Supporting Information

Cesium Carbonate-Catalyzed Synthesis of Phosphorothioates *via* S-Phosphination of Thioketones

Zu-Wei Chen,[a] Pratheepkumar Annamalai,[a] Rekha Bai,[a] Yongyi Hu,[d] Satpal Singh Badsara,[e] Kuo-Wei Huang,[d] and Chin-Fa Lee[a,b,c]*

[a]Department of Chemistry, National Chung Hsing University, Taichung, Taiwan 402, R.O.C

[b] i-Center for Advanced Science and Technology (iCAST), National Chung Hsing University, Taichung City 402, Taiwan, R.O.C.

[c] Innovation and Development Center of Sustainable Agriculture (IDCSA), National Chung Hsing University, Taichung City 402, Taiwan, R.O.C.

[d] KAUST Catalysis Center and Division of Physical Science and Engineering, King Abdullah University of Science and Technology, Thuwal 23955, Saudi Arabia

[e] MFOS Laboratory, Department of Chemistry, University of Rajasthan, JLN Marg, Jaipur, Rajasthan, India, 302004

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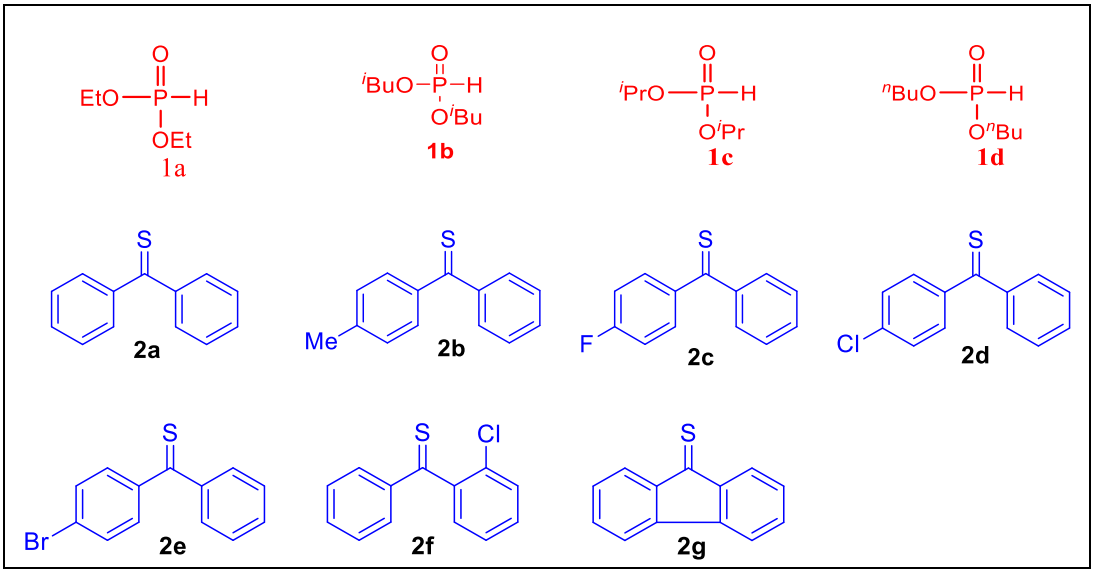
1. General information

Reagents, substrates, and solvents were purchased from commercial suppliers and used without purification. Anhydrous toluene uses calcium hydride to remove water, dry, and distill. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F_{254} (Merck). Chromatography was performed using silica gel 60 (43-63 um) (Merck) and Aluminum oxide 90 neutral (MN). ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were using $CDCl_3$ on *J*eol 400 MHz spectrometers. Tetramethylsilane (TMS) served as an internal standard for ^{1}H and ^{13}C NMR analysis. Chemical shifts in ^{1}H NMR and ^{13}C NMR spectra are reported as follows: Chloroform-d (referenced to 7.26 ppm for 1H and 77.0 ppm for ^{13}C). Coupling constants (*J*) are reported in hertz and peak multiplicities are reported using the following abbreviations: m = multiplet; s = singlet; d = doublet; t = triplet; q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets, tq = triplet of quartets, qd = quartet of doublets, br = broad signal. Low-Resolution Mass Spectrometry (LRMS) experiments were recorded on an Agilent Technologies 5977A with Agilent Technologies 7890B. High-Resolution Mass Spectrometry (HRMS) experiments were recorded on *J*eol *J*MS-HX-110 with EI (Electron Impact). All the phosphites **1a-d** commercially purchased and used without purification and all the thioketones **2a-g** were prepared from known literature methods.[1]

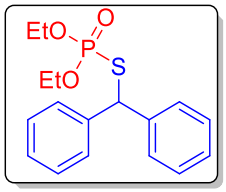


2. General procedure for Table 1

In a sealed tube, diphenylmethanethione **(2a)** (89.2 mg, 0.45 mmol), base (40 mol %) were added in a glove box with filled nitrogen, pluged the serum plug and removed it out of the glove box, then diethyl phosphites (**1a)** (41.4 mg, 0.3 mmol) and solvent (2 mL) were added, and kept in an oil bath for 6-18 hours at 80 to 100 ºC. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and filtered through a celite pad and concentrated under reduced pressure. The crude product thus obtained was purified by column chromatography using silica gel (300-400 mesh) (20-30% ethyl acetate in hexanes) to obtain the pure product of **3a**.

Representative example of Table 1

***S*-Benzhydryl *O*,*O*-diethyl phosphorothioate (3a)**

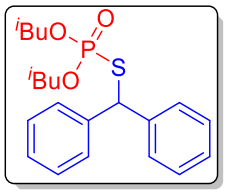


Yield: 87 mg, 86%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.6 Hz, 4H), 7.31 (t, J = 7.6 Hz, 4H), 7.25-7.20 (m, 2H), 5.64 (d, J = 11.6 Hz, 1H), 4.07-3.96 (m, 2H), 3.91-3.80 (m, 2H), 1.15 (t, J = 7.2 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 141.40 (d, J = 5.0 Hz), 128.5, 128.1, 127.3, 73.1 (d, J = 7.0 Hz), 54.0 (d, J = 3.0 Hz), 28.7 (d, J = 7.0 Hz), 18.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.05; HRMS (EI) m/z calcd for $C_{17}H_{21}O_3PS$ $[M]^+$ 336.0949; found: 336.0946.

3. General procedure for Table 2

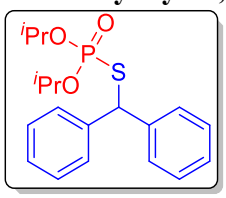
In a sealed tube, thioketones **2a-g** (0.45 mmol), cesium carbonate (40 mol %) were added in a glove box with filled nitrogen, plugged the serum plug and removed it out of the glove box, then a phosphites **1a-d** (0.3 mmol) and ethyl acetate (2 mL) were added, and kept in an oil bath for 12 hours at 80 ºC. After completion of the reaction, the reaction mixtures diluted with ethyl acetate and filtered through a celite pad and concentrated under reduced pressure. The crude products thus obtained were purified by column chromatography using silica gel (300-400 mesh) (20-30% ethyl acetate in hexanes) to obtain the pure products **3**.

***S*-Benzhydryl *O*,*O*-diisobutyl phosphorothioate (3b)**



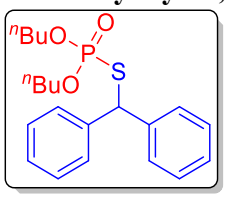
The title compound was prepared following the general procedure for Table 2, using diisobutyl phosphonate (**1b)** (58.3 mg, 0.3 mmol), diphenylmethanethione (**2a)** (89.2 mg, 0.45 mmol), providing **3b** as a colorless oil. Yield: 104 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.0 Hz, 3H), 7.30 (t, J = 7.6 Hz, 4H), 7.24-7.21 (m, 2H), 5.69 (d, J = 11.6 Hz, 1H), 3.73-3.67 (m, 2H), 3.56-3.50 (m, 2H), 1.84–1.71 (m, 2H), 0.83 (dd, J = 6.8 & 3.6 Hz, 12H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 141.2 (d, J = 6.0 Hz), 128.4, 128.0, 127.3, 63.3 (d, J = 6.0 Hz), 54.0 (d, J = 3.0 Hz), 15.6 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.99; HRMS (EI) m/z calcd for $C_{21}H_{29}O_3PS$ $[M]^+$ 392.1575; found: 392.1567.

***S*-Benzhydryl *O*,*O*-diisopropyl phosphorothioate (3c)**



The title compound was prepared following the general procedure for Table 2, using diisopropyl phosphonate (**1c)** (50 mg, 0.3 mmol), diphenylmethanethione (**2a)** (89.2 mg, 0.45 mmol), providing **3c** as a colorless oil. Yield: 83 mg, 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.42 (m, 4H), 7.33-7.28 (m, 4H), 7.24-7.20 (m, 2H), 5.70 (d, J = 12.0 Hz, 1H), 4.60- 4.48 (m, 2H), 1.22 (d, J = 6.4 Hz, 6H), 1.11 (d, J = 6.4 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 141.6 (d, J = 6.0 Hz), 128.4, 128.1, 127.2, 72.6 (d, J = 6.0 Hz), 54.2 (d, J = 3.0 Hz), 23.6 (d, J = 4.0 Hz), 23.2 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.69; HRMS (EI) m/z calcd for $C_{19}H_{25}O_3PS$ $[M]^+$ 364.1262; found: 346.1266.

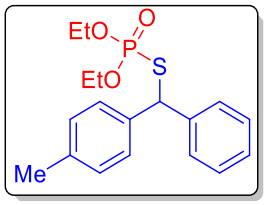
***S*-Benzhydryl *O*,*O*-dibutyl phosphorothioate (3d)**



The title compound was prepared following the general procedure for Table 2, using di-*n*-butyl phosphonate **1d** (58.3 mg, 0.3 mmol), diphenylmethanethione **2a** (89.2 mg, 0.45 mmol),

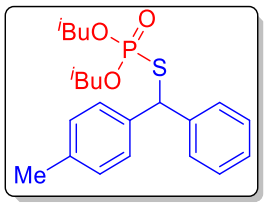
providing **3d** as a colorless oil. Yield: 88 mg, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 7.6 Hz, 4H), 7.27 (t, J = 7.6 Hz, 4H), 7.21-7.17 (m, 2H), 5.64 (d, J = 11.6 Hz, 1H), 3.96-3.88 (m, 2H), 3.78-3.71 (m, 2H), 1.49-1.41 (m, 4H), 1.29-1.20 (m, 4H), 0.83 (t, J = 7.4 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 141.3 (d, J = 6.0 Hz), 128.3, 127.9, 127.2, 66.9 (d, J = 6.0 Hz), 53.9 (d, J = 3.0 Hz), 31.7 (d, J = 7.0 Hz), 18.4, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.14; HRMS (EI) m/z calcd for $C_{21}H_{29}O_3PS$ $[M]^+$ 392.1575; found: 392.1573.

***O,O*-Diethyl *S*-(phenyl(*p*-tolyl)methyl) phosphorothioate (3e)**



The title compound was prepared following the general procedure for Table 2, using diethyl phosphonate (**1a)** (41.4 mg, 0.3 mmol), phenyl(*p*-tolyl)methanethione (**2b)** (95.5 mg, 0.45 mmol), providing **3e** as a colorless oil. Yield: 70 mg, 67%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, J = 7.6 & 1.6 Hz, 1H), 7.43-7.41 (m, 2H), 7.32-7.28 (m, 2H), 7.24 -7.14 (m, 4H), 5.89 (d, J = 12.0 Hz, 1H), 4.08-3.98 (m, 2H), 3.92-3.82 (m, 2H), 2.39 (s, 3H), 1.19 (td, J = 7.2 & 0.8 Hz, 3H), 1.14 (td, J = 7.2 & 0.8 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 140.7 (d, J = 5.0 Hz), 139.2 (d, J = 5.0 Hz), 135.6, 130.5, 128.6, 128.4 (d, J = 11.0 Hz), 127.3 (d, J = 16.0 Hz), 126.1, 63.4 (d, J = 6.0 Hz), 50.7 (d, J = 3.0 Hz), 19.6, 15.7 (d, J = 6.0 Hz), 15.6 (d, J = 8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.35; HRMS (EI) m/z calcd for $C_{18}H_{23}O_3PS$ $[M]^+$ 350.1106; found: 350.1114.

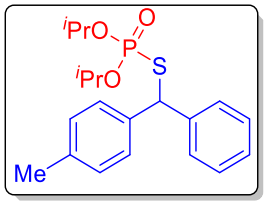
***O,O*-Diisobutyl *S*-(phenyl(*p*-tolyl)methyl) phosphorothioate (3f)**



The title compound was prepared following the general procedure for Table 2, using diisobutyl phosphonate (**1b)** (58.3 mg, 0.3 mmol), phenyl(*p*-tolyl)methanethione (**2b)** (95.5 mg, 0.45 mmol), providing **3f** as a colorless oil. Yield: 90 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.6 Hz, 1H), 7.42-7.39 (m, 2H), 7.30-7.24 (m, 2H), 7.22-7.13 (m, 4H), 5.92 (d, J = 12.0 Hz, 1H), 3.72-3.66 (m, 2H), 3.60-3.48 (m, 2H), 2.38 (s, 3H), 1.81-1.72 (m, 2H), 0.85-0.80 (m,

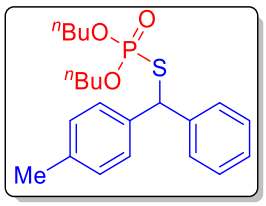
12H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 140.7 (d, J = 6.0 Hz), 139.2 (d, J = 4.0 Hz), 135.6, 130.5, 128.6, 128.3 (d, J = 4.0 Hz), 127.3 (d, J = 16.0 Hz), 126.1, 73.1 (d, J = 7.0 Hz), 50.7 (d, J = 3.0 Hz), 28.7 (d, J = 6.0 Hz), 28.6 (d, J = 6.0 Hz), 19.5, 18.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.48; HRMS (EI) m/z calcd for $C_{22}H_{31}O_3PS$ $[M]^+$ 406.1732; found: 406.1738.

***O,O*-Diisopropyl *S*-(phenyl(*p*-tolyl)methyl) phosphorothioate (3g)**



The title compound was prepared following the general procedure for Table 2, using diisopropyl phosphonate (**1c**) (50.0 mg, 0.3 mmol), phenyl(*p*-tolyl)methanethione (**2b**) (95.5 mg, 0.45 mmol), providing **3g** as a colorless oil. Yield: 93 mg, 82%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 2H), 7.36-7.28 (m, 4H), 7.23-7.19 (m, 1H), 7.11 (d, J = 8.0 Hz, 2H), 5.68 (d, J = 12.0 Hz, 1H), 4.60-4.49 (m, 2H), 2.30 (s, 3H), 1.25-1.22 (m, 6H), 1.12 (d, J = 6.4 Hz, 6H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 141.7 (d, J = 6.0 Hz), 138.5 (d, J = 6.0 Hz), 136.9, 129.0, 128.3, 128.0, 127.8, 127.1, 72.6 (d, J = 4.0 Hz), 72.5 (d, J = 4.0 Hz), 54.0 (d, J = 3.0 Hz), 23.6 (d, J = 6.0 Hz), 23.5 (d, J = 4.0 Hz), 23.2 (d, J = 7.0 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.87; HRMS (EI) m/z calcd for $C_{20}H_{27}O_3PS$ $[M]^+$ 378.1419; found: 378.1423.

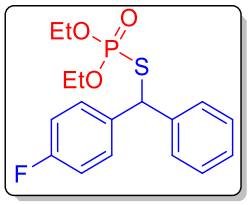
***O,O*-Dibutyl *S*-(phenyl(*p*-tolyl)methyl) phosphorothioate (3h)**



The title compound was prepared following the general procedure for Table 2, using dibutyl phosphonate **1d** (58.3 mg, 0.3 mmol), phenyl(*p*-tolyl)methanethione **2b** (95.5 mg, 0.45 mmol), providing **3h** as a colorless oil. Yield: 99 mg, 81%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.2 Hz, 2H), 7.33-7.29 (m, 4H), 7.25-7.20 (m, 1H), 7.12 (d, J = 7.6 Hz, 2H), 5.62 (d, J = 11.6 Hz, 1H), 3.97-3.89 (m, 2H), 3.81-3.73 (m, 2H), 2.31 (s, 3H), 1.50-1.43 (m, 4H), 1.30-1.24 (m, 4H), 0.86 (t, J = 7.2 Hz, 6H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 141.6 (d, J = 5.0 Hz), 138.4 (d, J = 6.0 Hz), 137.0, 129.1, 128.4, 128.0, 127.9, 127.2, 67.0 (d, J = 6.0 Hz), 53.9 (d, J = 4.0 Hz), 31.8 (d, J = 8.0 Hz), 20.9, 18.5, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.33; HRMS (EI) m/z

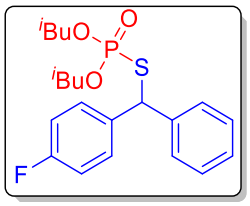
calcd for $C_{22}H_{31}O_3PS$ $[M]^+$ 406.1732; found: 406.1725.

***O,O*-Diethyl *S*-((4-fluorophenyl)(phenyl)methyl) phosphorothioate (3i)**



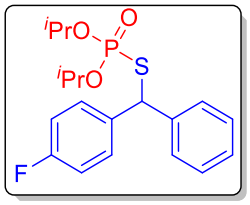
The title compound was prepared following the general procedure for Table 2, using diethyl phosphonate (**1a)** (41.4 mg, 0.3 mmol), (4-fluorophenyl)(phenyl)methanethione (**2c)** (97.3 mg, 0.45 mmol), providing **3i** as a colorless oil. Yield: 97 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 4H), 7.32 (t, J = 7.6 Hz, 2H), 7.30-7.24 (m, 1H), 7.00 (t, J = 8.6 Hz, 2H), 5.64 (d, J = 11.6 Hz, 1H), 4.06-3.99 (m, 2H), 3.90-3.83 (m, 2H), 1.20-1.15 (m, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 161.8 (d, J = 245.0 Hz), 141.0 (d, J = 6.0 Hz), 137.2 (d, J = 6.0 Hz), 129.8 (d, J = 9.0 Hz), 128.6, 128.0, 127.5, 115.3 (d, J = 22.0 Hz), 63.5 (d, J = 5.0 Hz), 53.3 (d, J = 3.0 Hz), 15.7 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.67; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.58; HRMS (EI) m/z calcd for $C_{17}H_{20}FO_3PS$ $[M]^+$ 354.0855; found: 354.0864.

***S*-((4-Fluorophenyl)(phenyl)methyl) *O,O*-diisobutyl phosphorothioate (3j)**



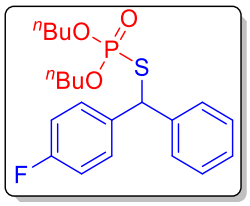
The title compound was prepared following the general procedure for Table 2, using diisobutyl phosphonate (**1b)** (58.3 mg, 0.3 mmol), (4-fluorophenyl)(phenyl)methanethione (**2c)** (97.3 mg, 0.45 mmol), providing **3j** as a colorless oil. Yield: 105 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.38 (m, 4H), 7.30 (t, J = 7.6 Hz, 2H), 7.28-7.17 (m, 1H), 6.98 (t, J = 8.6 Hz, 2H), 5.67 (d, J = 11.6 Hz, 1H), 3.73-3.66 (m, 2H), 3.56-3.50 (m, 2H), 1.82-1.72 (m, 2H), 0.82 (dd, J = 6.8, 2.6 Hz, 12H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 161.8 (d, J = 245.0 Hz), 141.1 (d, J = 6.0 Hz), 137.3 (d, J = 5.0 Hz) &137.2 (d, J = 5.0 Hz), 129.8 (d, J = 8.0 Hz), 128.5, 128.0, 127.4, 115.2 (d, J = 21.0 Hz), 73.2 (d, J = 7.0 Hz), 53.3 (d, J = 3.0 Hz), 28.7 (d, J = 8.0 Hz), 18.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.76; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.69; HRMS (EI) m/z calcd for $C_{21}H_{28}FO_3PS$ $[M]^+$ 410.1481; found: 410.1487.

***S*-((4-Fluorophenyl)(phenyl)methyl) *O,O*-diisopropyl phosphorothioate (3k)**



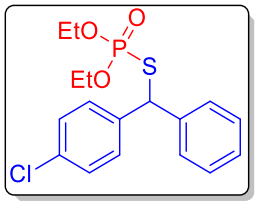
The title compound was prepared following the general procedure for Table 2, using diisopropyl phosphonate (**1c)** (50.0 mg, 0.3 mmol), (4-fluorophenyl)(phenyl)methanethione (**2c)** (97.3 mg, 0.45 mmol), providing **3k** as a colorless oil. Yield: 87 mg, 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 4H), 7.34-7.30 (m, 2H), 7.26-7.24 (m, 1H), 7.00 (t, J = 8.6 Hz, 2H), 5.69 (d, J = 11.6 Hz, 1H), 4.59-4.50 (m, 2H), 1.23 (d, J = 6.0 Hz, 6H), 1.13 (d, J = 6.0 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 161.8 (d, J = 245.0 Hz), 141.4 (d, J = 6.0 Hz), 137.6 (d, J = 6.0 Hz), 129.9 (d, J = 8.0 Hz), 128.6, 128.1, 127.5, 115.3 (d, J = 21.0 Hz), 72.8 (d, J = 6.0 Hz), 72.7 (d, J = 6.0 Hz), 53.6 (d, J = 3.0 Hz), 23.7 (d, J = 4.0 Hz), 23.3 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.39; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.91; HRMS (EI) m/z calcd for $C_{19}H_{24}FO_3PS$ $[M]^+$ 382.1168; found: 382.1171.

***O,O*-Dibutyl *S*-((4-fluorophenyl)(phenyl)methyl) phosphorothioate (3l)**



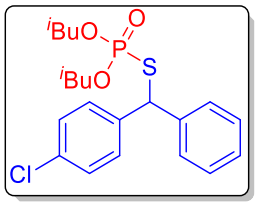
The title compound was prepared following the general procedure for Table 2, dibutyl phosphonate **(1d)** (58.3 mg, 0.3 mmol), (4-fluorophenyl)(phenyl)methanethione (**2c)** (97.3 mg, 0.45 mmol), providing **3l** as a colorless oil. Yield: 84 mg, 68%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.39 (m, 4H), 7.31 (t, J = 7.6 Hz, 2H), 7.26-7.22 (m, 1H), 6.98 (t, J = 8.6 Hz, 2H), 5.66 (d, J = 11.6 Hz, 1H), 3.97-3.91 (m, 2H), 3.84-3.77 (m, 2H), 1.53-1.45 (m, 4H), 1.32-1.23 (m, 4H), 0.86 (t, J = 7.4 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 161.7 (d, J = 246.0 Hz), 141.0 (d, J = 5.0 Hz), 137.3 (d, J = 5.0 Hz), 137.2 (d, J = 5.0 Hz), 129.8 (d, J = 8.0 Hz), 128.4, 127.9, 127.4, 115.2 (d, J = 21.0 Hz), 67.1 (d, J = 7.0 Hz), 67.0 (d, J = 7.0 Hz), 53.2 (d, J = 3.0 Hz), 31.7 (d, J = 7.0 Hz), 18.4, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.86; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.65; HRMS (EI) m/z calcd for $C_{21}H_{28}FO_3PS$ $[M]^+$ 410.1481; found: 410.1484.

***S*-((4-Chlorophenyl)(phenyl)methyl) *O,O*-diethyl phosphorothioate (3m)**



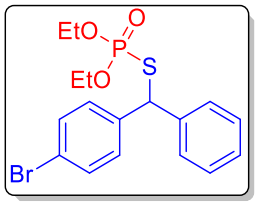
The title compound was prepared following the general procedure for Table 2, using diethyl phosphonate (**1a)** (41.4 mg, 0.3 mmol), (4-chlorophenyl)(phenyl)methanamine (**2d)** (104.7 mg, 0.45 mmol), providing **3m** as a colorless oil. Yield: 58 mg, 52%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.34 (m, 5H), 7.32-7.24 (m, 4H), 5.65 (d, J = 11.6 Hz, 1H), 4.07-3.97 (m, 2H), 3.92-3.82 (m, 2H), 1.18 (td, J = 7.0 & 0.9 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 141.0 (d, J = 6.0 Hz), 140.2 (d, J = 5.0 Hz), 133.4, 129.7, 128.8, 128.2, 127.8, 63.7 (d, J = 6.0 Hz), 53.6 (d, J = 3.0 Hz), 15.9 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.52; HRMS (EI) m/z calcd for $C_{17}H_{20}ClO_3PS$ $[M]^+$ 370.0559; found: 370.0551.

***S*-((4-Chlorophenyl)(phenyl)methyl) *O,O*-diisobutyl phosphorothioate (3n)**



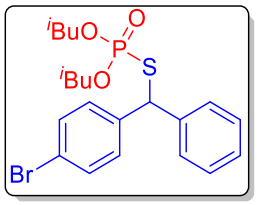
The title compound was prepared following the general procedure for Table 2, using diisobutyl phosphonate **(1b)** (58.3 mg, 0.3 mmol), (4-chlorophenyl)(phenyl)methanamine (**2d)** (104.7 mg, 0.45 mmol), providing **3n** as a yellow oil. Yield: 82 mg, 64%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.35 (m, 4H), 7.34-7.23 (m, 5H), 5.65 (d, J = 11.6 Hz, 1H), 3.73-3.67 (m, 2H), 3.58-3.51 (m, 2H), 1.83-1.73 (m, 2H), 0.85-0.82 (m, 12H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 141.0 (d, J = 6.0 Hz), 140.2 (d, J = 6.0 Hz), 133.3, 129.6, 128.7, 128.0, 127.6, 73.3 (d, J = 7.0 Hz), 53.4 (d, J = 3.0 Hz), 28.8 (d, J = 8. Hz), 18.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.61; HRMS (EI) m/z calcd for $C_{21}H_{28}ClO_3PS$ $[M]^+$ 426.1185; found: 426.1176.

***S*-((4-Bromophenyl)(phenyl)methyl) *O,O*-diethyl phosphorothioate (3o)**



The title compound was prepared following the general procedure for Table 2, using diethyl phosphonate **1a** (41.4 mg, 0.3 mmol), (4-bromophenyl)(phenyl)methanethione **2e** (124.7 mg, 0.45 mmol), providing **3o** as a yellow oil. Yield: 79 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.43 (m, 2H), 7.40-7.37 (m, 2H), 7.34-7.28 (m, 4H), 7.27-7.23 (m, 1H), 5.60 (d, J = 11.2 Hz, 1H), 4.07-4.02 (m, 2H), 3.92-3.82 (m, 2H), 1.18 (td, J = 7.0, 0.8 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 140.8 (d, J = 6.0 Hz), 140.5 (d, J = 6.0 Hz), 131.6, 129.9, 128.7, 128.0, 127.7, 121.4, 63.6 (d, J = 6.0 Hz), 53.5 (d, J = 3.0 Hz), 15.8 (d, J = 8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.49; HRMS (EI) m/z calcd for $C_{17}H_{20}BrO_3PS$ $[M]^+$ 414.0054; found: 414.0059.

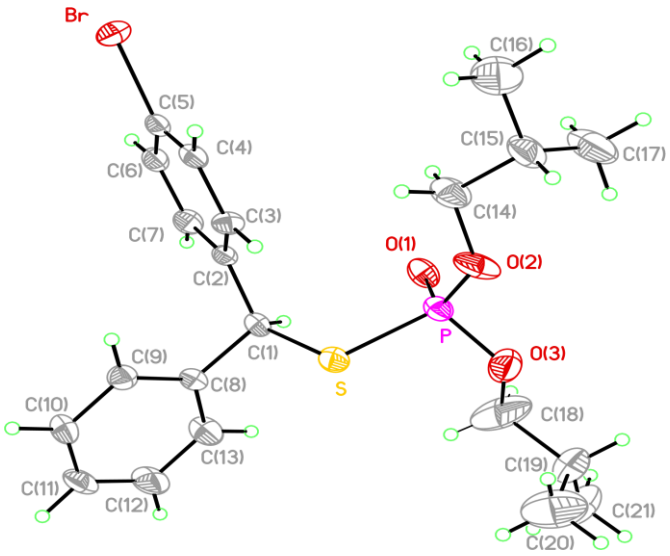
***S*-((4-Bromophenyl)(phenyl)methyl) *O,O*-diisobutyl phosphorothioate (3p)**



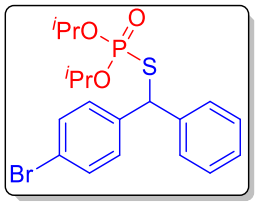
The title compound was prepared following the general procedure for Table 2, using diisobutyl phosphonate (**1b)** (58.3 mg, 0.3 mmol), (4-bromophenyl)(phenyl)methanethione (**2e)** (124.7 mg, 0.45 mmol), providing **3p** as a white solid, M.P: 86-87 ºC. Yield: 93 mg, 66%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42 (m, 2H), 7.40-7.37 (m, 2H), 7.34-7.30 (m, 4H), 7.27-7.22 (m, 1H), 5.64 (d, J = 11.6 Hz, 1H), 3.73-3.66 (m, 2H), 3.58-3.51 (m, 2H), 1.83-1.73 (m, 2H), 0.85-0.83 (m, 12H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 140.9 (d, J = 6.0 Hz), 140.7 (d, J = 5.0 Hz), 131.6, 130.0, 128.7, 128.0, 127.6, 121.4, 73.3 (d, J = 7.0 Hz), 53.5 (d, J = 3.0 Hz), 28.8 (d, J = 7.0 Hz), 18.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.57; HRMS (EI) m/z calcd for $C_{21}H_{28}BrO_3PS$ $[M]^+$ 470.0680; found: 470.0682.

Crystal data and structure refinement for 3p

Crystal data for **3p** Empirical formula, $C_{21}H_{28}BrO_3PS$; formula weight, 471.37; crystal color, habit: white, block; crystal dimensions, 0.450 x 0.360 x 0.050 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 6.0891(13) Å, b = 9.1440(19) Å, c = 39.857(9) Å; α = 90.00; β = 93.360(6)°; γ = 90.00; V = 2215.4(8) $Å^3$; space group, P 21/n; Z = 4; Dcalcd = 1.413 Mg/m^3; F000 = 976; λ(Mo-Kα) = 0.71073 Å; R (I≥2σ1) = 0.0848, wR2 = 0.2083. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **3p** CCDC # 2183574).

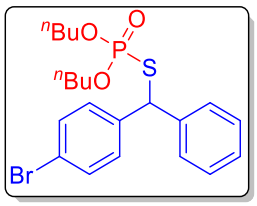


***S*-((4-Bromophenyl)(phenyl)methyl) *O,O*-diisopropyl phosphorothioate (3q)**



The title compound was prepared following the general procedure for Table 2, using diisopropyl phosphonate (**1c)** (50.0 mg, 0.3 mmol), (4-bromophenyl)(phenyl)methanethione (**2e)** (124.7 mg, 0.45 mmol), providing **3q** as a colorless oil. Yield: 113 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.33-7.30 (m, 4H), 7.26-7.22 (m, 1H), 5.65 (d, J = 11.6 Hz, 1H), 4.57–4.51 (m, 2H), 1.23 (dd, J = 6.8 & 4.8 Hz, 6H), 1.13 (d, J = 6.0 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 141.0 (d, J = 6.0 Hz), 140.8 (d, J = 6.0 Hz), 131.6, 130.0, 128.6, 128.1, 127.6, 121.3, 72.8 (d, J = 6.0 Hz), 53.6 (d, J = 3.0 Hz), 23.7 (d, J = 4.0 Hz), 23.3 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.21; HRMS (EI) m/z calcd for $C_{19}H_{24}BrO_3PS$ $[M]^+$ 442.0367; found: 442.0358.

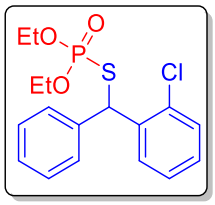
***S*-((4-Bromophenyl)(phenyl)methyl) *O,O*-dibutyl phosphorothioate (3r)**



The title compound was prepared following the general procedure for Table 2, using dibutyl phosphonate (**1d)** (58.3 mg, 0.3 mmol), (4-bromophenyl)(phenyl)methanethione (**2e)** (124.7 mg,

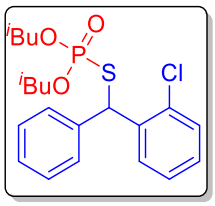
0.45 mmol), providing **3r** as a colorless oil. Yield: 109 mg, 77%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.42 (m, 2H), 7.40-7.36 (m, 2H), 7.34-7.30 (m, 4H), 7.27-7.23 (m, 1H), 5.61 (d, J = 11.2 Hz, 1H), 3.98-3.90 (m, 2H), 3.83-3.75 (m, 2H), 1.52-1.43 (m, 4H), 1.32-1.22 (m, 4H), 0.87 (td, J = 7.6 & 2.0 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 140.8 (d, J = 6.0 Hz), 140.6 (d, J = 5.0 Hz), 131.6, 129.9, 128.6, 128.0, 127.6, 121.4, 67.3 (d, J = 6.0 Hz), 53.4 (d, J = 3.0 Hz), 31.9 (d, J = 8.0 Hz), 18.5, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.69; HRMS (EI) m/z calcd for $C_{21}H_{28}BrO_3PS$ $[M]^+$ 470.0680; found: 470.0688.

***S*-((2-Chlorophenyl)(phenyl)methyl) *O,O*-diethyl phosphorothioate (3s)**



The title compound was prepared following the general procedure for Table 2, using diethyl phosphonate (**1a)** (41.4 mg, 0.3 mmol), (2-chlorophenyl)(phenyl)methanethione (**2f)** (104.7 mg, 0.45 mmol), providing **3s** as a colorless oil. Yield: 82 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, J = 8.0, 2.4 Hz, 1H), 7.45-7.42 (m, 2H), 7.37-7.18 (m, 6H), 6.08 (d, J = 12.0 Hz, 1H), 4.10-4.03 (m, 2H), 3.94-3.87 (m, 2H), 1.22-1.15 (m, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 140.1 (d, J = 5.0 Hz), 138.8 (d, J = 5.0 Hz), 133.1, 130.1, 129.8, 128.7, 128.6, 128.2, 127.6, 127.1, 63.5 (d, J = 9.0 Hz), 50.2 (d, J = 3.0 Hz), 15.8 (d, J = 3.0 Hz), 15.7 (d, J = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.35; HRMS (EI) m/z calcd for $C_{17}H_{20}ClO_3PS$ $[M]^+$ 370.0559; found: 370.0549.

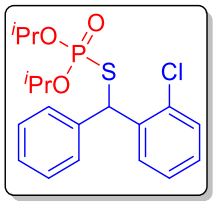
***S*-((2-Chlorophenyl)(phenyl)methyl) *O,O*-diisobutyl phosphorothioate (3t)**



The title compound was prepared following the general procedure for Table 2, using diisobutyl phosphonate **1b** (58.3 mg, 0.3 mmol), (2-chlorophenyl)(phenyl)methanethione **2f** (104.7 mg, 0.45 mmol), providing **3t** as a colorless oil. Yield: 111 mg, 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, J = 7.6 & 1.6 Hz, 1H), 7.44-7.41 (m, 2H), 7.36-7.20 (m, 6H), 6.12 (d, J = 12.0 Hz, 1H), 3.80-3.71 (m, 2H), 3.65-3.61 (m, 1H), 3.56-3.52 (m, 1H), 1.84-1.73 (m, 2H), 0.88-0.80 (m,

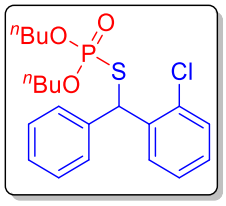
12H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 140.2 (d, J = 6.0 Hz), 138.9 (d, J = 5.0 Hz), 133.2, 130.1, 129.8, 128.7, 128.6, 128.2, 127.5, 127.0, 73.3 (d, J = 6.0 Hz), 73.2 (d, J = 7.0 Hz), 50.2 (d, J = 3.0 Hz), 28.8 (d, J = 7.0 Hz), 28.7 (d, J = 8.0 Hz), 18.6 (d, J = 3.0 Hz), 18.5 (d, J = 5.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.43; HRMS (EI) m/z calcd for $C_{21}H_{28}ClO_3PS$ $[M]^+$ 426.1158; found: 426.1183.

***S*-((2-Chlorophenyl)(phenyl)methyl) *O,O*-diisopropyl phosphorothioate (3u)**



The title compound was prepared following the general procedure for Table 2, using diisopropyl phosphonate (**1c)** (50.0 mg, 0.3 mmol), (2-chlorophenyl)(phenyl)methanethione (**2f)** (104.7 mg, 0.45 mmol), providing **3u** as a colorless oil. Yield: 101 mg, 85%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, J = 7.8 & 1.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.32-7.13 (m, 6H), 6.15 (d, J = 12.0 Hz, 1H), 4.70-4.50 (m, 2H), 1.27 (d, J = 6.2 Hz, 3H), 1.22 (d, J = 6.3 Hz, 3H), 1.16 (d, J = 6.3 Hz, 3H), 1.09 (d, J = 6.3 Hz, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 140.1 (d, J = 6.0 Hz), 138.7 (d, J = 5.0 Hz), 132.8, 130.0, 129.4, 128.4, 128.3, 128.0, 127.2, 126.8, 72.6 (d, J = 6.0 Hz), 50.2 (d, J = 3.0 Hz), 23.5 (d, J = 7.0 Hz), 23.4 (d, J = 7.0 Hz), 23.1 (d, J = 9.0 Hz), 23.0 (d, J = 9.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.03; HRMS (EI) m/z calcd for $C_{19}H_{24}ClO_3PS$ $[M]^+$ 398.0872, found: 398.0880.

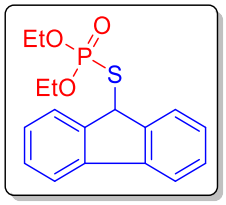
***O,O*-Dibutyl *S*-((2-chlorophenyl)(phenyl)methyl) phosphorothioate (3v)**



The title compound was prepared following the general procedure for Table 2, using di-*n*-butyl phosphonate (**1d)** (58.3 mg, 0.3 mmol), (2-chlorophenyl)(phenyl)methanethione (**2f)** (104.7 mg, 0.45 mmol), providing **3v** as a colorless oil. Yield: 99 mg, 77%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.34-7.17 (m, 6H), 6.11 (d, J = 12.4 Hz, 1H), 4.01-3.96 (m, 2H), 3.88-3.79 (m, 2H), 1.54-1.47 (m, 4H), 1.33-1.23 (m, 4H), 0.88-0.83 (m, 4H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 140.0 (d, J = 5.0 Hz), 138.7 (d, J = 5.0 Hz), 132.9, 129.9,

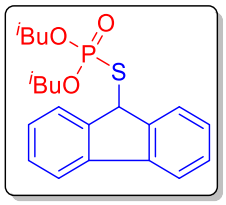
129.6, 128.5, 128.4, 128.0, 127.4, 126.9, 67.0 (d, J = 6.0 Hz), 66.9 (d, J = 6.0 Hz), 50.0 (d, J = 3.0 Hz), 31.7 (d, J = 7.0 Hz), 31.6 (d, J = 7.0 Hz), 18.4 (d, J = 5.0 Hz), 13.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.57; HRMS (EI) m/z calcd for $C_{21}H_{28}ClO_3PS$ $[M]^+$ 426.1185; found: 426.1176.

***O,O*-Diethyl *S*-(9*H*-fluoren-9-yl) phosphorothioate (3w)**



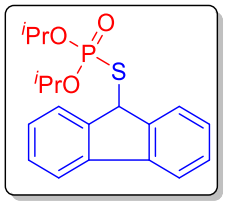
The title compound was prepared following the general procedure for Table 2, using diethyl phosphonate (**1a)** (41.4 mg, 0.3 mmol), 9*H*-fluorene-9-thione (**2g)** (88.3 mg, 0.45 mmol), providing **3w** as a yellow oil. Yield: 84 mg, 84%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 7.2 Hz, 2H), 7.42-7.33 (m, 4H), 5.47 (d, J = 15.6 Hz, 1H), 4.34-4.17 (m, 4H), 1.40 (t, J = 7.0 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 144.2 (d, J = 5.0 Hz), 140.3, 128.5, 127.7, 125.9, 120.0, 64.0 (d, J = 7.0 Hz), 48.4 (d, J = 4.0 Hz), 16.0 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.23; HRMS (EI) m/z calcd for $C_{17}H_{19}O_3PS$ $[M]^+$ 334.0793; found: 334.0802.

***S*-(9*H*-Fluoren-9-yl) *O,O*-diisobutyl phosphorothioate (3x)**



The title compound was prepared following the general procedure for Table 2, using diisobutyl phosphonate (**1b)** (58.3 mg, 0.3 mmol), 9*H*-fluorene-9-thione (**2g)** (88.3 mg, 0.45 mmol), providing **3x** as a yellow oil. Yield: 89 mg, 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.42-7.33 (m, 4H), 5.51 (d, J = 14.8 Hz, 1H), 4.04-3.91 (m, 4H), 2.10-1.99 (m, 2H), 1.00 (d, J = 6.8 Hz, 12H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 144.2 (d, J = 5.0 Hz), 140.2, 128.5, 127.7, 125.9, 119.9, 73.8 (d, J = 7.0 Hz), 48.1 (d, J = 4.0 Hz), 28.9 (d, J = 7.0 Hz), 18.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.31; HRMS (EI) m/z calcd for $C_{21}H_{27}O_3PS$ $[M]^+$ 390.1419; found: 390.1423.

***S*-(9*H*-Fluoren-9-yl) *O*,*O*-diisopropyl phosphorothioate (3y)**



The title compound was prepared following the general procedure for Table 2, using diisopropyl phosphonate (**1c)** (50.0 mg, 0.3 mmol), 9*H*-fluorene-9-thione (**2g)** (88.3 mg, 0.45 mmol), providing **3x** as an orange oil. Yield: 84 mg, 77%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 6.4 Hz, 2H), 7.41-7.33 (m, 4H), 5.52 (d, J = 14.4 Hz, 1H), 4.95-4.84 (m, 2H), 1.44 (d, J = 6.4 Hz, 6H), 1.42 (d, J = 6.4 Hz, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 144.3 (d, J = 5.0 Hz), 140.1, 128.4, 127.5, 125.97, 119.8, 73.2 (d, J = 7.0 Hz), 48.2 (d, J = 4.0 Hz), 23.7 (d, J = 4.0 Hz), 23.6 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.22; HRMS (EI) m/z calcd for $C_{19}H_{23}O_3PS$ $[M]^+$ 362.1106; found: 362.1111.

4. Computational Details

All calculations were performed using the Gaussian 16 Rev. B.01.[2] The hybrid gradient generalization approximation (hybrid GGA) functional B3LYP,[3] along with 6-31 basis sets, diffuse functions[4] and polarization functions[5] and the integration grid consisted of 99 radial shells and 590 angular points are employed. Geometry optimizations are performed at B3LYP/6-31G(d) level of theory. Following frequency calculations, ground states and transition states were identified by zero or one imaginary frequency, respectively. Intrinsic reaction coordinate (IRC) calculations are carried out for further verification of transition states. The single energy values of all species, solvated by ethyl acetate in integral equation formalism model (IEFPCM)[5], are further refined at the higher B3LYP/6-31++G(d,p) level of theory.

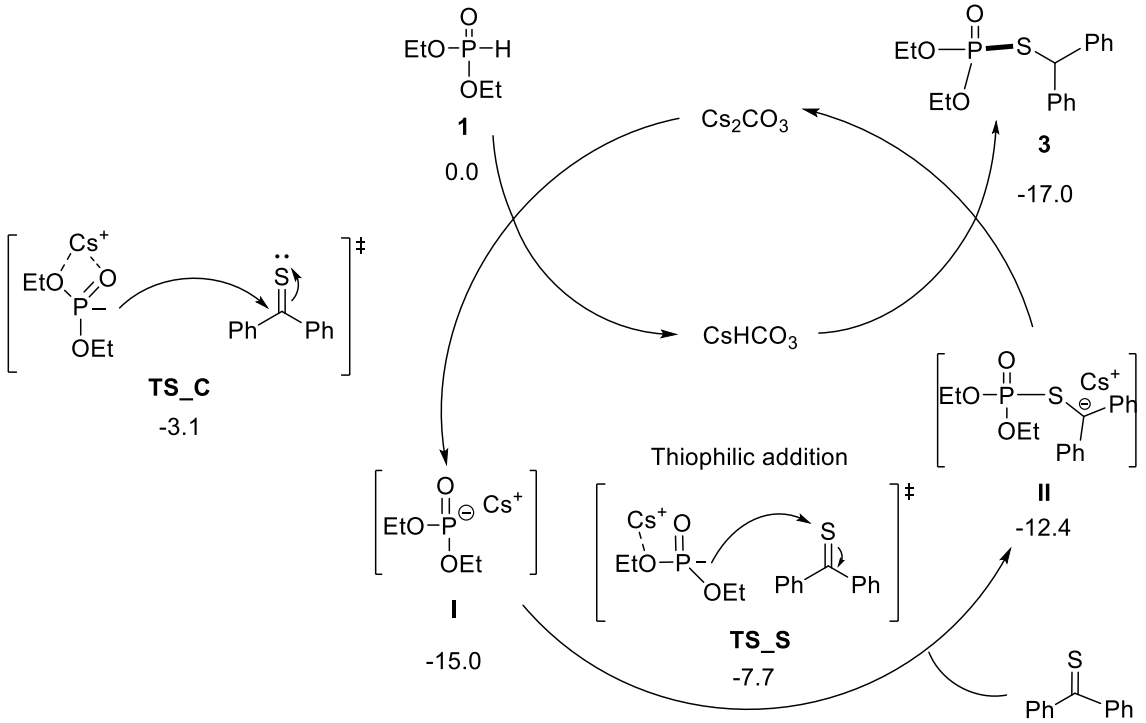


Figure 1. Single point energies under B3LYP(IEFPCM, EA)/6-31++G(d,p)/SDD || B3LYP/6-31G(d)/SDD, numbers in kcal/mol.

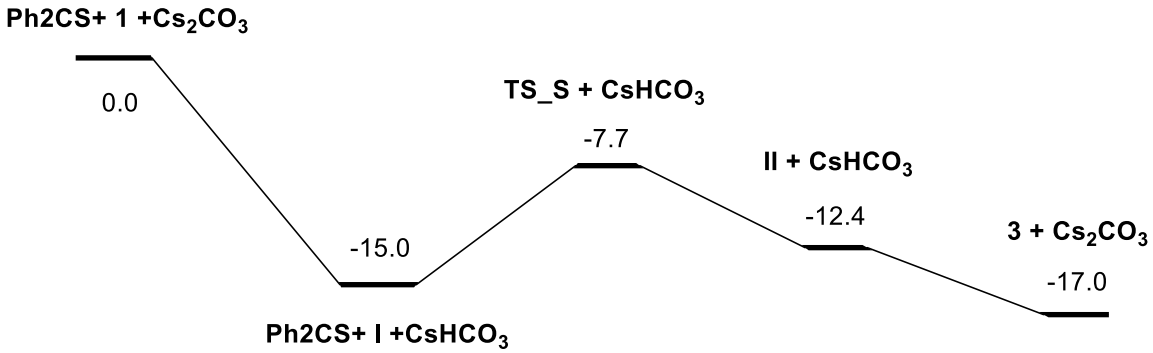


Figure 2. Single point energies under B3LYP(IEFPCM, EA)/6-31++G(d,p)/SDD || B3LYP/6-31G(d)/SDD, numbers in kcal/mol.

Supporting Information

Cartesian coordinates and single point energy of all species on B3LYP(IEFPCM, EA)/6-31++G(d,p)||B3LYP/6-31G(d) level of theory

Cs_2CO_3

-304.282231776

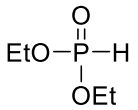
C	-0.159708000	0.019790000	-2.662817000
O	-0.471935000	0.069043000	-3.912118000
O	1.062280000	0.085817000	-2.260488000

O	-1.137427000	-0.104275000	-1.756025000
Cs	0.617249000	-0.107534000	0.435864000
Cs	-3.186625000	-0.143317000	-3.686857000

$CsHCO_3$

-284.677233841

C	-0.272601000	0.008634000	-2.633430000
O	-0.398107000	0.090046000	-3.877404000
O	1.028585000	0.061282000	-2.153890000
O	-1.181231000	-0.115370000	-1.759172000
H	0.923590000	-0.015270000	-1.191207000
Cs	-3.244667000	-0.108917000	-3.757710000



diEtOPHO

1

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C	-2.927315000	0.332760000	-4.639957000
H	-2.819791000	1.303342000	-4.147359000
H	-1.964374000	0.067471000	-5.094883000
O	-3.919126000	0.442247000	-5.690737000
P	-3.967576000	1.762873000	-6.627070000
O	-5.455259000	1.675600000	-7.228752000
C	-6.593824000	1.948883000	-6.372726000
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H	-6.651532000	1.161747000	-5.612914000
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H	-7.762246000	2.759165000	-8.000691000
H	-8.719762000	2.168264000	-6.624671000
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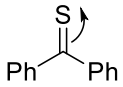

Ph2CS

Ph2CS

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C	-0.486699000	-1.003826000	-2.196524000
C	-2.000597000	0.874700000	-2.384642000
C	-0.375386000	-1.050633000	-3.582312000
C	-1.906558000	0.809423000	-3.774016000
C	-1.088595000	-0.147551000	-4.377131000
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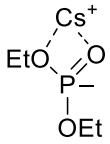

I

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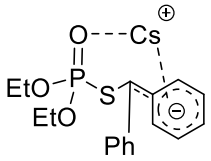
H	-7.658340000	2.783391000	-7.918216000
H	-7.601141000	3.236908000	-6.199198000
H	-8.695840000	1.950933000	-6.739340000
O	-2.842489000	1.806250000	-7.314218000
Cs	-3.709555000	4.420359000	-6.809974000



II

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H	0.752275000	3.505885000	-4.313864000
H	1.360738000	2.168572000	-5.317905000
O	-0.446701000	1.813163000	-4.349985000
P	-1.545234000	2.213816000	-5.486418000
O	-2.866165000	1.530457000	-4.838786000
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H	-2.633630000	-0.477788000	-5.330676000
C	-4.281556000	-0.187009000	-3.948447000
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H	-4.330357000	-1.236533000	-3.636691000
O	-1.783718000	3.685966000	-5.646545000
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C	0.820155000	4.608326000	-9.500045000

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H	1.767261000	4.987820000	-9.118438000
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Cs	-2.437910000	5.459883000	-7.820411000
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C	-3.918130000	0.848619000	-8.251832000
C	-4.211398000	0.201218000	-10.937022000
C	-5.083239000	0.226029000	-8.698398000
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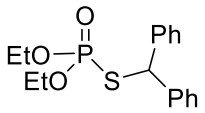

3

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C	-3.972955000	3.470058000	-4.719772000
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H	-4.774792000	3.550713000	-5.463002000
O	-2.707052000	3.327763000	-5.416086000
P	-2.440152000	2.006172000	-6.310235000
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H	-0.261536000	0.772412000	-5.163119000
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S	-3.335291000	2.485970000	-8.144278000
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H	-0.147578000	-2.299806000	-8.217110000
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C	-4.867767000	1.824504000	-10.784764000
C	-5.686405000	-0.250001000	-9.872716000
C	-5.883225000	1.801982000	-11.742811000
C	-6.699507000	-0.275813000	-10.831061000
C	-6.801314000	0.751477000	-11.771132000
H	-4.168172000	2.655992000	-10.770986000
H	-5.613972000	-1.052701000	-9.142790000
H	-5.956854000	2.610690000	-12.465042000
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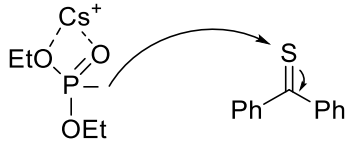

TS_S

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H	-2.965112000	-6.219438000	-2.598866000
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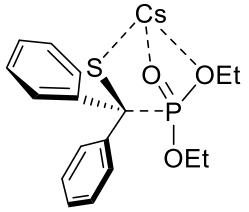

TS_C

TS_C

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H	-5.528607000	3.335137000	-8.300822000

H	-4.686693000	3.666691000	-6.780675000
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H	0.486469000	3.029351000	-8.973280000
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H	1.793608000	4.422453000	-10.553260000
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Cs	-1.909193000	1.301229000	-5.365075000
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C	-3.074652000	0.563723000	-10.860739000
C	-3.308531000	-2.123102000	-10.164399000
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H	-1.497509000	-1.817489000	-9.031049000
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H	-3.386359000	-3.174047000	-9.896595000
H	-4.872286000	0.274990000	-11.997392000
H	-5.085324000	-2.132896000	-11.390636000

5. References

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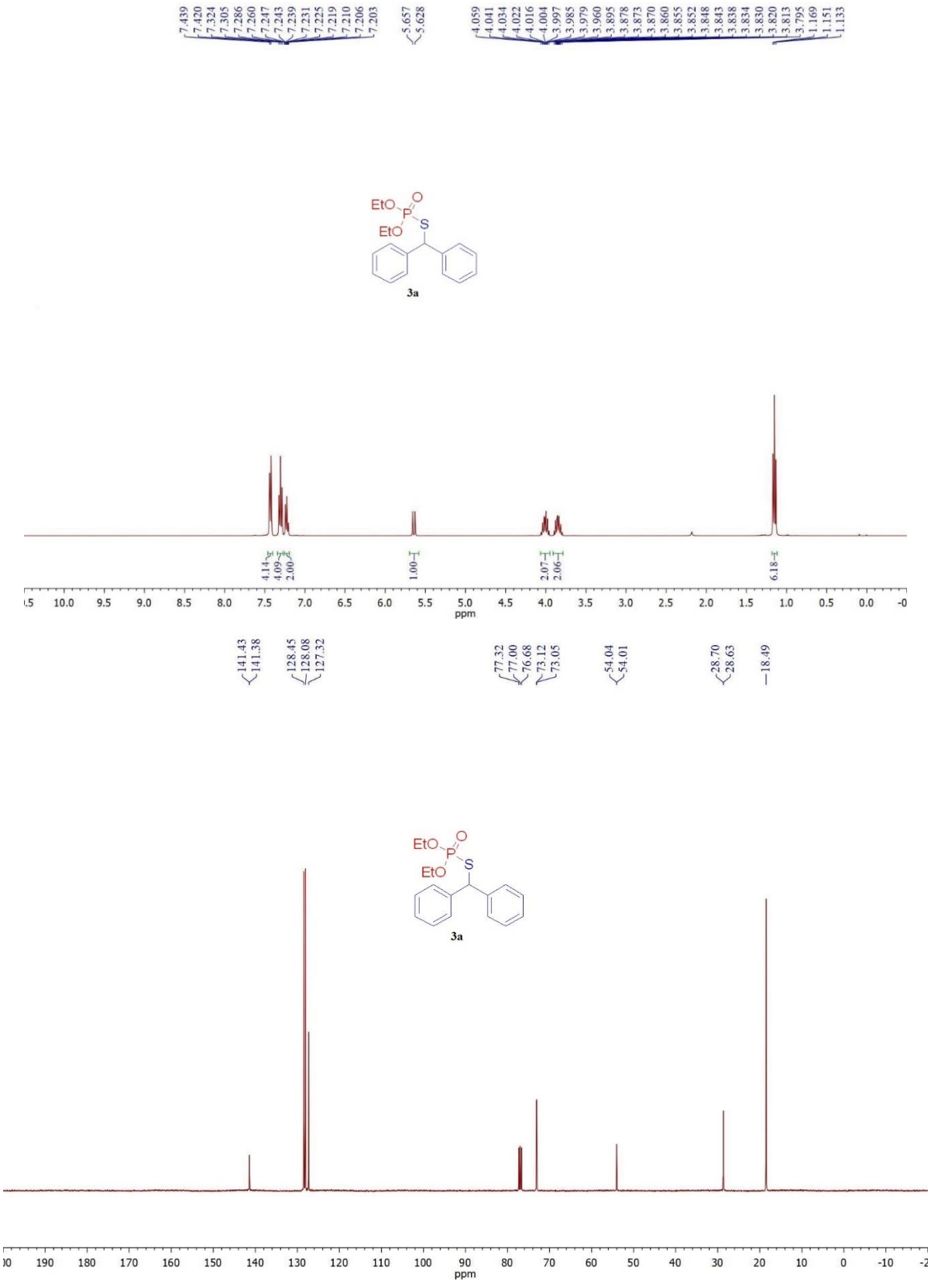
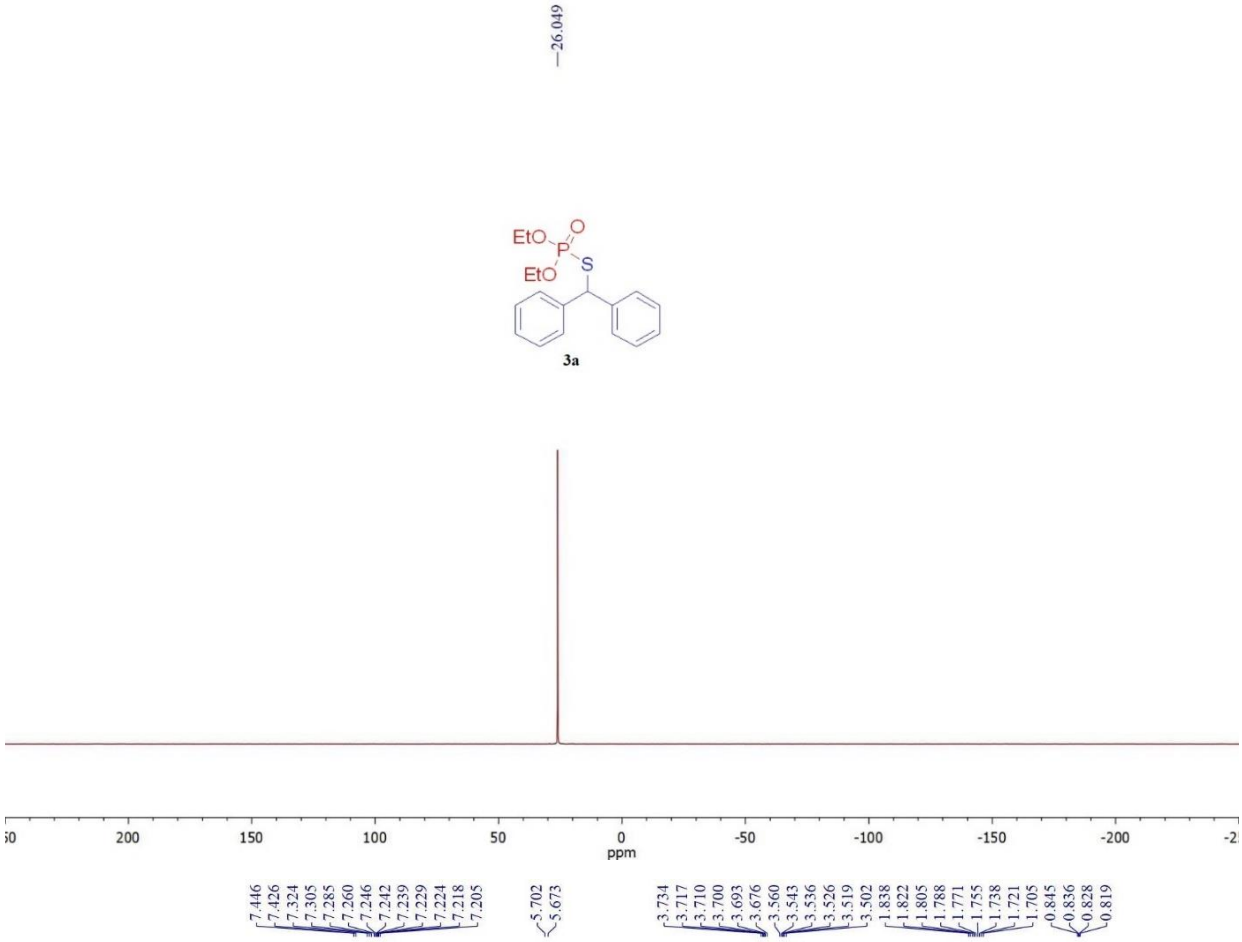
6. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra of compounds 3

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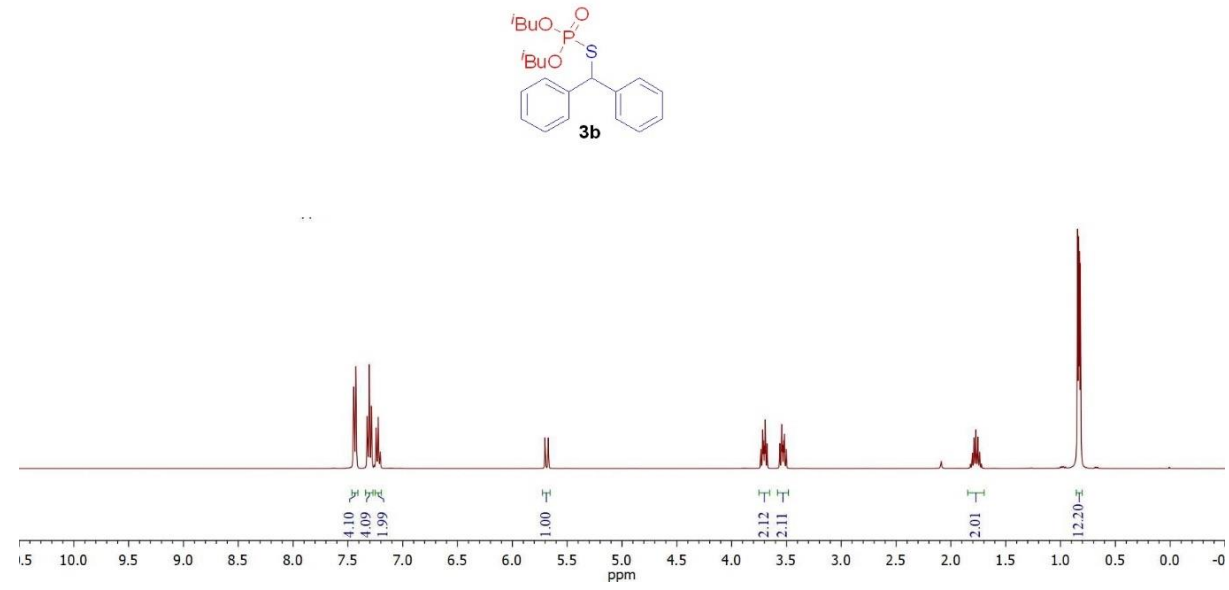
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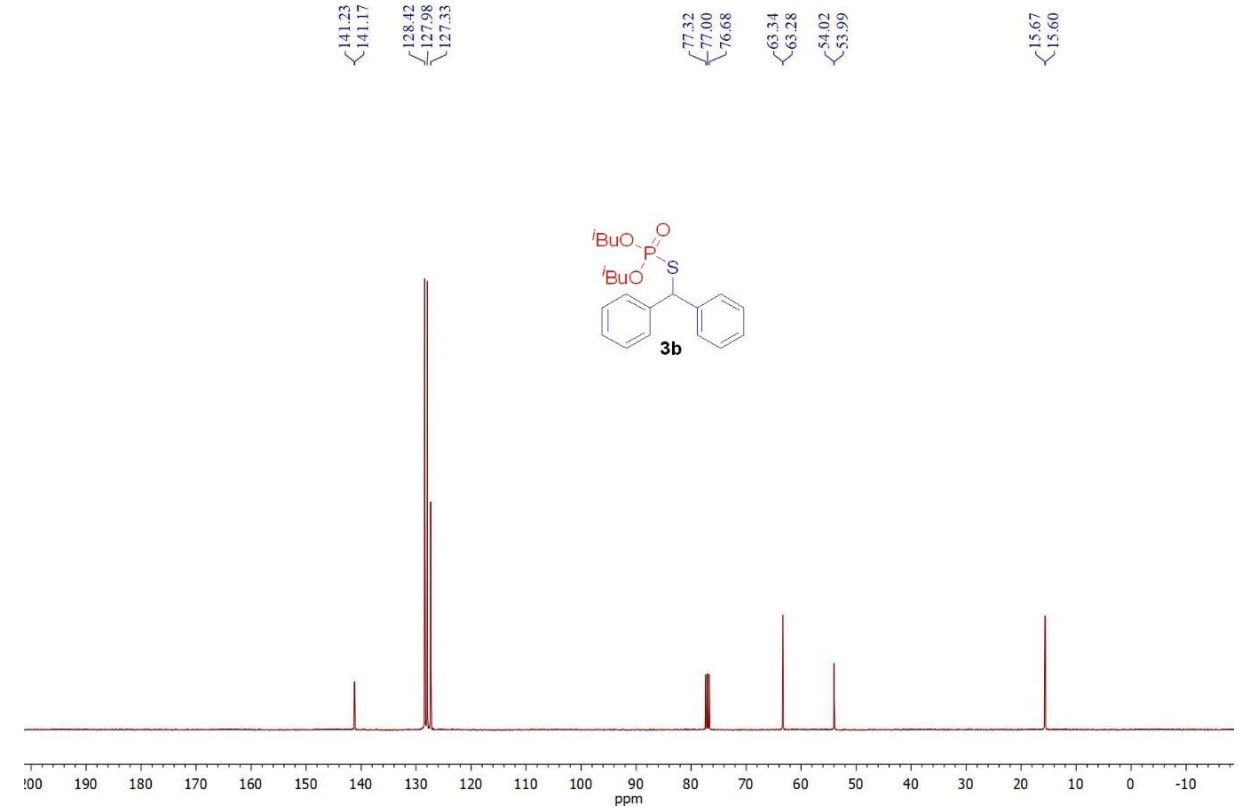
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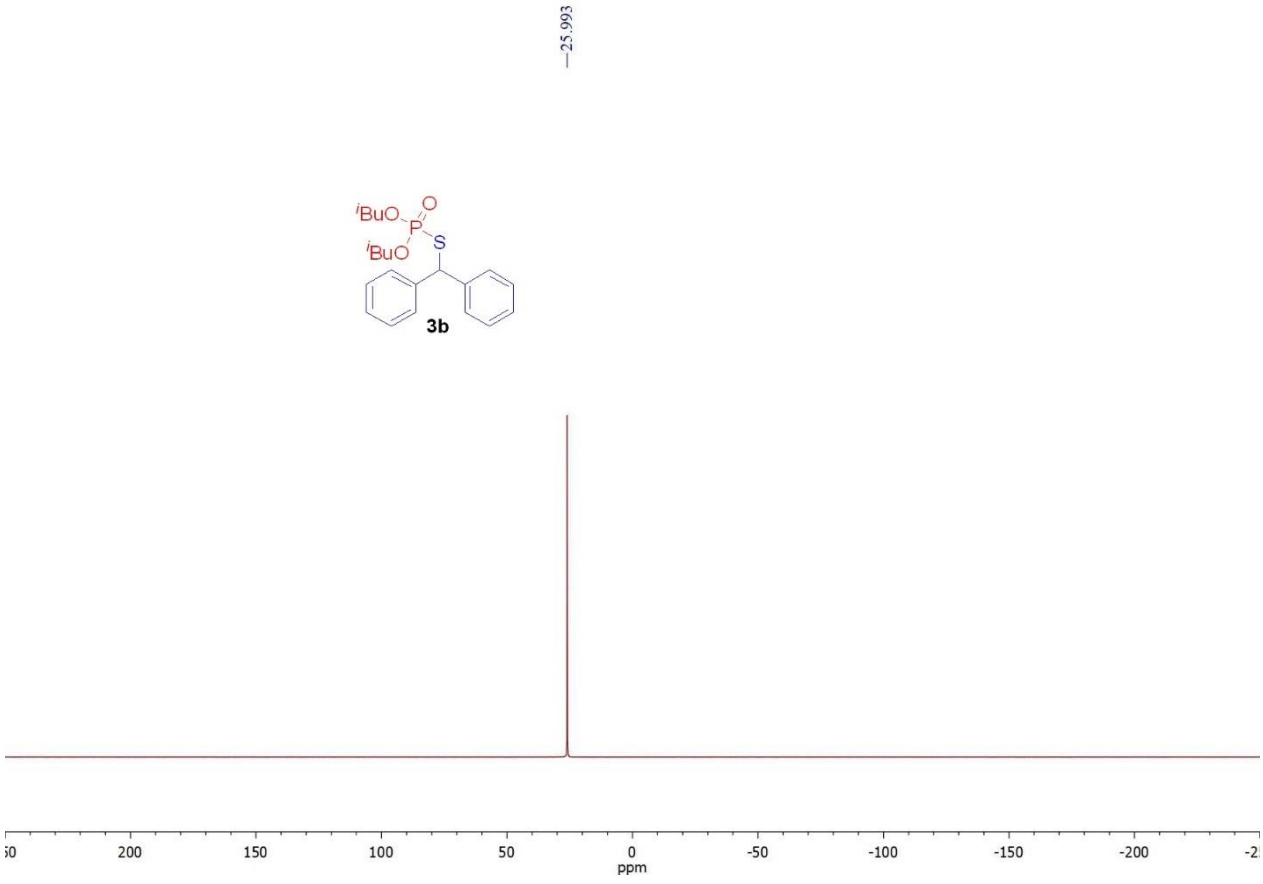
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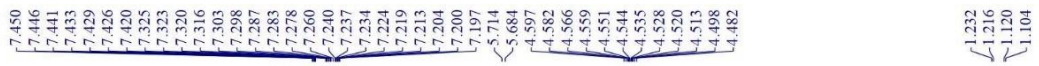
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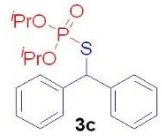
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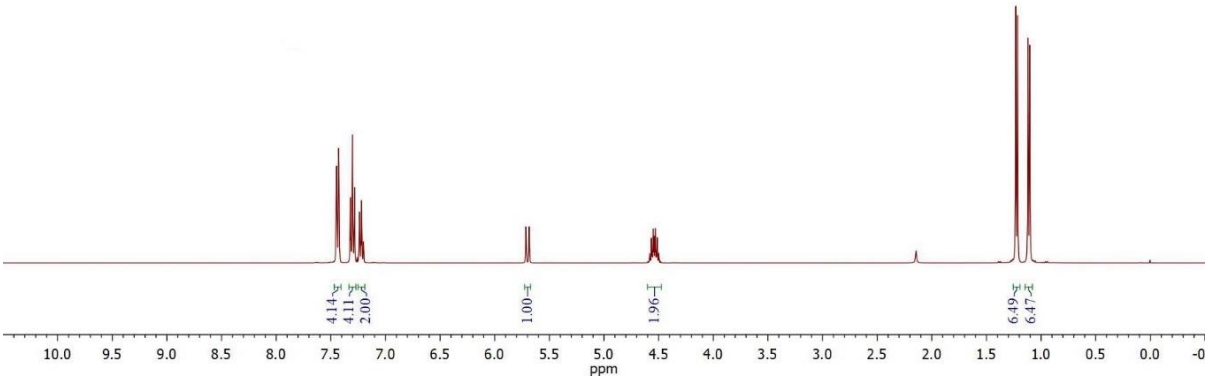
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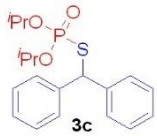
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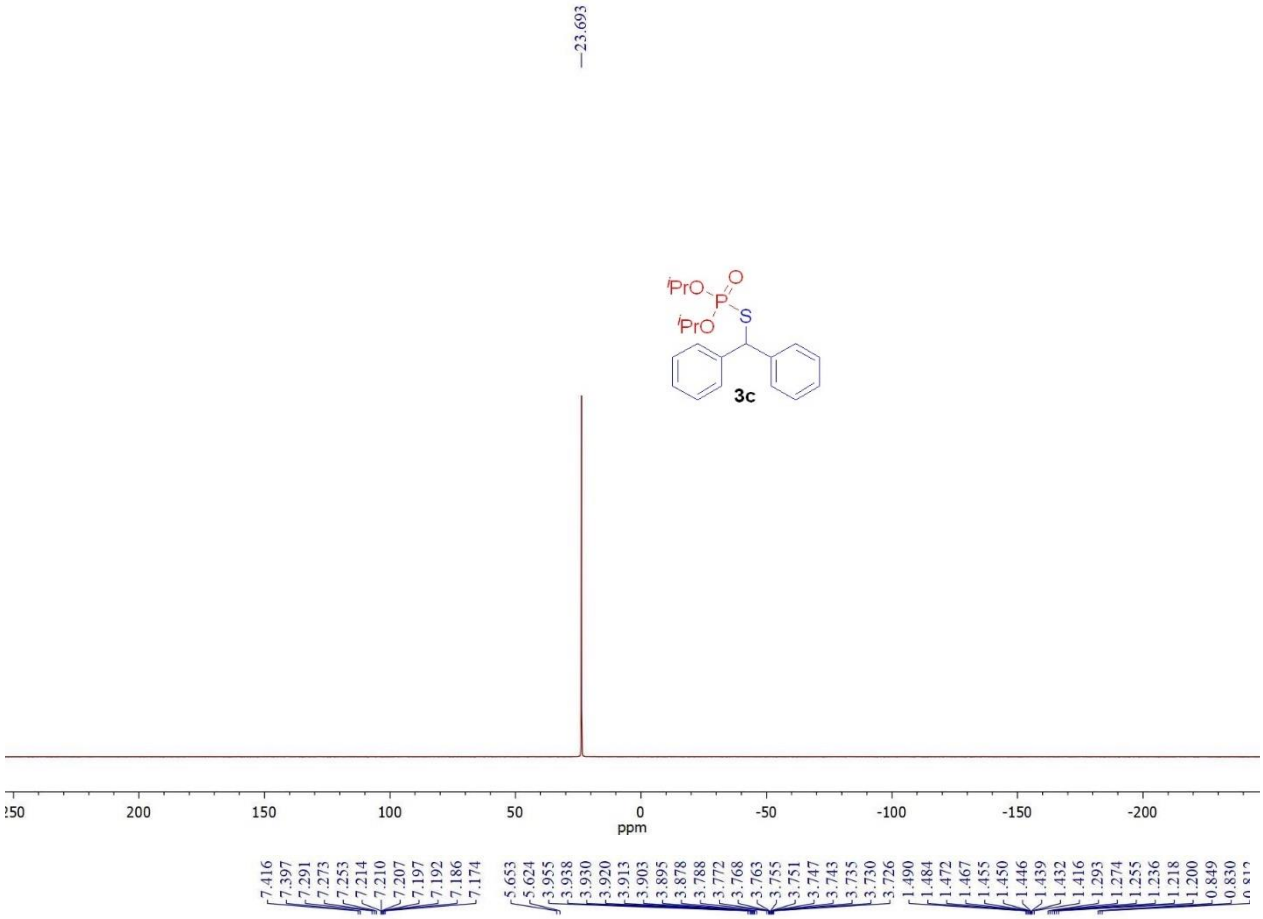
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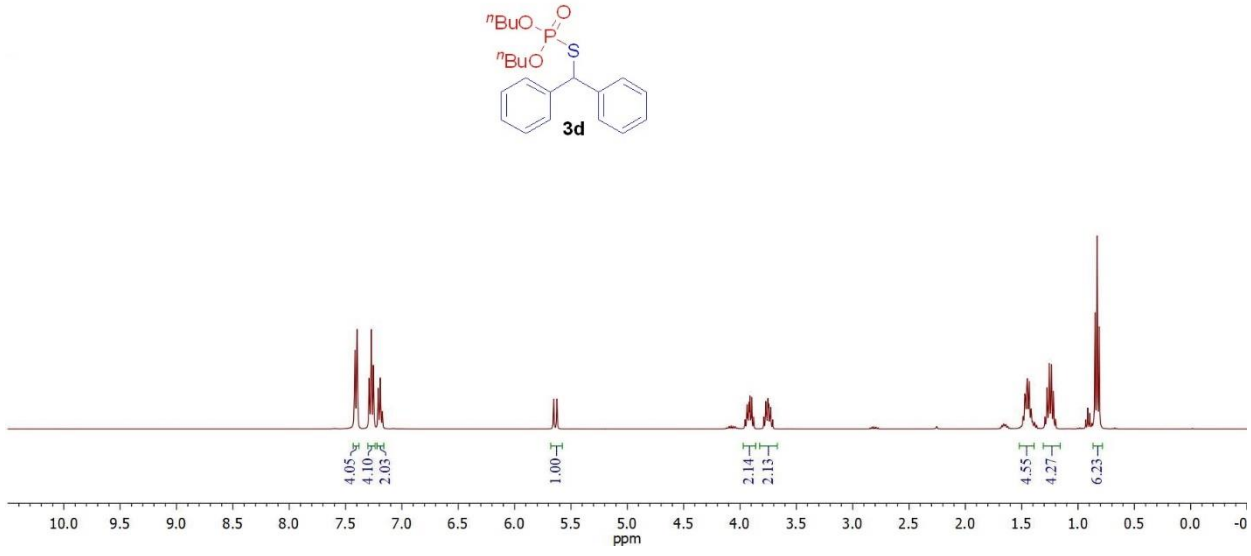
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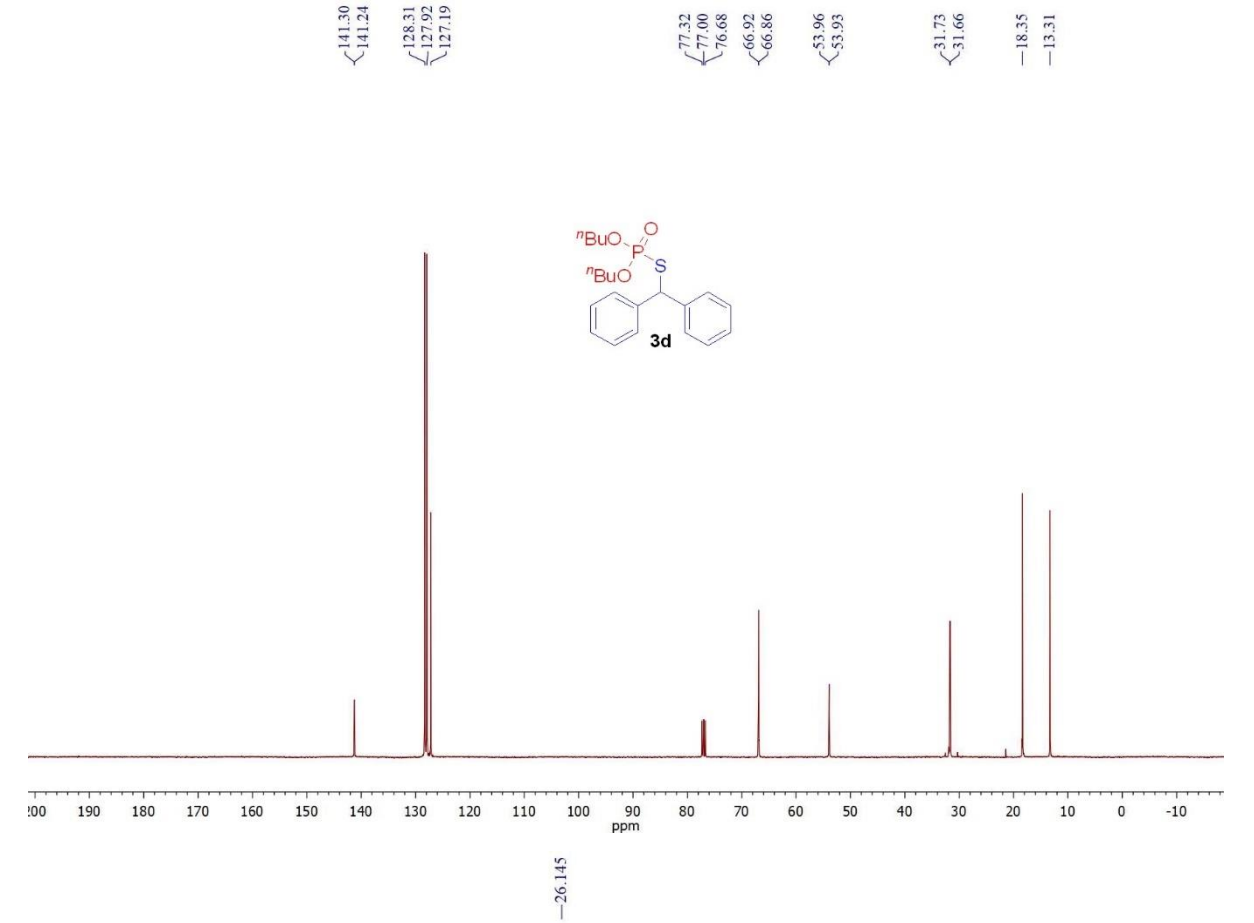
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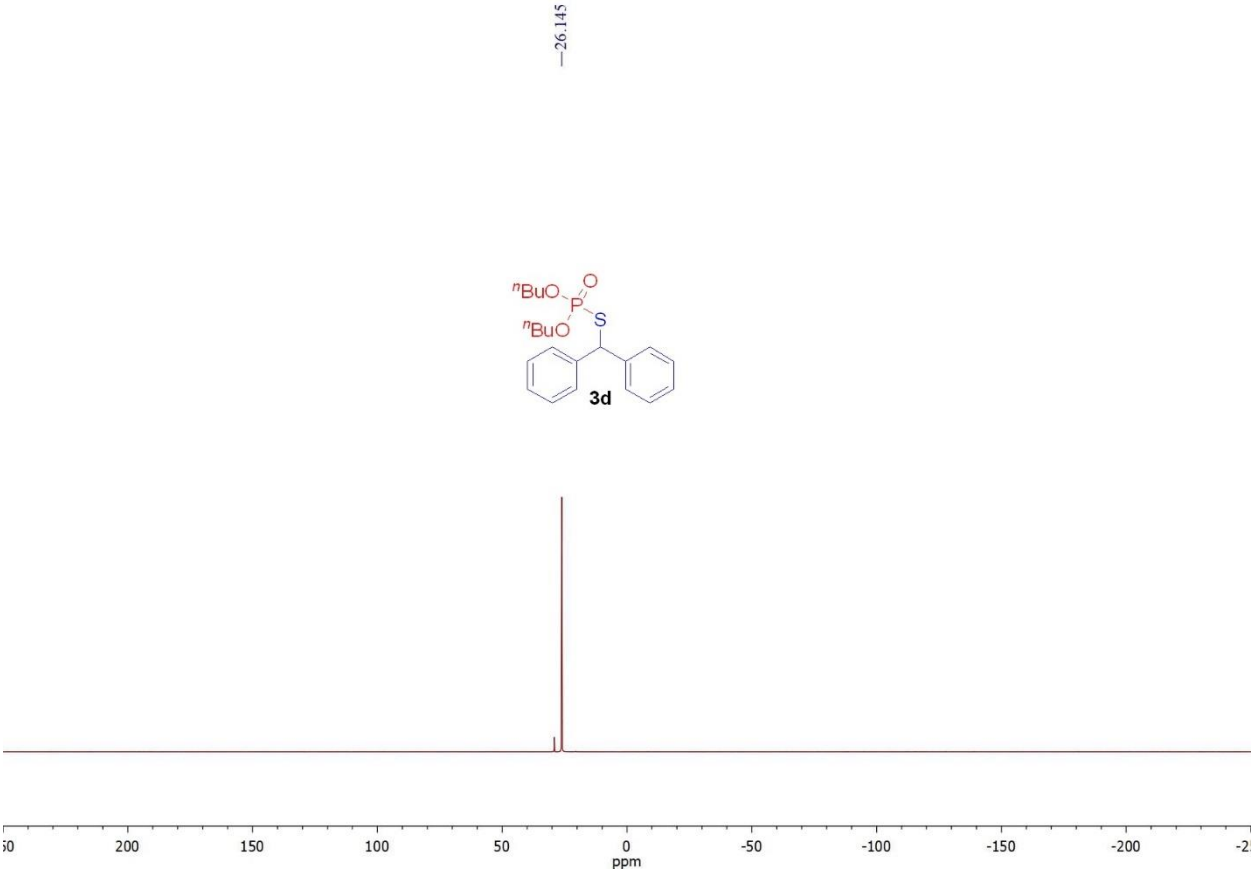
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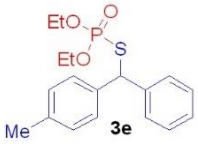
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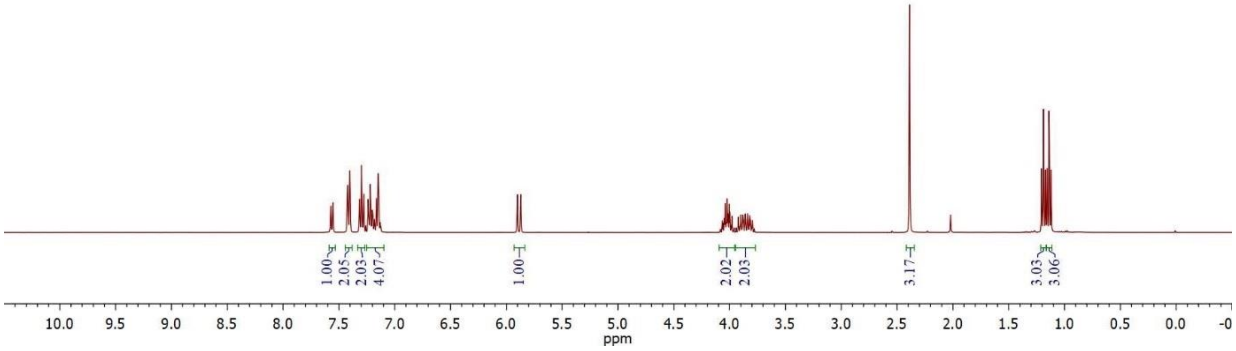
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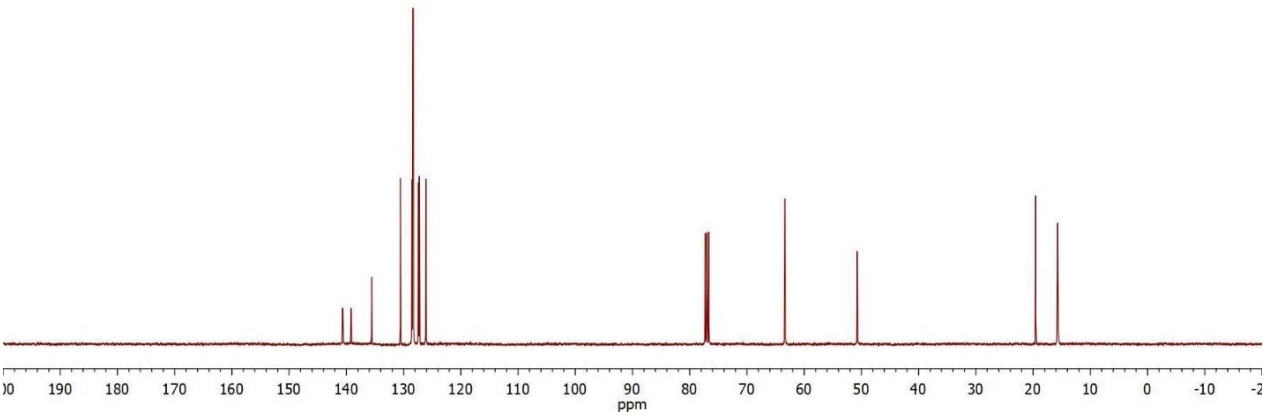
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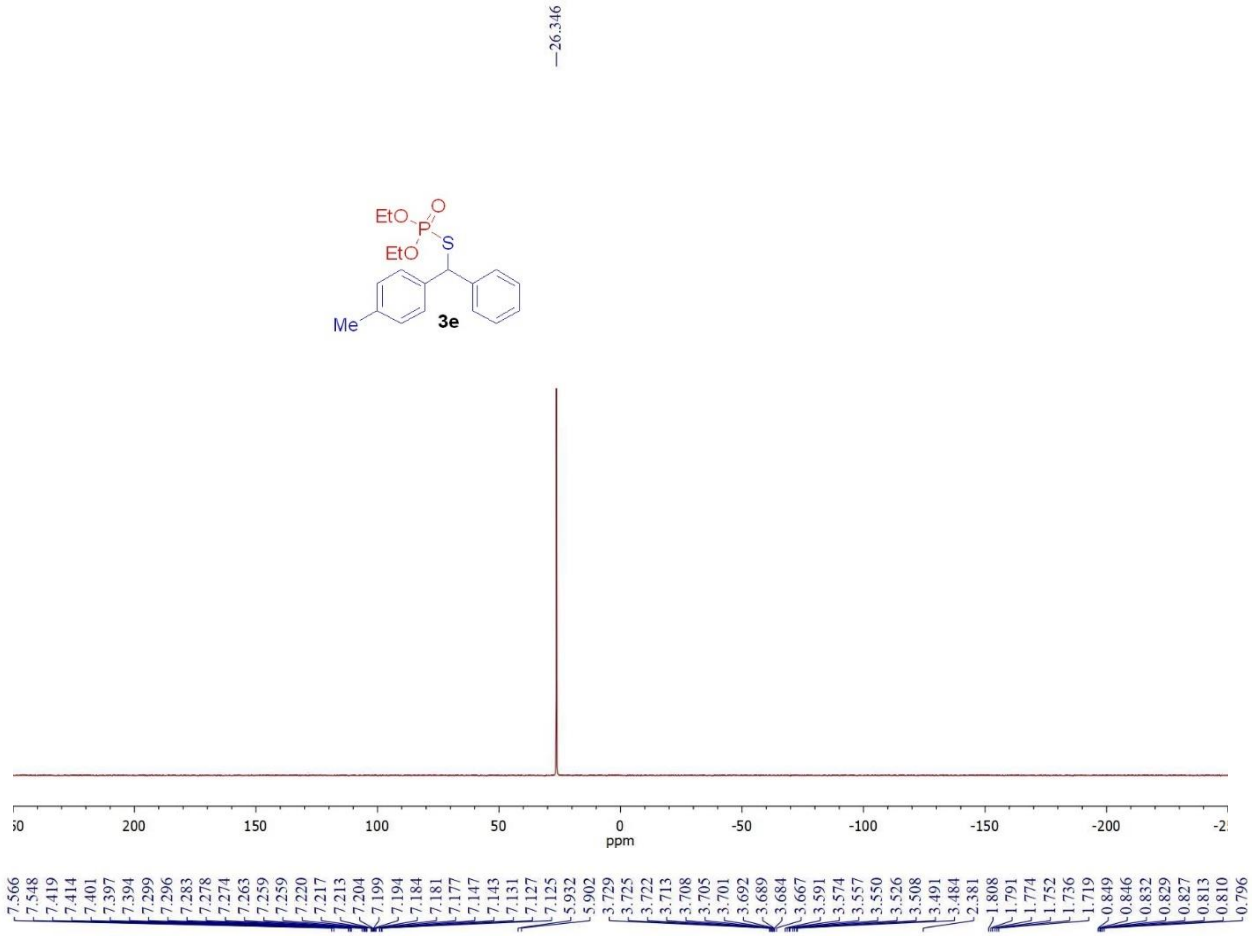
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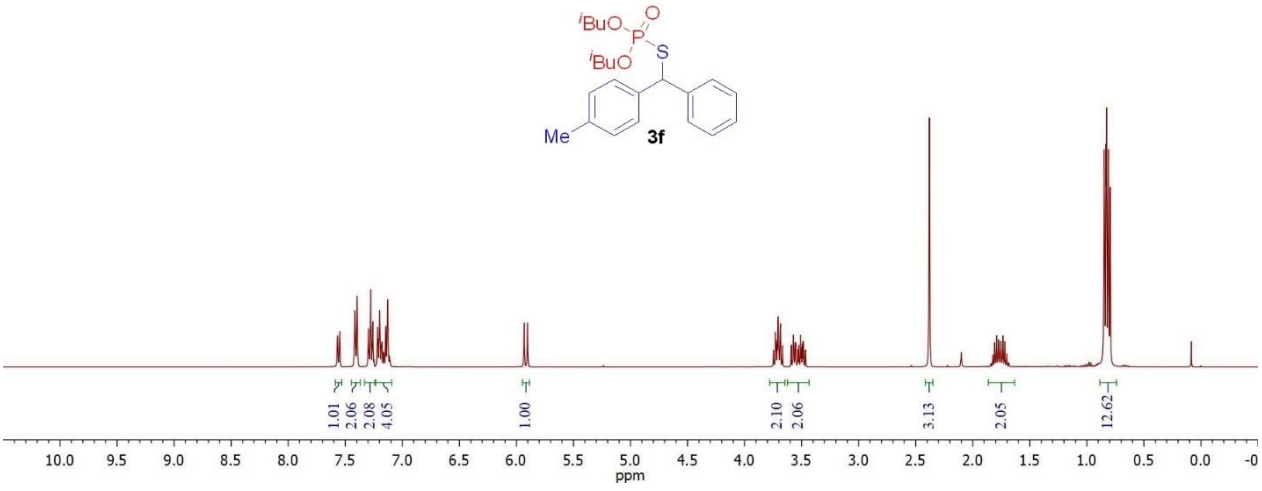
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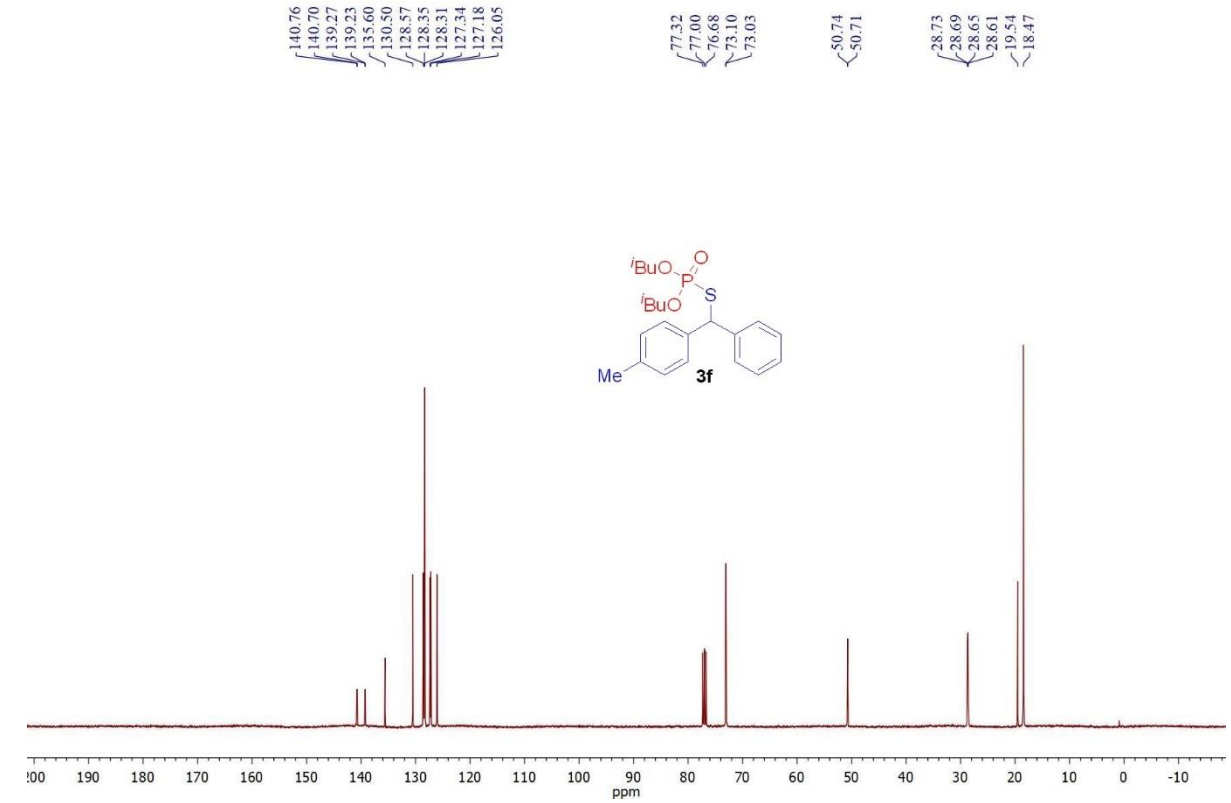
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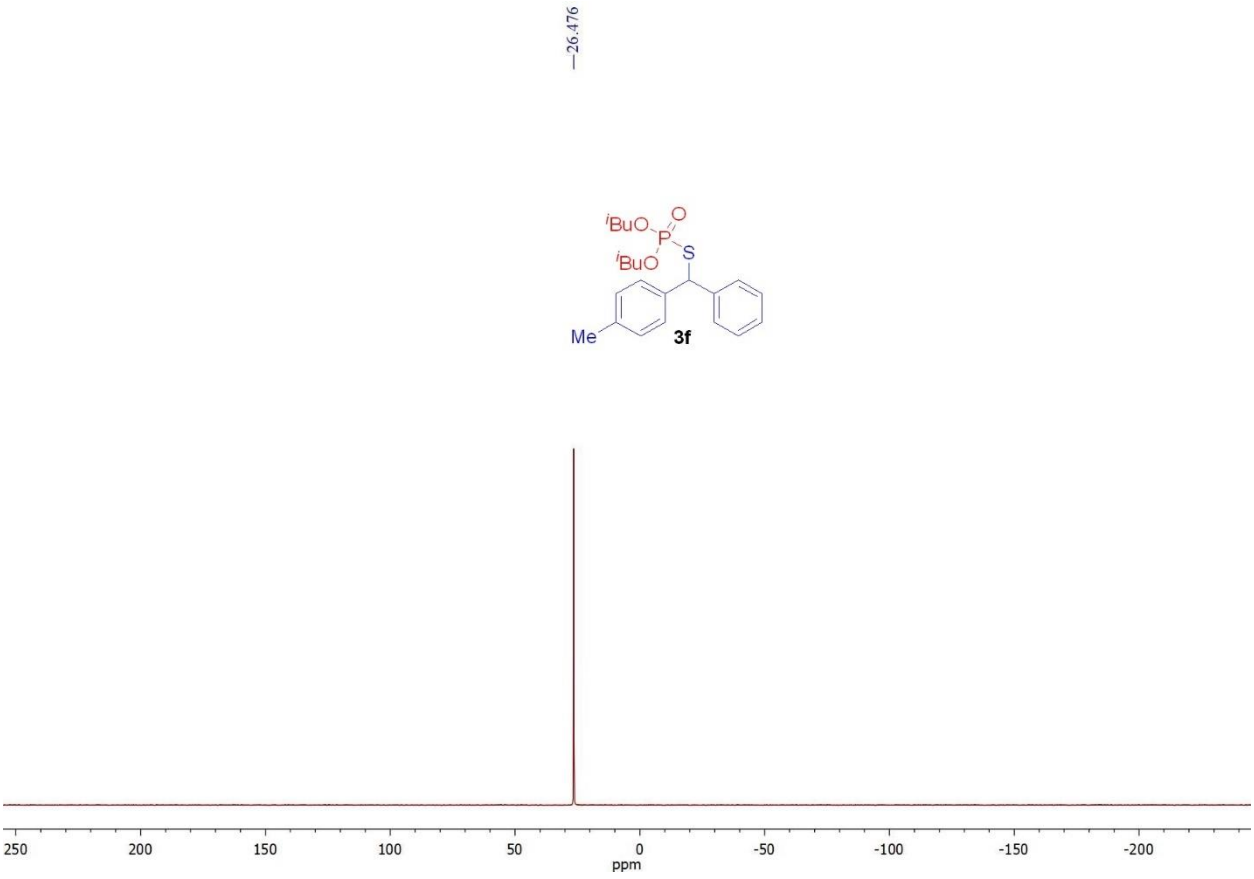
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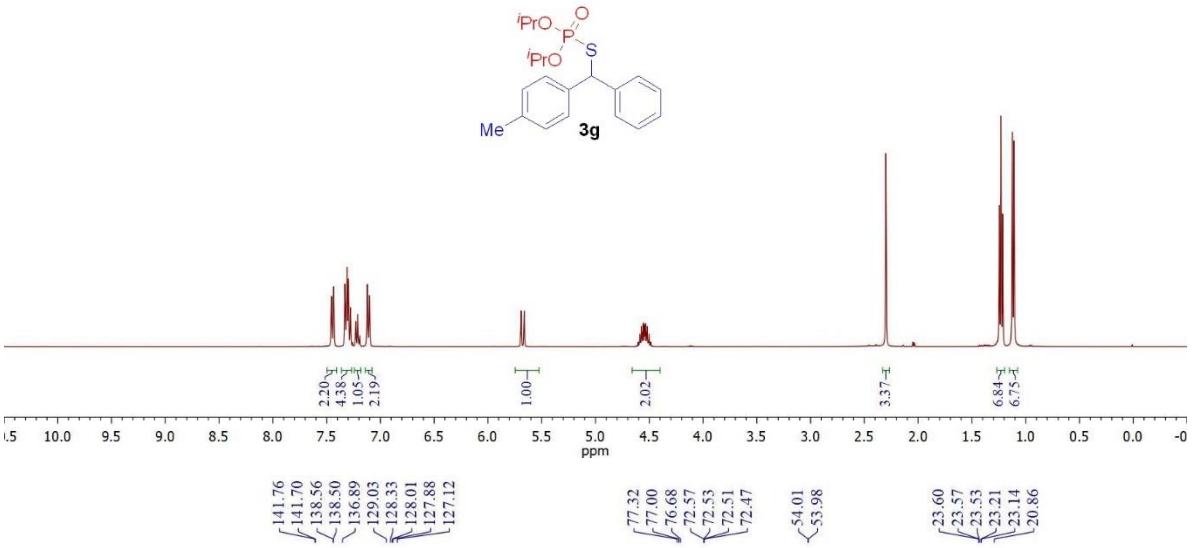
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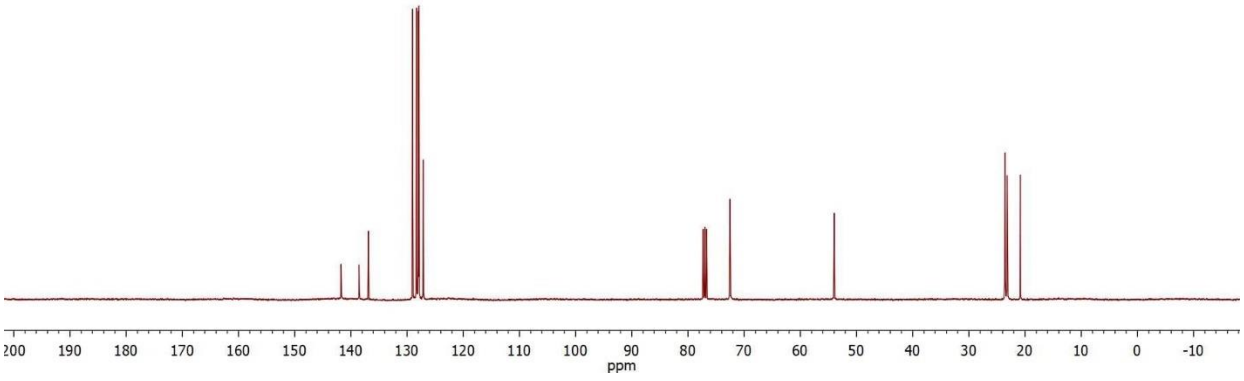
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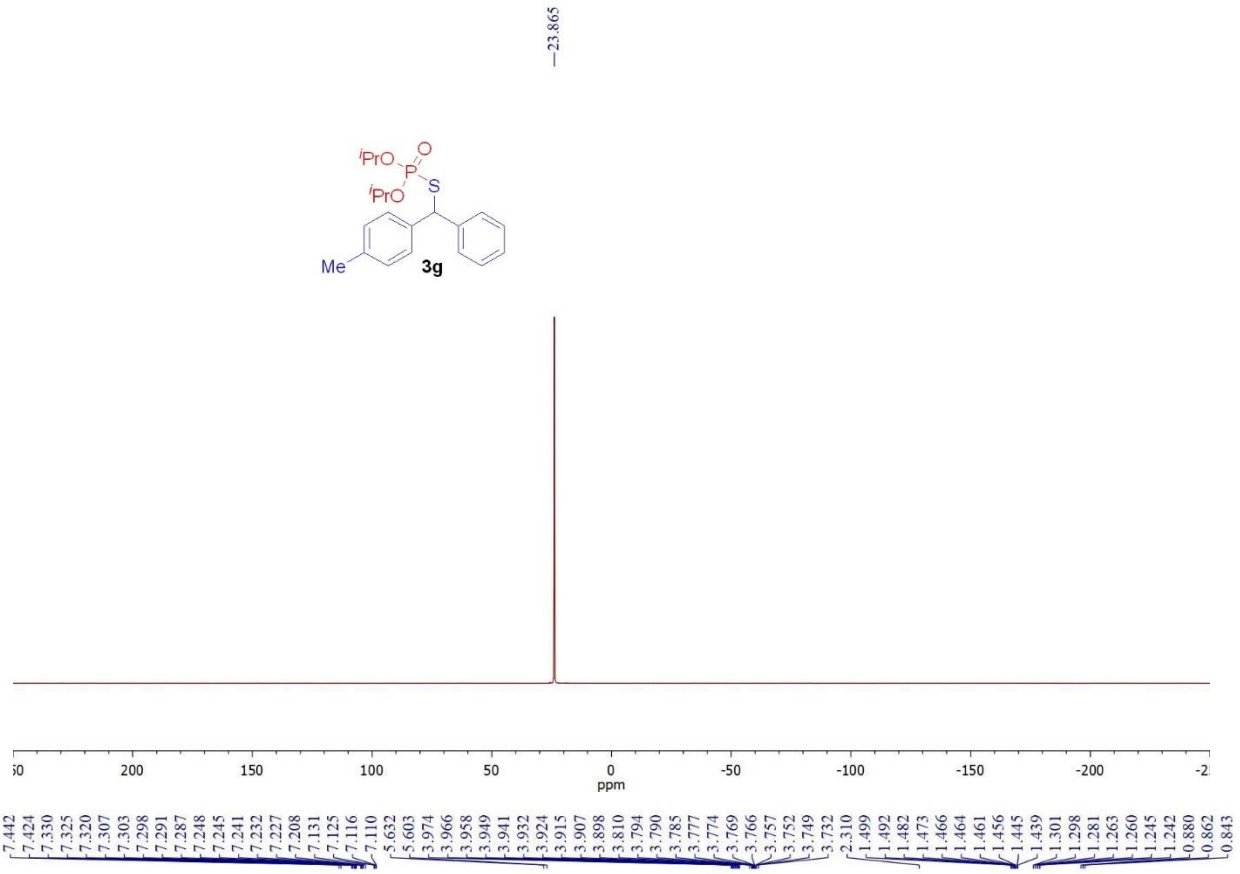
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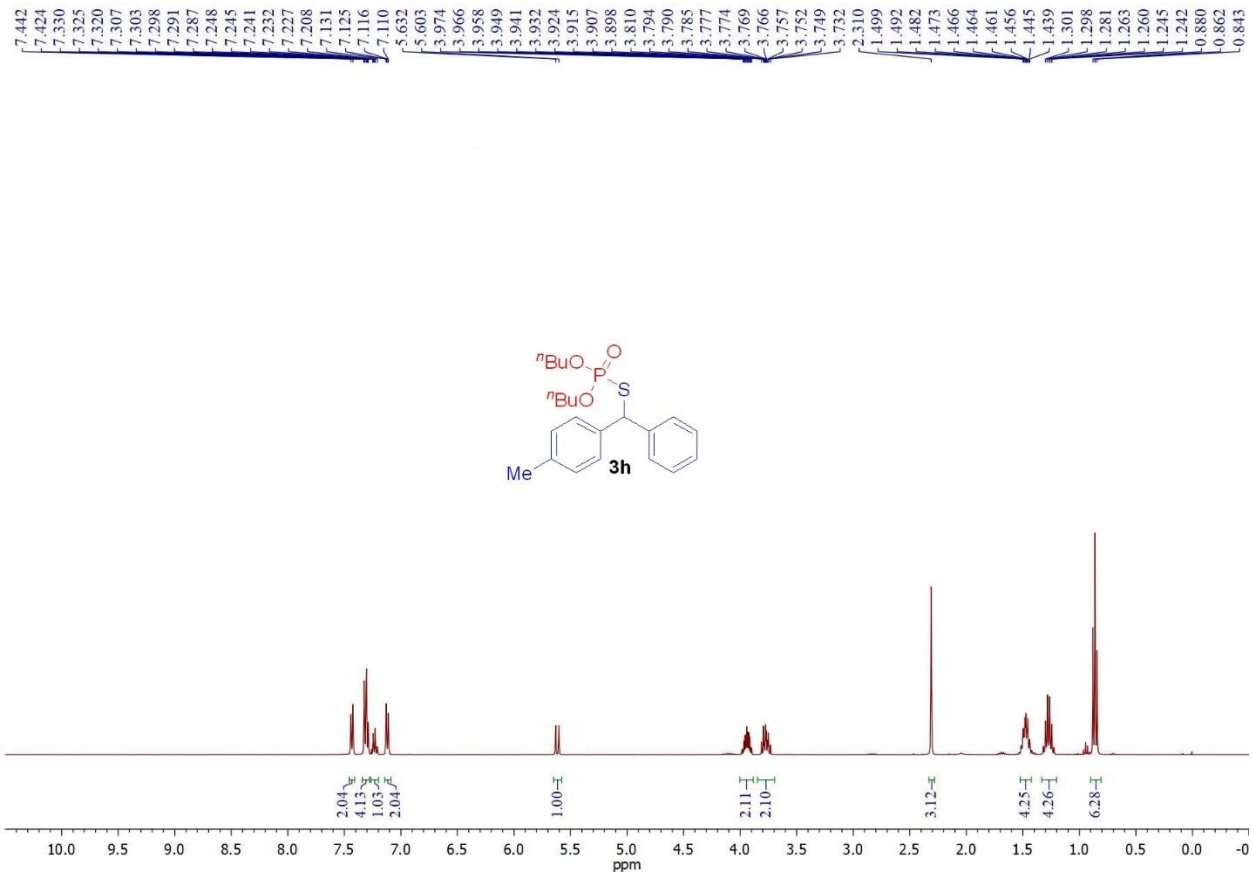
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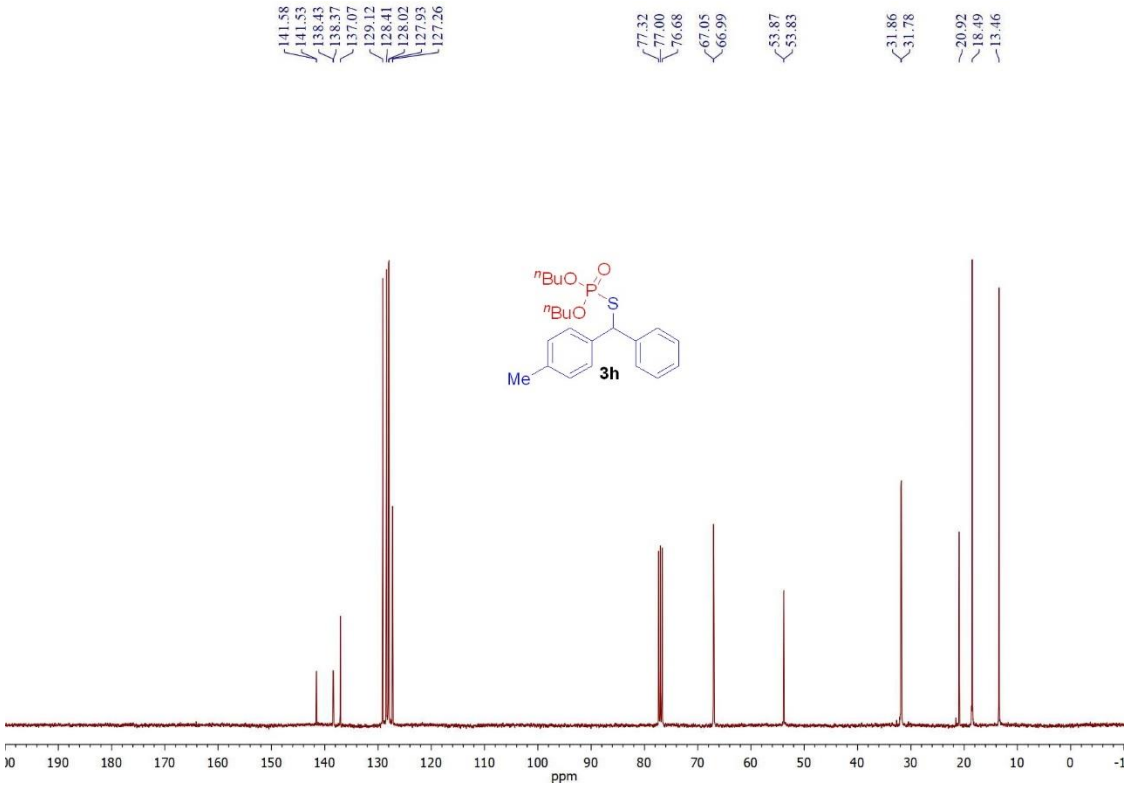
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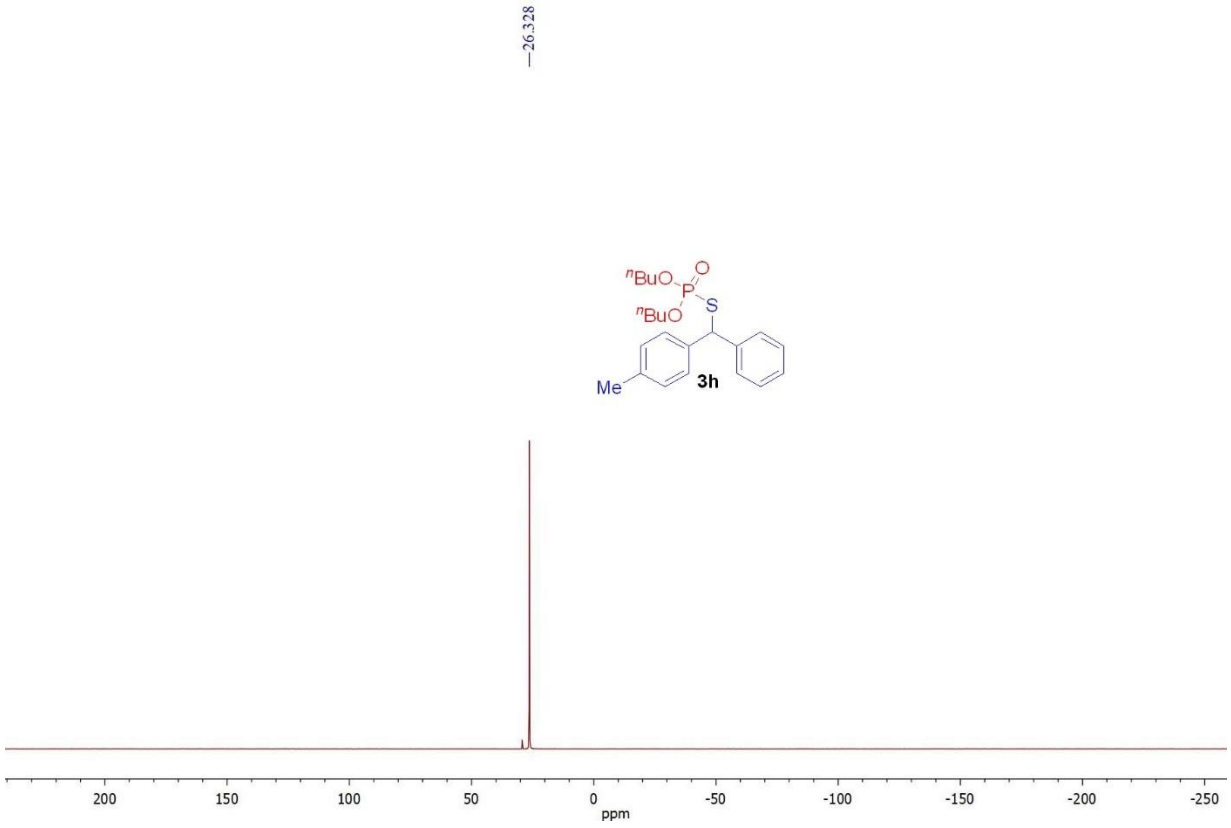
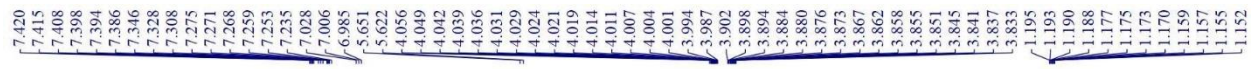

26.328
nBuO
nBuO
P
O
S
Me
3h
ppm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7.328
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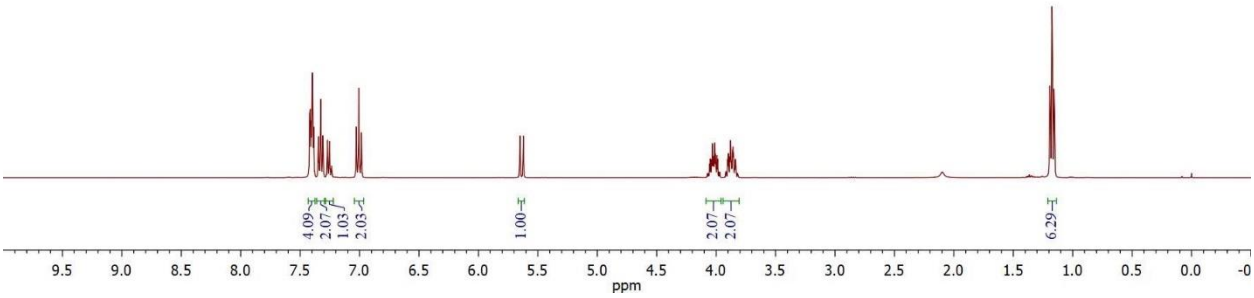
7.268
7.259
7.253
7.235
7.028
7.006
6.985
5.651
5.622
4.056
4.049
4.042
4.039
4.036
4.031
4.029
4.024
4.021
4.019
4.014
4.011
4.007
4.004
4.001
3.994
3.987
3.902
3.898
3.894
3.884
3.880
3.876
3.873
3.867
3.862
3.858
3.855
3.851
3.845
3.841
3.837
3.833
1.195
1.193
1.190
1.188
1.177
1.175
1.173
1.170
1.159
1.157
1.155
1.152


EtO
O
P
S
EtO
F
3i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1.03
2.03
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2.07
2.07
6.29
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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
-0
ppm


163.06
160.61
141.06
141.00
137.24
137.19
137.15
129.83
129.74
128.58
127.96
127.54
115.43
115.21
77.32
77.00
76.68
63.49
63.45
53.34
53.31
15.76
15.69


EtO
O
P
S
EtO
F
3i

00
190
180
170
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130
120
110
100
90
80
70
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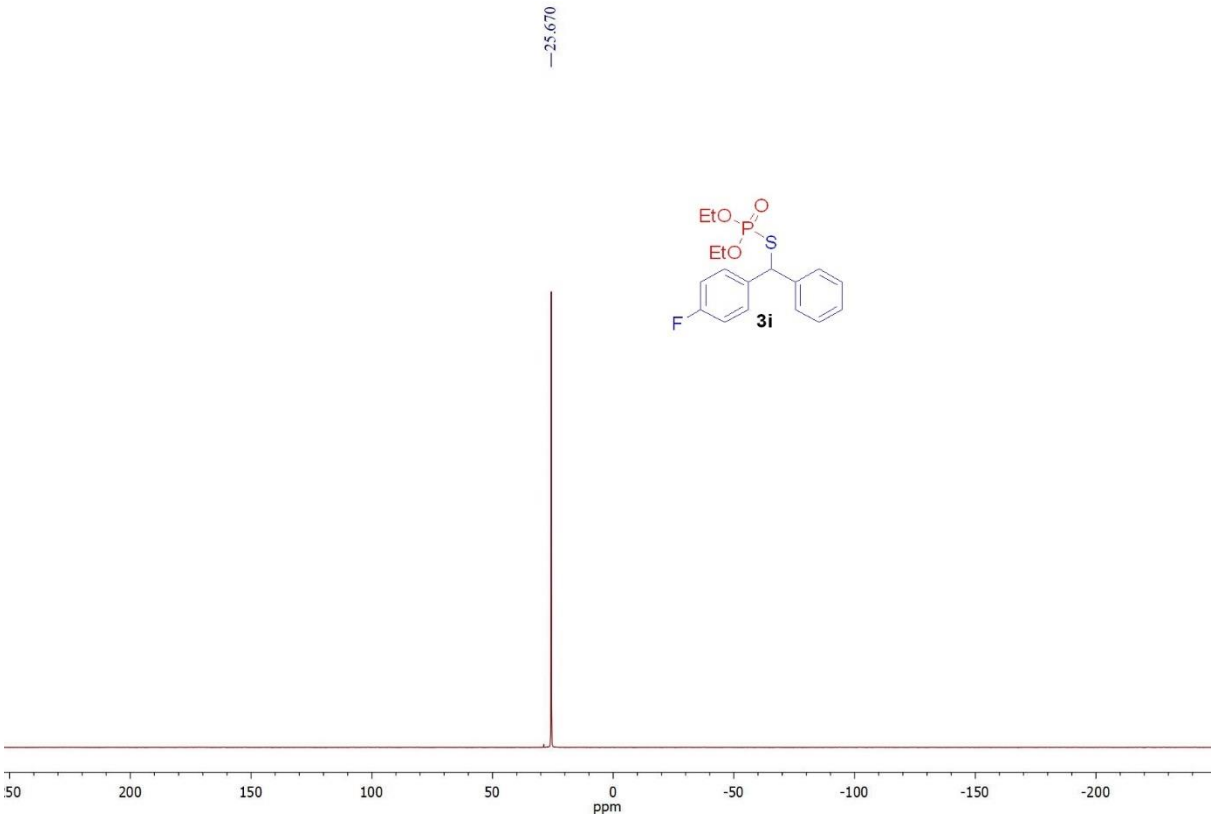
50
40
30
20
10
0
-10
ppm


25.670
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EtO
S
F
3i
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150
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ppm
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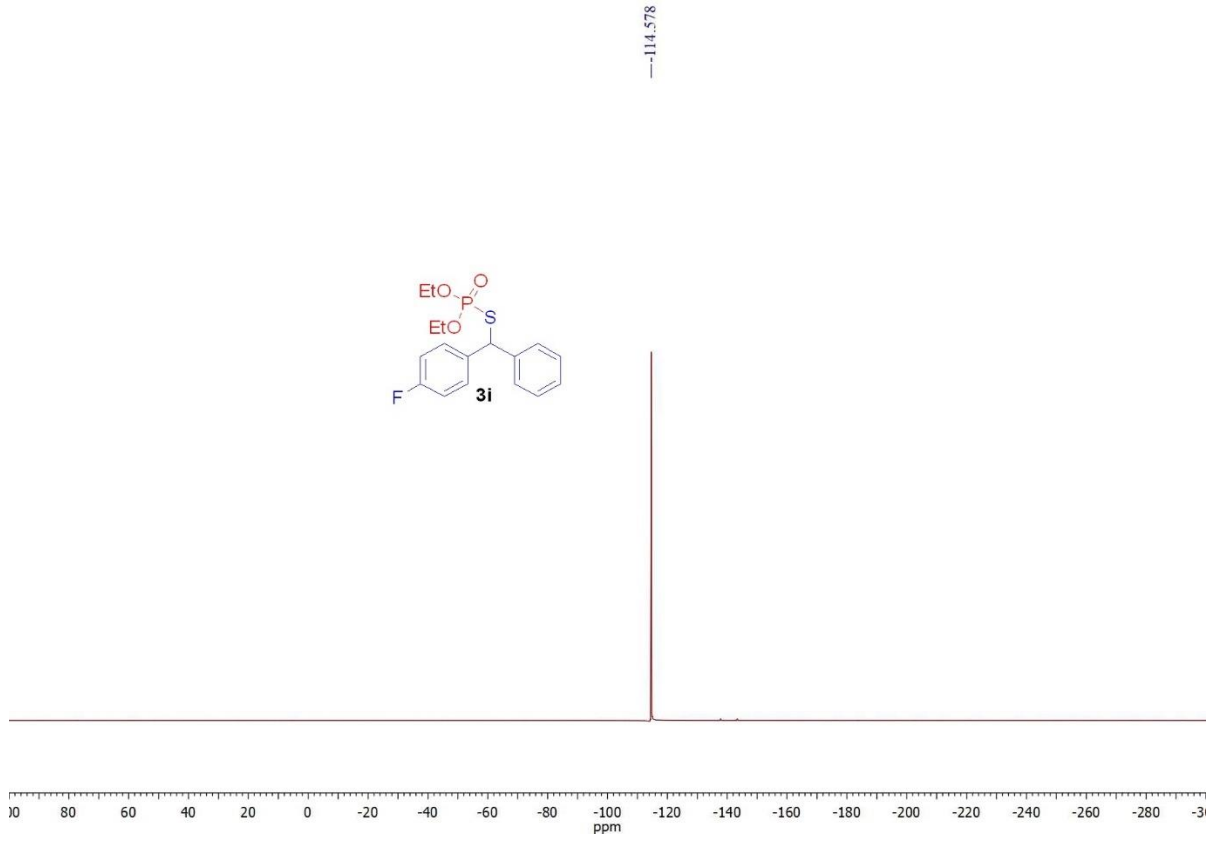
-150
-200


114.578
EtO
O
P
EtO
S
F
3i
80
60
40
20
0
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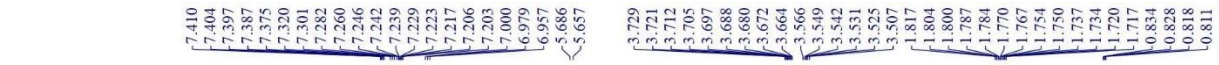
ppm
-120
-140
-160
-180
-200
-220
-240
-260
-280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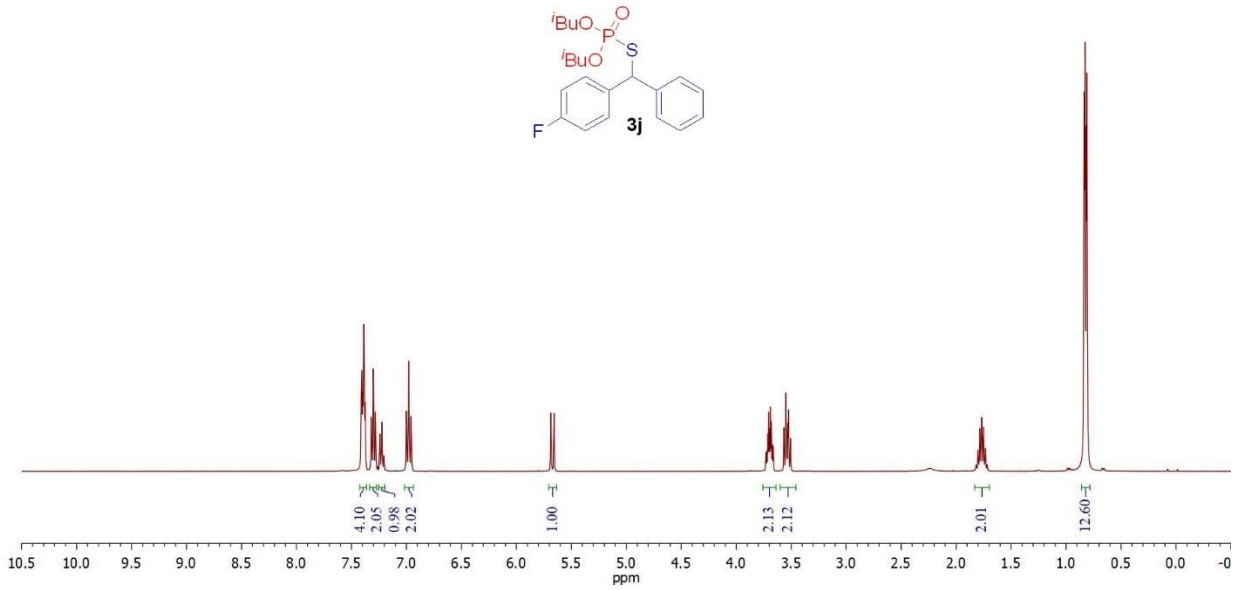
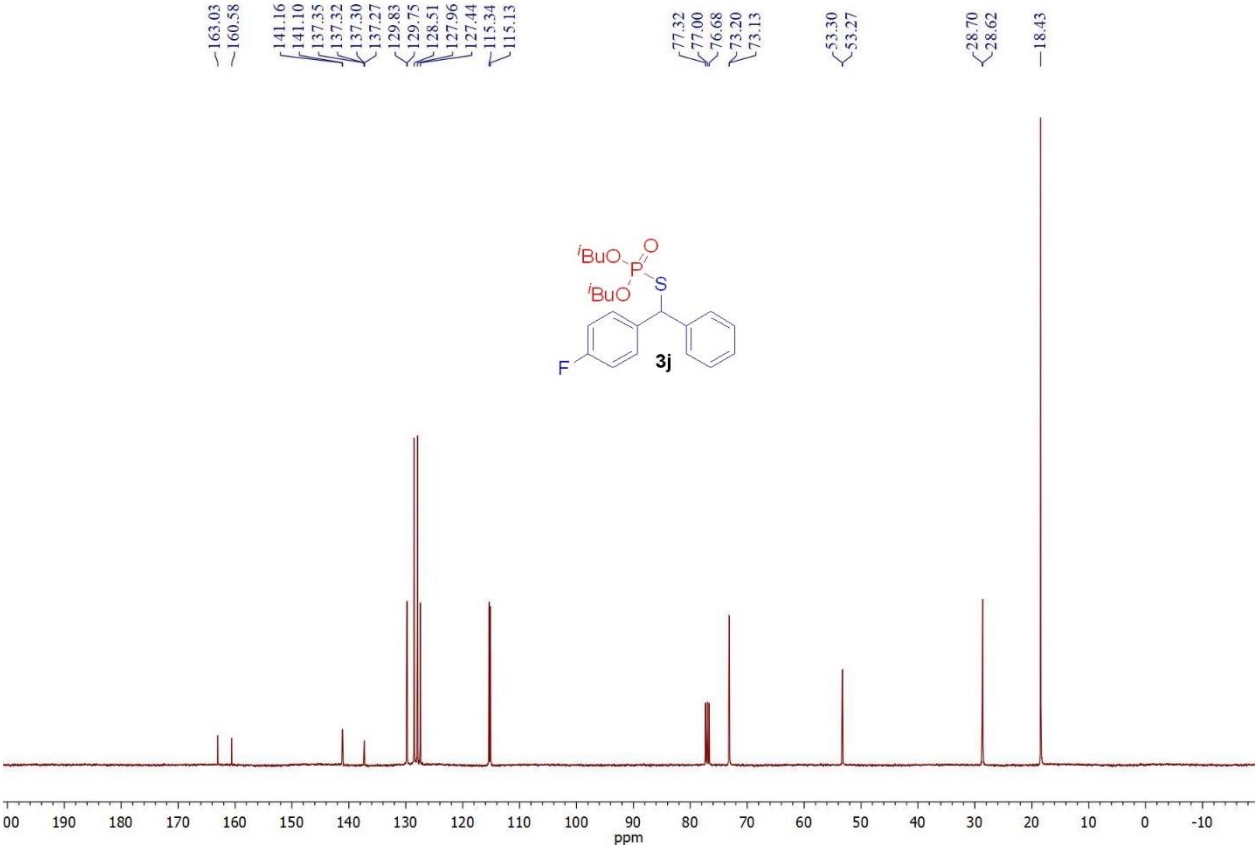
7.301
7.282
7.260
7.246
7.242
7.239
7.229
7.223
7.217
7.206
7.203
7.000
6.979
6.957
5.686
5.657
3.729
3.721
3.712
3.705
3.697
3.688
3.680
3.672
3.664
3.566
3.549
3.542
3.531
3.525
3.507
1.817
1.804
1.800
1.787
1.784
1.770
1.767
1.754
1.750
1.737
1.734
1.720
1.717
0.834
0.828
0.818
0.811


iBuO
iBuO
P
O
S
F
3j
4.10
2.05
0.98
2.02
1.00
2.13
2.12
2.01
12.60
10.5
10.0
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
-0
ppm


163.03
160.58
141.16
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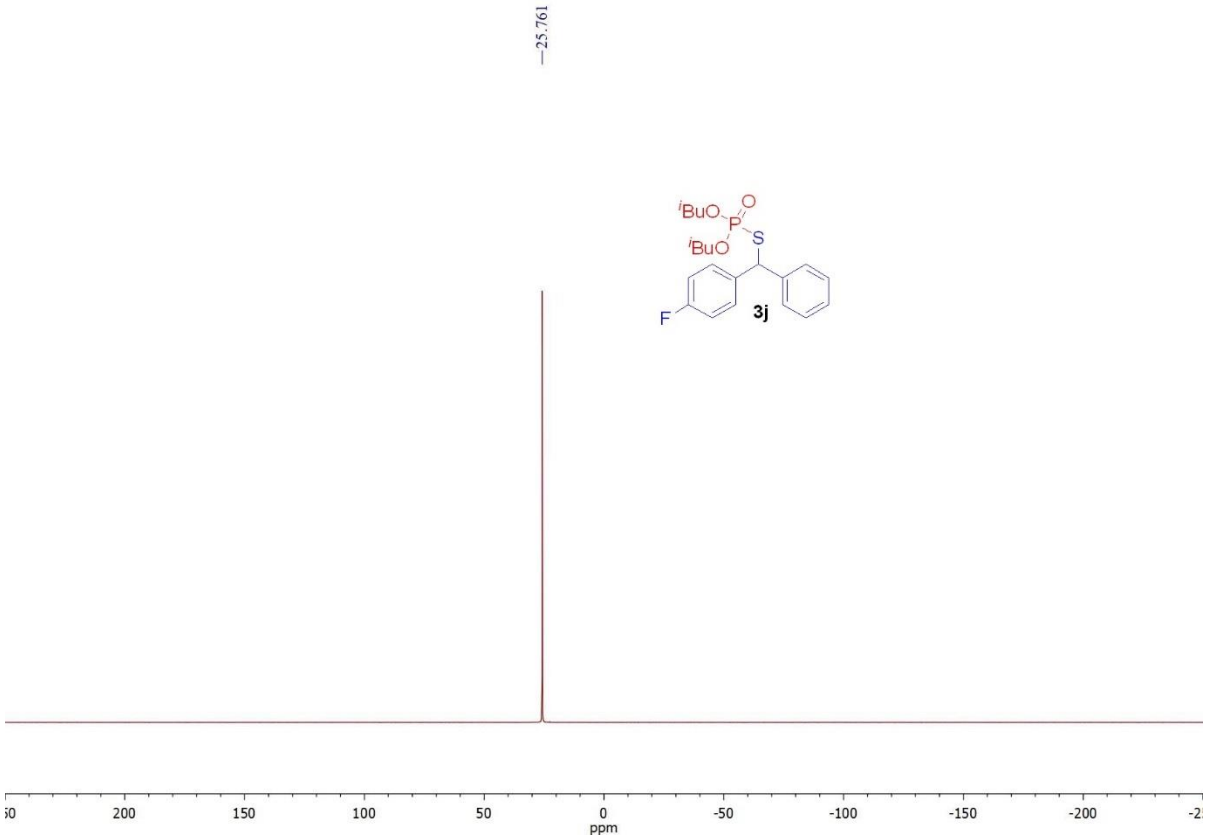
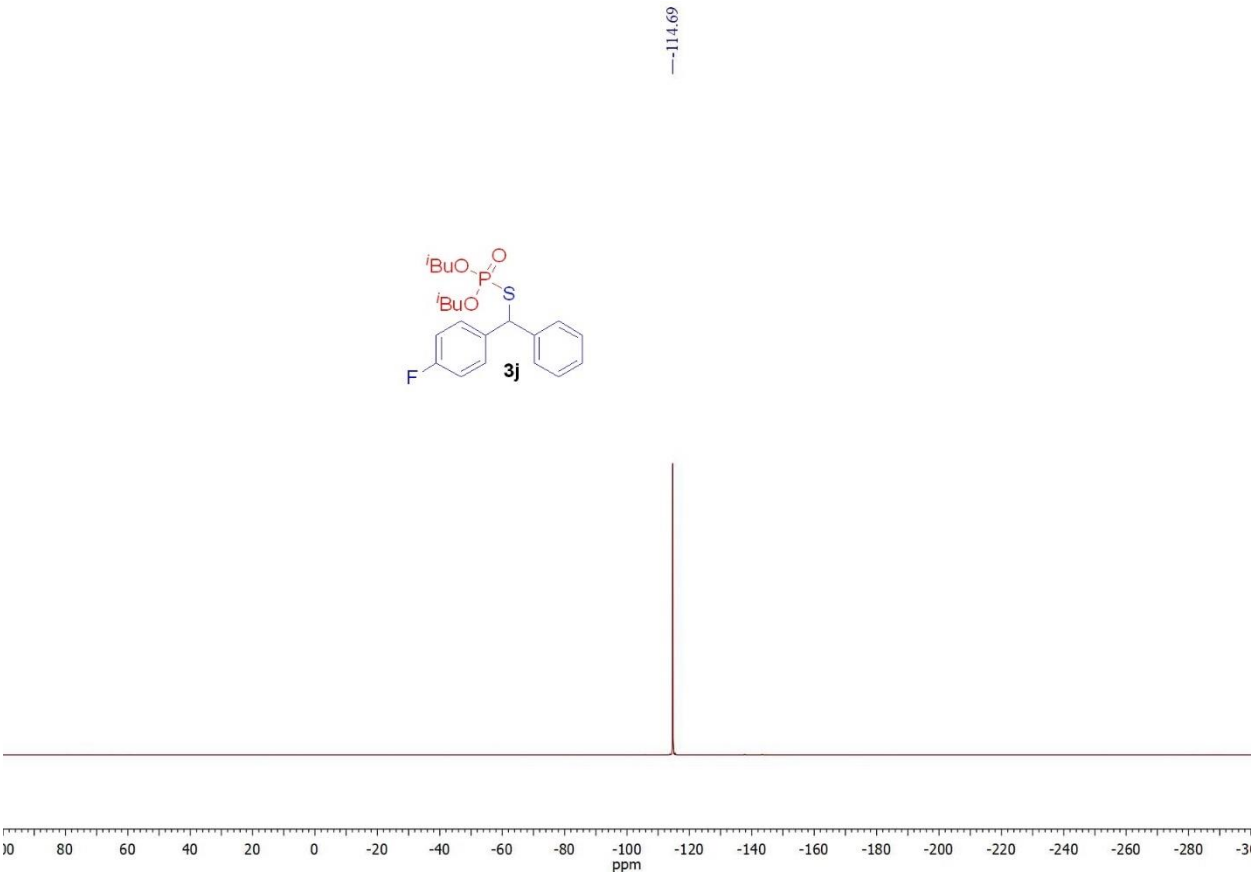
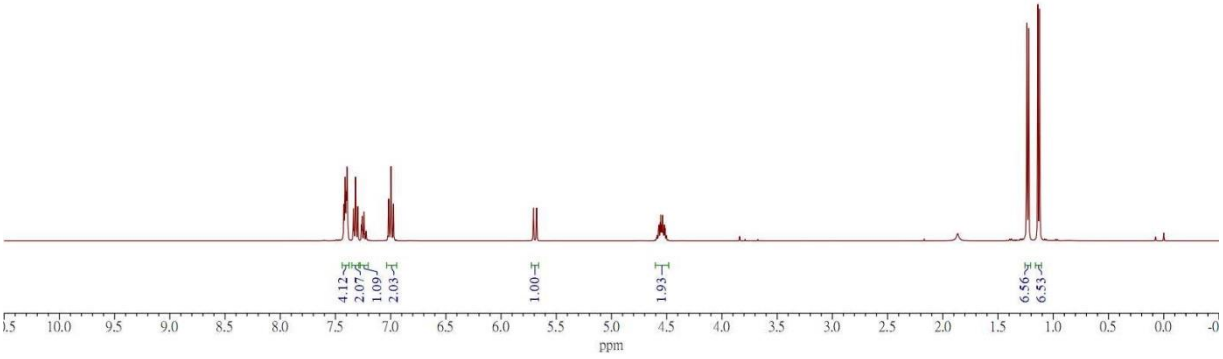
137.35
137.32
137.30
137.27
129.83
129.75
128.51
127.96
127.44
115.34
115.13
77.32
77.00
76.68
73.20
73.13
53.30
53.27
28.70
28.62
18.43
iBuO
iBuO
P
O
S
F
3j
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


25.761
iBuO
iBuO
P
O
S
F
3j
200
150
100
50
0
ppm
-50
-100
-150
-200


-114.69
iBuO
iBuO
P
O
S
F
3j
80
60
40
20
0
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280


7.425
7.418
7.412
7.408
7.402
7.396
7.394
7.389
7.340
7.338
7.335
7.331
7.318
7.314
7.302
7.298
7.265
7.262
7.258
7.255
7.246
7.240
7.222
7.018
6.996
6.975
5.708
5.679
4.591
4.585
4.576
4.570
4.563
4.560
4.554
4.548
4.544
4.538
4.532
4.529
4.523
4.517
4.507
4.501
1.240
1.238
1.225
1.223
1.140
1.125
0.000


iPrO
O
P
iPrO
S
F
3k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1.93
6.56
6.53
ppm


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160.65
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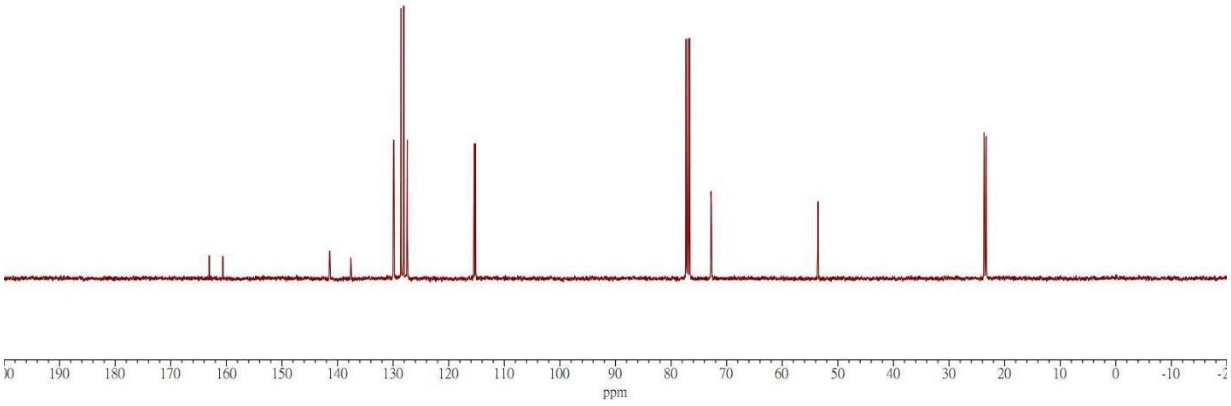
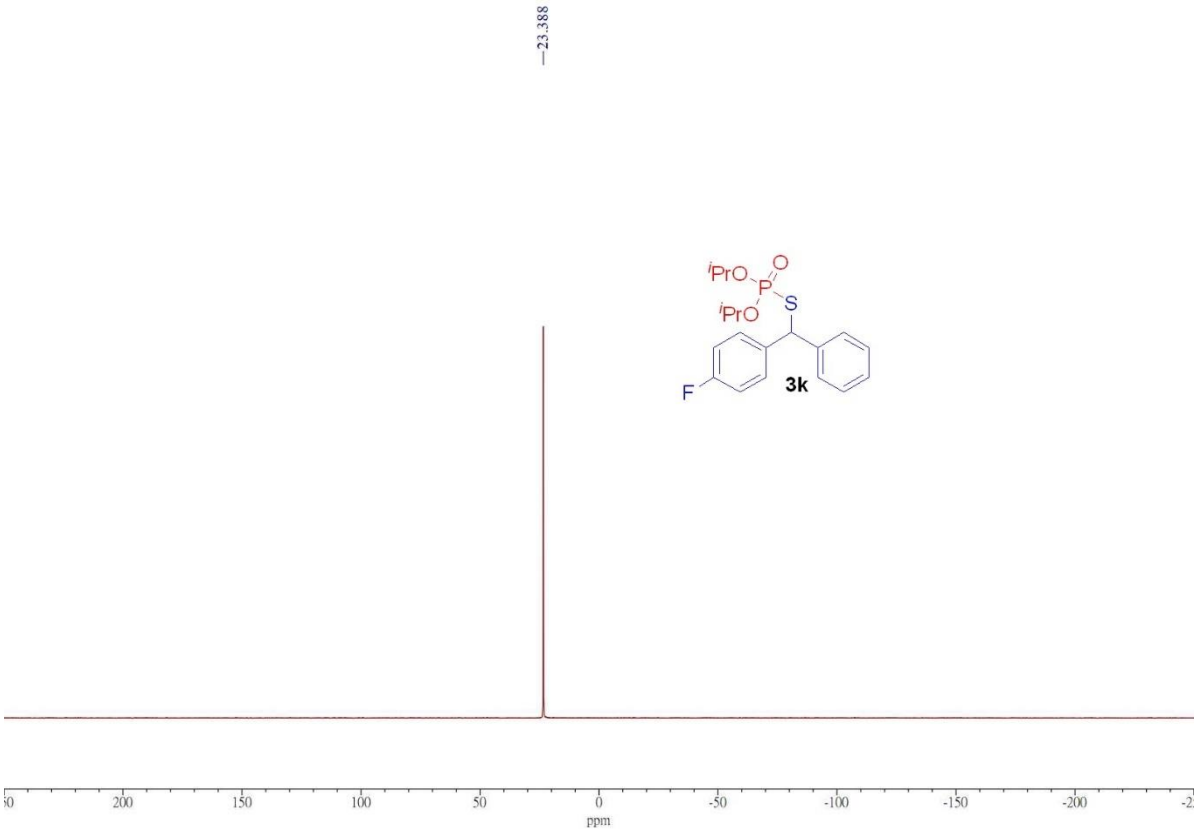
141.38
137.60
137.55
129.94
129.86
128.58
128.08
127.45
115.40
115.19
77.32
77.00
76.68
72.83
72.81
72.77
72.75
53.59
53.56
23.70
23.66
23.36
23.30


iPrO
O
P
iPrO
S
F
3k


ppm


23.388
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P
iPrO
S
F
3k
200
150
100
50
0
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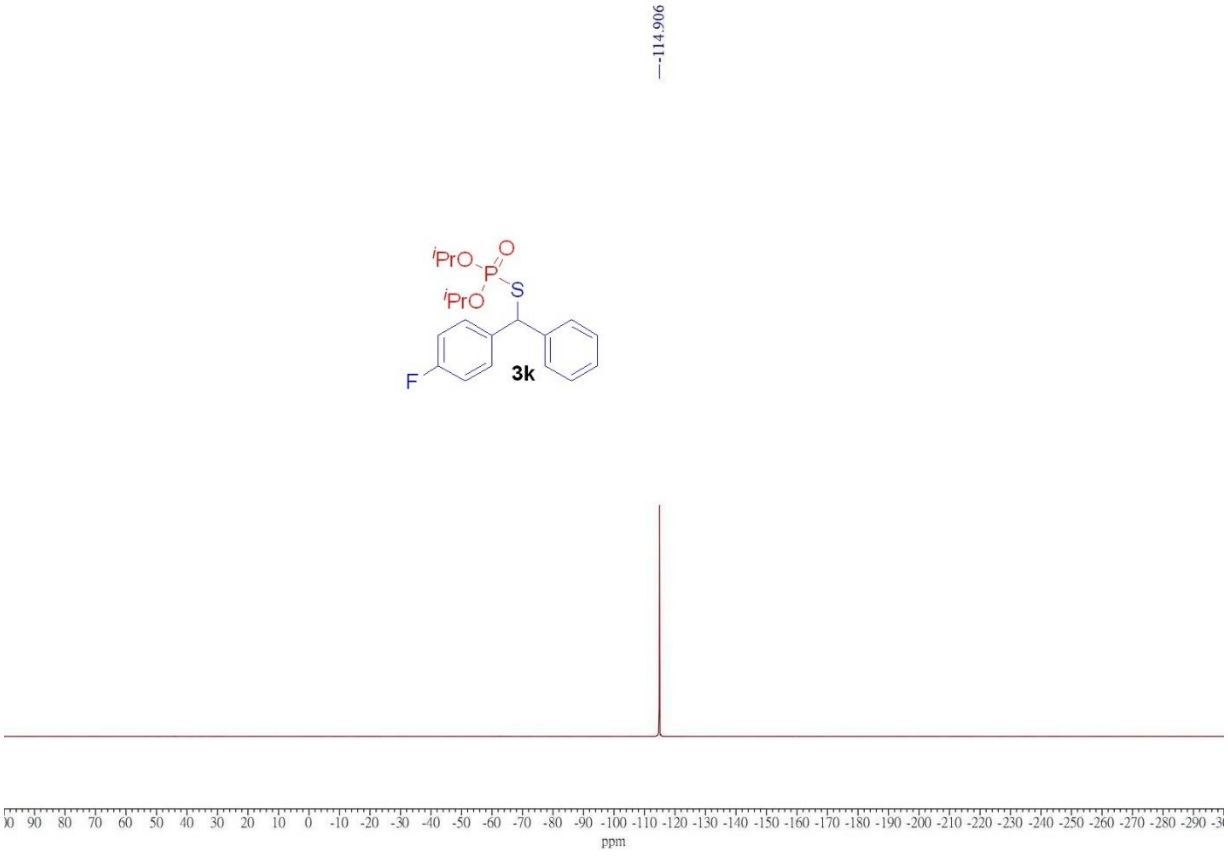
-100
-150
-200
ppm


-114.906
iPrO
O
P
iPrO
S
F
3k
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80
70
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50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
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-280
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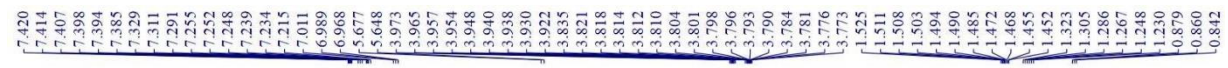
ppm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7.311
7.291
7.255
7.252
7.248
7.239
7.234
7.215
7.011
6.989
6.968
5.677
5.648
3.973
3.965
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3.954
3.948
3.940
3.938
3.930
3.922
3.835
3.821
3.818
3.814
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3.801
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3.796
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3.790
3.784
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3.776
3.773
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1.508
1.503
1.494
1.490
1.485
1.472
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1.248
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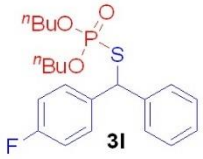
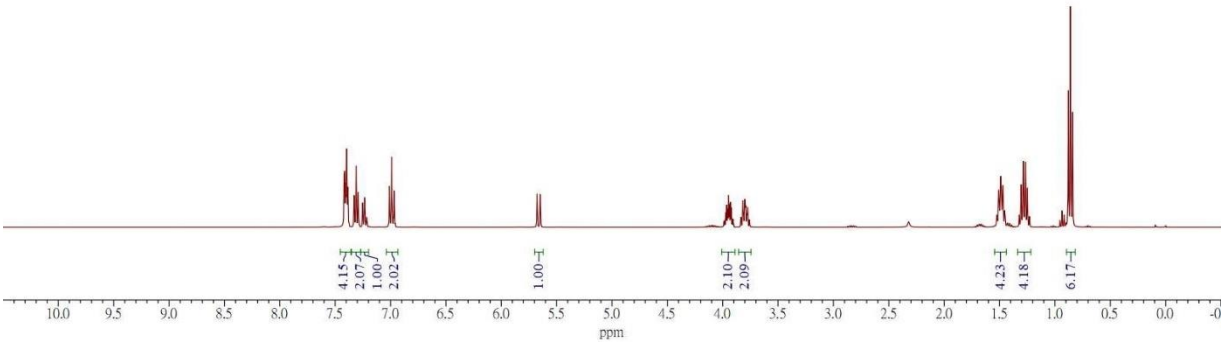
0.842


nBuO
O
P
S
nBuO
F

3l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2.10
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4.23
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6.17
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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
-0
ppm


162.97
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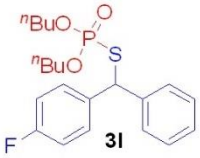
141.06
141.01
137.27
137.24
137.22
129.74
129.66
128.44
127.86
127.37
115.27
115.06
77.32
77.00
76.68
67.09
67.07
67.02
67.00
53.25
53.22
31.77
31.70
18.38
13.31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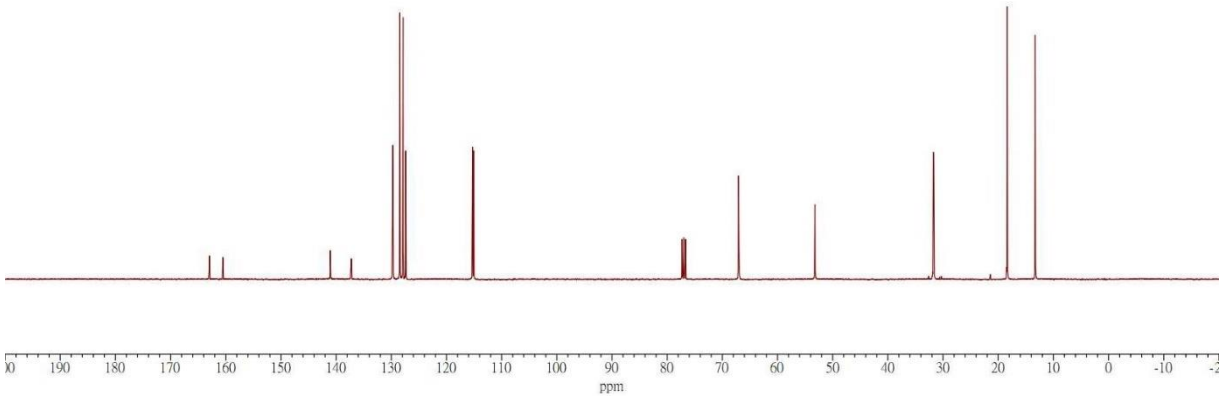
O
P
S
nBuO
F

3l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130
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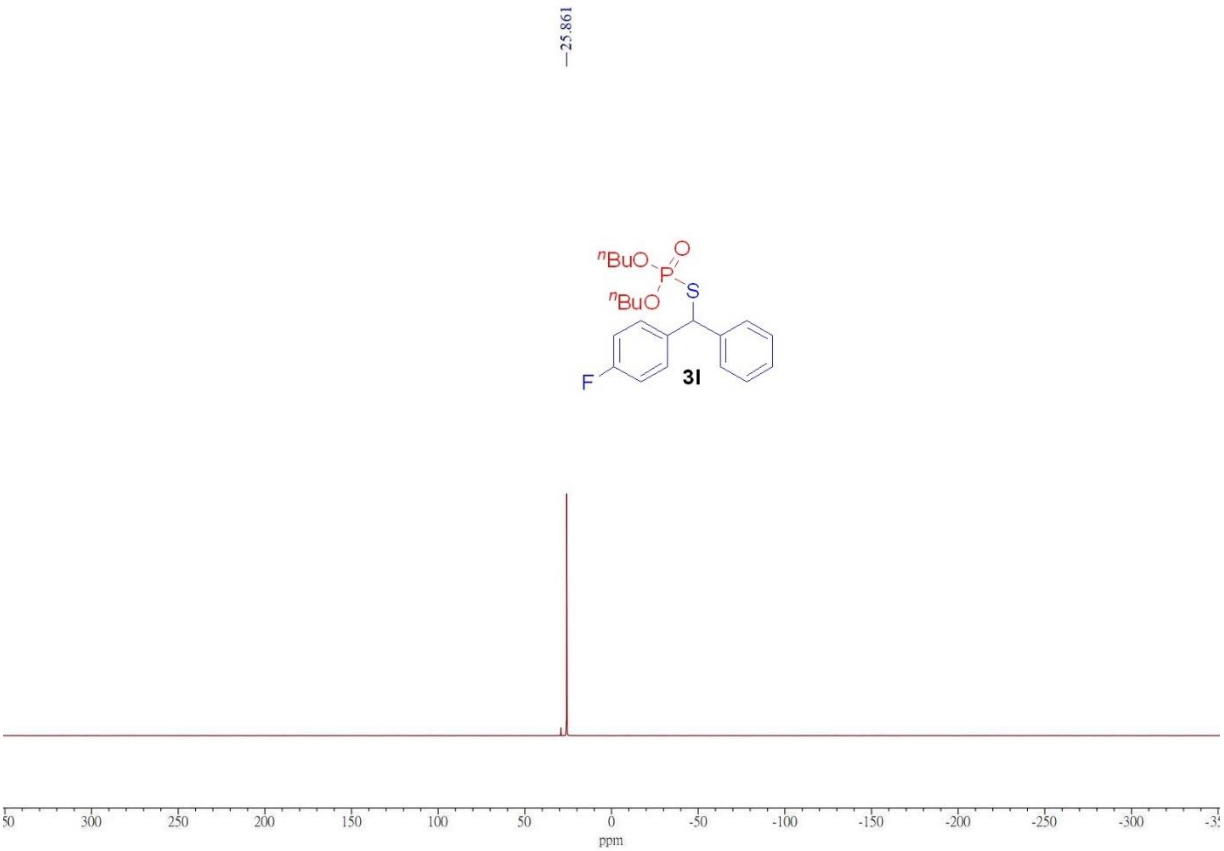
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


-25.861
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O
P
nBuO
S
F
3l
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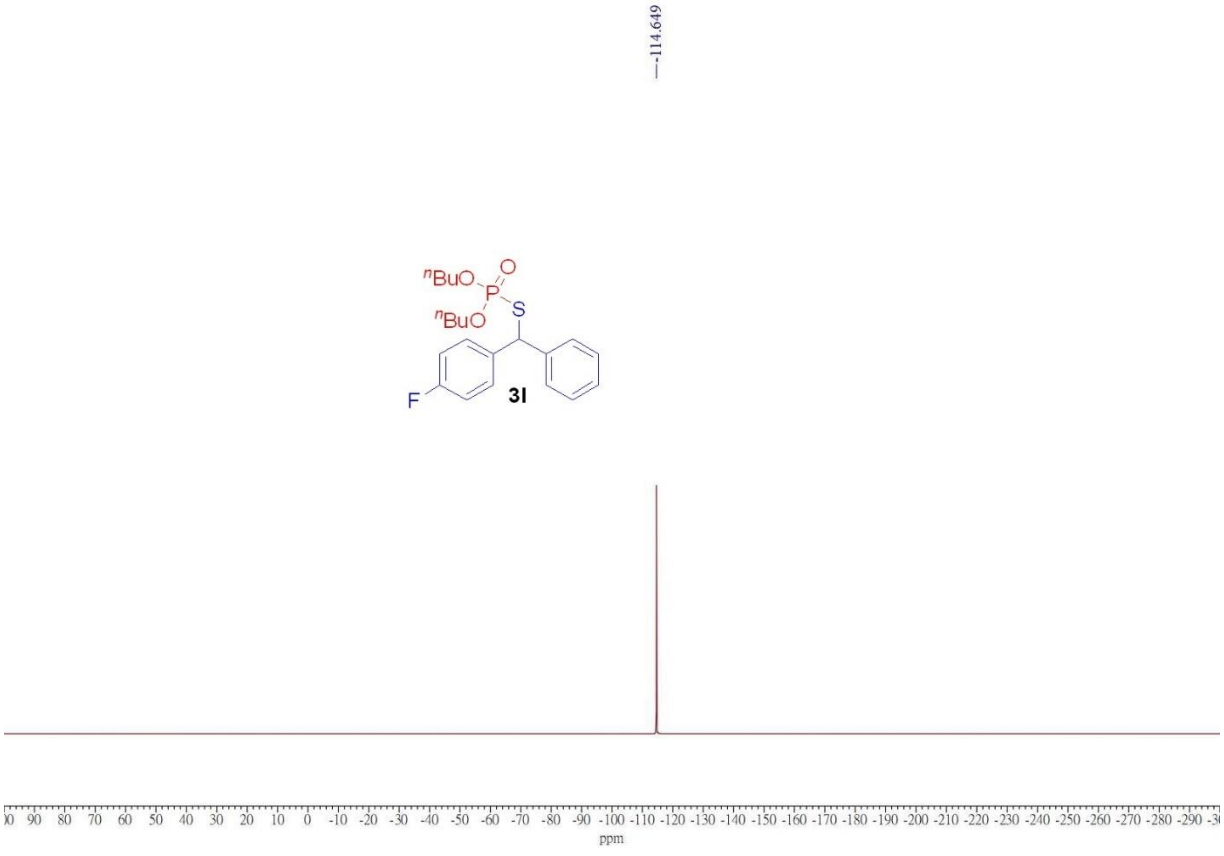
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
ppm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50
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0
-10
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-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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-270
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-290
ppm


7.404
7.400
7.394
7.382
7.379
7.374
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7.356
7.345
7.343
7.325
7.321
7.305
7.299
7.294
7.282
7.277
7.273
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7.255
7.249
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5.604
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4.051
4.046
4.036
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3.850
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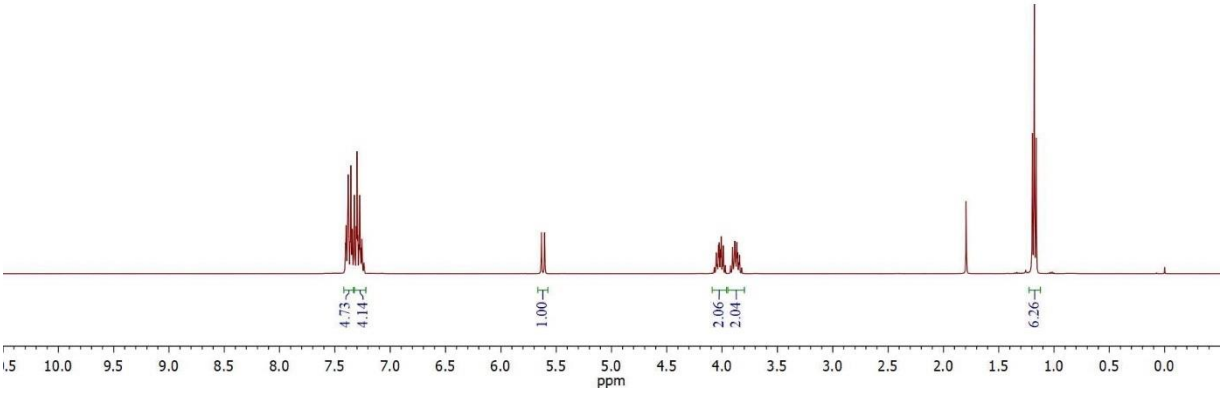
1.196
1.181
1.178
1.163


EtO
O
P
EtO
S
Cl
3m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8.5
8.0
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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


141.04
140.98
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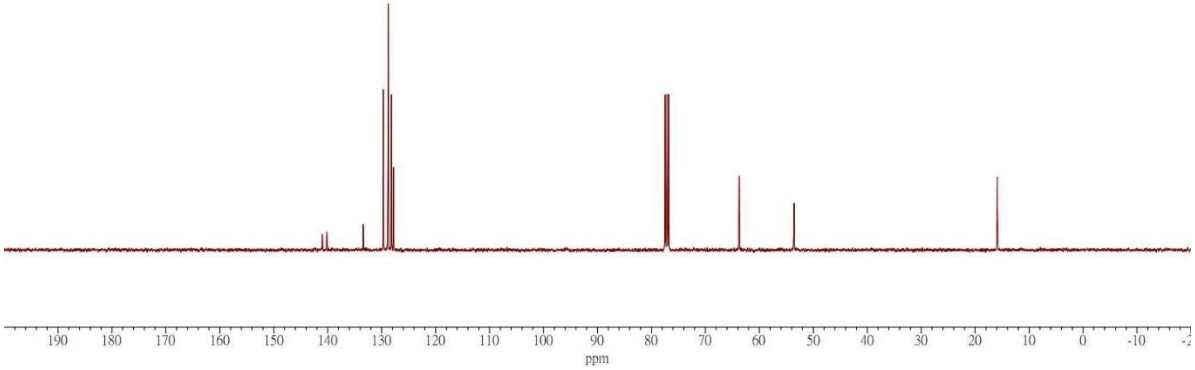
140.15
133.44
129.70
128.80
128.18
127.80
77.46
77.15
76.83
63.75
63.69
53.60
53.57
15.96
15.89


EtO
O
P
EtO
S
Cl
3m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100
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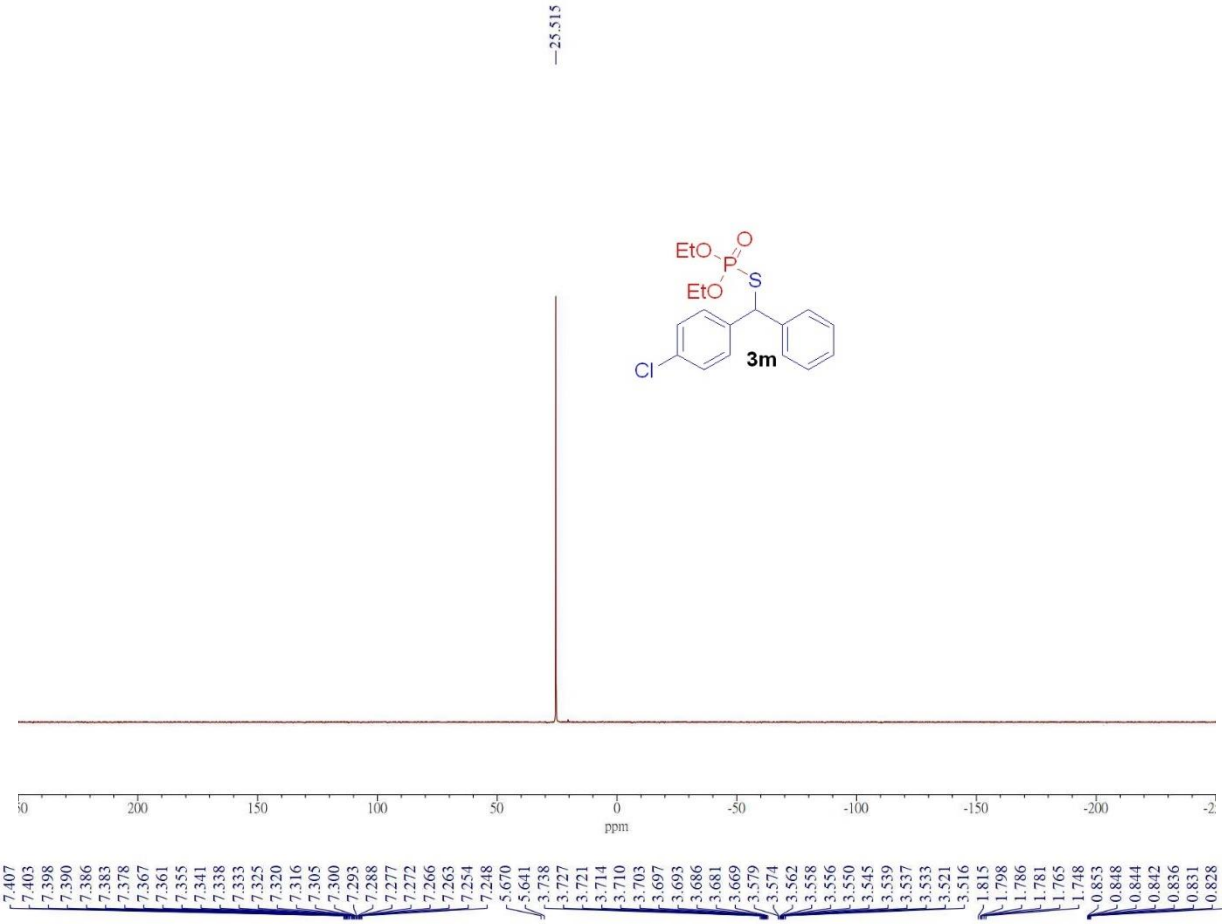
80
70
60
50
40
30
20
10
0
-10
ppm


25.515
EtO
O
P
EtO
S
Cl
3m
ppm
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7.361
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7.341
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7.333
7.325
7.320
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7.305
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1.815
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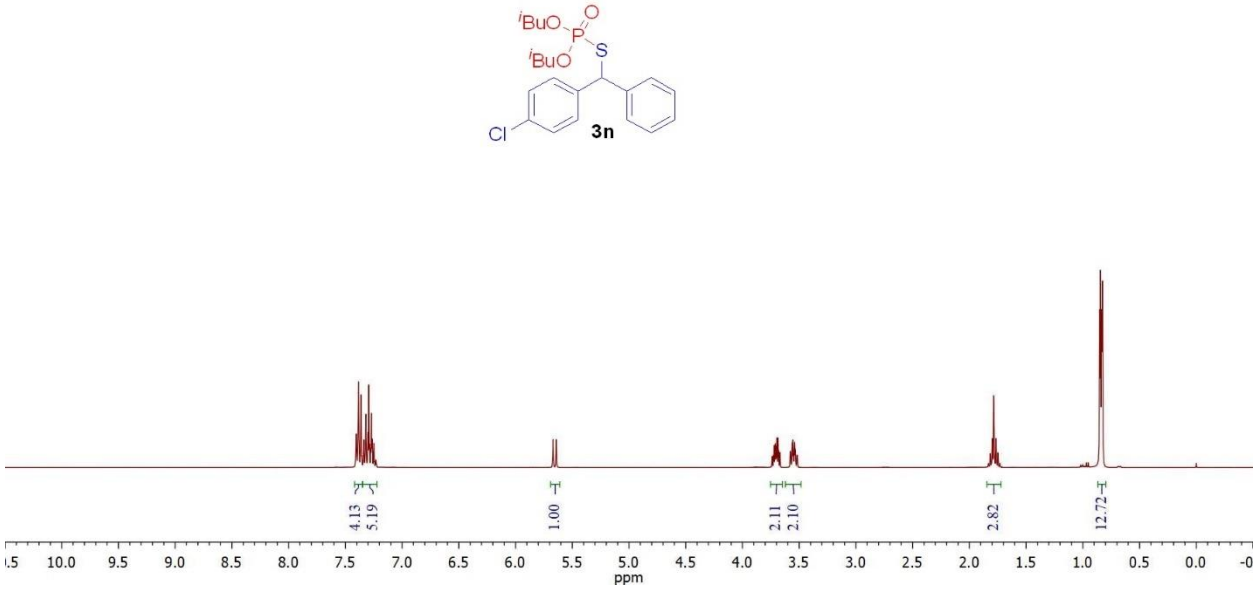
0.825


iBuO
O
P
iBuO
S
Cl
3n
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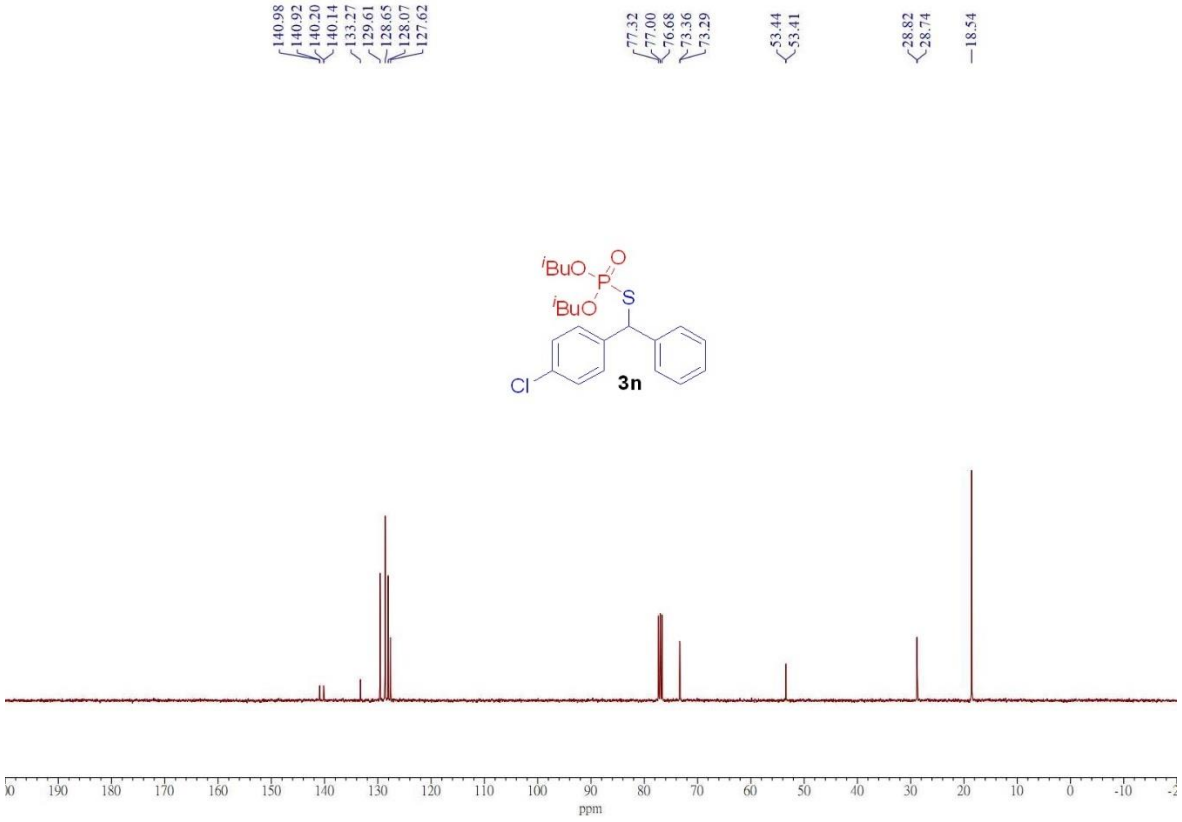
2.82
12.72
ppm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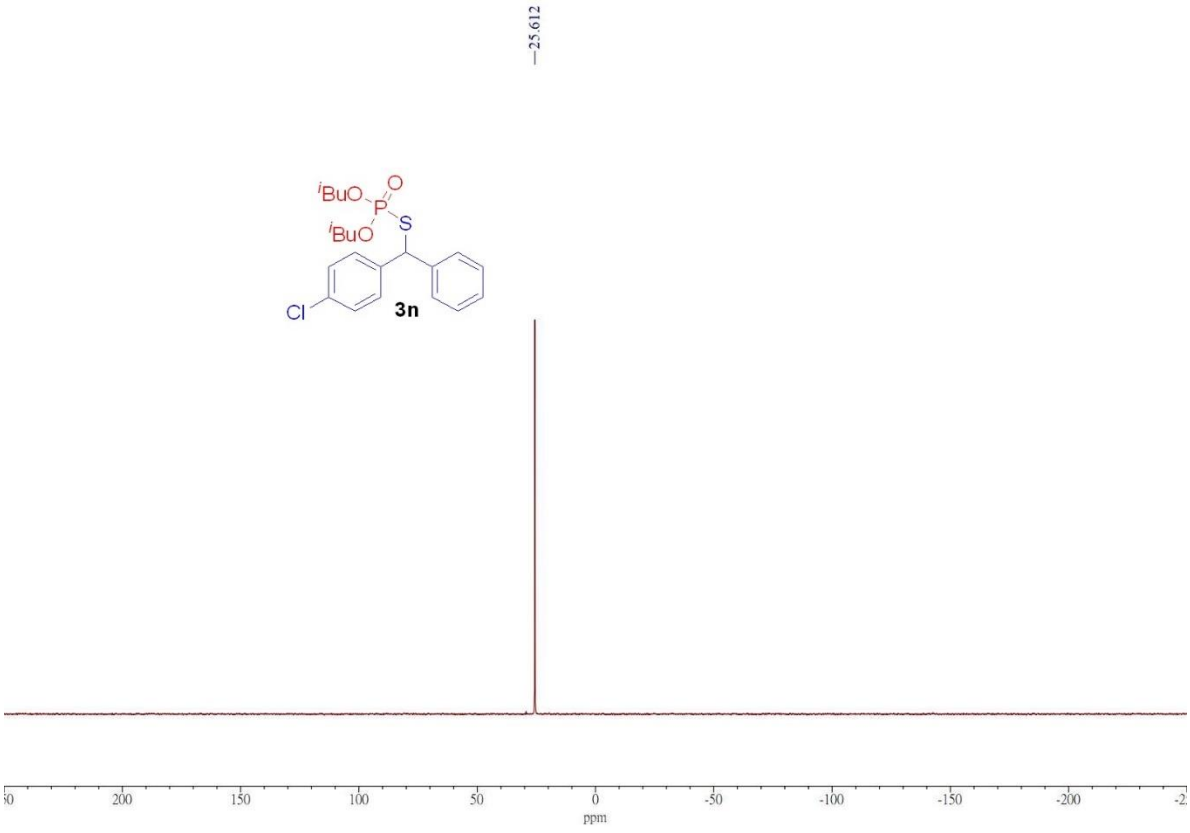
128.07
127.62
77.32
77.00
76.68
73.36
73.29
53.44
53.41
28.82
28.74
18.54
iBuO
iBuO
O
P
S
Cl
3n
ppm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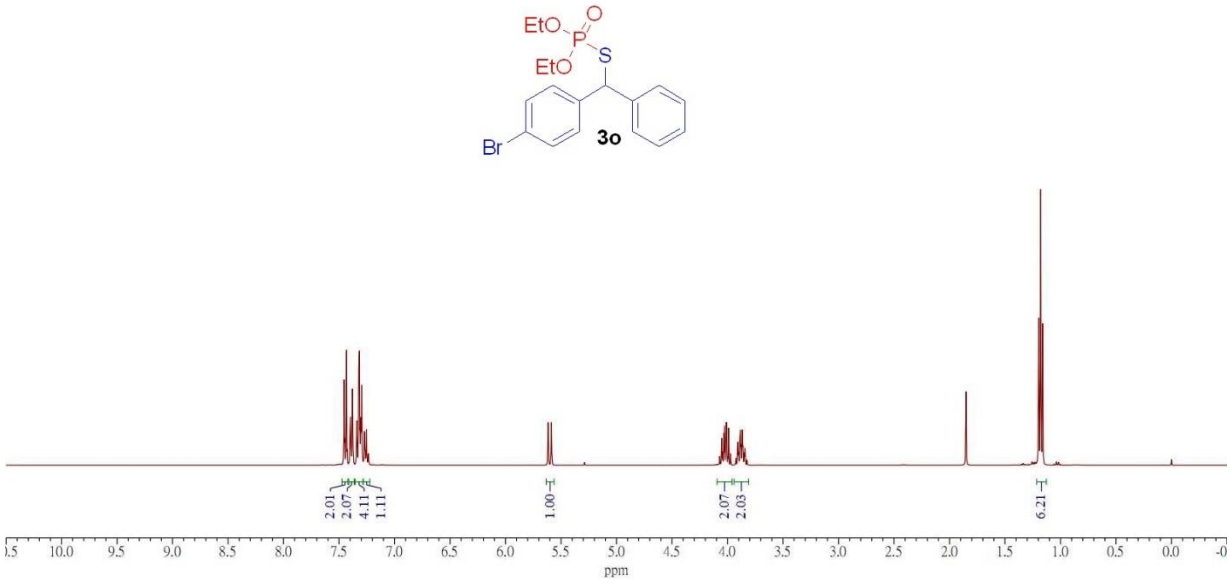
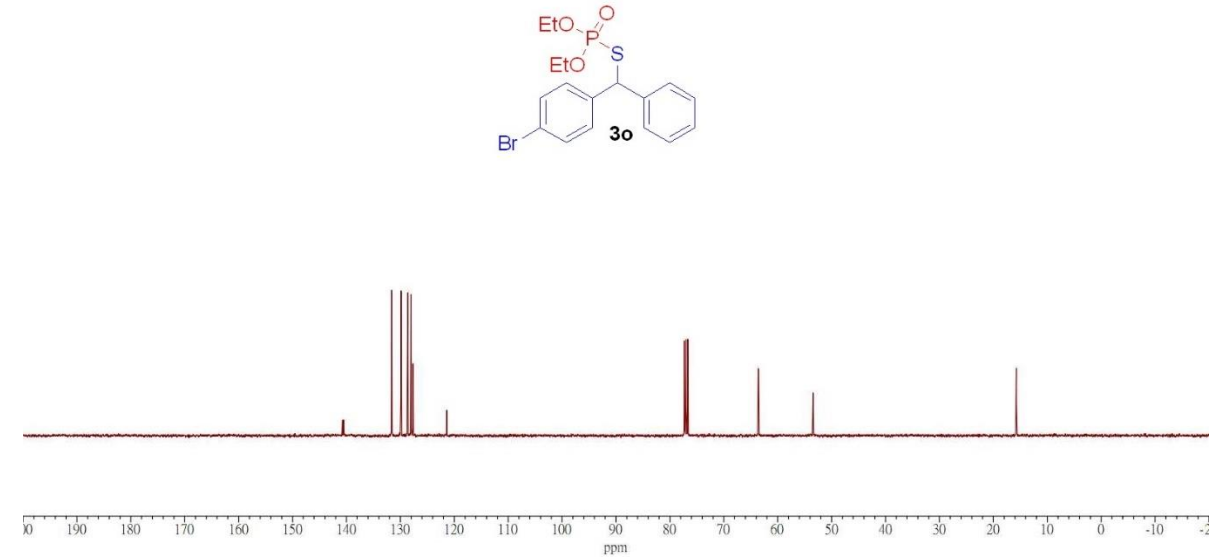
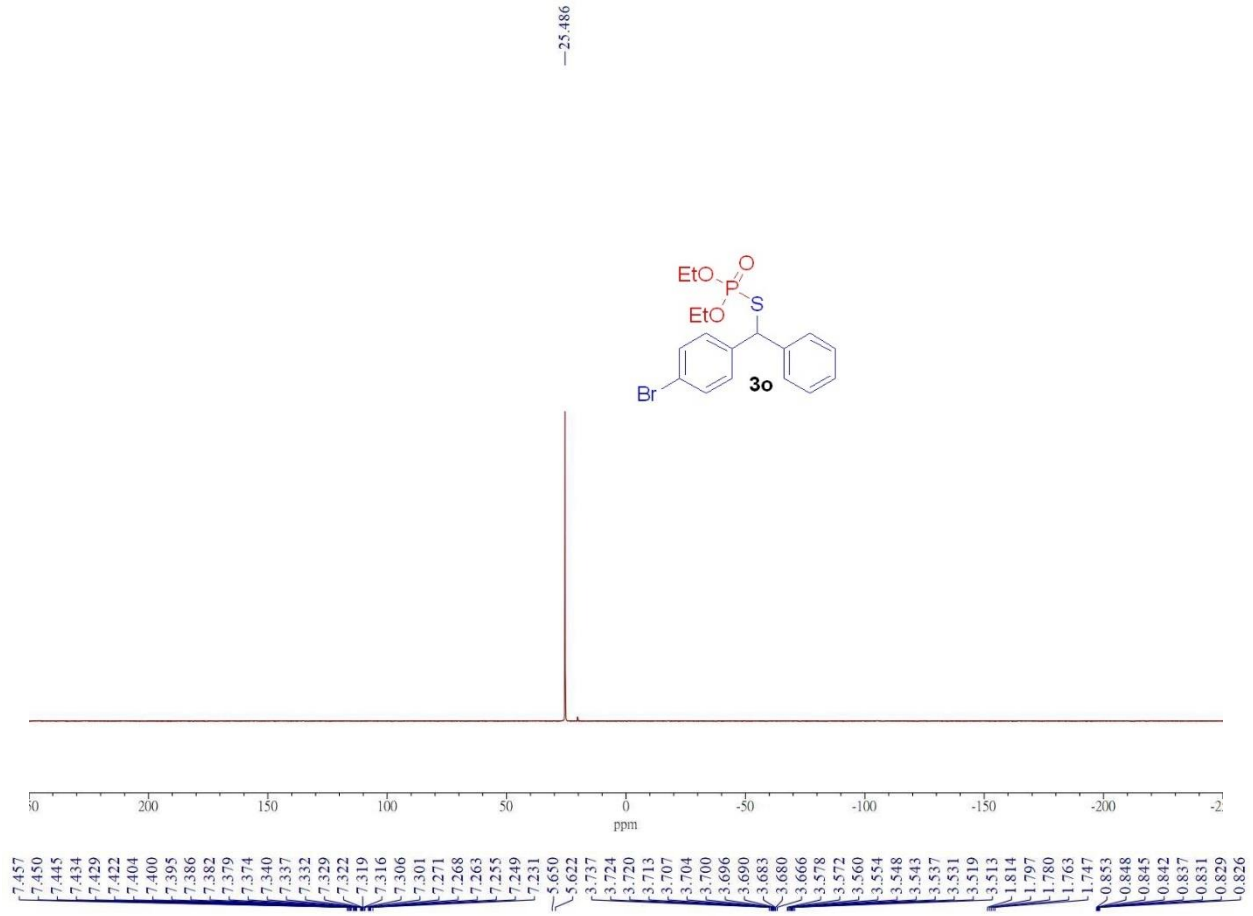
iBuO
iBuO
O
P
S
Cl
3n
ppm


EtO
EtO
O
P
S
Br
3o
2.01
2.07
4.11
1.11
1.00
2.07
2.03
6.21
ppm


EtO
EtO
O
P
S
Br
3o
ppm


25.486
EtO
O
P
S
EtO
Br
3o
ppm
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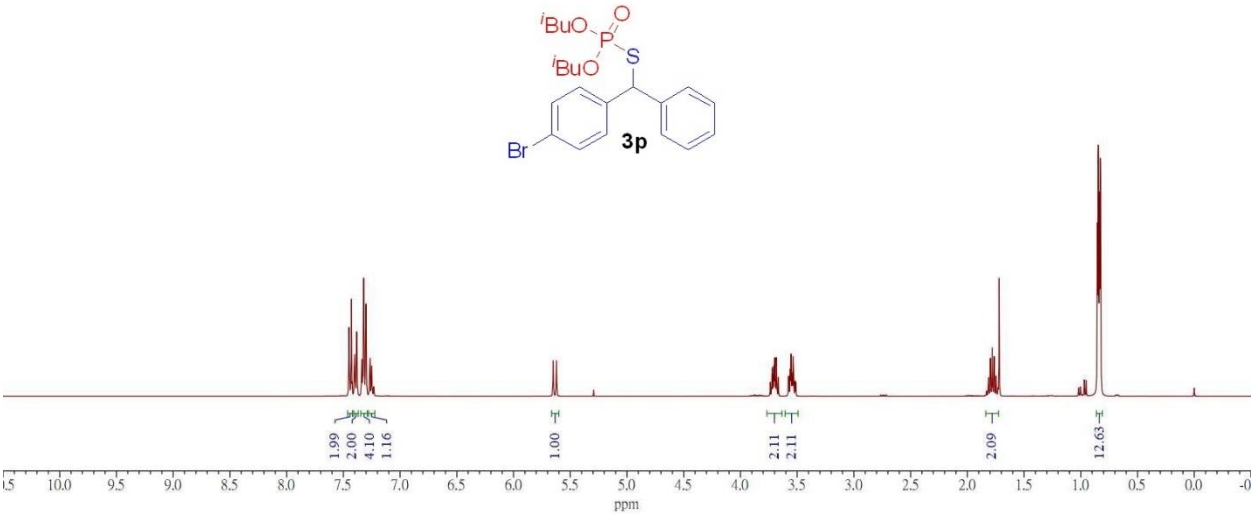
7.450
7.445
7.434
7.429
7.422
7.404
7.400
7.395
7.386
7.382
7.379
7.374
7.340
7.337
7.332
7.329
7.322
7.319
7.316
7.306
7.301
7.271
7.268
7.263
7.255
7.249
7.231
5.650
5.622
3.737
3.724
3.720
3.713
3.707
3.704
3.700
3.696
3.690
3.683
3.680
3.666
3.578
3.572
3.560
3.554
3.548
3.543
3.537
3.531
3.519
3.513
1.814
1.797
1.780
1.763
1.747
0.853
0.848
0.845
0.842
0.837
0.831
0.829
0.826


iBuO
O
P
S
iBuO
Br
3p
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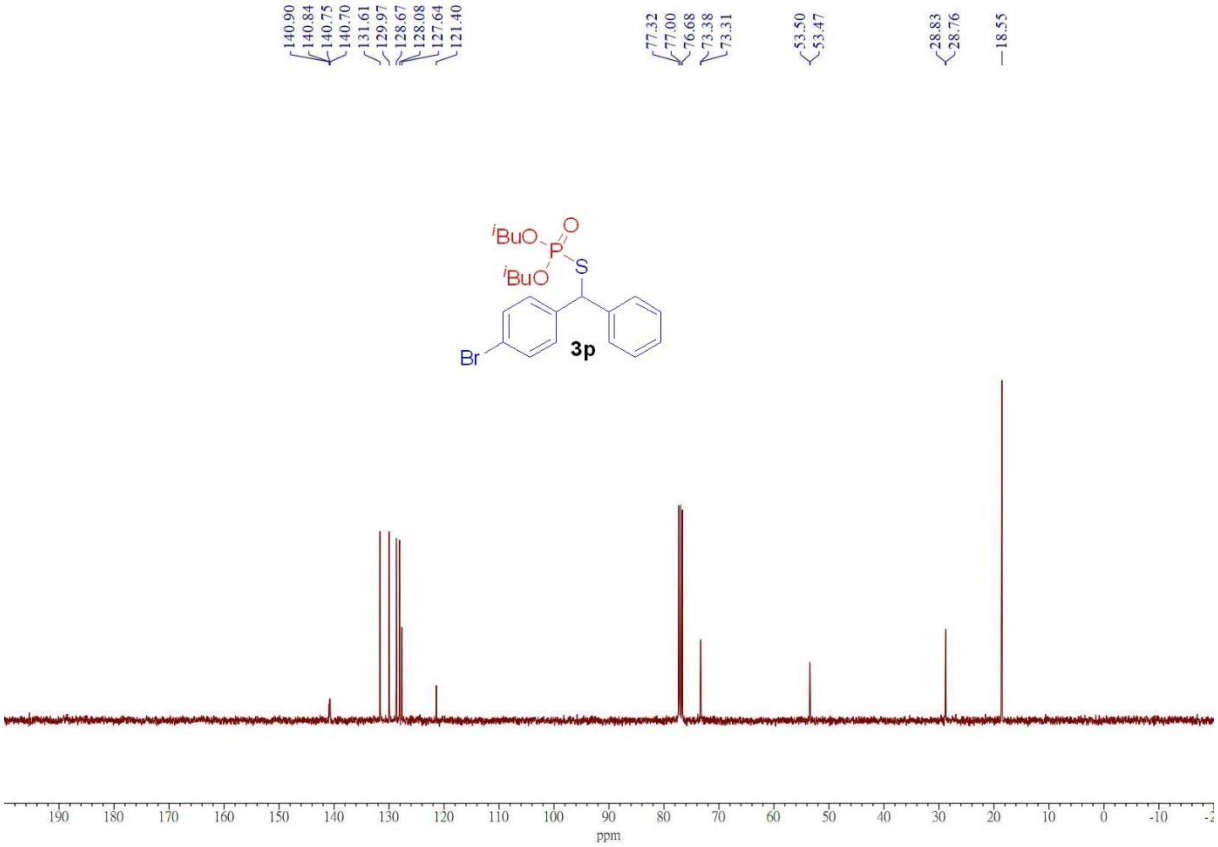
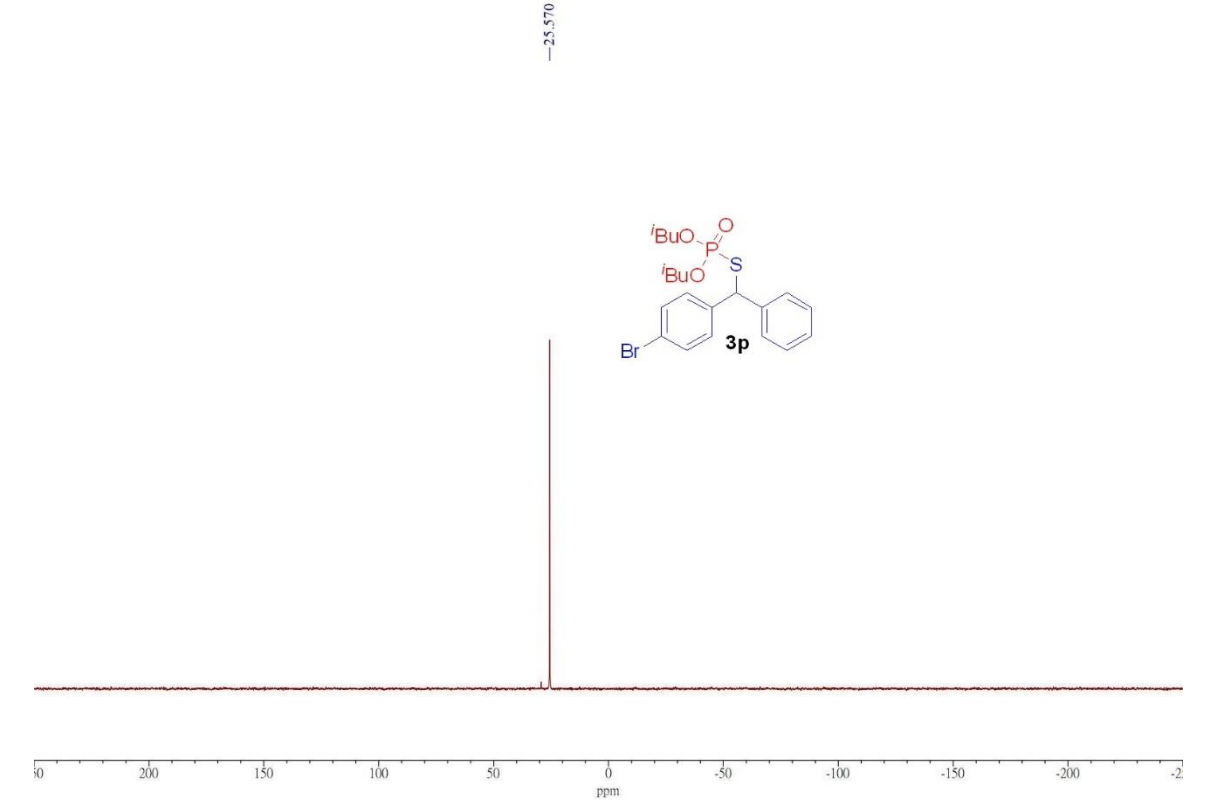
4.10
1.16
1.00
2.11
2.11
2.09
12.63
ppm


140.90
140.84
140.75
140.70
131.61
129.97
128.67
128.08
127.64
121.40
77.32
77.00
76.68
73.38
73.31
53.50
53.47
28.83
28.76
18.55
iBuO
iBuO
P
O
S
Br
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm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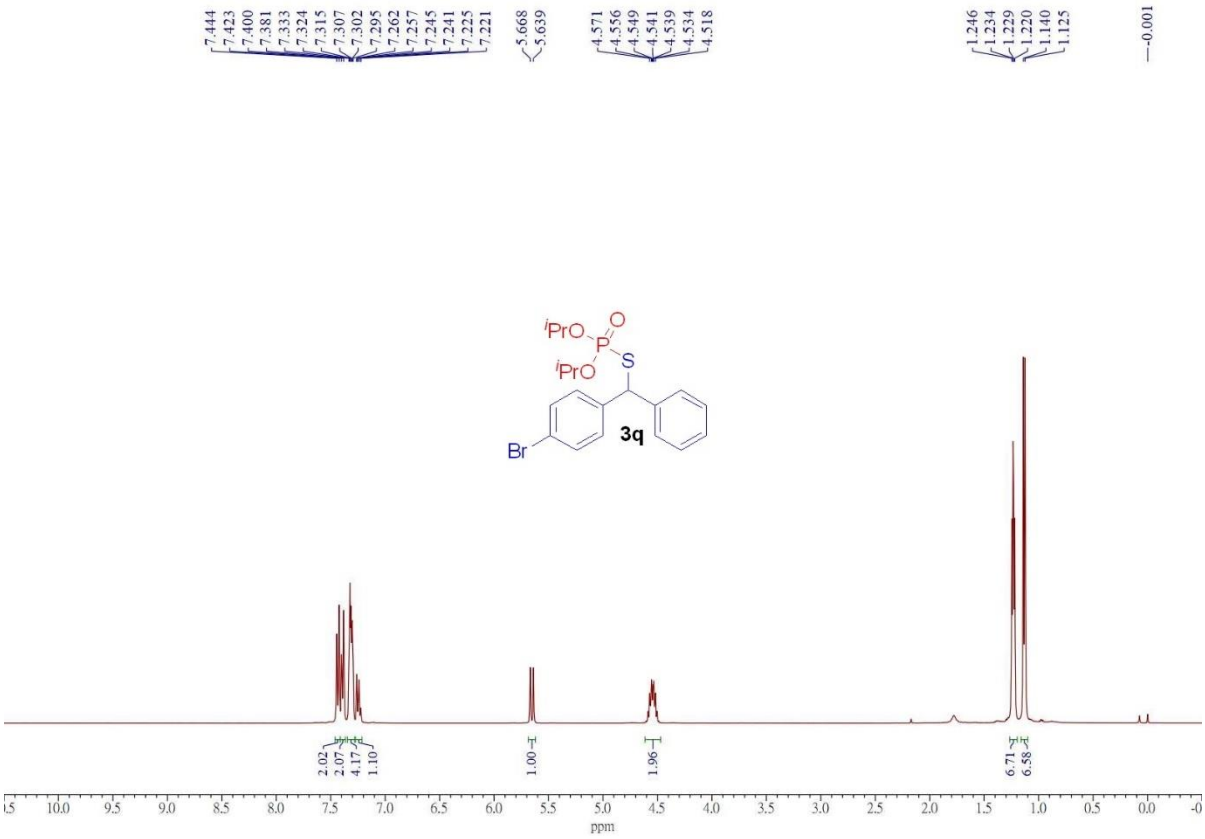
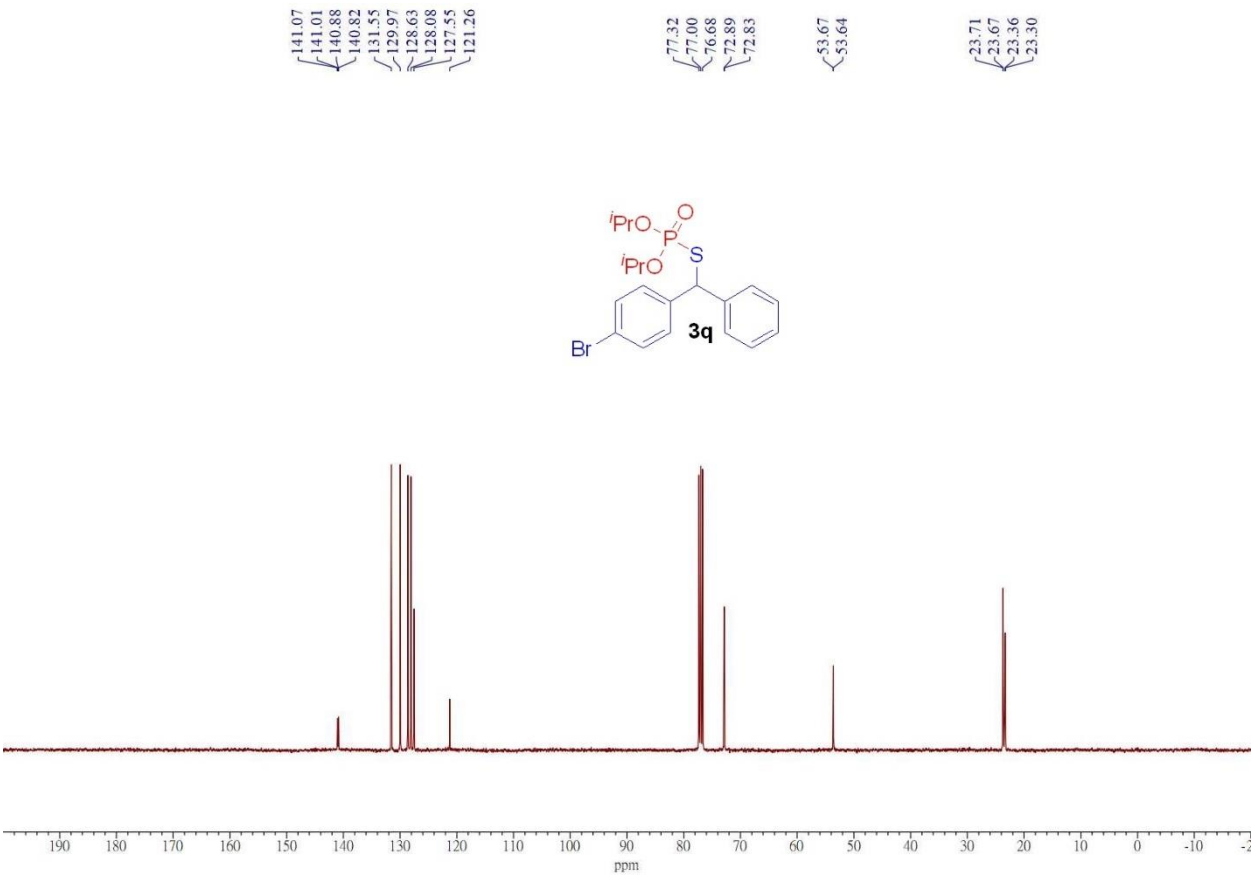
iBuO
iBuO
P
O
S
Br
3p
200 150 100 50 0 -50 -100 -150 -200
ppm


7.444
7.423
7.400
7.381
7.333
7.324
7.315
7.307
7.302
7.295
7.262
7.257
7.245
7.241
7.225
7.221
5.668
5.639
4.571
4.556
4.549
4.541
4.539
4.534
4.518
1.246
1.234
1.229
1.220
1.140
1.125
-0.001
iPrO
O
P
iPrO
S
Br
3q
2.02
2.07
4.17
1.10
1.00
1.96
6.71
6.58
ppm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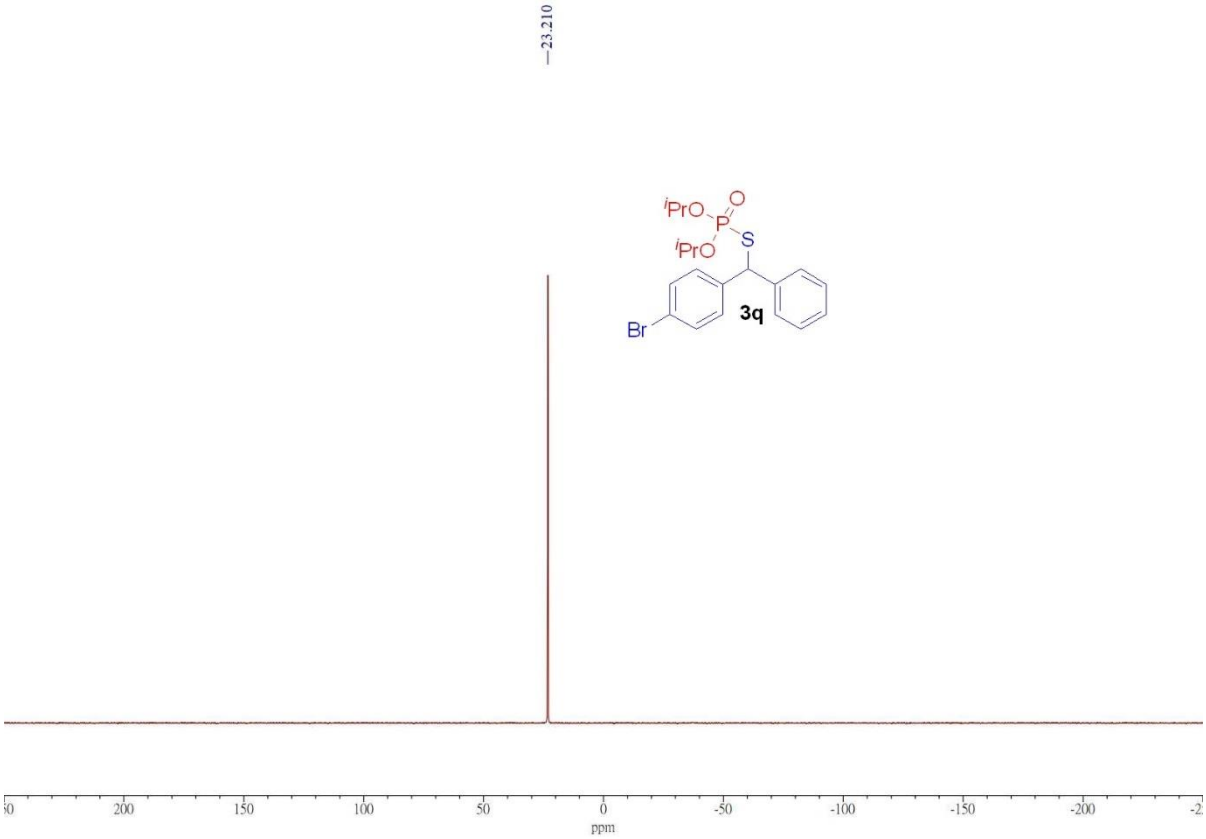
141.01
140.88
140.82
131.55
129.97
128.63
128.08
127.55
121.26
77.32
77.00
76.68
72.89
72.83
53.67
53.64
23.71
23.67
23.36
23.30
iPrO
O
P
iPrO
S
Br
3q
ppm


23.210
iPrO
iPrO
P
O
S
Br
3q
ppm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7.435
7.430
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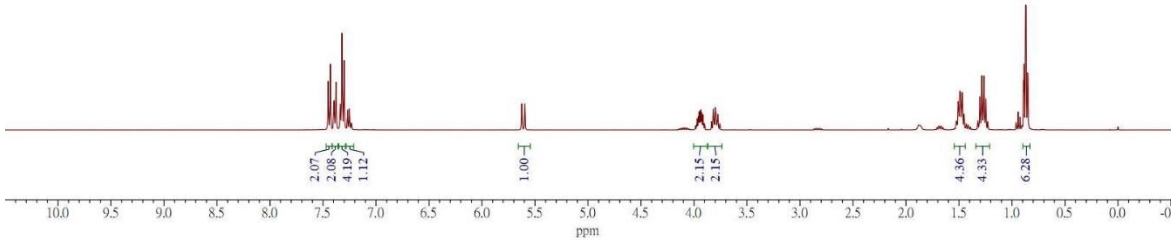
7.395
7.382
7.378
7.375
7.340
7.337
7.328
7.321
7.316
7.305
7.300
7.269
7.266
7.250
5.624
5.596
3.969
3.962
3.959
3.951
3.945
3.941
3.934
3.927
3.917
3.819
3.816
3.813
3.809
3.802
3.799
3.797
3.794
3.792
3.788
3.782
3.780
3.775
3.772
1.526
1.509
1.503
1.492
1.486
1.475
1.470
1.467
1.454
1.450
1.322
1.303
1.284
1.265
1.247
0.891
0.885
0.872
0.867
0.854
0.849


nBuO
nBuO
P
O
S
Br
3r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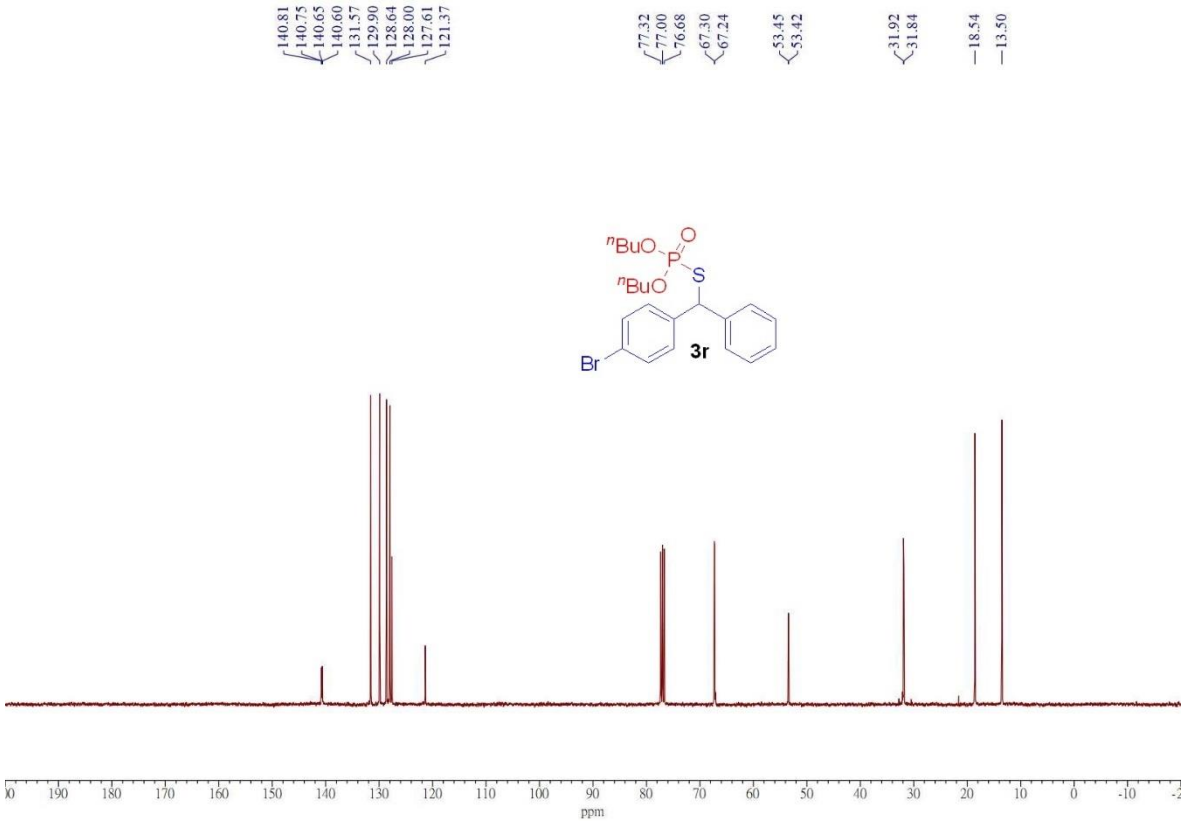
2.08
4.19
1.12
1.00
2.15
2.15
4.36
4.33
6.28
ppm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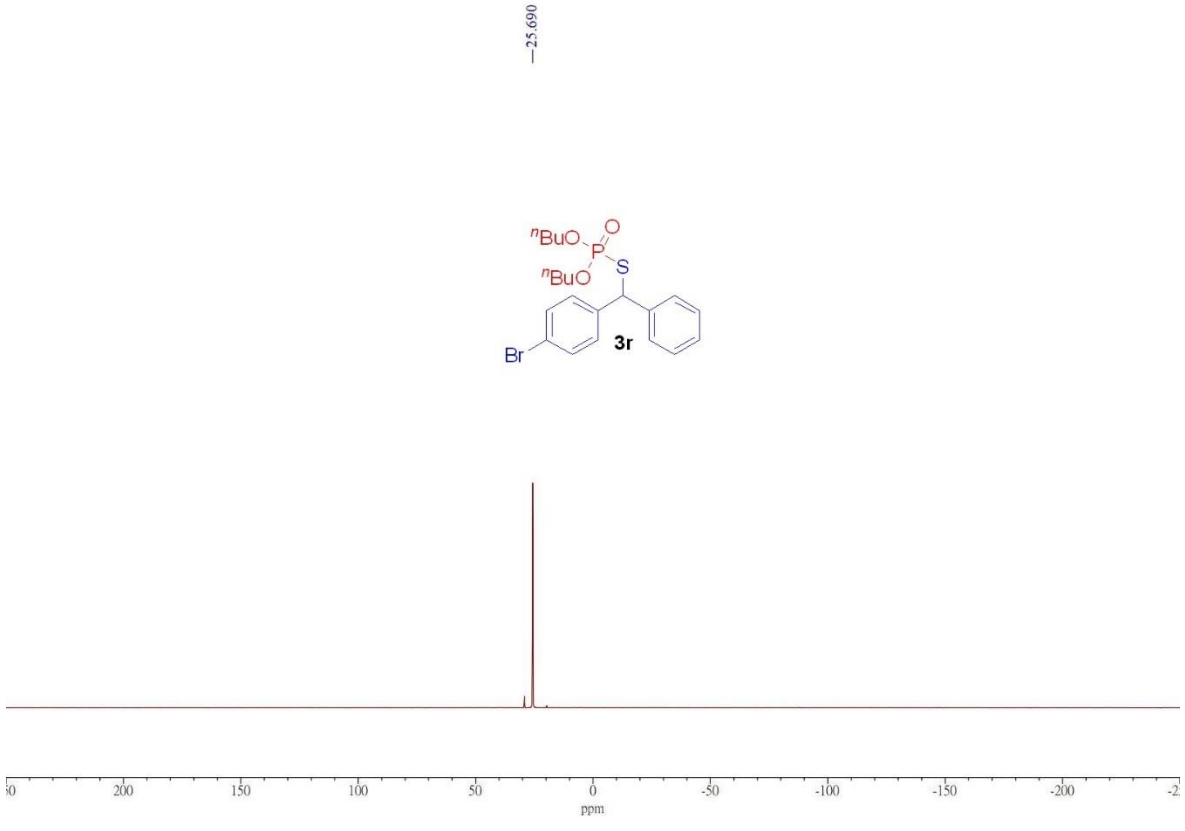
140.75
140.65
140.60
131.57
129.90
128.64
128.00
127.61
121.37
77.32
77.00
76.68
67.30
67.24
53.45
53.42
31.92
31.84
18.54
13.50
nBuO
nBuO
P
O
S
Br
3r
ppm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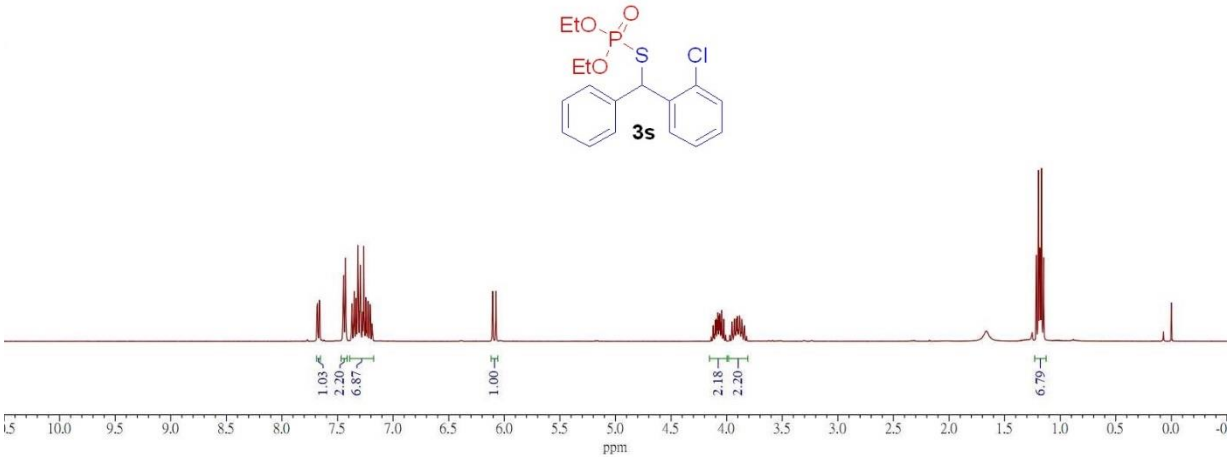
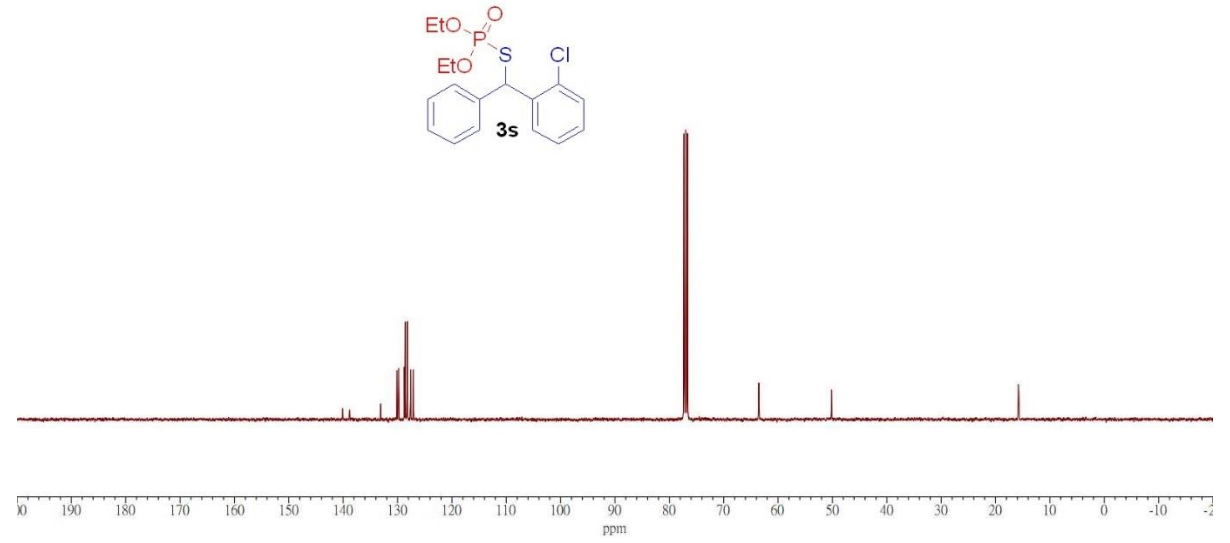
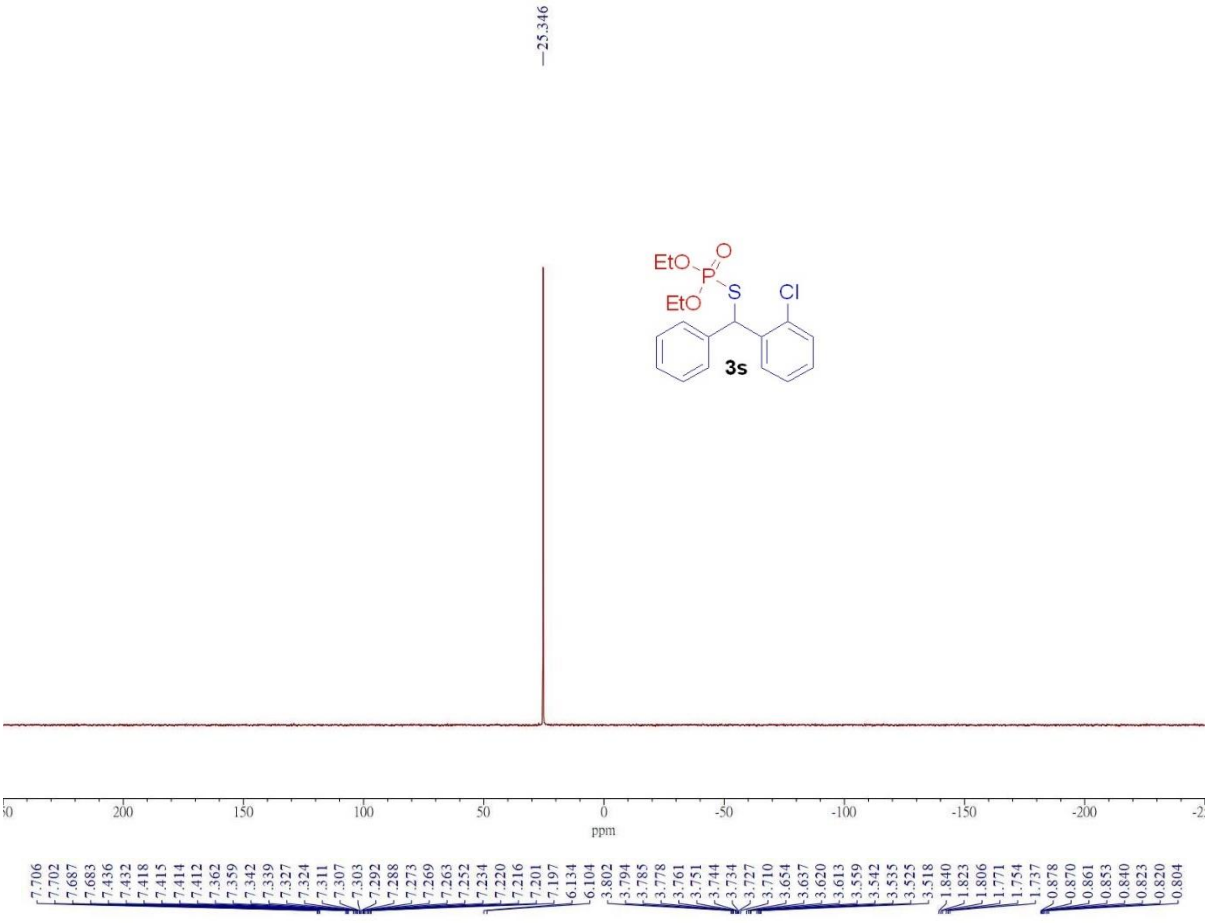
nBuO
nBuO
P
O
S
Br
3r
ppm


EtO
O
P
S
Cl
EtO
3s
1.03
2.20
6.87
1.00
2.18
2.20
6.79
ppm


EtO
O
P
S
Cl
EtO
3s
ppm


25.346
EtO
EtO
O
P
S
Cl
3s
ppm
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7.702
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7.683
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7.418
7.415
7.414
7.412
7.362
7.359
7.342
7.339
7.327
7.324
7.311
7.307
7.303
7.292
7.288
7.273
7.269
7.263
7.252
7.234
7.220
7.216
7.201
7.197
6.134
6.104
3.802
3.794
3.785
3.778
3.761
3.751
3.744
3.734
3.727
3.710
3.654
3.637
3.620
3.613
3.559
3.542
3.535
3.525
3.518
1.840
1.823
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1.737
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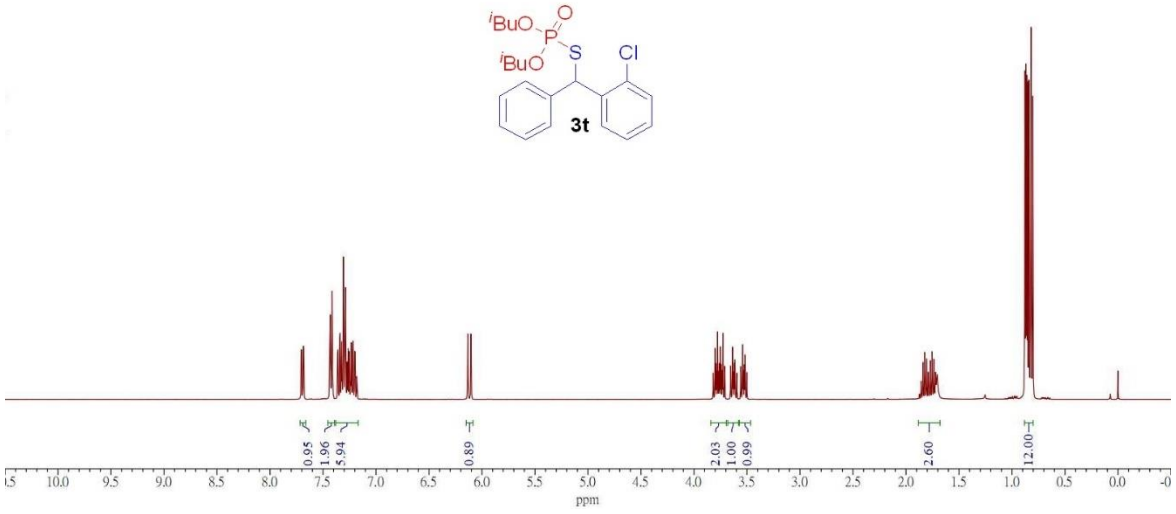
0.870
0.861
0.853
0.840
0.823
0.820
0.804


iBuO
iBuO
O
P
S
Cl
3t
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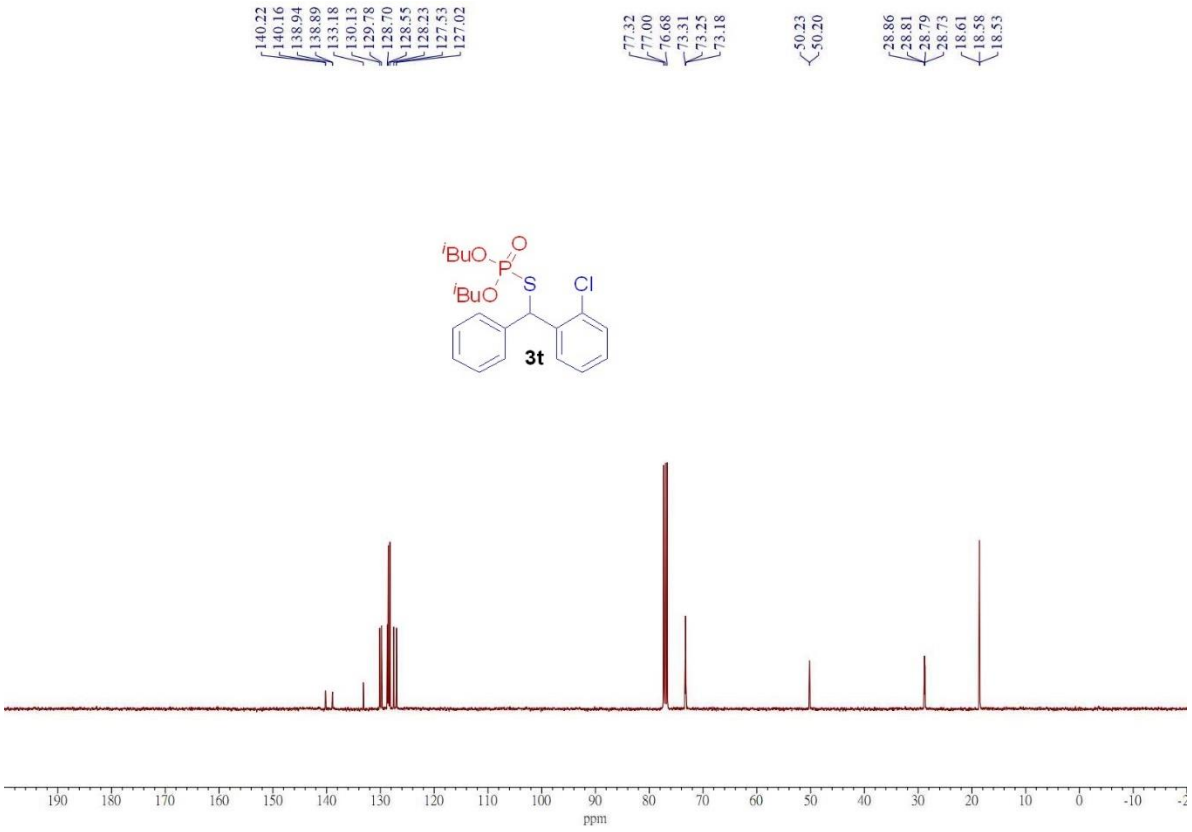
1.96
5.94
0.89
2.03
1.00
0.99
2.60
12.00
ppm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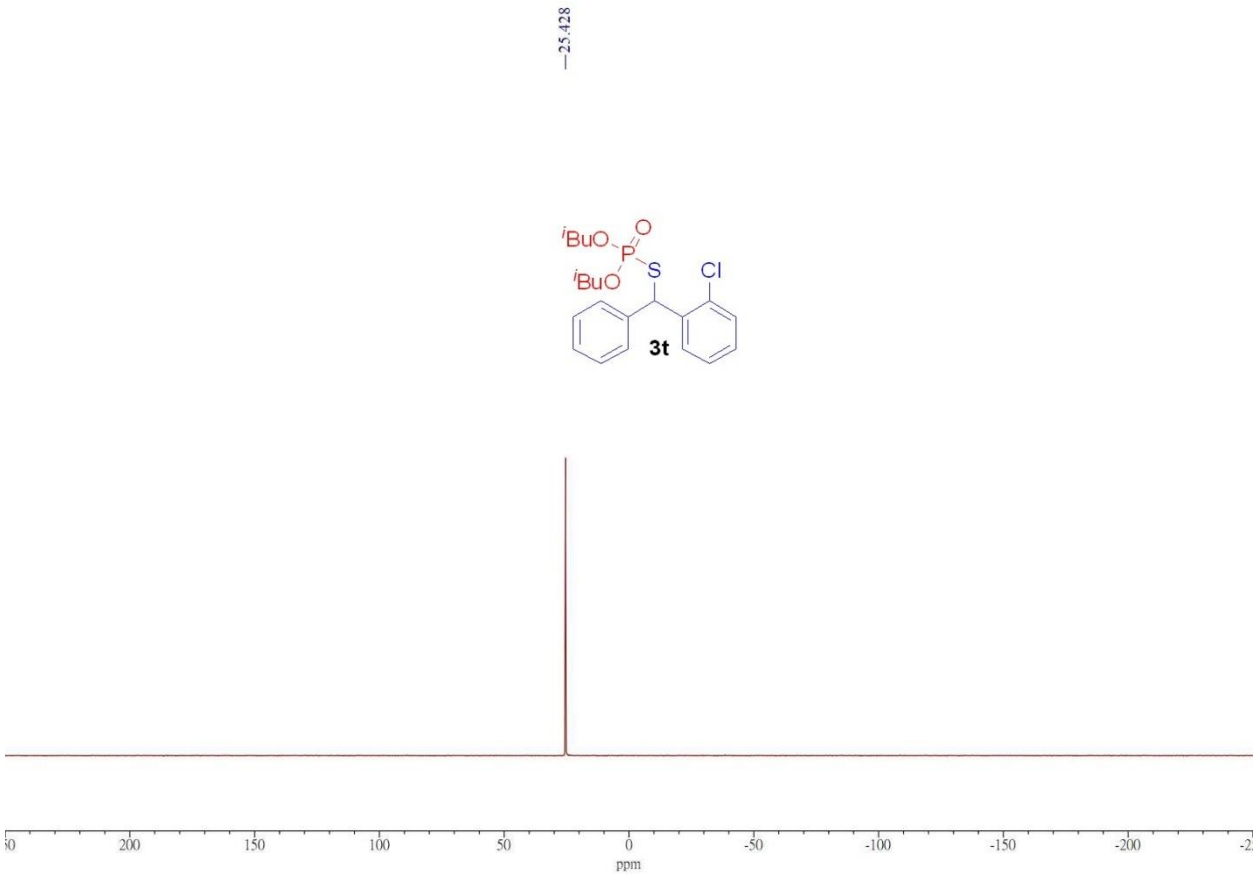
140.16
138.94
138.89
133.18
130.13
129.78
128.70
128.55
128.23
127.53
127.02
77.32
77.00
76.68
73.31
73.25
73.18
50.23
50.20
28.86
28.81
28.79
28.73
18.61
18.58
18.53
iBuO
iBuO
O
P
S
Cl
3t
ppm


25.428
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iBuO
O
P
S
Cl
3t
ppm


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7.427
7.418
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7.411
7.323
7.319
7.303
7.299
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7.289
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7.271
7.267
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7.255
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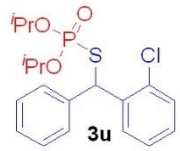
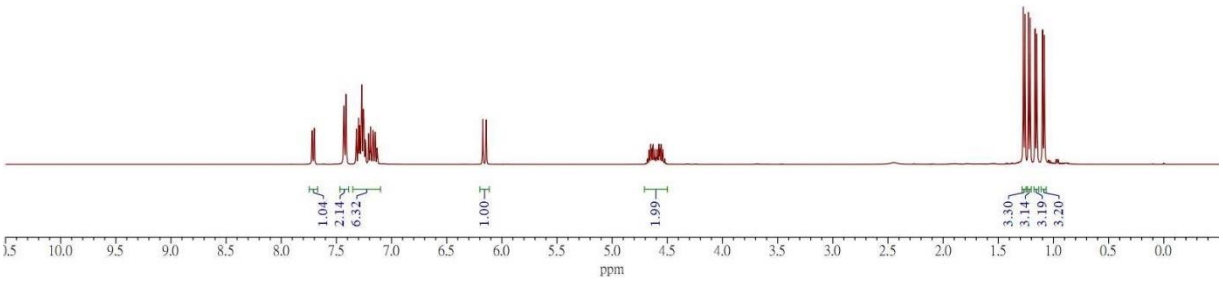
7.209
7.205
7.190
7.171
7.166
7.151
7.147
7.132
7.128
6.173
6.143
4.666
4.660
4.651
4.645
4.635
4.629
4.620
4.614
4.608
4.598
4.593
4.587
4.577
4.571
4.562
4.556
4.546
4.540
4.525
1.274
1.259
1.227
1.212
1.167
1.151
1.099
1.083


iPrO
O
P
iPrO
S
Cl
3u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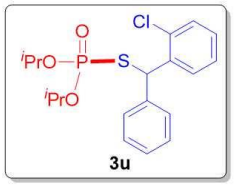
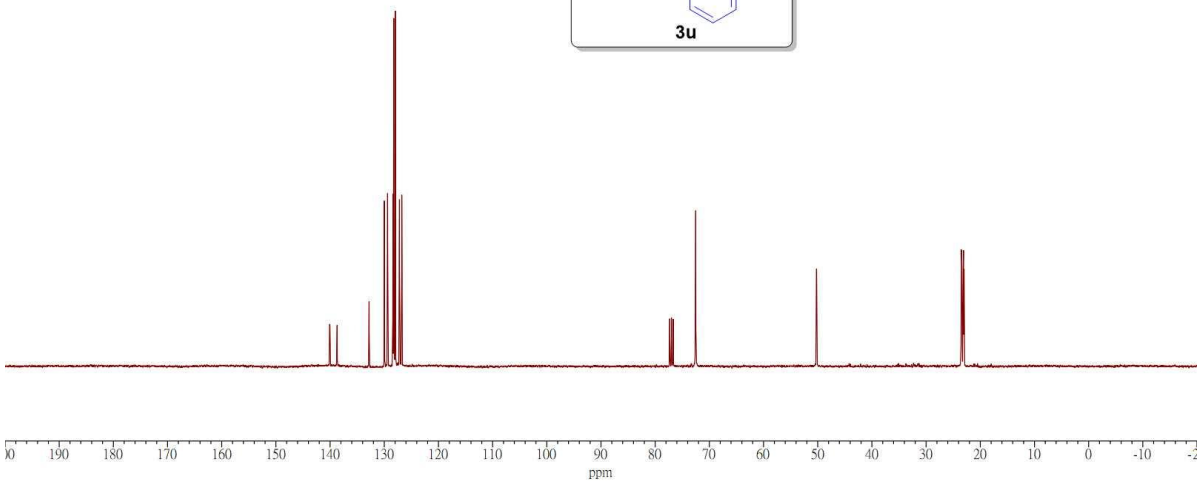
2.14
6.32
1.00
1.99
3.30
3.14
3.19
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


140.09
140.03
138.75
138.70
132.80
129.99
129.39
128.40
128.25
127.96
127.20
126.77
77.32
77.00
76.68
72.58
72.52
50.24
50.21
23.52
23.48
23.45
23.41
23.15
23.09
23.06
23.00


Cl
O
iPrO
P
S
iPrO
3u


190
180
170
160
150
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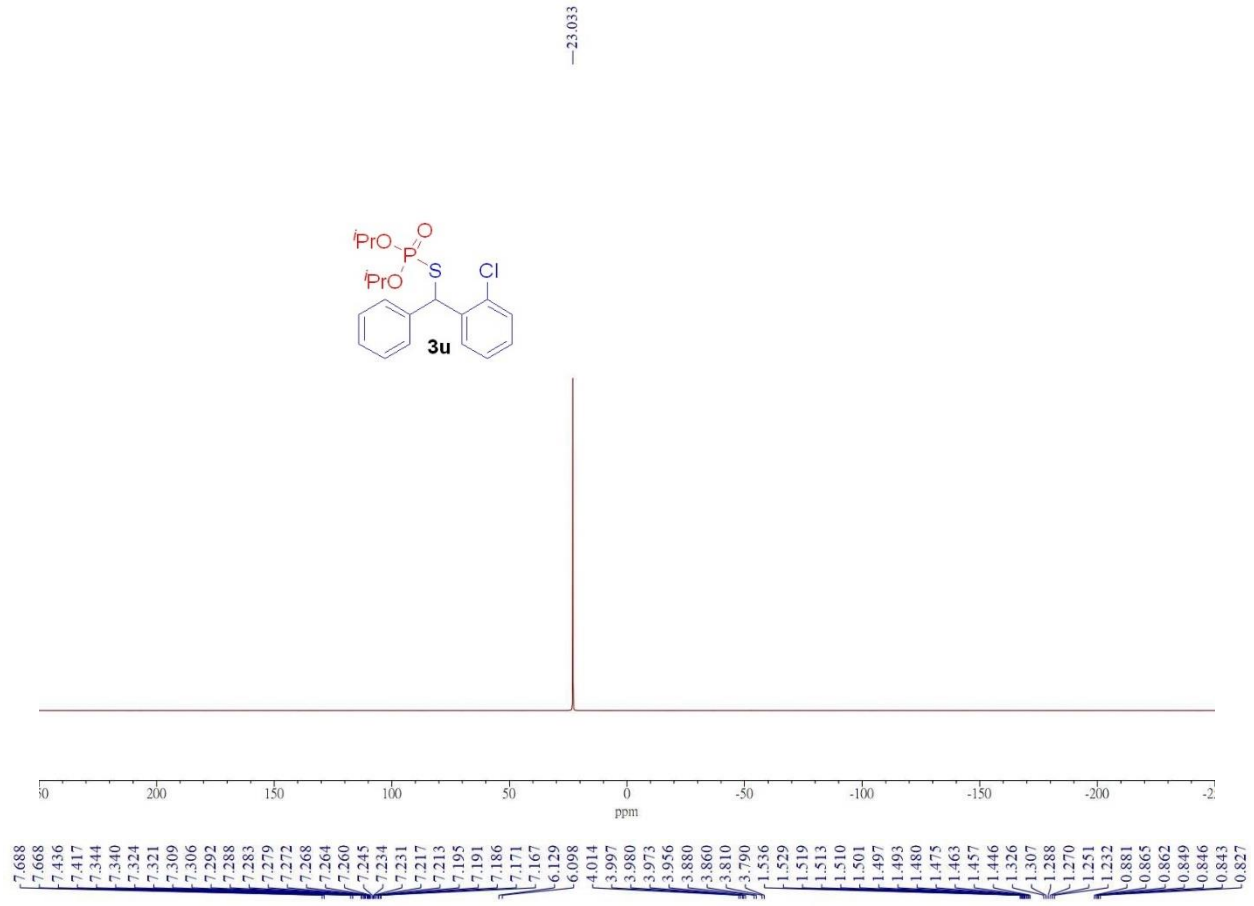
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


23.033
iPrO
iPrO
P
O
S
Cl
3u
ppm
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7.436
7.417
7.344
7.340
7.324
7.321
7.309
7.306
7.292
7.288
7.283
7.279
7.272
7.268
7.264
7.260
7.245
7.234
7.231
7.217
7.213
7.195
7.191
7.186
7.171
7.167
6.129
6.098
4.014
3.997
3.980
3.973
3.956
3.880
3.860
3.810
3.790
1.536
1.529
1.519
1.513
1.510
1.501
1.497
1.493
1.480
1.475
1.463
1.457
1.446
1.326
1.307
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1.251
1.232
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0.849
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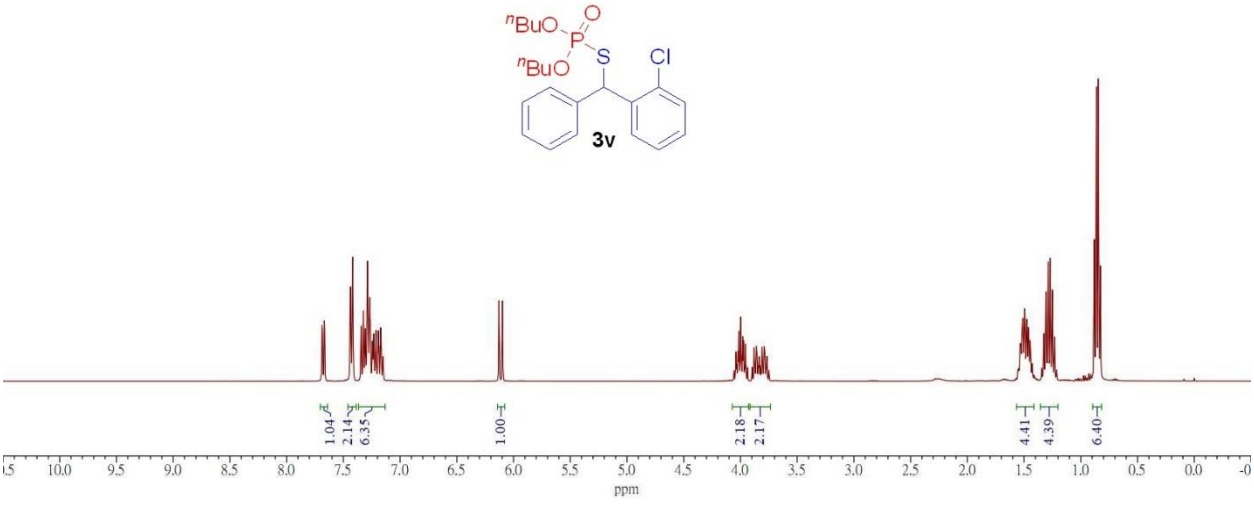
0.843
0.827


nBuO
nBuO
P
O
S
Cl
3v
1.04
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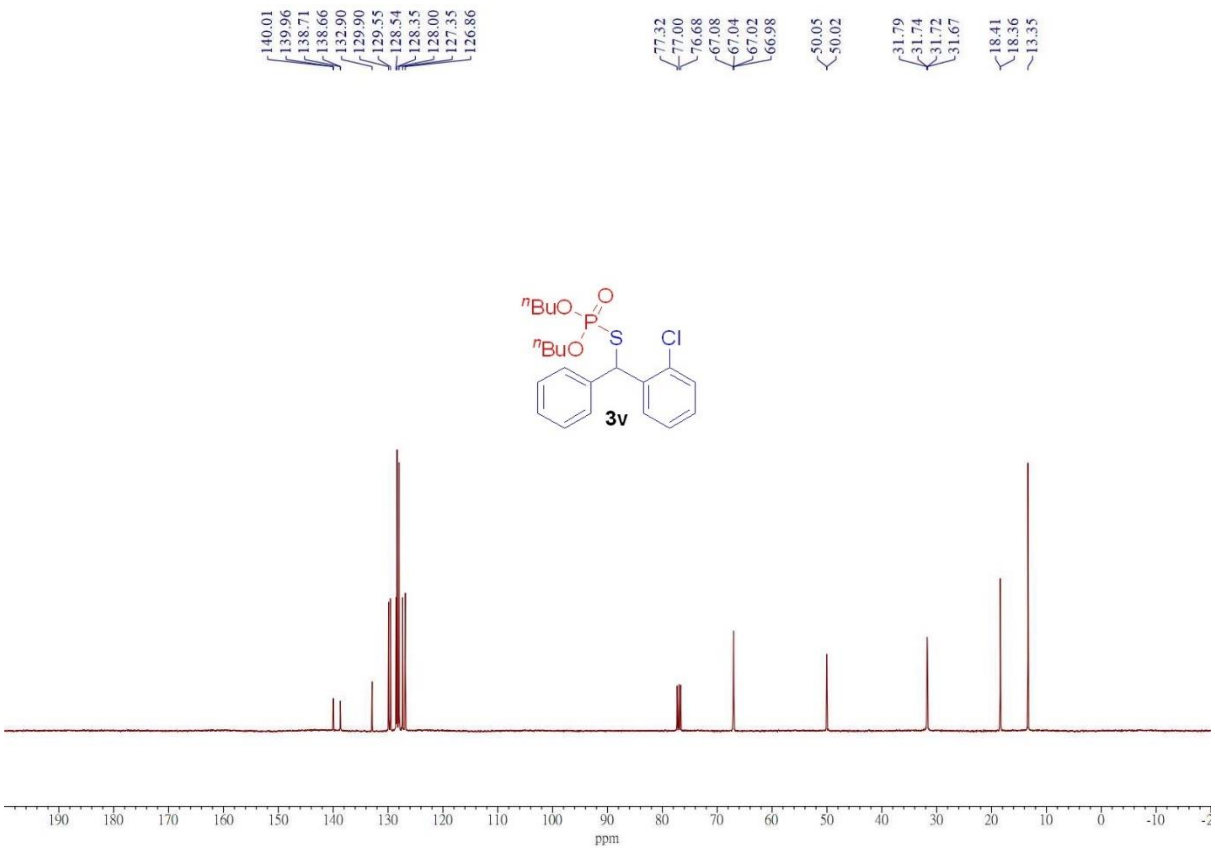
6.35
1.00
2.18
2.17
4.41
4.39
6.40
ppm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132.90
129.90
129.55
128.54
128.35
128.00
127.35
126.86
77.32
77.00
76.68
67.08
67.04
67.02
66.98
50.05
50.02
31.79
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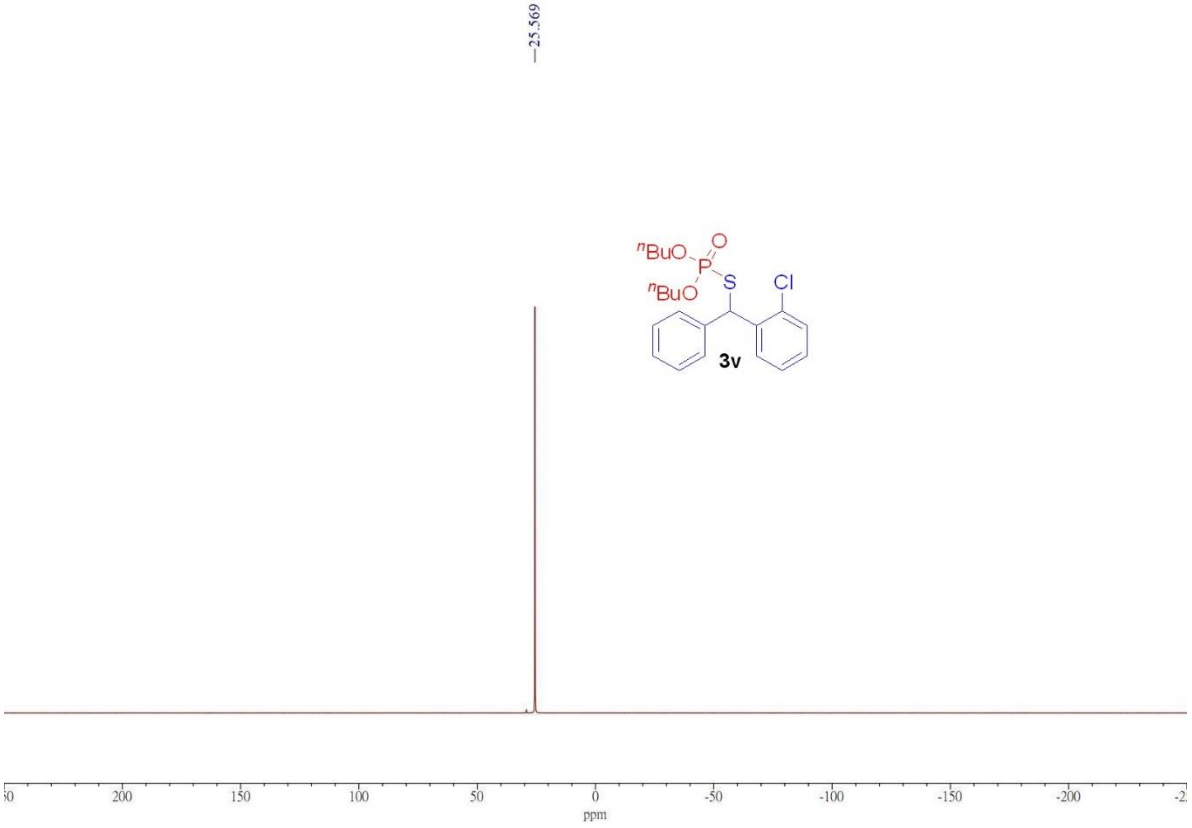
nBuO
nBuO
P
O
S
Cl
3v
ppm


25.569
nBuO
nBuO
P
O
S
Cl
3v
ppm


7.809
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7.700
7.421
7.404
7.401
7.385
7.382
7.368
7.365
7.349
7.346
7.331
7.327
7.260
5.490
5.451
4.341
4.323
4.316
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4.303
4.298
4.285
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4.277
4.260
4.256
4.252
4.239
4.234
4.231
4.221
4.217
4.213
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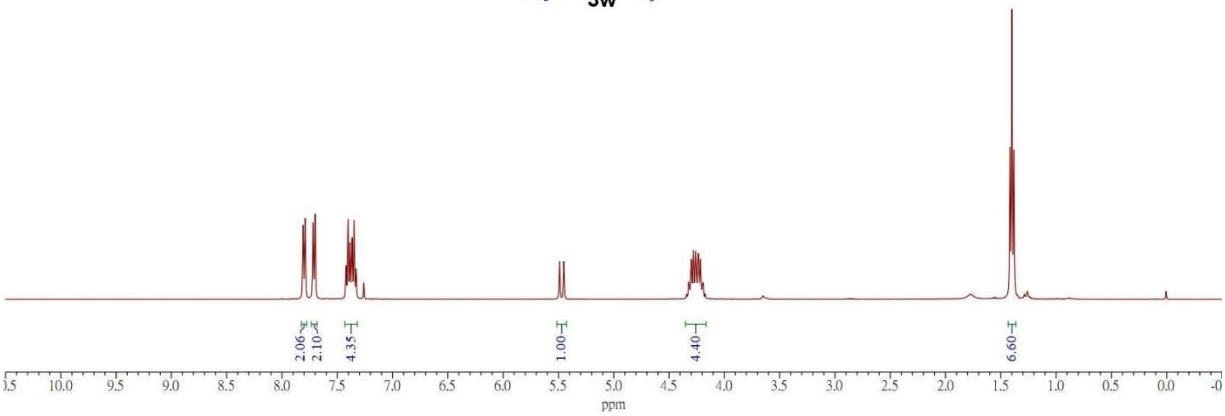
4.192
4.174
1.417
1.399
1.382


EtO
EtO
O
P
S

3w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2.10
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1.00
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6.60
ppm


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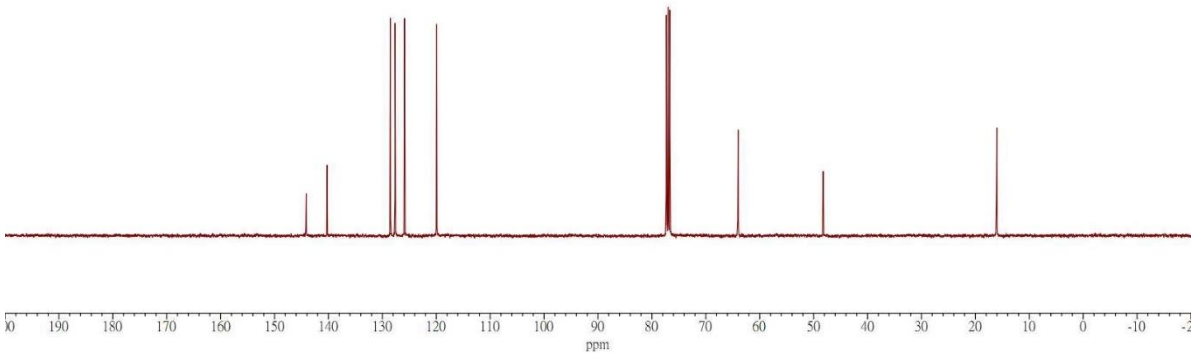
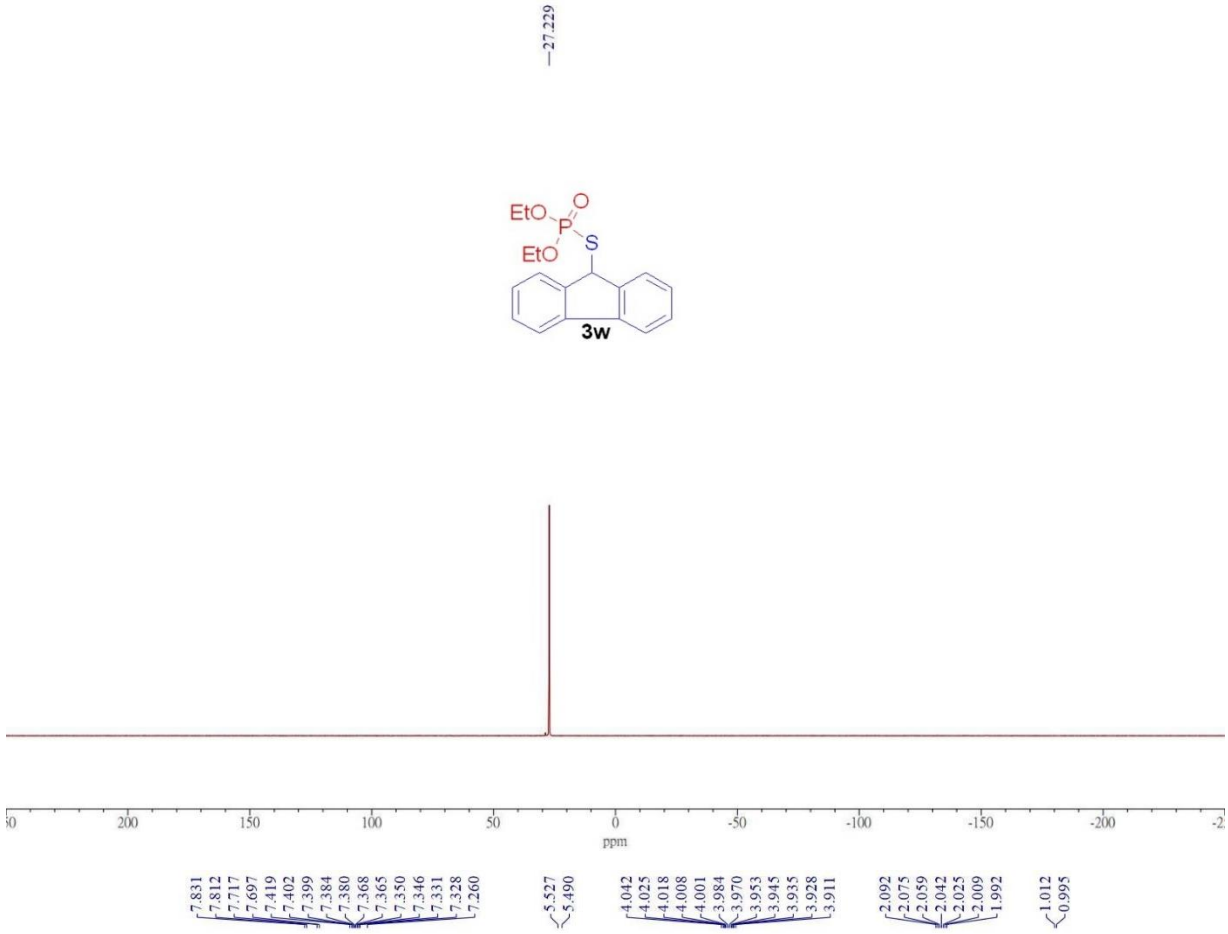
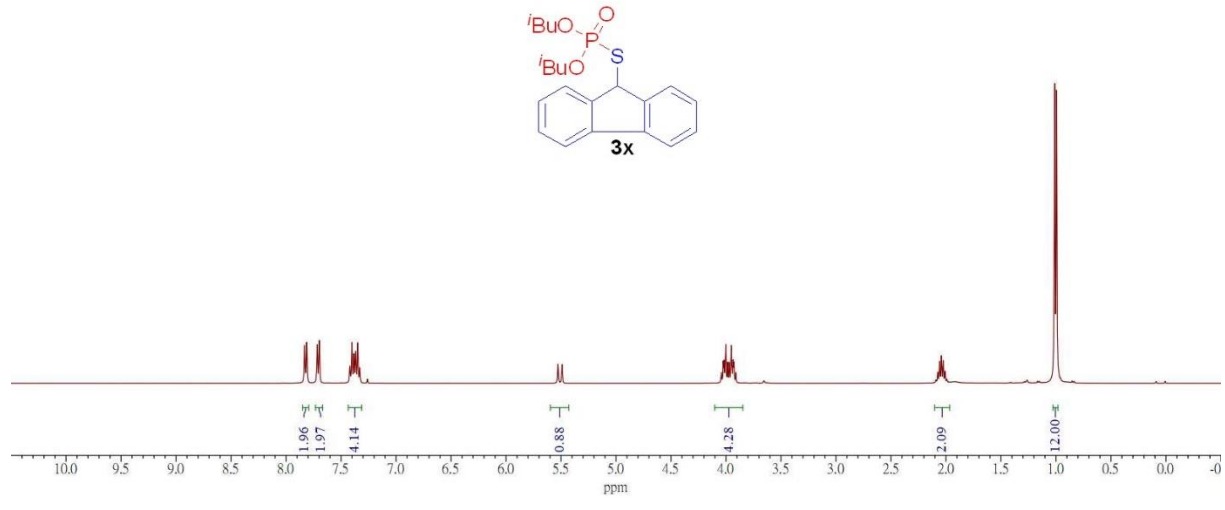
144.13
140.25
128.53
127.65
125.89
119.95
77.32
77.00
76.68
64.06
63.99
48.26
48.22
16.08
16.01

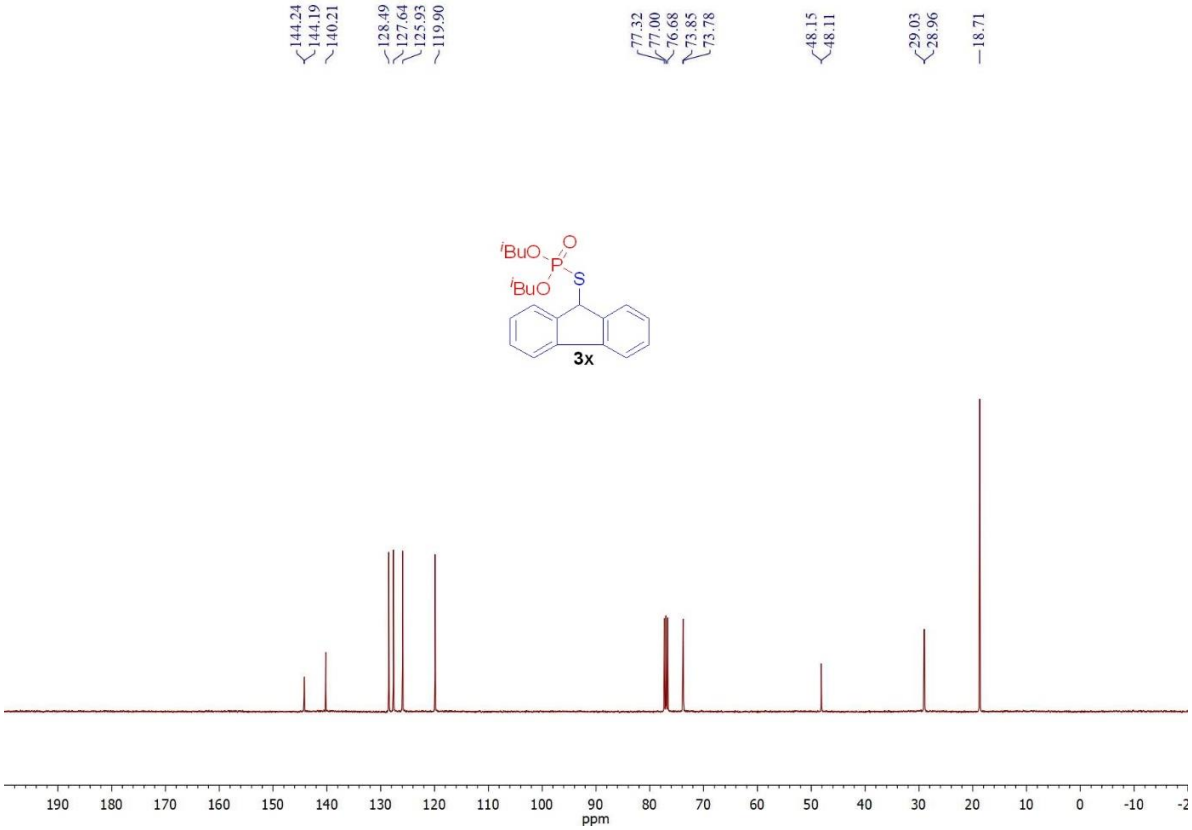

EtO
EtO
O
P
S

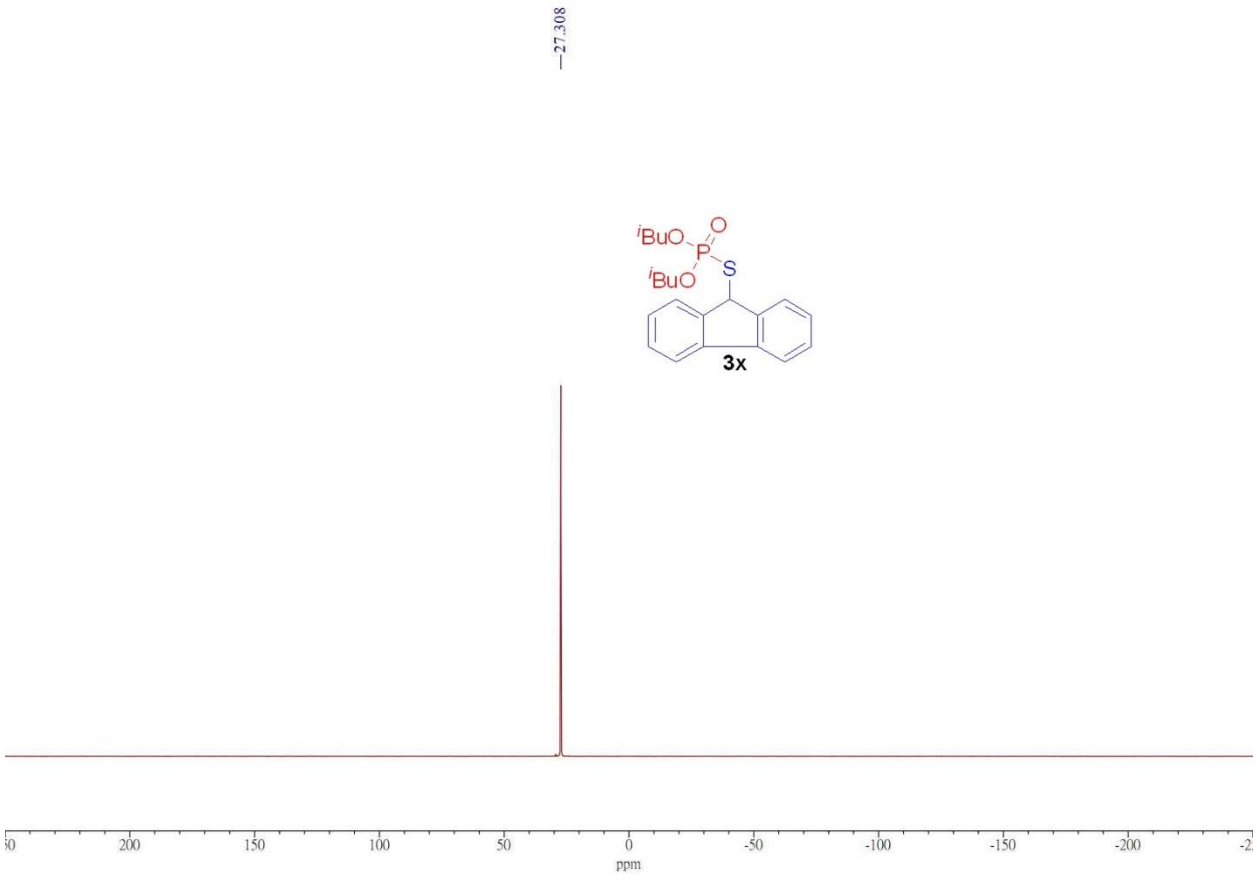
3w

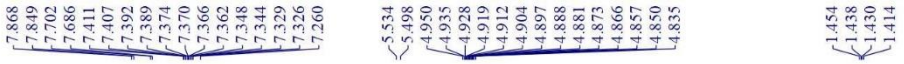

ppm

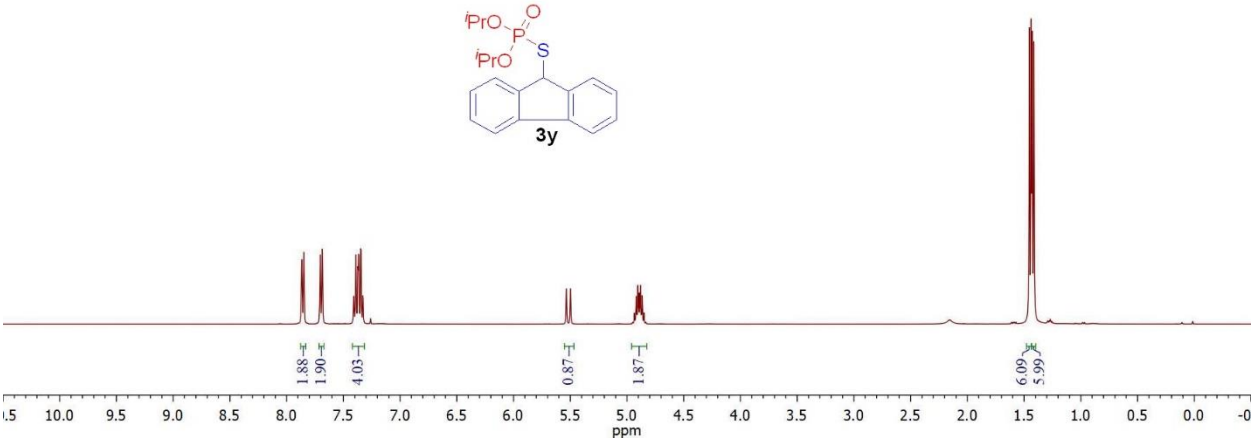

27.229
EtO
O
P
S
EtO
3w
ppm
7.831
7.812
7.717
7.697
7.419
7.402
7.399
7.384
7.380
7.368
7.365
7.350
7.346
7.331
7.328
7.260
5.527
5.490
4.042
4.025
4.018
4.008
4.001
3.984
3.970
3.953
3.945
3.935
3.928
3.911
2.092
2.075
2.059
2.042
2.025
2.009
1.992
1.012
0.995


iBuO
O
P
S
iBuO
3x
ppm
1.96
1.97
4.14
0.88
4.28
2.09
12.00

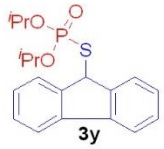

144.24
144.19
140.21
128.49
127.64
125.93
119.90
77.32
77.00
76.68
73.85
73.78
48.15
48.11
29.03
28.96
18.71
3x
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

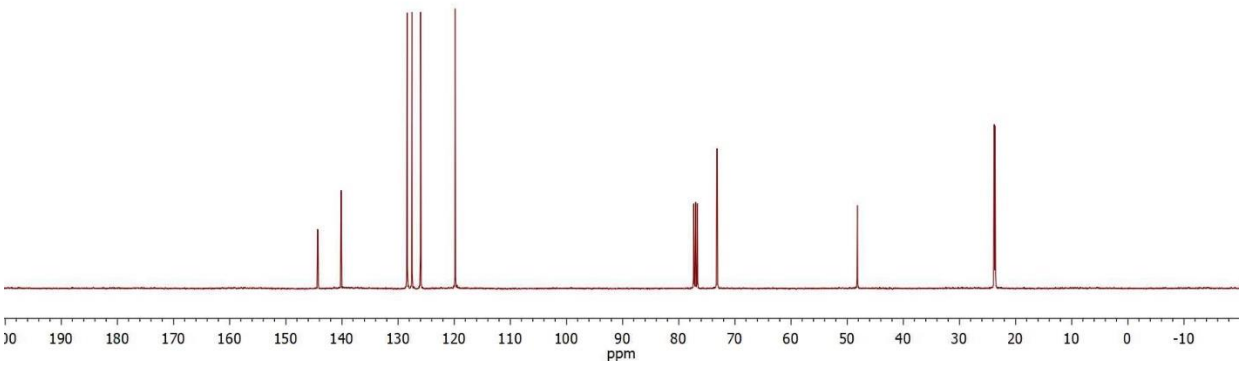

27.308
3x
200 150 100 50 0 -50 -100 -150 -200
ppm

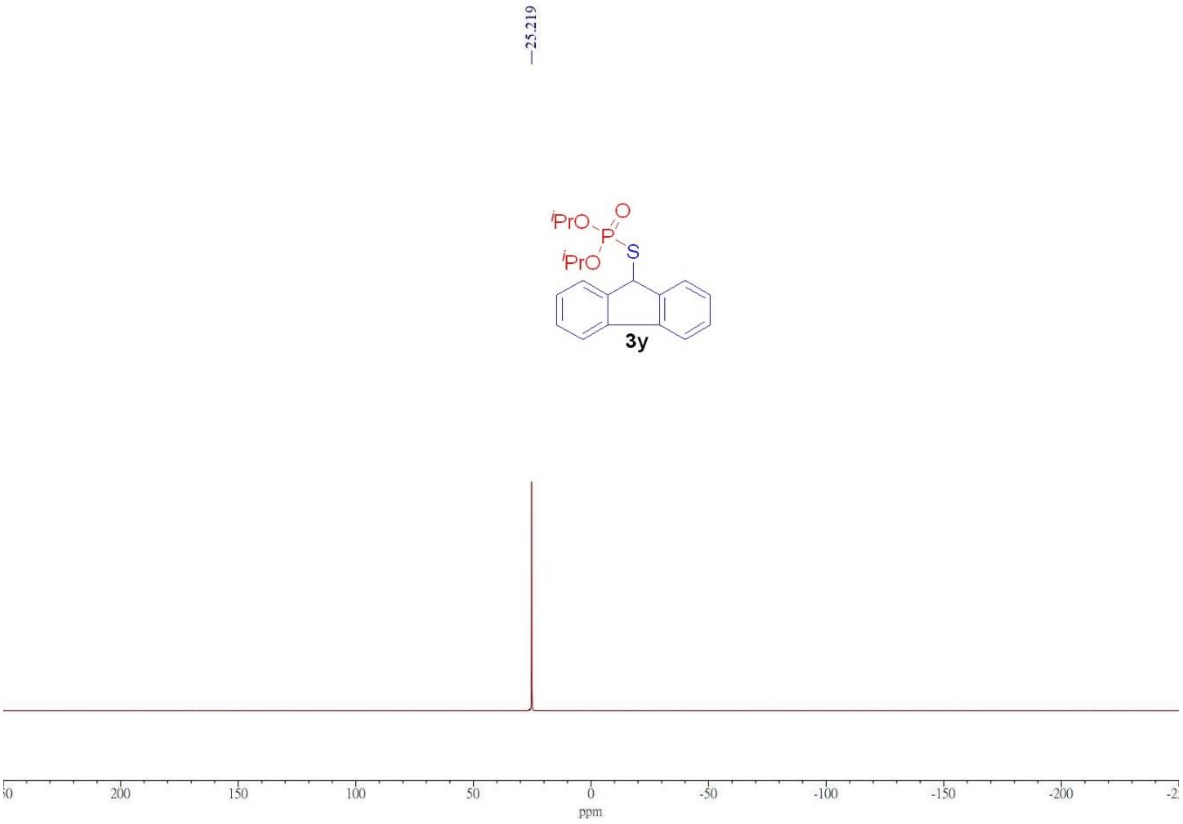

7.868
7.849
7.702
7.686
7.411
7.407
7.392
7.389
7.374
7.370
7.366
7.362
7.348
7.344
7.329
7.326
7.260
5.534
5.498
4.950
4.935
4.928
4.919
4.912
4.904
4.897
4.888
4.881
4.873
4.866
4.857
4.850
4.835
1.454
1.438
1.430
1.414


iPrO
O
P
S
iPrO
3y
1.88
1.90
4.03
0.87
1.87
6.09
5.99
ppm


144.31
144.26
140.14
128.38
127.52
125.97
119.80
77.32
77.00
76.68
73.21
73.14
48.21
48.18
23.81
23.77
23.66
23.60


iPrO
O
P
S
iPrO
3y


ppm


25.219
iPrO
O
P
S
iPrO
3y
200
150
100
50
0
-50
-100
-150
-200
ppm