Supporting Materials for:

A Novel Copper-Catalyzed Reductive Coupling of *N*-tosylhydrazones with *H*-phosphorus oxides

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1. General Infomations

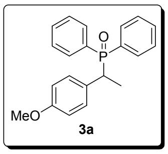
Solvents and reagents were reagent grade and used without purification unless otherwise noted. Anhydrous solvents were obtained as follow: THF and dioxane by distillation from sodium and benzophenone; All reactions were carried out in oven dried glassware under nitrogen or argon unless otherwise specified. All ^{1}H-NMR (400 MHz) spectra were recorded on a Bruker-DMX 400 using $CDCl_3$ solution in the presence of tetramethylsilane (TMS) as an internal standard and are reported in ppm (δ). Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; and br, broad. High and Low resolution fast atom bombardment (FAB) measurements were made with a JEOL JMS-AX505HA mass spectrometer.

2. General Procedures for Copper-Catalyzed Reductive Coupling

2 mmol diaryl phosphine oxide or *H*-phosphonate, 1 mmol *N*-Tosylhydrazone and 3 mmol K_2CO_3 were charged into 25 mL oven-dried flask, and backfilled with nitrogen three times. 5 mL fresh-distilled 1,4-dioxane or DMF was then injected into the flask, following by heating up to 110 ^{o}C for 2 hrs. The reaction was monitored by TLC until starting materials consumed, then removed all of the volatiles for further purification on silica chromatography. (Generally, 100% Ethyl Acetate was selected as eluent.)

3. Characterizations of Coupling Products (^{1}HNMR, ^{13}CNMR, ^{31}PNMR, HR-MS)

3a White solids.



[Ref. P. Cheruku, A. Paptchikhine, T. L. Church, P. G. Andersson, *J. Am. Chem. Soc.* **2009**, 131, 8285-8289.]

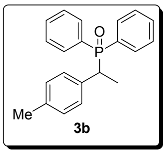
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.56 (dd, J = 16, 7.6 Hz, 3H), 3.59 (qu, J = 14.8, 7.6 Hz, 1H), 3.76 (s, 3H), 6.75 (d, J = 8.8 Hz, 2H), 7.16 (dd, J = 8.4, 2.4 Hz, 2H), 7.27-7.40 (m, 3H), 7.47-7.58 (m, 5H), 7.88-7.93 (m, 2H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 15.60 (d, $J_{C,P}$ = 2.0 Hz), 39.97 (d, $J_{C,P}$ = 67.4 Hz), 55.20, 113.70 (d, $J_{C,P}$ = 1.20 Hz), 127.99, 128.11, 128.58, 128.69, 129.77 (d, $J_{C,P}$ = 5.60 Hz), 130.14, 130.20, 131.13, 131.22, 131.24, 131.27, 131.35, 131.43, 131.63, 131.66, 131.69, 132.60 (d, $J_{C,P}$ = 13.5 Hz), 158.51 (d, $J_{C,P}$ = 2.2 Hz).

^{31}PNMR δ: 33.48.

HR-MS: calcd for $C_{21}H_{22}O_2P$ 337.1357 ([M + H^+]), found 337.1355.

3b White solids.



[Ref. (a) P. Cheruku, A. Paptchikhine, T. L. Church, P. G. Andersson, *J. Am. Chem. Soc.* **2009**, 131, 23, 8285-8289; (b) D. A. Jaeger, D. Bolikal, *J. Org. Chem.* **1986**, 51, 1350-1352.]

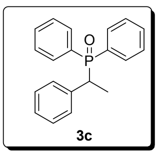
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.579 (dd, J = 16.0, 7.6 Hz, 3H), 2.293 (s, 3H), 3.606 (qu, J = 15.20, 7.6 Hz, 1H), 7.022 (d, J = 8 Hz, 2H), 7.131 (dd, J = 7.6, 1.6 Hz, 2H), 7.302-7.321 (m, 2H), 7.376-7.413 (m, 1H), 7.485-7.596 (m, 5H), 7.893-7.939 (m, 2H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 15.60 (d, $J_{C,P}$ = 2.60 Hz), 21.05, 40.40 (d, $J_{C,P}$ = 67.1 Hz), 127.98, 128.10, 128.58, 128.69, 128.97, 128.99, 129.02, 129.07, 131.13, 131.22, 131.25 (d, $J_{C,P}$ = 2.60 Hz), 131.31, 131.40, 131.63, 131.67 (d, $J_{C,P}$ = 3.0 Hz), 132.64 (d, $J_{C,P}$ = 3.30 Hz), 134.80 (d, $J_{C,P}$ = 5.70 Hz), 136.43 (d, $J_{C,P}$ = 2.40 Hz).

^{31}PNMR δ: 33.34.

HR-MS: calcd for $C_{21}H_{22}OP$ 321.1408 ([M + H^+]), found 321.1403.

3c White solids.



[Ref. (a) P.-Y. Renard, P. Vayron, E. Leclerc, A. Valleix, C. Mioskowski, *Angew. Chem. Int. Ed.* **2003**, 42, 2389-2392; (b) U. Berens, *Eur. Pat. Appl.* **2005**, 17pp. coden: EPXXDW EP 1582527 A1 20051005.]

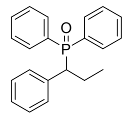
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.61 (dd, J = 16.0, 7.2 Hz, 3H), 3.63 (qu, J = 14.80, 7.2 Hz, 1H), 7.20-7.25 (m, 5H), 7.30-7.39 (m, 3H), 7.45-7.50 (m, 2H), 7.55-7.58 (m, 3H), 7.91-7.95 (m, 2H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 15.46 (d, $J_{C,P}$ = 2.80 Hz), 40.98 (d, $J_{C,P}$ = 66.7 Hz), 126.89 (d, $J_{C,P}$ = 2.30 Hz), 127.96, 128.07, 128.24, 128.26, 128.60, 128.71, 129.18, 129.23, 131.10, 131.19, 131.27 (d, $J_{C,P}$ = 2.70 Hz), 131.36, 131.44, 131.51, 131.60, 131.69 (d, $J_{C,P}$ = 2.50 Hz), 132.51 (d, $J_{C,P}$ = 13.4 Hz), 137.95 (d, $J_{C,P}$ = 5.40 Hz).

^{31}PNMR δ: 33.37.

HR-MS: calcd for $C_{20}H_{20}OP$ 307.1252 ([M + H^+]), found 307.1252.

3d White solids.



3d

[Ref. J. Mazuela, A. Paptchihine, O. Pàmies, P. G. Andersson, M. Diéguez, *Chem. Eur. J.* **2010**, 16, 4567-4576.]

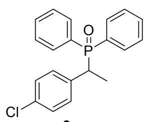
^{1}HNMR (400 MHz, $CDCl_3$) δ: 0.80 (t, J = 7.2 Hz, 3H), 1.94-2.16 (m, 2H), 3.27-3.32 (m, 1H), 7.15-7.25 (m, 7H), 7.31-7.34 (m, 1H), 7.41-7.46 (m, 2H), 7.51-7.58 (m, 3H), 7.88-7.92 (m, 2H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 12.75 (d, $J_{C,P}$ = 13.90 Hz), 22.64, 48.89 (d, $J_{C,P}$ = 67.2 Hz), 126.90 (d, $J_{C,P}$ = 2.60 Hz), 127.91, 128.03, 128.25 (d, $J_{C,P}$ = 1.90 Hz), 128.62, 128.73, 129.86, 129.92, 130.96, 131.05, 131.14 (d, $J_{C,P}$ = 2.70 Hz), 131.28, 131.37, 131.65 (d, $J_{C,P}$ = 2.40 Hz), 131.83 (d, $J_{C,P}$ = 14.10 Hz), 132.78 (d, $J_{C,P}$ = 18.60 Hz), 135.75 (d, $J_{C,P}$ = 5.50 Hz).

^{31}PNMR δ: 32.54.

HR-MS: calcd for $C_{21}H_{22}OP$ 321.1408 ([M + H$^+$]), found 321.1413.

3e White solids.



3e

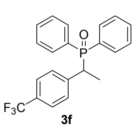
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.57 (dd, J = 15.6, 7.2 Hz, 3H), 3.61 (qu, J = 14.8, 7.2 Hz, 1H), 7.19 (s, 4H), 7.30-7.34 (m, 2H), 7.39-7.43 (m, 1H), 7.48-7.58 (m, 5H), 7.90-7.94 (m, 2H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 15.47 (d, $J_{C,P}$ = 2.50 Hz), 40.25 (d, $J_{C,P}$ = 66.50 Hz), 128.15, 128.26, 128.39 (d, $J_{C,P}$ = 1.8 Hz), 128.69, 128.80, 130.44, 130.49, 130.96, 131.04, 131.12, 131.25, 131.34, 131.49 (d, $J_{C,P}$ = 2.60 Hz), 131.85 (d, $J_{C,P}$ = 2.50 Hz), 132.06, 132.29, 132.74 (d, $J_{C,P}$ = 3.0 Hz), 136.56 (d, $J_{C,P}$ = 5.5 Hz).

^{31}PNMR δ: 32.95.

HR-MS: calcd for $C_{20}H_{19}ClOP$ 341.0862 ([M + H$^+$]), found 341.0854.

3f White solids.



3f

[Ref. (a) P. Cheruku, A. Paptchikhine, T. L. Church, P. G. Andersson, *J. Am. Chem. Soc.* **2009**, 131, 23, 8285-8289; (b) D. A. Jaeger, D. Bolikal, *J. Org. Chem.* **1986**, 51, 1350-1352.]

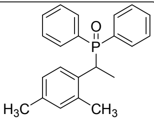
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.58 (dd, J = 16.0, 8.8 Hz, 3H), 3.68 (qu, J = 14.8, 7.6 Hz, 1H), 7.26-7.60 (m, 12H), 7.90-7.94 (m, 2H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 15.40 (d, $J_{C,P}$ = 2.90 Hz), 40.89 (d, d, $J_{C,P}$ = 65.80 Hz), 124.14 (q, $J_{C\text{-}F}$ = 270.0 Hz), 125.10-125.16 (m), 128.20, 128.31, 128.75, 128.87, 129.46, 129.51, 130.90, 130.99, 131.19, 131.28, 131.37, 131.61 (d, $J_{C,P}$ = 2.70 Hz), 131.86, 131.96 (d, $J_{C,P}$ = 2.70 Hz), 132.17, 142.32 (d, $J_{C,P}$ = 5.30 Hz).

^{31}PNMR δ: 32.83.

HR-MS: calcd for $C_{21}H_{19}F_3OP$ 375.1126 ([M + H$^+$]), found 375.1115.

3g White solids.



3g

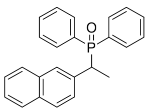
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.43 (dd, J = 16.40, 9.2 Hz, 3H), 1.85 (s, 3H), 2.17 (s, 3H), 3.70 (qu, J = 15.2, 7.6 Hz, 1H), 6.72 (s, 1H), 6.93 (d, J = 7.6 Hz, 1H), 7.10-7.14 (m, 2H), 7.23-7.28 (m, 3H), 7.44-7.52 (m, 4H), 7.80-7.84 (m, 2H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 15.82 (d, $J_{C,P}$ = 2.70 Hz), 19.56, 21.01, 35.39 (d, $J_{C,P}$ = 68.0 Hz), 127.18 (d, $J_{C,P}$ = 2.10 Hz), 127.89, 128.00, 128.61, 128.72, 128.85, 128.89, 130.83 (d, $J_{C,P}$ = 1.30 Hz), 130.99, 131.08, 131.21, 131.31 (d, $J_{C,P}$ = 2.60 Hz), 131.58, 131.66, 131.76 (d, $J_{C,P}$ = 2.60 Hz), 132.15 (d, $J_{C,P}$ = 4.0 Hz), 133.14, 133.48 (d, $J_{C,P}$ = 5.0 Hz), 135.45, 135.52, 136.35 (d, $J_{C,P}$ = 2.40 Hz).

^{31}PNMR δ: 33.74.

HR-MS: calcd for $C_{22}H_{24}OP$ 335.1565 ([M + H^+]), found 335.1562.

3h White solids.



3h

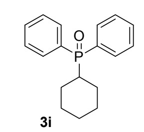
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.72 (dd, J = 15.6, 7.2 Hz, 3H), 4.51 (qu, J = 14.4, 6.8 Hz, 1H), 7.04-7.09 (m, 2H), 7.17-7.20 (m, 1H), 7.37-7.49 (m, 5H), 7.56-7.63 (m, 3H), 7.72 (d, J = 8.0 Hz, 1H), 7.8 (t, J = 5.20 Hz, 1H), 7.97-8.05 (m, 3H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 16.31 (d, $J_{C,P}$ = 2.80 Hz), 34.16 (d, $J_{C,P}$ = 74.6 Hz), 122.12-122.30 (m), 125.25, 125.70 (d, $J_{C,P}$ = 2.10 Hz), 126.00, 127.19 (d, $J_{C,P}$ = 5.20 Hz), 127.46 (d, $J_{C,P}$ = 1.90 Hz), 127.83, 127.94, 128.69, 128.80, 129.06, 130.75, 130.84, 131.16 (d, $J_{C,P}$ = 2.70 Hz), 131.40, 131.48, 131.74 (d, $J_{C,P}$ = 2.70 Hz), 131.99, 132.75, 132.93, 133.74, 134.83 (d, $J_{C,P}$ = 4.30 Hz).

^{31}PNMR δ: 33.87.

HR-MS: calcd for $C_{24}H_{22}OP$ 357.1408 ([M + H^+]), found 357.1405.

3i White solids.



3i

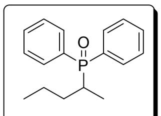
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.21-1.32 (m, 3H), 1.50-1.58 (m, 2H), 1.71-1.81 (m, 5H), 2.19-2.28 (m, 1H), 7.44-7.52 (m, 6H), 7.76-7.81 (m, 4H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 24.76 (d, $J_{C,P}$ = 2.40 Hz), 25.75, 26.33 (d, $J_{C,P}$ = 13.2Hz), 37.13 (d, $J_{C,P}$ = 72.6 Hz), 128.47, 128.58, 128.89 (d, $J_{C,P}$ = 12.7 Hz), 130.67 (d, $J_{C,P}$ = 11.3 Hz), 131.00, 131.08, 131.42 (d, $J_{C,P}$ = 2.40 Hz), 131.58, 132.52.

^{31}PNMR δ: 34.37.

HR-MS: calcd for $C_{18}H_{22}OP$ 285.1408 ([M + H^+]), found 285.1401.

3j White solids.



3j

[Ref. K. Goda, R. Okazaki, K.-Y. Akiba, N. Inamoto, *Bull. Chem. Soc. Jpn.* **1978**, 51, 260-264.]

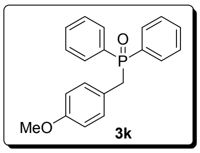
^{1}HNMR (400 MHz, $CDCl_3$) δ: 0.84 (t, J = 7.2 Hz, 3H), 1.16 (dd, J = 16.8, 9.6 Hz, 3H), 1.13-1.30 (m, 1H), 1.41-1.66 (m, 3H), 2.34-2.44 (m, 1H), 7.45-7.47 (m, 6H), 7.77-7.83 (m, 4H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 12.03 (d, $J_{C,P}$ = 2.40 Hz), 13.81, 20.58 (d, $J_{C,P}$ = 12.70 Hz), 30.89, 31.75 (d, $J_{C,P}$ = 70.90 Hz), 128.59 (dd, $J_{C,P}$ = 11.10, 3.70 Hz), 131.04, 131.12, 131.48 (dd, $J_{C,P}$ = 4.70, 2.40 Hz).

^{31}PNMR δ: 37.29.

HR-MS: calcd for $C_{17}H_{22}OP$ 273.1408 ([M + H^+]), found 273.1405.

3k White solids.



[Ref. C. Zhong, J. Zhu, J. Chang, X. Sun, *Tetrahedron Lett.* **2011**, 52, 2815-2817.]

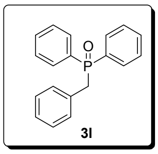
^{1}HNMR (400 MHz, $CDCl_3$) δ: 3.59 (d, J = 13.6 Hz, 2H), 3.75 (s, 3H), 6.73 (d, J = 8.4 Hz, 2H), 7.02 (dd, J = 8.8, 6.8 Hz, 2H), 7.42-7.53 (m, 6H), 7.67-7.71 (m, 4H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 37.12 (d, $J_{C,P}$ = 67.0 Hz), 55.20, 113.91 (d, $J_{C,P}$ = 2.50 Hz), 122.92 (d, $J_{C,P}$ = 8.1 Hz), 128.43, 128.55, 131.12, 131.16, 131.25, 131.76 (d, $J_{C,P}$ = 2.70 Hz), 131.93, 132.91, 158.54 (d, $J_{C,P}$ = 2.80 Hz).

^{31}PNMR δ: 29.42.

HR-MS: calcd for $C_{20}H_{20}O_2P$ 323.1201 ([M + H$^+$]), found 323.1195.

3l White solids.



[Ref. E. N. Tsvetkov, N. A. Bondarenko, I. G. Malakhova, M. I. Kabachnik, *Synthesis* **1986**, 3, 198-208.]

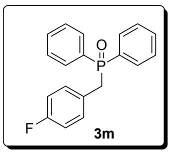
^{1}HNMR (400 MHz, $CDCl_3$) δ: 3.65 (d, J = 14.0 Hz, 2H), 7.10-7.19 (m, 5H), 7.42-7.53 (m, 6H), 7.67-7.72 (m, 4H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 38.16 (d, $J_{C,P}$ = 66.0 Hz), 126.79 (d, $J_{C,P}$ = 2.90 Hz), 128.38 (d, $J_{C,P}$ = 2.60 Hz), 128.44, 128.56, 130.17 (d, $J_{C,P}$ = 5.30 Hz), 131.15, 131.24, 131.80 (d, $J_{C,P}$ = 2.60 Hz), 131.88, 132.86.

^{31}PNMR δ: 27.93.

HR-MS: calcd for $C_{19}H_{18}OP$ 293.1095 ([M + H$^+$]), found 293.1086.

3m White solids.



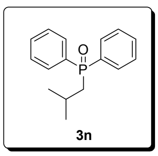
^{1}HNMR (400 MHz, $CDCl_3$) δ: 3.64 (d, J = 13.2 Hz, 2H), 6.88-6.92 (m, 2H), 7.07-7.11 (m, 2H), 7.45-7.56 (m, 6H), 7.68-7.73 (m, 4H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 37.23 **(**d, $J_{C,P}$ = 66.50 Hz**)**, 115.31 (dd, $J_{C\text{-}F}$ = 21.30, 2.40 Hz), 126.90 (dd, $J_{C\text{-}F}$ = 7.80, 3.10 Hz), 128.52, 128.63, 131.09, 131.18, 131.52-131.68 (m), 131.90 (d, $J_{C,P}$ = 2.70 Hz), 132.67, 161.93 (dd, $J_{C\text{-}F}$ = 243.90, 3.20 Hz).

^{31}PNMR δ: 29.23.

HR-MS: calcd for $C_{19}H_{17}FOP$ 311.1001 ([M + H$^+$]), found 311.0996.

3n White solids.



[Ref. D. C. Morrison, *J. Am. Chem. Soc.* **1950**, 72, 4820-4821.]

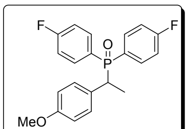
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.04 (d, J = 6.4 Hz, 6H), 2.138-2.27 (m, 3H), 7.46-7.54 (m, 6H), 7.76-7.80 (m, 4H).

^{13}CNMR (100 MHz, $CDCl_3$) δ: 23.62 (d, $J_{C,P}$ = 3.80 Hz), 24.67 (d, $J_{C,P}$ = 8.90 Hz), 38.38 (d, $J_{C,P}$ = 70.70 Hz), 128.50, 128.61, 130.61, 130.70, 131.46 (d, $J_{C,P}$ = 2.50 Hz), 133.55, 134.51.

^{31}PNMR δ: 29.21.

HR-MS: calcd for $C_{16}H_{20}OP$ 259.1252 ([M + H$^+$]), found 259.1245.

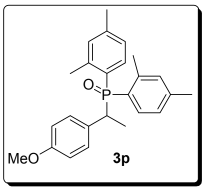
3o White solids.



3o

[1]HNMR (400 MHz, $CDCl_3$) δ: 1.55 (dd, J = 16.4, 9.2 Hz, 3H), 3.53 (qu, J = 14.8, 7.2 Hz, 1H), 3.76 (s, 3H), 6.76 (d, J = 8.4 Hz, 2H), 6.96-7.01 (m, 2H), 7.10-7.13 (m, 2H), 7.21-7.29 (m, 2H), 7.41-7.47 (m, 2H), 7.85-7.91 (m, 2H).
[13]CNMR (100 MHz, $CDCl_3$) δ: 15.45 (d, $J_{C,P}$ = 2.40 Hz), 40.30 (d, $J_{C,P}$ = 68.50 Hz), 55.21, 113.85 (d, $J_{C,P}$ =1.90 Hz), 115.50 (dd, $J_{C\text{-}F}$ = 21.2, 8.7 Hz), 116.13 (dd, $J_{C\text{-}F}$ = 21.1, 9.0 Hz), 127.34 (dd, $J_{C\text{-}F}$ = 16.0, 3.4 Hz), 128.31 (dd, $J_{C\text{-}F}$ = 21.0, 3.6 Hz), 129.28 (d, $J_{C,P}$ = 5.70Hz), 130.11 (d, $J_{C,P}$ = 5.50 Hz), 133.48-133.87 (m), 158.71 (d, $J_{C,P}$ = 2.50 Hz), 163.58 (dd, $J_{C\text{-}F}$ = 35.5, 3.2 Hz), 166.10 (dd, $J_{C\text{-}F}$ = 36.0, 3.3 Hz).
[31]PNMR δ: 32.57.
HR-MS: calcd for $C_{21}H_{20}F_2O_2P$ 373.1169 ([M + H$^+$]), found 373.1144.

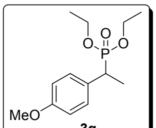
3p White solids.



3p

[1]HNMR (400 MHz, $CDCl_3$) δ: 1.69 (dd, J = 15.2, 8.0 Hz), 2.10 (s, 3H), 2.24 (s, 3H), 2.35 (s, 3H), 2.36 (s, 3H), 2.37 (s, 3H), 3.69-3.74 (m, 1H), 3.76 (s, 3H), 6.74 (d, J = 8.4 Hz, 2H), 7.03-7.14 (m, 4H), 7.22-7.24 (m, 2H), 7.65-7.81 (m, 2H).
[13]CNMR (100 MHz, $CDCl_3$) δ: 14.22, 16.60 (d), 20.88-21.41 (m), 38.62 (d, $J_{C,P}$ = 67.70 Hz), 55.23, 113.65 (d), 125.62-126.41 (m), 128.48, 128.83, 130.20 (d), 131.00 (d), 131.77, 131.87, 132.10-132.26 (m), 133.00 (d), 133.65 (d), 141.12-142.88 (m), 158.39 (d).
HR-MS: calcd for $C_{25}H_{30}O_2P$ 393.1983, found 393.1980.

3q Colorless oil.

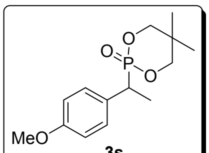


3q

[Ref. D.-Y. Wang, X.-P. Hu, J. Deng, S.-B. Yu, Z.-C. Duan, Z. Zheng, *J. Org. Chem.* **2009**, 74, 4408-4410; N. S. Goulioukina, T. M. Dolgina, I. P. Beletskaya, J.-C. Henry, D. Lavergne, V. Ratovelomanana-Vidal, J.-P. Genet, *Tetrahedron: Asymmetry*, **2001**, 12, 319-328.]

[1]HNMR (400 MHz, $CDCl_3$) δ: 1.16 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.56 (dd, J = 18.4, 7.8 Hz, 3H), 3.12 (dq, J = 22.4, 7.2 Hz, 1H), 3.80 (s, 3H), 3.82 (m, 1H), 3.93 (m, 1H), 4.01 (m, 2H), 6.87 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H).
[13]CNMR (100 MHz, $CDCl_3$) δ: 15.8, 16.4 (d, J = 5.0 Hz), 16.5 (d, J = 5.0 Hz), 37.5 (d, J = 138.0 Hz), 55.3, 61.9 (d, J = 6.0 Hz), 62.2 (d, J = 6.0 Hz), 113.9, 129.7 (d, J = 5.0 Hz), 130.0 (d, J = 6.0 Hz), 158.7.

3s White solids.

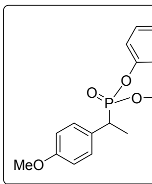


3s

[1]HNMR (400 MHz, $CDCl_3$) δ: 0.89 (s, 3H), 0.91 (s, 3H), 1.62 (dd, J = 18.8, 11.2 Hz, 3H), 3.21-3.32 (m, 1H), 3.59-3.70 (m, 2H), 3.79 (s, 3H), 4.14-4.20 (m, 2H), 6.87 (d, J = 8.4 Hz, 2H), 7.26-7.29 (m, 2H).
[13]CNMR (100 MHz, $CDCl_3$) δ: 15.21 (d, $J_{C,P}$ = 4.60 Hz), 21.48 (d, $J_{C,P}$ = 14.70 Hz), 32.63 (d, $J_{C,P}$ = 5.80 Hz), 36.58 (d, $J_{C,P}$ = 134.50 Hz), 55.29, 74.82 (dd, $J_{C,P}$ = 6.5, 2.9 Hz), 113.96 (d, $J_{C,P}$ = 2.50 Hz), 129.14 (d, $J_{C,P}$ = 7.60 Hz), 129.66 (d, $J_{C,P}$ = 6.40 Hz), 158.81 (d, $J_{C,P}$ = 3.10 Hz).

HR-MS: calcd for $C_{14}H_{22}O_4P$ 285.1256, found 285.1258.

3t White solids.



3t

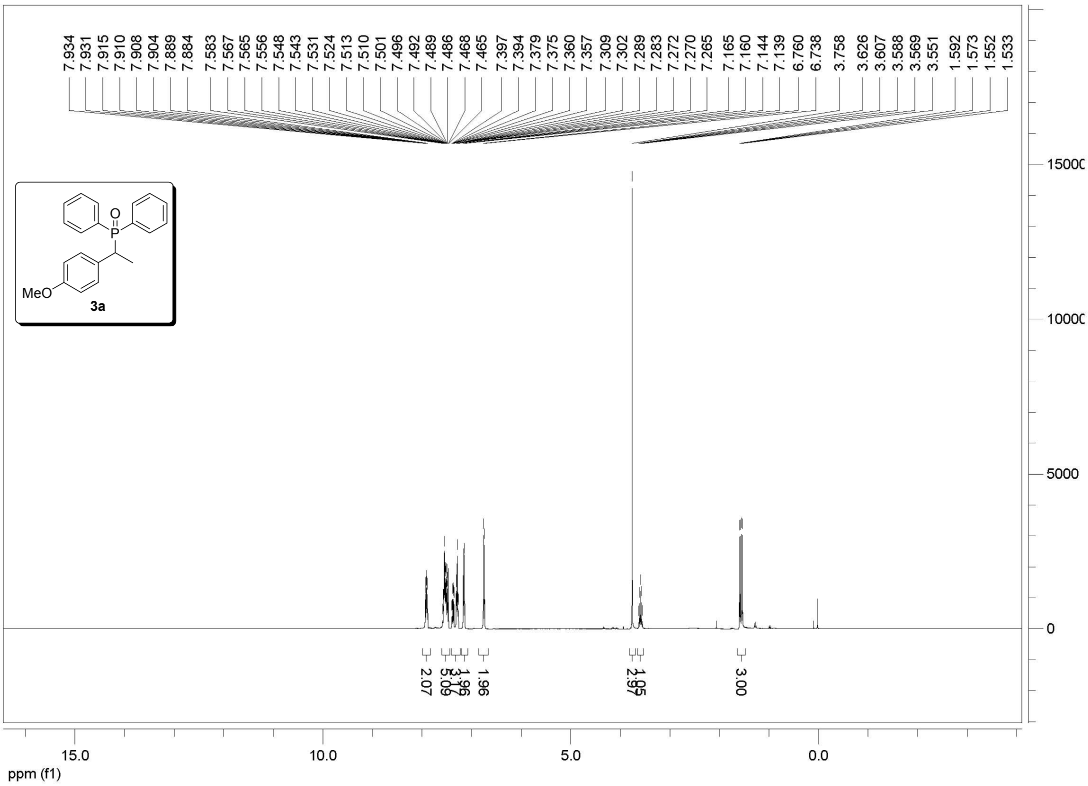
^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.81 (dd, J = 18.8, 12.4 Hz, 3H), 3.24-3.35 (m, 1H), 3.75 (s, 3H), 6.74 (d, J = 8.8 Hz, 2H), 7.22-7.27 (m, 4H), 7.31-7.37 (m, 3H), 7.42-7.51 (m, 3H), 7.94 (dd, J = 16.8, 9.6 Hz, 4H).

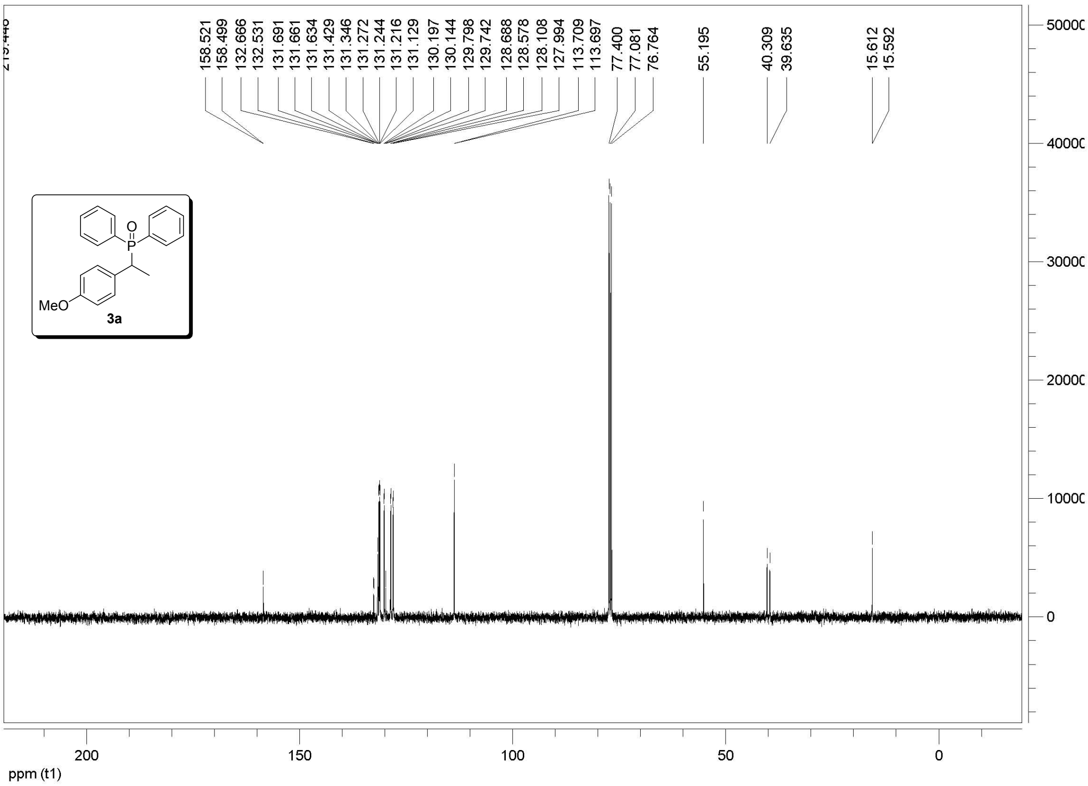
^{13}CNMR (100 MHz, $CDCl_3$) δ: 16.55 (d, $J_{C,P}$ = 3.90 Hz), 35.88 (d, $J_{C,P}$ = 129.0 Hz), 55.27, 114.12(d), 119.88 (d), 121.36, 121.88 (d), 125.66 (d), 126.61, 126.74, 126.90, 127.35, 128.24, 128.31, 128.51, 129.78, 129.85, 130.91, 131.13, 131.37, 131.84, 132.43 (d), 132.55, 145.90 (d), 148.12 (d), 158.99 (d).

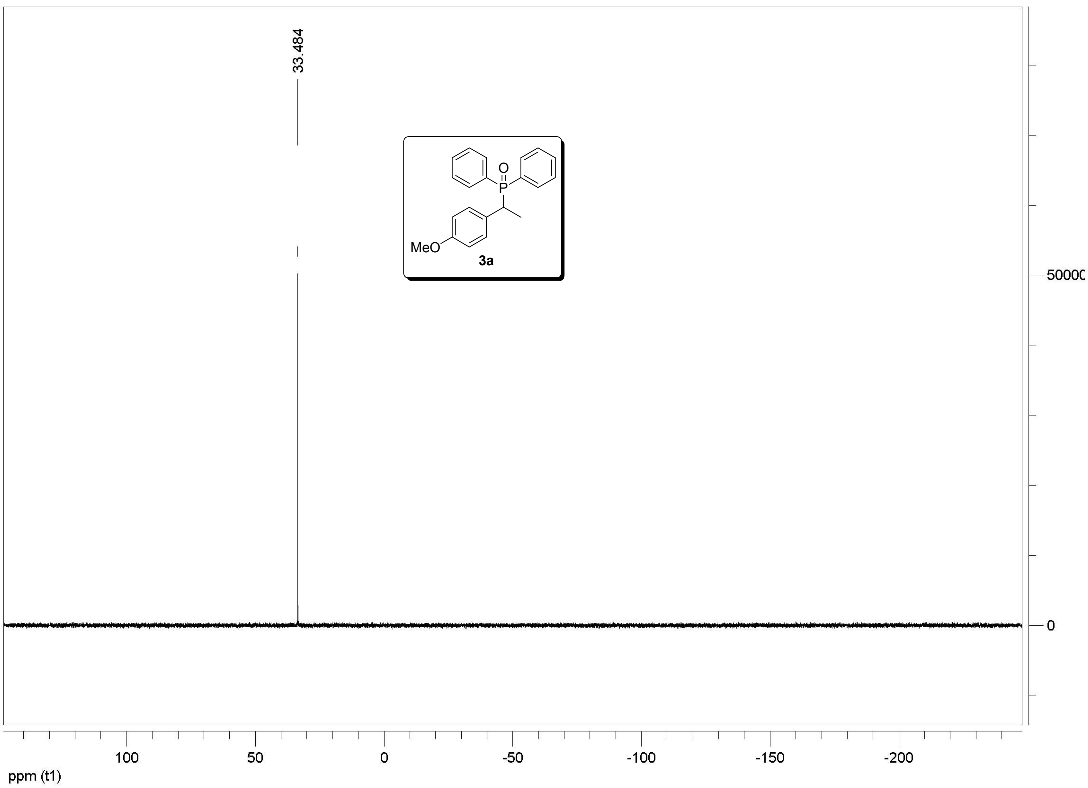
HR-MS: calcd for $C_{29}H_{23}NaO_4P$ 489.1232, found 489.1202.

4. Selected Spectra of Organophosphorus Products

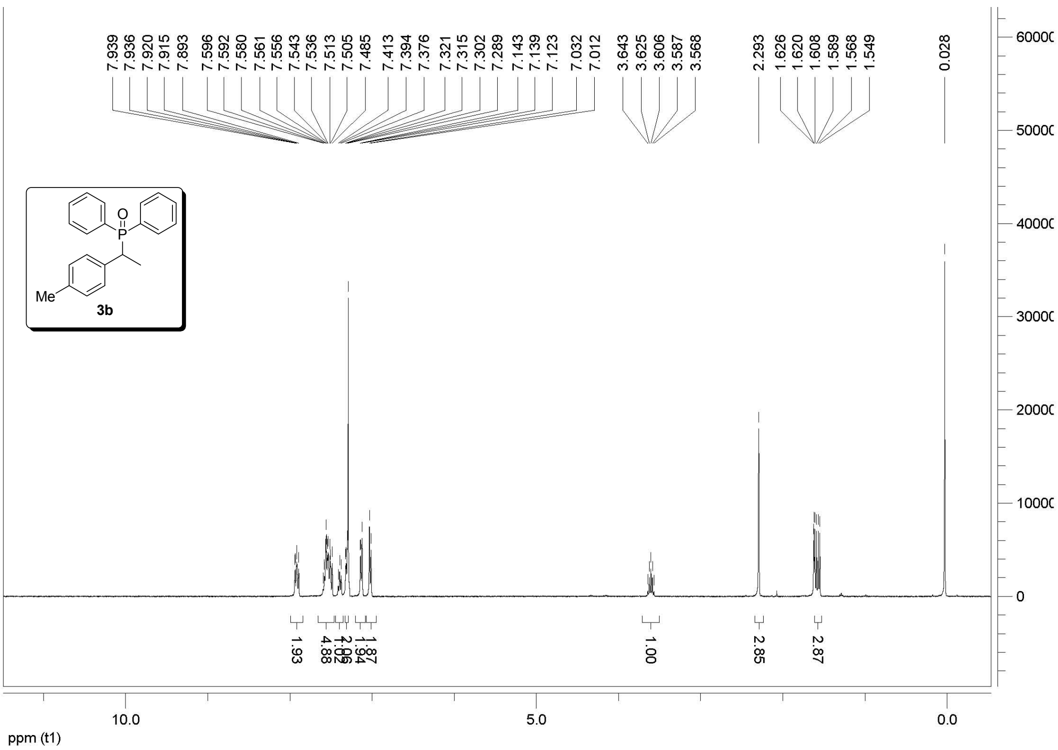
3a

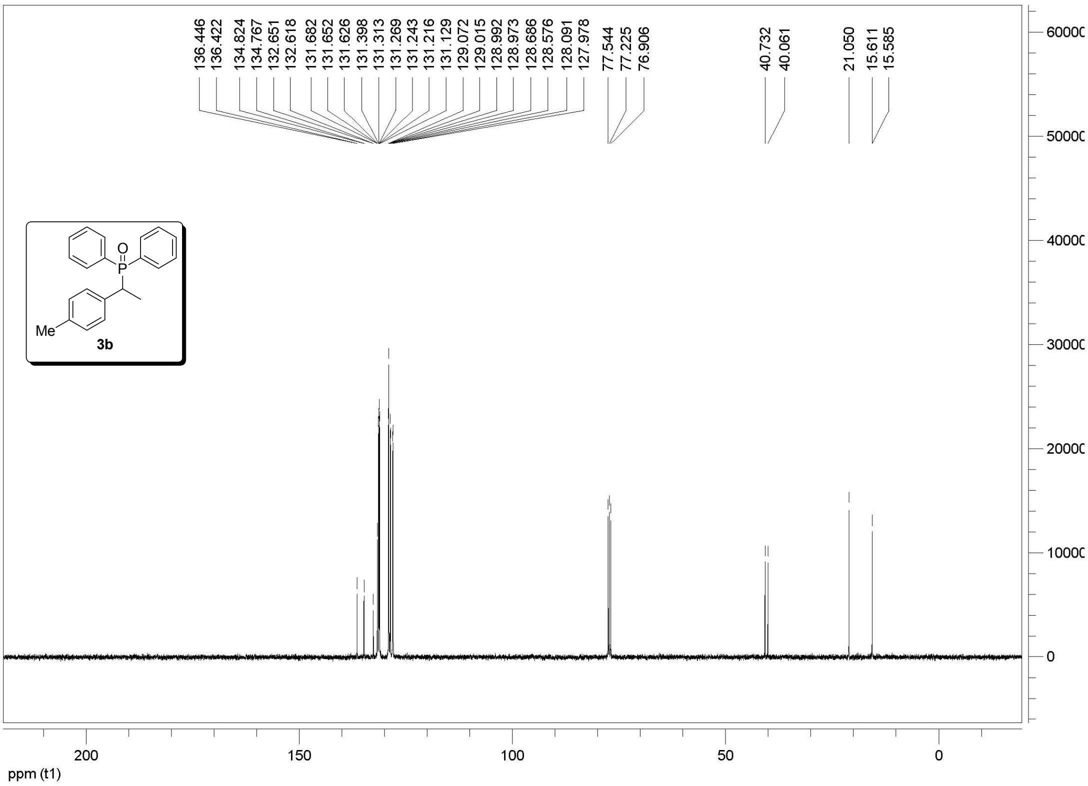


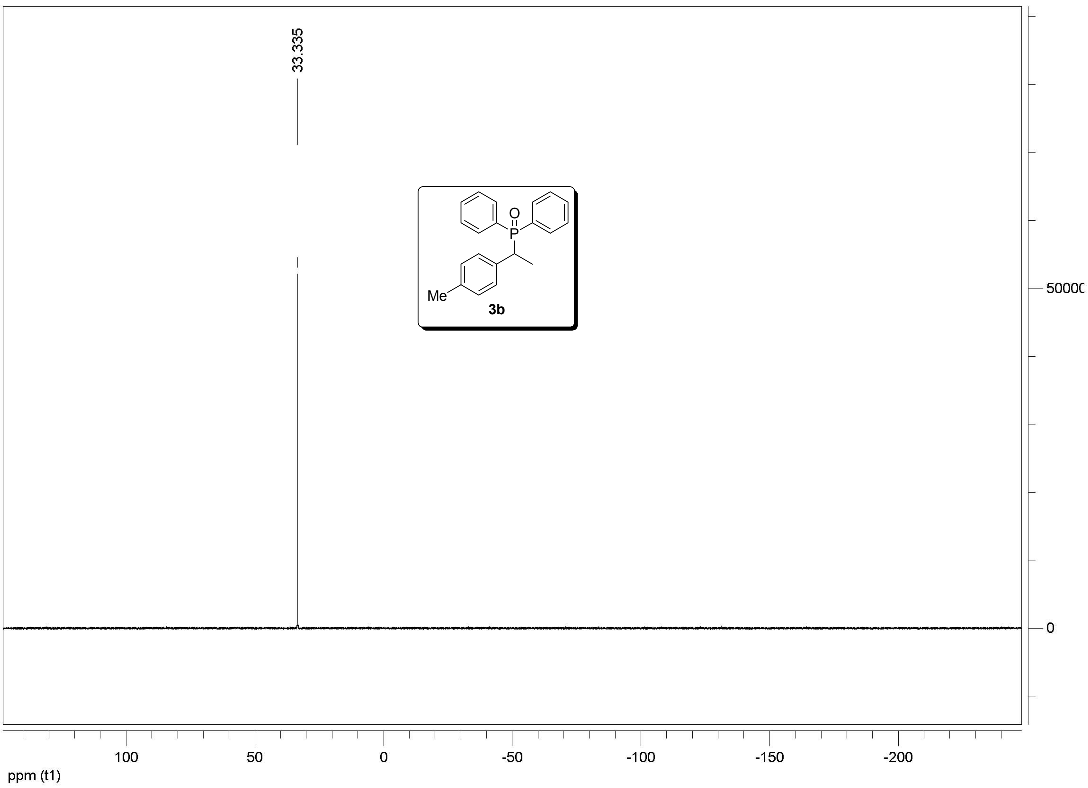



33.484
MeO
3a
50000
0
100
50
0
-50
-100
-150
-200
ppm (t1)

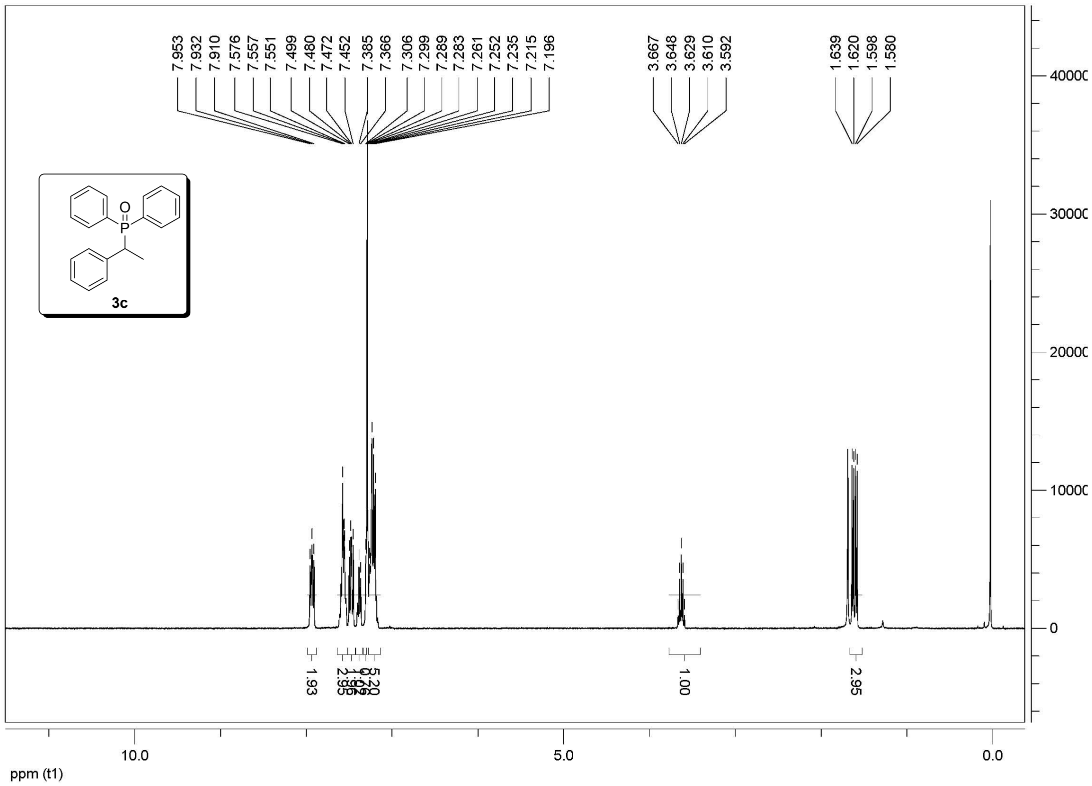
3b

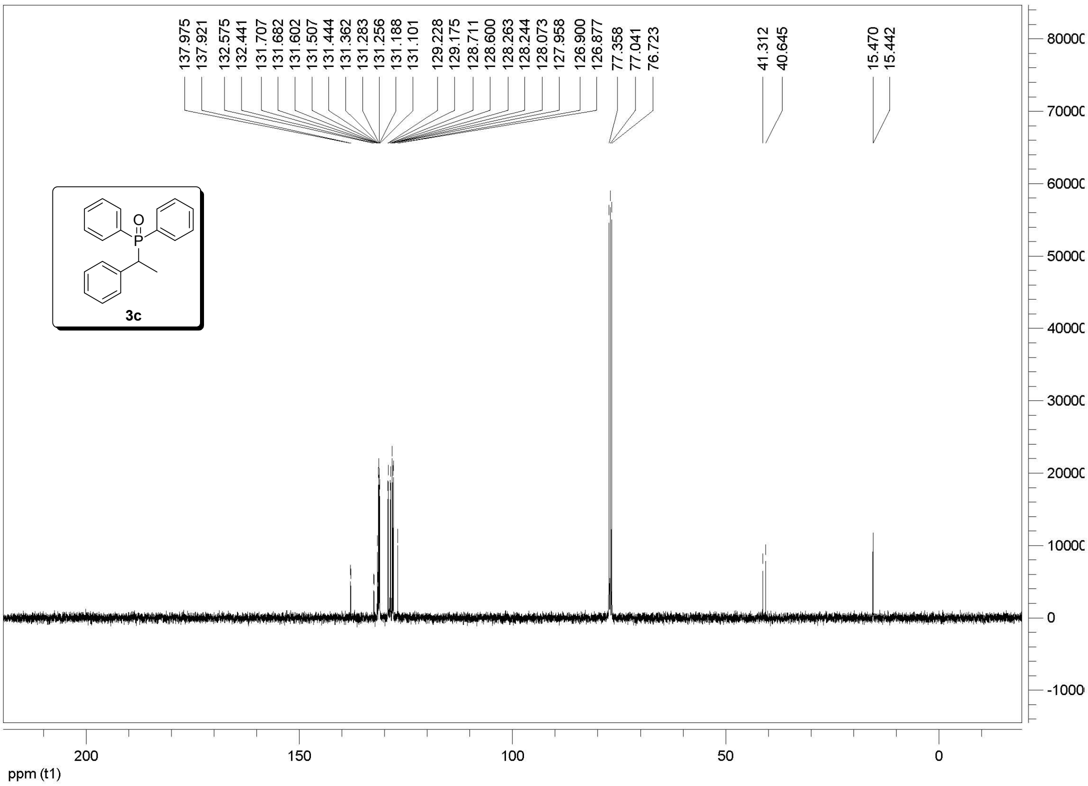

7.939
7.936
7.920
7.915
7.893
7.596
7.592
7.580
7.561
7.556
7.543
7.536
7.513
7.505
7.485
7.413
7.394
7.376
7.321
7.315
7.302
7.289
7.143
7.139
7.123
7.032
7.012
3.643
3.625
3.606
3.587
3.568
2.293
1.626
1.620
1.608
1.589
1.568
1.549
0.028
Me
3b
1.93
4.88
1.00
2.85
2.87
10.0
5.0
0.0
ppm (t1)


136.446
136.422
134.824
134.767
132.651
132.618
131.682
131.652
131.626
131.398
131.313
131.269
131.243
131.216
131.129
129.072
129.015
128.992
128.973
128.686
128.576
128.091
127.978
77.544
77.225
76.906
40.732
40.061
21.050
15.611
15.585
Me
3b
200
150
100
50
0
ppm (t1)

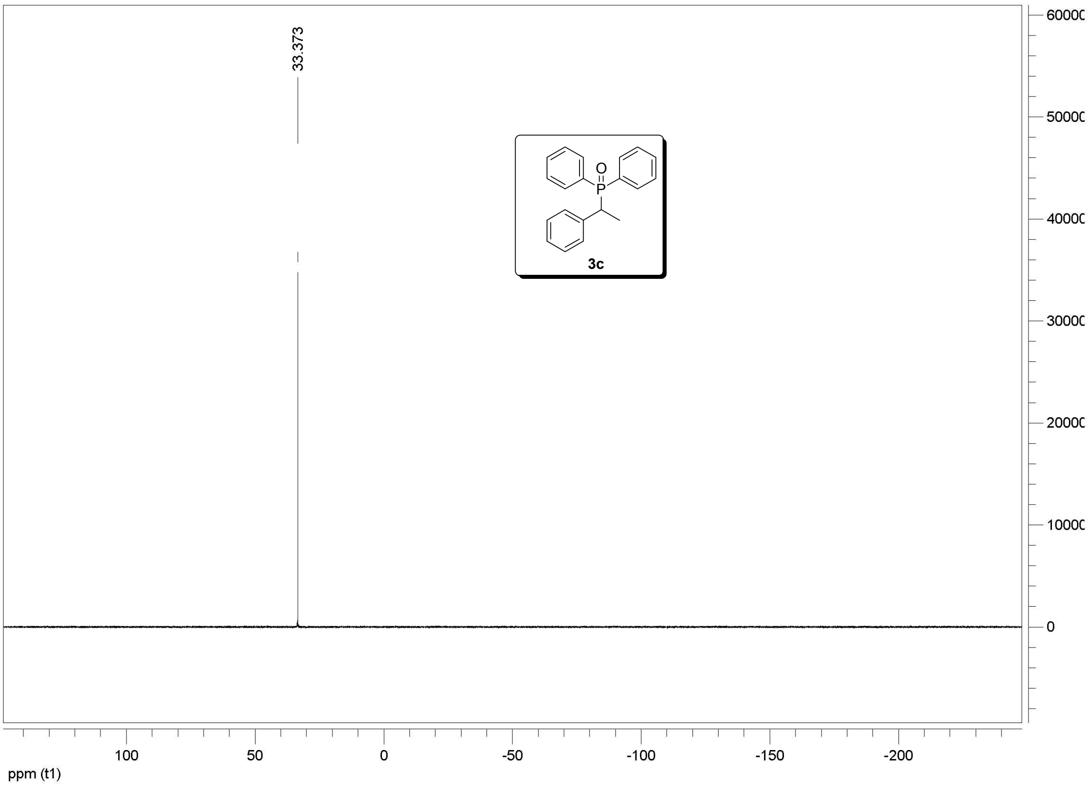

33.335
Me
3b
100
50
0
-50
-100
-150
-200
ppm (t1)

3c

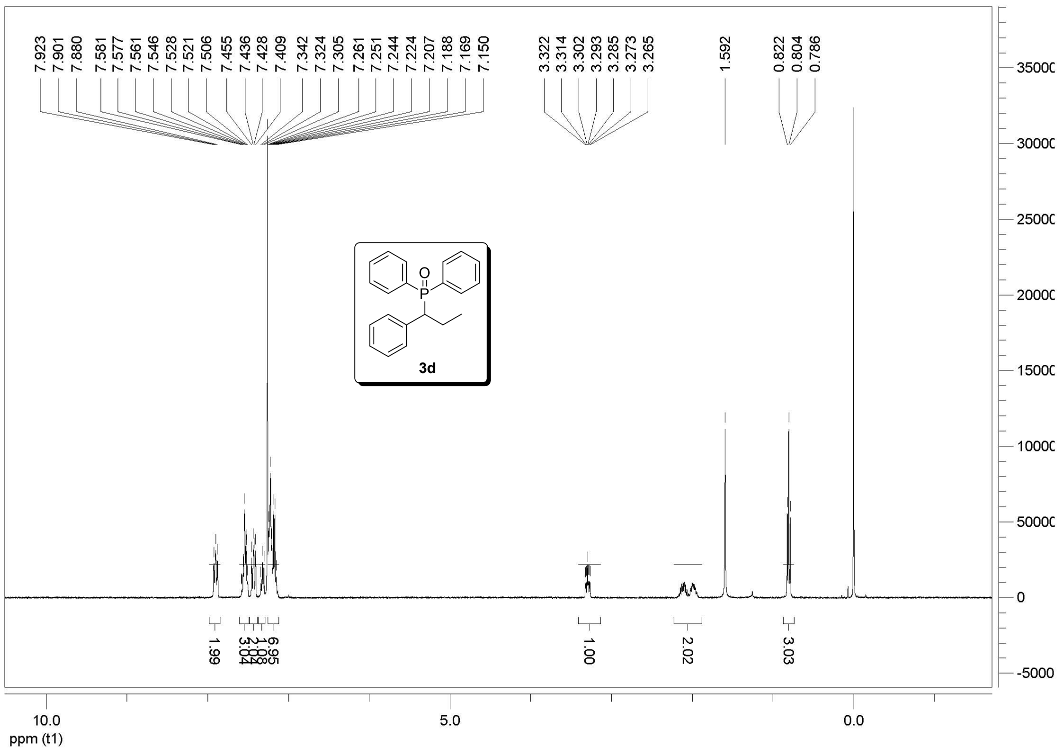

7.953
7.932
7.910
7.576
7.557
7.551
7.499
7.480
7.472
7.452
7.385
7.366
7.306
7.299
7.289
7.283
7.261
7.252
7.235
7.215
7.196
3.667
3.648
3.629
3.610
3.592
1.639
1.620
1.598
1.580
3c
1.93
1.00
2.95
10.0
5.0
0.0
ppm (t1)
40000
30000
20000
10000
0

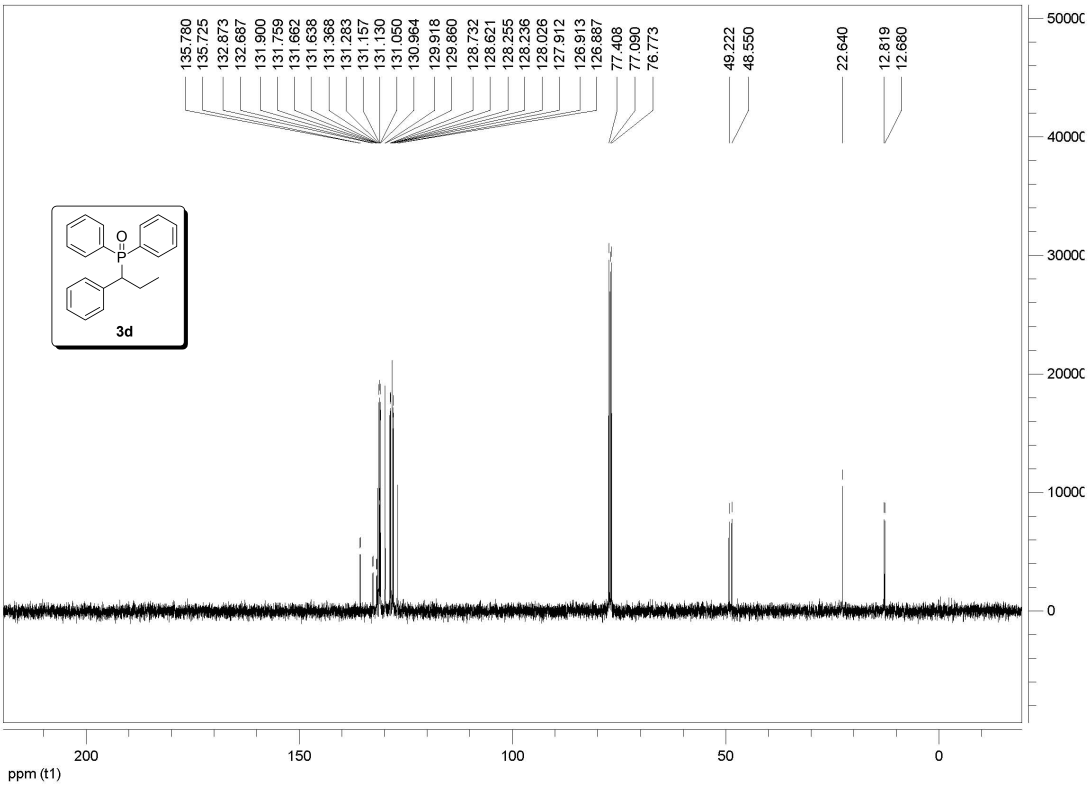

137.975
137.921
132.575
132.441
131.707
131.682
131.602
131.507
131.444
131.362
131.283
131.256
131.188
131.101
129.228
129.175
128.711
128.600
128.263
128.244
128.073
127.958
126.900
126.877
77.358
77.041
76.723
41.312
40.645
15.470
15.442
3c
200
150
100
50
0
ppm (t1)
80000
70000
60000
50000
40000
30000
20000
10000
0
-1000

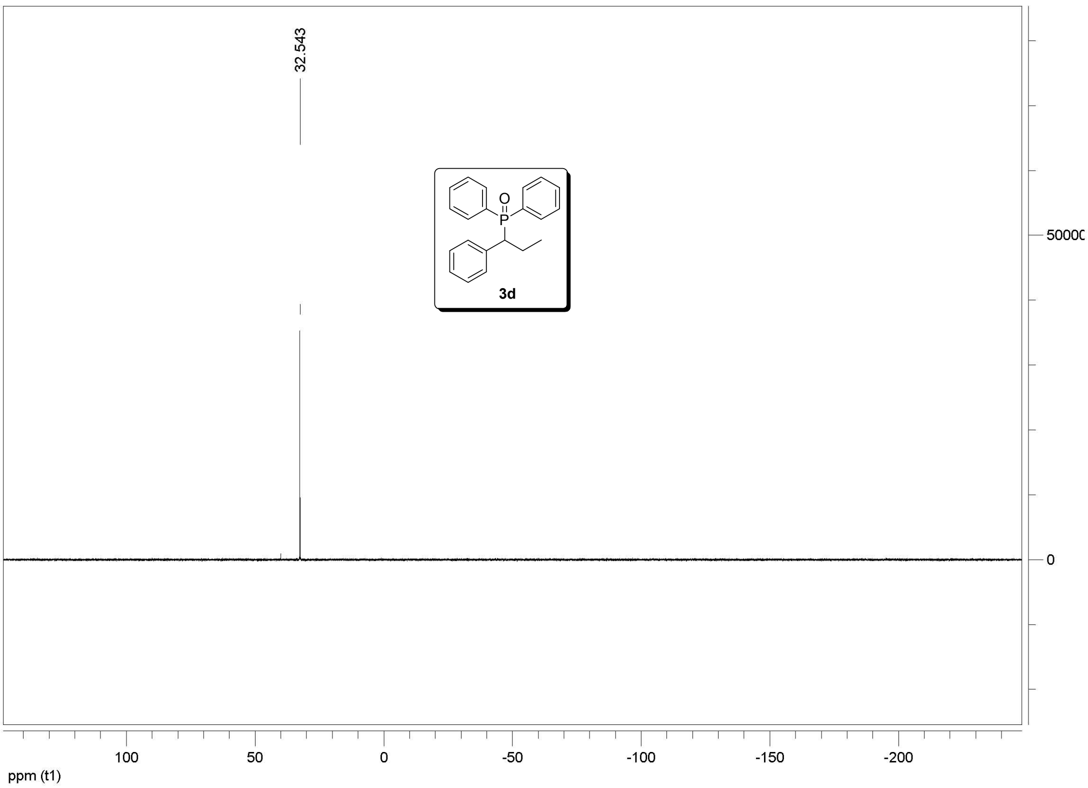
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



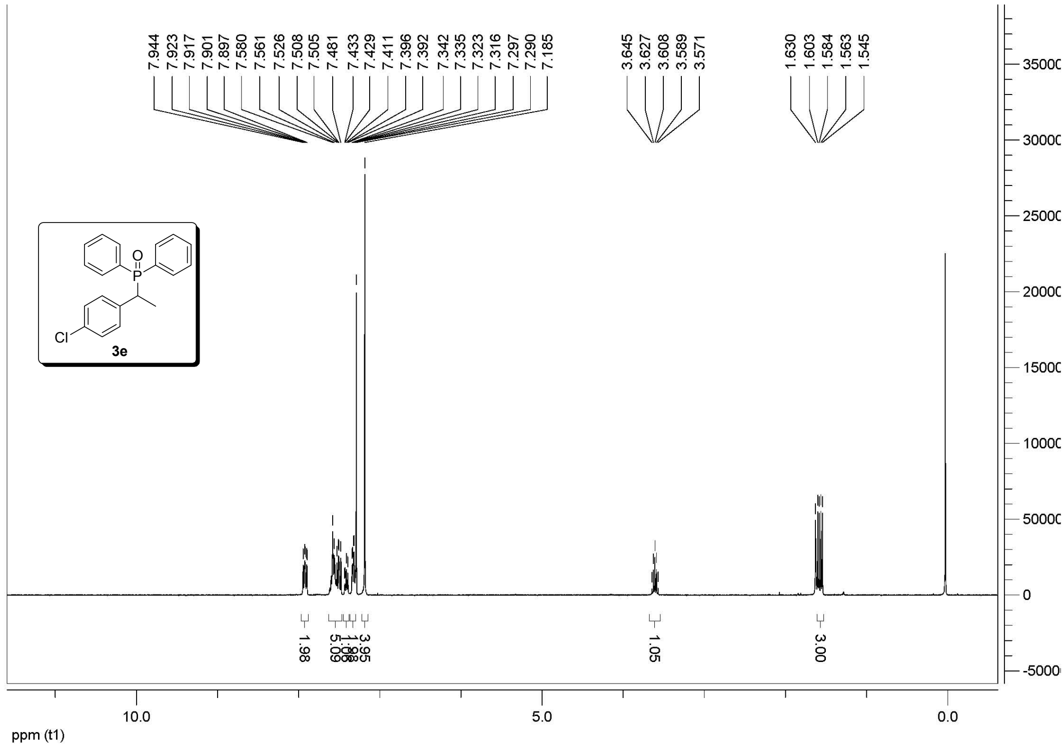
3d

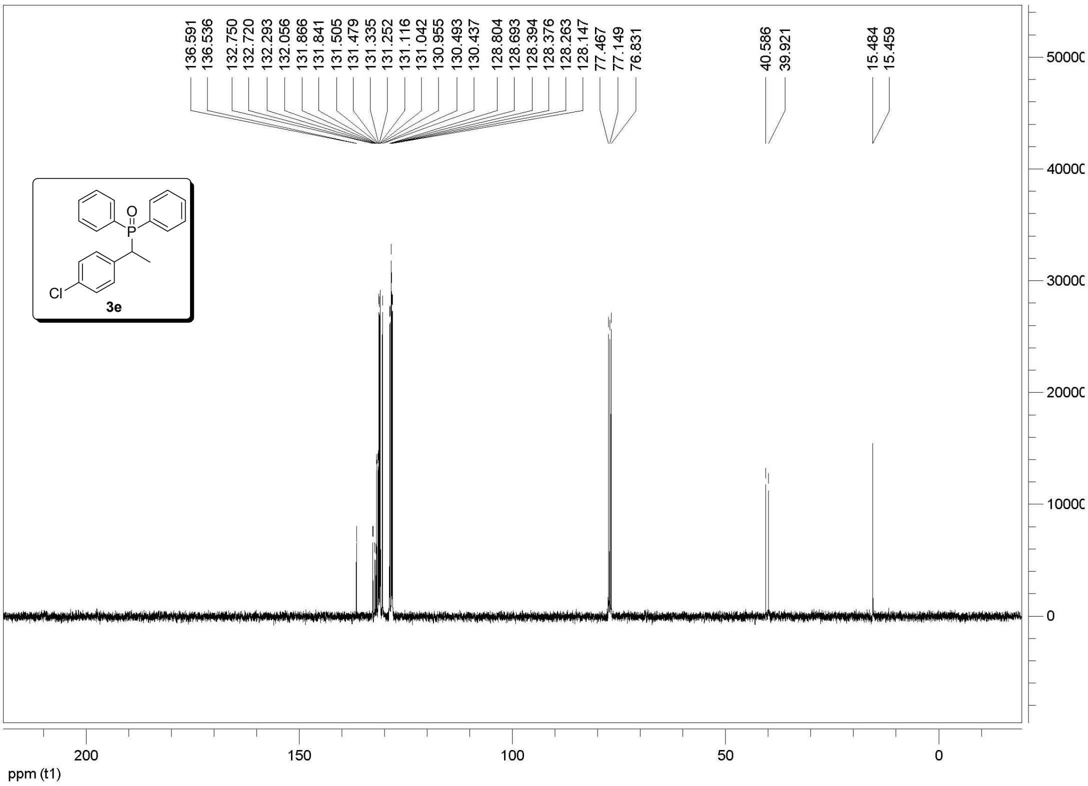


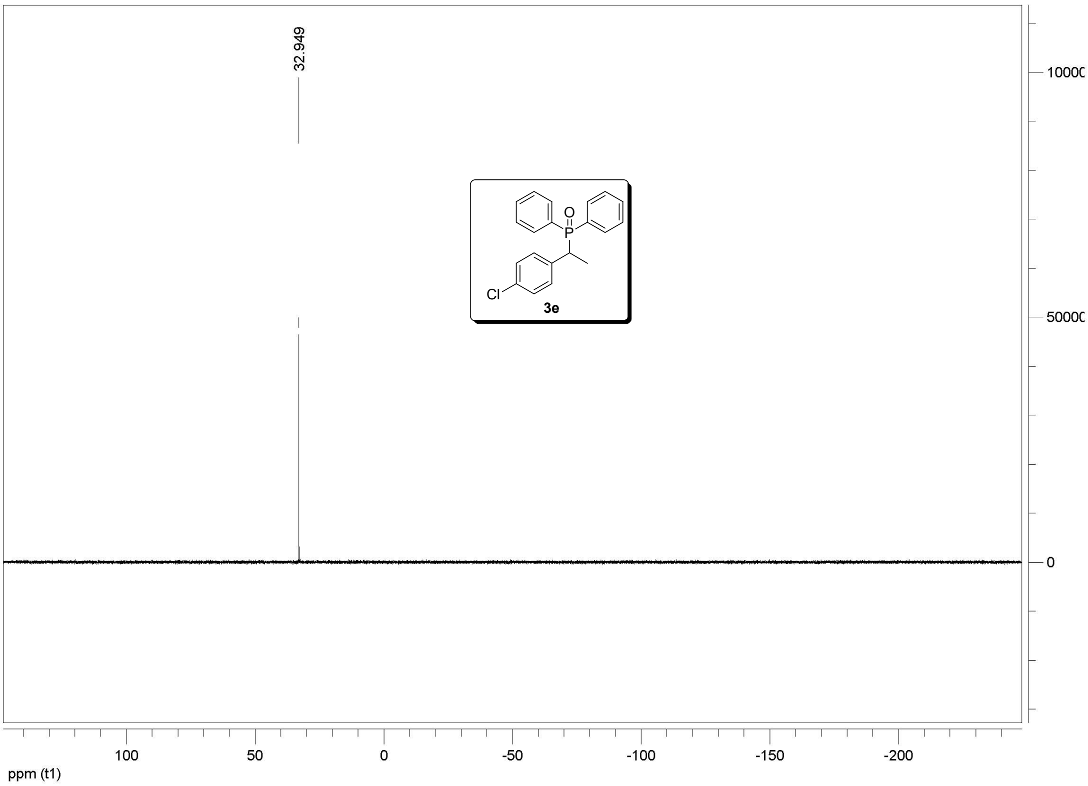

135.780
135.725
132.873
132.687
131.900
131.759
131.662
131.638
131.368
131.283
131.157
131.130
131.050
130.964
129.918
129.860
128.732
128.621
128.255
128.236
128.026
127.912
126.913
126.887
77.408
77.090
76.773
49.222
48.550
22.640
12.819
12.680
3d
200
150
100
50
0
ppm (t1)
50000
40000
30000
20000
10000
0


32.543
3d
100
50
0
-50
-100
-150
-200
ppm (t1)
50000
0

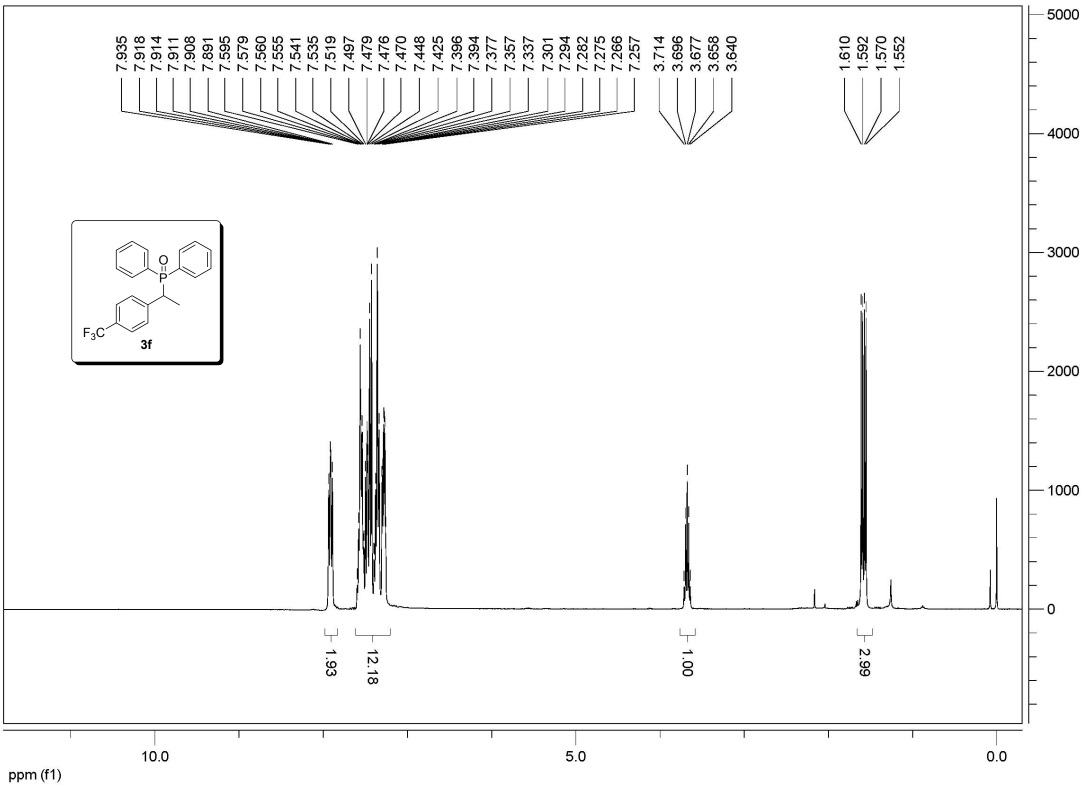
3e

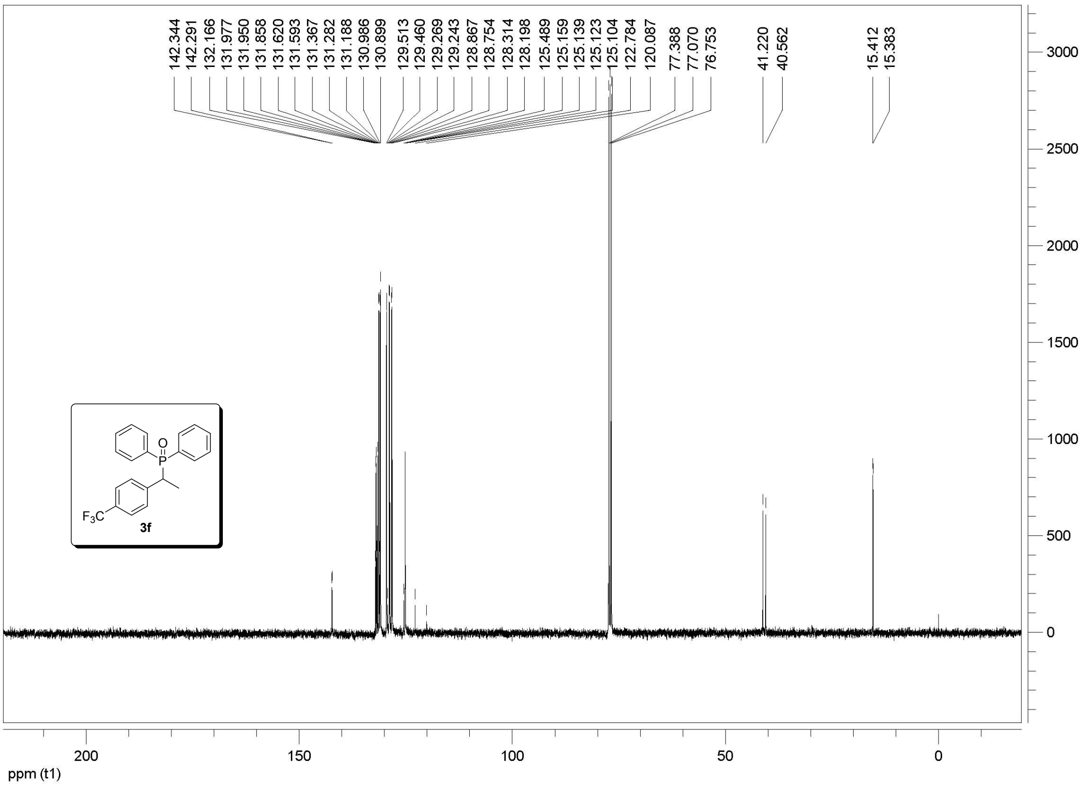


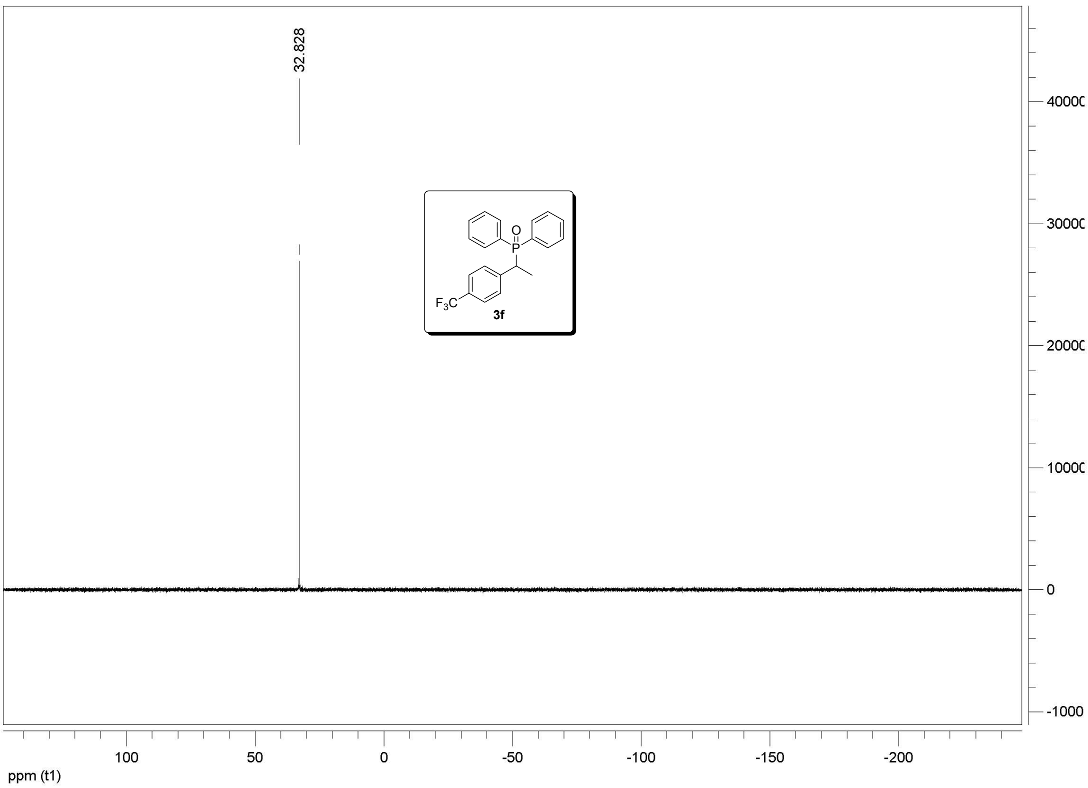



32.949
3e
100
50
0
-50
-100
-150
-200
ppm (t1)

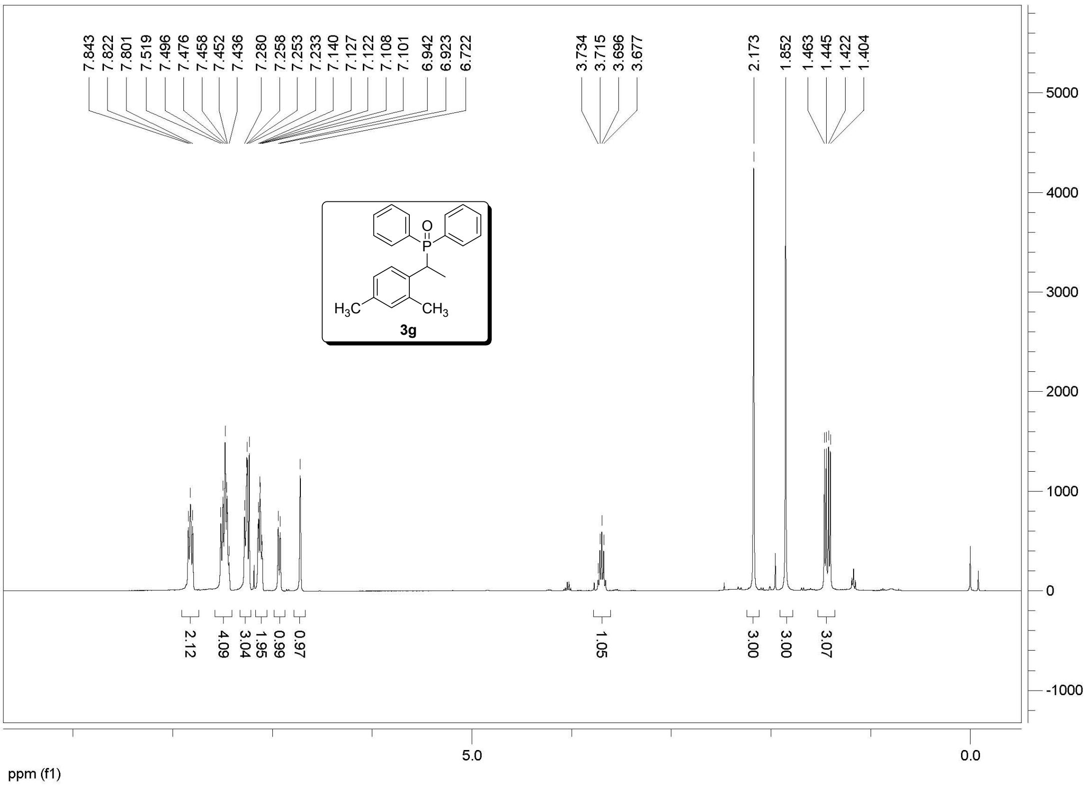
3f

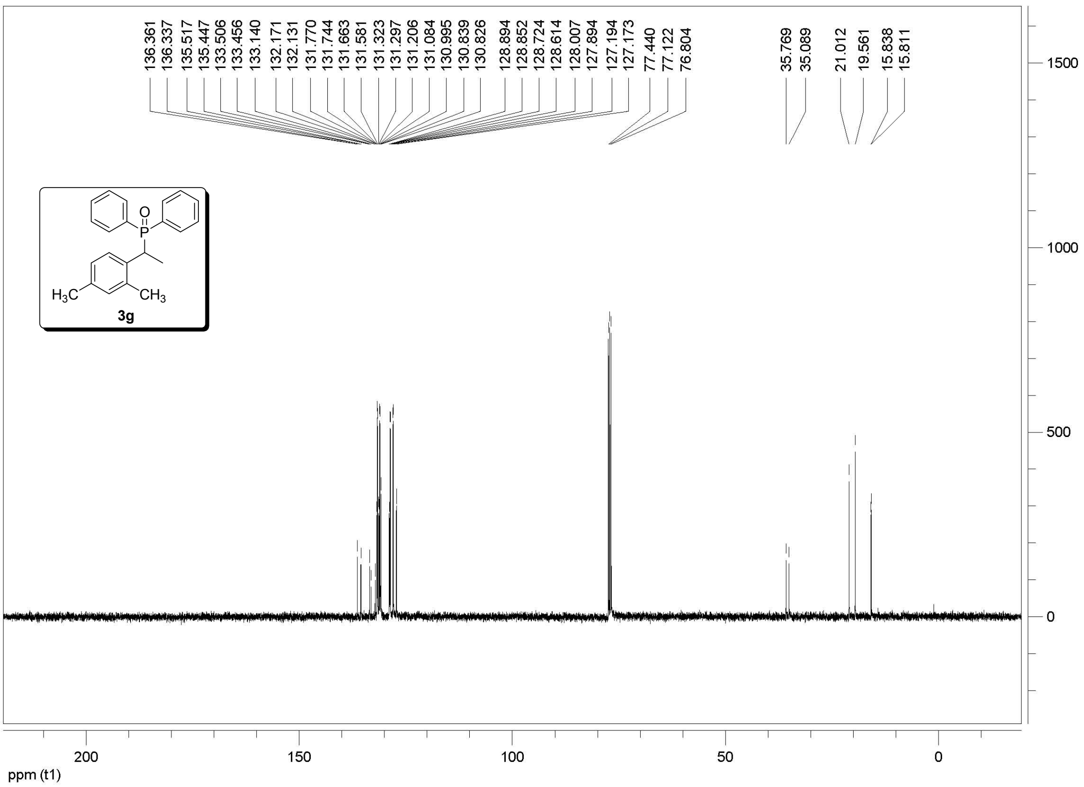

7.935
7.918
7.914
7.911
7.908
7.891
7.595
7.579
7.560
7.555
7.541
7.535
7.519
7.497
7.479
7.476
7.470
7.448
7.425
7.396
7.394
7.377
7.357
7.337
7.301
7.294
7.282
7.275
7.266
7.257
3.714
3.696
3.677
3.658
3.640
1.610
1.592
1.570
1.552
3f
1.93
12.18
1.00
2.99
10.0
5.0
0.0
ppm (f1)

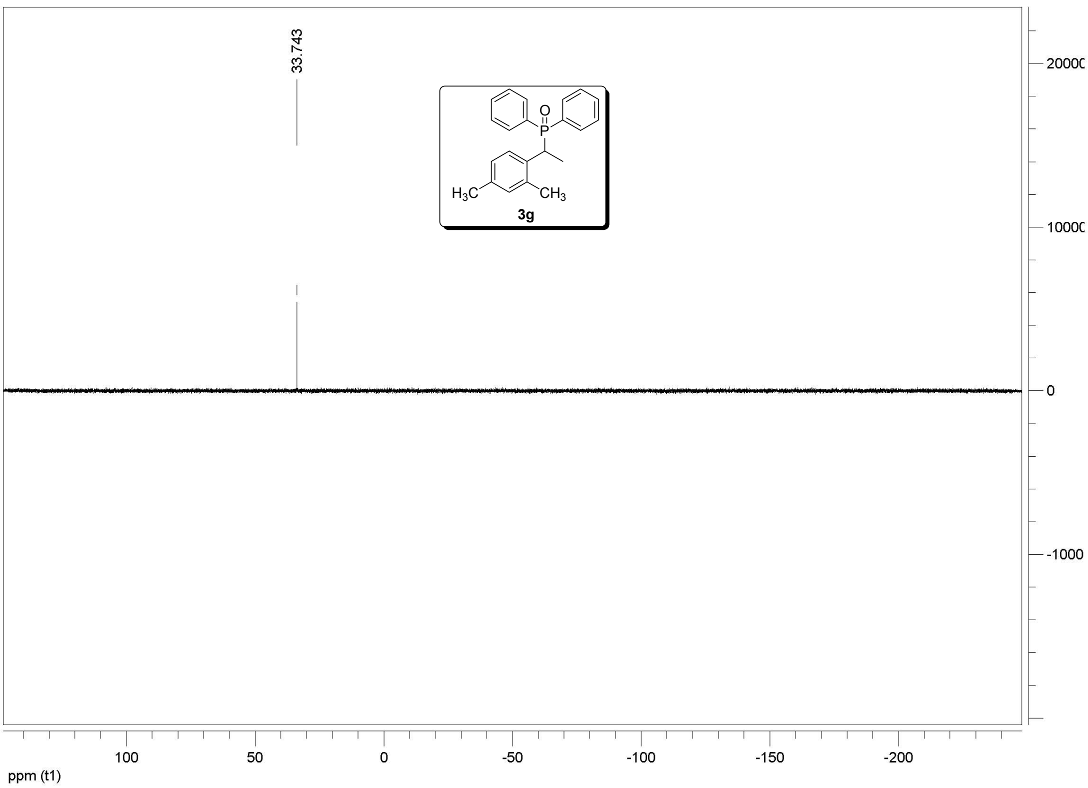

142.344
142.291
132.166
131.977
131.950
131.858
131.620
131.593
131.367
131.282
131.188
130.986
130.899
129.513
129.460
129.269
129.243
128.867
128.754
128.314
128.198
125.489
125.159
125.139
125.123
125.104
122.784
120.087
77.388
77.070
76.753
41.220
40.562
15.412
15.383
3000
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)
O
P
F_3C
3f


32.828
40000
30000
20000
10000
0
-1000
100
50
0
-50
-100
-150
-200
ppm (t1)
O
P
F_3C
3f

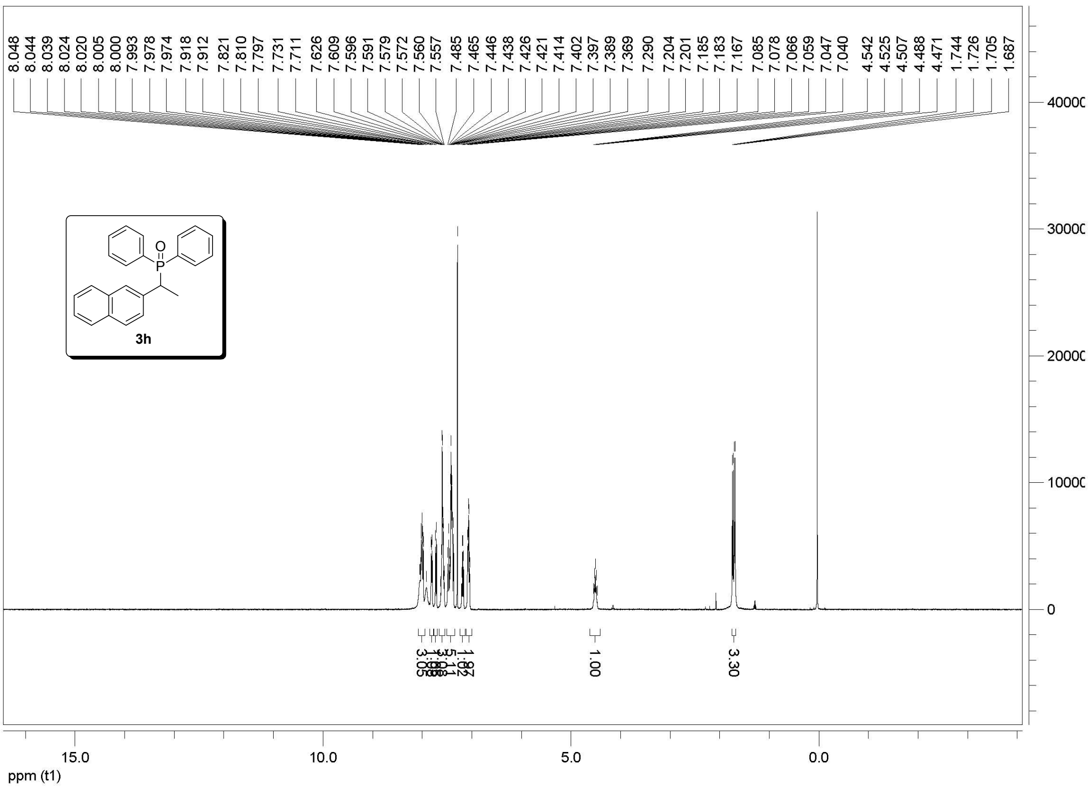
3g

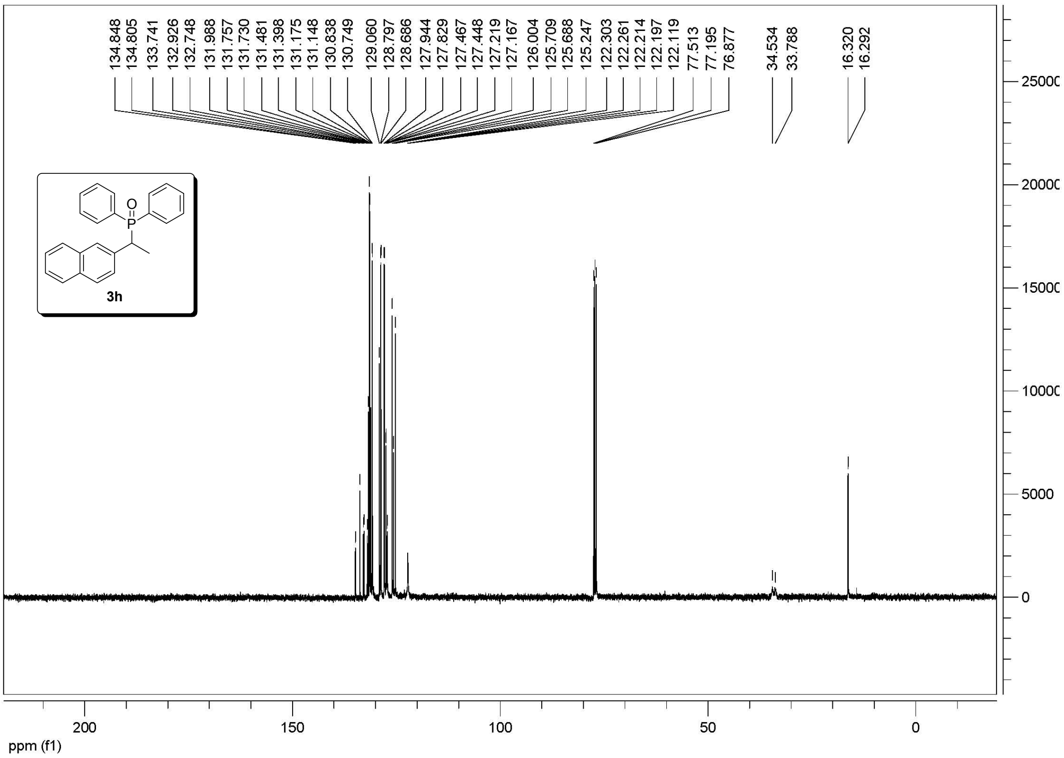

7.843
7.822
7.801
7.519
7.496
7.476
7.458
7.452
7.436
7.280
7.258
7.253
7.233
7.140
7.127
7.122
7.108
7.101
6.942
6.923
6.722
3.734
3.715
3.696
3.677
2.173
1.852
1.463
1.445
1.422
1.404
O
P
H_3C
CH_3
3g
2.12
4.09
3.04
1.95
0.99
0.97
1.05
3.00
3.00
3.07
5000
4000
3000
2000
1000
0
-1000
5.0
0.0
ppm (f1)

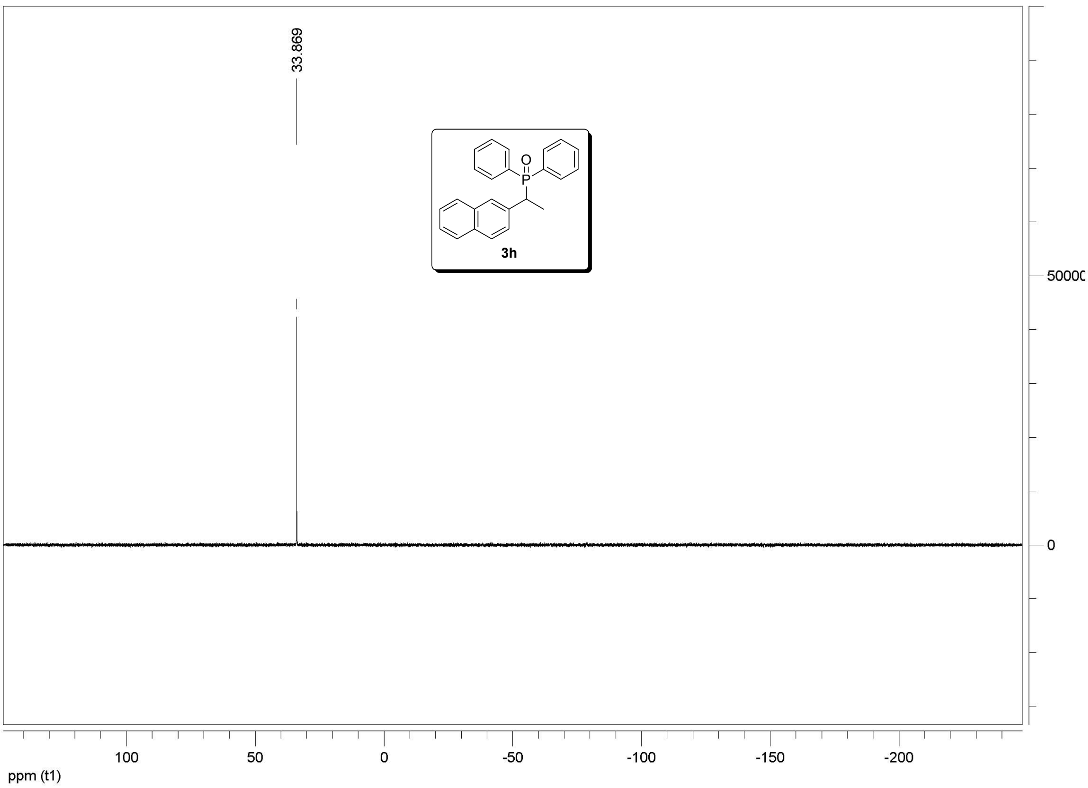

136.361
136.337
135.517
135.447
133.506
133.456
133.140
132.171
132.131
131.770
131.744
131.663
131.581
131.323
131.297
131.206
131.084
130.995
130.839
130.826
128.894
128.852
128.724
128.614
128.007
127.894
127.194
127.173
77.440
77.122
76.804
35.769
35.089
21.012
19.561
15.838
15.811
O
P
H_3C
CH_3
3g
1500
1000
500
0
200
150
100
50
0
ppm (t1)



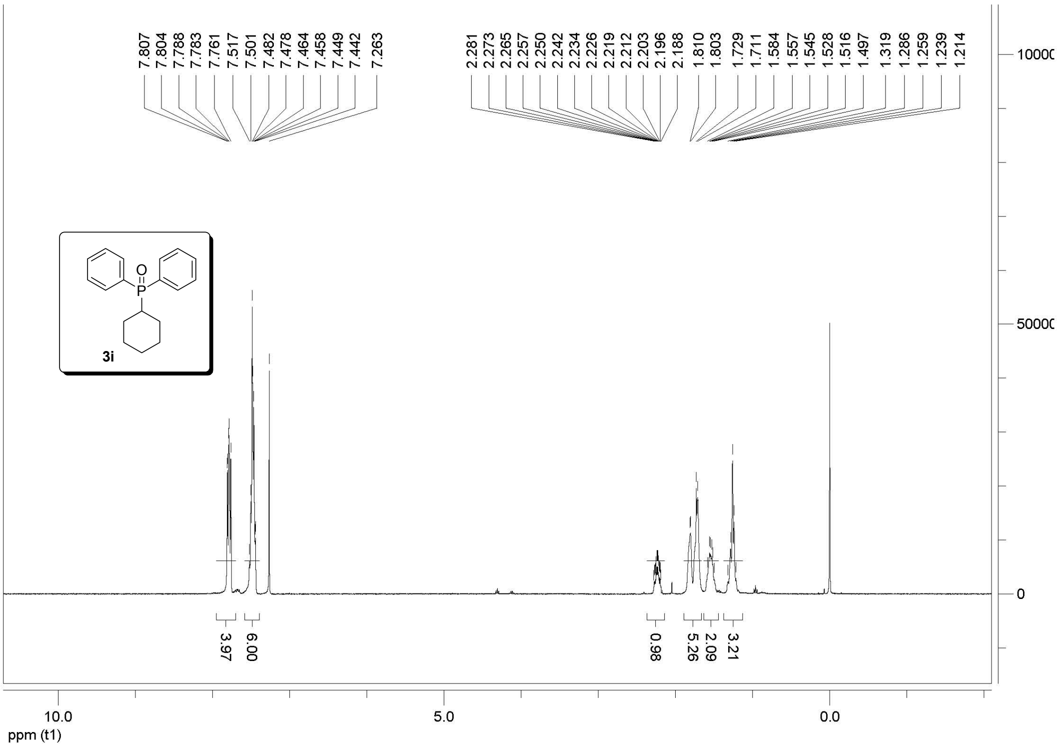
3h

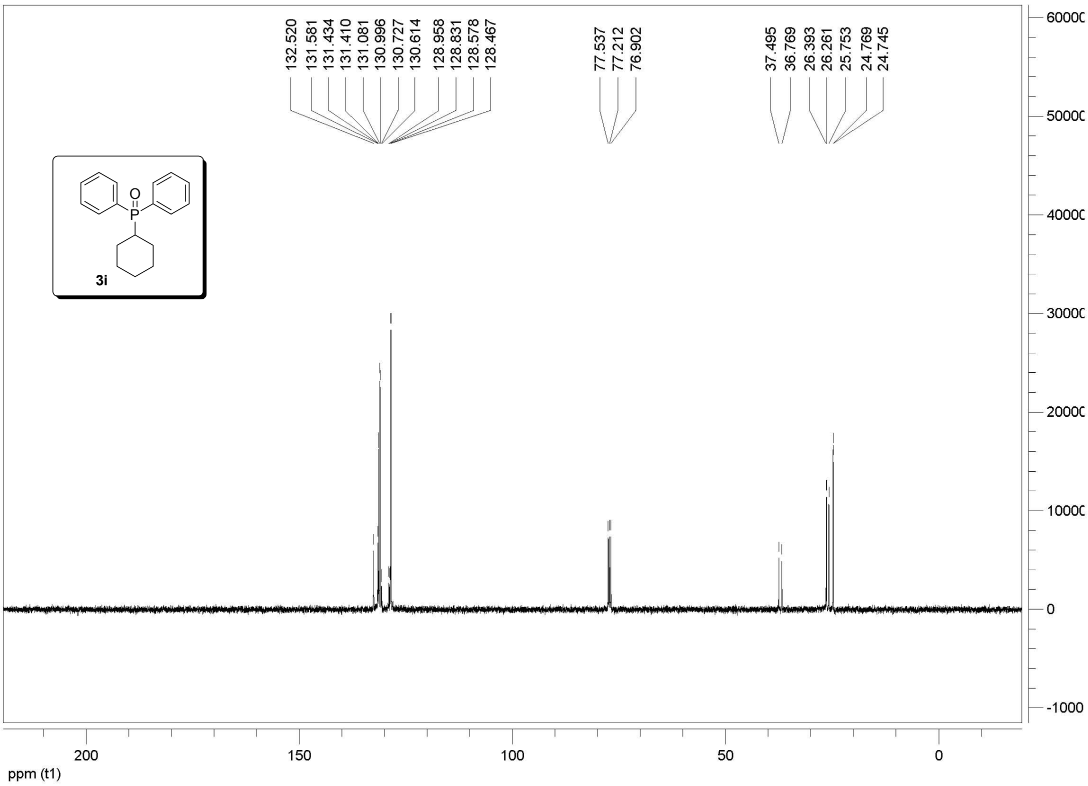


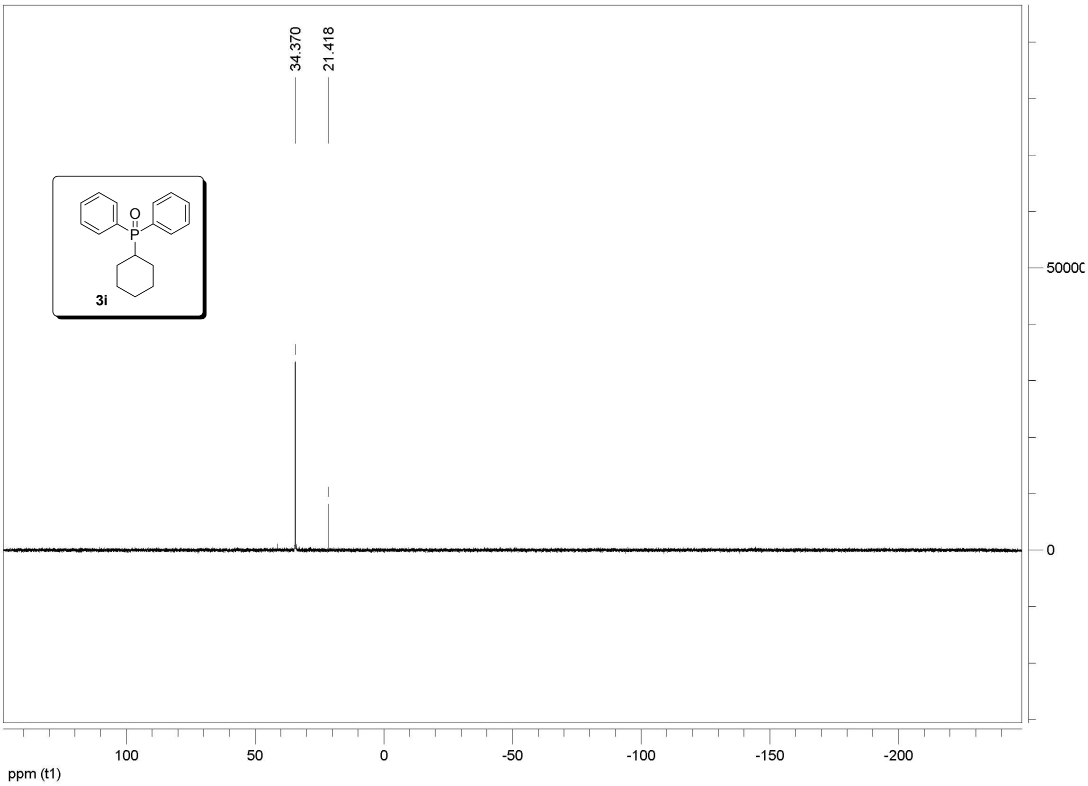

134.848
134.805
133.741
132.926
132.748
131.988
131.757
131.730
131.481
131.398
131.175
131.148
130.838
130.749
129.060
128.797
128.686
127.944
127.829
127.467
127.448
127.219
127.167
126.004
125.709
125.688
125.247
122.303
122.261
122.214
122.197
122.119
77.513
77.195
76.877
34.534
33.788
16.320
16.292
3h
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (f1)


33.869
3h
50000
0
100
50
0
-50
-100
-150
-200
ppm (t1)

3i


7.807
7.804
7.788
7.783
7.761
7.517
7.501
7.482
7.478
7.464
7.458
7.449
7.442
7.263
2.281
2.273
2.265
2.257
2.250
2.242
2.234
2.226
2.219
2.212
2.203
2.196
2.188
1.810
1.803
1.729
1.711
1.584
1.557
1.545
1.528
1.516
1.497
1.319
1.286
1.259
1.239
1.214
3i
3.97
6.00
0.98
5.26
2.09
3.21
10.0
5.0
0.0
ppm (t1)


132.520
131.581
131.434
131.410
131.081
130.996
130.727
130.614
128.958
128.831
128.578
128.467
77.537
77.212
76.902
37.495
36.769
26.393
26.261
25.753
24.769
24.745
3i
200
150
100
50
0
ppm (t1)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O
P
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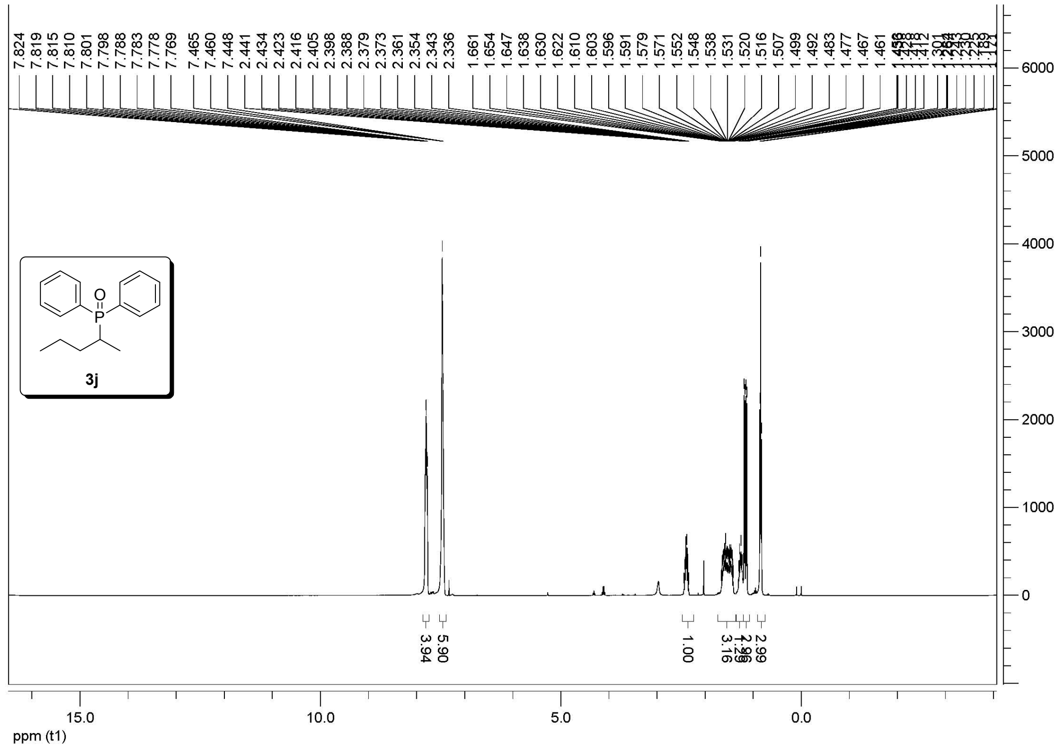
-100
-150
-200
ppm (t1)

3j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7.819
7.815
7.810
7.801
7.798
7.788
7.783
7.778
7.769
7.465
7.460
7.448
2.441
2.434
2.423
2.416
2.405
2.398
2.388
2.379
2.373
2.361
2.354
2.343
2.336
1.661
1.654
1.647
1.638
1.630
1.622
1.610
1.603
1.596
1.591
1.579
1.571
1.552
1.548
1.538
1.531
1.520
1.516
1.507
1.499
1.492
1.483
1.477
1.467
1.461
6000
5000
4000
3000
2000
1000
0
O
P
3j
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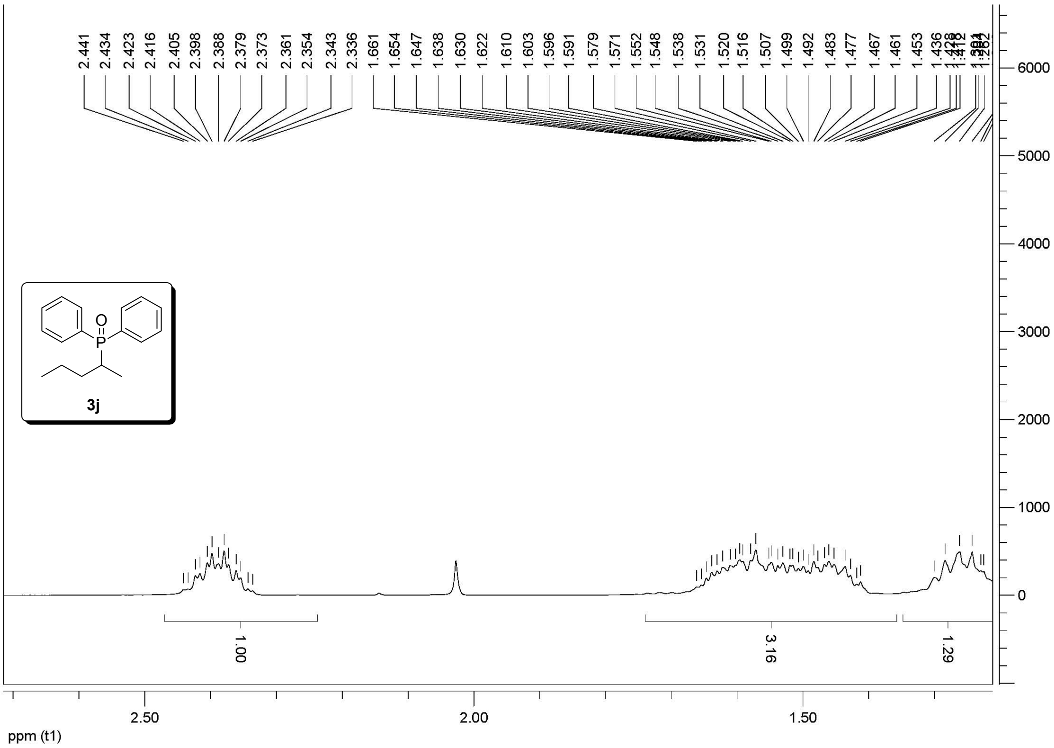
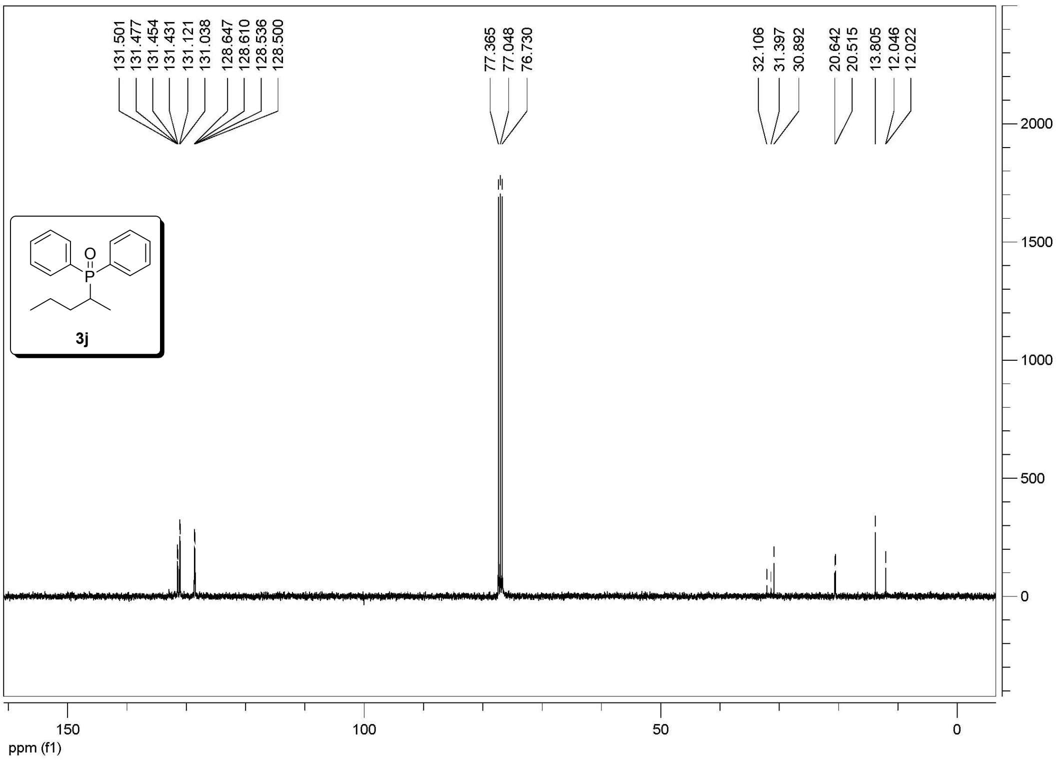
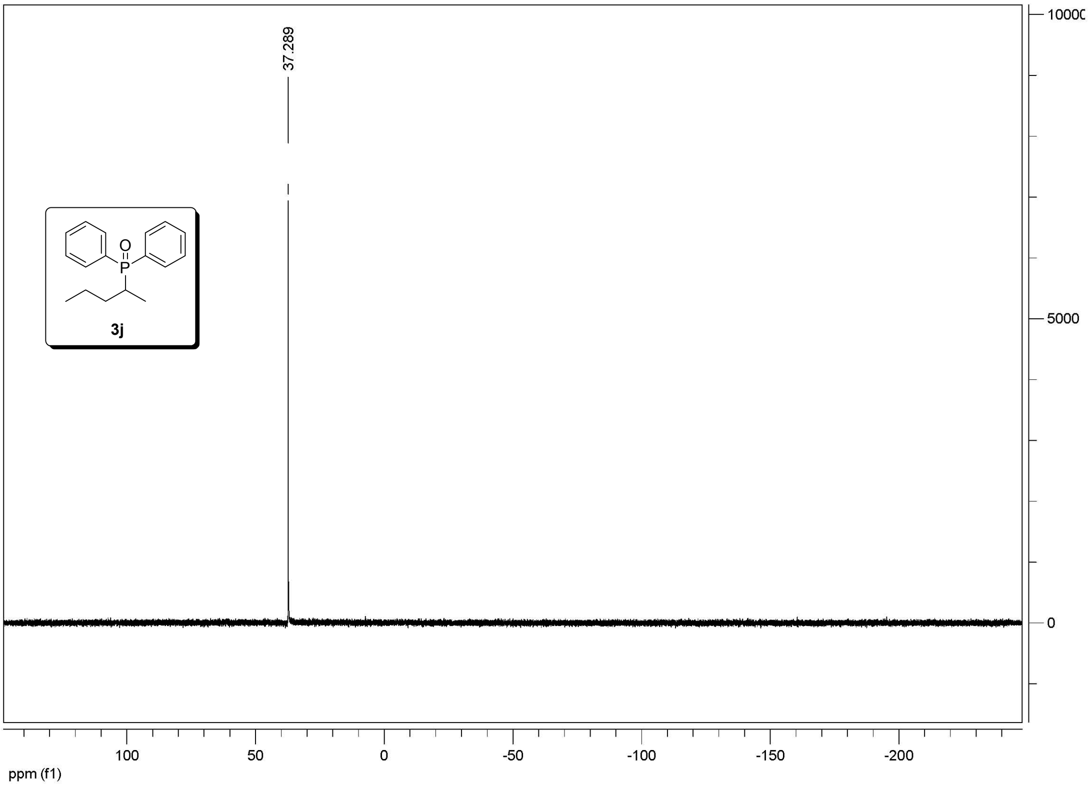
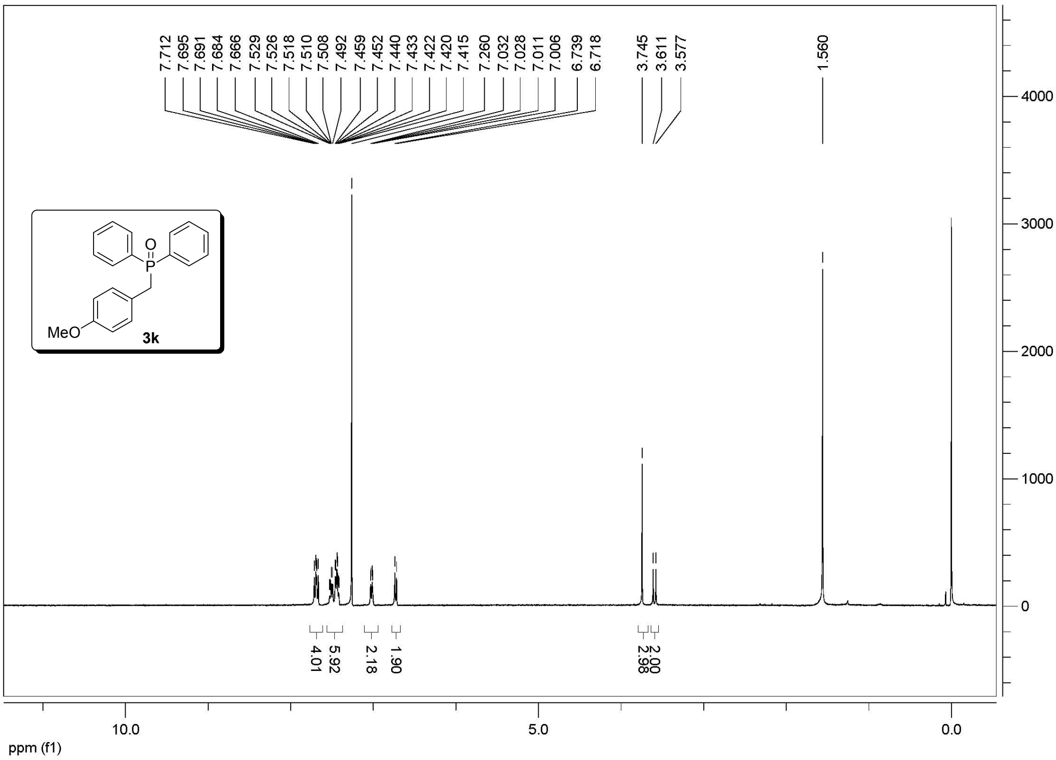
5.90
1.00
3.16
2.99
15.0
10.0
5.0
0.0
ppm (t1)

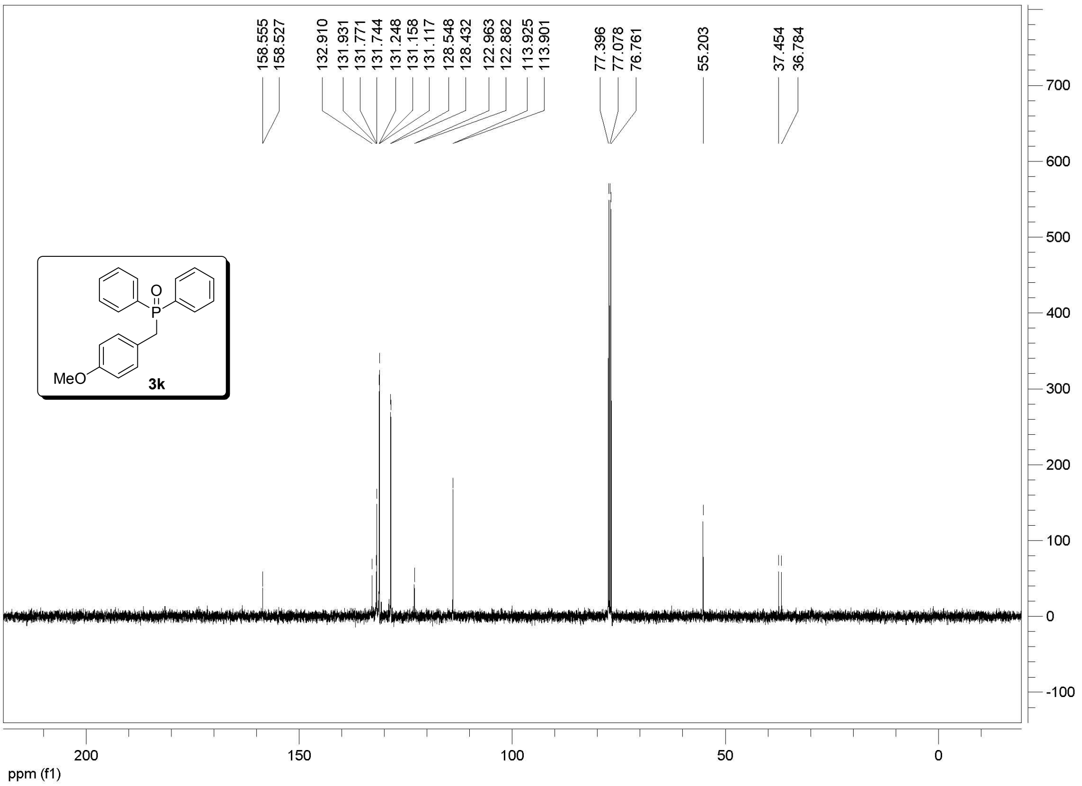

2.441
2.434
2.423
2.416
2.405
2.398
2.388
2.379
2.373
2.361
2.354
2.343
2.336
1.661
1.654
1.647
1.638
1.630
1.622
1.610
1.603
1.596
1.591
1.579
1.571
1.552
1.548
1.538
1.531
1.520
1.516
1.507
1.499
1.492
1.483
1.477
1.467
1.461
1.453
1.436
O
P
3j
6000
5000
4000
3000
2000
1000
0
1.00
3.16
1.29
2.50
2.00
1.50
ppm (t1)


131.501
131.477
131.454
131.431
131.121
131.038
128.647
128.610
128.536
128.500
77.365
77.048
76.730
32.106
31.397
30.892
20.642
20.515
13.805
12.046
12.022
O
P
3j
2000
1500
1000
500
0
150
100
50
0
ppm (f1)


37.289
3j
10000
5000
0
100
50
0
-50
-100
-150
-200
ppm (f1)

3k


7.712
7.695
7.691
7.684
7.666
7.529
7.526
7.518
7.510
7.508
7.492
7.459
7.452
7.440
7.433
7.422
7.420
7.415
7.260
7.032
7.028
7.011
7.006
6.739
6.718
3.745
3.611
3.577
1.560
MeO
3k
4.01
5.92
2.18
1.90
2.98
2.00
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)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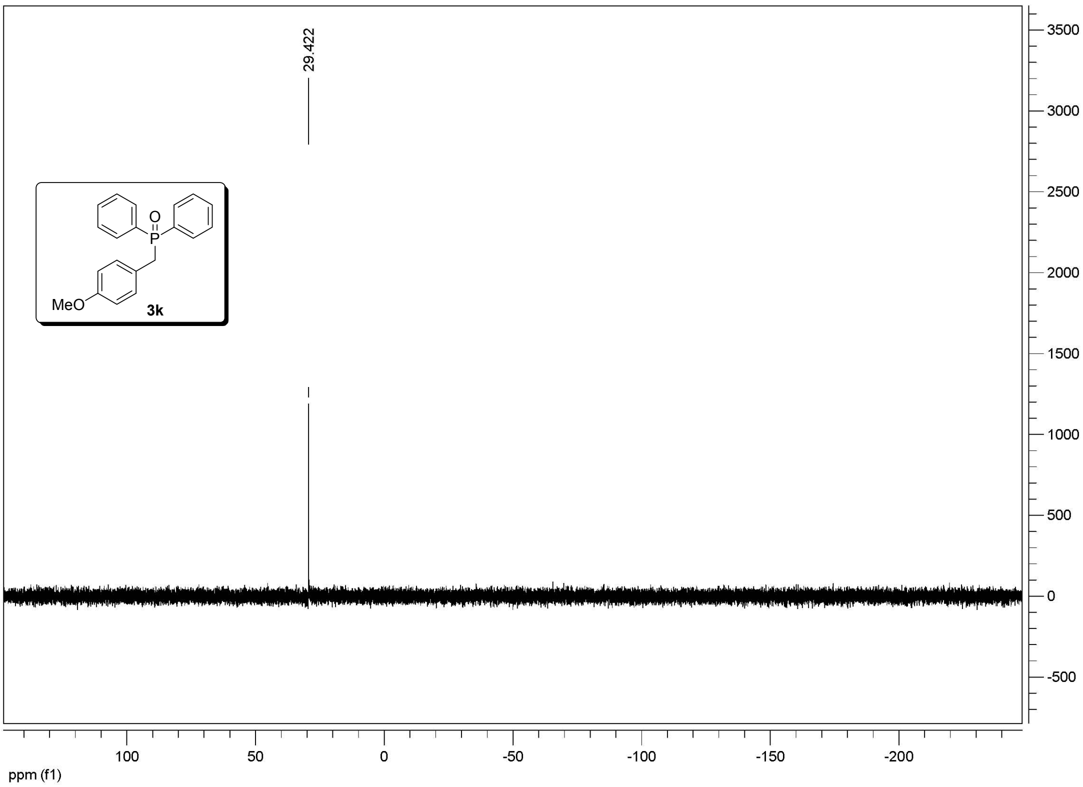
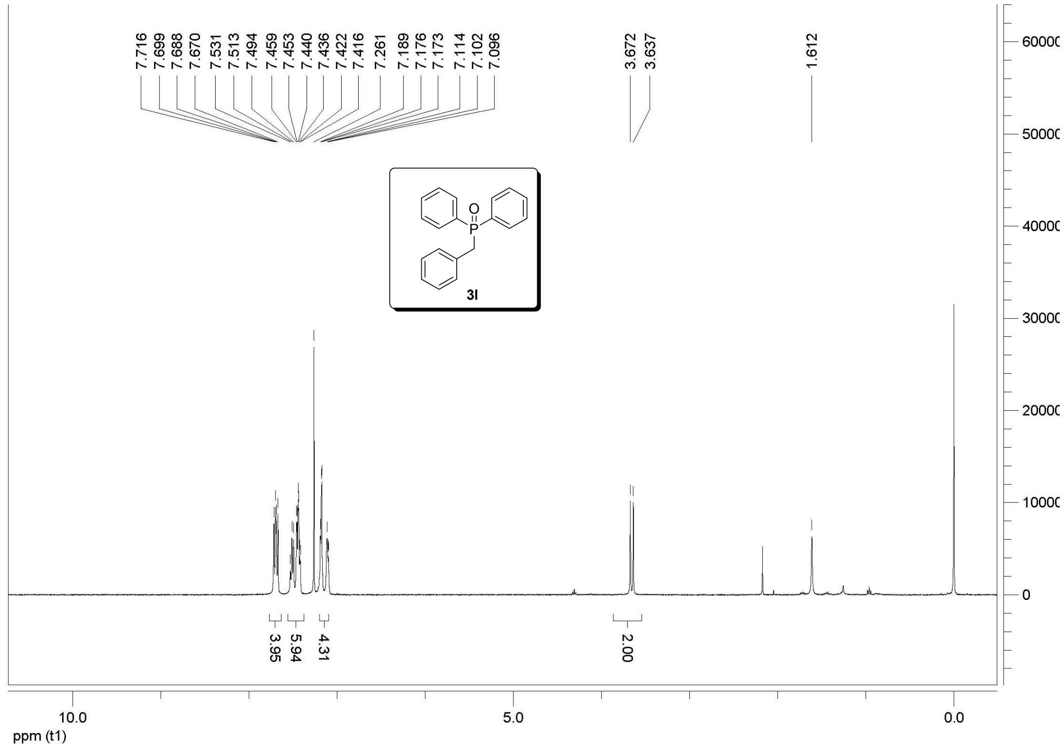
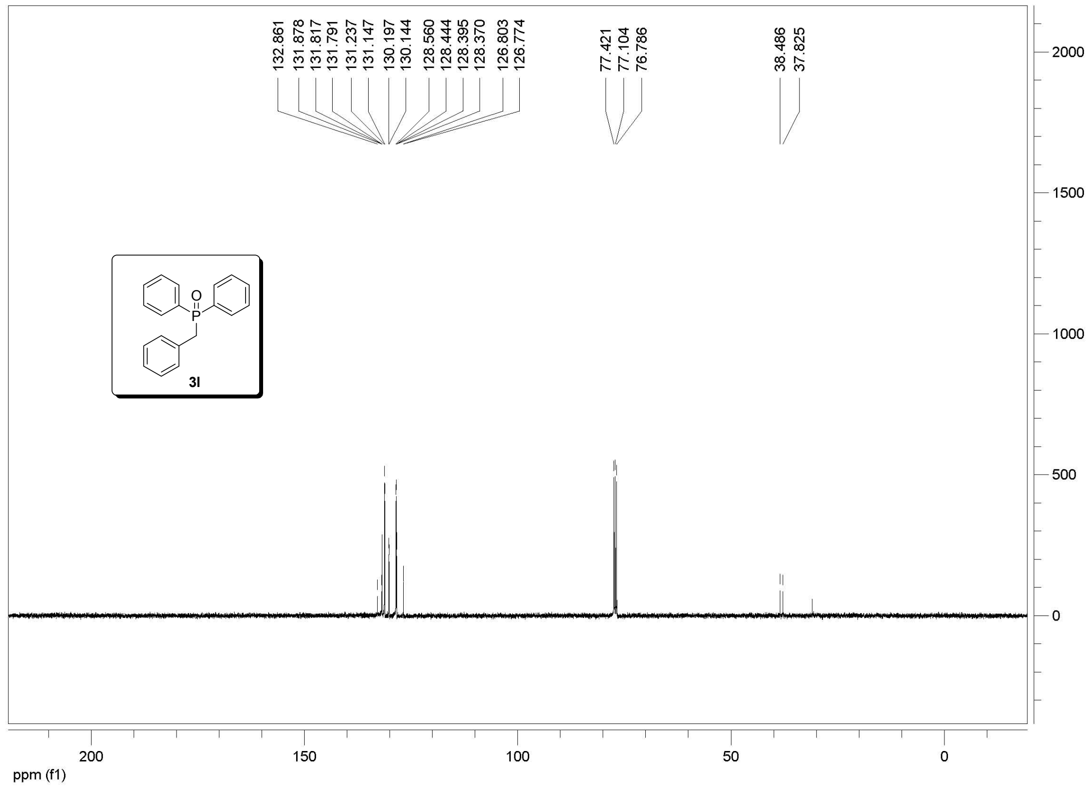
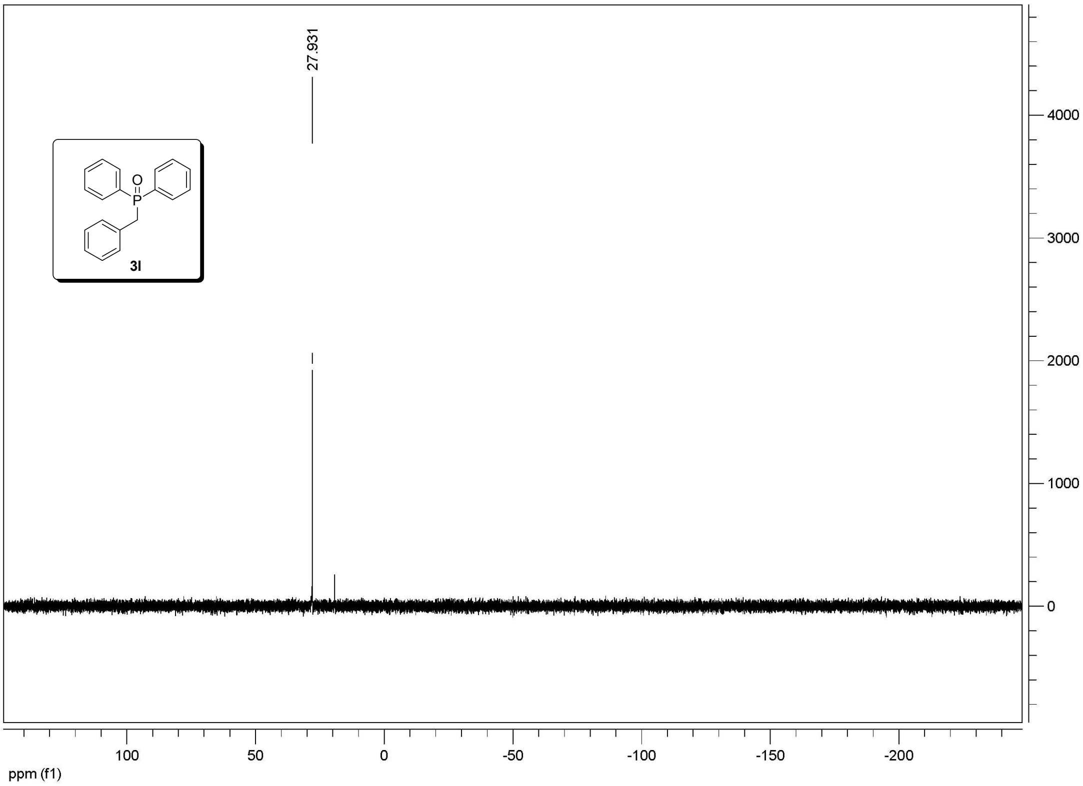
131.771
131.744
131.248
131.158
131.117
128.548
128.432
122.963
122.882
113.925
113.901
77.396
77.078
76.761
55.203
37.454
36.784
MeO
3k
ppm (f1)


29.422
MeO
3k
ppm (f1)

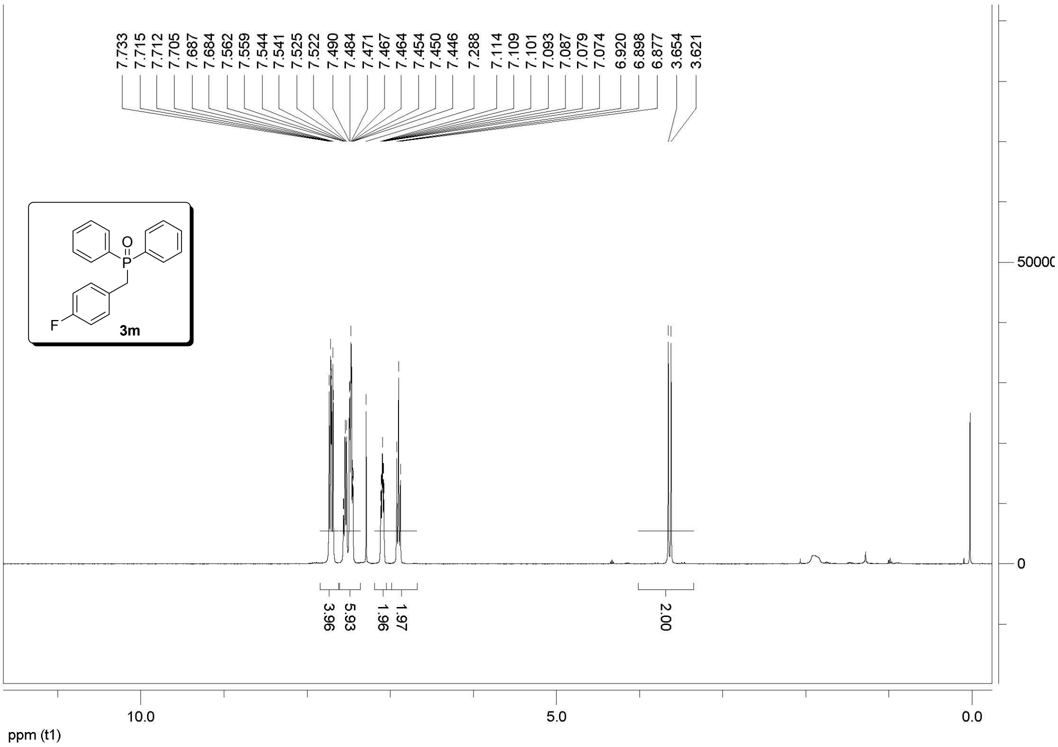
3l

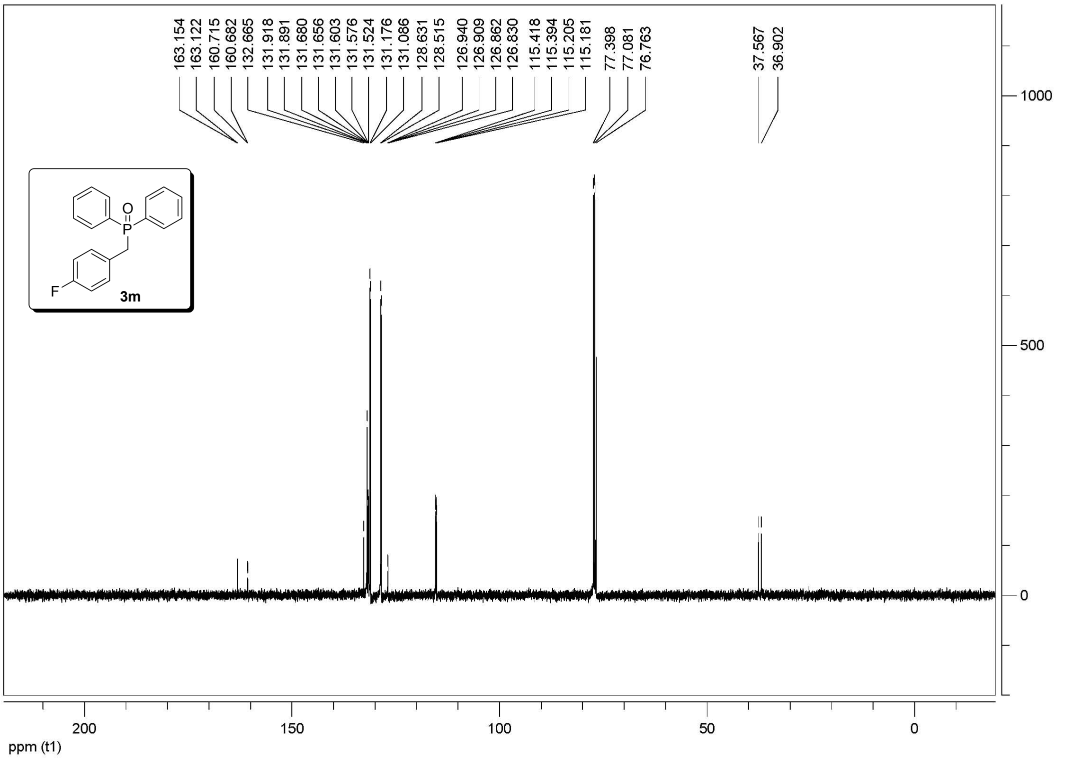

7.716
7.699
7.688
7.670
7.531
7.513
7.494
7.459
7.453
7.440
7.436
7.422
7.416
7.261
7.189
7.176
7.173
7.114
7.102
7.096
3.672
3.637
1.612
3l
3.95
5.94
4.31
2.00
10.0
5.0
0.0
ppm (t1)

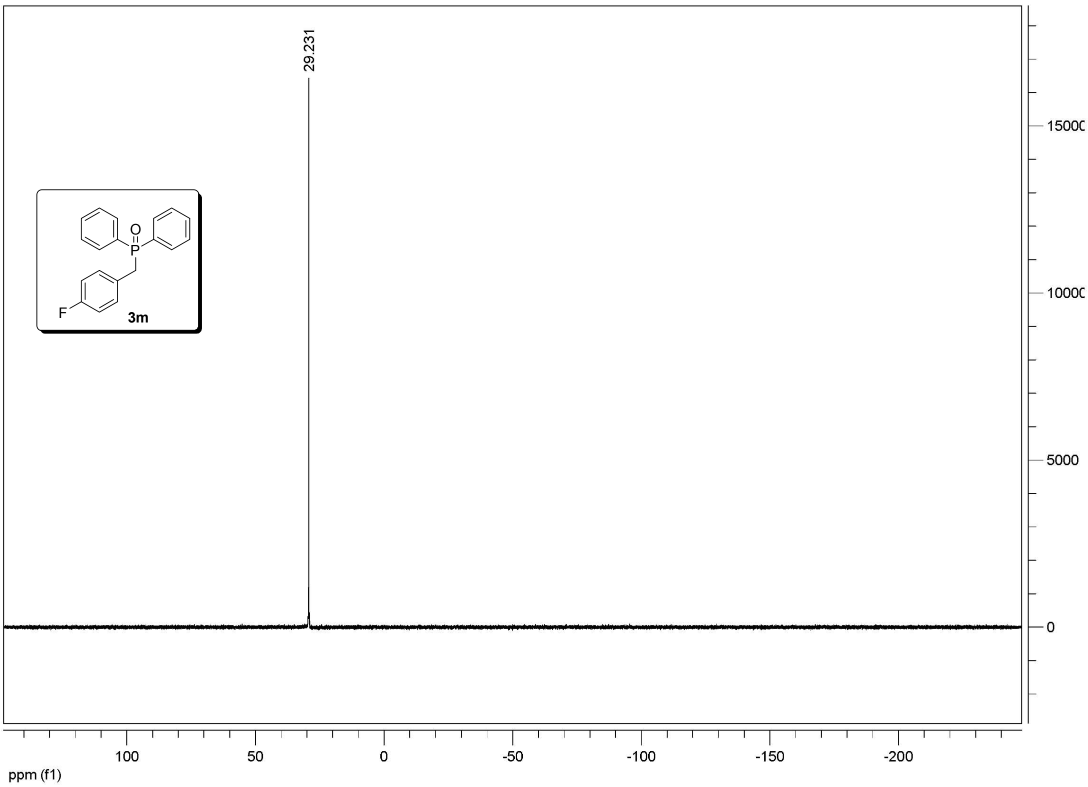

132.861
131.878
131.817
131.791
131.237
131.147
130.197
130.144
128.560
128.444
128.395
128.370
126.803
126.774
77.421
77.104
76.786
38.486
37.825
3l
200
150
100
50
0
ppm (f1)


27.931
3l
4000
3000
2000
1000
0
100
50
0
-50
-100
-150
-200
ppm (f1)

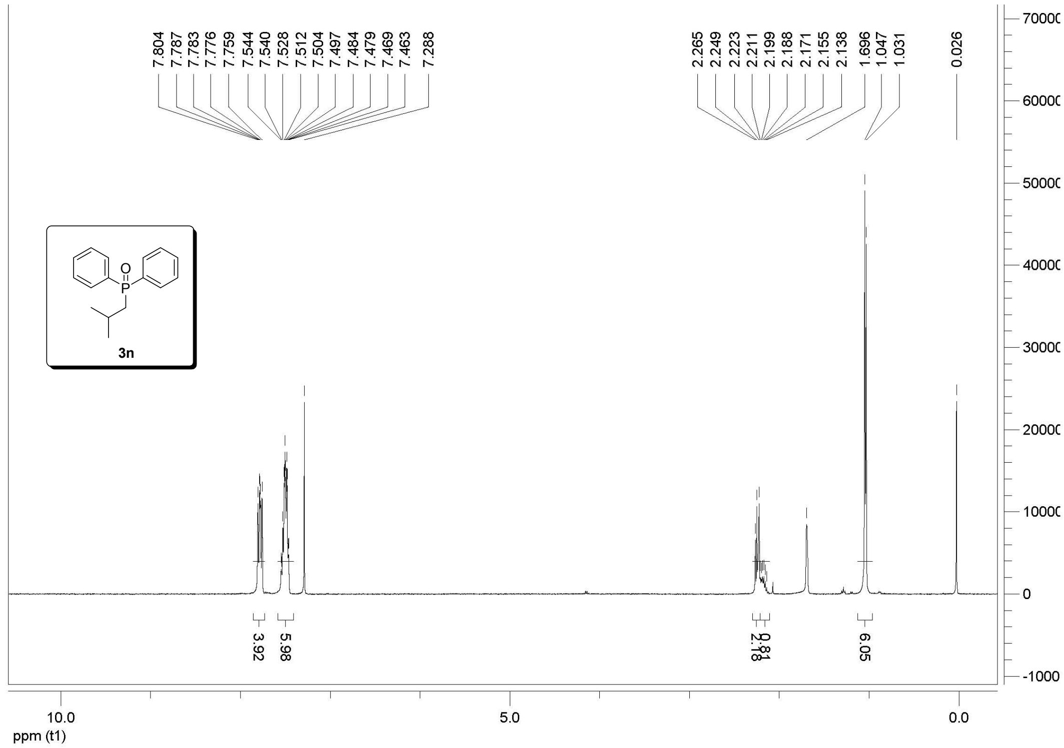
3m

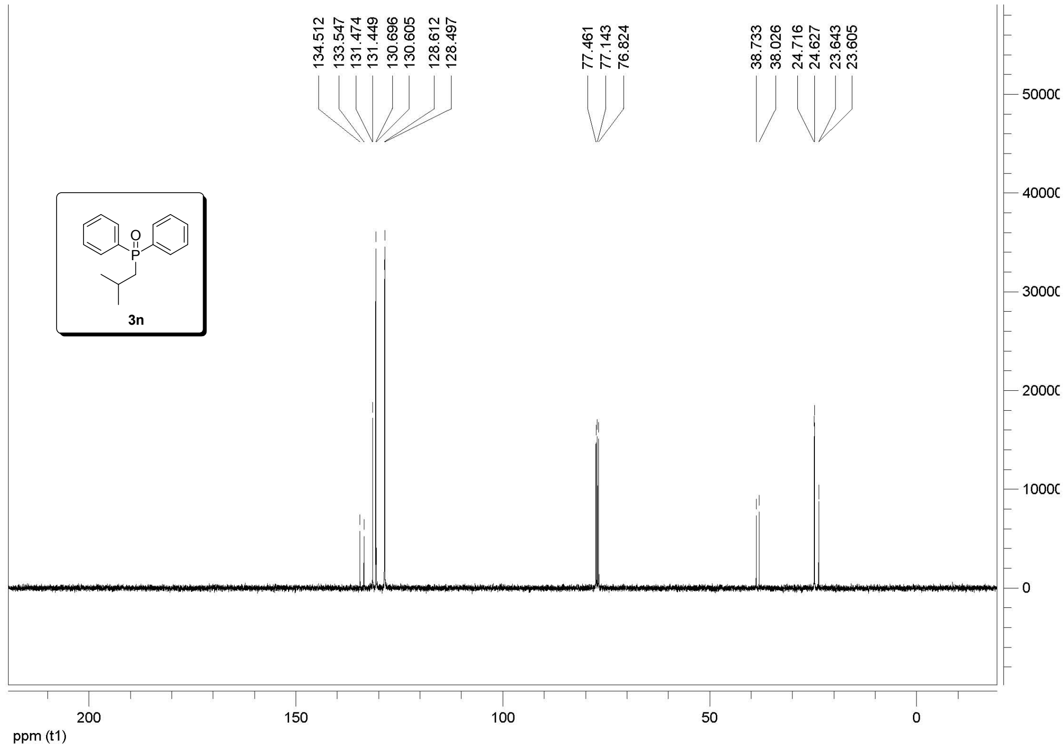

7.733
7.715
7.712
7.705
7.687
7.684
7.562
7.559
7.544
7.541
7.525
7.522
7.490
7.484
7.471
7.467
7.464
7.454
7.450
7.446
7.288
7.114
7.109
7.101
7.093
7.087
7.079
7.074
6.920
6.898
6.877
3.654
3.621
F
3m
50000
0
3.96
5.93
1.96
1.97
2.00
10.0
5.0
0.0
ppm (t1)


163.154
163.122
160.715
160.682
132.665
131.918
131.891
131.680
131.656
131.603
131.576
131.524
131.176
131.086
128.631
128.515
126.940
126.909
126.862
126.830
115.418
115.394
115.205
115.181
77.398
77.081
76.763
37.567
36.902
O
P
F
3m
1000
500
0
200
150
100
50
0
ppm (t1)


29.231
O
P
F
3m
15000
10000
5000
0
100
50
0
-50
-100
-150
-200
ppm (f1)

3n


7.804
7.787
7.783
7.776
7.759
7.544
7.540
7.528
7.512
7.504
7.497
7.484
7.479
7.469
7.463
7.288
2.265
2.249
2.223
2.211
2.199
2.188
2.171
2.155
2.138
1.696
1.047
1.031
0.026
3n
3.92
5.98
0.81
2.18
6.05
10.0
5.0
0.0
ppm (t1)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133.547
131.474
131.449
130.696
130.605
128.612
128.497
77.461
77.143
76.824
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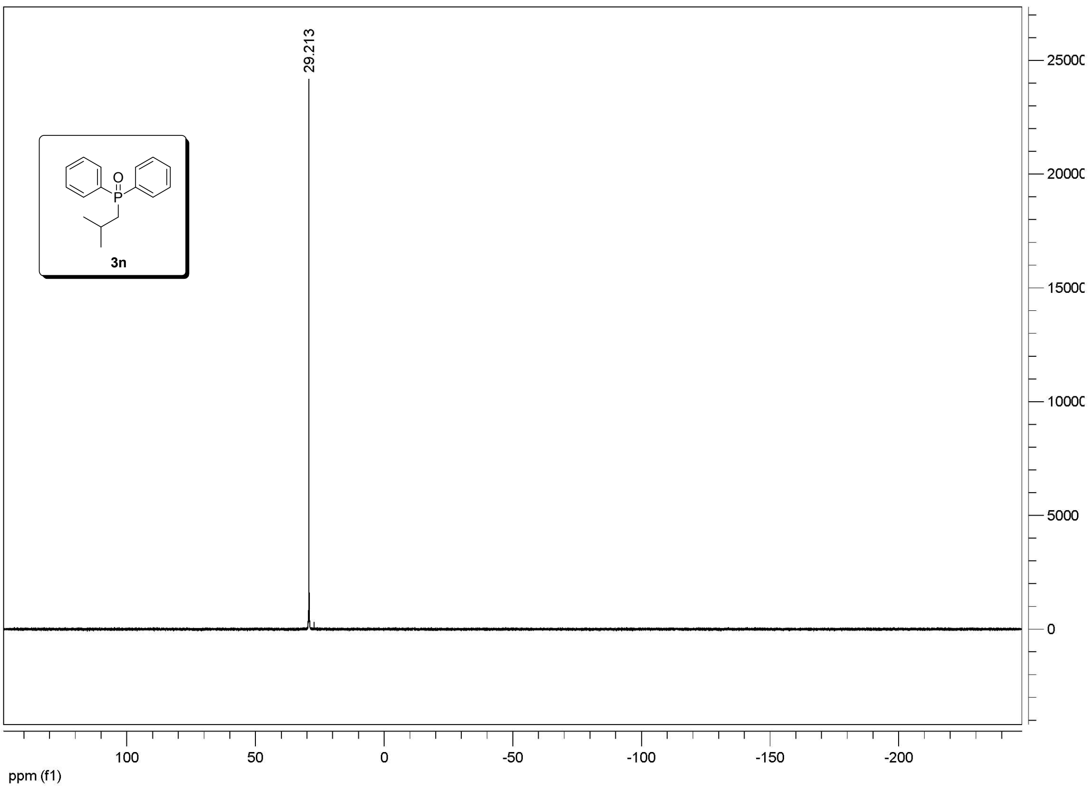
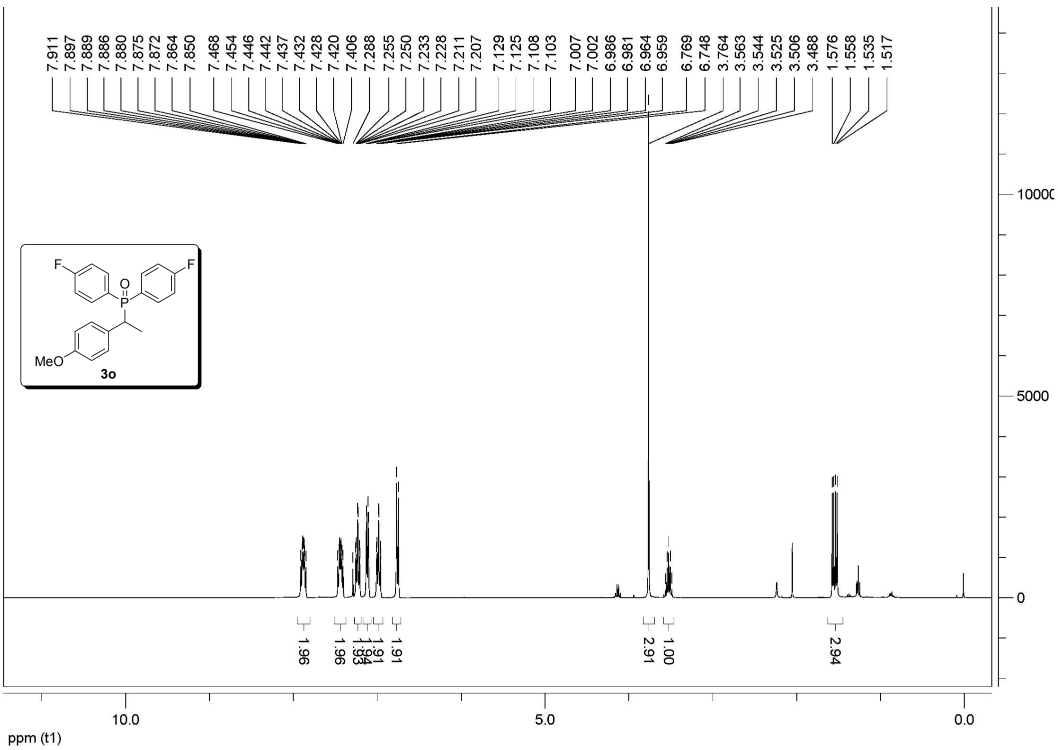
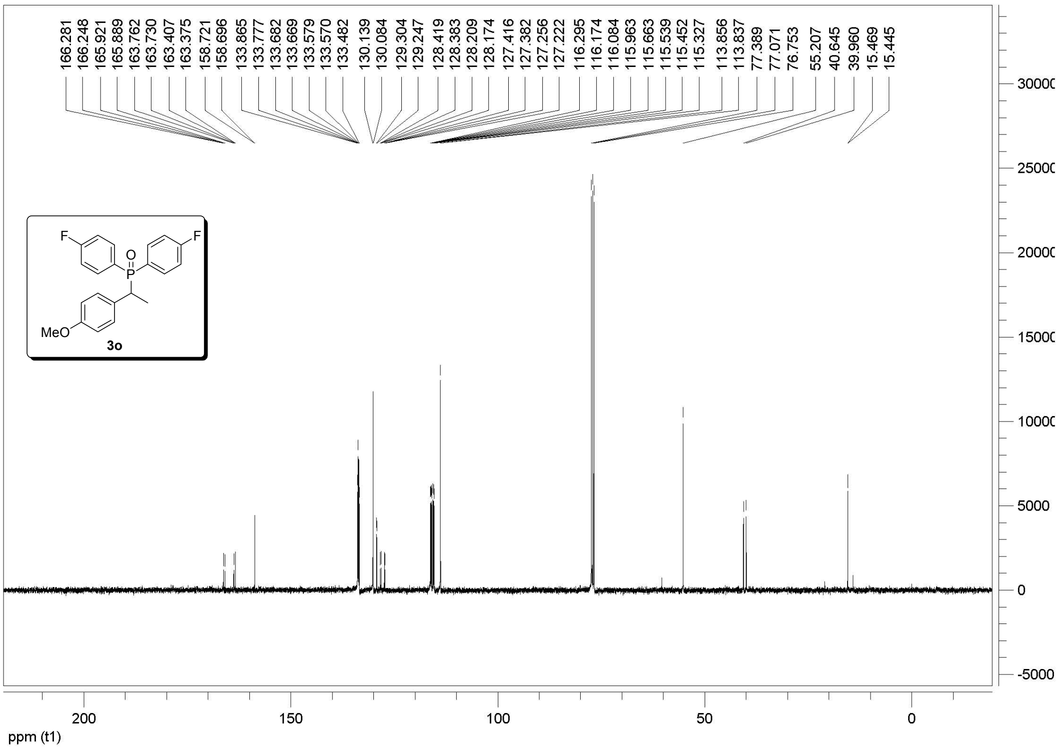
38.026
24.716
24.627
23.643
23.605
3n
200
150
100
50
0
ppm (t1)



3o




166.281
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165.921
165.889
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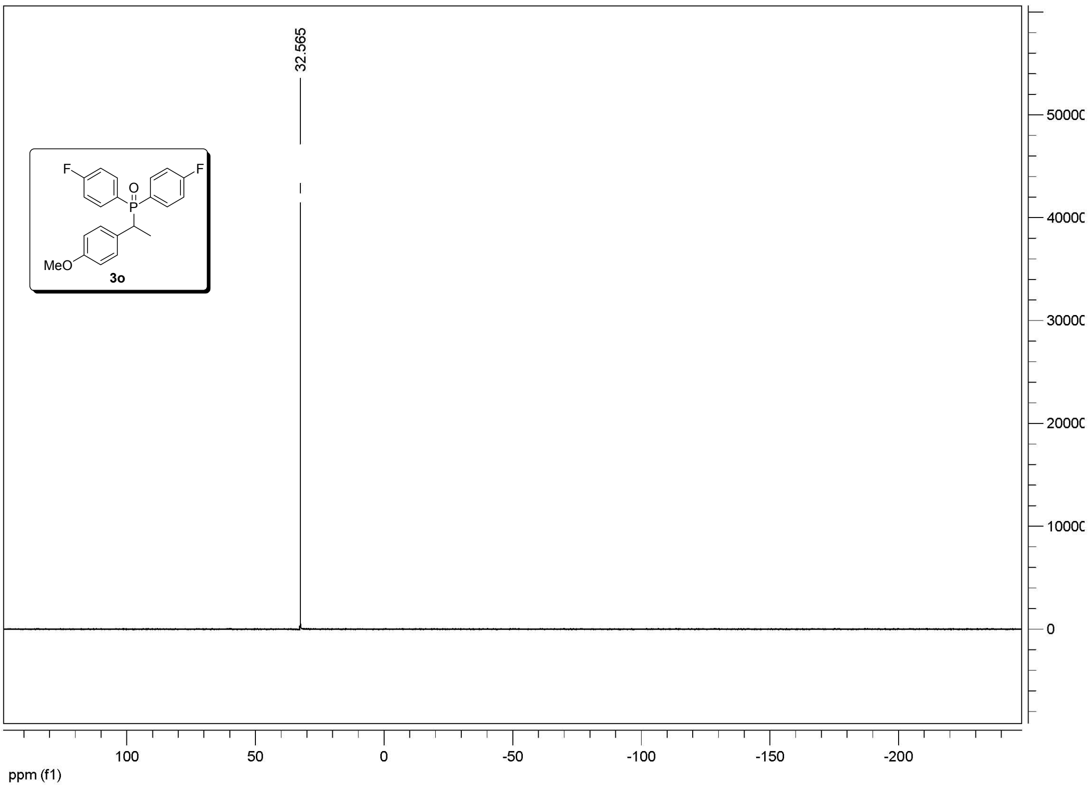
163.730
163.407
163.375
158.721
158.696
133.865
133.777
133.682
133.669
133.579
133.570
133.482
130.139
130.084
129.304
129.247
128.419
128.383
128.209
128.174
127.416
127.382
127.256
127.222
116.295
116.174
116.084
115.963
115.663
115.539
115.452
115.327
113.856
113.837
77.389
77.071
76.753
55.207
40.645
39.960
15.469
15.445
F
O
P
F
MeO
3o
ppm (t1)


32.565
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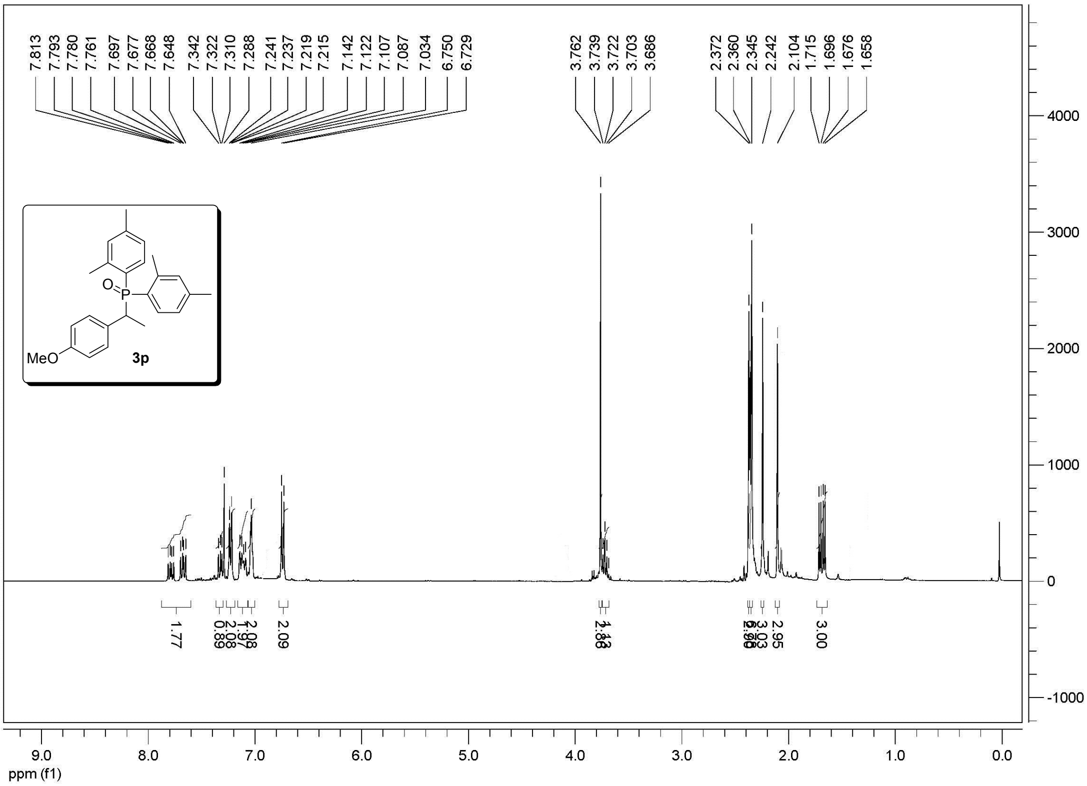
O
P
F
MeO
3o
ppm (f1)

3p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7.648
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7.322
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7.288
7.241
7.237
7.219
7.215
7.142
7.122
7.107
7.087
7.034
6.750
6.729
3.762
3.739
3.722
3.703
3.686
2.372
2.360
2.345
2.242
2.104
1.715
1.696
1.676
1.658
MeO
3p
1.77
0.89
2.08
1.97
2.08
2.09
2.95
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
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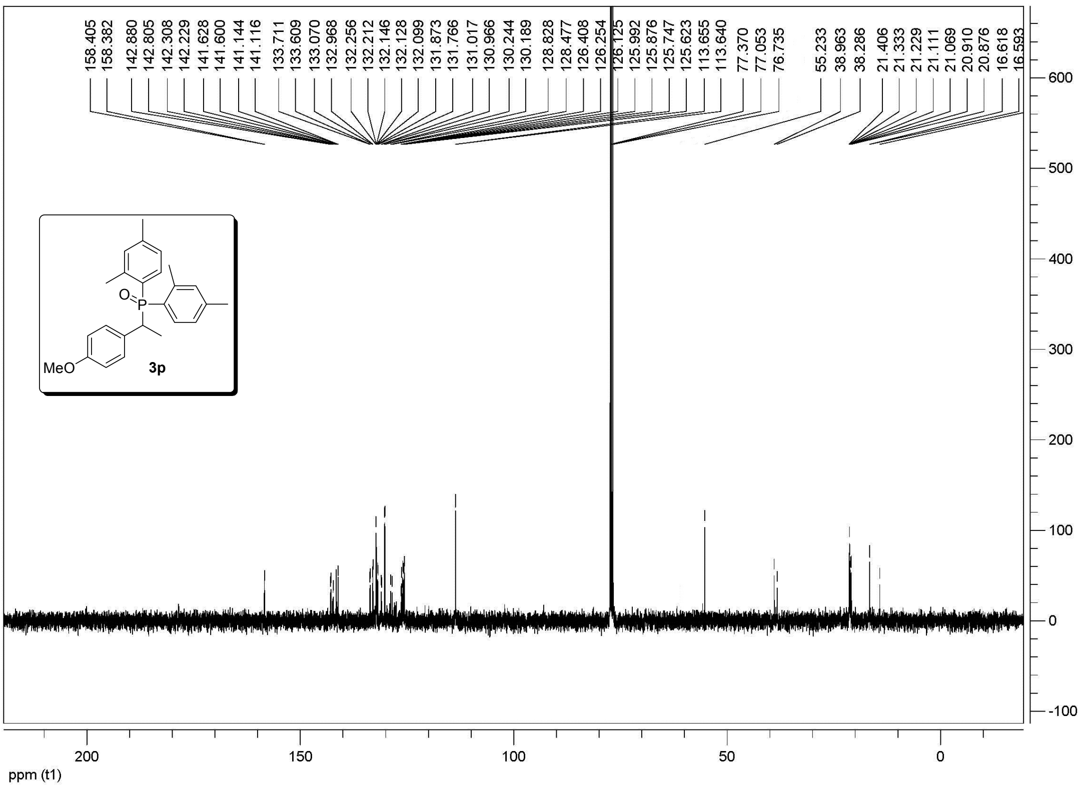
3000
2000
1000
0
-1000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142.229
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141.600
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141.116
133.711
133.609
133.070
132.968
132.256
132.212
132.146
132.128
132.099
131.873
131.766
131.017
130.966
130.244
130.189
128.828
128.477
126.408
126.254
126.125
125.992
125.876
125.747
125.623
113.655
113.640
77.370
77.053
76.735
55.233
38.963
38.286
21.406
21.333
21.229
21.111
21.069
20.910
20.876
16.618
16.593
MeO
3p
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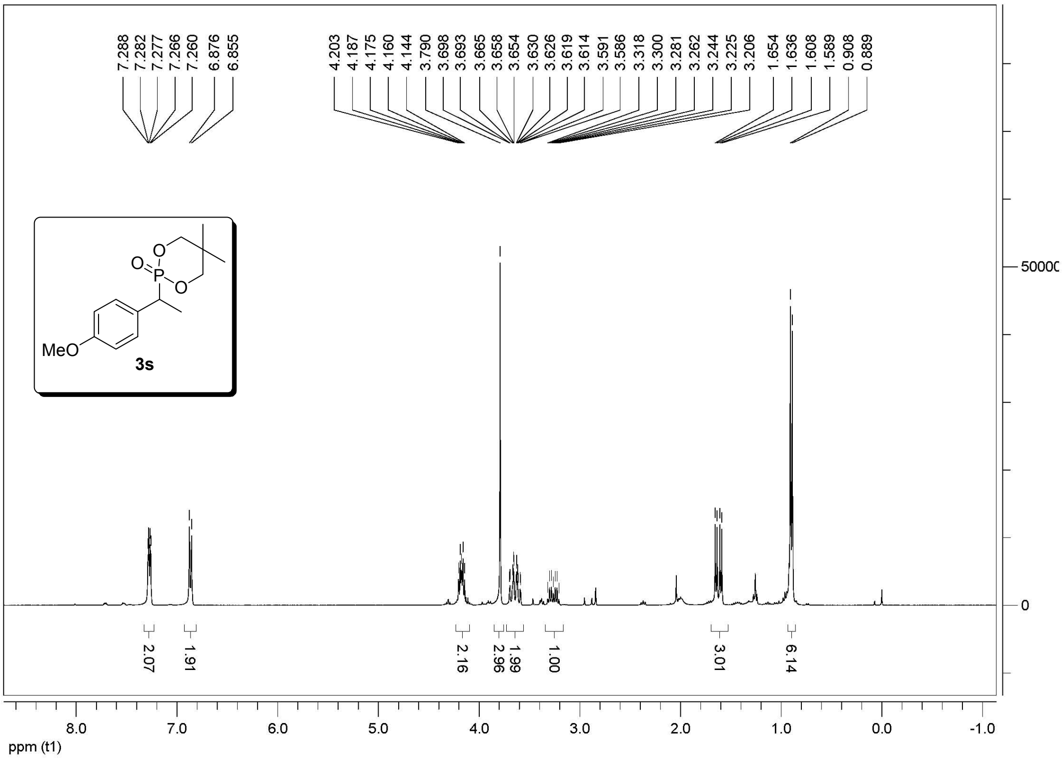
150
100
50
0
ppm (t1)
600
500
400
300
200
100
0
-100

3s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7.260
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6.855
4.203
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4.175
4.160
4.144
3.790
3.698
3.693
3.665
3.658
3.654
3.630
3.626
3.619
3.614
3.591
3.586
3.318
3.300
3.281
3.262
3.244
3.225
3.206
1.654
1.636
1.608
1.589
0.908
0.889
MeO
3s
2.07
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2.16
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1.99
1.00
3.01
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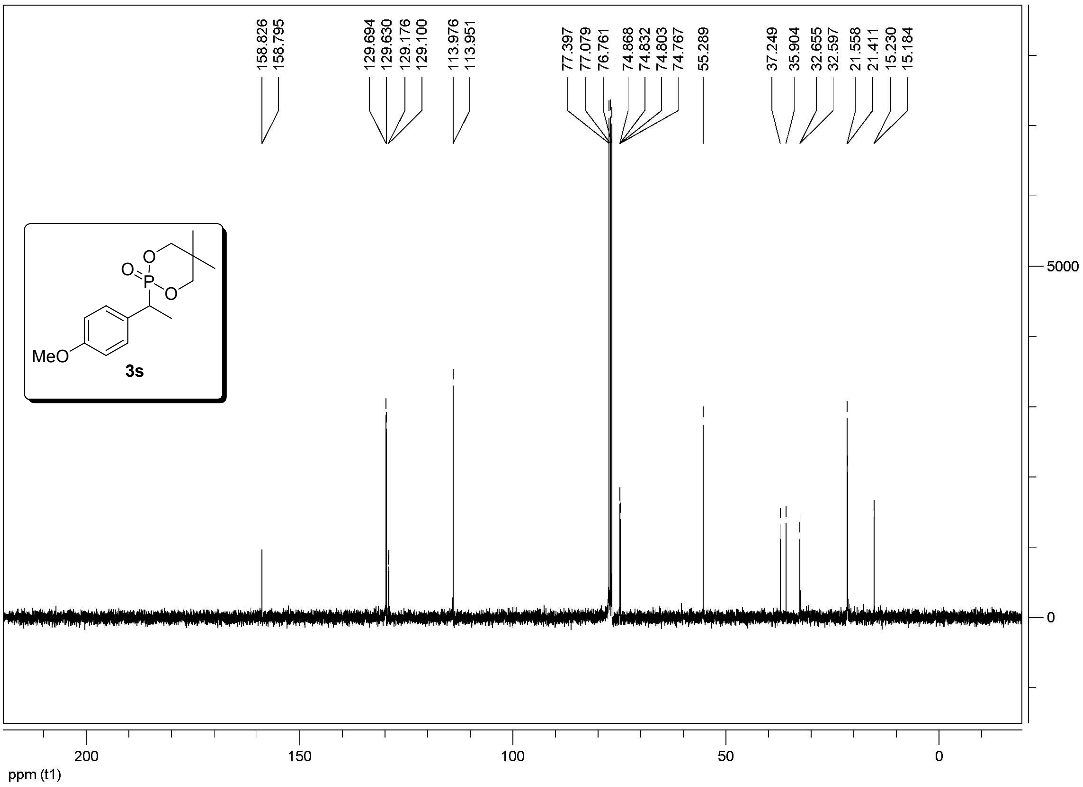
50000
0
ppm (t1)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77.079
76.761
74.868
74.832
74.803
74.767
55.289
37.249
35.904
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32.597
21.558
21.411
15.230
15.184
MeO
3s
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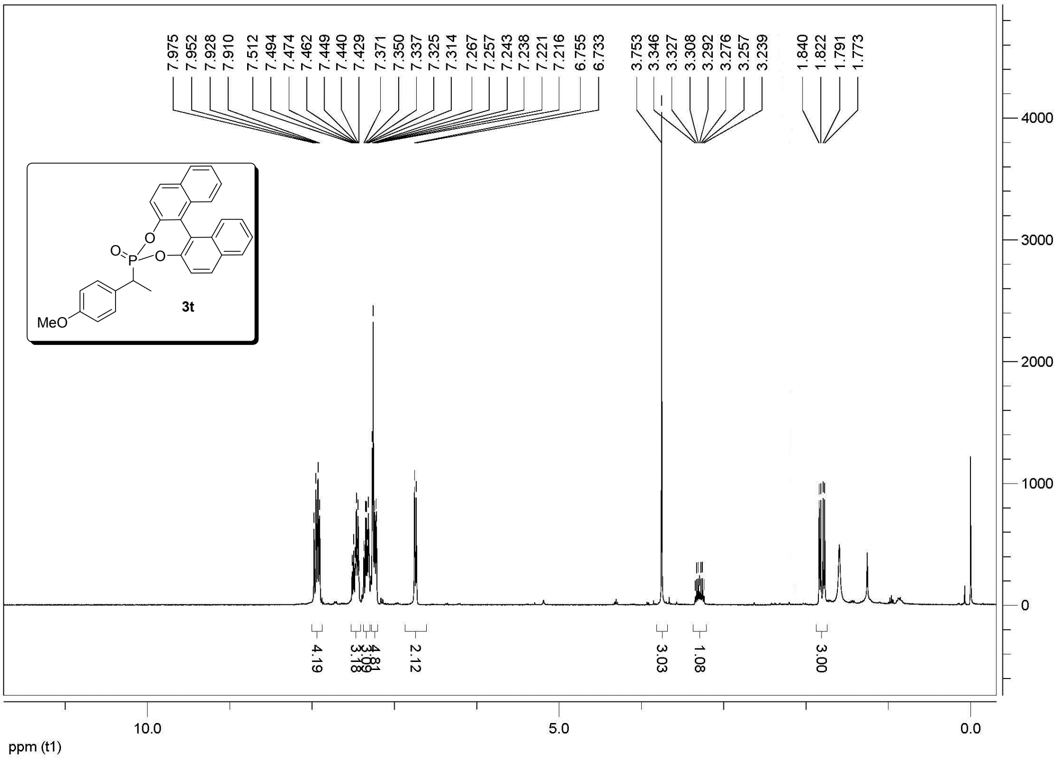
0
ppm (t1)

3t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7.462
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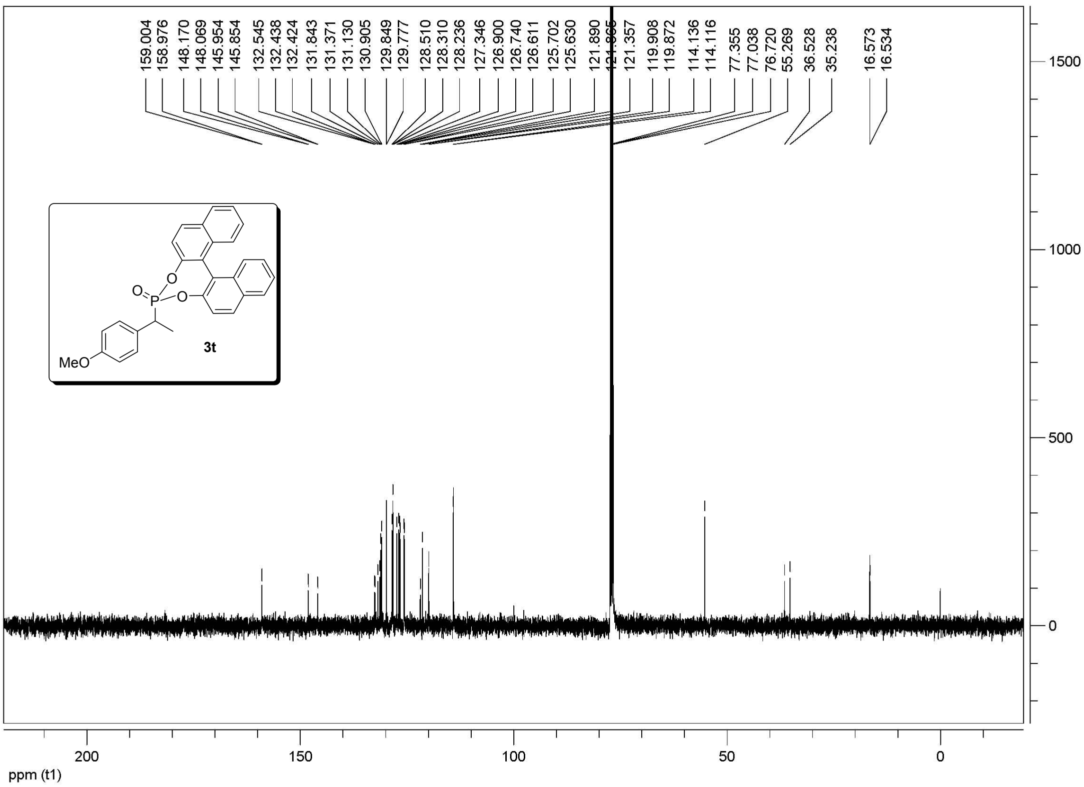
7.429
7.371
7.350
7.337
7.325
7.314
7.267
7.257
7.243
7.238
7.221
7.216
6.755
6.733
3.753
3.346
3.327
3.308
3.292
3.276
3.257
3.239
1.840
1.822
1.791
1.773
4.19
3.18
3.09
4.81
2.12
3.03
1.08
3.00
10.0
5.0
0.0
ppm (t1)
4000
3000
2000
1000
0
3t
MeO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129.849
129.777
128.510
128.310
128.236
127.346
126.900
126.740
126.611
125.702
125.630
121.890
121.357
119.908
119.872
114.136
114.116
77.355
77.038
76.720
55.269
36.528
35.238
16.573
16.534
200
150
100
50
0
ppm (t1)
1500
1000
500
0
3t
MeO