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Thieme

SUPPLEMENTARY INFORMATION

Cycloaddition / Aromatization Sequence for the Synthesis of 2,3-Disubstituted Benzenephosphonates

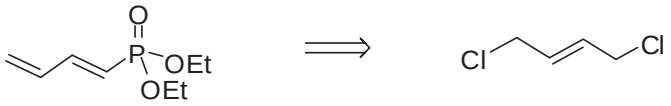
*Elise Villemin and Jacqueline Marchand-Brynaert**

Université catholique de Louvain,
Institute of Condensed Matter and Nanosciences (ICMN),
Molecules, Solids and Reactivity (MOST),
Bâtiment Lavoisier, Place Louis Pasteur 1, L4.01.02, 1348 Louvain-la-Neuve, Belgium
jacqueline.marchand@uclouvain.be

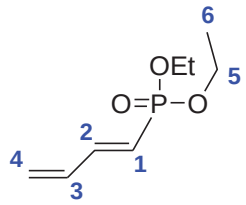
CONTENT

I. Synthesis and characterization

Product 1: Diethyl 1-phosphonobuta-1,3-diene



Diethyl 1-phosphonobuta-1,3-diene **(1)** was prepared according to the procedure described in the literature.[1]



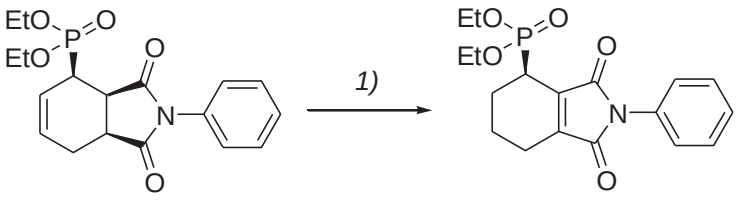
$C_8H_{14}O_3P$

MW = 190.18 g.mol^{-1}

CAS Registry Number: 25145-58-8

Rf [silica gel, ethyl acetate] = 0.5.
IR (ν, cm^{-1}): 2989 (m), 2930 (w), 1632 (m, C=C), 1584 (m), 1392 (w), 1246 (s, P=O), 1217 (s), 1051 (s), 1024 (s, P-O), 962 (s, P-O), 744 (s).
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (ddd, $^2J_{2,P}$ = 20.8 Hz, $^3J_{1,2}$ = 16.9 Hz, $^3J_{2,3}$ = 10.6 Hz, C(2)-H,1H), 6.24 (dtd, $^3J_{3,4a}$ = 17.0 Hz, $^3J_{2,3}$ = $^3J_{3,4b}$ = 10.3 Hz and $^4J_{1,3}$ = 1.1 Hz, 1H, C(3)-H), 5.56 (dd, $^2J_{1,P}$ = 18.5 Hz and $^3J_{1,2}$ = 17.5 Hz, C(1)-H, 1H), 5.56 (d, $^3J_{3,4a}$ = 16.9 Hz, C(4)-Ha, 1H), 5.27 (d, $^3J_{3,4b}$ = 9.9 Hz, C(4)-Hb, 1H), 3.92 (app. q., $^3J_{5,6}$ = $^3J_{5,P}$ = 7.1 Hz, C(5)-H, 4H), 1.16 (t, $^3J_{5,6}$ = 7.1 Hz, C(6)-H , 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 148.5 (d, $^4J_{4,P}$ = 5.8 Hz, C(4)), 135.7 (d, $^2J_{2,P}$ = 26.7 Hz, C(2)), 125.0 (s, C(3)), 118.1 (d, $^1J_{1,P}$ = 189.3 Hz, C(1)), 61.8 (d, $^2J_{5,P}$ = 5.4 Hz, C(5)), 16.4 (s, C(6)).
^{31}P NMR (121 MHz, $CDCl_3$): δ 19.33,

Product 5: diethyl 1,2,3-hexahydro-1,3-dioxo-2-phenyl-1*H*-isoindol-4-yl-4-phosphonate

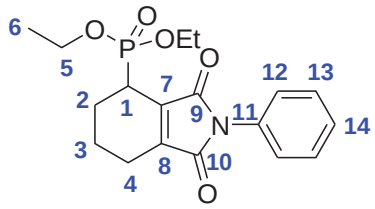


Reagents and conditions :
1) $CHCl_3$, EtOH, 70°C, a few min
2) $RhCl_3$.x H_2O, H_2O, 70°C, overnight

A solution of **4** (100 mg, 0.28 mmol) in chloroform (650 µL) and ethanol (650 µL) is stirred at 70°C during a few minutes. A solution of *x*-hydrated rhodium (III) chloride (26 mg, 0.13 mmol) and water (130 µL) is added to the precedent hot solution. The resultant mixture is

[1] (a) Griffin, C. E.; Daniewski, W. M. *J. Org. Chem.* **1970**, *35*, 1691-1693; (b) Monbaliu, J-C.; Marchand-Brynaert, J. *Synthesis* **2009**, *11*, 1876–1880.

stirred at 70°C overnight. The aqueous layer is extracted with ethyl acetate (4x) and the combined organic portions were dried over magnesium sulphate. The solvent is removed under reduced pressure and the brown oil was purified by column chromatography to afford **5** as a brown oil, (17 mg, 17%).



$C_{18}H_{22}NO_5P$

MW= 363.44 g.mol^{-1}

Rf [silica gel, ethyl acetate] = 0.4.

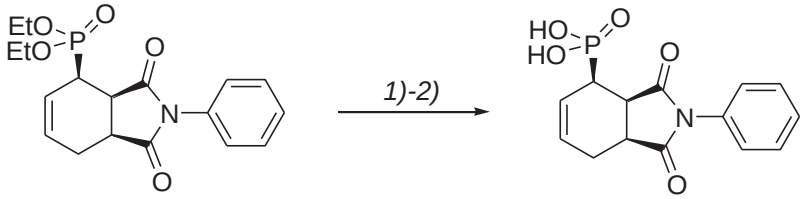
^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.48-7.42 (m, C(12)-H, 2H), 7.35-7.31 (m, C(13)-H and C(14)-H, 3H), 4.21 (q, $^3J_{5,6}$ = 7.2 Hz, C(5)-H, 2H), 4.13 (q, $^3J_{5',6'}$ = 7.4 Hz, C(5')-H, 2H), 2.62 (ddd, $^1J_{1,P}$ = 19.9 Hz, $^3J_{1,7}$ = $^3J_{1,2}$ = 5.9 Hz, C(1)-H, 1H), 2.45-1.69 (m, C(7), C(8) and C(2)), 1.37 (t, $^3J_{6,P}$ = 7.6 Hz, C(6)-H, 3H), 1.31 (t, $^3J_{6,P}$ = 7.4 Hz, C(6)-H, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ : 169.2 (s, C(9)), 168.4 (s, C(10)), 123.2 (d, $^4J_{4,P}$ = 10.8 Hz, C(4)), 136.6 (d, $^3J_{3,P}$ = 10.0 Hz, C(3)), 131.9 (s, C(11)), 129.1 (s, C(13)), 127.7 (s, C(14)), 126.1 (s, C(12)), 62.8 (d, $^2J_{5,P}$ = 6.8 Hz, C(5)), 62.7 (d, $^2J_{5',P}$ = 9.9 Hz, C(5')), 30.1 (d, $^1J_{1,P}$ = 139.3 Hz, C(1)), 23.2 (d, $^2J_{7,P}$ = 4.5 Hz, C(7)), 20.1 (s, C(2)), 18.5 (s, C(8)), 16.5 (d, $^3J_{6,P}$ = 5.9 Hz, C(6)).

^{31}P NMR (121 MHz, $CDCl_3$) δ : 24.74.

MS (APCI, positive mode) m/z (%) = 364.98 (20) **[M+H]**, 363.96 (100) **[M]**, 336.04 (14) **[M-CH_2=CH_2]**, 308.06 (11) **[M-2 CH_2=CH_2]**.

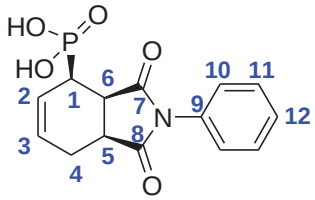
Product 7: 2,3,3a,4,7,7a-hexahydro-1,3-dioxo-2-phenyl-1*H*-isoindolin-4-yl-4-phosphonic acid



Reagents and conditions :

1) TMSBr, CH_3CN, RT, overnight
2) MeOH, RT, 1h

A solution of **4** (60 mg, 0.165 mmol), trimethylsilyl bromide (68 µL, 78 mg, 0.512 mmol) in anhydrous acetonitrile (0.8 mL) is stirred at room temperature overnight. The ethyl bromide by-product, the excess of trimethylsilyl bromide and the solvent are evaporated under reduced pressure. The reaction mixture is then hydrolyzed with an excess of methanol at room temperature during 1h. The solvent is evaporated to afford **7** as a brown oil (51 mg, 100%).

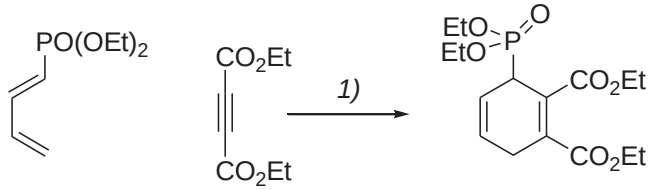


$C_{14}H_{14}NO_5P$

MW= 307.24 g.mol^{-1}

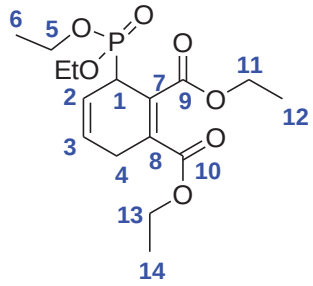
IR (υ, cm^{-1}): 3773-2752 (large band, m, OH), 1736 (w, C=O), 1712 (s, C=O), 1645 (m, C=C), 1633 (m, C=C), 1595 (w), 1495 (m), 1389 (m), 1188 (s, P=O), 1022 (m, P-O), 958 (m, P-O).
^{1}H NMR(500 MHz, MeOD) δ : . 7.20 (app. t, $^{3}J_{10,11}$ = $^{3}J_{11,12}$ = 7.3 Hz, C(11)-H, 2H), 7.14 (t, $^{3}J_{11,12}$ = 7.0 Hz, C(12)-H, 1H), 7.07 (d, $^{3}J_{10,11}$= 7.5 Hz, C(10)-H, 2H), 5.94-5.86 (m, C(3)-H, 1H), 5.79-5.38 (m, C(2)-H, 1H), 3.27 (dd, $^{3}J_{6,P}$= 20.0 Hz and $^{3}J_{1,6}$ = 6.7 Hz, C(6)-H, 1H), 3.18 (td, $^{3}J_{4',5}$ = $^{3}J_{5,6}$ = 8.8 Hz and $^{3}J_{4,5}$ = 4.1 Hz, C(5)-H, 1H), 2.84 (dt, $^{1}J_{1,P}$ = 22.3 Hz and $^{3}J_{1,2}$ = $^{3}J_{1,6}$ = 5.0 Hz, C(1)-H, 1H), 2.49 (dq, $^{2}J_{4,4'}$ = 16.4 Hz and $^{3}J_{4,5}$ = $^{3}J_{3,4}$ = $^{5}J_{4,P}$ = 3.8 Hz, C(4)-H, 1H), 2.24-2.28 (m, C(4)-H', 1H).
^{13}C NMR (125 MHz, MeOD) δ : 180.9 (s, C(8)), 178.6 (d, $^{3}J_{7,P}$ = 2.3 Hz, C(7)), 133.8 (s, C(9)), 131.00 (d, $^{3}J_{3,P}$= 11.9 Hz, C(3)), 129.87 (s, C(11)), 129.53 (s, C(12)), 128.2 (s, C(10)), 126.0 (d, $^{2}J_{2,P}$= 7.5 Hz, C(2)), 42.3 (d, $^{2}J_{6,P}$ = 3.5 Hz, C(6)), 40.4 (d, $^{3}J_{5,P}$ = 8.0 Hz, C(5)), 36.2 (d, $^{1}J_{1,P}$ = 141.6 Hz, C(1)), 23.6 (s, C(4)).
^{31}P NMR (202 MHz, MeOD) δ : 24.74.
HRMS (MALDI-TOF, negative mode) m/z (%) [M-H]: Calcd for $C_{14}H_{13}NO_5P$: 306.0531, Found: 306.0546 (100).

Product 9b: diethyl (2,3-ethyldicarboxylate)-cyclohexa-2,5-dienyl phosphonate



Reagents and conditions :
1) neat, 120°C

A neat mixture of diene **1** (300 mg, 1.58 mmol) and diethyl acetylenedicarboxylate (759 µL, 805 mg, 4.73 mmol) is vigorously stirred at 120°C in a pressure tube overnight. The reaction mixture is directly purified by column chromatography to afford **9b** as a yellow oil (233 mg, 41 %).



$C_{16}H_{25}O_7P$

MW= 360.34 g.mol^{-1}

Rf [silica gel, ethyl acetate] = 0.3.
IR (υ, cm^{-1}): 2986 (m), 1722 (s, C=O), 1715 (s, C=O), 1674 (s, C=C), 1637 (m, CH=CH), 1475 (m), 1446 (m), 1391 (m), 1367 (m), 1245 (s, P=O), 1022 (s, P-O), 957 (s, P-O), 747 (s).
^{1}H NMR (500 MHz, $CDCl_3$) δ : 5.92 (dddd, $^{3}J_{3,4}$ = 15.1 Hz, $^{3}J_{2,3}$ = 10.6 Hz, $^{3}J_{3,4'}$ = 5.3 Hz and $^{4}J_{3,P}$= 1.5 Hz, C(3)-H, 1H), 5.89 (ddt, $^{3}J_{2,3}$ = 9.9 Hz, $^{3}J_{2,P}$ = 4.6 Hz and $^{4}J_{2,4'}$ = $^{4}J_{2,4}$ = 2.6 Hz, C(2), 1H), 4.28-4.14 (m, C(11)-H and C(12)-H, 4H), 4.14-4.04 (m, C(5)-H and C(5')-H, 4H), 4.00 (ddt, $^{1}J_{1,P}$ = 30.7 Hz, $^{3}J_{1,2}$ = 6.7 Hz, $^{3}J_{1,3}$ = 4.5 Hz, C(1)-H, 1H), 3.14 (dddt, *J* = 30.7 Hz, $^{2}J_{4,4'}$ = 22.2 Hz, $^{3}J_{3,4}$ = 6.5 Hz and $^{4}J_{2,4}$ = $^{4}J_{4,13}$ = 2.2 Hz, C(4)-H, 1H), 2.91 (ddt, $^{2}J_{4,4'}$ =

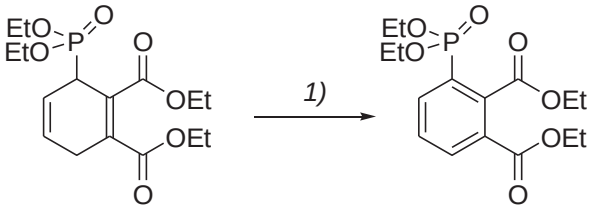
22.2 Hz, $^{5}J_{4',P}$ = 16.1 Hz and $^{3}J_{3,4'}$= 4.5 Hz, C(4)-H', 1H), 1,29 (t, $^{3}J_{11,12}$ = $^{3}J_{13,14}$ = 7.2 Hz, C(12)-H and C(14), 6H) 1,28 (t, $^{3}J_{5,6}$ = 6.7 Hz, C(6)-H, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ : 167.7 (s, C(9) or C(10)), 166.3 (s, C(10) or C(9)), 136.3 (d, $^{3}J_{8,P}$ = 10.9 Hz, C(8)), 128.3 (d, $^{2}J_{7,P}$ = 9.9 Hz, C(7)), 125.6 (d, $^{3}J_{3,P}$ = 11.0 Hz, C(3)), 120.7 (d, $^{2}J_{2,P}$ = 10.8 Hz, C(2)), 62.9 (d, $^{2}J_{5,P}$ = 7.2 Hz, C(5)), 62.7 (d, $^{2}J_{5',P}$ = 6.9 Hz, C(5')), 61.3 (s, C(11) or C(12)), 61.2 (s, C(12) or C(11)), 39.1 (d, $^{1}J_{1,P}$ =138.6 Hz, C(1)), 28.5 (d, $^{4}J_{4,P}$ = 6.6 Hz, C(4)), 16.4 (d, $^{3}J_{6,P}$ = 5.5 Hz, C(6)), 16.3 (d, $^{3}J_{6',P}$ = 5.7 Hz, C(6')), 13.9 (s, C(13) or C(14)), 13.8 (s, C(14) or C(13)).

^{31}P NMR (202 MHz, $CDCl_3$) δ : 22.42.

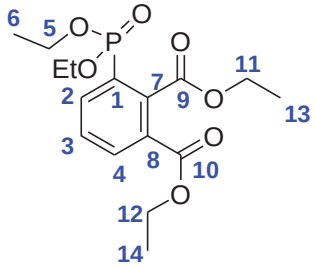
HRMS (MALDI-TOFpositive mode) m/z (%) [M+Na]: Calcd for $C_{16}H_{25}O_7PNa$: 383.1236, Found: 383.1225 (100).

Product 10b: 3-diethylphosphono-1,2-diethylester-phthalic acid



Reagents and conditions :
1) Pd/C (cat), $PhNO_2$, anhydrous toluene

A solution of **9b** (192 mg, 0.53 mmol), nitrobenzene (269 µL, 321 mg, 2.60 mmol) and palladium on charcoal (10 mol%, 124 mg, 0.06 mmol) in anhydrous toluene (10.4 mL) is stirred under reflux at least 24h. The reaction mixture is filtered through a celite pad, rinsed with a solution of dichloromethane: methanol (1:1) and concentrated under reduced pressure. The reaction mixture is purified by column chromatography to afford **10b** as a yellow oil (94 mg, 49 %).



$C_{16}H_{23}O_7P$

MW= 358.32 g.mol^{-1}

Rf [silica gel, ethyl acetate] = 0.6.

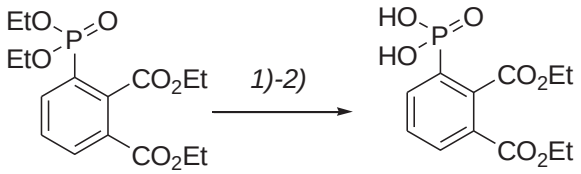
IR (υ, cm^{-1}): 2980 (w), 1722 (s, C=O), 1651 (w, C=C), 1578 (m, C=C), 1470 (m, C=C), 1443 (m, C=C), 1392 (m), 1367 (m), 1250 (s, P=O), 1141 (s), 1109 (s), 1009 (s, P-O), 947 (s, P-O), 754 (s), 694 (m).

^{1}H NMR (500 MHz, $CDCl_3$) δ : . 8.16- (d, $^{3}J_{3,4}$ = 6.9 Hz, C(4)-H, 1H), 8.13 (dd, $^{3}J_{2,P}$ = 13.4 Hz and $^{3}J_{2,3}$ = 7.7 Hz, C(2)-H, 1H), 7.58 (td, $^{3}J_{2,3}$ = $^{3}J_{3,4}$ = 7.8 Hz and $^{4}J_{3,P}$ = 3.3 Hz, C(3)-H, 1H), 4.44 (q, $^{3}J_{11,13}$ or $^{3}J_{12,14}$ = 7.2 Hz, C(11)-H or C(12)-H, 2H), 4.37 (q, $^{3}J_{12,14}$ or $^{3}J_{11,13}$ = 7.1 Hz, C(12)-H or C(11)-H, 2H), 4.22-4.14 (m, C(5)-H, 2H) ; 4.13-4.05 (m, C(5)-H, 2H) ; 1,41 (t, $^{3}J_{11,13}$ or $^{3}J_{12,14}$ = 7.2 Hz, C(13)-H or C(14)-H, 3H), 1,38 (t, $^{3}J_{12,14}$ or $^{3}J_{11,13}$ = 7.7 Hz, C(14)-H or C(13)-H, 3H), 1,34 (t, $^{3}J_{5,6}$ = 7.1 Hz, C(6)-H, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ : 167.7 (d, $^{3}J_{9,P}$ = 5.5 Hz, C(9)), 165.1 (s, C(10)), 138.8 (d, $^{2}J_{7,P}$ = 11.2 Hz, C(7)), 137.4 (d, $^{3}J_{3,P}$ = 8.2 Hz, C(3)), 133.9 (d, $^{4}J_{4,P}$ = 2.1 Hz, C(4)), 129.3 (d, $^{3}J_{8,P}$ = 13.6 Hz, C(8)), 129.0 (d, $^{3}J_{3,P}$ = 13.9 Hz, C(3)), 127.3 (d, $^{1}J_{1,P}$ =184.2 Hz, C(1)), 62.7

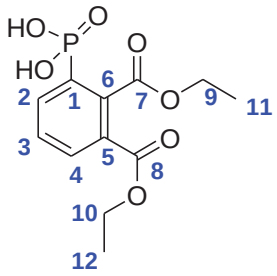
(d, $^{2}J_{5,P}$ = 5.2 Hz, C(5)), 62.1 (s, C(12) or C(11)), 61.9 (s, C(11) or C(12)), 16.3 (d, $^{3}J_{6,P}$ = 6.5 Hz, C(6)), 14.2 (s, C(13) or C(14)), 13.9 (s, C(14) or C(13)).
^{31}P NMR (202 MHz, $CDCl_3$) δ : 15.39.
HRMS (MALDI-TOF, positive mode) m/z (%) [M+Na]: Calcd for $C_{16}H_{23}O_7PNa$: 381.1079, Found: 381.1079 (100).

Product 11b: 3-phosphonic acid-1,2-diethylester-phthalic acid



Reagents and conditions :
1) TMSBr, CH_3CN, reflux
2) MeOH, RT, 1h

A solution of **10b** (45.8 mg, 0.13 mmol), trimethylsilyl bromide (52 µL, 60.7 mg, 0.40 mmol) in anhydrous acetonitrile (1.2 mL) is stirred under reflux. The ethyl bromide by-product, the excess of trimethylsilyl bromide and the solvent are evaporated under reduced pressure. The reaction mixture is then hydrolyzed with an excess of methanol (6 mL) at room temperature during 1h. The solvent is evaporated to afford **11b** as an orange oil (29.4 mg, 76 %).



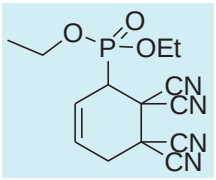
$C_{12}H_{15}O_7P$

MW= 302.22 g.mol^{-1}

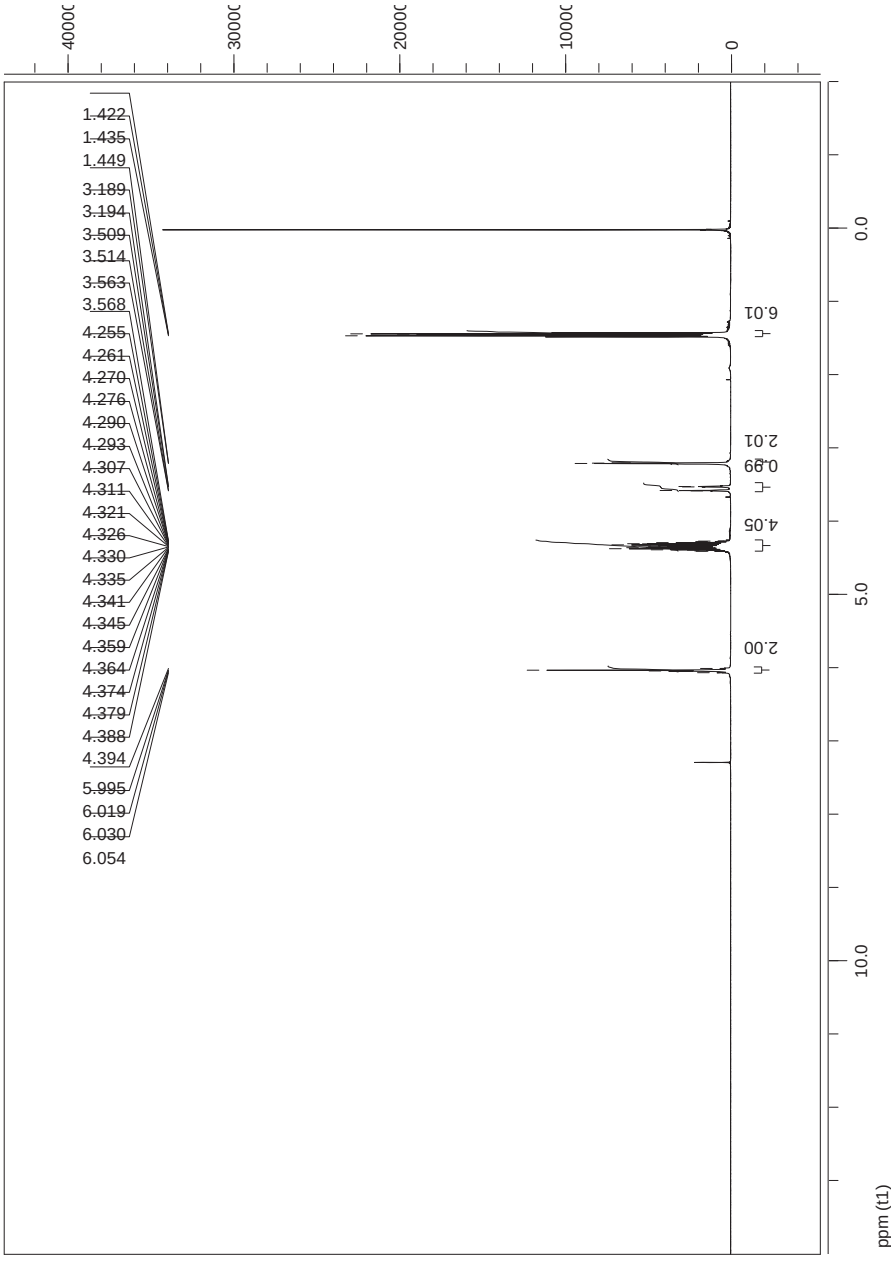
IR (υ, cm^{-1}): 3500-3000 (large band, m, OH), 3149 (w), 1772 (m, C=O), 1699 (s, C=O), 1578 (w, C=C), 1445 (m, C=C), 1290 (s), 1149 (m, P=O), 1116 (m), 1014 (s, P-O), 939 (m, P-O), 766 (m), 694 (w).
^{1}H NMR (500 MHz, MeOD) δ : . 8.13 (dd, $^{3}J_{2,P}$ = 12.4 Hz and $^{3}J_{2,3}$ = 7.9 Hz, C(2)-H, 1H), 8.12 (d, $^{3}J_{3,4}$ = 7.9 Hz, C(4)-H, 1H), 7.65 (td, $^{3}J_{2,3}$ = $^{3}J_{3,4}$ = 7.8 Hz and $^{4}J_{3,P}$ = 2.7 Hz, C(3)-H, 1H), 4.37 (q, $^{3}J_{9,11}$ or $^{3}J_{10,12}$ = 7.2 Hz, C(9)-H or C(10)-H, 2H), 4.35 (q, $^{3}J_{9,11}$ or $^{3}J_{10,12}$ = 7.1 Hz, C(10)-H or C(9)-H, 2H), 1.37 (t, $^{3}J_{9,11}$ or $^{3}J_{10,12}$ = 7.1 Hz, C(11)-H or C(12)-H, 3H), 1.36 (t, $^{3}J_{10,12}$ or $^{3}J_{9,11}$ = 7.1 Hz, C(12)-H or C(11)-H, 3H).
^{13}C NMR (125 MHz, MeOD) δ : 170.0 (d, $^{3}J_{7,P}$ = 4.6 Hz, C(7)), 166.9 (s, C(8)), 139.0 (d, $^{2}J_{6,P}$ = 10.9 Hz, C(6)), 137.4 (d, $^{2}J_{2,P}$ = 8.5 Hz, C(2)), 133.9 (d, $^{4}J_{4,P}$ = 1.7 Hz, C(4)), 132.2 (d, $^{1}J_{1,P}$ = 182.7 Hz, C(1)), 130.3 (d, $^{3}J_{5,P}$ = 13.1 Hz, C(5)), 130.5 (d, $^{3}J_{3,P}$ = 13.7 Hz, C(3)), 63.2 (s, C(9) or C(10)), 62.9 (s, C(9) or C(10)), 14.4 (s, C(12) or C(11)), 14.1 (s, C(11) or C(12)).
^{31}P NMR (202 MHz, MeOD) δ : 12.30.
HRMS (MALDI-TOF, negative mode) m/z (%) [M-H]: Calcd for $C_{12}H_{14}O_7P$: 301.0477, Found: 301.0487 (100); **[M-H-CH_2=CH_2]:**.227.0099 (5).

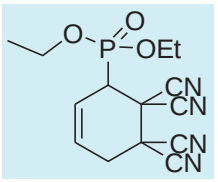
II. NMR spectra

A. Product 2

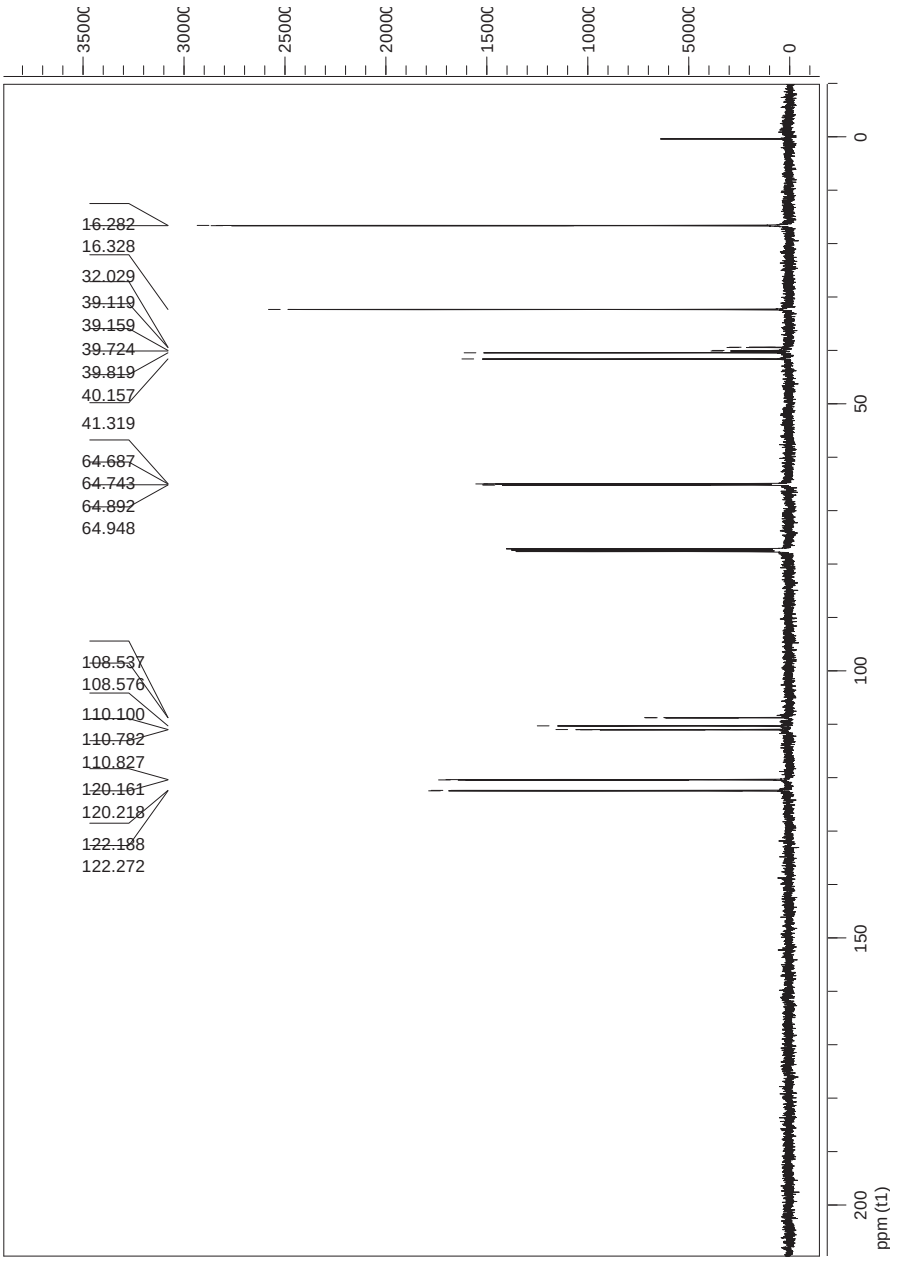


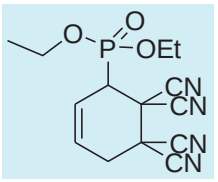
^{1}H NMR spectrum



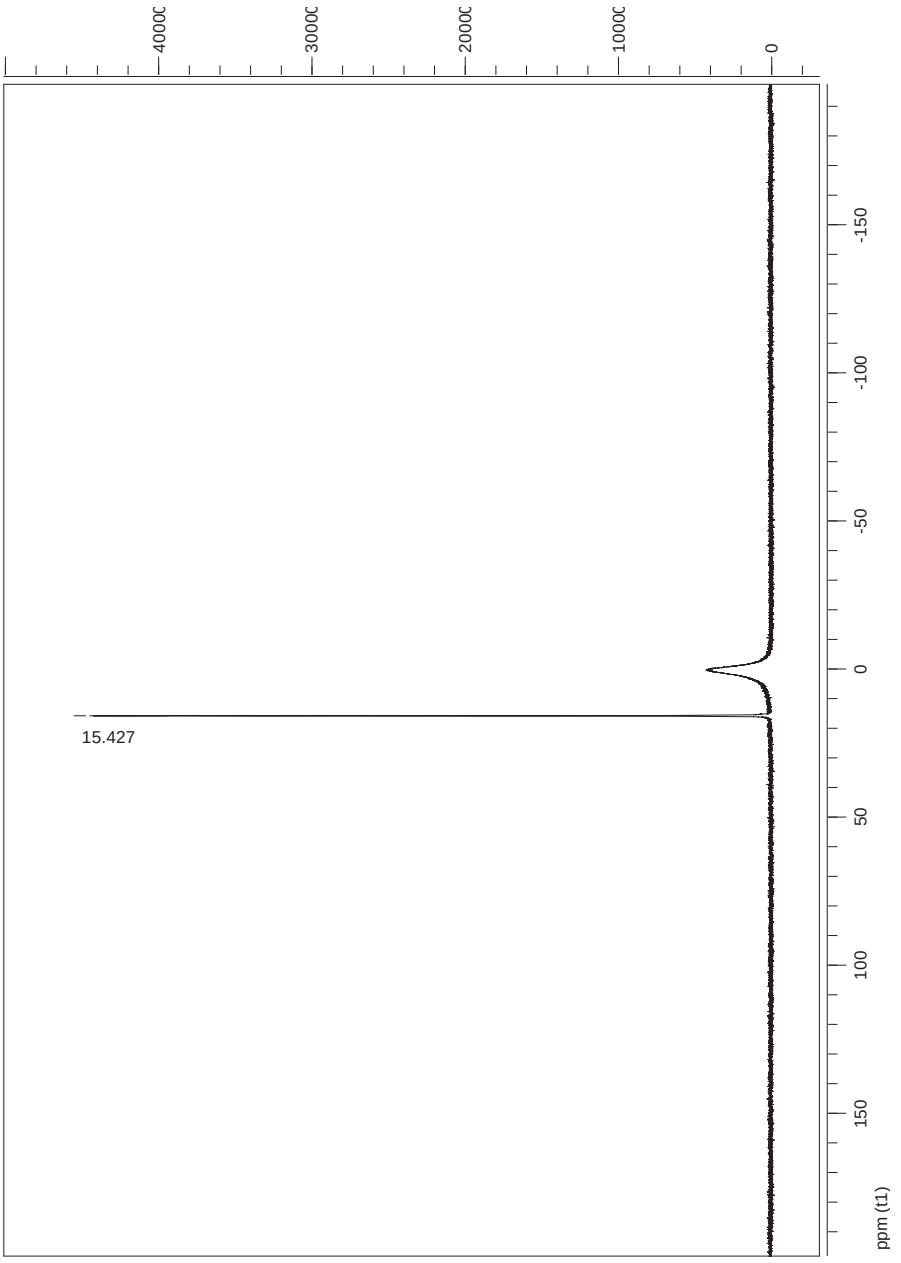


^{13}C NMR spectrum

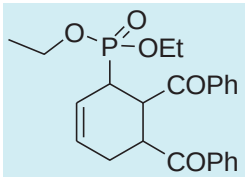




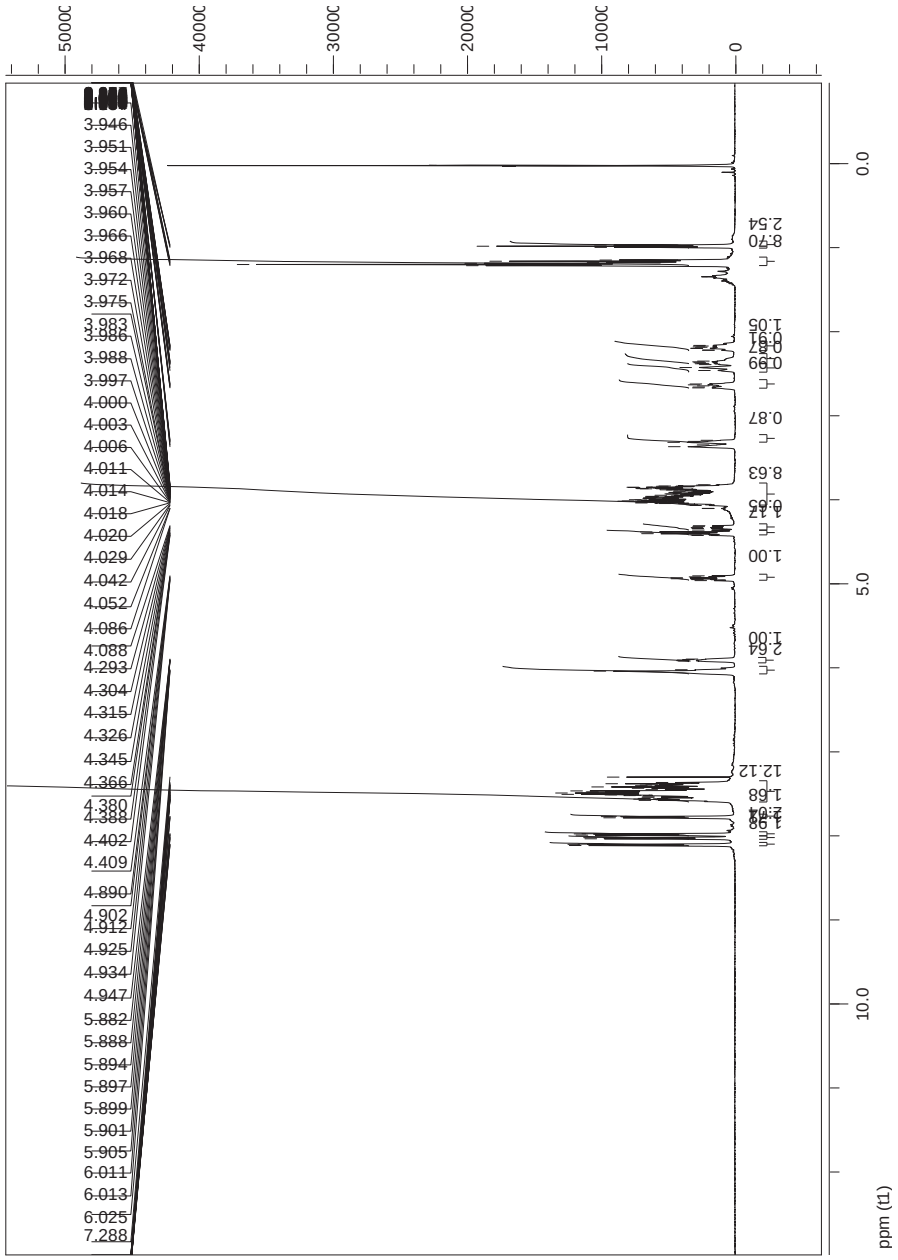
^{31}P NMR spectrum

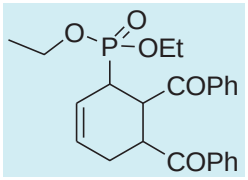


B. Product 3

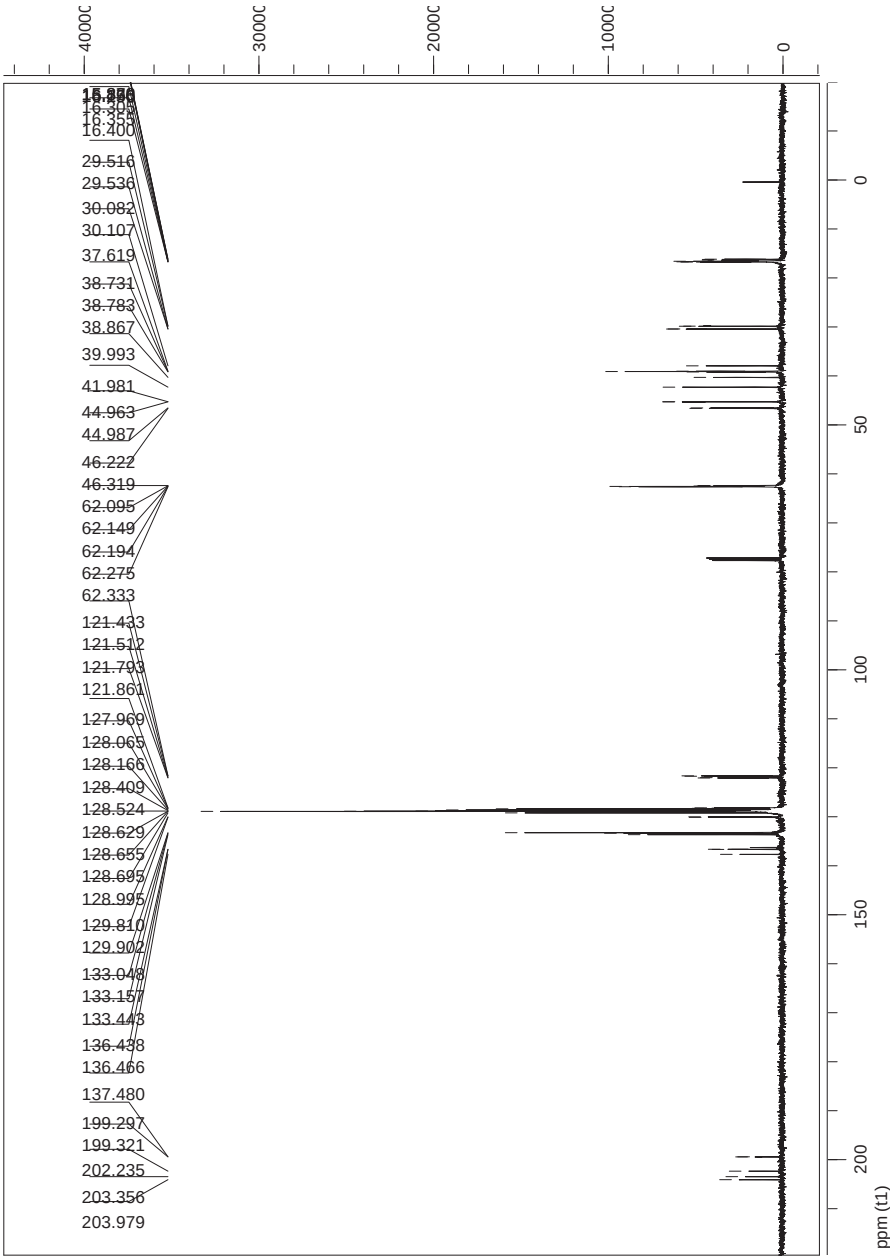


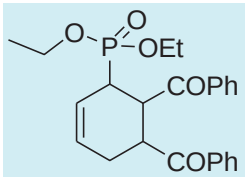
^{1}H NMR spectrum



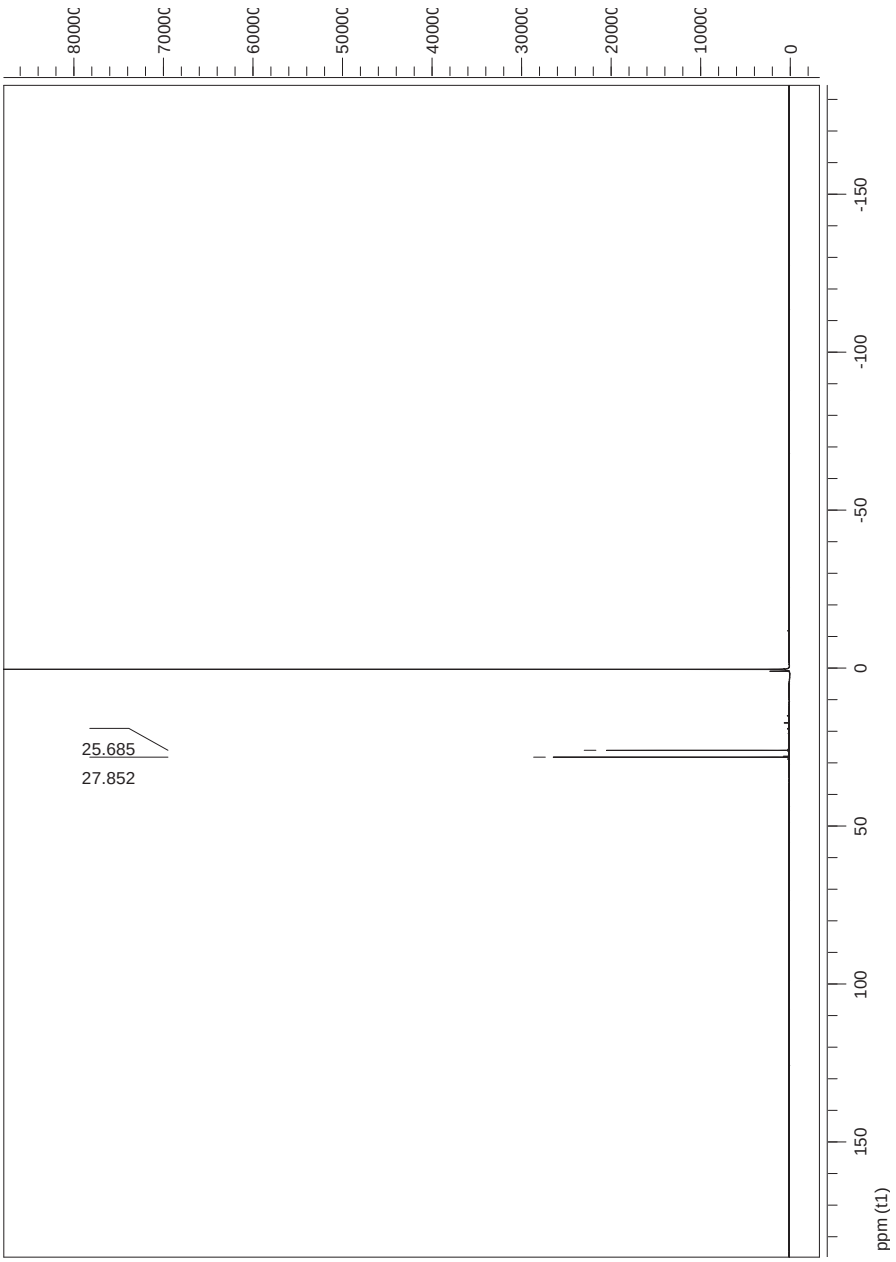


^{13}C NMR spectrum

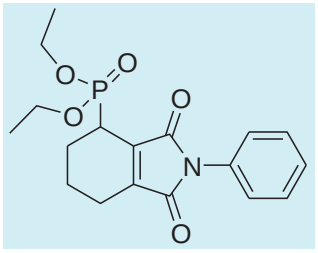




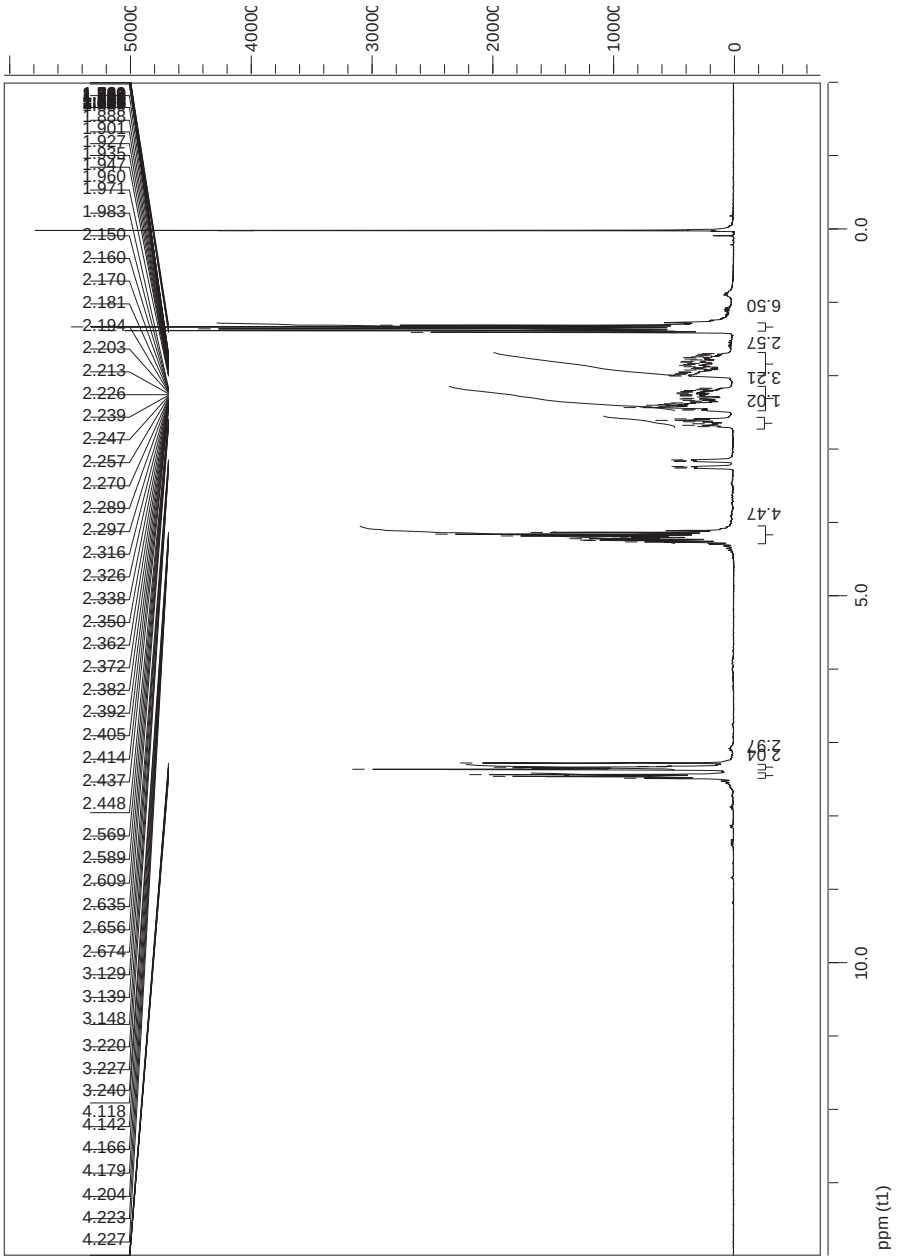
^{31}P NMR spectrum

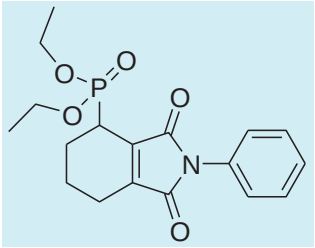


C. Product 5

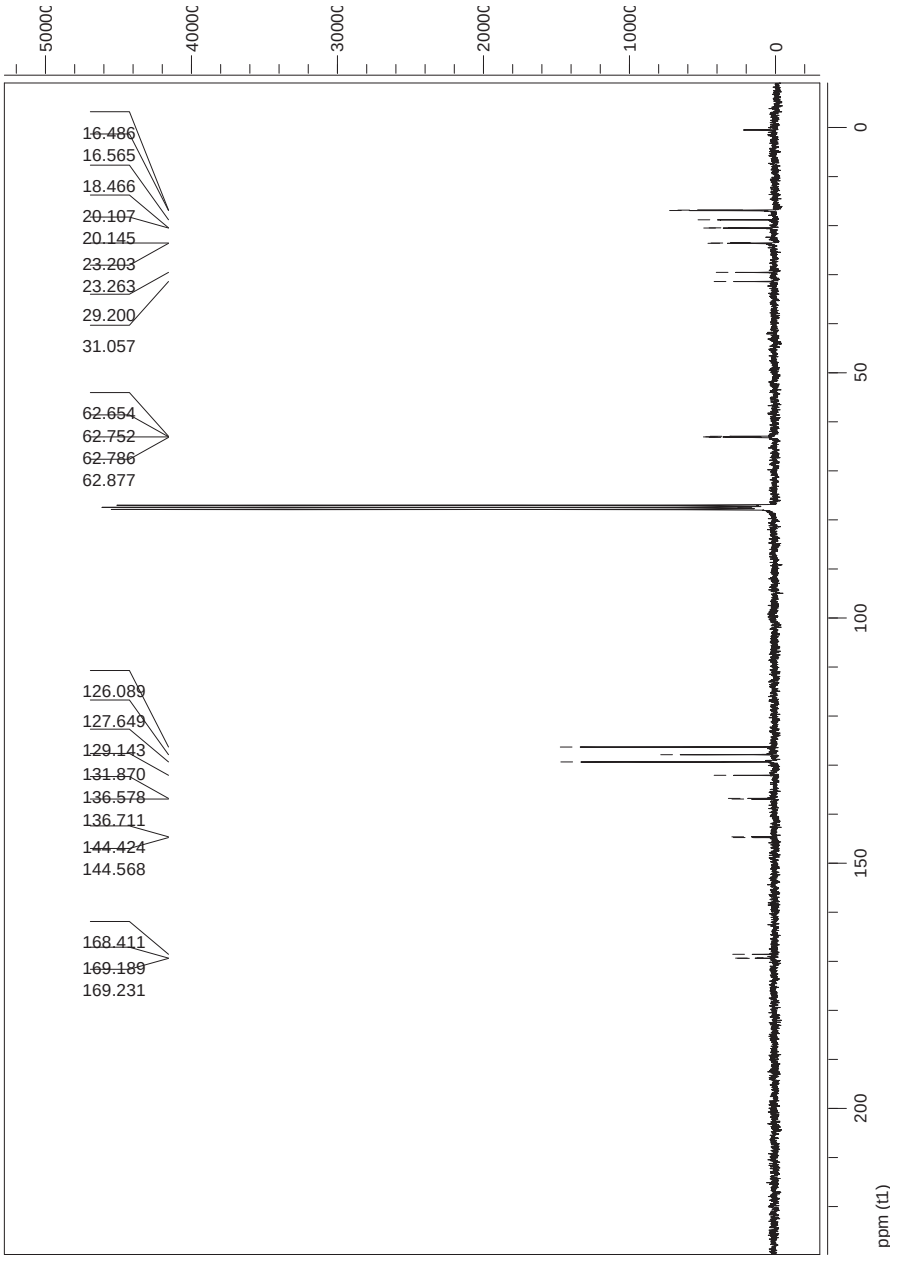


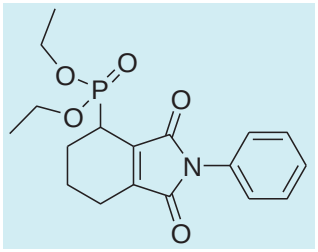
^{1}H NMR spectrum



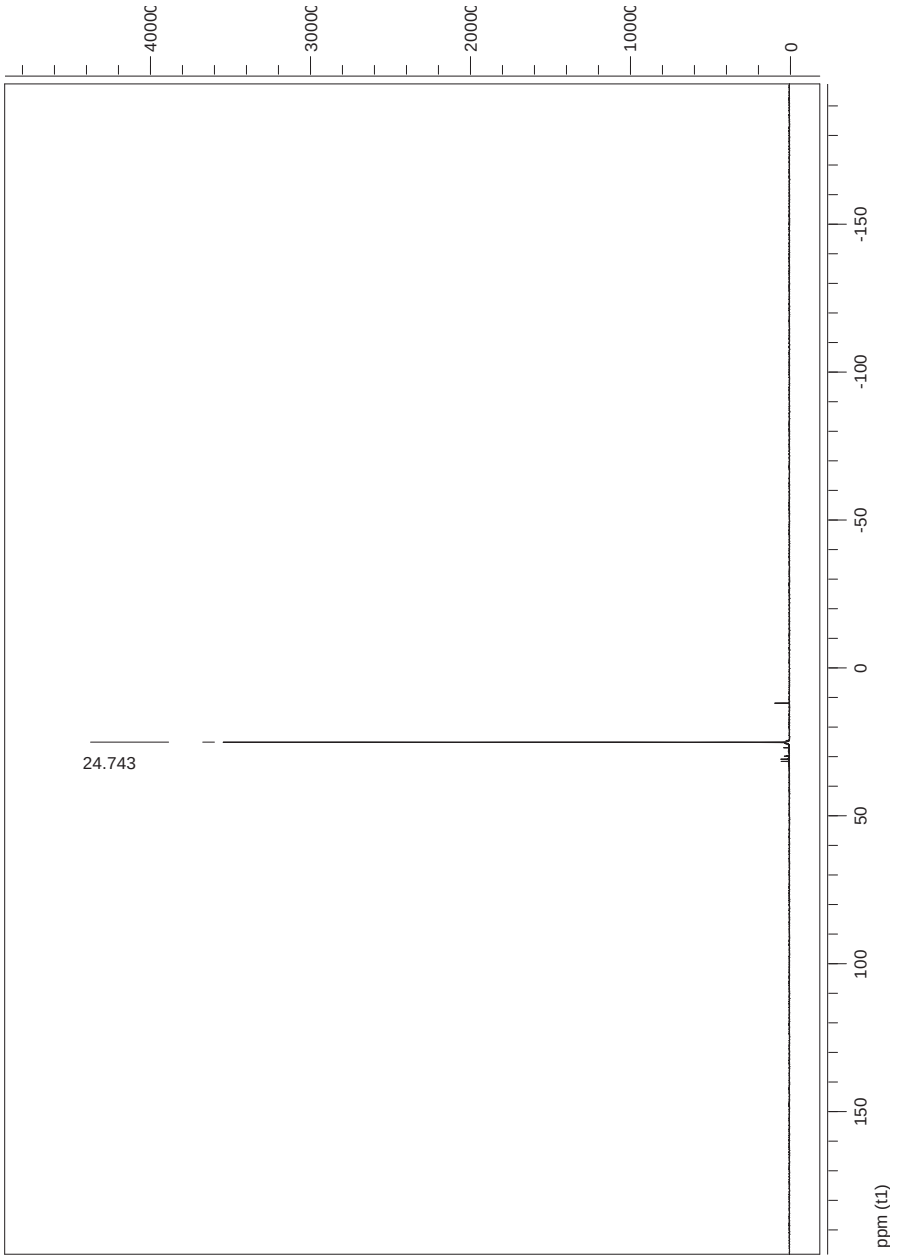


^{13}C NMR spectrum

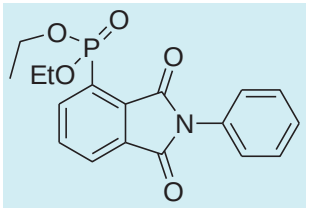




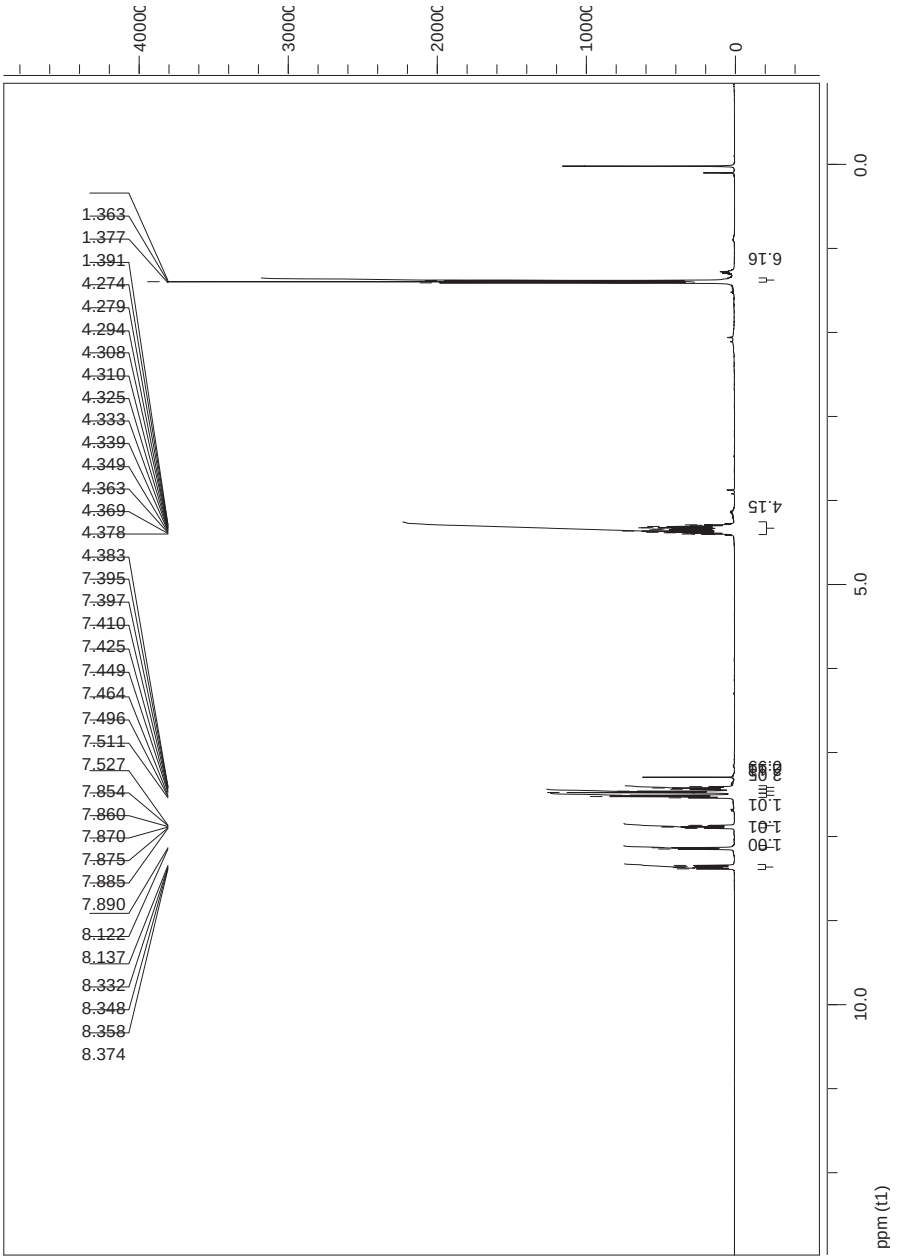
^{31}P NMR spectrum

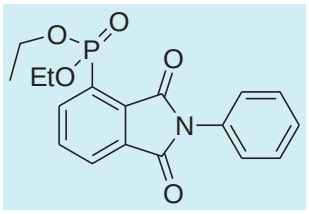


D. Product 6

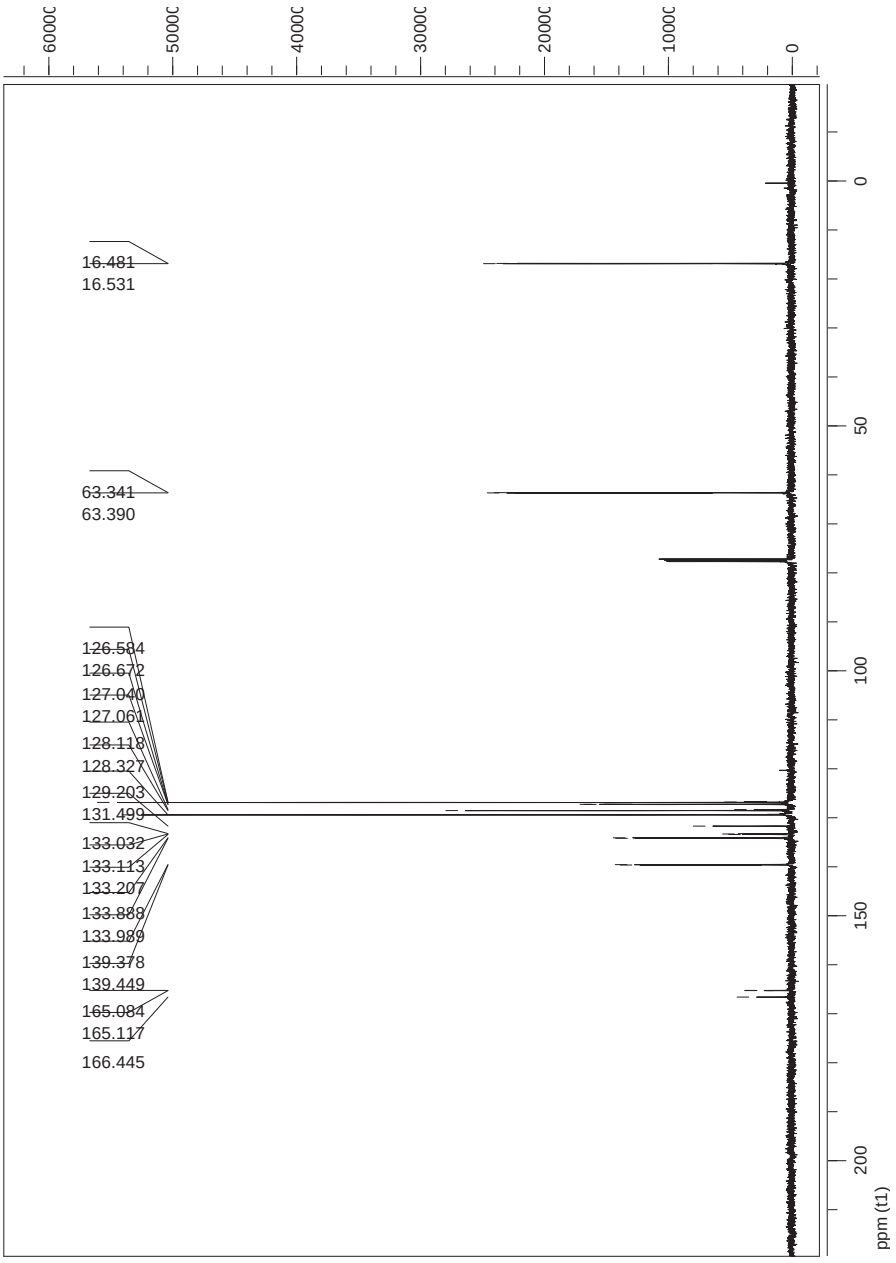


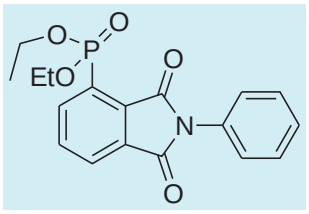
^{1}H NMR spectrum



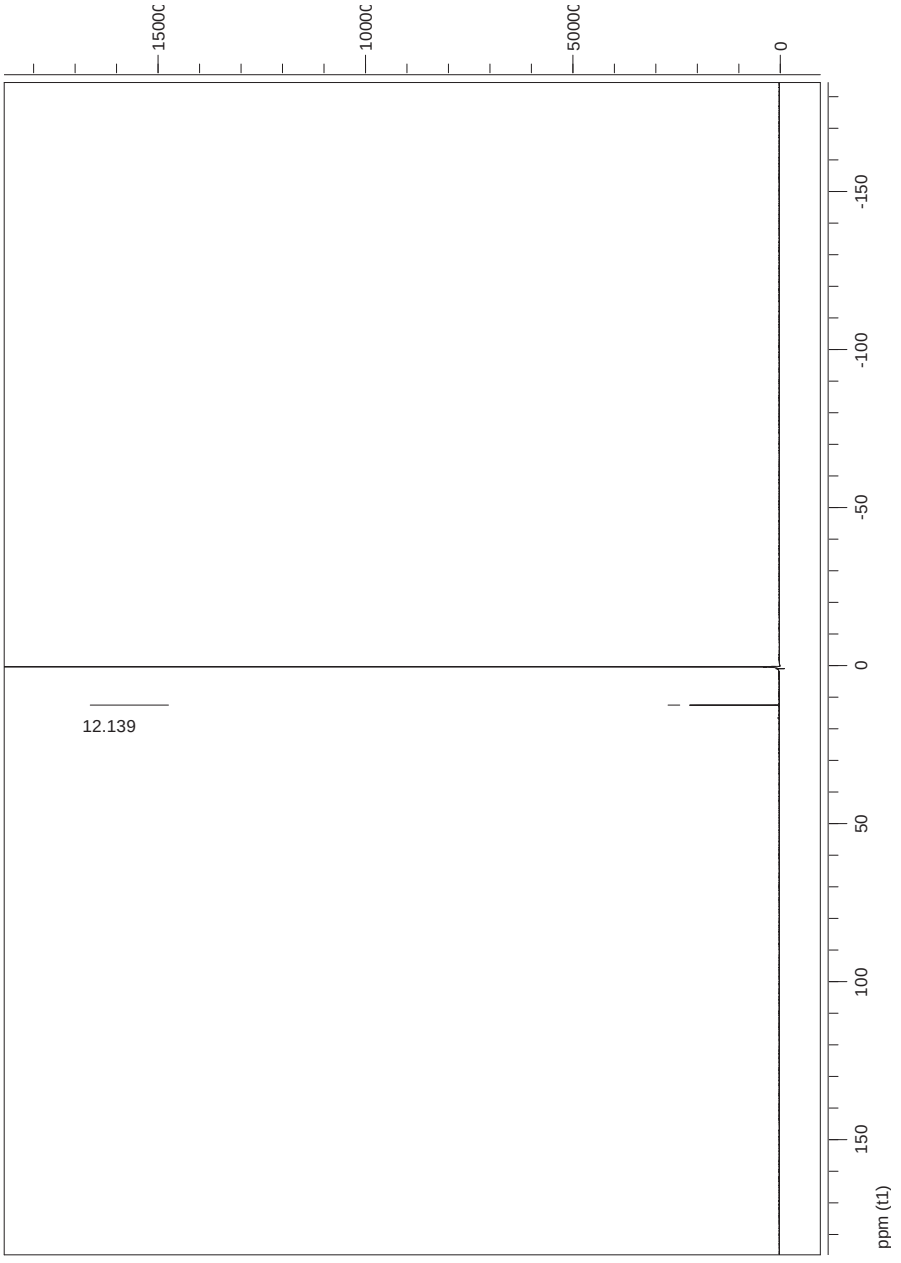


^{13}C NMR spectrum

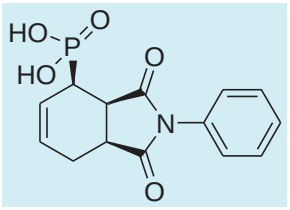




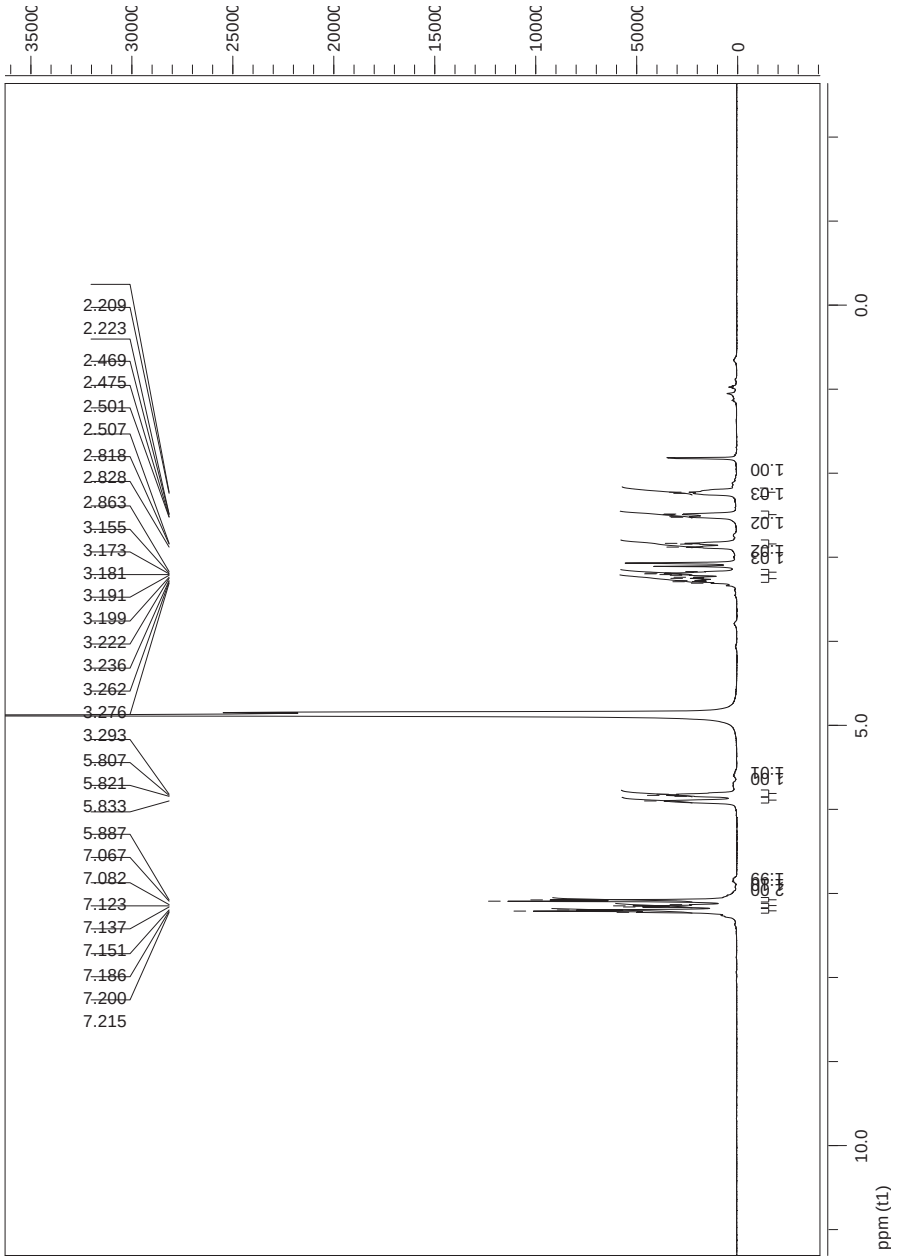
^{31}P NMR spectrum

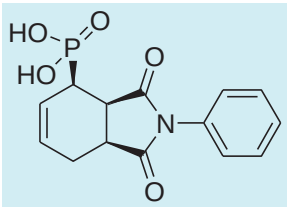


E. Product 7

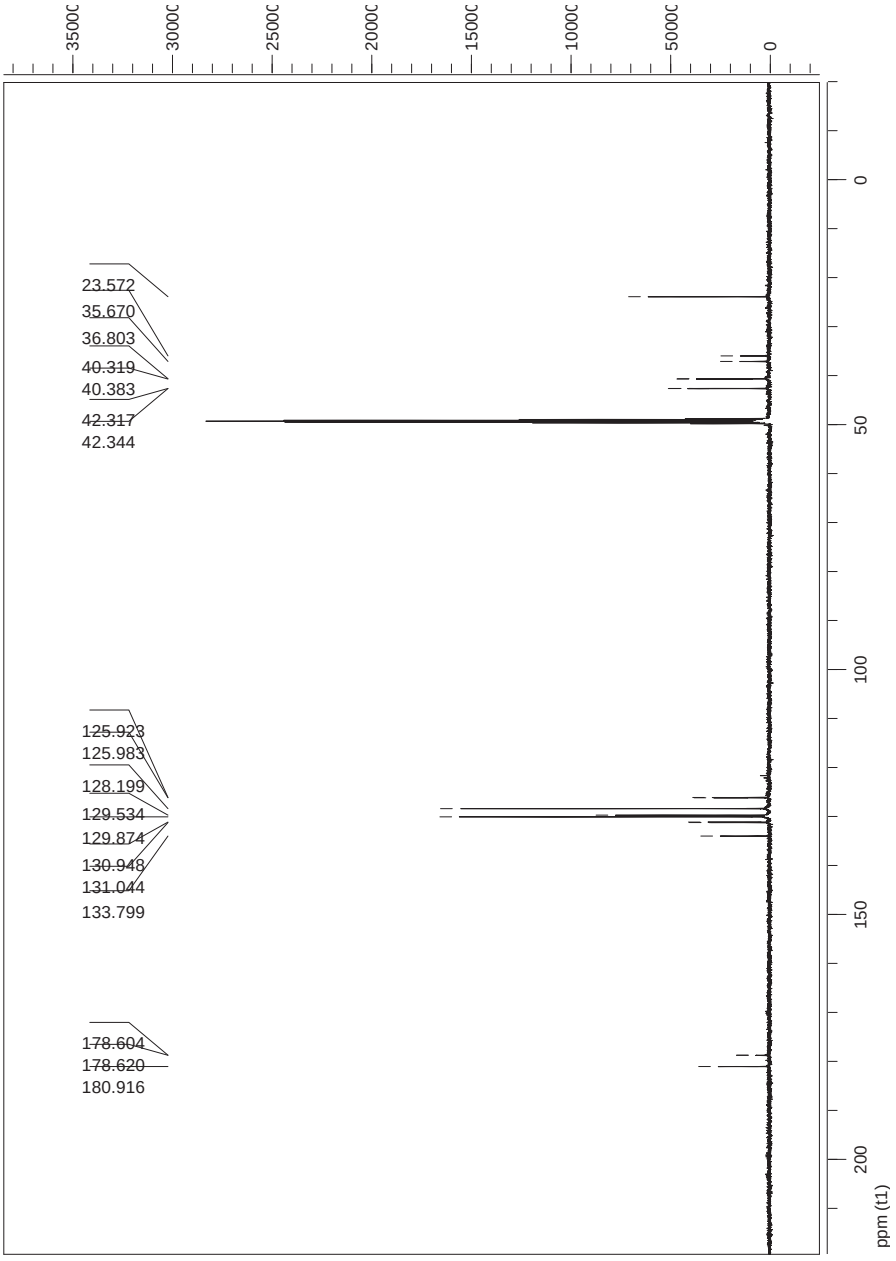


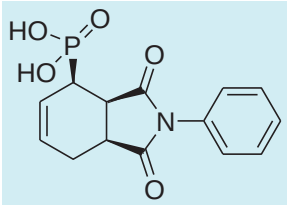
^{1}H NMR spectrum



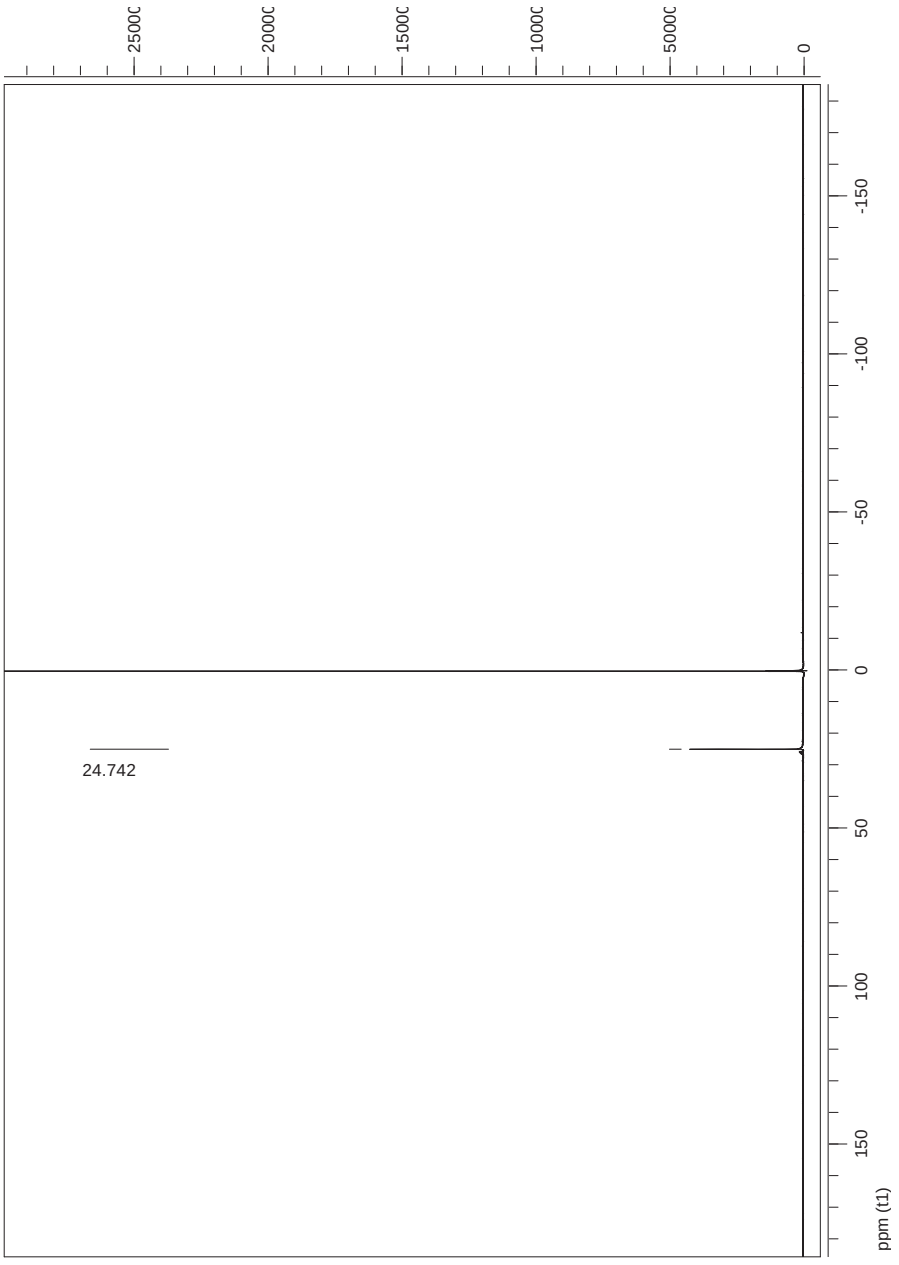


^{13}C NMR spectrum

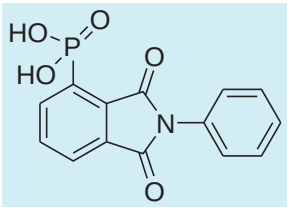




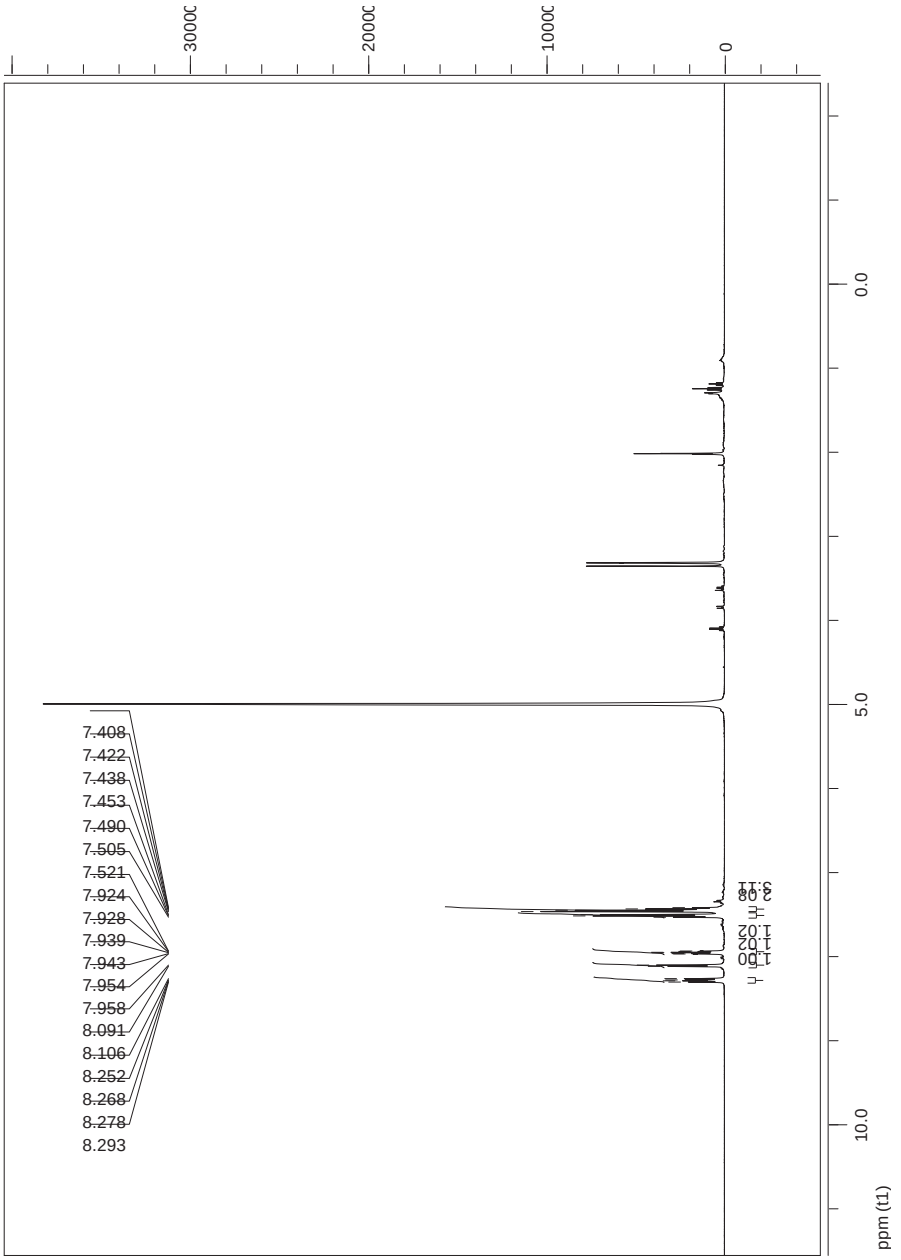
^{31}P NMR spectrum

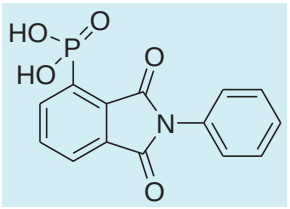


F. Product 8

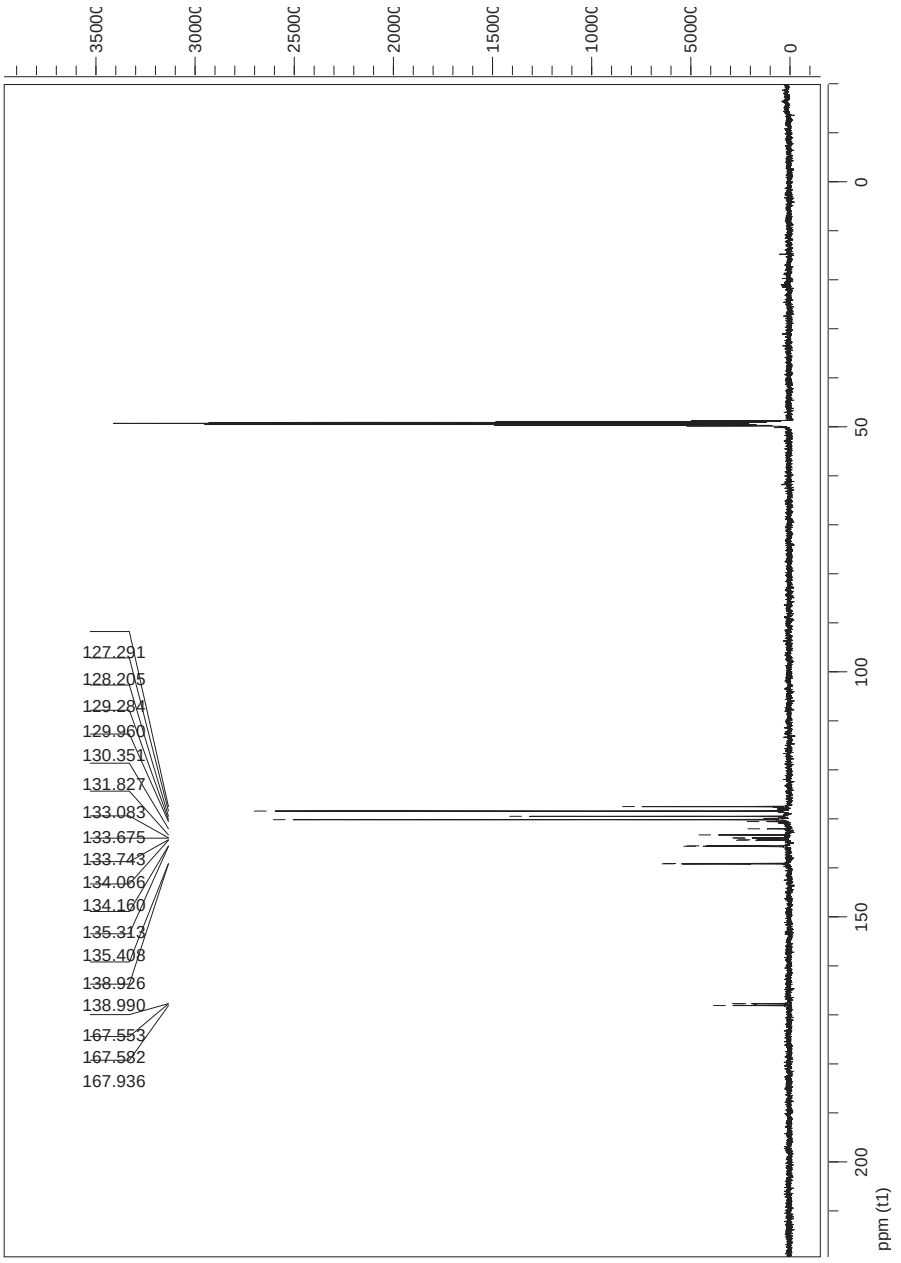


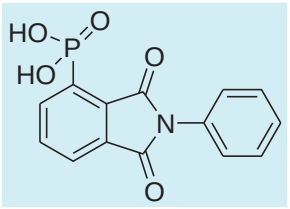
^{1}H NMR spectrum



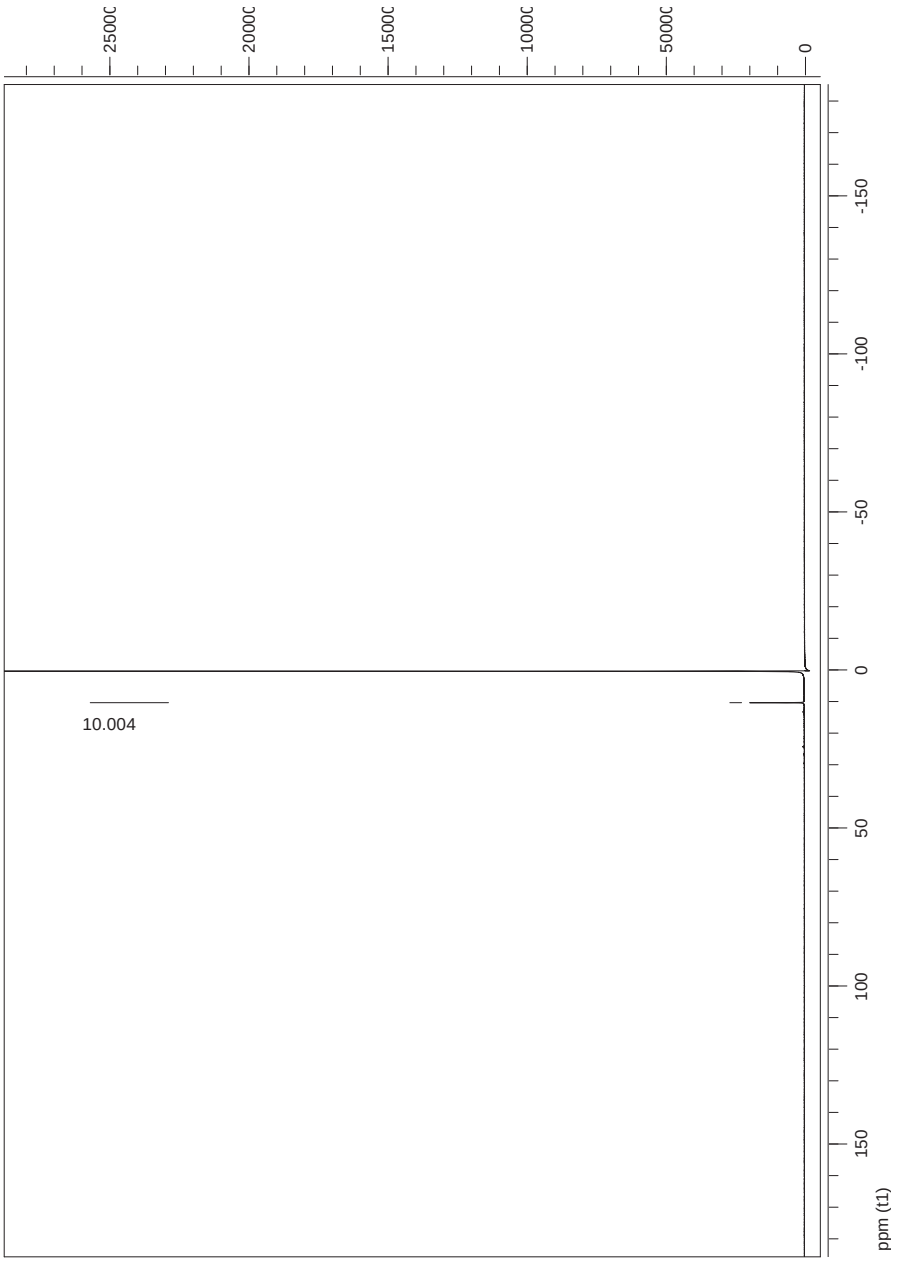


^{13}C NMR spectrum

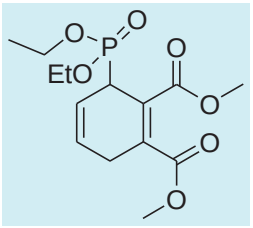




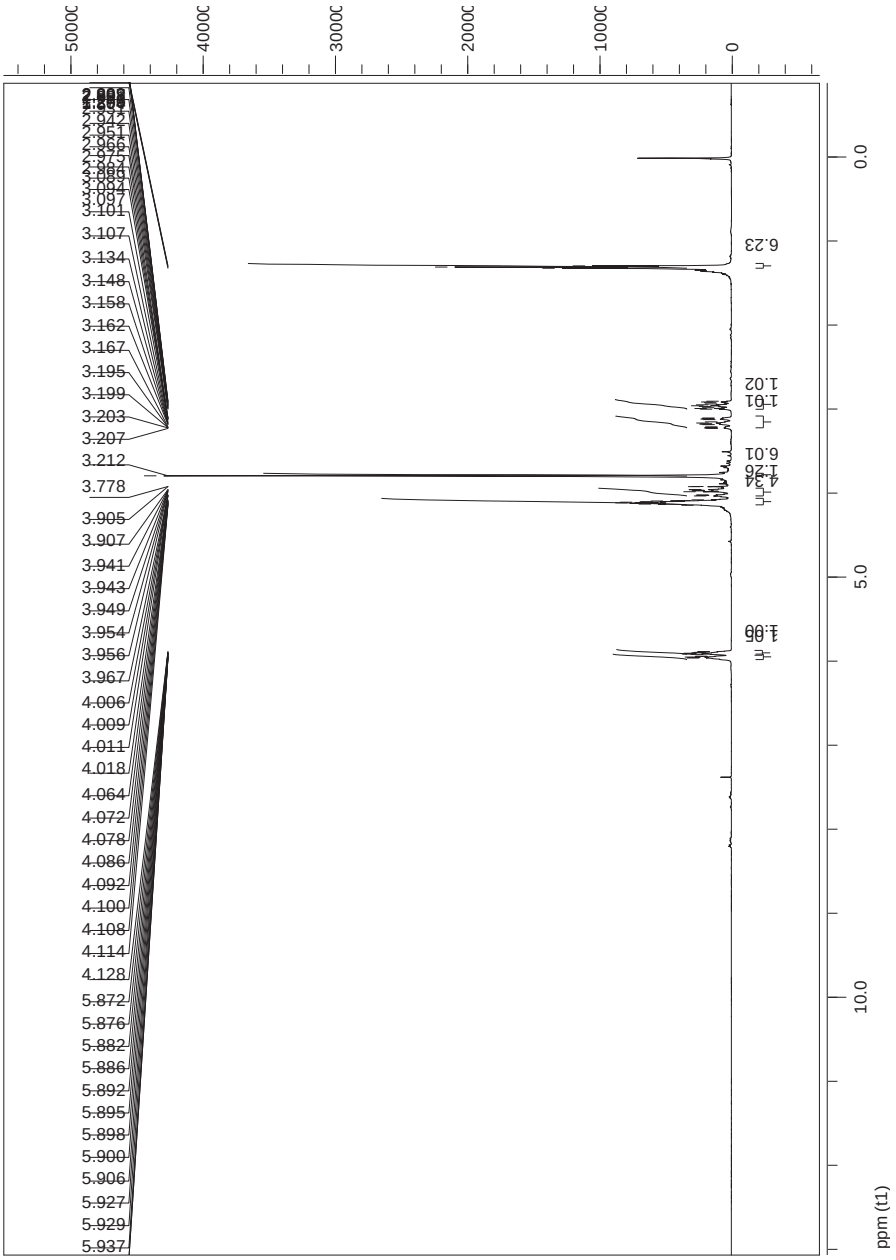
^{31}P NMR spectrum

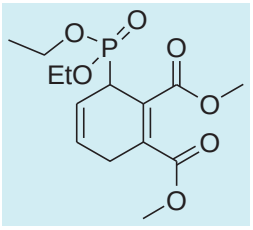


G. Product 9a

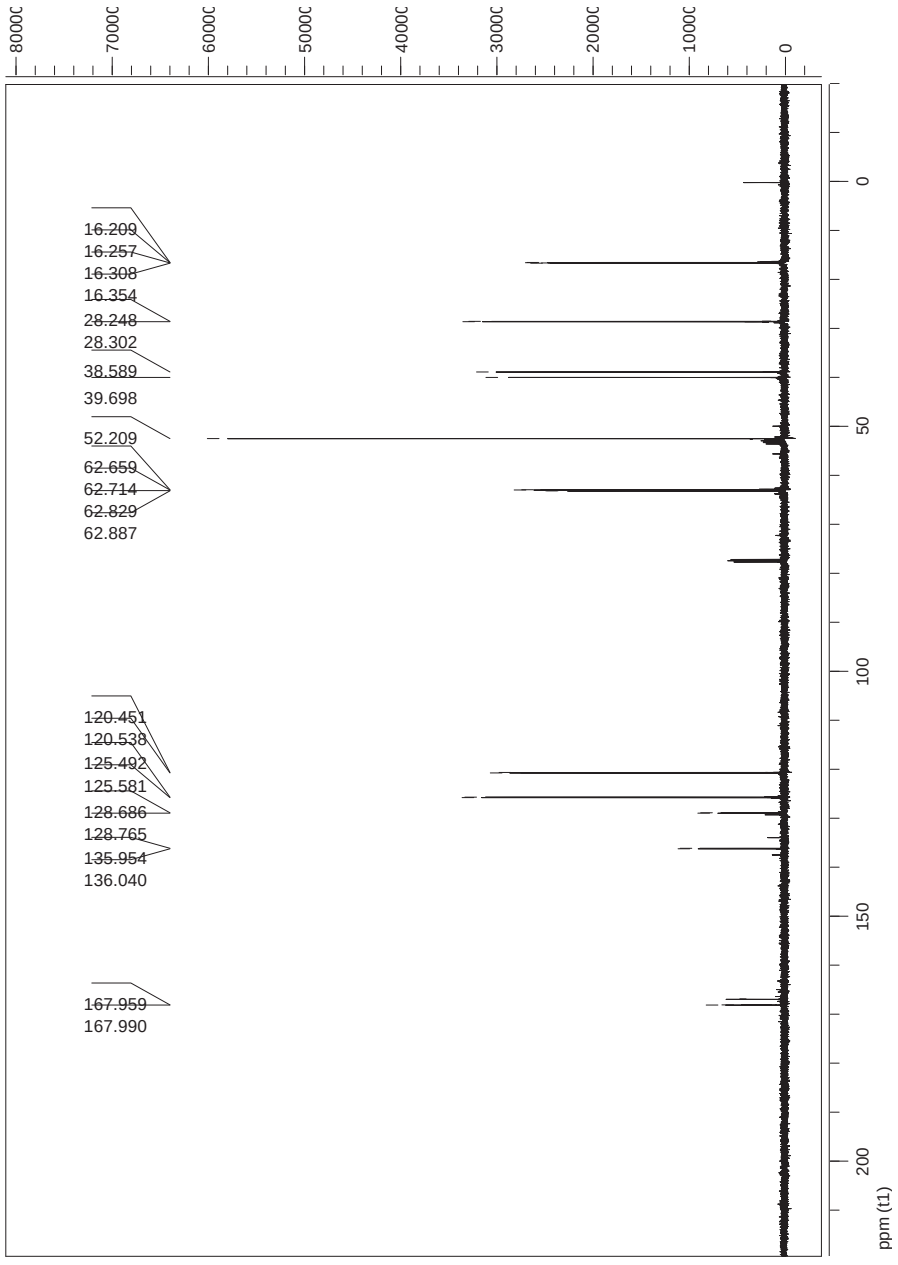


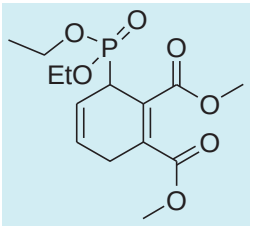
^{1}H NMR spectrum



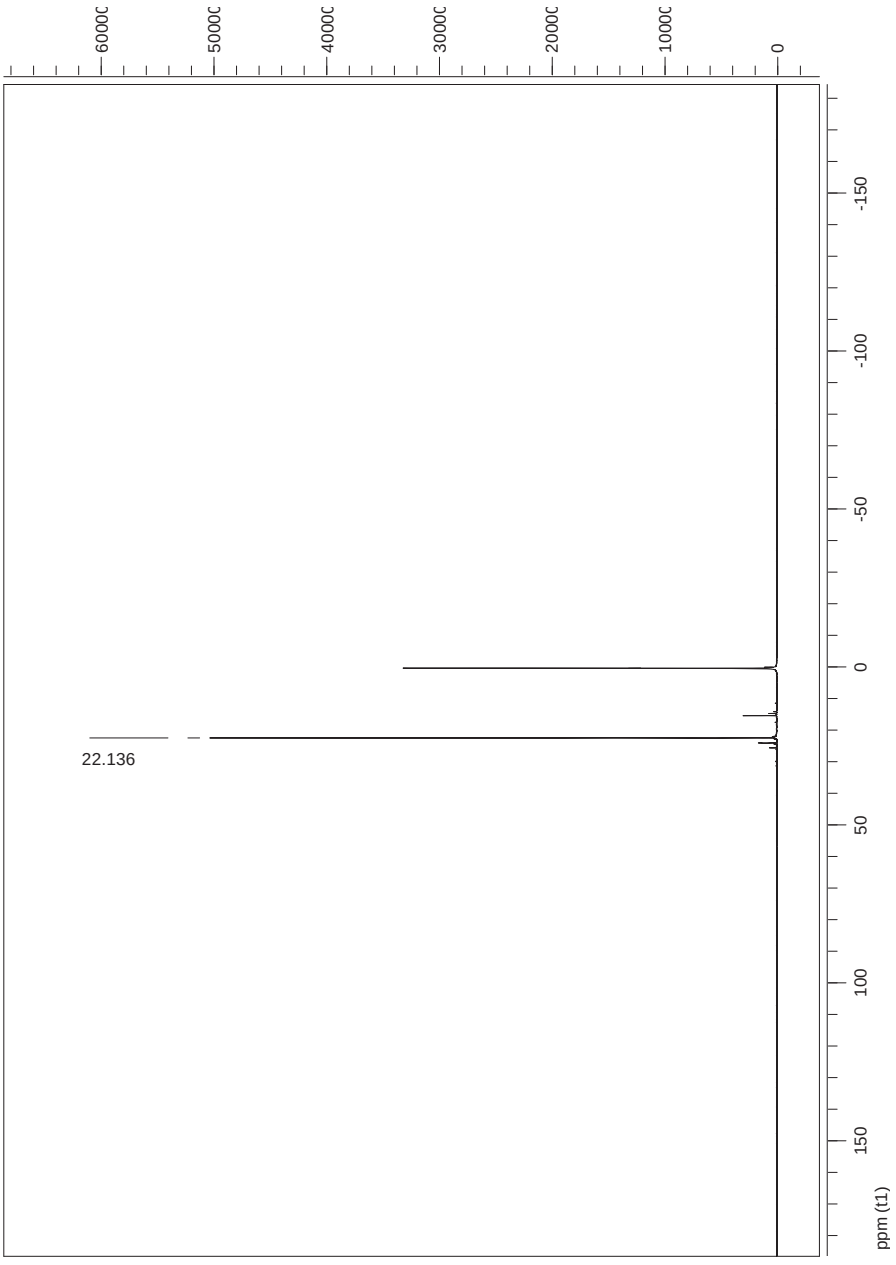


^{13}C NMR spectrum

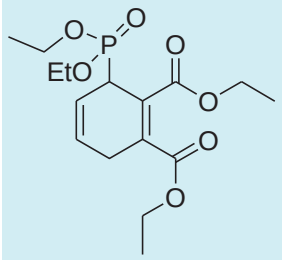




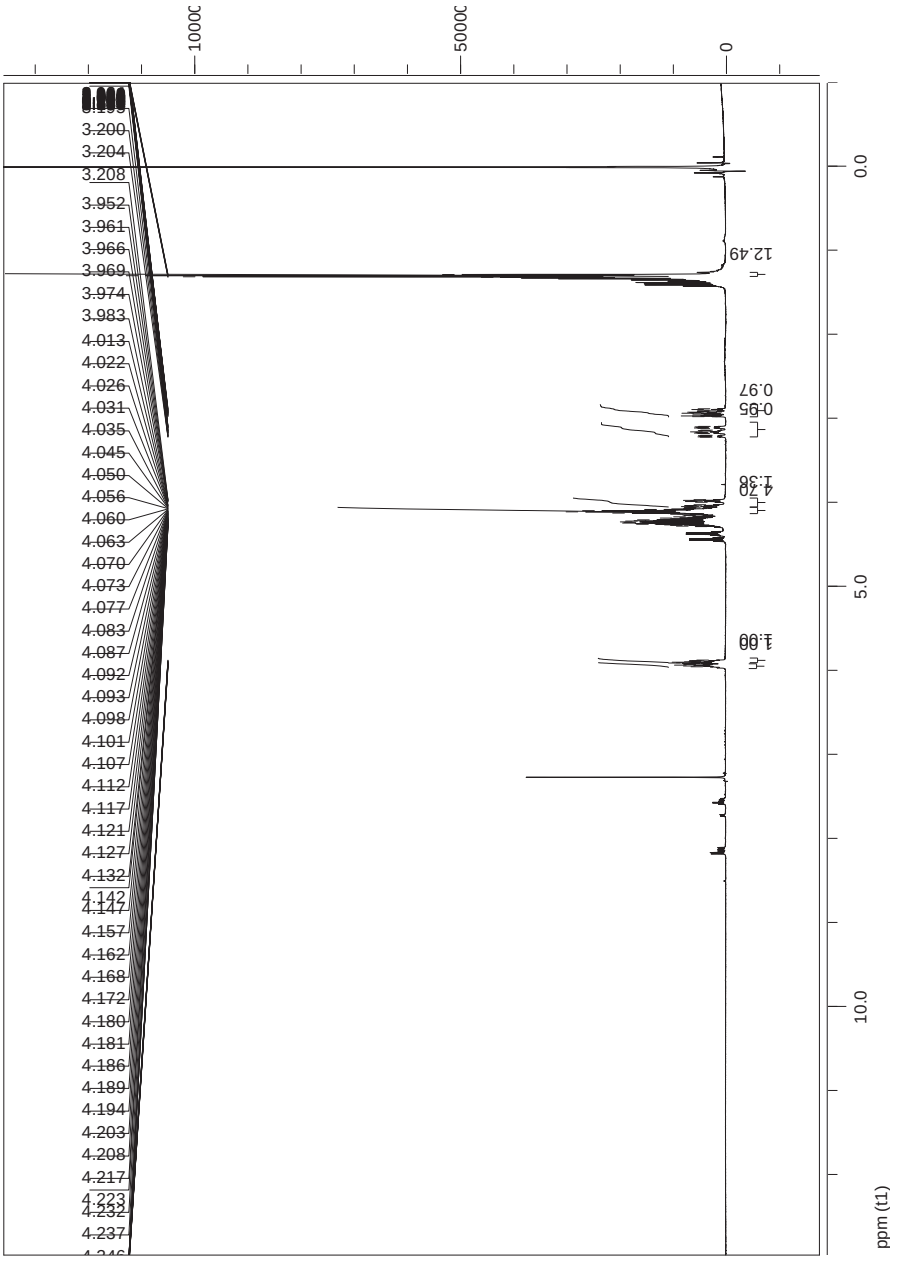
^{31}P NMR spectrum

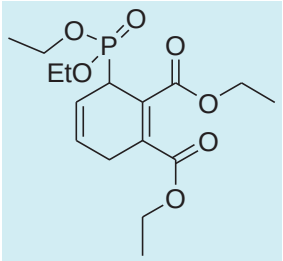


H. Product 9b

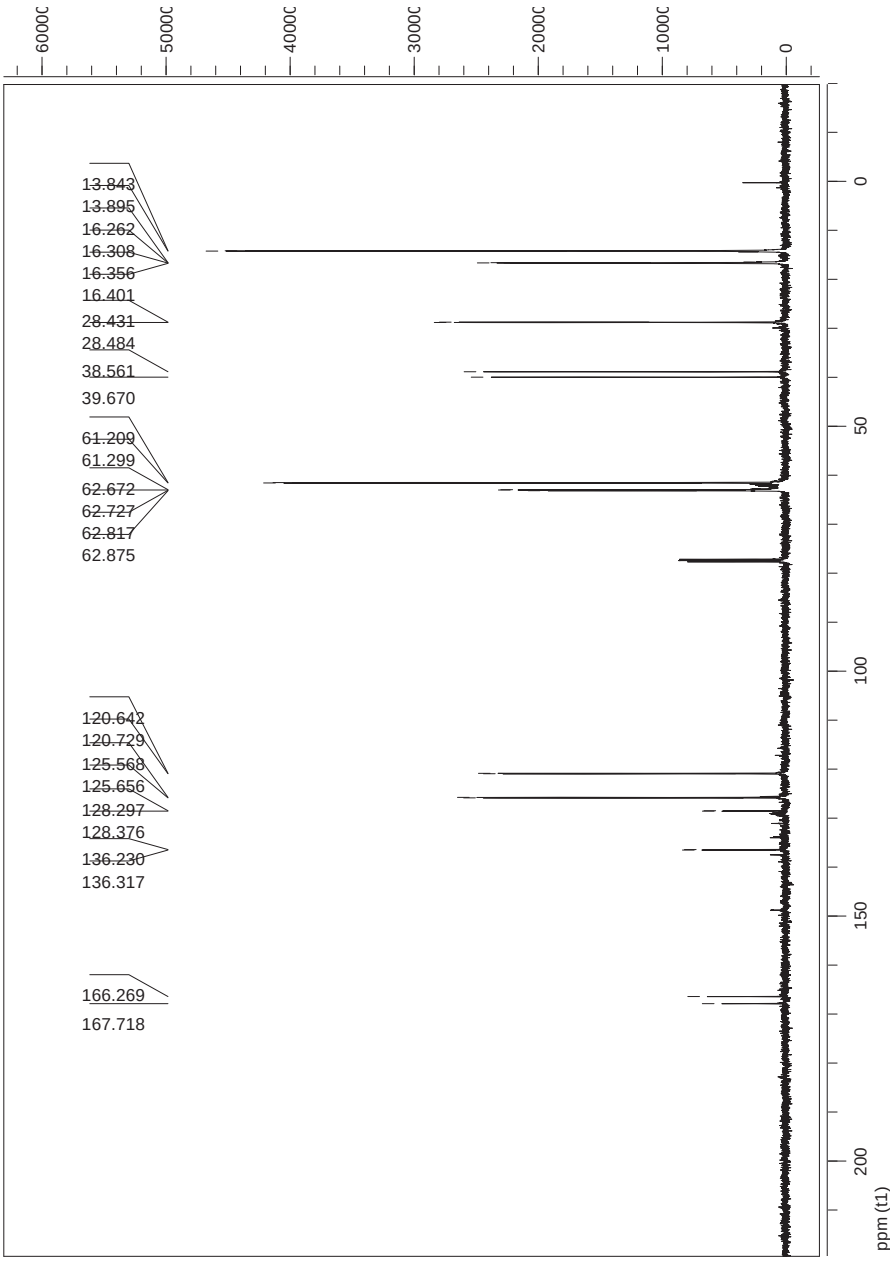


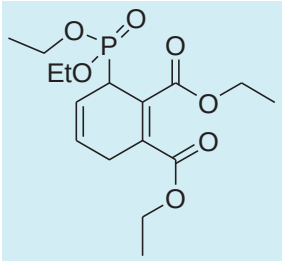
^{1}H NMR spectrum



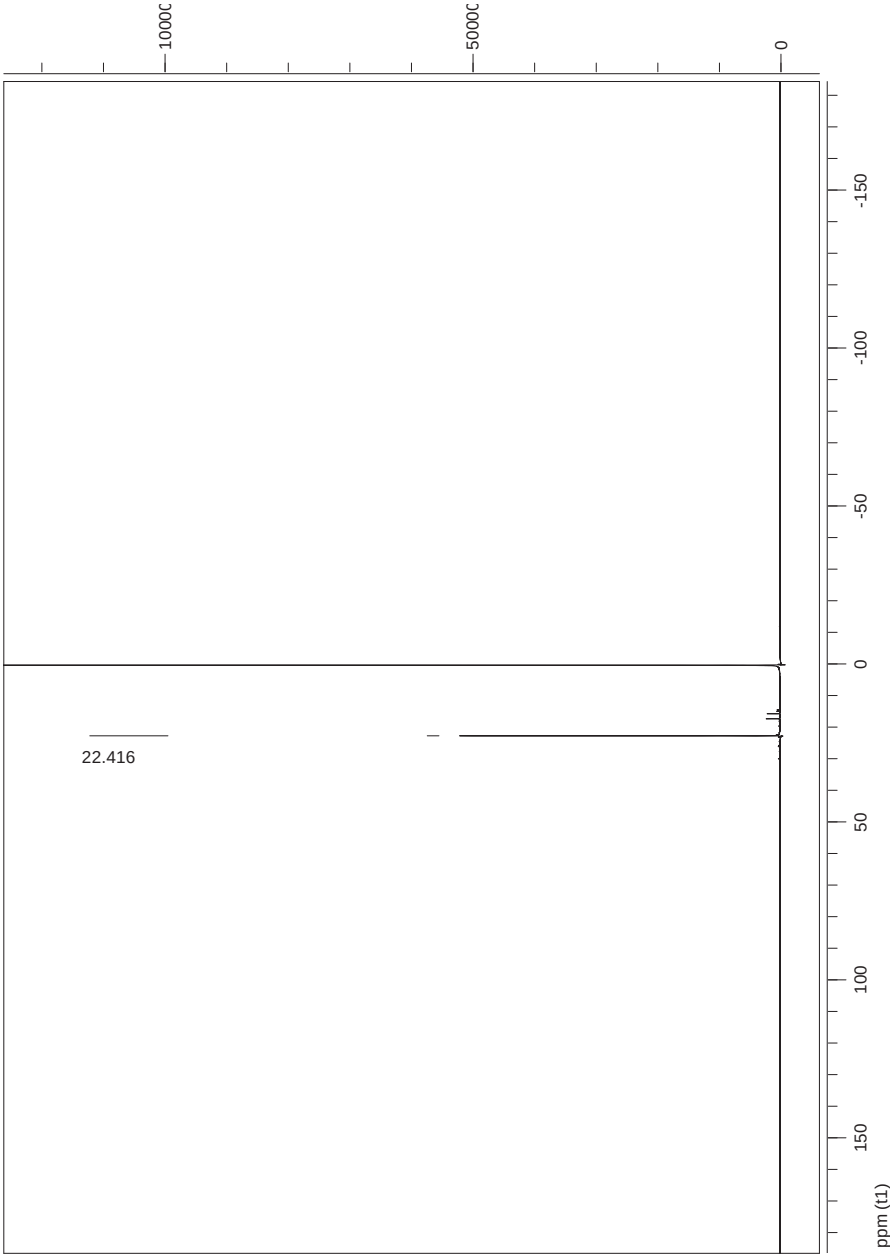


^{13}C NMR spectrum

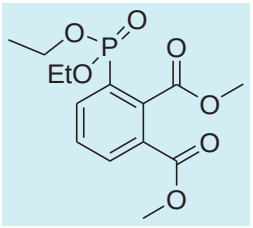




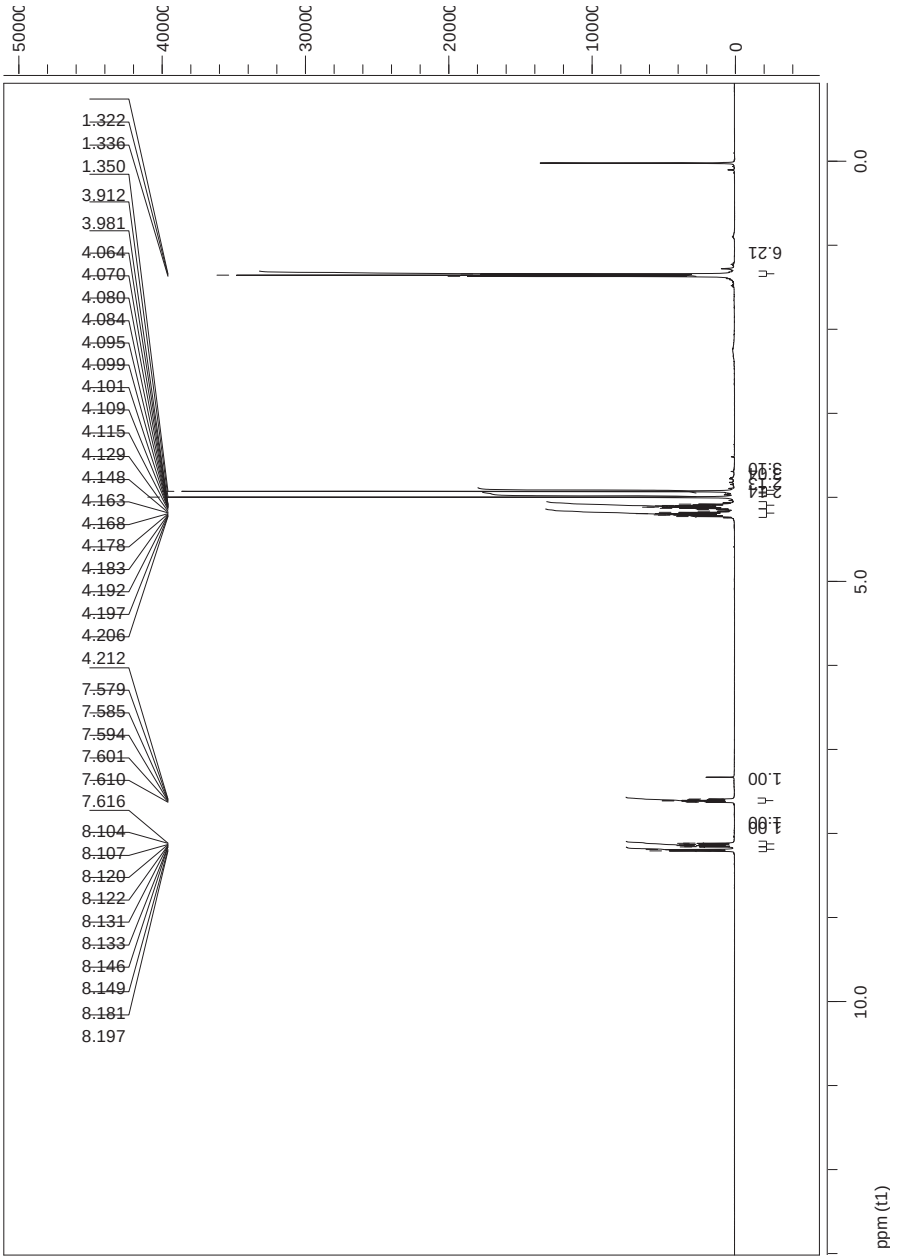
^{31}P NMR spectrum



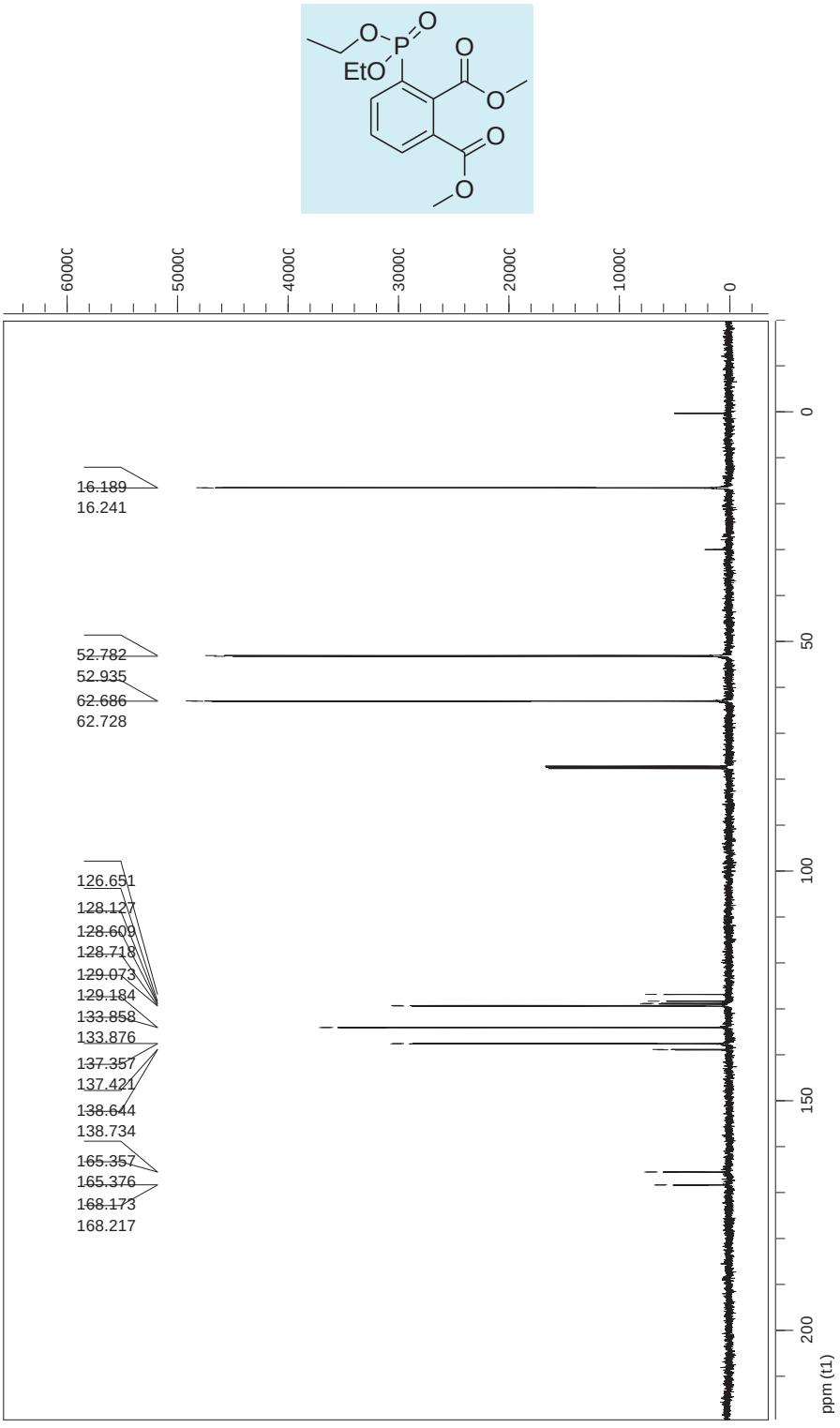
I. Product 10a



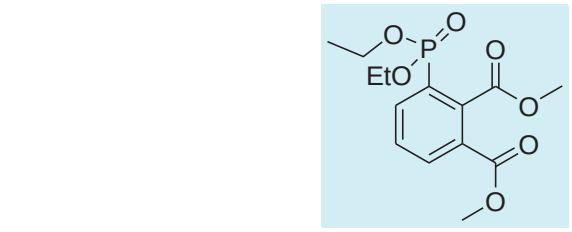
^{1}H NMR spectrum

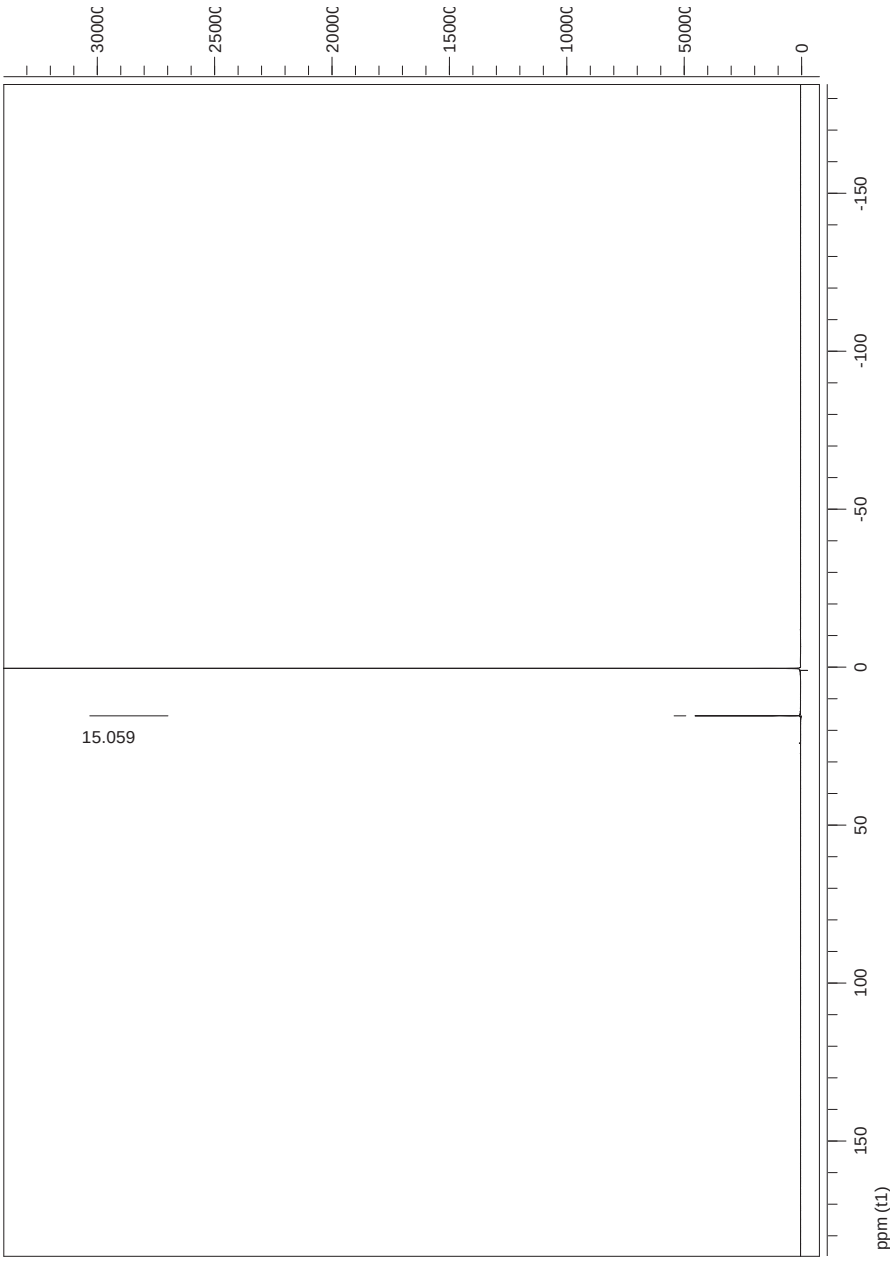


^{13}C NMR spectrum

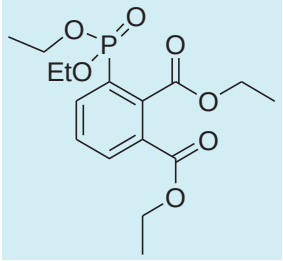


^{31}P NMR spectrum

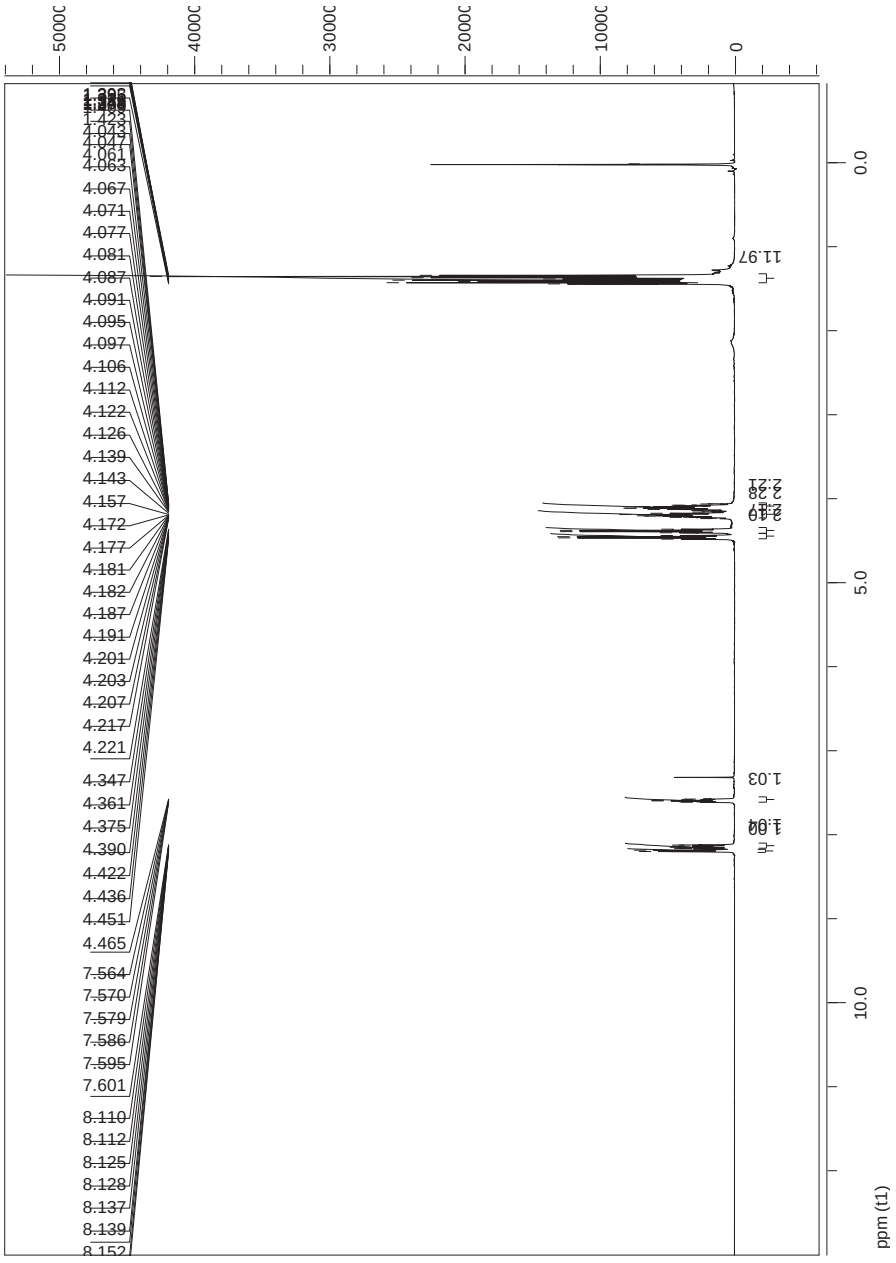


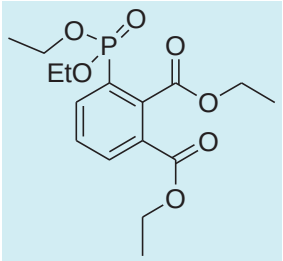


J. Product 10b

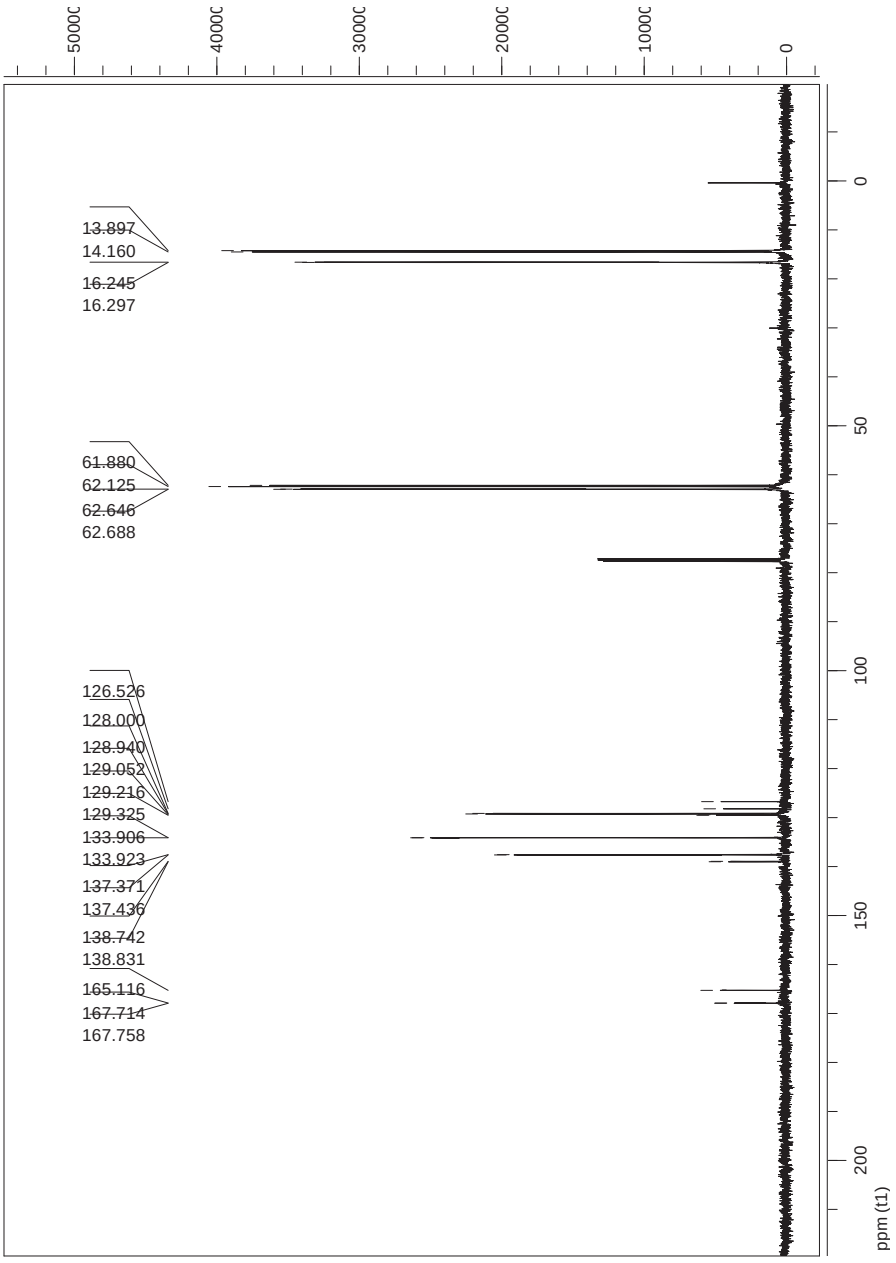


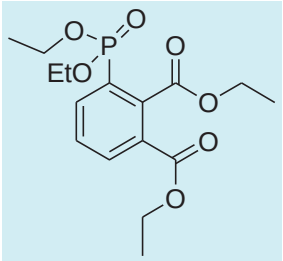
^{1}H NMR spectrum



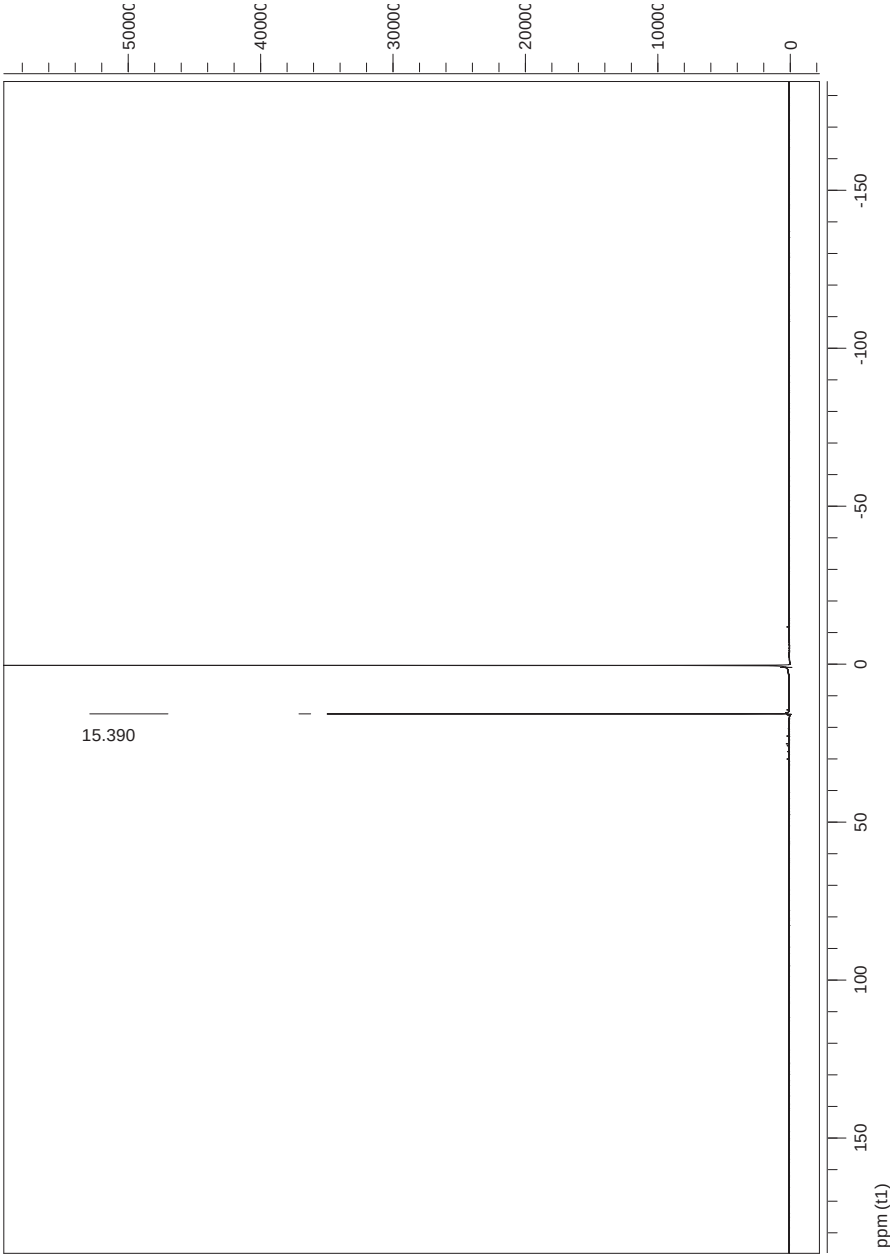


^{13}C NMR spectrum

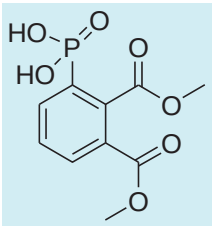




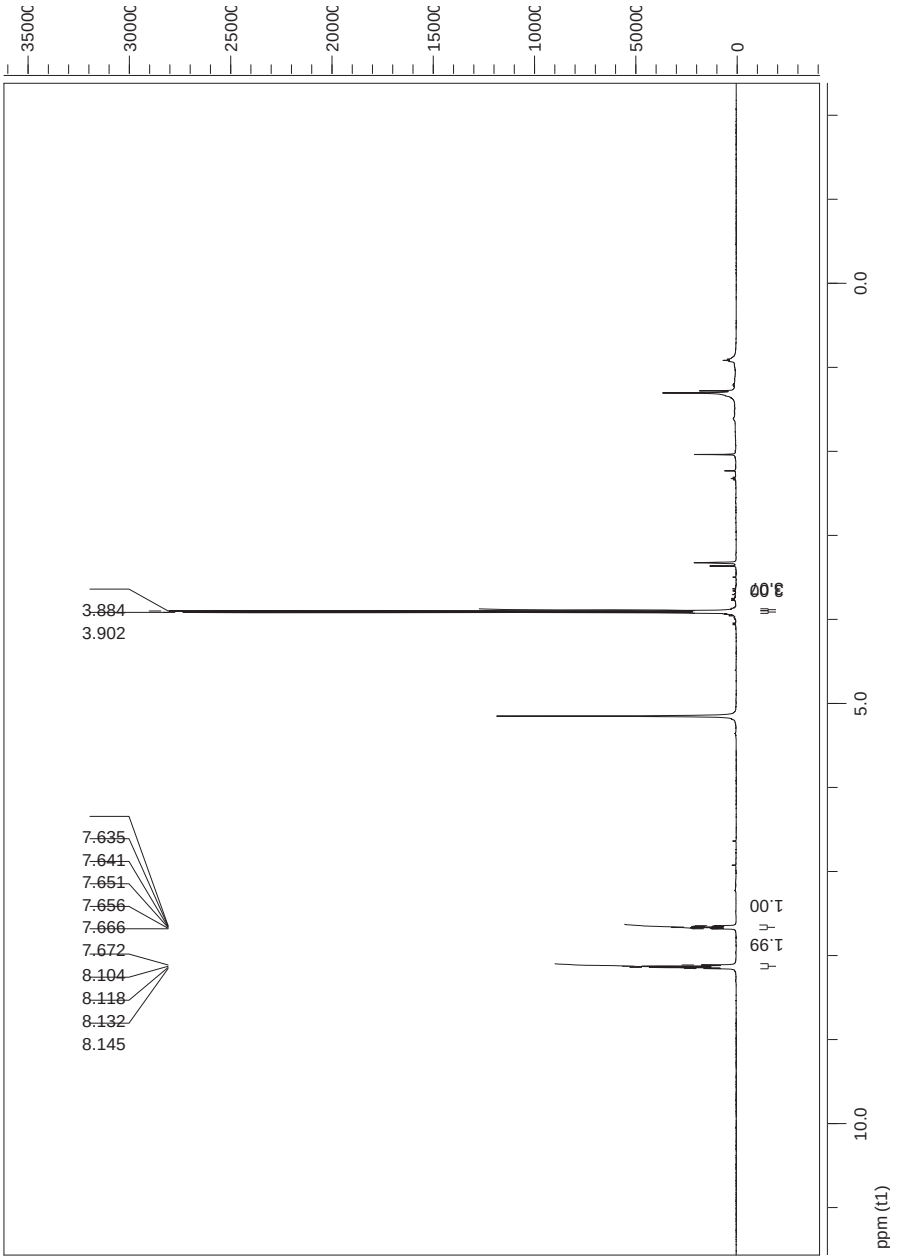
^{31}P NMR spectrum

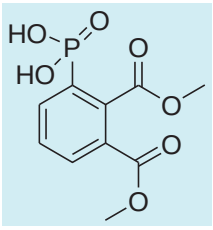


K. Product 11a

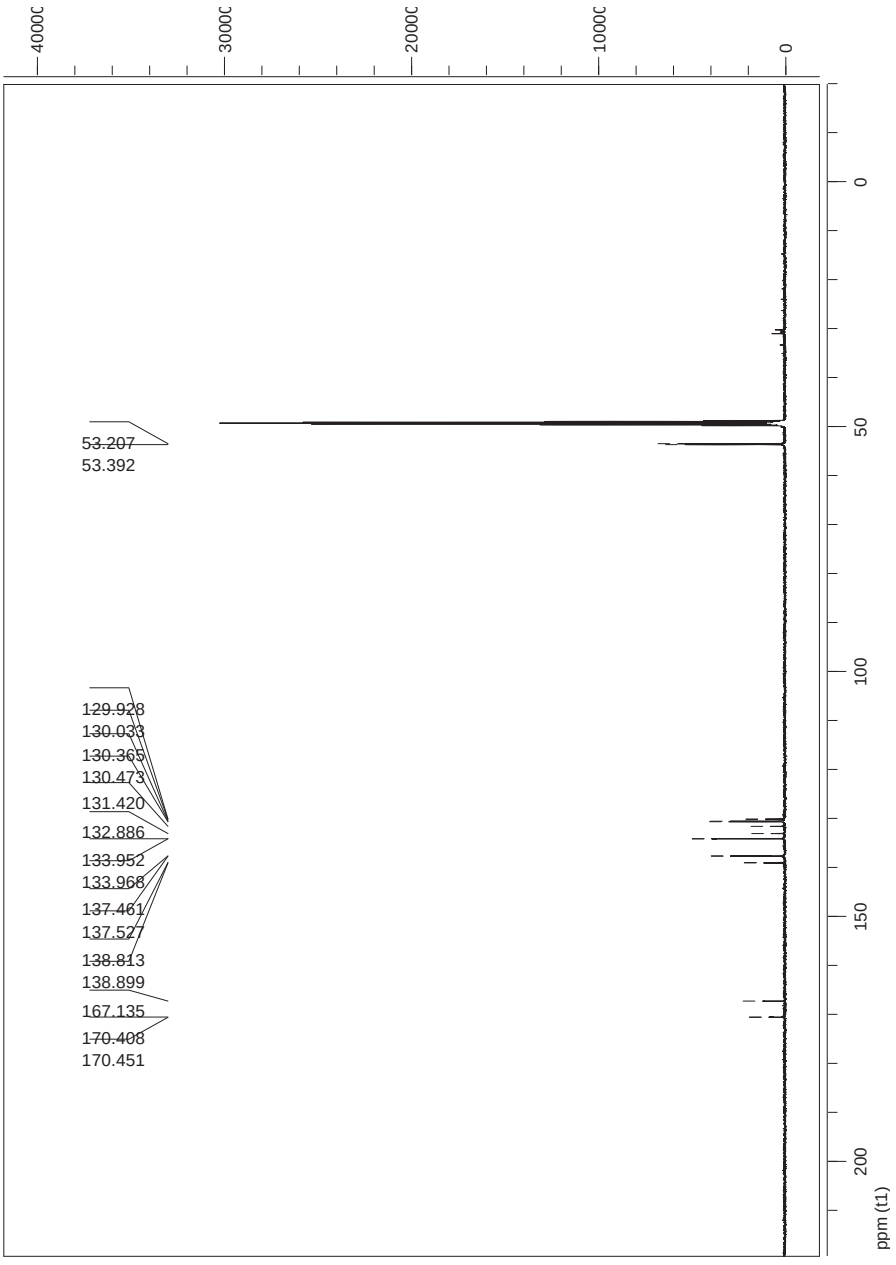


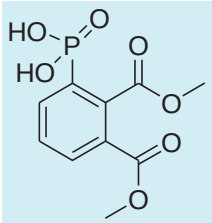
^{1}H NMR spectrum



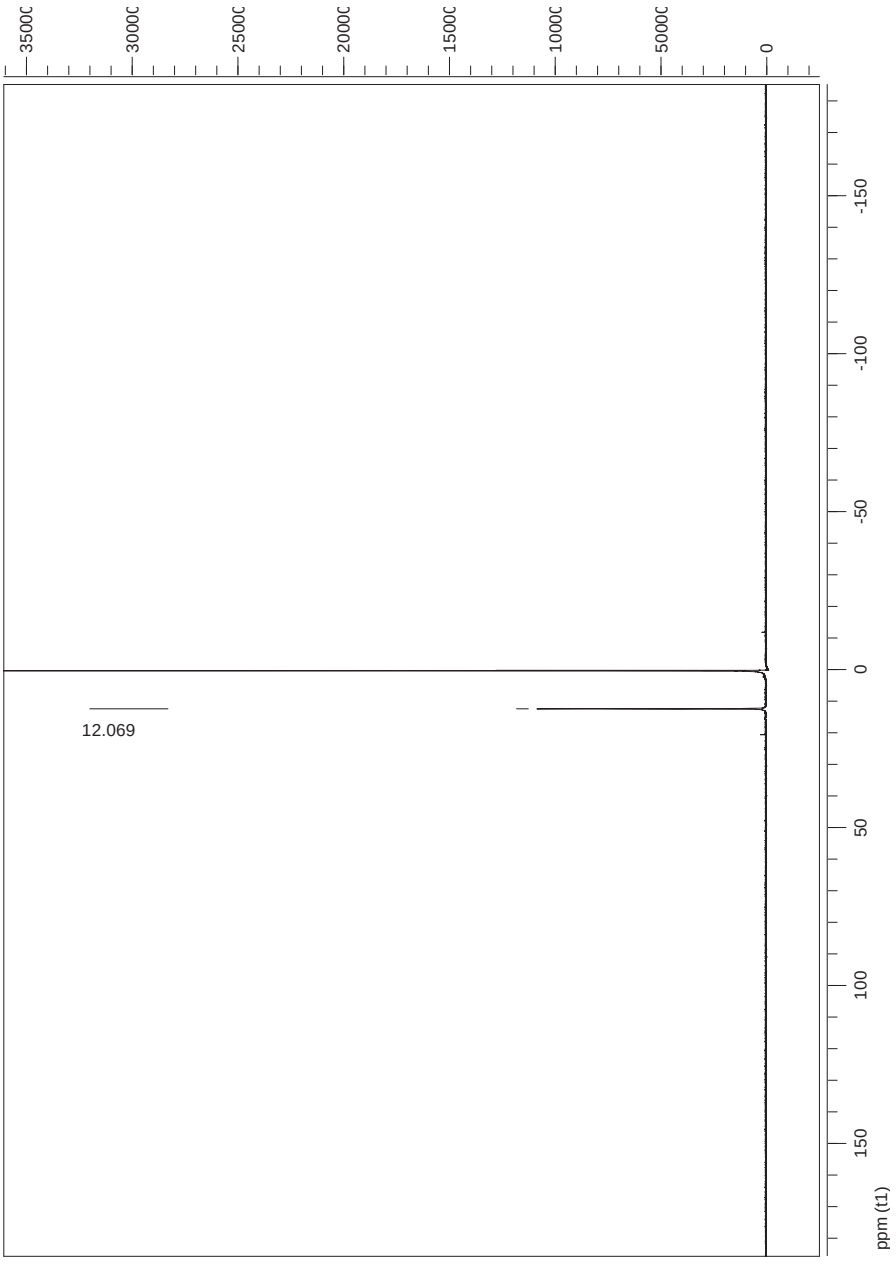


^{13}C NMR spectrum

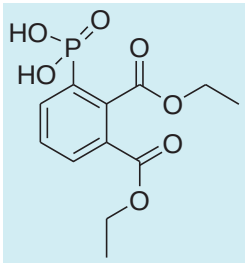




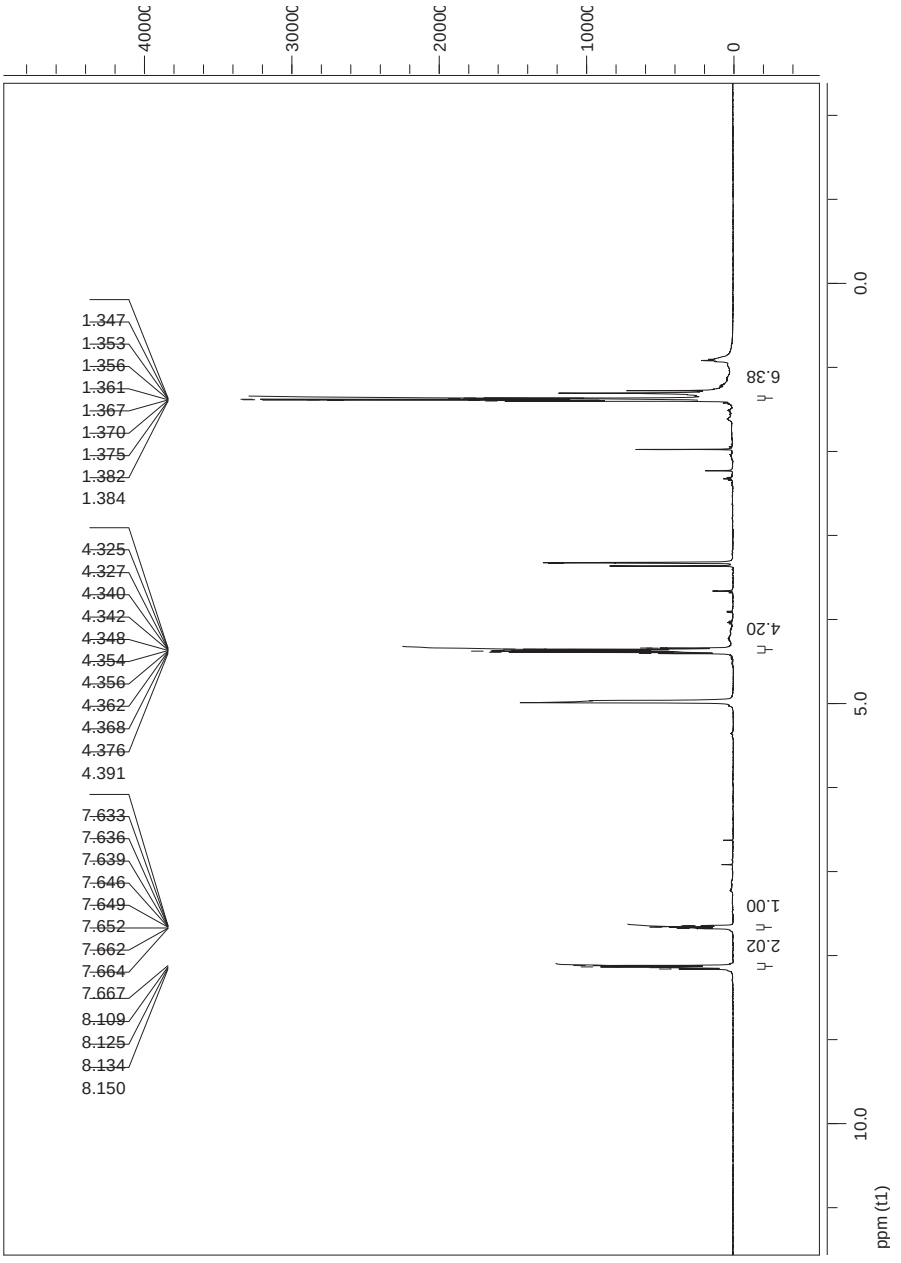
^{31}P NMR spectrum

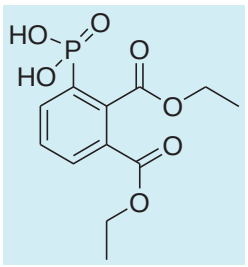


L. Product 11b

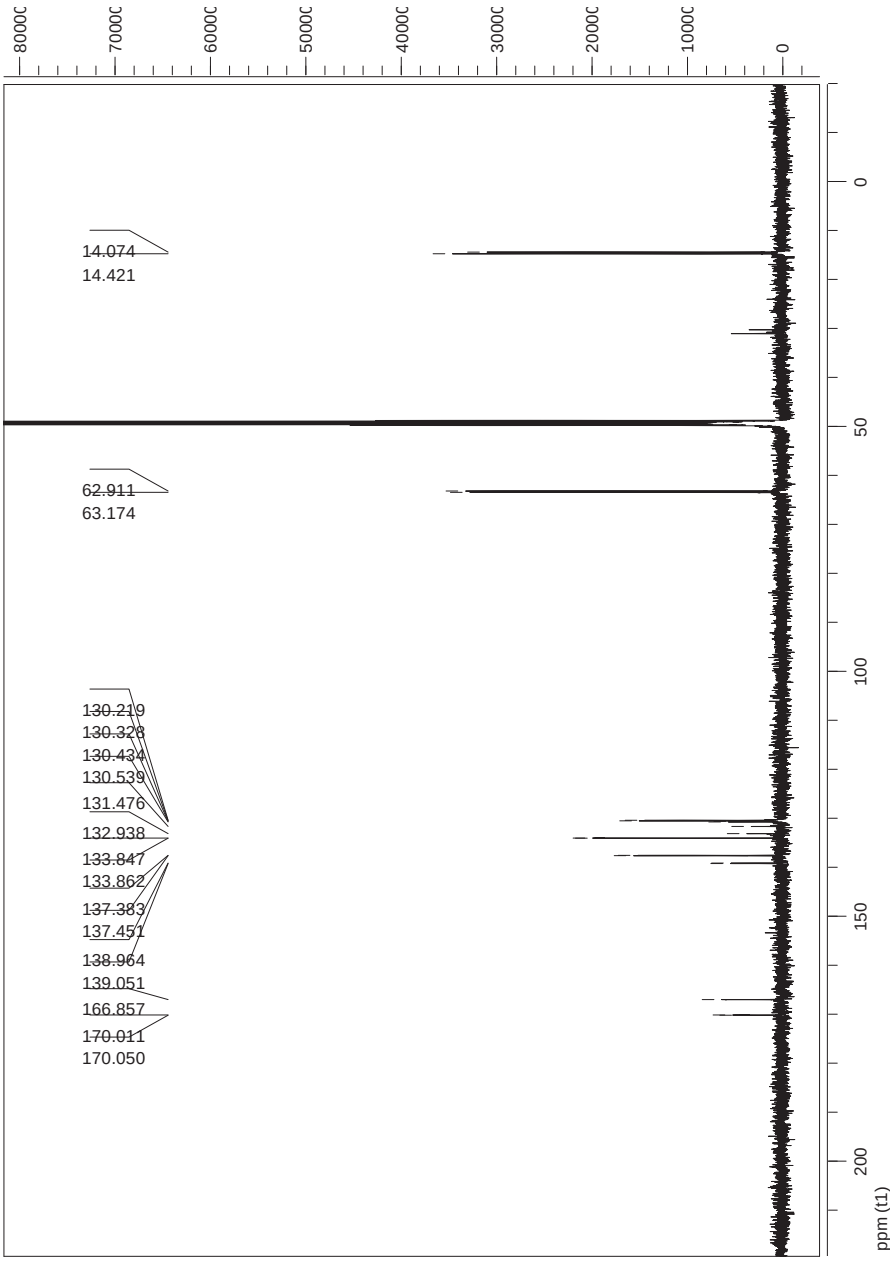


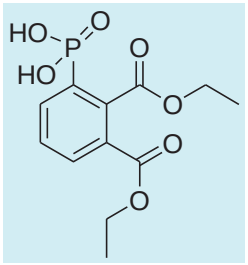
^{1}H NMR spectrum



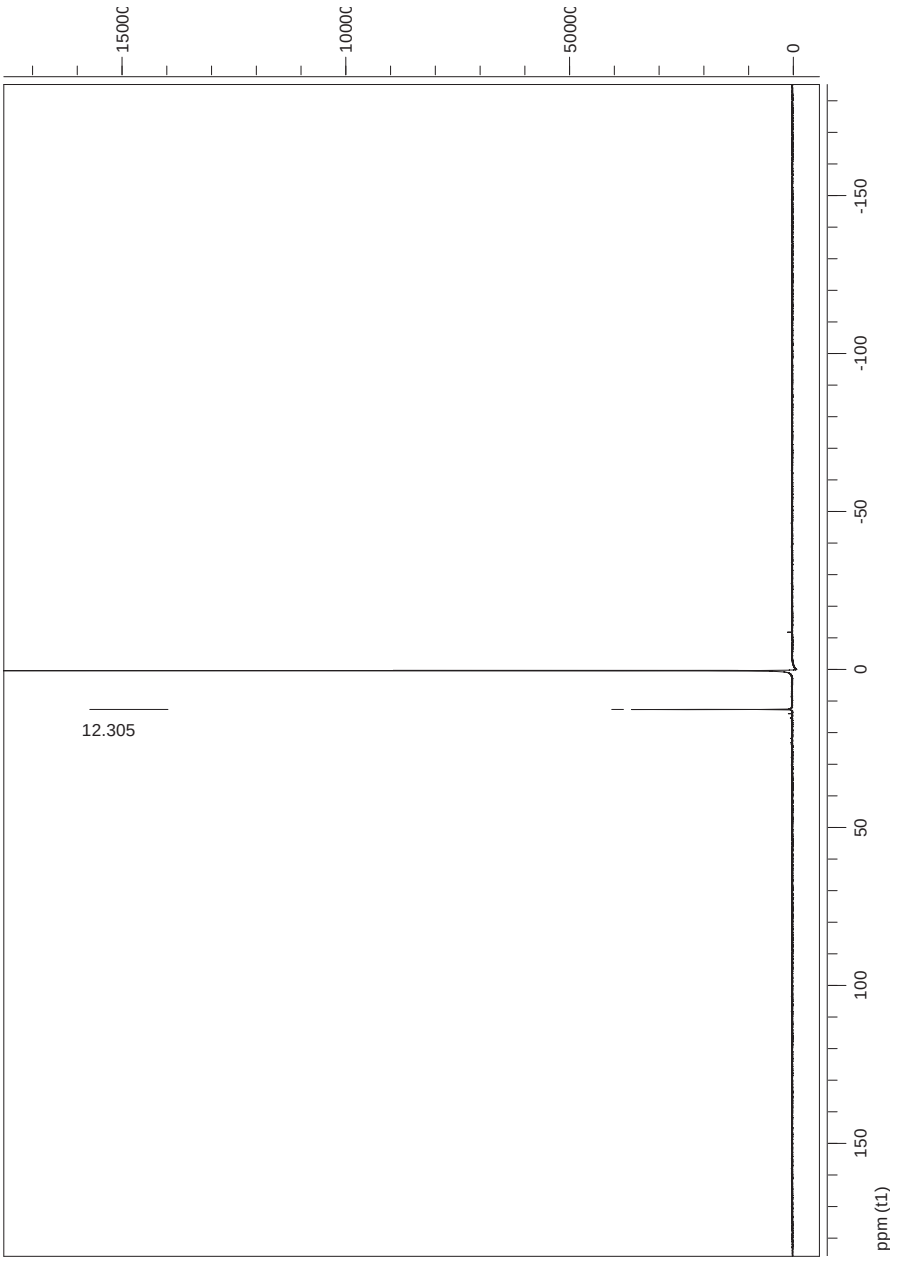


^{13}C NMR spectrum

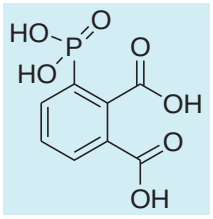




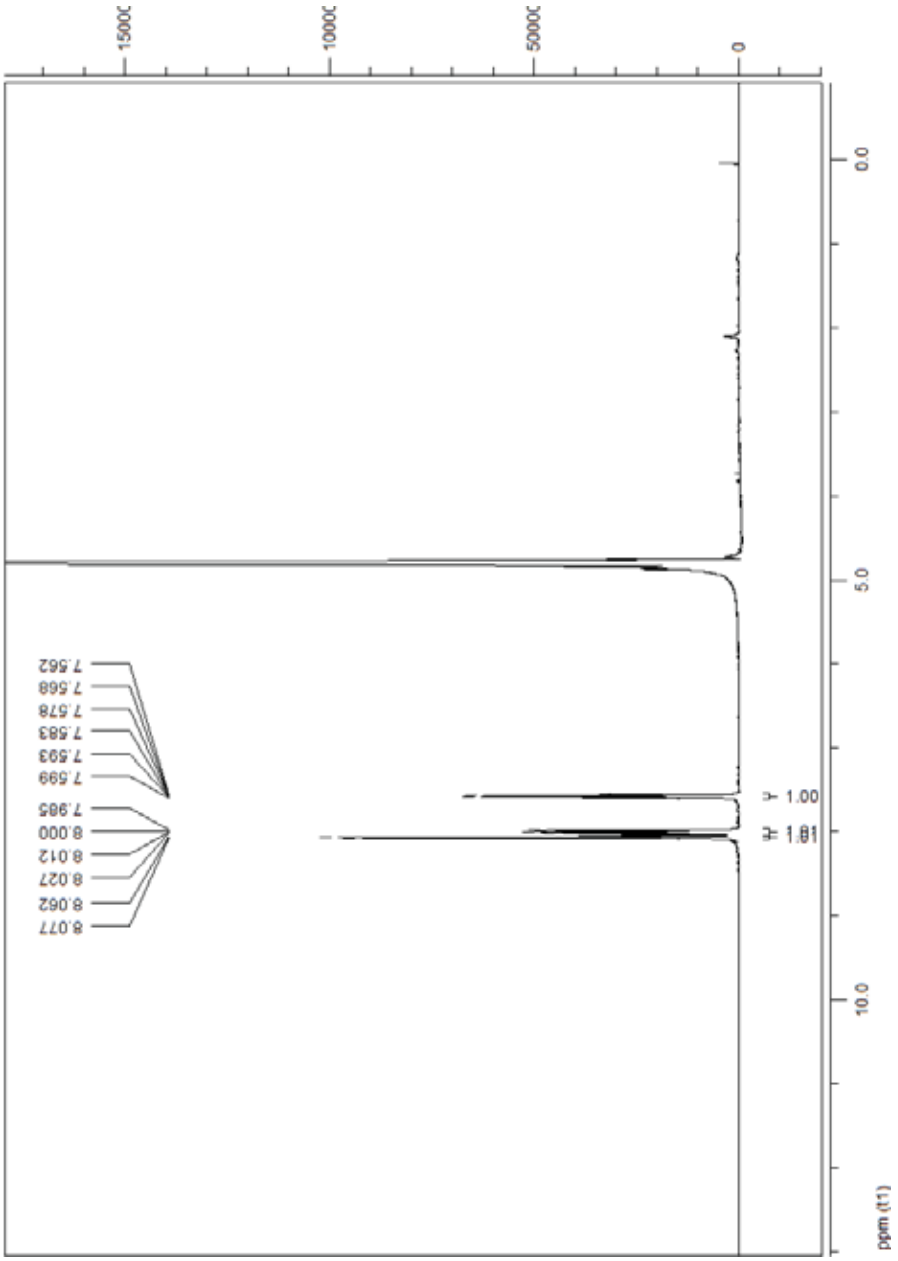
^{31}P NMR spectrum

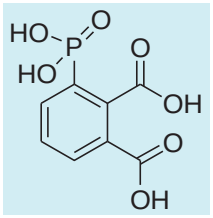


M. Product 12

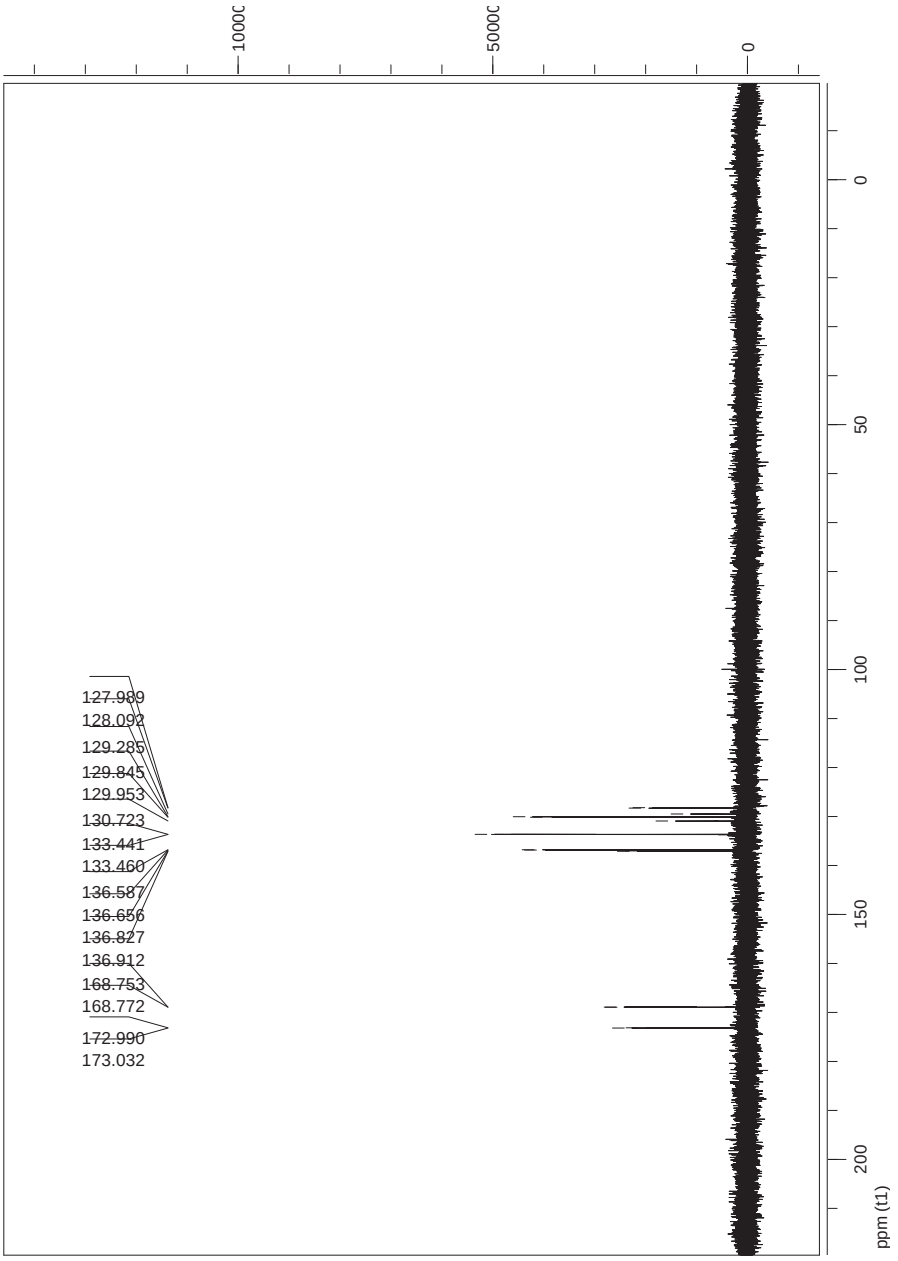


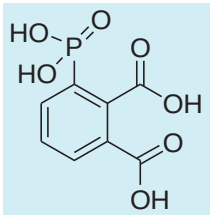
^{1}H NMR spectrum





^{13}C NMR spectrum





^{31}P NMR spectrum