

**Exploring the Versatility of Dithieno[2,3-*b*;3',2'-*e*]-4-keto-1,4-  
dihydrophosphinines**

**Supporting Information**

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# Table of Contents

<b>SI.1.0 General Methods and Experimental Setup .....</b>	<b>1</b>
<b>SI.2.0 Chapter 2: Phosphorus Modifications on the Dithieno[2,3-<i>b</i>:3',2'-<i>e</i>]-4-keto-1,4-dihydrophosphinine .....</b>	<b>3</b>
SI.2.1 Experimental for precursor compounds .....	3
SI.2.2 Nuclear Magnetic Resonance Spectra .....	6
SI.2.3 Solid-state structures .....	50
SI.2.4 Density-Functional Theory Calculation Coordinates (X,Y,Z) .....	63
SI.2.5 Cyclic Voltammetry- Oxidation Regime .....	69
SI.2.6 Mass Spectrometry .....	70
<b>SI.3.0 Chapter 3: Ketone Modifications of the Dithieno[2,3-<i>b</i>:3',2'-<i>e</i>]-4-keto-1,4-dihydrophosphinine Toward Stronger Electron Acceptors.....</b>	<b>75</b>
SI 3.1 Nuclear Magnetic Resonance Spectra .....	75
SI 3.2 Solid-State Structures .....	93
SI 3.3 Density-Functional Theory Calculation Coordinates (X,Y,Z) .....	101
SI 3.4 Cyclic Voltammetry – Oxidation Regime .....	106
SI 3.5 Mass Spectrometry .....	107
<b>SI.4.0 Chapter 4: Extending the Conjugation of the Dithieno[2,3-<i>b</i>:3',2'-<i>e</i>]-4-keto-1,4-dihydrophosphinine Core.....</b>	<b>110</b>

SI.4.1 Nuclear Magnetic Resonance Spectra.....	110
SI.4.2 Solid-State Structures.....	141
SI.4.3 $E_T(30)$ Values vs. Emission Maxima.....	158
SI.4.4 Density-Functional Theory Calculation Coordinates (X,Y, Z) .....	159
SI.4.5 Cyclic Voltammetry – Oxidation Regime .....	171
SI.4.6 Mass Spectrometry.....	172
<b>SI.5.0 Chapter 5 Conclusion and Future Outlook Supporting Information .....</b>	<b>176</b>
SI.5.1 Nuclear Magnetic Resonance Spectrum.....	176
SI.5.2 Solid-state Structures.....	177
SI.5.3 Density-Functional Theory Calculation Coordinates (X, Y, Z).....	181
<b>SI.6.0 References .....</b>	<b>196</b>

## SI.1.0 General Methods and Experimental Setup

Most reactions were performed under an inert argon atmosphere using standard Schlenk line techniques. Solvents were dried using an MBraun SPS solvent purification system. The reagents used were purchased from Sigma Aldrich, Fischer, or Oakwood Chemicals and used as received. The bis(triphenylphosphine)palladium (II) dichloride was obtained from the Le lab at York University Canada. Compound **2-3O** was synthesized according to the literature procedure.<sup>1</sup>

**NMR:**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR, additional to the COSY, HSQC, HMBC, DEPT-135 experiments were obtained from Bruker NEO 300, 400 or 600 MHz spectrometers. The various deuterated solvents used were purchased from Sigma Aldrich or ACP chemicals. The multiplicity of peaks is described as singlet (s), doublet (d), doublet of doublet (dd), or multiplet (m). Select experiments were conducted and thereafter elucidated by Dr. Howard Hunter at York University, Toronto, Canada.

**XRD:** The single crystals were diffracted on a Bruker D8 Quest Eco diffractometer by Jesse LeBlanc or Casey Lenart at York University, Toronto, Canada. The solid-state structures were solved using OLEX2 and the graphics were done on Mercury.

**DFT:** The density functional theory calculations were done with a B3LYP 6-31G+(d) basis set using the polarization continuum model (PCM) for solvation in  $\text{CH}_2\text{Cl}_2$  using Gaussian 16.<sup>2</sup> For **2-3Au** a LANL2MB basis set was used. Time-dependent density functional theory calculations were done using a TD-SCF CAM B3LYP 6-31G+(d) basis set using the PCM model in  $\text{CH}_2\text{Cl}_2$ .

Orbitals were viewed on Gaussview. The calculations were done on the Cedar or Graham clusters provided by the Digital research alliance of Canada. Some calculations were done with the help of Dr. Avik Battacharjee at York University, Toronto, Canada.

**Microwave Reactions:** All microwave reactions were done using an Anton Paar Monowave 2000 in G10 or G30 pressure vials with a Teflon cap.

**Optical studies:** The absorption data were obtained on an Agilent Cary 5000 UV-vis spectrophotometer using standard quartz cuvettes. The emission data was obtained on an Edinburg FS5 spectrometer with a standard cuvette holder module for emission and an integrating sphere for the quantum yield measurements. The solutions for chapters two and three were done at a concentration of  $5 \times 10^{-5}$  M and for chapter four they were prepared at  $5 \times 10^{-6}$  M.

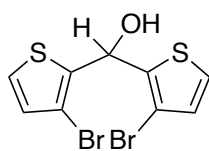
**Cyclic Voltammetry:** The experiments were performed using a Metrohm Autolab Potentiostat with NOVA software in dry  $\text{CH}_3\text{CN}$  with tetrabutylammonium hexafluorophosphate as the electrolyte. The solutions were done at a concentration of 2 mg/mL for a total volume of 10 mL. The standard scan rate was 0.1 V/s unless stated otherwise for specific experiments.

**Mass Spectrometry:** The experiments were done by Maxime Rossato at the YSciCore mass spectrometry facility at York University, Toronto Canada. Other analysis was done at the AIMS mass spectrometry laboratory at the University of Toronto, Canada.

## SI.2.0 Chapter 2: Phosphorus Modifications on the Dithieno[2,3-*b*:3',2'-*e*]-4-keto-1,4-dihydrophosphinine

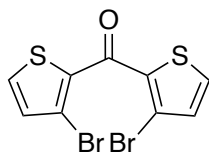
### SI.2.1 Experimental for precursor compounds

Synthesis of compound **2-4**:



3-Bromothiophene (10 g, 61.3 mmol) was added dropwise to lithium diisopropylamide (61.3 mmol) in 100 mL dry THF at 0 °C under argon and allowed to stir for 30 minutes. Methyl formate (3.9 g, 64.4 mmol) was then added dropwise to the mixture and allowed to stir for 3 hours at 0 °C. The reaction was quenched with ammonium chloride and extracted with Et<sub>2</sub>O. The organic layer was dried with MgSO<sub>4</sub> and gravity filtered to give a brown oil. The oil was purified using column chromatography using a 1:6 ratio of ethyl acetate to hexanes, to give a yellow oil (40% yield, 8.7 g). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 7.26 (d, 2H, <sup>3</sup>J<sub>H-H</sub>= 5.5Hz), 6.95 (d, 2H, <sup>3</sup>J<sub>H-H</sub>=5.4Hz), 6.40 (d, 1H, <sup>3</sup>J<sub>H-H</sub>= 3.6Hz), 3.92 (d, 1H, <sup>3</sup>J<sub>H-H</sub>= 3.7Hz).

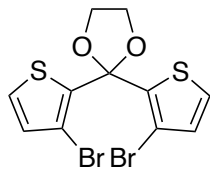
Synthesis of Ketone **2-5**:



Pyridinium chlorochromate (7.9 g, 37 mmol) was added at 0 °C to a mixture of **2-4** (8.7 g, 24.6 mmol), and molecular sieves (5.3 g) in 90 mL dry dichloromethane. The mixture was allowed to stir for a few minutes at 0 °C, then at room temperature overnight. The reaction was quenched with 100 mL Et<sub>2</sub>O and passed through an Al<sub>2</sub>O<sub>3</sub> plug after which a yellow powder

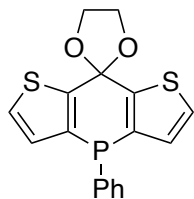
was obtained (85% yield, 7.4 g).  $^1\text{H NMR}$  (300MHz,  $\text{CDCl}_3$ ):  $\delta = 7.58\text{ppm}$  (d, 2H,  $^3J_{\text{H-H}} = 5.1\text{Hz}$ ), 7.12 (d, 2H,  $^3J_{\text{H-H}} = 5.1\text{Hz}$ ).

#### Synthesis of Protected Ketone **2-6**:



Compound **2-5** (7.4 g, 21 mmol), *p*-toluenesulfonic acid (0.4 g, 2 mmol) and ethylene glycol (130 g, 2090 mmol) were added to 150 mL benzene under argon. The mixture was refluxed under a Dean-Stark head for 120 hours. After cooling, 250 mL  $\text{NaHCO}_3$  was added and the organics extracted with benzene. The benzene layer was washed with distilled  $\text{H}_2\text{O}$  (x3) and brine (x3). Thereafter the organic layer was dried with  $\text{MgSO}_4$  and gravity filtered. All volatiles were removed and the residue was washed with cold  $\text{Et}_2\text{O}$  to give a yellow powder (82% yield, 6.2 g).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.30$  (d,  $J = 5.3$  Hz, 2H), 7.00 (d,  $J = 5.3$  Hz, 2H), 4.23 (s, 4H).

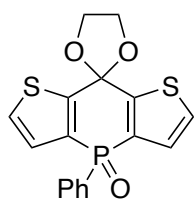
#### Synthesis of Protected Dithienoketophosphinine **2-7**:



To compound **2-6** (2.1 g, 5.2 mmol) in 150 mL  $\text{Et}_2\text{O}:\text{THF}$  (3:1), *n*BuLi (0.7 g, 1.6 M, 10 mmol) was added dropwise at  $-78^\circ\text{C}$ . After all, *n*BuLi was added, the mixture stirred for 30 minutes at  $-78^\circ\text{C}$ , then for another 30 minutes at room temperature.  $\text{PhPCl}_2$  (0.98 g, 5.5 mmol) was added dropwise at  $-78^\circ\text{C}$  and the mixture was allowed to stir at  $-78^\circ\text{C}$  for a few minutes and

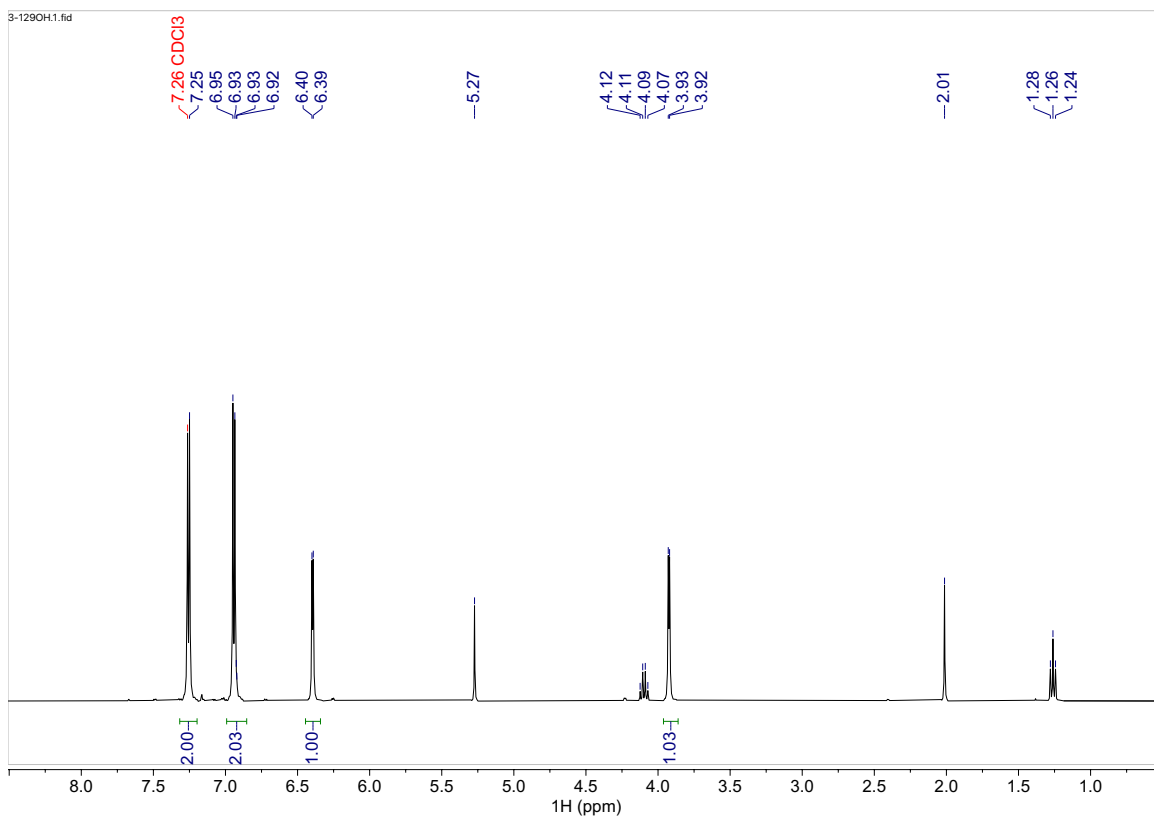
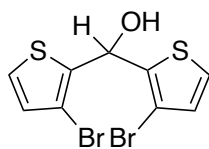
the cold bath was quickly switched to a warm water bath and let stir overnight under argon. The solvent was removed and the brown residue was taken up in Et<sub>2</sub>O and passed thru neutral Al<sub>2</sub>O<sub>3</sub>. All volatiles were removed to give a white powder (65% yield, 1.1 g). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ = -36.5 ppm. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.45 (m, 7H, Ar), 6.87 (dd, *J*<sub>HH</sub> = 5.1, *J*<sub>HP</sub> = 2.9 Hz, 2H), 4.45 (m, 4H, -OCH<sub>2</sub>-).

Oxidation of **2-7** toward **2-7O**:

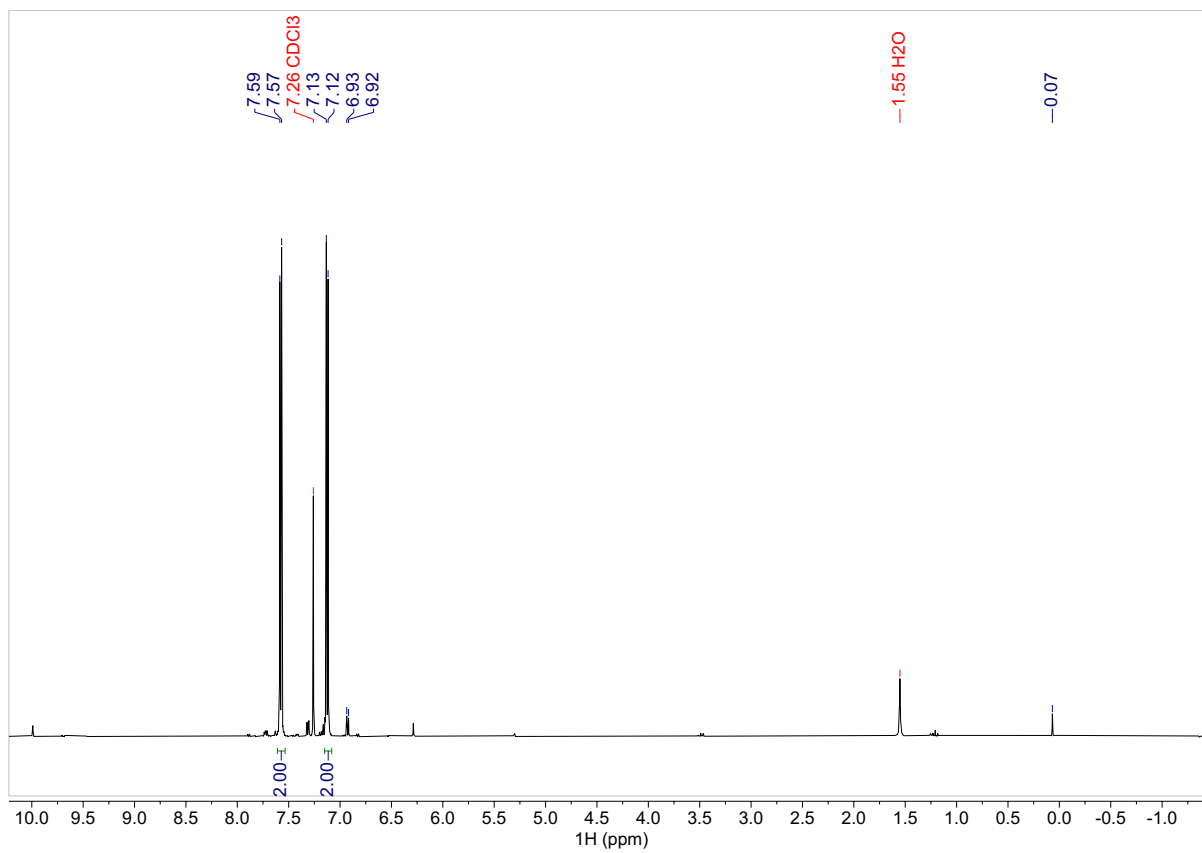
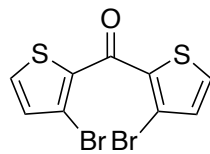


Compound **2-7** (1.1 g, 3.2 mmol) was dissolved in 30 mL CHCl<sub>3</sub>:THF and 0.3 mL hydrogen peroxide was added then stirred overnight at room temperature. The mixture was quenched with water and extracted with CHCl<sub>3</sub>. The organic layer was washed with brine (x3) and dried with MgSO<sub>4</sub> then gravity filtered. Upon removing all volatiles, a tan solid remained (100% yield, 1.1 g). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ = 2.3 ppm. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.80 (m, 2H, -th), 7.45 (m, 5H, -ph), 7.35 (t, *J* = 4.7 Hz, 2H), 4.55 (m, 4H, -OCH<sub>2</sub>-).

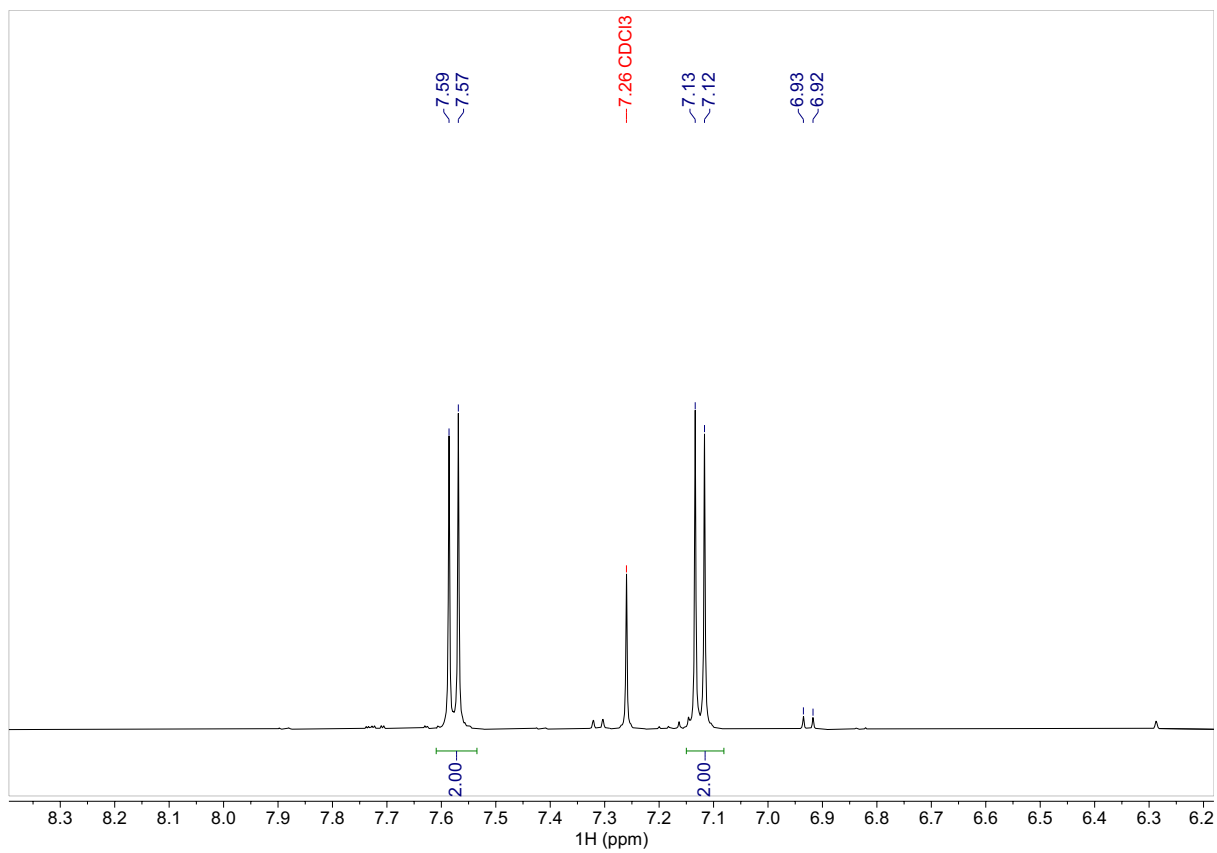
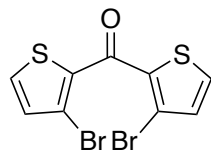
## SI.2.2 Nuclear Magnetic Resonance Spectra



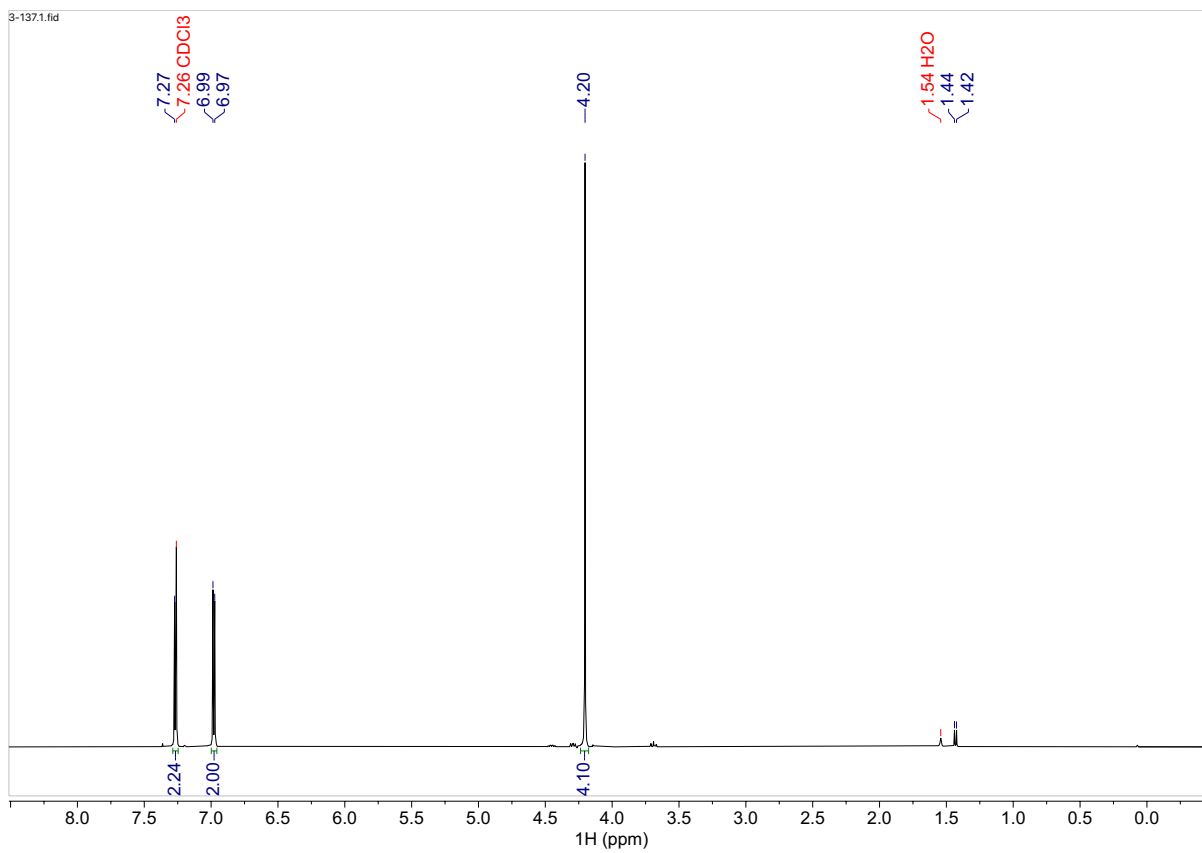
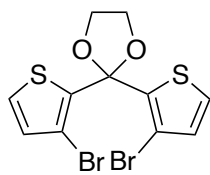
**Figure S2-1.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of compound 2-4.



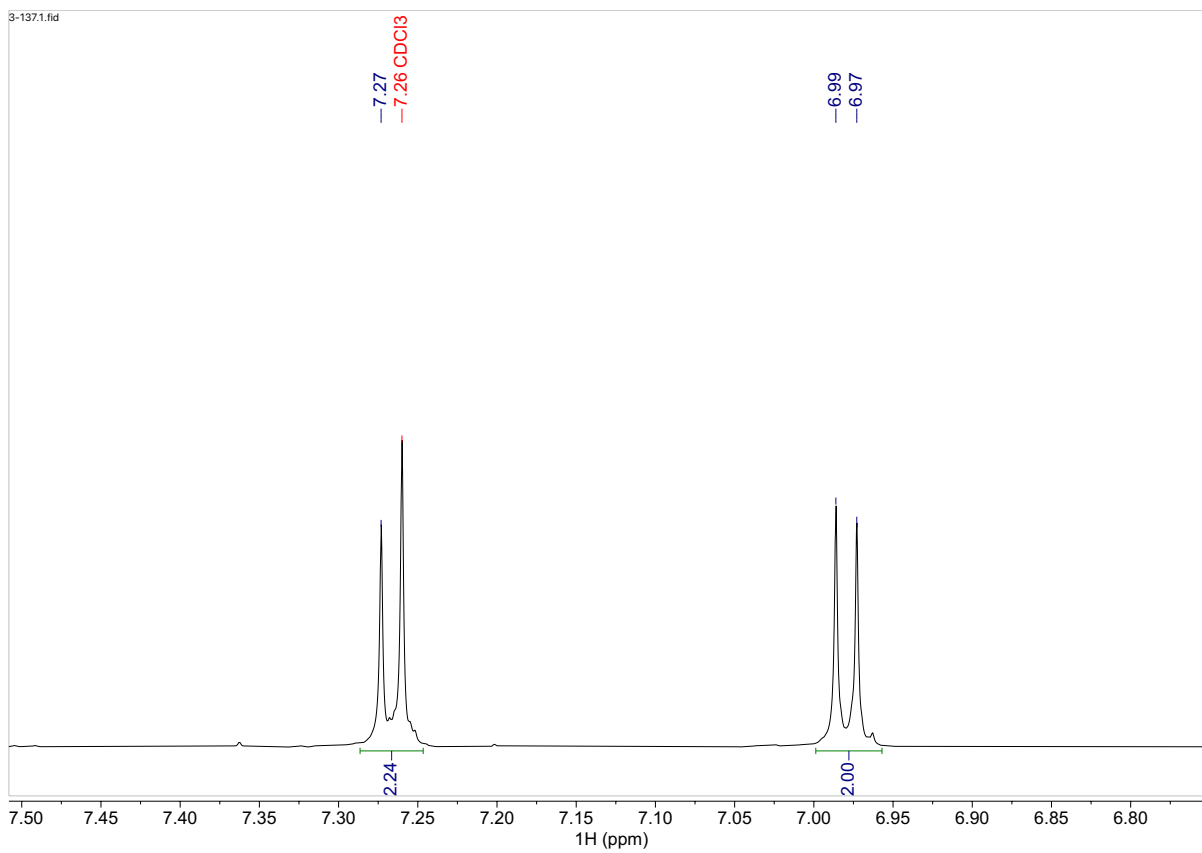
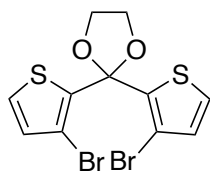
**Figure S2-2.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of compound 2-5.



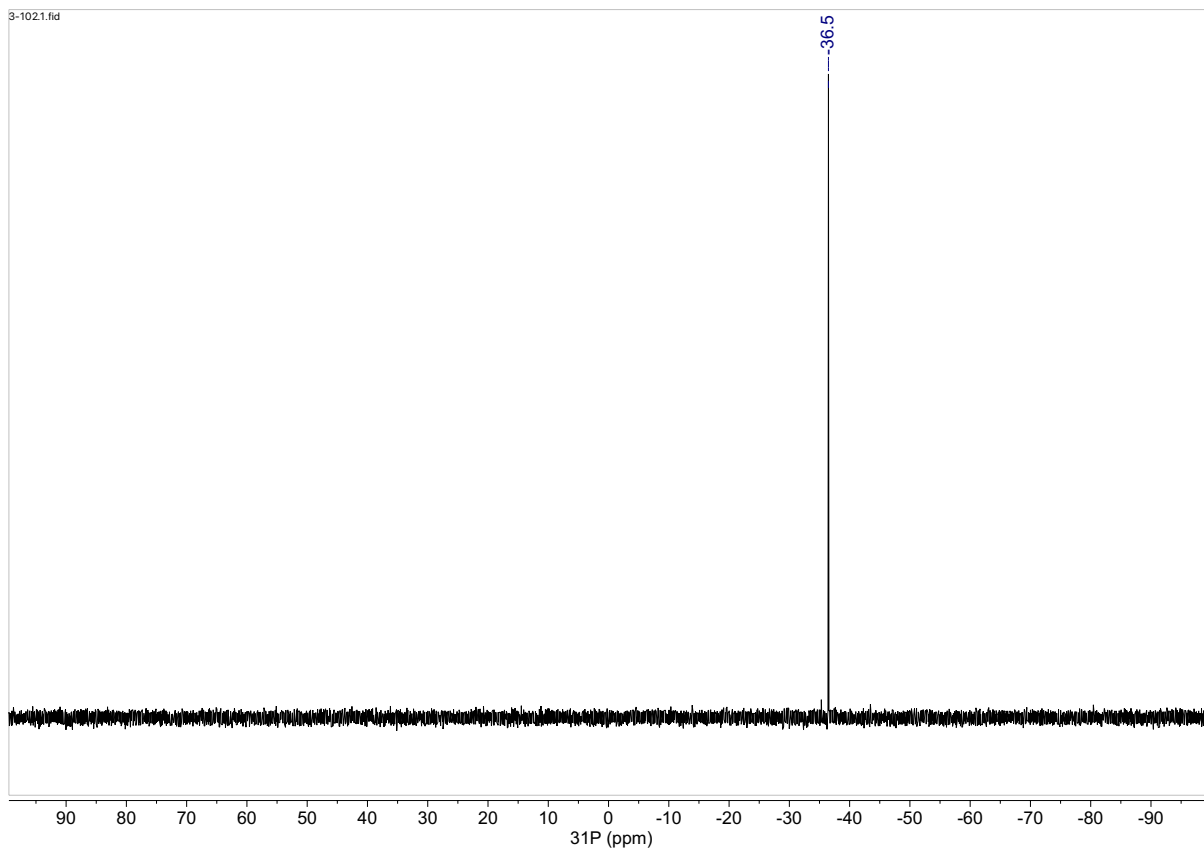
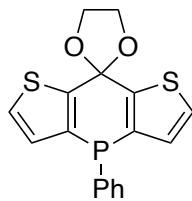
**Figure S2-3.** <sup>1</sup>H NMR spectrum zoomed (400 MHz, CDCl<sub>3</sub>) of compound **2-5**.



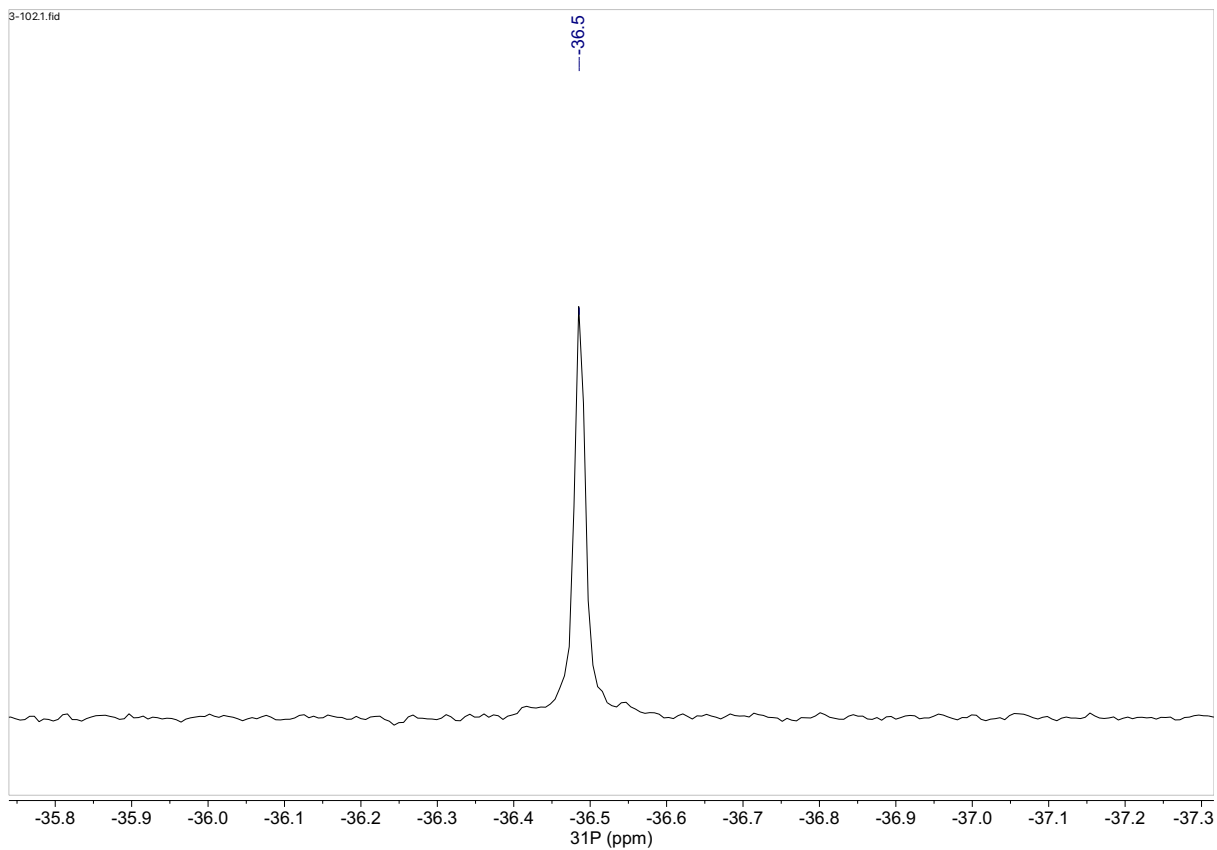
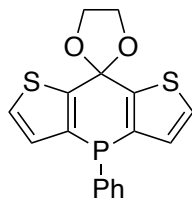
**Figure S2-4.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of compound 2-6.



**Figure S2-5.** <sup>1</sup>H NMR spectrum zoomed (400 MHz, CDCl<sub>3</sub>) of compound 2-6.



**Figure S2-6.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of compound 2-7.



**Figure S2-7.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CDCl}_3$ ) of compound 2-7.

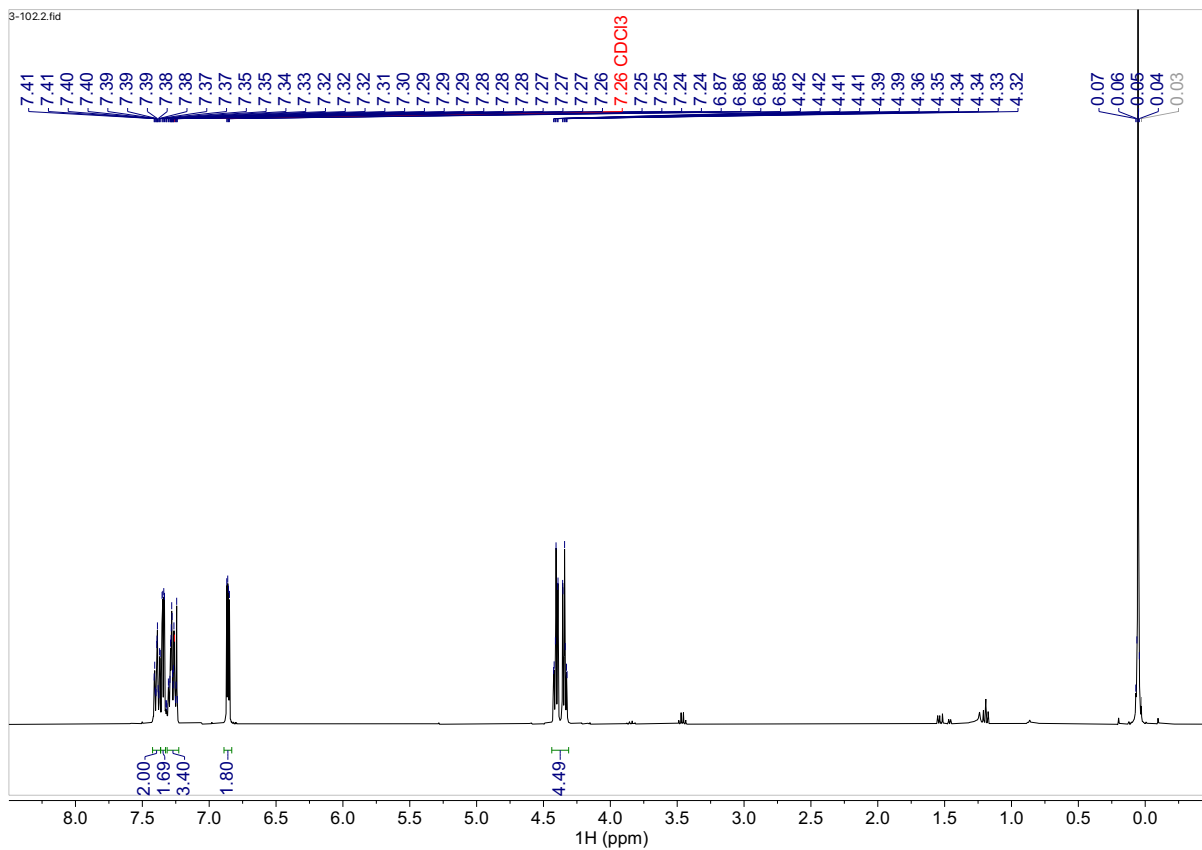
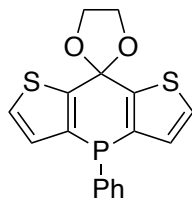
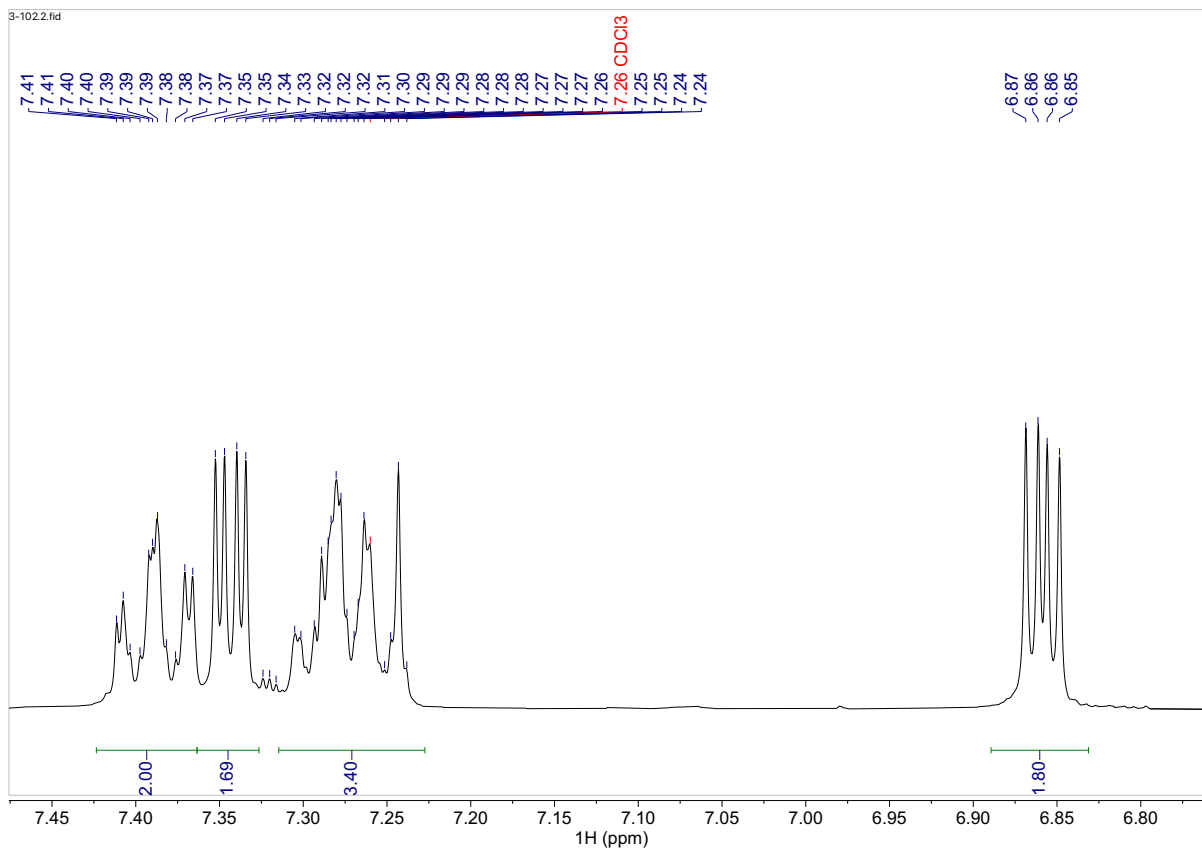
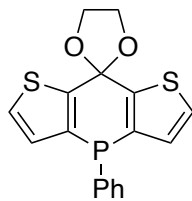
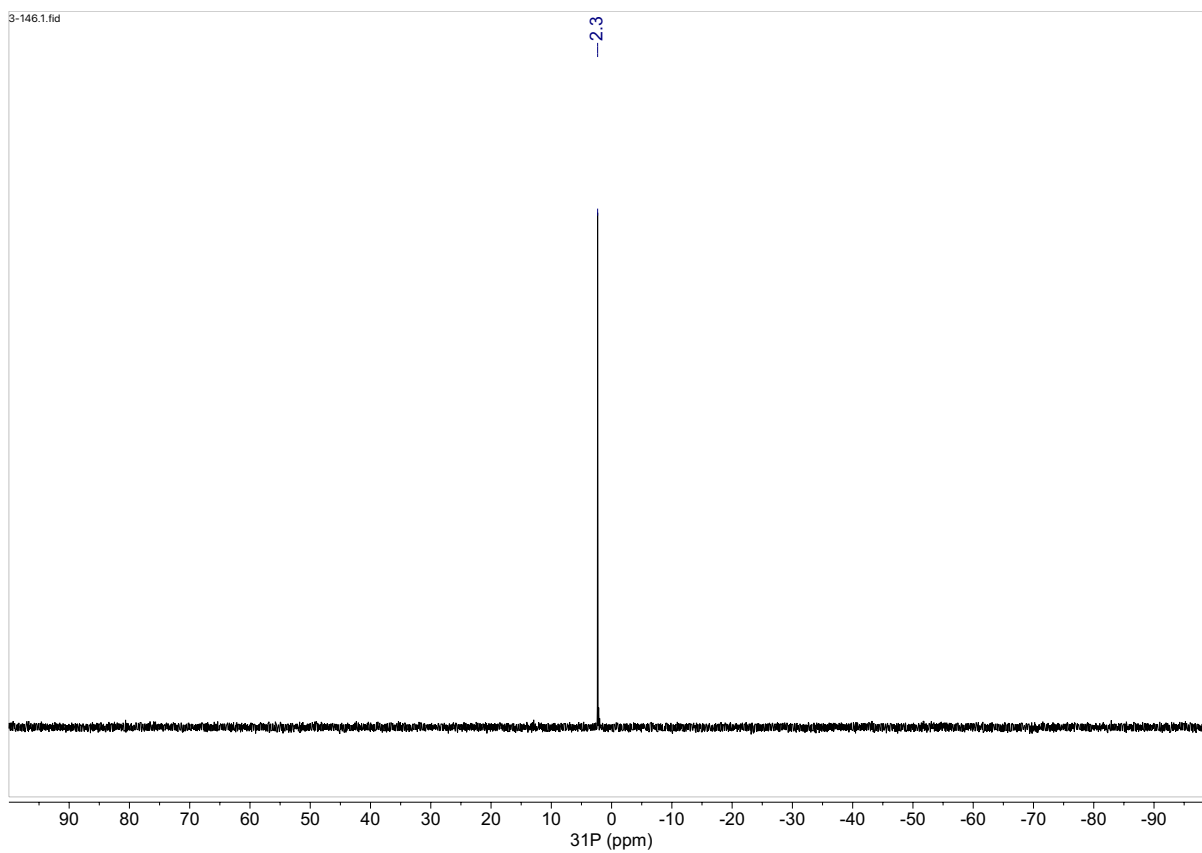
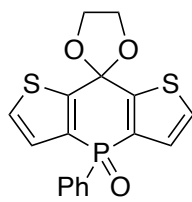


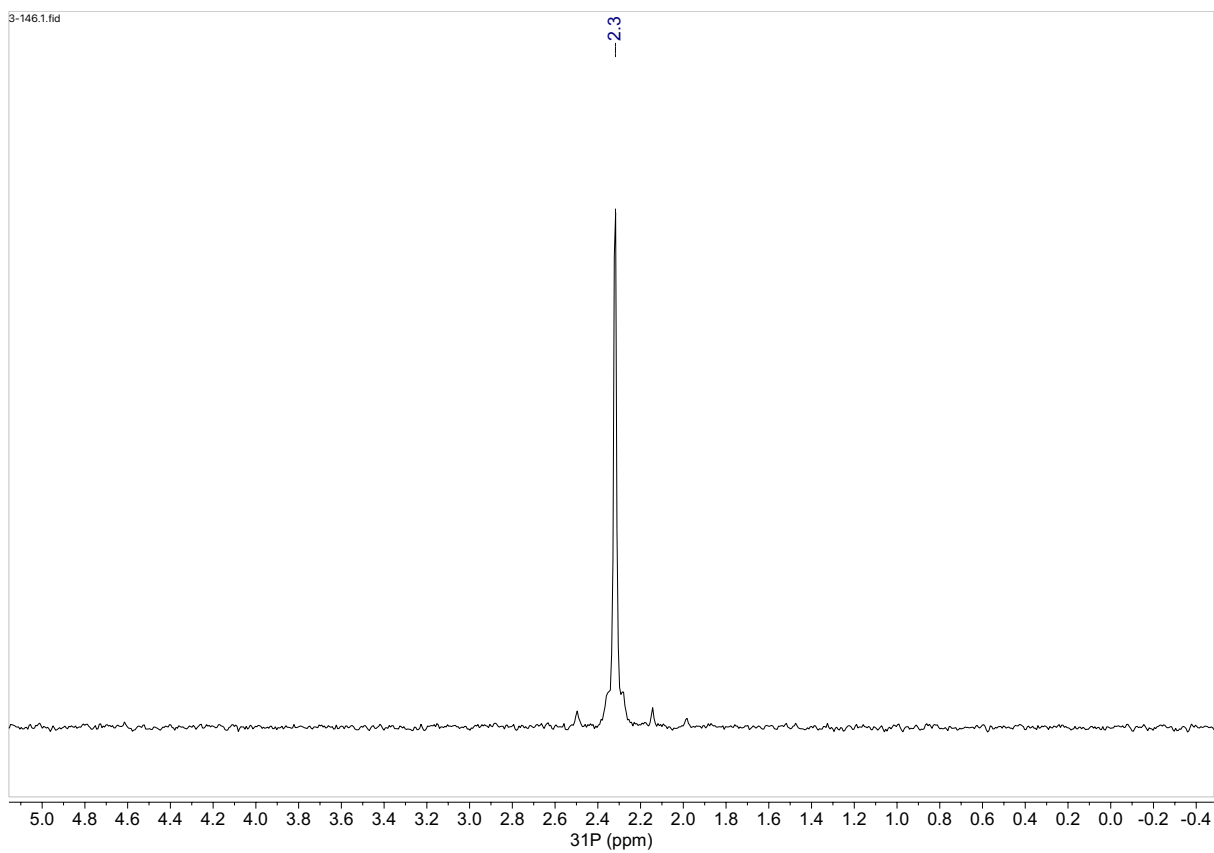
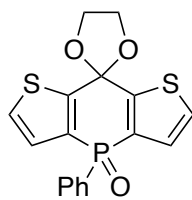
Figure S2-8.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of compound 2-7.



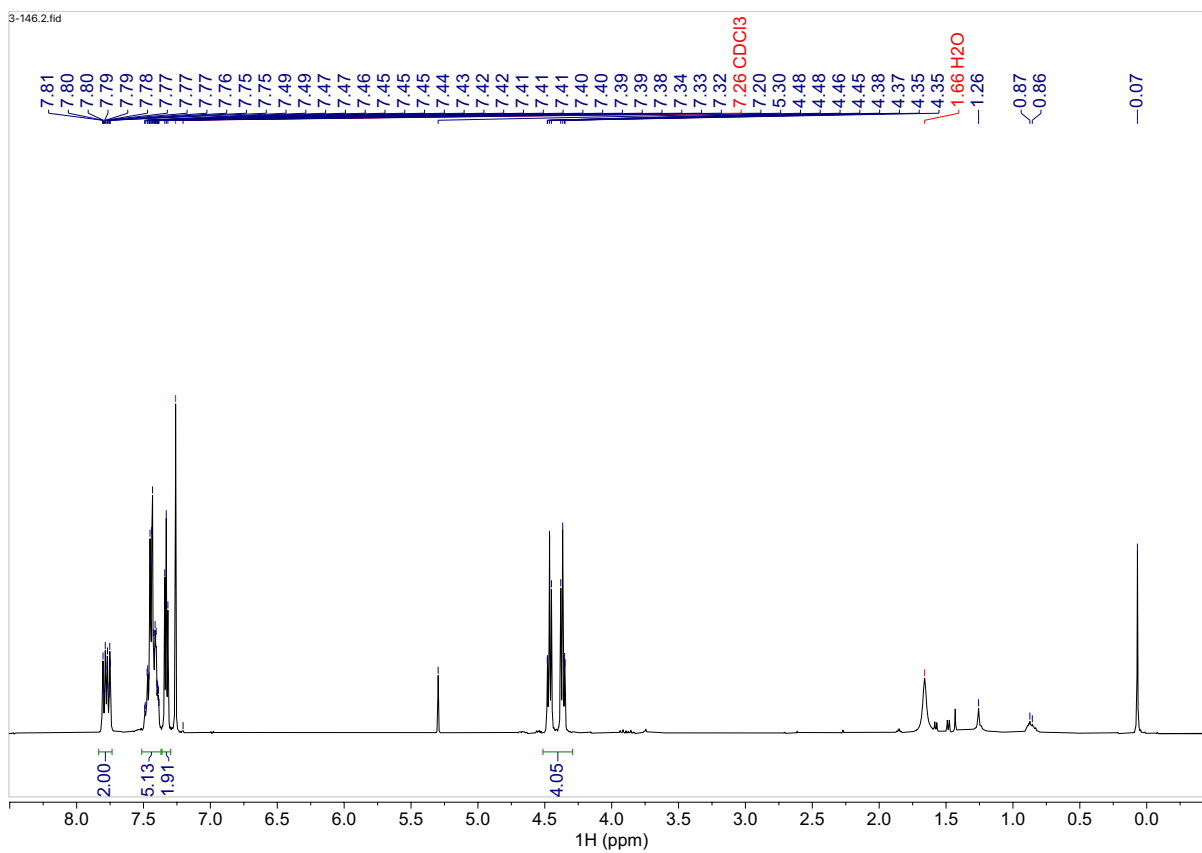
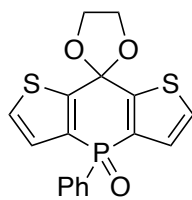
**Figure S2-9.**  $^1\text{H}$  NMR spectrum zoomed (400 MHz,  $\text{CDCl}_3$ ) of compound 2-7.



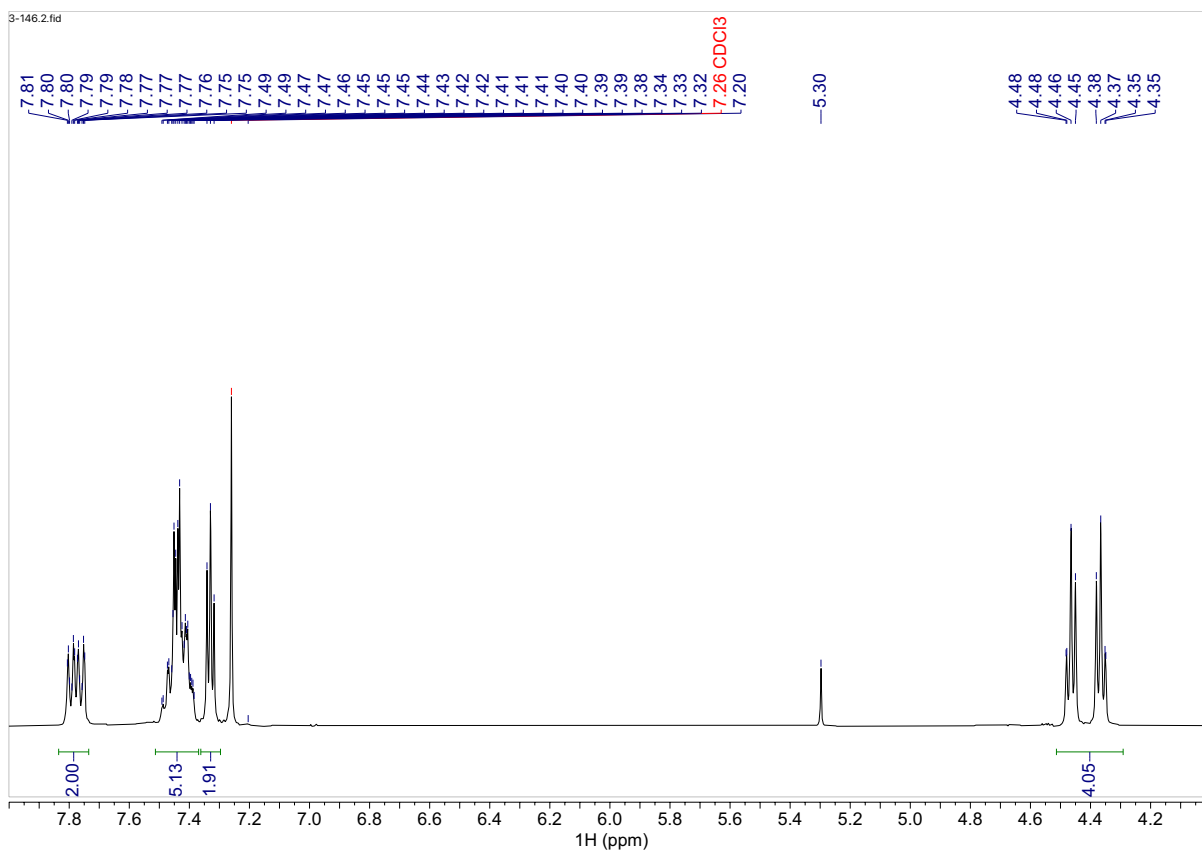
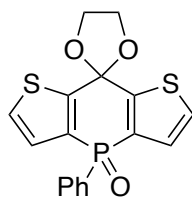
**Figure S2-10.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of compound 2-70.



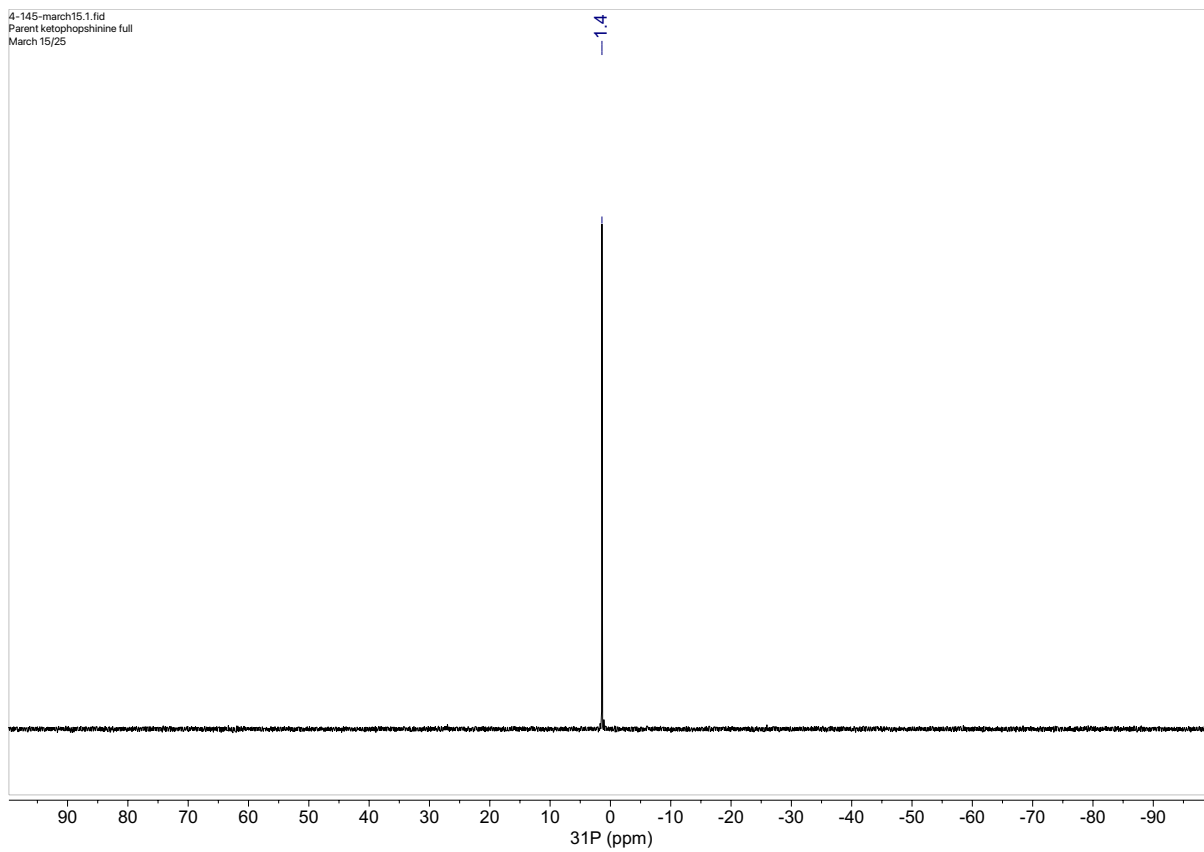
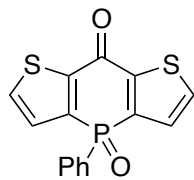
**Figure S2-11.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CDCl}_3$ ) of compound **2-7O**.



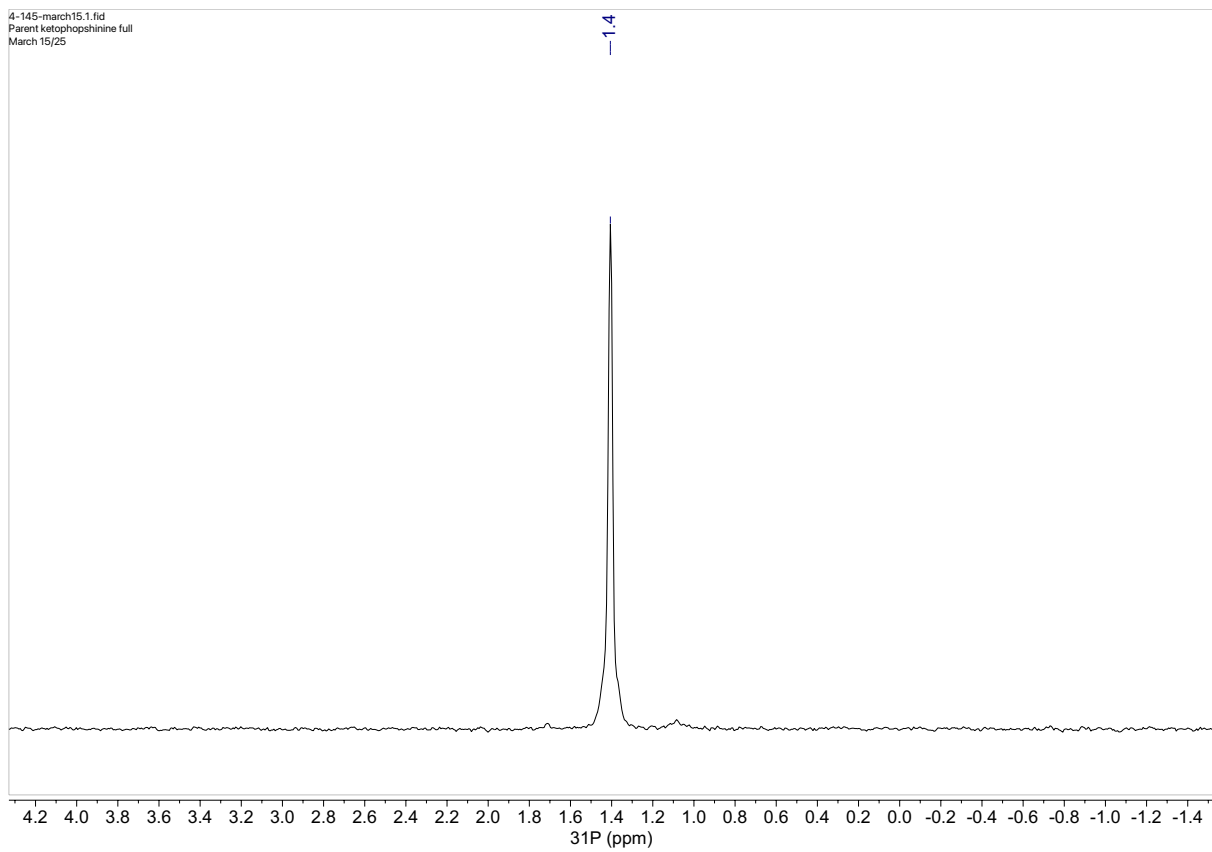
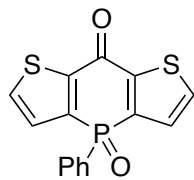
**Figure S2-12.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of compound **2-70**.



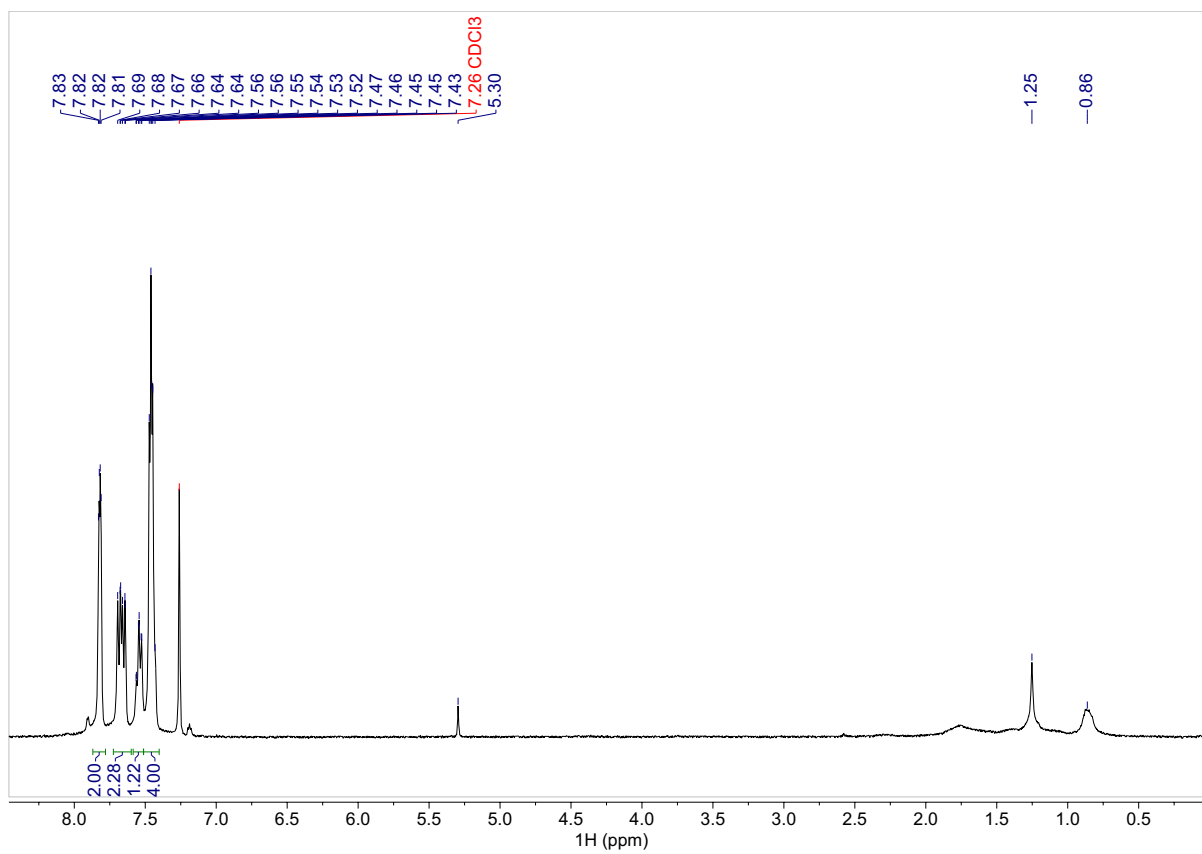
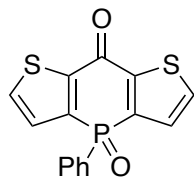
**Figure S2-13.**  $^1\text{H}$  NMR spectrum zoomed (400 MHz,  $\text{CDCl}_3$ ) of compound **2-7O**.



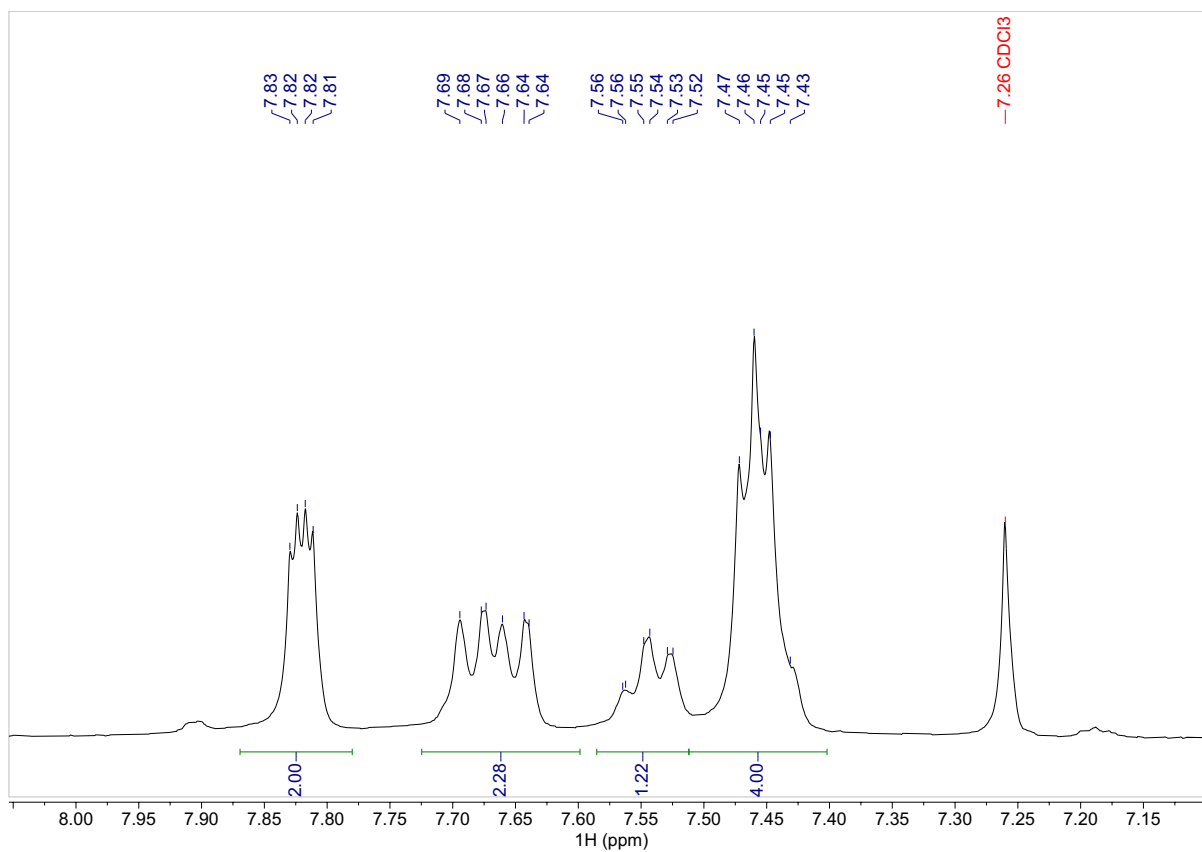
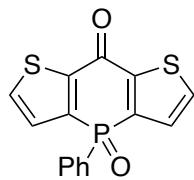
**Figure S2-14.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of compound 2-30.



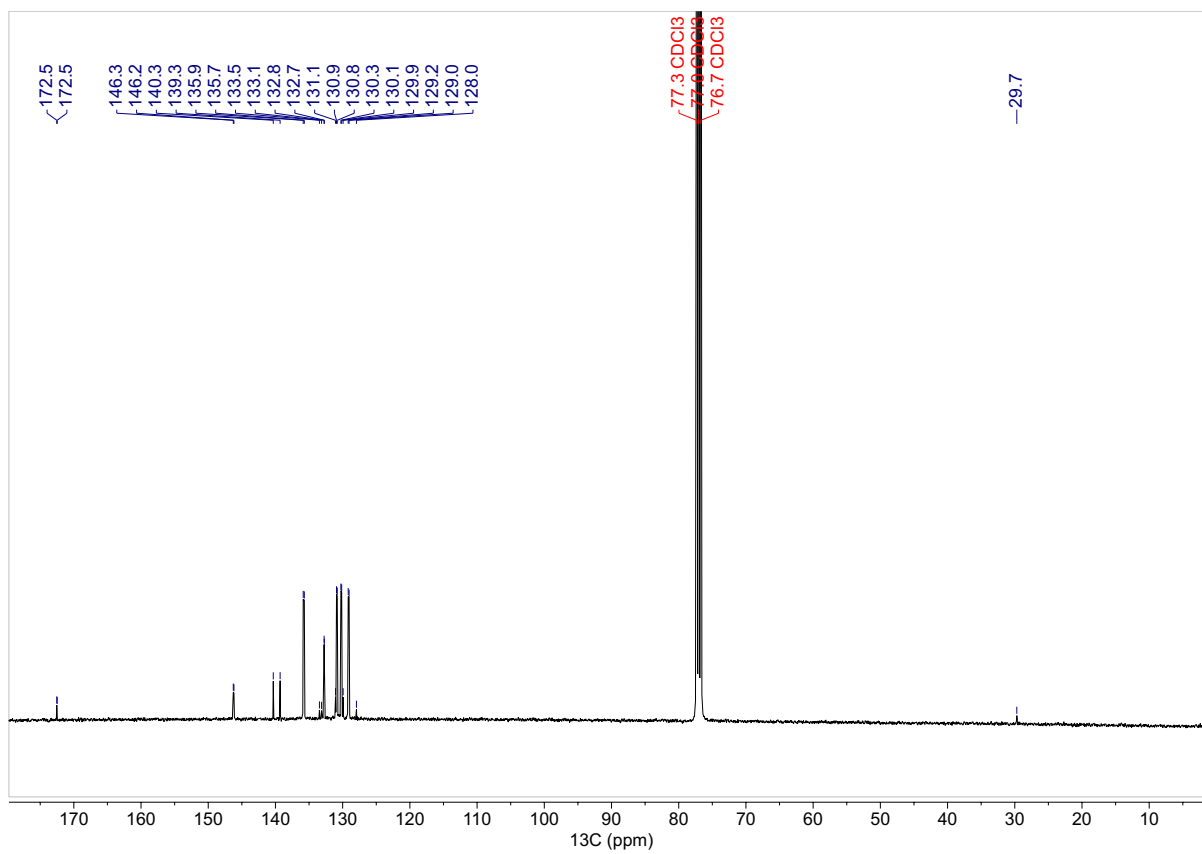
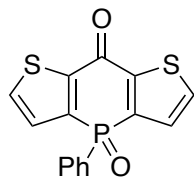
**Figure S2-15.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CDCl}_3$ ) of compound **2-30**.



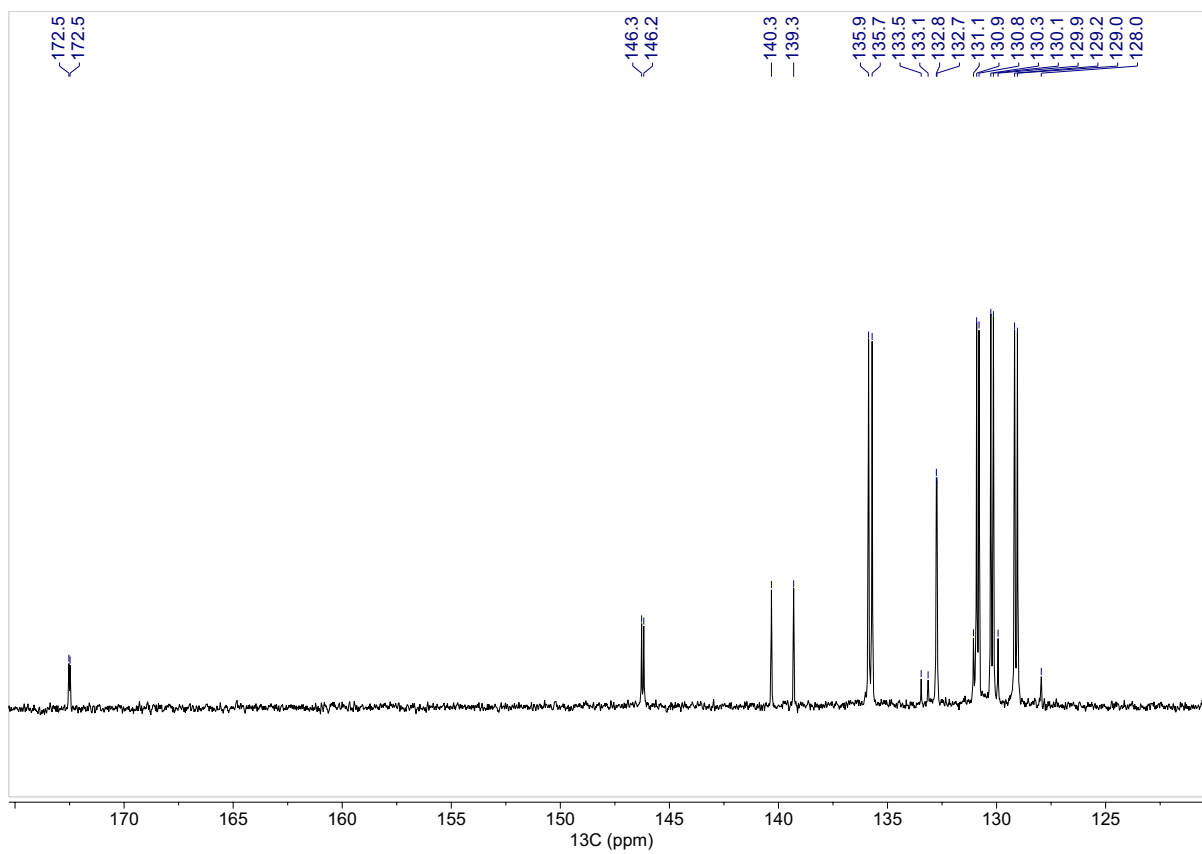
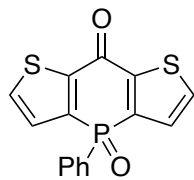
**Figure S2-16.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of compound 2-30.



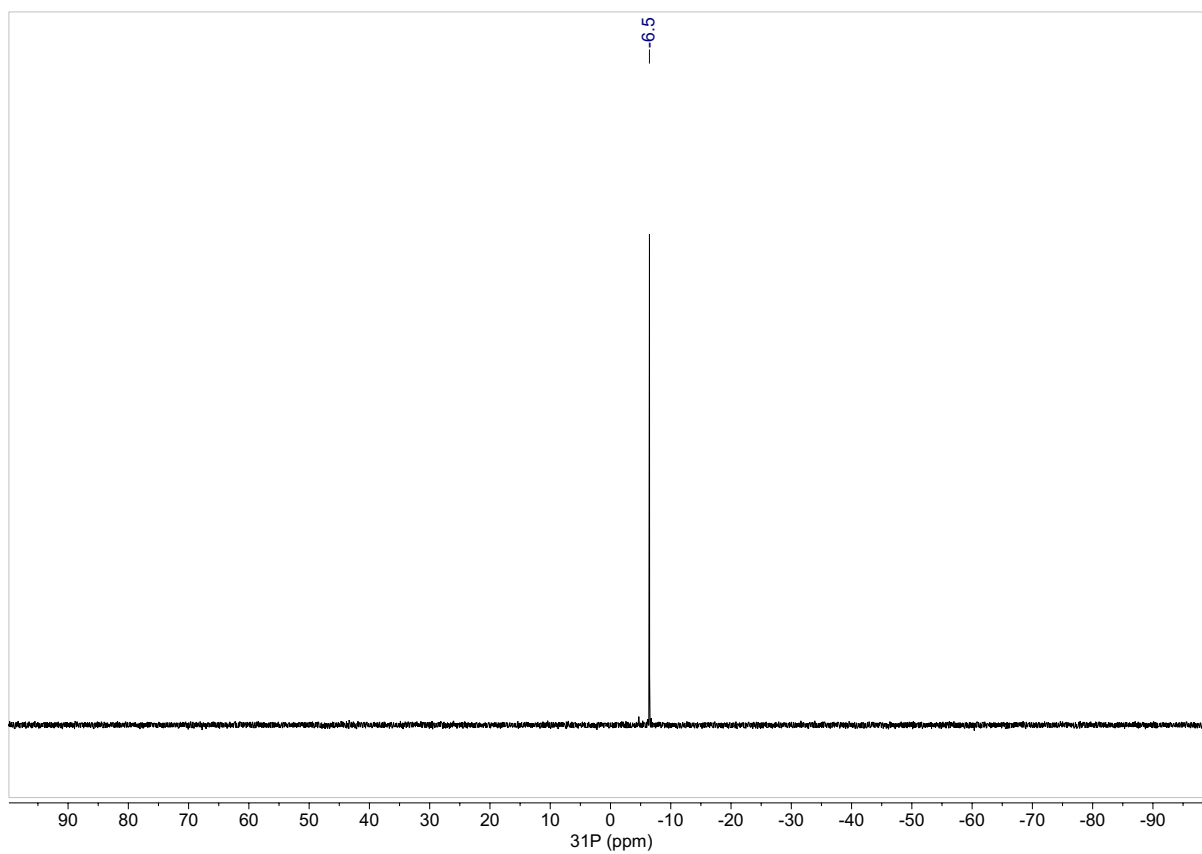
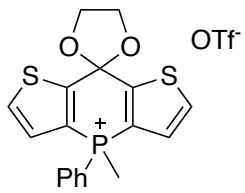
**Figure S2-17.** <sup>1</sup>H NMR spectrum zoomed (400 MHz, CDCl<sub>3</sub>) of compound **2-30**.



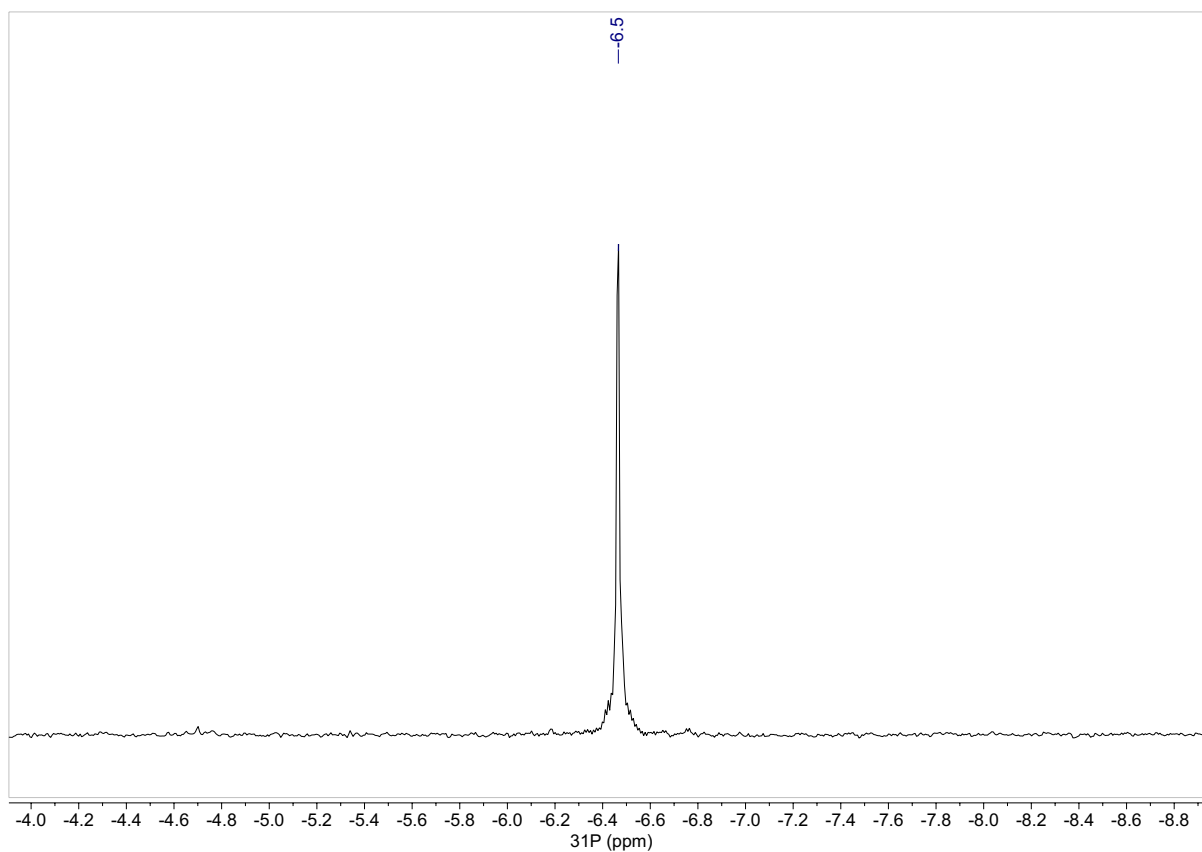
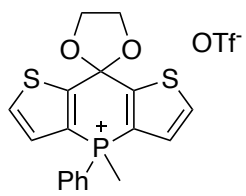
**Figure S2-18.** <sup>13</sup>C NMR spectrum (100.6 MHz, CDCl<sub>3</sub>) of compound 2-3O.



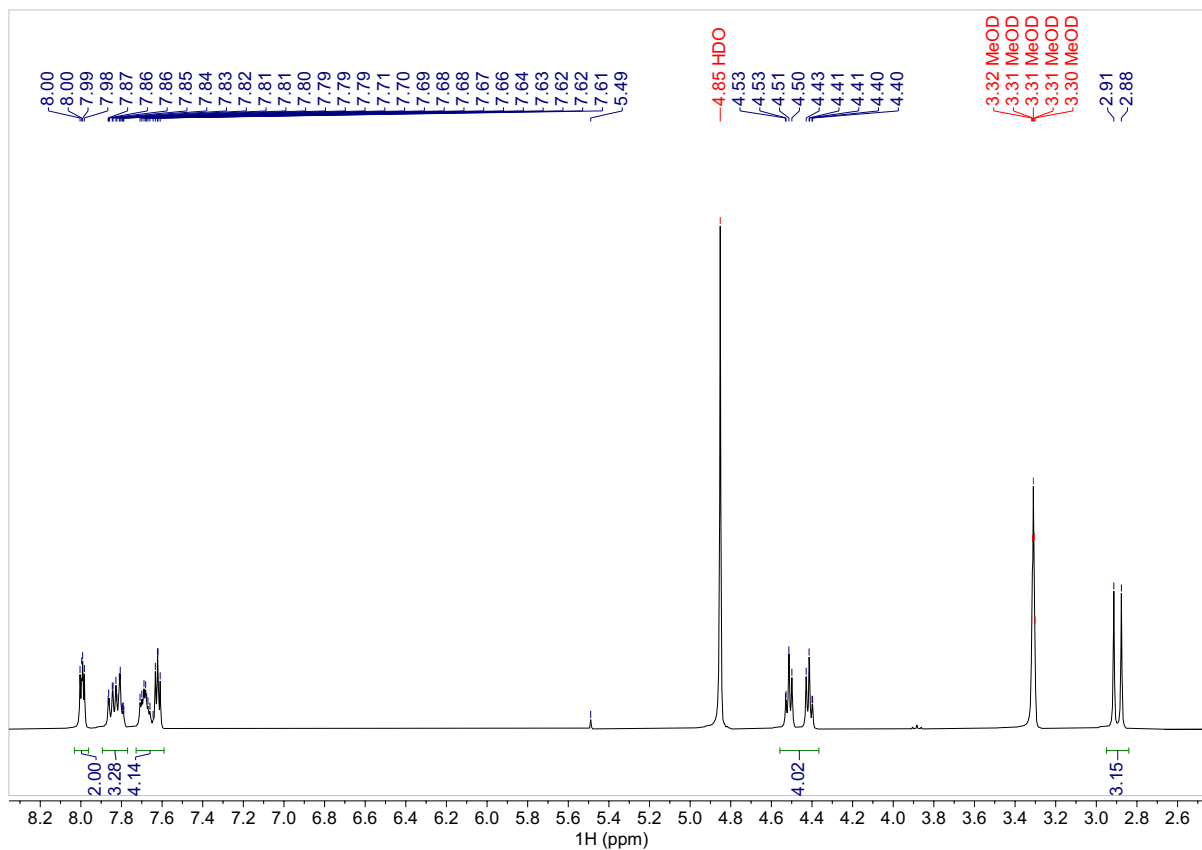
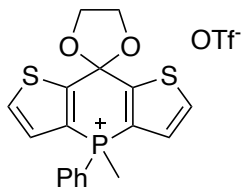
**Figure S2-19.** <sup>13</sup>C NMR spectrum zoomed (100.6 MHz, CDCl<sub>3</sub>) of compound 2-30.



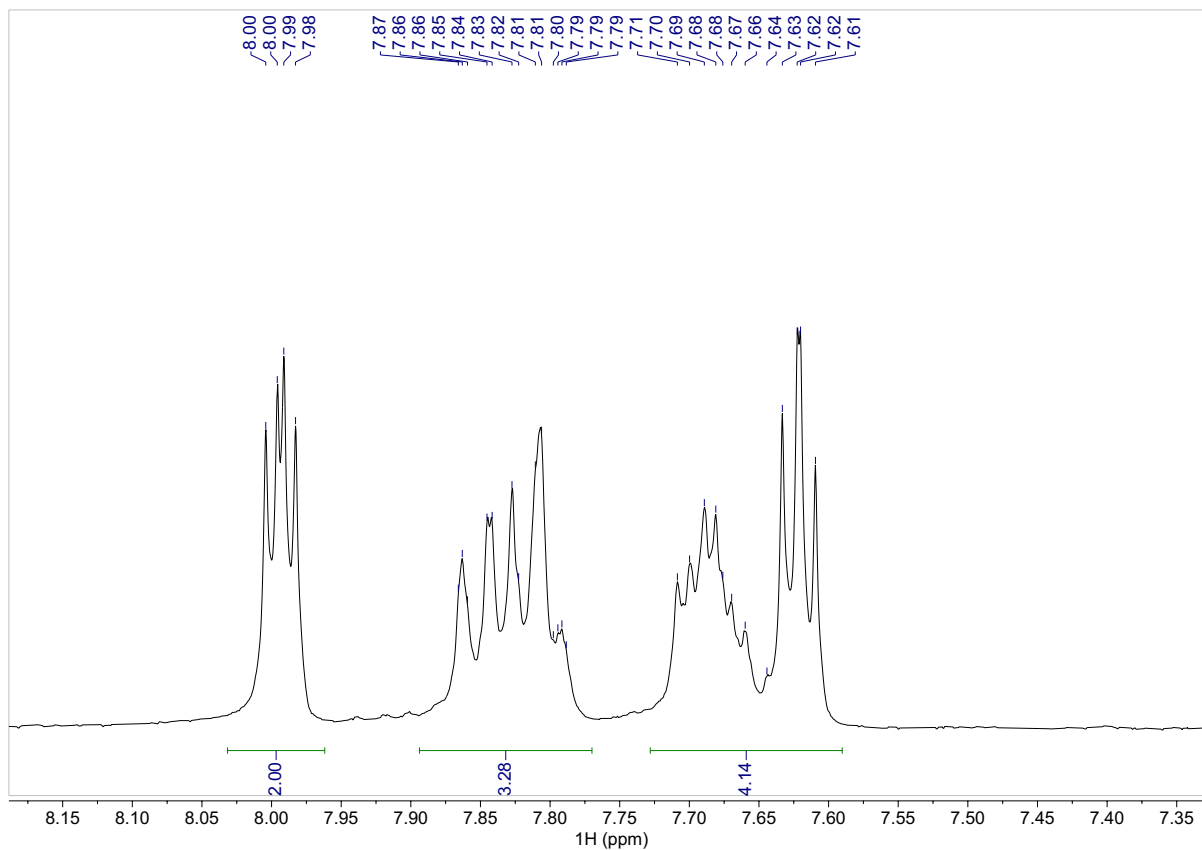
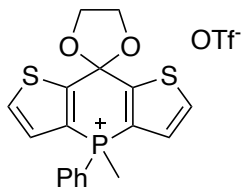
**Figure S2-20.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, MeOD) of compound **2-8Me**.



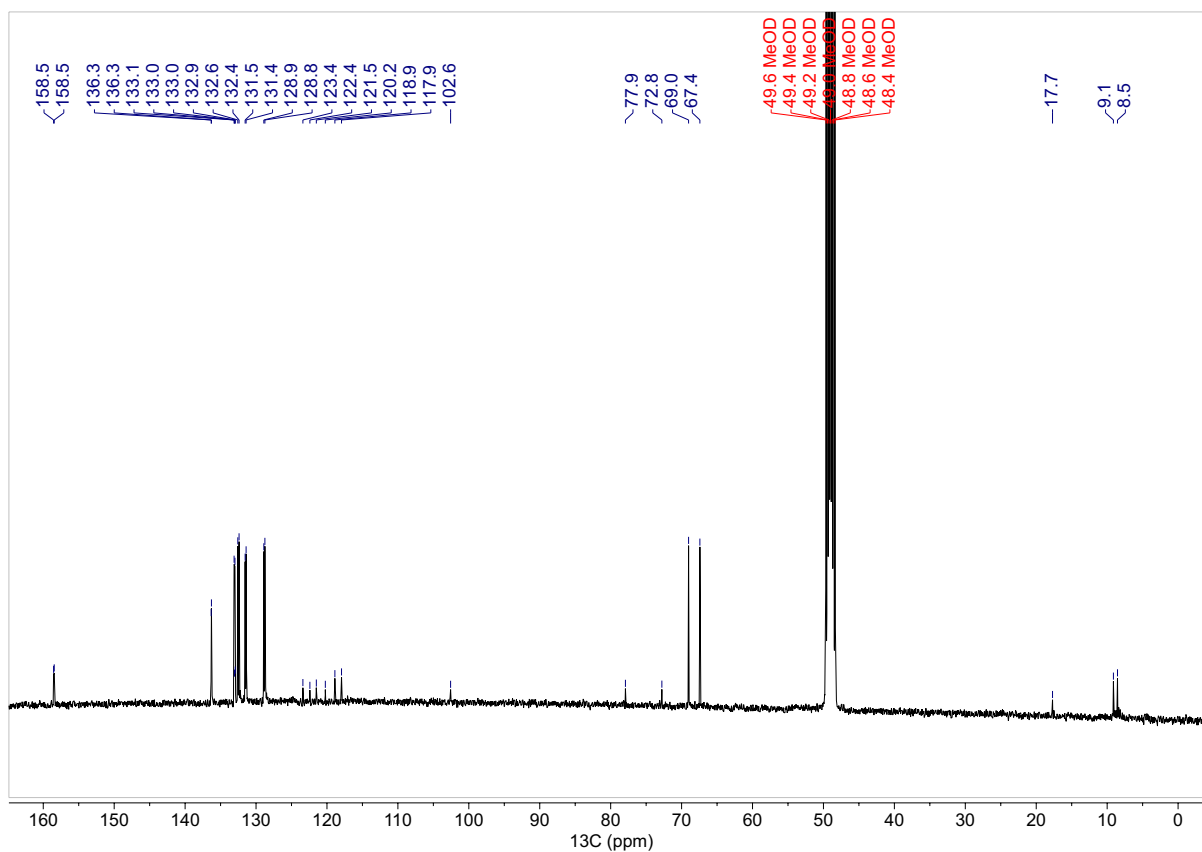
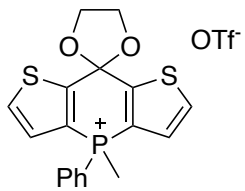
**Figure S2-21.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum zoomed (162 MHz, MeOD) of compound **2-8Me**.



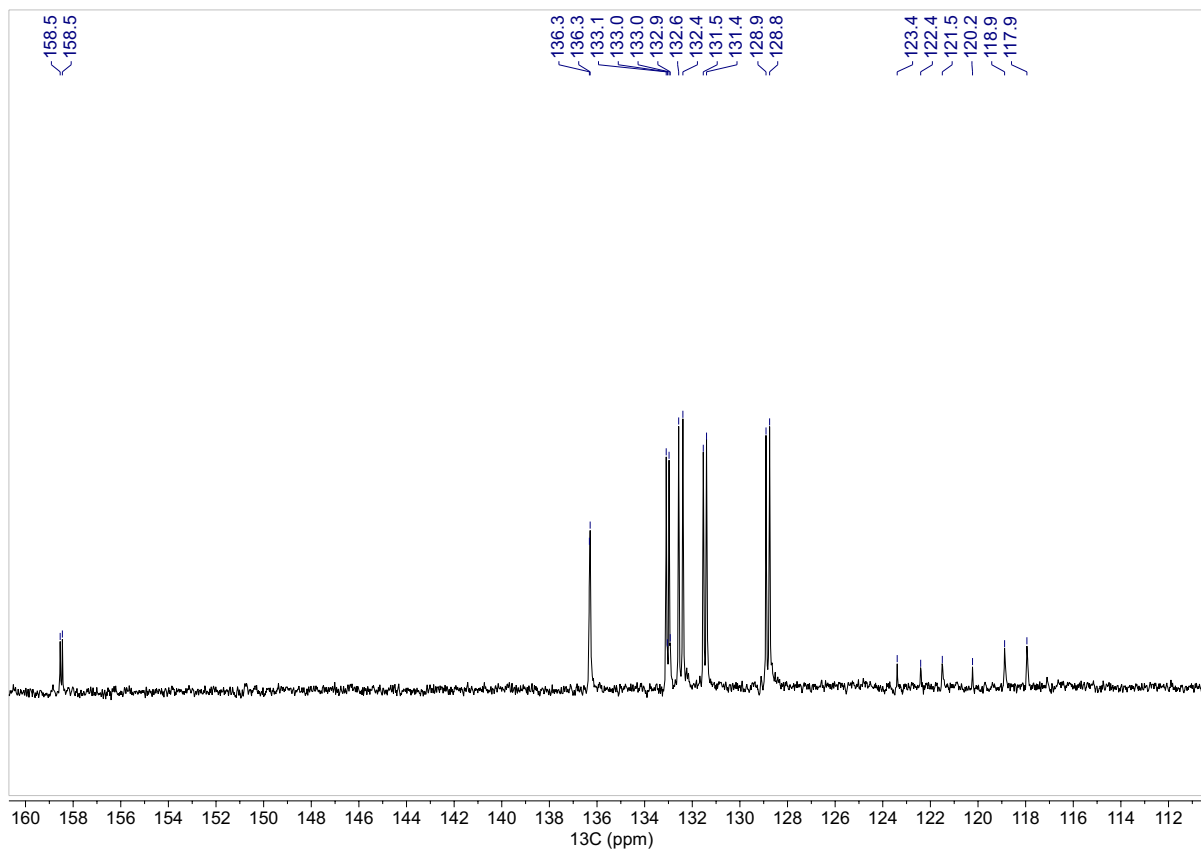
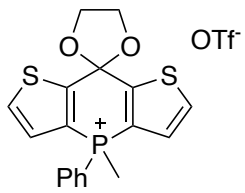
**Figure S2-22.**  $^1\text{H}$  NMR spectrum (400 MHz, MeOD) of compound **2-8Me**.



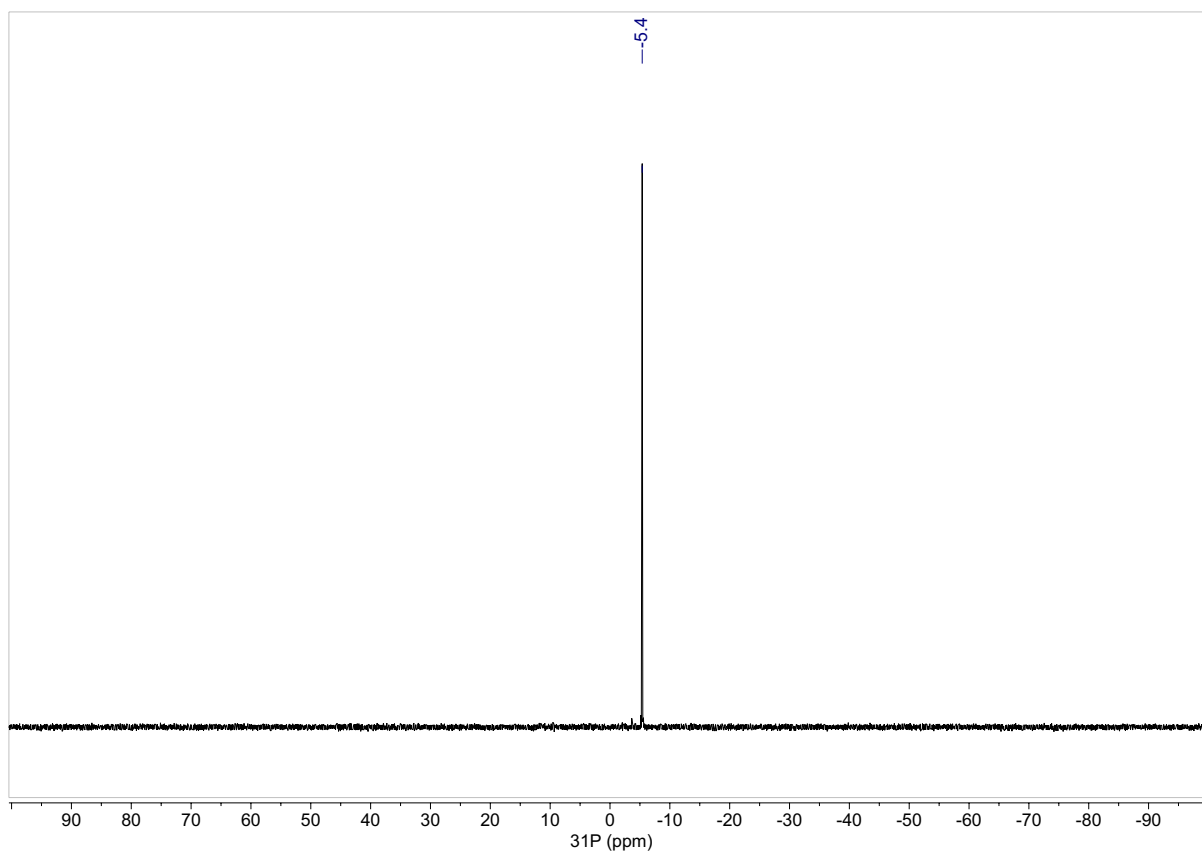
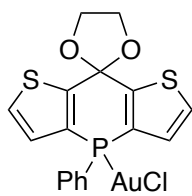
**Figure S2-23.**  $^1\text{H}$  NMR spectrum zoomed (400 MHz, MeOD) of compound **2-8Me**.



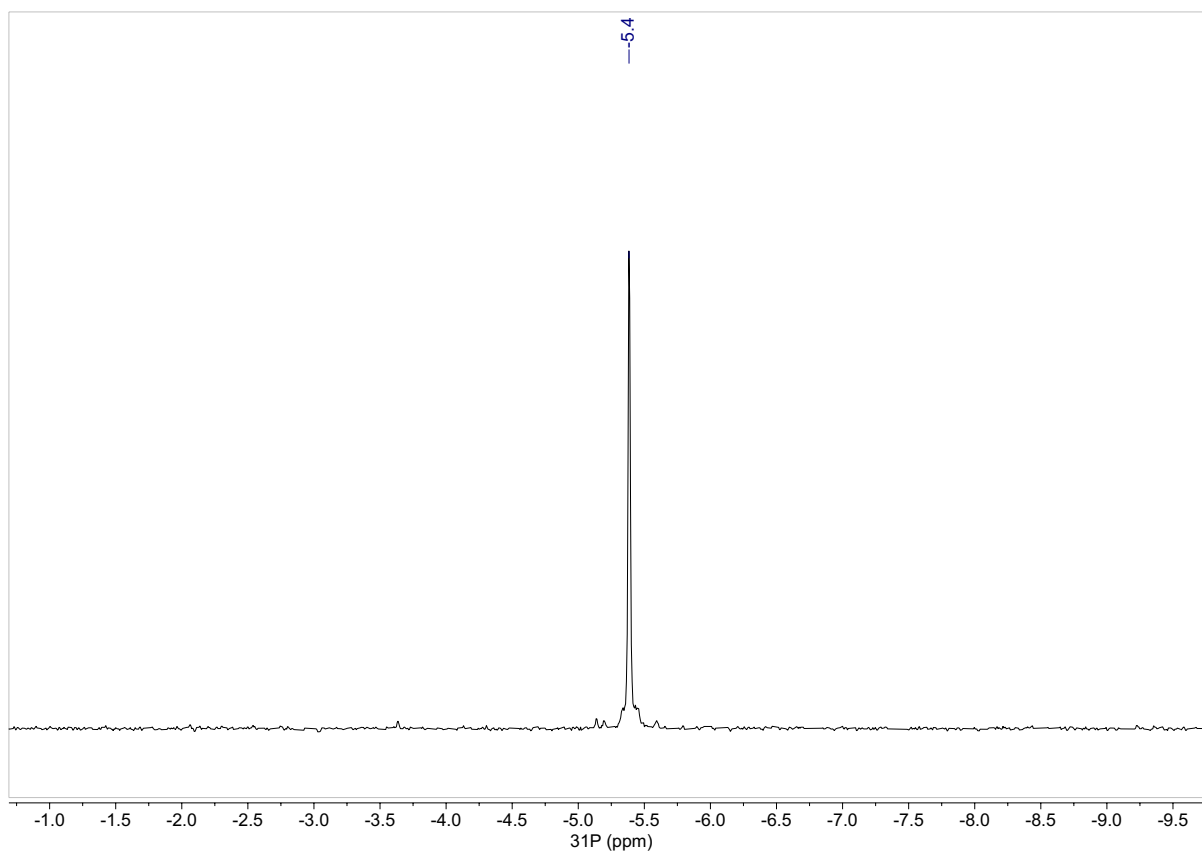
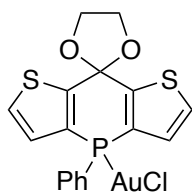
**Figure S2-24.**  $^{13}\text{C}$  NMR spectrum (100.6 MHz, MeOD) of compound **2-8Me**.



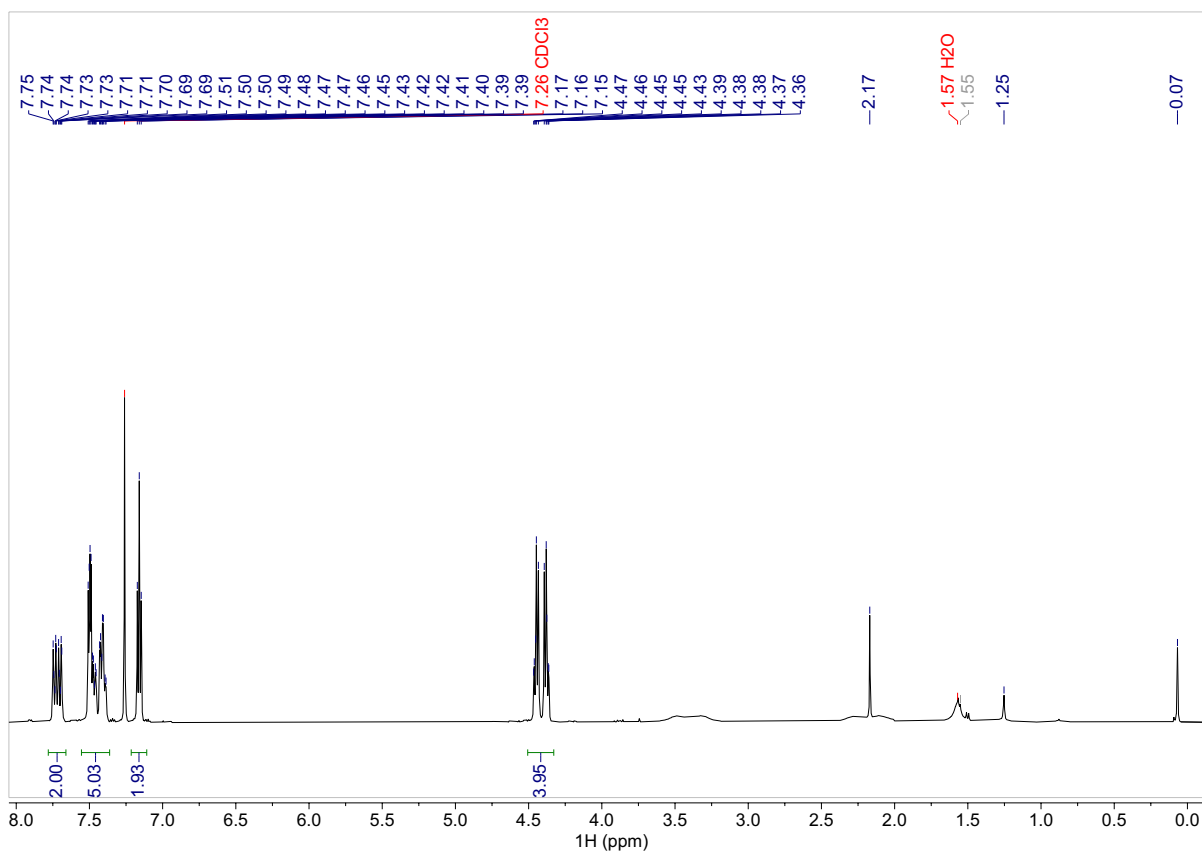
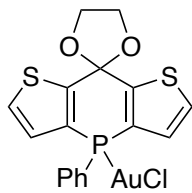
**Figure S2-25.**  $^{13}\text{C}$  NMR spectrum zoomed (100.6 MHz, MeOD) of compound **2-8Me**.



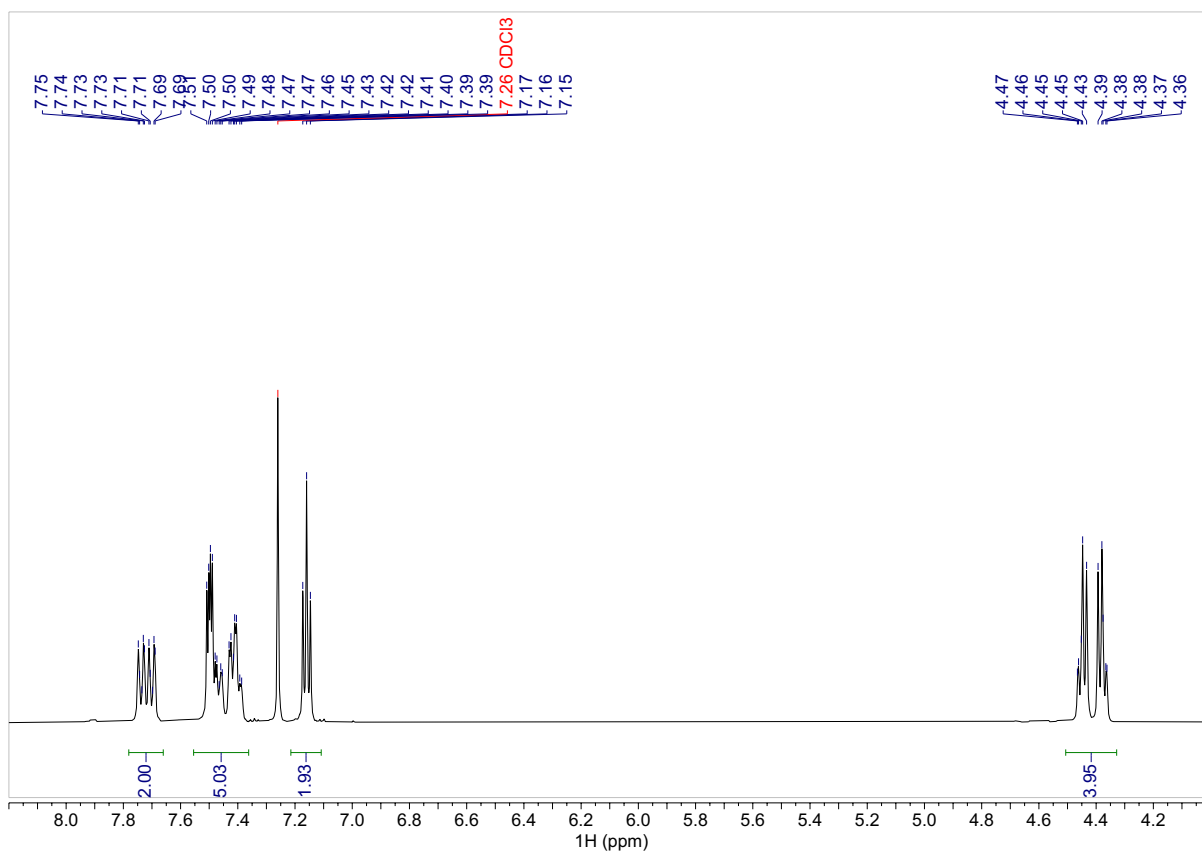
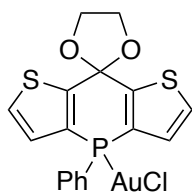
**Figure S2-26.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of compound 2-8Au.



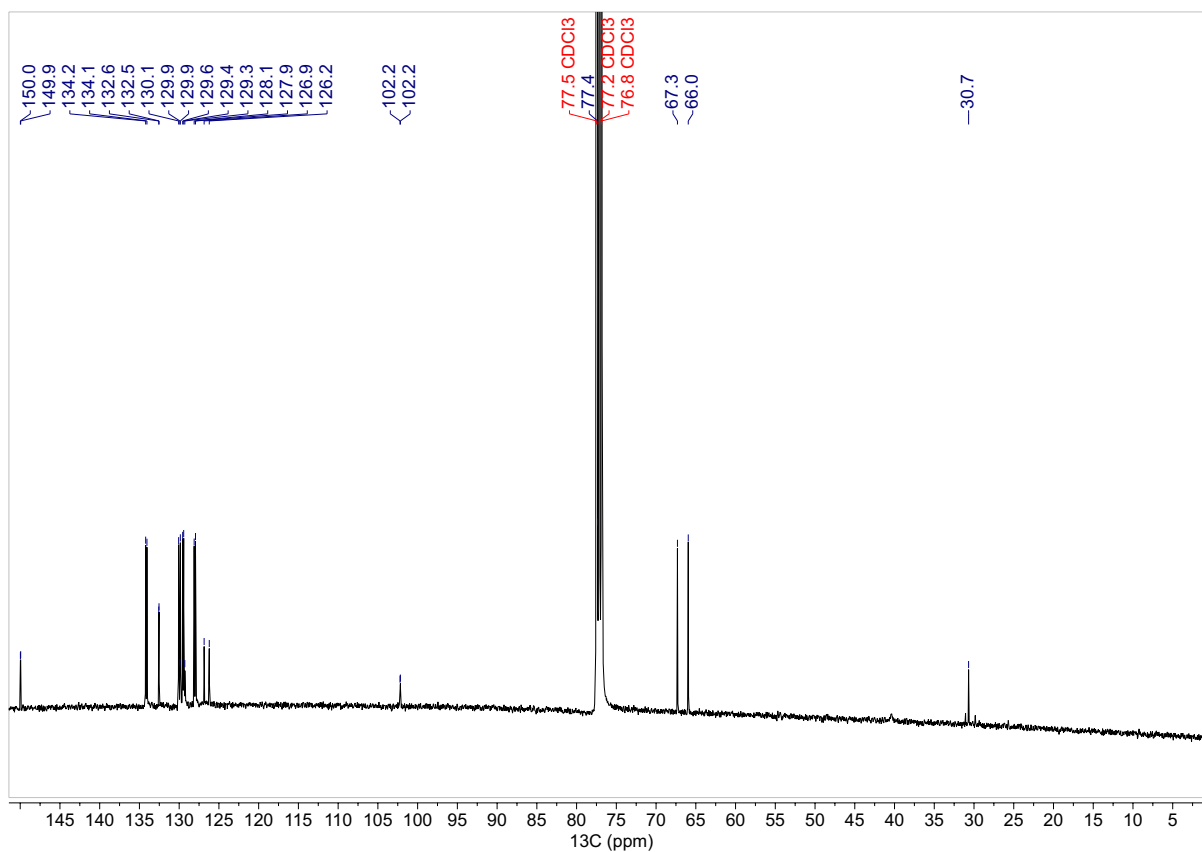
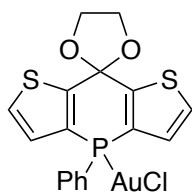
**Figure S2-27.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CDCl}_3$ ) of compound **2-8Au**.



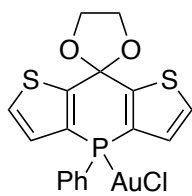
**Figure S2-28.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of compound **2-8Au**.



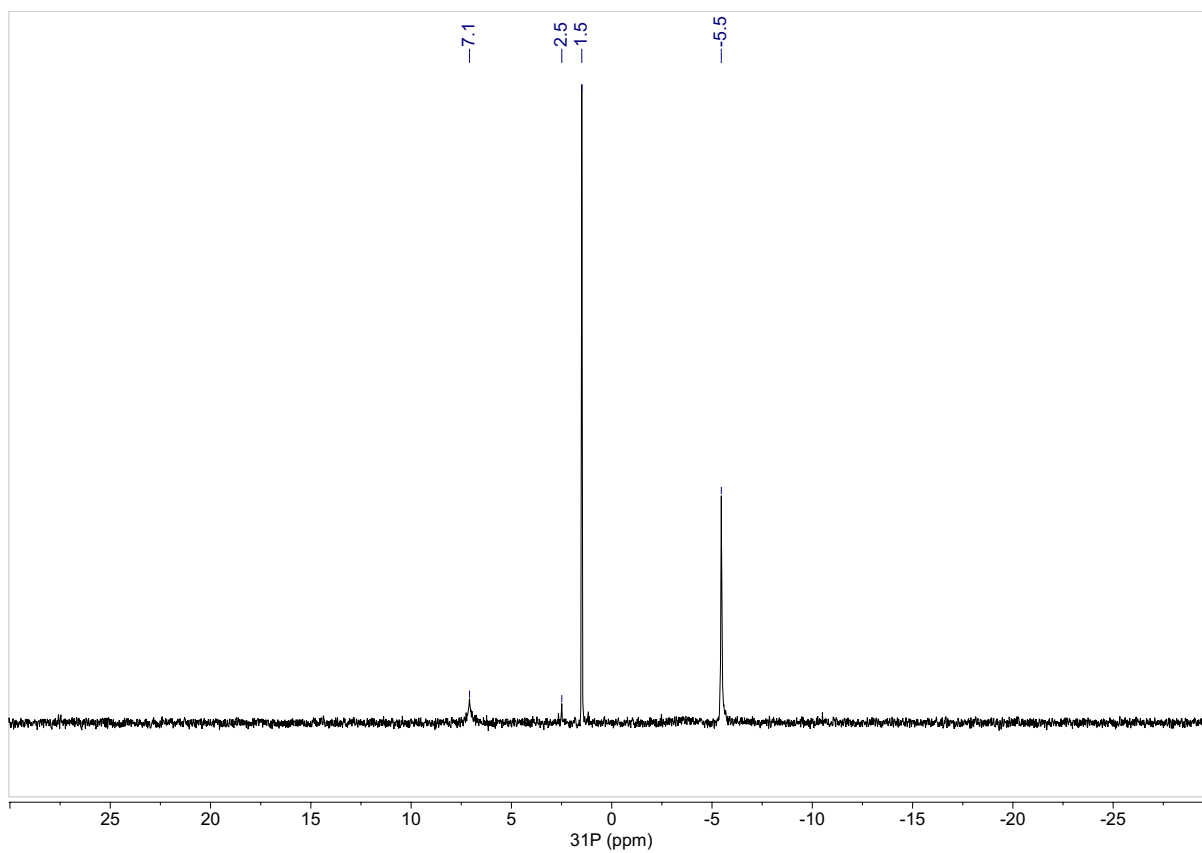
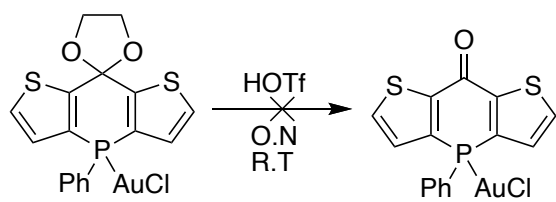
**Figure S2-29.** <sup>1</sup>H NMR spectrum zoomed (400 MHz, CDCl<sub>3</sub>) of compound **2-8Au**.



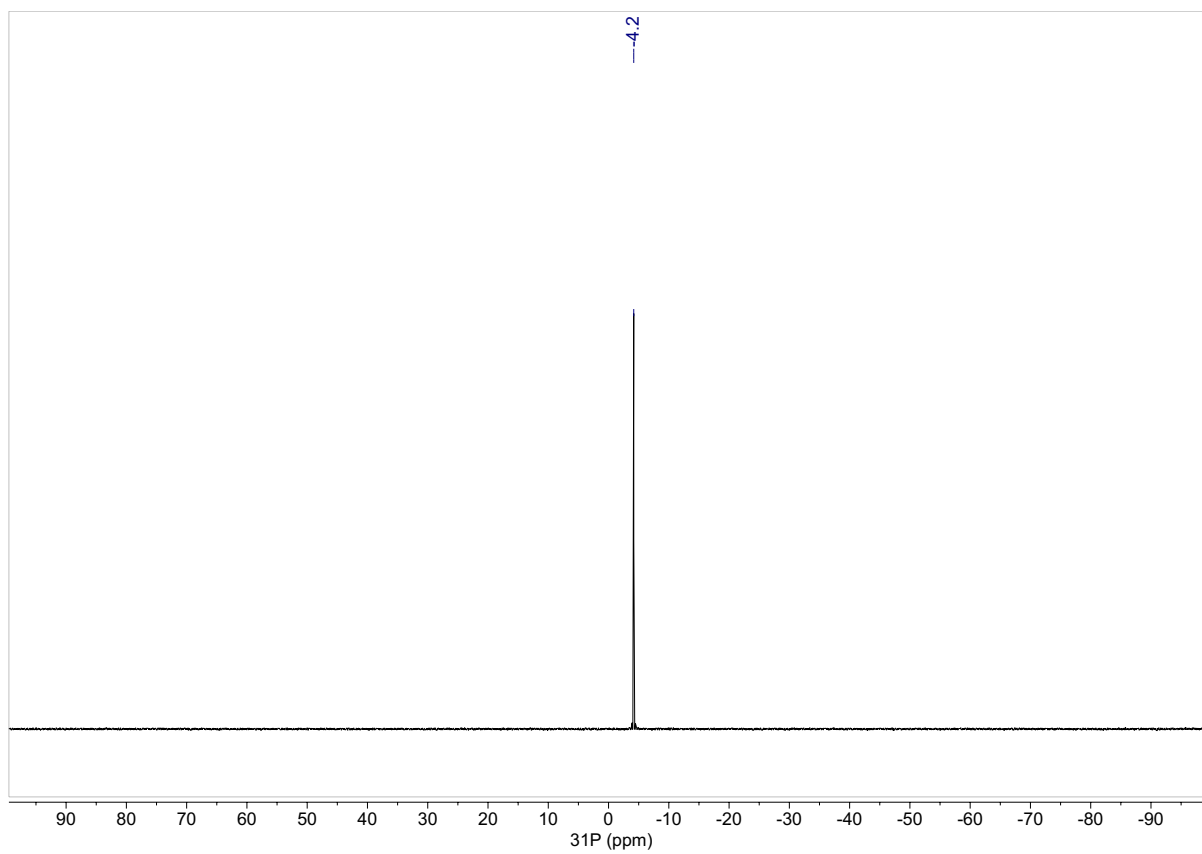
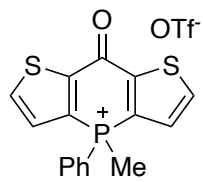
**Figure S2-30.** <sup>13</sup>C NMR spectrum (100.6 MHz, CDCl<sub>3</sub>) of compound **2-8Au**.



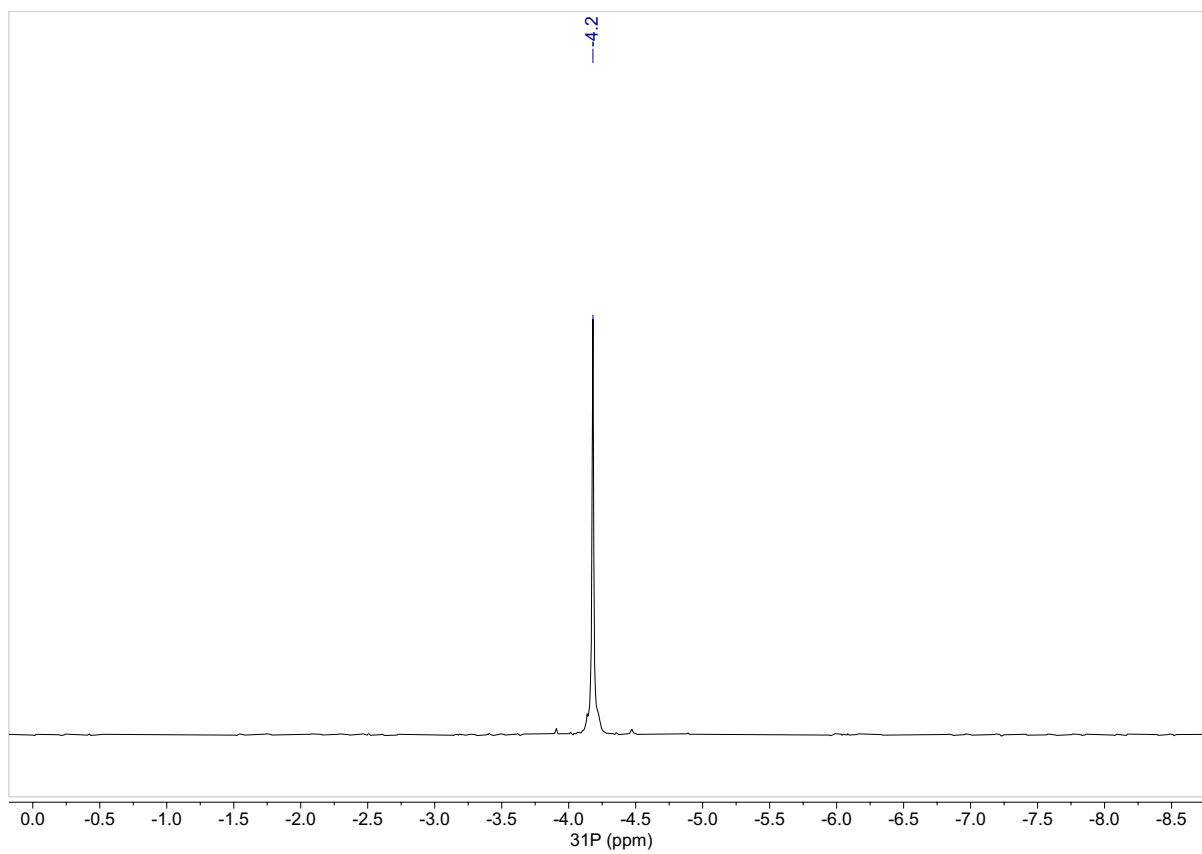
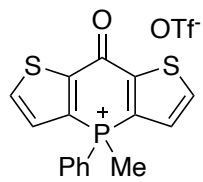
**Figure S2-31.**  $^{13}\text{C}$  NMR spectrum zoomed (100.6 MHz,  $\text{CDCl}_3$ ) of compound **2-8Au**.



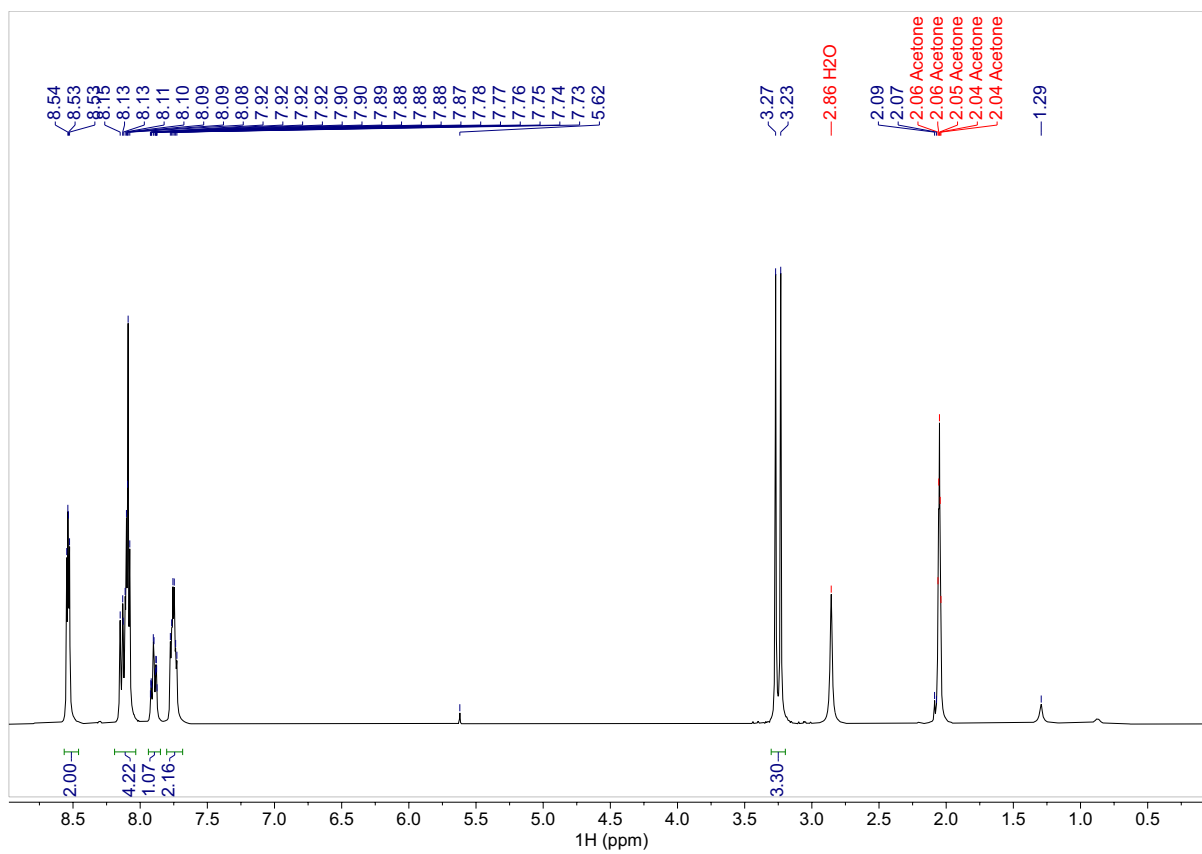
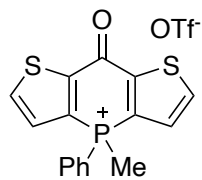
**Figure S2-32.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of crude reaction mixture from failed deprotection using triflic acid.



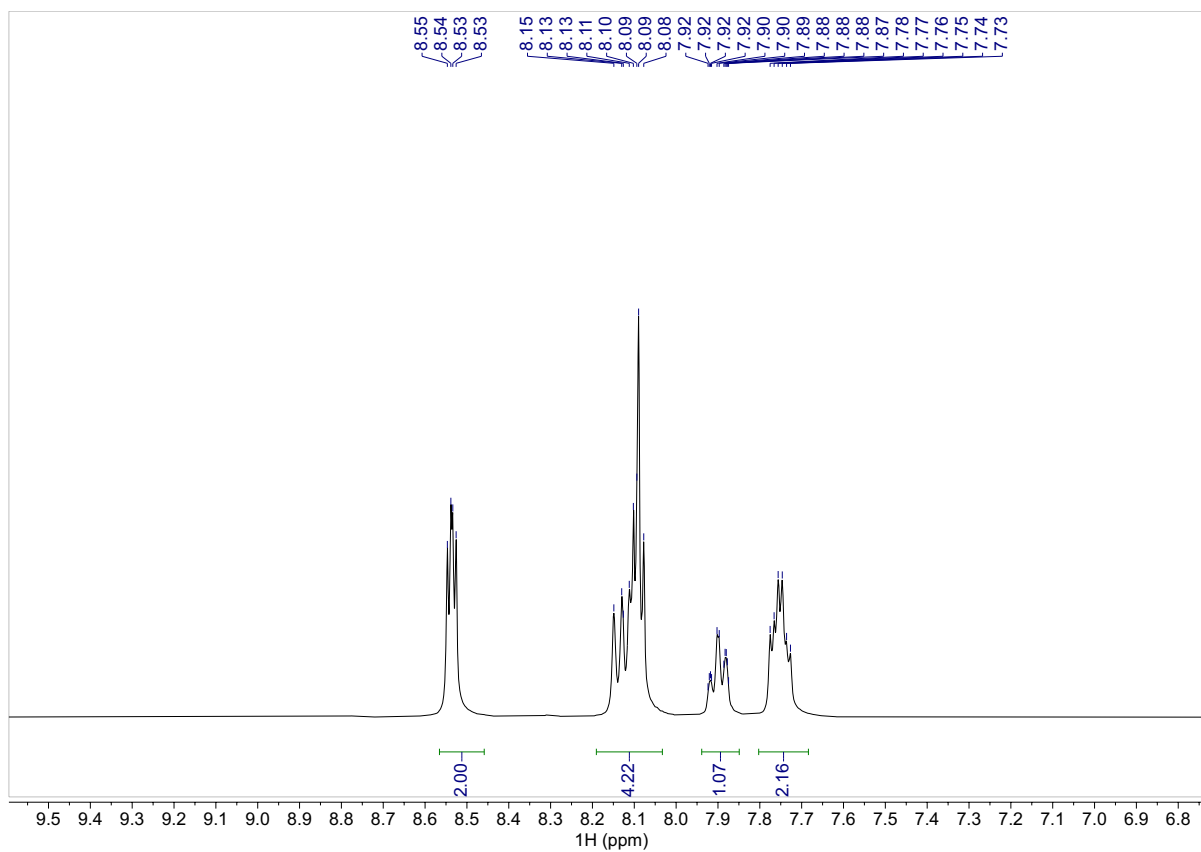
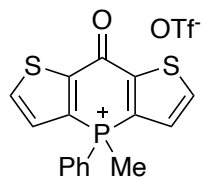
**Figure S2-33.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $(\text{CD}_3)_2\text{CO}$ ) of compound **2-3Me**.



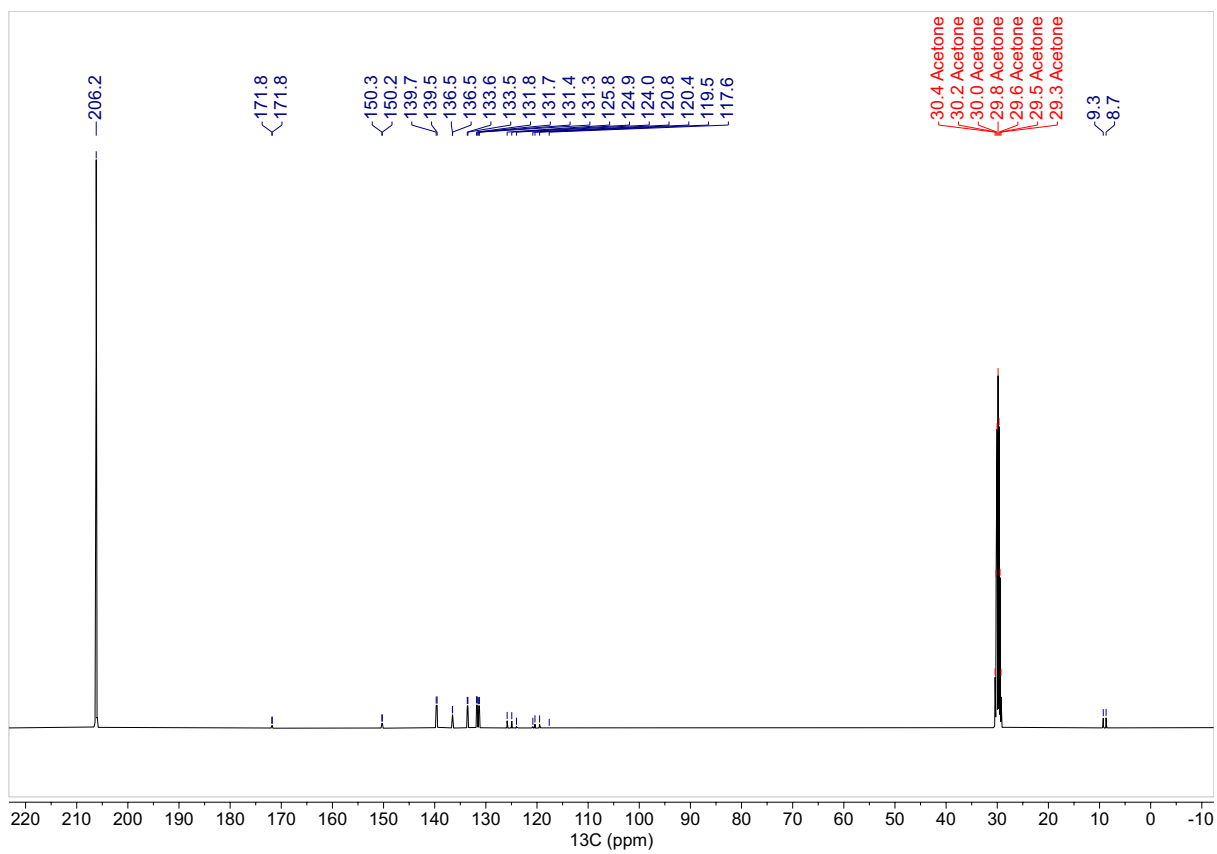
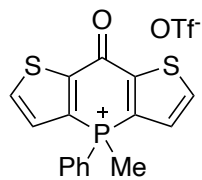
**Figure S2-34.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum zoomed (162 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) of compound **2-3Me**.



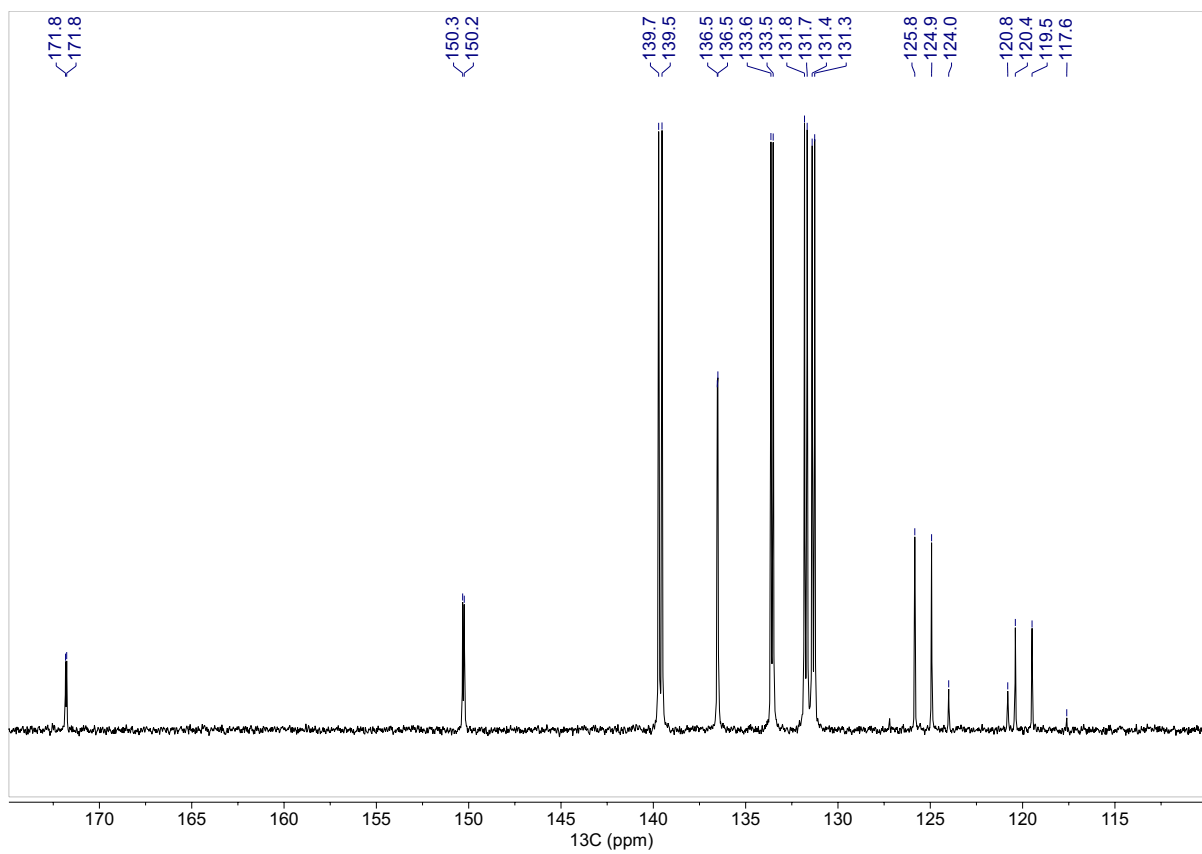
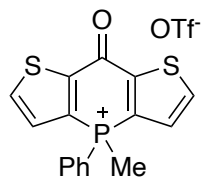
**Figure S2-35.**  $^1\text{H}$  NMR spectrum (400 MHz,  $(\text{CD}_3)_2\text{CO}$ ) of compound **2-3Me**.



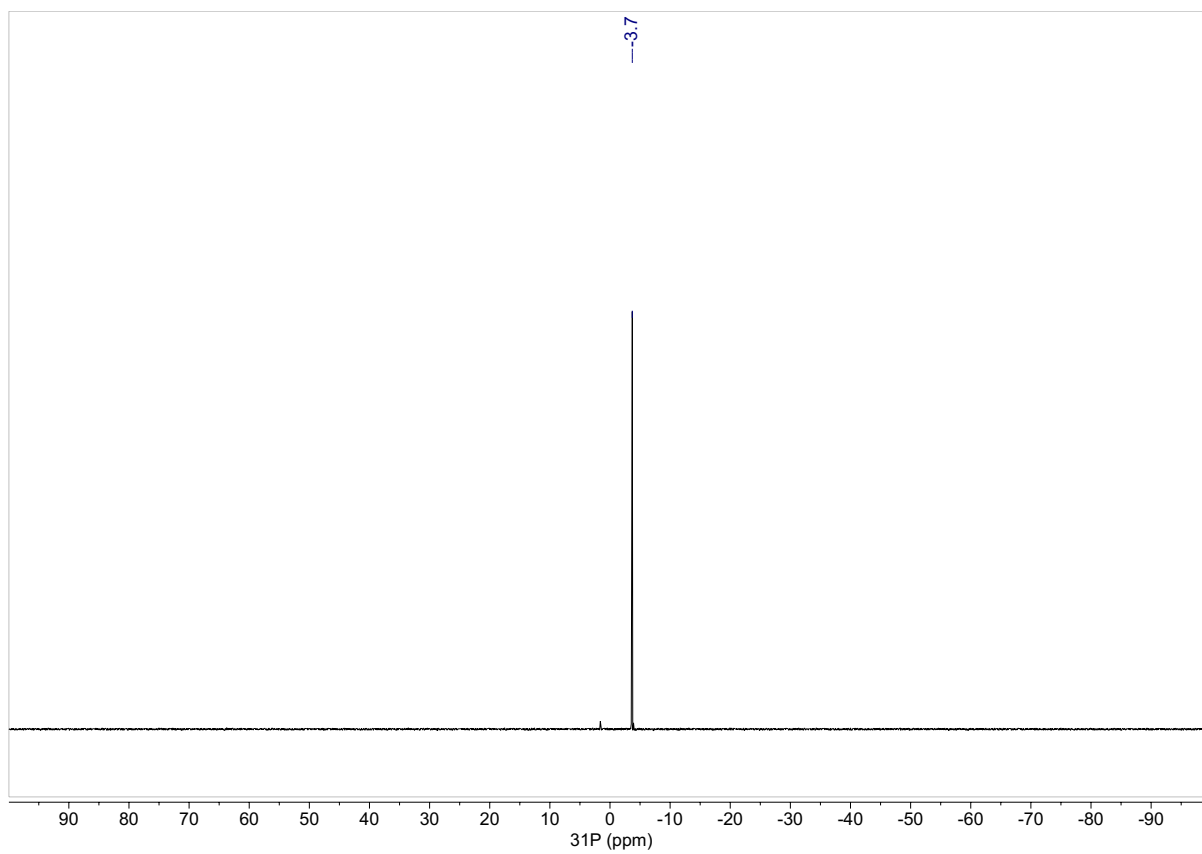
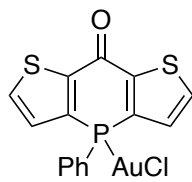
**Figure S2-36.**  $^1\text{H}$  NMR spectrum zoomed (400 MHz,  $(\text{CD}_3)_2\text{CO}$ ) of compound **2-3Me**.



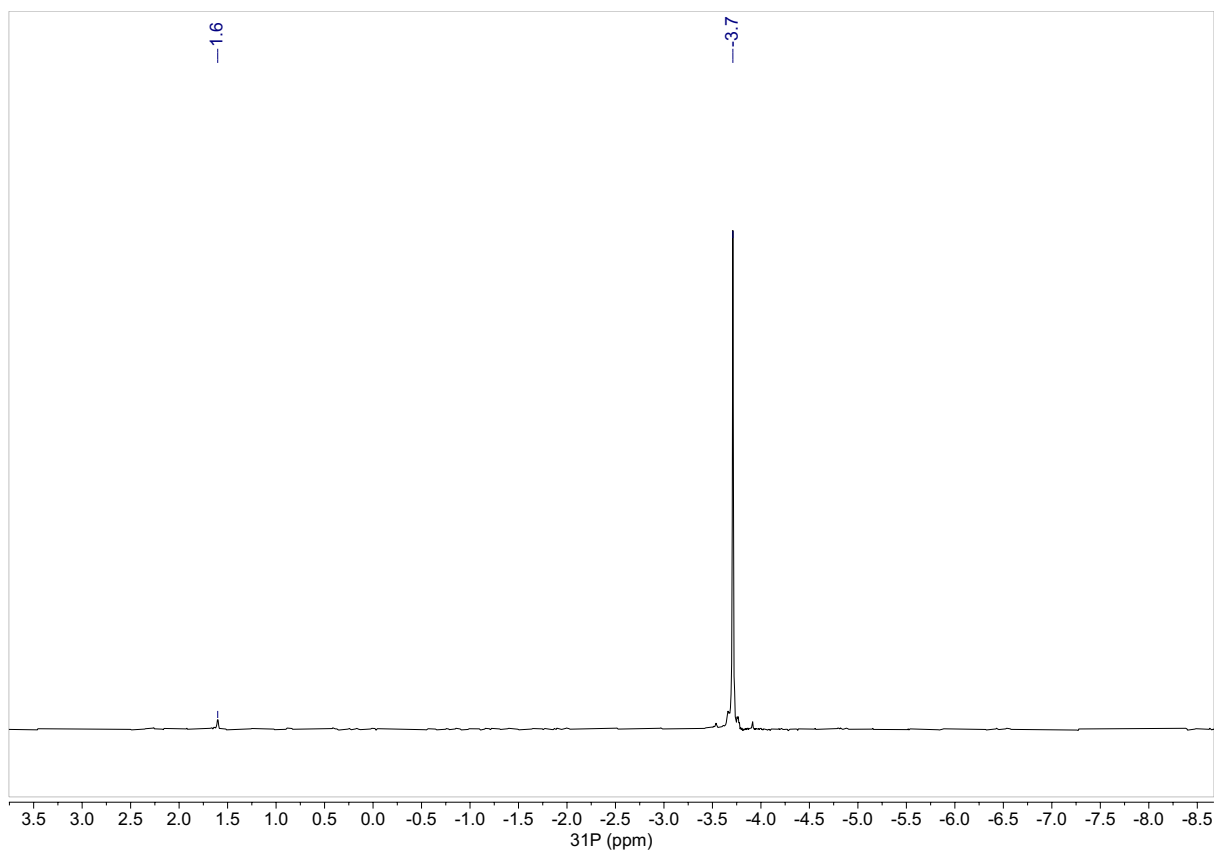
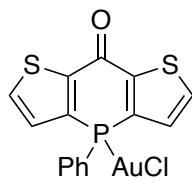
**Figure S2-37.** <sup>13</sup>C NMR spectrum (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) of compound 2-3Me.



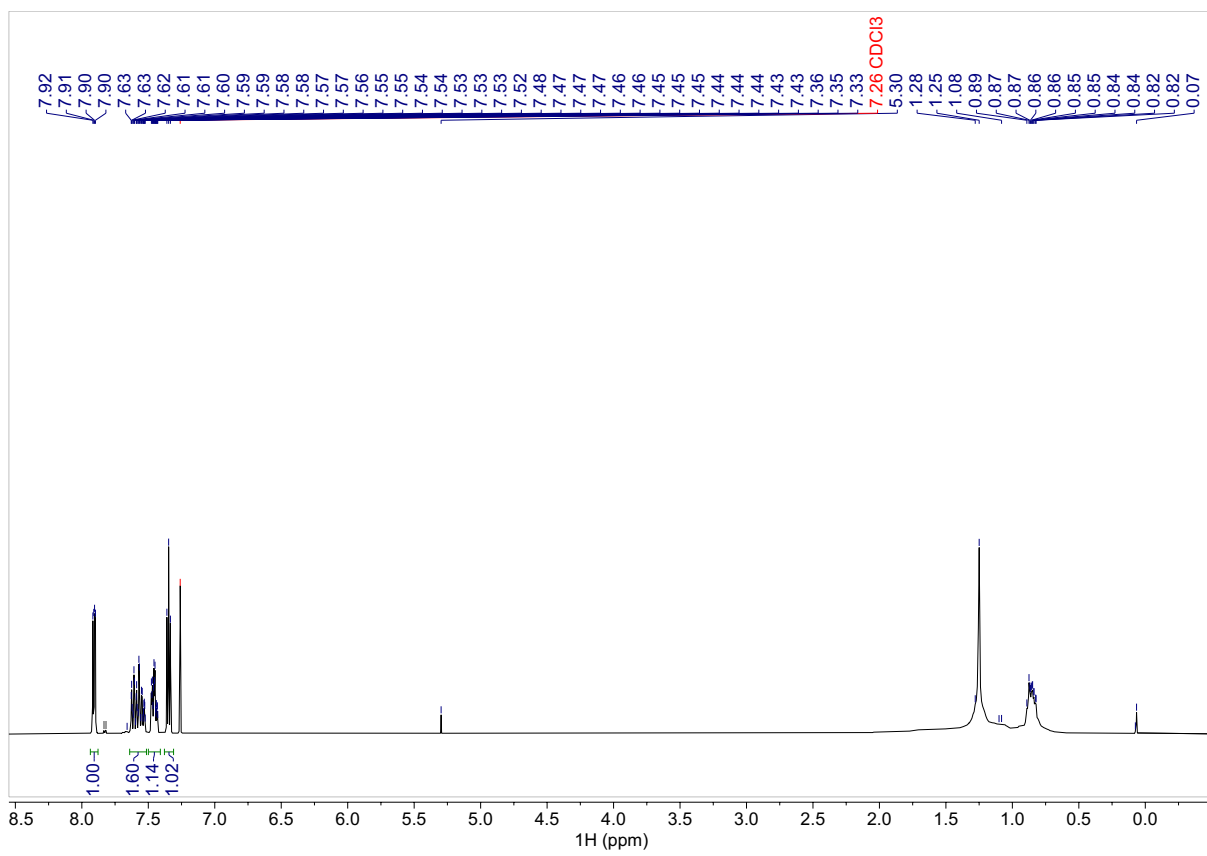
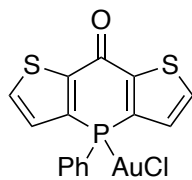
**Figure S2-38.** <sup>13</sup>C NMR spectrum zoomed (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) of compound 2-3Me.



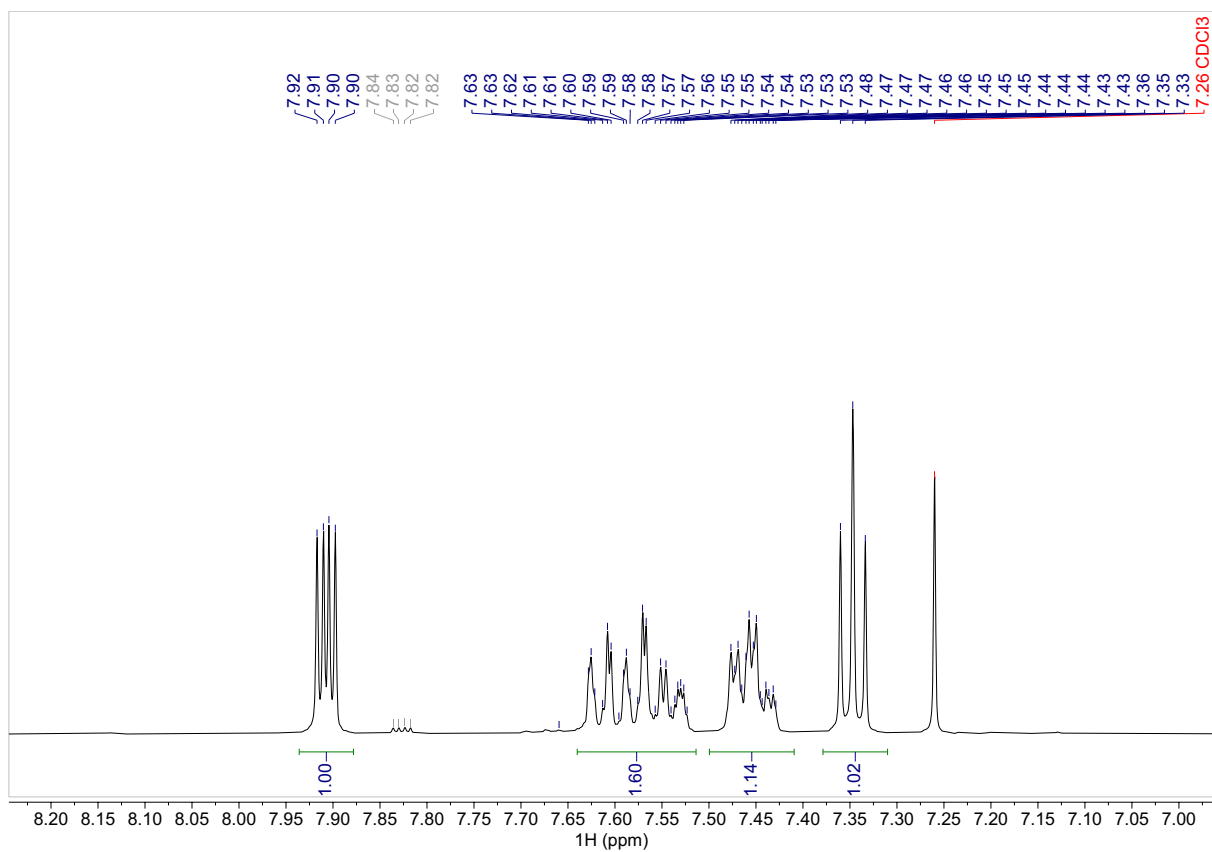
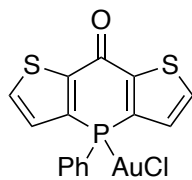
**Figure S2-39.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of compound **2-3Au**.



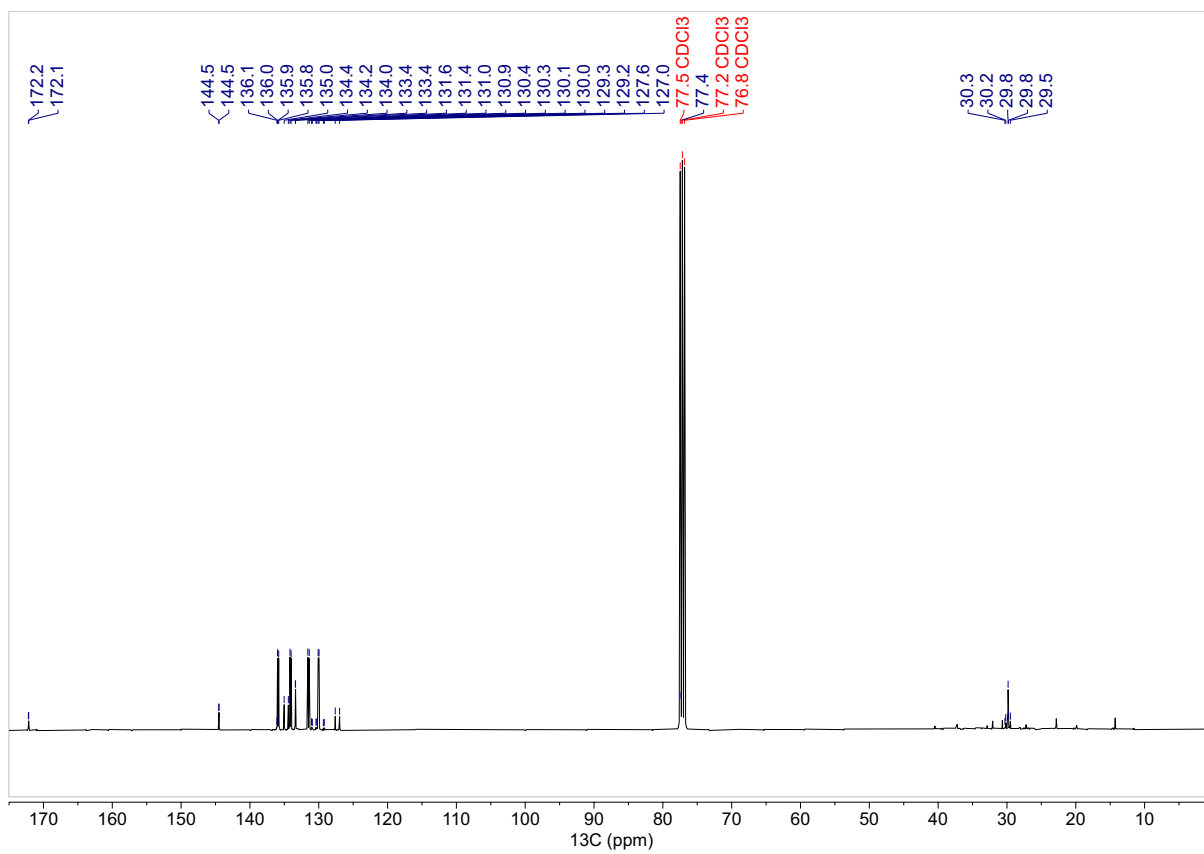
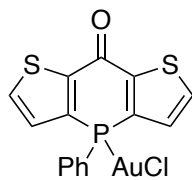
**Figure S2-40.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CDCl}_3$ ) of compound 2-3Au.



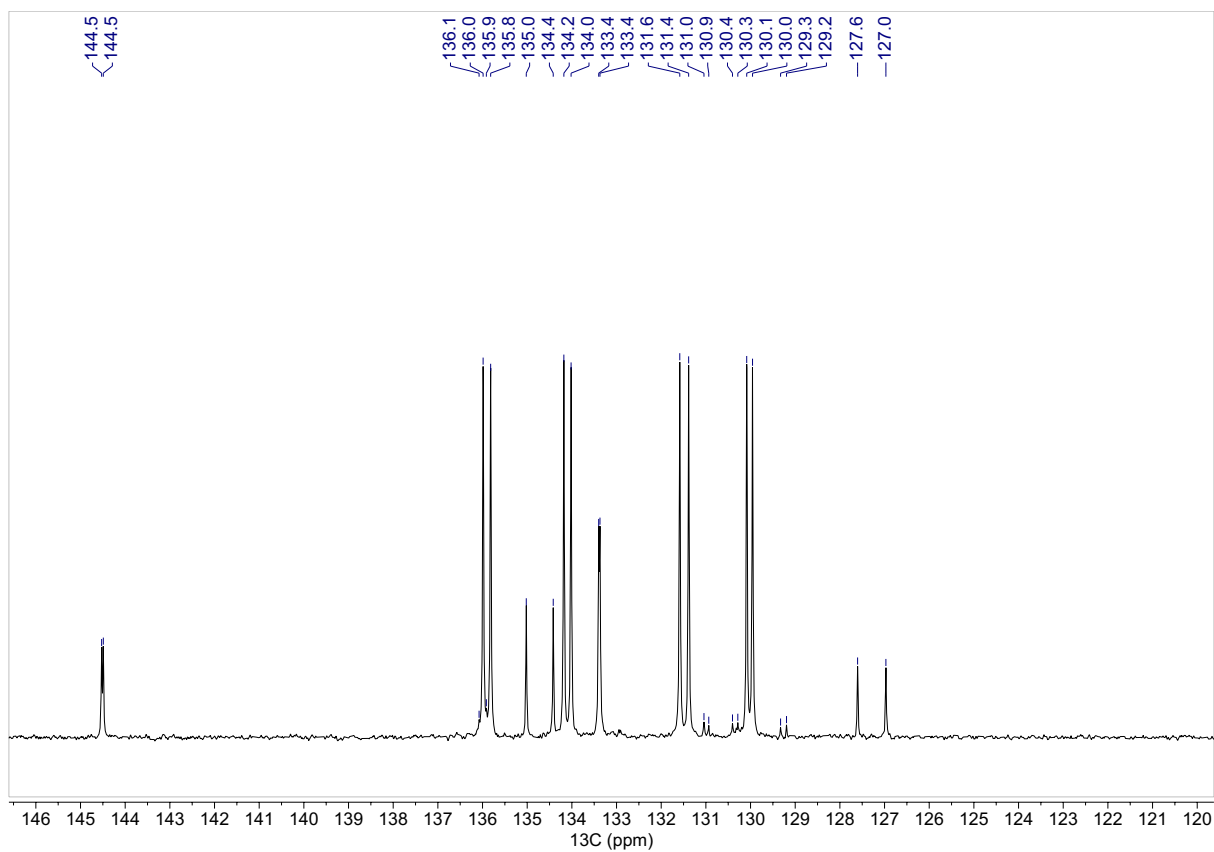
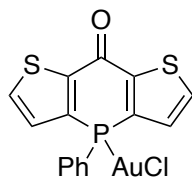
**Figure S2-41.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of compound **2-3Au**.



**Figure S2-42.** <sup>1</sup>H NMR spectrum zoomed (400 MHz, CDCl<sub>3</sub>) of compound 2-3Au.



**Figure S2-43.** <sup>13</sup>C NMR spectrum (100.6 MHz, CDCl<sub>3</sub>) of compound 2-3Au.

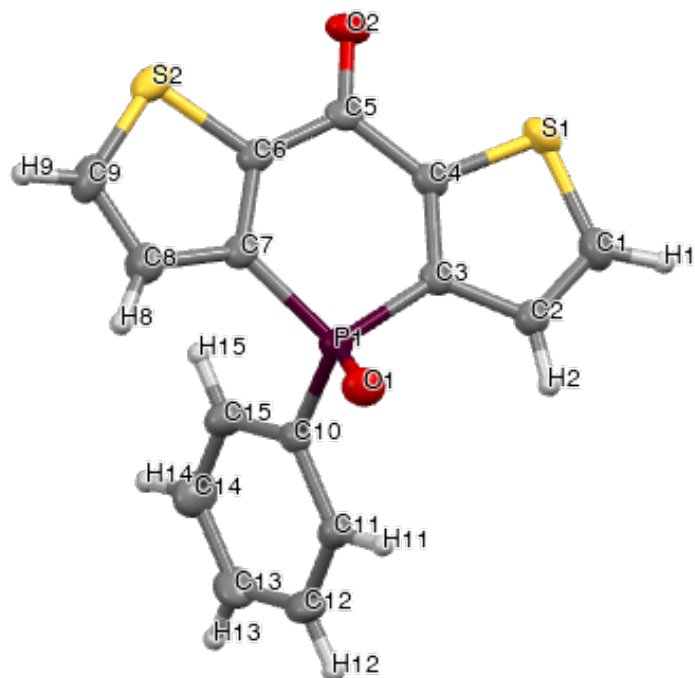


**Figure S2-44.**  $^{13}\text{C}$  NMR spectrum zoomed (100.6 MHz,  $\text{CDCl}_3$ ) of compound 2-3Au.

### SI.2.3 Solid-state structures

**Table S2-1.** Crystal data and structure refinement for **2-30**.

Identification code	4_159_A
Empirical formula	C <sub>15</sub> H <sub>9</sub> O <sub>2</sub> PS <sub>2</sub>
Formula weight	316.31
Temperature/K	173.00
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	7.1012(3)
b/Å	11.2755(5)
c/Å	17.1138(7)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1370.29(10)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.533
μ/mm <sup>-1</sup>	0.501
F(000)	648.0
Crystal size/mm <sup>3</sup>	0.25 × 0.2 × 0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.326 to 56.632
Index ranges	-9 ≤ h ≤ 9, -15 ≤ k ≤ 14, -22 ≤ l ≤ 22
Reflections collected	29749
Independent reflections	3413 [R <sub>int</sub> = 0.0478, R <sub>sigma</sub> = 0.0273]
Data/restraints/parameters	3413/0/181
Goodness-of-fit on F <sup>2</sup>	1.046
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0280, wR <sub>2</sub> = 0.0643
Final R indexes [all data]	R <sub>1</sub> = 0.0361, wR <sub>2</sub> = 0.0684
Largest diff. peak/hole / e Å <sup>-3</sup>	0.20/-0.28
Flack parameter	0.05(3)



**Figure S2-45.** Labelled solid-state structure of **2-3O** shown as thermal ellipsoids (50% probability).

**Table S2-2.** Bond lengths for **2-3O**.

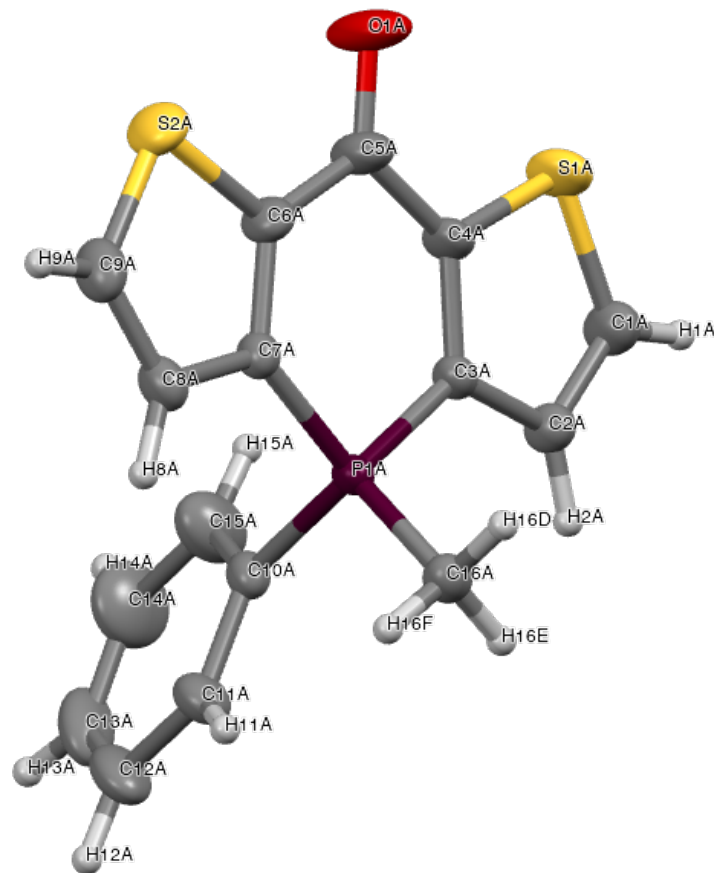
<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>	<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>
S2	C6	1.723(3)	C11	C10	1.391(3)
S2	C9	1.700(3)	C10	C15	1.394(3)
S1	C4	1.719(3)	C3	C4	1.384(3)
S1	C1	1.706(3)	C3	C2	1.412(4)
P1	O1	1.4850(18)	C4	C5	1.460(4)
P1	C10	1.797(2)	C5	C6	1.463(4)
P1	C3	1.798(2)	C7	C6	1.386(3)
P1	C7	1.797(3)	C7	C8	1.415(4)
O2	C5	1.232(3)	C9	C8	1.370(4)
C13	C12	1.389(4)	C1	C2	1.360(4)
C13	C14	1.380(4)	C15	C14	1.383(4)
C12	C11	1.382(4)			

**Table S2-3.** Bond angles for **2-30**.

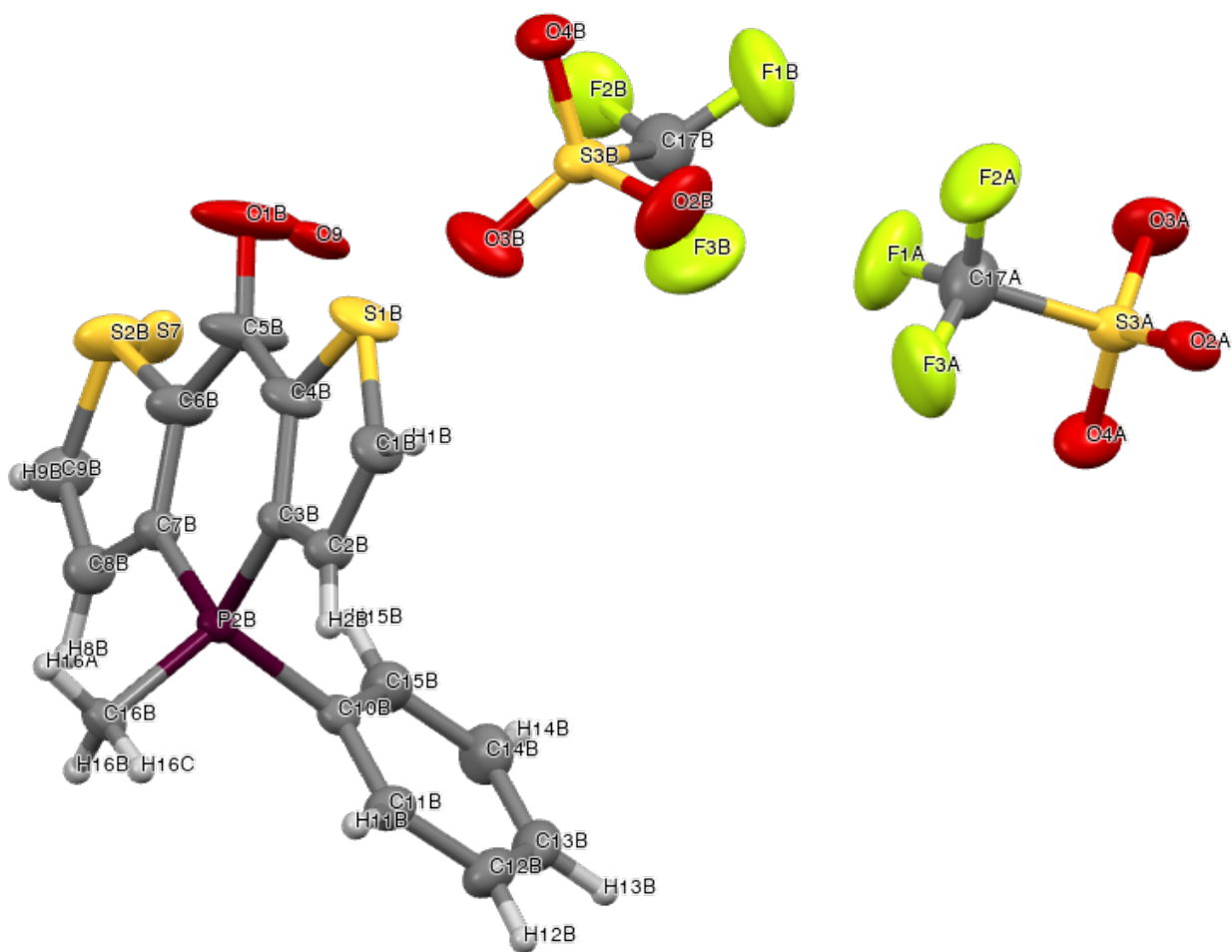
<b>Atom Atom Atom</b>	<b>Angle/°</b>	<b>Atom Atom Atom</b>	<b>Angle/°</b>
C9 S2 C6	91.41(13)	C3 C4 C5	128.2(2)
C1 S1 C4	91.46(13)	C5 C4 S1	120.45(17)
O1 P1 C10	112.09(11)	O2 C5 C4	121.5(3)
O1 P1 C3	112.45(11)	O2 C5 C6	122.1(3)
O1 P1 C7	115.80(12)	C4 C5 C6	116.4(2)
C10 P1 C3	107.25(11)	C6 C7 P1	122.7(2)
C7 P1 C10	106.58(11)	C6 C7 C8	111.8(2)
C7 P1 C3	101.84(12)	C8 C7 P1	125.47(19)
C14 C13 C12	119.9(3)	C5 C6 S2	120.25(18)
C11 C12 C13	119.8(3)	C7 C6 S2	111.7(2)
C12 C11 C10	120.5(3)	C7 C6 C5	128.1(2)
C11 C10 P1	118.13(19)	C8 C9 S2	112.8(2)
C11 C10 C15	119.3(2)	C9 C8 C7	112.3(2)
C15 C10 P1	122.61(19)	C2 C1 S1	112.6(2)
C4 C3 P1	122.71(19)	C1 C2 C3	112.5(2)
C4 C3 C2	112.1(2)	C14 C15 C10	120.0(3)
C2 C3 P1	124.99(18)	C13 C14 C15	120.4(3)
C3 C4 S1	111.35(19)		

**Table S2-4.** Crystal data and structure refinement for **2-3Me**.

Identification code	1_11_0_0m_a
Empirical formula	C <sub>19.25</sub> H <sub>16.5</sub> F <sub>3</sub> O <sub>4.75</sub> PS <sub>3</sub>
Formula weight	507.97
Temperature/K	150.00
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	13.0863(11)
b/Å	14.7632(12)
c/Å	23.1467(18)
α/°	90
β/°	93.047(3)
γ/°	90
Volume/Å <sup>3</sup>	4465.5(6)
Z	8
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.511
μ/mm <sup>-1</sup>	0.456
F(000)	2080.0
Crystal size/mm <sup>3</sup>	0.25 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.66 to 66.434
Index ranges	-20 ≤ h ≤ 20, -22 ≤ k ≤ 22, -35 ≤ l ≤ 35
Reflections collected	155229
Independent reflections	17066 [R <sub>int</sub> = 0.0383, R <sub>sigma</sub> = 0.0226]
Data/restraints/parameters	17066/0/619
Goodness-of-fit on F <sup>2</sup>	1.124
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0614, wR <sub>2</sub> = 0.1405
Final R indexes [all data]	R <sub>1</sub> = 0.0735, wR <sub>2</sub> = 0.1471
Largest diff. peak/hole / e Å <sup>-3</sup>	0.81/-0.59



**Figure S2-46.** Labelled solid-state structure of **2-3Me** shown as thermal ellipsoids (50% probability).



**Figure S2-47.** Labeled solid-state structure of **2-3Me** shown as thermal ellipsoids (50% probability). Second system in unit cell including triflate anions.

**Table S2-5.** Bond lengths for **2-3Me**.

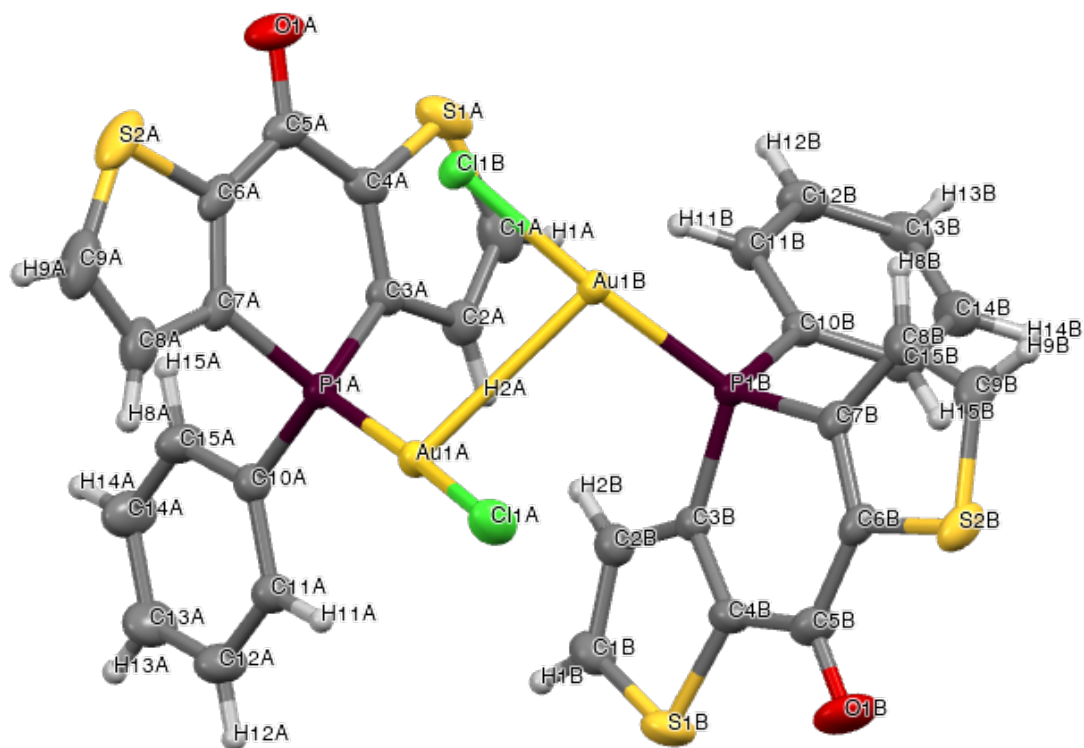
<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>	<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>
S1A	C4A	1.713(2)	C5A	C4A	1.464(3)
S1A	C1A	1.704(3)	C5A	C6A	1.468(3)
S2A	C6A	1.716(2)	C4A	C3A	1.381(3)
S2A	C9A	1.711(3)	C3A	C2A	1.414(3)
S1B	C1B	1.703(2)	C10A	C15A	1.385(4)
S1B	C4B	1.716(2)	C10A	C11A	1.392(3)
S2B	C6B	1.727(3)	C15A	C14A	1.388(4)
S2B	C9B	1.683(3)	C14A	C13A	1.369(6)
S3A	O2A	1.4476(17)	C13A	C12A	1.378(5)
S3A	O4A	1.4372(19)	C1A	C2A	1.364(3)
S3A	O3A	1.4346(19)	C11A	C12A	1.396(3)
S3A	C17A	1.822(3)	C7A	C6A	1.385(3)
S3B	O2B	1.441(2)	C7A	C8A	1.413(3)
S3B	O3B	1.424(2)	C9A	C8A	1.371(3)
S3B	O4B	1.4312(18)	C13B	C14B	1.377(4)
S3B	C17B	1.812(3)	C13B	C12B	1.381(4)
P1A	C3A	1.7659(19)	C14B	C15B	1.393(3)
P1A	C10A	1.787(2)	C15B	C10B	1.395(3)
P1A	C16A	1.784(2)	C10B	C11B	1.395(3)
P1A	C7A	1.7790(19)	C3B	C2B	1.416(3)
P2B	C10B	1.787(2)	C3B	C4B	1.373(3)
P2B	C3B	1.7815(18)	C2B	C1B	1.371(3)
P2B	C7B	1.773(2)	C12B	C11B	1.386(3)
P2B	C16B	1.781(2)	C7B	C6B	1.376(3)
F1A	C17A	1.326(3)	C7B	C8B	1.418(3)
F2A	C17A	1.330(4)	C6B	C5B	1.466(3)
F3A	C17A	1.326(4)	C6B	S7	1.697(8)
F1B	C17B	1.324(4)	C5B	C4B	1.463(3)
F2B	C17B	1.342(4)	C5B	O9	1.328(14)
F3B	C17B	1.318(4)	C9B	C8B	1.368(3)
O1A	C5A	1.229(3)	C9B	S7	1.881(8)
O1B	C5B	1.235(4)			

**Table S2-6. Bond angles for 2-3Me.**

Atom Atom Atom	Angle/°	Atom Atom Atom	Angle/°
C1A S1A C4A	91.52(11)	C5A C6A S2A	120.82(16)
C9A S2A C6A	91.88(11)	C7A C6A S2A	111.04(16)
C1B S1B C4B	91.32(10)	C7A C6A C5A	128.03(18)
C9B S2B C6B	92.02(12)	C8A C9A S2A	112.31(18)
O2A S3A C17A	102.85(12)	C9A C8A C7A	111.9(2)
O4A S3A O2A	114.31(11)	C14B C13B C12B	120.7(2)
O4A S3A C17A	103.13(14)	C13B C14B C15B	120.2(2)
O3A S3A O2A	114.69(12)	C14B C15B C10B	119.3(2)
O3A S3A O4A	115.55(13)	C15B C10B P2B	120.66(16)
O3A S3A C17A	104.00(14)	C11B C10B P2B	119.08(15)
O2B S3B C17B	102.97(16)	C11B C10B C15B	120.13(19)
O3B S3B O2B	114.64(17)	C2B C3B P2B	126.36(14)
O3B S3B O4B	116.40(14)	C4B C3B P2B	121.13(15)
O3B S3B C17B	103.89(14)	C4B C3B C2B	112.38(17)
O4B S3B O2B	113.65(14)	C1B C2B C3B	111.69(19)
O4B S3B C17B	102.92(14)	C2B C1B S1B	112.75(16)
C3A P1A C10A	107.56(10)	C13B C12B C11B	120.1(2)
C3A P1A C16A	112.63(10)	C12B C11B C10B	119.7(2)
C3A P1A C7A	104.17(9)	C6B C7B P2B	120.91(15)
C16A P1A C10A	110.10(10)	C6B C7B C8B	112.91(19)
C7A P1A C10A	111.42(9)	C8B C7B P2B	126.07(16)
C7A P1A C16A	110.82(10)	C7B C6B S2B	110.44(16)
C3B P2B C10B	109.37(9)	C7B C6B C5B	128.1(2)
C7B P2B C10B	108.60(9)	C7B C6B S7	114.6(3)
C7B P2B C3B	104.23(9)	C5B C6B S2B	121.38(17)
C7B P2B C16B	112.59(10)	C5B C6B S7	115.8(3)
C16B P2B C10B	111.20(10)	O1B C5B C6B	119.9(3)
C16B P2B C3B	110.60(9)	O1B C5B C4B	122.7(3)
O1A C5A C4A	121.1(2)	C4B C5B C6B	117.09(19)
O1A C5A C6A	122.2(2)	O9 C5B C6B	122.8(8)
C4A C5A C6A	116.68(18)	O9 C5B C4B	110.2(7)
C5A C4A S1A	121.09(16)	C3B C4B S1B	111.86(16)
C3A C4A S1A	111.33(15)	C3B C4B C5B	127.60(18)
C3A C4A C5A	127.58(18)	C5B C4B S1B	120.43(16)
C4A C3A P1A	122.19(15)	C8B C9B S2B	113.08(18)
C4A C3A C2A	112.61(17)	C8B C9B S7	109.9(3)
C2A C3A P1A	125.20(15)	C9B C8B C7B	111.4(2)
C15A C10A P1A	119.22(19)	F1A C17A S3A	111.1(2)
C15A C10A C11A	120.1(2)	F1A C17A F2A	108.2(3)
C11A C10A P1A	120.62(18)	F2A C17A S3A	110.9(2)
C10A C15A C14A	119.8(3)	F3A C17A S3A	110.9(2)
C13A C14A C15A	120.1(3)	F3A C17A F1A	108.1(3)
C14A C13A C12A	120.7(3)	F3A C17A F2A	107.5(3)
C2A C1A S1A	112.89(17)	F1B C17B S3B	112.0(2)
C1A C2A C3A	111.6(2)	F1B C17B F2B	107.0(3)
C10A C11A C12A	119.2(3)	F2B C17B S3B	110.5(2)
C13A C12A C11A	120.0(3)	F3B C17B S3B	112.7(3)
C6A C7A P1A	120.99(15)	F3B C17B F1B	108.7(3)
C6A C7A C8A	112.82(18)	F3B C17B F2B	105.7(3)
C8A C7A P1A	126.11(16)	C6B S7 C9B	86.4(3)

**Table S2-7.** Crystal data and structure refinement for **2-3Au**

Identification code	CT_1_112_0m_a
Empirical formula	C <sub>15</sub> H <sub>9</sub> AuClOPS <sub>2</sub>
Formula weight	532.73
Temperature/K	173.00
Crystal system	triclinic
Space group	P-1
a/Å	8.0944(3)
b/Å	13.5467(4)
c/Å	14.8103(5)
α/°	86.3350(10)
β/°	87.2270(10)
γ/°	74.6330(10)
Volume/Å <sup>3</sup>	1561.89(9)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	2.266
μ/mm <sup>-1</sup>	9.953
F(000)	1000.0
Crystal size/mm <sup>3</sup>	0.075 × 0.075 × 0.075
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.274 to 61.012
Index ranges	-11 ≤ h ≤ 11, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	64763
Independent reflections	9541 [R <sub>int</sub> = 0.0399, R <sub>sigma</sub> = 0.0242]
Data/restraints/parameters	9541/0/379
Goodness-of-fit on F <sup>2</sup>	1.053
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0206, wR <sub>2</sub> = 0.0384
Final R indexes [all data]	R <sub>1</sub> = 0.0314, wR <sub>2</sub> = 0.0428
Largest diff. peak/hole / e Å <sup>-3</sup>	1.96/-0.81



**Figure S2-48.** Labeled solid-state structure of 2-3Au shown as thermal ellipsoids (50% probability).

**Table S2-8.** Bond lengths for **2-3Au**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1B	Au1A	3.08200(18)	C3B	C2B	1.413(4)
Au1B	C11B	2.3030(7)	C3B	C4B	1.375(4)
Au1B	P1B	2.2316(7)	C3A	C2A	1.417(4)
Au1A	P1A	2.2279(8)	C3A	C4A	1.382(4)
Au1A	C11A	2.2934(8)	C7B	C6B	1.383(4)
P1A	C10A	1.803(3)	C7B	C8B	1.414(4)
P1A	C3A	1.795(3)	C2A	C1A	1.361(5)
P1A	C7A	1.794(3)	C12B	C11B	1.383(4)
P1B	C3B	1.799(3)	C10B	C11B	1.388(4)
P1B	C7B	1.800(3)	C10B	C15B	1.397(4)
P1B	C10B	1.807(3)	C11A	C12A	1.392(5)
S2B	C6B	1.723(3)	C4A	C5A	1.460(5)
S2B	C9B	1.705(4)	C2B	C1B	1.369(5)
S1B	C4B	1.712(3)	C6B	C5B	1.457(5)
S1B	C1B	1.704(4)	C4B	C5B	1.461(5)
S1A	C4A	1.721(3)	C7A	C6A	1.370(5)
S1A	C1A	1.699(4)	C7A	C8A	1.419(5)
S2A	C6A	1.722(3)	C5A	C6A	1.465(5)
S2A	C9A	1.706(5)	C8B	C9B	1.368(5)
O1A	C5A	1.228(4)	C15B	C14B	1.375(5)
O1B	C5B	1.226(4)	C15A	C14A	1.374(5)
C10A	C11A	1.391(4)	C8A	C9A	1.359(5)
C10A	C15A	1.398(4)	C12A	C13A	1.374(5)
C13B	C12B	1.381(5)	C14A	C13A	1.389(5)
C13B	C14B	1.384(5)			

**Table S2-9.** Bond angles for **2-3Au**.

<b>Atom Atom Atom</b>	<b>Angle/°</b>	<b>Atom Atom Atom</b>	<b>Angle/°</b>
C11B Au1B Au1A	86.29(2)	C11B C10B C15B	119.8(3)
P1B Au1B Au1A	97.05(2)	C15B C10B P1B	120.8(2)
P1B Au1B C11B	174.83(3)	C10A C11A C12A	119.4(3)
P1A Au1A Au1B	101.08(2)	C12B C11B C10B	119.9(3)
P1A Au1A C11A	171.17(3)	C3A C4A S1A	111.2(3)
C11A Au1A Au1B	81.77(2)	C3A C4A C5A	127.8(3)
C10A P1A Au1A	118.07(11)	C5A C4A S1A	120.9(2)
C3A P1A Au1A	117.85(10)	C1B C2B C3B	112.5(3)
C3A P1A C10A	104.51(14)	C7B C6B S2B	111.0(2)
C7A P1A Au1A	106.02(10)	C7B C6B C5B	129.1(3)
C7A P1A C10A	107.26(14)	C5B C6B S2B	119.7(2)
C7A P1A C3A	101.51(15)	C3B C4B S1B	111.8(2)
C3B P1B Au1B	114.26(10)	C3B C4B C5B	127.8(3)
C3B P1B C7B	100.90(14)	C5B C4B S1B	120.5(2)
C3B P1B C10B	106.63(14)	C6A C7A P1A	122.5(3)
C7B P1B Au1B	117.70(10)	C6A C7A C8A	113.1(3)
C7B P1B C10B	104.88(14)	C8A C7A P1A	124.1(3)
C10B P1B Au1B	111.31(10)	O1A C5A C4A	121.9(4)
C9B S2B C6B	91.71(16)	O1A C5A C6A	121.8(3)
C1B S1B C4B	91.70(16)	C4A C5A C6A	116.3(3)
C1A S1A C4A	91.70(17)	C9B C8B C7B	112.1(3)
C9A S2A C6A	91.51(19)	C7A C6A S2A	111.0(3)
C11A C10A P1A	120.2(2)	C7A C6A C5A	128.2(3)
C11A C10A C15A	120.1(3)	C5A C6A S2A	120.8(3)
C15A C10A P1A	119.7(2)	C14B C15B C10B	119.8(3)
C12B C13B C14B	120.3(3)	C14A C15A C10A	119.9(3)
C2B C3B P1B	124.1(2)	C2A C1A S1A	112.6(3)
C4B C3B P1B	123.6(2)	C2B C1B S1B	112.1(3)
C4B C3B C2B	112.0(3)	C15B C14B C13B	120.2(3)
C2A C3A P1A	125.4(2)	C8B C9B S2B	112.5(3)
C4A C3A P1A	122.5(2)	C9A C8A C7A	111.6(4)
C4A C3A C2A	112.0(3)	O1B C5B C6B	122.2(3)
C6B C7B P1B	122.2(2)	O1B C5B C4B	122.1(3)
C6B C7B C8B	112.6(3)	C6B C5B C4B	115.7(3)
C8B C7B P1B	125.2(2)	C13A C12A C11A	119.9(3)
C1A C2A C3A	112.4(3)	C15A C14A C13A	119.8(3)
C13B C12B C11B	120.0(3)	C12A C13A C14A	120.9(3)
C11B C10B P1B	119.4(2)	C8A C9A S2A	112.8(3)

## SI.2.4 Density-Functional Theory Calculation Coordinates (X,Y,Z)

### 2-30

C	-0.40207700	-1.40500000	0.53379000
C	-1.61877700	1.24965800	-0.11248700
C	-1.61929100	-1.24911400	-0.11227400
C	-2.30221500	0.00038300	-0.47838500
P	0.60969600	-0.00006700	1.08560700
C	-1.02025600	3.62579700	0.24209100
H	-1.01527300	4.70835100	0.26422700
C	-0.06134900	2.77393300	0.73540800
H	0.84567000	3.11222600	1.22398200
C	-0.40149200	1.40519400	0.53352700
C	-1.02169000	-3.62542200	0.24274300
H	-1.01714300	-4.70797300	0.26510000
C	-0.06251700	-2.77383600	0.73602600
H	0.84429200	-3.11239500	1.22480500
S	-2.34890900	2.78851200	-0.47427900
S	-2.34997600	-2.78774900	-0.47385400
O	-3.39315200	0.00056000	-1.05952300
C	2.11424700	-0.00045300	0.05398800
C	3.35889200	0.00062800	0.69931500
C	2.05352700	-0.00171500	-1.34907600
C	4.53650500	0.00047800	-0.05503600

H	3.39925600	0.00155900	1.78450700
C	3.23136400	-0.00185900	-2.09776600
H	1.09419800	-0.00260500	-1.86088600
C	4.47337400	-0.00075900	-1.45113700
H	5.49922800	0.00131900	0.44885900
H	3.18082600	-0.00284400	-3.18311700
H	5.38886300	-0.00088300	-2.03670200
O	0.92656800	0.00001100	2.56338300

### 2-3

C	0.35047300	-1.38765400	-0.60112800
C	1.60057800	1.23955900	-0.01441700
C	1.60055600	-1.23958600	-0.01438400
C	2.30840800	-0.00001500	0.30376000
P	-0.61279100	-0.00001000	-1.29123100
C	0.92614400	3.61501000	-0.22381900
H	0.88737500	4.69674700	-0.18961500
C	-0.02438500	2.76195000	-0.72403700
H	-0.95752600	3.10006200	-1.16240500
C	0.35049000	1.38763400	-0.60115300
C	0.92609500	-3.61503300	-0.22375300
H	0.88730900	-4.69676800	-0.18952400
C	-0.02441900	-2.76196900	-0.72399200

H	-0.95756400	-3.10007600	-1.16235600
S	2.31118600	2.78386800	0.39442600
S	2.31114200	-2.78389600	0.39449200
O	3.43495400	-0.00001800	0.82772500
C	-2.15844100	0.00001500	-0.26960300
C	-3.38739100	-0.00010900	-0.94628600
C	-2.14729200	0.00015800	1.13589600
C	-4.59031700	-0.00009400	-0.23009000
H	-3.40676900	-0.00021700	-2.03338000
C	-3.34729000	0.00017700	1.84866200
H	-1.20282200	0.00025200	1.67391000
C	-4.57081200	0.00005200	1.16638900
H	-5.53662400	-0.00019300	-0.76450400
H	-3.32918800	0.00029000	2.93543100
H	-5.50360300	0.00007000	1.72415200

### **2-3Me**

C	-0.43416800	-1.39832000	0.44376300
C	-1.65321500	1.28462100	-0.14713300
C	-1.70571800	-1.21877200	-0.08735000
C	-2.39922800	0.04182400	-0.40316800
P	0.59116600	0.00664000	0.89541100
C	-0.94202000	3.64932400	0.01703400

H	-0.89864800	4.73004700	-0.02935700
C	0.03296100	2.79495400	0.47362800
H	0.99307700	3.13134900	0.84930400
C	-0.37685600	1.43411600	0.38098100
C	-1.09755200	-3.60182800	0.18970500
H	-1.10200500	-4.68440900	0.19566100
C	-0.08410700	-2.77016900	0.60165600
H	0.86245900	-3.12865700	0.99044600
S	-2.35412800	2.82421000	-0.52744600
S	-2.47445200	-2.74220100	-0.39066200
O	-3.54099300	0.05387400	-0.86592300
C	2.18107100	-0.06020000	0.03707900
C	3.37680400	0.22245000	0.71641800
C	2.19991400	-0.37073500	-1.33463500
C	4.58764100	0.19359300	0.02065900
H	3.37856400	0.45952500	1.77523800
C	3.41431100	-0.39595900	-2.01838600
H	1.27973500	-0.59565600	-1.86654000
C	4.60676300	-0.11362600	-1.34220400
H	5.51244300	0.40954000	0.54698200
H	3.42910000	-0.63840600	-3.07665800
H	5.55089800	-0.13588500	-1.87875000
C	0.81927600	0.04856000	2.70018900

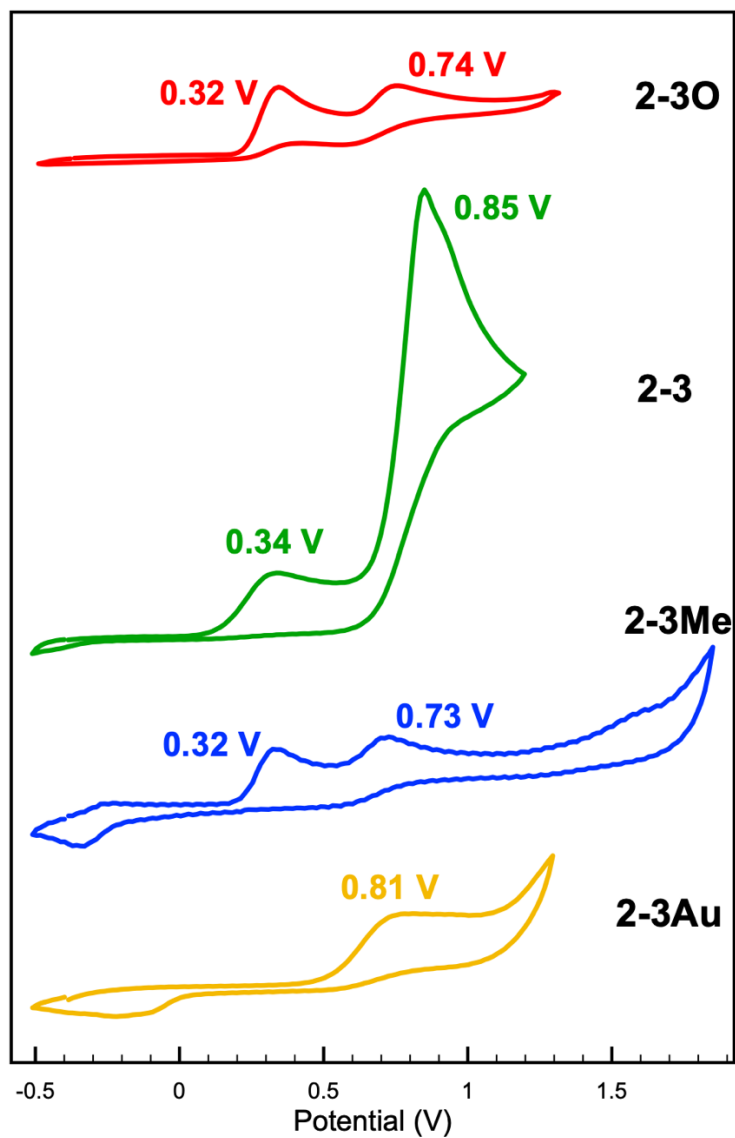
H	1.39083000	-0.82417100	3.02771800
H	1.33739900	0.96334500	2.99944400
H	-0.17138000	0.03165100	3.16303600

### **2-3Au**

C	-1.12404500	-0.14809300	-1.40494900
C	-2.34481300	-0.78832700	1.24715900
C	-2.34479600	-0.78926300	-1.24672600
C	-3.02875000	-1.15337600	0.00035300
P	-0.08707100	0.34806300	-0.00021000
C	-1.73514200	-0.45178800	3.62373100
H	-1.72402900	-0.44066800	4.70638000
C	-0.77499600	0.04088900	2.77414500
H	0.14018100	0.51354300	3.11296900
C	-1.12401500	-0.14714100	1.40492300
C	-1.73505400	-0.45453700	-3.62354400
H	-1.72390300	-0.44427700	-4.70620000
C	-0.77501800	0.03894500	-2.77430400
H	0.14012300	0.51144200	-3.11343700
S	-3.06881100	-1.15867300	2.78609200
S	-3.06866600	-1.16092300	-2.78538700
O	-4.12232900	-1.73133400	0.00055700
C	-0.05668900	2.17891000	-0.00069100

C	1.17034500	2.85784100	-0.00094400
C	-1.25926800	2.90720500	-0.00078300
C	1.19501200	4.25652200	-0.00131900
H	2.10232300	2.29984400	-0.00090600
C	-1.22831400	4.30192300	-0.00118200
H	-2.21659000	2.39282400	-0.00052100
C	-0.00140200	4.97772100	-0.00146000
H	2.14875300	4.77654200	-0.00152600
H	-2.15997300	4.86063600	-0.00129200
H	0.01888000	6.06407100	-0.00178600
Au	1.98387400	-0.65136300	0.00020700
Cl	4.11965800	-1.71162400	0.00064200

## SI.2.5 Cyclic Voltammetry- Oxidation Regime

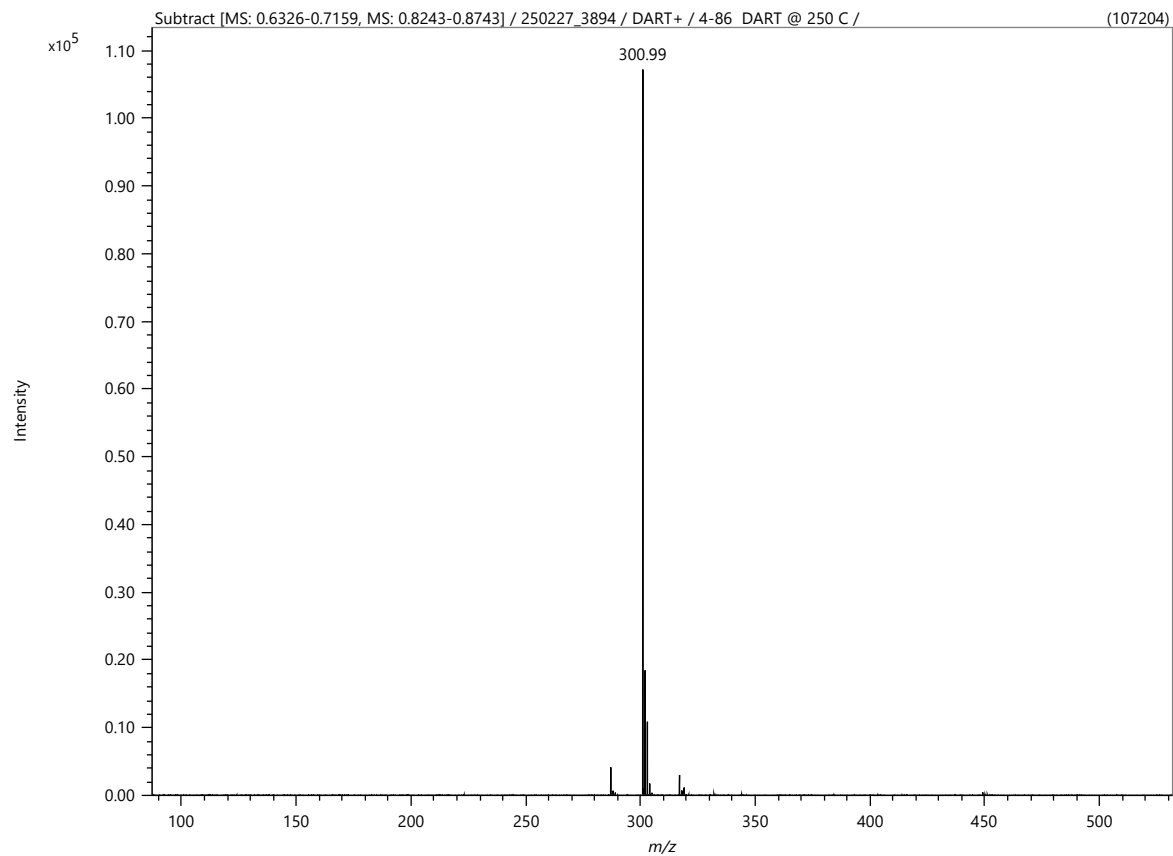


**Figure S2-49.** Cyclic voltammograms for oxidations of **2-3O** (red), **2-3** (green), **2-3Me** (blue) and **2-3Au** (yellow). Potentials are referenced to Fc/Fc<sup>+</sup>. Scan rate 100 mV/s with tetrabutylammonium hexafluorophosphate as supporting electrolyte. All experiments performed in dry CH<sub>3</sub>CN under argon.

## SI.2.6 Mass Spectrometry

DART IONIZATION

AccuTOF 4G



1 / 1

AIMS Mass Spectrometry Laboratory, University of Toronto

2025-02-27

**Figure S2-50.** Mass spectrometry result for compound **2-3**.

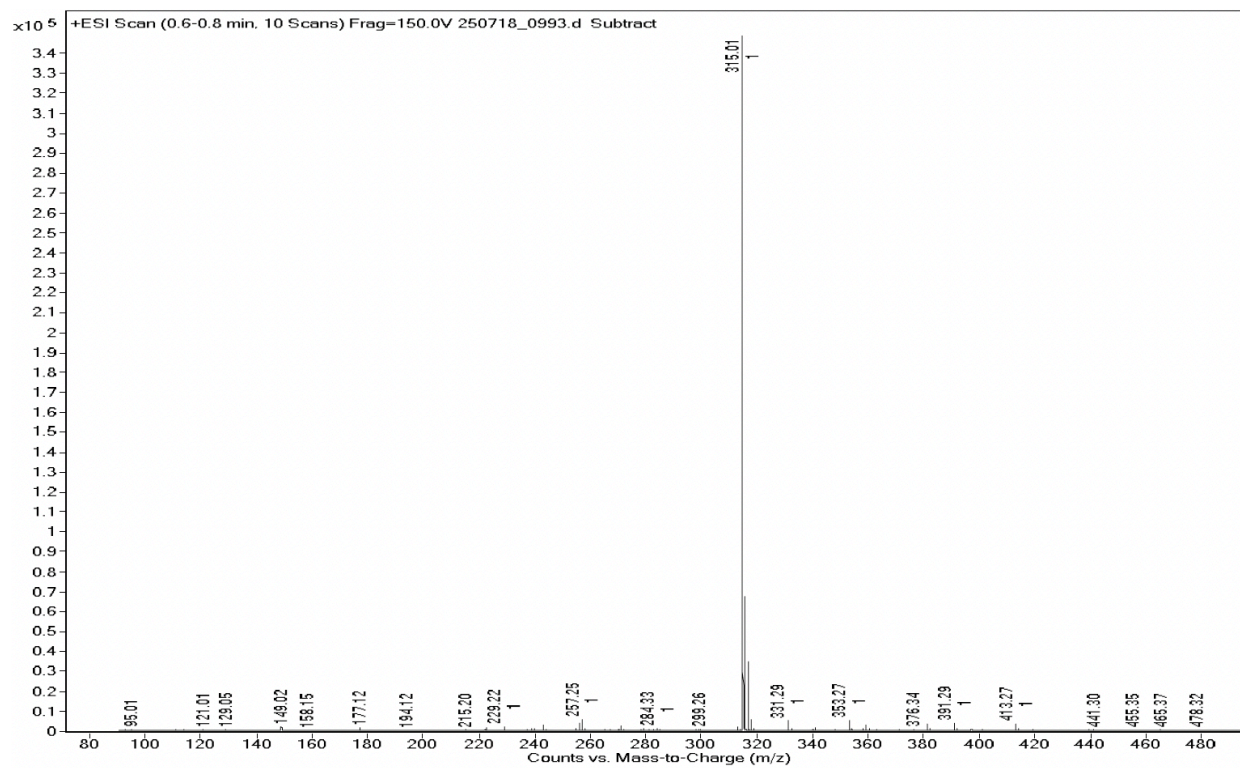
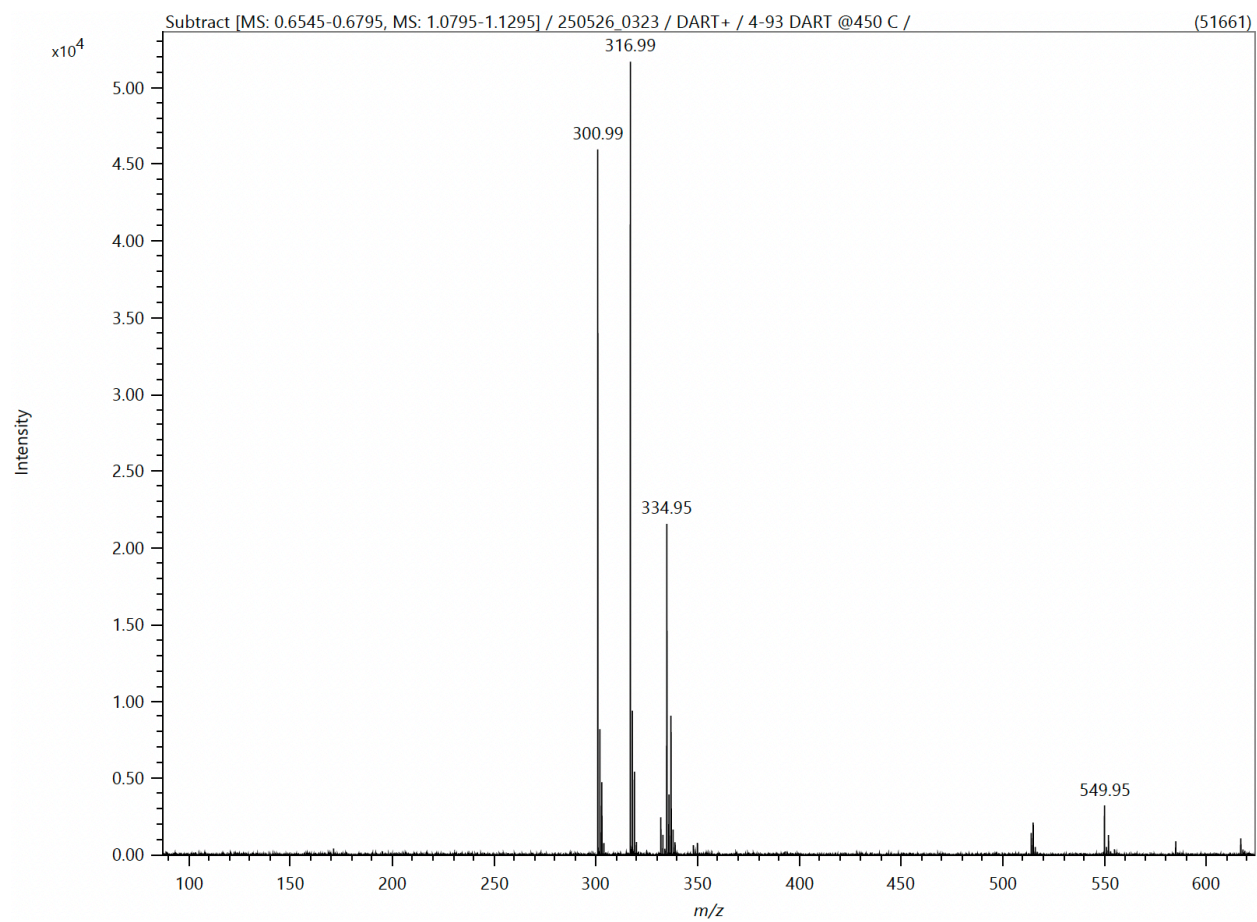


Figure S2-51. Mass spectrometry result for compound 2-3Me.



**Figure S2-52.** Mass spectrometry result for compound **2-3Au**.

## Analysis report

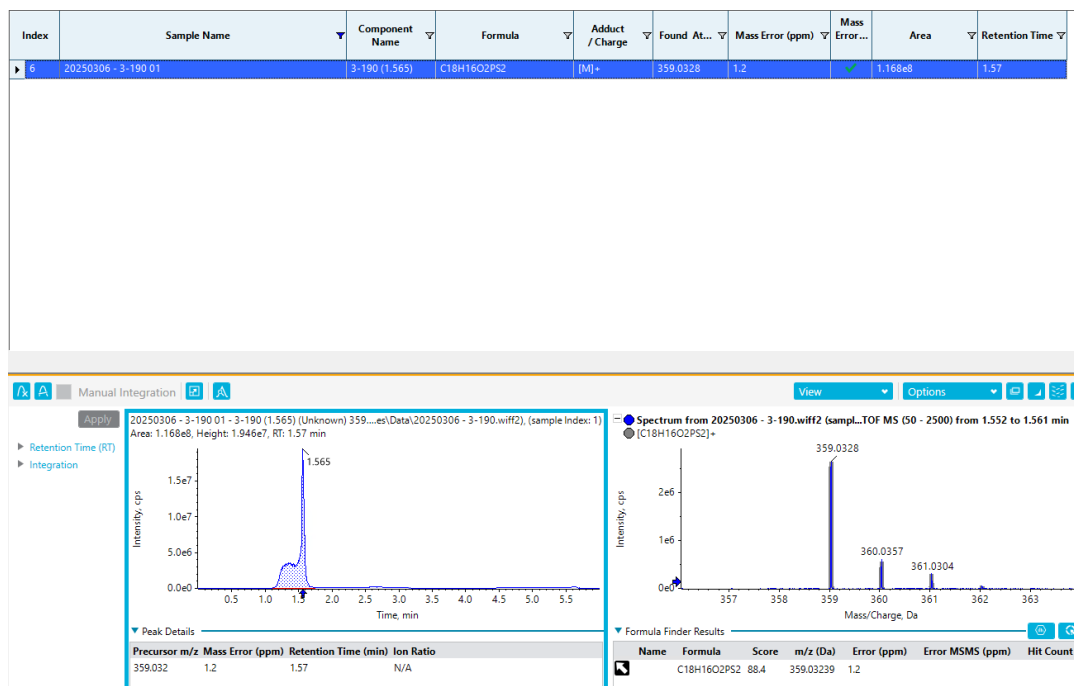
### Analysis summary:

**Analysis request submission date:** 3/5/2020

**Analysis completion date:** 3/9/2020

**Contact:** jeevafio@yorku.ca

### Results:



**Figure S2-53.** Mass spectrometry result for compound 2-8Me.

YSci Core – MS facility

Faculty of Science, **Department of Chemistry**

402 Life Science Building, 4700 Keele street, M3J 1P3, Toronto, Ontario, CANADA.

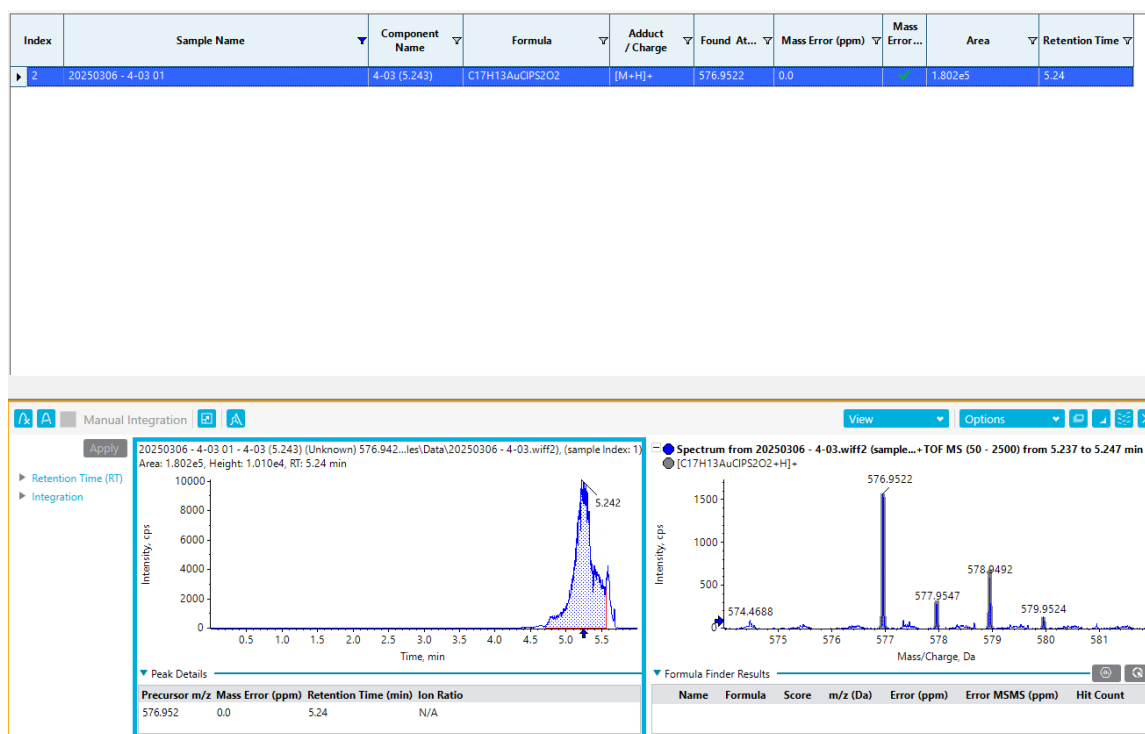
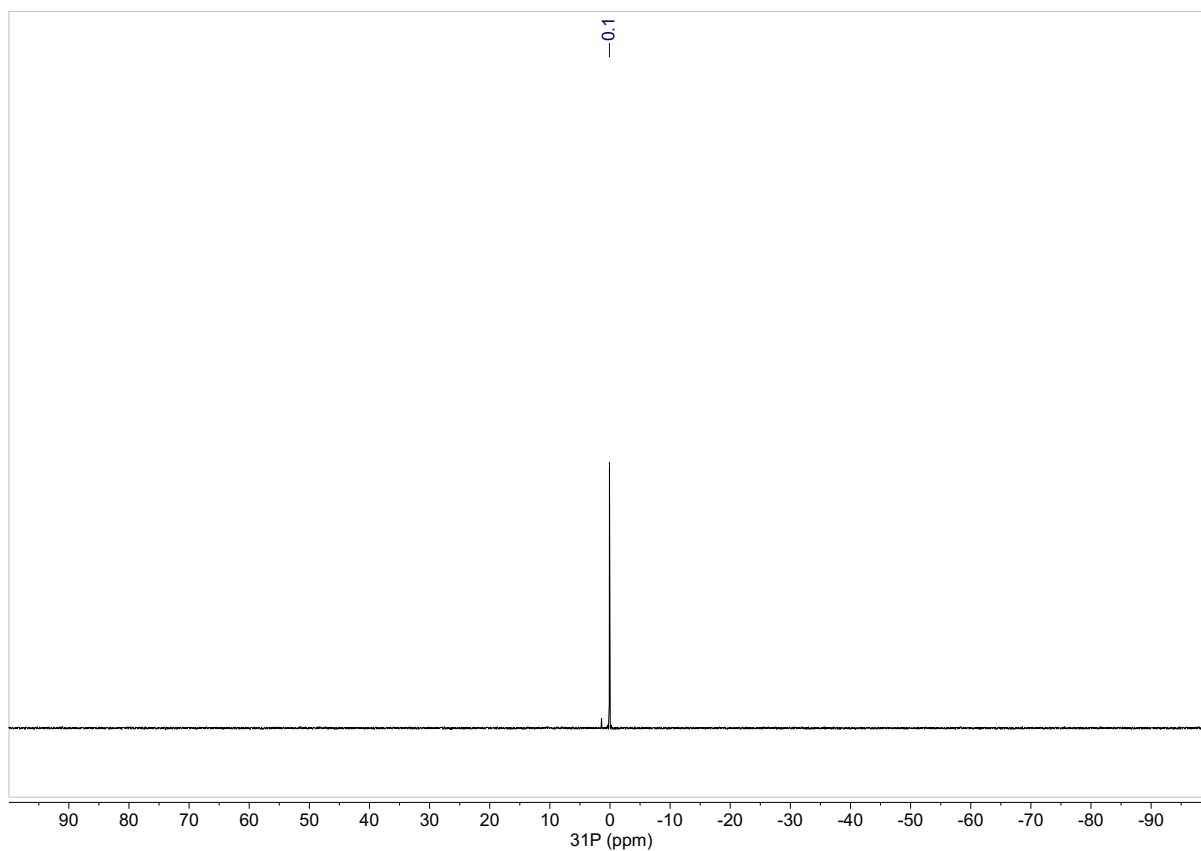
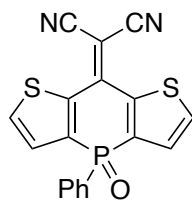


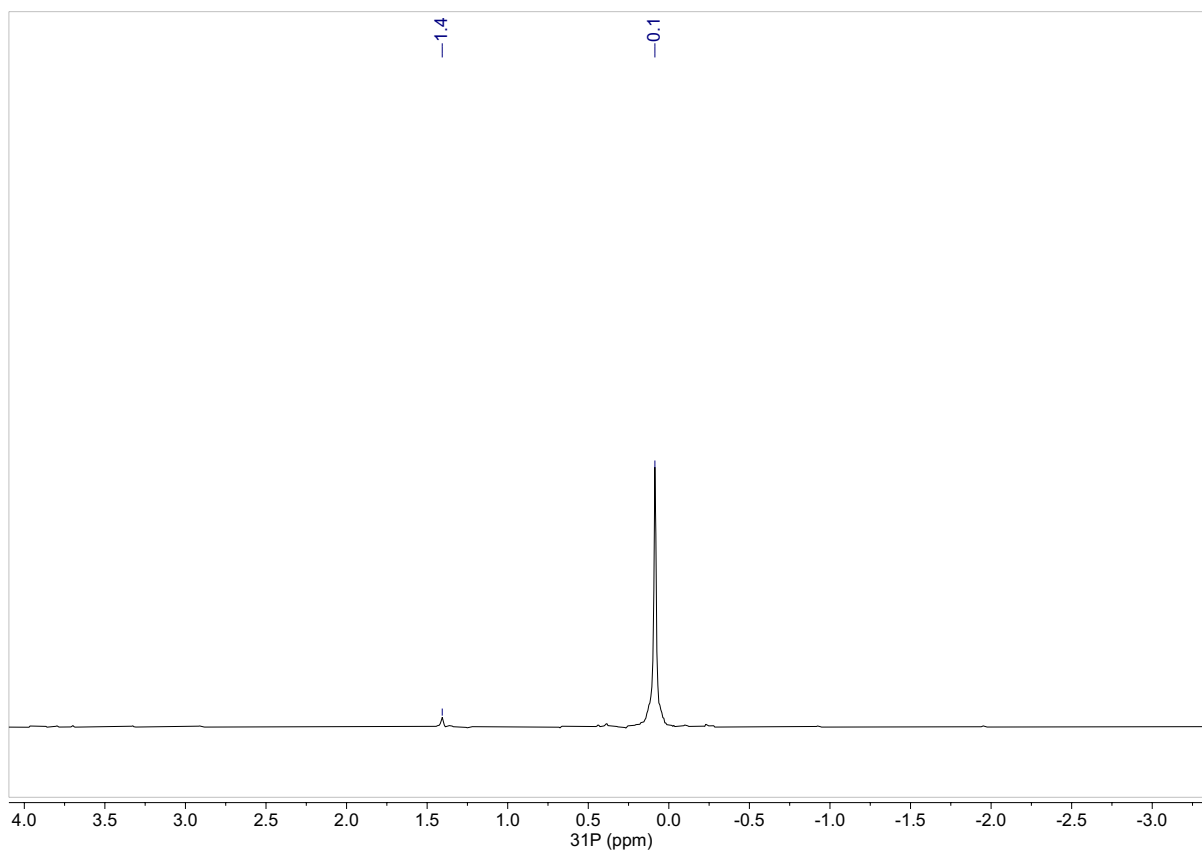
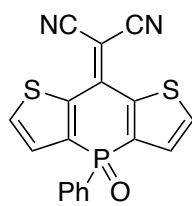
Figure S2-54. Mass spectrometry result for compound **2-8Au**.

# SI.3.0 Chapter 3: Ketone Modifications of the Dithieno[2,3-b:3',2'-e]-4-keto-1,4-dihydrophosphinine Toward Stronger Electron Acceptors

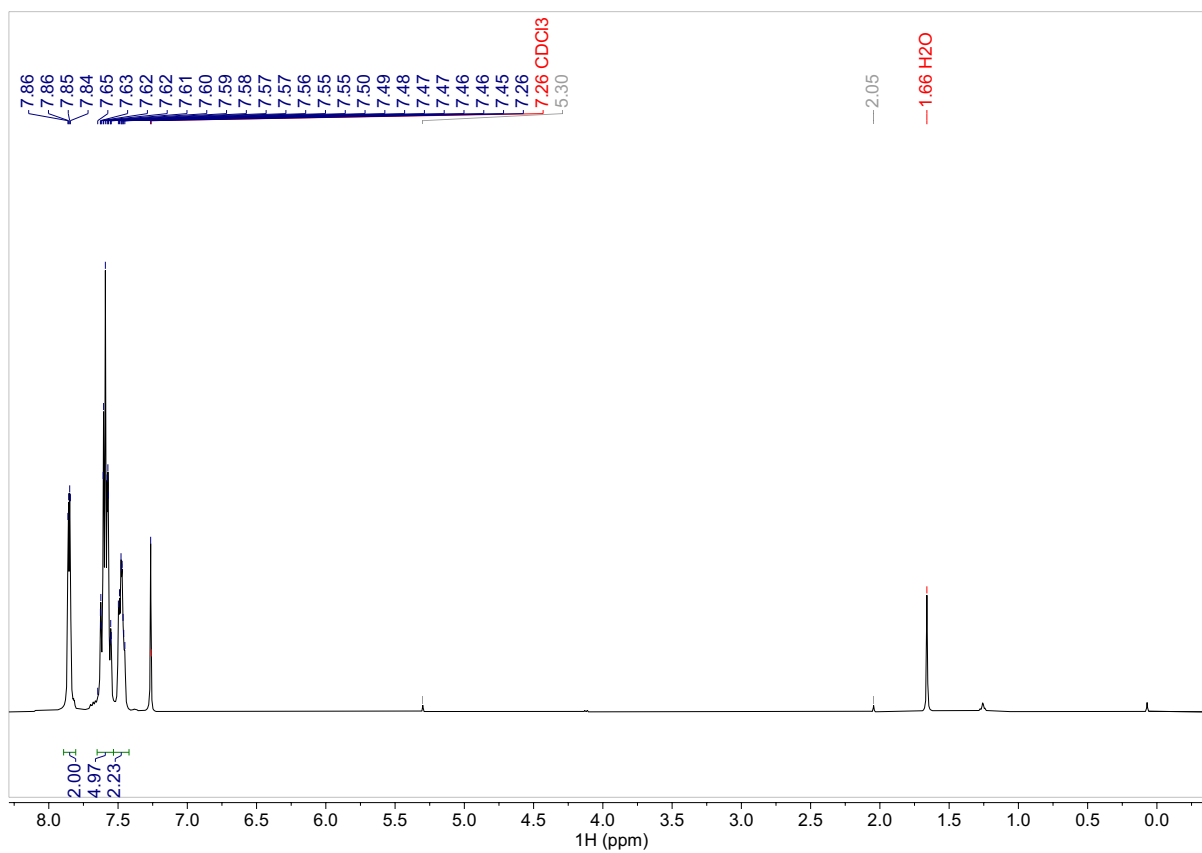
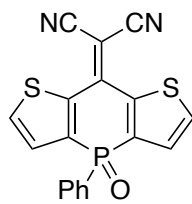
## SI 3.1 Nuclear Magnetic Resonance Spectra



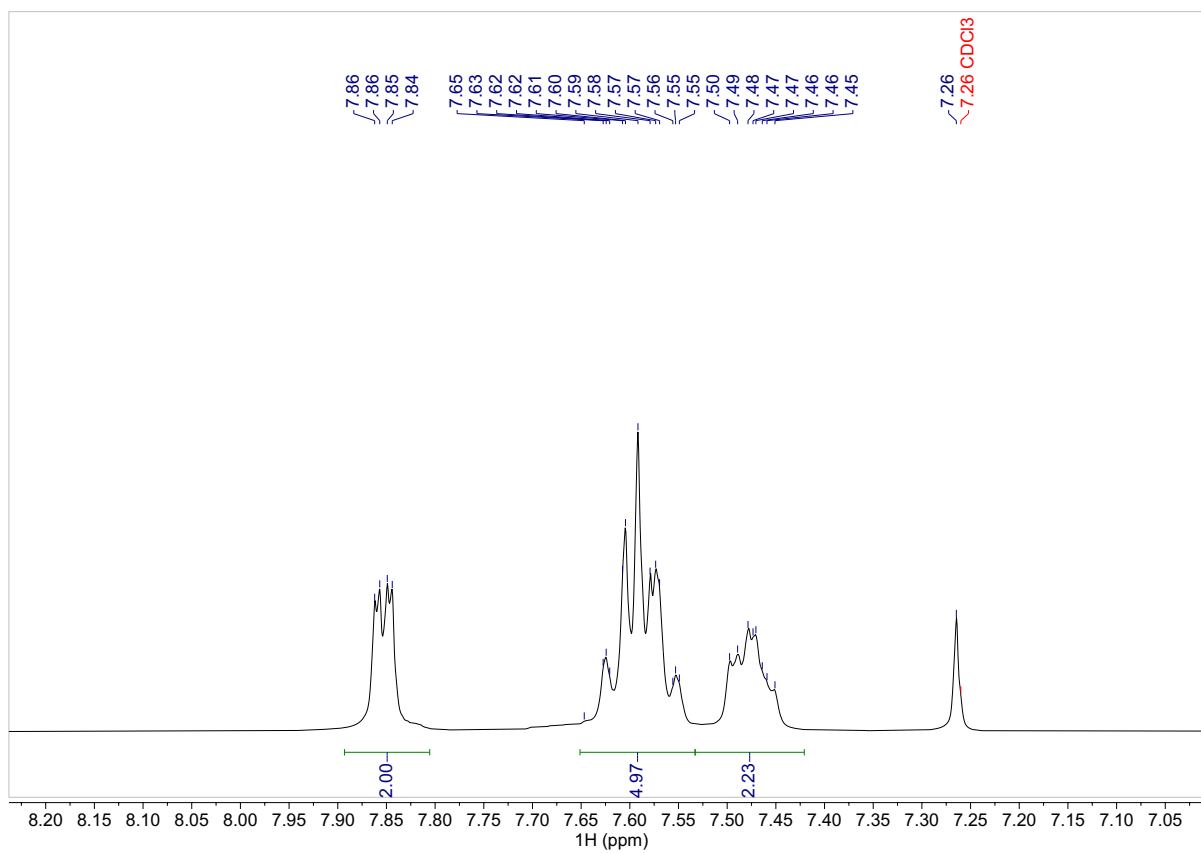
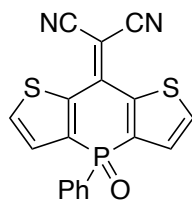
**Figure S3-1.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of compound **3-70**.



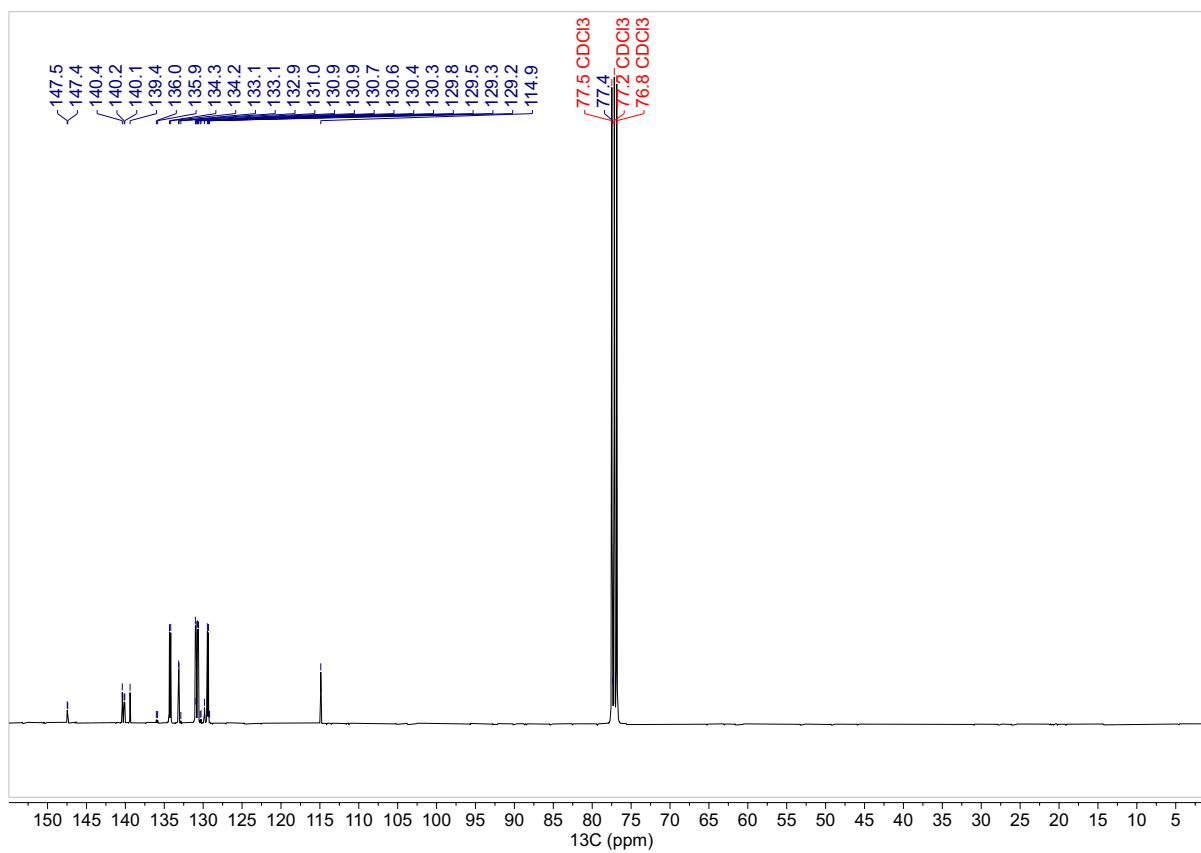
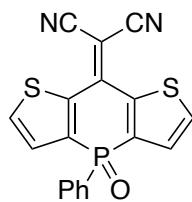
**Figure S3-2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CDCl}_3$ ) of compound **3-70**.



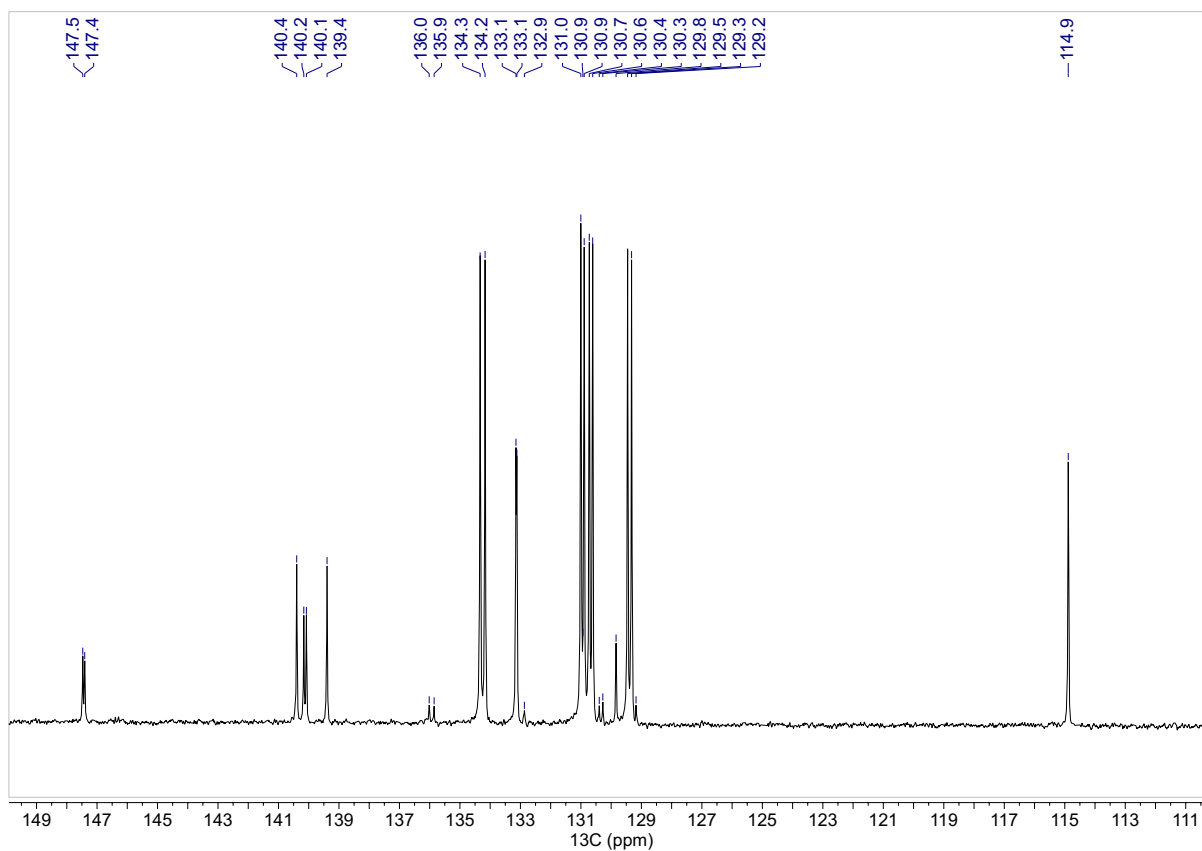
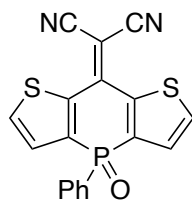
**Figure S3-3.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of compound **3-7O**.



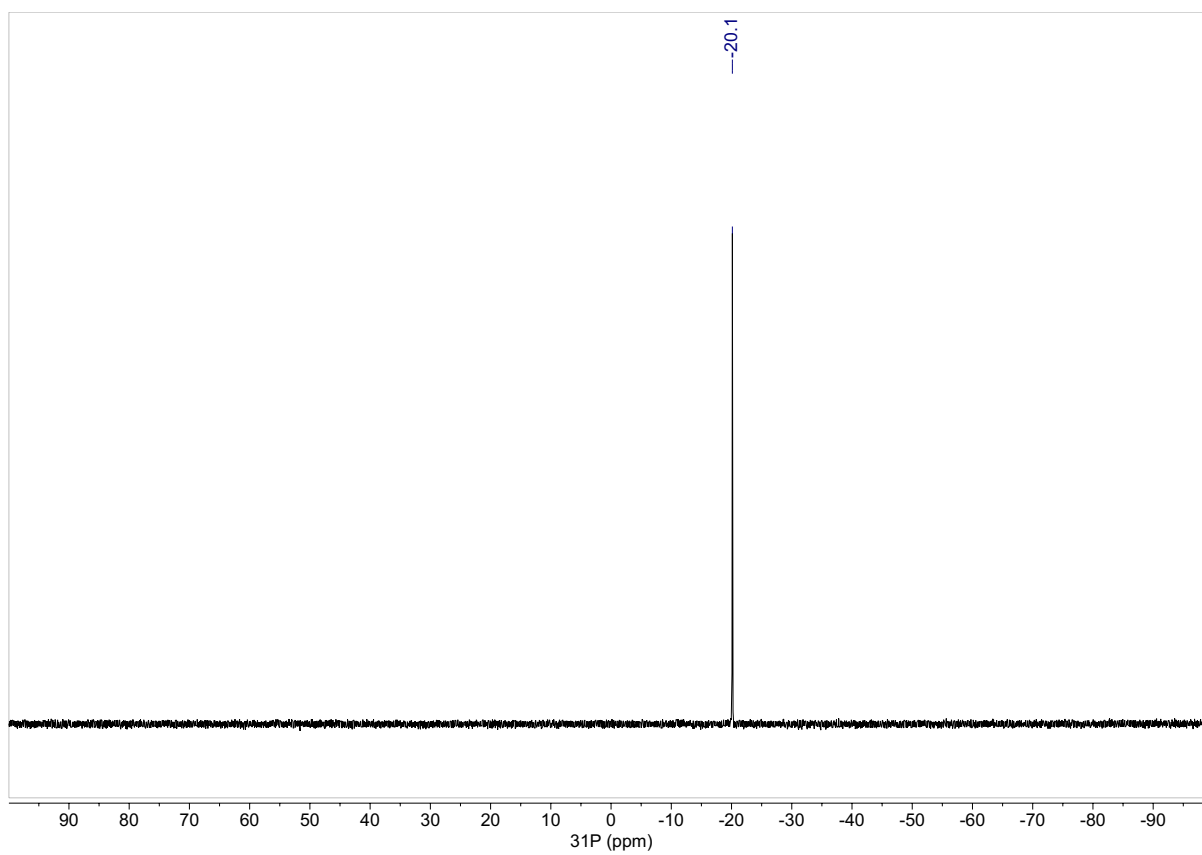
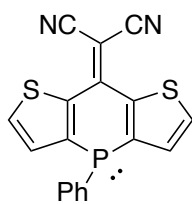
**Figure S3-4.**  $^1\text{H}$  NMR spectrum zoomed (400 MHz,  $\text{CDCl}_3$ ) of compound **3-70**.



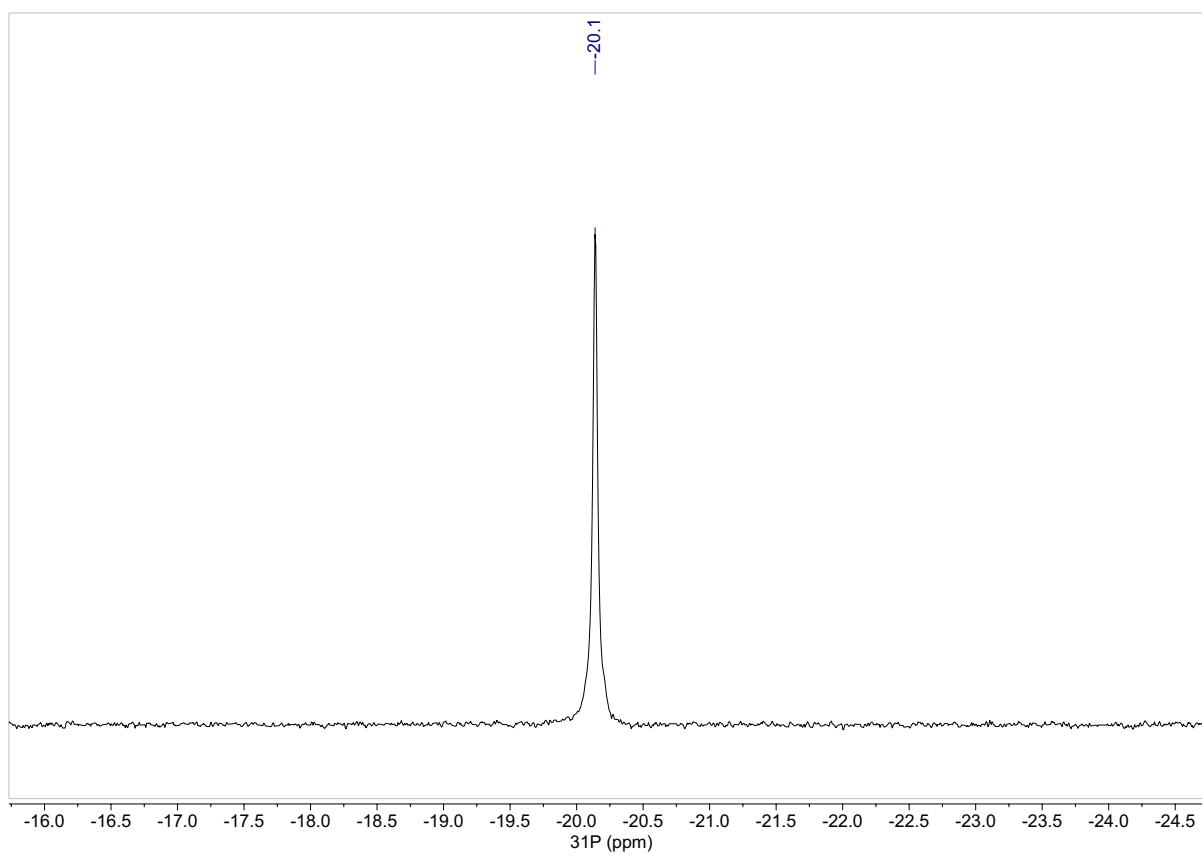
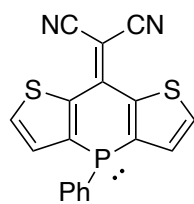
**Figure S3-5.** <sup>13</sup>C NMR spectrum (100.6 MHz, CDCl<sub>3</sub>) of compound **3-70**.



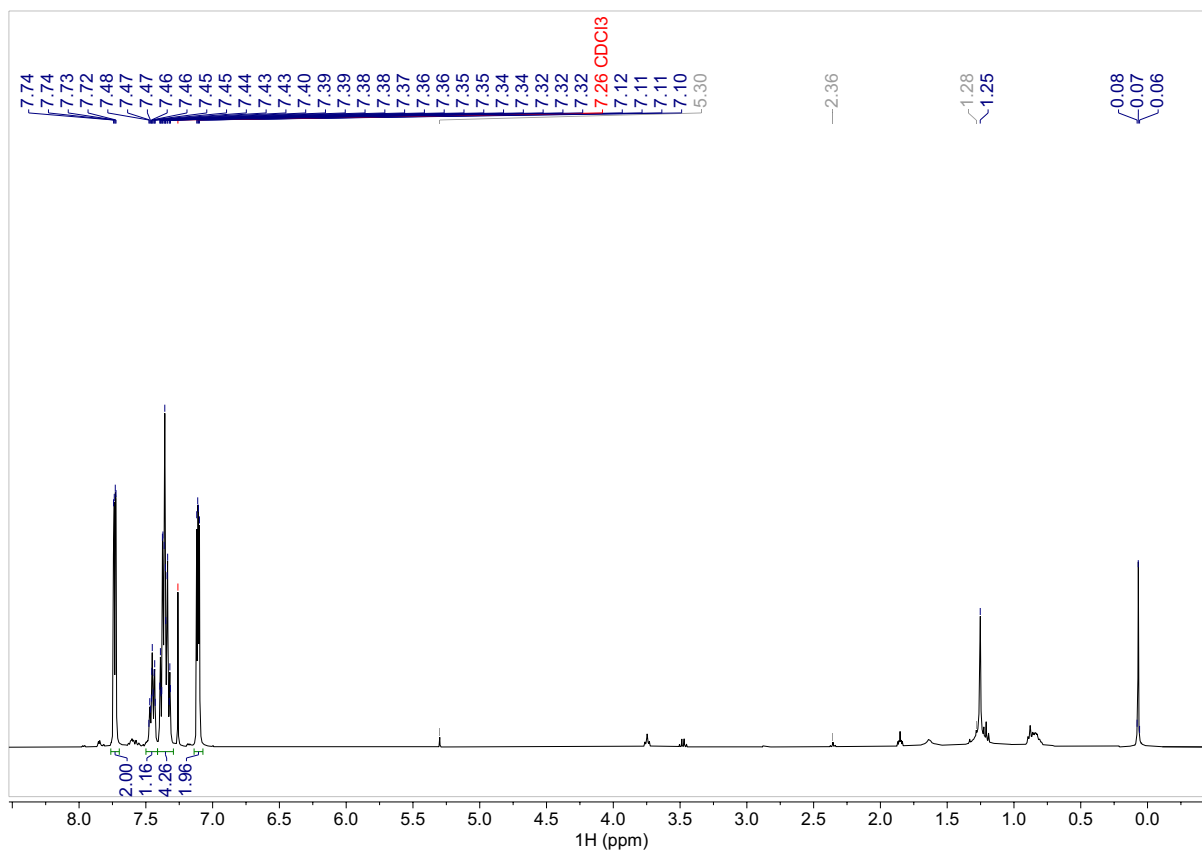
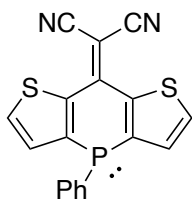
**Figure S3-6.**  $^{13}\text{C}$  NMR spectrum zoomed (100.6 MHz,  $\text{CDCl}_3$ ) of compound **3-7O**.



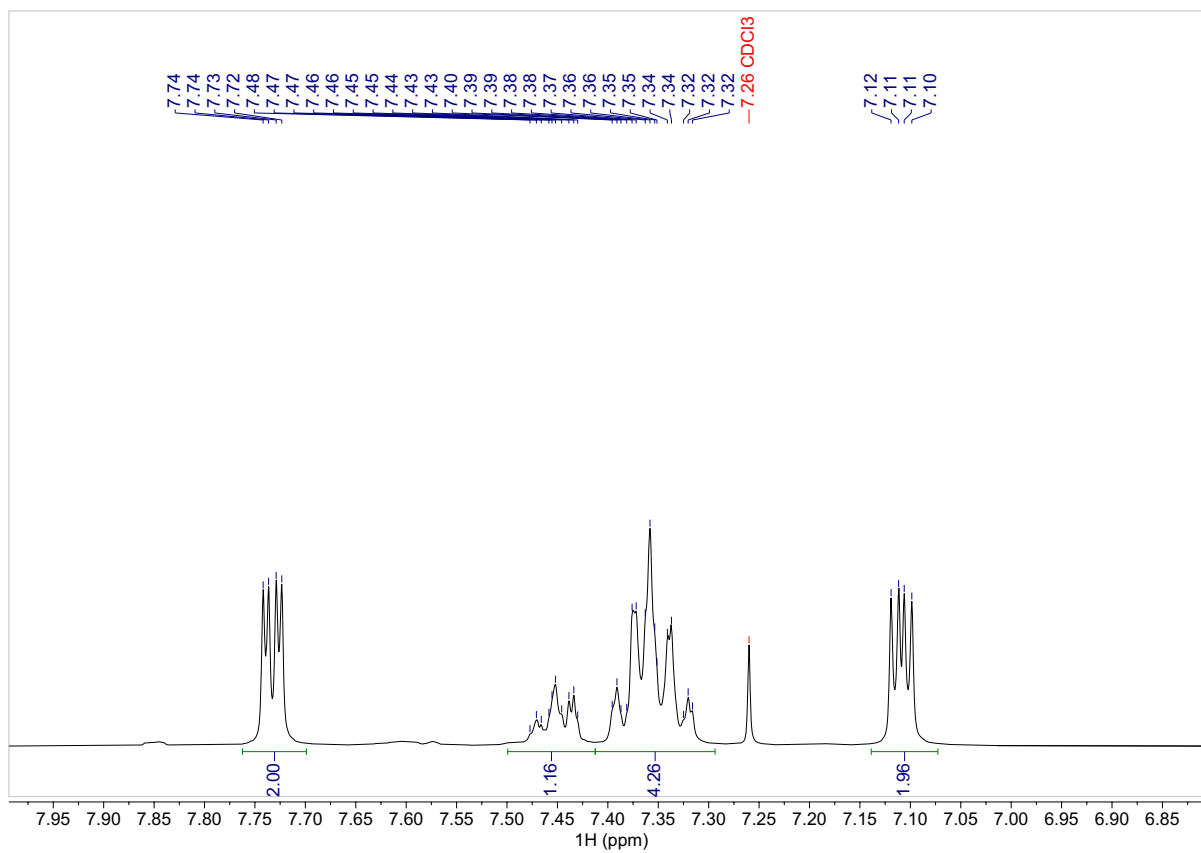
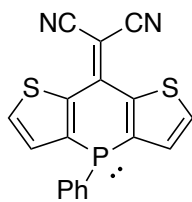
**Figure S3-7.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of compound 3-7.



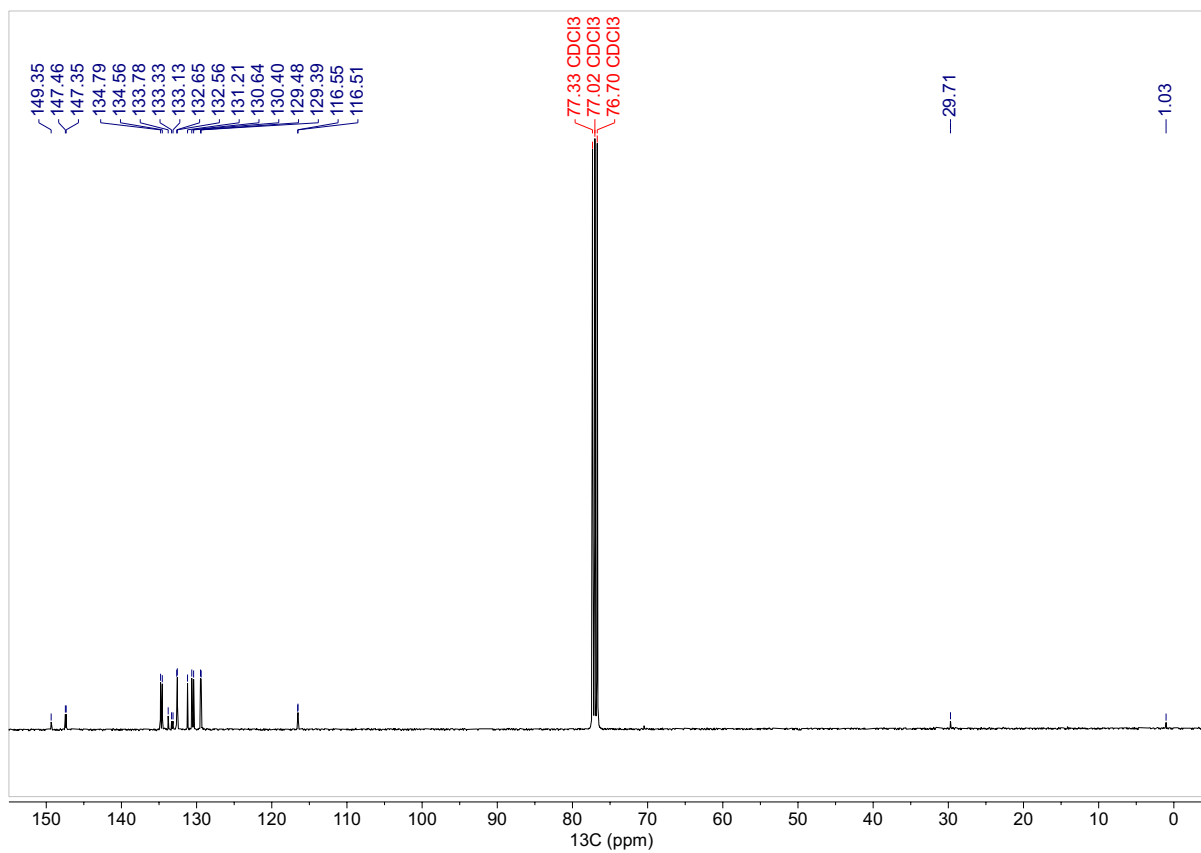
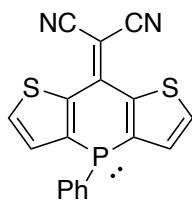
**Figure S3-8.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CDCl}_3$ ) of compound 3-7.



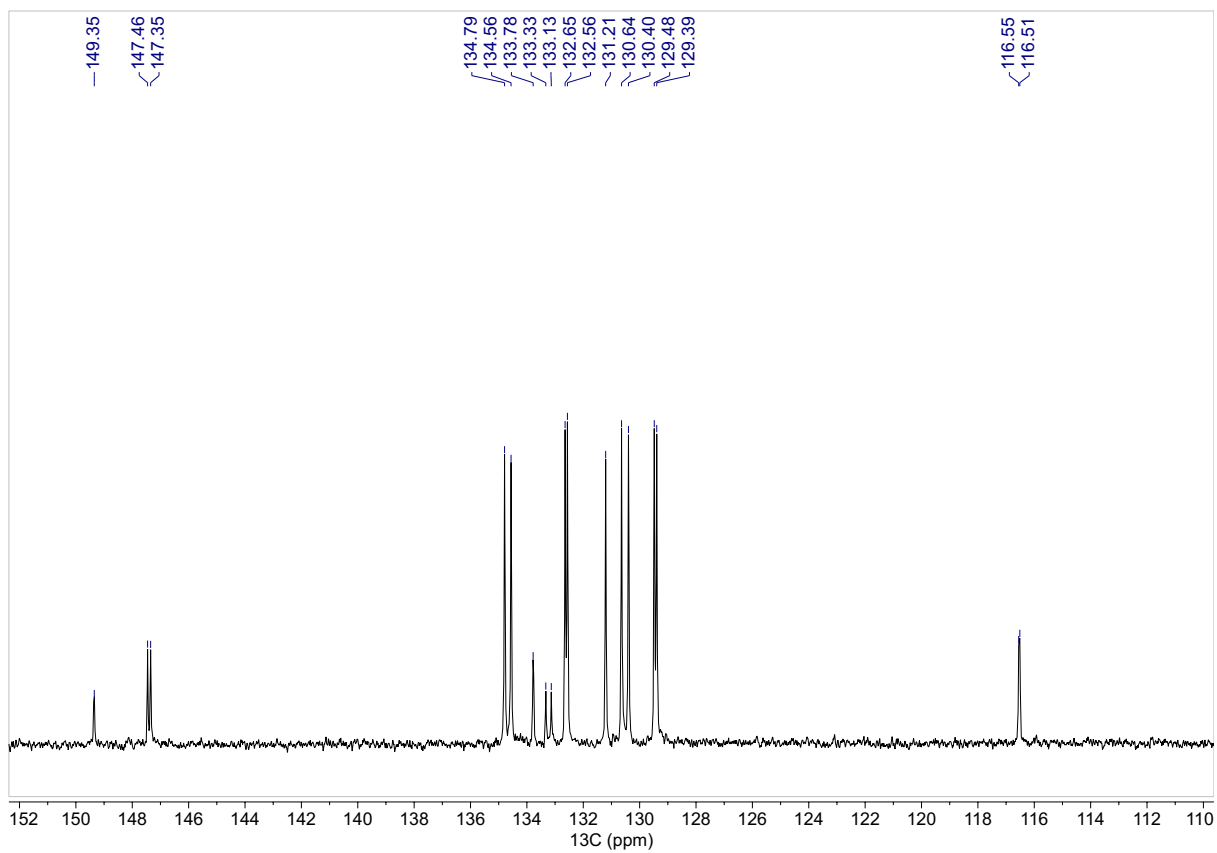
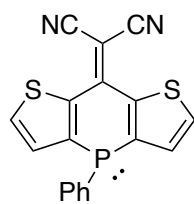
**Figure S3-9.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of compound 3-7.



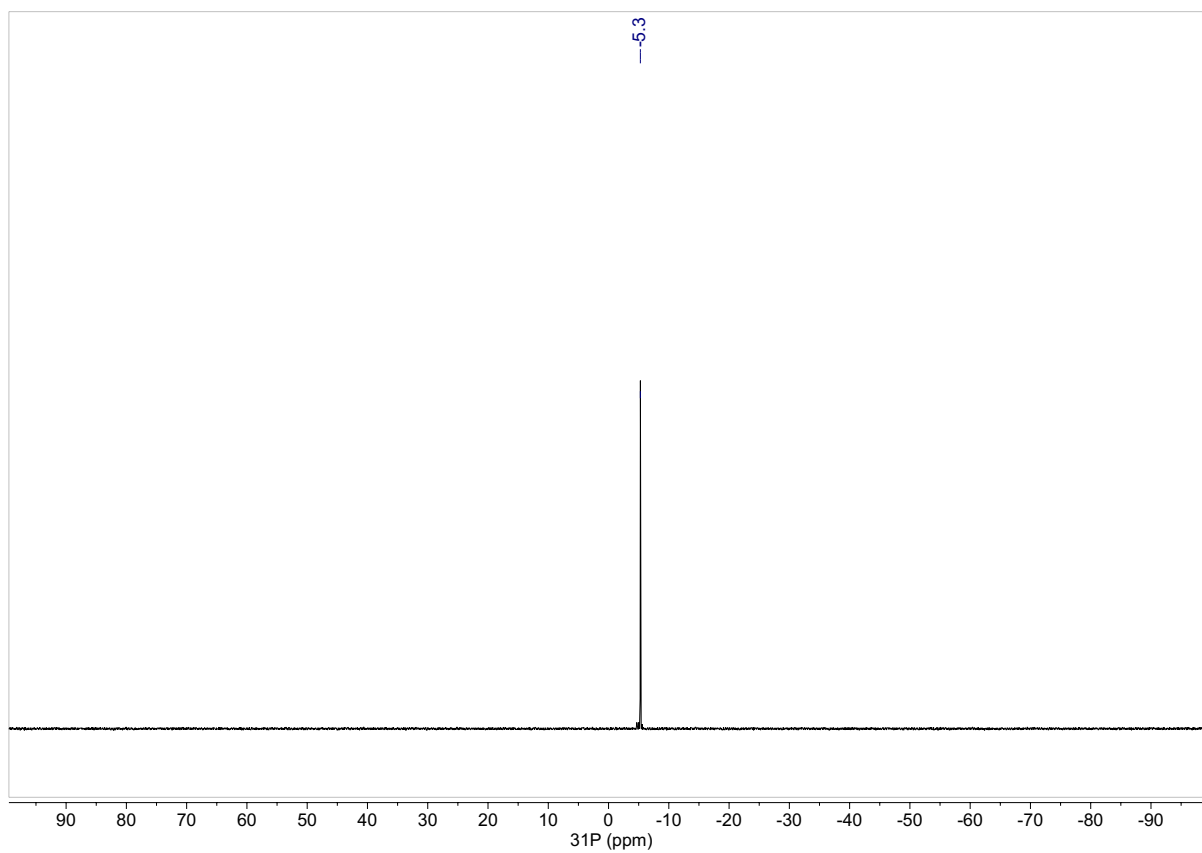
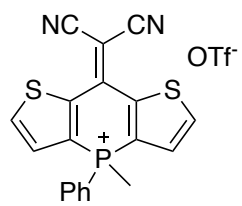
**Figure S3-10.**  $^1\text{H}$  NMR spectrum zoomed (400 MHz,  $\text{CDCl}_3$ ) of compound **3-7**.



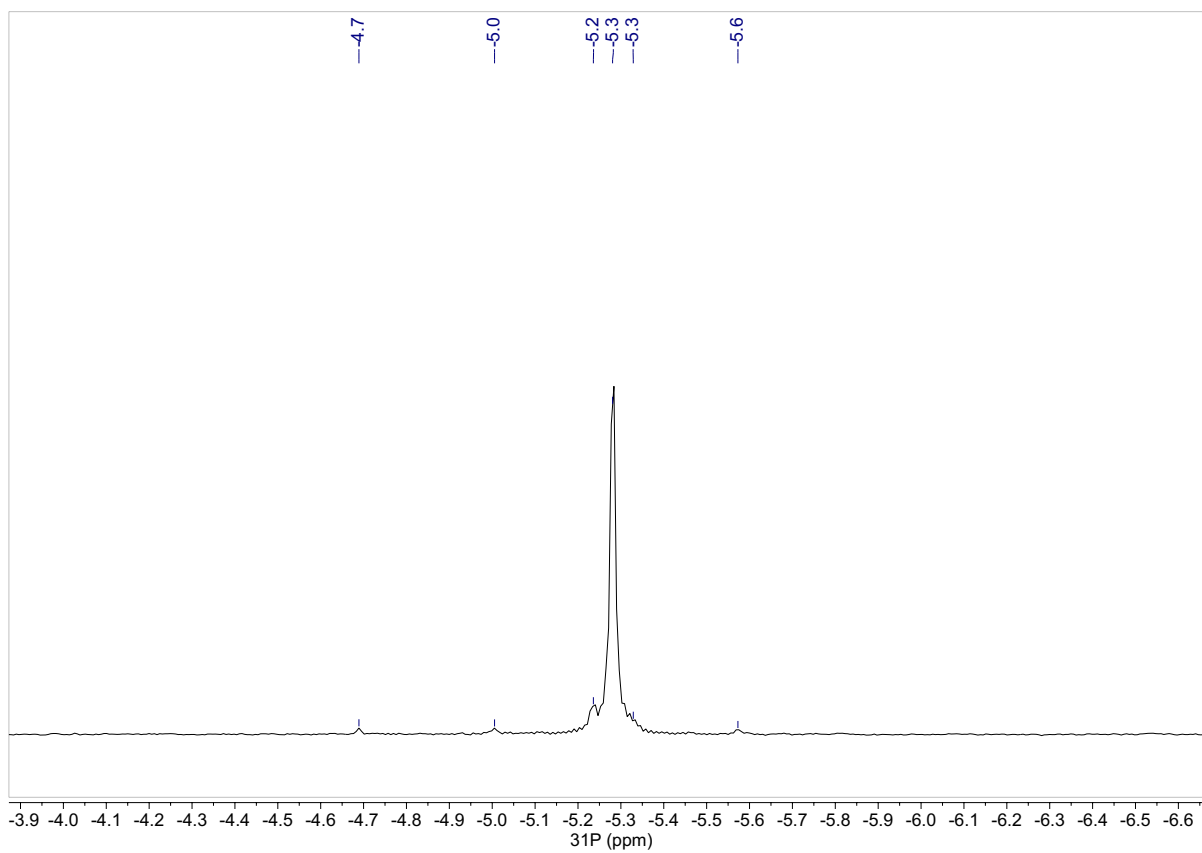
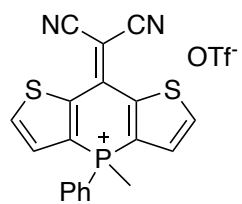
**Figure S3-11.** <sup>13</sup>C NMR spectrum (100.6 MHz, CDCl<sub>3</sub>) of compound 3-7.



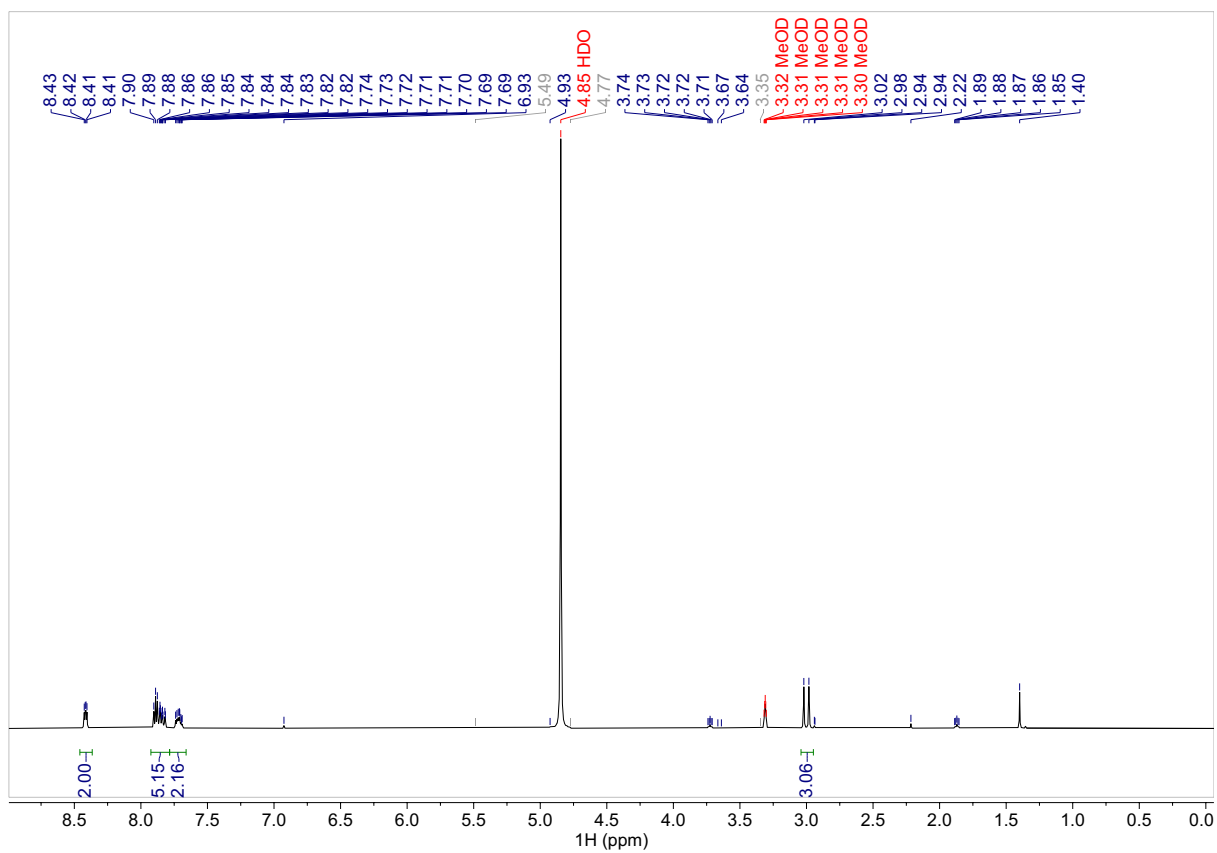
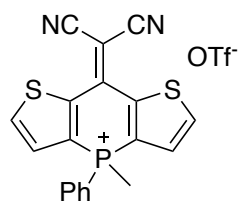
**Figure S3-12.**  $^{13}\text{C}$  NMR spectrum zoomed (100.6 MHz,  $\text{CDCl}_3$ ) of compound 3-7.



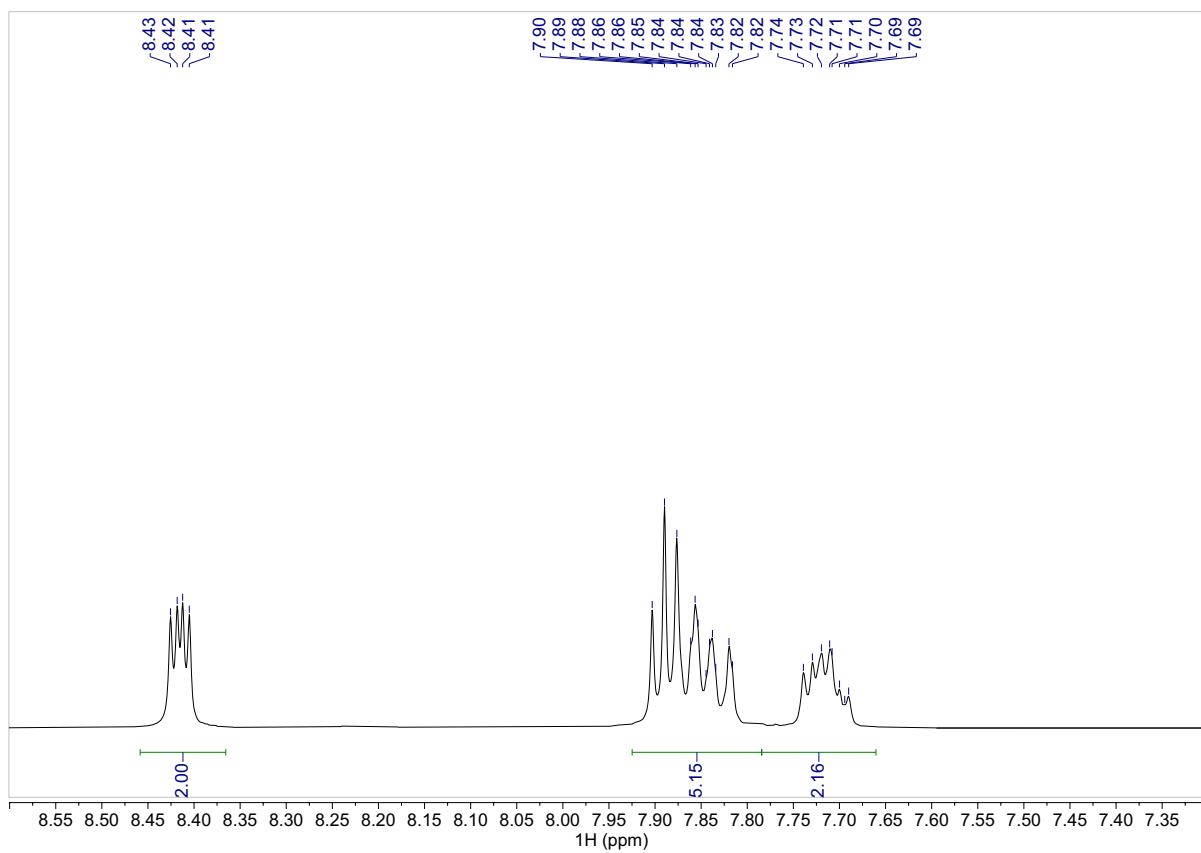
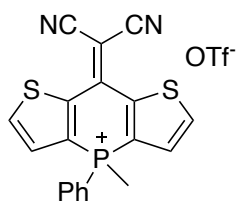
**Figure S3-13.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz, MeOD) of compound 3-7Me.



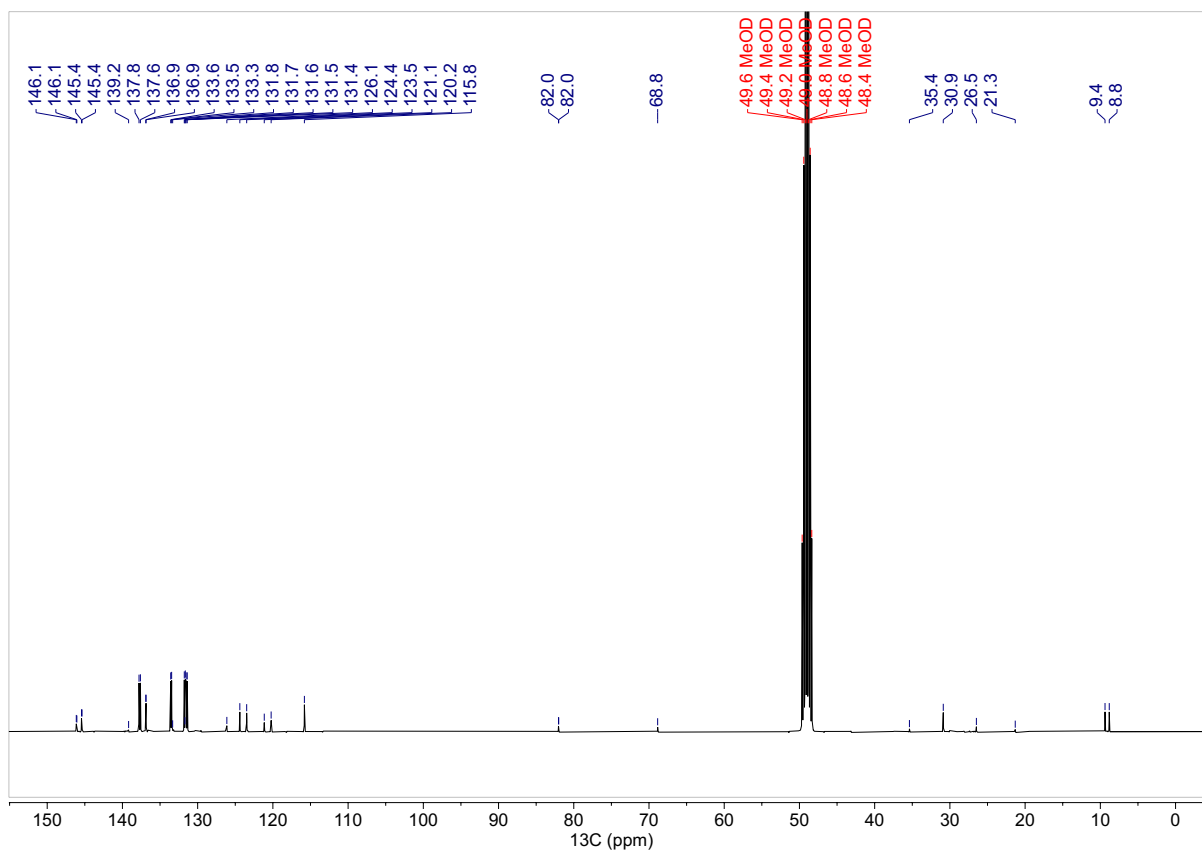
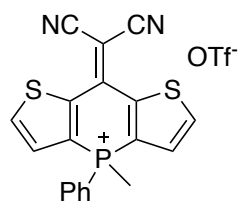
**Figure S3-14.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz, MeOD) of compound **3-7Me**.



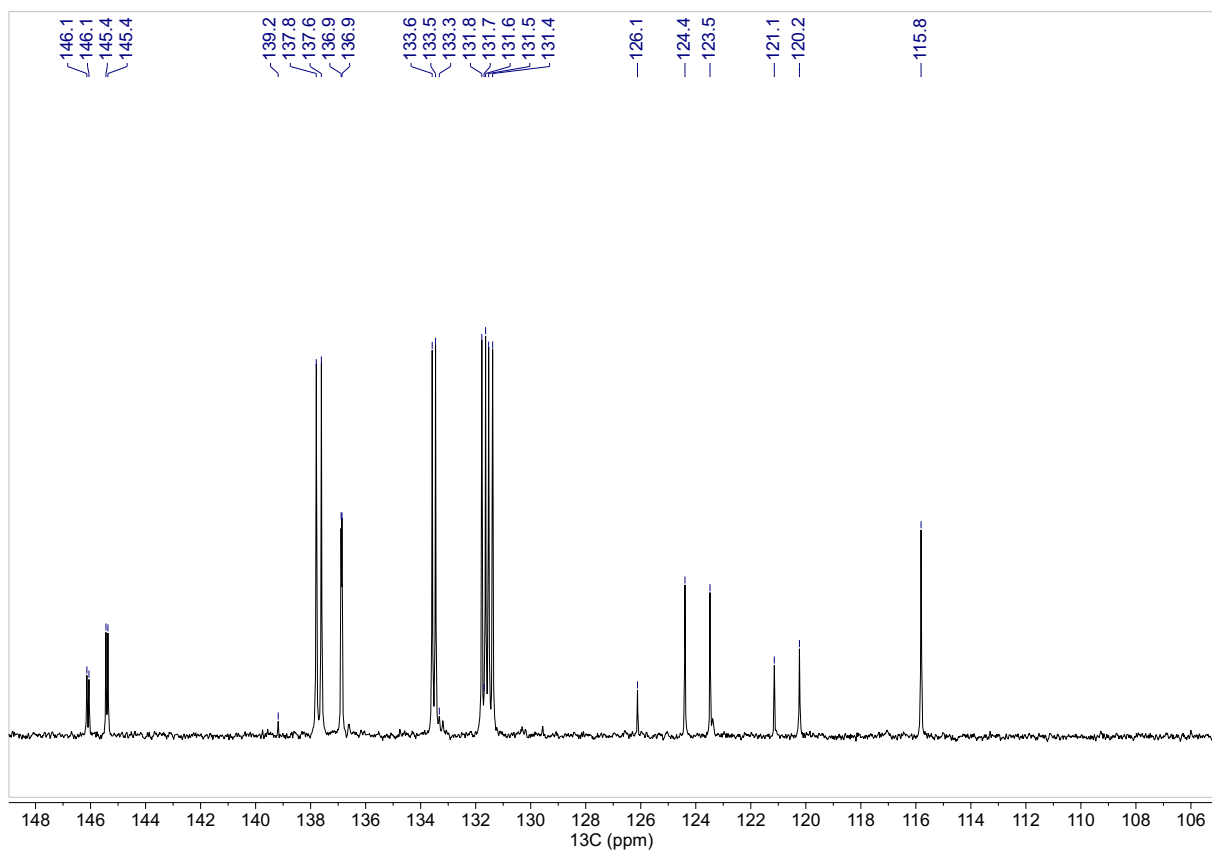
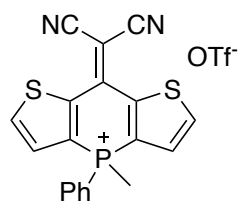
**Figure S3-15.**  $^1\text{H}$  NMR spectrum (400 MHz, MeOD) of compound **3-7Me**.



**Figure S3-16.** <sup>1</sup>H NMR spectrum zoomed (400 MHz, MeOD) of compound 3-7Me.



**Figure S3-17.** <sup>13</sup>C NMR spectrum (100.6 MHz, MeOD) of compound 3-7Me.

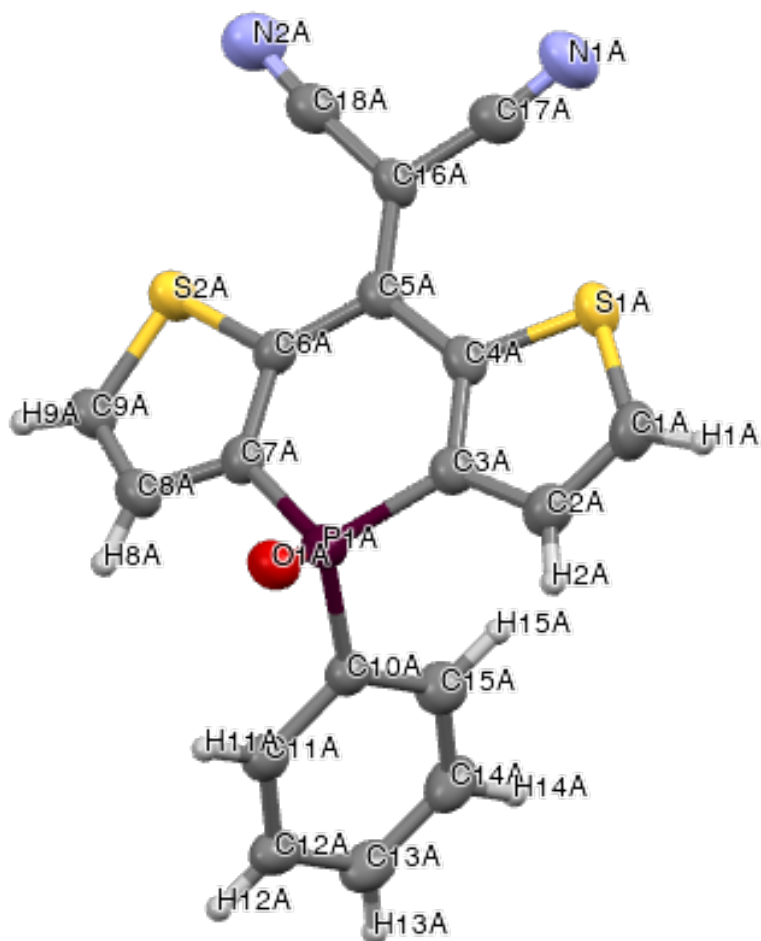


**Figure S3-18.** <sup>13</sup>C NMR spectrum zoomed (100.6 MHz, MeOD) of compound **3-7Me**.

### SI 3.2 Solid-State Structures

**Table S3-1.** Crystal data and structure refinement for **3-7O**.

Identification code	CT_1_126_2_a
Empirical formula	C <sub>18</sub> H <sub>9</sub> N <sub>2</sub> OPS <sub>2</sub>
Formula weight	364.391
Temperature/K	173.00
Crystal system	orthorhombic
Space group	Pna2 <sub>1</sub>
a/Å	13.8271(10)
b/Å	22.0958(18)
c/Å	10.4132(8)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	3181.4(4)
Z	8
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.522
μ/mm <sup>-1</sup>	0.442
F(000)	1491.5
Crystal size/mm <sup>3</sup>	0.15 × 0.15 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.32 to 56.56
Index ranges	-19 ≤ h ≤ 19, -31 ≤ k ≤ 31, -14 ≤ l ≤ 14
Reflections collected	82961
Independent reflections	7902 [R <sub>int</sub> = 0.0974, R <sub>sigma</sub> = 0.0604]
Data/restraints/parameters	7902/1/437
Goodness-of-fit on F <sup>2</sup>	1.080
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0455, wR <sub>2</sub> = 0.1027
Final R indexes [all data]	R <sub>1</sub> = 0.0760, wR <sub>2</sub> = 0.1217
Largest diff. peak/hole / e Å <sup>-3</sup>	0.48/-0.45
Flack parameter	0.02(3)



**Figure S3-19.** Labelled solid-state structure of **3-7O** shown as thermal ellipsoids (50% probability).

**Table S3-2.** Bond lengths for **3-7O**.

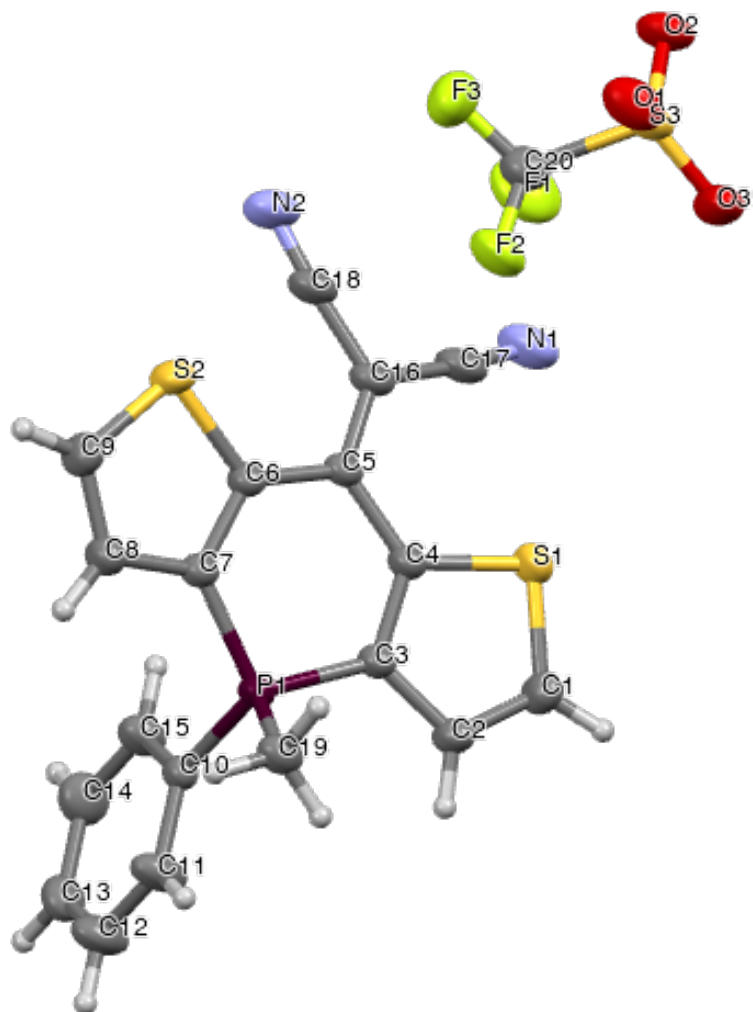
<b>Atom Atom</b>	<b>Length/Å</b>	<b>Atom Atom</b>	<b>Length/Å</b>
S1A C4A	1.742(3)	C10A C15A	1.392(5)
S1A C1A	1.697(4)	C10A C11A	1.398(5)
S2A C6A	1.732(3)	C15A C14A	1.381(5)
S2A C9A	1.699(4)	C14A C13A	1.383(6)
S1B C4B	1.741(3)	C13A C12A	1.383(6)
S1B C1B	1.687(4)	C4A C3A	1.401(5)
S2B C9B	1.693(4)	C3A C2A	1.420(5)
S2B C6B	1.738(4)	C2A C1A	1.375(5)
P1A O1A	1.481(2)	C12A C11A	1.376(5)
P1A C7A	1.788(4)	C8A C9A	1.346(5)
P1A C10A	1.798(3)	C13B C14B	1.352(7)
P1A C3A	1.773(4)	C13B C12B	1.362(7)
P1B O1B	1.484(3)	C14B C15B	1.407(6)
P1B C10B	1.791(4)	C15B C10B	1.375(5)
P1B C3B	1.771(4)	C10B C11B	1.398(6)
P1B C7B	1.782(4)	C3B C4B	1.385(5)
N2A C18A	1.150(5)	C3B C2B	1.423(5)
N1A C17A	1.121(5)	C4B C5B	1.475(5)
N2B C18B	1.159(5)	C5B C16B	1.364(5)
N1B C17B	1.155(5)	C5B C6B	1.475(5)
C18A C16A	1.432(5)	C16B C18B	1.427(6)
C16A C5A	1.367(5)	C16B C17B	1.437(5)
C16A C17A	1.462(5)	C1B C2B	1.353(6)
C5A C6A	1.472(5)	C7B C8B	1.411(5)
C5A C4A	1.446(5)	C7B C6B	1.383(5)
C6A C7A	1.388(5)	C8B C9B	1.359(6)
C7A C8A	1.413(5)	C12B C11B	1.395(6)

**Table S3-3. Bond angles for 3-7O.**

<b>Atom Atom Atom</b>	<b>Angle/°</b>	<b>Atom Atom Atom</b>	<b>Angle/°</b>
C1A S1A C4A	93.29(19)	C2A C3A P1A	122.4(3)
C9A S2A C6A	92.09(17)	C2A C3A C4A	113.6(3)
C1B S1B C4B	92.41(19)	C1A C2A C3A	112.2(4)
C6B S2B C9B	92.3(2)	C2A C1A S1A	112.1(3)
C7A P1A O1A	114.38(15)	C11A C12A C13A	120.3(4)
C10A P1A O1A	114.28(15)	C12A C11A C10A	120.2(4)
C10A P1A C7A	104.55(16)	C9A C8A C7A	112.3(3)
C3A P1A O1A	113.15(15)	C8A C9A S2A	112.9(3)
C3A P1A C7A	101.18(17)	C12B C13B C14B	121.3(4)
C3A P1A C10A	108.15(17)	C15B C14B C13B	119.9(4)
C10B P1B O1B	112.44(16)	C10B C15B C14B	119.8(4)
C3B P1B O1B	113.49(15)	C15B C10B P1B	124.2(3)
C3B P1B C10B	108.40(17)	C11B C10B P1B	116.2(3)
C7B P1B O1B	115.52(16)	C11B C10B C15B	119.6(4)
C7B P1B C10B	104.72(16)	C4B C3B P1B	125.0(3)
C7B P1B C3B	101.30(17)	C2B C3B P1B	122.1(3)
C16A C18A N2A	174.5(4)	C2B C3B C4B	112.6(3)
C5A C16A C18A	126.8(3)	C3B C4B S1B	109.7(3)
C17A C16A C18A	108.8(3)	C5B C4B S1B	124.4(3)
C17A C16A C5A	124.4(3)	C5B C4B C3B	125.9(3)
C6A C5A C16A	120.2(3)	C16B C5B C4B	121.3(3)
C4A C5A C16A	122.2(3)	C6B C5B C4B	116.5(3)
C4A C5A C6A	117.6(3)	C6B C5B C16B	122.2(3)
C5A C6A S2A	124.6(3)	C18B C16B C5B	125.2(3)
C7A C6A S2A	109.5(3)	C17B C16B C5B	125.0(4)
C7A C6A C5A	125.9(3)	C17B C16B C18B	109.8(3)
C6A C7A P1A	123.7(3)	C16B C18B N2B	174.8(4)
C8A C7A P1A	123.2(3)	C16B C17B N1B	175.0(5)
C8A C7A C6A	113.2(3)	C2B C1B S1B	112.8(3)
C15A C10A P1A	122.6(3)	C1B C2B C3B	112.6(4)
C11A C10A P1A	118.1(3)	C8B C7B P1B	123.4(3)
C11A C10A C15A	119.2(3)	C6B C7B P1B	123.4(3)
C14A C15A C10A	120.2(4)	C6B C7B C8B	113.2(3)
C13A C14A C15A	120.2(4)	C9B C8B C7B	112.5(4)
C12A C13A C14A	120.0(4)	C8B C9B S2B	112.4(3)
C16A C17A N1A	172.0(5)	C5B C6B S2B	123.0(3)
C5A C4A S1A	124.5(3)	C7B C6B S2B	109.6(3)
C3A C4A S1A	108.8(3)	C7B C6B C5B	127.4(3)
C3A C4A C5A	126.5(3)	C11B C12B C13B	120.1(4)
C4A C3A P1A	123.4(3)	C12B C11B C10B	119.4(4)

**Table S3-4.** Crystal data and structure refinement for **3-7Me**.

Identification code	4_137_0m_a
Empirical formula	C <sub>20</sub> H <sub>12</sub> F <sub>3</sub> N <sub>2</sub> O <sub>3</sub> PS <sub>3</sub>
Formula weight	512.47
Temperature/K	173.00
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	10.6082(4)
b/Å	12.9407(4)
c/Å	16.1172(5)
α/°	90
β/°	102.3080(10)
γ/°	90
Volume/Å <sup>3</sup>	2161.68(13)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.575
μ/mm <sup>-1</sup>	0.469
F(000)	1040.0
Crystal size/mm <sup>3</sup>	0.2 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.074 to 56.628
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21
Reflections collected	55441
Independent reflections	5376 [R <sub>int</sub> = 0.0535, R <sub>sigma</sub> = 0.0268]
Data/restraints/parameters	5376/0/290
Goodness-of-fit on F <sup>2</sup>	1.027
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0354, wR <sub>2</sub> = 0.0856
Final R indexes [all data]	R <sub>1</sub> = 0.0519, wR <sub>2</sub> = 0.0935
Largest diff. peak/hole / e Å <sup>-3</sup>	0.38/-0.37



**Figure S3-20.** Labelled solid-state structure of **3-7Me** shown as thermal ellipsoids (50% probability).

**Table S3-5.** Bond Lengths for **3-7Me**.

<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>	<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>
S1	C1	1.694(2)	C7	C8	1.412(2)
S1	C4	1.7308(17)	C8	C9	1.362(3)
S2	C6	1.7256(17)	C10	C11	1.383(2)
S2	C9	1.697(2)	C10	C15	1.388(3)
P1	C3	1.7684(17)	C11	C12	1.392(3)
P1	C7	1.7649(17)	C12	C13	1.366(3)
P1	C10	1.7895(17)	C13	C14	1.376(3)
P1	C19	1.7837(18)	C14	C15	1.383(3)
N1	C17	1.141(3)	C16	C18	1.431(3)
N2	C18	1.145(3)	C16	C17	1.436(3)
C1	C2	1.357(3)	S3	O1	1.4386(16)
C2	C3	1.413(2)	S3	O2	1.4386(14)
C3	C4	1.386(2)	S3	O3	1.4386(16)
C4	C5	1.465(2)	S3	C20	1.816(2)
C5	C6	1.464(2)	F1	C20	1.331(3)
C5	C16	1.382(2)	F2	C20	1.333(2)
C6	C7	1.393(2)	F3	C20	1.318(3)

**Table S3-6.** Bond Angles for **3-7Me**.

<b>Atom Atom Atom</b>	<b>Angle/°</b>	<b>Atom Atom Atom</b>	<b>Angle/°</b>
C1 S1 C4	92.49(9)	C8 C9 S2	112.68(14)
C9 S2 C6	92.79(9)	C11 C10 P1	120.08(14)
C3 P1 C10	113.08(8)	C11 C10 C15	119.75(17)
C3 P1 C19	107.38(9)	C15 C10 P1	120.17(13)
C7 P1 C3	102.86(8)	C10 C11 C12	119.68(19)
C7 P1 C10	111.94(8)	C13 C12 C11	120.4(2)
C7 P1 C19	111.35(9)	C12 C13 C14	120.06(19)
C19 P1 C10	110.00(8)	C13 C14 C15	120.45(19)
C2 C1 S1	112.89(14)	C14 C15 C10	119.67(18)
C1 C2 C3	111.55(16)	C5 C16 C18	125.08(17)
C2 C3 P1	122.41(13)	C5 C16 C17	125.06(17)
C4 C3 P1	123.52(13)	C18 C16 C17	109.71(16)
C4 C3 C2	113.93(15)	N2 C18 C16	173.0(2)
C3 C4 S1	109.11(12)	N1 C17 C16	173.7(2)
C3 C4 C5	125.99(15)	O1 S3 O2	114.85(9)
C5 C4 S1	124.90(12)	O1 S3 O3	115.99(11)
C6 C5 C4	116.97(14)	O1 S3 C20	102.13(10)
C16 C5 C4	121.20(16)	O2 S3 O3	114.10(9)
C16 C5 C6	121.79(16)	O2 S3 C20	103.29(10)
C5 C6 S2	124.13(13)	O3 S3 C20	104.05(10)
C7 C6 S2	109.01(13)	F1 C20 S3	111.25(15)
C7 C6 C5	126.86(15)	F1 C20 F2	107.23(17)
C6 C7 P1	122.57(13)	F2 C20 S3	111.85(16)
C6 C7 C8	114.00(15)	F3 C20 S3	111.85(15)
C8 C7 P1	123.34(13)	F3 C20 F1	107.20(19)
C9 C8 C7	111.51(17)	F3 C20 F2	107.20(18)

### SI 3.3 Density-Functional Theory Calculation Coordinates (X,Y,Z)

#### 3-7O

C	0.32089300	-1.37463200	0.99361500
C	-0.96921200	1.24486300	0.48469900
C	-0.96908500	-1.24484900	0.48485800
C	-1.59180200	-0.00005400	0.01389200
P	1.48943200	0.00017700	1.13404000
C	-0.41318000	3.55705900	1.25870700
H	-0.45720700	4.60807000	1.51618800
C	0.63760000	2.69089300	1.42130500
H	1.59382900	2.96572100	1.85188900
C	0.32075400	1.37483900	0.99340400
C	-0.41275100	-3.55695100	1.25895400
H	-0.45663800	-4.60795700	1.51647800
C	0.63790800	-2.69063700	1.42153200
H	1.59417000	-2.96533500	1.85212800
S	-1.78992800	2.79872600	0.55826800
S	-1.78958300	-2.79882900	0.55845000
C	2.51272200	0.00004900	-0.38132000
C	3.90482400	0.00018900	-0.21524300
C	1.96332900	-0.00020300	-1.67247400
C	4.74037400	0.00007600	-1.33603600
H	4.31861400	0.00039000	0.78917400

C	2.80102400	-0.00030900	-2.78822400
H	0.88527200	-0.00031600	-1.81414200
C	4.19036700	-0.00017300	-2.62018000
H	5.81915900	0.00017500	-1.20371600
H	2.37129700	-0.00049500	-3.78637900
H	4.84108700	-0.00026500	-3.49083800
O	2.32776200	0.00036900	2.38104800
C	-2.68969500	-0.00012500	-0.83980600
C	-3.31510800	-1.17719600	-1.35876000
C	-3.31490600	1.17689900	-1.35912800
N	-3.88019100	2.07670600	-1.83718600
N	-3.88056900	-2.07704600	-1.83653100

### 3-7

C	-0.33430800	-1.35968800	-0.50001300
C	0.99499100	1.23595300	-0.08809000
C	0.99487800	-1.23597300	-0.08807800
C	1.76886300	-0.00004700	-0.04644400
P	-1.27428400	0.00010700	-1.24623400
C	0.08714500	3.55987100	0.12277700
H	-0.03777200	4.61514200	0.33175600
C	-0.83271600	2.69035200	-0.39911400
H	-1.83747000	2.98219800	-0.68402700

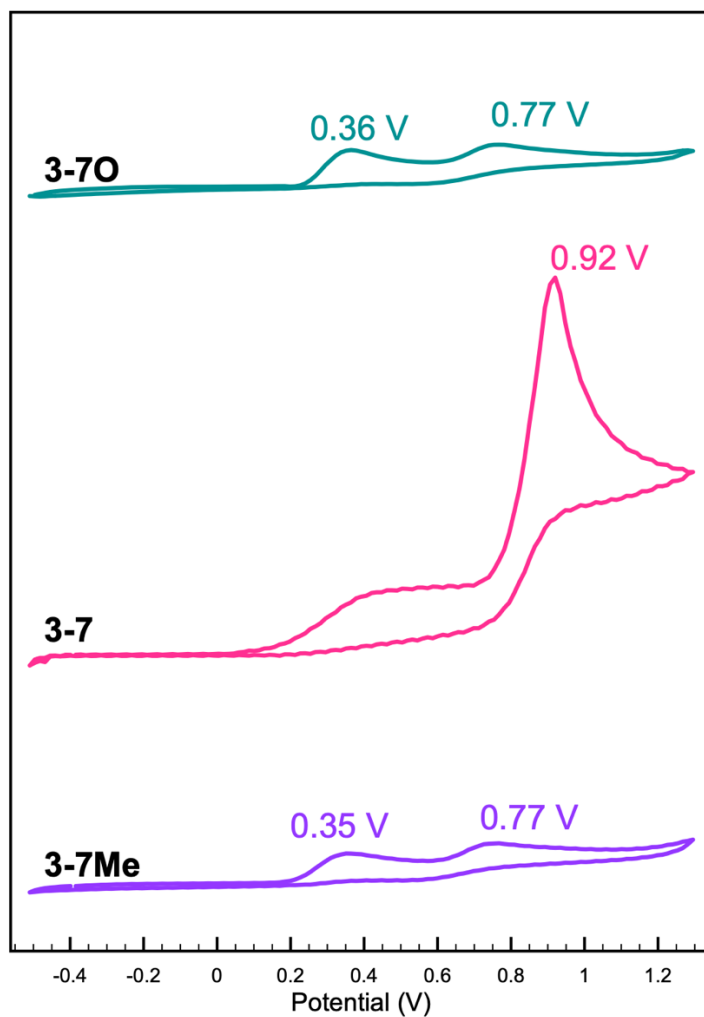
C	-0.33419000	1.35981400	-0.50000400
C	0.08685800	-3.55985500	0.12247800
H	-0.03816100	-4.61513600	0.33135000
C	-0.83294000	-2.69020300	-0.39930800
H	-1.83771700	-2.98193400	-0.68426400
S	1.59733300	2.80321100	0.45837000
S	1.59710500	-2.80336000	0.45815600
C	-2.87292500	0.00015100	-0.31953700
C	-4.05815200	0.00003500	-1.07057300
C	-2.94633500	0.00017900	1.08461400
C	-5.30208700	-0.00004800	-0.42876300
H	-4.01139100	0.00000400	-2.15676700
C	-4.18754200	0.00007800	1.72229100
H	-2.03644300	0.00031100	1.67891500
C	-5.36700800	-0.00004700	0.96630800
H	-6.21407200	-0.00010300	-1.01959900
H	-4.23595800	0.00008100	2.80806400
H	-6.33191500	-0.00015300	1.46632900
C	3.16961000	-0.00007300	0.02907200
C	3.98904900	-1.16768900	0.03147600
C	3.98909100	1.16751100	0.03090600
N	4.75079100	2.05157800	0.02355200
N	4.75070100	-2.05180100	0.02463900

### 3-7Me

C	0.23962500	-1.35843000	0.95038300
C	-0.98451300	1.30282000	0.38405600
C	-1.07108000	-1.18557500	0.49929900
C	-1.66573300	0.06171900	0.00029400
C	-0.30174400	3.64157600	0.95370500
H	-0.29482100	4.71027000	1.12626000
C	0.72451200	2.75072000	1.13930100
H	1.71049400	3.04188600	1.48139900
C	0.33231300	1.42019400	0.83434900
C	-0.55733900	-3.50289000	1.29277900
H	-0.62912700	-4.54739500	1.56801700
C	0.53546600	-2.67943500	1.38331900
H	1.50235600	-3.00802900	1.74655400
S	-1.73278100	2.88539100	0.38172000
S	-1.93533300	-2.69780800	0.65899600
C	2.60119700	-0.13024900	-0.36585500
C	3.84688200	0.51309300	-0.26703500
C	2.25911500	-0.83820400	-1.53042500
C	4.74362500	0.44414400	-1.33409100
H	4.12662200	1.06482100	0.62493800
C	3.16426900	-0.89997900	-2.59039000

H	1.30221600	-1.34492600	-1.61088000
C	4.40365500	-0.25988700	-2.49347000
H	5.70694200	0.93912500	-1.25636300
H	2.90112000	-1.45157400	-3.48789600
H	5.10609300	-0.31218200	-3.32028500
C	-2.78995200	0.06145700	-0.81714800
C	-3.47089300	-1.11091800	-1.27175600
C	-3.39904400	1.23080300	-1.37058000
N	-3.96282400	2.11582300	-1.87643200
N	-4.08847300	-1.99853200	-1.70508700
C	2.26102800	0.04230400	2.59365800
H	2.90283900	-0.83693200	2.69223100
H	2.87543600	0.94245800	2.67505800
H	1.51047800	0.04745000	3.38824800
P	1.40666100	-0.00579500	0.98997000

### SI 3.4 Cyclic Voltammetry – Oxidation Regime



**Figure S3-21.** Cyclic voltammograms for oxidations of **3-7O** (turquoise), **3-7** (pink), **3-7Me** (purple). Potentials are referenced to  $\text{Fc}/\text{Fc}^+$ . Scan rate 100 mV/s with tetrabutylammonium hexafluorophosphate as supporting electrolyte. All experiments performed in dry  $\text{CH}_3\text{CN}$  under argon.

## SI 3.5 Mass Spectrometry

Index	Sample Name	Component Name	Formula	Adduct / Charge	Found At...	Mass Error (ppm)	Mass Error...	Area	Retention Time
24	20250306 - 4-85 01	4-85 (2.449)	C18H9N2OPS2	[M+H] <sup>+</sup>	364.9970	0.8	✓	1.872e7	2.45

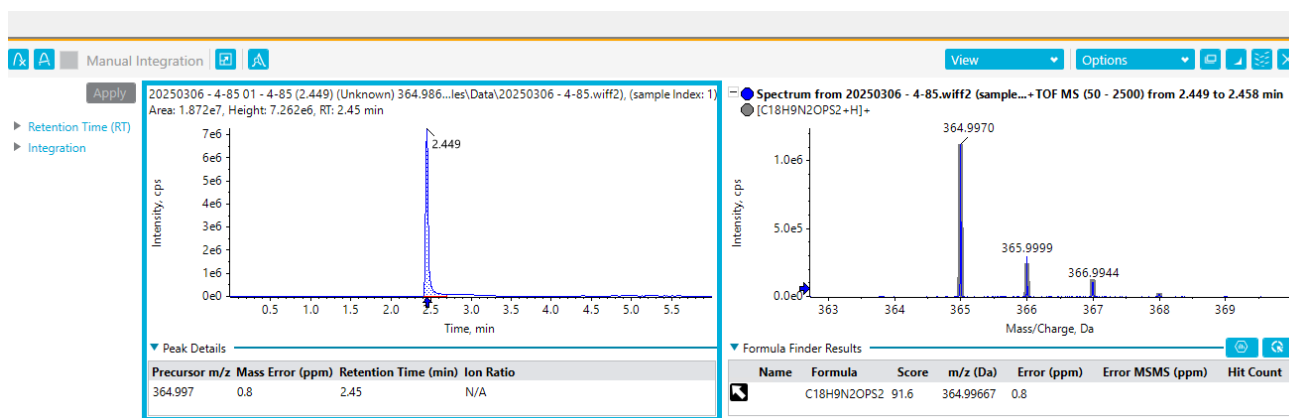
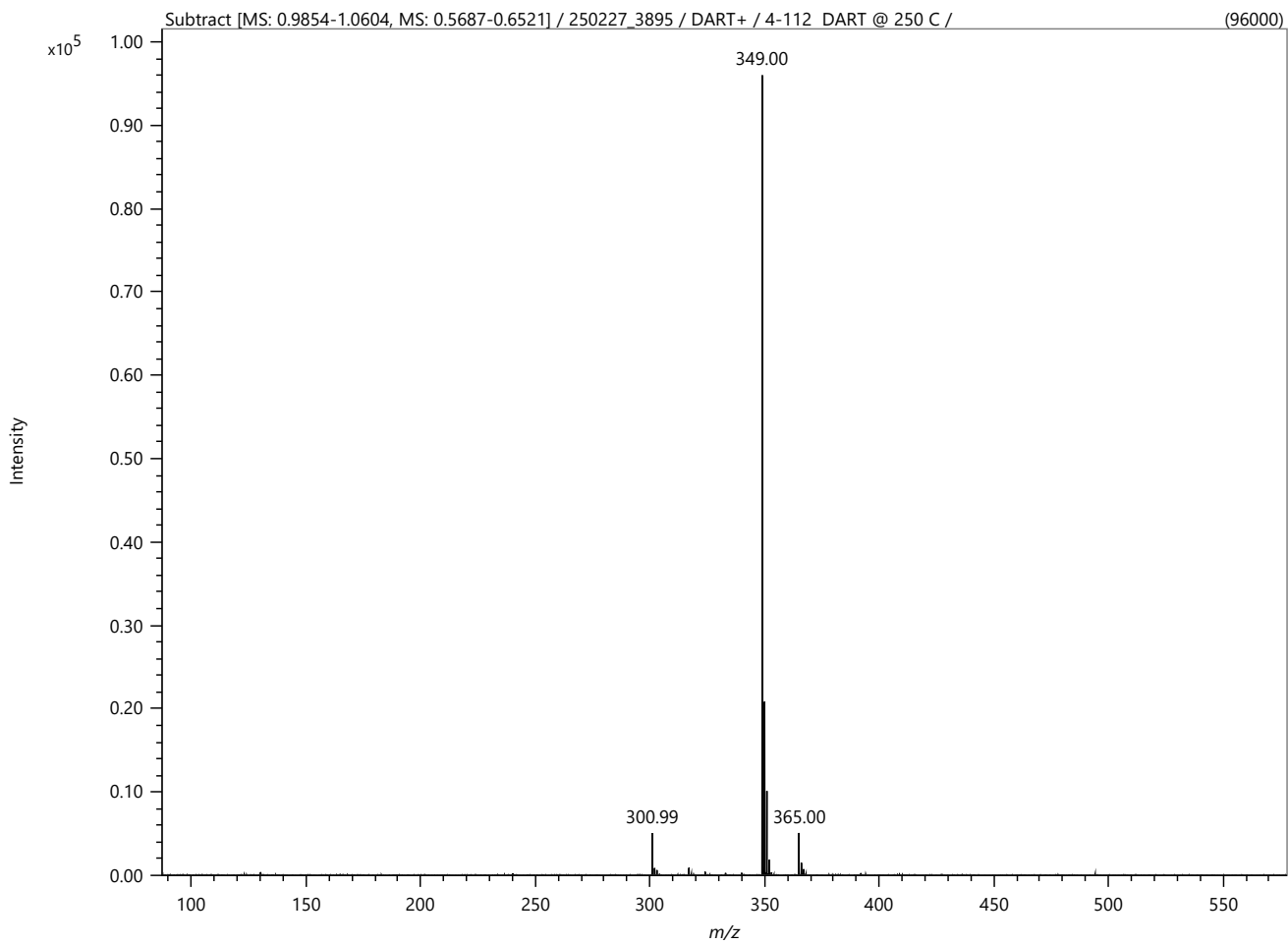


Figure S3-22. Mass spectrometry result for compound 3-7O.



1 / 1

**Figure S3-23.** Mass spectrometry result for compound **3-7**.

YSci Core – MS facility

Faculty of Science, **Department of Chemistry**

402 Life Science Building, 4700 Keele street, M3J 1P3, Toronto, Ontario, CANADA.

Index	Sample Name	Component Name	Formula	Adduct / Charge	Found At...	Mass Error (ppm)	Mass Error...	Area	Retention Time
20	20250306 - 4-172.01	4-172 (1.605)	C <sub>19</sub> H <sub>12</sub> N <sub>2</sub> PS <sub>2</sub>	[M] <sup>+</sup>	363.0181	1.9	✓	2.051e7	1.61

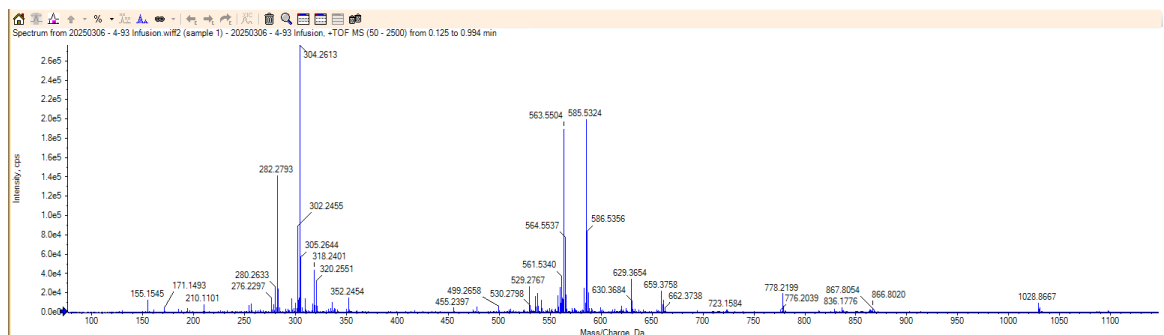
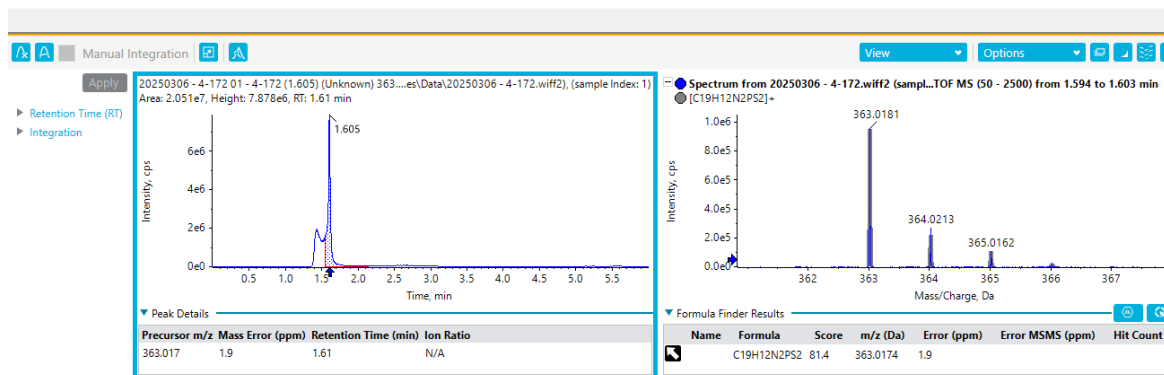
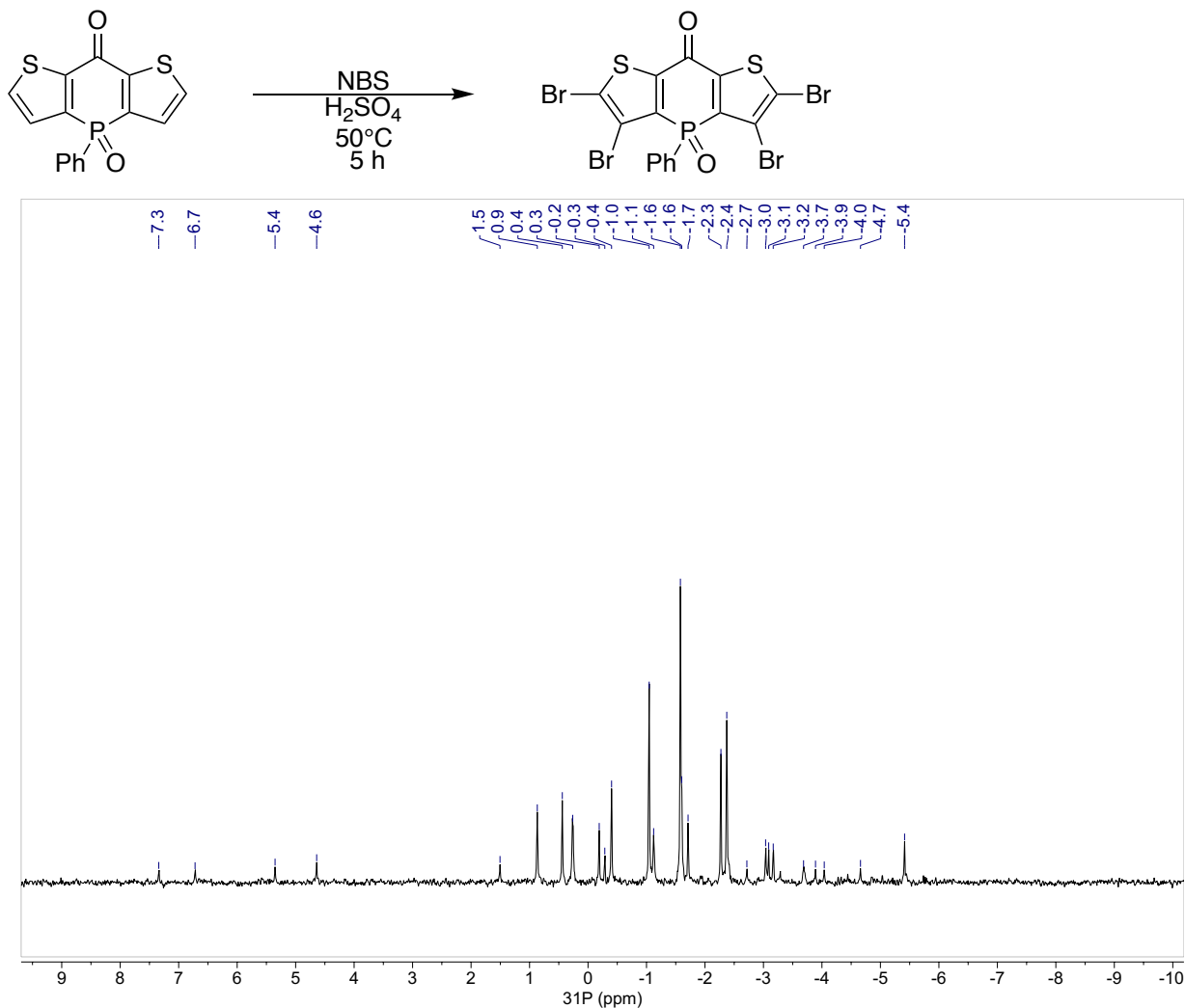


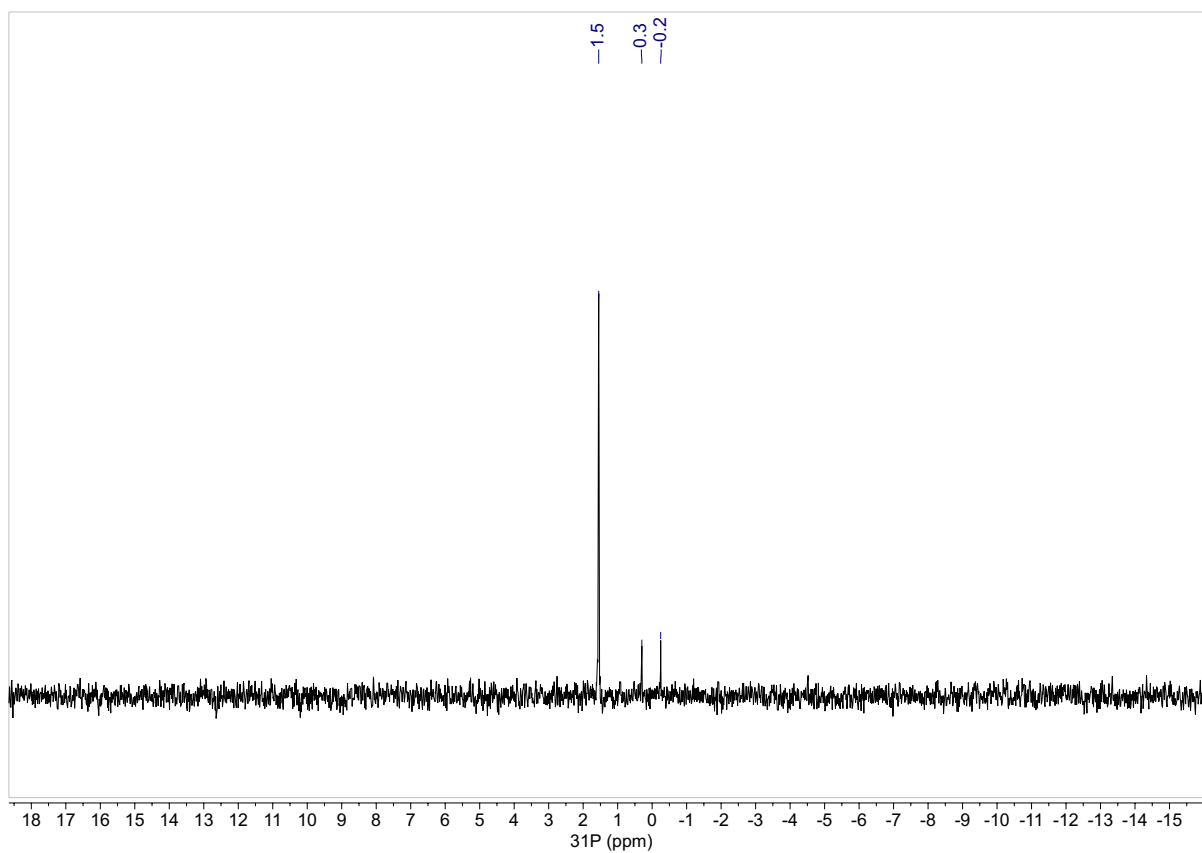
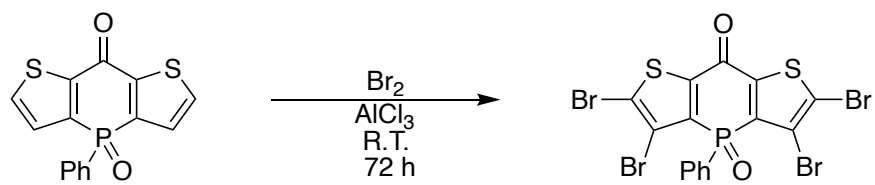
Figure S3-24. Mass spectrometry result for compound 3-7Me.

## SI.4.0 Chapter 4: Extending the Conjugation of the Dithieno[2,3-*b*:3',2'-*e*]-4-keto-1,4-dihydrophosphinine Core

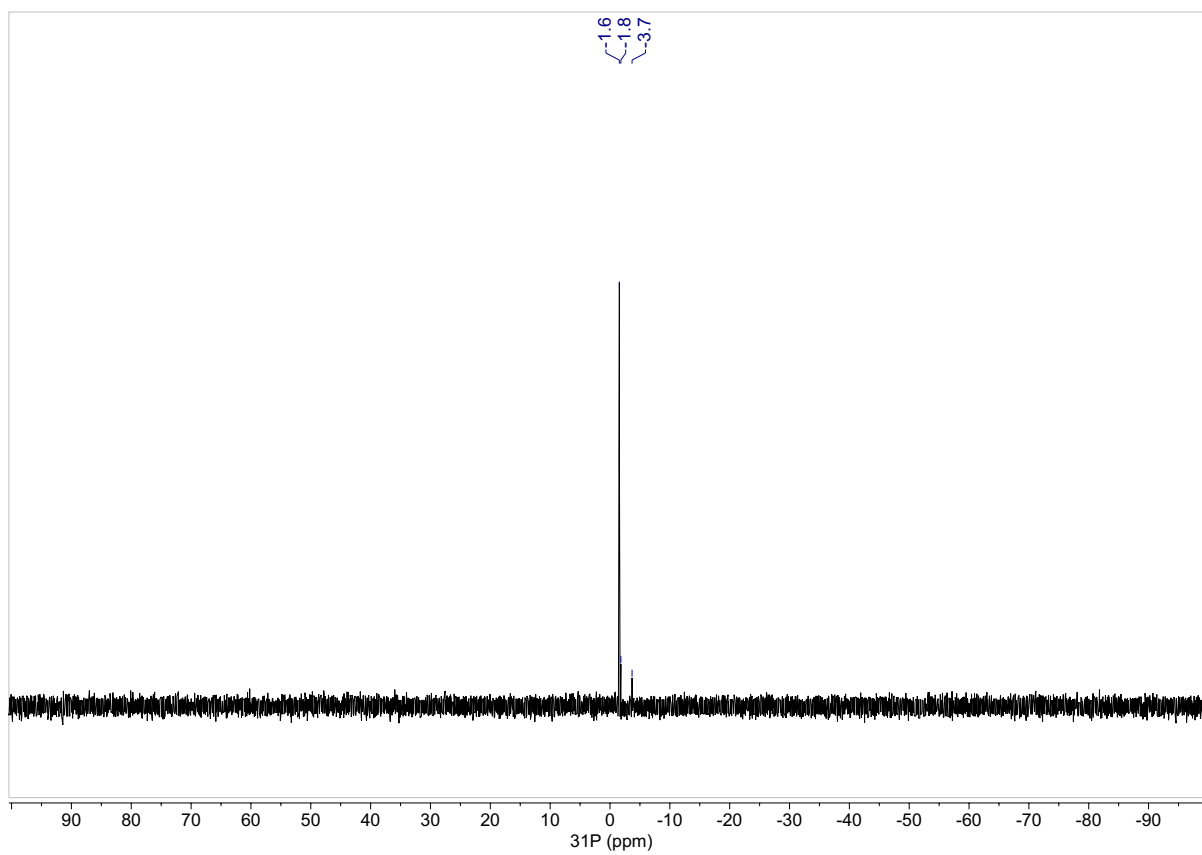
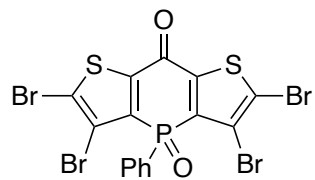
### SI.4.1 Nuclear Magnetic Resonance Spectra



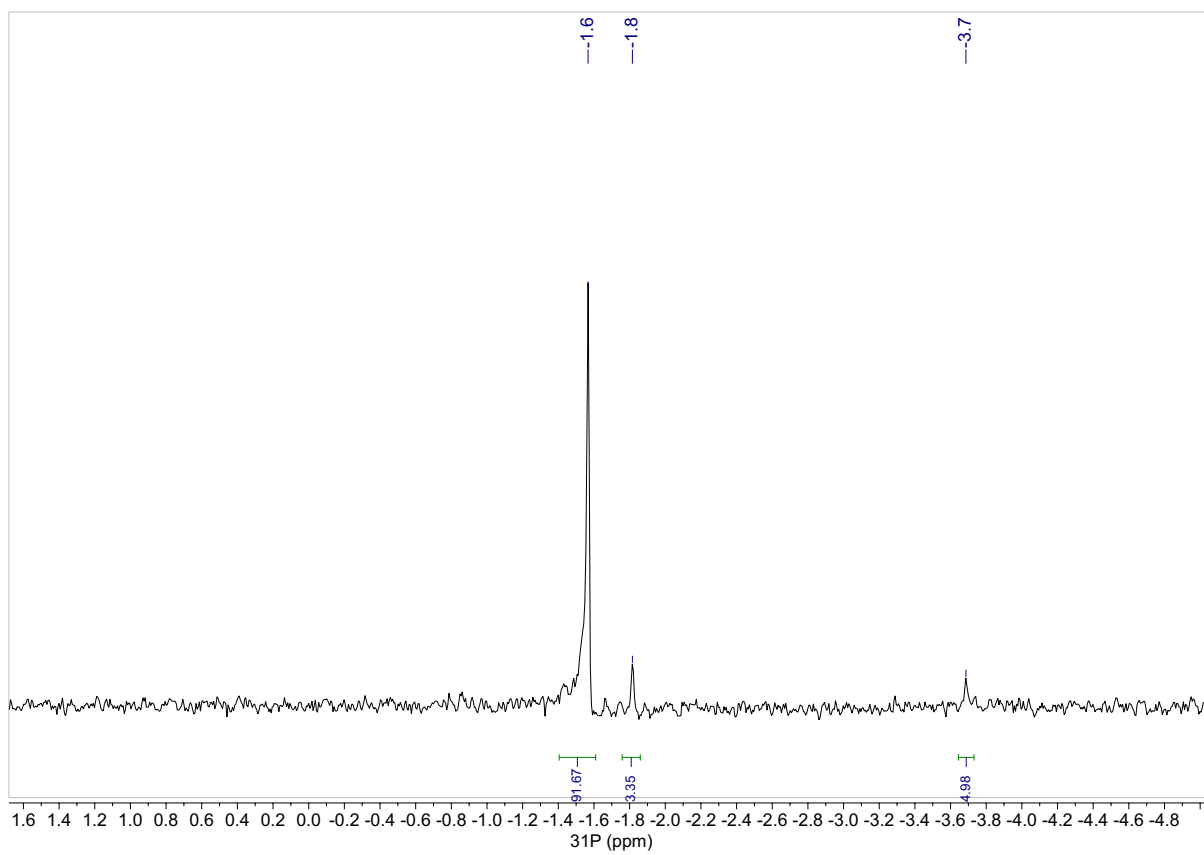
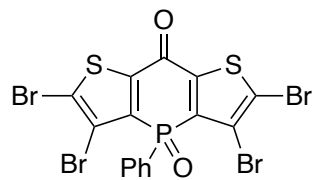
**Figure S4-1.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, CDCl<sub>3</sub>) of reaction from Scheme 4-2A.



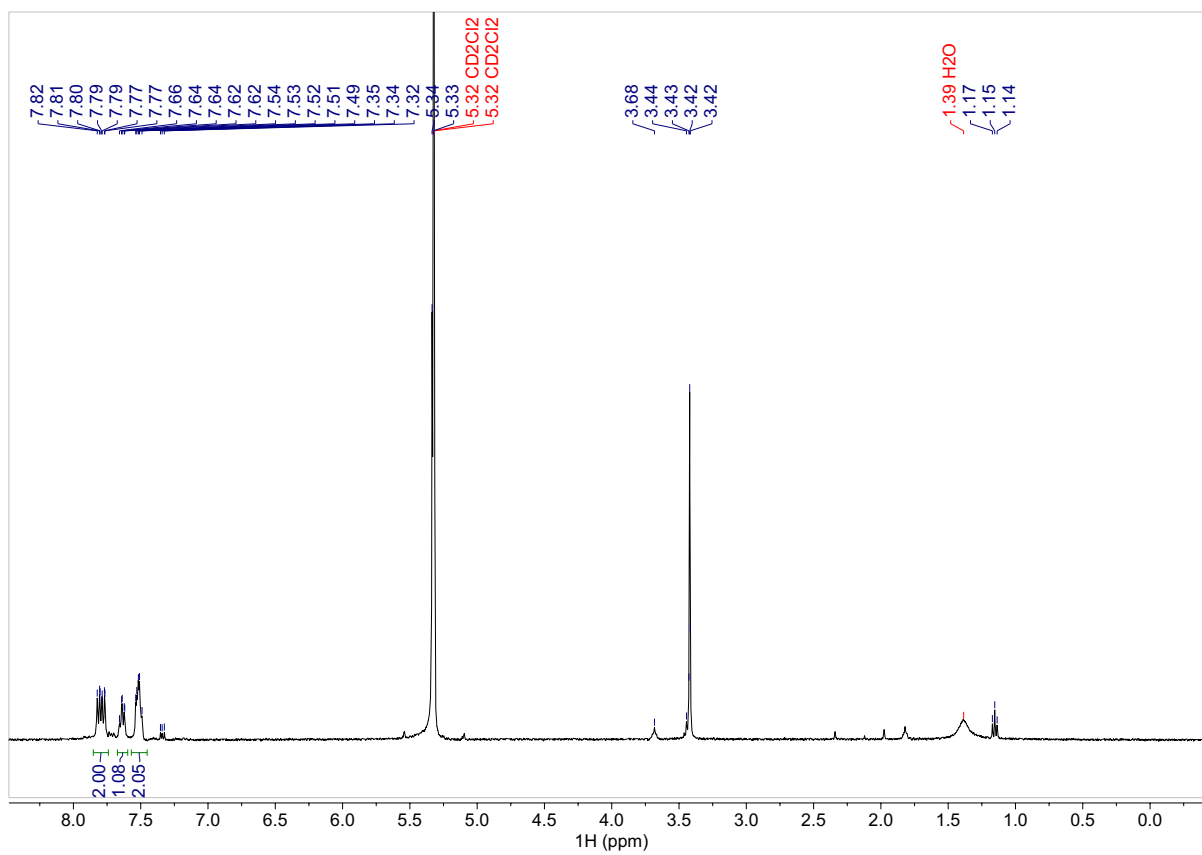
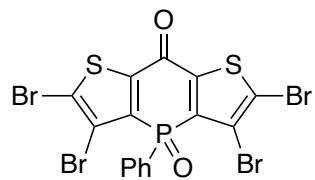
**Figure S4-2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CDCl}_3$ ) of reaction Scheme 4-2B.



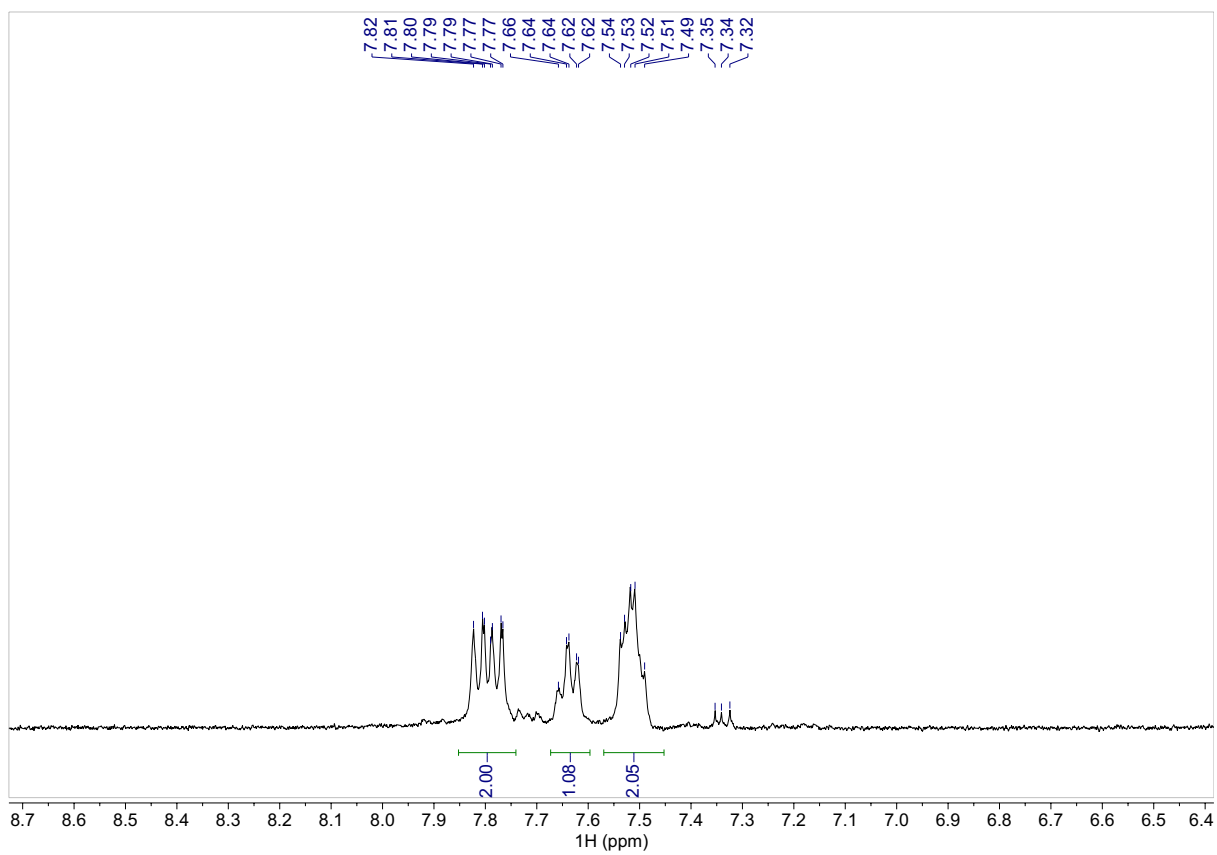
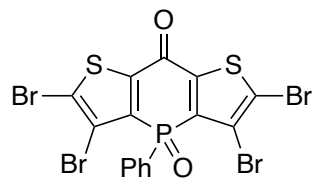
**Figure S4-3.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound 4-5.



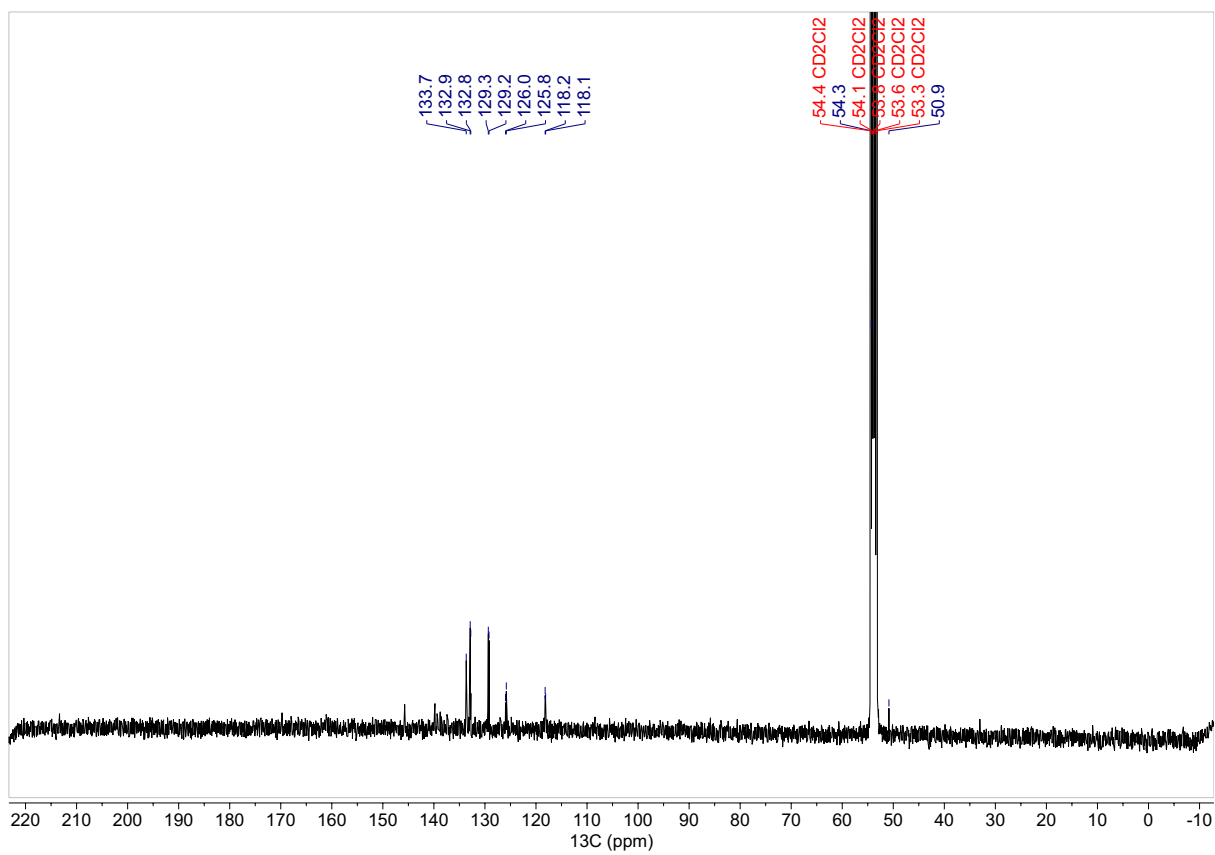
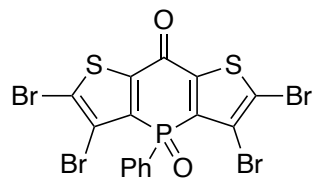
**Figure S4-4.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound 4-5.



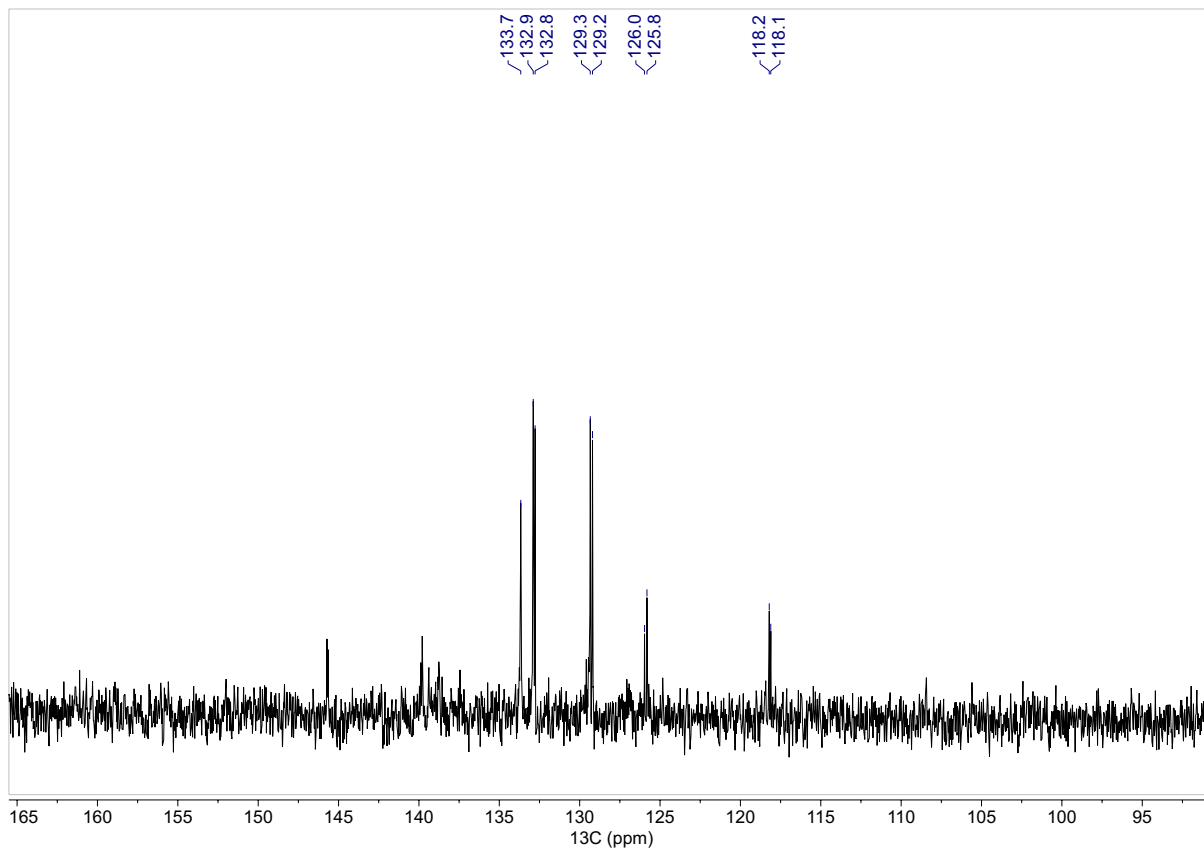
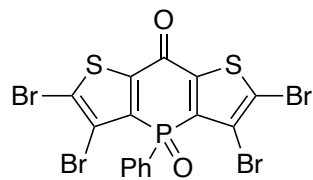
**Figure S4-5.** <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-5.



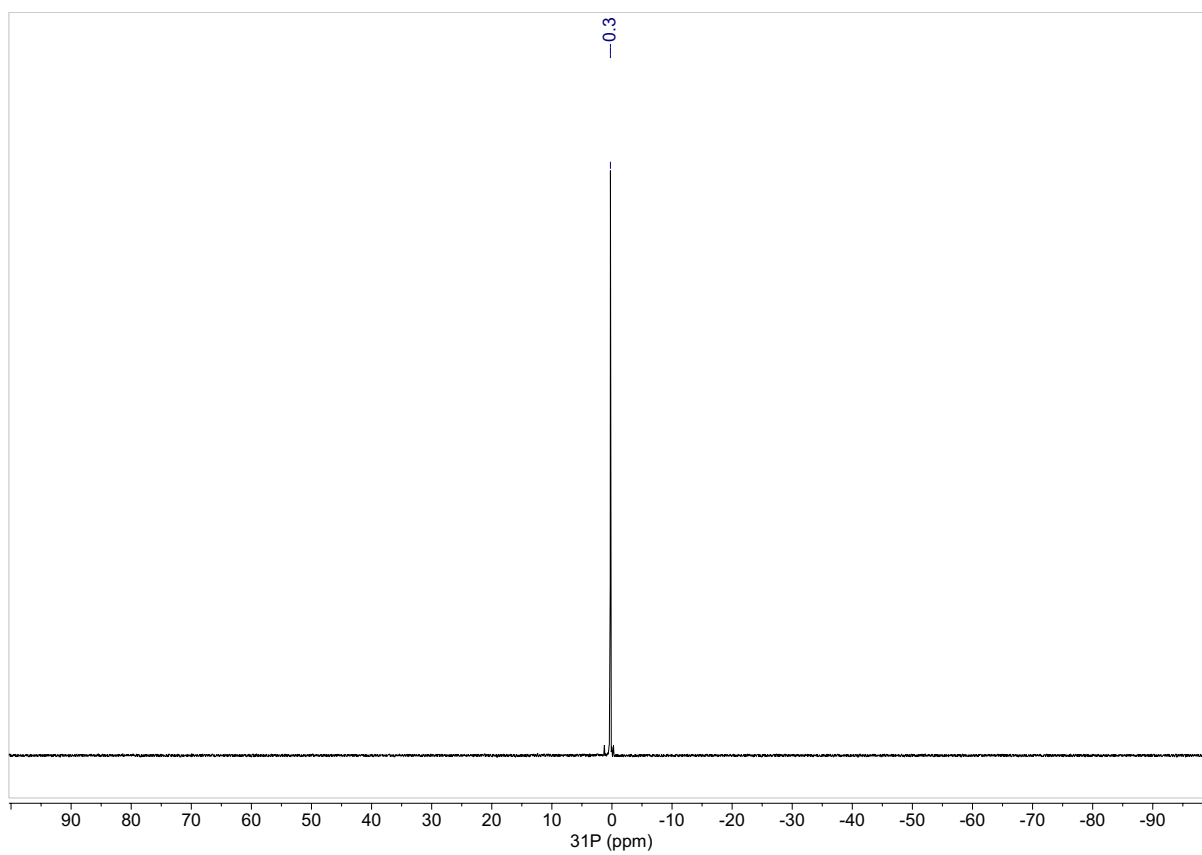
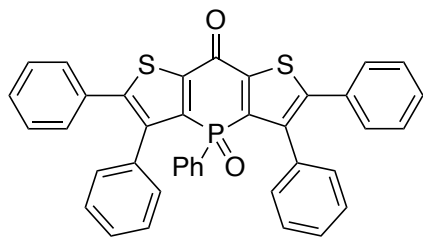
**Figure S4-6.**  $^1\text{H}$  NMR spectrum zoomed (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound 4-5.



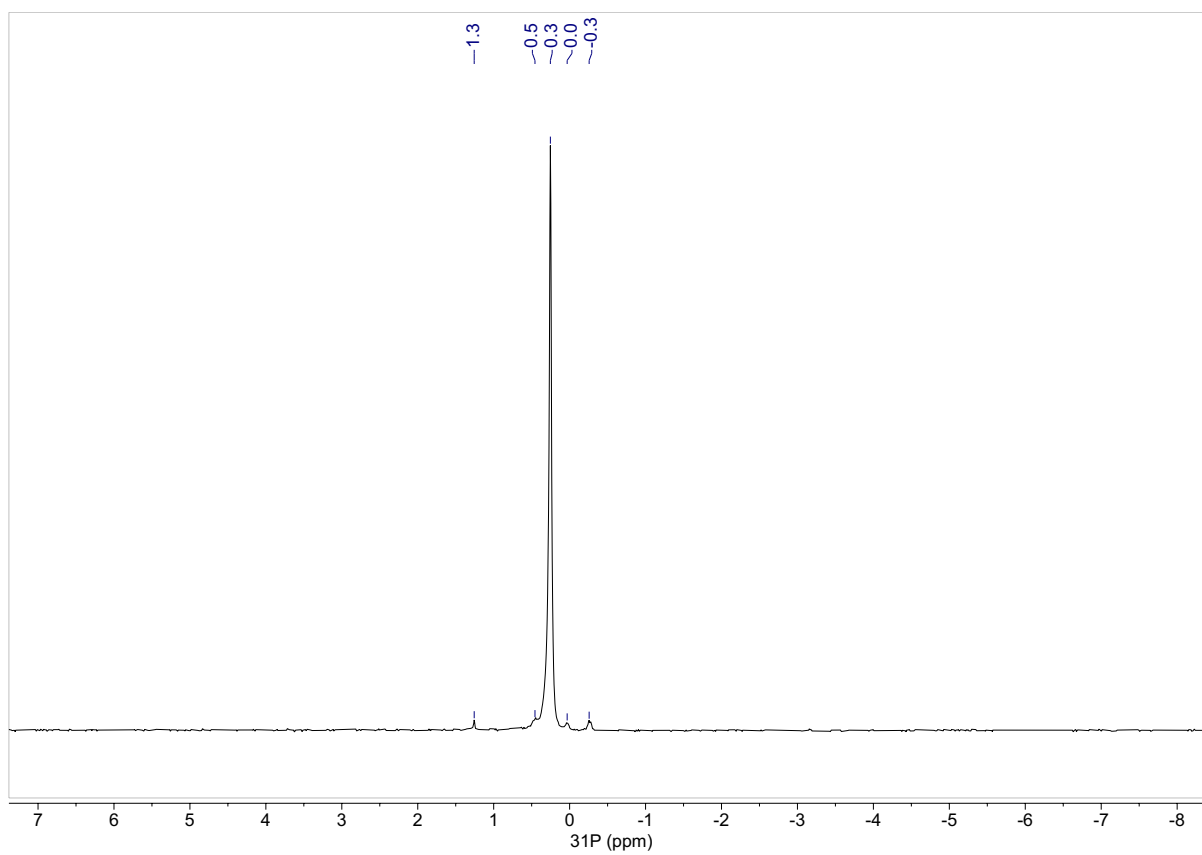
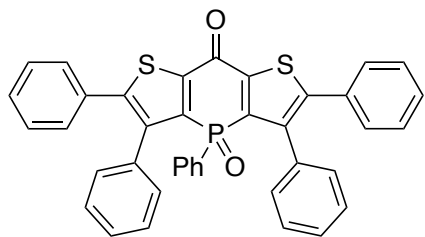
**Figure S4-7.** <sup>13</sup>C NMR spectrum (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-5.



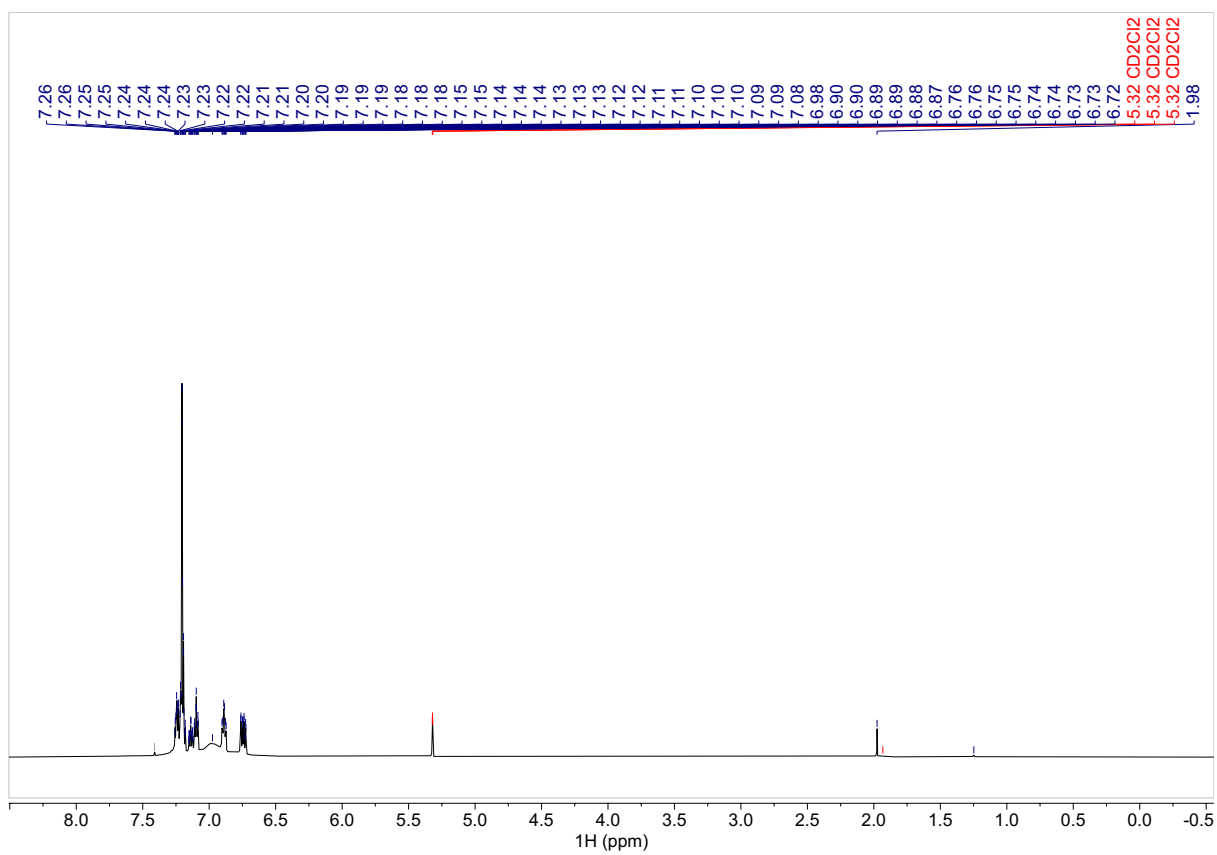
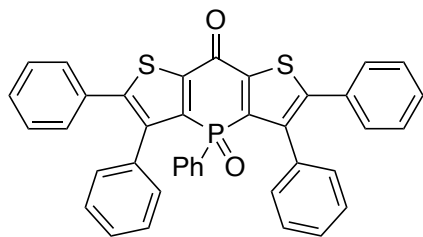
**Figure S4-8.** <sup>13</sup>C NMR spectrum zoomed (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-5.



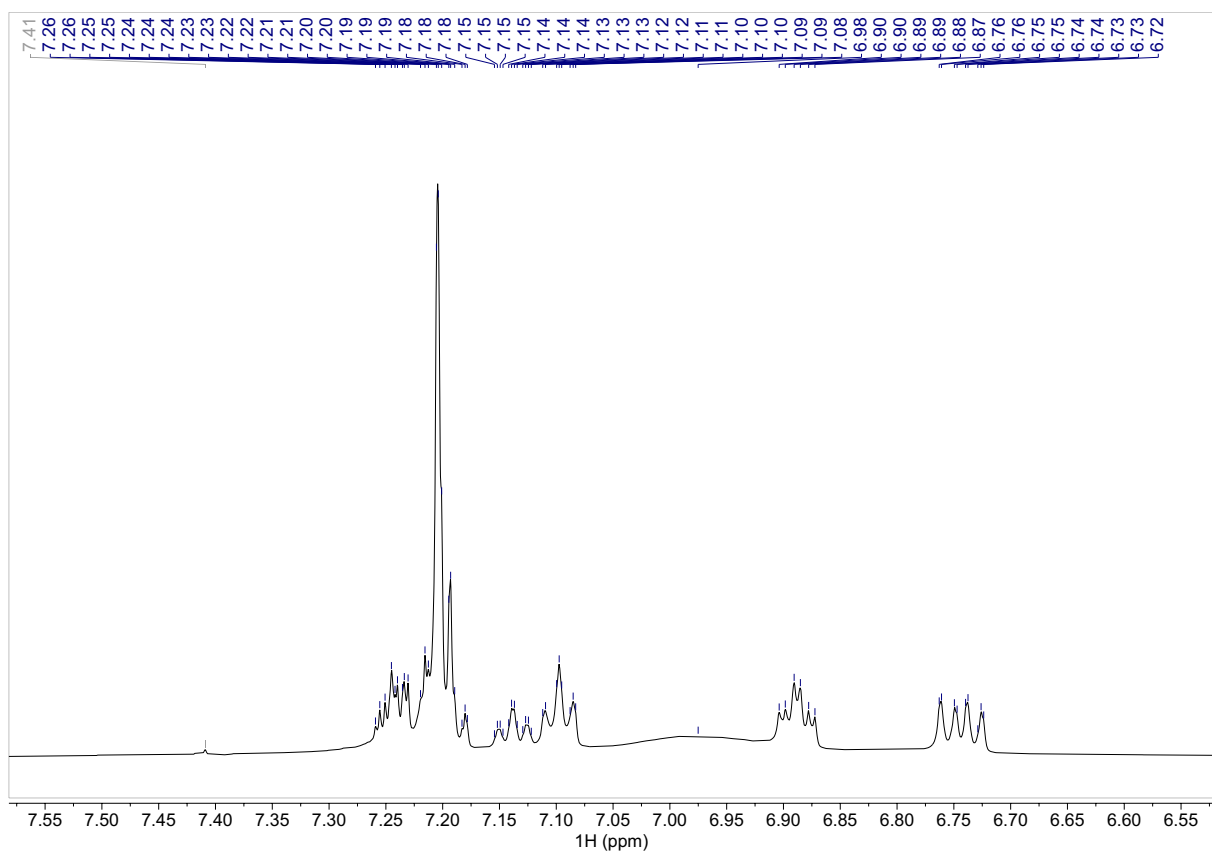
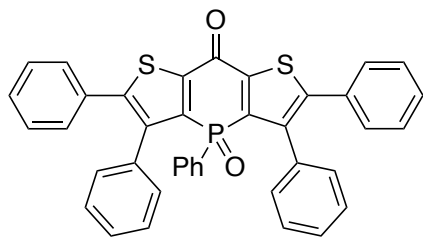
**Figure S4-9.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound 4-7.



**Figure S4-10.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum zoomed (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound 4-7.



**Figure S4-11.** <sup>1</sup>H NMR spectrum (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-7.



**Figure S4-12.**  $^1\text{H}$  NMR spectrum zoomed (600 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound 4-7.

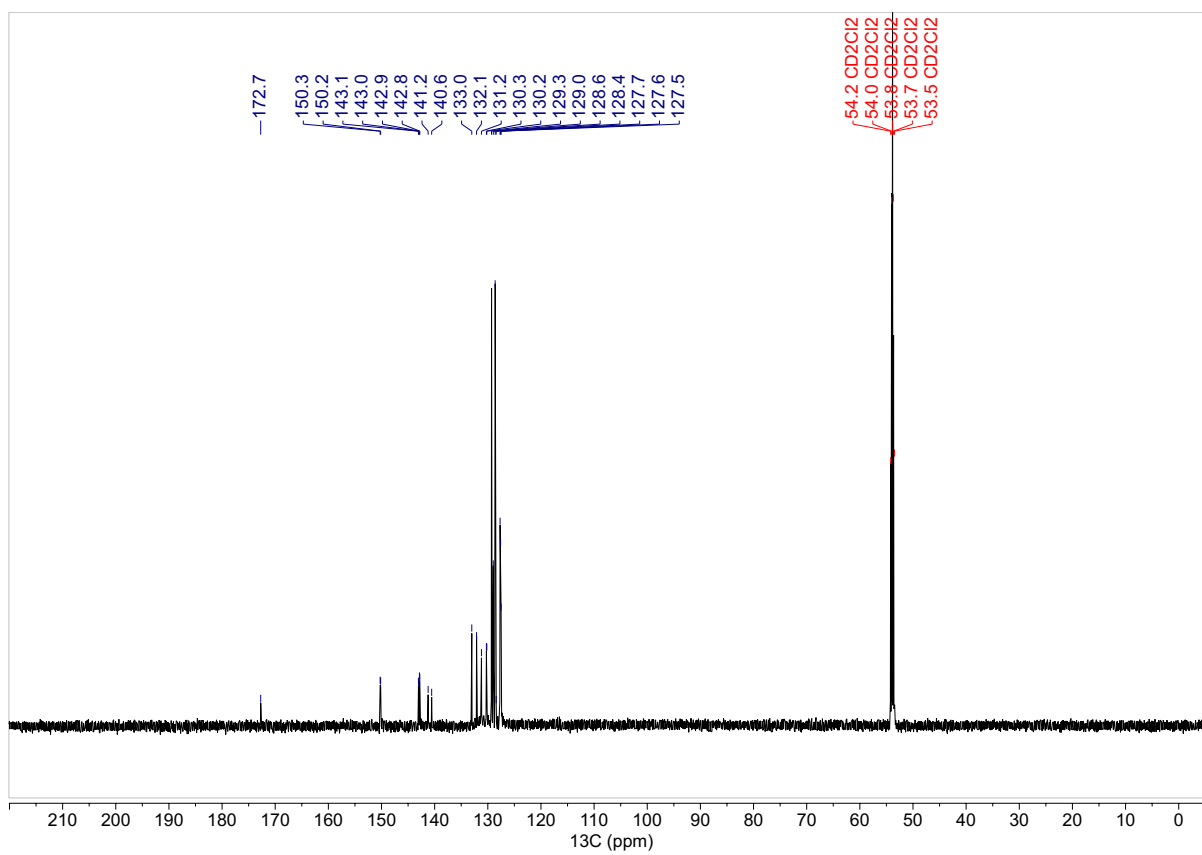
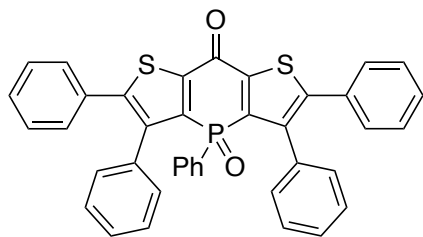
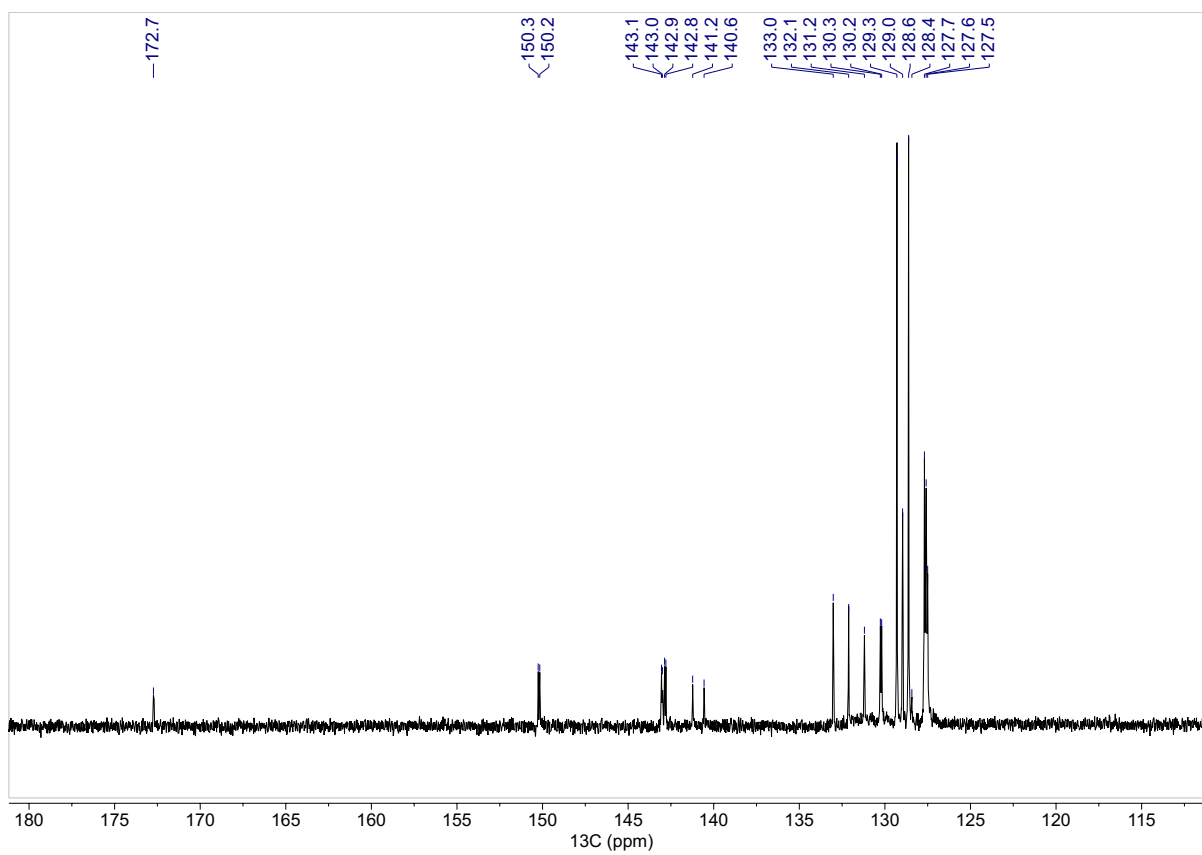
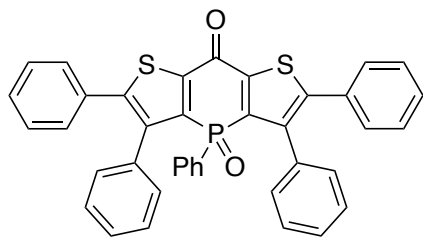
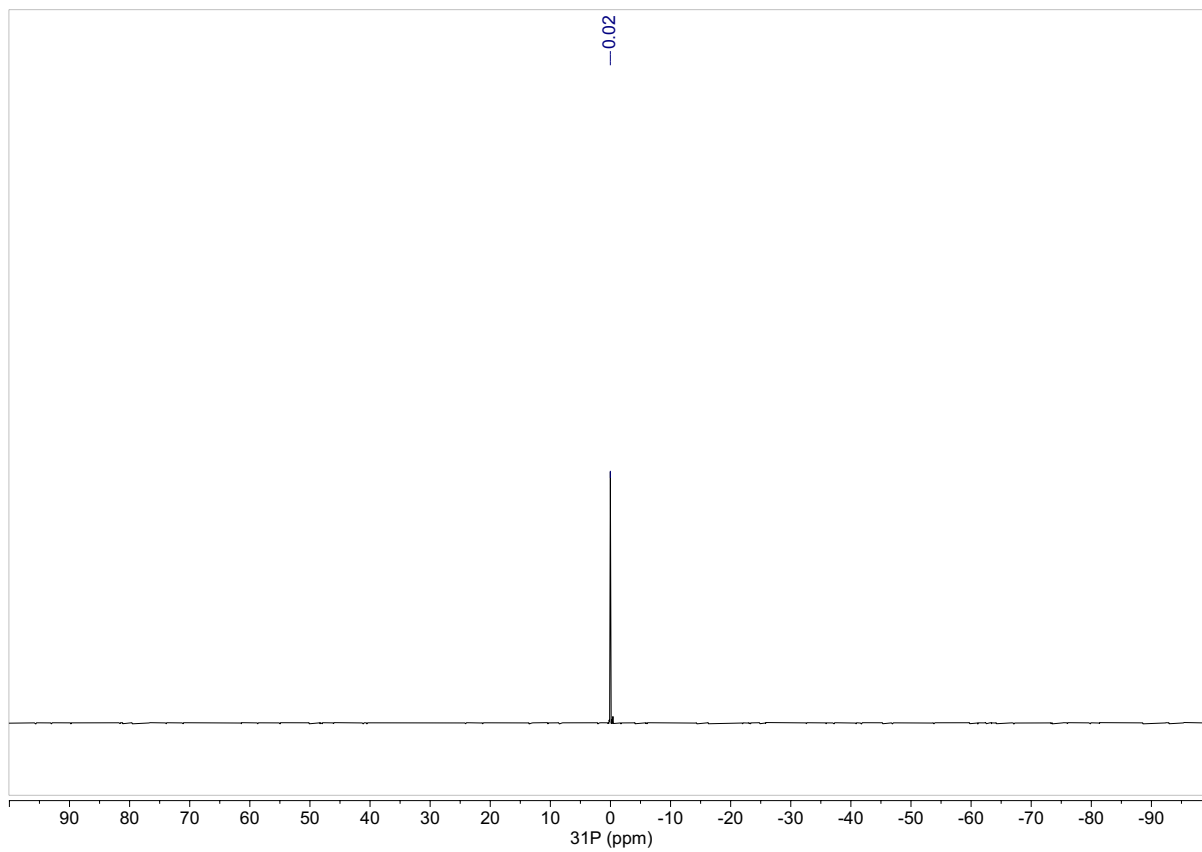
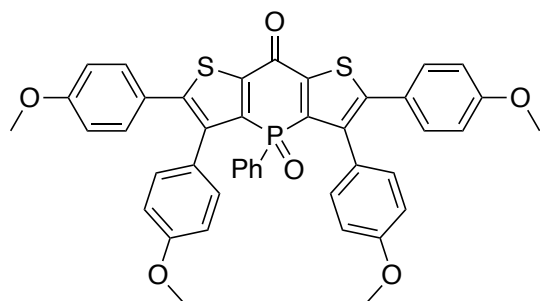


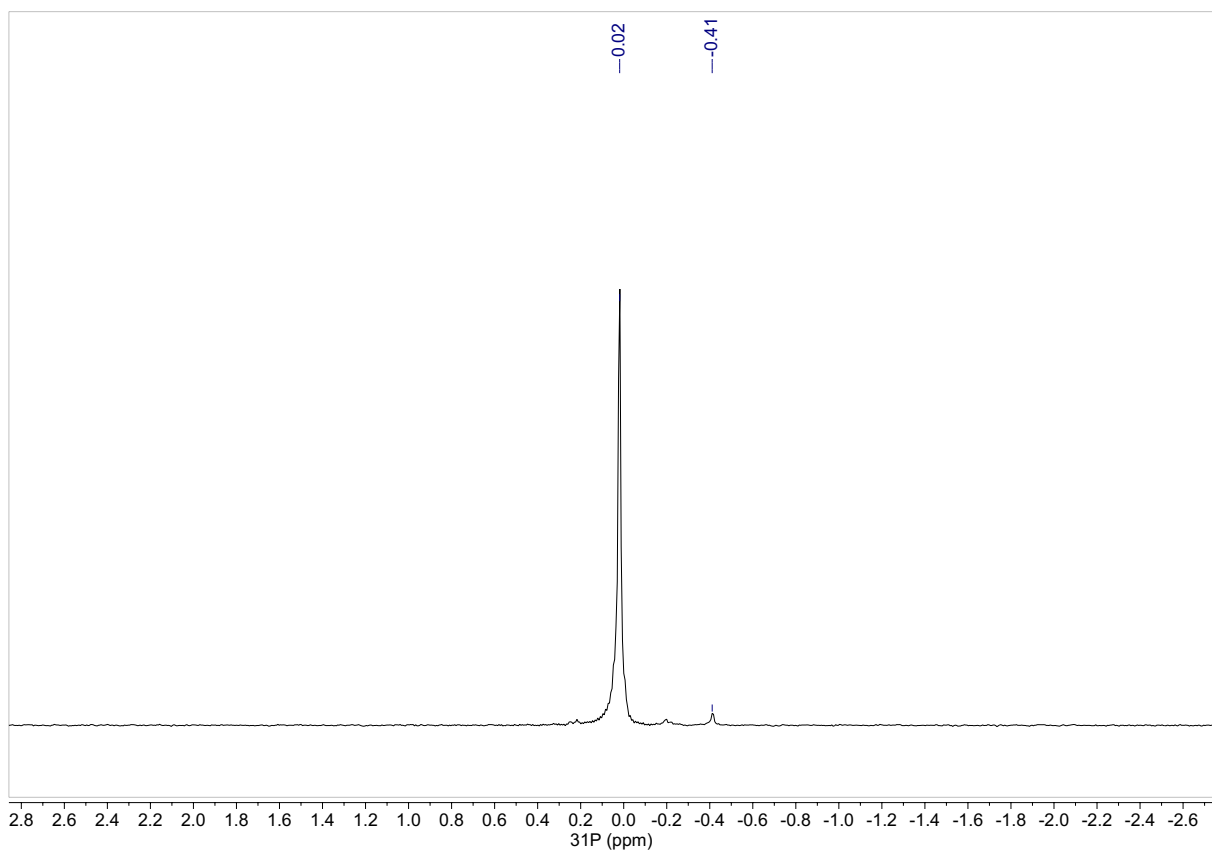
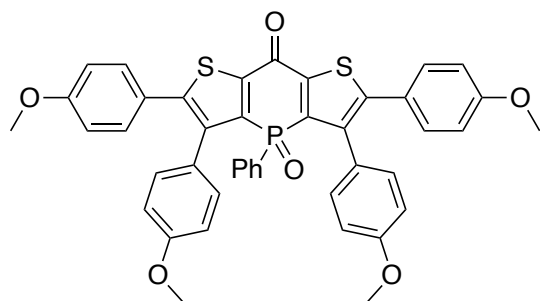
Figure S4-13.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound 4-7.



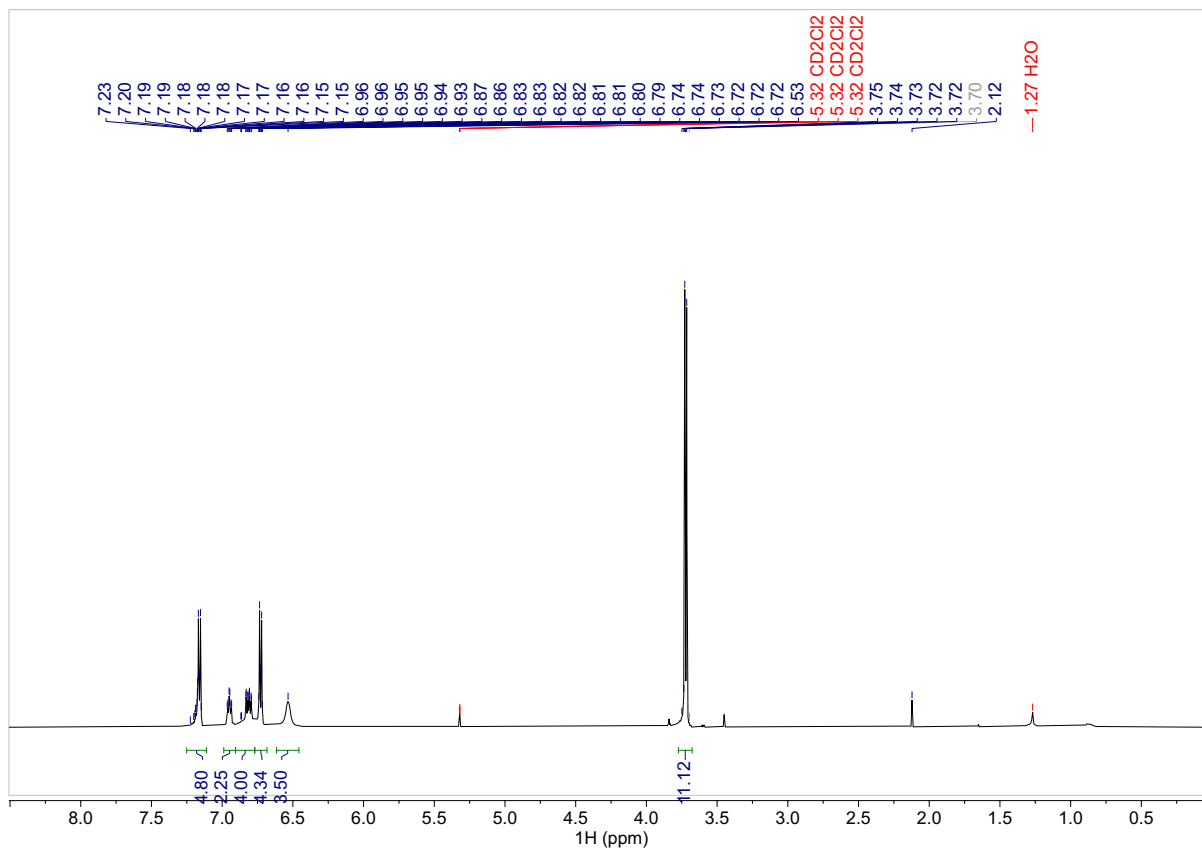
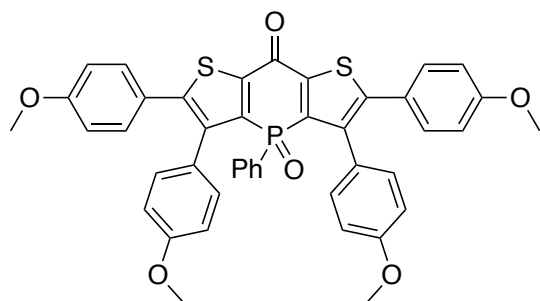
**Figure S4-14.**  $^{13}\text{C}$  NMR spectrum zoomed (150 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound 4-7.



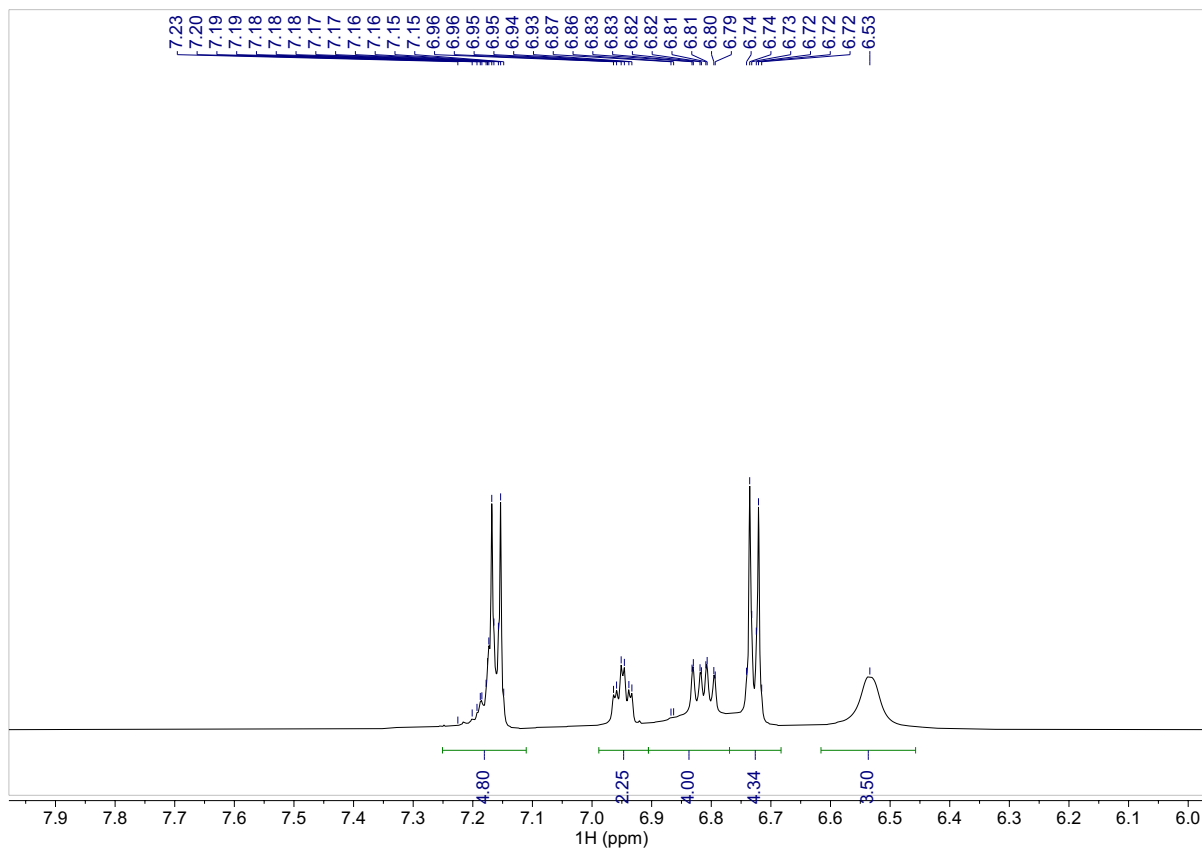
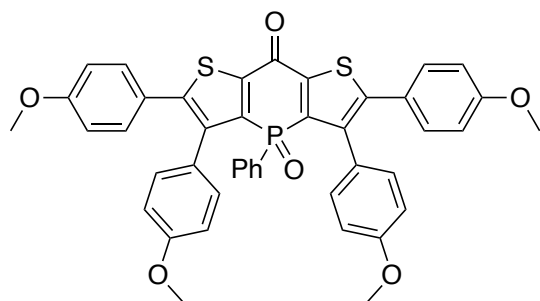
**Figure S4-15.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of compound **4-8**.



**Figure S4-16.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum zoomed (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-8.

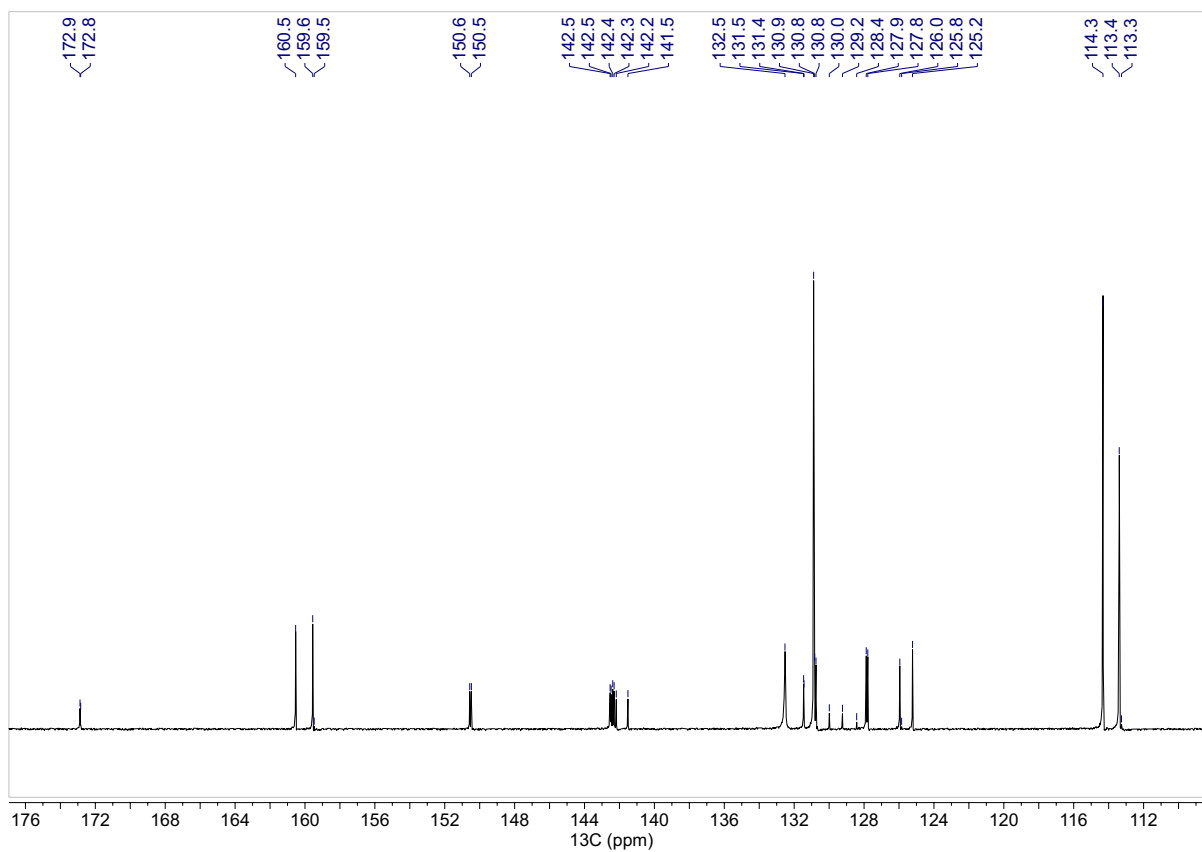
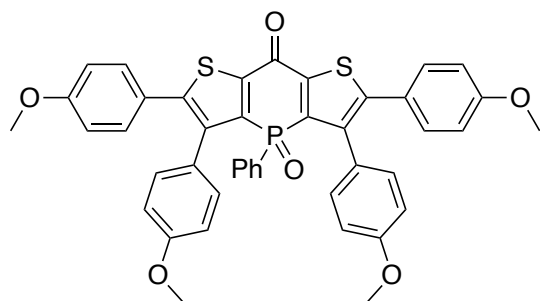


**Figure S4-17.** <sup>1</sup>H NMR spectrum (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-8.

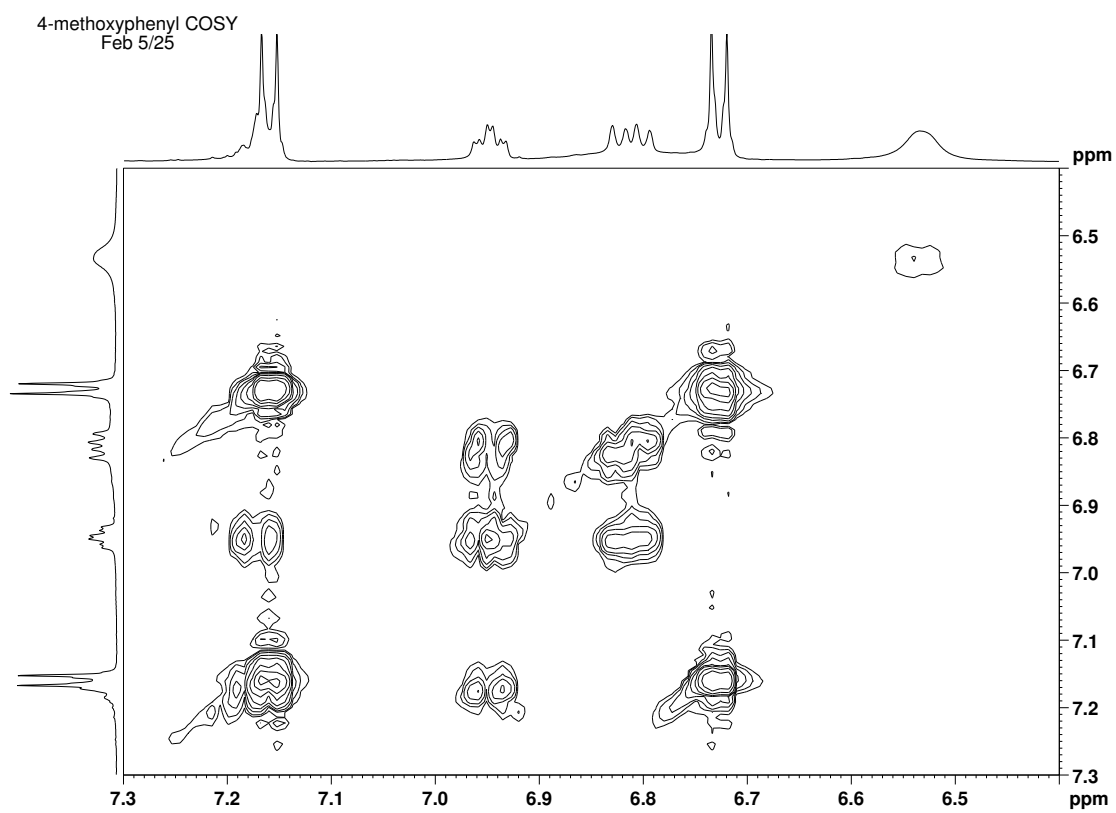
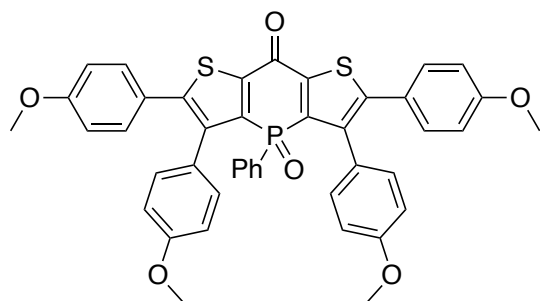


**Figure S4-18.** <sup>1</sup>H NMR spectrum zoomed (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-8.

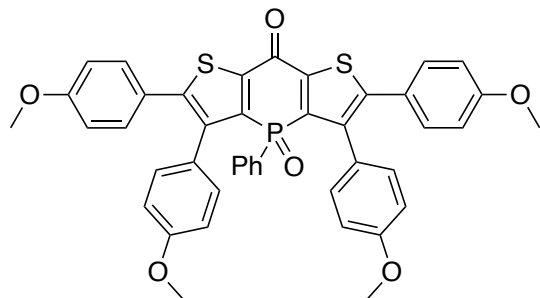




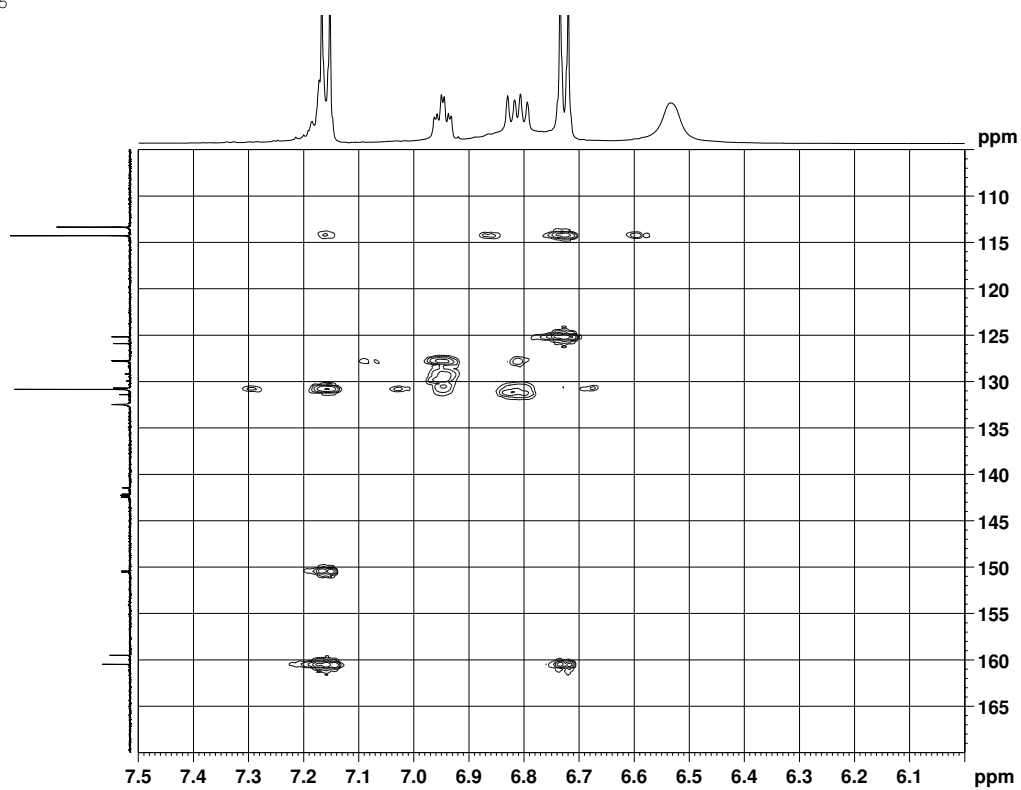
**Figure S4-20.** <sup>13</sup>C NMR spectrum zoomed (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-8.



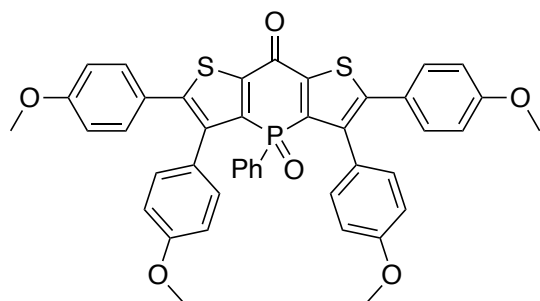
**Figure S4-21.** 2D COSY NMR spectrum of compound 4-8 (600 MHz).



4-methoxyphenyl HMBC 1H-13C  
Feb 5/25



**Figure S4-22.** 2D  $^1\text{H}$ - $^{13}\text{C}$  HMBC of compound **4-8** (600 MHz).



4-methoxyphenyl HMBC 1H-13C  
Feb 5/25

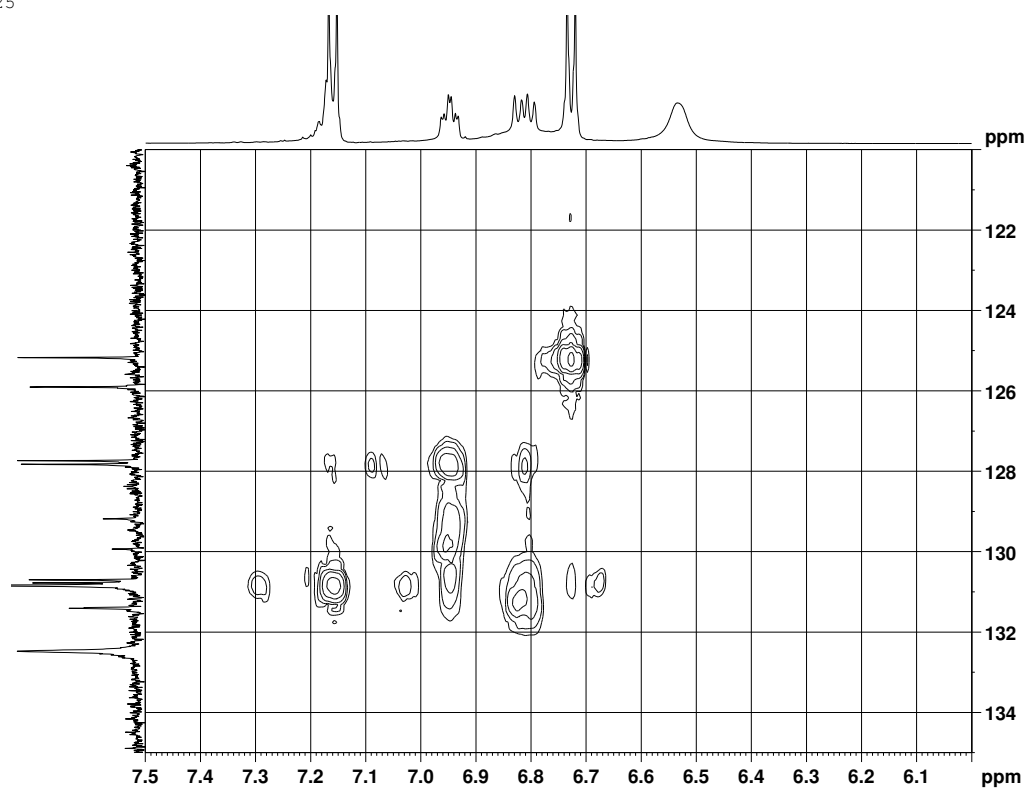
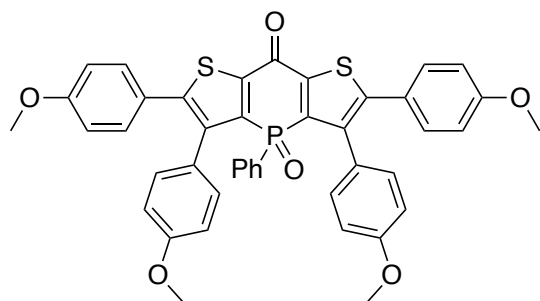
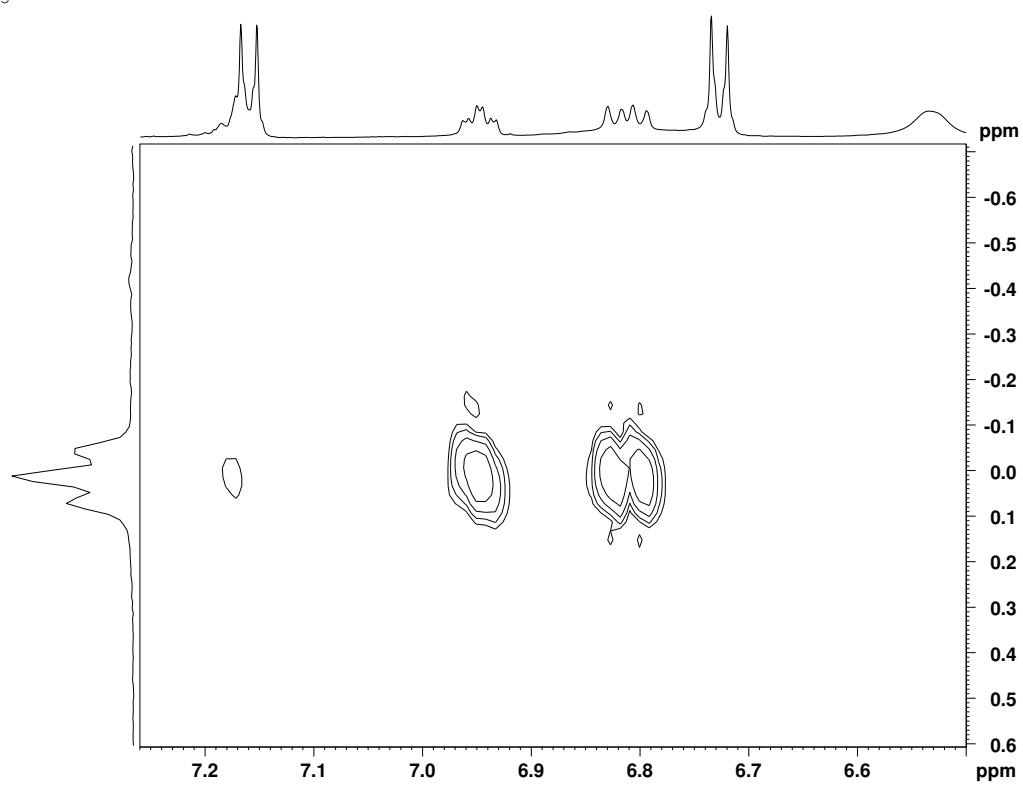


Figure S4-23. 2D  $^1\text{H}$ - $^{13}\text{C}$  HMBC of compound 4-8 zoomed (600 MHz).

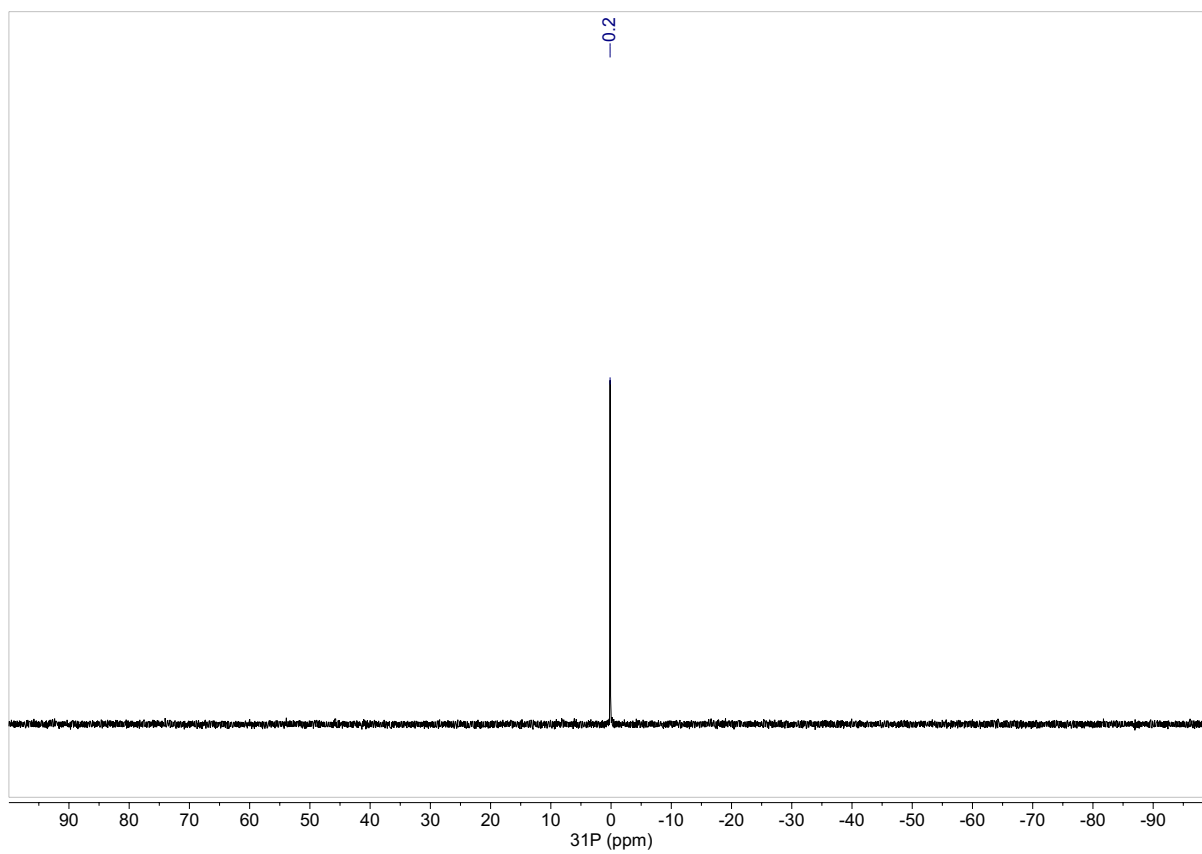
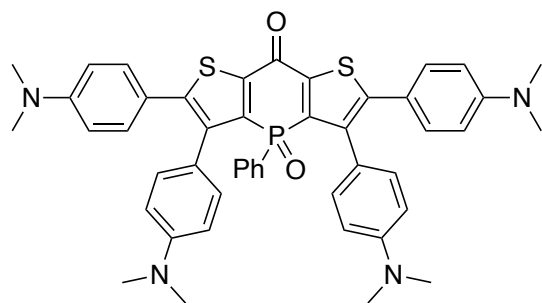


4-methoxyphenyl  $^{31}\text{P}$  HMBC  
Feb 6/25

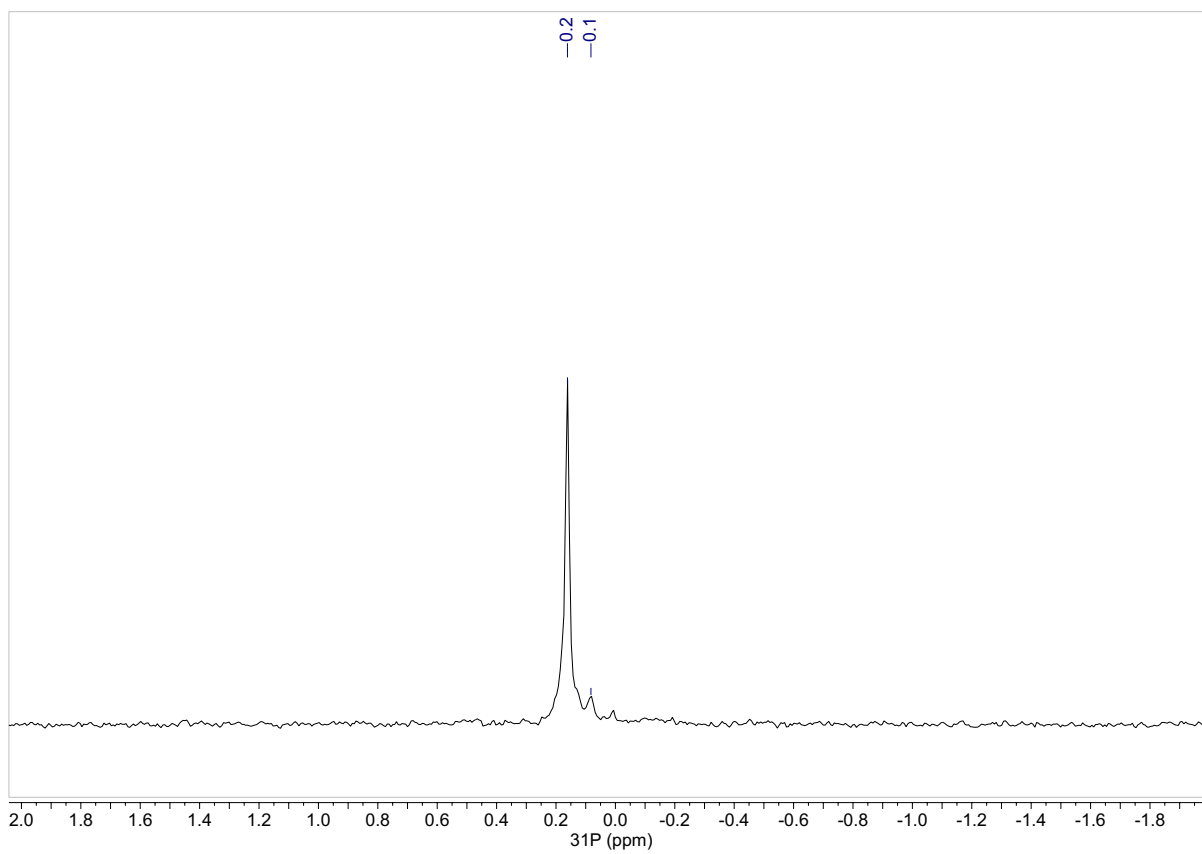
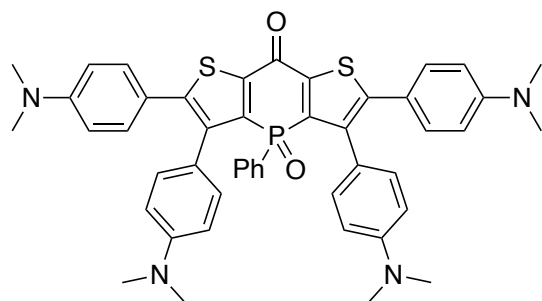


**Figure S4-24.** 2D  $^{31}\text{P}$ - $^1\text{H}$  HMBC of compound **4-8** (600 MHz).

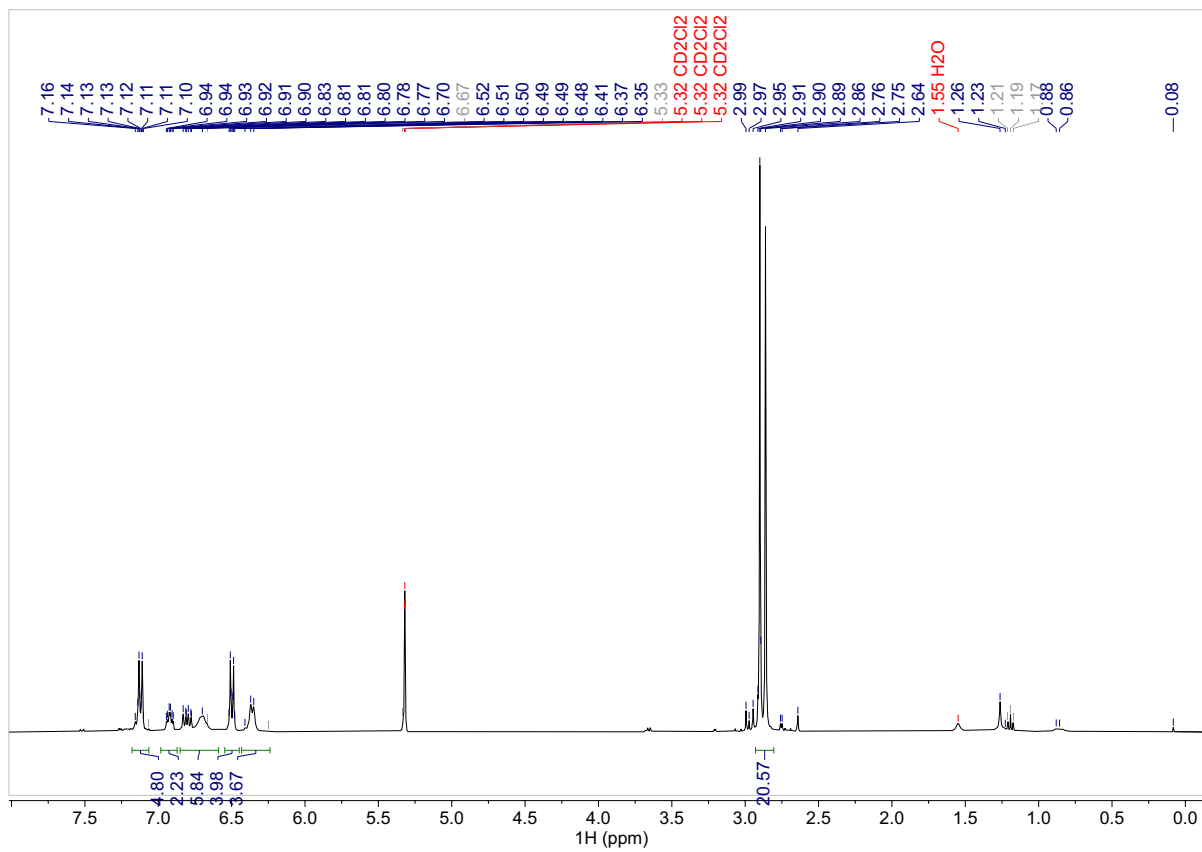
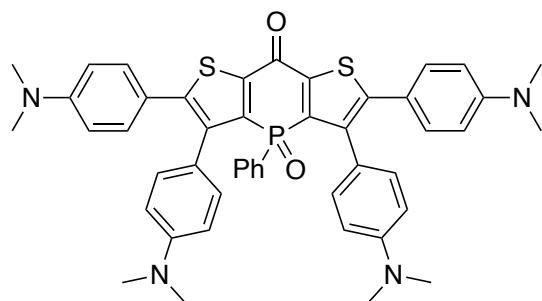




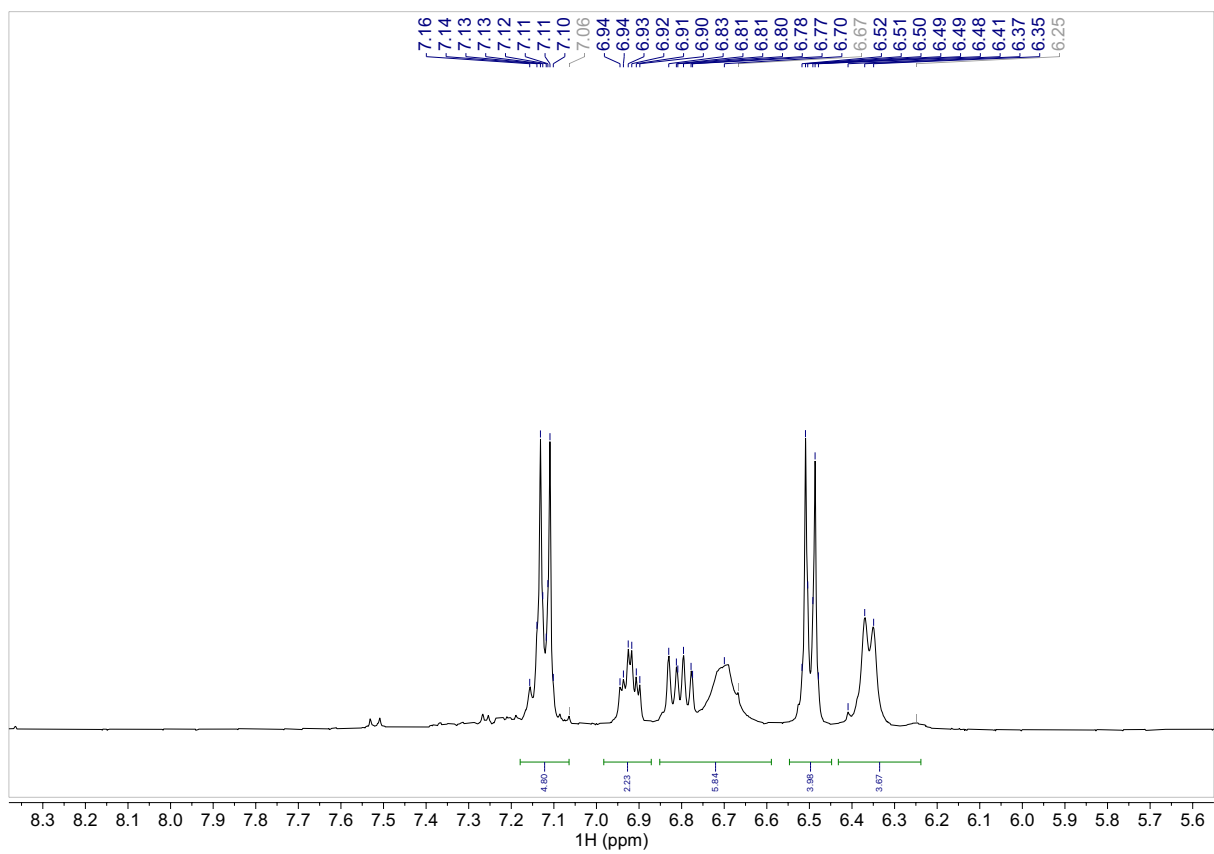
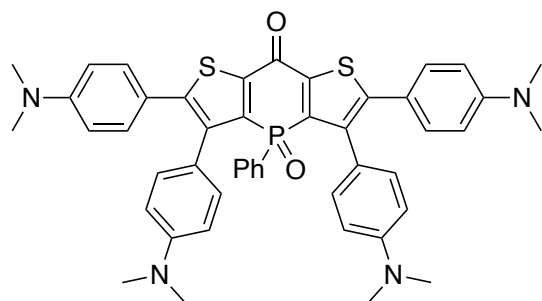
**Figure S4-26.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-9.



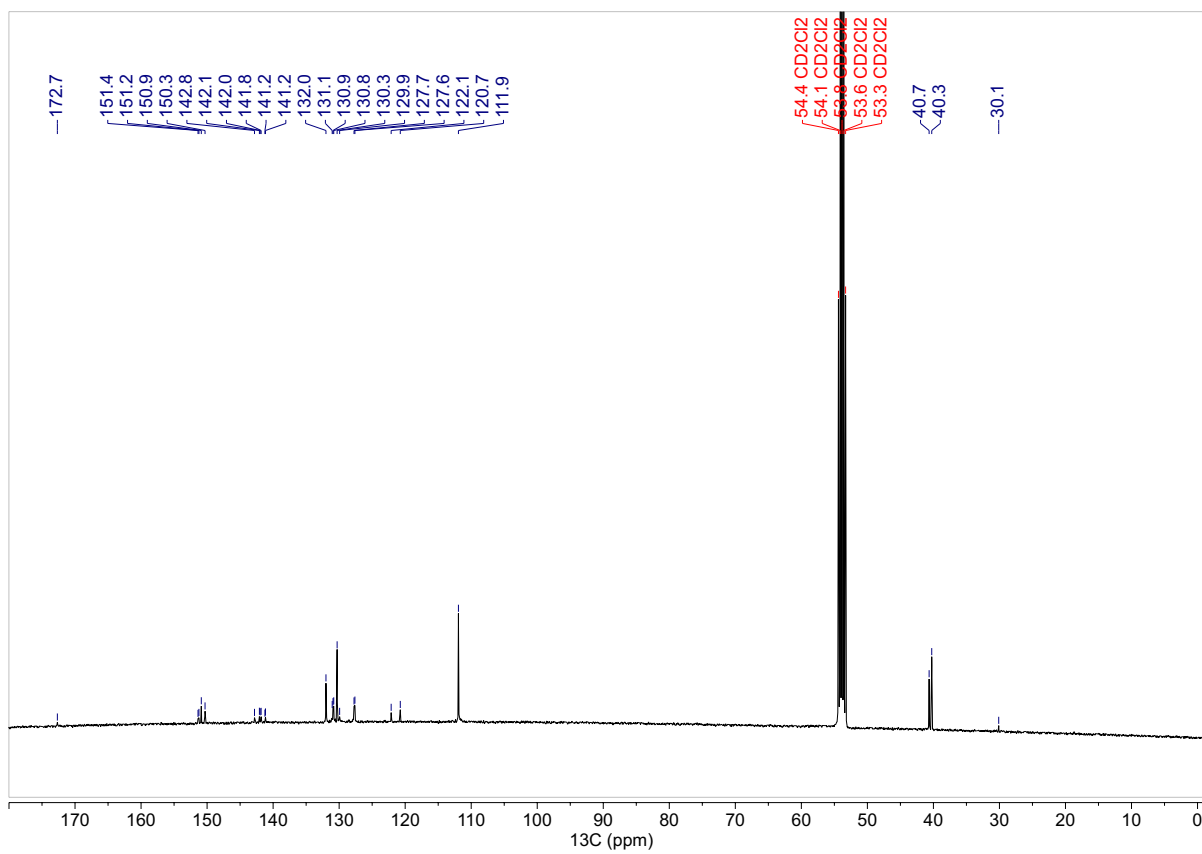
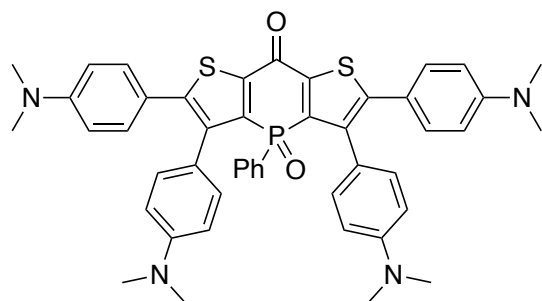
**Figure S4-27.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum zoomed (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-9.



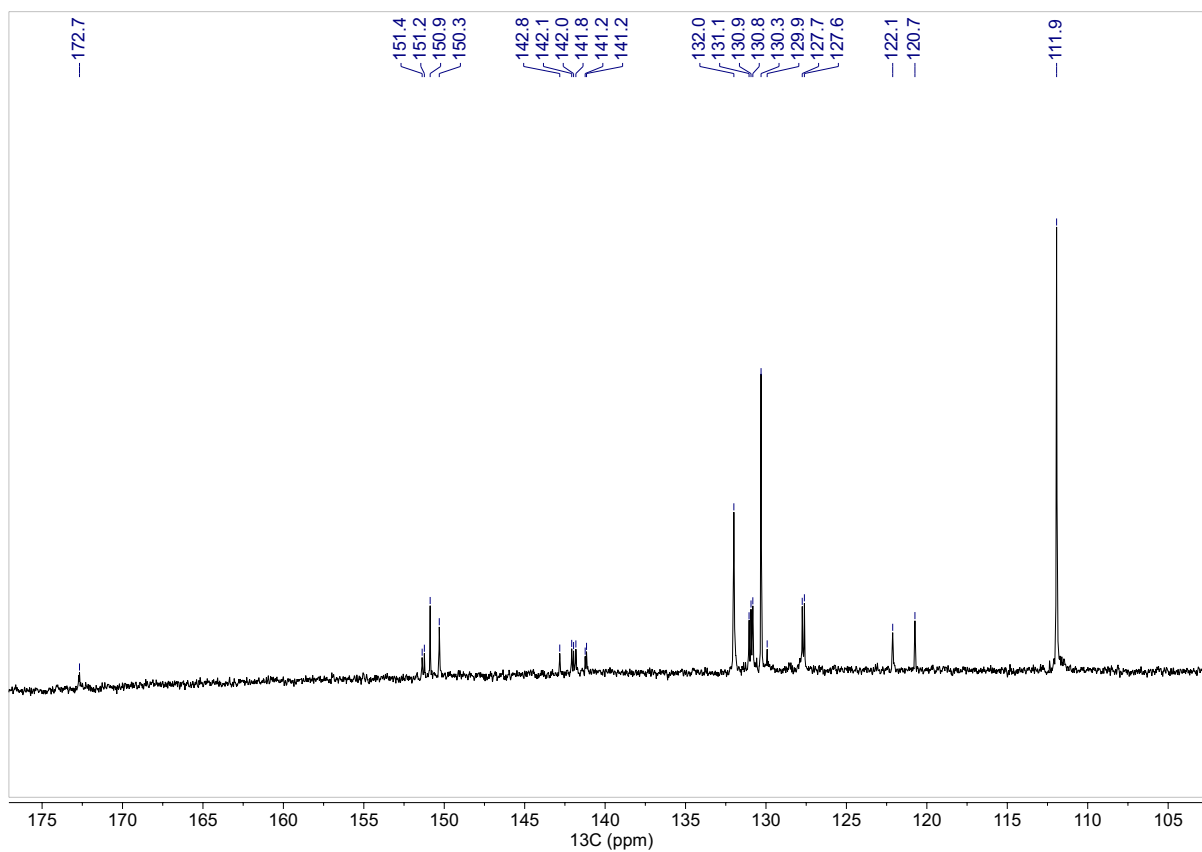
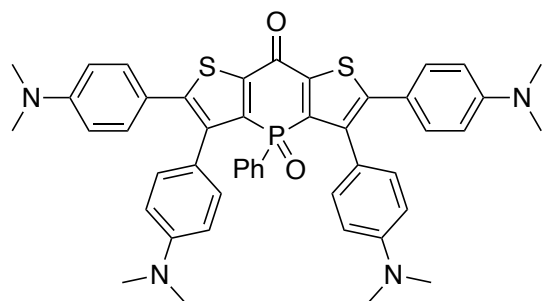
**Figure S4-28.** <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound **4-9**.



**Figure S4-29.** <sup>1</sup>H NMR spectrum zoomed (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-9.

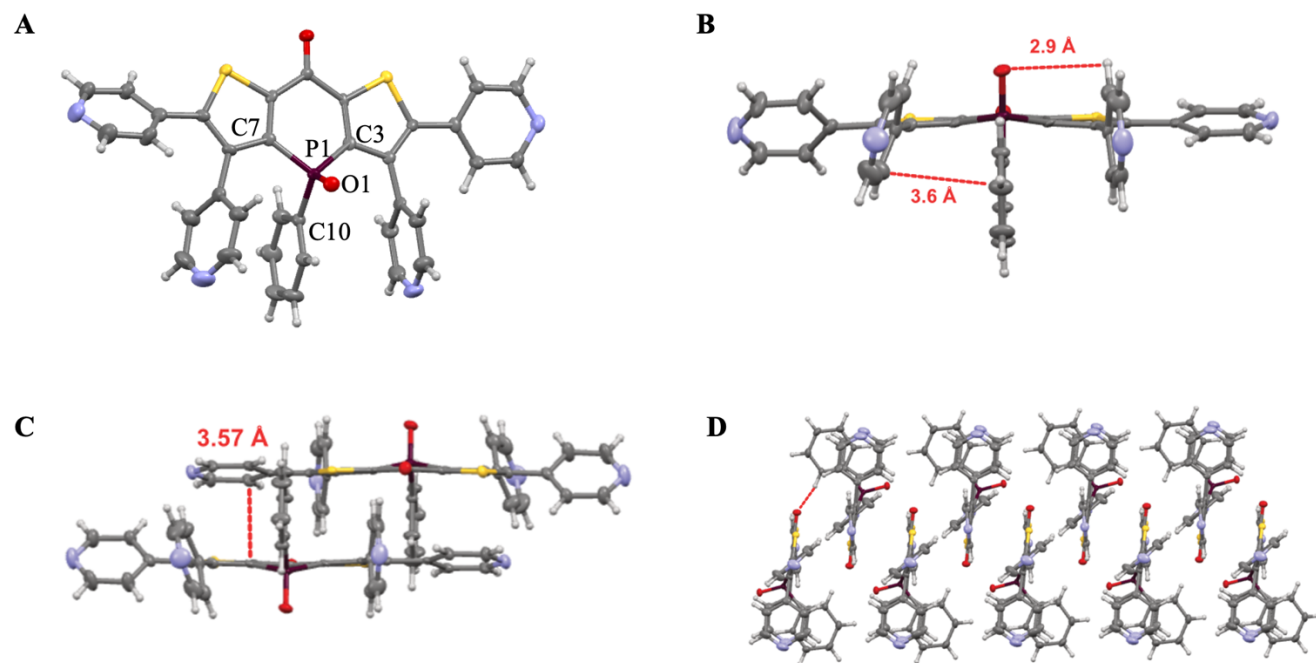


**Figure S4-30.** <sup>13</sup>C NMR spectrum (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-9.

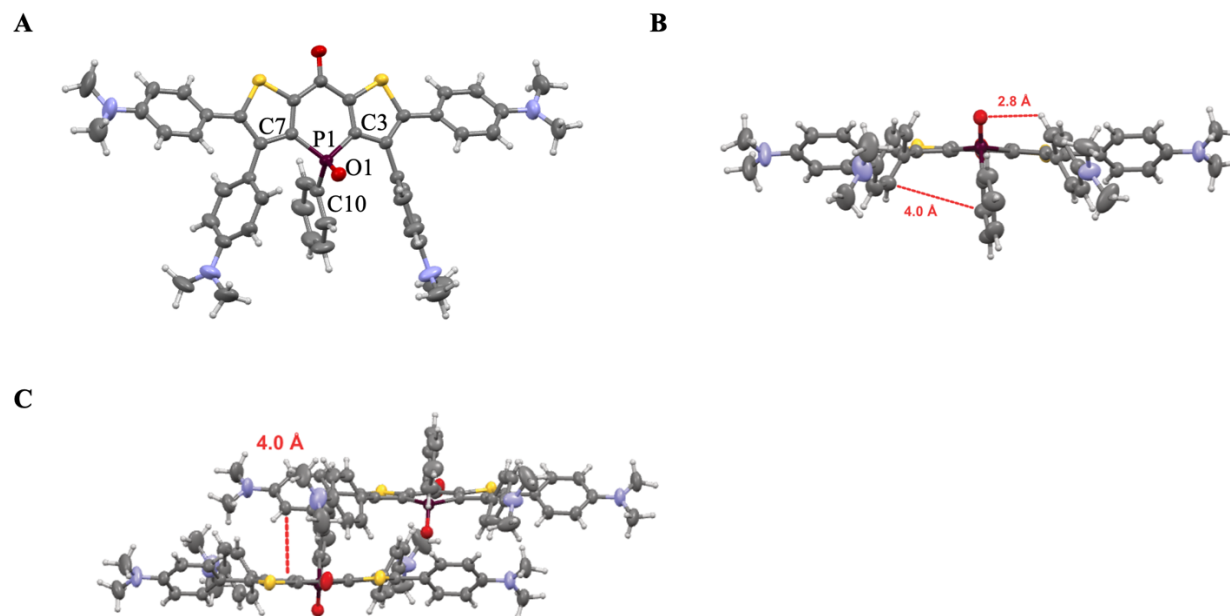


**Figure S4-31.** <sup>13</sup>C NMR spectrum zoomed (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound 4-9.

## SI.4.2 Solid-State Structures



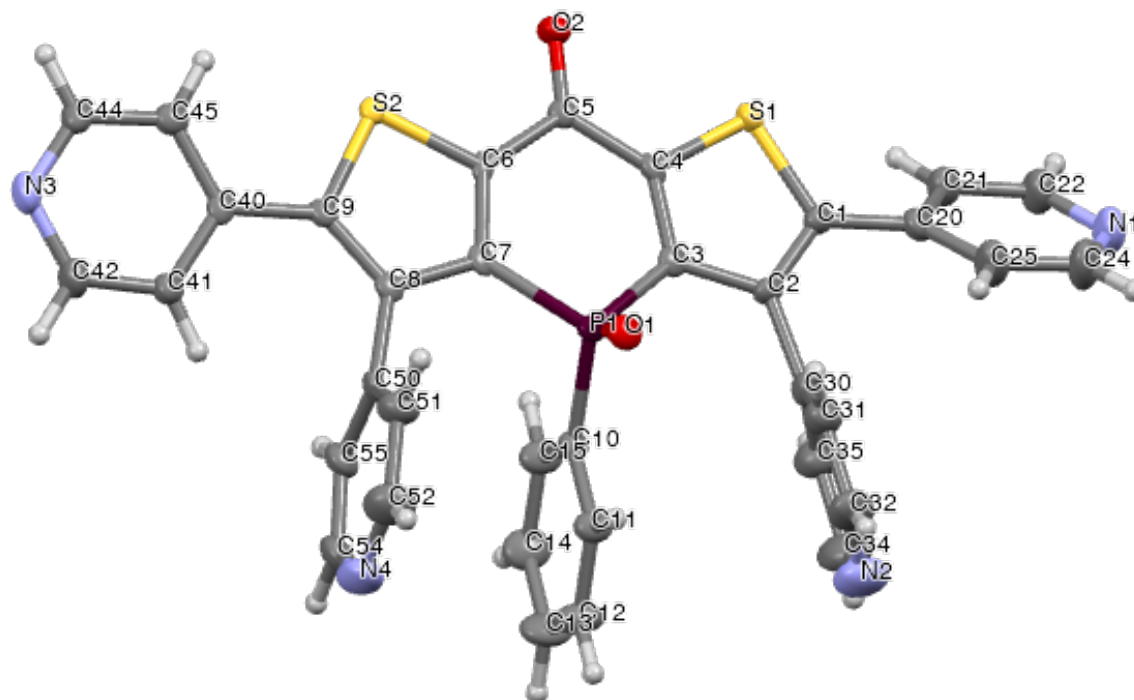
**Figure S4-32.** (A) Structure of 4-6 in the solid state, thermal ellipsoids at 50% probability; (B) intramolecular  $\pi$ -stacking and hydrogen bonding interactions; (C) intermolecular  $\pi$ -stacking; (D) bulk packing with some intermolecular hydrogen-bonding interactions shown as red dashes. Selected bond lengths: P1-C3 1.803(4) Å, P1-C7 1.798(5) Å, P1-C10 1.790(4) Å, P1-O1 1.487(3) Å. Selected bond Angles C7-P1-C3 100.9(2) °.



**Figure S4-33.** (A) Structure of **4-9** in the solid state, thermal ellipsoids at 50% probability; (B) intramolecular  $\pi$ -stacking and hydrogen bonding interactions; (C) intermolecular  $\pi$ -stacking. Selected bond lengths: P1-C3 1.810(2) Å, P1-C7 1.805(2) Å, P1-C10 1.788(2) Å, P1-O1 1.484(2) Å. Selected bond Angles C7-P1-C3 101.89(9) °.

**Table S4-1.** Crystal data and structure refinement for **4-6**.

Identification code	4_169_2_0m_a
Empirical formula	C <sub>36</sub> H <sub>23</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> PS <sub>2</sub>
Formula weight	709.620
Temperature/K	173.00
Crystal system	triclinic
Space group	P-1
a/Å	6.9933(4)
b/Å	14.6227(7)
c/Å	17.9962(8)
α/°	67.858(2)
β/°	86.207(2)
γ/°	79.715(2)
Volume/Å <sup>3</sup>	1677.20(15)
Z	2
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.405
μ/mm <sup>-1</sup>	0.405
F(000)	729.7
Crystal size/mm <sup>3</sup>	0.1 × 0.05 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.56 to 55.76
Index ranges	-9 ≤ h ≤ 9, -19 ≤ k ≤ 19, -24 ≤ l ≤ 24
Reflections collected	57014
Independent reflections	7998 [R <sub>int</sub> = 0.1132, R <sub>sigma</sub> = 0.0753]
Data/restraints/parameters	7998/0/397
Goodness-of-fit on F <sup>2</sup>	1.057
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0932, wR <sub>2</sub> = 0.1902
Final R indexes [all data]	R <sub>1</sub> = 0.1165, wR <sub>2</sub> = 0.2014
Largest diff. peak/hole / e Å <sup>-3</sup>	1.21/-0.94



**Figure S4-34.** Labelled solid-state structure of 4-6 shown as thermal ellipsoids (50% probability).

**Table S4-2.** Bond lengths for 4-6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.715(4)	C45	C44	1.372(6)
S1	C4	1.718(4)	C22	C21	1.371(6)
S2	C6	1.712(4)	C3	C2	1.415(6)
S2	C9	1.737(4)	C10	C11	1.392(6)
P1	O1	1.487(3)	C10	C15	1.398(6)
P1	C3	1.803(4)	C11	C12	1.377(6)
P1	C10	1.789(4)	C12	C13	1.393(7)
P1	C7	1.799(4)	C13	C14	1.381(7)
O2	C5	1.226(5)	C14	C15	1.380(7)
N3	C44	1.335(6)	C7	C8	1.430(5)
N3	C42	1.342(6)	C8	C50	1.491(6)
N1	C24	1.340(7)	C50	C51	1.371(6)
N1	C22	1.327(7)	C50	C55	1.389(6)
C24	C25	1.376(7)	C51	C52	1.397(7)
C25	C20	1.387(7)	C52	N4	1.335(8)
C20	C1	1.471(6)	N4	C54	1.327(7)
C20	C21	1.404(6)	C54	C55	1.379(7)
C1	C2	1.381(6)	C42	C41	1.381(6)
C4	C5	1.453(6)	C2	C30	1.491(6)
C4	C3	1.380(6)	C30	C31	1.386(7)
C5	C6	1.476(5)	C30	C35	1.389(7)
C6	C7	1.377(6)	C31	C32	1.377(7)
C9	C40	1.474(5)	C32	N2	1.327(8)
C9	C8	1.376(6)	N2	C34	1.299(8)
C40	C45	1.398(6)	C34	C35	1.389(8)
C40	C41	1.408(6)			

**Table S4-3.** Bond angles for 4-6.

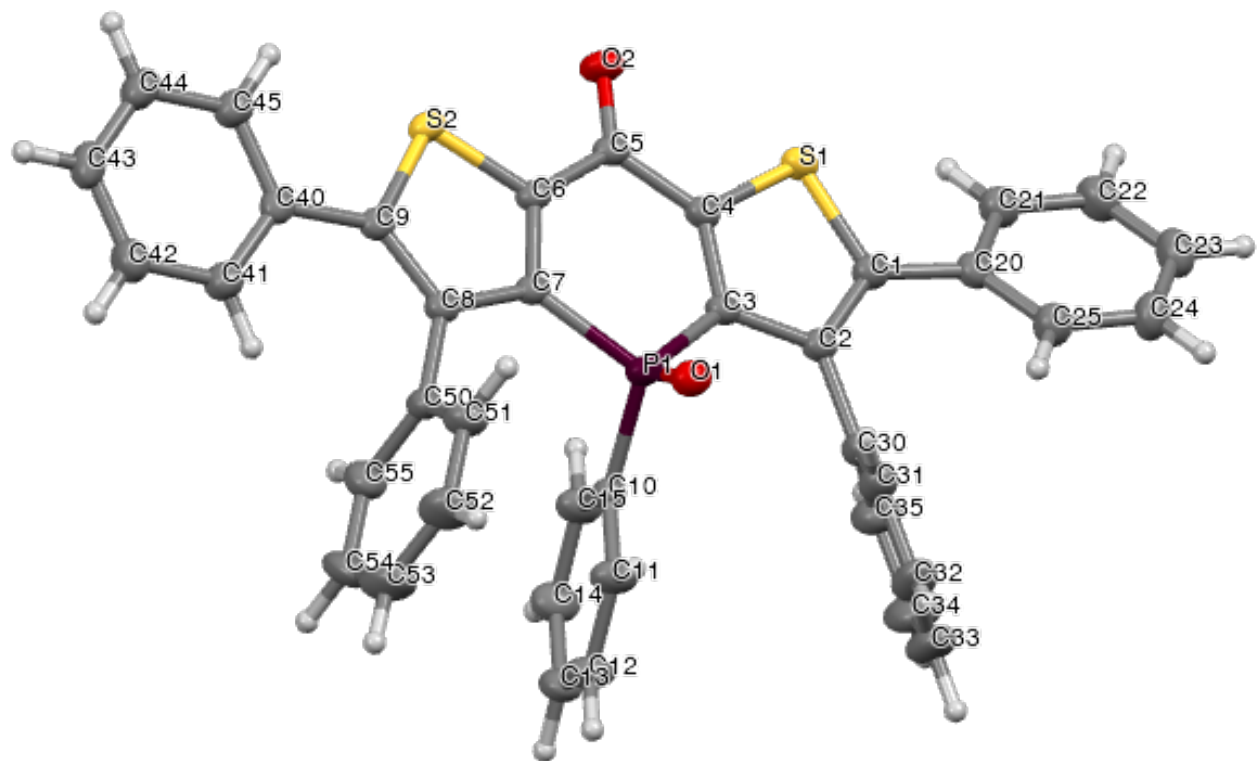
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	S1	C1	91.9(2)	C2	C3	P1	124.5(3)
C9	S2	C6	91.63(19)	C2	C3	C4	112.7(4)
C3	P1	O1	112.06(17)	C11	C10	P1	118.4(3)
C10	P1	O1	113.26(18)	C15	C10	P1	121.7(3)
C10	P1	C3	108.62(19)	C15	C10	C11	120.0(4)
C7	P1	O1	112.69(18)	C12	C11	C10	120.4(4)
C7	P1	C3	100.95(18)	C13	C12	C11	119.6(4)
C7	P1	C10	108.49(18)	C14	C13	C12	120.0(5)
C42	N3	C44	115.7(4)	C15	C14	C13	121.0(4)
C22	N1	C24	115.9(4)	C14	C15	C10	119.0(4)
C25	C24	N1	124.3(5)	C6	C7	P1	121.6(3)
C20	C25	C24	119.2(5)	C8	C7	P1	125.0(3)
C1	C20	C25	121.1(4)	C8	C7	C6	112.7(3)
C21	C20	C25	116.8(4)	C7	C8	C9	111.8(4)
C21	C20	C1	122.1(4)	C50	C8	C9	128.4(4)
C20	C1	S1	120.4(3)	C50	C8	C7	119.8(4)
C2	C1	S1	111.8(3)	C51	C50	C8	121.1(4)
C2	C1	C20	127.8(4)	C55	C50	C8	120.4(4)
C5	C4	S1	120.3(3)	C55	C50	C51	118.4(4)
C3	C4	S1	111.4(3)	C52	C51	C50	118.3(5)
C3	C4	C5	128.3(4)	N4	C52	C51	123.9(5)
C4	C5	O2	122.9(4)	C54	N4	C52	116.4(4)
C6	C5	O2	121.5(4)	C55	C54	N4	124.1(5)
C6	C5	C4	115.5(3)	C54	C55	C50	118.8(5)
C5	C6	S2	119.4(3)	C41	C42	N3	124.2(4)
C7	C6	S2	112.0(3)	C42	C41	C40	119.5(4)
C7	C6	C5	128.6(3)	C3	C2	C1	112.2(3)
C40	C9	S2	117.3(3)	C30	C2	C1	125.7(4)
C8	C9	S2	111.8(3)	C30	C2	C3	122.1(4)
C8	C9	C40	130.8(4)	C31	C30	C2	122.1(4)
C45	C40	C9	121.6(4)	C35	C30	C2	120.7(4)
C41	C40	C9	122.6(4)	C35	C30	C31	117.2(4)
C41	C40	C45	115.8(4)	C32	C31	C30	119.3(5)
C44	C45	C40	120.0(4)	N2	C32	C31	123.4(6)
C45	C44	N3	124.6(4)	C34	N2	C32	117.4(5)
C21	C22	N1	124.5(5)	C35	C34	N2	124.3(6)
C22	C21	C20	119.2(4)	C34	C35	C30	118.5(5)
C4	C3	P1	122.4(3)				

**Table S4-4. Torsion angles for 4-6.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C1	C20	C25	136.7(4)	C5	C6	S2	C9	178.8(3)
S1	C1	C20	C21	-40.8(4)	C5	C6	C7	C8	-178.9(4)
S1	C1	C2	C3	1.1(3)	C6	S2	C9	C40	178.9(2)
S1	C1	C2	C30	178.7(3)	C6	S2	C9	C8	1.1(2)
S1	C4	C5	O2	-0.5(4)	C6	C5	C4	C3	-5.6(4)
S1	C4	C5	C6	176.7(3)	C6	C7	P1	C3	-17.5(3)
S1	C4	C3	P1	172.06(15)	C6	C7	P1	C10	-131.5(3)
S1	C4	C3	C2	-0.4(3)	C6	C7	C8	C9	-0.4(4)
S2	C6	C5	O2	0.0(3)	C6	C7	C8	C50	178.6(3)
S2	C6	C5	C4	-177.2(3)	C9	S2	C6	C7	-1.3(2)
S2	C6	C7	P1	-169.29(15)	C9	C40	C45	C44	-179.3(4)
S2	C6	C7	C8	1.3(3)	C9	C40	C41	C42	178.7(4)
S2	C9	C40	C45	-10.4(4)	C9	C8	C50	C51	-96.7(5)
S2	C9	C40	C41	170.7(3)	C9	C8	C50	C55	87.1(5)
S2	C9	C8	C7	-0.6(3)	C40	C9	C8	C7	-178.0(4)
S2	C9	C8	C50	-179.5(3)	C40	C9	C8	C50	3.1(5)
P1	C3	C4	C5	-5.8(4)	C45	C40	C9	C8	166.9(4)
P1	C3	C2	C1	-172.7(4)	C45	C40	C41	C42	-0.3(4)
P1	C3	C2	C30	9.5(4)	C45	C44	N3	C42	-1.3(5)
P1	C10	C11	C12	179.6(4)	C44	N3	C42	C41	0.7(5)
P1	C10	C15	C14	-179.0(4)	C44	C45	C40	C41	-0.3(5)
P1	C7	C6	C5	10.5(4)	C21	C20	C1	C2	139.8(4)
P1	C7	C8	C9	169.7(3)	C3	P1	C10	C11	124.0(3)
P1	C7	C8	C50	-11.3(4)	C3	P1	C10	C15	-55.1(3)
O1	P1	C3	C4	-104.7(3)	C3	P1	C7	C8	173.2(2)
O1	P1	C3	C2	66.8(3)	C3	C2	C30	C31	-69.4(5)
O1	P1	C10	C11	-1.2(3)	C3	C2	C30	C35	106.6(5)
O1	P1	C10	C15	179.7(3)	C10	P1	C3	C2	-59.0(3)
O1	P1	C7	C6	102.2(3)	C10	P1	C7	C8	59.1(2)
O1	P1	C7	C8	-67.1(2)	C10	C11	C12	C13	0.3(5)
O2	C5	C4	C3	177.2(4)	C10	C15	C14	C13	-1.6(6)
O2	C5	C6	C7	-179.8(4)	C11	C10	P1	C7	-127.1(3)
N3	C44	C45	C40	1.2(5)	C11	C10	C15	C14	1.9(5)
N3	C42	C41	C40	0.1(6)	C11	C12	C13	C14	0.1(6)
N1	C24	C25	C20	-0.8(7)	C12	C11	C10	C15	-1.3(6)
N1	C22	C21	C20	1.0(7)	C12	C13	C14	C15	0.6(7)
C24	N1	C22	C21	-2.9(6)	C15	C10	P1	C7	53.8(4)
C24	C25	C20	C1	-178.8(5)	C7	P1	C3	C2	-173.0(3)
C24	C25	C20	C21	-1.2(7)	C7	C8	C50	C51	84.5(4)
C25	C24	N1	C22	2.8(8)	C7	C8	C50	C55	-91.7(4)
C25	C20	C1	C2	-42.8(6)	C8	C9	C40	C41	-12.0(5)
C25	C20	C21	C22	1.2(5)	C8	C50	C51	C52	-175.2(5)
C20	C1	S1	C4	179.4(4)	C8	C50	C55	C54	174.2(4)
C20	C1	C2	C3	-179.4(5)	C50	C51	C52	N4	0.4(6)
C20	C1	C2	C30	-1.8(6)	C50	C55	C54	N4	2.0(5)
C1	S1	C4	C5	178.9(2)	C51	C50	C55	C54	-2.2(5)
C1	S1	C4	C3	0.8(2)	C51	C52	N4	C54	-0.7(7)
C1	C20	C21	C22	178.7(5)	C52	C51	C50	C55	1.1(6)
C1	C2	C3	C4	-0.4(4)	C52	N4	C54	C55	-0.5(6)
C1	C2	C30	C31	113.1(5)	C2	C30	C31	C32	176.2(5)
C1	C2	C30	C35	-70.9(5)	C2	C30	C35	C34	-175.0(5)
C4	S1	C1	C2	-1.1(3)	C30	C31	C32	N2	-2.0(6)
C4	C5	C6	C7	3.0(4)	C30	C35	C34	N2	-0.8(7)
C4	C3	P1	C10	129.4(3)	C31	C30	C35	C34	1.2(5)
C4	C3	P1	C7	15.5(4)	C31	C32	N2	C34	2.4(7)
C4	C3	C2	C30	-178.2(3)	C32	C31	C30	C35	0.0(6)
C5	C4	C3	C2	-178.2(4)	C32	N2	C34	C35	-1.0(7)

**Table S4-5.** Crystal data and structure refinement for 4-7.

Identification code	4_152_a
Empirical formula	C <sub>39</sub> H <sub>25</sub> O <sub>2</sub> PS <sub>2</sub>
Formula weight	620.738
Temperature/K	173.00
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	17.6725(6)
b/Å	7.2277(2)
c/Å	24.9932(8)
α/°	90
β/°	108.884(1)
γ/°	90
Volume/Å <sup>3</sup>	3020.59(16)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.365
μ/mm <sup>-1</sup>	0.265
F(000)	1290.0
Crystal size/mm <sup>3</sup>	0.15 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.82 to 56.82
Index ranges	-23 ≤ h ≤ 23, -9 ≤ k ≤ 9, -33 ≤ l ≤ 33
Reflections collected	122877
Independent reflections	7577 [R <sub>int</sub> = 0.0498, R <sub>sigma</sub> = 0.0187]
Data/restraints/parameters	7577/0/397
Goodness-of-fit on F <sup>2</sup>	1.069
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0377, wR <sub>2</sub> = 0.0905
Final R indexes [all data]	R <sub>1</sub> = 0.0450, wR <sub>2</sub> = 0.0944
Largest diff. peak/hole / e Å <sup>-3</sup>	0.53/-0.38



**Figure S4-35.** Labelled solid-state structure of 4-7 shown as thermal ellipsoids (50% probability).

**Table S4-6.** Bond lengths for 4-7.

<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>	<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>
S1	C1	1.7210(15)	C20	C25	1.397(2)
S1	C4	1.7054(14)	C20	C21	1.397(2)
S2	C6	1.7061(14)	C23	C24	1.385(3)
S2	C9	1.7288(15)	C23	C22	1.386(3)
P1	O1	1.4869(11)	C10	C11	1.391(2)
P1	C3	1.8076(14)	C10	C15	1.390(2)
P1	C7	1.8072(14)	C11	C12	1.390(2)
P1	C10	1.7983(15)	C12	C13	1.381(3)
O2	C5	1.2301(17)	C13	C14	1.385(2)
C1	C2	1.393(2)	C14	C15	1.391(2)
C1	C20	1.475(2)	C25	C24	1.389(2)
C2	C3	1.429(2)	C30	C35	1.386(2)
C2	C30	1.493(2)	C30	C31	1.393(2)
C3	C4	1.3830(19)	C35	C34	1.393(3)
C4	C5	1.466(2)	C34	C33	1.372(3)
C5	C6	1.459(2)	C33	C32	1.374(3)
C6	C7	1.3836(19)	C32	C31	1.395(2)
C7	C8	1.427(2)	C50	C51	1.388(2)
C8	C9	1.3912(19)	C50	C55	1.394(2)
C8	C50	1.4922(19)	C51	C52	1.393(2)
C9	C40	1.479(2)	C52	C53	1.365(3)
C40	C41	1.397(2)	C53	C54	1.382(3)
C40	C45	1.406(2)	C54	C55	1.400(3)
C41	C42	1.390(2)	C44	C45	1.385(2)
C42	C43	1.378(2)	C21	C22	1.387(2)
C43	C44	1.387(3)			

**Table S4-7.** Bond angles for 4-7.

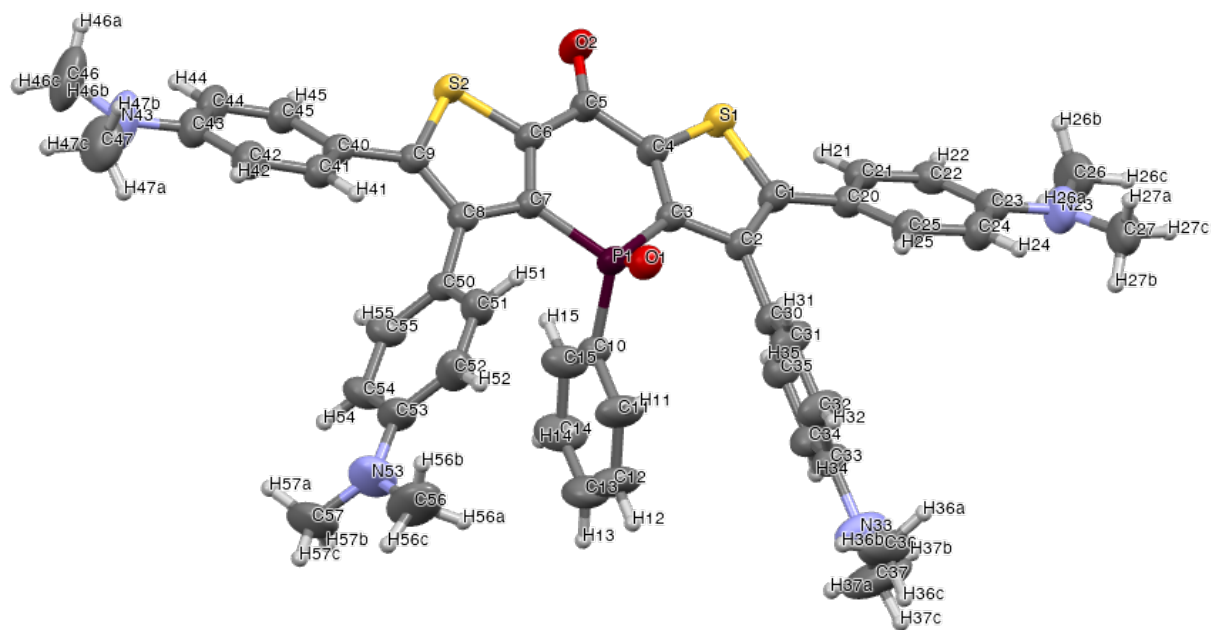
<b>Atom</b>	<b>Atom</b>	<b>Atom</b>	<b>Angle<sup>o</sup></b>	<b>Atom</b>	<b>Atom</b>	<b>Atom</b>	<b>Angle<sup>o</sup></b>
C4	S1	C1	92.13(7)	C42	C41	C40	120.94(15)
C9	S2	C6	92.30(7)	C43	C42	C41	120.87(16)
C3	P1	O1	112.51(6)	C44	C43	C42	119.08(15)
C7	P1	O1	112.64(6)	C25	C20	C1	121.26(14)
C7	P1	C3	101.68(6)	C21	C20	C1	120.31(14)
C10	P1	O1	112.58(6)	C21	C20	C25	118.25(14)
C10	P1	C3	107.45(7)	C22	C23	C24	119.53(16)
C10	P1	C7	109.34(6)	C11	C10	P1	118.26(12)
C2	C1	S1	111.52(11)	C15	C10	P1	122.08(11)
C20	C1	S1	117.16(11)	C15	C10	C11	119.65(14)
C20	C1	C2	131.03(13)	C12	C11	C10	119.97(15)
C3	C2	C1	111.93(12)	C13	C12	C11	120.11(15)
C30	C2	C1	124.32(13)	C14	C13	C12	120.33(15)
C30	C2	C3	123.71(13)	C15	C14	C13	119.75(16)
C2	C3	P1	125.93(11)	C14	C15	C10	120.19(15)
C4	C3	P1	121.44(11)	C24	C25	C20	120.65(15)
C4	C3	C2	111.98(12)	C25	C24	C23	120.42(16)
C3	C4	S1	112.41(11)	C35	C30	C2	119.79(15)
C5	C4	S1	118.71(10)	C31	C30	C2	121.03(15)
C5	C4	C3	128.88(13)	C31	C30	C35	119.18(15)
C4	C5	O2	121.71(13)	C34	C35	C30	120.30(19)
C6	C5	O2	122.37(13)	C33	C34	C35	120.1(2)
C6	C5	C4	115.92(12)	C32	C33	C34	120.33(17)
C5	C6	S2	119.30(10)	C31	C32	C33	120.19(19)
C7	C6	S2	112.11(11)	C32	C31	C30	119.91(18)
C7	C6	C5	128.59(13)	C51	C50	C8	119.99(13)
C6	C7	P1	121.88(11)	C55	C50	C8	120.28(15)
C8	C7	P1	125.28(10)	C55	C50	C51	119.73(15)
C8	C7	C6	112.28(12)	C52	C51	C50	120.24(17)
C9	C8	C7	112.19(12)	C53	C52	C51	120.1(2)
C50	C8	C7	121.70(12)	C54	C53	C52	120.40(18)
C50	C8	C9	126.11(13)	C55	C54	C53	120.38(18)
C8	C9	S2	111.11(11)	C54	C55	C50	119.10(19)
C40	C9	S2	117.23(10)	C45	C44	C43	120.57(15)
C40	C9	C8	131.66(13)	C44	C45	C40	121.04(16)
C41	C40	C9	122.89(13)	C22	C21	C20	120.94(15)
C45	C40	C9	119.62(14)	C21	C22	C23	120.20(16)
C45	C40	C41	117.50(14)				

**Table S4-8.** Torsion angles for 4-7.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C1	C2	C3	-1.25(12)	C4	C3	P1	C10	127.90(12)
S1	C1	C2	C30	176.53(10)	C4	C3	C2	C30	-176.01(12)
S1	C1	C20	C25	146.90(12)	C4	C5	C6	C7	-2.09(16)
S1	C1	C20	C21	-28.10(14)	C5	C6	S2	C9	179.52(12)
S1	C4	C3	P1	169.79(6)	C5	C6	C7	C8	-179.09(15)
S1	C4	C3	C2	-1.53(12)	C6	S2	C9	C8	-0.01(9)
S1	C4	C5	O2	3.16(13)	C6	S2	C9	C40	179.25(9)
S1	C4	C5	C6	-177.04(11)	C6	C7	P1	C10	-126.22(12)
S2	C6	C5	O2	-2.43(13)	C6	C7	C8	C9	-1.06(14)
S2	C6	C5	C4	177.77(11)	C6	C7	C8	C50	179.51(12)
S2	C6	C7	P1	-170.80(6)	C7	P1	C10	C11	-115.39(11)
S2	C6	C7	C8	1.05(11)	C7	P1	C10	C15	65.83(11)
S2	C9	C8	C7	0.60(11)	C7	C6	S2	C9	-0.60(11)
S2	C9	C8	C50	180.00(9)	C7	C8	C9	C40	-178.52(11)
S2	C9	C40	C41	172.66(11)	C7	C8	C50	C51	82.71(16)
S2	C9	C40	C45	-7.19(14)	C7	C8	C50	C55	-97.58(16)
P1	C3	C2	C1	-169.07(13)	C8	C7	P1	C10	63.03(13)
P1	C3	C2	C30	13.14(15)	C8	C9	C40	C41	-8.3(2)
P1	C3	C4	C5	-9.79(15)	C8	C9	C40	C45	171.90(17)
P1	C7	C6	C5	9.06(15)	C8	C50	C51	C52	178.69(16)
P1	C7	C8	C9	170.46(12)	C8	C50	C55	C54	-178.41(16)
P1	C7	C8	C50	-8.97(14)	C9	C8	C50	C51	-96.64(17)
P1	C10	C11	C12	-179.24(13)	C9	C8	C50	C55	83.07(17)
P1	C10	C15	C14	178.86(14)	C9	C40	C41	C42	-179.93(16)
O2	C5	C4	C3	-177.28(13)	C9	C40	C45	C44	179.46(14)
O2	C5	C6	C7	177.71(14)	C40	C9	C8	C50	0.9(2)
O1	P1	C3	C2	62.41(9)	C40	C41	C42	C43	0.6(2)
O1	P1	C3	C4	-107.64(10)	C40	C45	C44	C43	0.35(19)
O1	P1	C7	C6	107.83(10)	C41	C40	C45	C44	-0.39(17)
O1	P1	C7	C8	-62.92(9)	C41	C42	C43	C44	-0.7(2)
O1	P1	C10	C11	10.60(10)	C42	C41	C40	C45	-0.1(2)
O1	P1	C10	C15	-168.18(12)	C42	C43	C44	C45	0.2(2)
C1	S1	C4	C3	0.70(9)	C20	C1	C2	C30	-10.0(2)
C1	S1	C4	C5	-179.67(9)	C20	C25	C24	C23	-0.4(2)
C1	C2	C3	C4	1.79(14)	C20	C21	C22	C23	-0.31(19)
C1	C2	C30	C35	-61.28(18)	C10	C11	C12	C13	0.7(2)
C1	C2	C30	C31	118.79(16)	C10	C15	C14	C13	0.0(2)
C1	C20	C25	C24	-174.72(16)	C11	C10	C15	C14	0.09(18)
C1	C20	C21	C22	175.11(15)	C11	C12	C13	C14	-0.6(2)
C2	C1	S1	C4	0.34(12)	C12	C11	C10	C15	-0.4(2)
C2	C1	C20	C25	-26.3(2)	C12	C13	C14	C15	0.2(2)
C2	C1	C20	C21	158.75(17)	C25	C20	C21	C22	-0.05(18)
C2	C3	P1	C7	-176.85(12)	C25	C24	C23	C22	0.0(2)
C2	C3	P1	C10	-62.05(14)	C24	C23	C22	C21	0.3(2)
C2	C3	C4	C5	178.88(11)	C24	C25	C20	C21	0.4(2)
C2	C30	C35	C34	-179.81(17)	C30	C35	C34	C33	0.1(2)
C2	C30	C31	C32	179.88(15)	C30	C31	C32	C33	-0.3(2)
C3	P1	C7	C6	-12.82(9)	C35	C30	C31	C32	-0.05(19)
C3	P1	C7	C8	176.43(9)	C35	C34	C33	C32	-0.5(3)
C3	P1	C10	C11	135.03(11)	C34	C35	C30	C31	0.1(2)
C3	P1	C10	C15	-43.76(11)	C34	C33	C32	C31	0.6(3)
C3	C2	C1	C20	172.20(11)	C50	C51	C52	C53	-0.2(2)
C3	C2	C30	C35	116.25(17)	C50	C55	C54	C53	-0.3(2)
C3	C2	C30	C31	-63.68(17)	C51	C50	C55	C54	1.30(18)
C3	C4	C5	C6	2.52(18)	C51	C52	C53	C54	1.2(2)
C4	S1	C1	C20	-174.11(9)	C52	C51	C50	C55	-1.0(2)
C4	C3	P1	C7	13.10(13)	C52	C53	C54	C55	-0.9(2)

**Table S4-9.** Crystal data and structure refinement for **4-9**.

Identification code	4_186_a
Empirical formula	C <sub>51</sub> H <sub>51</sub> N <sub>6</sub> O <sub>2</sub> PS <sub>2</sub>
Formula weight	875.118
Temperature/K	173.00
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	14.3469(6)
b/Å	23.1144(10)
c/Å	13.9566(6)
α/°	90
β/°	95.734(2)
γ/°	90
Volume/Å <sup>3</sup>	4605.1(3)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.262
μ/mm <sup>-1</sup>	0.198
F(000)	1850.4
Crystal size/mm <sup>3</sup>	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.26 to 61.16
Index ranges	-20 ≤ h ≤ 20, -33 ≤ k ≤ 33, -19 ≤ l ≤ 19
Reflections collected	234864
Independent reflections	14100 [R <sub>int</sub> = 0.0898, R <sub>sigma</sub> = 0.0421]
Data/restraints/parameters	14100/6/589
Goodness-of-fit on F <sup>2</sup>	1.066
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0566, wR <sub>2</sub> = 0.1328
Final R indexes [all data]	R <sub>1</sub> = 0.1166, wR <sub>2</sub> = 0.1672
Largest diff. peak/hole / e Å <sup>-3</sup>	0.50/-0.54



**Figure S4-36.** Labelled solid-state structure of **4-9** shown as thermal ellipsoids (50% probability). Acetonitrile omitted for clarity.

**Table S4-10.** Bond lengths for 4-9.

<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>	<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>
P1	O1	1.4838(15)	C34	C33	1.386(3)
P1	C10	1.788(2)	C1	C20	1.472(3)
P1	C3	1.810(2)	N33	C33	1.395(3)
P1	C7	1.805(2)	N33	C36	1.424(4)
S2	C9	1.725(2)	N33	C37	1.403(4)
S2	C6	1.712(2)	C45	C44	1.377(3)
S1	C4	1.716(2)	C51	C52	1.390(3)
S1	C1	1.727(2)	C52	C53	1.397(4)
O2	C5	1.232(2)	C20	C25	1.396(3)
C2	C3	1.428(3)	C53	C54	1.392(4)
C2	C30	1.487(3)	C53	N53	1.393(3)
C2	C1	1.390(3)	C41	C42	1.380(3)
C10	C15	1.371(3)	C23	C24	1.404(3)
C10	C11	1.387(3)	C54	C55	1.380(3)
C3	C4	1.382(3)	C33	C32	1.392(3)
C30	C35	1.389(3)	C42	C43	1.404(3)
C30	C31	1.378(3)	N53	C57	1.434(4)
C50	C8	1.489(3)	N53	C56	1.435(4)
C50	C51	1.381(3)	C24	C25	1.380(3)
C50	C55	1.392(3)	C32	C31	1.394(3)
C40	C9	1.471(3)	C43	C44	1.396(4)
C40	C45	1.399(3)	C43	N43	1.373(3)
C40	C41	1.393(3)	C15	C14	1.384(4)
N23	C23	1.380(3)	N43	C47	1.413(4)
N23	C27	1.448(4)	N43	C46	1.435(4)
N23	C26	1.450(4)	C11	C12	1.383(4)
C9	C8	1.392(3)	C12	C13	1.358(4)
C5	C6	1.464(3)	C14	C13	1.369(4)
C5	C4	1.463(3)	N01C	C01F	1.134(4)
C7	C6	1.382(3)	C01F	C01I	1.453(5)
C7	C8	1.426(3)	C01H	C01O	1.440(11)
C21	C22	1.378(3)	C01H	C16	1.43(2)
C21	C20	1.395(3)	C01O	N01Q	1.129(10)
C22	C23	1.404(3)	N01R	C16	1.139(19)
C34	C35	1.377(3)			

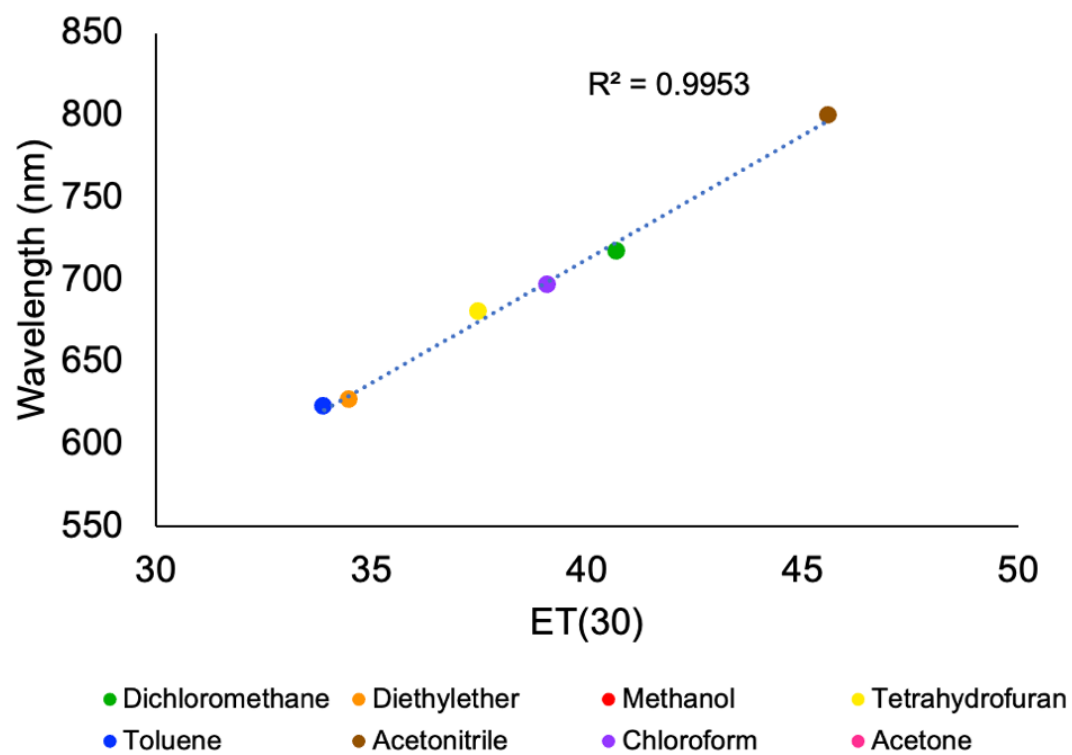
**Table S4-11. Bond angles for 4-9.**

Atom Atom Atom	Angle <sup>o</sup>	Atom Atom Atom	Angle <sup>o</sup>
C10 P1 O1	113.17(9)	C2 C1 S1	111.75(15)
C3 P1 O1	113.49(9)	C20 C1 S1	119.06(15)
C3 P1 C10	104.77(10)	C20 C1 C2	129.15(18)
C7 P1 O1	112.17(9)	C36 N33 C33	119.7(2)
C7 P1 C10	110.56(10)	C37 N33 C33	119.8(2)
C7 P1 C3	101.90(9)	C37 N33 C36	119.8(3)
C6 S2 C9	91.74(10)	C44 C45 C40	122.1(2)
C1 S1 C4	91.71(10)	C52 C51 C50	121.2(2)
C30 C2 C3	124.71(18)	C53 C52 C51	121.2(2)
C1 C2 C3	111.98(17)	C1 C20 C21	121.71(19)
C1 C2 C30	123.02(18)	C25 C20 C21	117.1(2)
C15 C10 P1	122.60(16)	C25 C20 C1	121.09(19)
C11 C10 P1	117.93(18)	C34 C35 C30	121.8(2)
C11 C10 C15	119.0(2)	C54 C53 C52	117.3(2)
C2 C3 P1	125.38(14)	N53 C53 C52	121.8(3)
C4 C3 P1	122.41(15)	N53 C53 C54	121.0(3)
C4 C3 C2	112.19(18)	C42 C41 C40	121.1(2)
C35 C30 C2	119.47(19)	C22 C23 N23	121.6(2)
C31 C30 C2	123.08(19)	C24 C23 N23	121.2(2)
C31 C30 C35	117.5(2)	C24 C23 C22	117.2(2)
C51 C50 C8	122.85(19)	C55 C54 C53	121.1(2)
C55 C50 C8	119.5(2)	N33 C33 C34	121.1(2)
C55 C50 C51	117.6(2)	C32 C33 C34	117.6(2)
C45 C40 C9	120.5(2)	C32 C33 N33	121.2(2)
C41 C40 C9	122.16(19)	C54 C55 C50	121.6(2)
C41 C40 C45	117.3(2)	C43 C42 C41	121.3(2)
C27 N23 C23	120.2(2)	C57 N53 C53	120.5(3)
C26 N23 C23	119.6(2)	C56 N53 C53	120.0(3)
C26 N23 C27	119.1(2)	C56 N53 C57	118.9(3)
C40 C9 S2	118.19(15)	C25 C24 C23	121.2(2)
C8 C9 S2	111.88(15)	C31 C32 C33	120.9(2)
C8 C9 C40	129.92(18)	C44 C43 C42	117.7(2)
C6 C5 O2	121.93(19)	N43 C43 C42	121.6(2)
C4 C5 O2	121.78(19)	N43 C43 C44	120.6(2)
C4 C5 C6	116.29(17)	C14 C15 C10	120.2(2)
C6 C7 P1	121.28(15)	C24 C25 C20	121.5(2)
C8 C7 P1	125.98(15)	C32 C31 C30	121.2(2)
C8 C7 C6	112.41(17)	C43 C44 C45	120.5(2)
C5 C6 S2	118.68(15)	C47 N43 C43	121.6(3)
C7 C6 S2	112.27(16)	C46 N43 C43	121.5(3)
C7 C6 C5	128.97(18)	C46 N43 C47	116.3(3)
C3 C4 S1	112.34(15)	C12 C11 C10	120.2(3)
C5 C4 S1	119.66(15)	C13 C12 C11	120.2(3)
C5 C4 C3	127.99(19)	C13 C14 C15	120.3(3)
C20 C21 C22	122.0(2)	C14 C13 C12	120.1(3)
C23 C22 C21	121.0(2)	C01I C01F N01C	178.3(4)
C9 C8 C50	122.48(18)	C16 C01HC01O	25.6
C7 C8 C50	125.65(17)	N01QC01OC01H	178.4(10)
C7 C8 C9	111.67(18)	N01RC16 C01H	177(2)
C33 C34 C35	121.0(2)		

**Table S4-12. Torsion angles for 4-9.**

A	B	C	D	Angle <sup>o</sup>	A	B	C	D	Angle <sup>o</sup>
P1	C10	C15	C14	171.5(2)	C9	S2	C6	C7	-1.43(14)
P1	C10	C11	C12	-171.9(2)	C9	C40	C45	C44	-179.3(2)
P1	C3	C2	C30	9.3(2)	C9	C40	C41	C42	178.5(2)
P1	C3	C2	C1	-176.80(19)	C9	C8	C50	C51	-114.3(2)
P1	C3	C4	S1	177.92(14)	C9	C8	C50	C55	61.7(2)
P1	C3	C4	C5	-2.0(2)	C9	C8	C7	C6	-0.3(2)
P1	C7	C6	S2	-172.55(14)	C5	C6	C7	C8	-175.4(2)
P1	C7	C6	C5	10.9(2)	C5	C4	S1	C1	179.51(19)
P1	C7	C8	C50	-11.9(2)	C7	P1	C10	C15	54.09(16)
P1	C7	C8	C9	173.16(19)	C7	P1	C10	C11	-133.82(18)
S2	C9	C40	C45	37.8(2)	C7	P1	C3	C4	8.18(14)
S2	C9	C40	C41	-140.27(17)	C7	C6	C5	C4	-2.5(3)
S2	C9	C8	C50	-175.96(14)	C7	C8	C50	C51	71.2(2)
S2	C9	C8	C7	-0.79(18)	C7	C8	C50	C55	-112.7(2)
S2	C6	C5	O2	0.5(2)	C6	S2	C9	C8	1.26(14)
S2	C6	C5	C4	-178.95(17)	C4	S1	C1	C20	-176.48(14)
S2	C6	C7	C8	1.24(18)	C4	C3	C2	C1	1.7(2)
S1	C4	C3	C2	-0.58(18)	C21	C22	C23	C24	-0.4(3)
S1	C4	C5	O2	-1.8(2)	C21	C20	C25	C24	-0.8(3)
S1	C4	C5	C6	177.71(17)	C22	C21	C20	C1	177.9(2)
S1	C1	C2	C3	-1.99(18)	C22	C21	C20	C25	1.6(3)
S1	C1	C2	C30	172.05(14)	C22	C23	N23	C27	175.2(2)
S1	C1	C20	C21	-35.2(2)	C22	C23	N23	C26	7.2(3)
S1	C1	C20	C25	140.91(18)	C22	C23	C24	C25	1.2(3)
O1	P1	C10	C15	-179.12(17)	C8	C50	C51	C52	176.5(2)
O1	P1	C10	C11	-7.03(16)	C8	C50	C55	C54	-176.4(2)
O1	P1	C3	C2	65.67(13)	C8	C9	C40	C45	-142.4(2)
O1	P1	C3	C4	-112.63(15)	C8	C9	C40	C41	39.5(3)
O1	P1	C7	C6	109.70(15)	C34	C35	C30	C31	-0.8(3)
O1	P1	C7	C8	-63.20(13)	C34	C33	N33	C36	176.6(3)
O2	C5	C6	C7	176.9(2)	C34	C33	N33	C37	6.4(4)
O2	C5	C4	C3	178.2(2)	C34	C33	C32	C31	-0.6(3)
C2	C3	P1	C10	-58.3(2)	C1	C2	C30	C35	-59.0(2)
C2	C3	P1	C7	-173.52(18)	C1	C2	C30	C31	121.3(2)
C2	C3	C4	C5	179.45(18)	C1	C20	C25	C24	-177.1(2)
C2	C30	C35	C34	179.4(2)	N33	C33	C34	C35	-179.2(2)
C2	C30	C31	C32	-179.2(2)	N33	C33	C32	C31	179.5(3)
C2	C1	S1	C4	1.41(18)	C45	C40	C41	C42	0.4(3)
C2	C1	C20	C21	147.3(2)	C45	C44	C43	C42	1.0(3)
C2	C1	C20	C25	-36.6(3)	C45	C44	C43	N43	-177.4(3)
C10	P1	C3	C4	123.44(15)	C51	C50	C55	C54	-0.1(3)
C10	P1	C7	C6	-122.95(15)	C51	C52	C53	C54	0.9(3)
C10	P1	C7	C8	64.15(13)	C51	C52	C53	N53	-178.2(3)
C10	C15	C14	C13	0.2(3)	C52	C51	C50	C55	0.4(3)
C10	C11	C12	C13	-0.2(3)	C52	C53	C54	C55	-0.7(3)
C3	P1	C10	C15	-54.98(16)	C52	C53	N53	C57	179.3(3)
C3	P1	C10	C11	117.11(18)	C52	C53	N53	C56	-10.2(3)
C3	P1	C7	C6	-12.02(14)	C20	C21	C22	C23	-1.0(3)
C3	P1	C7	C8	175.08(14)	C20	C25	C24	C23	-0.6(3)
C3	C2	C30	C35	114.3(2)	C35	C30	C31	C32	1.1(3)
C3	C2	C30	C31	-65.4(3)	C35	C34	C33	C32	0.9(3)
C3	C2	C1	C20	175.64(17)	C41	C40	C45	C44	-1.2(3)
C3	C4	S1	C1	-0.46(18)	C41	C42	C43	C44	-1.7(3)
C3	C4	C5	C6	-2.3(3)	C41	C42	C43	N43	176.6(3)
C30	C2	C3	C4	-172.3(2)	C54	C53	N53	C57	0.2(3)
C30	C2	C1	C20	-10.3(3)	C54	C53	N53	C56	170.7(3)
C30	C35	C34	C33	-0.2(3)	C55	C54	C53	N53	178.5(3)
C30	C31	C32	C33	-0.4(3)	C42	C43	N43	C47	0.8(3)
C50	C8	C9	C40	4.2(3)	C42	C43	N43	C46	171.6(3)
C50	C8	C7	C6	174.7(2)	C24	C23	N23	C27	-5.5(3)
C50	C51	C52	C53	-0.8(3)	C24	C23	N23	C26	-173.5(3)
C50	C55	C54	C53	0.3(3)	C32	C33	N33	C36	-3.5(3)
C40	C9	S2	C6	-178.89(18)	C32	C33	N33	C37	-173.7(3)
C40	C9	C8	C7	179.4(2)	C15	C10	C11	C12	0.5(3)
C40	C45	C44	C43	0.5(3)	C15	C14	C13	C12	0.1(4)
C40	C41	C42	C43	1.1(3)	C44	C43	N43	C47	179.1(3)
N23	C23	C22	C21	178.9(2)	C44	C43	N43	C46	-10.1(4)
N23	C23	C24	C25	-178.1(2)	C11	C10	C15	C14	-0.5(3)
C9	S2	C6	C5	175.56(14)	C11	C12	C13	C14	-0.1(4)

### SI.4.3 $E_T(30)$ Values vs. Emission Maxima



**Figure S4-37.**  $E_T(30)$  values vs emission maxima for **4-9** after removing outliers acetone and methanol.  $R^2$  value changes to 0.99.

#### SI.4.4 Density-Functional Theory Calculation Coordinates (X,Y, Z)

4-7

C	-1.45281600	-0.65422900	-0.08671700
C	1.21074000	-2.03329400	0.08429400
C	-1.28355100	-2.00555200	0.16992900
C	-0.03878300	-2.76857300	0.29323100
P	-0.02788400	0.44709800	-0.40651800
C	3.61670700	-1.41884400	-0.10211700
C	2.77756400	-0.32829100	-0.32413100
C	1.39216800	-0.69331300	-0.21995000
C	-3.68435000	-1.36057000	0.00975000
C	-2.83392800	-0.27420700	-0.18189800
S	2.72074900	-2.87299000	0.23038800
S	-2.80195200	-2.82987600	0.31571100
O	-0.04336300	-3.97929400	0.55643100
C	0.09202200	1.59924700	1.00402500
C	0.24662600	2.96606400	0.73819500
C	0.04373800	1.14597400	2.33186300
C	0.35090800	3.87510300	1.79479700
H	0.27951400	3.31122600	-0.29057200
C	0.14664000	2.05699700	3.38468700
H	-0.07815000	0.08766600	2.55038800
C	0.30048100	3.42251400	3.11646200

H	0.47041200	4.93447600	1.58405100
H	0.10597100	1.70246900	4.41108400
H	0.38038100	4.13052600	3.93718100
O	-0.09938200	1.14185000	-1.74453300
C	-5.16061400	-1.40902600	-0.01031100
C	-5.92692200	-0.44899100	0.67677500
C	-5.82903000	-2.44013000	-0.69778000
C	-7.32085200	-0.51663700	0.66853100
H	-5.42958100	0.34229500	1.22759300
C	-7.22365700	-2.50478800	-0.70358900
H	-5.25512200	-3.18222600	-1.24643200
C	-7.97488700	-1.54267200	-0.02171200
H	-7.89622000	0.23099500	1.20807700
H	-7.72147200	-3.30408200	-1.24599700
H	-9.06043000	-1.59227600	-0.02682200
C	-3.33011600	1.09209500	-0.52625900
C	-3.87135800	1.33860600	-1.79843100
C	-3.29436700	2.13712800	0.40933300
C	-4.36172000	2.60372400	-2.12928100
H	-3.90213200	0.53617900	-2.53072800
C	-3.78744500	3.40284000	0.07930200
H	-2.88853200	1.95824300	1.40099200
C	-4.32163900	3.64002400	-1.19052900

H	-4.77377300	2.77926400	-3.11964400
H	-3.75505300	4.20113500	0.81631000
H	-4.70427000	4.62452800	-1.44701600
C	5.09150600	-1.48959700	-0.14672000
C	5.80877000	-0.90590400	-1.20780300
C	5.80457400	-2.17517700	0.85477800
C	7.19994700	-1.00087800	-1.25910900
H	5.27356100	-0.38950200	-1.99810700
C	7.19683100	-2.26750400	0.80063600
H	5.26864700	-2.62150900	1.68842900
C	7.89965900	-1.67978800	-0.25554400
H	7.73733000	-0.54860100	-2.08841600
H	7.73073600	-2.79486700	1.58662000
H	8.98315400	-1.75147100	-0.29791600
C	3.29223600	1.05105400	-0.56507500
C	4.06327000	1.69079700	0.42059700
C	3.04667900	1.72150500	-1.77407200
C	4.57626500	2.97124000	0.20372600
H	4.25696600	1.18278200	1.36159300
C	3.56354200	3.00174000	-1.99177800
H	2.44742200	1.24215000	-2.54099000
C	4.32955500	3.63028300	-1.00526700
H	5.16689000	3.45308500	0.97868800

H 3.36666300 3.50640900 -2.93419500

H 4.73020300 4.62620800 -1.17619300

**4-8**

C -1.42436700 -0.88489700 0.10282600

C 1.24677500 -2.25556400 0.20799500

C -1.24656300 -2.25566400 0.20799700

C 0.00013900 -3.01898000 0.28272700

P 0.00002500 0.26401000 0.04878600

C 3.64945600 -1.61583100 0.00052700

C 2.80398300 -0.50659200 -0.01531600

C 1.42451800 -0.88478400 0.10279700

C -3.64925800 -1.61605100 0.00054000

C -2.80385200 -0.50676300 -0.01528300

S 2.76008300 -3.10380100 0.18020400

S -2.75983400 -3.10396400 0.18031800

O 0.00019000 -4.25558100 0.38008200

C -0.00009900 1.14002900 1.65215500

C 0.00006600 2.54082000 1.64649500

C -0.00046000 0.44589700 2.87218600

C -0.00014000 3.24408800 2.85432700

H 0.00031700 3.07132700 0.69931500

C -0.00066200 1.15120800 4.07727000

H	-0.00057400	-0.64146800	2.88884600
C	-0.00051300	2.55134600	4.06877100
H	-0.00001900	4.33081300	2.84496200
H	-0.00095000	0.61002500	5.01956900
H	-0.00069700	3.09917800	5.00746200
O	-0.00000900	1.19789400	-1.13675200
C	-5.11755800	-1.67707400	-0.10887100
C	-5.94803300	-0.78083100	0.59749800
C	-5.73821200	-2.65822600	-0.90015900
C	-7.33075500	-0.86340800	0.50894300
H	-5.50471800	-0.02212900	1.23311200
C	-7.12854900	-2.75084100	-0.99945100
H	-5.13016700	-3.35535000	-1.47062900
C	-7.93437600	-1.84823900	-0.29211400
H	-7.96370500	-0.17511800	1.06148200
H	-7.56277000	-3.51798300	-1.62992300
C	-3.30063000	0.88591600	-0.21893500
C	-3.74993100	1.29742100	-1.47954600
C	-3.36525000	1.80815000	0.83998200
C	-4.24513800	2.58720800	-1.69561500
H	-3.71055000	0.60300700	-2.31471500
C	-3.85840600	3.09408800	0.64311500
H	-3.03485100	1.51428000	1.83226900

C	-4.30007100	3.49360400	-0.62807100
H	-4.57753600	2.86700000	-2.68875000
H	-3.90819500	3.80285000	1.46480600
C	5.11774100	-1.67685500	-0.10894000
C	5.73838500	-2.65826300	-0.89992000
C	5.94825900	-0.78036800	0.59709800
C	7.12872000	-2.75092900	-0.99920700
H	5.13034400	-3.35555100	-1.47019300
C	7.33097000	-0.86299300	0.50854300
H	5.50497600	-0.02143300	1.23244900
C	7.93457500	-1.84812300	-0.29217200
H	7.56290800	-3.51825900	-1.62947600
H	7.96394400	-0.17451700	1.06082300
C	3.30064000	0.88613100	-0.21899200
C	3.36531000	1.80828500	0.84000000
C	3.74973700	1.29777700	-1.47962300
C	3.85835400	3.09427300	0.64319600
H	3.03504000	1.51427600	1.83228900
C	4.24481900	2.58762400	-1.69563200
H	3.71029000	0.60344000	-2.31485500
C	4.29984100	3.49392300	-0.62801400
H	3.90819100	3.80296900	1.46494000
H	4.57701900	2.86755300	-2.68879500

O	-9.29672600	-1.84561900	-0.31545400
O	9.29691800	-1.84557900	-0.31547500
O	4.76407300	4.77539900	-0.72365600
O	-4.76445000	4.77502600	-0.72374400
C	-9.97214500	-2.83067200	-1.10197100
H	-11.03644300	-2.63810900	-0.96295900
H	-9.71591500	-2.73060300	-2.16314200
H	-9.73273700	-3.84261800	-0.75501200
C	-5.22356500	5.24288700	-1.99325300
H	-5.53694500	6.27495200	-1.83102200
H	-4.41935200	5.21601900	-2.73807600
H	-6.07664400	4.65163900	-2.34694700
C	5.22345500	5.24322600	-1.99308000
H	5.53701900	6.27522100	-1.83076200
H	6.07646100	4.65182000	-2.34668400
H	4.41933900	5.21655500	-2.73801700
C	9.97230200	-2.83111700	-1.10140800
H	9.71622800	-2.73151500	-2.16266300
H	11.03660900	-2.63865300	-0.96233500
H	9.73270000	-3.84286500	-0.75400500

**4-9**

C	-1.42607000	-1.05765000	0.07257600
C	1.24464100	-2.42844400	0.18531900
C	-1.24485200	-2.42822900	0.18517900
C	-0.00016200	-3.19035400	0.25769300
P	0.00000900	0.08885400	0.00761600
C	3.65422200	-1.78849100	-0.02332000
C	2.80415000	-0.67831200	-0.04566300
C	1.42590600	-1.05785500	0.07275000
C	-3.65437600	-1.78820700	-0.02369800
C	-2.80430000	-0.67805100	-0.04596100
S	2.75958600	-3.27672600	0.16476600
S	-2.75986100	-3.27645200	0.16450900
O	-0.00030200	-4.42995500	0.35424200
C	-0.00002600	0.97616000	1.60644900
C	0.00000600	2.37660100	1.59301800
C	-0.00015300	0.28990800	2.83065800
C	-0.00007800	3.08724000	2.79657200
H	0.00009100	2.90058500	0.64226000
C	-0.00023300	1.00203700	4.03192700
H	-0.00016800	-0.79739000	2.85309600
C	-0.00020000	2.40209500	4.01543900
H	-0.00005800	4.17403300	2.78063200

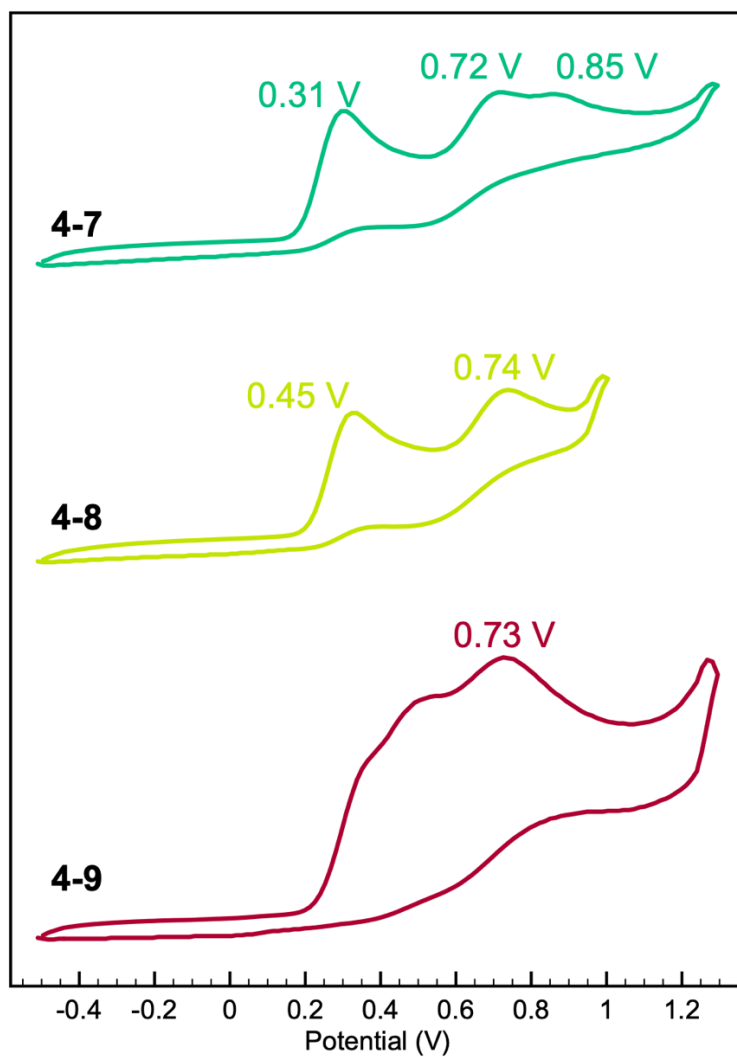
H	-0.00032700	0.46619300	4.97736700
H	-0.00026700	2.95553000	4.95094700
O	0.00012200	1.01747000	-1.18274700
C	-5.11751800	-1.85466900	-0.12896000
C	-5.95812400	-0.90842200	0.49138500
C	-5.74966800	-2.90413400	-0.82649000
C	-7.34221200	-0.99653800	0.41629100
H	-5.52196200	-0.09583500	1.06215600
C	-7.13256800	-3.00403900	-0.91538300
H	-5.14645600	-3.65463900	-1.33162400
C	-7.97823700	-2.04257700	-0.30320500
H	-7.93223700	-0.24668400	0.92974800
H	-7.55414400	-3.83143600	-1.47349800
C	-3.29614400	0.71359900	-0.26012600
C	-3.76499000	1.11909500	-1.51900300
C	-3.35753700	1.65160000	0.77971900
C	-4.26026600	2.40125300	-1.74023100
H	-3.74450800	0.41591400	-2.34817300
C	-3.85428400	2.93838200	0.57908300
H	-3.02574300	1.37213600	1.77630400
C	-4.30664100	3.35890300	-0.69589200
H	-4.60827500	2.65394200	-2.73478600
H	-3.88407500	3.61517800	1.42481700

C	5.11733600	-1.85510300	-0.12845300
C	5.74948300	-2.90480100	-0.82567700
C	5.95796700	-0.90865000	0.49159900
C	7.13237000	-3.00484400	-0.91442500
H	5.14625400	-3.65530500	-1.33079500
C	7.34204100	-0.99686000	0.41668400
H	5.52179200	-0.09575600	1.06192300
C	7.97803800	-2.04339400	-0.30215600
H	7.55401400	-3.83224800	-1.47249500
H	7.93214100	-0.24673400	0.92968000
C	3.29616200	0.71327300	-0.25986300
C	3.35782700	1.65126400	0.77997300
C	3.76494500	1.11868300	-1.51878700
C	3.85476900	2.93795500	0.57928500
H	3.02610900	1.37182700	1.77658200
C	4.26043300	2.40076000	-1.74006400
H	3.74424900	0.41551300	-2.34795900
C	4.30707800	3.35839400	-0.69573400
H	3.88473600	3.61476500	1.42500400
H	4.60835300	2.65337400	-2.73466700
N	9.35015200	-2.11836000	-0.40615400
C	9.96905900	-3.29227400	-1.00941500
H	11.05137900	-3.15755000	-1.02014700

H	9.74070300	-4.21481500	-0.45418200
H	9.63860700	-3.42467600	-2.04657700
C	10.18760500	-1.19967800	0.35494100
H	11.23409900	-1.38953100	0.11299100
H	9.96812700	-0.15751900	0.09440600
H	10.05672200	-1.31883800	1.44146600
N	4.76285500	4.65093200	-0.91537400
N	-4.76223600	4.65148900	-0.91552600
N	-9.35050700	-2.11698200	-0.40810100
C	5.44303400	4.96215800	-2.16638700
H	5.69933400	6.02301400	-2.17573100
H	6.36873000	4.37908900	-2.30197300
H	4.78958100	4.77283200	-3.02491200
C	5.03432300	5.51237700	0.22829500
H	5.82027600	5.10707900	0.88668900
H	5.35839600	6.48985700	-0.13319300
H	4.13023700	5.66496600	0.82793400
C	-5.44230000	4.96286300	-2.16655000
H	-6.36817000	4.38006300	-2.30212700
H	-5.69829200	6.02379300	-2.17594700
H	-4.78890000	4.77330400	-3.02506300
C	-5.03331000	5.51309300	0.22811200
H	-5.35734600	6.49057600	-0.13340100

H	-5.81915800	5.10797800	0.88674000
H	-4.12905400	5.66562200	0.82751800
C	-9.96928100	-3.29279000	-1.00792000
H	-9.74300600	-4.21352100	-0.44873100
H	-11.05144400	-3.15692800	-1.02157400
H	-9.63686300	-3.42931100	-2.04382800
C	-10.18785800	-1.20123300	0.35673100
H	-9.96719100	-0.15818800	0.10116500
H	-11.23427800	-1.38889400	0.11267100
H	-10.05820600	-1.32554200	1.44288200

#### SI.4.5 Cyclic Voltammetry – Oxidation Regime



**Figure S4-38.** Cyclic voltammograms for oxidations of **4-7**, **4-8**, and **4-9**. Potentials are referenced to  $\text{Fc}/\text{Fc}^+$ . Scan rate 100 mV/s with tetrabutylammonium hexafluorophosphate as supporting electrolyte. All experiments performed in dry  $\text{CH}_3\text{CN}$  under argon.

## SL4.6 Mass Spectrometry

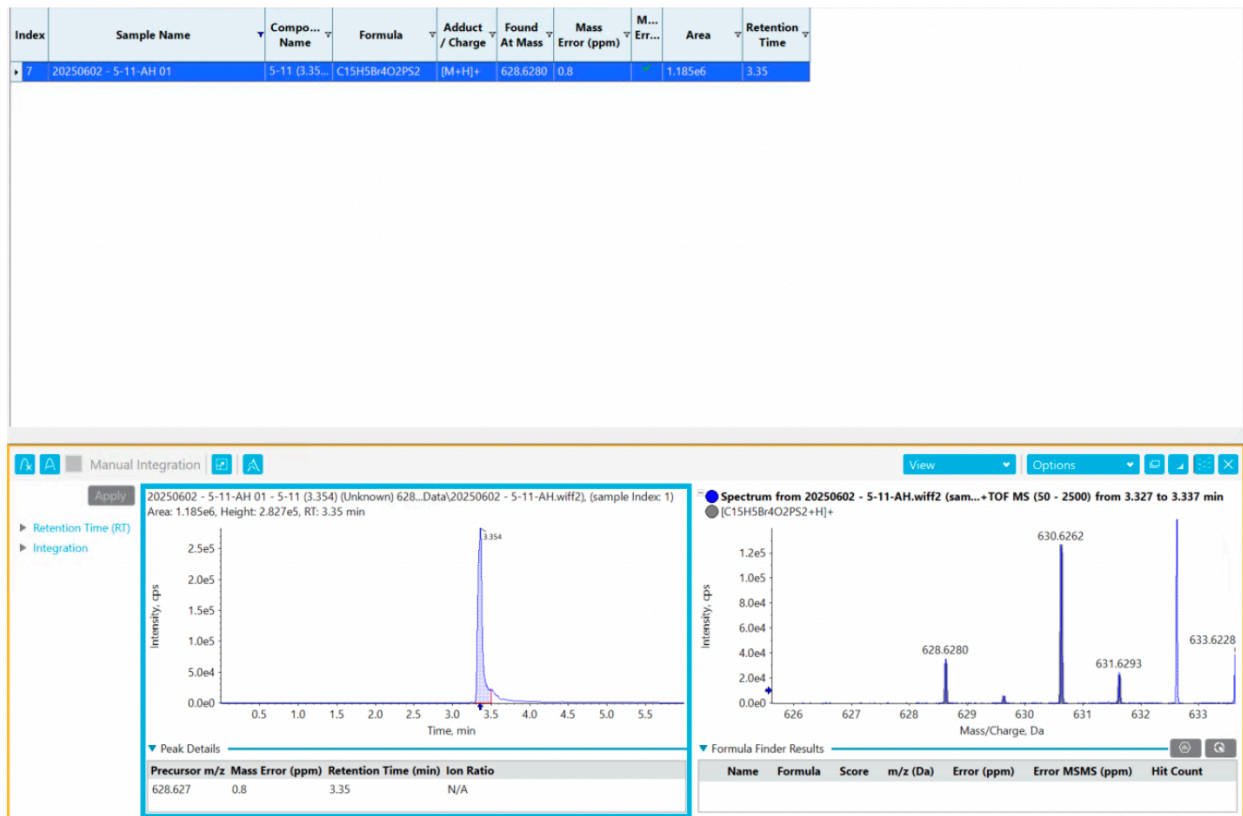


Figure S4-39. Mass spectrometry result for compound 4-5.

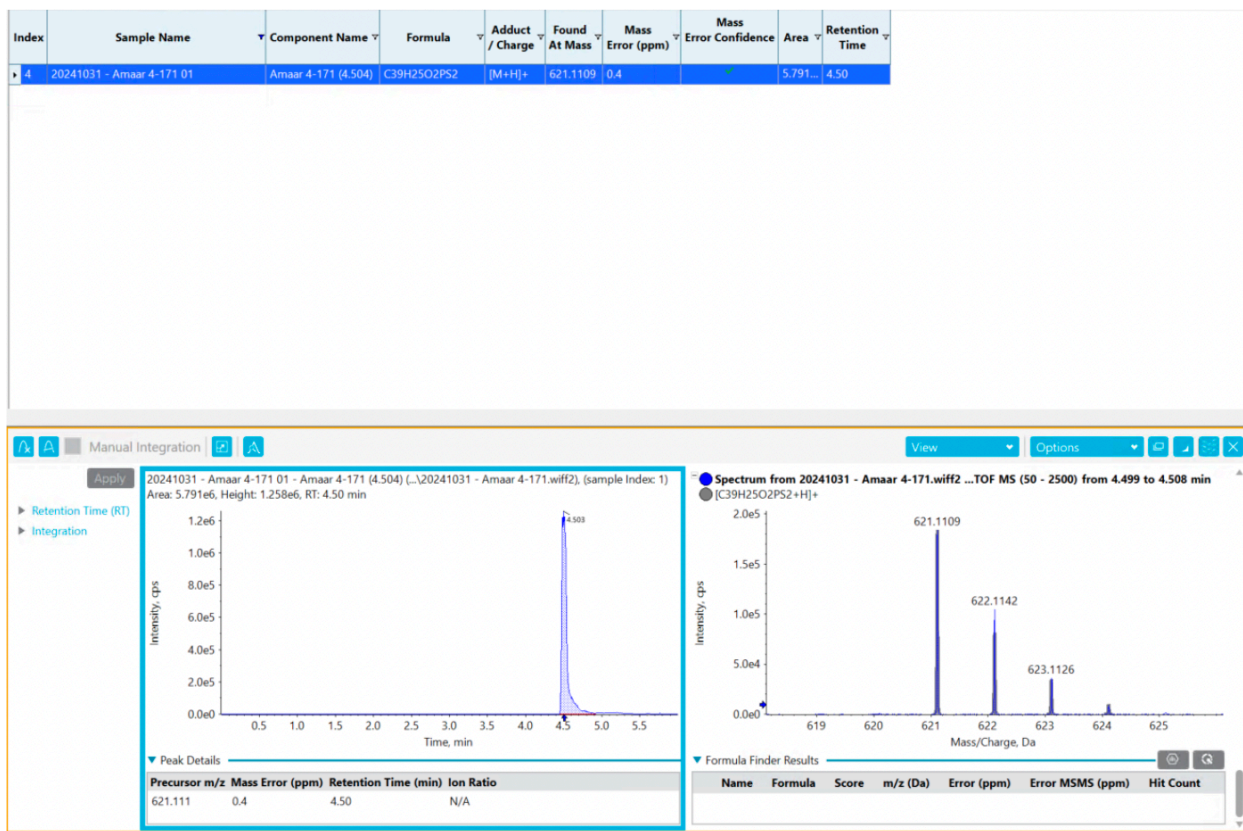


Figure S4-40. Mass spectrometry result for compound 4-7.

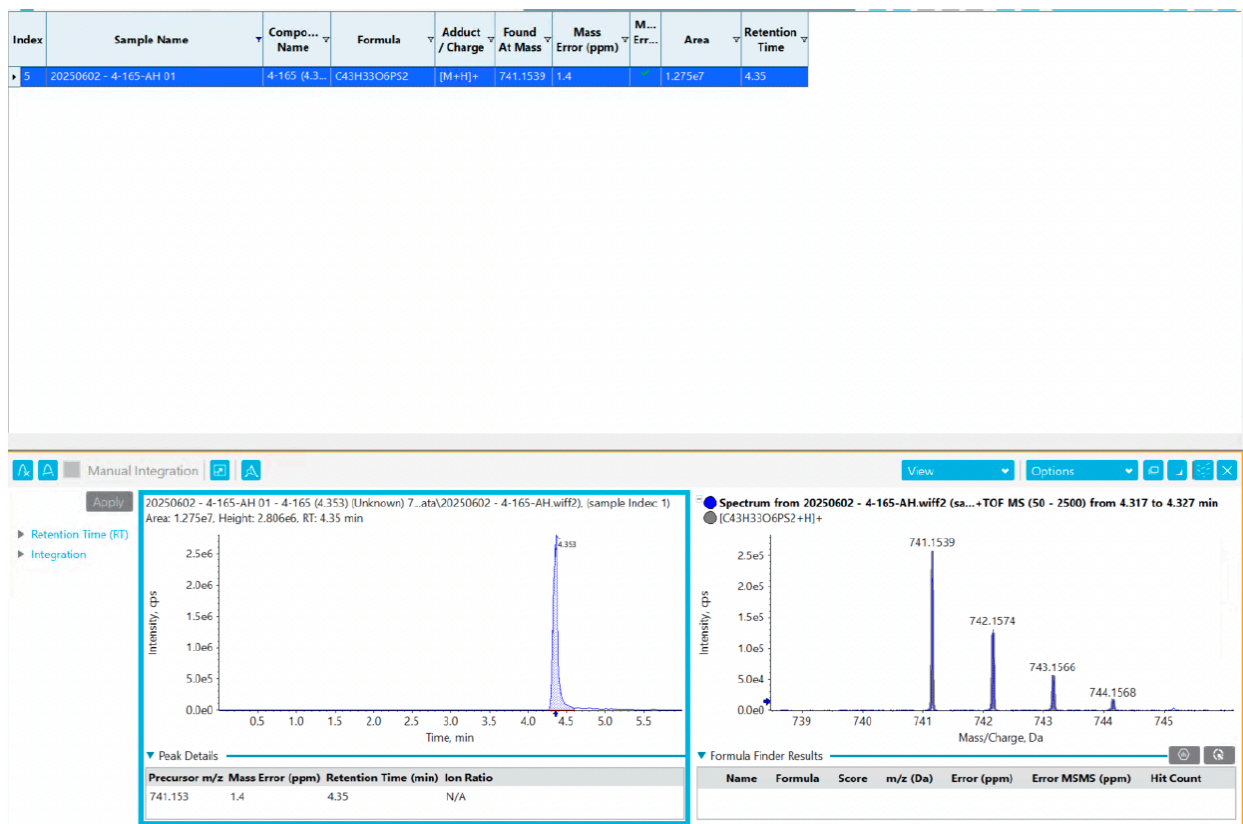


Figure S4-41. Mass spectrometry result for compound 4-8.

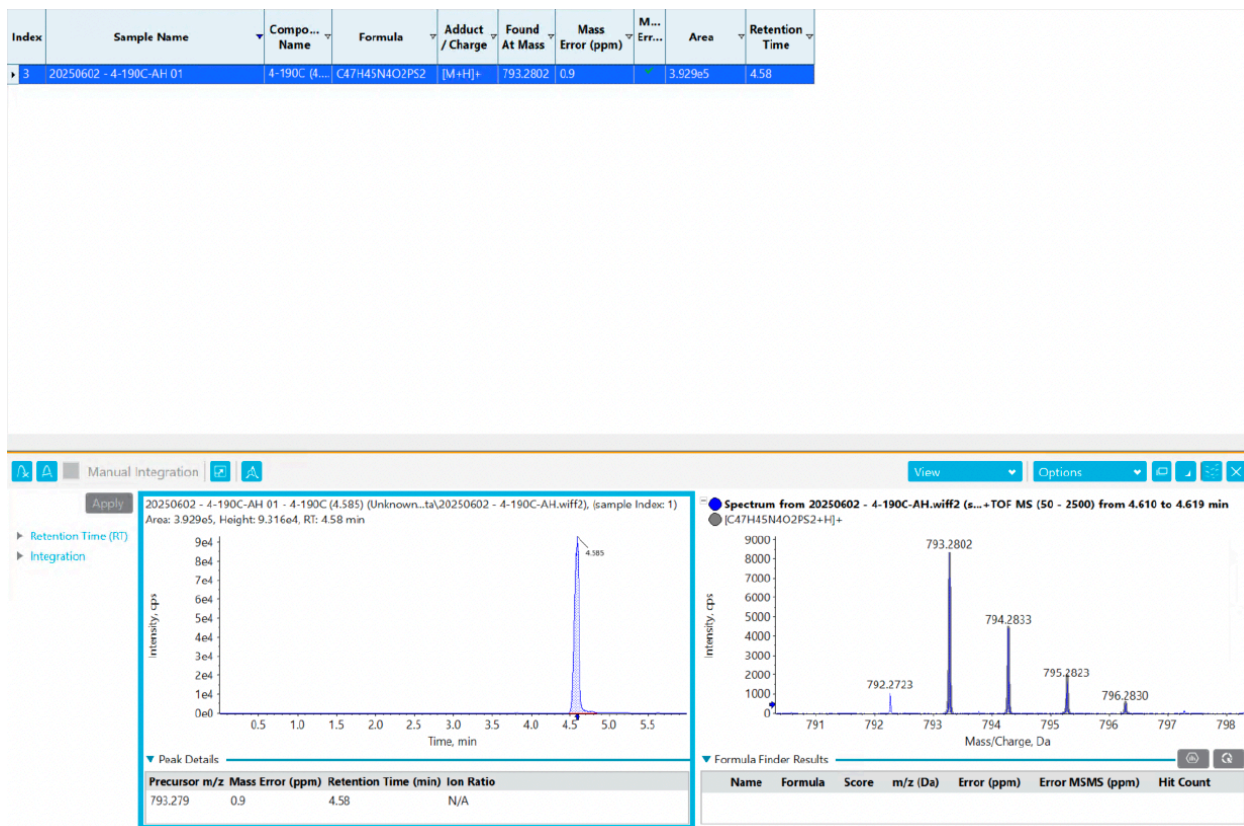
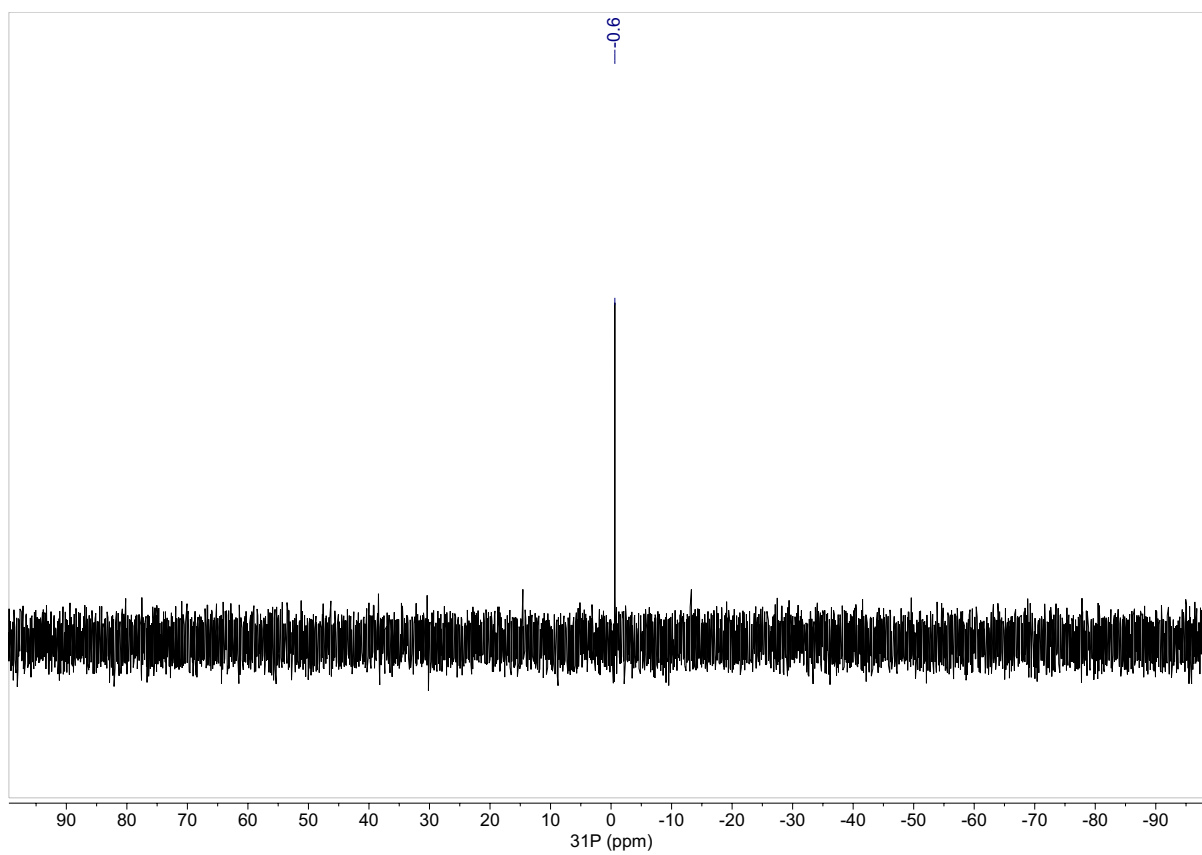
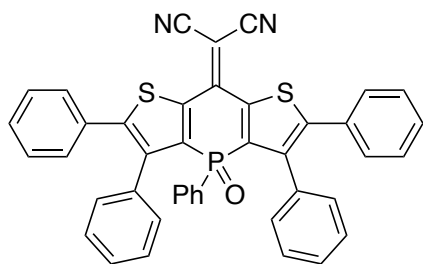


Figure S4-42. Mass spectrometry result for compound 4-9.

## SI.5.0 Chapter 5 Conclusion and Future Outlook Supporting Information

### SI.5.1 Nuclear Magnetic Resonance Spectrum

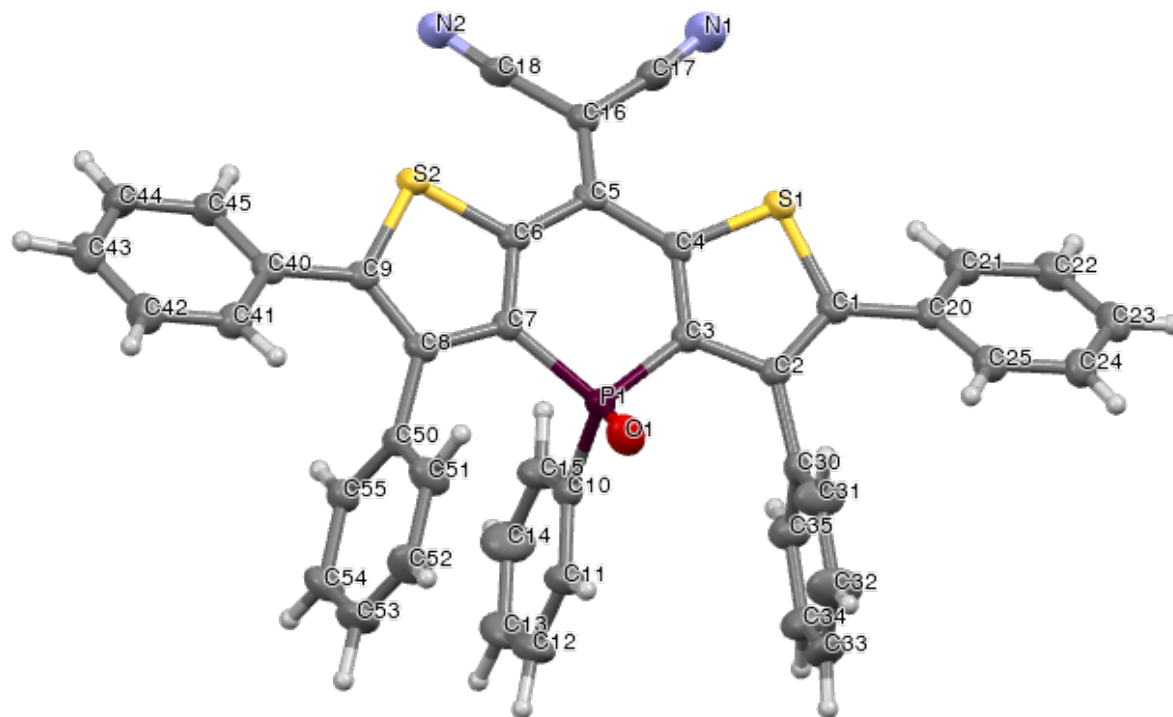


**Figure S5-1.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, CDCl<sub>3</sub>) of compound 5-2.

## SI.5.2 Solid-state Structures

**Table S5-1.** Crystal data and structure refinement for **5-2**.

Identification code	4_197_0m_a
Empirical formula	C <sub>42</sub> H <sub>25</sub> N <sub>2</sub> OPS <sub>2</sub>
Formula weight	668.785
Temperature/K	173.00
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	6.6574(5)
b/Å	23.4062(17)
c/Å	20.6047(13)
α/°	90
β/°	93.639(3)
γ/°	90
Volume/Å <sup>3</sup>	3204.2(4)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.386
μ/mm <sup>-1</sup>	0.255
F(000)	1386.1
Crystal size/mm <sup>3</sup>	0.15 × 0.05 × 0.025
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.32 to 54.96
Index ranges	-9 ≤ h ≤ 9, -32 ≤ k ≤ 32, -28 ≤ l ≤ 28
Reflections collected	139113
Independent reflections	7351 [R <sub>int</sub> = 0.1957, R <sub>sigma</sub> = 0.0851]
Data/restraints/parameters	7351/0/533
Goodness-of-fit on F <sup>2</sup>	1.139
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0759, wR <sub>2</sub> = 0.1443
Final R indexes [all data]	R <sub>1</sub> = 0.1104, wR <sub>2</sub> = 0.1571
Largest diff. peak/hole / e Å <sup>-3</sup>	0.57/-0.63



**Figure S5-2.** Labelled solid-state structure of **5-2** shown as thermal ellipsoids (50% probability).

**Table S5-2.** Bond lengths for **5-2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.728(3)	C43	C44	1.369(6)
S1	C4	1.732(3)	C21	C22	1.390(5)
S2	C6	1.735(3)	C16	C17	1.427(5)
S2	C9	1.719(3)	C16	C18	1.440(5)
P1	O1	1.480(2)	C8	C7	1.421(4)
P1	C7	1.794(3)	C8	C50	1.493(4)
P1	C3	1.791(3)	C3	C2	1.421(4)
P1	C10	1.793(3)	C2	C30	1.489(4)
N1	C17	1.149(4)	C30	C35	1.385(5)
N2	C18	1.149(4)	C30	C31	1.389(5)
C23	C24	1.378(6)	C35	C34	1.388(5)
C23	C22	1.382(6)	C34	C33	1.387(6)
C24	C25	1.390(5)	C33	C32	1.359(7)
C25	C20	1.379(5)	C32	C31	1.380(6)
C20	C1	1.481(4)	C10	C15	1.378(5)
C20	C21	1.410(5)	C10	C11	1.390(5)
C1	C2	1.377(4)	C15	C14	1.385(6)
C4	C5	1.469(5)	C14	C13	1.388(6)
C4	C3	1.385(4)	C13	C12	1.360(6)
C5	C6	1.460(4)	C12	C11	1.393(6)
C5	C16	1.377(5)	C50	C51	1.386(5)
C6	C7	1.387(4)	C50	C55	1.391(5)
C9	C40	1.476(4)	C51	C52	1.383(5)
C9	C8	1.370(4)	C52	C53	1.374(6)
C40	C41	1.404(5)	C53	C54	1.382(6)
C40	C45	1.389(5)	C54	C55	1.380(5)
C41	C42	1.381(5)	C45	C44	1.387(5)
C42	C43	1.381(6)			

**Table S5-3.** Bond angles for **5-2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	S1	C1	93.24(16)	C16	C17	N1	173.2(4)
C9	S2	C6	92.71(15)	C16	C18	N2	172.8(4)
C7	P1	O1	114.36(15)	C7	C8	C9	111.9(3)
C3	P1	O1	113.05(15)	C50	C8	C9	125.5(3)
C3	P1	C7	100.91(15)	C50	C8	C7	122.5(3)
C10	P1	O1	114.08(16)	C6	C7	P1	123.5(2)
C10	P1	C7	104.89(15)	C8	C7	P1	122.3(2)
C10	P1	C3	108.44(15)	C8	C7	C6	114.1(3)
C22	C23	C24	119.1(4)	C4	C3	P1	124.2(2)
C25	C24	C23	121.0(4)	C2	C3	P1	121.5(2)
C20	C25	C24	120.5(4)	C2	C3	C4	114.2(3)
C1	C20	C25	121.3(3)	C3	C2	C1	112.5(3)
C21	C20	C25	118.7(3)	C30	C2	C1	125.5(3)
C21	C20	C1	120.0(3)	C30	C2	C3	121.9(3)
C20	C1	S1	118.3(2)	C35	C30	C2	121.2(3)
C2	C1	S1	110.7(2)	C31	C30	C2	120.4(3)
C2	C1	C20	130.9(3)	C31	C30	C35	118.2(3)
C5	C4	S1	124.4(2)	C34	C35	C30	121.3(4)
C3	C4	S1	109.3(2)	C33	C34	C35	119.2(4)
C3	C4	C5	126.1(3)	C32	C33	C34	119.8(4)
C6	C5	C4	116.7(3)	C31	C32	C33	121.2(4)
C16	C5	C4	121.2(3)	C32	C31	C30	120.3(4)
C16	C5	C6	121.9(3)	C15	C10	P1	121.3(3)
C5	C6	S2	123.5(2)	C11	C10	P1	118.7(3)
C7	C6	S2	109.3(2)	C11	C10	C15	119.9(3)
C7	C6	C5	127.2(3)	C14	C15	C10	119.8(4)
C40	C9	S2	118.1(2)	C13	C14	C15	120.2(4)
C8	C9	S2	111.8(2)	C12	C13	C14	119.9(4)
C8	C9	C40	130.1(3)	C11	C12	C13	120.5(4)
C41	C40	C9	121.8(3)	C12	C11	C10	119.6(4)
C45	C40	C9	120.5(3)	C51	C50	C8	120.8(3)
C45	C40	C41	117.7(3)	C55	C50	C8	120.6(3)
C42	C41	C40	120.8(3)	C55	C50	C51	118.6(3)
C43	C42	C41	120.3(4)	C52	C51	C50	120.7(4)
C44	C43	C42	119.6(4)	C53	C52	C51	120.0(4)
C22	C21	C20	119.9(4)	C54	C53	C52	120.2(4)
C21	C22	C23	120.7(4)	C55	C54	C53	119.8(4)
C17	C16	C5	125.6(3)	C54	C55	C50	120.7(3)
C18	C16	C5	125.0(3)	C44	C45	C40	120.9(3)
C18	C16	C17	109.2(3)	C45	C44	C43	120.6(4)

### SI.5.3 Density-Functional Theory Calculation Coordinates (X, Y, Z)

4-6

C	-1.45089100	-0.65143100	-0.07432100
C	1.21271400	-2.02770300	0.10308100
C	-1.28520500	-2.00223900	0.18356700
C	-0.03815300	-2.76460500	0.31469200
P	-0.02871100	0.45445400	-0.39072900
C	3.61226400	-1.42035900	-0.09751500
C	2.77572100	-0.32990300	-0.32017100
C	1.39017300	-0.68930000	-0.20732300
C	-3.67982600	-1.36307600	0.01192100
C	-2.83188900	-0.27627200	-0.17671000
S	2.71951900	-2.87027300	0.24733800
S	-2.80021600	-2.83054800	0.32095000
O	-0.04182900	-3.97130700	0.58255600
C	0.08985900	1.60777300	1.01627200
C	0.26247700	2.97162000	0.74270600
C	0.02297600	1.16269000	2.34644800
C	0.36770500	3.88560800	1.79480100
H	0.30694600	3.31135200	-0.28744900
C	0.12719800	2.07946400	3.39396200
H	-0.11520300	0.10795500	2.57163000
C	0.30010700	3.44124100	3.11846500

H	0.50098700	4.94205200	1.57861100
H	0.07214800	1.73221200	4.42204100
H	0.38083400	4.15327500	3.93544500
O	-0.10133300	1.14570200	-1.72939300
C	-5.15538100	-1.40783600	-0.01475300
C	-5.93537700	-0.44465200	0.64496500
C	-5.83641100	-2.43889100	-0.68266000
C	-7.32530100	-0.55106200	0.59851000
H	-5.47529100	0.36583000	1.19894800
C	-7.23129200	-2.45430900	-0.66624400
H	-5.29542700	-3.20862300	-1.22483600
H	-7.94216100	0.18681300	1.10675200
H	-7.77151200	-3.24418000	-1.18341900
C	-3.32562200	1.08728200	-0.52878900
C	-3.87771200	1.33991200	-1.79164100
C	-3.27859500	2.15071000	0.38111800
C	-4.34698800	2.62127200	-2.08250400
H	-3.93618300	0.55552900	-2.54012700
C	-3.77733500	3.39604200	-0.00660400
H	-2.87238200	2.01693900	1.37858600
H	-4.77606400	2.83575300	-3.05891200
H	-3.75212500	4.23211900	0.68910800
C	5.08627100	-1.48984200	-0.15196400

C	5.81009000	-0.91133700	-1.20682800
C	5.81823100	-2.17066400	0.83426200
C	7.19950100	-1.03049800	-1.21930400
H	5.30504900	-0.39057900	-2.01305400
C	7.20800900	-2.23218300	0.72716200
H	5.32155500	-2.63123300	1.68315700
H	7.77384300	-0.59004100	-2.03130400
H	7.78855400	-2.75146600	1.48648000
C	3.29017400	1.04593600	-0.57014600
C	4.08595100	1.69314000	0.38637400
C	3.02060700	1.73536000	-1.75980100
C	4.56733900	2.97400200	0.11558500
H	4.32314600	1.21253500	1.33067600
C	3.55341600	3.01414600	-1.93498300
H	2.40450400	1.29222100	-2.53385200
H	5.18295800	3.49106900	0.84861000
H	3.35699900	3.56231000	-2.85398600
N	-7.97982200	-1.53213600	-0.04226200
N	-4.30590600	3.64397300	-1.21407100
N	4.31586100	3.63762800	-1.02374300
N	7.90374100	-1.67530500	-0.27561600

**5-1**

C	-1.45475600	-0.79709600	0.04444000
C	1.21432800	-2.16421800	0.17145300
C	-1.29189100	-2.16091300	0.21550400
C	-0.03766500	-2.91939300	0.35085900
P	-0.03723300	0.34369600	-0.15883600
C	3.60280100	-1.56721900	-0.06540300
C	2.76755900	-0.46128400	-0.22208300
C	1.38313700	-0.81404300	-0.08385100
C	-3.67578300	-1.53961400	-0.02294100
C	-2.83362300	-0.43310200	-0.08977800
S	2.71141100	-3.02162700	0.24684200
S	-2.79279000	-3.01443900	0.22740700
O	-0.03360700	-4.12737600	0.57973100
C	0.08155900	1.39064100	1.32509600
C	0.18171300	2.77759900	1.13325300
C	0.08333400	0.85976500	2.62599900
C	0.28204900	3.62779500	2.23777900
H	0.17426700	3.18181700	0.12547500
C	0.18285200	1.71486900	3.72456200
H	0.00414700	-0.21098800	2.79382900
C	0.28237200	3.09786500	3.53147000
H	0.35769900	4.70109800	2.08683500

H	0.18120400	1.30241100	4.72926300
H	0.35878300	3.75969800	4.38956100
O	-0.12017500	1.14174400	-1.43522100
C	-5.14355800	-1.60168100	-0.12797700
C	-5.97792400	-0.66359900	0.50377300
C	-5.76649400	-2.63924400	-0.84820900
C	-7.35306300	-0.78016600	0.40509100
H	-5.57582100	0.14348700	1.10256900
C	-7.14436800	-2.70965700	-0.91395500
H	-5.18774700	-3.38767800	-1.37712500
H	-8.02775800	-0.08618500	0.88951400
H	-7.66055200	-3.49110400	-1.45812300
C	-3.30798800	0.95484400	-0.35222500
C	-3.76153900	1.32818200	-1.62689500
C	-3.31408100	1.92344300	0.65946000
C	-4.19229400	2.62270900	-1.85210600
H	-3.76861300	0.62227600	-2.44941100
C	-3.75756400	3.20673900	0.38250100
H	-2.98715300	1.69018300	1.66595600
H	-4.54588000	2.96037500	-2.81932500
H	-3.78406500	3.98483000	1.13465100
C	5.06901500	-1.65522100	-0.18661200
C	5.76115700	-1.01994900	-1.23395600

C	5.82418900	-2.41984600	0.71987800
C	7.13363700	-1.14667100	-1.33286800
H	5.24253500	-0.45031400	-1.99501000
C	7.19636600	-2.51538600	0.57322000
H	5.36010000	-2.92996600	1.55625300
H	7.70375800	-0.68140600	-2.12776500
H	7.81221700	-3.09063800	1.25295100
C	3.27301300	0.92172200	-0.43328200
C	4.13205900	1.51835700	0.50244900
C	2.91460800	1.67276900	-1.56555800
C	4.60316700	2.80323100	0.29201800
H	4.42821500	0.99990700	1.40668900
C	3.41750500	2.95050400	-1.73016300
H	2.24562000	1.27439600	-2.31748200
H	5.26152700	3.30191800	0.99156000
H	3.18032000	3.56301000	-2.59165400
N	-7.91994400	-1.78865000	-0.29453800
N	-4.18495600	3.54078700	-0.85514700
N	4.24804200	3.49842100	-0.81124800
N	7.83385800	-1.88070200	-0.43622800
C	9.30258300	-2.02039800	-0.59688800
H	9.50291600	-2.77410800	-1.36120100
H	9.71671900	-1.05854300	-0.89758100

H	9.73389900	-2.32679900	0.35450400
C	4.78054500	4.86451000	-1.04343600
H	5.43394500	4.84203100	-1.91731900
H	3.94652400	5.54677300	-1.21392900
H	5.34309100	5.17790900	-0.16592500
C	-4.66403300	4.91850700	-1.13694300
H	-4.08127900	5.33421200	-1.96022200
H	-5.72147600	4.87798000	-1.40381400
H	-4.52888500	5.52794400	-0.24550000
C	-9.39677500	-1.91649400	-0.36776200
H	-9.69005600	-2.04288900	-1.41035900
H	-9.70428800	-2.78425300	0.21846400
H	-9.84900500	-1.01282700	0.03678100

## 5-2

C	1.39946800	0.26150200	0.00409700
C	-1.24107100	1.63344500	0.19028500
C	1.24097600	1.63351300	0.19015200
C	-0.00004400	2.33296300	0.51852800
P	-0.00002000	-0.90263100	0.08989700
C	-3.58029400	0.97009000	-0.45891100
C	-2.73399500	-0.12721200	-0.33526500
C	-1.39957800	0.26143100	0.00423100

C	3.58019600	0.97015000	-0.45904000
C	2.73388700	-0.12715400	-0.33537200
S	-2.75817500	2.45318500	-0.09848300
S	2.75806000	2.45325600	-0.09866400
C	0.00007100	-1.62459000	1.76836700
C	-0.00009700	-3.02119700	1.88700300
C	0.00026400	-0.82535900	2.92228300
C	-0.00007000	-3.61395600	3.15300100
H	-0.00025100	-3.63454800	0.99128200
C	0.00029400	-1.42090800	4.18507300
H	0.00038400	0.25915800	2.84563400
C	0.00012700	-2.81599600	4.30099600
H	-0.00020500	-4.69719500	3.24016700
H	0.00044900	-0.79792200	5.07527100
H	0.00014900	-3.27809200	5.28462800
O	-0.00001700	-1.94179700	-1.00052900
C	5.00961800	1.02549800	-0.82542800
C	5.94111700	0.15206200	-0.23345400
C	5.46977700	1.97794500	-1.75461500
C	7.29351800	0.22783900	-0.56863300
H	5.60700800	-0.57636200	0.49767500
C	6.82363200	2.04995700	-2.08726900
H	4.76300000	2.65074900	-2.23308600

C	7.74011300	1.17471300	-1.49652600
H	8.00005700	-0.45101600	-0.09863600
H	7.15960700	2.78672500	-2.81185000
C	3.18527100	-1.52794800	-0.58488800
C	3.49641000	-1.94927200	-1.88685900
C	3.33679000	-2.43161400	0.47742300
C	3.94312600	-3.25107700	-2.12271200
H	3.38042700	-1.25655100	-2.71613800
C	3.78538900	-3.73425800	0.24151100
H	3.11278800	-2.11341700	1.49204400
C	4.08903000	-4.14773100	-1.05884200
H	4.17506500	-3.56503500	-3.13712300
H	3.89969300	-4.42282800	1.07479600
C	-5.00971400	1.02542400	-0.82530400
C	-5.46991400	1.97791300	-1.75441600
C	-5.94118300	0.15193000	-0.23336100
C	-6.82377900	2.04991000	-2.08704600
H	-4.76316700	2.65077000	-2.23286100
C	-7.29359000	0.22768400	-0.56851600
H	-5.60704200	-0.57651200	0.49773400
C	-7.74022600	1.17460300	-1.49634500
H	-7.15978400	2.78671700	-2.81157200
H	-8.00010400	-0.45121500	-0.09854500

C	-3.18525700	-1.52802100	-0.58490600
C	-3.33640900	-2.43193400	0.47725300
C	-3.49663300	-1.94912800	-1.88689100
C	-3.78486200	-3.73459000	0.24117300
H	-3.11223900	-2.11391100	1.49189300
C	-3.94320000	-3.25095800	-2.12291600
H	-3.38094700	-1.25622100	-2.71605600
C	-4.08872600	-4.14784900	-1.05920300
H	-3.89888200	-4.42335000	1.07433900
H	-4.17532100	-3.56473500	-3.13734200
C	-0.00005100	3.58914500	1.12891700
C	1.16960200	4.30640000	1.52771600
C	-1.16969200	4.30637500	1.52779300
N	2.05064900	4.96844400	1.90852000
N	-2.05071400	4.96842100	1.90864700
H	8.79389600	1.23047900	-1.75580900
H	4.43730200	-5.16081600	-1.24245100
H	-4.43688400	-5.16095200	-1.24293500
H	-8.79401500	1.23035600	-1.75560700

**5-13**

C	1.47158000	0.19092200	-0.00856800
C	-1.22226000	1.58121200	0.19132400
C	1.29601600	1.54416600	0.20070500
C	0.04789500	2.30979900	0.36650300
P	0.00481900	-0.88244700	0.37526100
C	-3.63210100	1.09143000	-0.09802700
C	-2.84976200	-0.08043300	-0.17168000
C	-1.44032100	0.22655600	0.03300500
C	3.69283400	0.99172700	-0.11882900
C	2.86875400	-0.14721100	-0.25544300
S	-2.65872400	2.50456600	0.15408600
S	2.76011900	2.42079900	0.20180100
O	0.06382200	3.51533000	0.58884200
C	0.02703000	-1.10686400	2.18567400
C	0.14252200	-2.42165400	2.66772300
C	-0.06175500	-0.03867800	3.09375200
C	0.17401500	-2.66038400	4.04378200
H	0.20293200	-3.25684000	1.97726700
C	-0.02816100	-0.28407600	4.46603900
H	-0.16082700	0.98639600	2.75147700
C	0.09112600	-1.59461500	4.94246200
H	0.26231500	-3.67958600	4.40802300

H	-0.09794700	0.54760400	5.16078700
H	0.11612700	-1.78214300	6.01192600
O	-0.01969000	-2.19188000	-0.36804800
P	5.52554600	1.37241500	-0.10692700
P	3.28553900	-1.82242800	-0.96811200
P	-5.43866500	1.52795800	-0.18761600
P	-3.37500400	-1.79744100	-0.67572100
C	-5.56133900	3.31981000	0.24469000
H	-5.13819700	3.89981500	-0.58099000
H	-4.92714700	3.47864000	1.12171300
C	-6.34481100	0.61464500	1.14276800
H	-6.28956900	1.28302400	2.00935600
H	-5.76237500	-0.26572000	1.41879800
C	-6.02281500	1.24688300	-1.92824100
H	-6.61249600	0.32765400	-1.93399600
H	-5.11035600	1.07052400	-2.50652500
C	-5.17056400	-1.95241900	-1.01971900
H	-5.73568500	-1.58458200	-0.16368600
H	-5.40276400	-1.32917100	-1.88261500
C	-2.97836000	-3.03416200	0.62058200
H	-3.19376000	-3.99972200	0.14798800
H	-1.89901100	-3.00995000	0.77212300
C	-2.49546200	-2.21791400	-2.23225000

H	-1.43441000	-2.25771800	-1.97894400
H	-2.80430500	-3.24477800	-2.46184400
C	2.94743700	-3.16768300	0.23482600
H	1.86586600	-3.20413600	0.37203300
H	3.22688900	-4.08976600	-0.28760300
C	2.25836100	-1.98697700	-2.48216500
H	1.21799300	-1.95751200	-2.15332900
H	2.43837700	-3.00258900	-2.85284000
C	5.03448500	-2.03515000	-1.48825000
H	5.35754500	-1.16250100	-2.05307900
H	5.64552500	-2.11356100	-0.58830400
C	6.19017700	1.23784700	-1.83589400
H	6.79048300	0.32393000	-1.85873700
H	5.31967200	1.08896100	-2.48218900
C	6.31160700	0.18441500	1.06268100
H	6.31704100	-0.77883600	0.55379600
H	5.62341100	0.10216800	1.91127200
C	5.63079700	3.09376400	0.57032100
H	5.01267600	3.73022500	-0.07053300
H	5.14612900	3.04237400	1.55218600
C	7.01559800	3.75485300	0.72095200
H	7.50497200	3.92842900	-0.23610000
H	6.84457700	4.73034200	1.18697200

H	7.68934700	3.19408300	1.36706900
C	7.74084300	0.49173200	1.54309100
H	8.10766200	-0.39978100	2.06122200
H	8.43093000	0.70215000	0.72118300
H	7.76461400	1.31795200	2.25484100
C	7.03078500	2.40853800	-2.36983900
H	6.48584300	3.35583800	-2.35238900
H	7.97317400	2.51794600	-1.82920700
H	7.27082800	2.18466800	-3.41406900
C	5.24519900	-3.29959600	-2.34747400
H	4.91355800	-4.21072300	-1.84207000
H	4.74435900	-3.22828600	-3.31574200
H	6.31860400	-3.39869700	-2.53404700
C	2.55512400	-0.94438700	-3.57156100
H	1.84247100	-1.08712200	-4.38962500
H	2.44367400	0.08132000	-3.20582100
H	3.56051900	-1.05474300	-3.98897600
C	3.69867700	-3.04521500	1.56873400
H	3.48782300	-2.09826000	2.07517600
H	3.37114600	-3.85635900	2.22565400
H	4.78121700	-3.14140500	1.44452700
C	-2.76655200	-1.28157300	-3.41852800
H	-2.13679900	-1.59696200	-4.25599400

H	-3.80554000	-1.32679100	-3.75817000
H	-2.51589400	-0.24163400	-3.18494500
C	-5.59694500	-3.40438200	-1.32230200
H	-5.45399800	-4.06714600	-0.46575700
H	-6.66497100	-3.39349100	-1.55824700
H	-5.07301500	-3.82012700	-2.18683900
C	-3.74600400	-2.88578000	1.94167300
H	-3.39545200	-3.65870600	2.63220000
H	-3.56683800	-1.91461700	2.41308900
H	-4.82445300	-3.02449800	1.81789700
C	-6.83568900	2.37504100	-2.58674600
H	-6.31091300	3.33333900	-2.57909400
H	-6.98927900	2.09175200	-3.63278300
H	-7.82007000	2.49949800	-2.13205500
C	-6.98526700	3.80883500	0.57515600
H	-6.91622900	4.87759800	0.79948600
H	-7.68370100	3.68953400	-0.25402600
H	-7.39594600	3.31556200	1.45948100
C	-7.80454800	0.24314600	0.83654800
H	-7.89023500	-0.47861700	0.01923400
H	-8.22740700	-0.22061500	1.73302300
H	-8.41647500	1.11505100	0.59274200

## SI.6.0 References

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