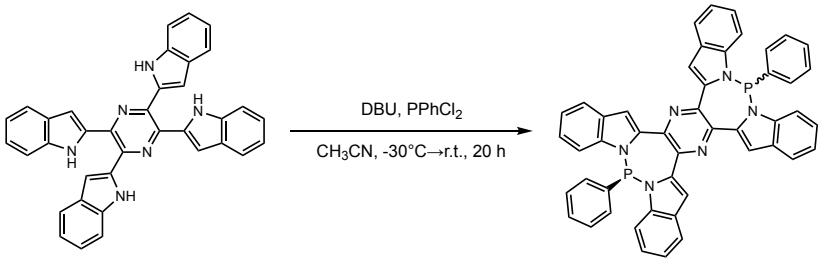
2NH: In a 1-necked Schlenk flask, 1,2,4,5-tetrabromobenzene (200 mg, 0.508 mmol, 1.0 eqv.) was mixed with 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (617.5 mg, 2.540 mmol, 5.0 eqv), tris (dibenzylideneacetone)dipalladium (0) (93 mg, 0.102 mmol, 0.2 eqv.), tri-tert-butylphosphonium tetrafluoroborate (147 mg, 0.507 mmol, 1.0 eqv.) and potassium phosphate (1941 mg, 9.144 mmol, 18 eqv.) in degassed THF 40 mL and water 10 mL. To complete the reaction, the resulting mixture was degassed for 15 min, and heated to 75 °C for 48 hours. Finally, the reaction mixture was allowed to cool to room temperature, after which it was poured into 30 mL of water. The organic layer was extracted with DCM, dried over anhydrous Na_2SO_4. The solvent of mixture was removed under vacuum. The product was obtained by washing Et_2O, followed by recrystallization from DCM. Isolated yield: 227.1 mg, 83.7%, white powder solid. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz, δ): 10.50 (s, 4H), 8.03 (s, 2H), 7.50 (d, J = 7.9 Hz, 4H), 7.35 (d, J = 8.1 Hz, 4H), 7.10 (ddd, J = 8.2, 7.0. 1.2 Hz, 4H), 7.06 – 6.95 (m, 4H), 6.46 (d, J = 2.2 Hz, 4H) ppm. ^{13}C NMR ($(CD_3)_2CO$, 101 MHz, δ): 138.02, 137.62, 133.32, 132.06, 129.87, 122.75, 121.28, 120.40, 112.16, 103.31 ppm. HRMS: m/z = 539.2234 ($[M+H]^+$, Calcd. 539.2231).



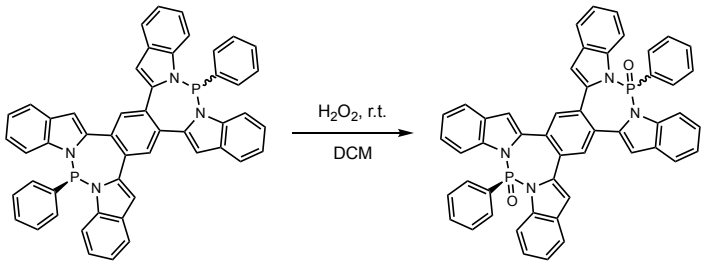
3NH: In a 1-necked Schlenk flask, 2,3,5,6-tetrachloropyrazine (200 mg, 0.918 mmol, 1.0 eqv.) was mixed with 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (1115 mg, 4.586 mmol, 5.0 eqv.), palladium (II) acetate (20.6 mg, 0.092 mmol, 0.1 eqv.), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (85.7 mg, 0.184 mmol, 0.2 eqv.) and potassium phosphate (1169 mg, 5.507 mmol, 6.0 eqv.) in degassed toluene 40 mL and water 10 mL. To complete the reaction, the resulting mixture was degassed for 15 min, heated to 80 °C for 48 hours. Finally, the reaction mixture was allowed to cool to room temperature, after which it was poured into 30 mL of water. The organic layer was extracted with DCM, dried over anhydrous Na_2SO_4. The solvent of mixture was removed under vacuum, The product was obtained by washing Et_2O, followed by recrystallization from DCM. Isolated yield: 223.3 mg, 45 %, yellow powder solid. ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 9.022 (s, 4H), 7.60 (d, J = 7.9 Hz, 4H), 7.47 (d, J = 8.2 Hz, 4H), 7.31 (t, J = 7.3 Hz, 4H), 7.23 (s, 4H), 7.17 (t, J = 7.5 Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 138.39, 136.63, 133.28, 128.59, 124.21, 121.84, 120.73, 111.52, 105.58 ppm. HRMS: m/z = 541.2138 ($[M+H]^+$, Calcd. 541.2136).



2t/2c: Under N_2 atmosphere, **2** (80 mg, 0.149 mmol, 1.0 eqv.), DBU (0.133 ml, 0.889 mmol, 6.0 eqv.) and 140 mL dry MeCN were added in a 200 mL flask. The solution was cooled to -30 °C in glove box refrigerator for 30 min, then the dichlorophenylphosphine (0.43 mL, 0.312 mmol, 2.1 eqv. 10 % in dry tol) was slowly added. The mixture was allowed up to room temperature slowly and stirred for 20 hours. Finally, the solvent of mixture was removed under vacuum. The residue was purified by silica gel column chromatography (dichloromethane/petroleum ether, from 0:10 to 9:1, v/v). Isolated yield: 101.8 mg, 91 % based the *cis*-/*trans*-mixtures, white powder solid. Due to the slow oxidation of P-center of **2t/2c** during chromatography, it was very hard to fully separate the trans- and cis-isomers of **2**.

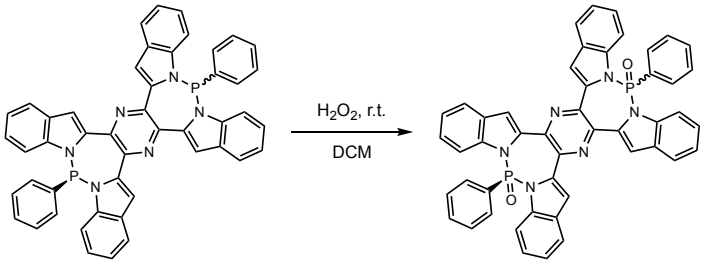


3t/3c: Under N_2 atmosphere, **3NH** (80 mg, 0.148 mmol, 1.0 eqv.), DBU (0.133 ml, 0.888 mmol, 6.0 eqv.) and 80 mL dry MeCN were added in a 200 ml flask. The solution was cooled to -30 °C in glove box refrigerator for 30 min, then the dichlorophenylphosphine (0.48 ml, 0.350 mmol, 2.6 eqv. 10% in dry tol, V:V) was slowly added. The mixture was allowed up to room temperature slowly and stirred for 20 hours. Finally, the solvent of mixture was removed under vacuum. The residue was purified by silica gel column chromatography (THF/petroleum ether, from 0:10 to 5:5, v/v). Isolated yield: 105.8 mg, 95 % based the *cis*-/*trans*-mixtures, yellow powder solid. Due to the slow oxidation of P-center of **3t/3c** during chromatography, it was very hard to fully separate the trans- and cis-isomers of **3**.

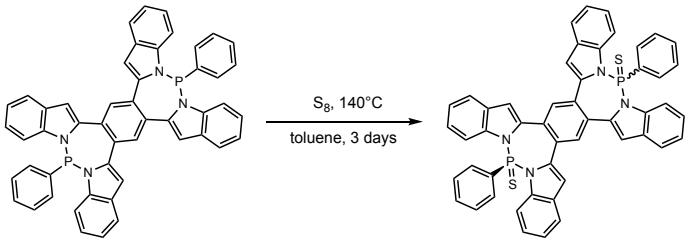


2Ot/2Oc: **2t/2c** (50 mg, 0.066 mmol) was dissolved in 30 ml DCM, and 2 ml H_2O_2 (30% in H_2O) was added. The solution was stirred for overnight at room temperature. Then, the mixture was separated and the aqueous phase was extracted with CH_2Cl_2 (3×30 mL), organic layer was dried over anhydrous Na_2SO_4. The solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (dichloromethane/petroleum ether, 1:1, v/v). Isolated yield of **2Ot/2Oc** mixture: 43.8 mg, 84%.

2Oc: Product was obtained as a faint yellow powder solid.^{1}H NMR ($CDCl_3$, 500 MHz, δ): 8.71 (dd, J = 8.4, 1.0 Hz, 4H), 7.90 (s, 2H), 7.69 (d, J = 7.7, 4H), 7.42 – 7.35 (m, 4H), 7.34 – 7.27 (m, 6H), 7.16 – 7.12 (m, 4H), 7.09 (d, J = 2.9 Hz, 4H), 7.11 – 7.03 (m, 4H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 126 MHz, δ): 141.9 (d, J = 4.1 Hz), 137.7 (d, J = 5.9 Hz), 134.0 (d, J = 3.1 Hz), 131.7, 131.3, 130.4, 130.2, 130.1, 129.9 (d, J = 8.3 Hz), 128.6 (d, J = 15.7 Hz), 125.1, 123.3, 120.8, 116.1, 111.8 (d, J = 6.9 Hz) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, δ) 14.4 ppm. HRMS(APCI-TOF) m/z: $[M+H]^+$ Calcd. For $C_{50}H_{33}N_4P_2O_2^+$ 783.2074; Found 783.2066.
2Ot: Product was obtained as a pale green powder solid. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz, δ): 8.66 (d, J = 8.0 Hz, 4H), 7.69 (d, J = 7.6 Hz, 4H), 7.64 (s, 2H), 7.45 – 7.42 (m, 2H), 7.40 - (m, 18H), 6.98 (s, 4H) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, δ) 14.4 ppm. HRMS(APCI-TOF) m/z: $[M+H]^+$ Calcd. For $C_{50}H_{33}N_4P_2O_2^+$ 783.2074; Found 783.2058. ^{13}C NMR spectrum cannot be obtained due to its low solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. Single crystal of **2Ot** was obtained and solved.



3Ot/3Oc: **3t/3c** (50 mg, 0.066 mmol) was dissolved in 40 mL DCM, and 2 ml H_2O_2 (30% in H_2O) was added. The solution was stirred for overnight at room temperature. Then, the mixture was separated and the aqueous phase was extracted with DCM (3×30 mL), organic layer was dried over anhydrous Na_2SO_4. The solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (THF/petroleum ether, 3:7). Isolated yield of **3Ot/3Oc** mixture: 45.3 mg, 87 %.
3Oc: Product was obtained as an orange powder solid. ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 8.75 (d, J = 8.5 Hz, 4H), 7.77 (d, J = 7.8 Hz, 4H), 7.70 (s, 4H), 7.46 (t, J = 7.7 Hz, 4H), 7.37 (t, J = 7.5 Hz, 4H), 7.31 – 7.28 (m, 2H), 7.03 (td, J = 11.1, 6.3 Hz, 4H), 6.98 – 6.90 (m, 4H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 126 MHz, δ): 142.3 (d, J = 4.2 Hz), 139.7, 136.1 (d, J = 5.8 Hz), 134.0, 131.6, 130.1 (d, J = 12.1 Hz), 129.5 (d, J = 8.1 Hz), 128.8 (d, J = 15.6 Hz), 126.2, 123.7, 121.7, 116.3, 115.5 (d, J = 6.8 Hz) ppm. ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$, δ) 13.7 ppm. HRMS(APCI-TOF) m/z: $[M+H]^+$ Calcd. For $C_{48}H_{31}N_6P_2O_2^+$ 785.1979; Found 785.1964.
3Ot: Product was obtained as an orange powder solid.^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.75 (d, J = 8.5 Hz, 4H), 7.73 (d, J = 7.9 Hz, 4H), 7.46 (t, J = 7.5 Hz, 4H), 7.39 – 7.30 (m, 10H), 7.21 (td, J = 7.5, 3.8 Hz, 4H), 7.15 – 7.05 (m, 4H) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz, δ): 142.0 (d, *J* = 4.2 Hz), 139.9, 136.5 (d, *J* = 14.1 Hz), 134.0 (d, *J* = 3.3 Hz), 130.7 (d, *J* = 12.1 Hz), 130.3, 129.5, 128.8 (d, *J* = 15.6 Hz), 126.0, 123.6, 121.7, 116.1, 114.7 (d, *J* = 6.5 Hz) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, δ) 13.9 ppm. HRMS(APCI-TOF) m/z: $[M+H]^+$ Calcd. For $C_{48}H_{31}N_6P_2O_2^+$ 785.1979; Found 785.1965.

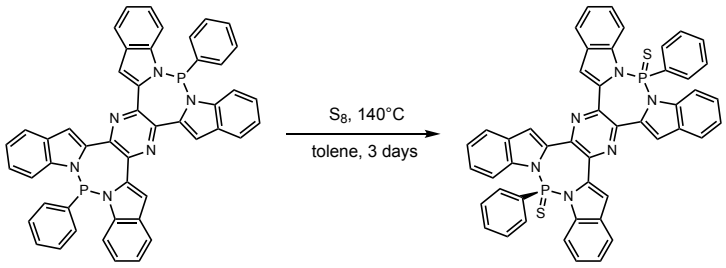


2St/2Sc: Under N_2 atmosphere, **2t/2c** (153.3 mg, 0.204 mmol 1.0 eqv.) and sublimed sulfur powder (163.4 mg, 5.10 mmol, 25.0 eqv.) were added to 10 mL toluene in a 100 mL flask. The solution was stirred for 3 days under dark at 140 °C. After cooling to room temperature, the solvent of mixture was removed under vacuum,

the residue was purified by silica gel column chromatography (dichloromethane/petroleum ether 3:2). Isolated yield of **2St/2Sc** mixture: 52%.

2Sc: Product was obtained as a pale green powder solid. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.94 (sbr, 4H), 7.80 (s, 2H), 7.67 – 7.66 (m, 4H), 7.34 – 7.26 (m, 10H), 7.4 – 7.18 (m, 4H), 7.14 – 7.09 (m, 4H), 7.01 (d, J = 1.7 Hz, 4H) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, δ) 46.5 ppm. HRMS(APCI-TOF) m/z: $[M+H]^+$ Calcd. For $C_{50}H_{32}N_4P_2S_2^+$ 815.1617; Found 815.1623. ^{13}C NMR spectrum cannot be obtained due to its low solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. Single crystal of **2Sc** was obtained and solved.

2St: Product was obtained as a white powder solid. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 9.27 (d, J = 8.5 Hz, 4H), 7.62 (d, J = 7.5 Hz, 4H), 7.36 – 7.32 (m, 4H), 7.30 – 7.26 (m, 4H), 7.20 (s, 2H), 7.18 – 7.16 (m, 3H), 7.14 – 7.11 (m, 7H), 6.60 (d, J = 1.7 Hz, 4H) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, δ) 46.4 ppm. HRMS(APCI-TOF) m/z: $[M+H]^+$ Calcd. For $C_{50}H_{33}N_4P_2S_2^+$ 815.1617; Found 815.1605. ^{13}C NMR spectrum cannot be obtained due to its low solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. Single crystal of **2St** was obtained and solved.



3St/3Sc: Under N_2 atmosphere, **3t/3c** (112.9 mg, 0.150 mmol, 1.0 eqv.) and sublimed sulfur powder (118.4 mg, 3.750 mmol 25.0 eqv.) were added to 10 mL toluene in a 100 mL flask. The solution was stirred for 7 days under dark at 140 °C. After cooling to room temperature, the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (dichloromethane/petroleum ether 2:3). Isolated yield of **3St/3Sc** mixture: 54%.

3Sc: Product was obtained as a yellow powder solid. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 9.26 (d, J = 8.5 Hz, 4H), 7.78 (d, J = 7.7 Hz, 4H), 7.70 (d, J = 1.5 Hz, 4H), 7.46 – 7.39 (t, J = 7.1, 4H), 7.36 (t, J = 7.1 Hz, 4H), 7.23 (d, J = 6.3 Hz, 2H), 7.10 – 7.01 (m, 4H), 6.93 (dd, J =15.6, 7.5 Hz, 4H) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, δ) 45.0 ppm. HRMS(APCI-TOF) m/z: $[M+H]^+$ Calcd. For $C_{48}H_{31}N_6P_2S_2^+$ 817.1522; Found 817.1502. ^{13}C NMR spectrum cannot be obtained due to its low solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. Single crystal of **3Sc** was obtained and solved.

3St: Product was obtained as a yellow powder solid. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 9.26 (d, J = 8.6 Hz, 4H), 7.71 (d, J = 7.6 Hz, 4H), 7.42 (t, J = 7.3 Hz, 4H), 7.33 (t, J = 7.3 Hz, 4H), 7.19 (d, J = 1.6 Hz, 4H), 7.16 – 7.01 (m, 10H) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, δ) 45.2 ppm. HRMS(APCI-TOF) m/z: $[M+H]^+$ Calcd. For $C_{48}H_{31}N_6P_2S_2^+$ 817.1522; Found 817.1496. ^{13}C NMR spectrum cannot be obtained due to its low solubility in $CDCl_3$, THF-d_6, acetone-d_6, and acetonitrile-d_3. Single crystal of **3St** was obtained and solved.

1a was purified by flash chromatography by using PE and DCM as eluent (from 9:1 to 5:5 by volume). Product was obtained as a white solid. The NMR spectra of this compound were previously reported by our group.[S2] ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 8.03 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 7.8 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.19 (t, J = 15.0 Hz, 2H), 7.12 – 7.10 (m, 2H),7.02 – 6.94 (m, 3H), 6.87 – 6.84 (m, 2H), 6.82 (s, 2H) ppm. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz, δ): 38.5 ppm.

1aO: Whit solid product was obtained. The NMR spectra of this compound were previously reported by our group.[S2] ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.70 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 7.7 Hz, 2H), 7.42 – 740 (m,

2H), 7.39 – 7.34 (m, 2H), 7.29 – 7.24 (m, 5H), 7.18 – 16 (m, 2H), 7.15 – 7.11 (m, 2H), 6.85 (d, J = 2.8 Hz, 2H) ppm. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz, δ): 15.0 ppm.

1S: Under N_2 atmosphere, **2** (153.3 mg, 0.204 mmol 1.0 eqv.) and sublimed sulfur powder (163.4 mg, 5.10 mmol, 25.0 eqv.) were added to 10 mL toluene in a 100 mL flask. The solution was stirred for 3 days under dark at 140 °C. After cooling to room temperature, the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (dichloromethane/petroleum ether 3:2). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 9.32 (d, J = 8.5 Hz, 2H), 7.64 – 7.61 (m, 2H), 7.34 – 7.27 (m, 6H), 7.18 – 7.10 (m, 5H), 7.07 – 7.02 (m, 2H), 6.80 (d, J = 3.0 Hz, 2H), ppm. ^{13}C $\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, δ): 142.1 (d, J = 6.1 Hz), 142.0, 138.3 (d, J = 137.2 Hz), 131.7, 131.4, 130.7 (d, J = 8.2 Hz), 130.1, 128.8, 128.5 (d, J = 26.0 Hz), 128.2, 123.8, 122.9 120.8, 116.4, 110.1 (J = 6.0 Hz) ppm. $^{31}P\{1H\}$ NMR ($CDCl_3$, 162 MHz, δ): 46.9 ppm.

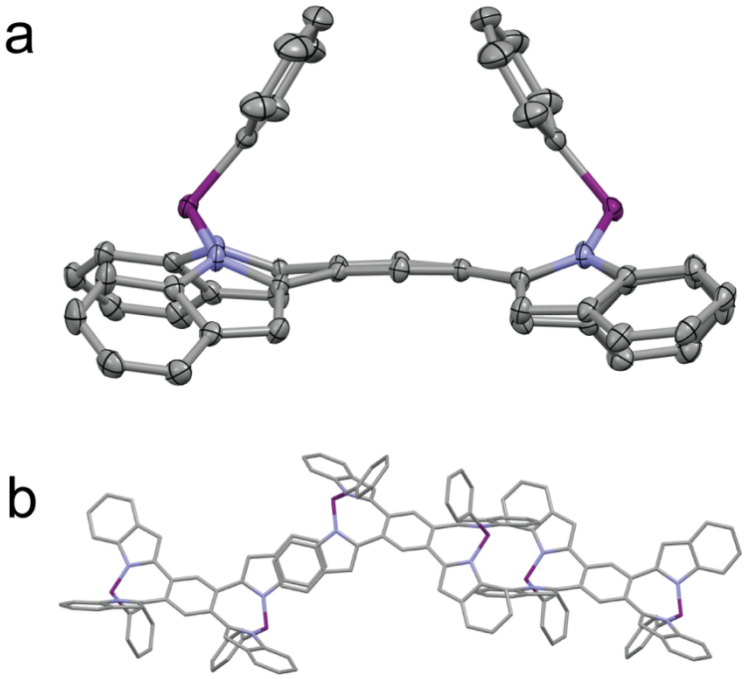


Figure S1. Crystal structure of **2c** at 50% probability level (hydrogen atoms are omitted for clarity).

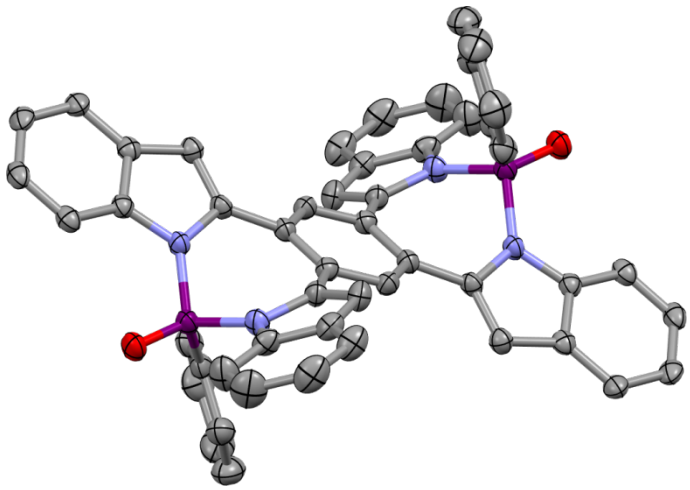


Figure S2. Crystal structure of **2Ot** at 50% probability level (hydrogen atoms are omitted for clarity).

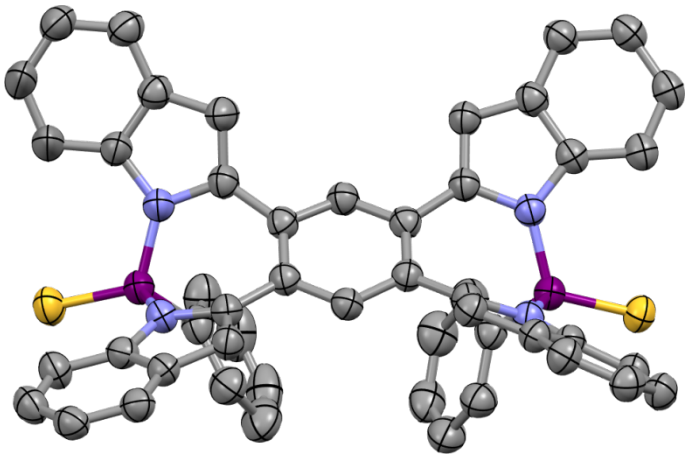


Figure S3. Crystal structure of **2Sc** at 50% probability level (hydrogen atoms are omitted for clarity).

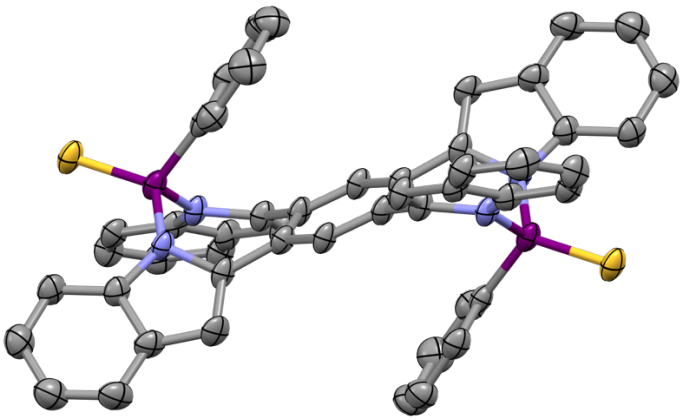


Figure S4. Crystal structure of **2St** at 50% probability level (hydrogen atoms are omitted for clarity).

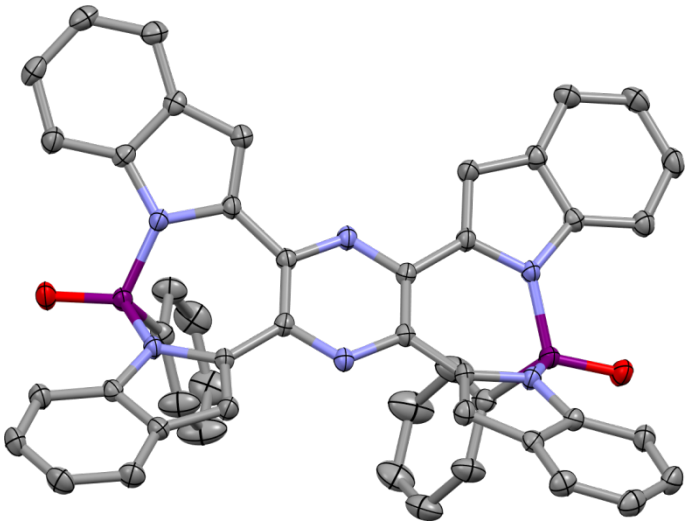


Figure S5. Crystal structure of **3Oc** at 50% probability level (hydrogen atoms are omitted for clarity).

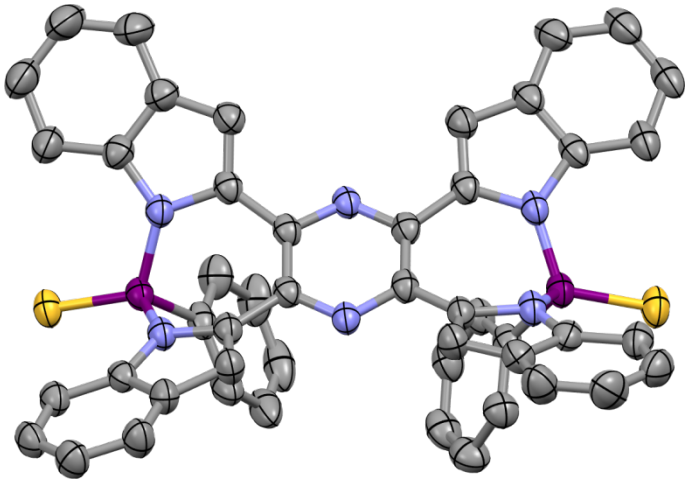


Figure S6. Crystal structure of **3Sc** at 50% probability level (hydrogen atoms are omitted for clarity).

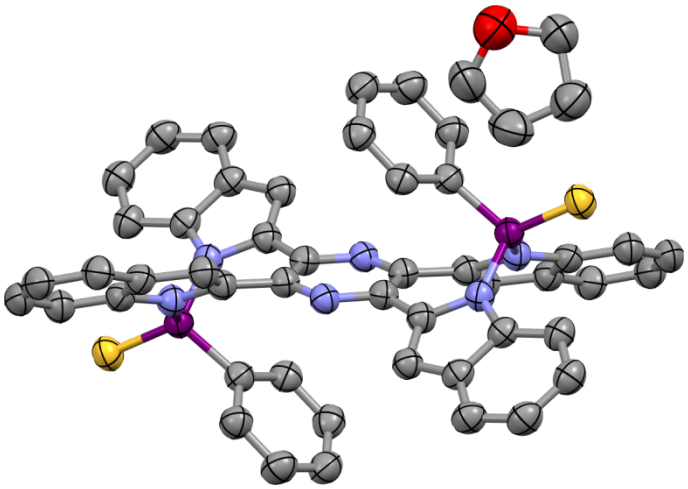


Figure S7. Crystal structure of **3St**: at 50% probability level (hydrogen atoms are omitted for clarity)

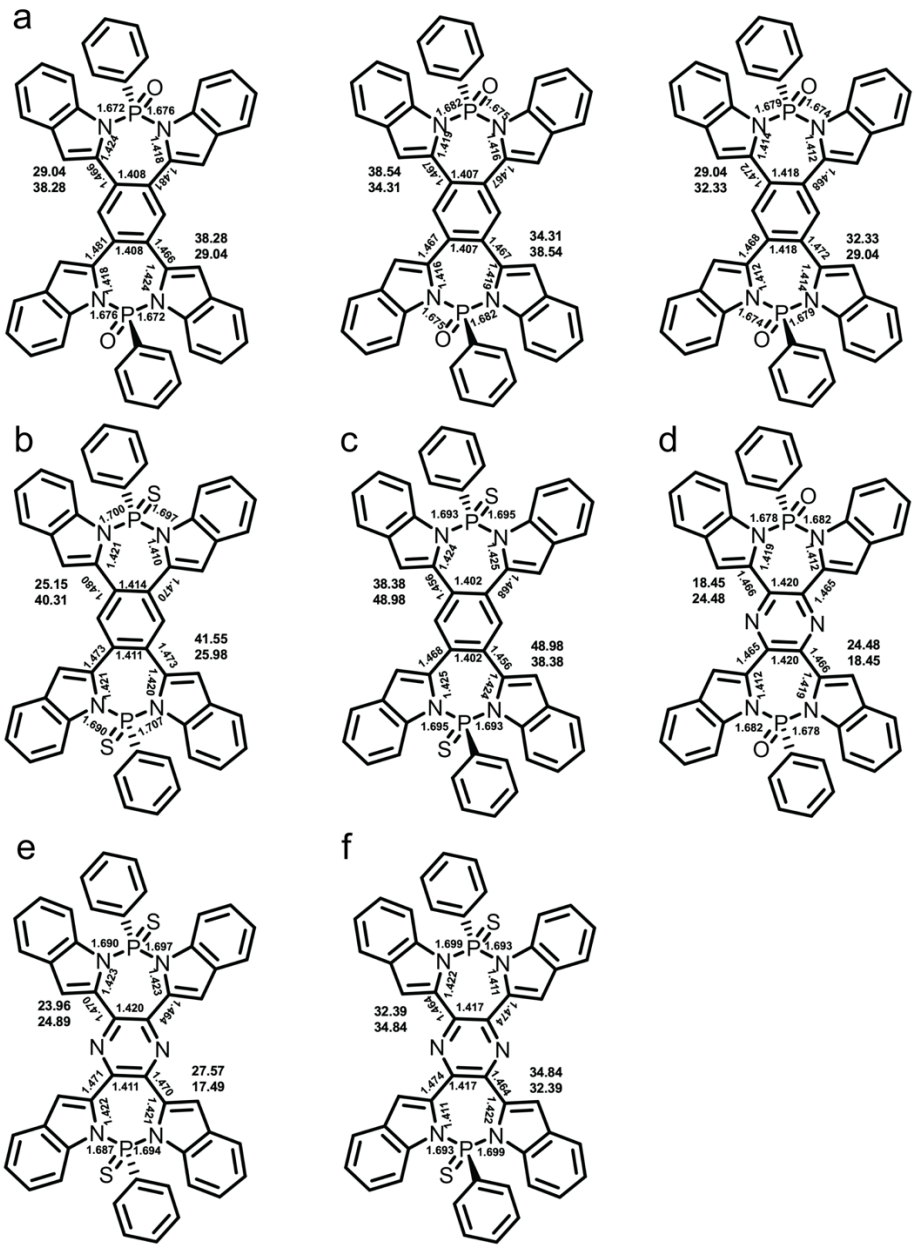


Figure S8. Bond length (Å) and torsion angles (º, between central benzene and indole) of (a) **2Ot**, (b) **2Sc**, (c) **2St**, (d) **3Oc**, (de) **3Sc**, and (f) **3St** in the single crystals.

Table S1. Crystal data and structure refinement for **2c**.

Using Olex2,[S3] the structure was solved by Direct Methods (ShelXT)[S4] and refined with ShelXL[S5] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. The voids (440Å^3) contain 1 disordered CH_3CH_2OH. However, a satisfactory disorder model for the solvent was not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density (100e-).[S6]

Compound	**2c**
Empirical Formula	$C_{50}H_{32}N_4P_2$
Formula Wright	750.73
Temperature / K	149.99
Crystal system	monoclinic
Space group	P2/n
a/Å	11.5627(8)
b/Å	11.9783(9)
c/Å	16.2773(12)
α/ °	90
β/ °	106.758(2)
γ/ °	90
Volume / Å^3	2158.7(3)
Z	2
ρ_{calc} g/cm^3	1.155
μ / mm^{-1}	0.138
F(000)	780.0
Crystal size / mm^3	0.20×0.15×0.10
Radiation	MoKα (λ = 0.71073)
2θ range for data collection / °	5.01 to 53.83
Index ranges	-14 ⩽ h ⩽ 14, -14 ⩽ k ⩽ 14, -20 ⩽ l ⩽ 20
Reflections collected	36182
Independent reflections	4428[R_{int} = 0.0627, R_{sigma} = 0.0324]
Data/restraints/parameters	4428/0/253
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.1030
Final R indexes [all data]	R_1 = 0.0582, wR_2 = 0.1121
Largest diff. peak/hole -3 (e. Å)	0.22/-0.35

Table S2. Crystal data and structure refinement for **2Ot**.

Using Olex2,[S3] the structure was solved by Direct Methods (ShelXT)[S4] and refined with ShelXL[S5] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. The voids (1071Å^3) contain 1 disordered C_4H_8O. However, a satisfactory disorder model for the solvent was not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density (263e-).[S6]

Compound	**2Ot**
Empirical Formula	$C_{50}H_{32}N_4O_2P_2$
Formula Wright	782.74
Temperature / K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	14.7824(9)
b/Å	16.2853(10)
c/Å	17.2541(11)
α/ °	71.492(3)
β/ °	64.708(3)
γ/ °	85.731(3)
Volume / Å^3	3552.2(4)
Z	3
ρ_{calc} g/cm^3	1.098
μ / mm^{-1}	0.132
F(000)	1218.0
Crystal size / mm^3	0.20×0.15×0.10
Radiation	MoKα (λ = 0.71073)
2θ range for data collection / °	4.38 to 53.016
Index ranges	-18 ⩽ h ⩽ 18, -20 ⩽ k ⩽ 20, -21 ⩽ l ⩽ 21
Reflections collected	75856
Independent reflections	14647 [R_{int} = 0.0792, R_{sigma} = 0.0559]
Data/restraints/parameters	14647/0/784
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0527, wR_2 = 0.1430
Final R indexes [all data]	R_1 = 0.0858, wR_2 = 0.1610
Largest diff. peak/hole -3 (e. Å)	0.35/-0.44

Table S3. Crystal data and structure refinement for **3Oc**.

Using Olex2,[S3] the structure was solved by Direct Methods (ShelXT)[S4] and refined with ShelXL[S5] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. The voids (816Å^3) contain 1 disordered CH_3CH_2OH. However, a satisfactory disorder model for the solvent was not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density (214e-).[S6]

Compound	**3Oc**
Empirical Formula	$C_{48}H_{30}N_6O_2P_2$
Formula Wright	784.72
Temperature / K	155.36
Crystal system	monoclinic
Space group	C2/c
a/Å	15.6939(9))
b/Å	21.6201(13)
c/Å	12.6481(8)
α/ °	90
β/ °	96.801(2)
γ/ °	90
Volume / Å^3	4261.3(4)
Z	4
ρ_{calc} g/cm^3	1.223
μ / mm^{-1}	0.148
F(000)	1624.0
Crystal size / mm^3	0.20×0.15×0.10
Radiation	MoKα (λ = 0.71073)
2θ range for data collection / °	4.346 to 52.91
Index ranges	-19 ⩽ h ⩽ 19, -27 ⩽ k ⩽ 27, -15 ⩽ l ⩽ 15
Reflections collected	55519
Independent reflections	4385 [R_{int} = 0.0852, R_{sigma} = 0.0315]
Data/restraints/parameters	4385/0/262
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0426, wR_2 = 0.1063
Final R indexes [all data]	R_1 = 0.0596, wR_2 = 0.1157
Largest diff. peak/hole -3 (e. Å)	0.24/-0.40

Table S4. Crystal data and structure refinement for **2Sc**.

Using Olex2,[S3] the structure was solved by Direct Methods (ShelXT)[S4] and refined with ShelXL[S5] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. The voids (1900Å³) contain 1 disordered CH_2Cl_2. However, a satisfactory disorder model for the solvent was not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density (304e-).[S6]

Compound	**2Sc**
Empirical Formula	$C_{50}H_{32}N_4P_2S_2$
Formula Wright	814.85
Temperature / K	150.0
Crystal system	monoclinic
Space group	C2/c
a/Å	23.4279(13)
b/Å	24.5056(13)
c/Å	16.8462(9)
α/°	90
β/°	114.755(2)
γ/°	90
Volume / Å^3	8782.9(8)
Z	8
ρ_{calc} g/cm^3	1.232
μ / mm^{-1}	2.087
F(000)	3376.0
Crystal size / mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range for data collection / °	5.5 to 149.138
Index ranges	-29 ⩽ h ⩽ 29, -29 ⩽ k ⩽ 30, -20 ⩽ l ⩽ 20
Reflections collected	36671
Independent reflections	8960 [R_{int} = 0.0408, R_{sigma} = 0.0381]
Data/restraints/parameters	8960/0/523
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0696, wR_2 = 0.1842
Final R indexes [all data]	R_1 = 0.0732, wR_2 = 0.1915
Largest diff. peak/hole-3 (e. Å)	0.80/-0.31

Table S5. Crystal data and structure refinement for **2St**.

Using Olex2,[S3] the structure was solved by Direct Methods (ShelXT)[S4] and refined with ShelXL[S5] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. The voids (1224Å³) contain 0.8 disordered C_4H_8O. However, a satisfactory disorder model for the solvent was not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density (256e-).[S6]

Compound	**2St**
Empirical Formula	$C_{25}H_{16}N_2PS$
Formula Wright	407.43
Temperature / K	150.15
Crystal system	monoclinic
Space group	C2/c
a/Å	30.400(3)
b/Å	9.1777(9)
c/Å	17.2567(14)
α/ °	90
β/ °	92.615(4)
γ/ °	90
Volume / Å^3	4809.6(8)
Z	8
ρ_{calc} g/cm^3	1.125
μ / mm^{-1}	1.249
F(000)	1688.0
Crystal size / mm^3	0.2 × 0.15 × 0.1
Radiation	GaKα (λ = 1.34139)
2θ range for data collection / °	9.778 to 116.45
Index ranges	-38 ⩽ h ⩽ 37, -11 ⩽ k ⩽ 11, -14 ⩽ l ⩽ 21
Reflections collected	29209
Independent reflections	4991 [R_{int} = 0.1298, R_{sigma} = 0.1009]
Data/restraints/parameters	4991/0/262
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0855, wR_2 = 0.2193
Final R indexes [all data]	R_1 = 0.1103, wR_2 = 0.2324
Largest diff. peak/hole-3 (e. Å)	0.52/-0.95

Table S6. Crystal data and structure refinement for **3Sc** (DCM).

Using Olex2,[S3] the structure was solved by Direct Methods (ShelXT)[S4] and refined with ShelXL[S5] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. The voids (1990 Å³) contain 0.9 disordered $C_2H_2Cl_2$. However, a satisfactory disorder model for the solvent was not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density (336e-).[S6]

Compound	**3Sc**
Empirical Formula	$C_{48}H_{30}N_6P_2S_2$
Formula Wright	816.84
Temperature / K	150.0
Crystal system	monoclinic
Space group	C2/c
a/Å	28.1290(9)
b/Å	12.5102(3)
c/Å	28.4072(9)
α/ °	90
β/ °	115.1160(10)
γ/ °	90
Volume / Å^3	9051.3(5)
Z	8
ρ_{calc} g/cm^3	1.199
μ / mm^{-1}	0.227
F(000)	3376.0
Crystal size / mm^3	0.2 × 0.15 × 0.12
Radiation	MoKα(λ = 0.71073)
2θ range for data collection / °	4.346 to 52.752
Index ranges	-35 ⩽ h ⩽ 35, -15 ⩽ k ⩽ 15, -35 ⩽ l ⩽ 35
Reflections collected	51774
Independent reflections	9258 [R_{int} = 0.0618, R_{sigma} = 0.0388]
Data/restraints/parameters	9258/0/523
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1445
Final R indexes [all data]	R_1 = 0.0710, wR_2 = 0.1604
Largest diff. peak/hole-3 (e. Å)	0.25/-0.25

Table S7. Crystal data and structure refinement for **3St** (THF).

Using Olex2,[S3] the structure was solved by Direct Methods (ShelXT)[S4] and refined with ShelXL[S5] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model.

Compound	**3St (THF)**
Empirical Formula	$C_{56}H_{46}N_6O_2P_2S_2$
Formula Wright	961.05
Temperature / K	150.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.4368(7)
b/Å	9.9144(6)
c/Å	20.5690(12)
α/°	90
β/°	90.445(2)
γ/°	90
Volume / Å^3	2332.2(2)
Z	2
ρ_{calc} g/cm^3	1.369
μ / mm^{-1}	2.093
F(000)	1004.0
Crystal size / mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range for data collection / °	8.818 to 149.634
Index ranges	-14 ≤ h ≤ 14, -12 ≤ k ≤ 12, -25 ≤ l ≤ 25
Reflections collected	33911
Independent reflections	4754 [R_{int} = 0.0385, R_{sigma} = 0.0291]
Data/restraints/parameters	4754/0/307
Goodness-of-fit on F^2	1.103
Final R indexes [I>=2σ (I)]	R_1 = 0.0711, wR_2 = 0.1923
Final R indexes [all data]	R_1 = 0.0731, wR_2 = 0.1963
Largest diff. peak/hole-3 (e. Å)	0.70/-0.31

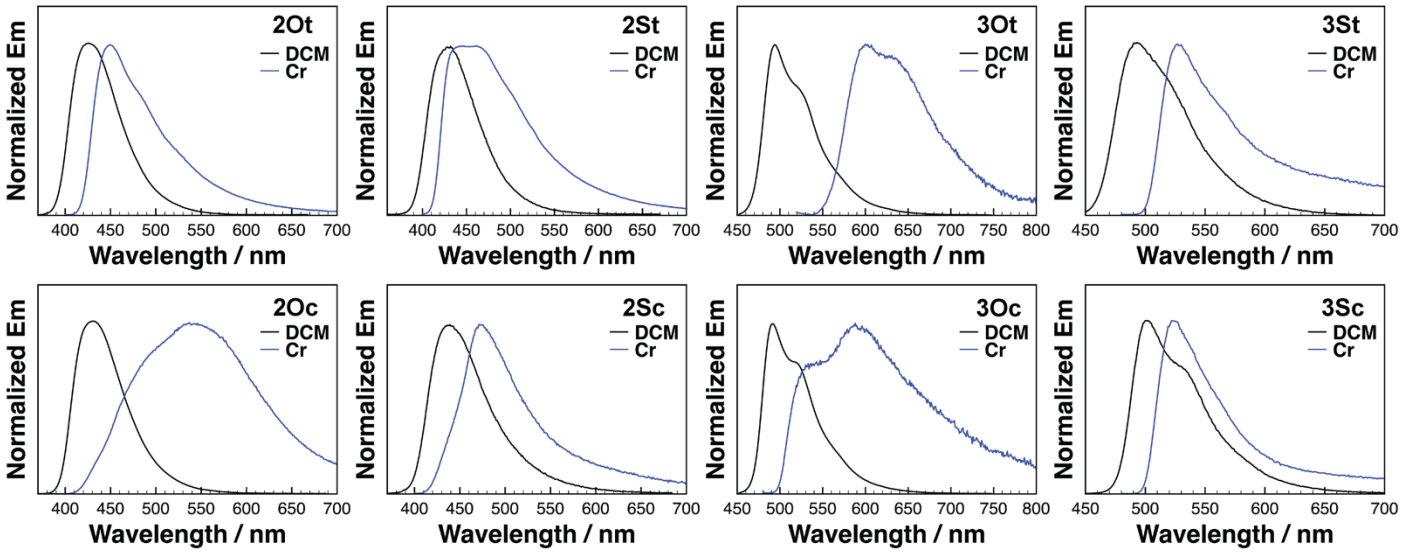


Figure S9. Emission spectra of DPP-PAHs in the solid state.

Theoretical Calculations:

Density functional theory (DFT) were employed to optimize the structures of the molecules at the ground state at the level of b31yp/6-31g(d). Time-dependent (TD) DFT were employed for the energy calculations of the molecules having the structure optimized in the ground state at the level of b31yp/6-31+g(d). The frequency of the compounds was calculated based on their optimized structures. The results show positive frequency values, which suggest that the optimized structures are indeed local minima.

Table S8. TD-DFT of DPP-PAHs.

Compound	LUMO (eV)	HOMO (eV)	S_0-S_1 Wavelength (nm) Energy gap (eV)	S_0-S_1 Oscillator strength
2Ot	-2.13	-5.65	395.85 3.52	0.4014
2Oc	-2.13	-5.58	405.69 3.46	0.0582
3Ot	-2.43	-5.58	467.73 3.15	0.2889
3Oc	-2.46	-5.55	479.10 3.09	0.2864

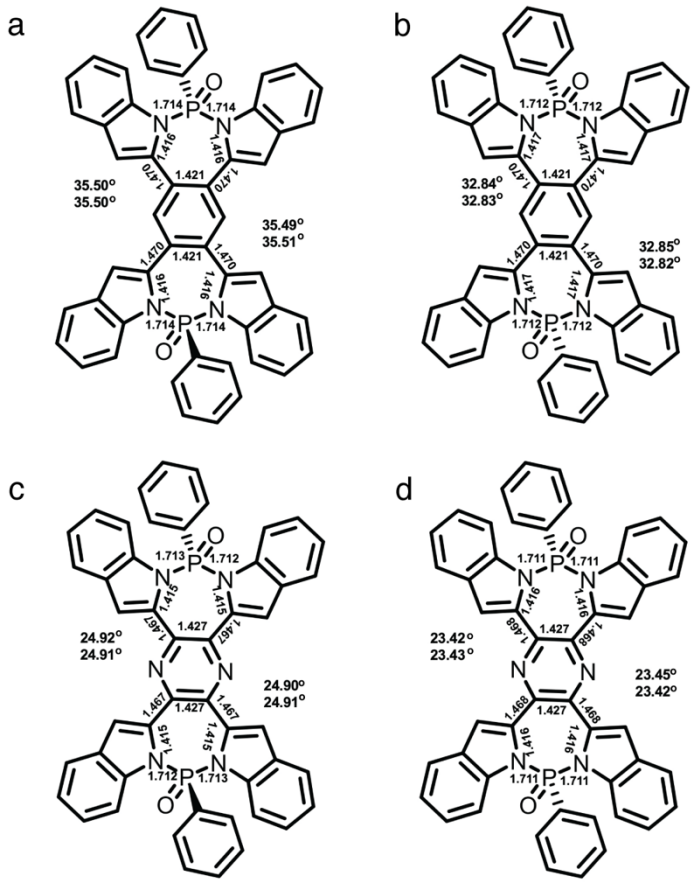


Figure S10. Bond length (Å) and torsion angles (º, between central benzene and indole) of (a) **2Ot**, (b) **2Oc**, (c) **3Ot**, and (d) **3Oc** in the optimized structures.

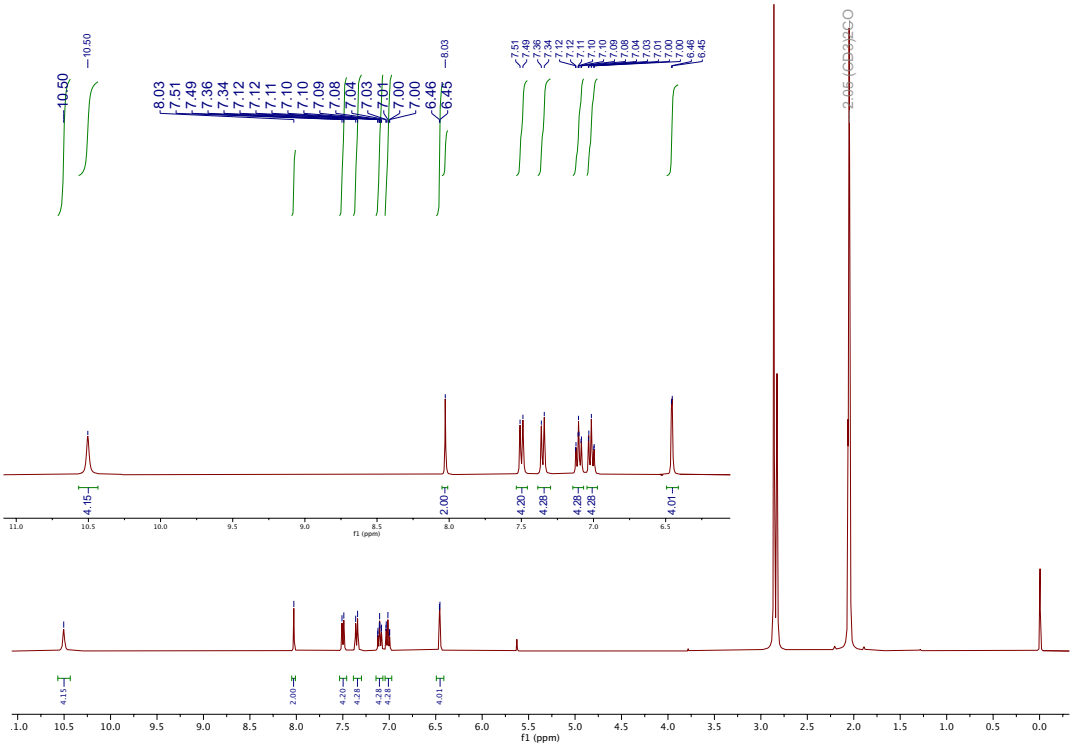


Figure S11. ^{1}H NMR spectrum (400 MHz, $(CD_3)_2CO$, 298K) of **2NH**.

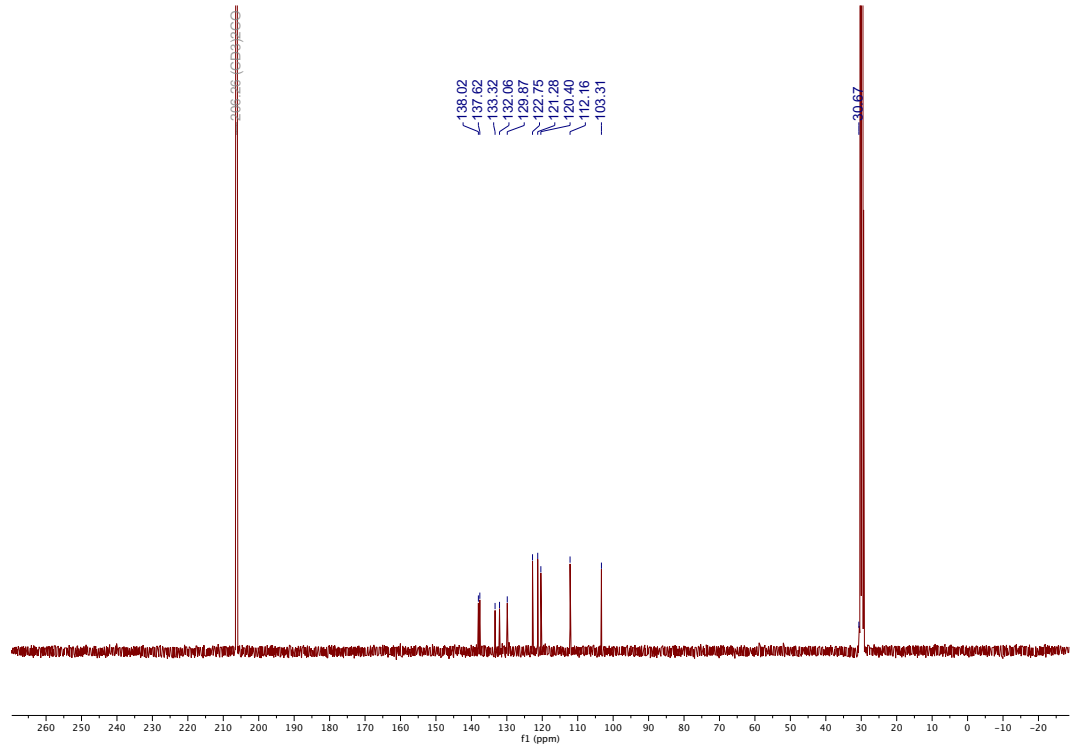


Figure S12. ^{13}C $\{^{1}H\}$ NMR spectrum (101 MHz, $(CD_3)_2CO$, 298K) of **2NH**.

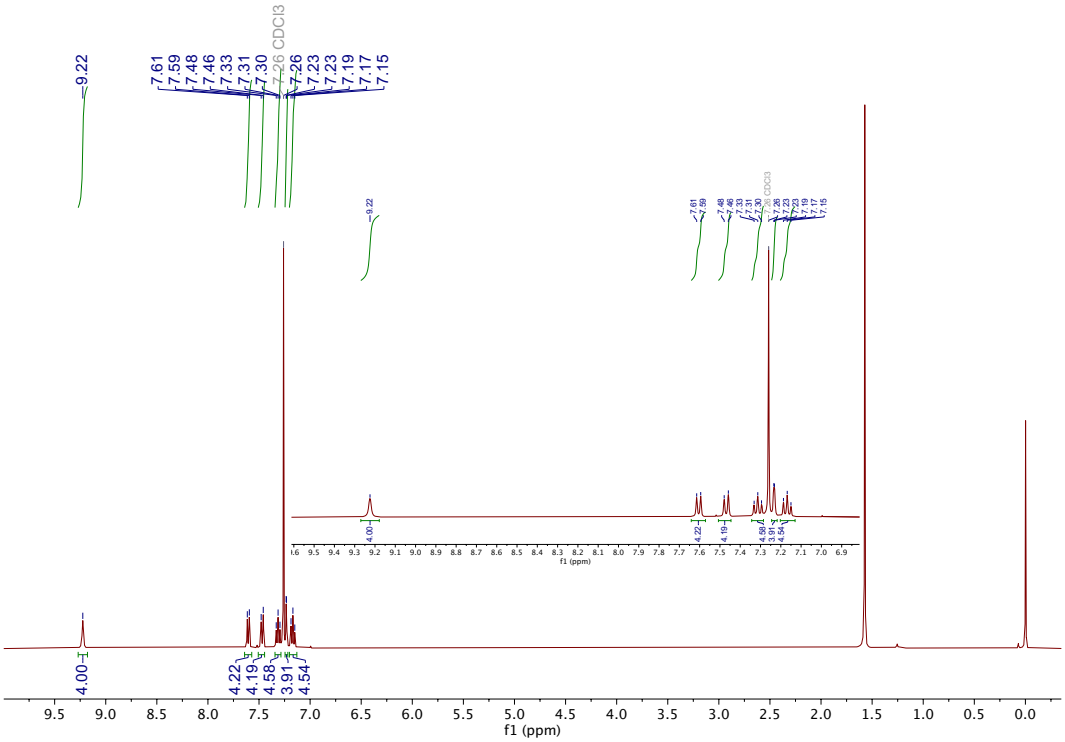


Figure S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **3NH**.

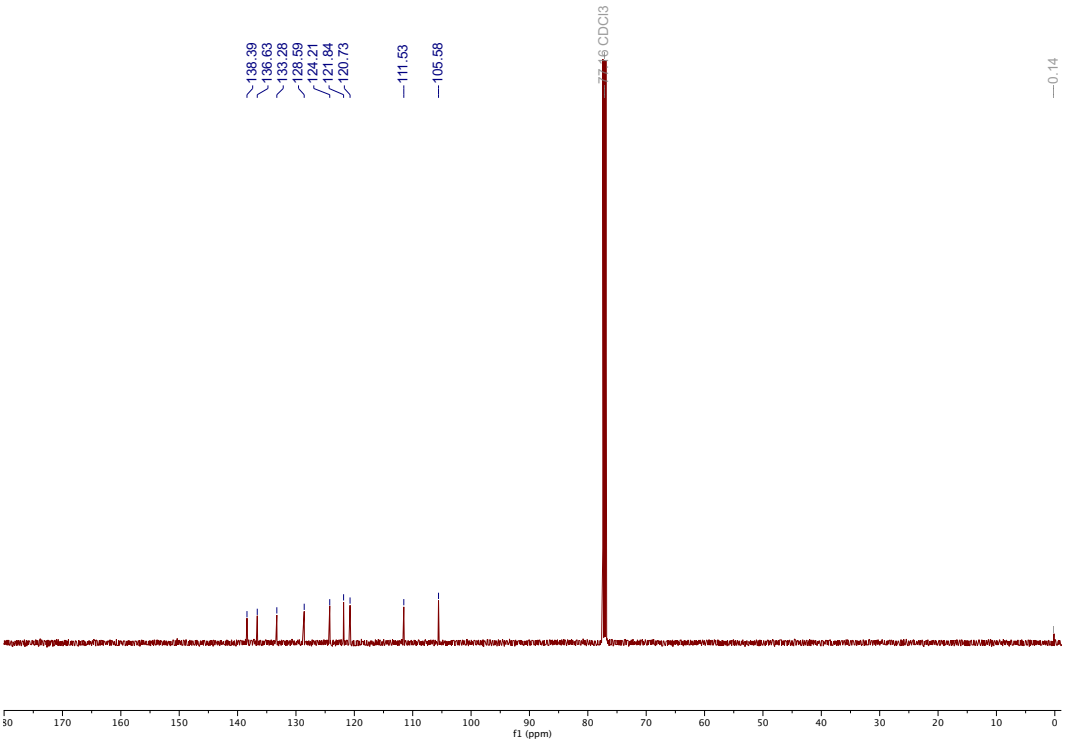


Figure S14. ^{13}C $\{^{1}$H$\}$ NMR spectrum (126 MHz, $CDCl_3$, 298K) of **3NH**.

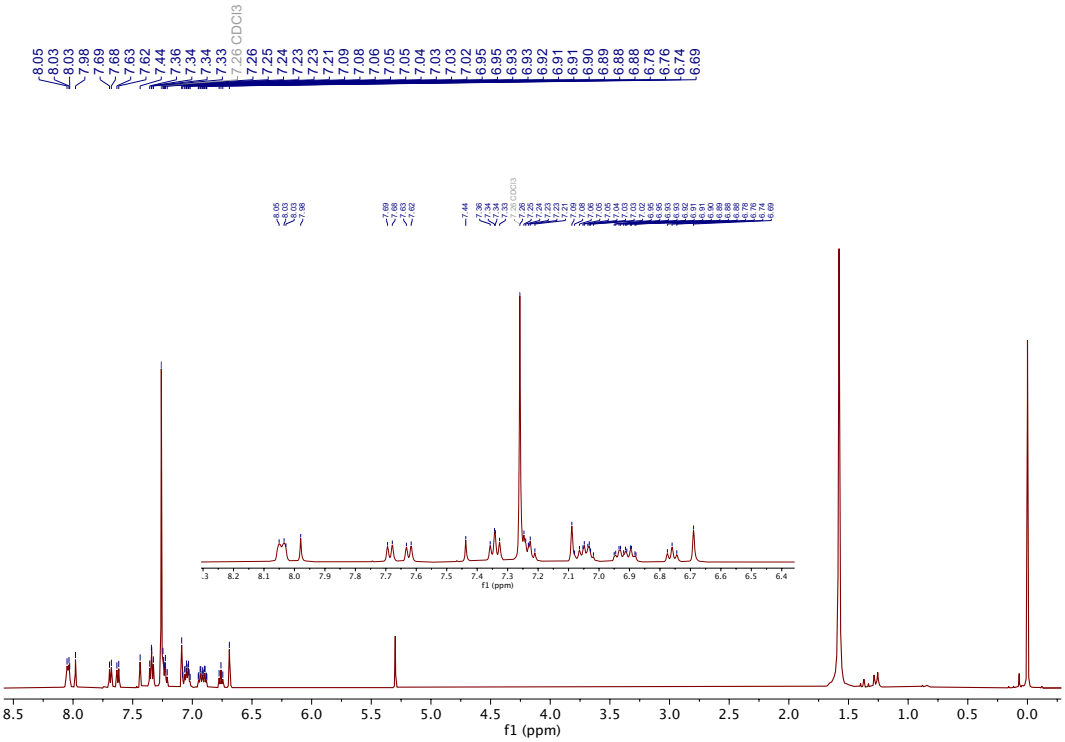


Figure S15. ^{11}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2t/c** mixture.

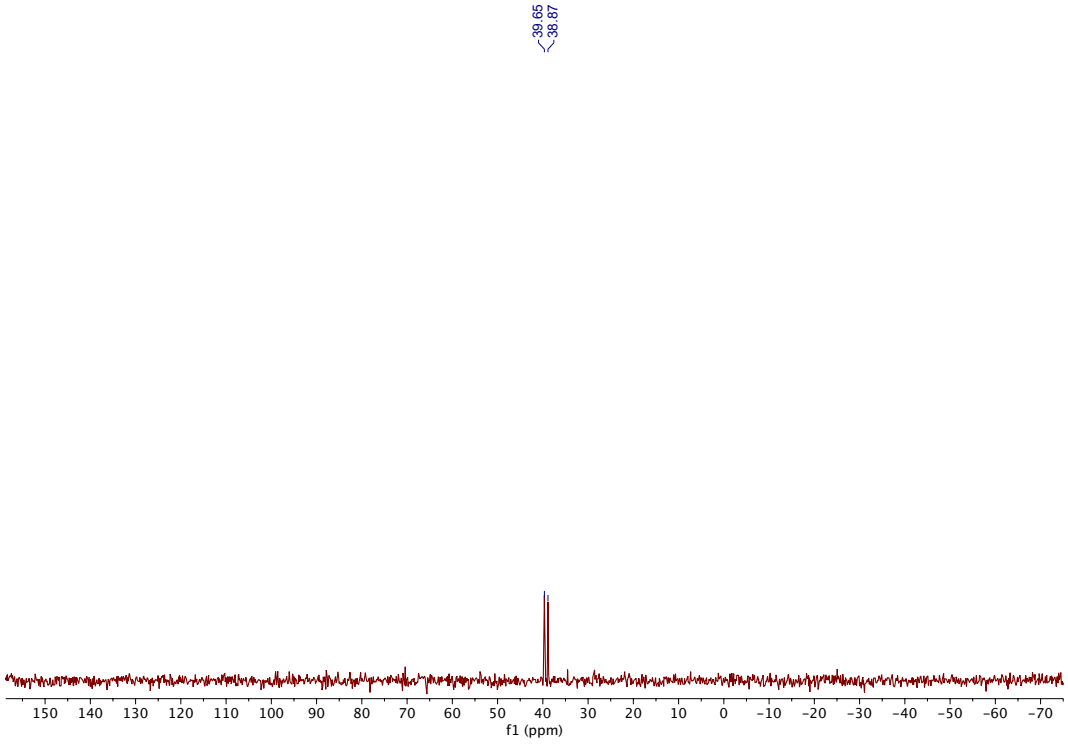


Figure S16. $^{1\ 31}$P $\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298K) of **2t/c** mixture.

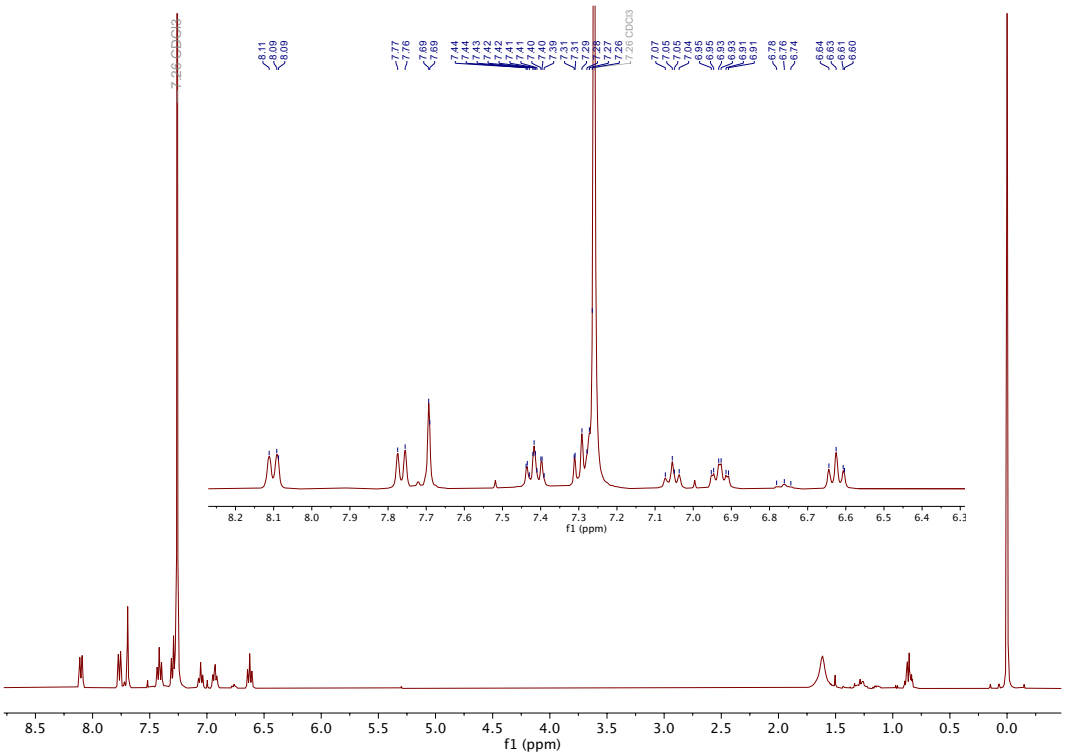


Figure S17. ^{11}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **3t/c** mixture.

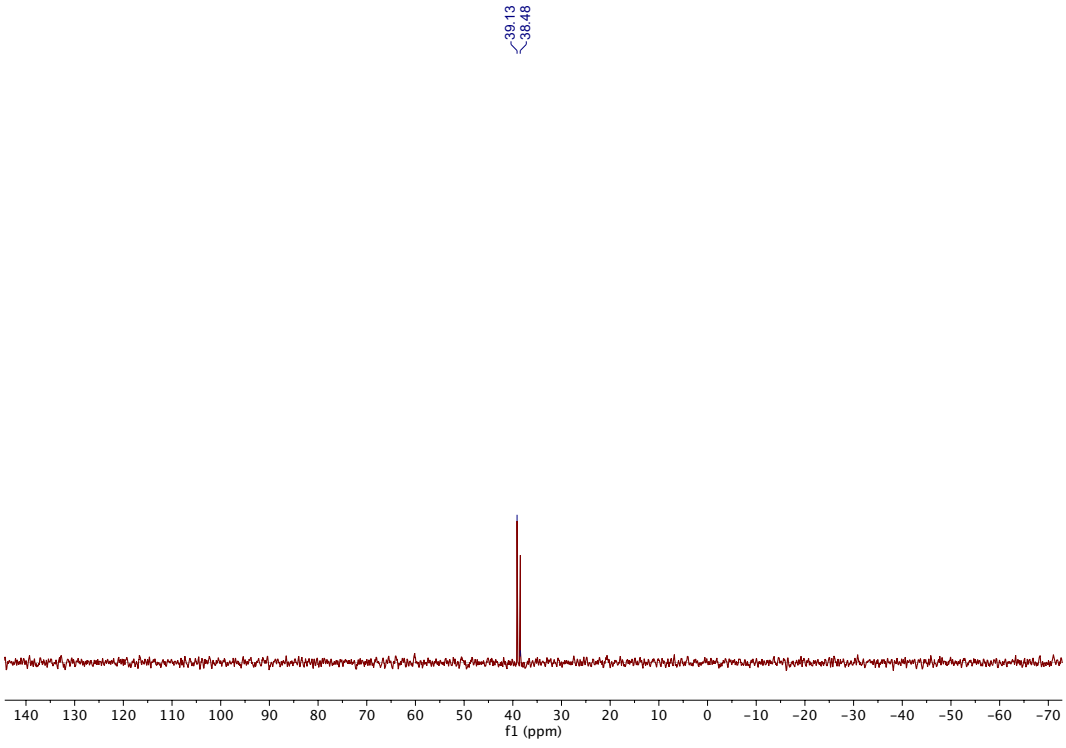


Figure S18. ^{1} ^{31}P {^{1}H} NMR spectrum (162 MHz, $CDCl_3$, 298K) of **3t/c** mixture.

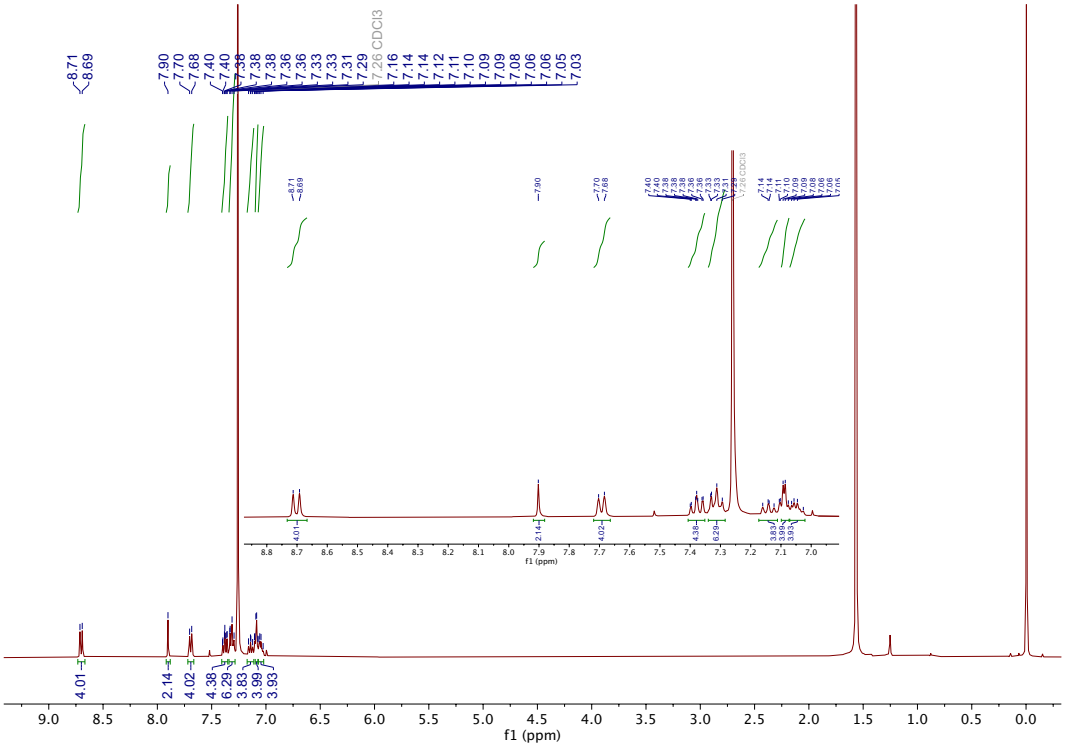


Figure S19. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **2Oc**.

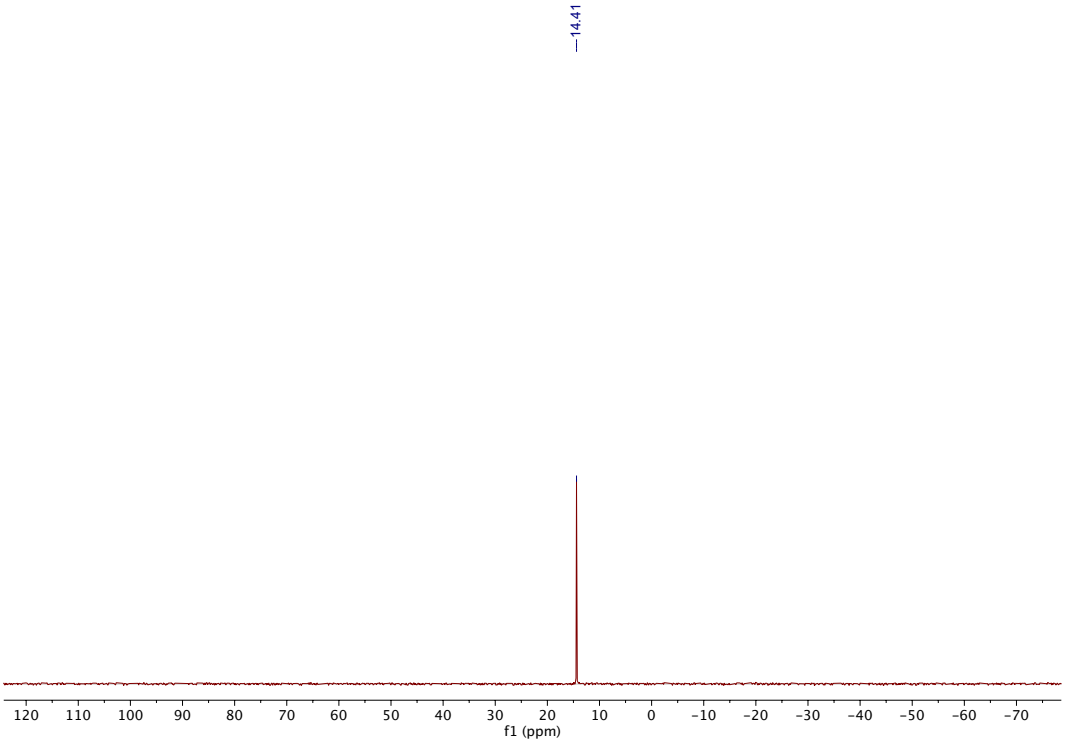


Figure S20. ^{31}P {^{1}H} NMR spectrum (162 MHz, $CDCl_3$, 298K) of **2Oc**.

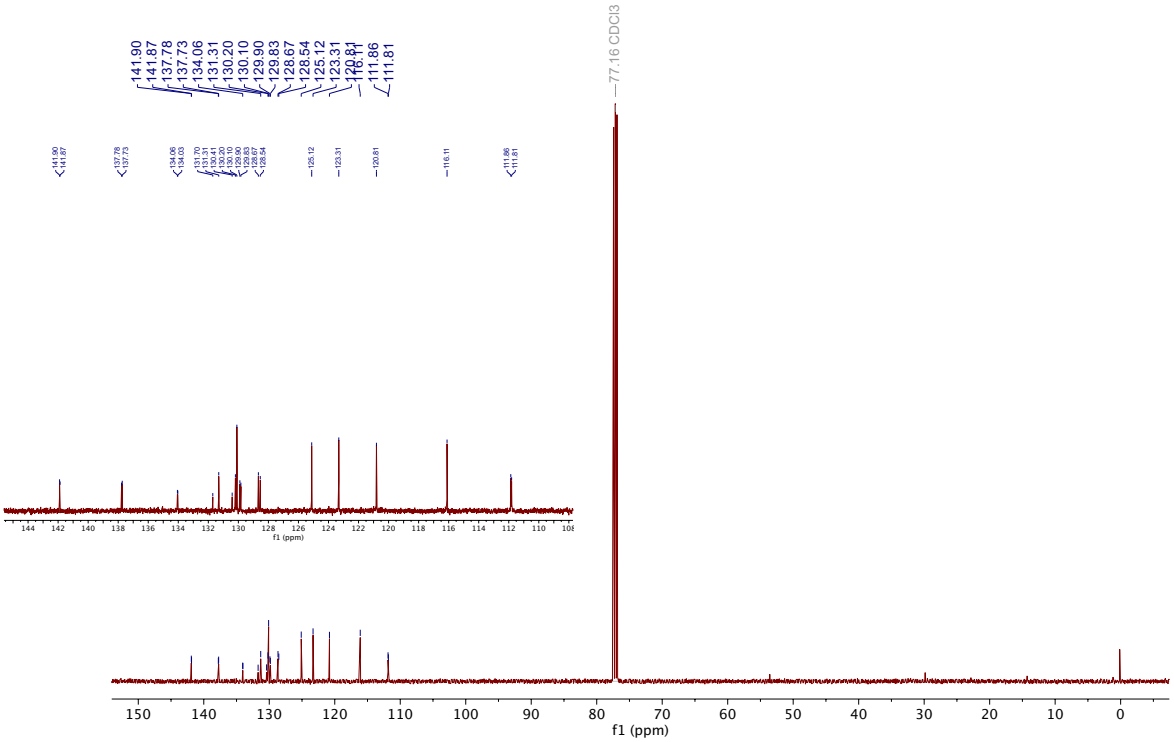


Figure S21. ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$, 298K) of **2Oc**.

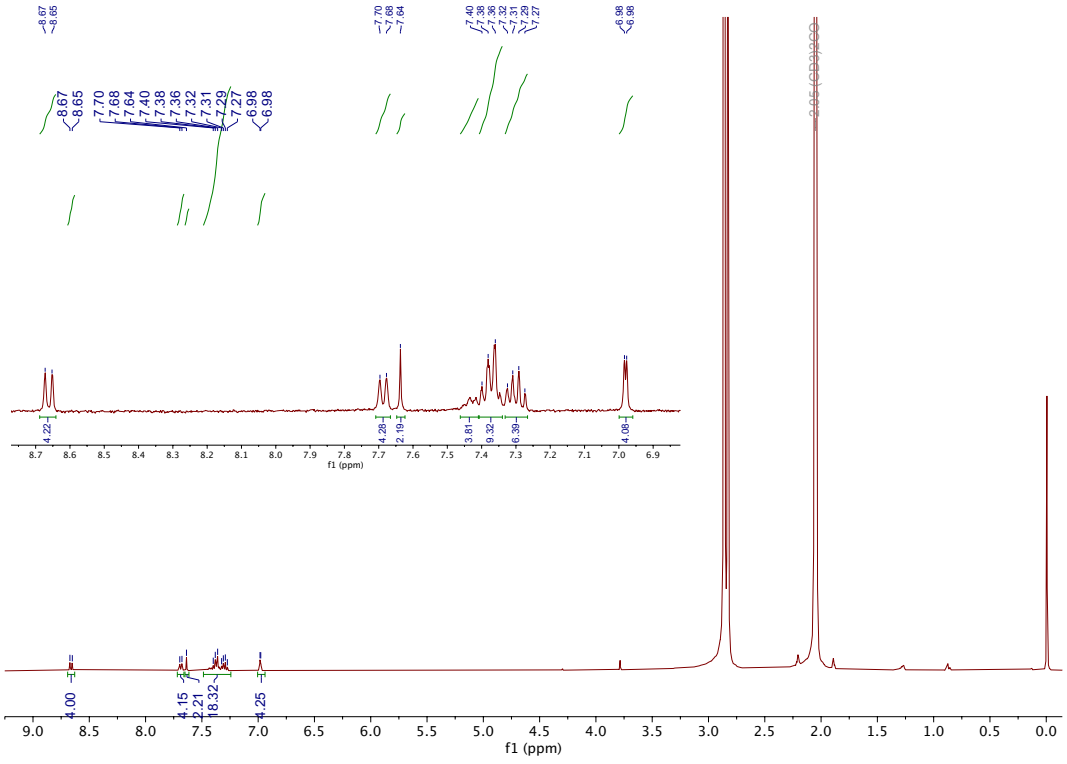


Figure S22. ^{1}H NMR spectrum (400 MHz, $(CD_3)_2CO$, 298K) of **2Ot**.

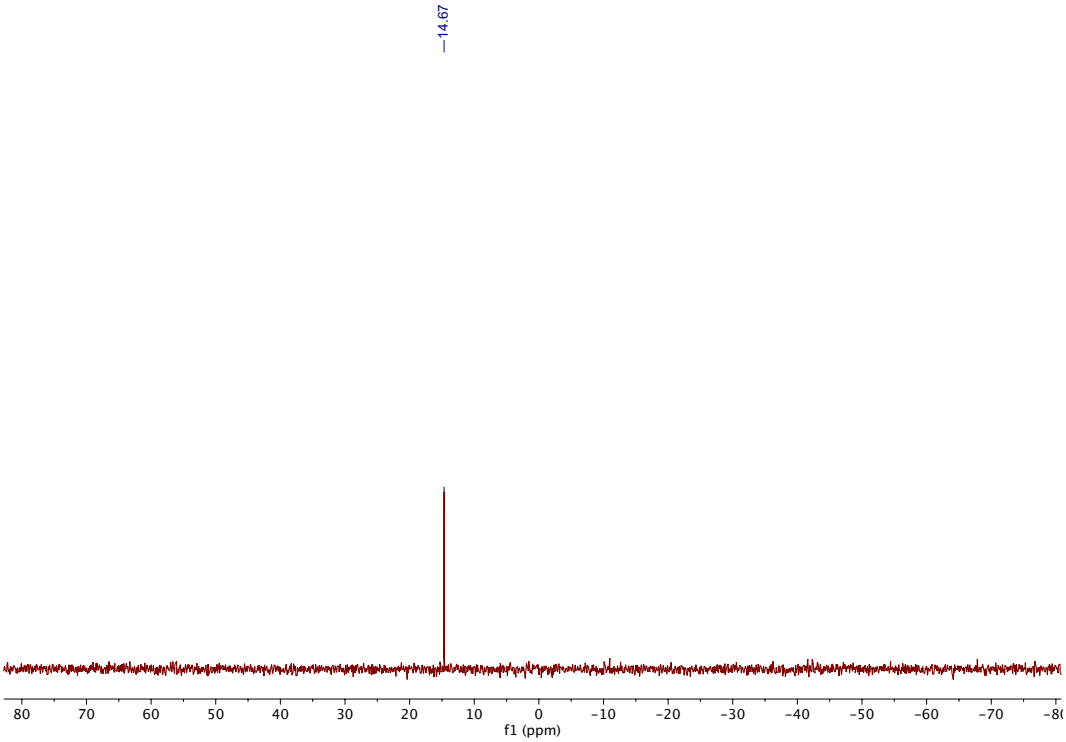


Figure S23. ^{31}P $\{^{1}H\}$ NMR spectrum (202 MHz, $CDCl_3$, 298K) of **2Ot**.

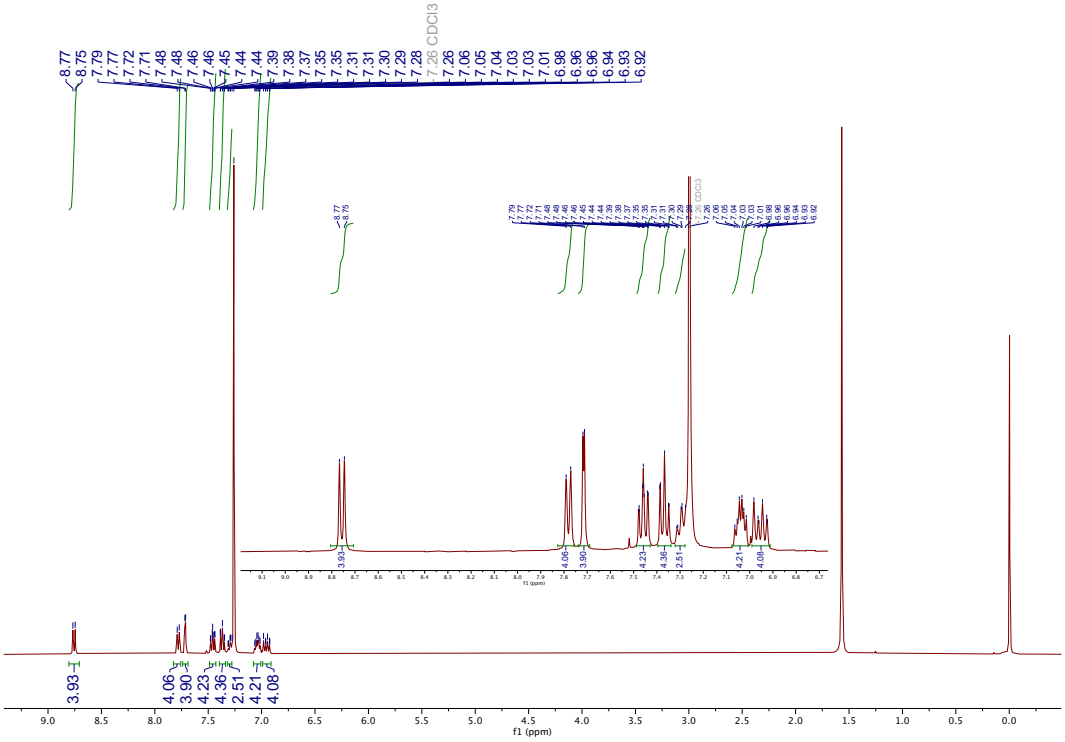


Figure S24. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of **3Oc**.

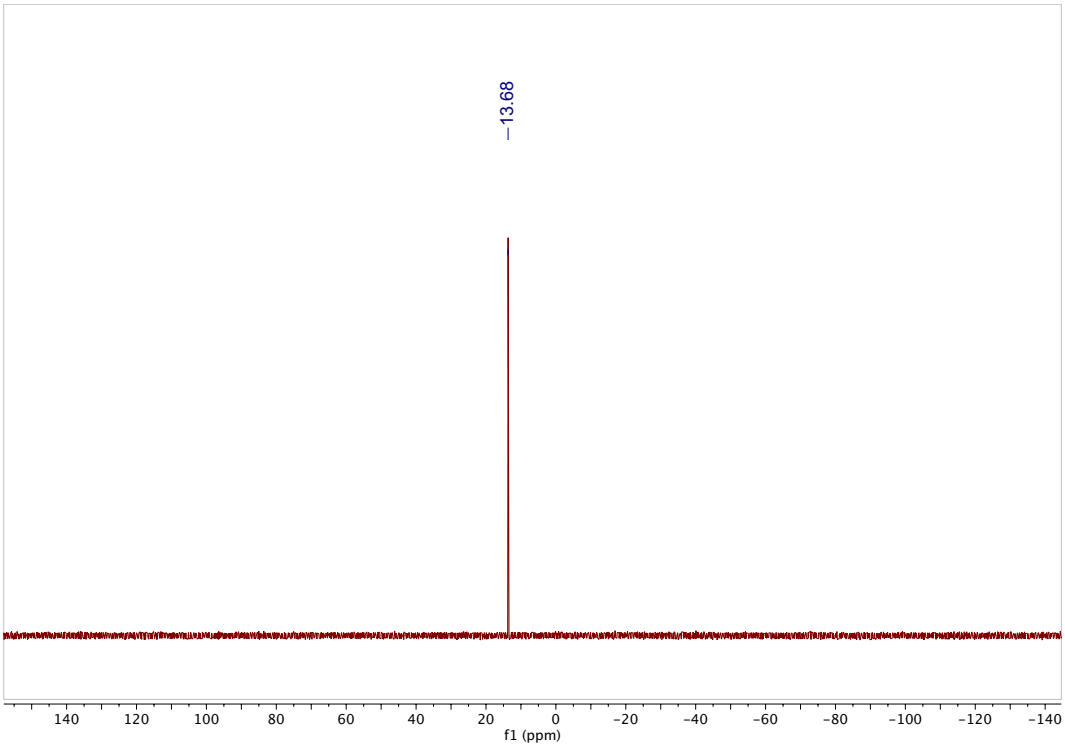


Figure S25. ^{31}P $\{^{1}H\}$ NMR spectrum (202 MHz, $CDCl_3$, 298K) of **3Oc**.

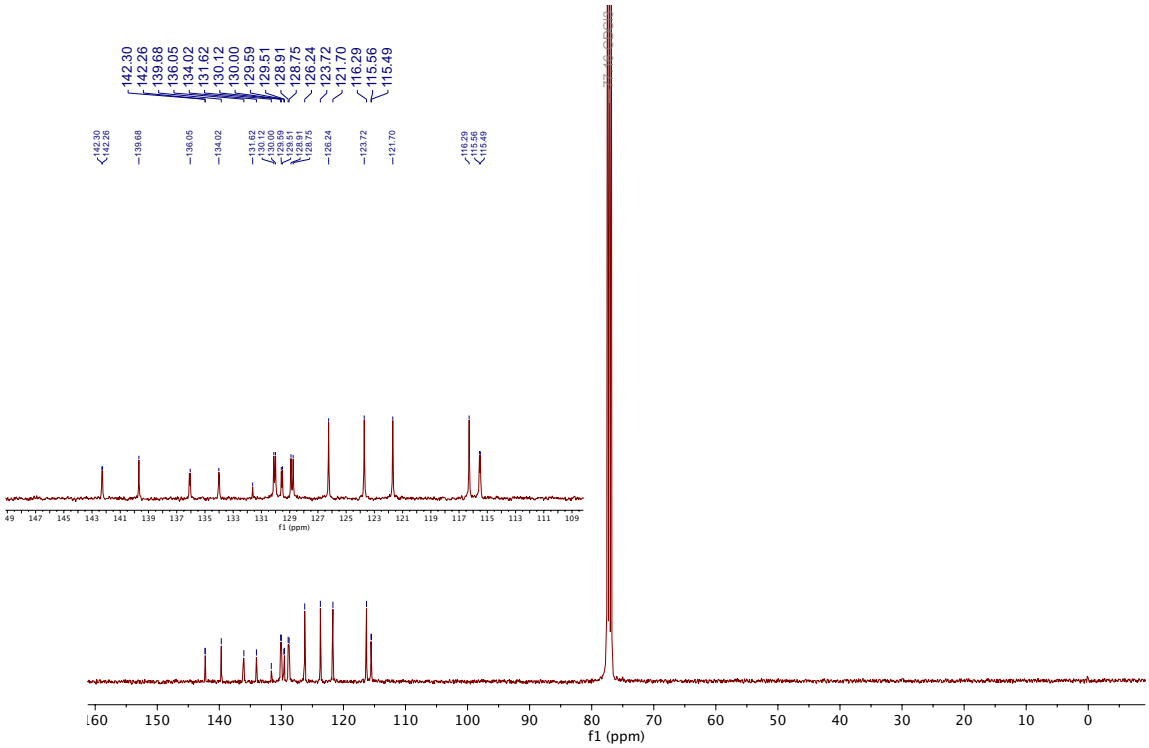


Figure S26. ^{13}C $\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298K) of **3Oc**.

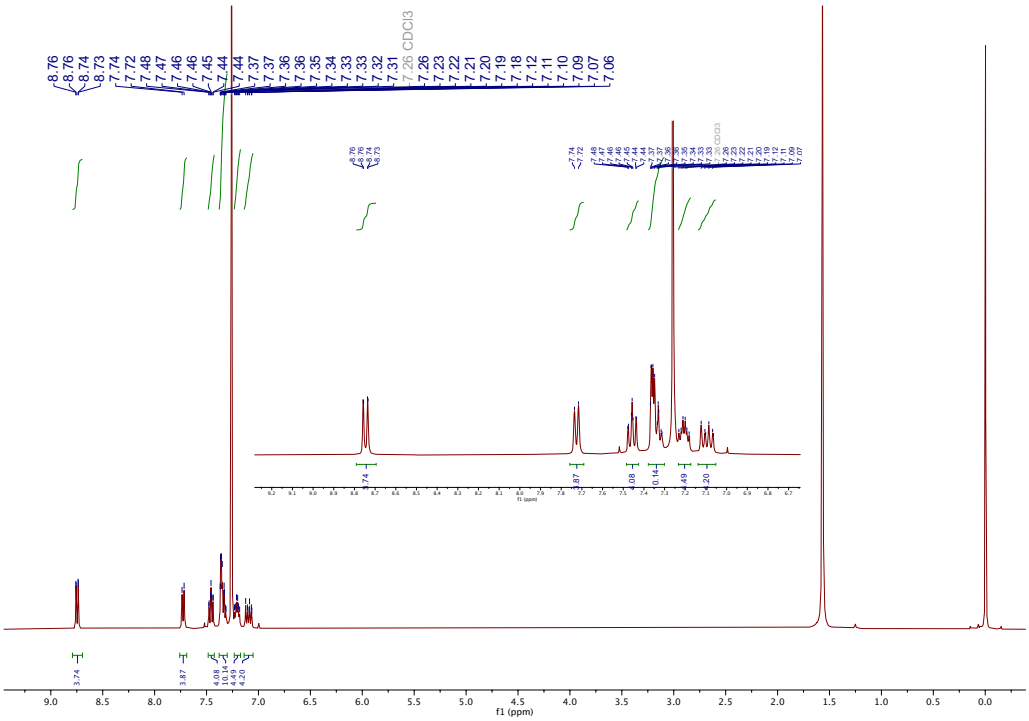


Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **3Ot**.

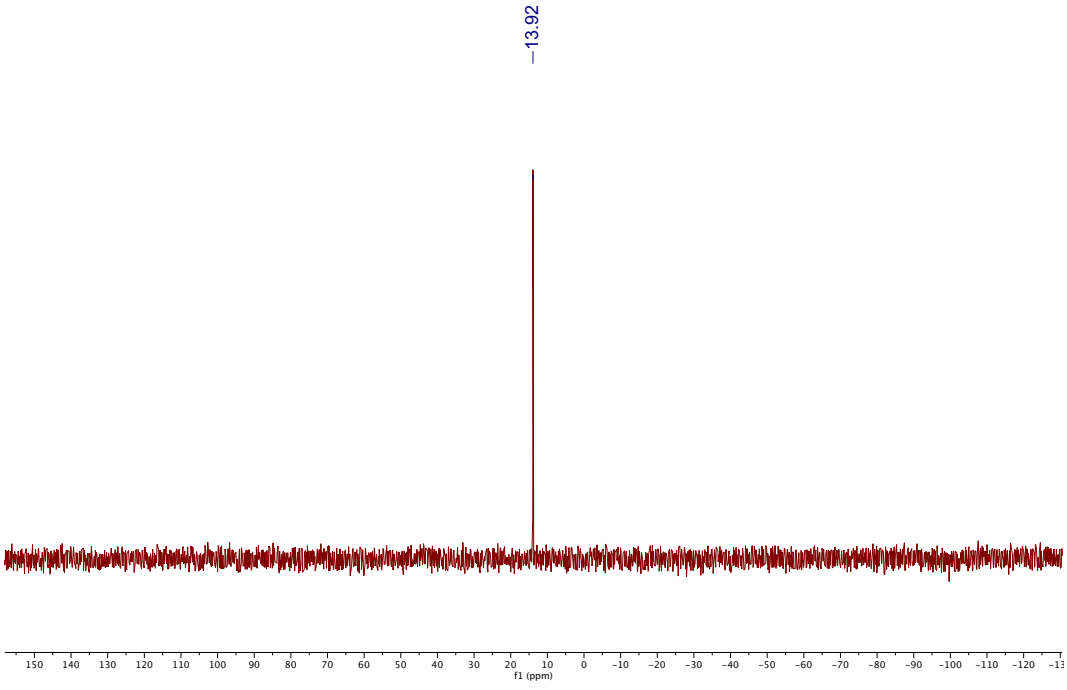


Figure S28. ^{31}P {^{1}H} NMR spectrum (162 MHz, $CDCl_3$, 298K) of **3Ot**.

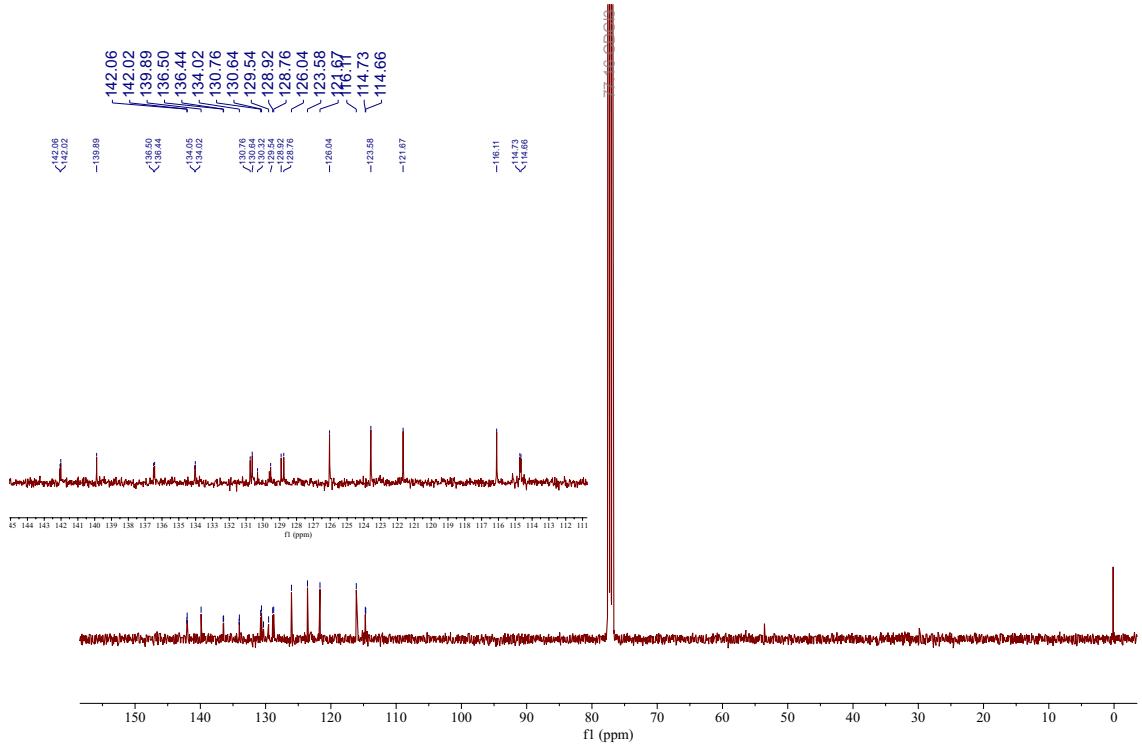


Figure S29. ^{13}C {^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 298K) of **3Ot**.

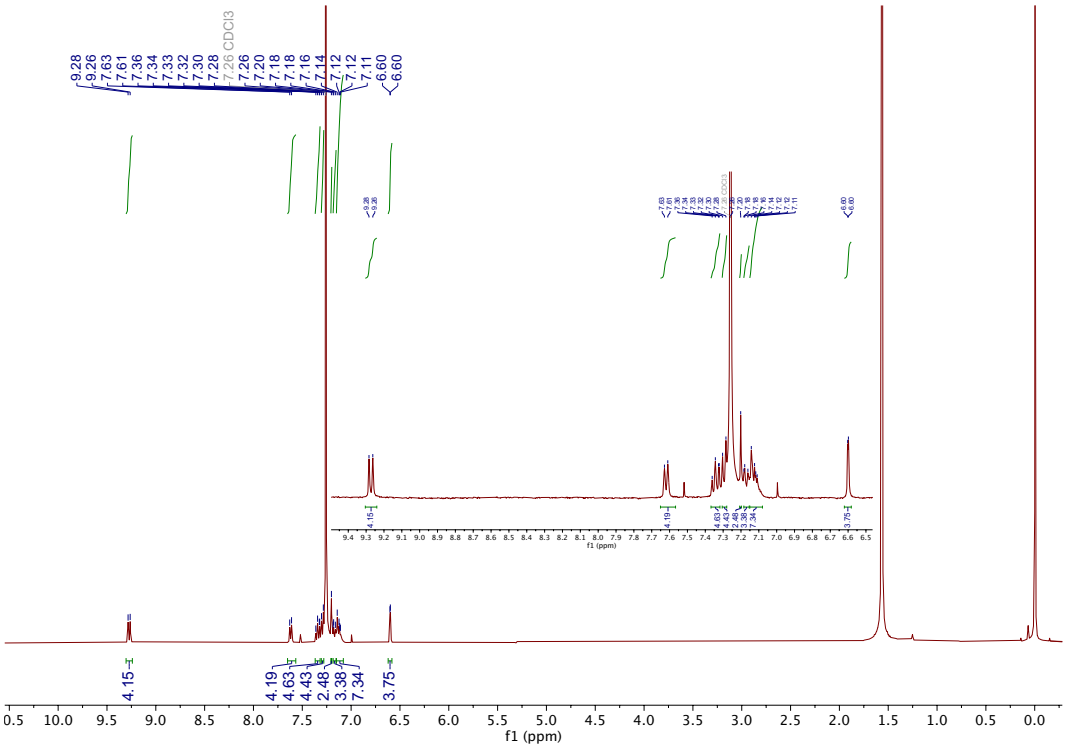


Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2St**.

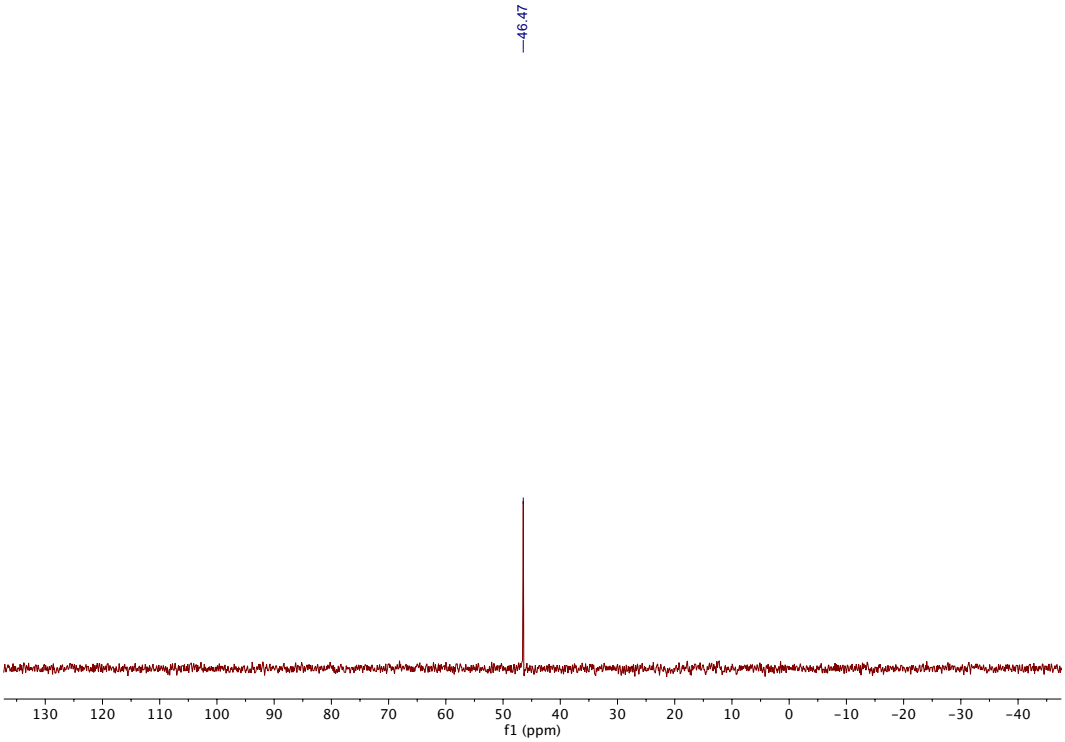


Figure S31. ^{31}P $\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298K) of **2St**.

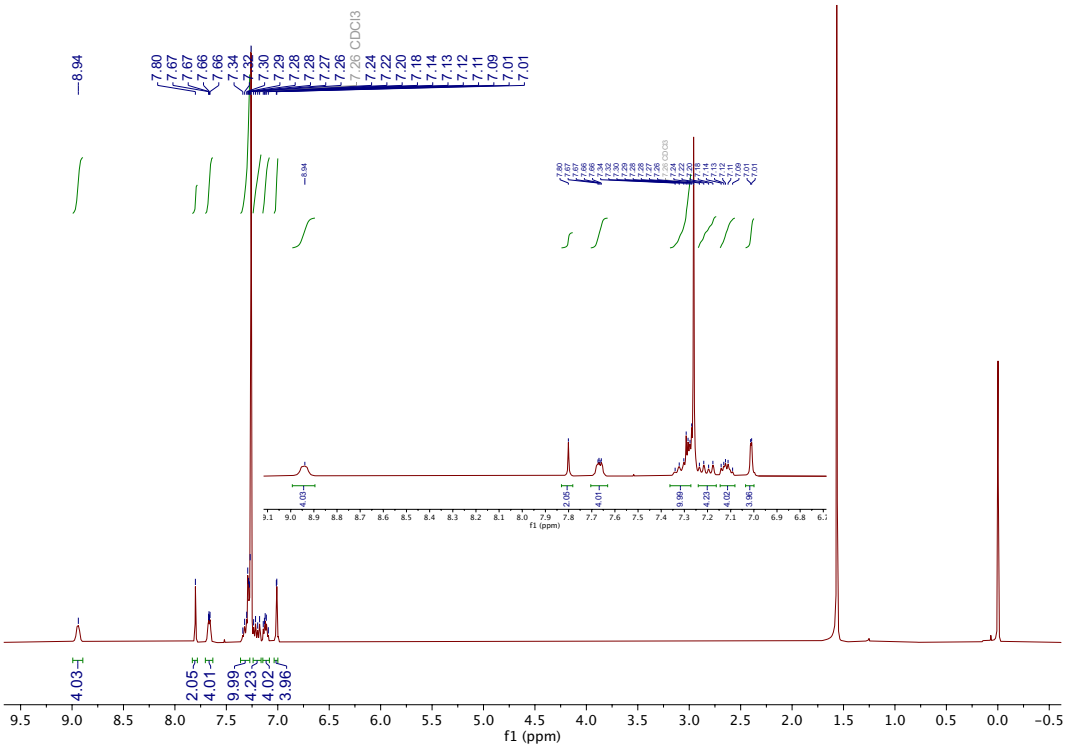


Figure S32. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2Sc**.

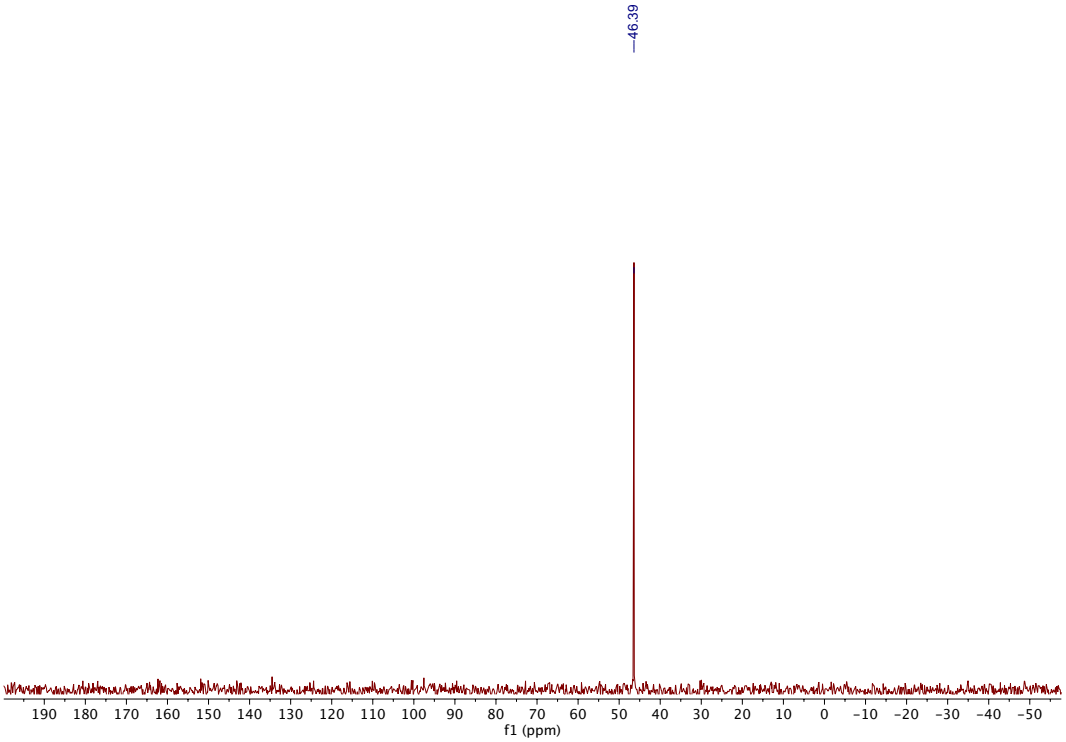


Figure S33. ^{31}P $\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298K) of **2Sc**.

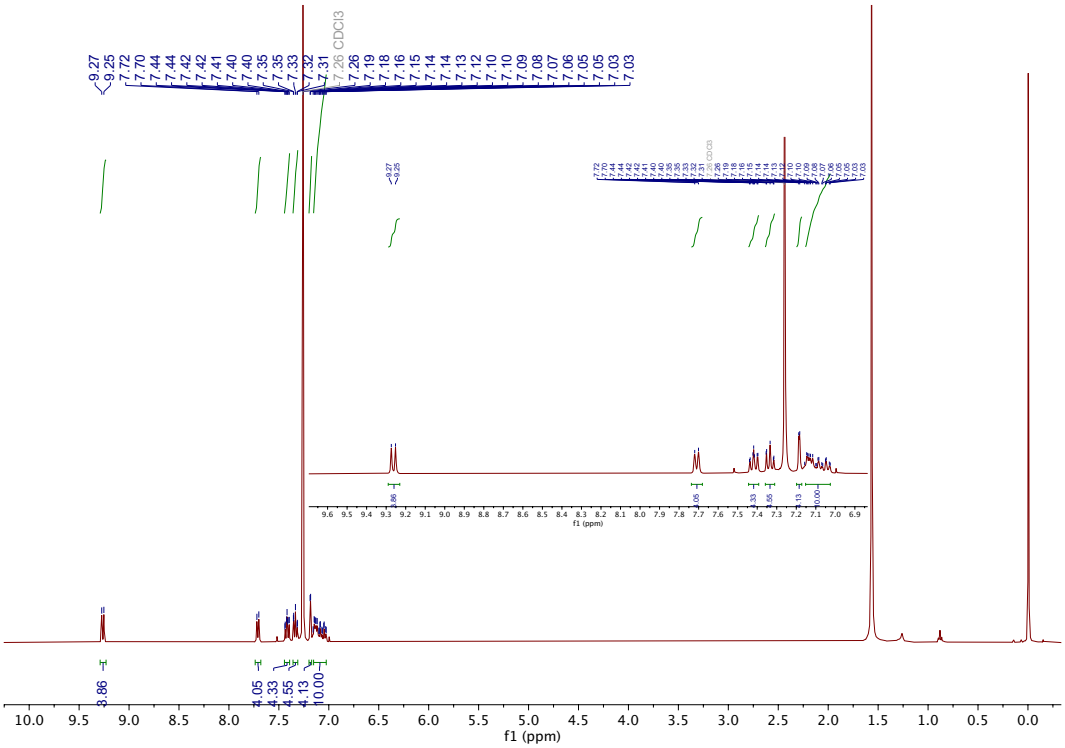


Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **3St**.

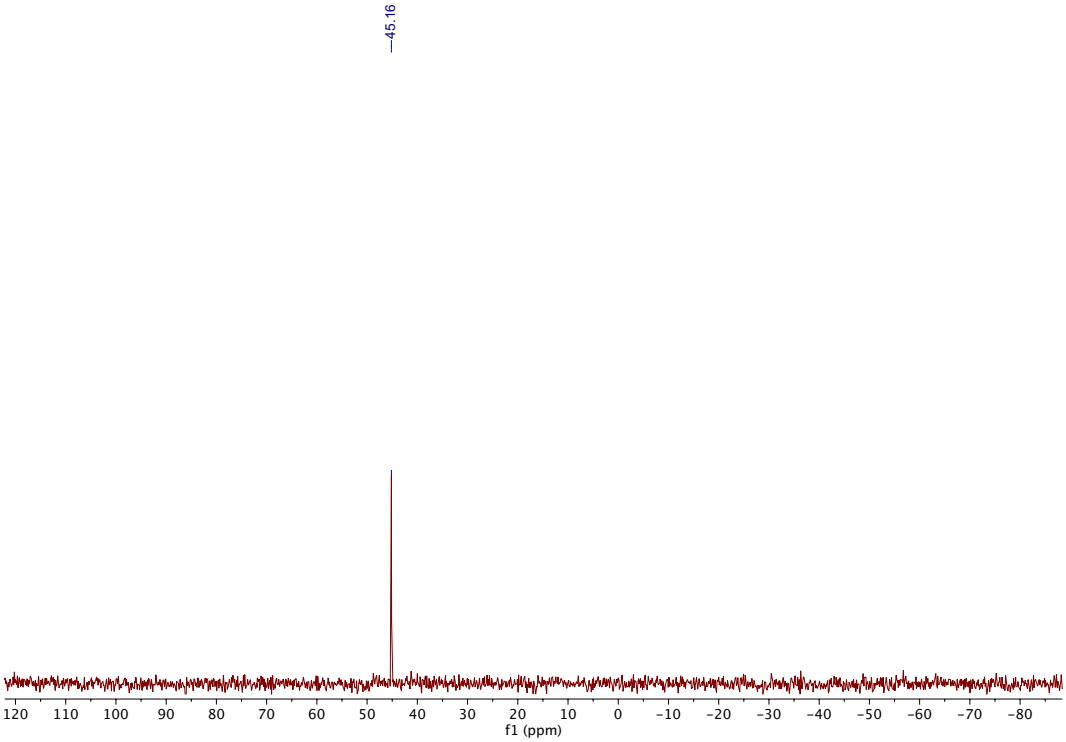


Figure S35. ^{31}P $\{^{1}H\}$ NMR spectrum (400 MHz, $CDCl_3$, 298K) of **3St**.

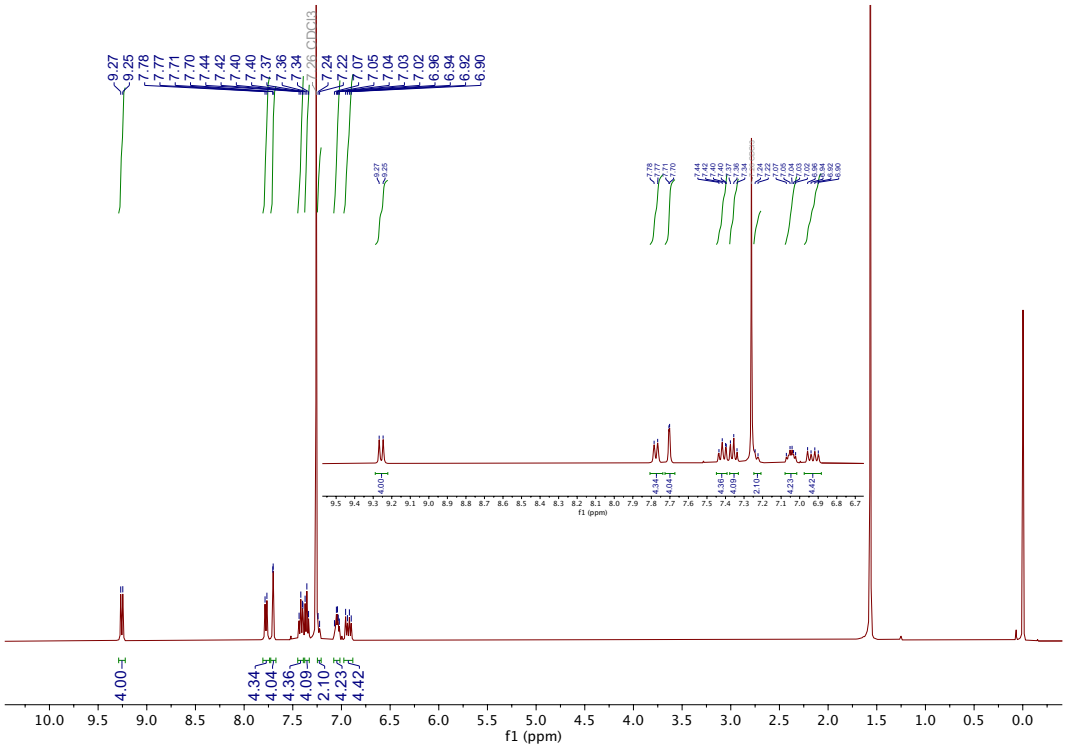


Figure S36. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **3Sc**.

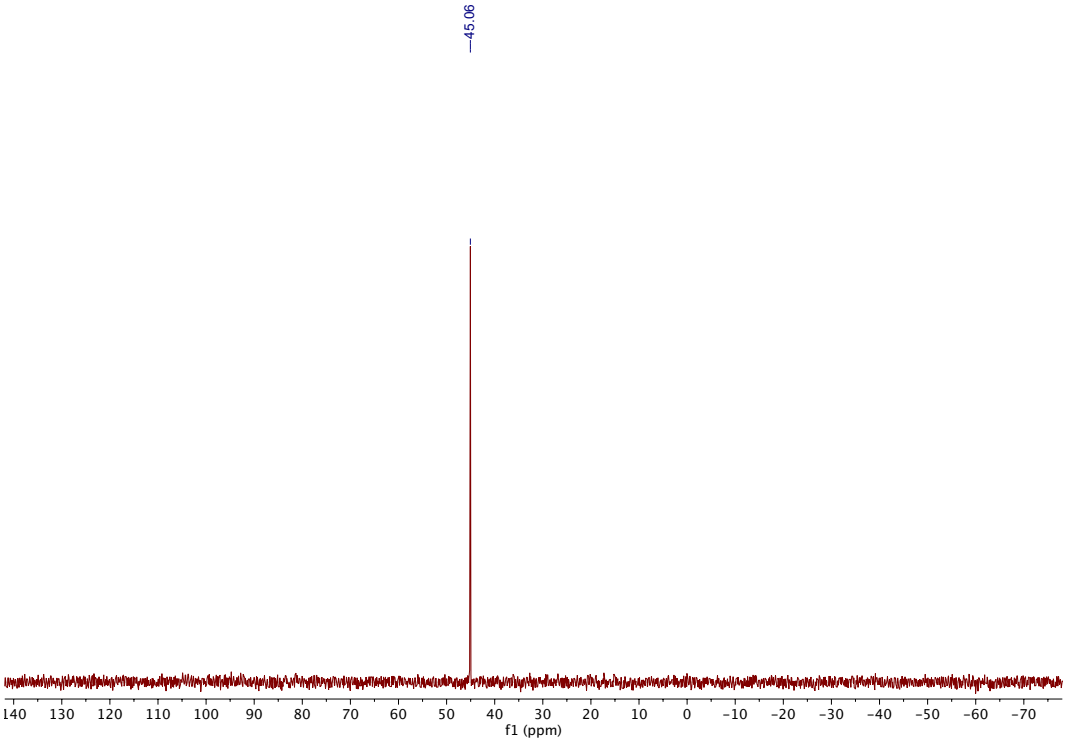


Figure S37. ^{31}P $\{^{1}H\}$ NMR spectrum (400 MHz, $CDCl_3$, 298K) of **3Sc**.

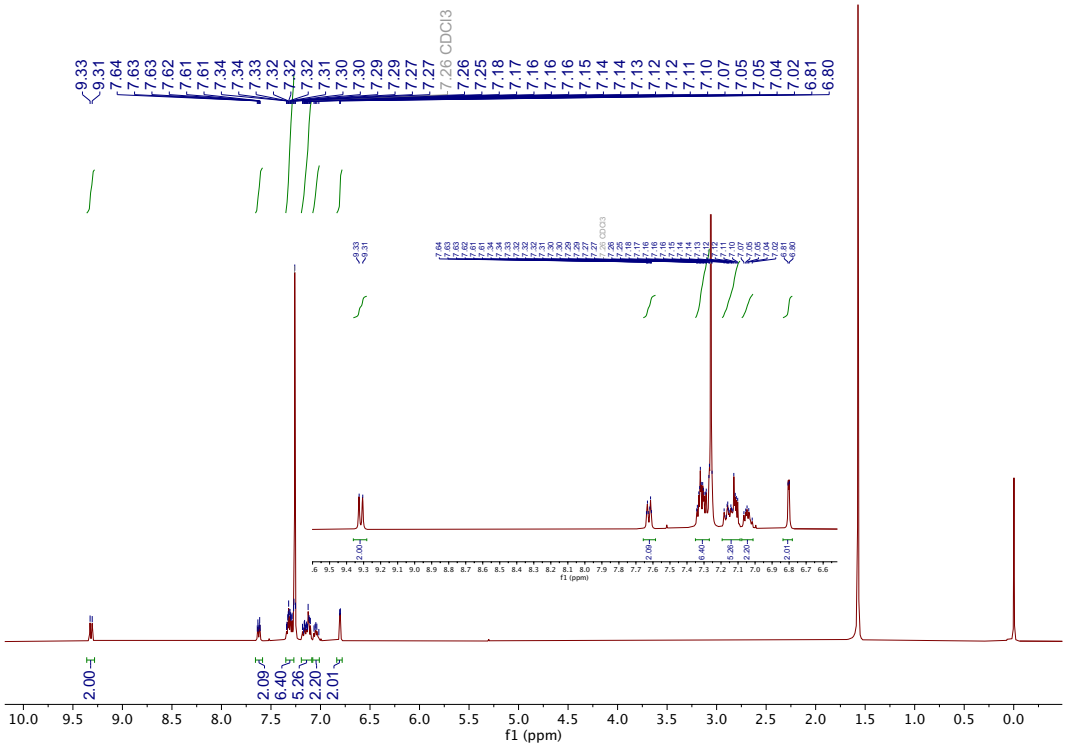


Figure S38. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **1S**.

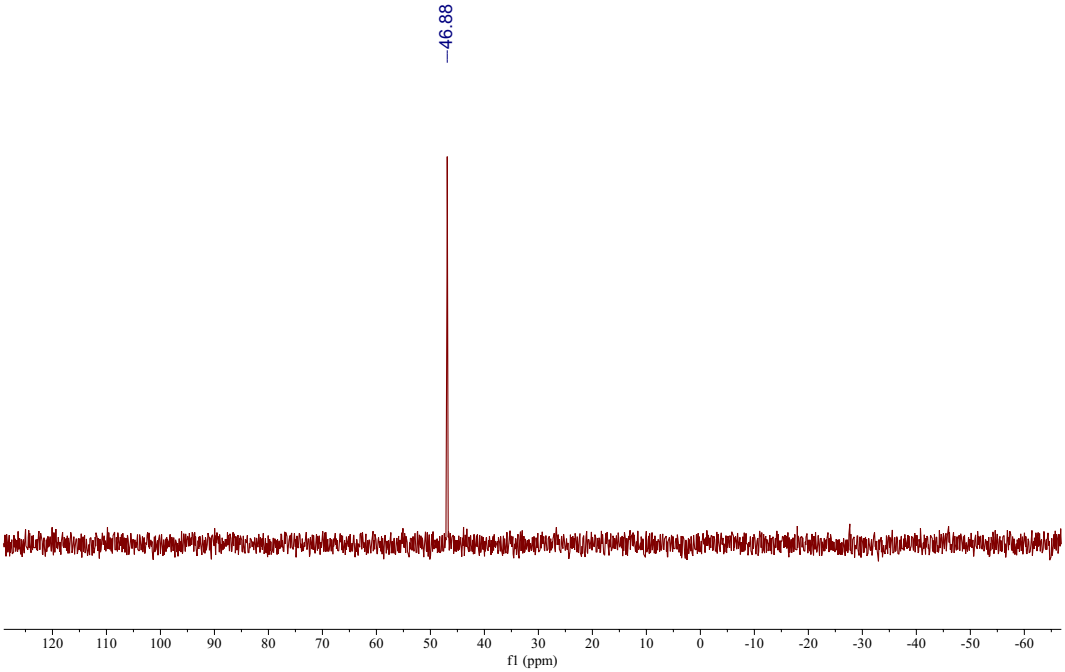


Figure S39. ^{31}P $\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298K) of **1S**.

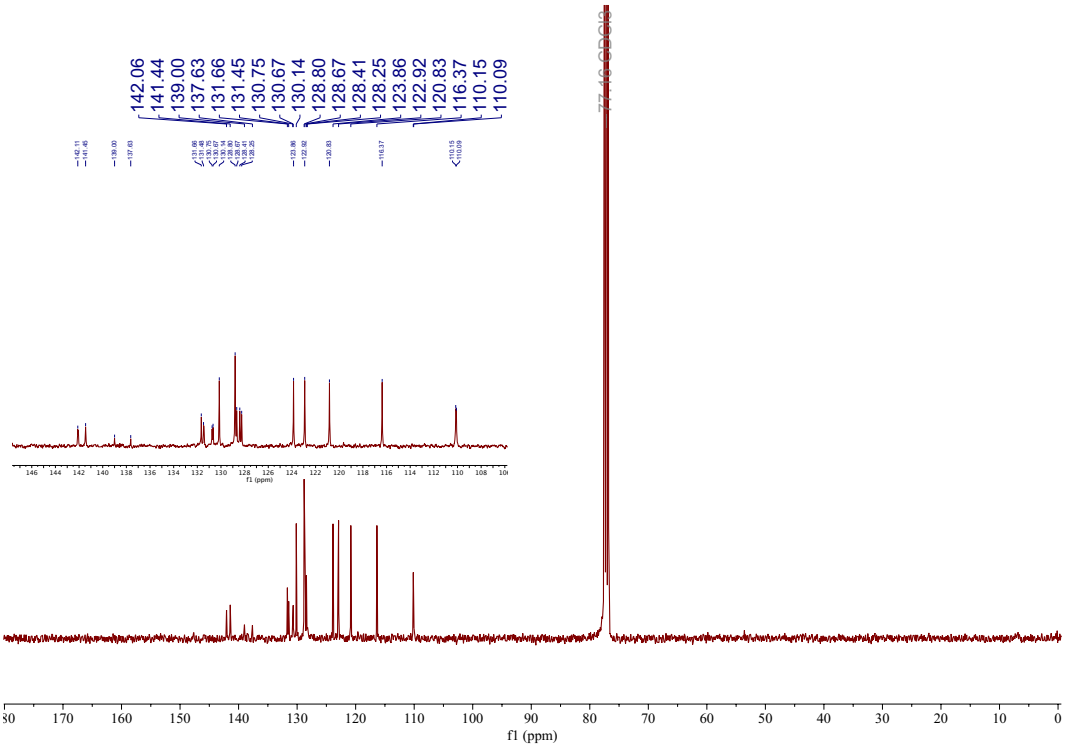


Figure S40. ^{13}C $\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 298K) of **1S**.

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