Electronic Supplementary Material (ESI) for Green Chemistry.

Direct synthesis of α-aminophosphonates from biomass resources catalyzed by $HReO_4$

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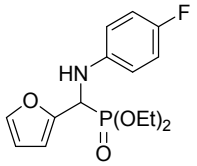
1. General information

Carbohydrates, anilines, H-phosphonates and the catalyst $HReO_4$ (75-80% aqueous solution) were obtained from commercial suppliers and were used without further purification. Flash chromatography was performed on MN Kieselgel 60M 230-400 mesh. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were measured on a Bruker Avance II^{+} 400 MHz and 300 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard.

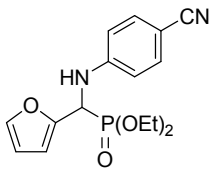
2. General procedure for the conversion of carbohydrates into α-aminophosphonates catalyzed by $HReO_4$

To a Schlenk flask equipped with a J. Young tap containing a solution of carbohydrate (1.0 mmol of pentose) in 1,4-dioxane (5 mL) was added $HReO_4$ (5 mol%). The reaction mixture was stirred in a closed Schlenk at 140 °C during 2 h. After cooling the reaction mixture to room temperature, aniline (1.0 mmol) and $HP(O)(OEt)_2$ (1.2 mmol) were added and the mixture was stirred at 140 ° C for 1 h. Then, water (3.0 mL) was added and the mixture was stirred at 80 °C for 1 h. The reaction mixture was cooled to ambient temperature and extracted with ethyl acetate (2 × 10.0 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified by flash chromatography with appropriate mixtures of *n*-hexane:ethyl acetate, affording the α-aminophosphonates.

3. Characterization of the products

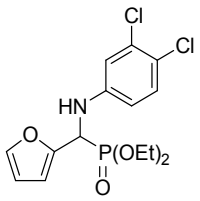


^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.37 (s, 1H, H_{fur}), 6.83 (t, 2H, J = 8.73, 8.55 Hz, H_{arom}), 6.59 (dd, 2H, J = 8.76, 4.26 Hz, H_{arom}), 6.36 (brs, 1H, H_{fur}), 6.31 (brs, 1H, H_{fur}), 4.79 (d, 1H, J = 23.71 Hz, C<u>H</u>), 4.46 (s, 1H, N-<u>H</u>), 4.19-4.13 (m, 2H, -OC<u>H</u>$_2$CH$_3$), 4.06-3.98 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 3.92-3.84 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 1.29 (t, 3H, J = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$), 1.19 (t, 3H, J = 7.05 Hz, -OCH$_2$C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 158.2 (d, J = 236.77 Hz, Cq), 149.3 (d, J = 1.95 Hz, C_q), 142.6 (d, J = 3.13 Hz, CH_{fur}), 142.4 (d, J = 2.28 Hz, C_q), 115.7 (d, J = 22.50 Hz, CH_{arom}), 115.2 (d, J = 7.56 Hz, CH_{arom}), 110.9 (d, J = 2.52 Hz, CH_{fur}), 108.9 (d, J = 7.01 Hz, CH_{fur}), 63.6 (d, J = 7.0 Hz, -O<u>C</u>H$_2$CH$_3$), 63.4 (d, J = 6.9 Hz, -O<u>C</u>H$_2$CH$_3$), 51.1 (d, J = 159.61 Hz, <u>C</u>H), 16.5 (d, J = 5.68 Hz, -OCH$_2$<u>C</u>H$_3$), 16.4 (d, J = 5.82 Hz, -OCH$_2$<u>C</u>H$_3$).^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 20.36 (s). Anal. Calcd. for $C_{15}H_{19}FNO_4P$: C, 55.05; H, 5.85; N, 4.28. Found: C, 55.32; H, 6.07; N, 4.51.

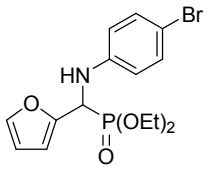


^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.40 (s, 1H, H_{fur}), 7.37 (s, 2H, H_{arom}), 6.66 (d, 2H, J = 8,61 Hz, H_{arom}), 6.40 (brs, 1H, H_{fur}), 6.33 (brs, 1H, H_{fur}), 5.38 (t, J = 7.95, 7.65 Hz, 1H, N-<u>H</u>), 4.90 (dd,

1H, *J* = 8.85, 23.47 Hz, C<u>H</u>), 4.21-4.14 (m, 2H, -OC<u>H</u>$_2$CH$_3$), 4.08-3.98 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 3.91-3.78 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 1.27 (t, 3H, *J* = 7.05 Hz, -OCH$_2$C<u>H</u>$_3$), 1.18 (t, 3H, *J* = 7.05 Hz, -OCH$_2$C<u>H</u>$_3$).^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 149.7 (d, *J* = 11.76 Hz, C_q), 148.3 (d, *J* = 2.00 Hz, C_q), 142.9 (d, *J* = 3,09 Hz, CH_{fur}), 133,6 (s, CH_{arom}), 120,0 (*s*, -<u>C</u>N), 113,4 (s, CH_{arom}), 111,0 (d, *J* = 2.57 Hz, CH_{fur}), 109.2 (d, *J* = 6.73 Hz, CH_{fur}), 100.6 (s, C_q), 63.7 (d, *J* = 7.03 Hz, -O<u>C</u>H$_2$CH$_3$), 63.6 (d, *J* = 6.96 Hz, -O<u>C</u>H$_2$CH$_3$), 49.4 (d, *J* = 159.55 Hz, <u>C</u>H), 16.5 (d, *J* = 5.74 Hz, -OCH$_2$<u>C</u>H$_3$), 16.3 (d, *J* = 5.66 Hz, -OCH$_2$<u>C</u>H$_3$). ^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 19.36 (s). Anal. Calcd. for $C_{16}H_{19}N_2O_4P$: C, 57.48; H, 5.73; N, 8.38. Found: C, 57.73; H, 6.07; N, 8.59.

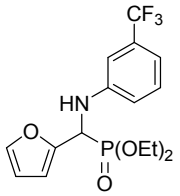


^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.38 (s, 1H, H_{fur}), 7.15 (d, 1H, *J* = 8.73 Hz, H_{arom}), 6.76 (d, 1H, *J* = 2.70 Hz, H_{arom}), 6.50 (dd, 1H, *J* = 2.70, 8.76 Hz, H_{arom}), 6.39 (brs, 1H, H_{fur}), 6.32 (brs, 1H, H_{fur}), 4.8 (d, 1H, *J* = 22.54 Hz, C<u>H</u>), 4.19-4.15 (m, 2H, -OC<u>H</u>$_2$CH$_3$), 4.06-4.01 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 3.90-3.81 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 1.29 (t, 3H, *J* = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$), 1.19 (t, 3H, *J* = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 148.7 (d, *J* = 1.95 Hz, C_q), 145.9 (d, *J* = 13.12 Hz, C_q), 142.8 (d, *J* = 3.11 Hz, CH_{fur}), 132.8 (s, C_q), 130.6 (s, CH_{arom}), 121.5 (s, C_q), 115.3 (s, CH_{arom}), 113.5 (s, CH_{arom}), 111.0 (d, *J* = 2.54 Hz, CH_{fur}), 109.2 (d, *J* = 6.91 Hz, CH_{fur}), 63.6 (d, *J* = 6.98 Hz, -O<u>C</u>H$_2$CH$_3$), 50.2 (d, *J* = 159.91 Hz, <u>C</u>H), 16.5 (d, *J* = 5.66 Hz, -OCH$_2$<u>C</u>H$_3$), 16.4 (d, *J* = 5.78 Hz, -OCH$_2$<u>C</u>H$_3$). ^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 19,73 (s). Anal. Calcd. for $C_{15}H_{18}Cl_2NO_4P$: C, 47.64; H, 4.80; N, 3.70. Found: C, 47.96; H, 5.02; N, 3,99.

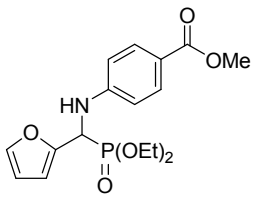


^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.36 (s, 1H, H_{fur}), 7.20 (d, 2H, *J* = 8.75 Hz, H_{arom}), 6.53 (d, 2H, *J* = 8.75 Hz, H_{arom}), 6.34 (brs, 1H, H_{fur}); 6.30 (brs, 1H, H_{fur}), 4.77 (dd, 1H, *J* = 8.71, 23.44 Hz, C<u>H</u>), 4.67 (brs, 1H, N-<u>H</u>), 4.18-4.11 (m, 2H, -OC<u>H</u>$_2$CH$_3$), 4.05-4.00 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 3.89-3.80 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 1.28 (t, 3H, *J* = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$), 1.18 (t, 3H, *J* = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 149.0 (d, *J* = 1.92 Hz, C_q), 145.2 (d, *J* =

13.20 Hz, C_q), 142.6 (d, *J* = 3.16 Hz, CH_{fur}), 131.9 (s, CH_{arom}), 115.6 (s, CH_{arom}), 110.9 (d, *J* = 2.56 Hz, CH_{fur}), 110.7 (s, C_q), 109.0 (d, *J* = 9.96 Hz, CH_{fur}), 63.5 (t, *J* = 6.60 Hz, -O<u>C</u>H_2CH_3), 50.2 (d, *J* = 159.55 Hz, <u>C</u>H), 16.5 (d, *J* = 5.66 Hz, -OCH_2<u>C</u>H_3), 16.3 (d, *J* = 5.66 Hz, -OCH_2<u>C</u>H_3). ^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 20.06 (*s*). Anal. Calcd. for $C_{15}H_{19}BrNO_4P$: C, 46.41; H, 4.93; N, 3.61. Found: C, 46.67; H, 5.16; N, 3.89.

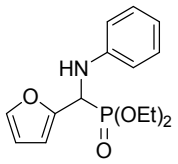


^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.38 (s, 1H, H_{fur}), 7.23 (t, 1H, *J* = 7.85 Hz, H_{arom}); 6.97 (s, 1H, H_{arom}), 6.92 (s, 1H, H_{arom}), 6.80 (d, 1H, *J* = 8.01 Hz, H_{arom}), 6.41 (s, 1H, H_{fur}), 6.32 (s, 1H, H_{fur}), 5.05 (t, 1H, *J* = 8.67, 6.57 Hz, N-<u>H</u>), 4,90 (dd, 1H, *J* = 9.21, 23.26 Hz, C<u>H</u>), 4.21-4.14 (m, 2H, -OC<u>H</u>$_2$$CH_3$), 4.10-4.05 (m, 1H, -OC<u>H</u>$_2$$CH_3$), 3.91-3.83 (m, 1H, -OC<u>H</u>$_2$$CH_3$), 1.28 (t, 3H, *J* = 7.04 Hz, -OCH_2C<u>H</u>$_3$), 1.20 (t, 3H, *J* = 7.02 Hz, -OCH_2C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 148.8 (d, *J* = 1.86 Hz, C_q), 146.6 (d, *J* = 12.90 Hz, C_q), 142.8 (d, *J* = 3.10 Hz, CH_{fur}), 131.5 (d, *J* = 31.80 Hz, C_q), 129.7 (s, CH_{arom}), 124.25 (d, *J* = 272.29 Hz, C_q), 116.7 (s, CH_{arom}), 115.2 (s, CH_{arom}), 110.9 (d, *J* = 2.22 Hz, CH_{arom}), 110.5 (d, *J* = 3.63 Hz, CH_{fur}), 109.2 (d, *J* = 7.01 Hz, CH_{fur}), 63.6 (d, *J* = 6.84 Hz, -O<u>C</u>H_2CH_3), 50.0 (d, *J* = 159.98 Hz, <u>C</u>H), 16.5 (d, *J* = 5.76 Hz, -OCH_2<u>C</u>H_3), 16.3 (d, *J* = 5.93 Hz, -OCH_2<u>C</u>H_3). ^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 20.00 (*s*). Anal. Calcd. for $C_{16}H_{19}F_3NO_4P$: C, 69.10; H, 5.27; N, 7.33. Found: C, 69.33; H, 5.48; N, 7.59.

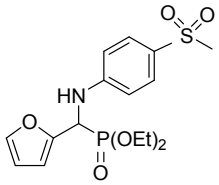


^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.82 (d, 2H, *J* = 8.68 Hz, H_{arom}), 7.37 (s, 1H, H_{fur}), 6.63 (d, 2H, *J* = 8.68 Hz, H_{arom}), 6.38 (brs, 1H, H_{fur}), 6.31 (brs, 1H, H_{fur}), 5.10 (t, *J* = 8.58, 6.81 Hz, 1H, N-<u>H</u>), 4.94 (dd, 1H, *J* = 9.03, 23.80 Hz, C<u>H</u>), 4.17-4.00 (m, 4H, -OC<u>H</u>$_2$$CH_3$), 3.80 (s, 3H, -COOC<u>H</u>$_3$), 1.28-1.15 (m, 6H, -OCH_2C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 167.1 (s, -<u>C</u>$OOCH_3$), 150.1 (d, *J* = 11.61 Hz, C_q), 148.7 (d, *J* = 1.92 Hz, C_q), 142.8 (d, *J* = 3.06 Hz, CH_{fur}), 131.5 (s, CH_{arom}), 120.1 (s, C_q), 112.7 (s, CH_{arom}), 110.9 (d, *J* = 2.52 Hz, CH_{fur}), 109.1 (d, *J* = 7.11 Hz, CH_{fur}), 63.6 (d, *J* = 7.11 Hz, -O<u>C</u>H_2CH_3), 51.7 (s, -COO<u>C</u>H_3), 49.5 (d, *J* = 159.40 Hz, <u>C</u>H), 16.5 (d, *J* = 5.81 Hz, -OCH_2<u>C</u>H_3), 16.3 (d, *J* = 5.70 Hz, -OCH_2<u>C</u>H_3). ^{31}P NMR (121.49 MHz,

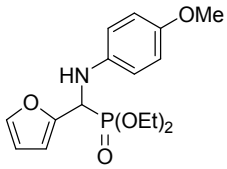
$CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 19.73 (*s*). Anal. Calcd. for $C_{17}H_{22}NO_6P$: C, 55.58; H, 6.04; N, 3.81. Found: C, 55.92; H, 6.32; N, 4.16.



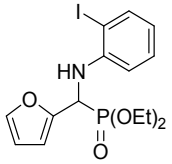
^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.37 (s, 1H, H_{fur}), 7.14 (t, 2H, *J* = 7.62, 7.89 Hz, H_{arom}), 6.74 (t, 1H, *J* = 7.32 Hz, H_{arom}), 6.66 (d, 2H, *J* = 7.89 Hz, H_{arom}), 6.38 (brs, 1H, H_3), 6.31 (brs, 1H, H_{fur}), 4.90 (dd, 1H, *J* = 9.06, 23.86 Hz, C<u>H</u>), 4.57 (t, *J* = 7.44, 7.77 Hz, 1H, N-<u>H</u>), 4.21-4.13 (m, 2H, -OC<u>H</u>$_2$CH$_3$), 4.09-4.01 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 3.90-3.82 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 1.29 (t, 3H, *J* = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$), 1.19 (t, 3H, *J* = 7.05 Hz, -OCH$_2$C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 149.4 (d, *J* = 1.92 Hz, C_q), 146.1 (d, *J* = 13.21 Hz, C_q), 142.5 (d, *J* = 3.15 Hz, CH_{fur}), 129.2 (s, CH_{arom}), 118.9 (s, CH_{arom}), 113.9 (s, CH_{arom}), 110.8 (d, *J* = 2.55 Hz, CH_{fur}), 108.8 (d, *J* = 7.10 Hz, CH_{fur}), 63.5 (d, *J* = 6.89 Hz, -O<u>C</u>H$_2$CH$_3$), 63.3 (d, *J* = 6.91 Hz, -O<u>C</u>H$_2$CH$_3$), 50.2 (d, *J* = 159.58 Hz, <u>C</u>H), 16.5 (d, *J* = 5.71 Hz -OCH$_2$<u>C</u>H$_3$), 16.3 (d, *J* = 5.68 Hz, -OCH$_2$<u>C</u>H$_3$). ^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 20.49 (*s*). Anal. Calcd. for $C_{15}H_{20}NO_4P$: C, 58.25; H, 6.52; N, 4.53. Found: C, 58.39; H, 6.72; N, 4.2.



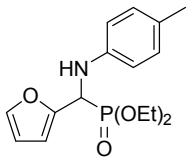
^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.67 (d, 2H, *J* = 8.49 Hz, H_{arom}), 7.38 (s, 1H, H_{fur}), 6.72 (d, 2H, *J* = 8.55 Hz, H_{arom}), 6.41 (brs, 1H, H_{fur}), 6.34 (brs, 1H, H_{fur}), 5.39 (t, *J* = 8.25, 7.35 Hz, 1H, N-<u>H</u>), 4.93 (dd, 1H, *J* = 8.81, 23.51 Hz, C<u>H</u>), 4.21-4.12 (m, 2H, -OC<u>H</u>$_2$CH$_3$), 4.09-3.98 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 3.89-3.81 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 2.96 (s, 3H, -SO$_2$C<u>H</u>$_3$), 1.27 (t, 3H, *J* = 7.02 Hz, -OCH$_2$C<u>H</u>$_3$), 1.19 (t, 3H, *J* = 7.02 Hz, -OCH$_2$C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 150.7 (s, C_q), 150.5 (s, C_q), 148.4 (d, *J* = 2.08 Hz, C_q), 143.0 (d, *J* = 3.07 Hz, CH_{fur}), 129.3 (d, *J* = 9.12 Hz, CH_{arom}), 113.1 (s, CH_{arom}), 111.0 (d, *J* = 2.42 Hz, CH_{fur}), 109.3 (d, *J* = 6.69 Hz, CH_{fur}), 63.8 (d, *J* = 6.91 Hz, -O<u>C</u>H$_2$CH$_3$), 63.6 (d, *J* = 7.03 Hz, -O<u>C</u>H$_2$CH$_3$), 49.5 (d, *J* = 159.54 Hz, <u>C</u>H), 45.0 (s, -SO$_2$<u>C</u>H$_3$), 16.5 (d, *J* = 5.60 Hz, -OCH$_2$<u>C</u>H$_3$), 16.4 (d, *J* = 5.70 Hz, -OCH$_2$<u>C</u>H$_3$). ^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 19.34 (*s*). Anal. Calcd. for $C_{17}H_{25}NO_6PS$: C, 50.74; H, 6.26; N, 3.48. Found: C, 51.91; H, 6.42; N, 3.64.



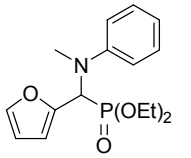
^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.35 (s, 1H, H_{fur}), 6.71(d, 2H, *J* = 8.87 Hz, H_{arom}), 6.60 (d, 2H, *J* = 8.87 Hz, H_{arom}), 6.34 (brs, 1H, H_{fur}), 6.29 (brs, 1H, H_{fur}), 4.79 (d, 1H, *J* = 23.80 Hz, C<u>H</u>), 4.21-4.12 (m, 2H, -OC<u>H</u>$_2$CH$_3$), 4.08-4.00 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 3.92-3.78 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 3.67 (s, 3H, -OC<u>H</u>$_3$), 1.28 (t, 3H, *J* = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$), 1.17 (t, 3H, *J* = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 153.1 (s, C_q), 149.6 (d, *J* = 1.86 Hz, C_q), 142.4 (d, *J* = 3.16 Hz, CH_{fur}), 140.1 (d, *J* = 14.28 Hz, C_q), 115.6 (s, CH_{arom}), 114.7 (s, CH_{arom}), 110.8 (d, *J* = 2.56 Hz, CH_{fur}), 108.8 (d, *J* = 7.15 Hz, CH_{fur}), 63.5 (d, *J* = 6.86 Hz, -O<u>C</u>H$_2$CH$_3$), 63.2 (d, *J* = 6.93 Hz, -O<u>C</u>H$_2$CH$_3$), 55.5 (s, -O<u>C</u>H$_3$), 51.3 (d, *J* = 159.70 Hz, <u>C</u>H), 16.5 (d, *J* = 5.71 Hz, -OCH$_2$<u>C</u>H$_3$), 16.3 (d, *J* = 5.80 Hz, -OCH$_2$<u>C</u>H$_3$). ^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 20.65 (*s*). Anal. Calcd. for $C_{16}H_{22}NO_5P$: C, 56.63; H, 6.53; N, 4.13. Found: C, 56.89; H, 6.85; N, 4.39.



^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.66 (dd, 1H, *J* = 1.25, 7.87 Hz, H_{arom}), 7.40 (s, 1H, H_{fur}), 7.14 (t, 1H, *J* = 7.87 Hz, H_{arom}), 6.55 (d, 1H, *J* = 7.87 Hz, H_{arom}), 6.49 (t, 1H, *J* = 7.87 Hz, H_{arom}), 6.38 (t, 1H, *J* = 3.26 Hz, H_{fur}), 6.33 (brs, 1H, H_{fur}), 5.05 (t, 1H, *J* = 7.97 Hz, N-<u>H</u>), 4.90 (dd, 1H, *J* = 8.72, 23.43 Hz, C<u>H</u>), 4.24-4.14 (m, 2H, -OC<u>H</u>$_2$CH$_3$), 4.13-4.04 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 4.01-3.93 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 1.32 (t, 3H, *J* = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$), 1.23 (t, 3H, *J* = 7.07 Hz, -OCH$_2$C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 149.0 (d, *J* = 2.62 Hz, C_q), 145.7 (d, *J* = 12.55 Hz, C_q), 142.8 (d, *J* = 3.18 Hz, CH_{fur}), 139.3 (s, CH_{arom}), 129.4 (s, CH_{arom}), 120.0 (s, CH_{arom}), 112.0 (s, CH_{arom}), 111.0 (d, *J* = 2.70 Hz, CH_{fur}), 109.0 (d, *J* = 7.02 Hz, CH_{fur}), 86.5 (s, C_q), 63.9 (d, *J* = 7.00 Hz, -O<u>C</u>H$_2$CH$_3$), 63.7 (d, *J* = 6.72 Hz, -O<u>C</u>H$_2$CH$_3$), 50.9 (d, *J* = 158.66 Hz, <u>C</u>H), 16.6 (d, *J* = 5.80 Hz, -OCH$_2$<u>C</u>H$_3$), 16.5 (d, *J* = 5.80 Hz, -OCH$_2$<u>C</u>H$_3$). ^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 19.37 (*s*). Anal. Calcd. for $C_{15}H_{19}INO_4P$: C, 41.40; H, 4.40; N, 3.22. Found: C, 41.69; H, 4.73; N, 3.48.

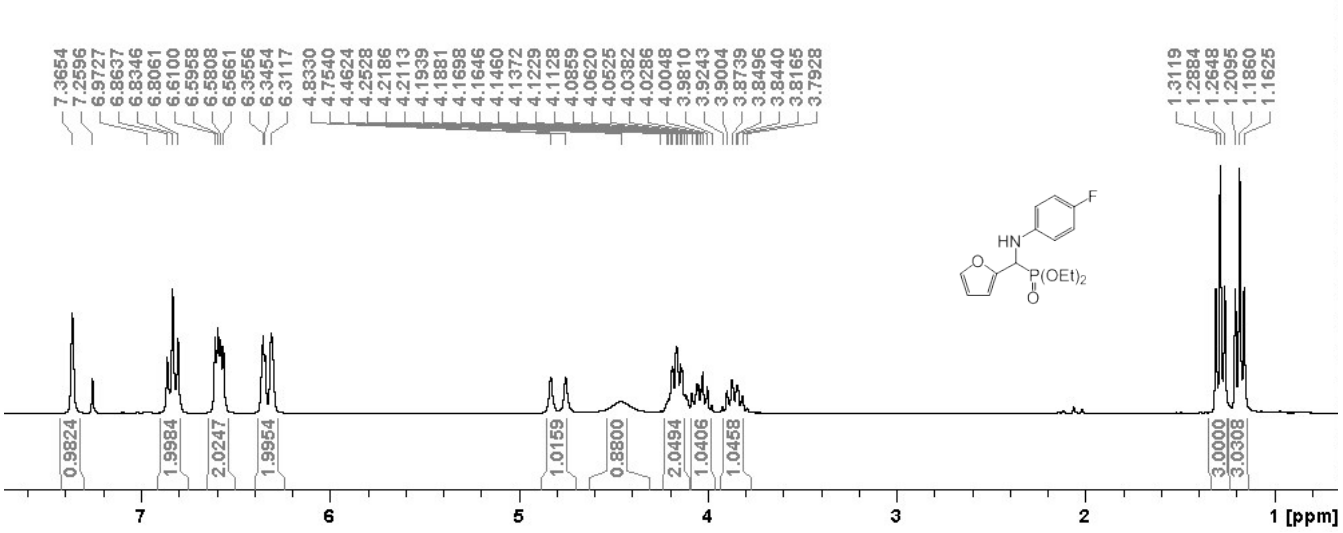


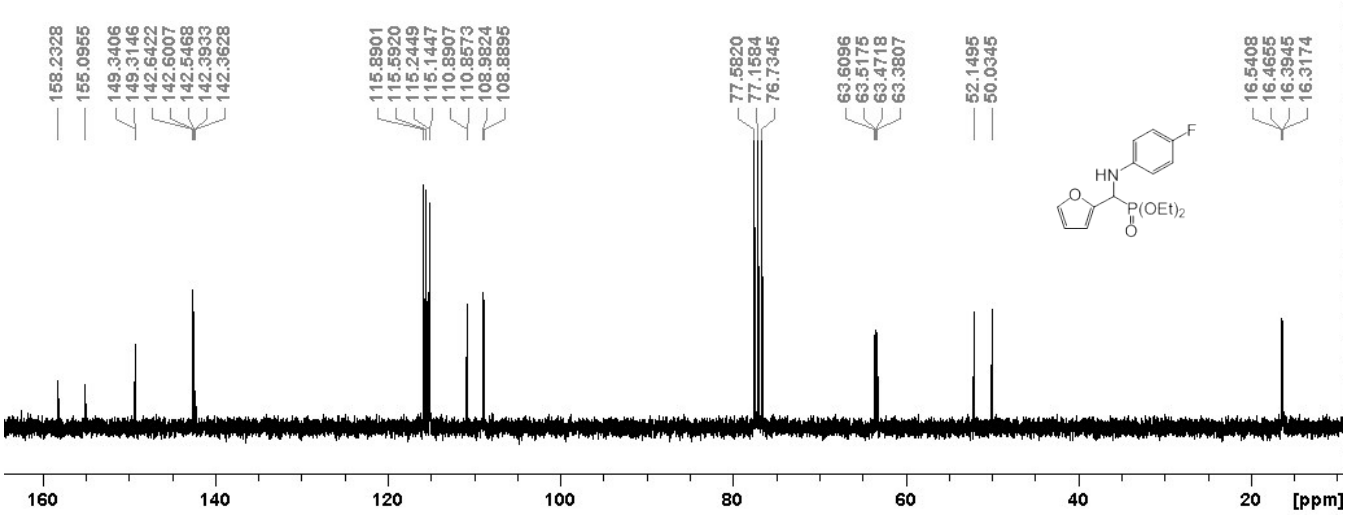
^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.35 (s, 1H, H_{fur}), 6.94 (d, 2H, *J* = 8.19 Hz, H_{arom}), 6.58 (d, 2H, *J* = 8.19 Hz, H_{arom}), 6.36 (brs, 1H, H_{fur}), 6.29 (brs, 1H, H_{fur}), 4.86 (dd, 1H, *J* = 9.51, 23.92 Hz, C<u>H</u>), 4.46 (t, 1H, *J* = 9.00, 8.84 Hz, N-<u>H</u>), 4.22-4.14 (m, 2H, -OC<u>H</u>$_2$CH$_3$), 4.11-3.98 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 3.93-3.79 (m, 1H, -OC<u>H</u>$_2$CH$_3$), 2.19 (s, 3H, -C<u>H</u>$_3$), 1.28 (t, 3H, *J* = 7.10 Hz, -OCH$_2$C<u>H</u>$_3$), 1.18 (t, 3H, *J* = 7.13 Hz, -OCH$_2$C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 149.5 (d, *J* = 1.82 Hz, C_q), 143.7 (d, *J* = 13.80 Hz, C_q), 142.3 (d, *J* = 3.18 Hz, CH_{fur}), 129.6 (s, CH_{arom}), 128.0 (s, C_q), 114.0 (s, CH_{arom}), 110.7 (d, *J* = 2.59 Hz, CH_{fur}), 108.7 (d, *J* = 7.12 Hz, CH_{fur}), 63.4 (d, *J* = 6.80 Hz, -O<u>C</u>H$_2$CH$_3$), 63.2 (d, *J* = 6.98 Hz, -O<u>C</u>H$_2$CH$_3$), 50.5 (d, *J* = 159.73 Hz, <u>C</u>H), 20.3 (s, -<u>C</u>H$_3$), 16.4 (d, *J* = 5.72 Hz, -OCH$_2$<u>C</u>H$_3$), 16.2 (d, *J* = 5.80 Hz, -OCH$_2$<u>C</u>H$_3$). ^{31}P NMR (121.49 MHz, $CDCl_3$, *o*-H_3PO_4 as internal standard) δ (ppm): 20.62 (*s*). Anal. Calcd. for $C_{16}H_{22}NO_4P$: C, 59.44; H, 6.86; N, 4.33. Found: C, 59.67; H, 7.05; N, 4.58.

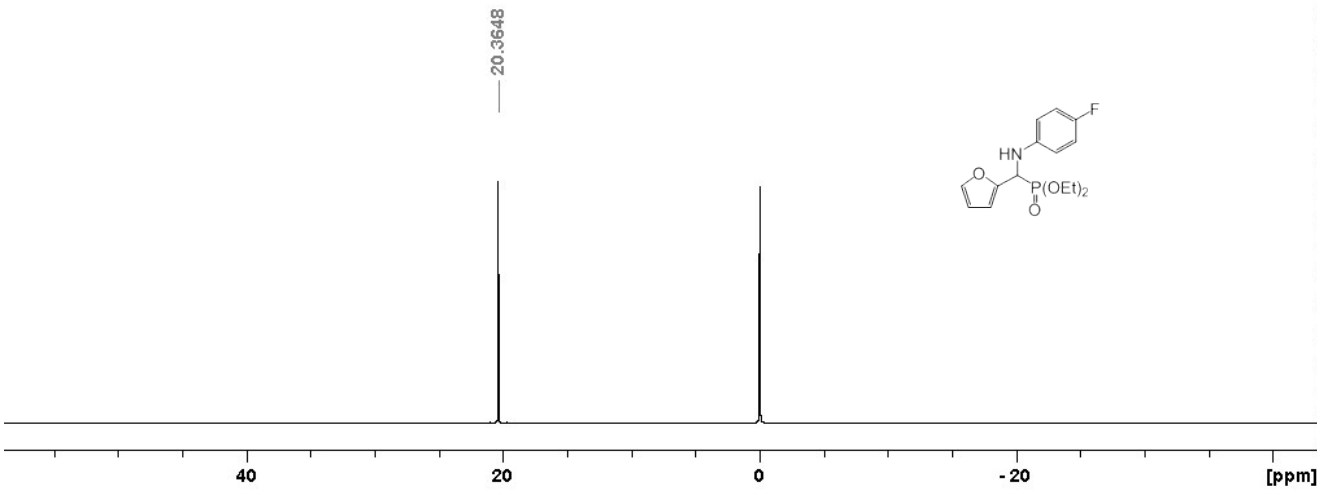


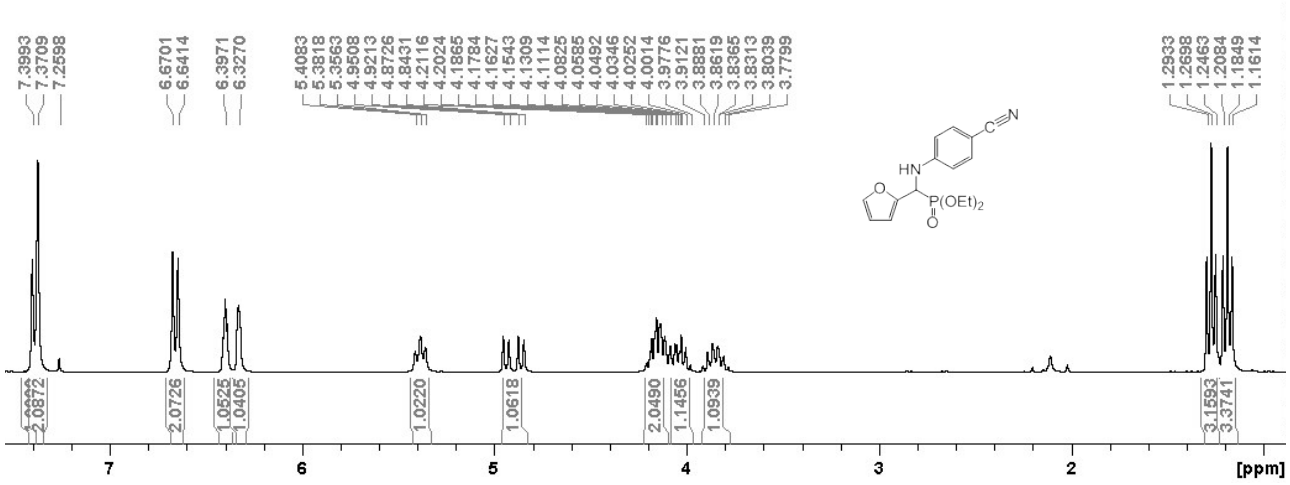
^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm): 7.35 (s, 1H, H_{fur}), 7.24 (t, 2H, *J* = 7.23, 8.82 Hz, H_{arom}), 6.92 (d, 2H, *J* = 8.55 Hz, H_{arom}), 6.78 (t, 1H, *J* = 7.17, 6.45 Hz, H_{arom}), 6.62 (brs, 1H, H_{fur}), 6.33 (brs, 1H, H_{fur}), 5.31 (d, 1H, *J* = 24.58 Hz, C<u>H</u>), 4.20-3.98 (m, 4H, -OC<u>H</u>$_2$CH$_3$), 2,92 (s, 3H, -NC<u>H</u>$_3$), 1.20 (t, 6H, *J* = 7.01 Hz, -OCH$_2$C<u>H</u>$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 149.9 (d, *J* = 6.49 Hz, C_q), 147.7 (d, *J* = 14.28 Hz, C_q), 142.56 (d, *J* = 3.16 Hz, CH_{fur}), 129.0 (s, CH_{arom}), 118.3 (s, CH_{arom}), 114.1 (d, *J* = 2.56 Hz, CH_{arom}), 110.6 (d, *J* = 7.15 Hz, CH_{fur}), 110.2 (s, CH_{fur}), 62.4 (d, *J* = 7.16 Hz, -O<u>C</u>H$_2$CH$_3$), 63.1 (d, *J* = 7.10 Hz, -O<u>C</u>H$_2$CH$_3$), 56.0 (d, *J* = 166.31 Hz, <u>C</u>H), 34.27 (s, -N<u>C</u>H$_3$), 16.3 (d, *J* = 5.54 Hz, -OCH$_2$<u>C</u>H$_3$), 16.1 (d, *J* = 5.68 Hz, -OCH$_2$<u>C</u>H$_3$). ^{31}P NMR (121.49 MHz, $CDCl_3$) δ (ppm): 19.61 (*s*). Anal. Calcd. for $C_{16}H_{22}NO_4P$: C, 59.44; H, 6.86; N, 4.33. Found: C, 59.69; H, 7.14; N, 4.71.

4. NMR spectra





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4.1309
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4.0492
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4.0252
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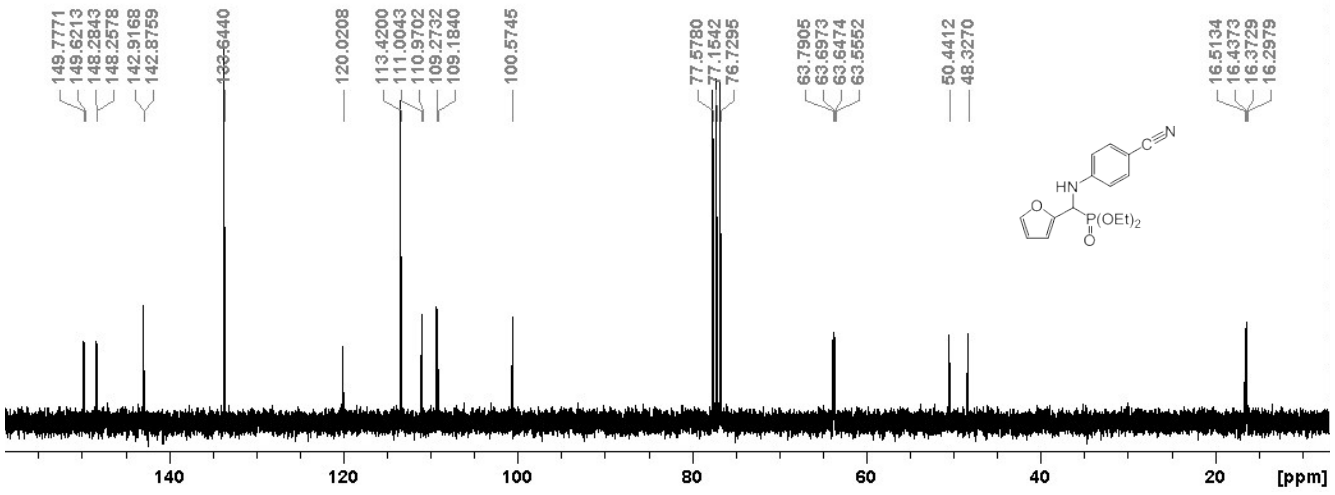
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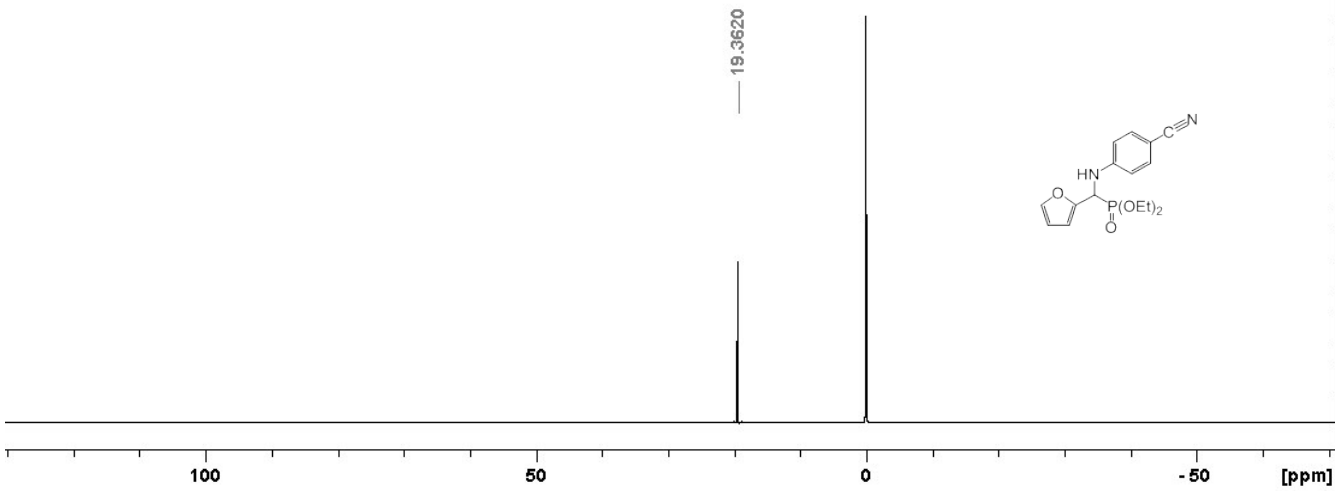
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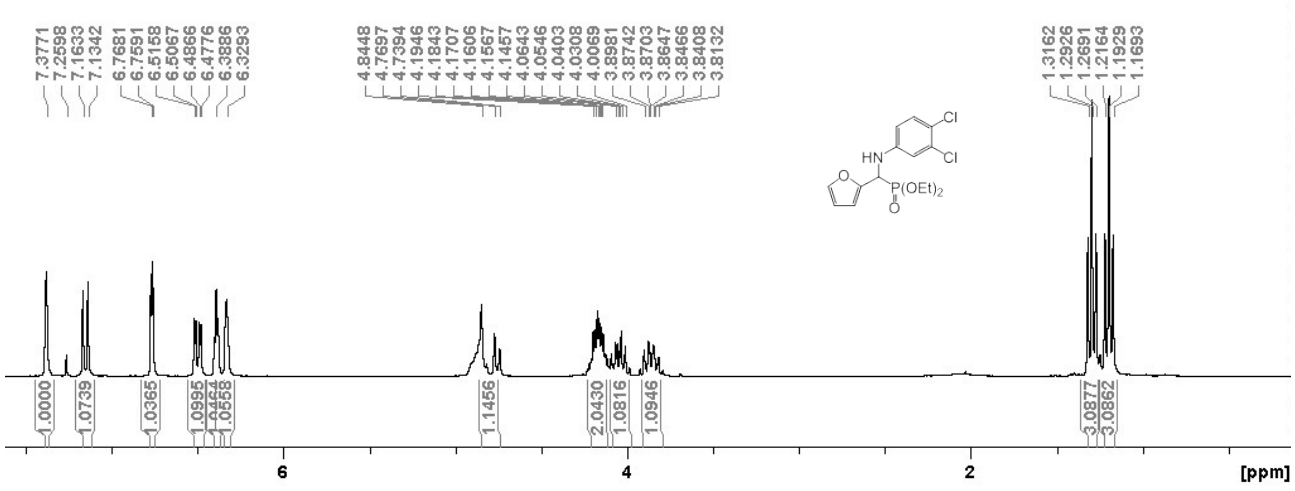
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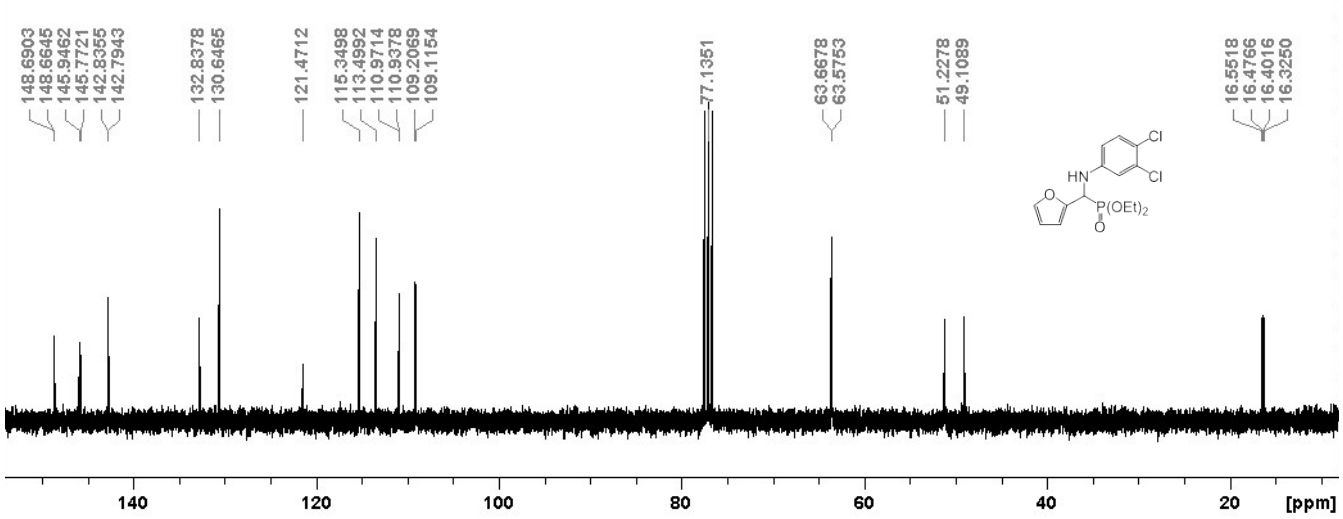
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51.2278
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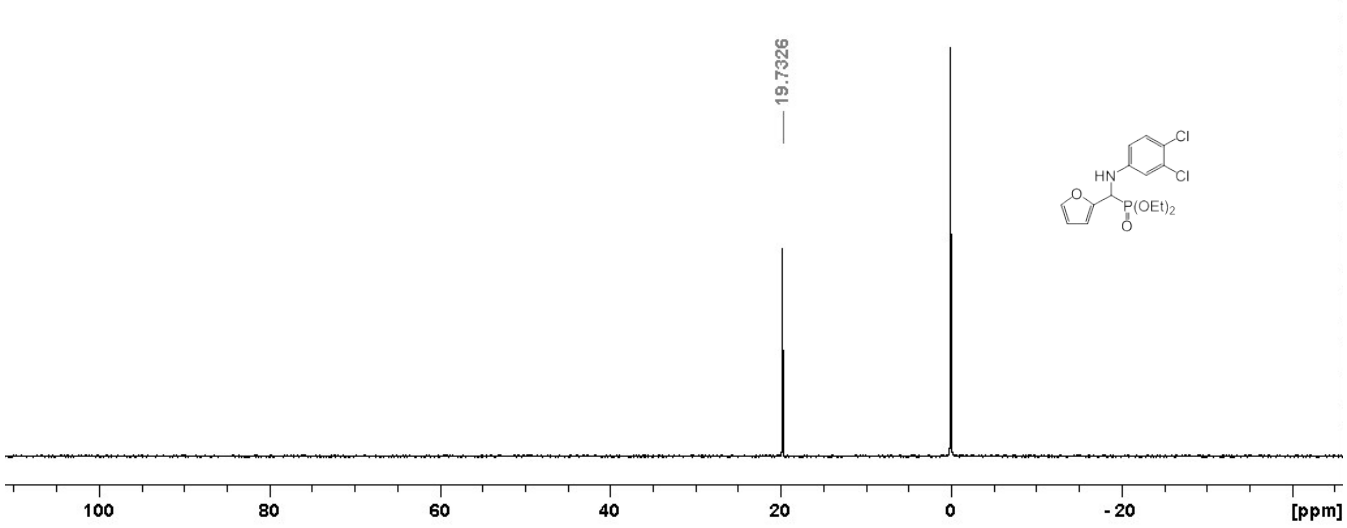
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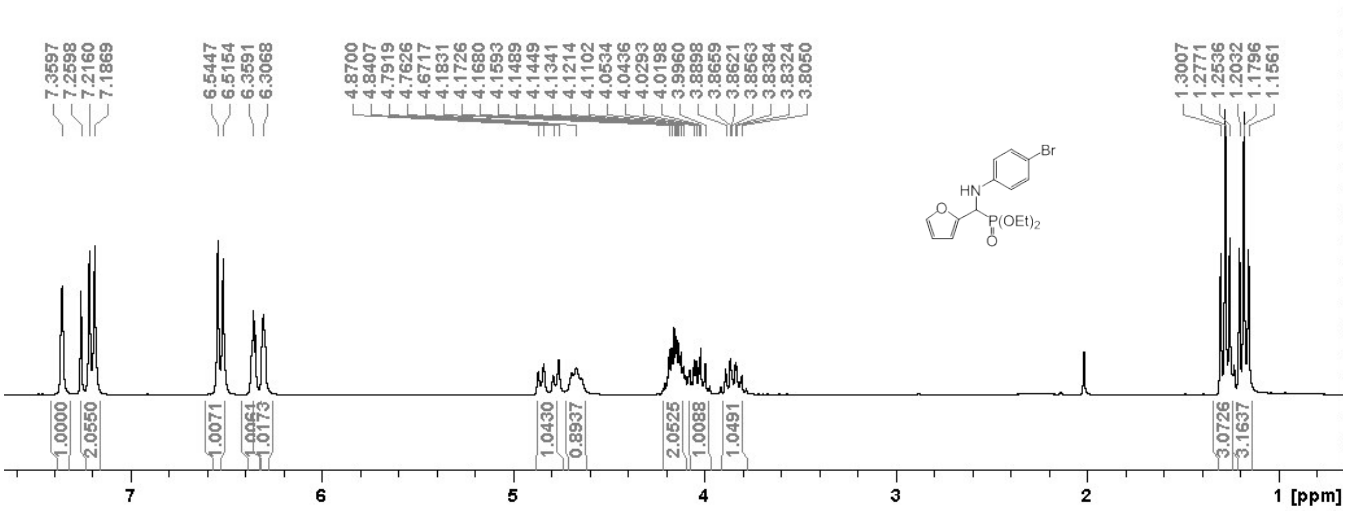
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3
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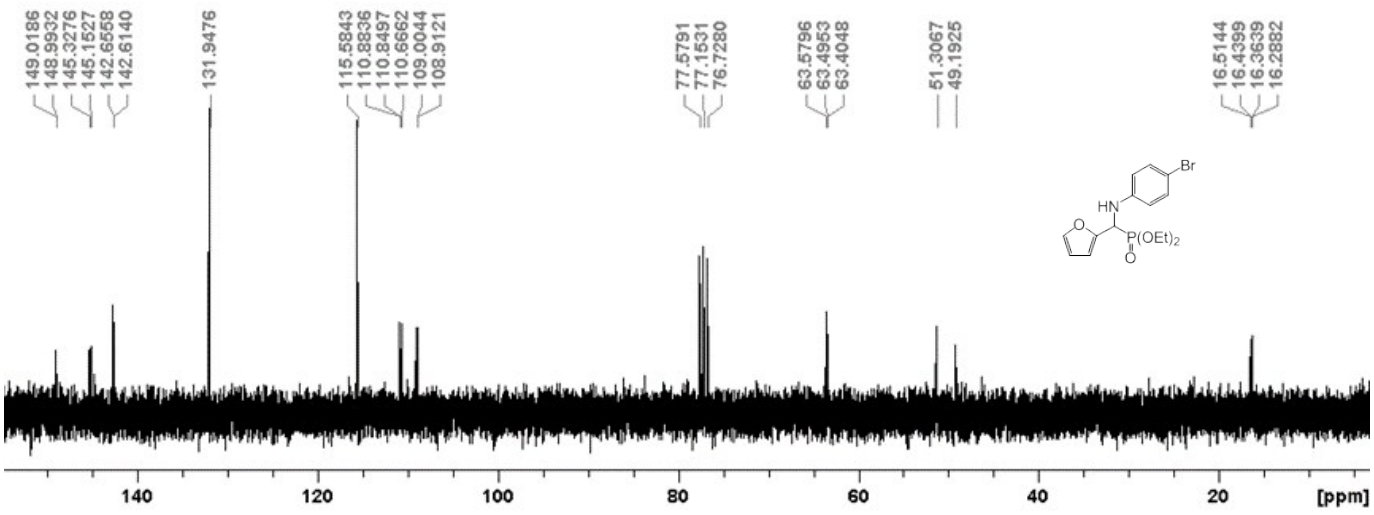
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51.3067
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16.5144
16.4399
16.3639
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O
P(OEt)2
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120
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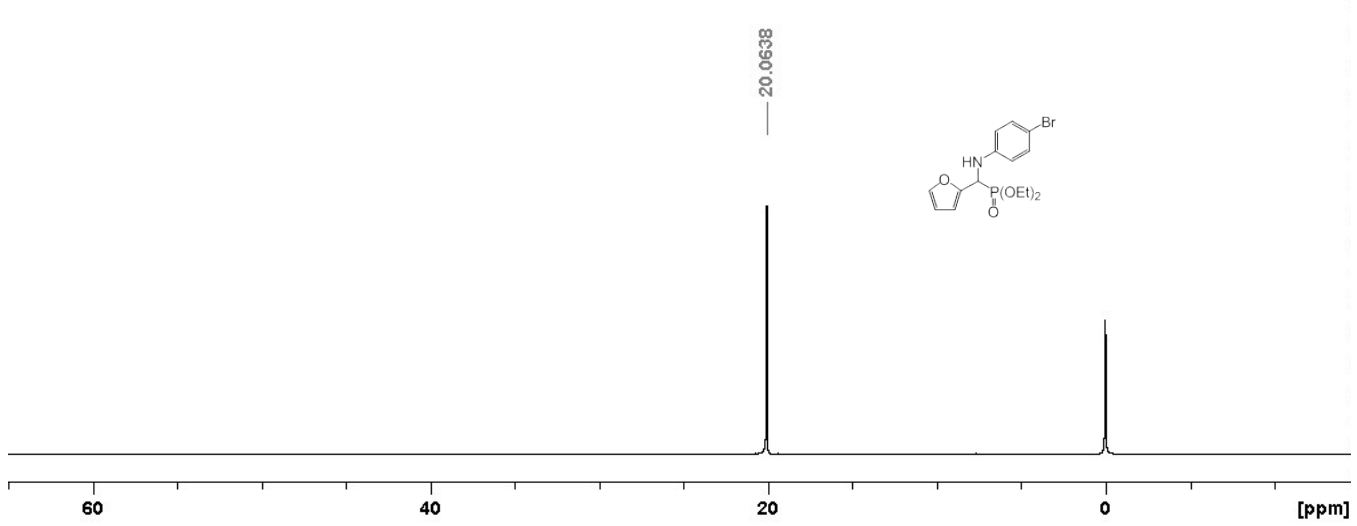
60
40
20
[ppm]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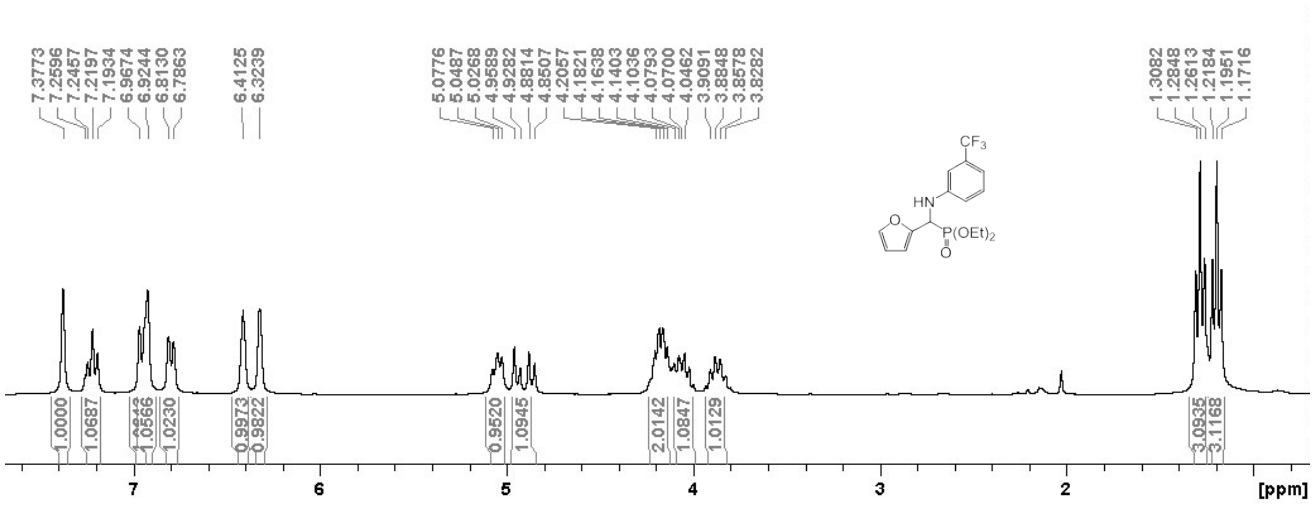
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4.0700
4.0462
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3.8848
3.8578
3.8282
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CF3
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O
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0.9520
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1.0847
1.0129
3.0935
3.1168
7
6
5
4
3
2
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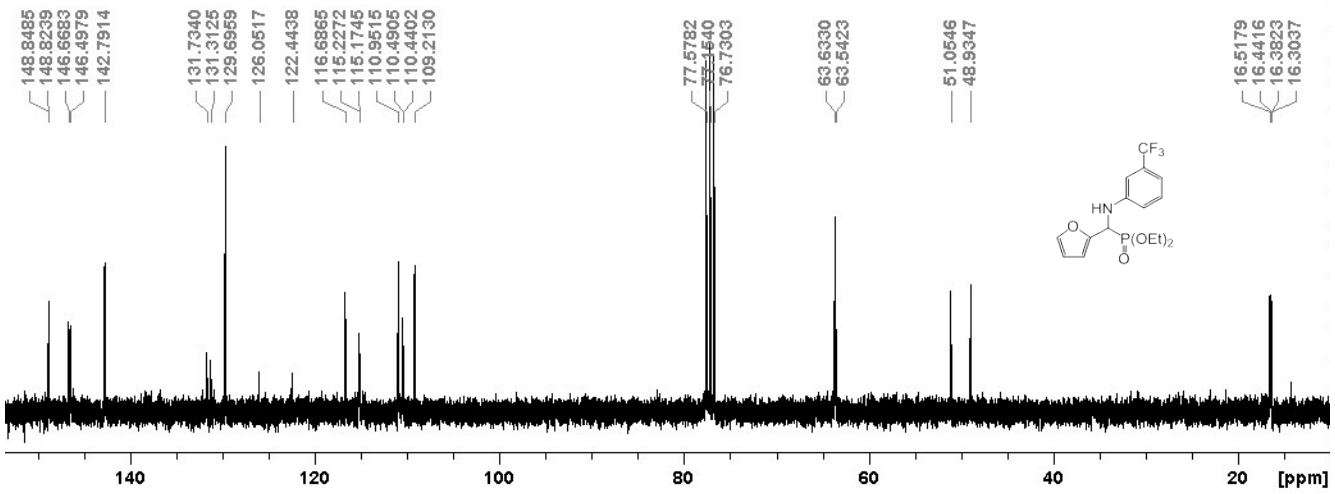
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115.1745
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77.1640
76.7303
63.6330
63.5423
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48.9347
16.5179
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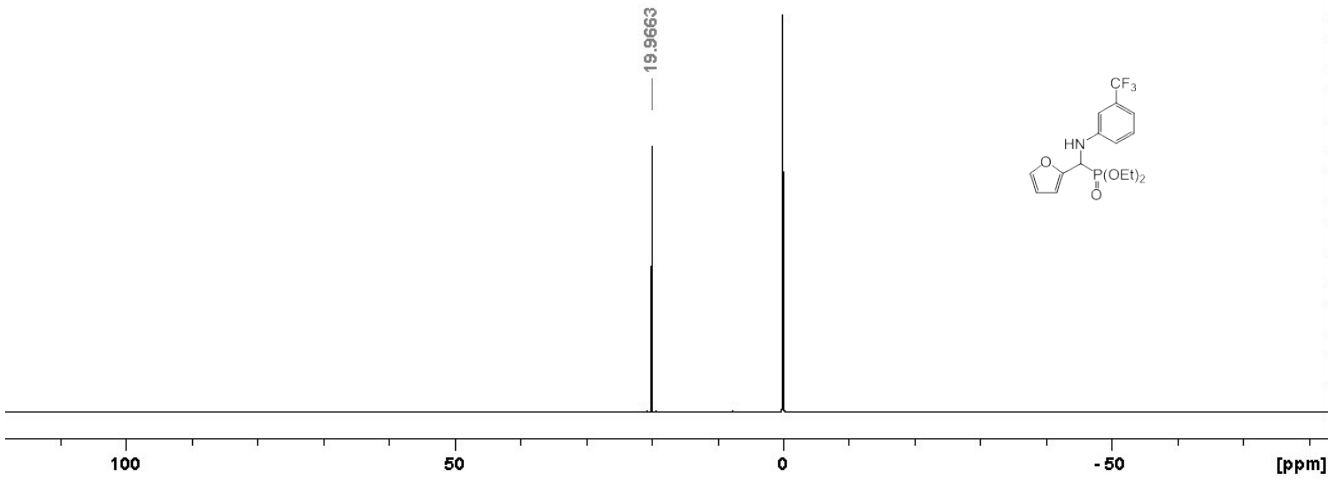
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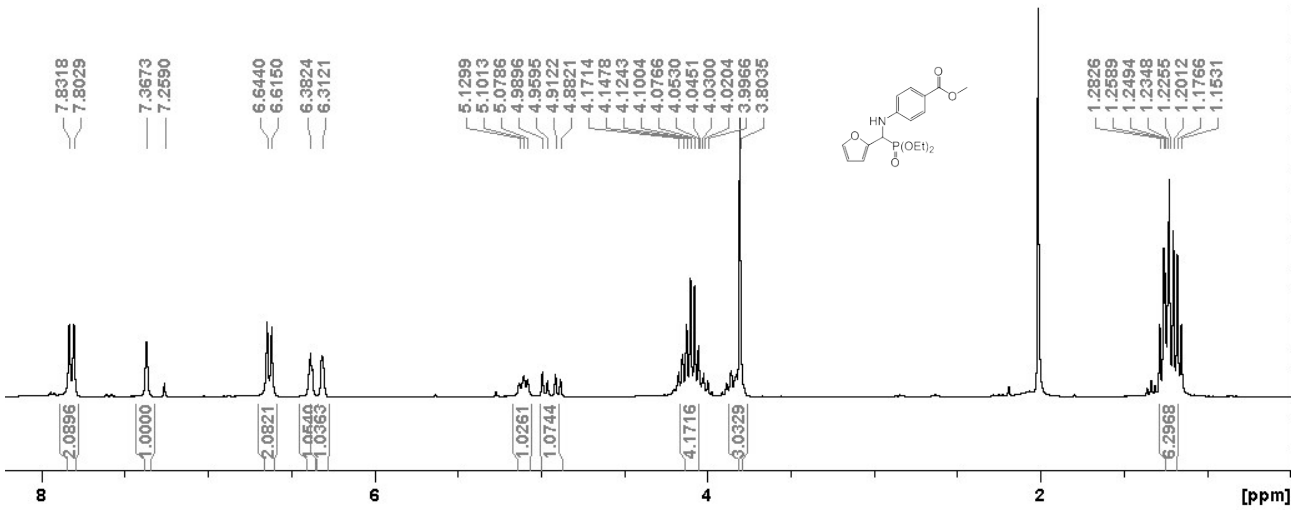
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4.0300
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1.2589
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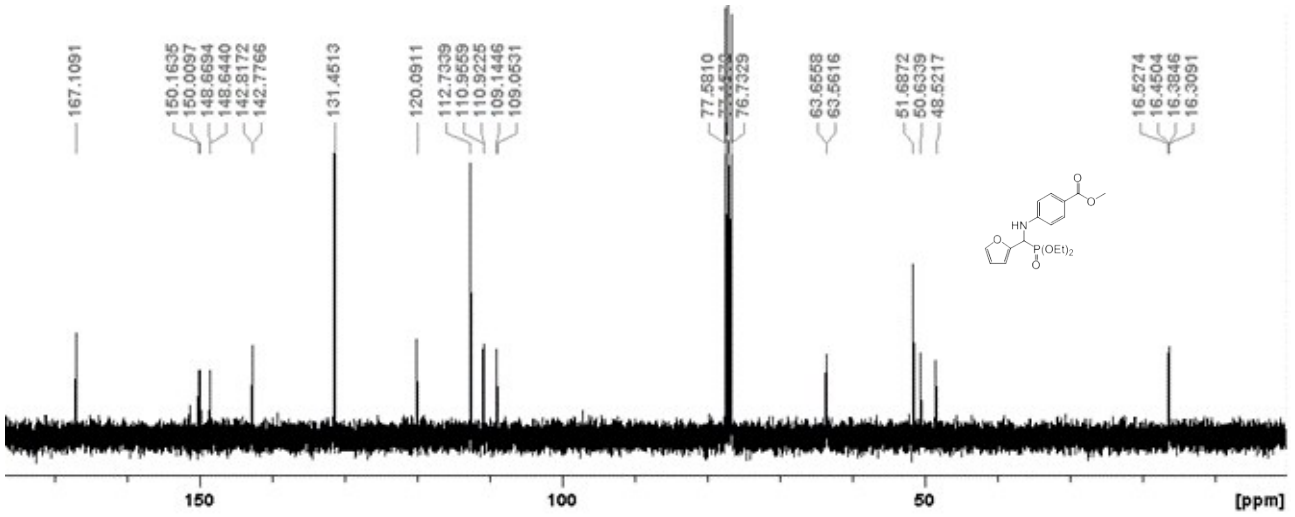
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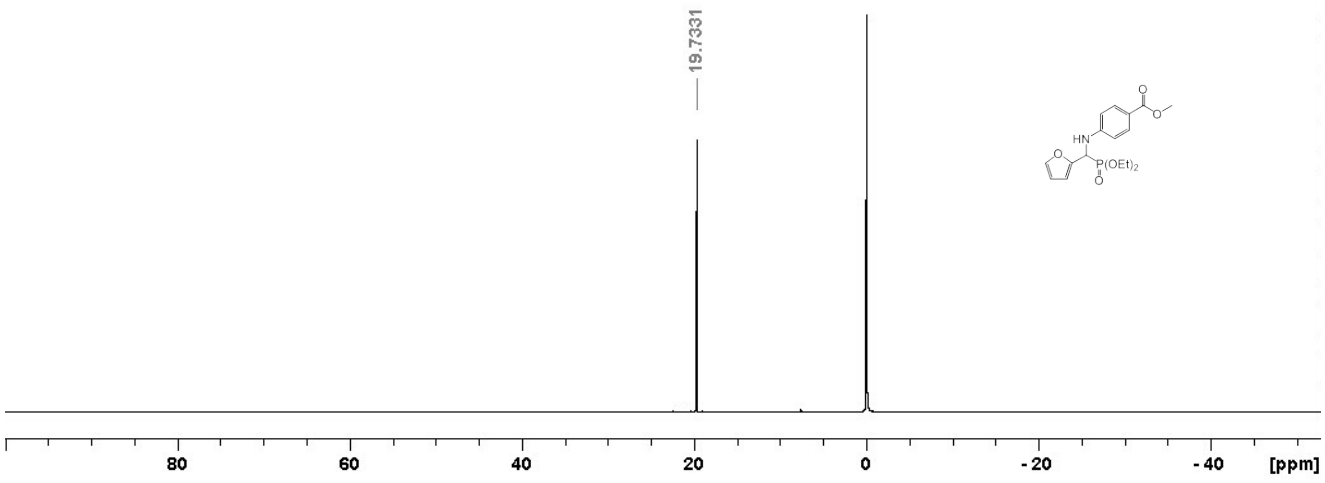
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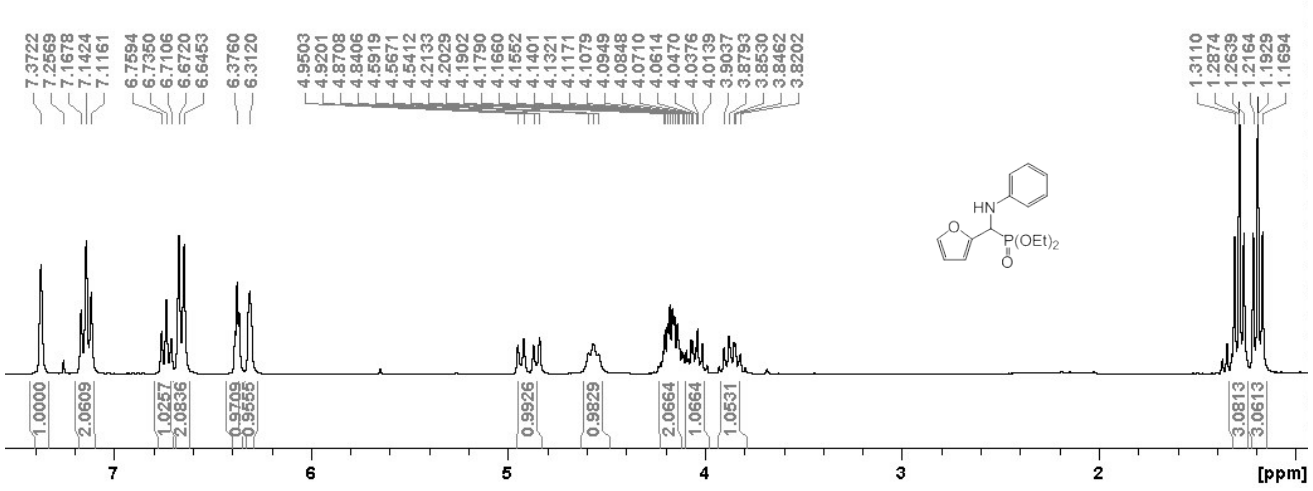
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4.1552
4.1401
4.1321
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4.0949
4.0848
4.0710
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4.0376
4.0139
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3.8793
3.8530
3.8462
3.8202
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1.2639
1.2164
1.1929
1.1694
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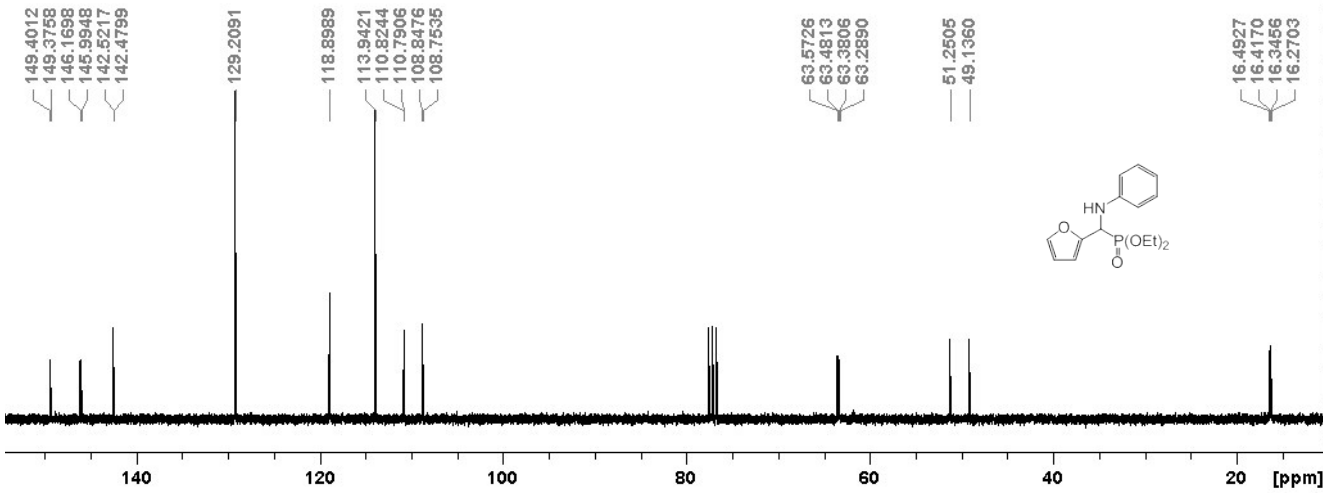
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108.8476
108.7535
63.5726
63.4813
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63.2890
51.2505
49.1360
16.4927
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HN
O
P(OEt)2
O
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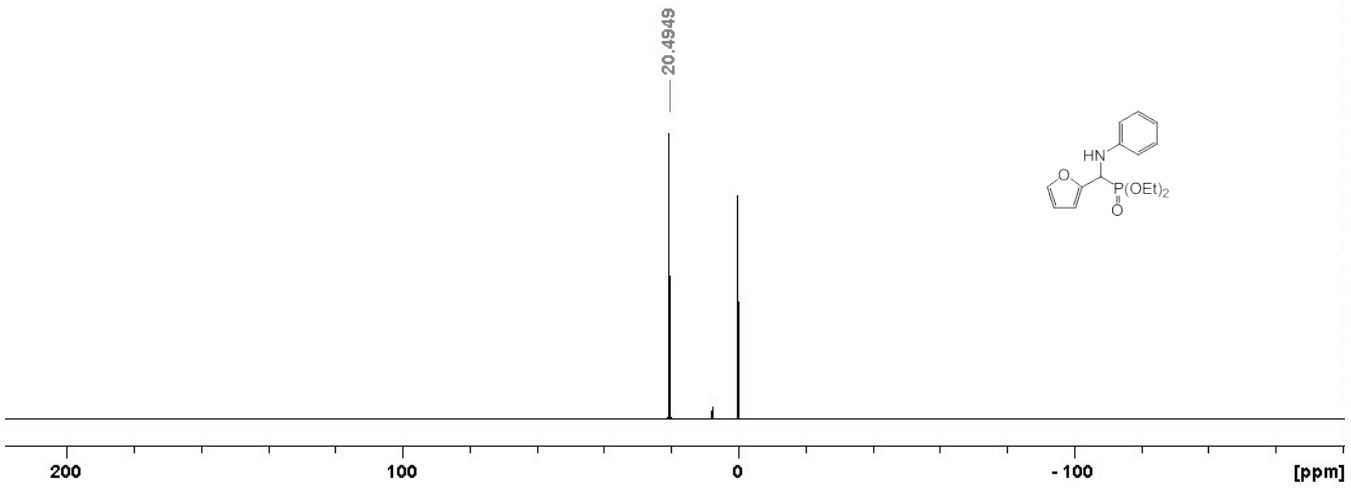
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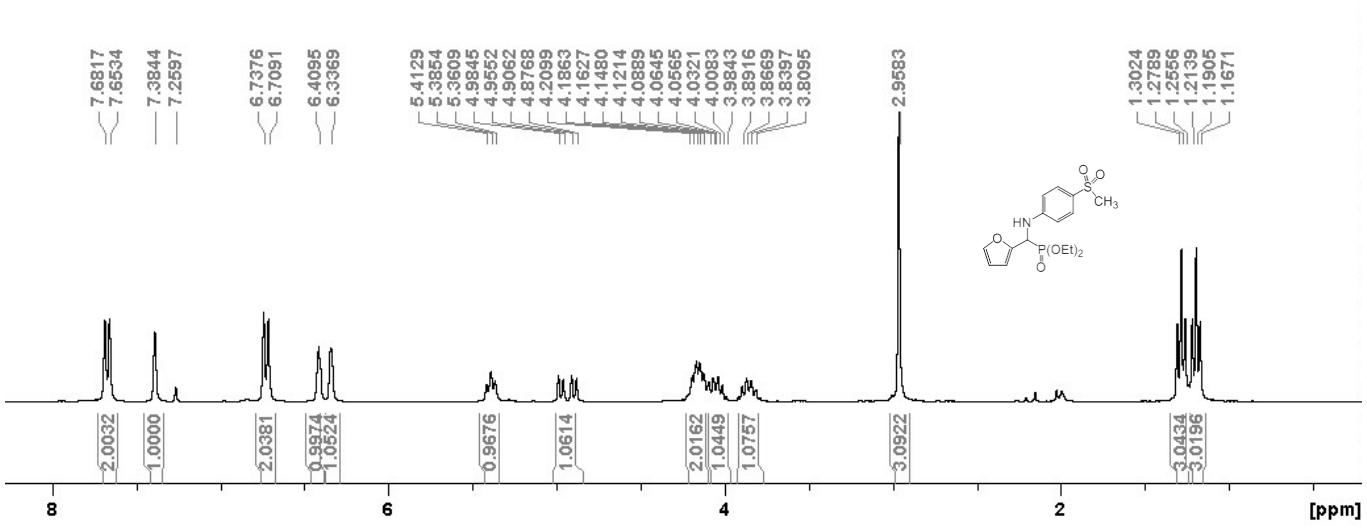
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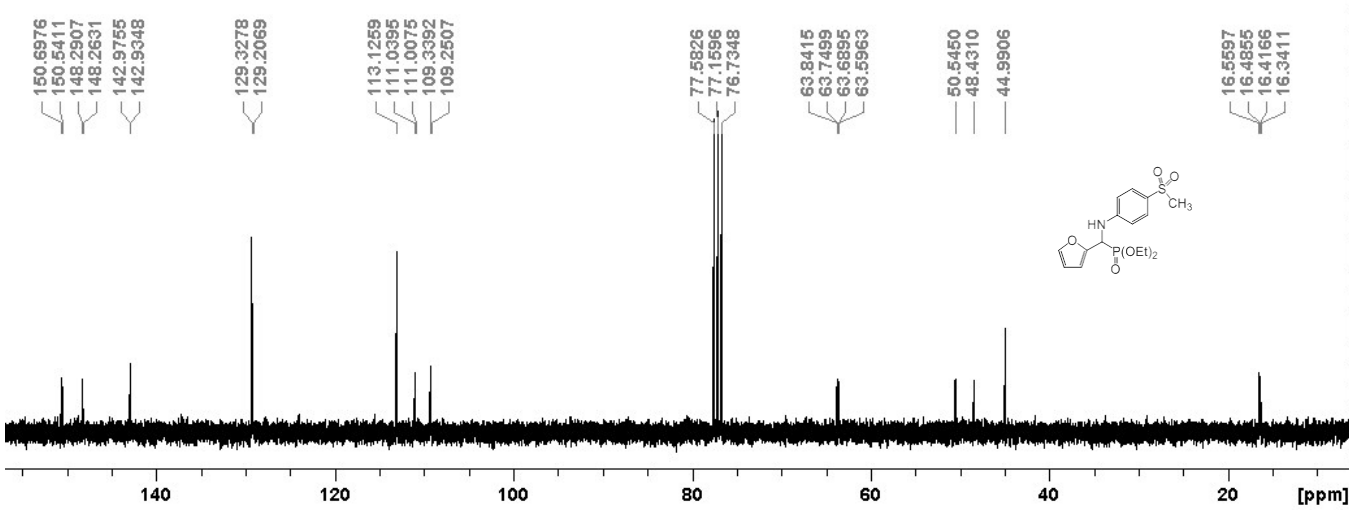
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50.5450
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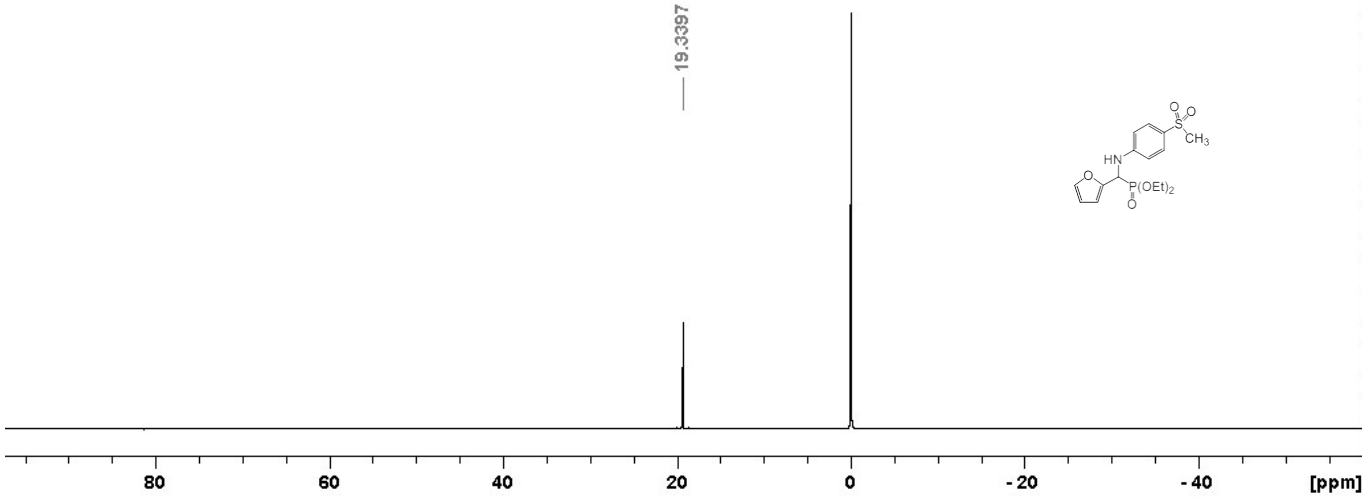
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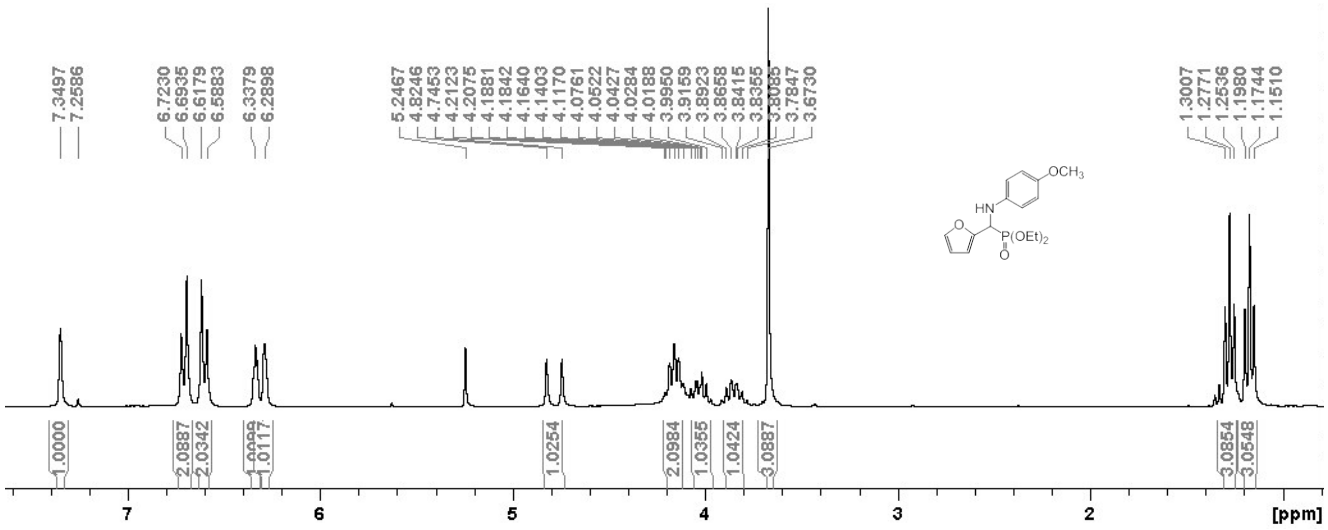
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4.1640
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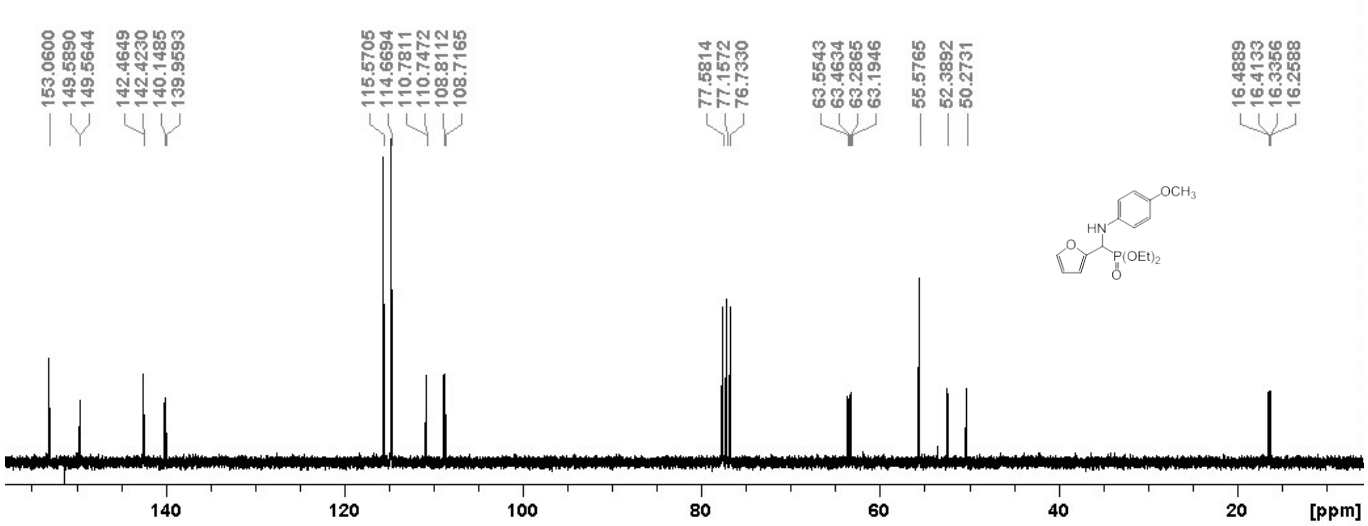
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P(OEt)2
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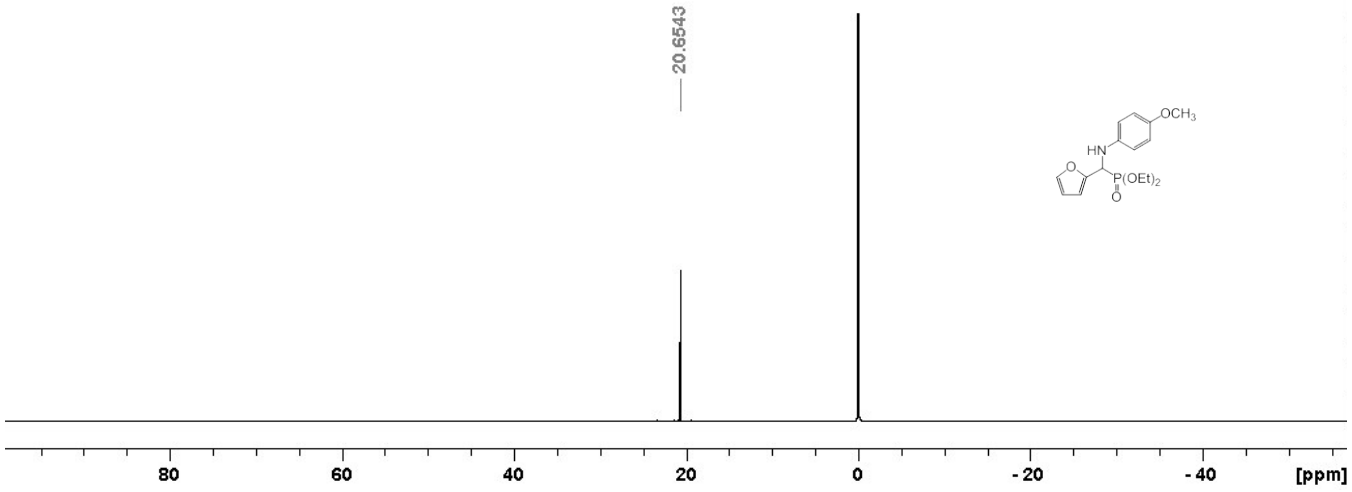
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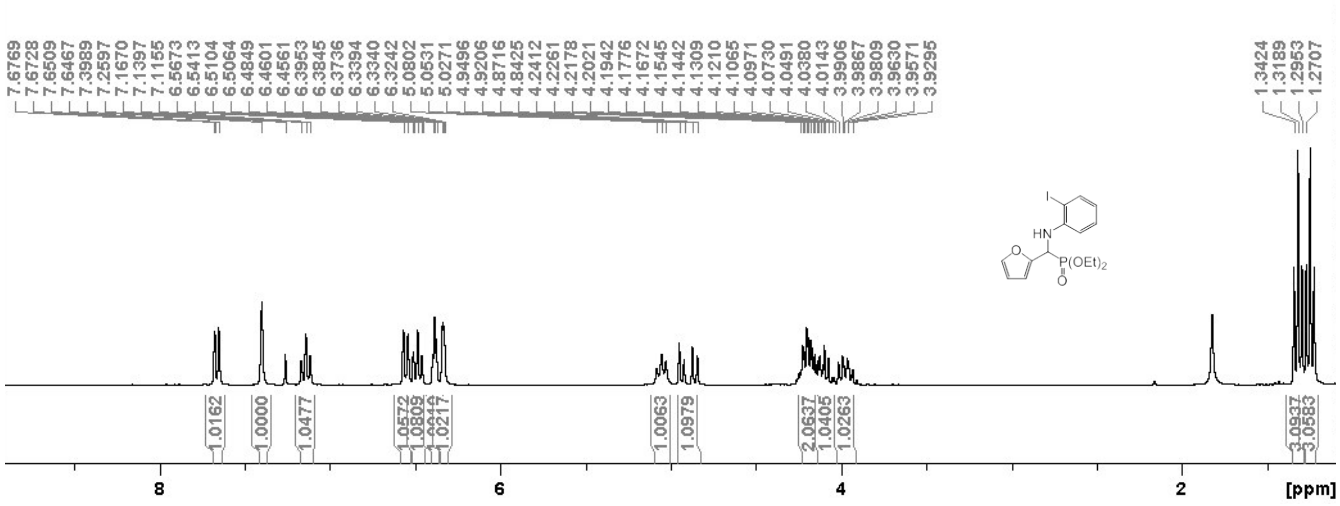
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6.4849
6.4601
6.4561
6.3953
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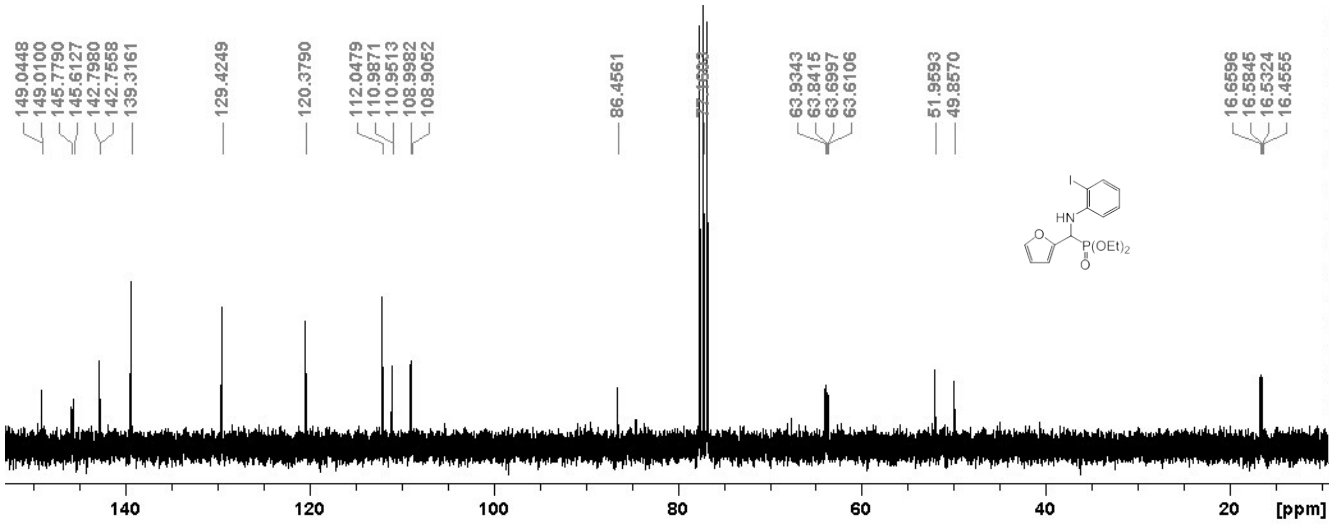
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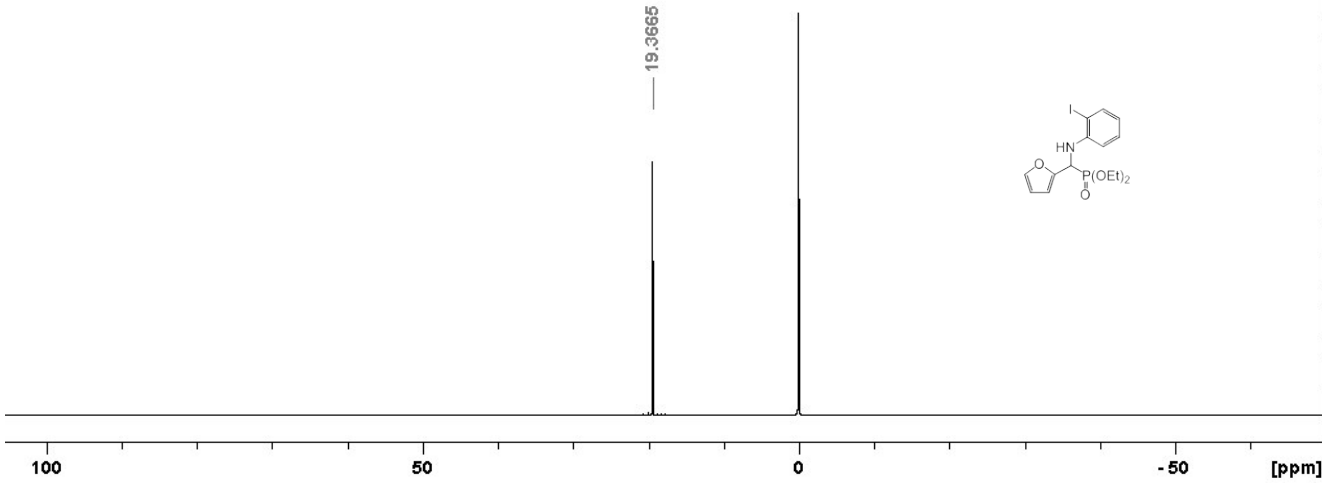
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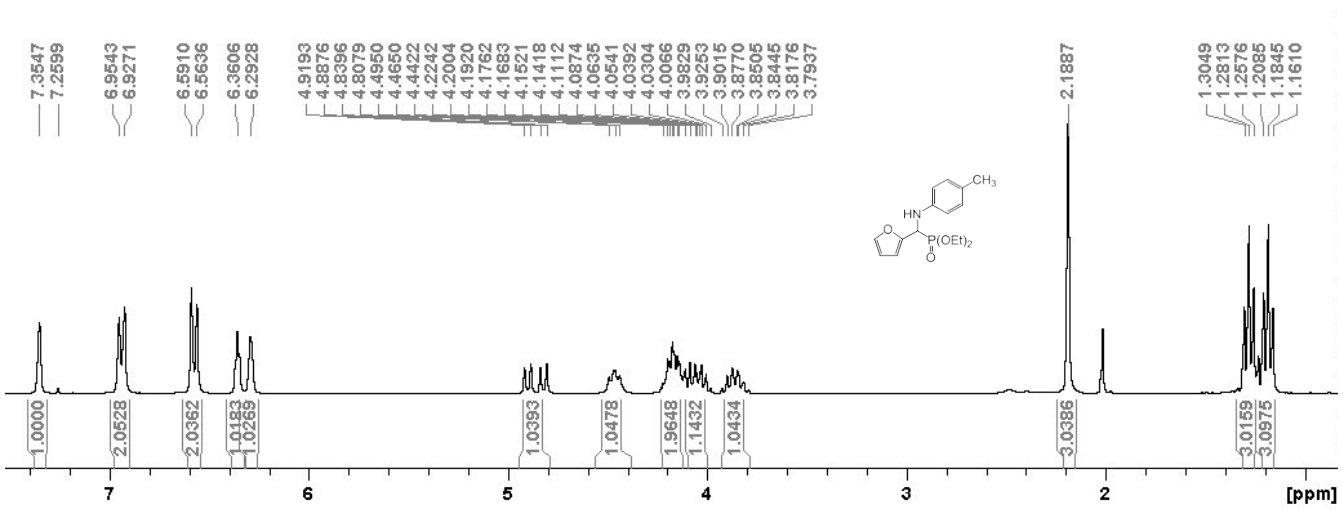
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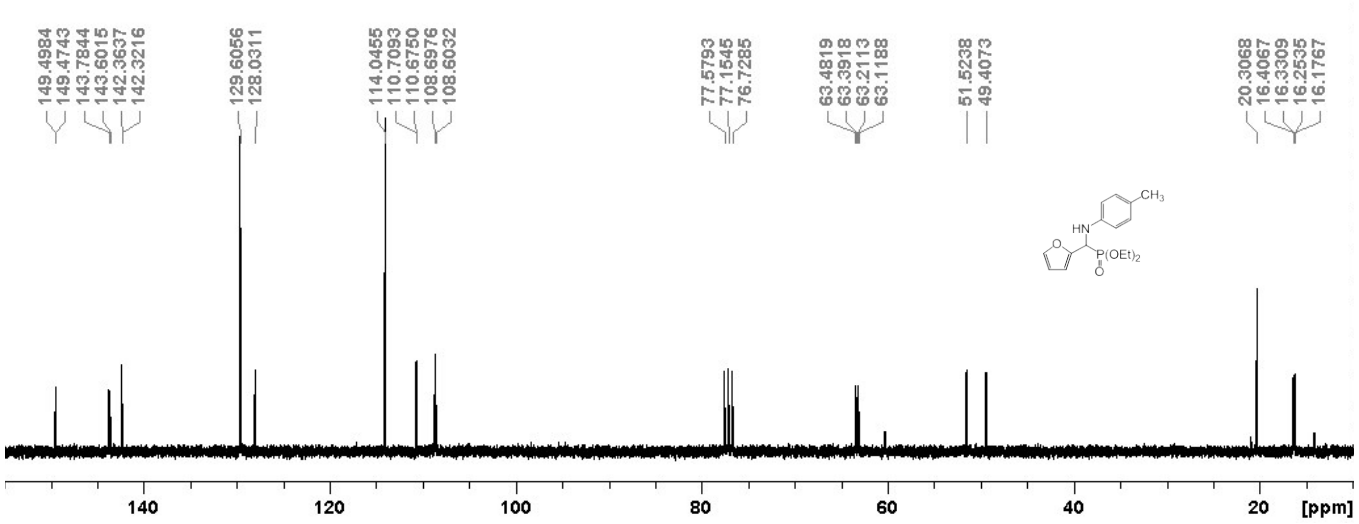
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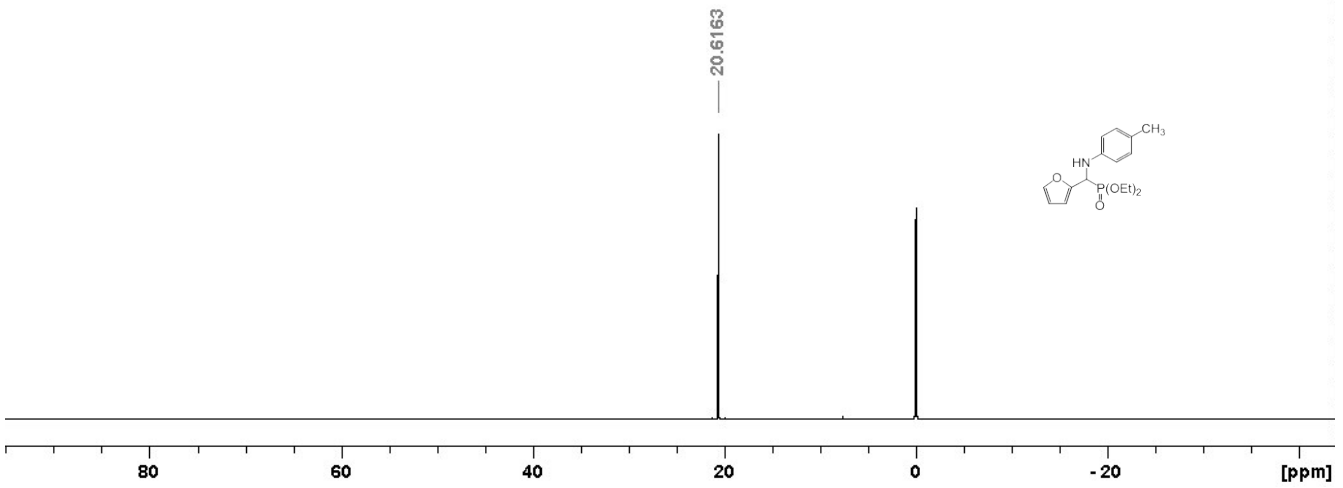
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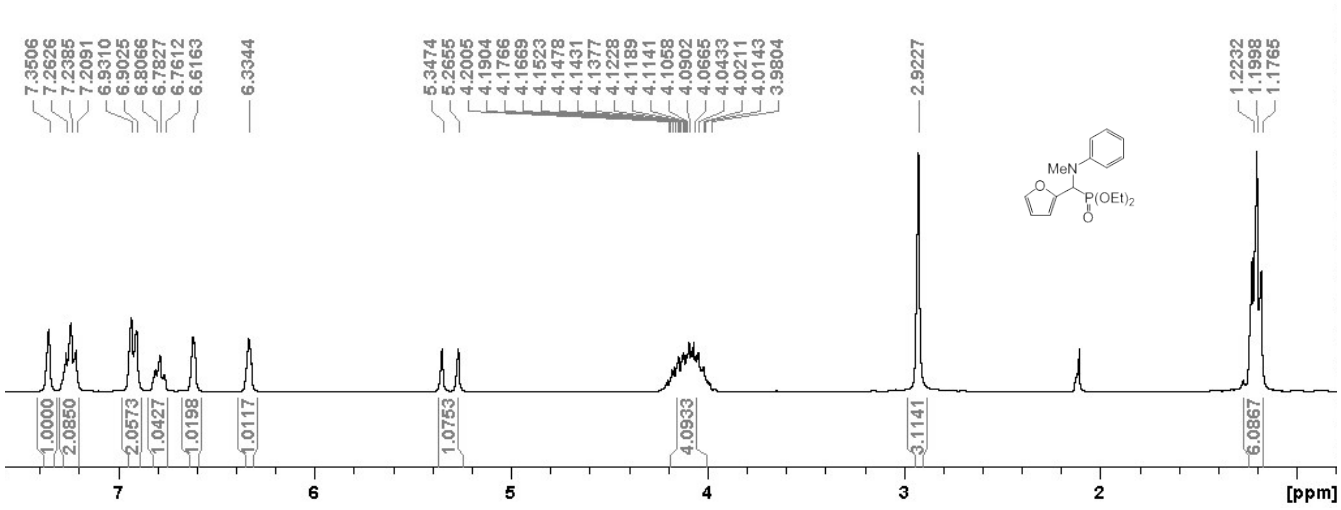
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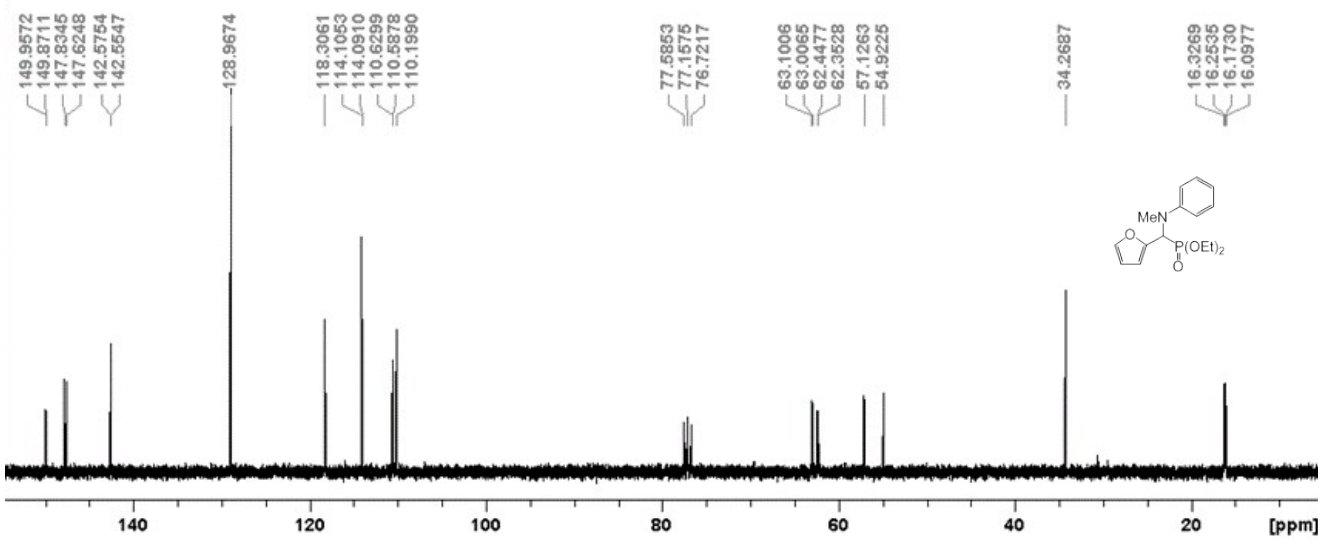
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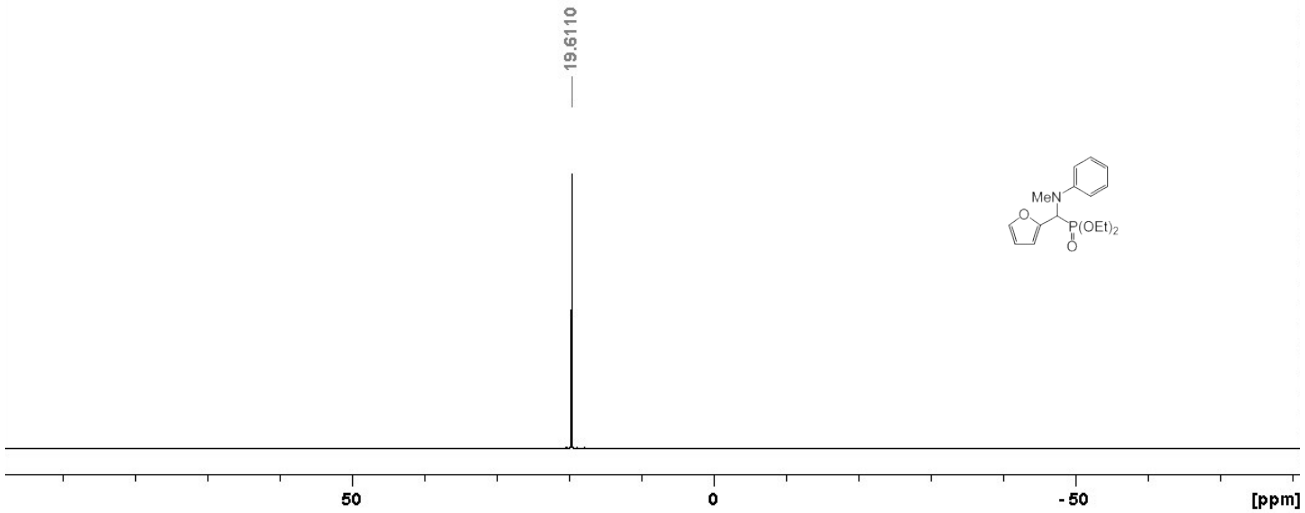
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