Electronic Supplementary Information for

$Mn(OAc)_3$-Mediated Synthesis of β-Hydroxyphosphonates from P(O)-H Compounds and Alkenes

Yuzhen Gao,[a] Ju Wu,[a] Jian Xu,[a] Pengbo Zhang,[a] Guo Tang,[a,*] and Yufen Zhao[a,b]

[a] Department of Chemistry, College of Chemistry and Chemical Engineering, and the Key Laboratory for Chemical Biology of Fujian Province, Xiamen University, Xiamen, Fujian 361005, China
Fax: (86)592-2185780; E-mail: t12g21@xmu.edu.cn

[b] Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084,China

Table of Contents

General and Experimental Section

General

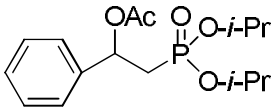
All reactions were carried out under N_2. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Bruker AVⅢ 400M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard or 85% H_3PO_4 as external standard for ^{31}P NMR (162 MHz). Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.23 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Chemical shifts of common trace ^{1}H NMR impurities (ppm): H_2O: 1.56, $CHCl_3$: 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.

Typical procedure for the synthesis of β-hydroxyphosphonates:

An oven-dried Schlenk tube containing $Mn(OAc)_3{\cdot}2H_2O$ (1.5 mmol) was evacuated and purged with nitrogen three times. Alkene (0.50 mmol), *H*-phosphonate (1.0 mmol) and CH_3COOH (3 mL) were sequentially added to the system at room temperature. The reaction mixture was heated with stirring at 80 ^{o}C for 8 hours. The reaction solution was concentrated in vacuo and then added 15 mL saturated sodium bicarbonate solution and extracted with EtOAc (3×10 mL). The combined organic layer was concentrated in vacuo, and then added 2 mL of 1 M NaOH (in CH_3OH) solution. The mixture was stirred at room temperature for 1 hour, and then neutralized by 1 M hydrochloric acid. The solution was extracted with EtOAc (3×10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography using petroleum ether–AcOEt (3:1-1:1, v/v) as the eluent to give the corresponding β-hydroxyphosphonates.

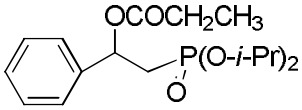
Spectral Data

*2-(Diisopropoxyphosphoryl)-1-phenylethyl acetate (**3a**) (CAS no: 54051-30-8).*



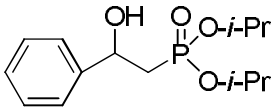
Colourless oil; 143 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32 – 7.20 (m, 5H), 6.05 (m, 1H), 4.60 (m, 2H), 2.44 (m, 1H), 2.18 (m, 1H), 2.00 (s, 1H), 2.31 (s, 3H), 1.25 – 1.15 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.5 (s), 140.1 (d, *J* = 10.8 Hz), 128.5 (s), 128.3 (s), 126.6 (s), 70.9 (d, *J* = 1.8 Hz), 70.5 (d, *J* = 6.7 Hz), 70.4 (d, *J* = 6.6 Hz), 34.5 (d, *J* = 141.6 Hz), 23.96 (d, *J* = 3.7 Hz), 23.8 (t, *J* = 5.1 Hz), 21.1 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 23.4. MS-ESI: *m/z* 351.1 ($[M+Na]^+$).

*2-(Diisopropoxyphosphoryl)-1-phenylethyl propionate (**3b**).*



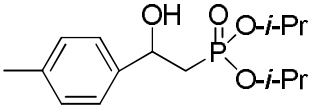
Colourless oil; 125 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 – 7.27 (m, 5H), 6.09(m, 1H), 4.65 (m, 2H), 2.52 – 2.19 (m, 4H), 1.30 – 1.21 (m, 12H), 1.12 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.1 (s), 140.4 (d, *J* = 10.5 Hz), 128.6 (s), 128.4 (s), 126.67(s), 71.0 (d, *J* = 1.8 Hz), 70.6 (d, *J* = 6.5 Hz), 70.45 (d, *J* = 6.7 Hz), 34.9 (d, *J* = 141.2 Hz), 27.8 (s), 24.13 (d, *J* = 3.6 Hz), 24.0 (t, *J* = 4.1 Hz), 9.0 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 23.5. HRMS-ESI: *m/z* found 365.1490 ($[M+Na]^+$, $C_{17}H_{27}NaO_5P^+$ calcd. 365.1494).

*Diisopropyl (2-hydroxy-2-phenylethyl)phosphonate (**4a**) (CAS no: 72019-17-1).*



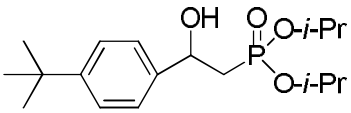
Light yellow solid; 124 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40 – 7.26 (m, 5H), 5.09 (m, 1H), 4.83 – 4.66 (m, 2H), 2.16 (m, 2H), 1.38 – 1.28 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.8 (d, *J* = 15.7 Hz), 128.4 (s), 127.6 (s), 125.6 (s), 70.8 (d, *J* = 6.5 Hz), 70.7 (d, *J* = 6.8 Hz), 68.8 (d, *J* = 4.4 Hz), 37.8 (d, *J* = 137.3 Hz), 24.0 (t, *J* = 3.5 Hz), 23.88 (d, *J* = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.0. MS-ESI: *m/z* 309.1 ($[M+Na]^+$).

*Diisopropyl (2-hydroxy-2-(p-tolyl)ethyl)phosphonate (**4b**).*



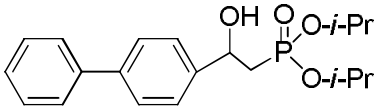
White solid; 135 mg, 90% yield, m.p. 97.1-98.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.28 – 7.26 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.13 (d, *J* = 8.0 Hz, 2H), 5.03 (m, 1H), 4.70 (m, 2H), 2.32 (s, 3H), 2.13 (m, 2H), 1.34 – 1.26 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.8 (d, *J* = 16.3 Hz), 137.2 (s), 129.1 (s), 125.5 (s), 70.8 (d, *J* = 6.5 Hz), 70.6(d, *J* = 6.8 Hz), 68.65 (d, *J* = 4.4 Hz), 37.3 (d, *J* = 136.5 Hz), 24.1 (t, *J* = 3.8 Hz), 23.9 (d, *J* = 4.8 Hz), 21.1 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.3. HRMS-ESI: *m/z* 323.1383 ($[M+Na]^+$, $C_{15}H_{25}NaO_4P^+$ calcd. 323.1388).

*Diisopropyl (2-hydroxy-2-(4-isobutylphenyl)ethyl)phosphonate (**4c**).*



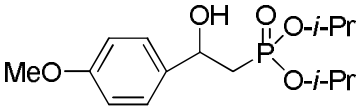
White solid; 137 mg, 80% yield, m.p. 95.0-96.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 – 7.30 (q, 4H, *J* = 8.5 Hz), 5.06 (m, 1H), 4.76 – 4.63 (m, 2H), 2.25 – 2.09 (m, 2H), 1.33 – 1.29 (m, 18H), 1.26 – 1.24 (d, 3H, *J* = 6.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.6 (s), 140.8 (d, *J* = 15.8 Hz), 125.4 (s), 70.85 (d, *J* = 6.5 Hz), 70.74 (d, *J* = 6.9 Hz), 68.7 (d, *J* = 4.4 Hz), 37.1 (d, *J* = 136.9 Hz), 34.6 (s), 31.4 (s), 24.1 (t, *J* = 3.7 Hz), 23.95 (d, *J* = 4.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.0. HRMS-ESI: *m/z* found 365.1856 ($[M+Na]^+$, $C_{18}H_{31}NaO_4P^+$ calcd. 365.1858).

*Diisopropyl (2-([1,1'-biphenyl]-4-yl)-2-hydroxyethyl)phosphonate (**4d**).*



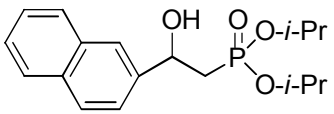
White solid; 100 mg, 55% yield, m.p. 78.2-79.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 – 7.56 (d, 4H, *J* = 7.9 Hz), 7.47 – 7.41 (m, 4H), 7.32 (m, 1H), 5.14 (m, 1H), 4.81 – 4.65 (m, 2H), 2.24 – 2.18 (m, 2H), 1.36 – 1.27 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.8 (d, *J* = 16.6 Hz), 141.0 (s), 140.7 (s), 128.9 (s), 127.41 (s), 127.36 (s), 127.2 (s), 126.2 (s), 70.17 (d, *J* = 6.3 Hz), 70.05 (d, *J* = 6.8 Hz), 68.75 (d, *J* = 4.6 Hz), 37.3 (d, *J* = 138.1 Hz), 24.2 (t, *J* = 2.8 Hz), 24.03 (d, *J* = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.2. HRMS-ESI: *m/z* found 385.1545 ($[M+Na]^+$, $C_{20}H_{27}NaO_4P^+$ calcd. 385.1545).

*Diisopropyl (2-hydroxy-2-(4-methoxyphenyl)ethyl)phosphonate (**4e**).*



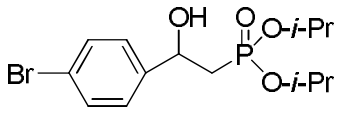
Yellow oil; 111 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.31 (d, 2H, *J* = 8.7 Hz), 6. 88 (d, 2H, *J* = 8.7 Hz), 5.05 (m, 1H), 4.81 – 4.67 (m, 2H), 3.81 (s, 3H), 2.18 – 2.11 (m, 2H), 1.38 – 1.29 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.3 (s), 135.95 (d, *J* = 17.1 Hz), 127.0 (s), 127.6 (s), 114.0 (s), 71.05 (d, *J* = 6.6 Hz), 70.95 (d, *J* = 6.9 Hz), 68.64 (d, *J* = 4.7 Hz), 55.5 (s), 37.4 (d, *J* = 136.1 Hz), 24.2 (t, *J* = 4.3 Hz), 24.12 (d, *J* = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.5. HRMS-ESI: *m/z* found 339.1336 ($[M+Na]^+$, $C_{15}H_{25}NaO_5P^+$ calcd. 339.1337).

*Diisopropyl (2-hydroxy-2-(naphthalen-2-yl)ethyl)phosphonate (**4f**).*



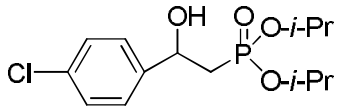
White solid; 118 mg, 70% yield, m.p. 77.4-78.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7,87 (s, 1H), 7.84 – 7.82 (m, 3H), 7.51 – 7.44 (m, 3H), 5.27 (m, 1H), 4.79 – 4.65 (m, 2H), 2.28 – 2.22 (m, 2H), 1.36 – 1.24 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 141.2 (d, *J* = 15.7 Hz), 133.4 (s), 133.0 (s), 128.3 (s), 128.1 (s), 127.7 (s), 126.2 (s), 125.9 (s), 124.3 (s), 123.8 (s), 71.0 (d, *J* = 6.6 Hz), 70.85 (d, *J* = 6.7 Hz), 69.03 (d, *J* = 4.5 Hz), 37.3 (d, *J* = 137.5 Hz), 24.1 (t, *J* = 3.4 Hz), 23.95 (d, *J* = 4.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.2. HRMS-ESI: *m/z* found 359.1387 ($[M+Na]^+$, $C_{18}H_{25}NaO_4P^+$ calcd. 359.1388).

*Diisopropyl (2-(4-bromophenyl)-2-hydroxyethyl)phosphonate (**4g**).*



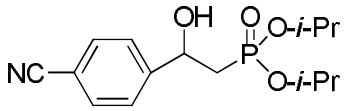
Light yellow solid; 151 mg, 83% yield, m.p. 71.1-72.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45 (d, 2H, *J* = 8.4 Hz), 7.26 (d, 2H, *J* = 8.4 Hz), 5.03 (m, 1H), 4.77 – 4.64 (m, 2H), 2.14 – 2.08 (m, 2H), 1.34 – 1.26 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.9 (d, *J* = 16.2 Hz), 131.6 (s), 127.5 (s), 121.4 (s), 71.14 (d, *J* = 6.6 Hz), 70.0 (d, *J* = 6.9 Hz), 68.33 (d, *J* = 4.3 Hz), 37.2 (d, *J* = 137.1 Hz), 24.1 (t, *J* = 3.6 Hz), 23.97 (d, *J* = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 26.6. HRMS-ESI: *m/z* found 387.0337 ($[M+Na]^+$, $C_{14}H_{22}BrNaO_4P^+$ calcd. 387.0337).

*Diisopropyl (2-(4-chlorophenyl)-2-hydroxyethyl)phosphonate (**4h**).*



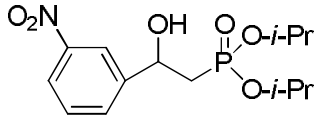
Light yellow solid; 134 mg, 84% yield, m.p. 66.6-67.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.34 – 7.28 (m, 4H), 5.04 (m, 1H), 4.74 – 4.62 (m, 2H), 2.19 – 2.02 (m, 2H), 1.33 – 1.25 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.48 (d, *J* = 15.7 Hz), 133.1 (s), 128.5 (s), 127.1 (s), 70.96 (d, *J* = 6.5 Hz), 70.8 (d, *J* = 6.8 Hz), 68.24 (d, *J* = 4.0 Hz), 37.2 (d, *J* = 138.2 Hz), 24.0 (t, *J* = 3.8 Hz), 23.88 (d, *J* = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 26.5. HRMS-ESI: *m/z* found 343.0842 ($[M+Na]^+$, $C_{14}H_{22}ClNaO_4P^+$ calcd. 343.0842).

*Diisopropyl (2-(4-cyanophenyl)-2-hydroxyethyl)phosphonate (**4i**).*



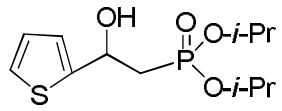
Yellow oil; 39 mg, 25% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66 (d, 2H, *J* = 8.1 Hz), 7.53 (d, 2H, *J* = 8.1 Hz), 5.12 (m, 1H), 4.82 – 4.66 (m, 2H), 2.19 – 2.05 (m, 2H), 1.39 – 1.27 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.1 (d, *J* = 16.9 Hz), 132.5 (s), 126.5 (s), 118.9 (s), 111.6 (s), 71.46 (d, *J* = 6.5 Hz), 71.33 (d, *J* = 6.9 Hz), 68.44 (d, *J* = 4.7 Hz), 37.1 (d, *J* = 137.7 Hz), 24.2 (t, *J* = 5.2 Hz), 23.09 (d, *J* = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 26.5. HRMS-ESI: *m/z* found 334.1182 ($[M+Na]^+$, $C_{15}H_{22}NNaO_4P^+$ calcd. 334.1184).

*Diisopropyl (2-hydroxy-2-(3-nitrophenyl)ethyl)phosphonate (**4j**).*



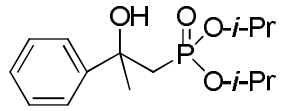
Light yellow solid; 55 mg, 33% yield, m.p. 55.4-56.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.26 (s, 1H), 8.12 (m, 1H), 7.74 (d, 1H *J* = 7.73 Hz), 7.52 (t, 1H *J* = 7.93 Hz), 4.79 – 4.65 (m, 3H), 2.19 – 2.10 (m, 2H), 1.36 – 1.24 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.5 (s), 146.1 (d, *J* = 16.4 Hz), 132.0 (s), 129.6 (s), 122.7 (s), 120.9 (s), 71.4 (d, *J* = 6.4 Hz), 71.25 (d, *J* = 6.8 Hz), 68.2 (d, *J* = 4.4 Hz), 37.1 (d, *J* = 137.8 Hz), 24.14 (m), 24.02 (d, *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 26.3. HRMS-ESI: *m/z* found 354.1080 ($[M+Na]^+$, $C_{14}H_{22}NNaO_6P^+$ calcd. 354.1082).

*Diisopropyl (2-hydroxy-2-(thiophen-2-yl)ethyl)phosphonate (**4k**).*



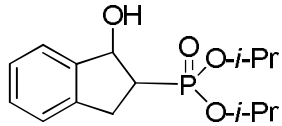
Light yellow solid; 85 mg, 58% yield, m.p.64.3-65.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.2 (m, 1H), 6.97 – 6.93 (m, 2H), 5.33 (m, 1H), 4.77 – 4.65 (m, 2H), 2.32 – 2.26 (m, 2H), 1.34 – 1.28 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.9 (d, J = 18.6 Hz), 126.6 (s), 124.6 (s), 123.4 (s), 71.1 (d, J = 6.5 Hz), 70.9 (d, J = 6.8 Hz), 65.3 (d, J = 3.5 Hz), 37.4 (d, J = 138.1 Hz), 24.1 (m), 23.93 (d, J = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 26.2. HRMS-ESI: *m/z* found 315.0790 ($[M+Na]^+$, $C_{12}H_{21}NaO_4PS^+$ calcd. 315.0796).

*Diisopropyl (2-hydroxy-2-phenylpropyl)phosphonate (**4l**)(CAS no: 1334049-23-8).*



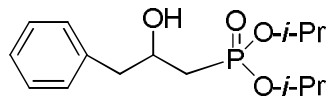
Yellow oil; 90 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (m, 2H), 7.32 (m, 2H), 7.22 (m, 1H), 4.72 – 4.62 (m, 1H), 4.30 (m, 1H), 2.46 – 2.25 (m, 2H), 1.62 (d, 3H, J = 2.2 Hz), 1.32 (t, 6H, J = 6.3 Hz), 1.17 (d, 3H, J = 6.1 Hz), 0.86 (d, 3H, J = 6.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.45 (d, J = 8.1 Hz), 128.1 (s), 126.7 (s), 124.8 (s), 72.13 (d, J = 5.0 Hz), 70.8 (d, J = 6.7 Hz), 70.65 (d, J = 6.7 Hz), 40.9 (d, J = 136.4 Hz), 32.4 (d, J = 13.3 Hz), 24.06 (m), 23.43 (d, J = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.1. MS-ESI: *m/z* 323.1 ($[M+Na]^+$).

*Diisopropyl (1-hydroxy-2,3-dihydro-1H-inden-2-yl)phosphonate (**4m**).*



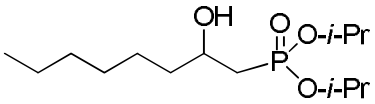
Yellow oil; 101 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40 (m, 1H), 7.23 – 7.15 (m, 3H), 5.44 (m, 1H), 4.75 – 4.67 (m, 2H), 3.6 (m, 1H), 3.03 (m, 1H), 2.50 (m, 1H), 1.32 – 1.24 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.8 (d, J = 13.8 Hz), 140.36 (d, J = 11.9 Hz), 128.2 (s), 127.0 (s), 124.45 (s), 124.41 (s), 76.2 (s), 70.55 (d, J = 6.6 Hz), 43.5 (d, J = 146.6 Hz), 31.6 (s), 24.1 (t, J = 3.4 Hz), 24.0 (t, J = 4.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 29.4. HRMS-ESI: *m/z* found 321.1236 ($[M+Na]^+$, $C_{15}H_{23}NaO_4P$+ calcd. 321.1232).

*Diisopropyl (2-hydroxy-3-phenylpropyl)phosphonate (**4n**).*



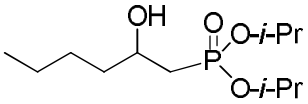
Colourless oil; 62 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30 (m, 2H), 7.21 (m, 3H), 4.73 – 4.66 (m, 2H), 4.22 (m, 1H), 2.92 (m, 1H), 2.76 (m, 1H), 1.98 – 1.81 (m, 2H), 1.31 – 1.27 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.9 (s), 129.6 (s), 128.5 (s), 126.6 (s), 70.8 (d, J = 2.1 Hz), 70.74 (d, J = 2.4 Hz), 68.87 (d, J = 4.9 Hz), 44.46 (d, J = 16.9 Hz), 34.0 (d, J = 139.7 Hz), 24.13 (d, J = 3.6 Hz), 24.05 (d, J = 4.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 28.2. HRMS-ESI: *m/z* found 323.1383 ($[M+Na]^+$, $C_{15}H_{25}NaO_4P^+$ calcd. 323.1388).

*Diisopropyl (2-hydroxyoctyl)phosphonate (**4o**).*



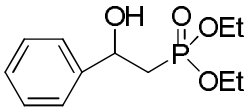
Colourless oil; 46 mg, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.70 (m, 2H), 3.94 (m, 1H), 1.95 – 1.75 (m, 2H), 1.59 – 1.53 (m, 1H), 1.48 – 1.40 (m, 2H), 1.34 – 1.24 (m, 19H), 0.88 – 0.84 (t, 3H, *J* = 6.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 70.75 (d, *J* = 2.0 Hz), 70.69 (d, *J* = 2.4 Hz), 66.69 (d, *J* = 5.7 Hz), 38.34 (d, *J* = 17.0 Hz), 34.8 (d, *J* = 138.8 Hz), 31.9 (s), 29.3 (s), 25.5 (s), 24.2 (d, *J* = 3.6 Hz), 24.13 (d, *J* = 4.8 Hz), 22.7 (s), 14.2 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 28.8. HRMS-ESI: *m/z* found 317.1852 ($[M+Na]^+$, $C_{14}H_{31}NaO_4P^+$ calcd. 317.1858).

*Diisopropyl (2-hydroxyhexyl)phosphonate (**4p**).*



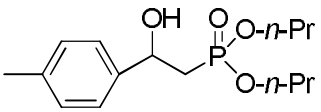
Colourless oil; 35 mg, 26% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.77 – 4.66 (m, 2H), 3.95 (m, 1H), 1.96 – 1.78 (m, 2H), 1.58 – 1.54 (m, 1H), 1.49 – 1.31 (m, 17H), 0.91 – 0.88 (t, 3H, *J* = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 70.81 (d, *J* = 2.0 Hz), 70.76 (d, *J* = 2.2 Hz), 66.73 (d, *J* = 5.7 Hz), 38.1 (d, *J* = 11.4 Hz), 34.8 (d, *J* = 138.9 Hz), 27.7 (s), 24.2 (d, *J* = 3.5 Hz), 24.15 (d, *J* = 4.8 Hz), 22.7 (s), 14.2 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 28.8. HRMS-ESI: *m/z* found 289.1542 ($[M+Na]^+$, $C_{12}H_{27}NaO_4P^+$ calcd. 289.1545).

*Diethyl (2-hydroxy-2-phenylethyl)phosphonate (**4q**) (CAS no: 72019-14-8).*



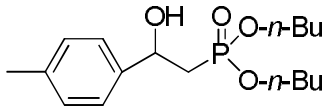
White solid; 103 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 – 7.23 (m, 5H), 5.09 (m, 1H), 4.10 – 4.00 (m, 2H), 2.20 (m, 2H), 1.28 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.85 (d, *J* = 15.0 Hz), 128.5 (s), 127.7 (s), 125.6 (s), 68.78 (d, *J* = 4.2 Hz), 62.07 (d, *J* = 6.3 Hz), 61.9 (d, *J* = 6.6 Hz), 36.0 (d, *J* = 136.7 Hz), 16.4 (t, *J* = 5.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 29.1. MS-ESI: *m/z* 281.0 ($[M+Na]^+$).

*Dipropyl (2-hydroxy-2-(p-tolyl)ethyl)phosphonate (**4r**).*



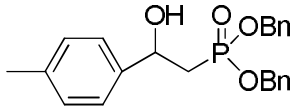
Colourless oil; 123 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26 (m, 2H), 7.13 (m, 2H), 5.05 (m, 1H), 3.95 (m, 4H), 2.32 (s), 2.20 (m, 2H), 1.65 (m, 4H), 0.93 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.9 (d, *J* = 15.5 Hz), 137.2 (s), 129.1 (s), 125.5 (s), 68.63 (d, *J* = 4.1 Hz), 67.48 (d, *J* = 6.5 Hz), 67.3 (d, *J* = 7.2 Hz), 35.9 (d, *J* = 136.0 Hz), 23.8 (t, *J* = 5.5 Hz), 21.1 (s), 10.0 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 28.4. HRMS-ESI: *m/z* found 323.1383 ($[M+Na]^+$, $C_{15}H_{25}NaO_4P^+$ calcd. 323.1388).

*Dibutyl (2-hydroxy-2-(p-tolyl)ethyl)phosphonate (**4s**).*



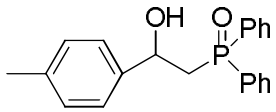
Colourless oil; 120 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26 (d, 2H, *J* = 8.0 Hz), 7.16 (d, 2H, *J* = 8.0 Hz), 5.06 (m, 1H), 4.06 – 4.00 (m, 4H), 2.33 (s), 2.28 – 2.10 (m, 2H), 1.64 (m, 4H), 1.40(m, 4H), 0.93 (q, 6H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.8 (d, *J* = 15.7 Hz), 137.5 (s), 129.3 (s), 125.6 (s), 68.8 (d, *J* = 4.4 Hz), 65.9 (d, *J* = 6.5 Hz), 65.8 (d, *J* = 7.0 Hz), 35.9 (d, *J* = 135.8 Hz), 32.6 (t, *J* = 6.0 Hz), 21.2 (s), 18.86 (d, *J* = 2.2 Hz), 13.7 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 28.5. HRMS-ESI: *m/z* found 351.1696 ($[M+Na]^+$, $C_{17}H_{29}NaO_4P^+$ calcd. 351.1701).

*Dibenzyl (2-hydroxy-2-(p-tolyl)ethyl)phosphonate (**4t**).*



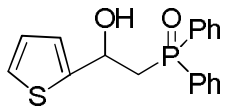
White solid; 91 mg, 46% yield, m.p. 79.2-80.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (m, 10H), 7.22 (d, 2H, *J* = 7.9 Hz), 7.16 (d, 2H, *J* = 8.0 Hz), 5.14 – 4.97 (m, 5H), 2.34 (s, 3H), 2.32 – 2.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.6 (d, *J* = 16.0 Hz), 137.6 (s), 136.6 (d, *J* = 6.1 Hz), 129.3 (s), 128.8 (d, *J* = 3.9 Hz), 128.7 (d, *J* = 5.9 Hz), 128.18 (d, *J* = 3.6 Hz), 125.6 (s), 68.74 (d, *J* = 4.4 Hz), 67.7 (d, *J* = 6.3 Hz), 67.6 (d, *J* = 6.6 Hz), 36.5 (d, *J* = 135.0 Hz), 21.2 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 29.6. HRMS-ESI: *m/z* found 419.1383 ($[M+Na]^+$, $C_{23}H_{25}NaO_4P^+$ calcd. 419.1388).

*(2-Hydroxy-2-(p-tolyl)ethyl)diphenylphosphine oxide (**4u**).*



White solid; 131 mg, 78% yield, m.p. 104.7-106.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (m, 2H), 7.69 (m, 2H), 7.56 – 7.41 (m, 6H), 7.21 (d, 2H, *J* = 7.8 Hz), 7.10 1(d, 2H, *J* = 7.7 Hz), 5.14 (t, 1H, *J* = 9.7 Hz), 2.77 (m, 1H), 2.57 (m, 1H), 2.30 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 141.1 (d, *J* = 13.2 Hz), 137.4 (s), 132.2 (s), 131.1 (d, *J* = 9.5 Hz), 130.56 (d, *J* = 9.7 Hz), 129.3 (s), 128.9 (t, *J* = 12.7 Hz), 125.6 (s), 69.1 (d, *J* = 4.1 Hz), 39.4 (d, *J* = 68.5 Hz), 21.2 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 33.8. HRMS-ESI: *m/z* found 359.1171 ($[M+Na]^+$, $C_{21}H_{21}NaO_2P^+$calcd. 359.1177).

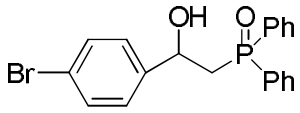
*(2-Hydroxy-2-(thiophen-2-yl)ethyl)diphenylphosphine oxide (**4v**).*



White solid; 107 mg, 65% yield, m.p. 153.6-155.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 (m, 4H), 7.50 (m, 6H), 7.17 (m, 1H), 6.87 (m, 2H), 5.45 (m, 2H), 2.92 (m, 1H), 2.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.2 (d, *J* = 14.8 Hz), 132,2 (m), 130.96 (d, *J* = 9.6 Hz), 130.6 (d, *J* = 9.8 Hz), 128.9 (m), 126.6 (s), 124.7 (s), 123.3

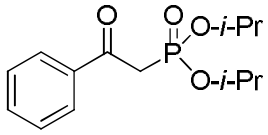
(s), 65.6 (d, J = 3.5 Hz), 39.5 (d, J = 68.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 32.9. HRMS-ESI: *m/z* found 351.0584 ($[M+Na]^+$, $C_{18}H_{17}NaO_2PS^+$calcd. 351.0585).

*(2-(4-Bromophenyl)-2-hydroxyethyl)diphenylphosphine oxide (**4w**).*



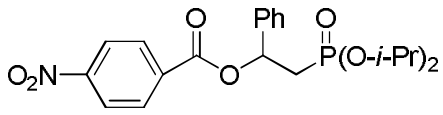
White solid; 134 mg, 67% yield, m.p. 143.4-144.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79 (m, 2H), 7.70 (m, 2H), 7.68 (m, 4H), 7.44 (m, 4H), 7.21 (d, 2H, J = 8.4 Hz), 5.19 – 5.11 (m, 2H), 2.74(m, 1H), 2.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.1 (d, J = 12.9 Hz), 132.38 (m), 131.7 (s), 131.1 (d, J = 9.4 Hz), 130.6 (d, J = 9.6 Hz), 129.05 (m), 127.5 (s), 121.5 (s), 68.9 (d, J = 4.2 Hz), 39.4 (d, J = 68.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 33.5. HRMS-ESI: *m/z* found 423.0126 ($[M+Na]^+$, $C_{20}H_{18}BrNaO_2P^+$calcd. 423.0125).

*Diisopropyl (2-oxo-2-phenylethyl)phosphonate (**5**) (CAS no: 57057-15-5).*



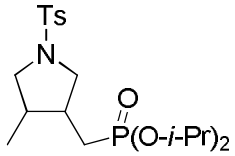
To a stirred ice-cold solution of **4a** (143 mg, 0.5 mmol) in dry CH_2Cl_2 (8 mL) was added Dess-Martin's reagent (318 mg, 0.75 mmol). The reaction mixture was allowed to warm to room temperature and further stirred for 30 min. The reaction was evaporated and the residue was subjected to silica gel column chromatography, eluting with petroleum ether/EtOAc (3/1), to give **5** (colourless oil; 136 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.92 – 7.90 (m, 2H), 7.48 – 7.44 (m, 1H), 7.37 – 7.34 (m, 2H), 4.67 – 4.56 (m, 2H), 3.49 (d, 2H, J = 22.8 Hz), 1.17 (d, 6H, J = 4.2 Hz), 1.16 (d, 6H, J = 4.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 192.0 (d, J = 6.7 Hz), 136.2 (s), 133.4 (s), 129.0 (s), 128.4 (s), 71.4 (d, J = 6.7 Hz), 39.6 (d, J = 130.2 Hz), 23.87 (d, J = 3.9 Hz), 23.65 (d, J = 5.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 17.7. MS-ESI: *m/z* 307.1 ($[M+Na]^+$).

*2-(Diisopropoxyphosphoryl)-1-phenylethyl 4-nitrobenzoate (**6**).*



A solution of diethyl azodicarboxylate (DEAD, 104 mg, 0.6 mmol) in CH_2Cl_2 (2.0 mL) was slowly added at rt via cannula to a solution of triphenylphosphine (144 mg, 0.55 mmol), 4-nitrobenzoic acid (92 mg, 0.55 mmol), and **4a** (143 mg, 0.5 mmol) in CH_2Cl_2 (1.0 mL), and the resulting mixture was stirred at rt for 2 h. The reaction was evaporated and the residue was subjected to silica gel column chromatography, eluting with petroleum ether/EtOAc (3/1), to give **6** (colourless oil; 153 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.26 (s, 4H), 7.45 – 7.43 (m, 2H), 7.38 – 7.29 (m, 3H), 6.35 – 6.29 (m, 1H), 4.72 – 4.62 (m, 2H), 2.71 – 2.61 (m, 1H), 2.43 – 2.33 (m, 1H), 1.25 – 1.22 (m, 6H), 1.20 (d, 6H, J = 6.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.7 (s), 150.8 (s), 139.7 (d, J = 11.4 Hz), 135.8 (s), 131.1 (s), 128.94 (s), 128.90 (s), 126.7 (s), 123.7 (s), 73.0 (d, J = 3.1 Hz), 70.9 (d, J = 6.9 Hz), 70.8 (d, J = 6.9 Hz), 35.0 (d, J = 142.0 Hz), 24.1 (m). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.9. HRMS-ESI: *m/z* found 458.1342 ($[M+Na]^+$, $C_{21}H_{26}NNaO_7P^+$ calcd. 458.1345).

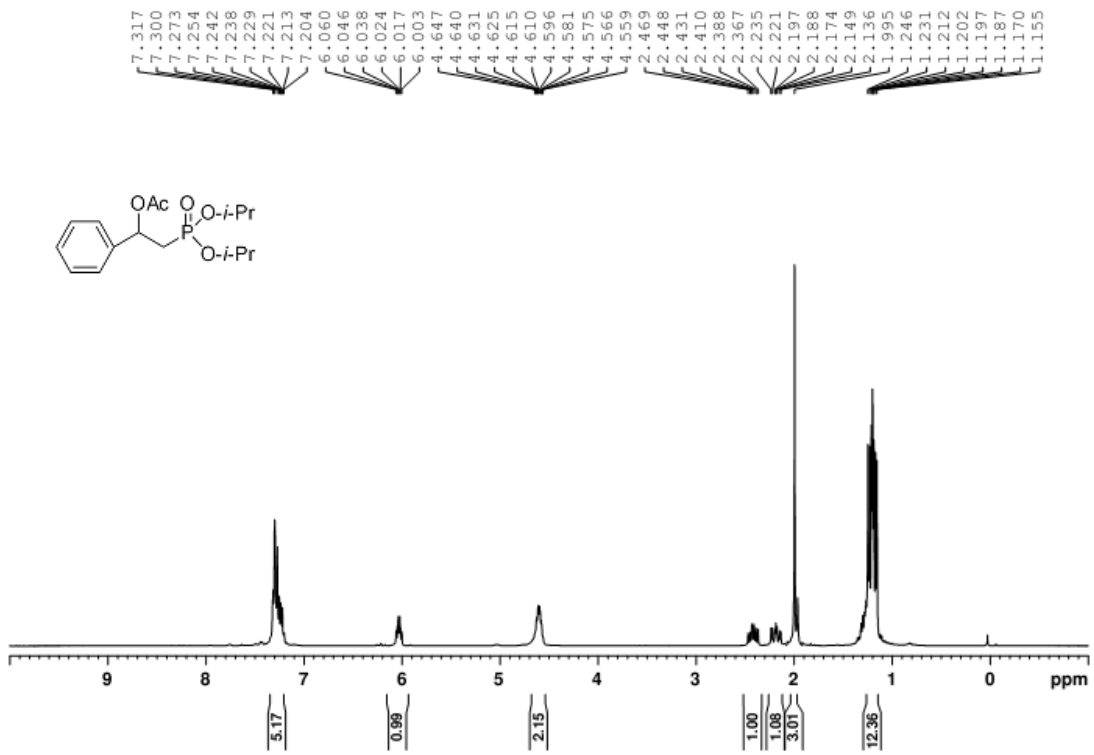
Diisopropyl ((4-methyl-1-tosylpyrrolidin-3-yl)methyl)phosphonate (7).



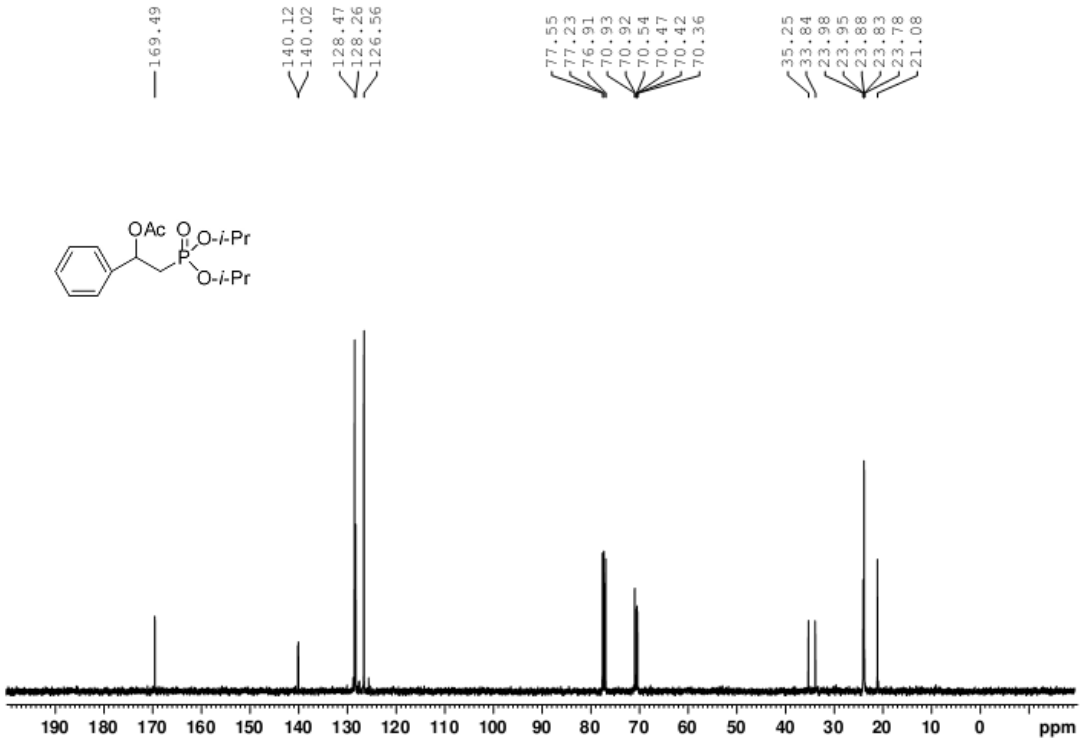
An oven-dried Schlenk tube containing $Mn(OAc)_3 \cdot 2H_2O$ (1.5 mmol, 402 mg) was evacuated and purged with nitrogen three times. N,N-Diallyl-4-methylbenzenesulfonamide (0.50 mmol, 126 mg), *H*-phosphonate (1.0 mmol, 166 mg) and CH_3COOH (3 mL) were sequentially added to the system at room temperature. The reaction mixture was heated with stirring at 60 ^oC for 8 hours. The reaction was evaporated and the residue was subjected to silica gel column chromatography, eluting with petroleum ether/EtOAc (1/1), to give **8** (colourless oil; 100 mg, 48% yield). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (d, 2H, J = 8.2 Hz), 7.31 (d, 2H, J = 8.1 Hz), 4.68 – 4.61 (m, 2H), 3.47 (dd, 1H, J = 10.0 Hz, J = 7.3 Hz), 3.32 (dd, 1H, J = 9.7 Hz, J = 6.2 Hz), 3.08 – 3.02 (m, 2H), 2.42 (s, 3H), 2.36 – 2.29 (m, 1H), 2.27 – 2.21 (m, 1H), 1.86 – 1.72 (m, 2H), 1.30 – 1.26 (m, 12H), 0.74 (d, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.5 (s), 134.2 (s), 129.8 (s), 127.6 (s), 70.6 (d, J = 6.7 Hz), 70.45 (d, J = 6.8 Hz), 54.6 (s), 51.5 (d, J = 9.0 Hz), 36.7 (d, J = 4.6 Hz), 36.1 (d, J = 12.5 Hz), 25.8 (d, J = 143.7 Hz), 24.2 (m), 21.7 (s), 13.3 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) 27.9. HRMS-ESI: *m/z* found 440.1635 ($[M+Na]^+$, $C_{19}H_{32}NNaO_5PS^+$ calcd. 440.1637).

^{31}P NMR, ^{1}H NMR and ^{13}C NMR spectra

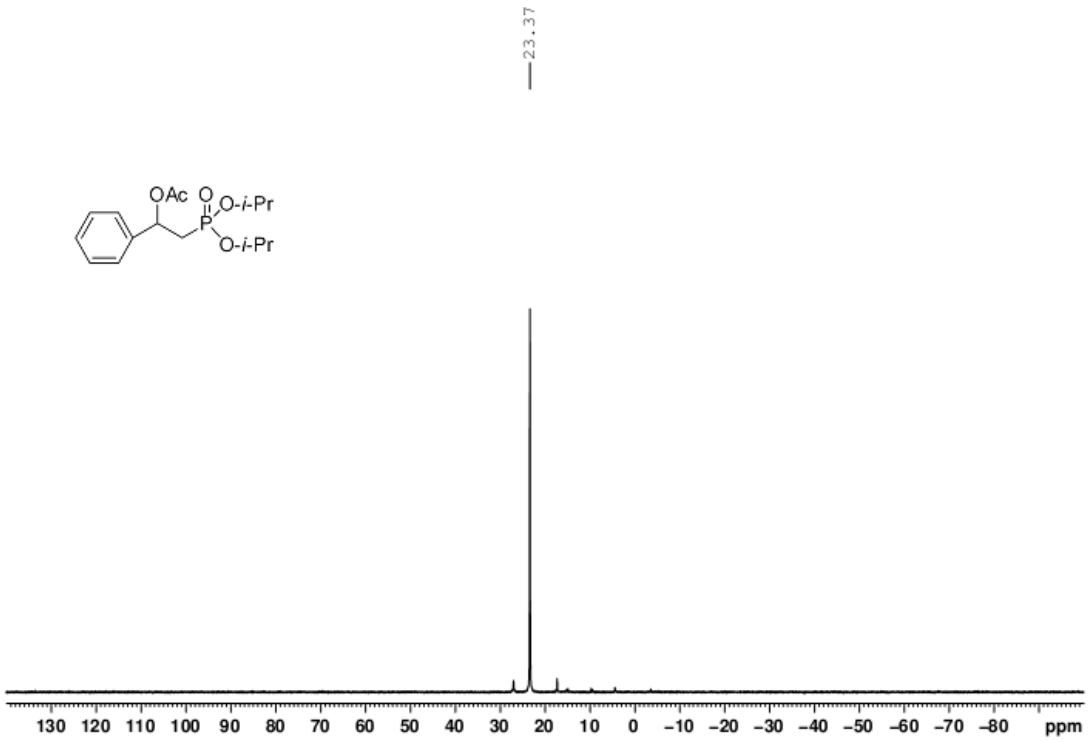
3a



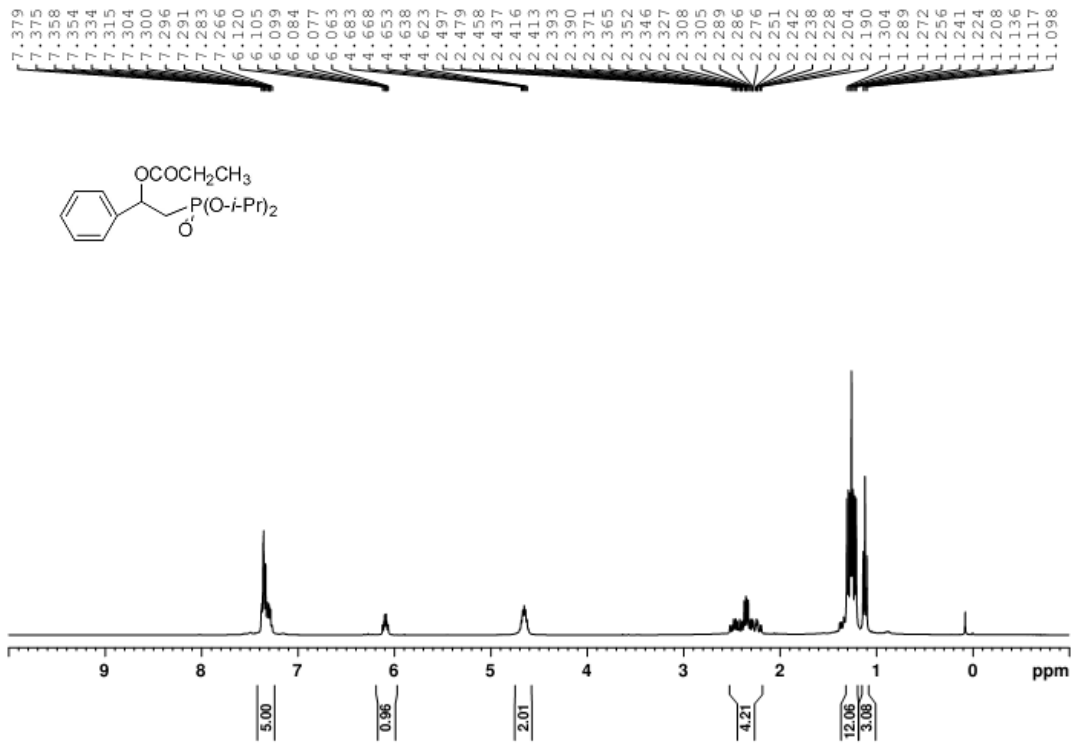
3a



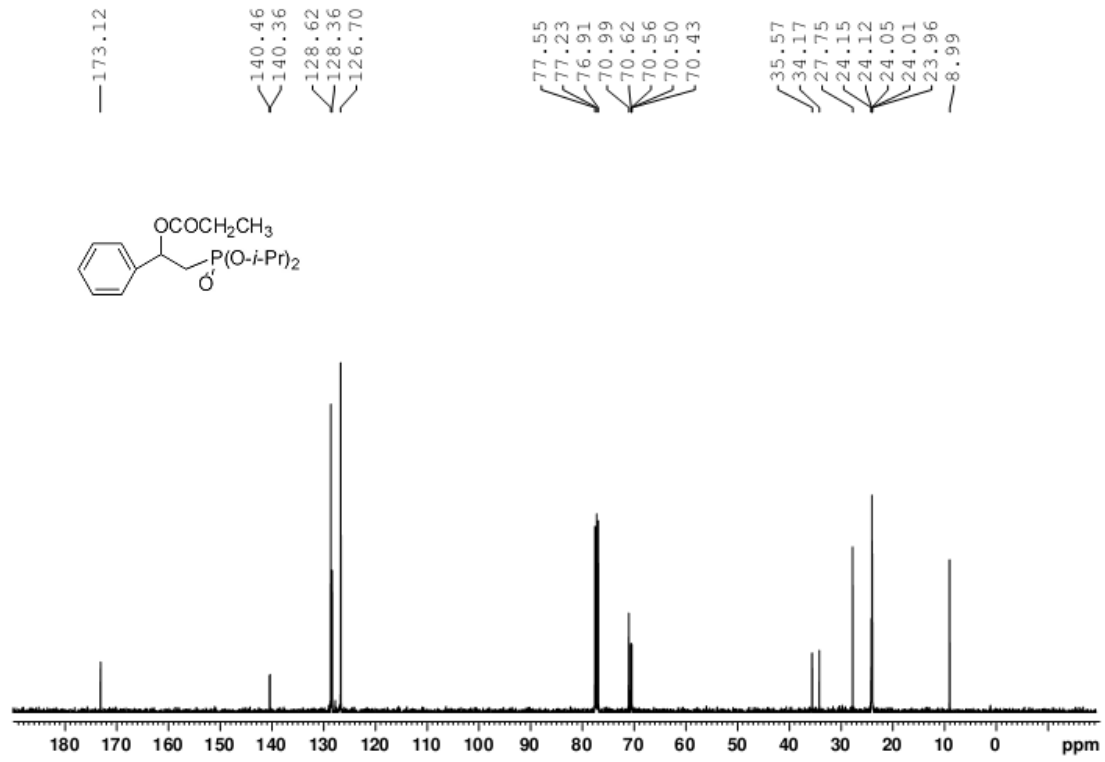
3a


23.37
OAc
O
O-i-Pr
P
O-i-Pr
130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 ppm

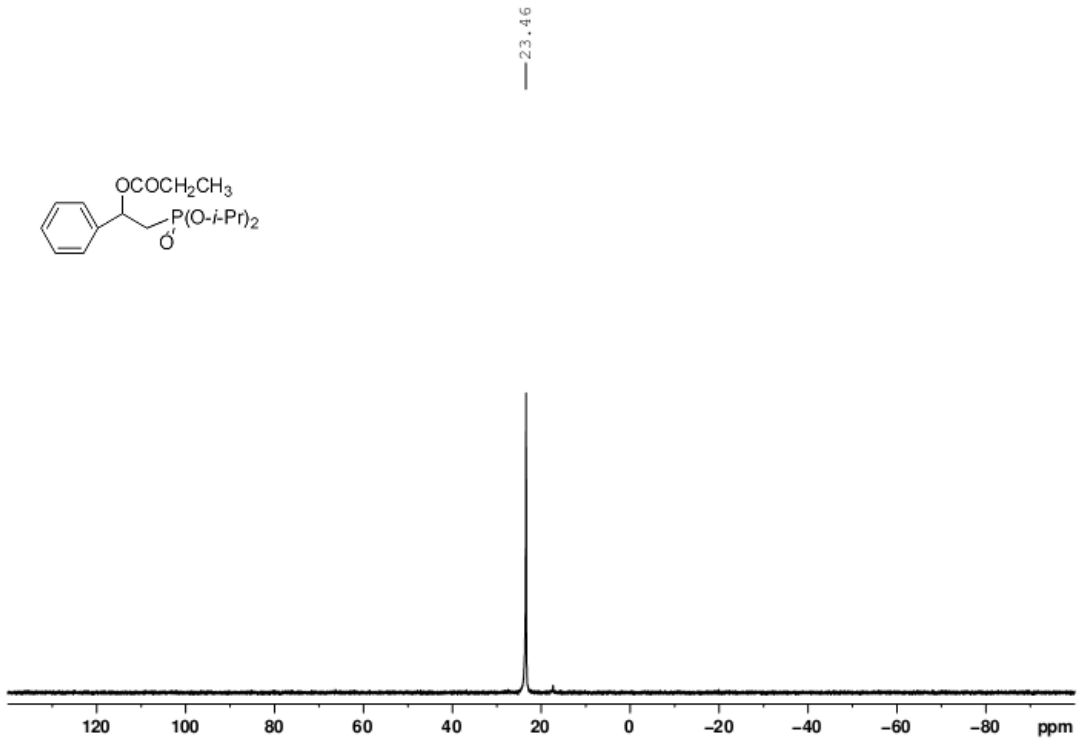
3b


7.379
7.375
7.358
7.354
7.334
7.315
7.304
7.300
7.296
7.291
7.283
7.266
6.120
6.105
6.099
6.084
6.077
6.063
4.683
4.668
4.653
4.638
4.623
2.497
2.479
2.458
2.437
2.416
2.413
2.393
2.390
2.371
2.365
2.352
2.346
2.327
2.308
2.305
2.289
2.286
2.276
2.251
2.242
2.238
2.228
2.204
2.190
1.304
1.289
1.272
1.256
1.241
1.224
1.208
1.136
1.117
1.098
OCOCH2CH3
P(O-i-Pr)2
O
9 8 7 6 5 4 3 2 1 0 ppm
5.00
0.96
2.01
4.21
12.06
3.08

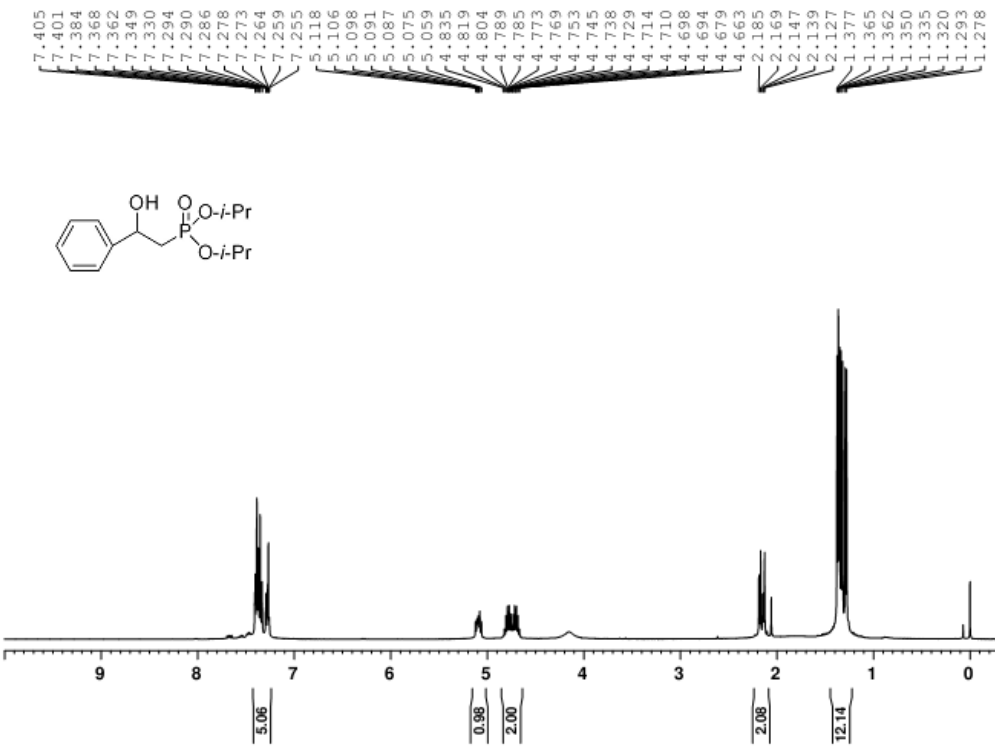
3b


173.12
140.46
140.36
128.62
128.36
126.70
77.55
77.23
76.91
70.99
70.62
70.56
70.50
70.43
35.57
34.17
27.75
24.15
24.12
24.05
24.01
23.96
8.99
OCOCH2CH3
P(O-i-Pr)2
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

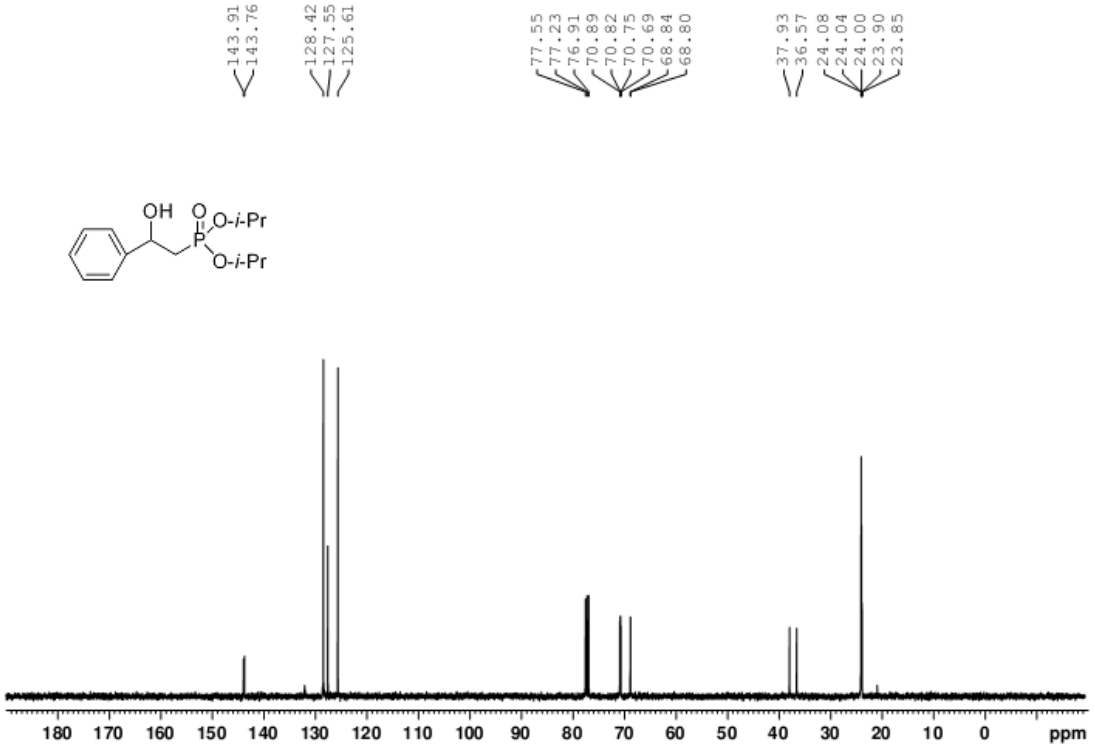
3b


23.46
OCOCH2CH3
P(O-i-Pr)2
O
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm

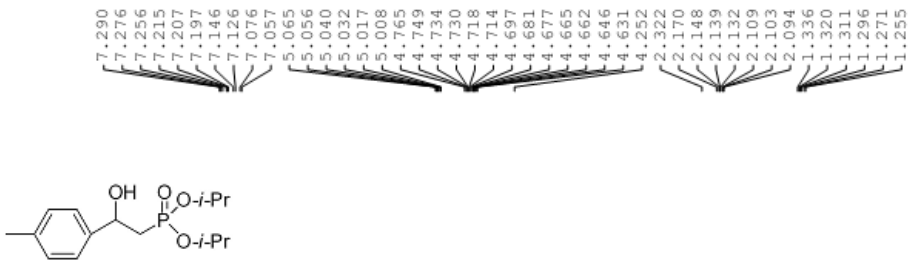
4a


7.405
7.401
7.384
7.368
7.362
7.349
7.330
7.294
7.290
7.286
7.278
7.273
7.264
7.259
7.255
5.118
5.106
5.098
5.091
5.087
5.075
5.059
4.835
4.819
4.804
4.789
4.785
4.773
4.769
4.753
4.745
4.738
4.729
4.714
4.710
4.698
4.694
4.679
4.663
2.185
2.169
2.147
2.139
2.127
1.377
1.365
1.362
1.350
1.335
1.320
1.293
1.278
OH
O
O-i-Pr
P
O-i-Pr
9
8
7
6
5
4
3
2
1
0
ppm
5.06
0.98
2.00
2.08
12.14

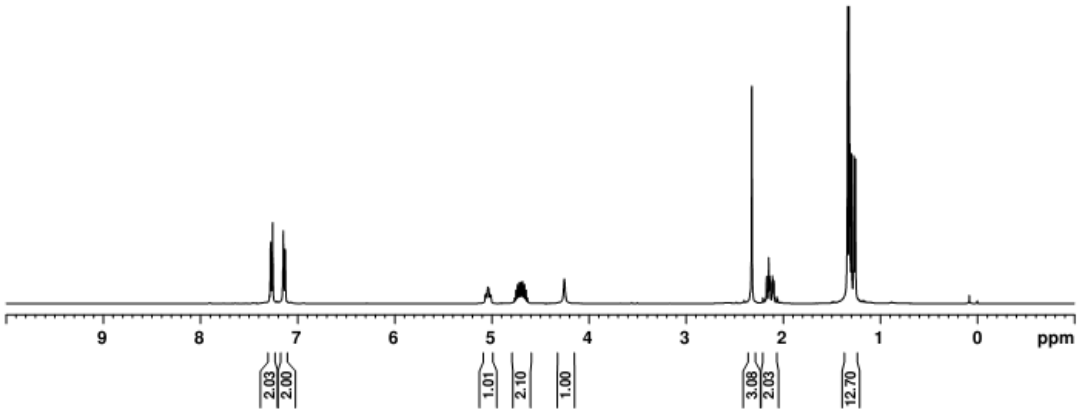
4a


143.91
143.76
128.42
127.55
125.61
77.55
77.23
76.91
70.89
70.82
70.75
70.69
68.84
68.80
37.93
36.57
24.08
24.04
24.00
23.90
23.85
OH
O
O-i-Pr
P
O-i-Pr
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4b

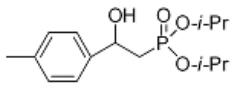

7.290
7.276
7.256
7.215
7.207
7.197
7.146
7.126
7.076
7.057
5.065
5.056
5.040
5.032
5.017
5.008
4.765
4.749
4.734
4.730
4.718
4.714
4.697
4.681
4.677
4.665
4.662
4.646
4.631
4.252
2.322
2.170
2.148
2.139
2.132
2.109
2.103
2.094
1.336
1.320
1.311
1.296
1.271
1.255

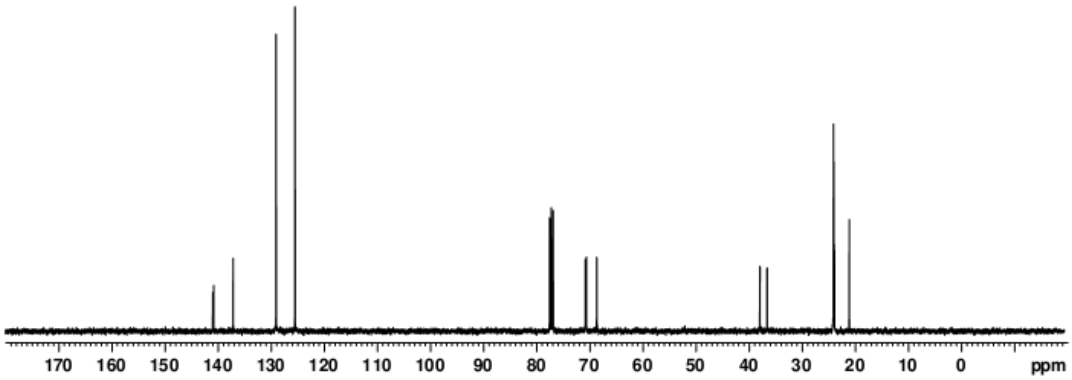
OH
O
O-i-Pr
P
O-i-Pr


9
8
7
6
5
4
3
2
1
0
ppm
2.03
2.00
1.01
2.10
1.00
3.08
2.03
12.70

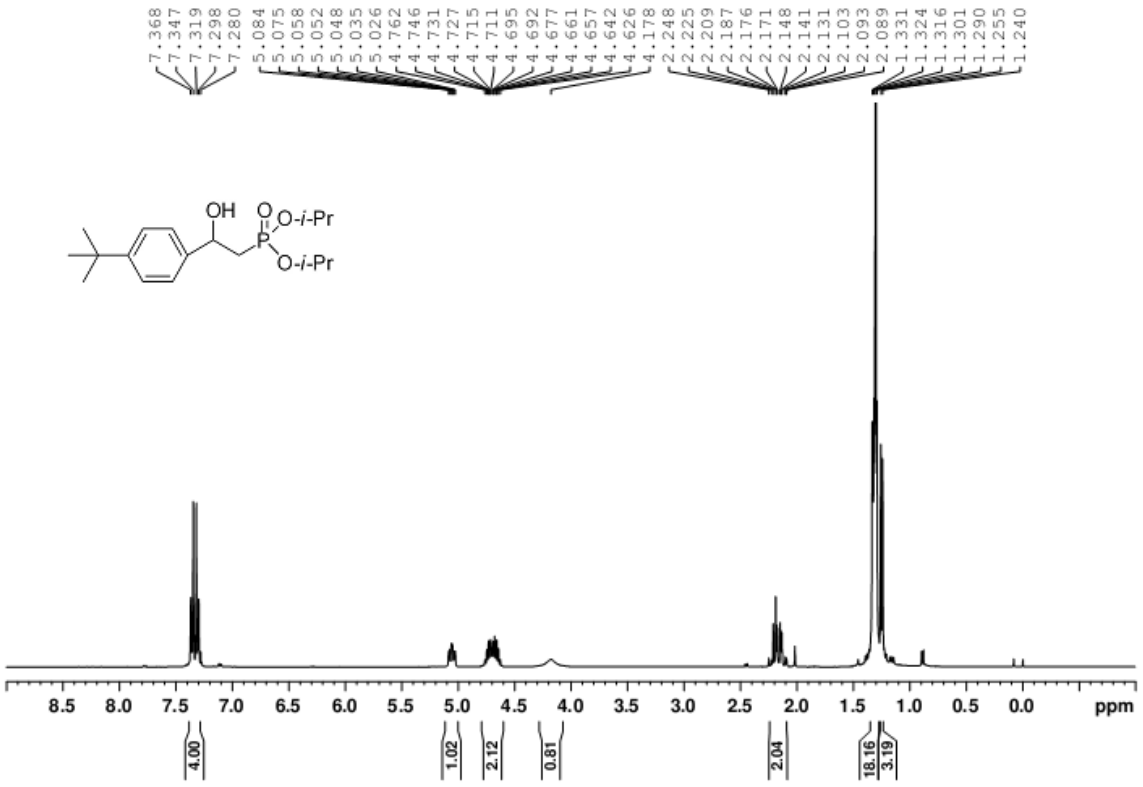
4b


140.96
140.80
137.17
129.09
125.53
77.55
77.23
76.91
70.81
70.75
70.68
70.62
68.69
68.65
37.95
36.59
24.11
24.07
24.03
23.93
23.88
21.11

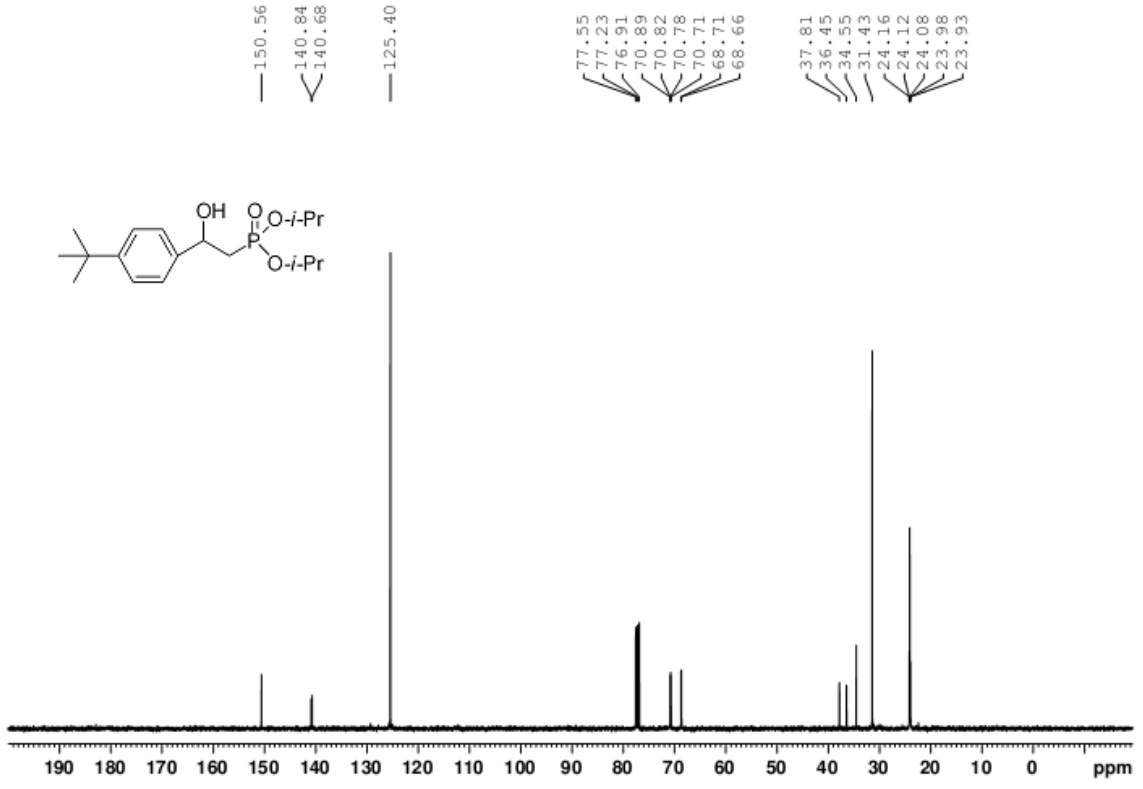

OH
O
O-i-Pr
P
O-i-Pr


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

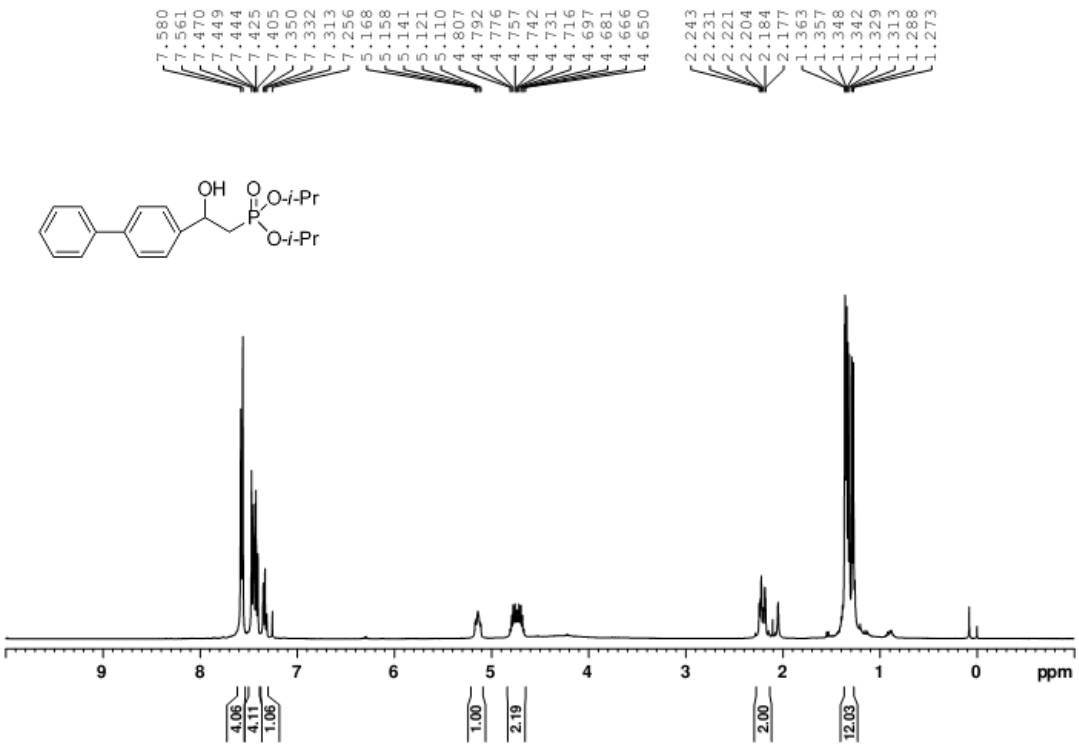
4c


7.368
7.347
7.319
7.298
7.280
5.084
5.075
5.058
5.052
5.048
5.035
5.026
4.762
4.746
4.731
4.727
4.715
4.711
4.695
4.692
4.677
4.661
4.657
4.642
4.626
4.178
2.248
2.225
2.209
2.187
2.176
2.171
2.148
2.141
2.131
2.103
2.093
2.089
1.331
1.324
1.316
1.301
1.290
1.255
1.240
OH
O
O-i-Pr
P
O-i-Pr
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.00
1.02
2.12
0.81
2.04
18.16
3.19

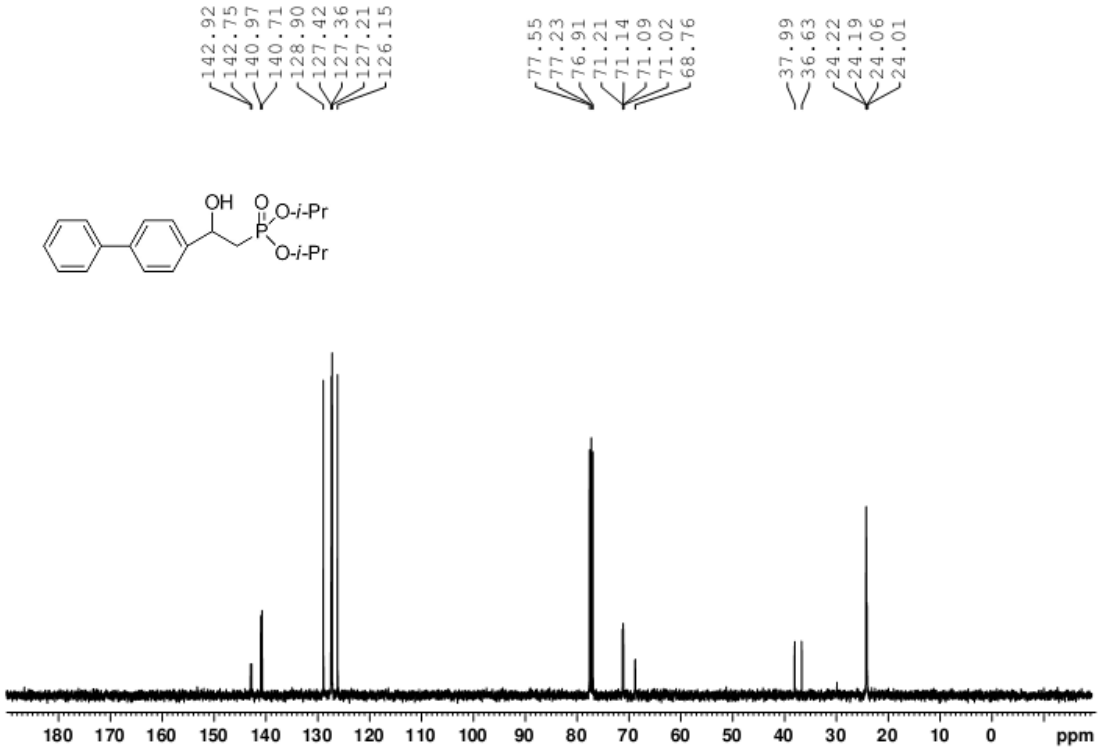
4c


150.56
140.84
140.68
125.40
77.55
77.23
76.91
70.89
70.82
70.78
70.71
68.71
68.66
37.81
36.45
34.55
31.43
24.16
24.12
24.08
23.98
23.93
OH
O
O-i-Pr
P
O-i-Pr
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

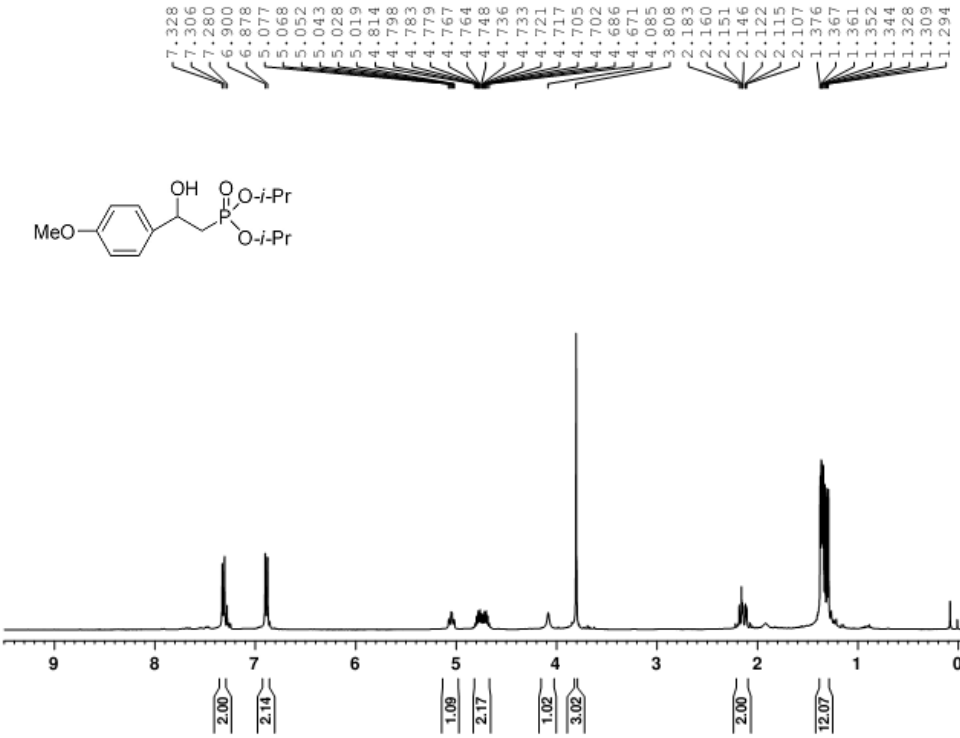
4d


7.580
7.561
7.470
7.449
7.444
7.425
7.405
7.350
7.332
7.313
7.256
5.168
5.158
5.141
5.121
5.110
4.807
4.792
4.776
4.757
4.742
4.731
4.716
4.697
4.681
4.666
4.650
2.243
2.231
2.221
2.204
2.184
2.177
1.363
1.357
1.348
1.342
1.329
1.313
1.288
1.273
OH
O
O-i-Pr
P
O-i-Pr
9
8
7
6
5
4
3
2
1
0
ppm
4.06
4.11
1.06
1.00
2.19
2.00
12.03

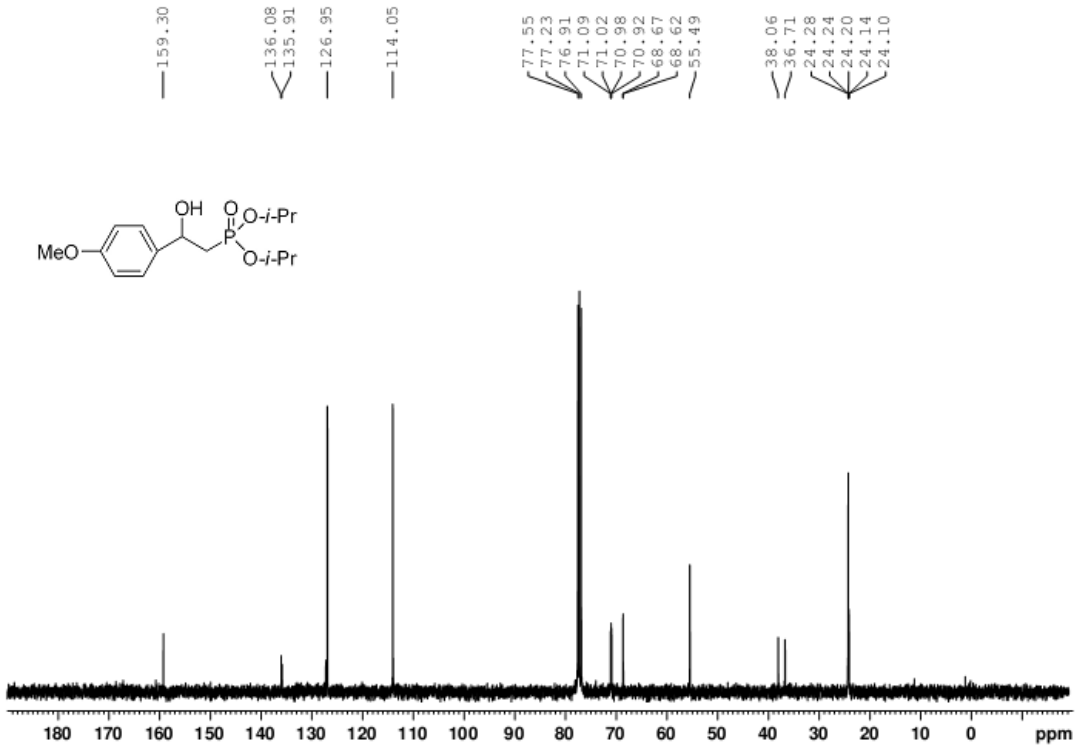
4d


142.92
142.75
140.97
140.71
128.90
127.42
127.36
127.21
126.15
77.55
77.23
76.91
71.21
71.14
71.09
71.02
68.76
37.99
36.63
24.22
24.19
24.06
24.01
OH
O
O-i-Pr
P
O-i-Pr
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

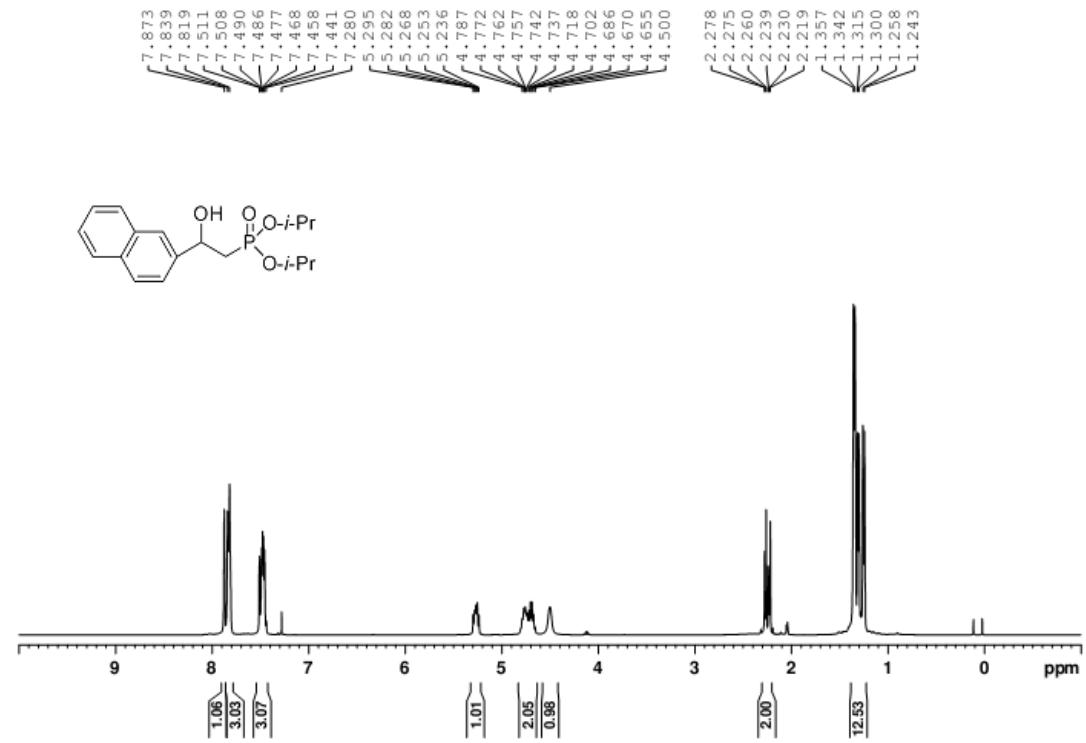
4e


7.328
7.306
7.280
6.900
6.878
5.077
5.068
5.052
5.043
5.028
5.019
4.814
4.798
4.783
4.779
4.767
4.764
4.748
4.736
4.733
4.721
4.717
4.705
4.702
4.686
4.671
4.085
3.808
2.183
2.160
2.151
2.146
2.122
2.115
2.107
1.376
1.367
1.361
1.352
1.344
1.328
1.309
1.294
OH
O
O-i-Pr
P
MeO
O-i-Pr
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.14
1.09
2.17
1.02
3.02
2.00
12.07

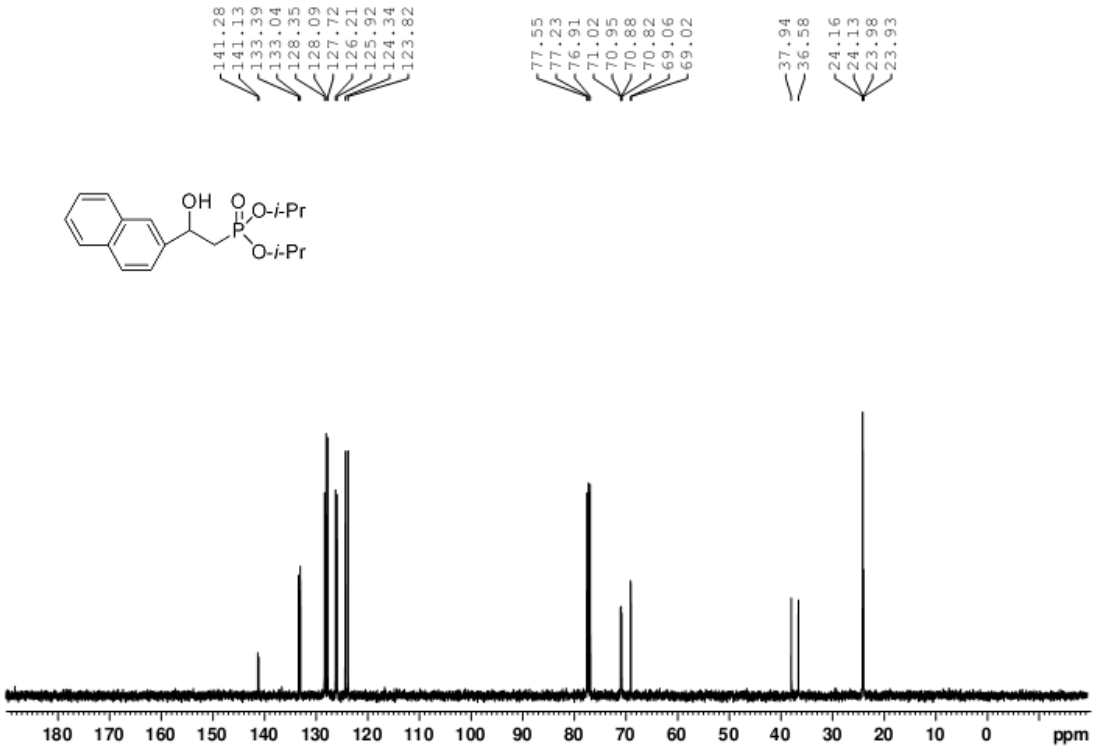
4e


159.30
136.08
135.91
126.95
114.05
77.55
77.23
76.91
71.09
71.02
70.98
70.92
68.67
68.62
55.49
38.06
36.71
24.28
24.24
24.20
24.14
24.10
OH
O
O-i-Pr
P
MeO
O-i-Pr
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

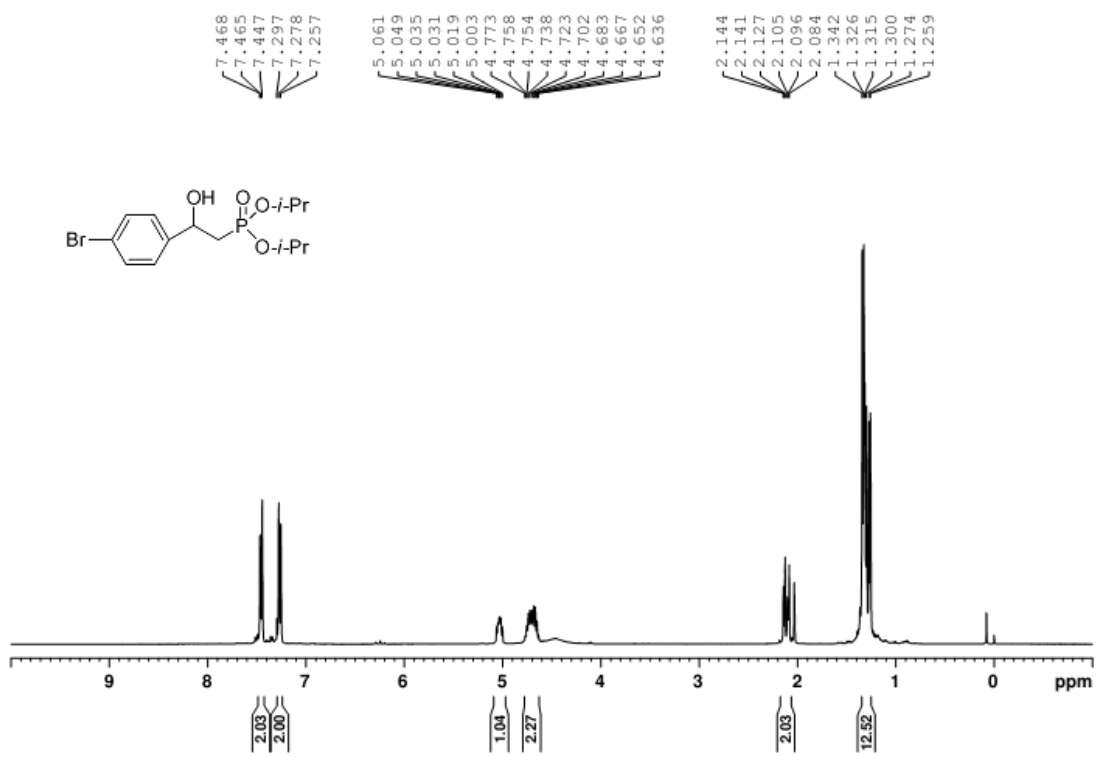
4f


7.873
7.839
7.819
7.511
7.508
7.490
7.486
7.477
7.468
7.458
7.441
7.280
5.295
5.282
5.268
5.253
5.236
4.787
4.772
4.762
4.757
4.742
4.737
4.718
4.702
4.686
4.670
4.655
4.500
2.278
2.275
2.260
2.239
2.230
2.219
1.357
1.342
1.315
1.300
1.258
1.243
OH
O
O-i-Pr
P
O-i-Pr
9
8
7
6
5
4
3
2
1
0
ppm
1.06
3.03
3.07
1.01
2.05
0.98
2.00
12.53

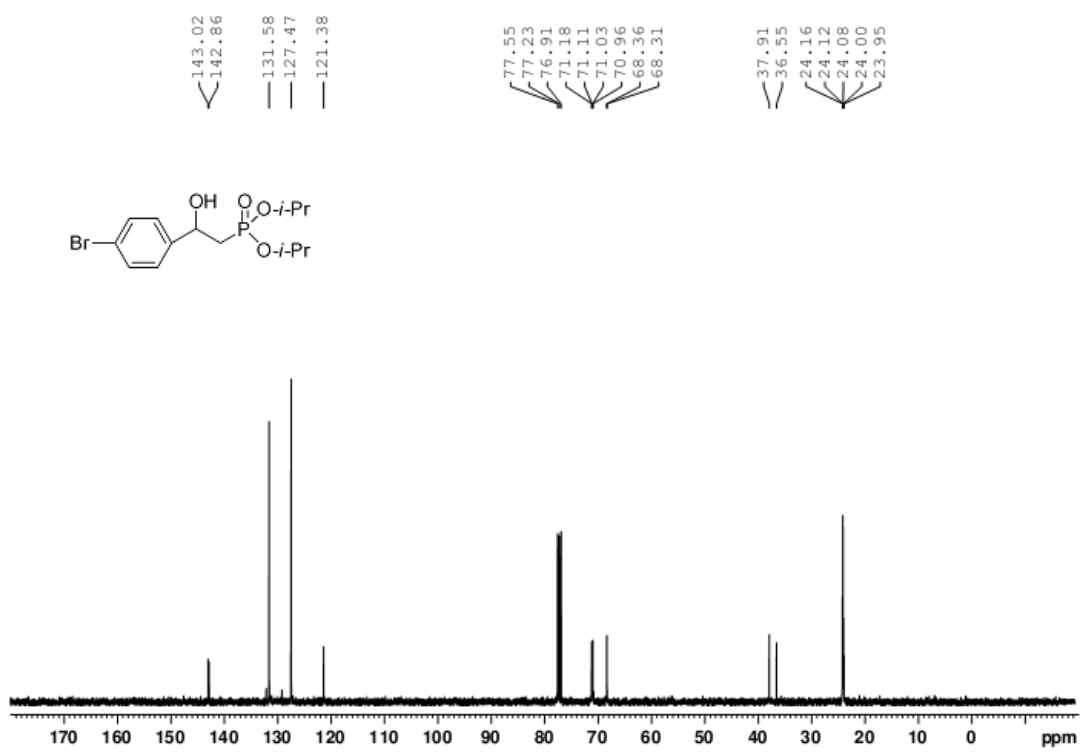
4f


141.28
141.13
133.39
133.04
128.35
128.09
127.72
126.21
125.92
124.34
123.82
77.55
77.23
76.91
71.02
70.95
70.88
70.82
69.06
69.02
37.94
36.58
24.16
24.13
23.98
23.93
OH
O
O-i-Pr
P
O-i-Pr
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

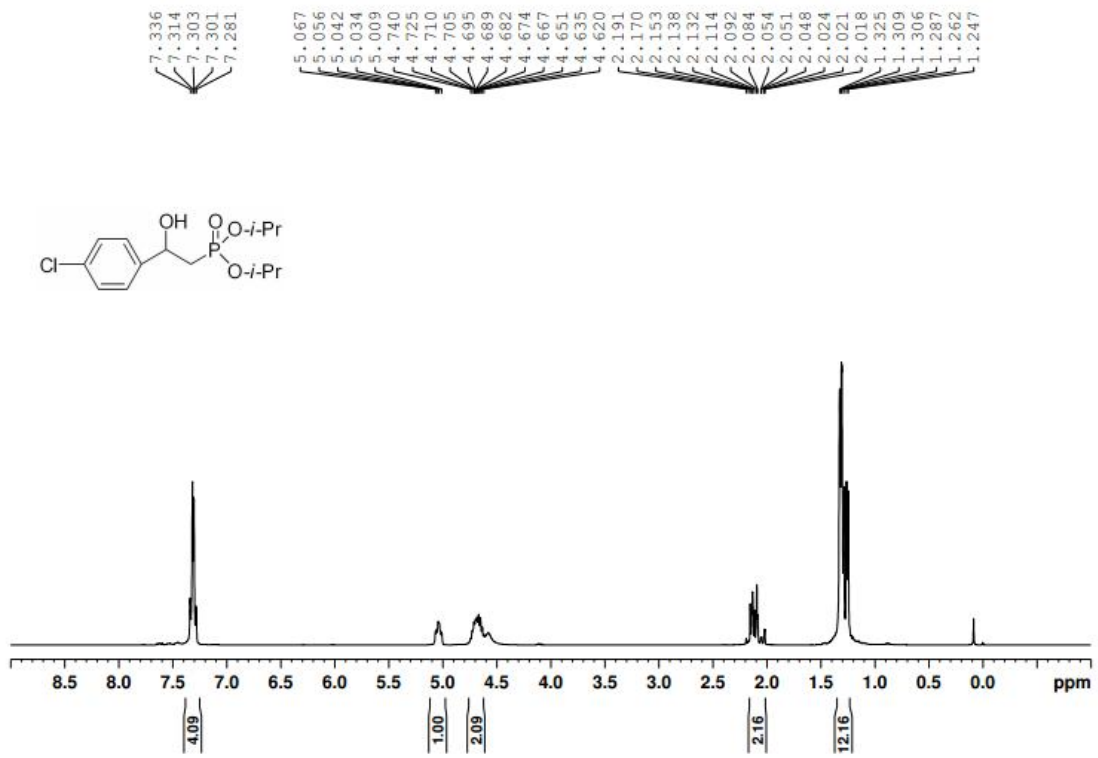
4g


7.468
7.465
7.447
7.297
7.278
7.257
5.061
5.049
5.035
5.031
5.019
5.003
4.773
4.758
4.754
4.738
4.723
4.702
4.683
4.667
4.652
4.636
2.144
2.141
2.127
2.105
2.096
2.084
1.342
1.326
1.315
1.300
1.274
1.259
OH
O
O-i-Pr
P
O-i-Pr
Br
9
8
7
6
5
4
3
2
1
0
ppm
2.03
2.00
1.04
2.27
2.03
12.52

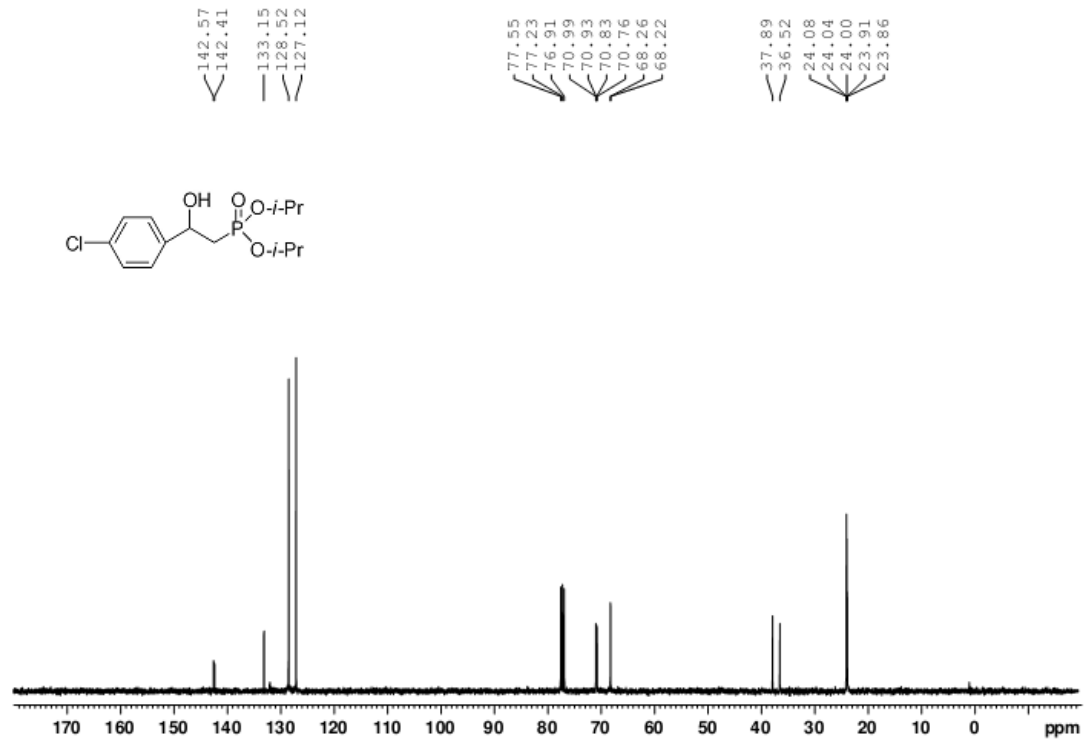
4g


143.02
142.86
131.58
127.47
121.38
77.55
77.23
76.91
71.18
71.11
71.03
70.96
68.36
68.31
37.91
36.55
24.16
24.12
24.08
24.00
23.95
OH
O
O-i-Pr
P
O-i-Pr
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

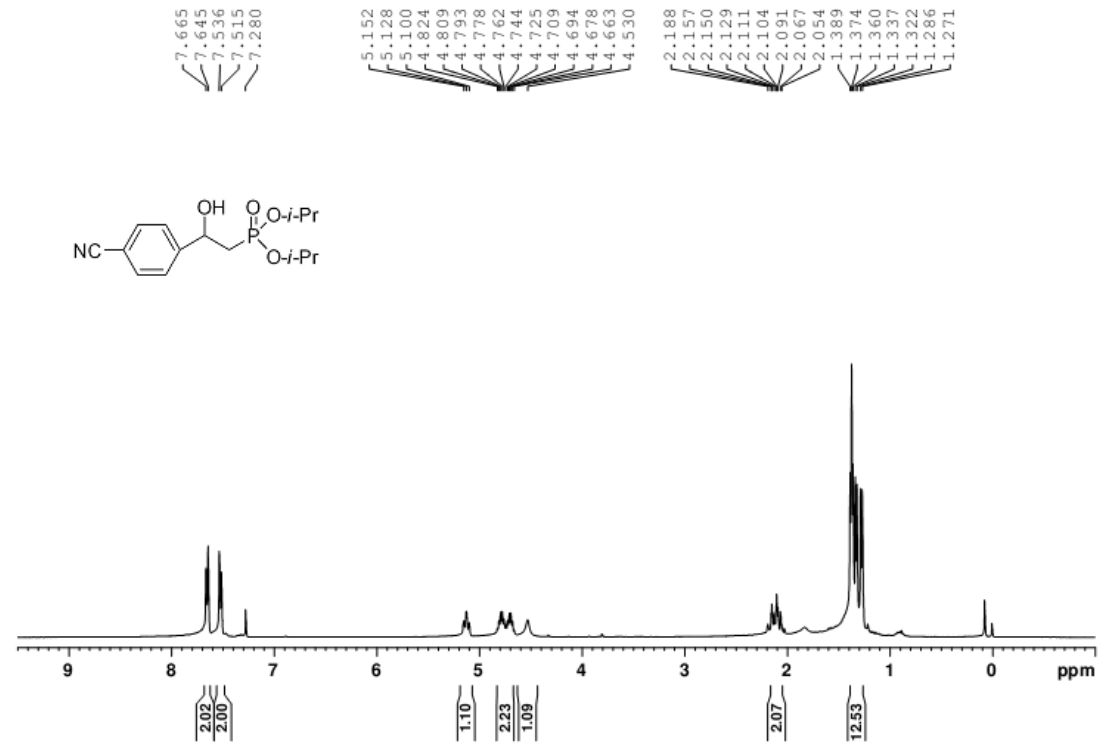
4h


7.336
7.314
7.303
7.301
7.281
5.067
5.056
5.042
5.034
5.009
4.740
4.725
4.710
4.705
4.695
4.689
4.682
4.674
4.667
4.651
4.635
4.620
2.191
2.170
2.153
2.138
2.132
2.114
2.092
2.084
2.054
2.051
2.048
2.024
2.021
2.018
1.325
1.309
1.306
1.287
1.262
1.247
OH
O
O-i-Pr
P
O-i-Pr
Cl
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.09
1.00
2.09
2.16
12.16

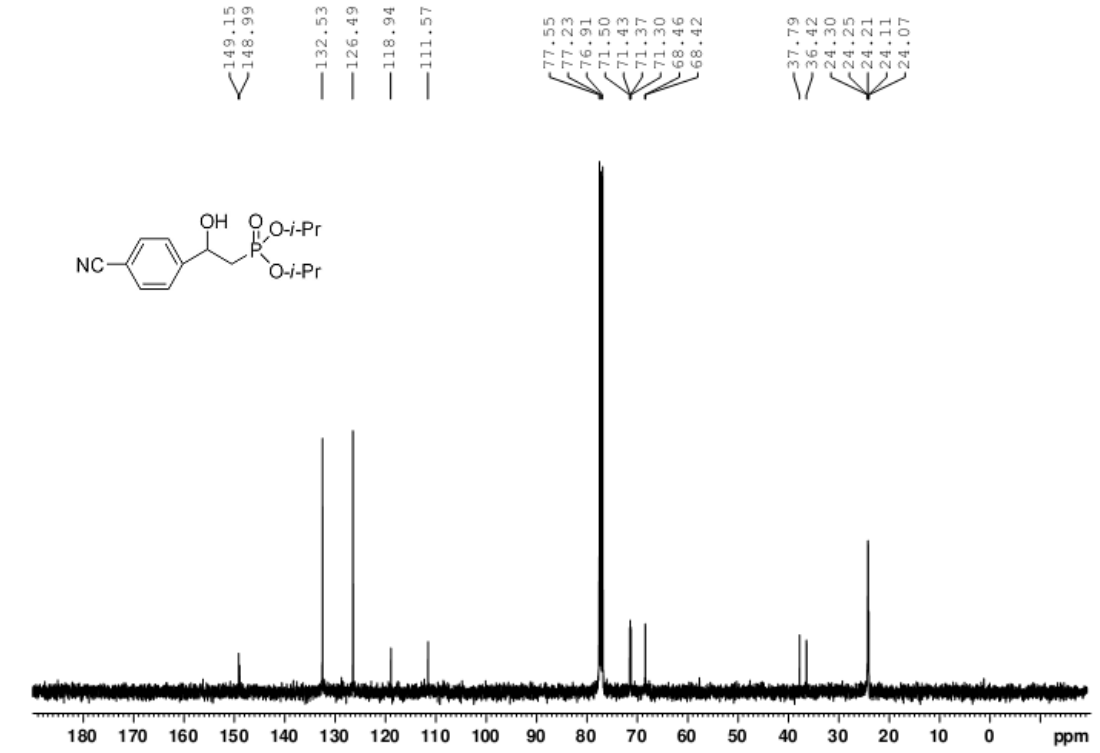
4h


142.57
142.41
133.15
128.52
127.12
77.55
77.23
76.91
70.99
70.93
70.83
70.76
68.26
68.22
37.89
36.52
24.08
24.04
24.00
23.91
23.86
OH
O
O-i-Pr
P
O-i-Pr
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

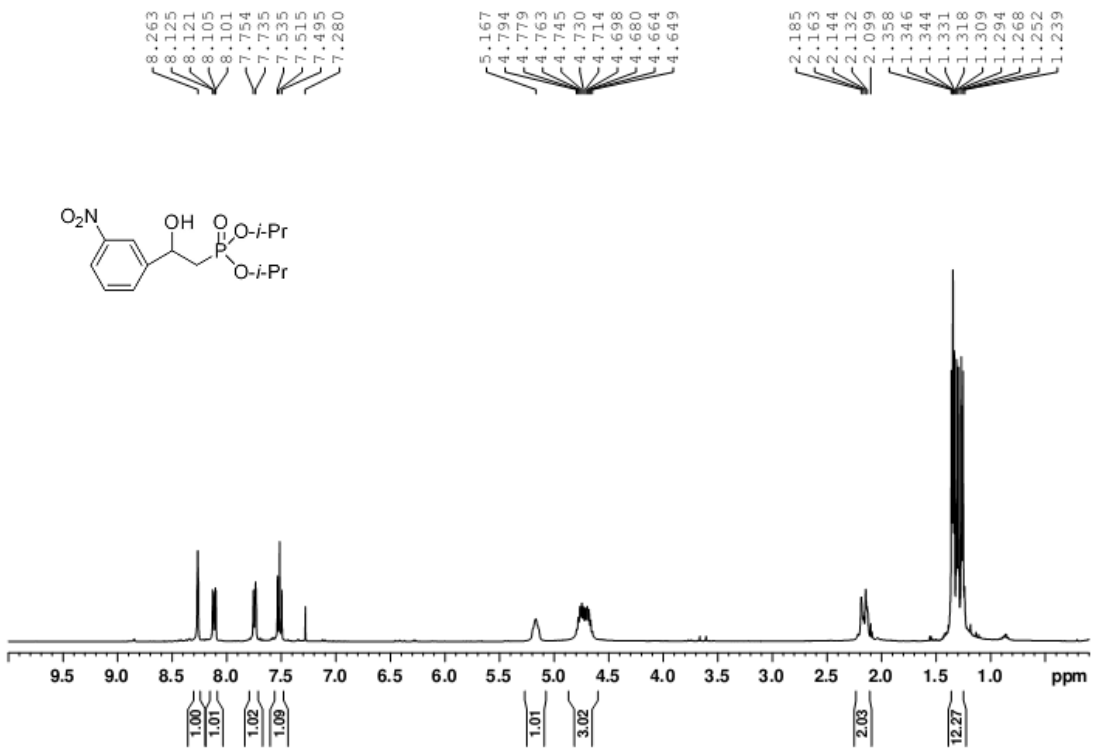
4i


7.665
7.645
7.536
7.515
7.280
5.152
5.128
5.100
4.824
4.809
4.793
4.778
4.762
4.744
4.725
4.709
4.694
4.678
4.663
4.530
2.188
2.157
2.150
2.129
2.111
2.104
2.091
2.067
2.054
1.389
1.374
1.360
1.337
1.322
1.286
1.271
OH
O
O-i-Pr
P
O-i-Pr
NC
9
8
7
6
5
4
3
2
1
0
ppm
2.02
2.00
1.10
2.23
1.09
2.07
12.53

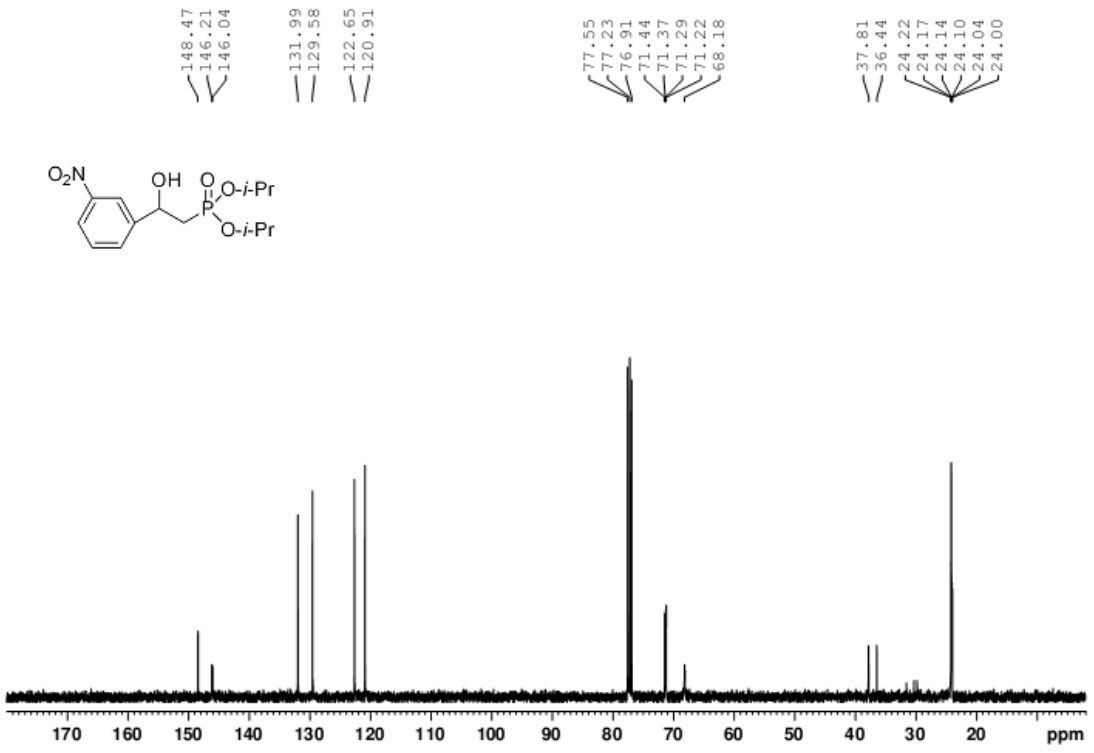
4i


149.15
148.99
132.53
126.49
118.94
111.57
77.55
77.23
76.91
71.50
71.43
71.37
71.30
68.46
68.42
37.79
36.42
24.30
24.25
24.21
24.11
24.07
OH
O
O-i-Pr
P
O-i-Pr
NC
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

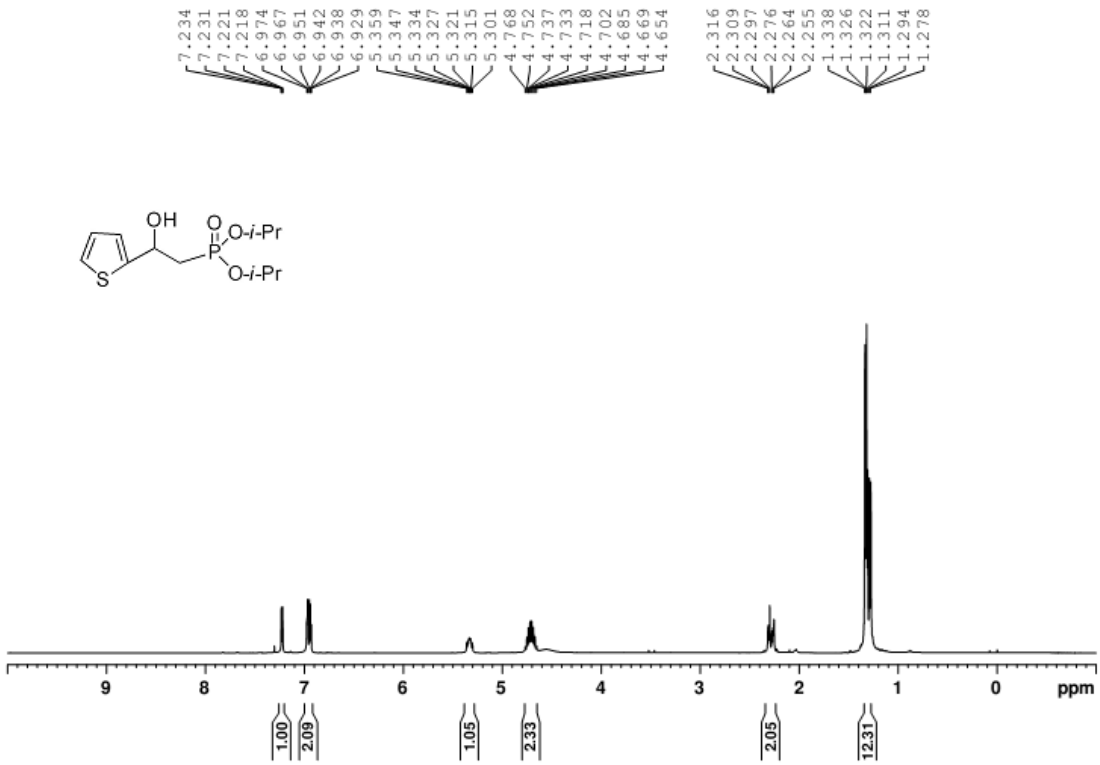
4j


8.263
8.125
8.121
8.105
8.101
7.754
7.735
7.535
7.515
7.495
7.280
5.167
4.794
4.779
4.763
4.745
4.730
4.714
4.698
4.680
4.664
4.649
2.185
2.163
2.144
2.132
2.099
1.358
1.346
1.344
1.331
1.318
1.309
1.294
1.268
1.252
1.239
O2N
OH
O
P
O-i-Pr
O-i-Pr
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 ppm
1.00
1.01
1.02
1.09
1.01
3.02
2.03
12.27

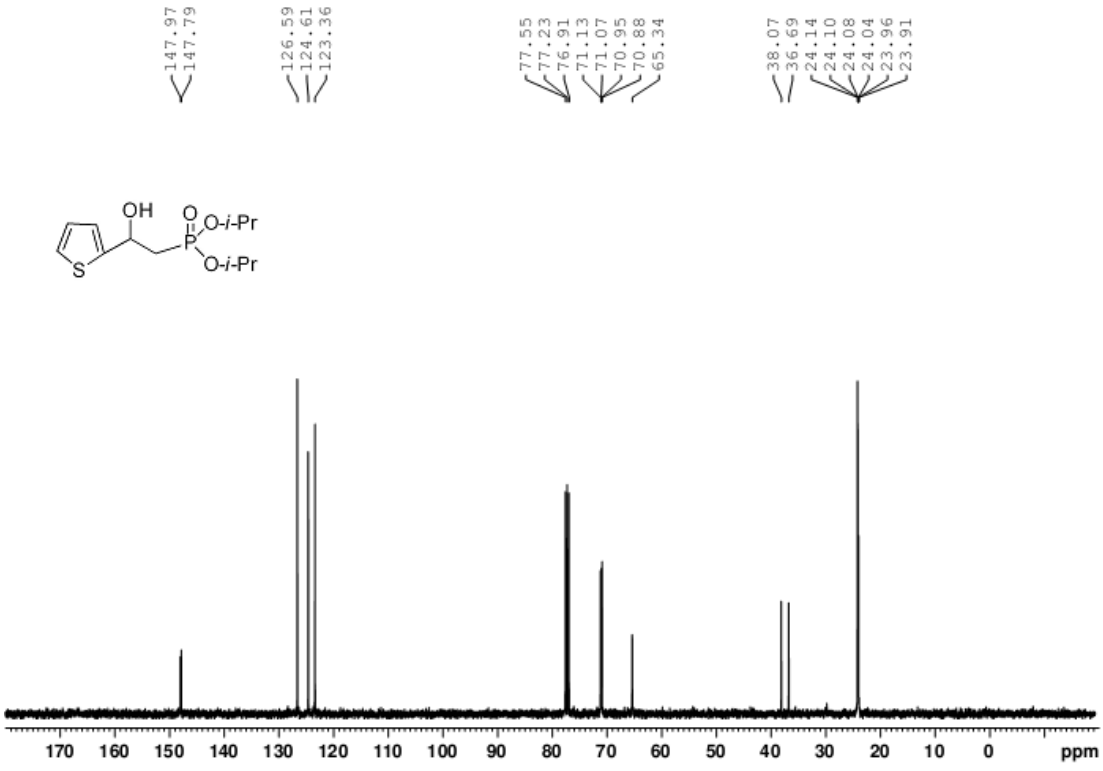
4j


148.47
146.21
146.04
131.99
129.58
122.65
120.91
77.55
77.23
76.91
71.44
71.37
71.29
71.22
68.18
37.81
36.44
24.22
24.17
24.14
24.10
24.04
24.00
O2N
OH
O
P
O-i-Pr
O-i-Pr
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

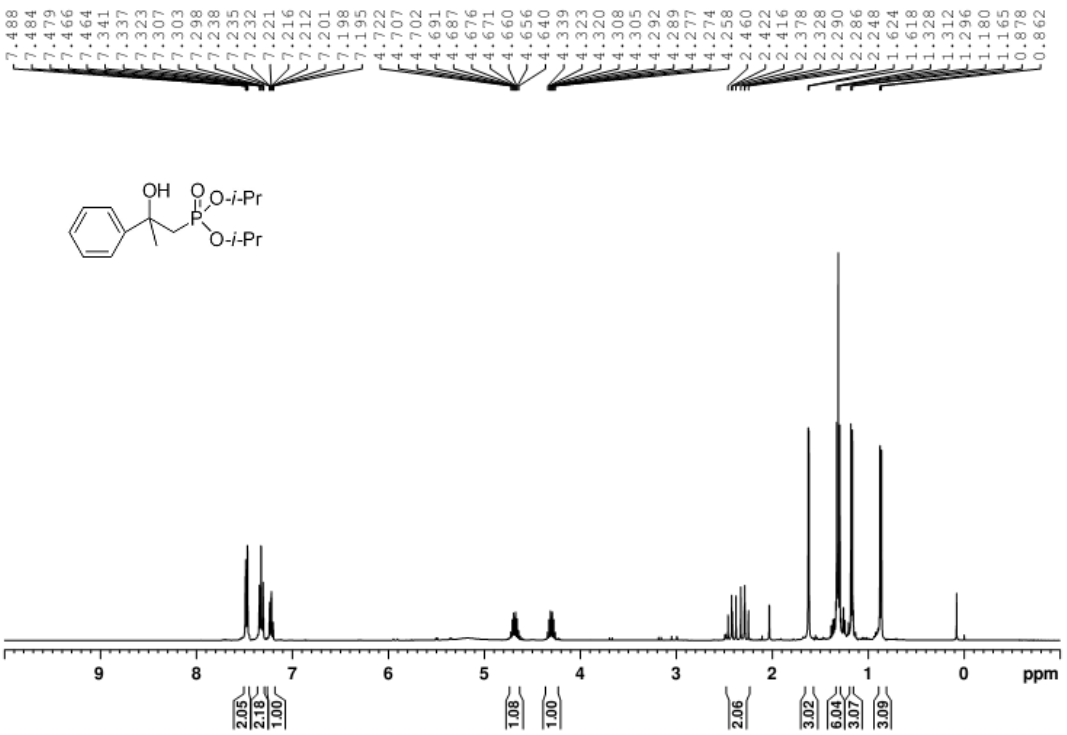
4k


7.234
7.231
7.221
7.218
6.974
6.967
6.951
6.942
6.938
6.929
5.359
5.347
5.334
5.327
5.321
5.315
5.301
4.768
4.752
4.737
4.733
4.718
4.702
4.685
4.669
4.654
2.316
2.309
2.297
2.276
2.264
2.255
1.338
1.326
1.322
1.311
1.294
1.278
OH
O
O-i-Pr
P
O-i-Pr
S
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.09
1.05
2.33
2.05
12.31

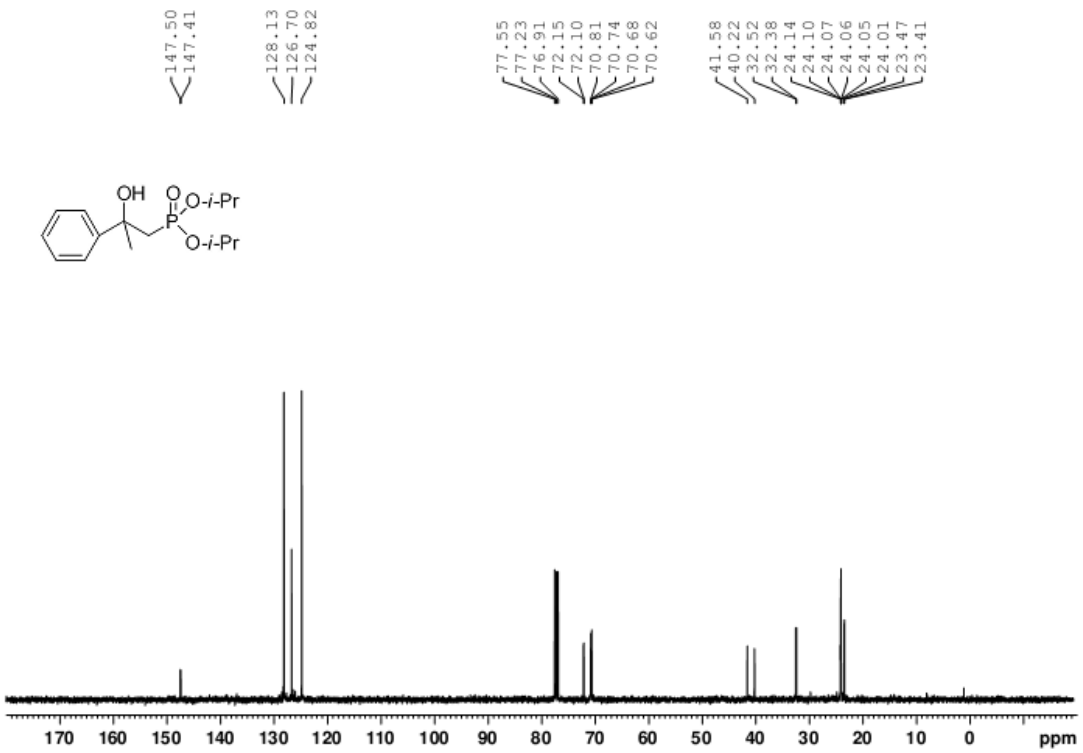
4k


147.97
147.79
126.59
124.61
123.36
77.55
77.23
76.91
71.13
71.07
70.95
70.88
65.34
38.07
36.69
24.14
24.10
24.08
24.04
23.96
23.91
OH
O
O-i-Pr
P
O-i-Pr
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

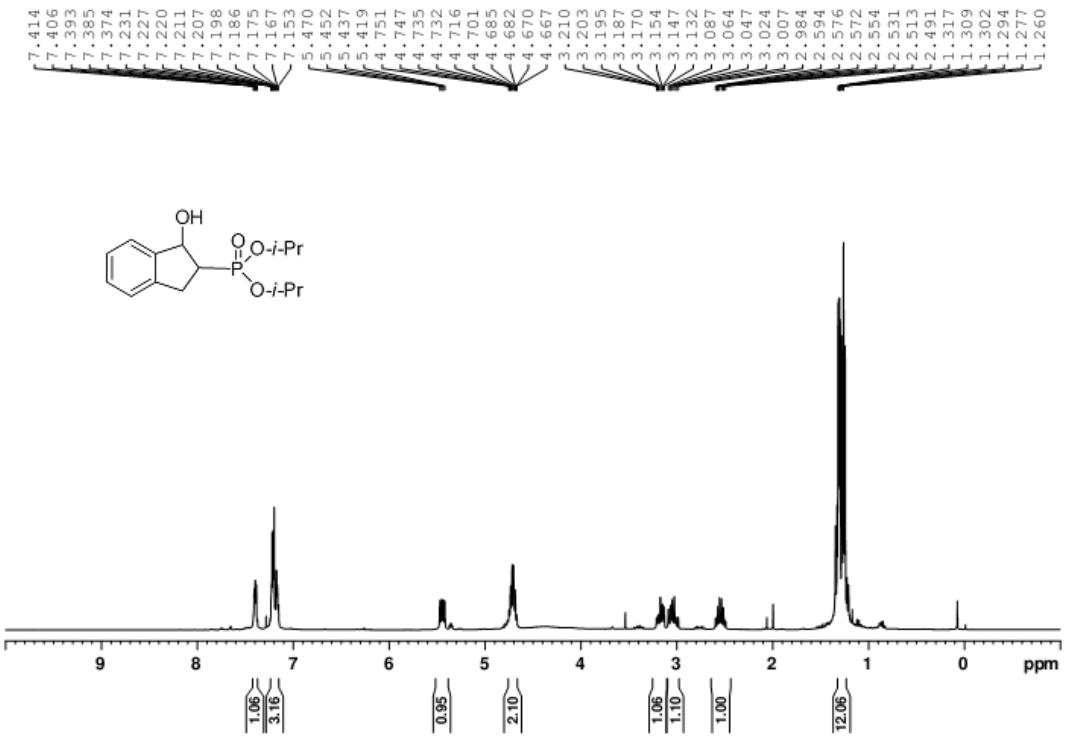
4l


7.488
7.484
7.479
7.466
7.464
7.341
7.337
7.323
7.307
7.303
7.298
7.238
7.235
7.232
7.221
7.216
7.212
7.201
7.198
7.195
4.722
4.707
4.702
4.691
4.687
4.676
4.671
4.660
4.656
4.640
4.339
4.323
4.320
4.308
4.305
4.292
4.289
4.277
4.274
4.258
2.460
2.422
2.416
2.378
2.328
2.290
2.286
2.248
1.624
1.618
1.328
1.312
1.296
1.180
1.165
0.878
0.862
OH
O
O-i-Pr
P
O-i-Pr
9
8
7
6
5
4
3
2
1
0
ppm
2.05
2.18
1.00
1.08
1.00
2.06
3.02
6.04
3.07
3.09

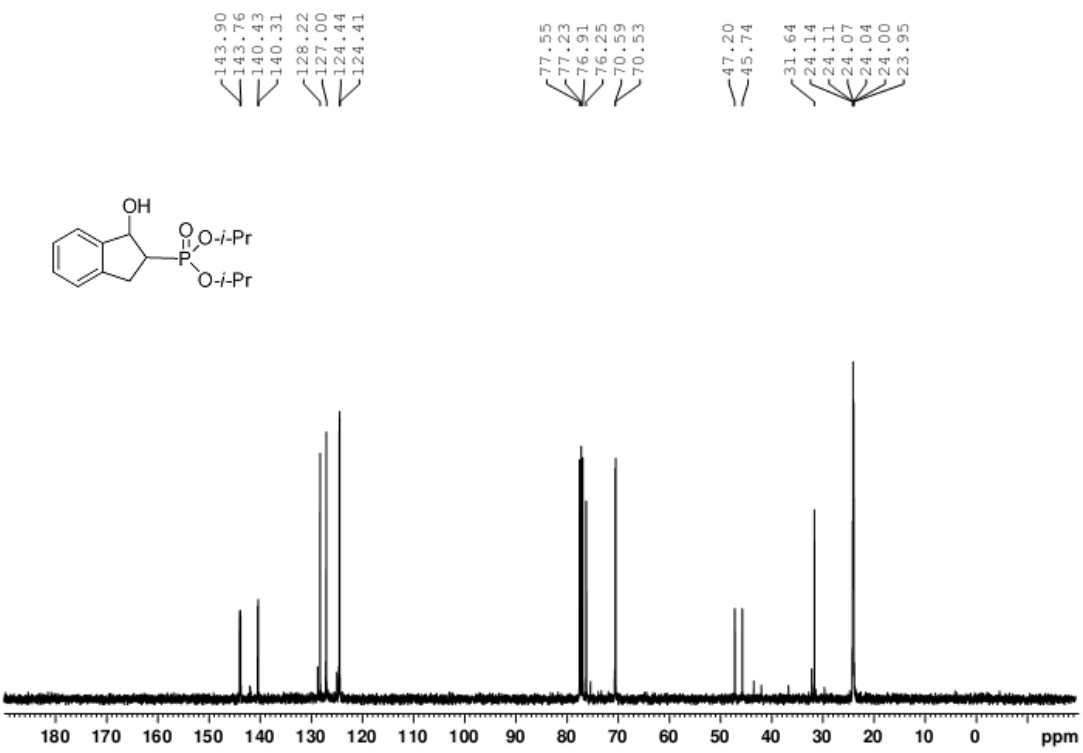
4l


147.50
147.41
128.13
126.70
124.82
77.55
77.23
76.91
72.15
72.10
70.81
70.74
70.68
70.62
41.58
40.22
32.52
32.38
24.14
24.10
24.07
24.06
24.05
24.01
23.47
23.41
OH
O
O-i-Pr
P
O-i-Pr
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

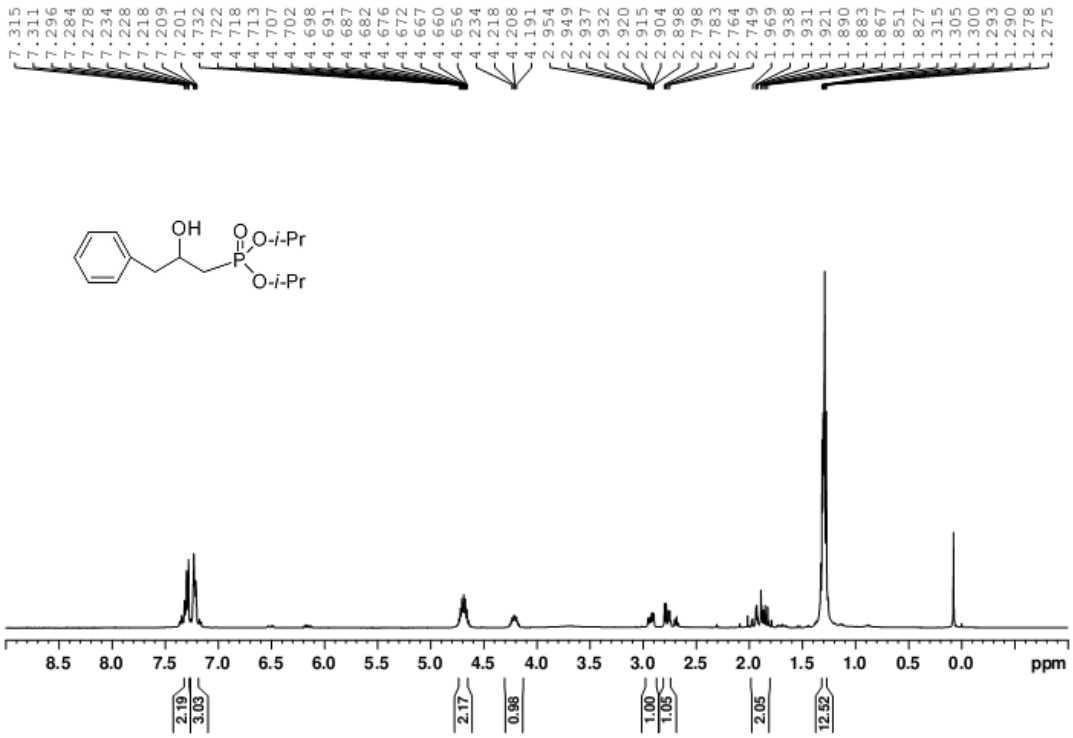
4m


7.414
7.406
7.393
7.385
7.374
7.231
7.227
7.220
7.211
7.207
7.198
7.186
7.175
7.167
7.153
5.470
5.452
5.437
5.419
4.751
4.747
4.735
4.732
4.716
4.701
4.685
4.682
4.670
4.667
3.210
3.203
3.195
3.187
3.170
3.154
3.147
3.132
3.087
3.064
3.047
3.024
3.007
2.984
2.594
2.576
2.572
2.554
2.531
2.513
2.491
1.317
1.309
1.302
1.294
1.277
1.260
OH
O
P
O-i-Pr
O-i-Pr
9
8
7
6
5
4
3
2
1
0
ppm
1.06
3.16
0.95
2.10
1.06
1.10
1.00
12.06

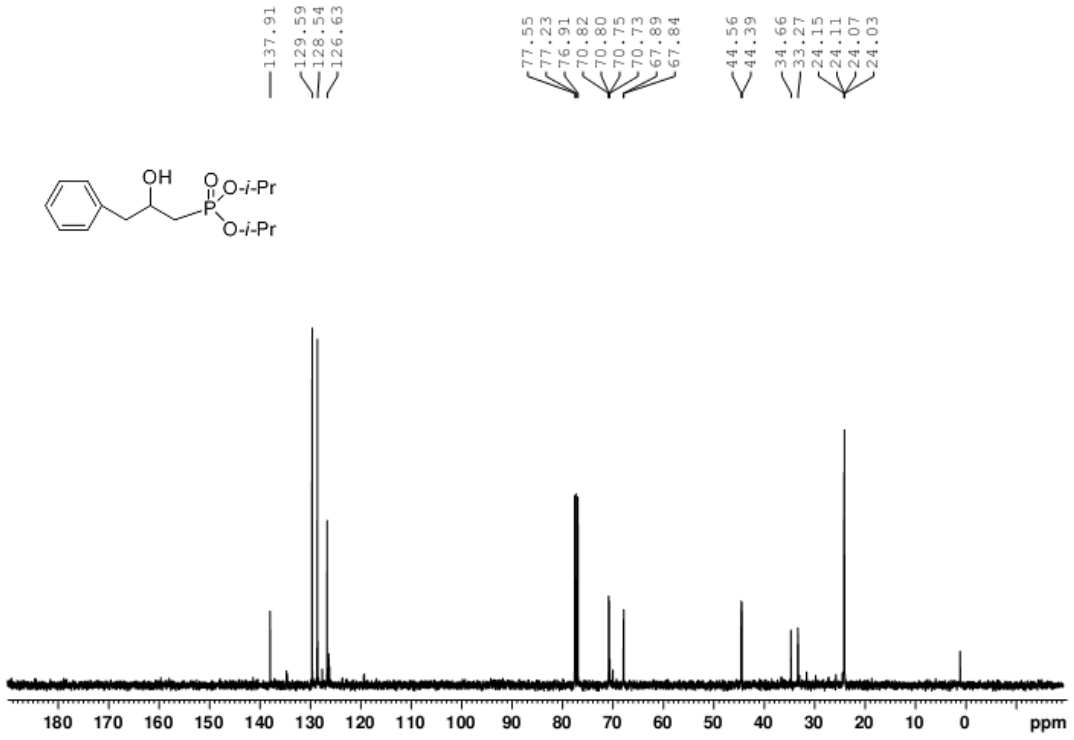
4m


143.90
143.76
140.43
140.31
128.22
127.00
124.44
124.41
77.55
77.23
76.91
76.25
70.59
70.53
47.20
45.74
31.64
24.14
24.11
24.07
24.04
24.00
23.95
OH
O
P
O-i-Pr
O-i-Pr
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

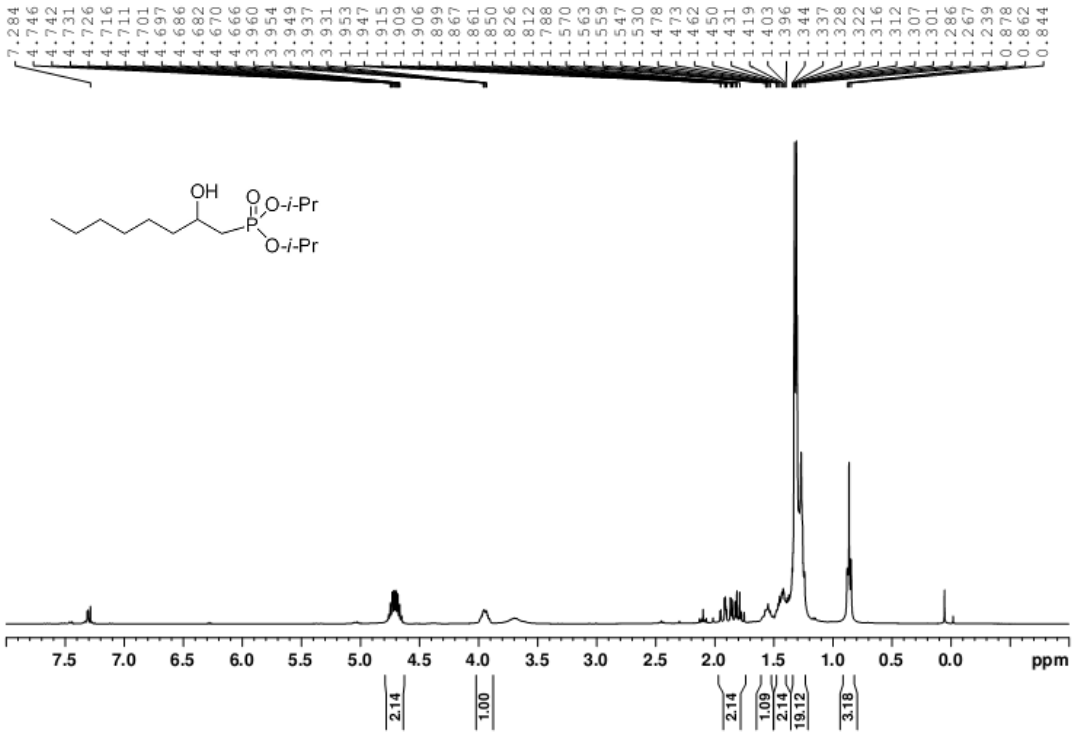
4n


7.315
7.311
7.296
7.284
7.278
7.234
7.228
7.218
7.209
7.201
4.732
4.722
4.718
4.713
4.707
4.702
4.698
4.691
4.687
4.682
4.676
4.672
4.667
4.660
4.656
4.234
4.218
4.208
4.191
2.954
2.949
2.937
2.932
2.920
2.915
2.904
2.898
2.798
2.783
2.764
2.749
1.969
1.938
1.931
1.921
1.890
1.883
1.867
1.851
1.827
1.315
1.305
1.300
1.293
1.290
1.278
1.275
OH
O
O-i-Pr
P
O-i-Pr
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.19
3.03
2.17
0.98
1.00
1.05
2.05
12.52

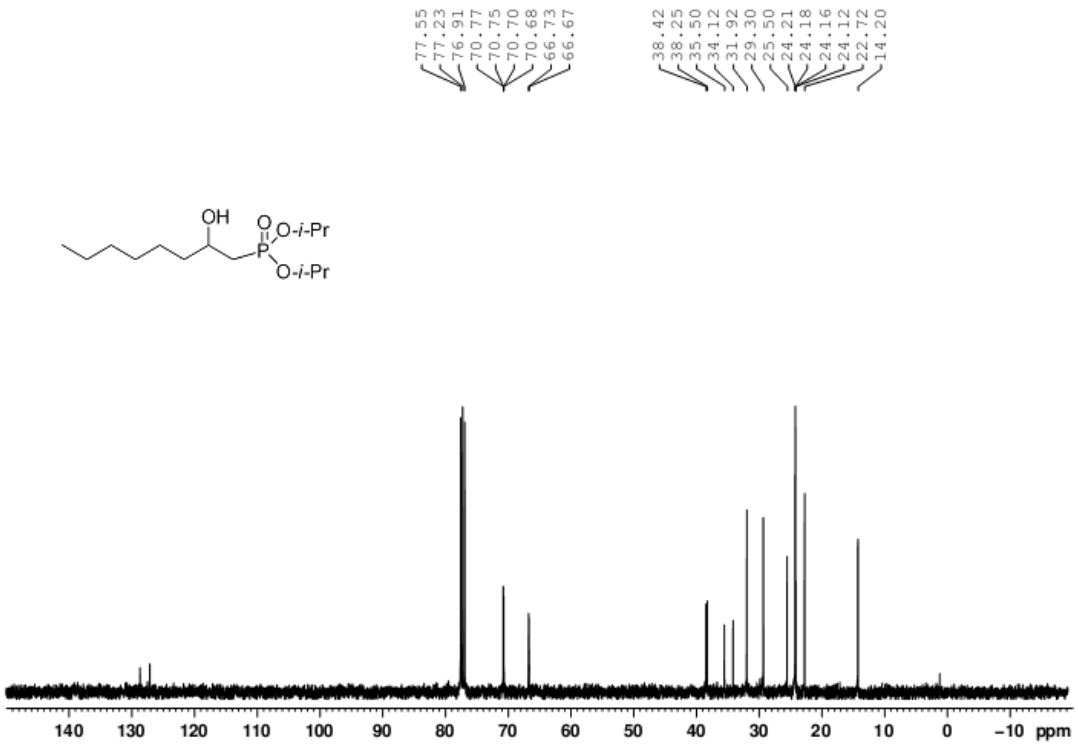
4n


137.91
129.59
128.54
126.63
77.55
77.23
76.91
70.82
70.80
70.75
70.73
67.89
67.84
44.56
44.39
34.66
33.27
24.15
24.11
24.07
24.03
OH
O
O-i-Pr
P
O-i-Pr
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

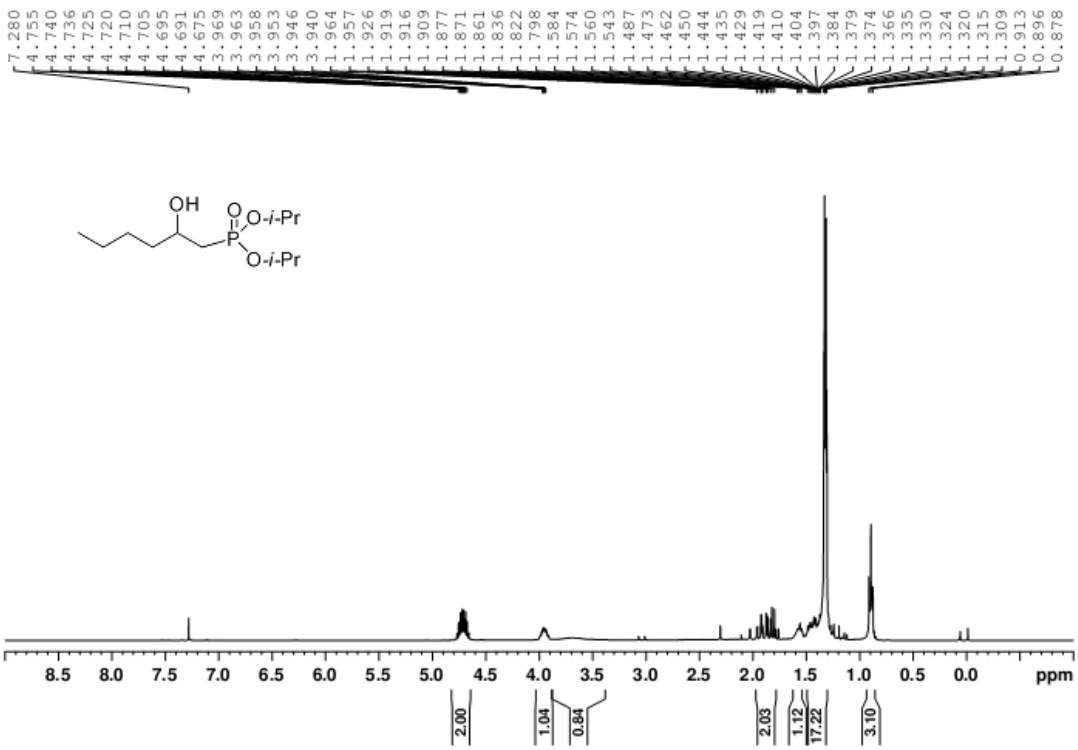
4o


7.284
4.746
4.742
4.731
4.726
4.716
4.711
4.701
4.697
4.686
4.682
4.670
4.666
3.960
3.954
3.949
3.937
3.931
1.953
1.947
1.915
1.909
1.906
1.899
1.867
1.861
1.850
1.826
1.812
1.788
1.570
1.563
1.559
1.547
1.530
1.478
1.473
1.462
1.450
1.431
1.419
1.403
1.396
1.344
1.337
1.328
1.322
1.316
1.312
1.307
1.301
1.286
1.267
1.239
0.878
0.862
0.844
OH
O
O-i-Pr
P
O-i-Pr
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.14
1.00
2.14
1.09
2.14
19.12
3.18

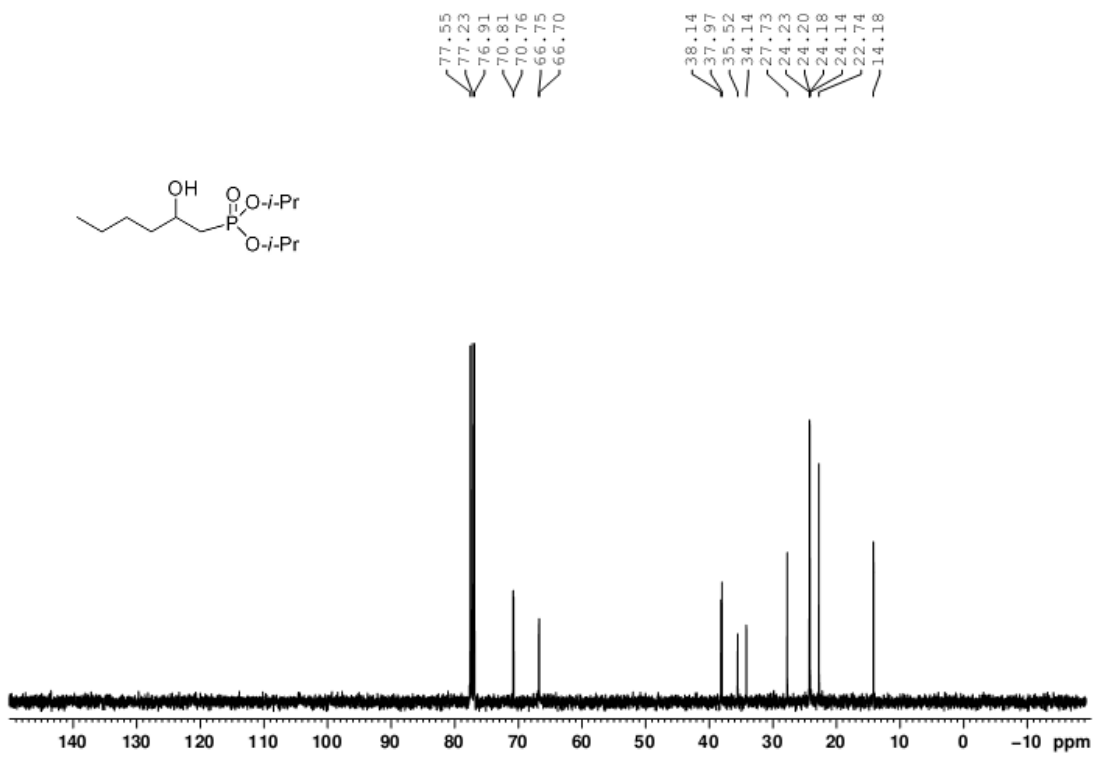
4o


77.55
77.23
76.91
70.77
70.75
70.70
70.68
66.73
66.67
38.42
38.25
35.50
34.12
31.92
29.30
25.50
24.21
24.18
24.16
24.12
22.72
14.20
OH
O
O-i-Pr
P
O-i-Pr
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
ppm

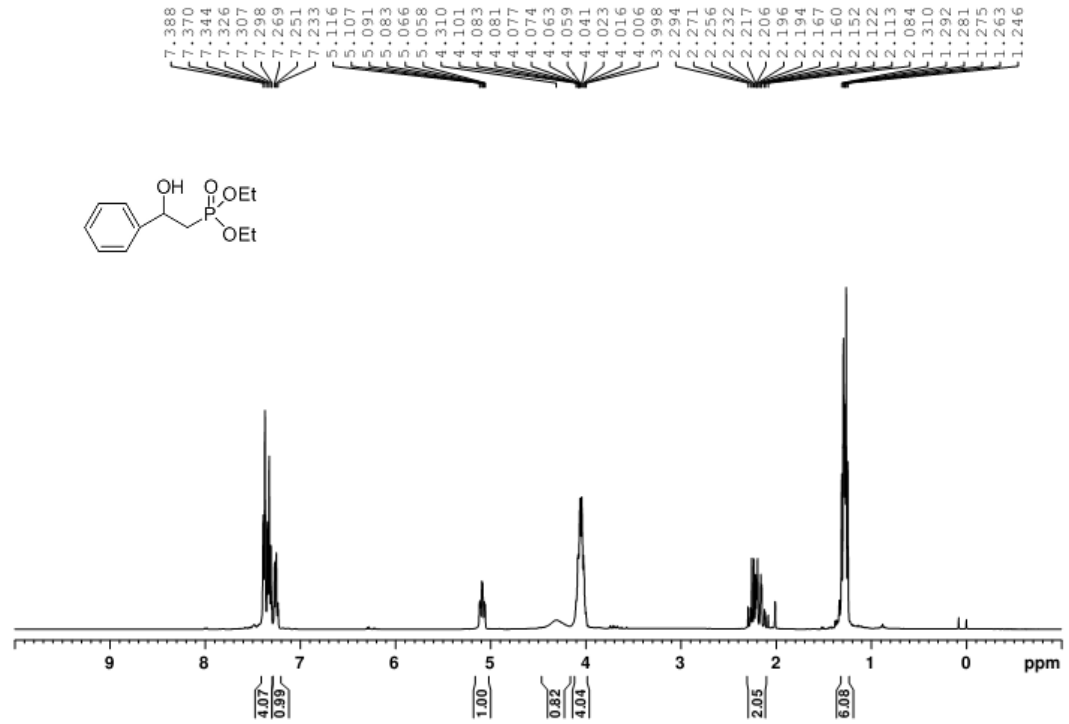
4p


7.280
4.755
4.740
4.736
4.725
4.720
4.710
4.705
4.695
4.691
4.675
3.969
3.963
3.958
3.953
3.946
3.940
1.964
1.957
1.926
1.919
1.916
1.909
1.877
1.871
1.861
1.836
1.822
1.798
1.584
1.574
1.560
1.543
1.487
1.473
1.462
1.450
1.444
1.435
1.429
1.419
1.410
1.404
1.397
1.384
1.379
1.374
1.366
1.335
1.330
1.324
1.320
1.315
1.309
0.913
0.896
0.878
OH
O
O-i-Pr
P
O-i-Pr
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.04
0.84
2.03
1.12
17.22
3.10

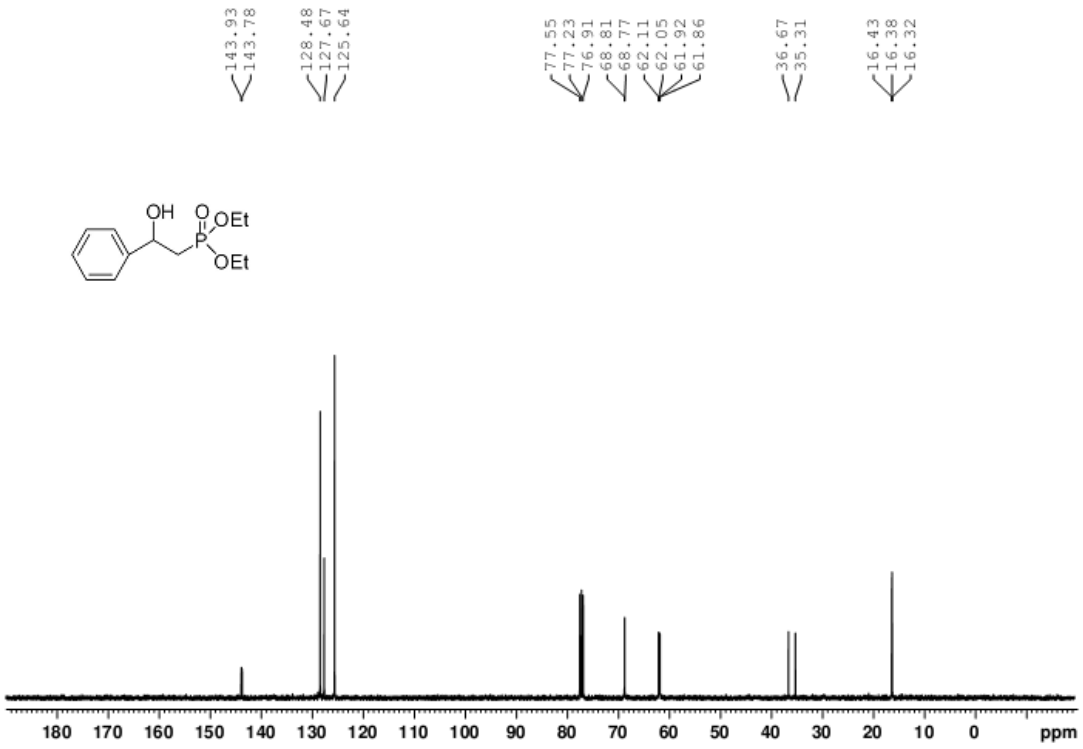
4p


77.55
77.23
76.91
70.81
70.76
66.75
66.70
38.14
37.97
35.52
34.14
27.73
24.23
24.20
24.18
24.14
22.74
14.18
OH
O
O-i-Pr
P
O-i-Pr
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

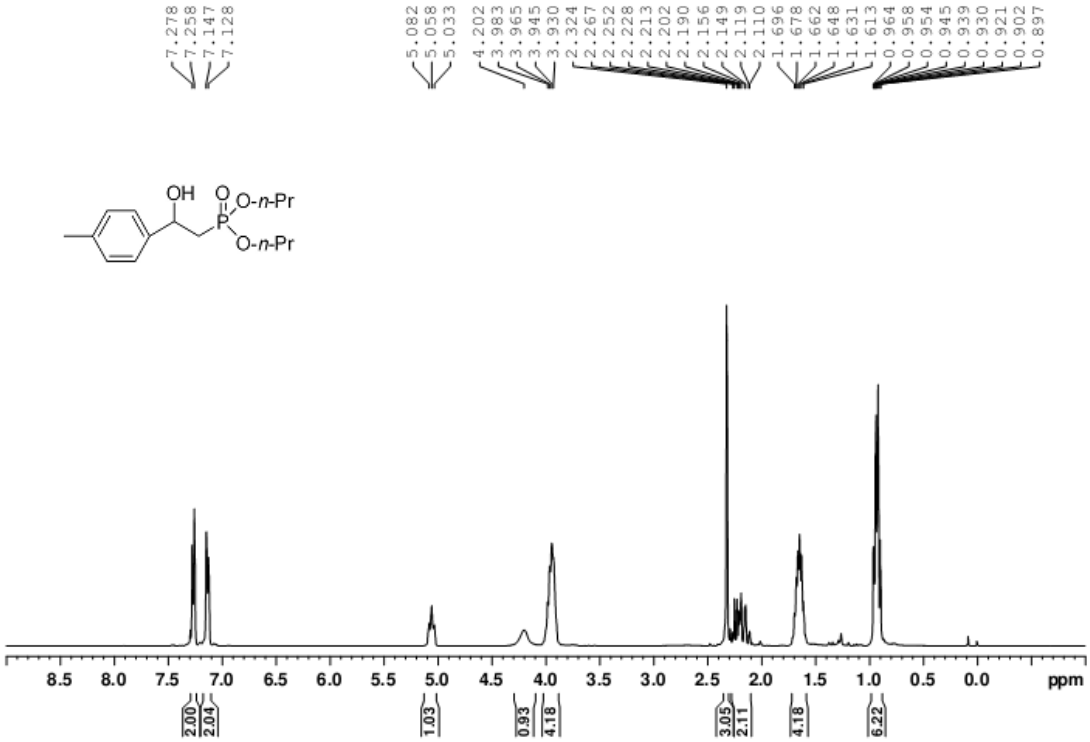
4q


7.388
7.370
7.344
7.326
7.307
7.298
7.269
7.251
7.233
5.116
5.107
5.091
5.083
5.066
5.058
4.310
4.101
4.083
4.081
4.077
4.074
4.063
4.059
4.041
4.023
4.016
4.006
3.998
2.294
2.271
2.256
2.232
2.217
2.206
2.196
2.194
2.167
2.160
2.152
2.122
2.113
2.084
1.310
1.292
1.281
1.275
1.263
1.246
OH
O
OEt
P
OEt
9
8
7
6
5
4
3
2
1
0
ppm
4.07
0.99
1.00
0.82
4.04
2.05
6.08

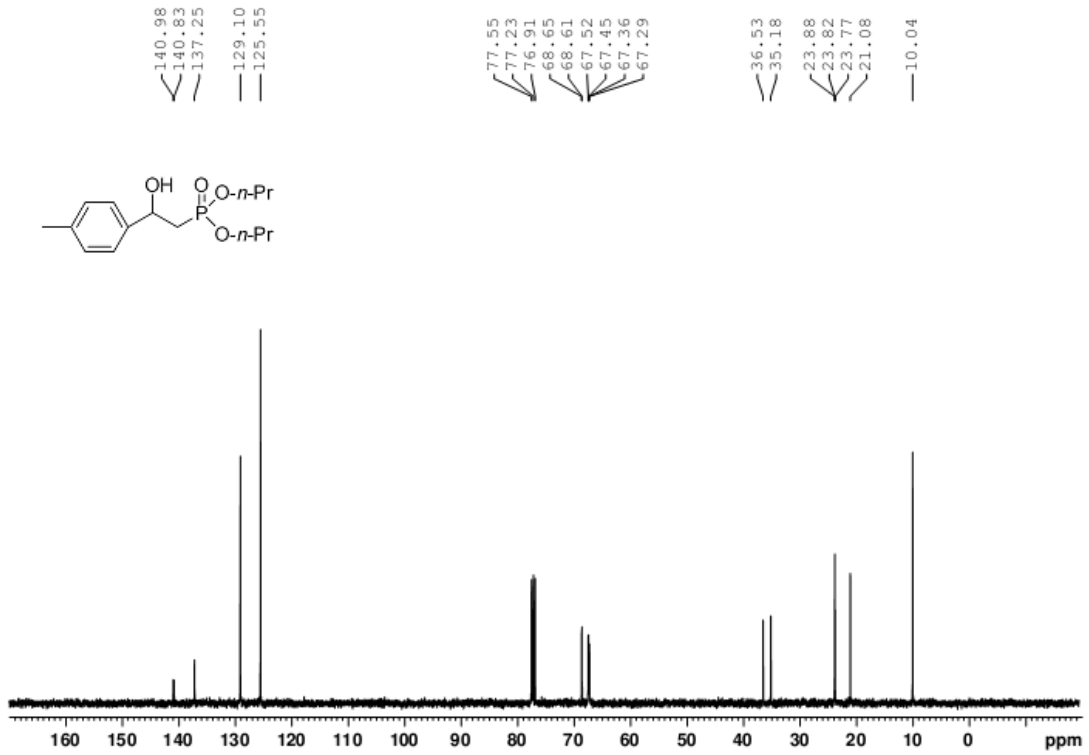
4q


143.93
143.78
128.48
127.67
125.64
77.55
77.23
76.91
68.81
68.77
62.11
62.05
61.92
61.86
36.67
35.31
16.43
16.38
16.32
OH
O
OEt
P
OEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

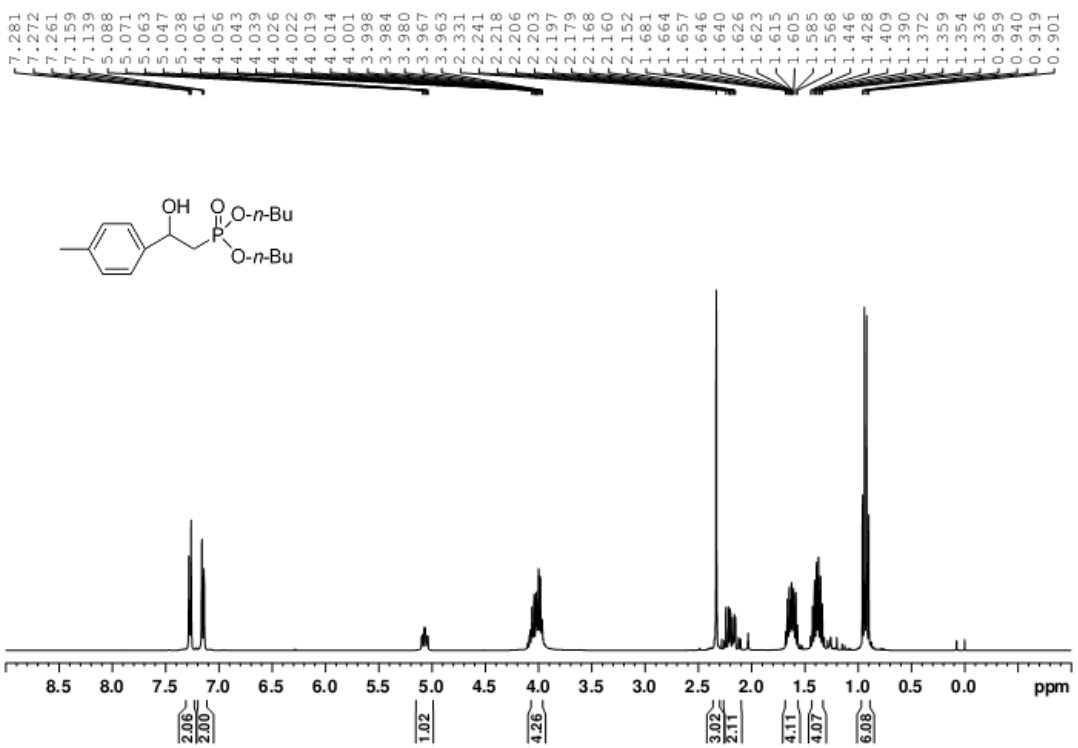
4r


7.278
7.258
7.147
7.128
5.082
5.058
5.033
4.202
3.983
3.965
3.945
3.930
2.324
2.267
2.252
2.228
2.213
2.202
2.190
2.156
2.149
2.119
2.110
1.696
1.678
1.662
1.648
1.631
1.613
0.964
0.958
0.954
0.945
0.939
0.930
0.921
0.902
0.897
OH
O
O-n-Pr
P
O-n-Pr
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
2.04
1.03
0.93
4.18
3.05
2.11
4.18
6.22

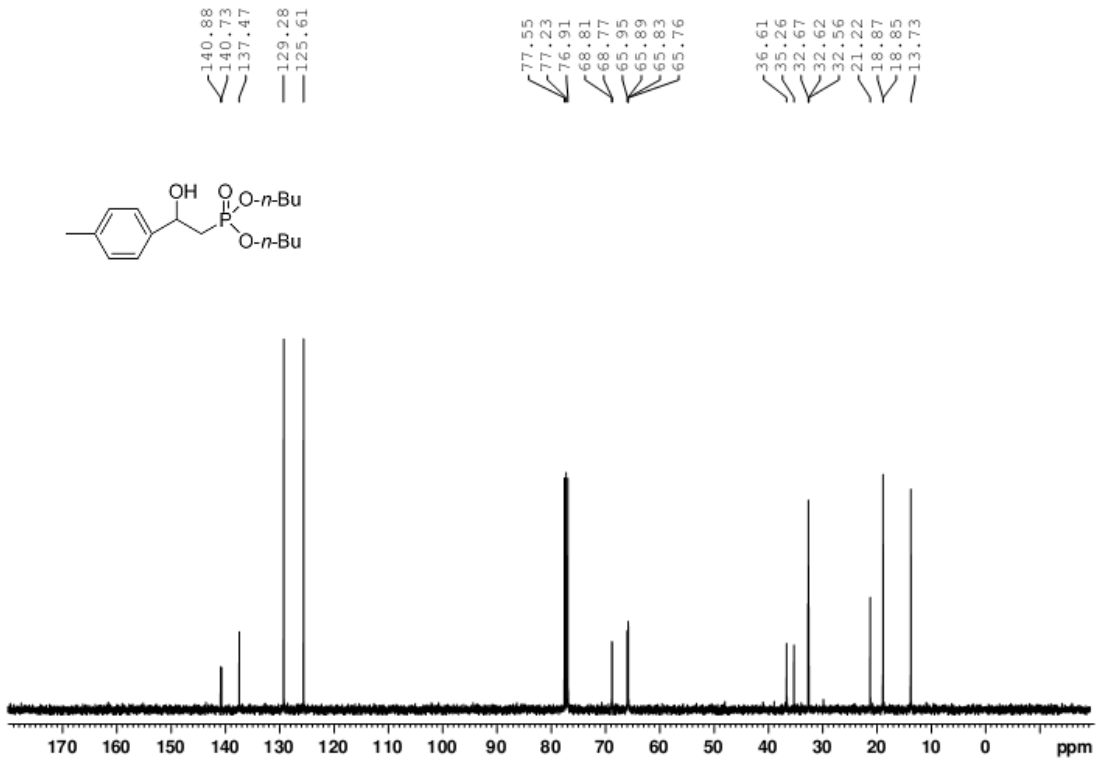
4r


140.98
140.83
137.25
129.10
125.55
77.55
77.23
76.91
68.65
68.61
67.52
67.45
67.36
67.29
36.53
35.18
23.88
23.82
23.77
21.08
10.04
OH
O
O-n-Pr
P
O-n-Pr
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

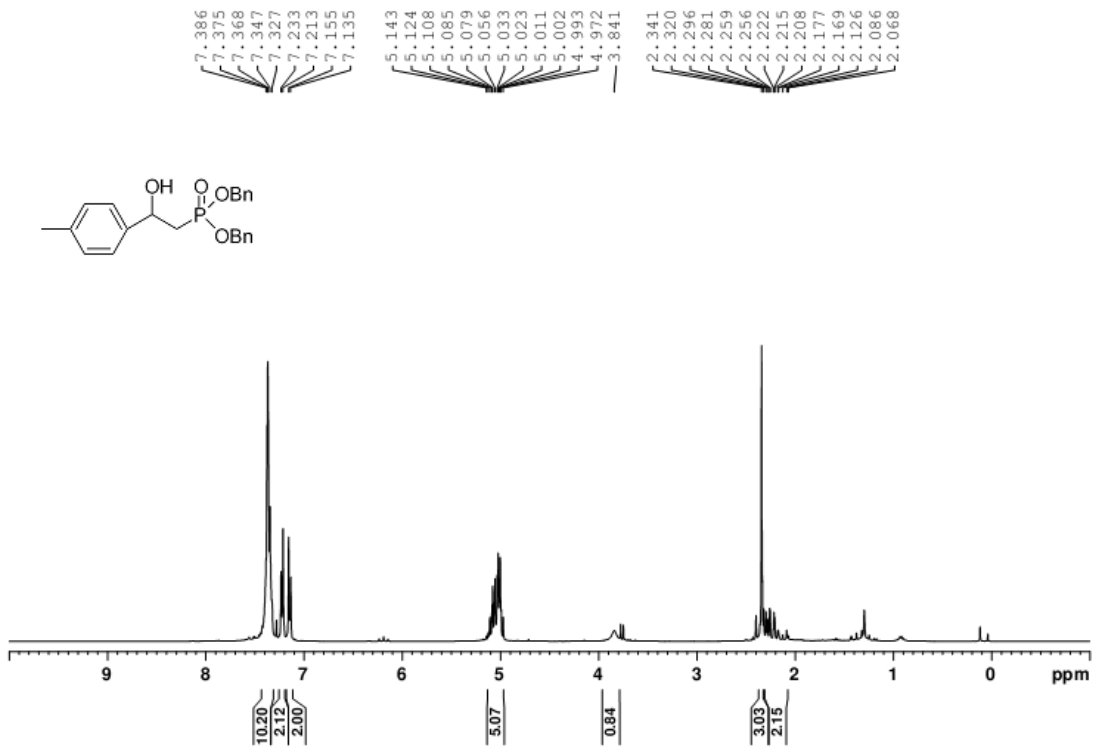
4s


7.281
7.272
7.261
7.159
7.139
5.088
5.071
5.063
5.047
5.038
4.061
4.056
4.043
4.039
4.026
4.022
4.019
4.014
4.001
3.998
3.984
3.980
3.967
3.963
2.331
2.241
2.218
2.206
2.203
2.197
2.179
2.168
2.160
2.152
1.681
1.664
1.657
1.646
1.640
1.626
1.623
1.615
1.605
1.585
1.568
1.446
1.428
1.409
1.390
1.372
1.359
1.354
1.336
0.959
0.940
0.919
0.901
OH
O
O-n-Bu
P
O-n-Bu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.06
2.00
1.02
4.26
3.02
2.11
4.11
4.07
6.08

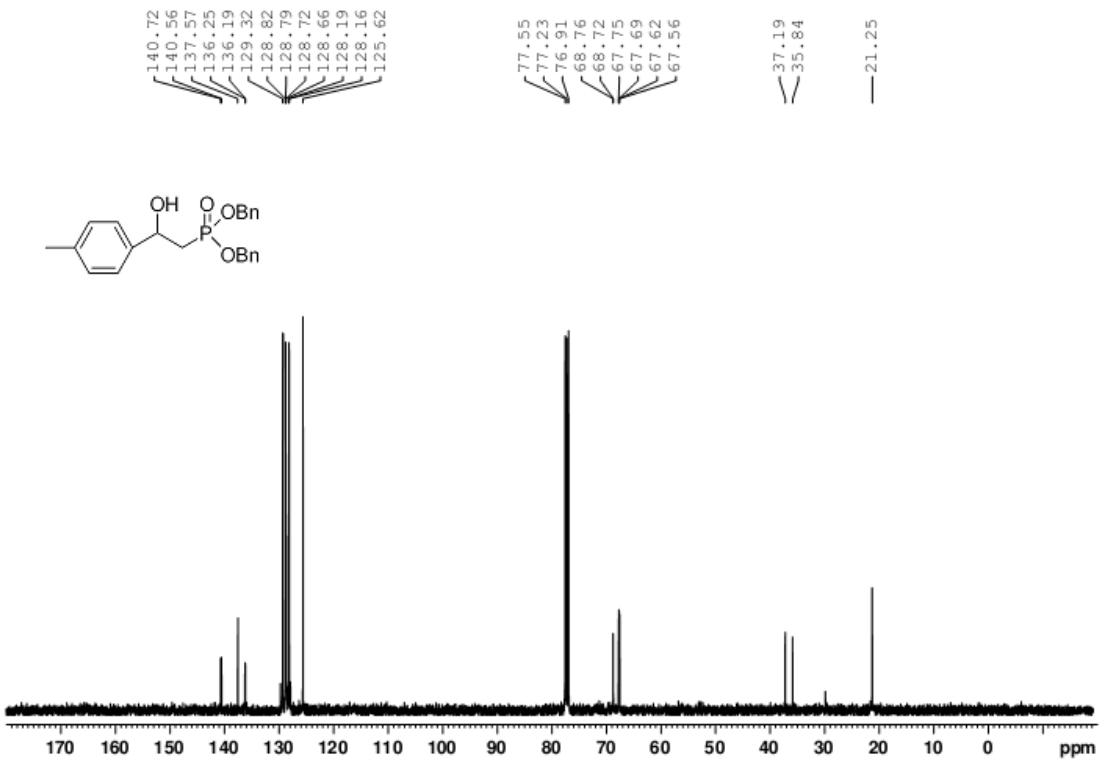
4s


140.88
140.73
137.47
129.28
125.61
77.55
77.23
76.91
68.81
68.77
65.95
65.89
65.83
65.76
36.61
35.26
32.67
32.62
32.56
21.22
18.87
18.85
13.73
OH
O
O-n-Bu
P
O-n-Bu
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

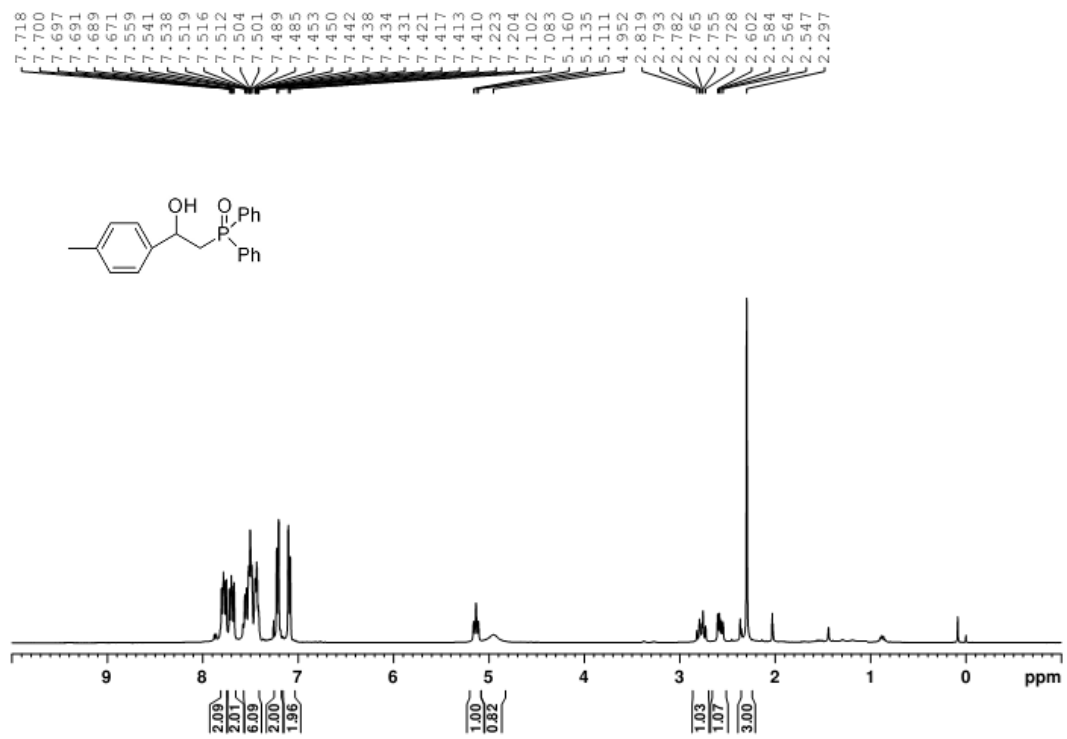
4t


7.386
7.375
7.368
7.347
7.327
7.233
7.213
7.155
7.135
5.143
5.124
5.108
5.085
5.079
5.056
5.033
5.023
5.011
5.002
4.993
4.972
3.841
2.341
2.320
2.296
2.281
2.259
2.256
2.222
2.215
2.208
2.177
2.169
2.126
2.086
2.068
OH
O
OBn
P
OBn
9
8
7
6
5
4
3
2
1
0
ppm
10.20
2.12
2.00
5.07
0.84
3.03
2.15

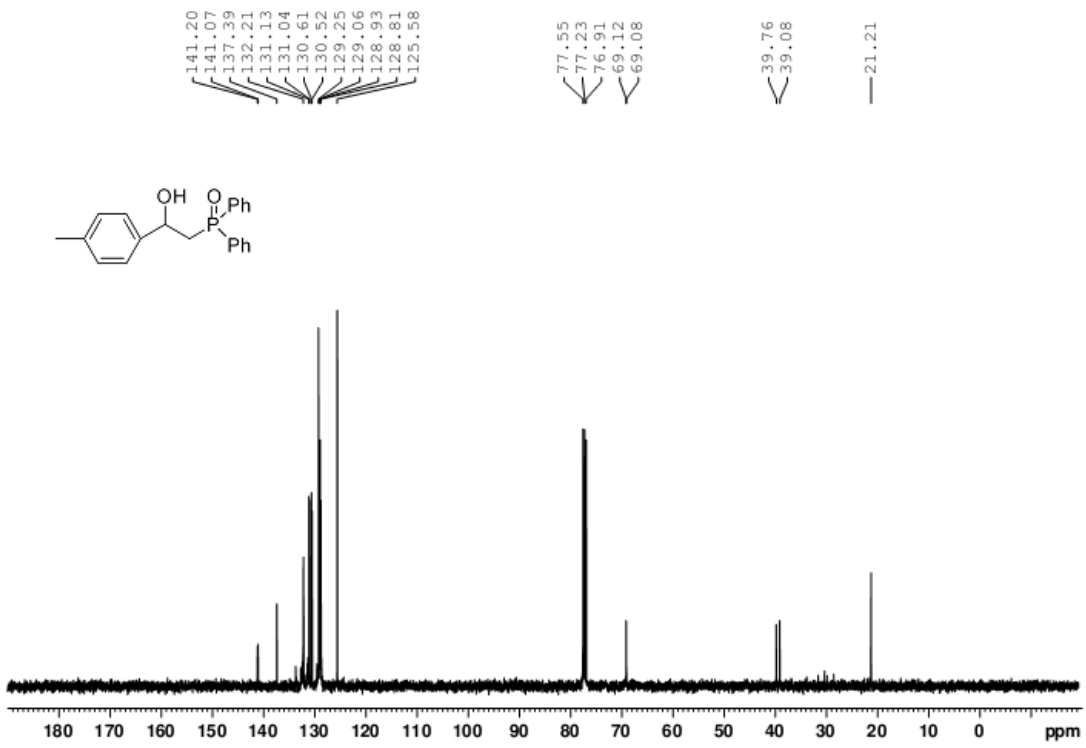
4t


140.72
140.56
137.57
136.25
136.19
129.32
128.82
128.79
128.72
128.66
128.19
128.16
125.62
77.55
77.23
76.91
68.76
68.72
67.75
67.69
67.62
67.56
37.19
35.84
21.25
OH
O
OBn
P
OBn
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

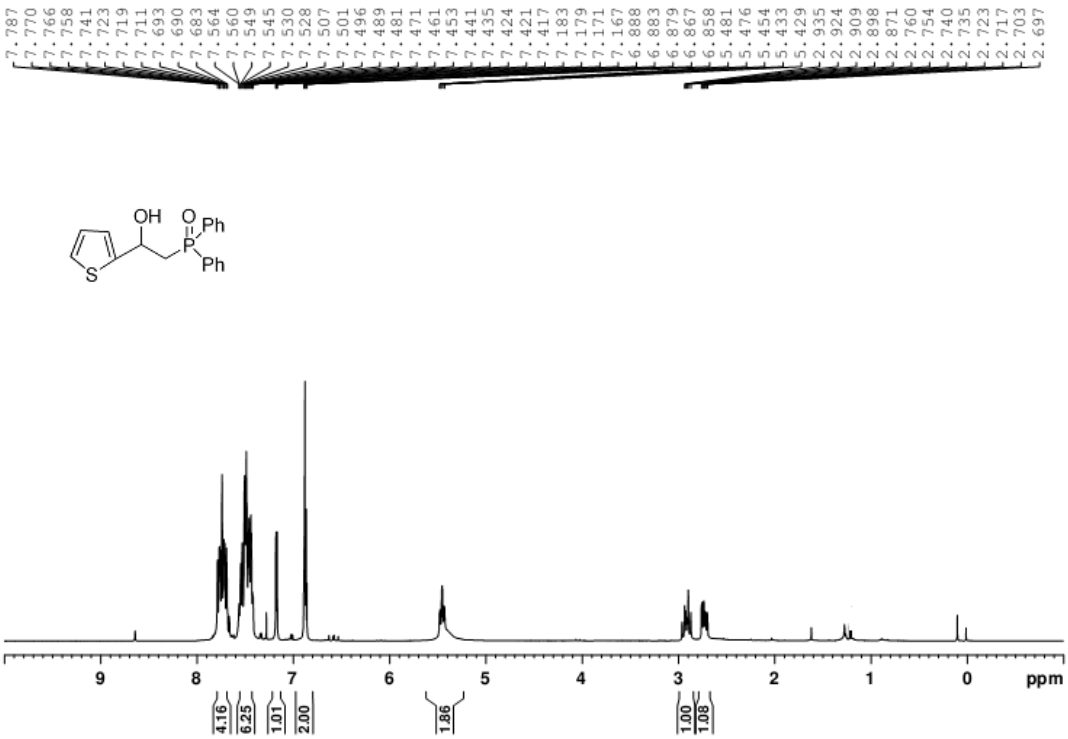
4u


7.718
7.700
7.697
7.691
7.689
7.671
7.559
7.541
7.538
7.519
7.516
7.512
7.504
7.501
7.489
7.485
7.453
7.450
7.442
7.438
7.434
7.431
7.421
7.417
7.413
7.410
7.223
7.204
7.102
7.083
5.160
5.135
5.111
4.952
2.819
2.793
2.782
2.765
2.755
2.728
2.602
2.584
2.564
2.547
2.297
OH
O
Ph
P
Ph
9
8
7
6
5
4
3
2
1
0
ppm
2.09
2.01
6.09
2.00
1.96
1.00
0.82
1.03
1.07
3.00

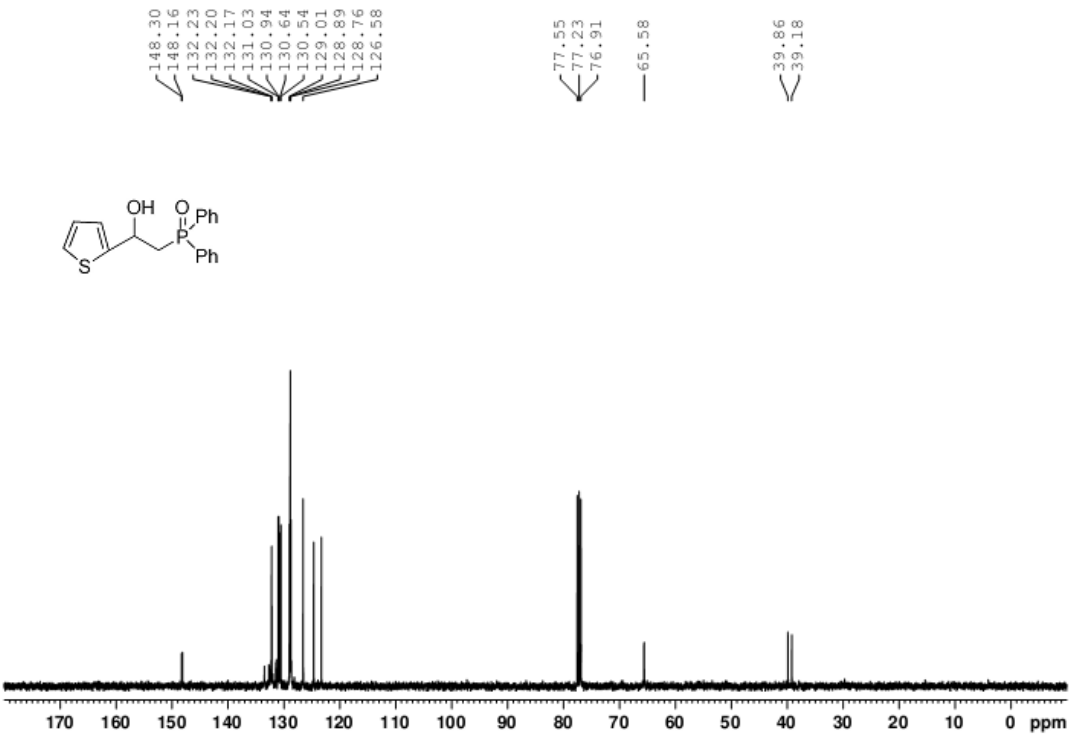
4u


141.20
141.07
137.39
132.21
131.13
131.04
130.61
130.52
129.25
129.06
128.93
128.81
125.58
77.55
77.23
76.91
69.12
69.08
39.76
39.08
21.21
OH
O
Ph
P
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

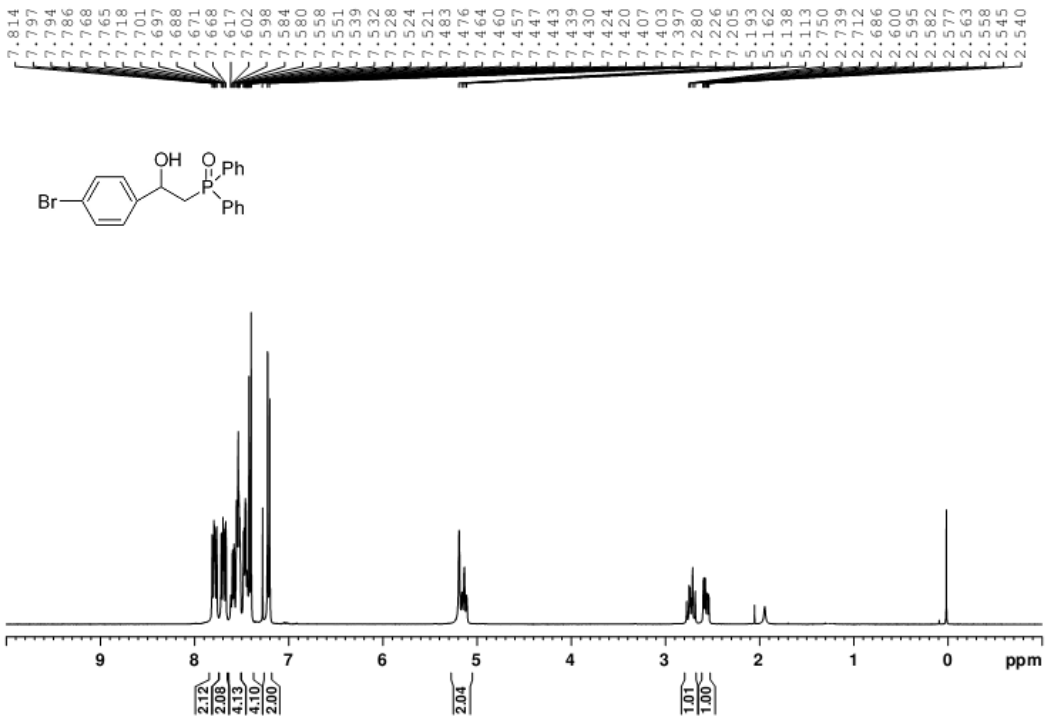
4v


7.787
7.770
7.766
7.758
7.741
7.723
7.719
7.711
7.693
7.690
7.683
7.564
7.560
7.549
7.545
7.530
7.528
7.507
7.501
7.496
7.489
7.481
7.471
7.461
7.453
7.441
7.435
7.424
7.421
7.417
7.183
7.179
7.171
7.167
6.888
6.883
6.879
6.867
6.858
5.481
5.476
5.454
5.433
5.429
2.935
2.924
2.909
2.898
2.871
2.760
2.754
2.740
2.735
2.723
2.717
2.703
2.697
OH
O
Ph
P
Ph
S
9
8
7
6
5
4
3
2
1
0
ppm
4.16
6.25
1.01
2.00
1.86
1.00
1.08

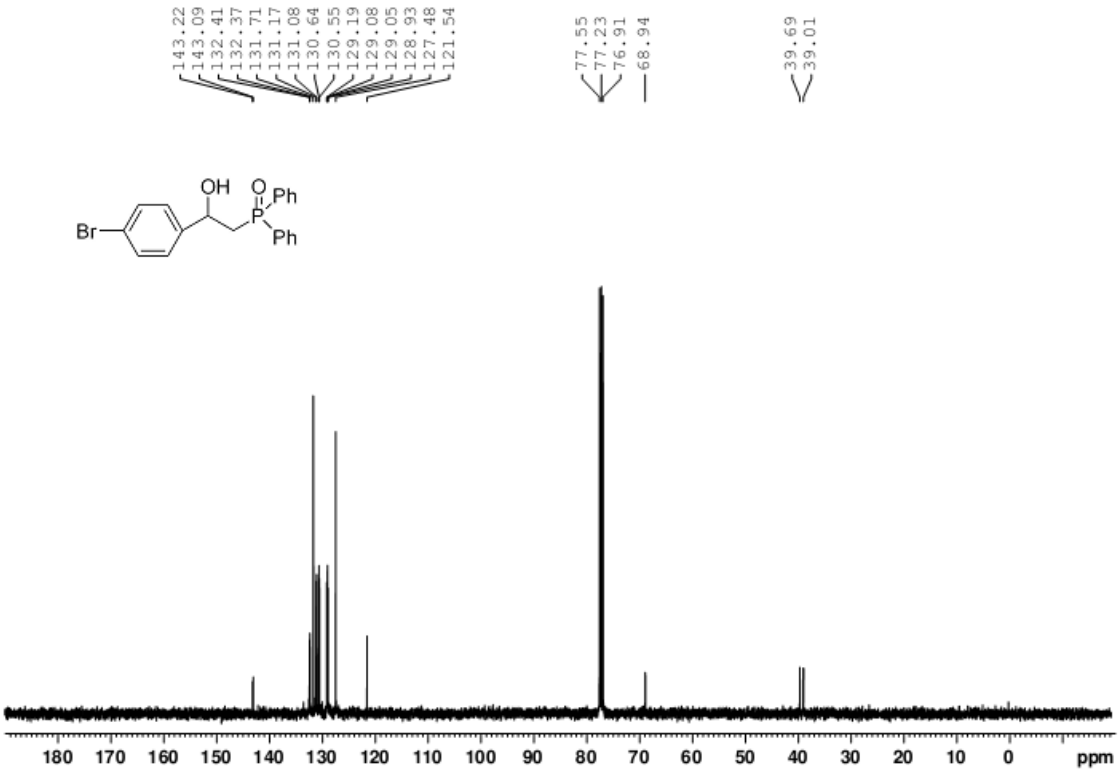
4v


148.30
148.16
132.23
132.20
132.17
131.03
130.94
130.64
130.54
129.01
128.89
128.76
126.58
77.55
77.23
76.91
65.58
39.86
39.18
OH
O
Ph
P
Ph
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

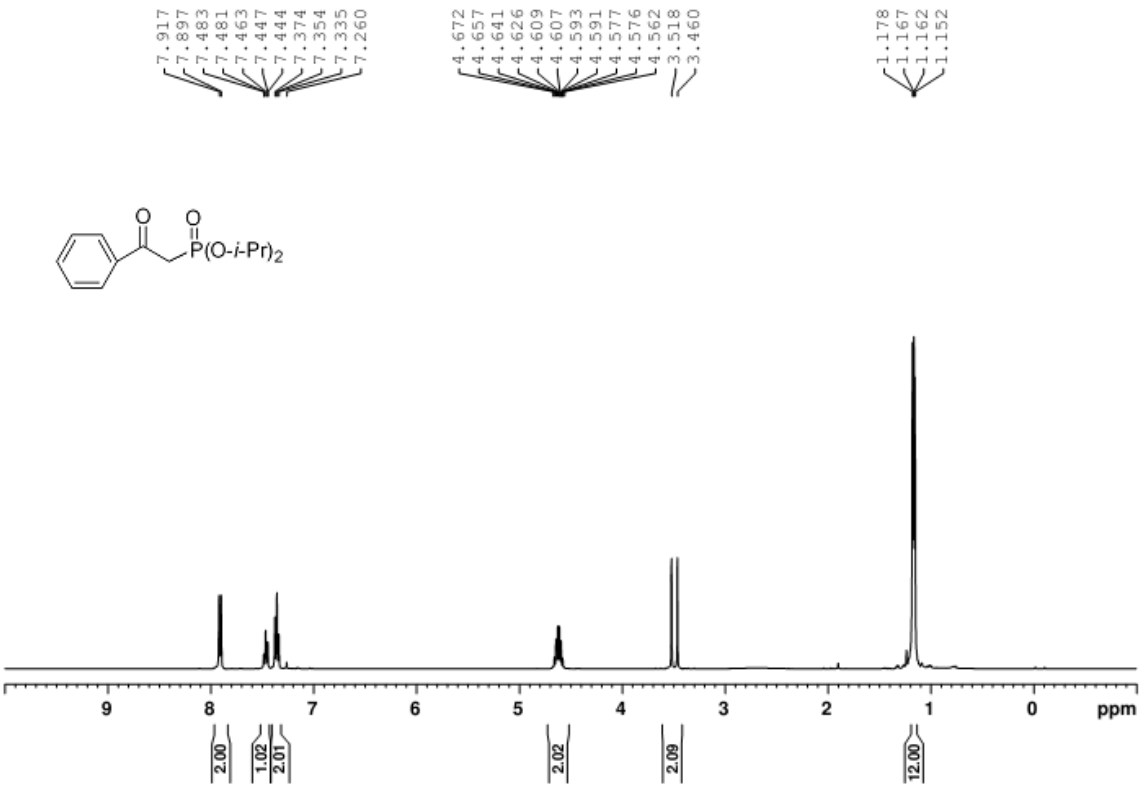
4w


7.814
7.797
7.794
7.786
7.768
7.765
7.718
7.701
7.697
7.688
7.671
7.668
7.617
7.602
7.598
7.584
7.580
7.558
7.551
7.539
7.532
7.528
7.524
7.521
7.483
7.476
7.464
7.460
7.457
7.447
7.443
7.439
7.430
7.424
7.420
7.407
7.403
7.397
7.280
7.226
7.205
5.193
5.162
5.138
5.113
2.750
2.739
2.712
2.686
2.600
2.595
2.582
2.577
2.563
2.558
2.545
2.540
OH
O
Ph
P
Ph
Br
9
8
7
6
5
4
3
2
1
0
ppm
2.12
2.08
4.13
4.10
2.00
2.04
1.01
1.00

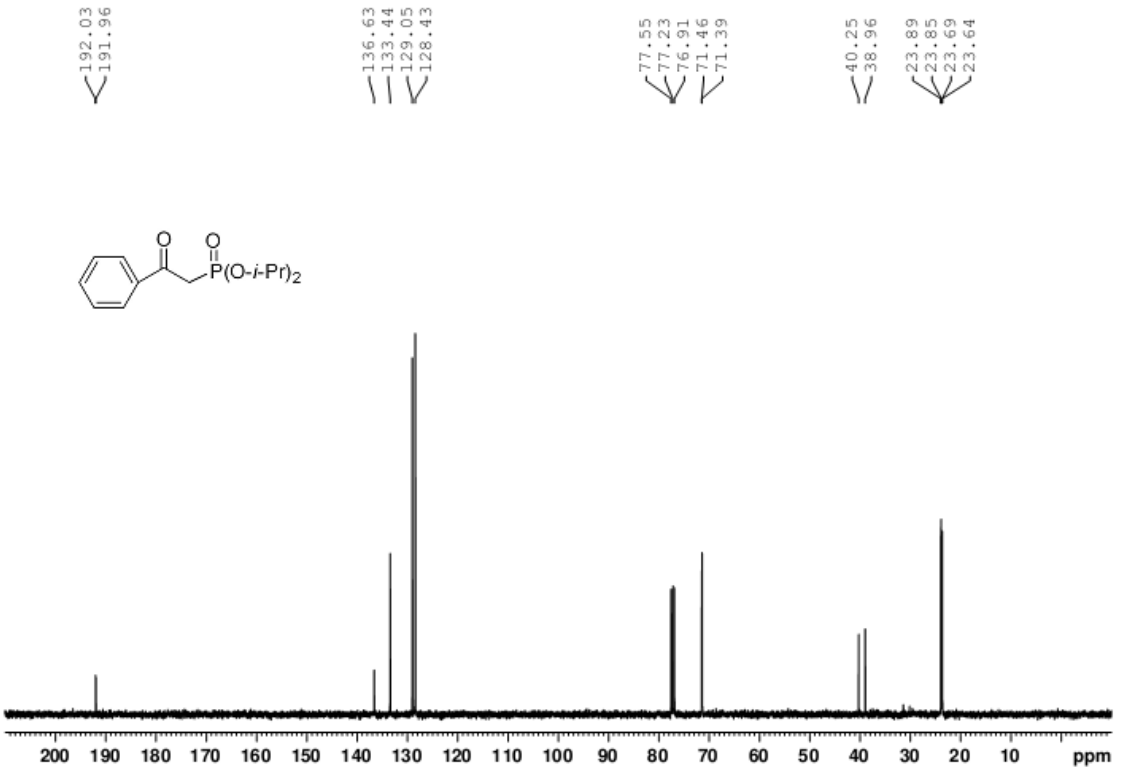
4w


143.22
143.09
132.41
132.37
131.71
131.17
131.08
130.64
130.55
129.19
129.08
129.05
128.93
127.48
121.54
77.55
77.23
76.91
68.94
39.69
39.01
OH
O
Ph
P
Ph
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

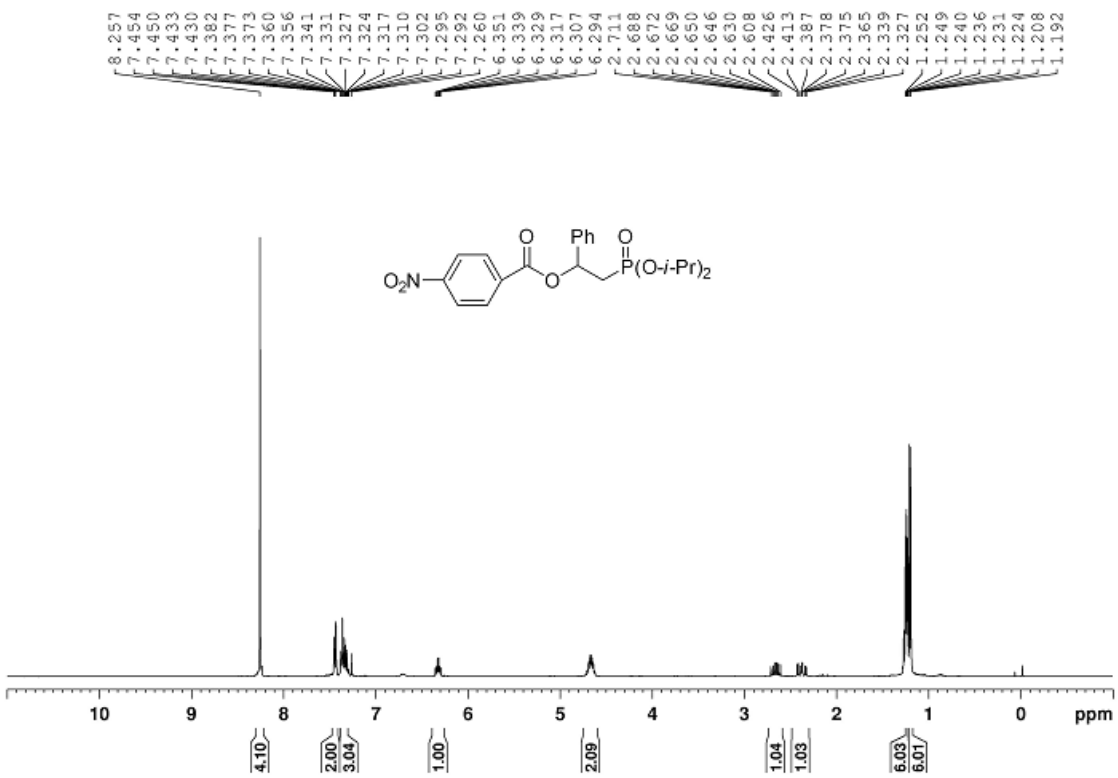
5


7.917
7.897
7.483
7.481
7.463
7.447
7.444
7.374
7.354
7.335
7.260
4.672
4.657
4.641
4.626
4.609
4.607
4.593
4.591
4.577
4.576
4.562
3.518
3.460
1.178
1.167
1.162
1.152
O
O
P(O-i-Pr)2
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.02
2.01
2.02
2.09
12.00

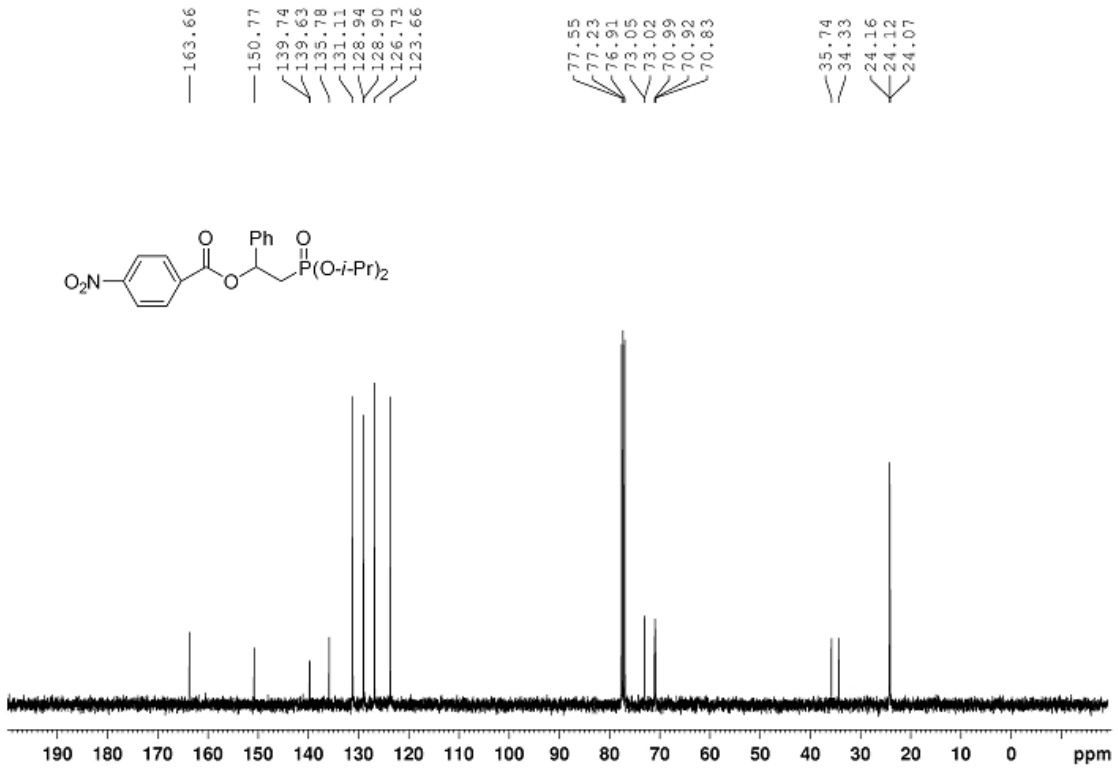
5


192.03
191.96
136.63
133.44
129.05
128.43
77.55
77.23
76.91
71.46
71.39
40.25
38.96
23.89
23.85
23.69
23.64
O
O
P(O-i-Pr)2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

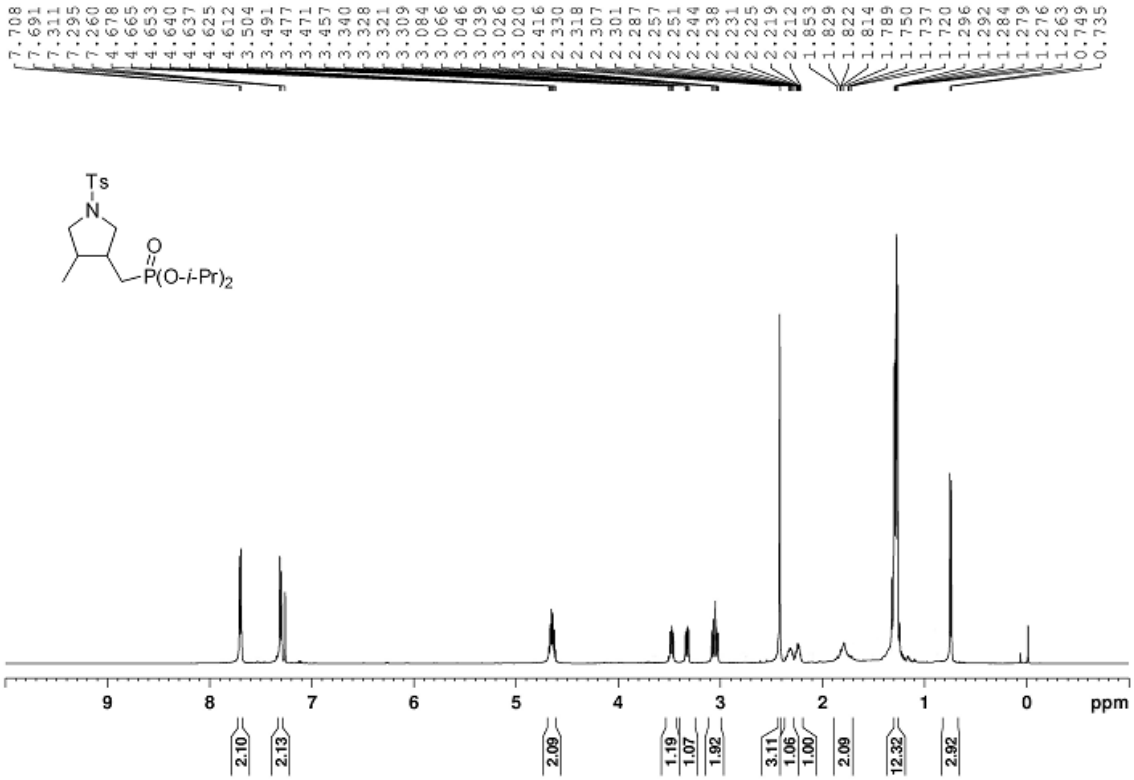
6


8.257
7.454
7.450
7.433
7.430
7.382
7.377
7.373
7.360
7.356
7.341
7.331
7.327
7.324
7.317
7.310
7.302
7.295
7.292
7.260
6.351
6.339
6.329
6.317
6.307
6.294
2.711
2.688
2.672
2.669
2.650
2.646
2.630
2.608
2.426
2.413
2.387
2.378
2.375
2.365
2.339
2.327
1.252
1.249
1.240
1.236
1.231
1.224
1.208
1.192
O
Ph
O
O2N
O
P(O-i-Pr)2
10
9
8
7
6
5
4
3
2
1
0
ppm
4.10
2.00
3.04
1.00
2.09
1.04
1.03
6.03
6.01

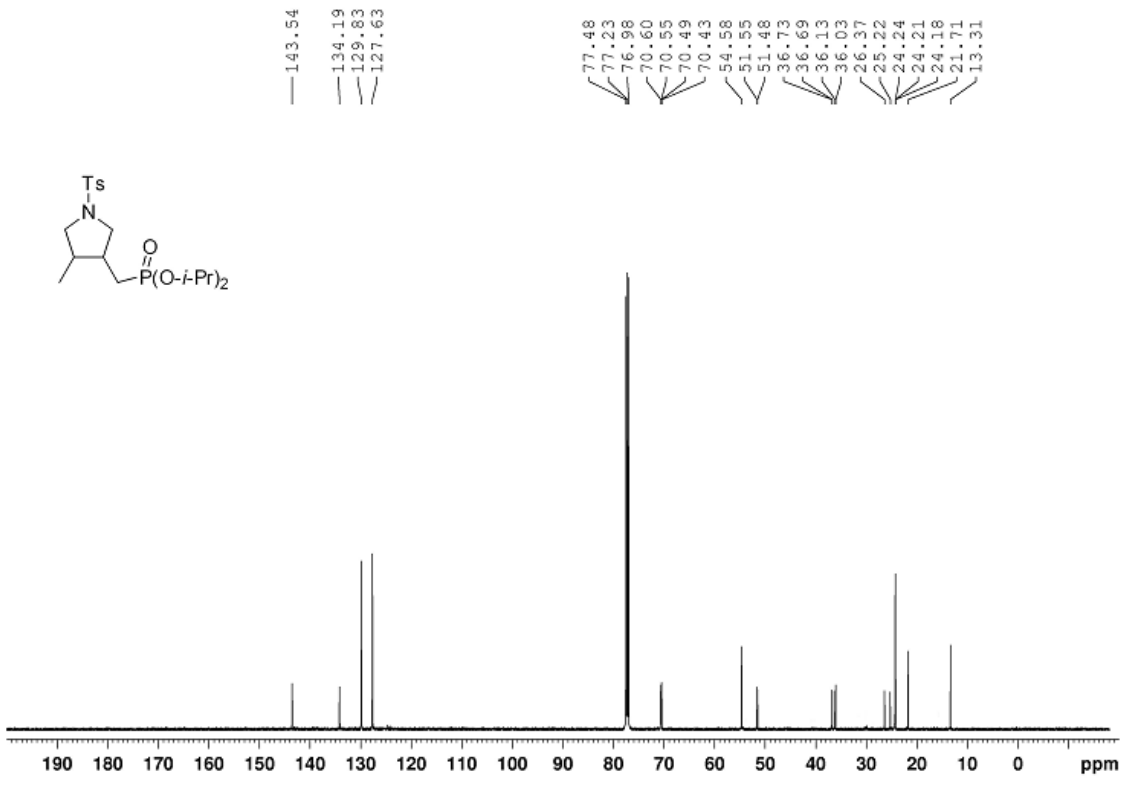
6


163.66
150.77
139.74
139.63
135.78
131.11
128.94
128.90
126.73
123.66
77.55
77.23
76.91
73.05
73.02
70.99
70.92
70.83
35.74
34.33
24.16
24.12
24.07
O
Ph
O
O2N
O
P(O-i-Pr)2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

7


7.708
7.691
7.311
7.295
7.260
4.678
4.665
4.653
4.640
4.637
4.625
4.612
3.504
3.491
3.477
3.471
3.457
3.340
3.328
3.321
3.309
3.084
3.066
3.046
3.039
3.026
3.020
2.416
2.330
2.318
2.307
2.301
2.287
2.257
2.251
2.244
2.238
2.231
2.225
2.219
2.212
1.853
1.829
1.822
1.814
1.789
1.750
1.737
1.720
1.296
1.292
1.284
1.279
1.276
1.263
0.749
0.735
Ts
N
O
P(O-i-Pr)2
9
8
7
6
5
4
3
2
1
0
ppm
2.10
2.13
2.09
1.19
1.07
1.92
3.11
1.06
1.00
2.09
12.32
2.92

7


143.54
134.19
129.83
127.63
77.48
77.23
76.98
70.60
70.55
70.49
70.43
54.58
51.55
51.48
36.73
36.69
36.13
36.03
26.37
25.22
24.24
24.21
24.18
21.71
13.31
Ts
N
O
P(O-i-Pr)2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm