Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-promoted Oxidative –Fluorination of Arylphosphine under Mild Condition

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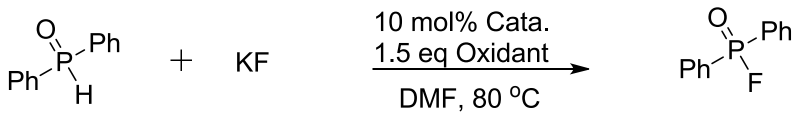
1. General information and materials

NMR spectra were obtained using a Brüker advance Ⅲ 400 spectrometer. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS) and $CDCl_3$, and all coupling constants are reported in hertz. The infrared spectra were obtained with KBr plates using Nexus 670 FT-IR spectrometer and only major peaks are reported in cm^{-1} . Mass spectra were mearsured using Bruker microTOF-Q II MS and measured in EI or ESI mode. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. DMF was purified and dried according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM). Substrates **1** were prepared according to the literature procedure,[1-2] **2n** was described in previous report.[3]

2. Table S1 Optimization different Catalysts and Oxidant[ab]



1a 2a

Entry	Cata.(mol%)	Fsource(equive)	Oxidant(equive)	Yield(%)
1	CuI (10)	KF (1.5)	DDQ (1.5)	69
2	$CuCl_2$ (10)	KF (1.5)	DDQ (1.5)	75
3	CuO (10)	KF (1.5)	DDQ (1.5)	59
4	$CuBr_2$ (10)	KF (1.5)	DDQ (1.5)	80
5	$Cu(OAc)_2$ (10)	KF (1.5)	DDQ (1.5)	64
6	$PdCl_2$ (10)	KF (1.5)	DDQ (1.5)	72
7	$Pd(TFA)_2$ (10)	KF (1.5)	DDQ (1.5)	69
8	$Pd(OAc)_2$ (10)	KF (1.5)	DDQ (1.5)	65
9	$Pd(acac)_2$ (10)	KF (1.5)	DDQ (1.5)	56
10	$FeCl_3$ (10)	KF (1.5)	DDQ (1.5)	52
11	Ag_2CO_3 (10)	KF (1.5)	DDQ (1.5)	49
12	AgTFA (10)	KF (1.5)	DDQ (1.5)	58
13	AgF (10)	KF (1.5)	DDQ (1.5)	55
14	AgOAc (10)	KF (1.5)	DDQ (1.5)	58
15	AgOTf (10)	KF (1.5)	DDQ (1.5)	60
16	$CuBr_2$ (10)	KF (1.5)	$K_2S_2O_8$ (1.5)	33
17	$CuBr_2$ (10)	KF (1.5)	$Cu(OAc)_2$ (1.5)	n.d.
18	$CuBr_2$ (10)	KF (1.5)	AgOAc (1.5)	17
18	$CuBr_2$ (10)	KF (1.5)	^{t}BuOOH (1.5)	trace
20	$CuBr_2$ (10)	KF (1.5)	CNA (1.5)	19
21	$CuBr_2$ (10)	KF (1.5)	$PhI(OAc)_2$ (1.5)	38
22	CuB_{r2} (10)	KF (1.5)	Oxone (1.5)	n.d.
23	$CuBr_2$ (10)	KF (1.5)	BQ (1.5)	n.d.
24		KF (1.5)	DDQ (1.5)	47
25[c]	$ZnBr_2$(5.0)	NaF (1.5)	DDQ (1.5)	57

26[c]	$Zn(OTf)_2$ (7.5)	NaF (1.5)	DDQ 1.5)	70
27[c]	$ZnCl_2$ (5.0)	NaF (1.5)	DDQ 1.5)	69

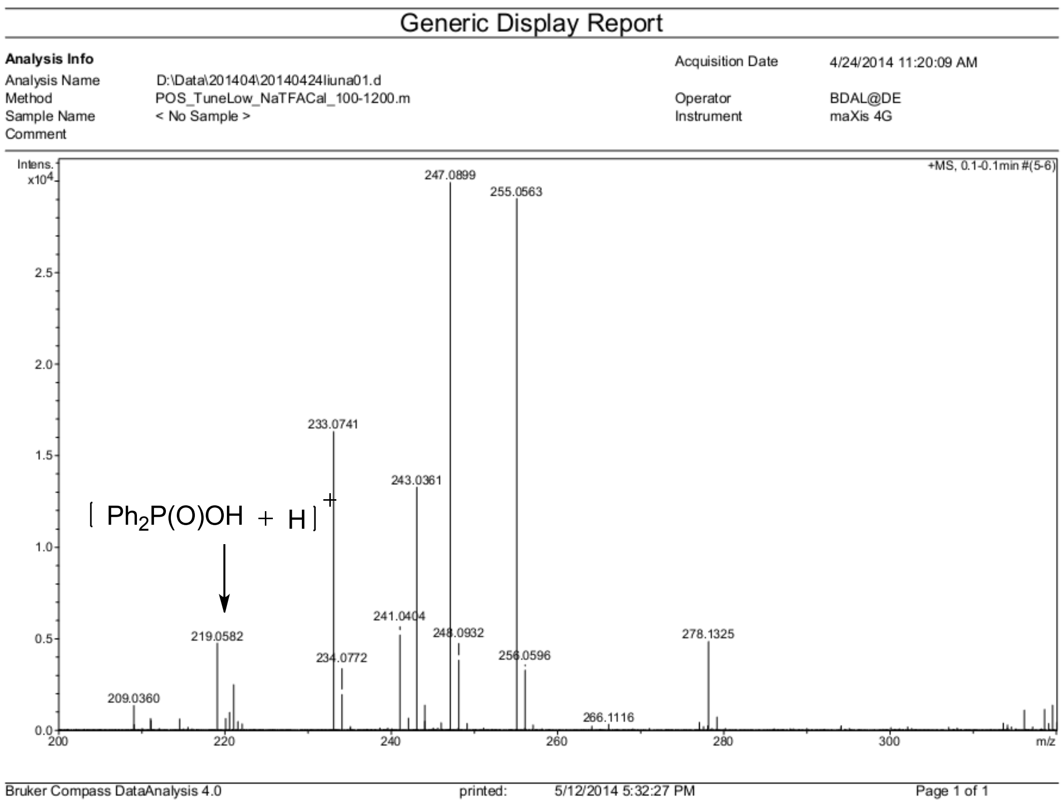
[a] All the reaction were carried out with Catalysts (10 mol%) in the presence of **1a** (0.3 mmol), KF (1.5 eq) and DDQ (1.5 eq) in 2.0 mL DMF at 80 °C under argon for 4 h. [b] Isolated yield. [c] R.T.

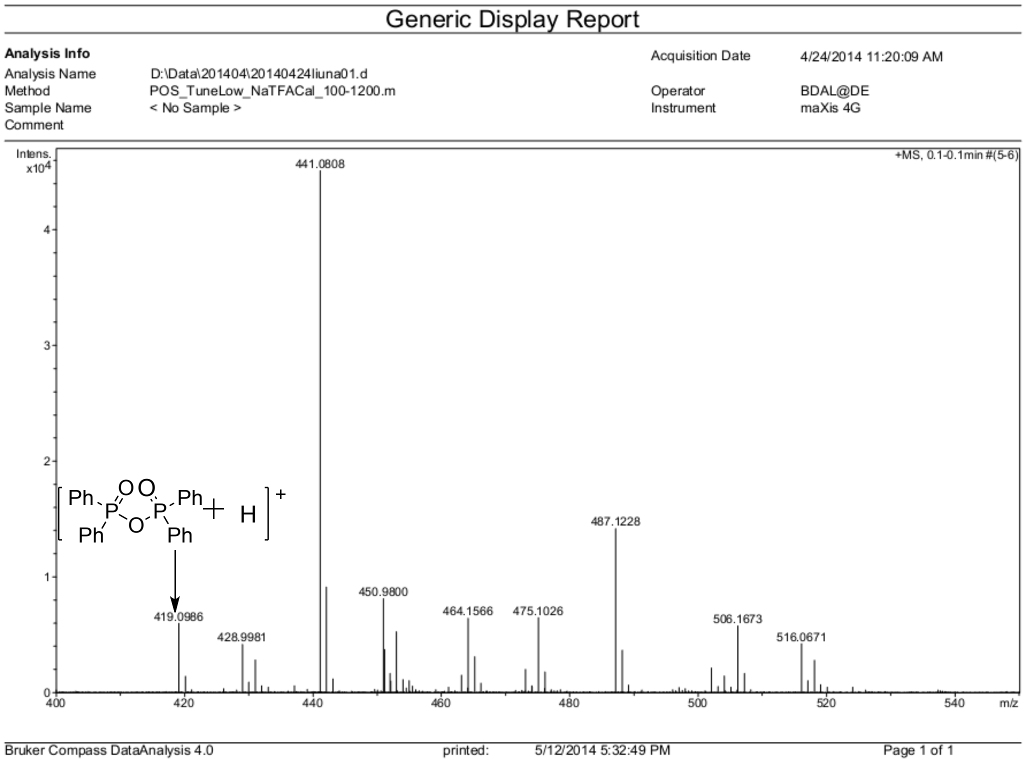
3. Preliminary mechanistic studies.

3.1 Analytical data of ESI-MS:

In a reaction tube, diphosphine oxide **1a** (0.30 mmol), NaF (0.45 mmol), DDQ (0.45 mmol), and $CuBr_2$ (0.015 mmol) were added and charged with Ar three times. Then, anhydrous DMF (1 mL) were added. The reaction mixture was stirred at RT for 10 min with vigorous stirring. The reaction was diluted with DMF(1/100) prior to the injection into the mass spectrometer.

The positive-ion mode of ESI-MS spectrum showed the signals corresponding to the A (m/z) 427.0441, 428.0471, 429.0481. The signal might mean that DDQ can easily react with diphenyl-phosphine oxide to form the intermediate A. On the other hand, a signal of m/z 219.0582 may be the Diphenylphosphinic acid. The signal of m/z 419.0986 illustrated that intermediate A easily react with Diphenylphosphinic acid to generate the molecular B, which can react with NaF to the final products.





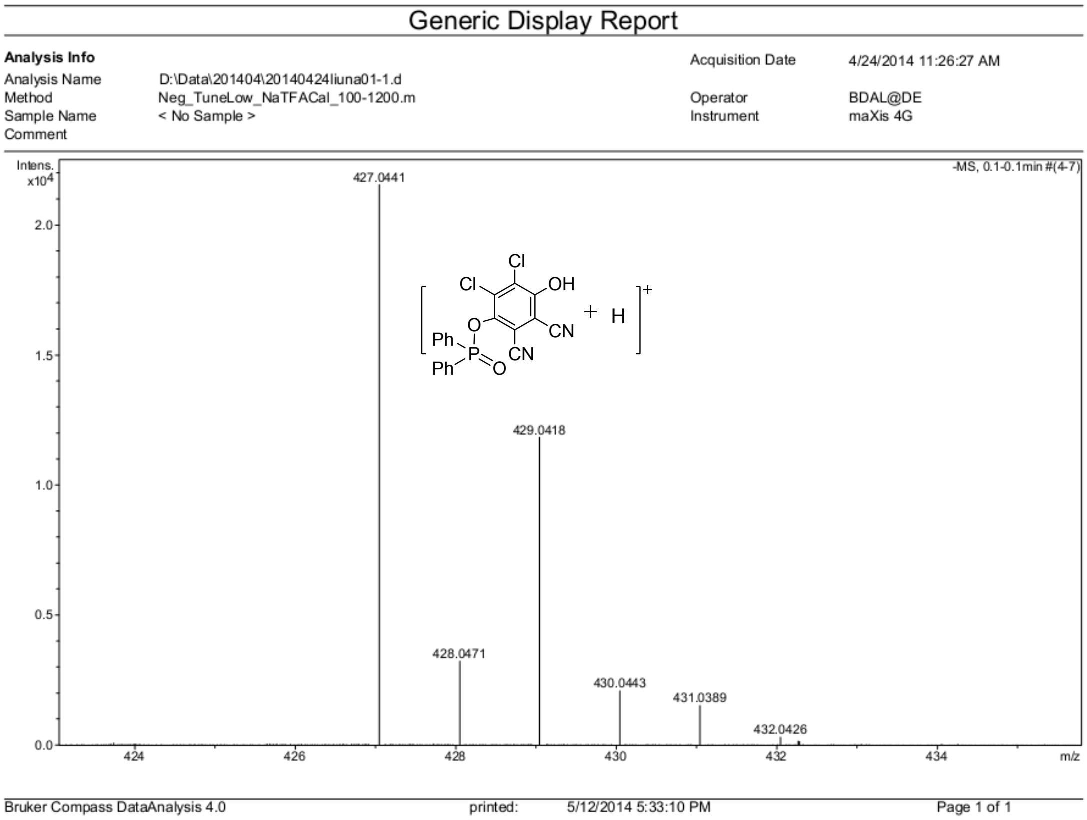


Figure S1. ESI-MS spectrum of the reaction solution.

We used $[Ph_2P(O)]_2O$ as the substrate under the reaction conditions resulted in the yield of 95% at 60 ^oC, but in the absence of the DDQ,only obtained 11% yield at 60 ^oC [Scheme S1, Eq. (1), (2)]. When the reactionwas degassed under conditions that the product was obtained in the yield of 85% [Scheme S1, Eq. (3)]. Chemical trapping of radicals using TEMPO (a well-known radical-trapping reagent) and AIBN under the reaction conditions [Scheme S1, Eq. (4), (5)]. As illustrated in Scheme S1, the addition of 3.0 equviallents of TEMPO and AIBN were performed under the standard condition. When TEMPO was added, the yield was decreased. Above all the reactions were carried out , the results were illustrated that the reaction was not go through the radical processure.

4. General Procedure for the Copper-promoted Oxidative–Fluorination of Arylphosphine.

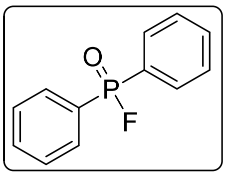
Method A: In a reaction tube, arylphosphine oxides **1** (0.30 mmol), NaF (0.45 mmol), DDQ (0.45 mmol), and $CuBr_2$ (0.015 mmol, 5.0 mol %) were added and charged with Ar three times. Then, anhydrous DMF (1 mL) were added. The mixture was stirred at room temperature for 4 h, until the reaction was completed. DMF was distilled under reduced pressure. The crude product was purified by flash chromatography on silica gel to give the desired products (PE : EA = 4:1).

Method B: In a reaction tube, arylphosphine oxides **1** (0.30 mmol), DDQ (0.45 mmol), and $CuBr_2$ (0.015 mmol, 5.0 mol %) were added and charged with Ar three times. Then, anhydrous DMF (1 mL) were added. The mixture was stirred at room temperature for 20 min, the nuleciliphilice was added slowly, the mixture was stirred until the reaction was completed. DMF was distilled under reduced pressure, The crude product was purified by flash chromatography on silica gel to give the desired products (PE : EA = 2:1).

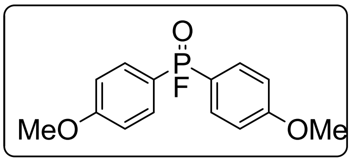
References:

1. S. Montel, T. Jia, P. J. Walsh. *Org. Lett.* 2014, **16**, 130-133.
2. Q. Xu, C.-Q. Zhao, L.-B. Han. *J. Am. Chem. Soc*. 2008, **130**, 12648-12655.
3. H. D. Durst, D. K. Rohrbaugh, P. Smith, J. M. Nilles, T. Connell , J. A. Laramee, S. Munavalli. *Phosphorus, Sulfur and Silicon.* 2008, **183**, 2655-2668.

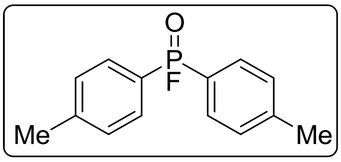
5. Characterization of new compounds.



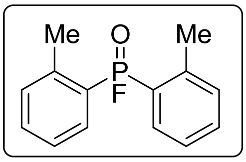
2a Yeld: 90%, pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 4H), 7.69 – 7.57 (m4 2H), 7.51 (m, 4H). ^{31}P NMR (400 MHz, $CDCl_3$) δ 40.94 (d, J = 1019.7 Hz). ^{19}F NMR (400 MHz, $CDCl_3$) δ -75.17 (d, J = 1019.8 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 133.35, 133.33, 131.45, 131.43, 131.34, 131.32, 129.38 (d, J = 22.3 Hz), 128.87, 128.73,127.97 (d, J = 22.3 Hz). MS : m/z (M+H): 221.



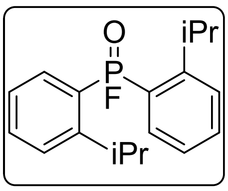
2b Yeld: 95%, faint orange solid. l.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (m, 4H), 6.99 (m, 4H), 3.85 (s, 6H). ^{31}P NMR (400 MHz, $CDCl_3$) δ 42.41 (d, J = 1008.3 Hz). ^{19}F NMR (400 MHz, $CDCl_3$) δ -72.64 (d, J = 1008.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 163.34, 163.31, 133.34, 133.32, 133.21, 133.19, 120.89 (d, J = 23.9 Hz), 119.40 (d, J = 23.9 Hz).114.31, 114.16, 55.31. IR(film/cm^{-1}) v_{max}: 3393, 2935, 2842, 1599, 1505, 1299, 1255, 1135, 1183. MS : m/z (M+H): 281.



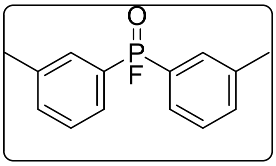
2c Yeld: 93%, white solid . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 4H), 7.30 (m,4H), 2.40 (s, 6H). ^{31}P NMR(400 MHz, $CDCl_3$) δ 42.11 (d, J = 1014.1 Hz). ^{19}F NMR (400 MHz, $CDCl_3$) δ -74.33 (d, J = 1014.3 Hz). ^{13}C NMR (400MHz, $CDCl_3$) δ 143.97, 143.94, 131.37, 131.35, 131.25, 131.23, 129.48, 129.34, 126.47 (d, J = 22.8 Hz), 125.04 (d, J = 22.8 Hz). 21.63. IR(film/cm^{-1}) v_{max} : 3392, 2923,2866, 1604, 1449, 1261, 1214, 1180, 1132, 1113. MS : m/z (M+H): 249.



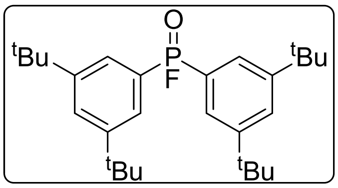
2e Yeld:75%, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.30 (m, 4H), 2.44 (s, 6H).^{31}P NMR (400 MHz, $CDCl_3$) δ 43.10 (d, J = 1018.4 Hz). ^{19}F NMR (400 MHz, $CDCl_3$) δ -74.57 (d, J = 1018.6 Hz). ^{13}C NMR (400 MHz,$CDCl_3$) δ 141.75, 141.63, 133.30, 133.27, 132.94, 132.91, 132.83, 132.79, 131.58, 131.45, 128.26 (d, J = 19.1 Hz), 126.91 (d, J = 19.1 Hz) 125.83, 125.69, 21.11, 21.07, 21.06. IR(film/cm^{-1}) v_{max} 3555, 3488, 3061, 2968, 2928, 1595, 1476, 1454, 1284, 1256, 1147, 758. MS : m/z (M+H): 249.



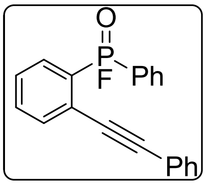
2f Yeld:18%,white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dt, J = 16.0, 8.2 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.31 (tt, J = 8.9, 4.4 Hz, 2H), 3.44 (dq, J = 13.4, 6.7 Hz, 2H), 1.08 (dd, J = 12.3, 6.7 Hz, 12H).^{31}P NMR (162 MHz, $CDCl_3$) δ 43.50 (d, J = 1017.2 Hz). ^{19}F NMR (400 MHz, $CDCl_3$) δ -71.19 (d, J = 1017.5 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.20, 153.07, 133.57, 133.54, 132.61, 132.57, 132.49, 132.45, 128.15 (d, J = 18.5 Hz)126.95, 126.88, 126.82, 126.79 (d, J = 18.5 Hz)125.95, 125.81, 31.61, 31.56, 23.83, 23.77. IR(film/cm^{-1}) v_{max} 3404, 2967, 2929, 1594, 1442, 1251, 1134, 830, 769. MS : m/z (M+H): 305.



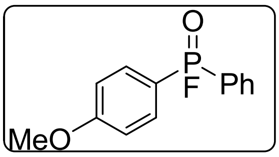
2g Yeld:80%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.56 (m, 4H), 7.44 – 7.35 (m, 4H), 2.40 (s, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.71 (d, *J* = 1019.7 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -75.51 (d, *J* = 1022.2 Hz).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.81, 138.67, 134.09, 134.06, 131.81, 131.79, 131.70, 131.68, 129.31 (d, *J* = 22.1 Hz) , 128.73, 128.58, 128.49, 128.47, 128.38, 128.36, 127.91 (d, *J* = 22.0 Hz) , 21.29. IR(film/cm^{-1}) v_{max} 3052, 2924, 2857, 1599, 1480, 1262, 1228, 1124.705, 567. MS : m/z (M+H): 249.



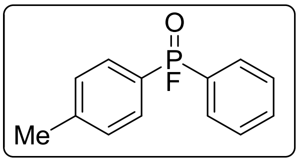
2h Yeld:55%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (t, *J* = 5.2 Hz, 2), 7.67 (s, 4), 1.33 (s, 36) ^{31}P NMR (400 MHz, $CDCl_3$) δ 43.64 (d, *J* = 1017.0 Hz).^{19}F NMR (400MHz Cl_3) δ -72.41 (d, *J* = 1017.2 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ151.45, 151.32, 128.76 (d, *J* = 21.8 Hz), 127.43, 127.40, 127.38 (d, *J* = 21.8 Hz) 125.61, 125.60, 125.49, 125.48, 35.02, 31.22. IR(film/cm^{-1}) v_{max} 3057, 2959, 905, 2870, 1594, 1477, 1427, 1364, 1255, 1154, 916, 878, 603. MS : m/z (M+H): 445.



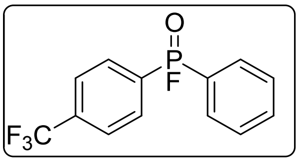
2i Yeld:73%, yellow oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (m, 1H), 7.91 – 7.79 (m, 2H), 7.73 – 7.47 (m, 4H), 7.43 (m, 2H), 7.38 – 7.28 (m, 5H).^{31}P NMR (400 MHz, $CDCl_3$) δ 39.56 (d, *J* = 1022.3 Hz).^{19}F NMR (400 MHz, $CDCl_3$) δ -76.31 (d, *J* = 1022.3 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 133.65, 133.54, 133.14, 133.11, 133.06, 133.02, 131.49, 131.44, 131.43, 131.33, 131.31, 130.56 (d, *J* = 19.4 Hz), 129.68 (d, *J* = 21.0 Hz),128.89, 128.56, 128.42, 128.24, 128.10, 127.97, 126.25, 126.15, 122.15, 96.49, 86.82, 86.76. IR(film/cm^{-1}) v_{max} 3402, 3060, 2925, 2855, 1588, 1492, 1440, 1257, 1140, 757, 692, 532. MS : m/z (M+H): 321.



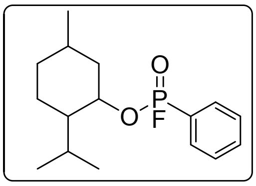
2j Yeld:84%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.68 (m,5H), 7.63 – 7.54 (m, 1H), 7.49 (td, *J* = 7.6, 3.9 Hz,2H), 7.00 (dd, *J* = 8.7, 2.8 Hz, 2H), 3.85 (s, 3H). ^{31}P NMR (400 MHz, $CDCl_3$) δ 41.64 (d, *J* = 1014.3 Hz). ^{19}F NMR (400 MHz, $CDCl_3$) δ -73.90 (d, *J* = 1014.2 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 163.57, 163.54, 133.58, 133.56, 133.45, 133.43, 133.12, 133.10, 131.29, 131.27, 128.79, 128.65, 120.30 (d, *J* = 22.9 Hz), 118.82 (d, *J* = 22.9 Hz)114.44, 114.29, 55.39. IR(film/cm^{-1}) v_{max}: 3396,2925,1597,1253,1133,534. MS : m/z (M+H): 251.



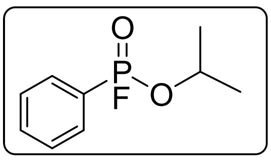
2k Yeld:83%, pale yellow oil [1]H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 2), 7.72 (dd, J = 12.9, 8.0 Hz, 2), 7.66 – 7.56 (m, 2), 7.51 (td, J = 7.6, 3.9 Hz, 1H), 7.32 (dd, J = 7.8, 3.5 Hz, 2H). 2.42 (s, 3H). [31]P NMR (400 MHz, $CDCl_3$) δ 41.45 (d, J = 1016.8 Hz). [19]F NMR (400 MHz, $CDCl_3$) δ -74.76 (d, J = 1017.1 Hz). [13]C NMR (400 MHz, $CDCl_3$) δ 144.21, 133.19, 133.17, 131.54, 131.52, 131.43, 131.40, 131.38, 131.29, 131.27, 129.82 (d, J = 22.8 Hz),129.61, 129.47, 128.81, 128.67, 128.42 (d, J = 22.7 Hz), 21.73. IR(film/cm^{-1}) v_{max} 3408, 2924, 1604, 1439, 1258, 1135, 536. MS : m/z (M+H): 235



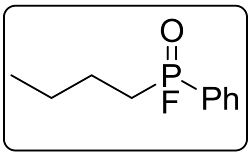
2l Yeld:47%, pale yellow oil [1]H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.89 – 7.81 (m, 2H), 7.78 (m, 2H), 7.78 (m, 2H), 7.67 (m, 1H), 7.55 (mz, 2H). [31]P NMR (400 MHz, $CDCl_3$) δ 38.72 (d, J = 1025.3 Hz).[19]F NMR (400 MHz, $CDCl_3$) δ -63.44,-75.17 (d, J = 1025.6 Hz) [13]C NMR (400 MHz, $CDCl_3$) δ 135.14, 134.84, 133.89, 133.87, 133.62, 132.48, 132.24, 132.02, 132.00, 131.90, 131.88, 131.66, 131.54, 131.52, 131.42, 131.40, 131.22, 131.12, 129.14, 129.00, 128.59, 128.48, 128.26, 127.05, 126.84, 125.86, 125.82, 125.78, 125.75, 125.72, 125.68, 125.64, 125.61, 124.60, 121.89. IR(film/cm^{-1}) v_{max} 3373, 3061, 2927, 2857, 2588, 1678, 1439, 1399, 1324, 1170, 1131, 965, 739, 567. MS : m/z (M+H): 289.



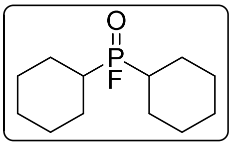
2mj Yeld:78%, pale yellow oil [1]H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 2H), 7.61 (m, 1H), 7.49 (m, 2H), 4.60 – 4.47 (m, 1H), 2.30 (d, J = 11.8 Hz, 1H), 2.24 – 2.13 (m, 1H), 1.94 (m, 1H), 1.69 (m, 2H), 1.53 – 1.14 (m, 4H), 1.04 (m, 1H), 0.95 (t, J = 7.3 Hz, 3H), 0.90 – 0.81 (m, 6H), 0.70 (d, J = 6.9 Hz, 2H).[31]P NMR (400 MHz, $CDCl_3$) δ 19.18 (d, J = 106.1 Hz), 12.74 (d, J = 103.6 Hz). [19]F NMR (400 MHz, $CDCl_3$) δ -59.22 (d, J = 919.0 Hz), -62.00 (d, J = 916.9 Hz). [13]C NMR (400 MHz, $CDCl_3$) δ 133.30, 131.48, 131.38, 128.65, 128.64, 128.49, 128.48, 126.60 (dd, J = 45.9, 31.2 Hz), 124.58 (dd, J = 46.4, 31.3 Hz), 80.43, 80.36, 80.05, 79.98, 48.28, 48.22, 48.15, 42.92, 42.83, 33.82, 31.52, 31.48, 25.81, 25.75, 22.84, 21.82, 21.73, 20.78, 20.67, 15.47. IR(film/cm^{-1}) v_{max} 3365, 2956, 2930, 2871, 1595, 1457, 1442, 1292, 1136, 1014, 996, 847. MS : m/z (M+H): 299



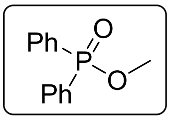
2n Yeld:44%, pale yellow oil. [1]H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 2H), 7.63 (m, 1H), 7.51 (dd, J = 12.6, 7.6 Hz,2H), 5.07 – 4.92 (m, 1H), 1.47 (d, J = 6.2 Hz, 3H), 1.38 (d, J = 6.2 Hz, 3H). ^{31}P NMR (400 MHz, $CDCl_3$) δ 15.92 (d, J = 1041.3 Hz). ^{19}F NMR (400 MHz, $CDCl_3$) δ -61.69 (d, J = 1041.0 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 133.43, 133.40, 131.62, 131.52, 128.69, 128.53, 126.31 (d, J = 30.7 Hz), 124.31 (d, J = 30.7 Hz),73.47, 73.41, 30.88, 23.89, 23.85, 23.77, 23.73. IR (film/cm^{-1}) v_{max} 3494, 3063, 2984, 2932, 1595, 1441, 1287, 1137, 1011, 995, 848. MS (M+H): 203



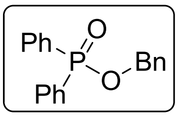
2o Yeld:65%, pale yellow oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m,2H), 7.67 – 7.56 (m, 1H), 7.51 (m, 2H), 2.16 – 1.94 (m, 2H), 1.69 – 1.49 (m, 2H), 1.47 – 1.32 (m, 2H), 0.87 (t, J = 7.3 Hz,3H). ^{31}P NMR (400MHz, $CDCl_3$) δ 55.62 (d, J = 1021.4 Hz).^{19}F NMR (400 MHz, $CDCl_3$) δ -75.55 (d, J = 1021.5 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 133.31, 133.29, 131.01, 130.99, 129.07 (d, J = 19.4 Hz), 127.77 (d, J = 19.2 Hz), 28.93 (d, J = 17.2 Hz), 27.97 (d, J = 17.2 Hz)., 23.59, 23.43, 23.29, 23.25, 13.35. IR (film/cm^{-1}) v_{max} 3404, 2958, 2931, 2870, 1594, 1439, 1165, 1128, 965, 741. MS : m/z (M+H): 201.



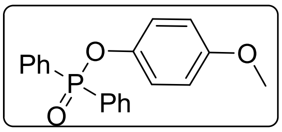
2pYeld:75%, pale yellow solid ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 – 1.89 (m, 2H), 1.89 – 1.73 (m, 8H), 1.69 (d, J = 1.5 Hz, 2H), 1.55 – 1.33 (m, 4H), 1.31 – 1.11 (m, 6H). ^{31}P NMR (400MHz, $CDCl_3$) δ 70.75 (d, J = 1036.4 Hz). ^{19}F NMR (400 MHz, $CDCl_3$) δ -94.88 (d, J = 1036.7 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 35.29 (d, J = 13.3 Hz), 34.43 (d, J = 13.3 Hz).25.90, 25.87, 25.76, 25.74, 25.53, 25.51, 24.61, 24.58, 24.54. IR (film/cm^{-1}) v_{max} 3453, 2930, 2854, 1448, 1279, 1245, 1202, 858. MS: m/z (M+H):233.



3aYeld:88%, pale yellow solid ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H), 7.52 (m, 2H), 7.44 (m, 4H), 3.76 (3H). ^{31}P NMR (400 MHz, $CDCl_3$) δ 33.22. ^{13}C NMR (400 MHz, $CDCl_3$) δ 132.16, 132.13, 131.63, 131.53, 130.26, 128.56, 128.43, 51.49, 51.43. MS : m/z (M+H): 233

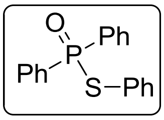


3b Yeld:81%, pale yellow solid ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 2H), 7.52 (t, J = 7.3 Hz,2H), 7.44 (dm, 4H), 7.39 – 7.28 (m, 4H), 5.08 (d, J = 6.8 Hz, 2H). ^{31}P NMR (400 MHz, $CDCl_3$) δ 32.32. ^{13}C NMR (400MHz, $CDCl_3$) δ 136.29, 136.22, 132.13, 132.10,, 131.65, 131.55, 131.26 (d, J = 136.7 Hz),128.51, 128.43, 128.38, 128.16, 127.74, 66.20, 66.15. MS : m/z (M+H): 309



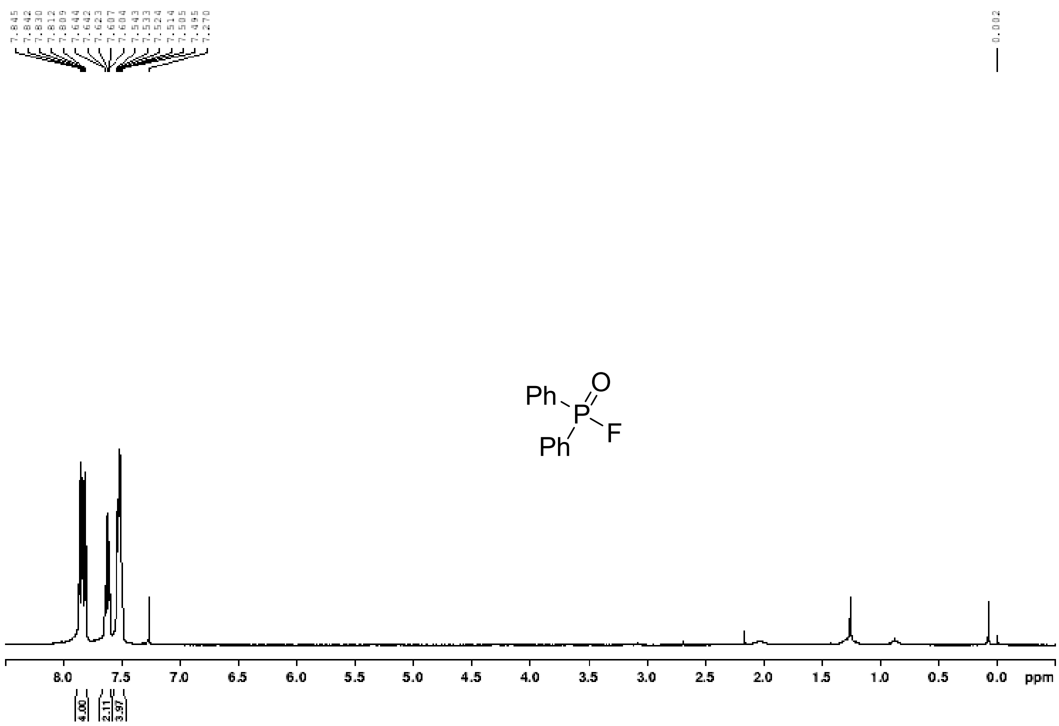
3d Yeld:46% , pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 4H), 7.54 (m, 2H), 7.46 (m, 4H), 7.12 – 7.07 (m, 2H), 6.78 – 6.71 (m, 2H), 3.72 (s, 3H). ^{31}P NMR (400 MHz, $CDCl_3$) δ

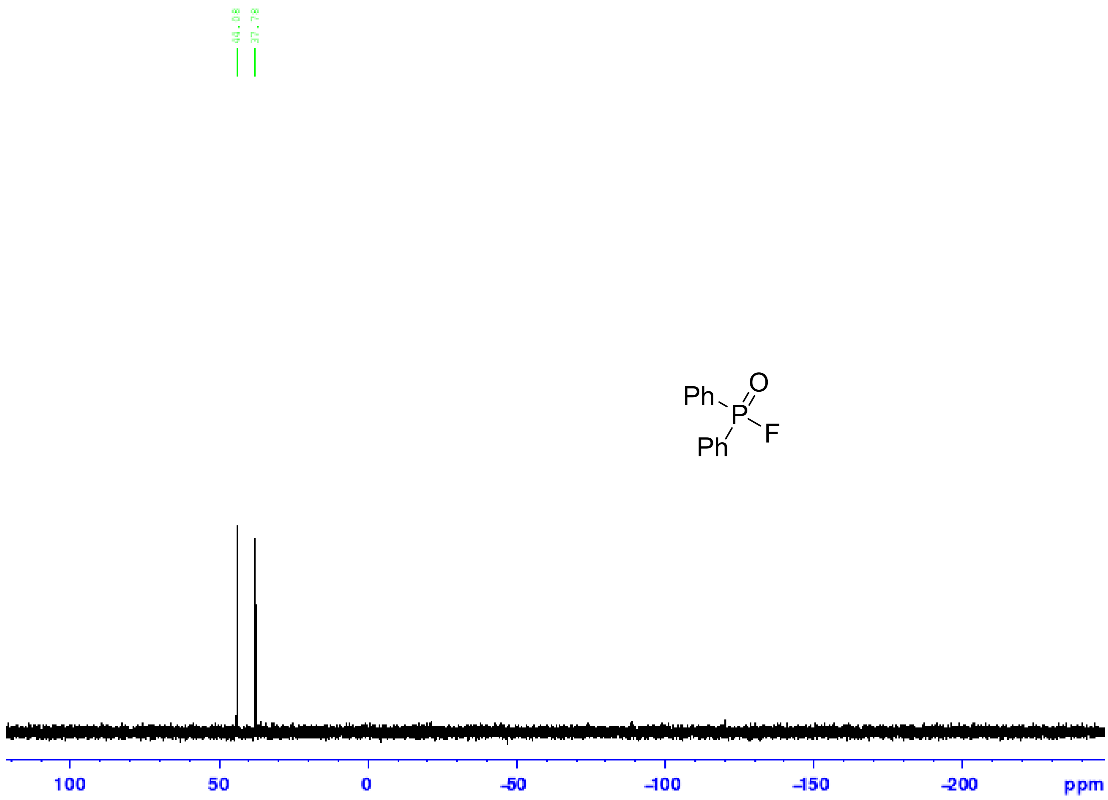
30.72. ^{13}C NMR (400 MHz, $CDCl_3$) δ 156.34, 144.14, 144.05, 132.47, 132.44, 131.82, 131.71, 130.59 (d, J = 138.5 Hz), 128.61, 128.48, 121.58, 121.54, 114.53, 55.45. MS : m/z (M+H): 325.



3e Yeld:81%, white solid. ^{1}H NMR (400 MHz, DMSO) δ 7.86 – 7.78 (m, 4H), 7.63 – 7.57 (m, 2H), 7.57 – 7.50 (m, 4H), 7.46 – 7.41 (m, 2H), 7.33 – 7.23 (m, 3H). ^{31}P NMR (400 MHz, DMSO) δ 39.58. ^{13}C NMR (400 MHz, DMSO) δ 134.66, 134.62, 132.41, 132.39, 132.34 (d, J = 106.0 Hz), 131.04, 130.94, 129.19, 129.03, 129.02, 128.85, 128.84, 128.74, 128.61, 127.04, 125.96, 125.91. MS: m/z (M+H): 311.

6. Charts

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P
F
Ph
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50
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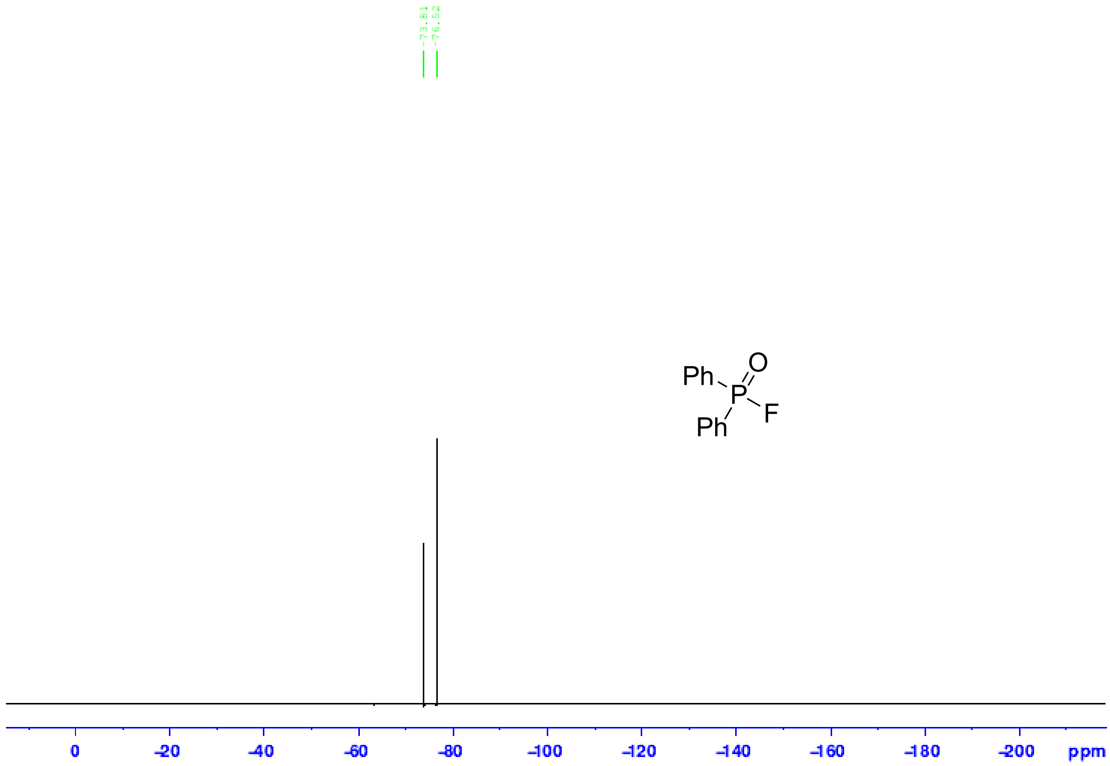
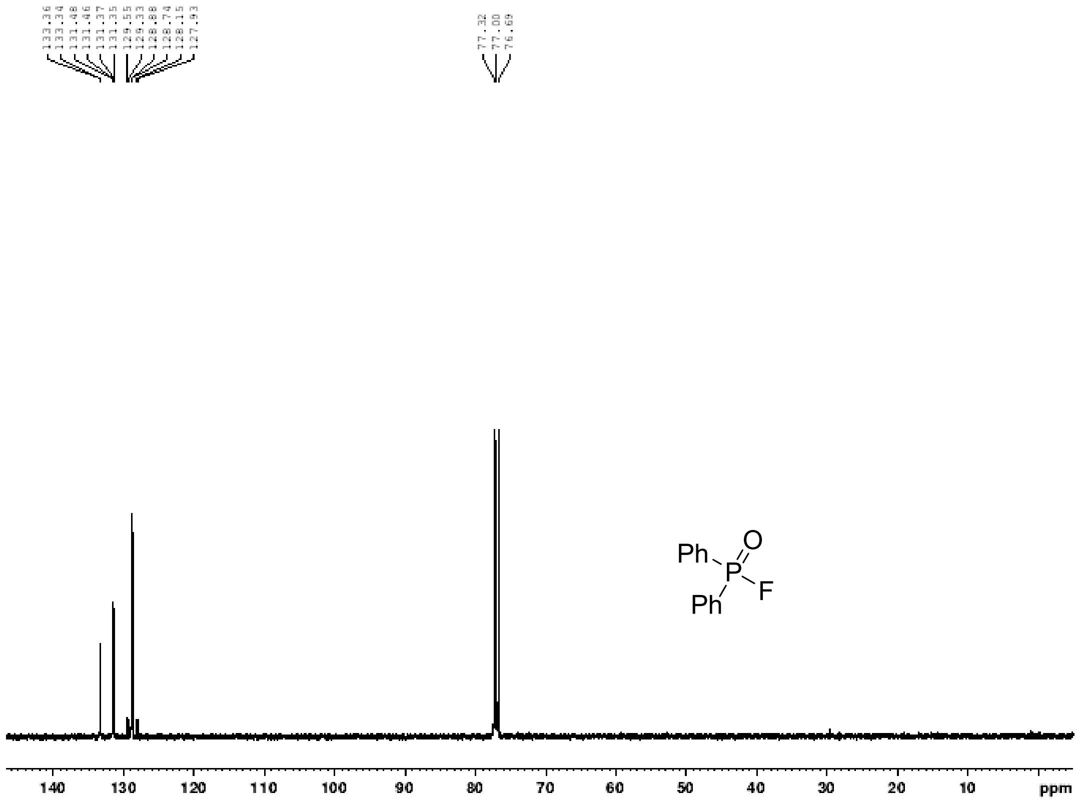
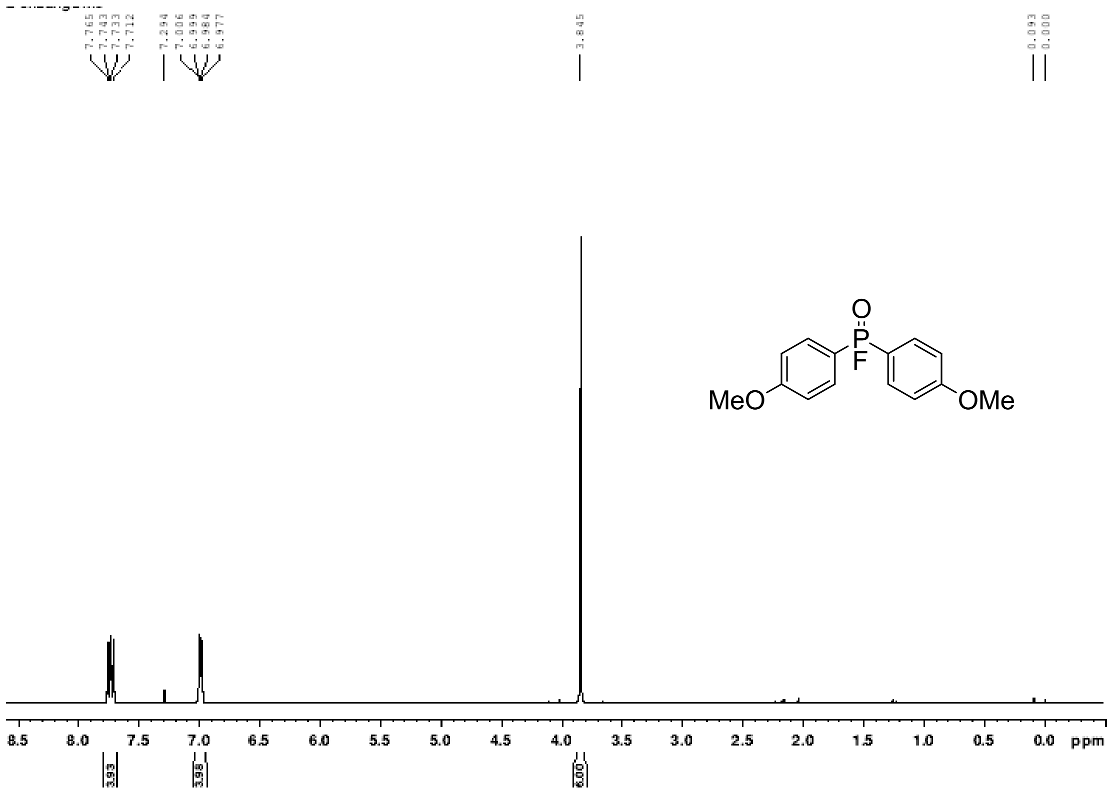
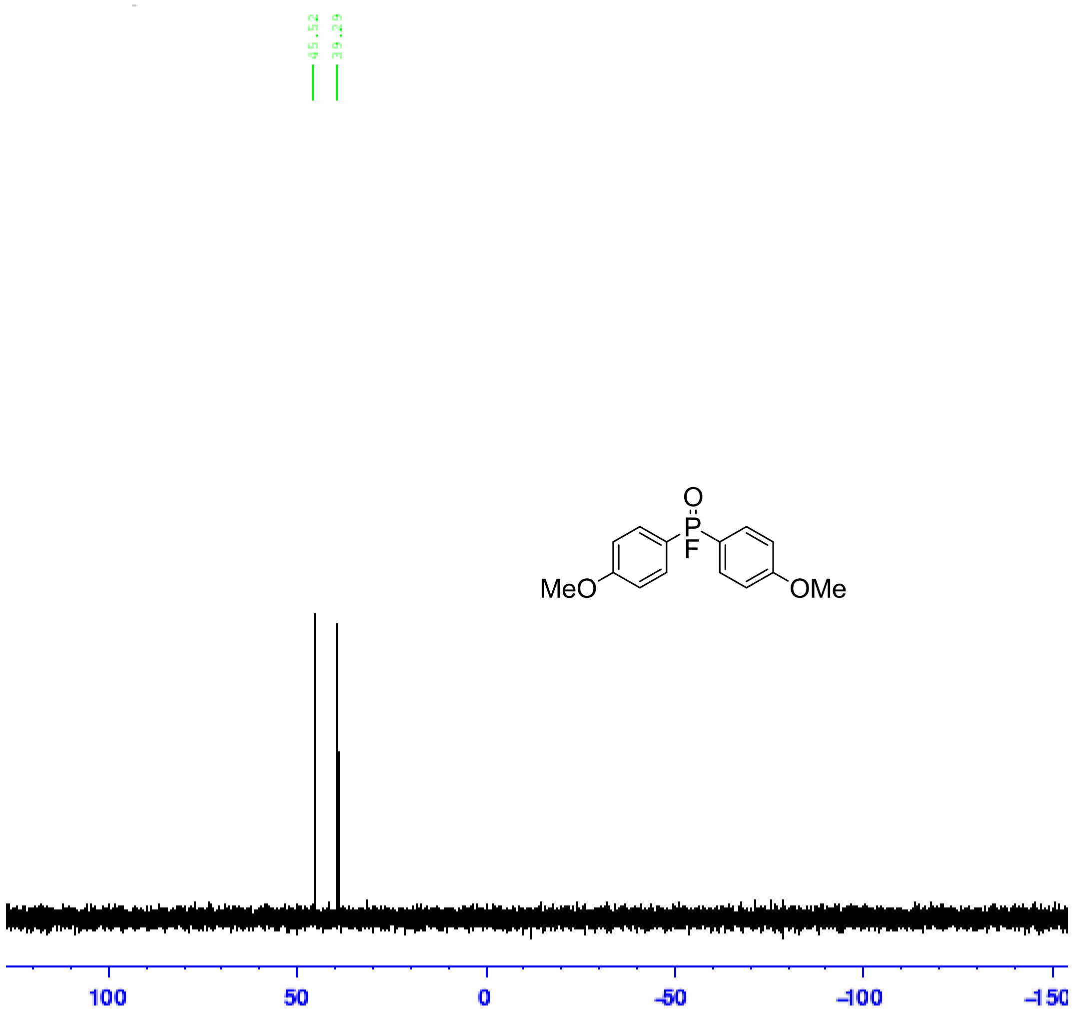
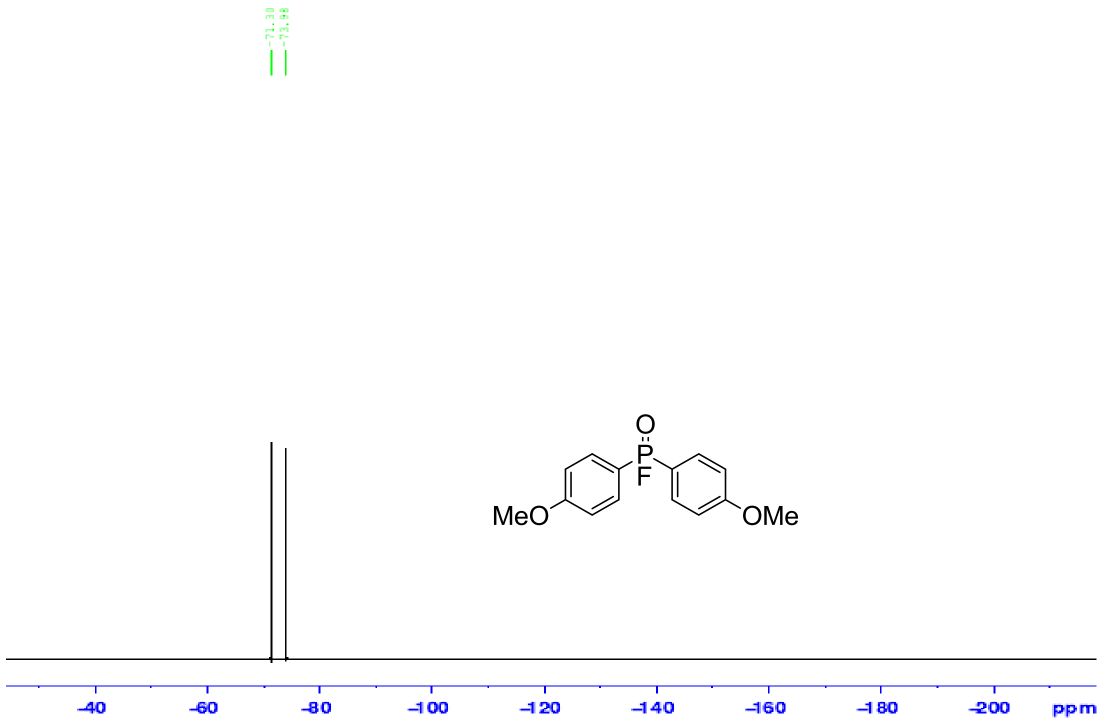
-100
-150
-200
ppm

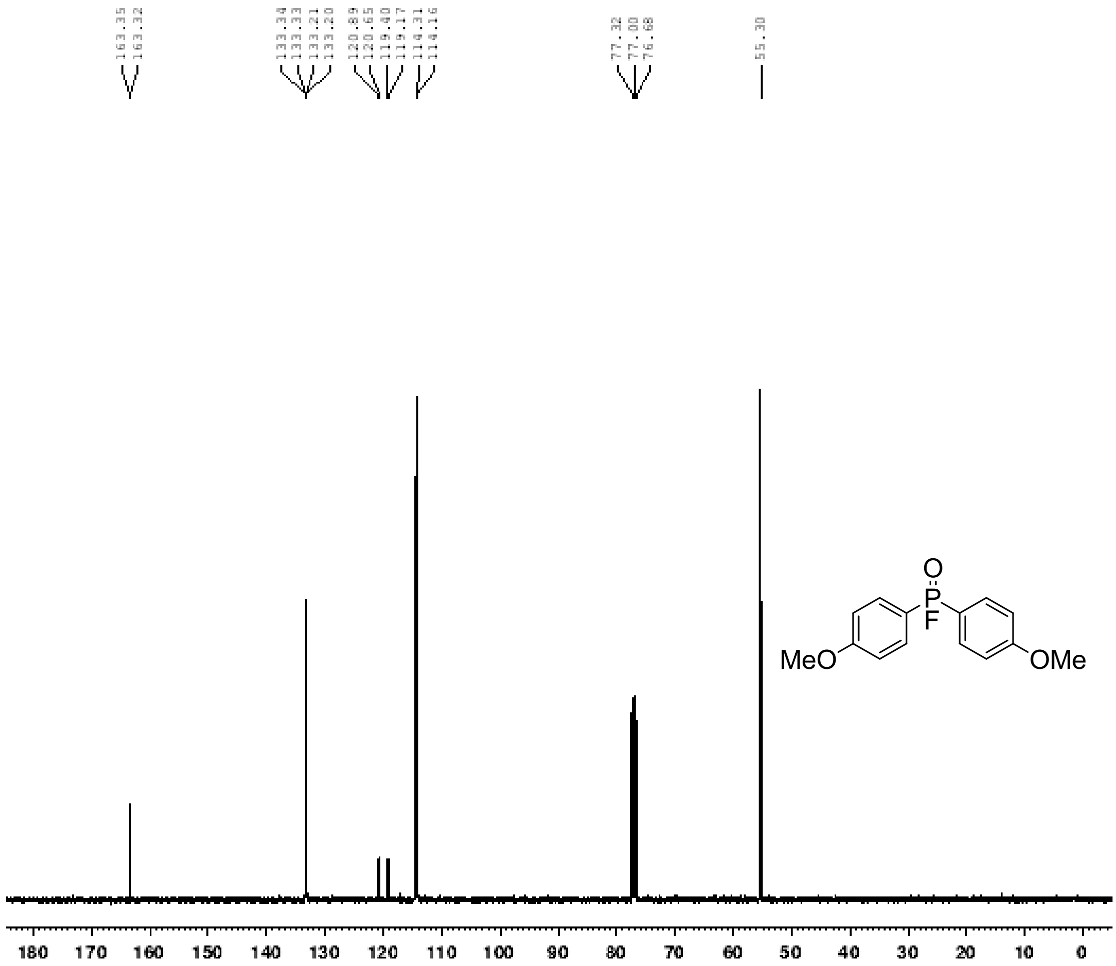

-73.81
-76.52
Ph
O
P
F
Ph
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

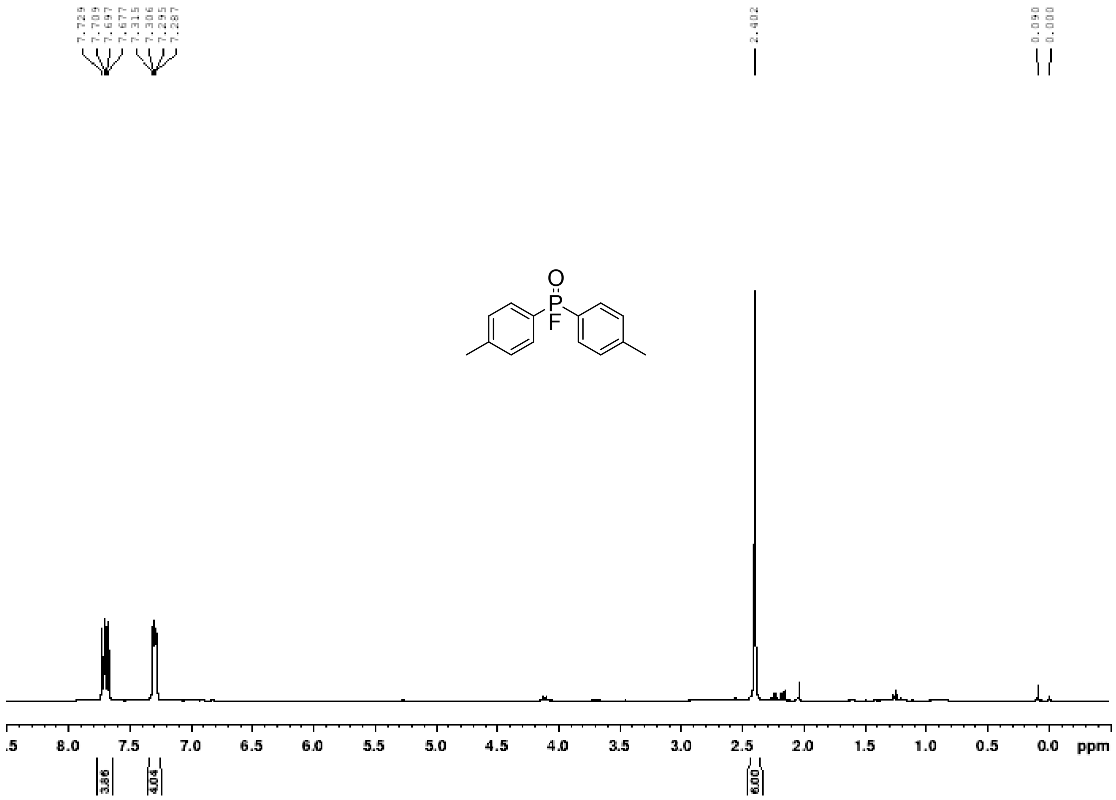

133.36
133.34
131.48
131.46
131.37
131.35
129.55
129.33
128.88
128.74
128.15
127.93
77.32
77.00
76.69
Ph
P
O
F
Ph
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.765
7.743
7.733
7.712
7.294
7.006
6.999
6.984
6.977
3.845
0.093
0.000
O
P
F
MeO
OMe
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
3.93
3.98
6.00


45.52
39.29
O
P
F
MeO
OMe
100 50 0 -50 -100 -150


-71.38
-73.98
MeO
OMe
O
P
F
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


163.35
163.32
133.34
133.33
133.21
133.20
120.89
120.65
119.40
119.17
114.31
114.16
77.32
77.00
76.68
55.30
MeO
OMe
O
P
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



7.729
7.709
7.697
7.677
7.315
7.306
7.295
7.287
2.402
0.090
0.000
O
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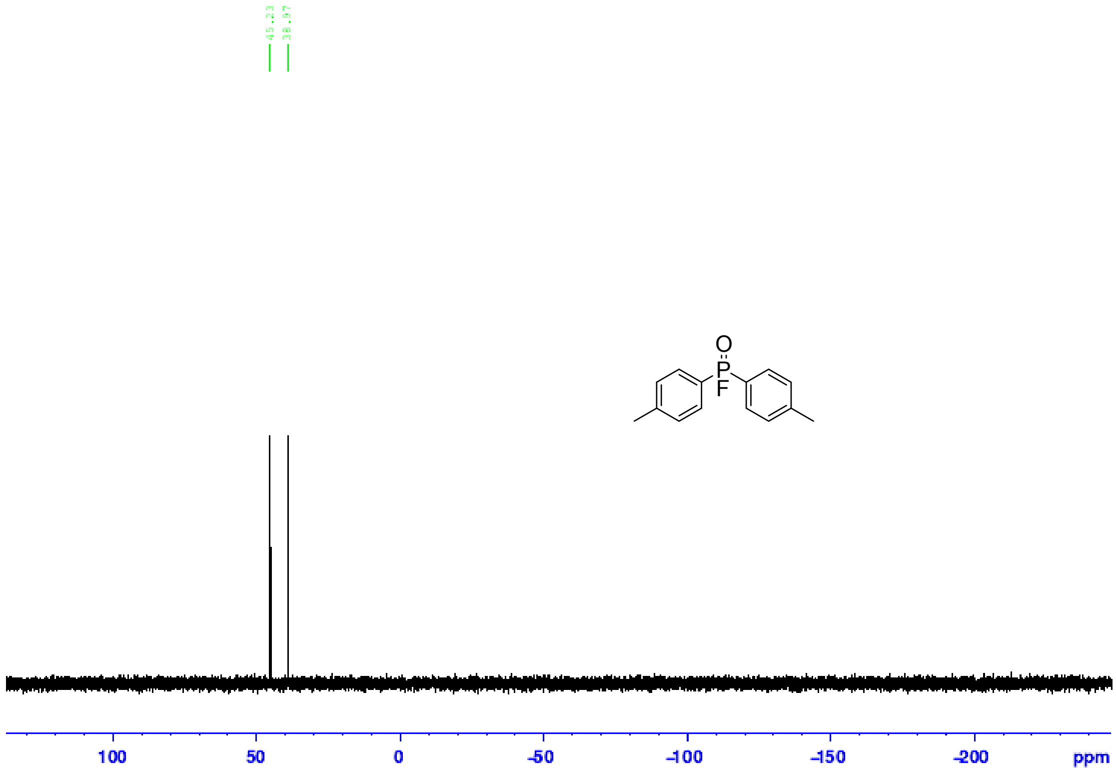
4.04
6.00
ppm



45.23
38.97
O
P
F
100
50
0
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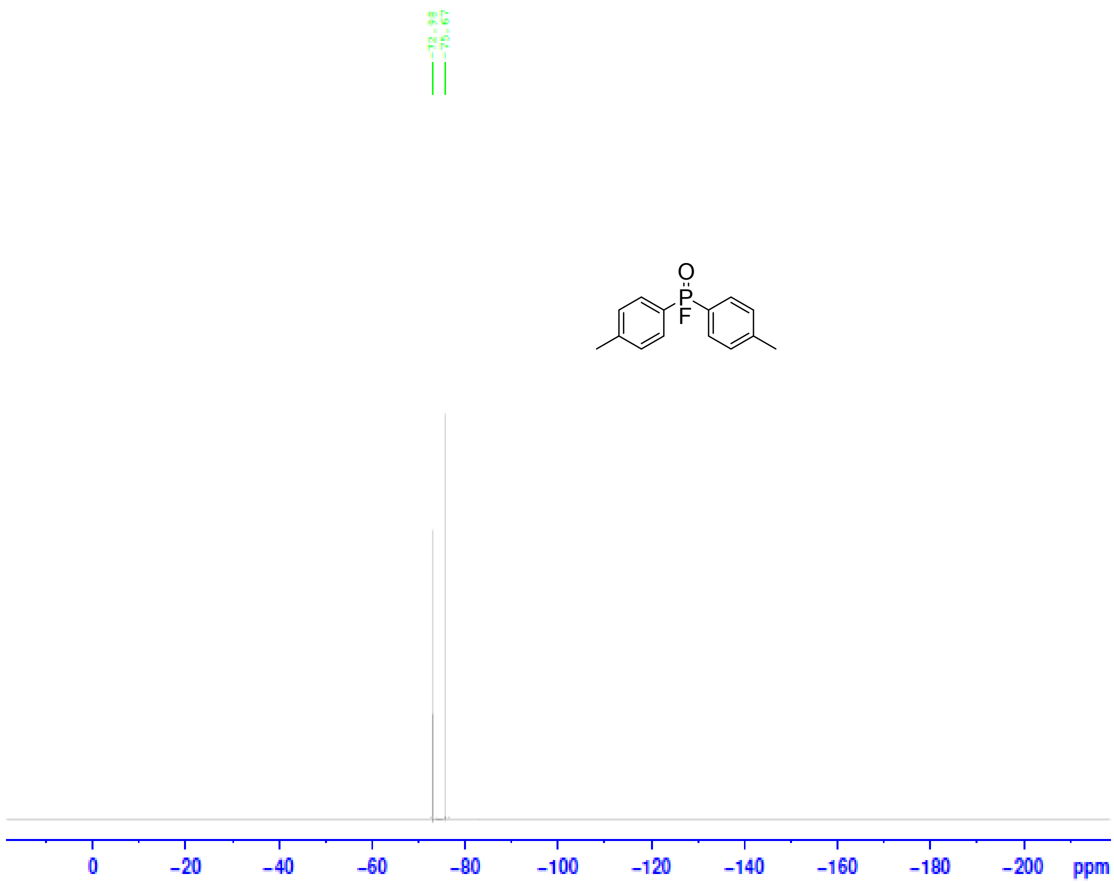
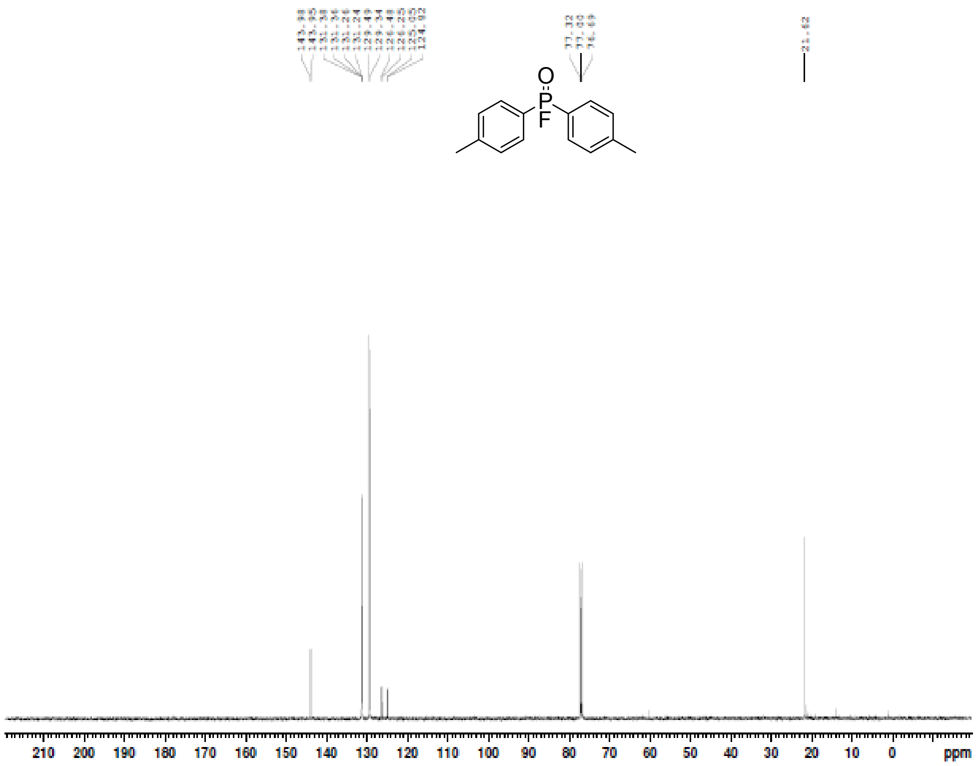
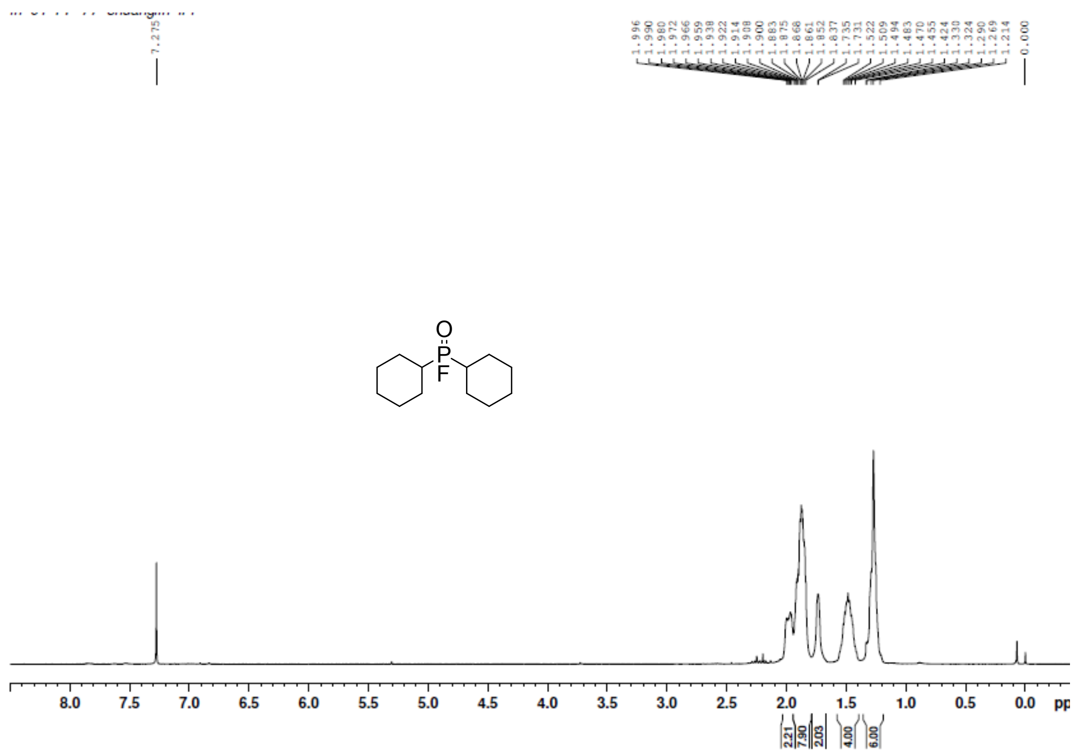
-100
-150
-200
ppm






7.275
0.000
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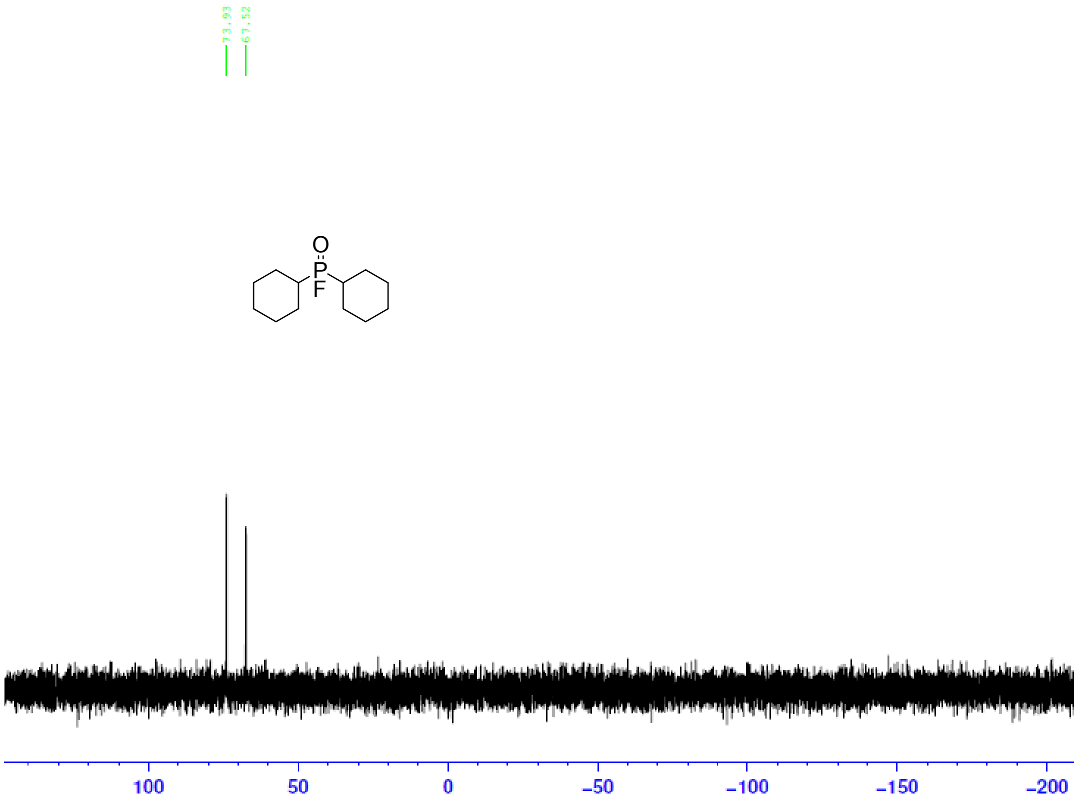
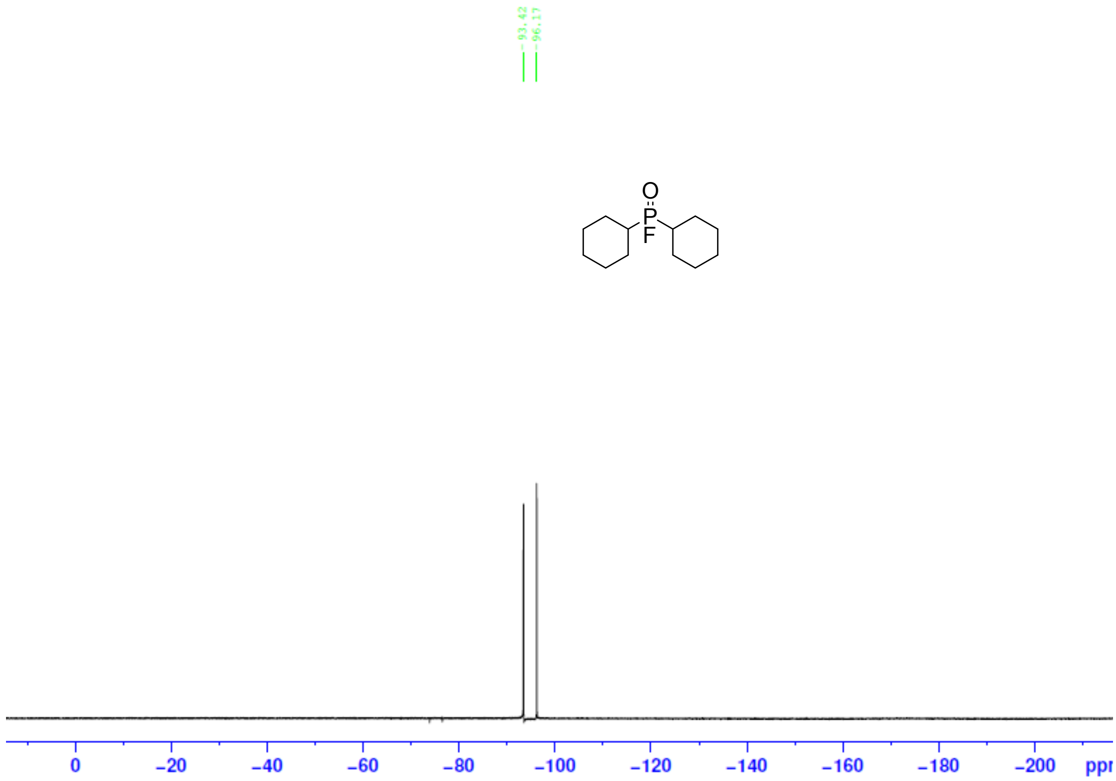
P
F
2.21
7.90
2.03
4.00
6.00


73.93
67.52
O
P
F
100
50
0
−50
−100
−150
−200


-93.42
-96.17
O
P
F
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-80
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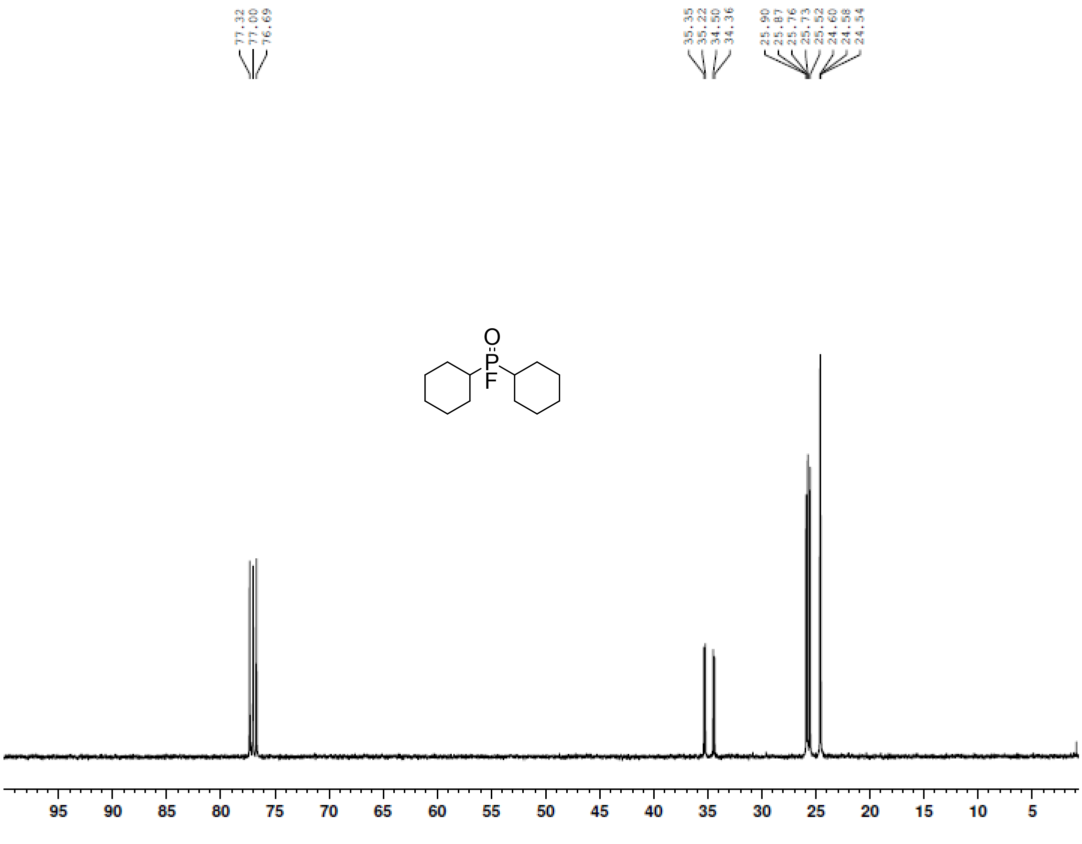
ppm


77.32
77.00
76.69
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35.22
34.50
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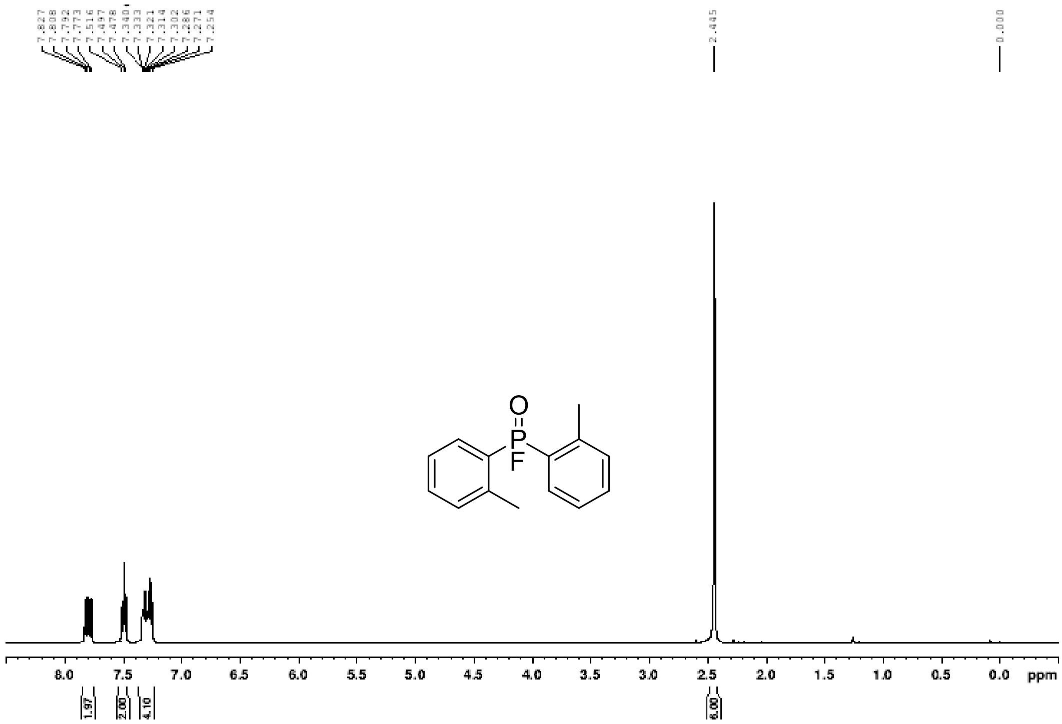
25.90
25.87
25.76
25.73
25.52
24.60
24.58
24.54
O
P
F
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5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7.773
7.516
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7.340
7.333
7.321
7.314
7.302
7.286
7.271
7.254
2.445
0.000
O
P
F
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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1.5
1.0
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ppm
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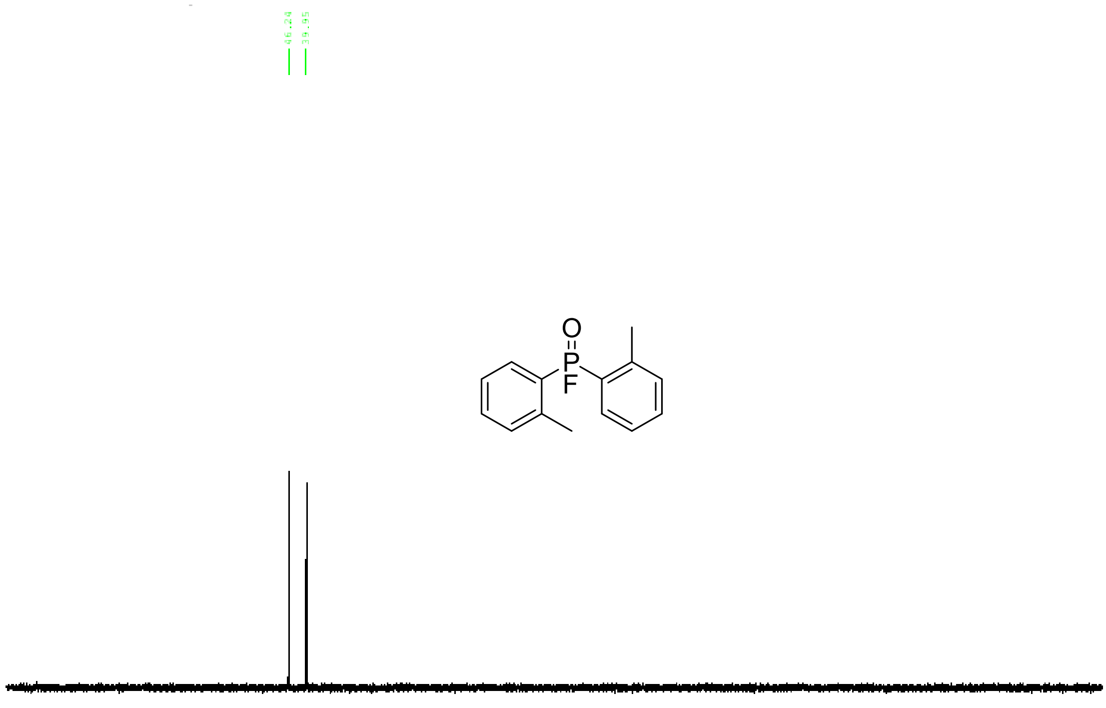
2.00
4.10
6.00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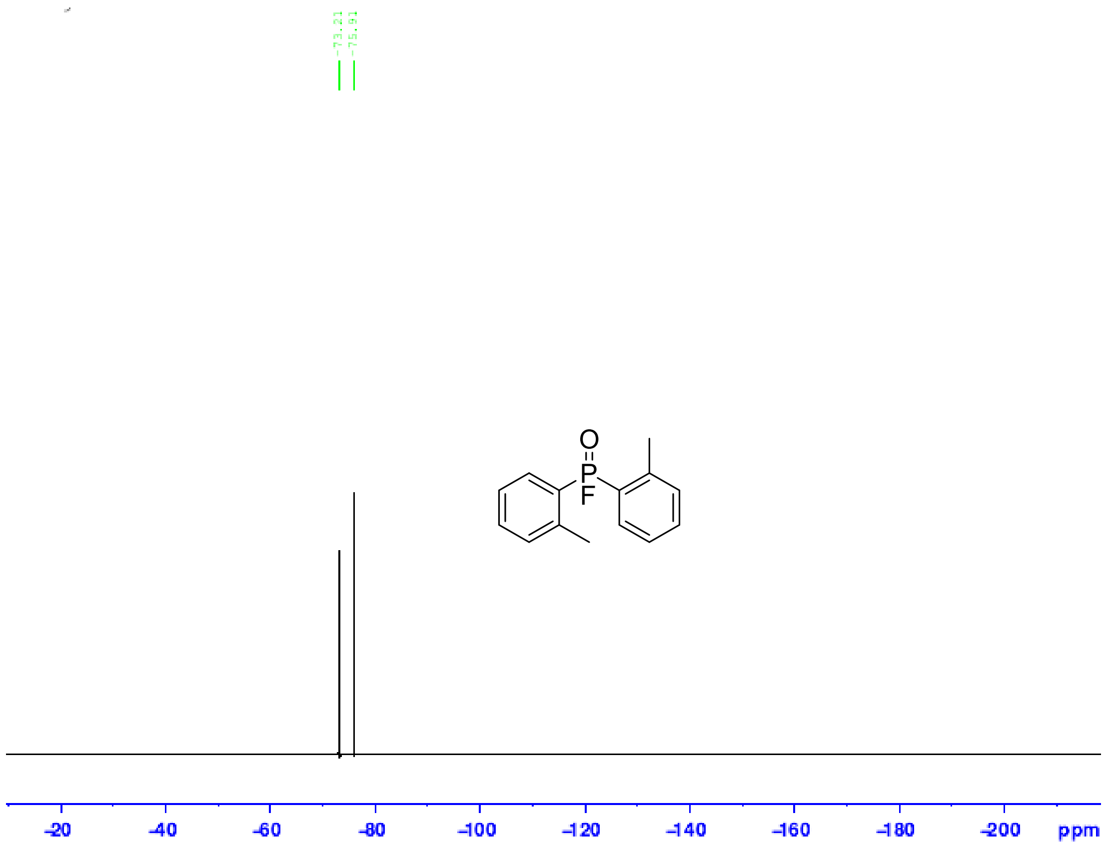
-150
-200
ppm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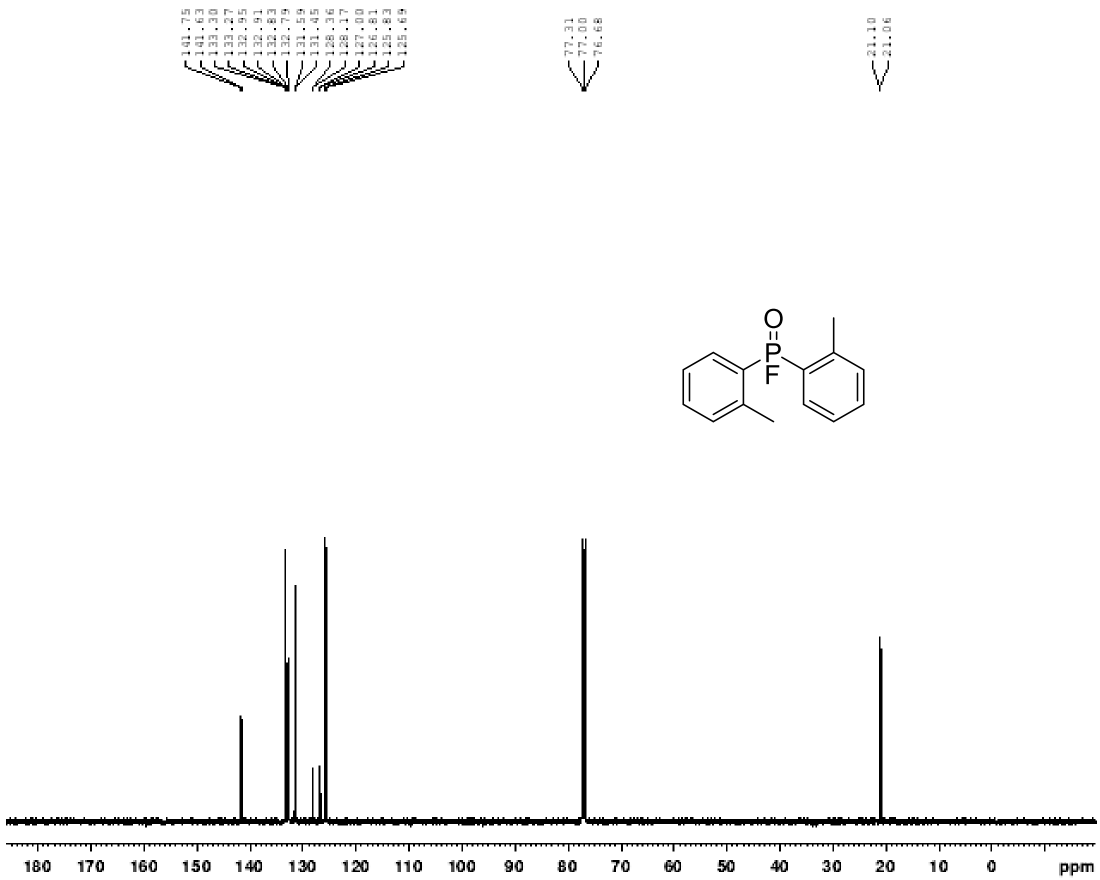
ppm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132.91
132.83
132.79
131.59
131.45
128.36
128.17
127.00
126.81
125.83
125.69
77.31
77.00
76.68
21.10
21.06
O
P
F
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130
120
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60
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20
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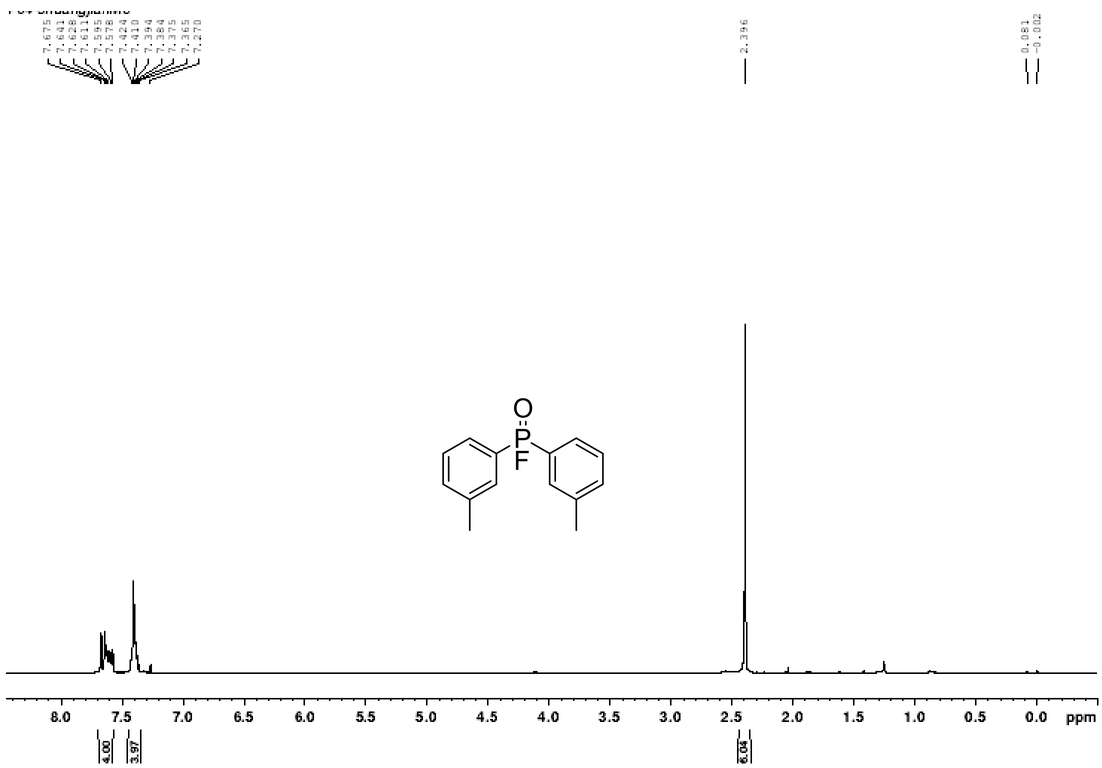

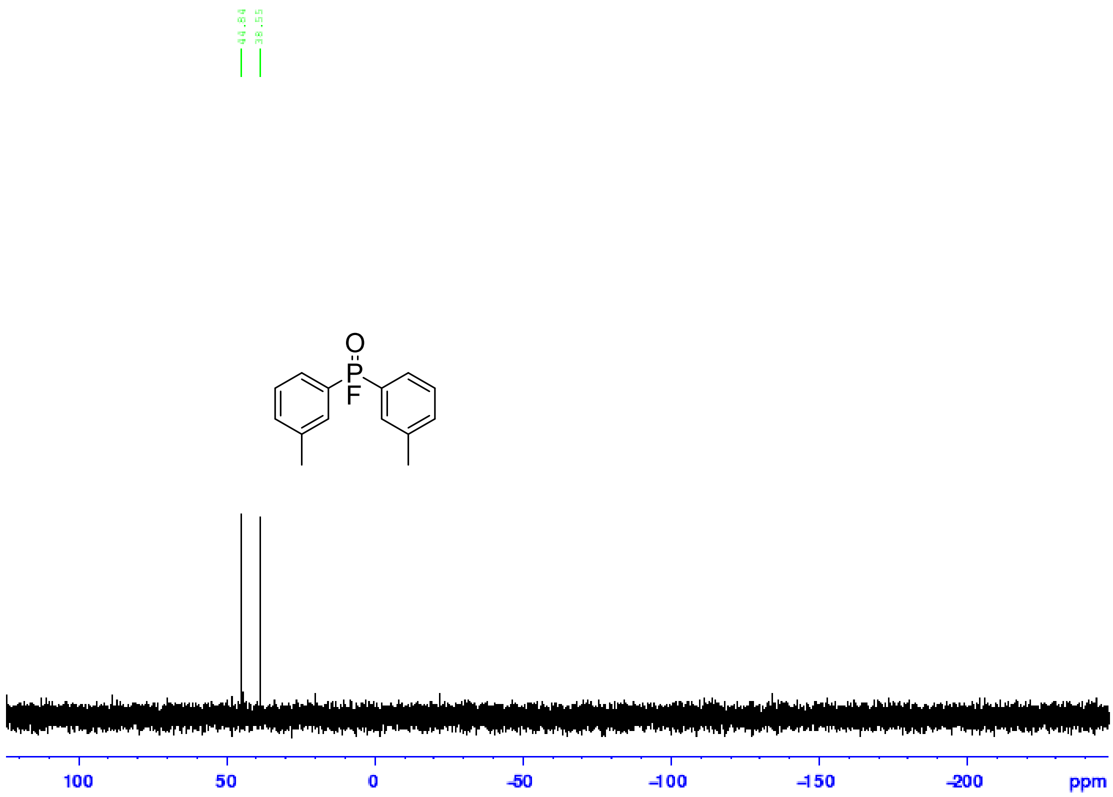

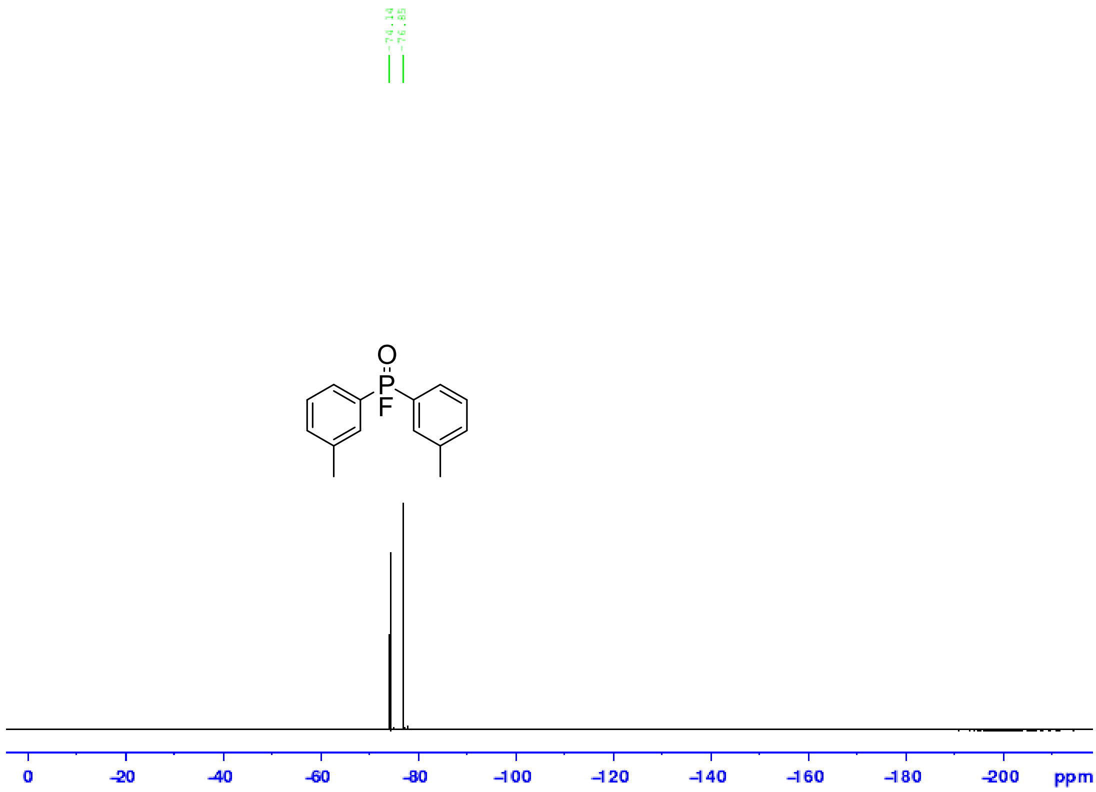

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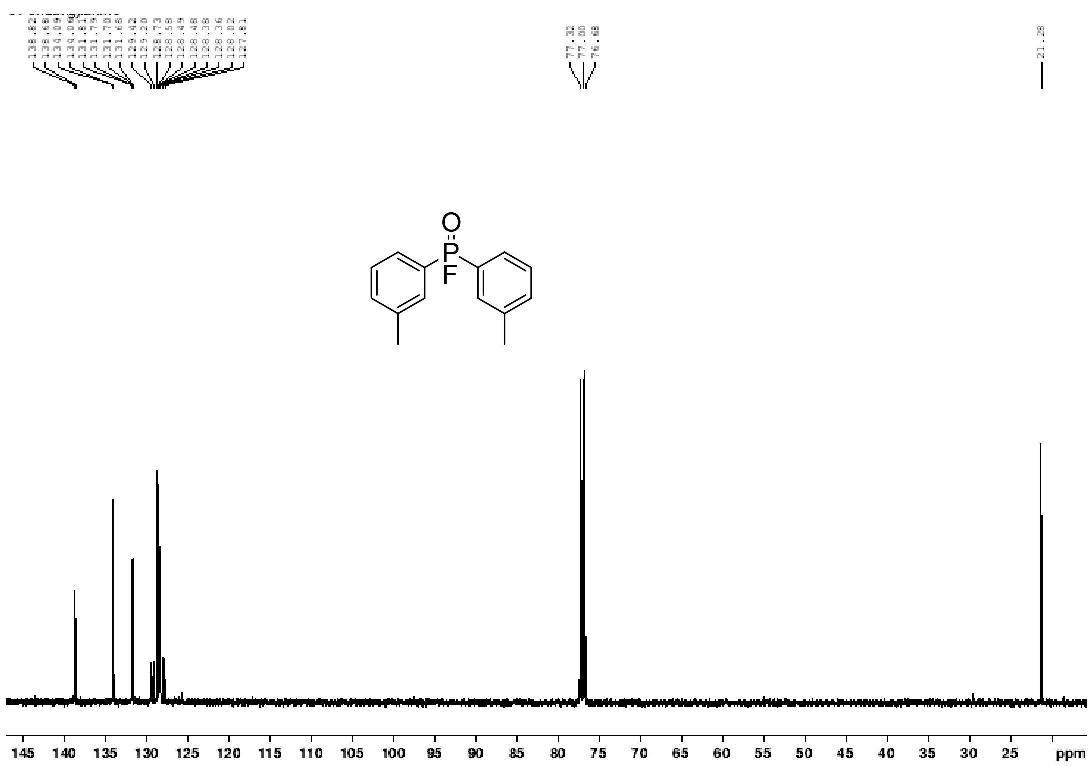
ppm



77.32
77.00
76.68
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145
140
135
130
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90
85
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75
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55
50
45
40
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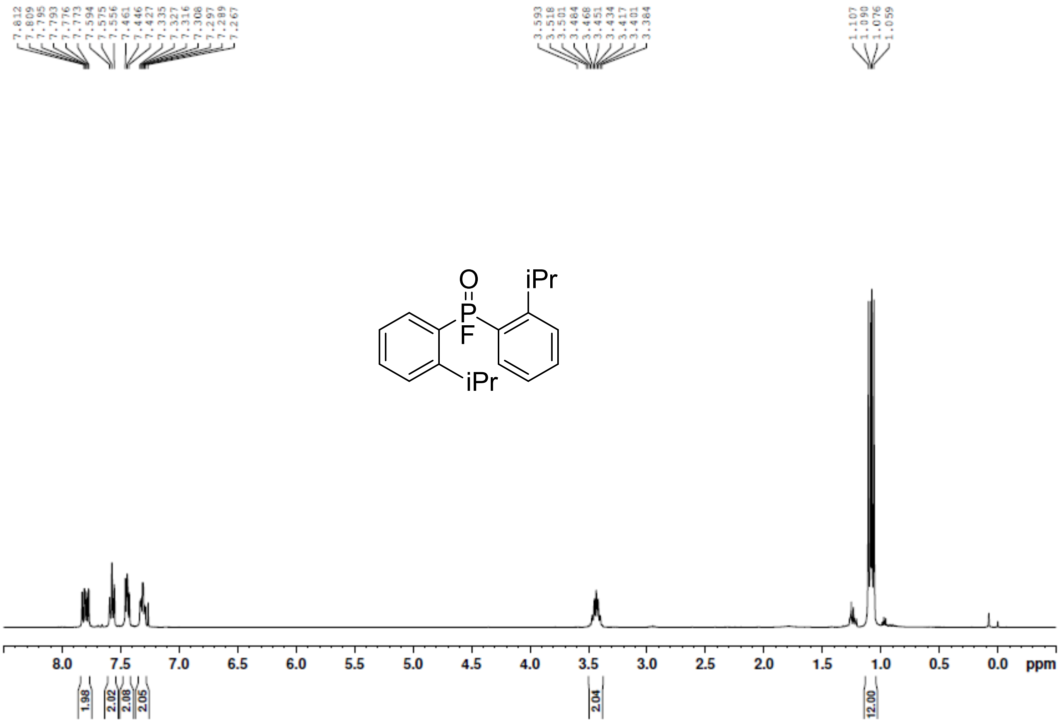
25
ppm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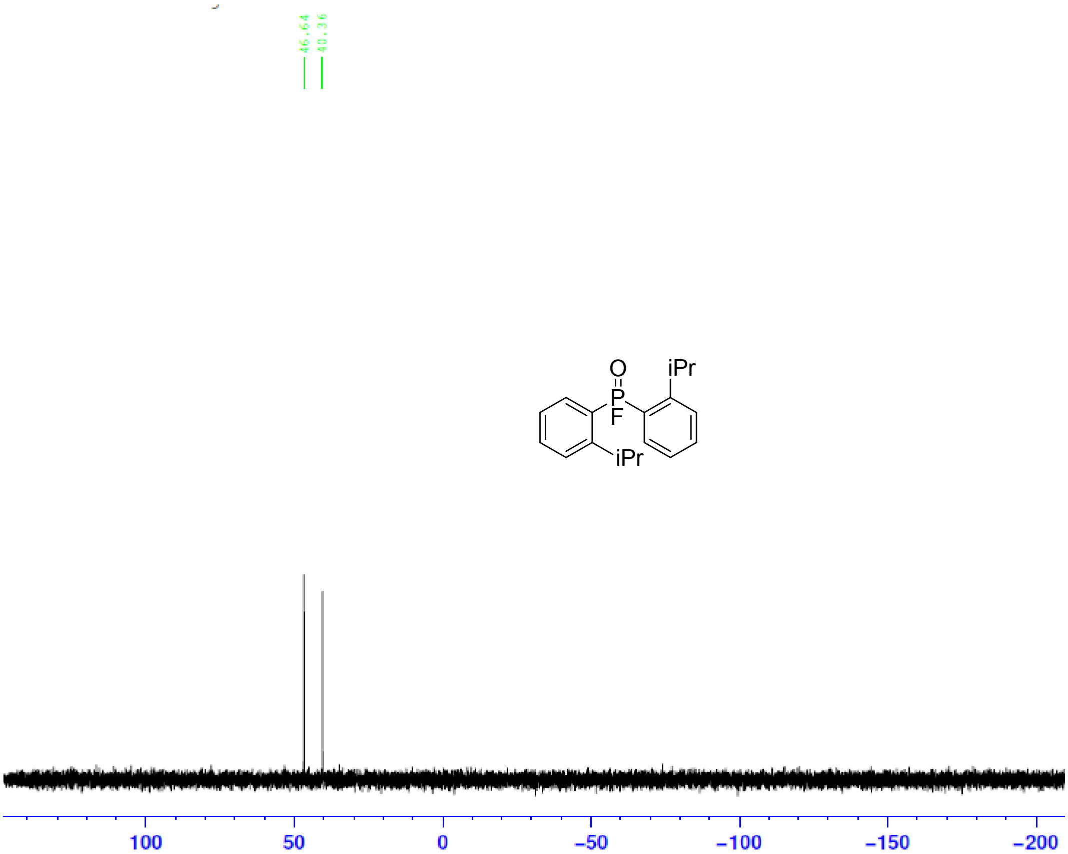
iPr
ppm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40.36
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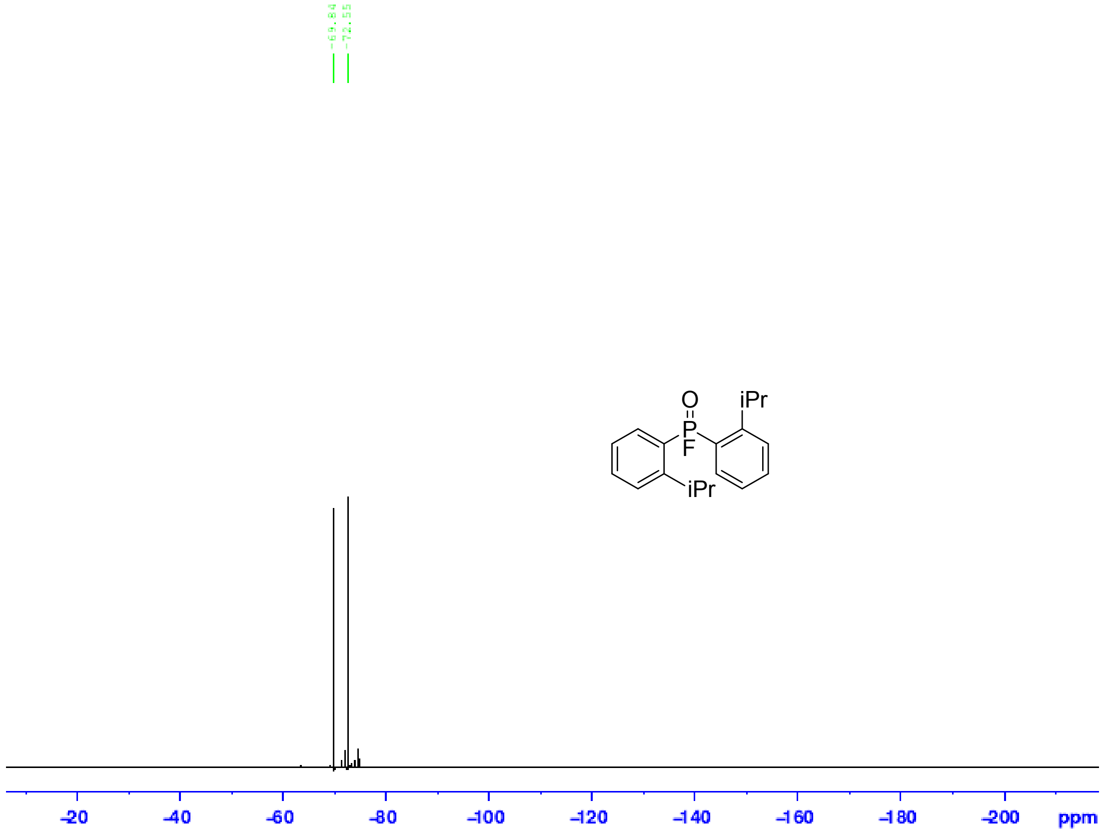
iPr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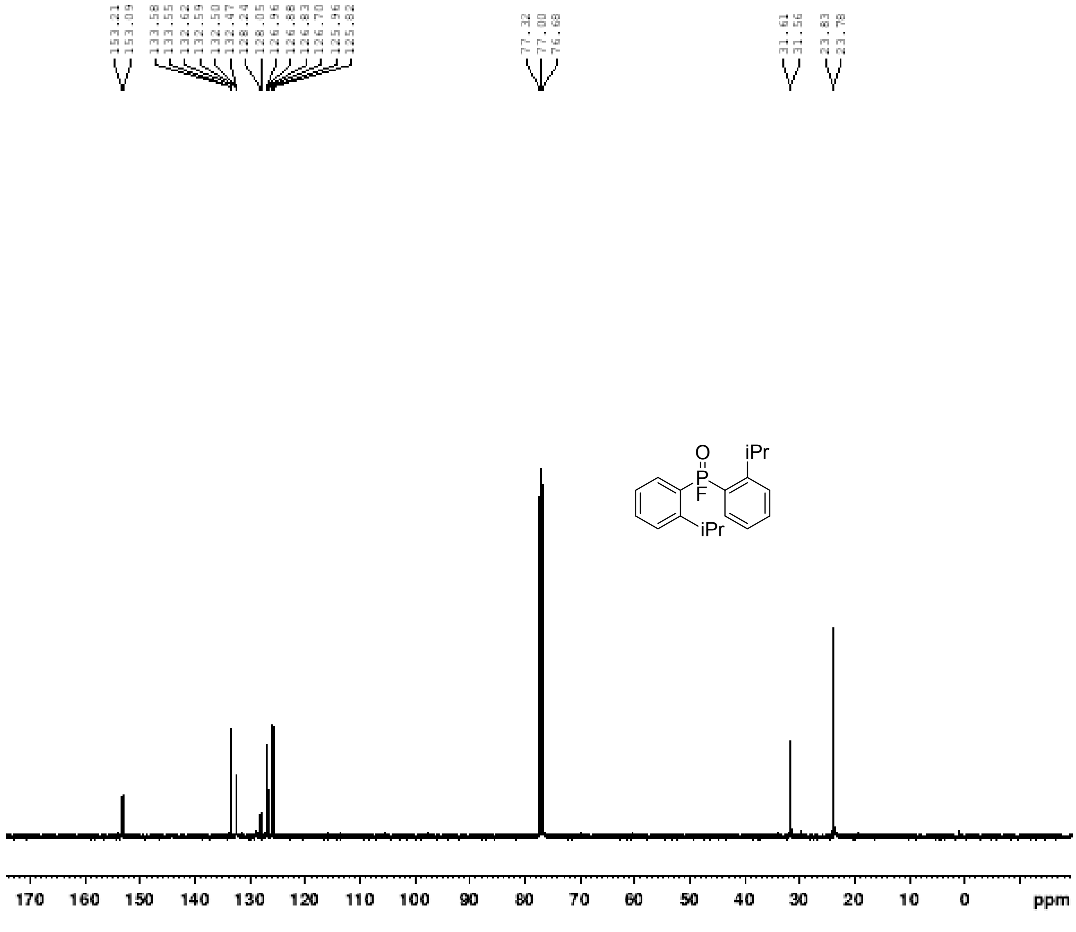
-180
-200
ppm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132.50
132.47
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128.05
126.96
126.88
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125.82
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77.00
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31.56
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23.78
iPr
iPr
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60
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20
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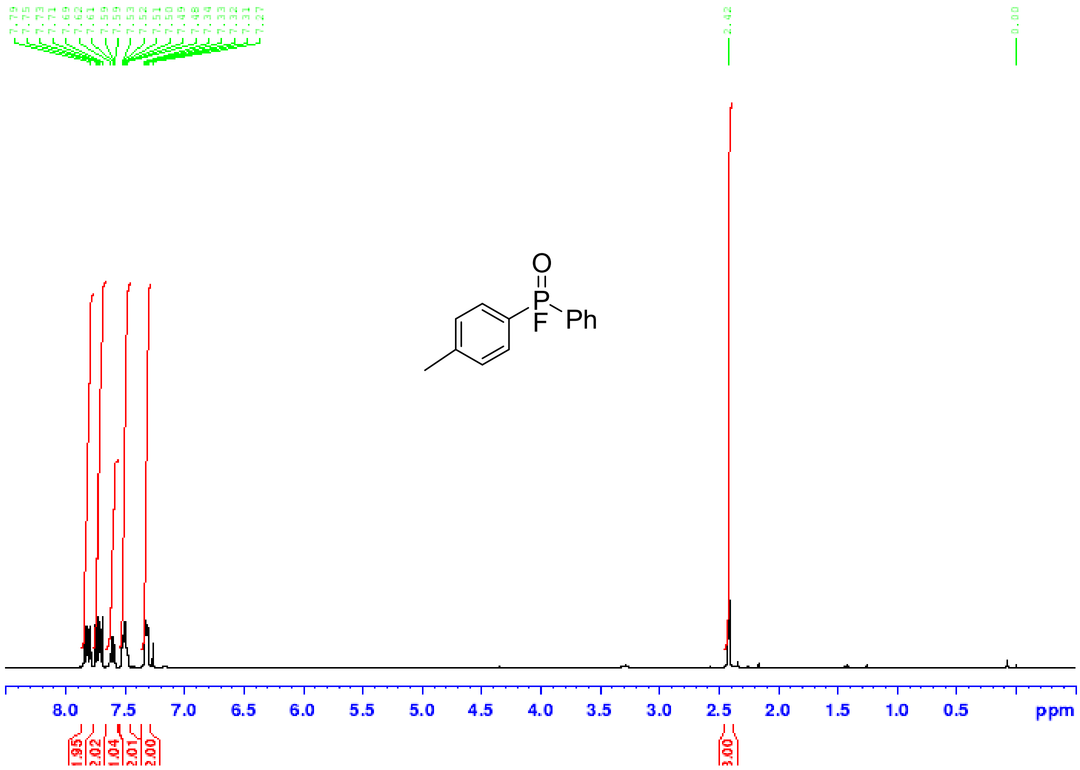
0
ppm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P
F
Ph
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7.0
6.5
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5.5
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4.5
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3.0
2.5
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ppm
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2.01
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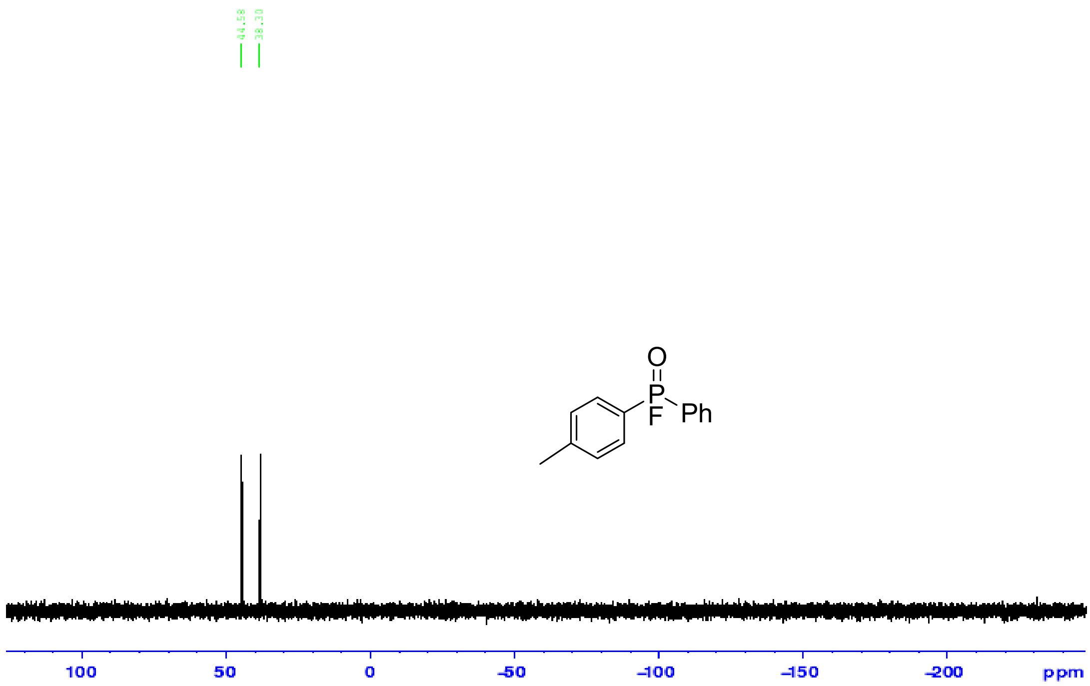
3.00
2.42
0.00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P
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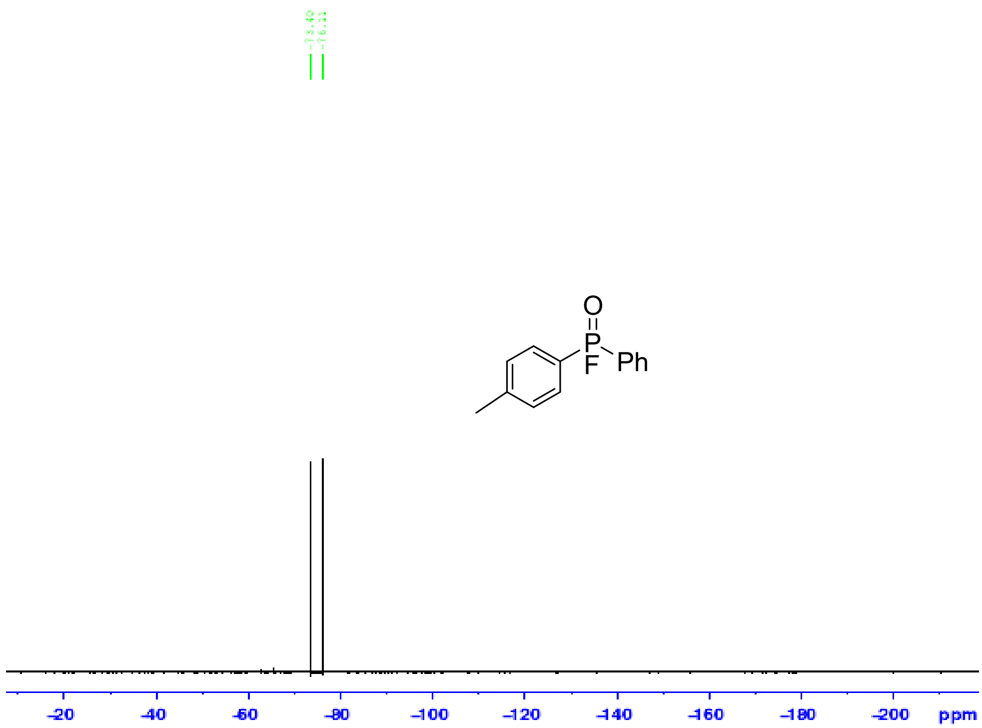
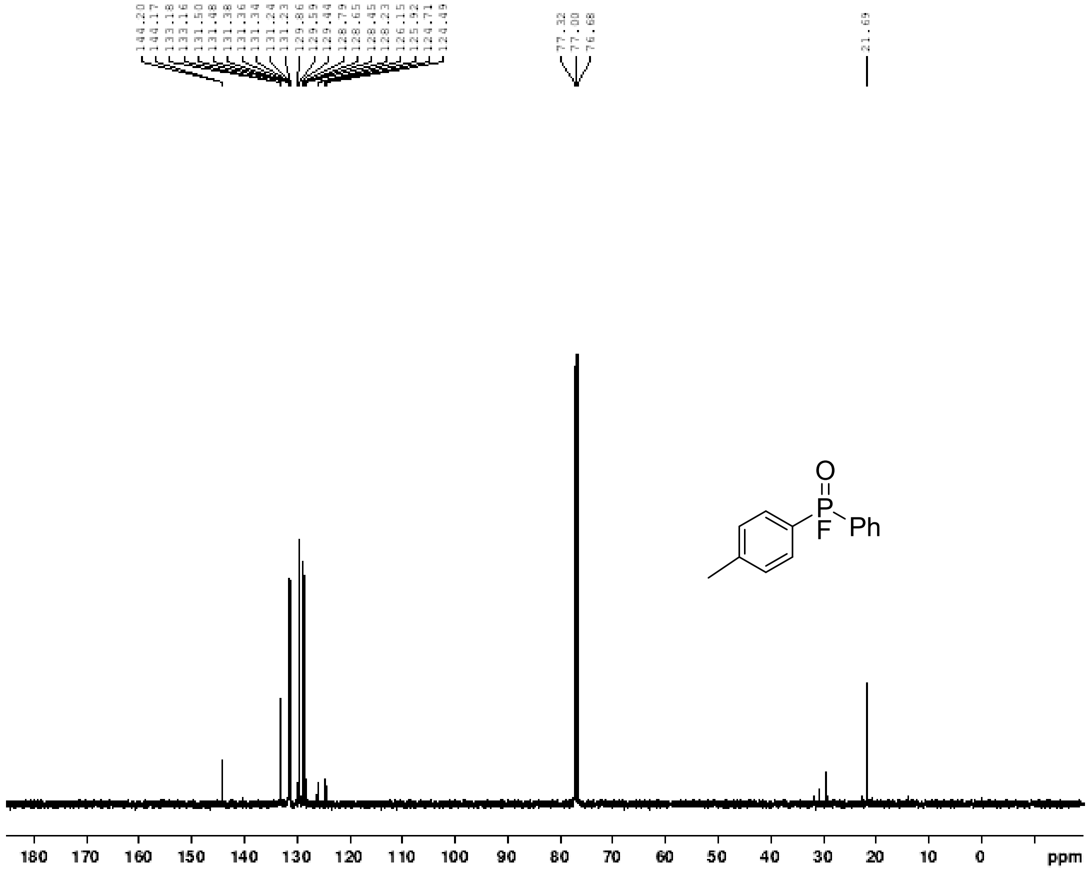
-200
ppm


O
P
F
Ph
-20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm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131.23
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128.65
128.45
128.23
126.15
125.92
124.71
124.49
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77.00
76.68
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O
P
F
Ph
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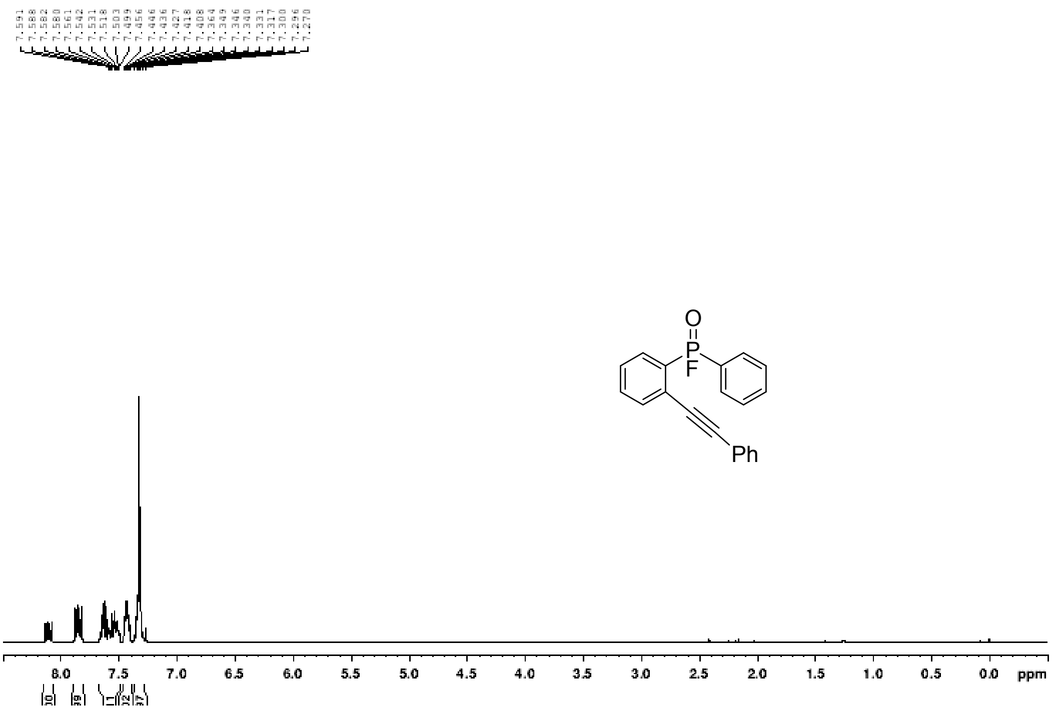
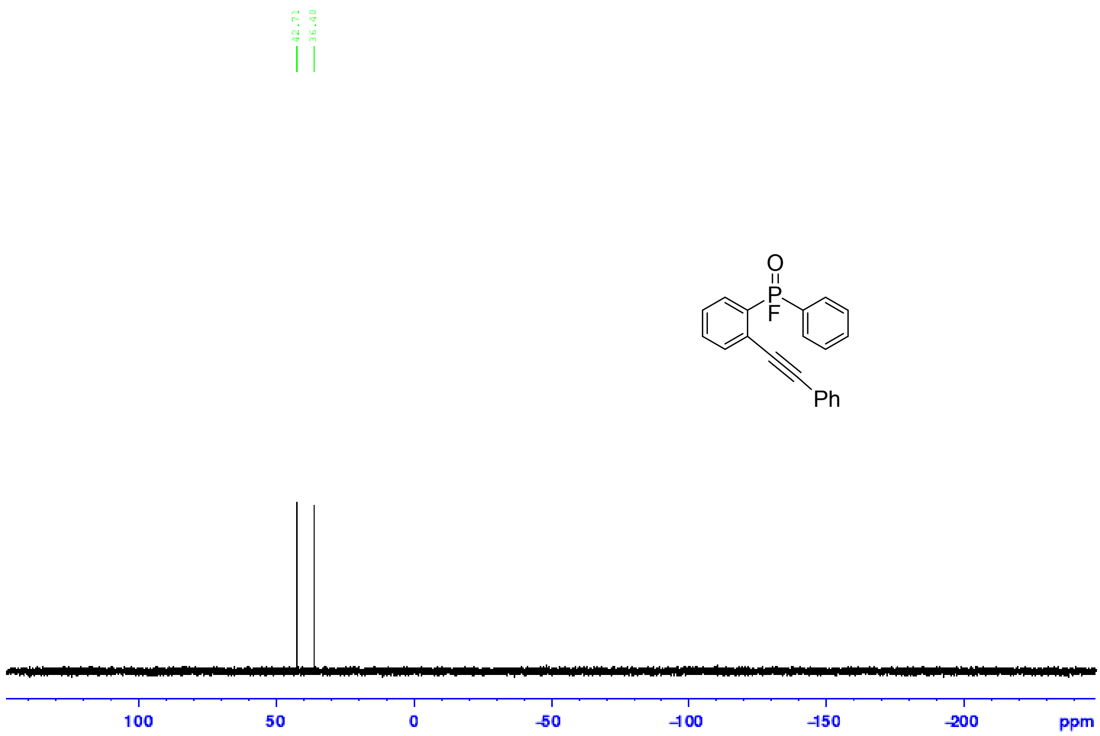
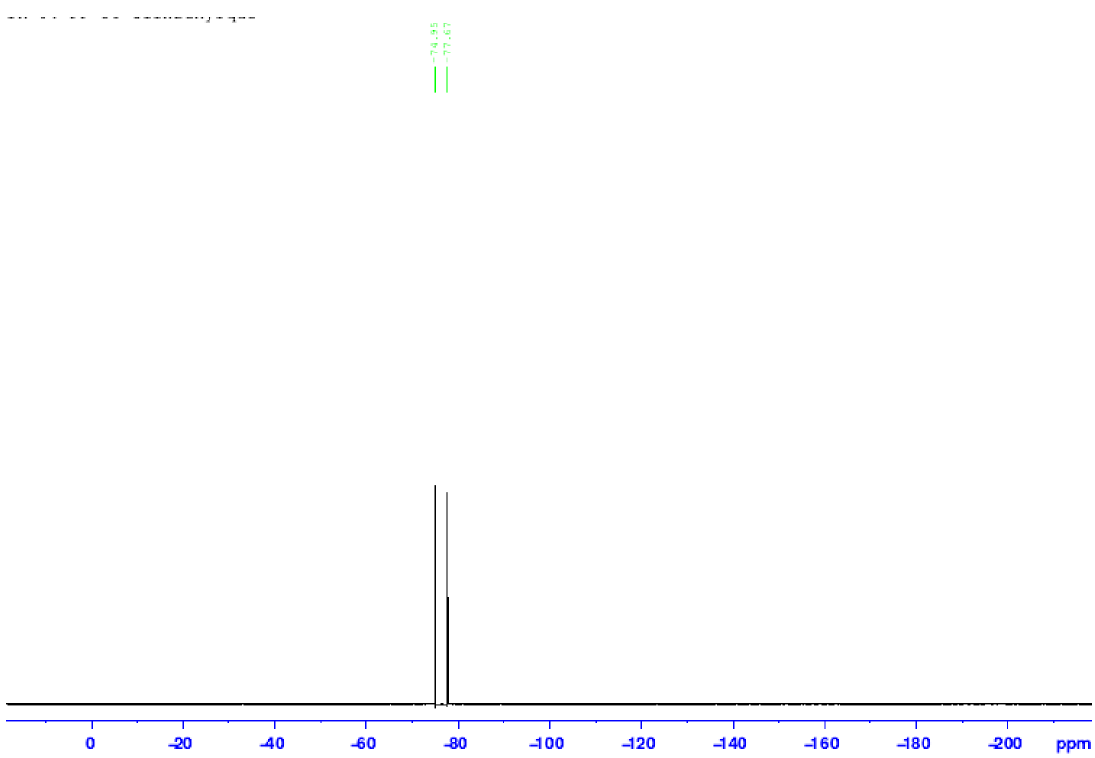
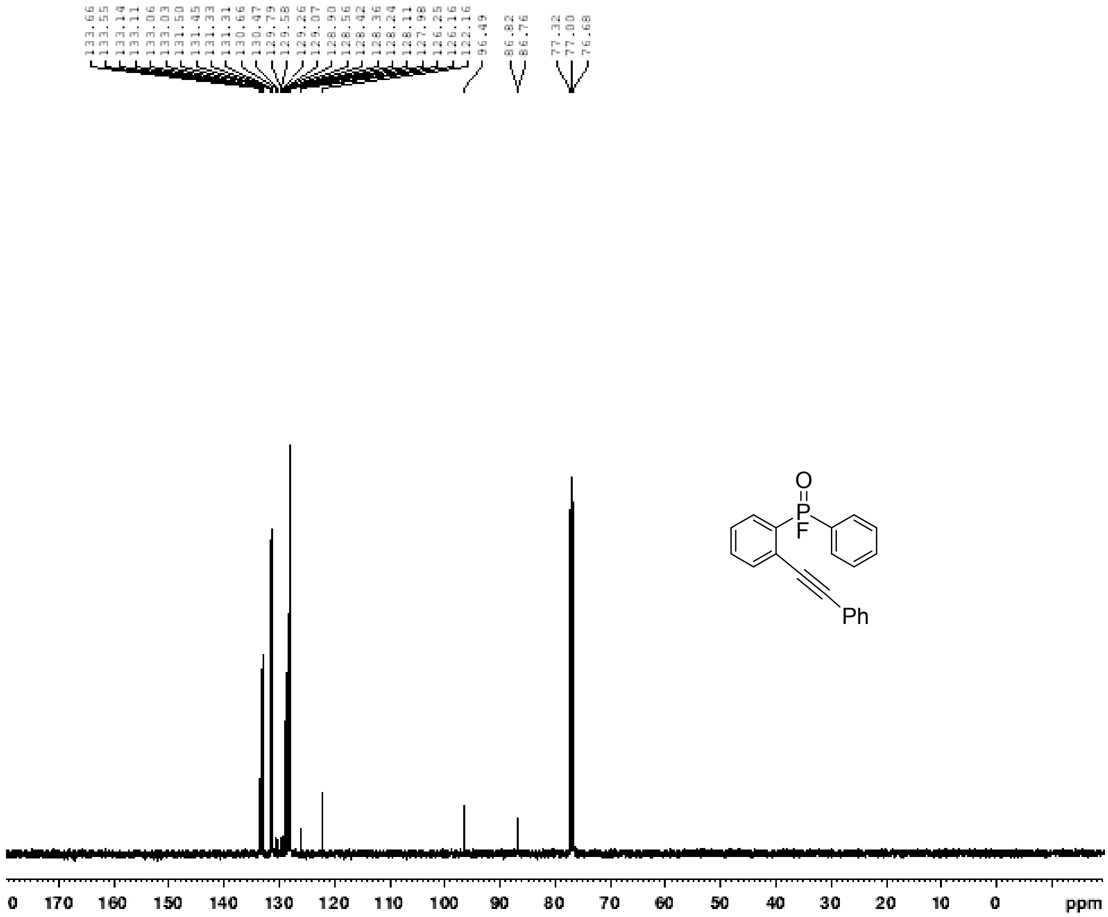
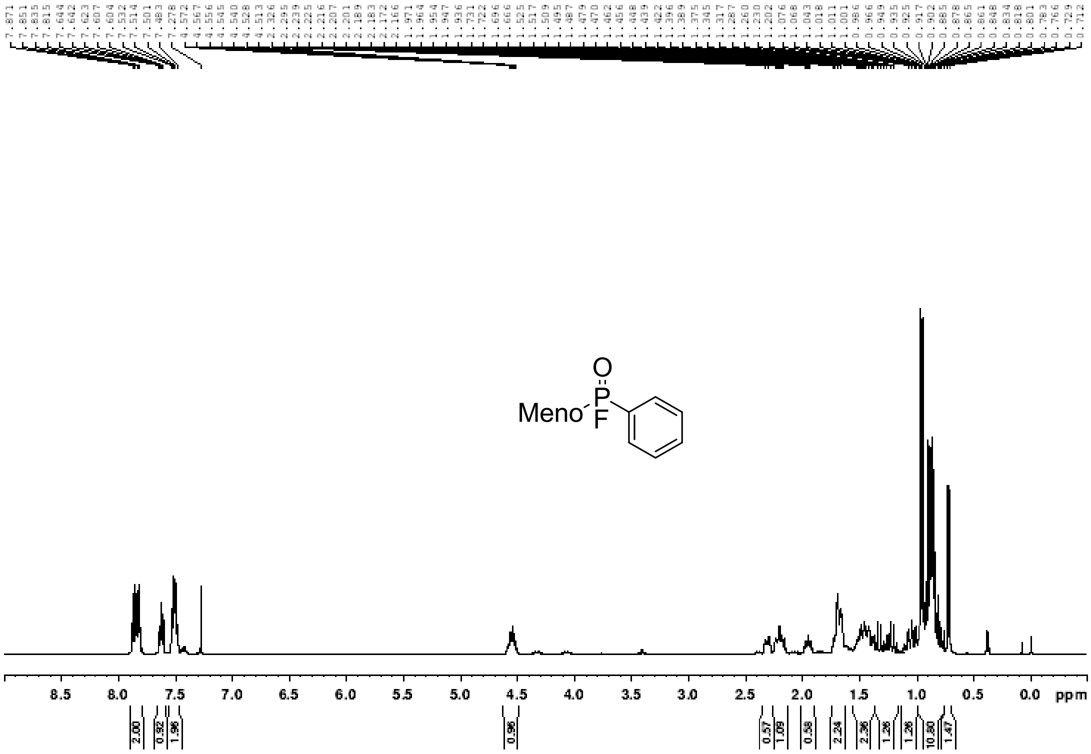
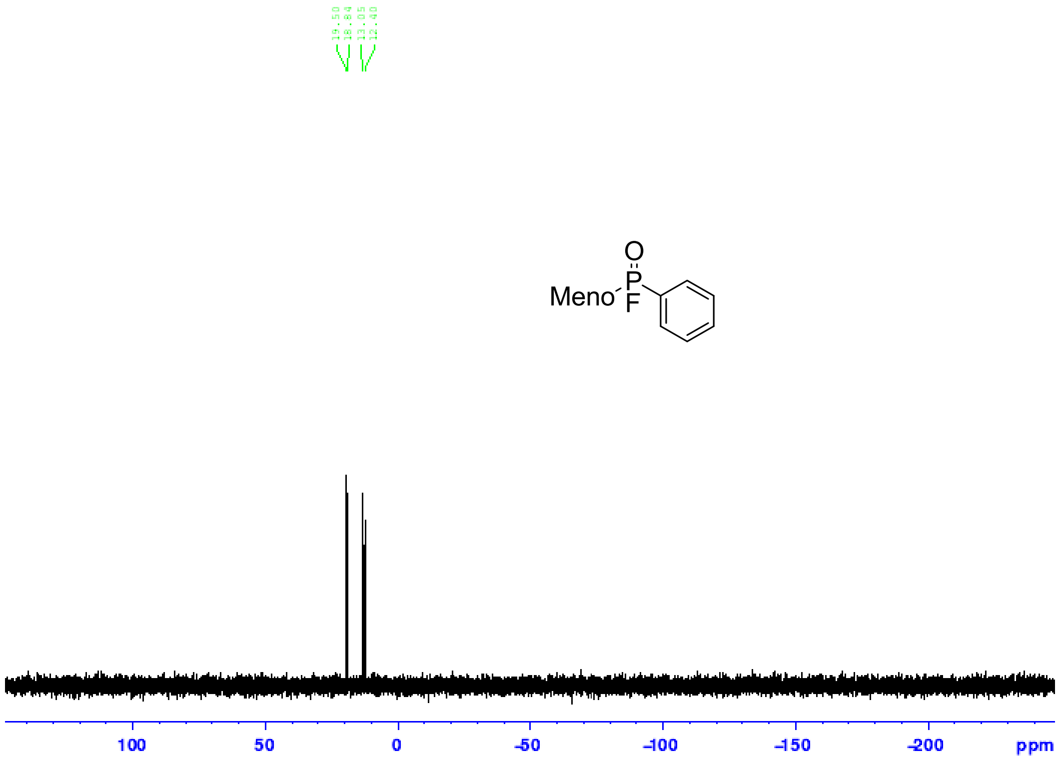


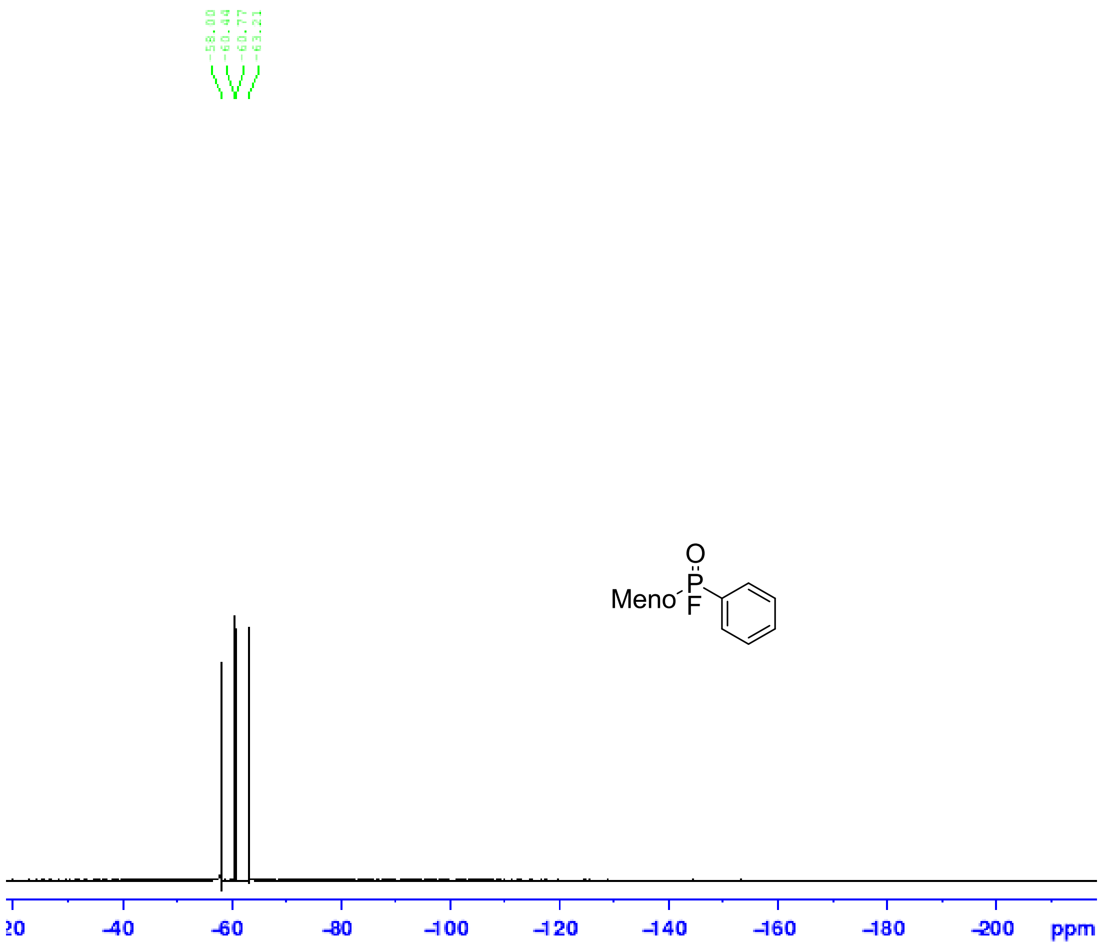



ppm

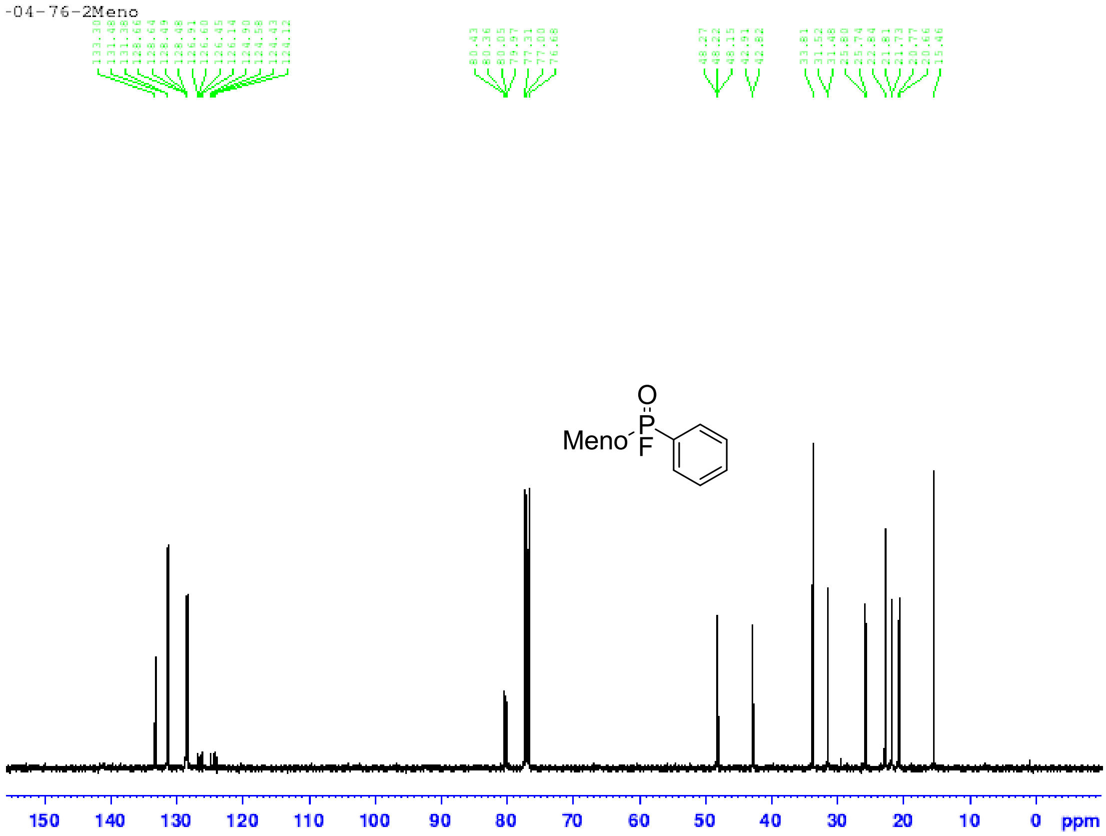

O
P
F
Ph
ppm


O
P
Meno
F
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

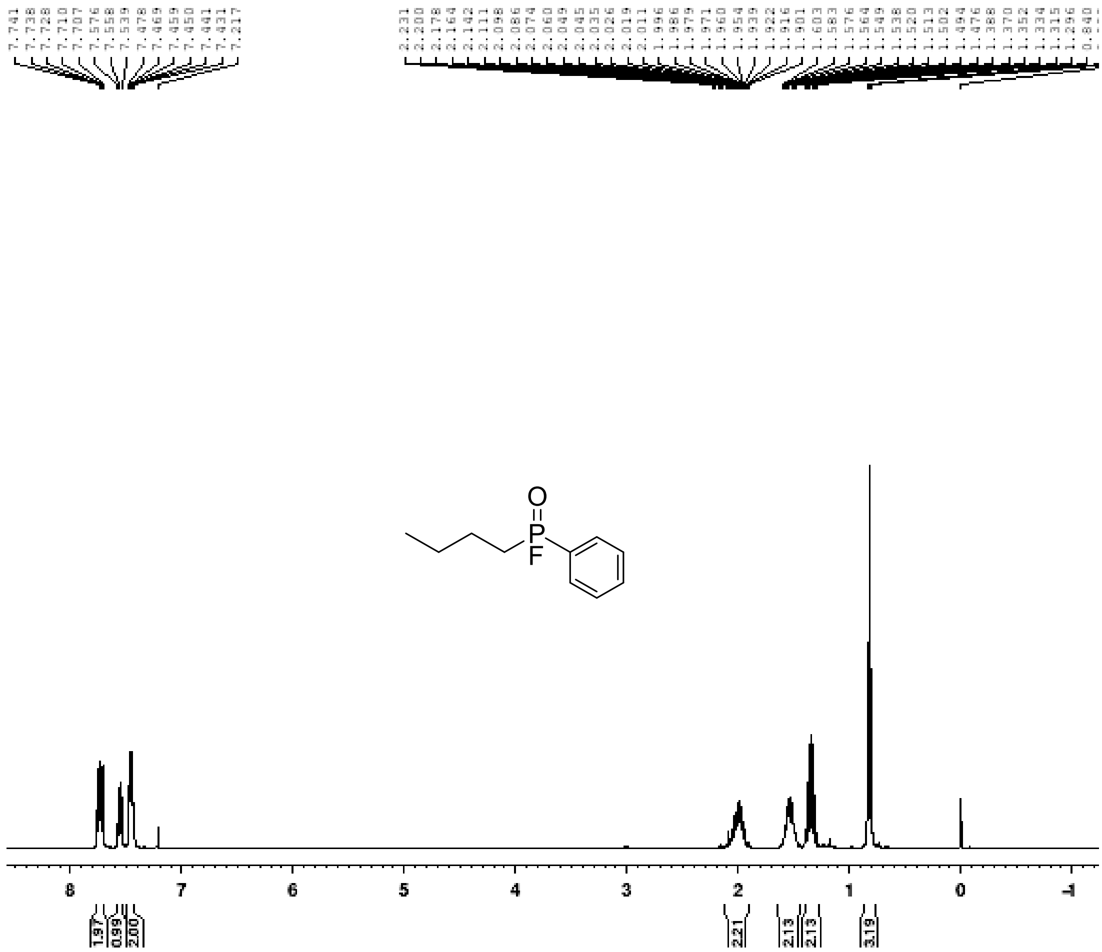

19.50
18.84
13.05
12.40
O
P
Meno
F
100
50
0
-50
-100
-150
-200
ppm

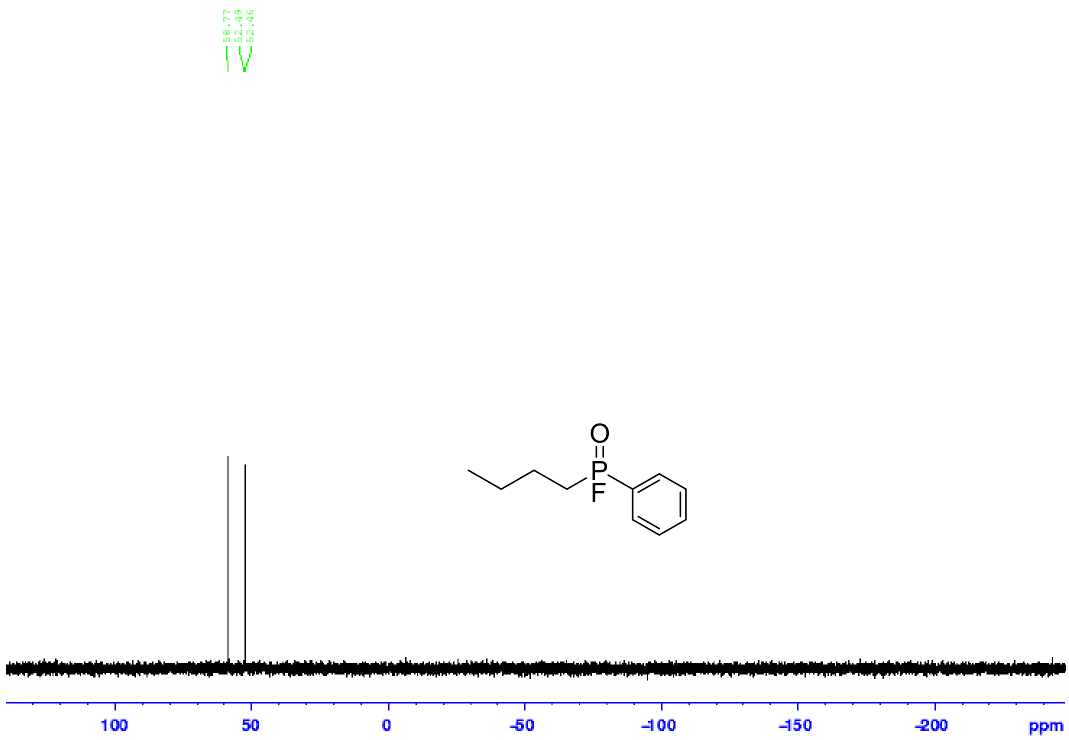


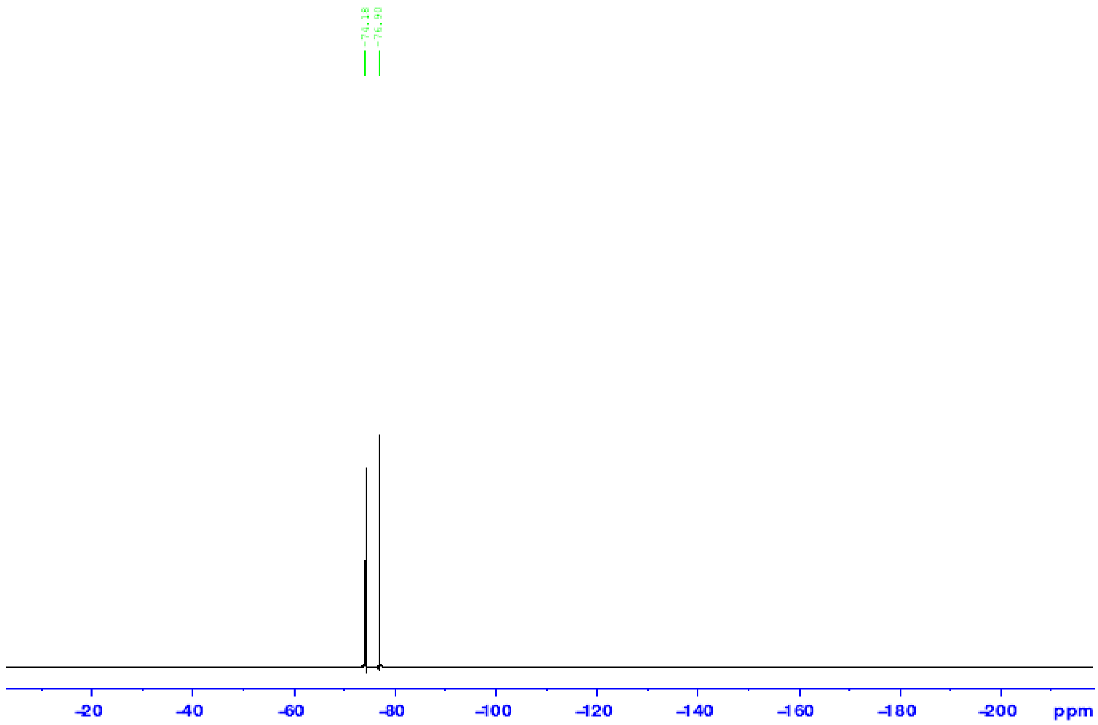
-58.00
-60.44
-60.77
-63.21
O
P
Meno
F
20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

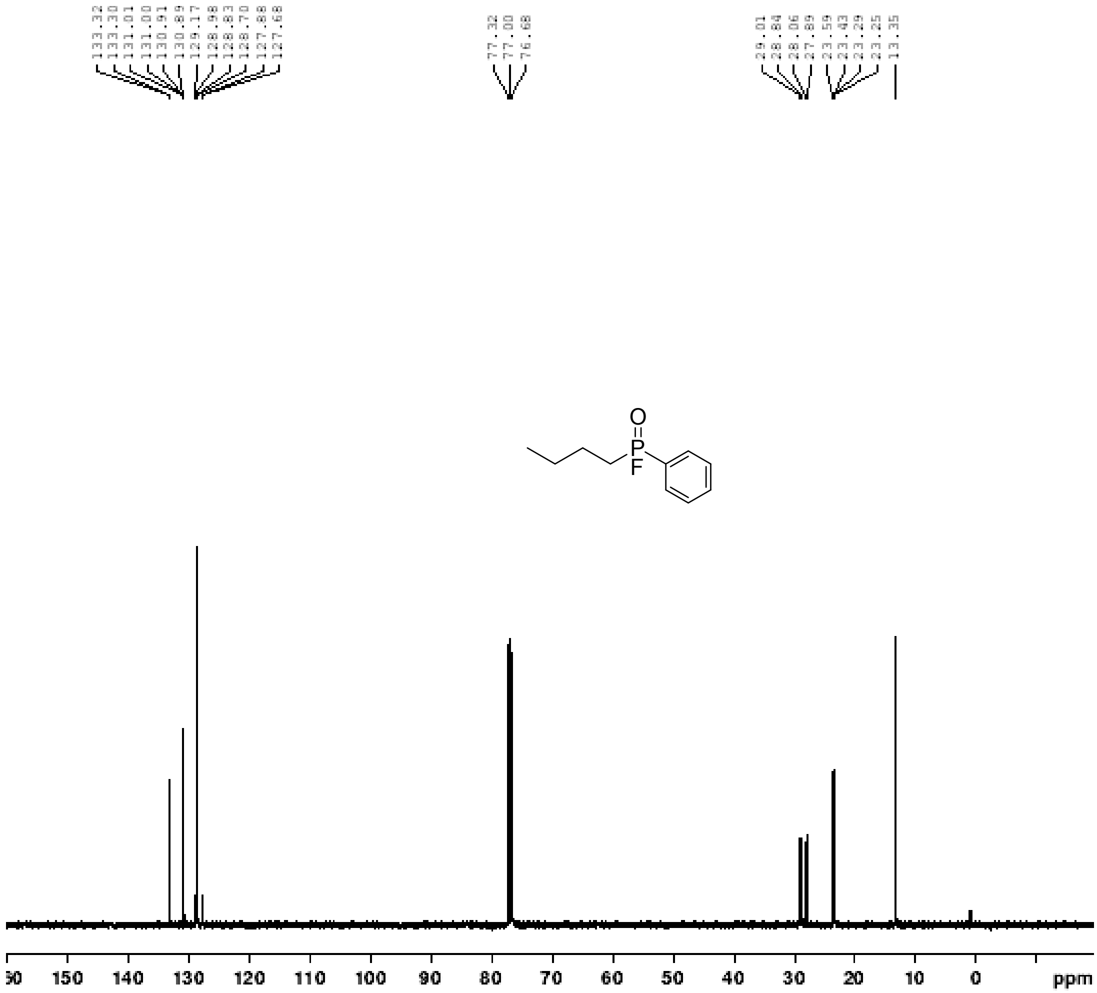


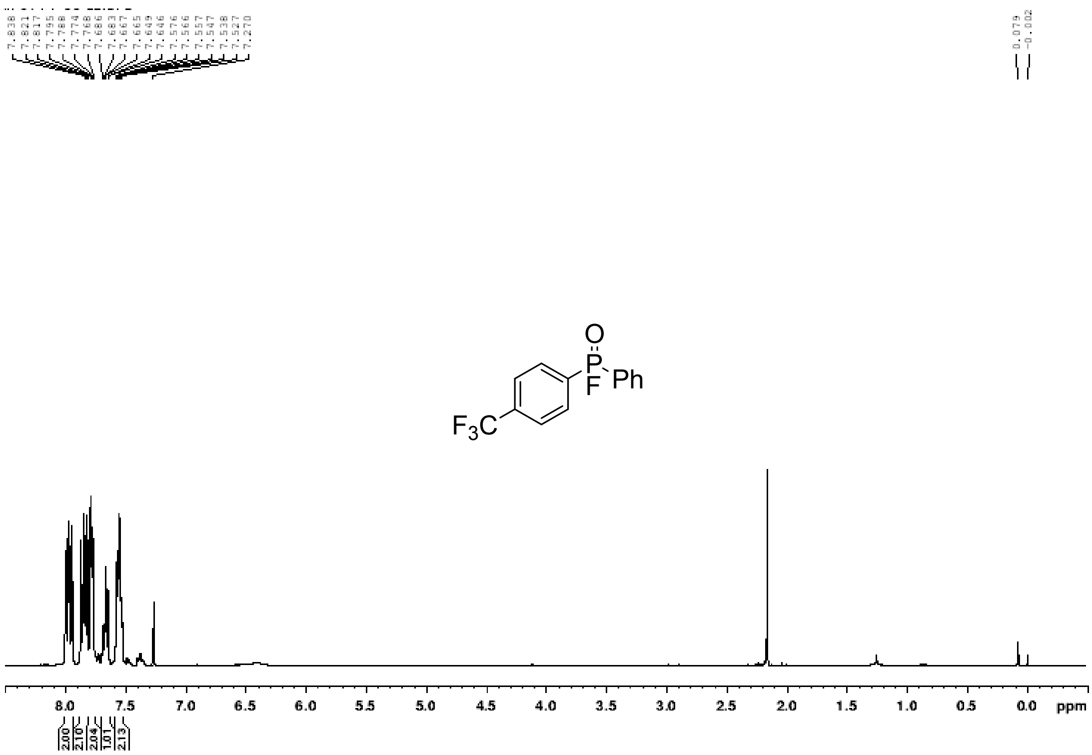
-04-76-2Meno
133.30
131.48
131.38
128.66
128.64
128.49
128.48
126.91
126.60
126.45
126.14
124.90
124.58
124.43
124.12
80.43
80.36
80.05
79.97
77.31
77.00
76.68
48.27
48.22
48.15
42.91
42.82
33.81
31.52
31.48
25.80
25.74
22.84
21.81
21.73
20.77
20.66
15.46
O
P
Meno
F
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.741
7.738
7.728
7.710
7.707
7.576
7.558
7.539
7.478
7.469
7.459
7.450
7.441
7.431
7.217
2.231
2.200
2.178
2.164
2.142
2.111
2.098
2.086
2.074
2.060
2.049
2.045
2.035
2.026
2.019
2.011
1.996
1.986
1.979
1.971
1.960
1.954
1.939
1.922
1.916
1.901
1.603
1.583
1.576
1.564
1.549
1.538
1.520
1.513
1.502
1.494
1.476
1.388
1.370
1.352
1.334
1.315
1.296
0.840
O
P
F
8
7
6
5
4
3
2
1
0
-1
1.97
0.99
2.00
2.21
2.13
2.13
3.19

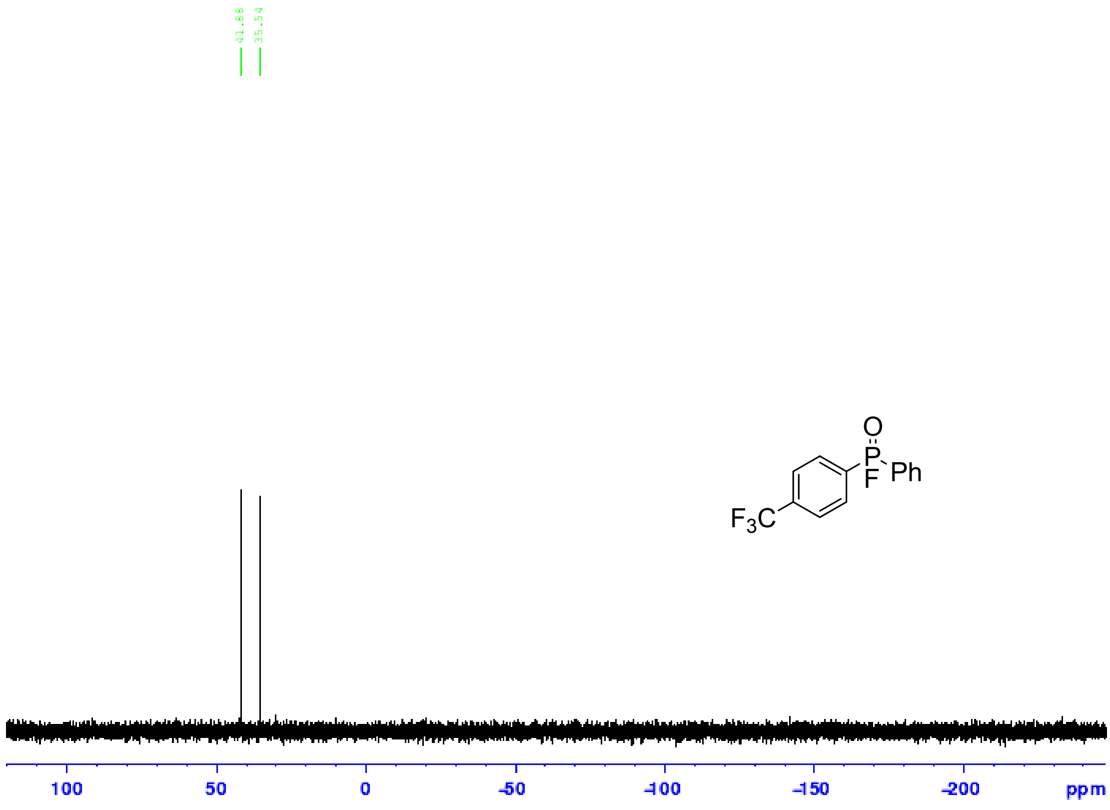

58.77
52.49
52.46
O
P
F
100
50
0
-50
-100
-150
-200
ppm



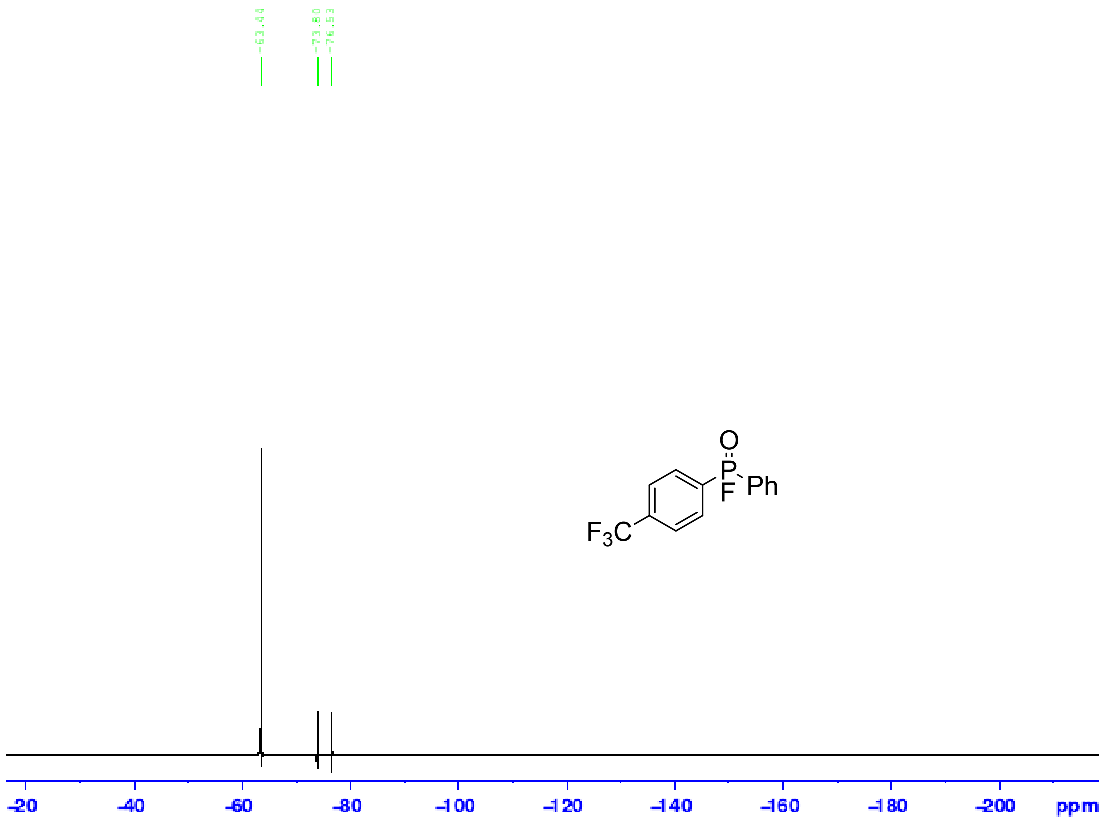




7.838
7.821
7.817
7.795
7.788
7.774
7.768
7.686
7.683
7.667
7.665
7.649
7.646
7.576
7.566
7.557
7.547
7.538
7.527
7.270
0.079
-0.002
O
P
Ph
F
F3C
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
2.10
2.04
1.01
2.13



41.88
35.54
O
P
Ph
F
F3C
100
50
0
-50
-100
-150
-200
ppm



-63.44
-73.80
-76.53
O
P
F
Ph
F3C
-20
-40
-60
-80
-100
-120
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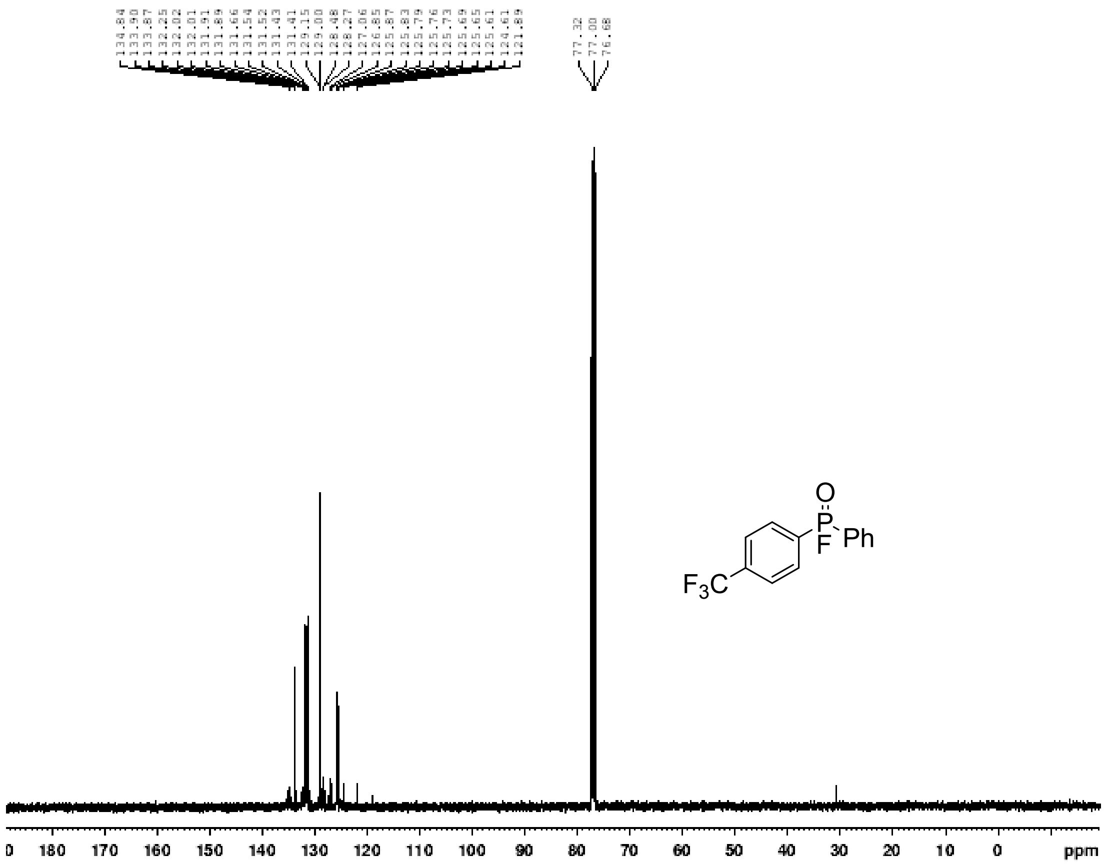
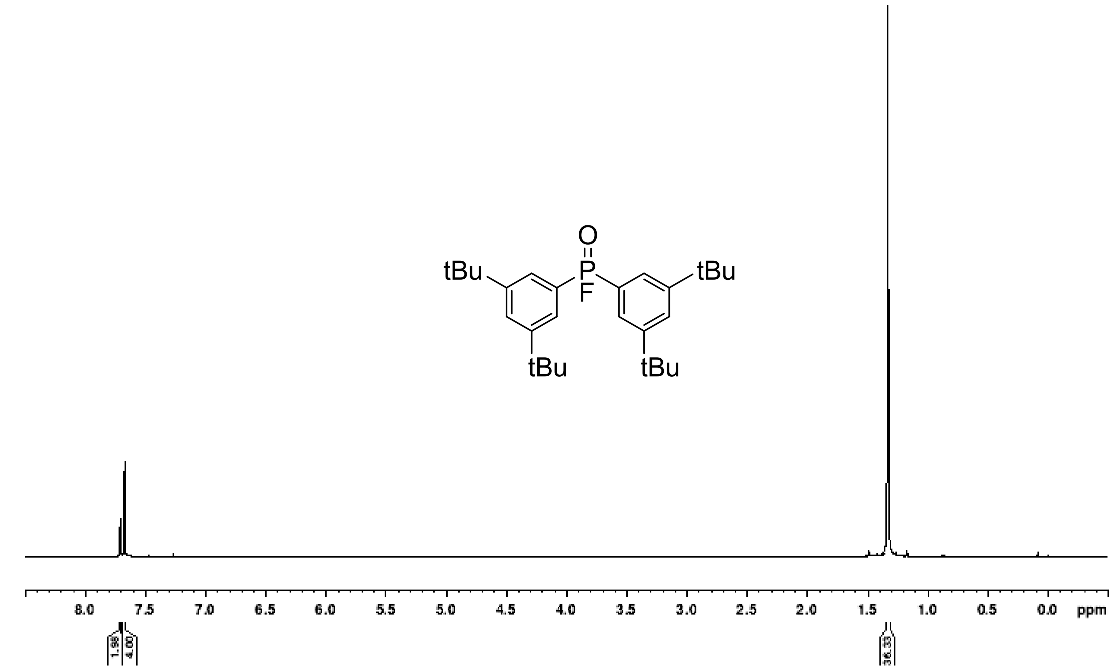
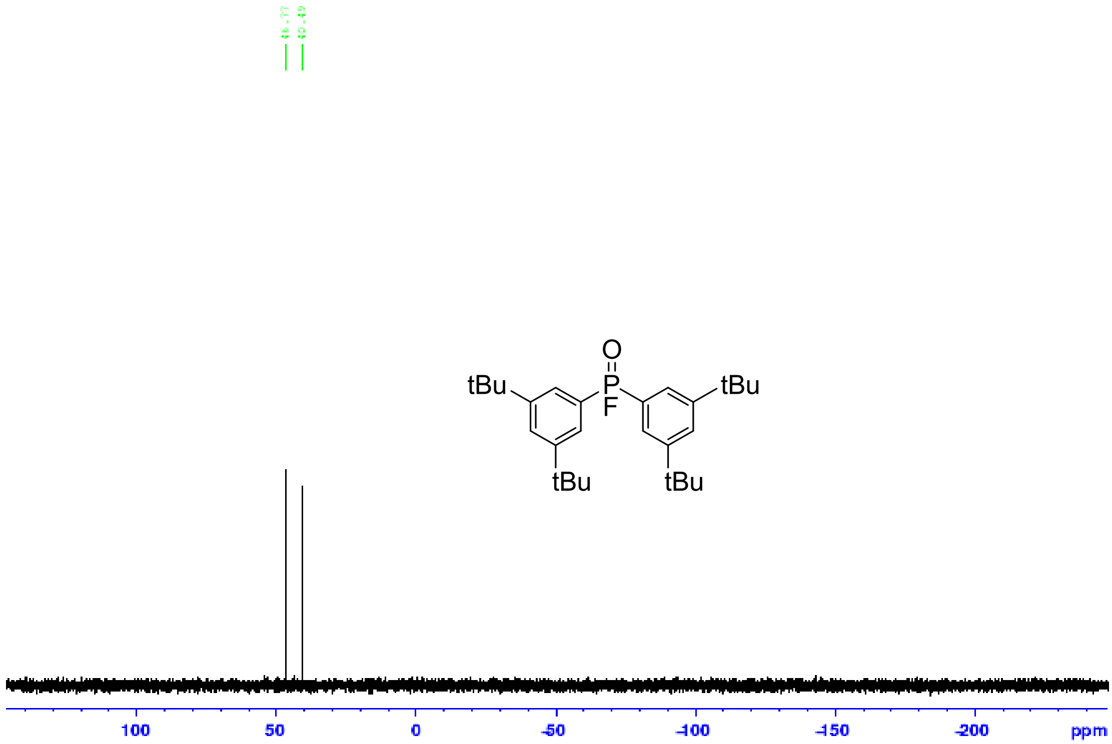
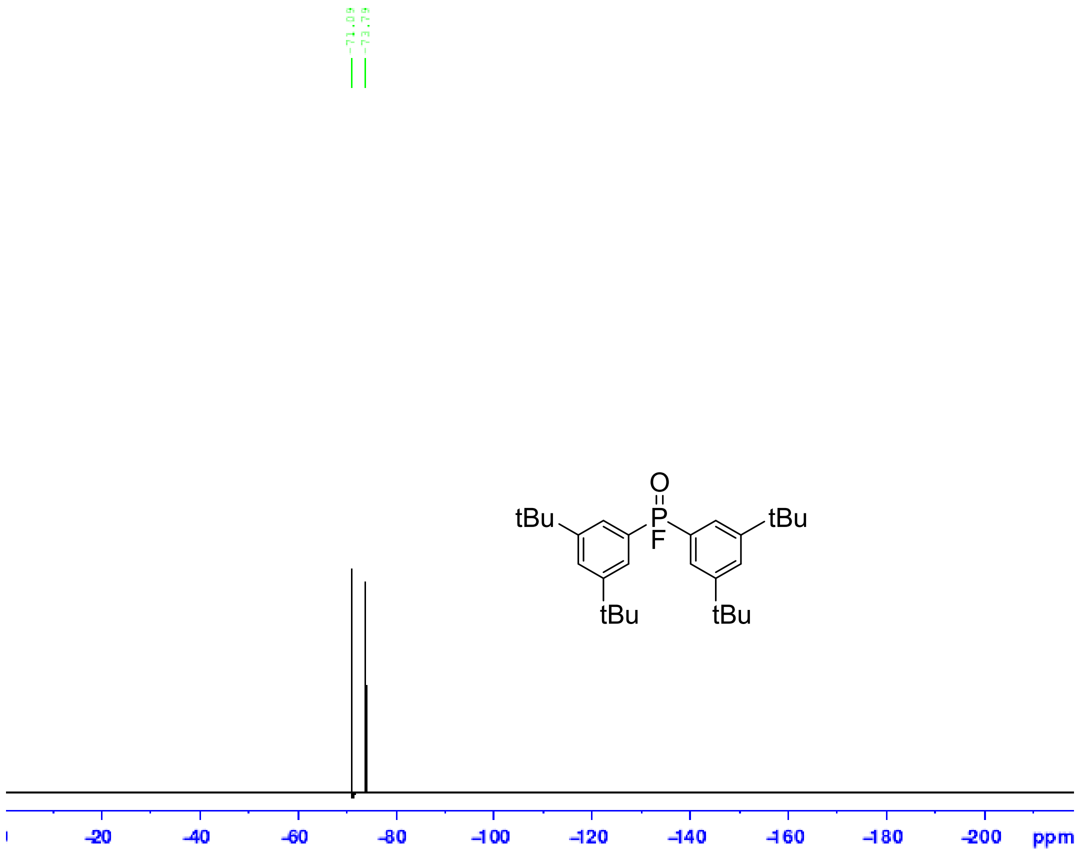
-160
-180
-200
ppm



134.84
133.90
133.87
132.25
132.02
132.01
131.91
131.89
131.66
131.54
131.52
131.43
131.41
129.15
129.00
128.48
128.27
127.06
126.85
125.87
125.83
125.79
125.76
125.73
125.69
125.65
125.61
124.61
121.89
77.32
77.00
76.68
O
P
F
Ph
F3C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
P
F
tBu
tBu
tBu
tBu
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
1.98
4.00
36.33


O
P
F
tBu
tBu
tBu
tBu
100 50 0 -50 -100 -150 -200 ppm


-71.09
-73.79
O
P
F
tBu
tBu
tBu
tBu
-20
-40
-60
-80
-100
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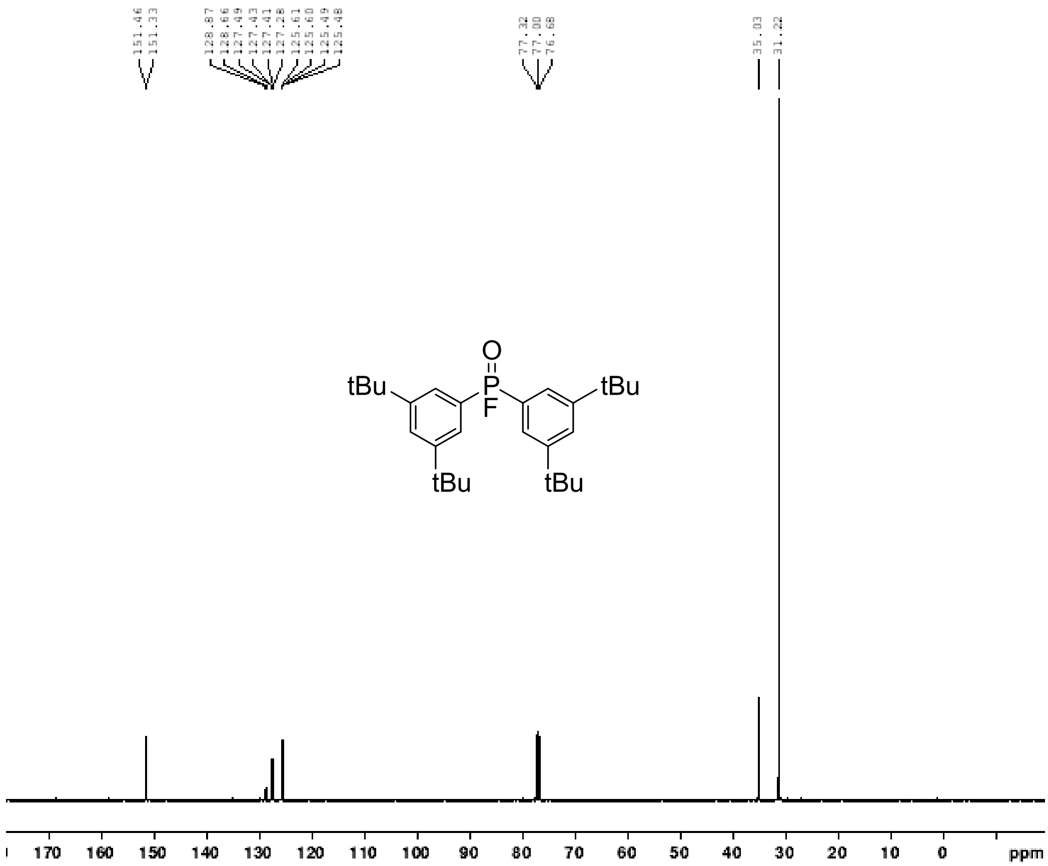
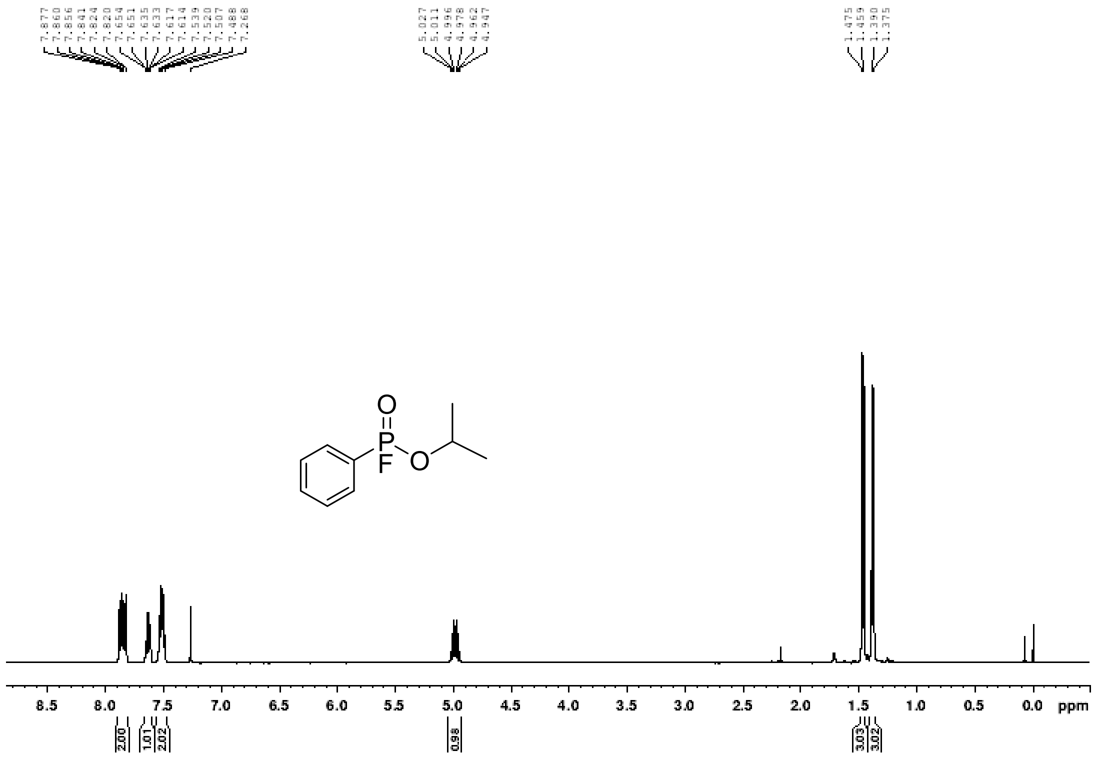
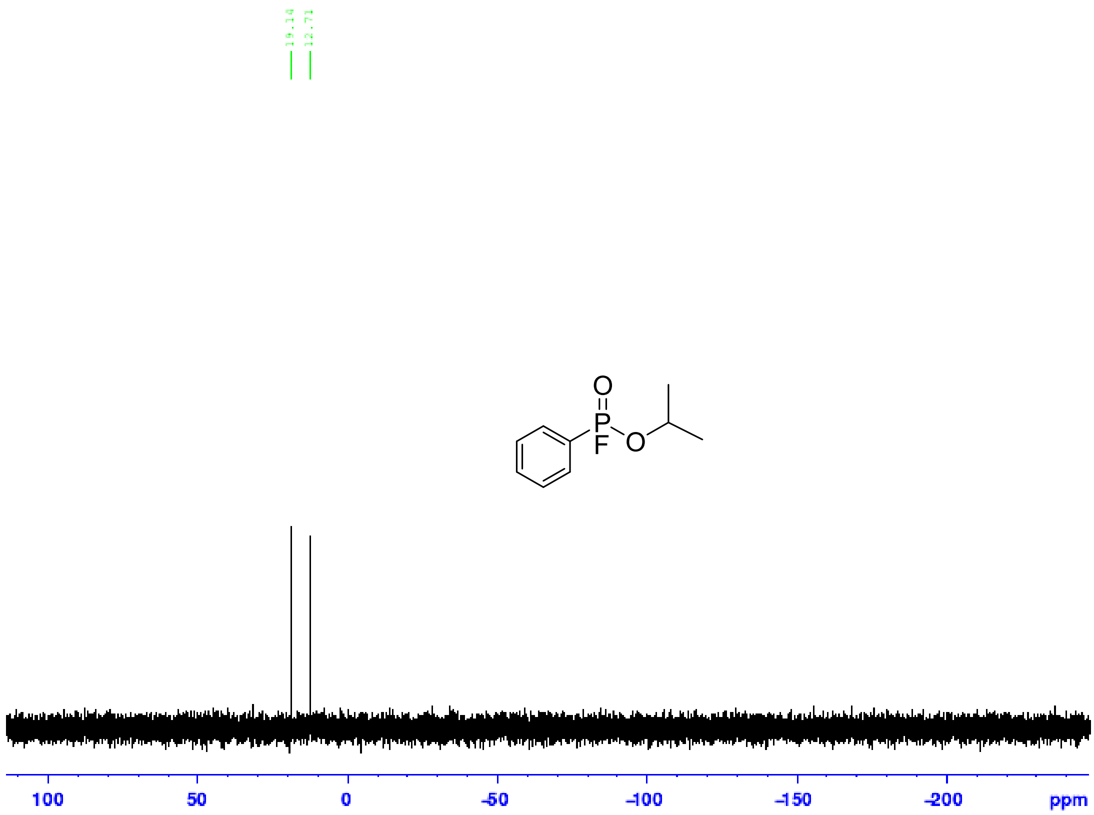
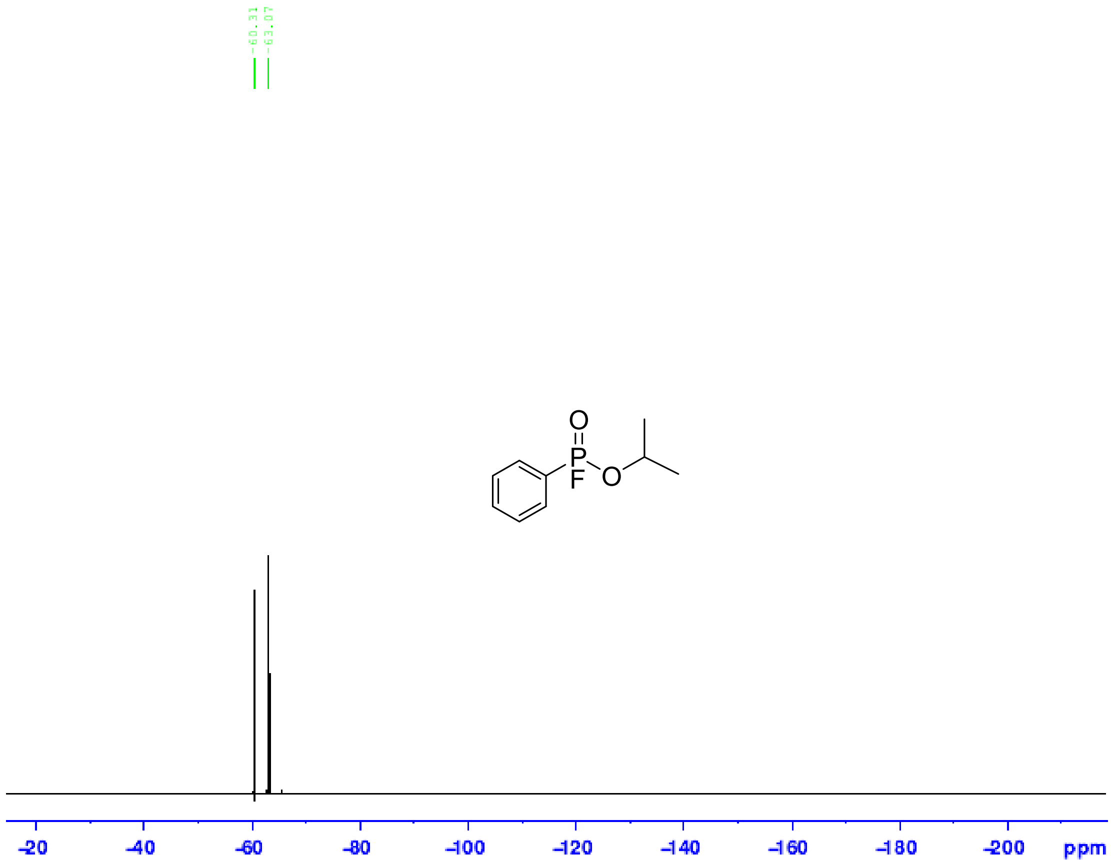
-140
-160
-180
-200
ppm


151.46
151.33
128.87
128.66
127.49
127.43
127.41
127.28
125.61
125.60
125.49
125.48
77.32
77.00
76.68
35.03
31.22
O
P
F
tBu
tBu
tBu
tBu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.877 7.860 7.856 7.841 7.824 7.820 7.654 7.651 7.635 7.633 7.617 7.614 7.539 7.520 7.507 7.488 7.268
5.027 5.011 4.996 4.978 4.962 4.947
1.475 1.459 1.390 1.375
O
P
F
O
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 1.01 2.02 0.98 3.03 3.02


12.71
O
P
F
O
100 50 0 -50 -100 -150 -200 ppm



-60.31
-63.07
O
P
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O
-20
-40
-60
-80
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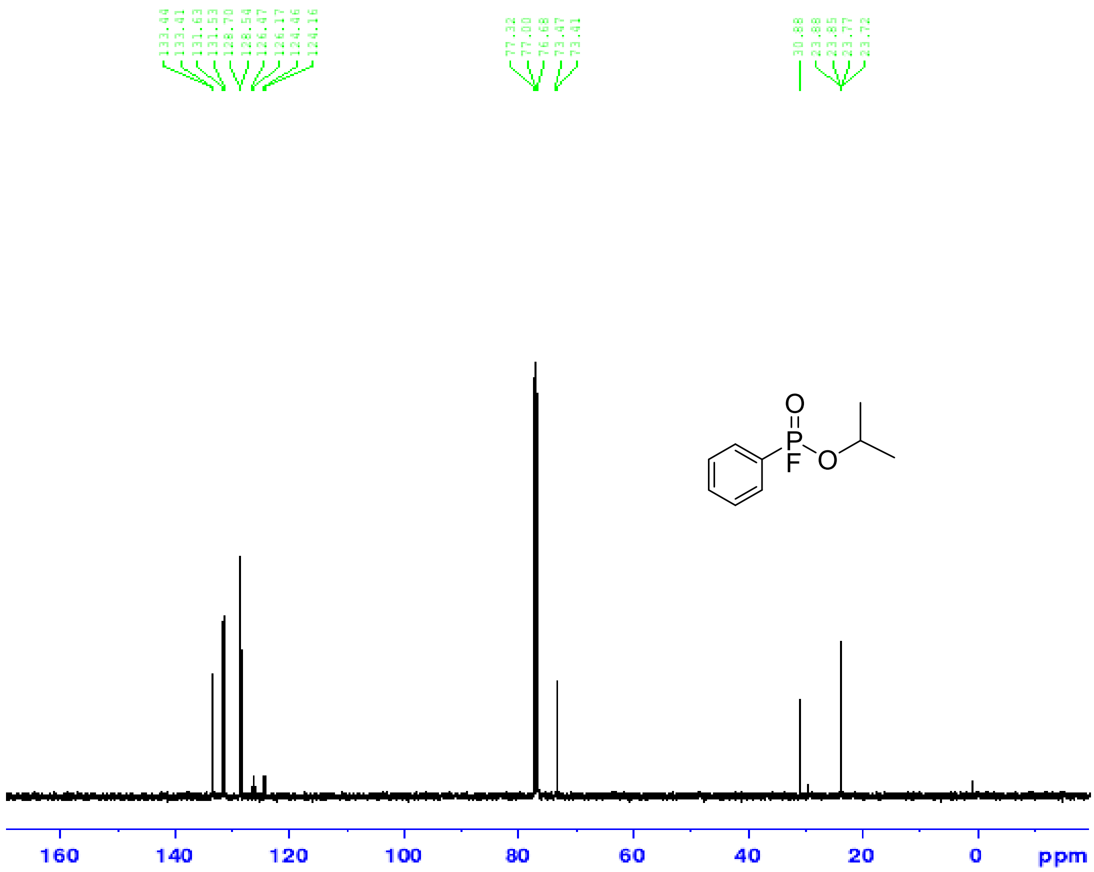
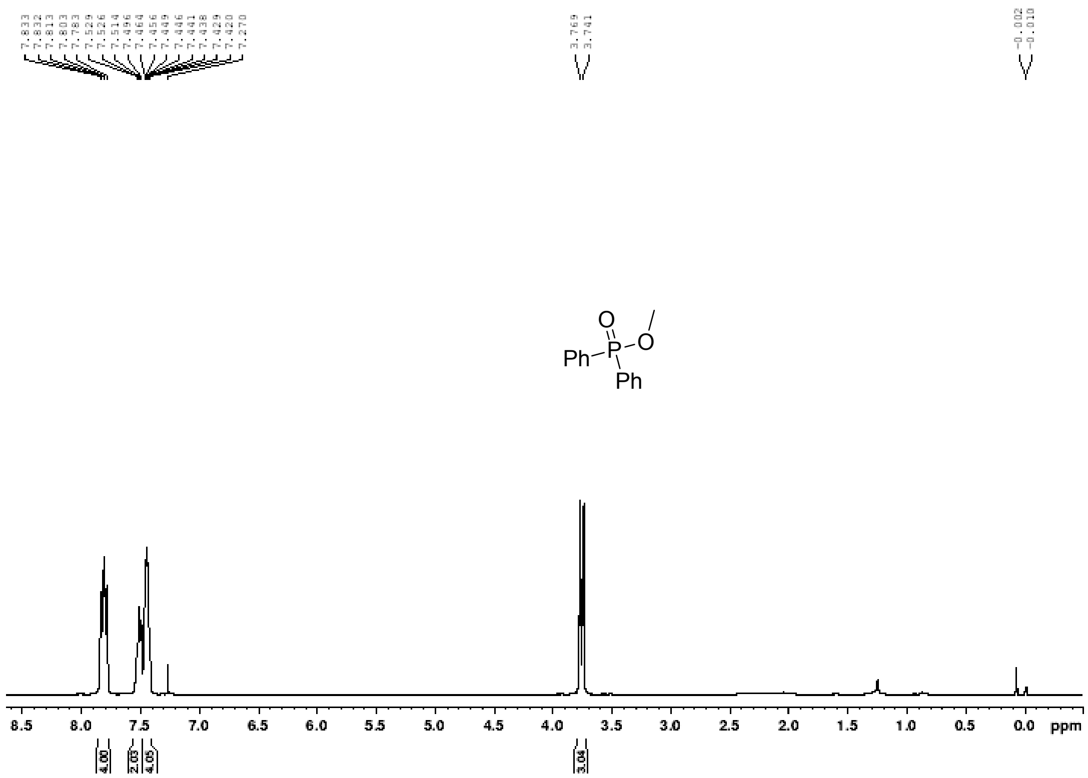
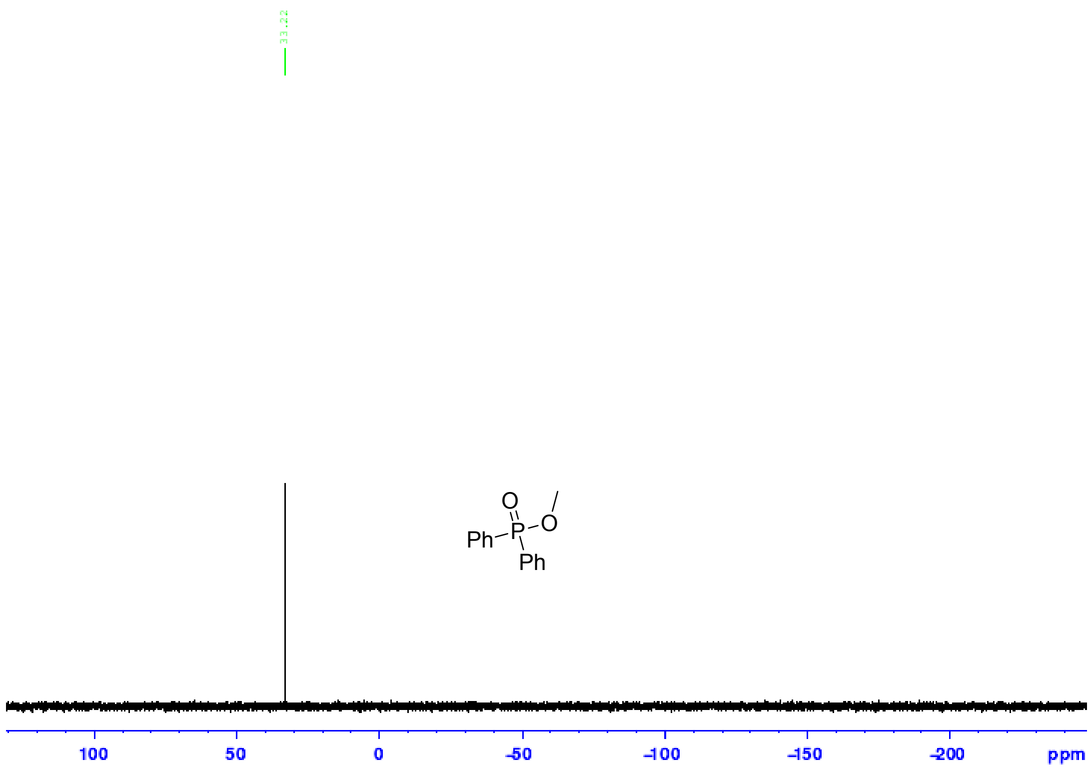
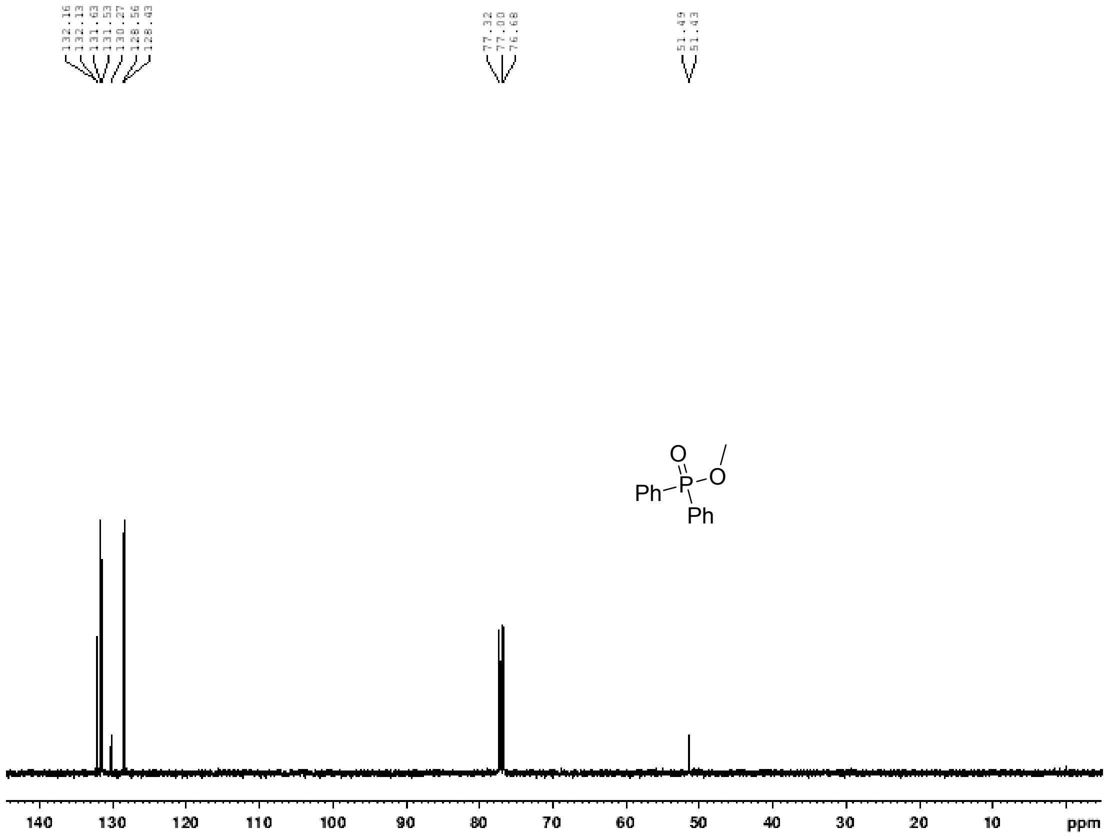
-160
-180
-200
ppm

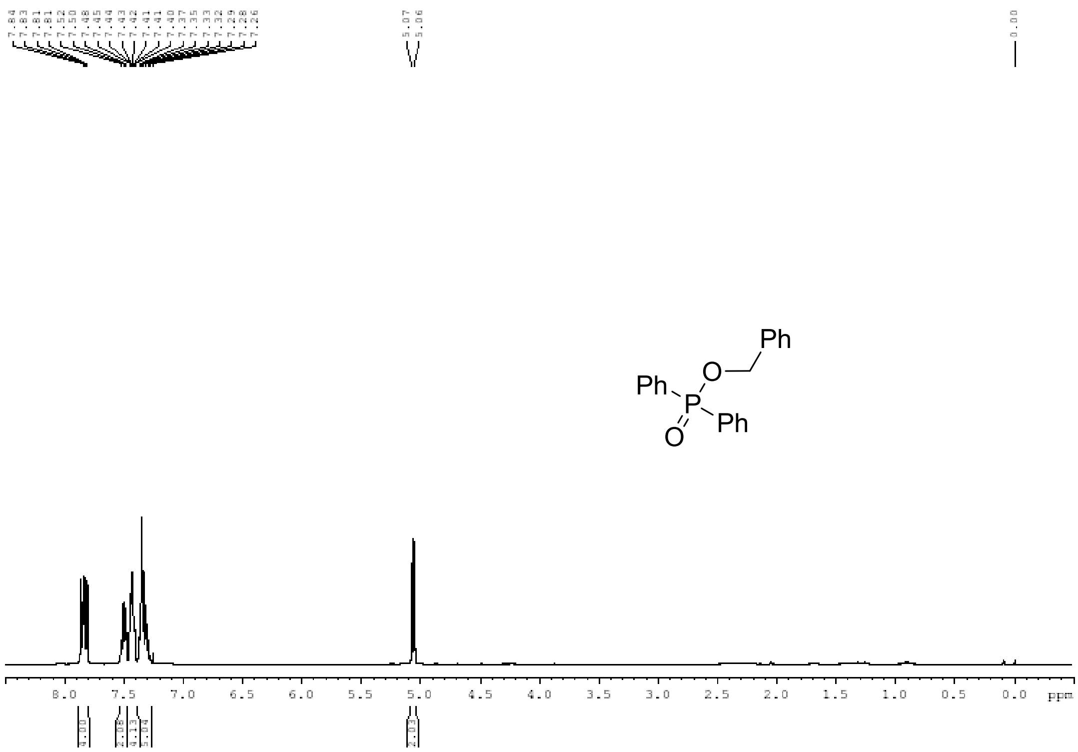


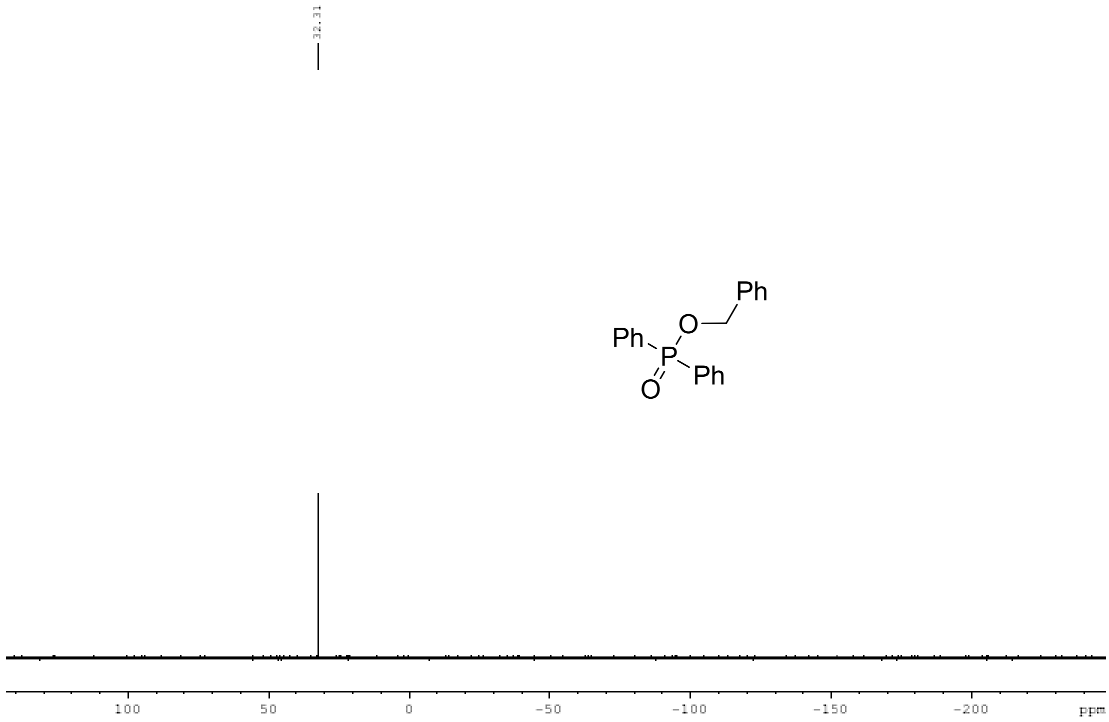
133.44
133.41
131.63
131.53
128.70
128.54
126.47
126.17
124.46
124.16
77.32
77.00
76.68
73.47
73.41
30.88
23.88
23.85
23.77
23.72
O
P
F
O
160
140
120
100
80
60
40
20
0
ppm

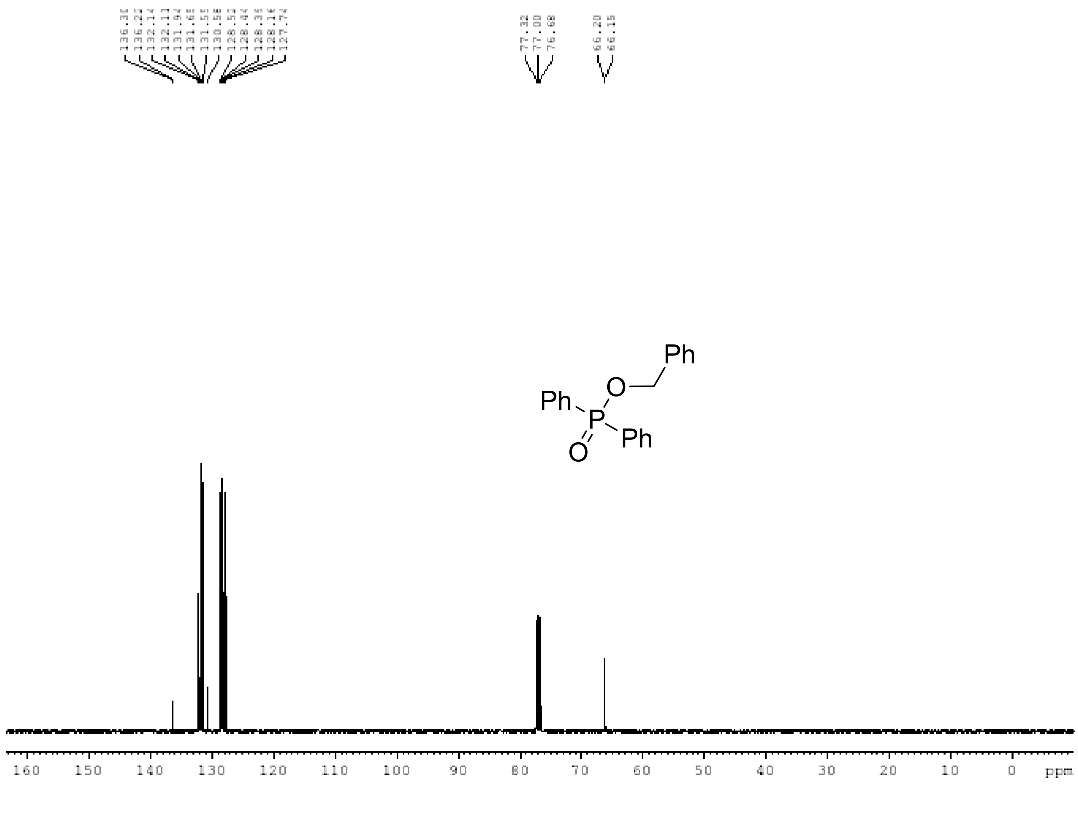

7.833
7.832
7.813
7.803
7.783
7.529
7.526
7.514
7.496
7.464
7.456
7.449
7.446
7.441
7.438
7.429
7.420
7.270
3.769
3.741
-0.002
-0.010
Ph
O
P
O
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.00
2.03
4.05
3.04

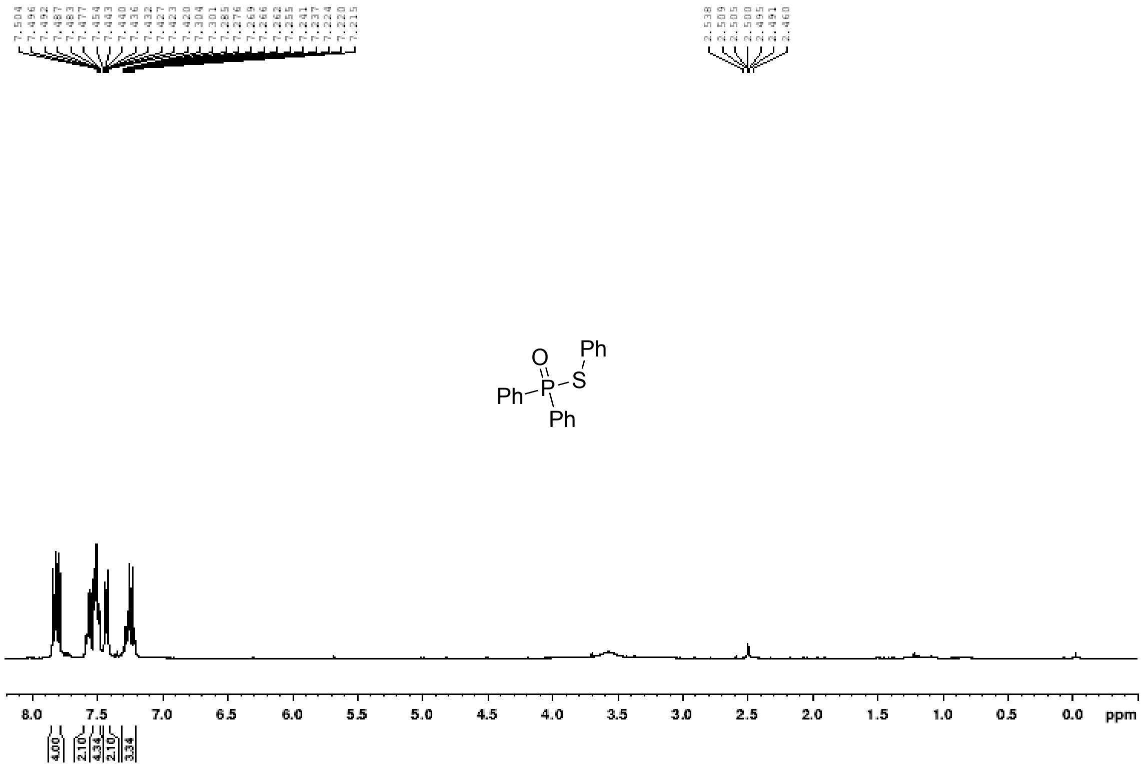

33.22
Ph
O
P
O
Ph
100
50
0
-50
-100
-150
-200
ppm

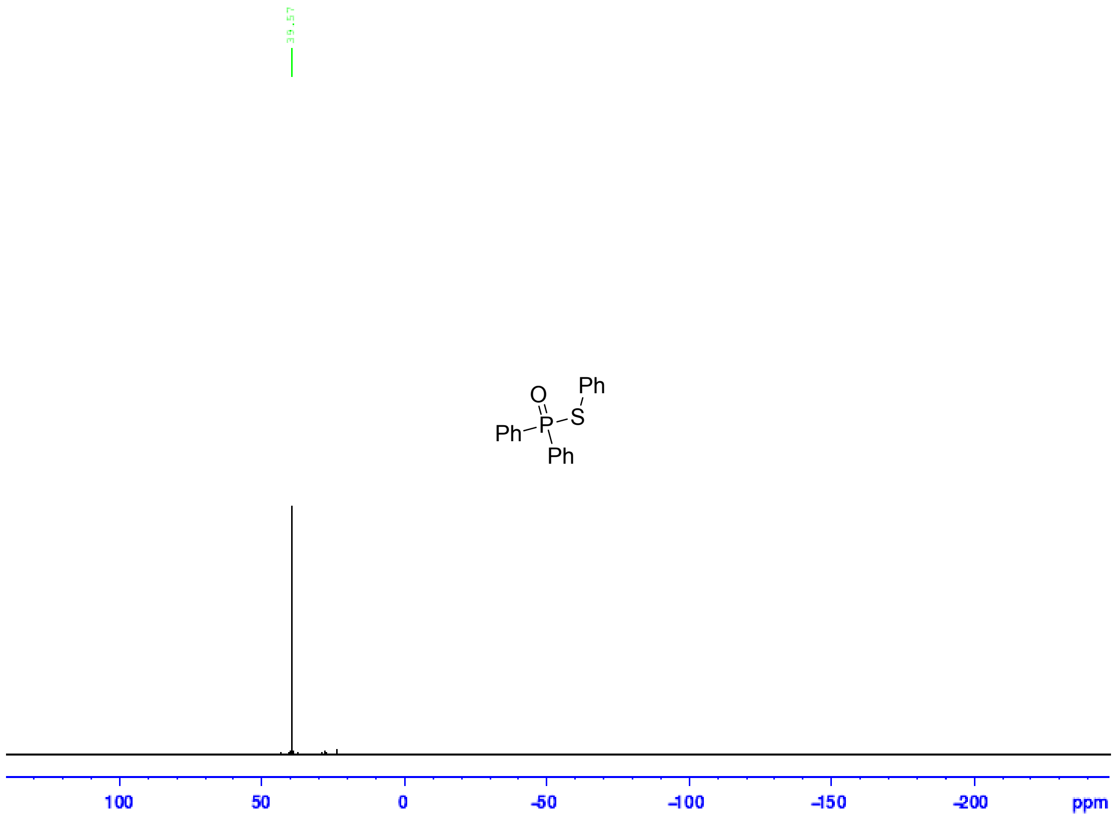

O
Ph
P
O
Ph
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

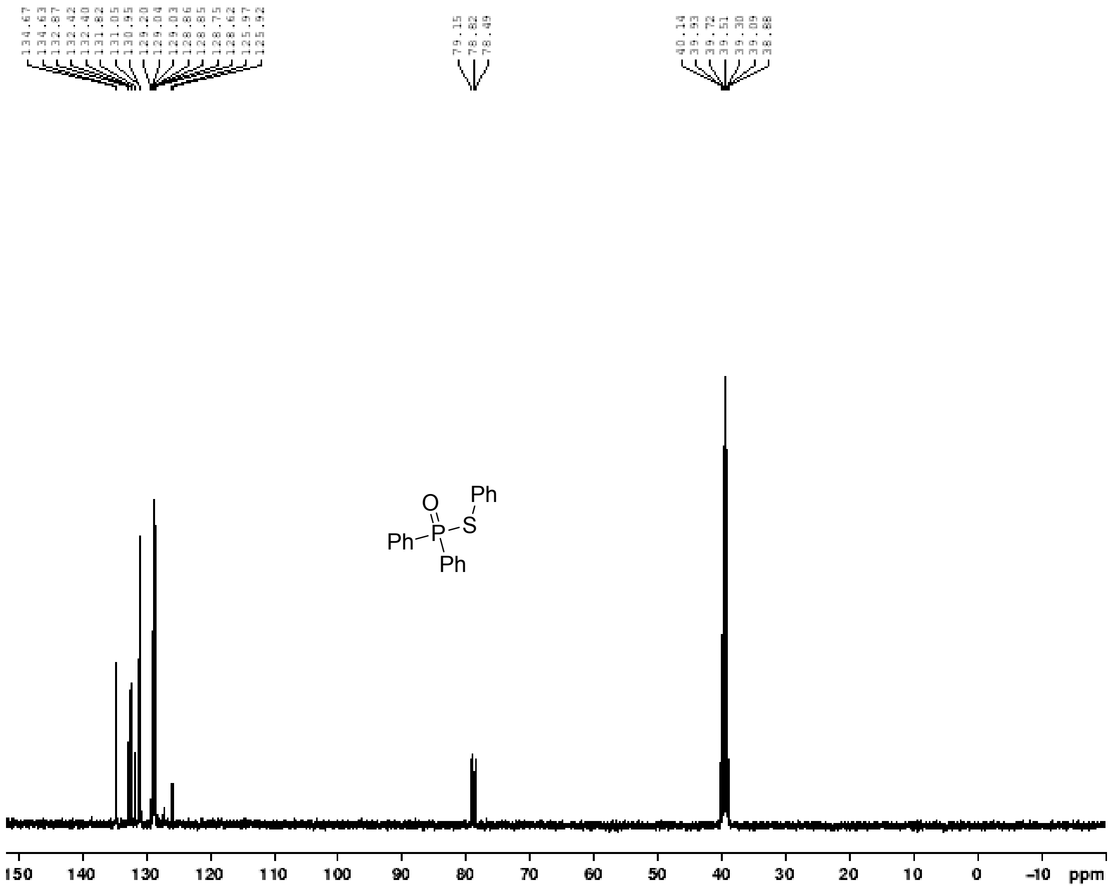

Ph
O
Ph
P
O
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

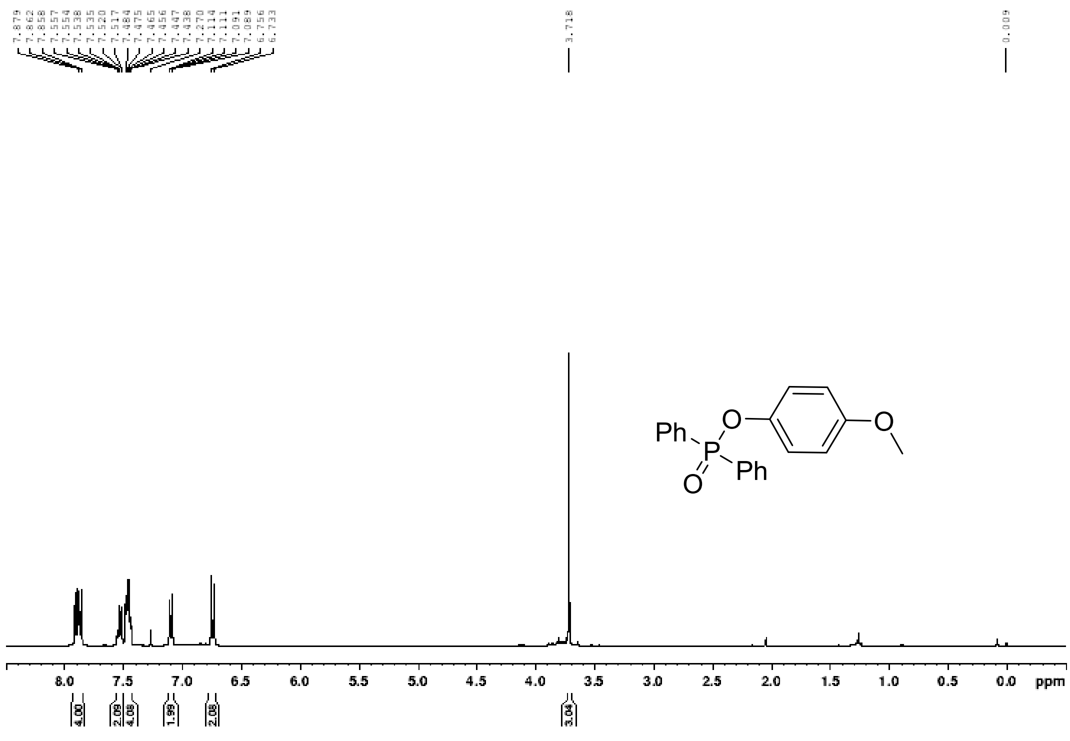

32.31
Ph
O
Ph
P
Ph
O
100
50
0
−50
−100
−150
−200
ppm

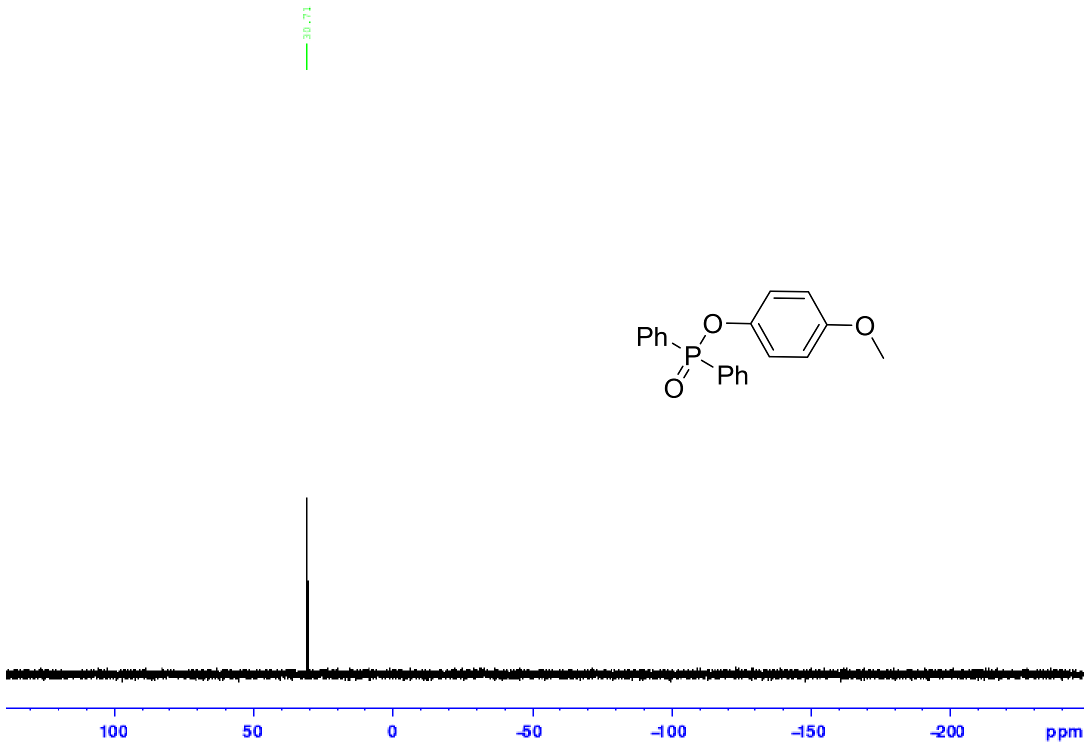

136.30
136.22
132.13
132.11
131.94
131.68
131.58
130.58
128.52
128.44
128.35
128.16
127.74
77.32
77.00
76.68
66.20
66.15
Ph
O
Ph
P
Ph
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

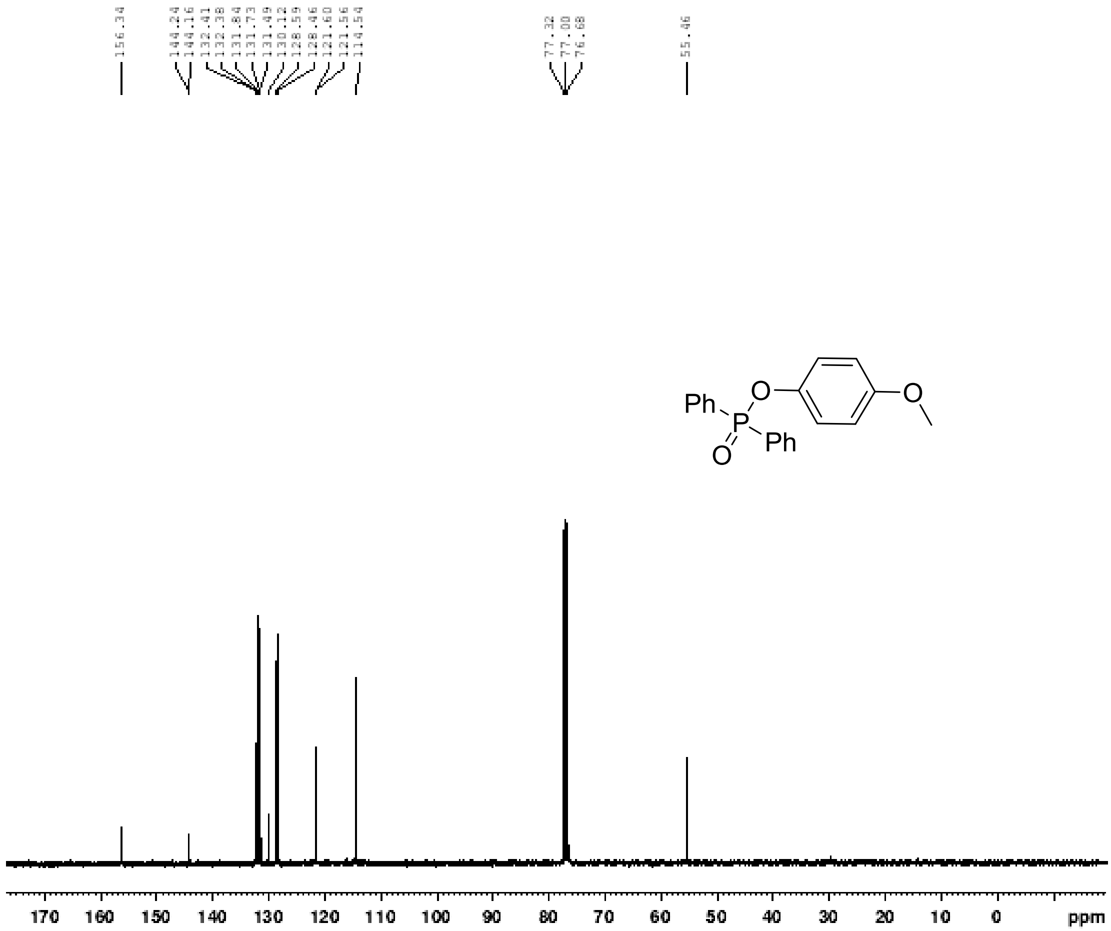

7.504
7.496
7.492
7.487
7.483
7.477
7.454
7.443
7.440
7.436
7.432
7.427
7.423
7.420
7.304
7.301
7.285
7.276
7.269
7.266
7.262
7.255
7.241
7.237
7.224
7.220
7.215
2.538
2.509
2.505
2.500
2.495
2.491
2.460
O
Ph
P
S
Ph
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.00
2.10
4.34
2.10
3.34


39.57
O
Ph
P
S
Ph
Ph
100
50
0
-50
-100
-150
-200
ppm


134.67
134.63
132.87
132.42
132.40
131.82
131.05
130.95
129.20
129.04
129.03
128.86
128.85
128.75
128.62
125.97
125.92
79.15
78.82
78.49
40.14
39.93
39.72
39.51
39.30
39.09
38.88
Ph
O
S
Ph
P
Ph
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
ppm


3.718
0.009
Ph
O
O
P
Ph
O
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
2.09
4.08
1.99
2.08
3.04


30.71
Ph
O
P
Ph
O
O
100
50
0
-50
-100
-150
-200
ppm


156.34
144.24
144.16
132.41
132.38
131.84
131.73
131.49
130.12
128.59
128.46
121.60
121.56
114.54
77.32
77.00
76.68
55.46
Ph
O
P
Ph
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm