Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

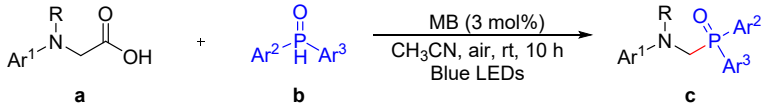
Photocatalytic decarboxylative phosphorylation of N-aryl glycines

Jiangwei Wen,*,† Xue Sun,† Kelu Yan, Tingtao Yan, Zhen Liu, Yang Li, Jianjing, Yang*
Key Laboratory of Green Natural Products and Pharmaceutical Intermediates in Colleges and Universities of Shandong Province, School of Chemistry and Chemical Engineering, Qufu Normal University, P. R. China.
E-mail: wenjy@qfnu.edu.cn, jjyang@whu.edu.cn
† These authors contributed equally.

1. General information

All glassware was oven dried at 100 °C for hours and cooled down under vacuum. N-aryl glycine and phosphine oxide was prepared according to reported procedures.[1] Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (b. p. 60-90 °C). ^{1}H, ^{13}C, and ^{19}F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to d-solvent peaks (77.00 ppm, chloroform).

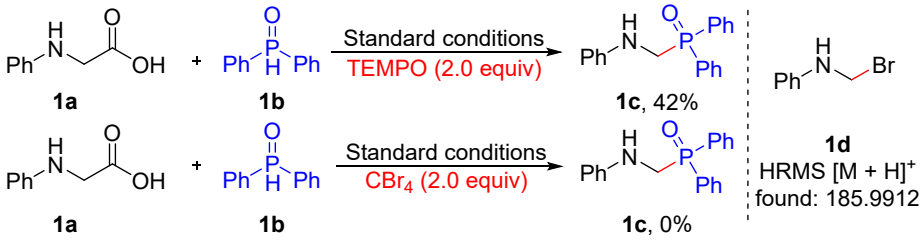
2. General procedure for photocatalytic decarboxylative phosphorylation of N-aryl glycines



a **b** **c**

In an oven-dried reaction tube (10 mL) equipped with a stir bar, N-aryl glycines **a** (0.5 mmol) and phosphine oxides **b** (0.25 mmol), and MB (3 mol%) were combined and added. Then, CH_3CN (2.0 mL) was slowly injected into the reaction tube. The reaction mixture was stirred and exposed to blue LED (460 nm) irradiation under room temperature for 10 h. When the reaction was finished, the reaction mixture was monitored by TLC and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl ether).

3. Radical inhibition experiments



1a **1b** **1c**, 42% **1a** **1b** **1c**, 0%

In an oven-dried reaction tube (10 mL) equipped with a stir bar, N-aryl glycines **a** (0.5 mmol) and phosphine oxides **b** (0.25 mmol), MB (3 mol%), and TEMPO or CBr_4 (0.5 mmol) were combined and added. Then, CH_3CN (2.0 mL) was slowly injected into the reaction tube. The reaction mixture was stirred and exposed to blue LED (460 nm) irradiation under room temperature for 10 h. When the reaction was finished, the reaction mixture was monitored by TLC and concentrated. The solution was concentrated in a vacuum and the desired product **1c** was obtained in a 42% yield. The detection of free radical species **1d** by high-resolution mass spectrometry (HRMS) further

confirmed this reaction may be a radical pathway.

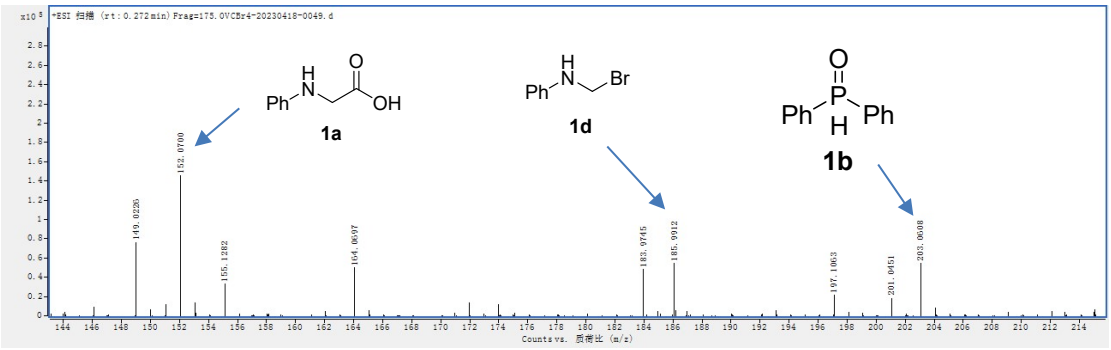
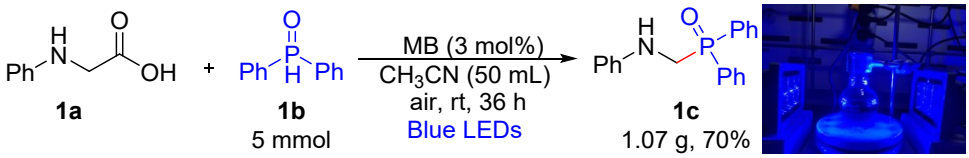


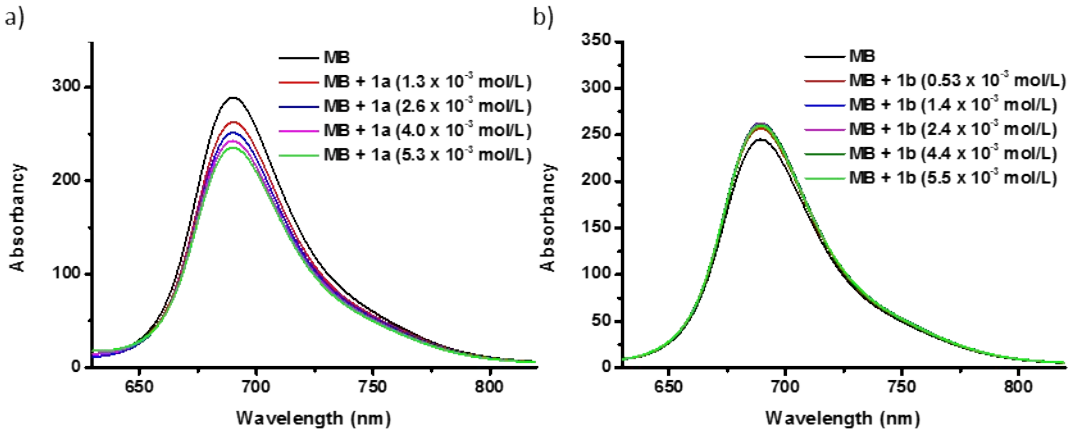
Figure S1. HRMS results of **1d**.

4. Large-scale synthesis of 1c.



In an oven-dried round bottom flask (100 mL) equipped with a stir bar, phenylalanine **1a** (10.0 mmol) and diphenylphosphine oxide **1b** (5.0 mmol), and MB (3 mol%) were combined and added. Then, CH_3CN (40.0 mL) was slowly injected into the round bottom flask. The reaction mixture was stirred and exposed to blue LED (460 nm) irradiation under room temperature for 36 h. When the reaction was finished, the reaction mixture was monitored by TLC and concentrated. The pure product **1c** (1.07 g, 70% yield) was obtained by flash column chromatography on silica gel (petroleum/ethyl ether = 1:1).

5. Fluorescence quenching experiments

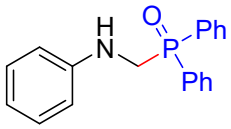


Quenching of MB fluorescence emission in the presence of **1a** or **1b**, the excitation wavelength was fixed at 425 nm, **MB** (1.0 x 10^{-3} mol/L). a) Varying concentrations of **1a**. b) Varying concentrations of **1b**.

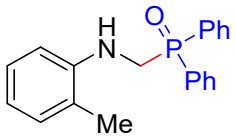
6. References

(1) (a) Pe´try, N.; Vanderbeeken, T.; Malher, A.; Bringer, Y.; Retailleau, P.; Bantreil, X.; Lamaty F. *Chem. Commun.,* **2019***, 55,* 9495-9498. (b) Li， C. J.； Lu, J.; Zhang, Z.-X.; Zhou, K.; Li, Y.; Qi, G. K. *Res. Chem. Intermed.* **2018**, *44*, 4547-45462.

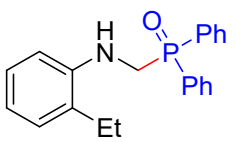
7. Detail descriptions for products



diphenyl((phenylamino)methyl)phosphine oxide (1c): yellow solid was obtained with 79% isolated yield (60.6 mg). m. p.: 128.2-129.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 4H), 7.52 (td, *J* = 7.5, 1.2 Hz, 2H), 7.48 – 7.42 (m, 4H), 7.14 (t, *J* = 7.9 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 4.38 (d, *J* = 5.7 Hz, 1H), 3.93 (dd, *J* = 8.5, 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7 (d, *J* = 11.0 Hz), 132.4 (d, *J* = 2.7 Hz), 131.2 (t, *J* = 8.0 Hz), 130.8 (d, *J* = 100.4 Hz), 129.2, 128.8 (d, *J* = 11.9 Hz), 118.6, 113.4, 43.8 (d, *J* = 79.0 Hz). HRMS (EI) calcd for $C_{19}H_{19}NOP$ $[M + H]^+$: 308.1199; found: 308.1198.

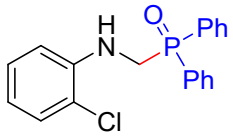


diphenyl((o-tolylamino)methyl)phosphine oxide (2c): white solid was obtained with 85% isolated yield (68.2 mg). m. p.: 120.5-122.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 4H), 7.56 (td, *J* = 7.4, 1.0 Hz, 2H), 7.49 (td, *J* = 7.6, 2.8 Hz, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 1H), 3.95 (d, *J* = 9.2 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6 (d, *J* = 11.0 Hz), 132.4 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 100.1 Hz), 131.1 (d, *J* = 9.5 Hz), 130.2, 128.8 (d, *J* = 11.8 Hz), 127.0, 123.4, 118.4, 110.3, 43.8 (d, *J* = 78.6 Hz), 17.3. HRMS (EI) calcd for $C_{20}H_{21}NOP$ $[M + H]^+$: 322.1355; found: 322.1354.

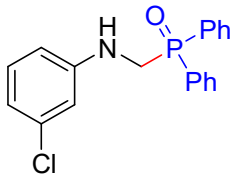


(((2-ethylphenyl)amino)methyl)diphenylphosphine oxide (3c): white solid was obtained with 75% isolated yield (62.8 mg). m. p.: 105-107 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 11.6, 7.3 Hz, 4H), 7.47 (t, *J* = 7.1 Hz, 2H), 7.40 (td, *J* = 7.6, 2.6 Hz, 4H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.3

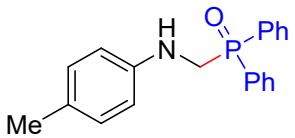
Hz, 1H), 6.67 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 4.02 (s, 1H), 3.86 (dd, J = 9.2, 5.2 Hz, 2H), 2.33 (q, J = 7.5 Hz, 2H), 1.02 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0 (d, J = 11.1 Hz), 132.4 (d, J = 2.7 Hz), 131.2 (d, J = 100.0 Hz), 131.1 (d, J = 9.5 Hz), 129.1, 128.8 (d, J = 11.8 Hz), 128.1, 126.9, 118.6, 110.6, 43.9 (d, J = 78.7 Hz), 23.8, 12.8. HRMS (EI) calcd for $C_{21}H_{23}NOP$ $[M + H]^+$: 336.1512; found: 336.1511.



(((2-chlorophenyl)amino)methyl)diphenylphosphine oxide (4c): white solid was obtained with 65% isolated yield (55.4 mg). m. p.: 132-134 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 4H), 7.57 (dd, J = 10.6, 4.2 Hz, 2H), 7.49 (td, J = 7.5, 2.6 Hz, 4H), 7.23 – 7.18 (m, 1H), 7.10 (dd, J = 11.4, 4.1 Hz, 1H), 6.74 – 6.60 (m, 2H), 4.70 (d, J = 5.3 Hz, 1H), 3.98 (dd, J = 8.9, 5.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3 (d, J = 9.6 Hz), 132.5 (d, J = 2.7 Hz), 131.2 (d, J = 9.5 Hz), 130.8 (d, J = 109.4 Hz), 129.2, 128.8 (d, J = 11.8 Hz), 127.7, 120.1, 118.6, 111.8, 43.9 (d, J = 78.2 Hz). HRMS (EI) calcd for $C_{19}H_{18}ClNOP$ $[M + H]^+$: 342.0809; found: 342.0807.

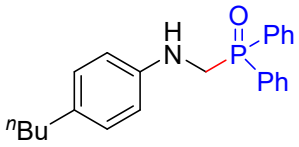


(((3-chlorophenyl)amino)methyl)diphenylphosphine oxide (5c): white solid was obtained with 64% isolated yield (54.5 mg). m. p.: 149-150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 4H), 7.70 (dd, J = 13.8, 7.2 Hz, 2H), 7.60 – 7.54 (m, 2H), 7.52 – 7.45 (m, 3H), 7.04 (t, J = 8.0 Hz, 1H), 6.69 (dd, J = 7.9, 0.9 Hz, 1H), 6.60 (t, J = 1.9 Hz, 1H), 6.52 (dd, J = 8.2, 2.1 Hz, 1H), 4.48 (s, 1H), 3.90 (d, J = 7.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7 (d, J = 10.4 Hz), 135.0, 132.5 (d, J = 2.7 Hz), 131.0 (d, J = 9.6 Hz), 130.6 (d, J = 101.8 Hz), 130.1, 128.9 (d, J = 11.9 Hz), 118.4, 112.9, 112.0, 43.6 (d, J = 78.2 Hz). HRMS (EI) calcd for $C_{19}H_{18}ClNOP$ $[M + H]^+$: 342.0809; found: 342.0807.

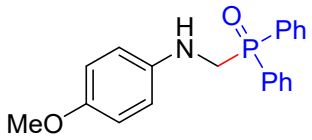


diphenyl((p-tolylamino)methyl)phosphine oxide (6c): white solid was obtained with 78% isolated yield (62.6 mg). m. p.: 161-162 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 4H), 7.47

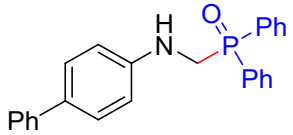
(t, J = 6.9 Hz, 2H), 7.39 (td, J = 7.6, 2.8 Hz, 4H), 6.90 (d, J = 8.3 Hz, 2H), 6.50 (d, J = 8.3 Hz, 2H), 4.05 (d, J = 4.0 Hz, 1H), 3.83 (d, J = 8.8 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3 (d, J = 11.6 Hz), 132.3 (d, J = 2.7 Hz), 131.2 (d, J = 100.0 Hz), 131.1 (d, J = 9.4 Hz), 129.7, 128.8 (d, J = 11.8 Hz), 127.9, 113.6, 44.2 (d, J = 79.2 Hz), 20.4. HRMS (EI) calcd for $C_{20}H_{21}NOP$ $[M + H]^+$: 322.1355; found: 322.1354.



(((4-butylphenyl)amino)methyl)diphenylphosphine oxide (7c): white solid was obtained with 66% isolated yield (59.9 mg). m. p.: 110-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.71 (m, 4H), 7.54 (td, J = 7.4, 1.1 Hz, 2H), 7.47 (td, J = 7.5, 2.8 Hz, 4H), 6.98 (d, J = 8.3 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 4.15 (d, J = 4.5 Hz, 1H), 3.91 (d, J = 8.4 Hz, 2H), 2.48 (t, J = 7.6 Hz, 2H), 1.58 – 1.46 (m, 2H), 1.38 – 1.25 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5 (d, J = 11.6 Hz), 133.2, 132.3 (d, J = 2.7 Hz), 131.2 (d, J = 99.9 Hz), 131.1 (d, J = 9.5 Hz), 129.1, 128.8 (d, J = 11.9 Hz), 113.5, 44.2 (d, J = 79.1 Hz), 34.7, 33.9, 22.3, 14.0. HRMS (EI) calcd for $C_{23}H_{27}NOP$ $[M + H]^+$: 364.1825; found: 364.1824.

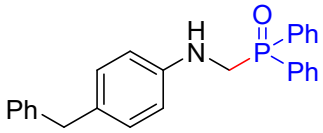


(((4-methoxyphenyl)amino)methyl)diphenylphosphine oxide (8c): Yellow liquid was obtained with 65% isolated yield (54.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 4H), 7.50 – 7.45 (m, 2H), 7.40 (td, J = 7.5, 2.8 Hz, 4H), 6.67 (d, J = 8.9 Hz, 2H), 6.55 (d, J = 8.9 Hz, 2H), 4.04 (d, J = 7.1 Hz, 1H), 3.82 (d, J = 8.6 Hz, 2H), 3.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 141.8 (d, J = 11.8 Hz), 132.3 (d, J = 2.8 Hz), 131.1 (d, J = 9.5 Hz), 131.0 (d, J = 100.0 Hz), 128.8 (d, J = 11.9 Hz), 114.8, 114.8, 55.7, 44.9 (d, J = 79.1 Hz). HRMS (EI) calcd for $C_{20}H_{21}NO_2P$ $[M + H]^+$: 338.1304; found: 338.1303

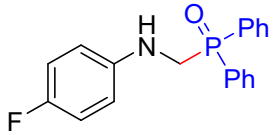


(([1,1'-biphenyl]-4-ylamino)methyl)diphenylphosphine oxide (9c): white solid was obtained with 68% isolated yield (65.1 mg). m. p.: 160-162 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 4H), 7.48 (td, J = 7.5, 1.2 Hz, 2H), 7.45 – 7.38 (m, 6H), 7.35 – 7.27 (m, 4H), 7.17 (dd, J = 8.7, 6.0 Hz,

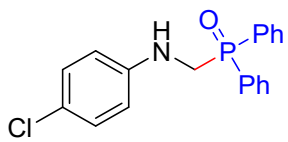
1H), 6.65 (d, *J* = 8.6 Hz, 2H), 4.34 (s, 1H), 3.89 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.0 (d, *J* = 10.9 Hz), 140.9, 132.4 (d, *J* = 2.8 Hz), 131.6, 131.1 (d, *J* = 9.5 Hz), 131.0 (d, *J* = 100.3 Hz), 128.9 (d, *J* = 11.9 Hz), 128.7, 127.9, 126.4, 126.3, 113.7, 43.9 (d, *J* = 78.6 Hz). HRMS (EI) calcd for $C_{25}H_{23}NOP$ $[M + H]^+$: 384.1512; found: 384.1511.



(((4-benzylphenyl)amino)methyl)diphenylphosphine oxide (10c): white solid was obtained with 70% isolated yield (69.4 mg). m. p.: 143-145 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 4H), 7.53 (td, *J* = 7.5, 1.1 Hz, 2H), 7.45 (td, *J* = 7.6, 2.8 Hz, 4H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.15 (dd, *J* = 11.3, 7.6 Hz, 3H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.20 (d, *J* = 5.7 Hz, 1H), 3.90 (dd, *J* = 8.6, 5.6 Hz, 2H), 3.85 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9 (d, *J* = 11.2 Hz), 141.8, 132.3 (d, *J* = 2.7 Hz), 131.3, 131.2 (d, *J* = 100.0 Hz), 131.1 (d, *J* = 9.5 Hz), 129.7, 128.8 (d, *J* = 12.0 Hz), 128.7, 128.3, 125.9, 113.7, 44.1 (d, *J* = 78.8 Hz), 41.0. HRMS (EI) calcd for $C_{26}H_{25}NOP$ $[M + H]^+$: 398.1168; found: 398.1167.

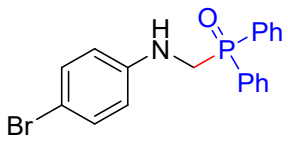


(((4-fluorophenyl)amino)methyl)diphenylphosphine oxide (11c): white solid was obtained with 70% isolated yield (56.8 mg). m. p.: 139-140.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 4H), 7.57 (td, *J* = 7.4, 1.2 Hz, 2H), 7.49 (td, *J* = 7.6, 2.9 Hz, 4H), 6.86 (t, *J* = 8.7 Hz, 2H), 6.59 (dd, *J* = 8.9, 4.3 Hz, 2H), 4.13 (d, *J* = 3.4 Hz, 1H), 3.88 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4 (d, *J* = 236.5 Hz), 144.0 (dd, *J* = 11.3, 2.0 Hz), 132.4 (d, *J* = 2.8 Hz), 131.1 (d, *J* = 9.5 Hz), 131.0 (d, *J* = 100.0 Hz), 128.8 (d, *J* = 11.9 Hz), 115.6 (d, *J* = 22.6 Hz), 114.4 (d, *J* = 7.6 Hz), 44.6 (d, *J* = 78.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -126.4. HRMS (EI) calcd for $C_{19}H_{18}FNOP$ $[M + H]^+$: 326.1105; found: 326.1104.

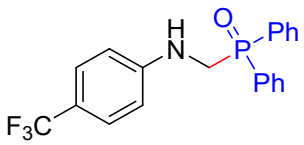


(((4-chlorophenyl)amino)methyl)diphenylphosphine oxide (**12c**): white solid was obtained with 83% isolated yield (70.7 mg). m. p.: 172-173.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 4H),

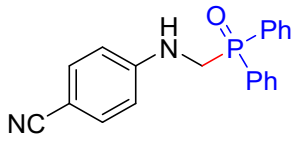
7.49 (td, J = 7.4, 1.3 Hz, 2H), 7.41 (td, J = 7.5, 2.9 Hz, 4H), 7.01 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 8.9 Hz, 2H), 4.31 (s, 1H), 3.81 (d, J = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2 (d, J = 10.8 Hz), 132.5 (d, J = 2.8 Hz), 131.1 (d, J = 9.5 Hz), 130.8 (d, J = 100.4 Hz), 129.0, 128.9 (d, J = 11.8 Hz), 123.2, 114.5, 44.0 (d, J = 78.1 Hz). HRMS (EI) calcd for $C_{19}H_{18}ClNOP$ $[M + H]^+$: 342.0809; found: 342.0807.



(((4-bromophenyl)amino)methyl)diphenylphosphine oxide (13c): white solid was obtained with 69% isolated yield (66.4 mg). m. p.: 72-74 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 4H), 7.56 (td, J = 7.4, 1.0 Hz, 2H), 7.47 (td, J = 7.6, 2.8 Hz, 4H), 7.21 (d, J = 8.7 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 4.43 (s, 1H), 3.87 (d, J = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7 (d, J = 10.6 Hz), 132.5 (d, J = 2.9 Hz), 131.9, 131.1 (d, J = 9.5 Hz), 130.8 (d, J = 100.3 Hz), 128.9 (d, J = 11.8 Hz), 115.0, 110.3, 43.8 (d, J = 78.2 Hz). HRMS (EI) calcd for $C_{19}H_{18}BrNOP$ $[M + H]^+$: 386.0304; found: 386.0303.

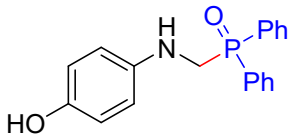


diphenyl(((4-(trifluoromethyl)phenyl)amino)methyl)phosphine oxide (14c): white solid was obtained with 63% isolated yield (59 mg). m. p.: 149-151 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.52 – 7.45 (m, 4H), 7.38 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 8.4 Hz, 2H), 4.75 (s, 1H), 3.95 (d, J = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1 (d, J = 9.9 Hz), 132.5 (d, J = 2.8 Hz), 131.0 (d, J = 9.5 Hz), 130.6 (d, J = 100.6 Hz), 128.9 (d, J = 12.0 Hz), 126.5 (q, J = 3.8 Hz), 124.7 (q, J = 270.3 Hz), 120.1 (d, J = 32.8 Hz), 112.6, 43.3 (d, J = 77.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.2. HRMS (EI) calcd for $C_{20}H_{18}F_3NOP$ $[M + H]^+$: 376.1073; found: 376.1072.

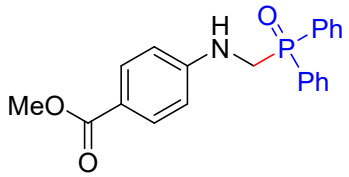


4-(((diphenylphosphoryl)methyl)amino)benzonitrile (15c): yellow solid was obtained with 35% isolated yield (29 mg). m. p.: 189-191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, J = 10.9, 7.9 Hz, 4H), 7.59 (t, J = 7.4 Hz, 2H), 7.50 (t, J = 7.0 Hz, 4H), 7.39 (d, J = 8.7 Hz, 2H), 5.10 (s, 1H), 3.96 (d, J = 3.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8 (d, J = 8.5 Hz), 133.6, 132.7 (d, J = 1.9 Hz), 131.0 (d, J = 9.2 Hz), 130.5 (d, J = 101.7 Hz), 129.0 (d, J = 11.6 Hz), 120.0, 112.9, 100.2, 43.1 (d, J = 76.6 Hz).

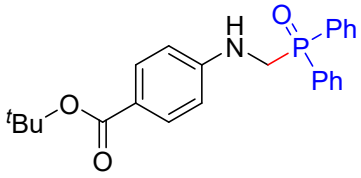
HRMS (EI) calcd for $C_{20}H_{18}N_2OP$ [M + H]$^+$: 333.1151; found: 333.1151.



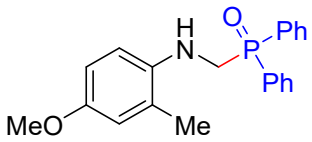
(((4-hydroxyphenyl)amino)methyl)diphenylphosphine oxide (16c): white solid was obtained with 50% isolated yield (40.3 mg). m. p.: 62-64 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 10.3, 8.0 Hz, 4H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.49 – 7.45 (m, 4H), 6.67 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 9.1 Hz, 2H), 4.33 (s, 1H), 3.92 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 142.3 (d, *J* = 2.4 Hz), 132.2, 131.2 (d, *J* = 9.1 Hz), 131.1 (d, *J* = 103.2 Hz), 128.7 (d, *J* = 11.3 Hz), 117.12, 116.0, 53.9 (d, *J* = 65.3 Hz). HRMS (EI) calcd for $C_{19}H_{19}NO_2P$ [M + H]$^+$: 324.1148; found: 324.1147.



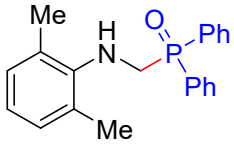
methyl 4-(((diphenylphosphoryl)methyl)amino)benzoate (17c): white solid was obtained with 72% isolated yield (65.7 mg). m. p.: 200-201 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.69 (dd, *J* = 11.4, 7.6 Hz, 4H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 6.5 Hz, 4H), 6.53 (d, *J* = 8.7 Hz, 2H), 4.94 (s, 1H), 3.90 (dd, *J* = 7.6, 3.7 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 151.4 (d, *J* = 9.1 Hz), 132.5 (d, *J* = 2.7 Hz), 131.3, 131.0 (d, *J* = 9.5 Hz), 130.7 (d, *J* = 101.2 Hz), 128.9 (d, *J* = 11.9 Hz), 119.6, 112.1, 51.5, 43.3 (d, *J* = 77.4 Hz). HRMS (EI) calcd for $C_{21}H_{21}NO_3P$ [M + H]$^+$: 366.1254; found: 366.1253.



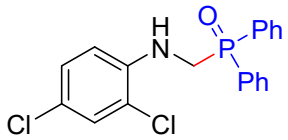
tert-butyl 4-(((diphenylphosphoryl)methyl)amino)benzoate (18c): white solid was obtained with 81% isolated yield (82.4 mg). m. p.: 170-172 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 6H), 7.56 (t, *J* = 7.3 Hz, 2H), 7.51 – 7.44 (m, 4H), 6.59 (d, *J* = 8.7 Hz, 2H), 4.81 (d, *J* = 5.4 Hz, 1H), 3.97 (d, *J* = 7.6 Hz, 2H), 1.55 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 150.9 (d, *J* = 9.5 Hz), 132.5 (d, *J* = 2.6 Hz), 131.2, 131.0 (d, *J* = 9.5 Hz), 130.7 (d, *J* = 106.4 Hz), 128.9 (d, *J* = 12.0 Hz), 121.7, 112.1, 80.0, 43.2 (d, *J* = 77.6 Hz), 28.3. HRMS (EI) calcd for $C_{24}H_{27}NO_3P$ [M + H]$^+$: 408.1723; found: 408.1720.



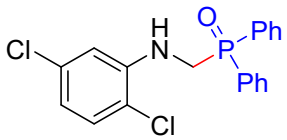
(((4-methoxy-2-methylphenyl)amino)methyl)diphenylphosphine oxide (19c): yellow solid was obtained with 87% isolated yield (76.3 mg). m. p.: 67-69 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 4H), 7.59 – 7.54 (m, 2H), 7.53 – 7.46 (m, 4H), 6.67 (s, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 3.91 (d, *J* = 8.9 Hz, 2H), 3.72 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 139.7 (d, *J* = 11.7 Hz), 132.4 (d, *J* = 2.9 Hz), 131.1 (d, *J* = 9.5 Hz), 131.0 (d, *J* = 100.0 Hz), 128.8 (d, *J* = 11.8 Hz), 125.5, 117.0, 111.9, 111.4, 55.7, 44.7 (d, *J* = 79.1 Hz), 17.5. HRMS (EI) calcd for $C_{21}H_{23}NO_2P$ $[M + H]^+$: 352.1461; found: 352.1460.



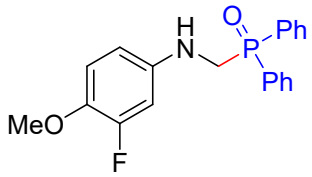
(((2,6-dimethylphenyl)amino)methyl)diphenylphosphine oxide (20c): yellow oil was obtained with 33% isolated yield (27.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 11.4, 7.5 Hz, 4H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.49 – 7.45 (m, 4H), 6.91 (d, *J* = 7.0 Hz, 2H), 6.79 (t, *J* = 7.5 Hz, 1H), 4.00 (d, *J* = 3.3 Hz, 1H), 3.81 (d, *J* = 7.5 Hz, 2H), 2.17 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3 (d, *J* = 10.2 Hz), 132.2 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 2.7 Hz), 131.5 (d, *J* = 100.4 Hz), 131.1 (d, *J* = 9.5 Hz), 128.8, 128.6 (d, *J* = 11.7 Hz), 48.0 (d, *J* = 74.3 Hz), 18.2. HRMS (EI) calcd for $C_{21}H_{23}NOP$ $[M + H]^+$: 336.1512; found: 336.1510.



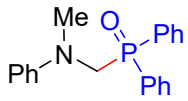
(((2,4-dichlorophenyl)amino)methyl)diphenylphosphine oxide (21c): white solid was obtained with 53% isolated yield (49.6 mg). m. p.: 169-170 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 4H), 7.58 (td, *J* = 7.4, 1.1 Hz, 2H), 7.50 (td, *J* = 7.6, 2.9 Hz, 4H), 7.22 (s, 1H), 7.06 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 1H), 4.71 (d, *J* = 5.7 Hz, 1H), 3.95 (dd, *J* = 8.5, 5.6 Hz, 2H^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2 (d, *J* = 9.1 Hz), 132.5 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 9.5 Hz), 130.6 (d, *J* = 100.0 Hz), 128.9 (d, *J* = 11.9 Hz), 128.8, 127.6, 122.6, 120.4, 112.4, 44.0 (d, *J* = 77.6 Hz). HRMS (EI) calcd for $C_{19}H_{17}Cl_2NOP$ $[M + H]^+$: 376.0419; found: 376.0417.



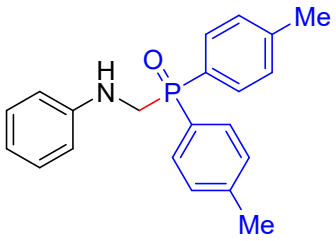
(((2,5-dichlorophenyl)amino)methyl)diphenylphosphine oxide (22c): white solid was obtained with 42% isolated yield (39.3 mg). m. p.: 148-150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 4H), 7.59 (td, *J* = 7.4, 1.3 Hz, 2H), 7.54 – 7.48 (m, 4H), 7.12 (d, *J* = 8.9 Hz, 1H), 6.64 – 6.62 (m, 1H), 6.62 (s, 1H), 4.86 (d, *J* = 5.6 Hz, 1H), 3.94 (dd, *J* = 8.7, 5.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2 (d, *J* = 9.4 Hz), 133.4, 132.6 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 100.4 Hz), 129.9, 128.9 (d, *J* = 11.8 Hz), 118.2, 118.2, 111.7, 43.6 (d, *J* = 77.4 Hz). HRMS (EI) calcd for $C_{19}H_{17}Cl_2NOP$ [M + H]$^{+}$: 376.0419; found: 376.0417.



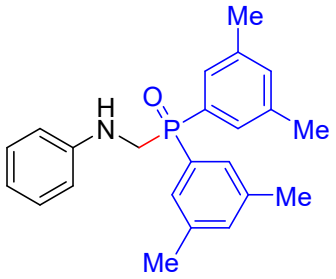
(((3-fluoro-4-methoxyphenyl)amino)methyl)diphenylphosphine oxide (23c): yellow oil was obtained with 72% isolated yield (63.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 4H), 7.57 (dd, *J* = 10.8, 4.1 Hz, 2H), 7.49 (td, *J* = 7.6, 2.8 Hz, 4H), 6.79 (t, *J* = 9.1 Hz, 1H), 6.43 (dd, *J* = 13.1, 2.7 Hz, 1H), 6.36 (d, *J* = 8.8 Hz, 1H), 3.88 (d, *J* = 8.2 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3 (d, *J* = 244.6 Hz), 142.5 (dd, *J* = 11.0, 9.0 Hz), 140.3 (d, *J* = 11.2 Hz), 132.6 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 9.7 Hz), 130.1 (d, *J* = 100.9 Hz), 128.9 (d, *J* = 11.9 Hz), 115.7 (d, *J* = 3.2 Hz), 108.8 (d, *J* = 3.3 Hz), 102.6 (d, *J* = 22.2 Hz), 57.3, 44.5 (d, *J* = 78.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.5. HRMS (EI) calcd for $C_{20}H_{20}NO_2P$ [M + H]$^{+}$: 356.1210; found: 356.1209.



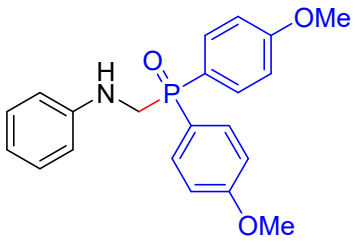
((methyl(phenyl)amino)methyl)diphenylphosphine oxide (24) white solid was obtained with 54% isolated yield (43.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 4H), 7.56 – 7.51 (m, 2H), 7.49 – 7.43 (m, 4H), 7.13 (t, *J* = 8.0 Hz, 2H), 6.70 (dd, *J* = 12.7, 7.9 Hz, 3H), 4.20 (d, *J* = 3.7 Hz, 2H), 2.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9 (d, *J* = 3.1 Hz), 132.1 (d, *J* = 2.7 Hz), 131.5 (d, *J* = 94.7 Hz), 131.3 (d, *J* = 9.1 Hz), 128.9, 128.6 (d, *J* = 11.3 Hz), 117.9, 113.4, 55.3 (d, *J* = 82.9 Hz), 39.9. HRMS (EI) calcd for $C_{20}H_{21}NOP$ [M + H]$^{+}$: 322.1352; found: 322.1351.



((phenylamino)methyl)di-p-tolylphosphine oxide (25c): white solid was obtained with 75% isolated yield (62.8 mg). m. p.: 120-122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 11.5, 8.1 Hz, 4H), 7.28 (dd, *J* = 7.9, 2.2 Hz, 4H), 7.16 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 4.26 (s, 1H), 3.88 (d, *J* = 9.0 Hz, 2H), 2.39 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7 (d, *J* = 11.3 Hz), 142.8 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 9.9 Hz), 129.5 (d, *J* = 12.2 Hz), 129.2, 127.9 (d, *J* = 102.7 Hz), 118.5, 113.4, 44.0 (d, *J* = 78.9 Hz), 21.6. HRMS (EI) calcd for $C_{27}H_{23}NOP$ $[M + H]^+$: 408.1512; found: 408.1511.

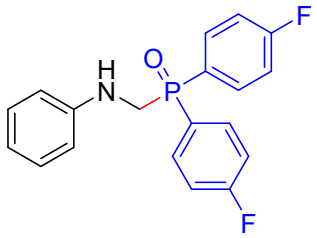


bis(3,5-dimethylphenyl)((phenylamino)methyl)phosphine oxide (26c): white solid was obtained with 70% isolated yield (63.5mg). m. p.: 130 - 132°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 11.9 Hz, 4H), 7.16 (t, *J* = 7.9 Hz, 4H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 2H), 4.28 (s, 1H), 3.89 (d, *J* = 8.7 Hz, 2H), 2.33 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9 (d, *J* = 10.7 Hz), 138.5 (d, *J* = 12.3 Hz), 134.0 (d, *J* = 2.8 Hz), 130.9 (d, *J* = 99.2 Hz), 129.1, 128.6 (d, *J* = 9.5 Hz), 118.4, 113.4, 43.8 (d, *J* = 77.6 Hz), 21.3. HRMS (EI) calcd for $C_{27}H_{23}NOP$ $[M + H]^+$: 364.1825; found: 364.1824.

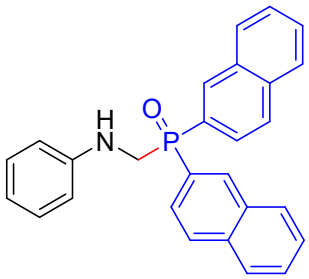


bis(4-methoxyphenyl)((phenylamino)methyl)phosphine oxide (27c): yellow solid was obtained with 65% isolated yield (59.6 mg). m. p.: 180-181 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 4H), 7.16 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.98 (dd, *J* = 8.8, 2.2 Hz, 4H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 2H), 4.25 (s, 1H), 3.84 (d, *J* = 5.2 Hz, 2H), 3.84 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7

(d, J = 2.8 Hz), 147.7 (d, J = 11.1 Hz), 133.0 (d, J = 10.9 Hz), 129.2, 122.4 (d, J = 106.9 Hz), 118.5, 114.3 (d, J = 12.9 Hz), 113.3, 55.3, 44.2 (d, J = 79.6 Hz). ^{19}F NMR (471 MHz, DMSO) δ -111.2. HRMS (EI) calcd for $C_{21}H_{23}NO_3P$ $[M + H]^+$: 368.1410; found: 368.1408.



bis(4-fluorophenyl)((phenylamino)methyl)phosphine oxide (28c): yellow solid was obtained with 93% isolated yield (79.7 mg). m. p.: 145-146 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.82 – 7.72 (m, 4H), 7.23 – 7.10 (m, 6H), 6.75 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 8.5 Hz, 2H), 3.95 (d, J = 8.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4 (dd, J = 254.8, 3.3 Hz), 147.4 (d, J = 10.8 Hz), 133.7 (dd, J = 11.1, 8.9 Hz), 129.2, 126.2 (dd, J = 103.9, 3.5 Hz), 118.7, 116.4 (dd, J = 21.5, 13.1 Hz), 113.4, 44.1 (d, J = 80.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -105.1. HRMS (EI) calcd for $C_{19}H_{17}F_2NOP$ $[M + H]^+$: 344.1010; found: 344.1008.

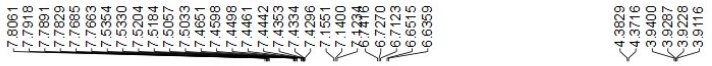


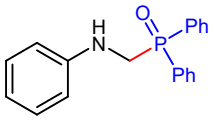
di(naphthalen-2-yl)((phenylamino)methyl)phosphine oxide (29c): yellow solid was obtained with 66% isolated yield (67.2 mg). m. p.: 191-193 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, J = 13.7 Hz, 2H), 8.00 (s, 1H), 7.94 – 7.86 (m, 6H), 7.76 (t, J = 9.1 Hz, 2H), 7.62 – 7.53 (m, 4H), 7.15 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.0 Hz, 3H), 4.15 (d, J = 8.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7 (d, J = 10.9 Hz), 134.9 (d, J = 2.2 Hz), 133.5 (d, J = 8.9 Hz), 132.5 (d, J = 13.0 Hz), 129.1 (d, J = 29.3 Hz), 128.8 (d, J = 11.8 Hz), 128.5, 127.6 (d, J = 101.0 Hz), 127.5 (d, J = 89.9 Hz), 125.6 (d, J = 10.6 Hz), 118.5, 113.5, 43.9 (d, J = 79.2 Hz). HRMS (EI) calcd for $C_{27}H_{23}NOP$ $[M + H]^+$: 408.1512; found: 408.1511.

Copies of product NMR Spectra

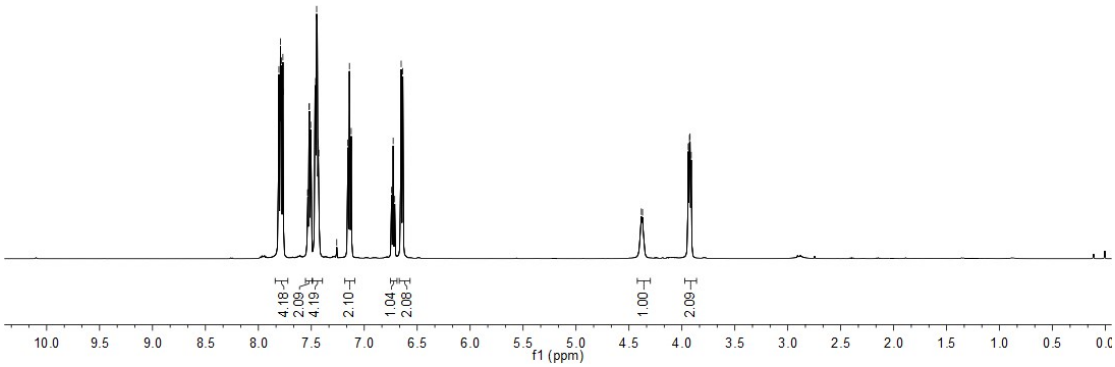
1c

^{1}H NMR

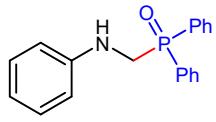




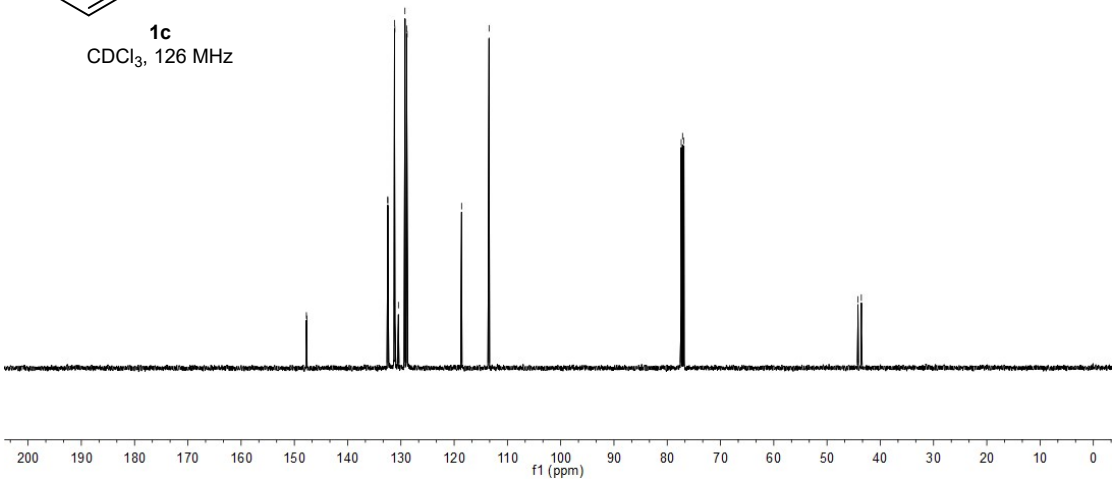
1c
$CDCl_3$, 500 MHz



^{13}C NMR

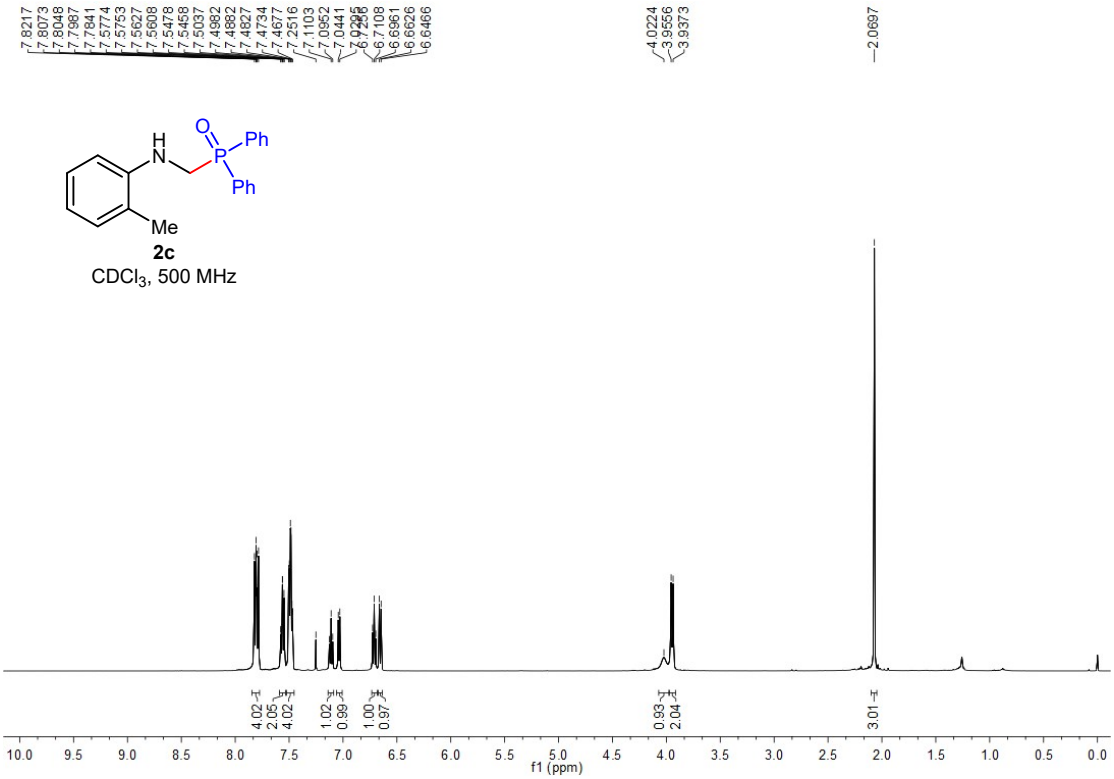


1c
$CDCl_3$, 126 MHz



2c

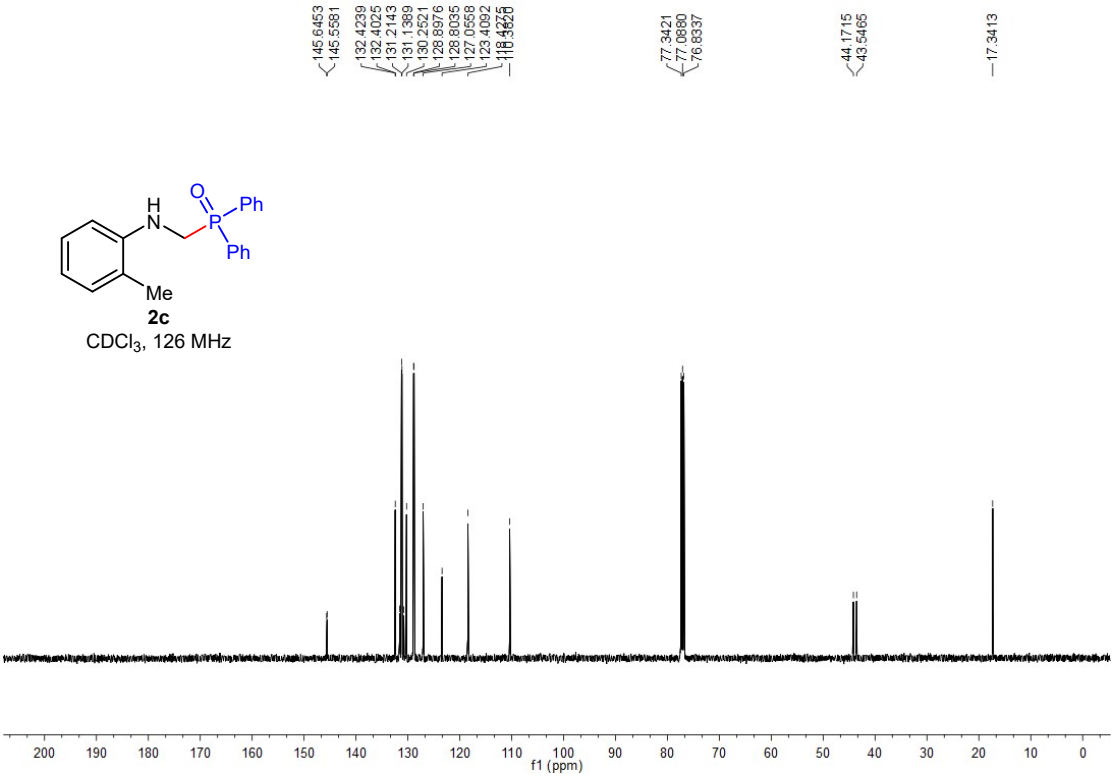
^{1}H NMR



2c

$CDCl_3$, 500 MHz

^{13}C NMR

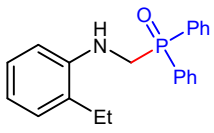


2c

$CDCl_3$, 126 MHz

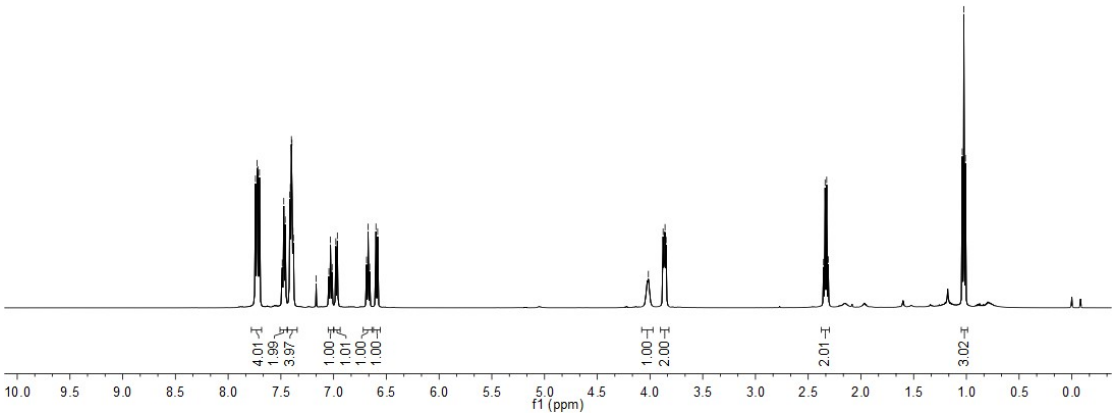
3c

^{1}H NMR

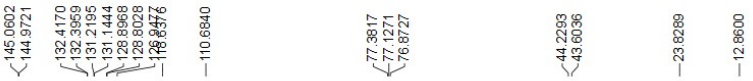


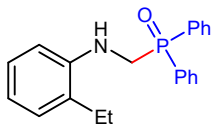
3c

$CDCl_3$, 500 MHz



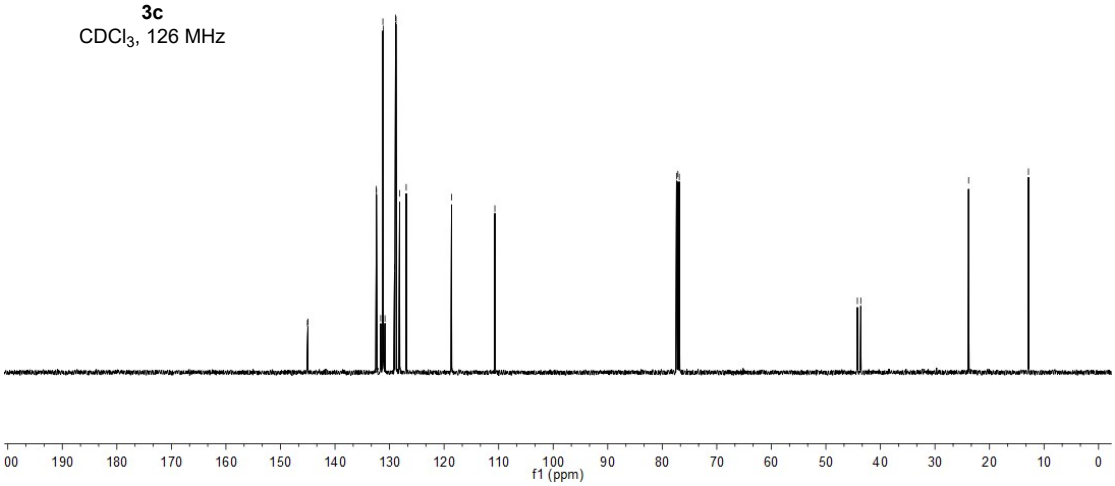
^{13}C NMR





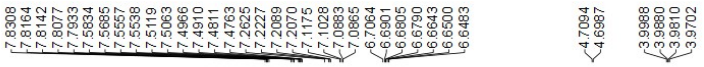
3c

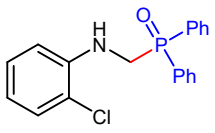
$CDCl_3$, 126 MHz



4c

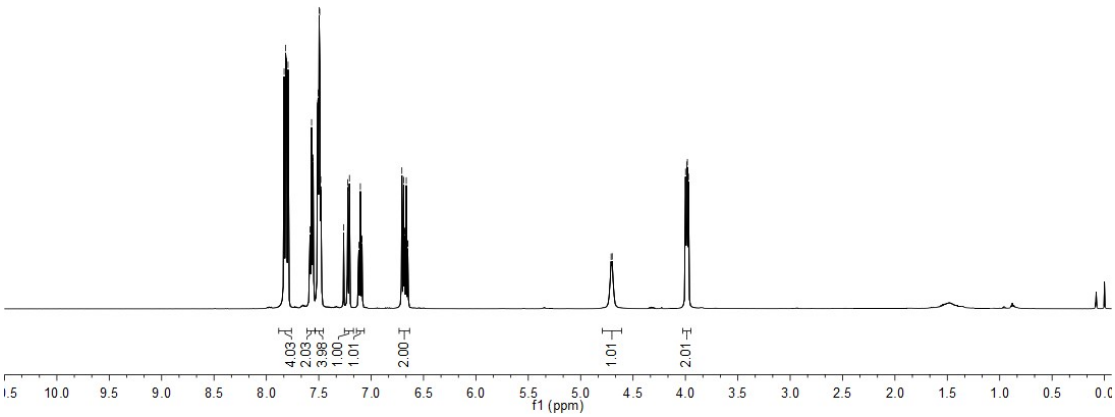
^{1}H NMR



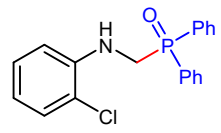


4c

$CDCl_3$, 500 MHz

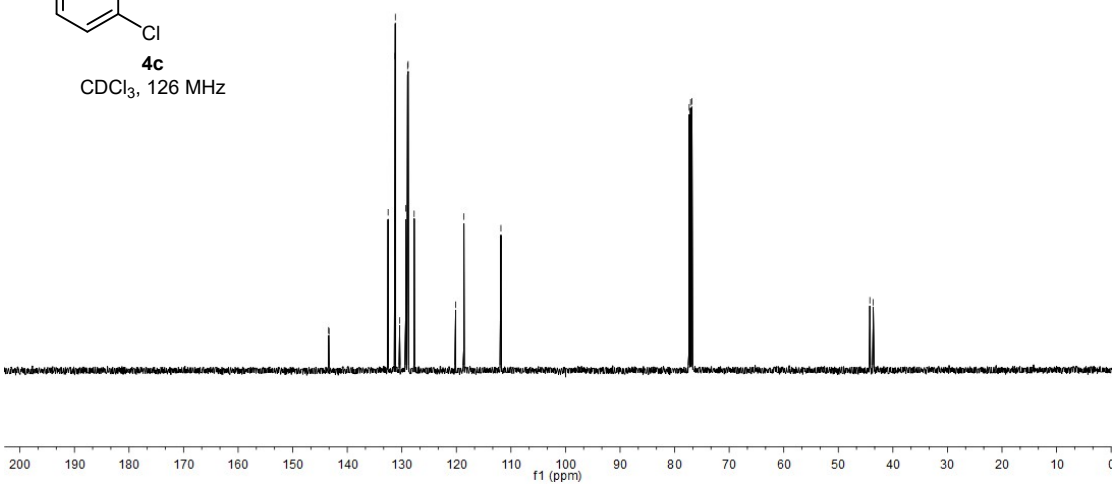


^{13}C NMR



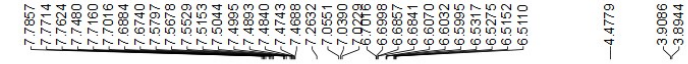
4c

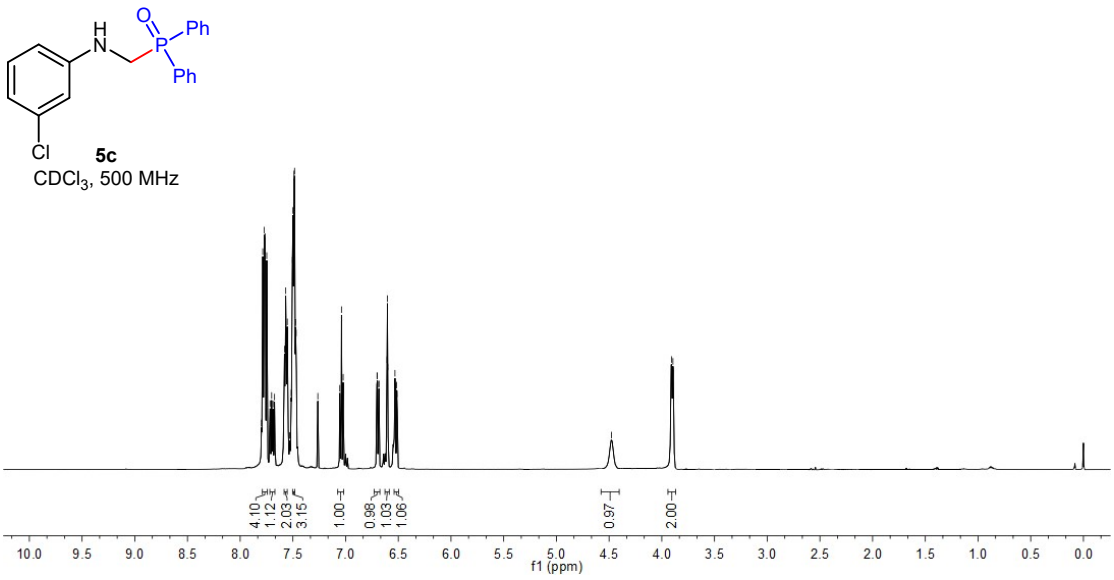
$CDCl_3$, 126 MHz



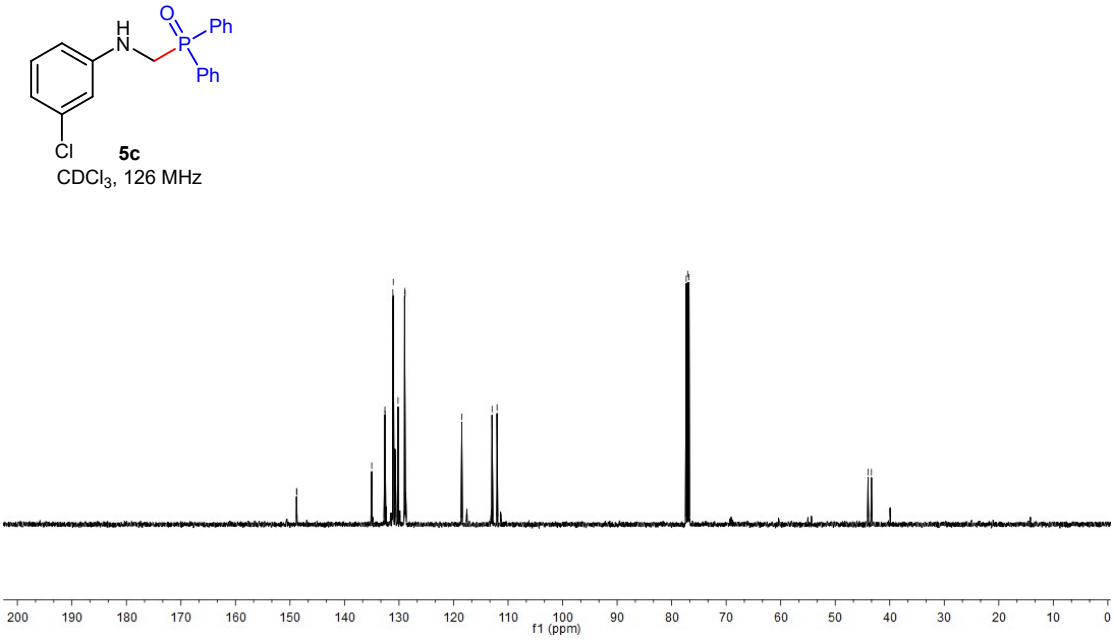
5c

^{1}H NMR



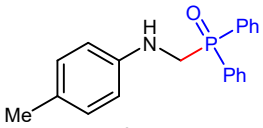


^{13}C NMR



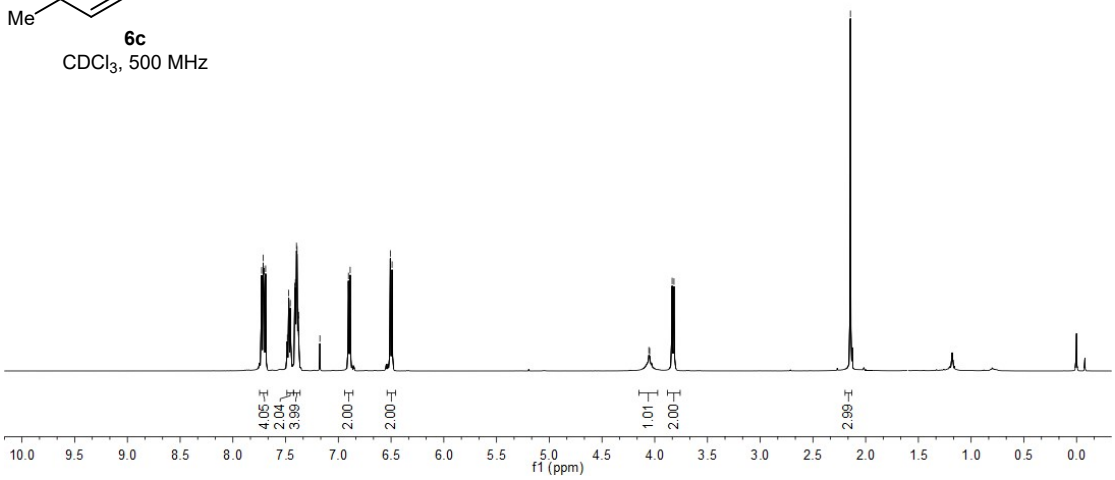
6c

^{1}H NMR

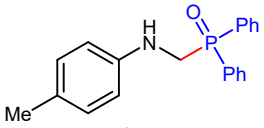


6c

$CDCl_3$, 500 MHz

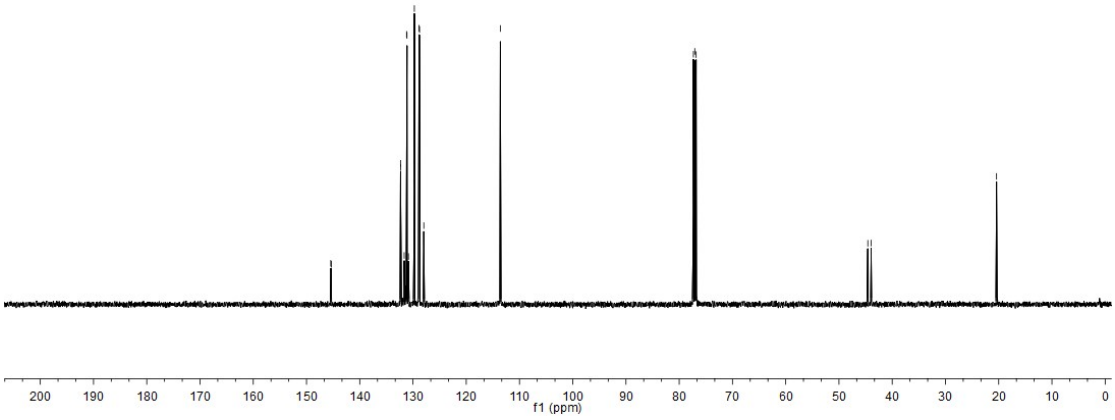


^{13}C NMR



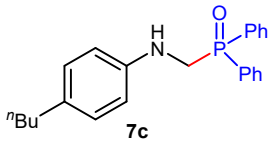
6c

$CDCl_3$, 126 MHz



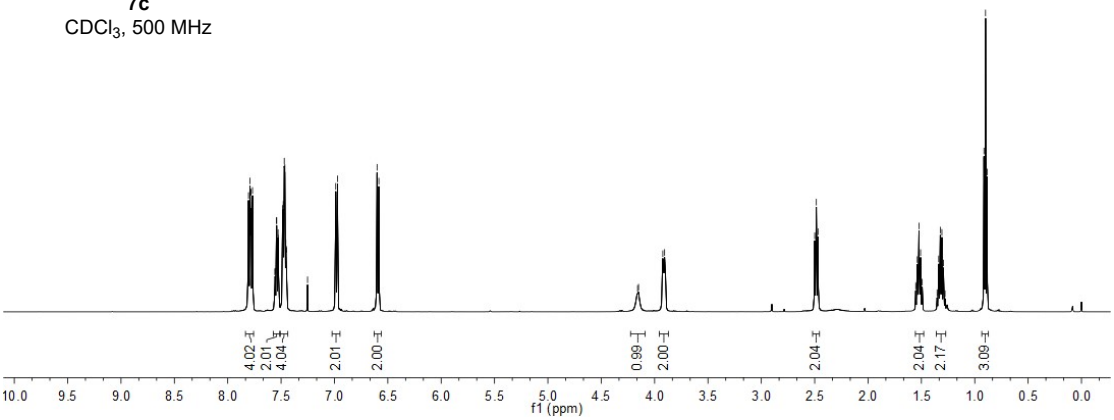
7c

^{1}H NMR

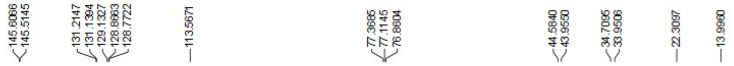


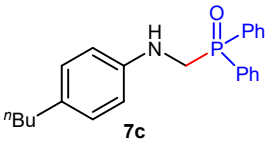
7c

$CDCl_3$, 500 MHz



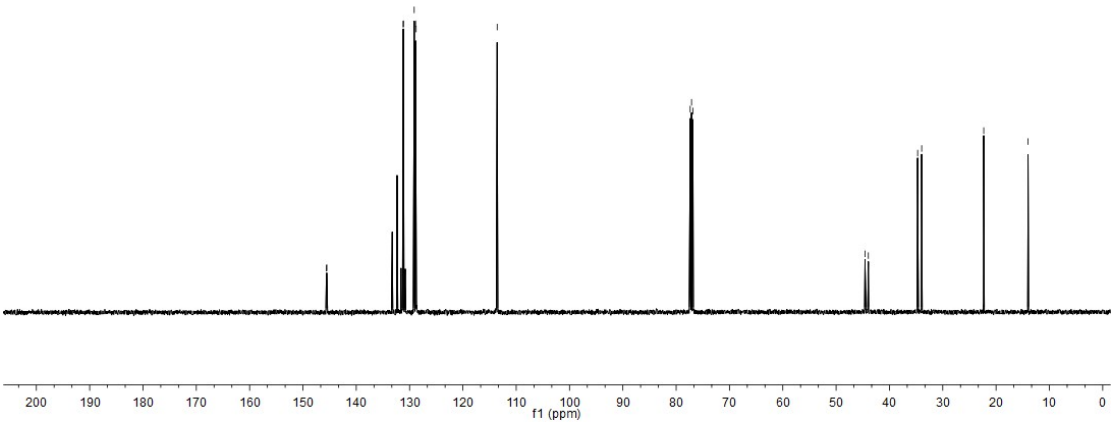
^{13}C NMR





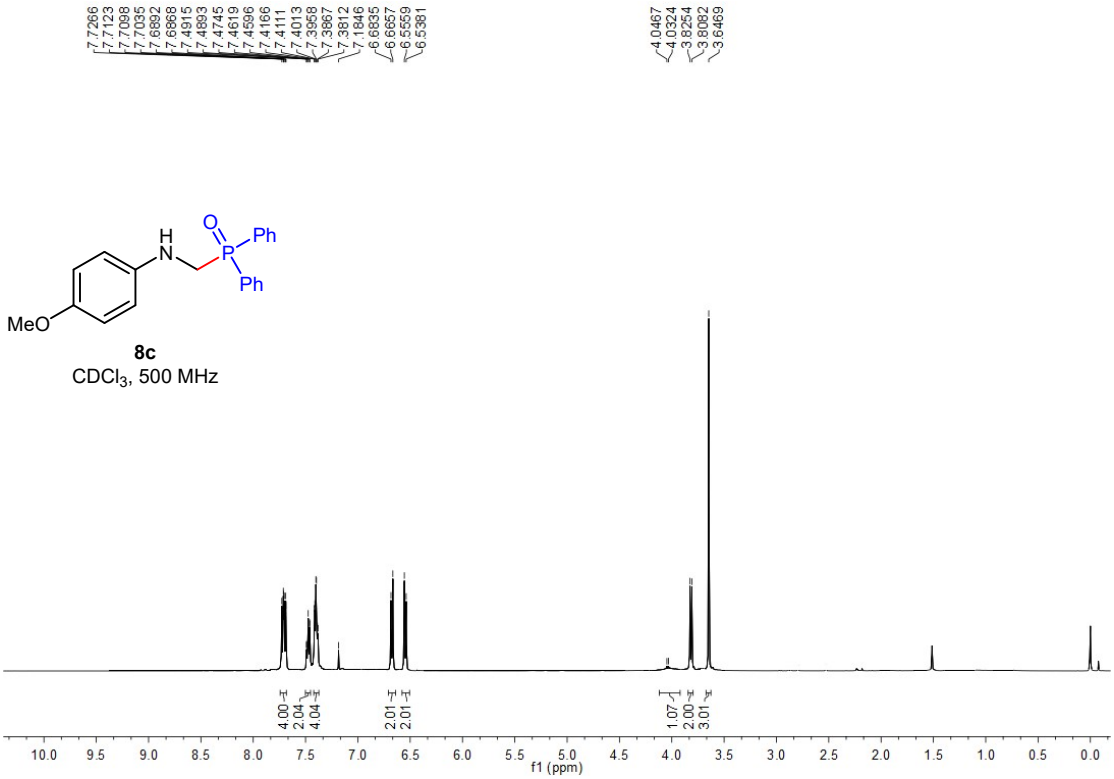
7c

$CDCl_3$, 126 MHz



8c

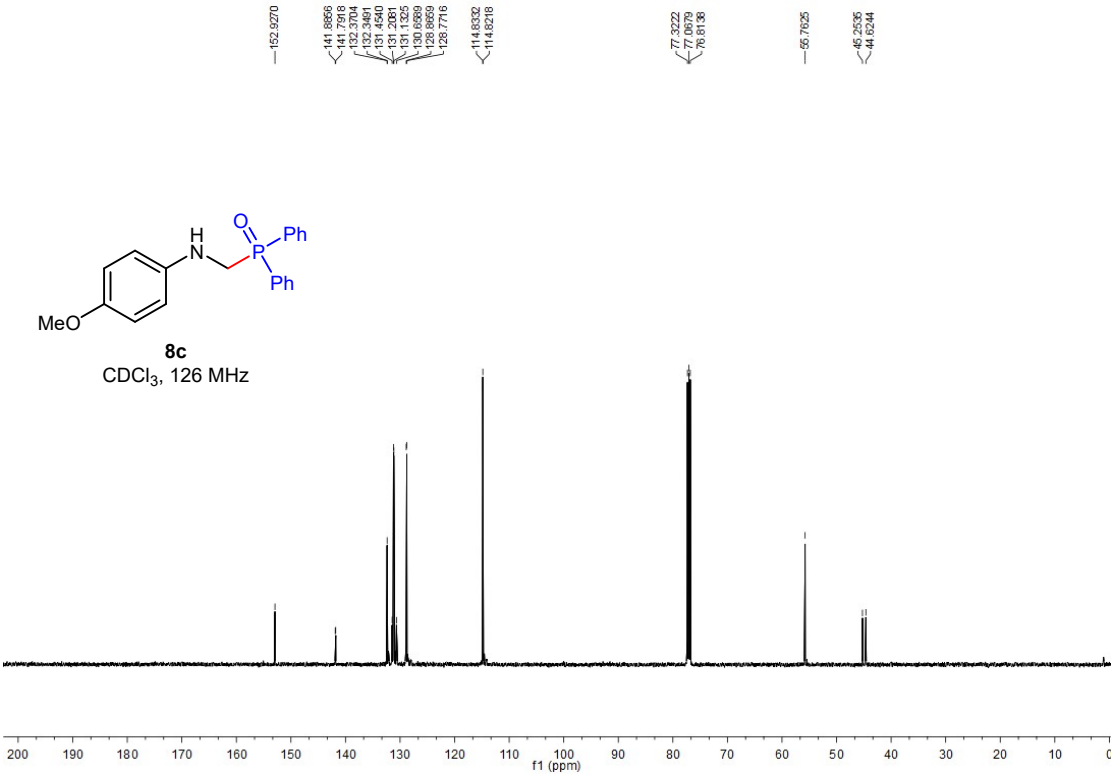
^{1}H NMR



8c

$CDCl_3$, 500 MHz

^{13}C NMR

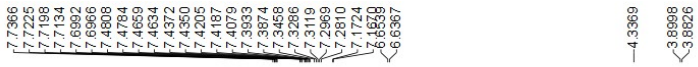


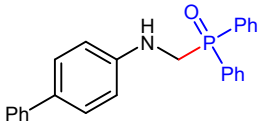
8c

$CDCl_3$, 126 MHz

9c

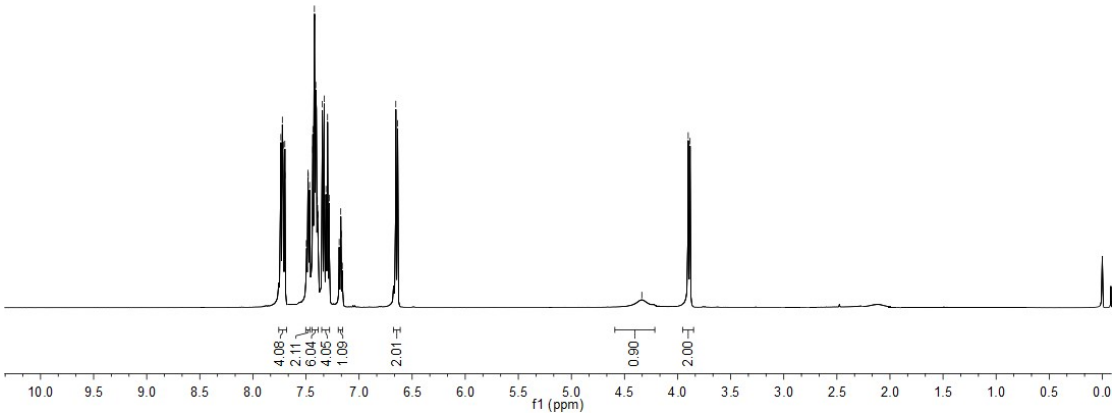
^{1}H NMR



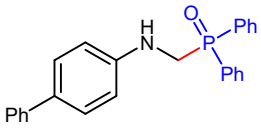


9c

$CDCl_3$, 500 MHz

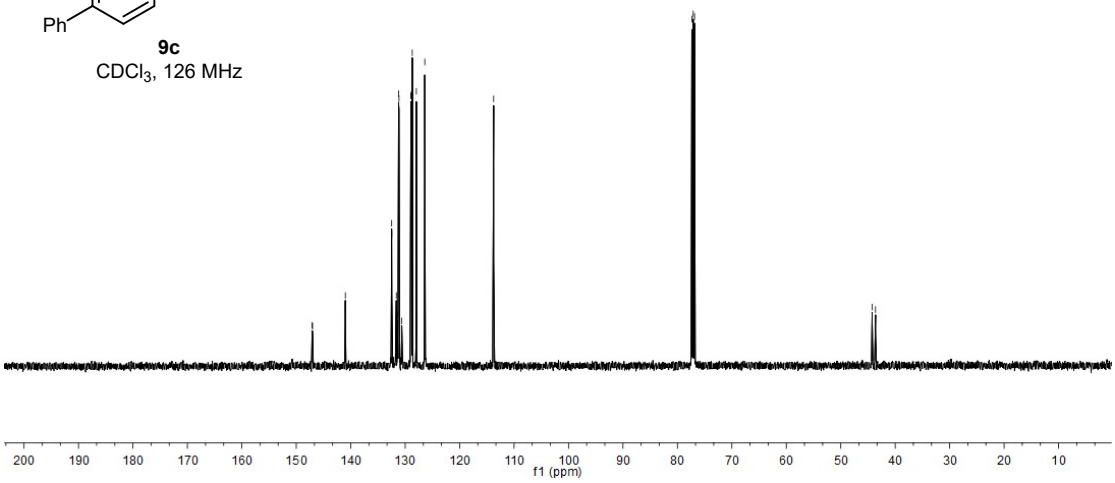


^{13}C NMR



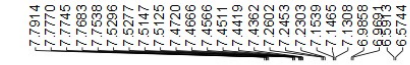
9c

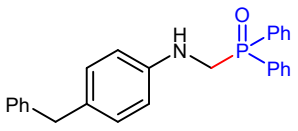
$CDCl_3$, 126 MHz



10c

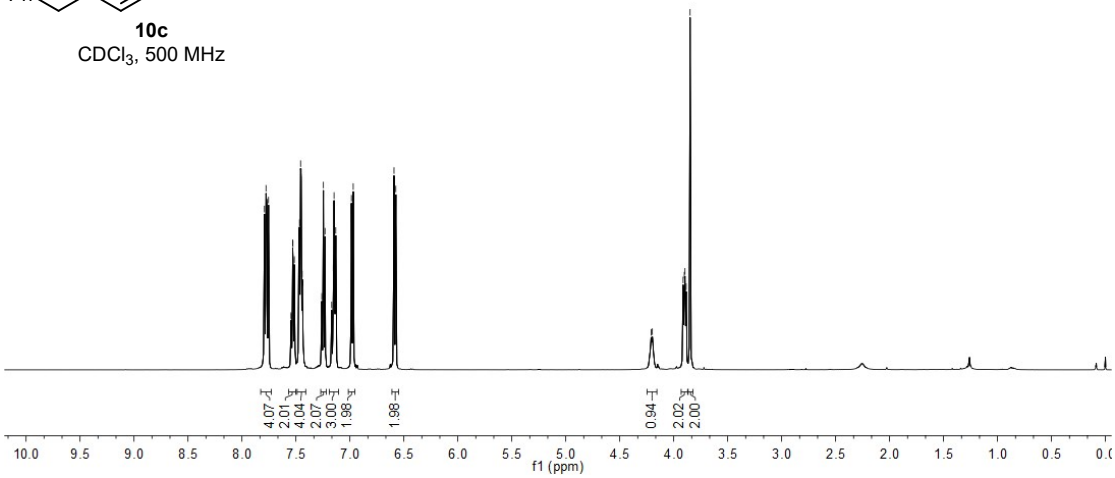
^{1}H NMR



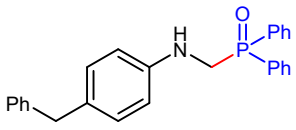


10c

$CDCl_3$, 500 MHz

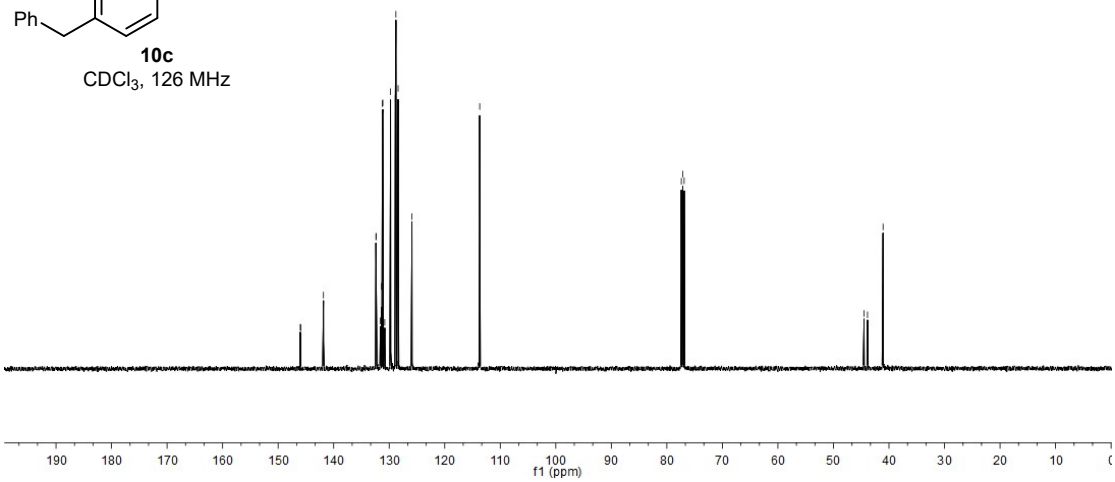


^{13}C NMR



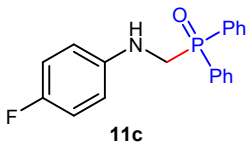
10c

$CDCl_3$, 126 MHz

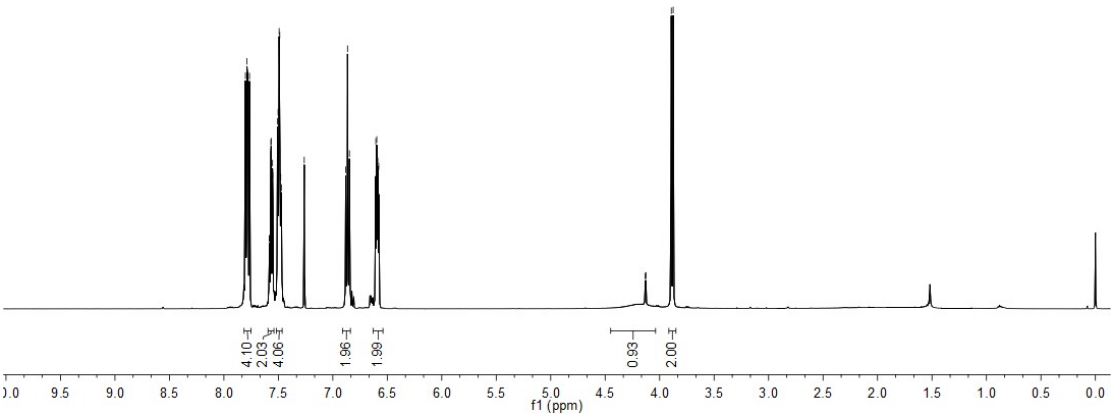


11c

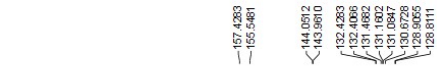
^{1}H NMR

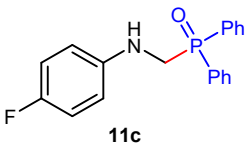


11c
$CDCl_3$, 500 MHz

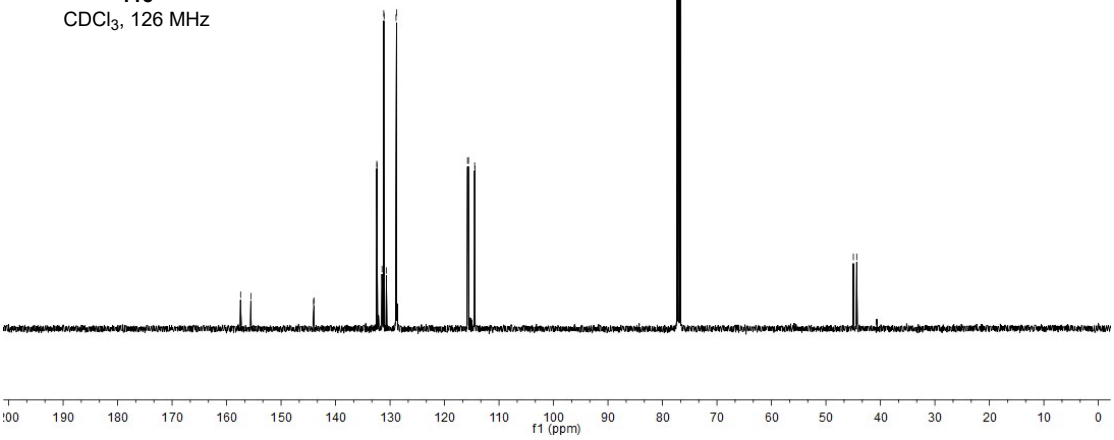


^{13}C NMR

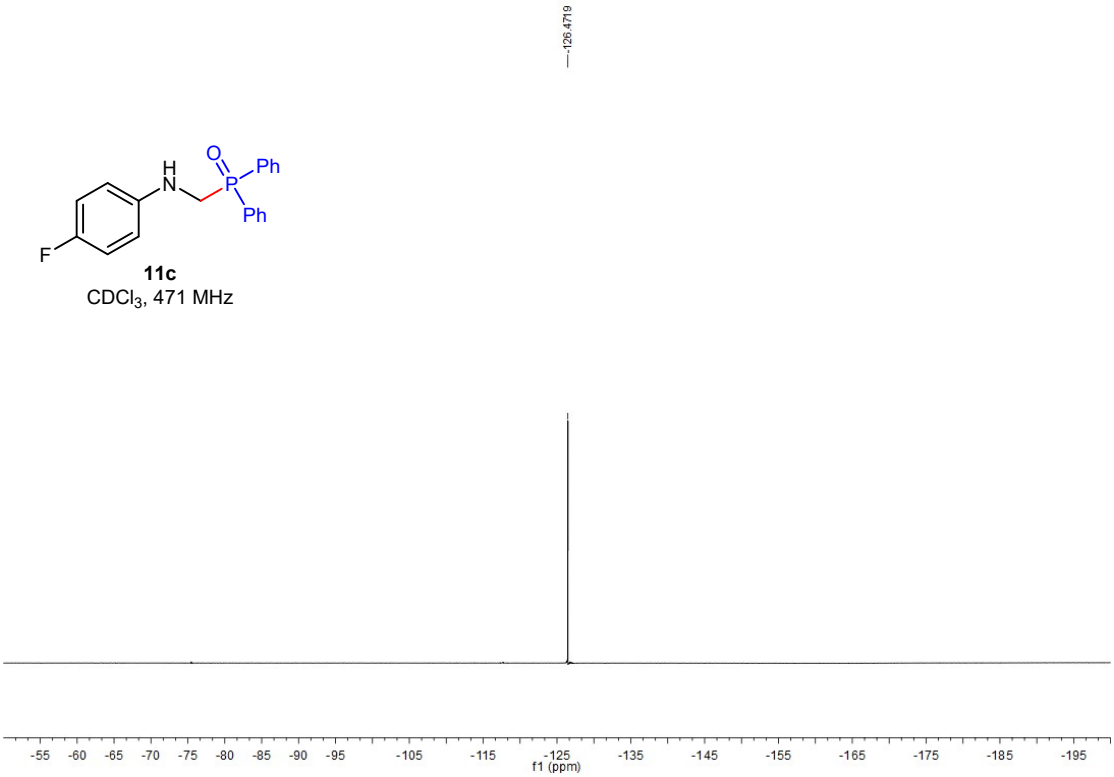




11c
$CDCl_3$, 126 MHz



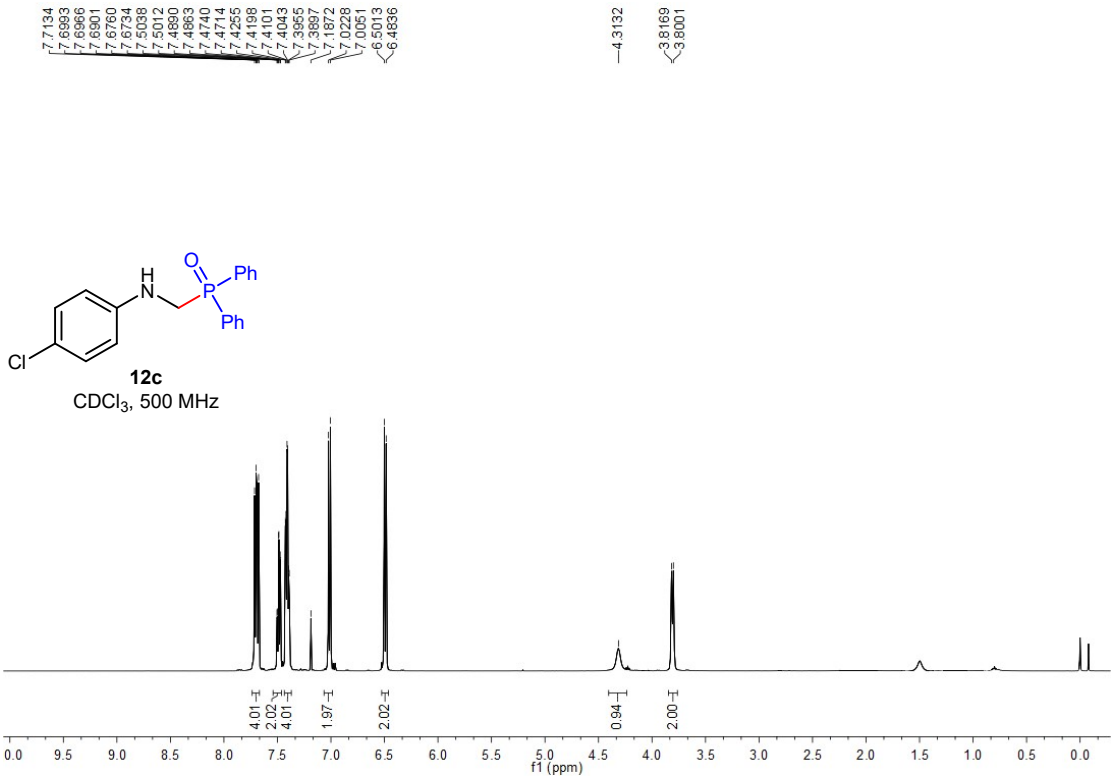
^{19}F NMR



11c
$CDCl_3$, 471 MHz

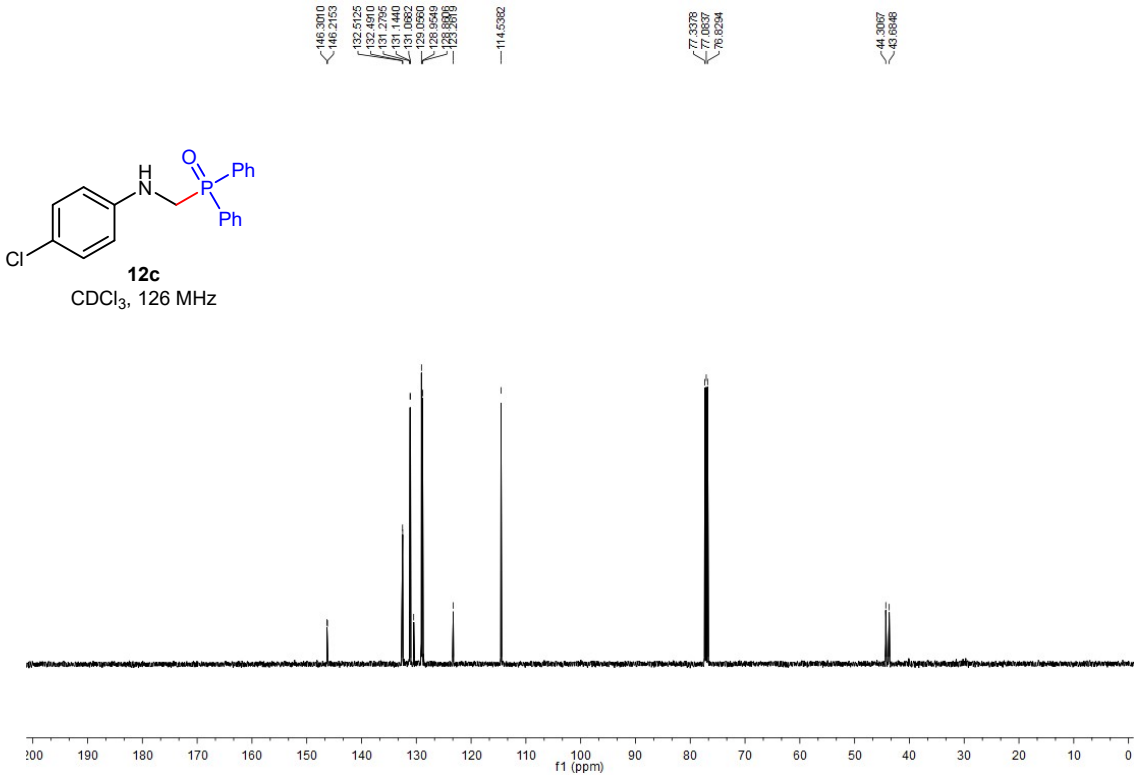
12c

^{1}H NMR



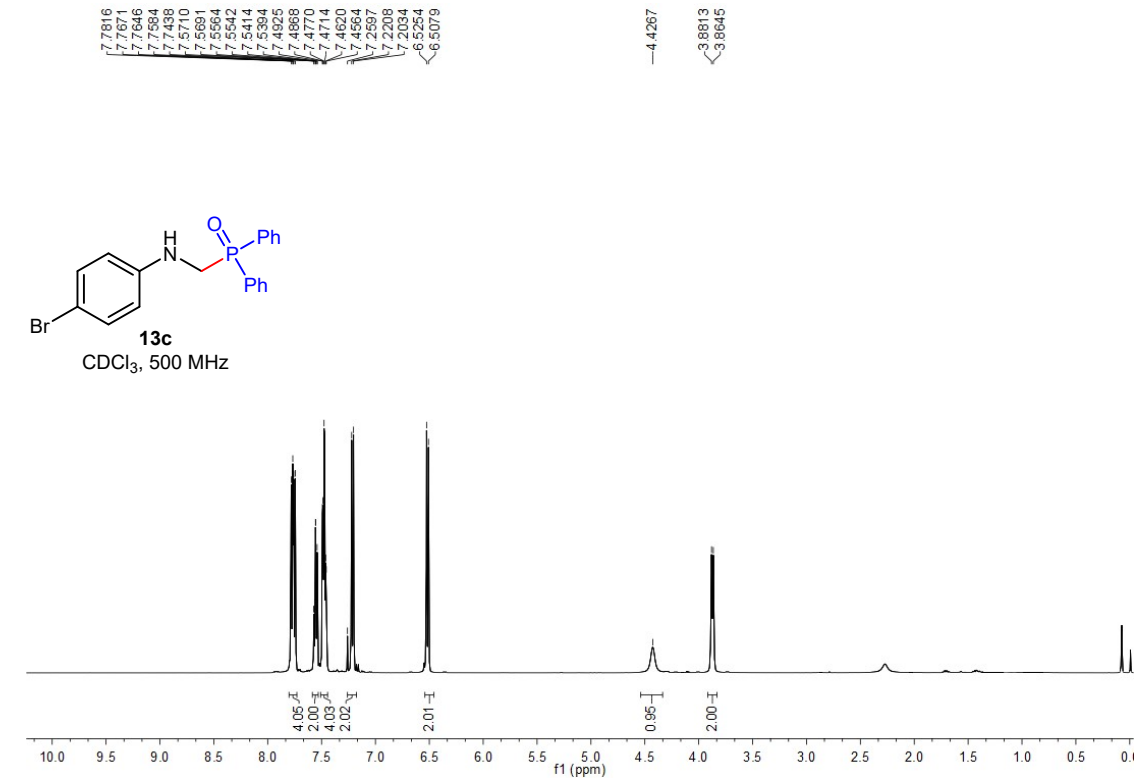
12c
$CDCl_3$, 500 MHz

^{13}C NMR

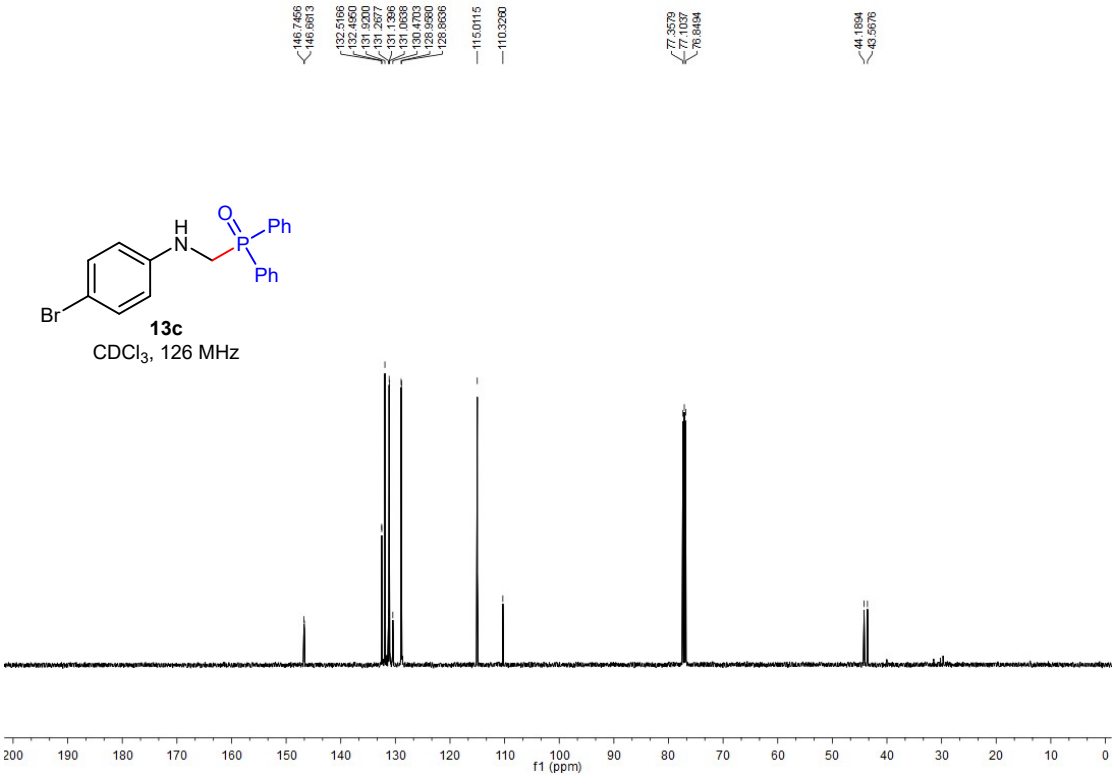


13c

^{1}H NMR

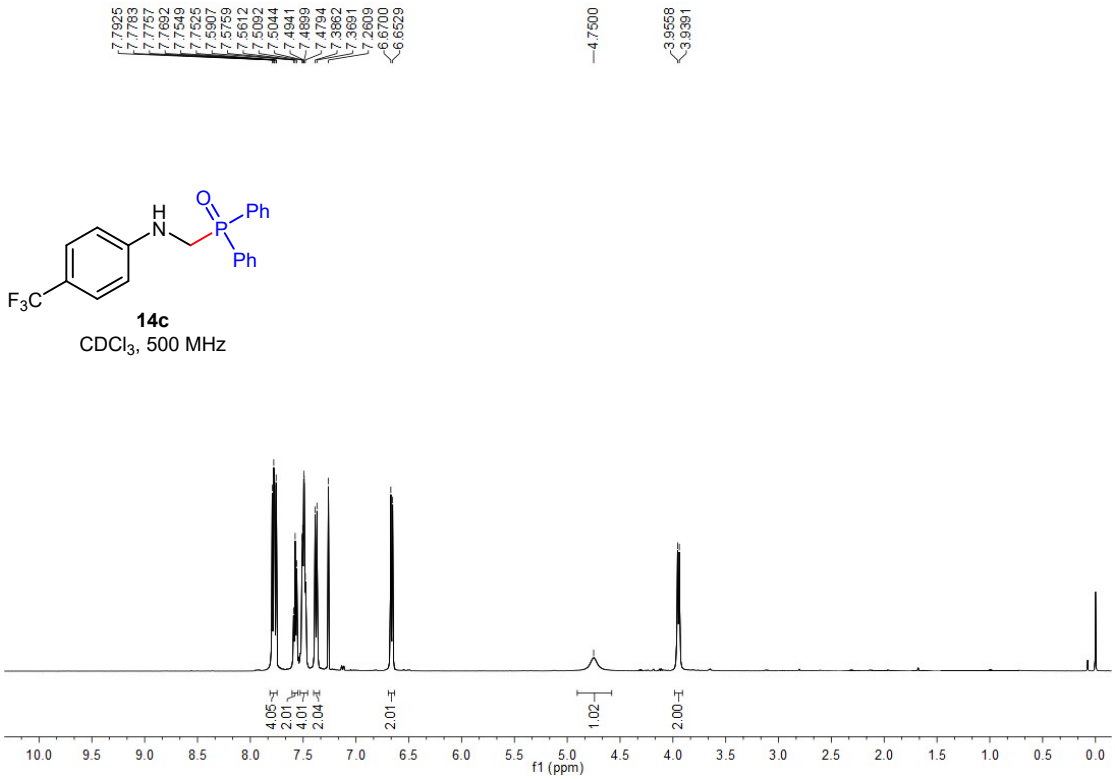


^{13}C NMR

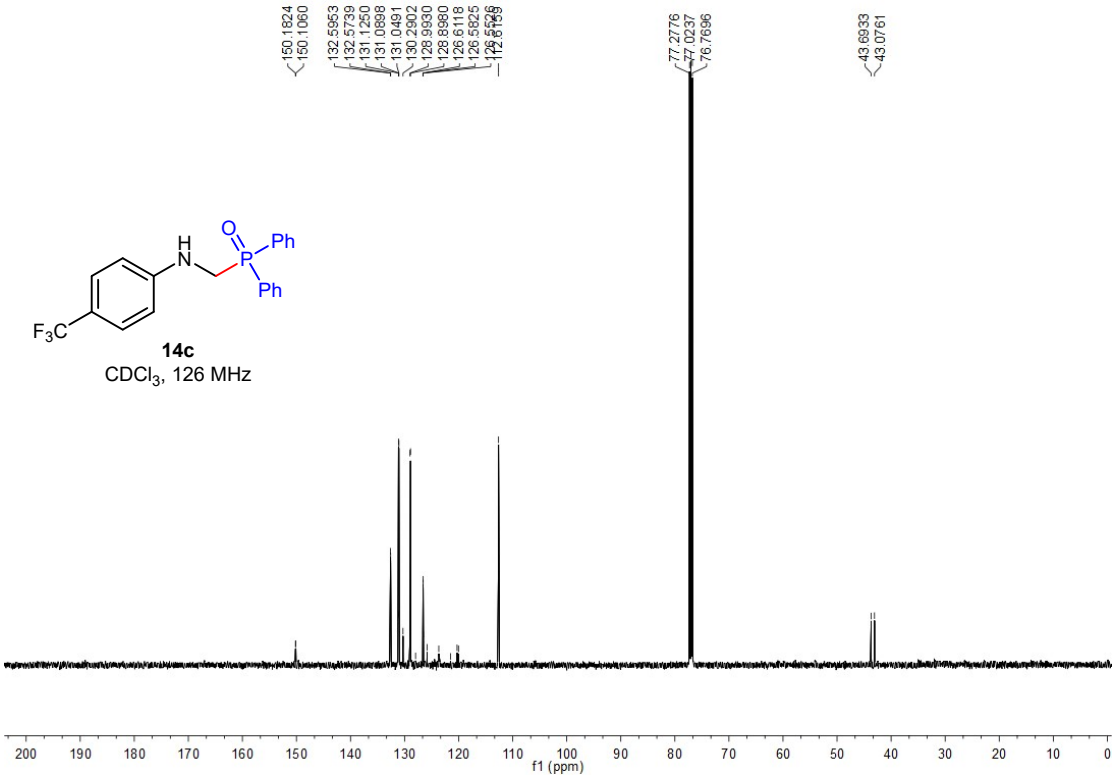


14c

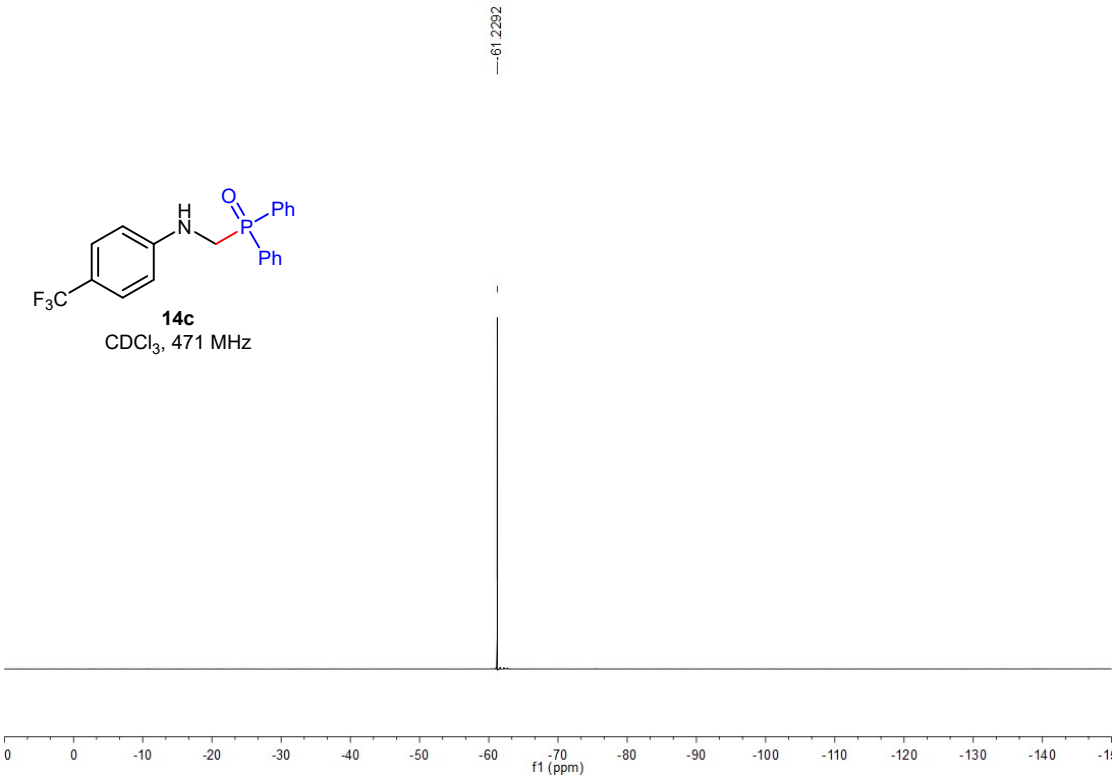
^{1}H NMR



^{13}C NMR

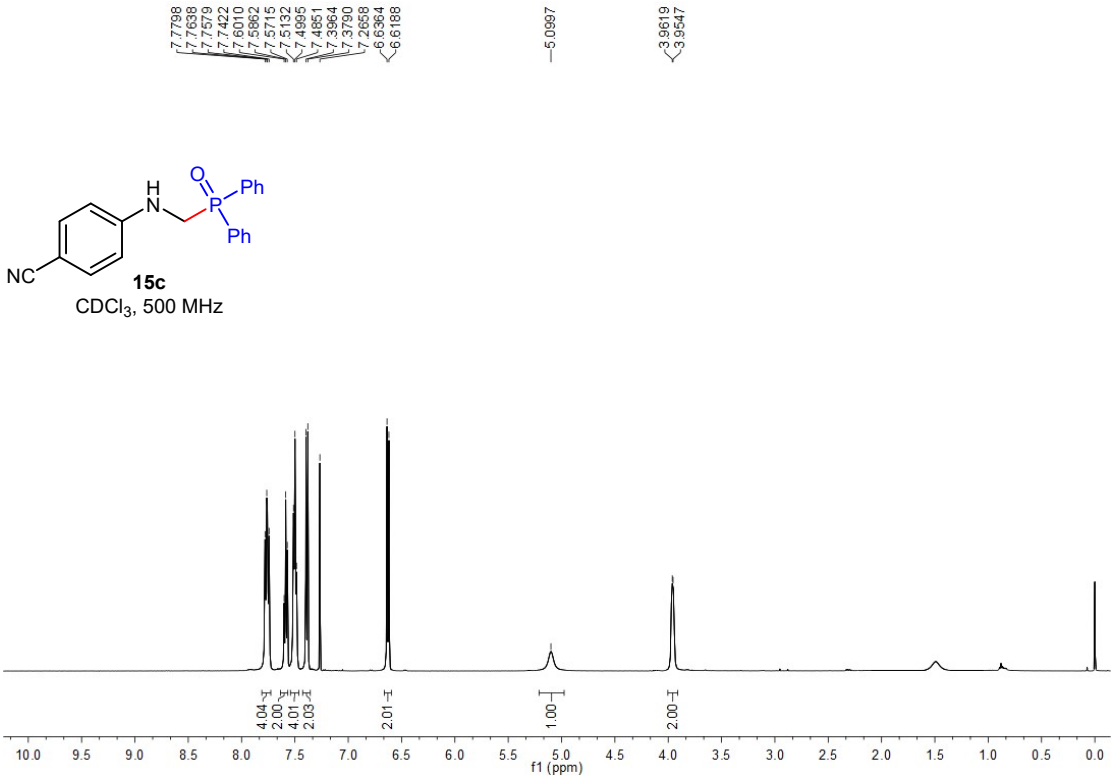


^{19}F NMR

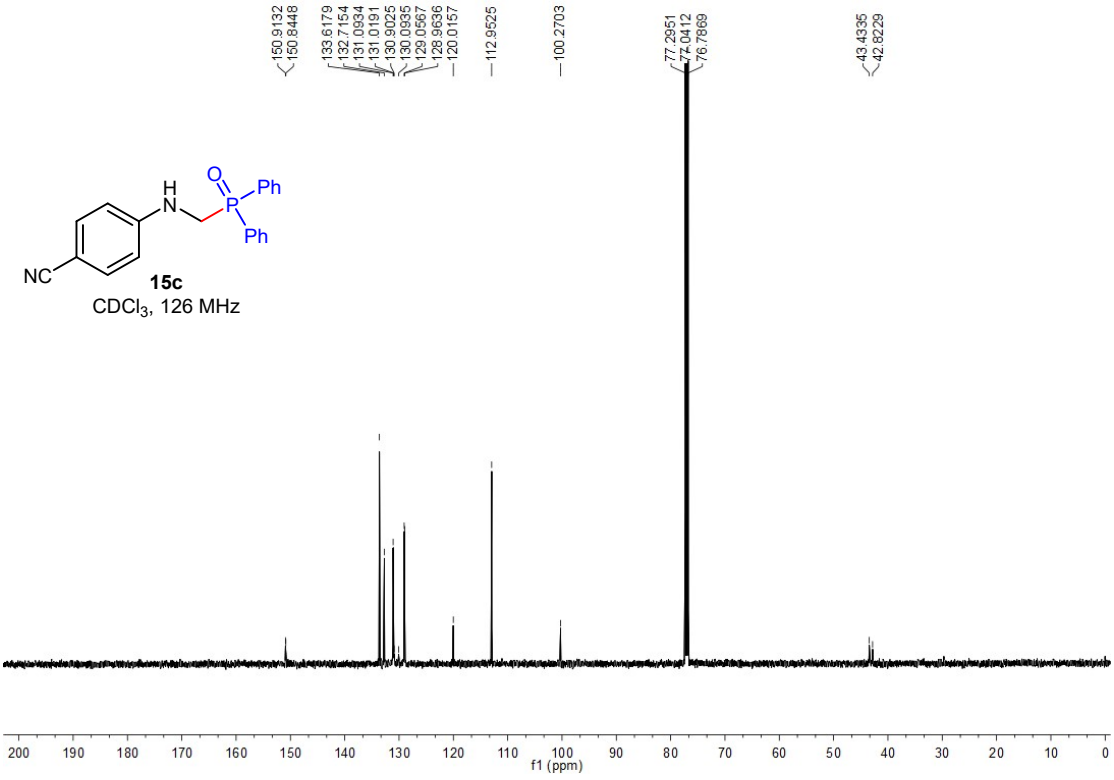


15c

^{1}H NMR

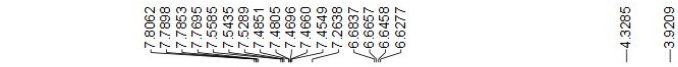


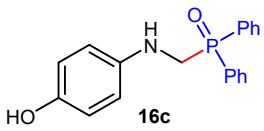
^{13}C NMR



16c

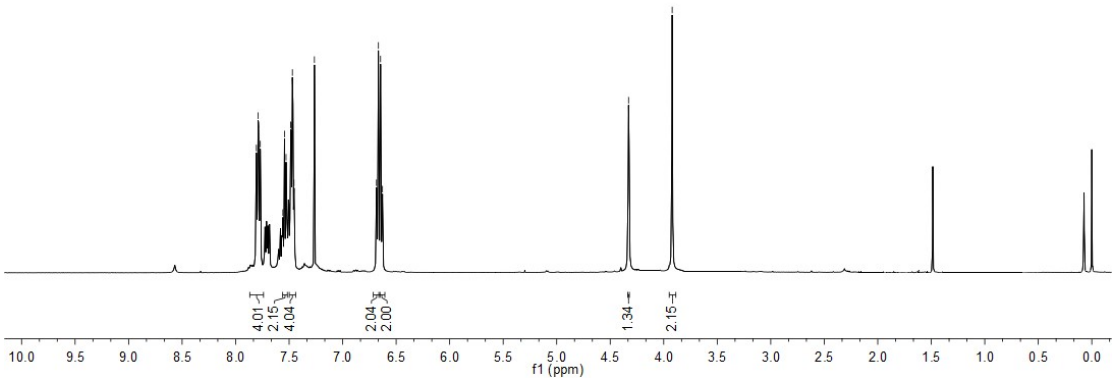
^{1}H NMR



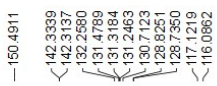


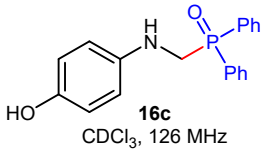
16c

$CDCl_3$, 500 MHz



^{13}C NMR



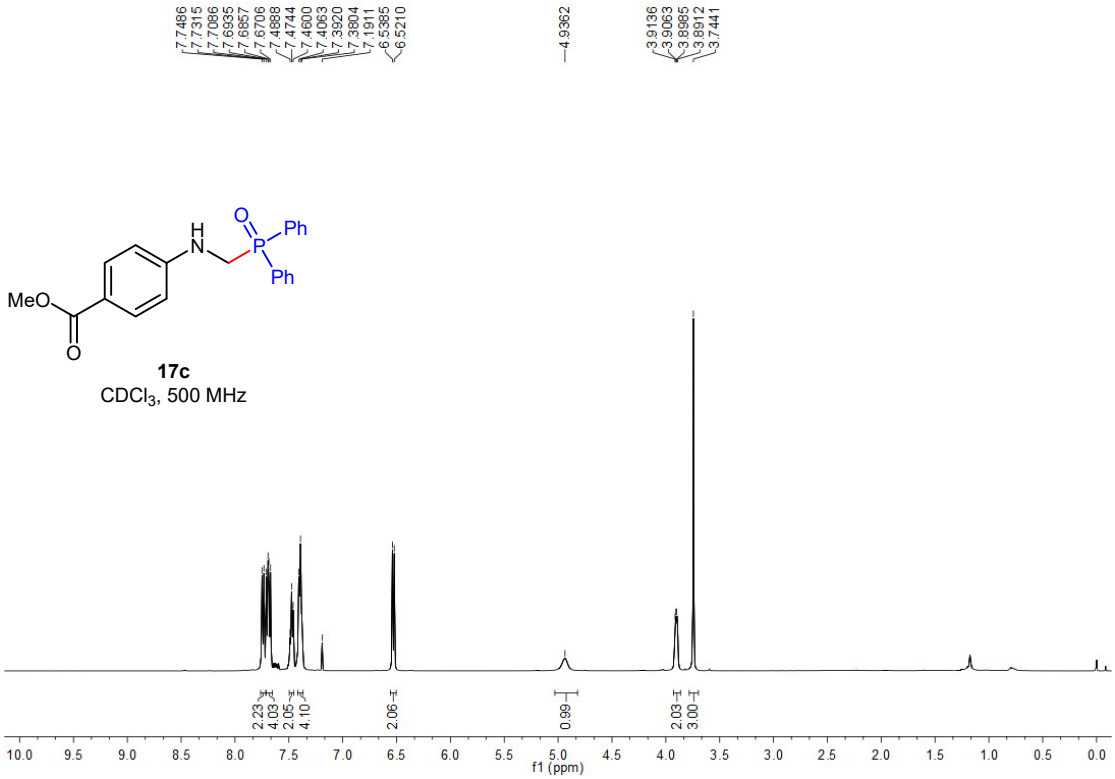


16c

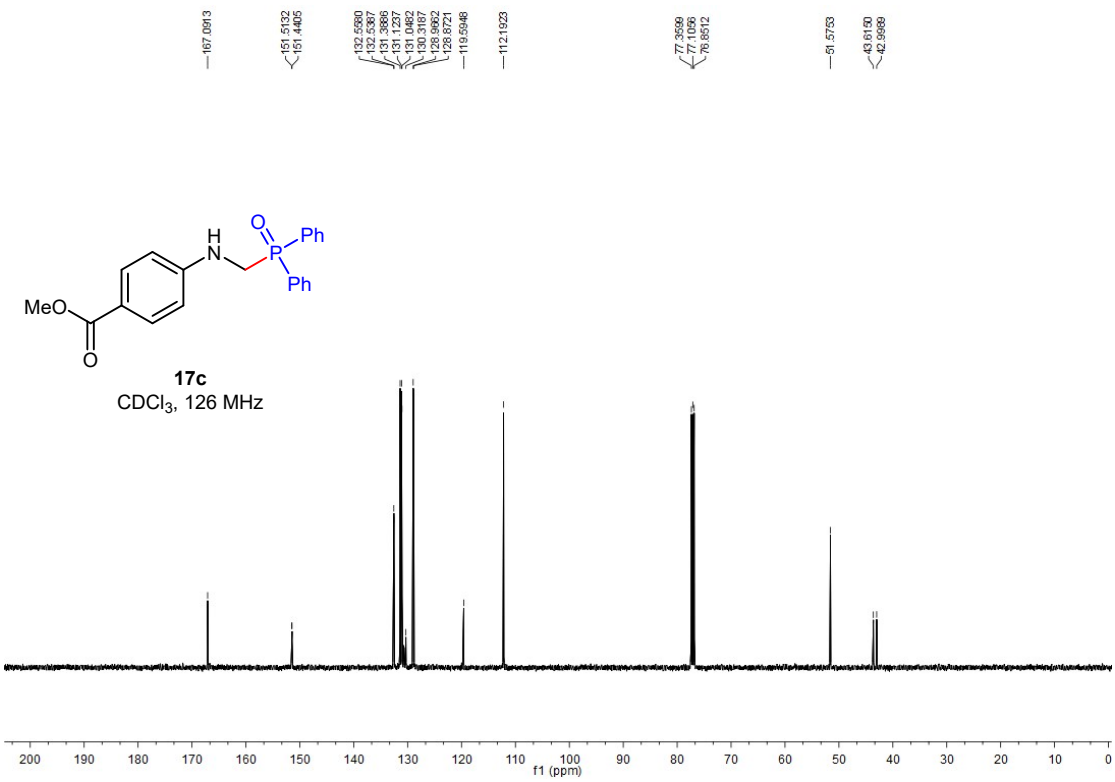
$CDCl_3$, 126 MHz

17c

^{1}H NMR

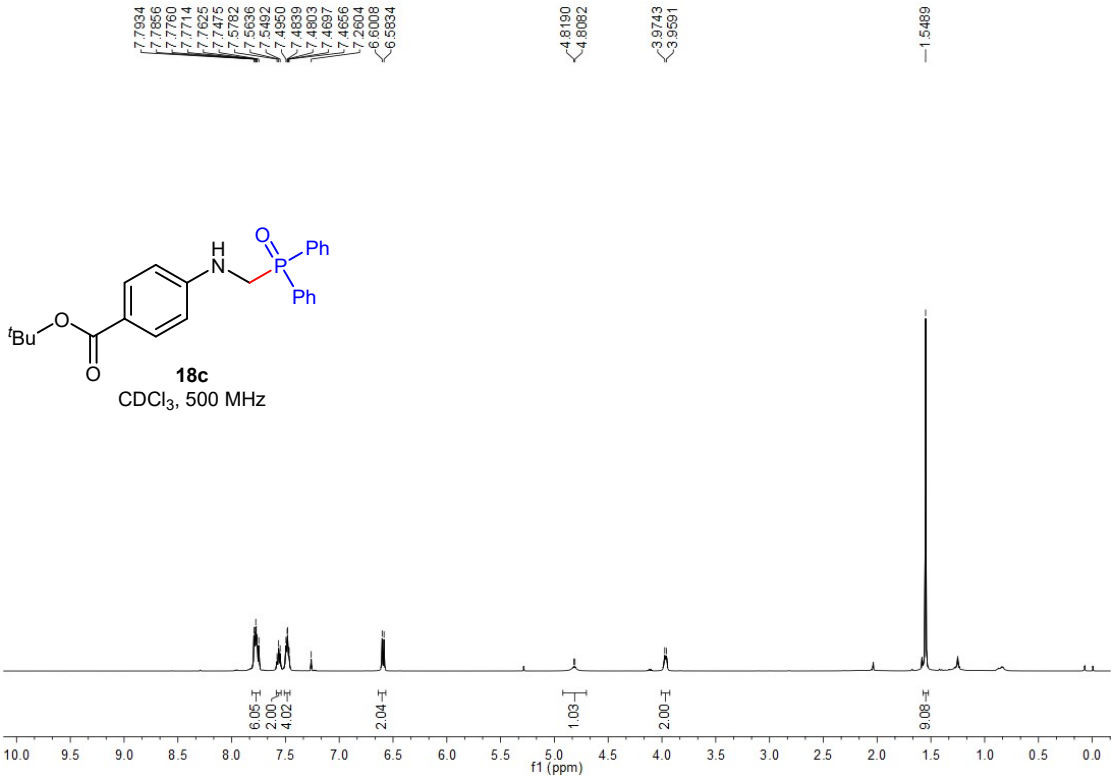


^{13}C NMR

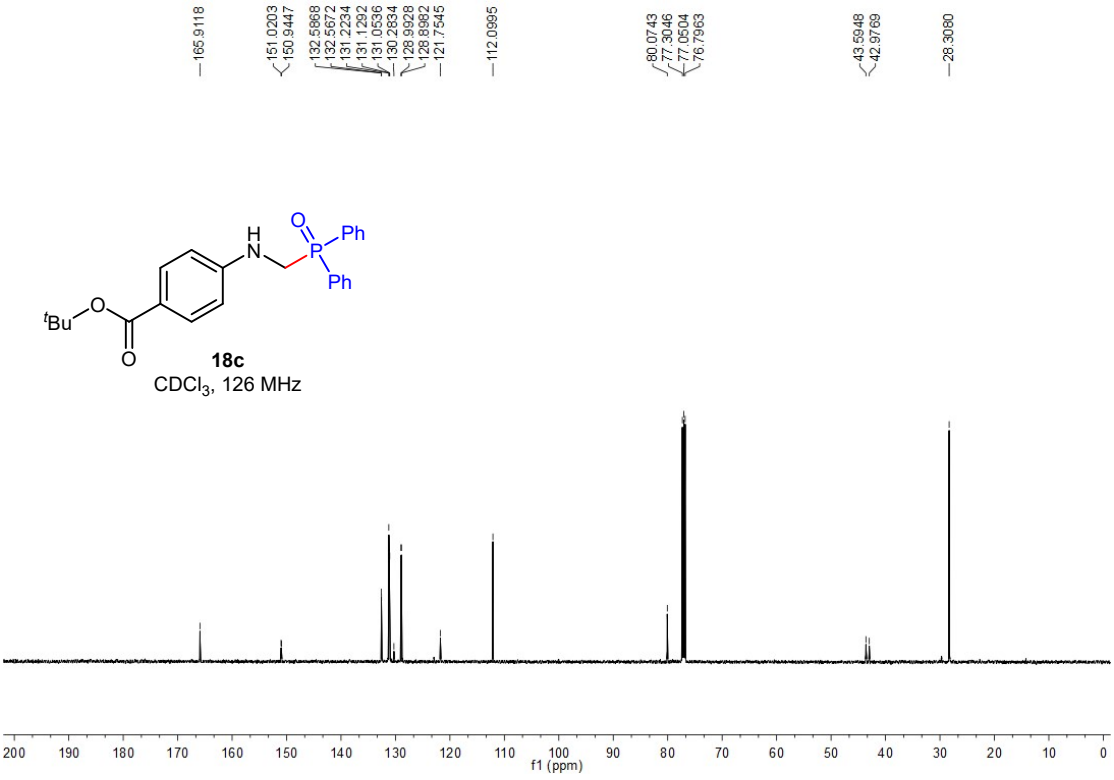


18c

^{1}H NMR

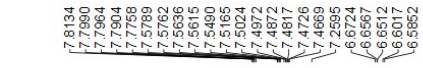


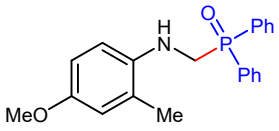
^{13}C NMR



19c

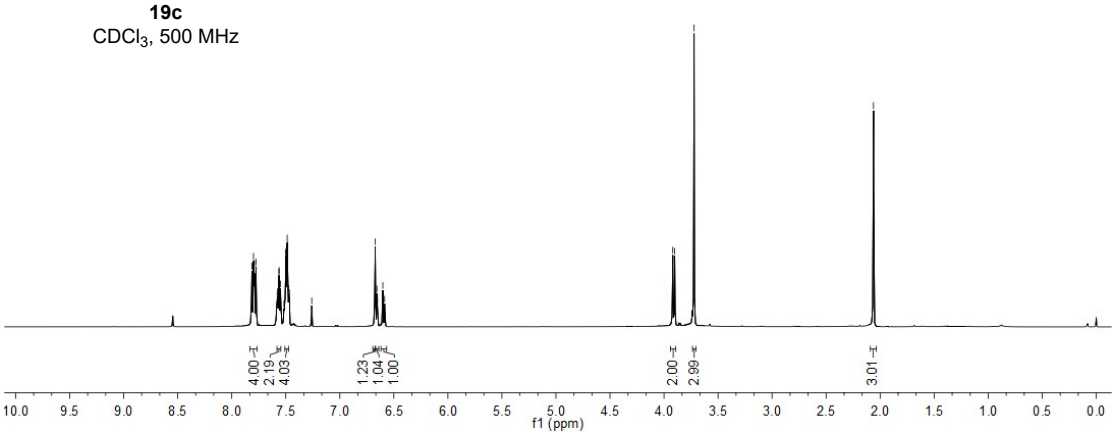
^{1}H NMR



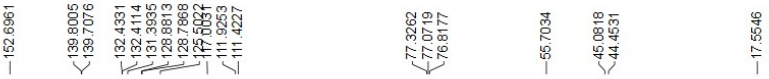


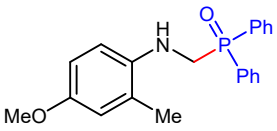
19c

$CDCl_3$, 500 MHz



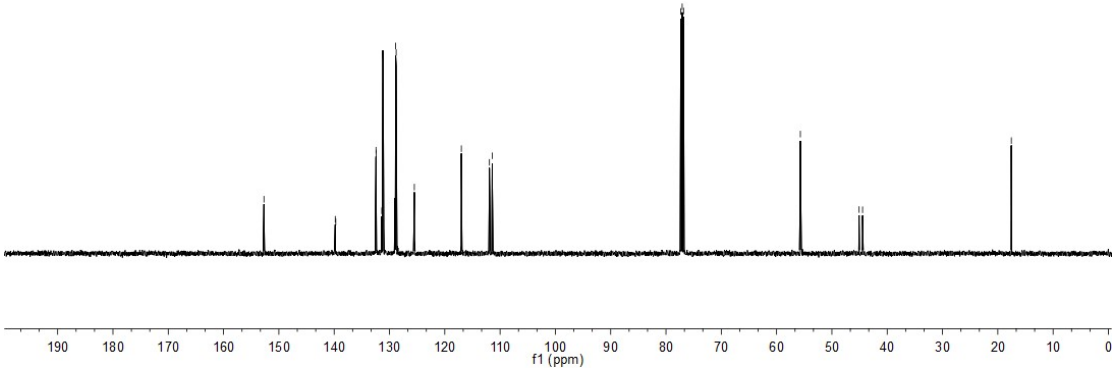
^{13}C NMR





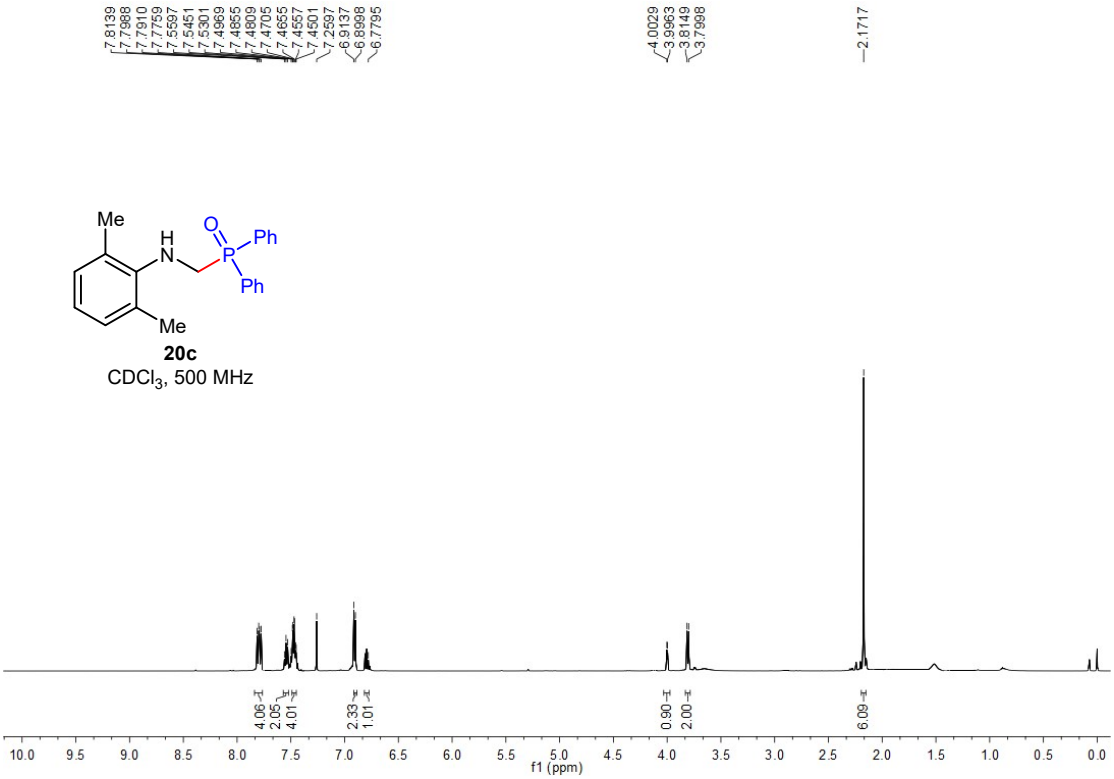
19c

$CDCl_3$, 126 MHz



20c

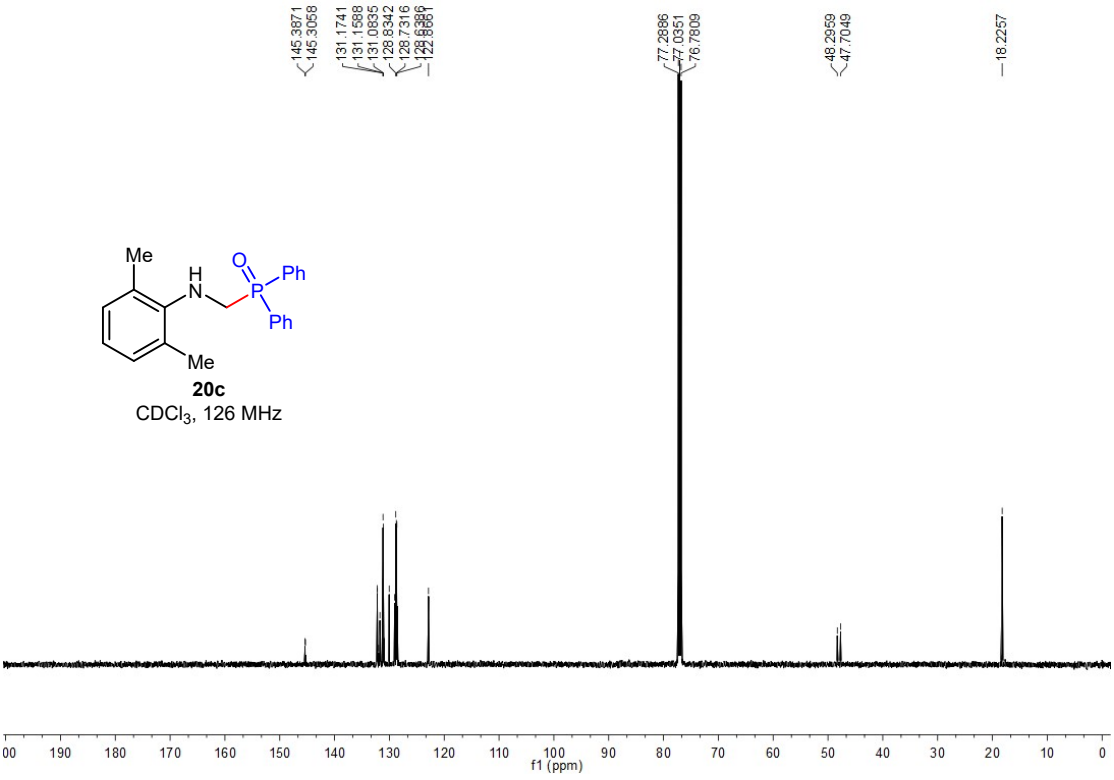
^{1}H NMR



20c

$CDCl_3$, 500 MHz

^{13}C NMR

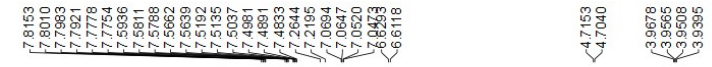


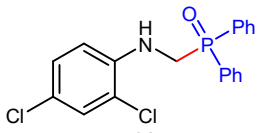
20c

$CDCl_3$, 126 MHz

21c

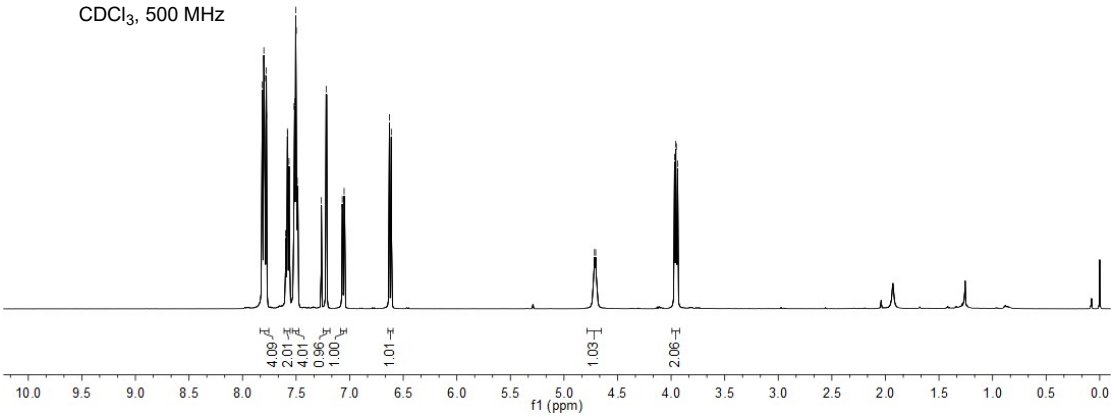
^{1}H NMR



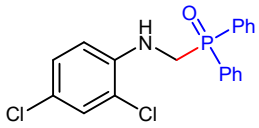


21c

$CDCl_3$, 500 MHz

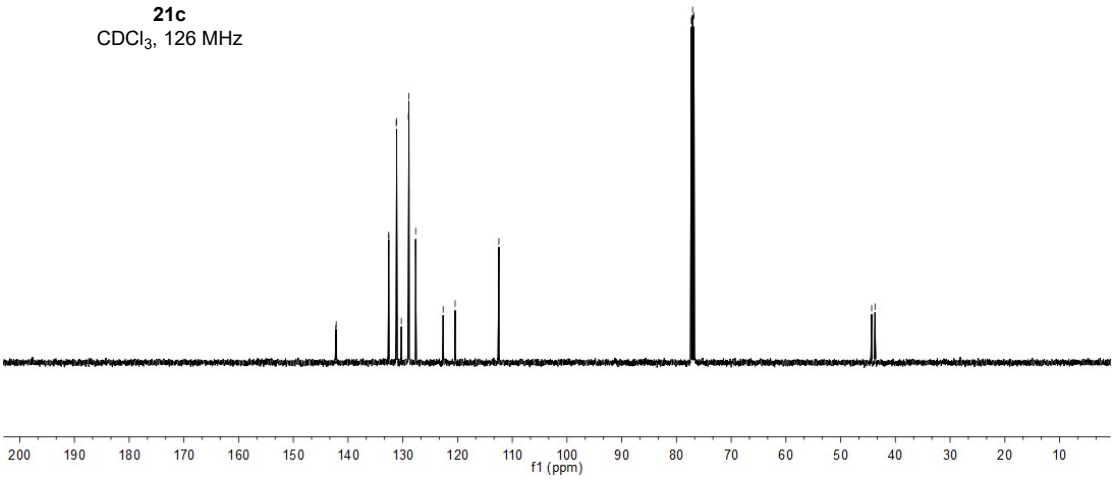


^{13}C NMR



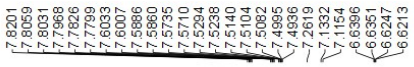
21c

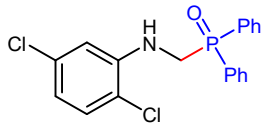
$CDCl_3$, 126 MHz



22c

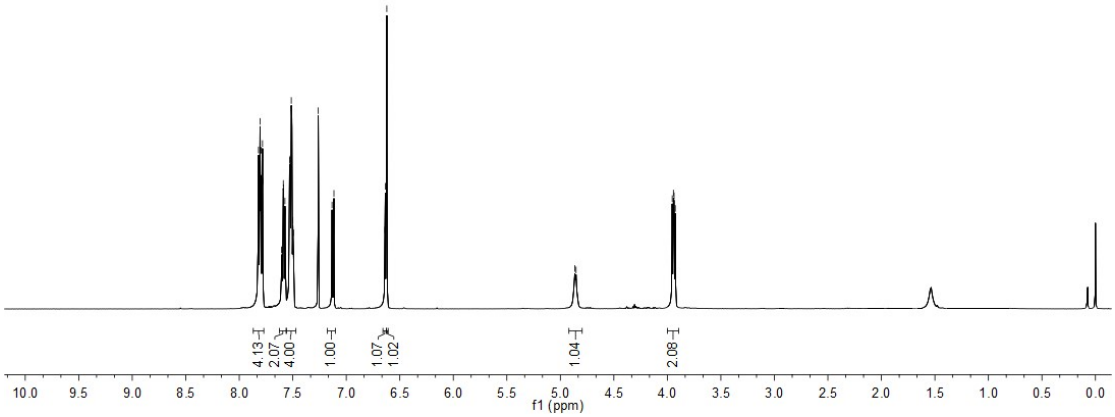
^{1}H NMR



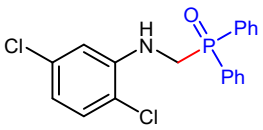


22c

$CDCl_3$, 500 MHz

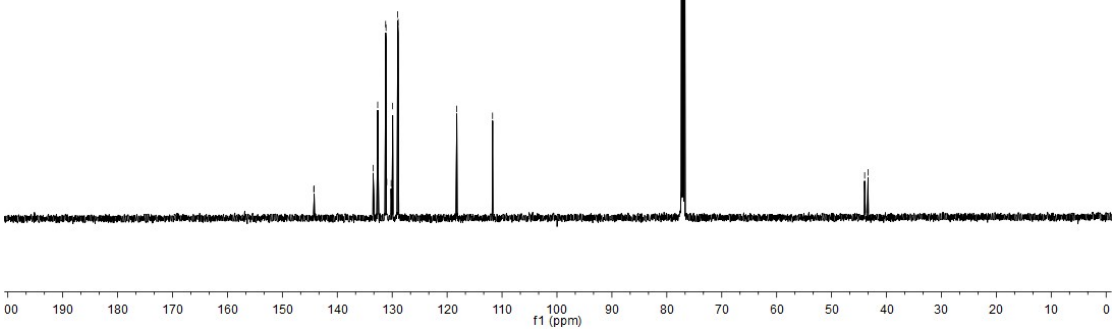


^{13}C NMR



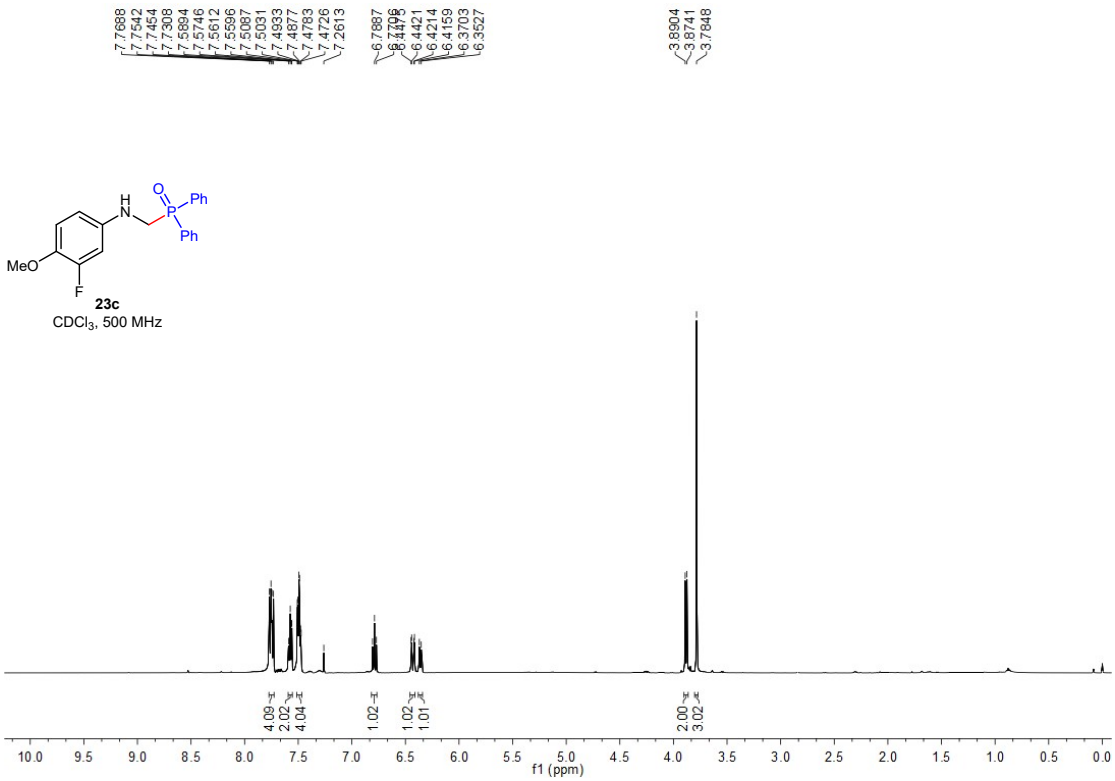
22c

$CDCl_3$, 126 MHz

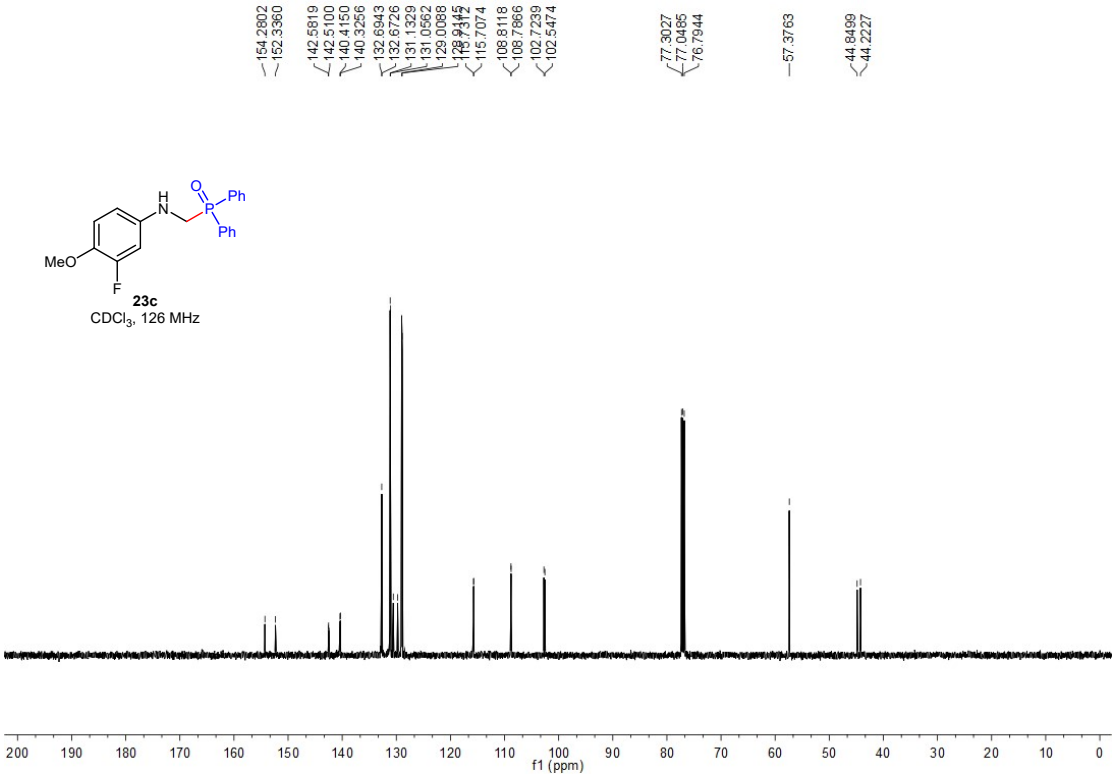


23c

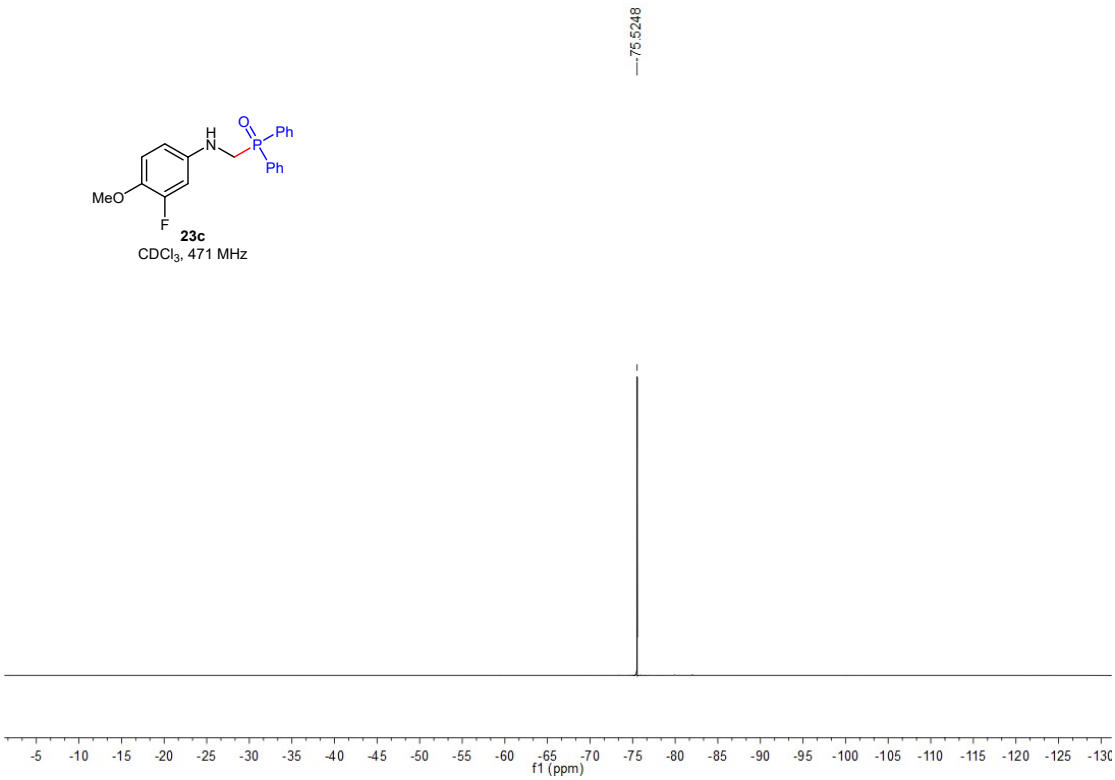
^{1}H NMR



^{13}C NMR

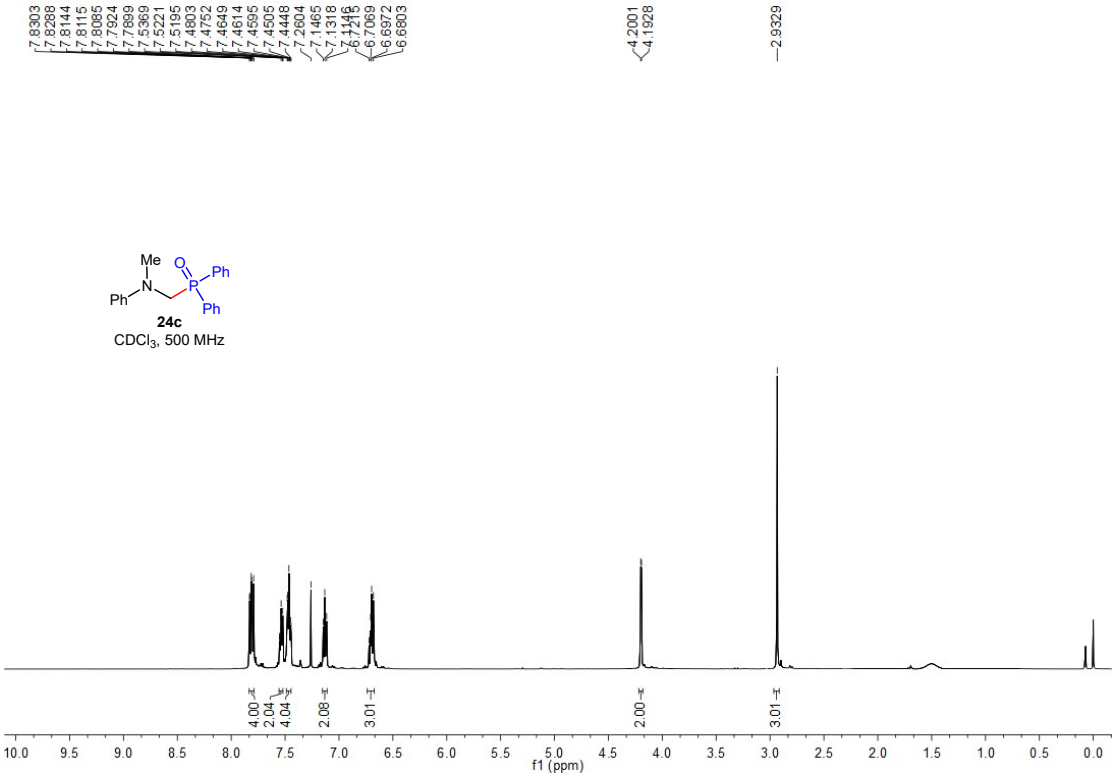


^{19}F NMR

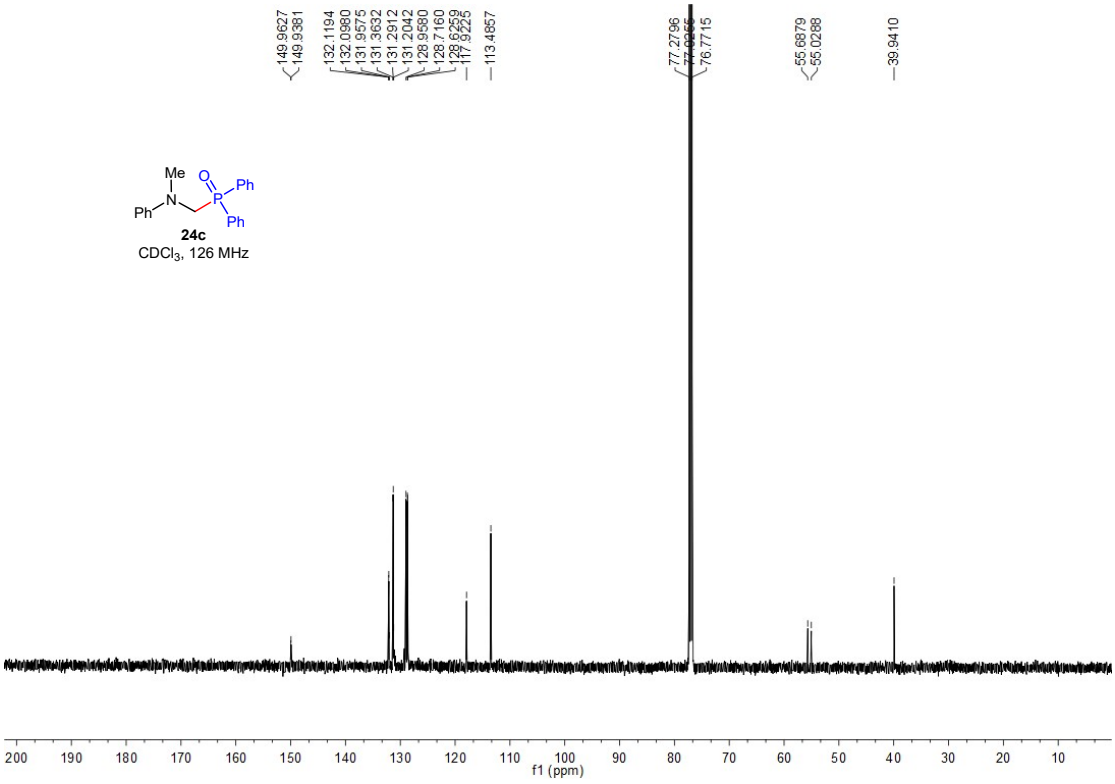


24c

^{1}H NMR

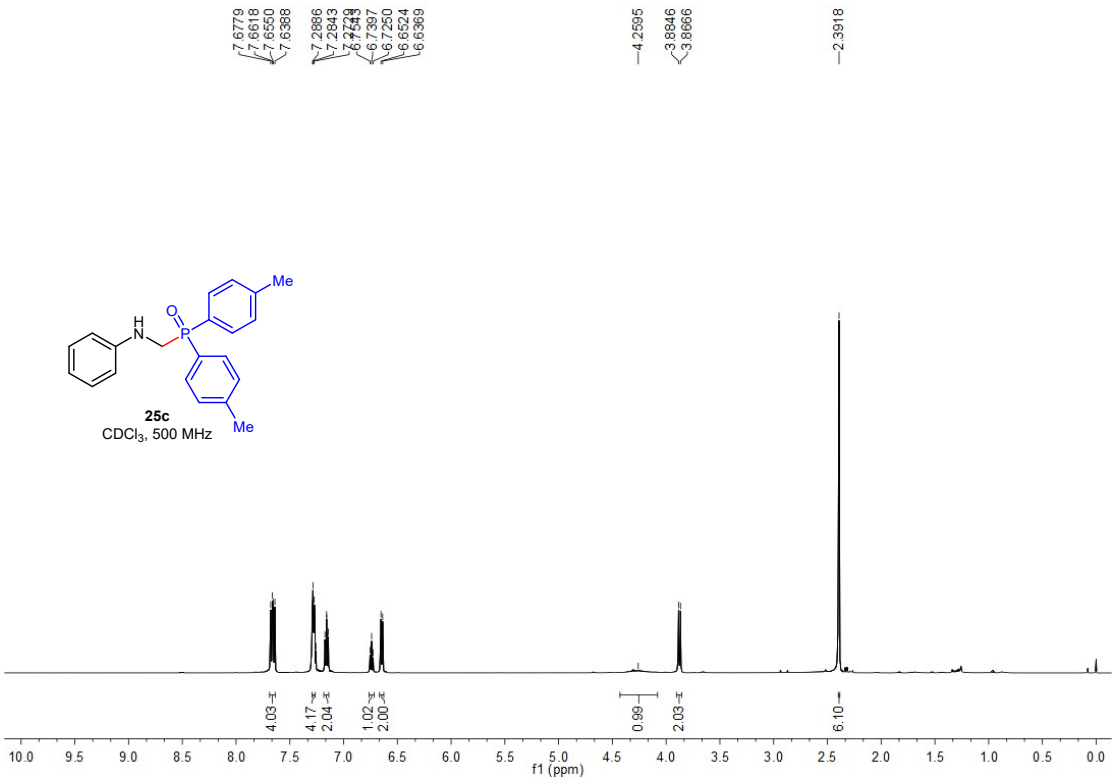


^{13}C NMR

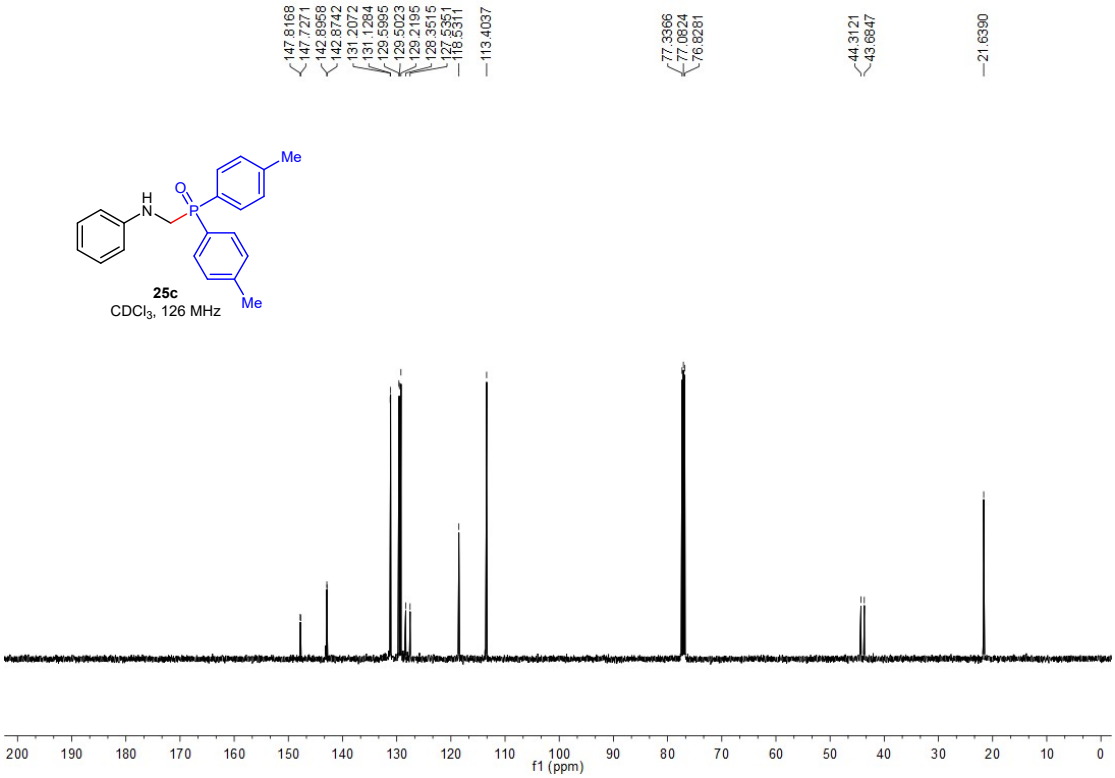


25c

^{1}H NMR

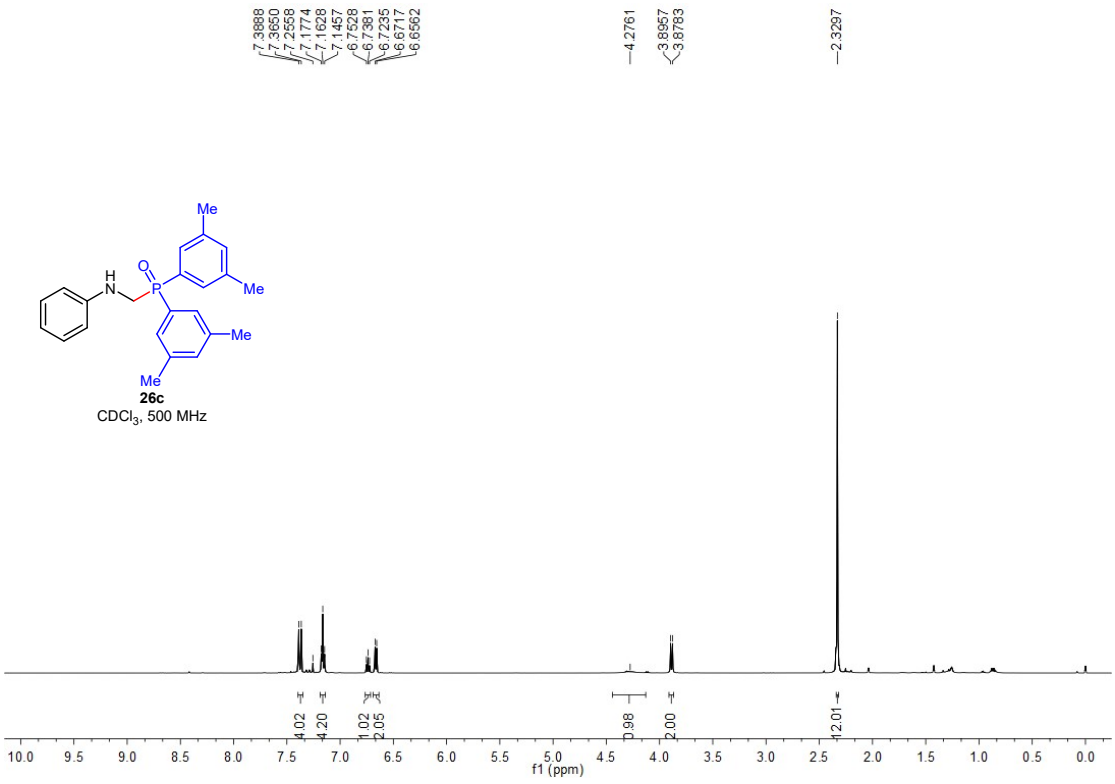


^{13}C NMR

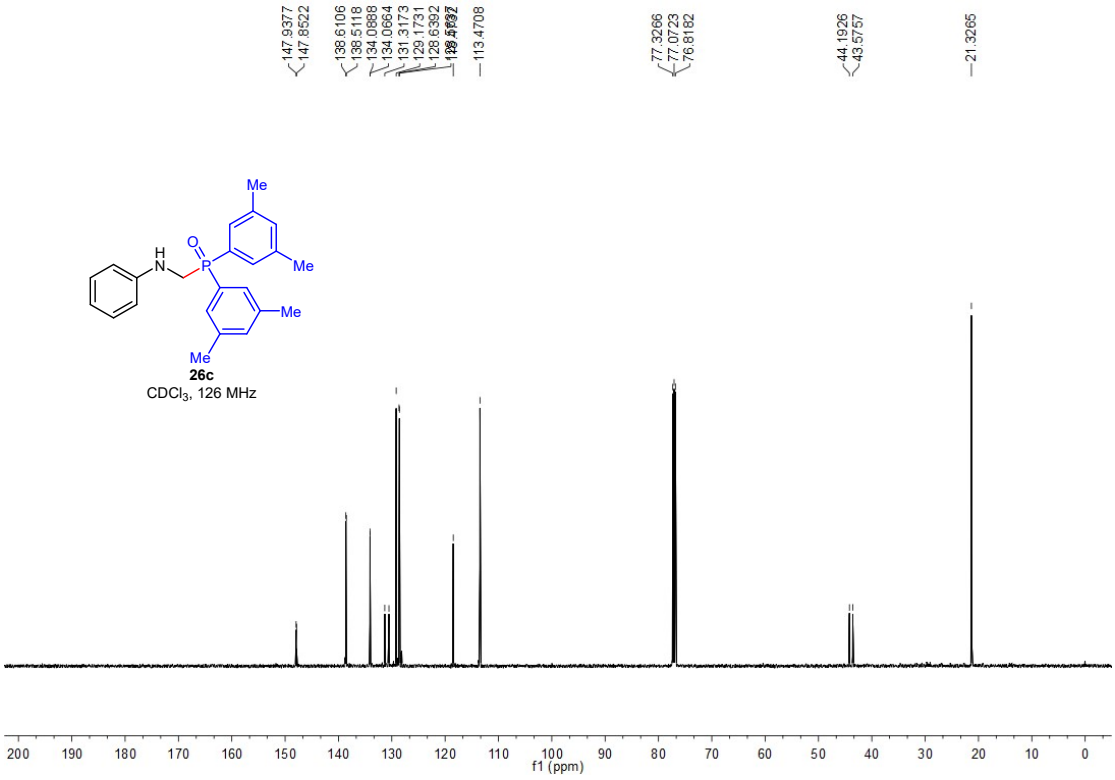


26c

^{1}H NMR

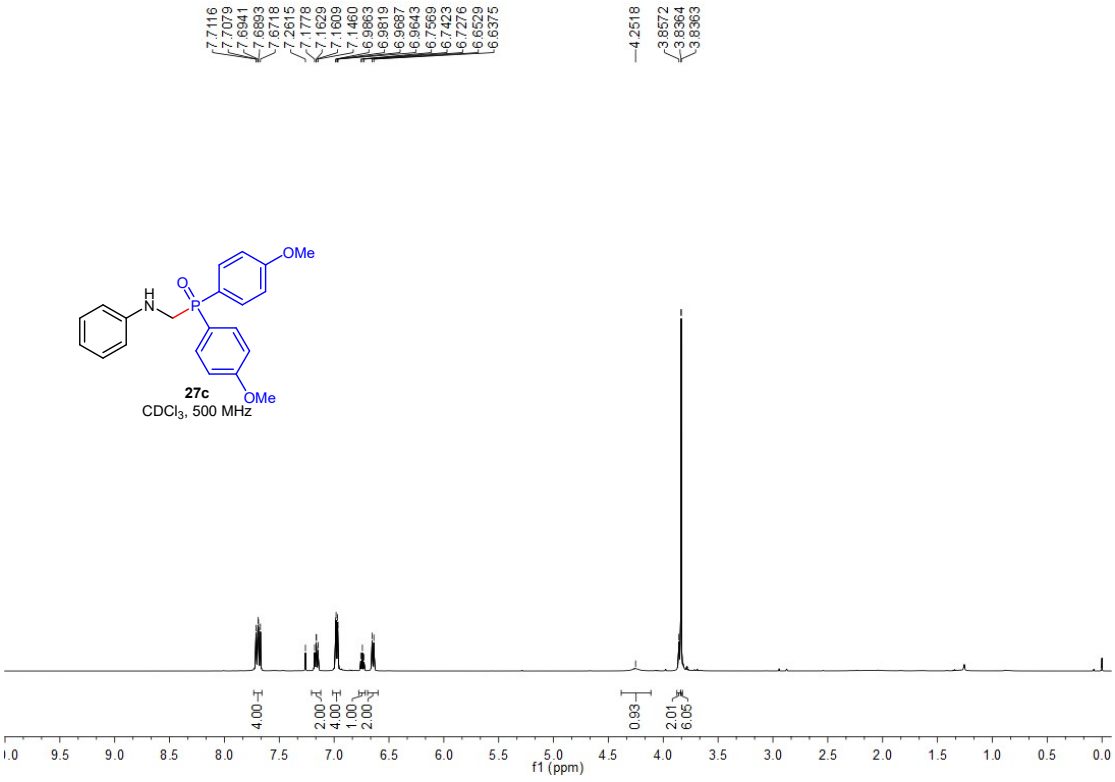


^{13}C NMR

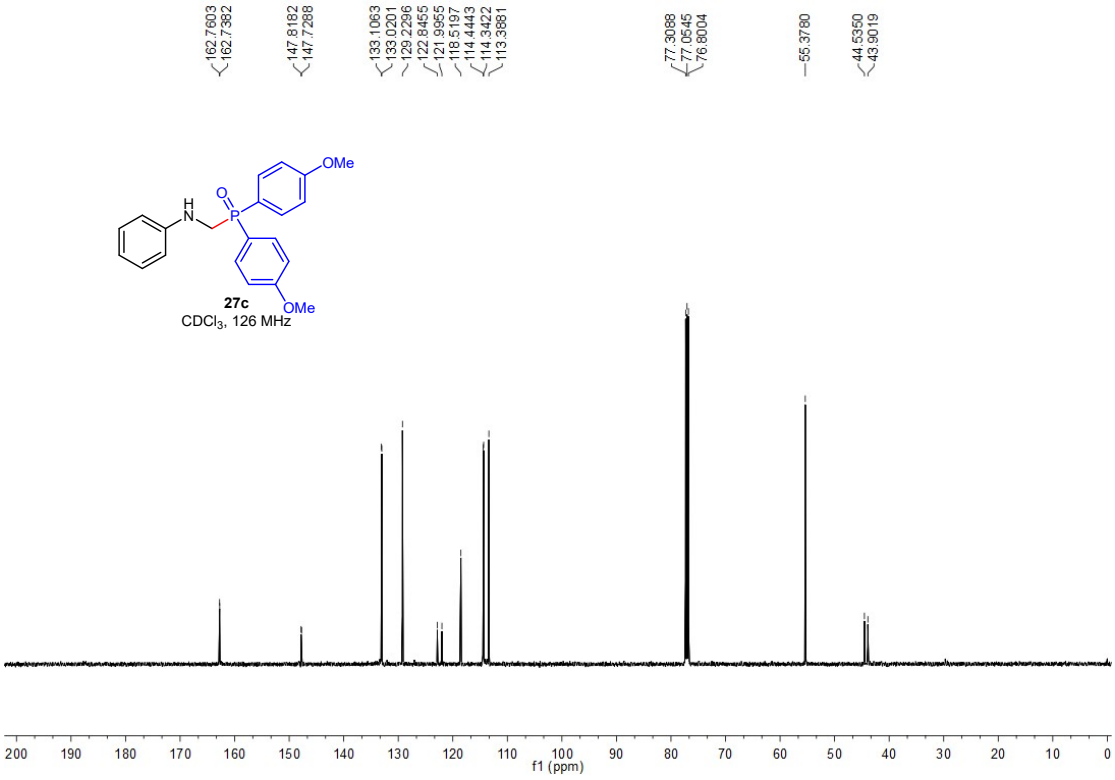


27c

^{1}H NMR

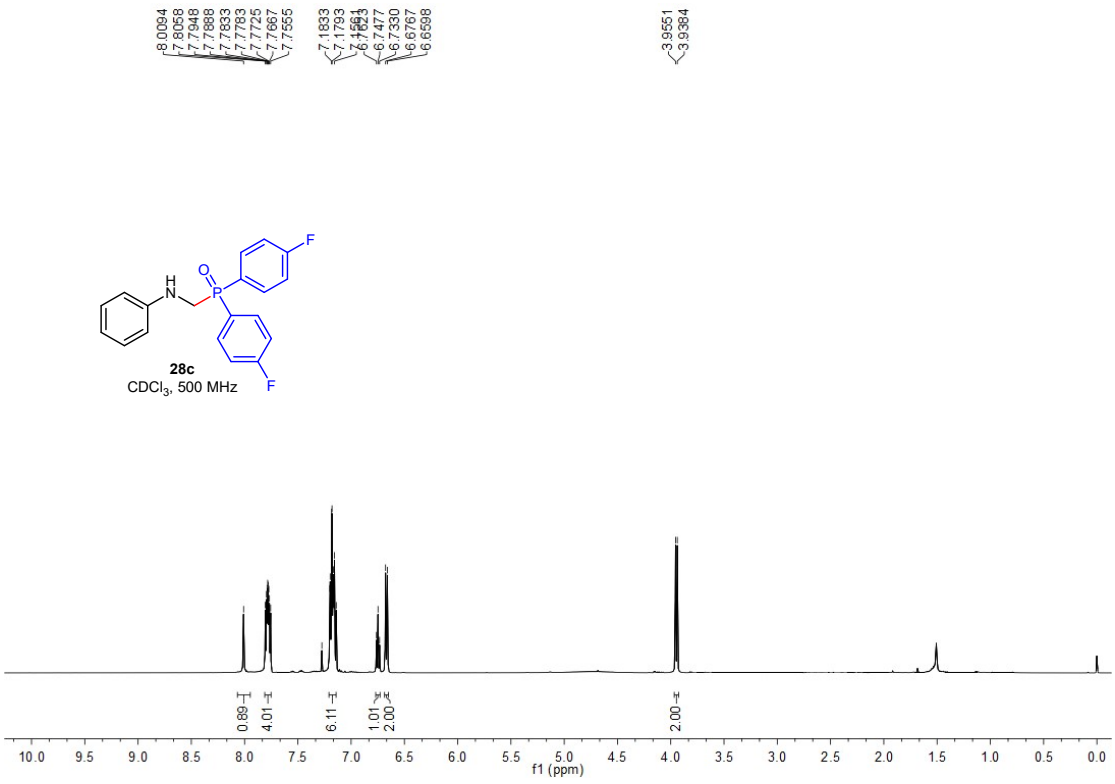


^{13}C NMR

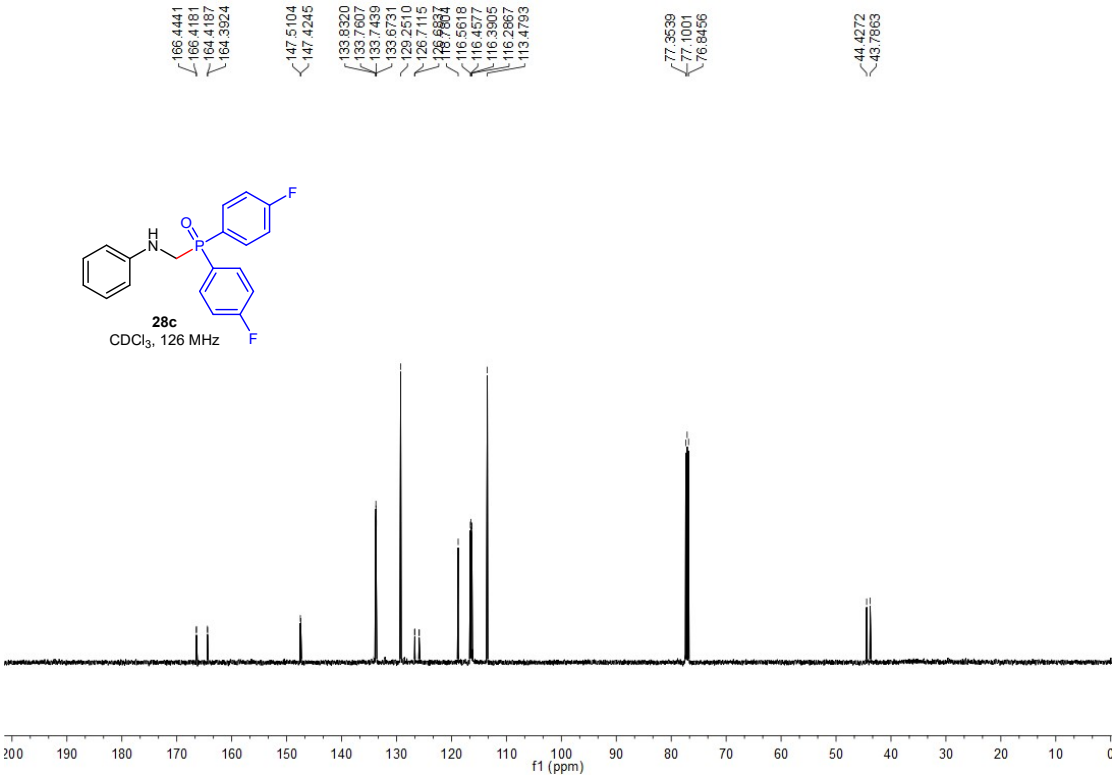


28c

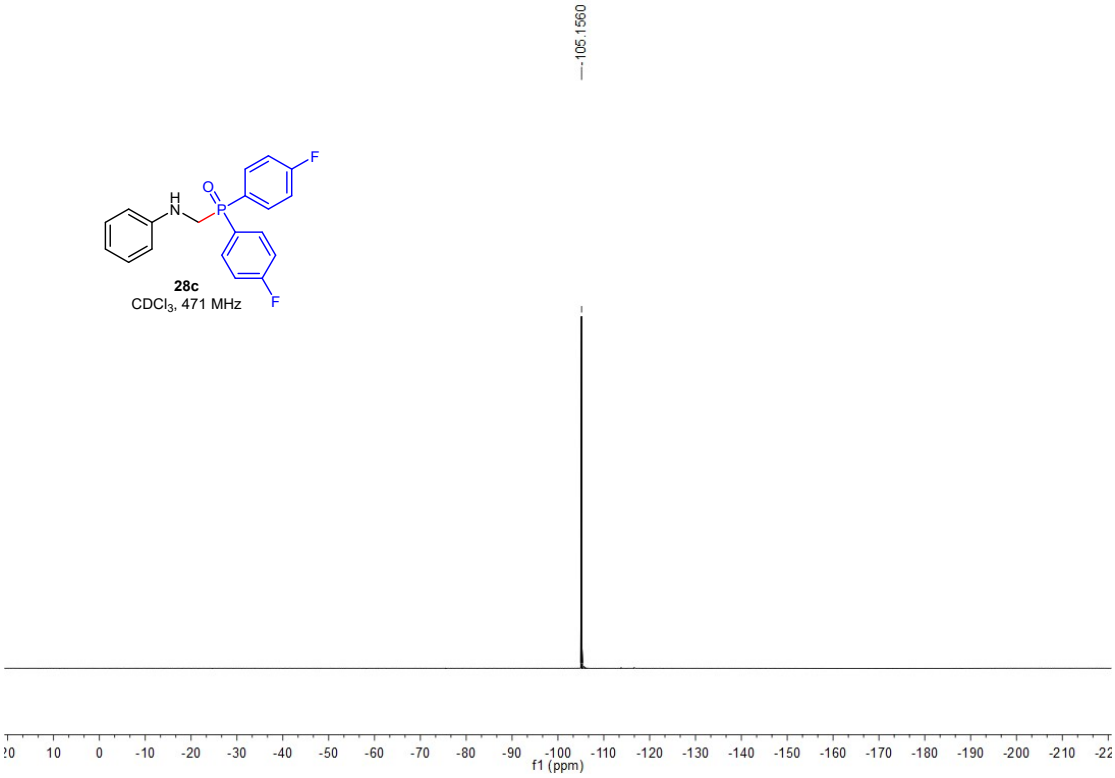
^{1}H NMR



^{13}C NMR

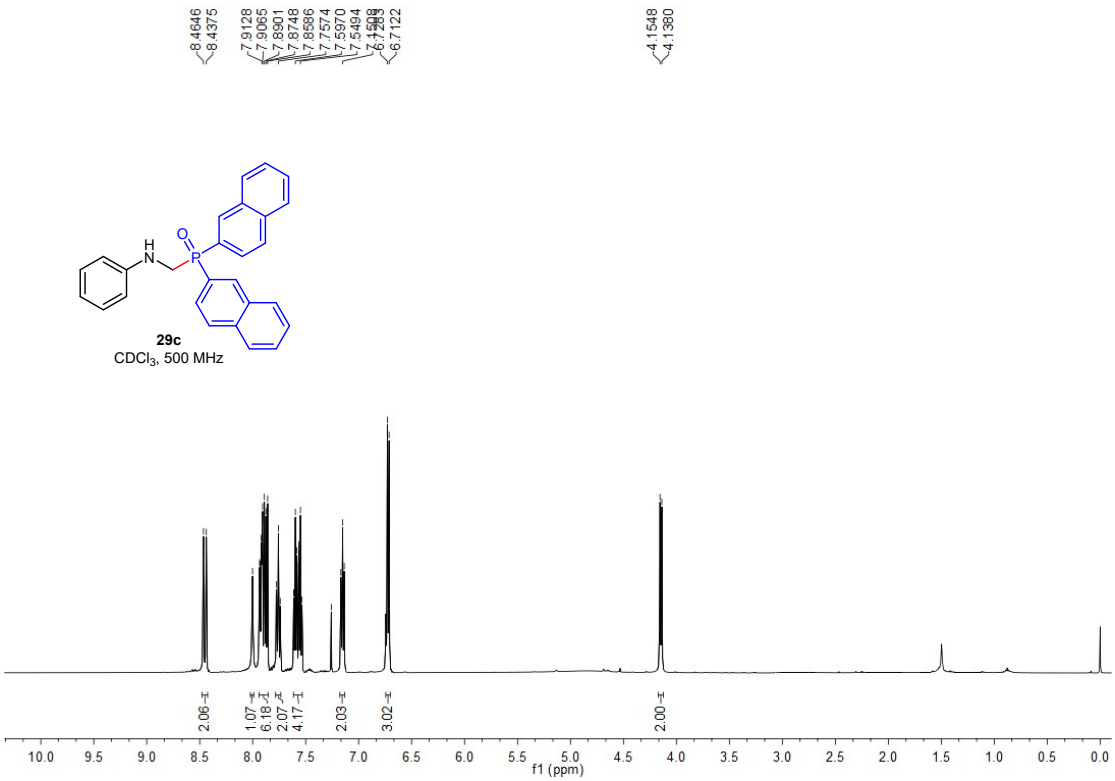


^{19}F NMR



29c

^{1}H NMR



^{13}C NMR