Hydrophosphorylation of Electron-Deficient Alkenes and Alkynes Mediated by Convergent Paired Electrolysis

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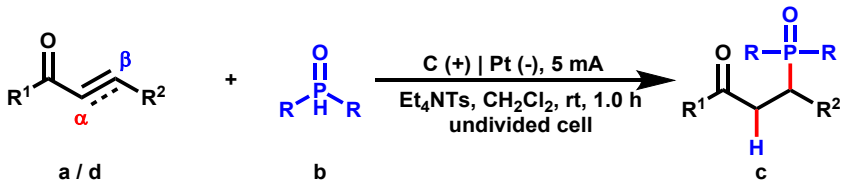
1. General information

All glassware was oven dried at 100 °C for hours and cooled down under vacuum. Diarylphosphane oxides and deuterated diphenylphosphane were synthesized according to previous reports.[1] Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China), the carbon rod (ϕ = 6.0 mm), Pt plates (1.0 x 1.0 cm^2), and Ni plates (1.5 x 1.5 cm^2) was purchased from Xuzhou Xinke Instrument and Meter Co. LTD. 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). ^1H, ^{13}C NMR, 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 tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively.

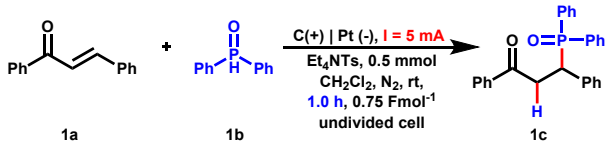
2. General Procedure



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **a/d** (0.25 mmol), **b** (0.5 mmol), and Et_4NTs (0.5 mmol, 142.5 mg) were combined and added. The flask was equipped with a carbon rods (ϕ = 6.0 mm) as the anode and Pt plates (1.0 x 1.0 cm^2) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, CH_2Cl_2 (10.0 mL) was slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under 25 °C for 1.0 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product **c** was obtained by flash column chromatography on silica gel.

3. Optimization of reaction conditions

Table S1. Optimization of reaction conditions [a]



1a 1b 1c

Entry	Deviation from standard conditions	Yield [b] (%)
1	none	94
2	without electricity	n. d.
3	$^{n}Bu_4NOAc$ instead of Et_4NTs	trace
4	$^{n}Bu_4NBF_4$ instead of Et_4NTs	20
5	$^{n}Bu_4NClO_4$ instead of Et_4NTs	80
6	$^{n}Bu_4NNO_3$ instead of Et_4NTs	78
7	Et_4NBr, $^{n}Bu_4NI$ instead of Et_4NTs	n. d.
8	DCE, DMF instead of CH_2Cl_2	60, 45
9	CH_3CN instead of CH_2Cl_2	trace
10	C(+)|C(-)	75
11	Pt(+)|C(-)	70
12	C(+)|Ni(-)	25
13	3 mA, 100 min	40
14	10 mA, 30 min	85

[a] Standard conditions: carbon rods as the anode, Pt plates (1 x 1 cm^2) as the cathode, constant current = 5 mA, **1a** (0.25 mmol), **1b** (0.5 mmol), Et_4NTs (0.5 mmol), CH_2Cl_2 (10.0 mL), rt, N_2, 1.0 h, 0.75 $Fmol^{-1}$. n. d. = not detected. DCE = 1,2-dichloroethane, DMF = N,N-dimethylacetamide. [b] Isolated yields.

4. Mechanistic Studies

4.1 Cyclic Voltammetry Experiment

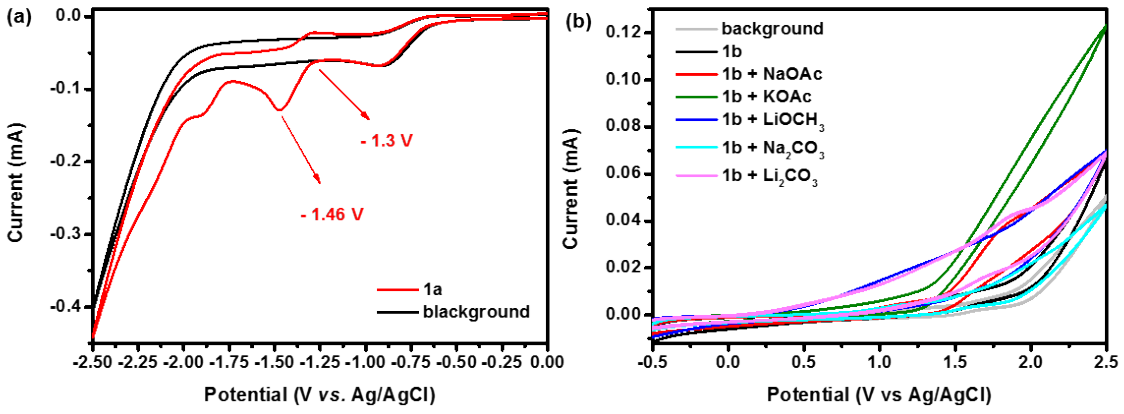


Figure S1. Cyclic Voltammetry at glass carbon as the working electrode, Pt plates (1.5 × 1.5 cm^2) as the counter electrode, Ag/AgCl as reference electrode. (a) **1a** (0.25 mM), in CH_2Cl_2 (10.0 mL) containing 0.1 M $^{n}Bu_4NBF_4$. (b) **1b** (0.5 mM). Base (2 mM) in CH_2Cl_2/EtOH (10.0 mL, v/v = 9/1) containing 0.1 M $^{n}Bu_4NBF_4$.

4.2 Deuterium Experiment

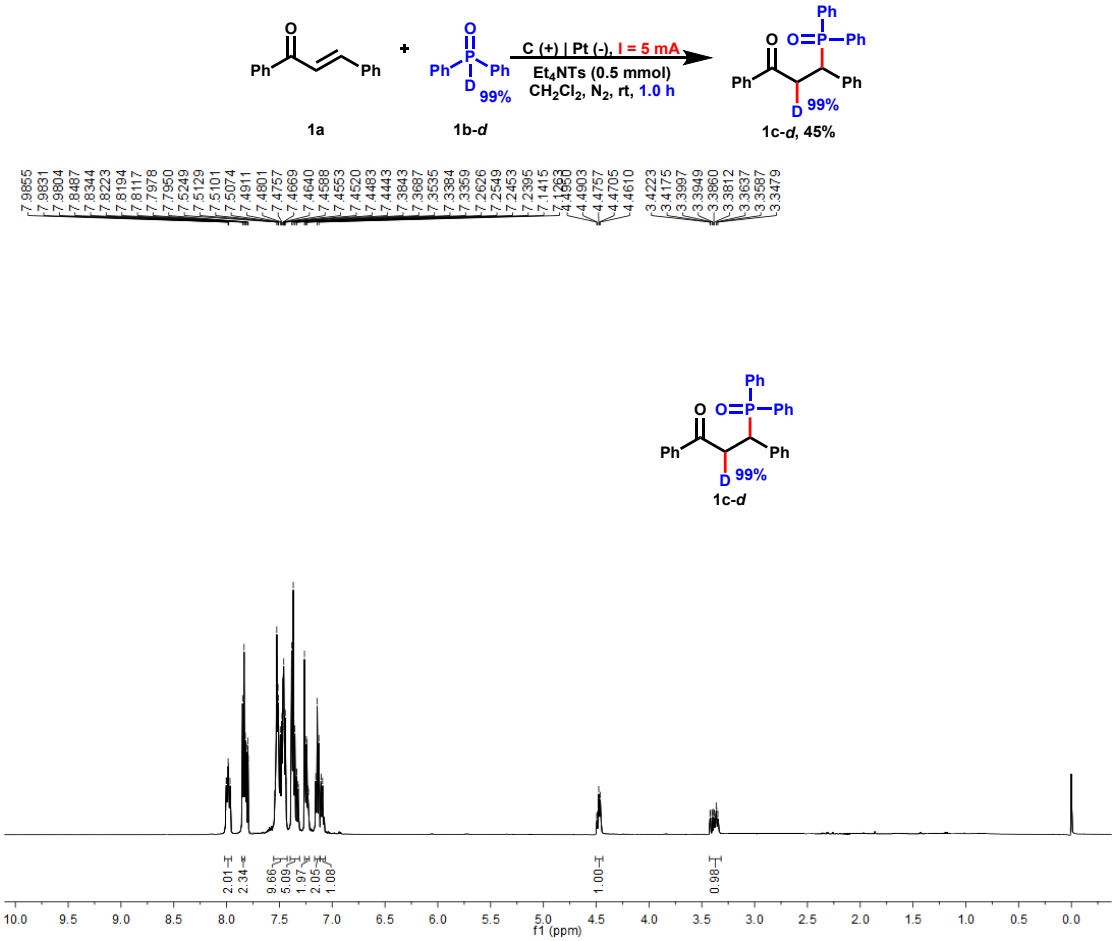
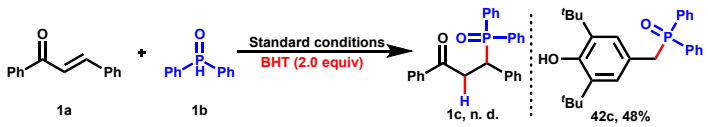


Figure S2. ^{1}H NMR resluts of **1c-*d***.

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, 1**a** (0.25 mmol, 52.0 mg), **1b-*d*** (0.5 mmol, 101.5 mg), and Et_4NTs (0.5 mmol, 142.5 mg) were combined and added. The flask was equipped with a carbon rods (ϕ = 6.0 mm) as the anode and Pt plates (1.0 x 1.0 cm^2) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, CH_2Cl_2 (10.0 mL) was slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under 25 °C for 1.0 h. When the reaction was finished, the pure product 1**c-*d*** was obtained by flash column chromatography on silica gel with a yield of 45%.

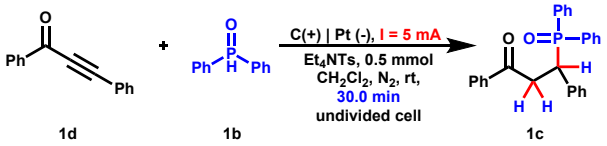
4.3 Radical trapping experiments



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1a** (0.25 mmol, 52.0 mg), **1b** (0.5 mmol, 101.0 mg), BHT (0.5 mmol, 110.0 mg), and Et_4NTs (0.5 mmol, 142.5 mg) were

combined and added. The flask was equipped with a carbon rods (ϕ = 6.0 mm) as the anode and Pt plates (1.0 x 1.0 cm^2) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, CH_2Cl_2 (10.0 mL) was slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under 25 °C for 1.0 h. When the reaction was finished, the solution was concentrated in a vacuum and not detected the desired product **1c**. The compound **42c** can be isolated in a yield of 48%.

4.4 HRMS results of 1d and 1b under standard conditions for 30 min (Figure S2 – S5).



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1d** (0.25 mmol, 51.5 mg), **1b** (0.5 mmol, 101.0 mg), and Et_4NTs (0.5 mmol, 142.5 mg) were combined and added. The flask was equipped with a carbon rods (ϕ = 6.0 mm) as the anode and Pt plates (1.0 x 1.0 cm^2) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, CH_2Cl_2 (10.0 mL) was slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under 25 °C for 30.0 min, and the corresponding composition was monitored by HRMS.

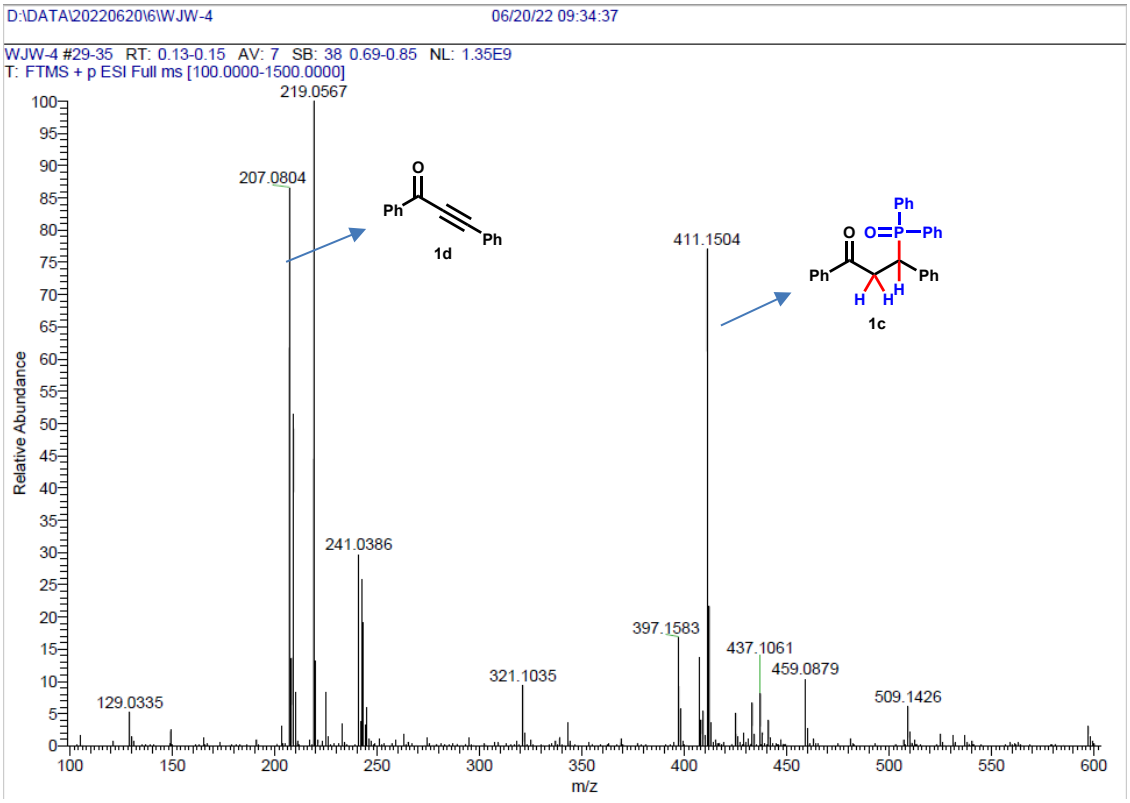


Figure S3. HRMS results of **1d** and **1b** under standard conditions for 30 min.

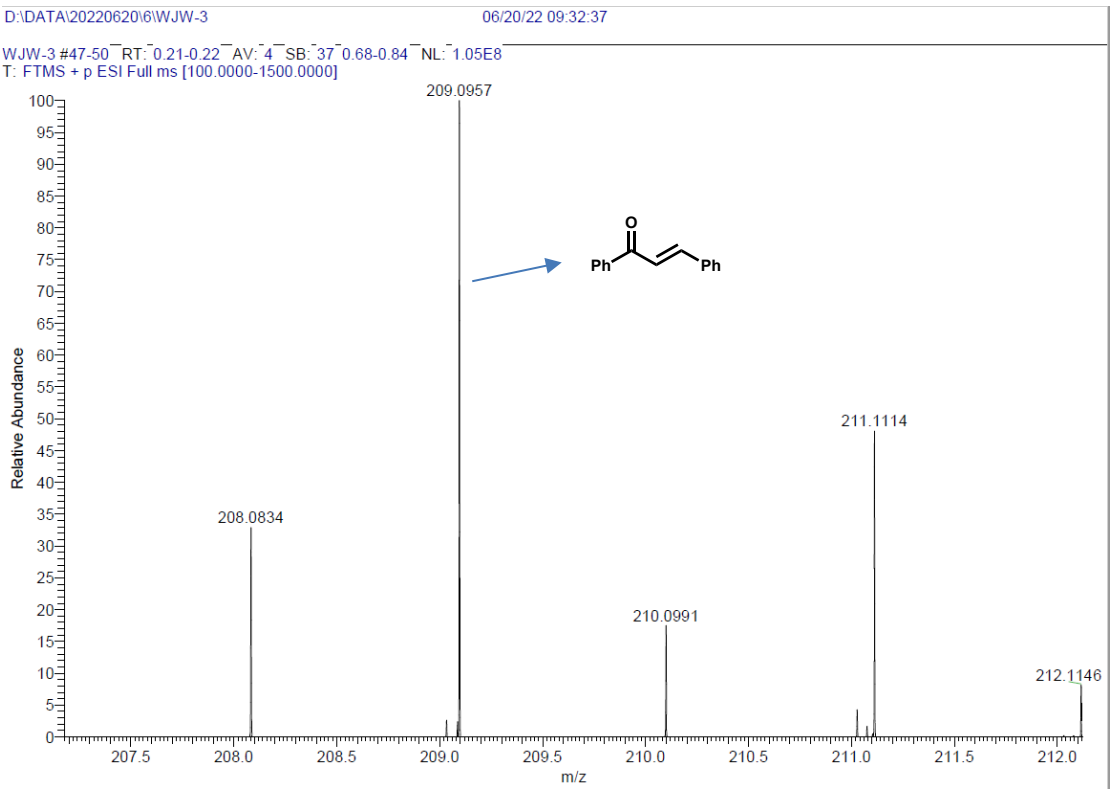


Figure S4. Zoomed in HRMS results of **1a**.

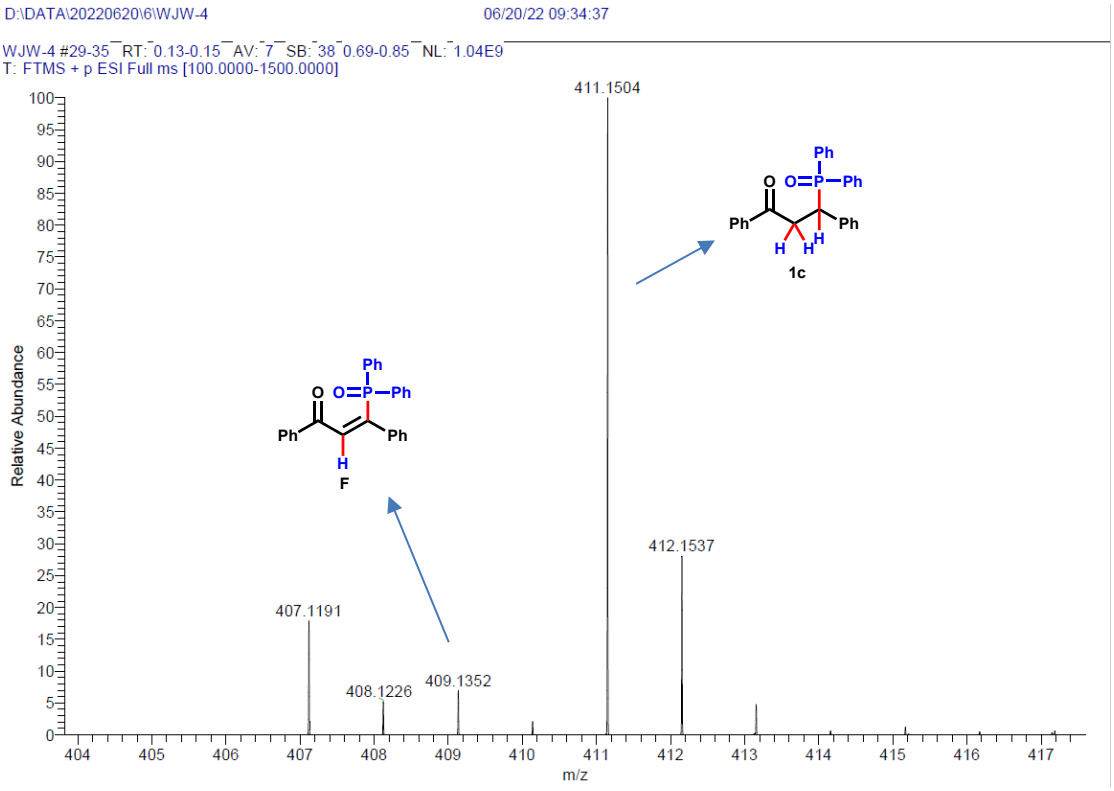


Figure S5. Zoomed in HRMS results of **1c** and byproduct **F** (trace).

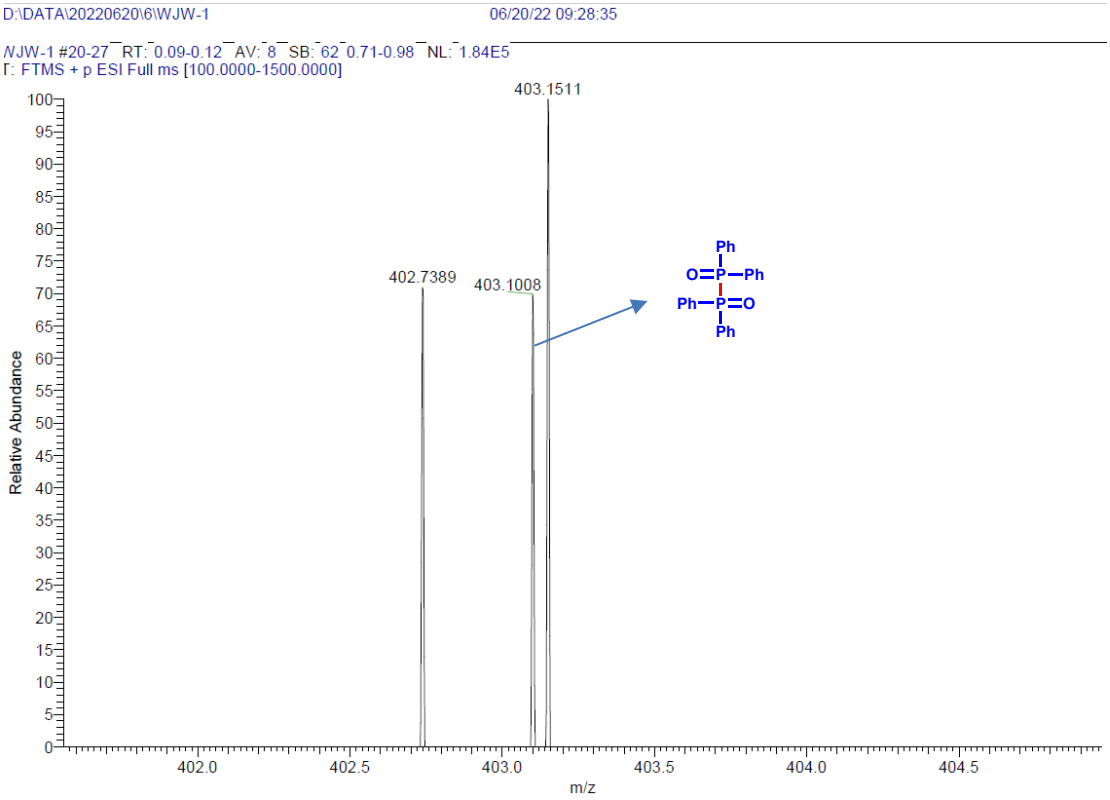
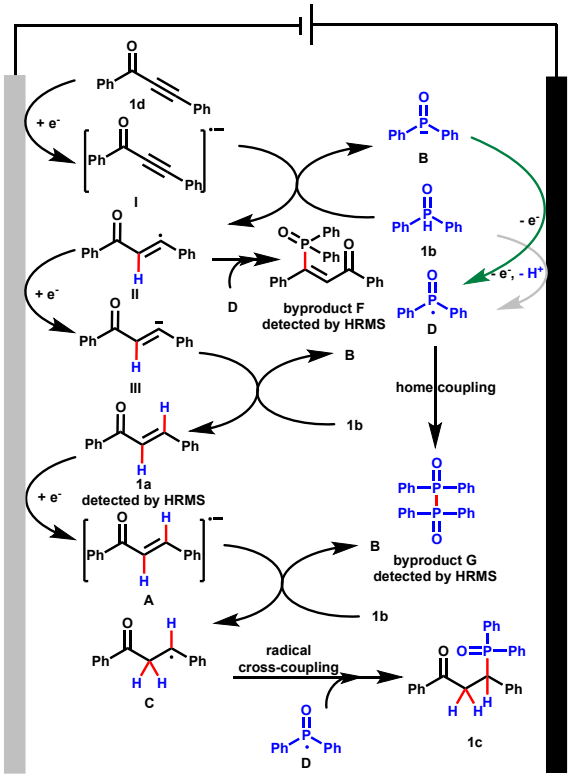


Figure S6. Zoomed in HRMS results of byproduct **G**.

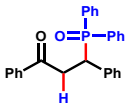


Scheme S1. Postulated reaction pathway for the hydrophosphorylation of ynones.

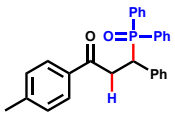
5. References

1. a) C.-J. Li, J. Lü, Z.-X. Zhang, K. Zhou, Y. Li, G.-H. Qi, *Res. Chem. Intermed.* **2018**, 44, 4547-4562; b) H.-F. Qian, C.-K. Li, Z.-H. Zhou, Z.-K. Tao, A. Shoberu, J.-P. Zou, *Org. Lett.* **2018**, 20, 18, 5947-5951.
2. a) C. Shan, F. Chen, J. Pan, Y. Gao, P. Xu, Y. Zhao, *J. Org. Chem.* **2017**, 82, 11659-11666; b) Z. Jiang, Y. Zhang, W. Ye, C.-H. Tan, *Tetrahedron Letters* **2007**, 48, 51-54; c) S. Liu, N. Shao, F.-Z. Li, X.-C. Yang, M.-C. Wang, *Org. Biomol. Chem*., **2017**, 15, 9465-9474; d) H. K. Lenker, M. E. Richard, K. P. Reese, A. F. Carter, J. D. Zawisky, E. F. Winter, T. W. Bergeron, K. S. Guydon, R.A. Stockland, Jr. *J. Org. Chem.* **2012**, 77, 1378-1385; e) A. Russo, A. Lattanzi, *Eur. J. Org. Chem.* **2010**, 6736-6739; f) Z. Huang, W. Liu, S. Li, Y. Yang, S. Guo, H. Cai, *Synlett* **2020**, 31, 1295-1297.

6. Detail descriptions for products.

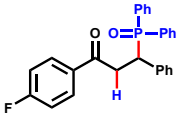


3-(diphenylphosphoryl)-1,3-diphenylpropan-1-one (1c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 94% isolated yield (96.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.84 (d, J = 7.7 Hz, 2H), 7.53 – 7.44 (m, 6H), 7.40 – 7.35 (m, 4H), 7.33 (d, J = 7.4 Hz, 1H), 7.24 (dd, J = 7.9, 2.8 Hz, 2H), 7.14 (t, J = 7.4 Hz, 2H), 7.10 (d, J = 7.2 Hz, 1H), 4.50 – 4.43 (m, 1H), 4.06 – 3.98 (m, 1H), 3.43 – 3.35 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6 (d, J_{C-P} = 13.3 Hz), 136.4, 135.9 (d, J_{C-P} = 5.6 Hz), 133.3, 132.0 (d, J_{C-P} = 2.7 Hz), 131.5 (d, J_{C-P} = 100.7 Hz), 131.4 (d, J_{C-P} = 2.8 Hz), 131.3 (d, J_{C-P} = 8.5 Hz), 131.2 (d, J_{C-P} = 94.9 Hz), 130.9 (d, J_{C-P} = 8.9 Hz), 129.8 (d, J_{C-P} = 5.7 Hz), 128.9 (d, J_{C-P} = 11.3 Hz), 128.5, 128.3 (d, J_{C-P} = 1.8 Hz), 128.1, 128.0, 127.0 (d, J_{C-P} = 2.3 Hz), 41.0 (d, J_{C-P} = 69.2 Hz), 38.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.4.

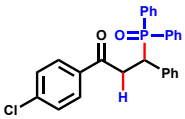


3-(diphenylphosphoryl)-3-phenyl-1-(p-tolyl)propan-1-one (2c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 82% isolated yield (87.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.58 – 7.50 (m, 3H), 7.46 – 7.40 (m, 2H), 7.35 – 7.27 (m, 3H), 7.25 – 7.20 (m, 2H), 7.18 – 7.11 (m, 3H), 4.25 – 4.19 (m, 1H), 3.38 – 3.28 (m, 1H), 3.00 – 2.89 (m, 1H), 1.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2 (d, J_{C-P} = 13.3 Hz), 144.2, 135.9 (d, J_{C-P} = 5.6 Hz), 133.9, 132.0 (d, J_{C-P} = 2.6 Hz), 131.9 (d, J_{C-P} = 100.5 Hz), 131.4 (d, J_{C-P} = 94.5 Hz), 131.3 (d, J_{C-P} = 2.7 Hz),

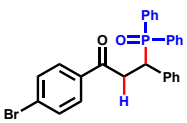
131.3 (d, $J_{C\text{-}P}$ = 8.5 Hz), 130.9 (d, $J_{C\text{-}P}$ = 8.9 Hz), 129.8 (d, $J_{C\text{-}P}$ = 5.7 Hz), 129.2, 128.9 (d, $J_{C\text{-}P}$ = 11.2 Hz), 128.2 (d, $J_{C\text{-}P}$ = 1.8 Hz), 128.2, 128.0 (d, $J_{C\text{-}P}$ = 11.8 Hz), 127.0 (d, $J_{C\text{-}P}$ = 2.4 Hz), 41.0 (d, $J_{C\text{-}P}$ = 69.1 Hz), 38.8, 21.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.4.



3-(diphenylphosphoryl)-1-(4-fluorophenyl)-3-phenylpropan-1-one (3c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 73% isolated yield (78.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.81 – 7.74 (m, 2H), 7.45 – 7.36 (m, 5H), 7.32 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.18 – 7.12 (m, 2H), 7.08 – 7.04 (m, 2H), 7.03 – 6.98 (m, 1H), 6.97 – 6.91 (m, 2H), 4.41 – 4.34 (m, 1H), 3.94 – 3.85 (m, 1H), 3.34 – 3.24 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1 (d, $J_{C\text{-}P}$ = 13.2 Hz), 165.8 (d, $J_{C\text{-}F}$ = 255.4 Hz), 132.8 (d, $J_{C\text{-}P}$ = 2.4 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 100.7 Hz), 131.4 (d, $J_{C\text{-}P}$ = 97.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.5 Hz), 130.9 (d, $J_{C\text{-}P}$ = 8.9 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 129.8 (d, $J_{C\text{-}P}$ = 5.7 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.2 Hz), 128.3 (d, $J_{C\text{-}P}$ = 1.7 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.8 Hz), 127.1 (d, $J_{C\text{-}P}$ = 2.3 Hz), 115.6 (d, $J_{C\text{-}F}$ = 21.9 Hz), 41.1 (d, $J_{C\text{-}P}$ = 69.0 Hz), 38.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.3.

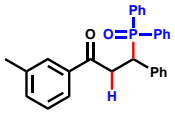


1-(4-chlorophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (4c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 62% isolated yield (68.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.79 – 7.74 (m, 2H), 7.55 – 7.49 (m, 3H), 7.48 – 7.43 (m, 2H), 7.38 – 7.31 (m, 5H), 7.27 – 7.22 (m, 2H), 7.17 – 7.12 (m, 2H), 7.12 – 7.07 (m, 1H), 4.48 – 4.40 (m, 1H), 4.01 – 3.90 (m, 1H), 3.41 – 3.31 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6 (d, $J_{C\text{-}P}$ = 13.2 Hz), 139.8, 135.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 134.7, 132.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 100.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 94.5 Hz), 130.9 (d, $J_{C\text{-}P}$ = 8.9 Hz), 129.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 129.5, 128.9 (d, $J_{C\text{-}P}$ = 11.3 Hz), 128.8, 128.3 (d, $J_{C\text{-}P}$ = 1.8 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.8 Hz), 127.1 (d, $J_{C\text{-}P}$ = 2.4 Hz), 41.1 (d, $J_{C\text{-}P}$ = 68.9 Hz), 38.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.3.

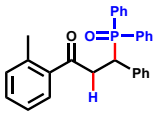


1-(4-bromophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (5c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 61% isolated yield (74.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.70 – 7.67 (m, 2H), 7.54 – 7.49 (m, 5H), 7.47 – 7.43 (m, 2H), 7.35 (t, J = 5.8 Hz, 3H), 7.26 – 7.21 (m, 2H), 7.14 (t, J = 7.1 Hz, 2H), 7.12 – 7.08 (m, 1H), 4.46 – 4.39 (m, 1H), 3.99 – 3.91 (m, 1H), 3.39 – 3.31 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8 (d, J_{C-P} = 13.2 Hz), 135.7 (d, J_{C-P} = 5.7 Hz), 135.1, 132.1 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 105.3 Hz), 131.8 (d, J_{C-P} = 102.8 Hz), 131.4 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 8.4 Hz), 130.9 (d, J_{C-P} = 8.9 Hz), 129.7 (d, J_{C-P} = 5.6 Hz), 129.6, 128.9 (d, J_{C-P} = 11.2 Hz), 128.6, 128.3 (d, J_{C-P} = 1.4 Hz), 128.1 (d, J_{C-P} = 11.8 Hz), 127.1 (d, J_{C-P} = 2.3 Hz), 41.1 (d, J_{C-P} = 68.6 Hz), 38.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.4.

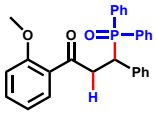


3-(diphenylphosphoryl)-3-phenyl-1-(m-tolyl)propan-1-one (6c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 68% isolated yield (72.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 7.67 – 7.62 (m, 2H), 7.54 – 7.49 (m, 3H), 7.48 – 7.43 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.28 (m, 2H), 7.27 – 7.21 (m, 3H), 7.16 – 7.11 (m, 2H), 7.11 – 7.06 (m, 1H), 4.51 – 4.44 (m, 1H), 4.07 – 3.98 (m, 1H), 3.42 – 3.32 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7 (d, J_{C-P} = 13.3 Hz), 138.3, 136.4, 135.9 (d, J_{C-P} = 5.6 Hz), 134.0, 132.0 (d, J_{C-P} = 2.6 Hz), 131.7 (d, J_{C-P} = 100.8 Hz), 131.5 (d, J_{C-P} = 94.5 Hz), 131.4 (d, J_{C-P} = 2.8 Hz), 131.3 (d, J_{C-P} = 8.5 Hz), 130.9 (d, J_{C-P} = 8.9 Hz), 129.8 (d, J_{C-P} = 5.7 Hz), 128.9 (d, J_{C-P} = 11.2 Hz), 128.7, 128.4, 128.2 (d, J_{C-P} = 1.8 Hz), 128.0 (d, J_{C-P} = 11.8 Hz), 127.0 (d, J_{C-P} = 2.3 Hz), 125.2, 41.0 (d, J_{C-P} = 69.2 Hz), 39.0, 21.2. ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.0.

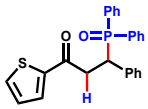


3-(diphenylphosphoryl)-3-phenyl-1-(o-tolyl)propan-1-one (7c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 72% isolated yield (76.3 mg). m. p. = 183-186 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.92 (m, 2H), 7.57 – 7.50 (m, 3H), 7.49 – 7.42 (m, 3H), 7.36 – 7.31 (m, 3H), 7.30 – 7.21 (m, 3H), 7.18 – 7.09 (m, 5H), 4.48 – 4.38 (m, 1H), 3.92 – 3.81 (m, 1H), 3.38 – 3.29 (m, 1H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7 (d, J_{C-P} = 13.3 Hz), 138.1, 137.3, 135.8 (d, J_{C-P} = 5.5 Hz), 132.0 (d, J_{C-P} = 2.8 Hz), 131.8, 131.6 (d, J_{C-P} = 81.0 Hz), 131.4, 131.4 (d, J_{C-P} = 86.4 Hz), 131.4 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 8.5 Hz), 131.0 (d, J_{C-P} = 8.9 Hz), 129.8 (d, J_{C-P} = 5.7 Hz), 128.9 (d, J_{C-P} = 11.3 Hz), 128.4, 128.3 (d, J_{C-P} = 1.8 Hz), 128.0 (d, J_{C-P} = 11.8 Hz), 127.0 (d, J_{C-P} = 2.3 Hz), 125.6, 41.6, 41.6 (d, J_{C-P} = 81.0 Hz), 20.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.0.

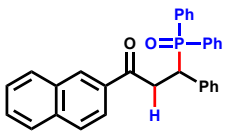
HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{28}H_{26}O_2P$: 425.1665; found: 425.1665.



3-(diphenylphosphoryl)-1-(2-methoxyphenyl)-3-phenylpropan-1-one (8c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 70% isolated yield (77.0 mg). m. p. = 179-181 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.55 – 7.44 (m, 5H), 7.41 – 7.32 (m, 3H), 7.32 – 7.28 (m, 2H), 7.28 – 7.22 (m, 2H), 7.15 – 7.07 (m, 3H), 6.88 – 6.82 (m, 2H), 4.50 – 4.44 (m, 1H), 4.06 – 3.97 (m, 1H), 3.77 (s, 3H), 3.52 – 3.43 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8 (d, J_{C-P} = 13.9 Hz), 158.6, 135.6 (d, J_{C-P} = 5.8 Hz), 133.7, 132.0 (d, J_{C-P} = 2.7 Hz), 131.5 (d, J_{C-P} = 2.8 Hz), 131.4 (d, J_{C-P} = 8.8 Hz), 131.0 (d, J_{C-P} = 9.0 Hz), 130.9 (d, J_{C-P} = 74.9 Hz), 130.7 (d, J_{C-P} = 70.4 Hz), 130.2, 130.0 (d, J_{C-P} = 5.8 Hz), 128.8 (d, J_{C-P} = 11.4 Hz), 128.1 (d, J_{C-P} = 0.7 Hz), 128.1 (d, J_{C-P} = 8.7 Hz), 127.5, 126.9 (d, J_{C-P} = 2.4 Hz), 120.4, 111.4, 55.4, 43.5, 41.3 (d, J_{C-P} = 69.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.0. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{28}H_{26}O_3P$: 441.1614; found: 441.1614.

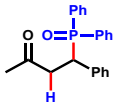


3-(diphenylphosphoryl)-3-phenyl-1-(thiophen-2-yl)propan-1-one (9c): yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 66% isolated yield (68.7 mg). m. p. = 149-152 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.89 – 7.84 (m, 2H), 7.61 – 7.56 (m, 2H), 7.53 – 7.49 (m, 4H), 7.42 – 7.36 (m, 3H), 7.35 – 7.29 (m, 2H), 7.06 – 6.98 (m, 2H), 6.82 – 6.76 (m, 1H), 4.87 – 4.80 (m, 1H), 4.00 – 3.91 (m, 1H), 3.40 – 3.30 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.3 (d, J_{C-P} = 12.6 Hz), 137.6 (d, J_{C-P} = 6.5 Hz), 136.3, 133.4 132.1 (d, J_{C-P} = 2.6 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 8.6 Hz), 131.2 (d, J_{C-P} = 96.0 Hz), 131.0 (d, J_{C-P} = 8.9 Hz), 131.0 (d, J_{C-P} = 95.0 Hz), 128.9 (d, J_{C-P} = 11.3 Hz), 128.5, 128.2, 128.1, 127.4 (d, J_{C-P} = 6.5 Hz), 126.7 (d, J_{C-P} = 2.5 Hz), 124.9 (d, J_{C-P} = 2.7 Hz), 39.9, 36.5 (d, J_{C-P} = 70.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.3. HkRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{25}H_{22}O_2PS$: 417.1073; found: 417.1069.

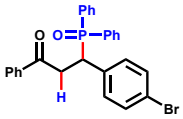


3-(diphenylphosphoryl)-1-(naphthalen-2-yl)-3-phenylpropan-1-one (10c): yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 61% isolated yield (70.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.02 (m, 2H), 7.89 (t, J = 8.3 Hz, 2H), 7.79 (t, J = 8.0 Hz, 2H), 7.51 (m, 7H), 7.42 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.25 (m, 2H), 7.15 (t, J = 7.5 Hz, 2H), 7.10 (d, J = 7.0 Hz, 1H), 4.55-4.51 (m, 1H), 4.16-4.23 (m, 1H), 3.48-3.55 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5 (d, J_{C-P} = 13.4 Hz), 135.9 (d, J_{C-P} = 5.6 Hz), 135.6, 133.6, 132.3, 132.1 (d, J_{C-P} = 2.6 Hz), 131.6 (d, J_{C-P} = 100.7 Hz), 131.4 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 8.5 Hz), 131.3 (d, J_{C-P} = 103.0 Hz), 130.9 (d, J_{C-P} = 8.9 Hz), 130.1, 129.8 (d, J_{C-P} = 5.7 Hz), 129.6, 128.9 (d, J_{C-P} = 11.2 Hz), 128.6, 128.3 (d, J_{C-P} = 2.5 Hz), 128.3, 128.1 (d, J_{C-P} = 11.8 Hz), 127.6, 127.1 (d, J_{C-P} = 2.3 Hz), 126.8, 123.5, 41.2 (d, J_{C-P} = 69.0 Hz), 38.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.6. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{31}H_6O_2P$: 461.1665; found: 461.1665.

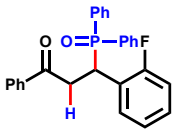


4-(diphenylphosphoryl)-4-phenylbutan-2-one (11c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 78% isolated yield (67.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.58 – 7.50 (m, 3H), 7.46 – 7.40 (m, 2H), 7.35 – 7.27 (m, 3H), 7.25 – 7.20 (m, 2H), 7.18 – 7.11 (m, 3H), 4.25 – 4.19 (m, 1H), 3.38 – 3.28 (m, 1H), 3.00 – 2.89 (m, 1H), 1.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.3 (d, J_{C-P} = 12.7 Hz), 135.8 (d, J_{C-P} = 5.5 Hz), 132.0 (d, J_{C-P} = 2.6 Hz), 131.4 (d, J_{C-P} = 101.7 Hz), 131.4 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 8.6 Hz), 131.3 (d, J_{C-P} = 101.5 Hz), 130.9 (d, J_{C-P} = 8.9 Hz), 129.7 (d, J_{C-P} = 5.7 Hz), 128.9 (d, J_{C-P} = 11.2 Hz), 128.3 (d, J_{C-P} = 1.7 Hz), 128.0 (d, J_{C-P} = 11.8 Hz), 127.1 (d, J_{C-P} = 2.3 Hz), 43.5, 41.1 (d, J_{C-P} = 68.7 Hz), 30.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.7.

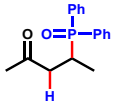


3-(4-bromophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (12c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 69% isolated yield (84.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.85 – 7.80 (m, 2H), 7.55 – 7.47 (m, 6H), 7.41 – 7.36 (m, 3H), 7.32 – 7.26 (m, 6H), 4.47 – 4.39 (m, 1H), 4.00 – 3.91 (m, 1H), 3.40 – 3.31 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4 (d, J_{C-P} = 13.2 Hz), 135.2 (d, J_{C-P} = 5.7 Hz), 133.5, 132.6 (d, J_{C-P} = 2.7 Hz), 132.1 (d, J_{C-P} = 2.8 Hz), 131.6 (d, J_{C-P} = 3.4 Hz), 131.4 (d, J_{C-P} = 5.8 Hz), 131.4 (d, J_{C-P} = 1.6 Hz), 131.3 (d, J_{C-P} = 100.5 Hz), 131.2 (d, J_{C-P} = 8.6 Hz), 131.1 (d, J_{C-P} = 99.5 Hz), 130.8 (d, J_{C-P} = 8.8 Hz), 129.0 (d, J_{C-P} = 11.3 Hz), 128.7 (d, J_{C-P} = 12.3 Hz), 128.6, 128.2 (d, J_{C-P} = 11.8 Hz), 128.0, 121.1 (d, J

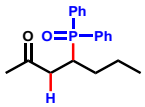
$_{C\text{-}P}$ = 2.9 Hz), 40.5 (d, $J_{C\text{-}P}$ = 68.9 Hz), 38.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.8.



3-(diphenylphosphoryl)-3-(2-fluorophenyl)-1-phenylpropan-1-one (13c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 68% isolated yield (72.8 mg). m. p. = 187-190 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H), 7.88 – 7.83 (m, 2H), 7.73 – 7.68 (m, 1H), 7.56 – 7.48 (m, 6H), 7.39 – 7.32 (m, 3H), 7.28 – 7.23 (m, 2H), 7.09 – 7.01 (m, 2H), 6.81 – 6.75 (m, 1H), 4.95 – 4.87 (m, 1H), 4.14 – 4.02 (m, 1H), 3.44 – 3.36 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1 (d, $J_{C\text{-}P}$ = 13.2 Hz), 160.4 (dd, $J_{C\text{-}F,\ C\text{-}P}$ = 246.3, 6.3 Hz), 136.2, 133.3, 132.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 101.6 Hz), 130.9 (d, $J_{C\text{-}P}$ = 95.2 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.5, 128.1, 128.1 (d, $J_{C\text{-}P}$ = 11.9 Hz), 124.3, 123.3 (dd, $J_{C\text{-}F,\ C\text{-}P}$ = 14.5, 5.4 Hz), 114.9 (d, $J_{C\text{-}F}$ = 23.1 Hz), 38.3, 32.4 (d, $J_{C\text{-}P}$ = 69.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.9 (d, J = 3.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.0. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{27}H_{23}FO_2P$: 429.1414; found: 429.1414.l

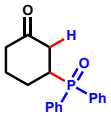


4-(diphenylphosphoryl)pentan-2-one (14c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 67% isolated yield (95.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 4H), 7.54 – 7.44 (m, 6H), 3.18 – 3.04 (m, 1H), 2.68 (dd, J = 9.2, 5.3 Hz, 2H), 2.07 (s, 3H), 1.13 (dd, J = 16.4, 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.0 (d, $J_{C\text{-}P}$ = 13.4 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.7 (d, $J_{C\text{-}P}$ = 95.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.6 (d, $J_{C\text{-}P}$ = 97.8 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.2 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.3 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 42.8, 30.5, 27.3 (d, $J_{C\text{-}P}$ = 73.9 Hz), 13.0 (d, $J_{C\text{-}P}$ = 2.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 37.3. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{20}O_2P$: 287.1195; found: 287.1194.

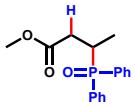


4-(diphenylphosphoryl)heptan-2-one (15c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 58% isolated yield (91.1 mg). m. p. = 112-114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H), 7.52 – 7.42 (m, 6H), 3.25 – 3.17 (m, 1H), 2.86 – 2.76 (m, 1H),

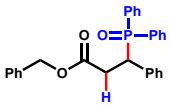
2.70 – 2.62 (m, 1H), 1.99 (s, 3H), 1.63 – 1.44 (m, 2H), 1.33 – 1.25 (m, 1H), 1.19 – 1.09 (m, 1H), 0.79 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.0 (d, J_{C-P} = 9.7 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 2.7 Hz), 131.6 (d, J_{C-P} = 97.1 Hz), 130.9 (d, J_{C-P} = 18.5 Hz), 128.7 (d, J_{C-P} = 11.5 Hz), 41.6, 31.1 (d, J_{C-P} = 72.9 Hz), 30.6 (d, J_{C-P} = 1.8 Hz), 30.0, 20.8 (d, J_{C-P} = 11.4 Hz), 13.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 37.3. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{19}H_{24}O_2P$: 315.1508; found: 315.1506.



3-(diphenylphosphoryl)cyclohexan-1-one (16c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 81% isolated yield (120.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.74 (m, 4H), 7.58 – 7.45 (m, 6H), 2.78 – 2.67 (m, 2H), 2.44 – 2.35 (m, 2H), 2.30 – 2.24 (m, 1H), 2.22 – 2.14 (m, 1H), 2.03 – 1.93 (m, 1H), 1.88 – 1.80 (m, 1H), 1.77 – 1.65 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6 (d, J_{C-P} = 14.2 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 132.1 (d, J_{C-P} = 2.8 Hz), 130.9 (d, J_{C-P} = 3.4 Hz), 130.8 (d, J_{C-P} = 3.4 Hz), 130.4 (d, J_{C-P} = 98.4 Hz), 129.9 (d, J_{C-P} = 97.7 Hz), 128.9 (d, J_{C-P} = 2.4 Hz), 128.8 (d, J_{C-P} = 2.4 Hz), 41.0, 39.2 (d, J_{C-P} = 3.2 Hz), 37.6 (d, J_{C-P} = 71.6 Hz), 26.3 (d, J_{C-P} = 15.6 Hz), 23.2 (d, J_{C-P} = 2.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.6.

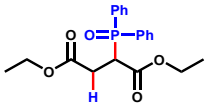


methyl 3-(diphenylphosphoryl)butanoate (17c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 41% isolated yield (61.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 4H), 7.54 – 7.46 (m, 6H), 3.62 (s, 3H), 3.03 – 2.93 (m, 1H), 2.66 – 2.59 (m, 1H), 2.51 – 2.43 (m, 1H), 1.20 (dd, J = 16.2, 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4 (d, J_{C-P} = 17.7 Hz), 131.8 (d, J_{C-P} = 6.9 Hz), 131.3 (d, J_{C-P} = 96.4 Hz), 131.0 (d, J_{C-P} = 8.8 Hz), 128.7 (d, J_{C-P} = 11.1 Hz), 51.9, 34.1, 29.2 (d, J_{C-P} = 73.3 Hz), 12.9 (d, J_{C-P} = 2.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.4.

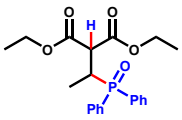


benzyl 3-(diphenylphosphoryl)-3-phenylpropanoate (18c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 53% isolated yield (116.6 mg). m. p. = 189-191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.57 – 7.49 (m, 3H), 7.44 (dd, J = 11.2, 7.6 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.28 – 7.21 (m, 7H), 7.18 – 7.13 (m, 3H), 7.06 (dd, J = 6.5, 3.0 Hz, 2H), 4.90 (s, 2H), 4.12 – 4.05 (m, 1H), 3.22 – 3.12 (m, 1H), 3.00 – 2.90 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$)

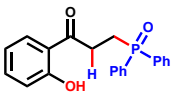
δ 171.2 (d, $J_{C\text{-}P}$ = 17.5 Hz), 135.4, 134.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 100.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 8.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 103.2 Hz), 129.7 (d, $J_{C\text{-}P}$ = 5.4 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.3 Hz), 128.4, 128.3 (d, $J_{C\text{-}P}$ = 1.7 Hz), 128.1, 128.0 (d, $J_{C\text{-}P}$ = 4.0 Hz), 127.8, 127.3 (d, $J_{C\text{-}P}$ = 2.4 Hz), 66.5, 43.0 (d, $J_{C\text{-}P}$ = 67.9 Hz), 34.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{28}H_{26}O_3P$: 441.1614; found: 441.1613.



diethyl 2-(diphenylphosphoryl)succinate (19c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 96% isolated yield (179.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 4H), 7.59 – 7.54 (m, 2H), 7.53 – 7.46 (m, 4H), 4.12 – 4.03 (m, 3H), 3.97 – 3.80 (m, 2H), 3.20 – 3.10 (m, 1H), 2.81 – 2.72 (m, 1H), 1.19 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2 (d, $J_{C\text{-}P}$ = 15.7 Hz), 168.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.6 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.5 (d, $J_{C\text{-}P}$ = 102.4 Hz), 129.6 (d, $J_{C\text{-}P}$ = 102.1 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.2 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.3 Hz), 61.3 (d, $J_{C\text{-}P}$ = 48.6 Hz), 44.5 (d, $J_{C\text{-}P}$ = 59.1 Hz), 30.7, 13.7 (d, $J_{C\text{-}P}$ = 70.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 30.2.

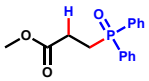


diethyl 2-(1-(diphenylphosphoryl)ethyl)malonate (20c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 74% isolated yield (143.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 4H), 7.55 – 7.43 (m, 6H), 4.21 – 4.12 (m, 2H), 3.98 – 3.89 (m, 1H), 3.86 – 3.76 (m, 2H), 3.42 – 3.33 (m, 1H), 1.31 – 1.23 (m, 6H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9 (d, $J_{C\text{-}P}$ = 9.3 Hz), 167.4 (d, $J_{C\text{-}P}$ = 9.1 Hz), 132.0 (d, $J_{C\text{-}P}$ = 3.8 Hz), 131.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 9.2 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.8 Hz), 130.9 (d, $J_{C\text{-}P}$ = 96.8 Hz), 130.5 (d, $J_{C\text{-}P}$ = 98.4 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.7 Hz), 61.6 (d, $J_{C\text{-}P}$ = 17.7 Hz), 50.5, 32.5 (d, $J_{C\text{-}P}$ = 71.3 Hz), 13.8 (d, $J_{C\text{-}P}$ = 20.6 Hz), 10.9 (d, $J_{C\text{-}P}$ = 2.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 30.3.

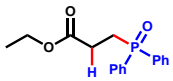


3-(diphenylphosphoryl)-1-(2-hydroxyphenyl)propan-1-one (21c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 47% isolated yield (82.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.98 (s, 1H), 7.79 (dd, J = 11.7, 7.4 Hz, 4H), 7.74 – 7.68 (m, 1H), 7.58 – 7.51 (m, 2H),

7.53 – 7.42 (m, 6H), 6.95 (d, J = 8.4 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 3.36 (q, J = 8.1 Hz, 2H), 2.72 (q, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.6 (d, $J_{C\text{-}P}$ = 13.7 Hz), 162.2, 136.6, 132.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.8 (d, $J_{C\text{-}P}$ = 100.8 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 129.9, 128.8 (d, $J_{C\text{-}P}$ = 11.8 Hz), 119.1, 118.9, 118.4, 30.4, 29.5 (d, $J_{C\text{-}P}$ = 42.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{20}O_3P$: 351.1145; found: 351.1145.

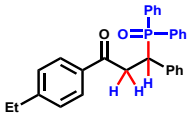


methyl 3-(diphenylphosphoryl)propanoate (22c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 85% isolated yield (122.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 4H), 7.56 – 7.51 (m, 2H), 7.51 – 7.46 (m, 4H), 3.62 (s, 3H), 2.69 – 2.61 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6 (d, $J_{C\text{-}P}$ = 16.8 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.5 (d, $J_{C\text{-}P}$ = 100.7 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.6 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.9 Hz), 52.0, 26.1 (d, $J_{C\text{-}P}$ = 2.2 Hz), 24.8 (d, $J_{C\text{-}P}$ = 73.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.3.



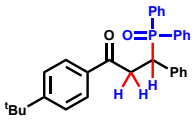
ethyl 3-(diphenylphosphoryl)propanoate (23c):[2] yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 72% isolated yield (108.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 4H), 7.58 – 7.41 (m, 6H), 4.08 (q, J = 7.1 Hz, 2H), 2.67 – 2.56 (m, 4H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3 (d, $J_{C\text{-}P}$ = 16.8 Hz), 132.0 (d, $J_{C\text{-}P}$ = 99.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.4 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.8 Hz), 60.9, 24.9 (d, $J_{C\text{-}P}$ = 73.1 Hz), 14.1. ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.3.

tert-butyl 3-(diphenylphosphoryl)propanoate (24c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 76% isolated yield (125.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.55 – 7.45 (m, 6H), 2.63 – 2.52 (m, 4H), 1.40 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5 (d, $J_{C\text{-}P}$ = 17.1 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.9 (d, $J_{C\text{-}P}$ = 100.1 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.8 Hz), 81.0, 27.9, 24.8 (d, $J_{C\text{-}P}$ = 73.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 36.5.

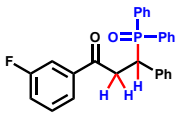


3-(diphenylphosphoryl)-1-(4-ethylphenyl)-3-phenylpropan-1-one (29c): white solid was obtained by

column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 63% isolated yield (69.0 mg). m. p. = 179-180 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.80 – 7.75 (m, 2H), 7.55 – 7.49 (m, 3H), 7.48 – 7.43 (m, 2H), 7.39 – 7.36 (m, 2H), 7.35 – 7.31 (m, 1H), 7.26 – 7.21 (m, 2H), 7.19 (d, J = 8.1 Hz, 2H), 7.16 – 7.11 (m, 2H), 7.11 – 7.06 (m, 1H), 4.51 – 4.43 (m, 1H), 4.06 – 3.95 (m, 1H), 3.40 – 3.31 (m, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2 (d, J_{C-P} = 13.2 Hz), 150.3, 136.0 (d, J_{C-P} = 5.6 Hz), 134.1, 131.9 (d, J_{C-P} = 2.6 Hz), 131.8 (d, J_{C-P} = 105.6 Hz), 131.6 (d, J_{C-P} = 98.5 Hz), 131.3 (d, J_{C-P} = 8.7 Hz), 130.9 (d, J_{C-P} = 8.9 Hz), 129.8 (d, J_{C-P} = 5.7 Hz), 128.9 (d, J_{C-P} = 11.2 Hz), 128.3, 128.2 (d, J_{C-P} = 1.7 Hz), 128.0 (d, J_{C-P} = 11.8 Hz), 128.0, 126.9, 41.0 (d, J = 69.2 Hz), 38.8, 28.9, 15.1. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.5. HRMS (EI) calcd for $C_{29}H_{28}O_2P$ $[M + H]^+$:439.1821; found: 439.1821.

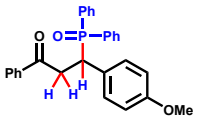


1-(4-(tert-butyl)phenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (30c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 51% isolated yield (59.4 mg). m. p. = 108-110 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.83 – 7.79 (m, 2H), 7.54 – 7.50 (m, 3H), 7.47 – 7.44 (m, 2H), 7.40 – 7.33 (m, 5H), 7.26 – 7.22 (m, 2H), 7.15 – 7.12 (m, 2H), 7.10 – 7.08 (m, 1H), 4.51 – 4.45 (m, 1H), 4.09 – 4.01 (m, 1H), 3.40 – 3.31 (m, 1H), 1.28 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1 (d, J_{C-P} = 13.4 Hz), 157.2, 135.8 (d, J_{C-P} = 5.8 Hz), 133.8, 132.0 (d, J_{C-P} = 2.6 Hz), 131.5 (d, J_{C-P} = 101.1 Hz), 131.4 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 8.5 Hz), 131.2 (d, J_{C-P} = 94.7 Hz), 130.9 (d, J_{C-P} = 9.0 Hz), 129.8 (d, J_{C-P} = 5.7 Hz), 128.9 (d, J_{C-P} = 11.3 Hz), 128.2 (d, J_{C-P} = 1.6 Hz), 128.1, 128.0, 127.0 (d, J_{C-P} = 2.3 Hz), 125.5, 41.0 (d, J_{C-P} = 69.4 Hz), 38.8, 35.0, 31.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.5. HRMS (EI) calcd for $C_{31}H_{32}O_2P$ $[M + H]^+$: 467.2134; found: 467.2134.

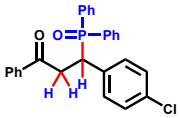


3-(diphenylphosphoryl)-1-(3-fluorophenyl)-3-phenylpropan-1-one (31c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 76% isolated yield (81.3 mg). m. p. = 142-145 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.91 (m, 2H), 7.88 – 7.76 (m, 1H), 7.61 (t, J = 6.8 Hz, 1H), 7.53 – 7.44 (m, 6H), 7.40 – 7.31 (m, 4H), 7.25 – 7.22 (m, 1H), 7.22 – 7.09 (m, 4H), 4.47 – 4.39 (m, 1H), 4.00 – 3.91 (m, 1H), 3.42 – 3.34 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6 (d, J_{C-P} = 11.1 Hz), 162.7 (d, J_{C-F} = 248.5 Hz), 132.0 (d, J_{C-F} = 2.4 Hz), 131.7 (d, J_{C-P} = 101.7 Hz), 131.6 (d, J

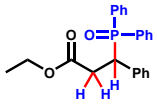
$_{C\text{-}P}$ = 9.4 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.4 Hz), 131.4 (d, $J_{C\text{-}P}$ = 100.7 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.5 Hz), 130.9 (d, $J_{C\text{-}P}$ = 8.9 Hz), 130.2 (d, $J_{C\text{-}P}$ = 7.7 Hz), 129.7 (d, $J_{C\text{-}P}$ = 5.7 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.3 Hz), 128.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 128.1 (d, $J_{C\text{-}P}$ = 11.8 Hz), 127.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 123.9, 120.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 114.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 41.1 (d, $J_{C\text{-}P}$ = 68.9 Hz), 39.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.4. HRMS (EI) calcd for $C_{27}H_{23}FO_2P$ [M + H] $^+$: 429.1414; found: 429.1408.



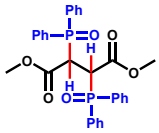
3-(diphenylphosphoryl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (32c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 74% isolated yield (81.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.85 – 7.82 (m, 2H), 7.52 – 7.47 (m, 6H), 7.38 – 7.34 (m, 3H), 7.31 – 7.26 (m, 4H), 6.70 – 6.67 (m, 2H), 4.46 – 4.39 (m, 1H), 4.01 – 3.92 (m, 1H), 3.68 (s, 3H), 3.38 – 3.29 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8 (d, $J_{C\text{-}P}$ = 13.5 Hz), 158.5 (d, $J_{C\text{-}P}$ = 2.3 Hz), 136.4, 133.3, 132.0 (t, $J_{C\text{-}P}$ = 49.1 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 100.3 Hz), 131.5 (d, $J_{C\text{-}P}$ = 103.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.5 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.8 Hz), 130.8 (d, $J_{C\text{-}P}$ = 5.7 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.2 Hz), 128.5, 128.1 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.1, 127.7 (d, $J_{C\text{-}P}$ = 5.7 Hz), 113.7 (d, $J_{C\text{-}P}$ = 1.6 Hz), 55.1, 40.1 (d, $J_{C\text{-}P}$ = 70.0 Hz), 39.1. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.0.



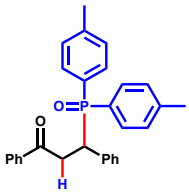
3-(4-chlorophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (33c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 68% isolated yield (75.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.82 (d, J = 7.8 Hz, 2H), 7.54 – 7.47 (m, 6H), 7.40 – 7.32 (m, 5H), 7.30 – 7.26 (m, 2H), 7.11 (d, J = 8.1 Hz, 2H), 4.48 – 4.41 (m, 1H), 4.00 – 3.91 (m, 1H), 3.41 – 3.31 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4 (d, $J_{C\text{-}P}$ = 13.2 Hz), 136.2, 134.6 (d, $J_{C\text{-}P}$ = 5.5 Hz), 133.5, 133.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.5 (d, $J_{C\text{-}P}$ = 100.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 94.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 5.7 Hz), 130.8 (d, $J_{C\text{-}P}$ = 8.9 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.3 Hz), 128.6, 128.4 (d, $J_{C\text{-}P}$ = 1.6 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.0, 40.5 (d, $J_{C\text{-}P}$ = 68.9 Hz), 38.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.3.



ethyl 3-(diphenylphosphoryl)-3-phenylpropanoate (34c):[2] yellow solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 30% isolated yield (56.7 mg). m. p. = 155-157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.59 – 7.52 (m, 3H), 7.48 – 7.43 (m, 2H), 7.37 – 7.32 (m, 1H), 7.28 – 7.22 (m, 4H), 7.18 – 7.11 (m, 3H), 4.13 – 4.04 (m, 1H), 3.91 (q, J = 7.1 Hz, 2H), 3.16 – 3.04 (m, 1H), 2.94 – 2.85 (m, 1H), 1.02 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3 (d, J_{C-P} = 17.2 Hz), 134.9 (d, J_{C-P} = 5.5 Hz), 132.0 (d, J_{C-P} = 2.6 Hz), 131.5 (d, J_{C-P} = 2.7 Hz), 131.4 (d, J_{C-P} = 8.6 Hz), 131.1 (d, J_{C-P} = 100.6 Hz), 131.0 (d, J_{C-P} = 8.9 Hz), 130.9 (d, J_{C-P} = 98.8 Hz), 129.7 (d, J_{C-P} = 5.5 Hz), 128.8 (d, J_{C-P} = 11.4 Hz), 128.2 (d, J_{C-P} = 1.8 Hz), 128.1 (d, J_{C-P} = 11.8 Hz), 127.2 (d, J_{C-P} = 2.4 Hz), 60.7, 42.9 (d, J_{C-P} = 68.1 Hz), 34.8, 13.9. HRMS (EI) calcd for $C_{23}H_{24}O_3P$ [M + H] $^{+}$: 379.1458; found: 379.1458.

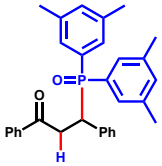


dimethyl 2,3-bis(diphenylphosphoryl)succinate (35c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 34% isolated yield (92.8 mg). m. p. = 89-91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 11.4, 6.8 Hz, 4H), 7.64 (dd, J = 11.5, 7.3 Hz, 4H), 7.56 (m, 6H), 7.43 (t, J = 7.3 Hz, 2H), 7.35 (t, J = 7.3 Hz, 4H), 4.70 (d, J = 4.2 Hz, 2H), 2.91 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 132.1 (d, J_{C-P} = 15.0 Hz), 131.9 (d, J_{C-P} = 115.2 Hz), 131.9 (t, J_{C-P} = 4.8 Hz), 131.7 (d, J_{C-P} = 115.3 Hz), 131.1 (t, J_{C-P} = 4.8 Hz), 51.7, 48.4 (dt, J_{C-P} = 44.4, 21.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.7. HRMS (EI) calcd for $C_{30}H_{29}O_6P_2$ [M + H] $^{+}$: 547.1434; found: 547.1434.

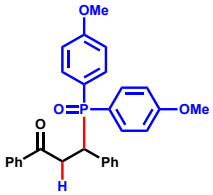


3-(di-p-tolylphosphoryl)-1,3-diphenylpropan-1-one (36c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 91% isolated yield (99.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 4H), 7.50 – 7.45 (m, 1H), 7.39 – 7.28 (m, 8H), 7.17 – 7.12 (m, 2H), 7.12 – 7.07 (m, 1H), 7.06 – 7.02 (m, 2H), 4.46 – 4.40 (m, 1H), 4.06 – 3.98 (m, 1H), 3.42 – 3.34 (m, 1H), 2.37 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8 (d, J_{C-P} = 13.3 Hz), 142.5 (d, J_{C-P} = 2.7 Hz), 141.8 (d, J_{C-P} = 2.9 Hz), 136.4, 136.0 (d, J_{C-P} = 5.7 Hz), 133.2, 131.2 (d, J_{C-P} = 8.9 Hz), 131.0 (d, J_{C-P} = 9.3 Hz), 129.8 (d, J_{C-P} = 5.6 Hz), 129.6 (d, J_{C-P} = 11.7 Hz), 128.8 (d, J_{C-P} = 12.3 Hz), 128.5, 128.3 (d,

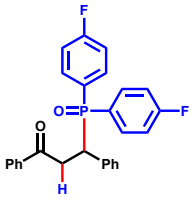
$J_{C\text{-}P}$ = 103.6 Hz), 128.2 (d, $J_{C\text{-}P}$ = 1.9 Hz), 128.1, 128.0 (d, $J_{C\text{-}P}$ = 97.6 Hz), 126.9 (d, $J_{C\text{-}P}$ = 2.5 Hz), 41.2 (d, $J_{C\text{-}P}$ = 69.2 Hz), 41.2 (d, $J_{C\text{-}P}$ = 69.2 Hz), 39.0, 21.5 (d, $J_{C\text{-}P}$ = 10.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.0.



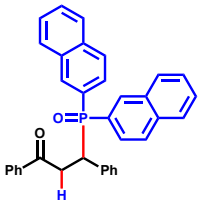
3-(bis(3,5-dimethylphenyl)phosphoryl)-1,3-diphenylpropan-1-one (37c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 88% isolated yield (102.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.56 (dd, J = 11.2, 1.6 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.40 – 7.34 (m, 4H), 7.17 – 7.11 (m, 3H), 7.09 (dd, J = 7.3, 1.7 Hz, 1H), 7.05 (dd, J = 11.6, 1.5 Hz, 2H), 6.95 (s, 1H), 4.46 – 4.39 (m, 1H), 4.08 – 4.00 (m, 1H), 3.43 – 3.34 (m, 1H), 2.34 (s, 6H), 2.17 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9 (d, $J_{C\text{-}P}$ = 13.2 Hz), 138.6 (d, $J_{C\text{-}P}$ = 12.1 Hz), 137.6 (d, $J_{C\text{-}P}$ = 12.6 Hz), 136.4, 136.0 (d, $J_{C\text{-}P}$ = 5.8 Hz), 133.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 133.2, 133.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 130.8 (d, $J_{C\text{-}P}$ = 100.6 Hz), 130.6 (d, $J_{C\text{-}P}$ = 94.4 Hz), 129.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 128.8 (d, $J_{C\text{-}P}$ = 8.7 Hz), 128.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.5, 128.2 (d, $J_{C\text{-}P}$ = 1.9 Hz), 128.1, 126.9 (d, $J_{C\text{-}P}$ = 2.4 Hz), 41.1 (d, $J_{C\text{-}P}$ = 68.5 Hz), 38.8, 21.2 (d, $J_{C\text{-}P}$ = 28.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.6. HRMS (EI) calcd for $C_{31}H_{32}O_2P$ [M + H] $^+$: 467.2134; found: 467.2135.



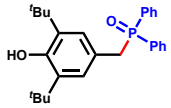
3-(bis(4-methoxyphenyl)phosphoryl)-1,3-diphenylpropan-1-one (38c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 90% isolated yield (105.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 4H), 7.50 – 7.46 (m, 1H), 7.39 – 7.30 (m, 6H), 7.18 – 7.13 (m, 2H), 7.12 – 7.08 (m, 1H), 7.02 – 6.99 (m, 2H), 6.76 – 6.72 (m, 2H), 4.42 – 4.36 (m, 1H), 4.05 – 3.97 (m, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.45 – 3.37 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8 (d, $J_{C\text{-}P}$ = 13.2 Hz), 162.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 162.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 136.4, 136.0 (d, $J_{C\text{-}P}$ = 5.7 Hz), 133.2, 133.1 (d, $J_{C\text{-}P}$ = 9.9 Hz), 132.8 (d, $J_{C\text{-}P}$ = 10.4 Hz), 129.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 128.5, 128.3 (d, $J_{C\text{-}P}$ = 1.8 Hz), 128.1, 127.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 122.6 (d, $J_{C\text{-}P}$ = 108.1 Hz), 122.0 (d, $J_{C\text{-}P}$ = 102.0 Hz), 114.5 (d, $J_{C\text{-}P}$ = 12.3 Hz), 113.6 (d, $J_{C\text{-}P}$ = 12.9 Hz), 55.2 (d, $J_{C\text{-}P}$ = 18.5 Hz), 41.5 (d, $J_{C\text{-}P}$ = 69.9 Hz), 38.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.6.



3-(bis(4-fluorophenyl)phosphoryl)-1,3-diphenylpropan-1-one (39c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 64% isolated yield (71.4 mg). m. p. = 194-196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.86 – 7.82 (m, 2H), 7.53 – 7.48 (m, 1H), 7.46 – 7.34 (m, 6H), 7.23 – 7.12 (m, 5H), 6.98 – 6.90 (m, 2H), 4.48 – 4.41 (m, 1H), 4.02 – 3.93 (m, 1H), 3.44 – 3.36 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4 (d, $J_{C\text{-}P}$ = 12.8 Hz), 164.9 (dd, $J_{C\text{-}F,\ C\text{-}P}$ = 250.5, 62.7 Hz), 136.2, 135.6 (d, $J_{C\text{-}P}$ = 5.7 Hz), 133.9 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 10.7, 9.4 Hz), 133.4 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 10.8, 9.5 Hz), 129.7 (d, $J_{C\text{-}P}$ = 5.8 Hz), 128., 128.4 (d, $J_{C\text{-}P}$ = 1.9 Hz), 128.0, 127.3 (d, $J_{C\text{-}P}$ = 2.5 Hz), 127.2 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 100.5, 51.5 Hz), 127.2 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 101.0, 51.5 Hz), 116.4 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 21.4, 12.3 Hz), 115.5 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 21.4, 12.9 Hz), 41.2 (d, $J_{C\text{-}P}$ = 70.2 Hz), 38.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -106.1, -106.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.4. HRMS (EI) calcd for $C_{27}H_{22}F_2O_2P$ $[M + H]^+$: 447.1320; found: 447.1315.



3-(di(naphthalen-2-yl)phosphoryl)-1,3-diphenylpropan-1-one (40c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 88% isolated yield (112.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, J = 12.7 Hz, 1H), 8.12 (dd, J = 13.3, 1.4 Hz, 1H), 8.00 – 7.93 (m, 3H), 7.86 – 7.79 (m, 3H), 7.75 – 7.68 (m, 3H), 7.59 – 7.51 (m, 3H), 7.50 – 7.45 (m, 3H), 7.45 – 7.38 (m, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.13 (t, J = 7.5 Hz, 2H), 7.09 – 7.03 (m, 1H), 4.77 – 4.70 (m, 1H), 4.16 – 4.06 (m, 1H), 3.53 – 3.44 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7 (d, $J_{C\text{-}P}$ = 13.2 Hz), 136.3, 135.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 134.7 (d, $J_{C\text{-}P}$ = 2.2 Hz), 134.4 (d, $J_{C\text{-}P}$ = 2.3 Hz), 133.8 (d, $J_{C\text{-}P}$ = 7.6 Hz), 133.4 (d, $J_{C\text{-}P}$ = 8.3 Hz), 133.3, 132.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 132.2 (d, $J_{C\text{-}P}$ = 12.9 Hz), 129.9 (d, $J_{C\text{-}P}$ = 5.7 Hz), 129.1 (d, $J_{C\text{-}P}$ = 109.7 Hz), 129.0 (d, $J_{C\text{-}P}$ = 10.6 Hz), 128.8, 128.6 (d, $J_{C\text{-}P}$ = 97.4 Hz), 128.5, 128.4 (d, $J_{C\text{-}P}$ = 1.6 Hz), 128.3, 128.1, 128.0 (d, $J_{C\text{-}P}$ = 7.3 Hz), 127.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 127.6, 127.2 (d, $J_{C\text{-}P}$ = 2.4 Hz), 127.1, 126.6, 125.7 (d, $J_{C\text{-}P}$ = 3.4 Hz), 125.6 (d, $J_{C\text{-}P}$ = 3.2 Hz), 41.0 (d, $J_{C\text{-}P}$ = 69.3 Hz), 39.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.6.

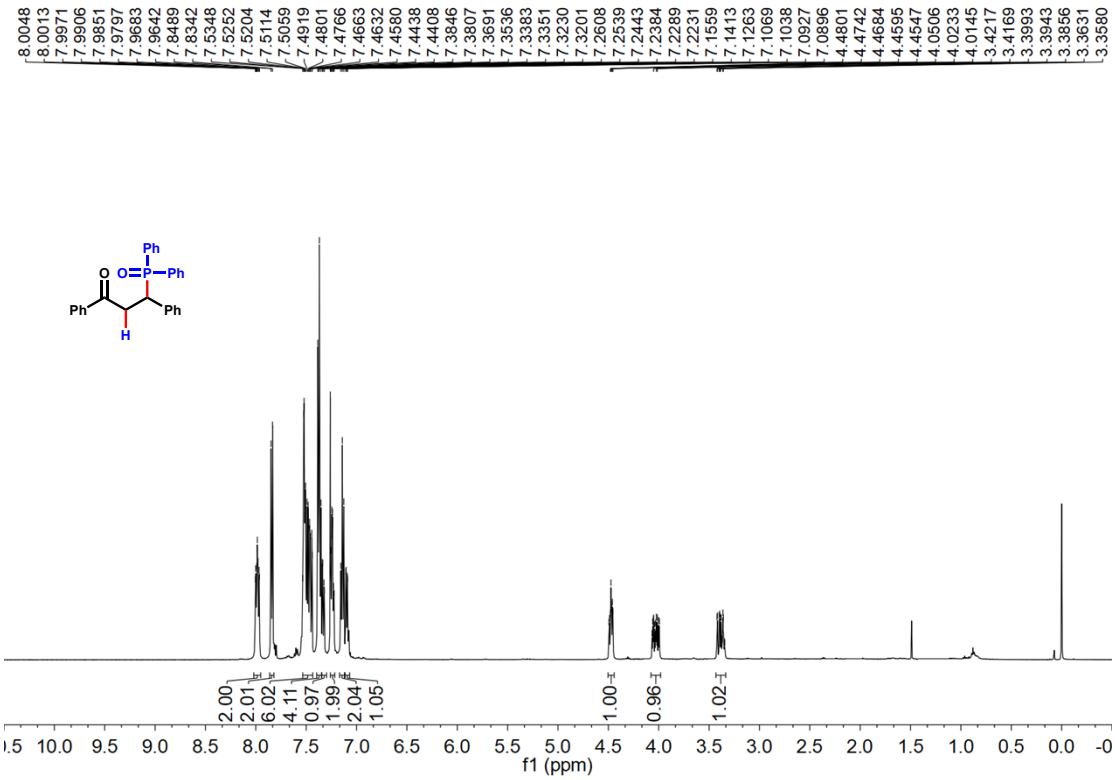


(3,5-di-tert-butyl-4-hydroxybenzyl)diphenylphosphine oxide (42c):[2] white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 48% isolated yield (50.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 4H), 7.52 – 7.47 (m, 2H), 7.44 – 7.39 (m, 4H), 6.74 (d, J = 2.2 Hz, 2H), 5.11 (s, 1H), 3.57 (d, J = 13.8 Hz, 2H), 1.28 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7 (d, $J_{C\text{-}P}$ = 3.5 Hz), 135.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.4 (d, $J_{C\text{-}P}$ = 97.9 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.4 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 126.9 (d, $J_{C\text{-}P}$ = 5.1 Hz), 121.2 (d, $J_{C\text{-}P}$ = 7.8 Hz), 38.1 (d, $J_{C\text{-}P}$ = 67.3 Hz), 34.1, 30.1.

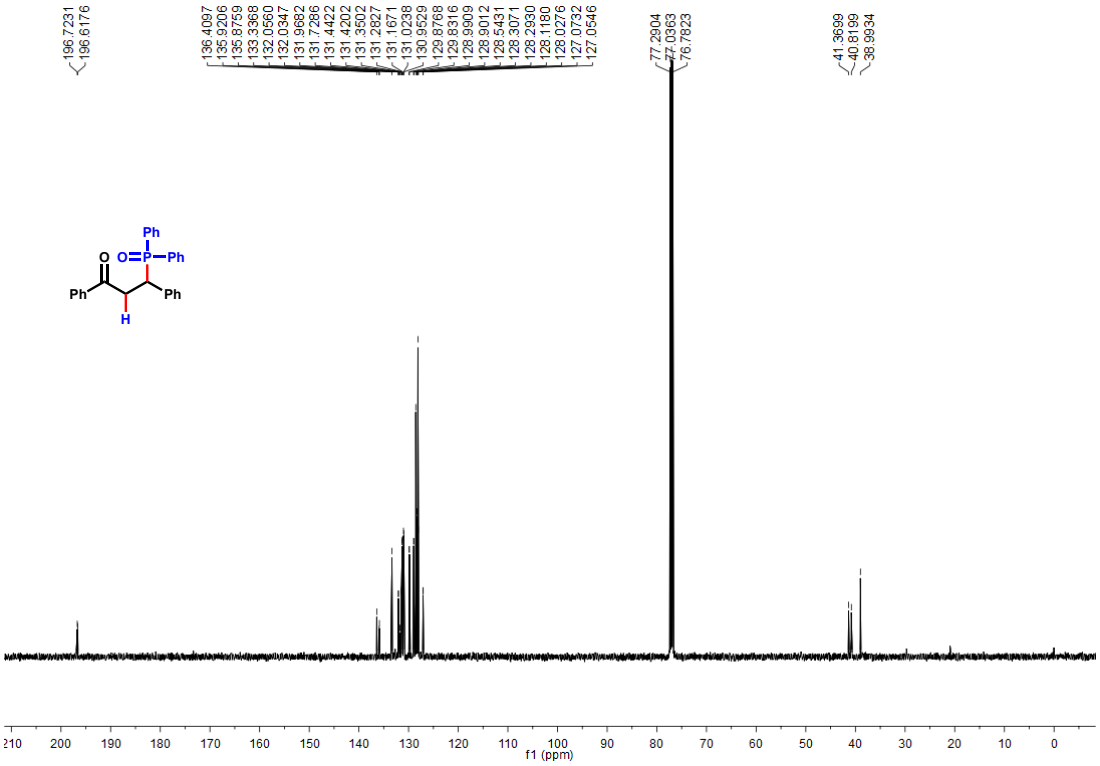
7. Copies of product NMR Spectra

1c

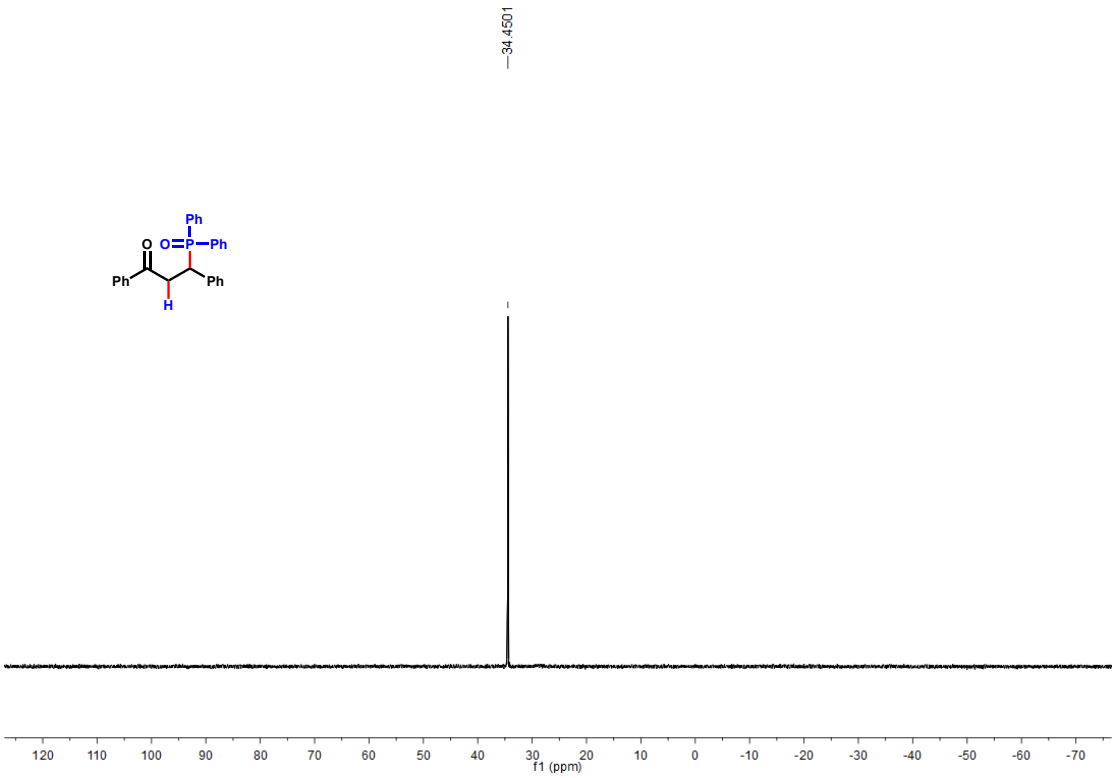
^{1}H NMR



^{13}C NMR

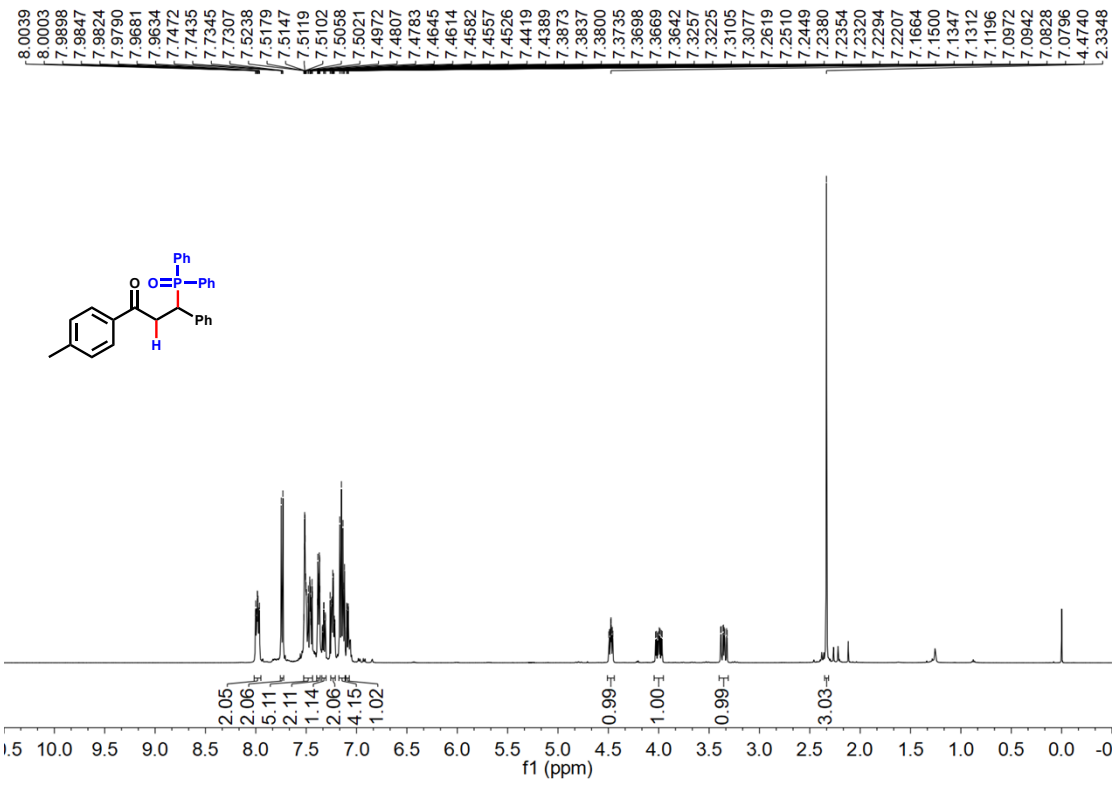


^{31}P NMR

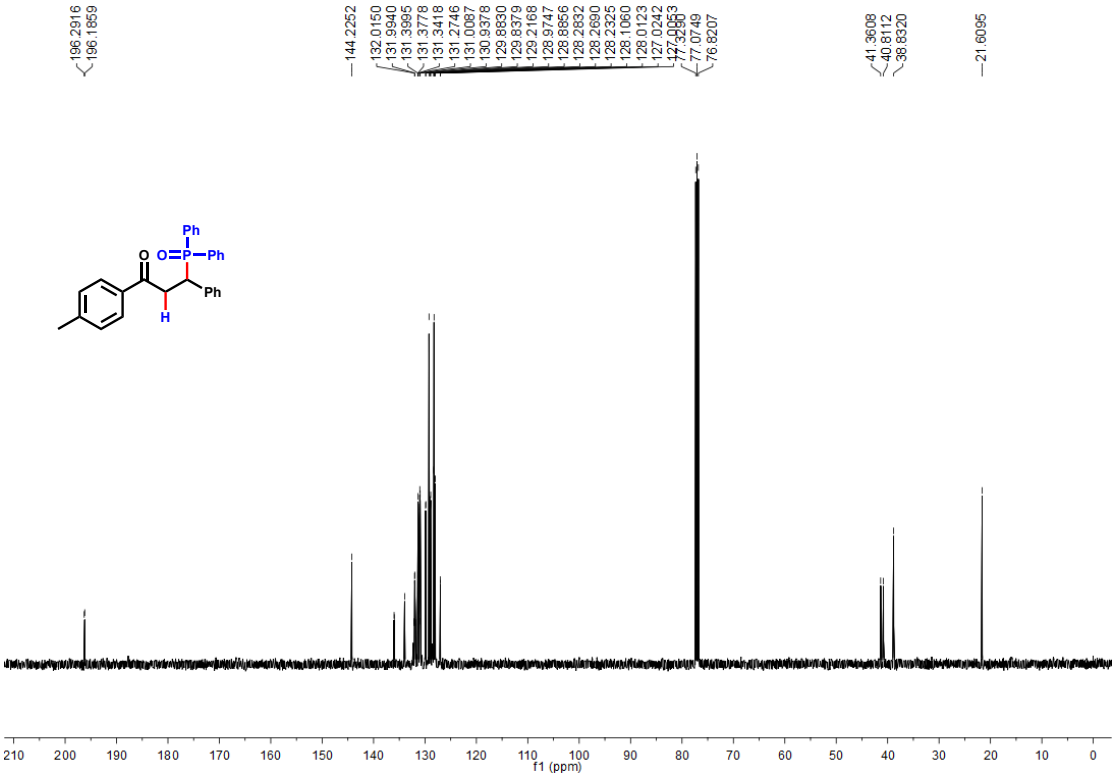


2c

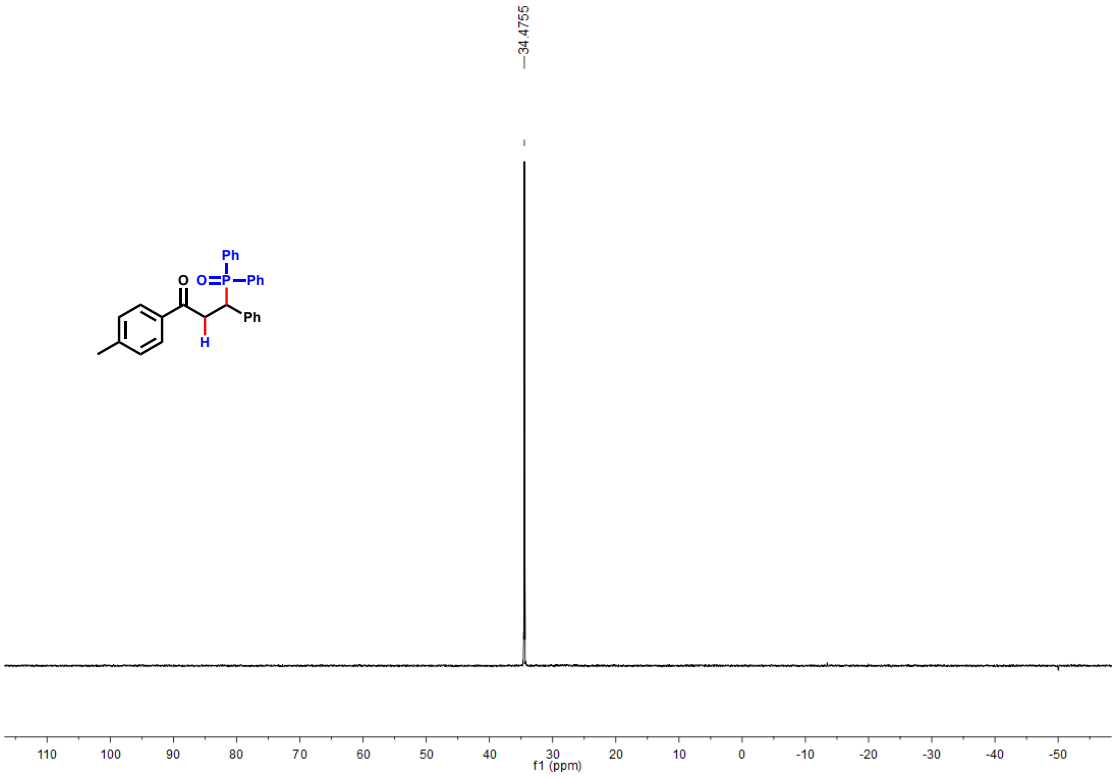
^{1}H NMR



^{13}C NMR

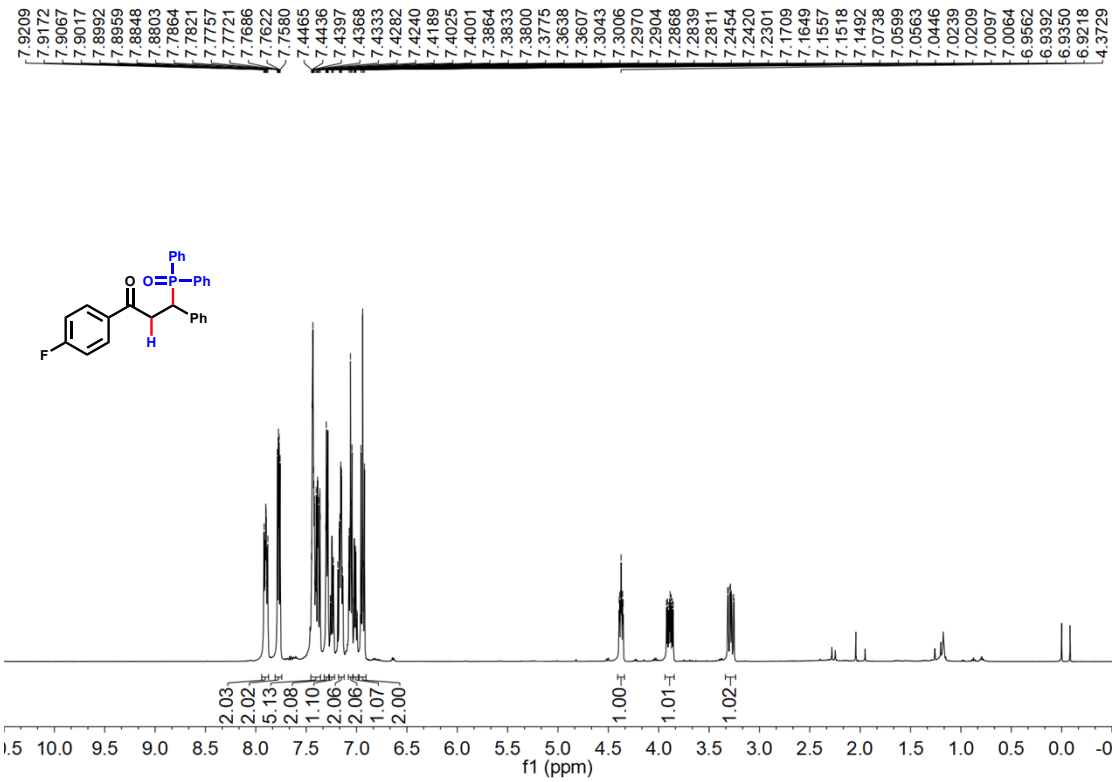


^{31}P NMR

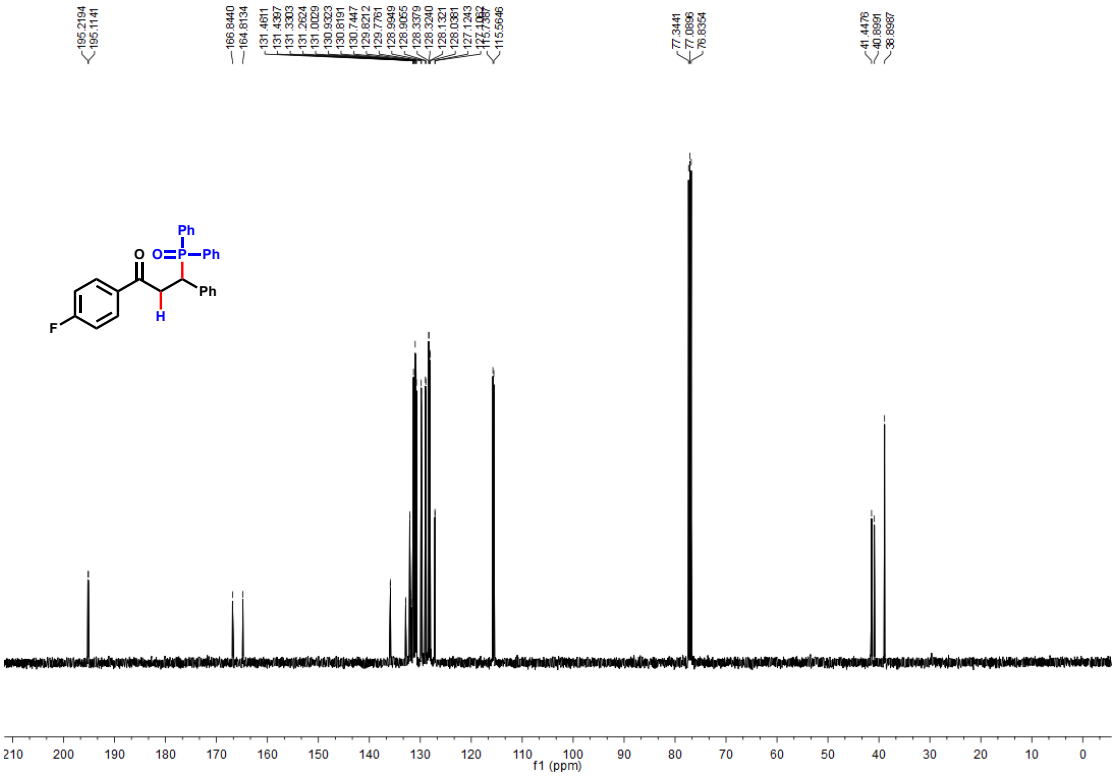


3c

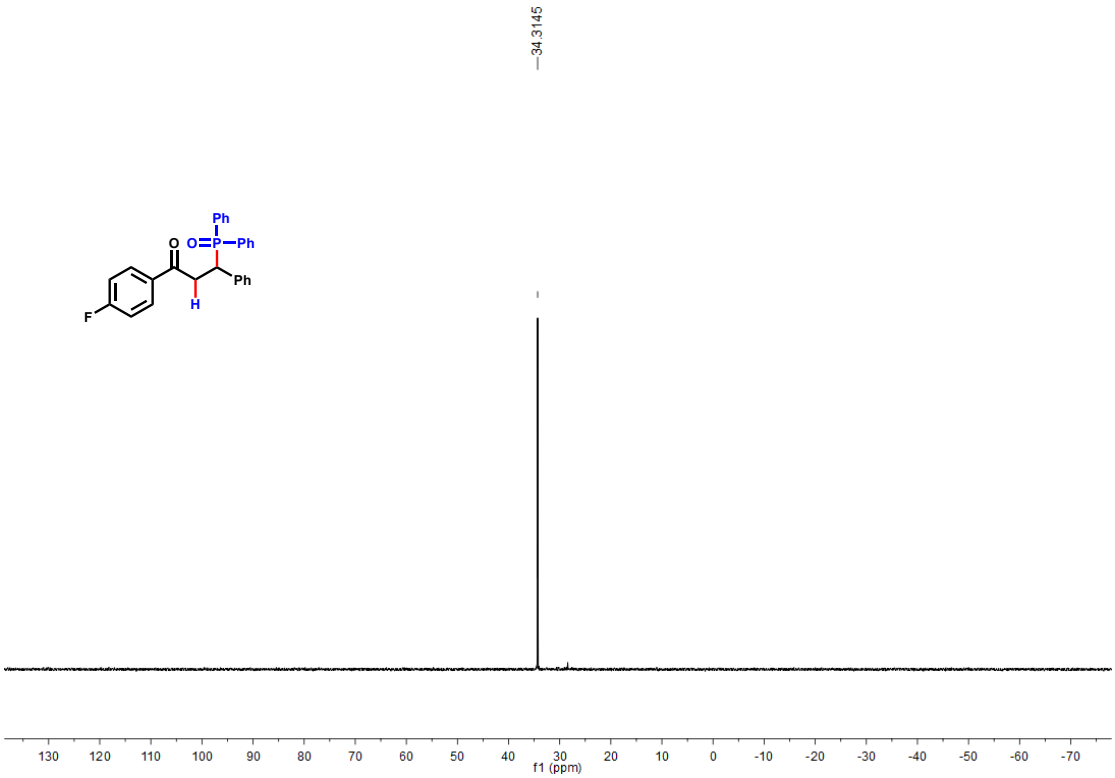
^{1}H NMR



^{13}C NMR

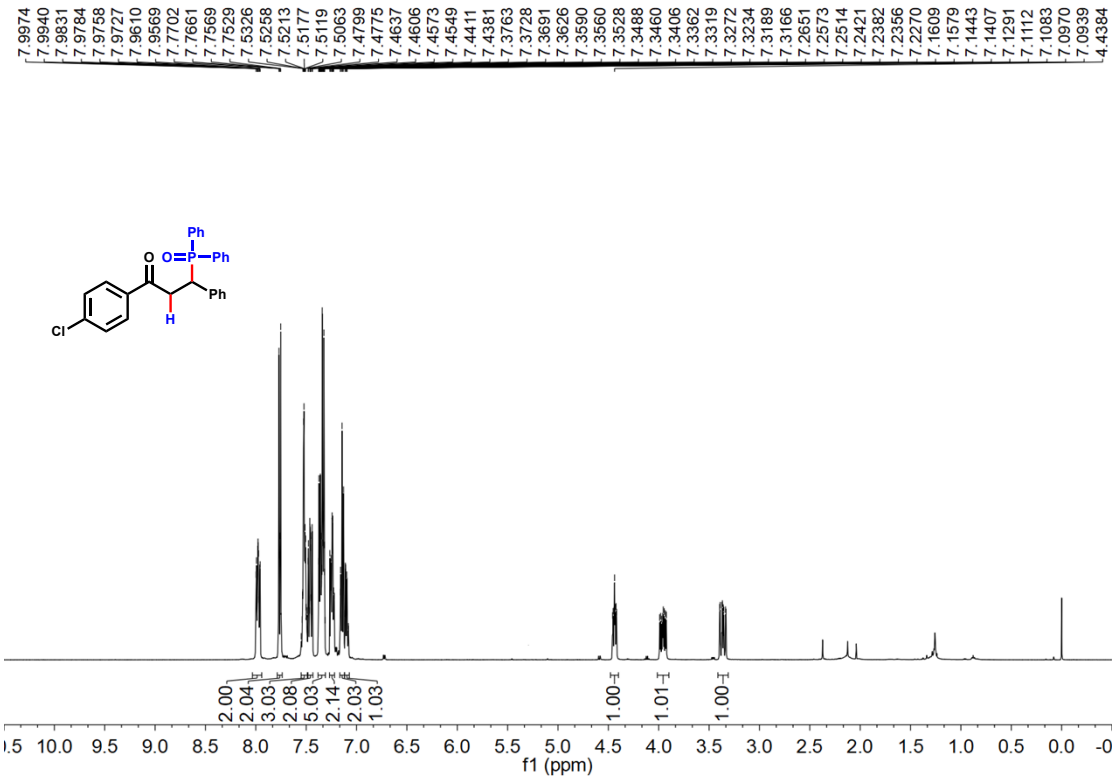


^{31}P NMR

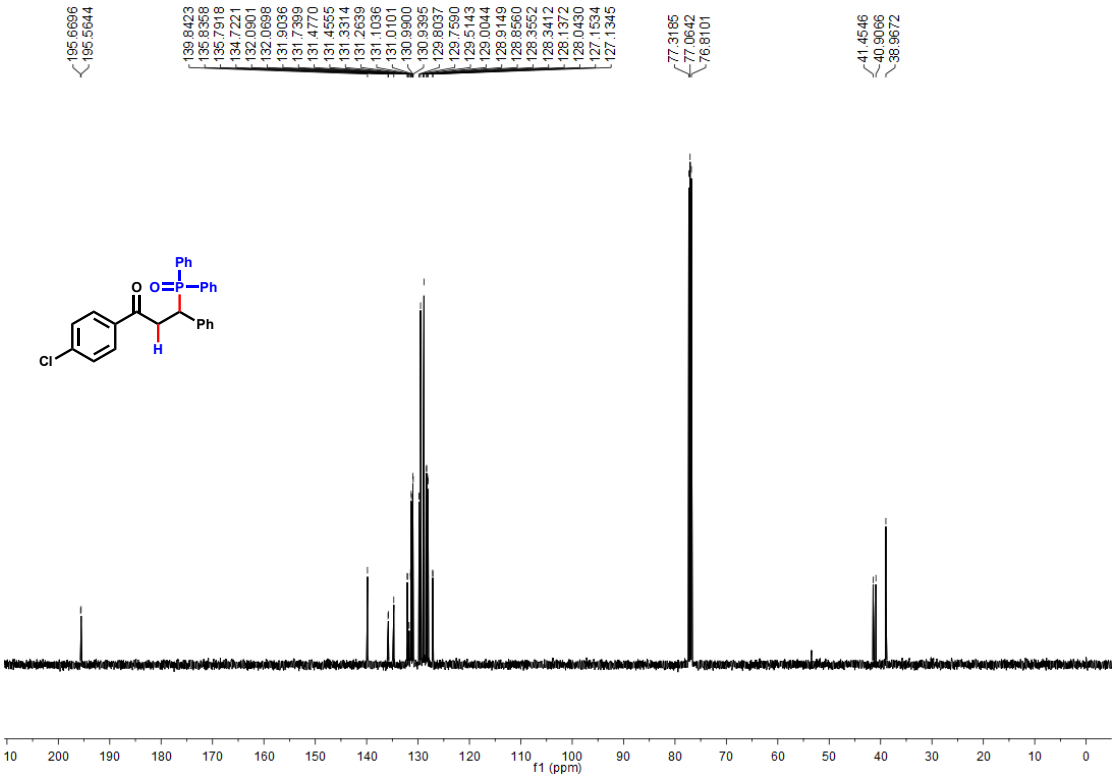


4c

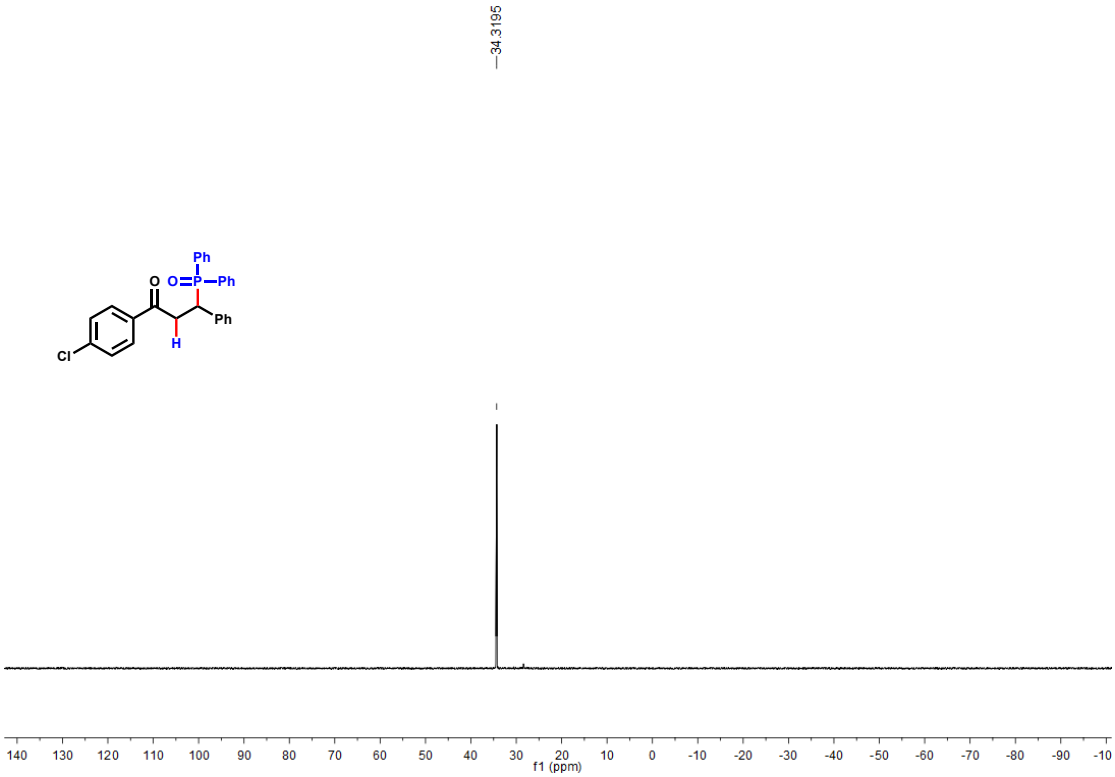
[1]H NMR



[13]C NMR

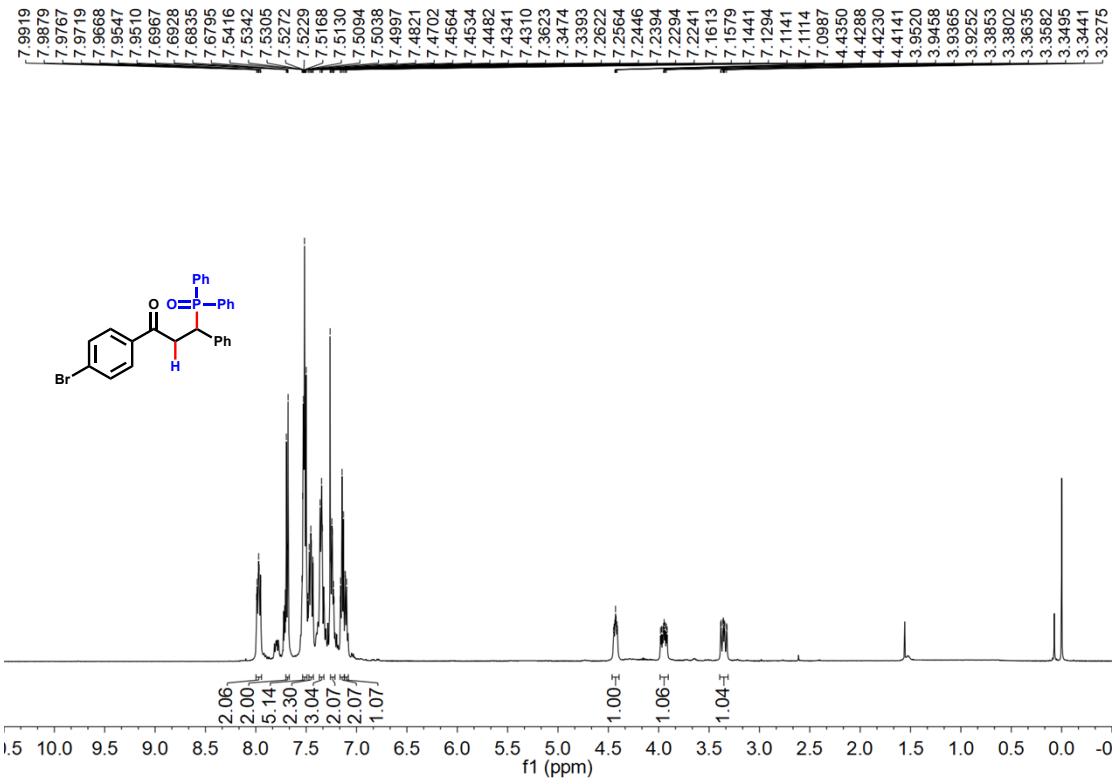


^{31}P NMR

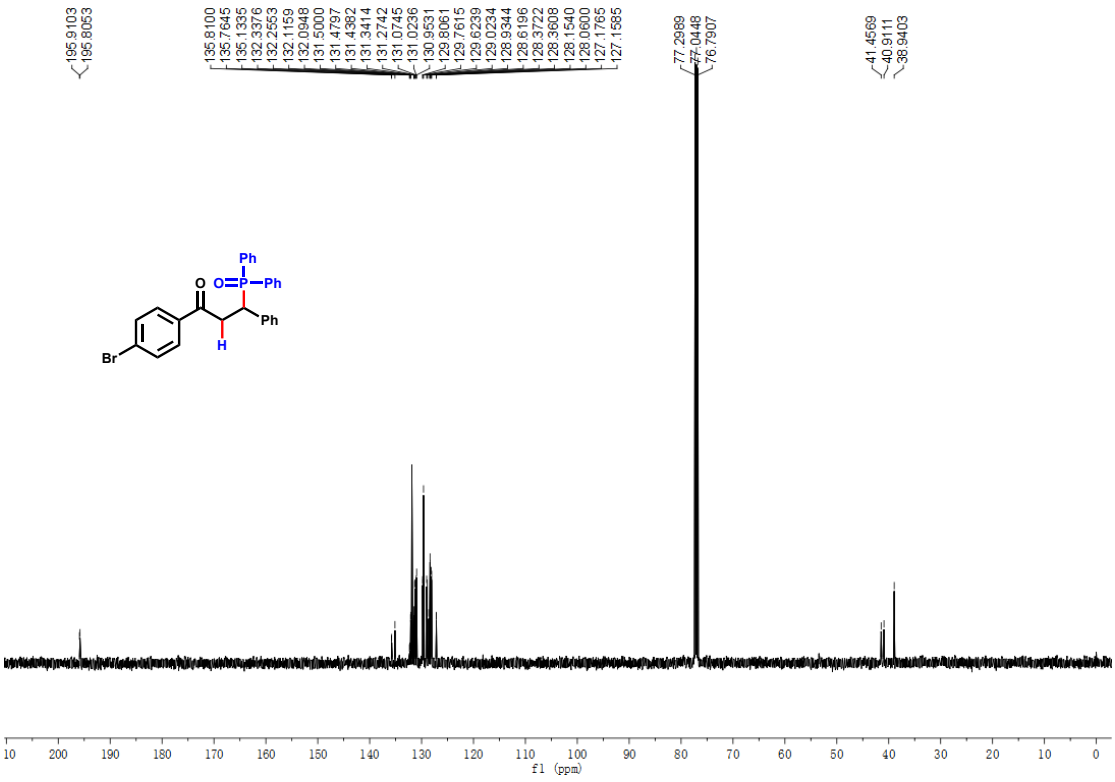


5c

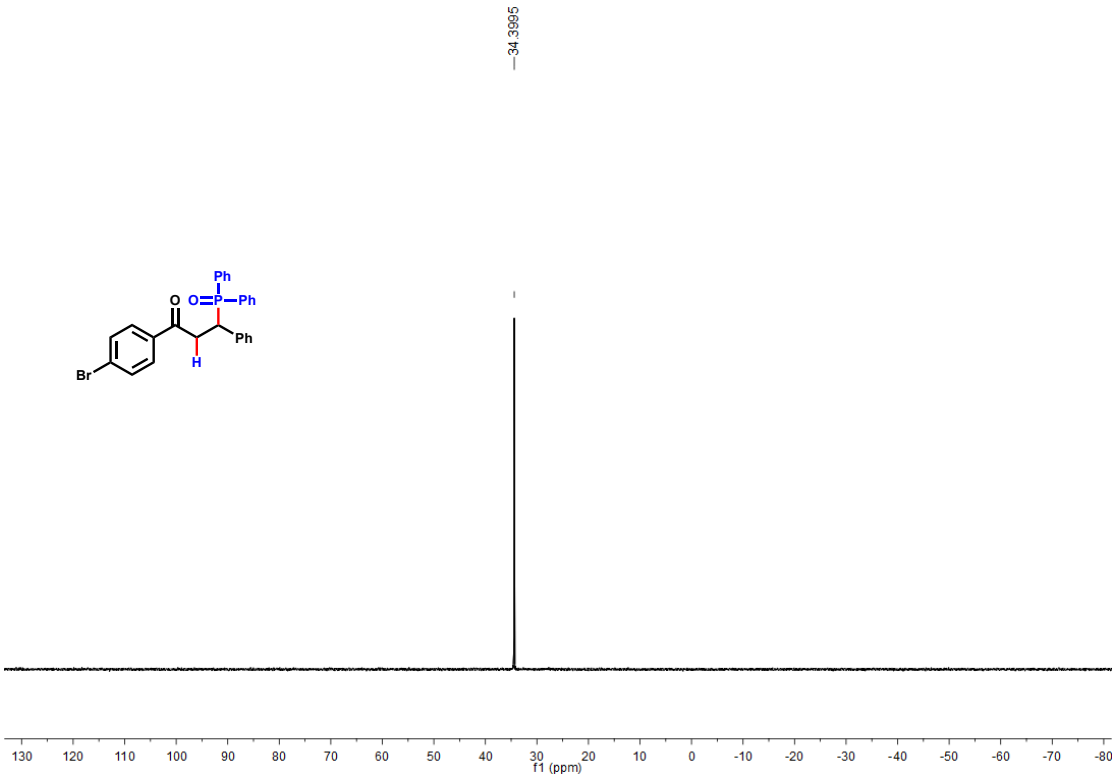
^{1}H NMR



^{13}C NMR

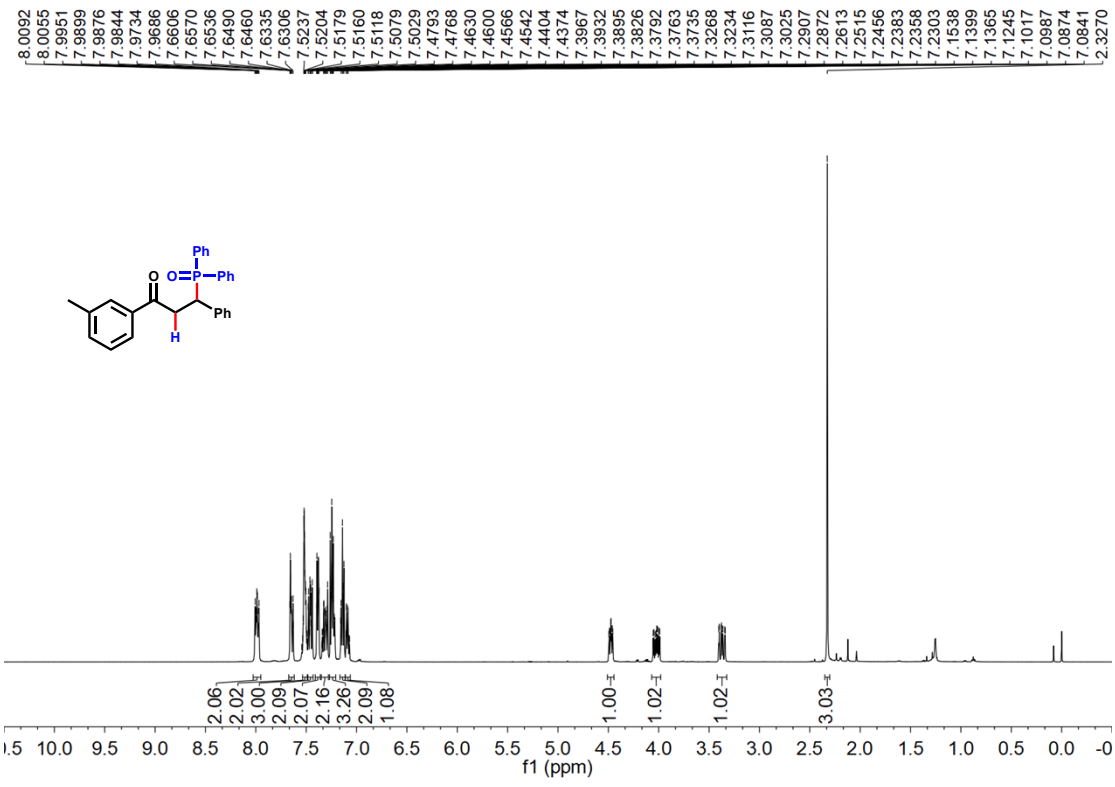


^{31}P NMR

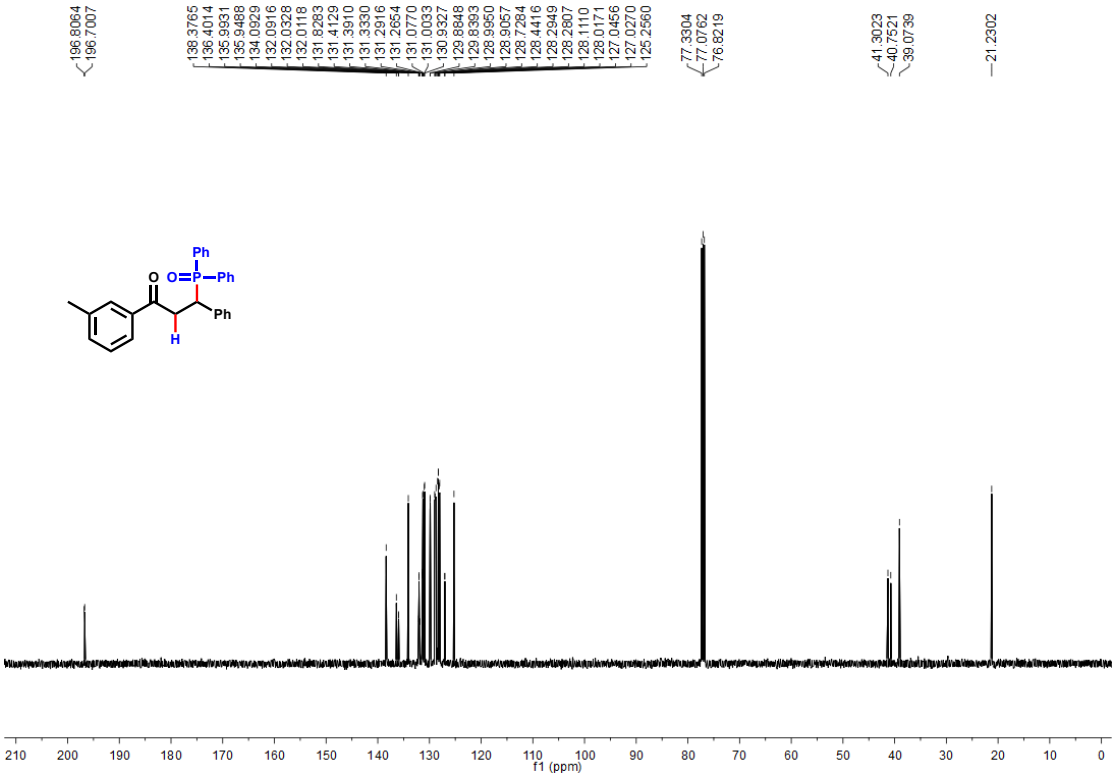

34.3995
Ph
O
O=P–Ph
Ph
H
Br
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

6c

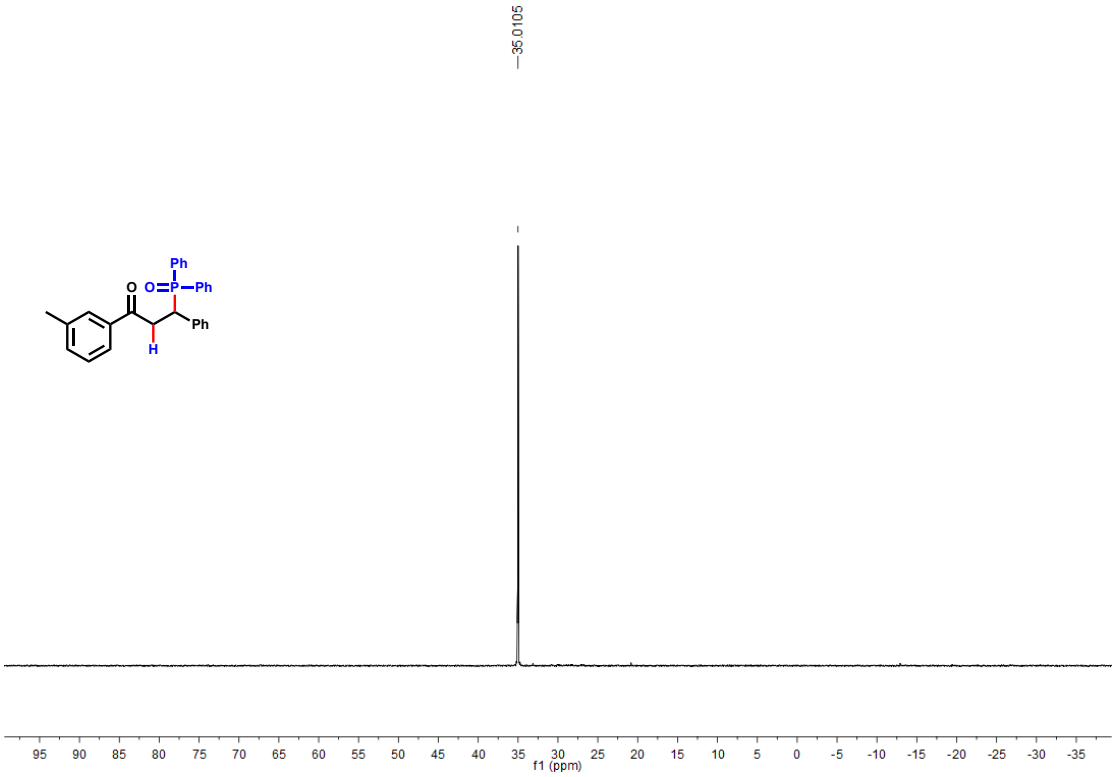
^{1}H NMR


8.0092 8.0055 7.9951 7.9899 7.9876 7.9844 7.9734 7.9686 7.6606 7.6570 7.6536 7.6490 7.6460 7.6335 7.6306 7.5237 7.5204 7.5179 7.5160 7.5118 7.5079 7.5029 7.4793 7.4768 7.4630 7.4600 7.4566 7.4542 7.4404 7.4374 7.3967 7.3932 7.3895 7.3826 7.3792 7.3763 7.3735 7.3268 7.3234 7.3116 7.3087 7.3025 7.2907 7.2872 7.2613 7.2515 7.2456 7.2383 7.2358 7.2303 7.1538 7.1399 7.1365 7.1245 7.1017 7.0987 7.0874 7.0841 2.3270
Ph
O
O=P–Ph
Ph
H
2.06 2.02 3.00 2.09 2.07 2.16 3.26 2.09 1.08 1.00 1.02 1.02 3.03
f1 (ppm)

^{13}C NMR

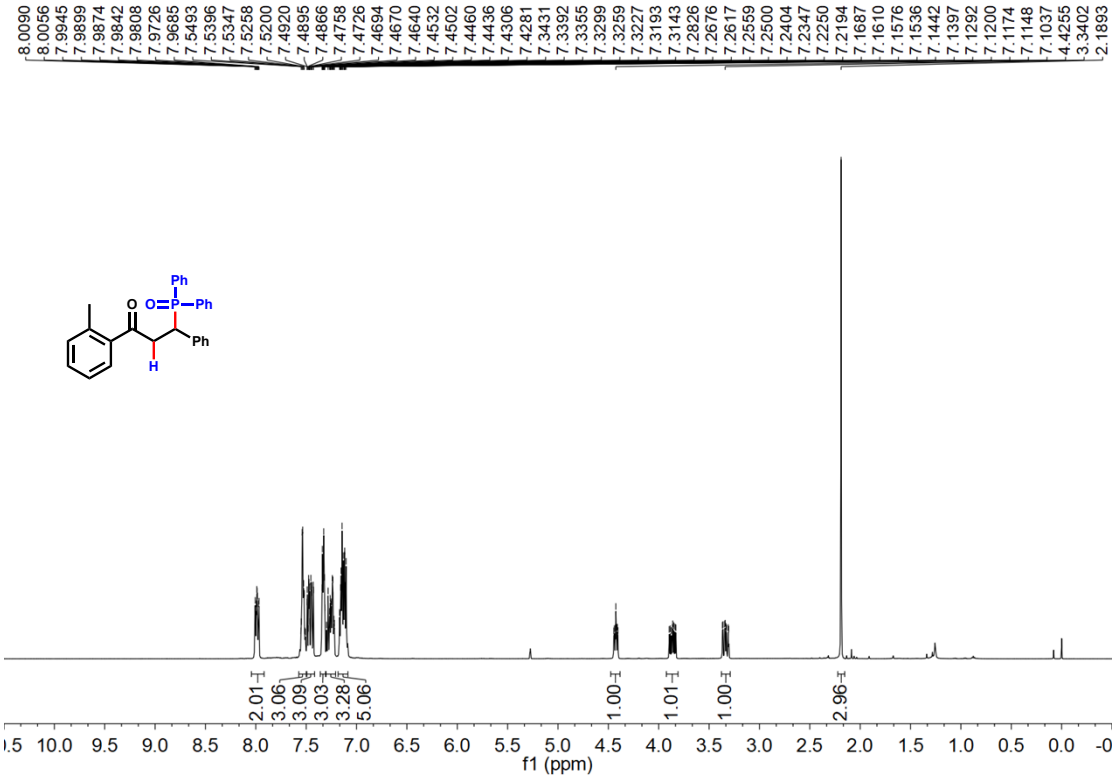


^{31}P NMR

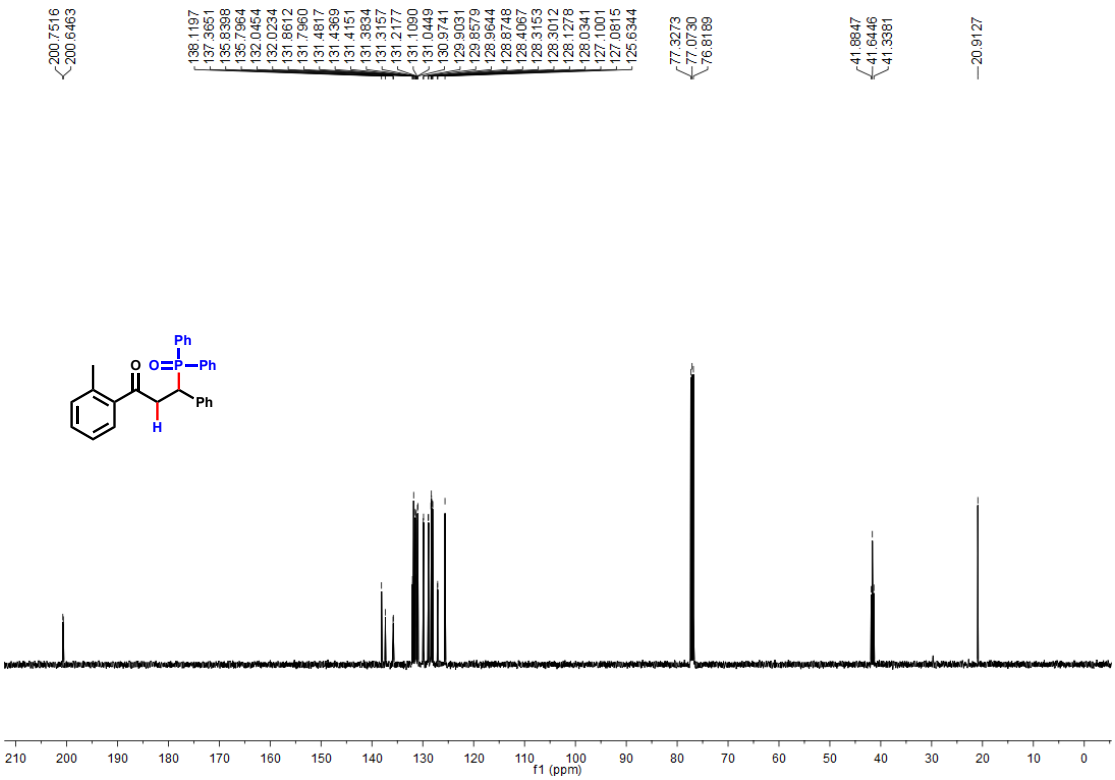


7c

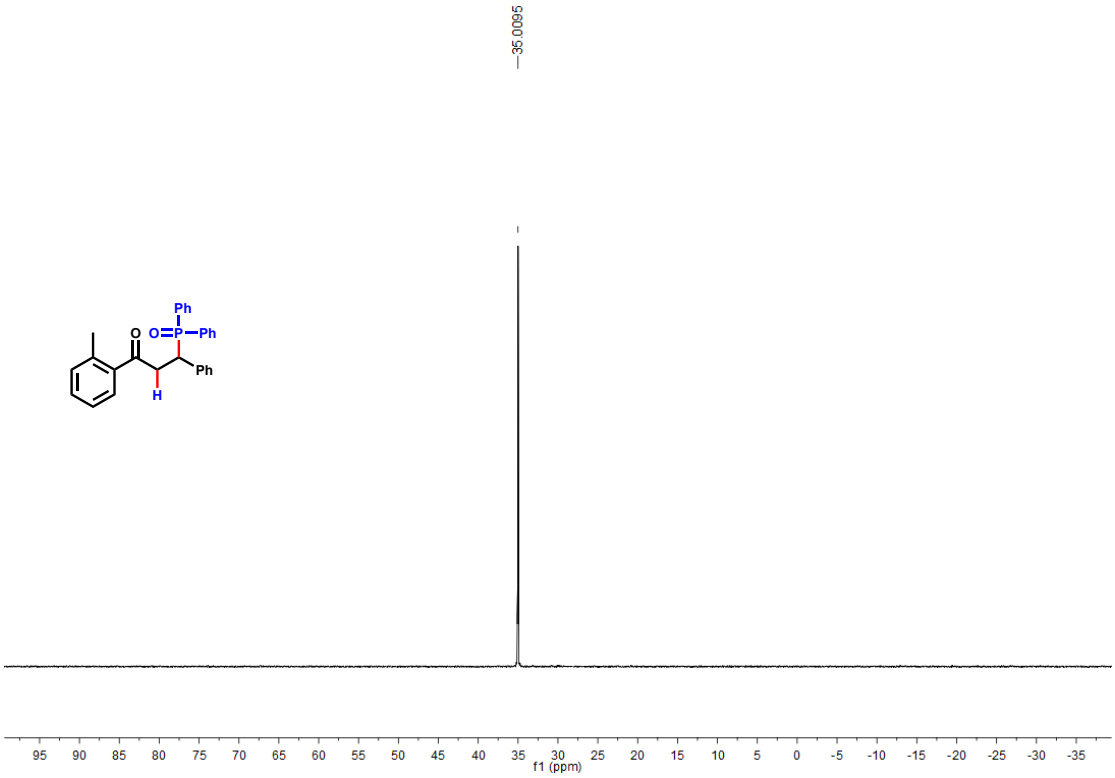
^{1}H NMR



^{13}C NMR

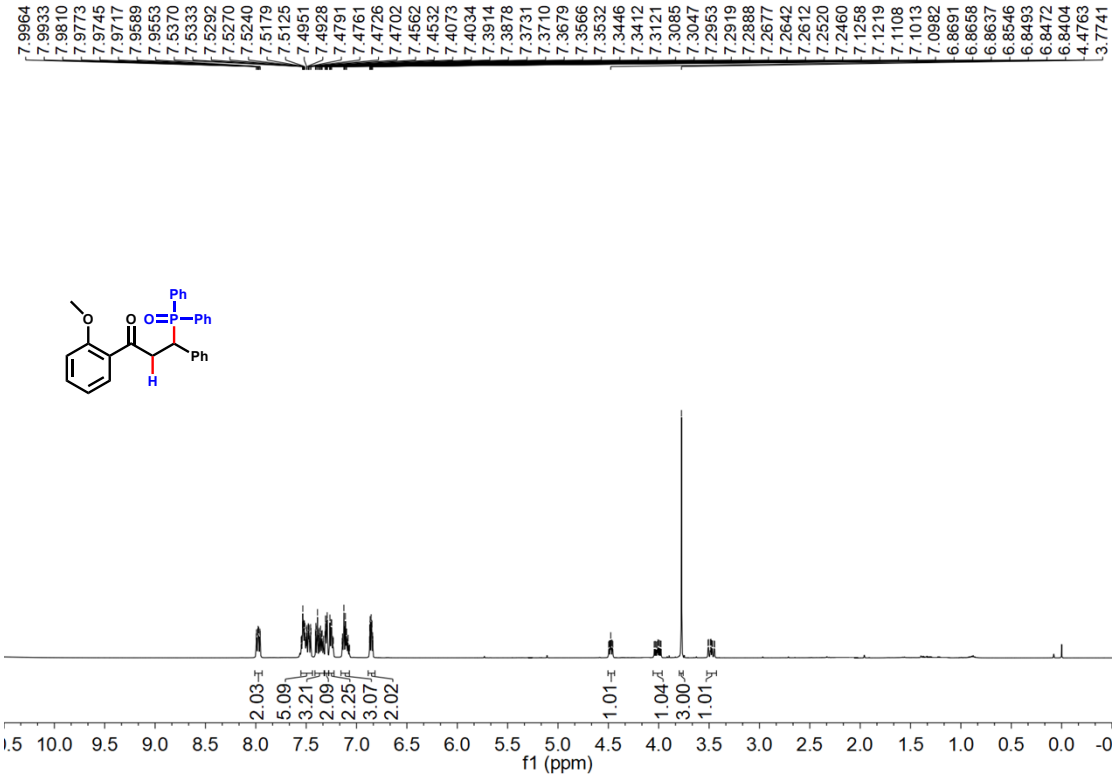


^{31}P NMR



8c

^{1}H NMR



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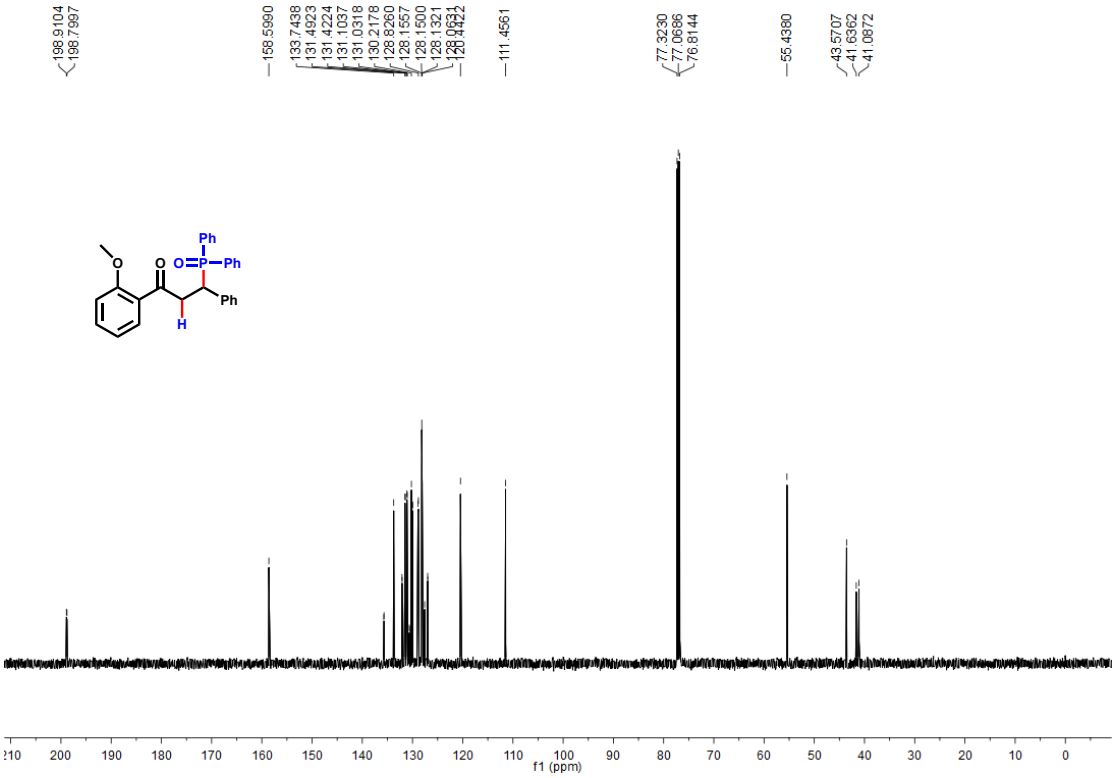

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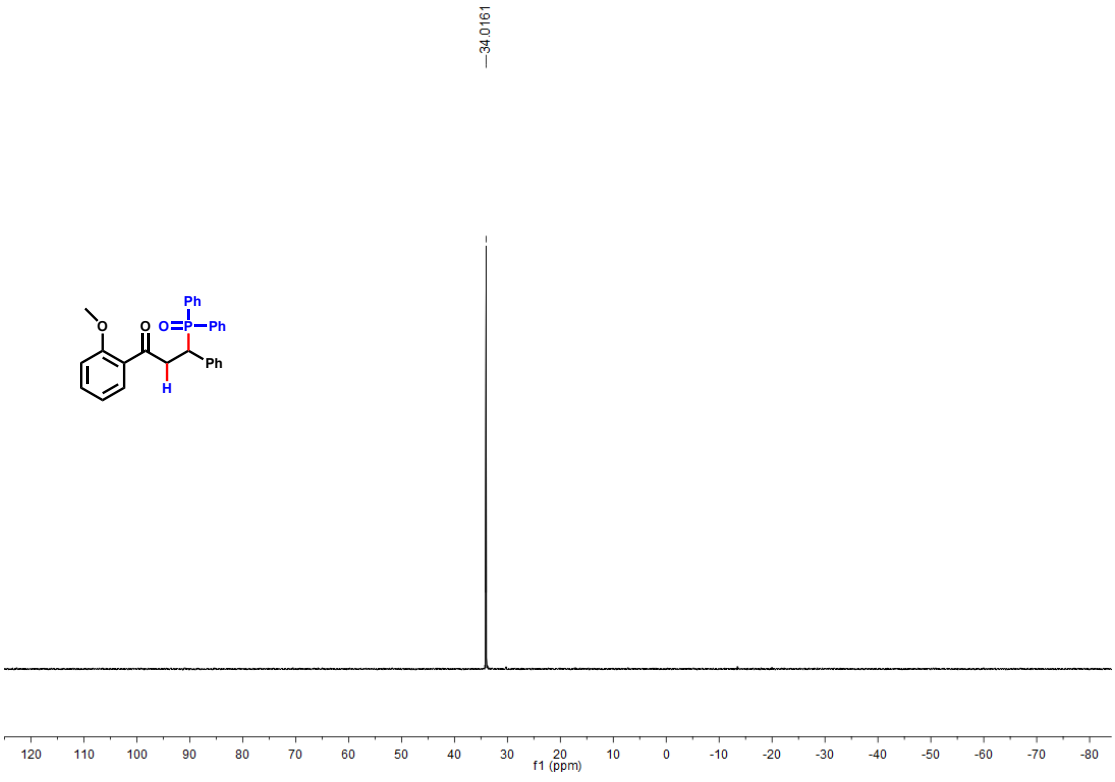
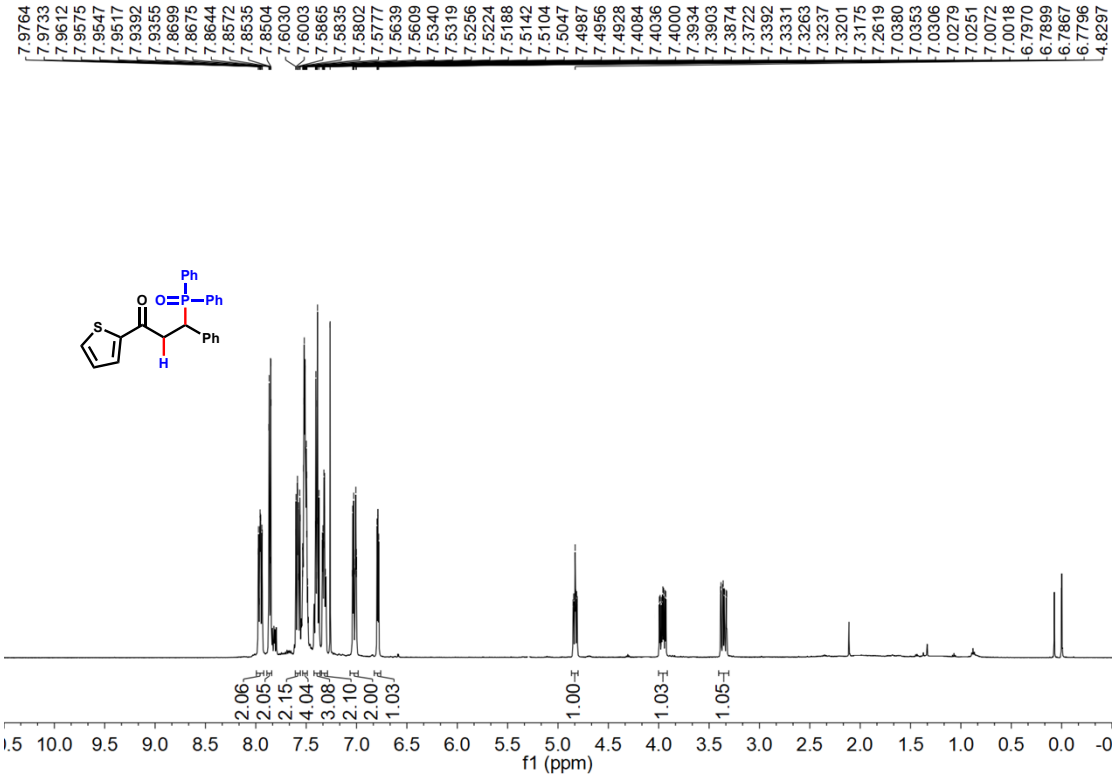
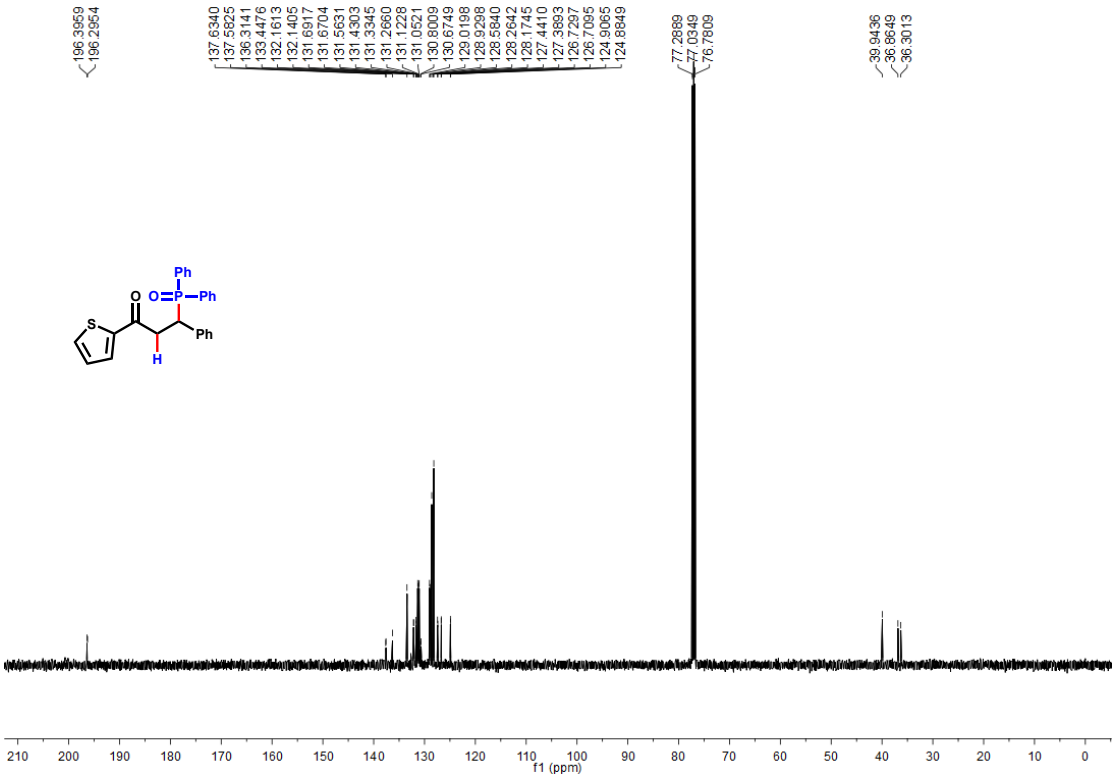


9c

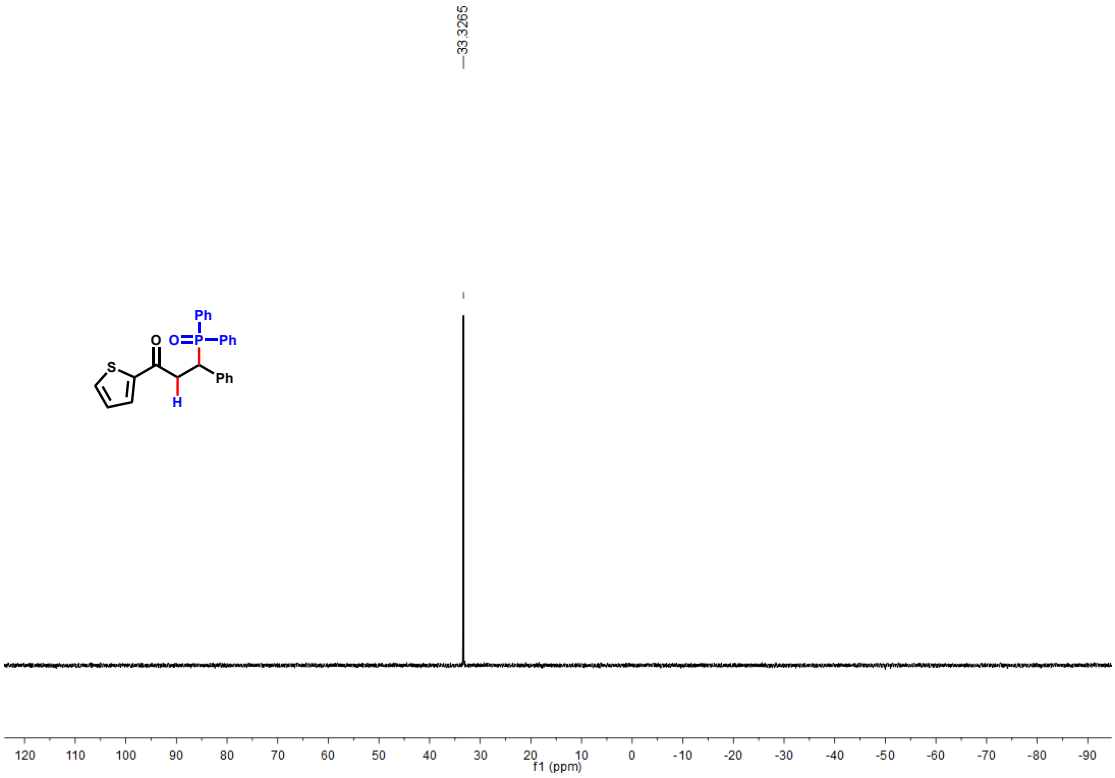
^{1}H NMR



^{13}C NMR

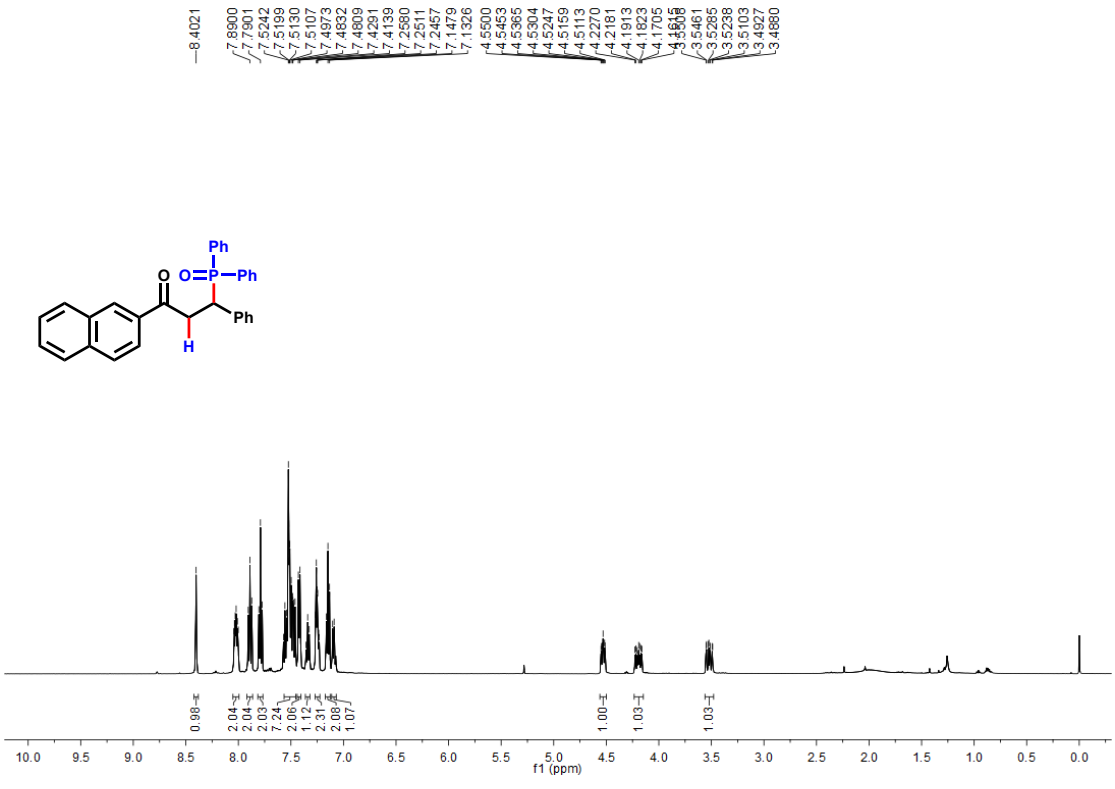


^{31}P NMR

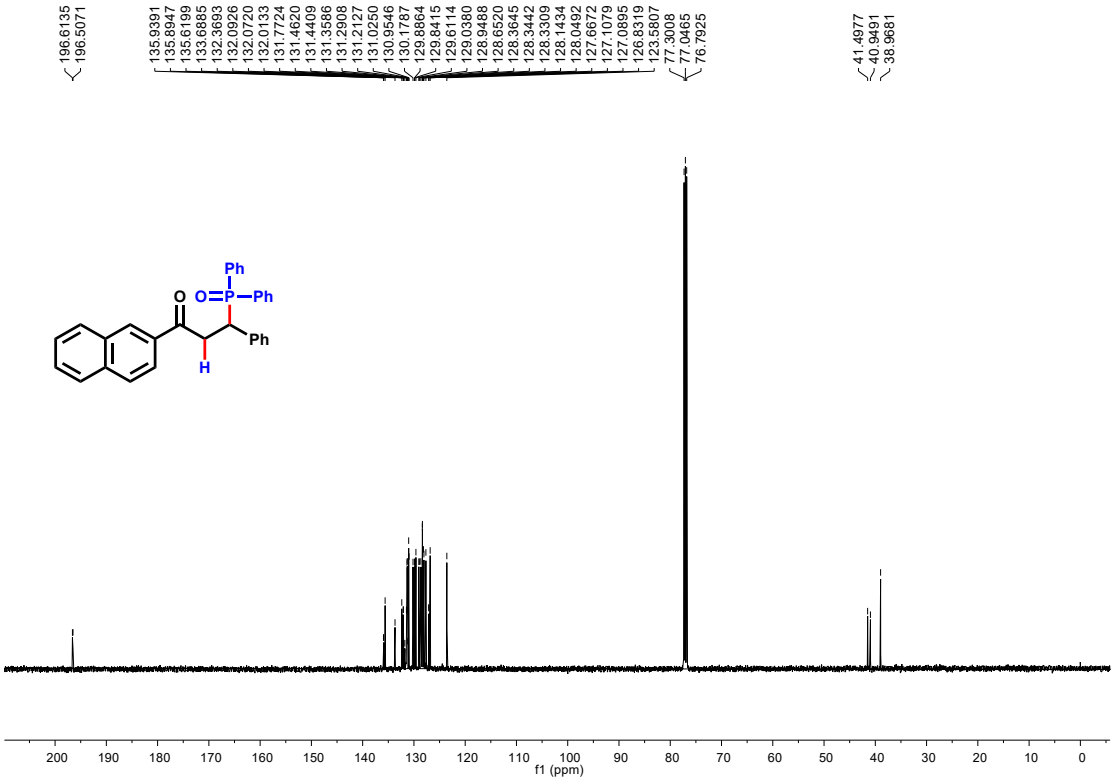


10c

^{1}H NMR



^{13}C NMR



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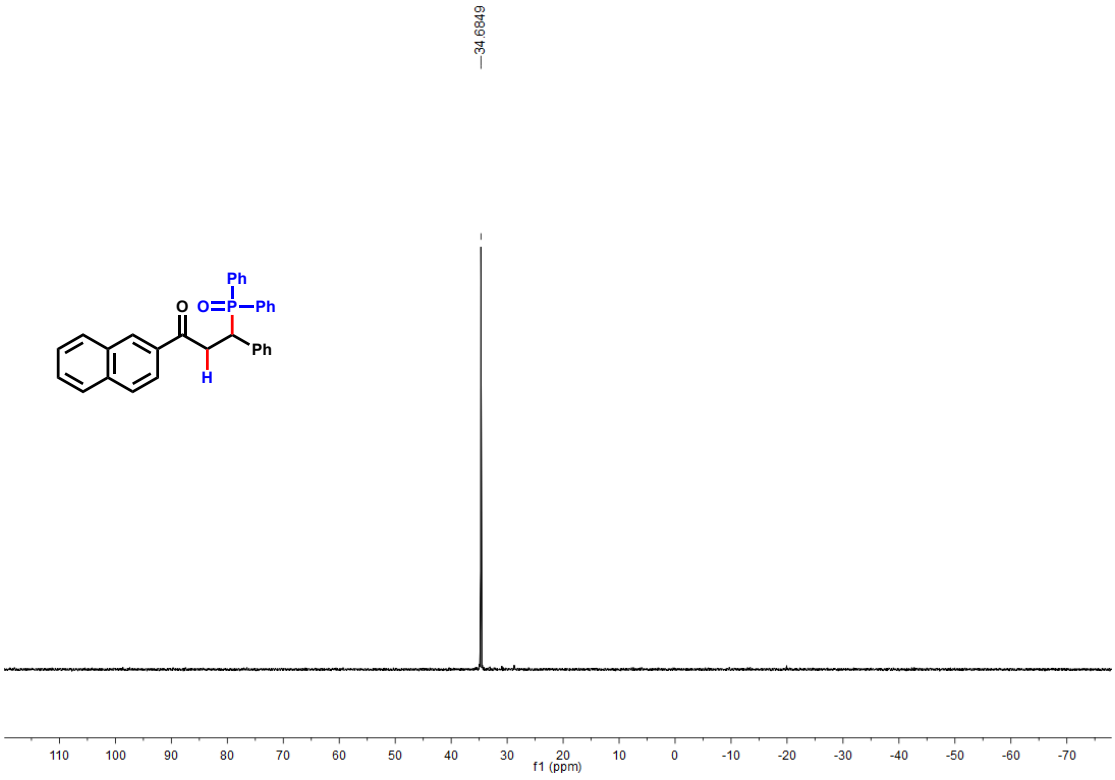
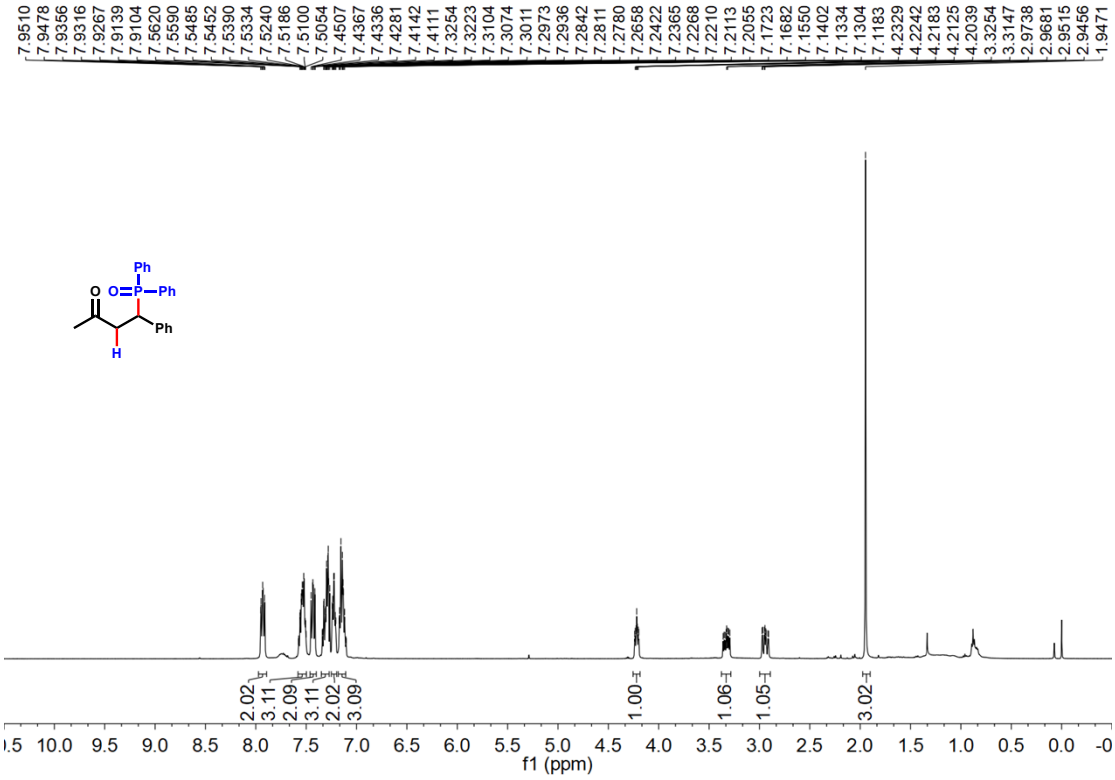
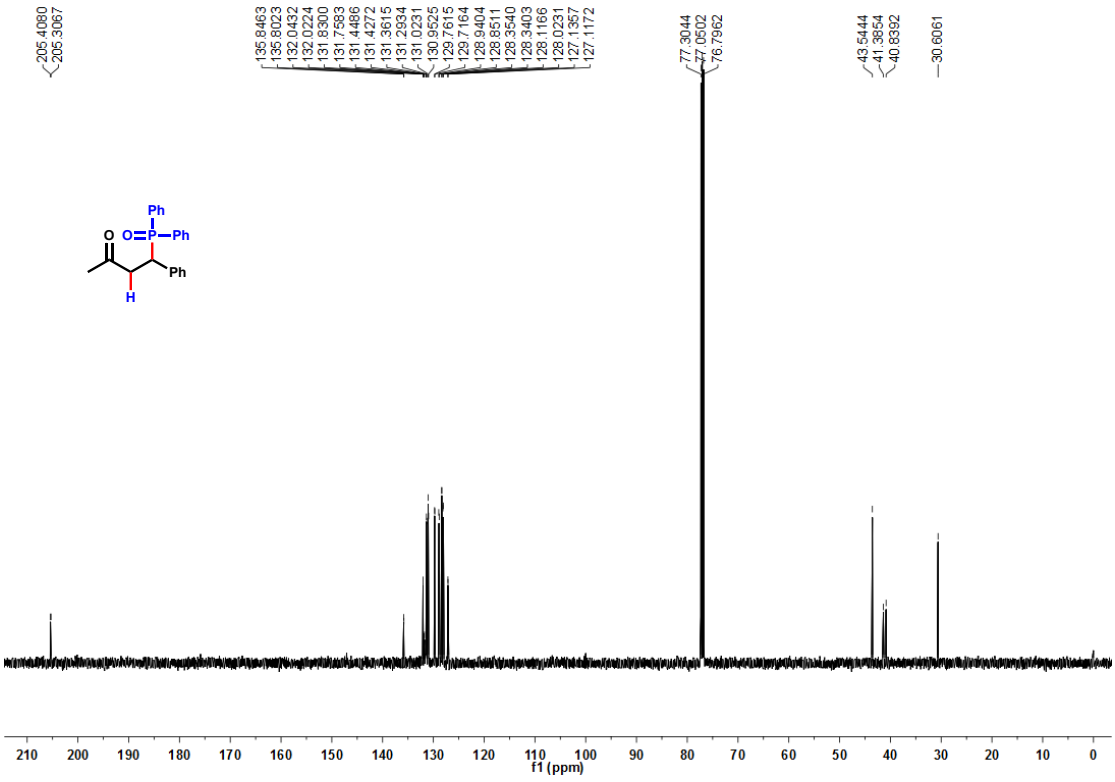


11c

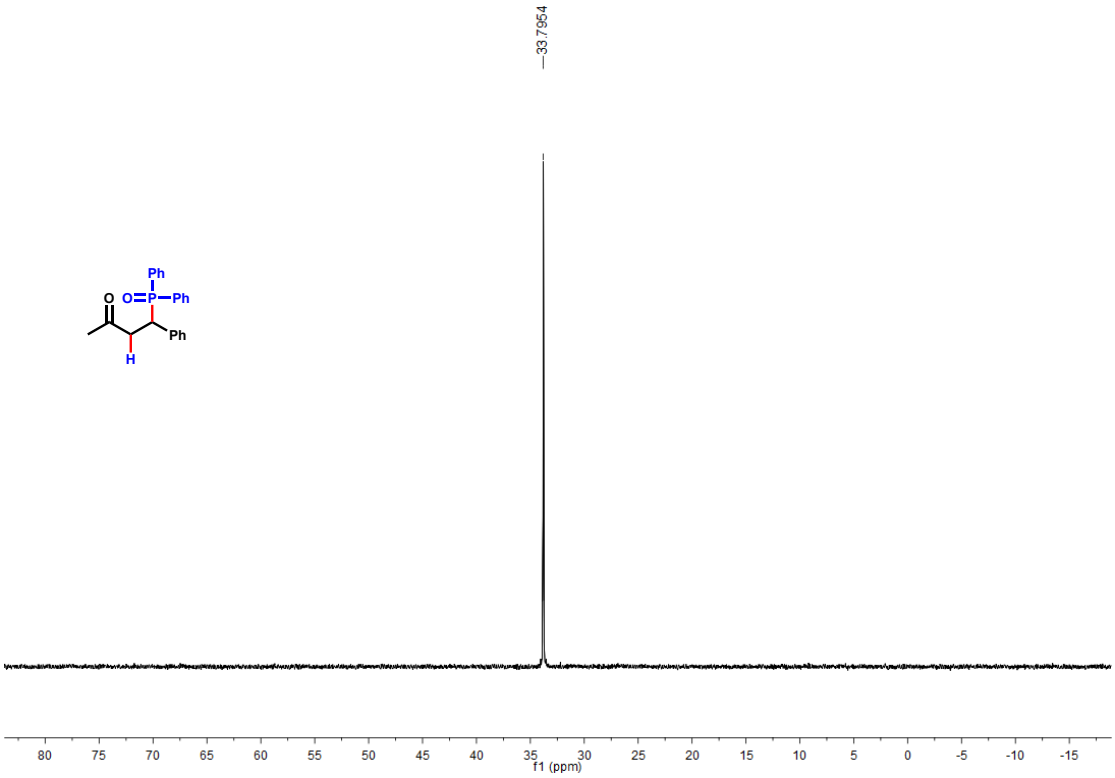
^{1}H NMR



^{13}C NMR

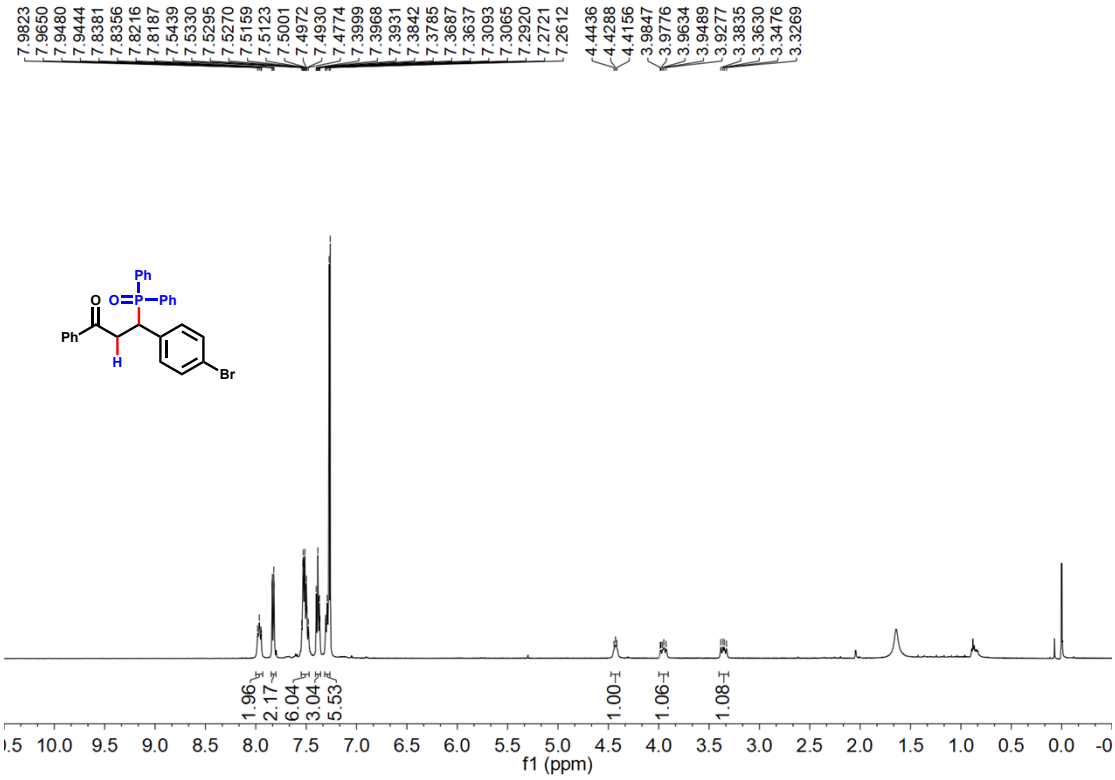


^{31}P NMR



12c

^{1}H NMR



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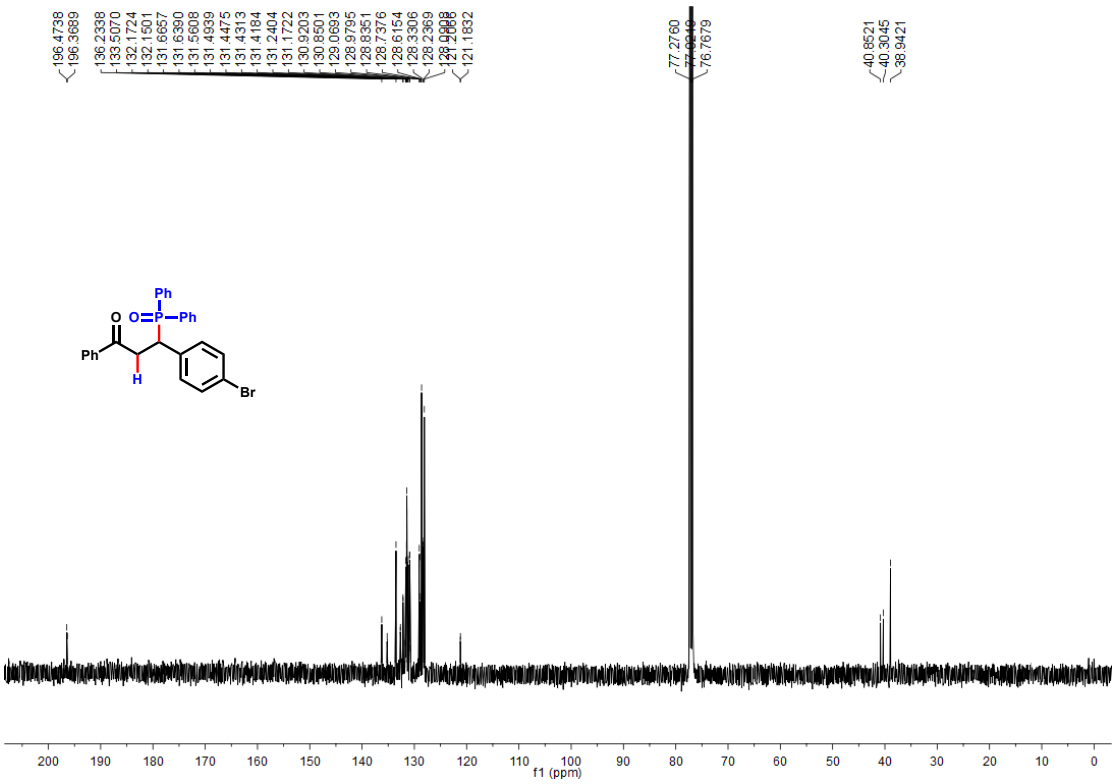

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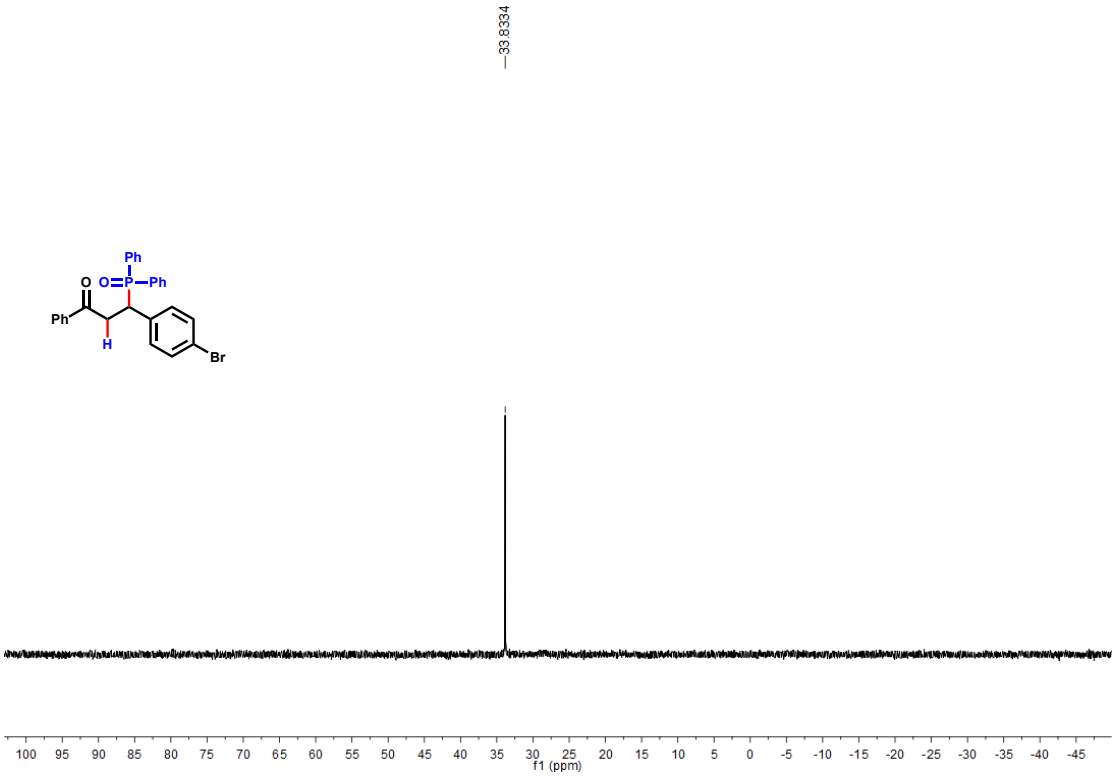

13c

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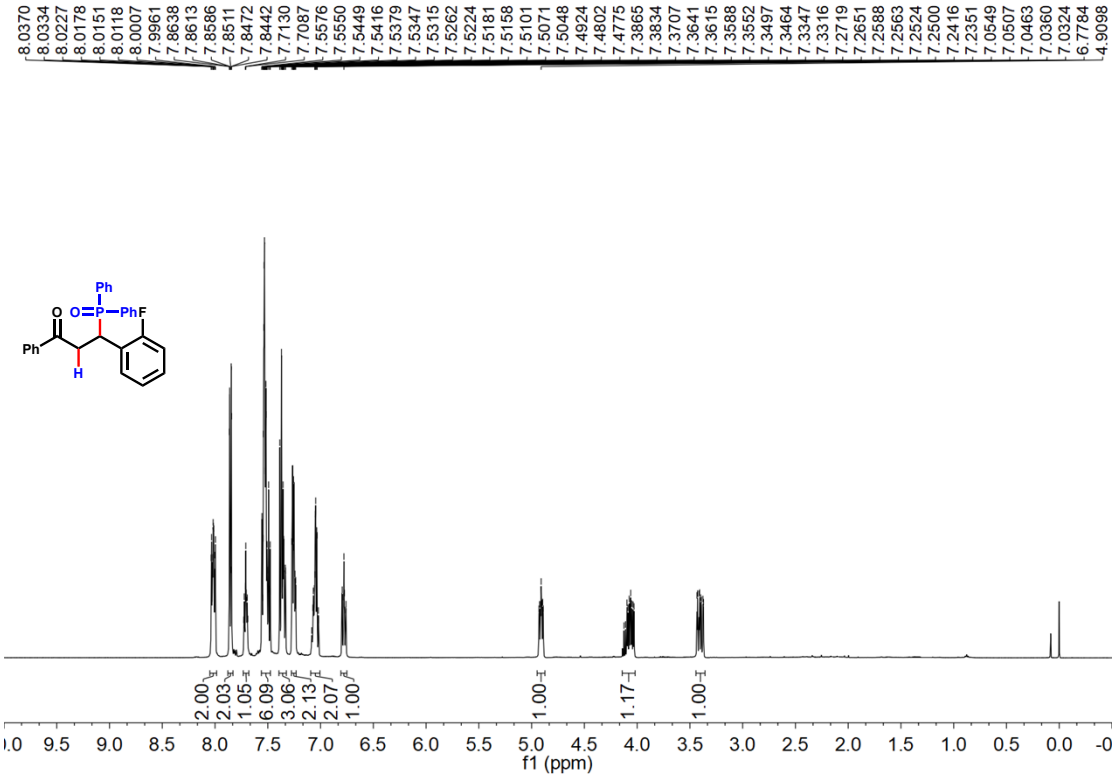

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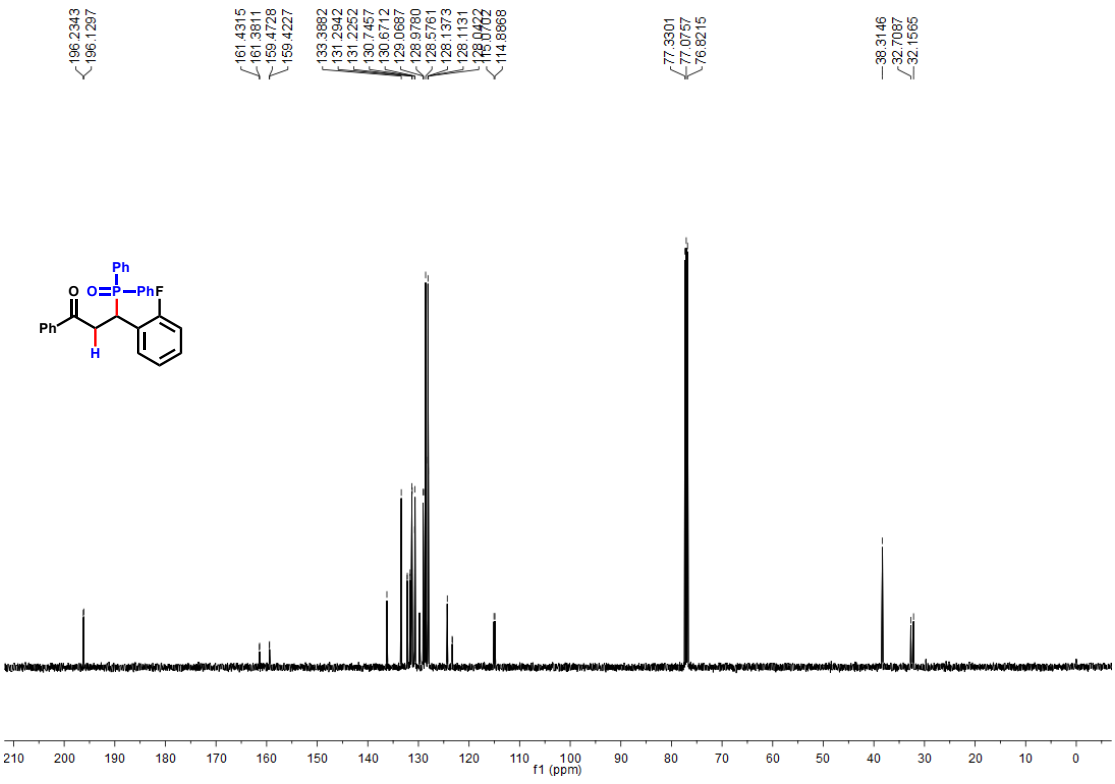

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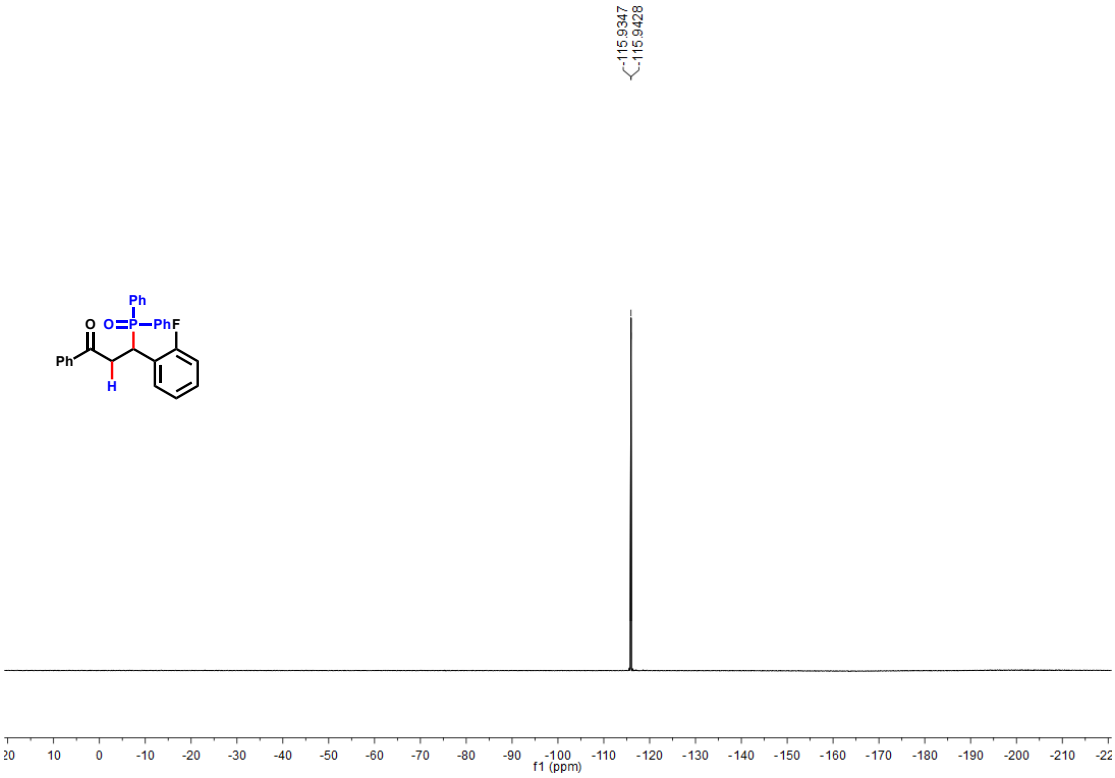
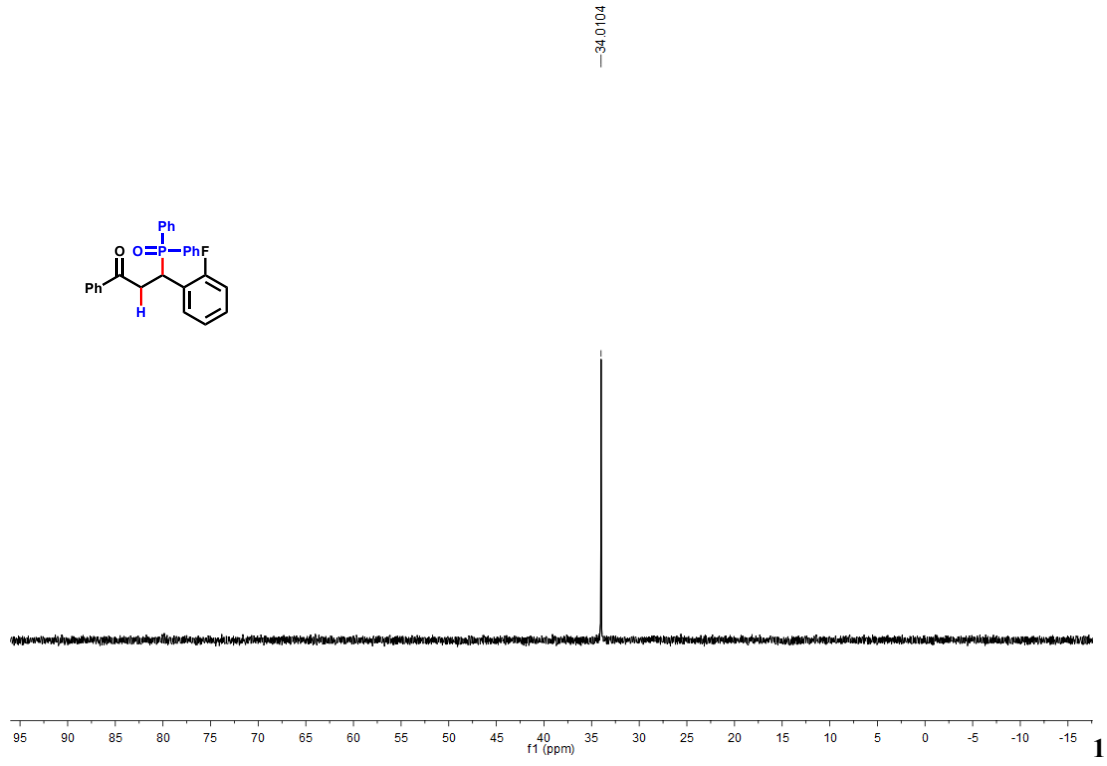


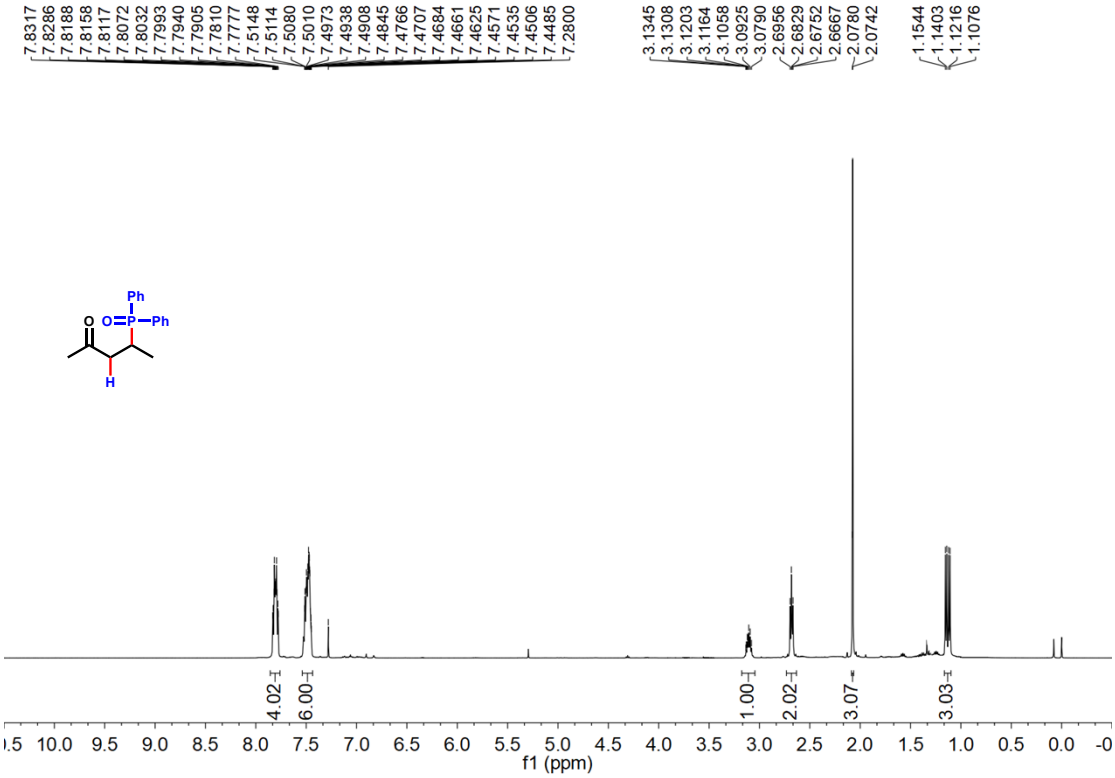
^{31}P NMR



1

4c

^{1}H NMR



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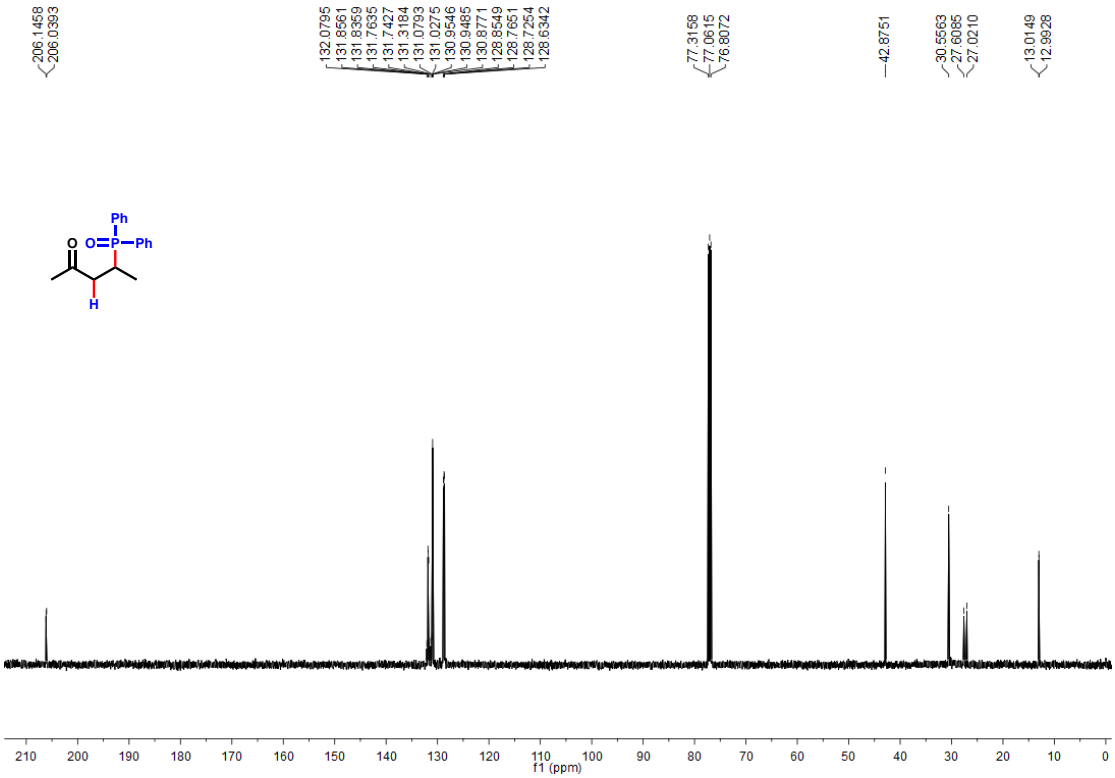

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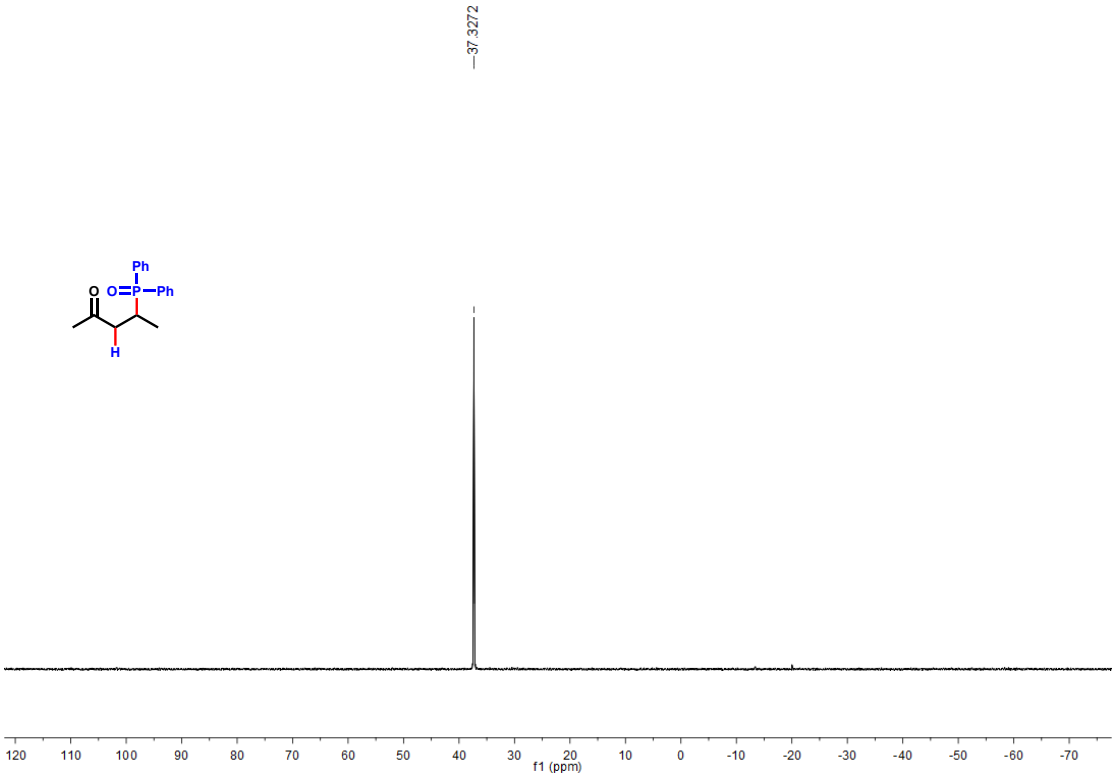
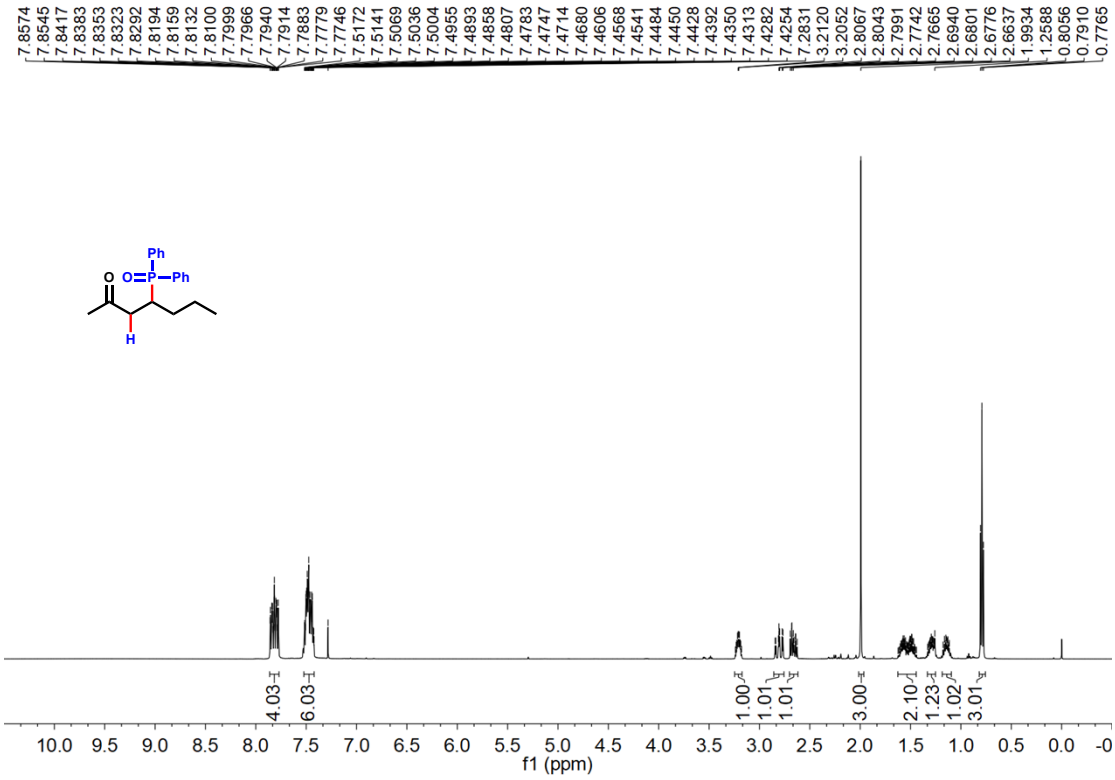
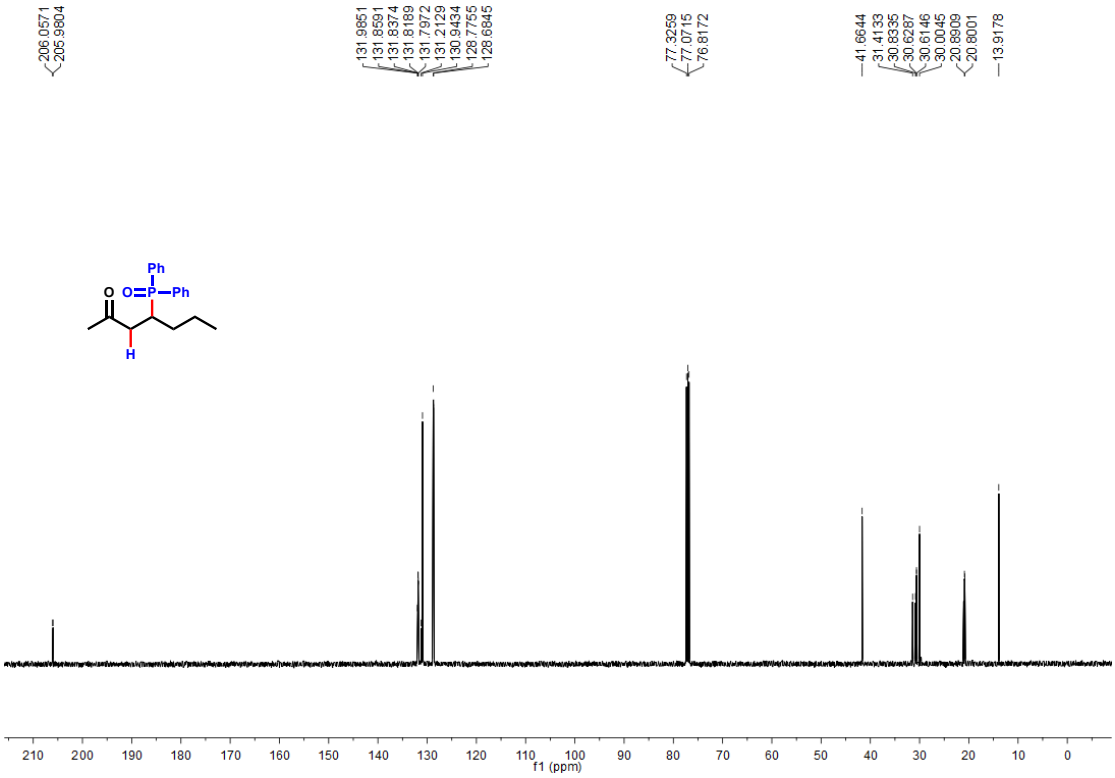


15c

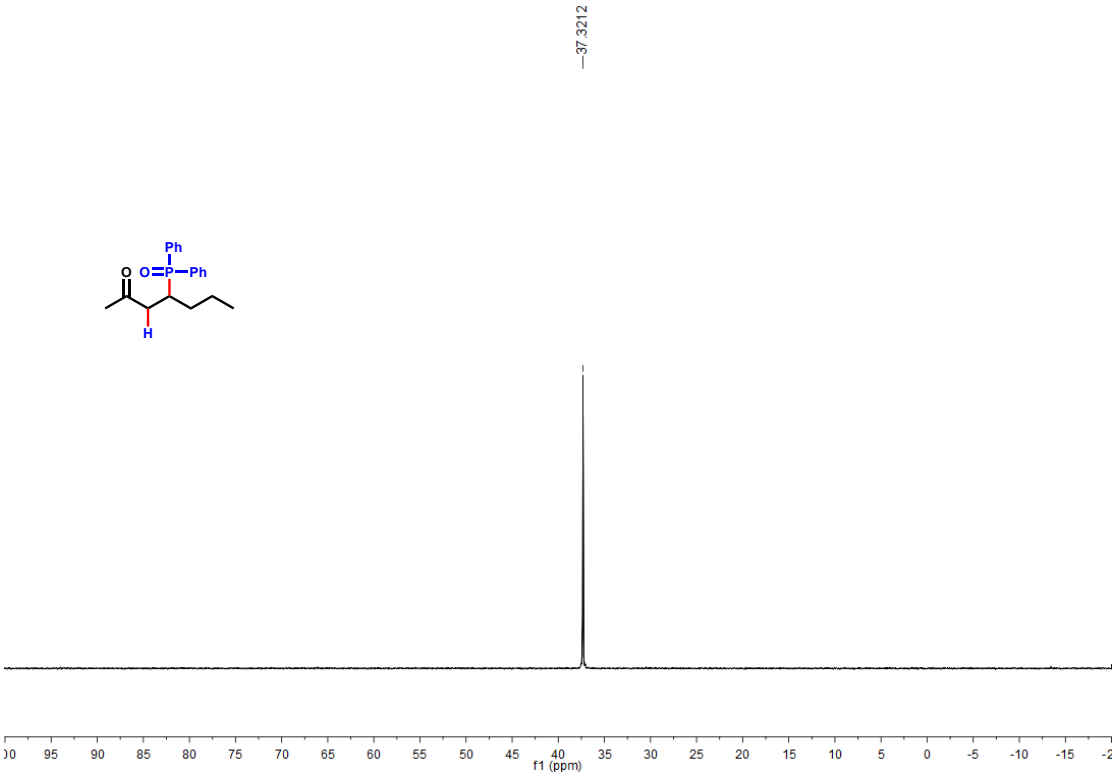
^{1}H NMR



^{13}C NMR

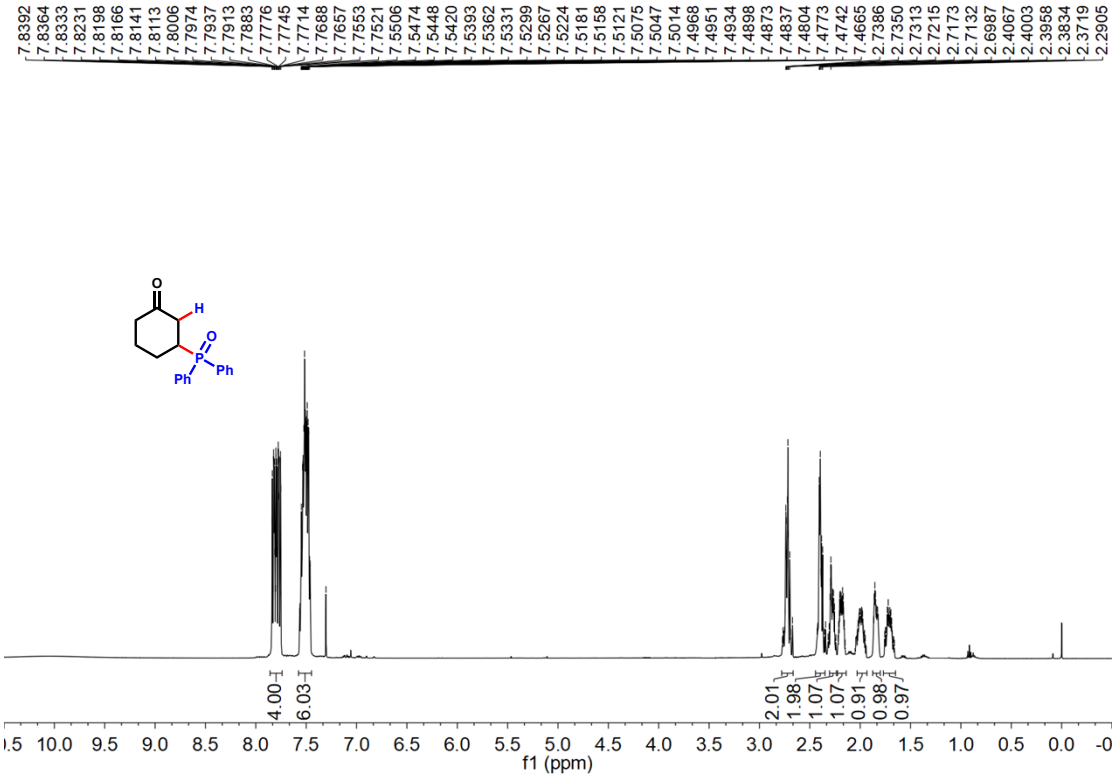


^{31}P NMR

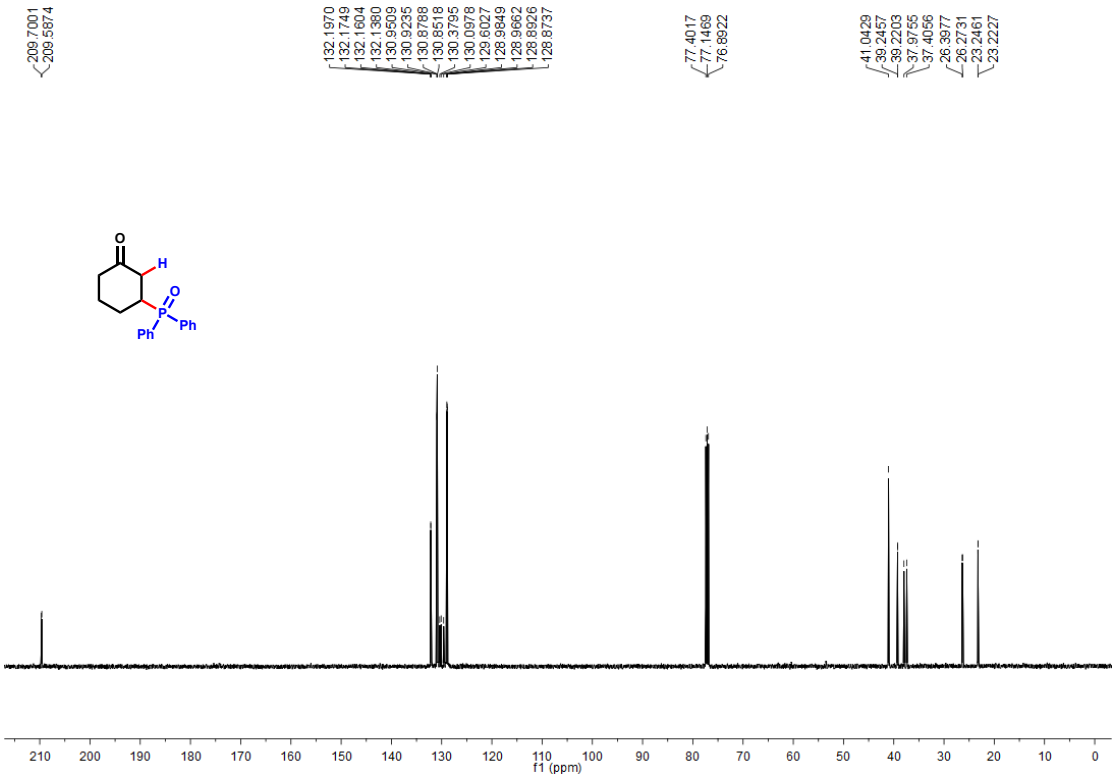


16c

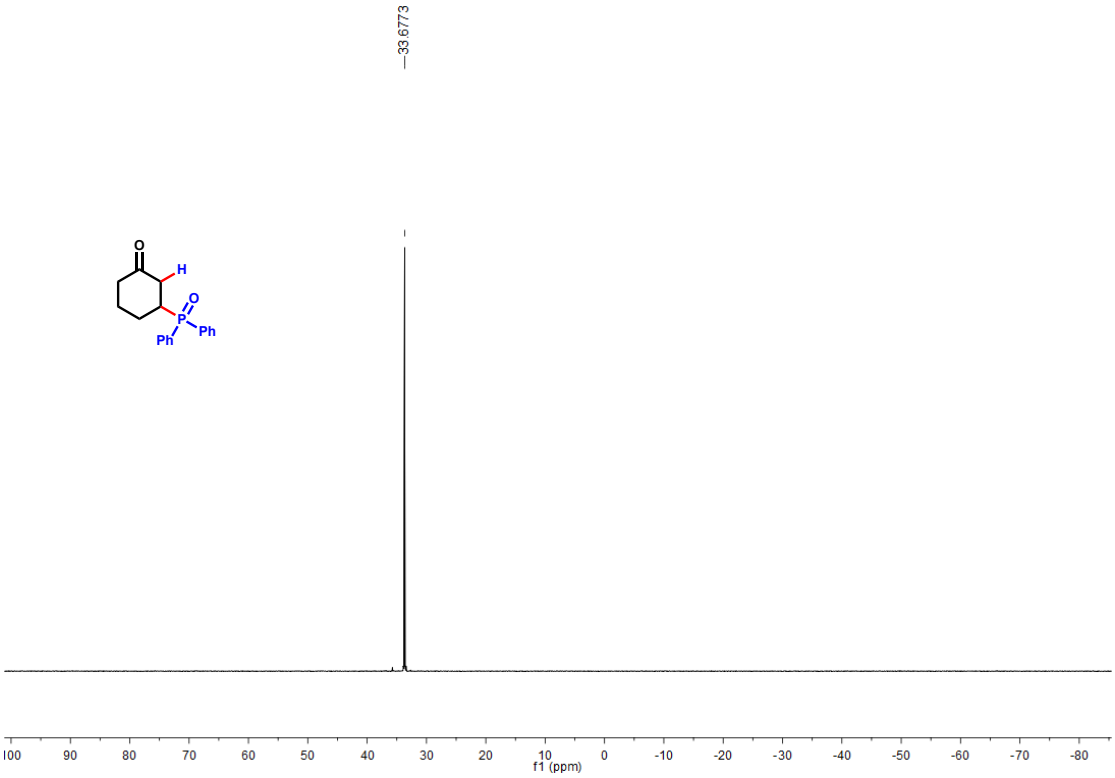
^{1}H NMR



^{13}C NMR

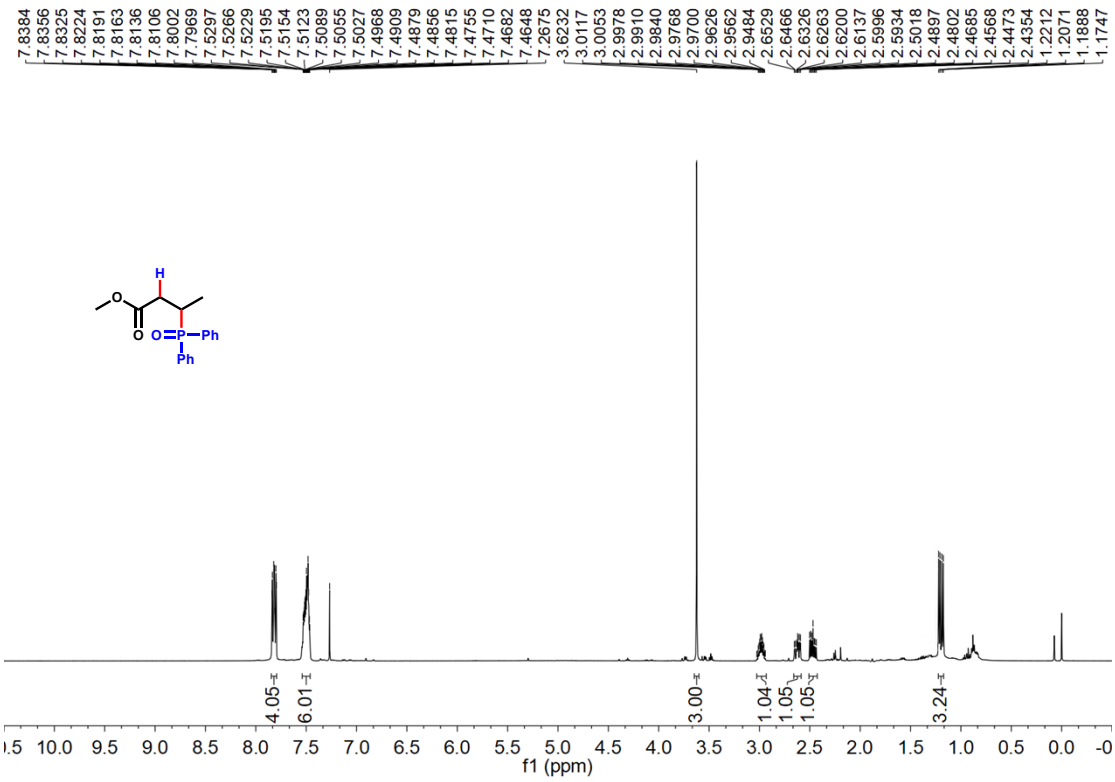


^{31}P NMR



17c

^{1}H NMR



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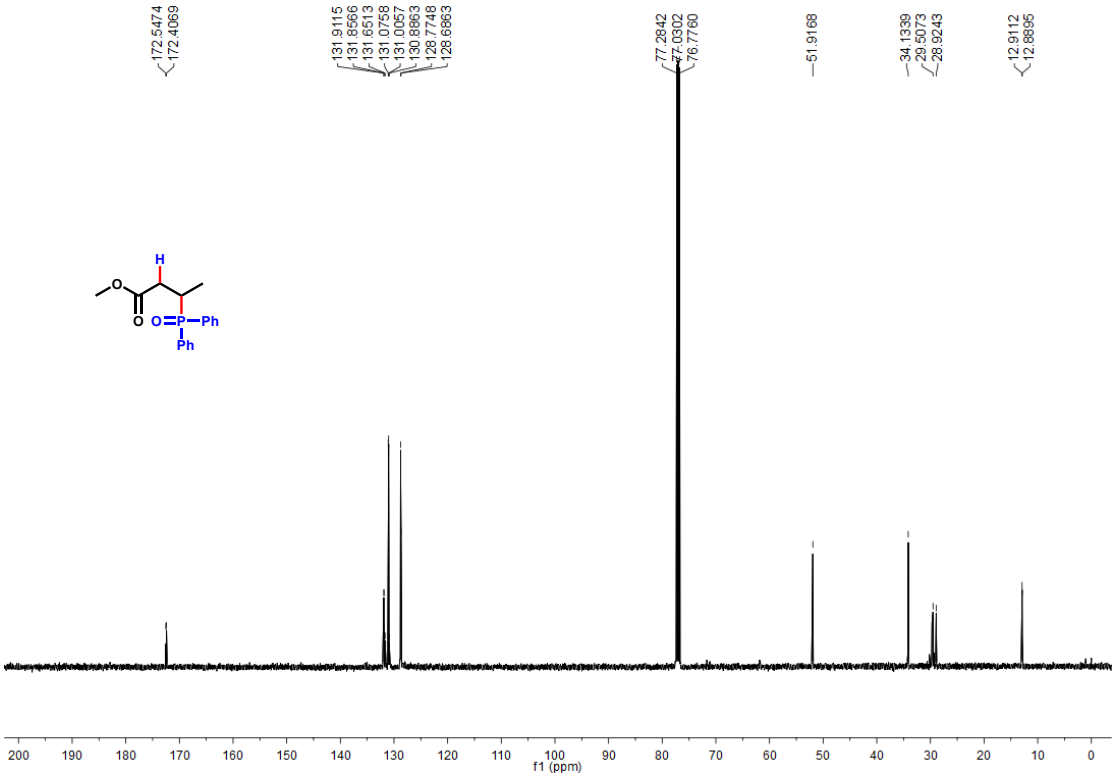
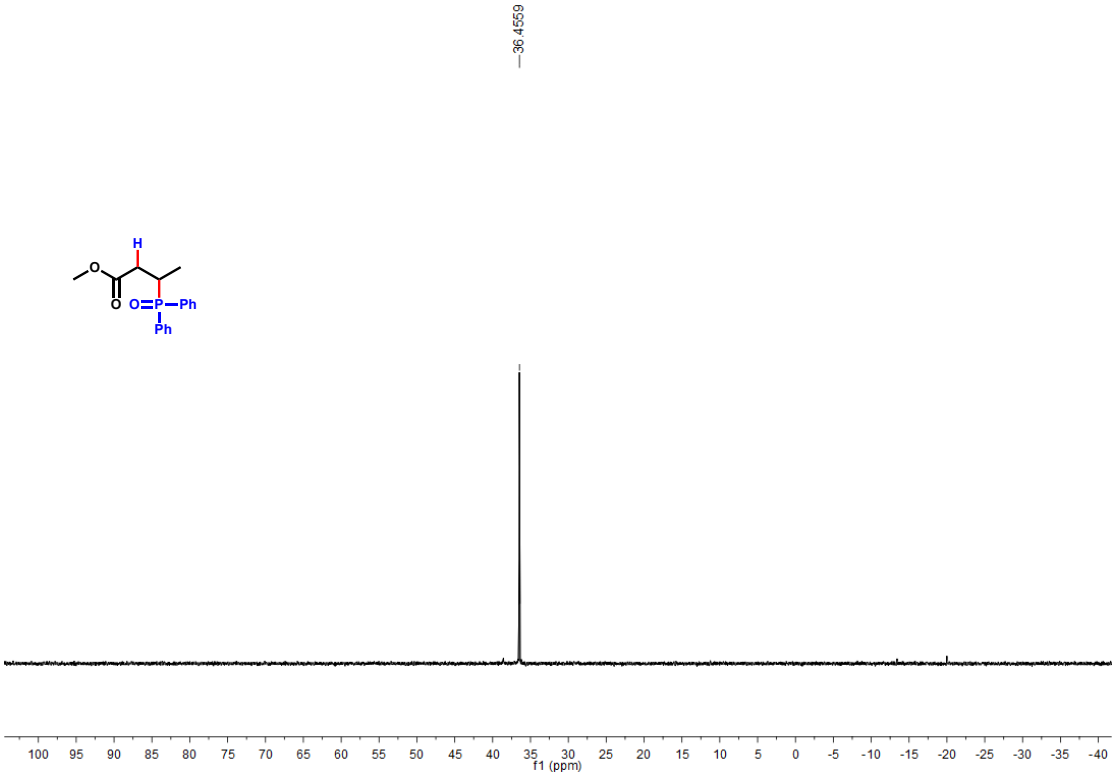
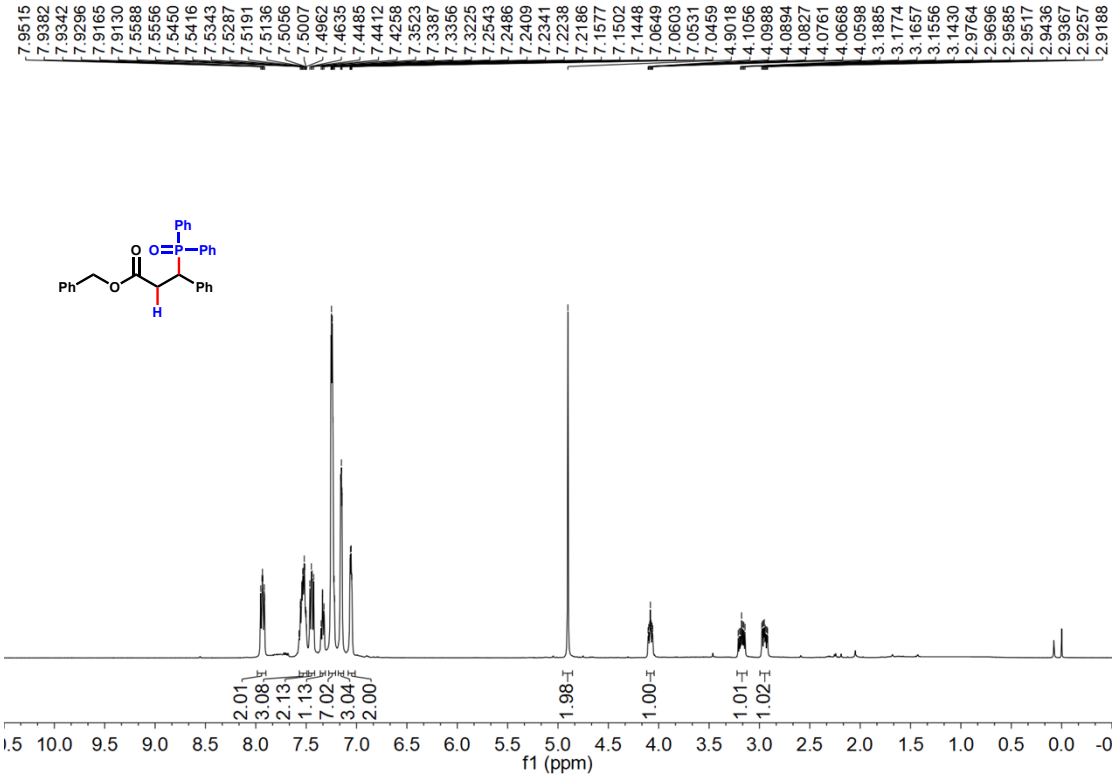


^{31}P NMR

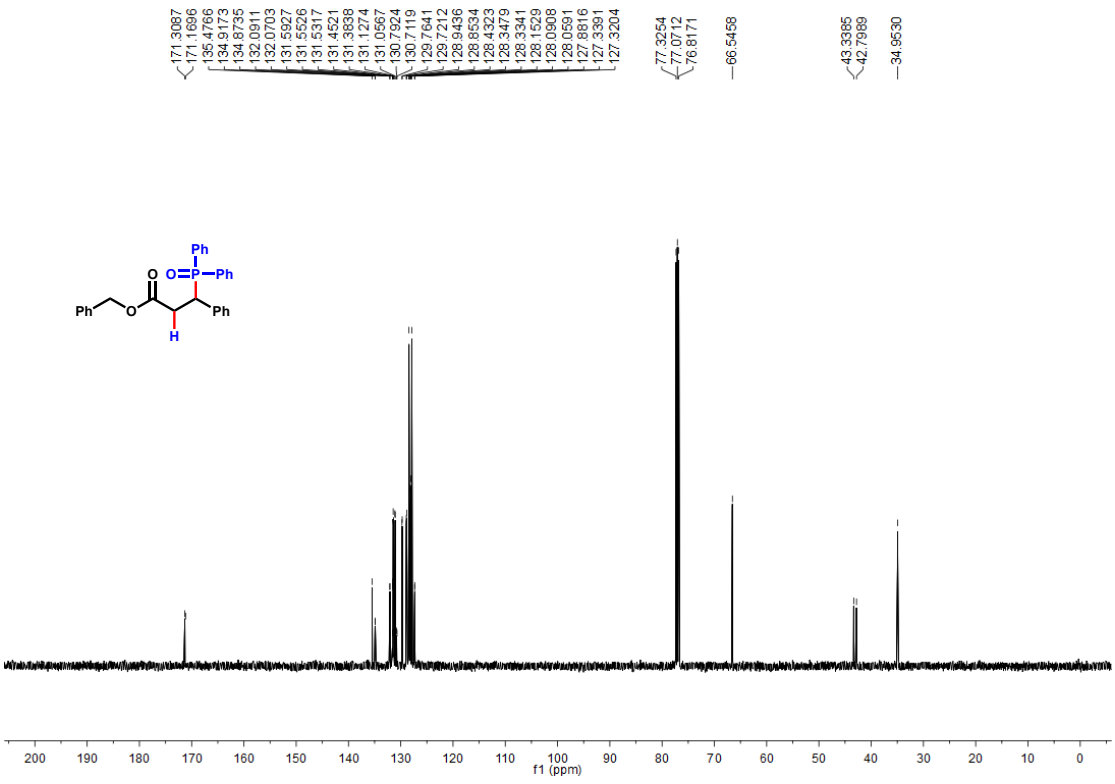


18c

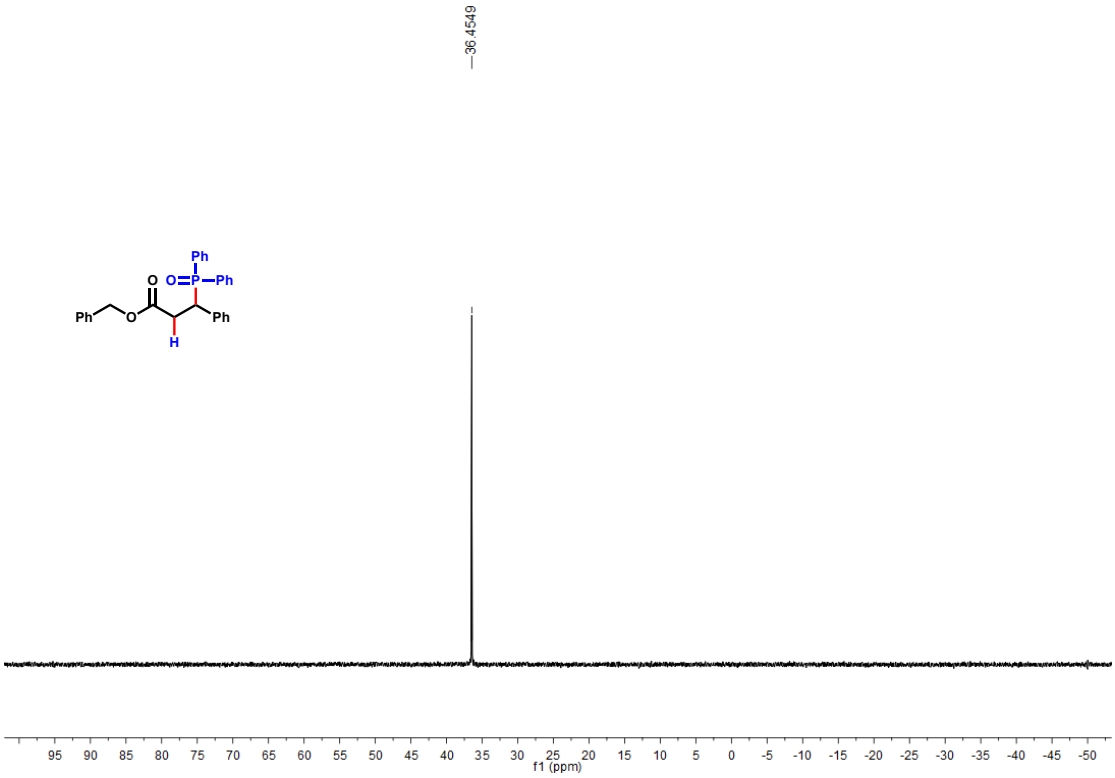
^{1}H NMR



^{13}C NMR

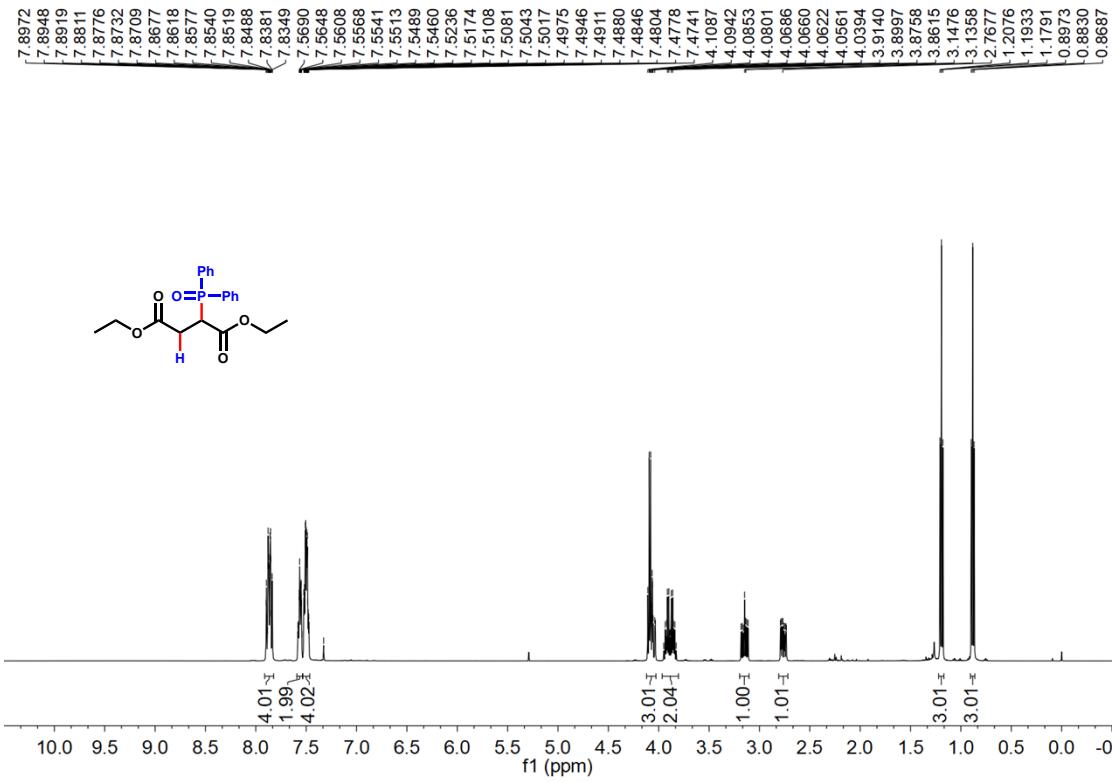


^{31}P NMR

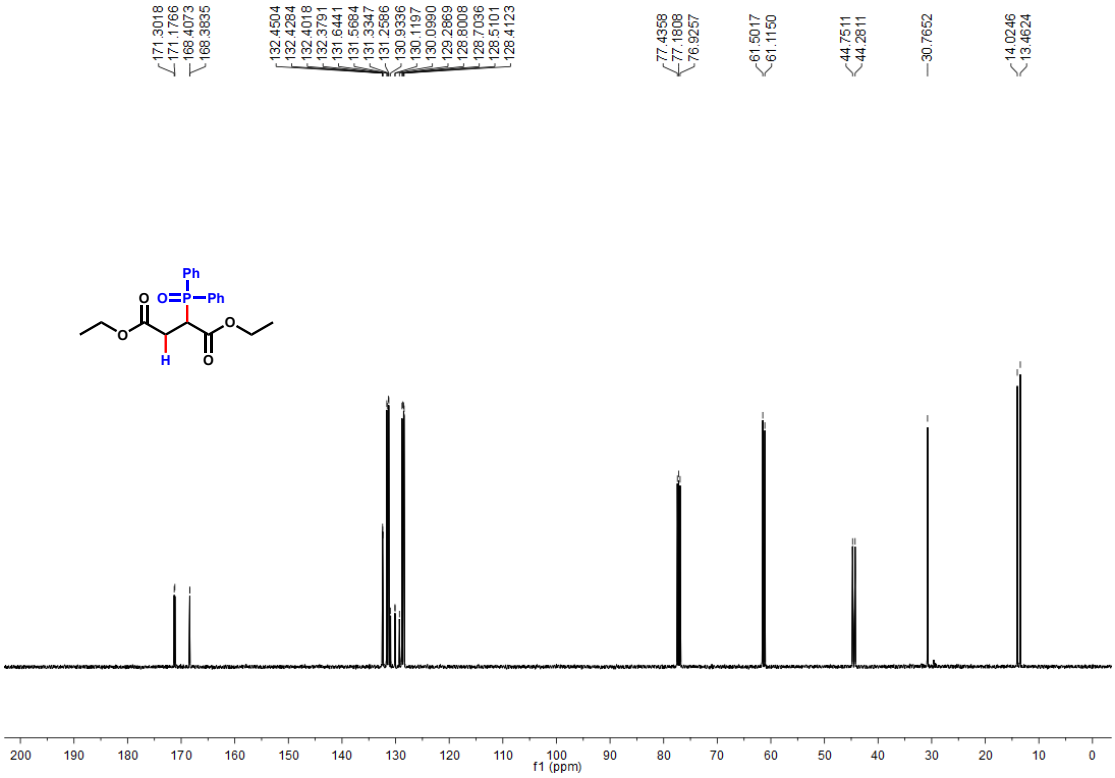


19c

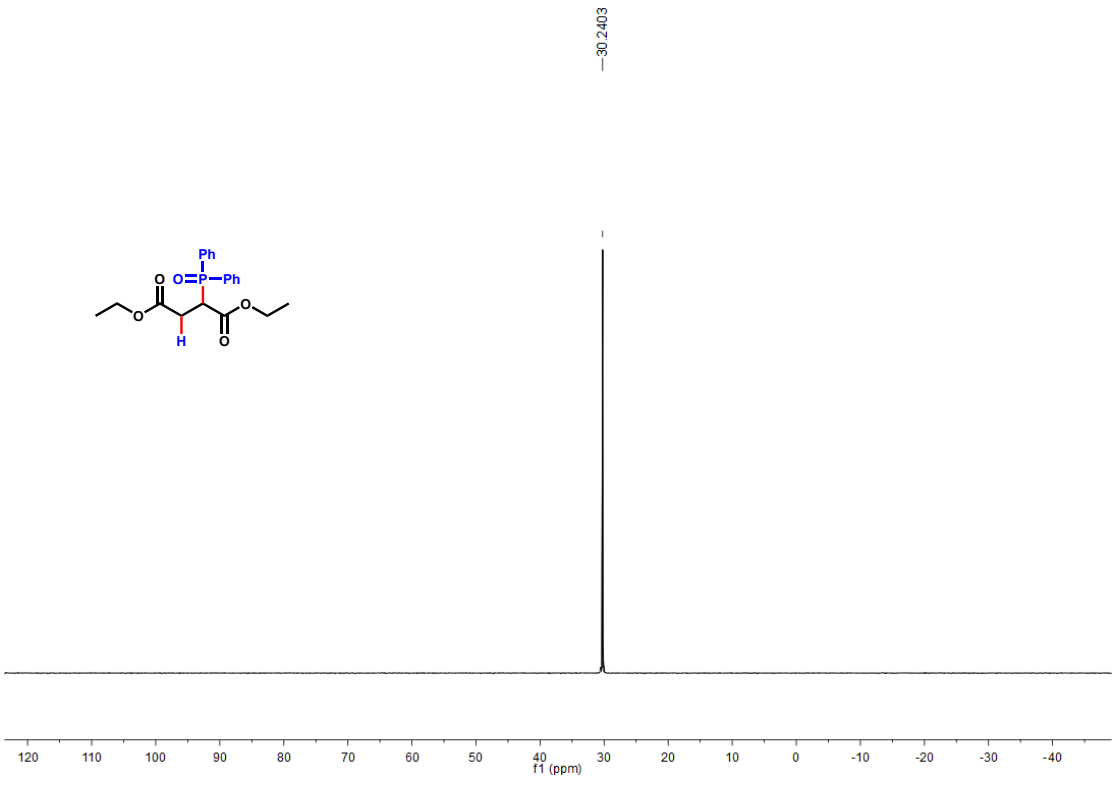
^{1}H NMR



^{13}C NMR

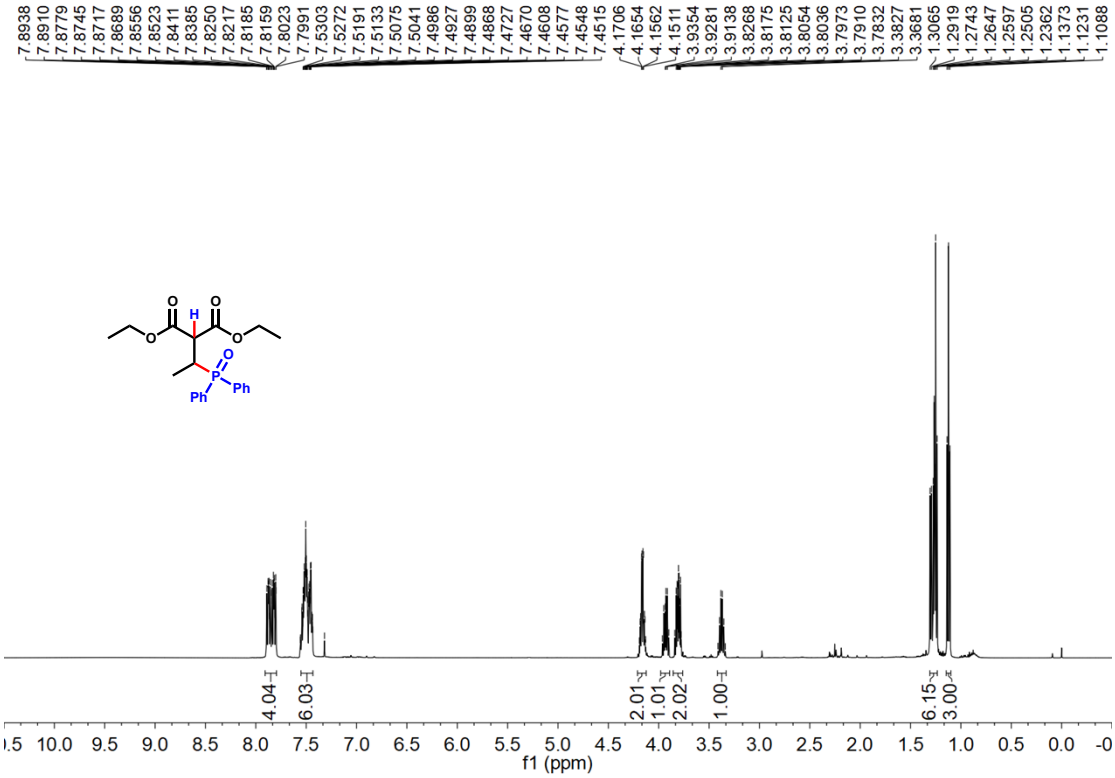


^{31}P NMR



20c

^{1}H NMR



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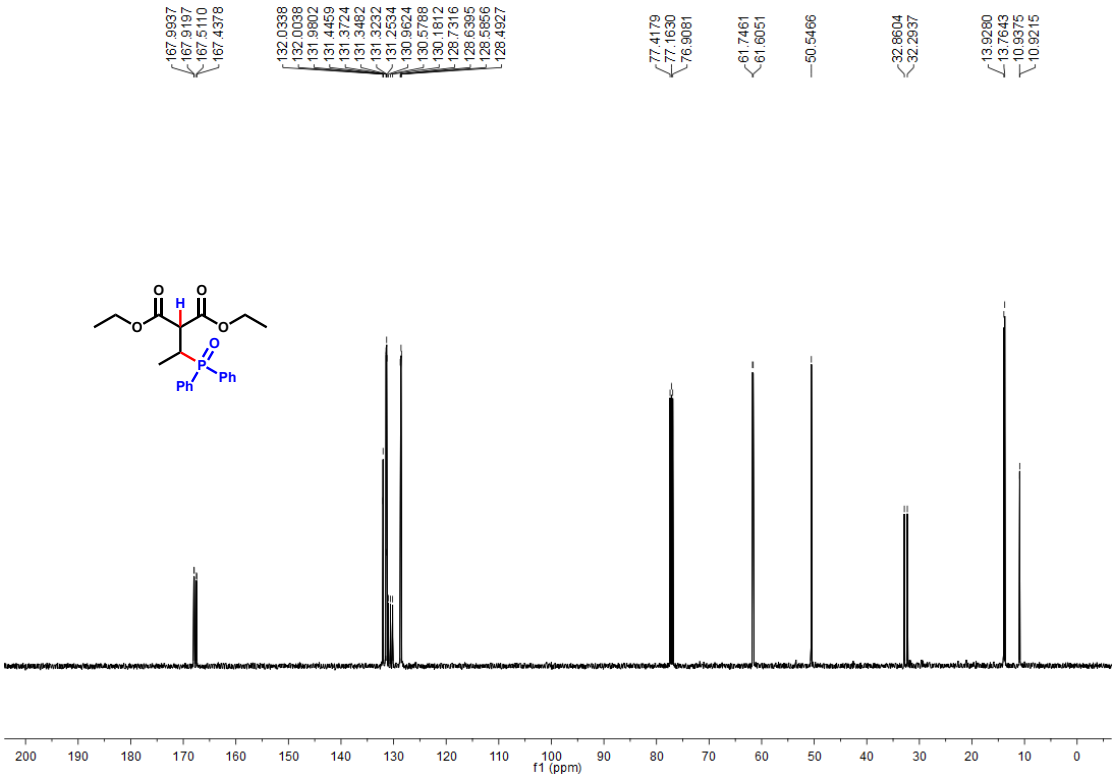

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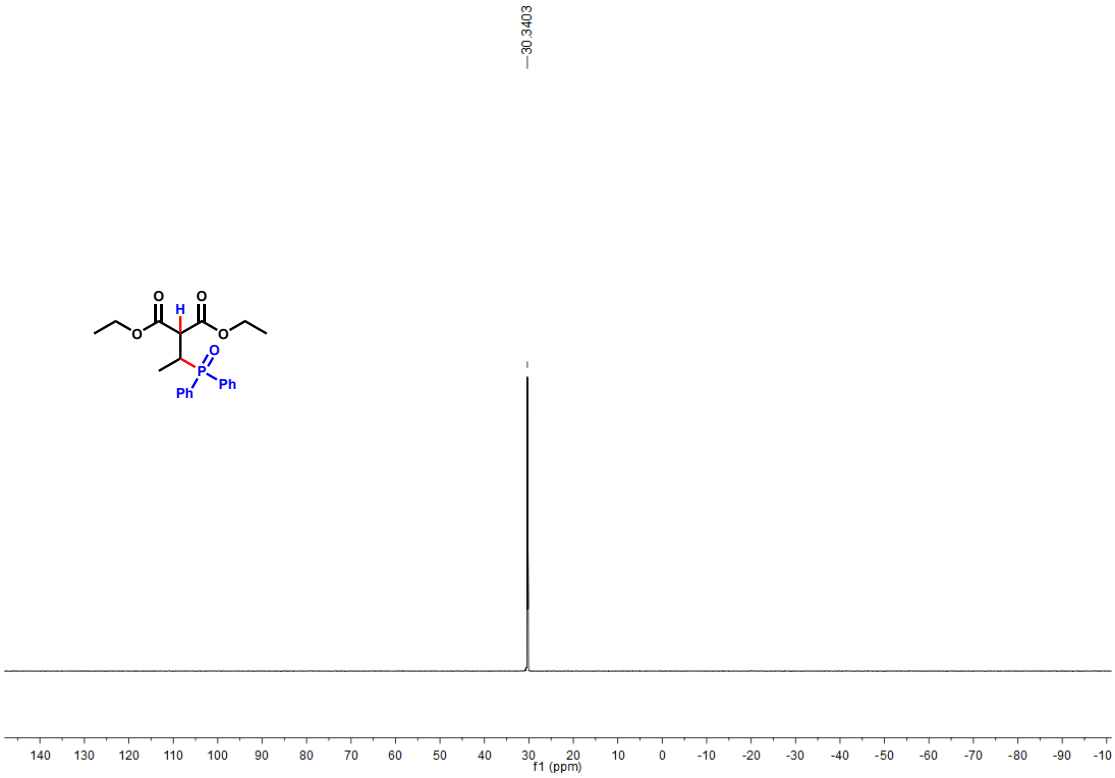
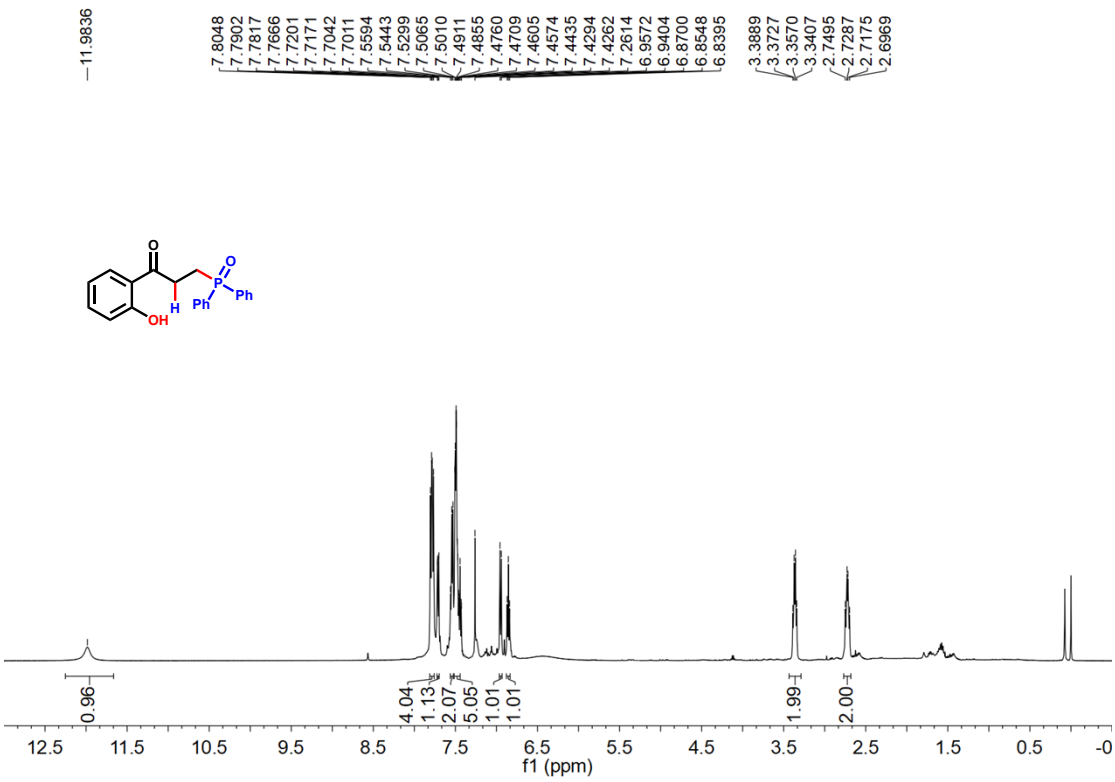


21c

^{1}H NMR



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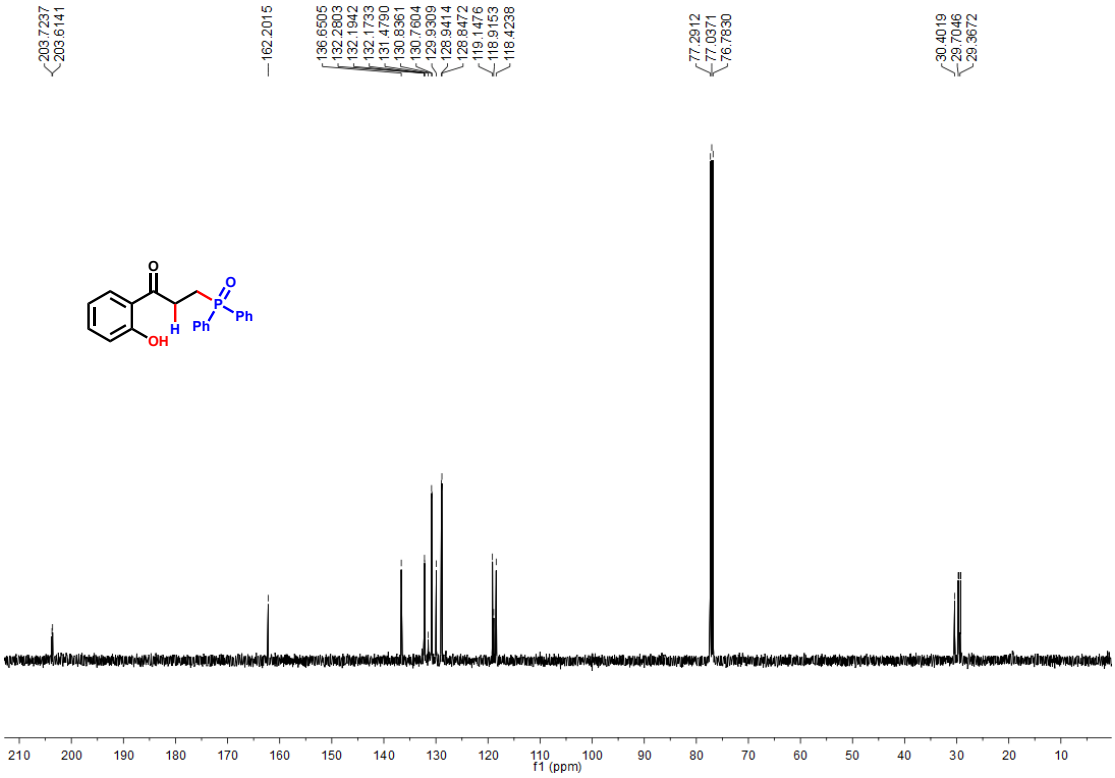

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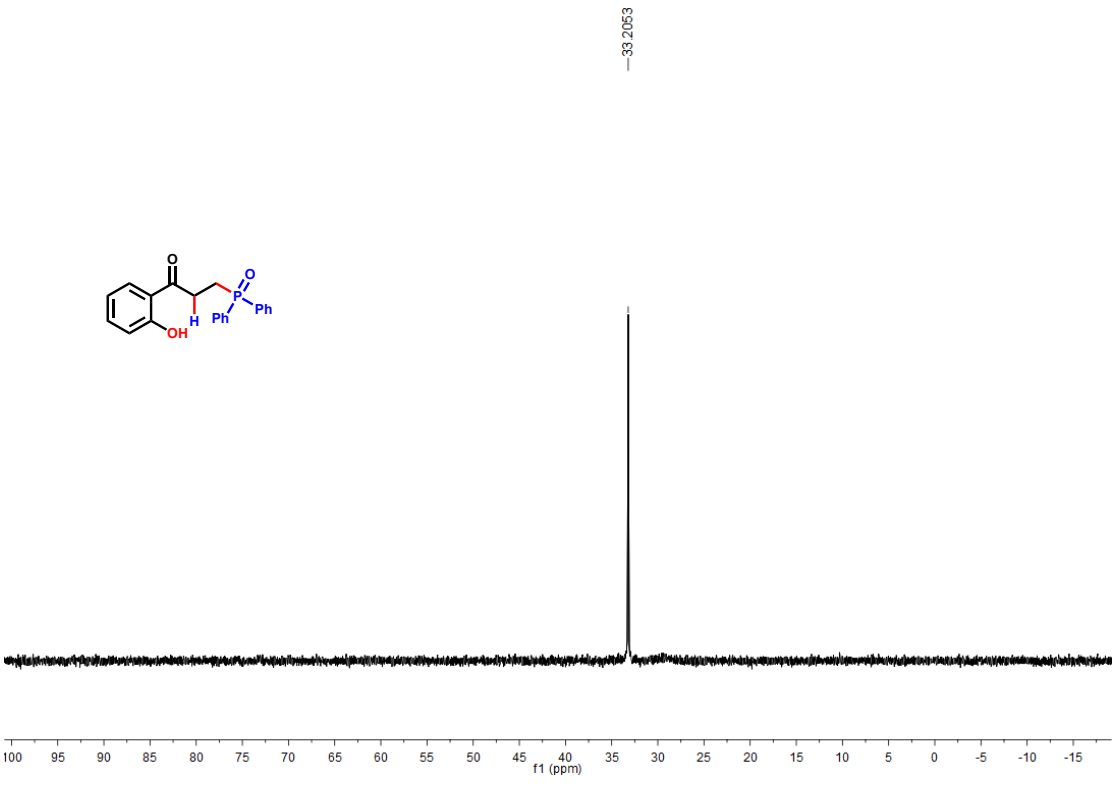

22c

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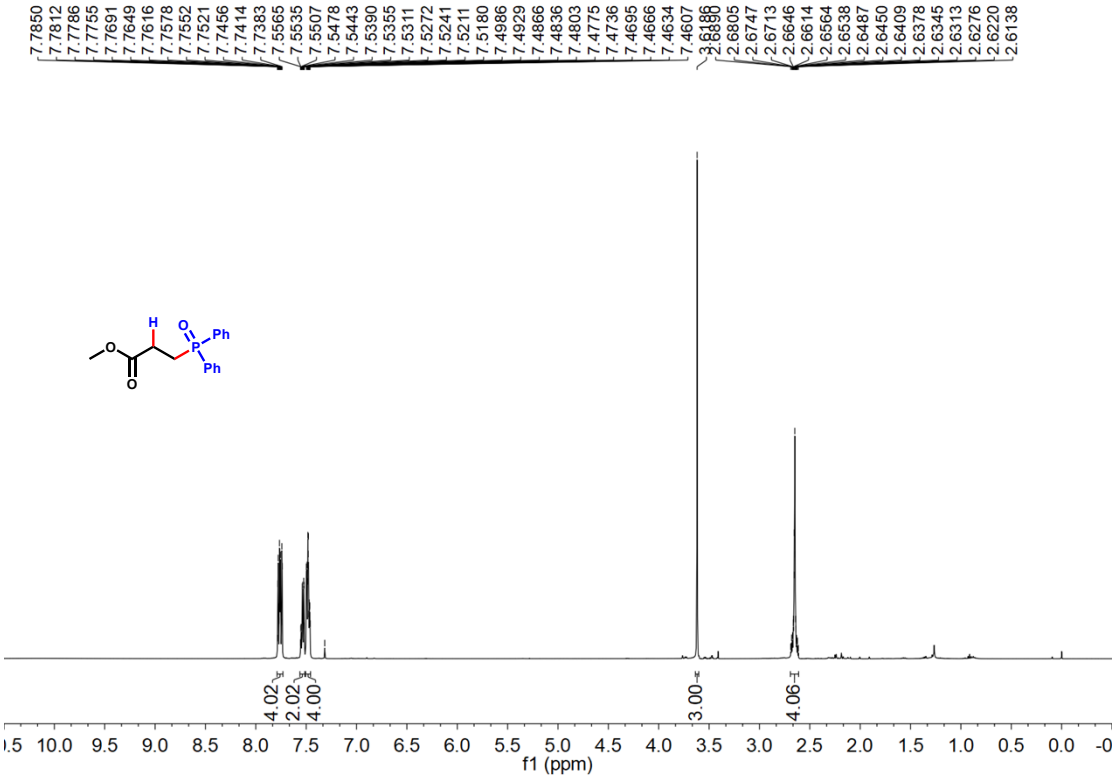

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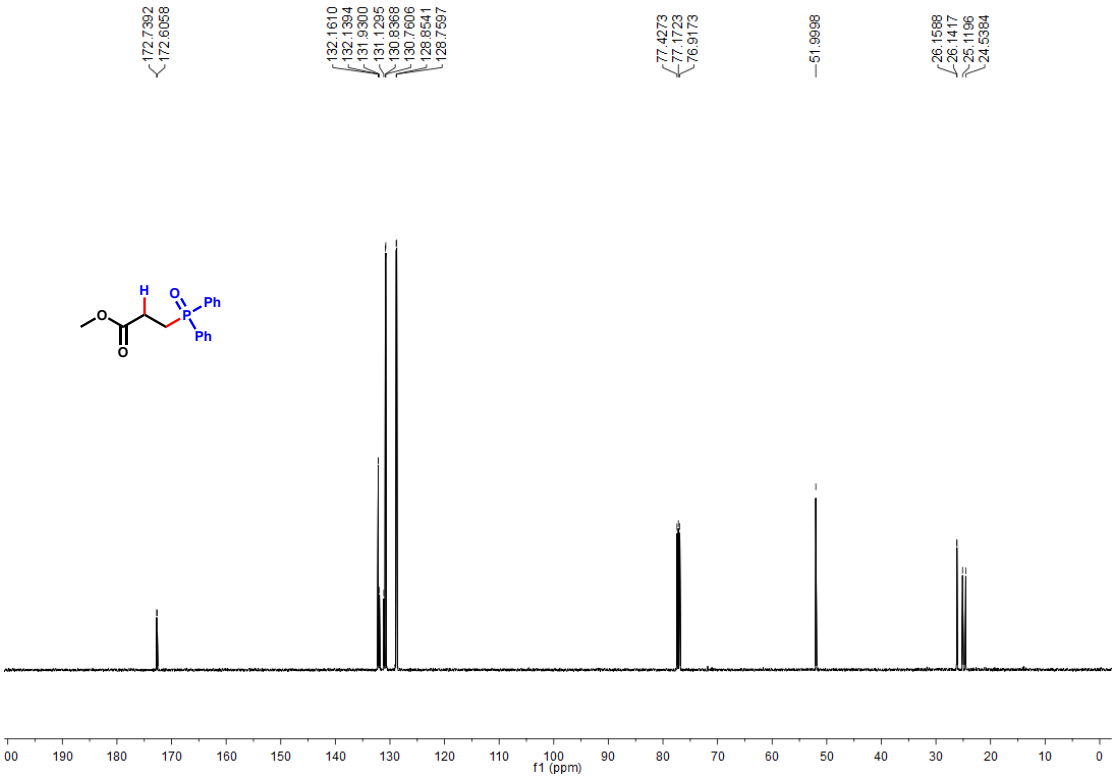

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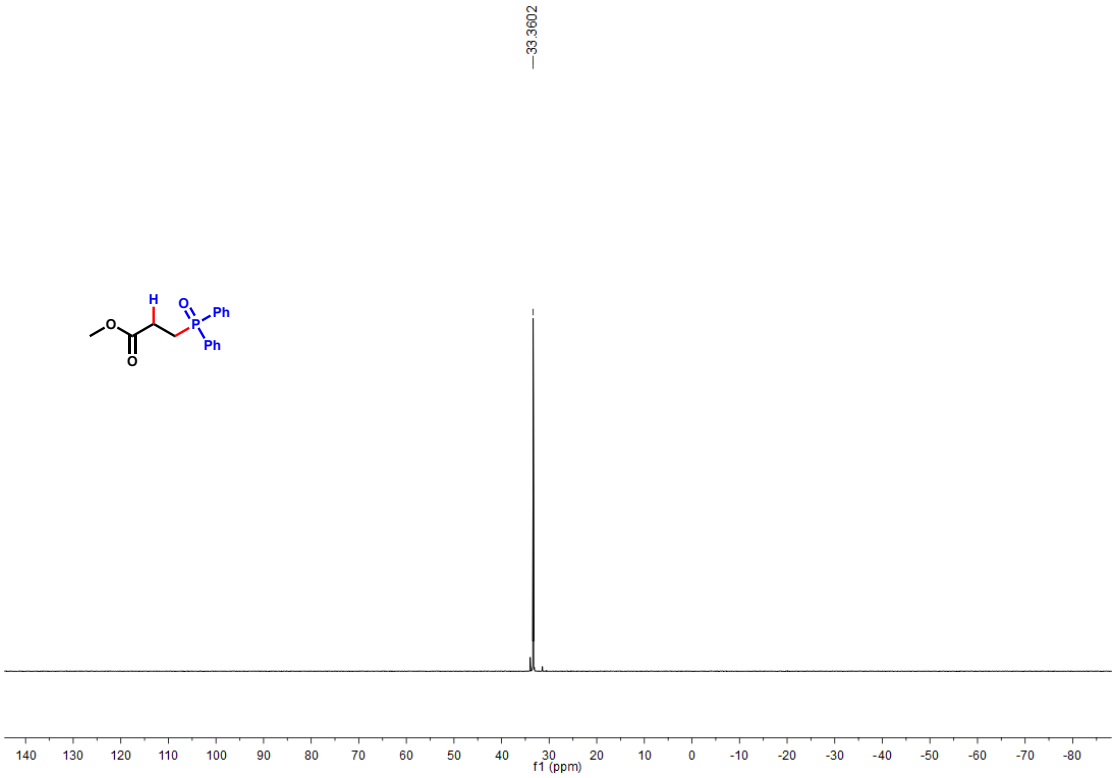
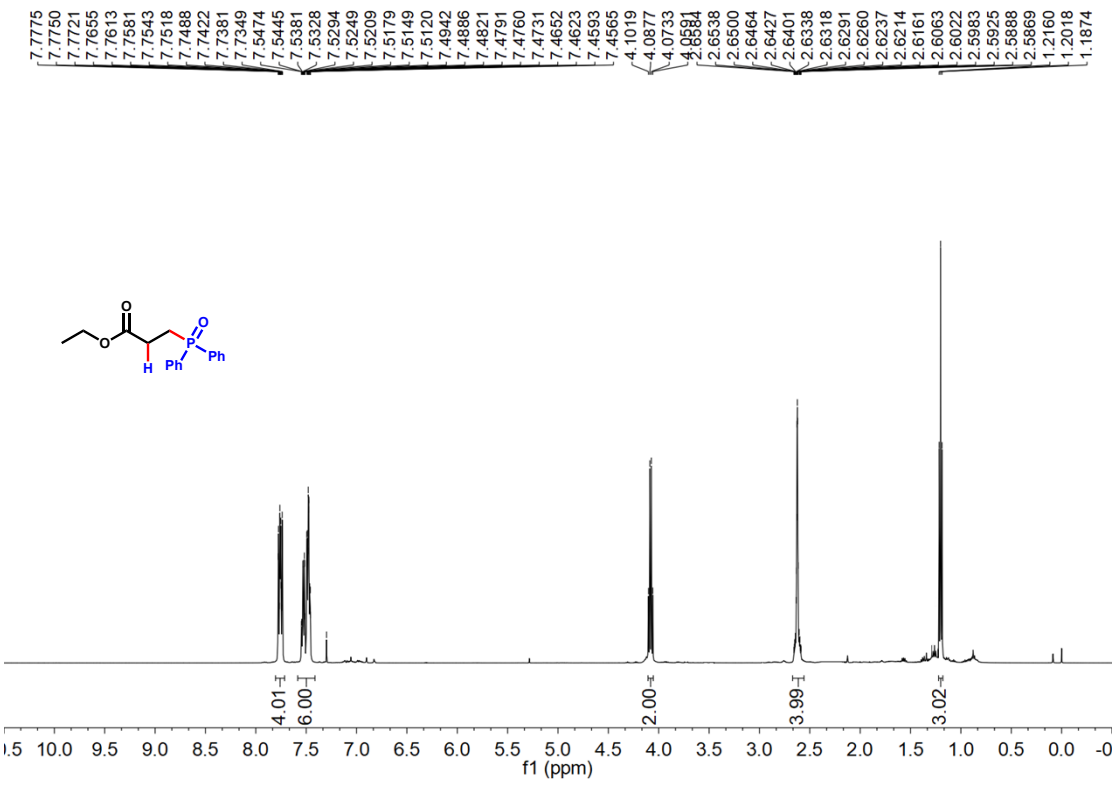


23c

^{1}H NMR



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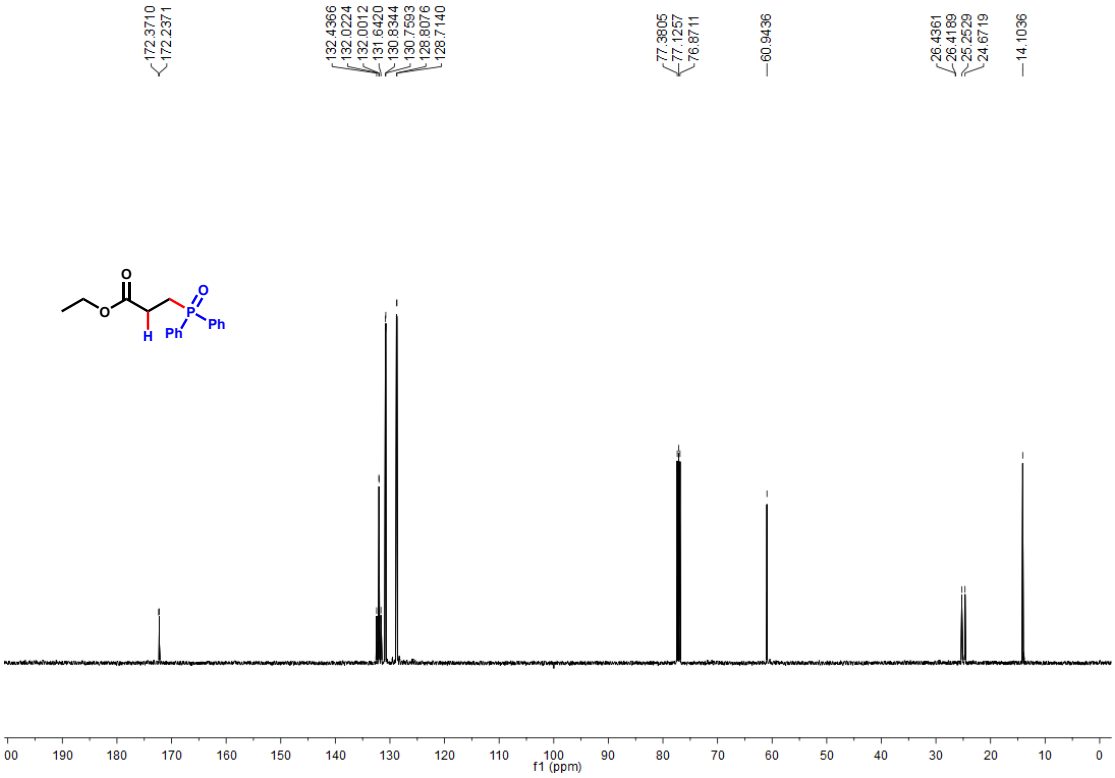
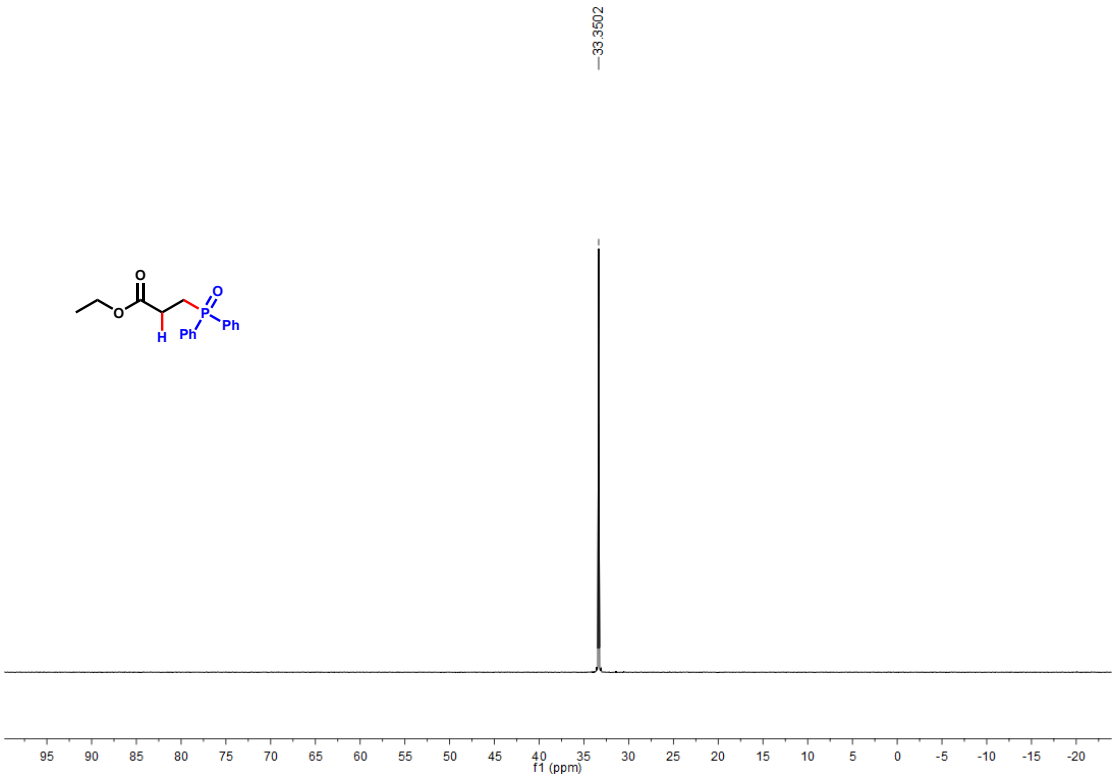
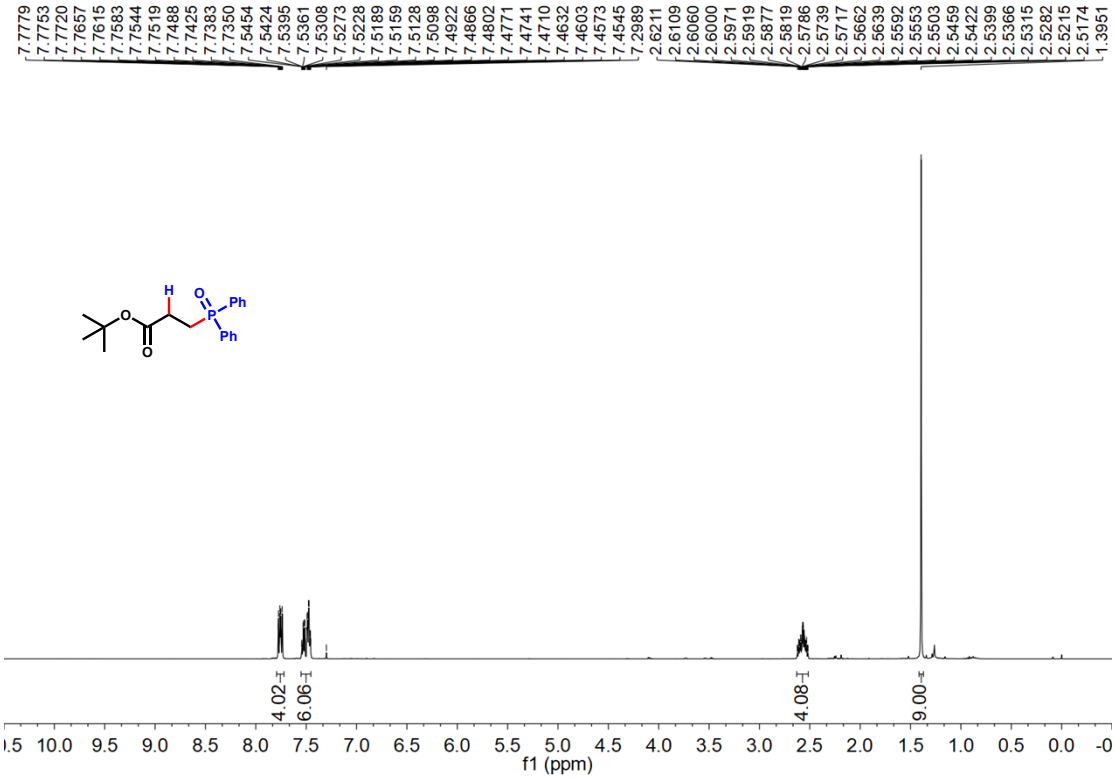


^{31}P NMR

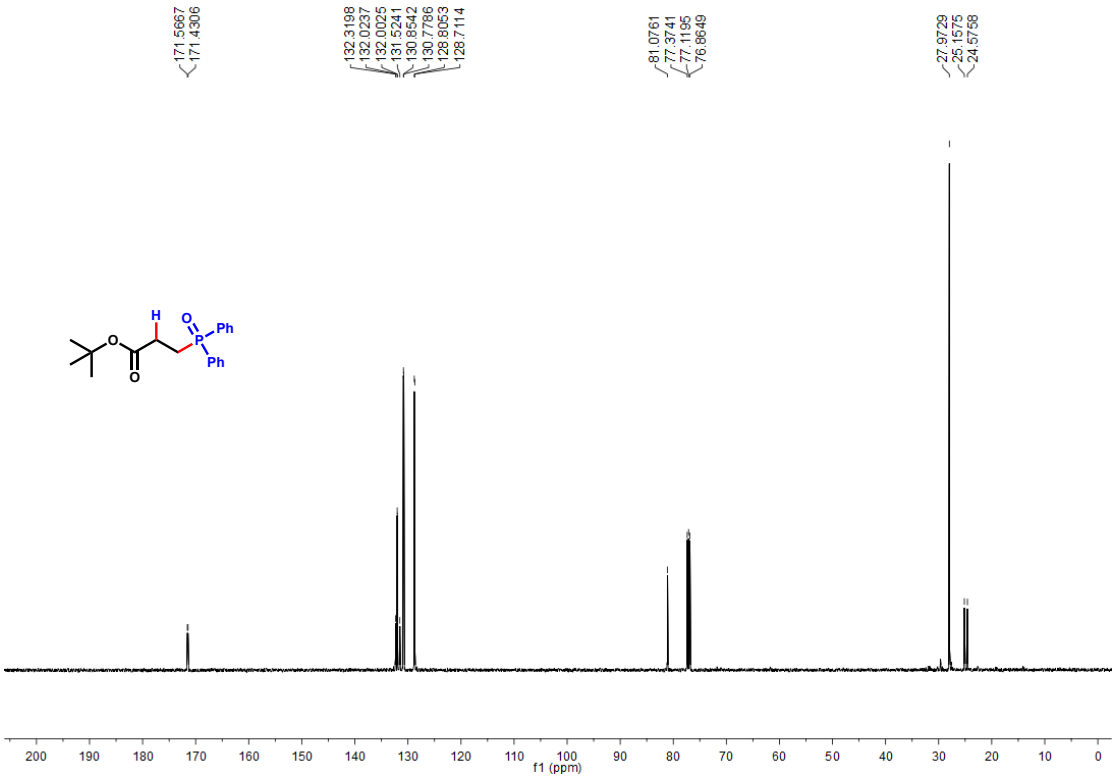


24c

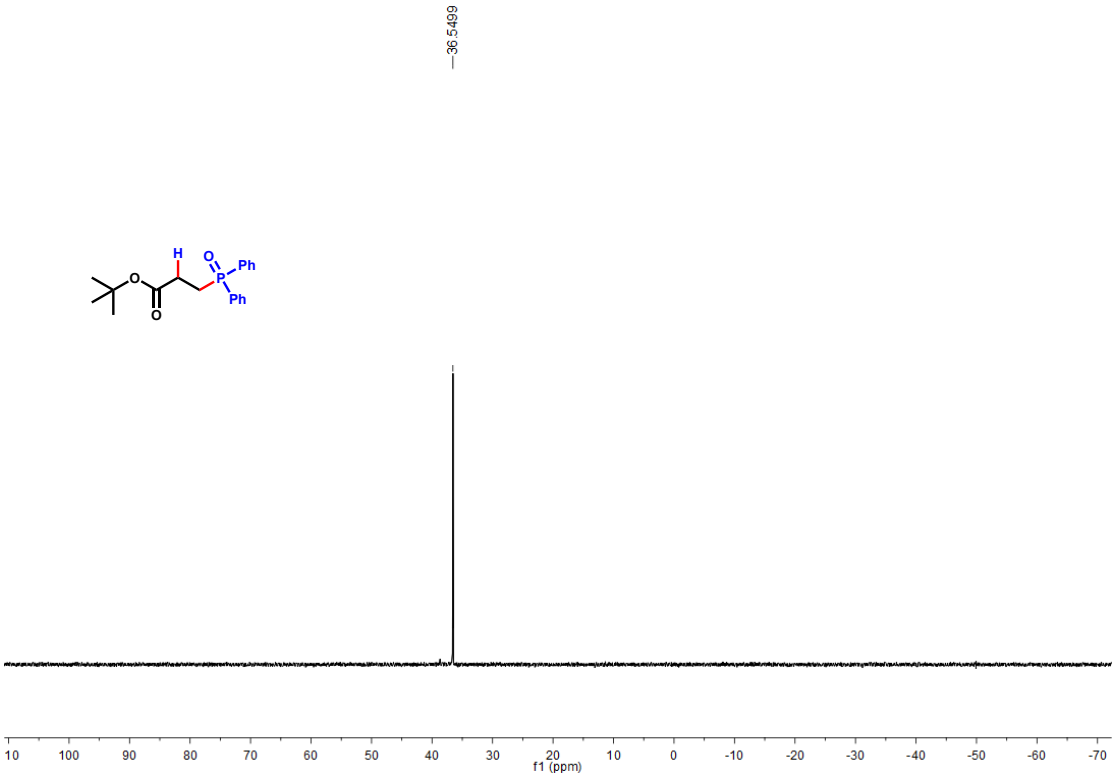
^{1}H NMR



^{13}C NMR

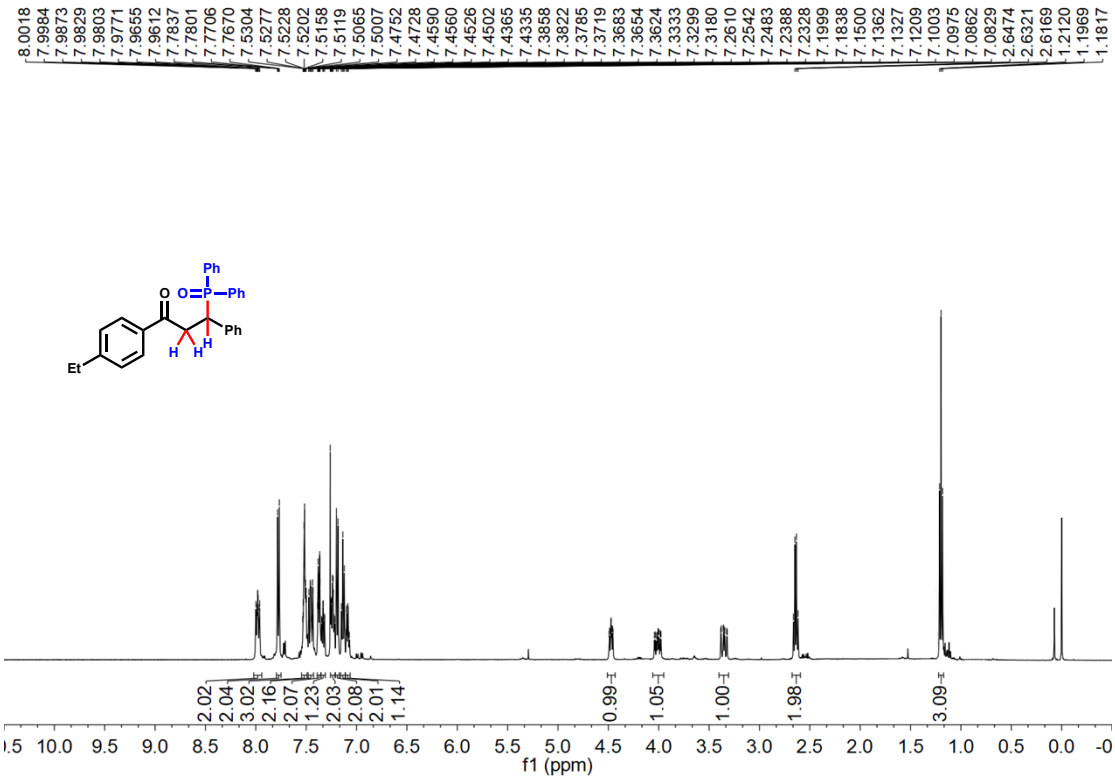


^{31}P NMR



29c

^{1}H NMR



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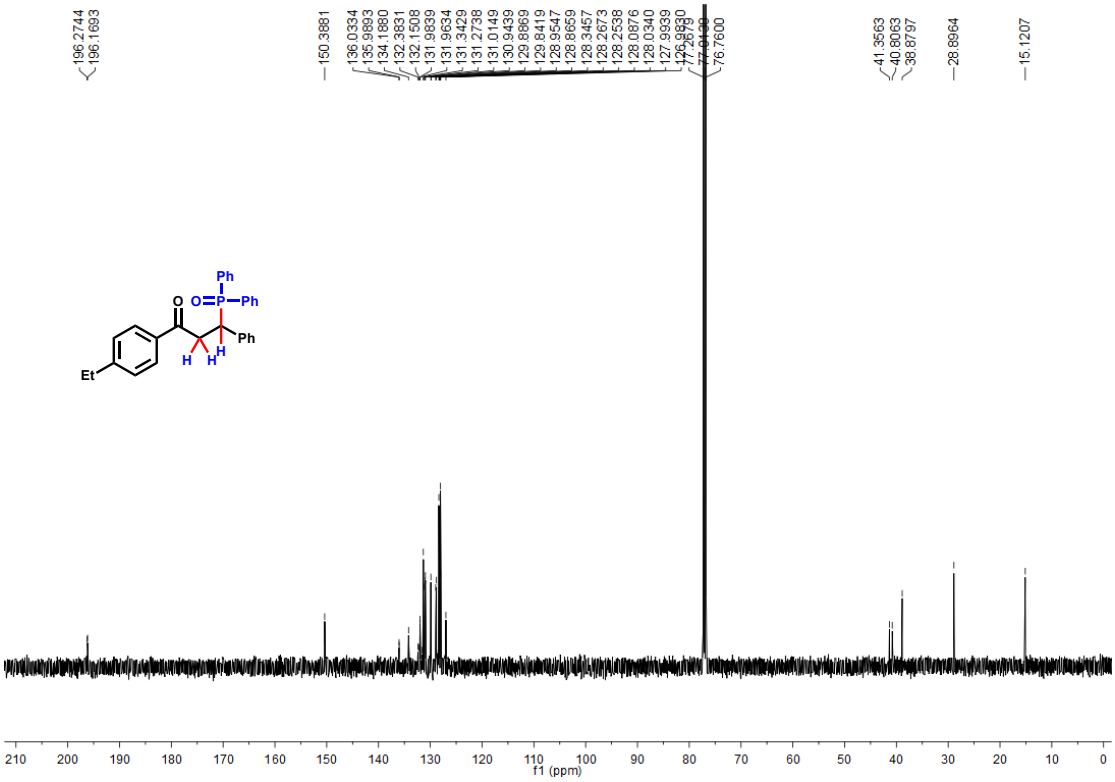

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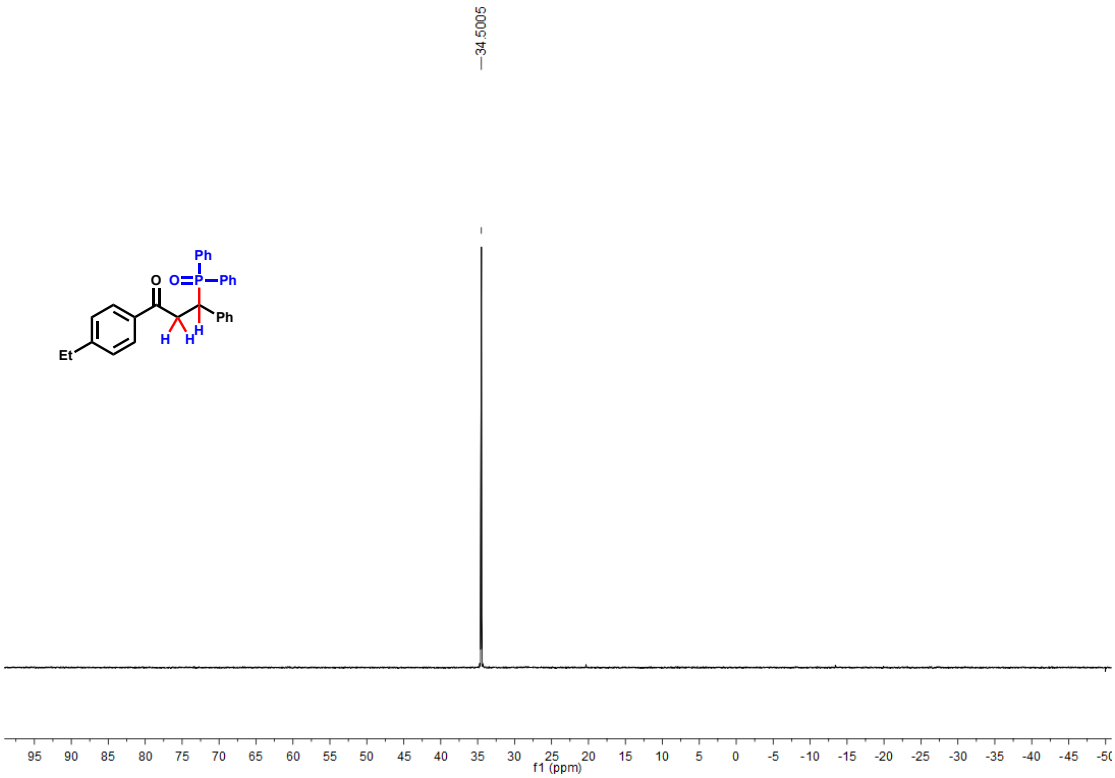
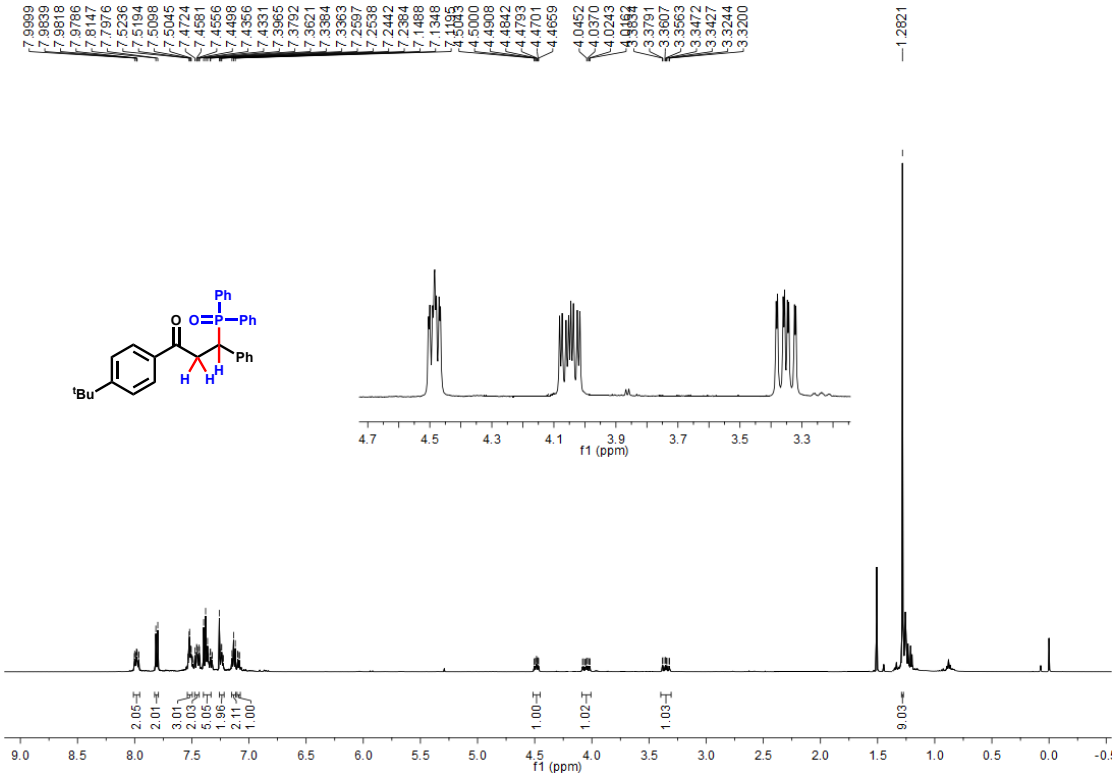


30c

^{1}H NMR



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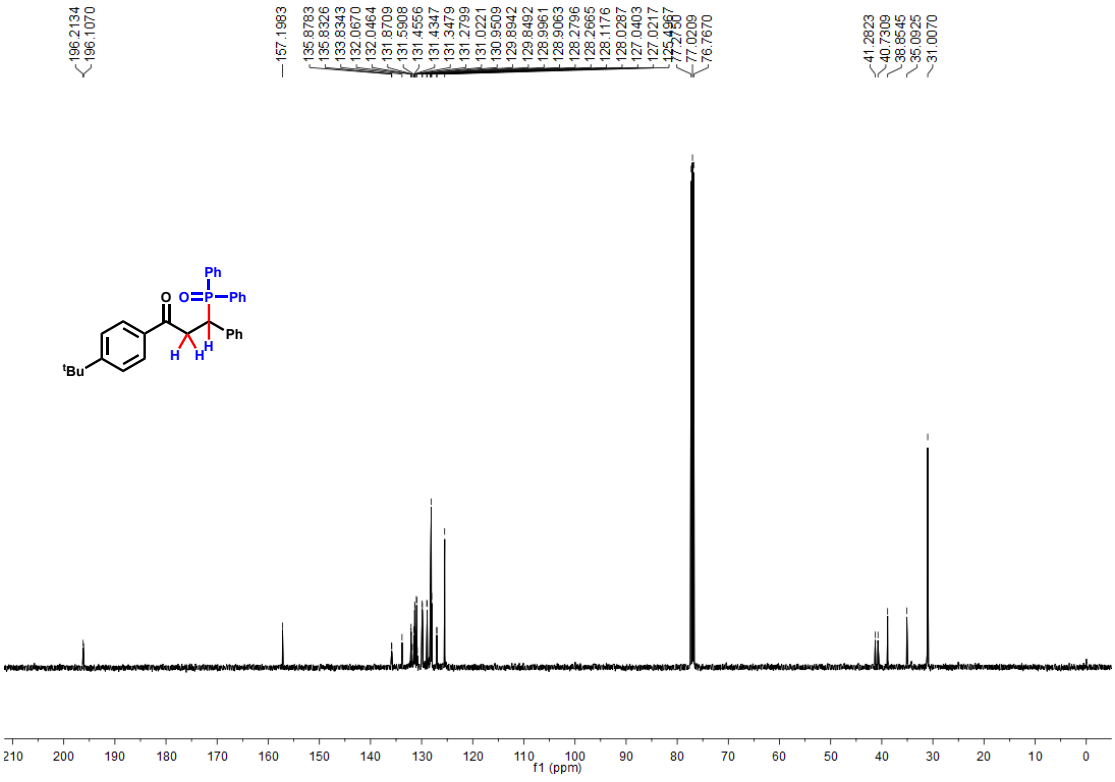

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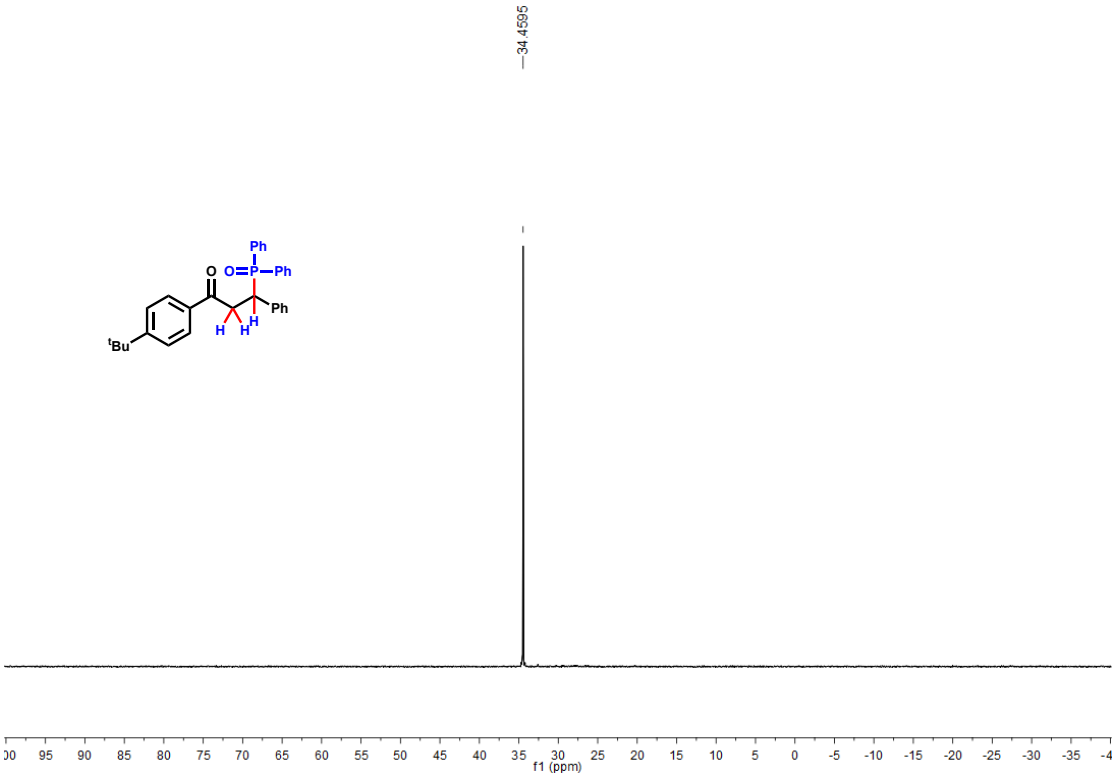

31c

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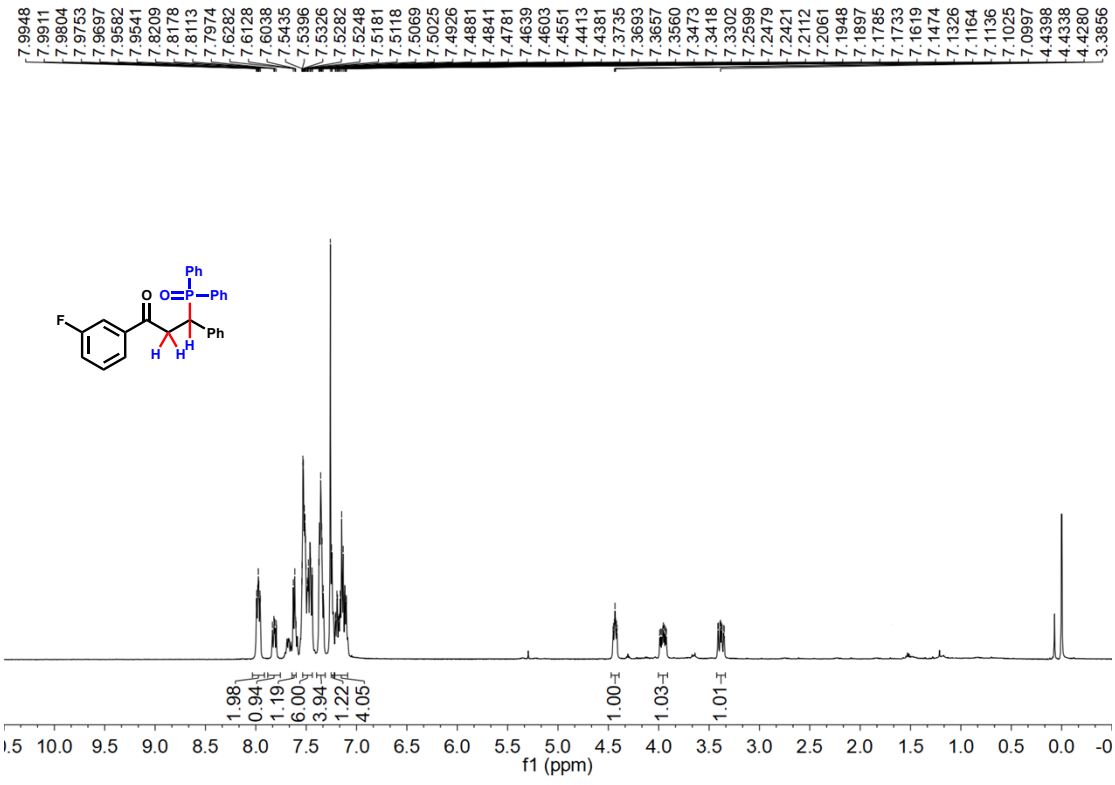

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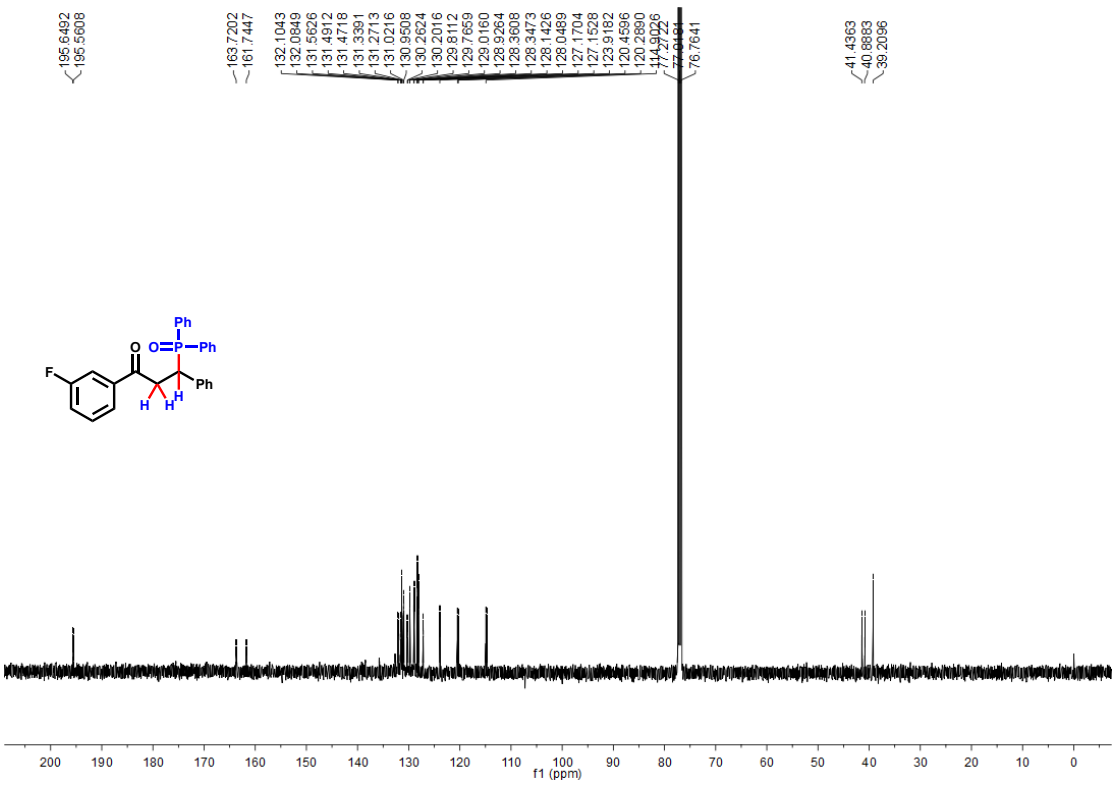
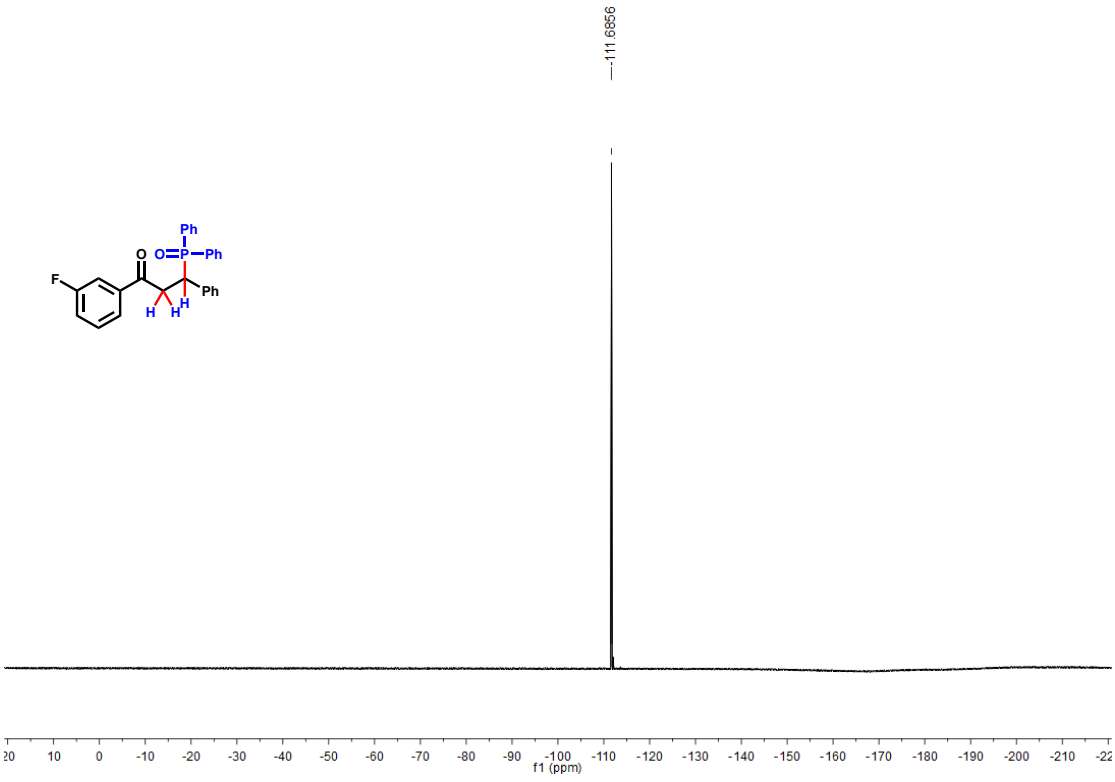


^{19}F NMR



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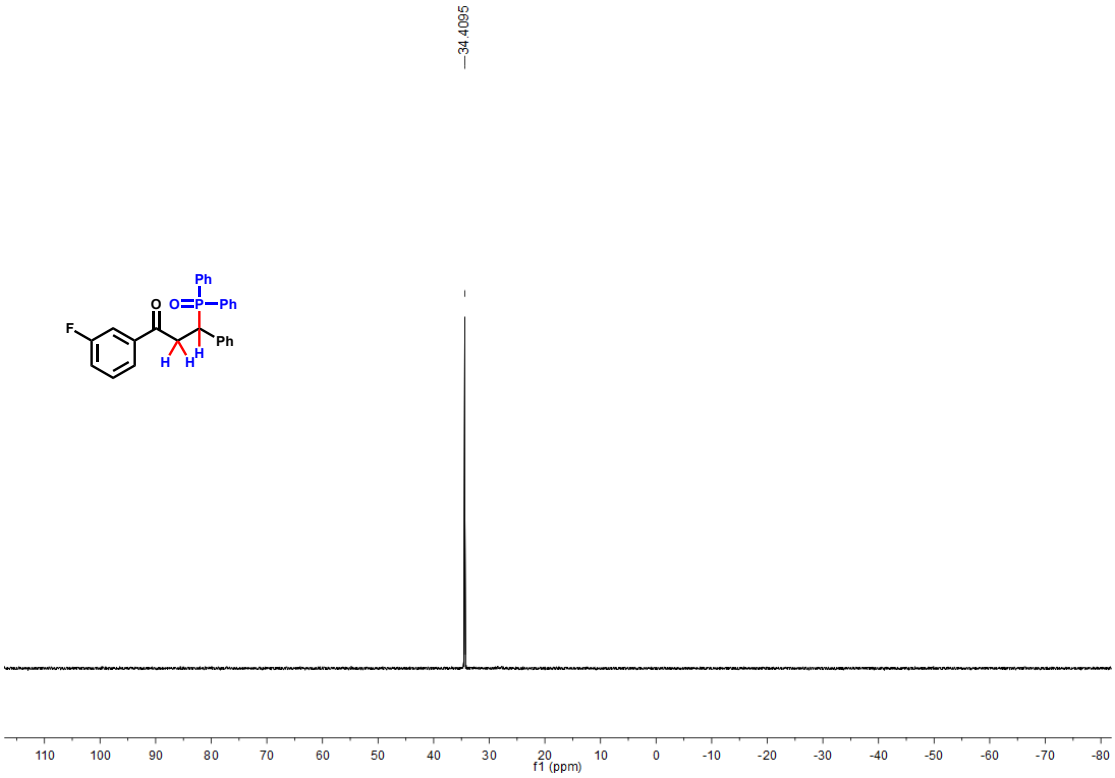

32c

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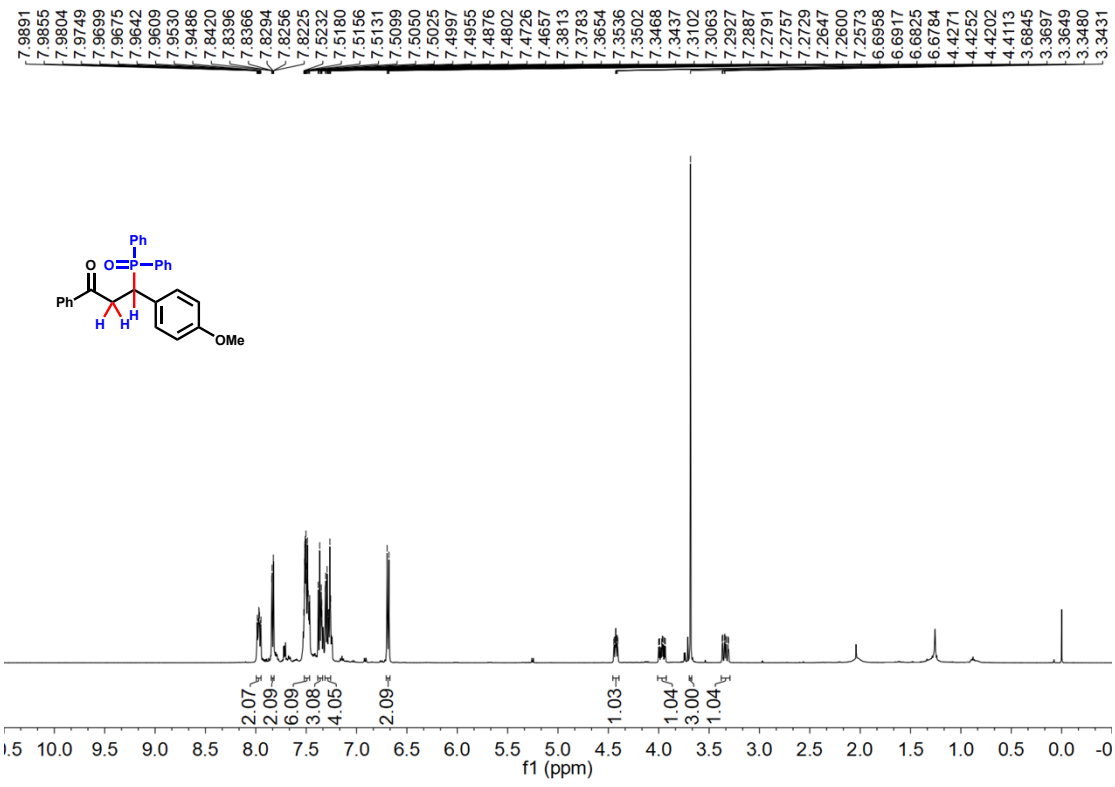

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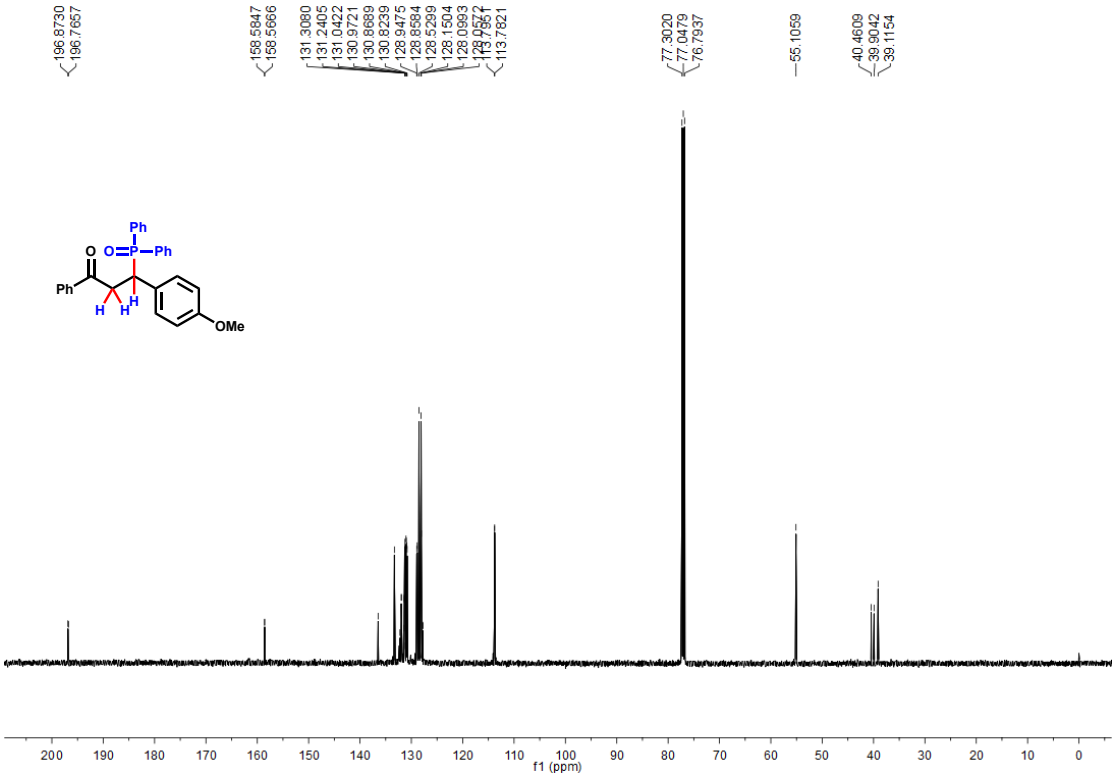

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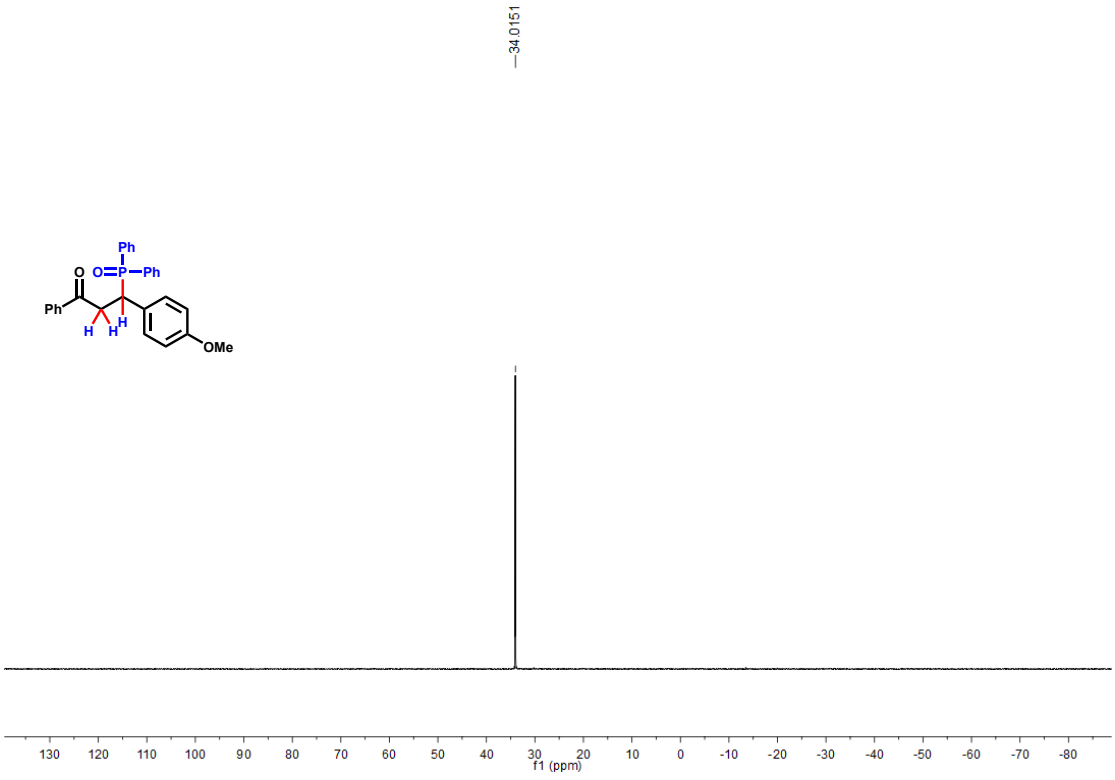

33c

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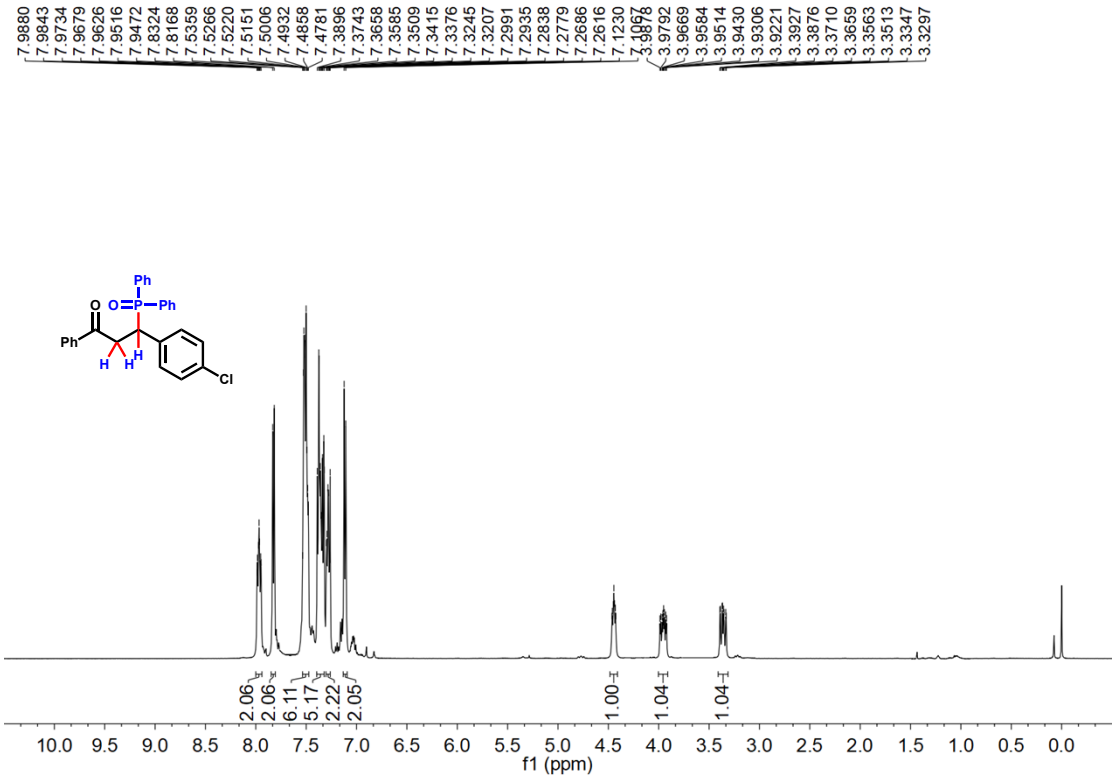

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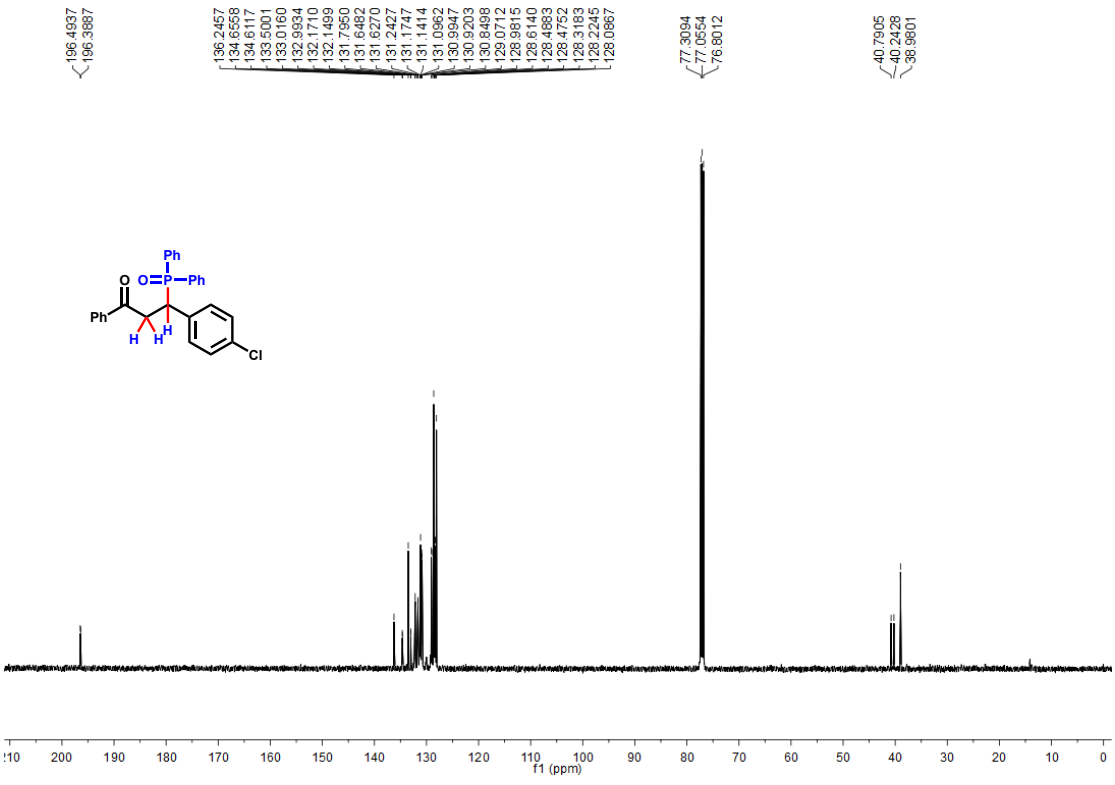

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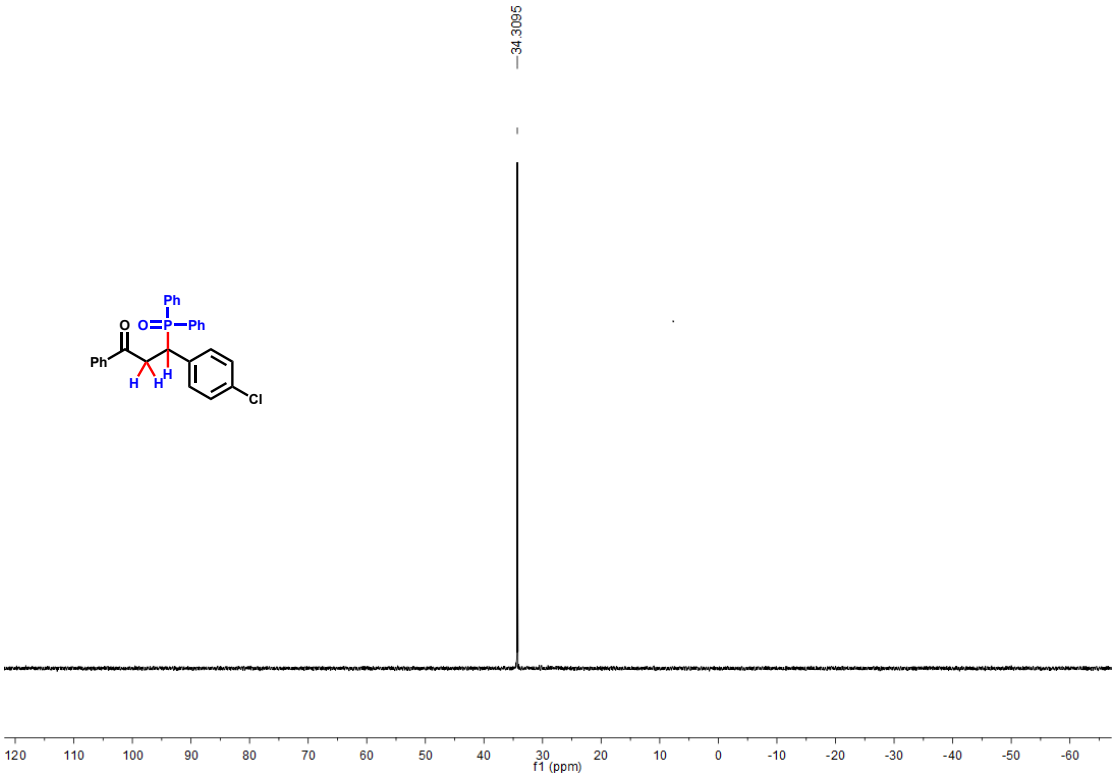

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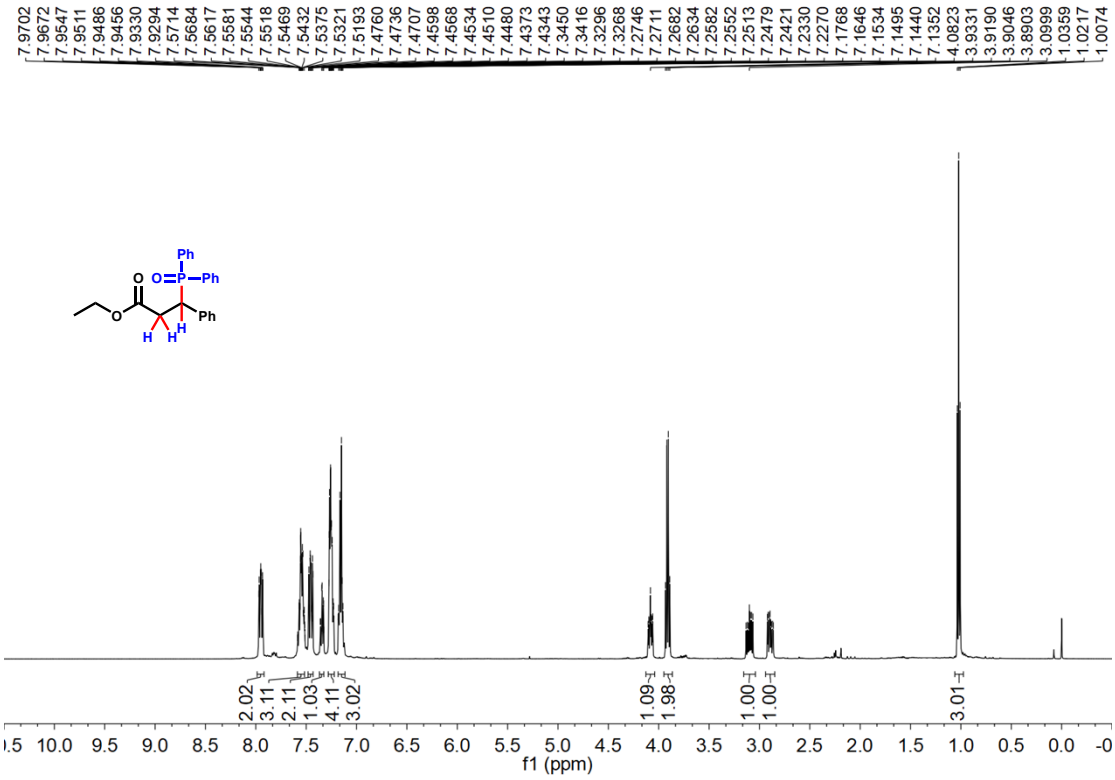

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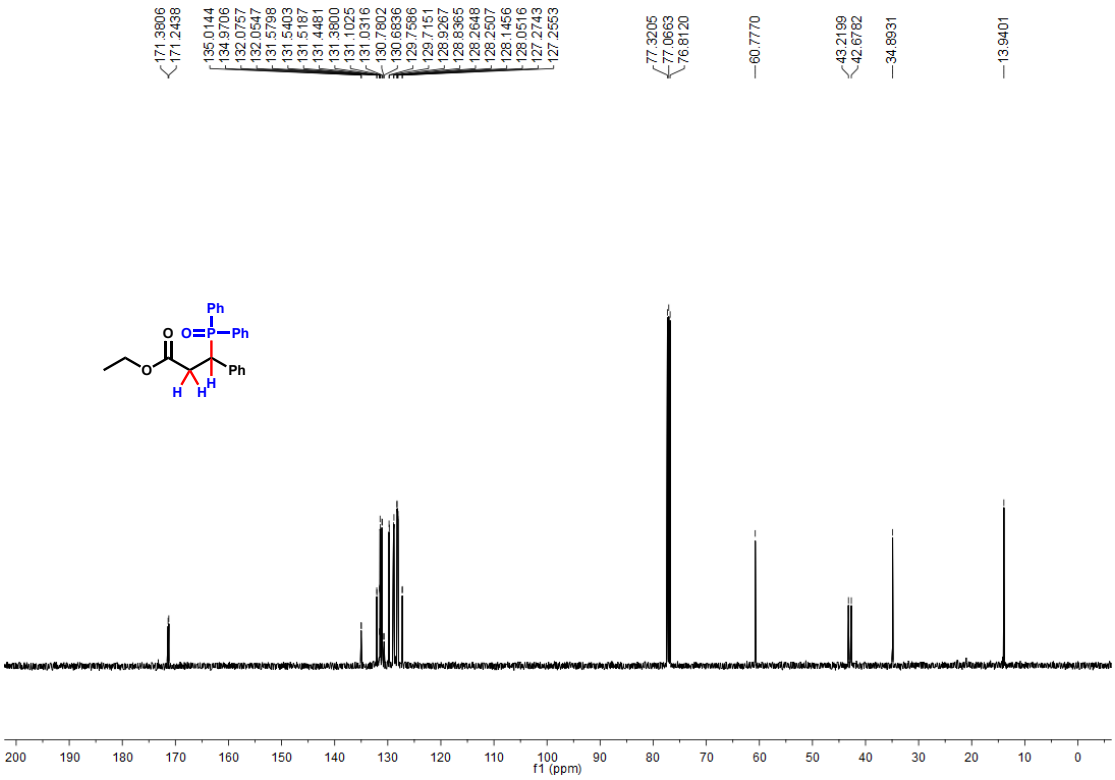

35c

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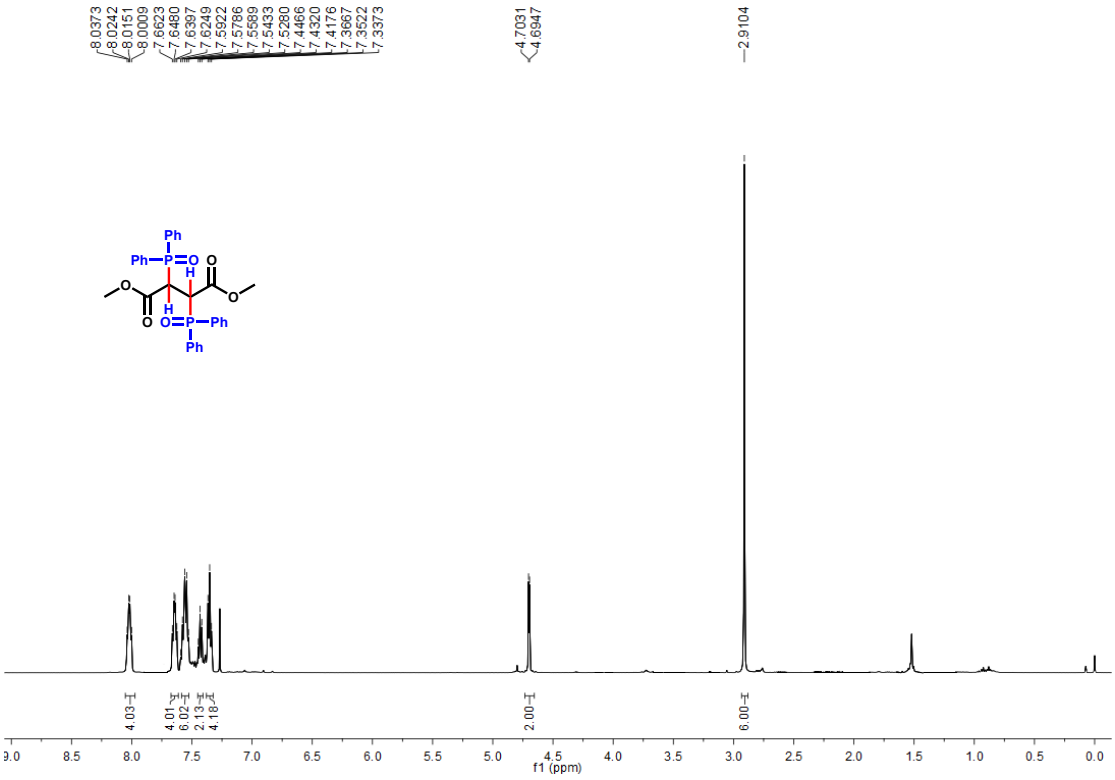

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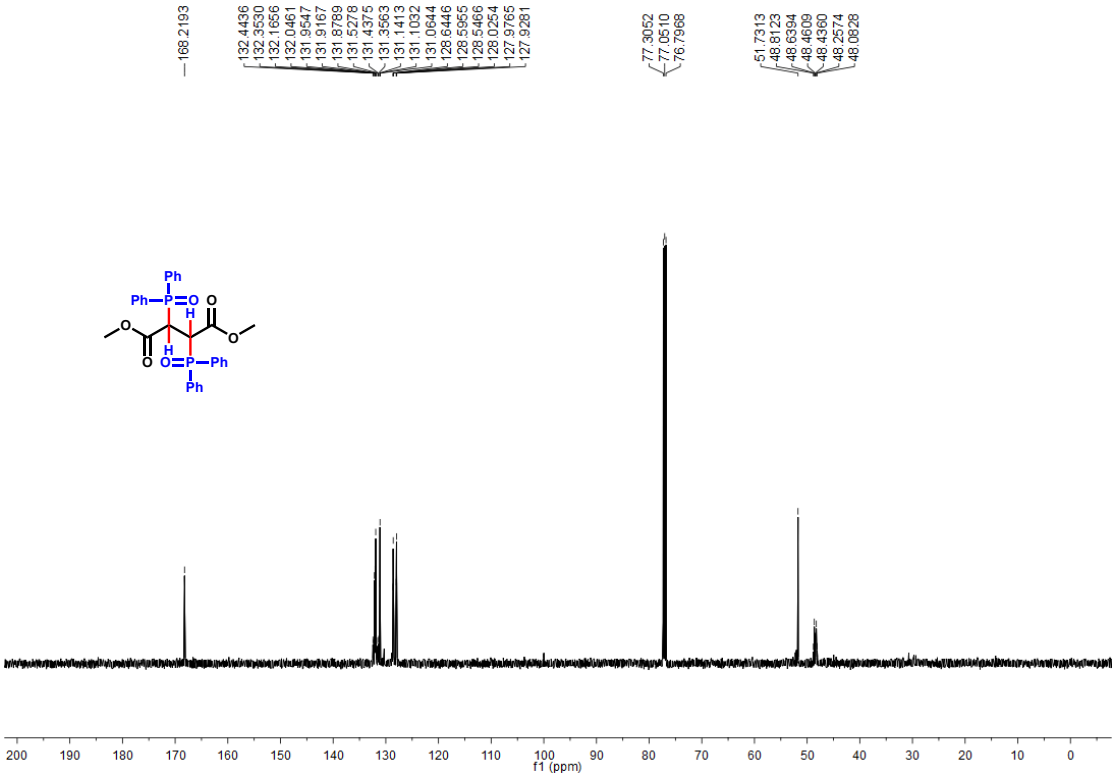

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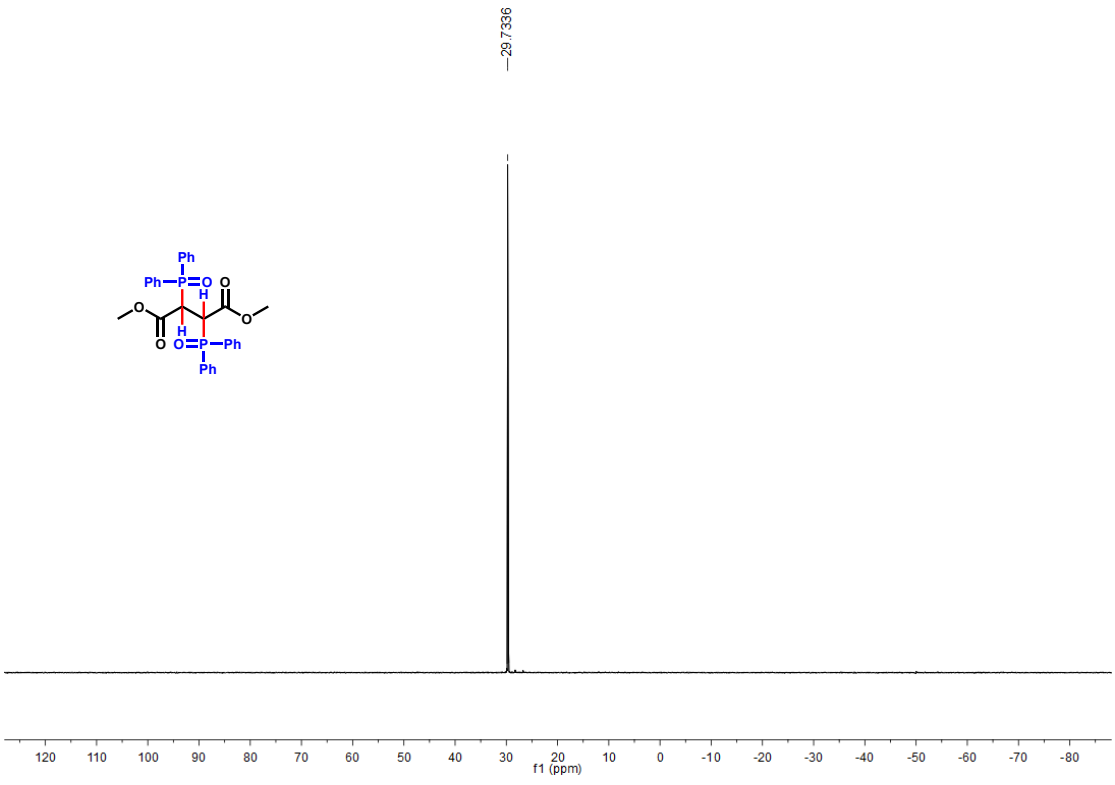
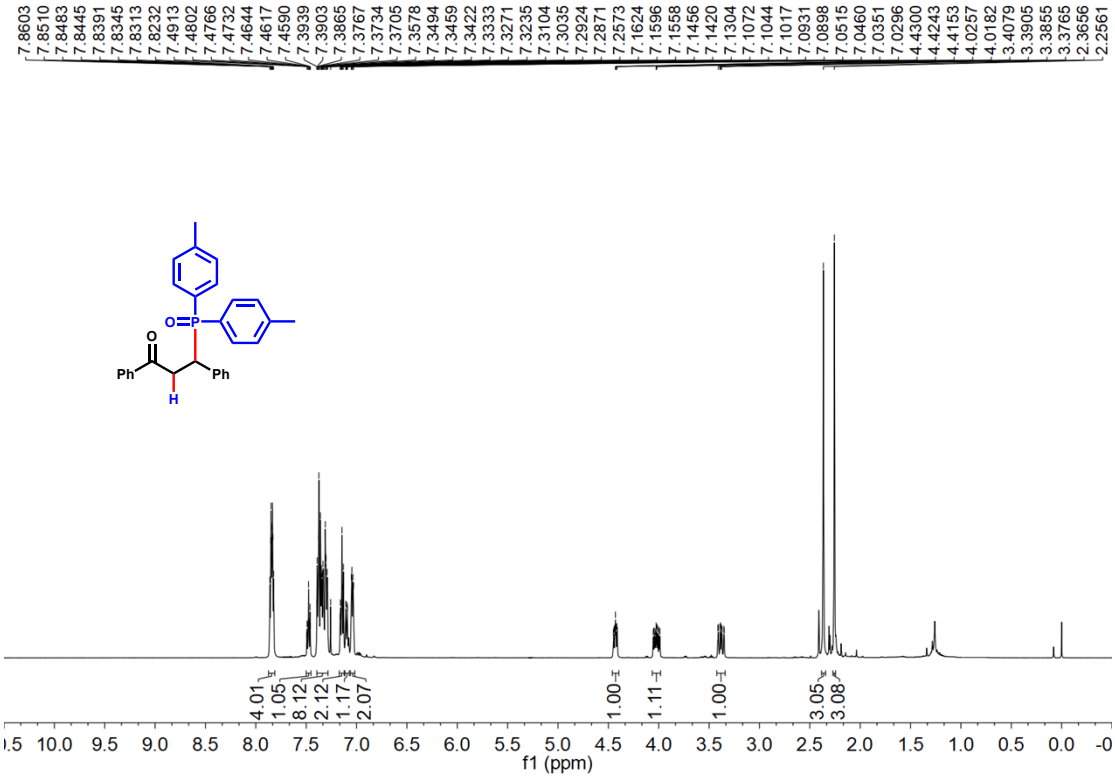


36c

^{1}H NMR



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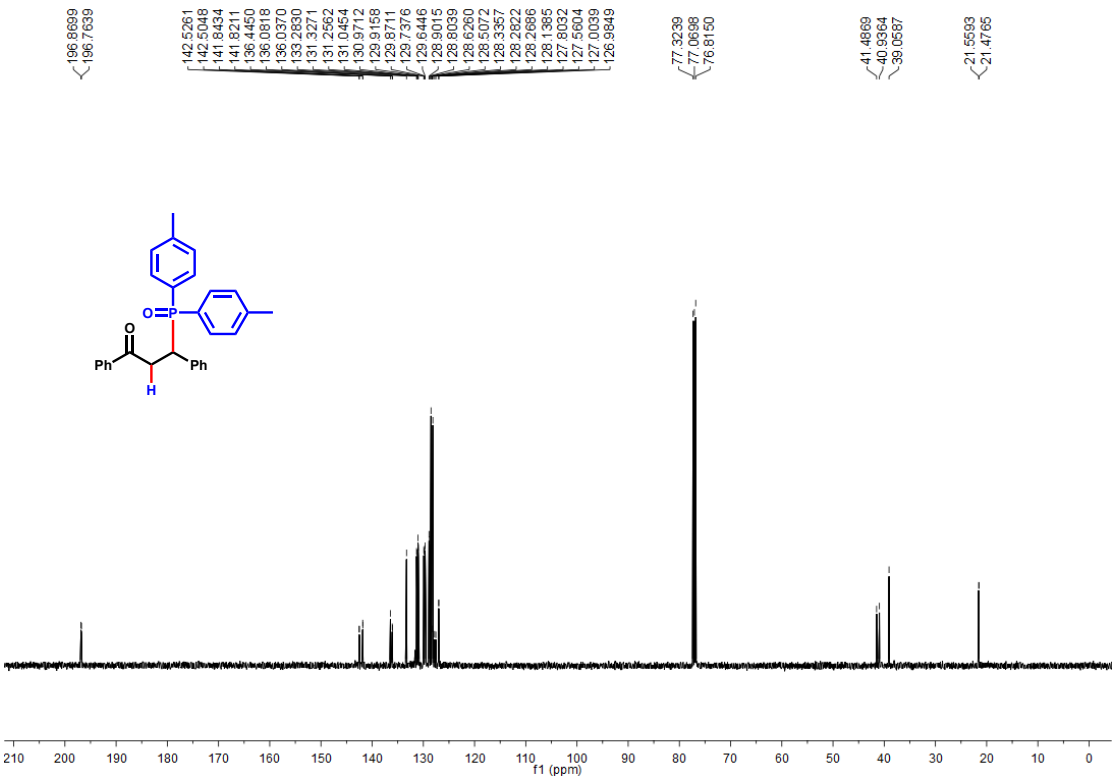

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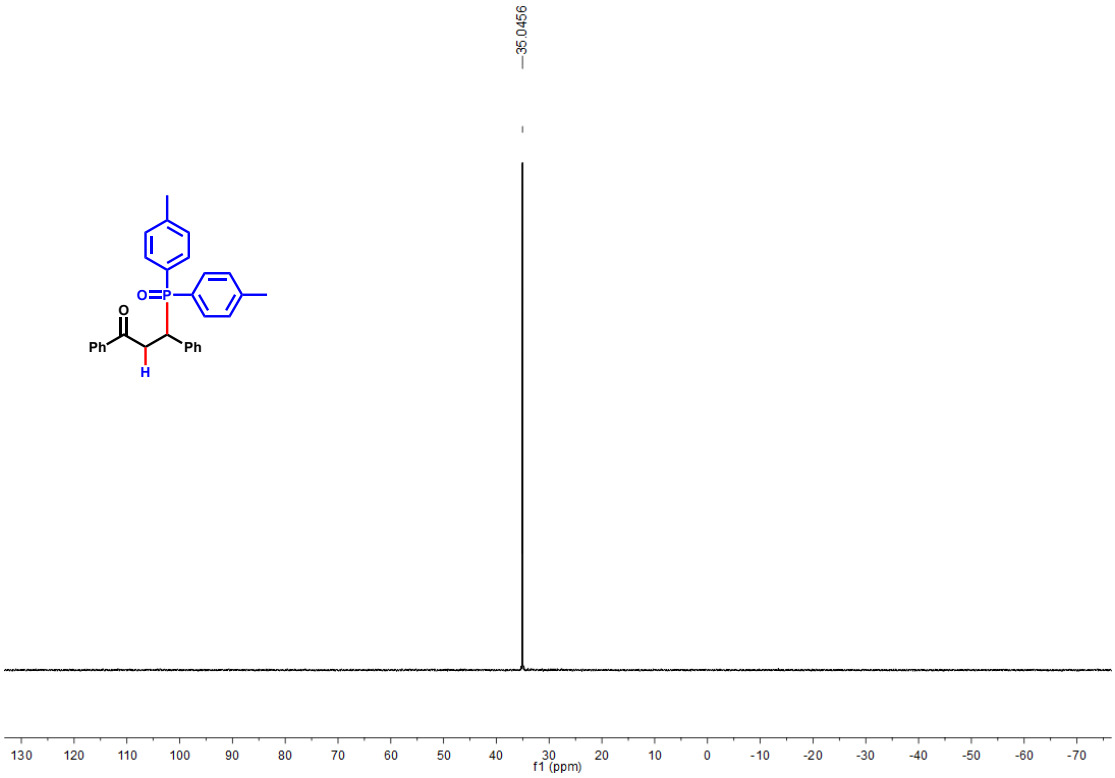

37c

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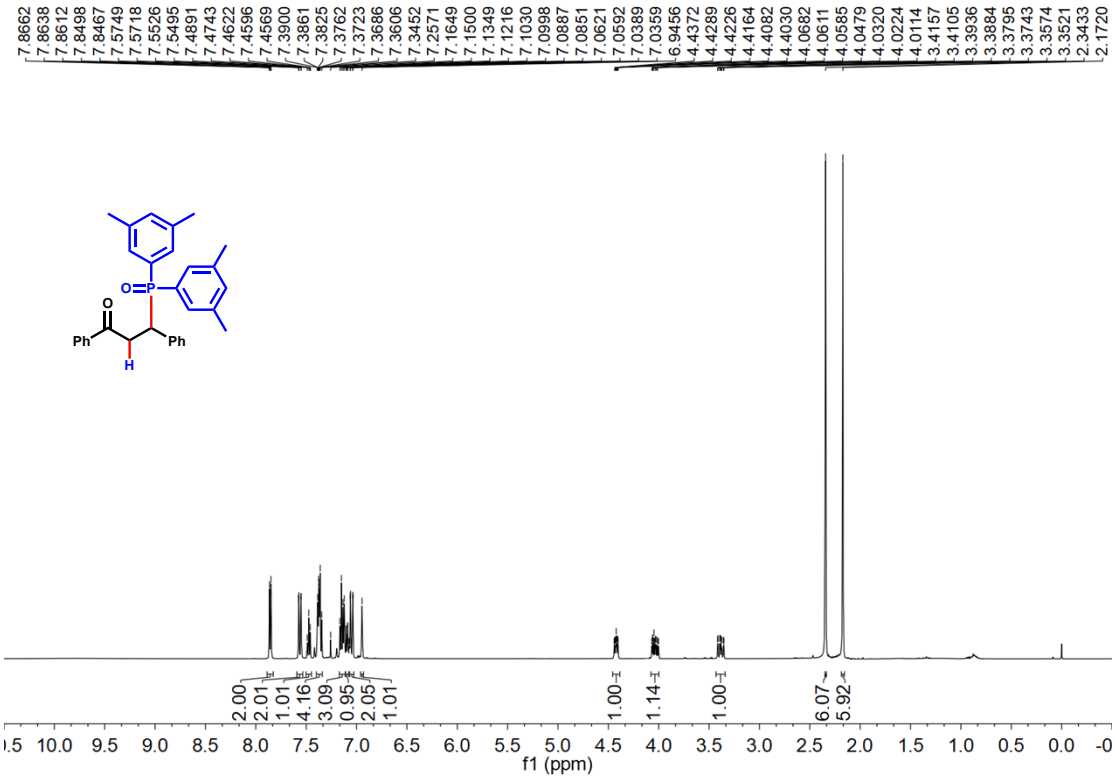

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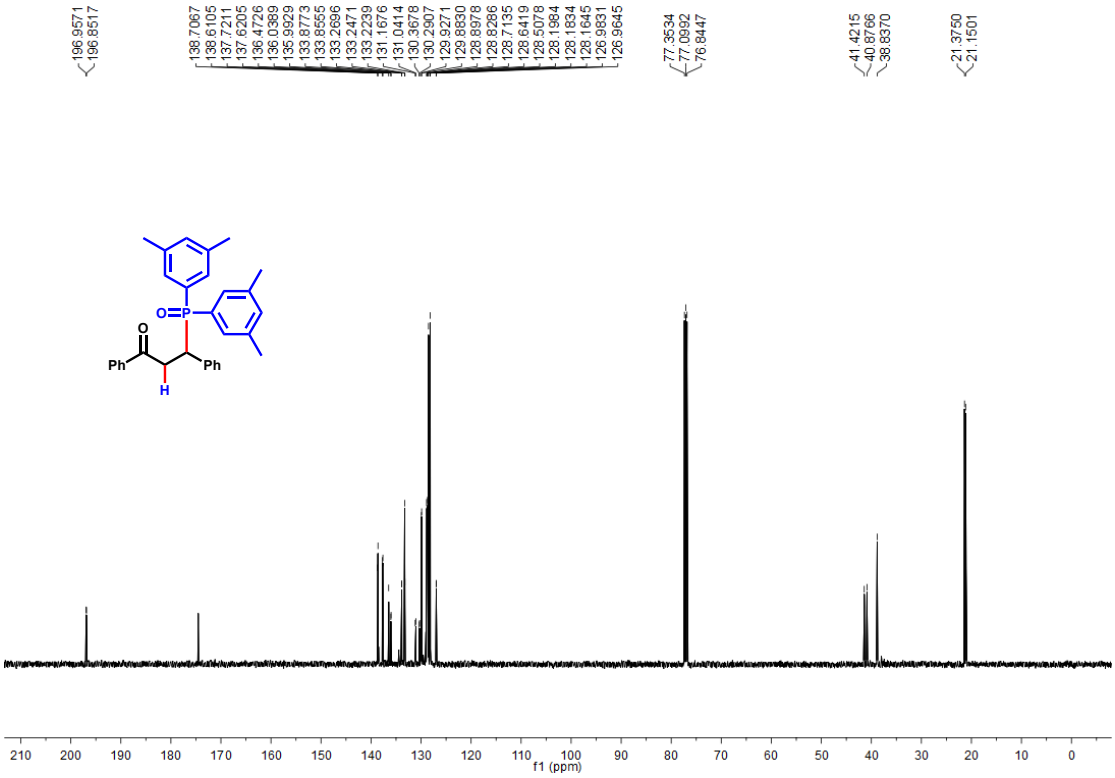

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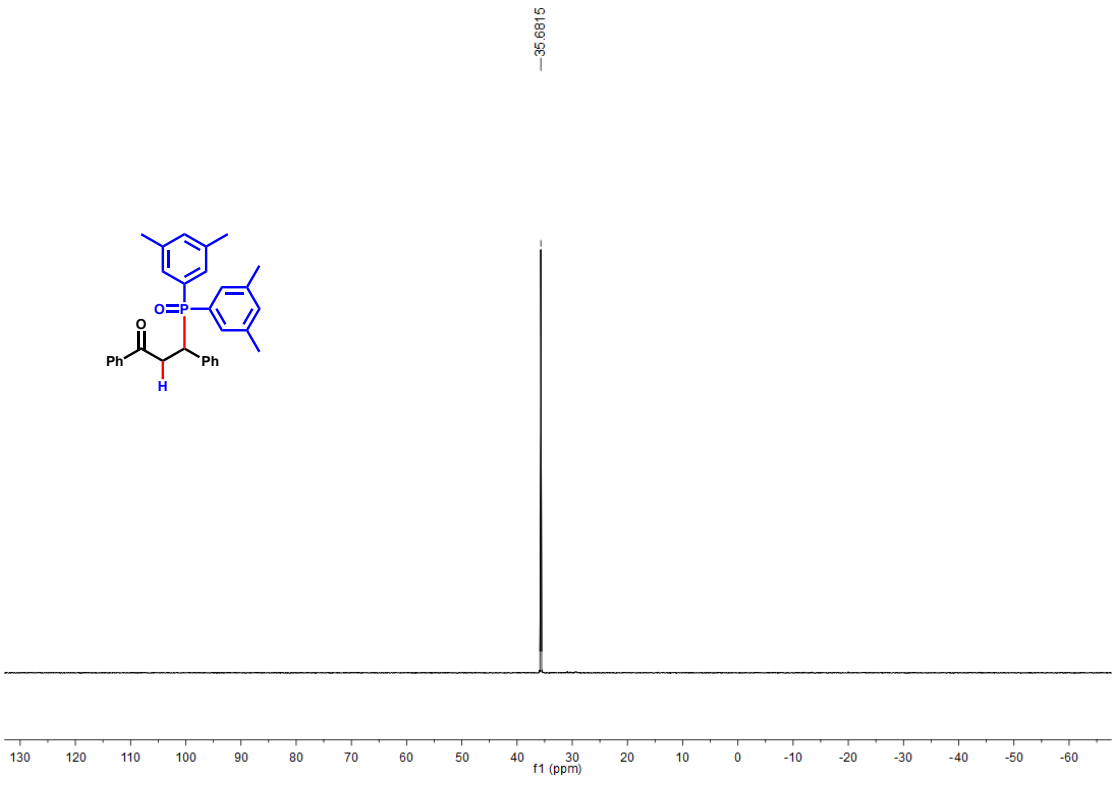

38c

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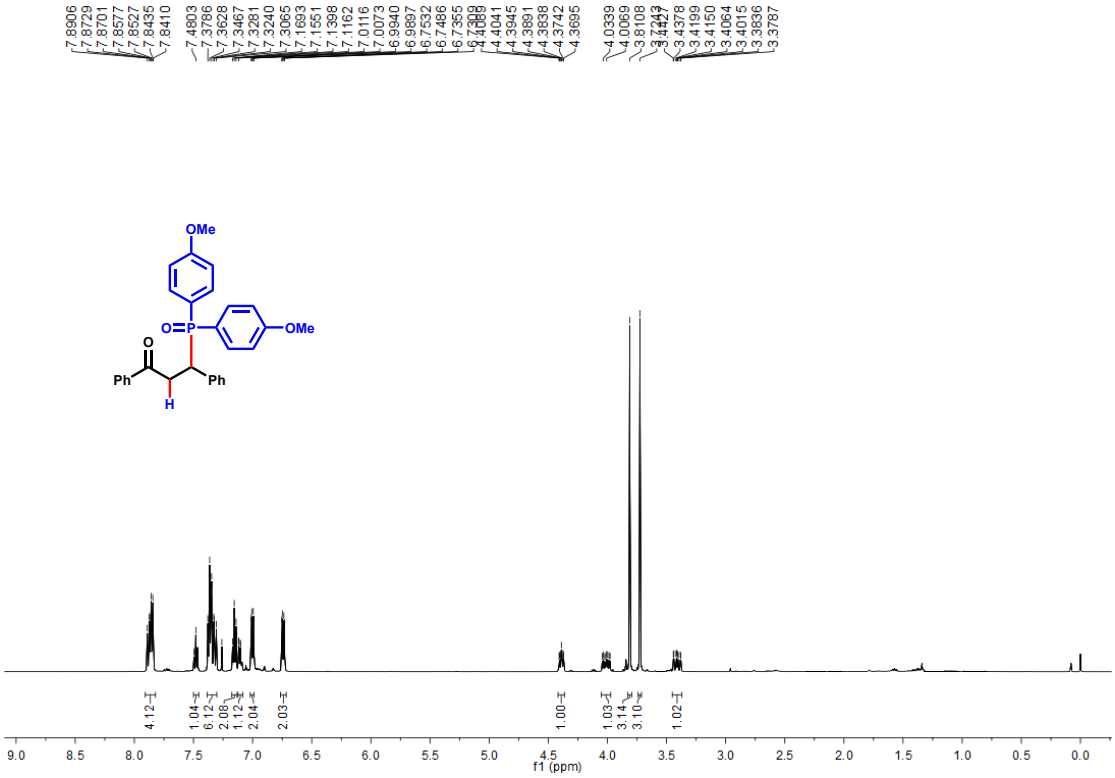

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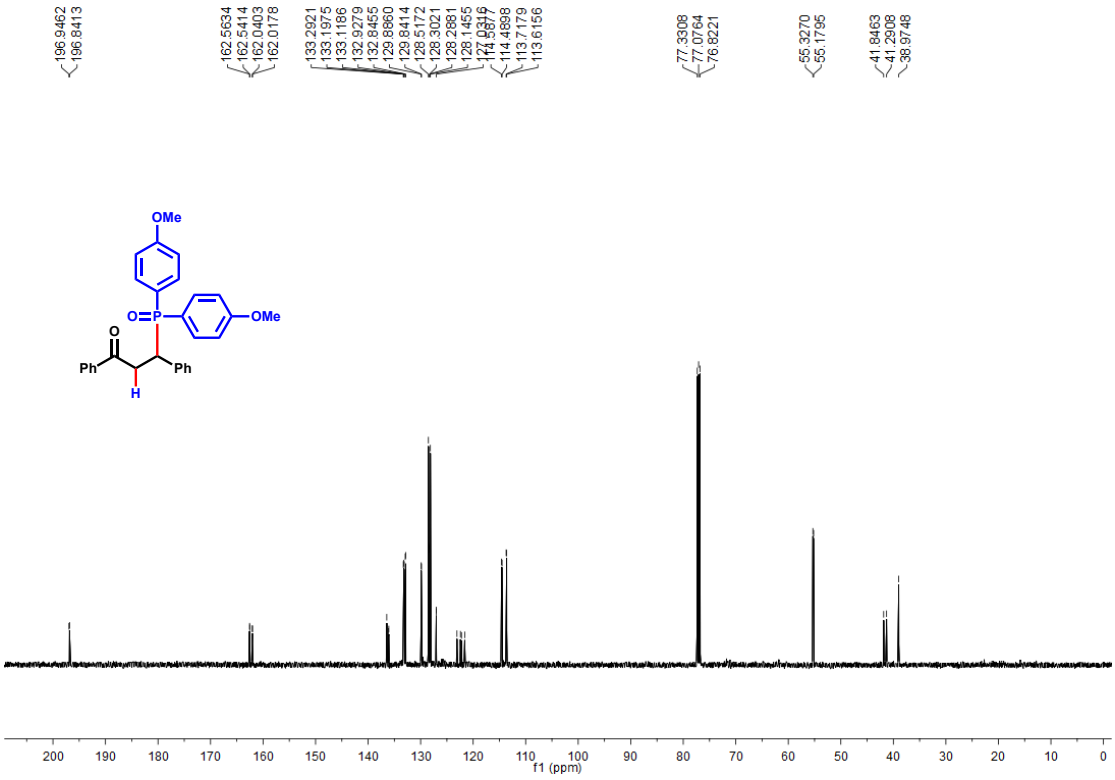

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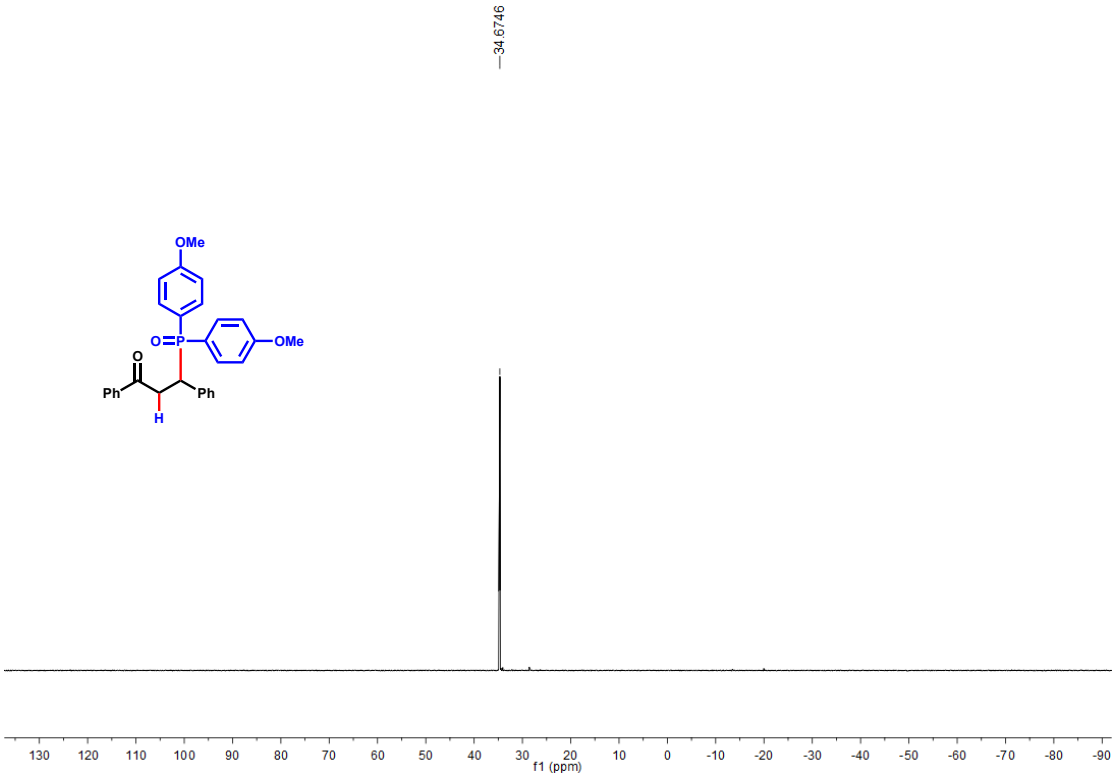

39c

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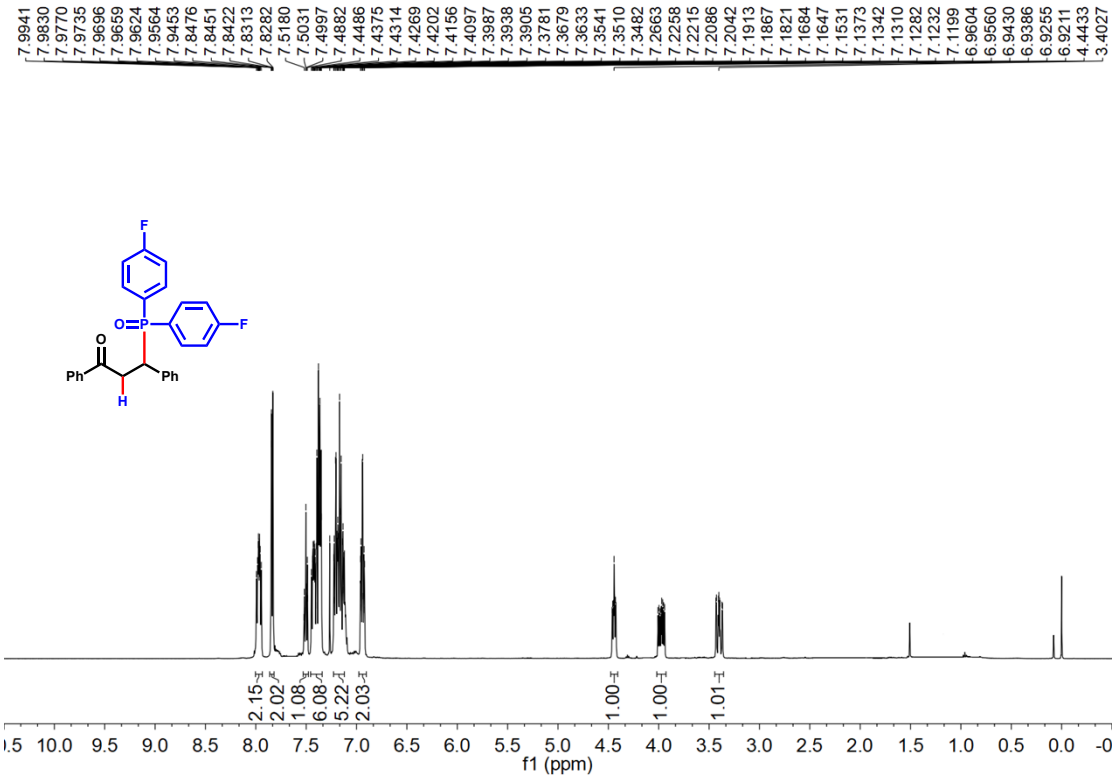

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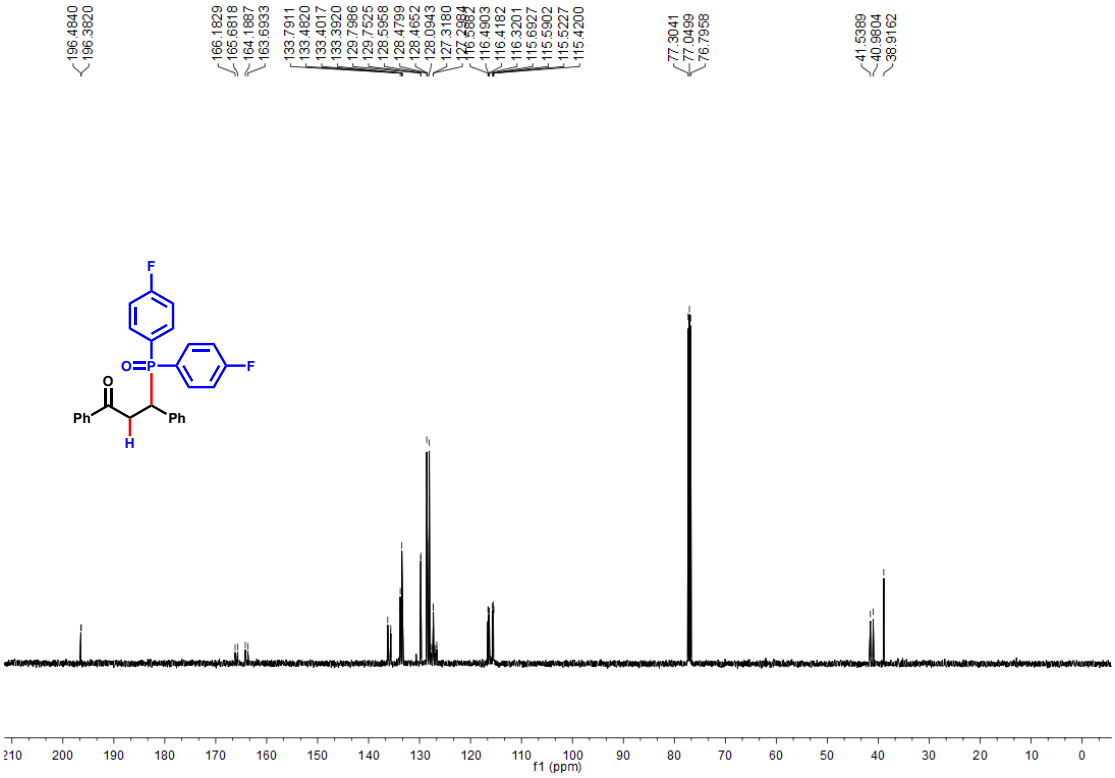
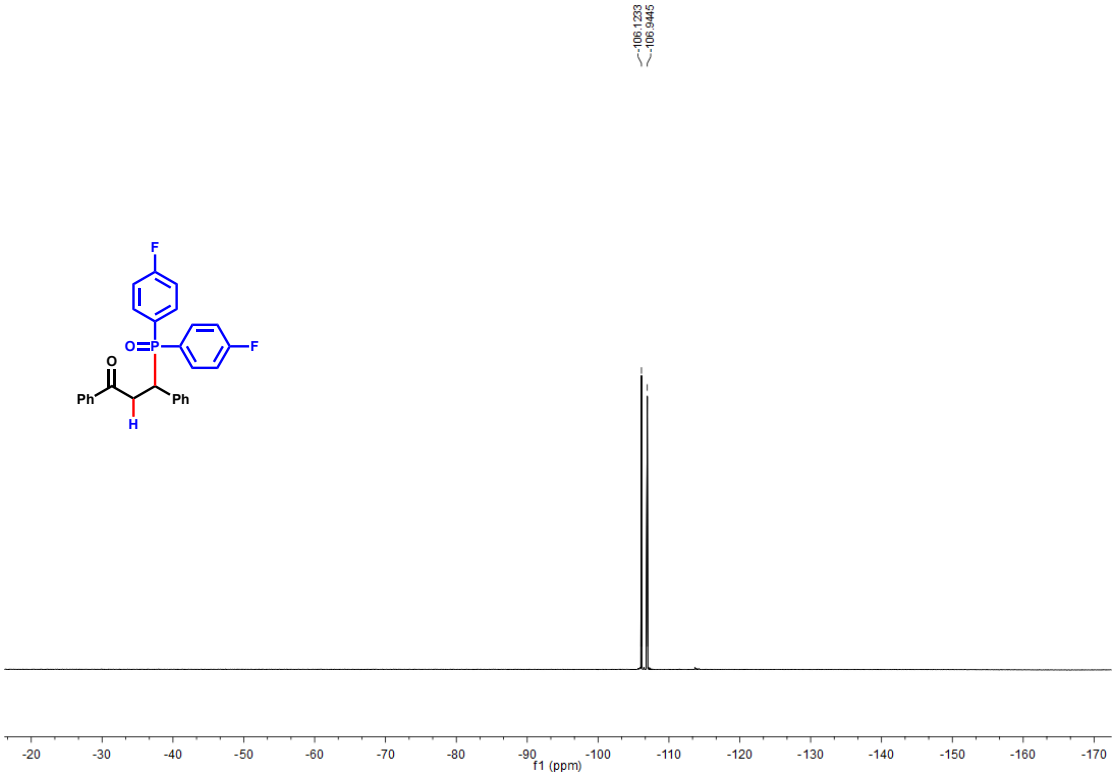
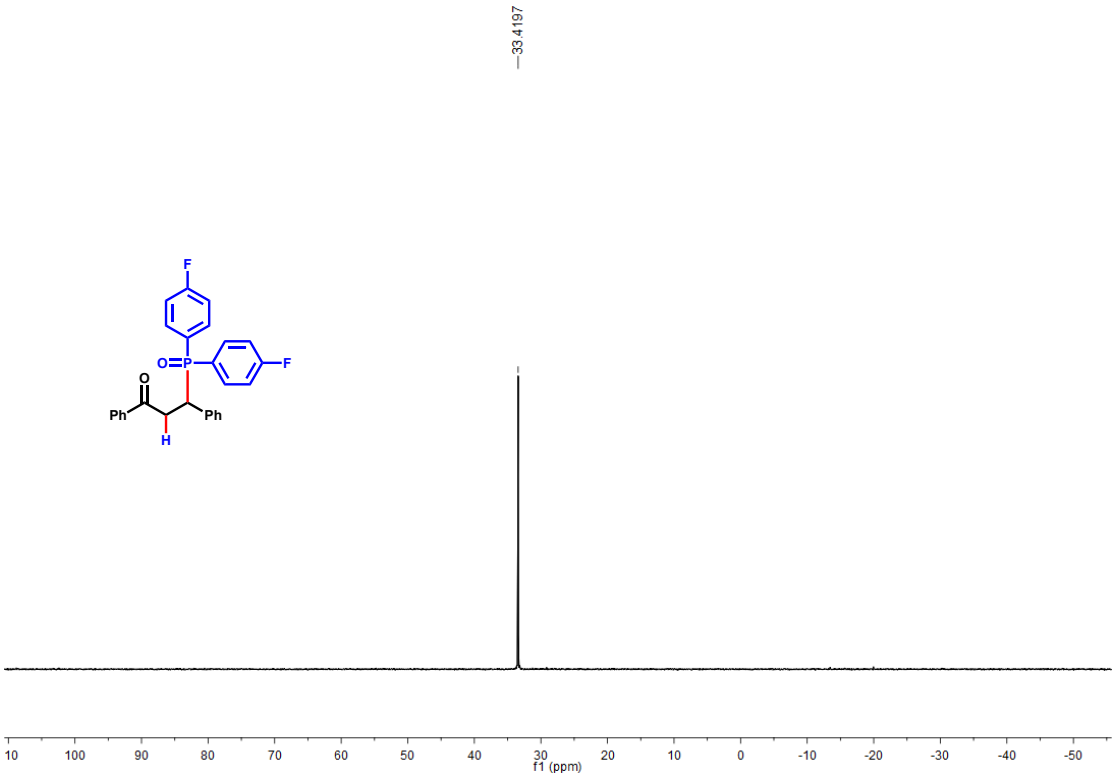


^{19}F NMR



^{31}P NMR



40c

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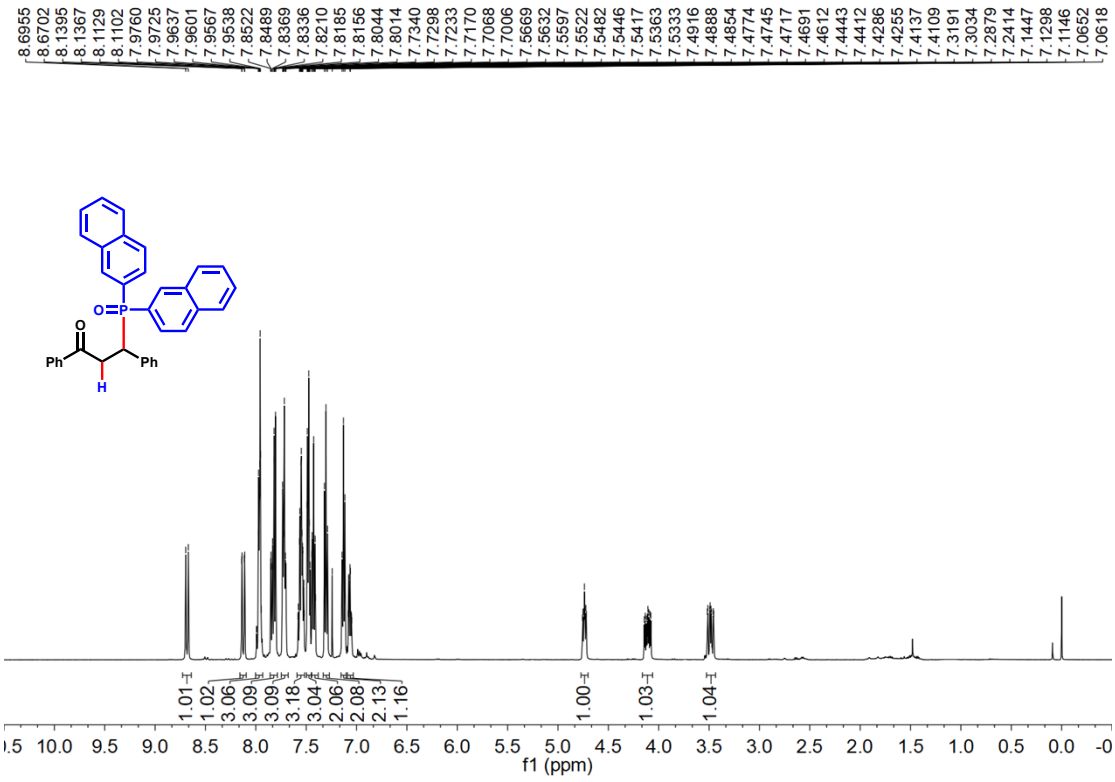

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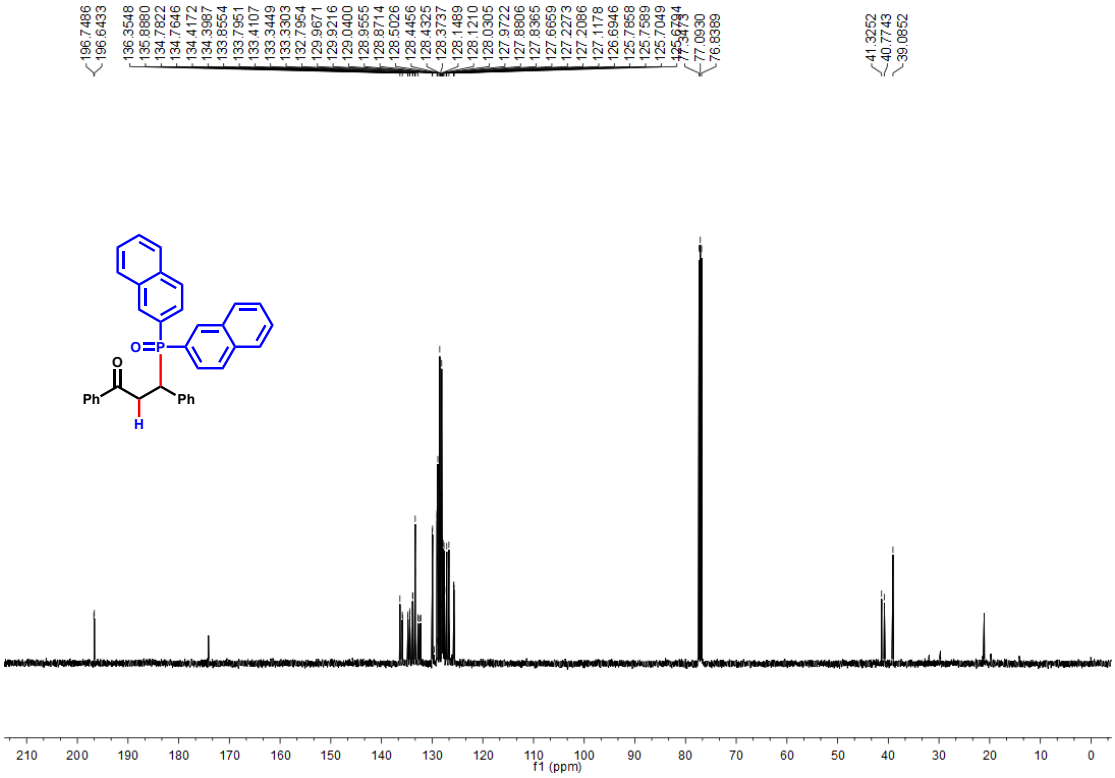

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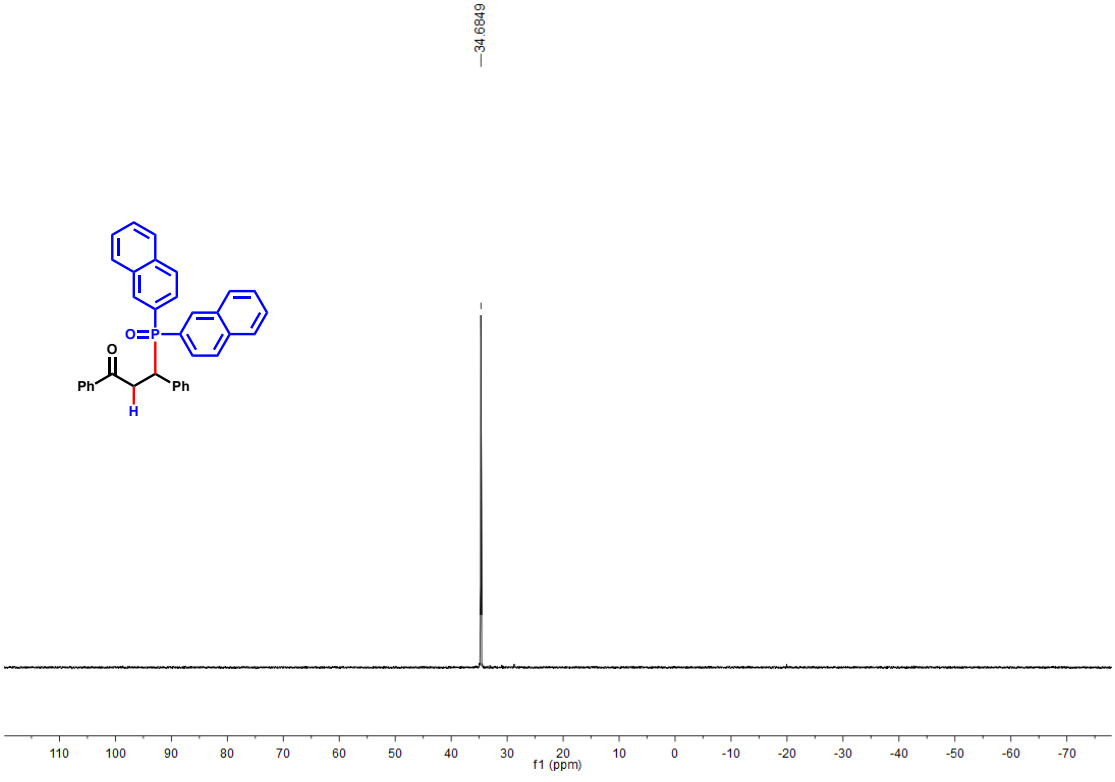
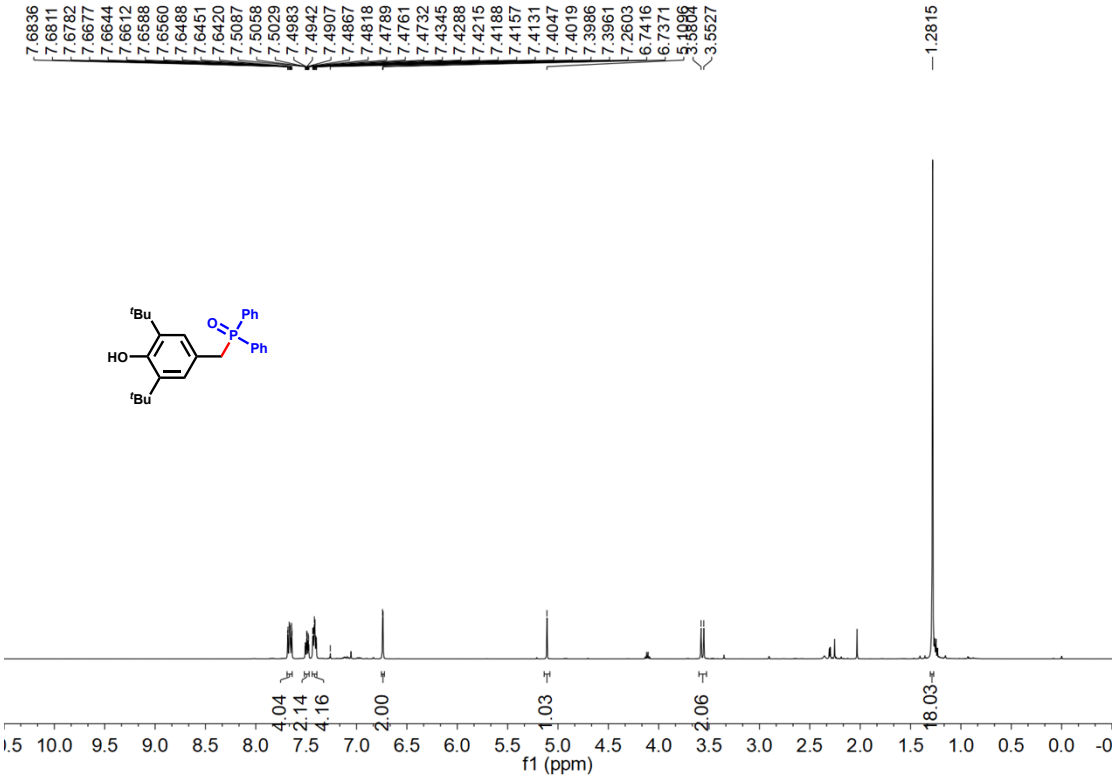


42c

^{1}H NMR



^{13}C NMR