Electronic Supplementary Information

for

Iron-catalyzed cascade cyclization of diaryldiyn-3-ones with P(O)H compounds: a rapid way for accessing 10-phosphorylated benzo[*b*]fluorenones

Yinwei Cao, Yue Ying, Jieyi Wu, Fushan Chen,* Guo Tang,* and Yufen Zhao

Department of Chemistry, College of Chemistry and Chemical Engineering, and the Key Laboratory for Chemical Biology of Fujian Province, Xiamen University, Xiamen, Fujian 361005, China.
E-mail: 17706925334@163.com; t12g21@xmu.edu.cn

Table of Contents

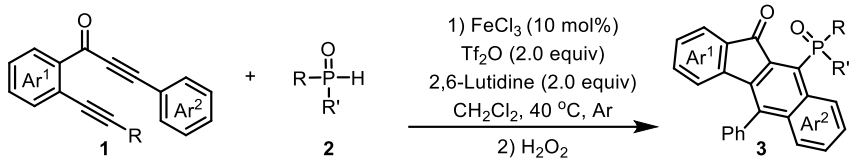
1	**General information**	**S2**
2	**General experimental procedures**	**S3**
3	**Characterization for products**	**S6**
4	**Photophysical properties of the selected products**	**S21**
5	**NMR spectrum of isolated products**	**S22**
6	**Crystallographic spectrum for 3a**	**S59**

1. General information.

All reactions were carried out under dry Ar (unless otherwise noted). All glassware was oven-dried prior to use. The commercially available reagents were purchased from TCI, Energy Chemical and Bide Pharmatech Ltd and used without further purification. 1,6-diyn-3-one derivatives were prepared from literary. Toluene, *N*, *N*-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, acetonitrile and dichloroethane (exact dry, water < 50 ppm) were purchased from Sinopharm Chemical Reagent Co., Ltd and used as the solvent. petroleum ether and ethyl acetate are all AR grade were obtained commercially and used as eluent without further purification. ^{1}H, ^{13}C, ^{31}P, ^{19}F and spectra were measured on Bruker AV 500M spectrometers with $CDCl_3$ as solvent. Data were reported relative to solvent peaks $CDCl_3$ 7.26 ppm for ^{1}H NMR and $CDCl_3$ 77.26 ppm for ^{13}C NMR. 85% H_3PO_4 as external standard for $^{31}P\{^{1}H\}$ NMR spectra. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constants in Hertz (Hz). The products were purified by column chromatography on silica gel 300-400 mesh. Isolated products were further characterized by HRMS (FT-ICR-MS) and an electrospray ionization source in positive-ion mode.

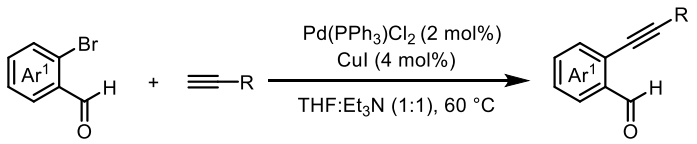
2 General experimental procedures

Iron-catalyzed cascade cyclization of diaryldiyn-3-ones with P(O)H compounds

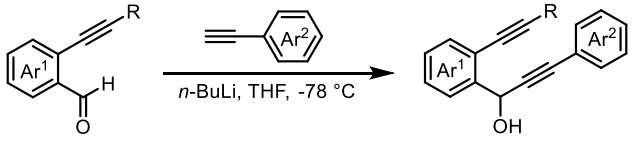


A schlenk tube containing diaryldiyn-3-ones (**1**, 0.30 mmol), P(O)H compounds (**2**, 0.60 mmol) and $FeCl_3$ (0.03 mmol) were evacuated and purged with argon three times. CH_2Cl_2 (3.0 mL), 2,6-Lutidine (0.60 mmol) and Tf_2O (0.60 mmol) were sequentially added to the system at room temperature. Then the system stirred at 40 °C for 4 h. Upon competition of reaction, saturated $NaHCO_3$ was added and the reaction was oxidized by H_2O_2 (30% aq. 0.5 mL) for 30 min under air. The resulting mixture was quenched with saturated $Na_2S_2O_3$ and extracted with ethyl acetate (3 x 10.0 mL). The combined organic layer was removed in vacuum, dried over with $MgSO_4$. The crude residues were purified by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent (8:1–2:1) to afford the desired phosphorylation products as yellow solids.

Preparation of Aryl-Fused 1,6-Diyn-3-ones

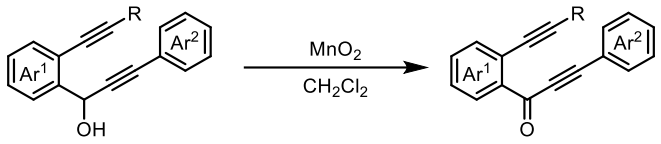


2′-Bromo-benzaldehyde derivatives (1.0 equiv), $Pd(PPh_3)_2Cl_2$ (2 mol%), and CuI (4 mol%) were dissolved in dry THF/Et_3N (1:1) in a round-bottom flask under a nitrogen atmosphere at room temperature. After 5 min of stirring, the corresponding terminal alkyne (1.2 equiv) was added and the reaction mixture was refluxed at 60 °C using an oil bath. After the completion of the reaction as indicated by TLC, the reaction mixture was filtered through Celite and the solvents were evaporated under reduced pressure. Finally, the crude product was purified by column chromatography (silica gel, hexanes/EtOAc) to get pure 2-(arylethynyl)benzaldehyde derivatives.



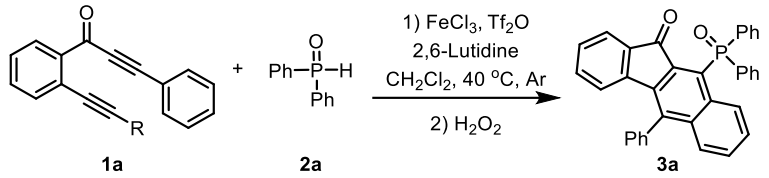
To a solution of alkyne (1.2 equiv) in dry THF at −78 °C, *n*-BuLi (2.5 M in hexanes, 1.2 equiv) was added slowly and stirred for 45 min at −78 °C and then a solution of 2-(arylethynyl)benzaldehyde derivatives (1.0 equiv) in THF was added slowly. The resulting mixture was allowed to stir for 2 h at room temperature. After completion of the reactionas mentioned by TLC, the reaction mixture was quenched by aqueous NH_4Cl solution and the organic layer was

extracted with EtOAc and dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure, and it was directly used for further reaction.



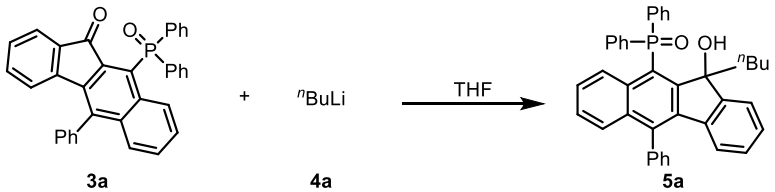
MnO_2 (15.0 equiv) was added in portions to a solution of the alcohol derivatives in CH_2Cl_2 and stirred at room temperature. After completion of the reaction as indicated by TLC, the reaction mixture was filtered through Celite and concentrated under reduced pressure. The residue was purified by column chromatography to yield the corresponding 1,6-diyn-3-ones.

Gram scale preparation of 3a

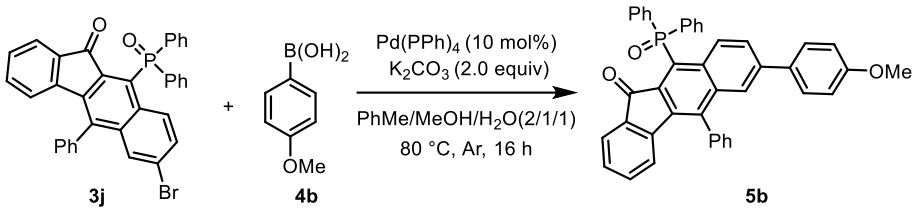


To a 50 mL Schlenk tube was added **1a** (1.55 g, 5.00 mmol), $FeCl_3$ (80.0 mg, 0.50 mmol), **2a** (2.02 g, 10.00 mmol) and 30 mL CH_2Cl_2. Then 2,6-lutidine (1.2 mL, 10.00 mmol) and Tf_2O (1.5 mL,10.00 mmol) was added. The mixture was stirred at 40°C oil bath for 12 h. Upon competition of reaction, saturated $NaHCO_3$ solution (10.0 mL) and 30% H_2O_2 (10.0 mL) were added and stirred for 1 h. The mixture was quenched with $Na_2S_2O_3$ solution. Then mixture was extracted with EA (3 x 30.0 mL), The combined organic layers were dried over $NaSO_4$, filtered, and concentrated in vacuo. The residue was separated by flash column chromatography to give **3a** as a yellow solid (1.34 g, 53% yield).

Further transformation of products



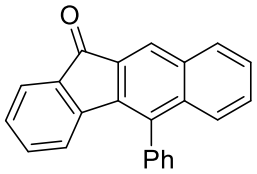
A stirred solution of compound **3a** (0.20 mmol) in anhydrous THF (2.0 mL) was added *n*-BuLi (100 μL, 2.5 M in hexane) at -40 °C. Then the mixture was stirred at room temperature overnight. TLC monitored the reaction to reach completion. The reaction was quenched by addition of saturated NH4Cl solution (3.0 mL). Extracted with EA (3 x 5.0 mL), the combined organic layers were washed with brine, dried over Na_2SO_4. The concentrated residue was purified by column chromatography to afford the desired product **5a** as a yellow solid (68.8 mg, 61% yield).



A mixture of **3j** (0.20 mmol, 1.0 equiv) and (4-methoxyphenyl)boronic acid (0.40 mmol, 2.0 equiv), $Pd(PPh)_4$ (0.02 mmol, 0.1 equiv), K_2CO_3 (0.20 mmol, 2.0 equiv), and the solvent ($PhMe/MeOH/H_2O$, 2.0 mL/1.0 mL /1.0 mL) added into a 10.0 mL Schlenk flask. The reaction was then carried out at 80 °C for 16 h under an argon atmosphere. After cooling, 3.0 mL H_2O was added and the product was extracted with CH_2Cl_2 (3 x 5.0 mL). The organic layer was dried with anhydrous sodium sulfate, the solvent was evaporated under a vacuum and crude product was purified by column chromatography to afford the desired product **5b** as a yellow solid (99.1 mg, 81% yield).

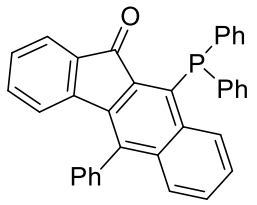
3. Characterization for products

5-phenyl-11H-benzo[b]fluoren-11-one (3a', new compound)



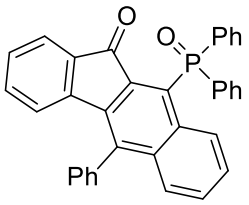
yellow solid; 18.4 mg, 20% yield; **m.p:** 218-220 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.91 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.66-7.63 (m, 2H), 7.58-7.52 (m, 5H), 7.40-7.35 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 192.4, 144.3, 141.4, 138.6, 136.9, 136.5, 135.7, 134.9, 134.0, 129.8, 129.4, 129.2, 129.0, 128.9, 128.3, 128.2, 127.0, 124.4, 120.9, 118.9; **FT-IR(film):**1705, 1277, 1181 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{23}H_{15}O^+$ 307.1117, found 307.1115.

10-(diphenylphosphaneyl)-5-phenyl-11H-benzo[b]fluoren-11-one (new compound)



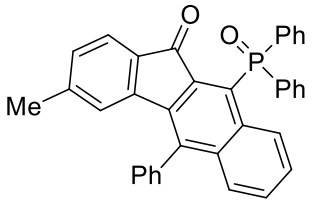
yellow gummy; 89.7 mg, 61% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.25 (d, *J* = 9.0 Hz, 1H), 7.66-7.62 (m, 4H), 7.55-7.52 (m, 4H), 7.50-7.44 (m, 4H), 7.34-7.29 (m, 6H), 7.21-7.11 (m, 3H), 6.24 (d, *J* = 7.4 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 192.5 (d, *J* = 1.8 Hz), 143.9, 138.4 (d, *J* = 19.8 Hz), 137.7, 137.2 (d, *J* = 41.1 Hz), 137.1, 136.9, 136.8, 136.7, 136.3, 135.9 (d, *J* = 7.8 Hz), 135.5, 134.4, 132.3 (d, *J* = 19.5 Hz), 130.8 (d, *J* = 10.3 Hz), 129.5 (d, *J* = 21.6 Hz), 128.7, 128.49 (d, *J* = 5.8 Hz), 128.46, 128.3, 128.0, 127.7, 126.1, 124.2, 123.7; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ -16.1; **FT-IR(film):**1708, 1195, 957, 908 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{35}H_{24}OP^+$ 491.1559, found 491.1551.

10-(diphenylphosphoryl)-5-phenyl-11*H*-benzo[b]fluoren-11-one (3a, new compound)



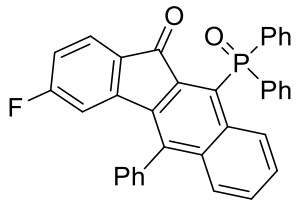
yellow solid; 107.8 mg, 71% yield; **m.p:** 260-263 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.66 (d, *J* = 9.0 Hz, 1H), 7.91-7.87 (m, 4H), 7.65-7.60 (m, 3H), 7.51-7.47 (m, 4H), 7.46-7.40 (m, 7H), 7.32 (d, *J* = 6.7 Hz, 1H), 7.13-7.08 (m, 2H), 6.16 (d, *J* = 7.2 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.3 (d, *J* = 3.5 Hz), 144.2, 139.0 (d, *J* = 2.2 Hz), 137.8 (d, *J* = 7.7 Hz), 137.4, 137.0 (d, *J* = 7.9 Hz), 136.5 (d, *J* = 6.9 Hz), 135.4, 135.1, 135.0 (d, *J* = 10.3 Hz), 134.2 (d, *J* = 110.3 Hz), 131.7 (d, *J* = 2.2 Hz), 131.6 (d, *J* = 11.1 Hz), 131.3 (d, *J* = 3.4 Hz), 130.7 (d, *J* = 89.1 Hz), 129.7, 129.5, 129.2, 129.0, 128.9, 128.4 (d, *J* = 13.0 Hz), 127.7, 127.6, 124.3, 124.0; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.6; **FT-IR(film):**1710, 1437, 1174, 1119 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{35}H_{24}O_2P^+$ 507.1508, found 507.1512.

10-(diphenylphosphoryl)-3-methyl-5-phenyl-11*H*-benzo[b]fluoren-11-one (3b, new compound)



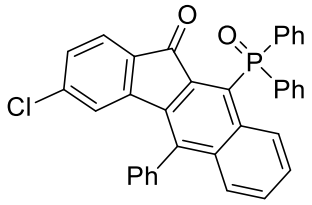
yellow solid; 120.1 mg, 77% yield; **m.p:** 258-259 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.69 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.66-7.63 (m, 4H), 7.54-7.48 (m, 4H), 7.46-7.42 (m, 7H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.92 (s, 1H), 2.07 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 190.8(d, *J* = 3.2 Hz), 146.1, 144.4, 138.7 (d, *J* = 2.5 Hz), 138.4 (d, *J* = 7.2 Hz), 137.4, 136.8 (d, *J* = 8.6 Hz), 136.4 (d, *J* = 6.6 Hz), 135.0 (d, *J* = 11.1 Hz), 134.3 (d, *J* = 109.6 Hz), 133.1, 131.52 (d, *J* = 2.2 Hz), 131.51 (d, *J* = 11.1 Hz), 131.2 (d, *J* = 4.3 Hz), 130.3 (d, *J* = 89.2 Hz), 129.65, 129.56, 129.4, 129.0, 128.7, 128.3 (d, *J* = 13.0 Hz), 127.51, 127.49, 124.8, 124.2, 22.4; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.6; **FT-IR(film):** 1707, 1437, 1173, 1119 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{36}H_{26}O_2P^+$ 521.1665, found 521.1668.

10-(diphenylphosphoryl)-3-fluoro-5-phenyl-11*H*-benzo[b]fluoren-11-one (3c, new compound)



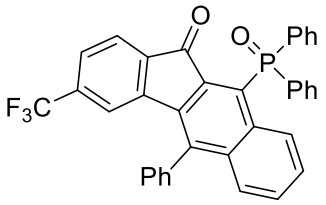
yellow solid; 107.0 mg, 68% yield; **m.p:** 245-247 °C; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 9.67 (d, *J* = 9.2 Hz, 1H), 7.90-7.87 (m, 4H), 7.68-7.64 (m, 3H), 7.54-7.44 (m, 9H), 7.41-7.40 (m, 2H), 7.35-7.33 (m, 1H), 7.77 (dt, J_1 = 8.5 Hz, J_2 = 2.1 Hz, 1H), 5.78 (dd, J_1 = 9.6 Hz, J_2 = 2.2 Hz, 1H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 189.4 (d, *J* = 3.2 Hz), 166.8 (d, *J* = 255.1 Hz), 146.7 (d, *J* = 10.9 Hz), 139.4 (d, *J* = 2.0 Hz), 137.6 (d, *J* = 6.6 Hz), 136.60 (d, *J* = 7.6 Hz), 136.56, 136.5 (d, *J* = 6.5 Hz), 134.0 (d, *J* = 109.6 Hz), 133.5 (d, *J* = 10.1 Hz), 131.6 (d, *J* = 2.0 Hz), 131.4 (d, *J* = 10.0 Hz), 131.2 (d, *J* = 3.6 Hz), 130.7 (d, *J* = 88.5 Hz), 129.7, 129.2, 129.1, 129.0, 128.3 (d, *J* = 12.8 Hz), 127.8, 127.6, 126.3, 126.2, 115.8 (d, *J* = 23.7 Hz), 111.4 (d, *J* = 25.8 Hz); **^{31}P NMR (CDCl$_3$, 202 MHz):** δ 33.3; **^{19}F NMR (CDCl$_3$, 471 MHz):** δ -103.01; **FT-IR(film):** 1713, 1611, 1436, 1176, 1119 cm^{-1}; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{35}H_{22}FNaO_2P^+$ 547.1234, found 547.1238.

3-chloro-10-(diphenylphosphoryl)-5-phenyl-11H-benzo[b]fluoren-11-one (3d, new compound)



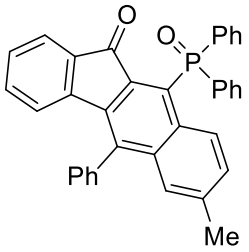
yellow solid; 115.0 mg, 71% yield; **m.p:** 261-263 °C; **^{1}H NMR (CDCl$_3$, 500 MHz):** δ 9.65 (d, *J* = 8.5 Hz, 1H), 7.90-7.88 (m, 4H), 7.69-7.64 (m, 3H), 7.55-7.48 (m, 5H), 7.47-7.44 (m, 4H), 7.42-7.40 (m, 2H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.08 (dd, J_1 = 8.2 Hz, J_2 = 1.0 Hz, 1H), 6.05 (d, *J* = 1.6 Hz, 1H); **^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz):** δ 190.0 (d, *J* = 3.4 Hz), 145.7, 141.3, 139.7 (d, *J* = 2.1 Hz), 137.6 (d, *J* = 6.8 Hz), 136.81, 136.78 (d, *J* = 5.5 Hz), 136.7 (d, *J* = 6.6 Hz), 134.1 (d, *J* = 109.6 Hz), 133.9 (d, *J* = 10.5 Hz), 133.6, 131.8 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 11.0 Hz), 131.4 (d, *J* = 4.4 Hz), 131.3 (d, *J* = 84.2 Hz), 129.9, 129.4, 129.3, 129.2, 129.1, 128.5 (d, *J* = 13.3 Hz), 128.1, 127.8, 125.3, 124.4; **^{31}P NMR (CDCl$_3$, 202 MHz):** δ 33.2; **FT-IR(film):** 1710, 1436, 1180, 1119 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{35}H_{23}ClO_2P^+$ 541.1119, found 541.1126.

10-(diphenylphosphoryl)-5-phenyl-3-(trifluoromethyl)-11*H*-benzo[b]fluoren-11-one (3e, new compound)



yellow solid; 115.4 mg, 67% yield; **m.p:** 255-257 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.69 (d, *J* = 8.5 Hz, 1H), 7.92-7.88 (m, 4H), 7.69-7.64 (m, 3H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.56-7.50 (m, 4H), 7.47-7.43 (m, 7H), 7.36 (d, *J* = 7.7 Hz, 1H), 6.33 (s, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 190.0 (d, *J* = 3.1 Hz), 144.5, 140.0 (d, *J* = 2.0 Hz), 137.6, 137.0 (d, *J* = 7.4 Hz), 136.8 (d, *J* = 7.8 Hz), 136.7 (d, *J* = 6.4 Hz), 136.6, 136.1 (q, *J* = 32.2 Hz), 133.96 (d, *J* = 109.6 Hz), 133.95 (d, *J* = 12.1 Hz), 131.9 (d, *J* = 88.0 Hz), 131.8 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 10.7 Hz), 131.5 (d, *J* = 3.9 Hz), 129.9, 129.6, 129.23, 129.21, 128.5 (d, *J* = 12.7 Hz), 128.2, 127.9, 125.9 (q, *J* = 3.3 Hz), 124.4, 123.3 (q, *J* = 274.5 Hz), 120.9 (q, *J* = 4.4 Hz); **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 32.9; **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -64.05; **FT-IR(film):** 1716, 1437, 1318, 1171, 1121 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{36}H_{23}F_3O_2P^+$ 575.1382, found 575.1390.

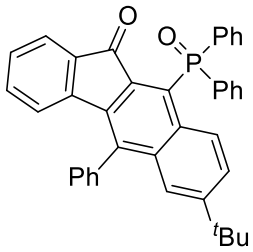
10-(diphenylphosphoryl)-7-methyl-5-phenyl-11*H*-benzo[b]fluoren-11-one (3f, new compound)



yellow solid; 113.9 mg, 73% yield; **m.p:** 252-255 °C;**^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.64 (d, *J* = 8.8 Hz, 1H), 7.93-7.89 (m, 4H), 7.66-7.61 (m, 3H), 7.50-7.48 (m, 2H), 7.46-7.41 (m, 6H), 7.36-7.32 (m, 2H), 7.28 (s, 1H), 7.11-7.06 (m, 2H), 6.13 (dd, J_1 = 7.3 Hz, J_2 = 1.6 Hz, 1H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.2(d, *J* = 3.3 Hz), 144.1, 139.6, 138.4 (d, *J* = 2.1 Hz), 137.5, 137.2 (d, *J* = 8.0 Hz), 136.7 (d, *J* = 7.0 Hz), 135.4, 135.2 (d, *J* = 10.9 Hz), 134.9, 134.7 (d, *J* = 6.1 Hz), 134.3 (d, *J* = 110.1 Hz), 131.53 (d, *J* = 2.0 Hz), 131.49 (d, *J* = 8.9 Hz), 131.0 (d, *J* = 3.5 Hz), 130.4 (d, *J* = 89.0 Hz), 129.7, 129.6, 129.4, 128.8, 128.7, 128.3 (d, *J* = 13.5 Hz), 126.8, 124.1,

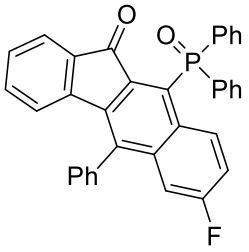
123.8, 22.0; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.7; **FT-IR(film):** 1709, 1437, 1174, 1120 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{36}H_{26}O_2P^+$ 521.1665, found 521.1668.

7-(tert-butyl)-10-(diphenylphosphoryl)-5-phenyl-11*H*-benzo[b]fluoren-11-one (3g, new compound)



yellow solid; 138.3 mg, 82% yield; **m.p:** 272-275 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.60 (d, J = 9.2 Hz, 1H), 7.92-7.88 (m, 4H), 7.66-7.59 (m, 4H), 7.51-7.48 (m, 2H), 7.46-7.41 (m, 7H), 7.33-7.32 (m, 1H), 7.13-7.08 (m, 2H), 6.18 (dd, J_1 = 7.0 Hz, J_2 = 1.7 Hz, 1H), 1.23 (s, 9H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.4 (d, J = 3.3 Hz), 152.2, 144.3, 139.1 (d, J = 3.3 Hz), 137.6, 137.2 (d, J = 7.7 Hz), 137.0 (d, J = 6.6 Hz), 135.5, 135.1 (d, J = 11.0 Hz), 134.9, 134.7 (d, J = 6.6 Hz), 134.2 (d, J = 109.55 Hz), 131.644 (d, J = 2.2 Hz), 131.636 (d, J = 11.1 Hz), 130.8 (d, J = 3.3 Hz),, 130.5 (d, J = 89.6 Hz), 129.6, 129.5, 128.82, 128.80, 128.4 (d, J = 12.2 Hz), 126.5, 124.2, 123.9, 123.0, 35.2, 30.9; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.5; **FT-IR(film):** 1710, 1610, 1436, 1174, 1118 cm^{-1}; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{39}H_{31}NaO_2P^+$ 585.1954, found 585.1954.

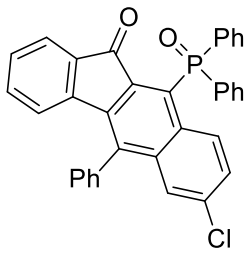
10-(diphenylphosphoryl)-7-fluoro-5-phenyl-11*H*-benzo[b]fluoren-11-one (3h, new compound)



yellow solid; 125.8 mg, 74% yield; **m.p:** 244-246 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.85 (dd, J_1 = 9.6 Hz, J_2 = 5.9 Hz, 1H), 7.88 (dd, J_1 = 12.8 Hz, J_2 = 7.5 Hz, 4H), 7.67-7.64 (m, 3H), 7.53-7.50 (m, 2H), 7.47-7.44 (m, 4H), 7.41-7.40 (m, 2H), 7.35-7.34 (m, 1H), 7.28-7.25 (m, 1H), 7.15-7.10 (m, 3H), 6.19-6.18 (m, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.0 (d, J = 3.3 Hz), 162.7 (d, J =

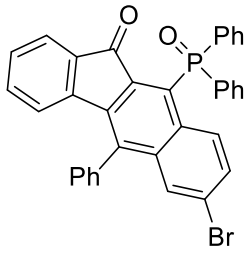
252.1 Hz), 143.9, 139.4 (dd, J_1 = 8.2 Hz, J_2 = 8.0 Hz), 138.2 (dd, J_1 = 5.5 Hz, J_2 = 2.5 Hz), 137.0 (dd, J_1 = 6.6 Hz, J_2 = 2.5 Hz), 136.9, 136.2 (d, J = 11.1 Hz), 135.5, 135.1, 134.3 (dd, J_1 = 8.8 Hz, J_2 = 3.2 Hz), 134.0 (d, J = 109.5 Hz), 133.5 (d, J = 6.6 Hz), 131.8 (d, J = 3.3 Hz), 131.6 (d, J = 10.0 Hz), 130.8 (d, J = 89.6 Hz), 130.0, 129.4, 129.3, 129.2, 128.5 (d, J = 13.3 Hz), 124.4, 124.1, 117.4 (d, J = 25.4 Hz), 111.6 (d, J = 23.2 Hz); **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.7; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$):** δ -101.05; **FT-IR(film):** 1712, 1611 1437, 1329, 1177cm^{-1}; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{35}H_{22}FNaO_2P^+$ 547.1234, found 547.1232.

7-chloro-10-(diphenylphosphoryl)-5-phenyl-11H-benzo[b]fluoren-11-one (3i, new compound)



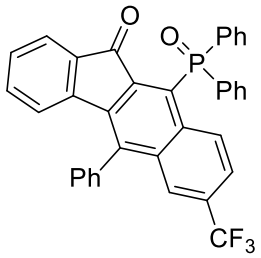
yellow solid; 124.8 mg, 77% yield; **m.p:** 268-269 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.76 (d, J = 8.8 Hz, 1H), 7.90-7.87 (m, 4H), 7.68-7.63 (m, 3H), 7.53-7.50 (m, 2H), 7.47-7.44 (m, 6H), 7.42-7.40 (m, 2H), 7.35-7.34 (m, 1H), 7.15-7.11 (m, 2H), 6.16-6.15 (m, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 190.9 (d, J = 3.3 Hz), 143.8, 138.2 (d, J = 8.8 Hz), 138.0 (d, J = 2.2 Hz), 137.7 (d, J = 7.7 Hz), 136.6, 136.2 (d, J = 11.1 Hz), 135.9, 135.4, 135.2, 134.8 (d, J = 6.6 Hz), 133.9 (d, J = 109.5 Hz), 132.9 (d, J = 3.3 Hz), 131.8 (d, J = 3.3 Hz), 131.6 (d, J = 10.0 Hz), 130.7 (d, J = 87.3 Hz), 129.9, 129.4, 129.3, 129.2, 128.5 (d, J = 12.2 Hz), 128.3, 126.4, 124.4, 124.1; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.9; **FT-IR(film):** 1713, 1596, 1489, 1437, 1172cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{35}H_{23}ClO_2P^+$ 541.1119, found 541.1119.

7-bromo-10-(diphenylphosphoryl)-5-phenyl-11H-benzo[b]fluoren-11-one (3j, new compound)



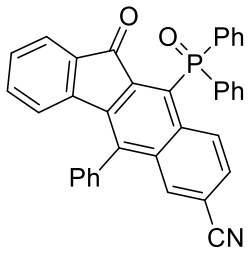
yellow solid; 110.4 mg, 63% yield; **m.p:** 254-257 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.69 (d, *J* = 9.2 Hz, 1H), 7.90-7.87 (m, 4H), 7.67-7.64 (m, 4H), 7.60-7.58 (m, 1H), 7.52-7.50 (m, 2H), 7.47-7.40 (m, 6H), 7.35-7.34 (m, 1H), 7.15-7.10 (m, 2H), 6.15 (d, *J* = 7.0 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 190.9 (d, *J* = 2.9 Hz), 143.7, 138.4 (d, *J* = 7.8 Hz), 137.9 (d, *J* = 1.7 Hz), 137.7 (d, *J* = 6.7 Hz), 136.5, 136.2 (d, *J* = 12.2 Hz), 135.3, 135.2, 135.0 (d, *J* = 6.5 Hz), 133.9 (d, *J* = 110.2 Hz), 132.8 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 2.3 Hz), 131.5 (d, *J* = 10.4 Hz), 130.9, 130.8 (d, *J* = 88.0 Hz), 129.9, 129.6, 129.4, 129.3, 129.2, 128.4 (d, *J* = 13.0 Hz), 124.6, 124.3, 124.1; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.8; **FT-IR(film):** 1711, 1587, 1477, 1430, 1189cm^{-1}; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{35}H_{22}BrNaO_2P^+$ 607.0433, found 607.0429.

10-(diphenylphosphoryl)-5-phenyl-7-(trifluoromethyl)-11H-benzo[b]fluoren-11-one (3k, new compound)



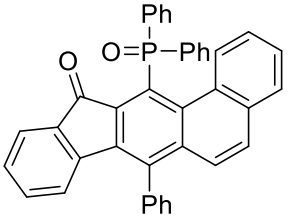
yellow solid; 79.2 mg, 46% yield; **m.p:** 262-264 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.86 (d, *J* = 9.1 Hz, 1H), 7.91-7.86 (m, 4H), 7.78 (s, 1H), 7.69-7.66 (m, 4H), 7.55-7.51 (m, 2H), 7.49-7.41 (m, 6H), 7.39-7.35 (m, 1H), 7.19-7.13 (m, 2H), 6.20-6.18 (m, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 190.8 (d, *J* = 3.1 Hz), 143.6, 139.3, 139.2 (d, *J* = 8.9 Hz), 137.8 (d, *J* = 7.3 Hz), 136.3 (d, *J* = 7.9 Hz), 136.09 (d, *J* = 9.8 Hz), 136.08, 135.2, 135.1, 135.6 (d, *J* = 109.7 Hz), 132.2 (d, *J* = 3.4 Hz), 131.7 (d, *J* = 2.2 Hz), 131.4 (d, *J* = 10.9 Hz), 130.7 (d, *J* = 88.3 Hz), 130.3 (q, *J* = 32.8 Hz), 129.8, 129.3, 129.24, 129.19, 128.3 (d, *J* = 13.2 Hz), 124.39 (q, *J* = 4.6 Hz), 124.36, 124.1, 123.8 (q, *J* = 272.4 Hz), 123.0 (q, *J* = 2.8 Hz); **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.5; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$):** δ -63.30; **FT-IR(film):**1711, 1592, 1498, 1437, 1177cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{36}H_{23}F_3O_2P^+$ 575.1328, found 575.1326.

10-(diphenylphosphoryl)-11-oxo-5-phenyl-11H-benzo[b]fluorene-7-carbonitrile (3l, new compound)



yellow solid; 84.6 mg, 53% yield; **m.p:** 241-243 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.85 (d, *J* = 8.9 Hz, 1H), 7.89-7.85 (m, 5H), 7.70-7.68 (m, 3H), 9.64 (d, *J* = 8.9 Hz, 1H), 7.55-7.52 (m, 2H), 7.48-7.46 (m, 4H), 7.40-7.36 (m, 3H), 7.19-7.15 (m, 2H), 7.21 (dd, J_1 = 6.4 Hz, J_2 = 1.8 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 190.6 (d, *J* = 2.2 Hz), 143.3, 140.0 (d, *J* = 6.6 Hz), 138.7, 138.0 (d, *J* = 6.6 Hz), 136.4 (d, *J* = 9.9 Hz), 136.3 (d, *J* = 7.7 Hz), 135.6, 135.4, 135.0, 133.3 (d, *J* = 111.6 Hz), 132.7, 132.3 (d, *J* = 3.3 Hz), 131.9, 131.4 (d, *J* = 11.0 Hz), 130.7 (d, *J* = 87.4 Hz), 130.0, 129.6, 129.5, 129.1, 128.4 (d, *J* = 13.3 Hz), 127.8, 124.5, 124.2, 118.6, 112.3; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.7; **FT-IR(film):** 2229, 1716, 1469, 1437, 1170, 1119 cm^{-1}; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{36}H_{22}NNaO_2P^+$ 554.1280, found 554.1267.

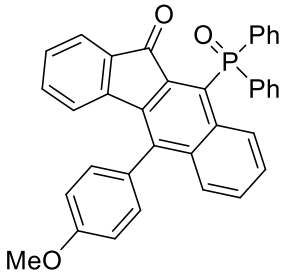
13-(diphenylphosphoryl)-7-phenyl-12H-indeno[1,2-b]phenanthren-12-one (3n, new compound)



yellow solid; 111.8 mg, 67% yield; **m.p:** 217-220 °C;**^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.71 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.96-7.91 (m, 6H), 7.67-7.61 (m, 2H), 7.54-7.41 (m, 11H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.18 (d, *J* = 7.8 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.3 (d, *J* = 3.1 Hz), 144.1, 138.8 (d, *J* = 2.1 Hz), 137.8 (d, *J* = 6.8 Hz), 137.1 (d, *J* = 7.8 Hz), 136.5 (d, *J* = 6.6 Hz), 135.4, 135.2 (d, *J* = 8.8 Hz), 135.1, 134.7, 134.3 (d, *J* = 110.0 Hz), 134.1 (d, *J* = 109.6 Hz), 133.8, 133.3, 131.7 (d, *J* = 3.3 Hz), 131.7 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 10.2 Hz), 131.5 (d, *J* = 11.1 Hz), 131.3 (d, *J* = 4.4 Hz), 130.8 (d, *J* = 88.9 Hz), 129.6, 129.2, 129.0, 128.7, 128.45 (d, *J* = 2.8 Hz), 128.44, 128.4 (d, *J* = 3.4 Hz), 128.3, 127.7, 127.3, 127.1, 124.3, 124.0; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.6; **FT-**

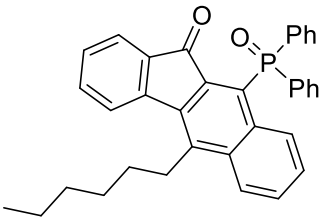
IR(film):1711, 1436, 1175, 1118 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{39}H_{26}O_2P^+$ 557.1665, found 557.1665.

10-(diphenylphosphoryl)-5-(4-methoxyphenyl)-11H-benzo[b]fluoren-11-one (3o, new compound)



yellow solid; 90.0 mg, 56% yield; **m.p:** 263-264 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.63 (d, *J* = 8.2 Hz, 1H), 7.91-7.86 (m, 4H), 7.56-7.42 (m, 9H), 7.35-7.30 (m, 3H), 7.18-7.08 (m, 4H) 6.31 (d, *J* = 7.6 Hz, 1H), 3.97 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.4 (d, *J* = 3.1 Hz), 160.1, 144.4, 139.0 (d, *J* = 2.4 Hz), 137.9 (d, *J* = 6.9 Hz), 137.5 (d, *J* = 7.8 Hz), 136.5 (d, *J* = 6.4 Hz), 135.7 (d, *J* = 10.4 Hz), 135.41, 135.37, 135.1, 134.3 (d, *J* = 109.7 Hz), 133.7, 131.7, 131.3 (d, *J* = 3.5 Hz), 131.1 (d, *J* = 84.3 Hz), 130.7, 129.3, 129.1, 128.9, 128.4 (d, *J* = 12.9 Hz), 127.6, 124.3, 124.1, 115.1, 55.7; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.8; **FT-IR(film):**1712, 1611, 1505, 1437, 1248, 1175, 1118 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{36}H_{26}O_3P^+$ 537.1614, found 537.1612.

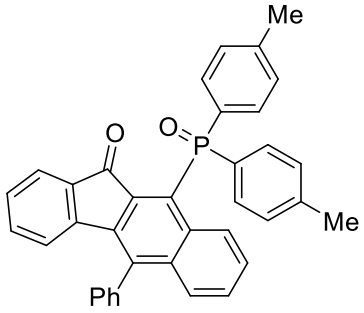
10-(diphenylphosphoryl)-5-hexyl-11H-benzo[b]fluoren-11-one (3p, new compound)



yellow solid; 90.9 mg, 59% yield; **m.p:**221-223 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.55 (d, *J* = 8.6 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.83-7.78 (m, 5H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.52-7.46 (m, 3H), 7.42-7.39 (m, 5H), 7.25 (t, *J* = 7.3 Hz, 1H), 3.42-3.39 (m, 2H), 1.87-1.81 (m, 2H), 1.71-1.66 (m, 2H), 1.49-1.39 (m, 4H), 0.96 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.2 (d, *J* = 3.3 Hz), 144.4, 139.7 (d, *J* = 2.2 Hz), 138.1 (d, *J* = 6.6 Hz), 136.4 (d, *J*

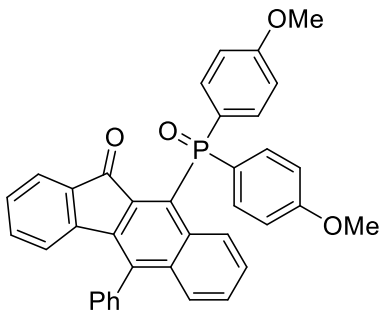
= 6.6 Hz), 163.1 (d, *J* = 8.4 Hz), 135.4, 135.3 (d, *J* = 3.3 Hz), 134.6 (d, *J* = 11.1 Hz), 139.2 (d, *J* = 110.0 Hz), 131.7 (d, *J* = 4.4 Hz), 131.4 (d, *J* = 3.3 Hz), 131.3 (d, *J* = 8.9 Hz), 129.12, 129.11 (d, *J* = 90.7 Hz), 126.6, 128.2 (d, *J* = 12.8 Hz), 127.3, 124.5, 124.4, 124.1, 31.7, 30.0, 29.2, 29.0, 22.7, 14.1; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.9; **FT-IR(film):**1708, 1437, 1177, 1117 cm^{-1}; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{35}H_{31}NaO_2P^+$ 537.1954, found 537.1950.

10-(di-p-tolylphosphoryl)-5-phenyl-11H-benzo[b]fluoren-11-one (3q, new compound)



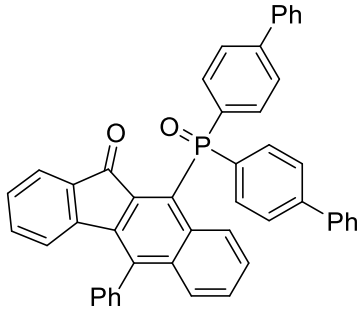
yellow solid; 115.3 mg, 72% yield; **m.p:** 267-270 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.64 (d, *J* = 9.1 Hz, 1H), 7.79-7.75 (m, 4H), 7.65-7.60 (m, 3H), 7.49-7.48 (m, 2H), 7.45-7.40 (m, 3H), 7.37-7.35 (m, 1H), 7.25-7.24 (m, 4H), 7.13-7.09 (m, 2H), 6.16 (d, *J* = 6.9 Hz, 1H), 2.38 (s, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.3 (d, *J* = 3.3 Hz), 144.2, 142.0 (d, *J* = 2.2 Hz), 138.8 (d, *J* = 2.2 Hz), 137.7 (d, *J* = 7.7 Hz), 137.5, 136.9 (d, *J* = 7.7 Hz), 136.5 (d, *J* = 6.6 Hz), 135.5, 135.05 (d, *J* = 11.1 Hz), 134.98, 131.6 (d, *J* = 11.1 Hz), 131.5 (d, *J* = 89.6 Hz), 131.4 (d, *J* = 4.4 Hz), 131.2 (d, *J* = 111.2 Hz), 129.7, 129.6, 129.15 (d, *J* = 13.3 Hz), 129.11, 128.9, 128.8, 127.58, 127.57, 124.3, 114.0, 21.9; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.4; **FT-IR(film):**1712, 1600, 1173, 1116, 1097 cm^{-1}; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{37}H_{27}NaO_2P^+$ 557.1641, found 557.1638.

10-(bis(4-methoxyphenyl)phosphoryl)-5-phenyl-11*H*-benzo[b]fluoren-11-one (3r, new compound)



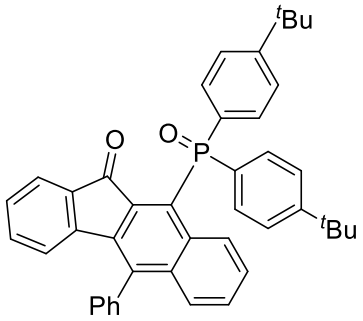
yellow solid; 110.4 mg, 65% yield; **m.p:** 235-238 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.60 (d, *J* = 8.6 Hz, 1H), 7.83-7.80 (m, 4H), 7.64-7.61 (m, 3H), 7.50-7.47 (m, 2H), 7.45-7.42 (m, 1H), 7.41-7.39 (m, 2H), 7.37-7.36 (m, 1H), 7.13-7.09 (m, 2H), 6.96-6.94 (m, 4H), 6.16-6.15 (m, 1H), 3.82 (s, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.4 (d, *J* = 3.3 Hz), 162.2 (d, *J* = 3.3 Hz), 144.1, 138.7 (d, *J* = 2.2 Hz), 137.6 (d, *J* = 6.9 Hz), 137.5, 136.9 (d, *J* = 7.8 Hz), 136.4 (d, *J* = 6.6 Hz), 135.5, 135.04 (d, *J* = 10.8 Hz), 134.97, 133.6 (d, *J* = 11.9 Hz), 132.2 (d, *J* = 89.7 Hz), 131.4 (d, *J* = 3.8 Hz), 129.7, 129.5, 129.1, 128.9, 128.8, 127.54, 127.52, 126.0 (d, *J* = 116.7 Hz), 124.3, 124.0, 113.9 (d, *J* = 13.7 Hz), 55.5; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 32.4; **FT-IR(film):**1712, 1597, 1504, 1254, 1179, 1119 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{37}H_{28}O_4P^+$ 567.1720, found 567.1725.

10-(di([1,1'-biphenyl]-4-yl)phosphoryl)-5-phenyl-11H-benzo[b]fluoren-11-one (3s, new compound)



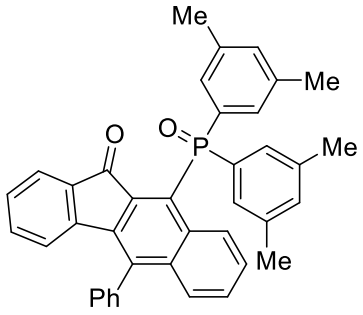
yellow solid; 146.1 mg, 74% yield; **m.p:** 228-230 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.76 (d, *J* = 8.4 Hz, 1H), 8.02-7.98 (m, 4H), 7.71-7.69 (m, 4H), 7.67-7.61 (m, 7H), 7.56-7.53 (m, 2H), 7.50-7.44 (m, 7H), 7.39-7.36 (m, 3H), 7.15-7.10 (m, 2H), 6.19 (d, *J* = 7.4 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.5 (d, *J* = 3.3 Hz), 144.4 (d, *J* = 3.3 Hz), 144.3, 140.5, 139.1 (d, *J* = 3.3 Hz), 137.8 (d, *J* = 7.7 Hz), 137.4, 137.1 (d, *J* = 7.7 Hz), 136.6 (d, *J* = 6.6 Hz), 135.4, 135.2, 135.1 (d, *J* = 8.8 Hz), 133.0 (d, *J* = 110.6 Hz), 132.1 (d, *J* = 11.1 Hz), 131.4 (d, *J* = 4.4 Hz), 130.7 (d, *J* = 89.6 Hz), 129.8, 129.5, 129.3, 129.10, 129.05, 128.92, 128.2, 127.8, 127.7, 127.5, 127.2 (d, *J* = 13.3 Hz), 124.4, 124.0; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.4; **FT-IR(film):**1710, 1598, 1483, 1171, 1120 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{47}H_{32}O_2P^+$ 659.2134 found 659.2134.

10-(bis(4-(tert-butyl)phenyl)phosphoryl)-5-phenyl-11H-benzo[b]fluoren-11-one (3t, new compound)



yellow solid; 61.2 mg, 33% yield; **m.p:** 255-257 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.67 (d, *J* = 8.8 Hz, 1H), 7.82-7.79 (m, 4H), 7.66-7.60 (m, 3H), 7.51-7.45 (m, 7H), 7.42-7.40 (m, 2H), 7.31-7.30 (m, 1H), 7.14-7.09 (m, 2H), 6.17 (d, *J* = 6.9 Hz, 1H), 1.31 (s, 18H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.0 (d, *J* = 3.3 Hz), 154.7 (d, *J* = 3.1 Hz), 144.0, 138.6 (d, *J* = 3.0 Hz), 137.6 (d, *J* = 6.8 Hz), 137.3, 136.7 (d, *J* = 7.8 Hz), 136.4 (d, *J* = 6.5 Hz), 135.4, 134.76 (d, *J* = 9.8 Hz), 134.75, 131.4 (d, *J* = 89.6 Hz), 131.33 (d, *J* = 10.9 Hz), 131.26 (d, *J* = 4.4 Hz), 130.9 (d, *J* = 110.2 Hz), 129.5, 129.3, 128.9, 128.7, 128.6, 127.40, 127.36, 125.2 (d, *J* = 13.1 Hz), 123.9, 123.8, 35.0, 31.1; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.6; **FT-IR(film):** 1712, 1599, 1470, 1177, 1092 cm^{-1}; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{43}H_{39}NaO_2P^+$ 641.2580 found 641.2574.

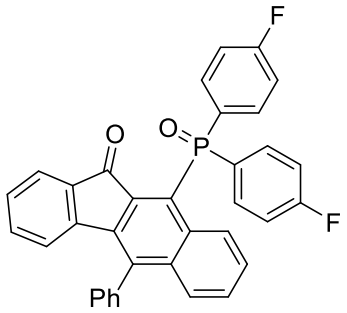
10-(bis(3,5-dimethylphenyl)phosphoryl)-5-phenyl-11H-benzo[b]fluoren-11-one (3u, new compound)



yellow solid; 82.6 mg, 49% yield; **m.p:**265-268 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.62 (d, *J* = 9.1 Hz, 1H), 7.66-7.60 (m, 3H), 7.52-7.43 (m, 9H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.14-7.09 (m, 4H), 6.20-6.18 (m, 1H), 2.31 (s, 12H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.0 (d, *J* = 3.3 Hz), 144.0, 138.6 (d, *J* = 2.2 Hz), 137.7 (d, *J* = 17.3 Hz), 137.6 (d, *J* = 6.6 Hz), 137.3, 136.8 (d, *J* = 7.7 Hz), 136.3 (d, *J* = 6.6 Hz), 135.4, 134.8 (d, *J* = 9.9 Hz), 134.7, 133.9 (d, *J* = 108.9 Hz), 133.3 (d, *J* = 3.3 Hz), 131.2 (d, *J* = 4.4 Hz), 131.0 (d, *J* = 86.9 Hz), 129.5, 129.4, 129.0 (d, *J* = 9.9 Hz), 128.9, 128.72, 128.66, 127.4, 127.3, 124.2, 123.8, 21.5; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 34.4; **FT-IR(film):**1712,

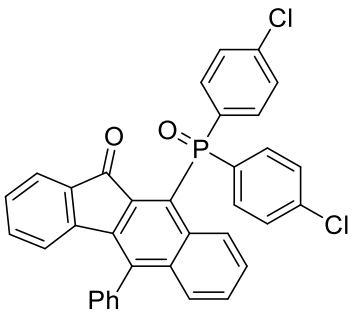
1600, 1470, 1175, 1131 cm^{-1}; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{39}H_{31}NaO_2P^+$ 585.1954 found 585.1954.

10-(bis(4-fluorophenyl)phosphoryl)-5-phenyl-11H-benzo[b]fluoren-11-one (3v, new compound)



yellow solid; 105.7 mg, 65% yield; **m.p:** 248-250 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.63 (d, *J* = 8.5 Hz, 1H), 7.93-7.86 (m, 3H), 7.66-7.61 (m, 3H), 7.54-7.40 (m, 8H), 7.36-7.34 (m, 1H), 7.15-7.09 (m, 4H), 6.18 (d, *J* = 7.0 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.3 (d, *J* = 4.4 Hz), 164.7 (d, *J* = 252.6 Hz), 144.0, 139.0, 137.6 (d, *J* = 6.6 Hz), 137.1, 136.5 (dd, J_1 = 8.0 Hz, J_2 = 5.7 Hz), 135.11, 135.06, 134.9 (d, *J* = 9.6 Hz), 134.0 (dd, J_1 = 9.6 Hz, J_2 = 9.0 Hz), 131.7, 131.3 (d, *J* = 10.2 Hz), 131.0, 129.6, 129.3, 129.1, 128.9, 128.8, 128.4 (d, *J* = 11.9 Hz), 127.6, 127.5, 124.2, 123.8, 115.5 (dd, J_1 = 21.1 Hz, J_2 = 12.8 Hz); **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 32.7; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$):** δ -105.80; **FT-IR(film):**1712, 1592, 1498, 1161, 1116 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{35}H_{22}F_2O_2P^+$ 543.1320, found 543.1320.

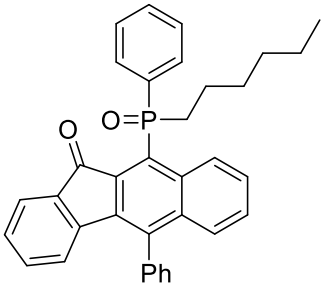
10-(bis(4-chlorophenyl)phosphoryl)-5-phenyl-11*H*-benzo[b]fluoren-11-one (3w, new compound)



yellow solid; 113.7 mg, 61% yield; **m.p:** 271-273 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.63 (d, *J* = 8.5 Hz, 1H), 7.82-7.79 (m, 4H), 7.66-7.61 (m, 3H), 7.53-7.46 (m, 3H), 7.43-7.37 (m, 7H), 7.16-

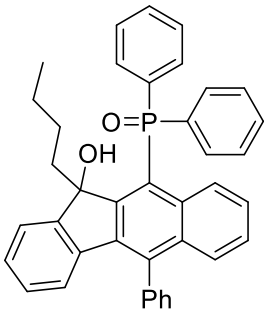
7.12 (m, 2H), 6.18-6.16 (m, 1H); **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz):** δ 191.5 (d, *J* = 2.1 Hz), 144.2, 139.4, 138.3 (d, *J* = 2.2 Hz), 137.7 (d, *J* = 7.0 Hz), 137.2, 137.1 (d, *J* = 8.0 Hz), 136.3 (d, *J* = 7.8 Hz), 135.4, 135.2, 135.1 (d, *J* = 8.7 Hz), 133.0 (d, *J* = 11.3 Hz), 132.5 (d, *J* = 111.4 Hz), 131.0 (d, *J* = 3.1 Hz), 129.8, 129.5 (d, *J* = 90.7 Hz), 129.44, 129.43, 129.2, 129.0, 138.9 (d, *J* = 13.4 Hz), 127.9, 127.8, 124.5, 124.1; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 32.0; **FT-IR(film):** 1709, 1481, 1275, 1180, 1086 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{35}H_{22}Cl_2O_2P^+$ 575.0729, found 575.0735.

10-(hexyl(phenyl)phosphoryl)-5-phenyl-11H-benzo[b]fluoren-11-one (3x, new compound)



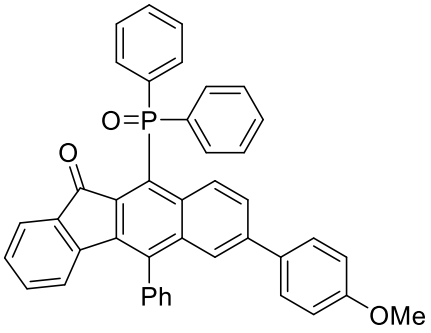
yellow solid; 83.3 mg, 54% yield; **m.p:** 209-211 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 10.23 (d, *J* = 8.7 Hz, 1H), 7.82-7.79 (m, 2H), 7.64-7.60 (m, 3H), 7.58-7.56 (m, 1H), 7.49-7.47 (m, 3H), 7.44-7.39 (m, 5H), 7.15-7.11 (m, 2H), 6.14-6.12 (m, 1H), 3.03-2.96 (m, 1H), 2.88-2.80 (m, 1H), 1.62-1.55 (m, 1H), 1.47-1.39 (m, 2H), 1.26-1.20 (m, 5H), 0.79 (t, *J* = 6.9 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz):** δ 192.3 (d, *J* = 3.3 Hz), 144.3, 138.9 (d, *J* = 2.2 Hz), 137.4, 137.3 (d, *J* = 5.5 Hz), 136.9 (d, *J* = 7.7 Hz), 136.4 (d, *J* = 103.9 Hz), 135.9 (d, *J* = 7.7 Hz), 135.31 (d, *J* = 11.1 Hz), 135.28 (d, *J* = 9.9 Hz), 131.3 (d, *J* = 2.2 Hz), 131.2 (d, *J* = 2.2 Hz), 130.9 (d, *J* = 79.6 Hz), 130.0 (d, *J* = 16.6 Hz), 129.9 (d, *J* = 9.9 Hz), 129.7 (d, *J* = 2.2 Hz), 129.5, 129.3, 128.9, 128.8, 128.4 (d, *J* = 12.2 Hz), 127.9, 127.5, 124.4, 124.0, 31.5, 30.9 (d, *J* = 15.6 Hz), 29.7 (d, *J* = 73.5 Hz), 22.6, 22.4 (d, *J* = 3.9 Hz), 14.2; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 42.8; **FT-IR(film):** 1716, 1437, 1322, 1281, 1127 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{35}H_{32}O_2P^+$ 515.2134 found 515.2136..

(11-butyl-11-hydroxy-5-phenyl-11H-benzo[b]fluoren-10-yl)diphenylphosphine oxide (5a, new compound)



Light yellow solid; 68.8 mg, 61% yield; **m.p:** 202-203 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.51 (s, 1H), 8.00-7.95 (m, 2H), 7.73-7.51 (m, 11H), 7.48-7.37 (m, 5H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.02-6.98 (m, 2H), 6.18 (d, *J* = 7.9 Hz, 1H), 2.82-2.74 (m, 1H), 2.26-2.19 (m, 1H), 0.88-0.77 (m, 1H), 0.62- 0.52 (m, 3H), 0.45 (t, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 160.0 (d, *J* = 6.8 Hz), 149.7, 138.7 (d, *J* = 2.8 Hz), 138.3, 137.8, 137.4 (d, *J* = 11.9 Hz), 136.1 (d, *J* = 107.7 Hz), 133.8 (d, *J* = 8.7 Hz), 132.6 (d, *J* = 3.6 Hz), 132.59 (d, *J* = 3.6 Hz), 132.57 (d, *J* = 10.3 Hz), 131.7 (d, *J* = 2.4 Hz), 131.5 (d, *J* = 103.7 Hz), 131.1 (d, *J* = 10.7 Hz), 129.7, 129.472, 129.465 (d, *J* = 10.3 Hz), 129.0 (d, *J* = 11.5 Hz), 128.9, 128.83, 128.80, 128.3, 128.2 (d, *J* = 7.6 Hz), 128.1, 127.3, 125.7, 125.2, 123.4, 123.3, 121.8 (d, *J* = 96.6 Hz), 83.8. (d, *J* = 3.2 Hz), 42.1, 26.6, 22.5, 13.7; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 35.3; **FT-IR(film):** 3626, 1437, 1154, 1117, 1098 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{39}H_{34}O_2P^+$ 565.2291 found 565.2294.

10-(diphenylphosphoryl)-7-(4-methoxyphenyl)-5-phenyl-11H-benzo[b]fluoren-11-one (5b, new compound)



yellow solid; 99.1 mg, 81% yield; **m.p:** 271-273 °C; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.74 (d, *J* = 9.3 Hz, 1H), 7.96 (m, 4H), 7.76 (d, *J* = 9.1 Hz, 1H), 7.67-7.62 (m, 4H), 7.54-7.45 (m, 10H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.15-7.09 (m, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 6.18 (t, *J* = 7.7 Hz, 1H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):** δ 191.2 (d, *J* = 3.6 Hz), 159.9, 144.1, 141.2, 139.0 (d, *J* = 2.3 Hz), 137.3, 137.2 (d, *J* = 6.8 Hz), 135.6 (d, *J* = 11.5 Hz), 135.5, 135.3 (d, *J* = 6.6 Hz), 135.0, 134.7,

133.1 (d, J = 101.3 Hz), 129.8, 129.5, 129.0, 128.9, 128.5 (d, J = 11.1 Hz), 128.3, 126.8, 124.5, 124.2, 124.0, 114.6, 55.5; **^{31}P NMR ($CDCl_3$, 202 MHz):** δ 33.8; **FT-IR(film):** 1708, 1605, 1493, 1249, 1178 cm^{-1}; **HRMS:** $[M+H]^+$ m/z calcd for $C_{42}H_{30}O_3P^+$ 613.1927 found 613.1932.

4. Photophysical properties of the selected products

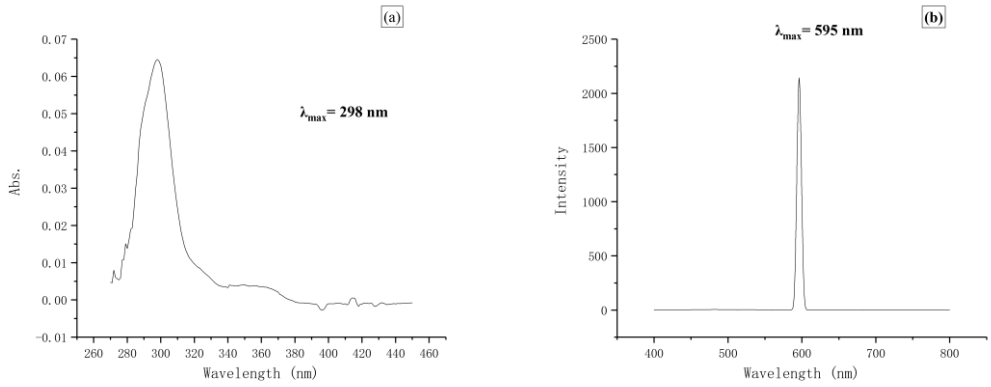


Figure S1. (a) Photoluminescence absorption spectrum of **3e** in solution of EtOH (5×10^{-6} M). **(b)** Photoluminescence emission spectrum of **3e** in solution of EtOH (5×10^{-6} M) upon excitation at 298 nm.

PL quantum yield of 3e, $\Phi_u=\Phi_s \times F_u/F_s \times A_s/A_u$= 33.1% (Using Rhodamine 6G as a reference)

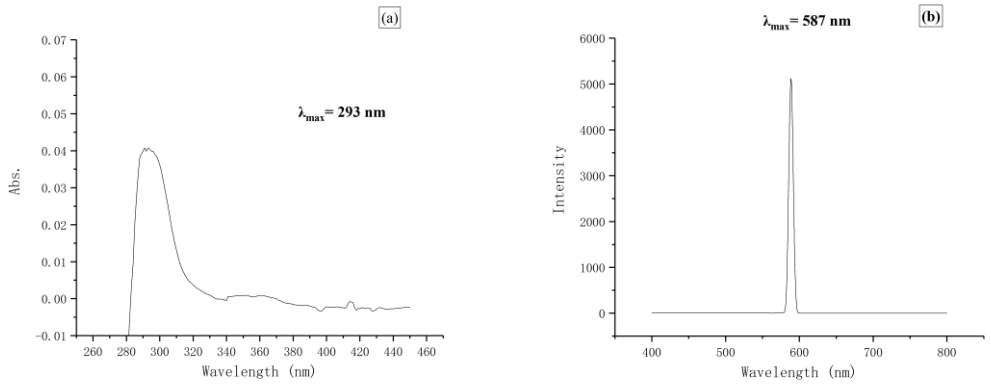
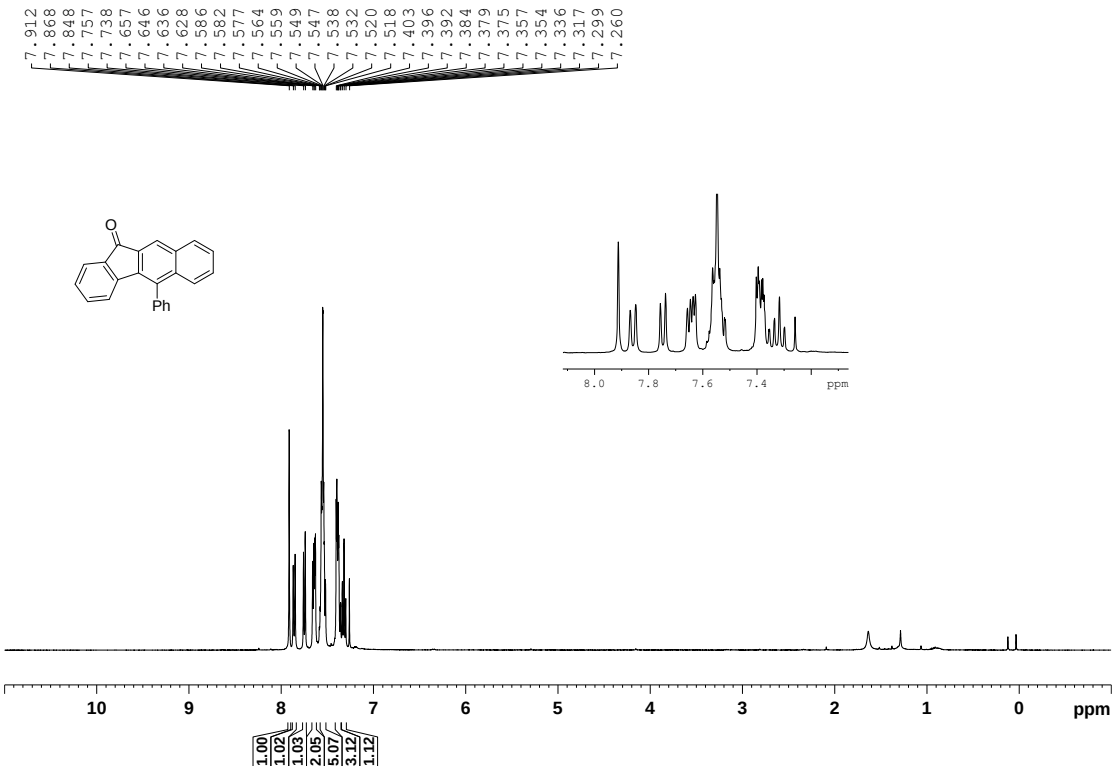


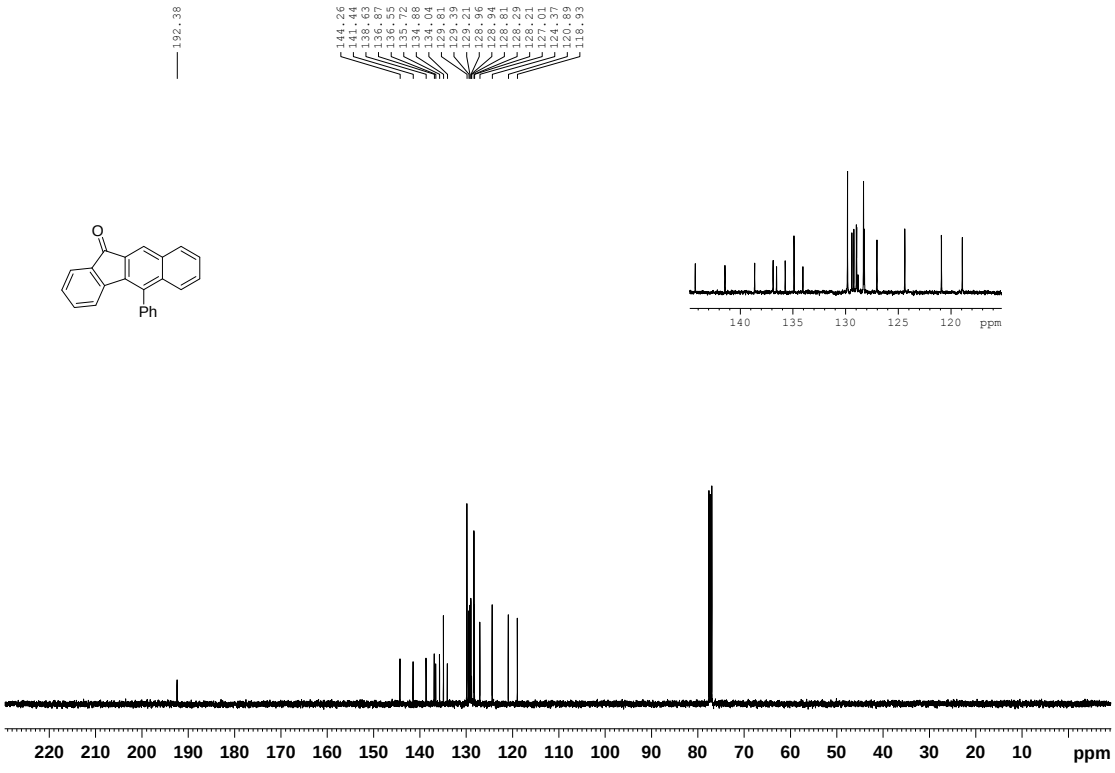
Figure S2. (a) Photoluminescence absorption spectrum of **3g** in solution of EtOH (2.5 x 10^{-6} M). **(b)** Photoluminescence emission spectrum of **3g** in solution of EtOH (2.5 x 10^{-6} M). upon excitation at 293 nm.

PL quantum yield of 3e, $\Phi_u=\Phi_s \times F_u/F_s \times A_s/A_u$= 24.8% (Using Rhodamine 6G as a reference)

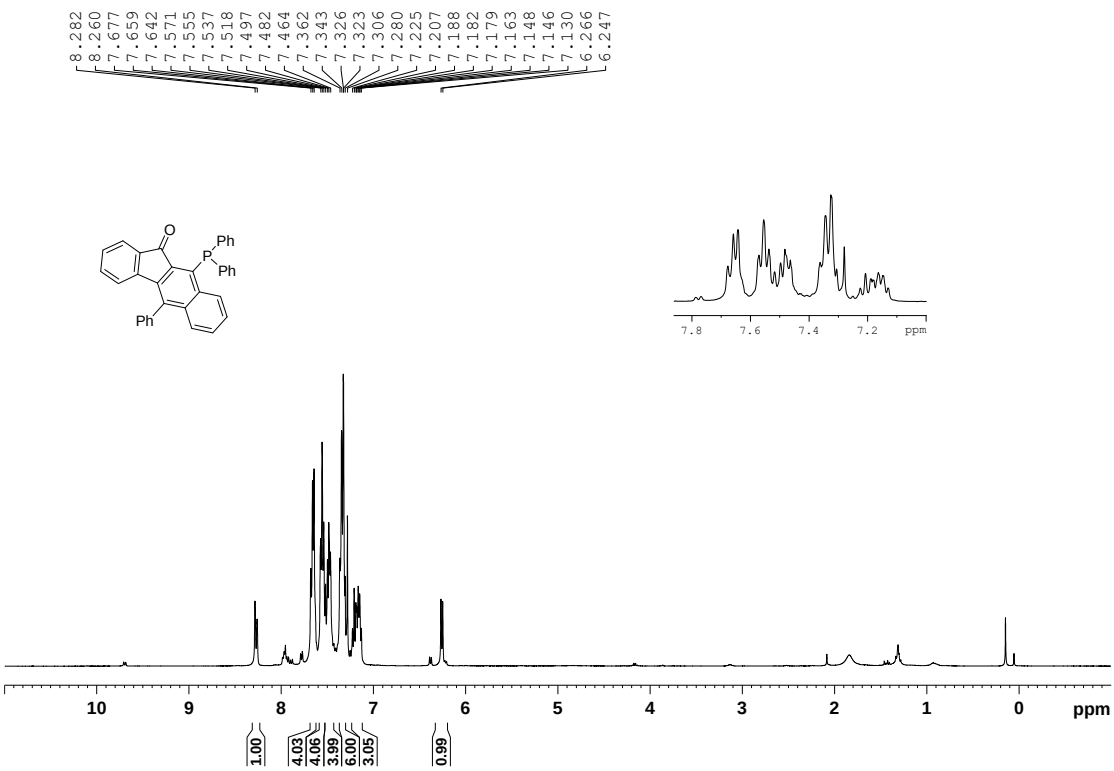
5. NMR spectrum of isolated products



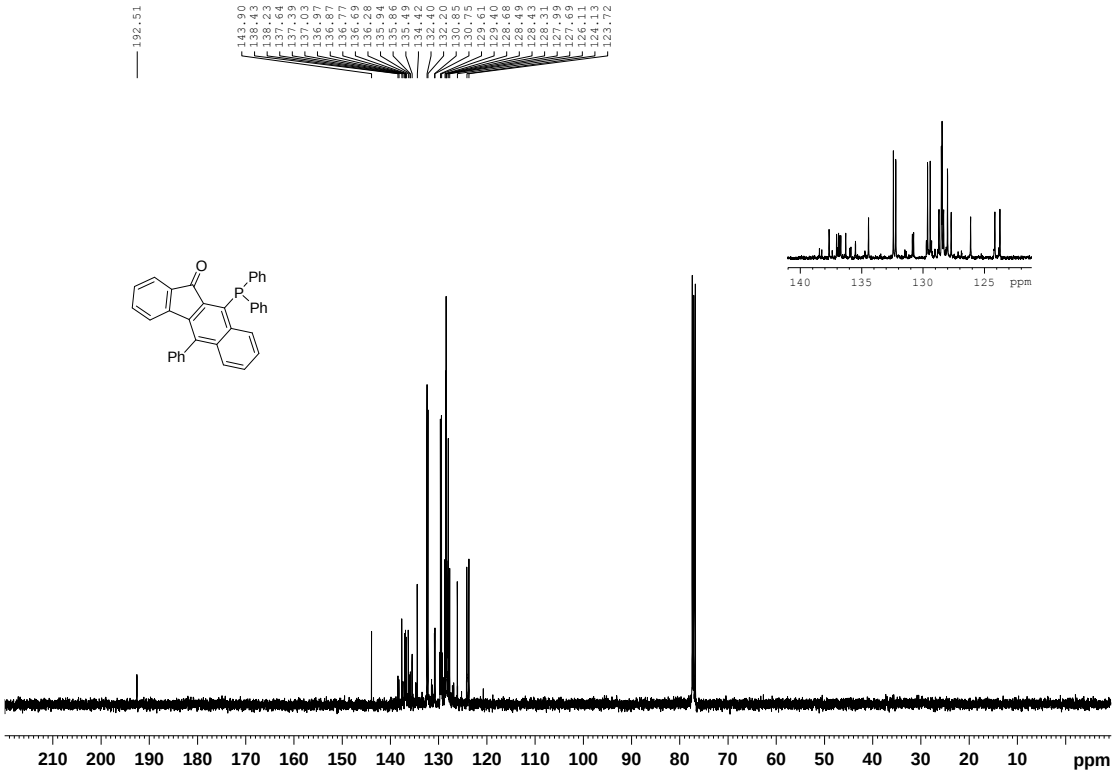
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3a'**



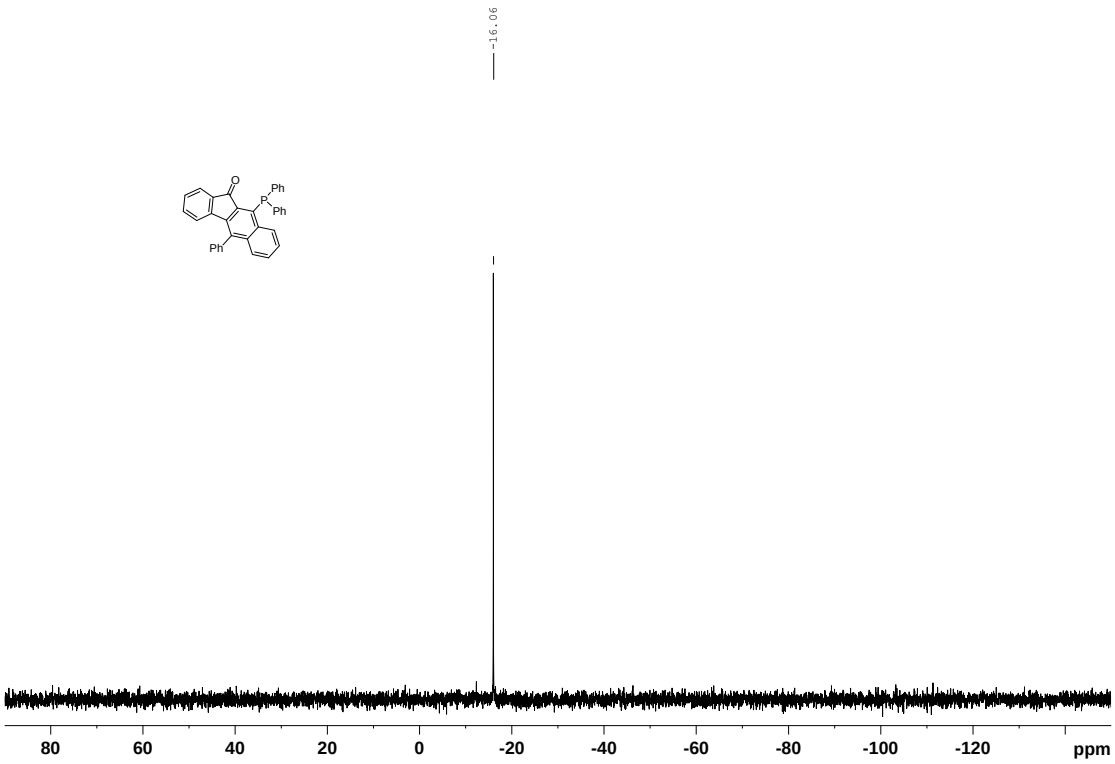
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3a'**



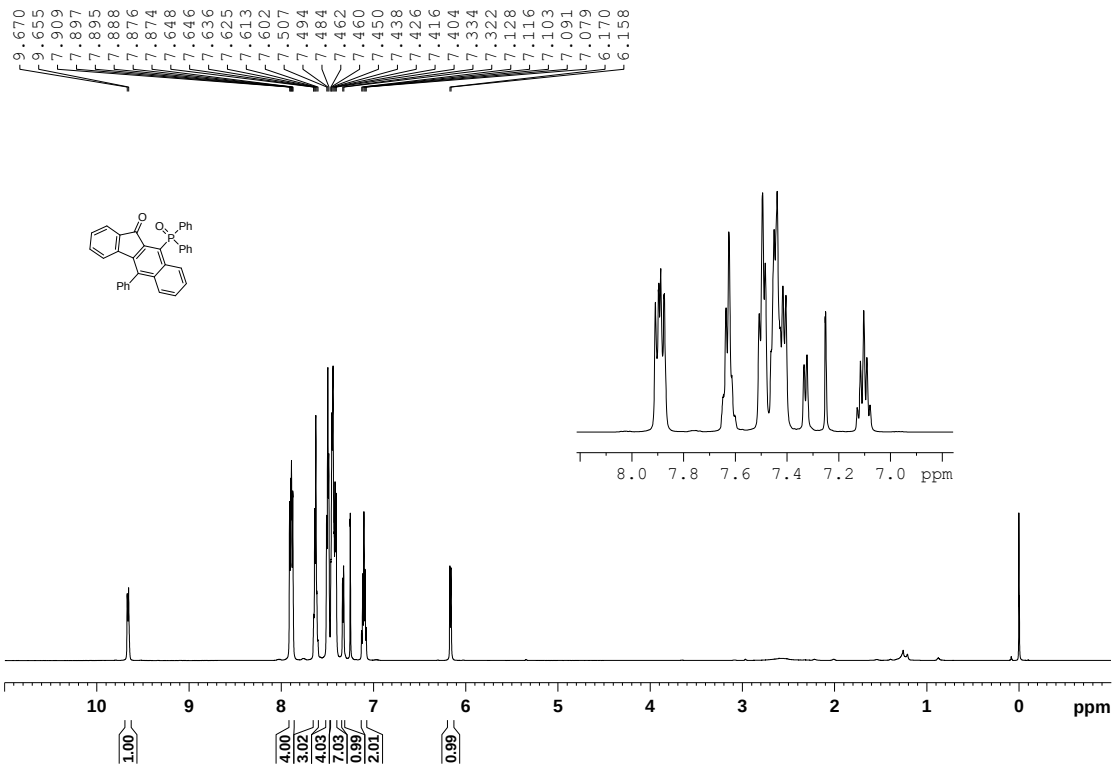
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound without oxidation



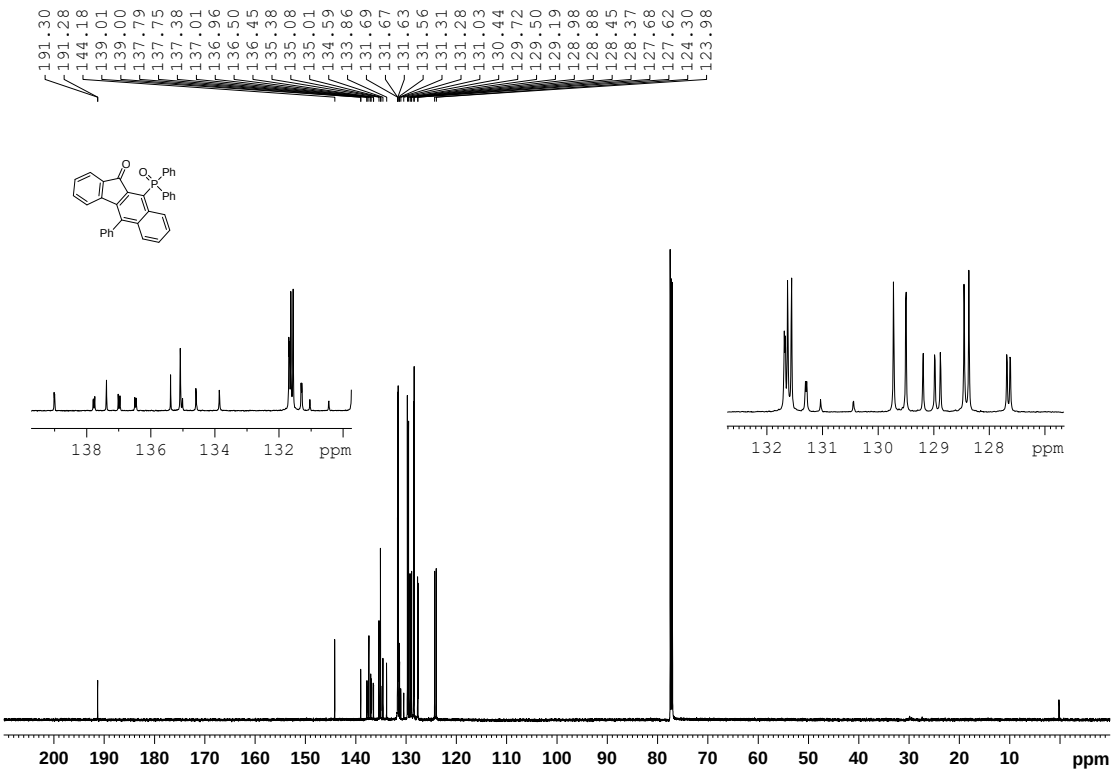
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound without oxidation



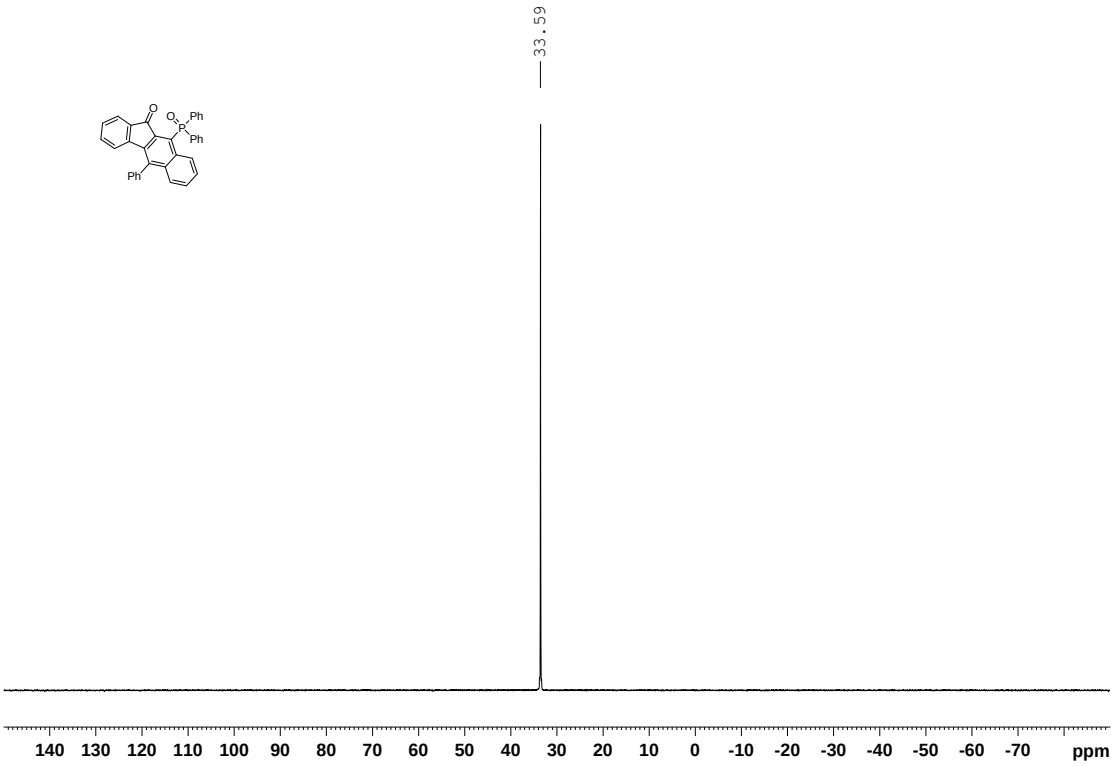
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound without oxidation



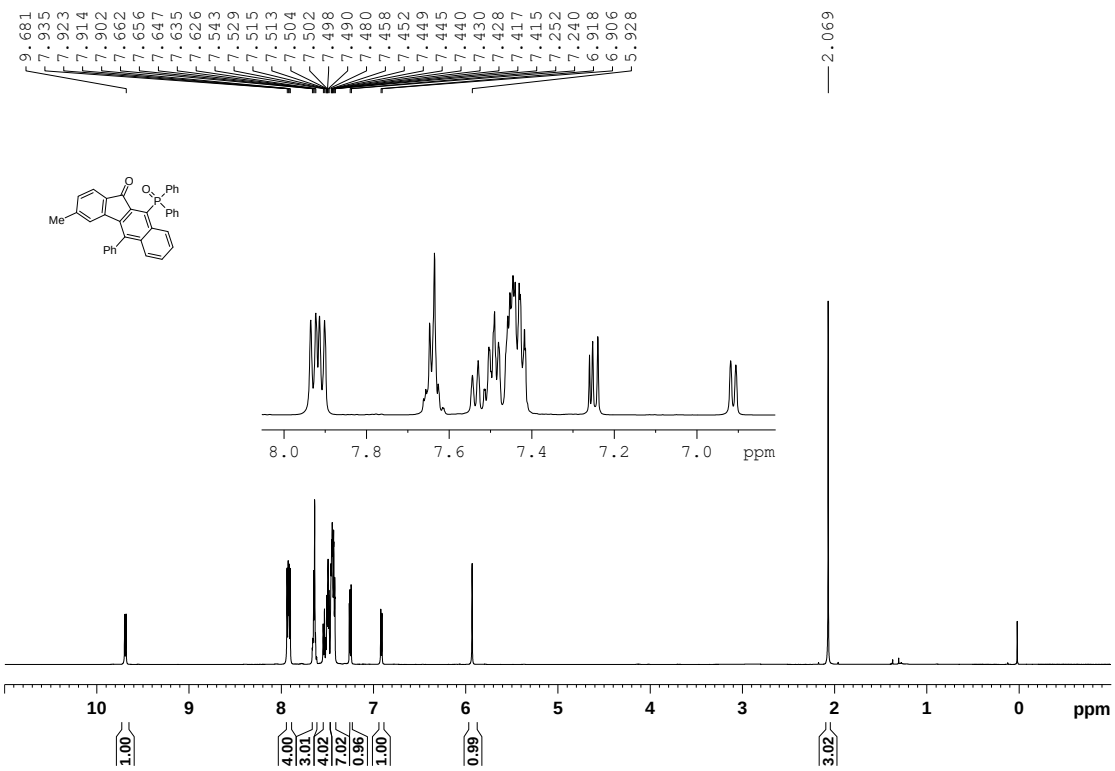
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3a**



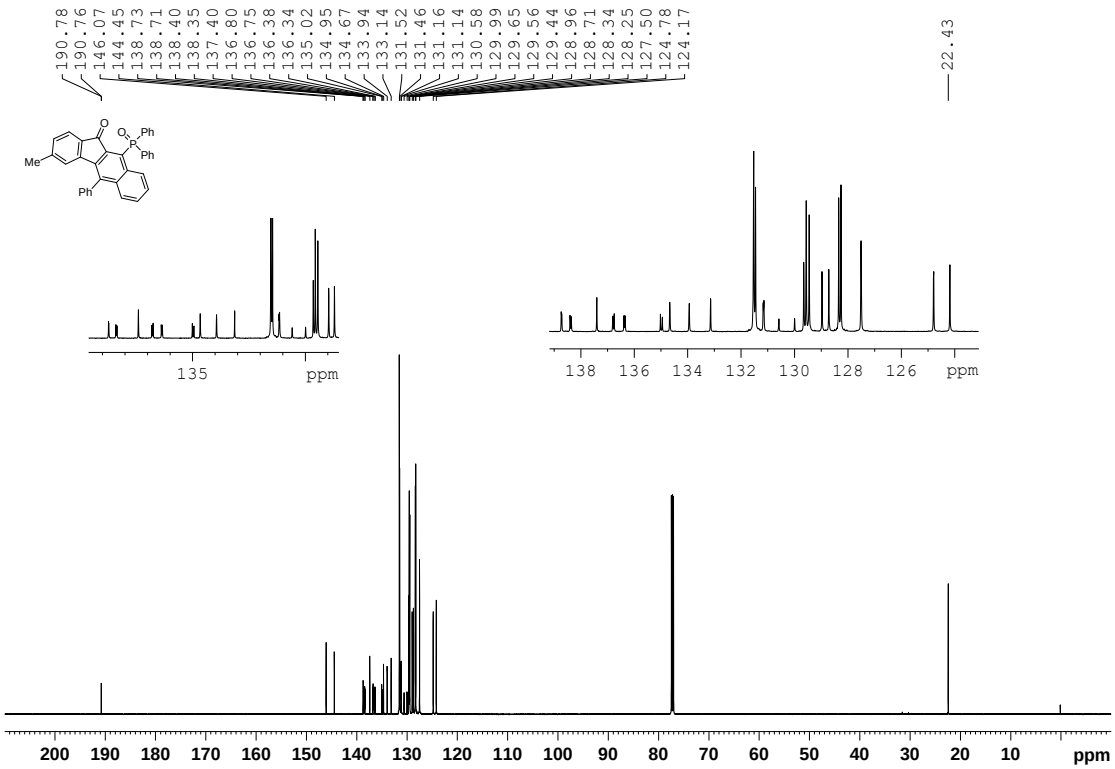
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3a**



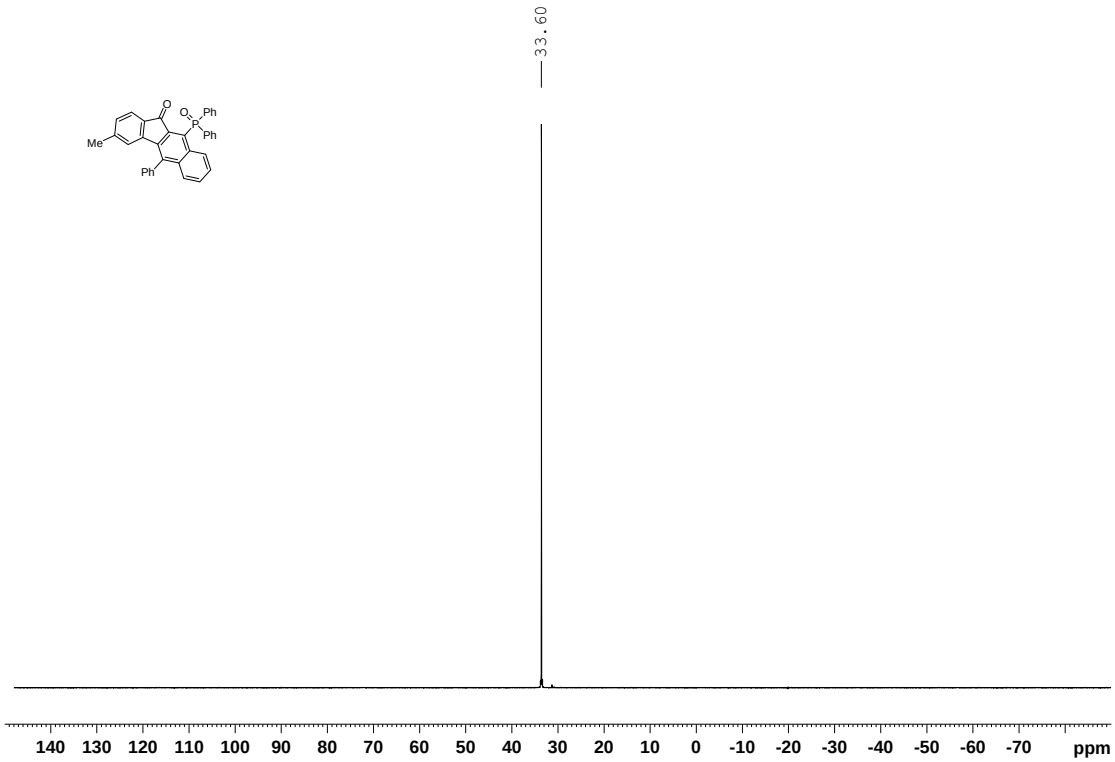
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3a**



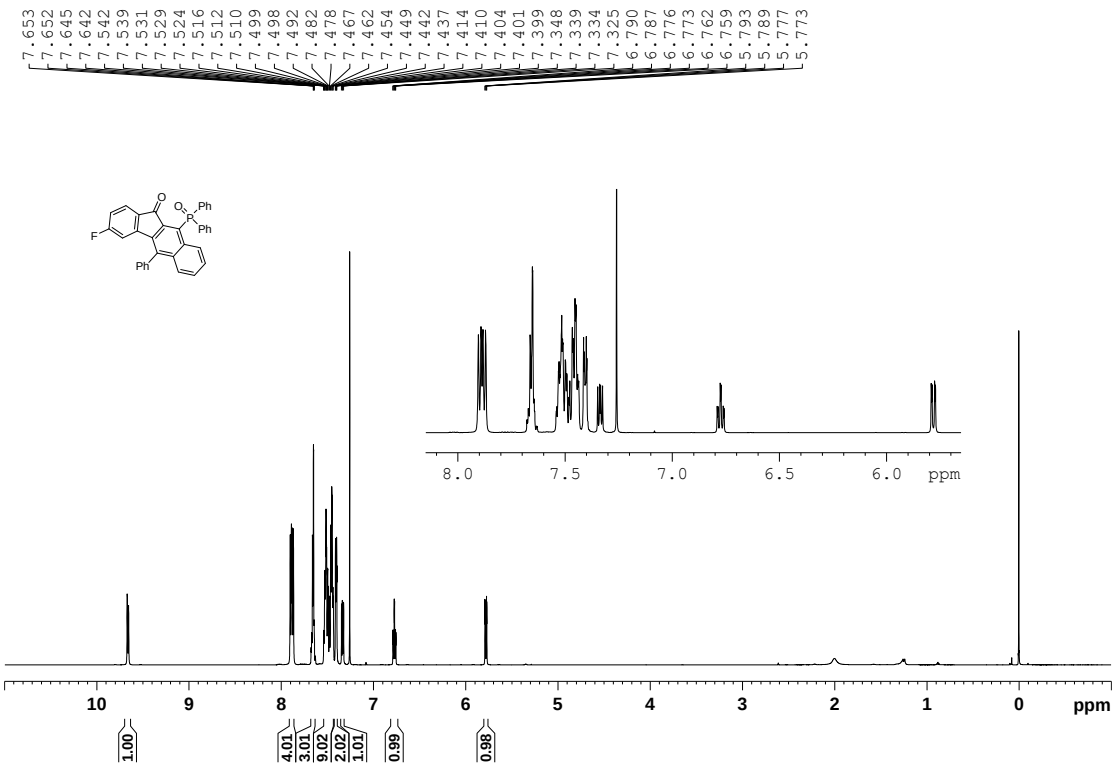
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3b**



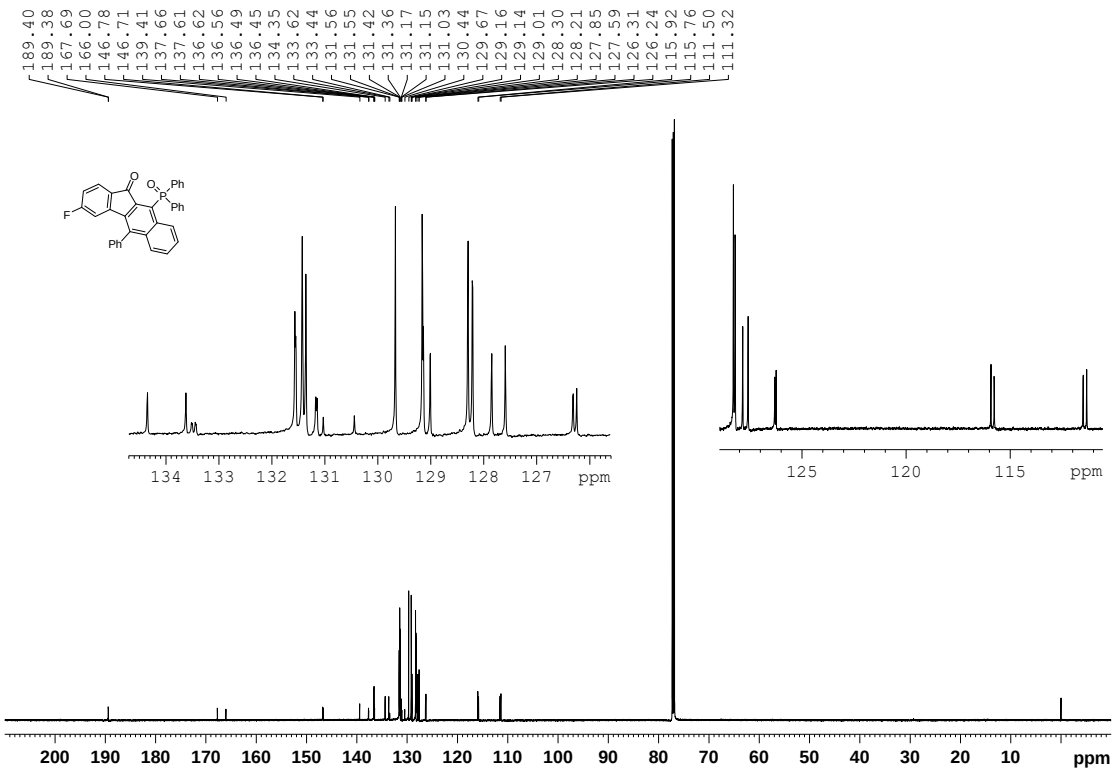
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3b**



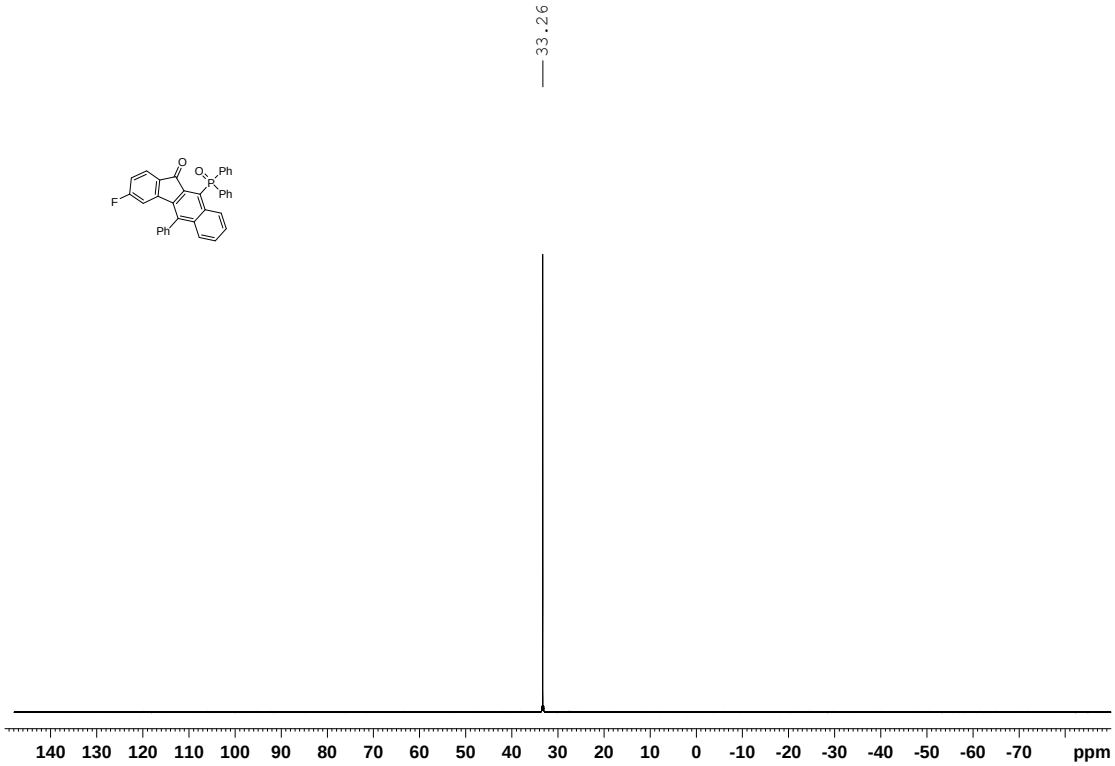
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3b**



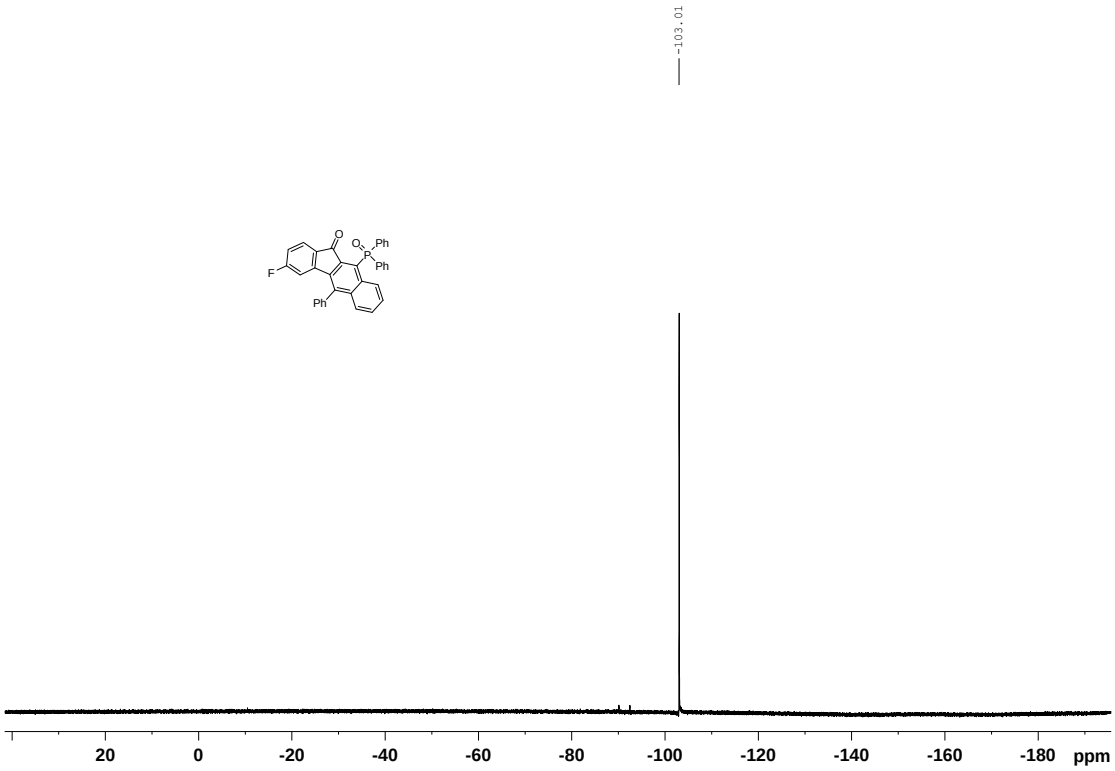
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3c**



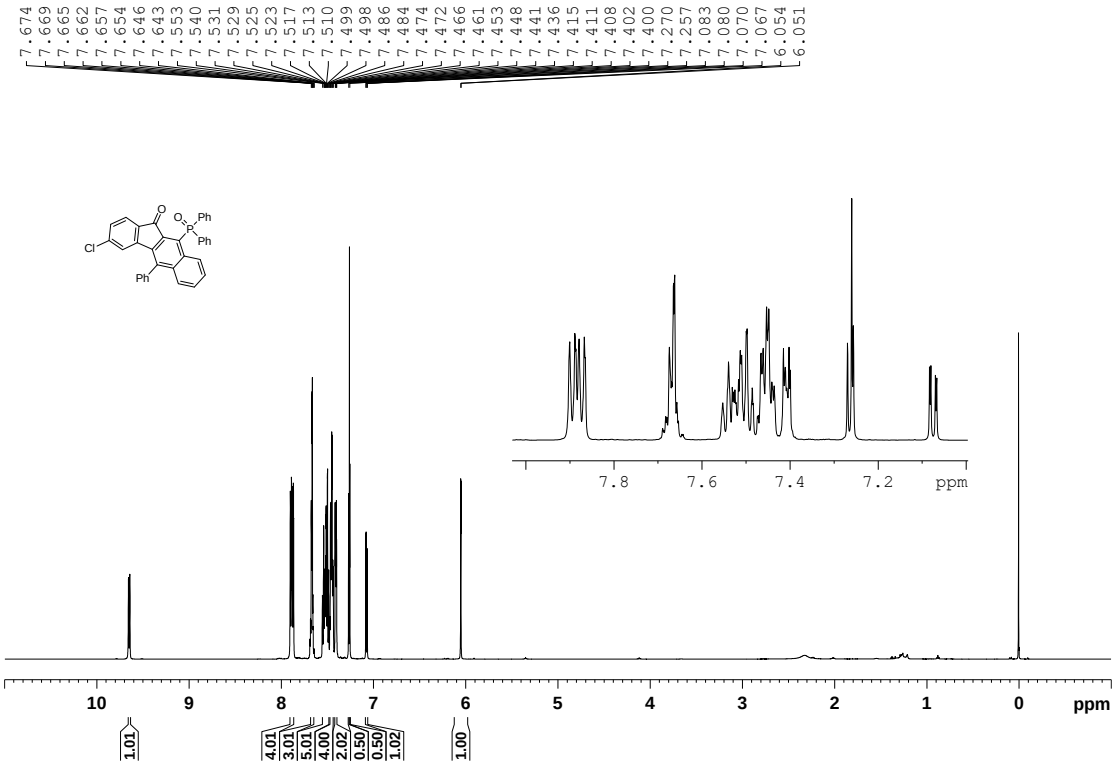
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3c**



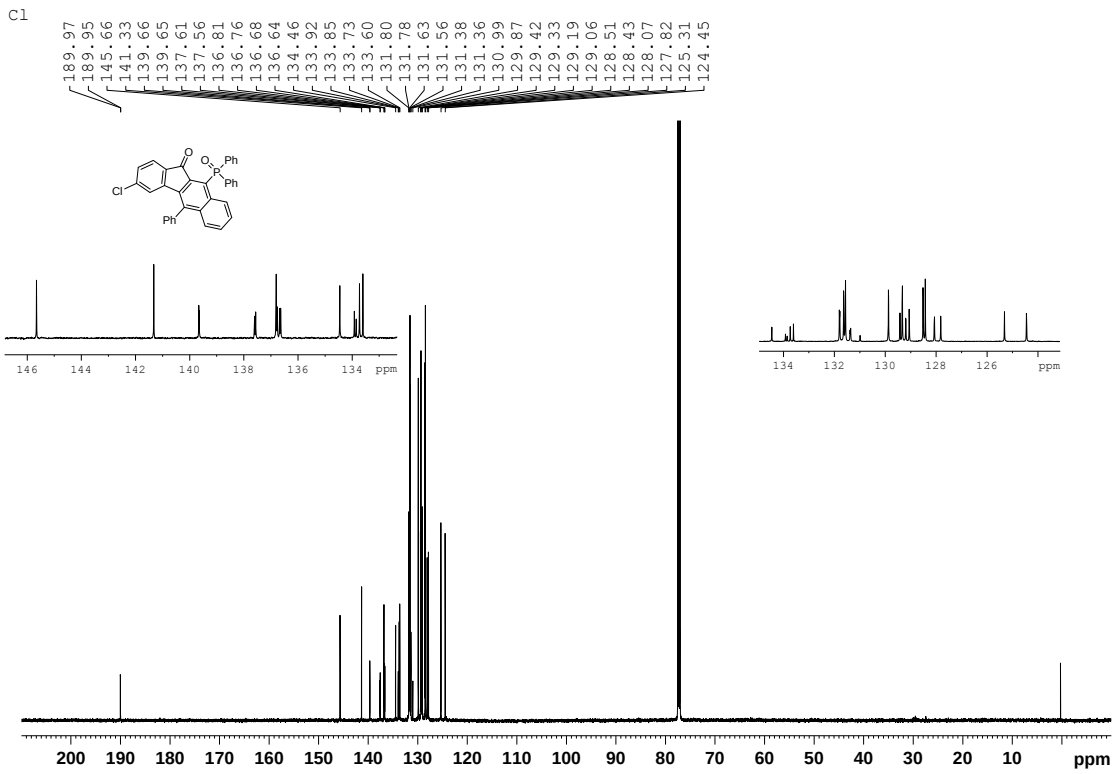
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3c**



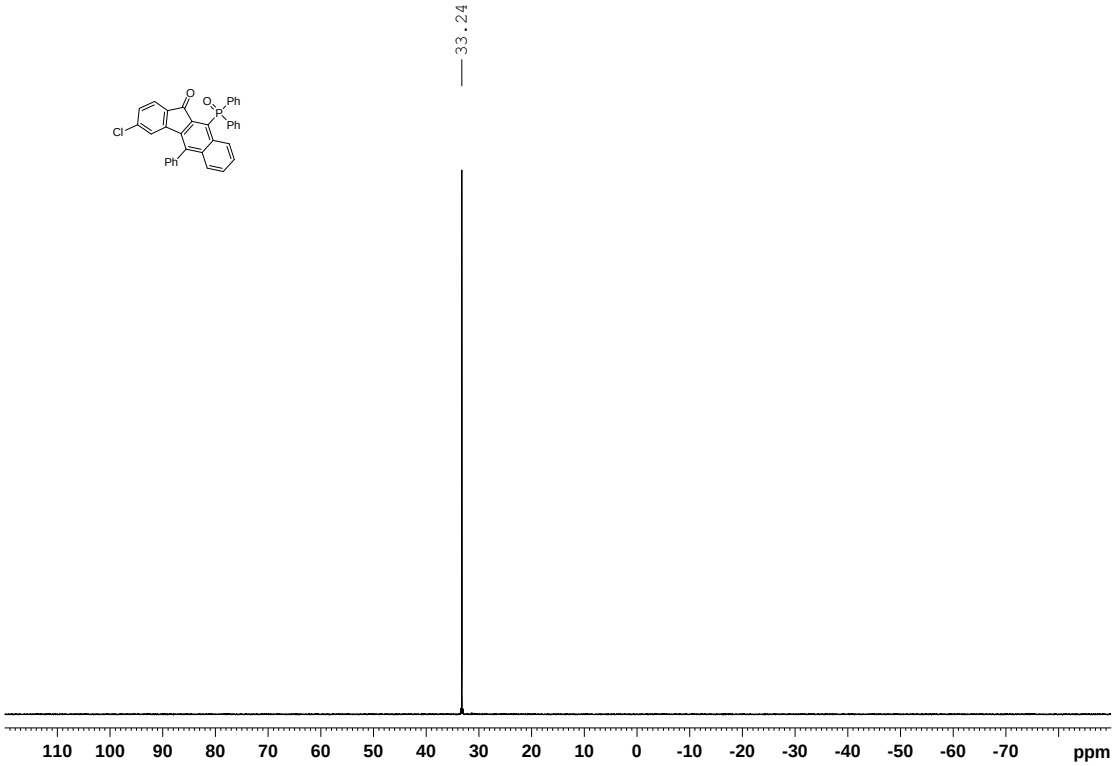
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) spectrum of compound **3c**



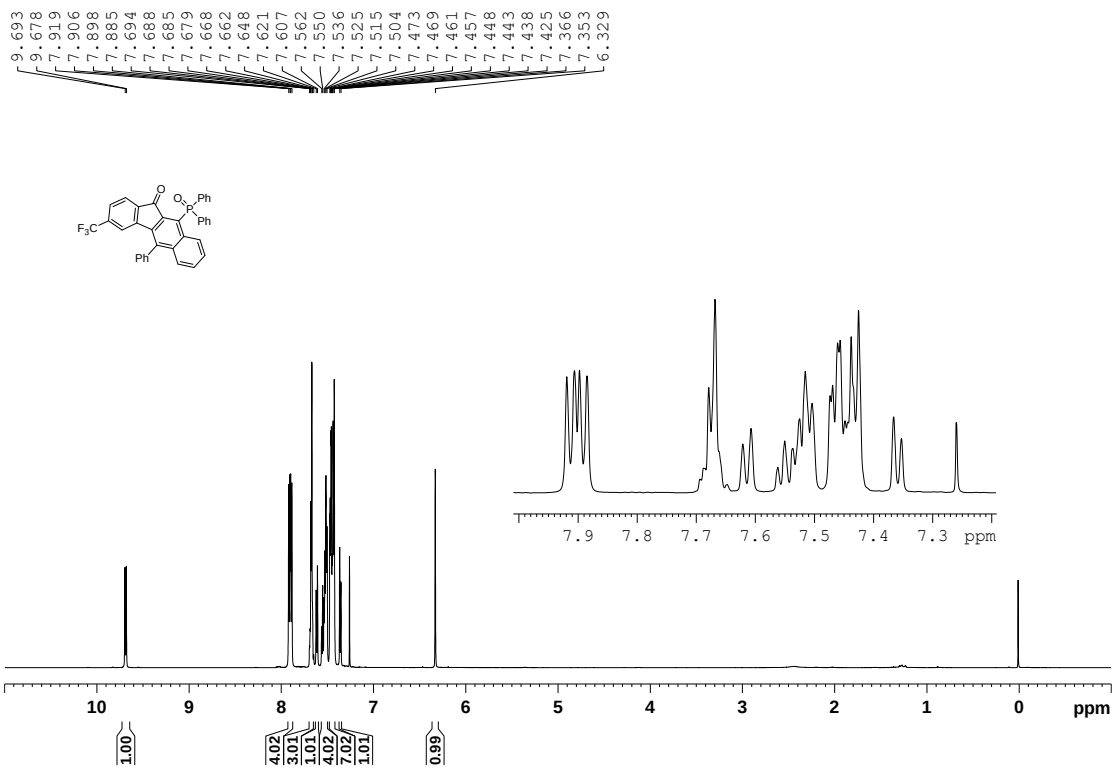
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3d**



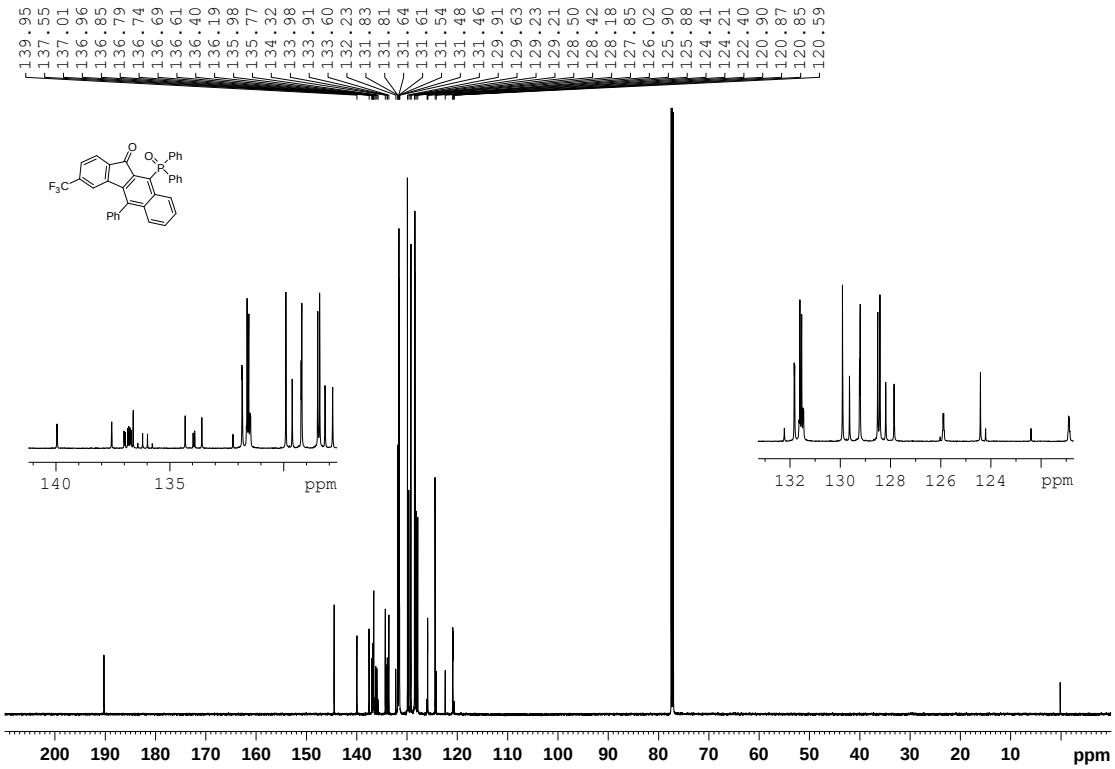
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3d**



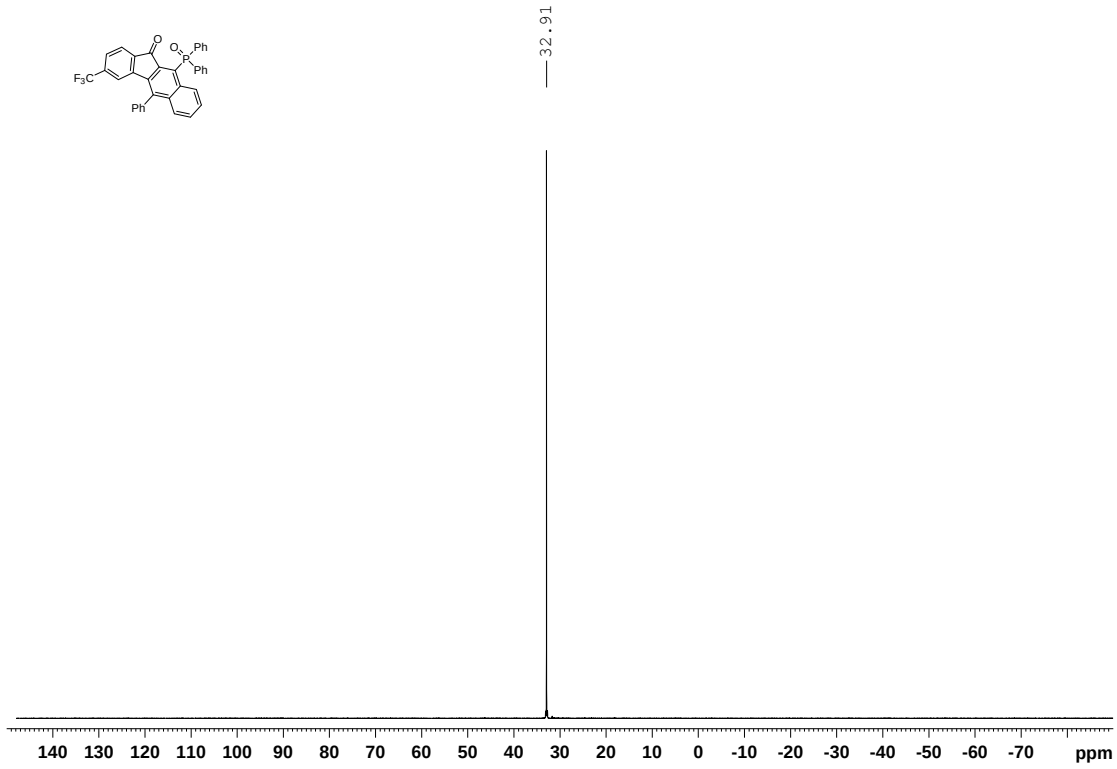
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3d**



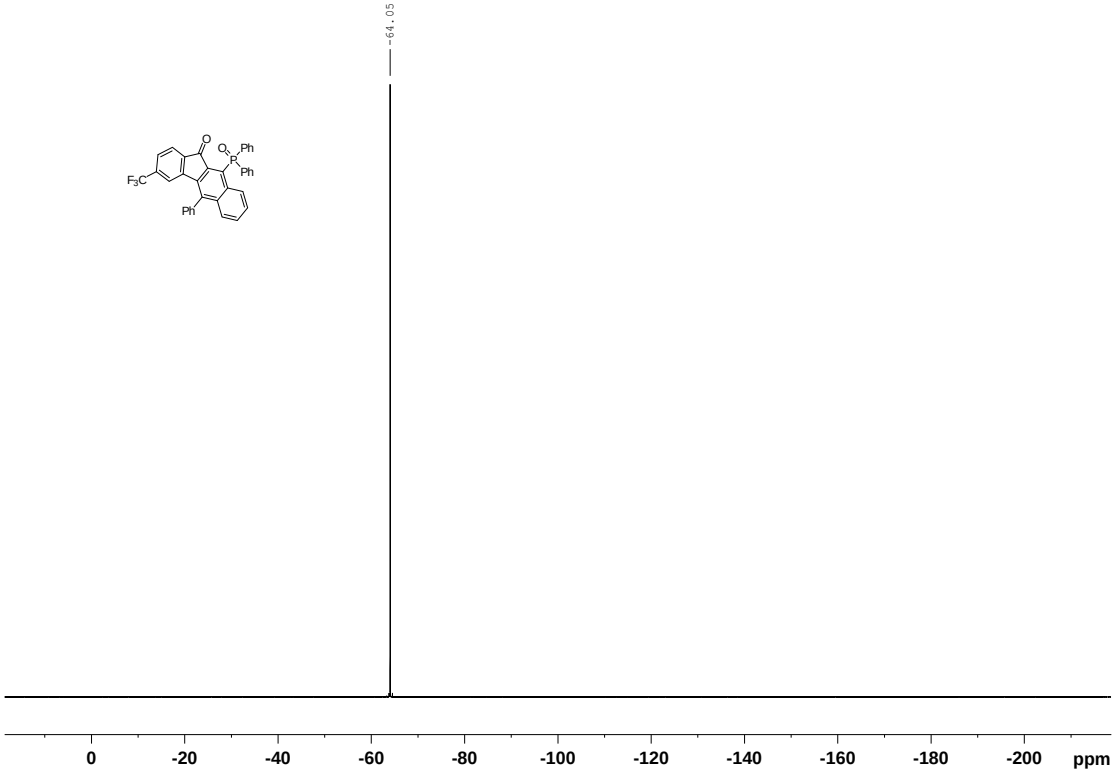
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3e**



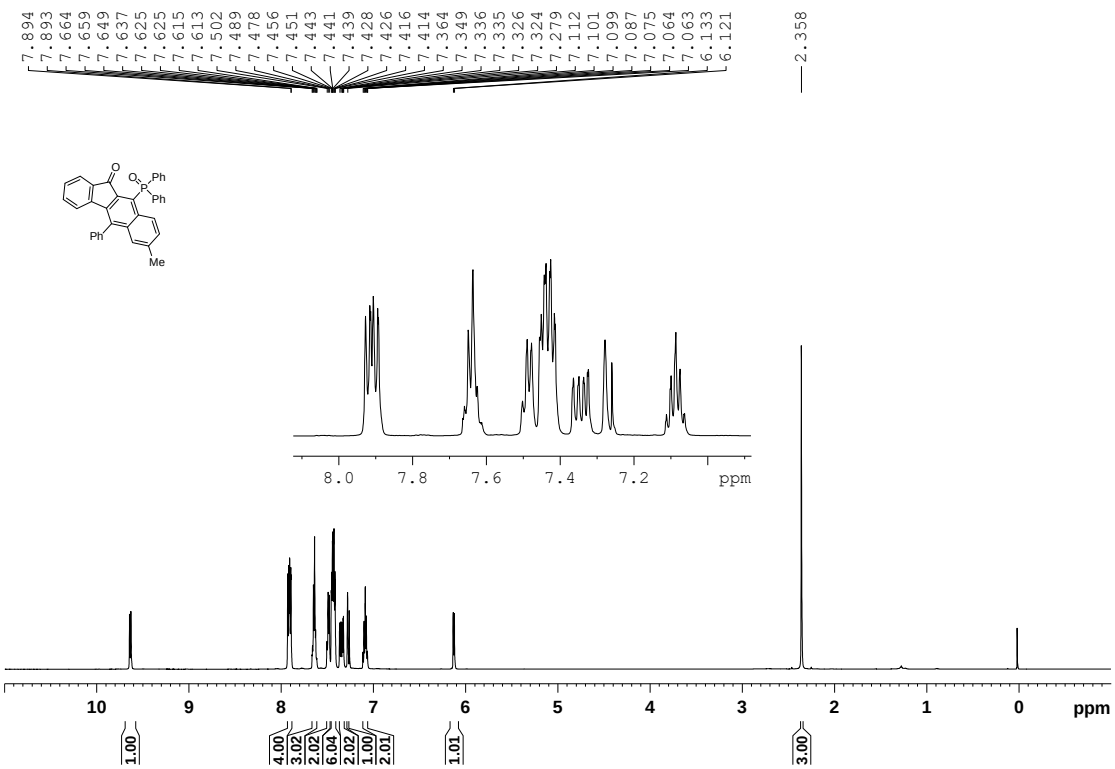
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3e**



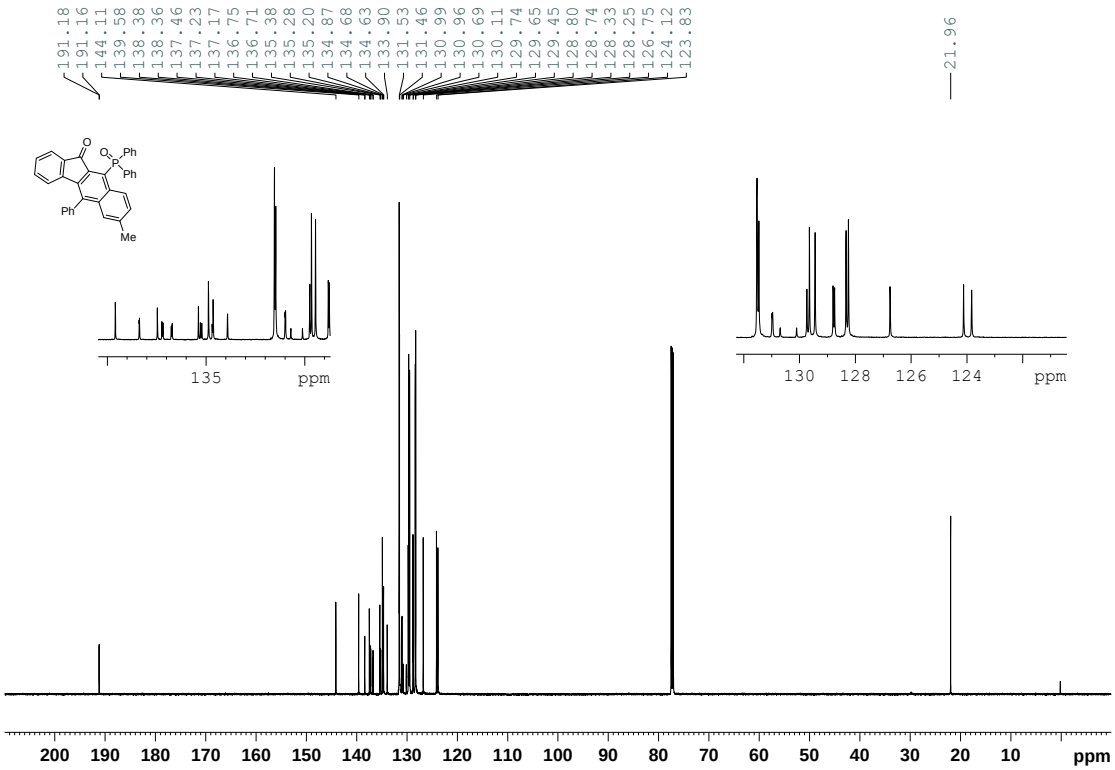
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3e**



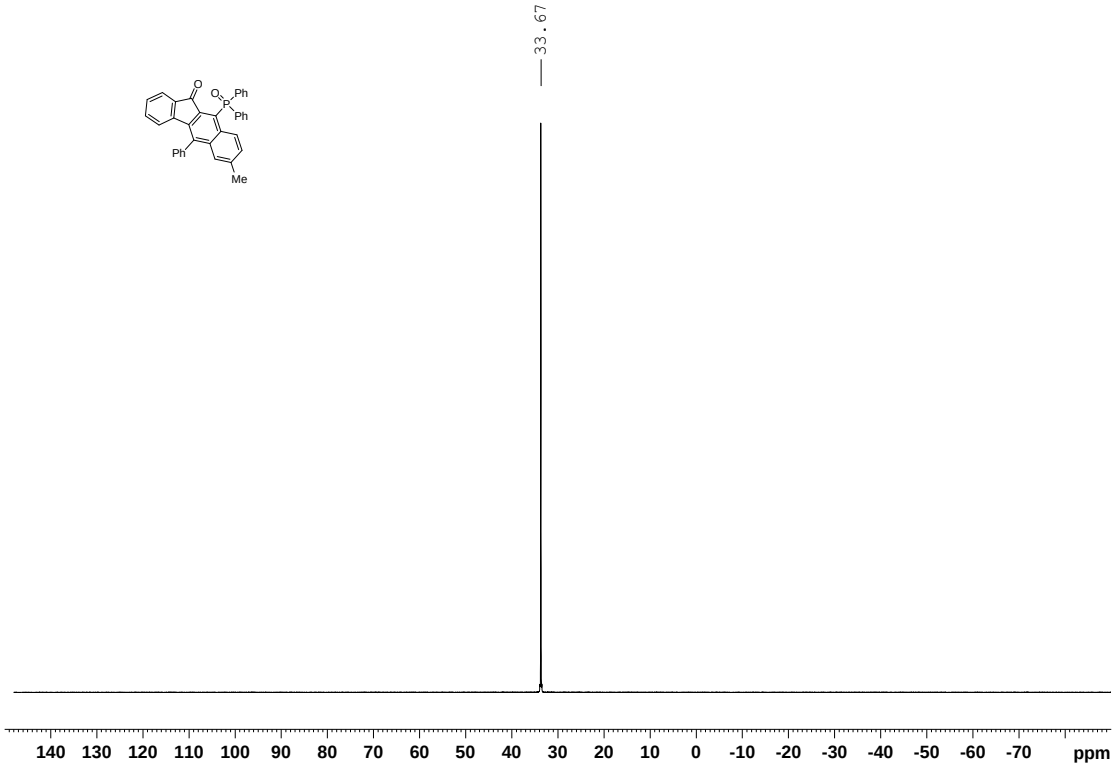
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) spectrum of compound **3e**



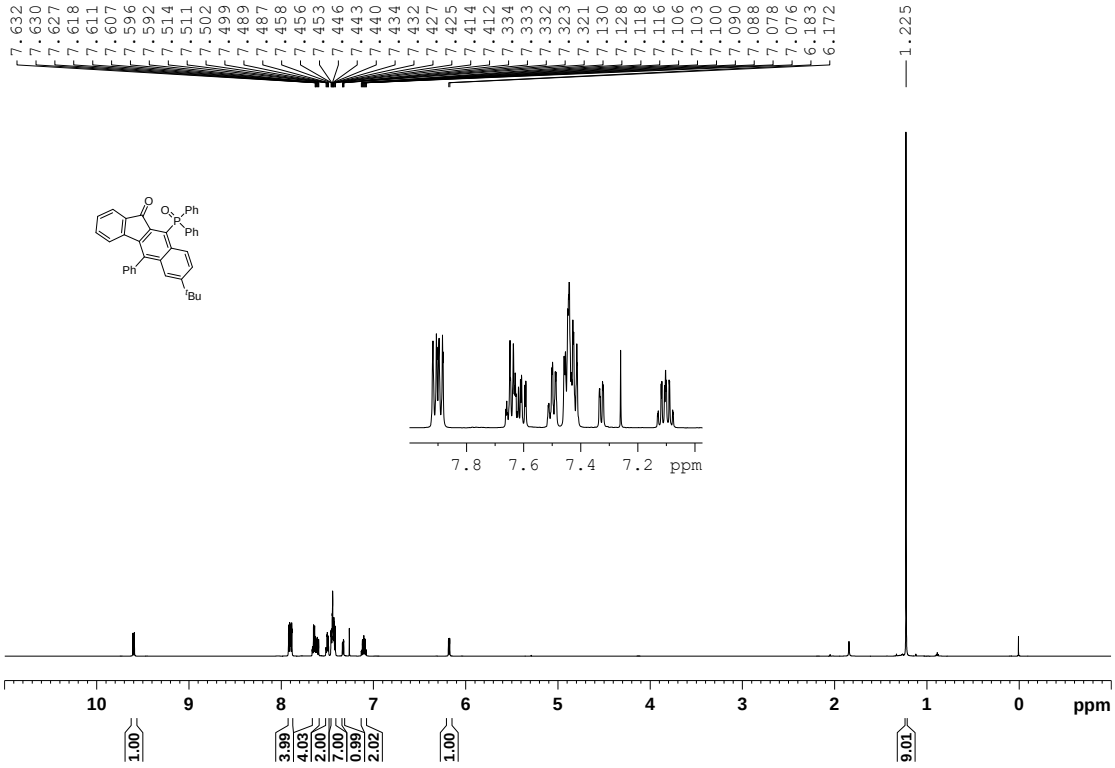
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3f**



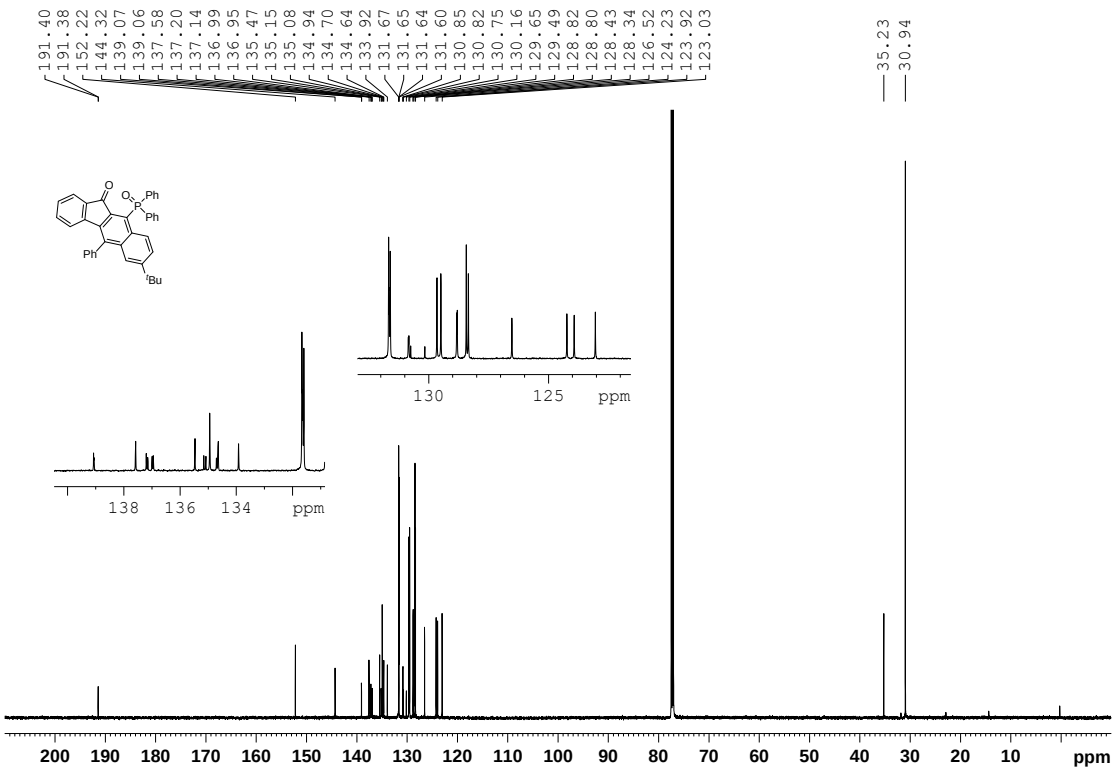
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3f**



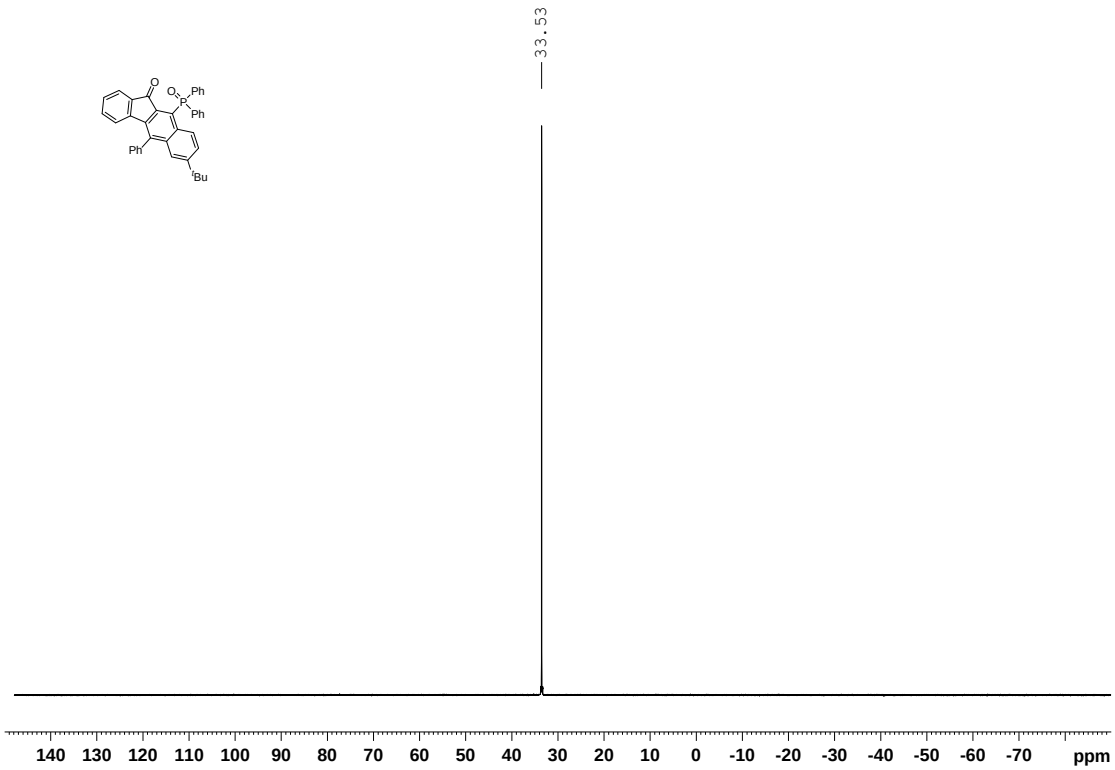
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3f**



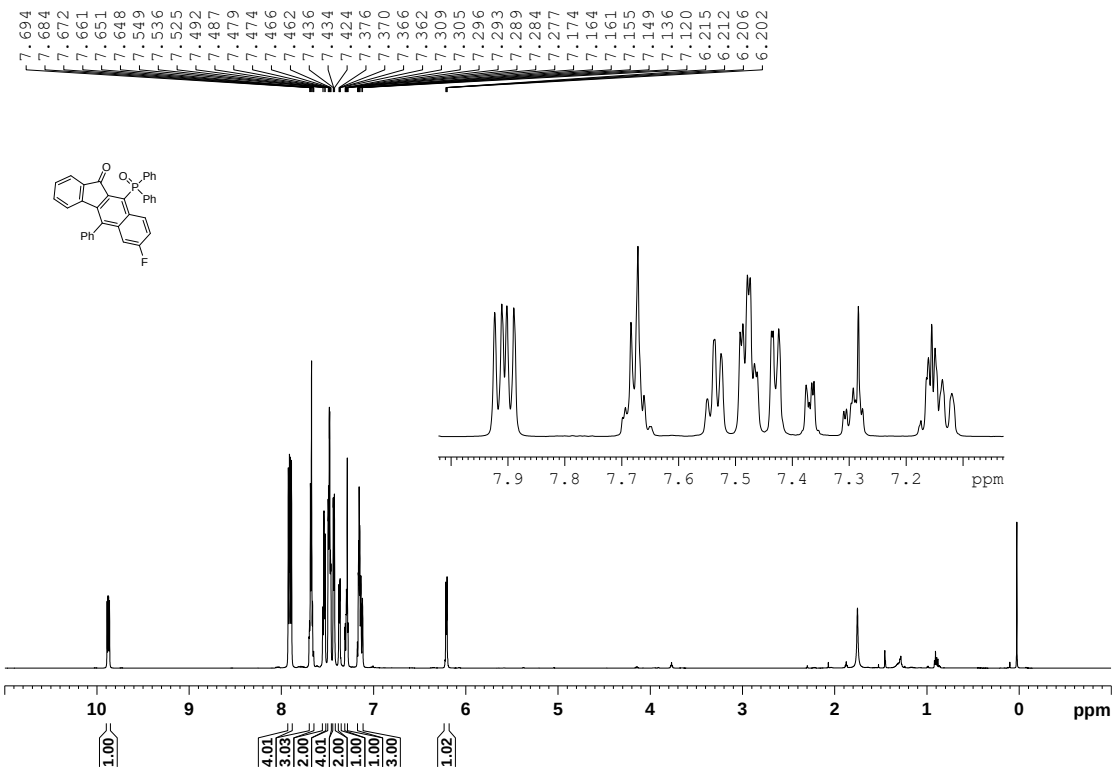
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3g**



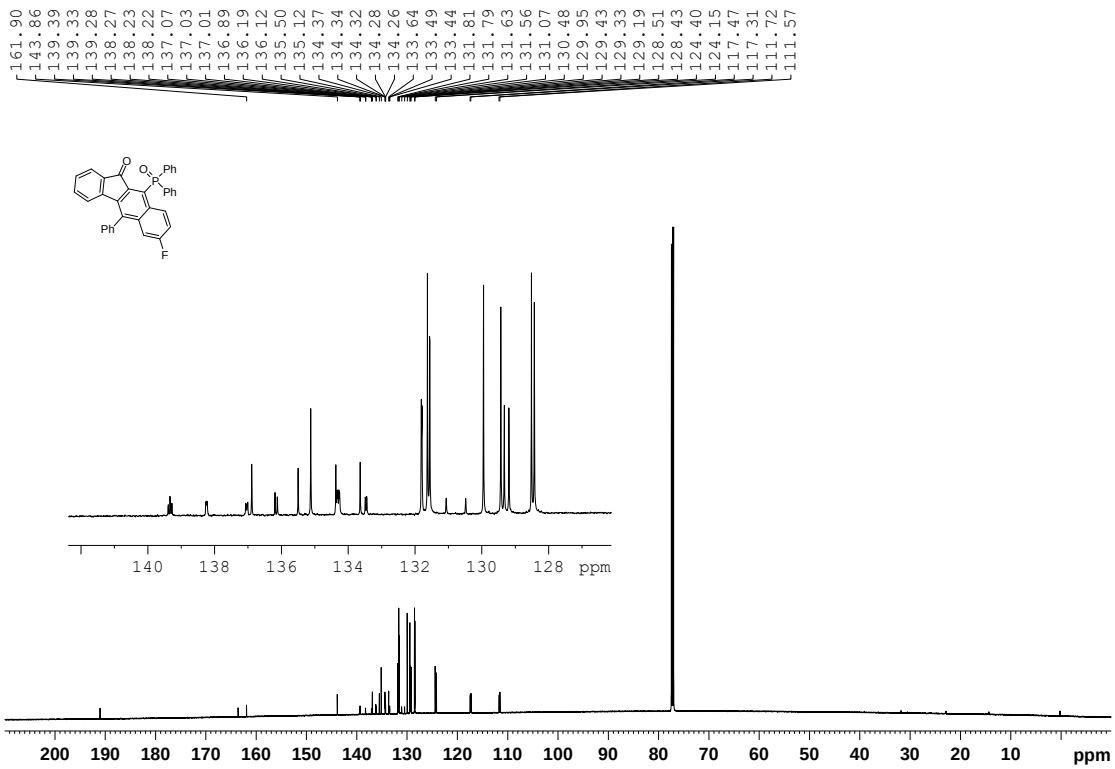
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3g**



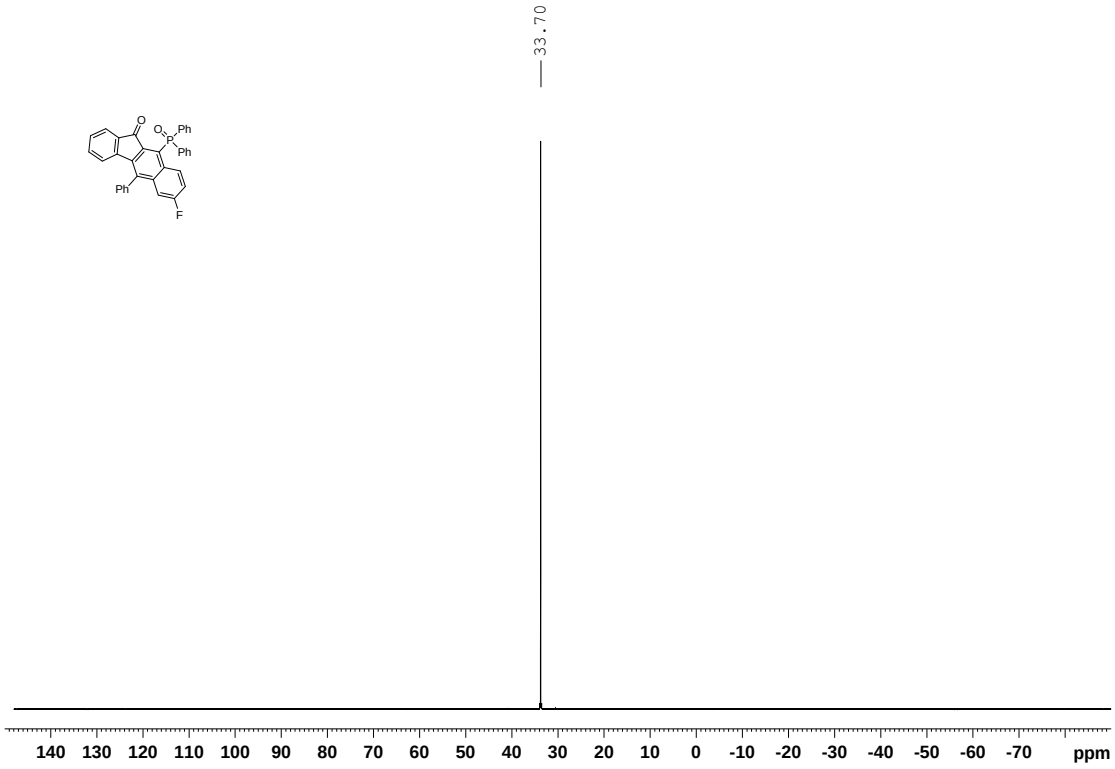
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3g**



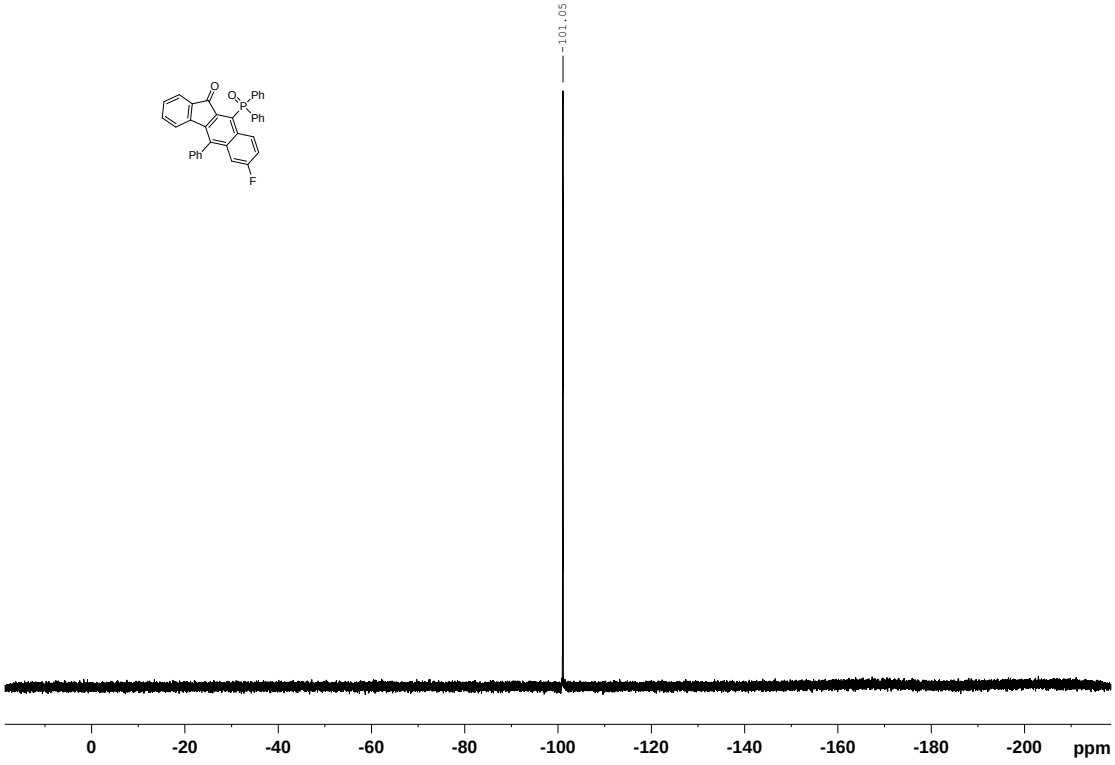
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3h**



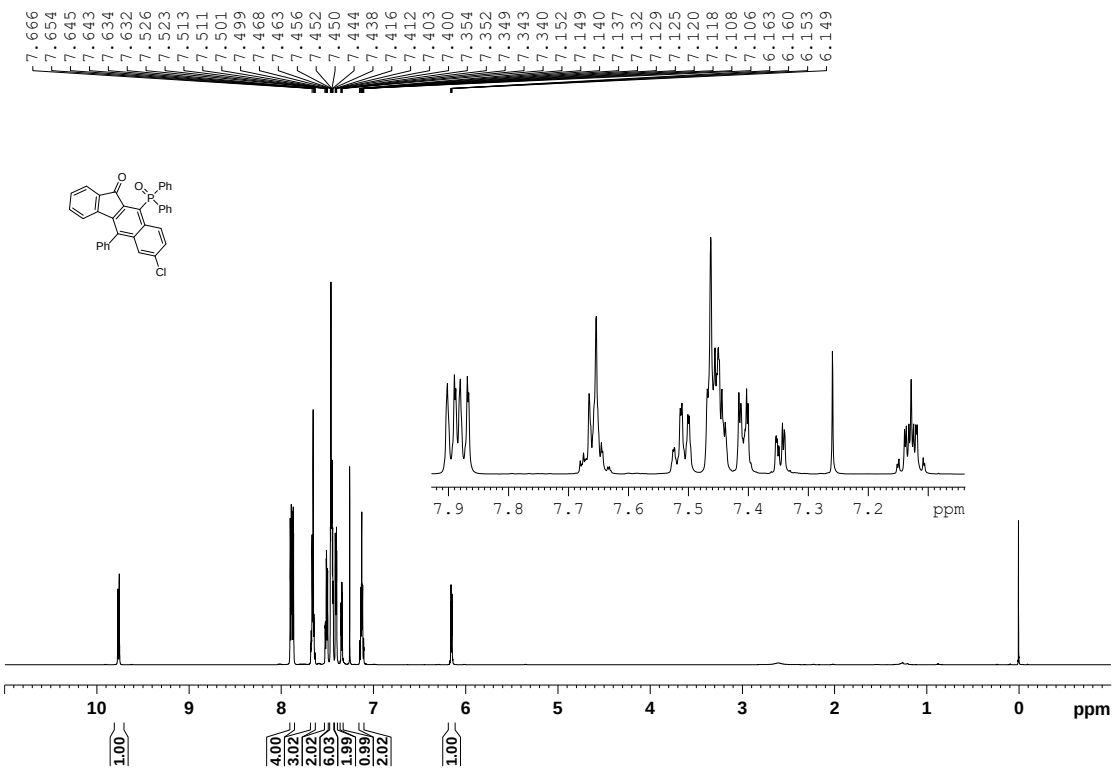
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3h**



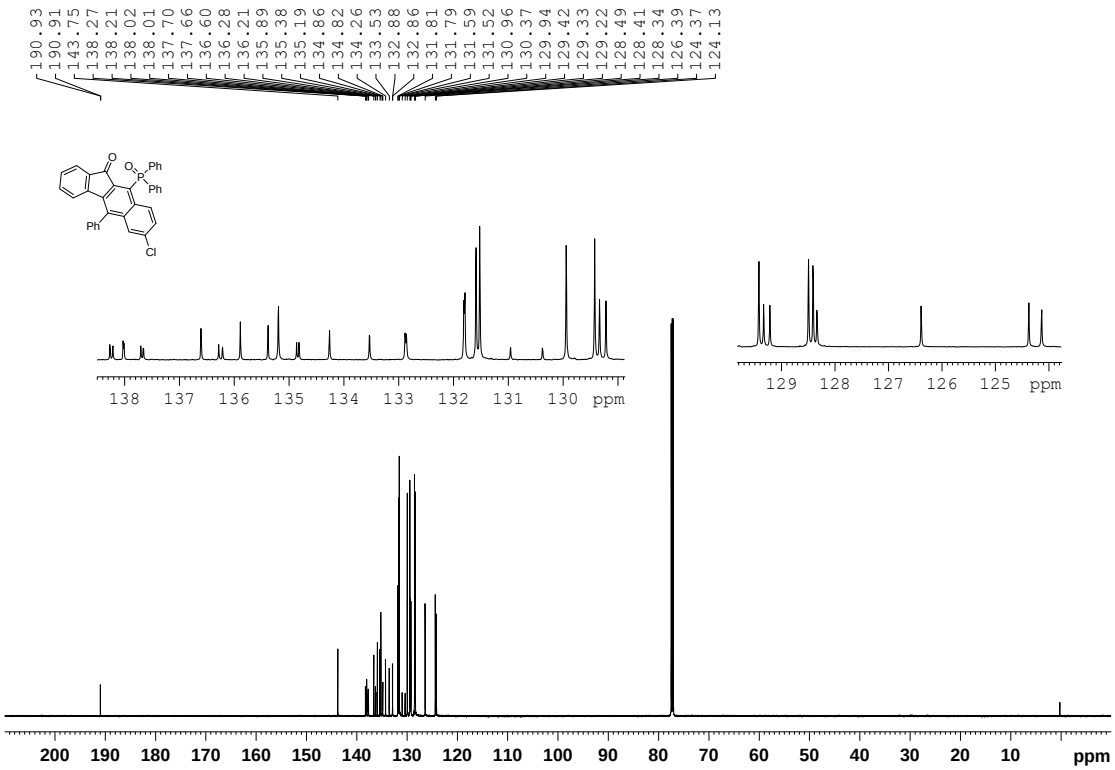
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3h**



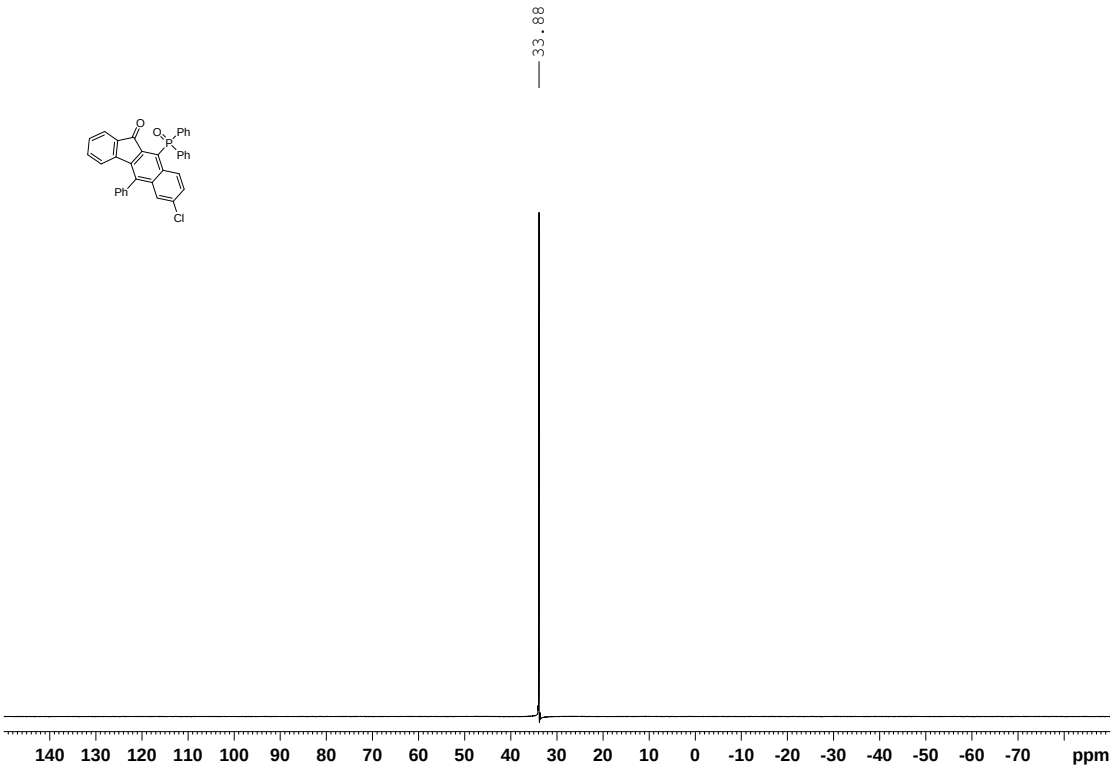
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) spectrum of compound **3h**



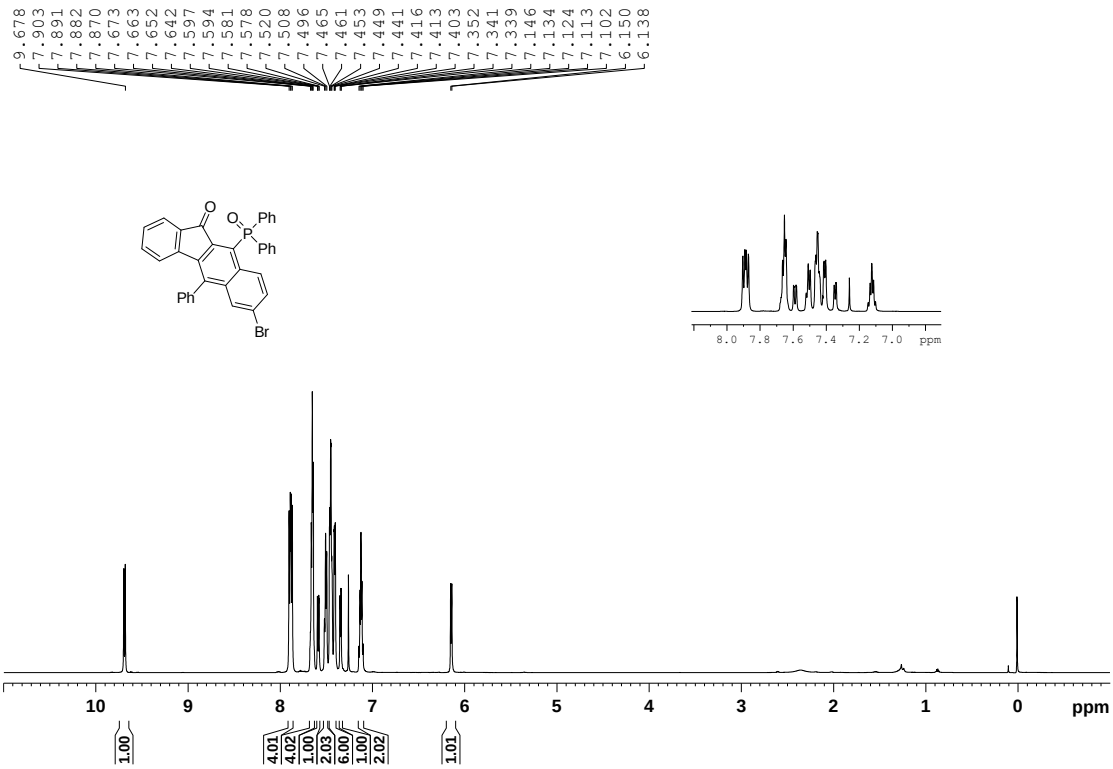
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3i**



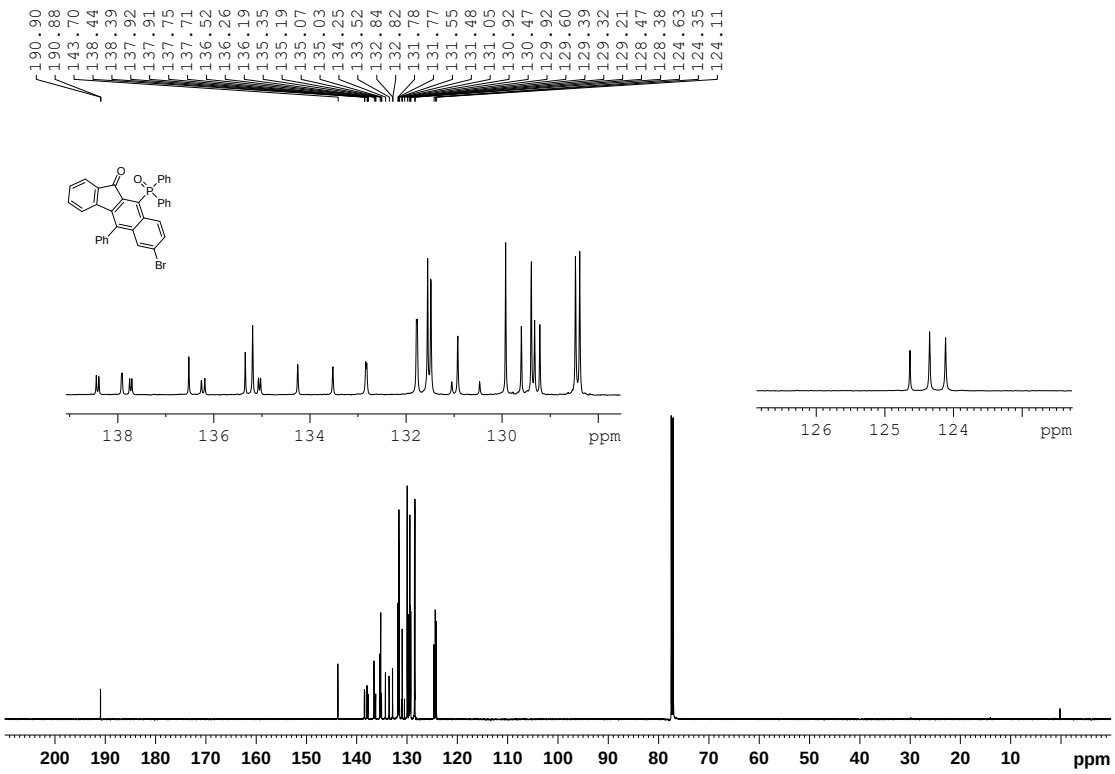
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3i**



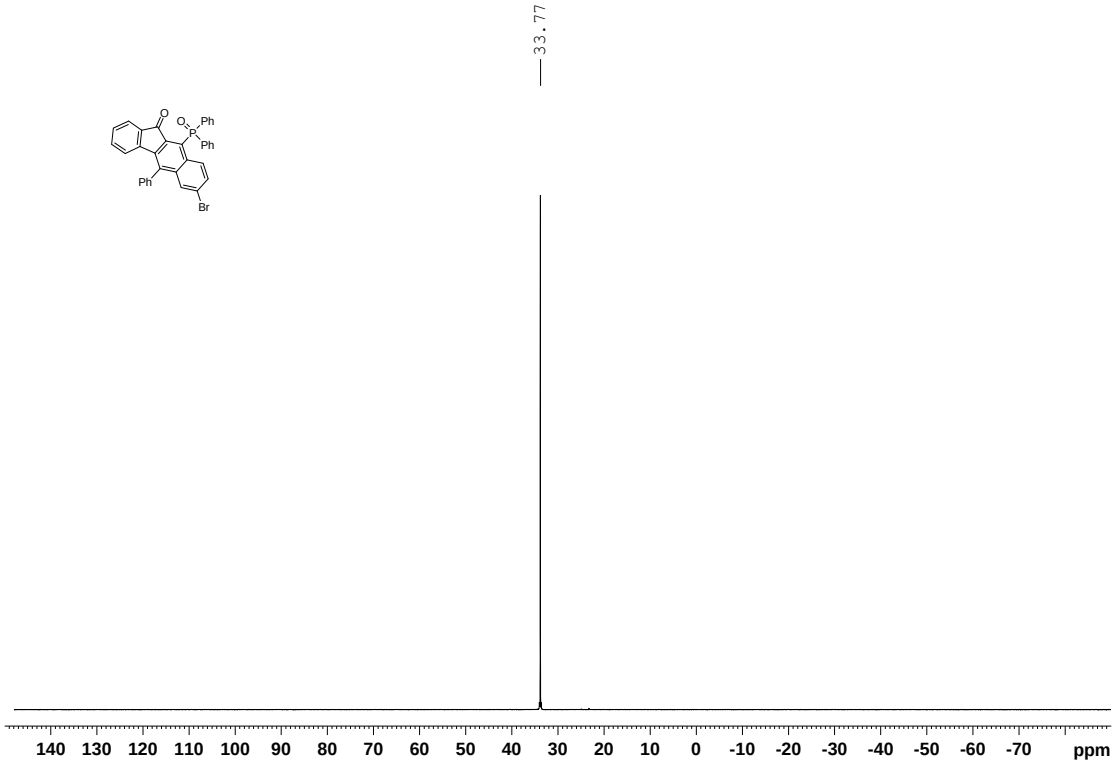
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3i**



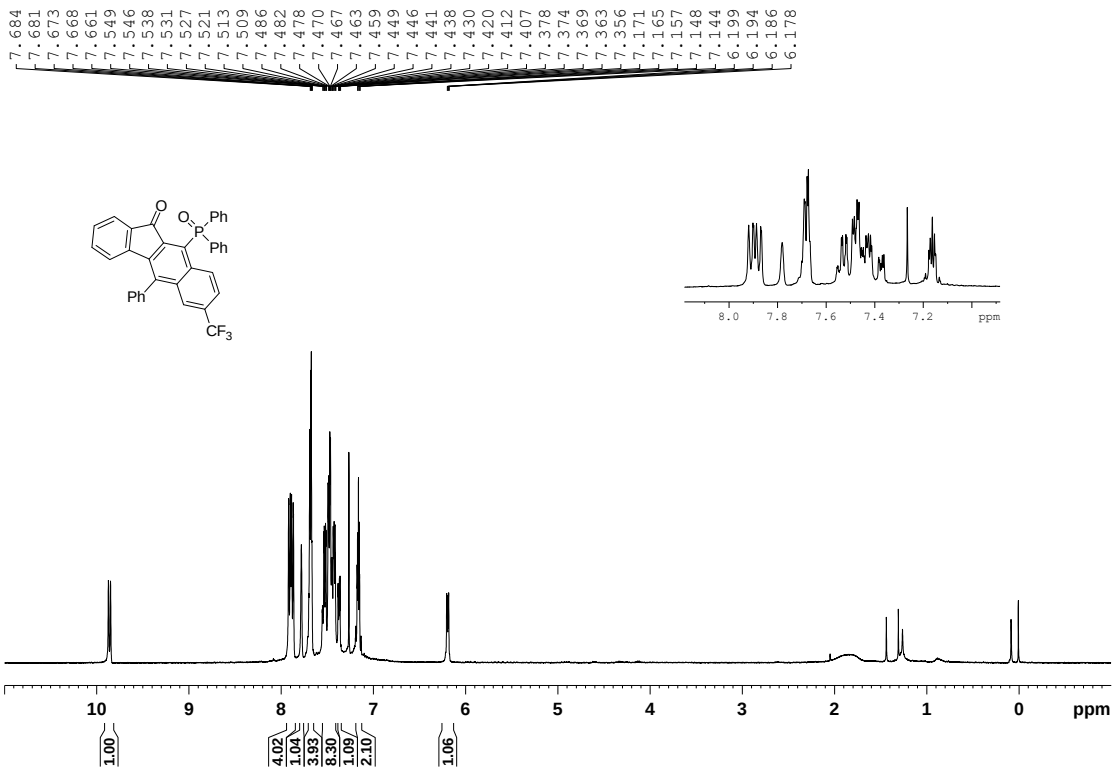
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3j**



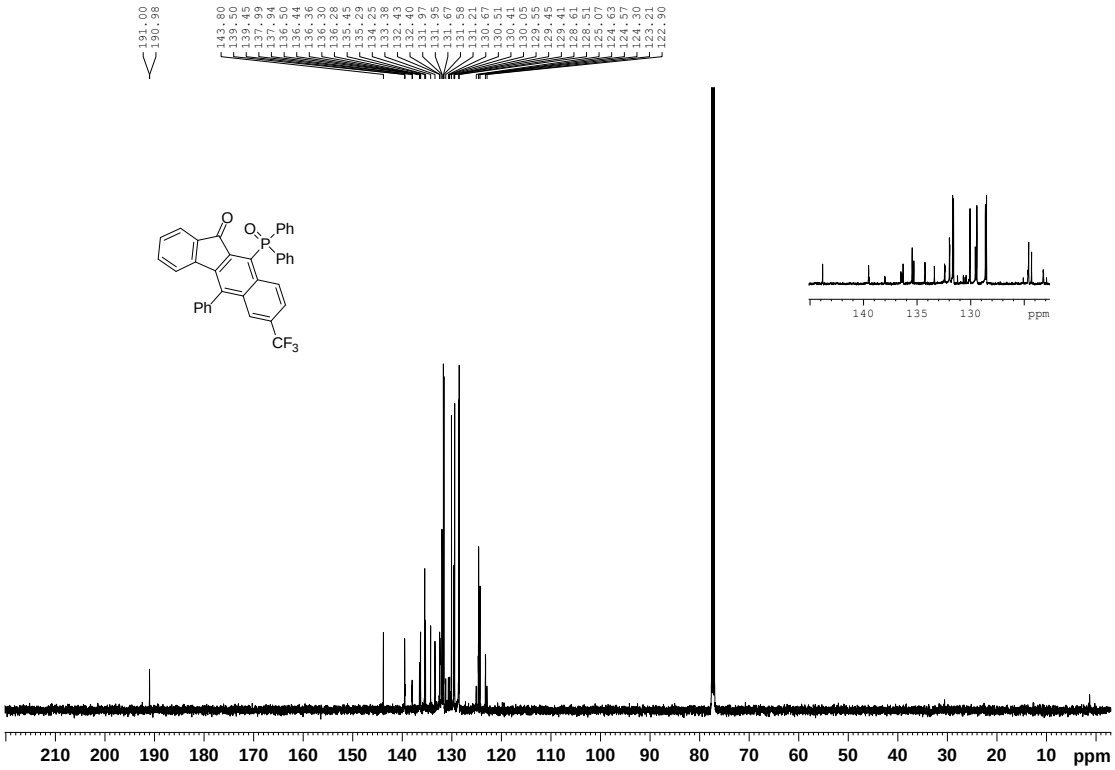
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3j**



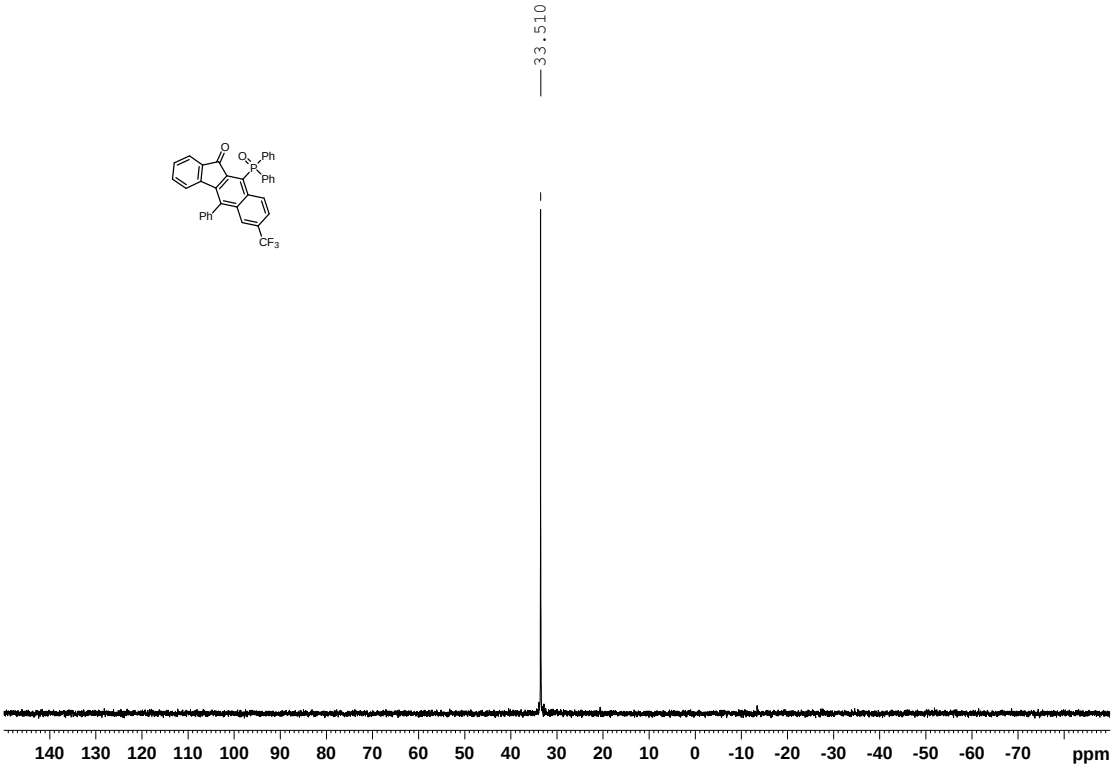
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3j**



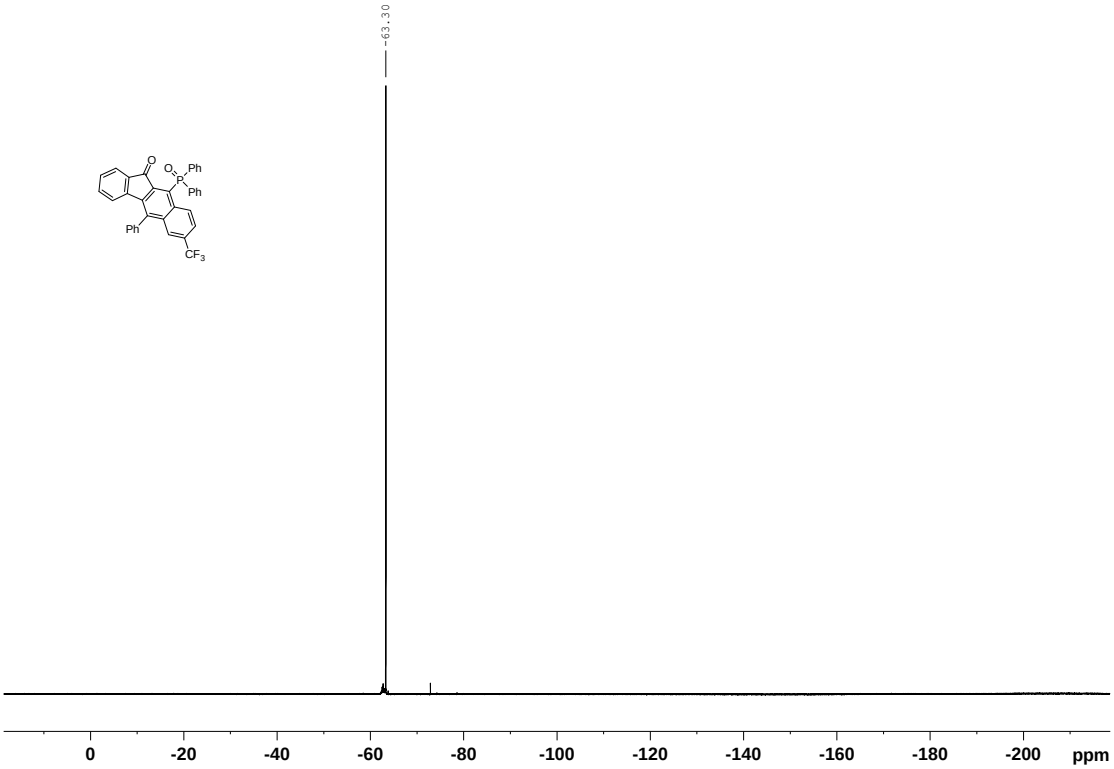
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **3k**



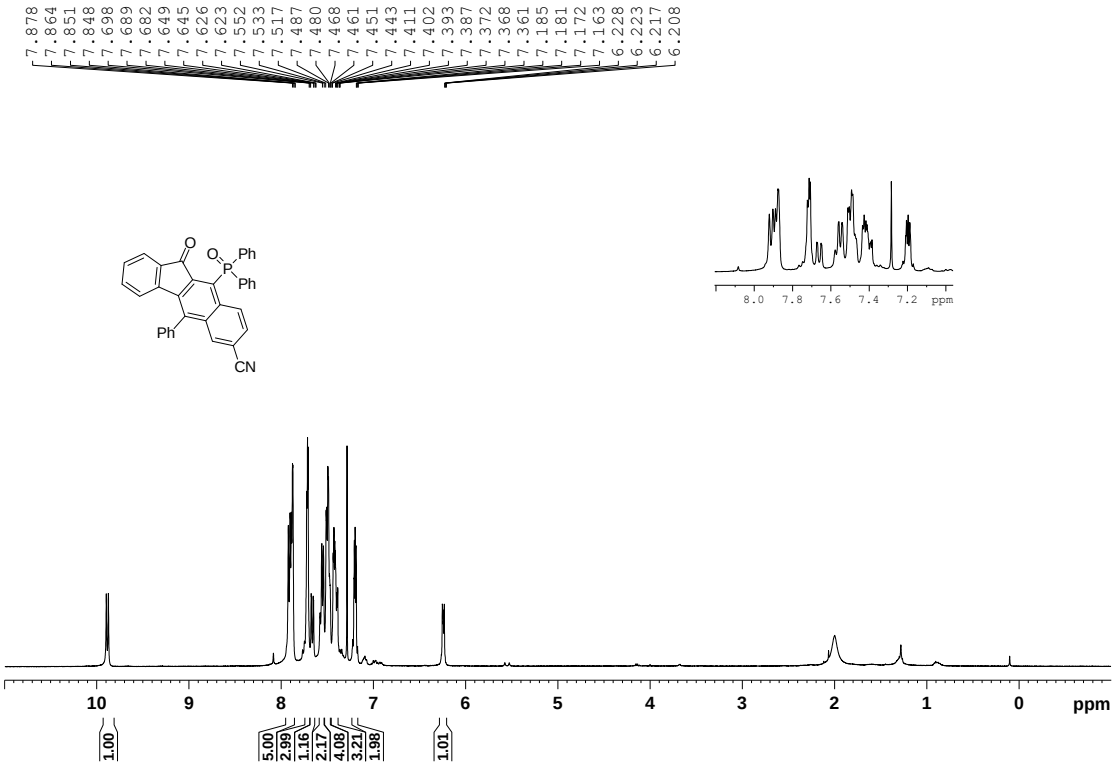
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3k**



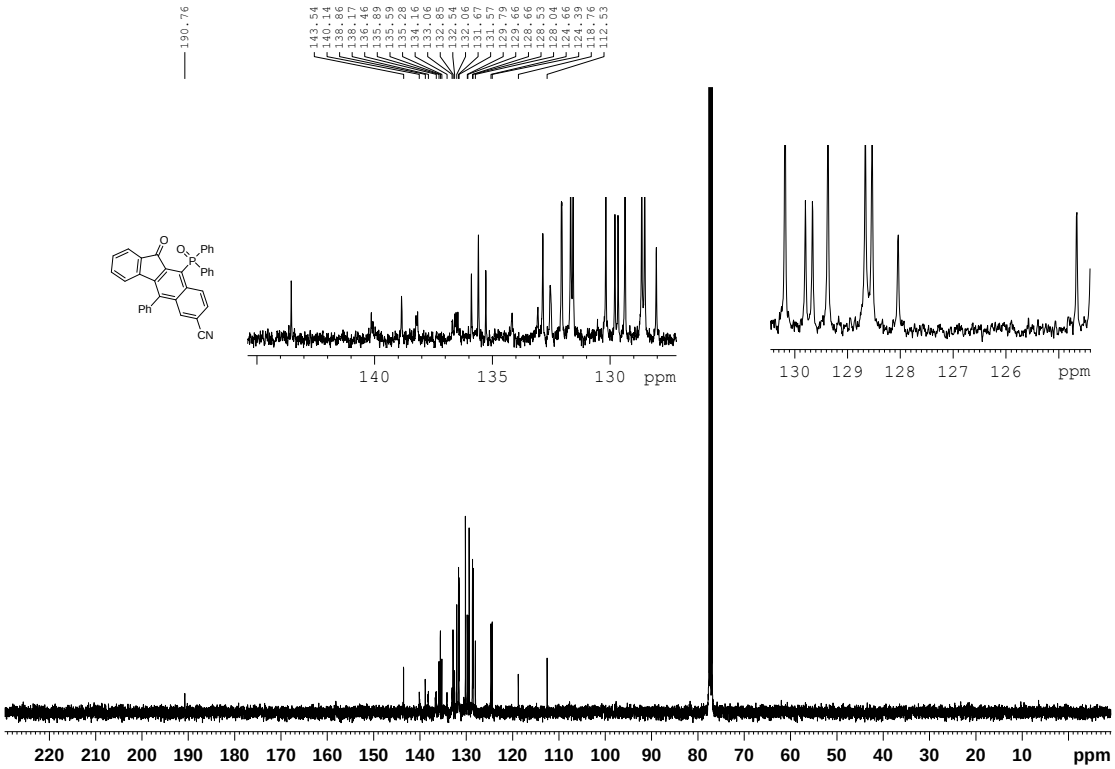
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3k**



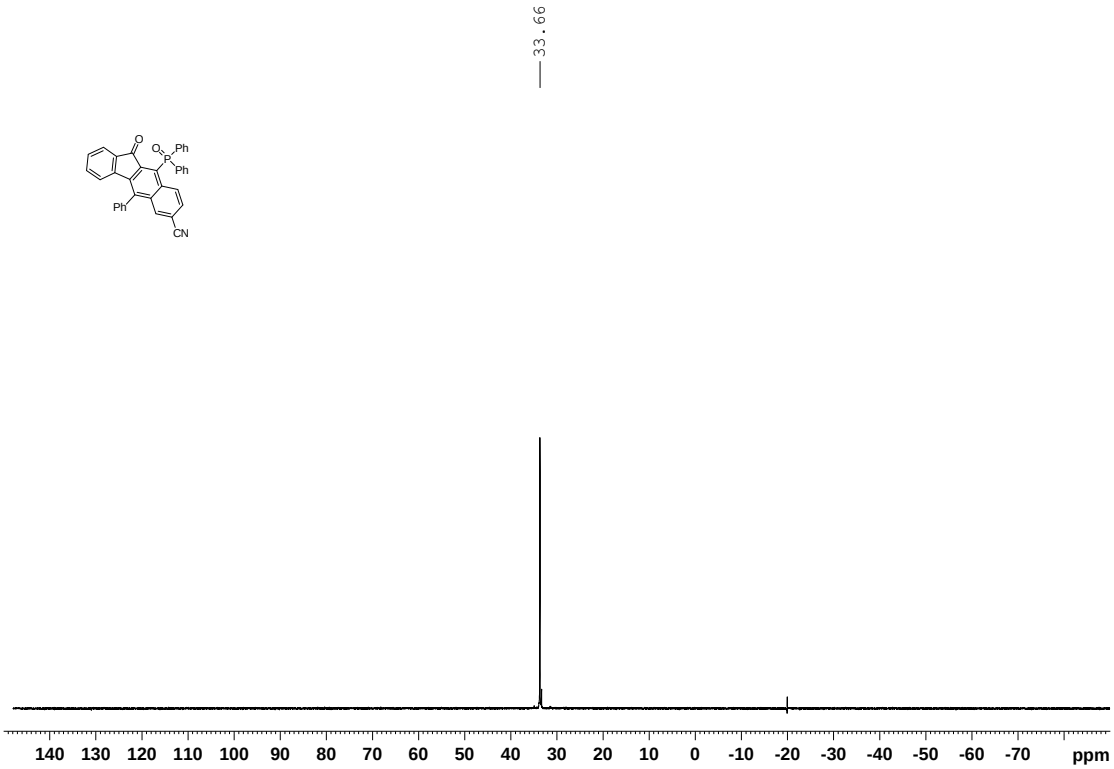
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) spectrum of compound **3k**



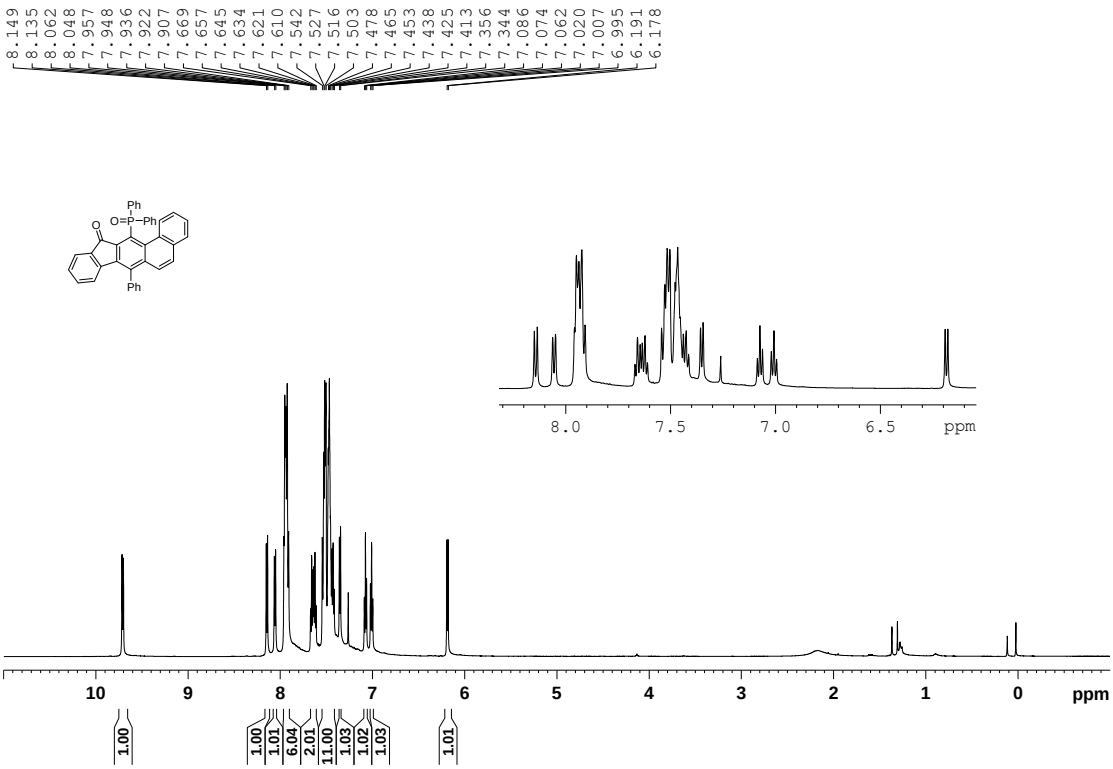
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3l**



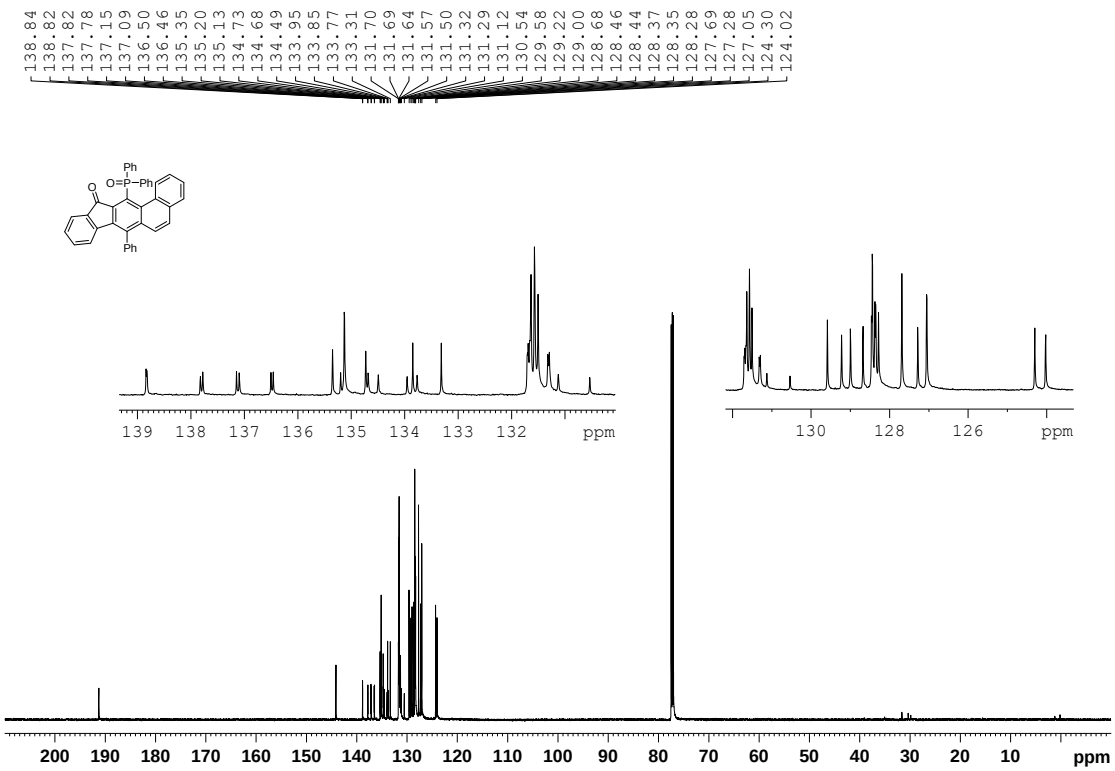
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3l**



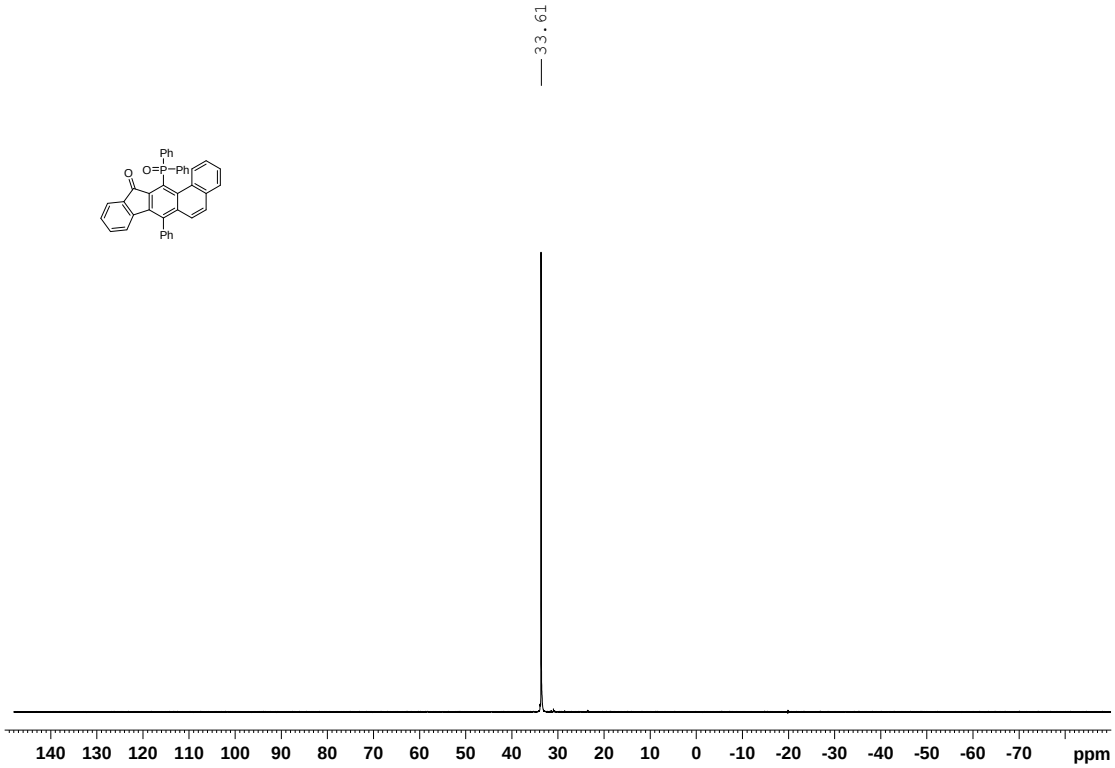
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3l**



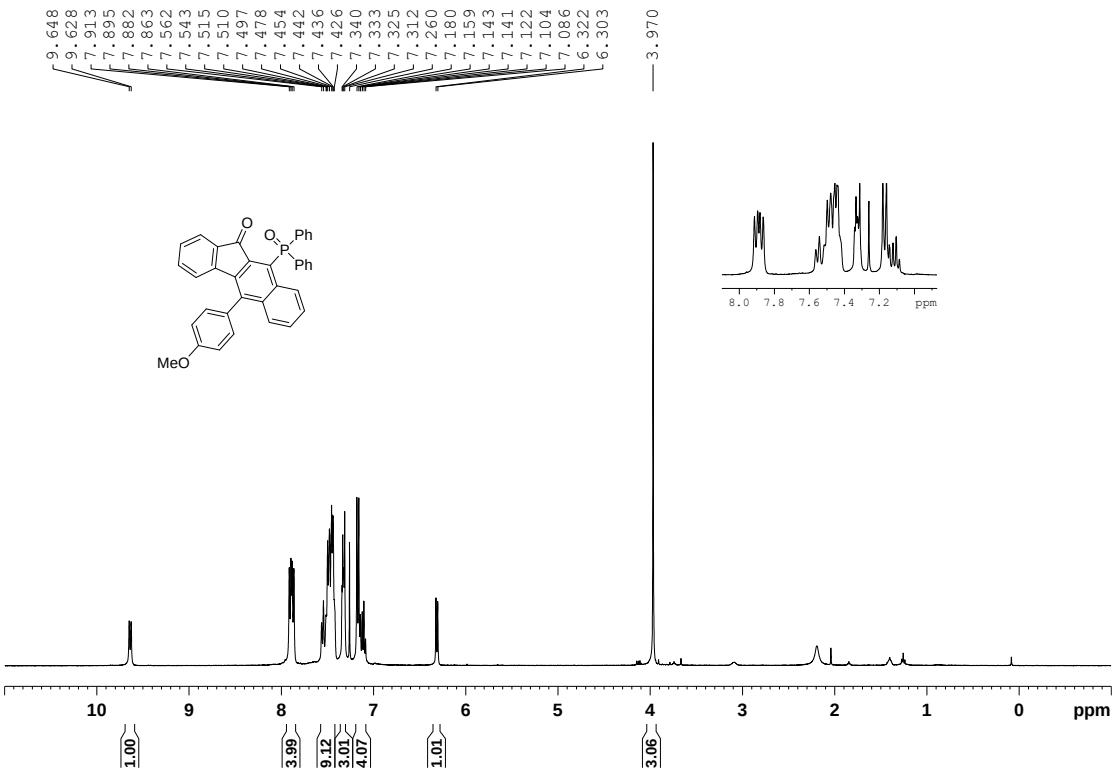
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3n**



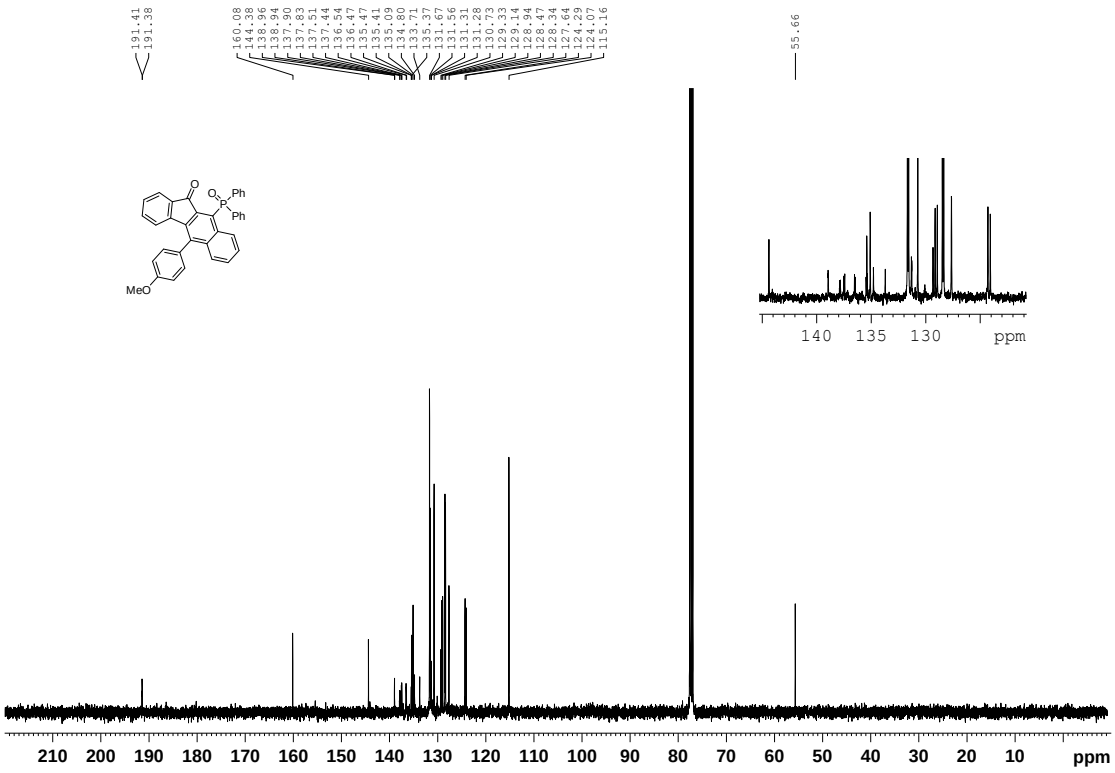
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3n**



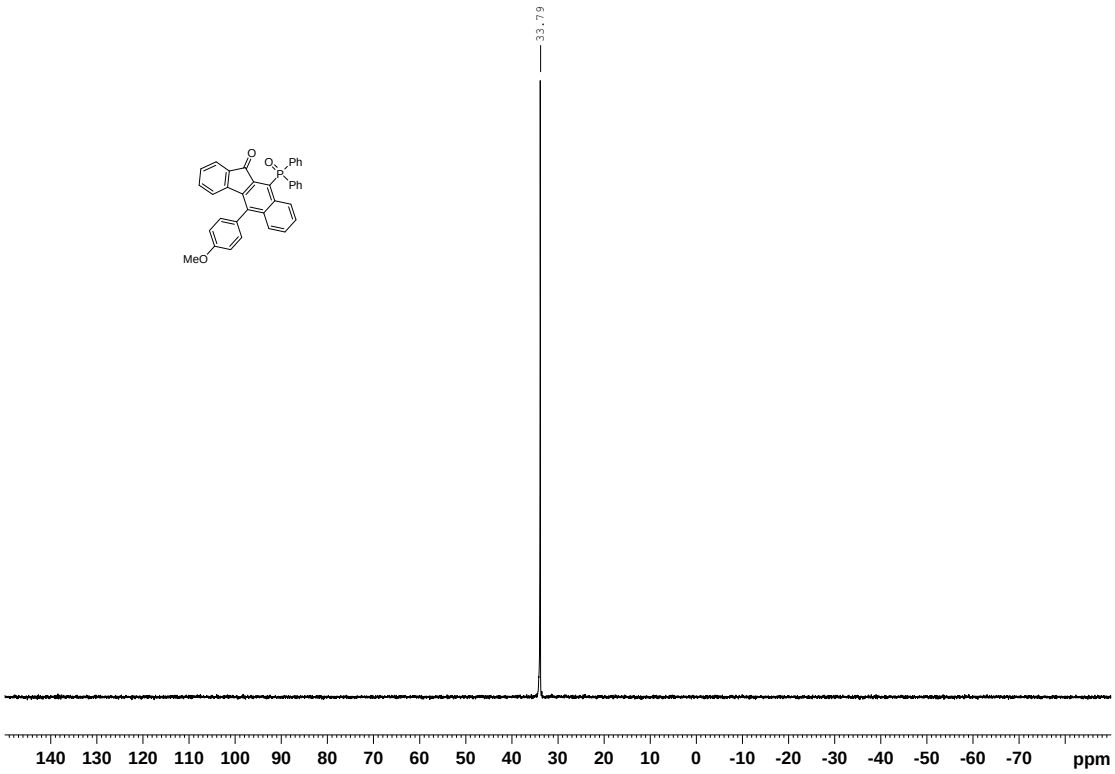
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3n**



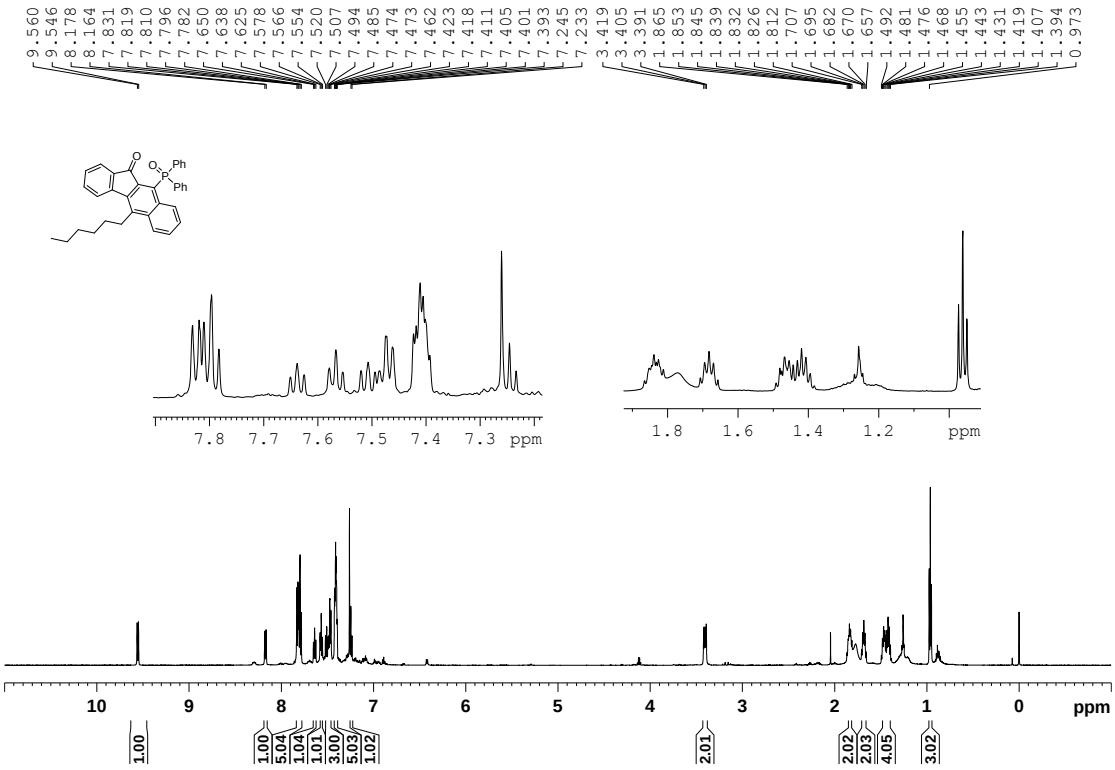
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3o**



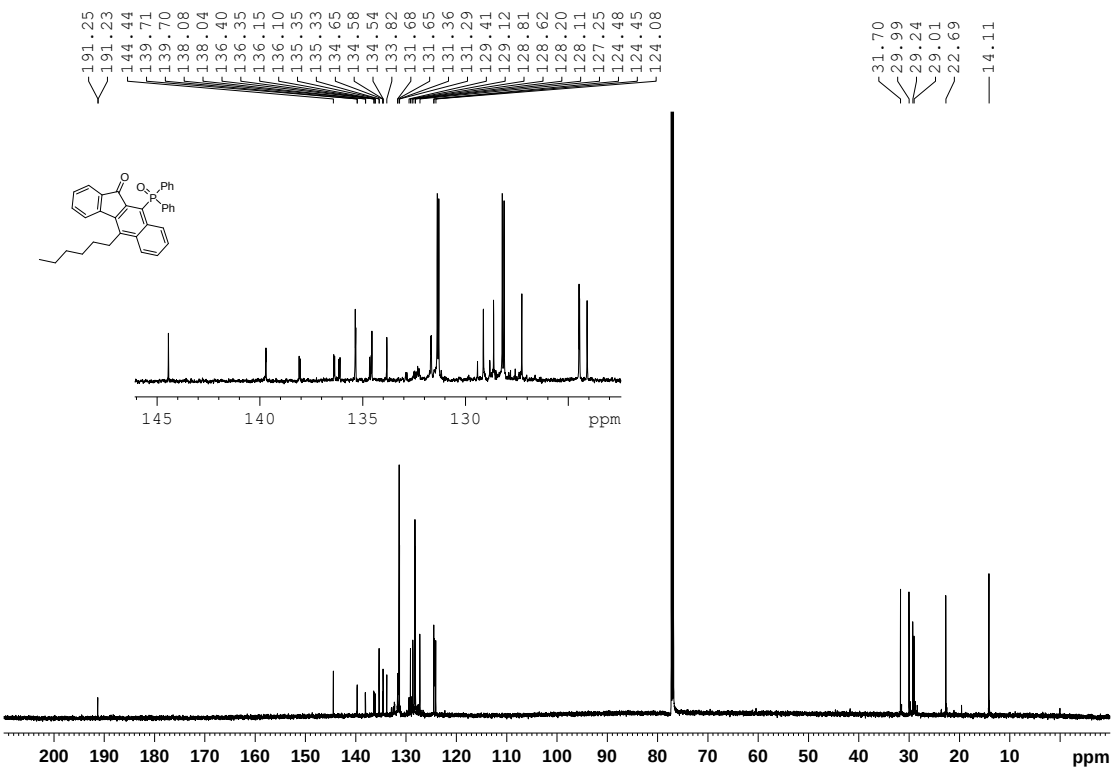
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3o**



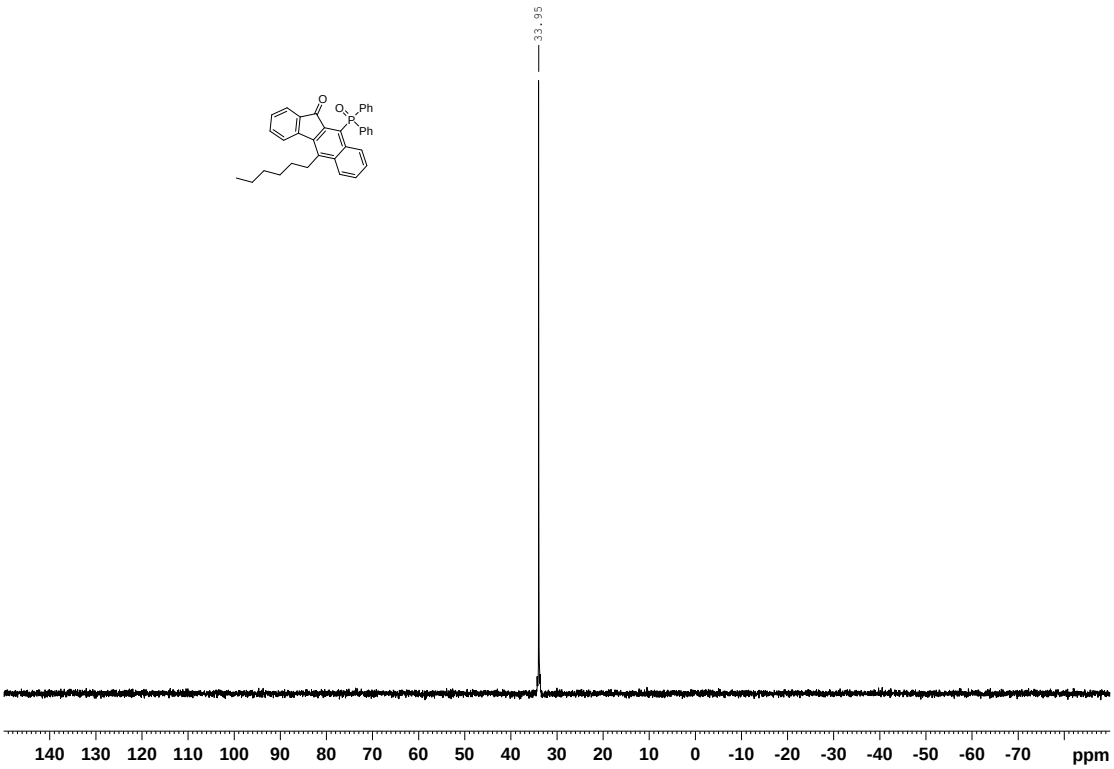
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3o**



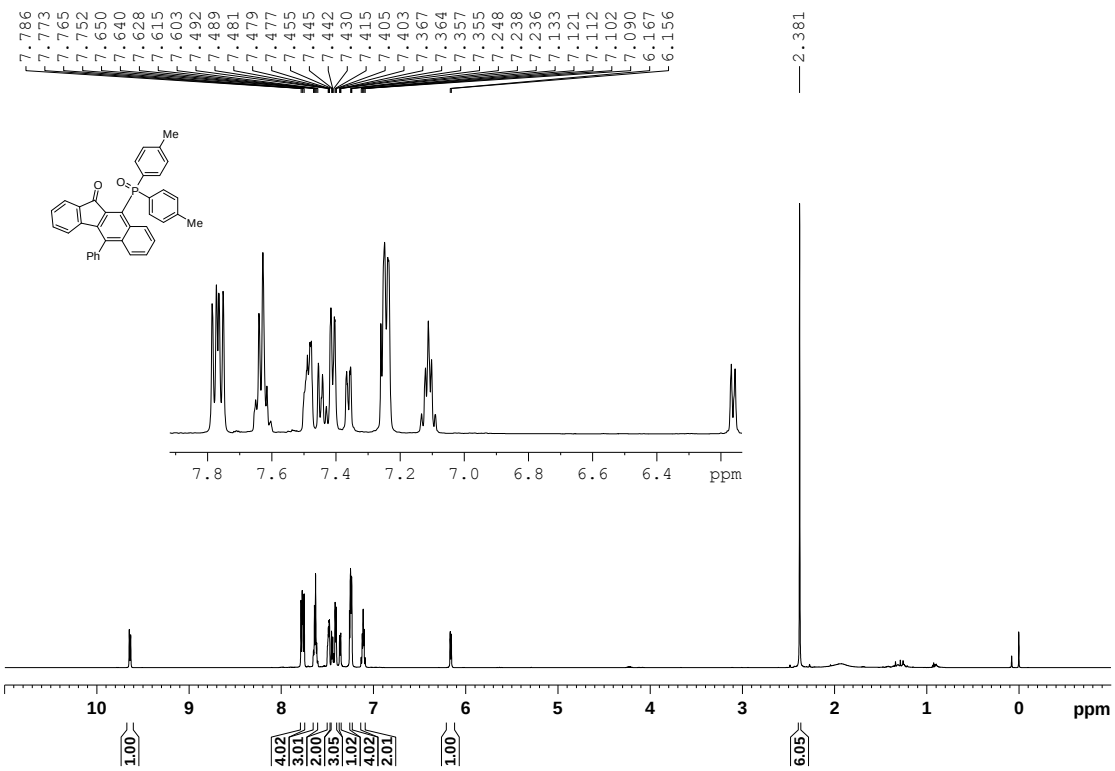
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3p**



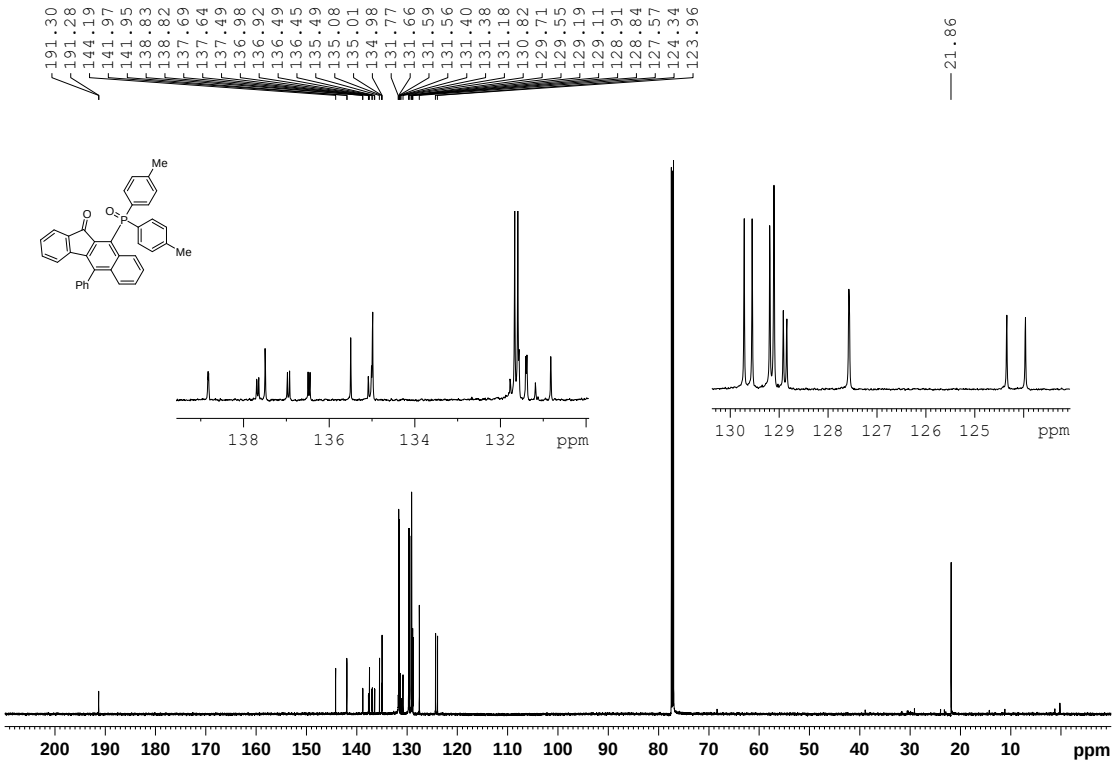
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3p**



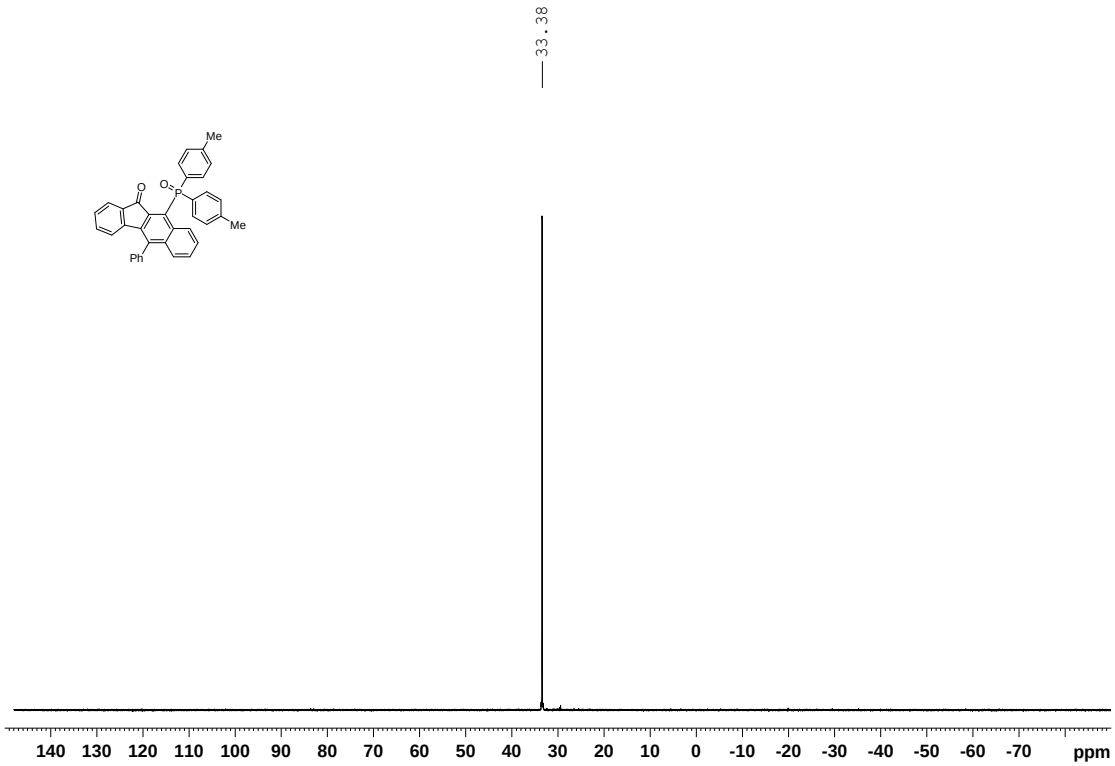
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3p**



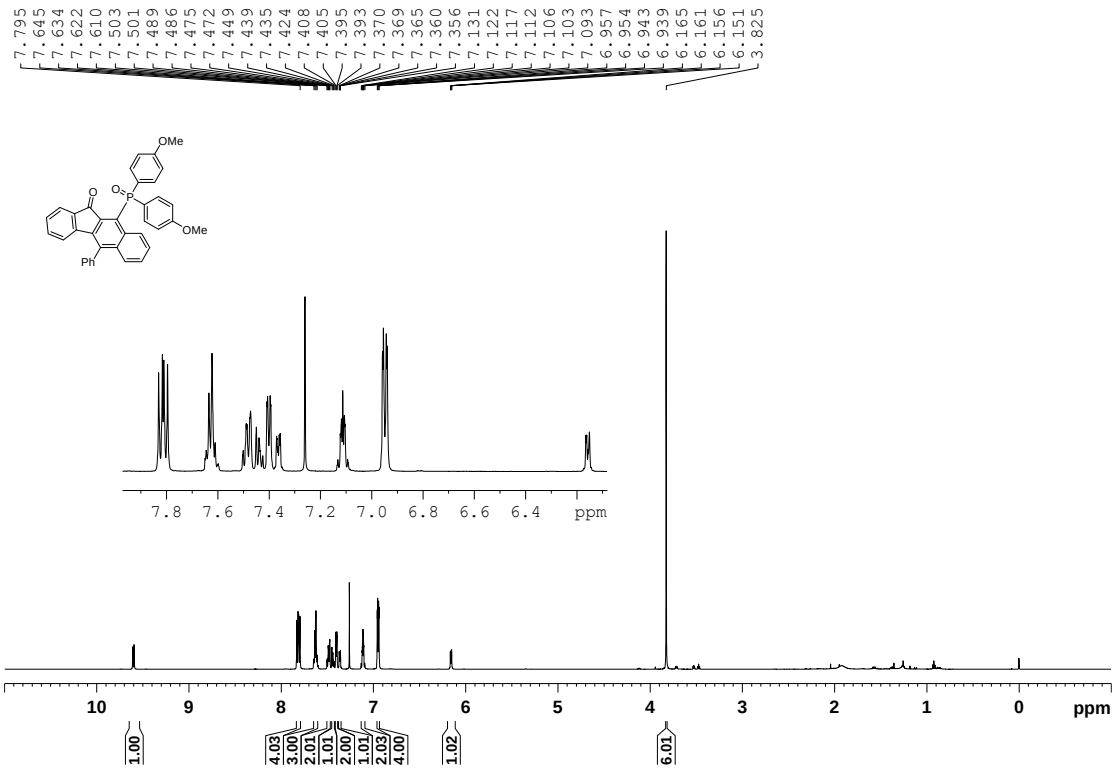
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3q**



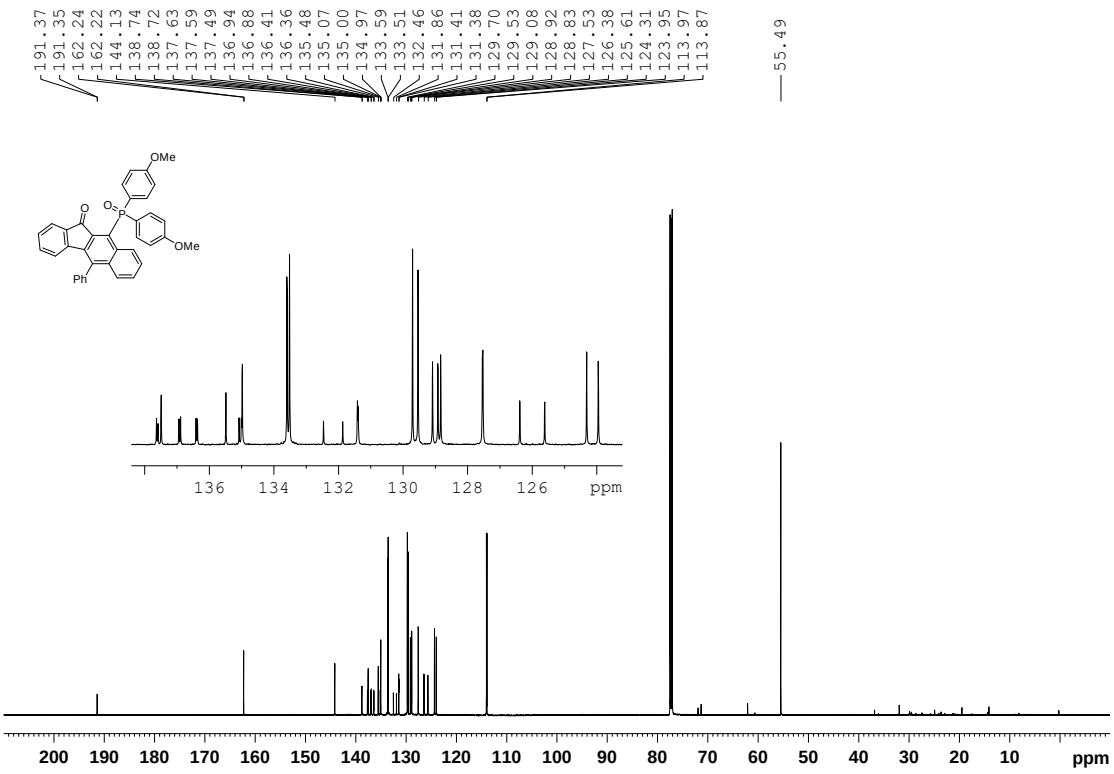
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3q**



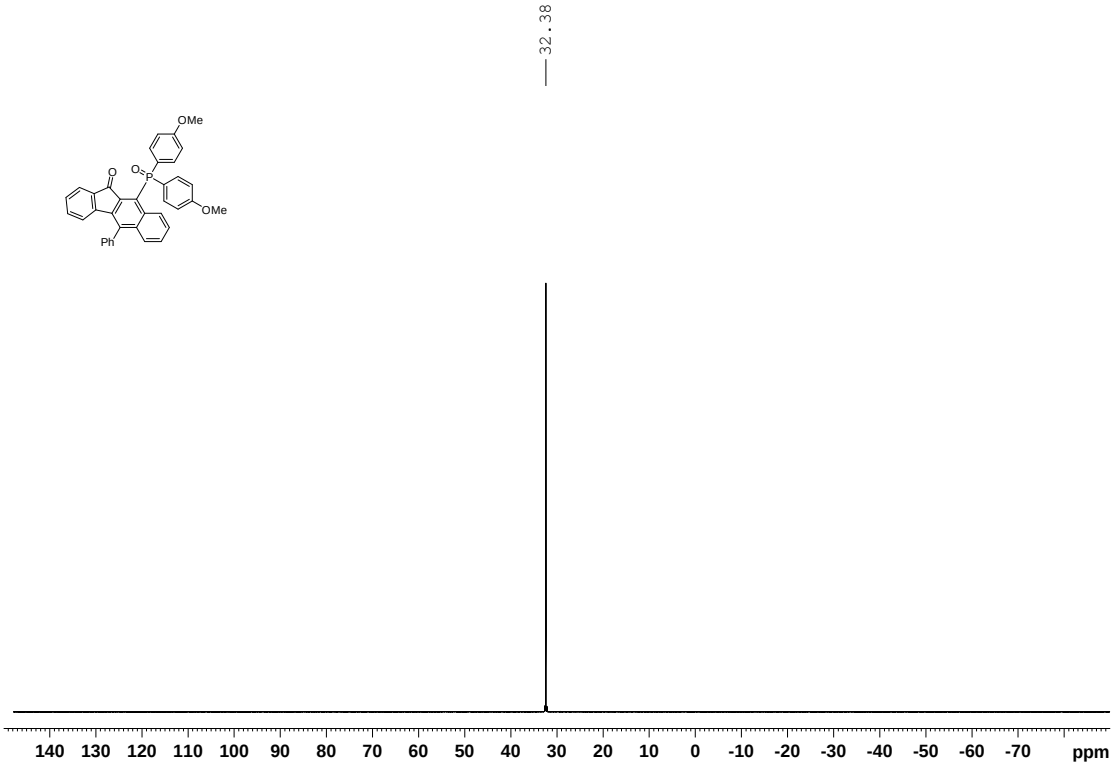
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3q**



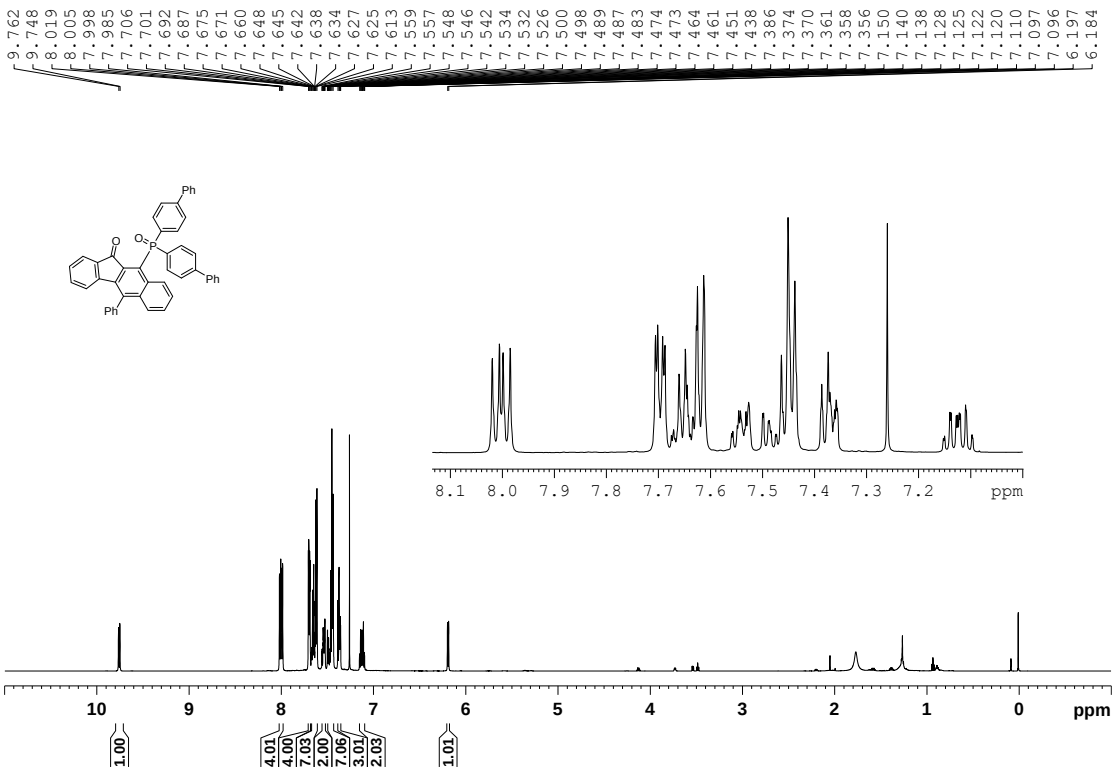
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3r**



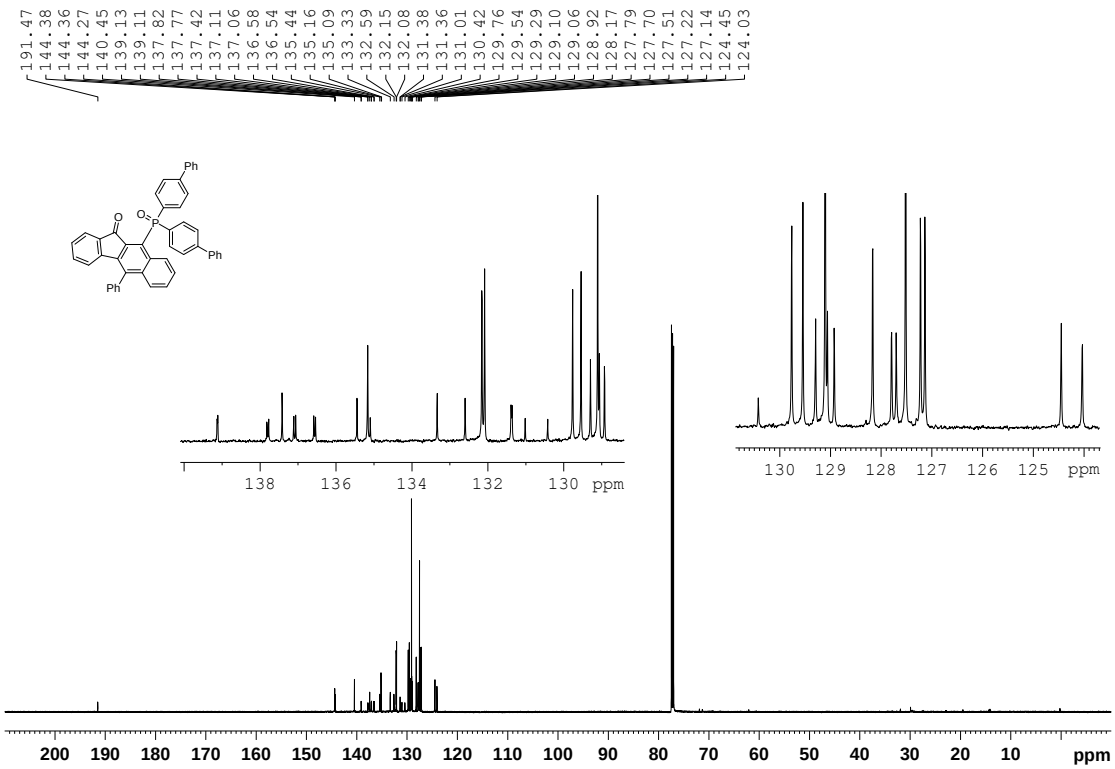
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3r**



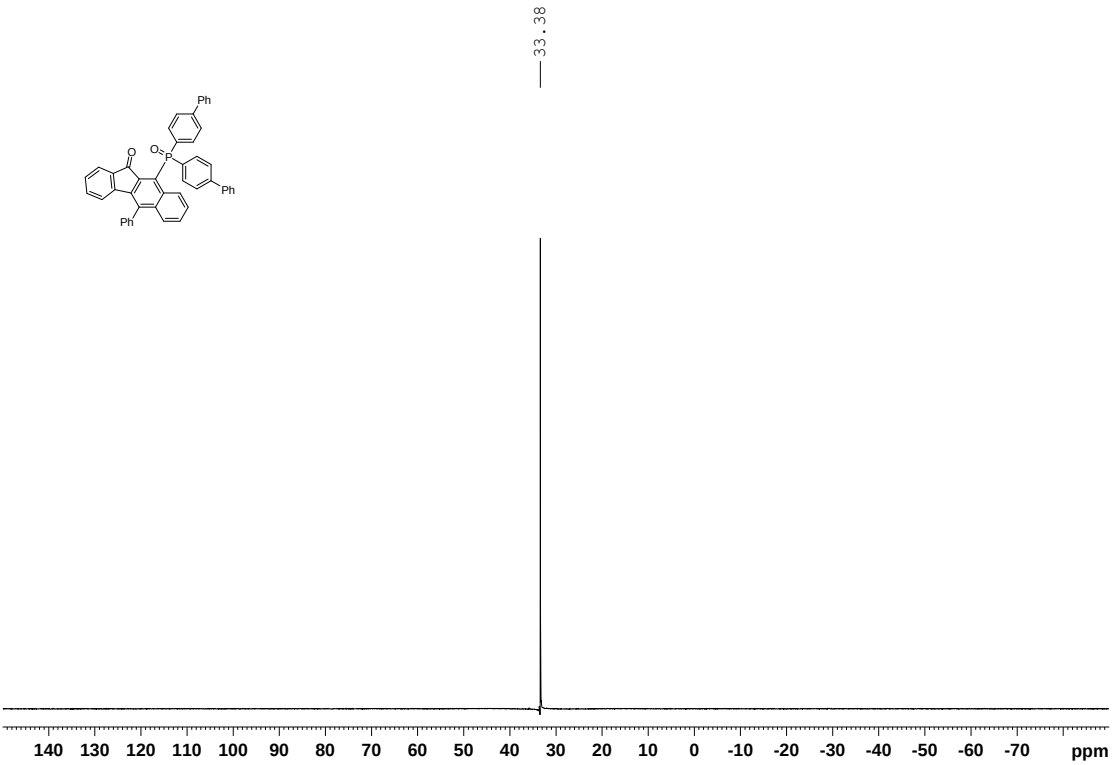
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3r**



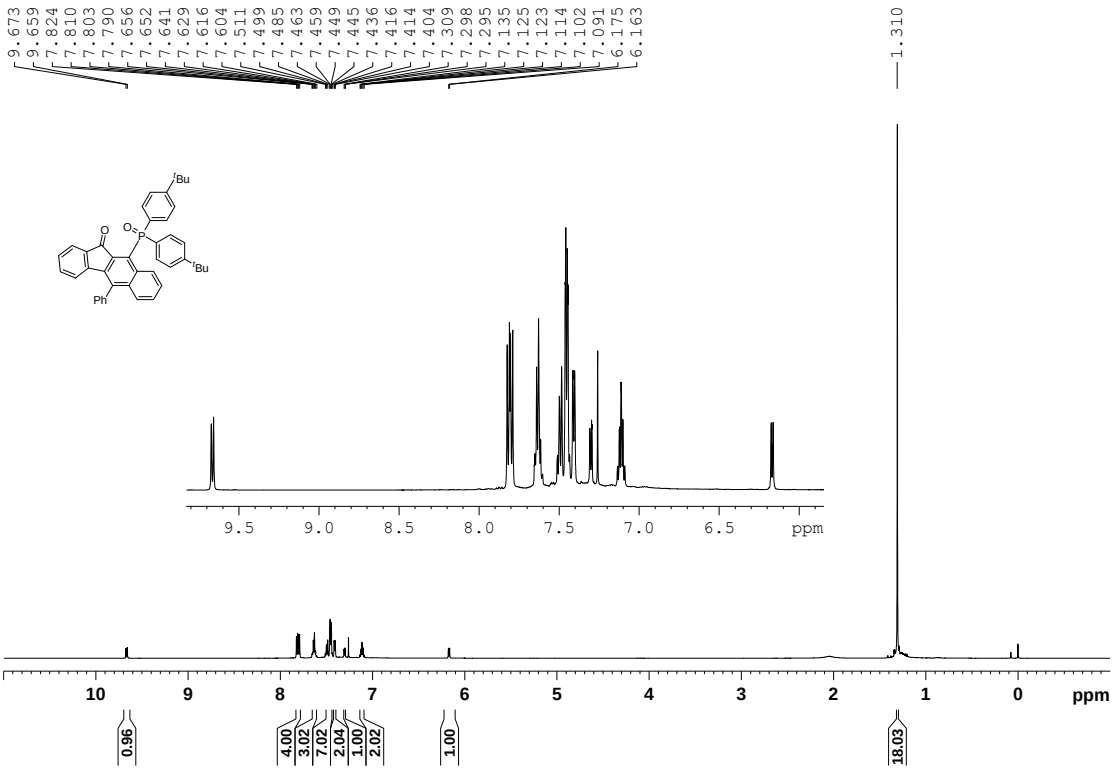
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3s**



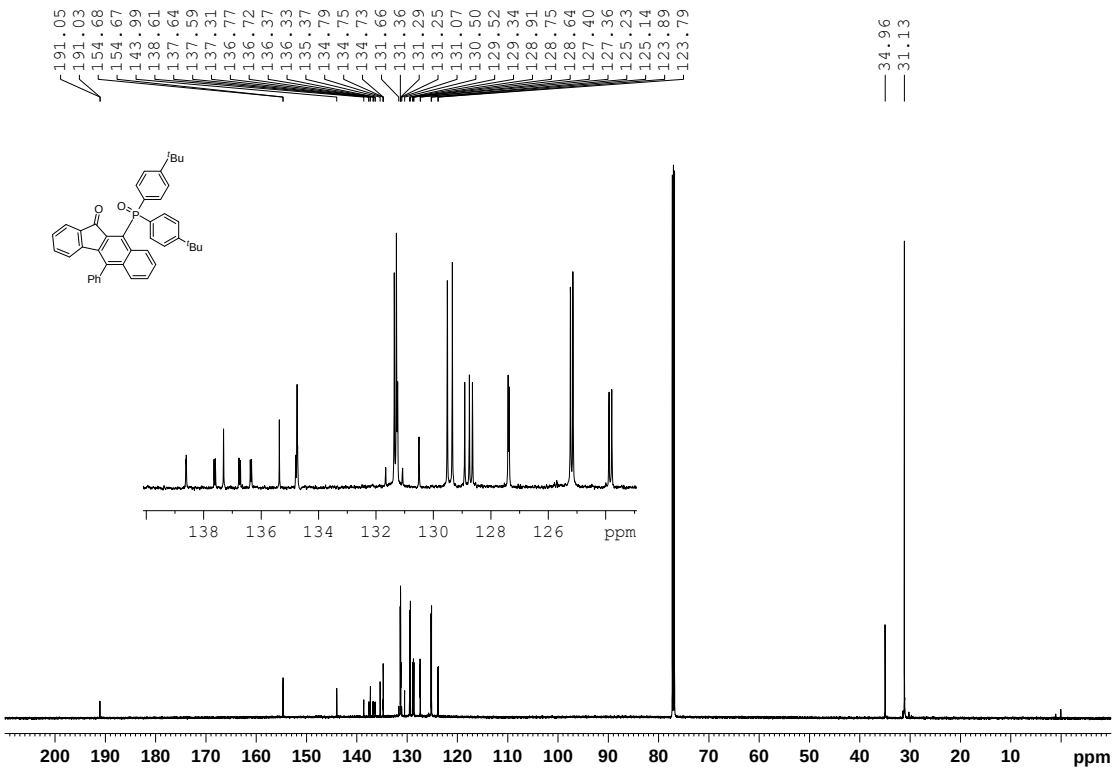
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3s**



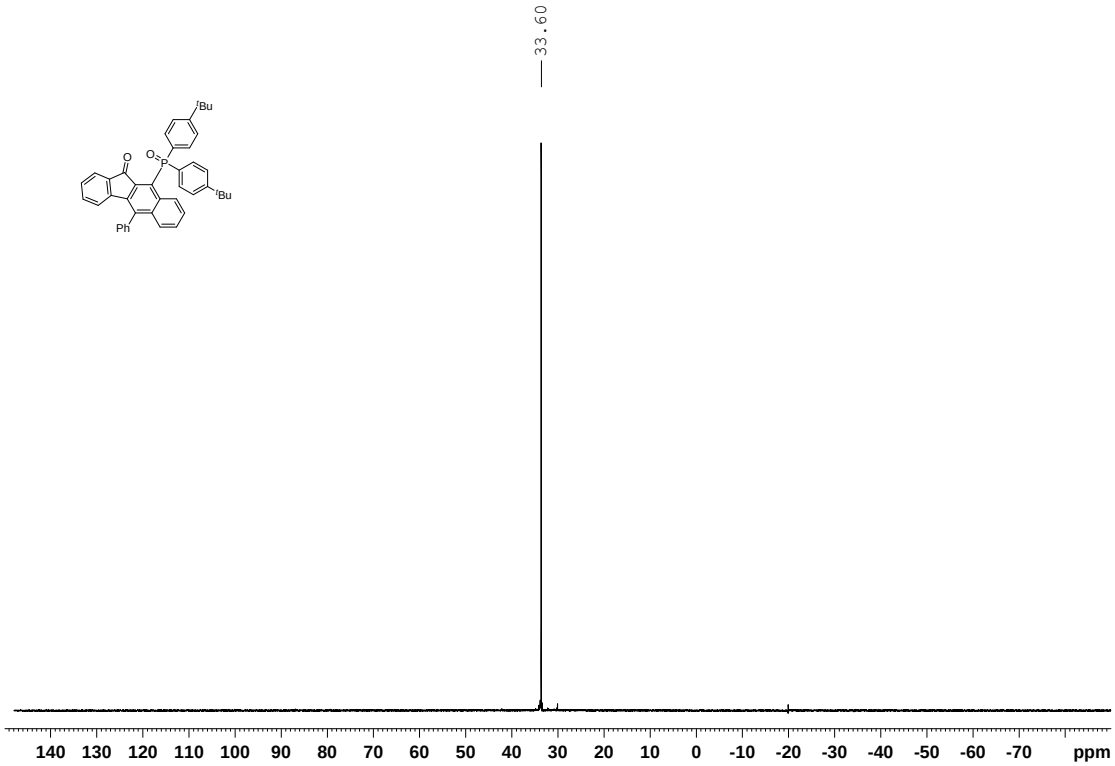
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3s**



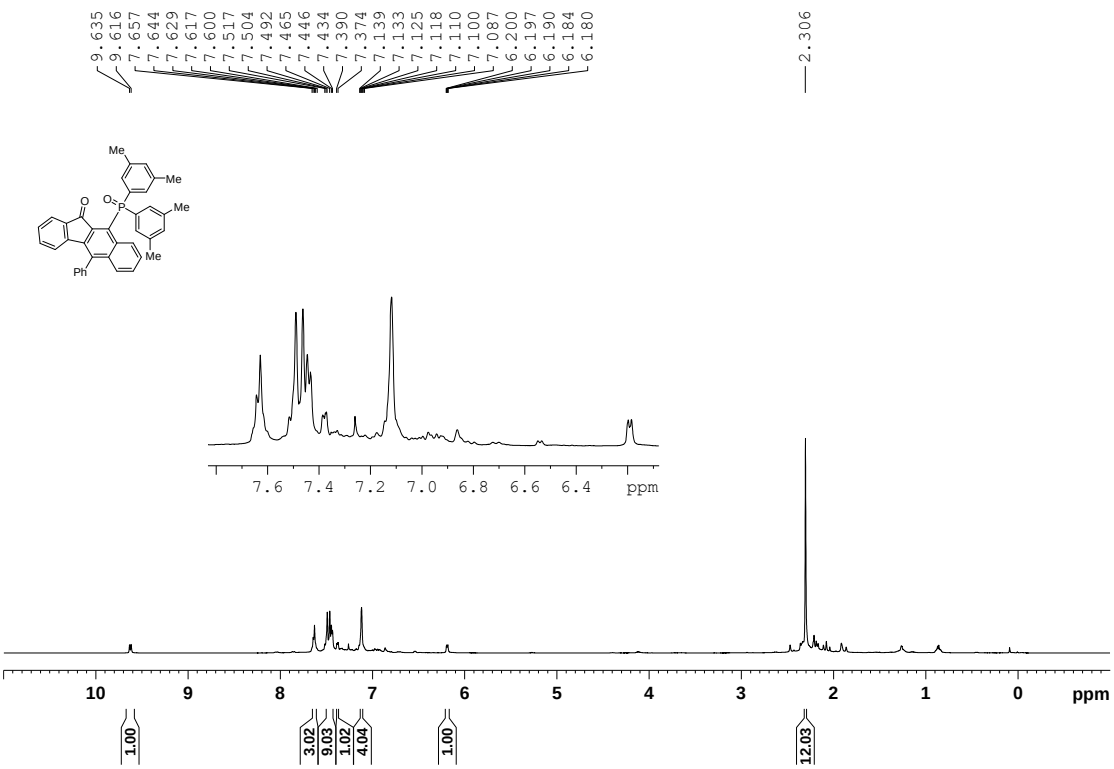
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3t**



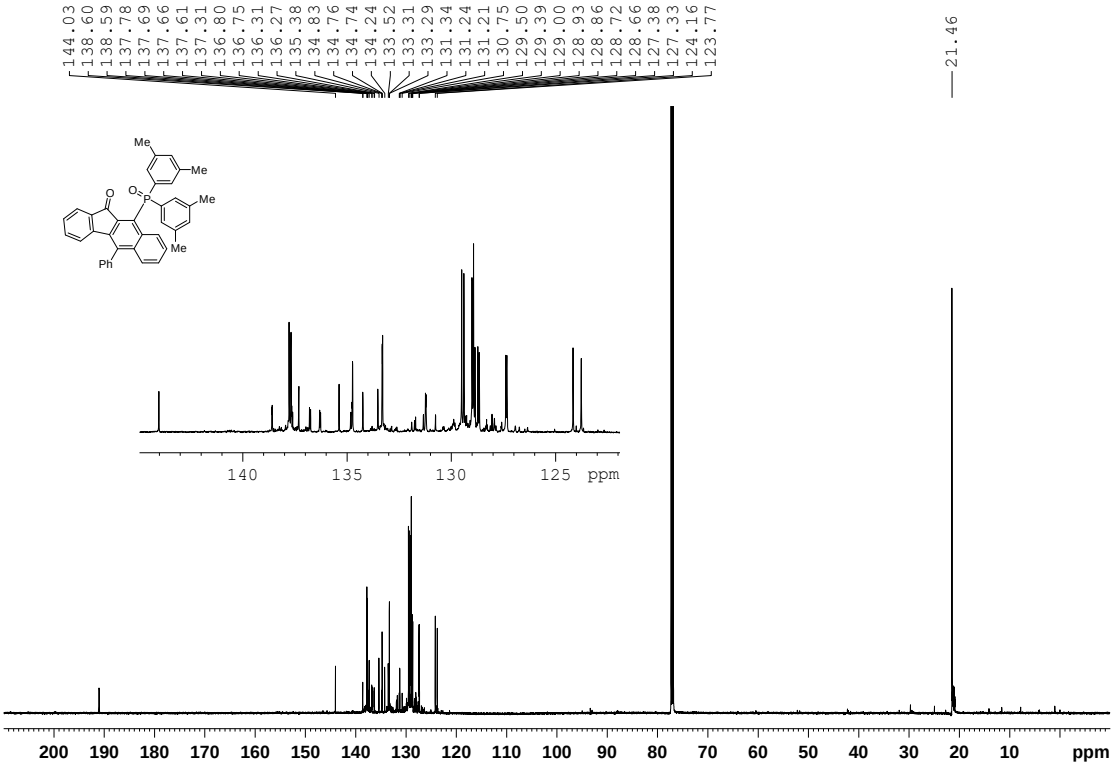
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3t**



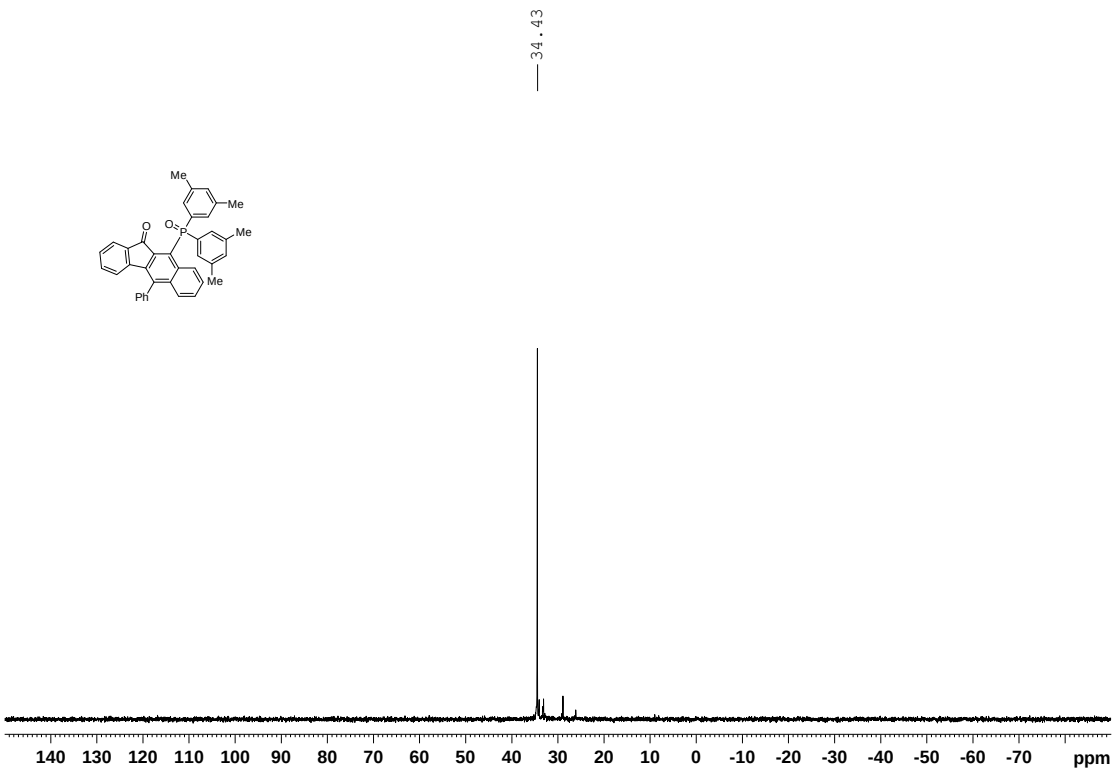
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3t**



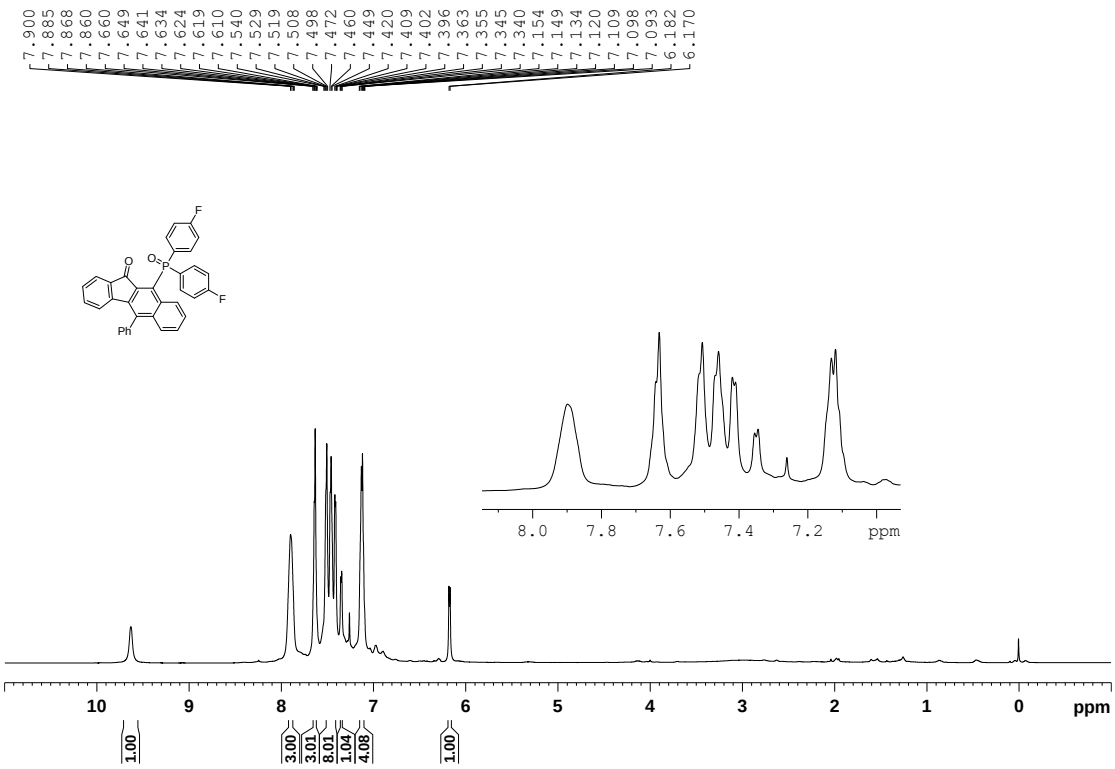
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3u**



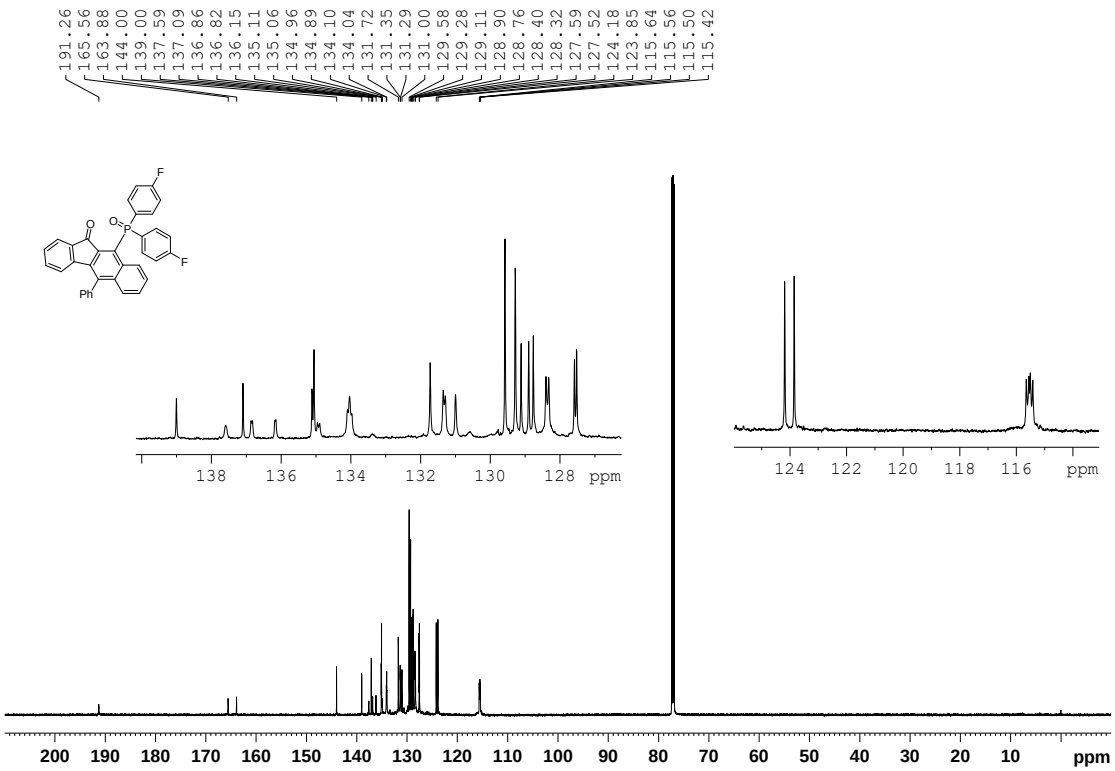
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3u**



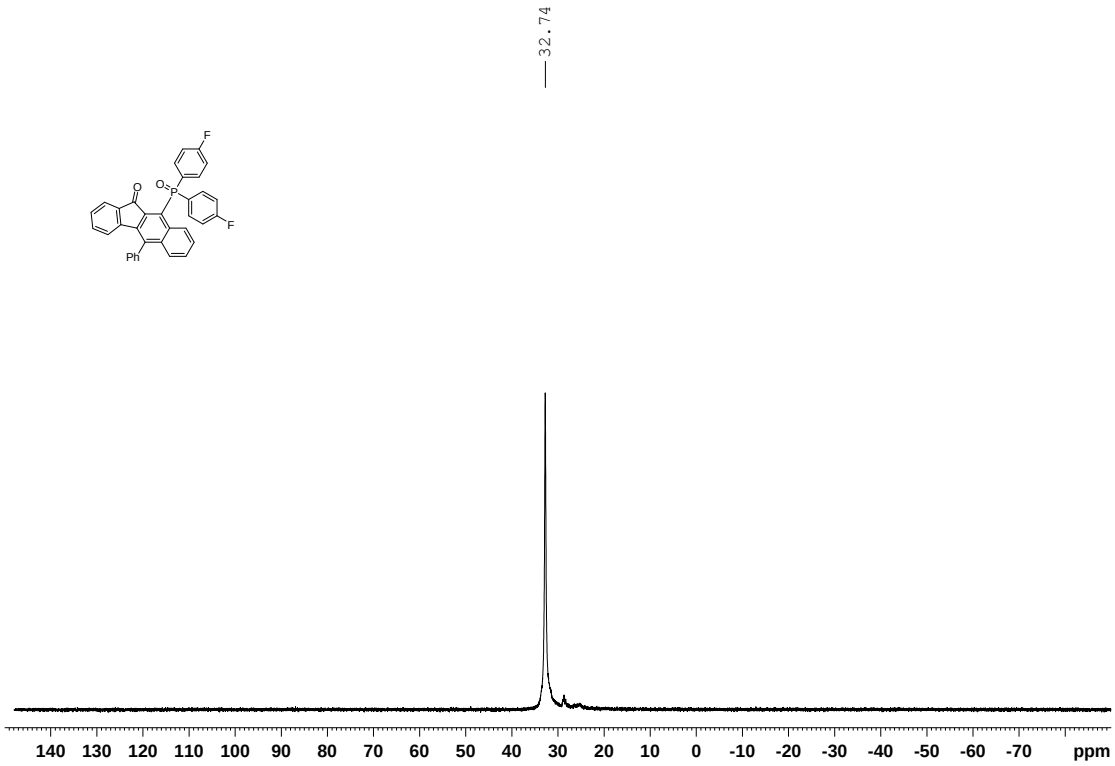
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3u**



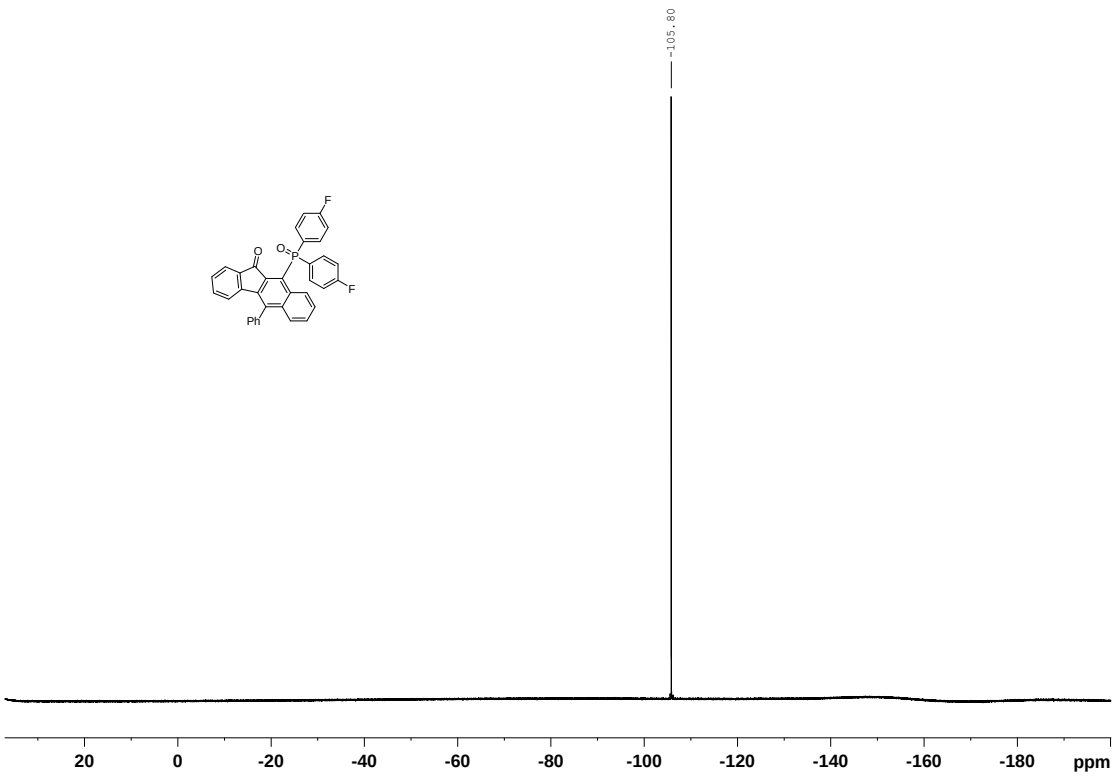
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3v**



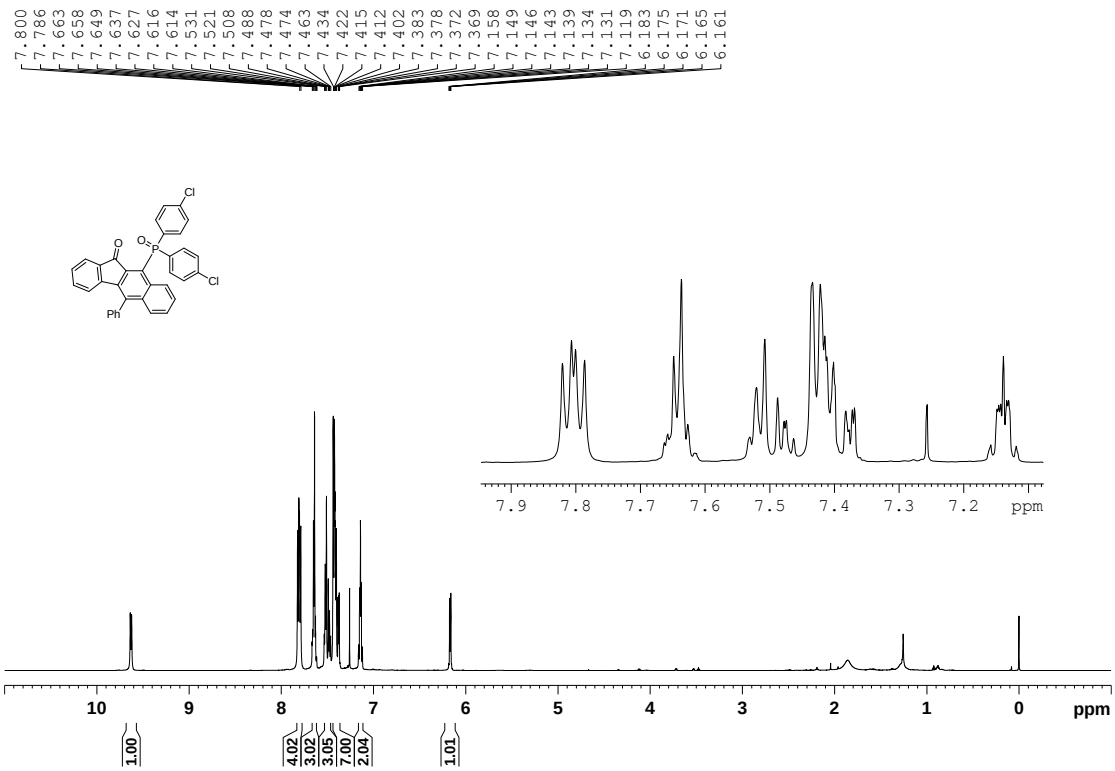
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3v**



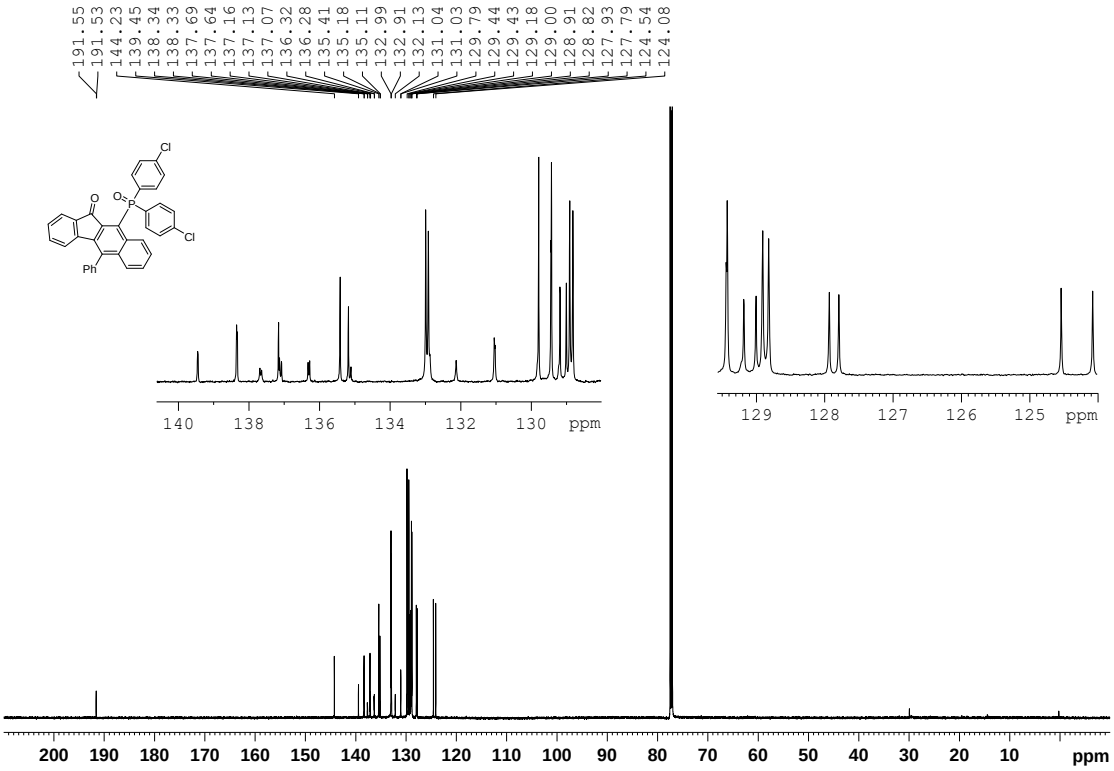
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3v**



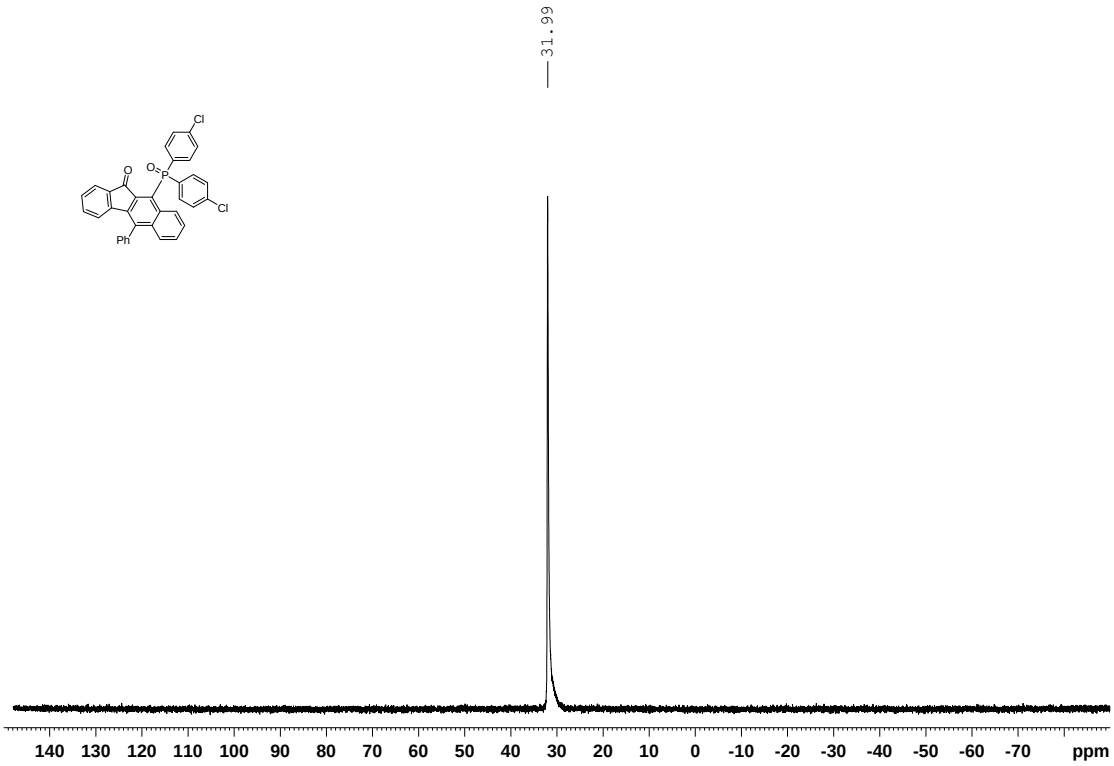
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) spectrum of compound **3v**



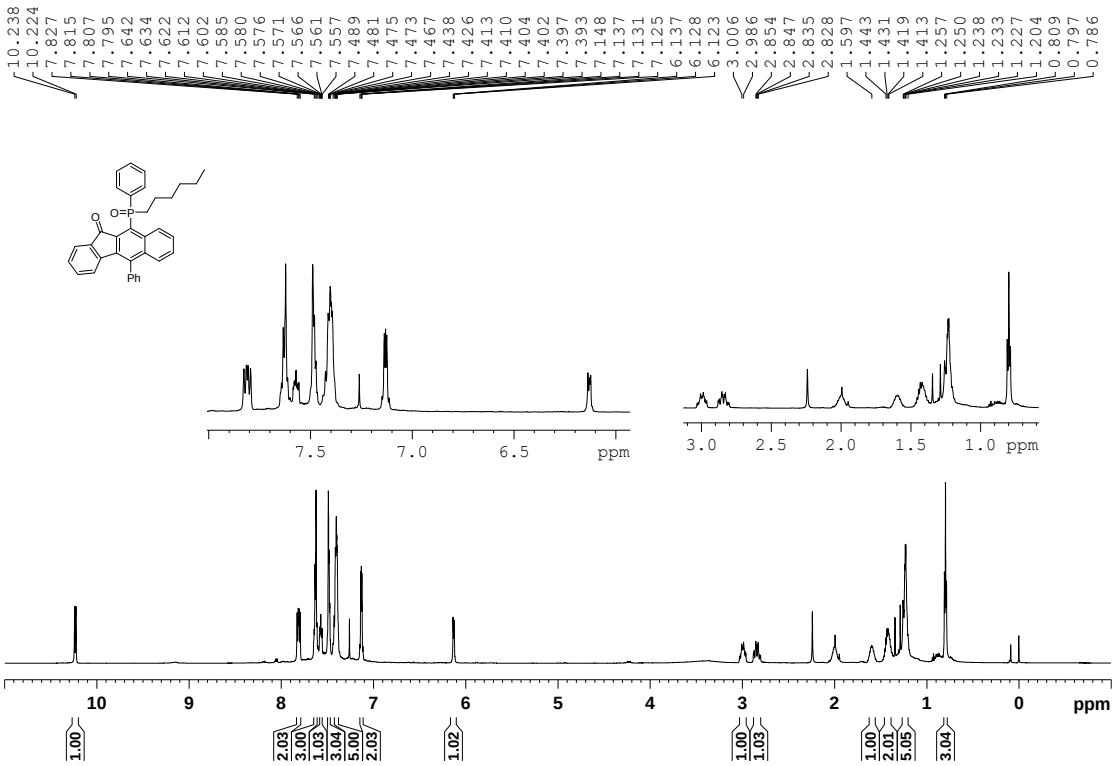
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3w**



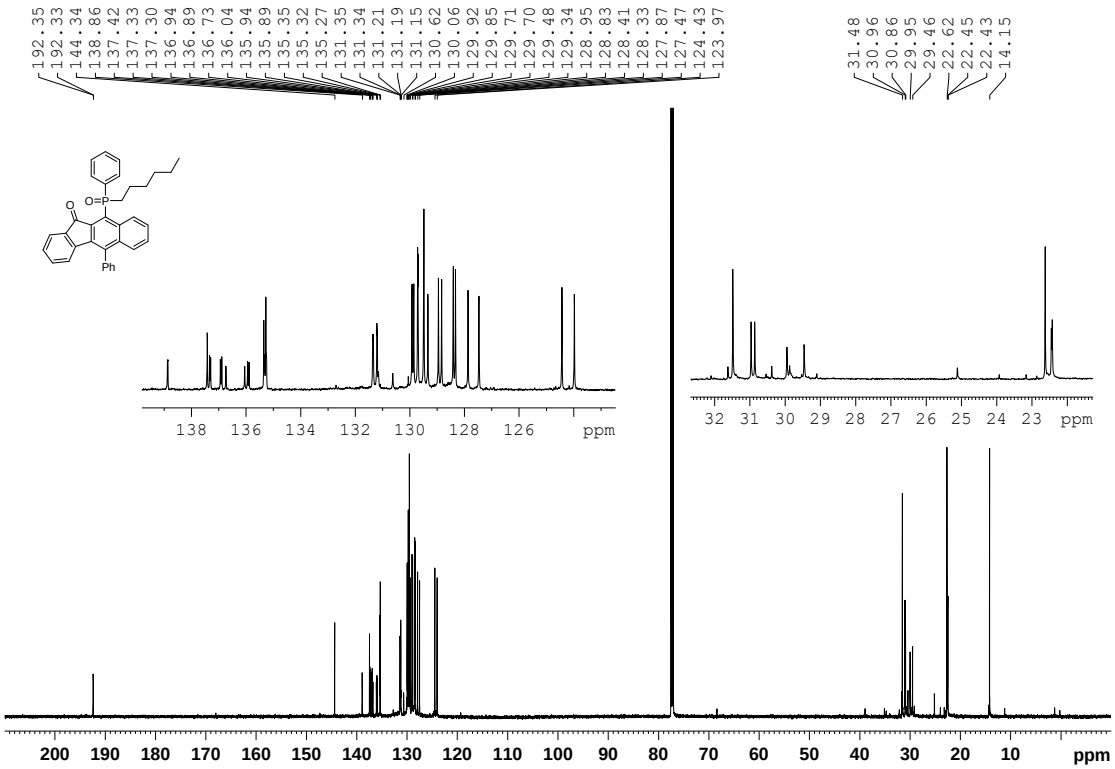
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3w**



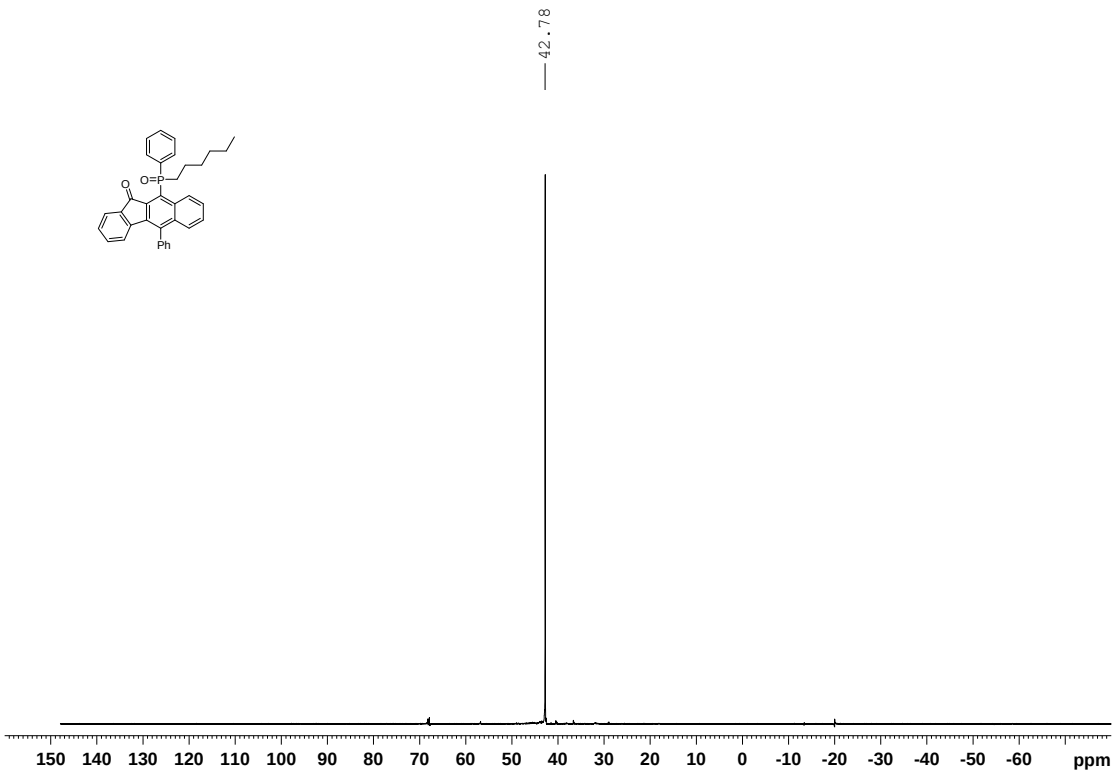
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3w**



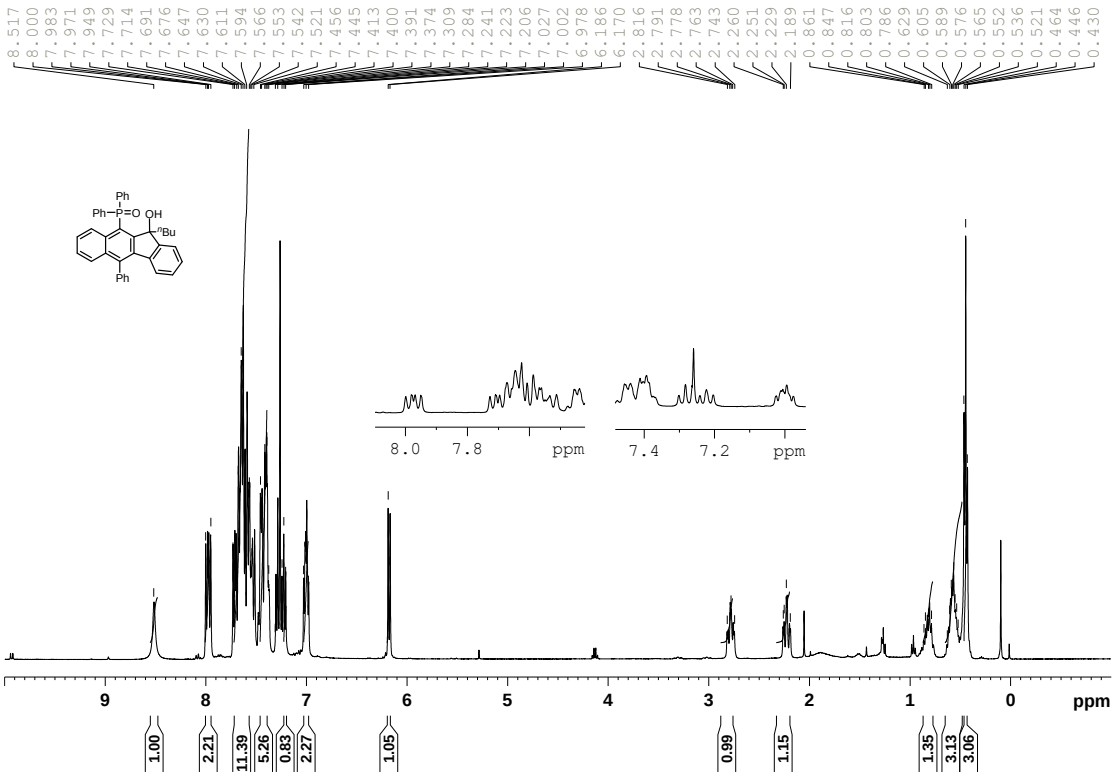
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3x**



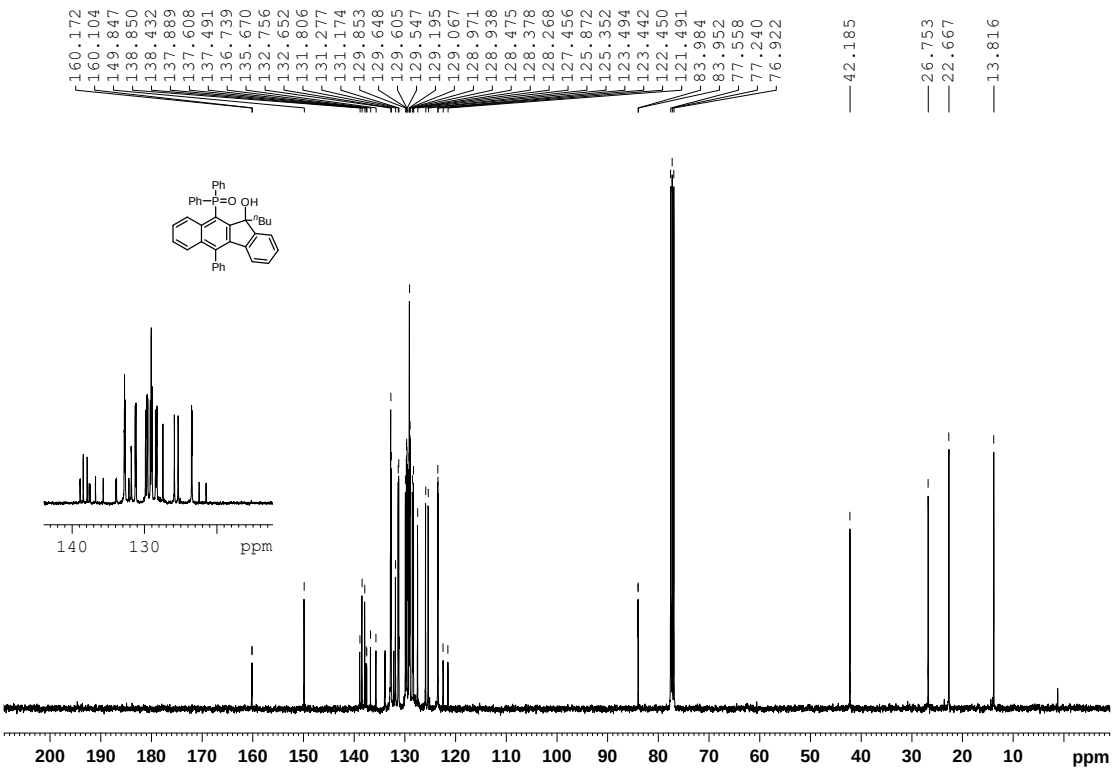
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **3x**



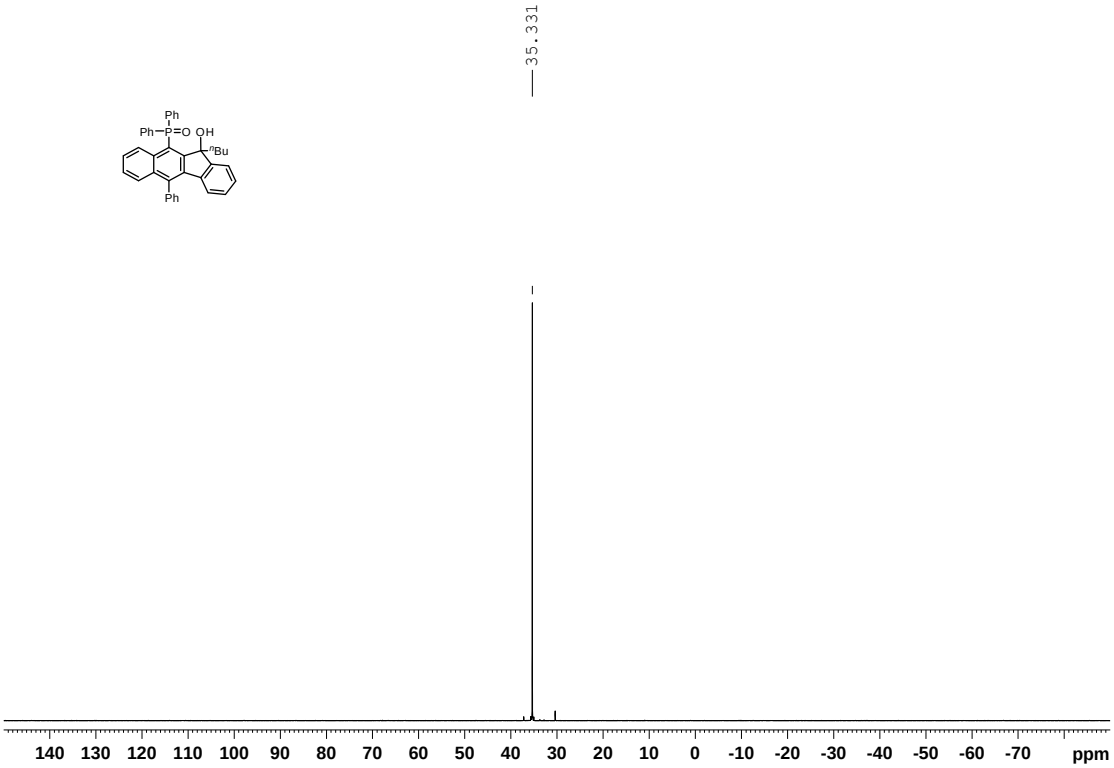
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **3x**



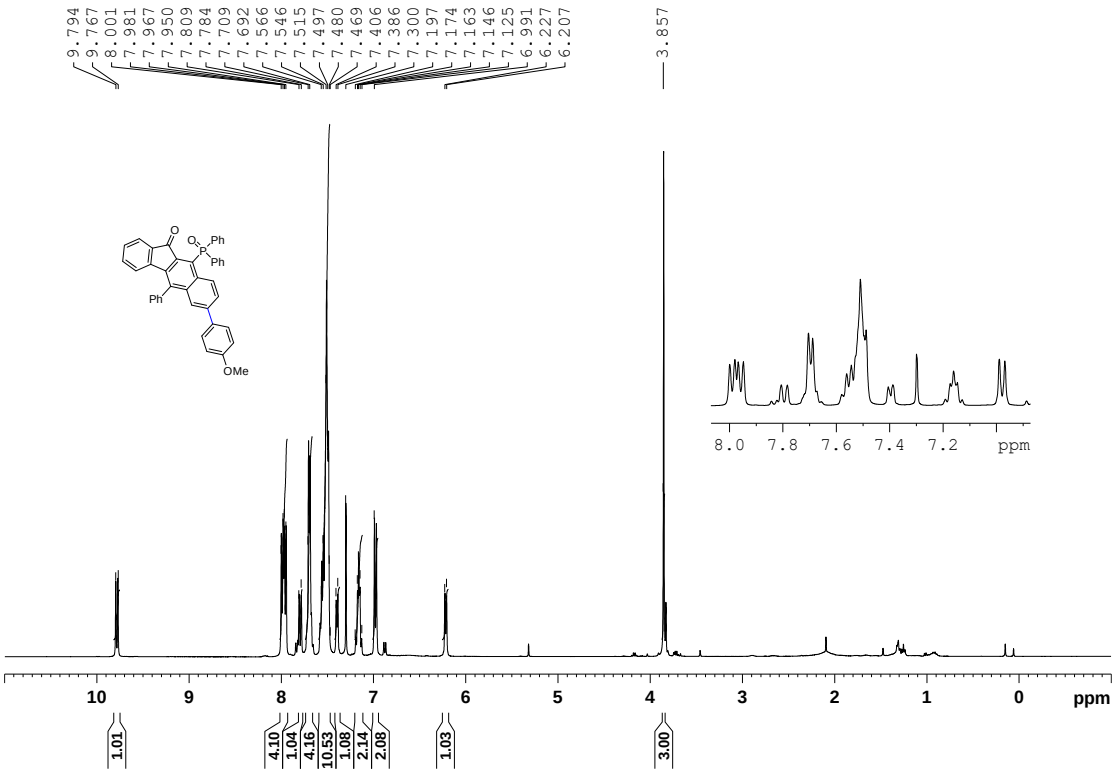
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5a**



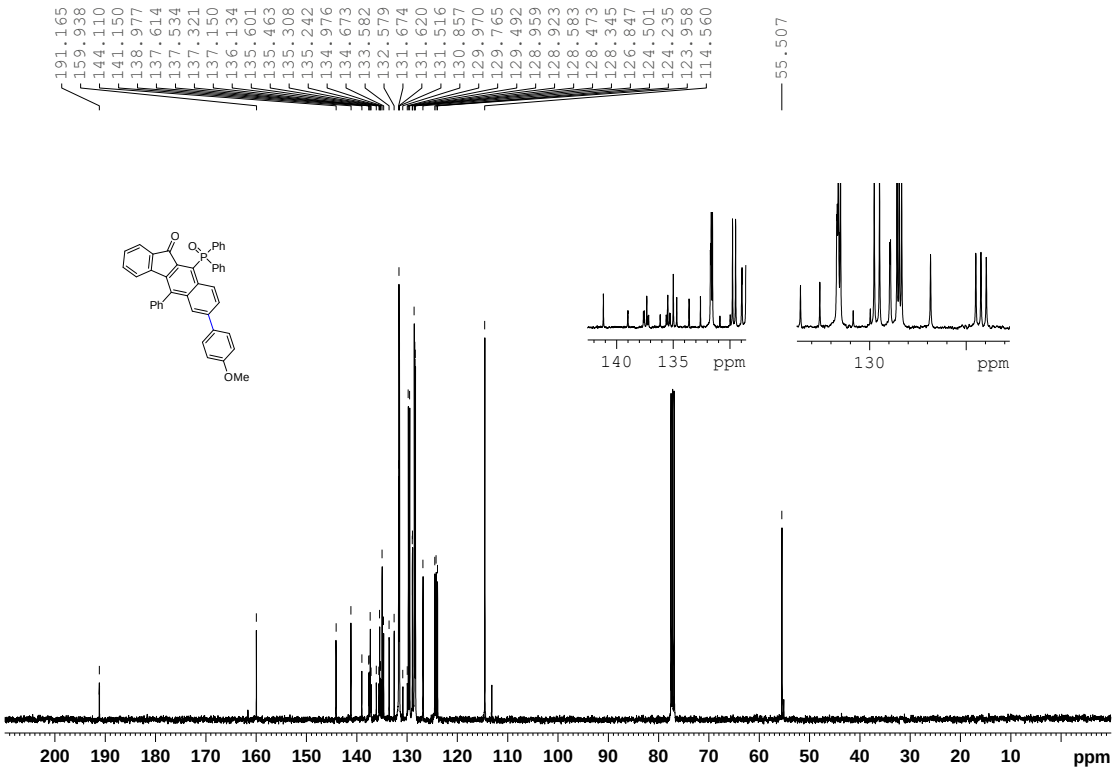
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **5a**



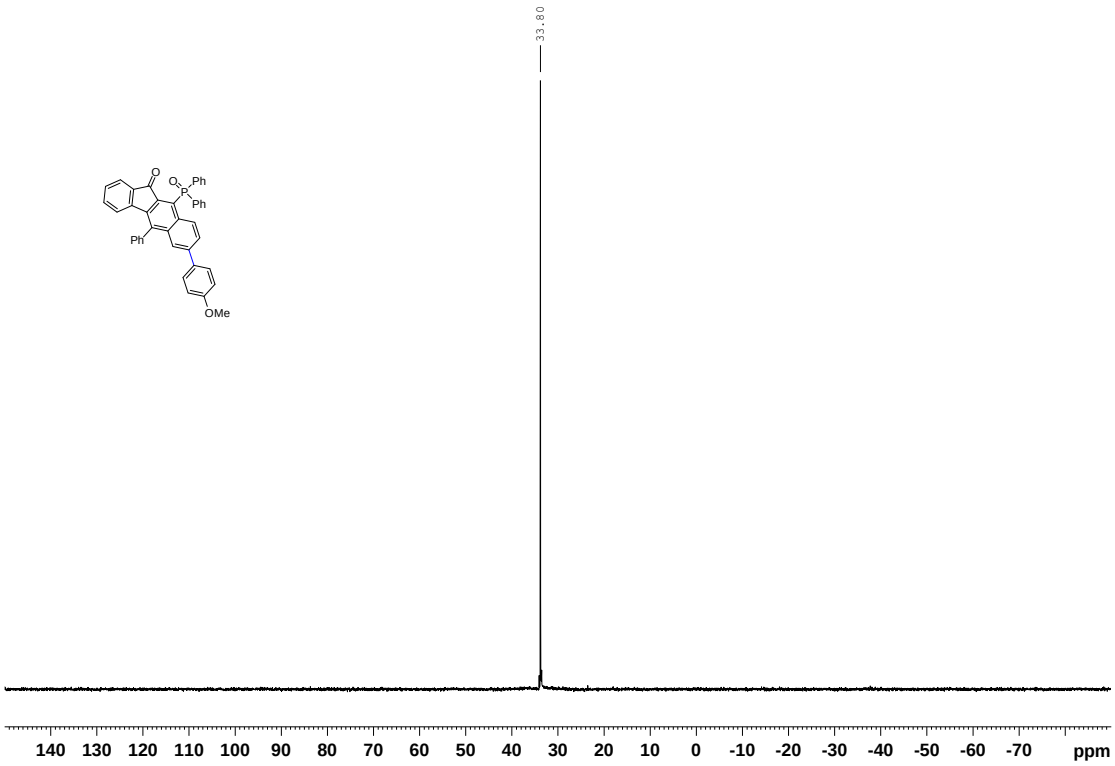
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5a**



$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5b**



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of compound **5b**



$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5b**

5. Crystallographic spectrum for 3a

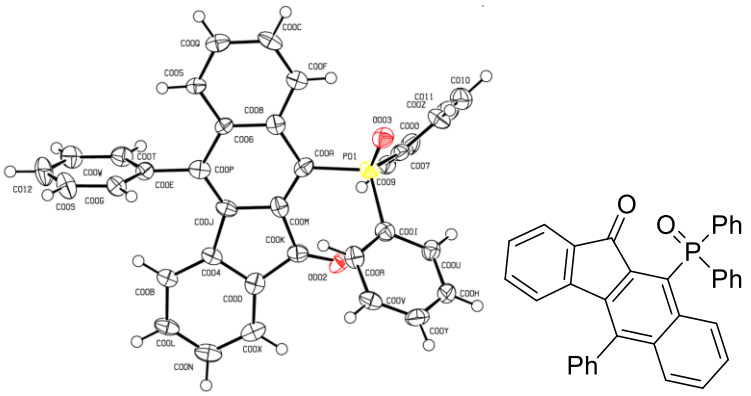


Table 1 Crystal data and structure refinement for 3a.

Identification code	exp_12276
Empirical formula	$C_{35}H_{23}O_2P$
Formula weight	506.50
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.9969(4)
b/Å	11.5978(5)
c/Å	26.9058(16)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2495.4(2)
Z	4
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.143
F(000)	1056.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.826 to 55.952
Index ranges	$-10 \le h \le 8$, $-13 \le k \le 15$, $-34 \le l \le 28$
Reflections collected	8060
Independent reflections	4515 [R_{int} = 0.0429, R_{sigma} = 0.0670]
Data/restraints/parameters	4515/0/343
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0673, wR_2 = 0.1553
Final R indexes [all data]	R_1 = 0.0800, wR_2 = 0.1641
Largest diff. peak/hole / e Å^{-3}	1.13/-0.43
Flack parameter	-0.01(9)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_12276. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
P01	9017.9(19)	658.0(12)	3563.5(5)	26.4(3)
O002	5975(6)	1785(3)	2951.1(14)	35.6(10)
O003	10056(5)	-28(3)	3913.7(14)	33.4(10)
C004	5201(7)	4218(5)	3716.1(19)	23.7(12)
C005	10546(6)	4217(5)	4707.1(18)	22.6(11)
C006	9455(7)	3721(4)	4359.1(19)	21.1(11)
C007	10001(7)	778(5)	2967(2)	26.3(12)
C008	9861(7)	2653(4)	4131.9(19)	25.1(12)
C009	9647(7)	1603(5)	2597(2)	27.6(12)
C00A	8685(7)	2139(5)	3783.9(19)	26.1(12)
C00B	4179(7)	5148(4)	3824.4(19)	24.7(11)
C00C	12522(7)	2683(5)	4555(2)	30.0(13)
C00D	4623(7)	3390(4)	3368(2)	27.0(13)
C00E	7461(7)	5435(4)	4482.6(19)	24.6(12)
C00F	11443(7)	2183(5)	4234(2)	27.1(13)
C00G	6633(7)	5469(5)	4936(2)	27.3(13)
C00H	5374(8)	-1616(5)	3187(2)	37.2(15)
C00I	7024(7)	-56(5)	3517(2)	28.7(12)
C00J	6838(7)	3835(5)	3899(2)	25.6(12)
C00K	5912(7)	2518(5)	3286.6(19)	27.1(12)
C00L	2611(7)	5203(5)	3599(2)	31.0(13)
C00M	7255(7)	2747(4)	3661.0(19)	26.0(12)
C00N	2055(8)	4396(5)	3271(2)	34.7(14)
C00O	10621(8)	1686(5)	2176(2)	32.5(14)
C00P	7891(7)	4300(5)	4241.1(19)	25.3(12)
C00Q	12076(8)	3726(5)	4810(2)	31.1(13)
C00R	5848(8)	73(5)	3901(2)	30.5(13)
C00S	6298(9)	6508(5)	5161(2)	39.8(16)
C00T	7918(8)	6464(5)	4260(2)	32.4(14)
C00U	6762(8)	-898(5)	3155(2)	29.0(13)
C00V	4455(7)	-657(5)	3928(2)	32.6(13)
C00W	7551(8)	7519(5)	4476(2)	36.1(15)
C00X	3064(8)	3478(5)	3145(2)	31.0(14)
C00Y	4255(8)	-1516(5)	3576(3)	39.6(15)
C00Z	11381(7)	35(6)	2883(2)	35.8(14)
C010	12336(8)	158(6)	2462(2)	42.0(16)
C011	11967(8)	962(5)	2113(2)	37.8(15)
C012	6748(10)	7528(6)	4933(3)	44.6(17)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for exp_12276. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P01	25.5(7)	29.4(7)	24.1(7)	1.0(6)	-0.9(6)	1.7(6)
O002	45(3)	42(2)	20.2(19)	-4.4(18)	2(2)	-21(2)
O003	36(2)	36(2)	28(2)	-0.3(18)	-8.7(19)	1(2)
C004	21(3)	26(3)	24(3)	11(2)	3(2)	1(2)
C005	21(3)	33(3)	14(2)	3(2)	-1(2)	-3(2)
C006	22(3)	24(2)	17(2)	2(2)	2(2)	-6(2)
C007	23(3)	33(3)	23(3)	-5(2)	-2(2)	-4(3)
C008	29(3)	24(3)	23(3)	6(2)	8(2)	-3(3)
C009	27(3)	29(3)	27(3)	-5(2)	2(2)	-3(2)
C00A	30(3)	32(3)	17(2)	-1(2)	2(2)	-8(2)
C00B	23(3)	27(3)	25(3)	9(2)	2(2)	1(2)
C00C	21(3)	39(3)	30(3)	16(3)	5(3)	7(3)
C00D	36(3)	23(3)	22(3)	9(2)	6(3)	-6(3)
C00E	25(3)	26(3)	23(3)	0(2)	1(2)	-2(2)
C00F	26(3)	31(3)	24(3)	8(2)	2(2)	0(3)
C00G	30(3)	26(3)	26(3)	6(2)	0(2)	4(2)
C00H	33(3)	36(3)	43(4)	-14(3)	-11(3)	7(3)
C00I	29(3)	30(3)	27(3)	3(3)	-3(3)	3(2)
C00J	21(3)	32(3)	24(3)	8(2)	-1(2)	3(2)
C00K	24(3)	32(3)	26(3)	4(2)	3(3)	-4(3)
C00L	21(3)	37(3)	35(3)	16(3)	-2(3)	4(3)
C00M	30(3)	25(3)	23(3)	4(2)	10(2)	1(2)
C00N	25(3)	47(4)	32(3)	18(3)	-4(3)	1(3)
C00O	37(4)	35(3)	25(3)	-6(2)	6(3)	-9(3)
C00P	26(3)	29(3)	21(3)	11(2)	1(2)	-2(3)
C00Q	28(3)	45(3)	20(3)	6(3)	-3(3)	-8(3)
C00R	37(3)	31(3)	23(3)	3(2)	7(3)	1(3)
C00S	50(4)	39(3)	31(3)	0(3)	4(3)	16(3)
C00T	30(3)	33(3)	34(3)	5(3)	1(3)	-2(3)
C00U	34(3)	27(3)	26(3)	-1(2)	-2(3)	1(3)
C00V	25(3)	37(3)	36(3)	8(3)	-1(3)	5(3)
C00W	38(4)	23(3)	47(4)	11(3)	-3(3)	3(3)
C00X	33(3)	37(3)	23(3)	10(3)	-5(3)	-12(3)
C00Y	27(3)	32(3)	59(4)	4(3)	-14(3)	-3(3)
C00Z	26(3)	44(3)	37(3)	1(3)	4(3)	8(3)
C010	35(4)	56(4)	36(3)	-13(3)	1(3)	4(3)
C011	34(3)	50(4)	28(3)	-6(3)	4(3)	-11(3)
C012	61(5)	25(3)	48(4)	-1(3)	1(4)	17(3)

Table 4 Bond Lengths for 3a

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P01	O003	1.486(4)	C00D	C00X	1.387(8)
P01	C007	1.792(6)	C00E	C00G	1.388(8)
P01	C00A	1.837(6)	C00E	C00P	1.508(8)
P01	C00I	1.801(6)	C00E	C00T	1.385(8)
O002	C00K	1.241(6)	C00G	C00S	1.375(8)
C004	C00B	1.384(8)	C00H	C00U	1.390(9)
C004	C00D	1.419(8)	C00H	C00Y	1.382(9)
C004	C00J	1.468(8)	C00I	C00R	1.404(8)
C005	C006	1.403(7)	C00I	C00U	1.395(8)
C005	C00Q	1.378(8)	C00J	C00M	1.454(8)
C006	C008	1.420(7)	C00J	C00P	1.359(8)
C006	C00P	1.455(8)	C00K	C00M	1.496(8)
C007	C009	1.411(8)	C00L	C00N	1.360(9)
C007	C00Z	1.418(8)	C00N	C00X	1.378(9)
C008	C00A	1.454(8)	C00O	C011	1.375(9)
C008	C00F	1.405(8)	C00R	C00V	1.401(8)
C009	C00O	1.377(8)	C00S	C012	1.381(9)
C00A	C00M	1.383(8)	C00T	C00W	1.386(8)
C00B	C00L	1.394(8)	C00V	C00Y	1.385(9)
C00C	C00F	1.351(8)	C00W	C012	1.386(9)
C00C	C00Q	1.437(8)	C00Z	C010	1.373(9)
C00D	C00K	1.460(8)	C010	C011	1.357(9)

Table 5 Bond Angles for 3a

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O003	P01	C007	111.3(3)	C00Y	C00H	C00U	120.9(6)
O003	P01	C00A	112.1(2)	C00R	C00I	P01	119.5(4)
O003	P01	C00I	107.0(3)	C00U	C00I	P01	120.2(4)
C007	P01	C00A	106.3(3)	C00U	C00I	C00R	119.2(5)
C007	P01	C00I	111.2(3)	C00M	C00J	C004	108.7(5)
C00I	P01	C00A	108.9(3)	C00P	C00J	C004	131.3(5)
C00B	C004	C00D	118.3(5)	C00P	C00J	C00M	120.0(5)
C00B	C004	C00J	133.8(5)	O002	C00K	C00D	127.7(5)
C00D	C004	C00J	107.9(5)	O002	C00K	C00M	125.6(5)
C00Q	C005	C006	121.1(5)	C00D	C00K	C00M	106.5(5)
C005	C006	C008	120.2(5)	C00N	C00L	C00B	123.0(6)

C005	C006	C00P	119.4(5)	C00A	C00M	C00J	121.8(5)
C008	C006	C00P	120.4(5)	C00A	C00M	C00K	131.6(5)
C009	C007	P01	126.7(4)	C00J	C00M	C00K	106.6(5)
C009	C007	C00Z	117.0(5)	C00L	C00N	C00X	120.0(6)
C00Z	C007	P01	116.0(4)	C011	C00O	C009	120.2(6)
C006	C008	C00A	119.1(5)	C006	C00P	C00E	120.3(5)
C00F	C008	C006	117.4(5)	C00J	C00P	C006	119.8(5)
C00F	C008	C00A	123.3(5)	C00J	C00P	C00E	119.8(5)
C00O	C009	C007	121.0(5)	C005	C00Q	C00C	118.2(5)
C008	C00A	P01	119.8(4)	C00V	C00R	C00I	120.5(5)
C00M	C00A	P01	121.2(4)	C00G	C00S	C012	120.2(6)
C00M	C00A	C008	118.7(5)	C00E	C00T	C00W	121.5(6)
C004	C00B	C00L	118.4(5)	C00H	C00U	C00I	119.8(6)
C00F	C00C	C00Q	120.5(5)	C00Y	C00V	C00R	119.4(6)
C004	C00D	C00K	109.7(5)	C012	C00W	C00T	118.5(6)
C00X	C00D	C004	121.9(5)	C00N	C00X	C00D	118.5(6)
C00X	C00D	C00K	128.4(5)	C00H	C00Y	C00V	120.3(6)
C00G	C00E	C00P	120.8(5)	C010	C00Z	C007	120.2(6)
C00T	C00E	C00G	118.8(5)	C011	C010	C00Z	121.4(6)
C00T	C00E	C00P	120.4(5)	C010	C011	C00O	120.2(6)
C00C	C00F	C008	122.2(5)	C00S	C012	C00W	120.6(6)
C00S	C00G	C00E	120.3(5)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H005	10230	4889	4871	27
H009	8742	2097	2637	33
H00B	4529	5721	4042	30
H00C	13563	2349	4611	36
H00F	11758	1504	4075	33
H00G	6304	4785	5088	33
H00H	5196	-2171	2943	45
H00L	1915	5820	3675	37
H00N	995	4464	3132	42
H00O	10369	2233	1935	39
H00Q	12801	4061	5039	37
H00R	5995	647	4138	37
H00S	5765	6524	5469	48

H00T	8483	6448	3958	39
H00U	7513	-978	2893	35
H00V	3672	-565	4181	39
H00W	7838	8205	4319	43
H00X	2707	2930	2916	37
H00Y	3363	-2028	3601	48
H00Z	11640	-535	3113	43
H010	13255	-322	2415	50
H011	12626	1025	1829	45
H012	6511	8227	5086	54