Supporting Information

Synthesis of Dibenzophospholes by Tf_2O-Mediated Intramolecular Phospha-Friedel-Crafts-Type Reaction

Kazutoshi Nishimura, Koji Hirano,* and Masahiro Miura*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Contents

Instrumentation and Chemicals

^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 400 MHz, 100 MHz, 162 MHz, and 162 MHz, respectively, for $CDCl_3$ and toluene-d_6 solutions. HRMS data were obtained by APCI using TOF or EI using a double focusing mass spectrometer. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel $60F_{254}$. Silica gel (Wakosil C-200) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-6AD (pump, SHIMADZU, 3.5 mL/min $CHCl_3$) and SPD-20A (UV detector, SHIMADZU, 254 nm) with two in-line GPC H-2001 (20 x 500 mm, particle size: 15 μm) and H-2002 columns (20 x 500 mm, particle size: 15 μm) (preparative columns, Shodex, $CHCl_3$ eluent). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was dried on a Glass Contour Solvent dispensing system (Nikko Hansen & Co., Ltd.) prior to use. All secondary phosphine oxides **1** were synthesized from the corresponding aryl bromides and $PhPCl_2$ according to the literature method.[1] All reactions were carried out under nitrogen atmosphere.

---

[1] Kuninobu, Y.; Yoshida, T.; Takai, K. *J. Org. Chem.* **2011**, *76*, 7370.

Experimental Procedures

Synthesis of **2a** (Table 1, entry 7, 0.10 mmol scale): In a Schlenk tube with pressure resistance, [1,1'-biphenyl]-2-yl(phenyl)phosphine oxide (**1a**, 0.10 mmol, 28 mg) was placed with a magnetic stir bar under N_2. Toluene (1.5 mL) was subsequently added by a syringe. The resulting mixture was stirred until it became homogeneous solution. Tf_2O (0.12 mmol, 20 μl) was then added by a syringe. The reaction mixture was heated at 90 ℃ in an oil bath for 8 h. After cooling, sat. $NaHCO_3$ aq was added. The resulting mixture was extracted three times with ethyl acetate (20 mL x 3). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The desired product 5-phenylbenzo[b]phosphindole 5-oxide (**2a**, 25 mg, 90%) was isolated by column chromatography on silica gel using ethyl acetate as eluent.

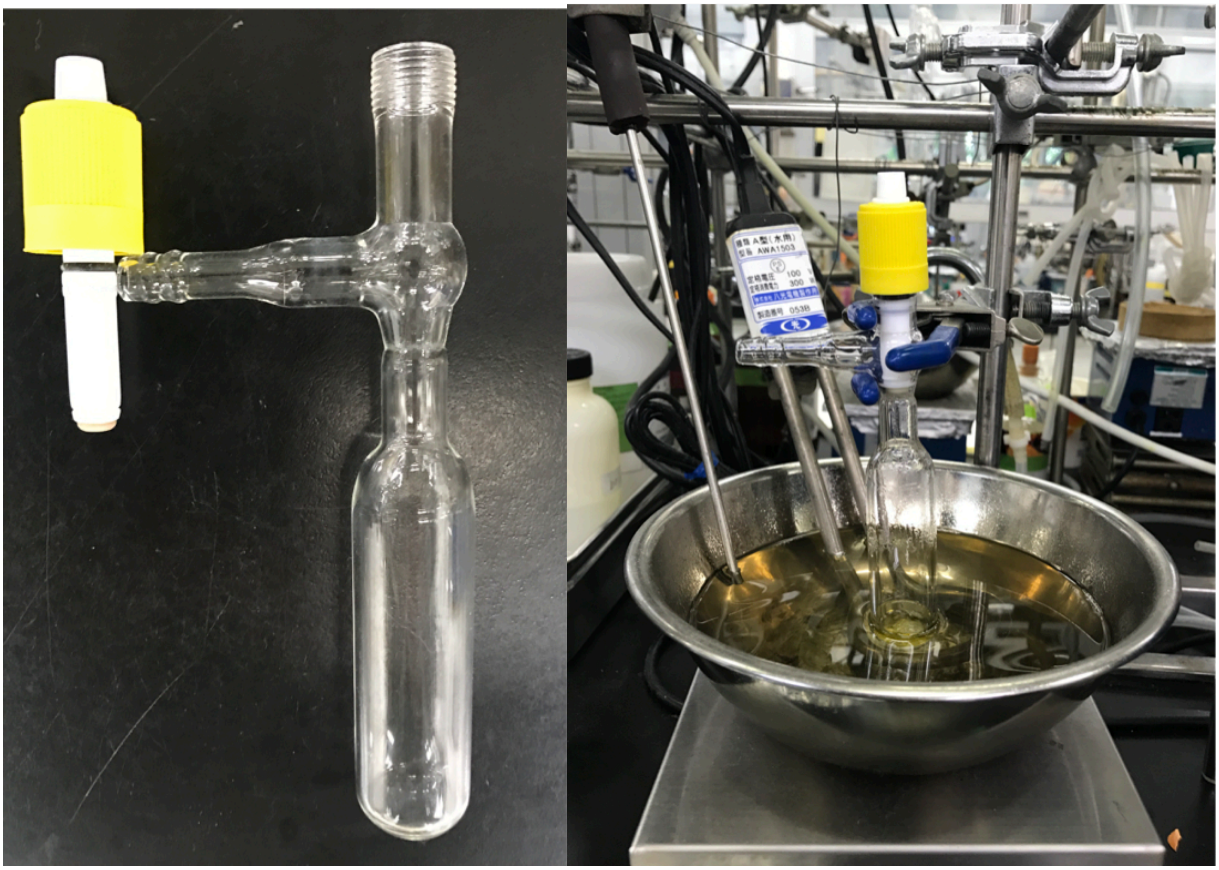


Figure S1. Photos of Schlenk flask used in this study: reaction set up (left); reaction progress (right).

Synthesis of **2a** (Table 1, entry 7, 1.0 mmol scale): In a Schlenk tube with pressure resistance, [1,1'-biphenyl]-2-yl(phenyl)phosphine oxide (**1a**, 1.0 mmol, 278 mg) was placed with a magnetic stir bar under N_2. Toluene (15 mL) was subsequently added by a syringe. The resulting mixture was

stirred until it became homogeneous solution. Tf_2O (1.2 mmol, 200 μl) was then added by a syringe. The reaction mixture was heated at 90 ℃ in an oil bath for 8 h. After cooling, sat. $NaHCO_3$ aq was added. The resulting mixture was extracted three times with ethyl acetate (20 mL x 3). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The desired product 5-phenylbenzo[b]phosphindole 5-oxide (**2a**, 183 mg, 66%) was isolated by column chromatography on silica gel using ethyl acetate as eluent.

Synthesis of **2r** (Scheme 5): In a Schlenk tube with pressure resistance, (thiophene-2,5-diylbis(2,1-phenylene))bis(phenylphosphine oxide) (**1r**, 0.10 mmol, 48 mg) was placed with a magnetic stir bar under N_2. Toluene (1.5 mL) was subsequently added by a syringe. The resulting mixture was stirred until it became homogeneous solution. Tf_2O (0.24 mmol, 40 μl) was then added by a syringe. The reaction mixture was heated at 90 ℃ in an oil bath for 24 h. After cooling, sat. $NaHCO_3$ aq was added. The resulting mixture was extracted eight times with chloroform (20 mL x 8). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The desired product 5,6-diphenyldiphosphindolo[3,2-b:2',3'-d]thiophene 5,6-dioxide (**2r**, 32 mg, 67% with ca. 1:1 *syn*/*anti* ratio) was isolated by column chromatography on silica gel using chloroform-methanol (10:1) as eluent.

X-Ray Analysis

The X-ray quality crystals of **2n** were grown from CH_2Cl_2/hexane.

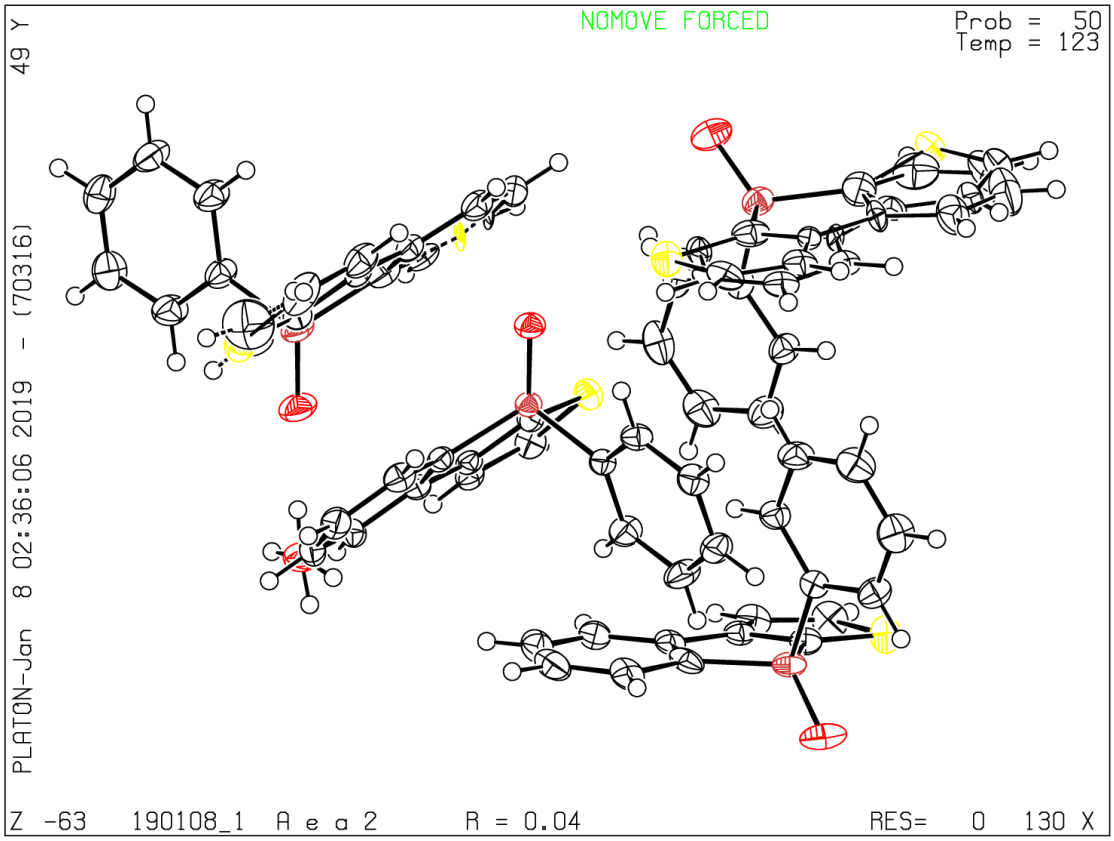


Figure S2. ORTEP drawing of **2n** (CCDC 1889358).

The X-ray quality crystals of *syn*-**2r** were grown from wet $CHCl_3$.

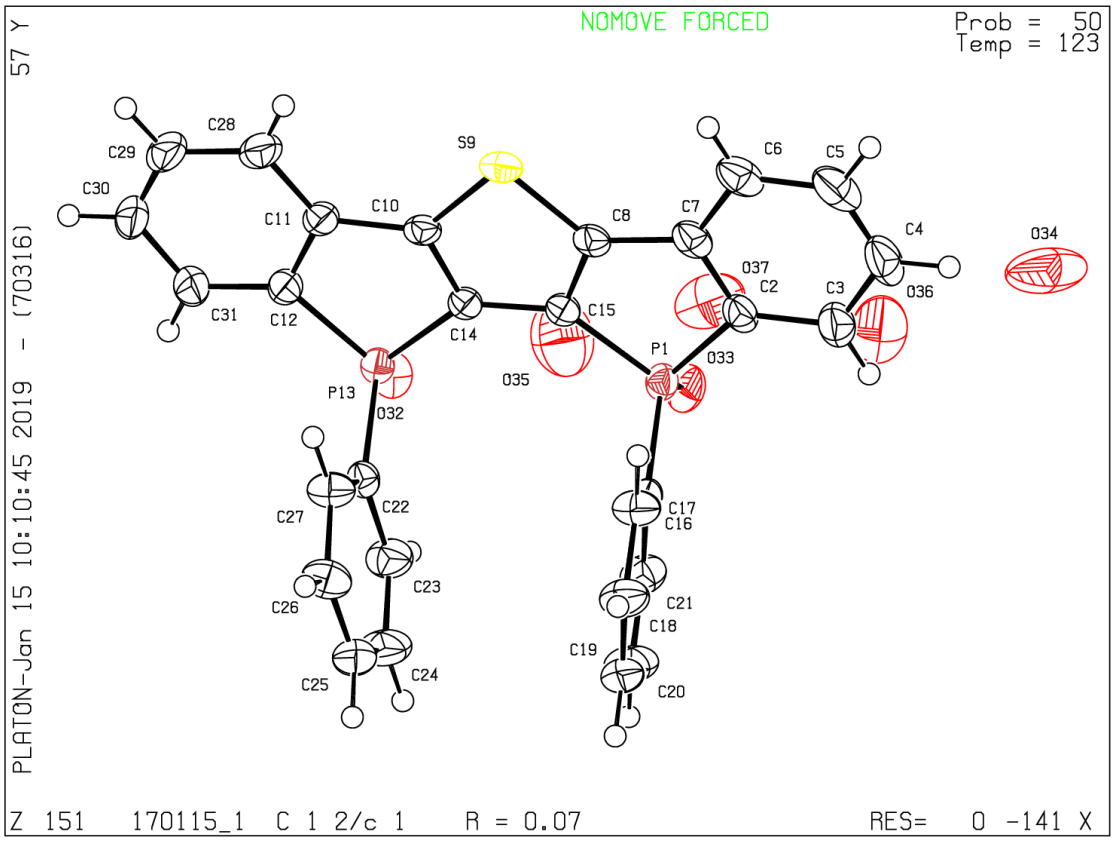


Figure S3. ORTEP drawing of *syn*-**2r** (CCDC 1891190).

NMR Studies for Mechanistic Discussion

We monitored the reaction mixture of **1a** with Tf_2O in toluene-d_8 by $^{19}F\{^1H\}$, ^{31}P, $^{31}P\{^1H\}$, and ^1H NMR (Figures S4–10). Upon treatment of **1a** with Tf_2O at room temperature, an original signal of Tf_2O (–72.5 ppm) still remained but a new signal appeared at –77.8 ppm (Figure S4). On the other hand, in the ^{31}P and $^{31}P\{^1H\}$ NMR the original signal of **1a** (15.7 ppm) immediately disappeared, and somewhat complicated spectra were obtained (Figures S5 and S6). The most informative signal was observed around 37–40 ppm, which may be corresponding to P–H species: the observed large coupling constant (564 Hz) was consistent with the $^1J_{P\text{-}H}$ coupling, and the ^1H-decoupled $^{31}P\{^1H\}$ NMR showed the singlet signal (Figure S5) while the doublet signal was observed in the ^{31}P NMR (Figure S6). Additionally, ^1H NMR also suggested the presence of P–H bond (around 8.2 ppm signal, Figure S7). These outcomes support the presence of a five-coordinated, Tf_2O adduct **A'** rather than our originally proposed phosphenium cation **A** (Scheme S1). After heating at 90 ˚C, there was no significant change in $^{19}F\{^1H\}$ NMR (Figure S8), but in the $^{31}P\{^1H\}$ NMR (Figure S9) the major signal was newly observed at 57.4 ppm (Figure S9), which was completely different from the signal of final product, dibenzophosphole oxide **2a** in toluene-d_8/$CDCl_3$ (32.1 ppm; isolated **2a** was hardly soluble in pure toluene-d_8). However, our control experiment using the isolated **2a** and TfOH showed a similar $^{31}P\{^1H\}$ signal (59.8) in toluene-d_8/$CDCl_3$ (Figure S10). Thus, the signal at 57.4 ppm in Figure S9 is assigned to be a complex of **2a** and TfOH.

On the basis of the above considerations, we propose the revised tentative reaction mechanism in Scheme S1b. The formed TfOH and CF_3SO_2H generally show similar signals to Tf_2O, and thus some $^{19}F\{^1H\}$ signals around –73 ppm are always observed during the course of reaction (Figures S4 and S8). However, the present NMR studies are still preliminary, and additional efforts are necessary for conclusive mechanistic statement.

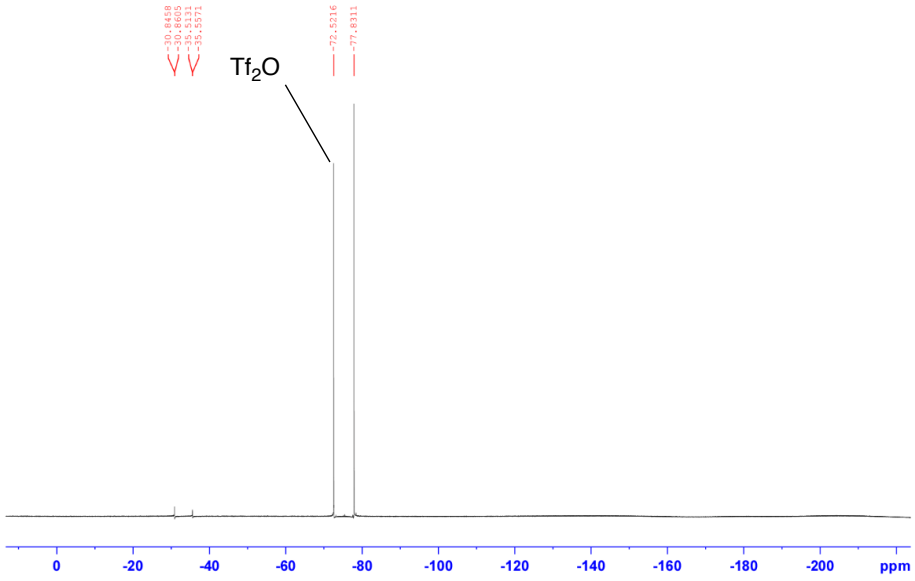


Figure S4. $^{19}F\{^{1}H\}$ NMR of **1a** and Tf_2O in toluene-d_8 at rt for 10 min.

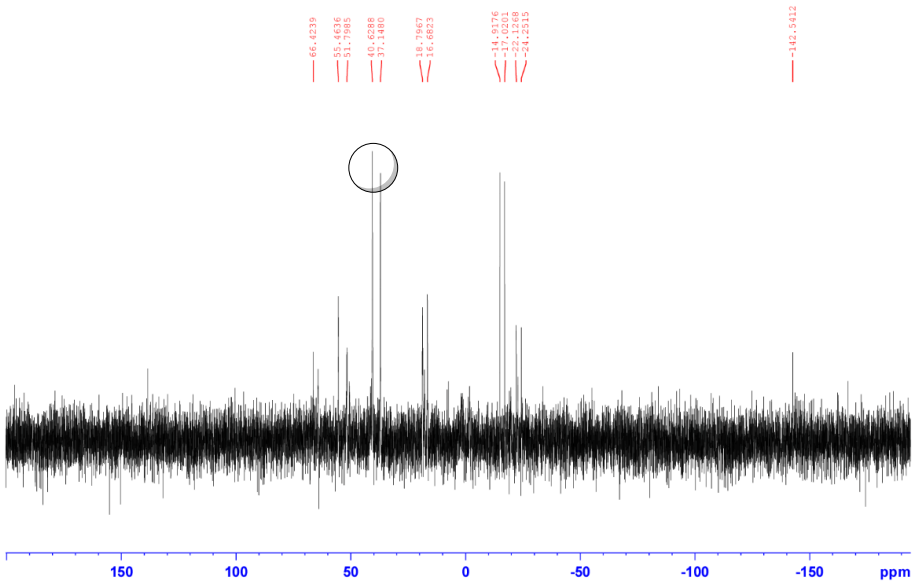


Figure S5. ^{31}P NMR of **1a** and Tf_2O in toluene-d_8 at rt for 10 min.

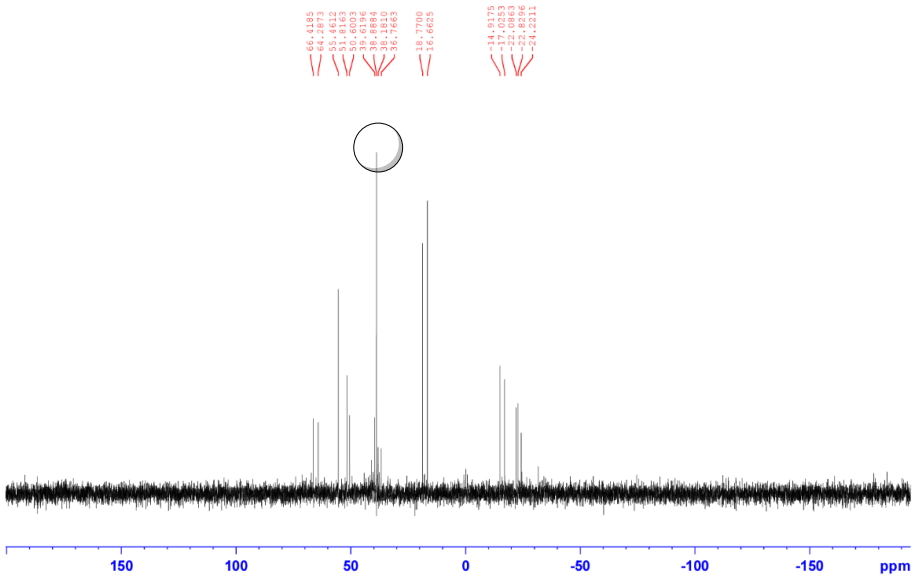


Figure S6. $^{31}P\{^{1}H\}$ NMR of **1a** and Tf_2O in toluene-d_8 at rt for 10 min.

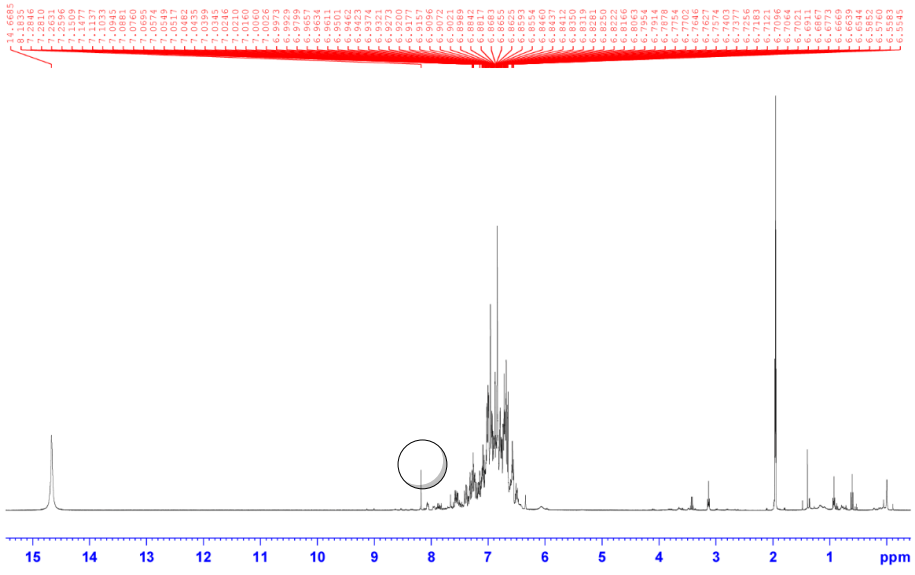


Figure S7. ^{1}H NMR of **1a** and Tf_2O in toluene-d_8 at rt for 10 min.

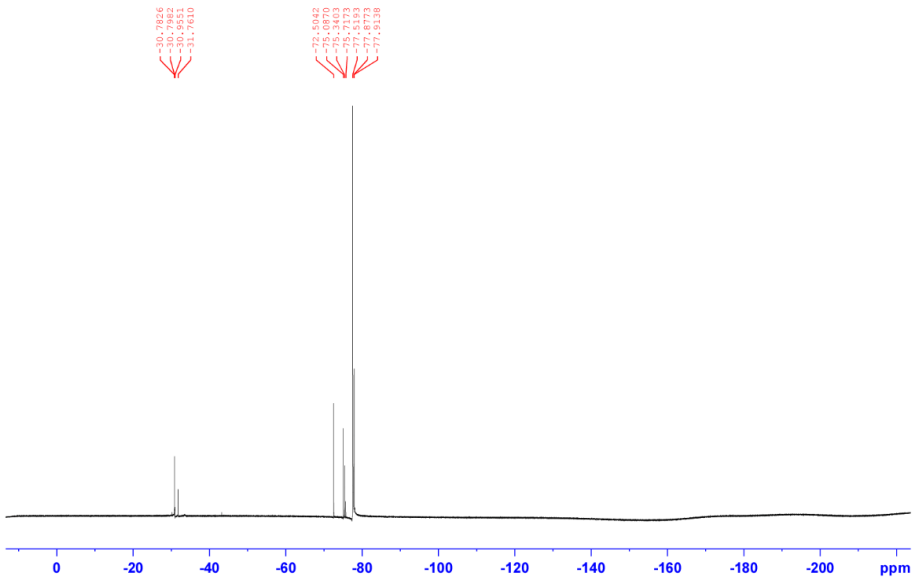


Figure S8. $^{19}F\{^{1}H\}$ NMR of **1a** and Tf_2O in toluene-d_8 at 90 ˚C for 8 h.

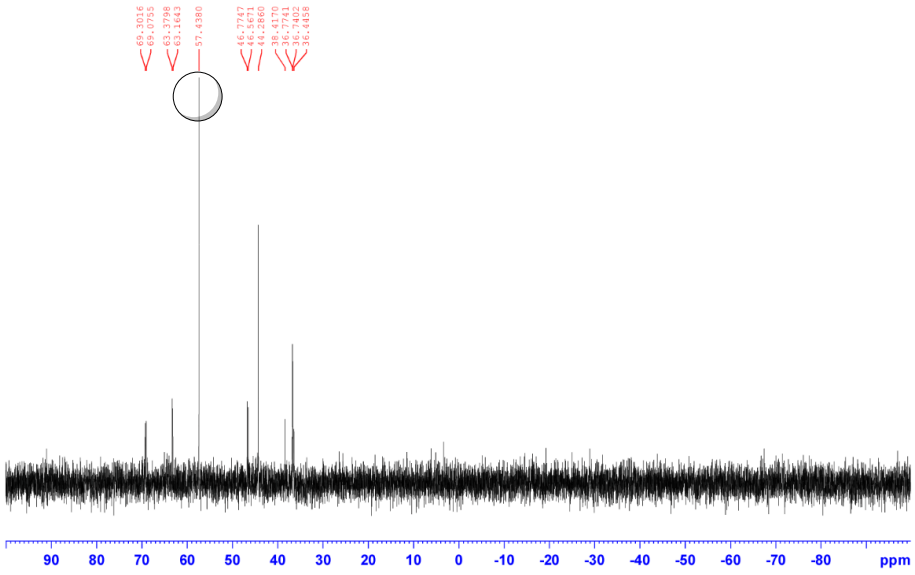


Figure S9. $^{31}P\{^{1}H\}$ NMR of **1a** and Tf_2O in toluene-d_8 at 90 ˚C for 8 h.

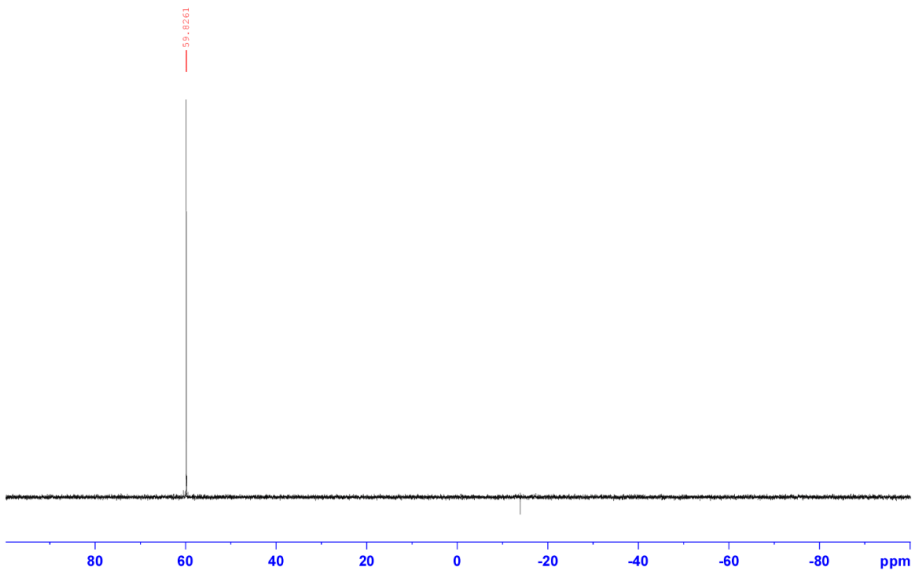
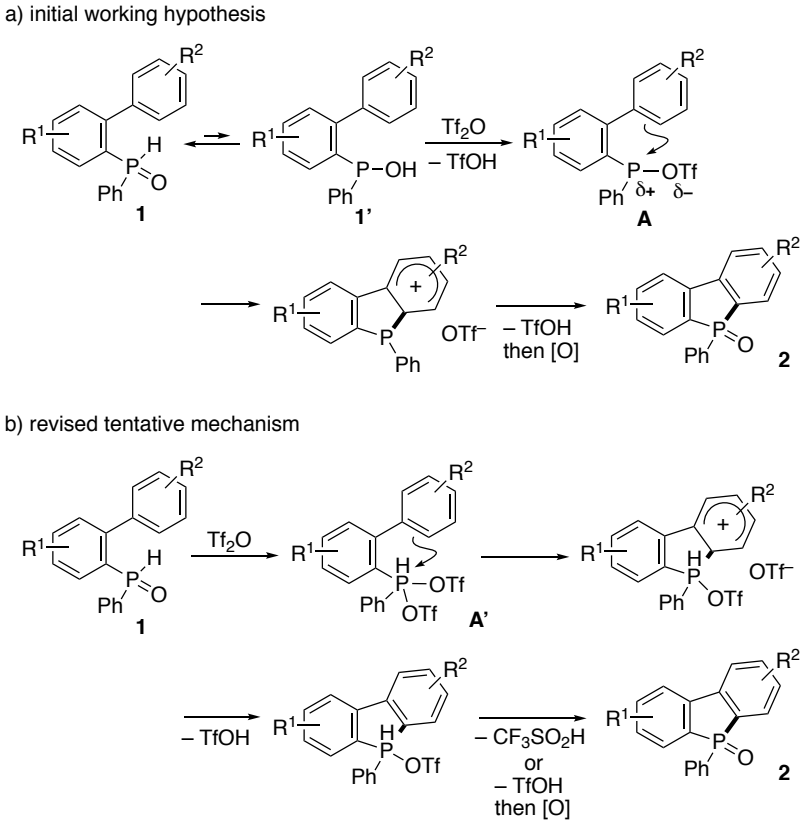


Figure S10. $^{31}P\{^{1}H\}$ NMR of **2a** and Tf_2O in toluene-d_8 at rt for 30 min.

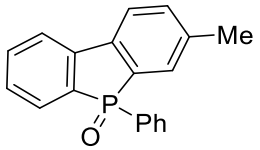
Scheme S1. Initial Working Hypothesis (a) and Revised Tentative Mechanism (b).



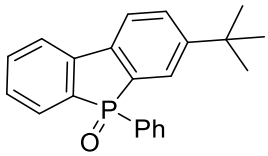
Characterization Data for Products

^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra for all compounds are attached in the last part.

The products **2a**, **2d**, **2e**, **2f**, **2g**, **2k**, **2l**, and **2n** are known, and their spectra data were in agreement with the reported values.[1,2]



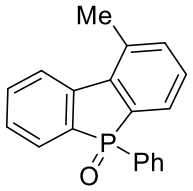
3-Methyl-5-phenylbenzo[*b*]phosphindole 5-oxide (2b): 22 mg (75%); white solid; m.p. 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 7.32-7.42 (m, 4H), 7.47-7.58 (m, 3H), 7.63-7.72 (m, 4H), 7.56 (dd, J = 7.7, 2.9, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 21.45 (1C), 121.01 (d, J = 10.2 Hz, 1C), 121.17 (d, J = 10.8 Hz, 1C), 128.84 (d, J = 12.5 Hz, 2C), 129.12 (d, J = 11.0 Hz, 1C), 129.99 (d, J = 9.5 Hz, 1C), 130.48 (d, J = 9.6 Hz, 1C), 131.17 (d, J = 102.3 Hz, 1C), 131.19 (d, J = 10.9 Hz, 2C), 132.23 (d, J = 2.9 Hz, 1C), 132.87 (d, J = 106.4 Hz, 1C), 133.10 (d, J = 105.9 Hz, 1C), 133.46 (d, J = 2.1 Hz, 1C), 134.26 (d, J = 2.1 Hz, 1C), 139.32 (d, J = 21.7 Hz, 1C), 139.87 (d, J = 11.3 Hz, 1C), 142.14 (d, J = 21.6 Hz, 1C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 33.68; HRMS (EI^+) m/z (M^+) calcd for $C_{19}H_{15}OP$: 290.0861, found: 290.0860.



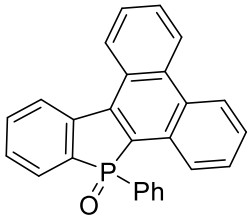
3-(*tert*-Butyl)-5-phenylbenzo[*b*]phosphindole 5-oxide (2c): 22 mg (66%); white solid; m.p. 62-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H), 7.34 (ddd, J = 7.2, 7.2, 3.6 Hz, 1H), 7.40 (ddd, J = 7.3, 7.3, 3.0 Hz, 2H), 7.50 (ddd, J = 7.3, 7.3, 1.4 Hz, 1H), 7.56 (dd, J = 7.6, 7.6, 1H), 7.61-7.76 (m, 6H), 7.79 (dd, J = 2.9, 7.7 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 31.30 (3C), 35.22 (1C), 121.03 (d, J = 10.8 Hz, 1C), 121.05 (d, J = 9.6 Hz, 1C), 126.73 (d, J = 10.0 Hz, 1C), 128.84 (d, J = 12.4 Hz, 2C), 129.14 (d, J = 11.1 Hz, 1C), 129.95 (d, J = 9.5 Hz, 1C), 130.88 (d, J = 2.1 Hz, 1C), 131.18 (d, J = 102.3 Hz, 1C), 131.22 (d, J = 10.9 Hz, 2C), 132.21 (d, J = 2.8 Hz, 1C), 132.64 (d, J = 106.4 Hz, 1C), 133.14 (d, J = 106.5 Hz, 1C), 133.44 (d, J = 2.1 Hz, 1C), 139.39 (d, J = 21.9 Hz, 1C), 141.95 (d, J = 21.7 Hz, 1C), 153.25 (d, J = 10.2 Hz, 1C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 34.28; HRMS (APCI)

[2] Unoh, Y.; Satoh, T.; Hirano, K.; Miura, M. *ACS Catal.* **2015**, *5*, 6634.

m/z $(M+H)^+$ calcd for $C_{22}H_{22}OP$: 333.1408, found: 333.1403.

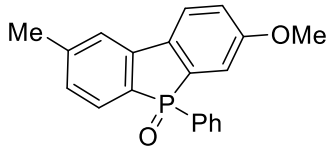


1-Methyl-5-phenylbenzo[*b*]phosphindole 5-oxide (2h): 21 mg (72%); white solid; m.p. 170-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (s, 3H), 7.29 (ddd, J = 7.4, 7.4, 3.5 Hz, 1H), 7.36-7.40 (m, 4H), 7.46-7.50 (m, 1H), 7.58-7.67 (m, 4H), 7.76 (ddd, J = 10.5, 7.4, 0.7 Hz, 1H), 7.79 (dd, J = 8.0, 3.5 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 23.06 (1C), 125.48 (d, J = 9.2 Hz, 1C), 127.91 (d, J = 9.6 Hz, 1C), 128.74 (d, J = 11.0 Hz, 1C), 128.80 (d, J = 12.5 Hz, 2C), 129.13 (d, J = 12.1 Hz, 1C), 130.28 (d, J = 9.4 Hz, 1C), 131.21 (d, J = 103.3 Hz, 1C), 131.23 (d, J = 10.8 Hz, 2C), 132.19 (d, J = 2.9 Hz, 1C), 133.42 (d, J = 2.2 Hz, 1C), 133.76 (d, J = 104.3 Hz, 1C), 133.96 (d, J = 106.0 Hz, 1C), 135.04 (d, J = 9.9 Hz, 1C), 136.98 (d, J = 2.1 Hz, 1C), 139.86 (d, J = 21.5 Hz, 1C), 143.240 (d, J = 21.6 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 32.58; HRMS (EI^+) m/z (M^+) calcd for $C_{19}H_{15}OP$: 290.0861, found: 290.0864.

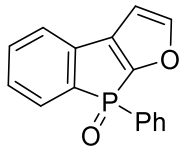


9-Phenyltribenzo[*b*,*e*,*g*]phosphindole 9-oxide (2i): 31 mg (83%); white solid; m.p. 192-193 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.38 (m, 2H), 7.43-7.47 (m, 2H), 7.54-7.58 (m, 1H), 7.63-7.70 (m, 2H), 7.72-7.86 (m, 5H), 8.30 (d, J = 8.0 Hz, 1H), 8.54 (dd, J = 8.0, 3.5 Hz, 1H), 8.68 (d, J = 8.4 Hz, 1H), 8.82-8.84 (m, 1H), 8.99-9.01 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 123.17 (1C), 124.22 (1C), 125.71 (d, J = 10.8 Hz, 1C), 125.95 (1C), 127.19 (d, J = 5.6 Hz,1C), 127.55 (1C), 127.99 (1C), 128.15 (d, J = 11.8 Hz, 1C), 128.19 (1C), 128.70 (1C), 128.99 (d, J = 12.4 Hz, 2C), 129.05 (d, J = 11.1 Hz, 1C), 129.45 (d, J = 8.9 Hz, 1C), 130.26 (d, J = 9.9 Hz, 1C), 130.32 (d, J = 111.0 Hz, 1C), 130.79 (1C), 131.00 (d, J = 101.6 Hz, 1C), 131.22 (d, J = 10.8 Hz, 2C), 132.29 (d, J = 2.8 Hz, 1C), 133.22 (d, J = 2.0 Hz, 1C), 134.09 (d, J = 1.5 Hz, 1C), 134.84 (d, J = 105.8 Hz, 1C), 139.62 (d, J = 19.7 Hz, 1C), 142.67 (d, J = 23.2 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 33.90; HRMS (EI^+) m/z (M^+) calcd

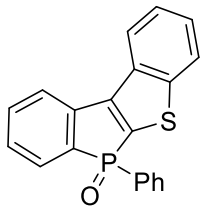
for $C_{26}H_{17}OP$: 376.1017, found: 376.1016.



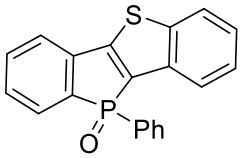
7-Methoxy-2-methyl-5-phenylbenzo[*b*]phosphindole 5-oxide (2j): 24 mg (76%); white solid; m.p. 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 3.80 (s, 3H), 7.08 (ddd, J = 8.5, 2.5, 0.7 Hz, 1H), 7.19 (dd, J = 10.9, 2.5 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H), 7.38-7.42 (m, 2H), 7.46-7.52 (m, 2H), 7.60 (dd, J = 7.8, 3.2 Hz, 1H), 7.64-7.69 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.34 (1C), 55.77 (1C), 114.01 (d, J = 10.9 Hz, 1C), 120.04 (d, J = 2.1 Hz,1C), 120.43 (d, J = 10.9 Hz, 1C), 122.25 (d, J = 12.1 Hz, 1C), 128.86 (d, J = 12.4 Hz, 2C), 130.46 (d, J = 9.6 Hz, 1C), 131.21 (d, J = 10.8 Hz, 2C), 131.22 (d, J = 102.0 Hz, 1C), 132.24 (d, J = 2.9 Hz, 1C), 132.64 (d, J = 107.1 Hz, 1C), 134.30 (d, J = 2.1 Hz, 1C), 134.52 (d, J = 105.7 Hz, 1C), 134.79 (d, J = 21.3 Hz, 1C), 138.52 (d, J = 11.0 Hz, 1C), 139.48 (d, J = 21.3 Hz, 1C), 160.61 (d, J = 13.8 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 33.68; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{20}H_{18}O_2P$: 321.1039, found: 321.1043.



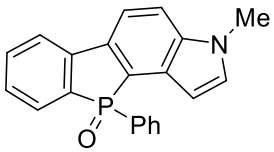
8-Phenylphosphindolo[2,3-*b*]furan 8-oxide (2m): 19 mg (73%); pale yellow solid; m.p. 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (dd, J = 1.7, 1.0 Hz, 1H), 7.29-7.33 (m, 1H), 7.41-7.44 (m, 1H), 7.45-7.49 (m, 2H), 7.50-7.60 (m, 3H), 7.71-7.75 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 105.81 (d, J = 8.4 Hz, 1C), 121.68 (d, J = 7.4 Hz, 1C), 128.75 (d, J = 12.0 Hz, 1C), 128.92 (d, J = 110.9 Hz, 1C), 129.09 (d, J = 13.2 Hz, 2C), 130.26 (d, J = 10.4 Hz, 1C), 131.36 (d, J = 11.4 Hz, 2C), 132.80 (d, J = 2.9 Hz, 1C), 133.13 (d, J = 1.9 Hz, 1C), 133.24 (d, J = 12.5 Hz, 1C), 135.42 (d, J = 113.0 Hz, 1C), 142.21 (d, J = 33.3 Hz, 1C), 152.45 (d, J = 132.1 Hz, 1C), 153.30 (d, J = 6.6 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 12.25; HRMS (EI^+) m/z (M^+) calcd for $C_{16}H_{11}O_2P$: 266.0497, found: 266.0499.



6-Phenylbenzo[*b*]phosphindolo[3,2-*d*]thiophene 6-oxide (2o): 28 mg (85%); white solid; m.p. 170-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.43 (m, 3H), 7.48-7.63 (m, 4H), 7.67-7.76 (m, 3H), 7.95 (d, J = 8.0 Hz, 1H), 8.04 (dd, J = 7.7, 3.5 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 121.76 (d, J = 9.8 Hz, 1C), 123.97 (1C), 124.31 (d, J = 1.4 Hz, 1C), 125.81 (1C), 126.80 (1C), 128.39 (d, J = 11.8 Hz, 1C), 129.06 (d, J = 13.0 Hz, 2C), 130.03 (d, J = 108.6 Hz, 1C), 130.23 (d, J = 10.2 Hz, 1C), 131.31 (d, J = 11.1 Hz, 2C), 132.71 (d, J = 2.9 Hz, 1C), 133.31 (d, J = 2.0 Hz, 1C), 133.49 (d, J = 11.8 Hz, 1C), 134.35 (d, J = 106.1 Hz, 1C), 137.32 (d, J = 109.1 Hz, 1C), 139.23 (d, J = 18.4 Hz, 1C), 146.90 (d, J = 21.8 Hz, 1C), 148.67 (d, J = 5.3 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 26.48; HRMS (EI$^+$) m/z (M^+) calcd for $C_{20}H_{13}OPS$: 332.0425, found: 332.0425.

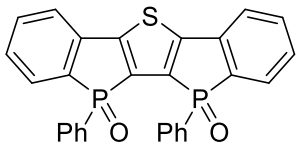


10-Phenylbenzo[*b*]phosphindolo[2,3-*d*]thiophene 10-oxide (2p): 28 mg (84%); pale yellow solid; m.p. 61-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.43 (m, 5H), 7.49-7.54 (m, 3H), 7.68 (dd, J = 10.3, 7.4 Hz, 1H), 7.74-7.81 (m, 3H), 7.86-7.88 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 122.08 (d, J = 8.8 Hz, 1C), 123.56 (d, J = 4.1 Hz, 2C), 125.62 (1C), 126.16 (1C), 129.09 (d, J = 12.6 Hz, 2C), 129.64 (d, J = 11.3 Hz, 1C), 129.69 (d, J = 9.8 Hz, 1C), 129.94 (d, J = 105.7 Hz, 1C), 130.74 (d, J = 107.9 Hz, 1C), 131.07 (d, J = 11.1 Hz, 2C), 132.61 (d, J = 2.9 Hz, 1C), 133.27 (d, J = 1.8 Hz, 1C), 136.24 (d, J = 12.5 Hz, 1C), 136.74 (d, J = 108.8 Hz, 1C), 137.63 (d, J = 18.6 Hz, 1C), 143.34 (d, J = 12.3 Hz, 1C), 154.78 (d, J = 27.3 Hz, 1C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 25.24; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{20}H_{14}OPS$: 333.0497, found: 333.0496.



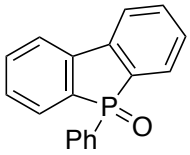
3-Methyl-10-phenyl-3*H*-phosphindolo[2,3-*e*]indole 10-oxide (2q): 17 mg (51% combined yield as a regiomixture of **2p** and **2p'**); pale yellow solid; m.p. 219-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H), 6.57 (dd, J = 3.1, 0.8 Hz, 1H), 7.10 (d, J = 3.1 Hz, 1H), 7.26-7.31 (m, 1H), 7.33-7.38 (m, 2H), 7.42-7.47 (m, 1H), 7.49-7.52 (m, 1H), 7.54 (ddd, J = 7.6, 1.3, 1.3 Hz, 1H), 7.66 (dd, J = 8.6, 2.7 Hz, 1H), 7.68-7.74 (m, 3H), 7.79 (dd, J = 7.7, 3.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 33.30 (1C),

100.70 (d, J = 2.5 Hz, 1C), 114.33 (d, J = 2.2 Hz, 1C), 114.54 (d, J = 10.8 Hz, 2C), 120.65 (d, J = 10.3 Hz, 1C), 123.22 (d, J = 108.1 Hz, 1C), 128.05 (d, J = 11.0 Hz, 1C), 128.56 (d, J = 10.5 Hz, 1C), 128.77 (d, J = 12.4 Hz, 2C), 129.87 (d, J = 9.8 Hz, 1C), 131.19 (d, J = 10.9 Hz, 1C), 131.64 (d, J = 101.0 Hz, 1C), 131.98 (d, J = 2.9 Hz, 1C), 132.38 (1C), 132.92 (d, J = 106.7 Hz, 1C), 133.22 (d, J = 1.9 Hz, 1C), 134.86 (d, J = 21.0 Hz, 1C), 137.74 (d, J = 11.9 Hz, 1C), 143.69 (d, J = 22.7 Hz, 1C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 33.69; HRMS (EI^+) m/z (M^+) calcd for $C_{21}H_{16}NOP$: 329.0970, found: 329.0965.

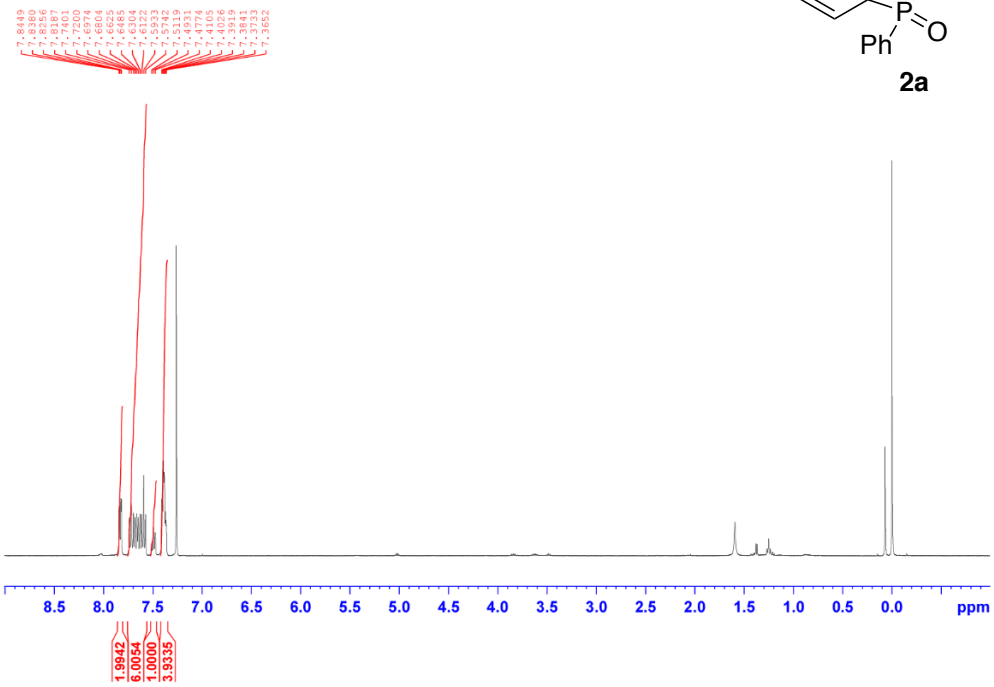


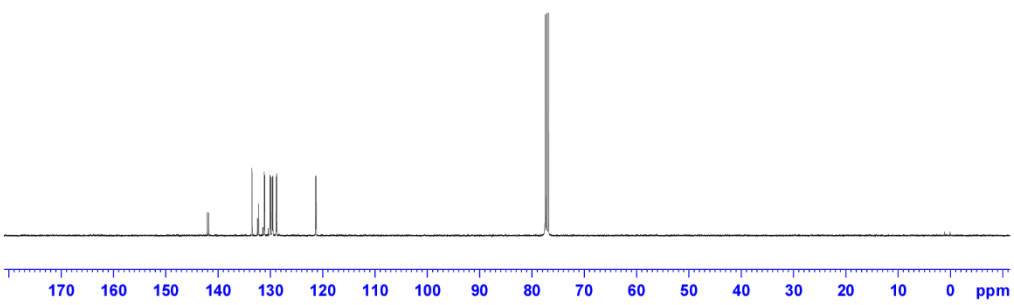
5,6-Diphenyldiphosphindolo[3,2-*b*:2',3'-*d*]thiophene 5,6-dioxide (2r, *syn* + *anti,* ca. 1:1 mixture): 32 mg (67%); pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$ + 5% D_2O): δ 7.05 (ddd, J = 7.7, 7.7, 3.2 Hz, 3H), 7.25-7.43 (m, 5H), 7.46-7.61 (m, 8H), 7.76 (dd, J = 9.9, 7.3 Hz, 1H), 7.89-7.94 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$ + 5% D_2O): δ 121.45 (d, J = 8.0 Hz, 2C), 121.53 (d, J = 8.1 Hz, 2C), 128.00 (d, J = 107.1 Hz, 2C), 128.71 (d, J = 13.1 Hz, 4C), 129.11 (d, J = 13.2 Hz, 4C), 129.38 (d, J = 11.3 Hz, 2C), 129.55 (d, J = 108.2 Hz, 2C), 129.56 (d, J = 11.6 Hz, 2C), 130.15 (d, J = 10.1 Hz, 2C), 130.31 (d, J = 9.4 Hz, 2C), 130.64 (d, J = 11.4 Hz, 4C), 131.4 (d, J = 11.5 Hz, 4C), 132.42 (d, J = 3.0 Hz, 2C), 132.96 (d, J = 2.9 Hz, 2C), 133.47 (d, J = 1.9 Hz, 2C),133.71 (d, J = 1.5 Hz, 2C), 134.84 (dd, J = 106.8, 15.0 Hz, 2C), 134.98 (d, J = 109.3 Hz, 2C), 135.03 (dd, J = 107.5, 15.1 Hz, 2C), 135.06 (d, J = 110.6 Hz, 2C), 136.97 (d, J = 2.1 Hz, 2C), 137.14 (d, J = 2.2 Hz, 2C), 156.33 (dd, J = 29.7, 13.0 Hz, 2C), 156.94 (dd, J = 28.8, 12.8 Hz, 2C); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$ + 5% D_2O): δ 23.90, 25.39; HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{28}H_{19}O_2P_2S$: 481.0575, found: 481.0575.

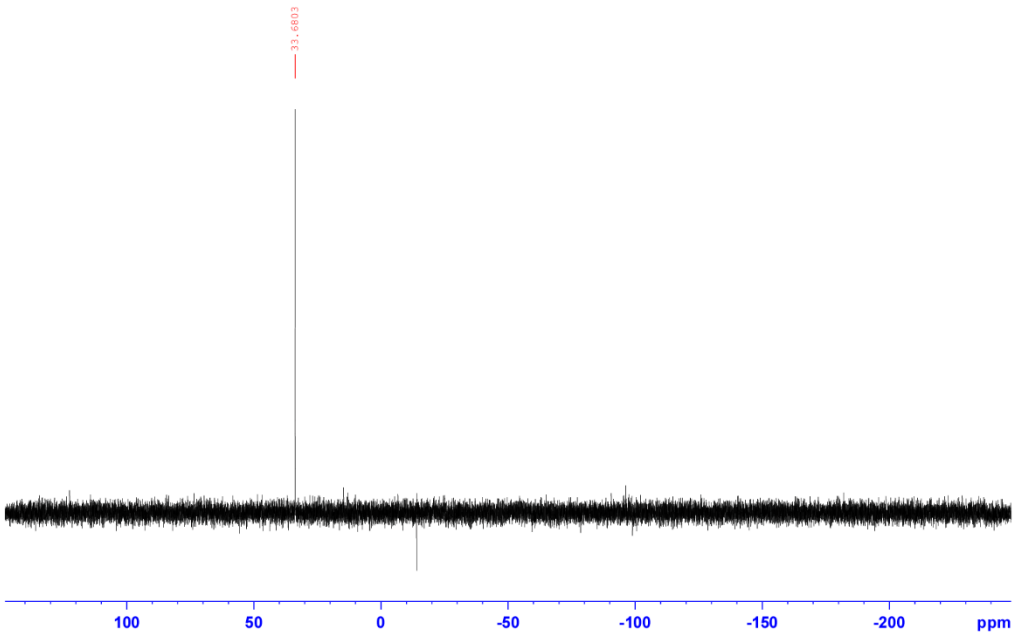
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2a**]



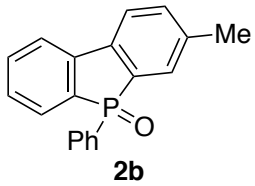
2a



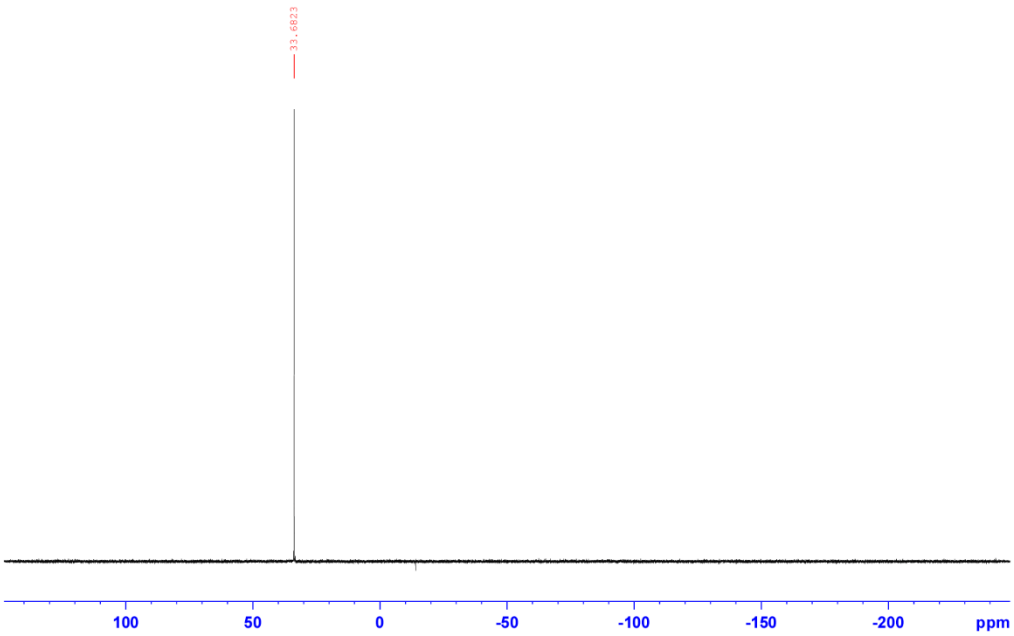



33.6803
100
50
0
-50
-100
-150
-200
ppm

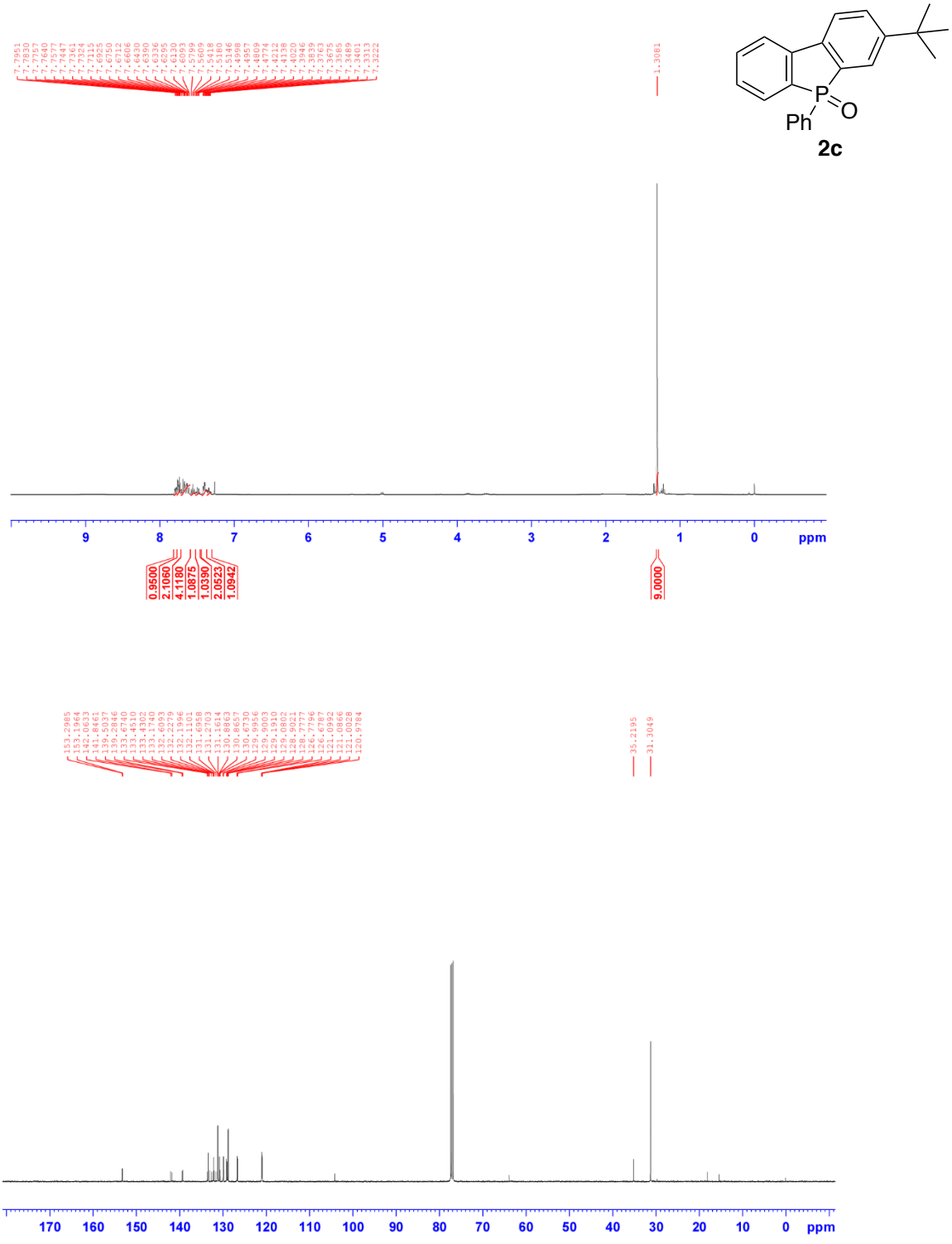
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2b**]

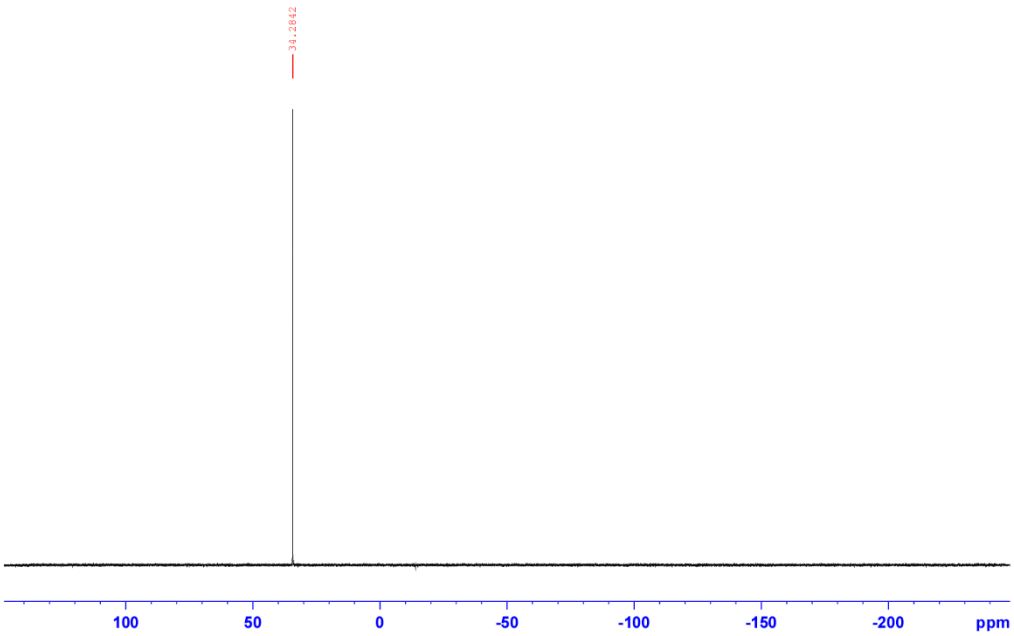


2b

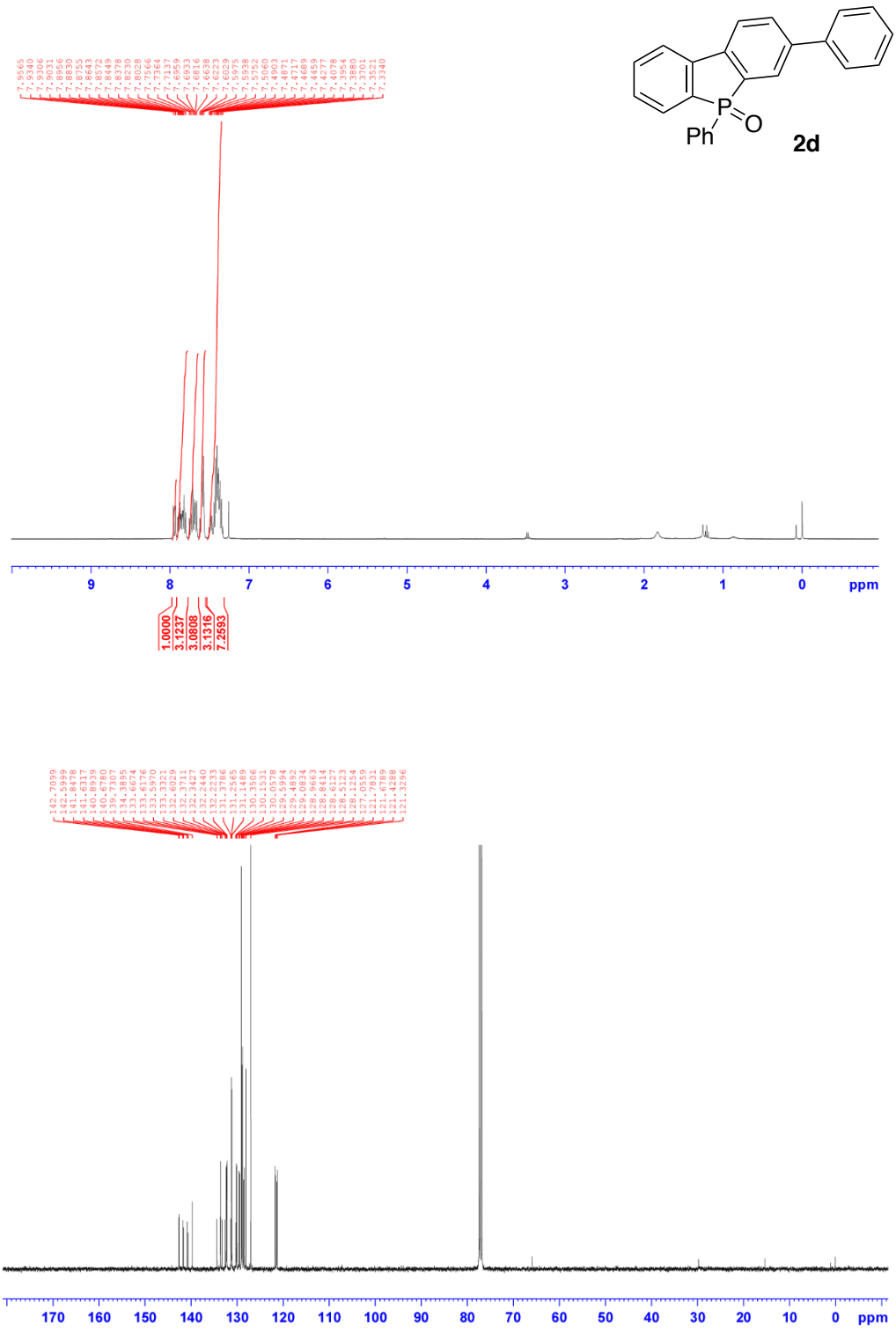

33.6823
100
50
0
-50
-100
-150
-200
ppm

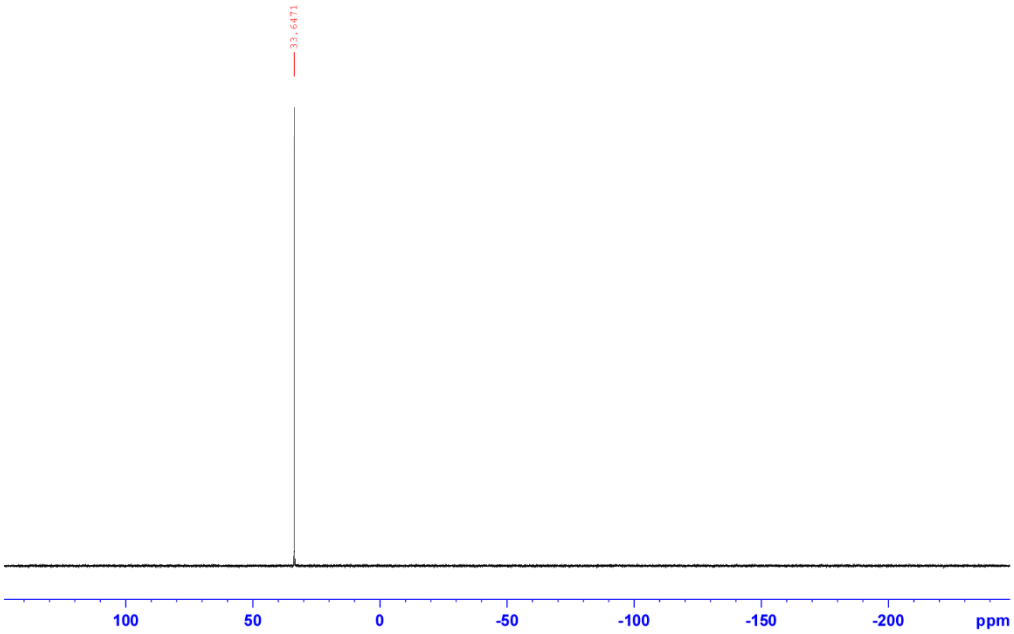
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2c**]



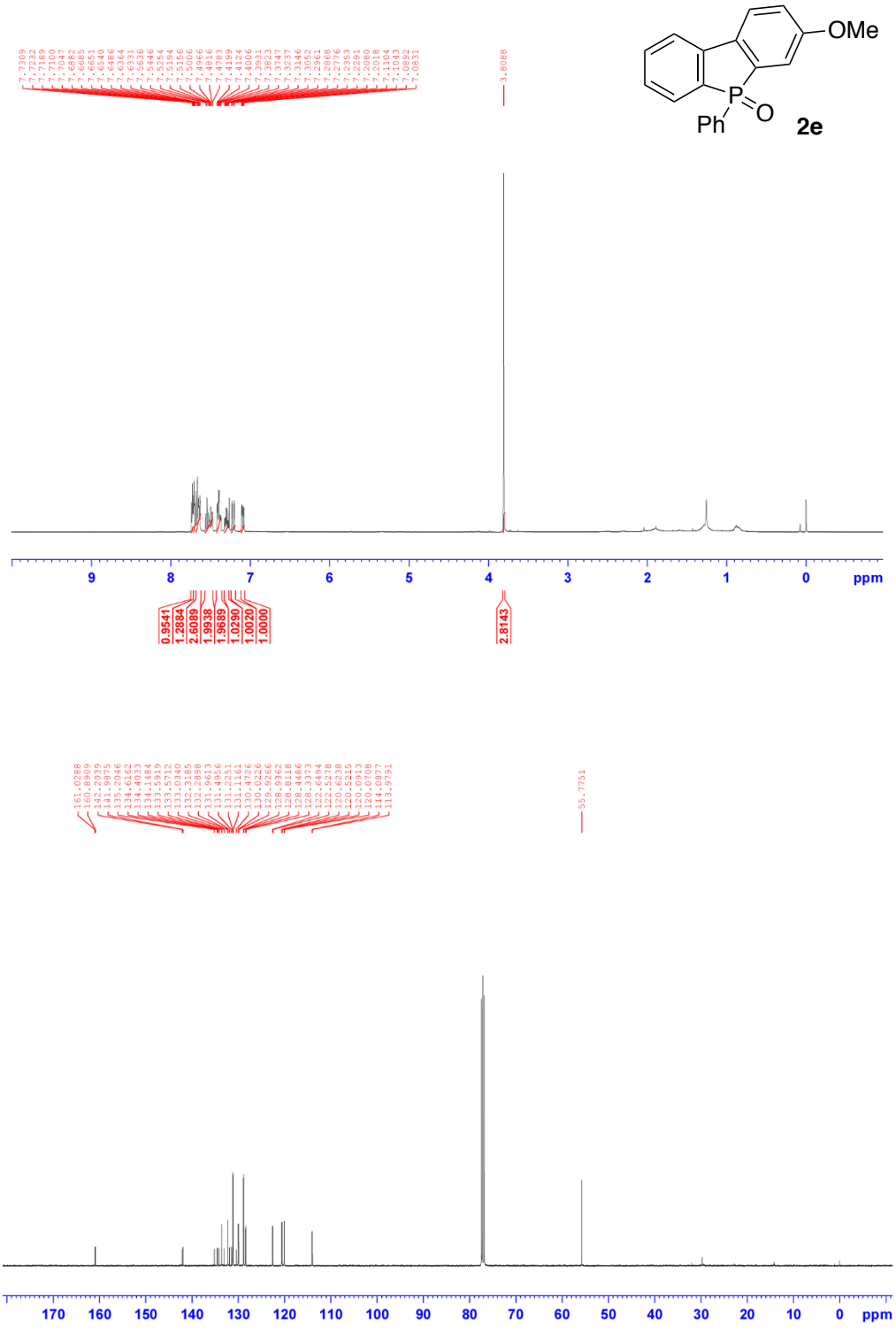

34.2842
100
50
0
-50
-100
-150
-200
ppm

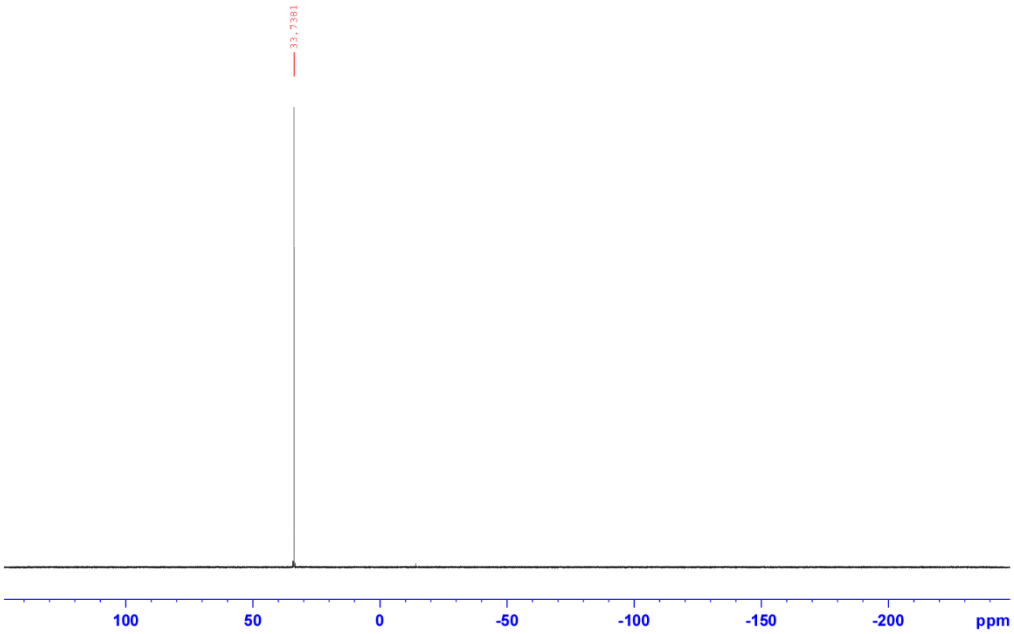
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2d**]



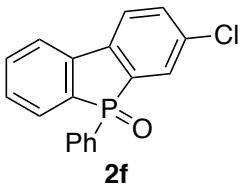

33.6471
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2e**]

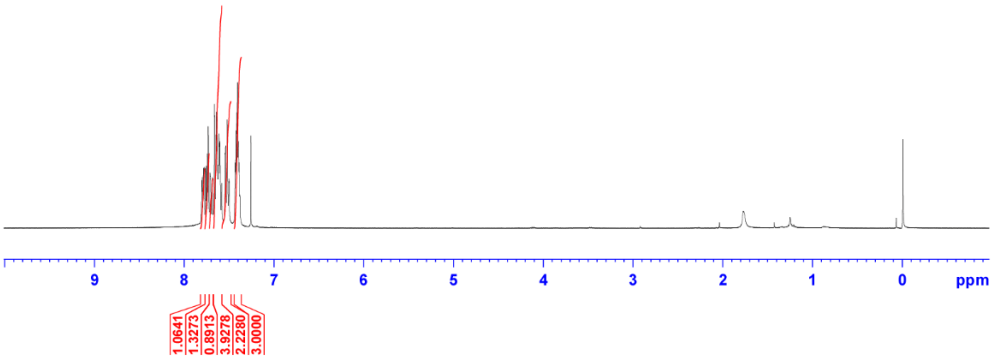


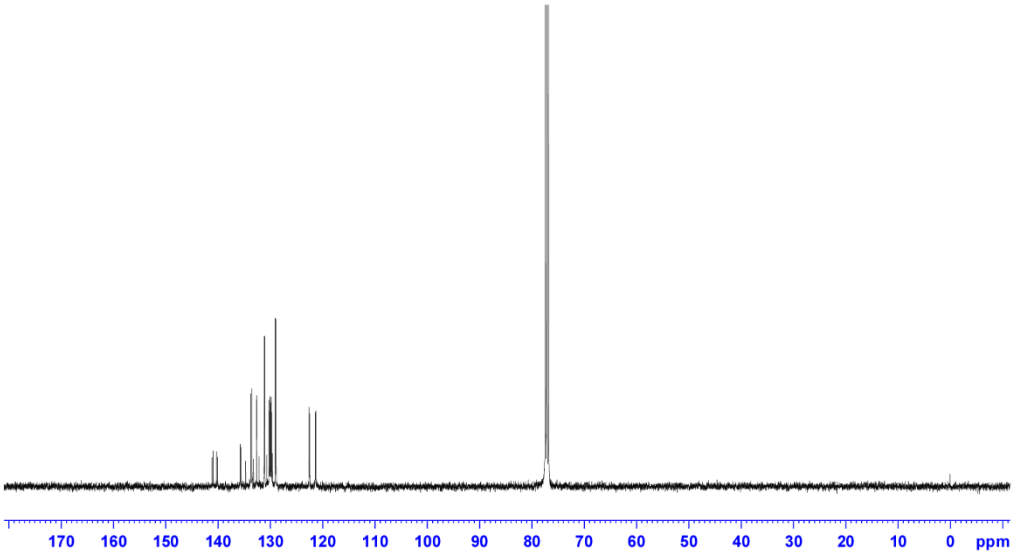

33.7381
100
50
0
-50
-100
-150
-200
ppm

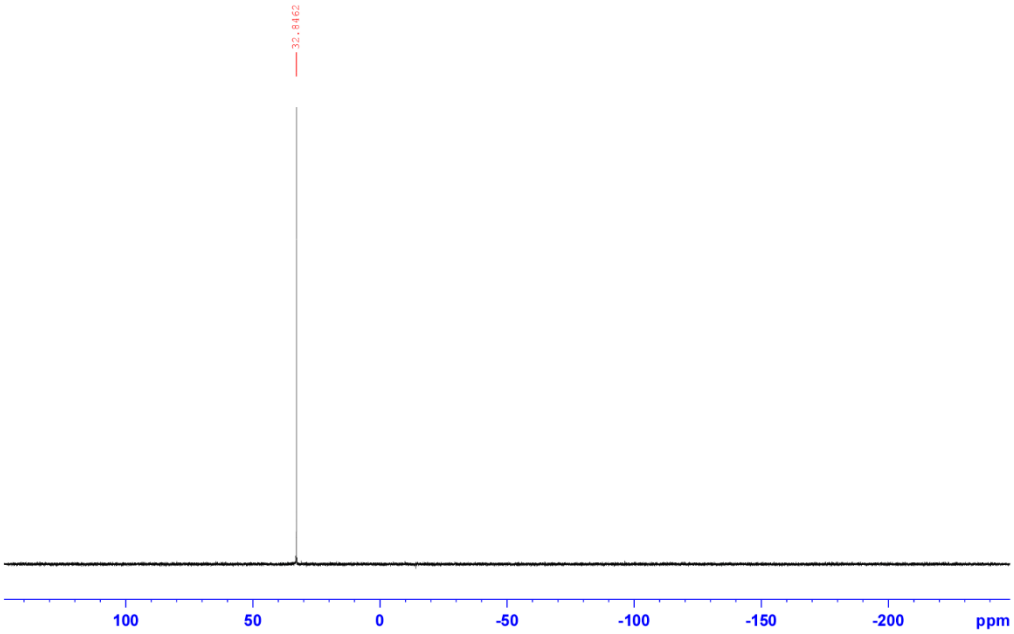
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2f**]



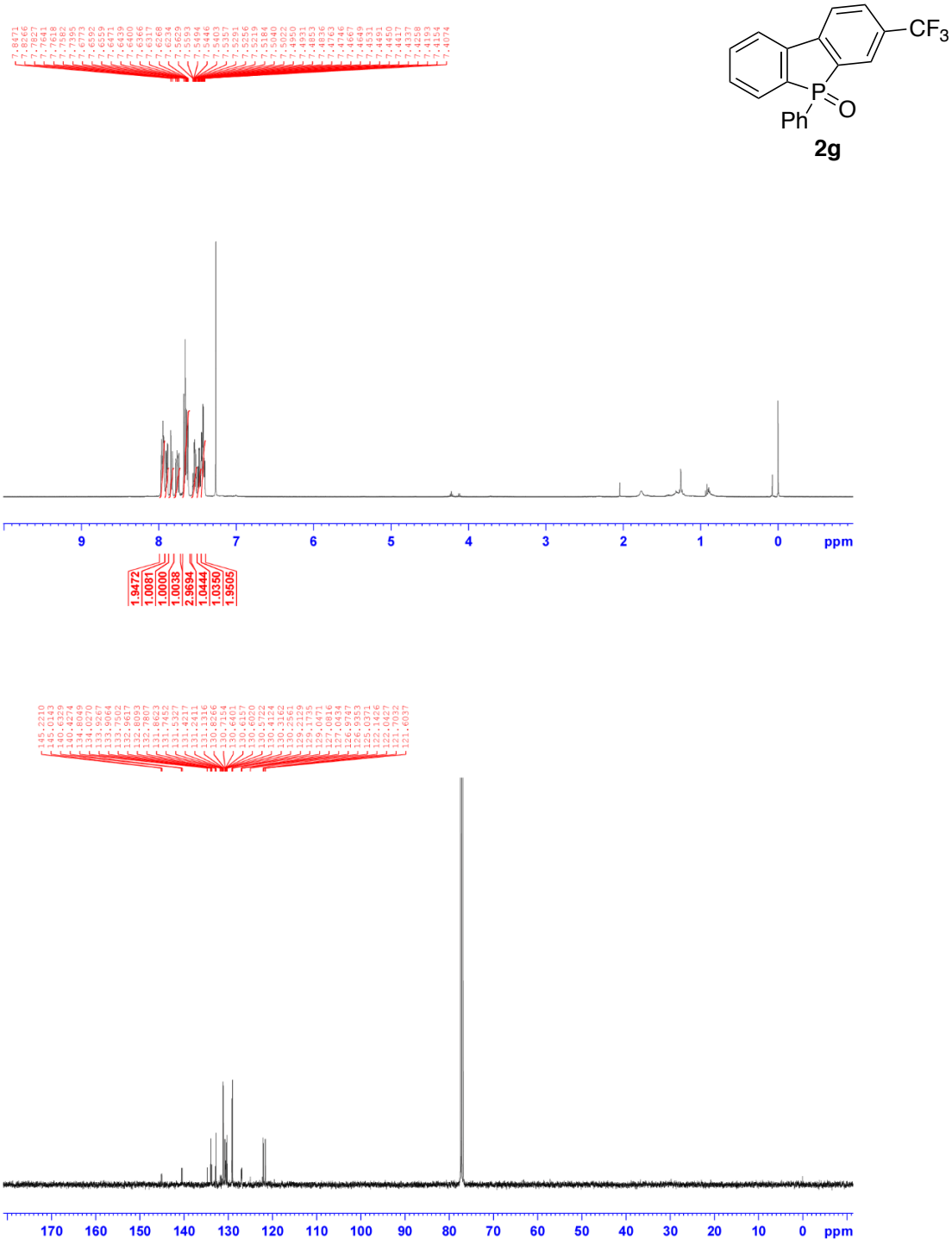
2f

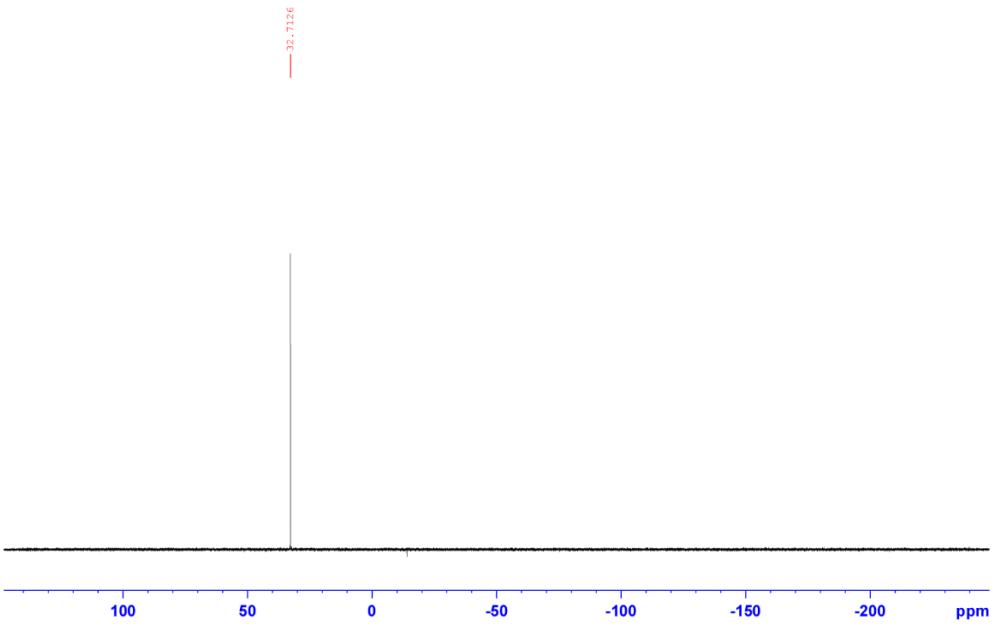




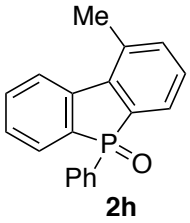

32.8462
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2g**]

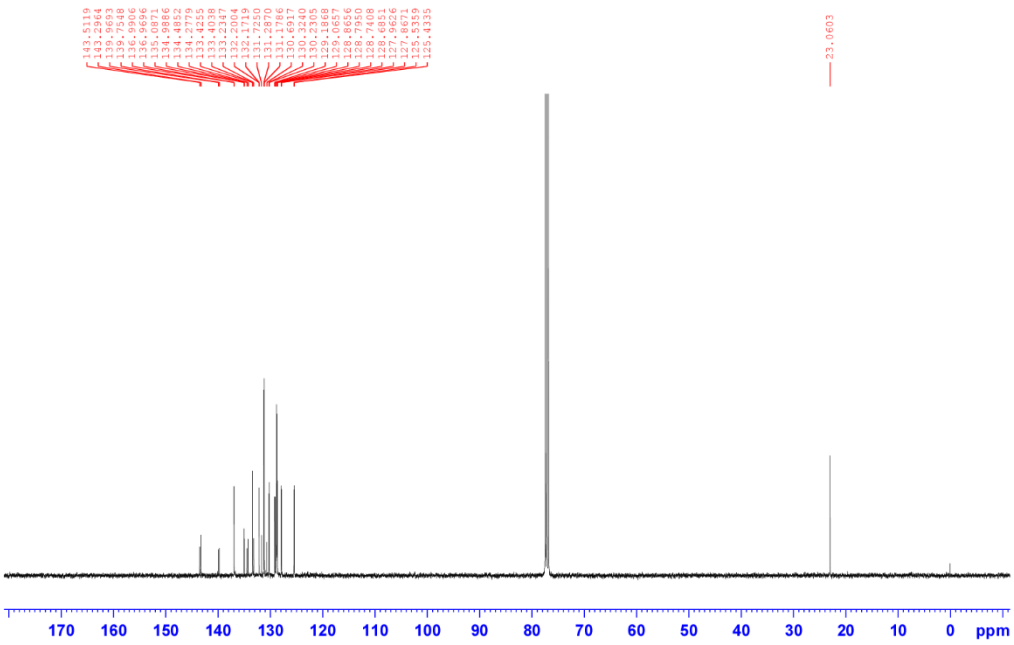


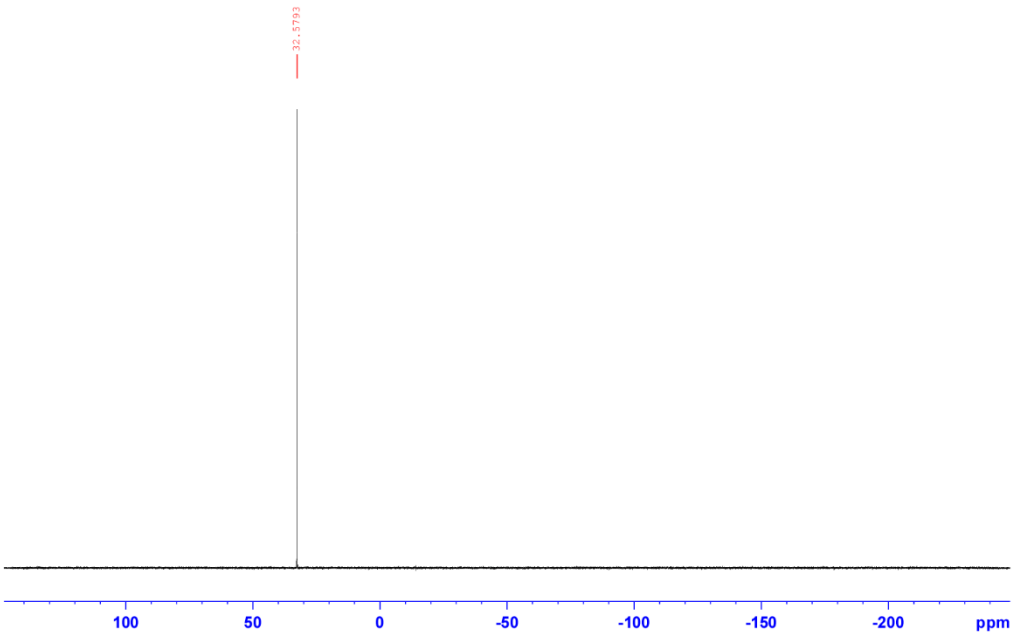

32.7126
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2h**]

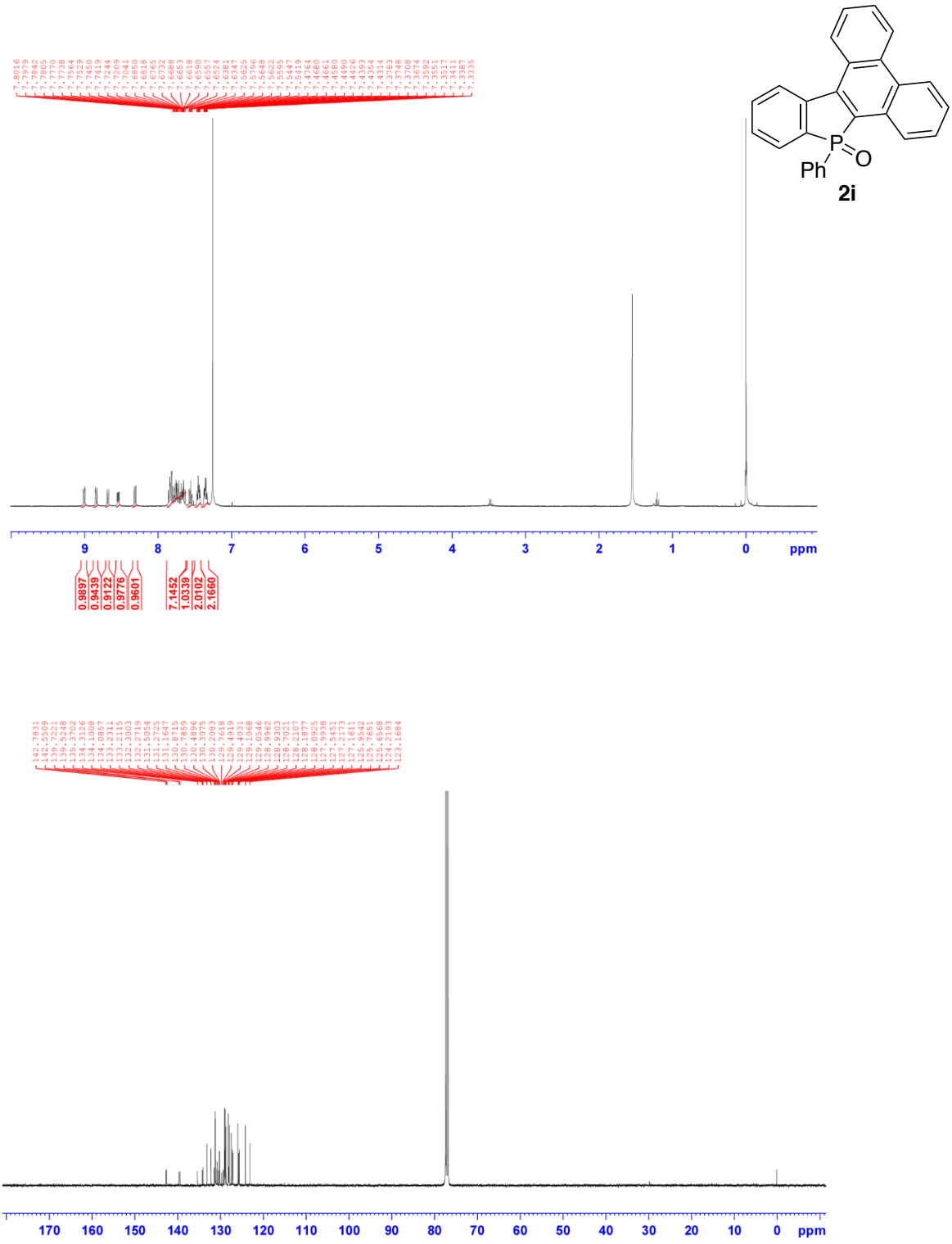


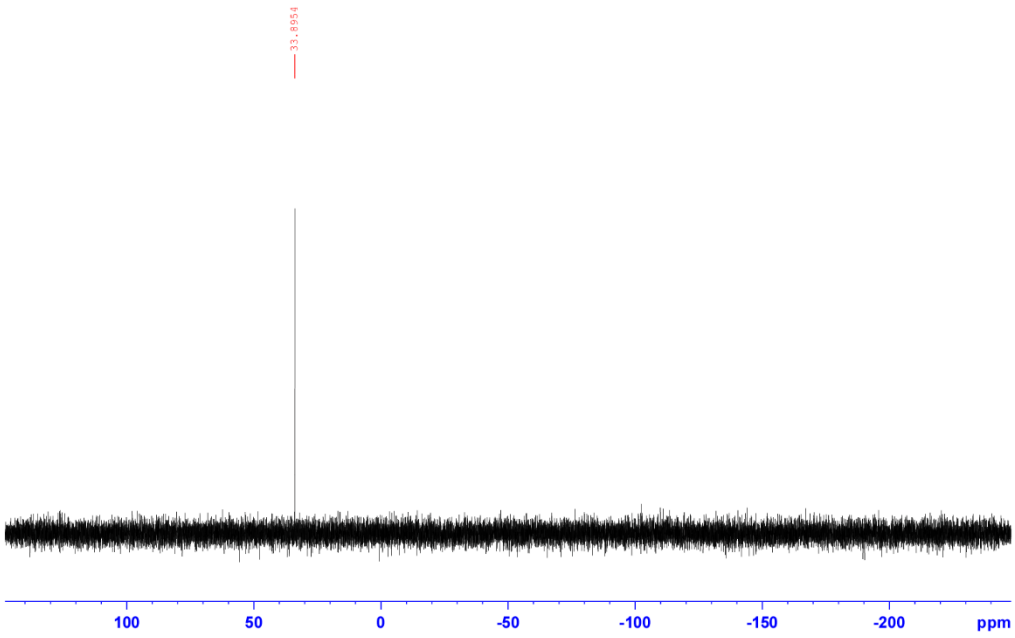
2h



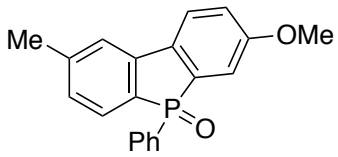

32.5793
100
50
0
-50
-100
-150
-200
ppm

[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2i**]

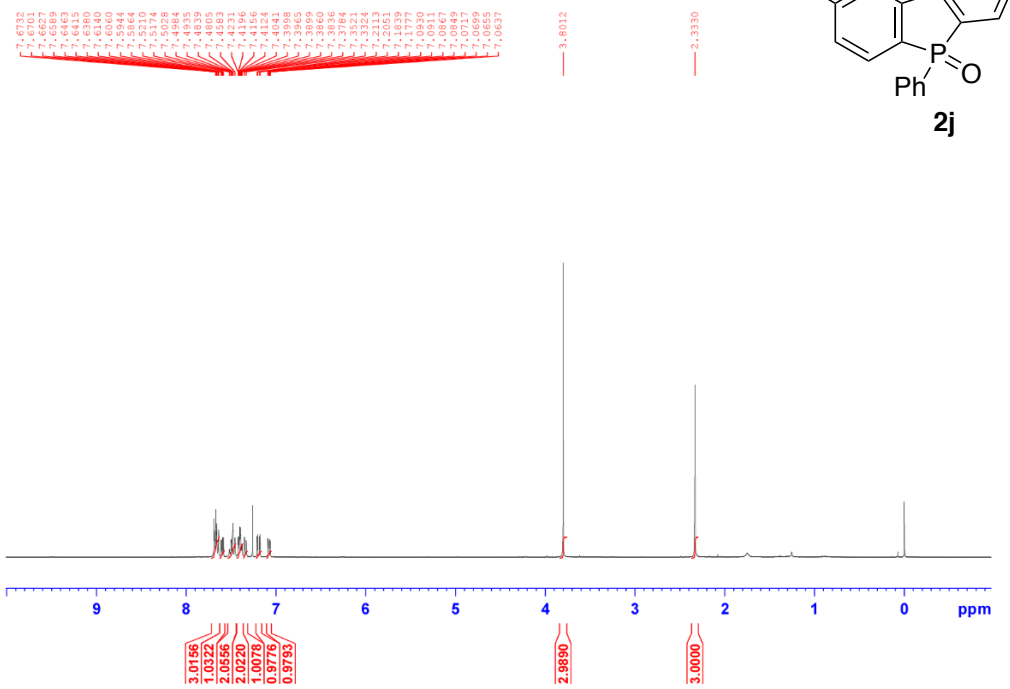


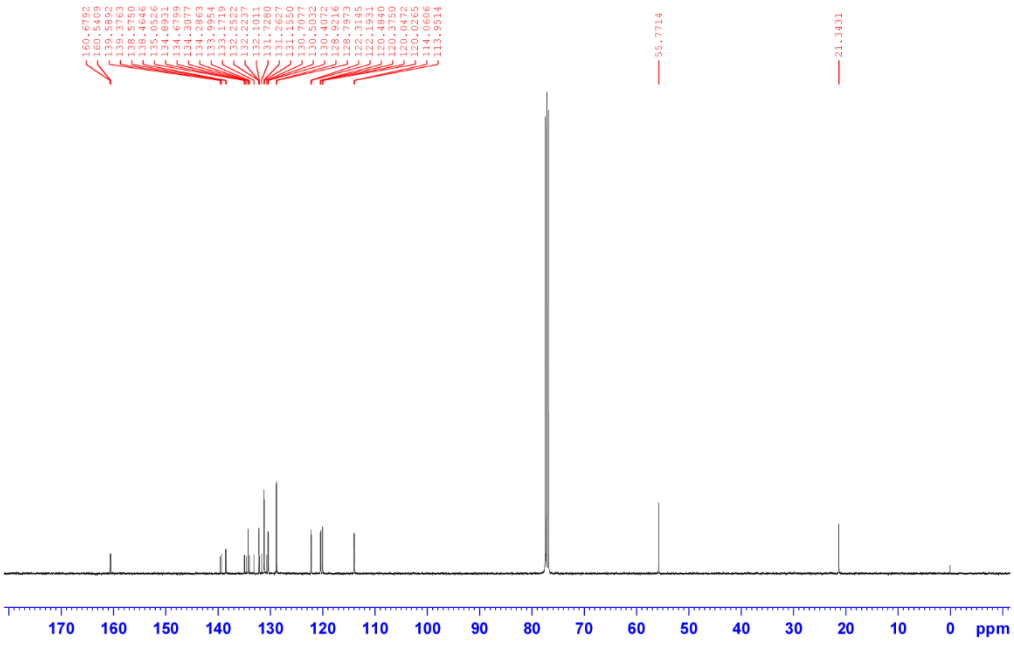

33.8954
100
50
0
-50
-100
-150
-200
ppm

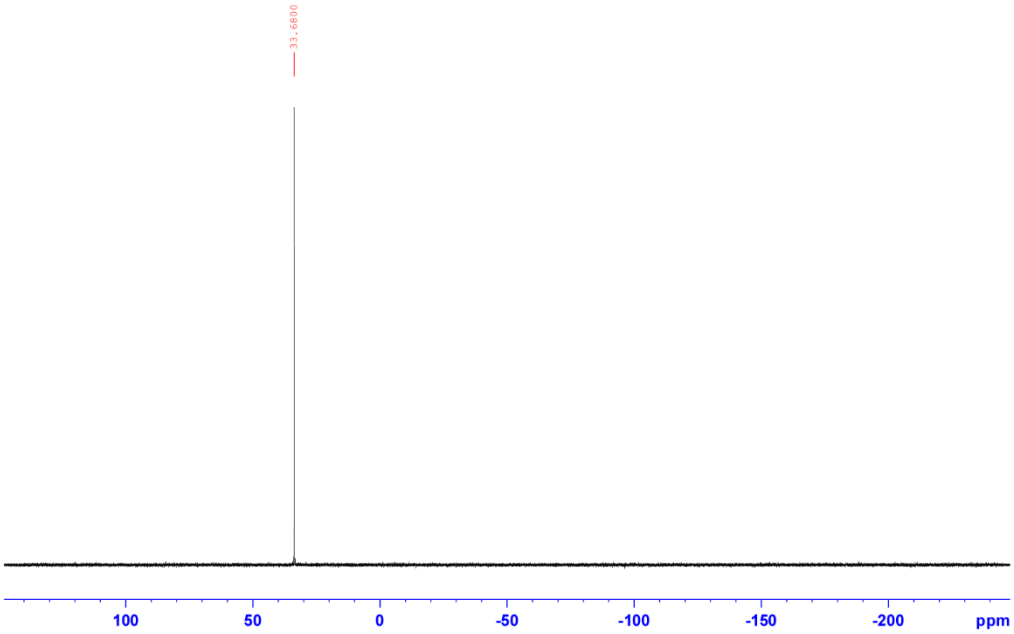
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2j**]



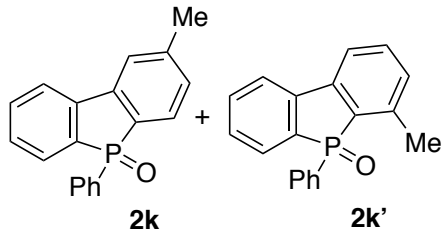
2j





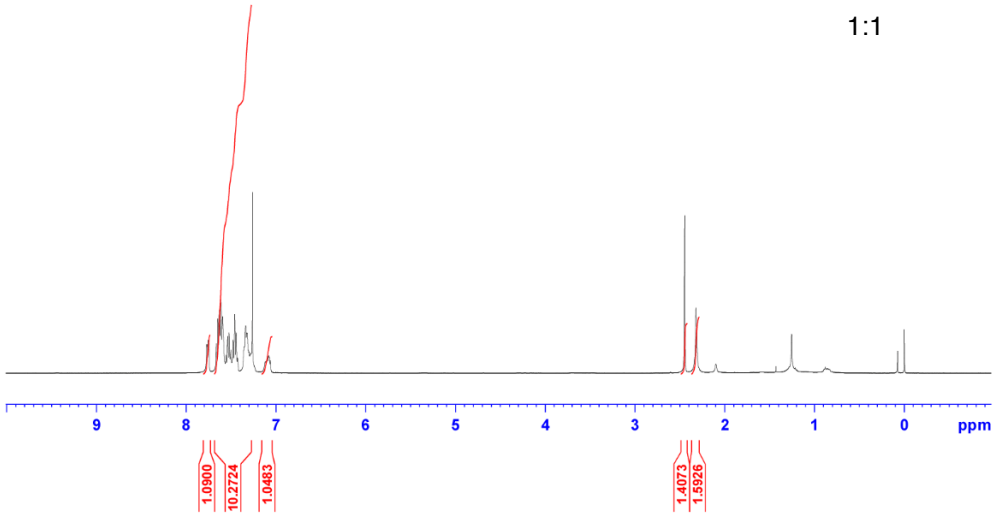

33.6800
100
50
0
-50
-100
-150
-200
ppm

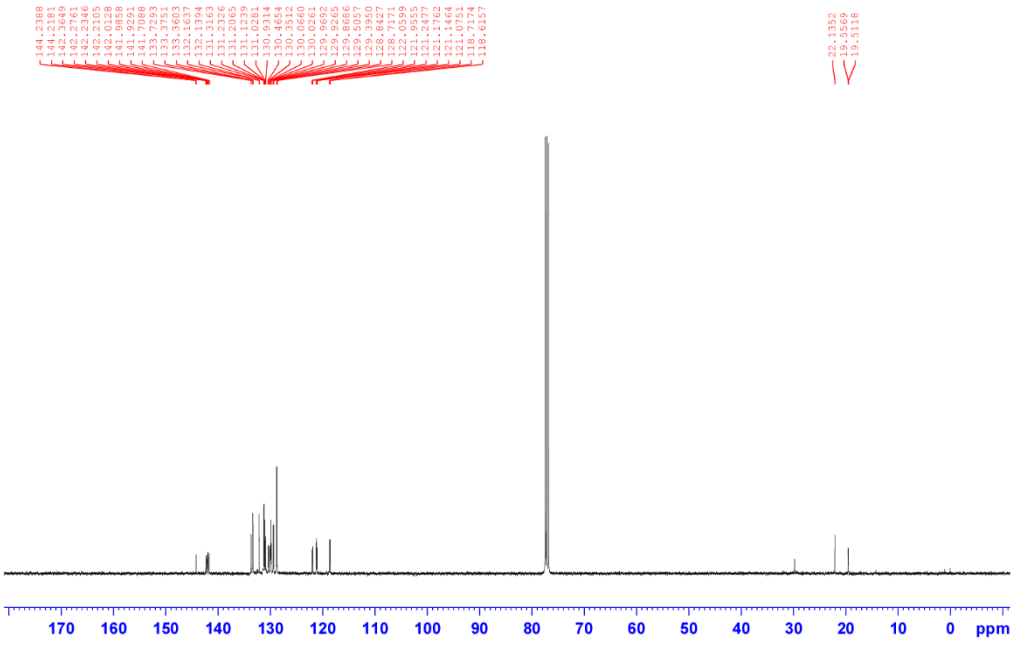
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2k** + **2k'**]

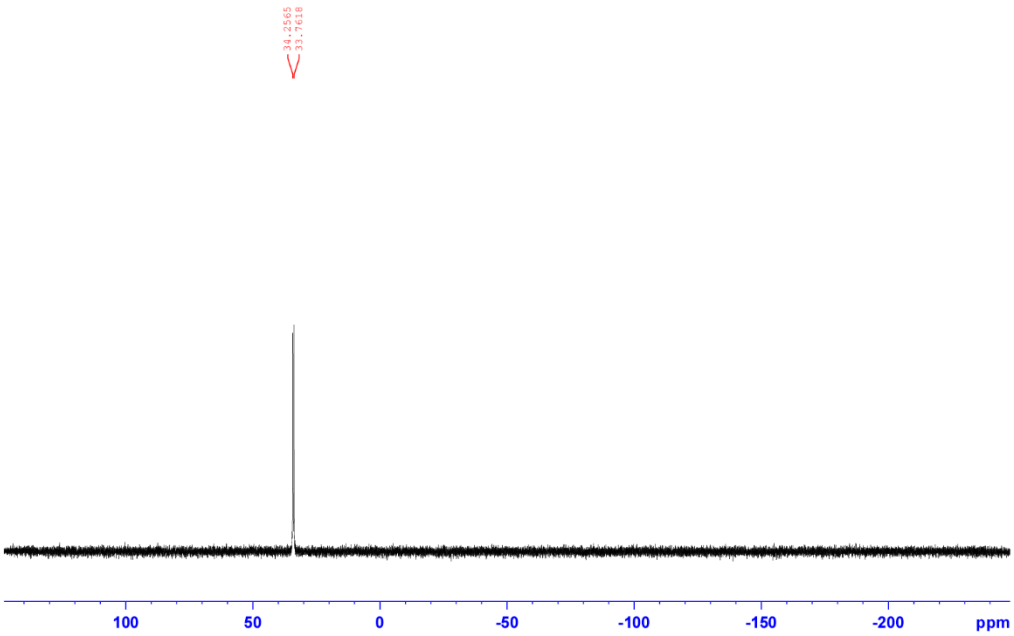


2k **2k'**

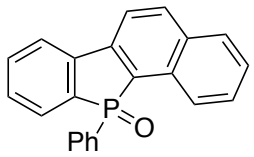
1:1



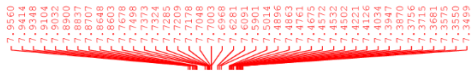


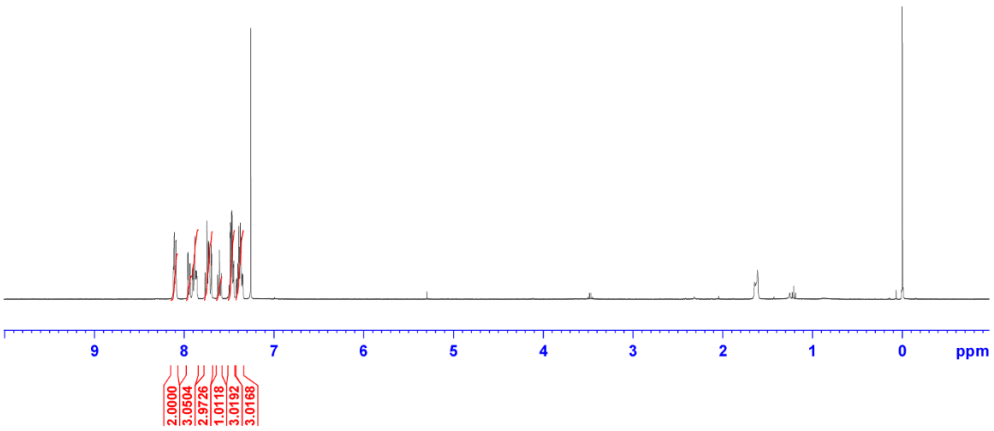

34.2565
33.7618
100
50
0
-50
-100
-150
-200
ppm

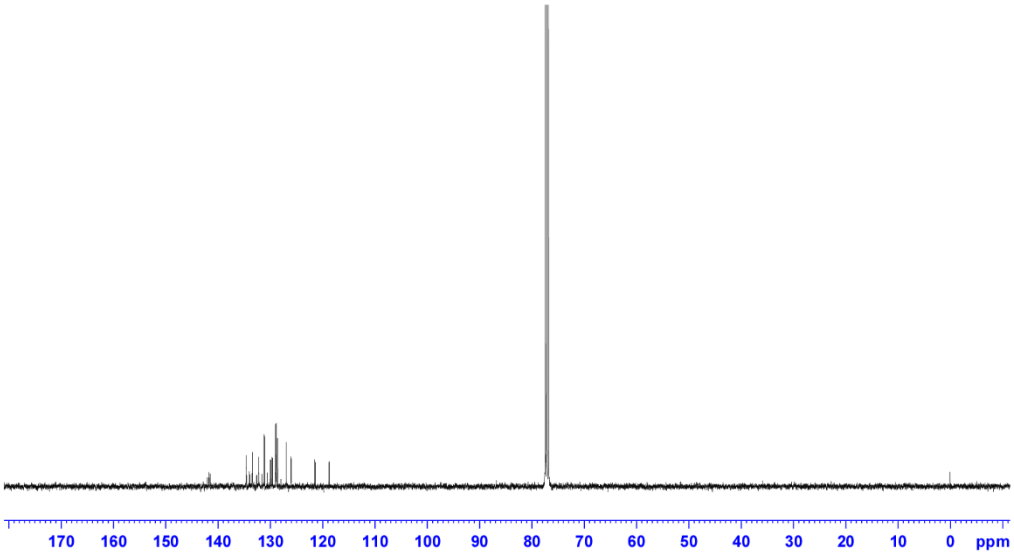
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2l**]

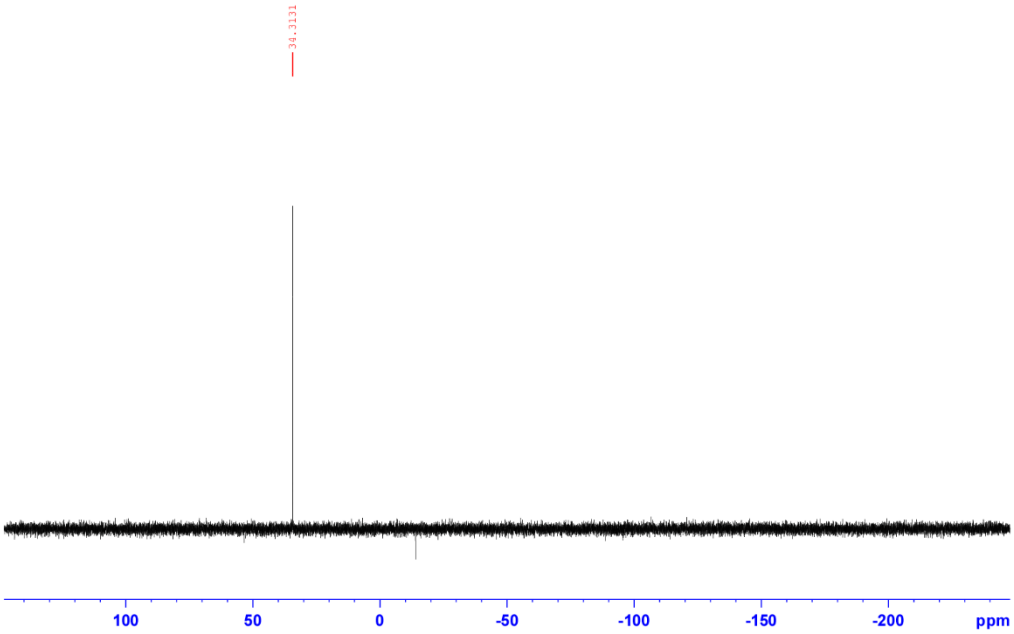


2l

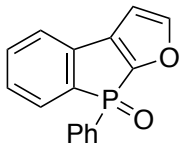




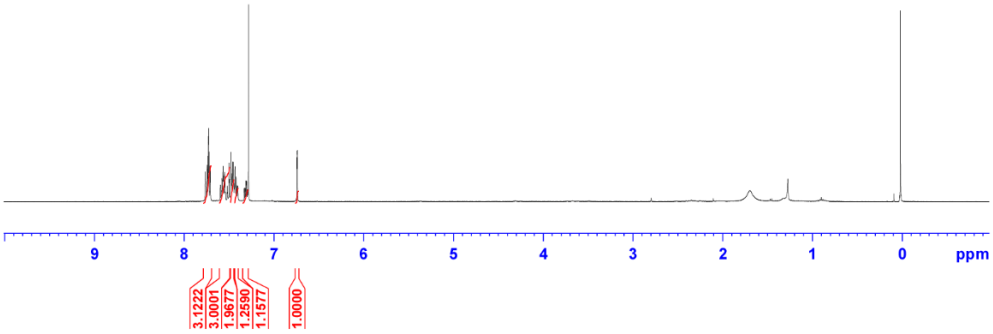


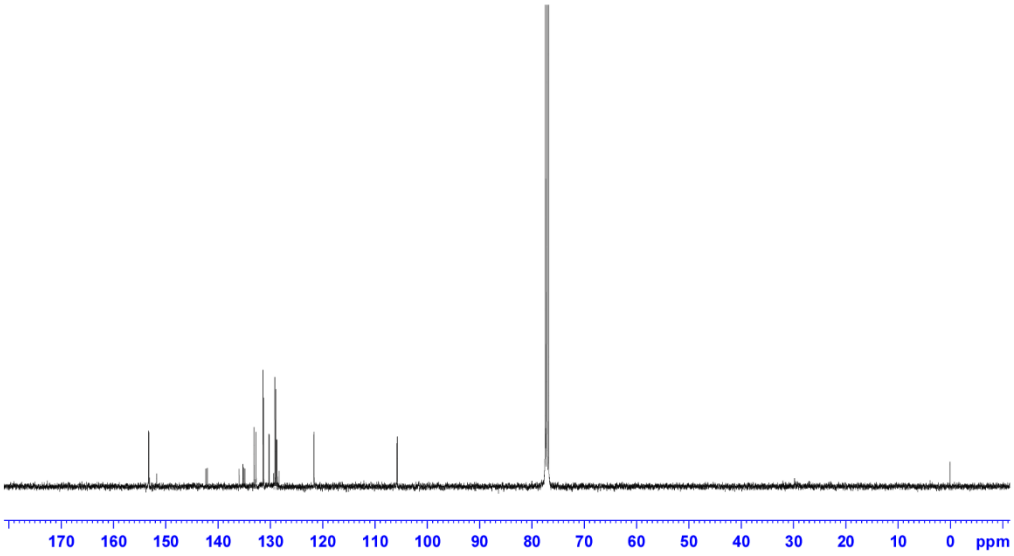

34.3131
100
50
0
-50
-100
-150
-200
ppm

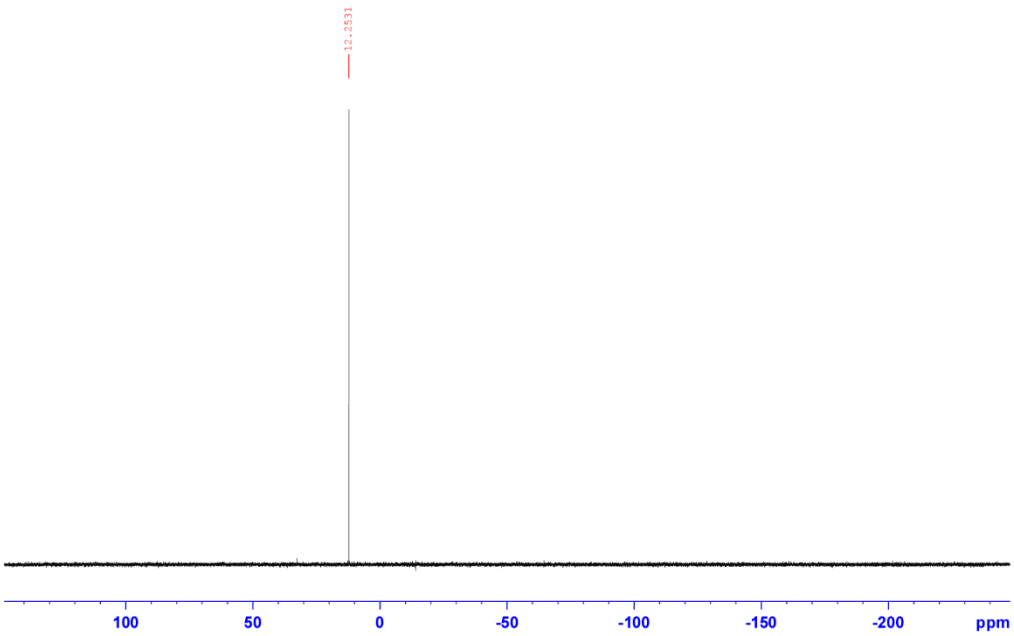
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2m**]



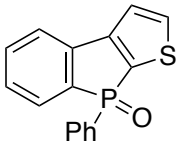
2m



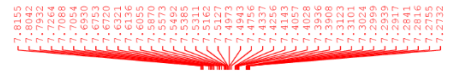


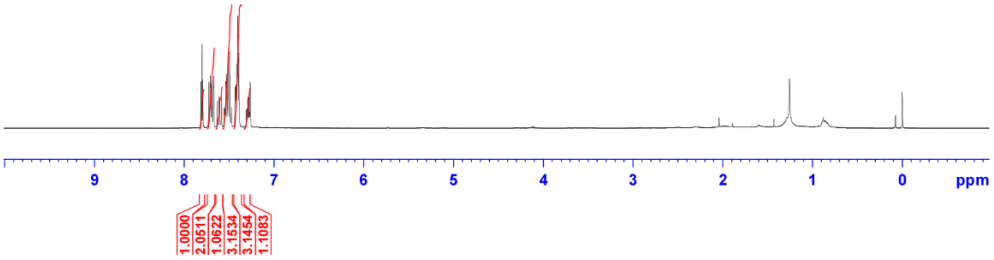

12.2531
100
50
0
-50
-100
-150
-200
ppm

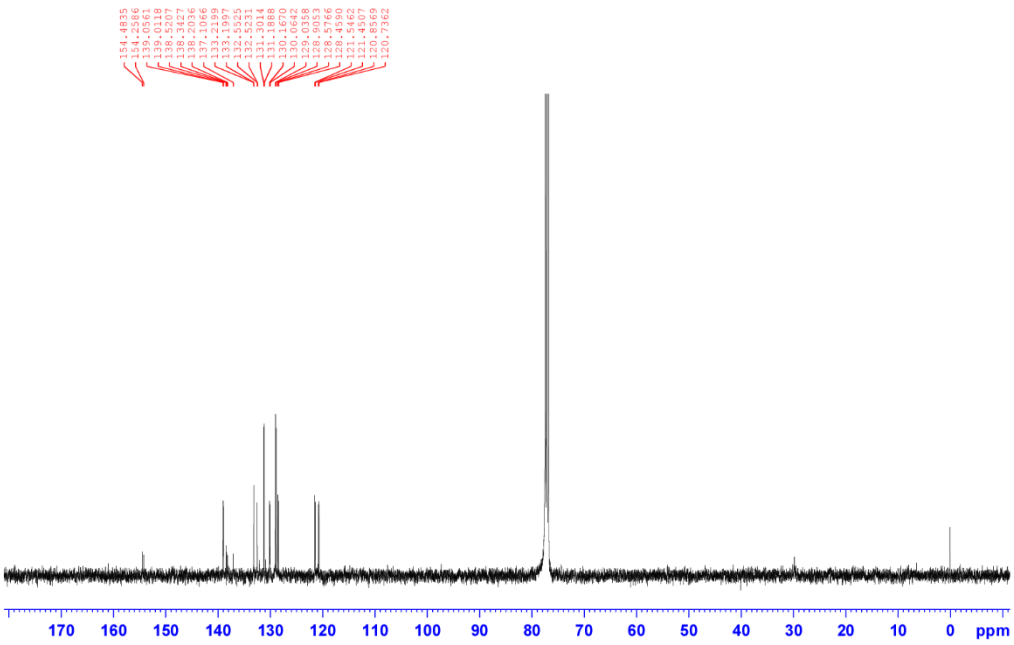
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2n**]

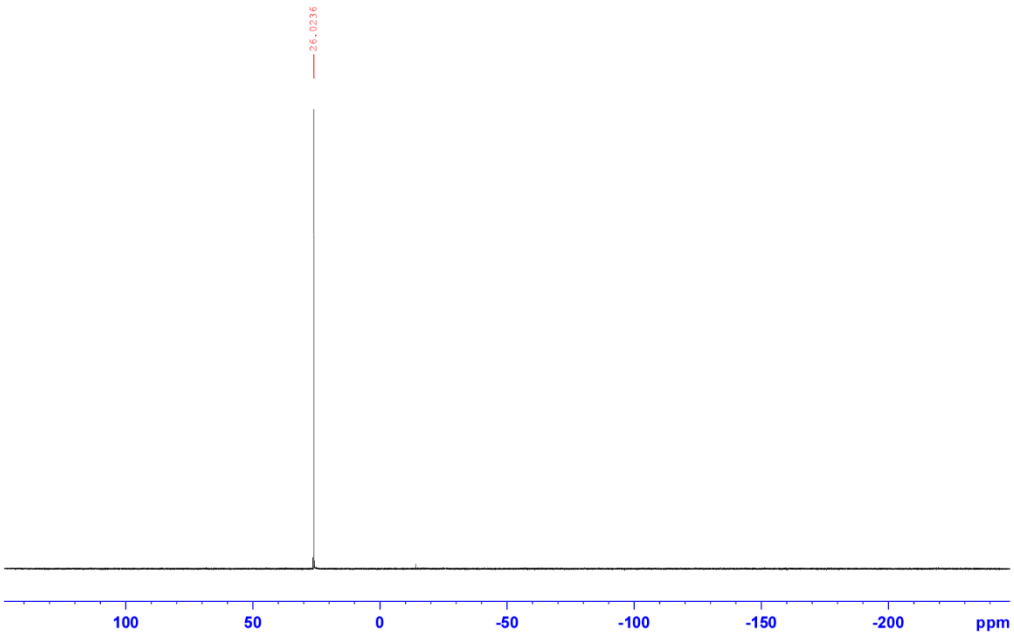


2n

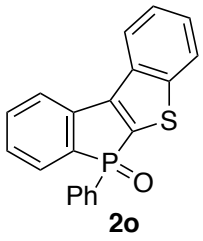




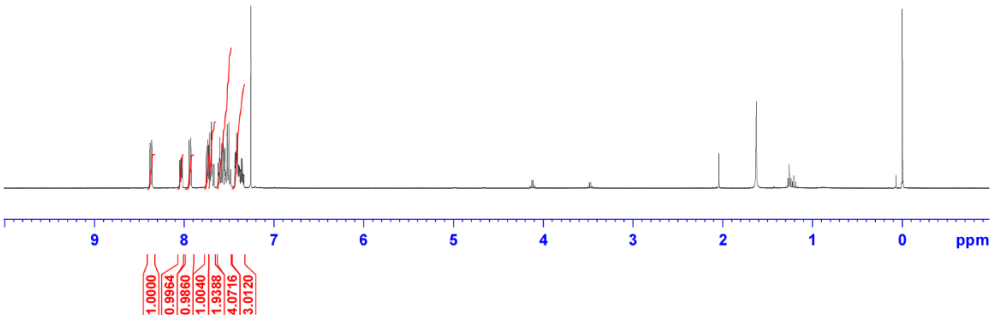


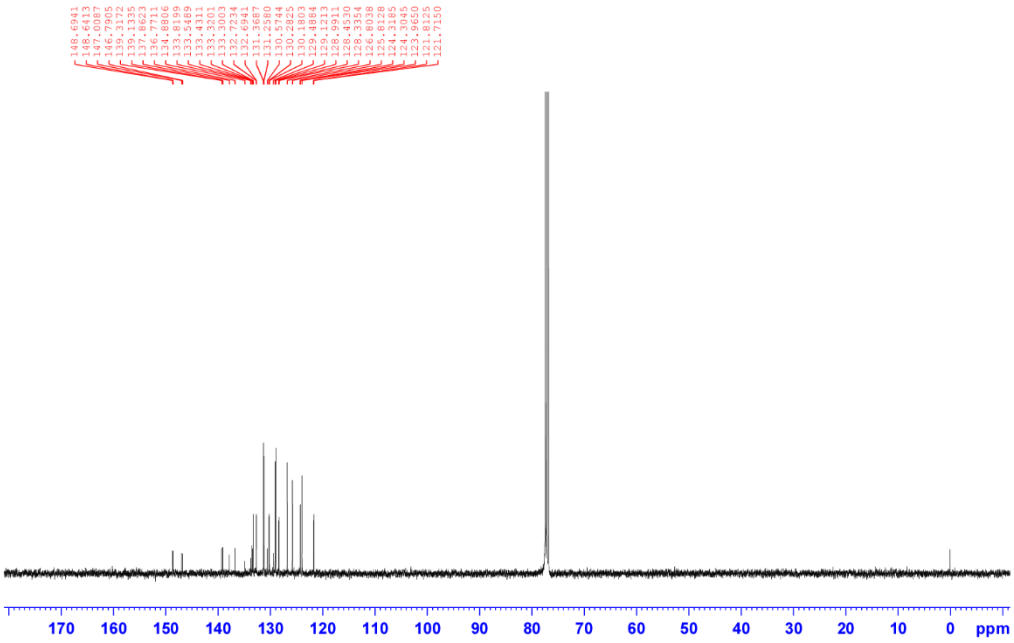

26.0236
100
50
0
-50
-100
-150
-200
ppm

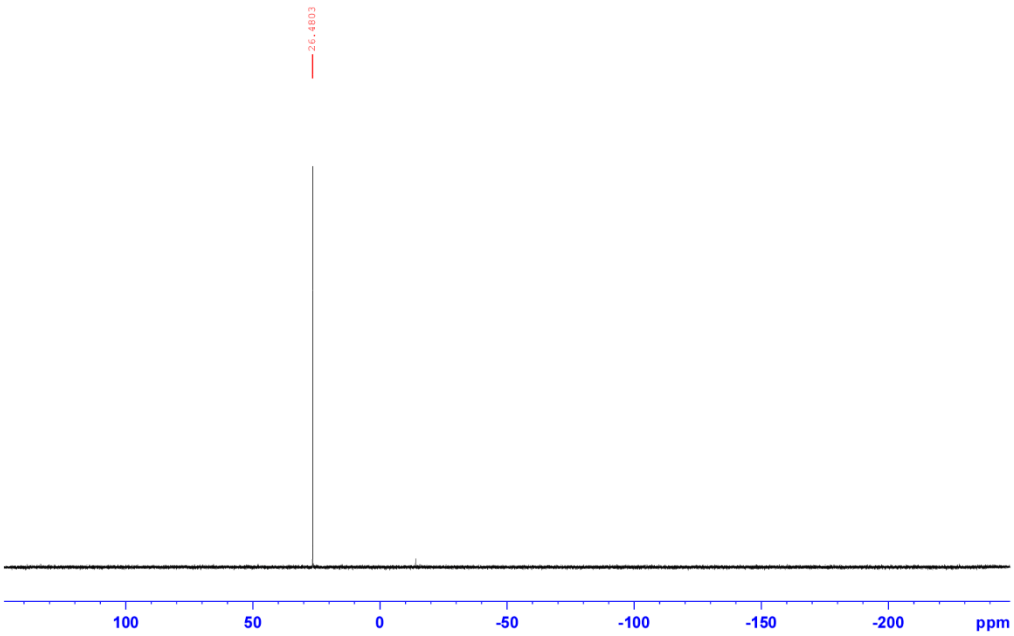
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2o**]



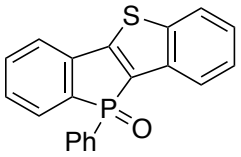
2o



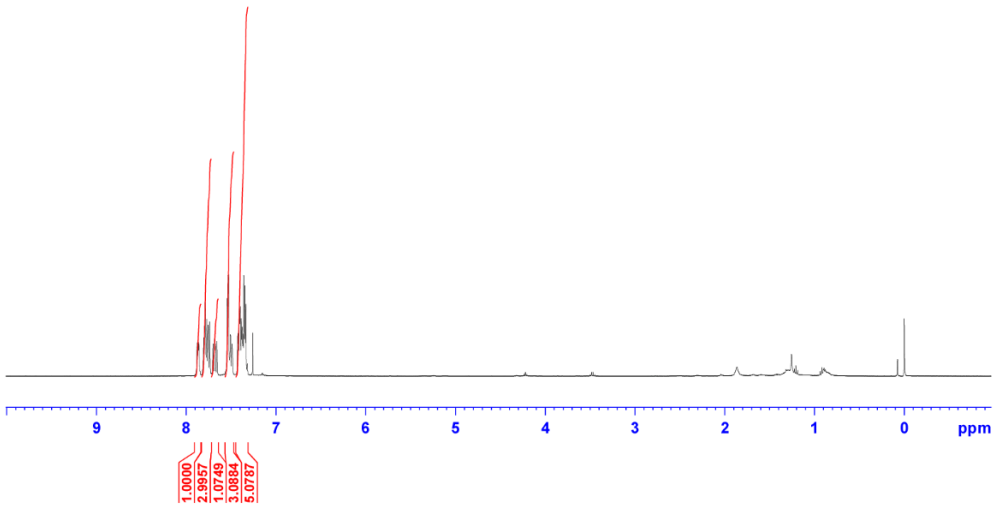


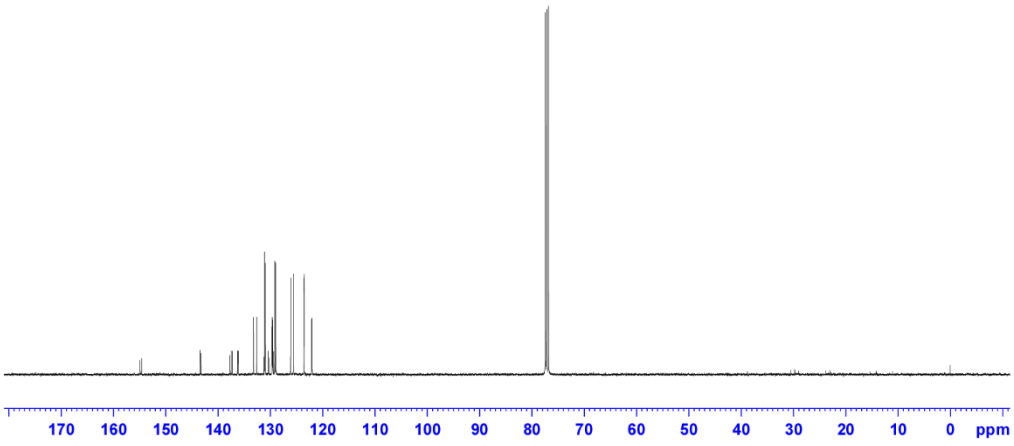

26.4803
100
50
0
-50
-100
-150
-200
ppm

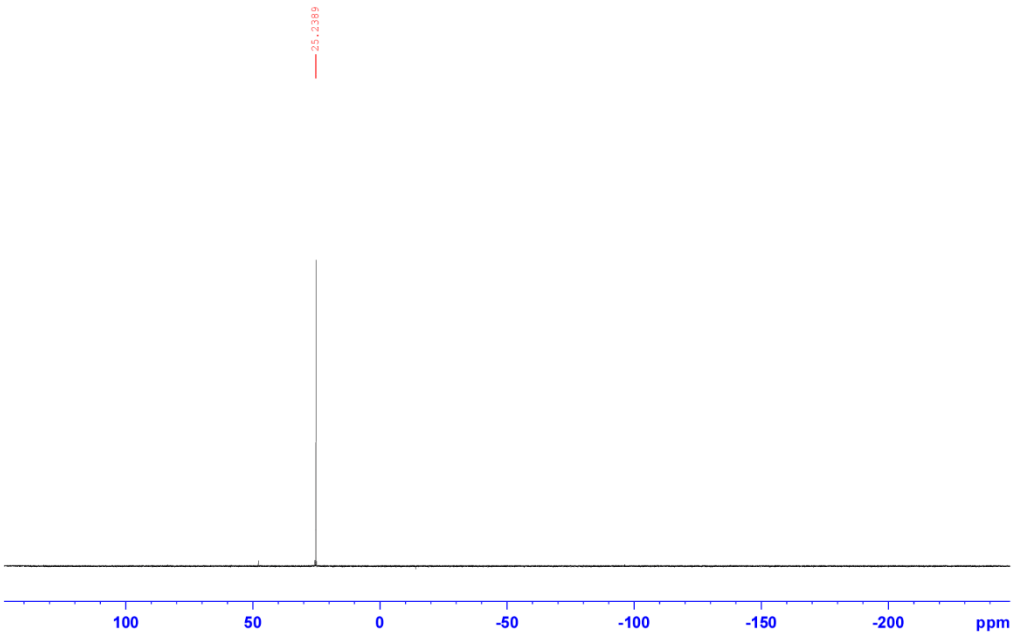
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2p**]



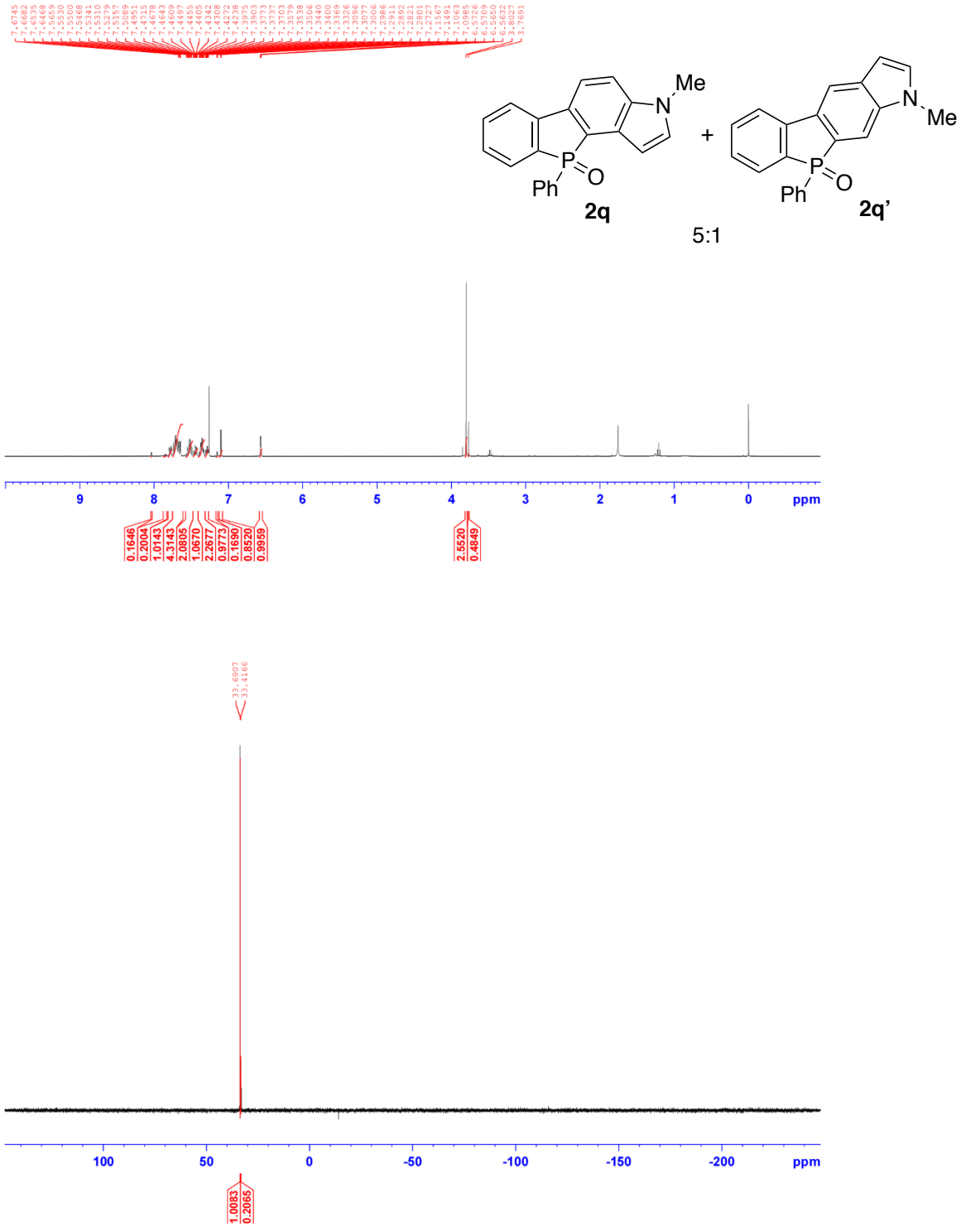
2p



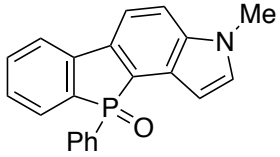



25.2389
100
50
0
-50
-100
-150
-200
ppm

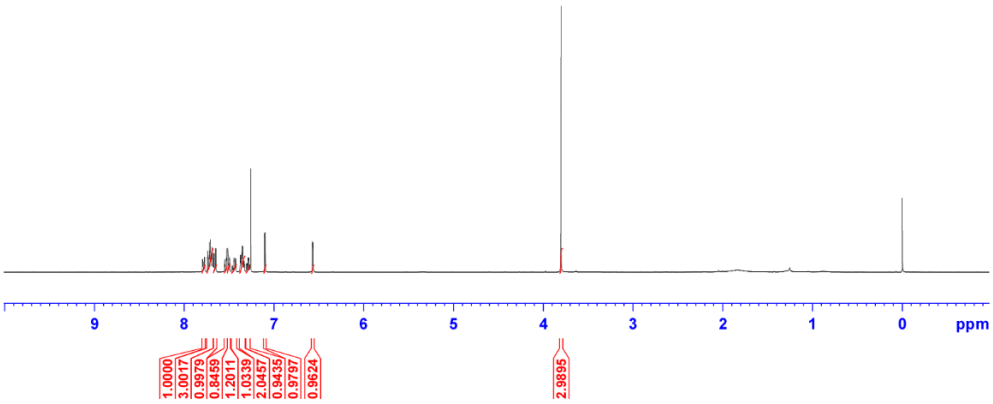
[^{1}H and ^{31}P{^{1}H} NMR Spectra of **2q** + **2q'**]

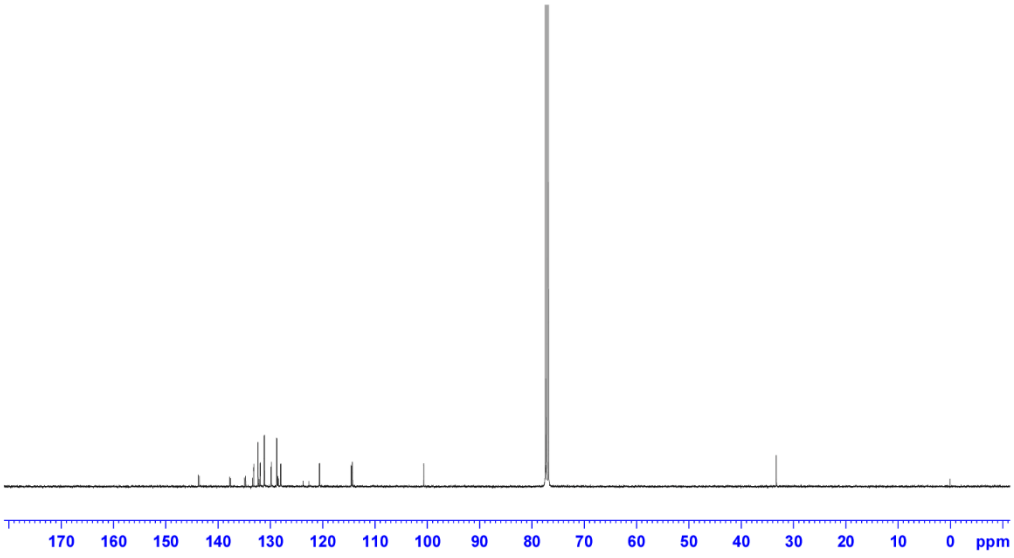


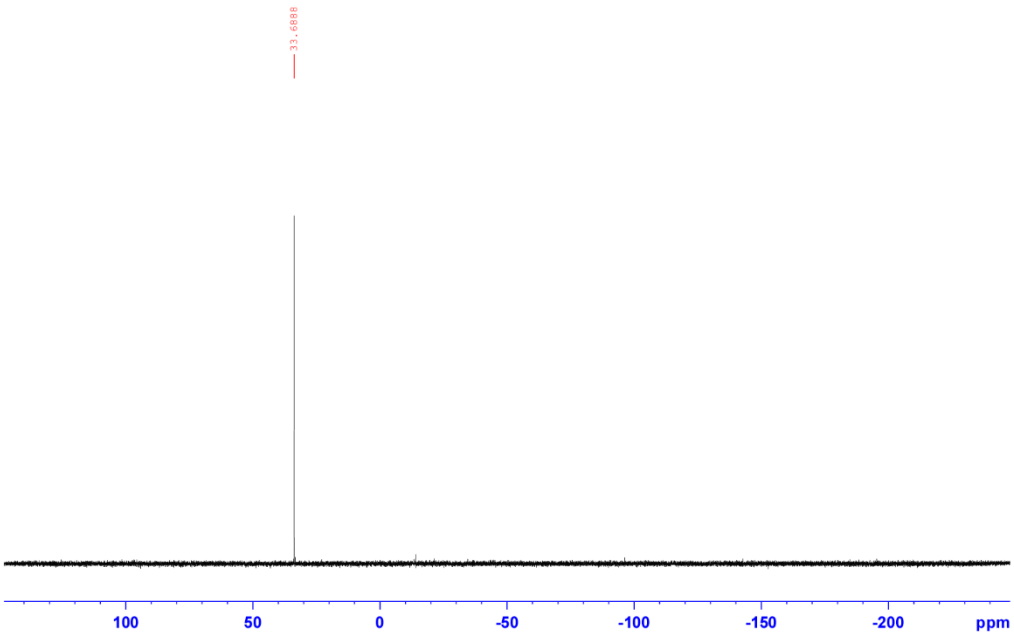
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2q**]



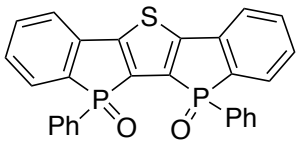
2q



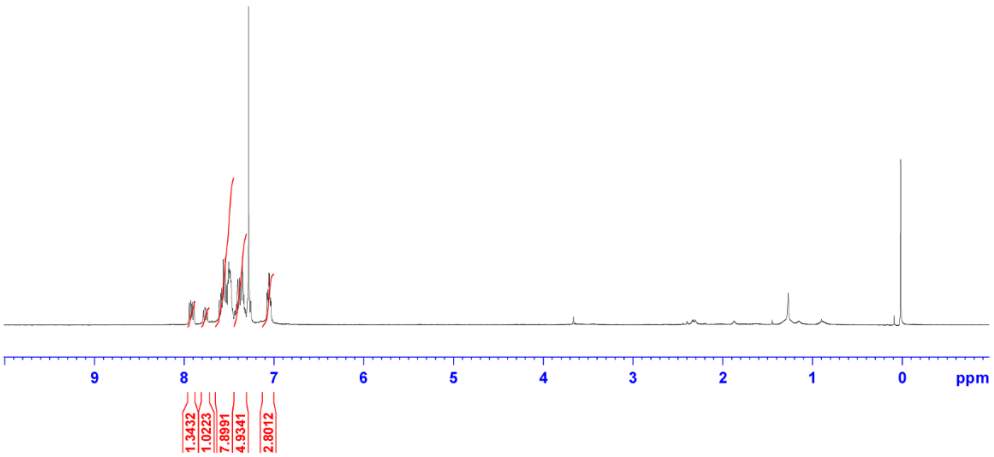


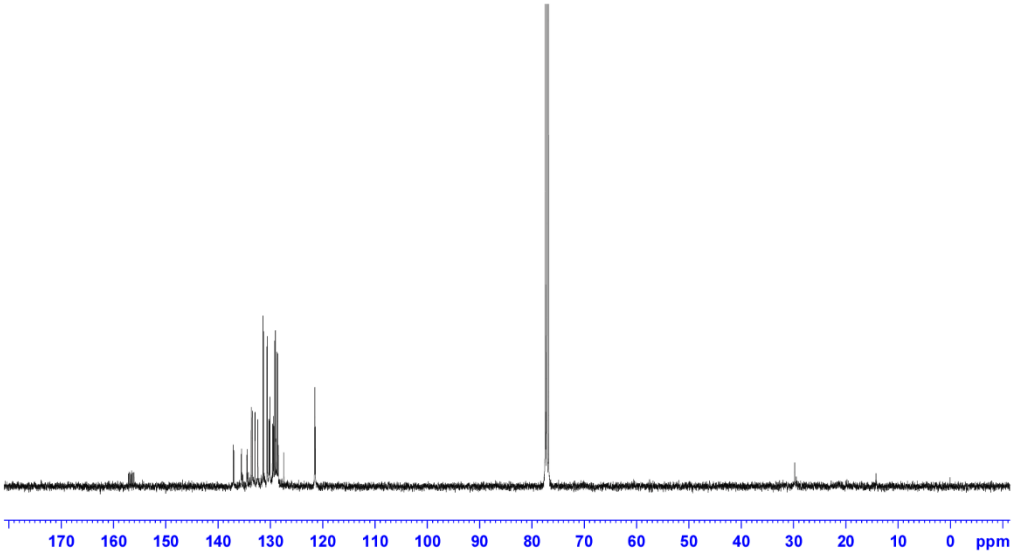

33.6888
100
50
0
-50
-100
-150
-200
ppm

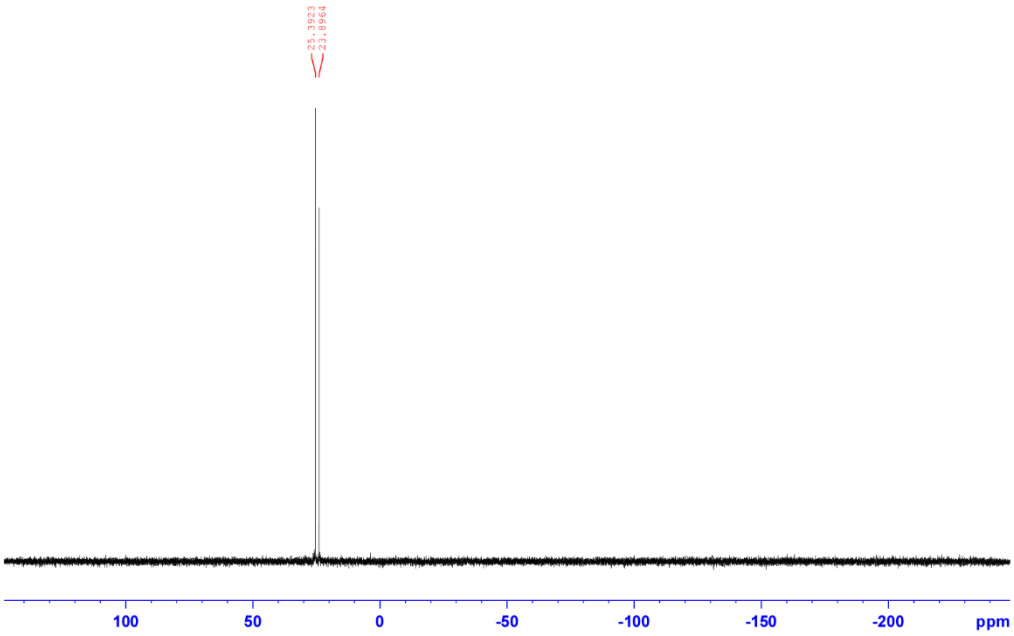
[^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR Spectra of **2r**]



2r *syn/anti* = ca. 1:1






25.3923
23.0964
100
50
0
-50
-100
-150
-200
ppm