Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Copper-Catalyzed Allylic C-H Phosphonation

Bin Yang,[a] Hong-Yu Zhang,[a] Shang-Dong Yang [a,b]*

[a] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China.

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China.

E-mail: yangshd@lzu.edu.cn

Contents

1. General information

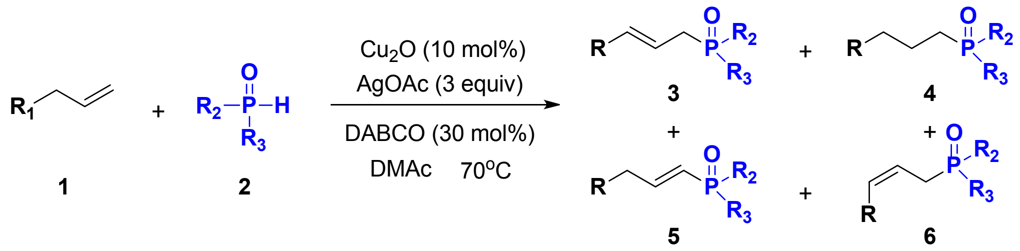
^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ 400 spectrometer in $CDCl_3$ with TMS as internal standard. ^{31}P NMR spectra were recorded on the same instrument. IR spectra were recorded on a Nexus 670 FT-IR spectrometer and only major peaks are reported in cm^{-1}. Mass spectra were mearsured using Bruker micro TOF-Q II. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. Methods for the Synthesis of Substrates:

1k[1] **, 1l**[2] **, 1m**[3] **, 1n**[4] **, 1p**[5] **, 1v**[6] were prepared according to the literature.

1b-1j and 1o, 1q, 1r, 1s, 2b, 2c were purchased from commercial source, and used without further purification.

3. Procedure for Cu_2O-Catalyzed Allylic C-H Phosphonation



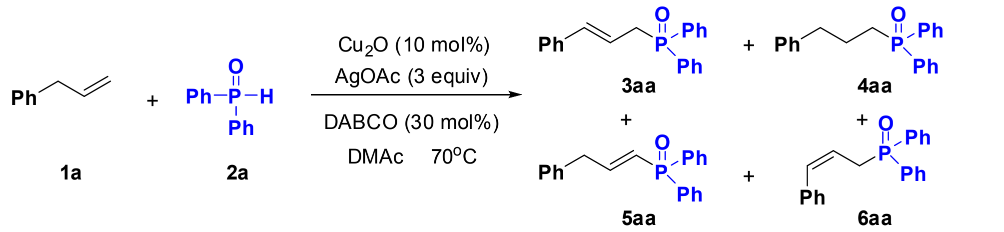
(**3ba-3ta and 3db, 3dc**) : To a Schlenk tube were added **2** (0.2 mmol), Cu_2O (10 mol %), AgOAc (0.6 mmol), 1, 4-diazabicyclooctane (30 mol %) and charged with argon for three times. Then, N, N-dimethylacetamide (2.0 mL) (dried with 4Å MS) and **1** (0.6 mmol) were added *via* syringe. The mixture was allowed to stir at 70 ℃ overnight. At the completion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organicphase was washed with water for three times and then dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel with dichloromethane/MeOH to give products **3, 4, 5** and **6** as a mixture.

Reference

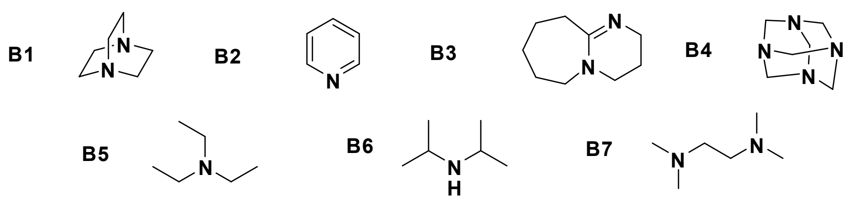
1 Smith, B. J.; Sulikowski, G. A. *Angew. Chem.* **2010**, *122,* 1643
2 Parsons, A. T.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2011**, *50,* 9120
3 Lipshutz, B. H.; Ghorai, S.; Leong, W. W. Y. *J. Org. Chem.* **2009**, *74*, 2854.
4 Wang, X.; Ye, Y. X.; Zhang, S. N.; Feng, J. J.; Xu, Y.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133,* 16410
5 Xu, J.; Fu, Y.; Luo, D.-F.; Jiang, Y.-Y.; Xiao, B.; Liu, Z.-J.; Gong, T.-J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133,* 15300

6 Norden, S.; Bender, M.; Rullkötter, J.; Christoffers, J. *Eur. J. Org. Chem.* **2011**, 4543

4. Detailed Optimization Information



Entry	Cu (10 mol %)	**1a / 2a**	AgOAc (equiv)	additive (equiv)	Solvent	T / °C	yield (%) [b]	**3aa:4aa:5aa:6aa** [c]
1	Cu_2O	2 : 1	2.0	-	DMAc	90	33	12 : 2 : 2 : 1
2	Cu_2O	1 : 2	2.0	-	DMAc	90	68	7 : 28 : 1 : 3
3[d]	Cu_2O	2 : 1	2.0	-	DMAc	90	n.d	-
4[e]	Cu_2O	2 : 1	2.0	-	DMAc	90	25	24 : 2 : 14 : 1
5[f]	Cu_2O	2 : 1	2.0	-	DMAc	90	n.d	-
6	Cu_2O	2 : 1	2.0	**B1** (2.0)	DMAc	90	56	43 : 10 : 1 : 2
7	Cu_2O	2 : 1	2.0	**B2** (2.0)	DMAc	90	33	44 : 2 : 12 : 3
8	Cu_2O	2 : 1	2.0	**B3** (2.0)	DMAc	90	trace	-
9	Cu_2O	2 : 1	2.0	**B1** (1.0)	DMAc	90	55	30 : 3 : 1 : 3
10	Cu_2O	2 : 1	2.0	**B1** (0.3)	DMAc	90	56	16 : 1 : 1 : 1
11	Cu_2O	2 : 1	2.0	**B1** (0.2)	DMAc	90	54	14 : 1 : 1.5 : 1
12	Cu_2O	2 : 1	2.0	**B1** (0.3)	THF	90	39	9 : 4 : 2 : 1
13	Cu_2O	2 : 1	2.0	**B1** (0.3)	Toluene	90	30	10 : 1 : 3 : 2
14	Cu_2O	2 : 1	2.0	**B1** (0.3)	MeCN	90	16	9 : 1 : 2.5 : 1
15	Cu_2O	2 : 1	2.0	**B4** (0.3)	DMAc	90	39	20 : 1 : 5 : 1
16	Cu_2O	2 : 1	2.0	**B5** (0.3)	DMAc	90	30	28 : 1 : 6 : 3
17	Cu_2O	2 : 1	2.0	**B6** (0.3)	DMAc	90	28	30 : 1 : 7 : 2.5
18	Cu_2O	2 : 1	2.0	**B7** (0.3)	DMAc	90	trace	-
19	Cu_2O	2 : 1	3.0	**B1** (0.3)	DMAc	70	64	14 : 1 : 2 : 1
20	Cu_2O	2 : 1	2.0	**B1** (0.3)	DMAc	50	trace	-
21	Cu_2O	3 : 1	2.0	**B1** (0.3)	DMAc	70	74	15 : 1 : 1 : 1.5
22	**Cu_2O**	**3 : 1**	**3.0**	**B1 (0.3)**	DMAc	**70**	**81**	**20 : 1 : 1 : 1.5**
23	Cu_2O	3 : 1	4.0	**B1** (0.3)	DMAc	70	70	20 : 1 : 1 : 2
24	CuTc	3 : 1	3.0	**B1** (0.3)	DMAc	70	64	10 : 1.6 : 1 : 1
25	$Cu(MeCN)_4PF_6$	3 : 1	3.0	**B1** (0.3)	DMAc	70	65	11 : 2 : 1 : 1
26	CuOTf	3 : 1	3.0	**B1** (0.3)	DMAc	70	71	9 : 2 : 1 : 1
27	$CuBr_2$	3 : 1	3.0	**B1** (0.3)	DMAc	70	42	13 : 2 : 1 : 2
28	-	3 : 1	3.0	**B1** (0.3)	DMAc	70	38	**4aa**
29	Cu_2O	3 : 1	-	**B1** (0.3)	DMAc	70	60	**4aa**

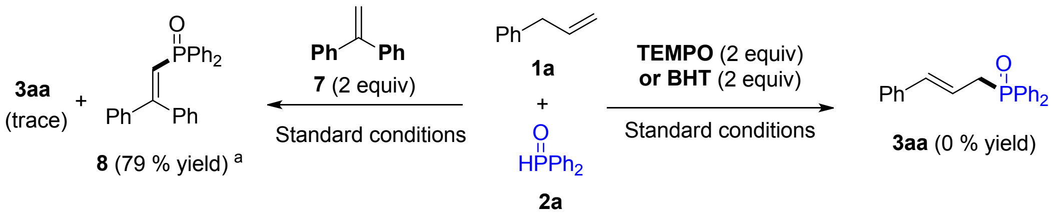


[a] The reactions were conducted on a 0.2 mmol scale, reaction conditions: **1a**, **2a**, Cu (10 mol %), AgOAc, DMAc (2.0 mL) and additive under Ar overnight. n.d = not detected. [b] Total

yield of isolated product. [c] Determined by ^1H NMR and ^{31}P NMR. [d] Ag_2CO_3 replaced AgOAc. [e] $AgNO_3$ replaced AgOAc. [f] $PhI(OAc)_2$ replaced AgOAc.

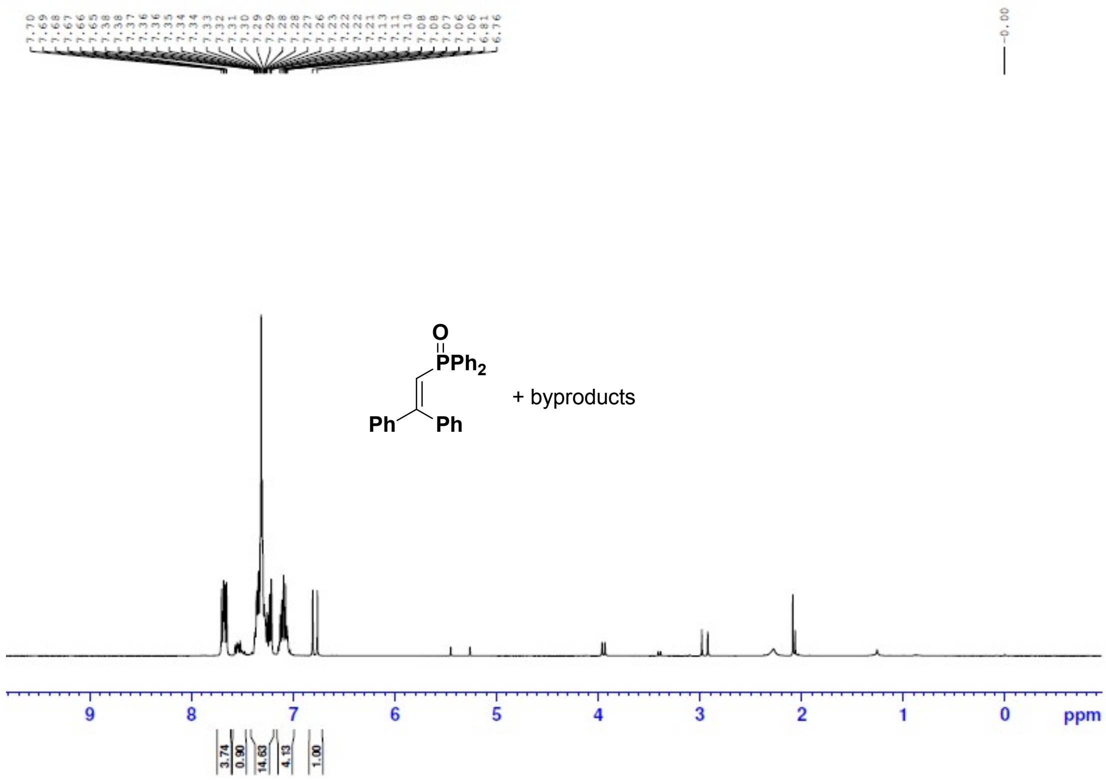
5. Preliminary Mechanistic Studies

a) Radical trapping experiments



[a] The total yield of 8(major) and byproducts.

To a Schlenk tube were added **2a** (0.2 mmol), Cu_2O (10 mol %), AgOAc (0.6 mmol), 1, 4-diazabicyclooctane (30 mol %), the radical scavenger (0.4 mmol) and charged with argon for three times. Then, N, N-dimethylacetamide (2.0 mL) and **1a** (0.6 mmol) were then added *via* syringe. The mixture was allowed to stir at 70 ℃ overnight. Then the reaction was monitored by TLC. When TEMPO or BHT (2, 6-Di-tert -butyl-4-methylphenol) was used as the radical scavenger, no product **3aa** was obtained. When 1, 1-diphenylethylene (**7**) was used as the radical scavenger, only trace **3aa** was detected, the trapping product **8** (HRMS calc. for $C_{26}H_{21}OP$ ($(M+H)^+$: 381.1403, found 381.1407) with other byproducts were obtained in a total 79 % yield (calculating based on **2a**).



b) Procedures for [$Ph_2P(O)Ag$] 9 used in reaction

To a Schlenk tube were added **9** (0.2 mmol), Cu_2O (10 mol %), AgOAc (0.6 mmol), 1, 4-diazabicyclooctane (30 mol %) and charged with argon for three times. Then, N, N-dimethylacetamide (2.0 mL) and **1** (0.6 mmol) were then added *via* syringe. The mixture was allowed to stir at 70 ^{o}C overnight. At the completion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organicphase was washed with a large amount of water for three times, with brine for once and then dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel with dichloromethane/MeOH to give products **3aa, 4aa, 5aa** and **6aa** as a mixture.

c) *p*H experiment

To a Schlenk tube were added **2** (0.4 mmol), Cu_2O (10 mol %), AgOAc (1.2 mmol), 1, 4-diazabicyclooctane (30 mol %) and charged with argon for three times. Then, N, N-dimethylacetamide (4.0 mL) and **1** (1.2 mmol) were then added *via* syringe. The mixture was allowed to stir at 70 ^{o}C. At different time points, the reaction was cooled to room temperature and the pH value was measured (*p*H were mearsured using METTLE TOLEDOFE20-FiveEasyTM *p*H). The *p*H values at different time points are listed in Table 1.

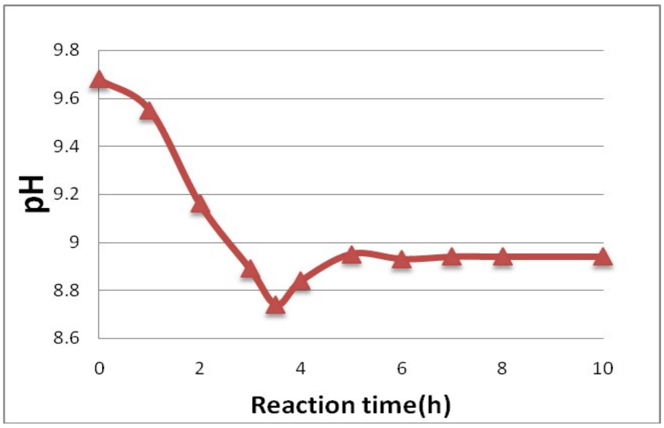


Table 1

Reaction Time (h)	0	1	2	3	3.5	4	5	6	7	8	10
pH	9.68	9.55	9.16	8.89	8.74	8.84	8.95	8.93	8.94	8.94	8.94

Temperature : 15℃

d) Composition of 3aa + 4aa under different equivalents of AgOAc

To a Schlenk tube were added **2** (0.2 mmol), Cu_2O (10 mol %), AgOAc (different equivalents are listed in Table 2), 1, 4-diazabicyclooctane (30 mol %) and charged with argon for three times. Then, N, N-dimethylacetamide (2.0 mL) and **1** (0.6 mmol) were then added *via* syringe. The mixture was allowed to stir at 70 ^{o}C overnight. At the completion of the reaction, water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organicphase was washed with a large amount of water for three times, with brine for once and then dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel with DCM/MeOH. Ignoring the small amounts of other byproducts, the ratio of **3aa/4aa** was determined by ^{31}P NMR.

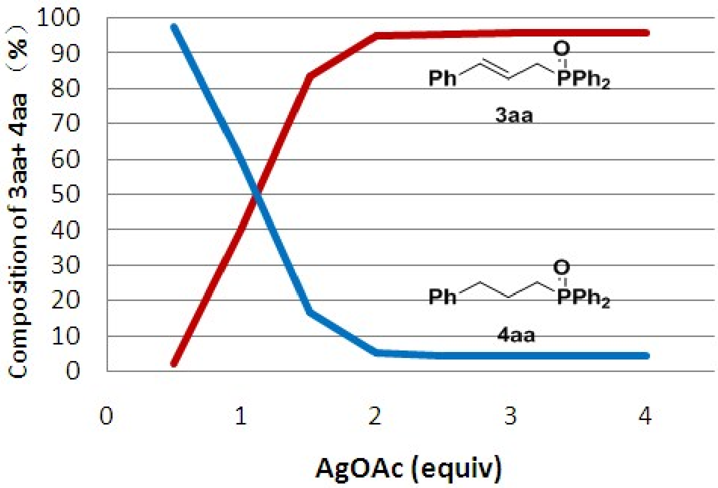
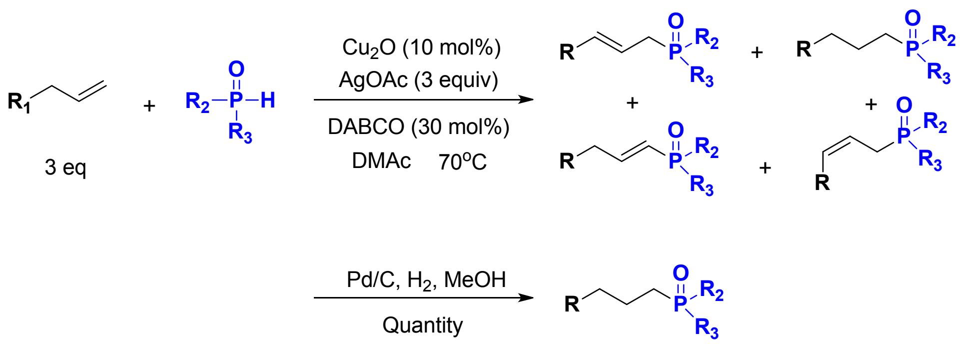
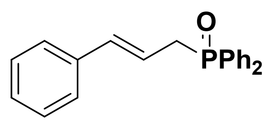


Table 2

AgOAc (equiv.)	0.5	1	1.5	2	2.5	3	4
3aa/3aa+4aa (%)	2.4	40.5	83.3	95	95.5	95.8	95.83
4aa/3aa+4aa (%)	97.6	59.5	16.6	5	4.5	4.2	4.17

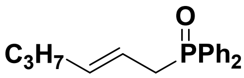
6. Characterization of the Products





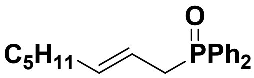
3aa

Selected major product, White solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.74 (m, 4H), 7.53-7.45 (m, 6H), 7.26-7.18 (m, 5H), 6.45-6.40 (m, 1H), 6.22-6.13 (m, 1H), 3.29 (dd, J_1 = 7.5 Hz, J_2 = 15.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7 (d, J_{C-P} = 3.0 Hz), 135.6 (d, J_{C-P} = 12.1 Hz), 132.4 (d, J_{C-P} = 98.1 Hz), 131.8 (d, J_{C-P} = 2.7 Hz), 131.0 (d, J_{C-P} = 9.1 Hz), 128.6 (d, J_{C-P} = 11.6 Hz), 128.4, 127.5, 126.2 (d, J_{C-P} = 1.6 Hz), 118.4 (d, J_{C-P} = 9.6 Hz), 35.6 (d, J_{C-P} = 68.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.97. IR (film) $υ_{max}$: 3404, 2926, 1437, 1184, 1119, 1069, 968, 731, 720, 694 cm^{-1}. HRMS calc. for $C_{21}H_{19}OP$ (M+H)$^+$:319.1246, found 319.1244.



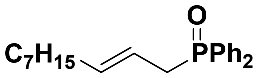
3ba

Selected major product, brown oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.70 (m, 4H), 7.52-7.42 (m, 6H), 5.52-5.36 (m, 2H), 3.07 (dd, J_1 = 6.9 Hz, J_2 = 10.4 Hz, 2H), 1.94-1.86 (m, 2H), 1.28-1.19 (m, 2H), 0.74 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2 (d, $J_{C\text{-}P}$ = 11.7 Hz), 132.6 (d, $J_{C\text{-}P}$ = 97.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 118.0 (d, $J_{C\text{-}P}$ = 5.9 Hz), 34.8 (d, $J_{C\text{-}P}$ = 69.2 Hz), 34.6 (d, $J_{C\text{-}P}$ = 2.1 Hz), 22.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 13.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.39. IR (film) υ_{max}: 3424, 2957, 2929, 1437, 1189, 1120, 968, 729, 719, 696 cm^{-1}. HRMS calc. for $C_{18}H_{21}OP$ (M+H) $^+$: 285.1403, found 285.1400.



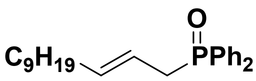
3ca

Selected major product, brown oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.69 (m, 4H), 7.51-7.42 (m, 6H), 5.52-5.36 (m, 2H), 3.06 (dd, J_1 = 6.9 Hz, J_2 = 14.4 Hz, 2H), 1.95-1.89 (m, 2H), 1.26-1.07 (m, 6H), 0.81 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 132.6 (d, $J_{C\text{-}P}$ = 97.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.6 Hz), 117.8 (d, $J_{C\text{-}P}$ = 9.2 Hz), 34.8 (d, $J_{C\text{-}P}$ = 69.2 Hz), 32.5 (d, $J_{C\text{-}P}$ = 2.2 Hz), 31.0, 28.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 22.3, 13.9. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.47. IR (film) υ_{max}: 3422, 2956 2926, 2855, 1437, 1188, 1120, 971, 719,696 cm^{-1}. HRMS calc. for $C_{20}H_{25}OP$ (M+H)$^+$: 313.1716, found 313.1713.



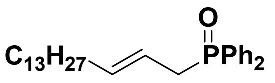
3da

Selected major product, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.70 (m, 4H), 7.52-7.43 (m, 6H), 5.53-5.36 (m, 2H), 3.07 (dd, J_1 = 6.9 Hz, J_2 = 14.5 Hz, 2H), 1.95-1.89 (m, 2H), 1.28-1.11 (m, 10H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5 (d, $J_{C\text{-}P}$ = 11.8 Hz), 132.6 (d, $J_{C\text{-}P}$ = 97.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 117.8 (d, $J_{C\text{-}P}$ = 9.2 Hz), 34.8 (d, $J_{C\text{-}P}$ = 69.2 Hz), 32.5 (d, $J_{C\text{-}P}$ = 2.0 Hz), 31.7, 29.0, 28.9, 28.8, 22.6, 14.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.52. IR (film) υ_{max}: 3412, 2926, 2854, 1437, 1188, 1120, 970, 719, 696 cm^{-1}. HRMS calc. for $C_{22}H_{29}OP$ (M+H)$^+$: 341.2029, found 341.2025.



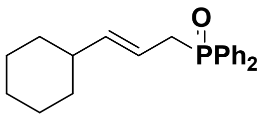
3ea

Selected major product, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.70 (m, 4H), 7.52-7.42 (m, 6H), 5.52-5.36 (m, 2H), 3.06 (dd, J_1 = 6.9 Hz, J_2 = 14.4 Hz, 2H), 1.95-1.89 (m, 2H), 1.30-1.11 (m, 14H), 0.87 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5 (d, J_{C-P} = 11.7 Hz), 132.6 (d, J_{C-P} = 97.5 Hz), 131.6 (d, J_{C-P} = 2.5 Hz), 131.0 (d, J_{C-P} = 9.0 Hz), 128.4 (d, J_{C-P} = 11.6 Hz), 117.8 (d, J_{C-P} = 9.1 Hz), 34.8 (d, J_{C-P} = 69.2 Hz), 32.6 (d, J_{C-P} = 2.1 Hz), 31.8, 29.4, 29.3, 29.2, 29.0 (d, J_{C-P} = 3.0 Hz), 28.9, 22.6, 14.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.44. IR (film) υ_{max}: 3422, 2925, 2854, 1462, 1438, 1190, 1118, 970, 724, 698 cm^{-1}. HRMS calc. for $C_{24}H_{33}OP$ $(M+H)^+$: 369.2342, found 369.2337.



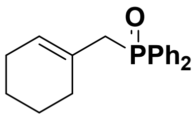
3fa

Selected major product, white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.70 (m, 4H), 7.52-7.42 (m, 6H), 5.52-5.36 (m, 2H), 3.07 (dd, J_1 = 6.8 Hz, J_2 = 14.4 Hz, 2H), 1.93-1.91 (m, 2H), 1.29-1.11 (m, 22H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4 (d, J_{C-P} = 11.7 Hz), 132.6 (d, J_{C-P} = 97.7 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 131.0 (d, J_{C-P} = 9.1 Hz), 128.4 (d, J_{C-P} = 11.5 Hz), 117.8 (d, J_{C-P} = 9.0 Hz), 34.8 (d, J_{C-P} = 69.2 Hz), 32.6, 31.8, 29.6, 29.5, 29.4, 29.3, 29.0, 28.9, 22.6, 14.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.40. IR (film) υ_{max}: 3399, 2916, 2851, 1469, 1438, 1184, 1120, 972, 719, 695 cm^{-1}. HRMS calc. for $C_{28}H_{41}OP$ $(M+H)^+$: 425.2968, found 425.2962.



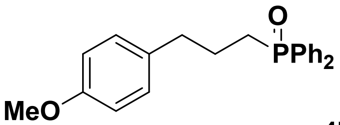
3ga

Selected major product, white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.69 (m, 4H), 7.52-7.41 (m, 6H), 5.39-5.37 (m, 2H), 3.07-3.02 (m, 2H), 1.88-1.82 (m, 1H), 1.63-1.50 (m, 4H), 1.24-1.03 (m, 4H), 0.93-0.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1 (d, J_{C-P} = 11.6 Hz), 132.6 (d, J_{C-P} = 97.8 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 128.3 (d, J_{C-P} = 11.6 Hz), 115.6 (d, J_{C-P} = 9.2 Hz), 40.7, 34.9 (d, J_{C-P} = 68.9 Hz), 33.0, 32.5 (d, J_{C-P} = 2.6 Hz), 26.0, 25.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.64. IR (film) υ_{max}: 3421, 2924, 2851, 1438, 1187, 1120, 969, 733, 720, 696 cm^{-1}. HRMS calc. for $C_{21}H_{25}OP$ $(M+H)^+$: 325.1716, found 325.1713.



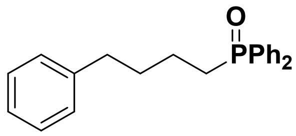
3ha

Selected major product, white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.72 (m, 4H), 7.51-7.42 (m, 6H), 5.40 (d, J = 2.8 Hz, 1H), 2.99 (d, J = 13.7 Hz, 2H), 1.96-1.88 (m, 4H), 1.52-1.40 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.2 (d, J_{C-P} = 96.9 Hz), 131.5 (d, J_{C-P} = 2.5 Hz), 131.0 (d, J_{C-P} = 8.9 Hz), 128.3 (d, J_{C-P} = 11.5 Hz), 127.5 (d, J_{C-P} = 10.0 Hz), 39.6 (d, J_{C-P} = 67.6 Hz), 30.2 (d, J_{C-P} = 2.3 Hz), 25.4 (d, J_{C-P} = 2.2 Hz), 22.7, 21.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.67. IR (film) υ_{max}: 3406, 2926, 2854, 1436, 1188, 1117, 920, 721, 695 cm^{-1}. HRMS calc. for $C_{19}H_{21}OP$ $(M+H)^+$: 297.1403, found 297.1405.



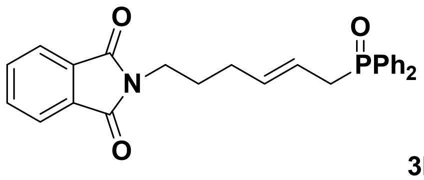
4ia

White solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.66 (m, 4H), 7.52-7.43 (m, 6H), 7.03 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H), 2.66 (t, J = 7.2 Hz, 2H), 2.27-2.20 (m, 2H), 1.98-1.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 132.9 (d, J_{C-P} = 97.5 Hz), 132.8, 131.6 (d, J_{C-P} = 2.5 Hz), 130.7 (d, J_{C-P} = 9.2 Hz), 129.4, 128.6 (d, J_{C-P} = 11.5 Hz), 113.8, 55.2, 35.7 (d, J_{C-P} = 14.7 Hz), 28.8 (d, J_{C-P} = 71.7 Hz), 23.1 (d, J_{C-P} = 3.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.46. IR (film) υ_{max}: 3408, 2926, 1512, 1438, 1245, 1179, 1119, 719, 697 cm^{-1}. HRMS calc. for $C_{22}H_{23}O_2P$ $(M+H)^+$: 351.1508, found 351.1505.



4ja

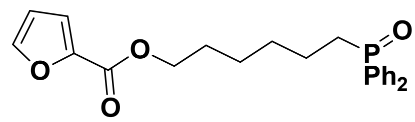
White solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.69 (m, 4H), 7.53-7.42 (m, 6H), 7.26-7.21 (m, 2H), 7.17-7.09 (m, 3H), 2.58 (t, J = 7.6 Hz, 2H), 2.31-2.24 (m, 2H), 1.75-1.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 133.1 (d, J_{C-P} = 97.2 Hz), 131.6 (d, J_{C-P} = 2.5 Hz), 130.1 (d, J_{C-P} = 9.2 Hz), 128.6 (d, J_{C-P} = 11.6 Hz), 128.3, 125.7, 35.3, 32.6 (d, J_{C-P} = 14.2 Hz), 29.6 (d, J_{C-P} = 71.4 Hz), 21.2 (d, J_{C-P} = 3.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.33. IR (film) υ_{max}: 3417, 2930, 2858, 1437, 1184, 1119, 743, 721, 697 cm^{-1}. HRMS calc. for $C_{22}H_{23}OP$ $(M+H)^+$:335.1559, found 335.1562.



3ka

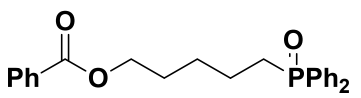
Selected major product, orange solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.73-7.66 (m, 6H), 7.50-7.42 (m, 6H), 5.54-5.43 (m, 2H), 3.52 (t, J = 7.2 Hz, 2H), 3.05 (dd, J_1 = 6.0 Hz, J_2 = 14.5 Hz, 2H), 2.02-1.96 (m, 2H), 1.63-1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 135.5 (d, J_{C-P} = 11.8 Hz), 133.8, 132.4 (d, J_{C-P} = 97.8 Hz), 132.0, 131.6 (d, J_{C-P} = 2.7 Hz), 130.9 (d, J_{C-P} = 9.0 Hz), 128.4 (d, J_{C-P} = 11.6 Hz), 123.0, 119.2 (d, J_{C-P} = 9.0 Hz), 37.3, 34.7 (d, J_{C-P} = 69.1 Hz), 29.8 (d, J_{C-P} = 1.9 Hz), 27.8 (d, J_{C-P} = 2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.42. IR (film) υ_{max}: 3413, 3057, 2934, 1770, 1711, 1437, 1397, 1188, 1120, 723, 697 cm^{-1}. HRMS calc. for $C_{26}H_{24}NO_3P$ $(M+H)^+$: 430.1567, found

430.1562.



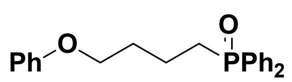
4la

White solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.70 (m, 4H), 7.54 (1s, 1H), 7.52-7.43 (m, 6H), 7.13 (d, J = 3.4 Hz, 1H), 6.48-6.47 (m, 1H), 4.24 (t, J = 6.6 Hz, 2H), 2.29-2.22 (m, 2H), 1.71-1.59 (m, 4H), 1.48-1.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 146.1, 144.7, 133.0 (d, J_{C-P} = 97.4 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 130.7 (d, J_{C-P} = 9.0 Hz), 128.6 (d, J_{C-P} = 11.4 Hz), 117.7, 111.7, 64.7, 30.4 (d, J_{C-P} = 14.4 Hz), 29.5 (d, J_{C-P} = 71.6 Hz), 28.3, 25.3, 21.3 (d, J_{C-P} = 3.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.41. IR (film) υ_{max}: 3419, 2929, 2859, 1720, 1580, 1474, 1438, 1298, 1182, 1120, 723, 697 cm^{-1}. HRMS calc. for $C_{23}H_{25}O_4P$ $(M+H)^+$: 397.1563, found 397.1559.



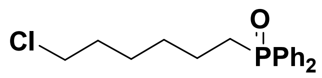
4ma

White solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-8.00 (m, 2H), 7.77-7.72 (m, 4H), 7.57-7.41 (m, 9H), 4.27 (t, J = 6.5 Hz, 2H), 2.33-2.27 (m, 2H), 1.79-1.67 (m, 4H), 1.60-1.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 132.9 (d, J_{C-P} = 97.6 Hz), 132.8, 131.7 (d, J_{C-P} = 2.7 Hz), 130.7 (d, J_{C-P} = 9.1 Hz), 130.3, 129.5, 128.6 (d, J_{C-P} = 11.6 Hz), 128.3, 64.6, 29.8 (d, J_{C-P} = 71.5 Hz), 28.3, 27.5 (d, J_{C-P} = 14.5 Hz), 21.3 (d, J_{C-P} = 3.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.29. IR (film) υ_{max}: 3411, 2930, 1717, 1451, 1276, 1182, 1118, 744, 714, 697 cm^{-1}. HRMS calc. for $C_{24}H_{25}O_3P$ $(M+H)^+$:393.1614, found 393.1612.



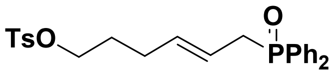
4na

White solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.71 (m, 4H), 7.53-7.43 (m, 6H), 7.27-7.22 (m, 2H), 6.94-6.90 (m, 1H), 6.84-6.82 (m, 2H), 3.93 (t, J = 6.0 Hz, 2H), 2.37-2.31 (m, 2H), 1.91-1.79 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 132.9 (d, J_{C-P} = 97.6 Hz), 131.7 (d, J_{C-P} = 2.3 Hz), 130.7 (d, J_{C-P} = 9.2 Hz), 129.4, 128.6 (d, J_{C-P} = 11.5 Hz), 120.6, 114.4, 68.9, 30.2 (d, J_{C-P} = 14.1 Hz), 29.3 (d, J_{C-P} = 71.6 Hz), 18.4 (d, J_{C-P} = 3.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.34. IR (film) υ_{max}: 3392, 2932, 1602, 1438, 1255, 1174, 1121, 751, 732, 694 cm^{-1}. HRMS calc. for $C_{22}H_{23}O_2P$ $(M+H)^+$: 351.1508, found 351.1504.



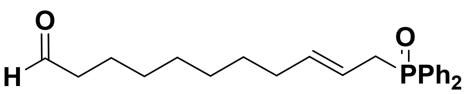
4oa

White solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.70 (m, 4H), 7.53-7.43 (m, 6H), 3.47 (t, J = 6.6 Hz, 2H), 2.29-2.22 (m, 2H), 1.74-1.59 (m, 4H), 1.44-1.40 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.0 (d, J_{C-P} = 97.4 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 130.7 (d, J_{C-P} = 9.2 Hz), 128.6 (d, J_{C-P} = 11.4 Hz), 44.8, 32.2, 30.0 (d, J_{C-P} = 14.2 Hz), 29.5 (d, J_{C-P} = 71.5 Hz), 26.2, 21.2 (d, J_{C-P} = 4.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.29. IR (film) $υ_{max}$: 3407, 2928, 2859, 1438, 1184, 1119, 1071, 720, 697 cm^{-1}. HRMS calc. for $C_{18}H_{22}ClOP$ $(M+H)^+$: 321.1170, found 321.1173.



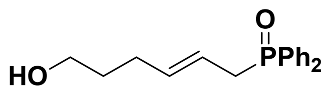
3pa

Selected major product, Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.69 (m, 6H), 7.55-7.45 (m, 6H), 7.34 (d, J = 8.0 Hz, 2H), 5.43-5.41 (m, 2H), 3.89 (t, J = 6.4 Hz, 2H), 3.04 (dd, J_1 = 4.0 Hz, J_2 = 13.5 Hz, 2H), 2.4 (s, 3H), 2.00-1.97 (m, 2H), 1.61-1.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 135.0 (d, J_{C-P} = 11.7 Hz), 133.2, 132.5 (d, J_{C-P} = 99.0 Hz), 131.8 (d, J_{C-P} = 2.6 Hz), 131.0 (d, J_{C-P} = 9.2 Hz), 129.8, 128.6 (d, J_{C-P} = 11.6 Hz), 127.8, 119.8 (d, J_{C-P} = 9.1 Hz), 69.6, 34.7 (d, J_{C-P} = 68.6 Hz), 28.3 21.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.18. IR (film) $υ_{max}$: 3395, 2924, 2856, 1597, 1438, 1179, 1120, 1096, 1043, 725, 696 cm^{-1}. HRMS calc. for $C_{25}H_{27}O_4P\ S$ $(M+H)^+$: 455.1440, found 455.1447.



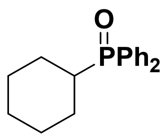
3qa

Selected major product, Coloress oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, J = 1.8 Hz, 1H), 7.75-7.70 (m, 4H), 7.54-7.44 (m, 6H), 5.53-5.37 (m, 2H), 3.08 (dd, J_1 = 6.9 Hz, J_2 = 14.4 Hz, 2H), 2.42-2.38 (m, 2H), 1.94-1.90 (m, 2H), 1.61-1.58 (m, 2H), 1.29-1.13 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.8, 137.3 (d, J_{C-P} = 11.7 Hz), 132.6 (d, J_{C-P} = 97.9 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 9.0 Hz), 128.5 (d, J_{C-P} = 11.6 Hz), 118.0 (d, J_{C-P} = 9.0 Hz), 43.8, 34.8 (d, J_{C-P} = 69.1 Hz), 32.5 (d, J_{C-P} = 2.1 Hz), 29.0 (d, J_{C-P} = 6.5 Hz), 28.9 (d, J_{C-P} = 2.9 Hz), 28.6, 22.0 ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.53. IR (film) $υ_{max}$: 3344, 2927, 2854, 1720, 1437, 1173, 1119, 969, 721, 696 cm^{-1}. HRMS calc. for $C_{23}H_{29}O_2P$ $(M+H)^+$: 369.1978, found 369.1976.



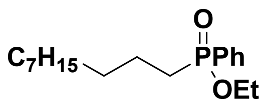
3ra

Selected major product, Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): 7.74-7.69 (m, 4H), 7.52-7.43 (m, 6H), 5.57-5.49 (m, 1H), 5.46-5.37 (m, 1H), 3.46 (t, J = 6.3 Hz, 2H), 3.06 (dd, J_1 = 7.2 Hz, J_2 = 14.1 Hz, 2H), 2.49 (s, 1H), 2.06-2.00 (m, 2H), 1.52-1.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8 (d, $J_{C\text{-}P}$ = 11.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 98.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 118.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 61.6, 34.6 (d, $J_{C\text{-}P}$ = 68.7 Hz), 31.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 29.1 (d, $J_{C\text{-}P}$ = 2.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.59. IR (film) υ_{max}: 3372, 3056, 2931, 2861, 1437, 1177, 1121, 968, 723, 696 cm^{-1}. HRMS calc. for $C_{18}H_{21}O_2P$ $(M+H)^+$: 301.1352, found 301.1348.



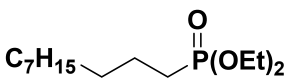
4sa

White solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.75 (m, 4H), 7.51-7.43 (m, 6H), 2.28-2.19 (m, 1H), 1.80-1.70 (m, 5H), 1.58-1.48 (m, 2H), 1.31-1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.1 (d, $J_{C\text{-}P}$ = 93.9 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.6 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.3 Hz), 37.2 (d, $J_{C\text{-}P}$ = 72.7 Hz), 26.3 (d, $J_{C\text{-}P}$ = 13.3 Hz), 25.7 (d, $J_{C\text{-}P}$ = 1.1 Hz), 24.7 (d, $J_{C\text{-}P}$ = 2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.36. IR (film) υ_{max}: 3401, 2928, 2854, 2219, 1438, 1179, 1118, 731, 698 cm^{-1}. HRMS calc. for $C_{18}H_{21}OP$ $(M+H)^+$: 285.1403, found 285.1405.



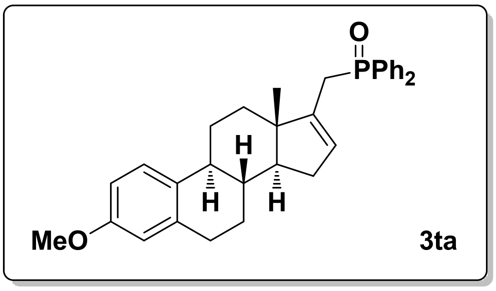
4db

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.74 (m, 2H), 7.56-7.52 (m, 1H), 7.50-7.45 (m, 2H), 4.12-4.02 (m, 1H), 3.88-3.79 (m, 1H), 1.97-1.77 (m, 2H), 1.63-1.41 (m, 2H), 1.33-1.22 (m, 17H), 0.86 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.6 (d, $J_{C\text{-}P}$ = 9.8 Hz), 131.1 (d, $J_{C\text{-}P}$ = 121.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.2 Hz), 60.4 (d, $J_{C\text{-}P}$ = 6.3 Hz), 31.8, 30.7 (d, $J_{C\text{-}P}$ = 15.9 Hz), 30.2, 29.4, 29.3, 29.2, 29.0, 22.6, 21.6 (d, $J_{C\text{-}P}$ = 3.5 Hz), 16.4 (d, $J_{C\text{-}P}$ = 6.5 Hz), 14.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 44.96. IR (film) υ_{max}: 3420, 2925, 2854, 1464, 1439, 1225, 1122, 1039, 952, 731, 693 cm^{-1}. HRMS calc. for $C_{18}H_{31}O_2P$ $(M+H)^+$: 311.2134, found 311.2133.



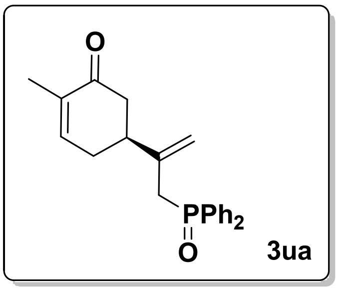
4dc

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.16-4.03 (m, 4H), 1.75-1.67 (m, 2H), 1.63-1.53 (m, 2H), 1.38-1.26 (m, 20H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.3 (d, $J_{C\text{-}P}$ = 6.5 Hz), 31.8, 30.6 (d, $J_{C\text{-}P}$ = 16.8 Hz), 29.4 (d, $J_{C\text{-}P}$ = 44.6 Hz), 29.3 (d, $J_{C\text{-}P}$ = 10.0 Hz), 26.4, 25.0, 22.6, 22.4 (d, $J_{C\text{-}P}$ = 5.1 Hz), 16.4 (d, $J_{C\text{-}P}$ = 5.9 Hz), 14.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.66. IR (film) υ_{max}: 3436, 2926, 2854, 1464, 1244, 1057, 1030, 960, 787, 722 cm^{-1}. HRMS calc. for $C_{14}H_{31}O_3P$ $(M+H)^+$: 279.2084, found 279.2081.



3ta

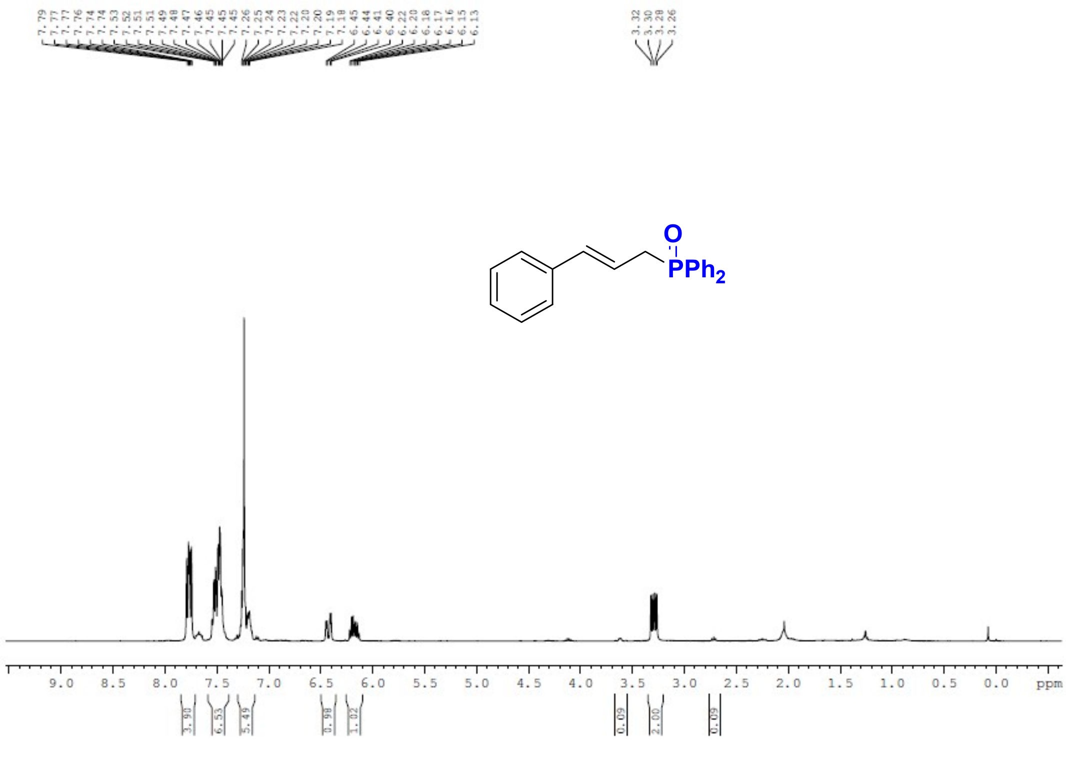
Brown oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.75 (m, 4H), 7.55-7.45 (m, 6H), 7.17 (d, J = 8.6 Hz, 1H), 6.72-6.69 (m, 1H), 6.63 (d, J = 2.6 Hz, 1H), 5.65 (d, J = 1.3 Hz, 1H), 3.77 (s, 3H), 3.16-3.00 (m, 2H), 2.89-2.85 (m, 2H), 2.33-2.10 (m, 3H), 1.93-1.85 (m, 1H), 1.78-1.74 (m, 1H), 1.56-1.25 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 143.8 (d, $J_{C\text{-}P}$ = 8.5 Hz), 138.0, 133.9, 133.2 (d, $J_{C\text{-}P}$ = 98.6 Hz), 132.9, 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 3.9 Hz), 131.0 (d, $J_{C\text{-}P}$ = 4.2 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.7 Hz), 126.0, 113.8, 111.4, 55.3, 55.2, 47.6 (d, $J_{C\text{-}P}$ = 6.2 Hz), 44.1, 37.4, 34.1, 31.4, 29.7 28.2 (d, $J_{C\text{-}P}$ = 69.8 Hz), 27.7, 26.3, 15.5 (d, $J_{C\text{-}P}$ = 1.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.85. IR (film) υ_{max}: 3396, 2927, 2852, 1609, 1499, 1437, 1197, 1119, 850, 737, 696 cm^{-1}. $[\alpha]^{20}$= +39 (c=15mg/ml in DCM). HRMS calc. for $C_{32}H_{35}O_2P$ $(M+H)^+$: 483.2447, found 483.2442.

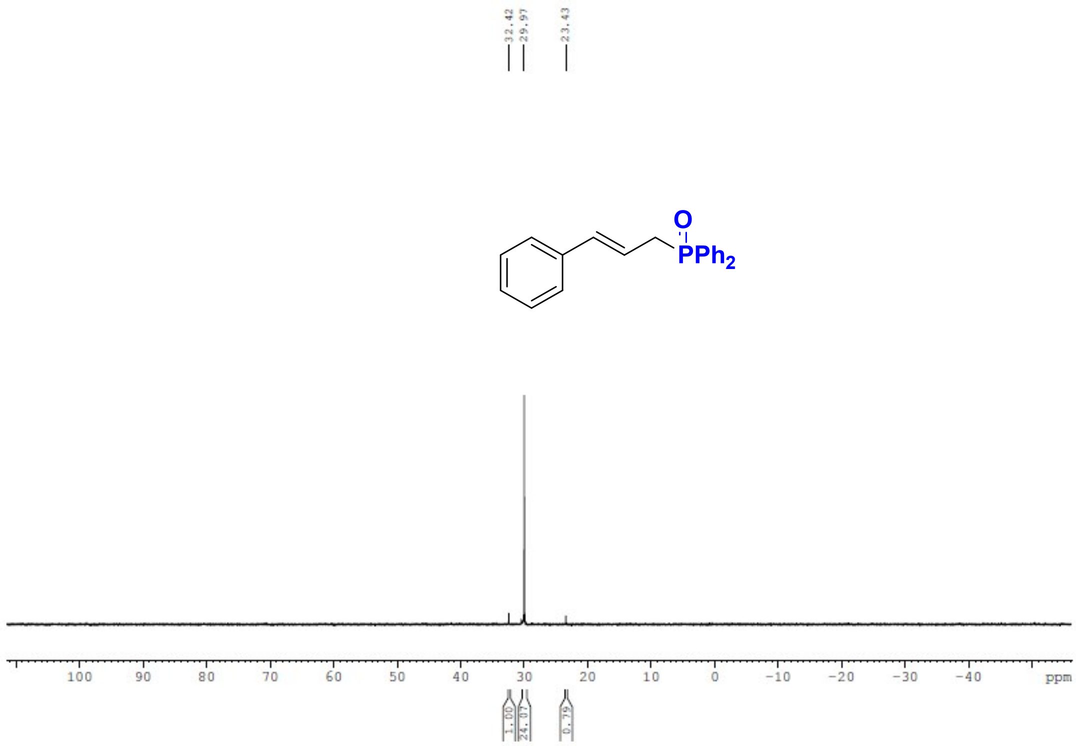


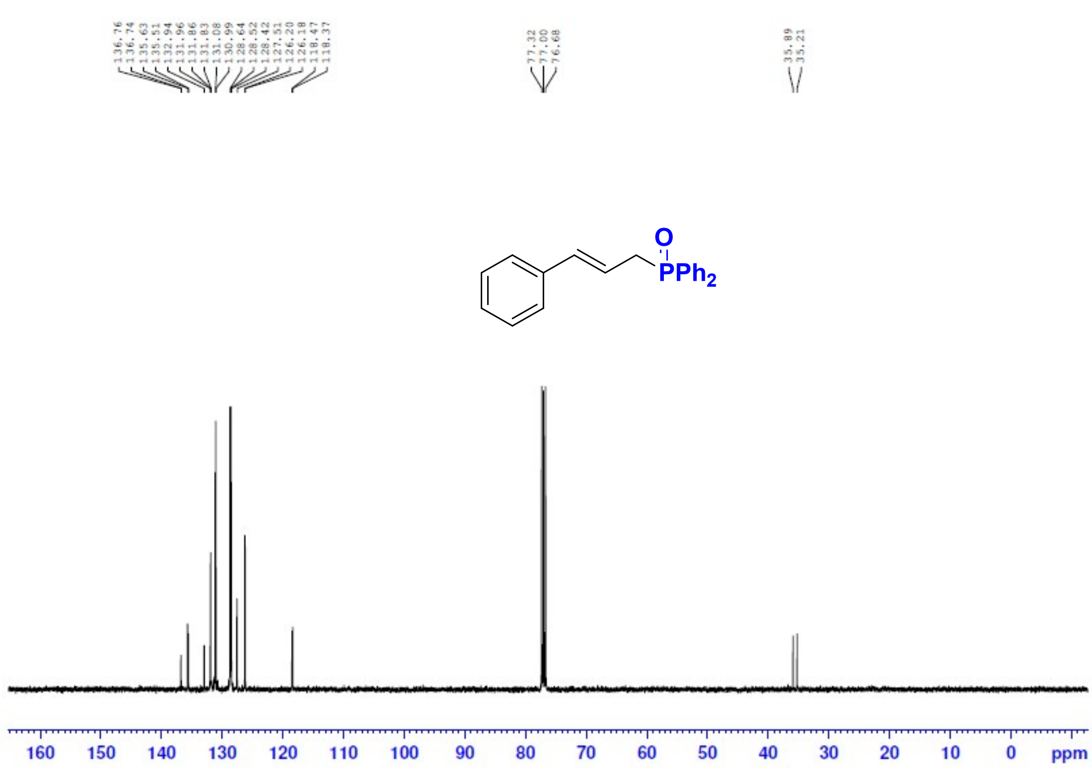
3ua

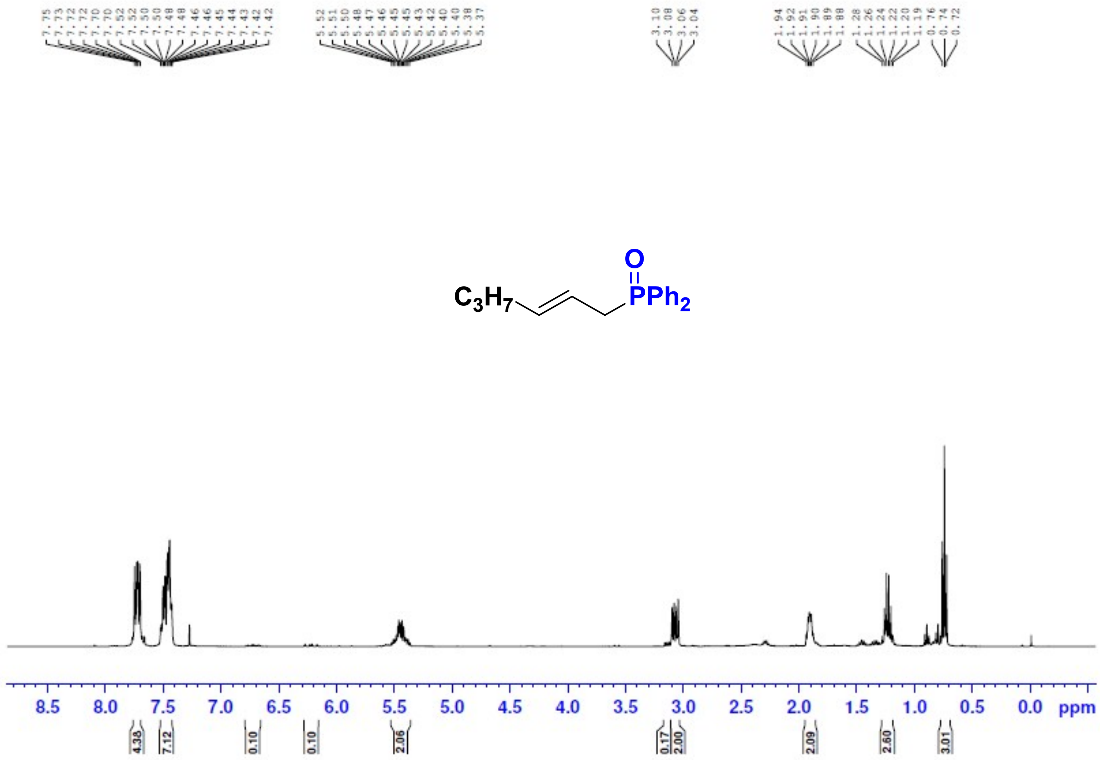
Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.71 (m, 4H), 7.53-7.45 (m, 6H), 6.68-6.67 (m, 1H), 4.87 (dd, J_1 = 4.2 Hz, J_2 = 20.6Hz, 2H), 3.19-3.07 (m, 2H), 2.88-2.82 (m, 1H), 2.57-2.49 (m, 2H), 2.31-2.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 144.3, 141.4 (d, $J_{C\text{-}P}$ = 9.1 Hz), 135.3, 132.5 (d, $J_{C\text{-}P}$ = 98.5 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.9 (dd, J_1= 2.3 Hz, J_2= 8.9 Hz), 128.5 (dd, J_1= 1.2 Hz, J_2 = 11.6 Hz), 115.2 (d, $J_{C\text{-}P}$ = 9.2 Hz), 43.1, 41.2 (d, $J_{C\text{-}P}$ = 2.4Hz), 36.6 (d, $J_{C\text{-}P}$ = 66.7 Hz), 31.2, 15.5 ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.45. $[\alpha]^{20}$= +13(c=10mg/ml in DCM). MS (ESI): $[M+H]^+$= 351.1484

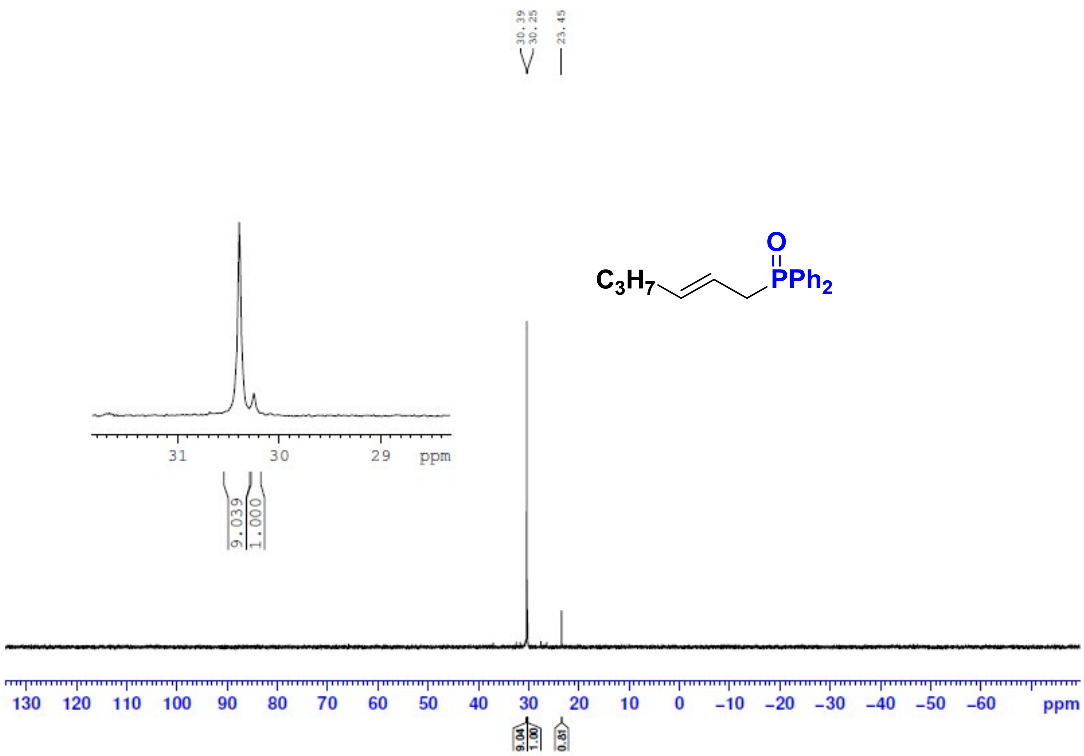
7. Charts of compounds

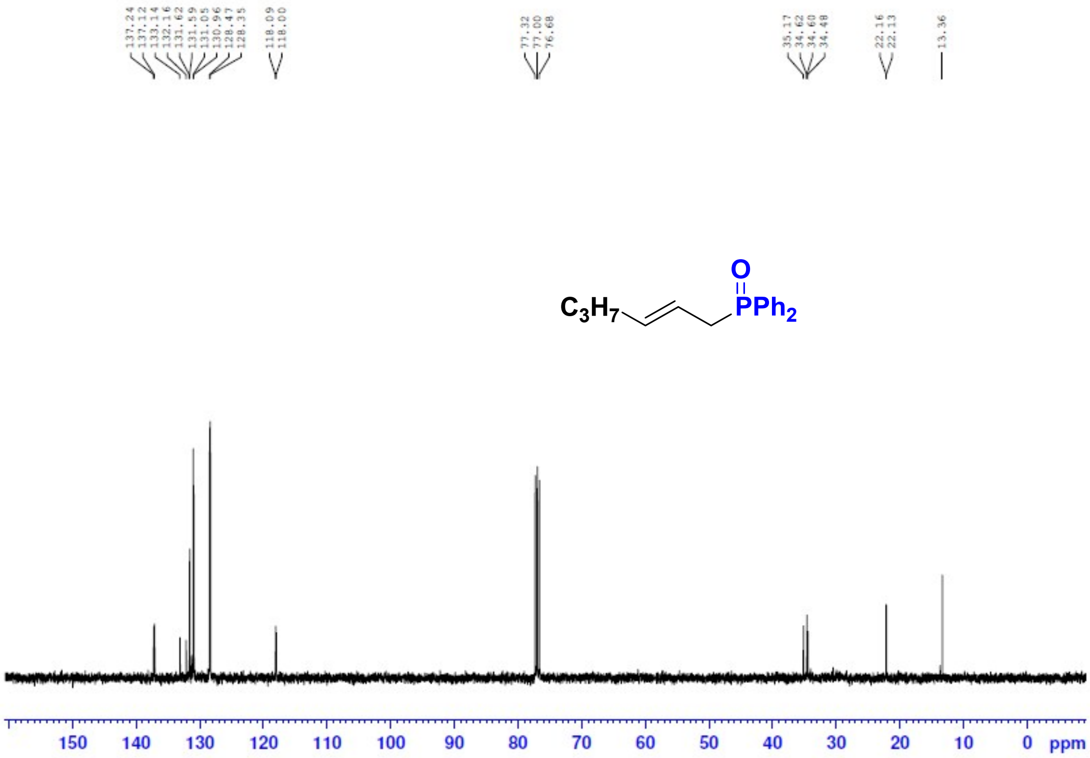



32.42
29.97
23.43
O
PPh2
1.00
24.87
0.79
ppm

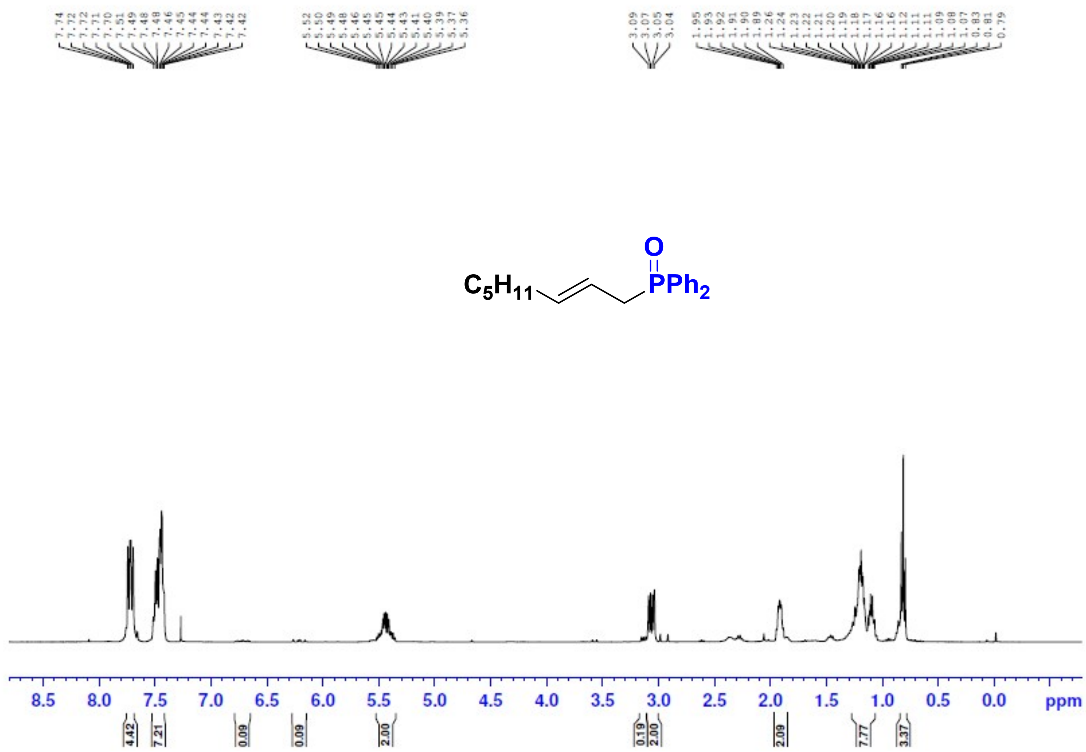

136.76
136.74
135.63
135.51
132.94
131.96
131.86
131.83
131.08
130.99
128.64
128.52
128.42
127.51
126.20
126.18
118.47
118.37
77.32
77.00
76.68
35.89
35.21
O
PPh2
ppm



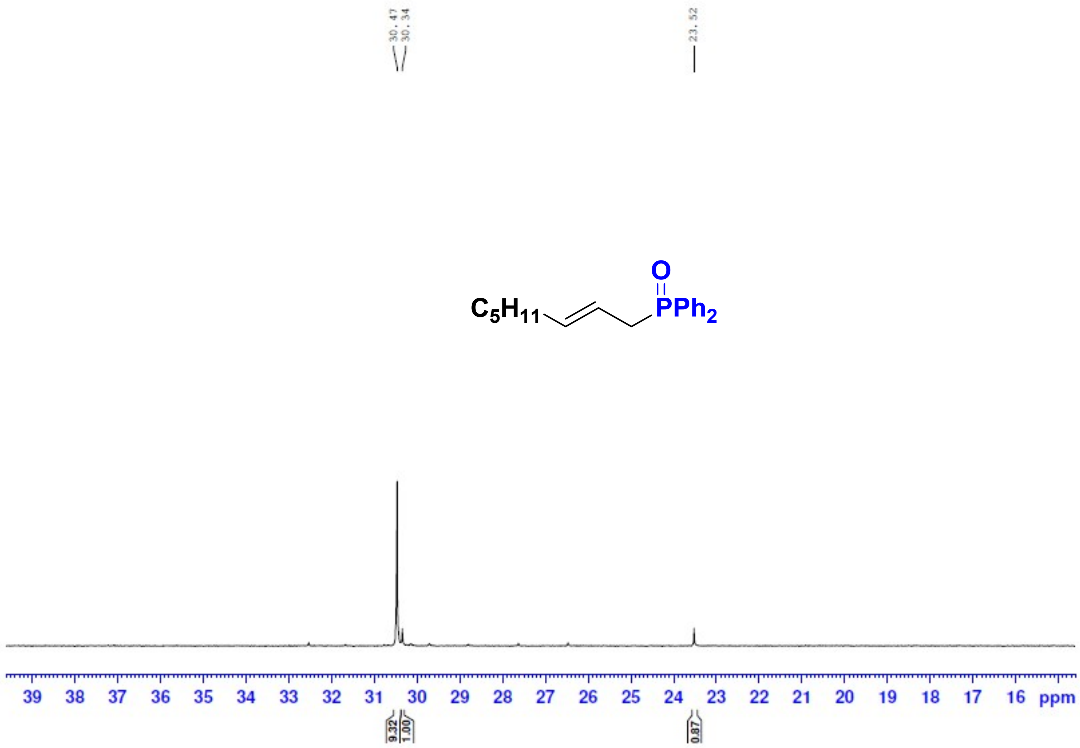


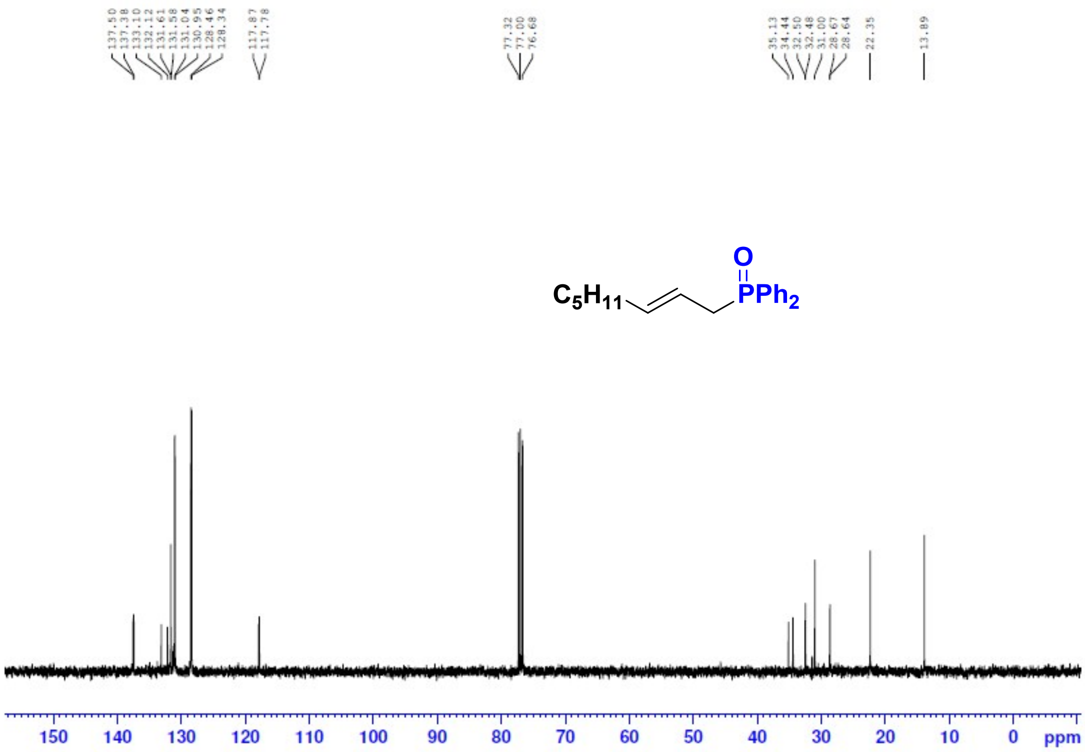


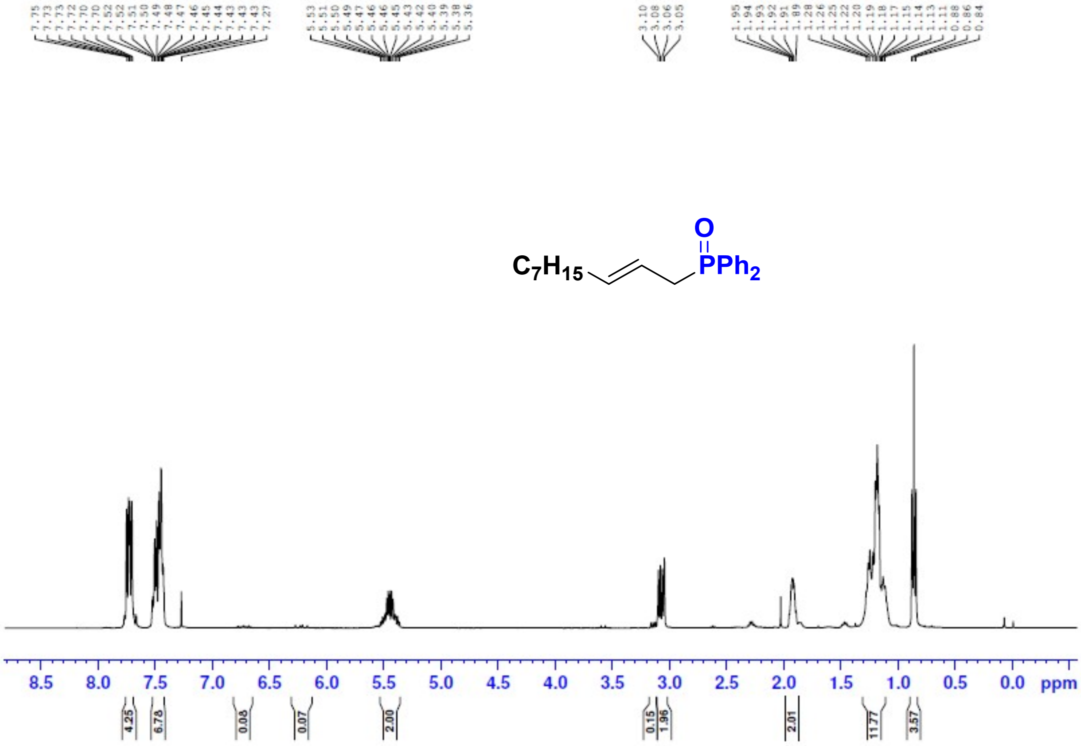
137.24
137.12
133.14
132.16
131.62
131.59
131.05
130.96
128.47
128.35
118.09
118.00
77.32
77.00
76.68
35.17
34.62
34.60
34.48
22.16
22.13
13.36
C_3H_7
O
PPh2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

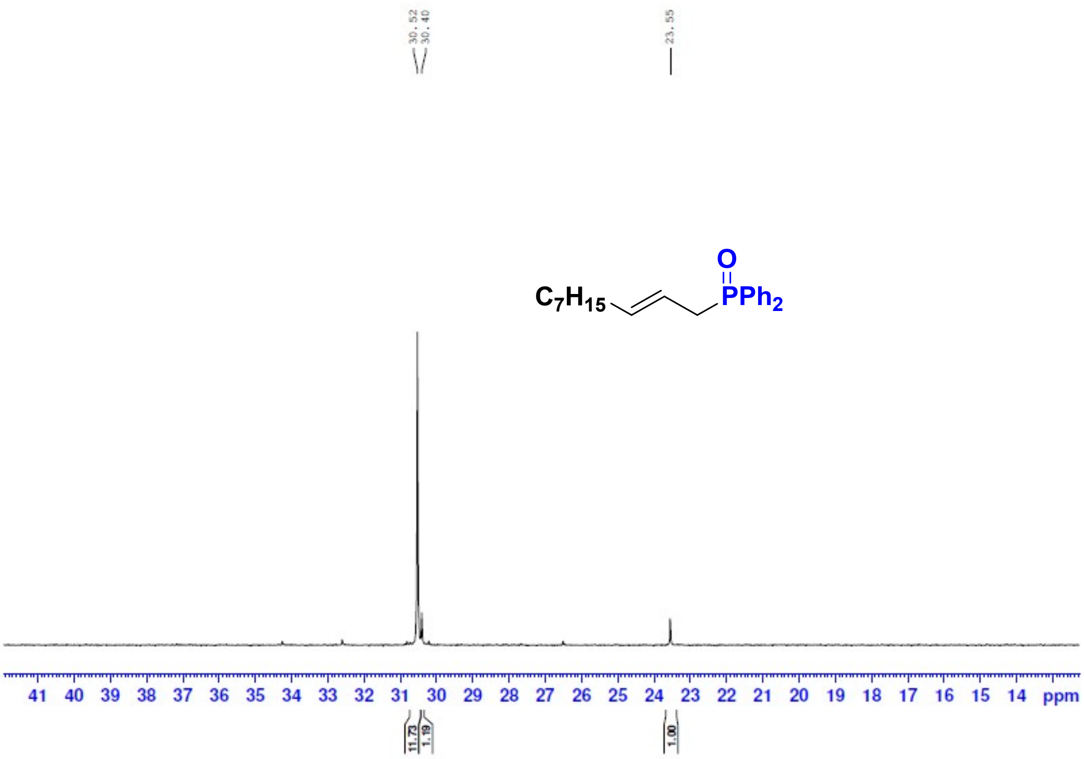


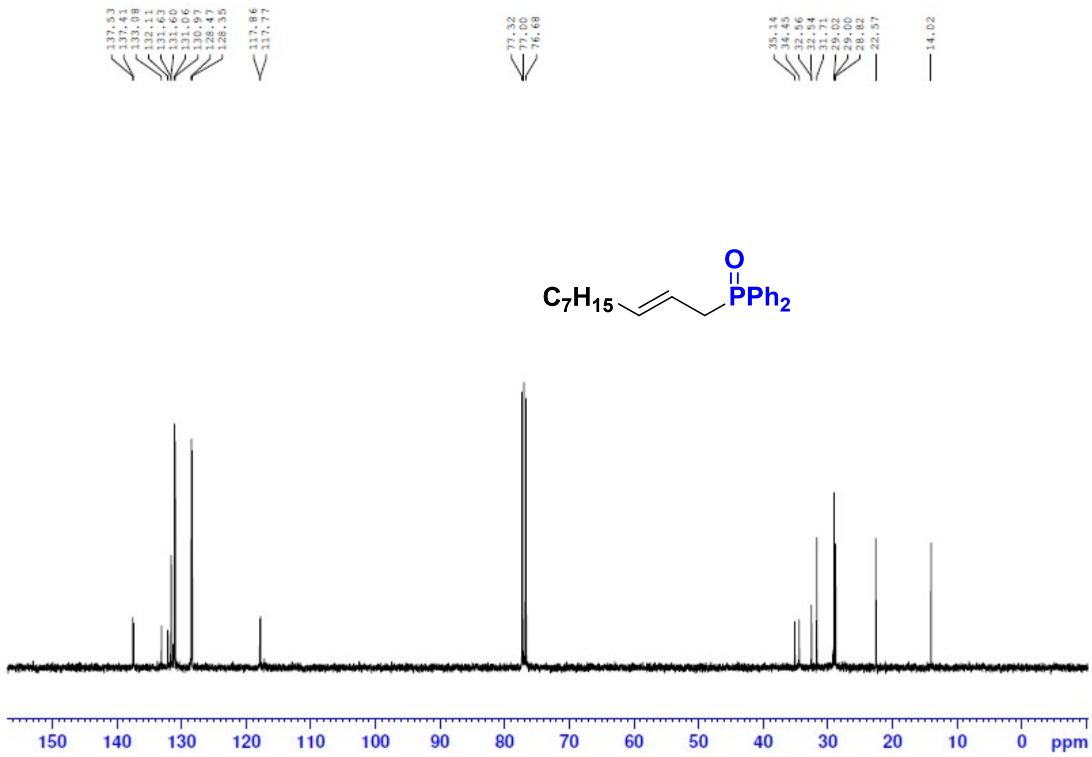
C_5H_{11}
O
PPh2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.42
7.21
0.09
0.09
2.00
0.19
2.00
2.09
7.77
3.37

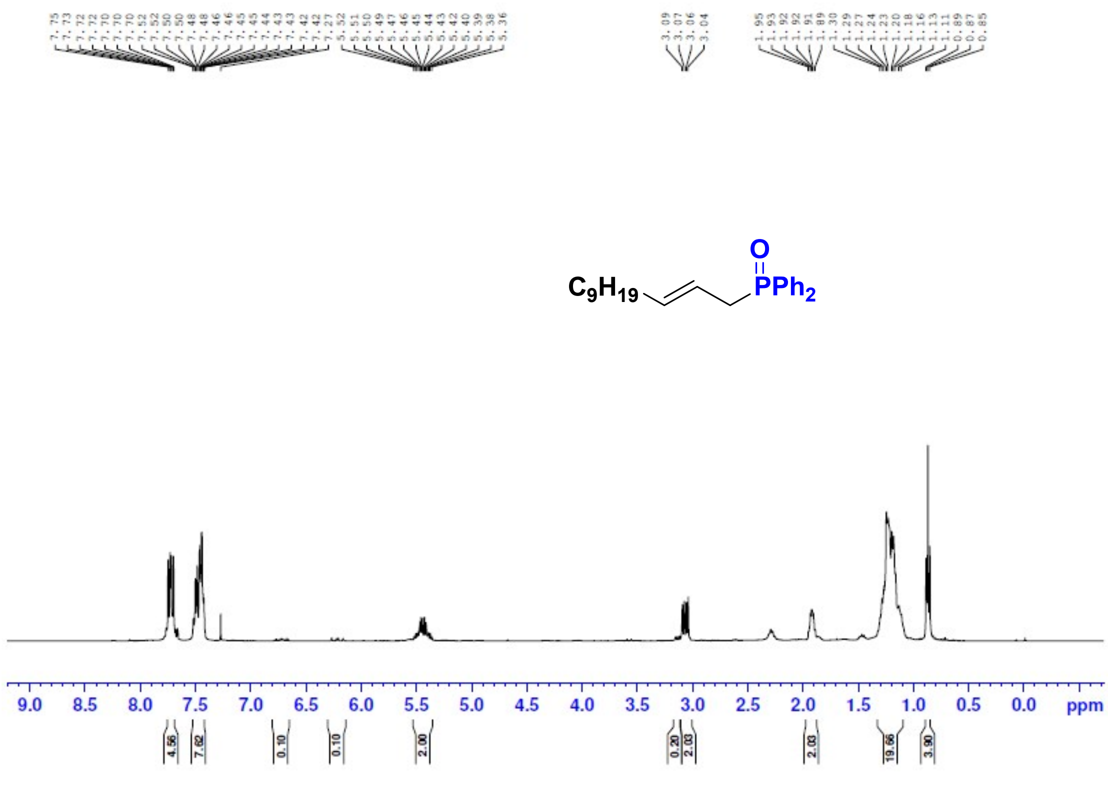

30.47
30.34
23.52
C5H11
O
PPh2
9.32
1.00
0.87
ppm

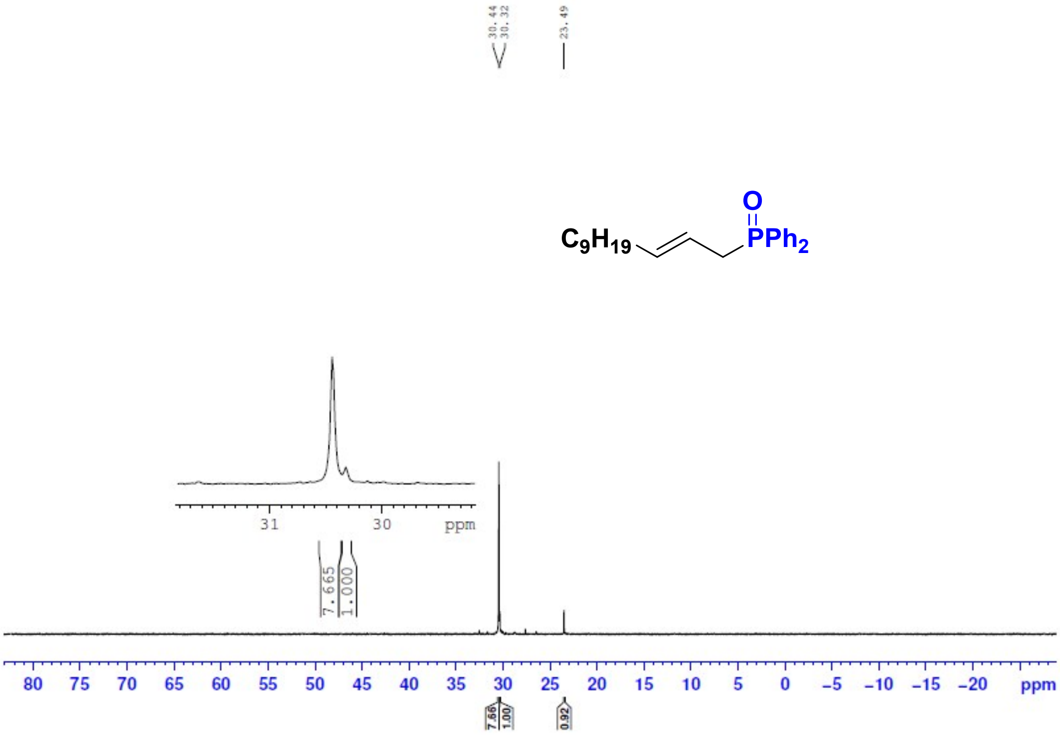

137.50
137.38
133.10
132.12
131.61
131.58
131.04
130.95
128.46
128.34
117.87
117.78
77.32
77.00
76.68
35.13
34.44
32.50
32.48
31.00
28.67
28.64
22.35
13.89
C5H11
O
PPh2
ppm

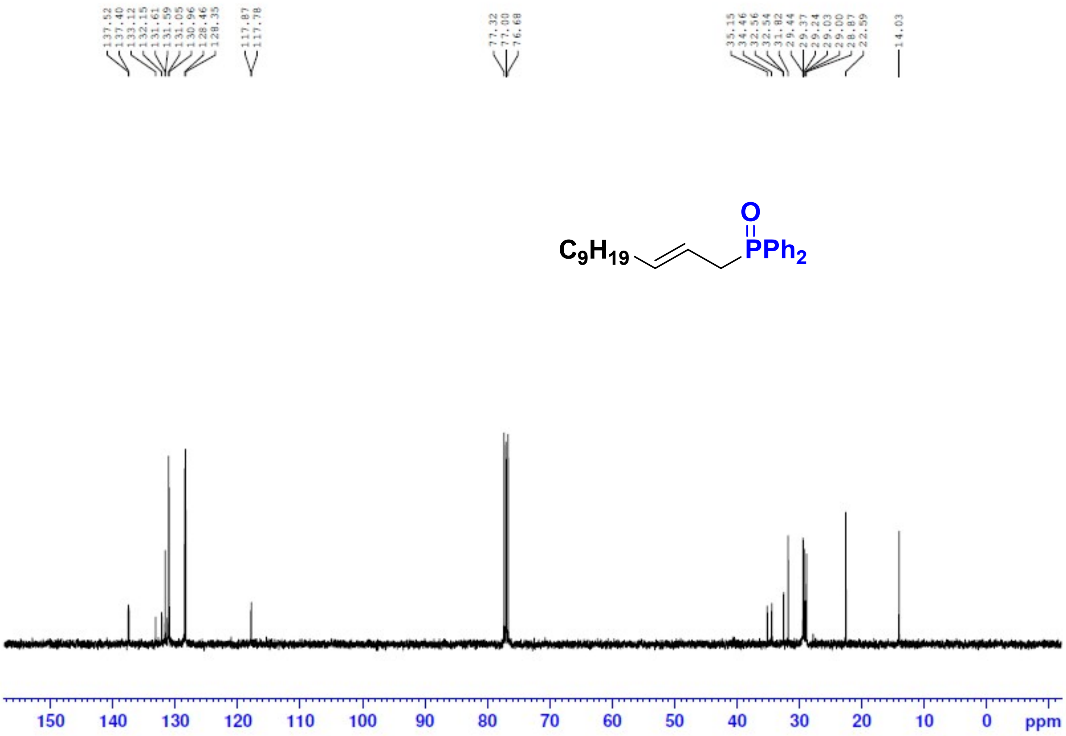

C7H15
O
PPh2
ppm

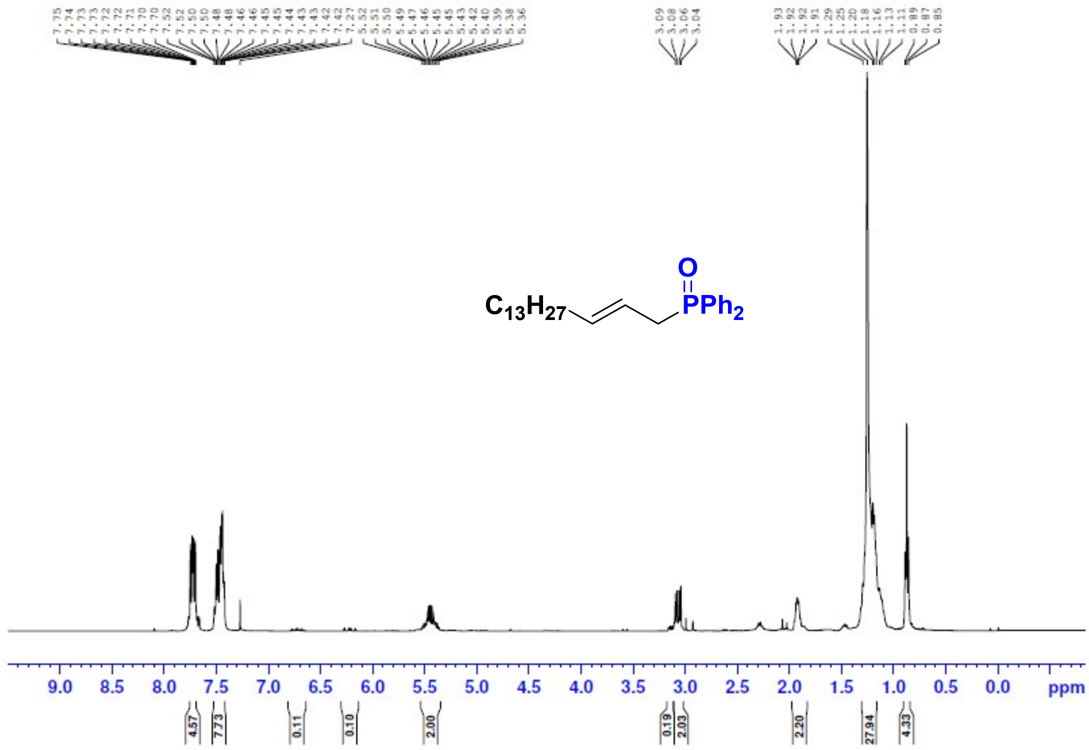

30.52
30.40
23.55
C7H15
O
PPh2
ppm



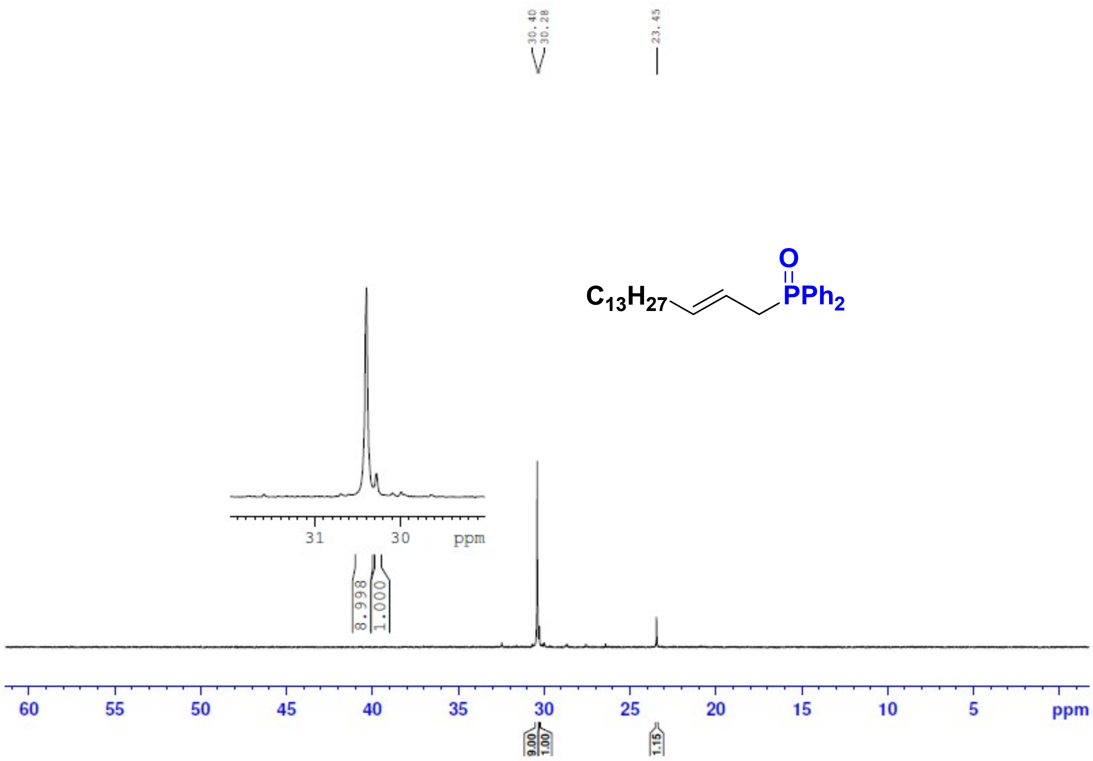



30.44
30.32
23.49
O
C9H19
PPh2
7.665
1.000
31
30
ppm
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 ppm
7.66
1.00
0.92

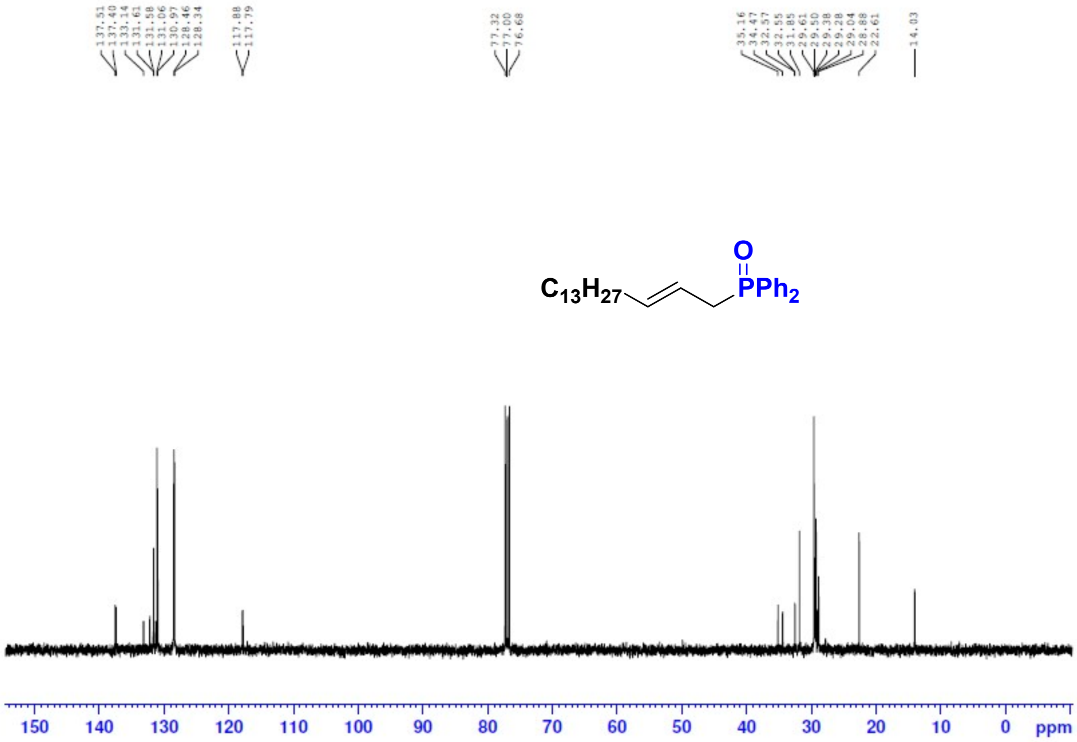

137.52
137.40
133.12
132.15
131.61
131.59
131.05
130.96
128.46
128.35
117.87
117.78
77.32
77.00
76.68
35.15
34.46
32.56
32.54
31.82
29.44
29.37
29.24
29.03
29.00
28.87
22.59
14.03
O
C9H19
PPh2
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

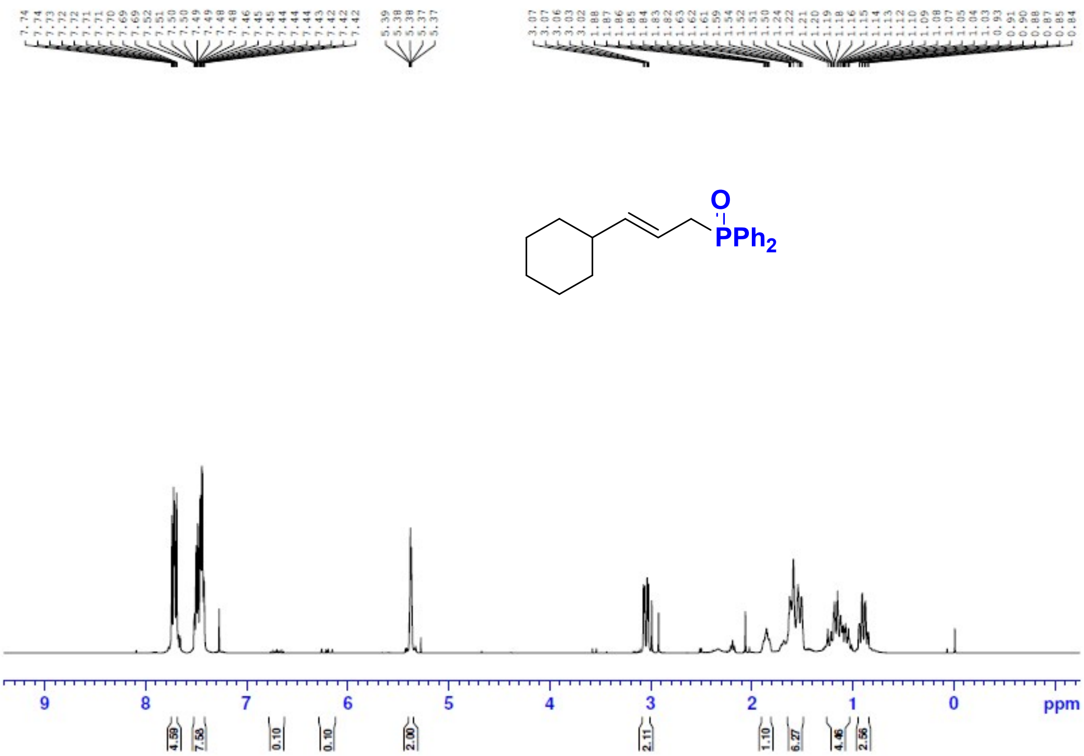


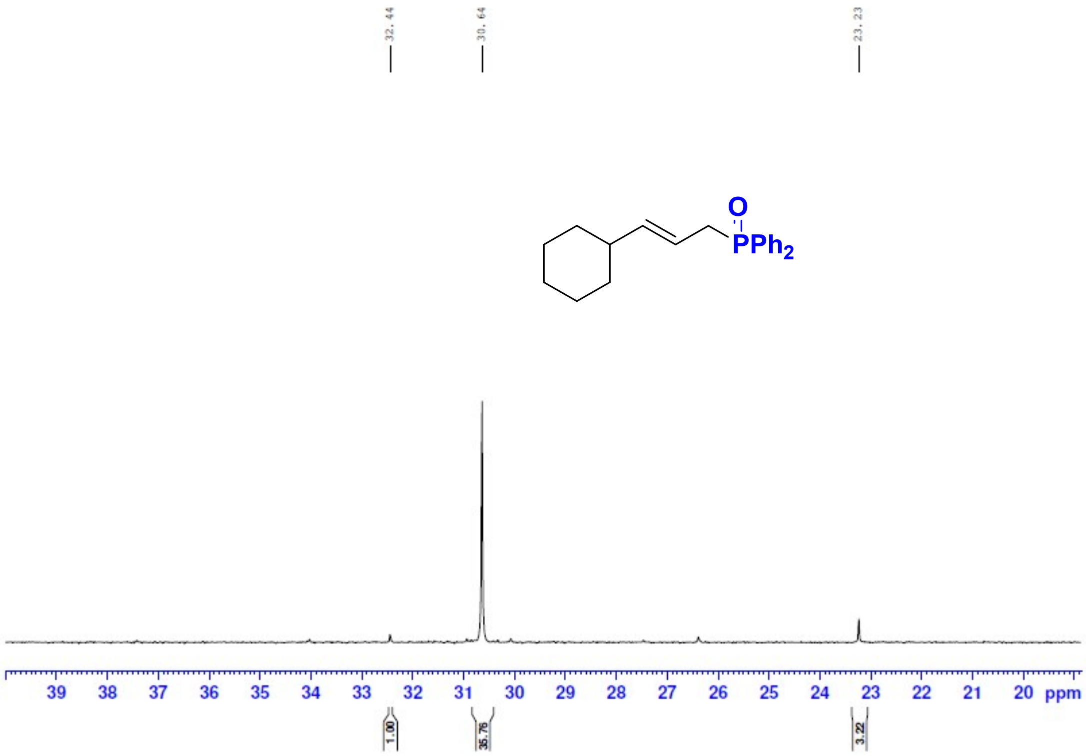
7.75 7.74 7.73 7.73 7.72 7.72 7.71 7.70 7.70 7.52 7.52 7.50 7.50 7.48 7.48 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.42 7.27 5.52 5.51 5.50 5.49 5.47 5.46 5.45 5.45 5.43 5.42 5.40 5.39 5.38 5.36
3.09 3.08 3.06 3.04
1.93 1.92 1.92 1.91 1.29 1.25 1.20 1.18 1.16 1.13 1.11 0.89 0.87 0.85
C13H27 PPh2 O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.57 7.73 0.11 0.10 2.00 0.19 2.03 2.20 27.94 4.33



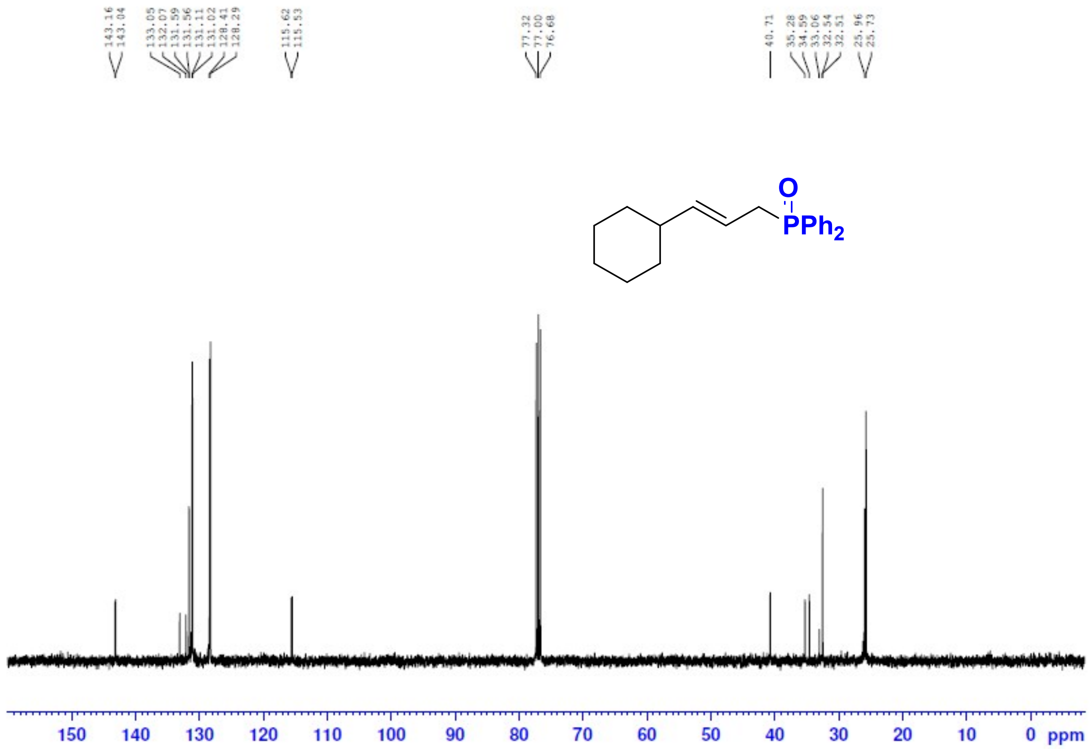
30.40 30.28
23.45
C13H27 PPh2 O
31 30 ppm
8.998 1.000
60 55 50 45 40 35 30 25 20 15 10 5 ppm
9.00 1.00 1.15


C13H27
O
PPh2
ppm

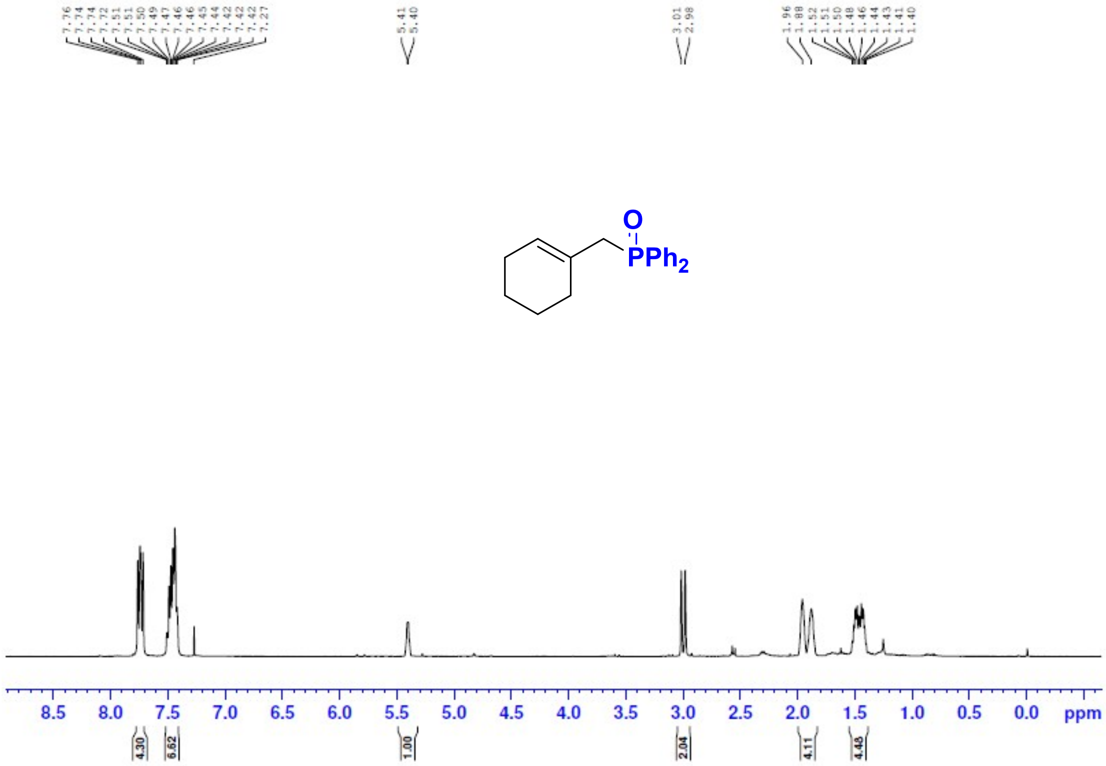

O
PPh2
ppm

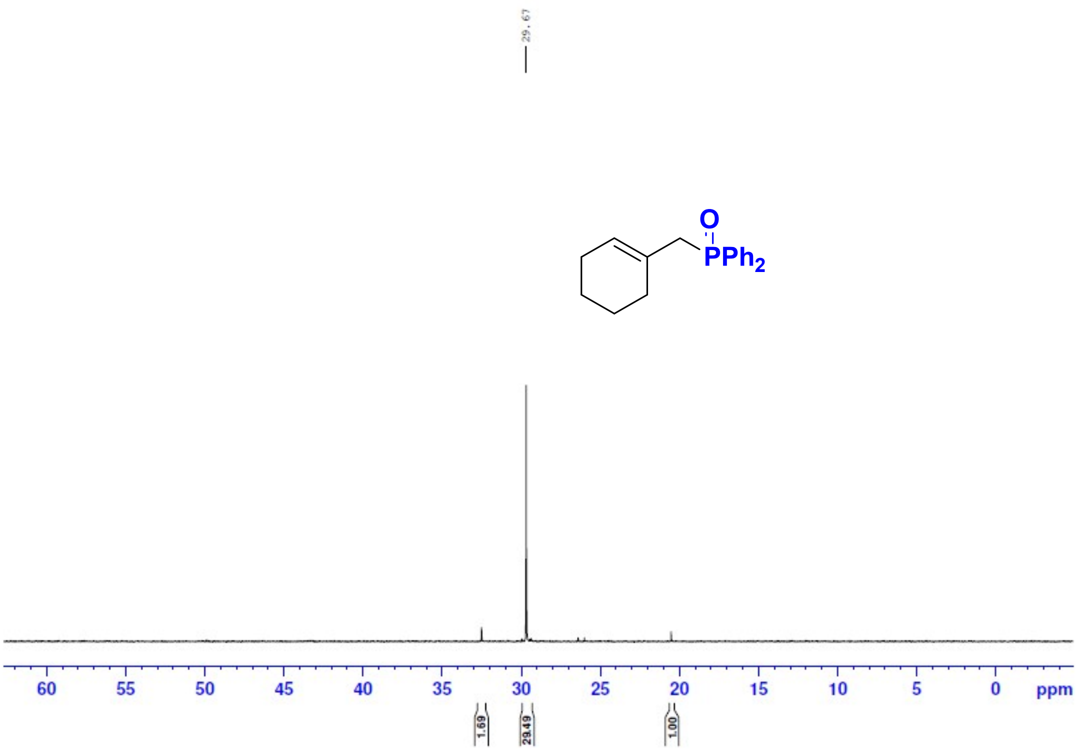


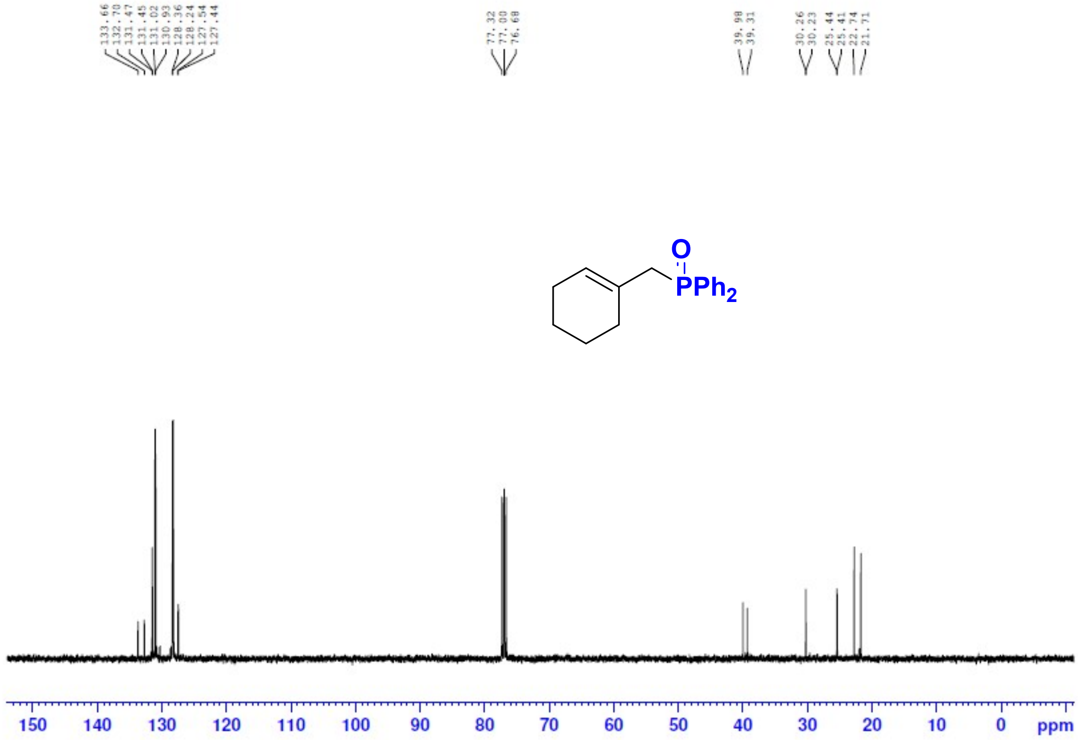
32.44
30.64
23.23
O
PPh2
39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 ppm
1.00
35.76
3.22

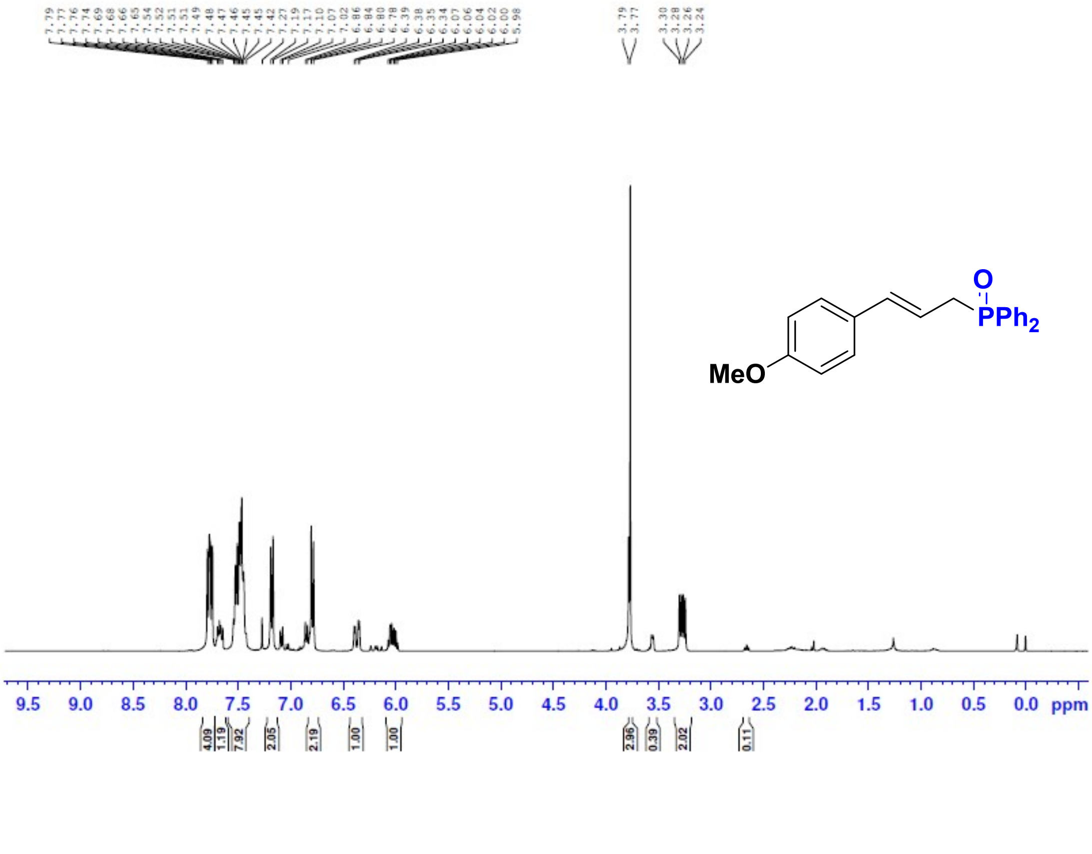


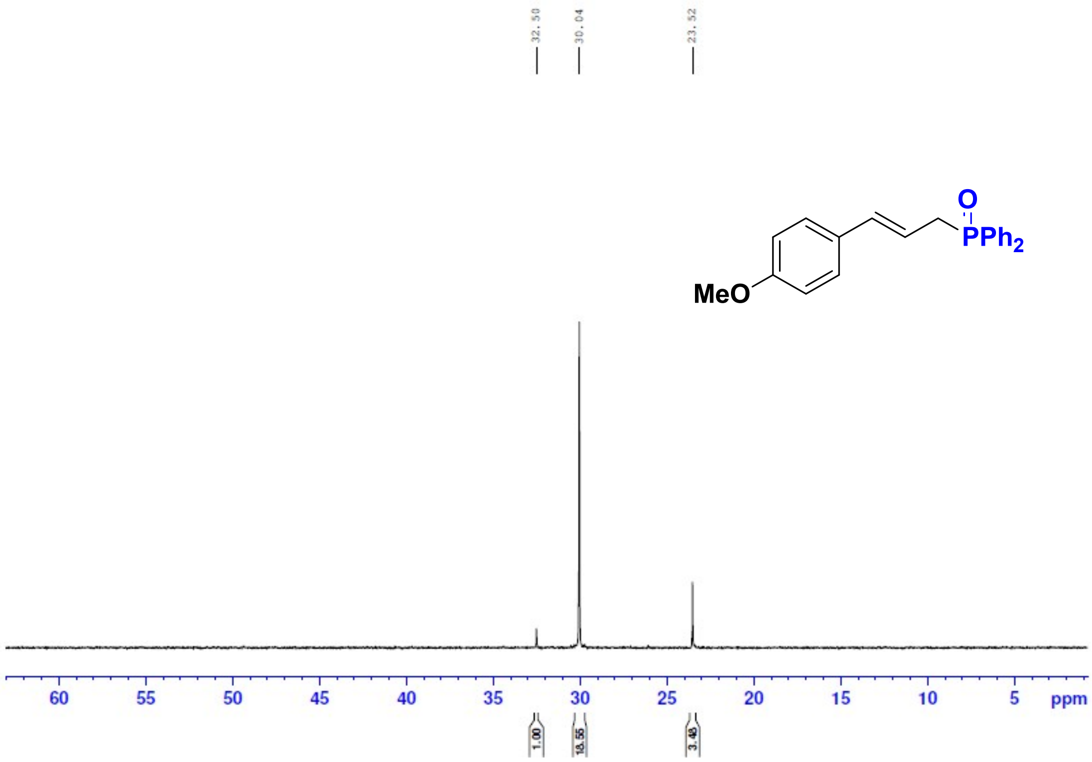
143.16
143.04
133.05
132.07
131.59
131.56
131.11
131.02
128.41
128.29
115.62
115.53
77.32
77.00
76.68
40.71
35.28
34.59
33.06
32.54
32.51
25.96
25.73
O
PPh2
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

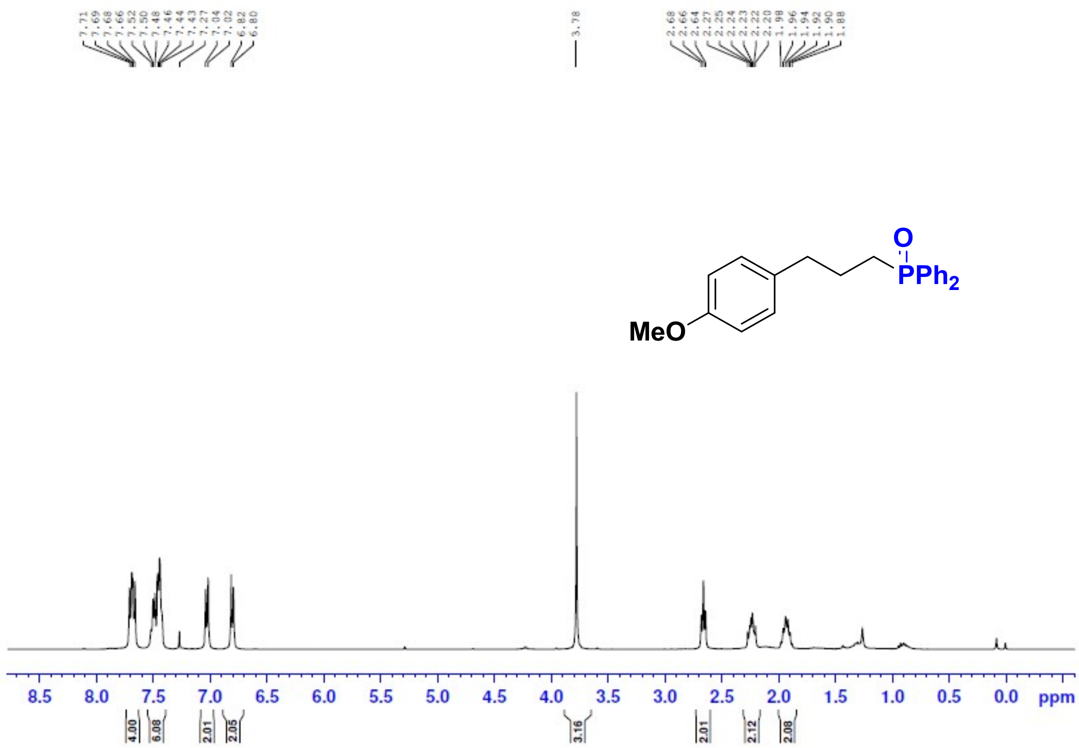


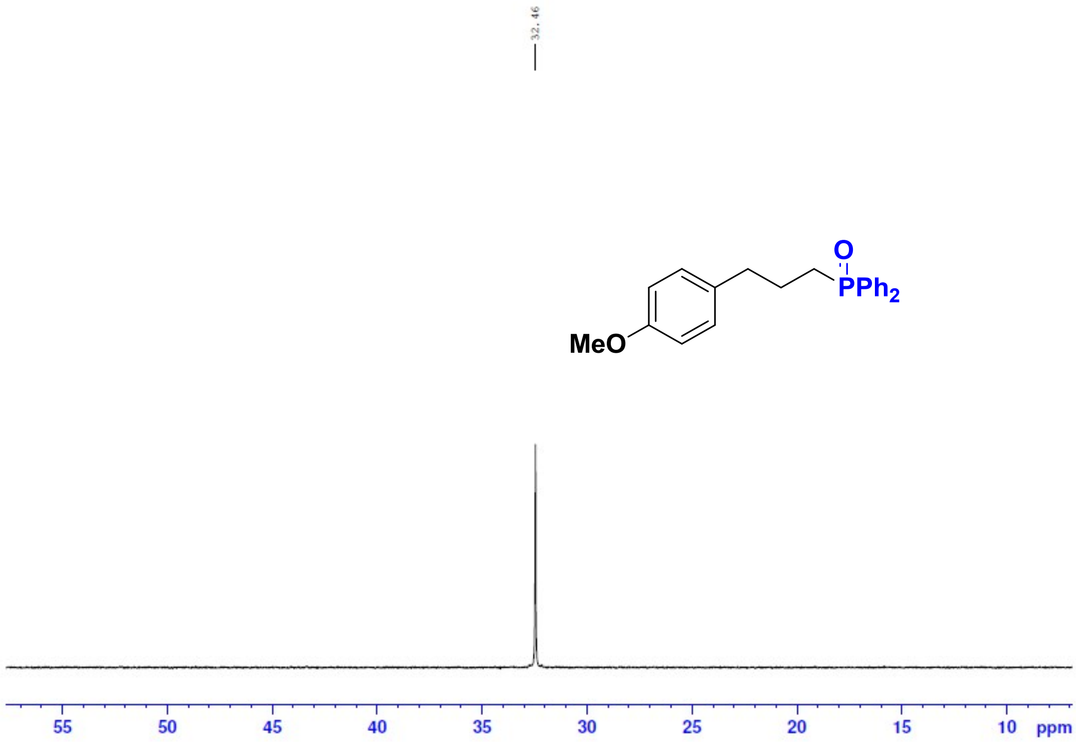


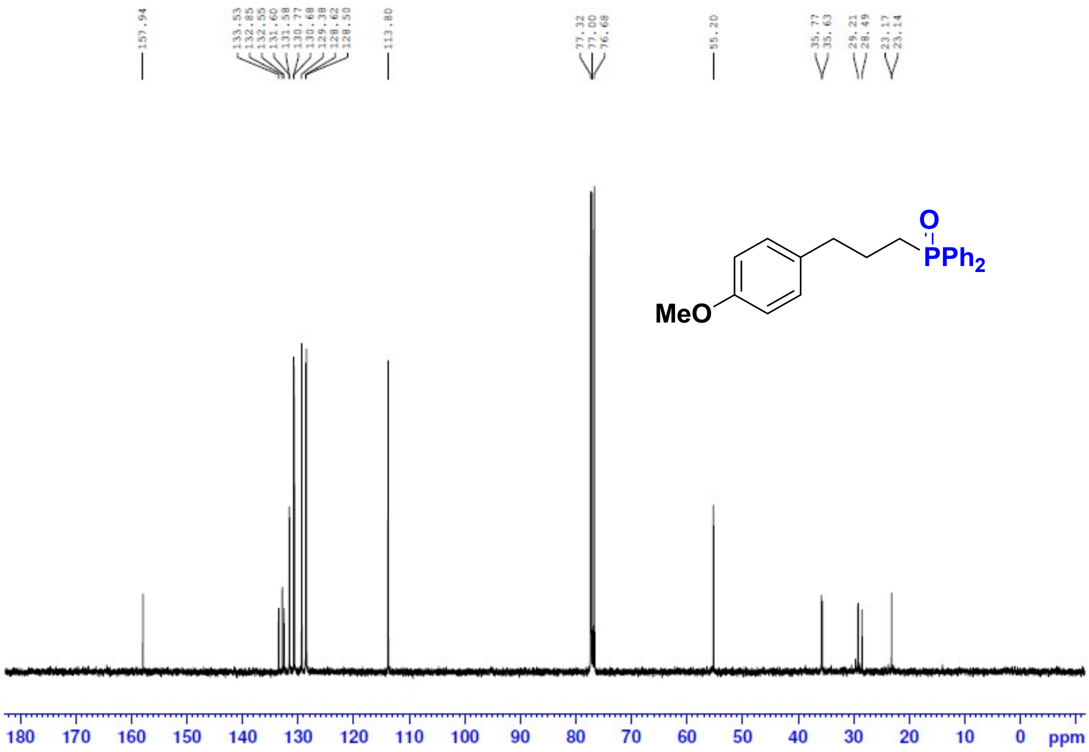

133.66
132.70
131.47
131.45
131.02
130.93
128.36
128.24
127.54
127.44
77.32
77.00
76.68
39.98
39.31
30.26
30.23
25.44
25.41
22.74
21.71
O
PPh2
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

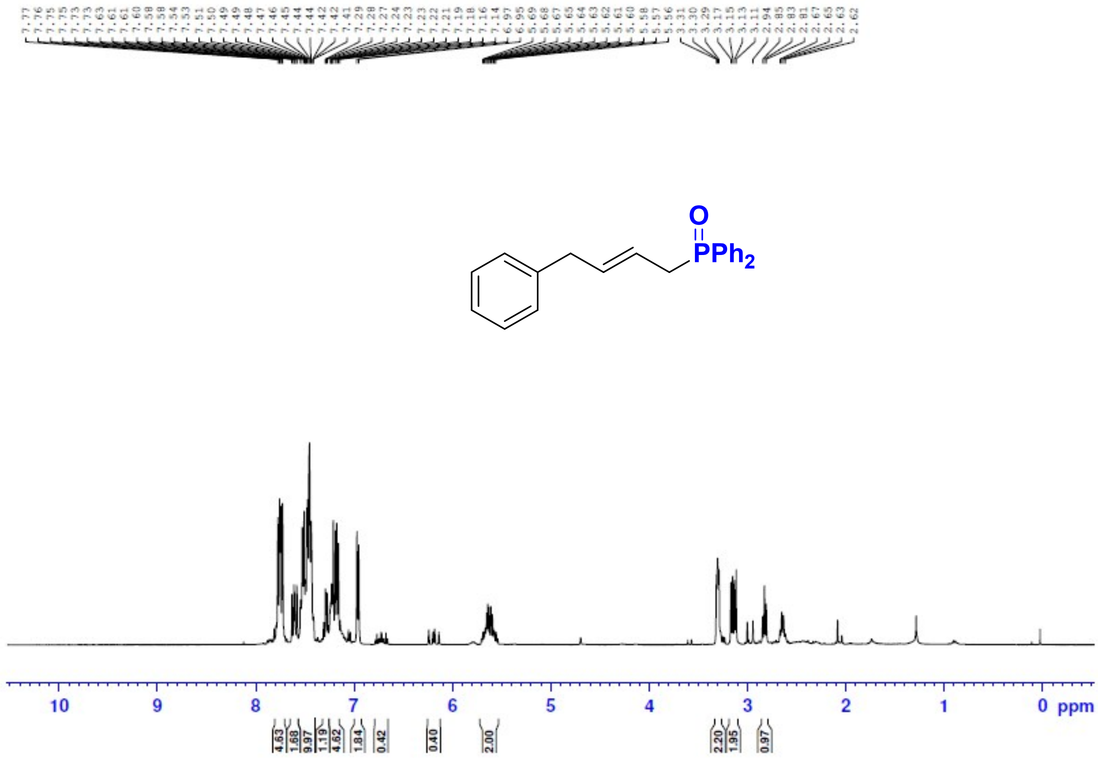

3.79
3.77
3.30
3.28
3.26
3.24
O
PPh2
MeO
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.09
1.19
7.92
2.05
2.19
1.00
1.00
2.96
0.39
2.02
0.11

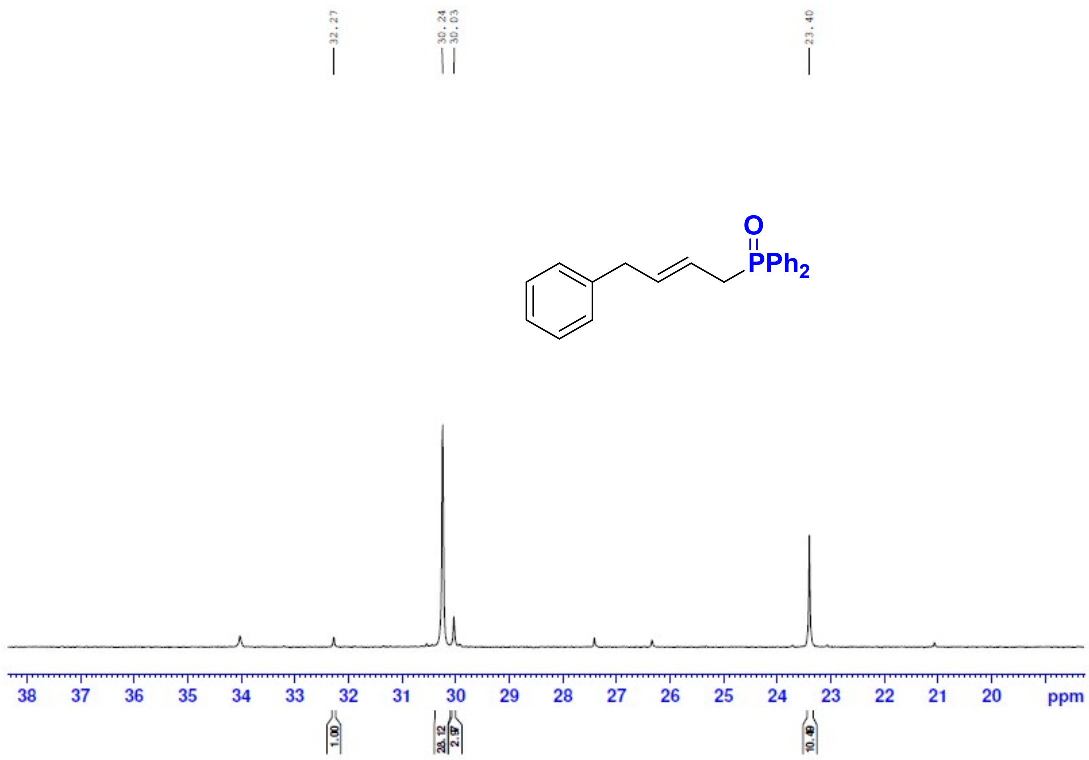

MeO
PPh2
O
ppm

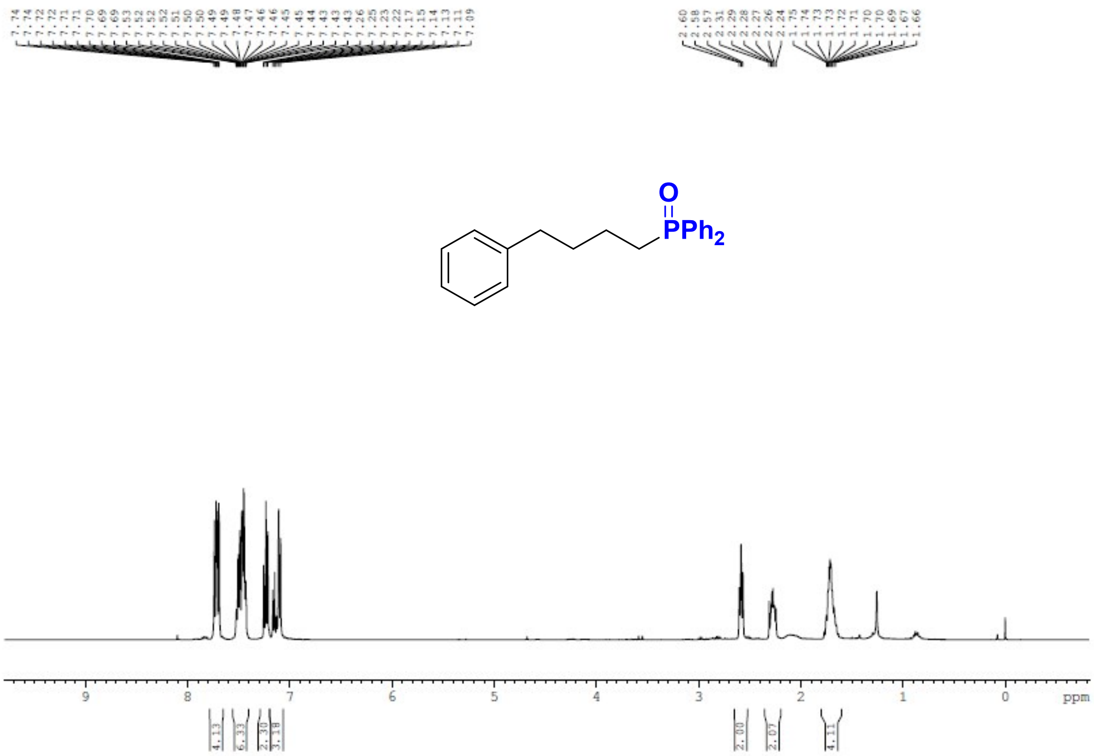

MeO
PPh2
O
ppm

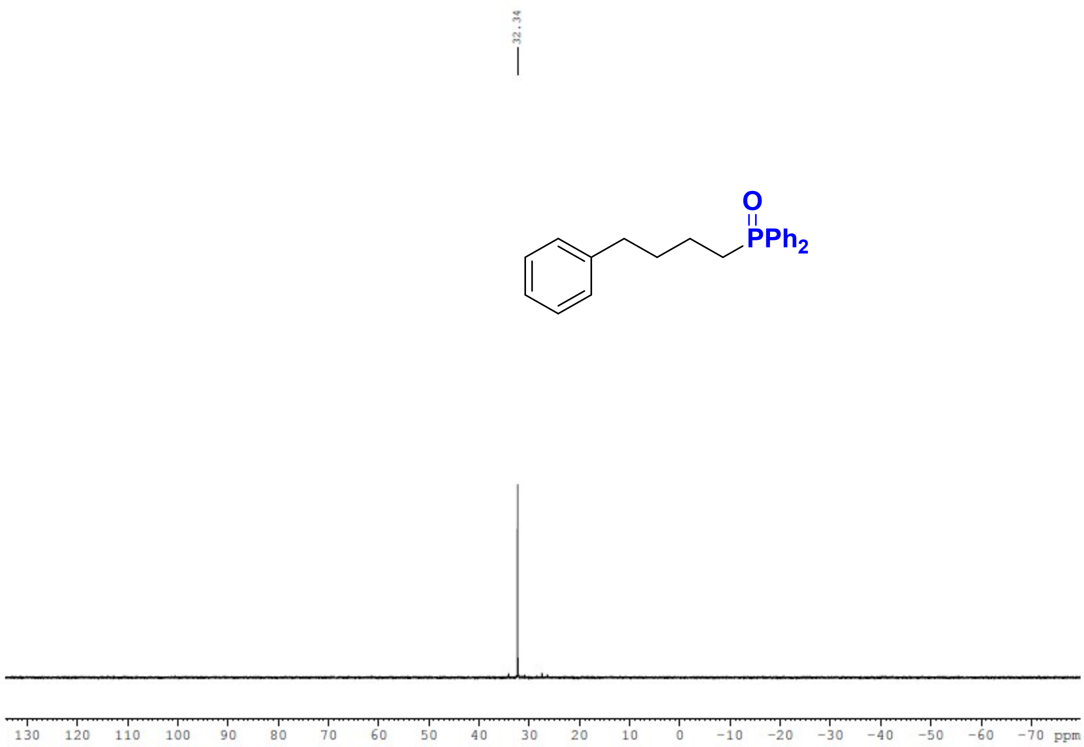

32.46
MeO
O
PPh2
55
50
45
40
35
30
25
20
15
10
ppm

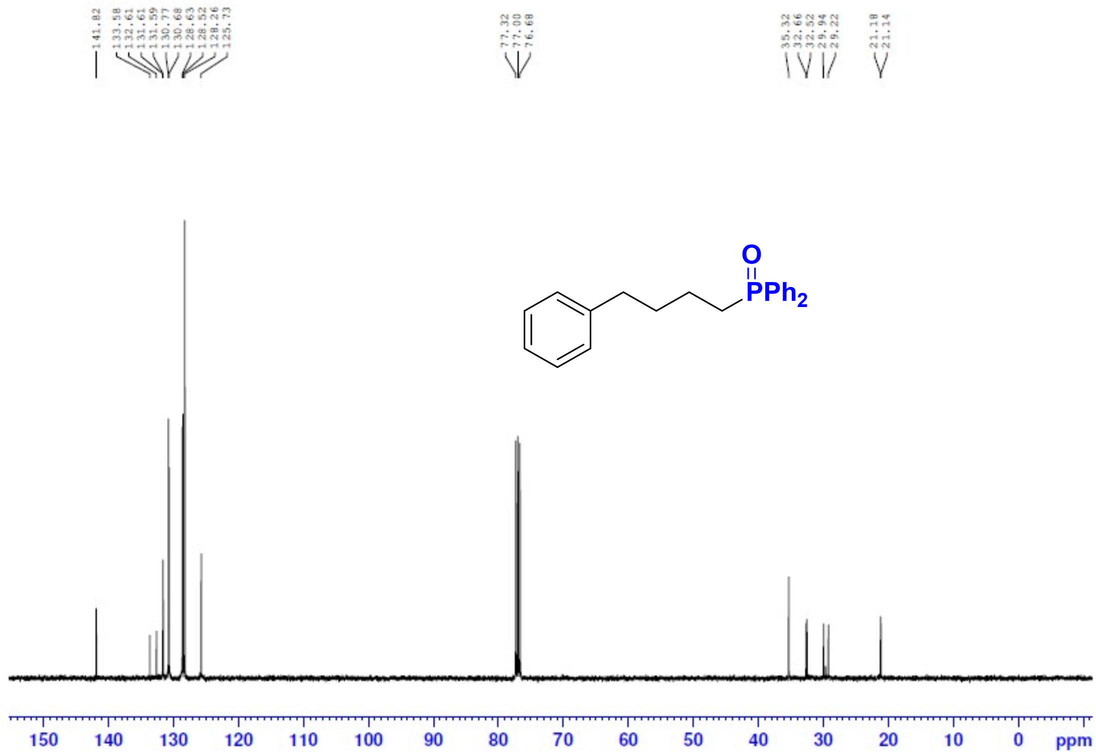

157.94
133.53
132.85
132.55
131.60
131.58
130.77
130.68
129.38
128.62
128.50
113.80
77.32
77.00
76.68
55.20
35.77
35.63
29.21
28.49
23.17
23.14
MeO
O
PPh2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

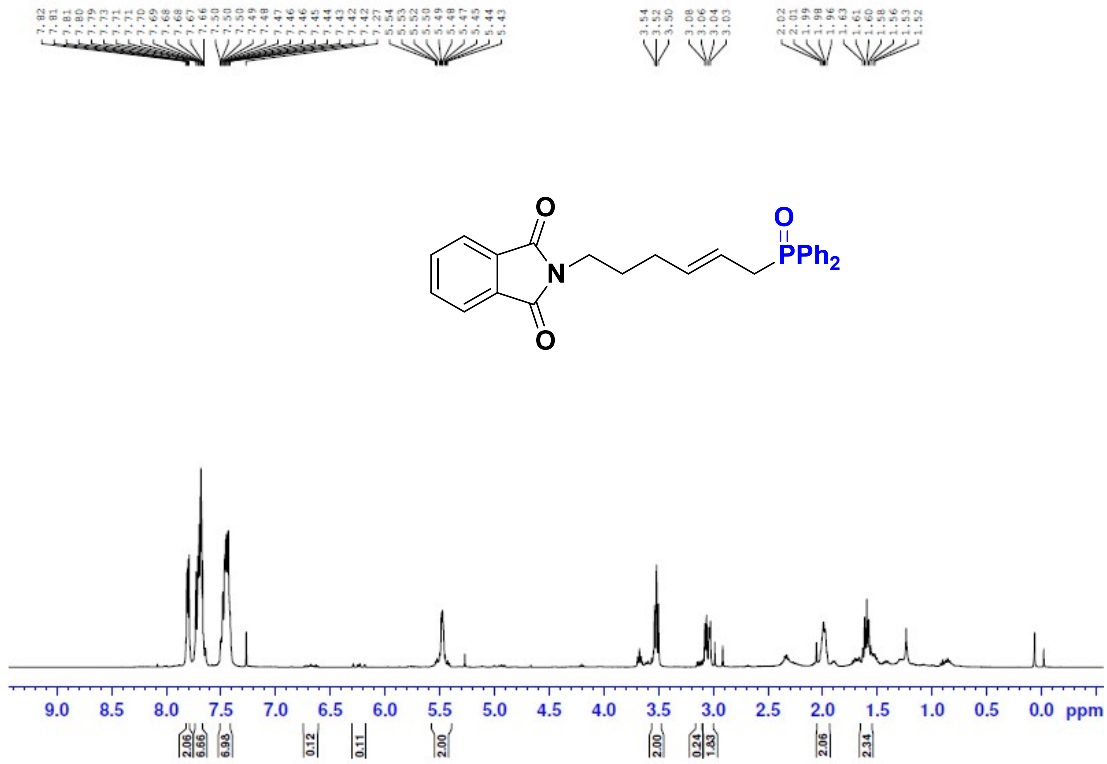


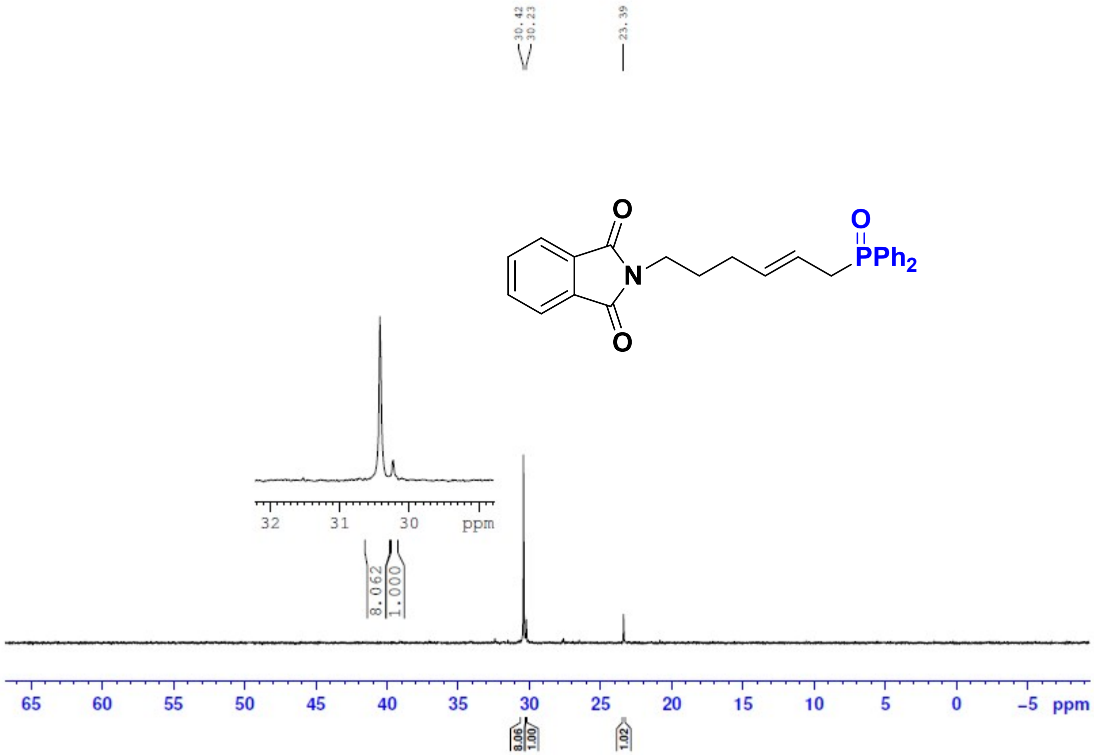


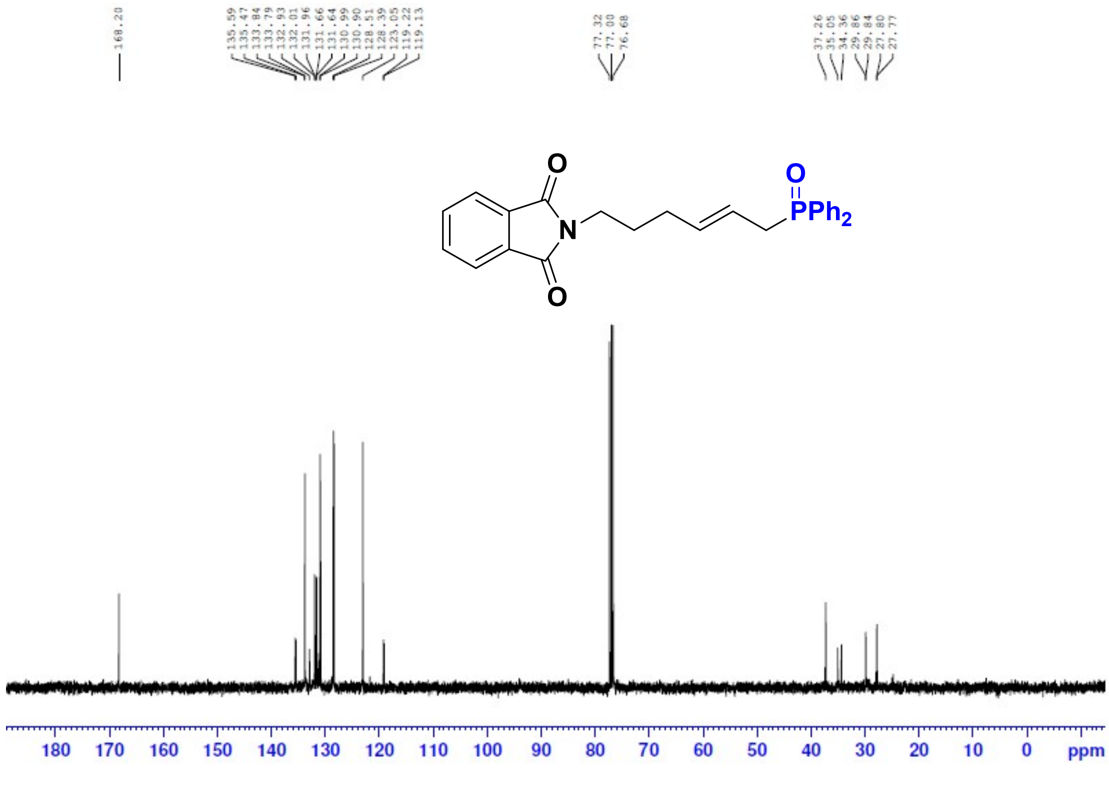

O
PPh2
ppm

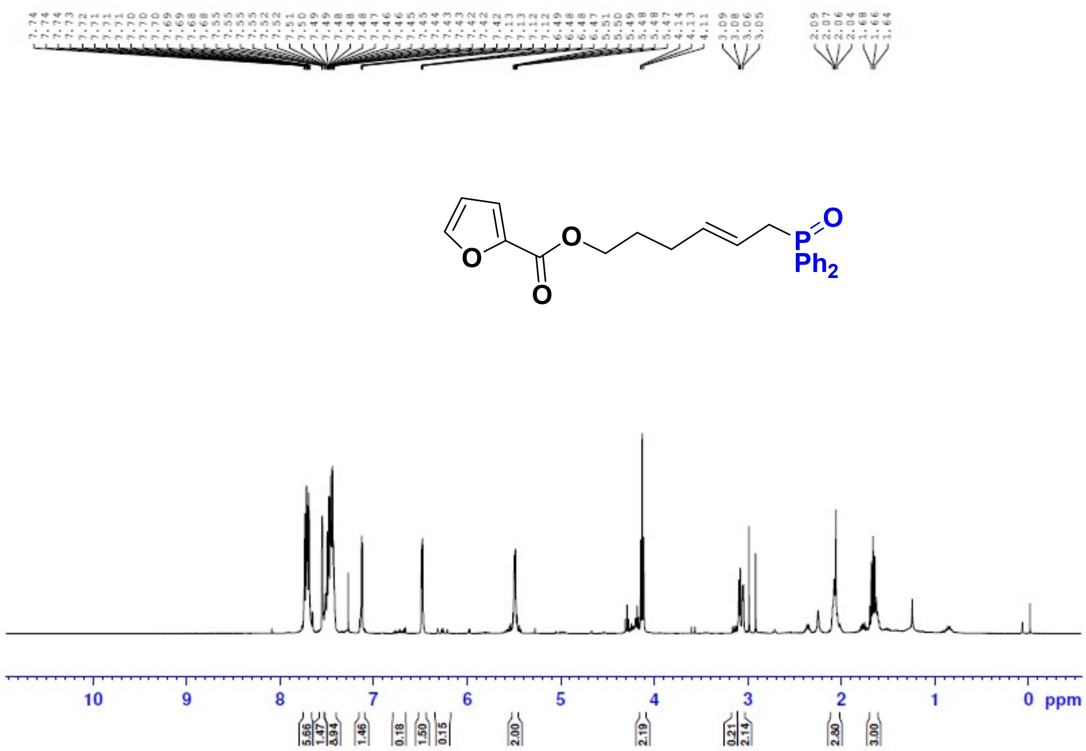

32.34
O
PPh2
ppm

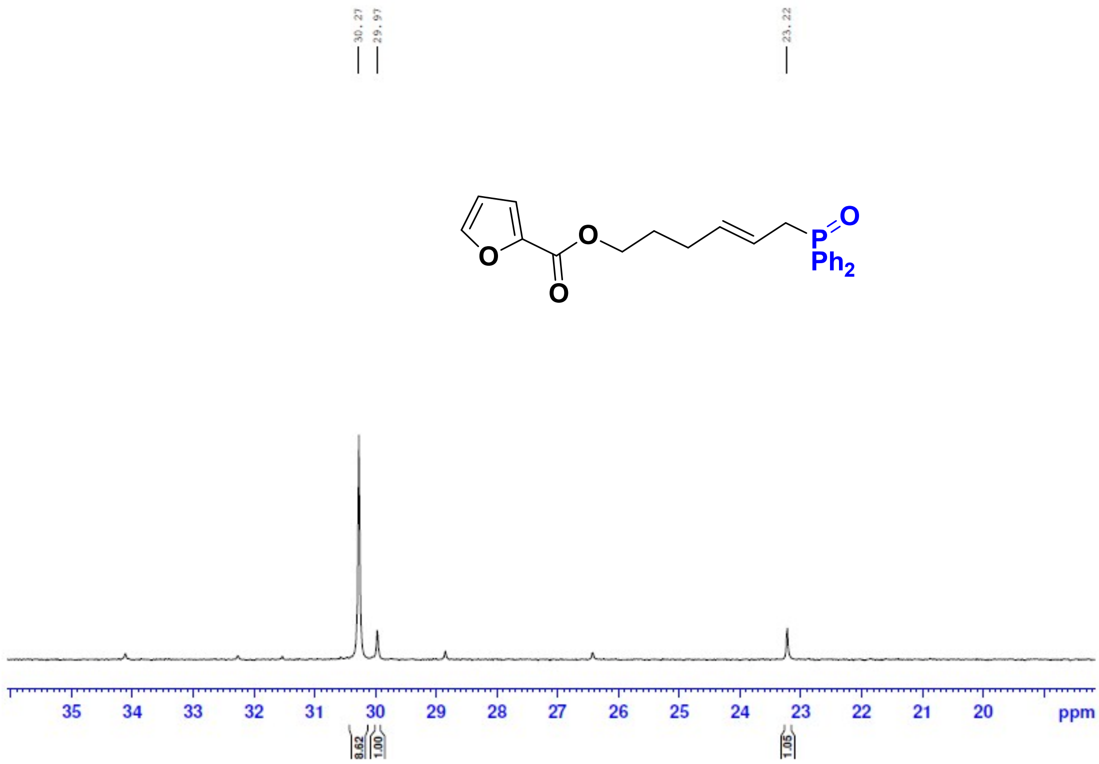


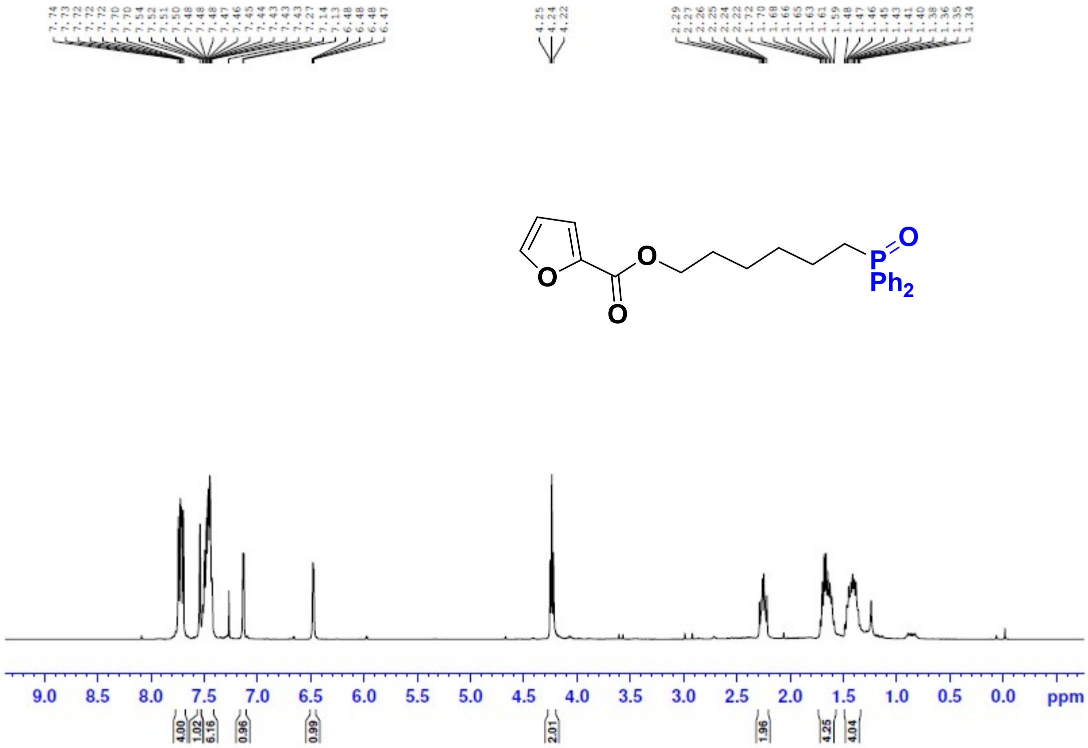


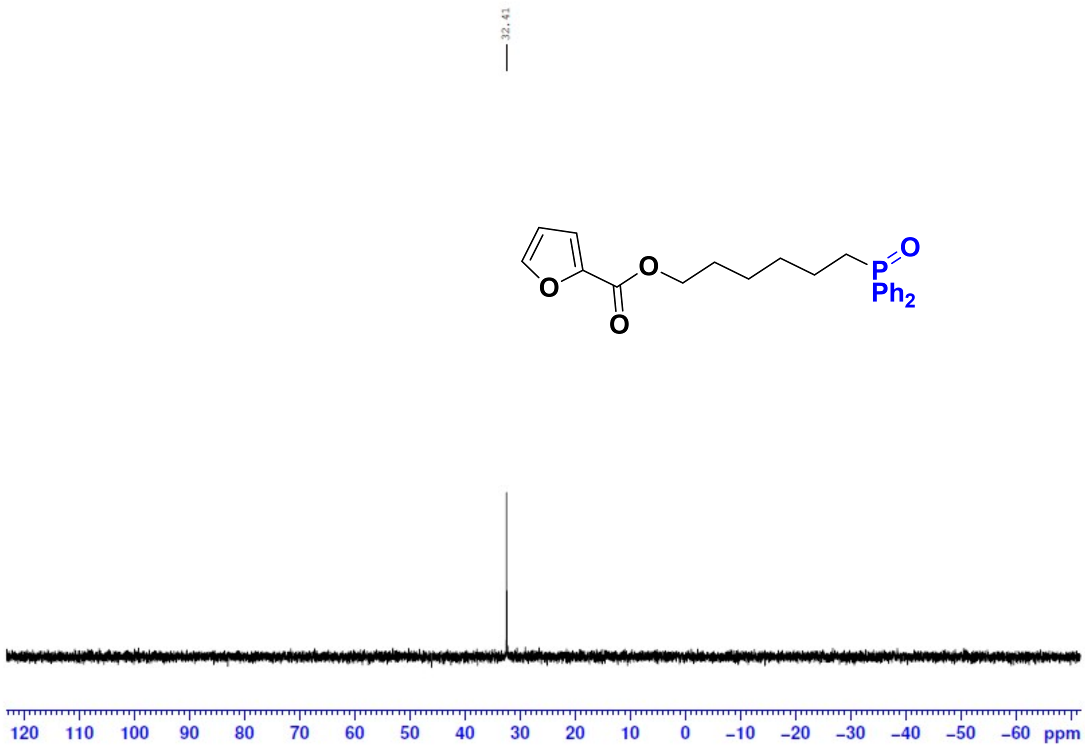

30.42
30.23
23.39
O
N
O
O
PPh2
32
31
30
ppm
8.062
1.000
65
60
55
50
45
40
35
30
25
20
15
10
5
0
–5
ppm
8.06
1.00
1.02

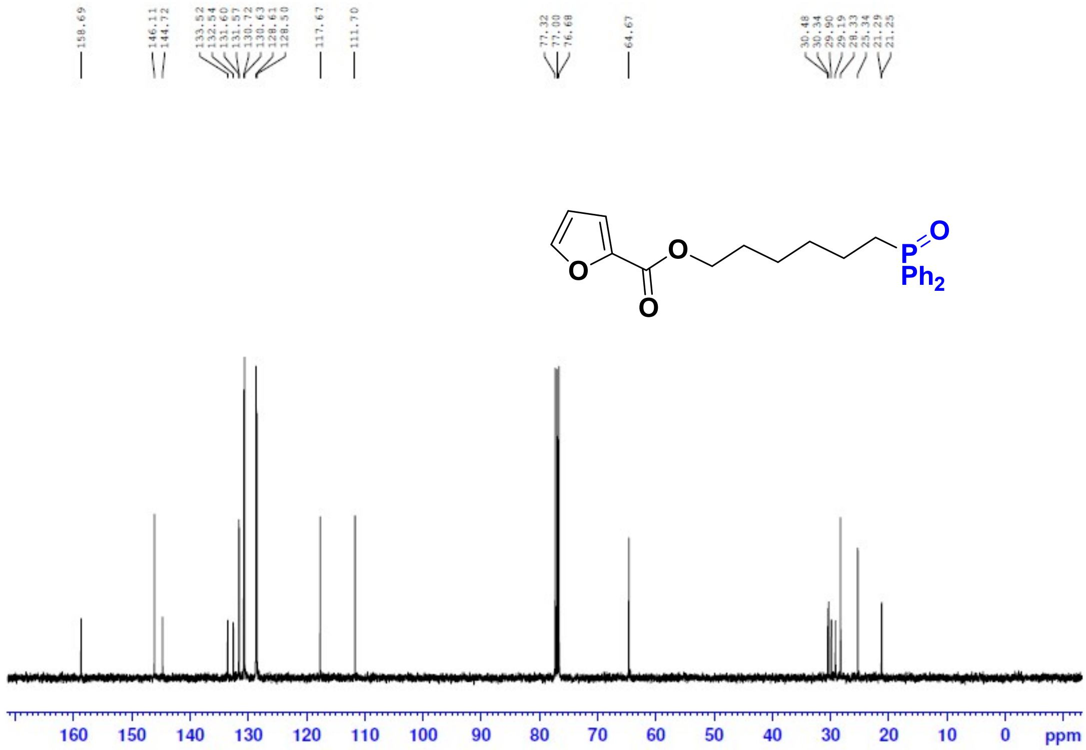

168.20
135.59
135.47
133.84
133.79
132.93
132.01
131.96
131.66
131.64
130.99
130.90
128.51
128.39
123.05
119.22
119.13
77.32
77.00
76.68
37.26
35.05
34.36
29.86
29.84
27.80
27.77
O
N
O
O
PPh2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



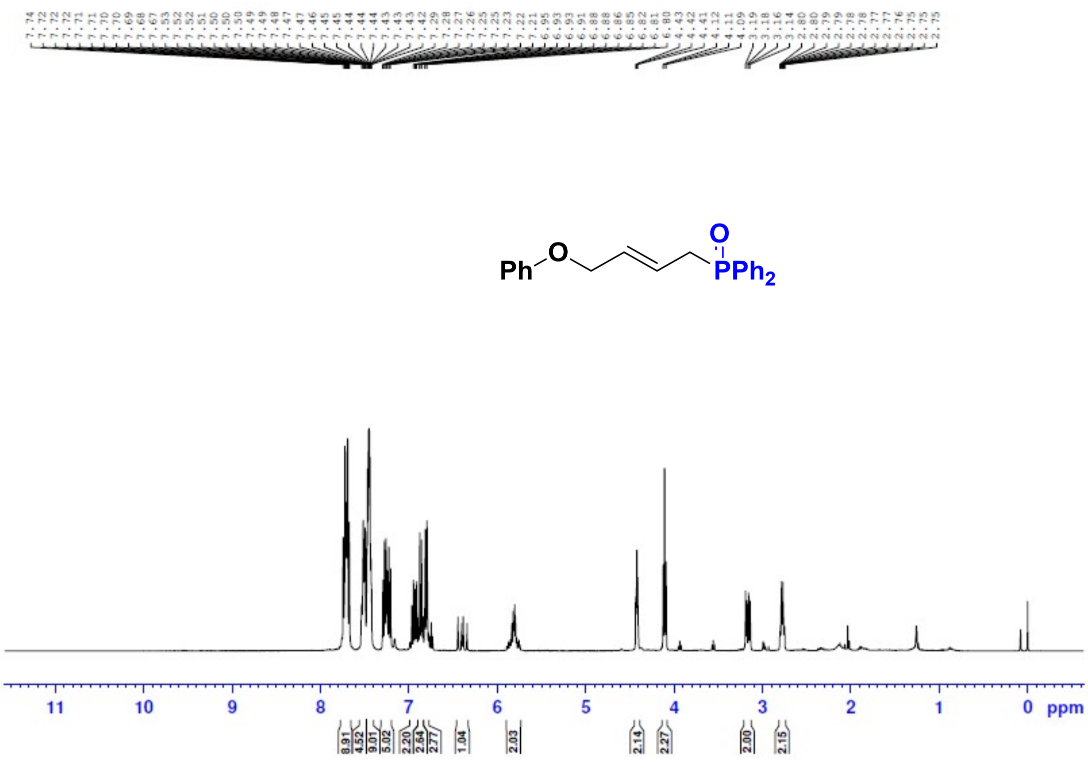



O
O
O
P
O
Ph2
ppm

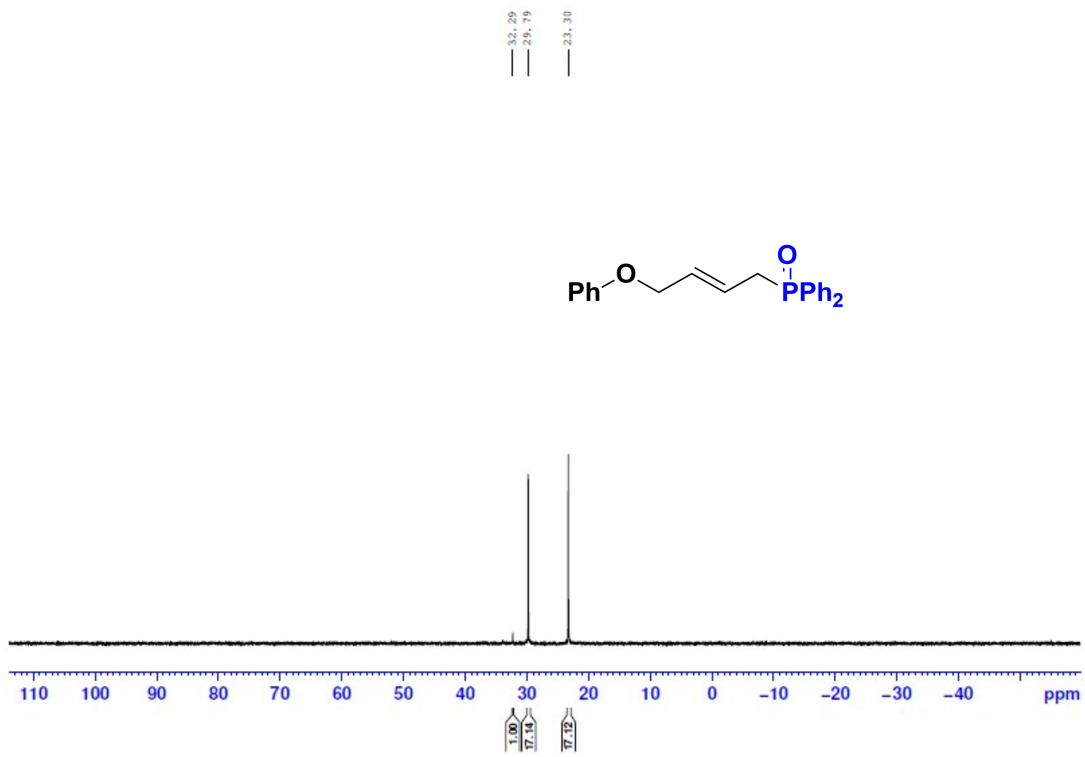

32.41
O
O
O
P
O
Ph2
ppm

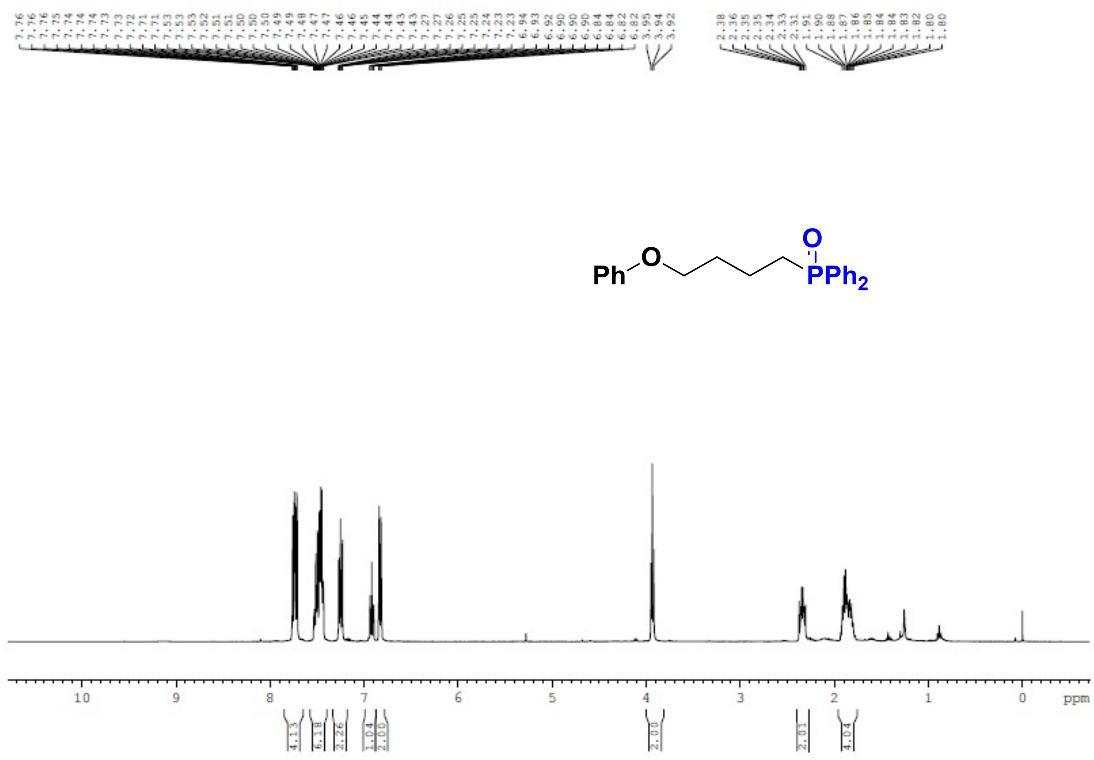


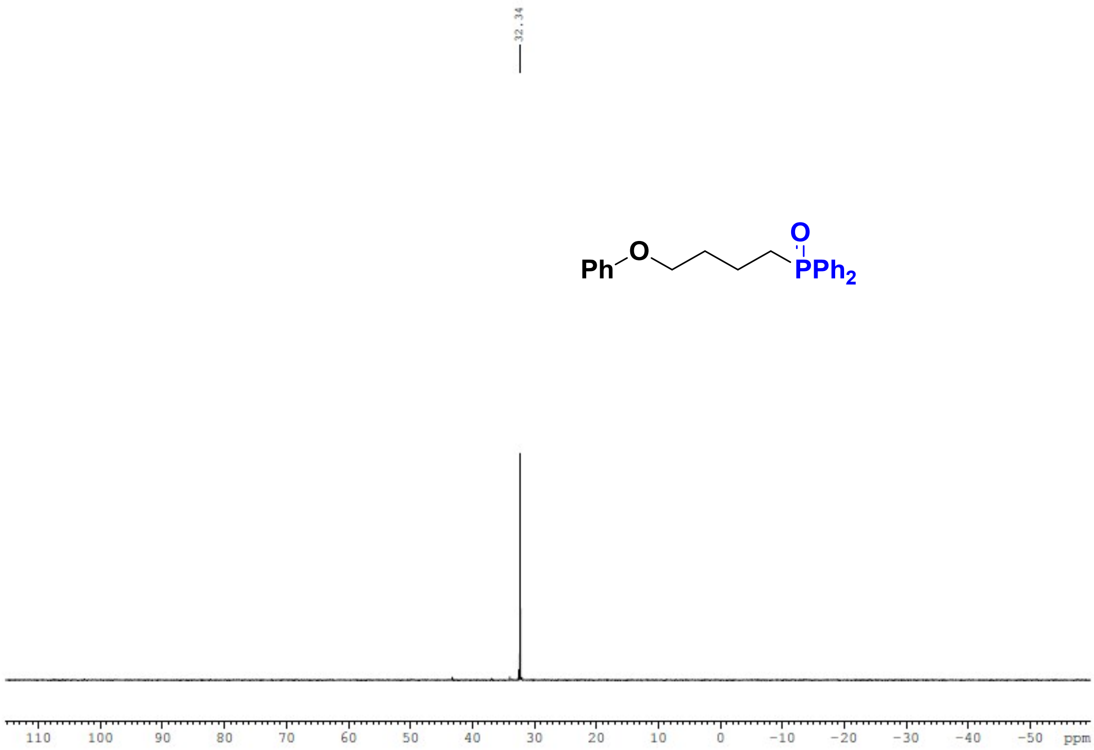
158.69
146.11
144.72
133.52
132.54
131.60
131.57
130.72
130.63
128.61
128.50
117.67
111.70
77.32
77.00
76.68
64.67
30.48
30.34
29.90
29.19
28.33
25.34
21.29
21.25
O
O
O
P
O
Ph2
ppm



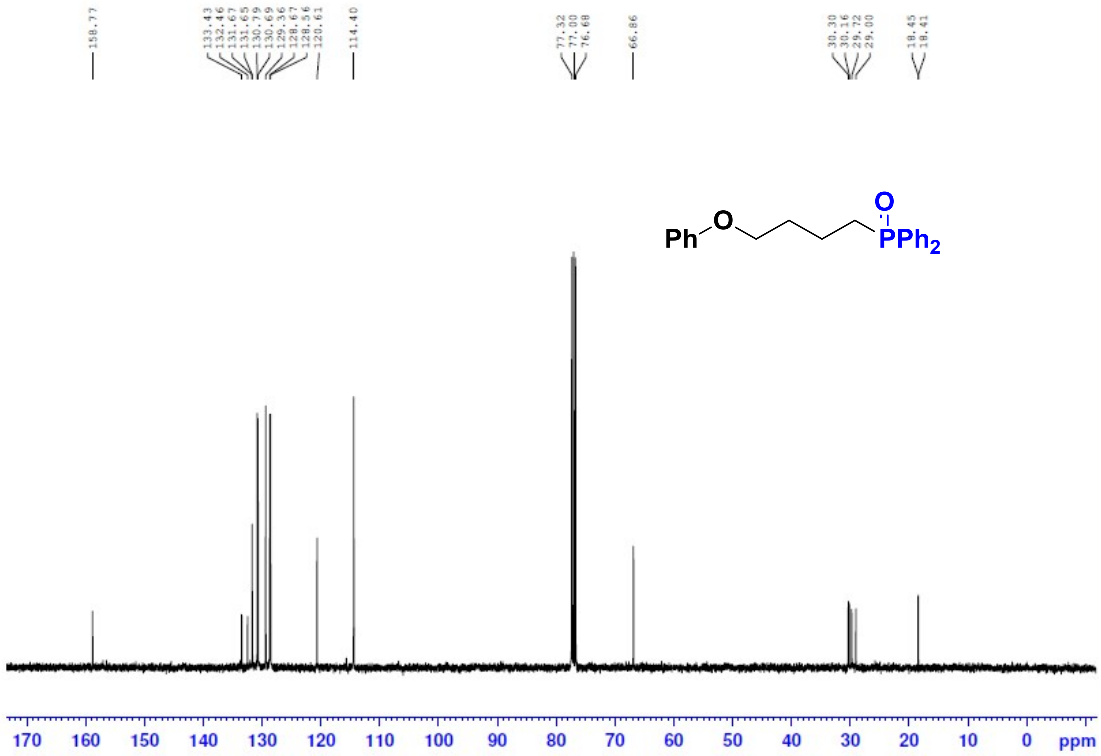
Ph
O
O
PPh2
ppm
8.91
4.52
9.01
5.02
2.20
2.64
2.77
1.04
2.03
2.14
2.27
2.00
2.15



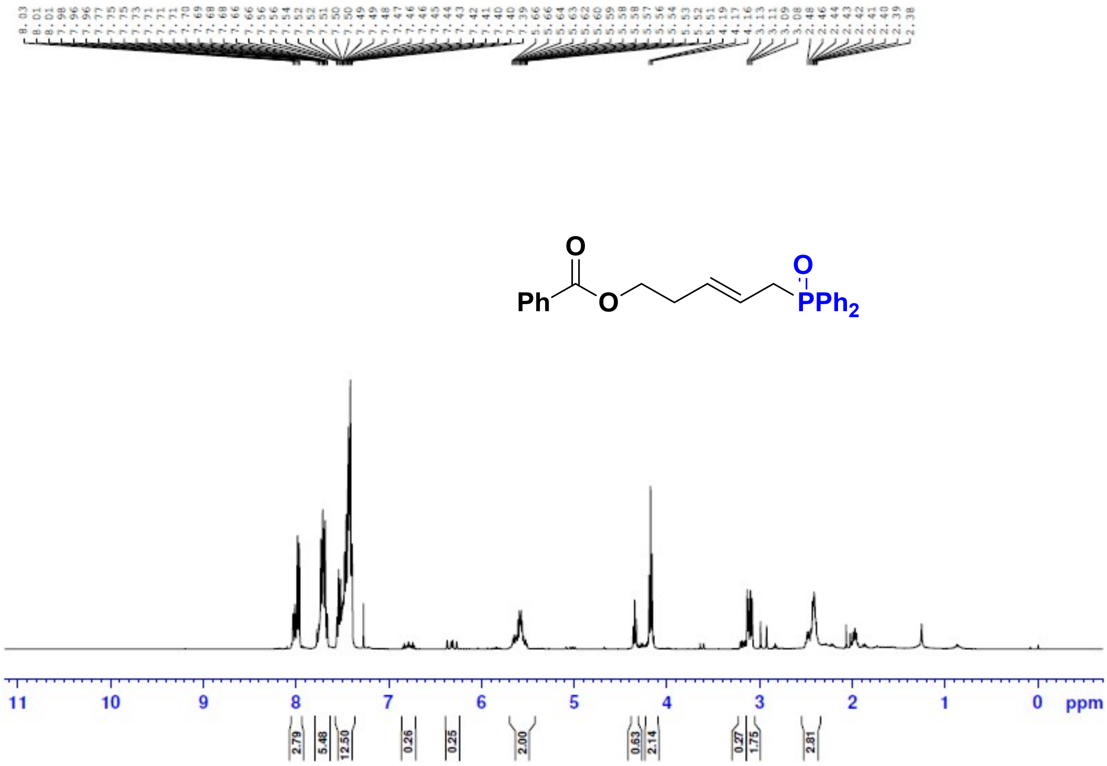


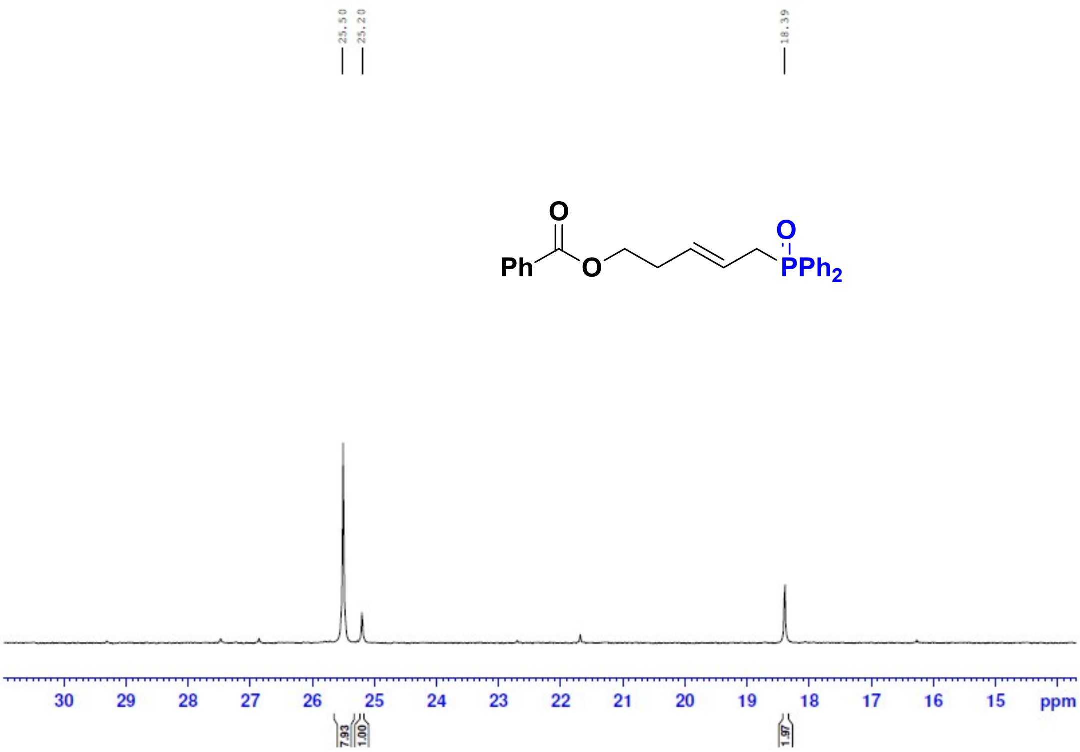


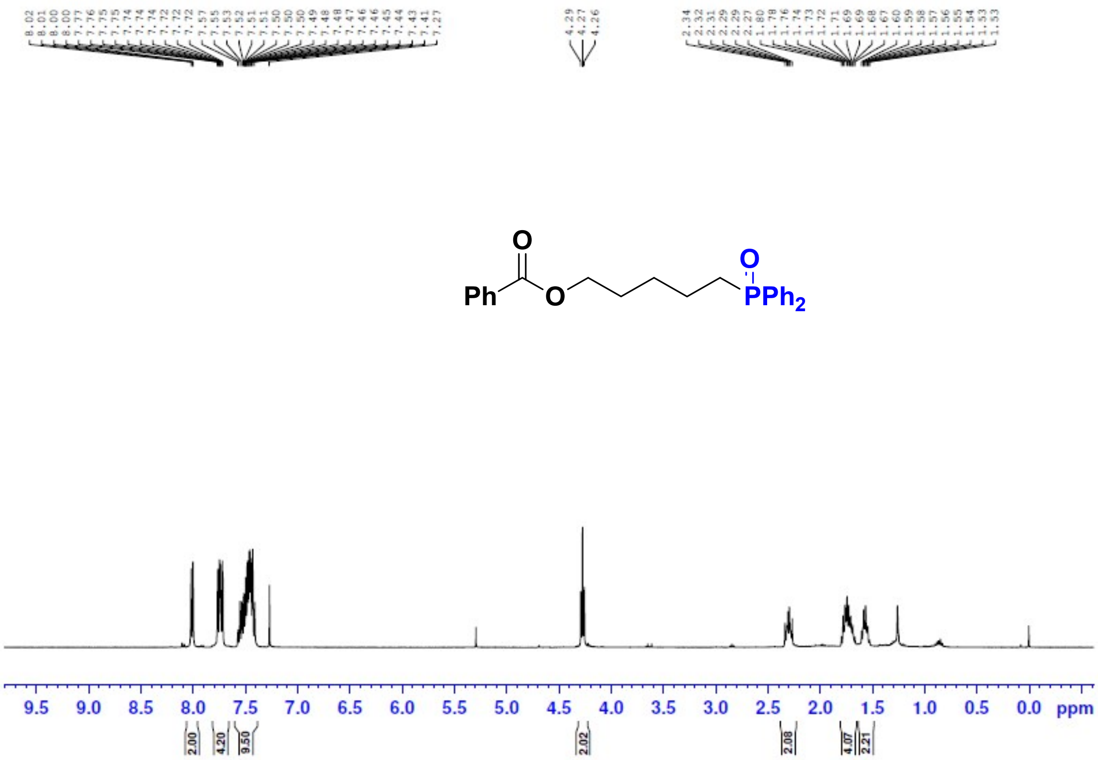
32.34
Ph
O
O
PPh2
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 ppm

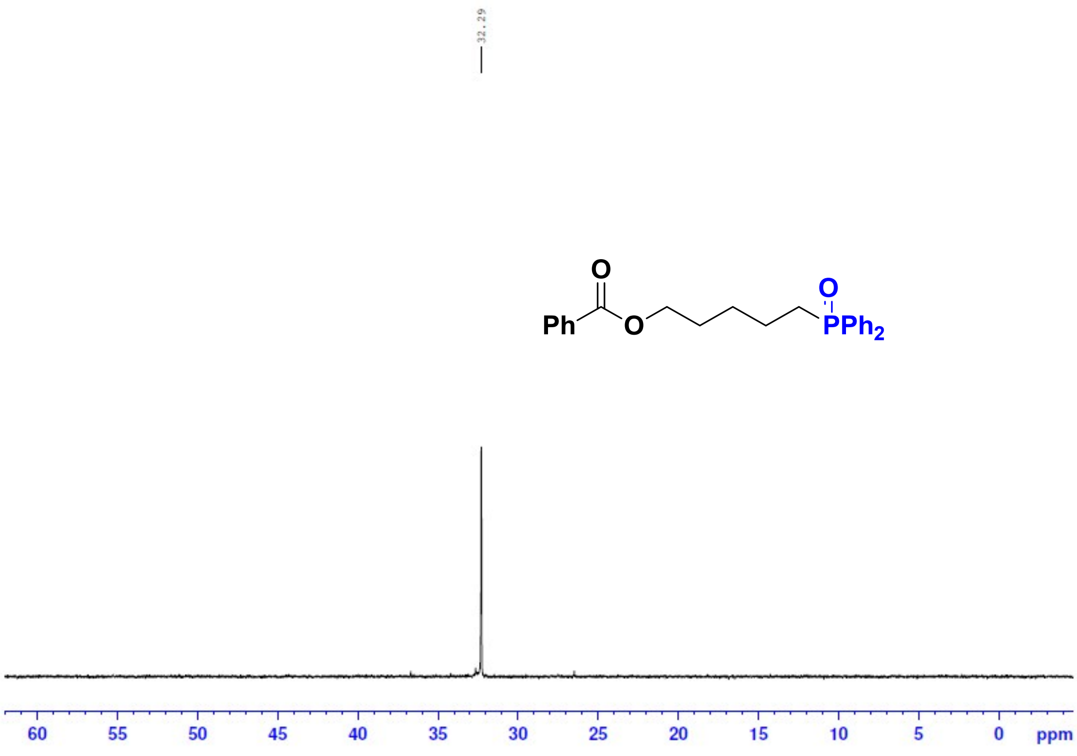


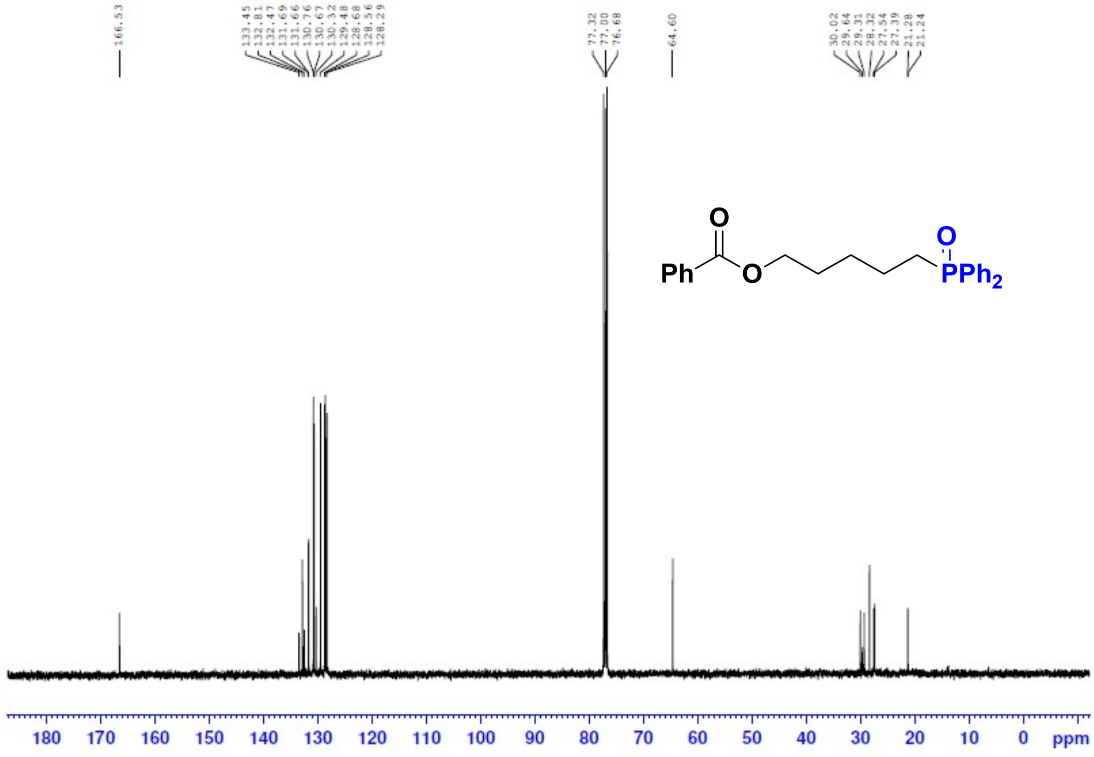
158.77
133.43 132.46 131.67 131.65 130.79 130.69 129.36 128.67 128.56 120.61
114.40
77.32 77.00 76.68
66.86
30.30 30.16 29.72 29.00
18.45 18.41
Ph
O
O
PPh2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

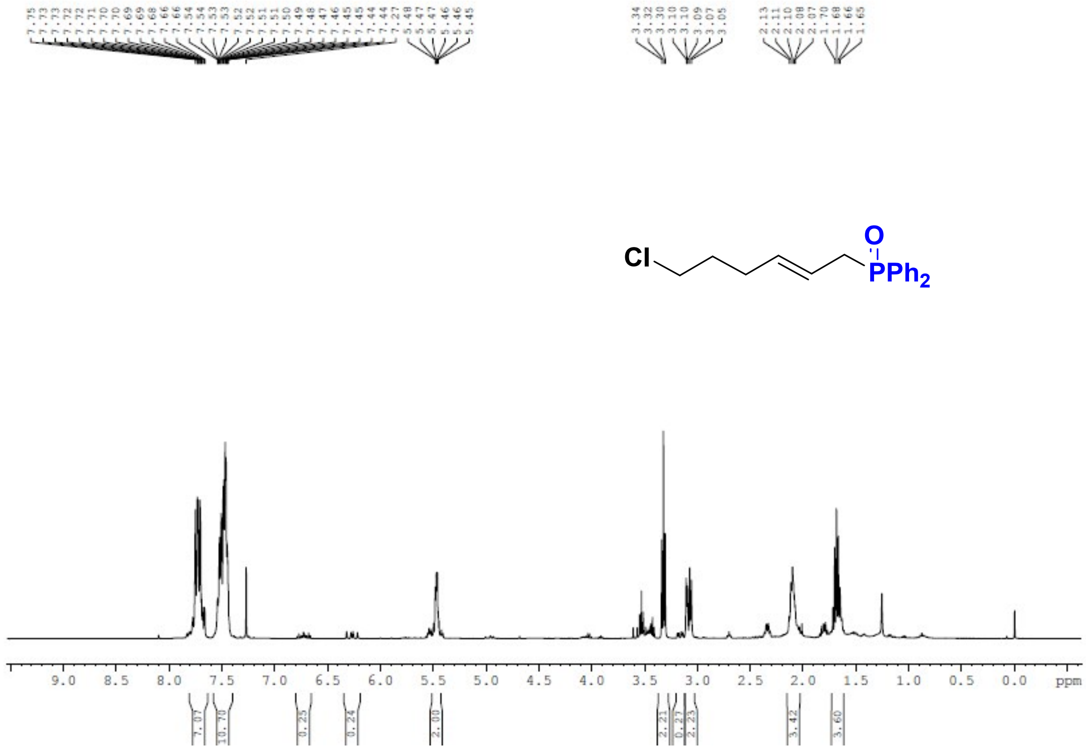

Ph
O
O
O
PPh2
ppm

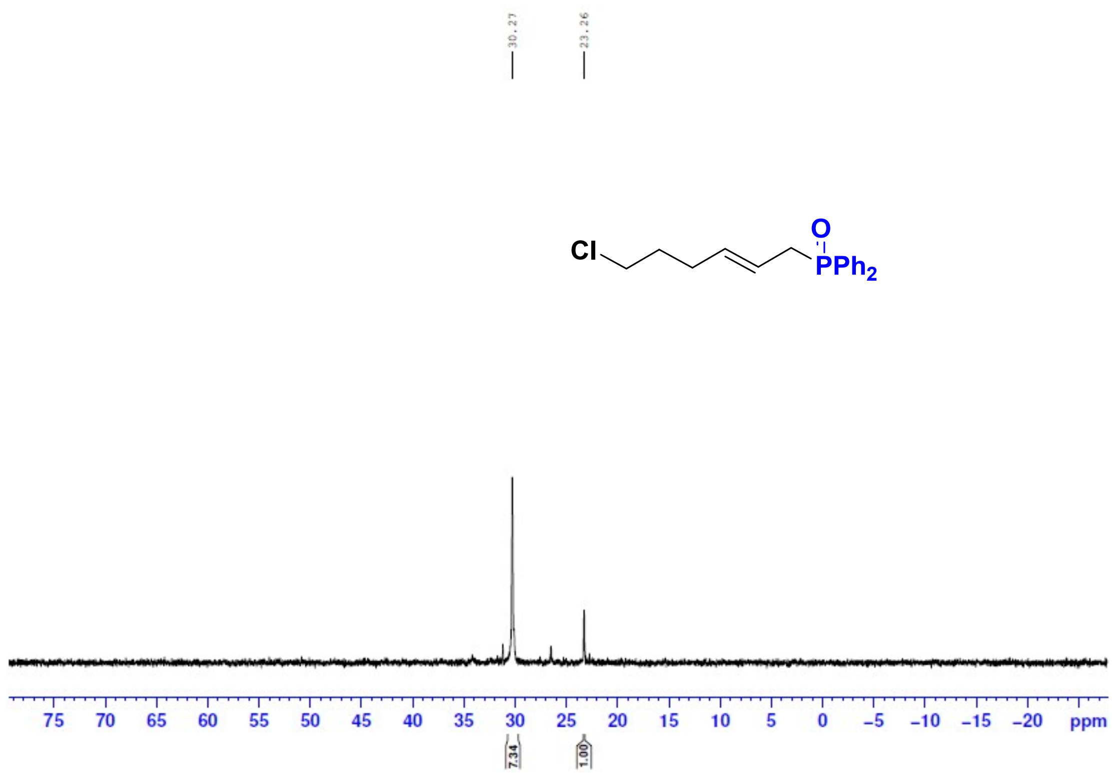

25.50
25.20
18.39
Ph
O
O
O
PPh2
ppm



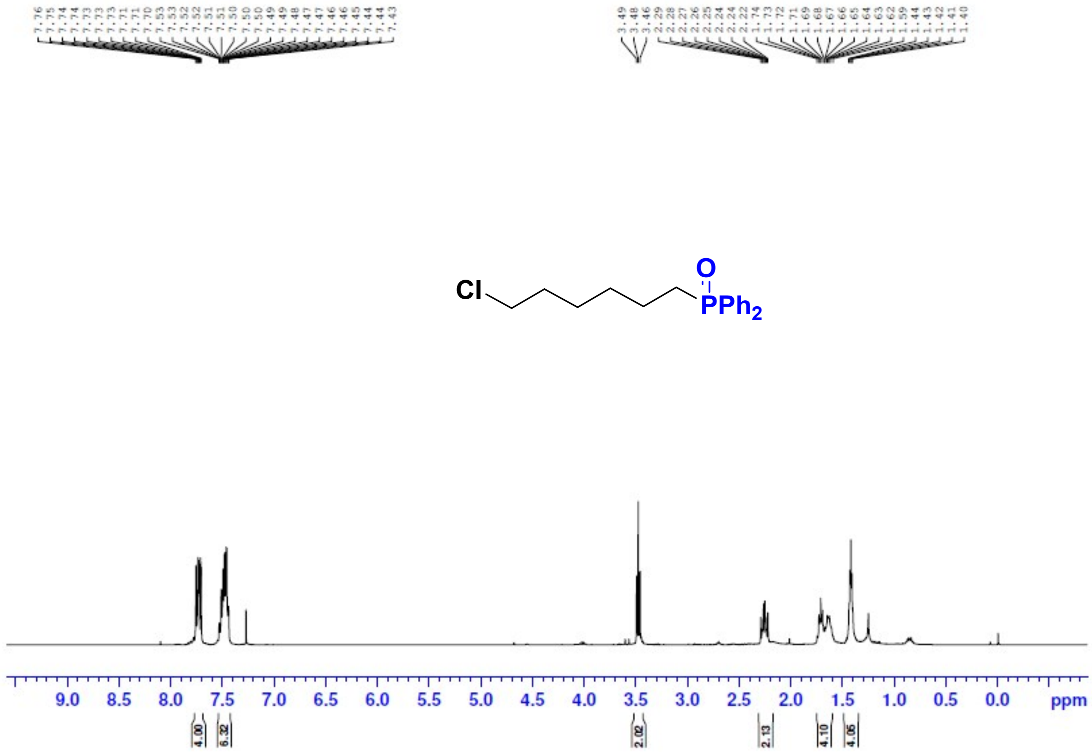



Ph
O
O
O
PPh2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

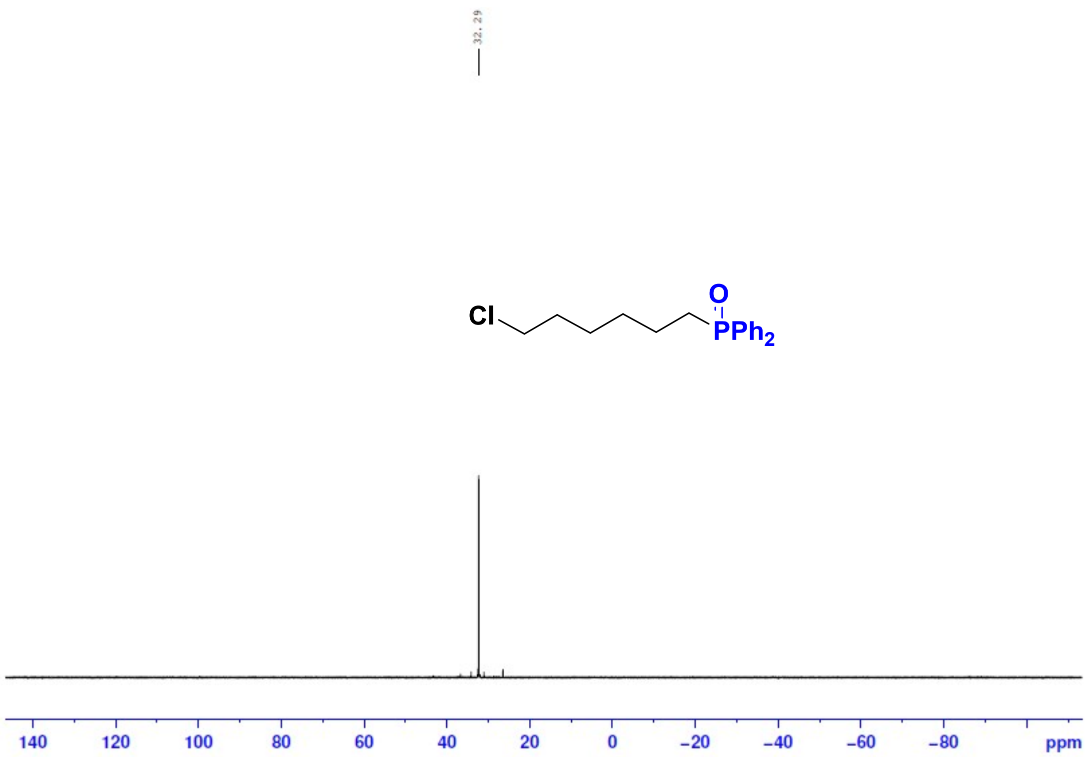

Cl
O
PPh2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

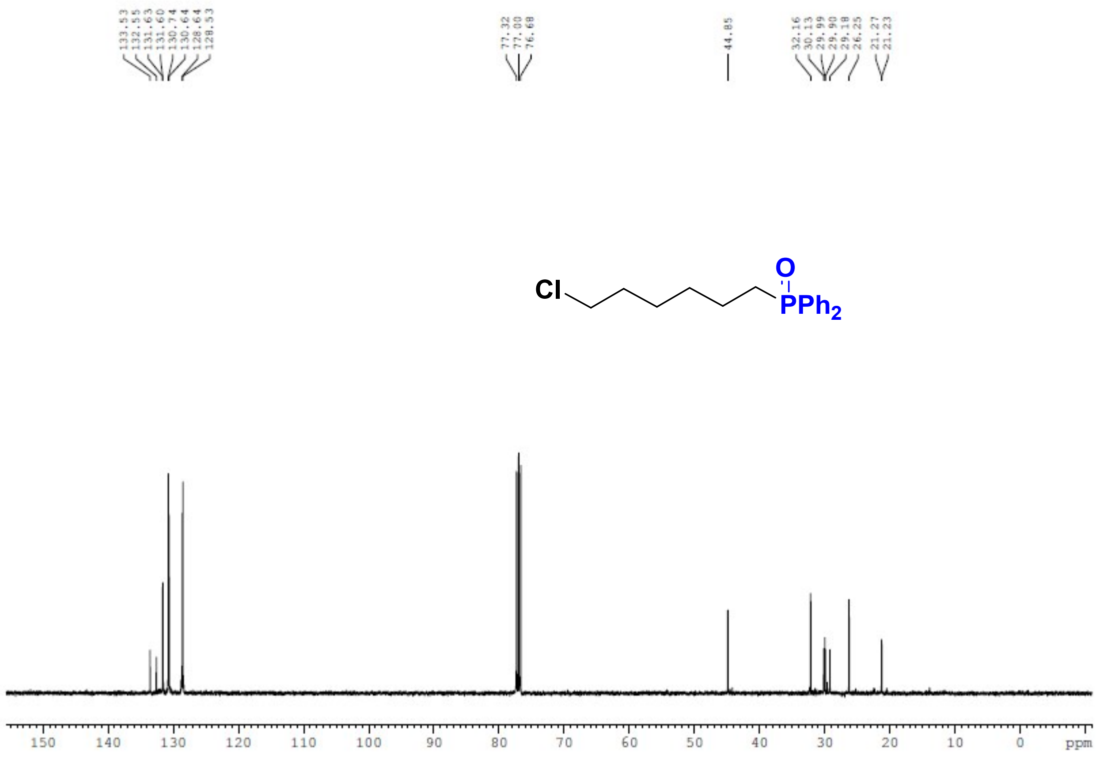


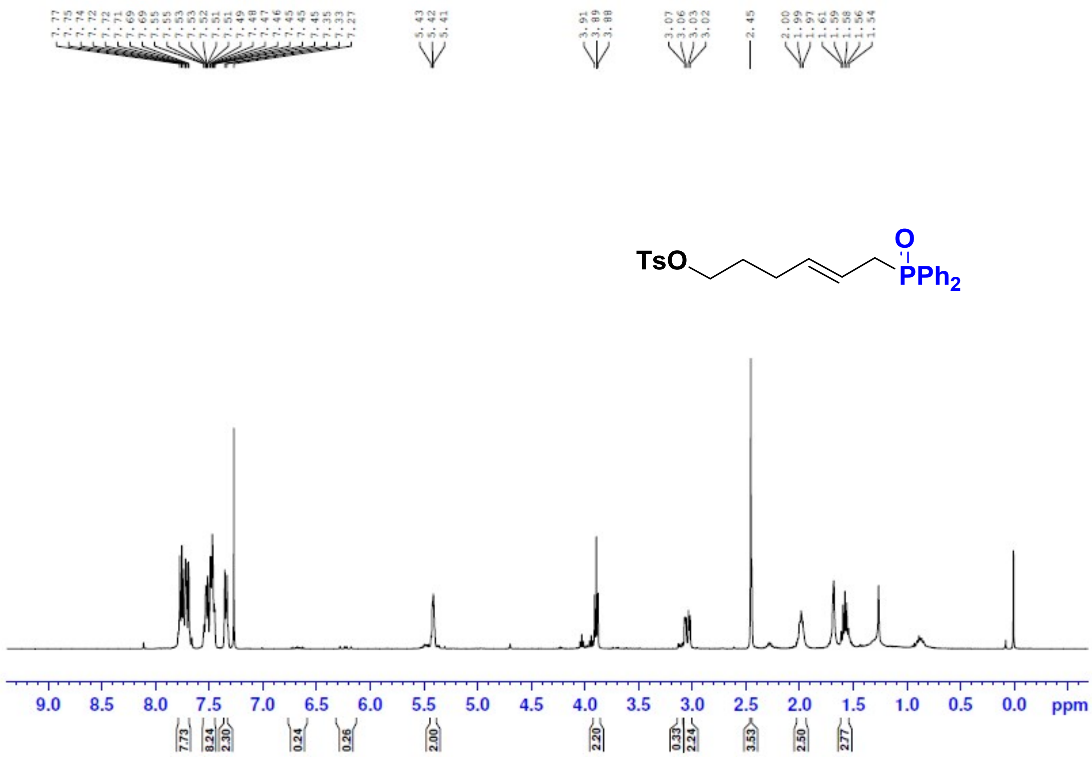
30.27
23.26
Cl
O
PPh2
ppm

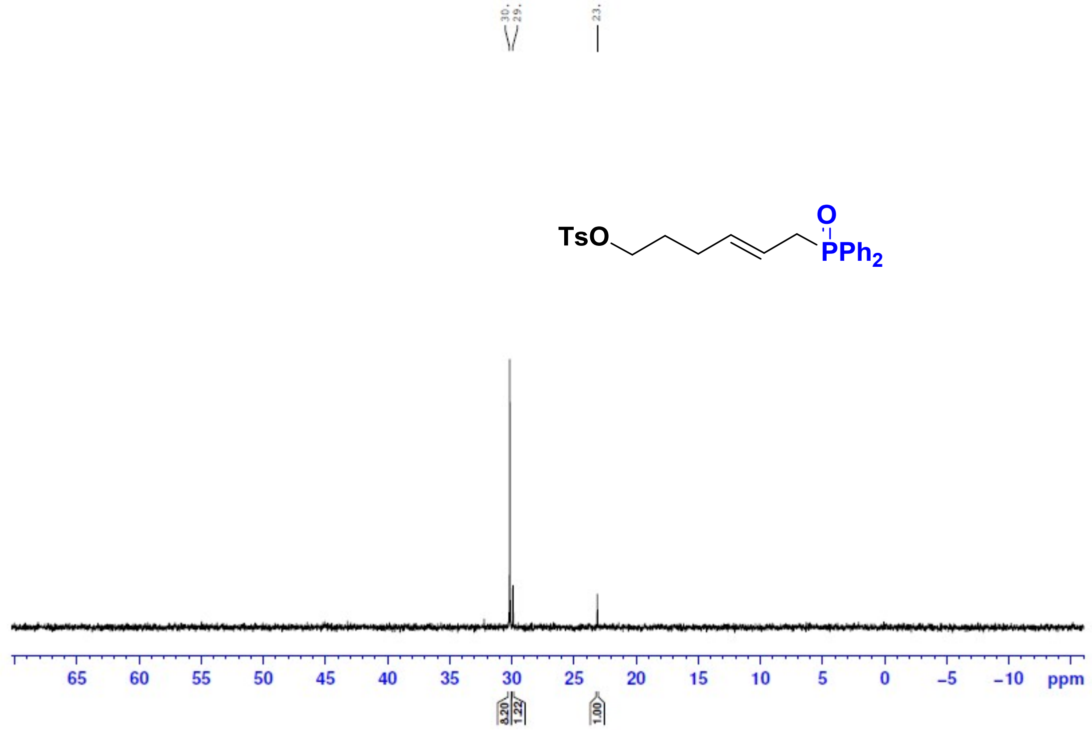


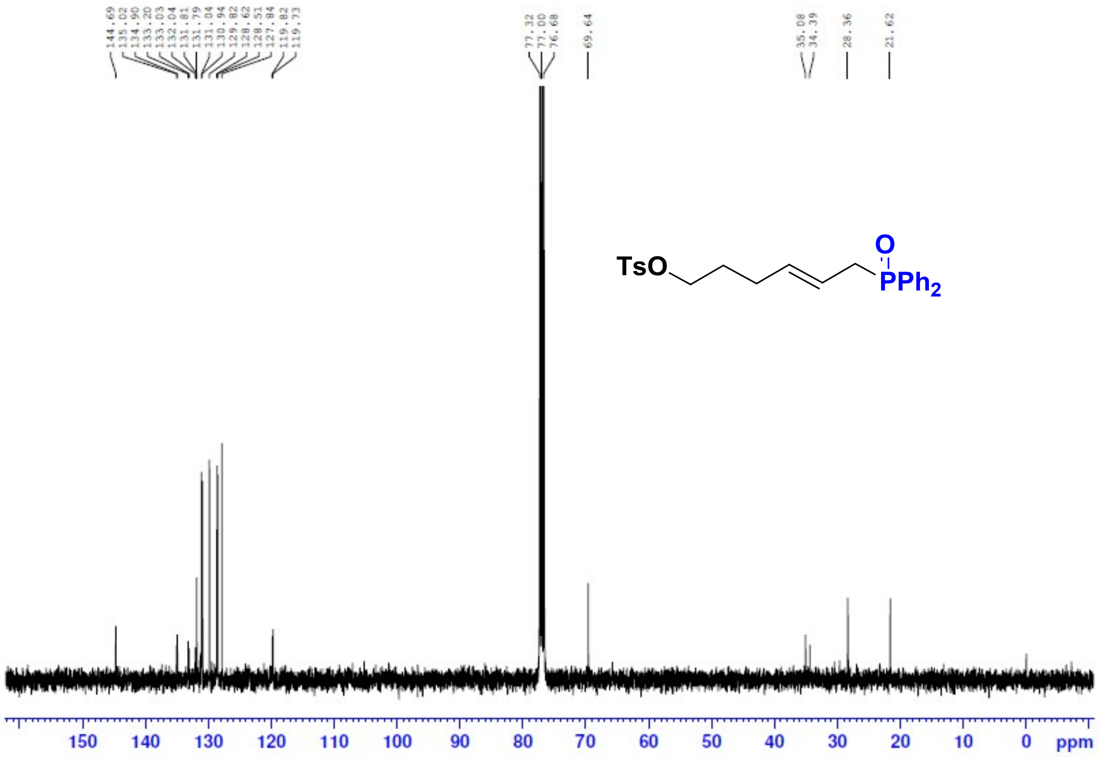
Cl
O
PPh2
ppm

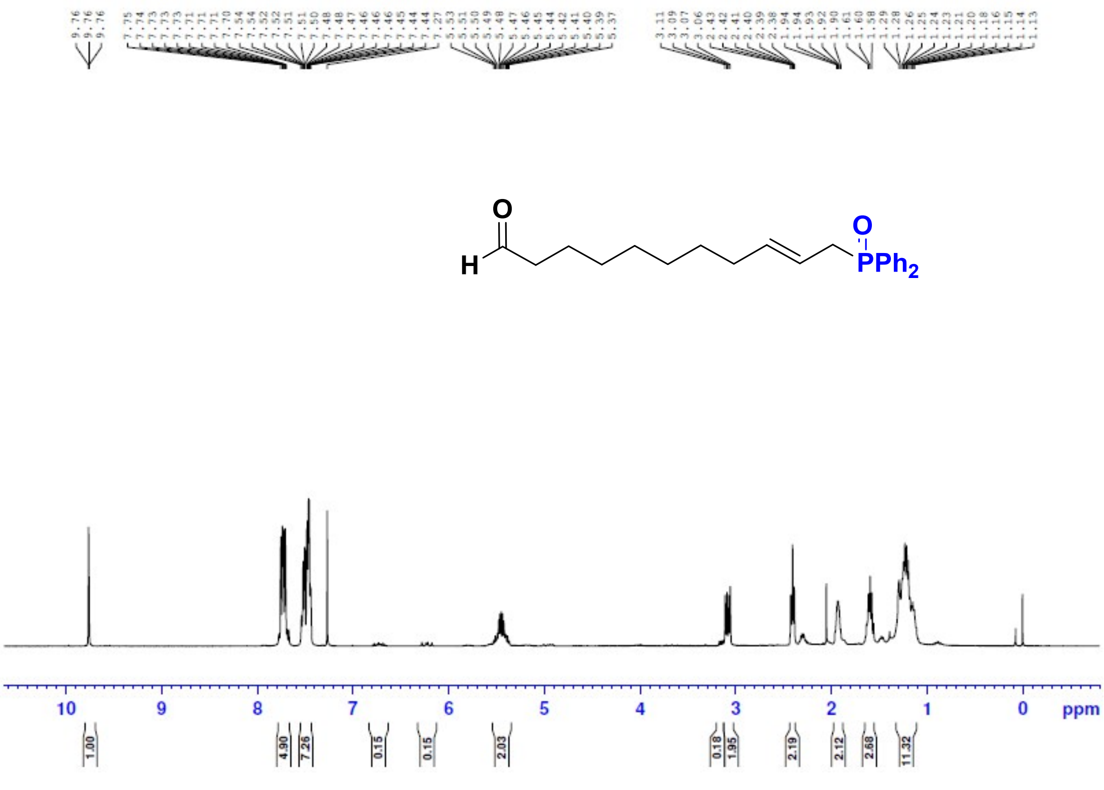

32.29
Cl
O
PPh2
140
120
100
80
60
40
20
0
−20
−40
−60
−80
ppm

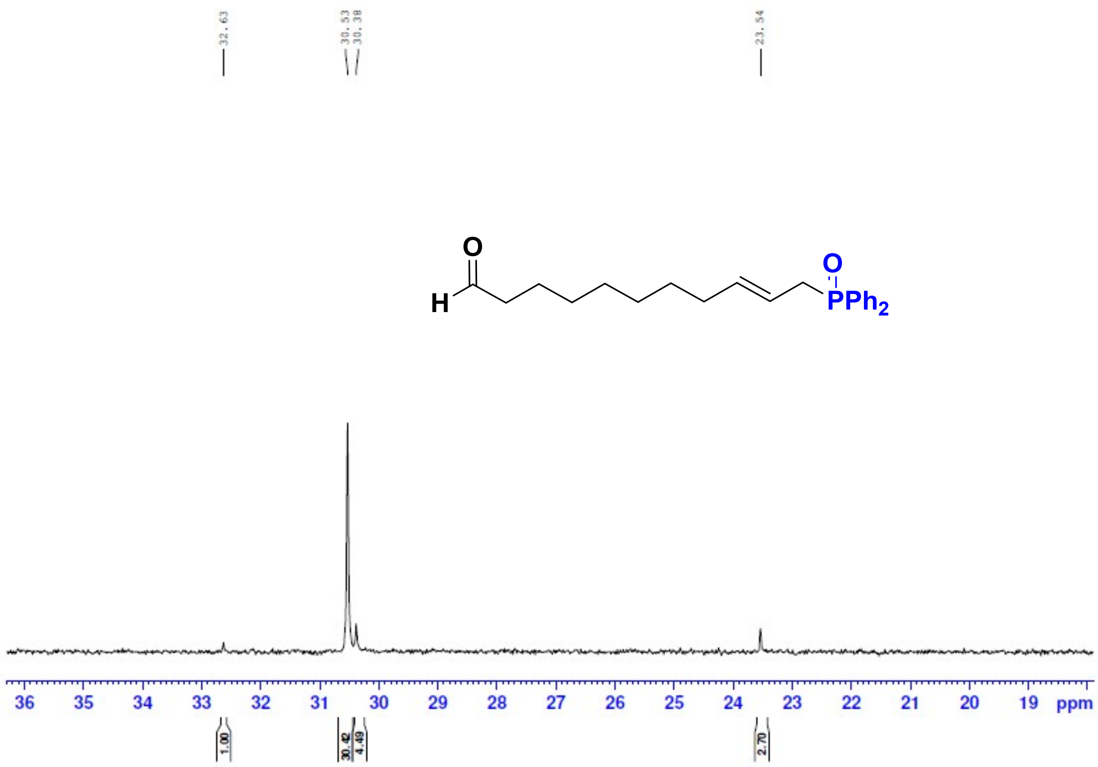

133.53
132.55
131.63
131.60
130.74
130.64
128.64
128.53
77.32
77.00
76.68
44.85
32.16
30.13
29.99
29.90
29.18
26.25
21.27
21.23
Cl
O
PPh2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

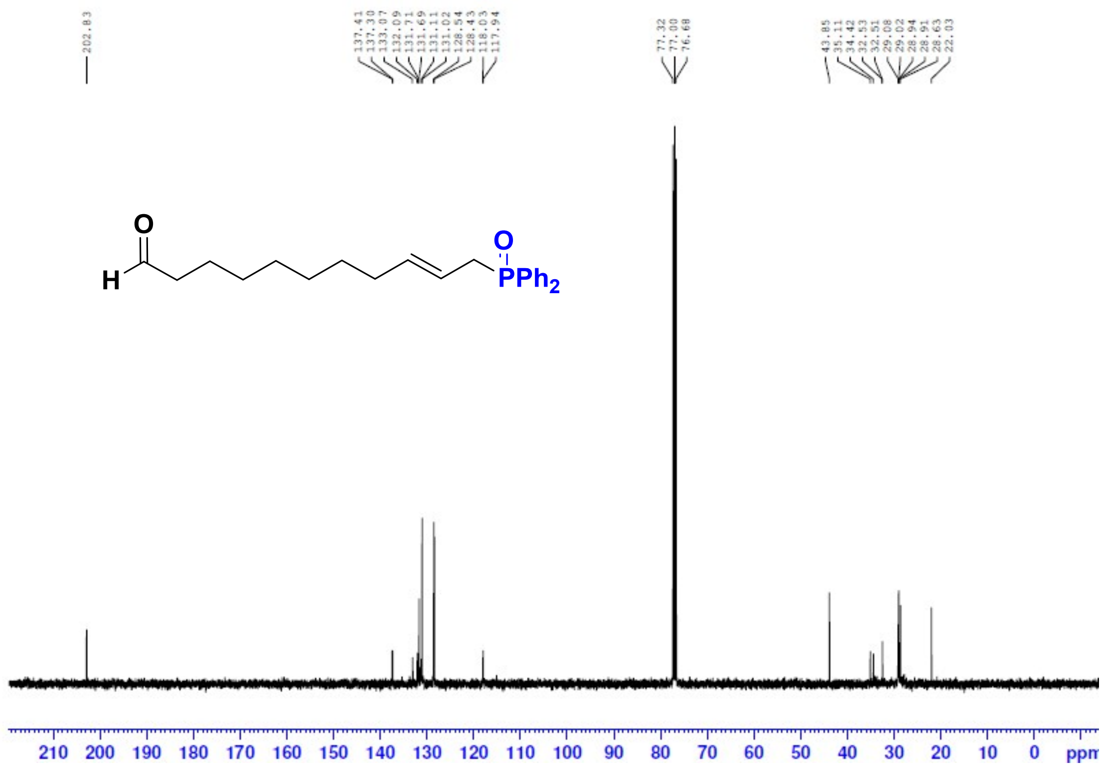

TsO
PPh2
O
ppm

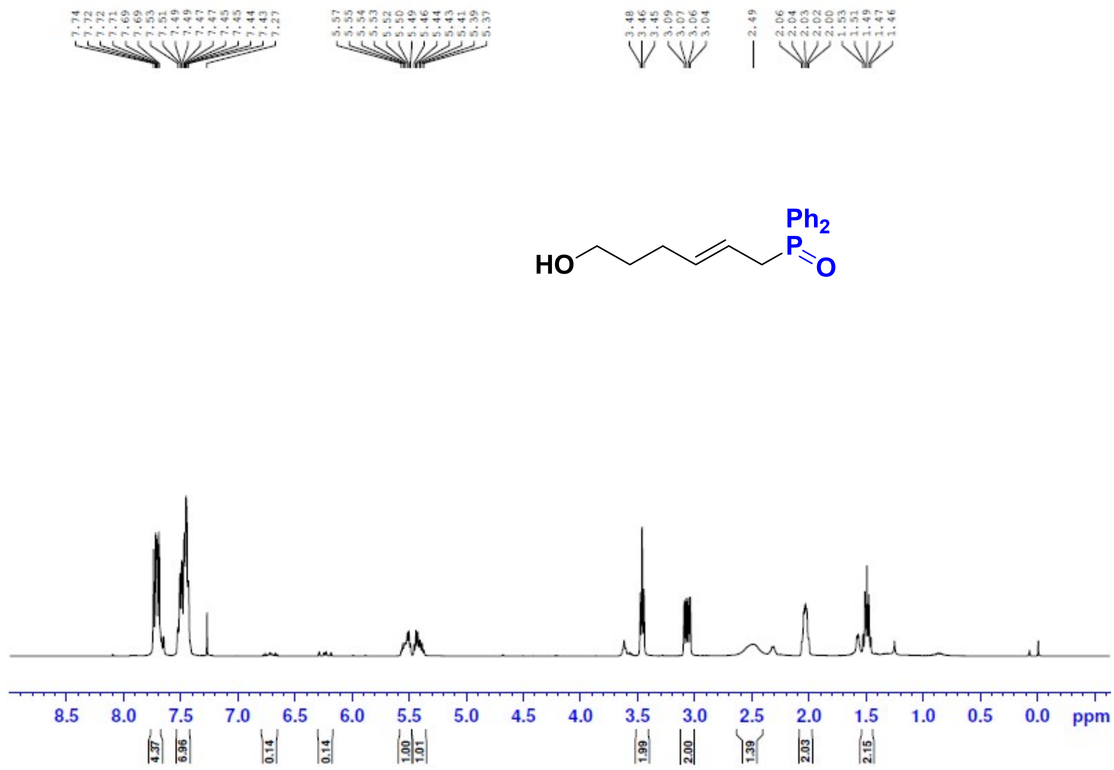

TsO
PPh2
O
ppm

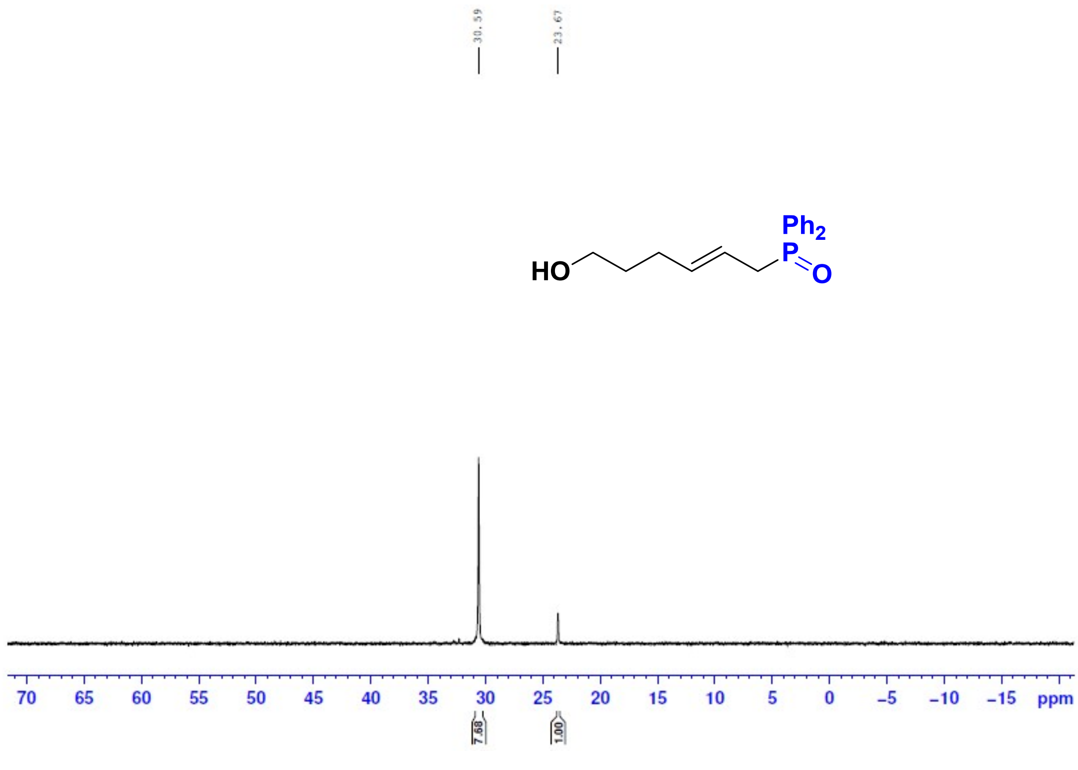

144.69
135.02
134.90
133.20
133.03
132.04
131.81
131.79
131.04
130.94
129.82
128.62
128.51
127.84
119.82
119.73
77.32
77.00
76.68
69.64
35.08
34.39
28.36
21.62
TsO
O
PPh2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

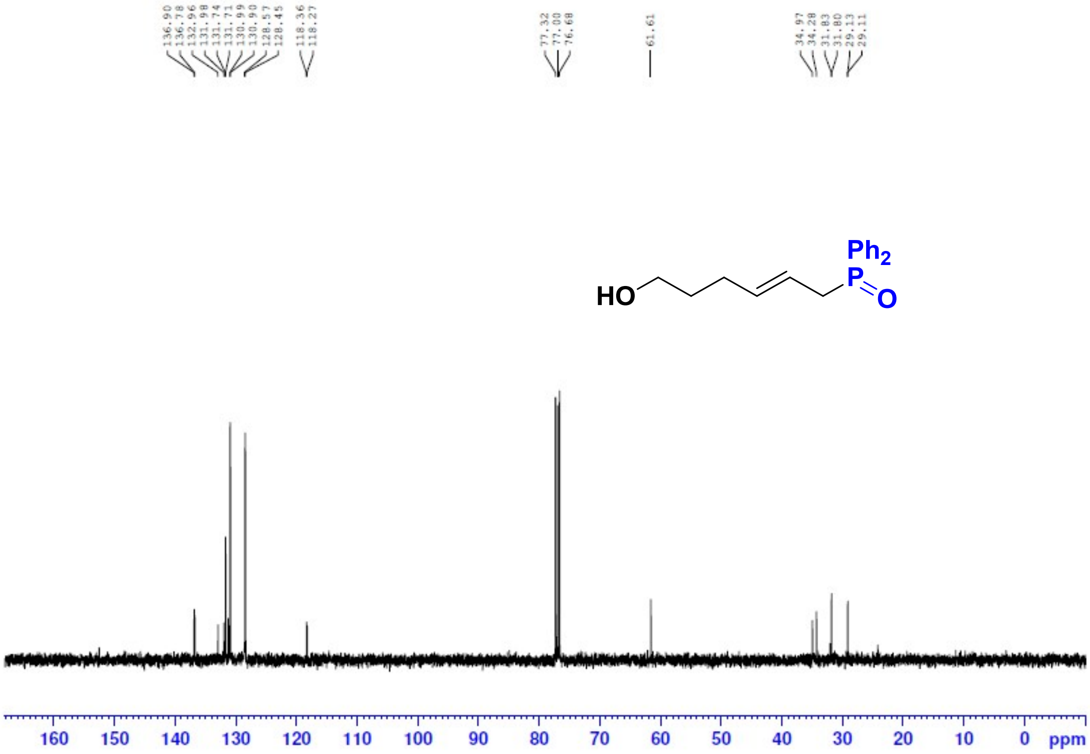

H
O
O
PPh2
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.90
7.26
0.15
0.15
2.03
0.18
1.95
2.19
2.12
2.68
11.32



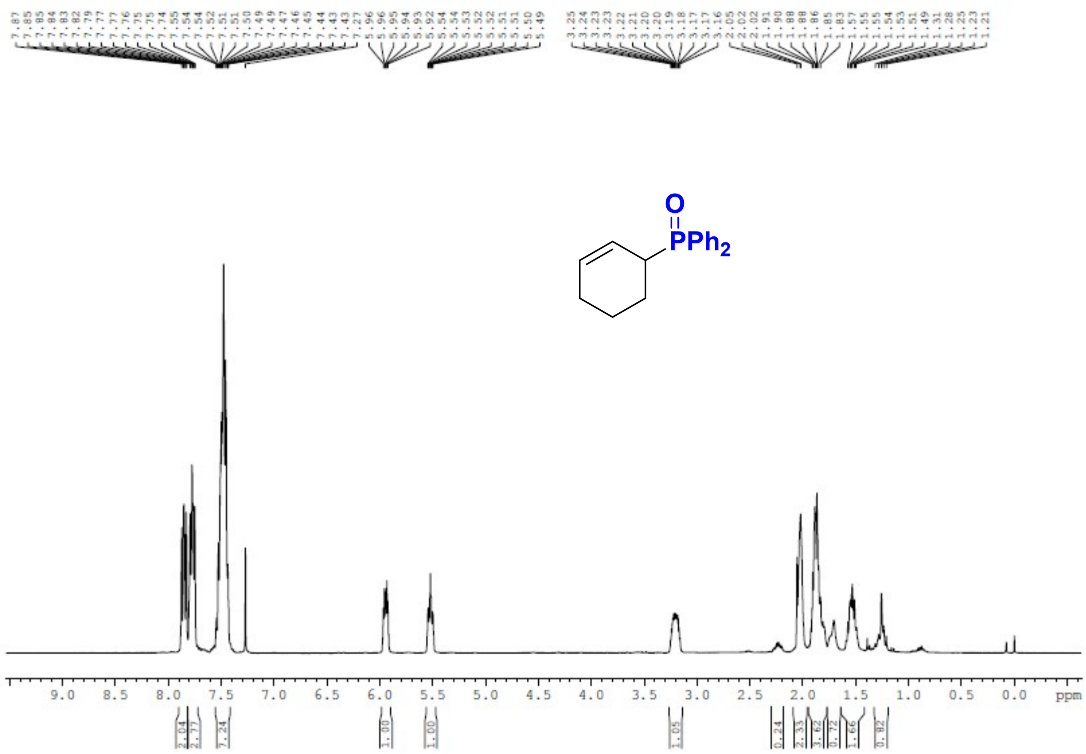




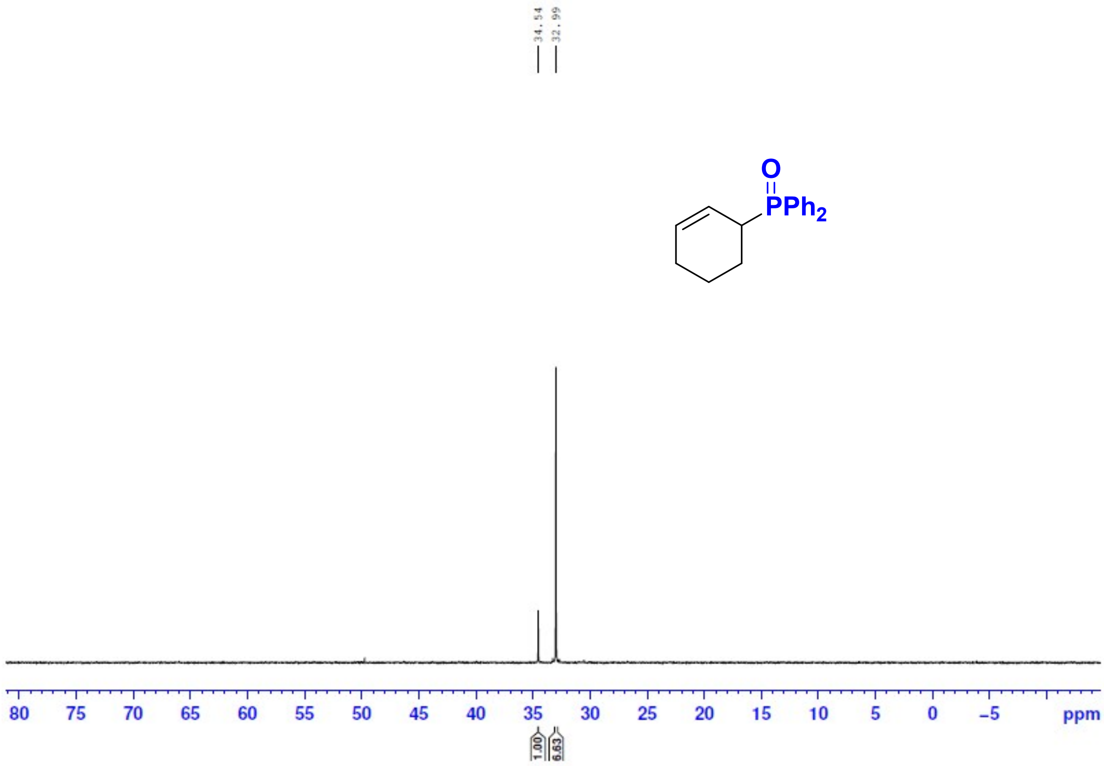


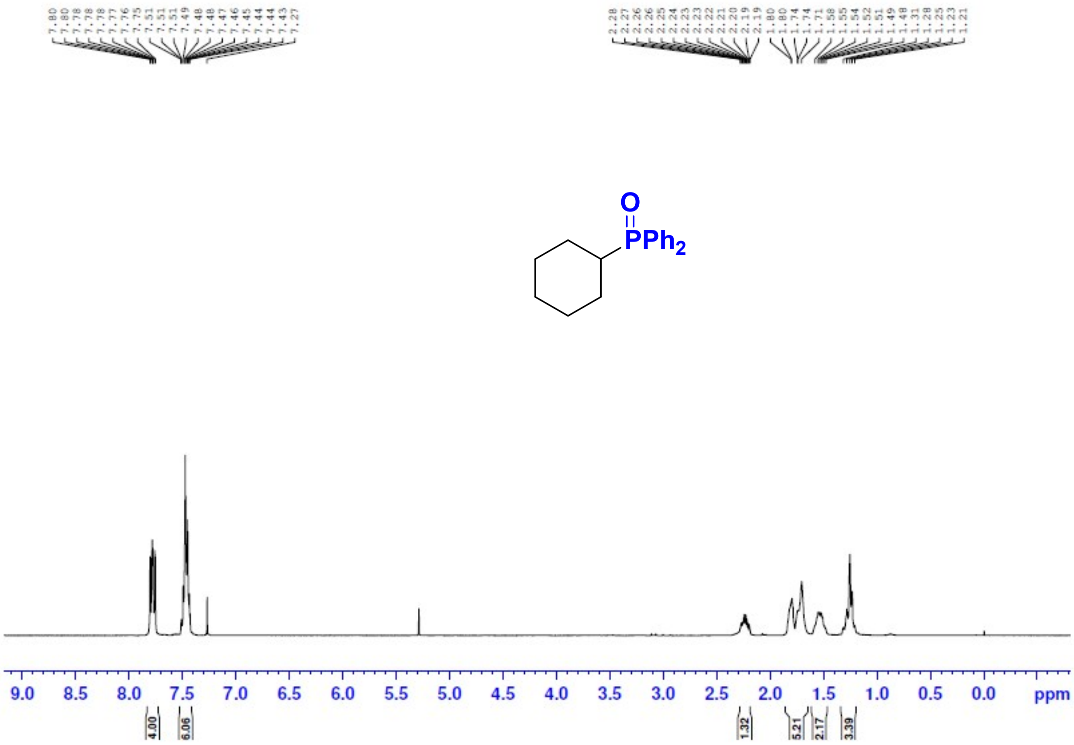


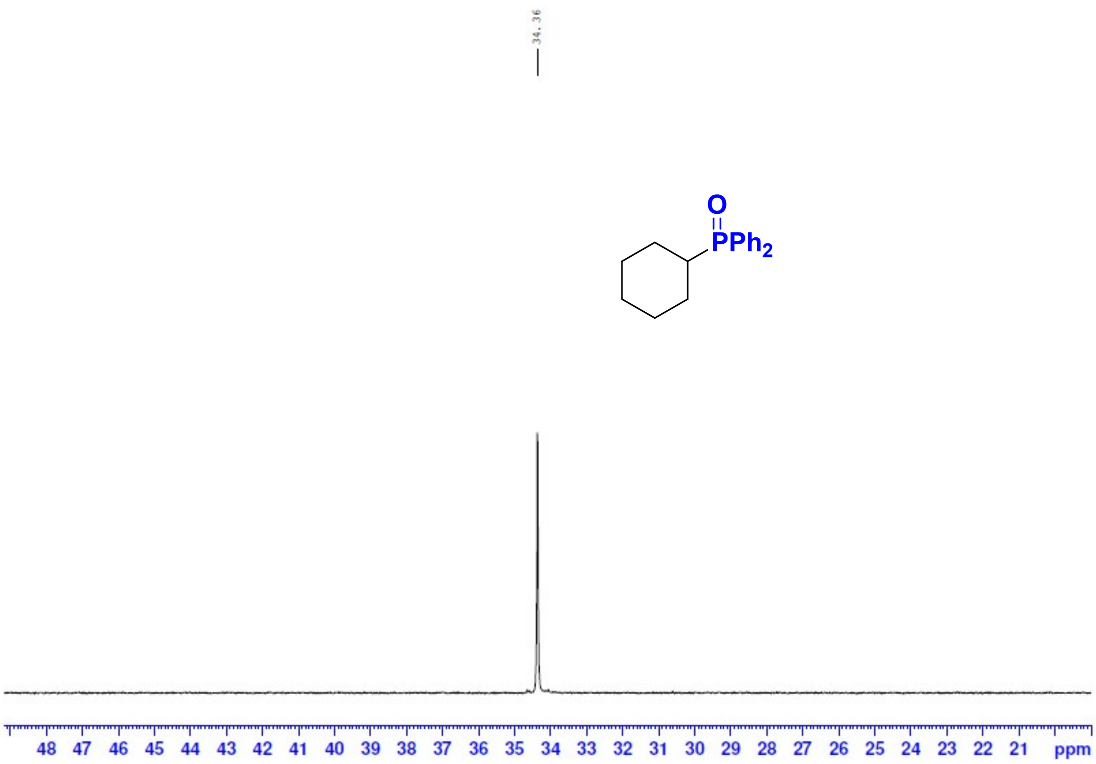
HO
Ph2
P
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



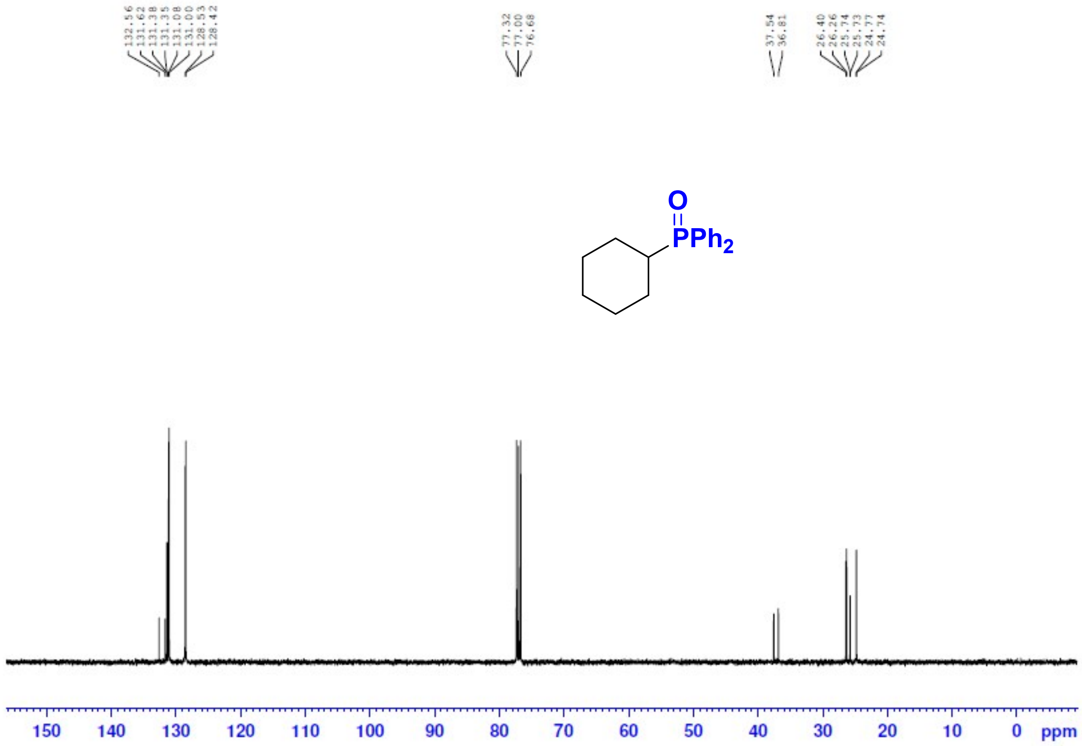
O
PPh2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


34.54
32.99
O
PPh2
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 ppm
1.00
6.63

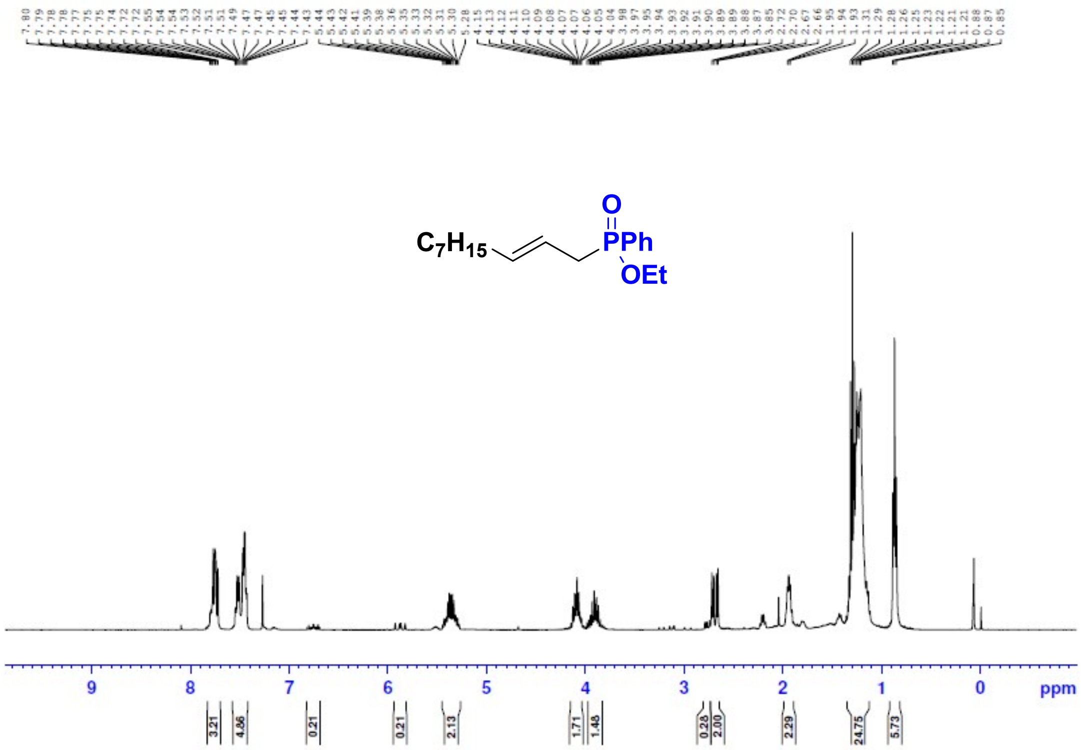

O
PPh2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.00
6.06
1.32
5.21
2.17
3.39

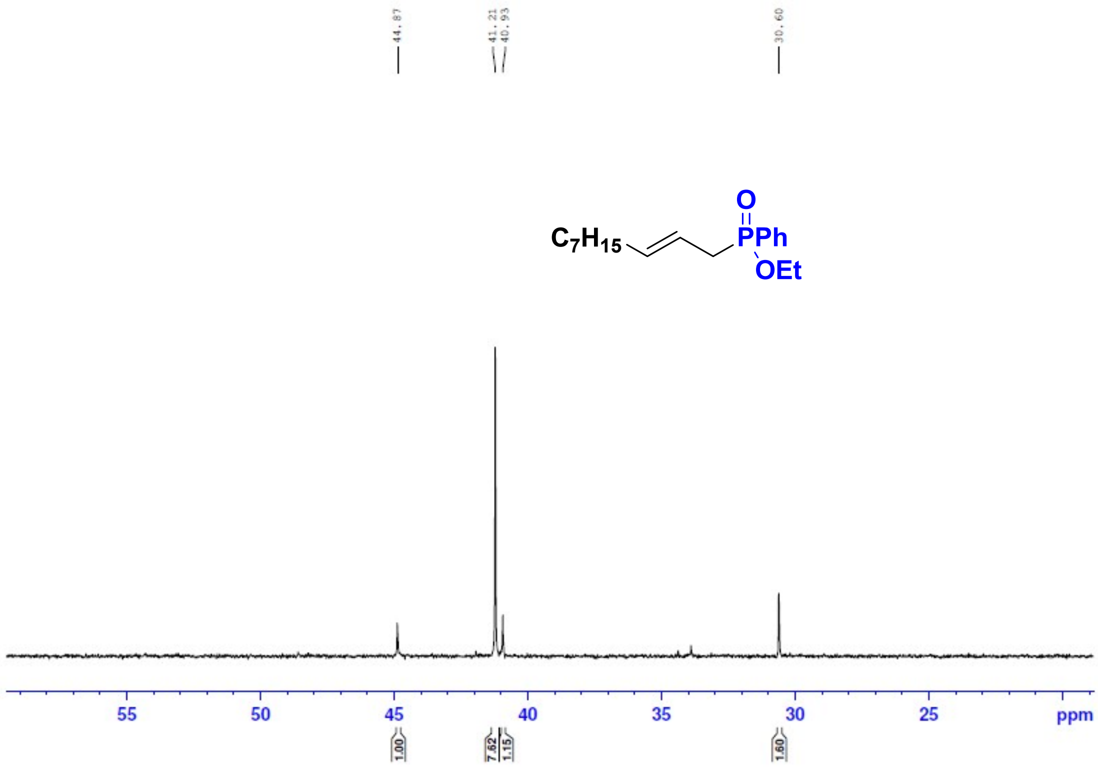


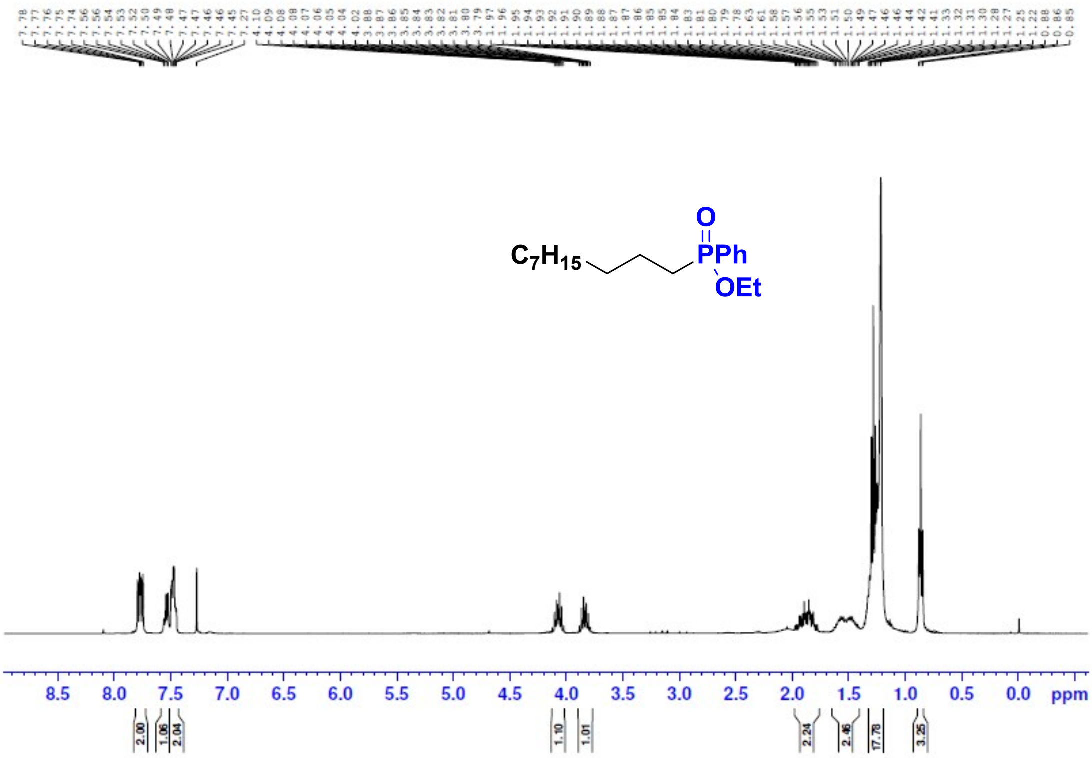
34.36
O
PPh2
48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 ppm

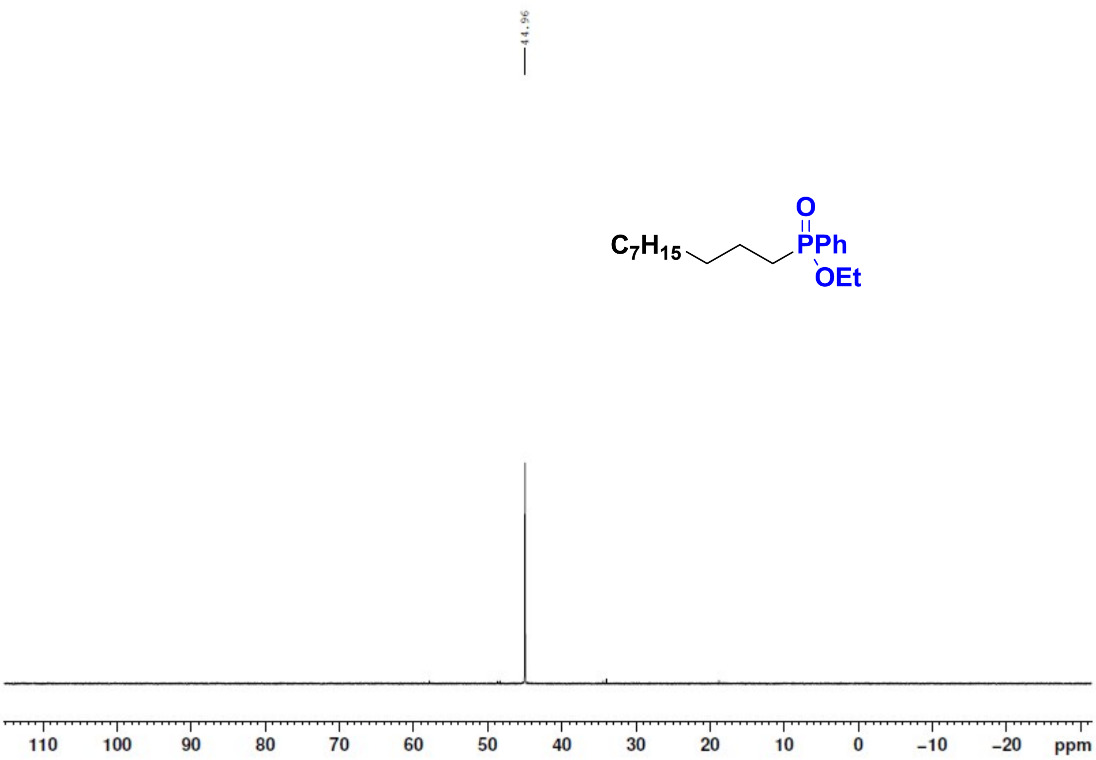


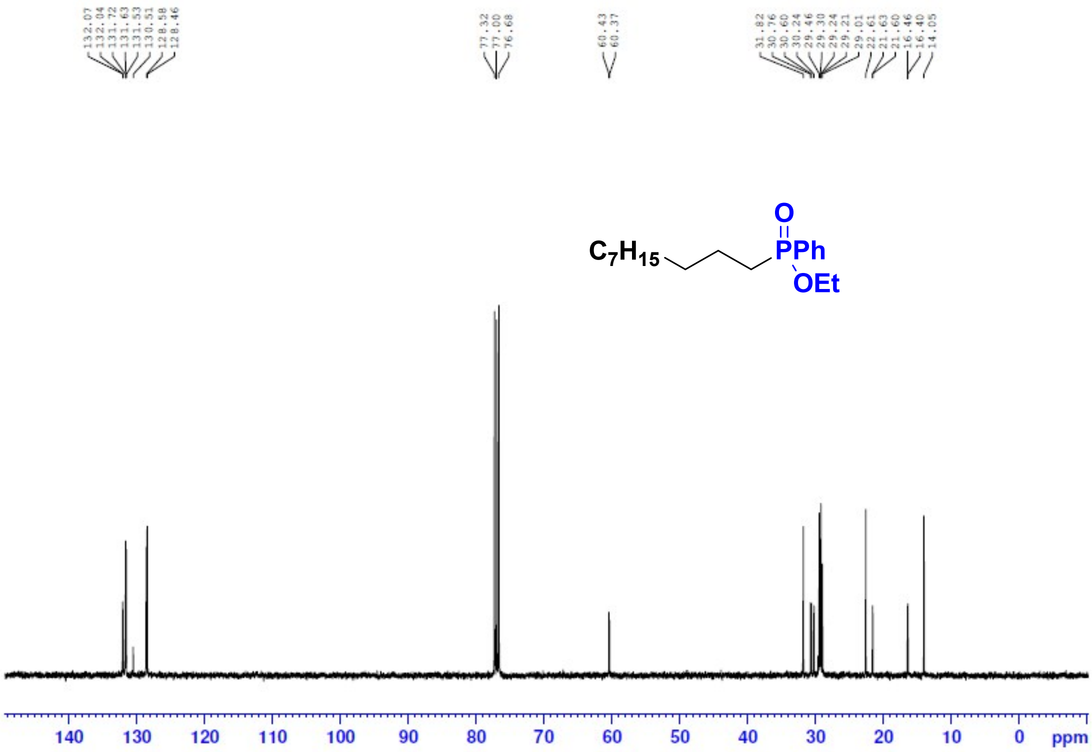
132.56
131.62
131.38
131.35
131.08
131.00
128.53
128.42
77.32
77.00
76.68
37.54
36.81
26.40
26.26
25.74
25.73
24.77
24.74
O
PPh2
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


C7H15
O
PPh
OEt
ppm

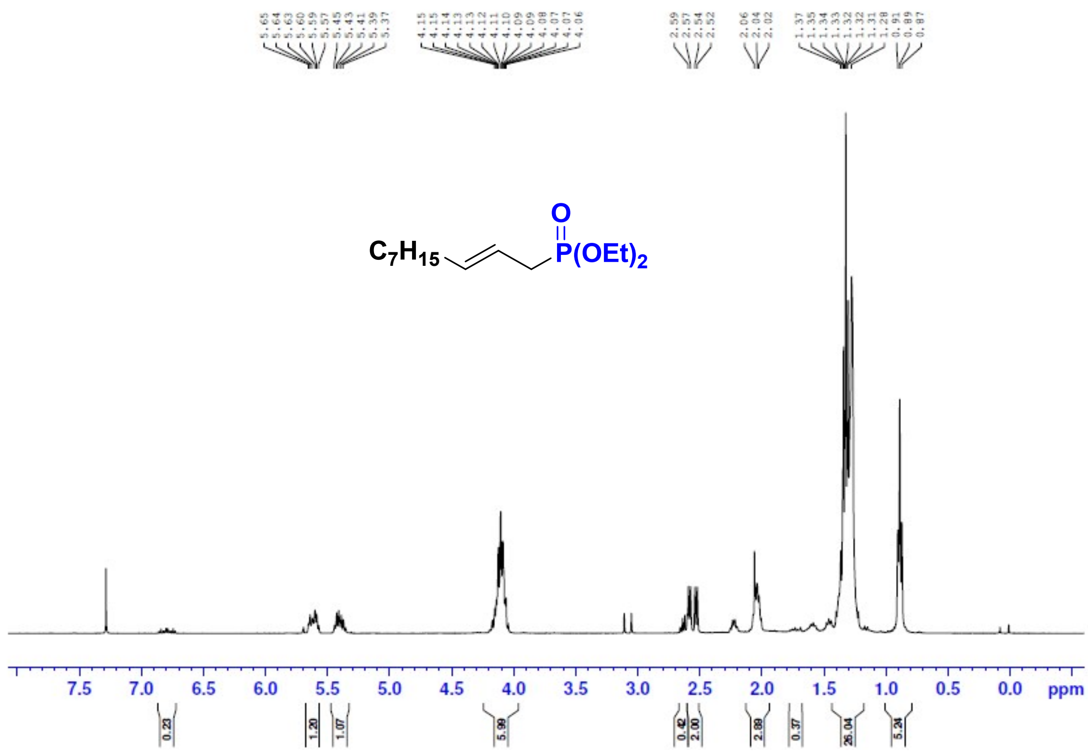

C7H15
O
PPh
OEt
ppm


O
C7H15
PPh
OEt
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00 1.06 2.04 1.10 1.01 2.24 2.46 17.78 3.25

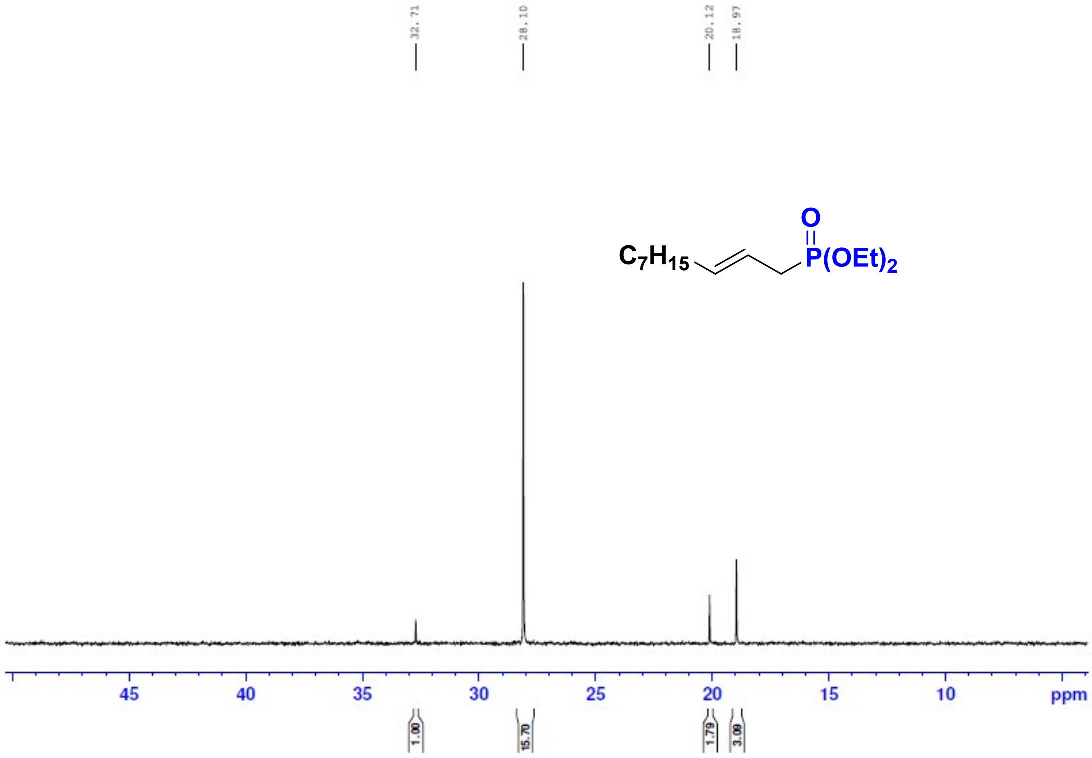

44.96
O
C7H15
PPh
OEt
110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 ppm



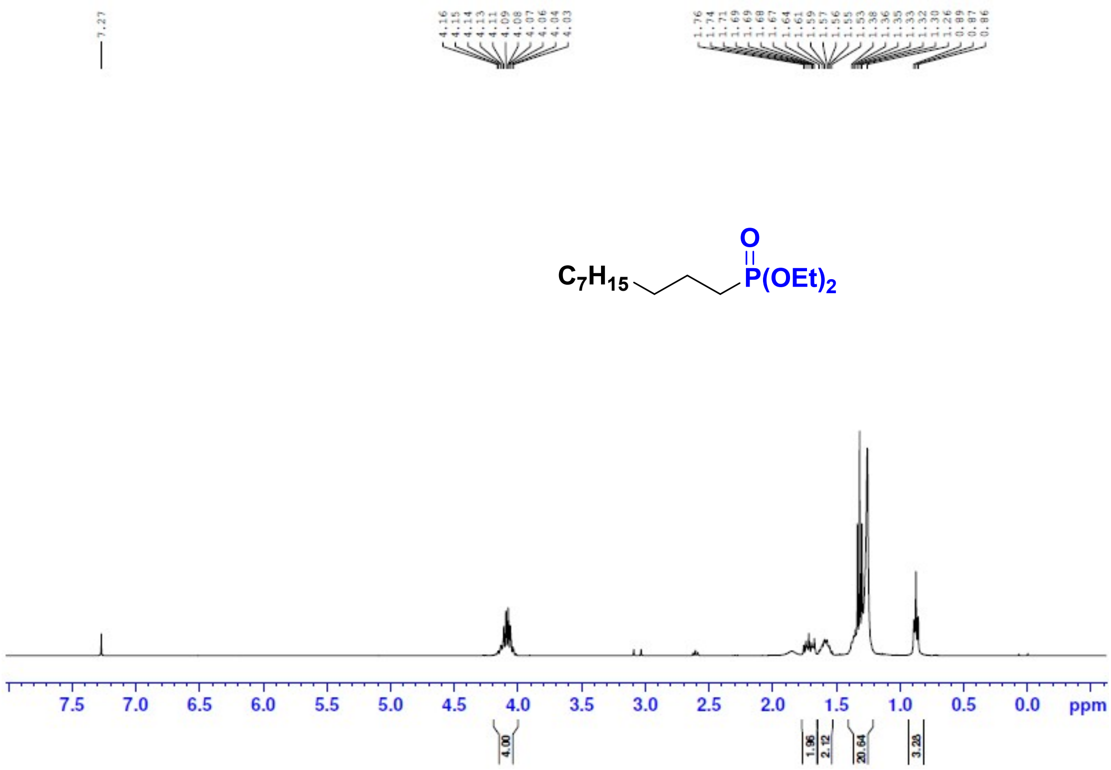
132.07
132.04
131.72
131.63
131.53
130.51
128.58
128.46
77.32
77.00
76.68
60.43
60.37
31.82
30.76
30.60
30.24
29.46
29.30
29.24
29.21
29.01
22.61
21.63
21.60
16.46
16.40
14.05
C7H15
O
PPh
OEt
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



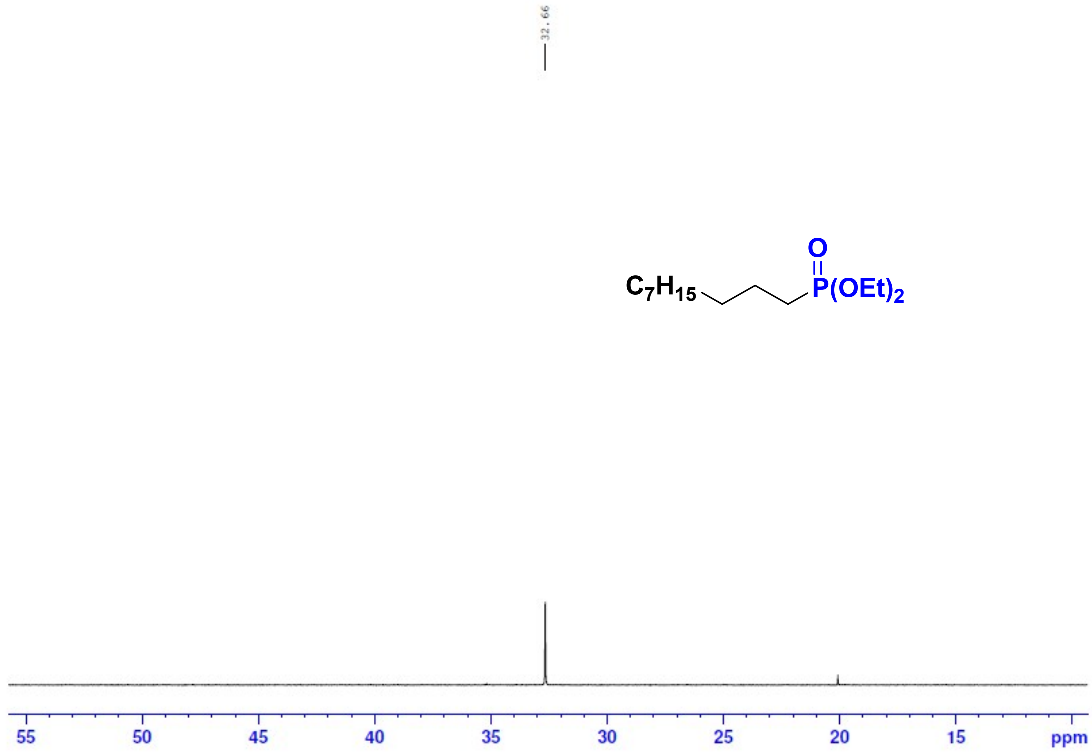
5.65
5.64
5.60
5.59
5.57
5.45
5.43
5.41
5.39
5.37
4.15
4.15
4.14
4.13
4.13
4.12
4.11
4.10
4.09
4.09
4.08
4.07
4.07
4.06
2.59
2.57
2.54
2.52
2.06
2.04
2.02
1.37
1.35
1.34
1.33
1.32
1.32
1.31
1.28
0.91
0.89
0.87
C7H15
O
P(OEt)2
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.23
1.20
1.07
5.99
0.42
2.00
2.89
0.37
26.04
5.24

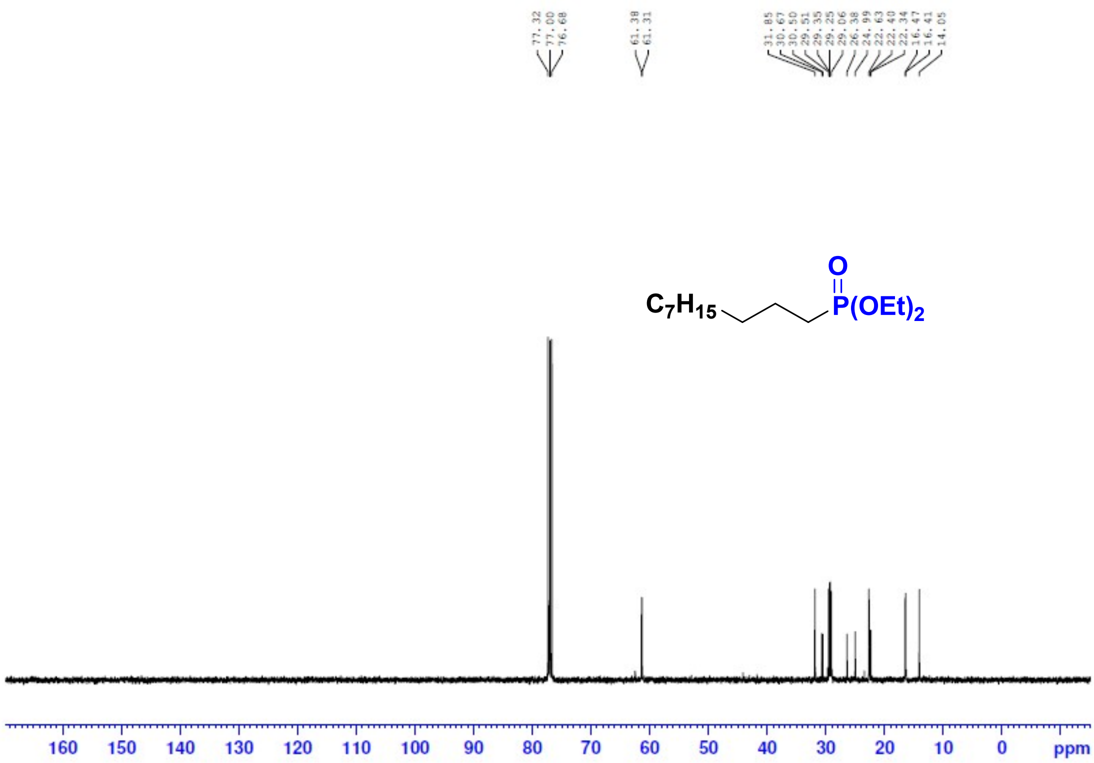


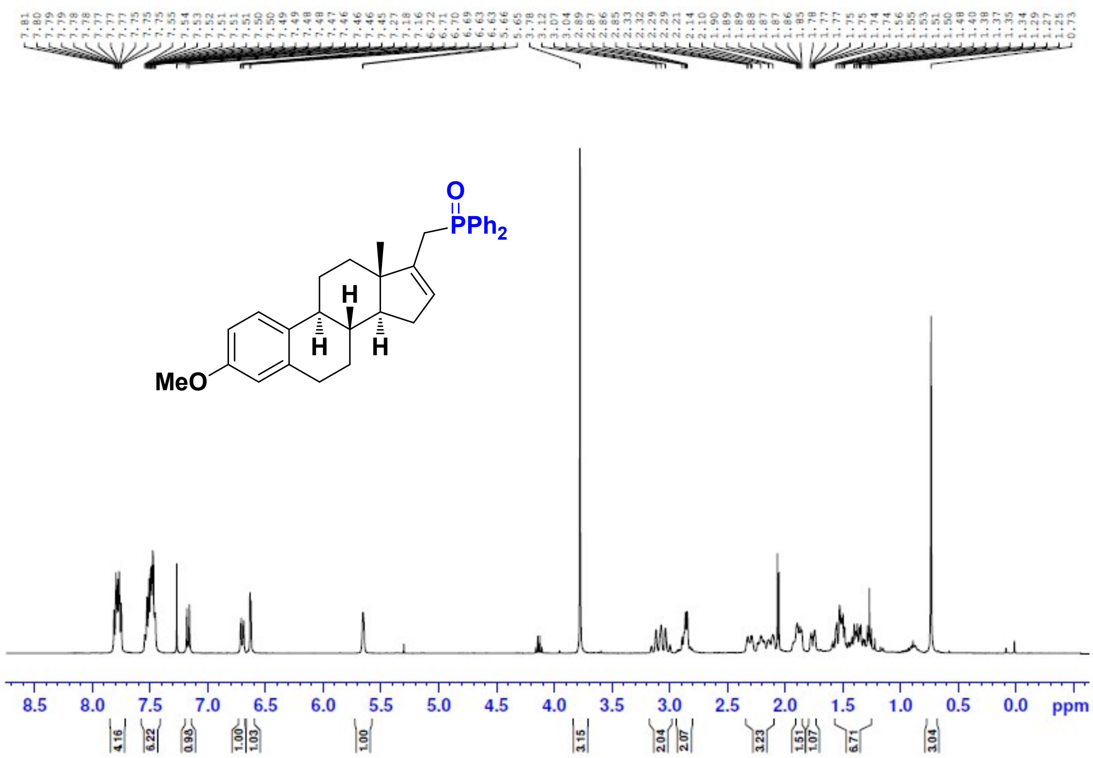
32.71
28.10
20.12
18.97
C_7H_{15}
O
P(OEt)2
45
40
35
30
25
20
15
10
ppm
1.00
15.70
1.79
3.09

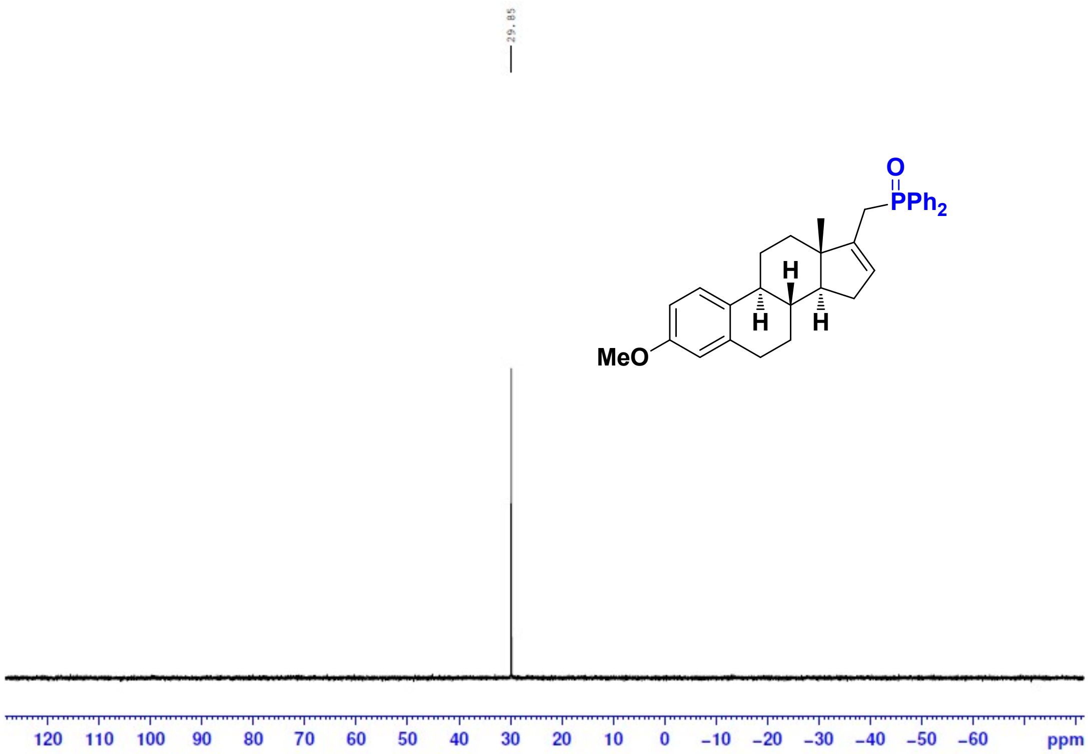


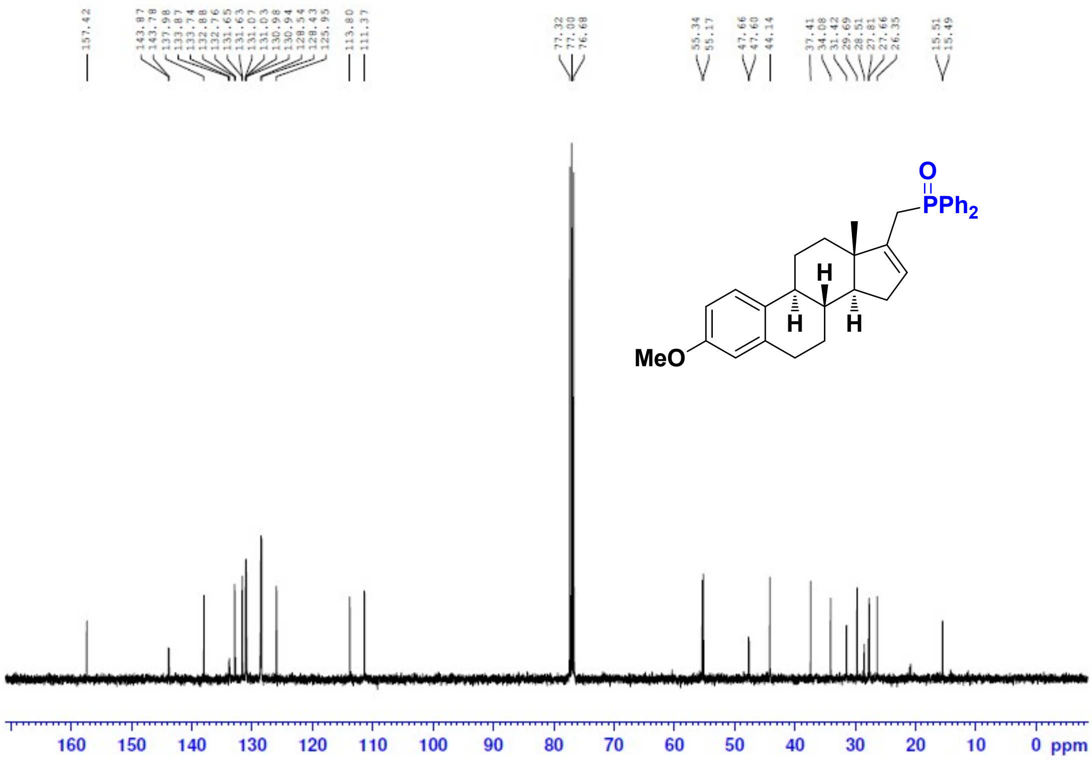
7.27
4.16
4.15
4.14
4.13
4.11
4.09
4.08
4.07
4.06
4.04
4.03
1.76
1.74
1.71
1.69
1.69
1.68
1.67
1.64
1.61
1.59
1.57
1.56
1.55
1.53
1.38
1.36
1.35
1.33
1.32
1.30
1.26
0.89
0.87
0.86
C_7H_{15}
O
P(OEt)2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.00
1.96
2.12
20.64
3.28


32.66
O
C7H15
P(OEt)2
55 50 45 40 35 30 25 20 15 ppm

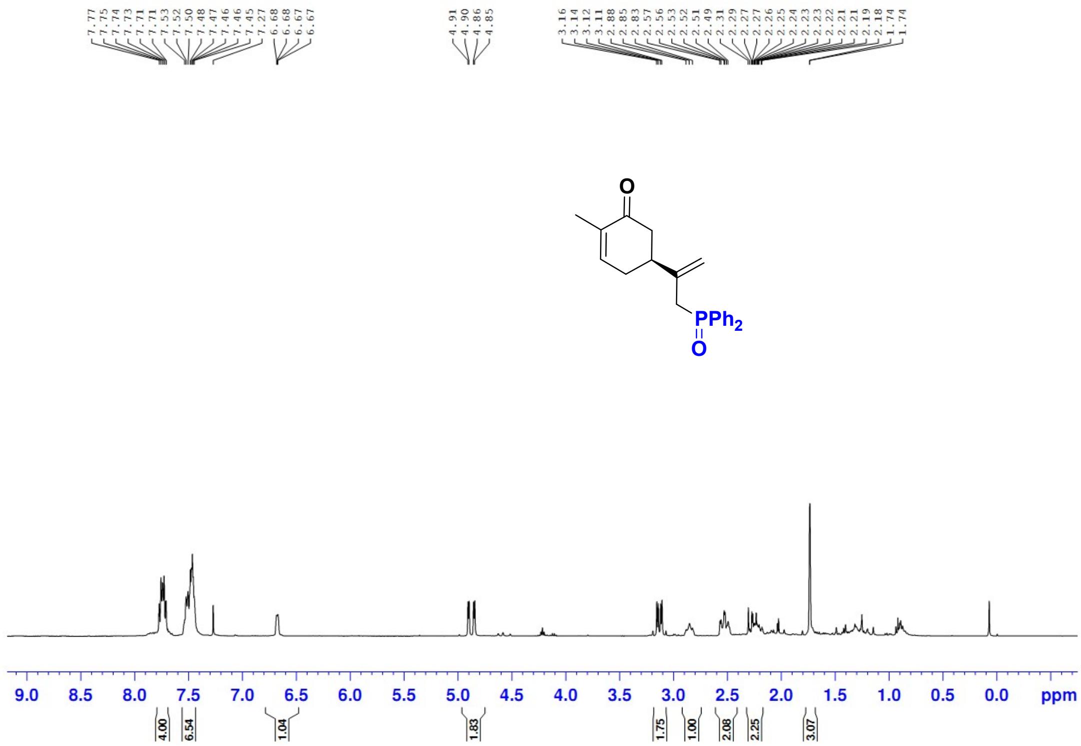

77.32
77.00
76.68
61.38
61.31
31.85
30.67
30.50
29.51
29.35
29.25
29.06
26.38
24.99
22.63
22.40
22.34
16.47
16.41
14.05
O
C7H15
P(OEt)2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



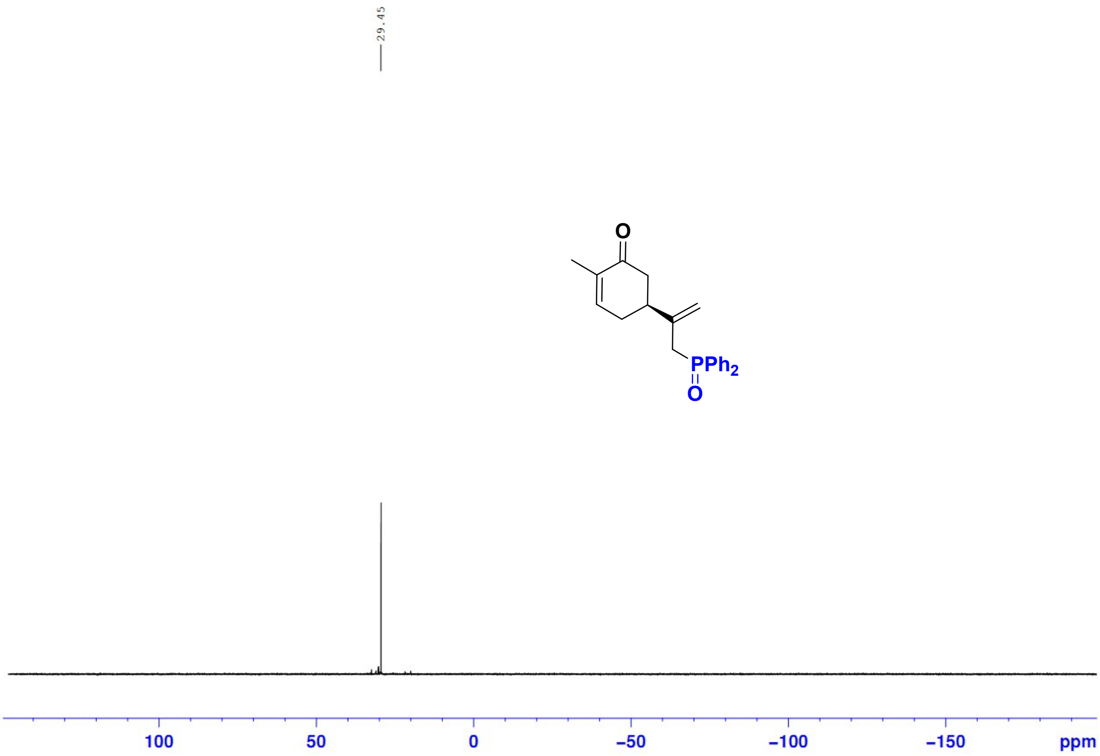




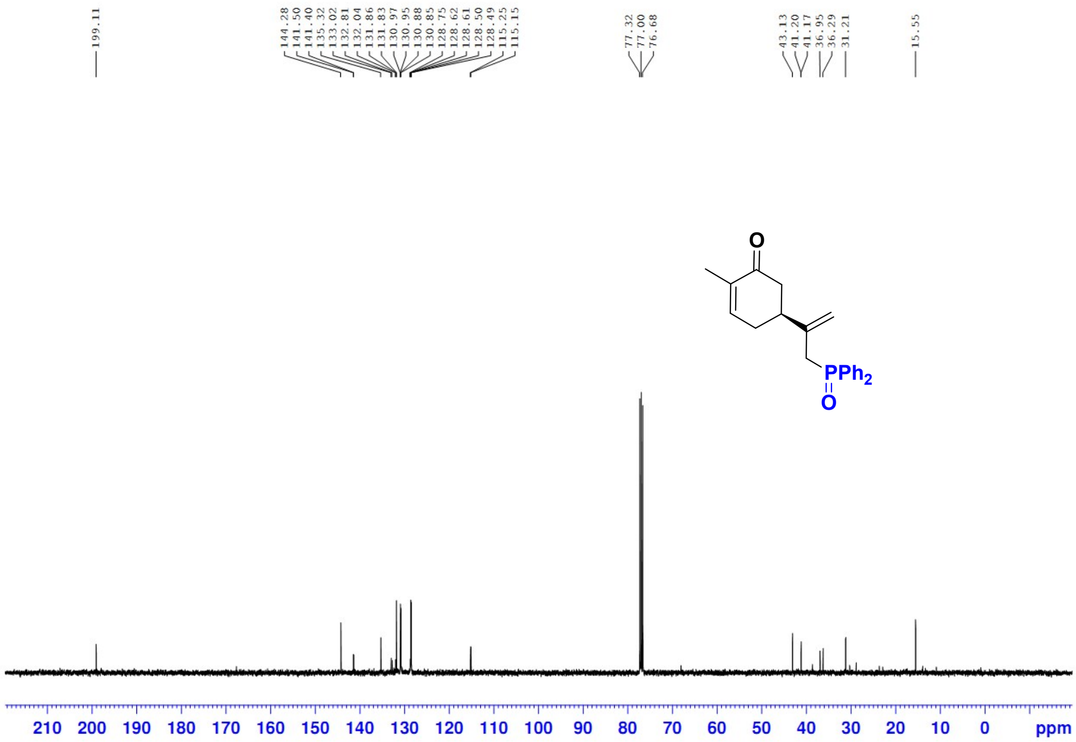
157.42
143.87
143.78
137.98
133.87
133.74
132.88
132.76
131.65
131.63
131.07
131.03
130.98
130.94
128.54
128.43
125.95
113.80
111.37
77.32
77.00
76.68
55.34
55.17
47.66
47.60
44.14
37.41
34.08
31.42
29.69
28.51
27.81
27.66
26.35
15.51
15.49
O
PPh2
H
H
H
MeO
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



7.77
7.75
7.74
7.73
7.71
7.71
7.53
7.52
7.50
7.48
7.47
7.46
7.46
7.45
7.27
6.68
6.68
6.67
6.67
4.91
4.90
4.86
4.85
3.16
3.14
3.12
3.11
2.88
2.85
2.83
2.57
2.56
2.53
2.52
2.51
2.49
2.31
2.29
2.27
2.27
2.26
2.25
2.24
2.23
2.23
2.22
2.21
2.21
2.19
2.18
1.74
1.74
O
PPh2
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.00
6.54
1.04
1.83
1.75
1.00
2.08
2.25
3.07



29.45
O
PPh2
O
100
50
0
–50
–100
–150
ppm



199.11
144.28
141.50
141.40
135.32
133.02
132.81
132.04
131.86
131.83
130.97
130.95
130.88
130.85
128.75
128.62
128.61
128.50
128.49
115.25
115.15
77.32
77.00
76.68
43.13
41.20
41.17
36.95
36.29
31.21
15.55
O
PPh2
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm