

Supporting Information for

Direct Transformation of Amides into  $\alpha$ -Amino Phosphonates  
via a Reductive Phosphination Process

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## 1. General:

All reactions were carried out under nitrogen atmosphere. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. THF was freshly distilled over sodium with the use of diphenyl ketone as an indicator. Infrared spectra were obtained on a Nicolet Avatar 330 FT-IR spectrometer. The data are reported in reciprocal centimetres ( $\text{cm}^{-1}$ ).  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were measured on Bruker AVIII 400M spectrometers with  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as internal standard or 85%  $\text{H}_3\text{PO}_4$  as external standard for  $^{31}\text{P}$  NMR (162 MHz). Chemical shifts were reported in units (ppm) by assigning TMS resonance in the  $^1\text{H}$  spectrum as 0.00 ppm and  $\text{CDCl}_3$  resonance in the  $^{13}\text{C}$  spectrum as 77.23 ppm. All coupling constants ( $J$  values) were reported in Hertz (Hz). The data is being reported as s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, and m = multiplet. Chemical shifts of common trace  $^1\text{H}$  NMR impurities (ppm):  $\text{H}_2\text{O}$ : 1.56,  $\text{CHCl}_3$ : 7.26. Column chromatography was performed on silica gel 300-400 mesh. The CAS number of the known compound was listed. The unknown products were further characterized by HRMS-ESI and IR.

### General Experimental Procedure of $\alpha$ -Amino Phosphonates from Secondary Amides

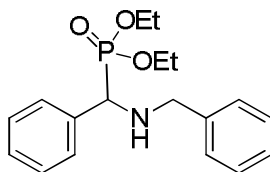
Treating secondary amide (0.3 mmol) in anhydrous THF (3.0 mL) with  $\text{Cp}_2\text{ZrHCl}$  (171 mg, 0.66 mmol) under nitrogen which was stirred at rt, then added  $H$ -phosphonate (0.36 mmol) until the suspension cleared (about 5 - 15 min) and the mixture was stirred at 60 °C for about 12 hours in a Schlenk tube. Then the reaction was quenched with saturated sodium bicarbonate (35.0 mL), and extracted with EtOAc (3 \* 5.0 mL). The combined organic extracts were washed with brine (10 mL), dried over  $\text{Na}_2\text{SO}_4$ , and evaporated to leave the crude product, which was purified by flash chromatography using petroleum–AcOEt (2:1, v/v) as the eluent to give the corresponding product **3a-s** and **3x-3aa**.

### General Experimental Procedure of $\alpha$ -Amino Phosphonates from Tertiary Amides

Treating tertiary amide (0.3 mmol) in anhydrous THF (3.0 mL) with  $\text{Cp}_2\text{ZrHCl}$  (93.3 mg, 0.36 mmol) under nitrogen which was stirred at rt, then added  $H$ -phosphonate (0.36 mmol) until the suspension cleared (about 5 - 15 min) and the mixture was stirred at 60 °C for about 12 hours in a Schlenk tube. Workup is the same as the above-mentioned method. A number of products were synthesized according to this procedure (**3t-3w**).

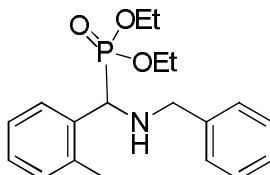
## 2. Spectral Data.

### Diethyl ((benzylamino)(phenyl)methyl)phosphonate (3a, CAS Number: 63000-01-1)



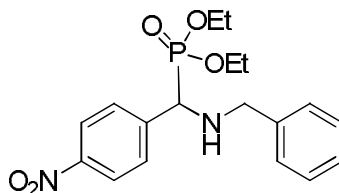
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.44 – 7.42 (m, 2H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 3H), 7.26 – 7.22 (m, 3H), 4.11 – 3.92 (m, 4H), 3.84 – 3.78 (m, 2H), 3.56 – 3.52 (d,  $J = 13.3$  Hz, 1H), 2.31 (s, 1H), 1.27 – 1.25 (t,  $J = 7.0$  Hz, 3H), 1.14 – 1.10 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 139.4 (s), 135.8 (d,  $J = 3.9$  Hz), 128.8 (d,  $J = 6.5$  Hz), 128.6 (d,  $J = 2.2$  Hz), 128.4 (d,  $J = 2.2$  Hz), 128.0 (d,  $J = 3.6$  Hz), 127.2 (s), 63.0 (d,  $J = 6.8$  Hz), 62.9 (d,  $J = 7.0$  Hz), 59.7 (d,  $J = 153.4$  Hz), 51.3 (d,  $J = 17.5$  Hz), 16.5 (d,  $J = 5.8$  Hz), 16.3 (d,  $J = 5.7$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.5. MS-ESI:  $m/z$  334.2 ( $[\text{M}+\text{H}]^+$ ).

### Diethyl ((benzylamino)(o-tolyl)methyl)phosphonate (3b, CAS Number: 1403485-47-1)



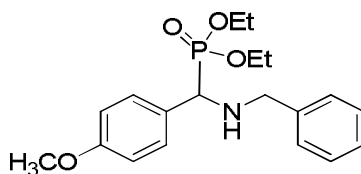
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.63 – 7.61 (m, 1H), 7.31 – 7.15 (m, 8H), 4.31 – 4.25 (d,  $J = 20.40$  Hz, 1H), 4.15 – 4.03 (m, 2H), 3.98 – 3.89 (m, 1H), 3.82 – 3.72 (m, 2H), 3.53 – 3.50 (d,  $J = 13.3$  Hz, 1H), 2.32 (s, 1H), 2.18 (s, 3H), 1.30 – 1.27 (t,  $J = 7.0$  Hz, 3H), 1.12 – 1.08 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 139.5 (s), 137.6 (d,  $J = 7.3$  Hz), 134.0 (d,  $J = 3.3$  Hz), 130.5 (d,  $J = 2.1$  Hz), 128.5 (s), 127.7 (m), 127.2 (s), 126.4 (d,  $J = 2.9$  Hz), 63.0 (d,  $J = 7.1$  Hz), 62.9 (d,  $J = 7.1$  Hz), 54.3 (d,  $J = 154.0$  Hz), 51.1 (d,  $J = 17.2$  Hz), 19.7 (s), 16.6 (d,  $J = 5.8$  Hz), 16.4 (d,  $J = 5.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 24.3. MS-ESI:  $m/z$  370.2 ( $[\text{M}+\text{Na}]^+$ ).

### Diethyl ((benzylamino)(4-nitrophenyl)methyl)phosphonate (3c, CAS Number: 272786-89-7)



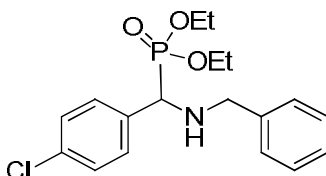
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.24 – 8.22 (d,  $J = 8.1$  Hz, 2H), 7.64 – 7.63 (d,  $J = 2.2$  Hz, 1H), 7.62 – 7.61 (d,  $J = 2.3$  Hz, 1H), 7.34 – 7.21 (m, 5H), 4.18 – 4.13 (d,  $J = 20.8$  Hz, 1H), 4.11 – 3.95 (m, 4H), 3.82 – 3.79 (d,  $J = 13.3$  Hz, 1H), 3.54 – 3.51 (d,  $J = 13.4$  Hz, 1H), 2.41 (s, 1H), 1.30 – 1.26 (t,  $J = 7.0$  Hz, 3H), 1.21 – 1.18 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 147.8 (d,  $J = 3.5$  Hz), 144.1 (d,  $J = 5.1$  Hz), 138.8 (s), 129.6 (d,  $J = 5.8$  Hz), 128.7 (s), 128.4 (s), 127.6 (s), 123.8 (d,  $J = 2.2$  Hz), 63.4 (d,  $J = 7.0$  Hz), 63.2 (d,  $J = 7.0$  Hz), 59.6 (d,  $J = 150.5$  Hz), 51.7 (d,  $J = 16.9$  Hz), 16.6 (d,  $J = 5.6$  Hz), 16.5 (d,  $J = 5.6$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 21.6. MS-ESI:  $m/z$  379.1 ( $[\text{M}+\text{H}]^+$ ).

**Diethyl ((benzylamino)(4-methoxyphenyl)methyl)phosphonate (3d, CAS Number: 171503-10-9)**



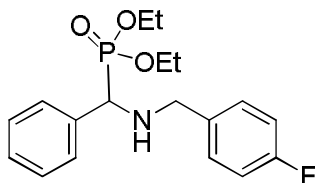
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.36 – 7.33 (m, 2H), 7.30 – 7.28 (m, 2H), 7.26 – 7.24 (m, 3H), 6.92 – 6.90 (d,  $J = 8.5$  Hz, 2H), 4.11 – 4.04 (m, 2H), 3.99 – 3.95 (m, 2H), 3.85 – 3.78 (m, 5H), 3.55 – 3.52 (d,  $J = 13.4$  Hz, 1H), 2.25 (s, 1H), 1.30 – 1.26 (t,  $J = 7.0$  Hz, 3H), 1.16 – 1.13 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 159.5 (d,  $J = 2.9$  Hz), 139.5 (s), 129.9 (d,  $J = 6.6$  Hz), 128.5 (s), 127.2 (s), 114.1 (d,  $J = 2.1$  Hz), 63.0 (d,  $J = 6.9$  Hz), 62.85 (d,  $J = 7.1$  Hz), 59.0 (d,  $J = 155.0$  Hz), 55.4 (s), 51.2 (d,  $J = 17.2$  Hz), 16.6 (d,  $J = 6.0$  Hz), 16.4 (d,  $J = 6.0$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.8. MS-ESI:  $m/z$  364.2 ( $[\text{M}+\text{H}]^+$ ).

**Diethyl ((benzylamino)(4-chlorophenyl)methyl)phosphonate (3e, CAS Number: 171503-17-6)**



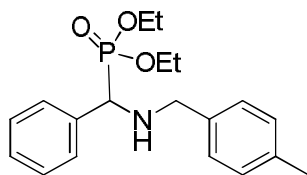
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.39 – 7.34 (m, 3H), 7.33 – 7.31 (m, 1H), 7.30 – 7.28 (m, 2H), 7.26 – 7.22 (m, 3H), 4.12 – 3.94 (m, 4H), 3.91 – 3.85 (m, 1H), 3.80 – 3.78 (d,  $J = 13.3$  Hz, 1H), 3.53 – 3.50 (d,  $J = 13.3$  Hz, 1H), 2.30 (s, 1H), 1.27 – 1.25 (t,  $J = 7.0$  Hz, 3H), 1.18 – 1.14 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 139.1 (s), 134.5 (d,  $J = 4.0$  Hz), 133.7 (d,  $J = 3.6$  Hz), 130.1 (d,  $J = 5.8$  Hz), 128.7 (d,  $J = 2.1$  Hz), 128.4 (d,  $J = 14.7$  Hz), 127.3 (s), 63.1 (d,  $J = 6.6$  Hz), 62.9 (d,  $J = 6.6$  Hz), 69.0 (d,  $J = 153.3$  Hz), 51.3 (d,  $J = 17.4$  Hz), 16.5 (d,  $J = 5.9$  Hz), 16.3 (d,  $J = 5.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 22.8. MS-ESI:  $m/z$  368.1 ( $[\text{M}+\text{H}]^+$ ).

**Diethyl (((4-fluorobenzyl)amino)(phenyl)methyl)phosphonate (3f)**



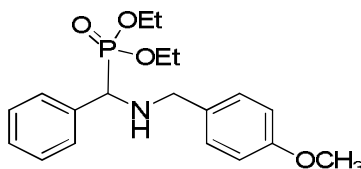
Yellow oil. IR (KBr)  $\nu_{\text{max}}$ : 3309, 2980, 1602, 1509, 1242, 1026, 823  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.43 – 7.33 (m, 5H), 7.32 – 7.19 (m, 2H), 7.00 – 6.96 (m, 2H), 4.11 – 3.92 (m, 4H), 3.82 – 3.75 (m, 2H), 3.54 – 3.50 (d,  $J = 13.2$  Hz, 1H), 2.28 (s, 1H), 1.30 – 1.26 (t,  $J = 7.0$  Hz, 3H), 1.14 – 1.10 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 162.2 (d,  $J = 244.4$  Hz), 135.5 (d,  $J = 63.8$  Hz), 130.0 (d,  $J = 7.7$  Hz), 128.8 (d,  $J = 6.2$  Hz), 128.6 (d,  $J = 2.2$  Hz), 128.1 (d,  $J = 2.8$  Hz), 127.9 (d,  $J = 11.7$  Hz), 115.3 (d,  $J = 21.2$  Hz), 63.1 (d,  $J = 7.4$  Hz), 63.0 (d,  $J = 7.4$  Hz), 59.7 (d,  $J = 153.5$  Hz), 50.6 (d,  $J = 17.4$  Hz), 16.6 (d,  $J = 5.9$  Hz), 16.4 (d,  $J = 5.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.4. HRMS-ESI:  $m/z$  374.1292 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{18}\text{H}_{23}\text{FNaO}_3\text{P}^+$  calcd. 374.1292).

**Diethyl (((4-methylbenzyl)amino)(phenyl)methyl)phosphonate (3g)**



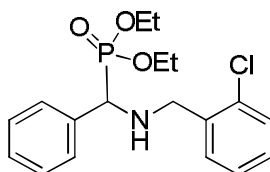
Yellow oil. IR (KBr)  $\nu_{\text{max}}$ : 3312, 2980, 1453, 1244, 1027, 963, 805, 700  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.44 – 7.30 (m, 5H), 7.15 – 7.09 (m, 4H), 4.09 – 3.92 (m, 4H), 3.84 – 3.78 (m, 4H), 3.85 – 3.75 (m, 2H), 3.51 – 3.48 (d,  $J$  = 13.4 Hz, 1H), 2.33 (s, 3H), 2.24 (s, 1H), 1.29 – 1.25 (t,  $J$  = 7.0 Hz, 3H), 1.14 – 1.10 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 136.8 (s), 136.4 (s), 136.0 (d,  $J$  = 4.3 Hz), 129.2 (s), 128.8 (d,  $J$  = 6.6 Hz), 128.5 (d,  $J$  = 2.1 Hz), 128.43 (s), 128.0 (d,  $J$  = 2.9 Hz), 63.0 (d,  $J$  = 6.7 Hz), 62.8 (d,  $J$  = 6.7 Hz), 59.7 (d,  $J$  = 154.2 Hz), 51.0 (d,  $J$  = 17.6 Hz), 21.2 (s), 16.5 (d,  $J$  = 5.8 Hz), 16.4 (d,  $J$  = 5.8 Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.5. HRMS-ESI:  $m/z$  370.1540 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{19}\text{H}_{26}\text{NNaO}_3\text{P}^+$  calcd. 370.1543).

**Diethyl (((4-methoxybenzyl)amino)(phenyl)methyl)phosphonate (3h, CAS Number: 183964-34-3)**



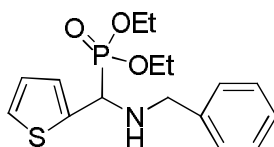
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.43 – 7.41 (d,  $J$  = 7.4 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.17 – 7.15 (d,  $J$  = 8.4 Hz, 2H), 6.85 – 6.83 (d,  $J$  = 8.4 Hz, 2H), 4.09 – 3.92 (m, 4H), 3.84 – 3.73 (m, 5H), 3.49 – 3.46 (d,  $J$  = 13.0 Hz, 1H), 2.24 (s, 1H), 1.29 – 1.25 (t,  $J$  = 7.2 Hz, 3H), 1.14 – 1.11 (t,  $J$  = 6.9 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 158.9 (s), 131.6 (s), 129.7 (s), 128.8 (d,  $J$  = 5.9 Hz), 128.6 (d,  $J$  = 2.2 Hz), 128.0 (d,  $J$  = 2.9 Hz), 113.9 (s), 63.1 (d,  $J$  = 7.0 Hz), 62.9 (d,  $J$  = 6.8 Hz), 59.6 (d,  $J$  = 153.6 Hz), 55.4 (s), 50.7 (d,  $J$  = 17.2 Hz), 16.6 (d,  $J$  = 6.1 Hz), 16.4 (d,  $J$  = 5.9 Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.5. MS-ESI:  $m/z$  364.2 ( $[\text{M}+\text{H}]^+$ ).

**Diethyl (((2-chlorobenzyl)amino)(phenyl)methyl)phosphonate (3i)**



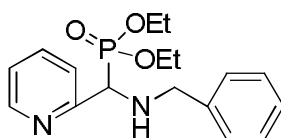
Yellow oil. IR (KBr)  $\nu_{\text{max}}$ : 3313, 2979, 2927, 1471, 1444, 1245, 1027, 964, 754  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.49 – 7.46 (m, 2H), 7.40 – 7.32 (m, 4H), 7.28 – 7.20 (m, 3H), 4.09 – 3.94 (m, 4H), 3.90 – 3.83 (m, 2H), 3.69 – 3.65 (d,  $J$  = 14.0 Hz, 1H), 2.50 (s, 1H), 1.28 – 1.27 (t,  $J$  = 7.0 Hz, 3H), 1.19 – 1.15 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 136.9 (s), 135.6 (d,  $J$  = 3.9 Hz), 134.1 (s), 130.6 (s), 129.7 (s), 128.9 (d,  $J$  = 6.2 Hz), 128.6 (d,  $J$  = 4.7 Hz), 128.1 (d,  $J$  = 2.6 Hz), 126.8 (s), 63.1 (d,  $J$  = 7.1 Hz), 62.9 (d,  $J$  = 6.9 Hz), 60.0 (d,  $J$  = 153.1 Hz), 49.2 (d,  $J$  = 17.8 Hz), 16.5 (d,  $J$  = 5.8 Hz), 16.3 (d,  $J$  = 5.9 Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.2. HRMS-ESI:  $m/z$  390.0993 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{18}\text{H}_{23}\text{ClNNaO}_3\text{P}^+$  calcd. 390.0996).

**Diethyl ((benzylamino)(thiophen-2-yl)methyl)phosphonate (3j, CAS Number: 169334-83-2)**



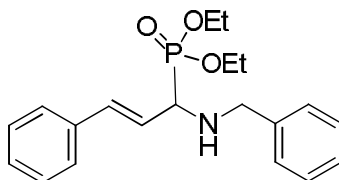
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.33 – 7.25 (m, 6H), 7.09 – 7.07 (m, 1H), 7.02 – 6.99 (m, 1H), 4.32 – 4.27 (d,  $J=20.1\text{ Hz}$ , 1H), 4.14 – 4.02 (m, 3H), 3.97 – 3.89 (m, 2H), 3.67 – 3.63 (d,  $J=13.3\text{ Hz}$ , 1H), 2.25 (s), 1.31 – 1.27 (t,  $J=7.0\text{ Hz}$ , 3H), 1.21 – 1.18 (t,  $J=7.0\text{ Hz}$ , 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 139.8 (s), 139.2 (s), 128.5 (s), 127.3 (s), 127.0 (s), 126.9 (s), 125.6 (d,  $J=3.4\text{ Hz}$ ), 63.3 (d,  $J=7.3\text{ Hz}$ ), 62.2 (d,  $J=7.3\text{ Hz}$ ), 55.2 (d,  $J=159.9\text{ Hz}$ ), 51.4 (d,  $J=16.1\text{ Hz}$ ), 16.6 (d,  $J=5.8\text{ Hz}$ ), 16.4 (d,  $J=5.8\text{ Hz}$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 21.6. MS-ESI:  $m/z$  362.2 ( $[\text{M}+\text{Na}]^+$ ).

**Diethyl ((benzylamino)(pyridin-2-yl)methyl)phosphonate (3k, CAS Number: 160514-83-0)**



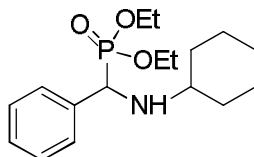
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.63 – 8.62 (m, 1H), 7.71 – 7.65 (m, 1H), 7.47 – 7.44 (m, 1H), 7.36 – 7.21 (m, 6H), 4.25 – 3.82 (m, 6H), 3.63 – 3.60 (d,  $J=13.1\text{ Hz}$ , 1H), 2.53 (s), 1.31 – 1.28 (t,  $J=7.0\text{ Hz}$ , 3H), 1.21 – 1.18 (t,  $J=7.0\text{ Hz}$ , 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 156.5 (s), 149.5 (s), 139.6 (s), 136.5 (s), 128.3 (d,  $J=6.7\text{ Hz}$ ), 127.3 (s), 123.9 (d,  $J=5.1\text{ Hz}$ ), 122.8 (s), 63.3 (d,  $J=6.6\text{ Hz}$ ), 62.9 (d,  $J=6.6\text{ Hz}$ ), 61.5 (d,  $J=152.7\text{ Hz}$ ), 52.3 (s), 52.2 (s), 16.5 (d,  $J=6.0\text{ Hz}$ ), 16.4 (d,  $J=5.9\text{ Hz}$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 22.2. MS-ESI:  $m/z$  357.2 ( $[\text{M}+\text{Na}]^+$ ).

**Diethyl (1-(benzylamino)-3-phenylallyl)phosphonate (3l, CAS Number: 359414-65-6)**



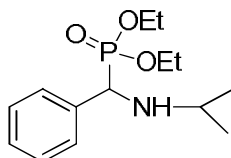
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.41 – 7.40 (m, 2H), 7.34 – 7.31 (m, 6H), 7.27 – 7.22 (m, 2H), 6.63 – 6.59 (m, 1H), 6.17 – 6.15 (m, 1H), 4.19 – 4.11 (m, 4H), 3.99 – 3.96 (d,  $J=13.6\text{ Hz}$ , 1H), 3.77 – 3.74 (d,  $J=13.3\text{ Hz}$ , 1H), 3.70 – 3.63 (m, 1H), 2.11 (s, 1H), 1.33 – 1.26 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 139.5 (s), 136.5 (d,  $J=2.9\text{ Hz}$ ), 134.5 (d,  $J=13.8\text{ Hz}$ ), 128.7 (s), 128.5 (s), 128.4 (s), 128.0 (s), 127.2 (s), 126.6 (d,  $J=2.1\text{ Hz}$ ), 124.3 (d,  $J=7.1\text{ Hz}$ ), 62.9 (d,  $J=7.3\text{ Hz}$ ), 62.8 (d,  $J=7.3\text{ Hz}$ ), 57.9 (d,  $J=155.9\text{ Hz}$ ), 51.3 (d,  $J=16.1\text{ Hz}$ ), 16.6 (d,  $J=3.6\text{ Hz}$ ), 16.5 (d,  $J=3.6\text{ Hz}$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.7. MS-ESI:  $m/z$  360.2 ( $[\text{M}+\text{H}]^+$ ).

**Diethyl ((cyclohexylamino)(phenyl)methyl)phosphonate (3m, CAS Number: 183963-90-8)**



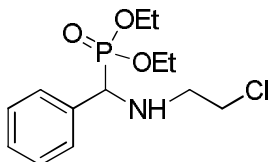
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.42 – 7.39 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.25 (m, 1H), 4.22 – 4.07 (m, 3H), 3.98 – 3.89 (m, 1H), 3.81 – 3.71 (m, 1H), 2.38 – 2.32 (m, 1H), 1.90 – 1.87 (m, 1H), 1.66 – 1.65 (m, 3H), 1.52 (s, 1H), 1.31 – 1.27 (t,  $J = 7.2$  Hz, 3H), 1.16 – 1.02 (m, 8H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 136.9 (s), 128.5 (d,  $J = 5.9$  Hz), 128.4 (d,  $J = 2.9$  Hz), 127.7 (d,  $J = 2.9$  Hz), 63.2 (d,  $J = 7.2$  Hz), 62.7 (d,  $J = 7.2$  Hz), 57.7 (d,  $J = 153.7$  Hz), 53.5 (d,  $J = 16.1$  Hz), 34.5 (s), 32.1 (s), 26.2 (s), 25.0 (s), 24.5 (s), 16.5 (d,  $J = 5.7$  Hz), 16.3 (d,  $J = 5.7$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 24.1. MS-ESI:  $m/z$  348.4 ( $[\text{M}+\text{Na}]^+$ ).

**Diethyl ((isopropylamino)(phenyl)methyl)phosphonate (3n, CAS Number: 874655-72-8)**



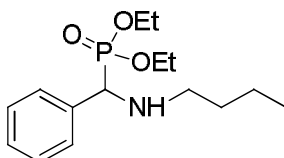
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.41 – 7.39 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.28 (m, 1H), 4.18 – 4.07 (m, 3H), 3.97 – 3.91 (m, 1H), 3.80 – 3.73 (m, 1H), 1.90 (s, 1H), 1.31 – 1.28 (t,  $J = 7.0$  Hz, 3H), 1.13 – 1.10 (t,  $J = 7.1$  Hz, 3H), 1.02 – 1.00 (d,  $J = 6.4$  Hz, 3H), 1.00 – 0.98 (d,  $J = 6.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 136.8 (s), 128.5 (m), 127.7 (d,  $J = 2.9$  Hz), 63.2 (d,  $J = 7.1$  Hz), 62.9 (d,  $J = 7.0$  Hz), 58.4 (d,  $J = 153.9$  Hz), 45.8 (d,  $J = 16.1$  Hz), 24.1 (s), 21.4 (s), 16.5 (d,  $J = 5.9$  Hz), 16.3 (d,  $J = 5.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.5. MS-ESI:  $m/z$  308.2 ( $[\text{M}+\text{Na}]^+$ ).

**Diethyl (((2-bromoethyl)amino)(phenyl)methyl)phosphonate (3o)**



Yellow oil. IR (KBr)  $\nu_{\text{max}}$ : 3306, 2980, 2929, 1453, 1391, 1244, 1027, 965, 701  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.44 – 7.29 (m, 5H), 4.01 – 3.96 (m, 4H), 3.89 – 3.85 (m, 1H), 3.60 – 3.55 (m, 2H), 2.90 – 2.83 (m, 2H), 2.36 (s, 1H), 1.29 – 1.26 (t,  $J = 7.0$  Hz, 3H), 1.18 – 1.15 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 135.5 (d,  $J = 5.0$  Hz), 128.5 (d,  $J = 3.6$  Hz), 128.1 (d,  $J = 2.9$  Hz), 63.1 (d,  $J = 7.3$  Hz), 62.9 (d,  $J = 7.3$  Hz), 60.6 (d,  $J = 153.7$  Hz), 49.1 (d,  $J = 16.9$  Hz), 44.4 (s), 16.5 (d,  $J = 5.8$  Hz), 16.3 (d,  $J = 5.6$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 22.8. HRMS:  $m/z$  328.0833 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{13}\text{H}_{21}\text{ClINNaO}_3\text{P}^+$  calcd. 328.0840).

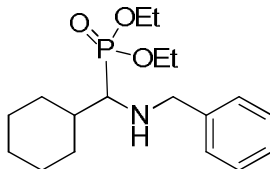
**Diethyl ((butylamino)(phenyl)methyl)phosphonate (3p, CAS Number: 157841-12-8)**



Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.43 – 7.27 (m, 5H), 4.10 – 3.94 (m, 4H), 3.84 – 3.80 (m, 1H), 2.54 – 2.40 (m, 2H), 1.45 – 1.40 (m, 2H), 1.36 – 1.30 (m, 2H), 1.29 – 1.26 (t,  $J = 7.0$  Hz, 3H), 1.16 – 1.12 (t,  $J = 7.1$  Hz, 2H), 0.88 – 0.84 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 136.4 (d,  $J = 4.3$  Hz), 128.6 (d,  $J = 6.6$  Hz), 128.5 (d,  $J = 2.7$  Hz), 127.8 (d,  $J = 3.3$  Hz), 62.5 (d,  $J = 4.3$  Hz).

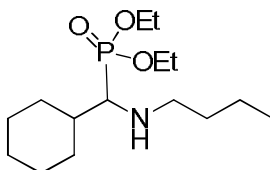
Hz), 62.8 (d,  $J = 7.0$  Hz), 61.3 (d,  $J = 152.4$  Hz), 47.9 (d,  $J = 16.8$  Hz), 32.1 (s), 20.4 (s), 16.6 (d,  $J = 5.6$  Hz), 16.4 (d,  $J = 5.7$  Hz), 4.1 (s).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.1. MS-ESI:  $m/z$  322.2 ( $[\text{M}+\text{Na}]^+$ ).

**Diethyl ((benzylamino)(cyclohexyl)methyl)phosphonate (3q)**



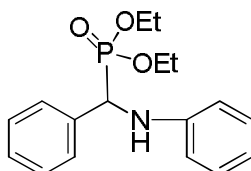
Yellow oil. IR (KBr)  $\nu_{\text{max}}$ : 3315, 2926, 2852, 1451, 1237, 1054, 1027, 957, 699  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.37 – 7.24 (m, 5H), 4.18 – 4.10 (m, 4H), 4.03 – 4.00 (d,  $J = 13.0$  Hz, 1H), 3.85 – 3.82 (d,  $J = 13.0$  Hz, 1H), 2.75 – 2.71 (d,  $J = 14.7$  Hz, 1H), 1.86 – 1.83 (d,  $J = 10.8$  Hz, 1H), 1.82 – 1.73 (m, 4H), 1.65 – 1.55 (m, 2H), 1.35 – 1.32 (t,  $J = 6.8$  Hz, 6H), 1.26 – 1.14 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 140.4 (s), 128.8 (d,  $J = 17.3$  Hz), 127.2 (s), 61.8 (d,  $J = 4.6$  Hz), 61.7 (d,  $J = 7.1$  Hz), 59.8 (d,  $J = 140.3$  Hz), 39.4 (d,  $J = 4.0$  Hz), 31.1 (d,  $J = 12.3$  Hz), 28.4 (d,  $J = 3.5$  Hz), 26.6 (t,  $J = 22.0$  Hz), 16.8 (d,  $J = 3.7$  Hz), 16.7 (d,  $J = 3.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 28.7. HRMS-ESI:  $m/z$  362.1849 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{18}\text{H}_{30}\text{NNaO}_3\text{P}^+$  calcd. 362.1856).

**Diethyl ((butylamino)(cyclohexyl)methyl)phosphonate (3r)**



Yellow oil. IR (KBr)  $\nu_{\text{max}}$ : 3326, 2927, 2853, 1451, 1239, 1056, 1029, 954  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 4.09 – 4.02 (m, 4H), 2.75 – 2.68 (m, 1H), 2.59 – 2.53 (m, 2H), 1.78 – 1.75 (m, 1H), 1.70 – 1.66 (m, 3H), 1.61 – 1.55 (m, 2H), 1.39 – 1.30 (m, 4H), 1.27 – 1.23 (m, 6H), 1.22 – 1.18 (m, 2H), 1.16 – 1.11 (m, 2H), 1.10 – 1.04 (m, 1H), 0.85 – 0.82 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 63.7 (d,  $J = 7.3$  Hz), 61.6 (d,  $J = 4.3$  Hz), 60.8 (d,  $J = 131.5$  Hz), 49.8 (d,  $J = 5.2$  Hz), 39.4 (d,  $J = 5.1$  Hz), 32.7 (s), 31.0 (d,  $J = 11.6$  Hz), 28.4 (d,  $J = 4.4$  Hz), 26.7 (d,  $J = 1.4$  Hz), 26.4 (d,  $J = 19.8$  Hz), 20.4 (s), 16.6 (d,  $J = 4.2$  Hz), 16.5 (d,  $J = 4.2$  Hz), 14.0 (s).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 28.6. HRMS-ESI:  $m/z$  328.2007 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{15}\text{H}_{32}\text{NNaO}_3\text{P}^+$  calcd. 328.2012).

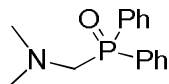
**Diethyl (phenyl(phenylamino)methyl)phosphonate (3s, CAS Number: 7236-88-6)**



Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.48 – 7.45 (m, 2H), 7.35 – 7.31 (t,  $J = 7.5$  Hz, 2H), 7.28 – 7.25 (m, 1H), 7.12 – 7.08 (m, 2H), 6.70 – 6.68 (t,  $J = 7.3$  Hz, 1H), 6.60 – 6.58 (d,  $J = 7.8$  Hz, 2H), 4.81 – 4.79 (m, 1H), 4.14 – 4.08 (m, 2H), 3.96 – 3.90 (m, 1H), 3.70 – 3.66 (m, 1H), 1.78 (s, 1H), 1.28 – 1.26 (t,  $J = 7.0$  Hz, 3H), 1.26 – 1.09 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm)

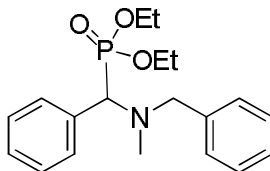
146.5 (d,  $J = 15.6$  Hz), 136.1 (s), 129.4 (s), 128.8 (d,  $J = 2.9$  Hz), 128.0 (d,  $J = 5.8$  Hz), 118.6 (s), 114.1 (s), 63.5 (d,  $J = 2.8$  Hz), 63.4 (d,  $J = 2.8$  Hz), 56.3 (d,  $J = 150.9$  Hz), 16.6 (d,  $J = 6.0$  Hz), 16.4 (d,  $J = 6.0$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 22.6. MS-ESI:  $m/z$  342.2 ( $[\text{M}+\text{Na}]^+$ ).

**((Dimethylamino)methyl)diphenylphosphine oxide (3t, CAS Number: 13119-20-5)**



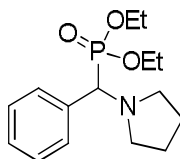
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.73 – 7.68 (m, 4H), 7.41 – 7.32 (m, 6H), 3.12 – 3.10 (d,  $J = 6.2$  Hz, 2H), 2.27 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 132.9 (s), 131.72 (d,  $J = 3.0$  Hz), 131.0 (d,  $J = 8.8$  Hz), 125.4 (d,  $J = 11.7$  Hz), 59.5 (d,  $J = 88.2$  Hz), 48.0 (d,  $J = 8.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 27.4. MS-ESI:  $m/z$  260.2 ( $[\text{M}+\text{H}]^+$ ).

**Diethyl ((benzyl(methyl)amino)(phenyl)methyl)phosphonate (3u)**



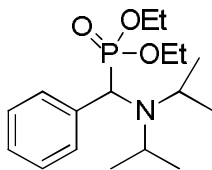
Yellow oil. IR (KBr)  $\nu_{\text{max}}$ : 2983, 1452, 1275, 1260, 1057, 1028, 962, 764, 750  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.50 – 7.49 (m, 2H), 7.48 – 7.29 (m, 7H), 7.26 – 7.24 (m, 1H), 4.27 – 4.21 (m, 2H), 4.08 – 4.02 (d,  $J = 24.0$  Hz, 1H), 3.94 – 3.83 (m, 2H), 3.74 – 3.70 (m, 1H), 3.37 – 3.41 (d,  $J = 13.4$  Hz, 1H), 2.41 (s, 3H), 1.39 – 1.36 (t,  $J = 7.1$  Hz, 3H), 1.03 – 0.99 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 139.2 (s), 132.2 (m), 131.96 (d,  $J = 8.7$  Hz), 129.0 (s), 128.3 (d,  $J = 13.2$  Hz), 128.1 (s), 127.2 (s), 65.0 (d,  $J = 162.2$  Hz), 62.7 (d,  $J = 7.2$  Hz), 62.3 (d,  $J = 7.2$  Hz), 59.9 (d,  $J = 12.4$  Hz), 40.0 (d,  $J = 5.8$  Hz), 16.7 (d,  $J = 5.8$  Hz), 16.3 (d,  $J = 5.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.1. HRMS-ESI:  $m/z$  370.1546 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{19}\text{H}_{26}\text{NNaO}_3\text{P}^+$  calcd. 370.1543).

**Diethyl (phenyl(pyrrolidin-1-yl)methyl)phosphonate (3v, CAS Number: 650634-09-6)**



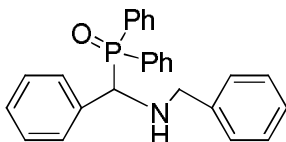
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.49 – 7.46 (m, 2H), 7.35 – 7.28 (m, 3H), 4.14 – 4.05 (m, 2H), 3.93 – 3.87 (m, 1H), 3.77 – 3.73 (d,  $J = 15.7$  Hz, 1H), 3.62 – 3.56 (m, 1H), 2.67 – 2.61 (m, 4H), 1.74 – 1.71 (m, 4H), 1.30 – 1.27 (t,  $J = 7.1$  Hz, 6H), 1.08 – 1.04 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 135.5 (s), 130.1 (d,  $J = 7.3$  Hz), 128.3 (s), 128.0 (s), 67.7 (d,  $J = 158.0$  Hz), 62.7 (d,  $J = 7.4$  Hz), 62.1 (d,  $J = 7.4$  Hz), 3.0 (d,  $J = 8.8$  Hz), 23.4 (s), 16.55 (d,  $J = 5.9$  Hz), 16.35 (d,  $J = 5.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 22.7. MS-ESI:  $m/z$  298.2 ( $[\text{M}+\text{H}]^+$ ).

**Diethyl ((diisopropylamino)(phenyl)methyl)phosphonate (3w)**



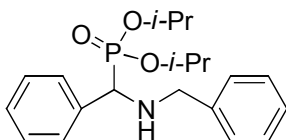
Yellow oil. IR (KBr)  $\nu_{\text{max}}$ : 2975, 2930, 1451, 1242, 1058, 1030, 959, 702  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.63 – 7.62 (m, 2H), 7.32 – 7.27 (m, 3H), 4.26 – 4.13 (m, 3H), 3.89 – 3.82 (m, 1H), 3.71 – 3.61 (m, 3H), 1.36 – 1.32 (t,  $J = 7.1$  Hz, 3H), 1.16 – 1.15 (d,  $J = 6.5$  Hz, 6H), 1.02 – 0.97 (t,  $J = 7.1$  Hz, 3H), 0.84 – 0.82 (d,  $J = 6.5$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 130.8 (s), 130.7 (s), 128.3 (s), 127.5 (s), 63.5 (d,  $J = 7.9$  Hz), 62.1 (d,  $J = 7.5$  Hz), 57.1 (d,  $J = 165.4$  Hz), 47.2 (d,  $J = 5.1$  Hz), 23.4 (d,  $J = 2.8$  Hz), 22.4 (s), 16.7 (d,  $J = 5.9$  Hz), 16.3 (d,  $J = 5.2$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 24.3. HRMS-ESI:  $m/z$  350.1854 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{17}\text{H}_{30}\text{NNaO}_3\text{P}^+$  calcd. 350.1856).

**((Benzylamino)(phenyl)methyl)diphenylphosphine oxide (3x, CAS Number: 38031-22-0)**



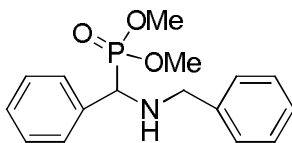
White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.85 – 7.79 (m, 2H), 7.59 – 7.55 (m, 1H), 7.50 – 7.44 (m, 4H), 7.39 – 7.35 (m, 1H), 7.32 – 7.21 (m, 10H), 7.16 – 7.14 (m, 2H), 4.39 – 4.36 (d,  $J = 10.5$  Hz, 1H), 3.84 – 3.81 (d,  $J = 13.1$  Hz, 1H), 3.51 – 3.48 (d,  $J = 13.5$  Hz, 1H), 2.58 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 139.1 (s), 135.2 (s), 132.0 (d,  $J = 8.5$  Hz), 131.86 (d,  $J = 2.9$  Hz), 131.55 (m), 130.6 (d,  $J = 21.9$  Hz), 129.15 (d,  $J = 5.1$  Hz), 128.8 (s), 128.4 (s), 128.3 (d,  $J = 2.2$  Hz), 128.03 (d,  $J = 11.7$  Hz), 127.8 (d,  $J = 2.9$  Hz), 127.2 (s), 61.2 (d,  $J = 79.9$  Hz), 51.0 (d,  $J = 14.5$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 31.5. MS-ESI:  $m/z$  398.2 ( $[\text{M}+\text{H}]^+$ ).

**Diisopropyl ((benzylamino)(phenyl)methyl)phosphonate (3y, CAS Number: 374544-01-1)**



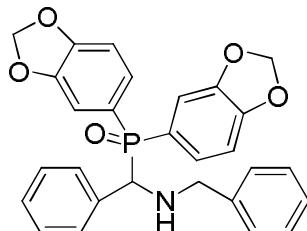
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.46 – 7.45 (m, 2H), 7.39 – 7.29 (m, 8H), 4.74 – 4.66 (m, 1H), 4.55 – 4.48 (m, 1H), 4.00 – 3.95 (d,  $J = 20.4$  Hz, 1H), 3.84 – 3.81 (d,  $J = 13.1$  Hz, 1H), 3.58 – 3.54 (d,  $J = 13.3$  Hz, 1H), 2.32 (s, 1H), 1.31 – 1.29 (m, 6H), 1.25 – 1.24 (d,  $J = 6.1$  Hz, 3H), 1.00 – 0.99 (d,  $J = 6.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 139.6 (s), 136.1 (d,  $J = 4.3$  Hz), 128.8 (d,  $J = 6.6$  Hz), 128.3 (d,  $J = 6.6$  Hz), 127.7 (d,  $J = 2.9$  Hz), 127.2 (s), 71.3 (d,  $J = 7.4$  Hz), 60.2 (d,  $J = 155.1$  Hz), 51.4 (d,  $J = 17.5$  Hz), 24.2 (t,  $J = 3.7$  Hz), 23.9 (d,  $J = 5.3$  Hz), 23.4 (d,  $J = 5.3$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 21.8. MS-ESI:  $m/z$  362.2 ( $[\text{M}+\text{H}]^+$ ).

**Dimethyl ((benzylamino)(phenyl)methyl)phosphonate (3z, CAS Number: 192868-43-2)**



Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.46 – 7.27 (m, 10H), 4.10 – 4.05 (d,  $J = 20.3$  Hz, 1H), 3.84 – 3.74 (m, 3H), 3.58 – 3.55 (m, 3H), 2.30 (s, 1H), 1.29 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 139.3 (s), 135.5 (d,  $J = 2.9$  Hz), 128.6 (d,  $J = 5.8$  Hz), 128.4 (d,  $J = 6.6$  Hz), 128.0 (d,  $J = 2.9$  Hz), 127.3 (s), 59.4 (d,  $J = 154.2$  Hz), 53.7 (d,  $J = 7.1$  Hz), 53.4 (d,  $J = 7.1$  Hz), 51.1 (d,  $J = 17.5$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 25.7. MS-ESI:  $m/z$  306.1 ( $[\text{M}+\text{H}]^+$ ).

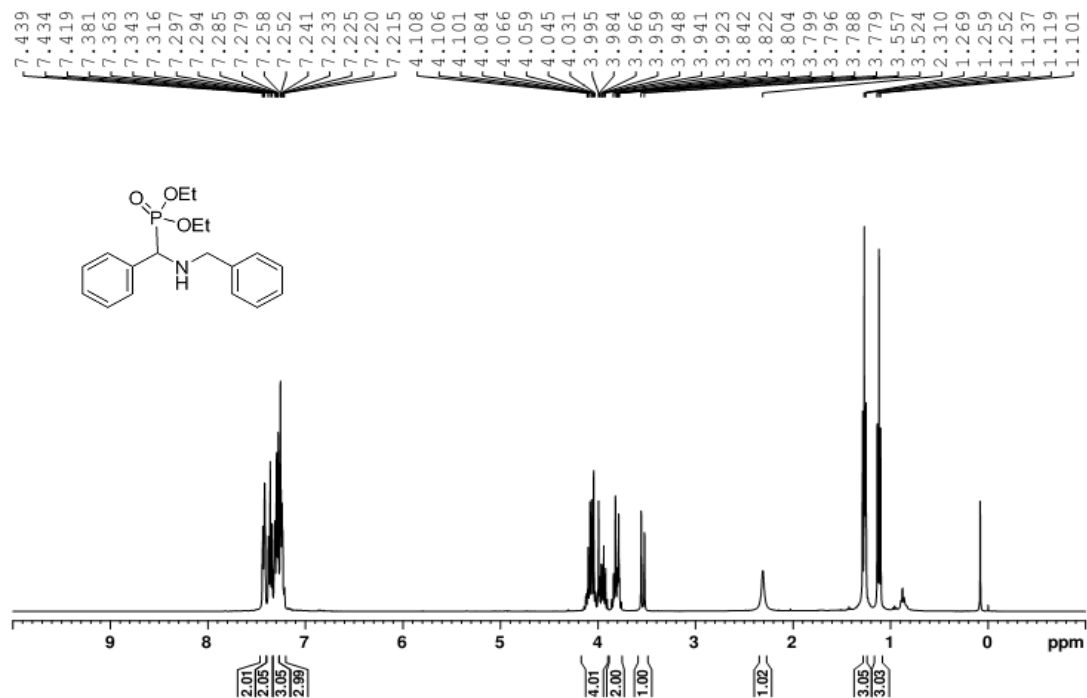
**Bis(benzo[d][1,3]dioxol-5-yl)((benzylamino)(phenyl)methyl)phosphine oxide (3aa)**



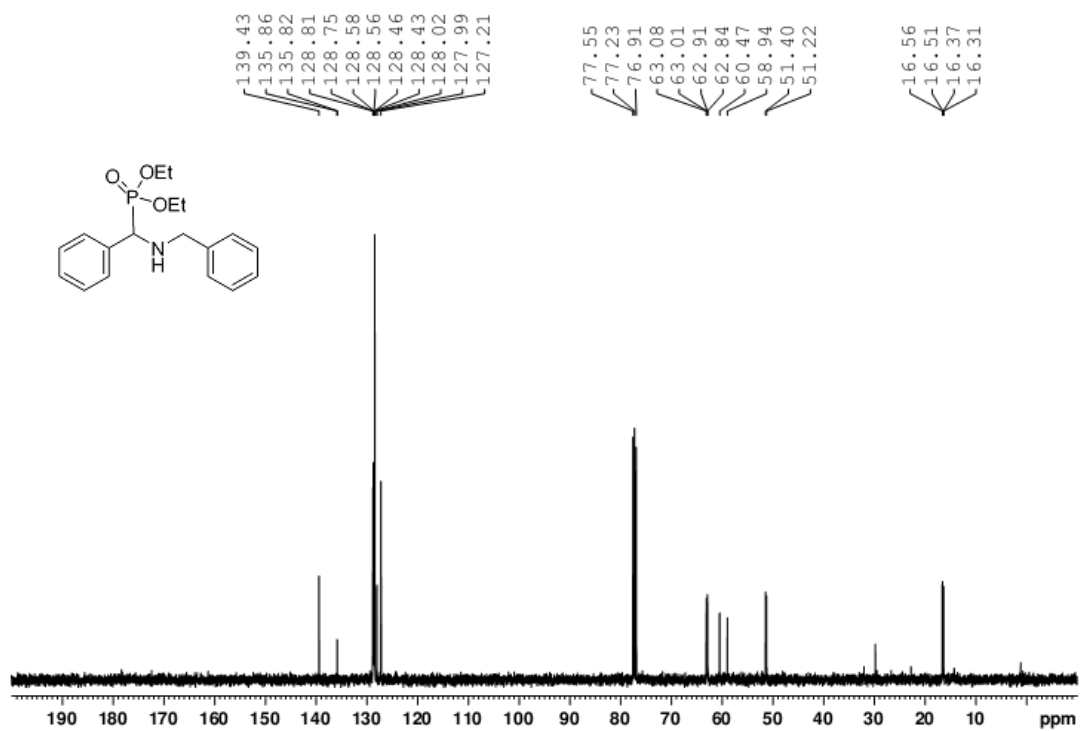
White solid. IR (KBr)  $\nu_{\text{max}}$ : 3026, 2897, 1480, 1424, 1241, 1038, 933, 700  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.30 – 7.18 (m, 10H), 7.15 – 7.13 (m, 2H), 6.99 – 6.94 (m, 1H), 6.87 – 6.84 (m, 2H), 6.67 – 6.64 (m, 1H), 5.99 – 5.98 (m, 2H), 5.87 – 5.86 (m, 2H), 4.29 – 4.26 (d,  $J = 11.07$  Hz, 1H), 3.84 – 3.80 (d,  $J = 13.3$  Hz, 1H), 3.50 – 3.47 (d,  $J = 13.3$  Hz, 1H), 2.50 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 150.8 (d,  $J = 2.2$  Hz), 150.5 (d,  $J = 2.9$  Hz), 147.8 (d,  $J = 17.6$  Hz), 147.5 (d,  $J = 17.6$  Hz), 139.1 (s), 135.3 (s), 129.2 (d,  $J = 5.1$  Hz), 128.8 (s), 128.3 (d,  $J = 4.3$  Hz), 128.8 (d,  $J = 2.4$  Hz), 127.4 (d,  $J = 9.9$  Hz), 127.25 (s), 127.0 (d,  $J = 9.6$  Hz), 111.6 (d,  $J = 11.8$  Hz), 111.1 (d,  $J = 11.8$  Hz), 108.4 (s), 101.5 (d,  $J = 16.2$  Hz), 61.6 (d,  $J = 81.8$  Hz), 51.1 (d,  $J = 14.7$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 31.6. HRMS-ESI:  $m/z$  508.1284 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{28}\text{H}_{24}\text{NNaO}_5\text{P}^+$  calcd. 508.1284).

3.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra of all products.

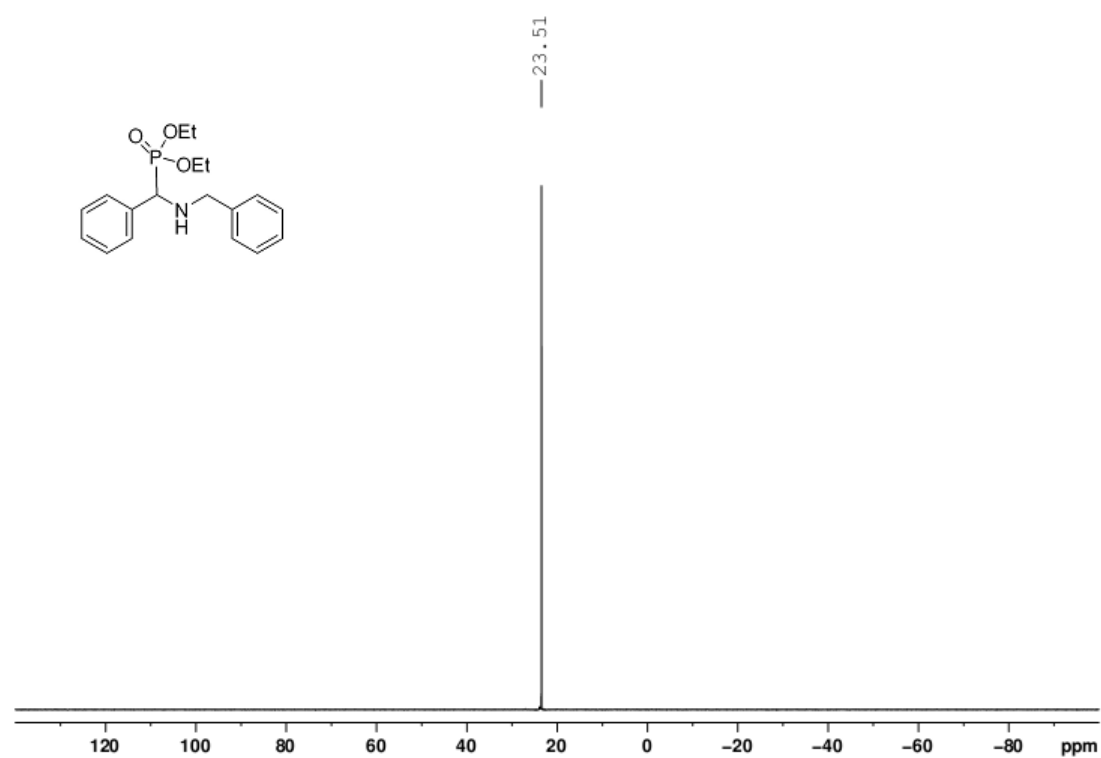
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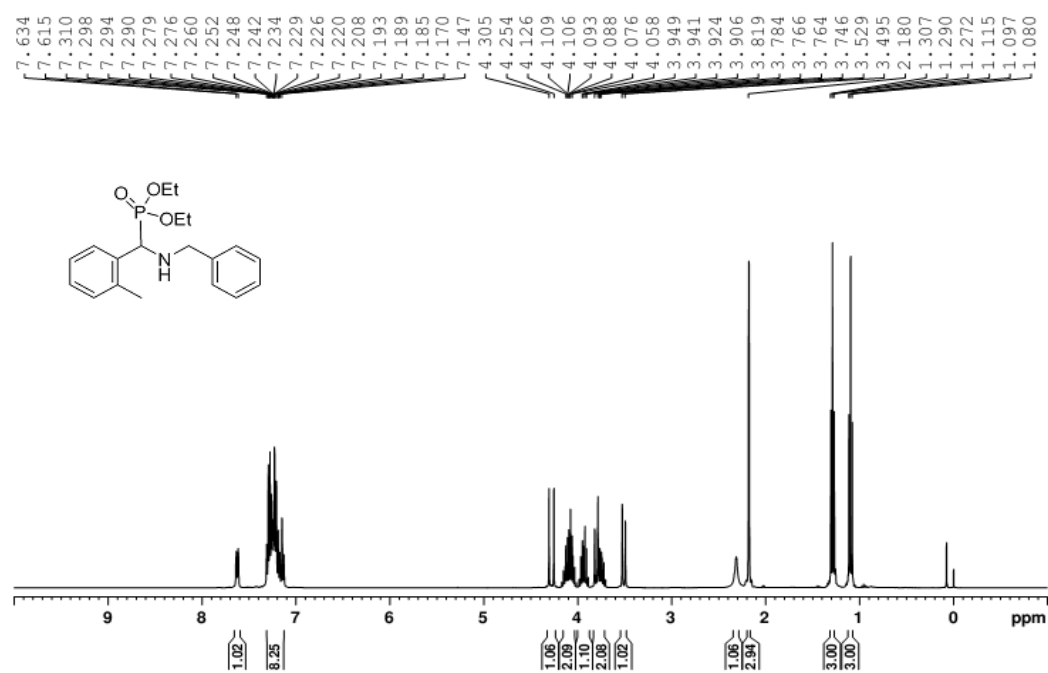
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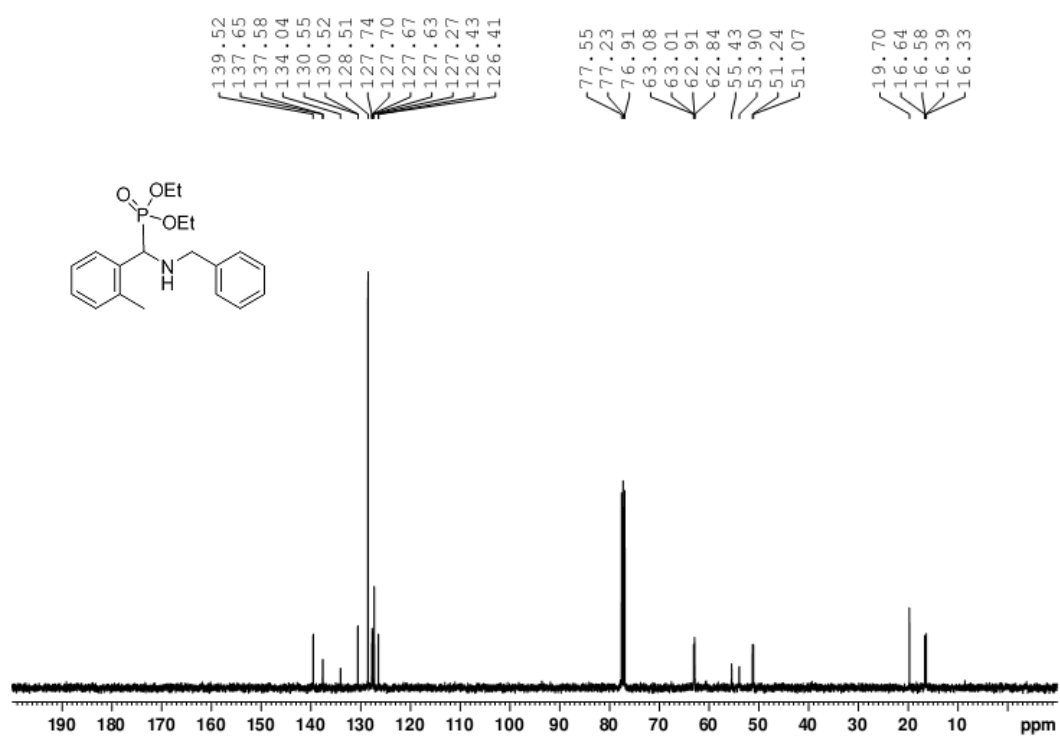
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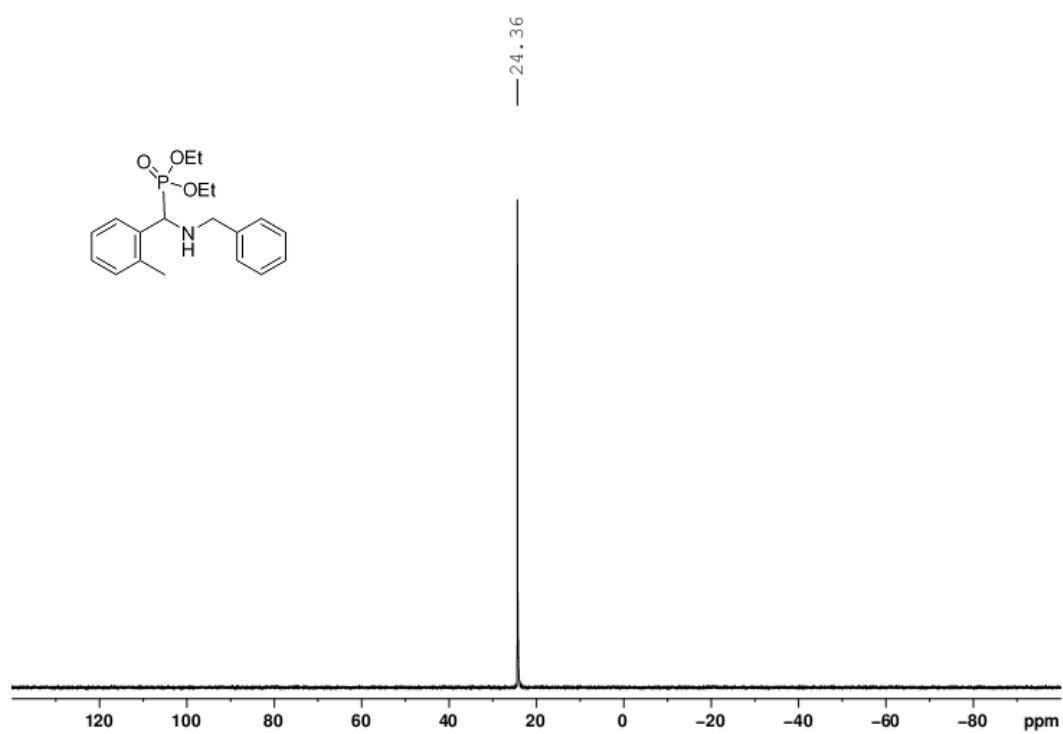
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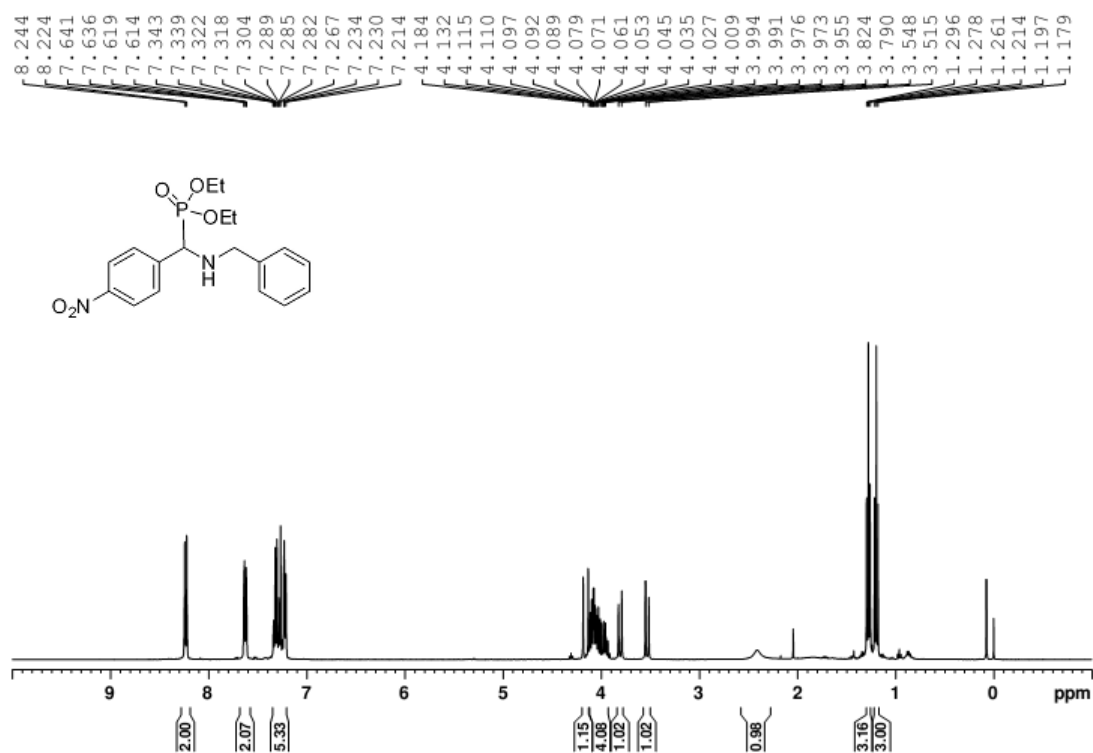
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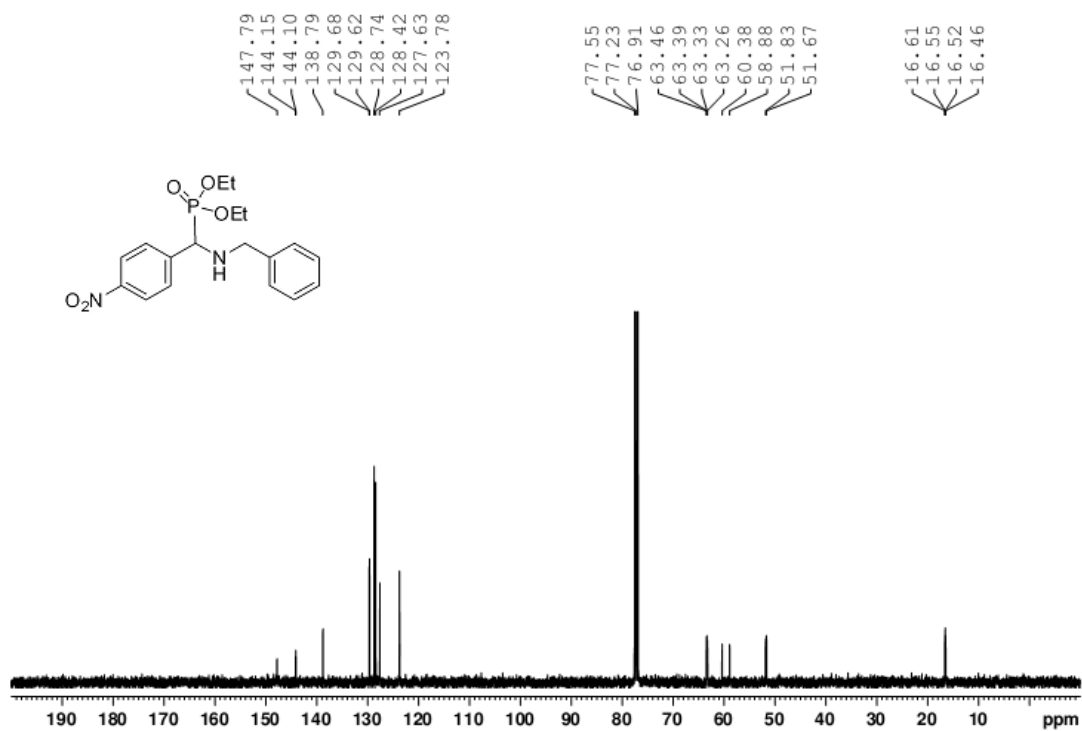
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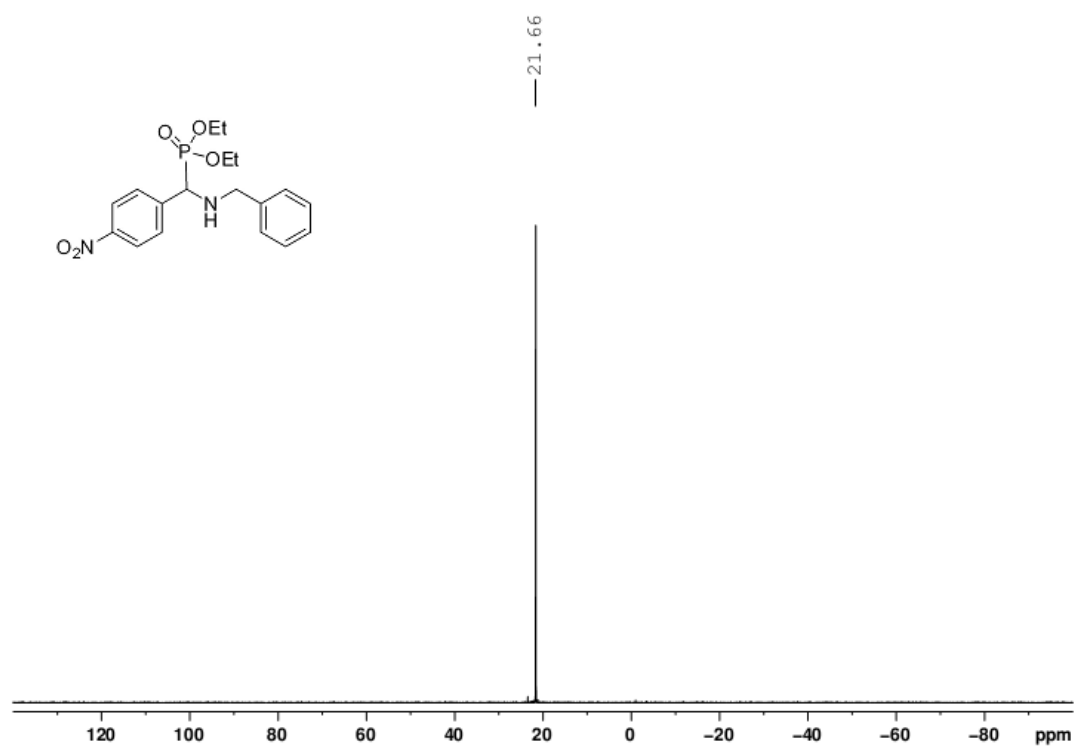
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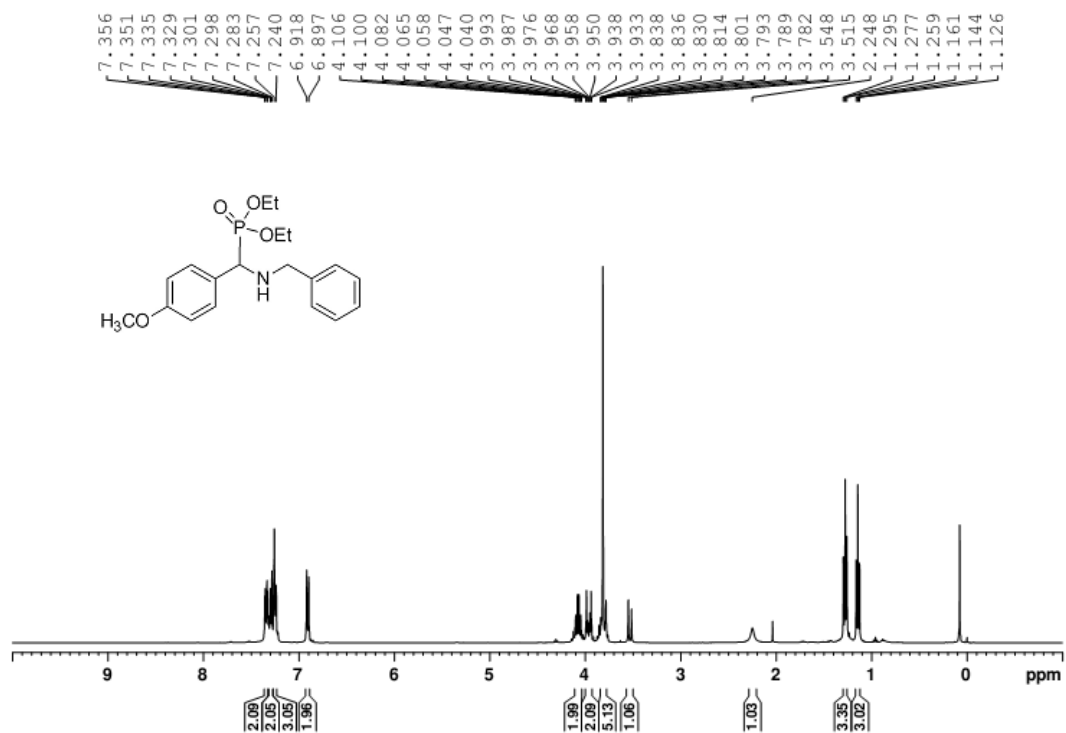
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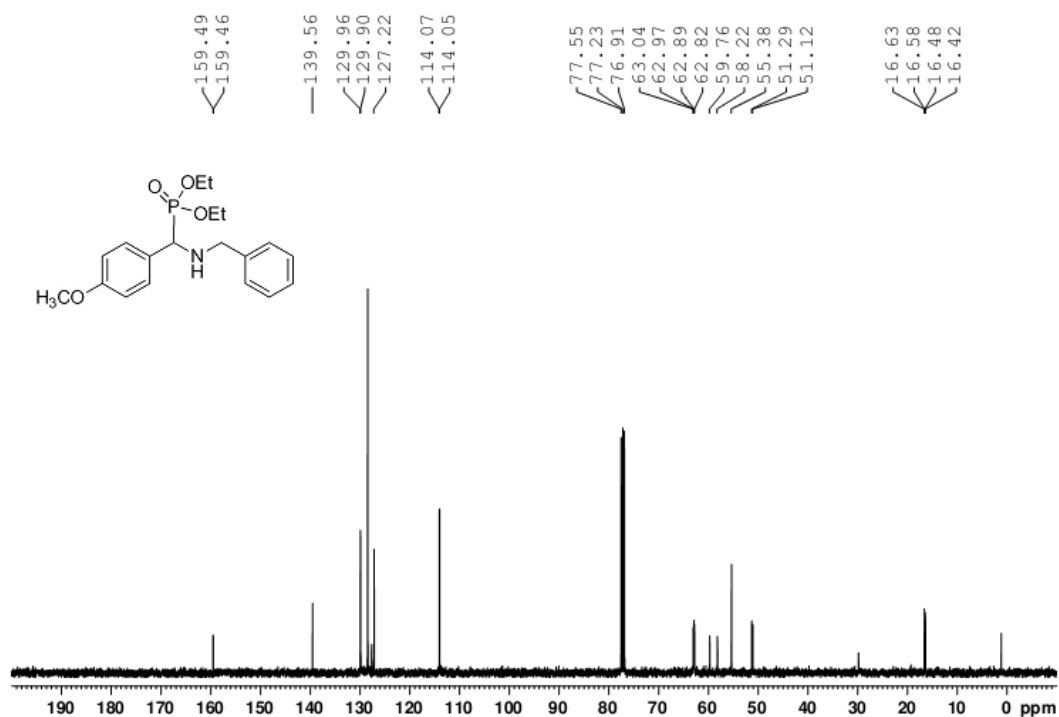
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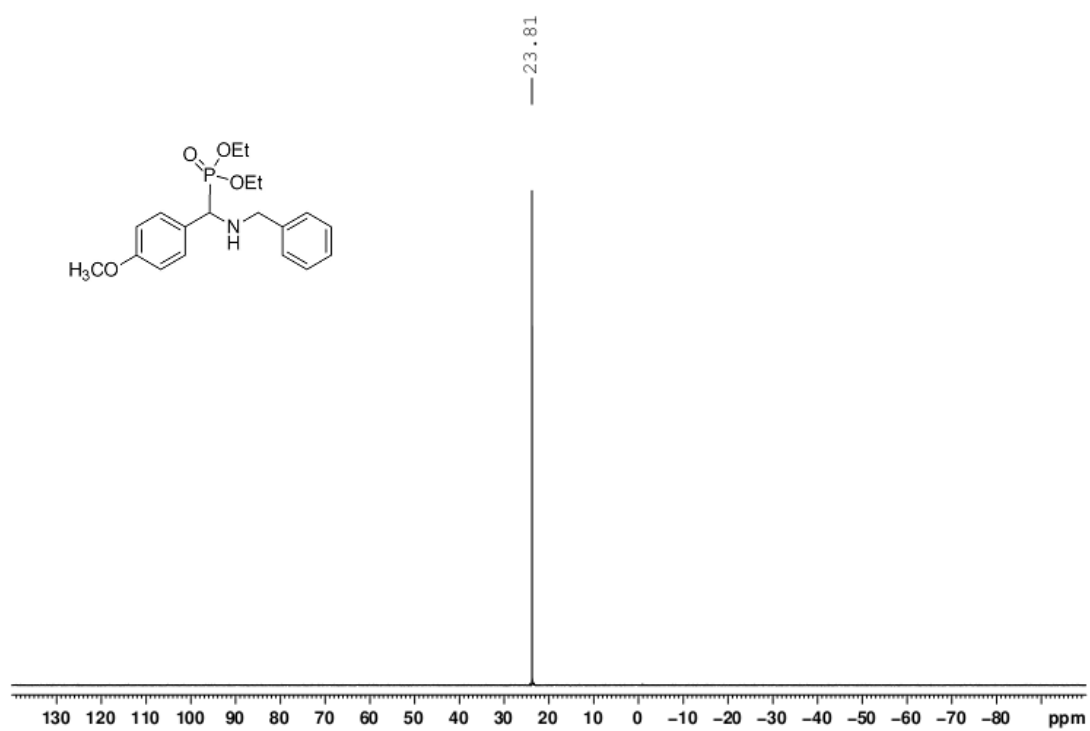
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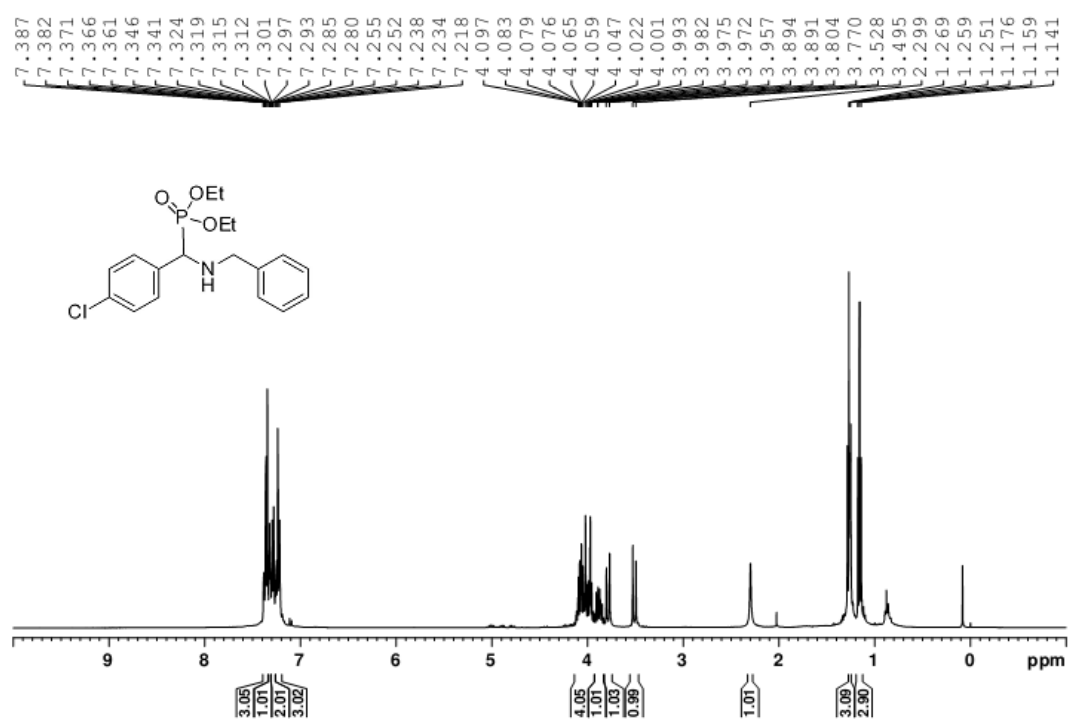
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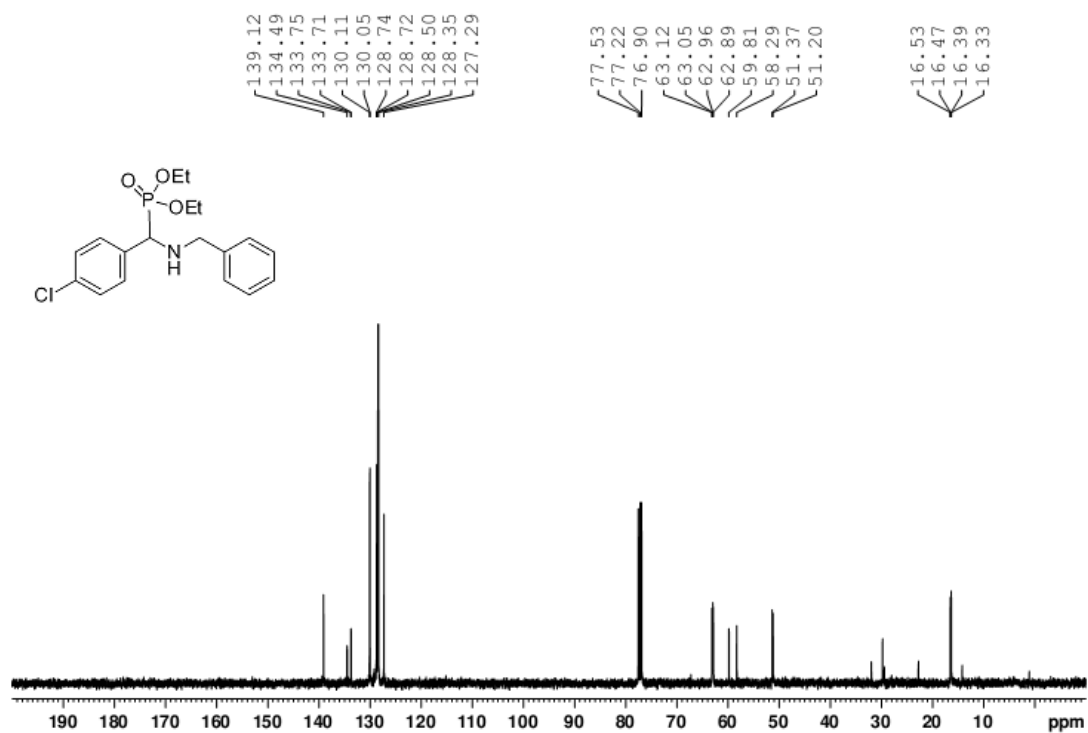
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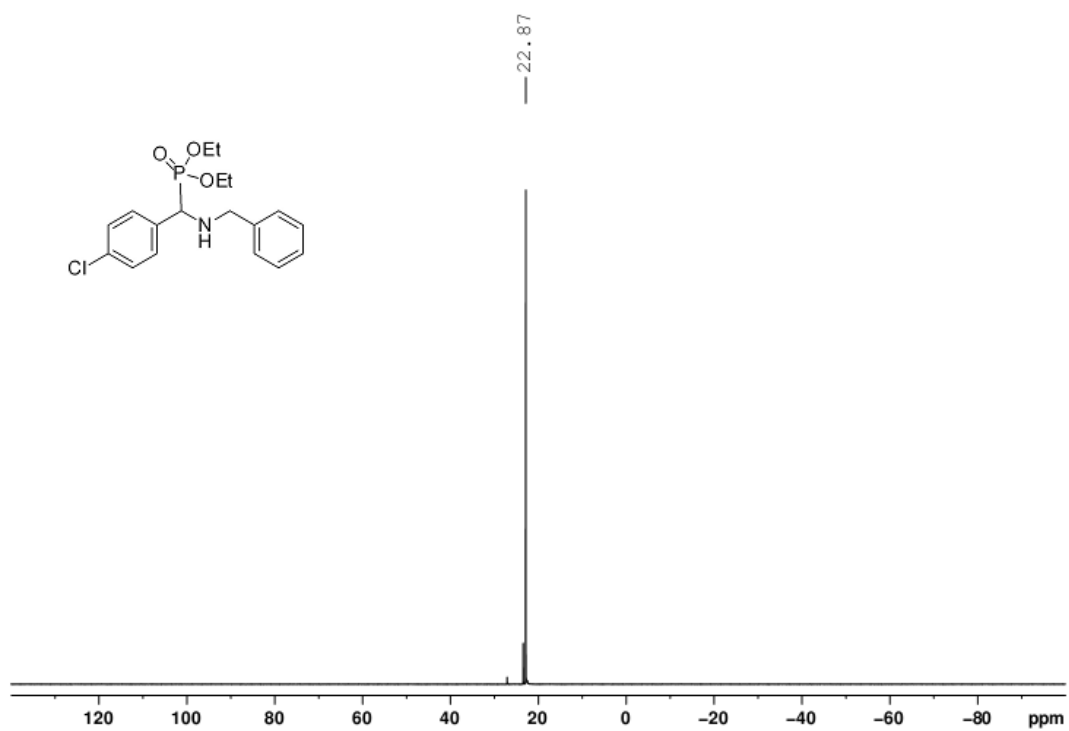
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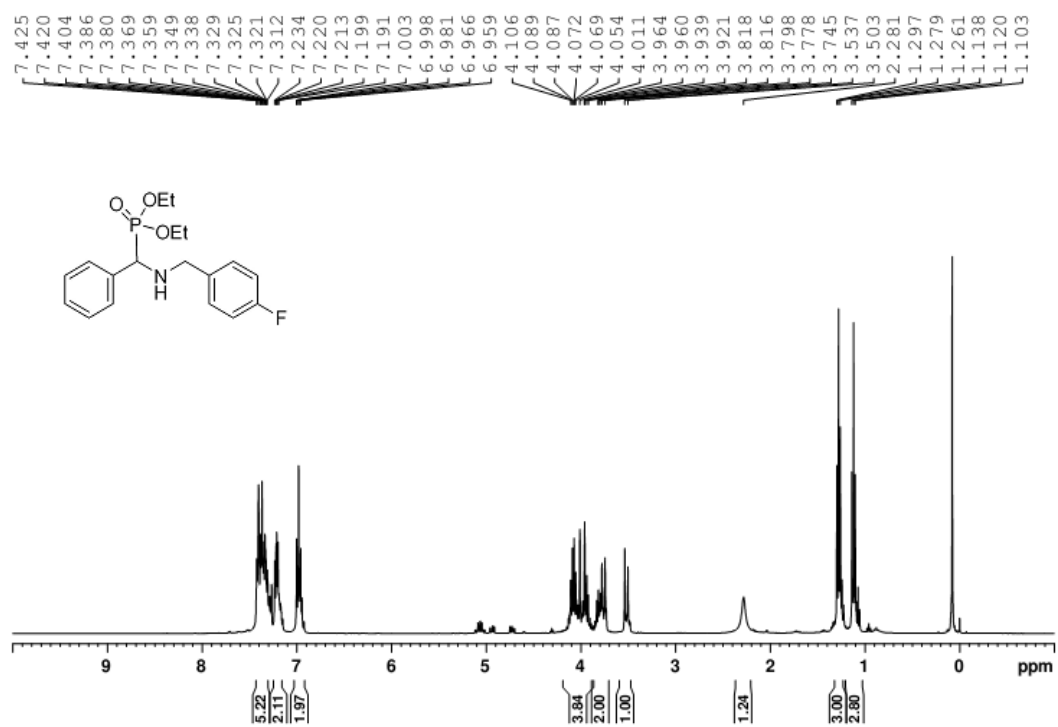
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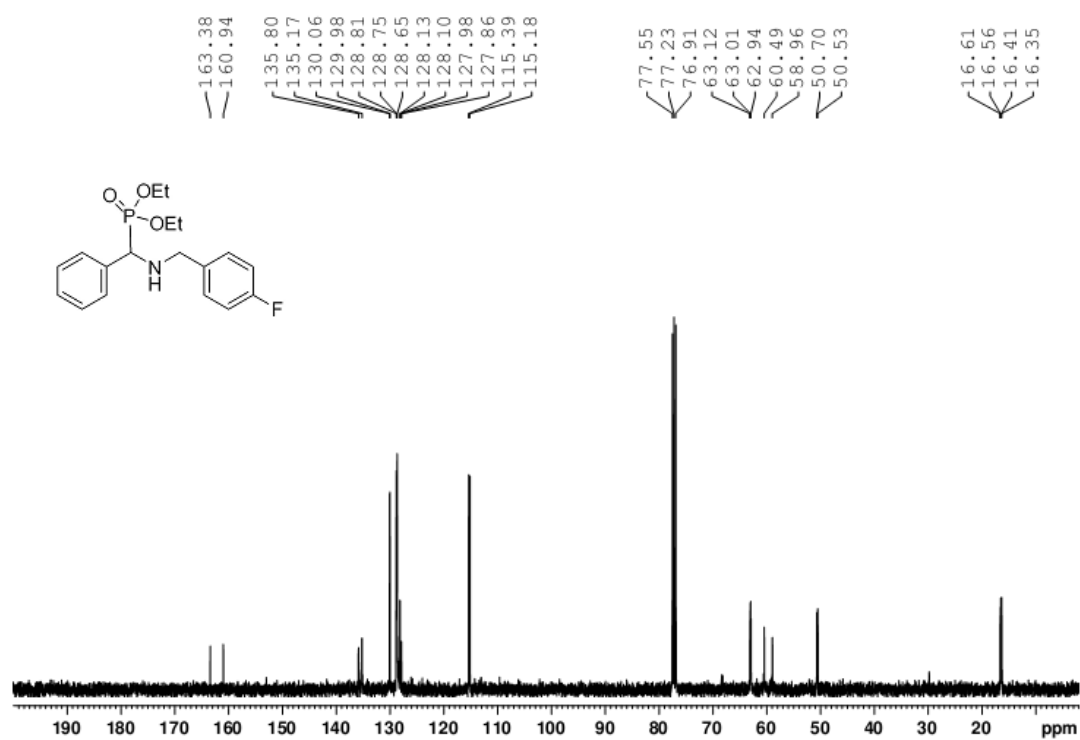
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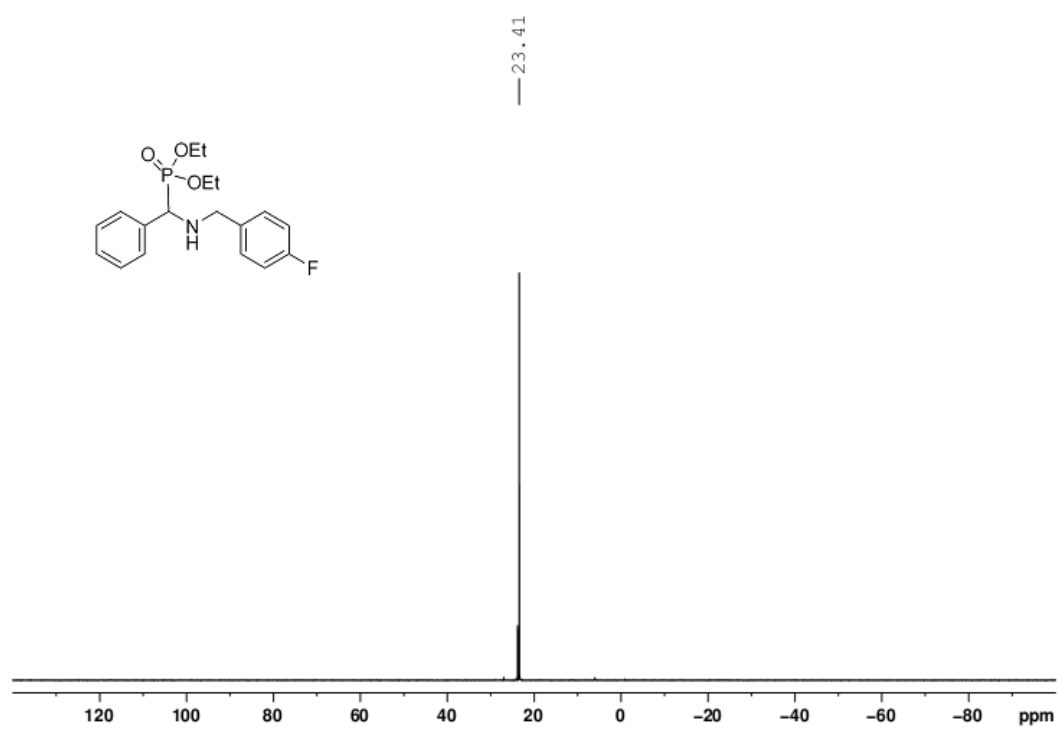
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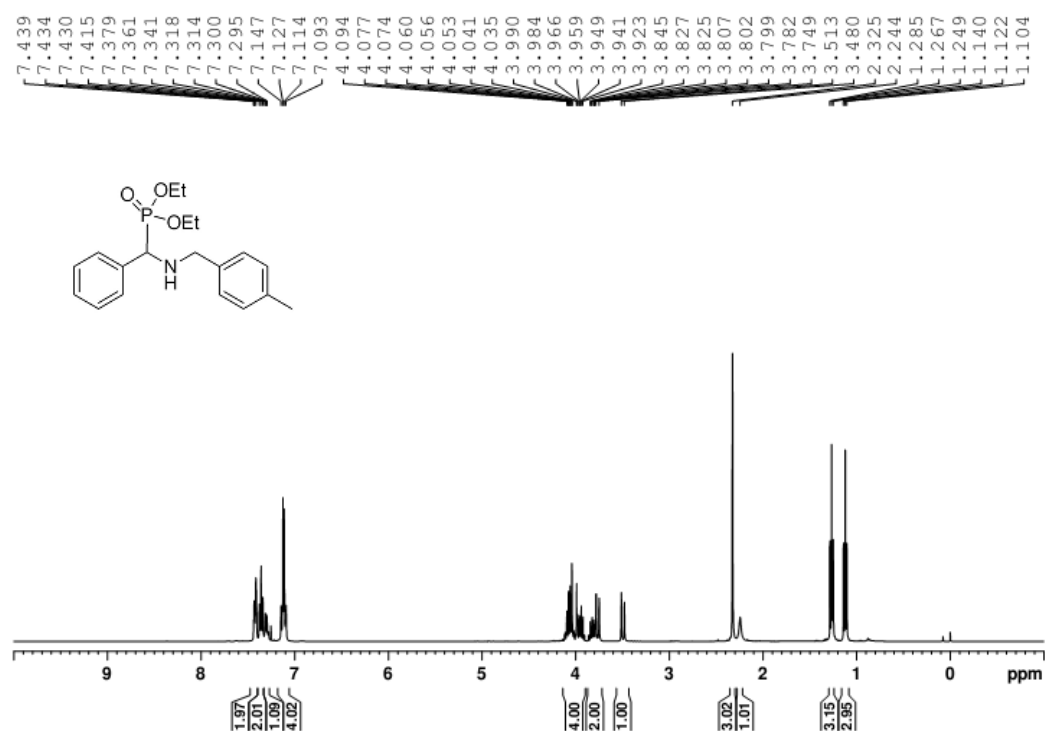
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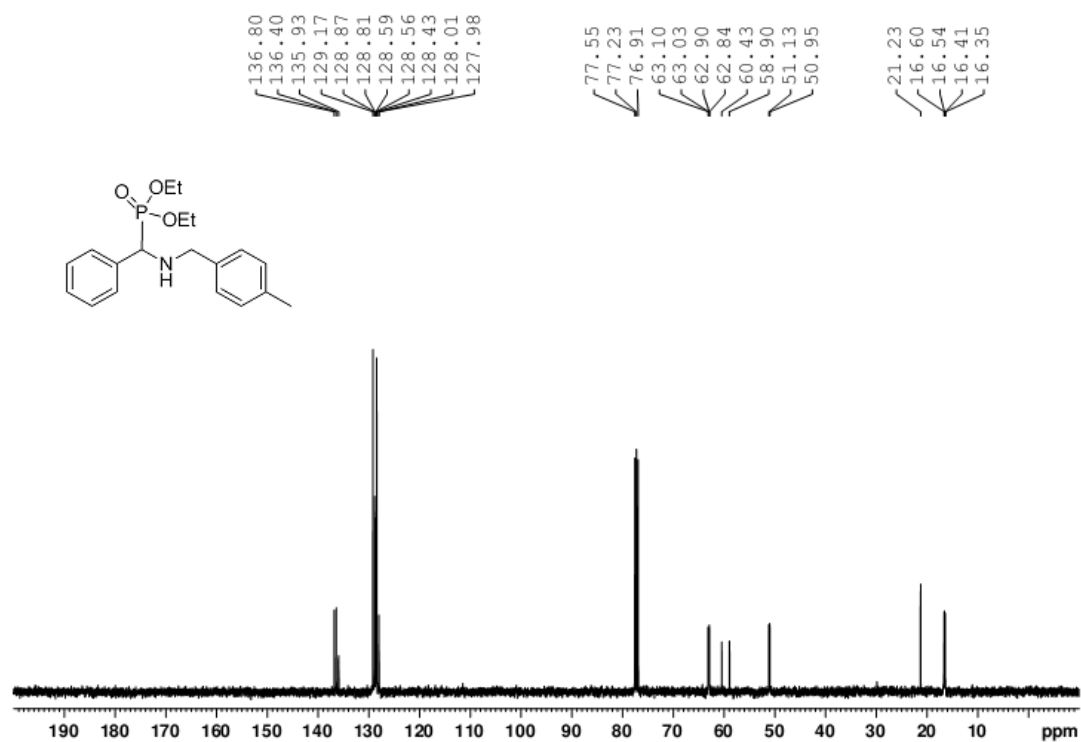
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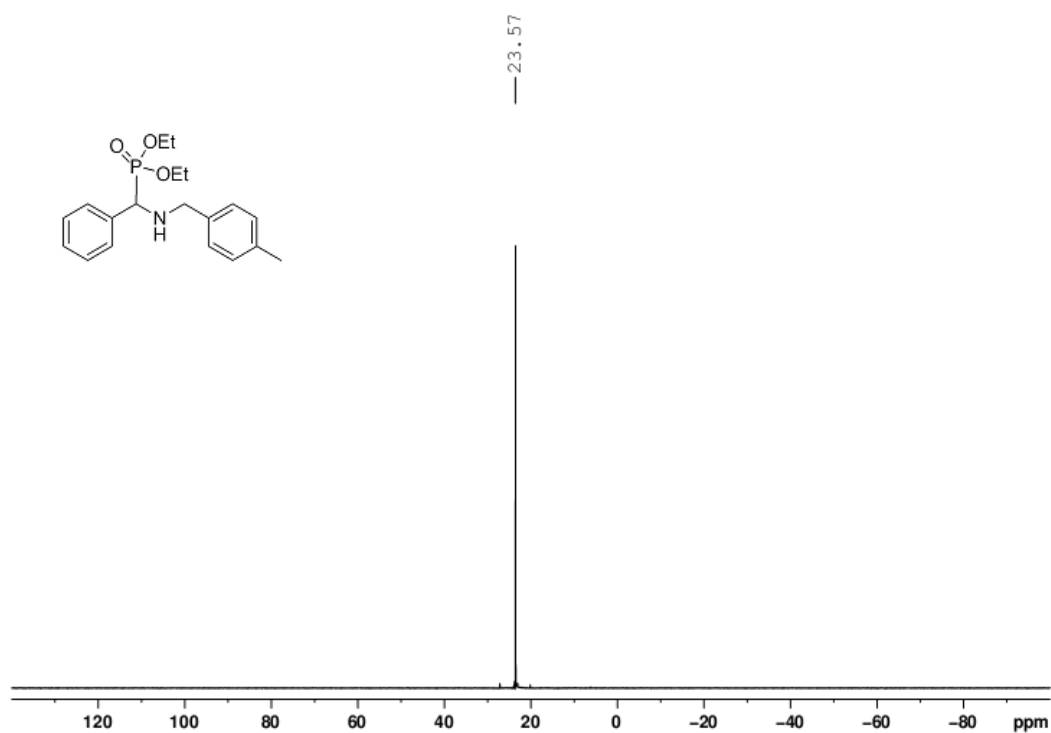
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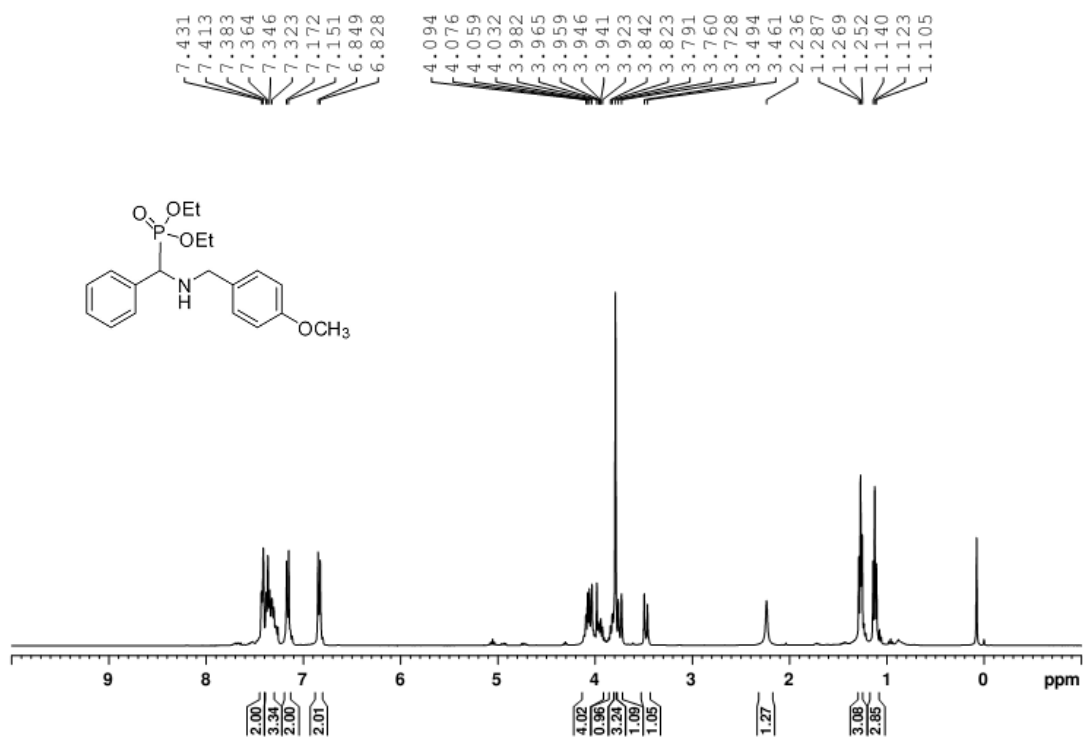
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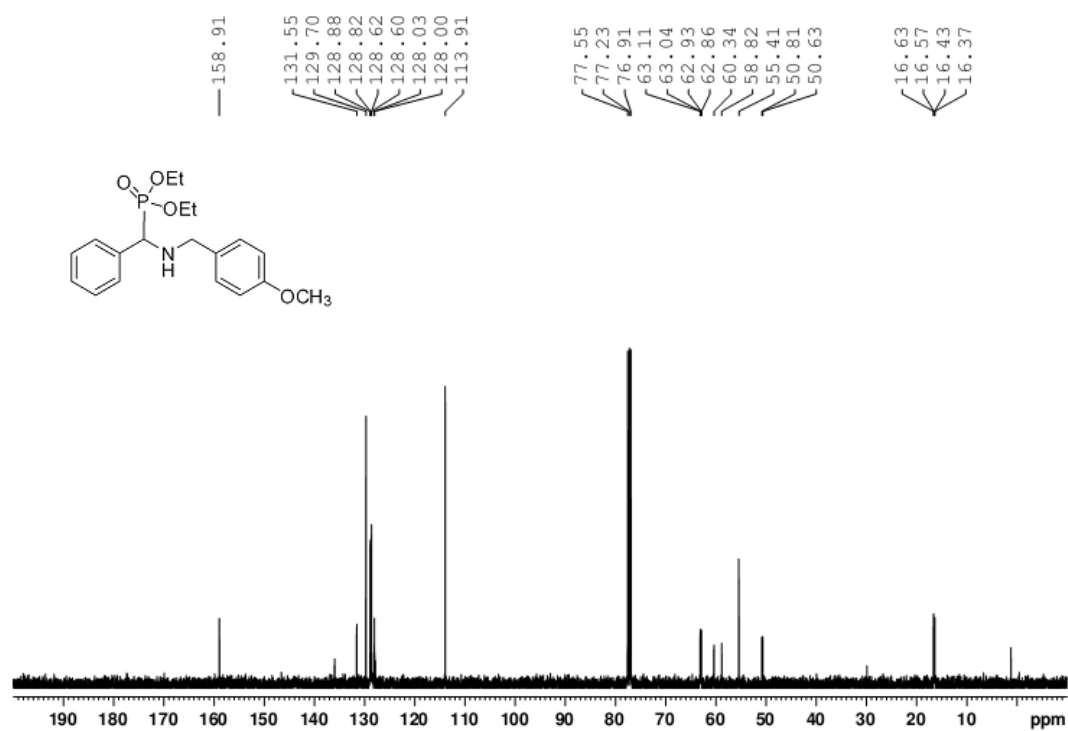
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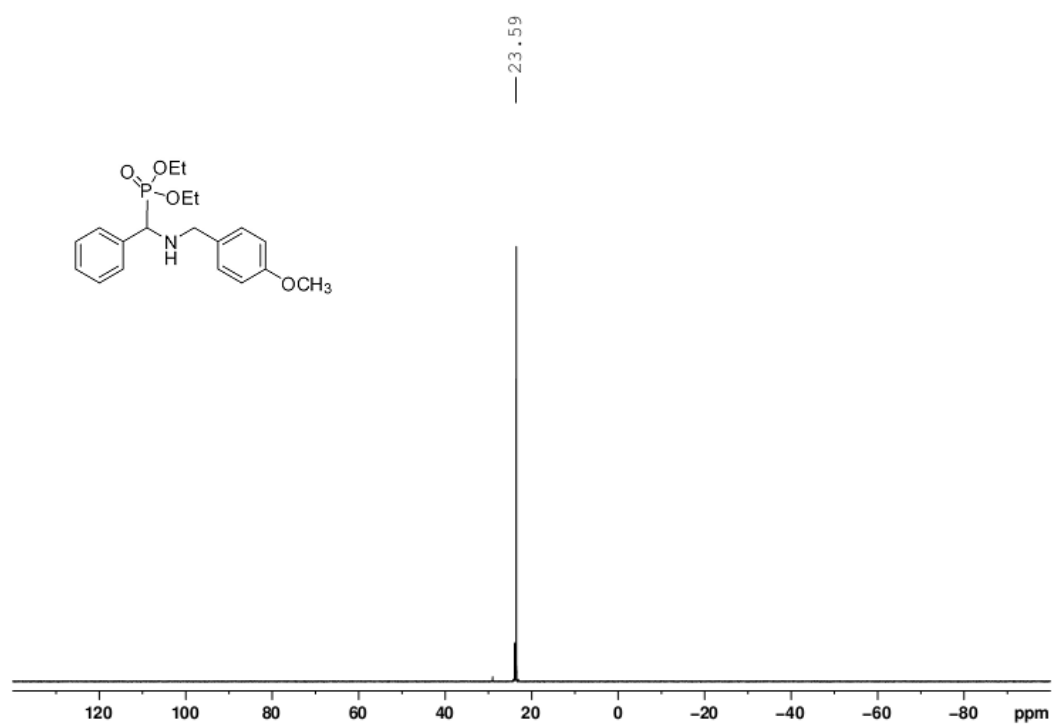
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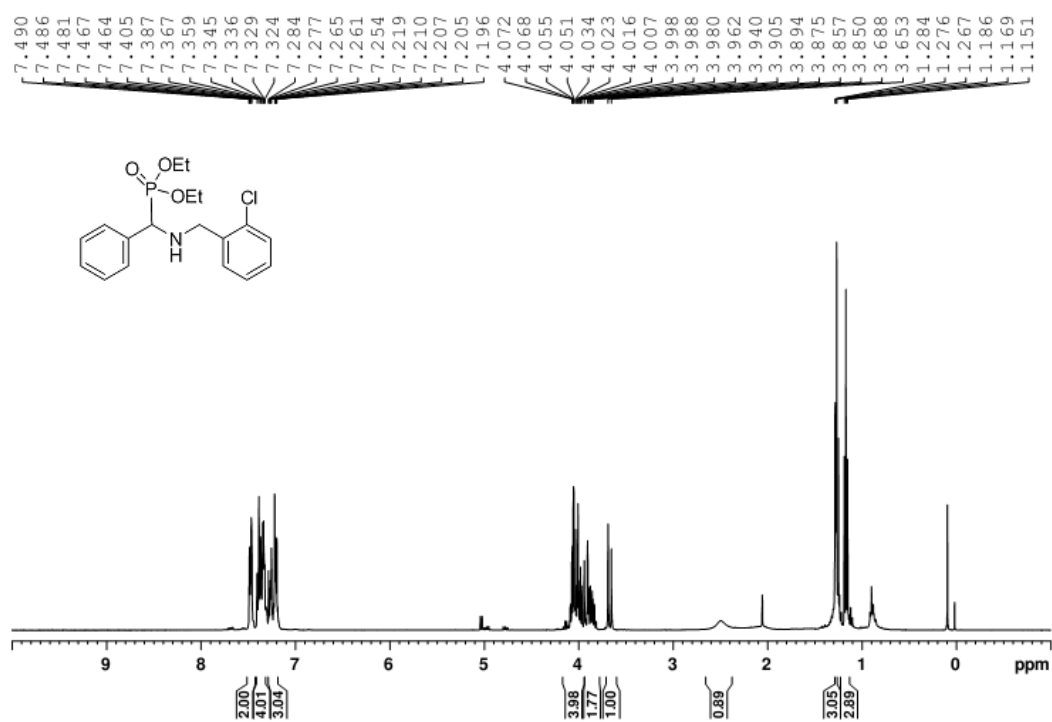
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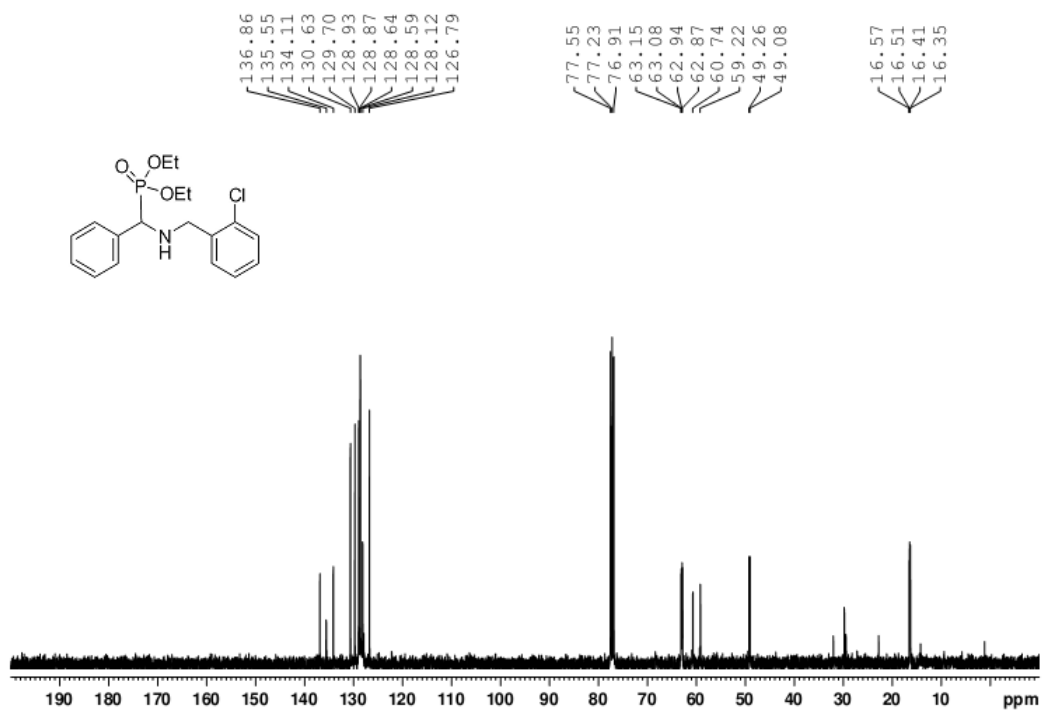
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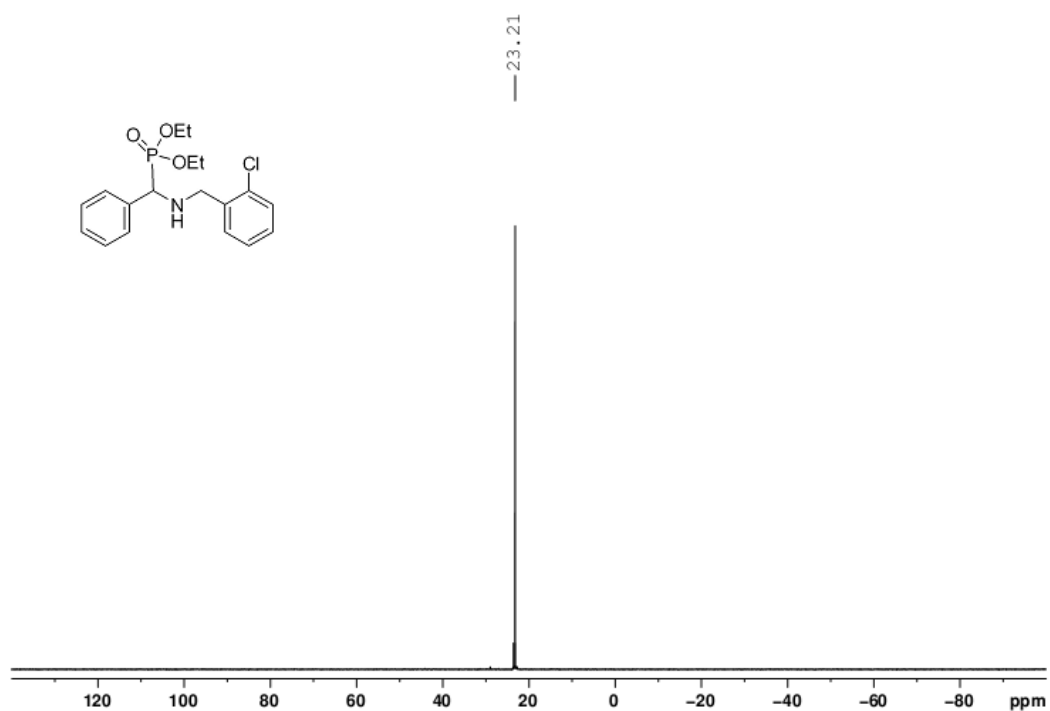
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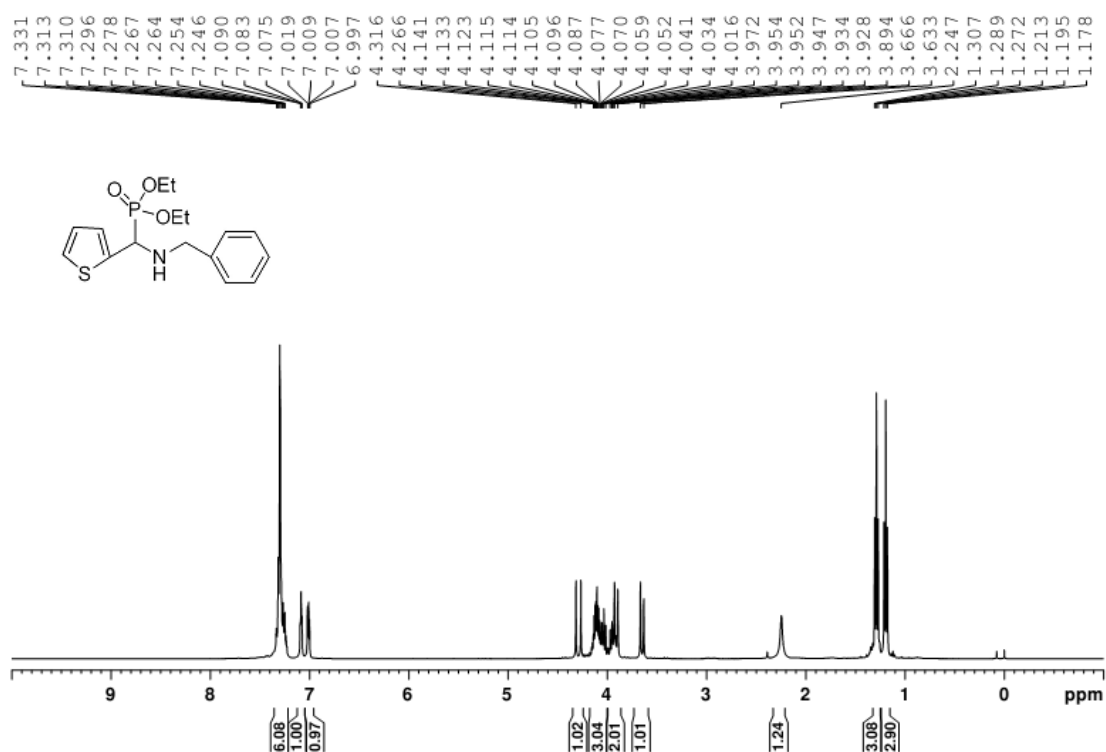
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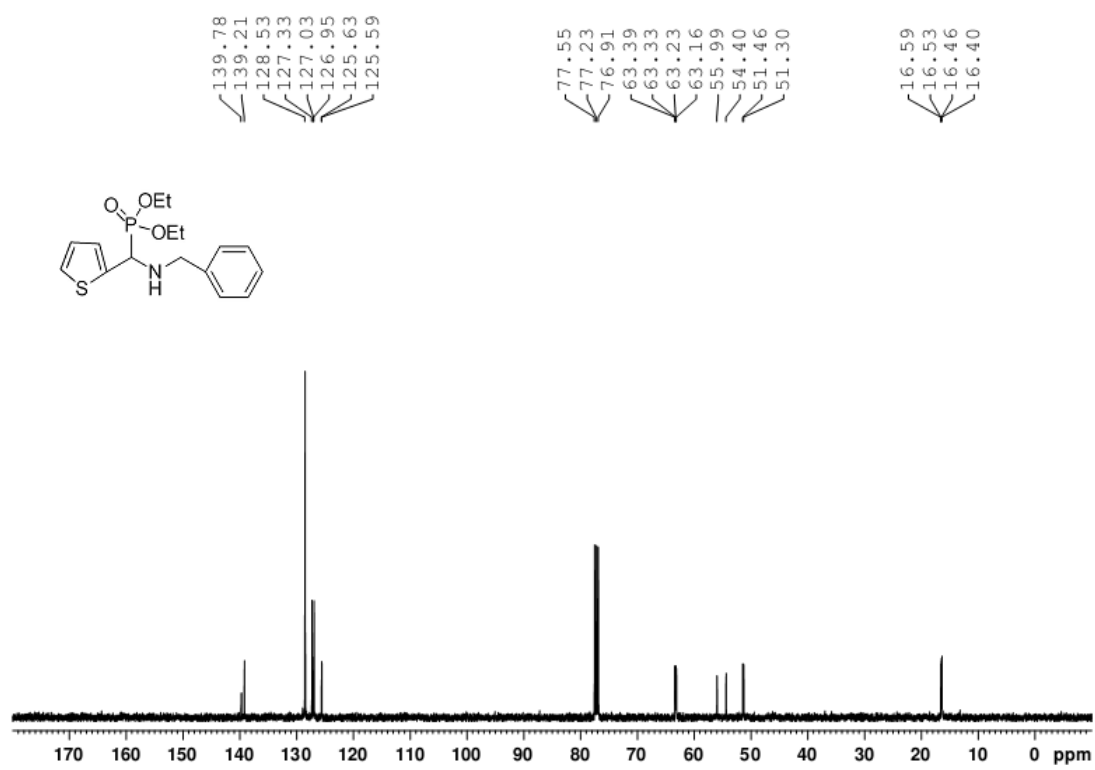
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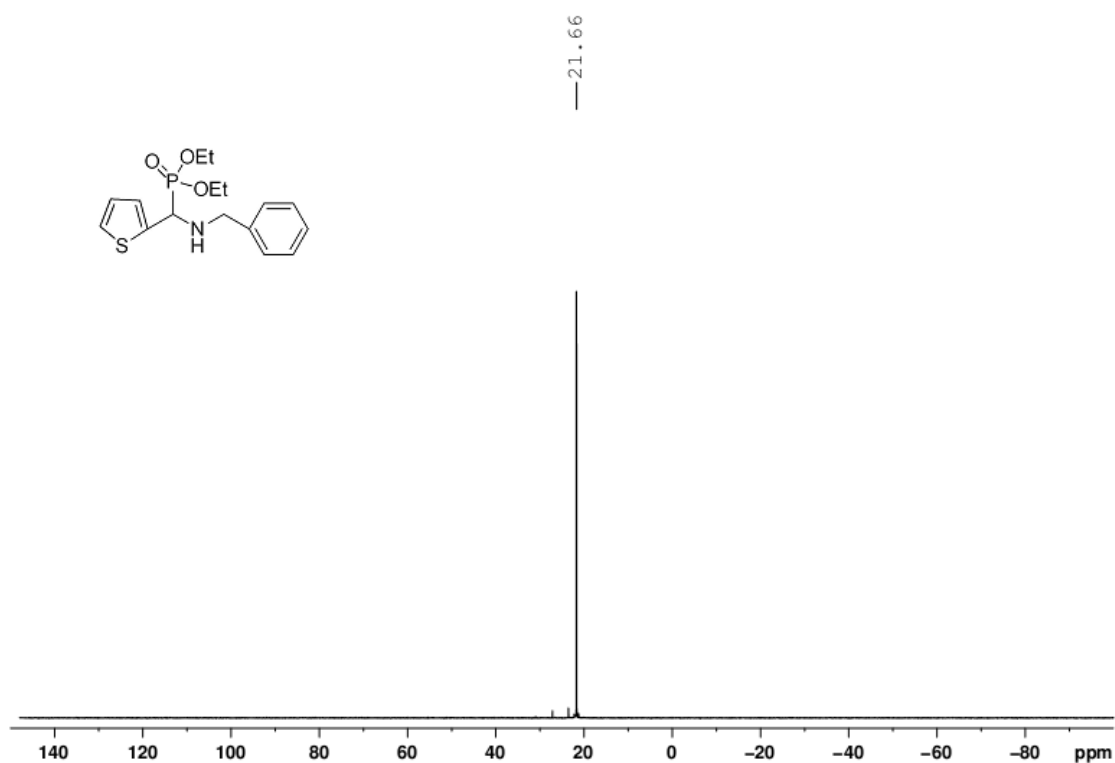
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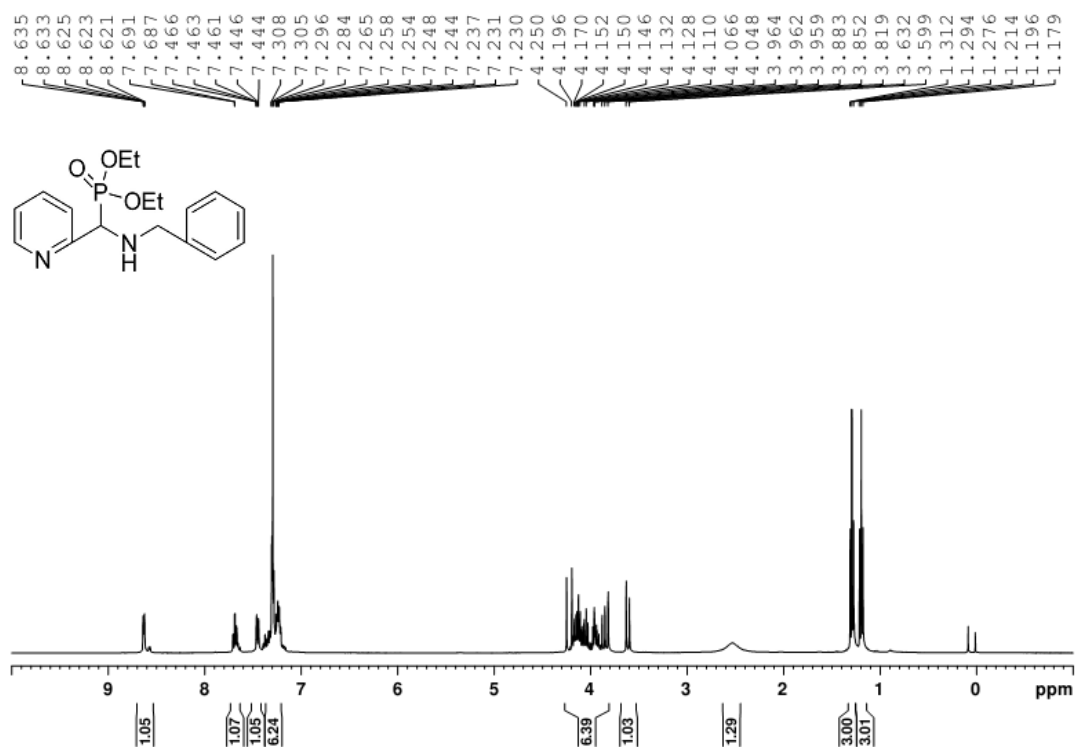
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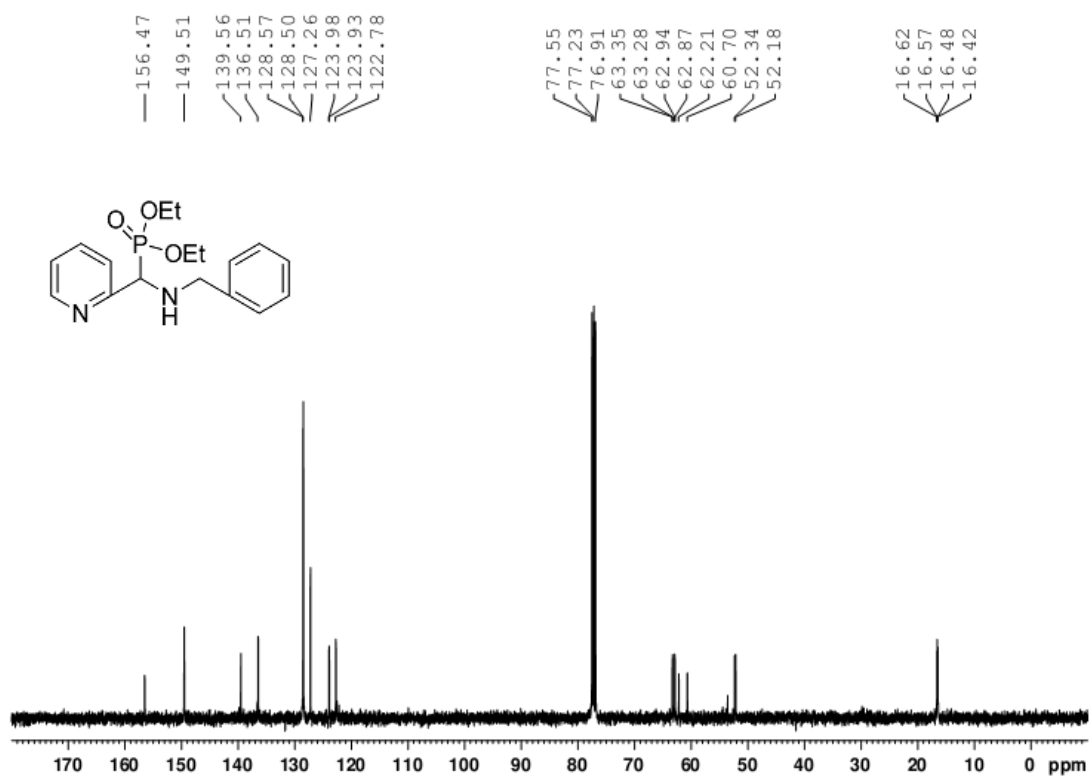
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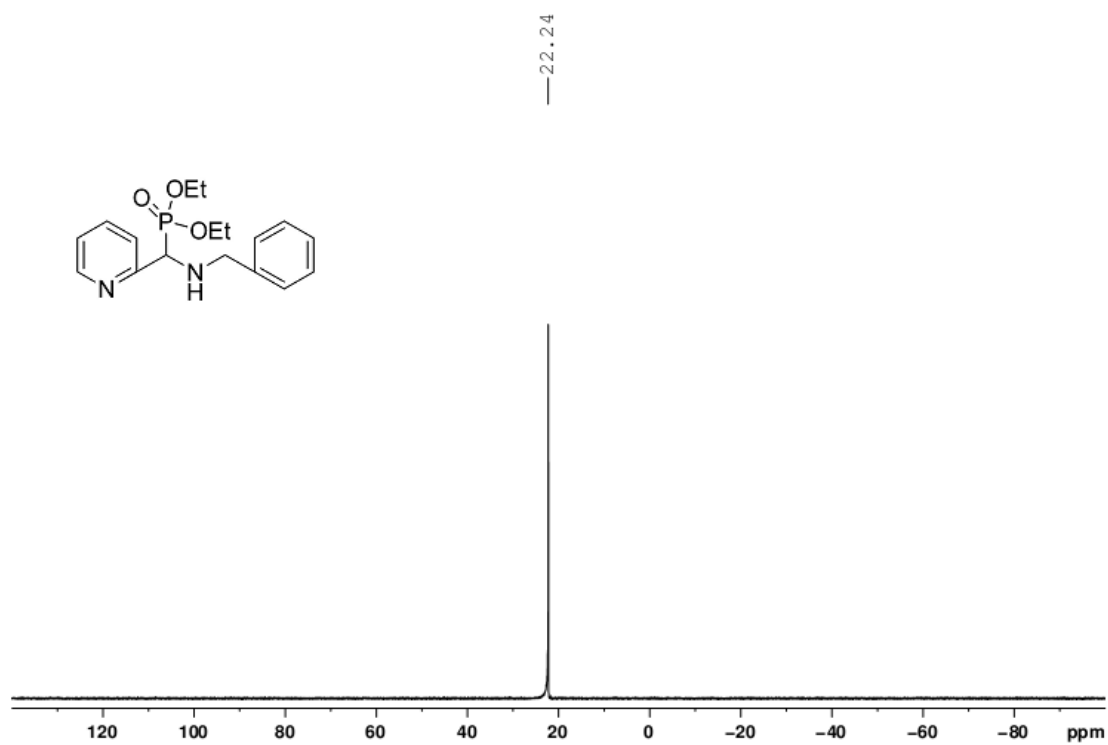
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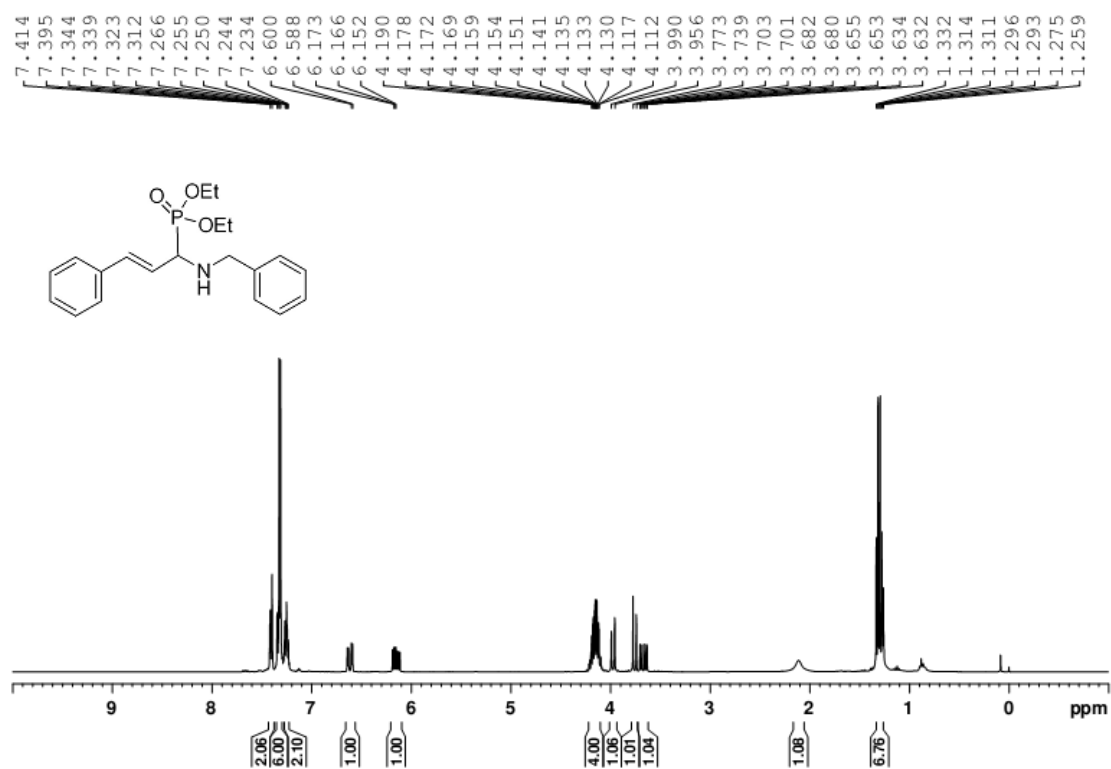
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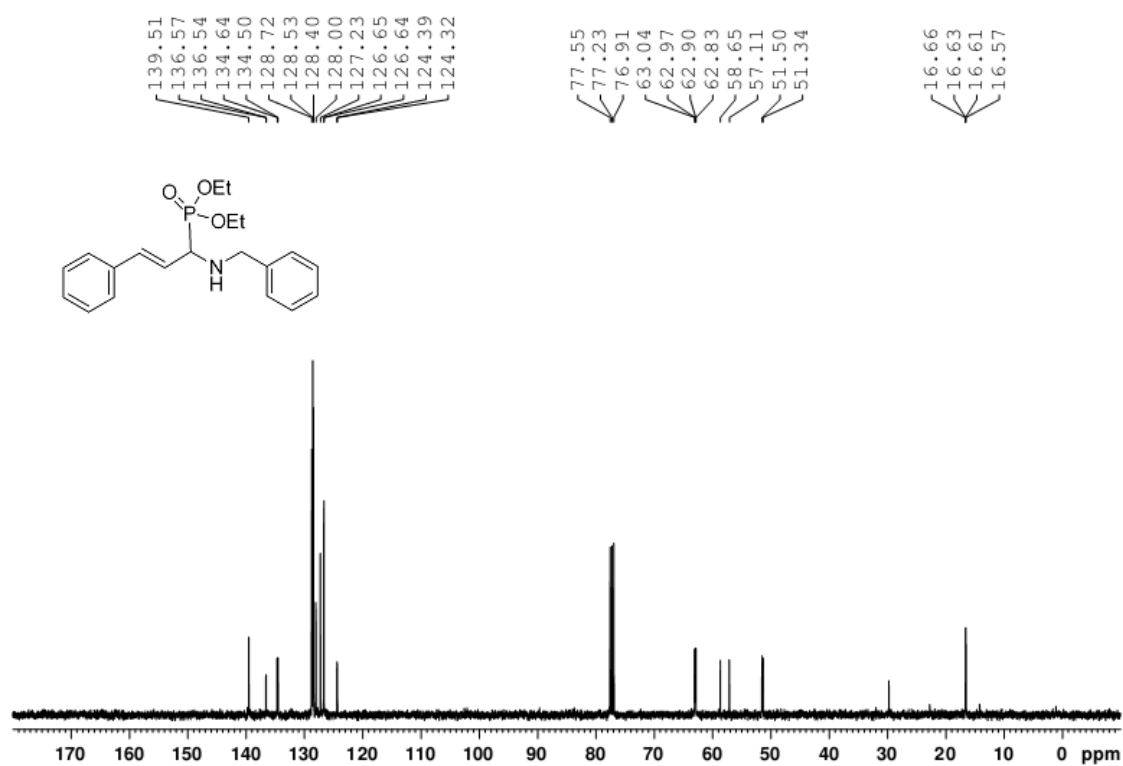
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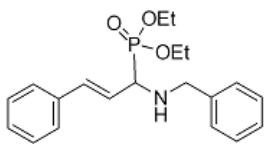
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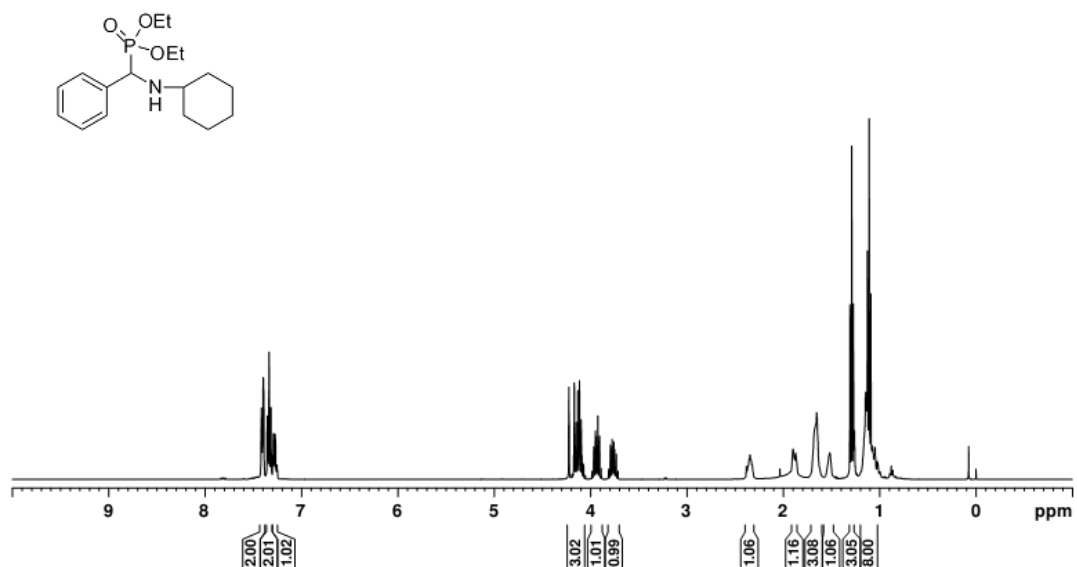
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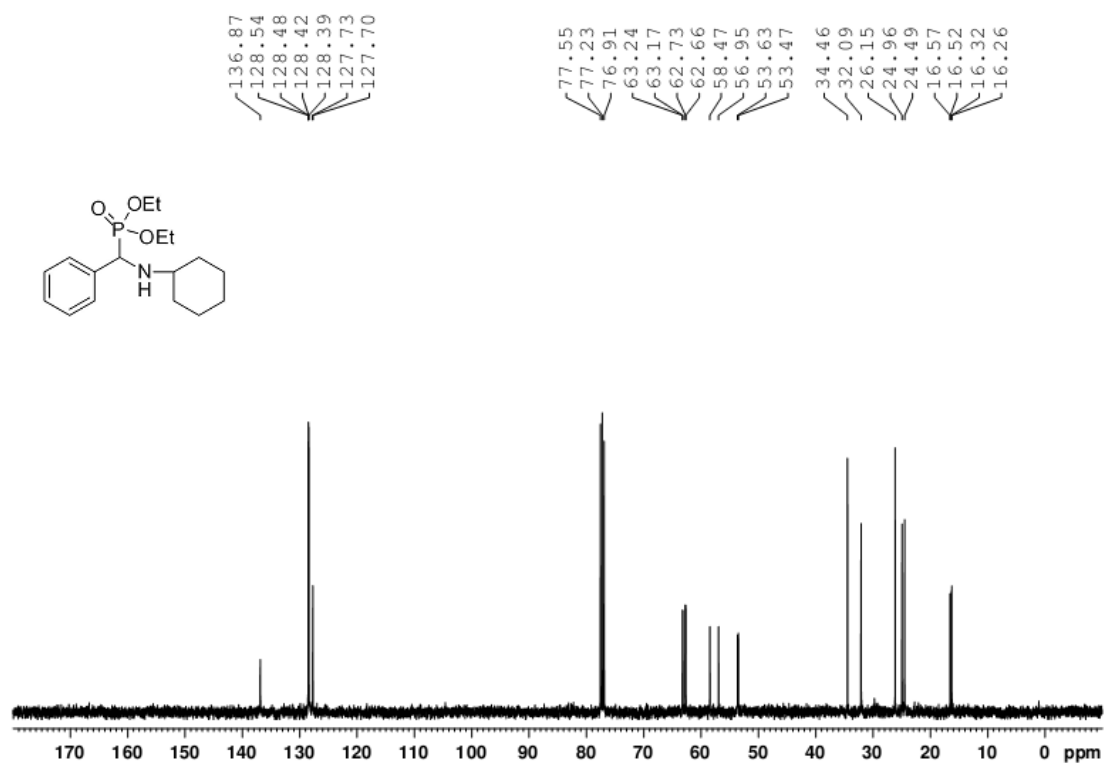
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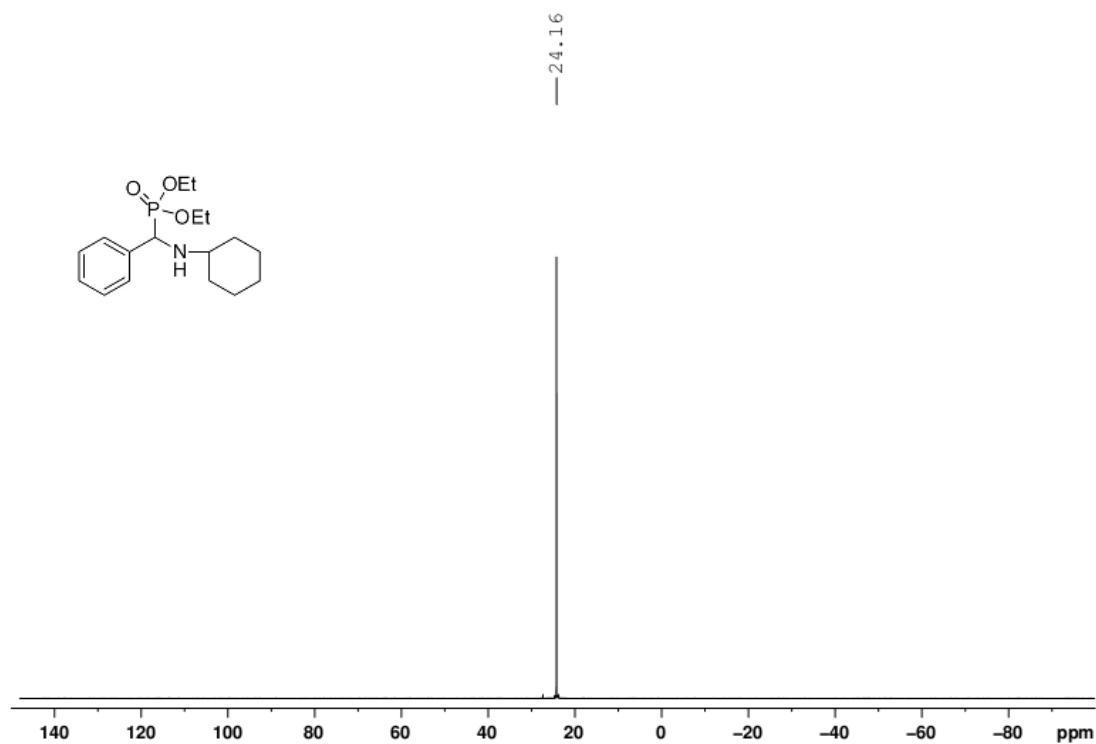
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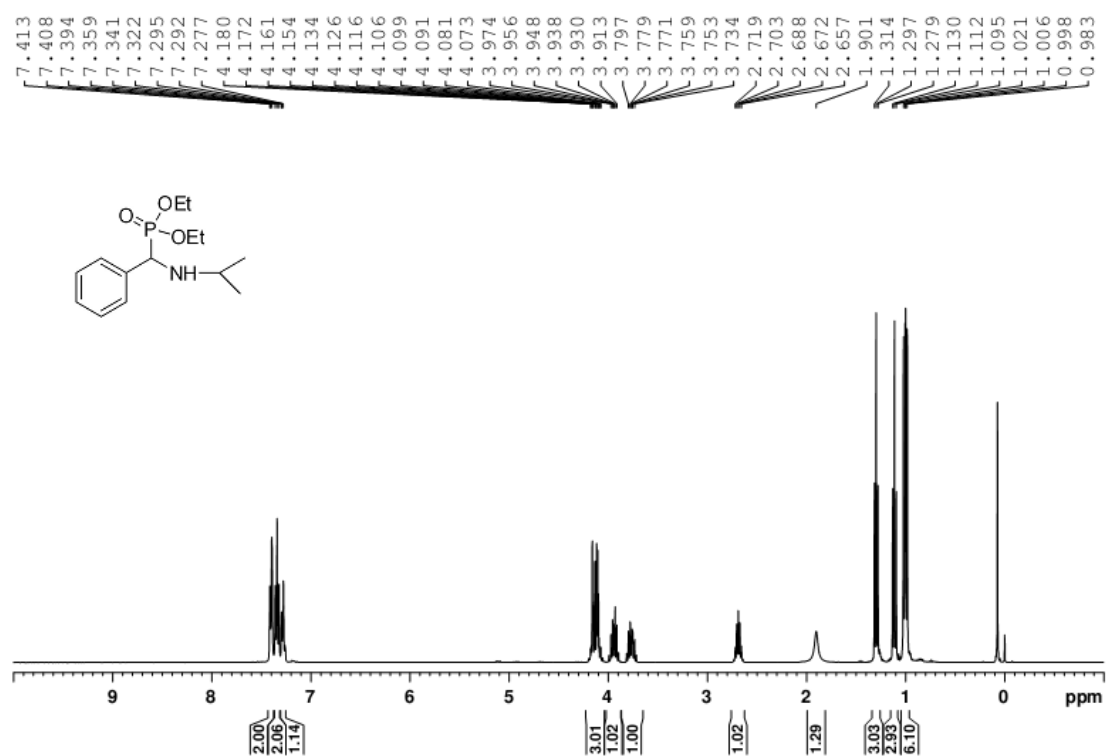
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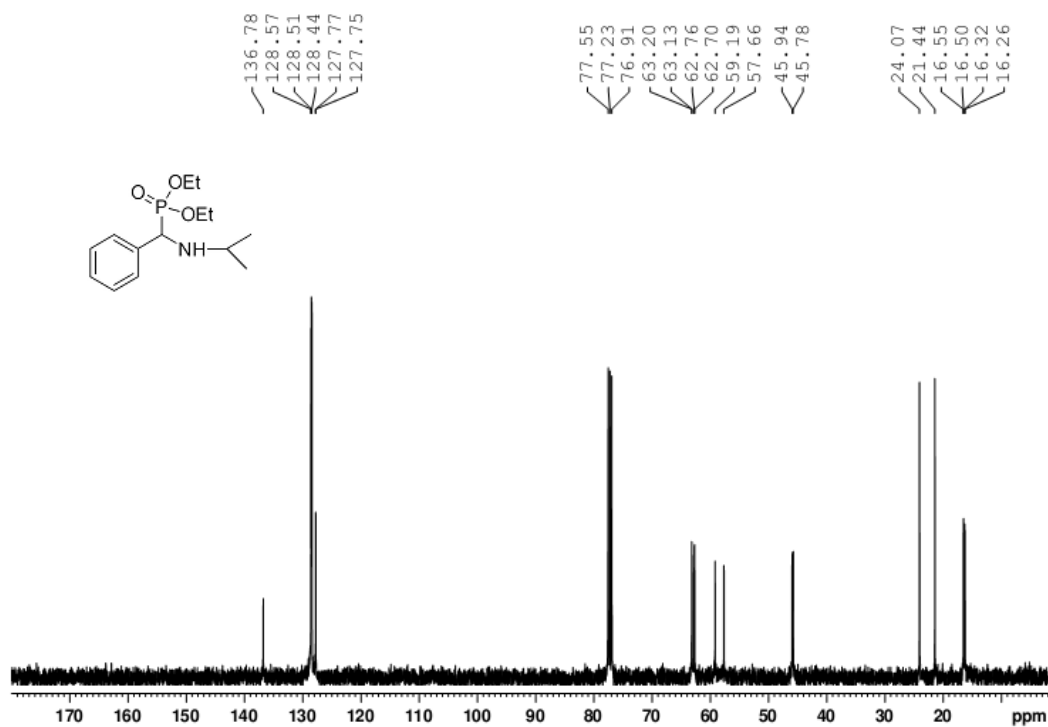
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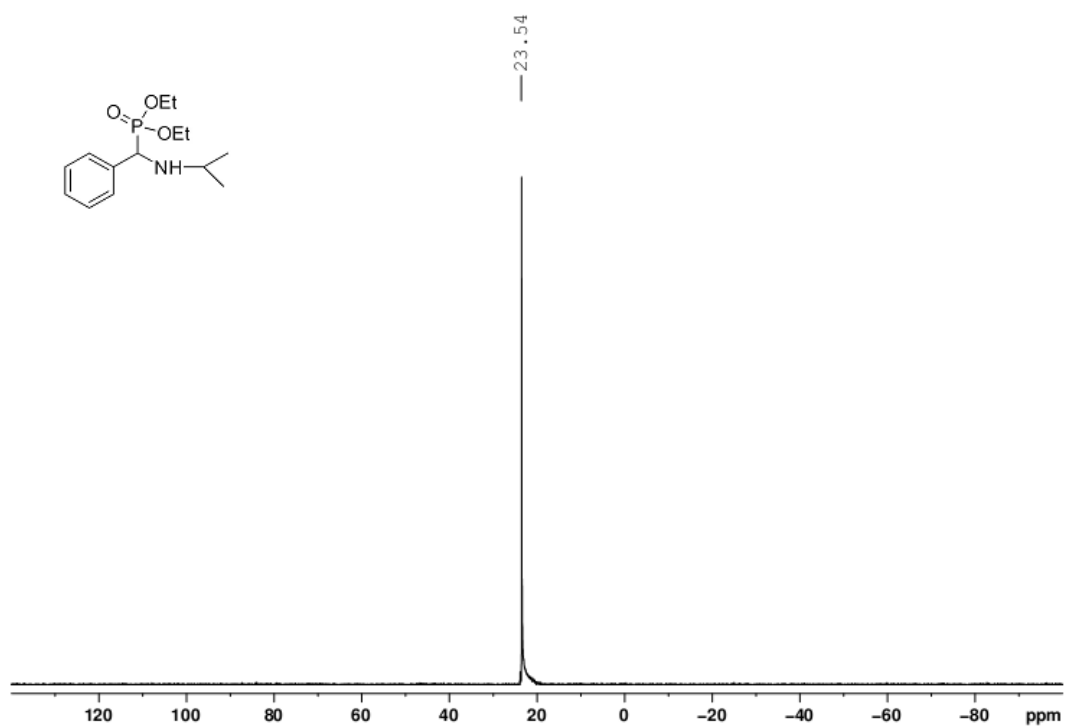
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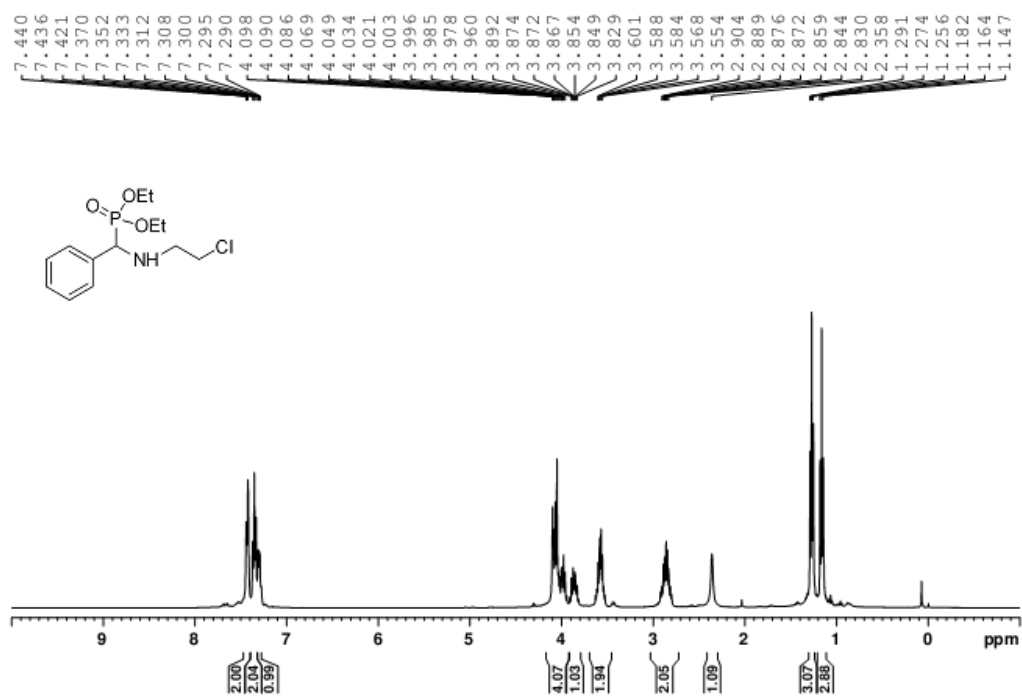
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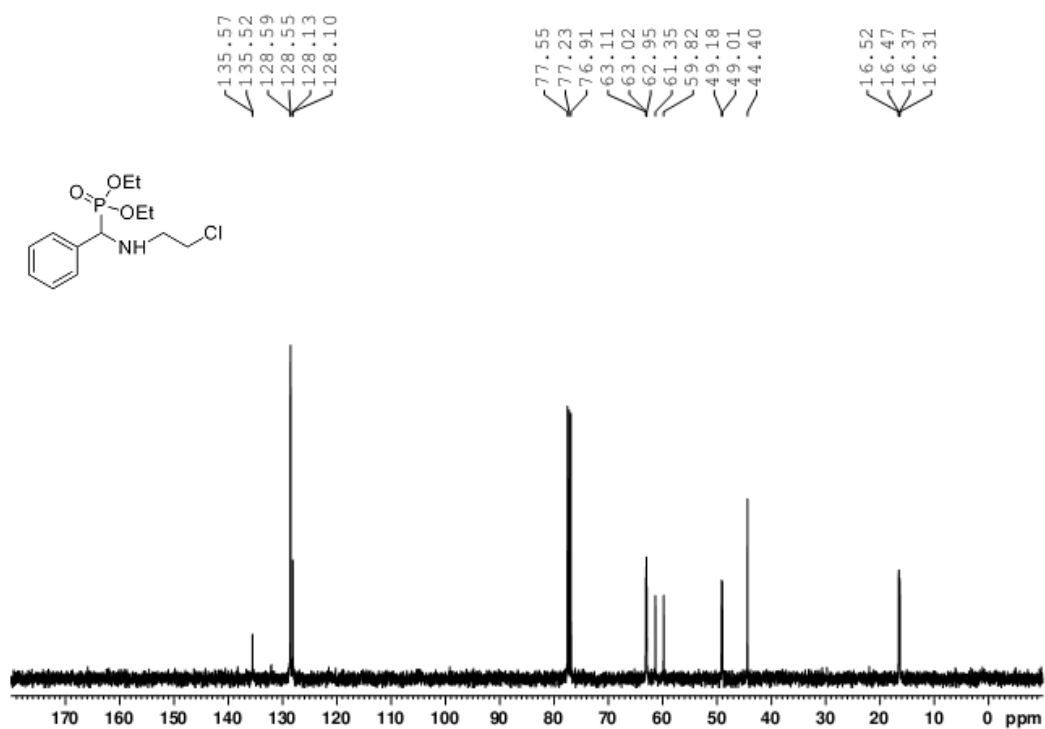
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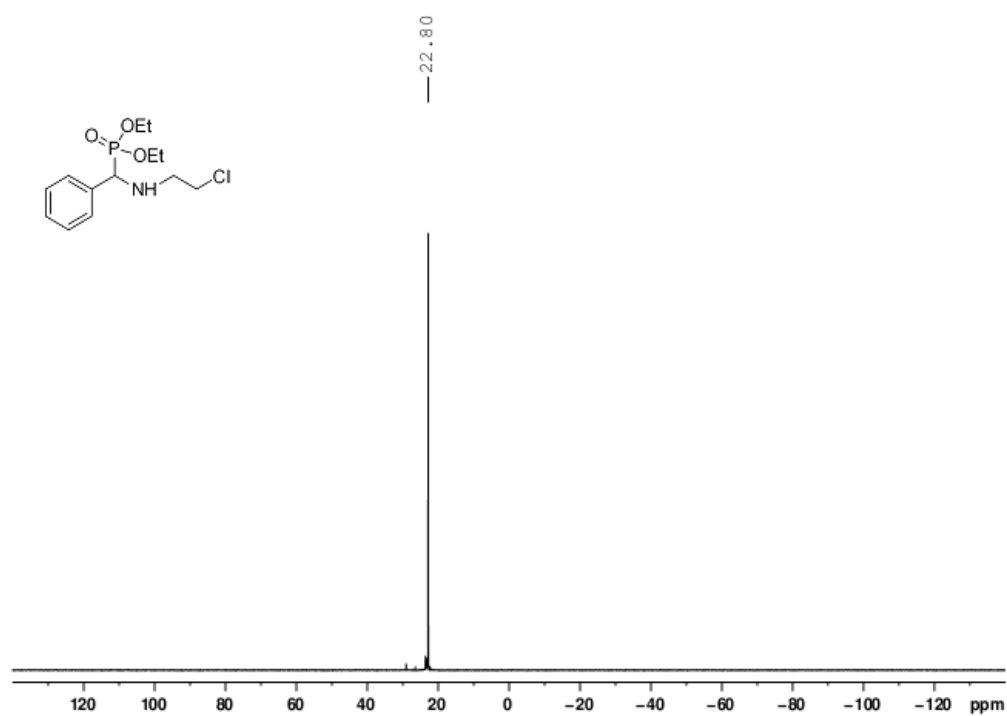
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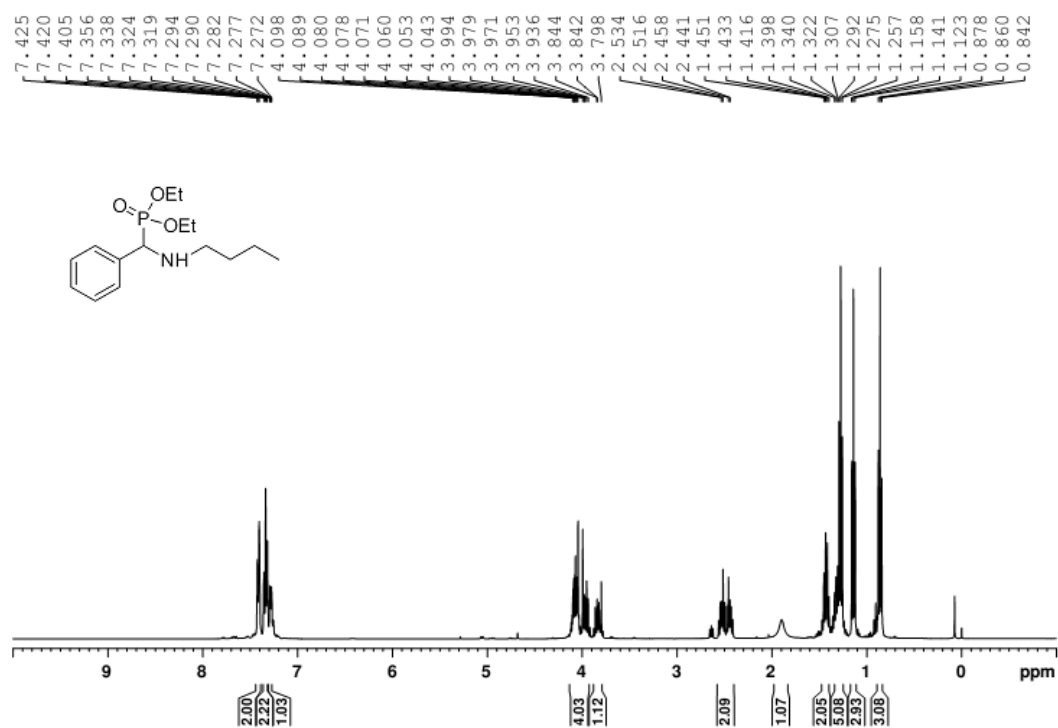
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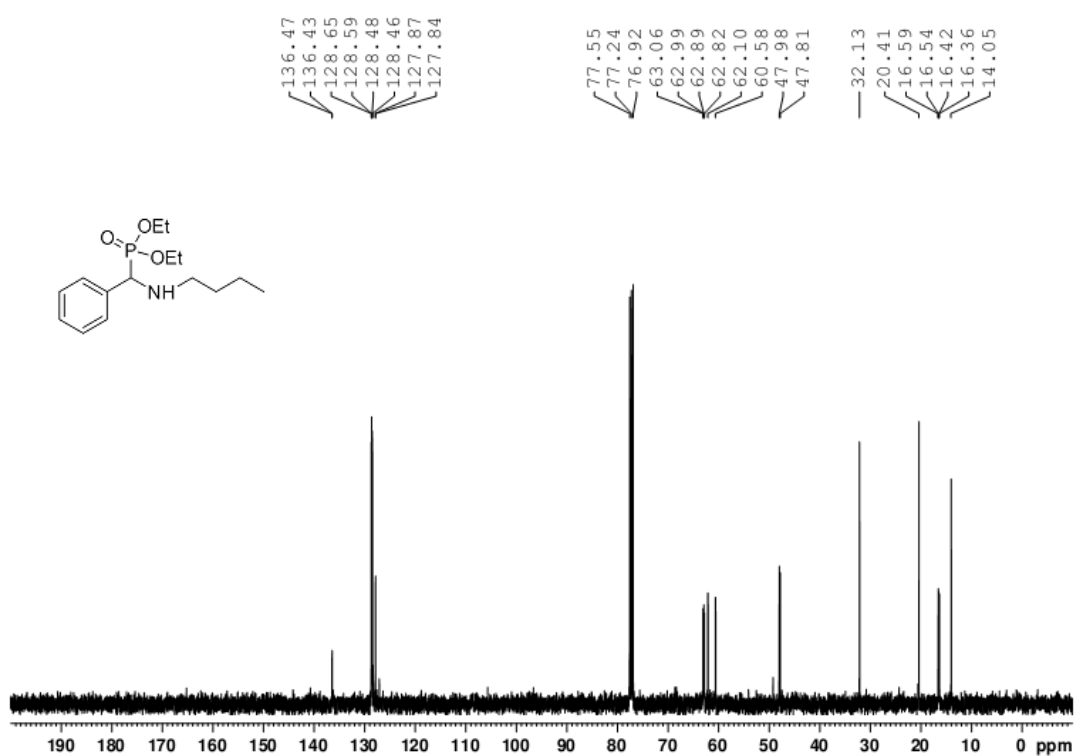
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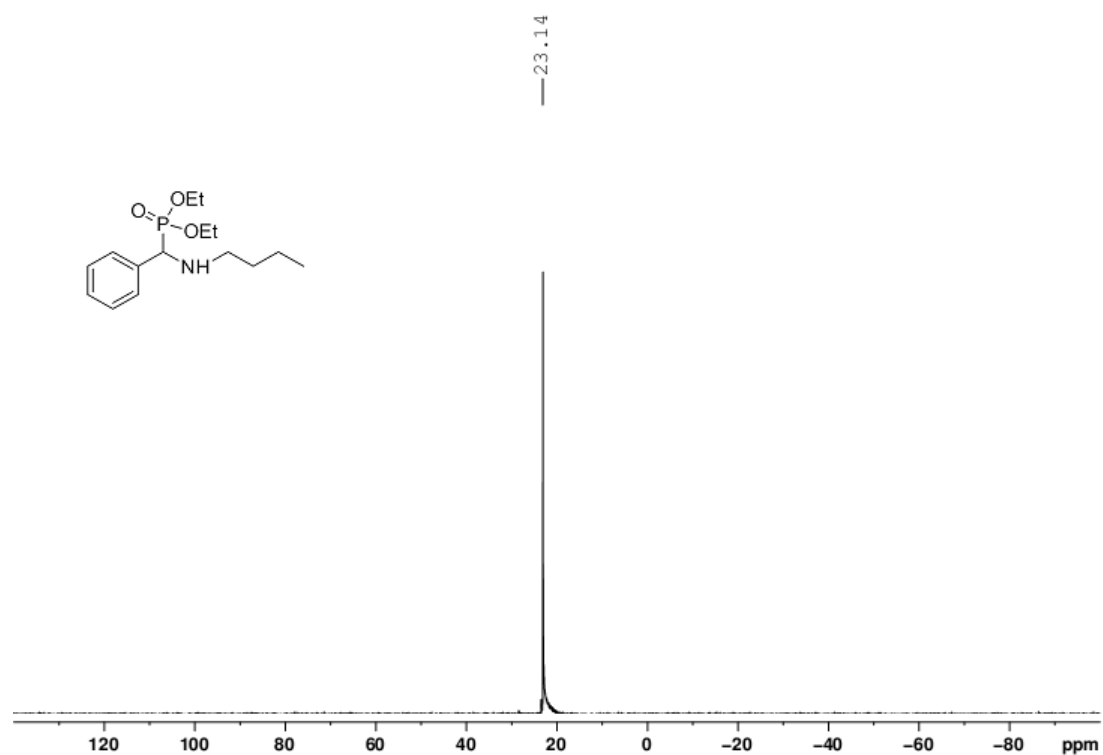
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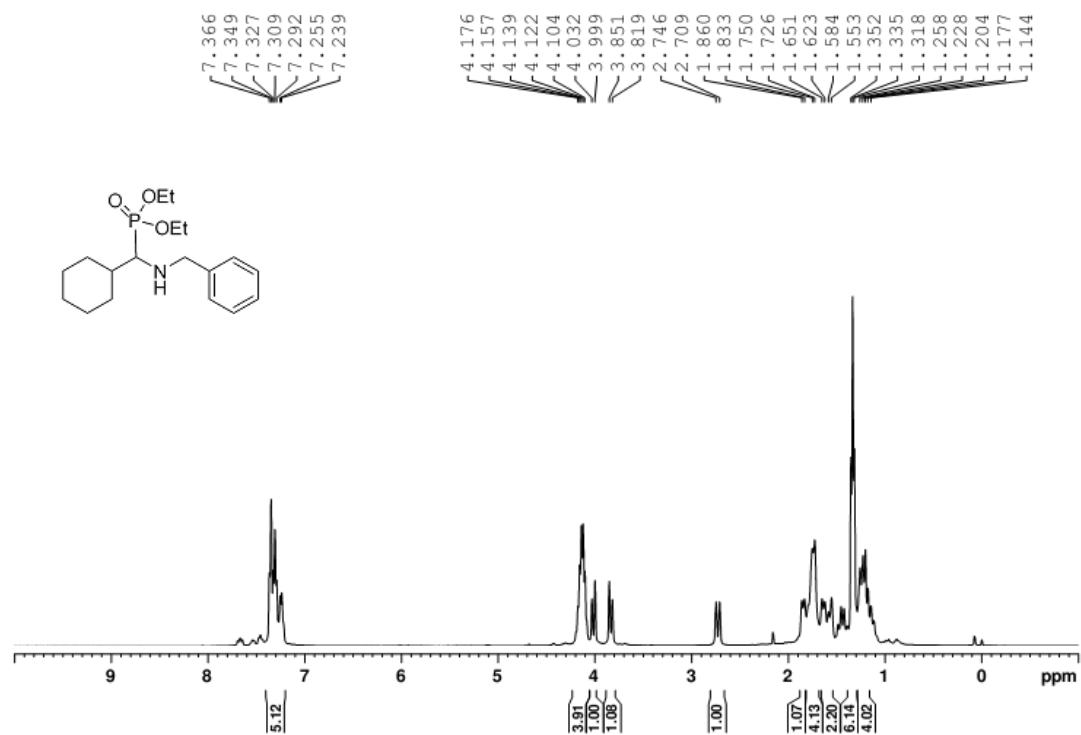
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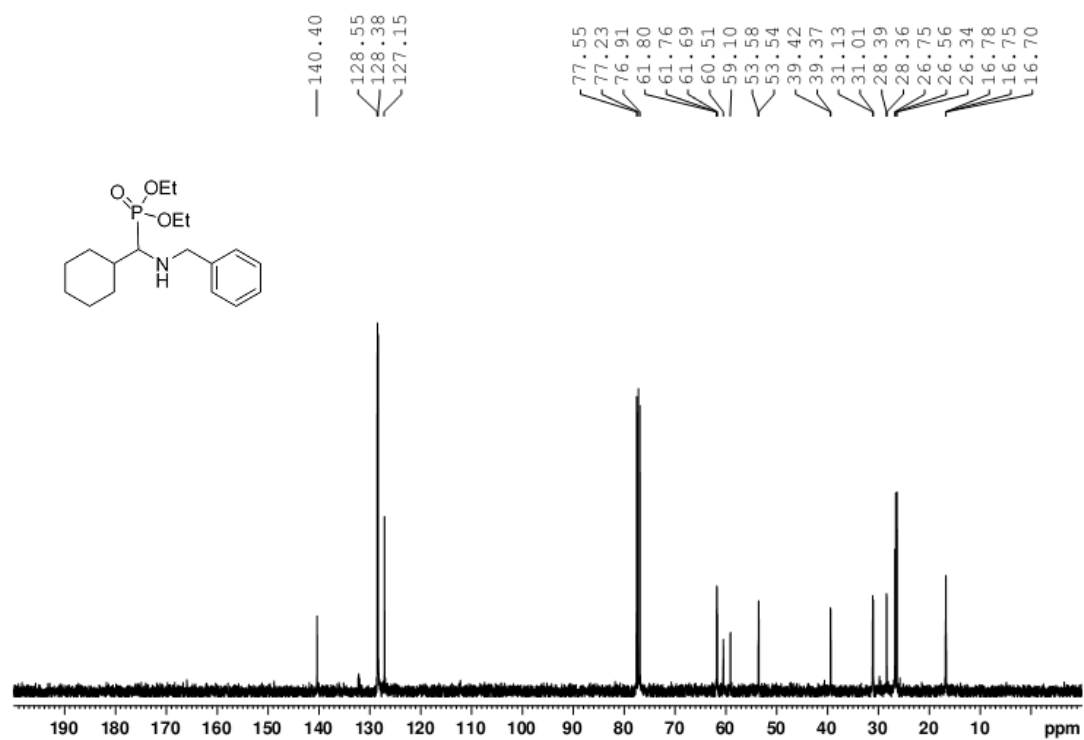
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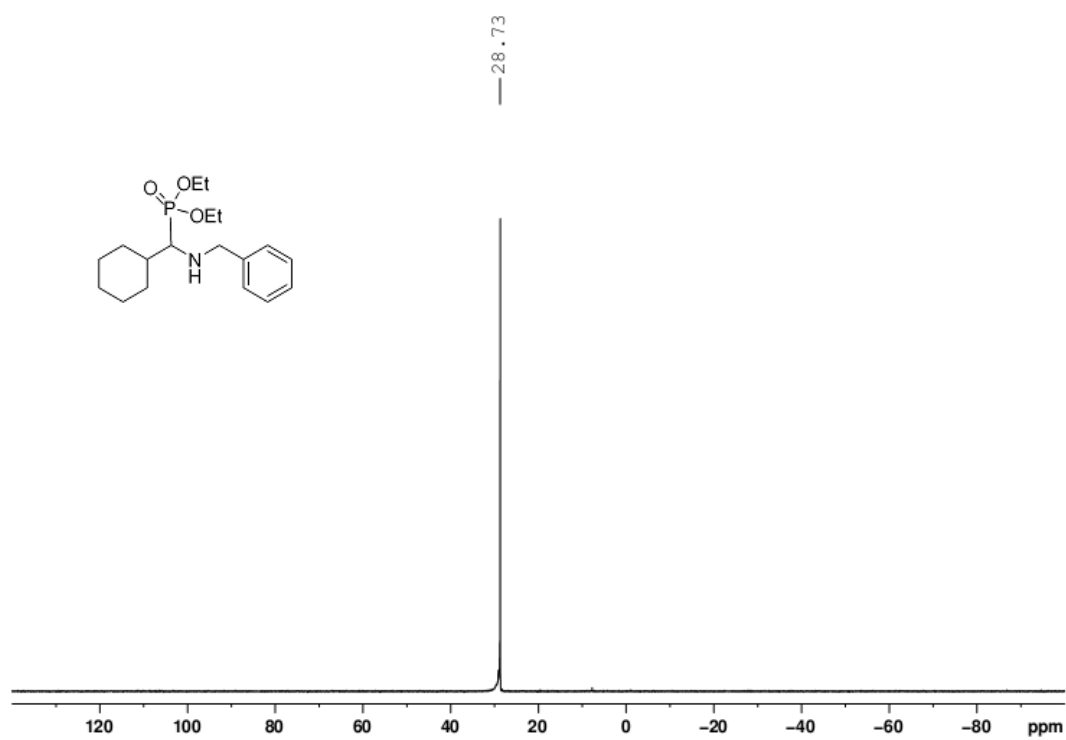
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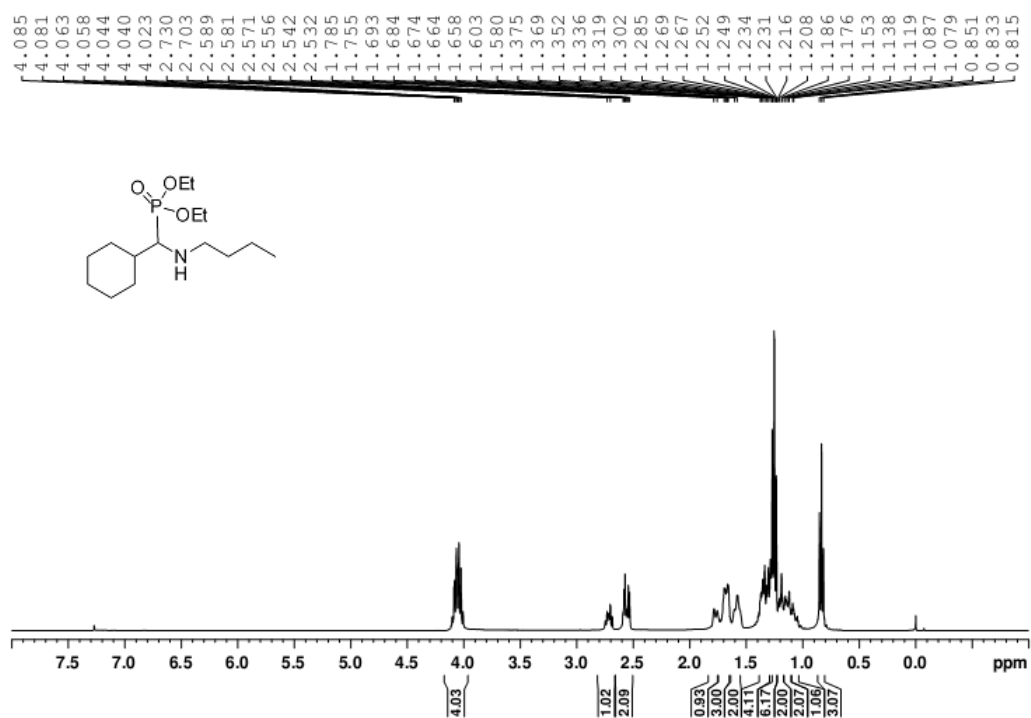
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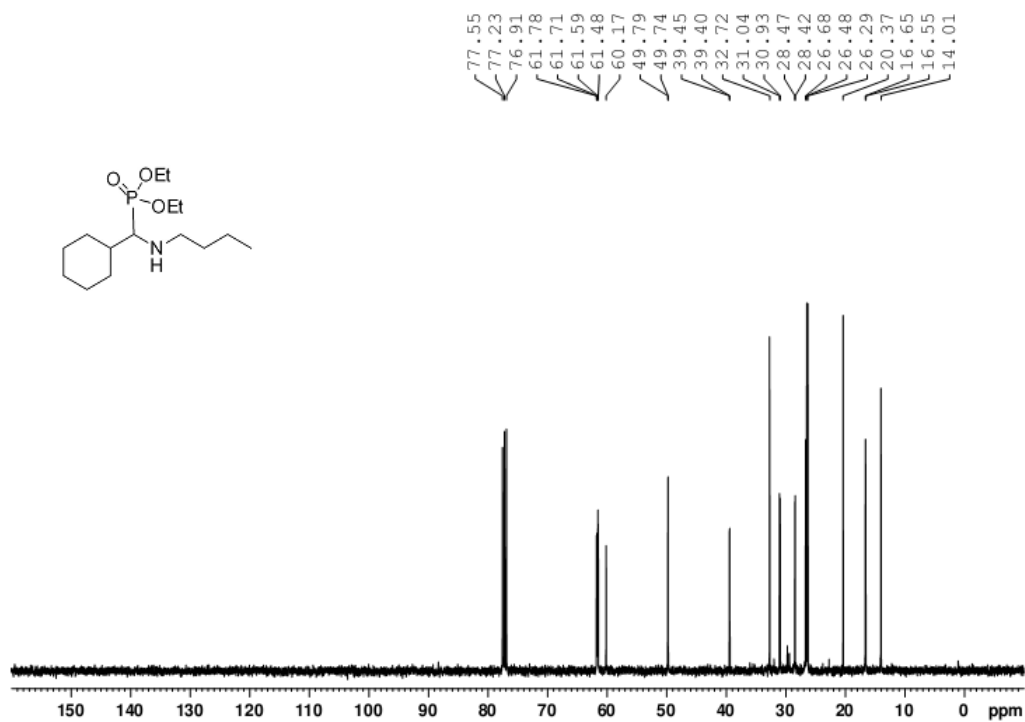
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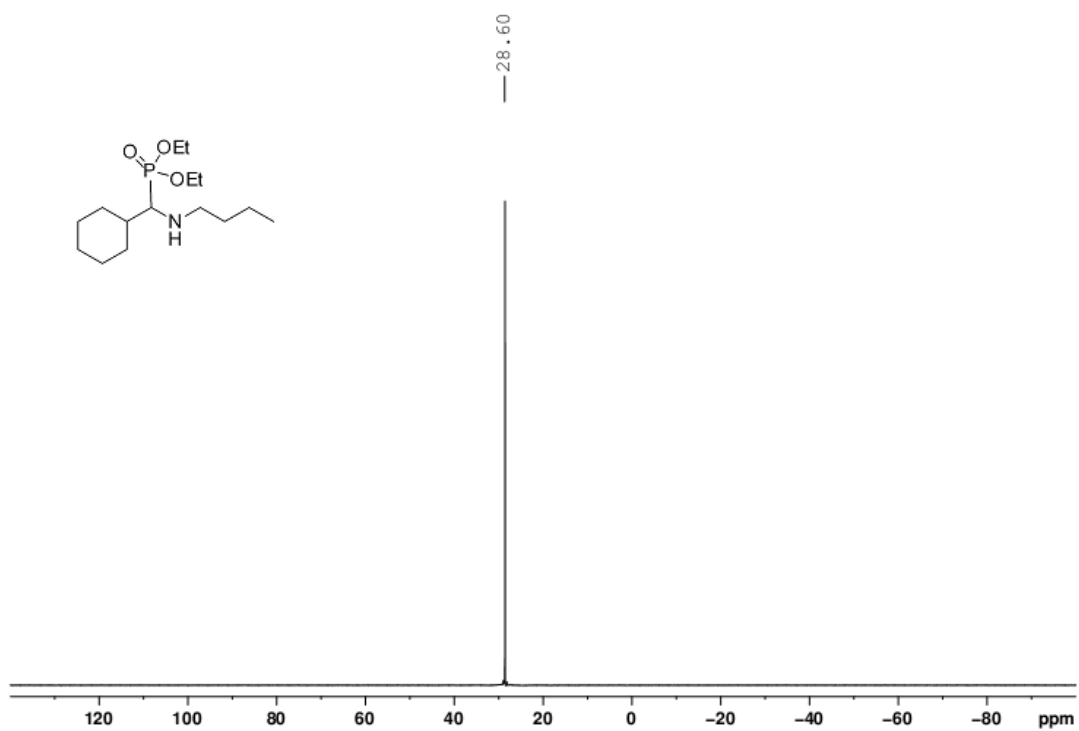
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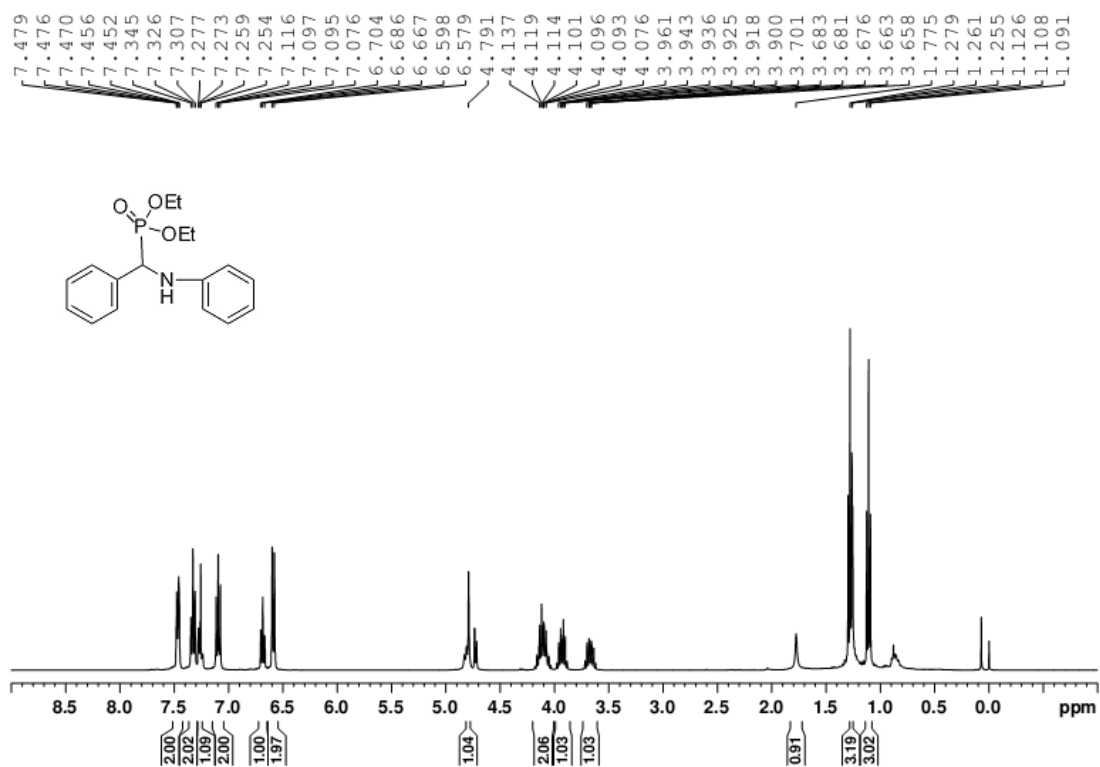
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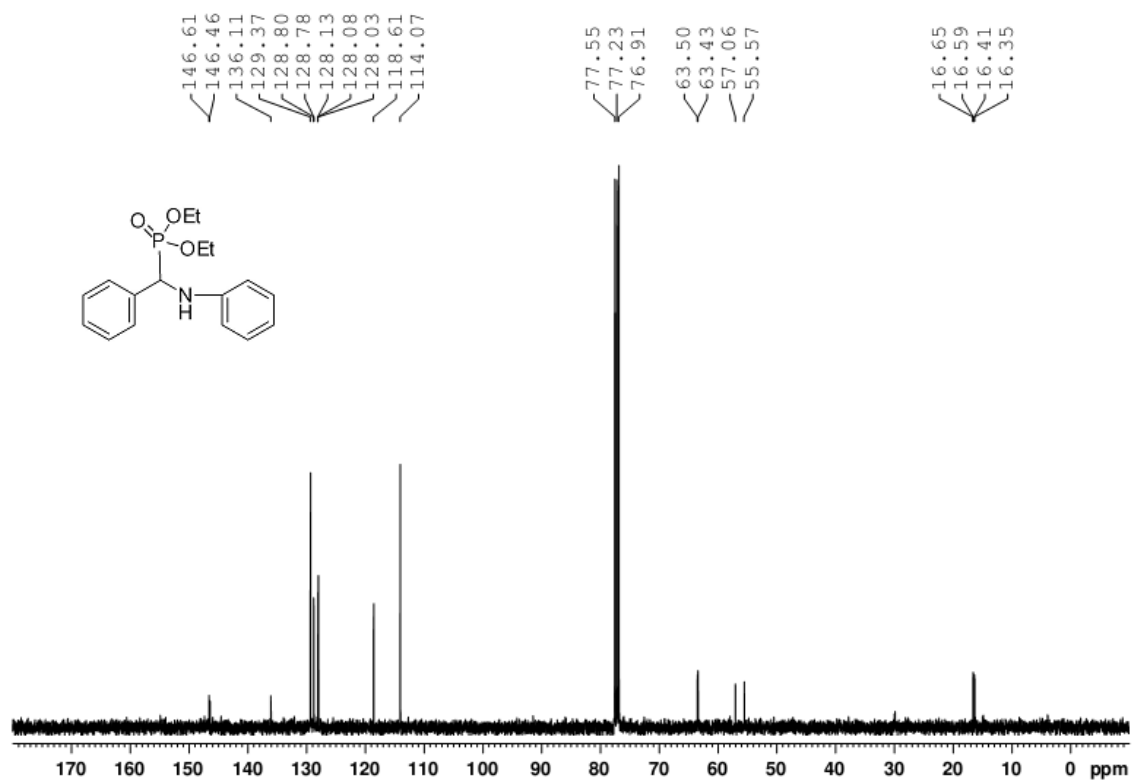
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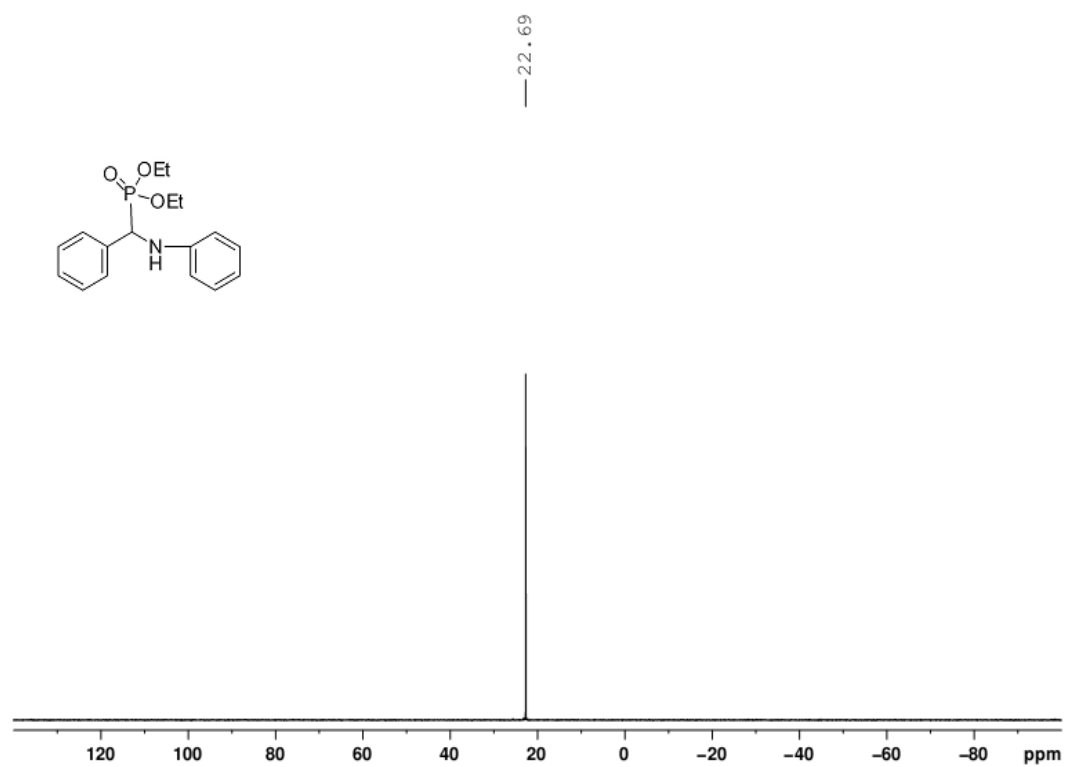
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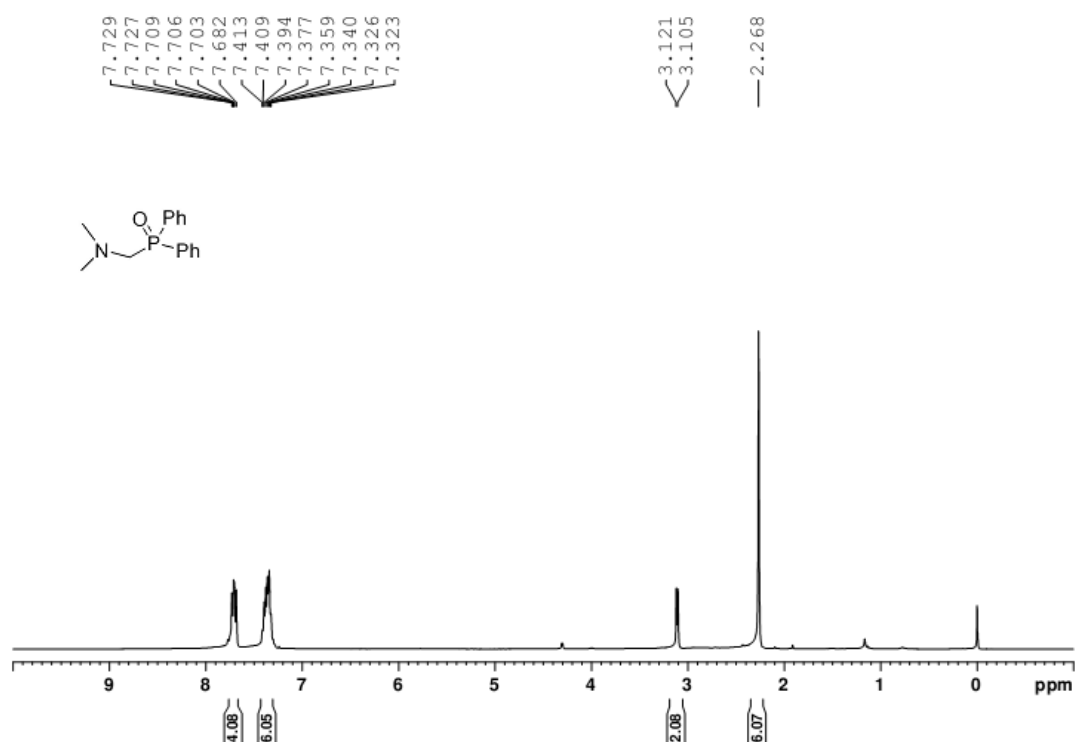
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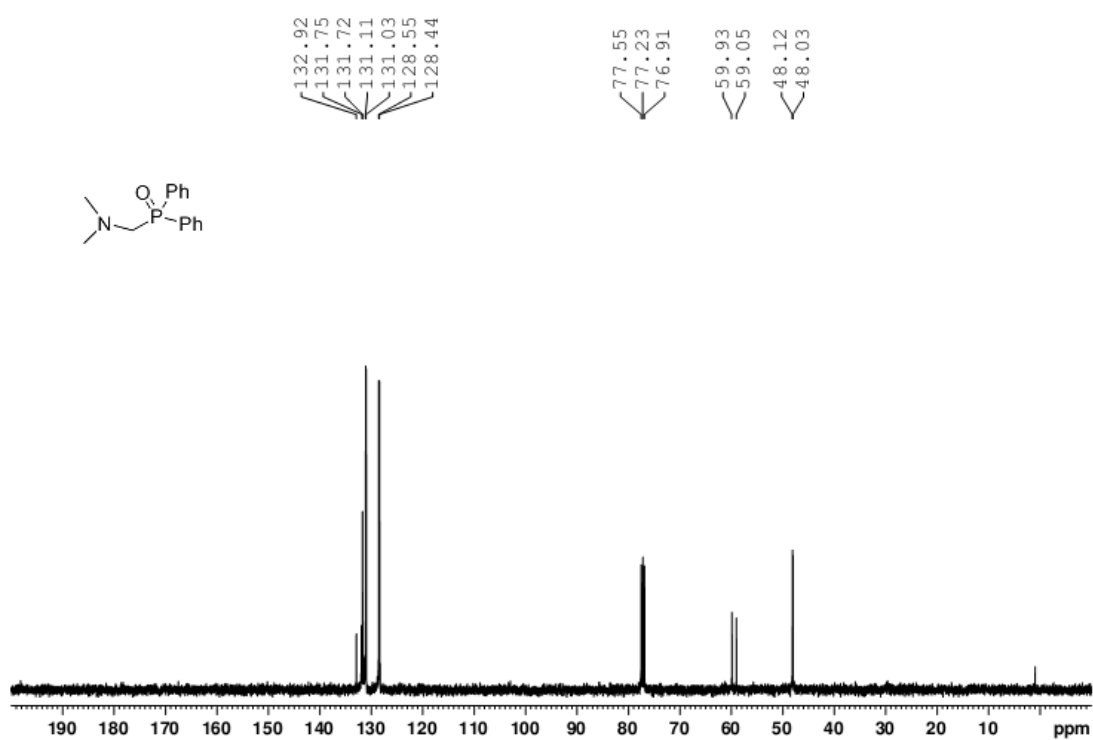
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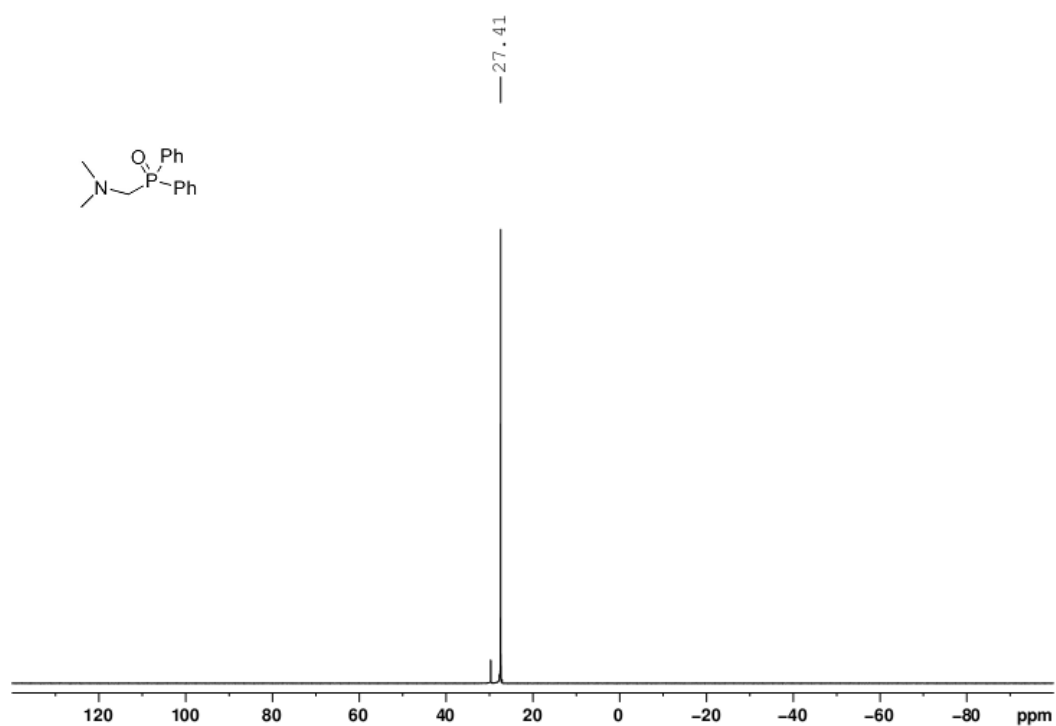
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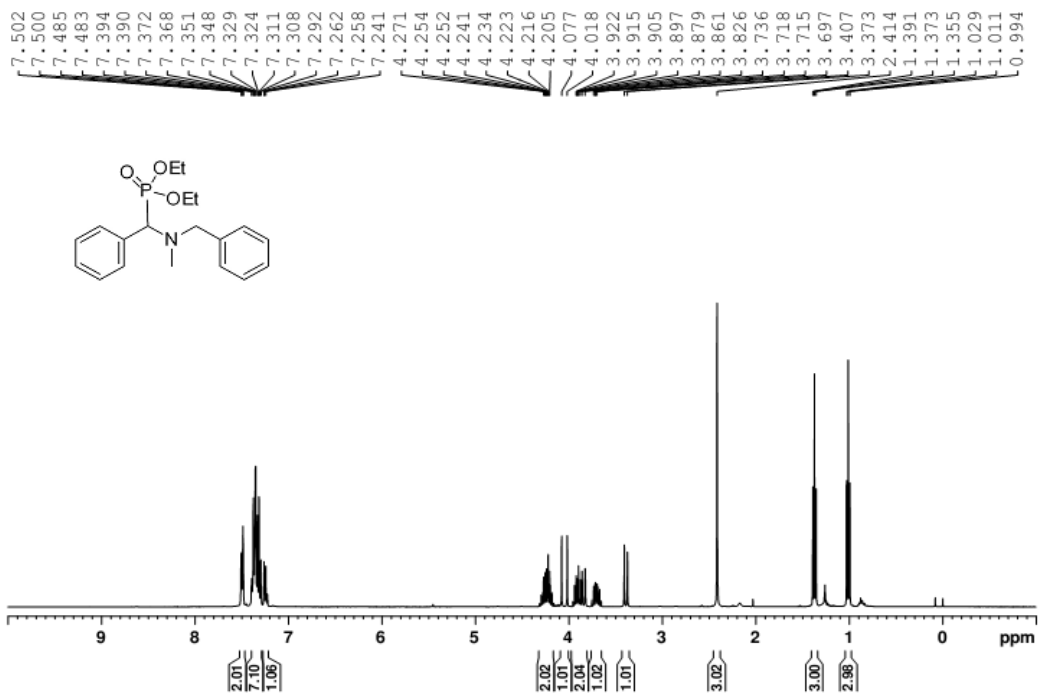
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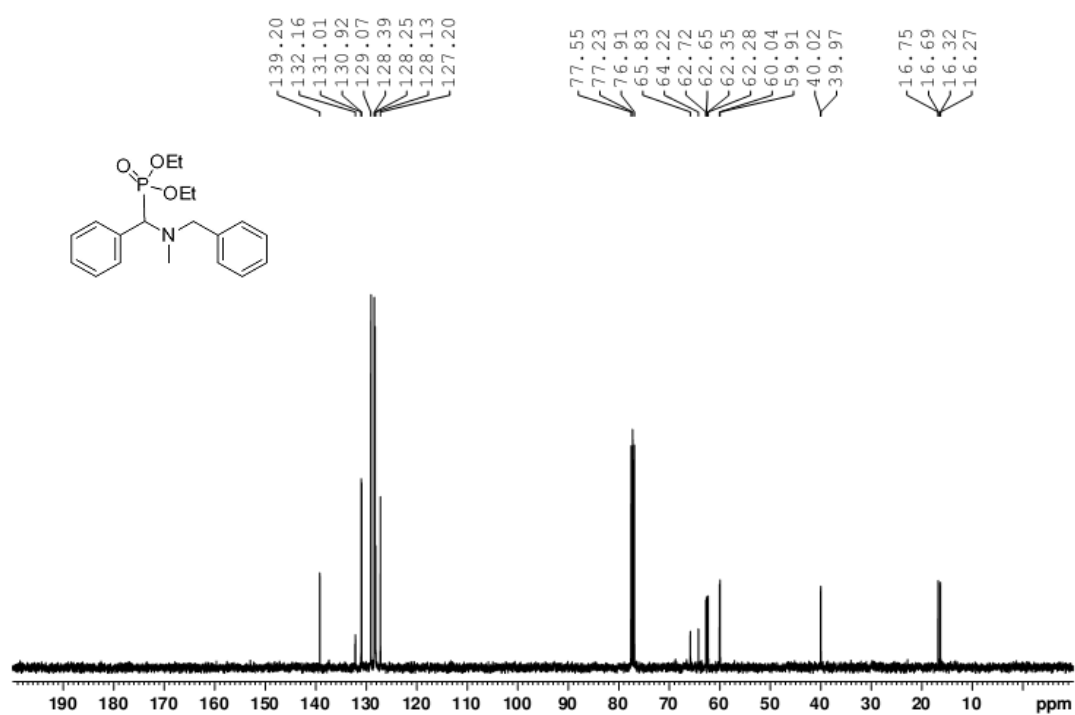
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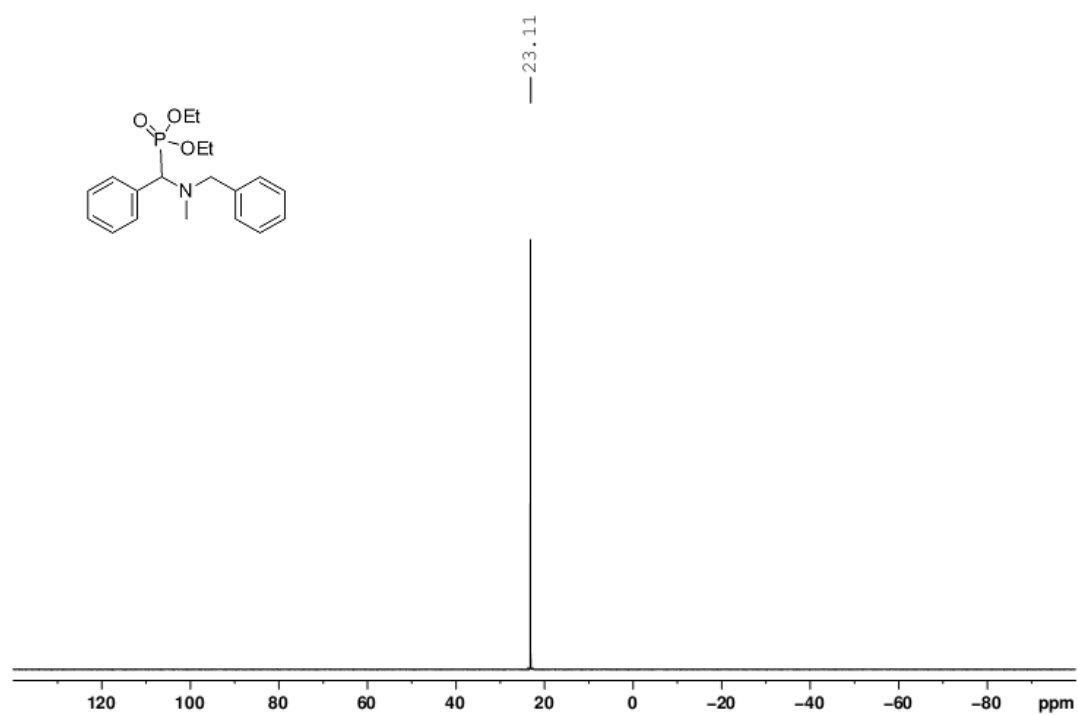
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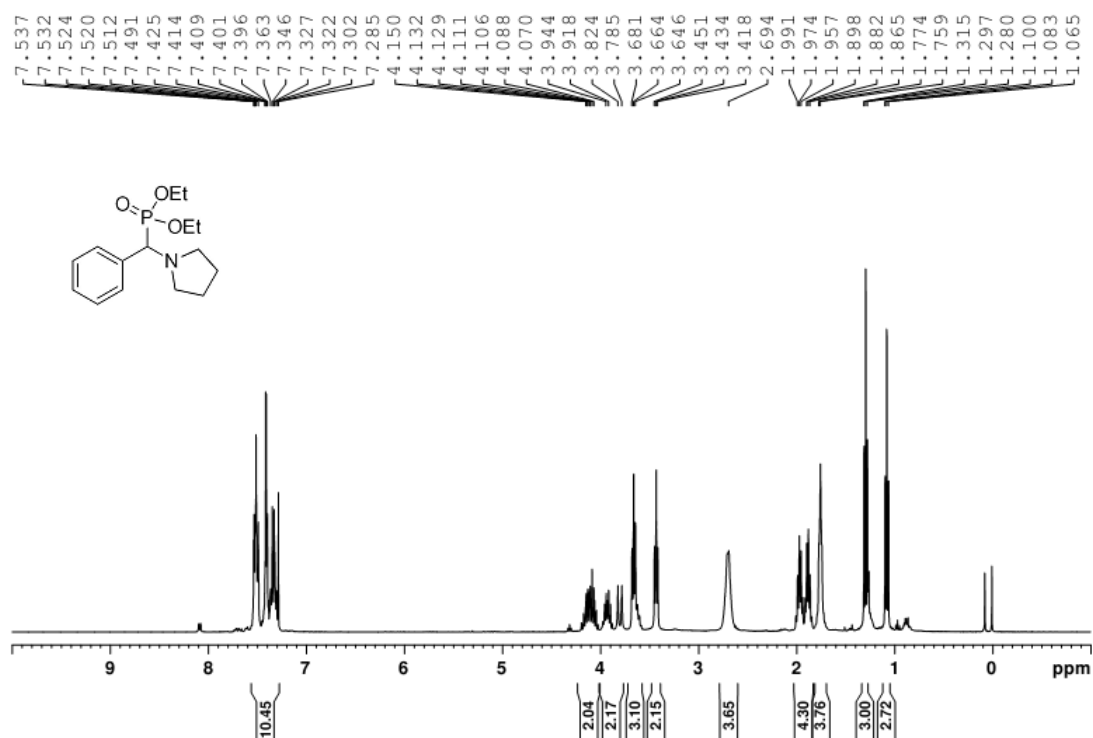
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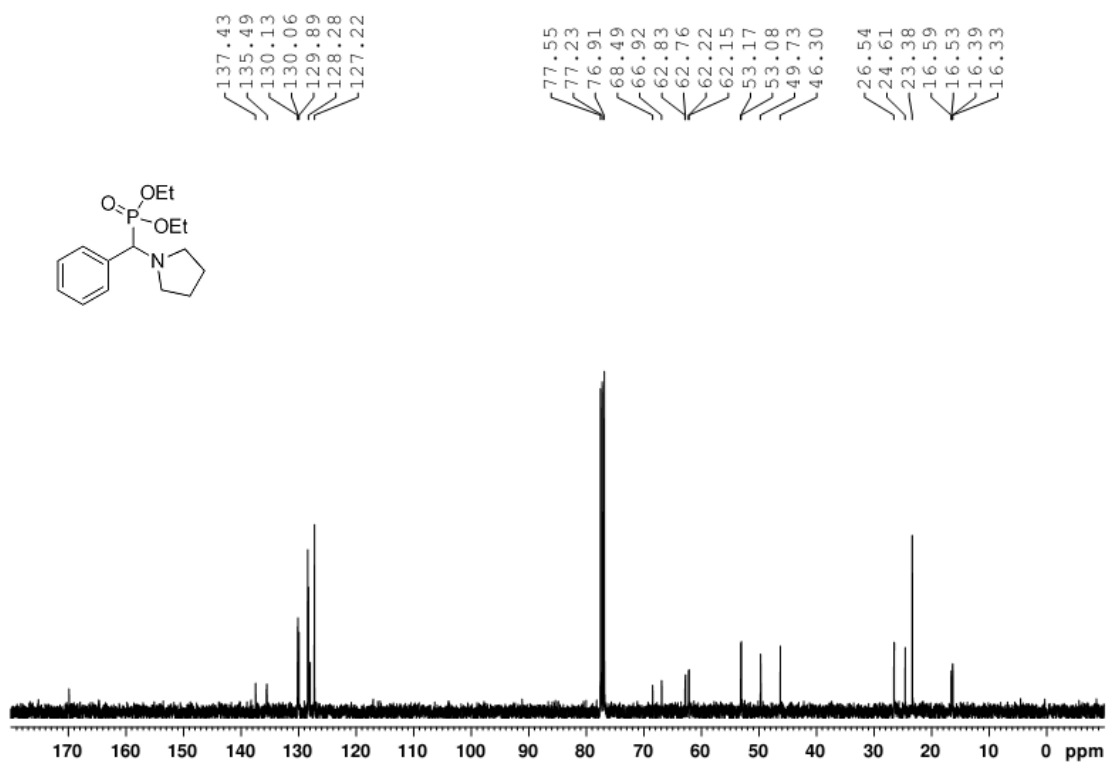
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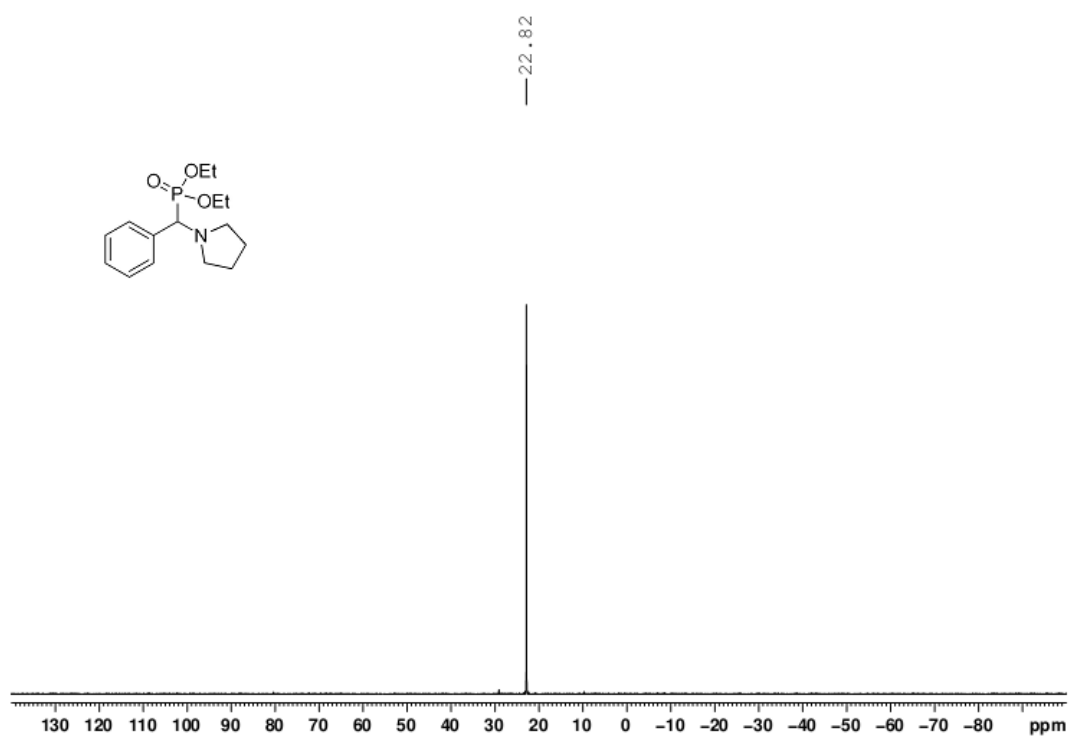
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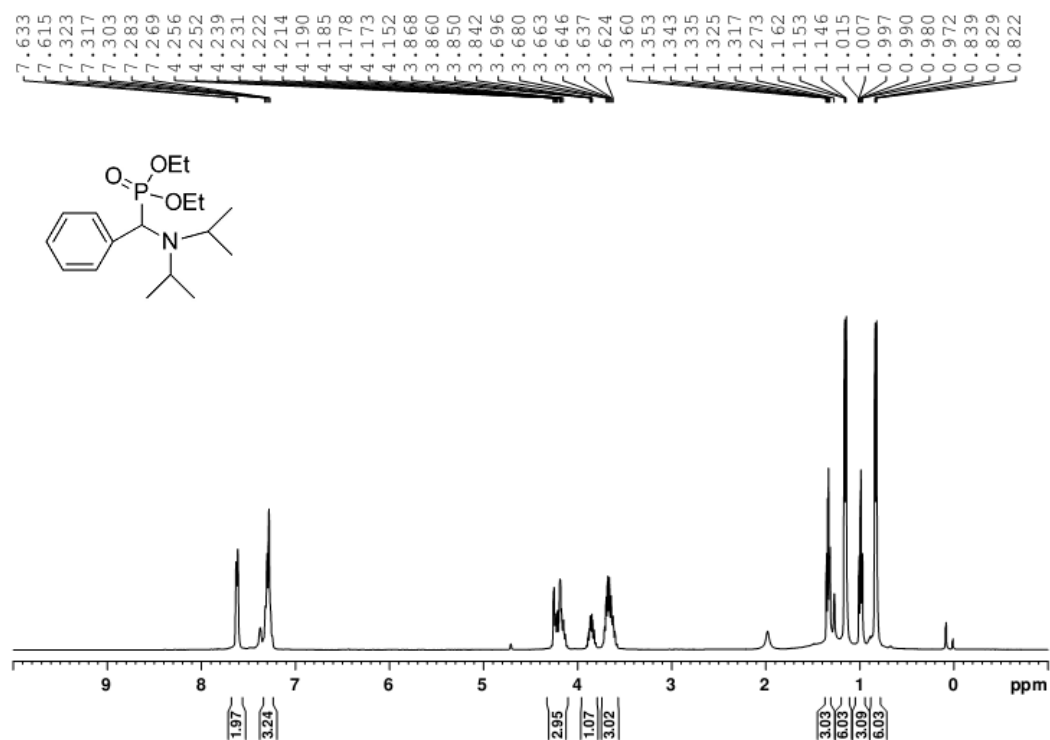
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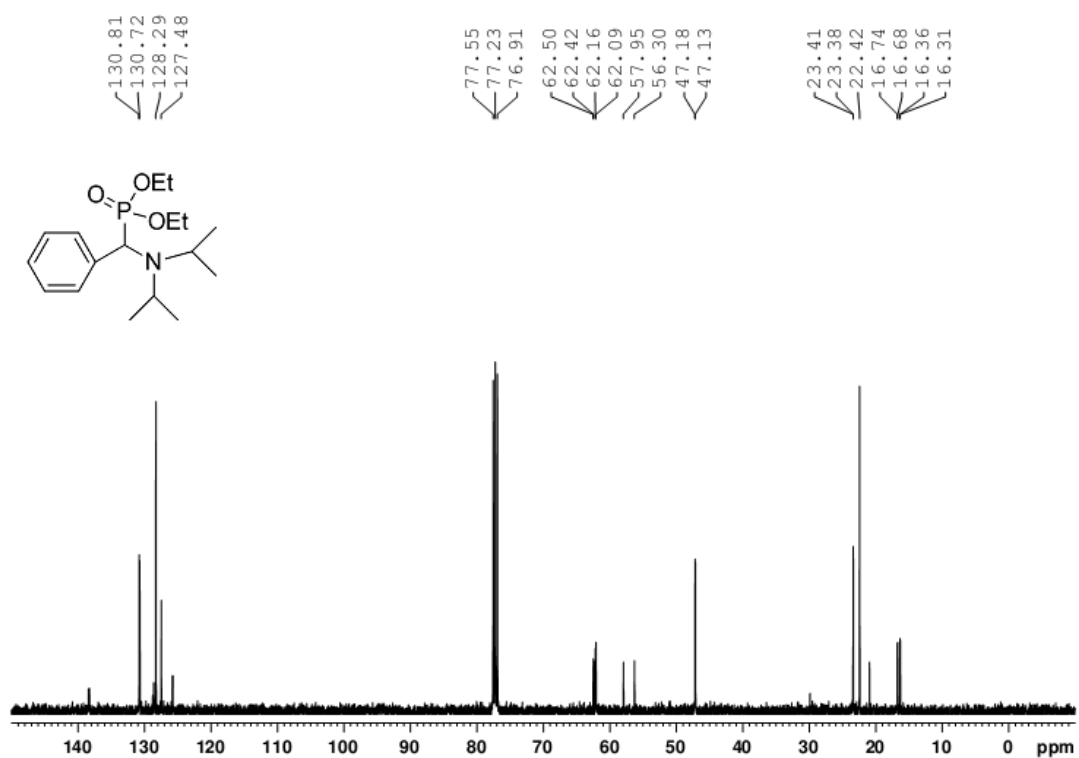
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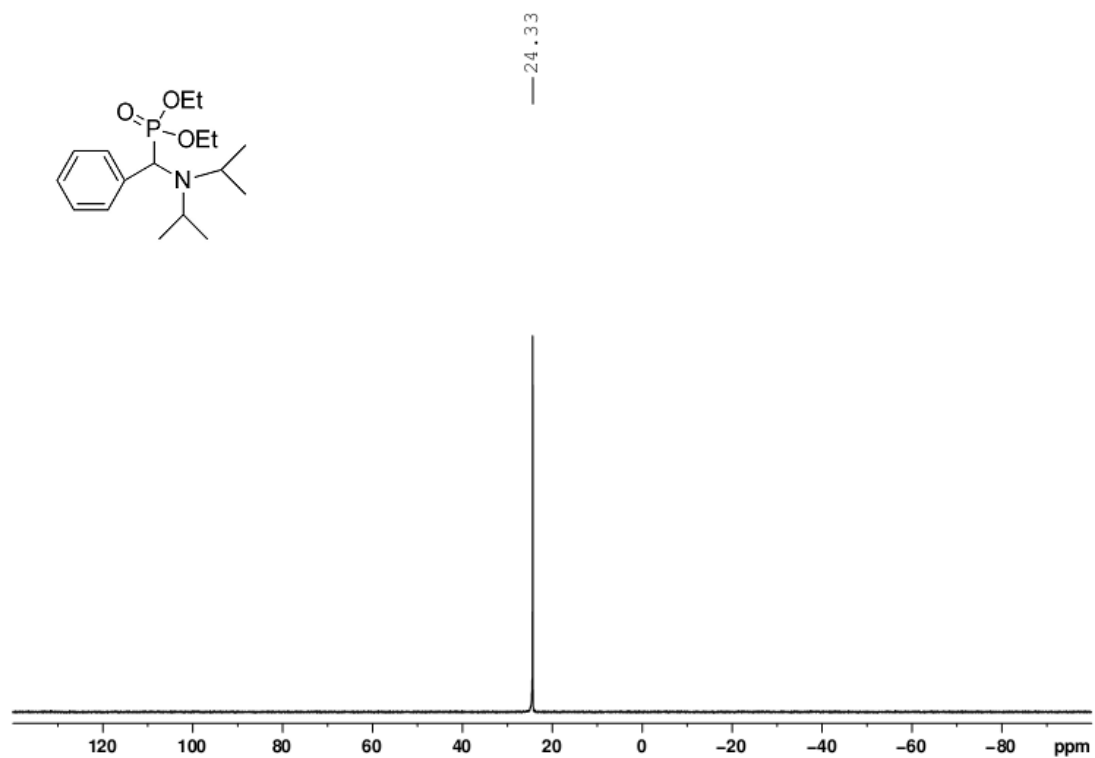
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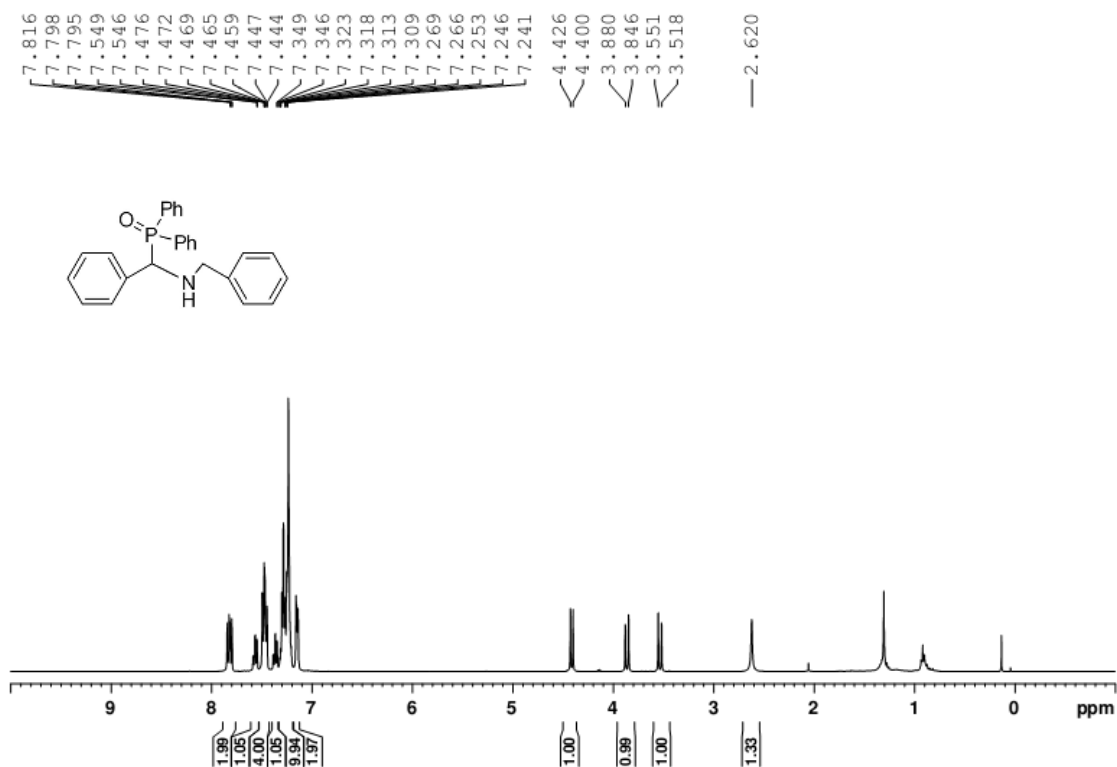
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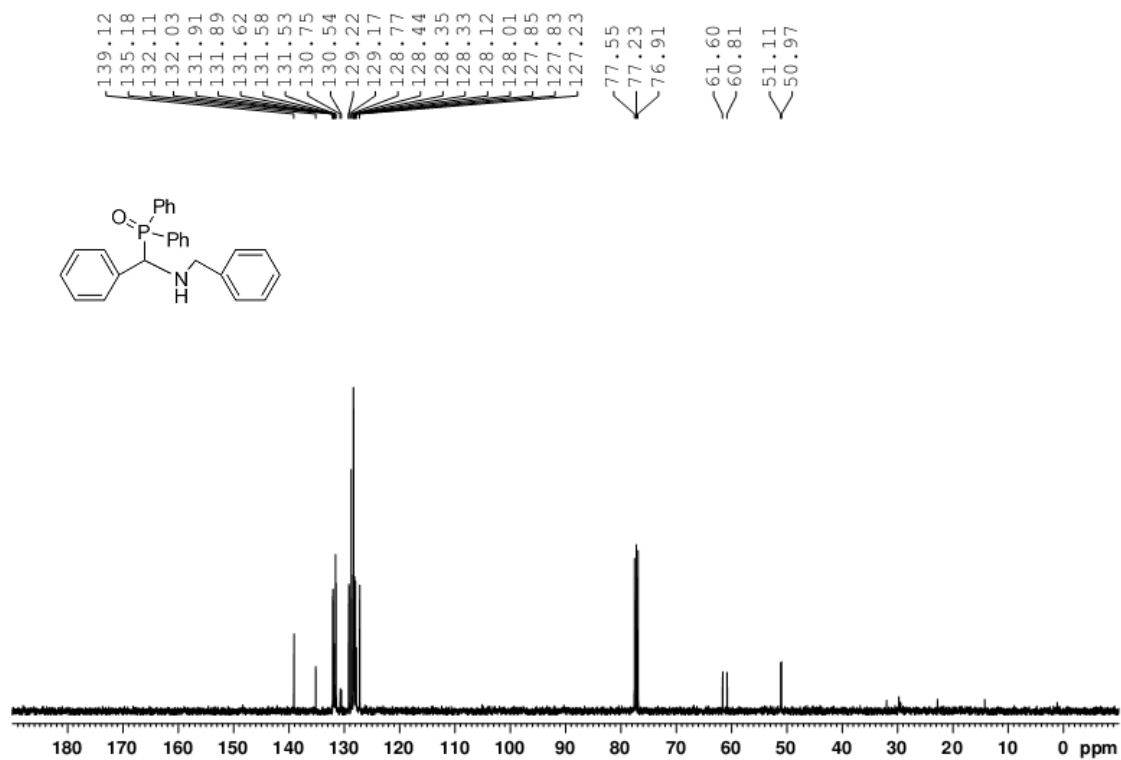
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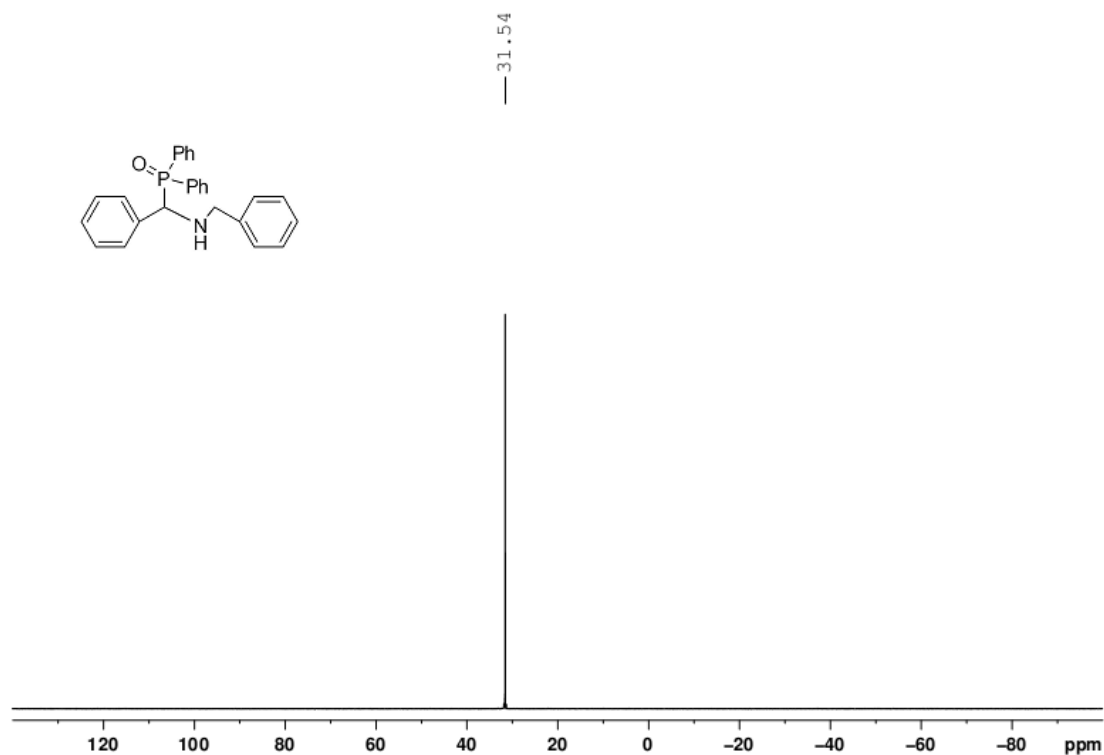
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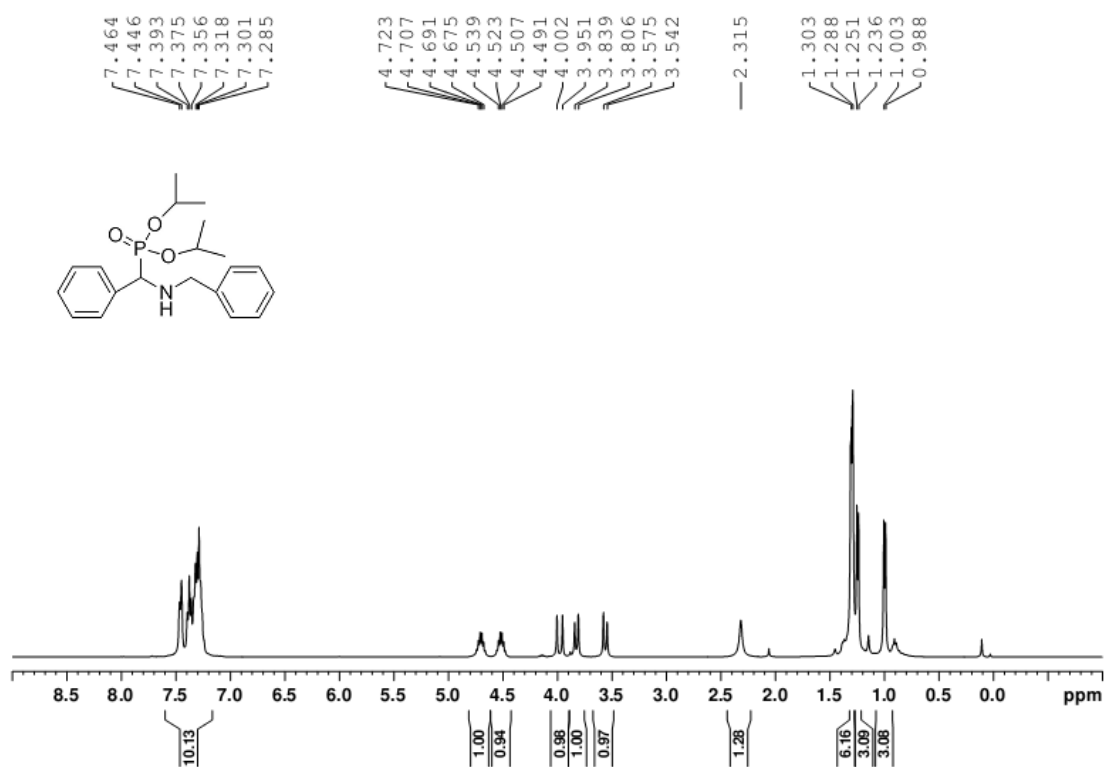
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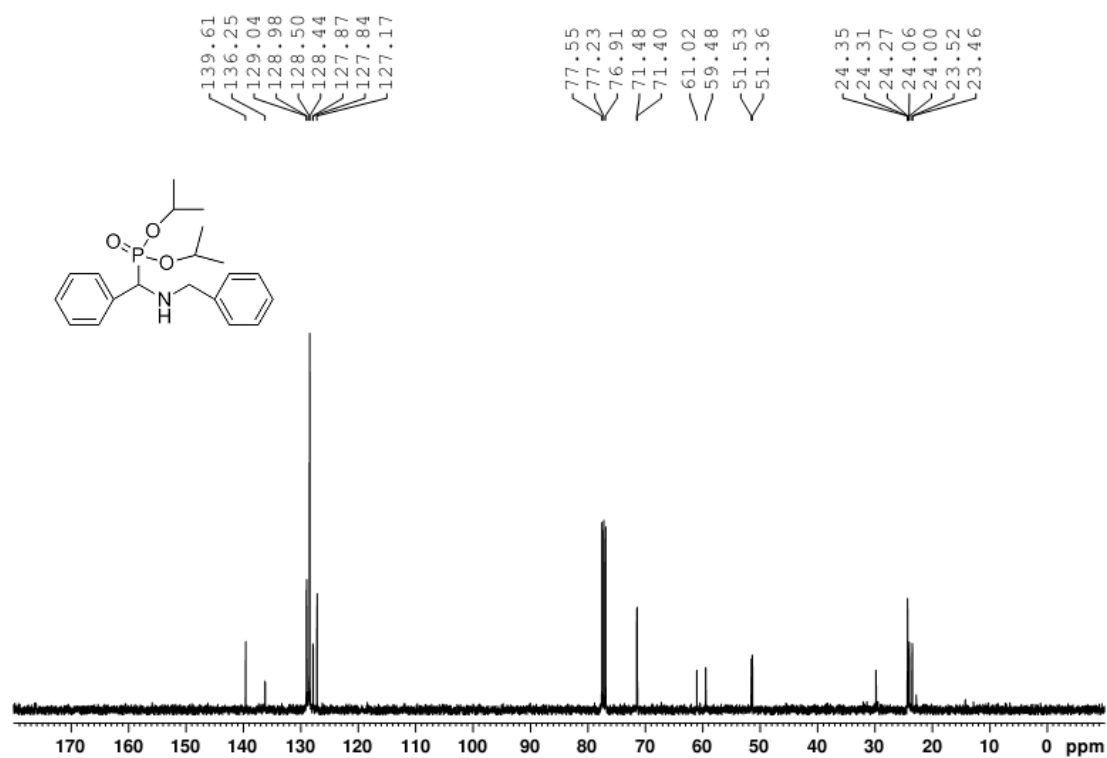
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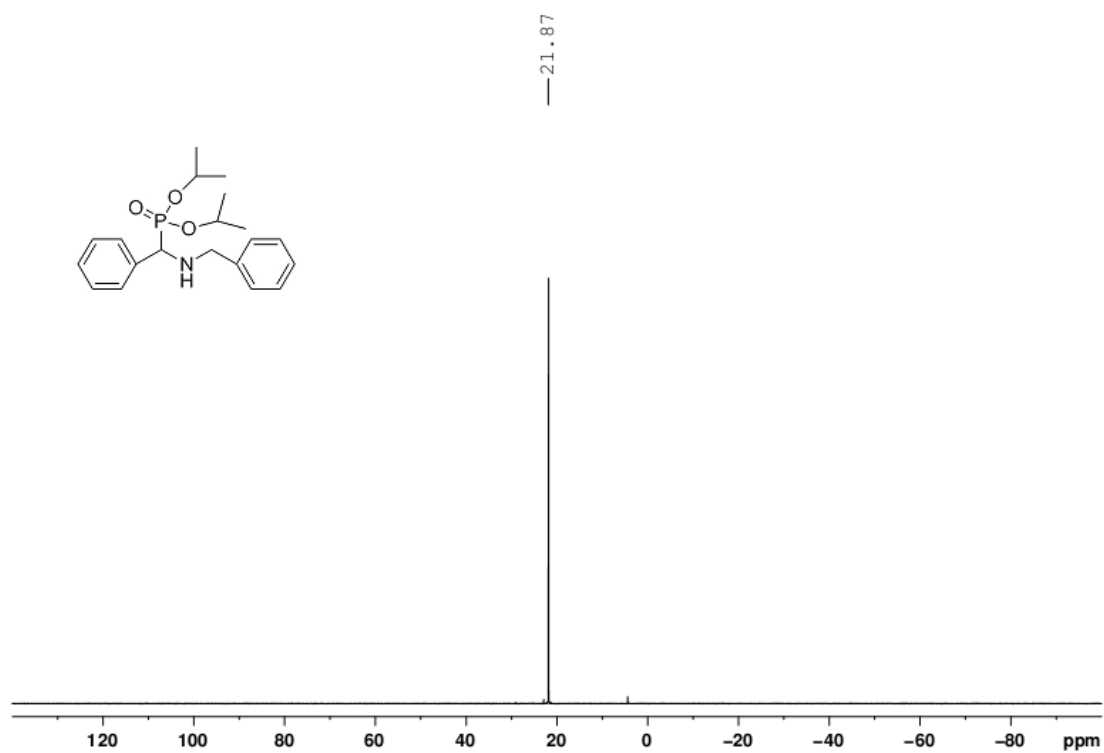
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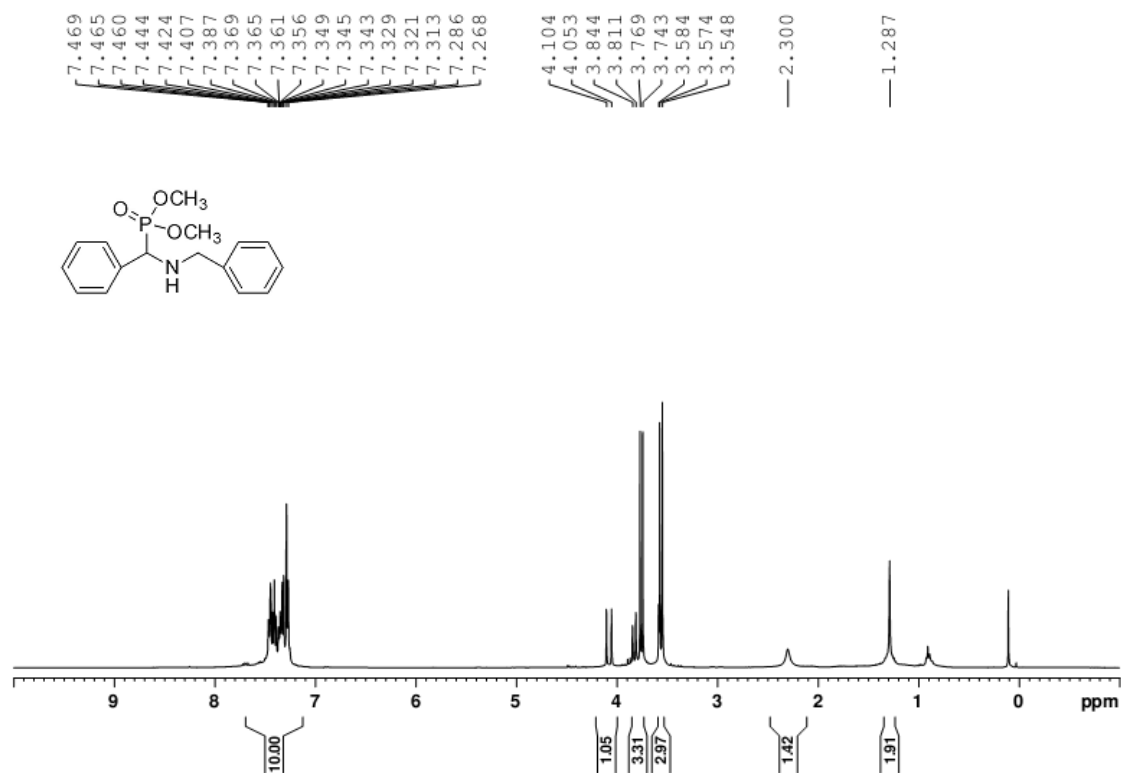
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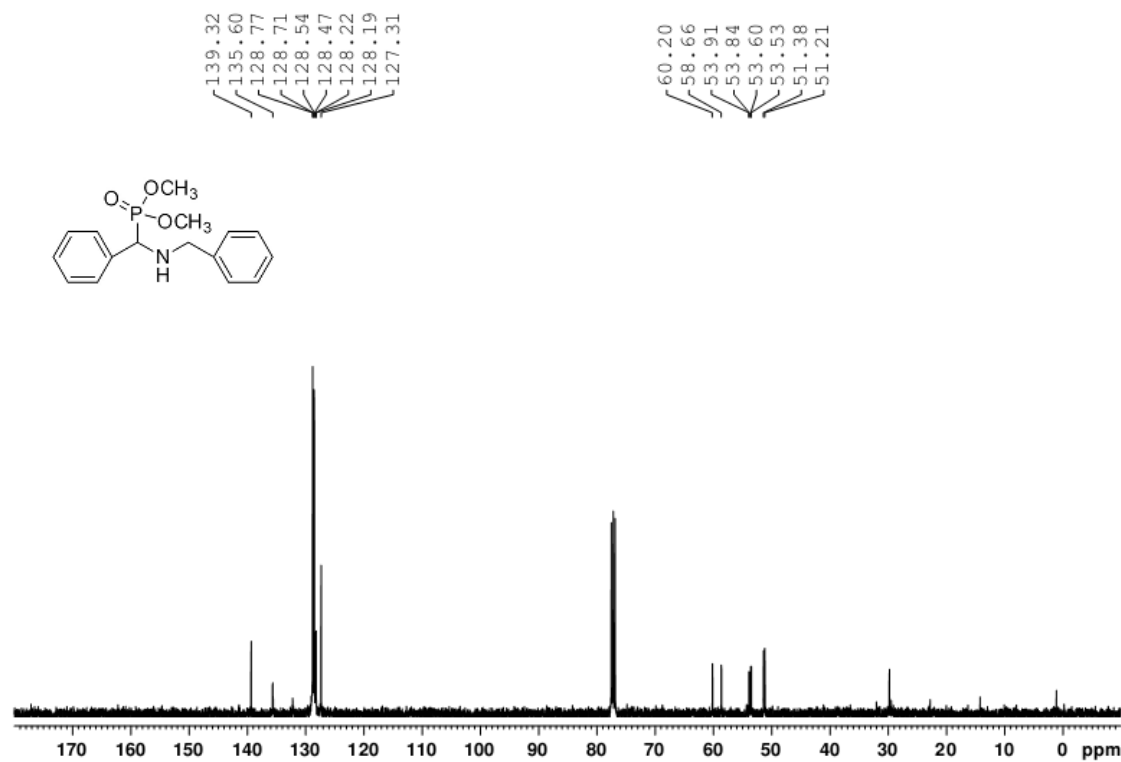
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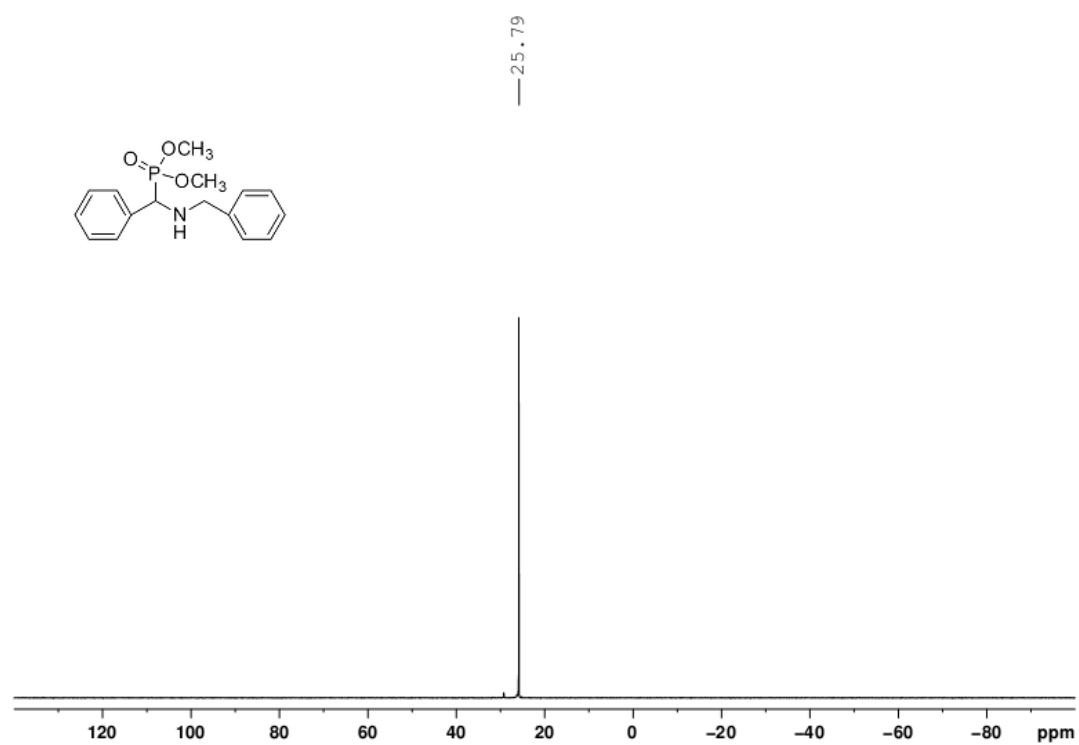
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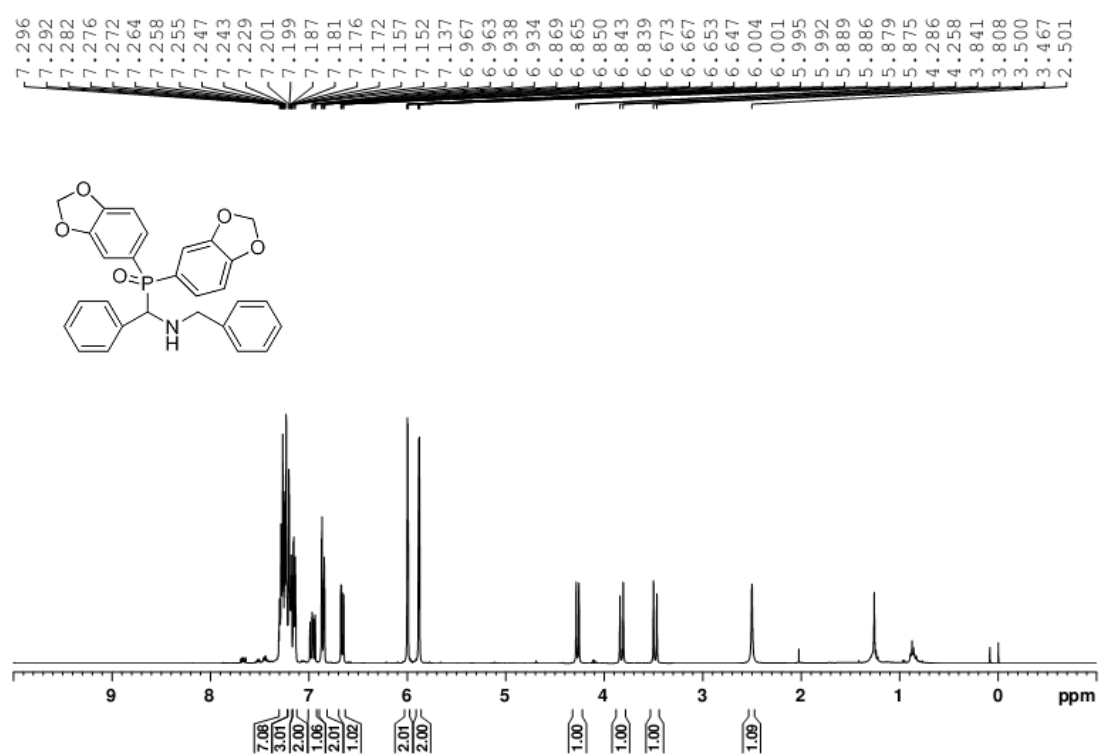
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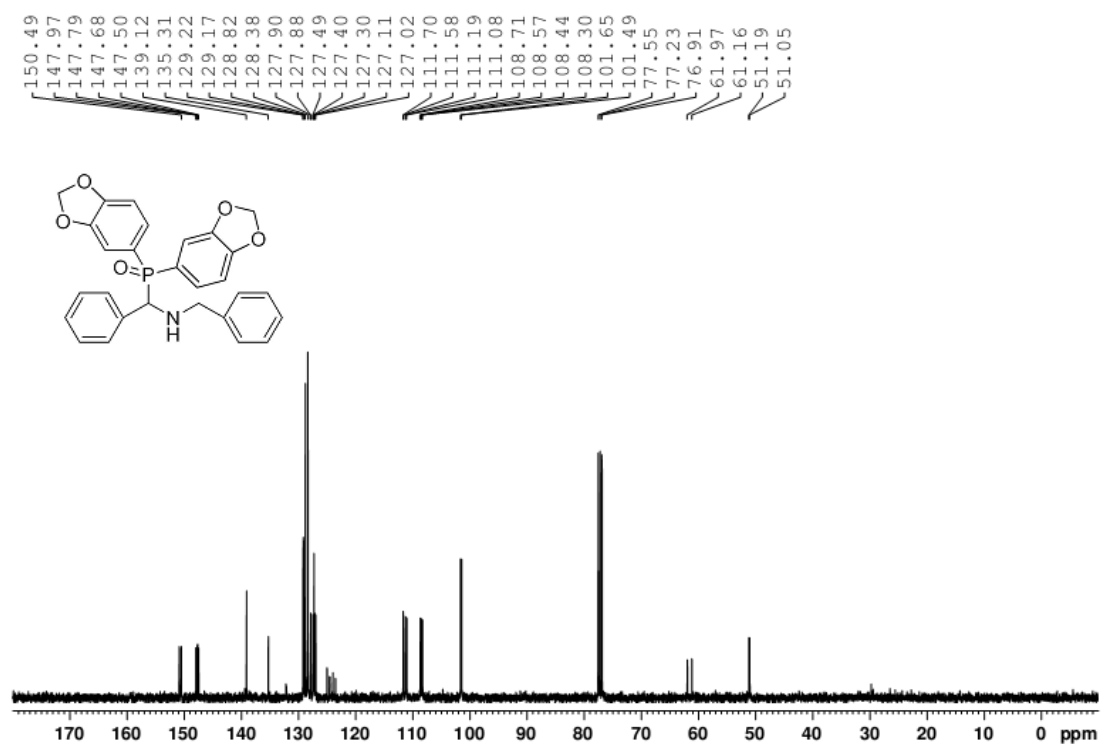
3z



3aa



3aa



3aa

