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Electronic Supplementary Information

Brønsted Base-Catalyzed α-Oxygenation of Carbonyl Compounds Utilizing [1,2]-Phospha-Brook Rearrangement

Azusa Kondoh[a] and Masahiro Terada*[a,b]

[a] Research and Analytical Center for Giant Molecules, Graduate School of Science Tohoku University, Aoba-Ku, Sendai 980-8578, Japan

[b] Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-Ku, Sendai 980-8578, Japan

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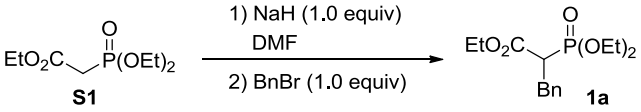
General Information

Unless otherwise noted, the reactions were carried out with dried glassware under argon atmosphere. ^{1}H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECA600 (243 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with 85% H_3PO_4 solution as an external standard (0.0 ppm in $CDCl_3$). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60N (spherical, neutral, 40-50 μm; Kanto Chemical Co., Inc.). High resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T FT-ICR-MS spectrometer at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University.

Materials: Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc., and other commercial suppliers and were used without purification. Dichloromethane, tetrahydrofuran and toluene were supplied from Kanto Chemical Co., Inc. as "Dehydrated solvent system". Other solvents were purchased from commercial suppliers as dehydrated solvents, and used under argon atmosphere.

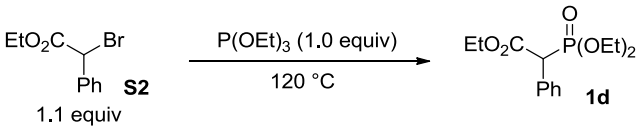
Experimental Procedure

Procedure for Preparation of α-Diethylphosphono Ester 1



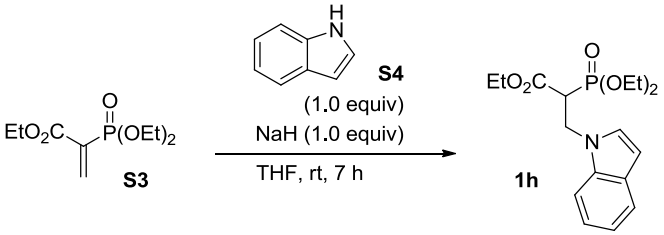
1a, **1c**, **1e**, **1f**, **1g**, **1j** and **1k** were synthesized via deprotonation of ethyl diethylphosphonoacetate (**S1**) by NaH followed by alkylation with the corresponding alkyl halides. For the synthesis of **1i**, THP-protected 4-bromo butan-1-ol was used for alkylation and the deprotection was then performed by treating with ethanol in the presence of a catalytic amount of $TsOH \cdot H_2O$. Synthesis of **1a** is representative. To a suspension of NaH (60%, dispersion in Paraffin Liquid, 0.40 g, 10 mmol) in DMF (20 mL) was added ethyl diethylphosphonoacetate (**S1**, 2.2 g, 10 mmol) dropwise at 0 °C. After stirred for 1 h at 0 °C, benzyl bromide (1.7 g, 10 mmol) was added dropwise. The resulting mixture was then allowed to warm to room temperature and stirred for 24 h. The reaction was quenched with H_2O, and the product was extracted with AcOEt. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (hexane/AcOEt = 1 : 1, twice) to provide **1a** (1.1 g, 3.6 mmol, 36%) as a colorless oil.

Synthesis of **1b** and **1d**



Synthesis of **1d** is representative. The mixture of α-bromophenylacetate (**S2**, 1.6 g, 6.5 mmol) and triethyl phosphite (0.64 g, 6.0 mmol) was heated at 120 °C for 5 h. After cooled to room temperature, the resulting mixture was directly purified by column chromatography (hexane/AcOEt = 1 : 1) to provide **1d** (1.0 g, 3.5 mmol, 58%) as a colorless oil.

Synthesis of **1h**[1]

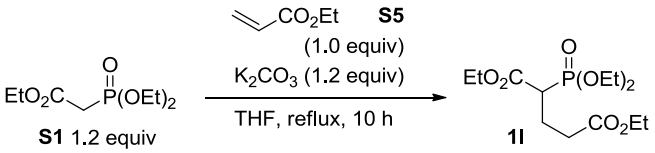


To a suspension of NaH (60%, dispersion in Paraffin liquid, 0.12 g, 3.0 mmol) in THF (8.0 mL) was added indole (**S4**, 0.35 g, 3.0 mmol) at 0 °C. After stirred for 5 min, a solution of vinyl phosphonate **S3** (0.71 g, 3.0 mmol) in THF (2.0 mL) was added dropwise. The resulting mixture was then allowed to warm to room temperature and stirred for 7 h. The reaction was quenched with H_2O, and the product was extracted with AcOEt. The combined

[1] H. Couthon-Gourvès, G. Simon, J.-P. Haelters and B. Corbel, *Synthesis*, 2006, 81.

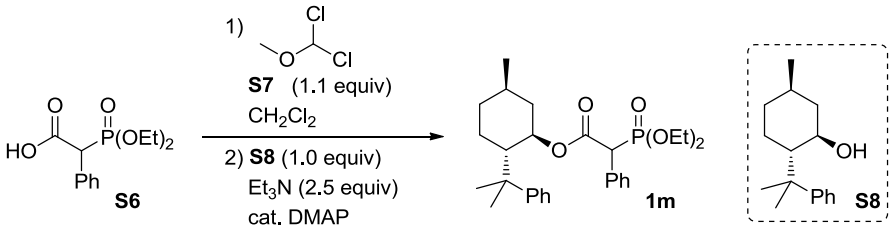
organic layer was dried over Na_2SO_4 and evaporated. The crude mixture was purified by column chromatography (hexane/AcOEt = 1 : 1) to provide **1h** (0.26 g, 0.73 mmol, 24%) as a red oil.

Synthesis of **1l**



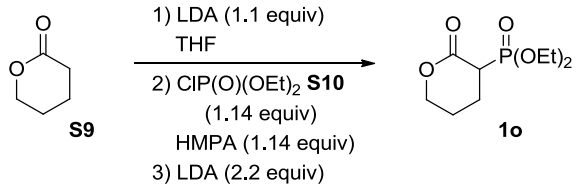
A mixture of **S1** (0.67 g, 3.0 mmol), ethyl acrylate (**S5**, 0.25 g, 2.5 mmol) and K_2CO_3 (0.42 g, 3.0 mmol) in THF (10 mL) was heated at reflux for 10 h. After cooled to room temperature, H_2O was added, and the product was extracted with AcOEt. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (hexane/AcOEt = 1 : 2) to afford **1l** (0.39 g, 1.2 mmol, 48 %) as a colorless oil.

Synthesis of **1m**, **1p** and **6**



1m, **1p** and **6** were synthesized via condensation of the carboxylic acid **S6**, which was formed by saponification of **1d**, and the corresponding alcohols or diethylamine. Synthesis of **1m** is representative. To a solution of **S6** (0.27 g, 1.0 mmol) in CH_2Cl_2 (5.0 mL) was added dichloromethyl methyl ether (**S7**, 0.13 g, 1.1 mmol) at ambient temperature. The mixture was stirred at that temperature for 1 h and then cooled to 0 °C. Et_3N (0.25 g, 2.5 mmol), a solution of alcohol **S8** (0.23 g, 1.0 mmol) in CH_2Cl_2 (1.0 mL), a catalytic amount of DMAP were sequentially added, and the resulting mixture was allowed to warm to room temperature. After stirred for 20 h, the reaction was quenched with H_2O. The product was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (hexane/AcOEt = 1 : 2) to afford **1m** (0.47 g, 0.97 mmol, 97 %) as a colorless oil.

Synthesis of **1n** and **1o**[2]

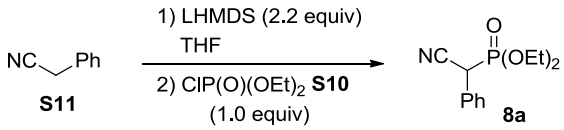


Synthesis of **1o** is representative. δ-Valerolactone (**S9**, 0.50 g, 5.0 mmol) was added to a solution of lithium

[2] J. A. Jackson, G. B. Hammond and D. F. Wiemer, *J. Org. Chem.*, 1989, **54**, 4750.

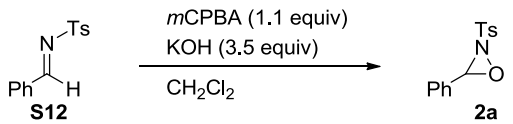
diisopropylamide (LDA, 5.5 mmol) in THF (15 mL) at -78 °C and the mixture was stirred for 45 min. HMPA (1.0 g, 5.7 mmol) and diethyl chlorophosphate (**S10**, 0.98 g, 5.7 mmol) were added, and the resulting mixture was warmed to room temperature, stirred for 45 min and then cooled to -78 °C. A solution LDA (11 mmol) in THF (15 mL) was added and the mixture was stirred at that temperature for 1 h, The mixture was then gradually warmed to room temperature and stirred at room temperature for 2 h. The reaction was quenched with a solution of acetic acid (1.3 g, 22 mmol) in Et_2O (30 mL). The resulting suspension was filtrated, and the filtrate was evaporated. The residue was purified by column chromatography (AcOEt) to provide **1o** (0.70 g, 3.0 mmol, 60 %) as a colorless oil.

Synthesis of **8**[3]



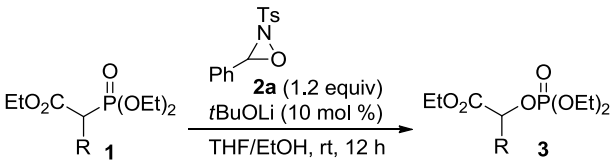
To a solution of LHMDS (1.0 M in THF, 11 mL, 11 mmol) was added phenylacetonitrile (**S11**, 0.59 g, 5.0 mmol) dropwise at -78 °C. After stirred for 30 min, **S10** (0.86 g, 5.0 mmol) was added. The resulting mixture was allowed to warm to 0 °C and stirred for 40 min. The reaction was quenched with 2N HCl aq. and the product was extracted with AcOEt. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (hexane/AcOEt = 1 : 1) to afford **8** (0.92 g, 3.6 mmol, 72 %) as a colorless oil.

Procedure for Preparation of Oxaziridines 2 and 5



Oxaziridines **2** and **5** were synthesized according to the procedure described in the literature.[4,5] Synthesis of **2a** is representative. KOH (1.5 g, 27 mmol) was added to a solution of *m*CPBA (assay 70%, 2.1 g, 8.4 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred vigorously for 5 min. Aldimine **S12** (2.0 g, 7.8 mmol) and CH_2Cl_2 (20 mL) were added, and the mixture was stirred for 25 min. The resulting suspension was then filtrated, and the filtrate was evaporated to yield **2a** (1.8 g, 6.6 mmol, 84%) as a white solid.

Typical Procedure for Brønsted Base-Catalyzed α-Oxygenation of Carbonyl Compounds

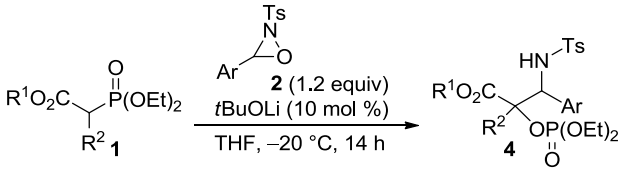


The reaction of **1a** with **2a** is representative (Table 1, entry 13). To a solution of **1a** (47 mg, 0.15 mmol) and **2a** (50

[3] B. Iorga, L. Ricard and P. Savignac, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3311.
[4] J. L. G. Ruano, J. Alemán, C. Fajado and P. Parra, *Org. Lett.*, 2005, **7**, 5493.
[5] F. A. Davis, J. C. Towson, D. B. Vashi, R. ThimmaReddy, J. P. McCauley Jr., M. E. Harakal and D. J. Gosciniak, *J. Org. Chem.*, 1990, **55**, 1254.

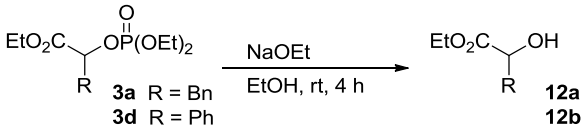
mg, 0.18 mmol) in mixed solvent of THF (1.2 mL) and ethanol (0.30 mL) was added a solution of *t*BuOLi in THF (1.0 M, 15 μL, 0.015 mmol). The resulting mixture was then stirred at room temperature for 12 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (hexane/AcOEt = 1 : 1) to provide **3a** (49 mg, 0.147 mmol, 98%) as a colorless oil.

Procedure for Reaction under Low Temperature Conditions



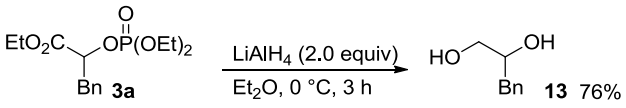
The reaction of **1p** with **2a** is representative (Table 2, entry 2). To a solution of **1p** (36 mg, 0.10 mmol) and **2a** (33 mg, 0.12 mmol) in THF (1.0 mL) was added a solution of *t*BuOLi in THF (1.0 M, 10 μL, 0.010 mmol) at -20 °C. The resulting mixture was then stirred at that temperature for 14 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was dried over Na_2SO_4 and evaporated. The crude mixture was purified by column chromatography (hexane/AcOEt = 1 : 1) to provide a mixture of **4pa** and **3p** (61 mg, **4pa**:**3p** = 95:5, **4pa** 0.092 mmol, 92%**; 3p** 4.8 μmol, 5%) as a colorless oil. In most cases, **4** and **3** were inseparable by silica gel column chromatography and the product was obtained as a mixture of **3** and **4**. Thus, the yield was calculated from the ratio of **3** and **4**, which was determined by ^1H NMR analysis. Further purification by using preparative HPLC enables the isolation of pure **4**.

Procedure for Transformation of 3 into 12 (Scheme 6)



The reaction of **3a** is representative. **3a** (33 mg, 0.10 mmol) was treated with 20% NaOEt solution in EtOH (1.0 mL). After the mixture was stirred at ambient temperature for 4 h, the reaction was quenched with a solution of HCl in Et_2O (2.0 M, 2.0 mL) at 0 ^oC and then H_2O was added. The product was extracted with AcOEt, dried over Na_2SO_4 and evaporated. The residual oil was purified by column chromatography (hexane/AcOEt = 3 : 1) to afford **12a** (17 mg, 0.088 mmol, 88%) as a colorless oil.

Procedure for Reduction of 3a into 13 (Scheme 6)

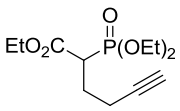


To a solution of **3a** (50 mg, 0.15 mmol) in Et_2O (3.0 mL) was added a solution of $LiAlH_4$ in Et_2O (1.0 M, 0.30 mL, 0.30 mmol) at 0 ^oC. The resulting mixture was stirred at that temperature for 3 h and then H_2O was added. The

product was extracted with AcOEt and washed with brine and 1 M aq. HCl. The combined organic layer was dried over Na_2SO_4 and evaporated. The crude mixture was purified by silica gel column chromatography (hexane/AcOEt = 1 : 2) to provide **13** (17 mg, 0.11 mmol, 76%) as a colorless oil. The reduction of **4da** into **14** were conducted under similar reaction conditions.

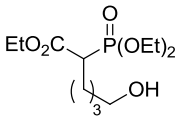
Analytical Data

Ethyl 2-diethylphosphonohex-5-ynoate (1g):



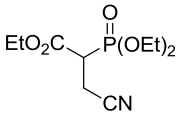
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.30 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 6.6 Hz, 3H), 1.35 (t, J = 6.6 Hz, 3H), 2.00 (t, J = 2.4 Hz, 1H), 2.01-2.12 (m, 1H), 2.17-2.28 (m, 2H), 2.32-2.40 (m, 1H), 3.19 (ddd, J = 23.4, 10.8, 4.2 Hz, 1H), 4.12-4.28 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 16.30 (d, J = 5.7 Hz), 16.33 (d, J = 4.3 Hz), 17.2 (d, J = 14.3 Hz), 25.7 (d, J = 4.2 Hz), 44.2 (d, J = 130.6 Hz), 61.5, 62.7 (d, J = 7.2 Hz), 62.8 (d, J = 7.2 Hz), 69.8, 82.2, 168.6 (d, J = 4.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.8; IR (ATR): 2982, 2938, 1731, 1445, 1369, 1249, 1153, 1017, 963 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{21}O_5P$ $[M+Na]^+$ 299.1019, Found 299.1019.

Ethyl 2-diethylphosphono-6-hydroxyhexanoate (1i):



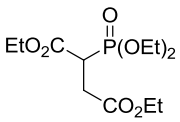
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 6.6 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.37-1.40 (m, 2H), 1.51-1.64 (m, 2H), 1.82-1.92 (m, 1H), 1.93-2.05 (m, 1H), 2.18 (brs, 1H), 2.94 (ddd, J = 22.8, 11.4, 4.2 Hz, 1H), 3.63 (t, J = 6.6 Hz, 2H), 4.09-4.27 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 16.2 (d, J = 5.7 Hz), 16.3 (d, J = 5.7 Hz), 24.5 (d, J = 15.8 Hz), 26.6 (d, J = 4.4 Hz), 32.0, 45.7 (d, J = 130.8 Hz), 61.3, 62.1, 62.6 (d, J = 7.2 Hz), 62.7 (d, J = 5.9 Hz), 169.2 (d, J = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.4; IR (ATR): 3431, 2982, 2934, 2868, 1732, 1445, 1392, 1368, 1237, 1151, 1020, 965 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{25}O_6P$ $[M+Na]^+$ 319.1281, Found 319.1281.

Ethyl 3-cyano-2-diethylphosphonopropanoate (1j):



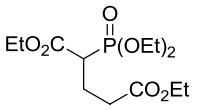
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.33 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 6.6 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H), 2.86 (ddd, J = 16.8, 10.8, 4.8 Hz, 1H), 3.00 (ddd, J = 17.4, 10.8, 10.8 Hz, 1H), 3.29 (ddd, J = 23.4, 9.6, 4.2 Hz, 1H), 4.15-4.23 (m, 4H), 4.25-4.36 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 15.8 (d, J = 2.9 Hz), 16.2 (d, J = 5.9 Hz), 16.3 (d, J = 5.7 Hz), 41.9 (d, J = 130.7 Hz), 62.5, 63.5 (d, J = 7.2 Hz), 63.6 (d, J = 5.9 Hz), 117.1 (d, J = 17.2 Hz), 166.4 (d, J = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.6; IR (ATR): 2984, 2938, 1733, 1369, 1252, 1178, 1095, 1015, 972 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_{18}NO_5P$ $[M+Na]^+$ 286.0815, Found 286.0815.

Diethyl 2-diethylphosphonobutandioate (1k):



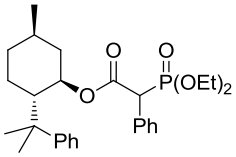
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 2.81 (ddd, J = 17.4, 9.0, 3.0 Hz, 1H), 3.07 (ddd, J = 18.0, 11.4, 7.2 Hz, 1H), 3.45 (ddd, J = 24.0, 11.4, 3.6 Hz, 1H), 4.10-4.30 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 14.1, 16.2 (d, J = 7.2 Hz), 16.3 (d, J = 7.2 Hz), 31.5, 41.2 (d, J = 130.8 Hz), 61.1, 61.7, 62.90 (d, J = 7.2 Hz), 62.94 (d, J = 7.2 Hz), 168.2 (d, J = 5.7 Hz), 171.1 (d, J = 18.8 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 21.9; IR (ATR): 2983, 2910, 1733, 1446, 1370, 1254, 1157, 1093, 1020, 967 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{23}O_7P$ $[M+Na]^+$ 333.1074, Found 333.1074.

Diethyl 2-diethylphosphonopentandioate (1l):



^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 2.16-2.30 (m, 2H), 2.36 (ddd, J = 16.2, 7.8, 7.8 Hz, 1H), 2.45 (ddd, J = 16.2, 8.4, 6.0 Hz, 1H), 3.05 (ddd, J = 23.4, 10.2, 4.8 Hz, 1H), 4.10-4.27 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 14.2, 16.32 (d, J = 5.7 Hz), 16.34 (d, J = 5.7 Hz), 22.3 (d, J = 4.4 Hz), 32.3 (d, J = 14.3 Hz), 44.6 (d, J = 130.7 Hz), 60.5, 61.5, 62.7 (d, J = 5.7 Hz), 62.8 (d, J = 7.2 Hz), 168.7 (d, J = 7.2 Hz), 172.3; ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.6; IR (ATR): 2982, 2910, 1731, 1446, 1370, 1251, 1151, 1094, 1018, 962 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{25}O_7P$ $[M+Na]^+$ 347.1230, Found 347.1230.

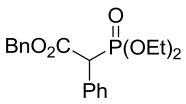
8-Phenylmenthyl 2-diethylphosphono-2-phenylacetate (1m):



60 : 40 diastereomixture

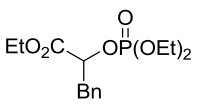
^{1}H NMR (600 MHz, $CDCl_3$) δ 0.70-2.10 (m, 23H), 3.44-3.54 (m, 1H), 3.76-4.14 (m, 4H), 4.75-4.86 (m, 1H), 7.10-7.50 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.1 (d, J = 5.7 Hz), 16.2 (d, J = 5.7 Hz), 16.3 (d, J = 5.9 Hz), 16.4 (d, J = 5.9 Hz), 21.6, 21.7, 24.5, 25.5, 26.5, 26.6, 27.1, 28.1, 31.1, 31.3, 34.4, 34.5, 39.5, 40.0, 40.6, 41.2, 50.2, 50.4, 51.2 (d, J = 129.3 Hz), 52.1 (d, J = 143.7 Hz), 62.8-63.0 (3C), 63.1 (d, J = 5.7 Hz), 75.97, 76.00, 124.9, 125.0, 125.3, 125.6, 127.6, 127.7, 127.9, 128.0, 128.1, 128.4, 129.2 (d, J = 5.9 Hz), 129.9 (d, J = 5.7 Hz), 130.6 (d, J = 8.6 Hz), 131.2 (d, J = 8.6 Hz), 151.5, 151.6, 166.6 (d, J = 4.4 Hz), 167.1; ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.4, 20.0; IR (ATR): 2955, 2925, 1728, 1496, 1455, 1256, 1209, 1148, 1049, 1022, 950 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{39}O_5P$ $[M+Na]^+$ 509.2427, Found 509.2427.

Benzyl 2-diethylphosphono-2-phenylacetate (1p):



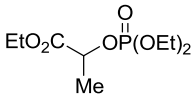
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.14 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H), 3.87-3.95 (m, 1H), 3.96-4.09 (m, 3H), 4.30 (d, J = 23.4 Hz, 1H), 5.15 (d, J = 12.6 Hz, 1H), 5.24 (d, J = 12.6 Hz, 1H), 7.29-7.37 (m, 8H), 7.50-7.55 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.16 (d, J = 5.7 Hz), 16.23 (d, J = 5.7 Hz), 52.2 (d, J = 133.5 Hz), 63.1 (d, J = 7.2 Hz), 63.4 (d, J = 7.2 Hz), 67.4, 128.0 (d, J = 2.9 Hz), 128.2, 128.3, 128.48, 128.52 (d, J = 2.9 Hz), 129.7 (d, J = 5.7 Hz), 130.7 (d, J = 8.7 Hz), 135.3, 167.5 (d, J = 3.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.1; IR (ATR): 2981, 2911, 1737, 1497, 1455, 1380, 1256, 1091, 1022, 888 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{23}O_5P$ $[M+Na]^+$ 385.1175, Found 385.1175.

Ethyl 2-diethylphosphoryloxy-3-phenylpropanoate (3a):



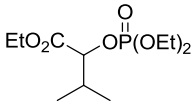
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.13 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H), 3.08 (dd, J = 13.8, 8.4 Hz, 1H), 3.23 (ddd, J = 14.4, 4.2, 2.2 Hz, 1H), 3.71 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 3.77 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.05 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.12 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 5.00 (t, J = 8.4, 4.2, 4.2 Hz, 1H), 7.21-7.32 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 15.89 (d, J = 8.7 Hz), 15.94 (d, J = 7.1 Hz), 39.2 (d, J = 7.2 Hz), 61.5, 63.7 (d, J = 5.7 Hz), 64.0 (d, J = 5.7 Hz), 76.1 (d, J = 5.7 Hz), 127.0, 128.4, 129.5, 135.6, 169.7; ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.5; IR (ATR): 2984, 2936, 1755, 1456, 1372, 1277, 1191, 1094, 1025, 978 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{23}O_6P$ $[M+Na]^+$ 353.1125, Found 353.1124.

Ethyl 2-diethylphosphoryloxypropanoate (3b):



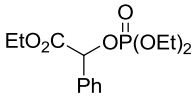
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.30 (t, J = 7.2 Hz, 3H), 1.34 (td, J = 7.2, 1.2 Hz, 3H), 1.35 (td, J = 7.2, 1.2 Hz, 3H), 1.56 (d, J = 7.2 Hz, 3H), 4.09-4.26 (m, 6H), 4.89 (dq, J = 8.4, 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 16.0 (d, J = 7.2 Hz) (2C), 19.2 (d, J = 5.9 Hz), 61.5, 63.9 (d, J = 5.7 Hz), 64.1 (d, J = 5.9 Hz), 71.7 (d, J = 5.9 Hz), 170.6 (d, J = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.3; IR (ATR): 2959, 2874, 1730, 1508, 1460, 1397, 1254, 1121, 1008 cm^{-1}; HRMS (ESI) Calcd for $C_9H_{19}O_6P$ $[M+Na]^+$ 277.0812, Found 277.0811.

Ethyl 2-diethylphosphoryloxy-3-methylbutanoate (3c):



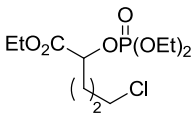
^{1}H NMR (600 MHz, $CDCl_3$) δ 0.97 (d, J = 7.2 Hz, 3H), 1.04 (d, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.34 (td, J = 7.2, 1.2 Hz, 3H), 1.35 (td, J = 7.2, 1.2 Hz, 3H), 2.23 (m, 1H), 4.09-4.29 (m, 6H), 4.61 (dd, J = 8.4, 4.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.2, 16.0 (d, J = 5.7 Hz), 16.1 (d, J = 7.2 Hz), 16.7, 18.5, 31.6 (d, J = 7.1 Hz), 61.2, 63.9 (d, J = 5.9 Hz), 64.1 (d, J = 5.7 Hz), 79.9 (d, J = 5.7 Hz), 169.8; ^{31}P NMR (243 MHz, $CDCl_3$) δ –0.8; IR (ATR): 2979, 2937, 2911, 1755, 1469, 1393, 1278, 1025, 979 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{23}O_6P$ $[M+Na]^+$ 305.1125, Found 305.1125.

Ethyl 2-diethylphosphoryloxy-2-phenylacetate (3d)[6]:



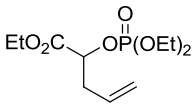
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.19 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 3.91-4.01 (m, 2H), 4.13-4.27 (m, 4H), 5.74 (d, J = 9.0 Hz, 1H), 7.33-7.42 (m, 3H), 7.45-7.50 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 15.8 (d, J = 7.2 Hz), 16.0 (d, J = 7.2 Hz), 61.8, 64.0 (d, J = 5.7 Hz), 64.3 (d, J = 5.7 Hz), 76.7 (d, J = 4.2 Hz), 127.2, 128.7, 129.2, 135.1 (d, J = 5.9 Hz), 168.8 (d, J = 5.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.4.

Ethyl 5-chloro-2-diethoxyphosphoryloxypentanoate (3e):



^{1}H NMR (600 MHz, $CDCl_3$) δ 1.30 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 1.86-2.12 (m, 4H), 3.58 (t, J = 6.0 Hz, 2H), 4.09-4.30 (m, 6H), 4.83 (ddd, J = 7.8, 7.8, 4.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 15.99 (d, J = 7.2 Hz), 16.04 (d, J = 5.9 Hz), 27.6, 30.3 (d, J = 7.2 Hz), 44.1, 61.6, 64.1 (d, J = 5.9 Hz), 64.2 (d, J = 5.7 Hz), 74.5 (d, J = 5.9 Hz), 169.8 (d, J = 2.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.1; IR (ATR): 2983, 2912, 2384, 1755, 1445, 1371, 1262, 1199, 1020 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{22}ClO_6P$ $[M+Na]^+$ 339.0735, Found 339.0735.

Ethyl 2-diethylphosphoryloxypent-4-enoate (3f)[7]:

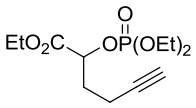


^{1}H NMR (600 MHz, $CDCl_3$) δ 1.29 (t, J = 7.2 Hz, 3H), 1.33 (td, J = 7.2, 0.6 Hz, 3H), 1.35 (td, J = 7.2, 0.6 Hz, 3H), 2.58-2.70 (m, 2H), 4.07-4.28 (m, 6H), 4.86 (ddd, J = 8.4, 7.2, 5.4 Hz, 1H), 5.15 (d, J = 10.2 Hz, 1H), 5.18 (dd, J = 17.4, 1.2 Hz, 1H), 5.81 (dddd, J = 17.4, 10.2, 7.2, 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 15.96 (d, J = 7.2 Hz), 15.98 (d, J = 7.2 Hz), 37.4 (d, J = 7.2 Hz),

[6] A. Baeza,C. Nájera, J. M. Sansano and J. M. Saá, *Chem. Eur. J.*, 2005, **11**, 3849.
[7] A. Kondoh and M. Terada, *Org. Lett.*, 2013, **15**, 4568.

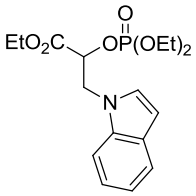
61.5, 64.0 (d, J = 5.9 Hz), 64.2 (d, J = 5.7 Hz), 74.6 (d, J = 4.4 Hz), 119.1, 131.5, 169.5 (d, J = 4.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.3.

Ethyl 2-diethylphosphoryloxyhex-5-ynoate (3g):



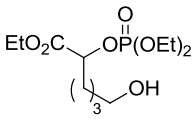
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.30 (t, J = 7.2 Hz, 3H), 1.34 (td, J = 7.2, 1.2 Hz, 3H), 1.36 (td, J = 7.2, 1.2 Hz, 3H), 2.01 (t, J = 2.4 Hz, 1H), 2.02-2.16 (m, 2H), 2.32-2.44 (m, 2H), 4.10-4.28 (m, 6H), 4.90 (ddd, J = 7.8, 7.8, 4.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 14.2, 16.01 (d, J = 5.7 Hz), 16.05 (d, J = 7.2 Hz), 32.0 (d, J = 5.9 Hz), 61.6, 64.1 (d, J = 5.9 Hz), 64.2 (d, J = 5.9 Hz), 69.6, 73.9 (d, J = 5.7 Hz), 82.2, 169.8 (d, J = 2.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.1; IR (ATR): 2984, 2940, 2911, 1738, 1473, 1373, 1262, 1185, 1021, 985 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{21}O_6P$ $[M+Na]^+$ 315.0968, Found 315.0968.

Ethyl 2-diethylphosphoryloxy-3-(1-indolyl)propanoate (3h):



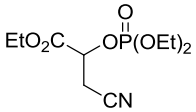
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.06 (td, J = 7.2, 1.2 Hz, 3H), 1.22 (td, J = 7.2, 1.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H), 3.62 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 3.72 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 3.99 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.08 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.14-4.25 (m, 2H), 4.52 (dd, J = 15.0, 7.2 Hz, 1H), 4.61 (ddd, J = 15.0, 4.2, 2.4 Hz, 1H), 5.12 (ddd, J = 8.4, 8.4, 4.2 Hz, 1H), 6.51 (d, J = 3.6 Hz, 1H), 7.10 (dd, J = 7.2, 7.2 Hz, 1H), 7.14 (d, J = 3.6 Hz, 1H), 7.22 (dd, J = 7.8, 7.8 Hz, 1H), 7.40 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 15.7 (d, J = 7.2 Hz), 15.9 (d, J = 7.2 Hz), 48.1 (d, J = 7.1 Hz), 62.2, 63.9 (d, J = 5.7 Hz), 64.3 (d, J = 5.4 Hz), 74.5 (d, J = 5.7 Hz), 102.3, 109.2, 119.8, 121.0, 121.9, 128.2, 128.6, 136.1, 168.1 (d, J = 2.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.5; IR (ATR): 2983, 2935, 1757, 1467, 1370, 1264, 1208, 1098, 1023, 972 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{24}NO_6P$ $[M+Na]^+$ 392.1233, Found 392.1233.

Ethyl 2-diethoxyphosphoryloxy-6-hydroxyhexanoate (3i):



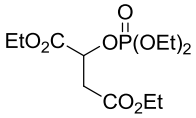
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.30 (td, J = 7.2, 1.2 Hz, 3H), 1.341 (t, J = 7.2 Hz, 3H), 1.343 (td, J = 7.2, 1.2 Hz, 3H), 1.47-1.70 (m, 4H), 1.87-1.94 (m, 3H), 3.60-3.70 (m, 2H), 4.10-4.28 (m, 6H), 4.77-4.82 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 16.01 (d, J = 7.1 Hz), 16.04 (d, J = 5.9 Hz), 20.8, 31.9, 32.7 (d, J = 5.9 Hz), 61.5, 62.3, 64.1 (d, J = 5.7 Hz), 64.2 (d, J = 5.7 Hz), 75.1 (d, J = 5.7 Hz), 170.2 (d, J = 3.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.1; IR (ATR): 3438, 2983, 2936, 2870, 1755, 1446, 1371, 1262, 1096, 1022, 983 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{25}O_7P$ $[M+Na]^+$ 335.1230, Found 335.1230.

Ethyl 3-cyano-2-diethylphosphoryloxypropanoate (3j):



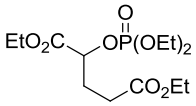
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.34 (t, J = 7.2 Hz, 3H), 1.376 (td, J = 7.2, 1.2 Hz, 3H), 1.378 (td, J = 7.2, 1.2 Hz, 3H), 2.98 (dd, J = 16.8, 6.6 Hz, 1H), 3.03 (dd, J = 16.8, 4.8 Hz, 1H), 4.16-4.28 (m, 4H), 4.28-4.35 (m, 2H), 5.04 (ddd, J = 9.0, 6.0, 4.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 15.97 (d, J = 7.2 Hz), 16.01 (d, J = 5.7 Hz), 22.5 (d, J = 5.7 Hz), 62.8, 64.7 (d, J = 5.9 Hz), 64.8 (d, J = 5.7 Hz), 70.2 (d, J = 5.9 Hz), 115.1, 167.1 (d, J = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.8; IR (ATR): 2983, 1746, 1469, 1382, 1238, 1092, 981, 888 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_{18}NO_6P$ $[M+Na]^+$ 302.0764, Found 302.0764.

Diethyl 2-diethylphosphoryloxybutanedioate (3k):



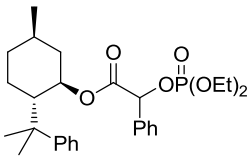
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.33 (td, J = 7.2, 1.2 Hz, 3H), 1.36 (td, J = 7.2, 1.2 Hz, 3H), 2.93 (d, J = 6.6 Hz, 2H), 4.07-4.30 (m, 8H), 5.17 (ddd, J = 9.0, 6.0, 6.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 14.1, 16.0 (d, J = 7.2 Hz) (2C), 38.1 (d, J = 5.7 Hz), 61.1, 61.9, 64.1 (d, J = 5.7 Hz), 64.3 (d, J = 5.7 Hz), 71.7 (d, J = 5.9 Hz), 168.9, 169.0 (d, J = 4.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.4; IR (ATR): 2984, 2940, 1737, 1447, 1374, 1239, 1178, 1094, 1019, 982 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{23}O_8P$ $[M+Na]^+$ 349.1023, Found 349.1022.

Diethyl 2-diethylphosphoryloxypentanedioate (3l):



^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 2.11-2.18 (m, 1H), 2.22-2.30 (m, 1H), 2.40-2.55 (m, 2H), 4.10-4.27 (m, 8H), 4.84 (ddd, J = 7.8, 7.8, 4.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 14.2, 16.0 (d, J = 5.7 Hz), 16.1 (d, J = 7.2 Hz), 28.2 (d, J = 7.2 Hz), 29.2, 60.6, 61.7, 64.1 (d, J = 5.9 Hz), 64.2 (d, J = 5.9 Hz), 74.2 (t, J = 5.7 Hz), 169.7 (d, J = 3.0 Hz), 172.3; ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.1; IR (ATR): 2983, 2914, 1733, 1445, 1373, 1238, 1180, 1094, 1019 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{25}O_8P$ $[M+Na]^+$ 363.1179, Found 363.1179.

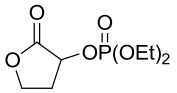
8-Phenylmenthyl 2-diethoxyphosphoryloxy-2-phenylacetate (3m):



Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.66-0.75 (m, 1H), 0.80 (s, 3H), 0.80-0.90 (m, 1H), 0.84 (d, J = 6.6 Hz, 3H), 1.02 (s, 3H), 1.03-1.08 (m, 1H), 1.15 (t, J = 7.2 Hz, 3H), 1.19-1.25 (m, 1H), 1.36 (t, J = 7.2 Hz, 3H), 1.35-1.50 (m, 2H), 1.75-1.82 (m, 1H), 1.98-2.06 (m, 1H), 3.85-3.97 (m, 2H), 4.13-4.26 (m, 2H), 4.79 (ddd, J = 10.8, 10.8, 4.2 Hz, 1H), 5.61 (d, J = 9.0 Hz, 1H), 7.08 (d, J = 7.2 Hz, 2H), 7.11 (dd, J = 7.2, 7.2 Hz, 1H), 7.20 (dd, J = 8.4, 7.2 Hz, 2H), 7.32-7.40 (m, 3H), 7.49 (d, J = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.1 Hz), 16.0 (d, J = 7.1 Hz), 21.6, 23.0, 27.3, 30.2, 31.3, 34.3, 40.1, 41.5, 50.4, 63.9 (d, J = 5.7 Hz), 64.2 (d, J = 5.7 Hz), 77.32, 77.33 (d, J = 4.4 Hz), 125.3, 125.7, 127.9, 128.0, 128.6, 129.4, 134.5 (d, J = 4.4 Hz), 149.7, 167.9 (d, J = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.4; IR (ATR): 2955, 2922, 2871, 1747, 1456, 1370, 1267, 1174, 1092, 1022, 964 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{39}O_6P$ $[M+Na]^+$ 525.2377, Found 525.2376.

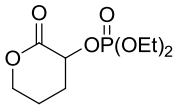
Minor diatereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.53-0.62 (m, 1H), 0.76 (d, J = 5.4 Hz, 3H), 0.74-0.82 (m, 1H), 1.03-1.12 (m, 1H), 1.20 (td, J = 7.2, 1.2 Hz, 3H), 1.21 (s, 3H), 1.32 (s, 3H), 1.37 (td, J = 7.2, 1.2 Hz, 3H), 1.37-1.44 (m, 1H), 1.56-1.66 (m, 2H), 1.68-1.74 (m, 1H), 1.92-2.00 (m, 1H), 3.89-4.01 (m, 2H), 4.15-4.29 (m, 2H), 4.78 (ddd, J = 10.8, 10.8, 4.8 Hz, 1H), 5.00 (d, J = 9.0 Hz, 1H), 7.10-7.15 (m, 2H), 7.21-7.25 (m, 1H), 7.26-7.30 (m, 3H), 7.30-7.34 (m, 2H), 7.38 (dd, J = 7.2, 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9 (d, J = 7.2 Hz), 16.1 (d, J = 7.2 Hz), 21.6, 24.4, 26.4, 28.2, 31.1, 34.4, 39.5, 40.4, 50.4, 63.8 (d, J = 5.9 Hz), 64.1 (d, J = 5.7 Hz), 76.2 (d, J = 4.4 Hz), 76.3, 125.2, 125.5, 127.1, 128.1, 128.4, 128.8, 135.2 (d, J = 5.7 Hz), 151.8, 167.9 (d, J = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.6.

2-Diethoxyphosphoryloxy-4-butanolide (3n):



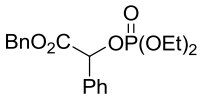
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.37 (td, J = 7.2, 1.2 Hz, 3H), 1.38 (td, J = 7.2, 1.2 Hz, 3H), 2.41-2.49 (m, 1H), 2.70-2.76 (m, 1H), 4.14-4.20 (m, 2H), 4.21-4.29 (m, 3H), 4.47 (ddd, J = 8.4, 8.4, 3.0 Hz, 1H), 5.05 (ddd, J = 9.6, 9.6, 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.98 (d, J = 5.7 Hz), 16.00 (d, J = 7.2 Hz), 30.2, 64.4 (d, J = 5.7 Hz), 64.67, 64.69 (d, J = 7.2 Hz), 70.7 (d, J = 5.7 Hz), 172.2 (d, J = 8.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.1; IR (ATR): 2985, 2919, 1792, 1755, 1445, 1394, 1262, 1100, 1017, 904 cm^{-1}; HRMS (ESI) Calcd for $C_8H_{15}O_6P$ [M+Na]$^+$ 261.0499, Found 261.0499.

2-Diethoxyphosphoryloxy-5-pentanolide (3o):



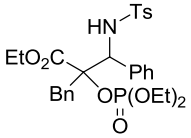
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.35 (t, J = 7.2 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H), 1.97-2.12 (m, 3H), 2.44-2.53 (m, 1H), 4.11-4.19 (m, 2H), 4.21-4.31 (m, 2H), 4.33-4.36 (m, 2H), 4.97 (ddd, J = 10.8, 10.8, 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.99 (d, J = 7.2 Hz), 16.01 (d, J = 5.7 Hz), 21.1, 26.9 (d, J = 4.4 Hz), 64.2 (d, J = 5.7 Hz), 64.7 (d, J = 5.7 Hz), 68.2, 70.8 (d, J = 4.4 Hz), 168.8 (d, J = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.2; IR (ATR): 2983, 2926, 1756, 1447, 1395, 1264, 1029 cm^{-1}; HRMS (ESI) Calcd for $C_9H_{17}O_6P$ [M+Na]$^+$ 275.0655, Found 275.0655.

Benzyl 2-diethoxyphosphoryloxy-2-phenylacetate (3p):



^{1}H NMR (600 MHz, $CDCl_3$) δ 1.17 (td, J = 7.2, 1.2 Hz, 3H), 1.30 (td, J = 7.2, 1.2 Hz, 3H), 3.89-4.00 (m, 2H), 4.10-4.22 (m, 2H), 5.16 (d, J = 12.0 Hz, 1H), 5.18 (d, J = 12.0 Hz, 1H), 5.80 (d, J = 8.4 Hz, 1H), 7.19-7.24 (m, 2H), 7.27-7.32 (m, 3H), 7.34-7.39 (m, 3H), 7.43-7.49 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9 (d, J = 5.9 Hz), 16.0 (d, J = 5.7 Hz), 64.0 (d, J = 5.7 Hz), 64.3 (d, J = 5.7 Hz), 67.3, 76.7 (d, J = 4.2 Hz), 127.2, 128.0. 128.3, 128.5, 128.7, 129.3, 134.9 (d, J = 6.0 Hz), 135.1, 168.7 (d, J = 6.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.4; IR (ATR): 2979, 2917, 1738, 1456, 1383, 1271, 1236, 1089, 888 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{23}O_6P$ [M+Na]$^+$ 401.1125, Found 401.1124.

Ethyl 2-benzyl-2-diethoxyphosphoryloxy-3-phenyl-3-(*N*-tosylamino)propioate (4aa):

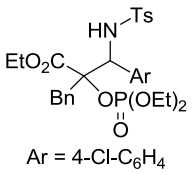


Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.04 (td, J = 7.2, 1.2 Hz, 3H), 1.19 (td, J = 7.2, 1.2 Hz, 3H), 1.42 (t, J = 7.2 Hz, 3H), 2.26 (s, 3H), 2.81 (d, J = 13.8 Hz, 1H), 3.26 (dd, J = 13.8, 7.8 Hz, 1H), 3.71-3.84 (m, 3H), 3.92 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.27 (dq, J = 10.8, 7.2 Hz, 1H), 4.33 (dq, J = 10.8, 7.2 Hz, 1H), 5.19 (d, J = 10.2 Hz, 1H), 6.90 (d, J = 7.8 Hz, 2H), 7.00-7.05 (m, 2H), 7.09 (dd, J = 7.2, 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.17-7.21 (m, 3H), 7.23 (d, J = 7.2 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 8.44 (d, J = 10.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.2, 15.8 (d, J = 8.6 Hz), 15.9 (d, J = 8.7 Hz), 21.2, 43.6 (d, J = 8.6 Hz), 62.8, 63.5 (d, J = 5.7 Hz), 64.0, 65.0 (d, J = 7.2 Hz), 91.9 (d, J = 10.1 Hz), 126.5, 127.3, 127.7, 127.8, 128.0, 128.8, 129.4, 130.2, 134.0, 134.2, 138.7, 142.0, 168.1; ^{31}P NMR (243 MHz, $CDCl_3$) δ –5.6; IR (ATR): 3132, 2983, 2908, 1762, 1455, 1336, 1239, 1162, 1035, 981 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{36}NO_8PS$ [M+Na]$^+$ 612.1792, Found 612.1791.

Minor diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3H), 1.21 (td, J = 7.2, 1.2 Hz, 3H), 1.31 (td, J = 7.2, 1.2 Hz, 3H), 2.26 (s, 3H), 3.68 (d, J = 15.0 Hz, 1H), 3.73 (d, J = 15.0 Hz, 1H), 3.75-3.83 (m, 2H), 4.00 (qd,

J = 7.2, 7.2 Hz, 2H), 4.17-4.27 (m, 2H), 5.14 (d, *J* = 9.6 Hz, 1H), 6.93 (dq, *J* = 8.4 Hz, 2H), 6.97 (dd, *J* = 8.4, 8.4 Hz, 2H), 7.02-7.08 (m, 3H), 7.22-7.31 (m, 3H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.5, 15.8 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 7.2 Hz), 21.3, 41.5, 61.7, 62.6, 64.7 (d, *J* = 7.2 Hz), 64.8 (d, *J* = 5.9 Hz), 90.9 (d, *J* = 5.7 Hz), 126.7, 127.1, 127.60, 127.63, 128.1, 128.8, 128.9, 130.2, 134.7, 134.9, 138.1, 142.4, 167.9 (d, *J* = 11.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –5.2.

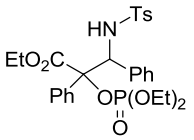
Ethyl 2-benzyl-3-(4-chlorophenyl)-2-diethoxyphosphoryloxy-3-(*N*-tosylamino)propioate (4ab):



Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.04 (td, *J* = 7.2, 1.2 Hz, 3H), 1.22 (td, *J* = 7.2, 1.2 Hz, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 2.31 (s, 3H), 2.77 (d, *J* = 13.3 Hz, 1H), 3.23 (dd, *J* = 13.2, 7.2 Hz, 1H), 3.73-3.87 (m, 3H), 3.95 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 4.26 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.33 (dq, *J* = 10.8, 7.2 Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 7.00-7.04 (m, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 7.15 (d, *J* = 9.0 Hz, 2H), 7.18-7.22 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 2H), 8.45 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.2, 15.8 (d, *J* = 8.7 Hz), 15.9 (d, *J* = 8.6 Hz), 21.3, 43.5 (d, *J* = 8.7 Hz), 62.9, 63.4, 63.5 (d, *J* = 7.2 Hz), 65.2 (d, *J* = 5.9 Hz), 91.6 (d, *J* = 8.7 Hz), 126.5, 127.4, 127.9, 128.1, 128.9, 130.1, 130.8, 132.6, 133.9, 134.0, 138.6, 142.5, 167.9; ^{31}P NMR (243 MHz, $CDCl_3$) δ –5.4; IR (ATR): 3131, 2983, 2907, 1762, 1598, 1495, 1340, 1239, 1162, 1091, 1033, 980 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{35}ClNO_8PS$ $[M+Na]^+$ 646.1402, Found 646.1401.

Minor diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.24 (td, *J* = 7.2, 1.2 Hz, 3H), 1.33 (td, *J* = 7.2, 1.2 Hz, 3H), 2.32 (s, 3H), 3.70 (s, 2H), 3.75-3.84 (m, 2H), 4.03 (qd, *J* = 7.2, 7.2 Hz, 2H), 4.18-4.26 (m, 2H), 5.10 (d, *J* = 9.6 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.95-6.99 (m, 4H), 7.23-7.31 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 4H), 7.70 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.5, 15.8 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 7.2 Hz), 21.3, 41.3, 61.7, 61.9, 64.9 (d, *J* = 7.2 Hz), 65.0 (d, *J* = 5.7 Hz), 90.8 (d, *J* = 5.7 Hz), 126.7, 127.2, 127.7, 128.2, 129.0, 130.2, 130.4, 133.4, 133.7, 134.4, 138.0, 142.8, 167.7 (d, *J* = 11.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –5.0.

Ethyl 2-diethoxyphosphoryloxy-2,3-diphenyl-3-(*N*-tosylamino)propioate (4da):

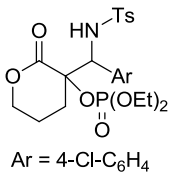


Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.19 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 2.27 (s, 3H), 3.86 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 3.95 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 4.15-4.26 (m, 2H), 4.31-4.43 (m, 2H), 5.52 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 2H), 6.84 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 7.24-7.30 (m, 3H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.44 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 15.9 (d, *J* = 8.6 Hz), 16.1 (d, *J* = 7.2 Hz), 21.3, 63.3, 63.9 (d, *J* = 5.7 Hz), 64.6, 65.1 (d, *J* = 5.7 Hz), 91.2 (d, *J* = 7.2 Hz), 126.2, 126.7, 127.1, 127.3, 128.2, 128.77 (2C), 128.84, 133.9, 135.9 (d, *J* = 8.7 Hz), 138.5, 142.2, 168.3; ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.7; IR (ATR): 3145, 2984, 2908, 1754, 1448, 1335, 1244, 1160, 1031, 981 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{34}NO_8PS$ $[M+Na]^+$ 598.1635, Found 598.1635.

Minor diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.2 Hz, 3H), 1.10 (td, *J* = 7.2, 1.2 Hz, 3H), 1.26 (td, *J* = 7.2, 1.2 Hz, 3H), 2.25 (s, 3H), 3.76 (m, 1H), 3.93-4.13 (m, 5H), 5.52 (d, *J* = 10.2 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.95 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.01-7.06 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.33-7.38 (m, 3H), 7.46 (d, *J* = 9.6 Hz, 1H), 7.68-7.73 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.6, 15.8 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 21.3,

62.1, 62.3, 64.5 (d, *J* = 7.2 Hz), 64.8 (d, *J* = 5.7 Hz), 89.3 (d, *J* = 5.7 Hz), 126.7, 127.5, 127.6, 127.8, 128.1, 128.8, 129.0, 129.2, 134.6, 135.4, 138.0, 142.3, 167.9 (d, *J* = 10.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.8.

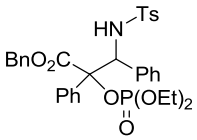
2-{(4-Chlorophenyl)-(*N*-tosylamino)methyl}-2-diethoxyphosphoryloxy-5-pentanolide (4ob):



Ar = 4-Cl-C_6H_4

^{1}H NMR (600 MHz, $CDCl_3$) *Major diastereomer*: δ 1.21 (t, *J* = 7.2 Hz, 3H), 1.31 (td, *J* = 7.2, 1.2 Hz, 3H), 1.75-1.88 (m, 1H), 1.89-1.97 (m, 1H), 2.07-2.13 (m, 1H), 2.37 (s, 3H), 2.43-2.50 (m, 1H), 3.94 (qd, *J* = 7.2, 7.2 Hz, 2H), 4.10-4.21 (m, 3H), 4.38 (m, 1H), 4.64 (brs, 1H), 6.11 (brs, 1H), 7.10-7.20 (m, 6H), 7.47 (d, *J* = 8.4 Hz, 2H); *Minor diastereomer*: δ 1.29-1.34 (m, 6H), 1.55-1.65 (m, 1H), 1.90-1.97 (m, 1H), 2.32 (s, 3H), 2.50-2.62 (m, 2H), 4.04-4.20 (m, 5H), 4.38-4.43 (m, 1H), 4.72 (d, *J* = 9.0 Hz, 1H), 6.58 (d, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) *Major diastereomer*: δ 15.8 (d, *J* = 8.7 Hz), 15.9 (d, *J* = 7.1 Hz), 21.4 (2C), 29.9, 61.8 (d, *J* = 8.7 Hz), 64.2 (d, *J* = 7.1 Hz), 64.7 (d, *J* = 5.7 Hz), 70.1, 81.3 (d, *J* = 7.2 Hz), 127.2, 128.3, 129.3, 130.6, 132.9, 134.6, 136.5, 143.4, 168.5; *Minor diastereomer*: δ 15.8 (d, *J* = 8.7 Hz), 15.9 (d, *J* = 7.1 Hz), 21.2, 21.3, 31.5, 62.7 (d, *J* = 8.7 Hz), 64.4 (d, *J* = 5.7 Hz), 64.7 (d, *J* = 5.7 Hz), 70.4, 81.2 (d, *J* = 7.4 Hz), 126.7, 128.4, 129.1, 129.8, 133.0, 134.4, 137.5, 143.1, 168.5; ^{31}P NMR (243 MHz, $CDCl_3$) *Major diastereomer*: δ –3.9; *Minor diastereomer*: δ –4.1; IR (ATR): 3156, 2983, 2935, 1743, 1494, 1339, 1266, 1164, 1032, 974 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{29}ClNO_8PS$ $[M+Na]^+$ 568.0938, Found 568.0938.

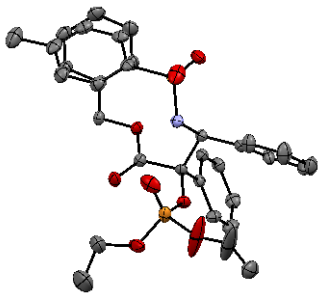
Benzyl 2-diethoxyphosphoryloxy-2,3-diphenyl-3-(*N*-tosylamino)propioate (4pa):

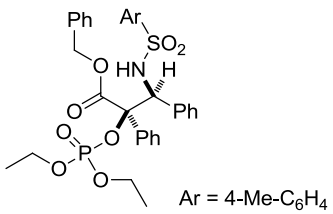


Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.13 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 2.27 (s, 3H), 3.75-3.90 (m, 2H), 4.02-4.17 (m, 2H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.34 (d, *J* = 12.0 Hz, 1H), 5.51 (d, *J* = 9.0 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 2H), 6.85 (dd, *J* = 7.2, 7.2 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.20 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.31-7.39 (m, 9H), 7.65 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 7.1 Hz), 15.9 (d, *J* = 7.2 Hz), 21.3, 63.9 (d, *J* = 7.5 Hz), 64.4, 65.0 (d, *J* = 7.5 Hz), 68.8, 90.9 (d, *J* = 7.2 Hz), 126.4, 126.7, 127.1, 127.3, 128.1, 128.4, 128.5, 128.75, 128.78, 128.87, 128.90, 134.0, 134.5, 135.6 (d, *J* = 8.7 Hz), 138.3, 142.3, 168.3; ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.8; IR (ATR): 3139, 2983, 2909, 1758, 1455, 1335, 1238, 1161, 1092, 1035, 985 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{36}NO_8PS$ $[M+Na]^+$ 660.1792, Found 660.1791; CCDC No. 1046578. A single crystal for single-crystal X-ray diffraction analysis was obtained by natural evaporation with hexane/AcOEt.

Figure S1. ORTEP diagram of **4pa**.

Hydrogens are omitted for clarity.

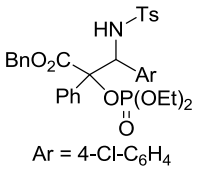




Ar = 4-Me-C_6H_4

Minor diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.05 (td, J = 7.2, 1.2 Hz, 3H), 1.16 (td, J = 7.2, 1.2 Hz, 3H), 2.24 (s, 3H), 3.65-3.74 (m, 1H), 3.93-4.03 (m, 3H), 4.90 (d, J = 12.0 Hz, 1H), 4.96 (d, J = 12.0 Hz, 1H), 5.58 (d, J = 9.6 Hz, 1H), 6.86 (d, J = 7.8 Hz, 2H), 6.90 (dd, J = 7.8, 7.8 Hz, 2H), 6.97-7.01 (m, 4H), 7.18-7.40 (m, 10H), 7.69-7.73 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7 (d, J = 7.2 Hz), 15.8 (d, J = 8.6 Hz), 21.3, 61.8, 64.6 (d, J = 5.9 Hz), 64.9 (d, J = 5.7 Hz), 67.9, 89.4 (d, J = 7.2 Hz), 126.7, 127.59, 127.62, 127.9, 128.1, 128.2, 128.3, 128.4, 128.8, 129.0, 129.2, 134.4 (2C), 135.2, 137.9, 142.3, 167.8 (d, J = 10.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.8.

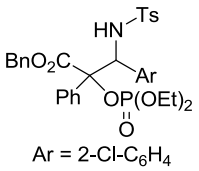
Benzyl 3-(4-chlorophenyl)-2-diethoxyphosphoryloxy-2-phenyl-3-(*N*-tosylamino)propioate (4pb):



Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.18 (td, J = 7.2, 1.2 Hz, 3H), 1.22 (td, J = 7.2, 1.2 Hz, 3H), 2.31 (s, 3H), 3.82-3.98 (m, 2H), 4.06-4.19 (m, 2H), 5.21 (d, J = 11.4 Hz, 1H), 5.34 (d, J =11.4 Hz, 1H), 5.45 (d, J = 8.4 Hz, 1H), 6.67 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 7.21 (dd, J = 7.2, 7.2 Hz, 2H), 7.26 (m, 1H), 7.32-7.38 (m, 9H), 7.74 (d, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.86 (d, J = 7.2 Hz), 15.94 (d, J = 7.2 Hz), 21.3, 63.8, 64.0 (d, J = 5.9 Hz), 65.2 (d, J = 5.7 Hz), 68.9, 90.6 (d, J = 8.6 Hz), 126.1, 126.7, 127.2, 128.3, 128.5, 128.6, 128.8, 128.9, 129.0, 130.2, 132.7, 133.4, 134.4, 135.4 (d, J = 7.2 Hz), 138.2, 142.7, 168.0; ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.5; IR (ATR): 3140, 2984, 1757, 1598, 1494, 1340, 1243, 1162, 1035, 987 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{35}ClNO_8PS$ $[M+Na]^+$ 694.1402, Found 694.1401.

Minor diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.06 (td, J = 7.2, 1.2 Hz, 3H), 1.19 (td, J = 7.2, 1.2 Hz, 3H), 2.30 (s, 3H), 3.65-3.74 (m, 1H), 3.93-4.06 (m, 3H), 4.94 (d, J = 12.0 Hz, 2H), 4.97 (d, J = 12.0 Hz, 1H), 5.52 (d, J = 9.6 Hz, 1H), 6.81 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 7.8 Hz, 2H), 6.99 (d, J = 6.6 Hz, 2H), 7.22-7.31 (m, 4H), 7.32-7.40 (m, 3H), 7.64-7.72 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7 (d, J = 7.2 Hz), 15.8 (d, J = 7.2 Hz), 21.3, 61.2, 64.7 (d, J = 5.7 Hz), 65.0 (d, J = 5.9 Hz), 68.0, 89.1 (d, J = 7.2 Hz), 126.7, 127.7, 127.8, 128.2, 128.3, 128.4, 128.5, 128.9, 129.2, 130.7, 132.9, 133.8, 134.3, 134.9, 137.8, 142.8, 167.7 (d, J = 10.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.7.

Benzyl 3-(2-chlorophenyl)-2-diethoxyphosphoryloxy-2-phenyl-3-(*N*-tosylamino)propioate (4pc):

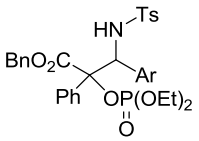


Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.14 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H), 2.27 (s, 3H), 3.90-4.03 (m, 4H), 5.26 (d, J = 12.0 Hz, 1H), 5.37 (d, J = 12.0 Hz, 1H), 5.90 (d, J = 7.8 Hz, 1H), 6.90-7.00 (m, 6H), 7.07 (dd, J = 7.2, 7.2 Hz, 2H), 7.14-7.20 (m, 3H), 7.31-7.38 (m, 6H), 7.44 (d, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.2 Hz), 15.9 (d, J = 8.7 Hz), 21.3, 58.9, 64.2 (d, J = 7.2 Hz), 64.7 (d, J = 5.7 Hz), 68.7, 89.8 (d, J = 7.1 Hz), 126.2, 126.4, 127.0, 127.7, 128.5, 128.55, 128.63, 128.7, 128.8, 129.0 (2C), 129.9, 133.1, 134.4, 134.5 (d, J = 5.7 Hz), 134.9, 137.2, 142.6, 168.2; ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.3; IR (ATR): 3167, 2984, 1756, 1496, 1448, 1342, 1247, 1163, 1028, 985 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{35}ClNO_8PS$ $[M+Na]^+$ 694.1402, Found 694.1401.

Minor diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.10 (td, J = 7.2, 1.2 Hz, 3H), 1.21 (td, J = 7.2, 1.2 Hz, 3H), 2.23 (s, 3H), 3.81-3.89 (m, 1H), 3.97-4.09 (m, 3H), 4.95 (d, J = 12.6 Hz, 1H), 5.06 (d, J = 12.6 Hz, 1H), 6.00 (d, J = 9.0 Hz, 1H), 6.84-6.92 (m, 4H), 6.93-6.99 (m, 2H), 7.02-7.08 (m, 2H), 7.19-7.30 (m, 6H), 7.32 (dd, J = 7.2, 7.2 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.2 Hz),

15.9 (d, *J* = 7.2 Hz), 21.3, 57.6, 64.4 (d, *J* = 7.2 Hz), 64.9 (d, *J* = 5.7 Hz), 67.9, 88.5 (d, *J* = 7.2 Hz), 126.5, 126.8, 127.8, 127.9, 128.2 (2C), 128.3, 128.90, 128.92, 129.0, 130.3, 130.4, 133.1, 134.57, 134.62, 135.0, 137.2, 142.6, 167.5 (d, *J* = 7.2 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.6.

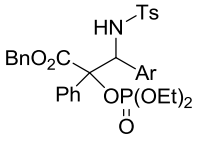
Benzyl 2-diethoxyphosphoryloxy-3-(4-nitrophenyl)-2-phenyl-3-(*N*-tosylamino)propioate (4pd):



Ar = 4-NO_2-C_6H_4

^{1}H NMR (600 MHz, $CDCl_3$) *Major diastereomer*: δ 1.23 (td, *J* = 7.2, 1.2 Hz, 3H), 1.24 (td, *J* = 7.2, 1.2 Hz, 3H), 2.29 (s, 3H), 3.95-4.07 (m, 2H), 4.08-4.20 (m, 2H), 5.20 (d, *J* = 12.0 Hz, 1H), 5.35 (d, *J* =12.0 Hz, 1H), 5.52 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.18-7.39 (m, 8H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.69 (d, *J* = 9.0 Hz, 2H), 8.00 (d, *J* = 6.6 Hz, 1H); *Minor diastereomer*: δ 1.10 (td, *J* = 7.2, 1.2 Hz, 3H), 1.20 (td, *J* = 7.2, 1.2 Hz, 3H), 2.23 (s, 3H), 3.75 (m, 1H), 3.92-4.01 (m, 3H), 4.97 (d, *J* = 12.0 Hz, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 5.61 (d, *J* = 9.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.18-7.40 (m, 10H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *Major diastereomer*: δ 15.90 (d, *J* = 7.2 Hz), 15.93 (d, *J* = 7.2 Hz), 21.3, 63.9, 64.2 (d, *J* = 10.2 Hz), 65.5 (d, *J* = 5.9 Hz), 69.0, 90.1 (d, *J* = 7.2 Hz), 122.0, 125.7, 126.7, 128.4, 128.5, 128.7, 128.9, 129.1, 129.2, 129.8, 134.2, 135.0 (d, *J* = 7.2 Hz), 137.9, 141.9, 143.1, 147.0, 167.6; *Minor diastereomer*: δ 15.7 (d, *J* = 7.1 Hz), 15.8 (d, *J* = 7.2 Hz), 21.2, 61.5, 64.7 (d, *J* = 7.2 Hz), 65.1 (d, *J* = 5.7 Hz), 68.2, 88.6 (d, *J* = 5.9 Hz), 122.4, 126.6, 127.5, 128.3, 128.5, 128.6, 128.7, 129.0, 129.4, 130.4, 134.0, 134.6, 137.7, 141.6, 143.1, 147.0, 167.5 (d, *J* = 11.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *Major diastereomer*: δ –3.8; *Minor diastereomer*: δ –4.4; IR (ATR): 3119, 2984, 1758, 1600, 1523, 1347, 1244, 1163, 1034 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{35}N_2O_{10}PS$ $[M+Na]^+$ 705.1642, Found 705.1642.

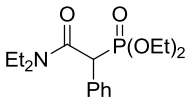
Benzyl 2-diethoxyphosphoryloxy-3-(3-methoxyphenyl)-2-phenyl-3-(*N*-tosylamino)propioate (4pe):



Ar = 3-MeO-C_6H_4

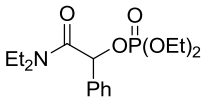
^{1}H NMR (600 MHz, $CDCl_3$) *Major diastereomer*: δ 1.12 (td, *J* = 7.2, 0.6 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 2.27 (s, 3H), 3.43 (s, 3H), 3.75-3.91 (m, 2H), 4.06-4.19 (m, 2H), 5.23 (d, *J* = 11.4 Hz, 1H), 5.36 (d, *J* =11.4 Hz, 1H), 5.52 (d, *J* = 9.0 Hz, 1H), 6.28 (s, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 6.53 (dd, *J* = 7.8, 2.4 Hz, 1H), 6.75 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 7.20-7.43 (m, 12H), 7.78 (d, *J* = 8.4 Hz, 1H); *Minor diastereomer*: δ 1.06 (td, *J* = 7.2, 1.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H), 2.25 (s, 3H), 3.53 (s, 3H), 3.66-3.74 (m, 1H), 3.93-4.03 (m, 3H), 4.90 (d, *J* = 12.0 Hz, 1H), 4.99 (d, *J* = 12.0 Hz, 1H), 5.58 (d, *J* = 10.2 Hz, 1H), 6.55-6.60 (m, 3H), 6.84 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 6.6 Hz, 2H), 7.20-7.44 (m, 8H), 7.64 (d, *J* = 10.2 Hz, 1H), 7.68-7.74 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) *Major diastereomer*: δ 15.7 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 21.3, 54.7, 63.9 (d, *J* = 5.7 Hz), 64.4, 65.1 (d, *J* = 5.7 Hz), 68.8, 91.1 (d, *J* = 7.2 Hz), 113.4, 113.9, 121.3, 126.4, 126.7, 128.0, 128.1, 128.4, 128.5, 128.7, 128.8, 128.9, 134.5, 135.2, 135.7 (d, *J* = 8.9 Hz), 138.4, 142.3, 158.5, 168.2; *Minor diastereomer*: δ 15.69 (d, *J* = 6.6 Hz), 15.73 (d, *J* = 7.2 Hz), 21.2, 54.7, 61.7, 64.6 (d, *J* = 7.1 Hz), 64.9 (d, *J* = 5.7 Hz), 67.8, 89.5 (d, *J* = 7.2 Hz), 113.9, 114.1, 121.7, 126.6, 126.7, 127.9, 128.1, 128.3, 128.4, 128.8, 128.9, 129.0, 134.4, 135.1, 135.6, 138.0, 142.3, 158.9, 167.7 (d, *J* = 11.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *Major diastereomer*: δ –4.8; *Minor diastereomer*: δ –4.9; IR (ATR): 3144, 2984, 1759, 1602, 1456, 1339, 1240, 1162, 1038 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{38}NO_9PS$ $[M+Na]^+$ 690.1903, Found 690.1903.

***N*,*N*-Diethyl-2-diethylphosphono-2-phenylacetamide (6):**



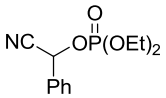
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.06 (t, J = 7.2 Hz, 3H), 1.10 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 3.25 (d, J = 7.2 Hz, 2H), 3.32 (qd, J = 7.2, 6.6 Hz, 1H), 3.46 (qd, J = 7.2, 6.6 Hz, 1H), 3.93-4.07 (m, 2H), 4.22 (qd, J = 7.2, 7.2 Hz, 2H), 4.42 (d, J = 22.8 Hz, 1H), 7.26-7.31 (m, 1H), 7.33 (dd, J = 7.2, 7.2 Hz, 2H), 7.47-7.51 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.7, 14.3, 16.2 (d, J = 7.2 Hz), 16.4 (d, J = 5.7 Hz), 40.6, 42.7, 50.4 (d, J = 142.2 Hz), 62.6 (d, J = 7.2 Hz), 63.4 (d, J = 5.7 Hz), 127.6, 128.6, 129.4 (d, J = 8.7 Hz), 132.3 (d, J = 8.6 Hz), 166.6 (d, J = 2.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.8; IR (ATR): 2979, 2933, 1638, 1432, 1254, 1056, 1027, 960 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{26}NO_4P$ [M+Na]$^+$ 350.1497, Found 350.1497.

***N*,*N*-Diethyl-2-diethoxyphosphoryloxy-2-phenylacetamide (7):**



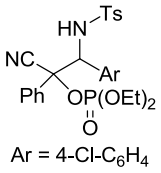
^{1}H NMR (600 MHz, $CDCl_3$) δ 0.99 (t, J = 7.2 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H), 1.16 (td, J = 7.2, 1.2 Hz, 3H), 1.34 (td, J = 7.2, 1.2 Hz, 3H), 3.15-3.26 (m, 2H), 3.31 (qd, J = 7.2, 7.2 Hz, 1H), 3.48 (qd, J = 7.2, 7.2 Hz, 1H), 3.92 (qd, J = 7.2, 7.2 Hz, 2H), 4.16-4.28 (m, 2H), 6.02 (d, J = 7.8 Hz, 1H), 7.35-7.42 (m, 3H), 7.48-7.53 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.6, 13.7, 15.8 (d, J = 7.2 Hz), 16.0 (d, J = 7.2 Hz), 40.6, 41.5, 63.8 (d, J = 5.7 Hz), 64.3 (d, J = 5.7 Hz), 76.0 (d, J = 4.2 Hz), 127.9, 128.9, 129.2, 135.6 (d, J = 5.7 Hz), 166.9 (d, J = 4.2 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.3; IR (ATR): 2980, 2935, 1660, 1456, 1363, 1272, 1028, 973 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{26}NO_5P$ [M+Na]$^+$ 366.1446, Found 366.1446.

2-Diethoxyphosphoryloxy-2-phenylacetonitrile (9)[8]:



^{1}H NMR (600 MHz, $CDCl_3$) δ 1.23 (td, J = 7.2, 1.2 Hz, 3H), 1.40 (td, J = 7.2, 1.2 Hz, 3H), 3.96-4.08 (m, 2H), 4.16-4.29 (m, 2H), 6.07 (d, J = 8.4 Hz, 1H), 7.45-7.49 (m, 3H), 7.55-7.59 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.2 Hz), 16.0 (d, J = 5.7 Hz), 64.7 (d, J = 5.9 Hz), 64.9 (d, J = 5.7 Hz), 66.5 (d, J = 4.4 Hz), 116.1 (d, J = 5.9 Hz), 127.5, 129.2, 130.6, 132.4 (d, J = 4.5 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ –1.7.

3-(4-Chlorophenyl)-2-diethoxyphosphoryloxy-2-phenyl-3-(*N*-tosylamino)propionitrile (11):



Ar = 4-Cl-C$_6$H$_4$

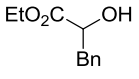
Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.17 (td, J = 7.2, 1.2 Hz, 3H), 1.26 (td, J = 7.2, 1.2 Hz, 3H), 2.33 (s, 3H), 3.88 (m, 1H), 3.97-4.15 (m, 3H), 4.91 (d, J = 9.0 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 6.78 (d, J = 8.4 Hz, 2H), 6.98-7.05 (m, 4H), 7.30-7.35 (m, 4H), 7.36-7.41 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.2 Hz) (2C), 21.4, 65.1 (d, J = 5.9 Hz), 65.6 (d, J = 5.7 Hz), 65.9 (d, J = 5.7 Hz), 81.0 (d, J = 8.6 Hz), 115.8 (d, J = 4.2 Hz), 126.1, 126.9, 127.9, 128.7, 129.2, 130.1 (2C), 131.5, 134.0 (d, J = 3.0 Hz), 134.6, 137.1, 143.4; ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.8; IR (ATR): 3132, 2983, 2910, 1495, 1451, 1340, 1262, 1165, 1091, 1026 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{28}ClN_2O_6PS$ [M+Na]$^+$ 585.0992, Found 585.0992.

Minor diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26 (td, J = 7.2, 1.2 Hz, 6H), 2.34 (s, 3H), 4.00-4.13 (m, 3H), 4.17 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.86 (d, J = 6.0 Hz, 1H), 6.09 (d, J = 6.0 Hz, 1H), 6.74 (d, J = 8.4 Hz, 2H),

[8] I. Micó and C. Nájera, *Tetrahedron*, 1993, **49**, 4327.

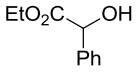
6.95 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.28-7.33 (m, 4H), 7.34-7.38 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9 (d, *J* = 7.2 Hz) (2C), 21.4, 65.1 (d, *J* = 5.9 Hz), 65.2 (d, *J* = 7.2 Hz), 66.2 (d, *J* = 7.2 Hz), 81.1 (d, *J* = 10.1 Hz), 115.0 (d, *J* = 2.9 Hz), 126.3, 127.0, 128.0, 128.6, 129.2, 130.0, 130.2, 131.5, 133.5, 134.7, 137.0, 143.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ –4.7

Ethyl 2-hydroxy-3-phenylpropanoate (12a)[9]:



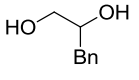
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 2.75 (d, *J* = 4.2 Hz, 1H), 2.97 (dd, *J* = 13.8, 6.6 Hz, 1H), 3.13 (dd, *J* = 13.2, 4.2 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.44 (ddd, *J* = 6.0, 6.0, 4.2 Hz, 1H), 7.21-7.26 (m, 3H), 7.30 (dd, *J* = 7.8, 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 40.4, 61.6, 71.0, 126.7, 128.2, 129.4, 136.2, 174.0.

Ethyl 2-hydroxy-2-phenylacetate (12b)[10]:



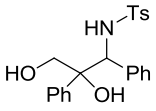
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.2 Hz, 3H), 3.47 (d, *J* = 4.2 Hz, 1H), 4.17 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.27 (dq, *J* = 10.8, 7.2 Hz, 1H), 5.16 (d, *J* = 4.2 Hz, 1H), 7.32 (m, 1H), 7.37 (m, 2H), 7.43 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 62.2, 72.9, 126.5, 128.4, 128.6, 138.4, 173.7.

3-Phenyl-1,2-propane-1,2-diol (13)[11]:



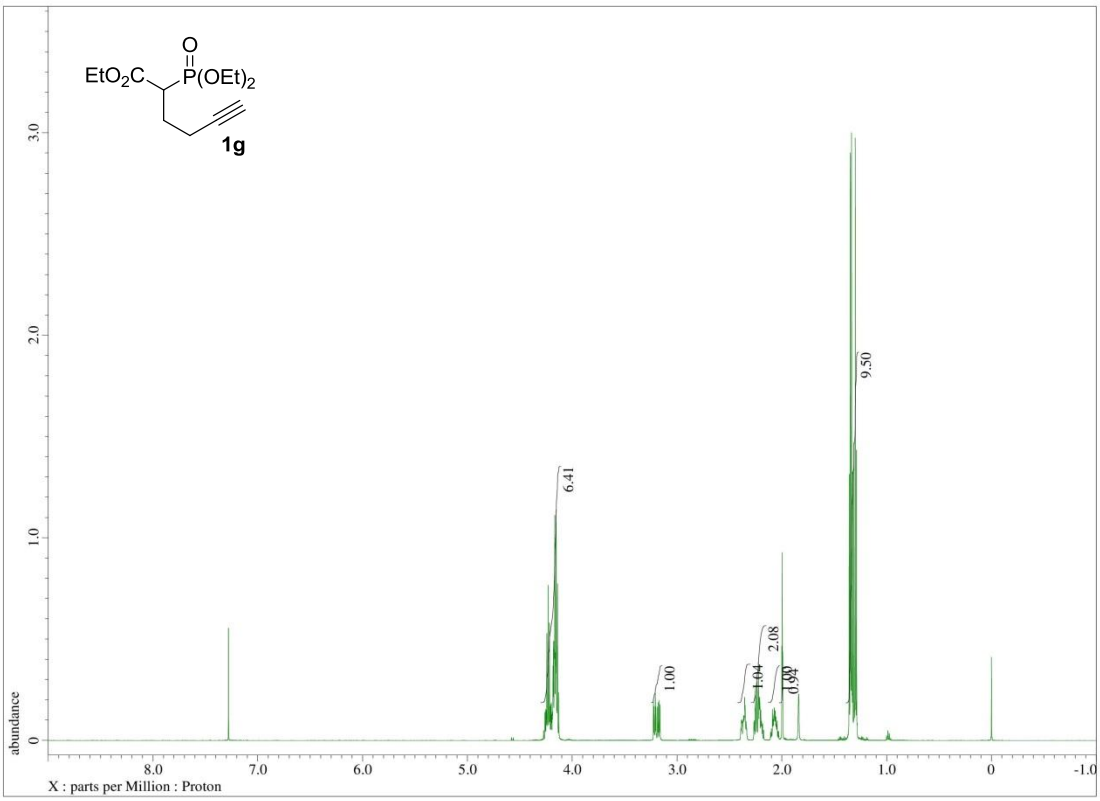
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.91 (t, *J* = 5.4 Hz, 1H), 2.04 (d, *J* = 3.6 Hz, 1H), 2.76 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.82 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.54 (m, 1H), 3.71 (m, 1H), 3.96 (m, 1H), 7.23 (m, 2H), 7.25 (m, 1H), 7.33 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 39.8, 66.0, 73.0, 126.6, 128.6, 129.3, 137.7.

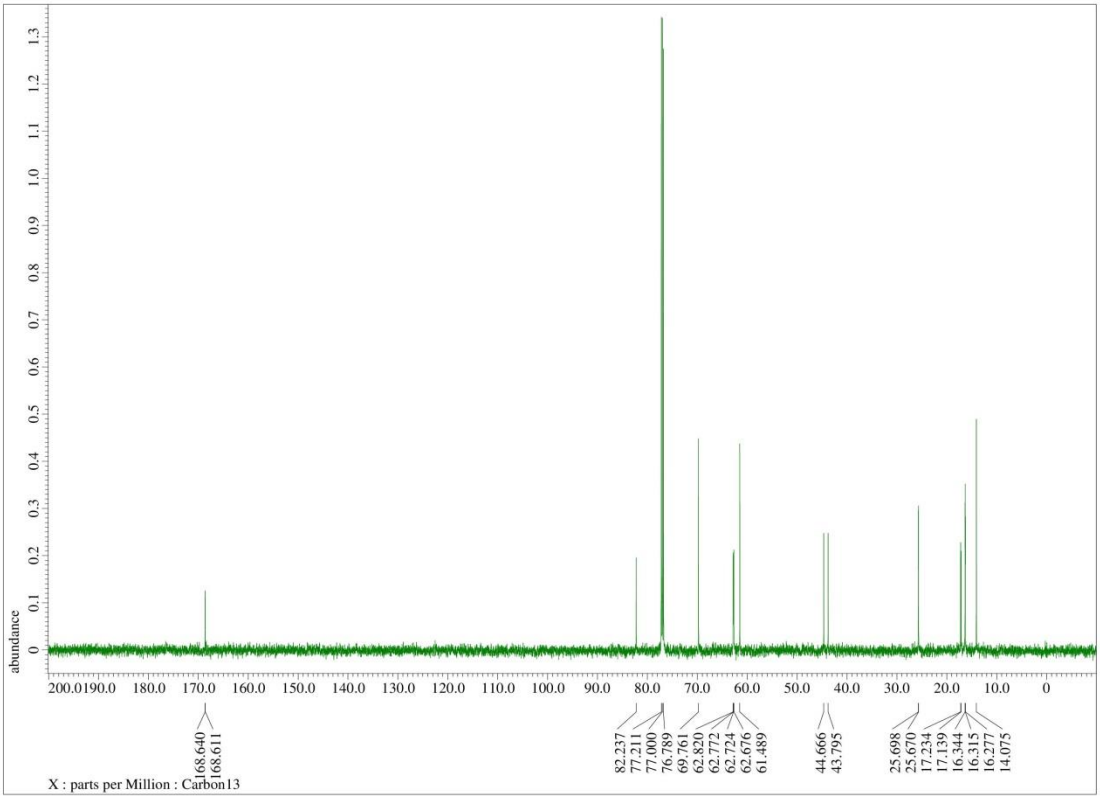
2,3-Diphenyl-3-(*N*-tosylamino)propane-1,2-diol (14):



^{1}H NMR (600 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.43 (brs, 1H), 3.53 (brs, 1H), 3.97 (d, *J* = 11.4 Hz, 1H), 4.13 (d, *J* = 11.4 Hz, 1H), 4.70 (d, *J* = 9.6 Hz, 1H), 5.62 (d, *J* = 10.2 Hz, 1H), 6.64 (d, *J* = 7.2 Hz, 2H), 6.86 (t, *J* = 7.2 Hz, 2H), 6.93-7.00 (m, 3H), 7.05-7.12 (m, 2H), 7.13-7.22 (m, 3H), 7.39 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.3, 63.0, 67.6, 78.7, 125.9, 127.0, 127.1, 127.4, 127.6, 128.0, 128.1, 129.1, 135.9, 136.7, 140.0, 143.1; IR (ATR): 3502, 3284, 3031, 2942, 1448, 1417, 1320, 1158, 1088 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{23}NO_4S$ $[M+Na]^+$ 420.1245, Found 420.1245.

[9] M. S. Kwon, I. S. Park, J. S. Jang, J. S. Lee and Park, *Org. Lett.*, 2007, **9**, 3417.
[10] L.-Q. Lu, Y. Li, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2013, **52**, 8382.
[11] A. D. Worthy, X. Sun and K. L. Tan, *J. Am. Chem. Soc.*, 2012, **134**, 7321.


EtO2C
O
P(OEt)2
1g
abundance
X : parts per Million : Proton
6.41
1.00
1.04
2.08
1.00
0.94
9.50


abundance
X : parts per Million : Carbon13
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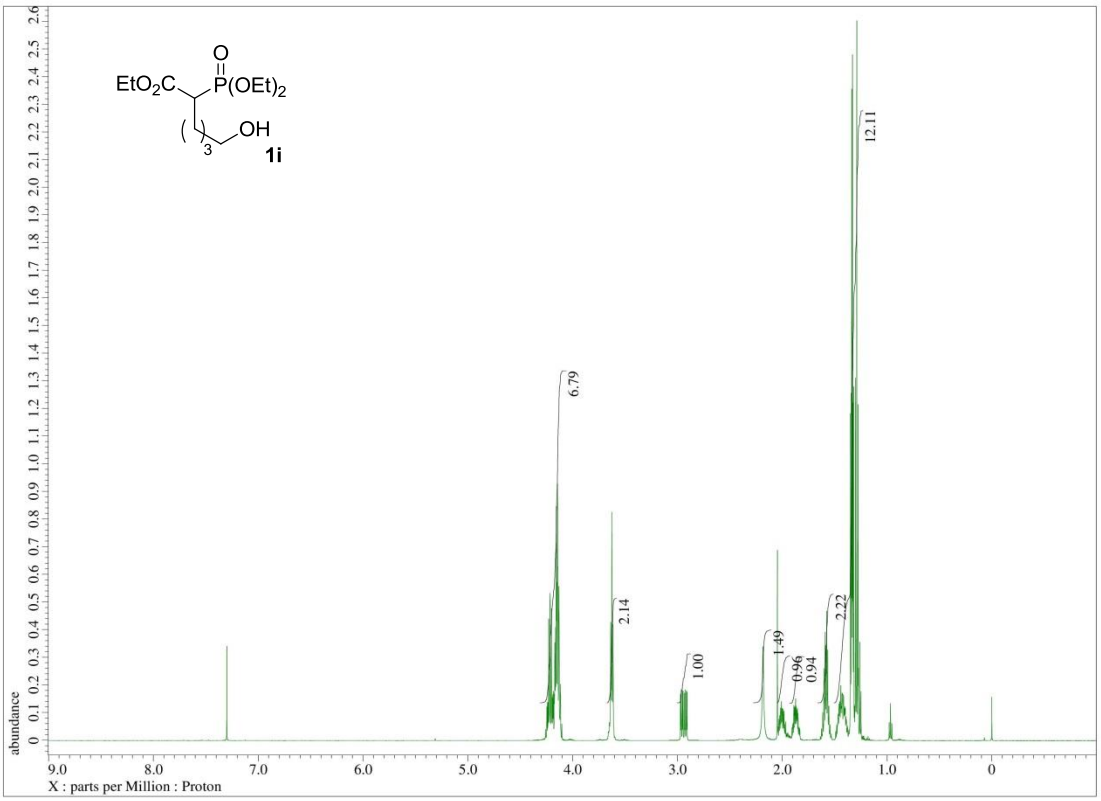
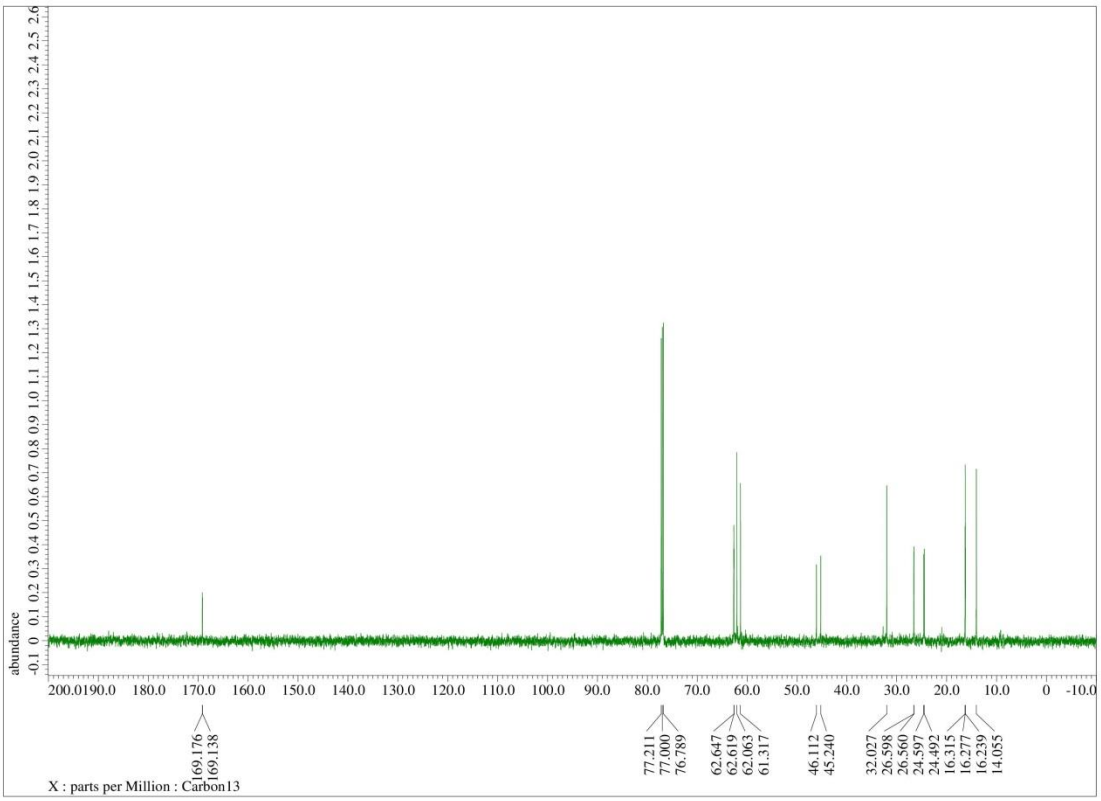
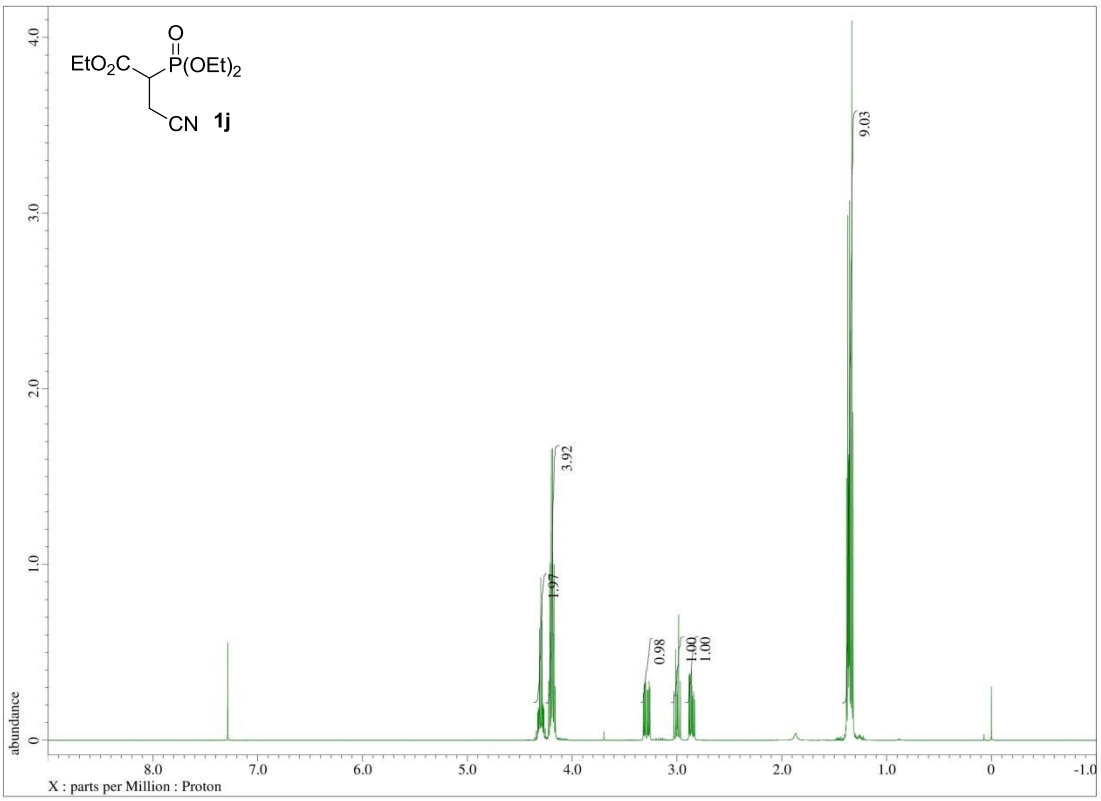
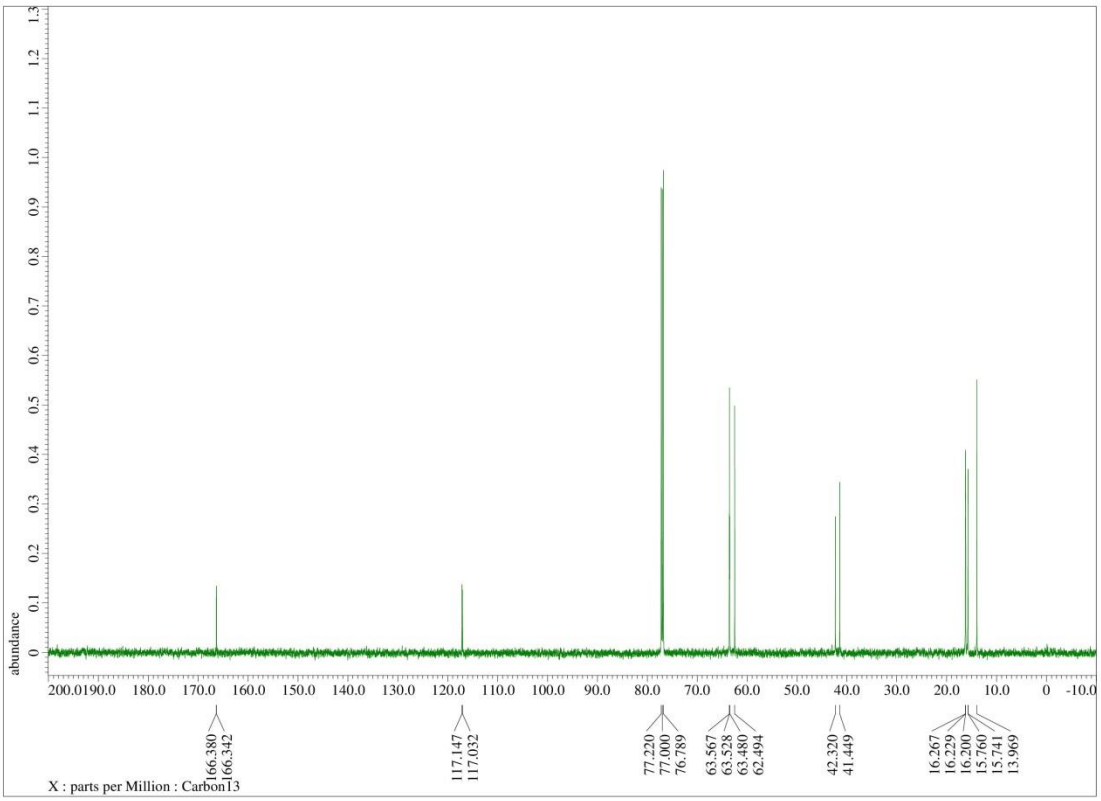
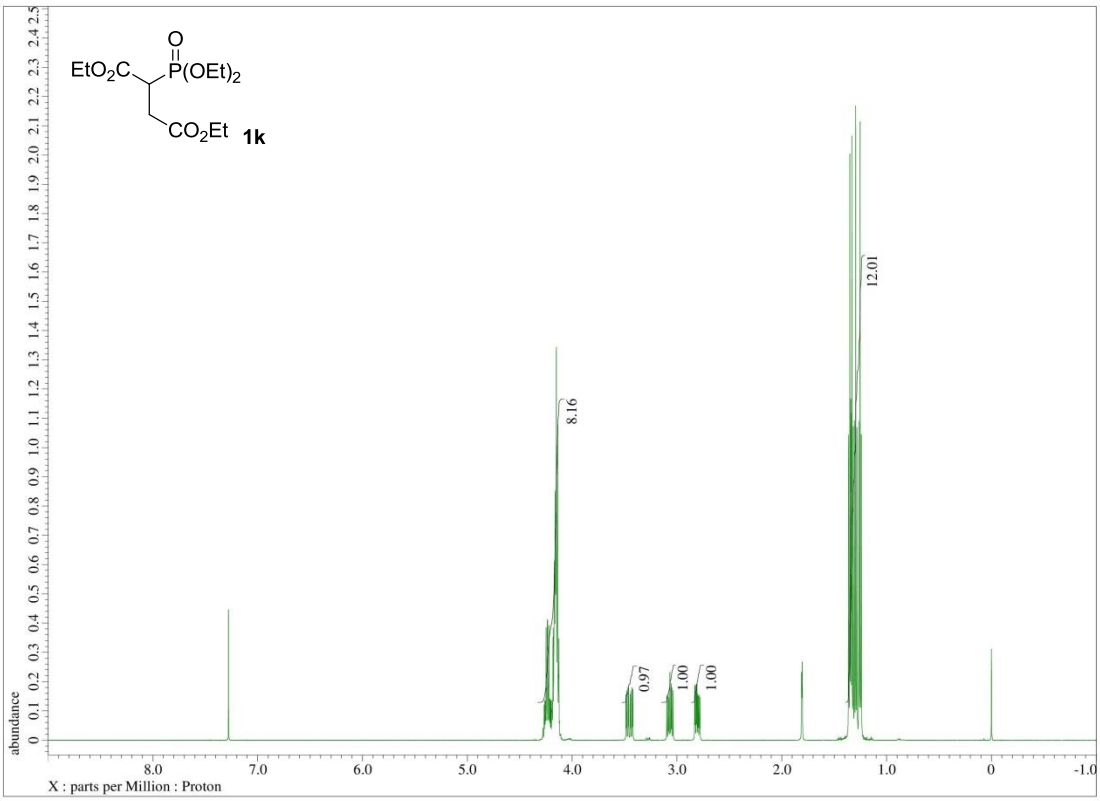
168.611
82.237
77.211
77.000
76.789
69.761
62.820
62.772
62.724
62.676
61.489
44.666
43.795
25.698
25.670
17.234
17.139
16.344
16.315
16.277
14.075


O
EtO2C
P(OEt)2
OH
3
1i
6.79
2.14
1.00
1.49
0.96
0.94
2.22
12.11
abundance
X : parts per Million : Proton


abundance
169.176
169.138
77.211
77.000
76.789
62.647
62.619
62.063
61.317
46.112
45.240
32.027
26.598
26.560
24.597
24.492
16.315
16.277
16.239
14.055
X : parts per Million : Carbon13


EtO2C
O
P(OEt)2
CN
1j
9.03
3.92
1.97
0.98
1.00
1.00
abundance
X : parts per Million : Proton


abundance
166.380
166.342
117.147
117.032
77.220
77.000
76.789
63.567
63.528
63.480
62.494
42.320
41.449
16.267
16.229
16.200
15.760
15.741
13.969
X : parts per Million : Carbon13


O
EtO2C
P(OEt)2
CO2Et
1k
abundance
X : parts per Million : Proton
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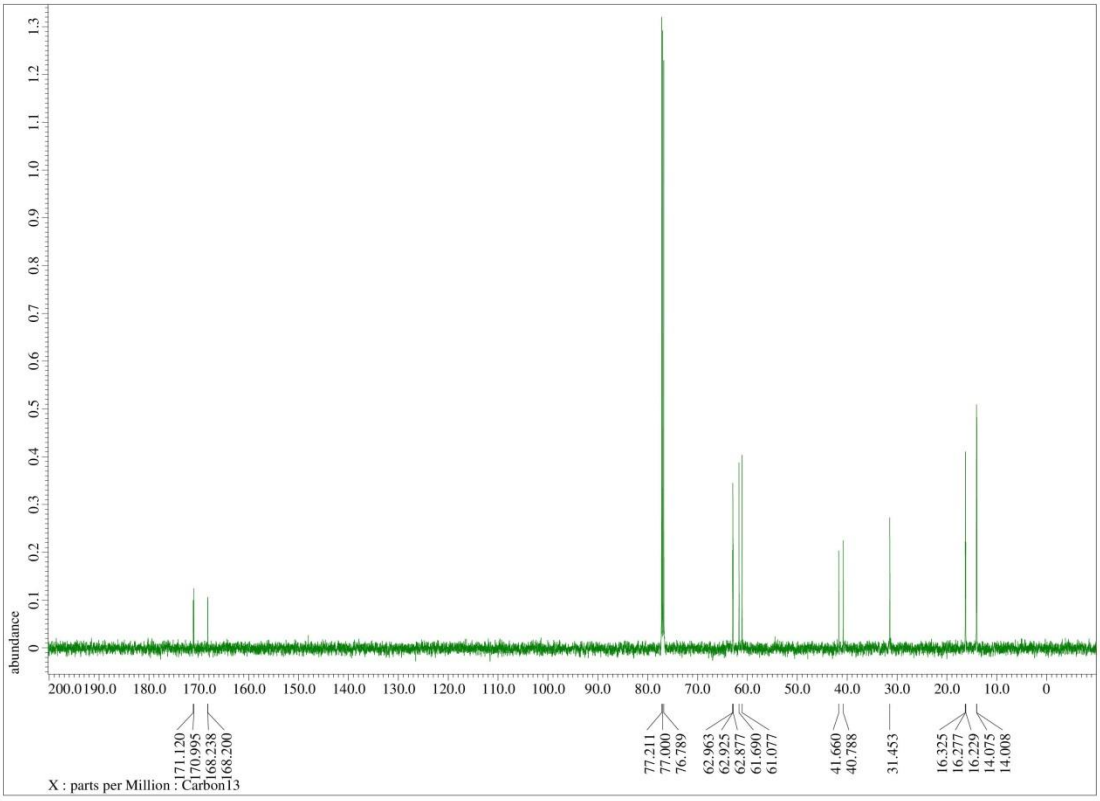
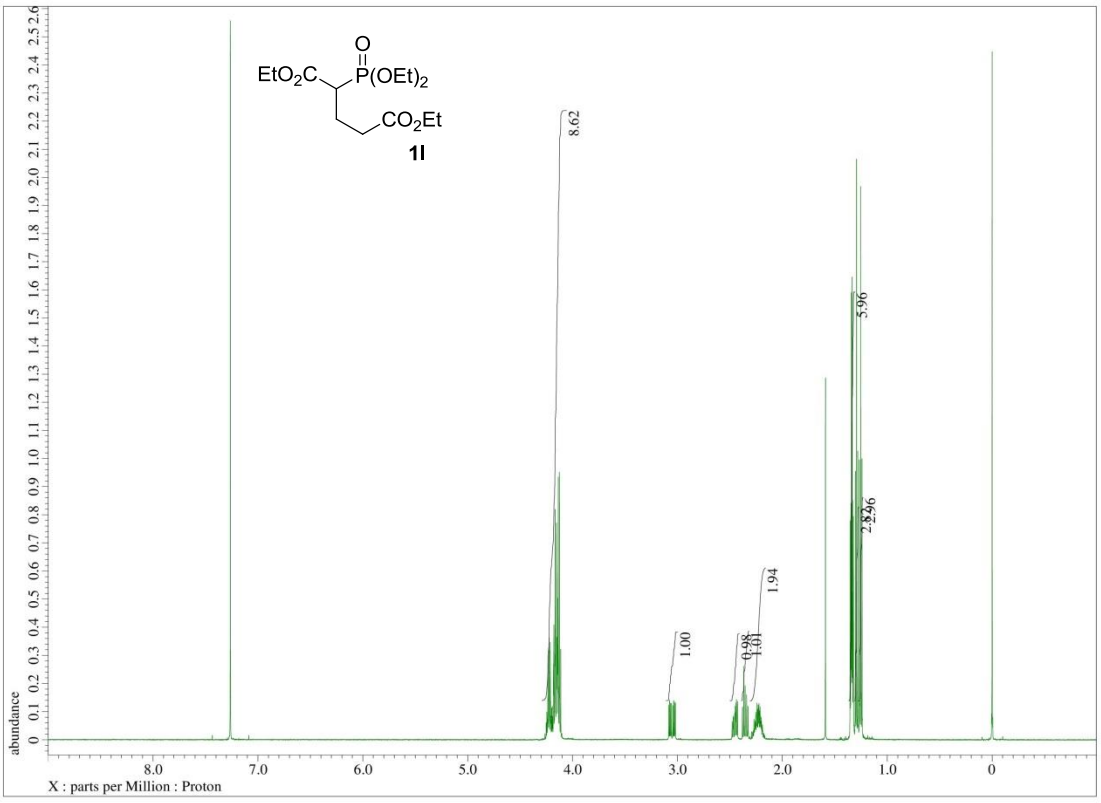
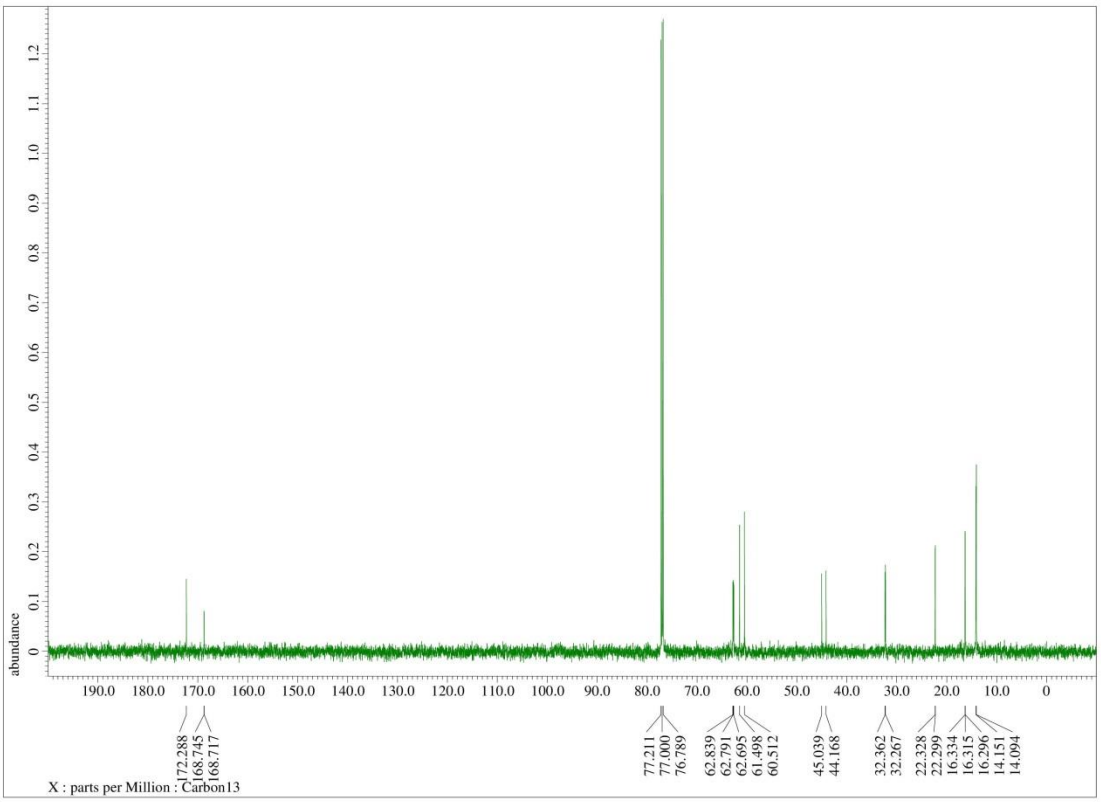
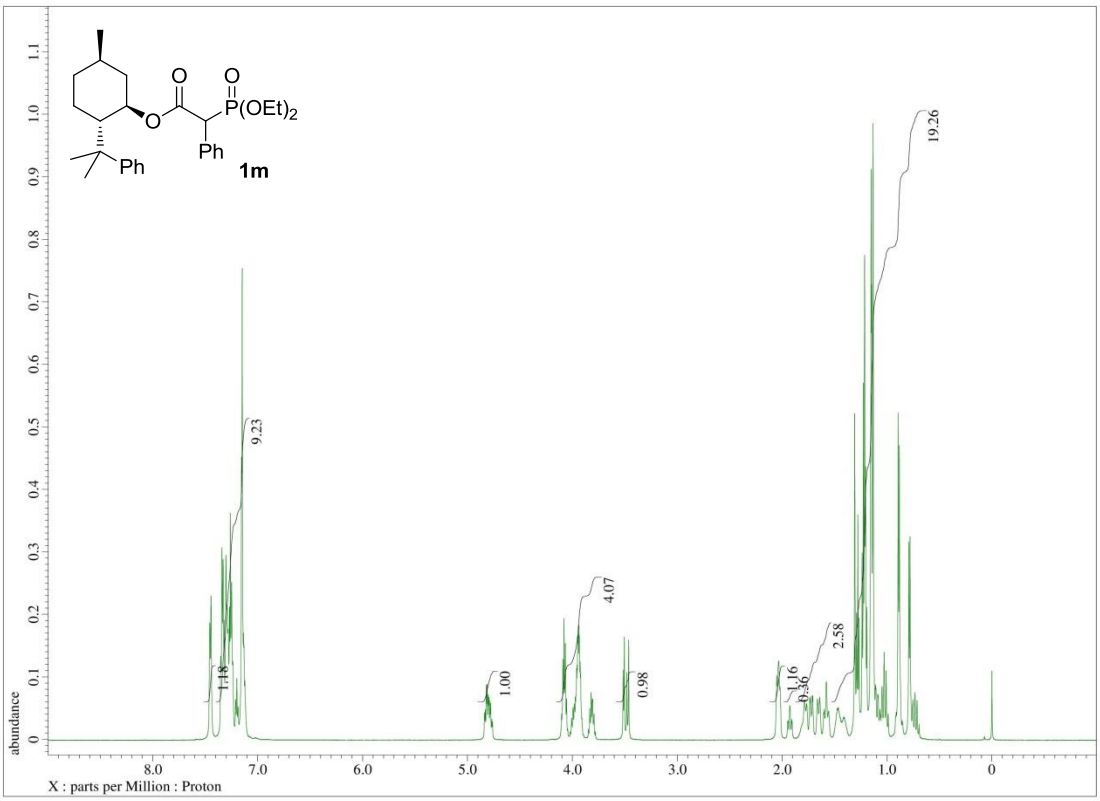
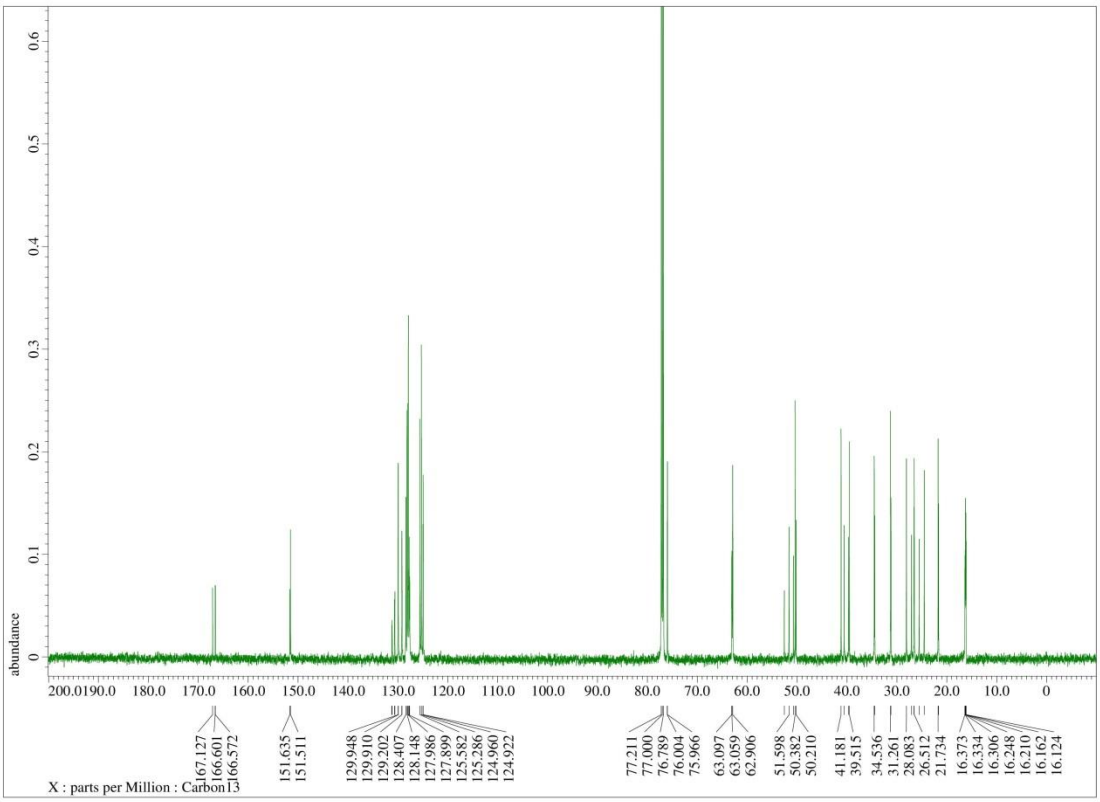
0.97
1.00
1.00
12.01


abundance
X : parts per Million : Carbon13
171.120
170.995
168.238
168.200
77.211
77.000
76.789
62.963
62.925
62.877
61.690
61.077
41.660
40.788
31.453
16.325
16.277
16.229
14.075
14.008


O
EtO2C
P(OEt)2
CO2Et
1l
8.62
5.96
2.96
1.94
1.00
abundance
X : parts per Million : Proton


172.288
168.745
168.717
77.211
77.000
76.789
62.839
62.791
62.695
61.498
60.512
45.039
44.168
32.362
32.267
22.328
22.299
16.334
16.315
16.296
14.151
14.094
abundance
X : parts per Million : Carbon13


O
O
P(OEt)2
O
Ph
Ph
1m
abundance
X : parts per Million : Proton
9.23
1.18
1.00
4.07
0.98
1.16
0.36
2.58
19.26


abundance
X : parts per Million : Carbon13
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166.601
166.572
151.635
151.511
129.948
129.910
129.202
128.407
128.148
127.986
127.899
125.582
125.286
124.960
124.922
77.211
77.000
76.789
76.004
75.966
63.097
63.059
62.906
51.598
50.382
50.210
41.181
39.515
34.536
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26.512
21.734
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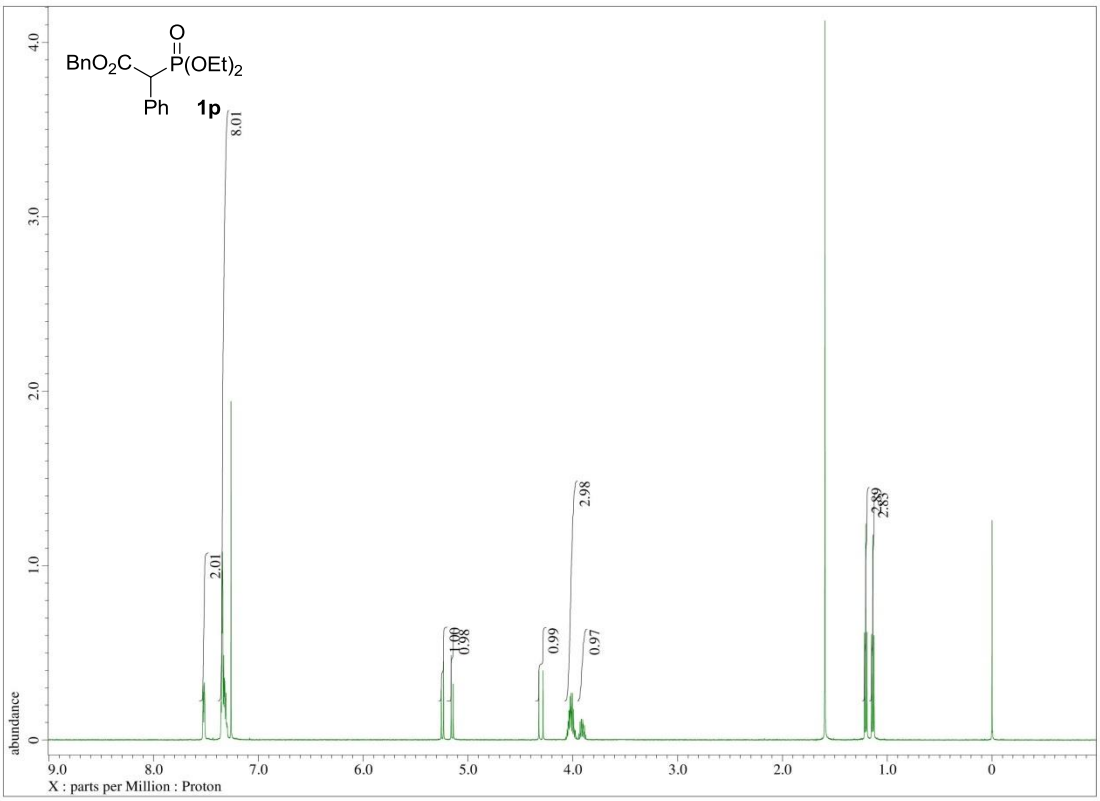
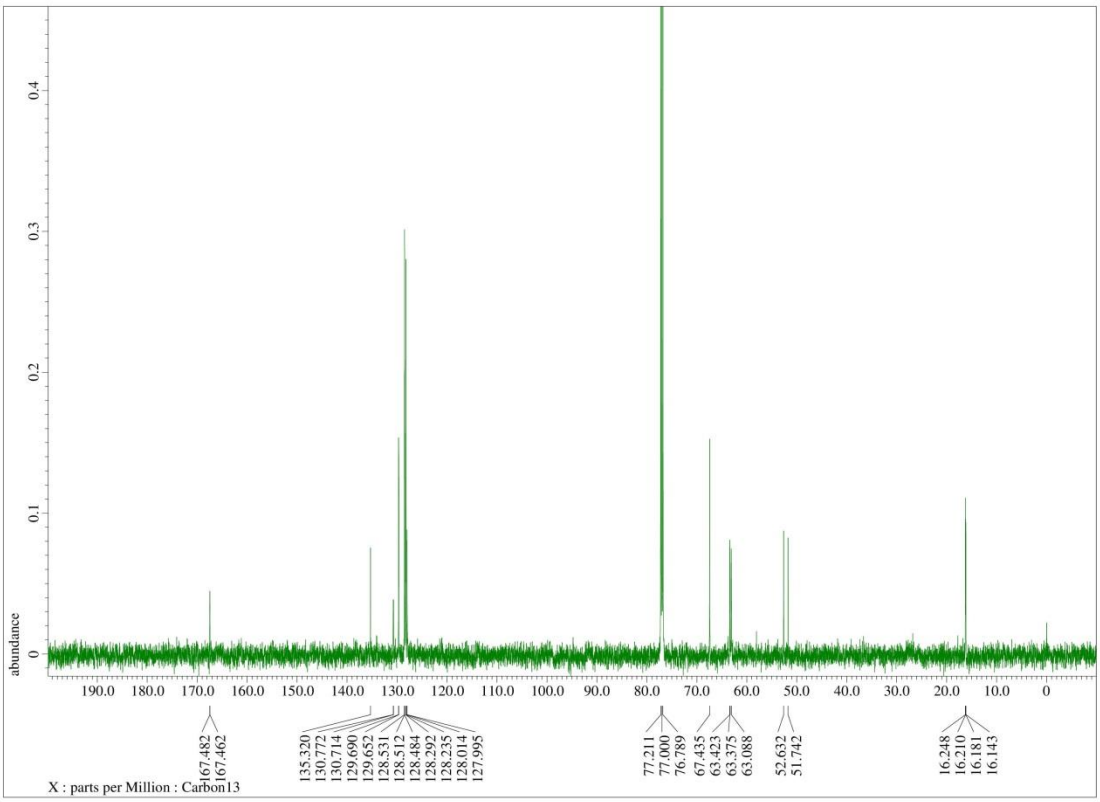
16.210
16.162
16.124


BnO2C
P(OEt)2
O
Ph
1p
8.01
2.01
2.98
0.99
0.97
abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13
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167.462
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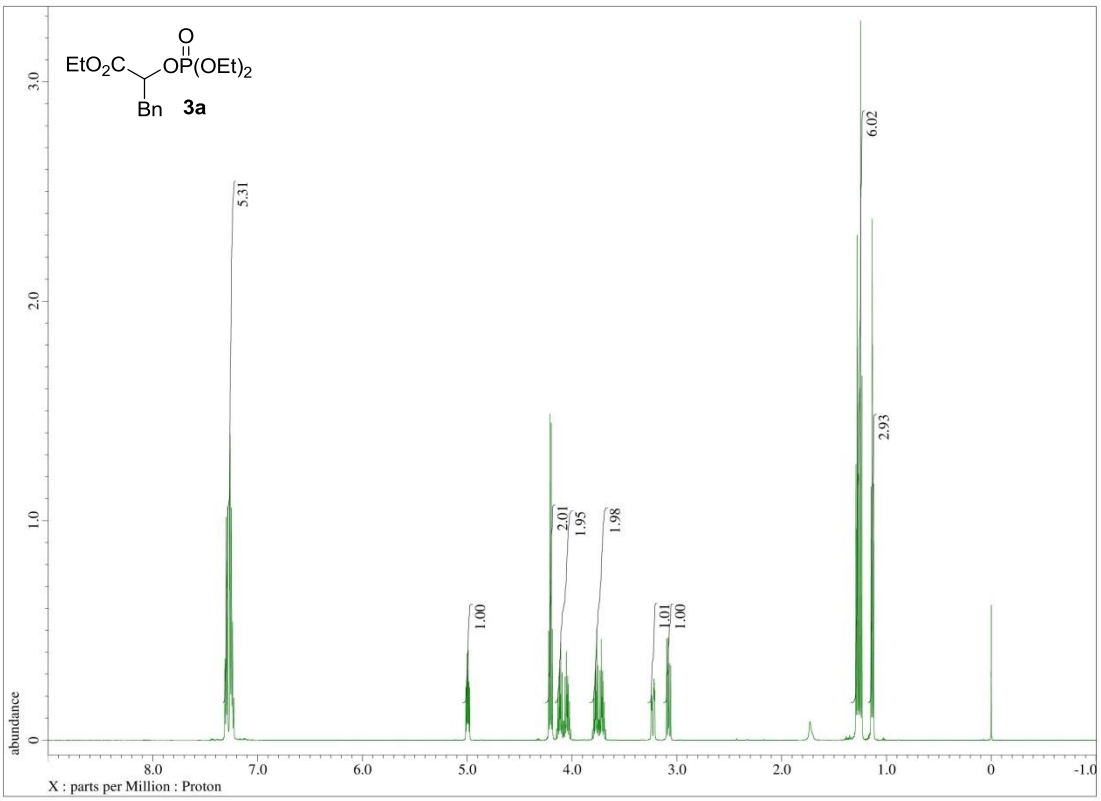
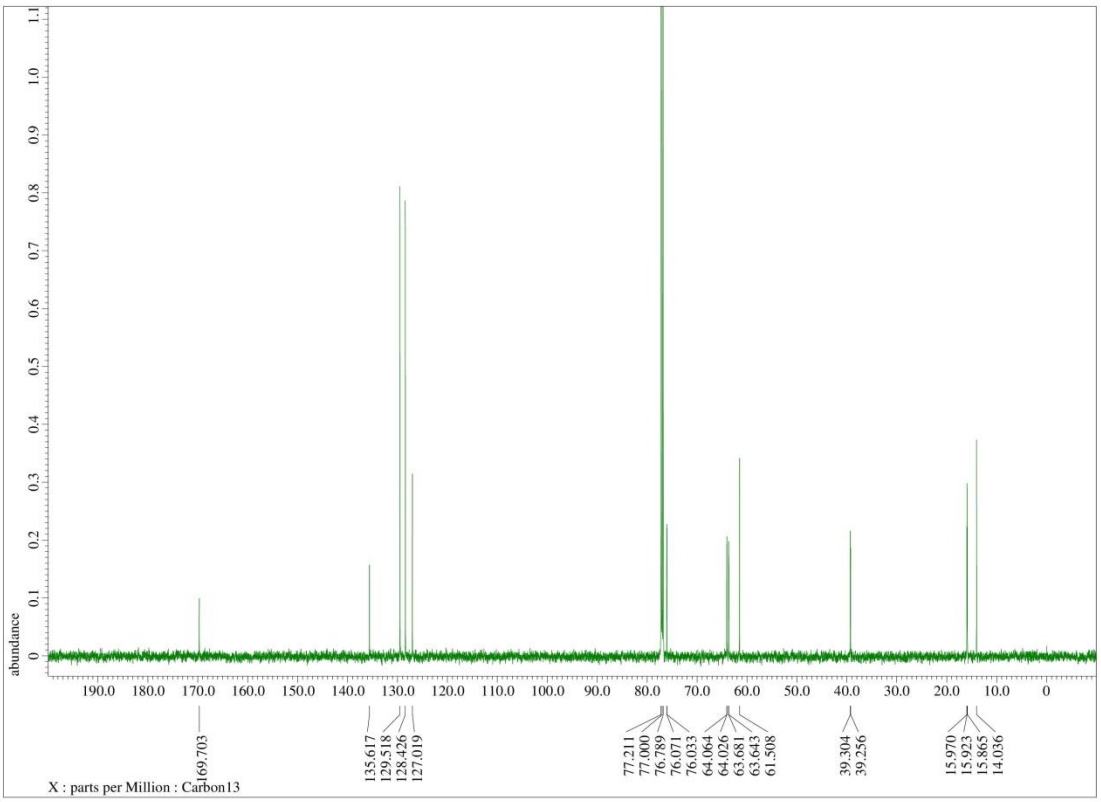
130.772
130.714
129.690
129.652
128.531
128.512
128.484
128.292
128.235
128.014
127.995
77.211
77.000
76.789
67.435
63.423
63.375
63.088
52.632
51.742
16.248
16.210
16.181
16.143


EtO2C
O
OP(OEt)2
Bn
3a
5.31
6.02
2.93
2.01
1.95
1.98
1.00
1.01
1.00
abundance
X : parts per Million : Proton


abundance
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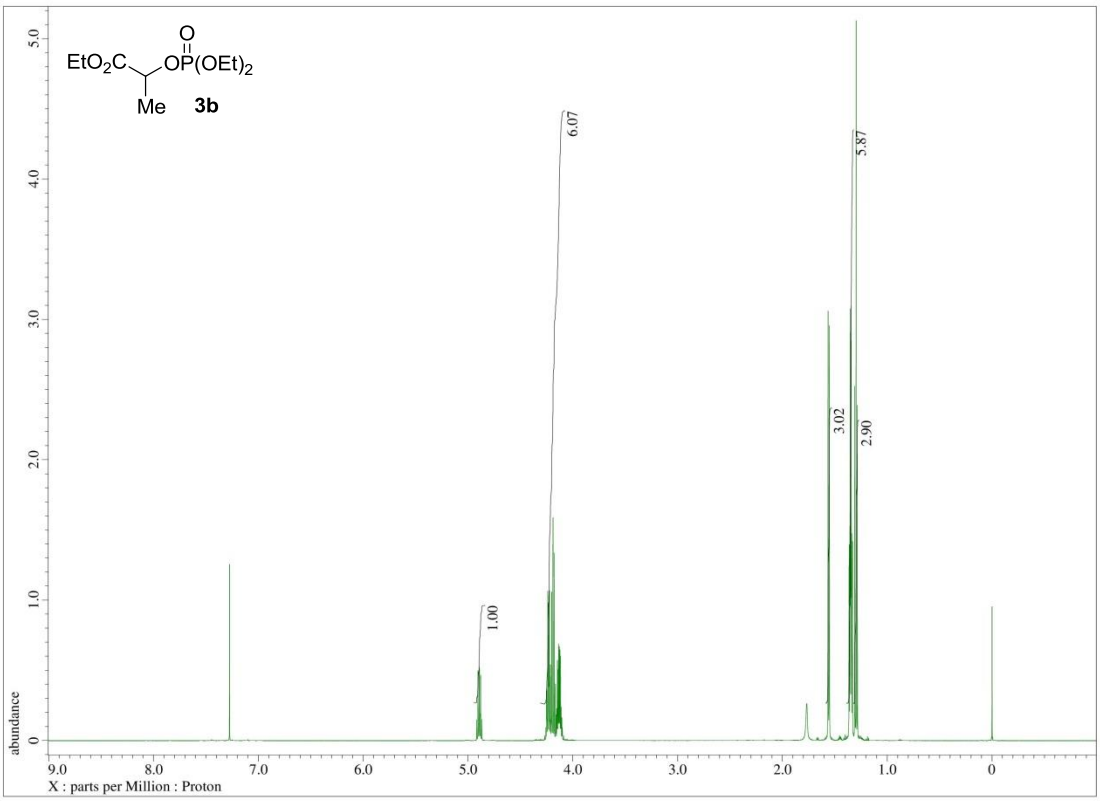
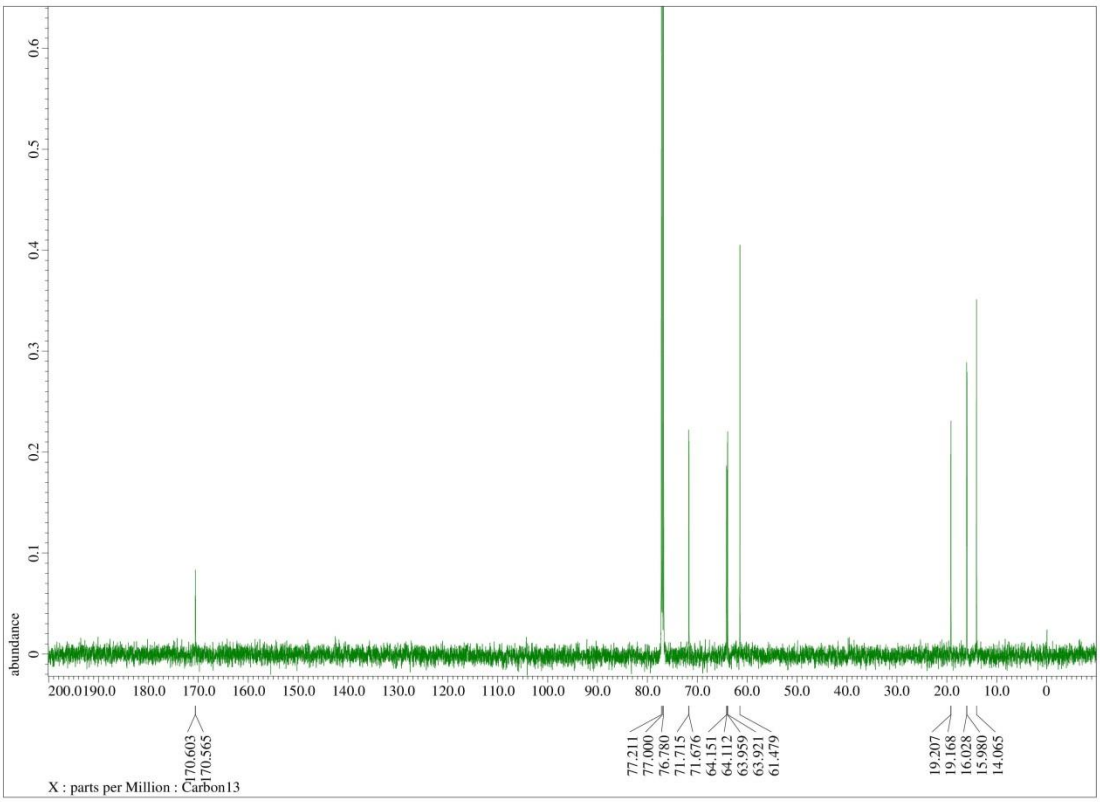
129.518
128.426
127.019
77.211
77.000
76.789
76.071
76.033
64.064
64.026
63.681
63.643
61.508
39.304
39.256
15.970
15.923
15.865
14.036
X : parts per Million : Carbon13


EtO2C
O
OP(OEt)2
Me
3b
6.07
5.87
3.02
2.90
1.00
abundance
X : parts per Million : Proton


abundance
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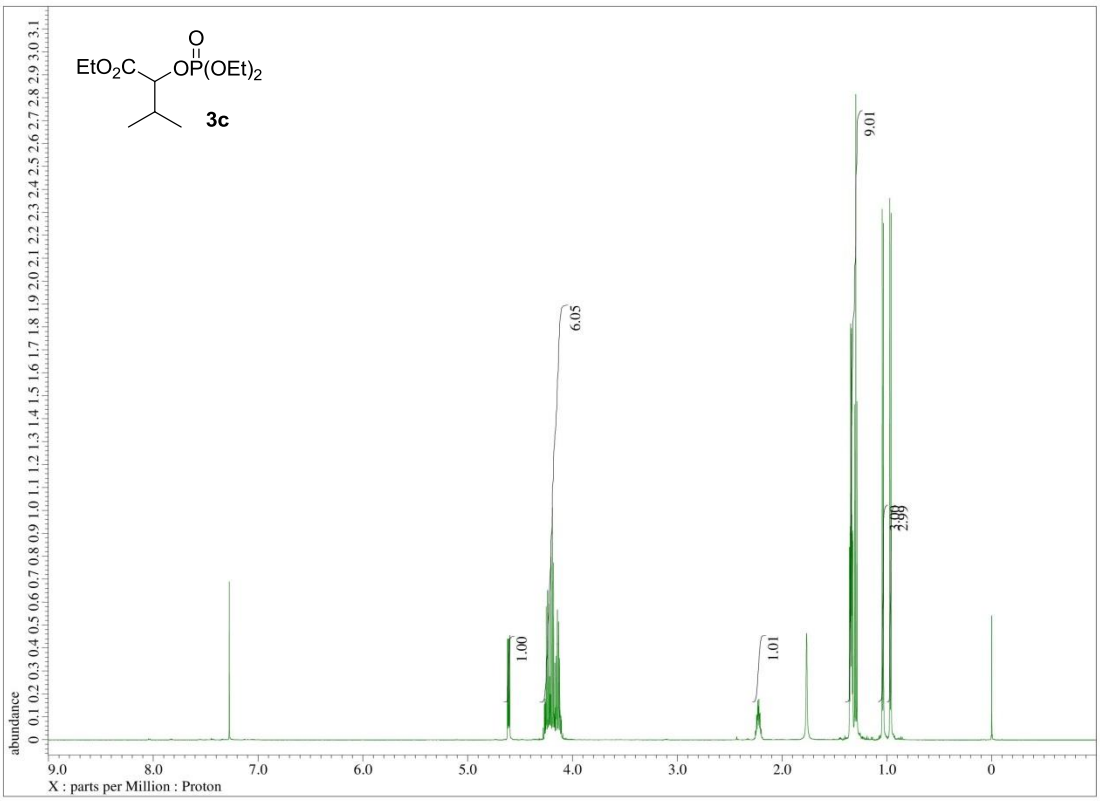
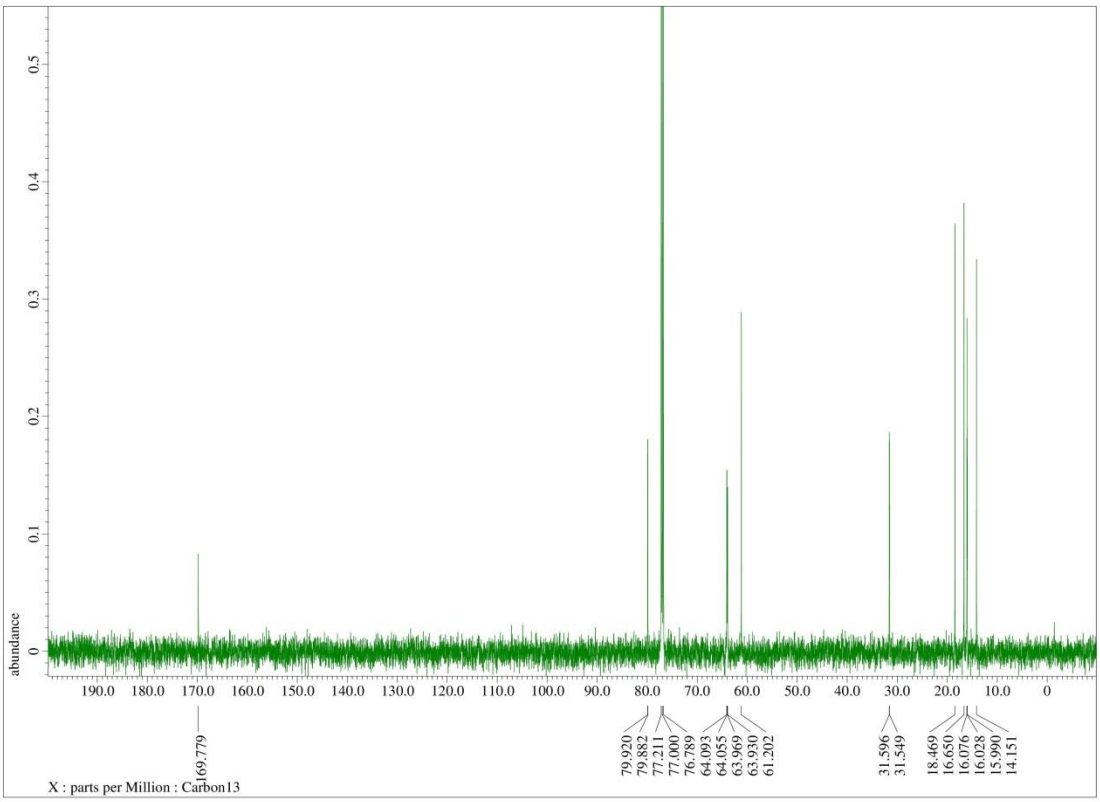
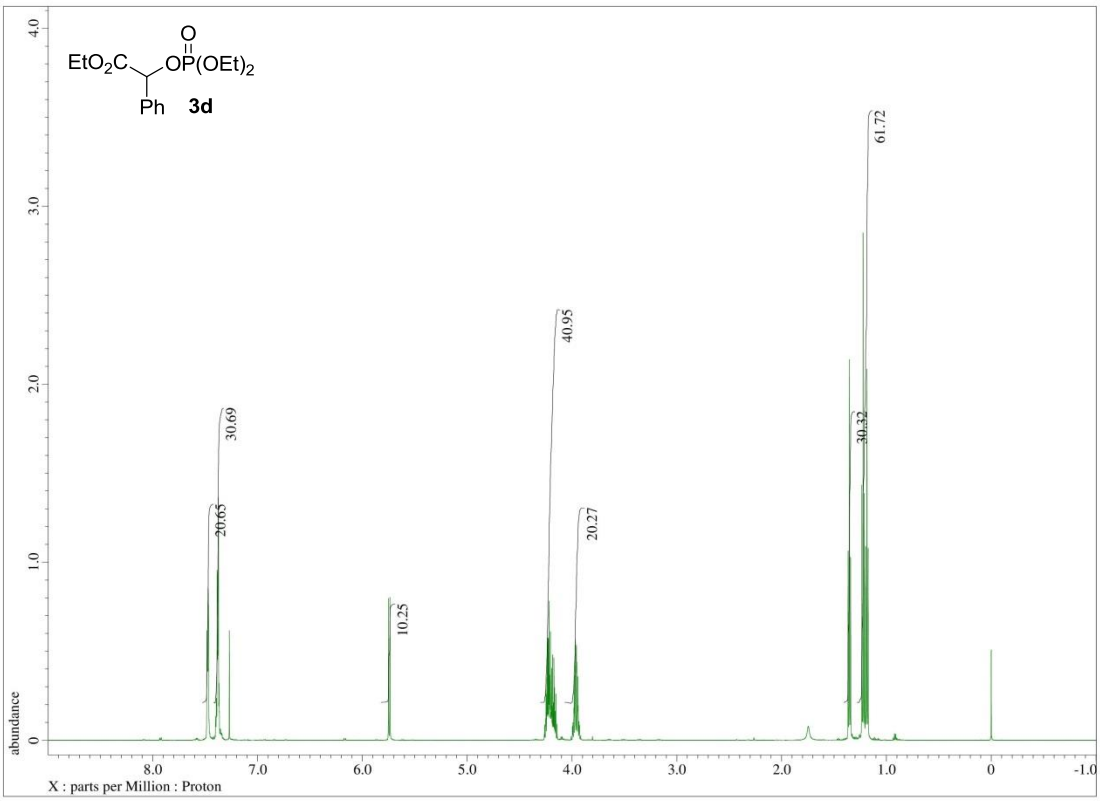
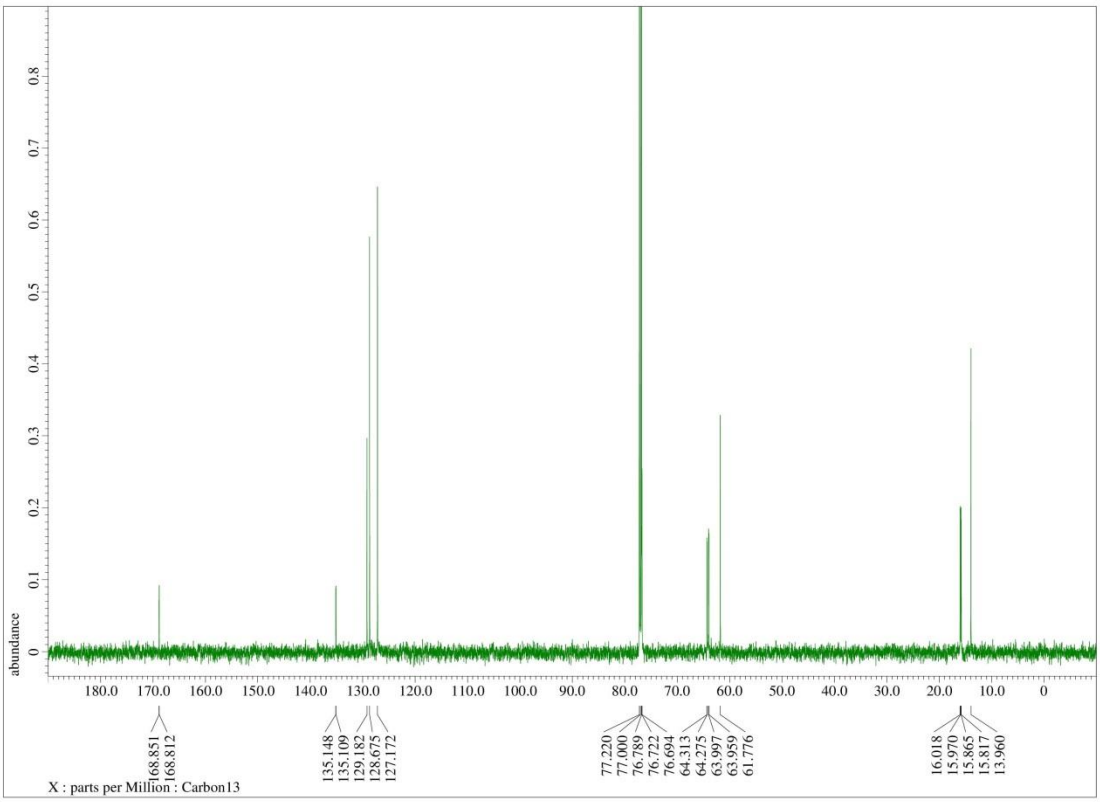
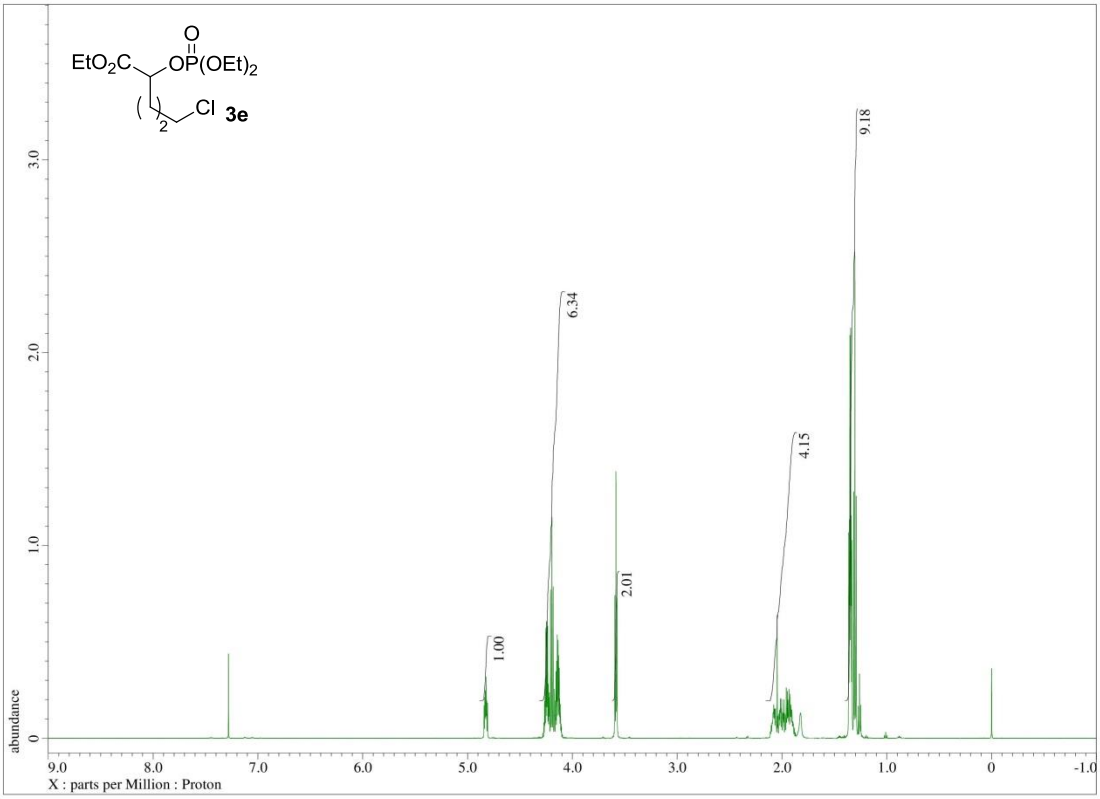
170.565
77.211
77.000
76.780
71.715
71.676
64.151
64.112
63.959
63.921
61.479
19.207
19.168
16.028
15.980
14.065
X : parts per Million : Carbon13

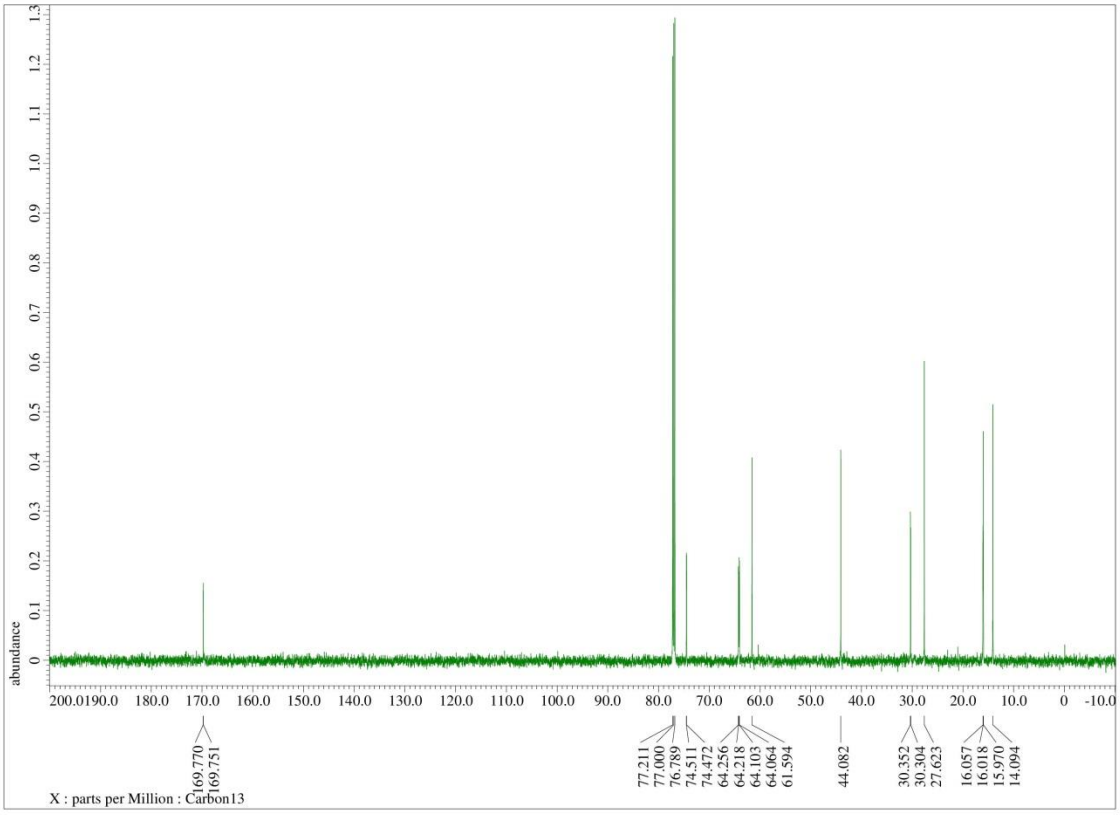

EtO2C
O
OP(OEt)2
3c
abundance
X : parts per Million : Proton
1.00
6.05
1.01
9.01
2.98
2.99

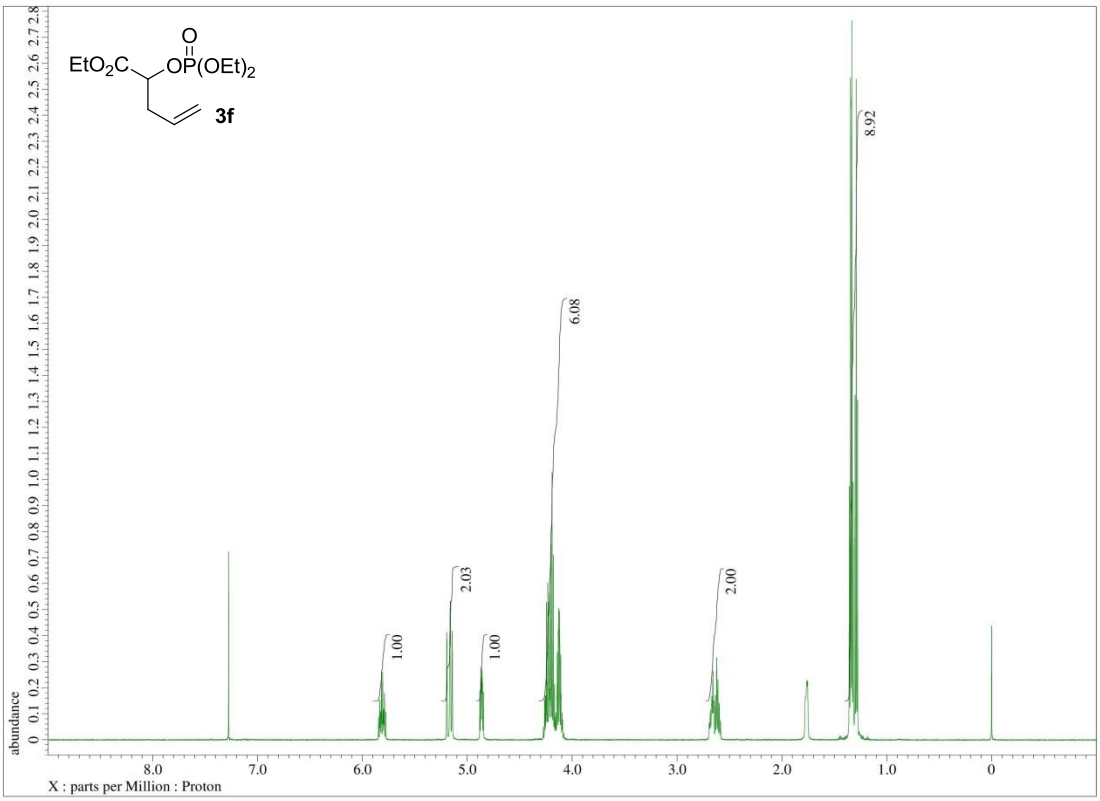

abundance
X : parts per Million : Carbon13
169.779
79.920
79.882
77.211
77.000
76.789
64.093
64.055
63.969
63.930
61.202
31.596
31.549
18.469
16.650
16.076
16.028
15.990
14.151

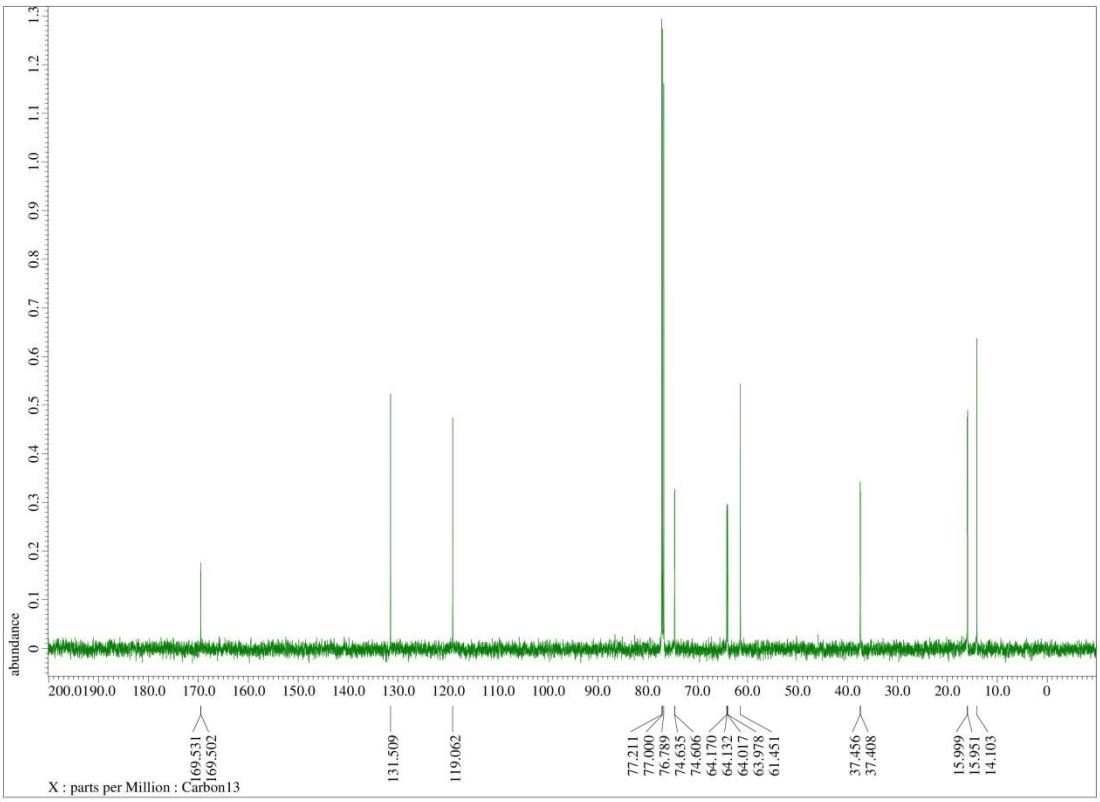

EtO2C
O
OP(OEt)2
Ph
3d
61.72
40.95
30.69
30.32
20.65
20.27
10.25
abundance
X : parts per Million : Proton

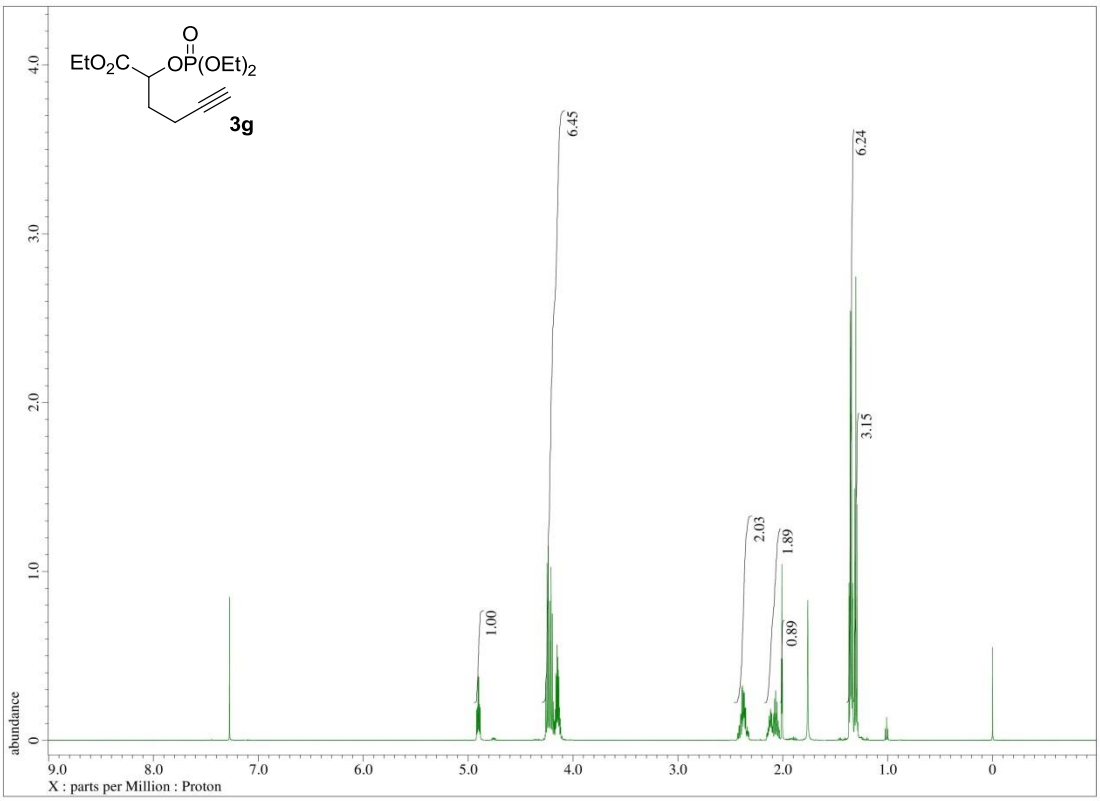

abundance
168.851
168.812
135.148
135.109
129.182
128.675
127.172
77.220
77.000
76.789
76.722
76.694
64.313
64.275
63.997
63.959
61.776
16.018
15.970
15.865
15.817
13.960
X : parts per Million : Carbon13

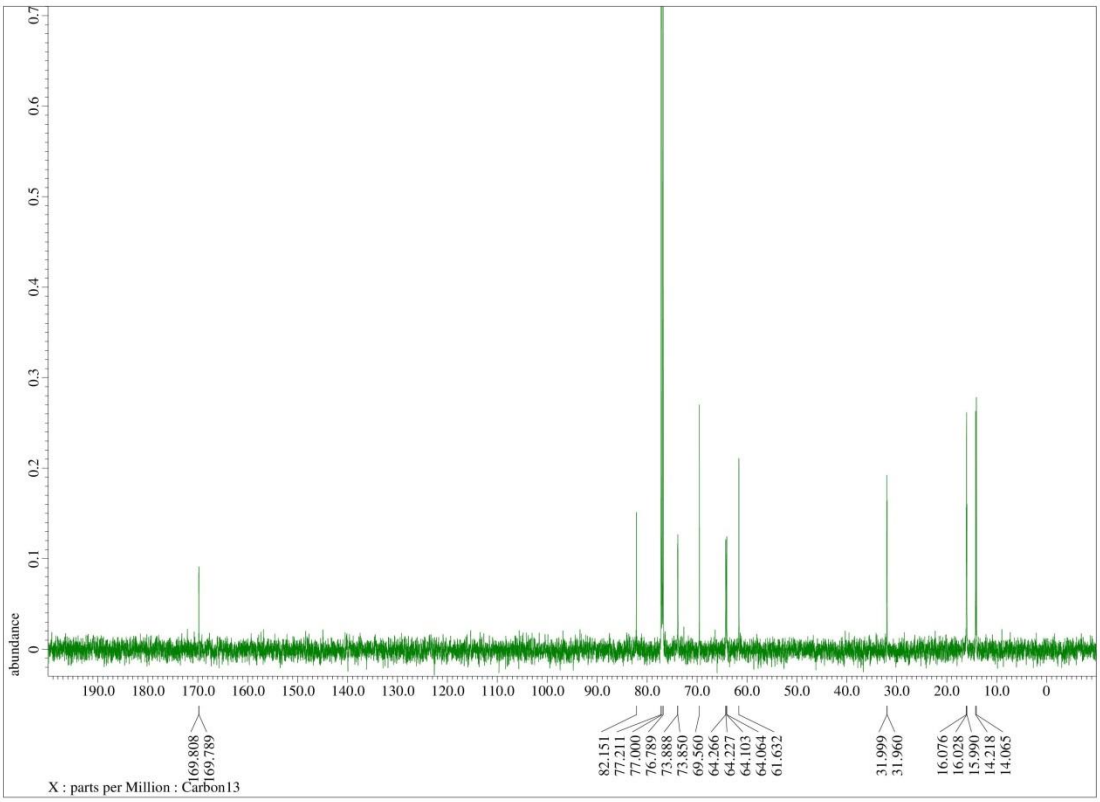

EtO2C
O
OP(OEt)2
Cl
2
3e
9.18
6.34
4.15
2.01
1.00
abundance
X : parts per Million : Proton

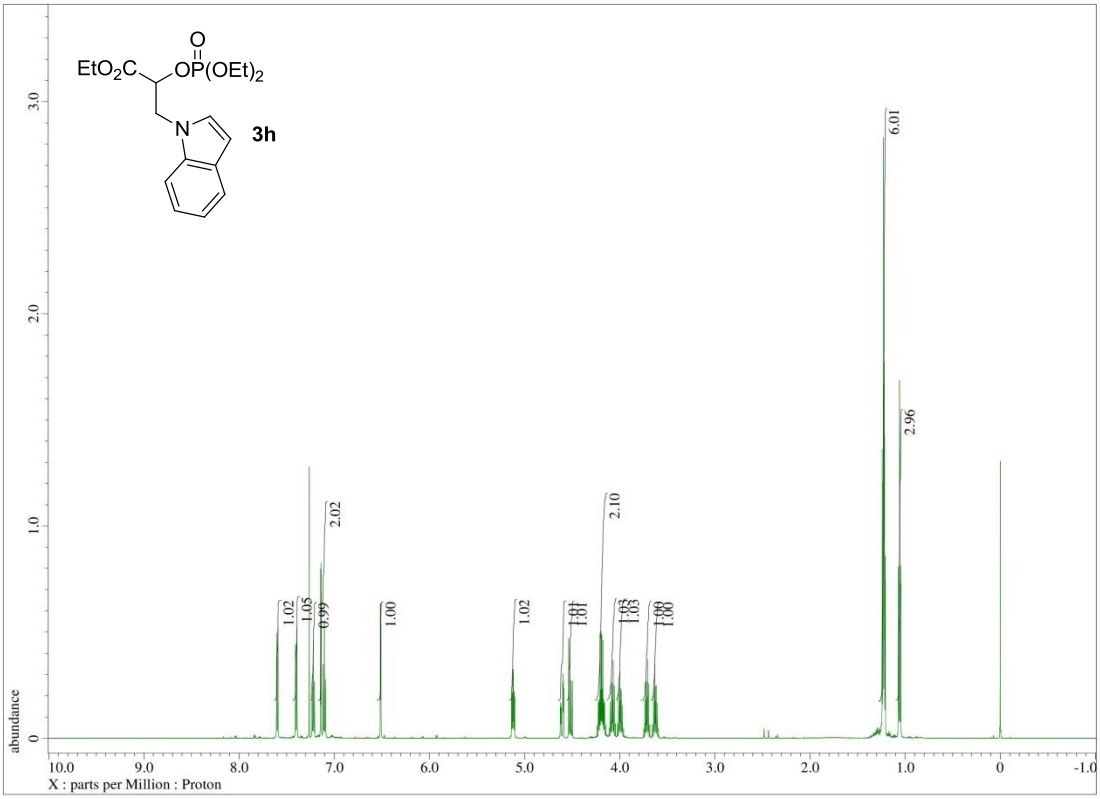

abundance
X : parts per Million : Carbon13
169.770
169.751
77.211
77.000
76.789
74.511
74.472
64.256
64.218
64.103
64.064
61.594
44.082
30.352
30.304
27.623
16.057
16.018
15.970
14.094

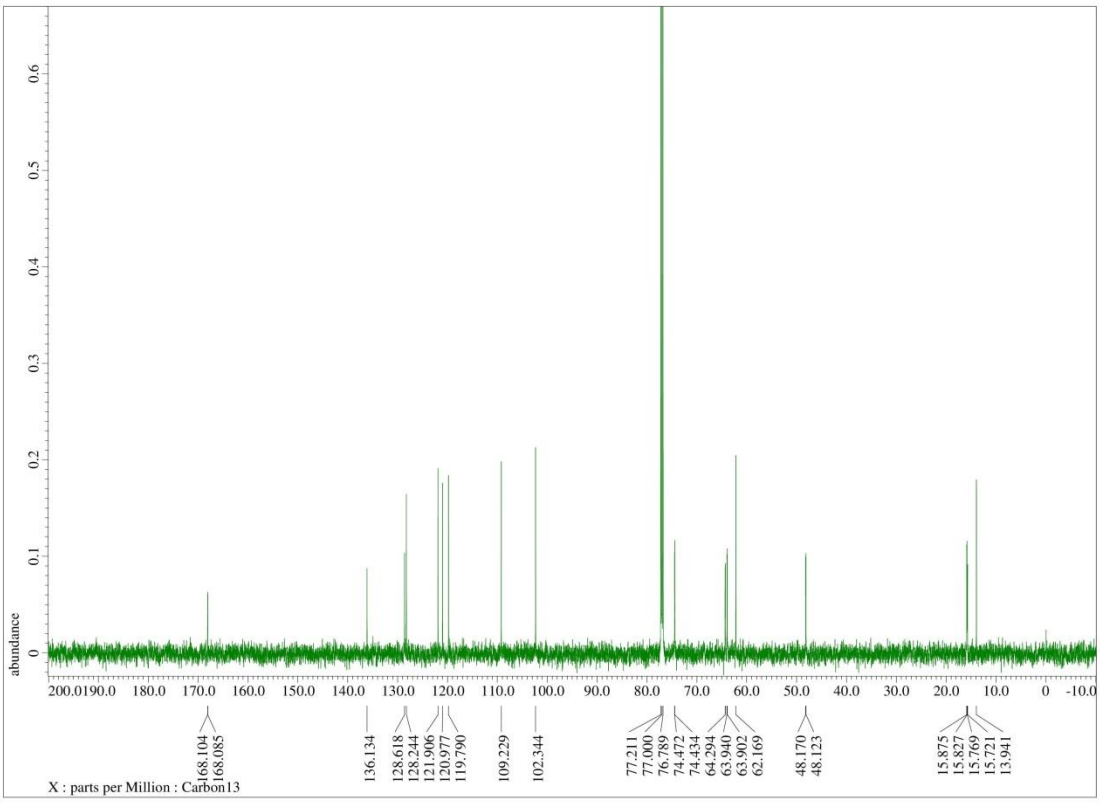

EtO2C
O
OP(OEt)2
3f
abundance
X : parts per Million : Proton
1.00
2.03
1.00
6.08
2.00
8.92

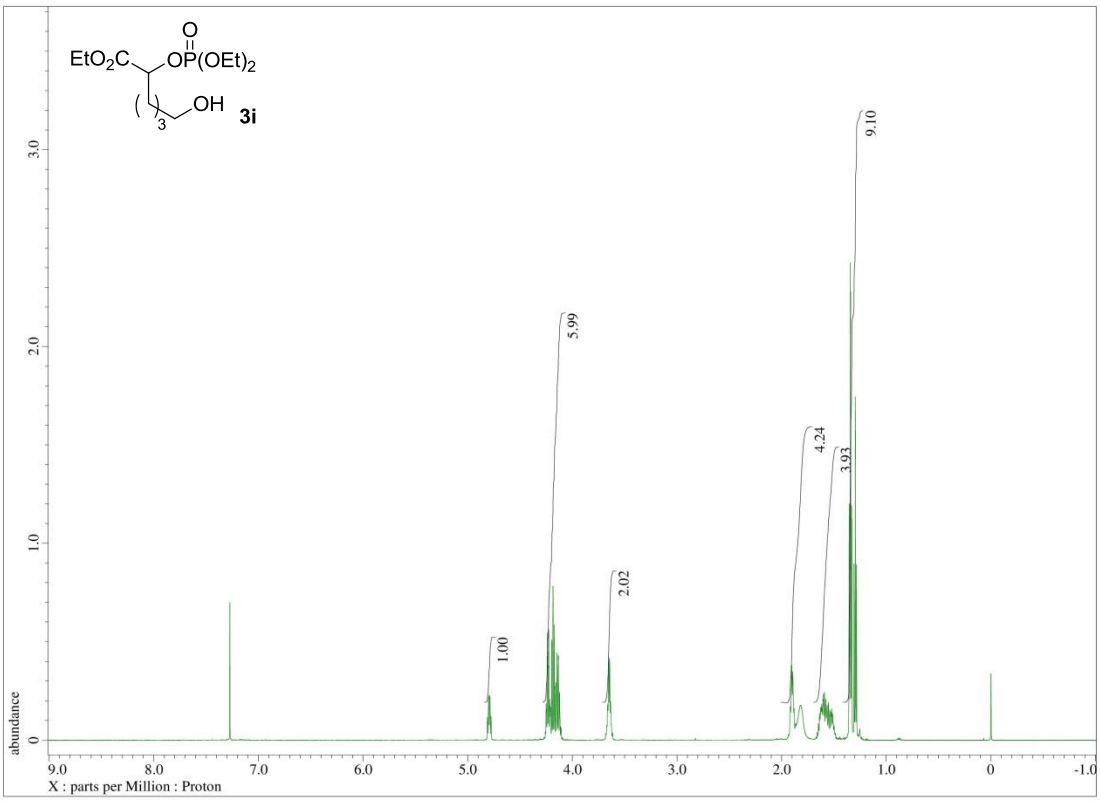

abundance
X : parts per Million : Carbon13
169.531
169.502
131.509
119.062
77.211
77.000
76.789
74.635
74.606
64.170
64.132
64.017
63.978
61.451
37.456
37.408
15.999
15.951
14.103

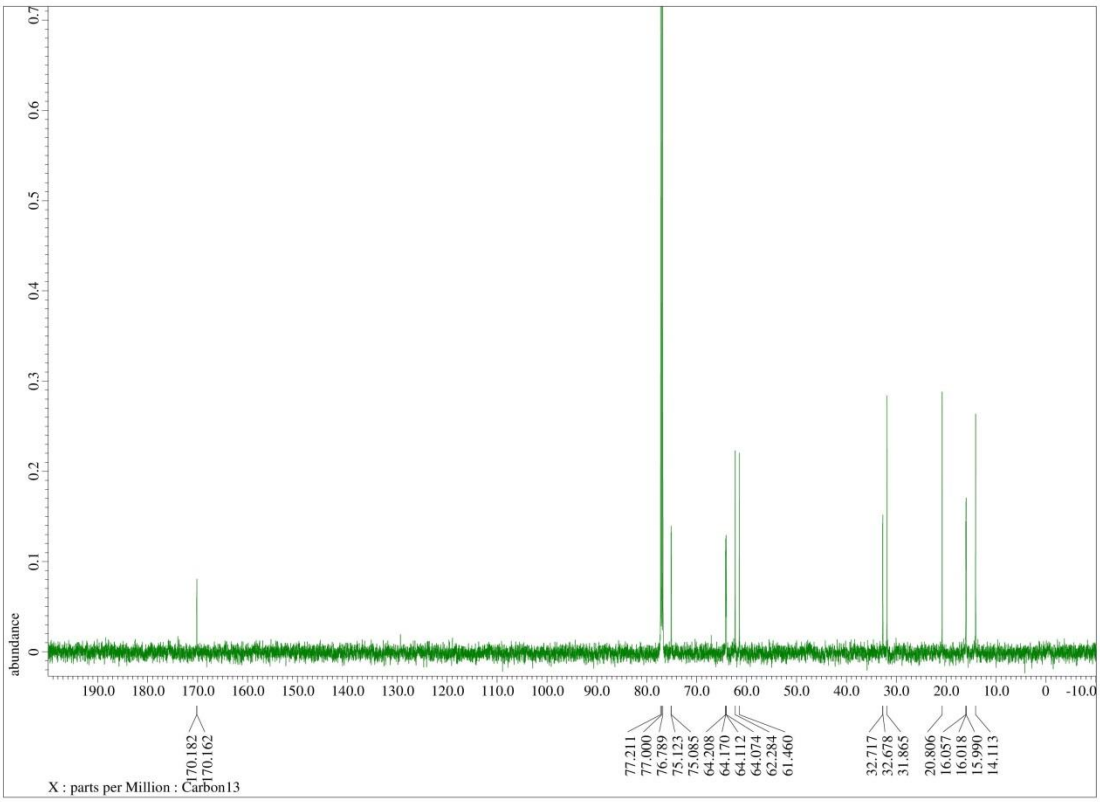

EtO2C
O
OP(OEt)2
3g
6.45
6.24
3.15
2.03
1.89
1.00
0.89
abundance
X : parts per Million : Proton

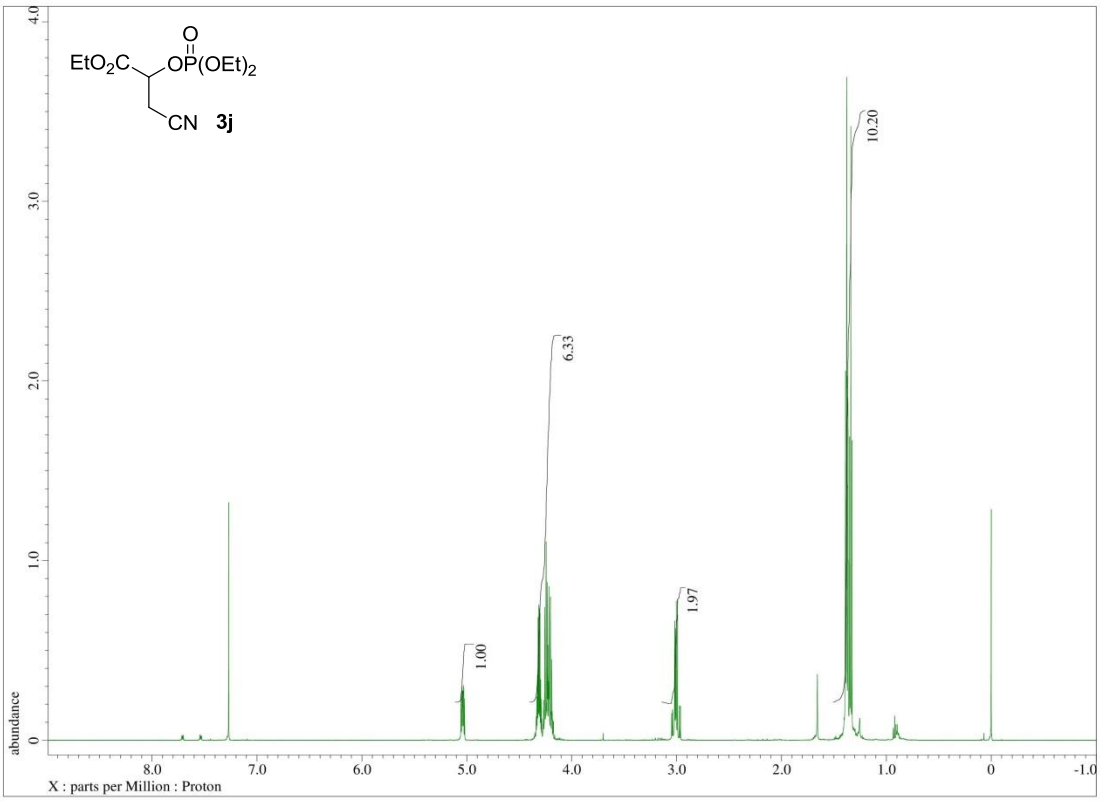

abundance
169.808
169.789
82.151
77.211
77.000
76.789
73.888
73.850
69.560
64.266
64.227
64.103
64.064
61.632
31.999
31.960
16.076
16.028
15.990
14.218
14.065
X : parts per Million : Carbon13

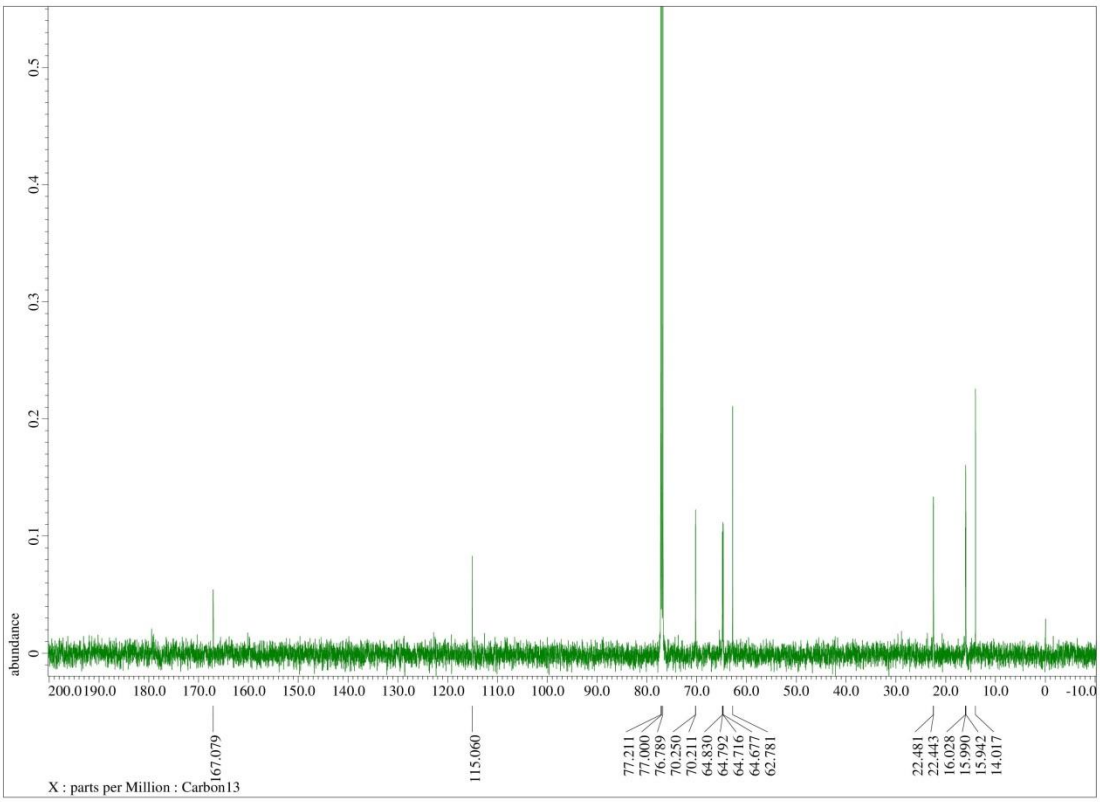

EtO2C
O
OP(OEt)2
N
3h
6.01
2.96
2.10
2.02
1.02
1.05
0.99
1.00
1.02
1.01
1.01
1.03
1.03
1.00
1.00
abundance
X : parts per Million : Proton

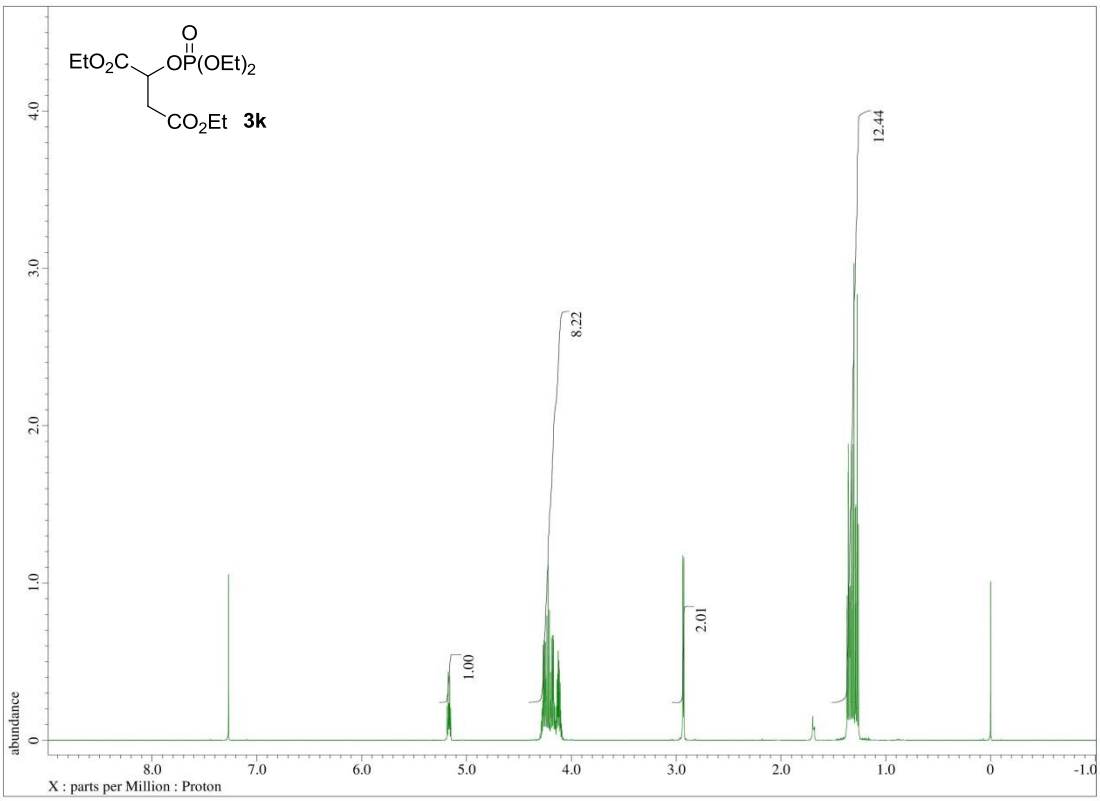

abundance
X : parts per Million : Carbon13
168.104
168.085
136.134
128.618
128.244
121.906
120.977
119.790
109.229
102.344
77.211
77.000
76.789
74.472
74.434
64.294
63.940
63.902
62.169
48.170
48.123
15.875
15.827
15.769
15.721
13.941

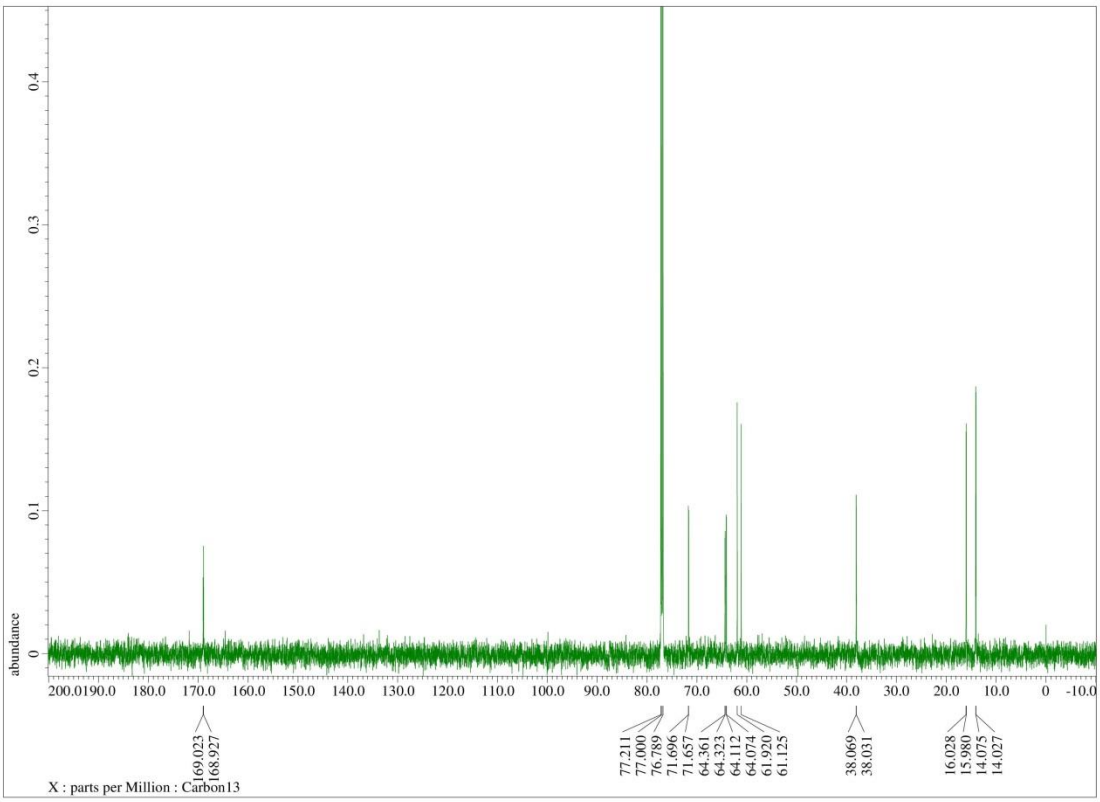

EtO2C
O
OP(OEt)2
OH
3
3i
abundance
X : parts per Million : Proton
1.00
5.99
2.02
4.24
3.93
9.10

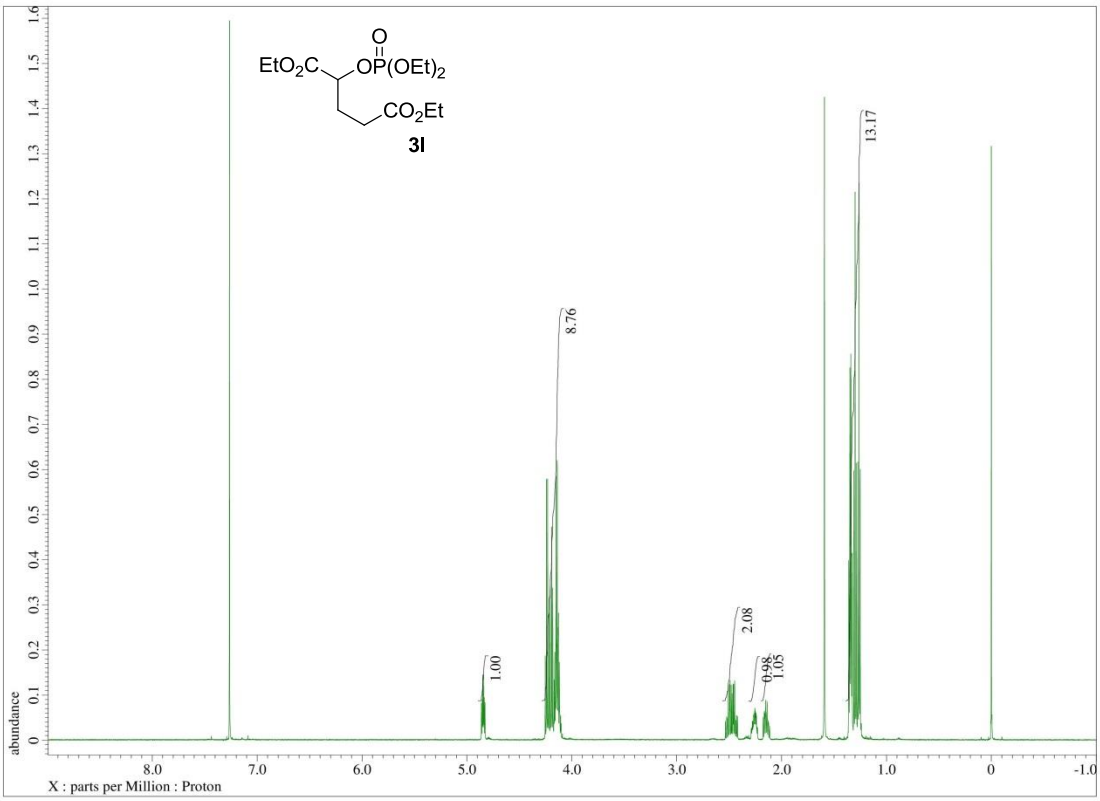

abundance
X : parts per Million : Carbon13
170.182
170.162
77.211
77.000
76.789
75.123
75.085
64.208
64.170
64.112
64.074
62.284
61.460
32.717
32.678
31.865
20.806
16.057
16.018
15.990
14.113

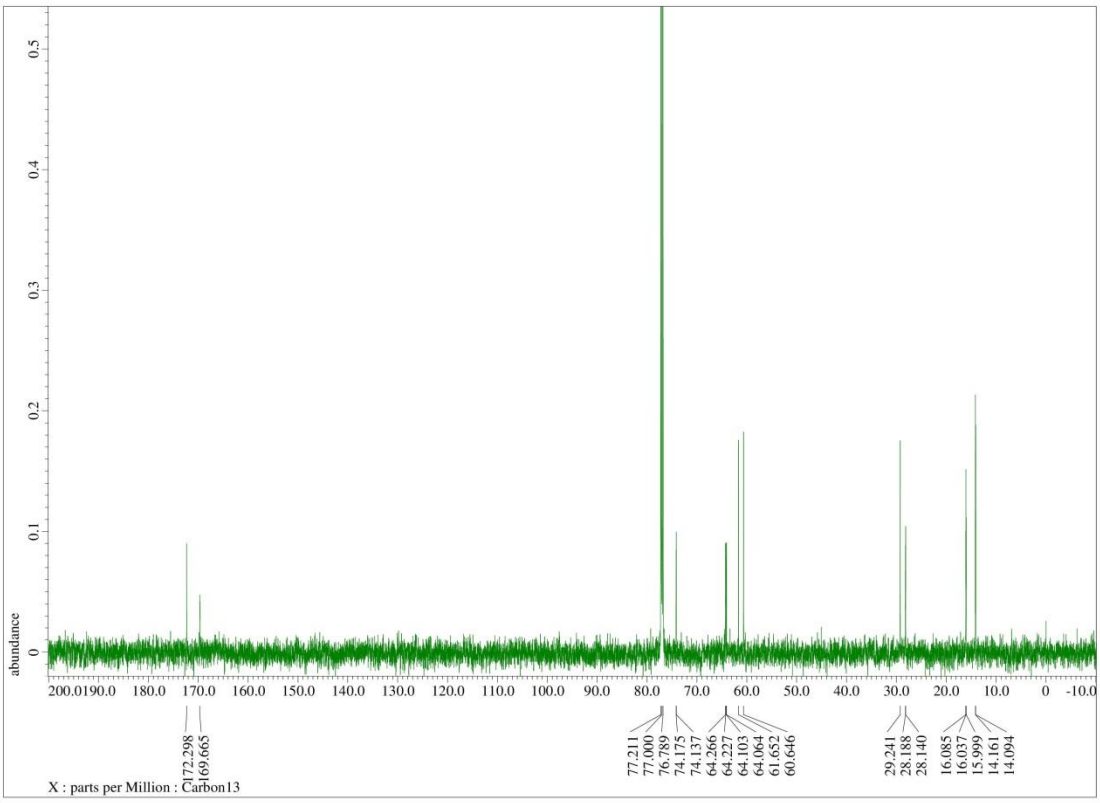

EtO2C
O
OP(OEt)2
CN
3j
10.20
6.33
1.97
1.00
abundance
X : parts per Million : Proton

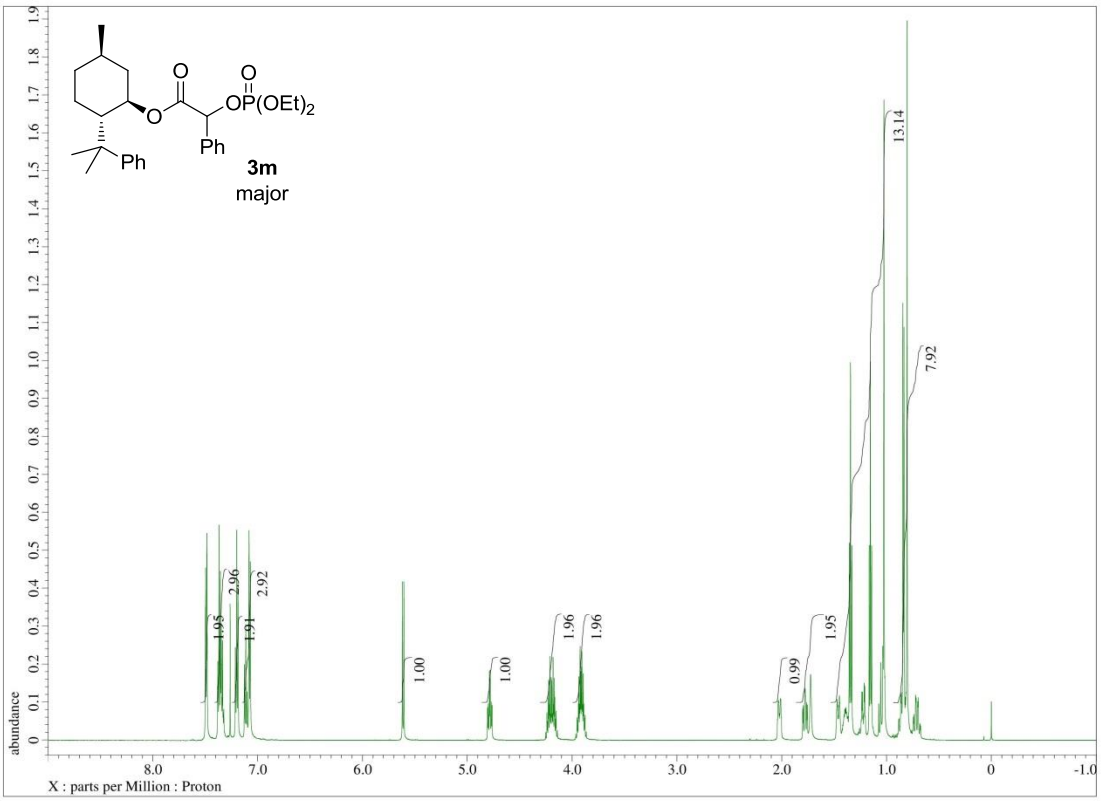

abundance
167.079
115.060
77.211
77.000
76.789
70.250
70.211
64.830
64.792
64.716
64.677
62.781
22.481
22.443
16.028
15.990
15.942
14.017
X : parts per Million : Carbon13

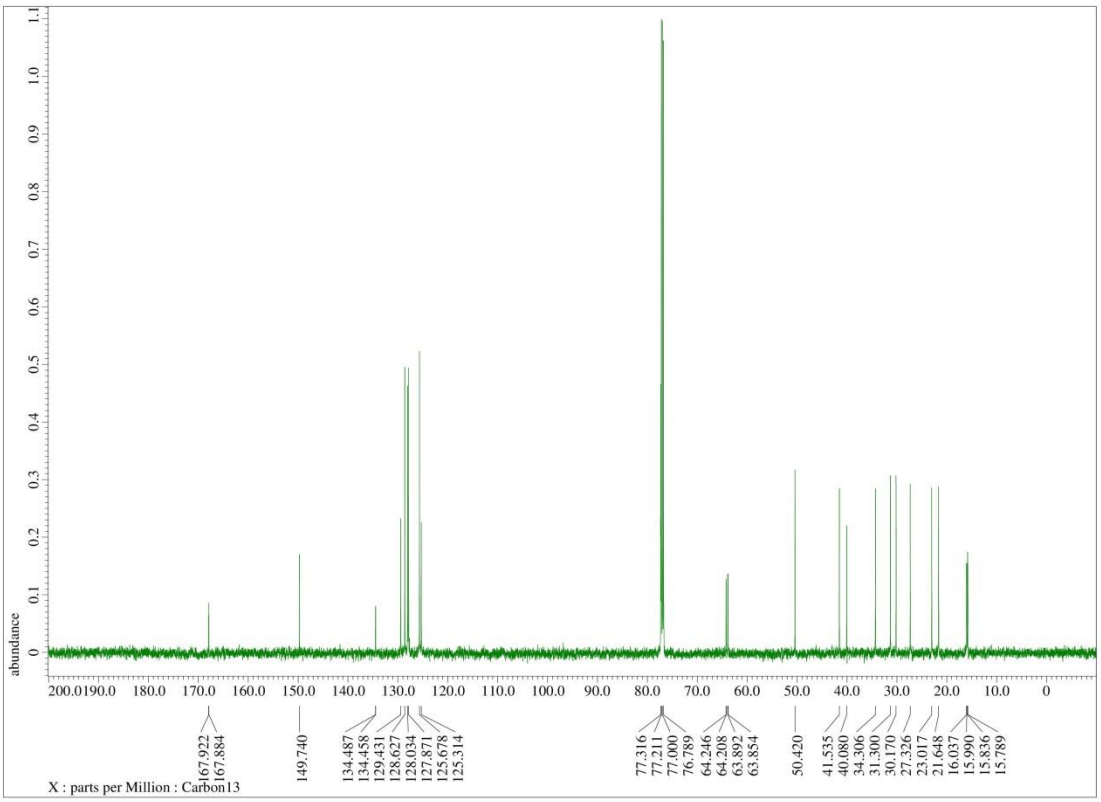

EtO2C
O
OP(OEt)2
CO2Et
3k
12.44
8.22
2.01
1.00
abundance
X : parts per Million : Proton

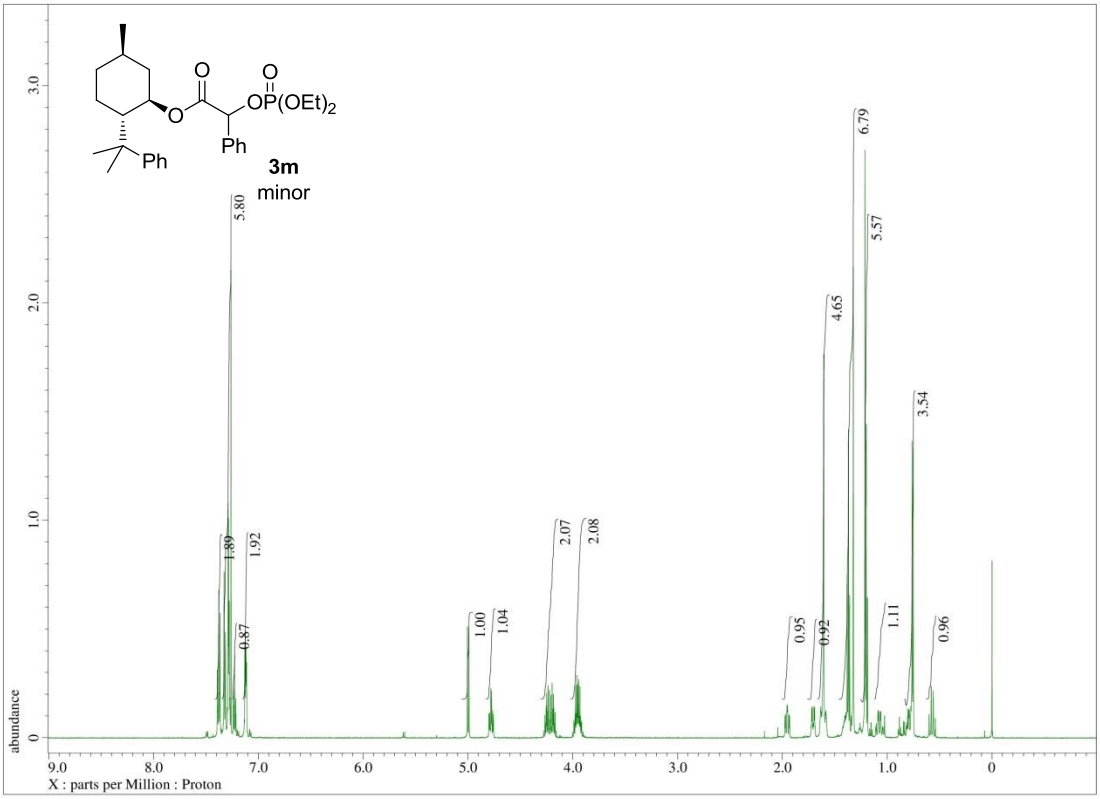

abundance
169.023
168.927
77.211
77.000
76.789
71.696
71.657
64.361
64.323
64.112
64.074
61.920
61.125
38.069
38.031
16.028
15.980
14.075
14.027
X : parts per Million : Carbon13

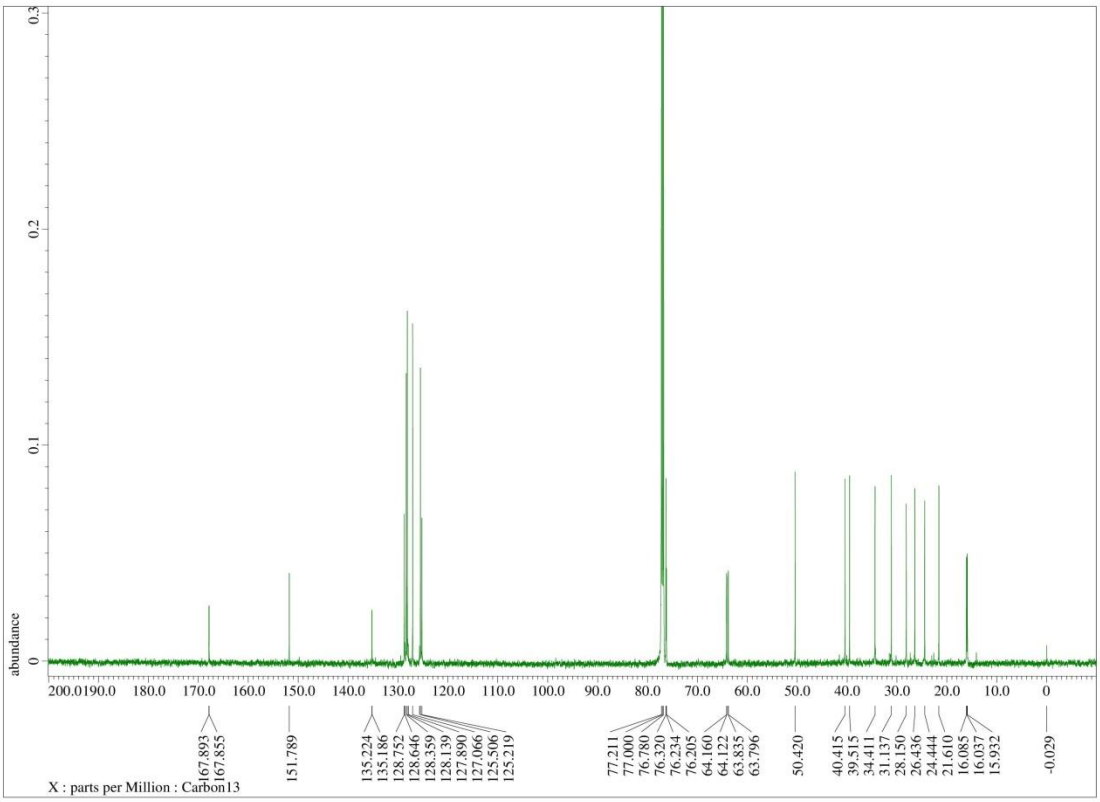

EtO2C
O
OP(OEt)2
CO2Et
3l
abundance
X : parts per Million : Proton
1.00
8.76
2.08
0.98
1.05
13.17

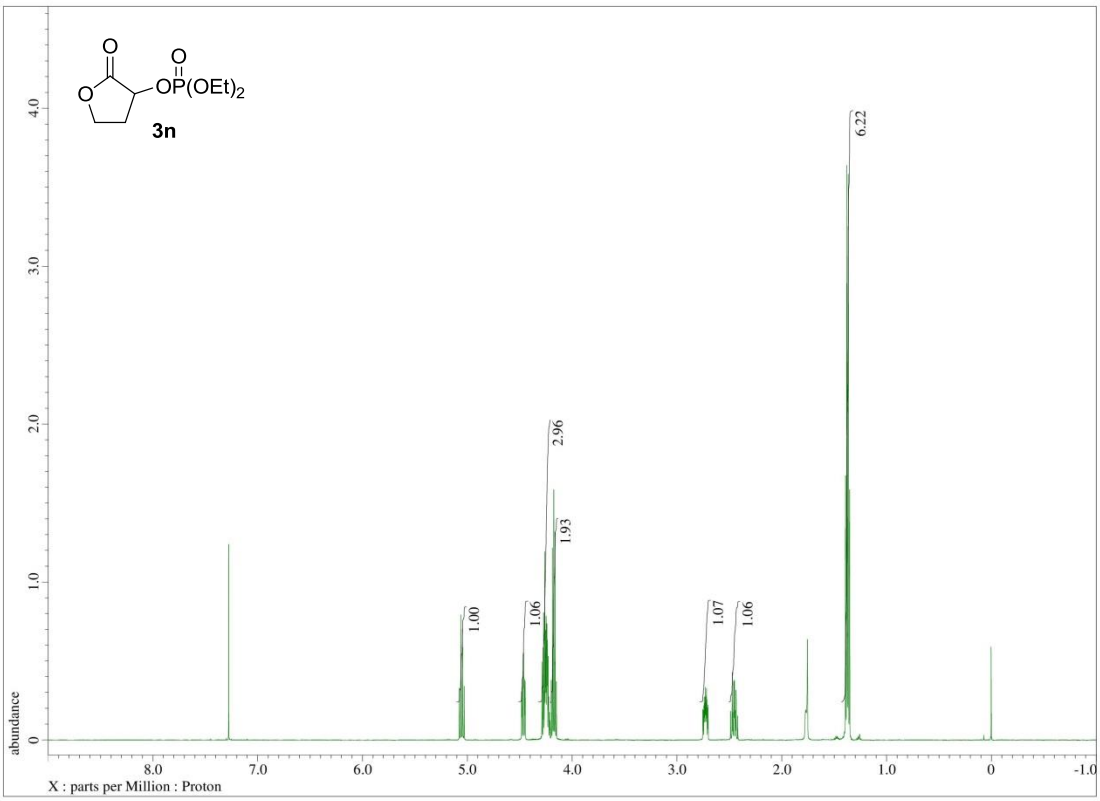

abundance
X : parts per Million : Carbon13
172.298
169.665
77.211
77.000
76.789
74.175
74.137
64.266
64.227
64.103
64.064
61.652
60.646
29.241
28.188
28.140
16.085
16.037
15.999
14.161
14.094

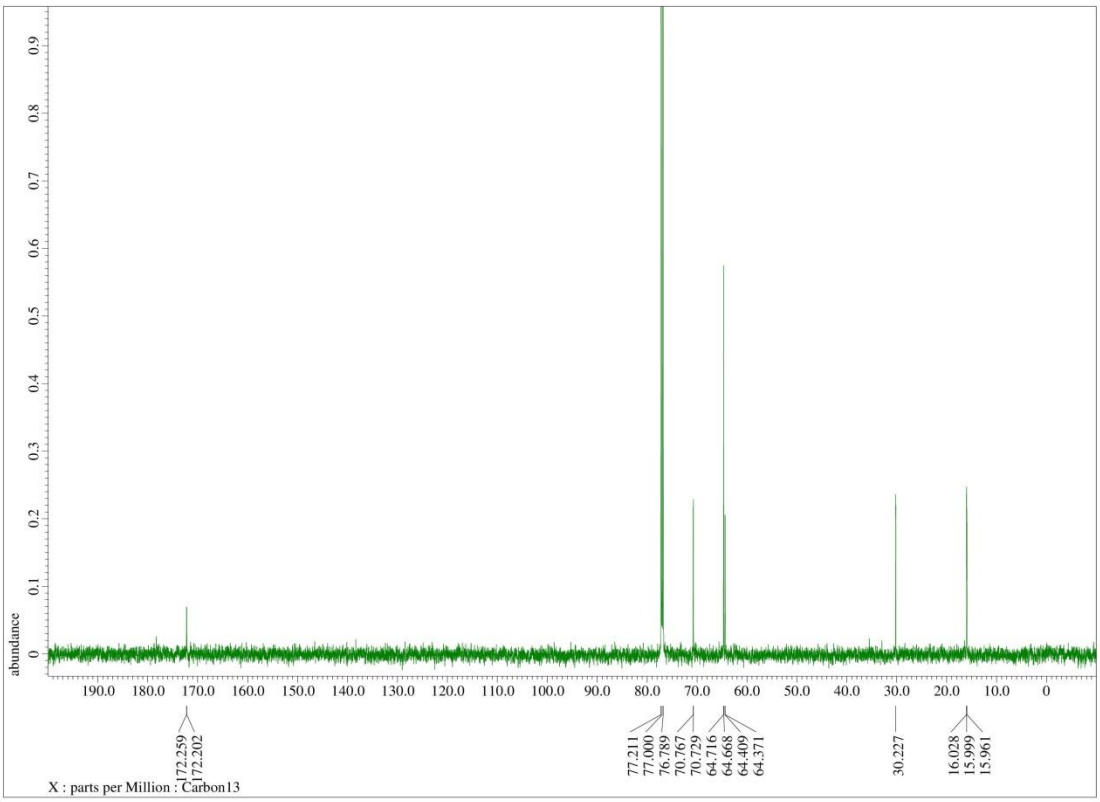

O
O
OP(OEt)2
O
Ph
Ph
3m
major
abundance
X : parts per Million : Proton
13.14
7.92
2.96
2.92
1.95
1.91
1.00
1.00
1.96
1.96
0.99
1.95

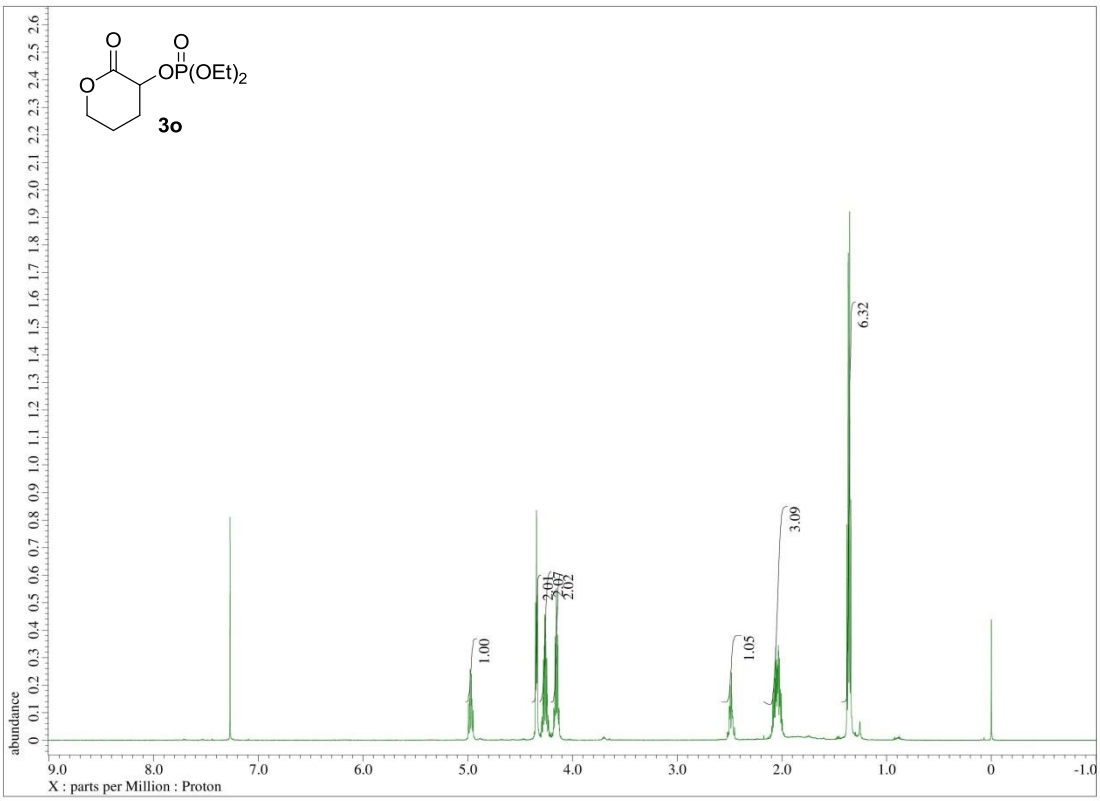

abundance
X : parts per Million : Carbon13
167.922
167.884
149.740
134.487
134.458
129.431
128.627
128.034
127.871
125.678
125.314
77.316
77.211
77.000
76.789
64.246
64.208
63.892
63.854
50.420
41.535
40.080
34.306
31.300
30.170
27.326
23.017
21.648
16.037
15.990
15.836
15.789

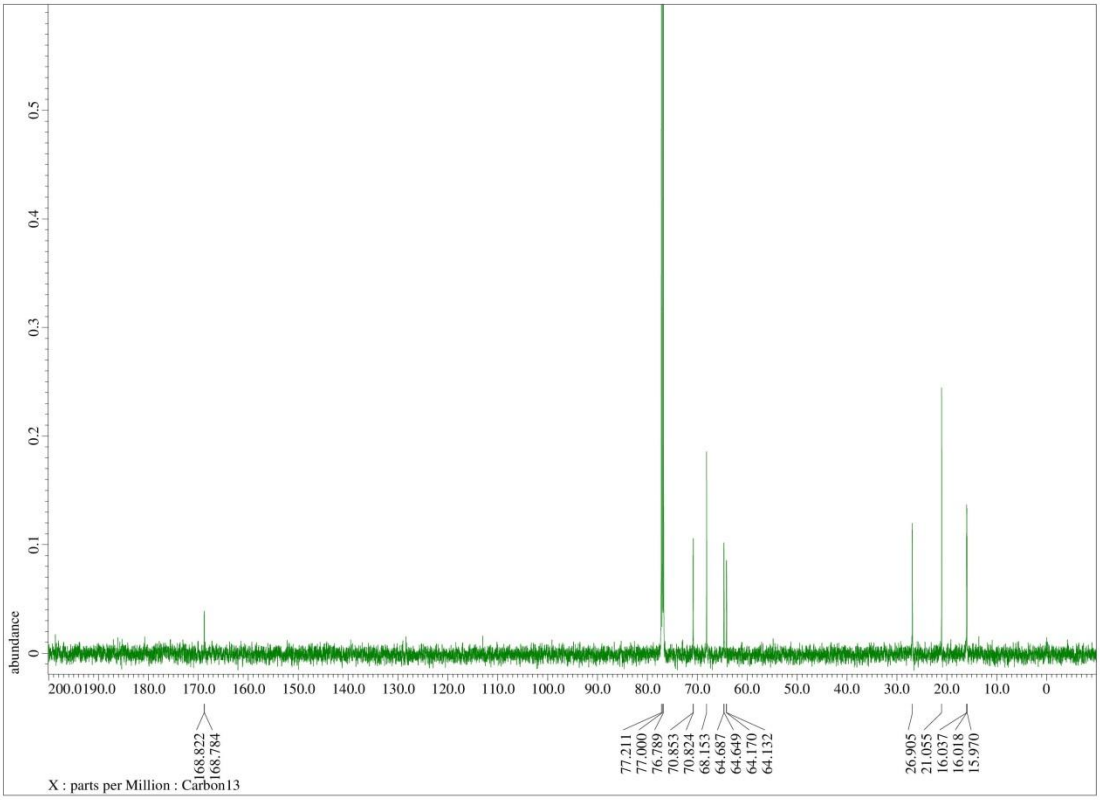

O
O
OP(OEt)2
Ph
O
Ph
3m
minor
5.80
1.89
1.92
0.87
1.00
1.04
2.07
2.08
0.95
0.92
4.65
6.79
5.57
1.11
3.54
0.96
abundance
X : parts per Million : Proton

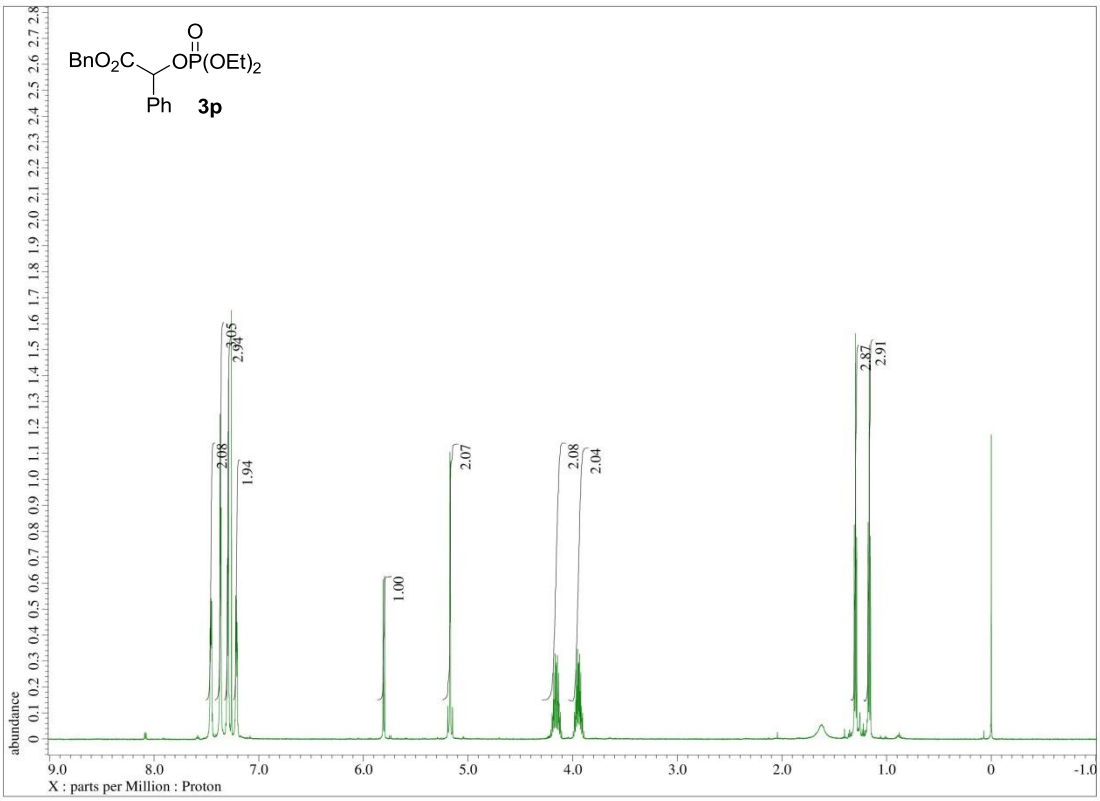

abundance
X : parts per Million : Carbon13
167.893
167.855
151.789
135.224
135.186
128.752
128.646
128.359
128.139
127.890
127.066
125.506
125.219
77.211
77.000
76.780
76.320
76.234
76.205
64.160
64.122
63.835
63.796
50.420
40.415
39.515
34.411
31.137
28.150
26.436
24.444
21.610
16.085
16.037
15.932
-0.029

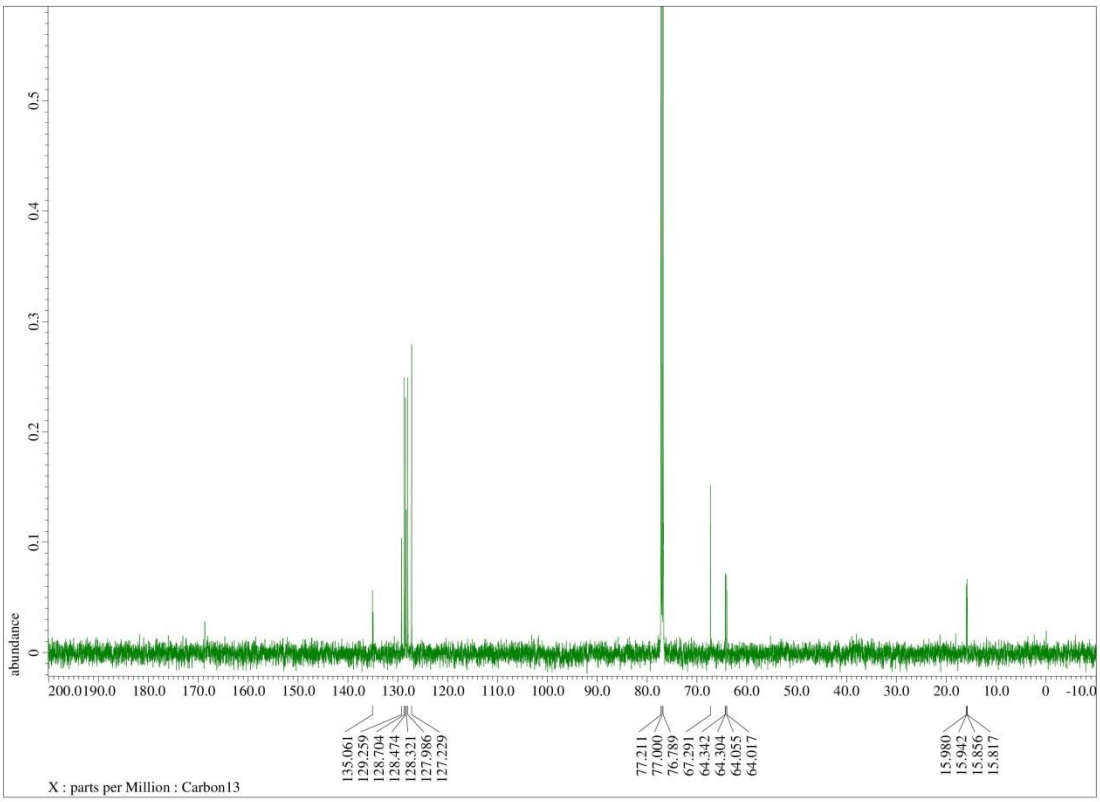

3n
abundance
X : parts per Million : Proton
1.00
1.06
2.96
1.93
1.07
1.06
6.22

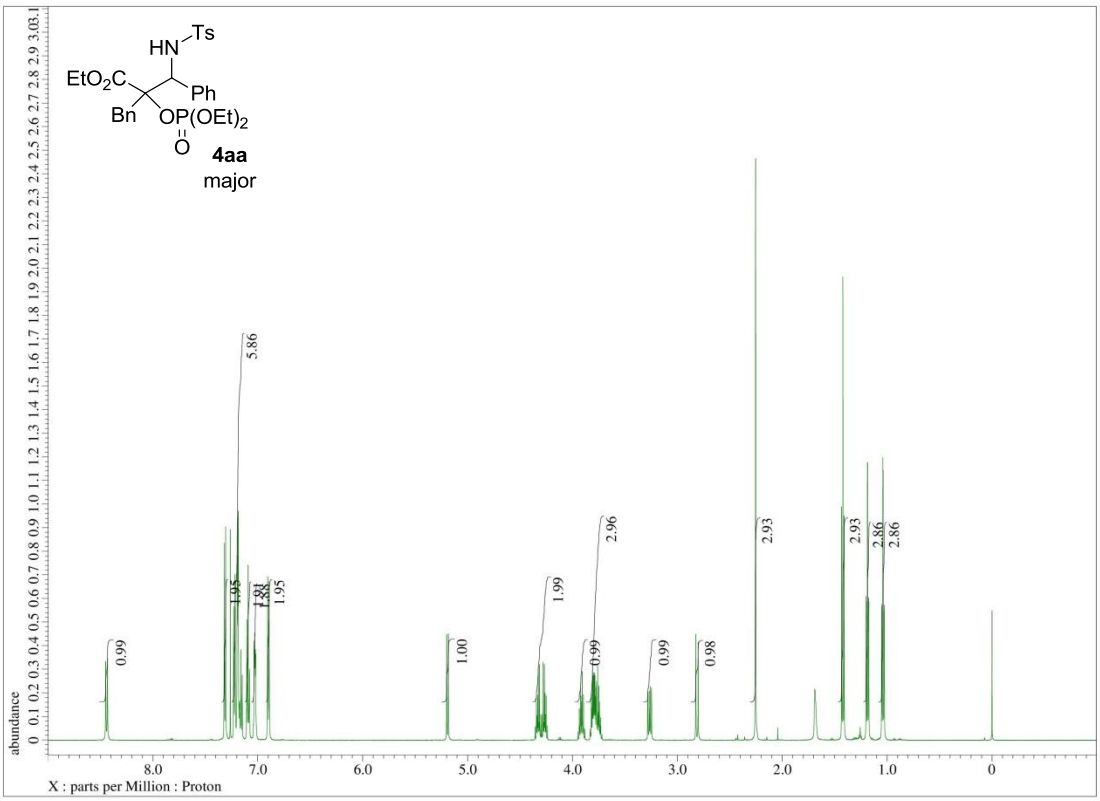

abundance
X : parts per Million : Carbon13
172.259
172.202
77.211
77.000
76.789
70.767
70.729
64.716
64.668
64.409
64.371
30.227
16.028
15.999
15.961

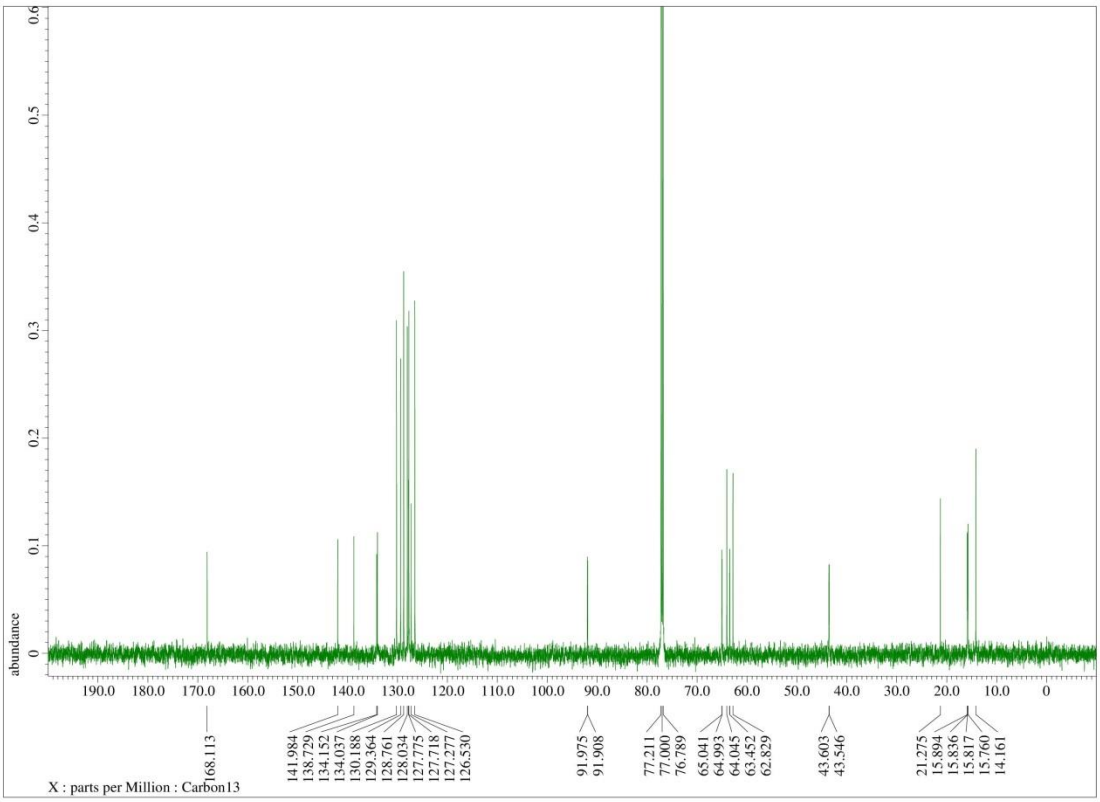

OP(OEt)2
3o
abundance
X : parts per Million : Proton
1.00
2.01
2.07
2.02
1.05
3.09
6.32

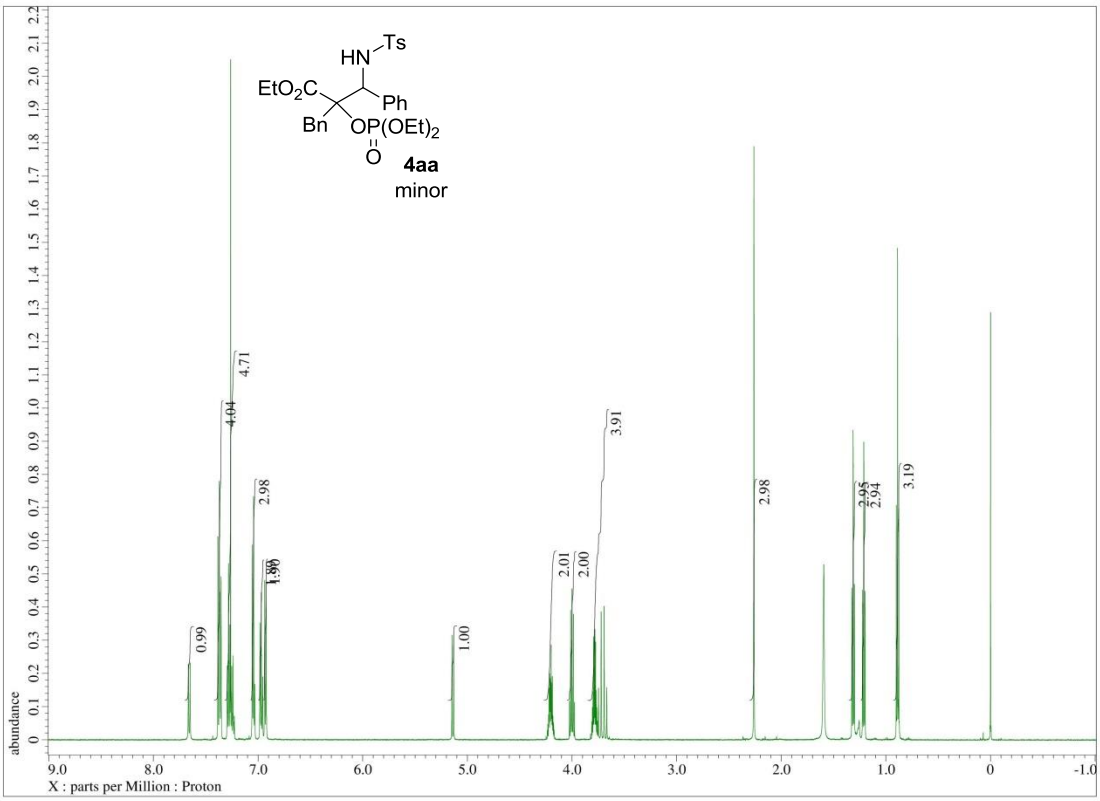

abundance
X : parts per Million : Carbon13
168.822
168.784
77.211
77.000
76.789
70.853
70.824
68.153
64.687
64.649
64.170
64.132
26.905
21.055
16.037
16.018
15.970

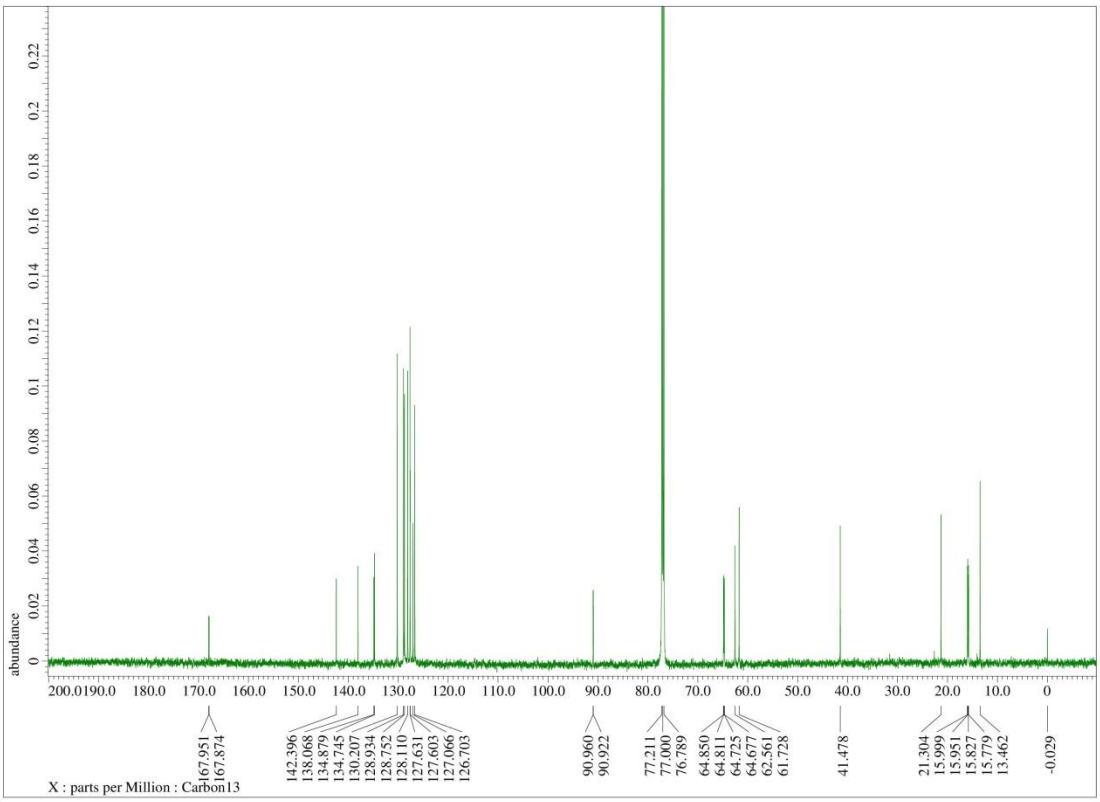

BnO2C
O
OP(OEt)2
Ph
3p
abundance
X : parts per Million : Proton
3.05
2.94
2.08
1.94
1.00
2.07
2.08
2.04
2.87
2.91

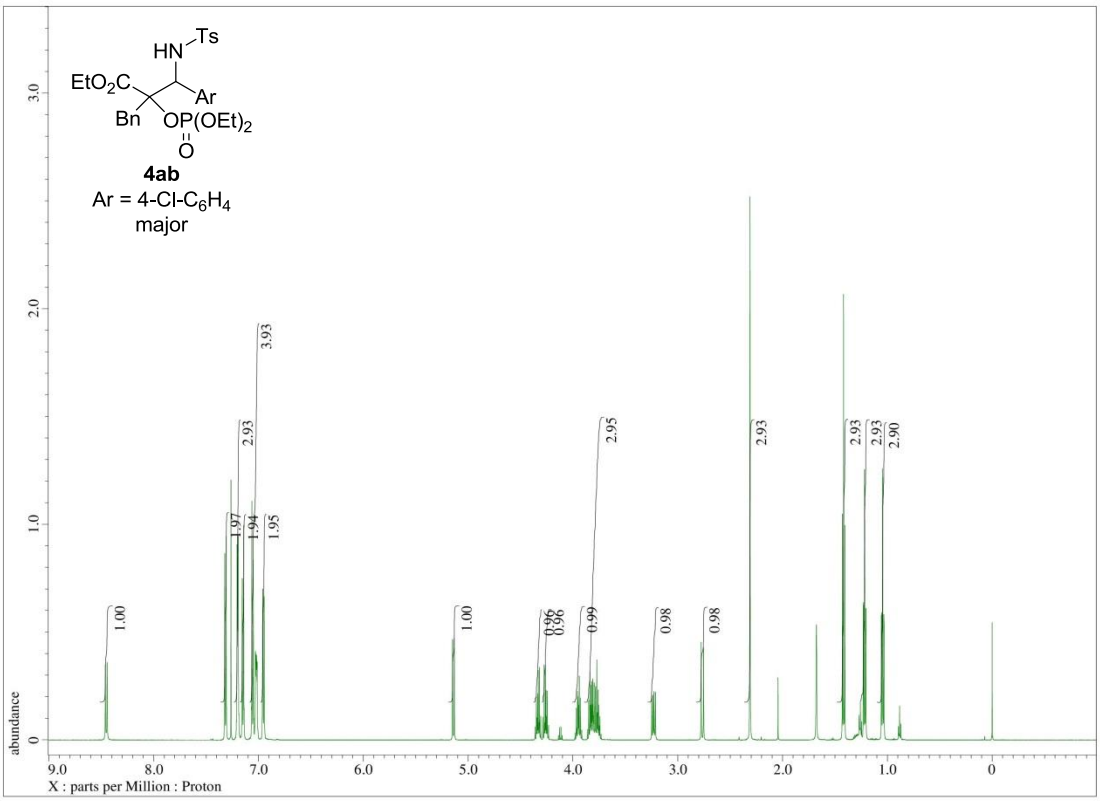

abundance
X : parts per Million : Carbon13
135.061
129.259
128.704
128.474
128.321
127.986
127.229
77.211
77.000
76.789
67.291
64.342
64.304
64.055
64.017
15.980
15.942
15.856
15.817

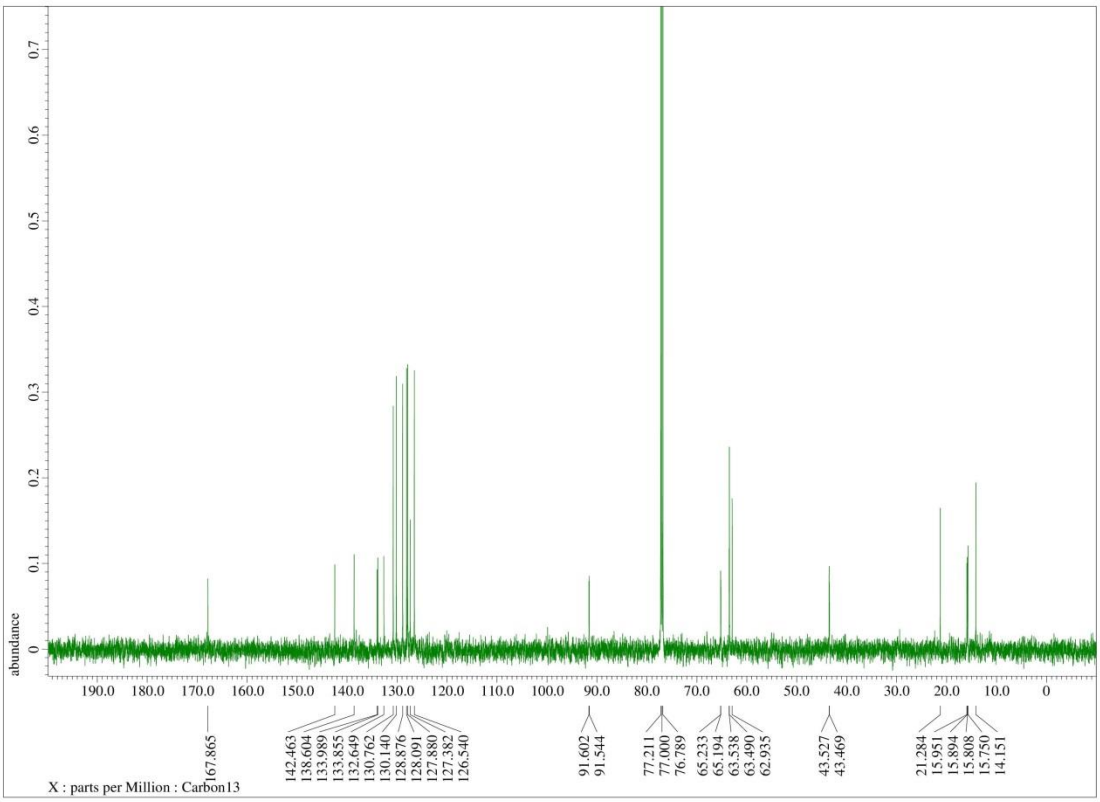

HN
Ts
EtO2C
Ph
Bn
OP(OEt)2
O
4aa
major
abundance
X : parts per Million : Proton

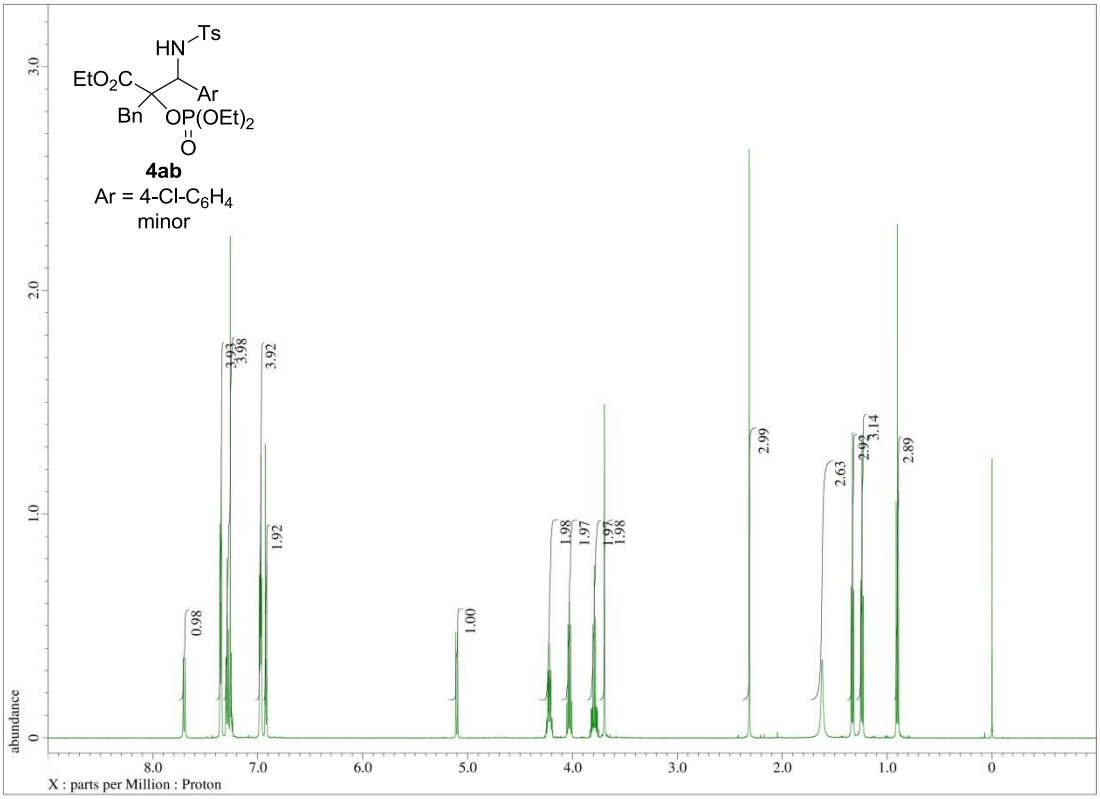

abundance
X : parts per Million : Carbon13

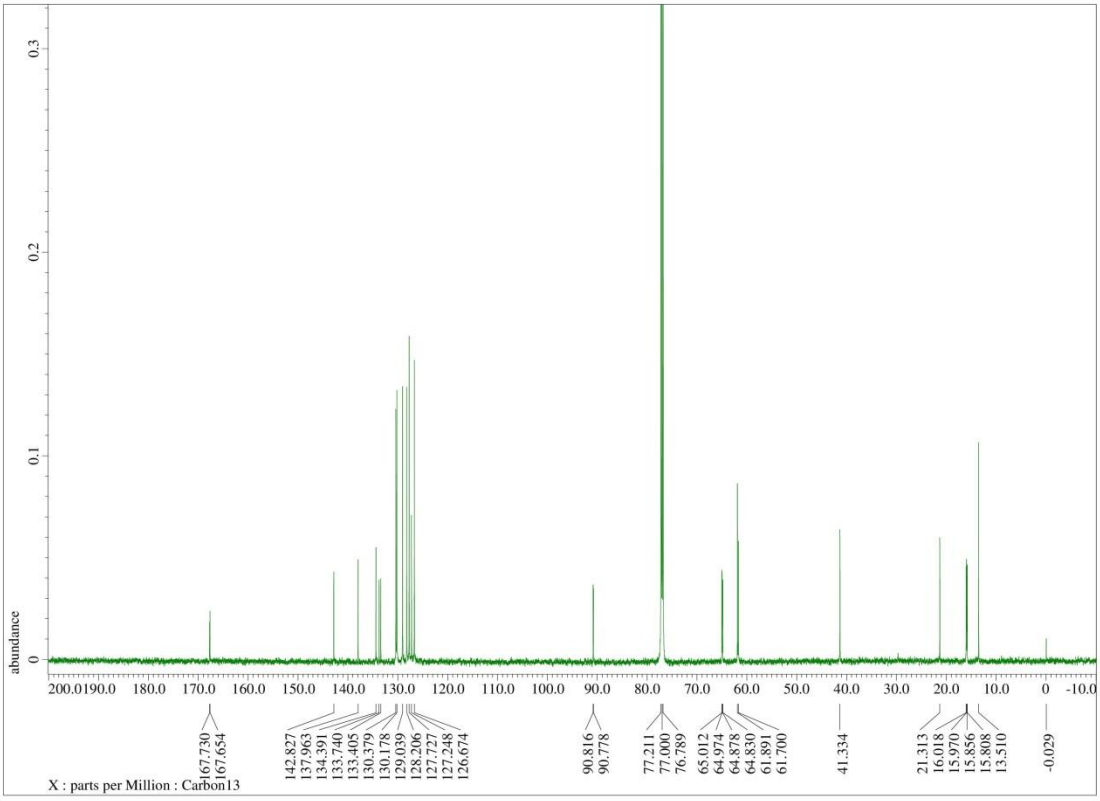

HN
Ts
EtO2C
Ph
Bn
OP(OEt)2
O
4aa
minor
abundance
X : parts per Million : Proton
0.99
4.04
4.71
2.98
1.00
2.01
2.00
3.91
2.98
2.95
2.94
3.19

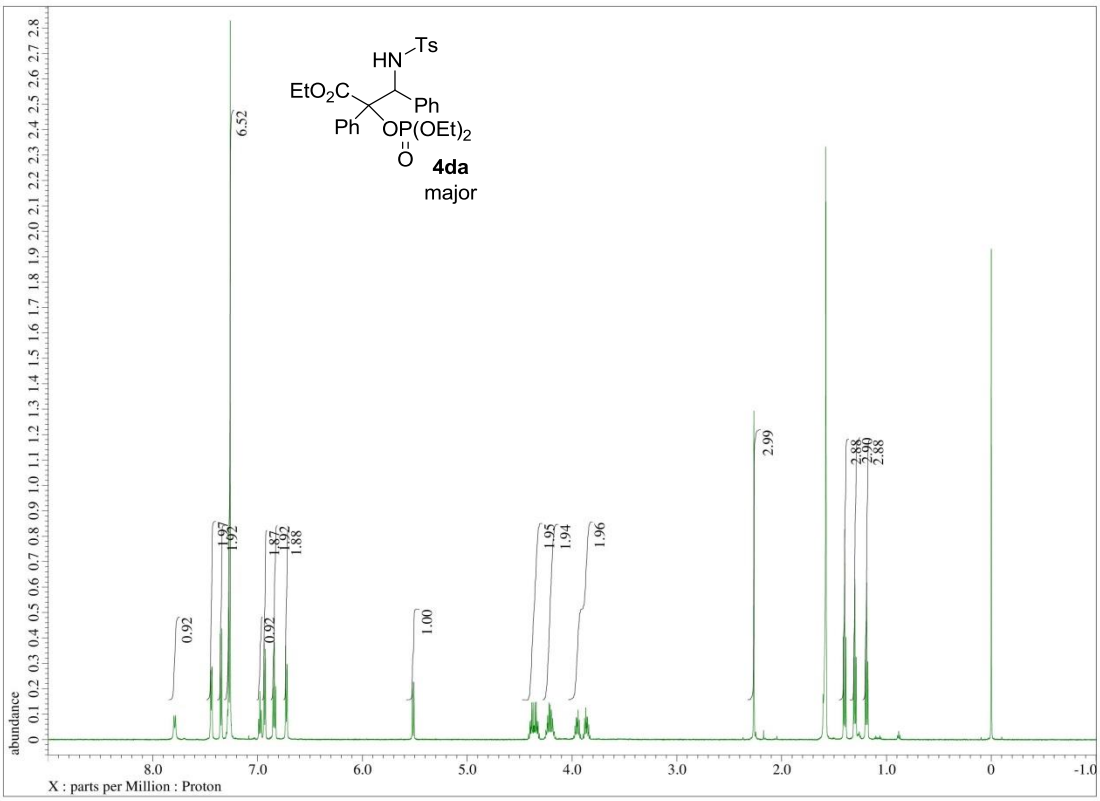

abundance
X : parts per Million : Carbon13
167.951
167.874
142.396
138.068
134.879
134.745
130.207
128.934
128.752
128.110
127.631
127.603
127.066
126.703
90.960
90.922
77.211
77.000
76.789
64.850
64.811
64.725
64.677
62.561
61.728
41.478
21.304
15.999
15.951
15.827
15.779
13.462
-0.029

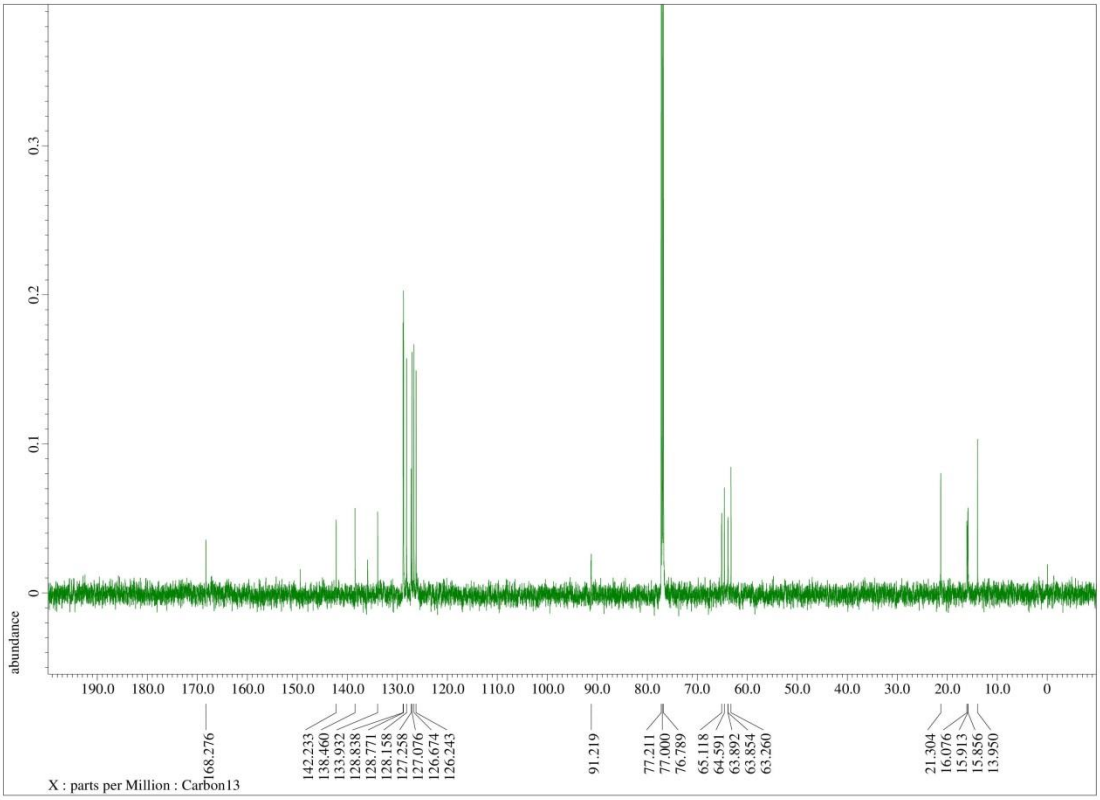

HN
Ts
EtO2C
Ar
Bn
OP(OEt)2
O
4ab
Ar = 4-Cl-C6H4
major
abundance
X : parts per Million : Proton

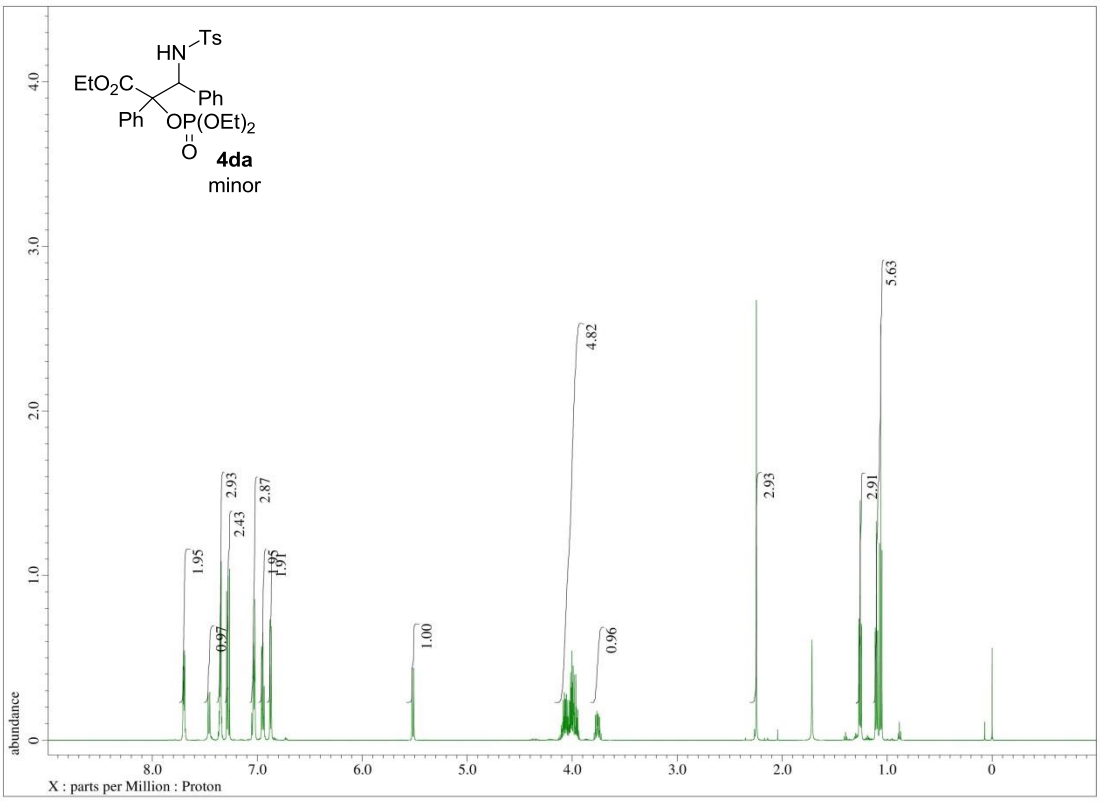

abundance
X : parts per Million : Carbon13

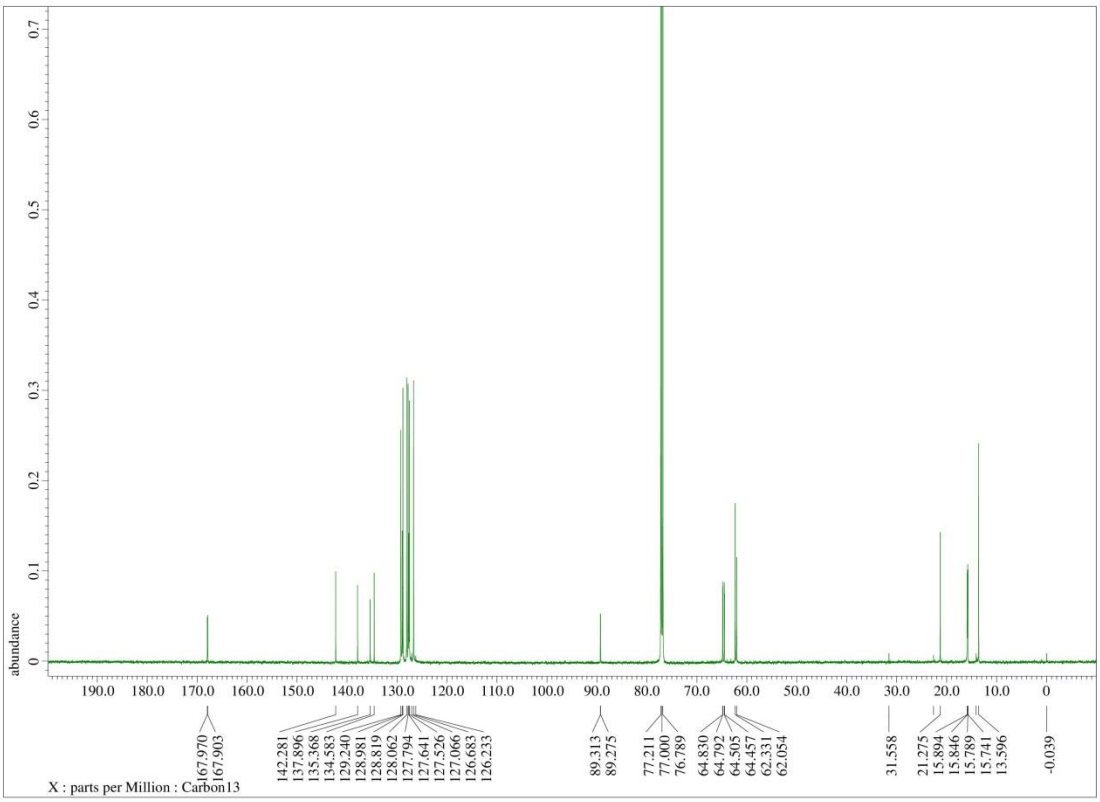

HN
Ts
EtO2C
Ar
Bn
OP(OEt)2
O
4ab
Ar = 4-Cl-C6H4
minor
abundance
X : parts per Million : Proton
0.98
3.93
3.98
3.92
1.92
1.00
1.98
1.97
1.97
1.98
2.99
2.63
2.93
3.14
2.89

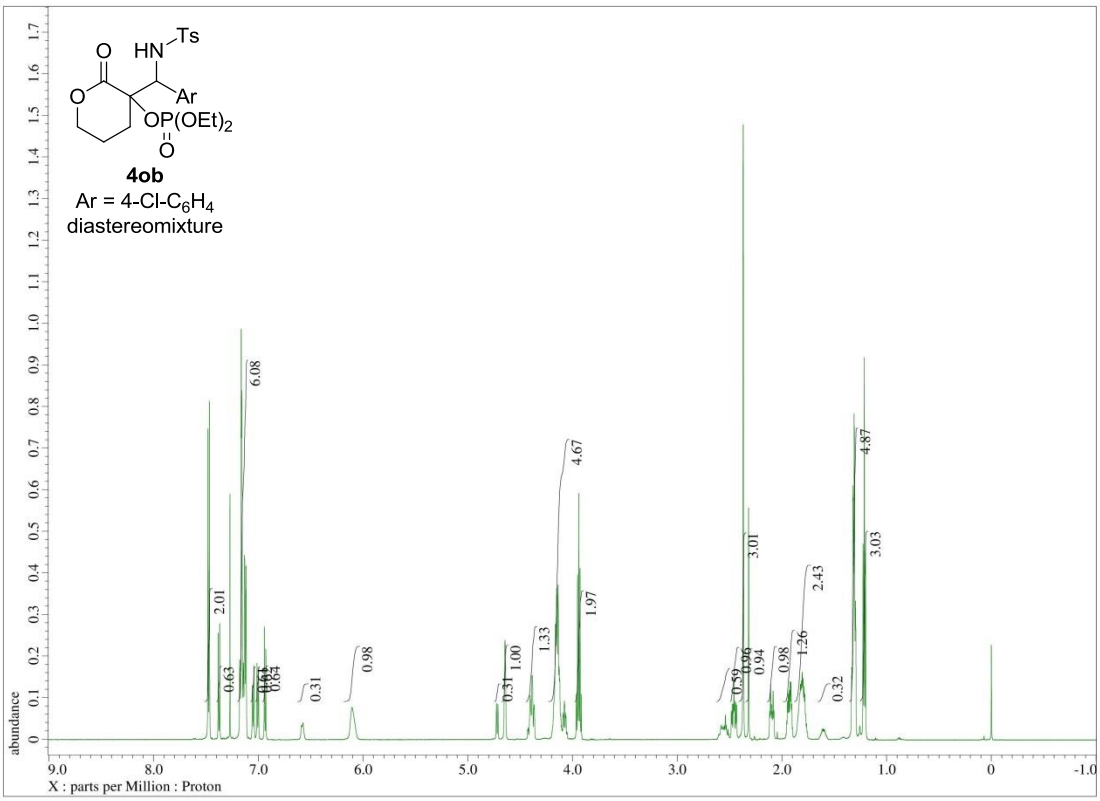

abundance
X : parts per Million : Carbon13
167.730
167.654
142.827
137.963
134.391
133.740
133.405
130.379
130.178
129.039
128.206
127.727
127.248
126.674
90.816
90.778
77.211
77.000
76.789
65.012
64.974
64.878
64.830
61.891
61.700
41.334
21.313
16.018
15.970
15.856
15.808
13.510
-0.029

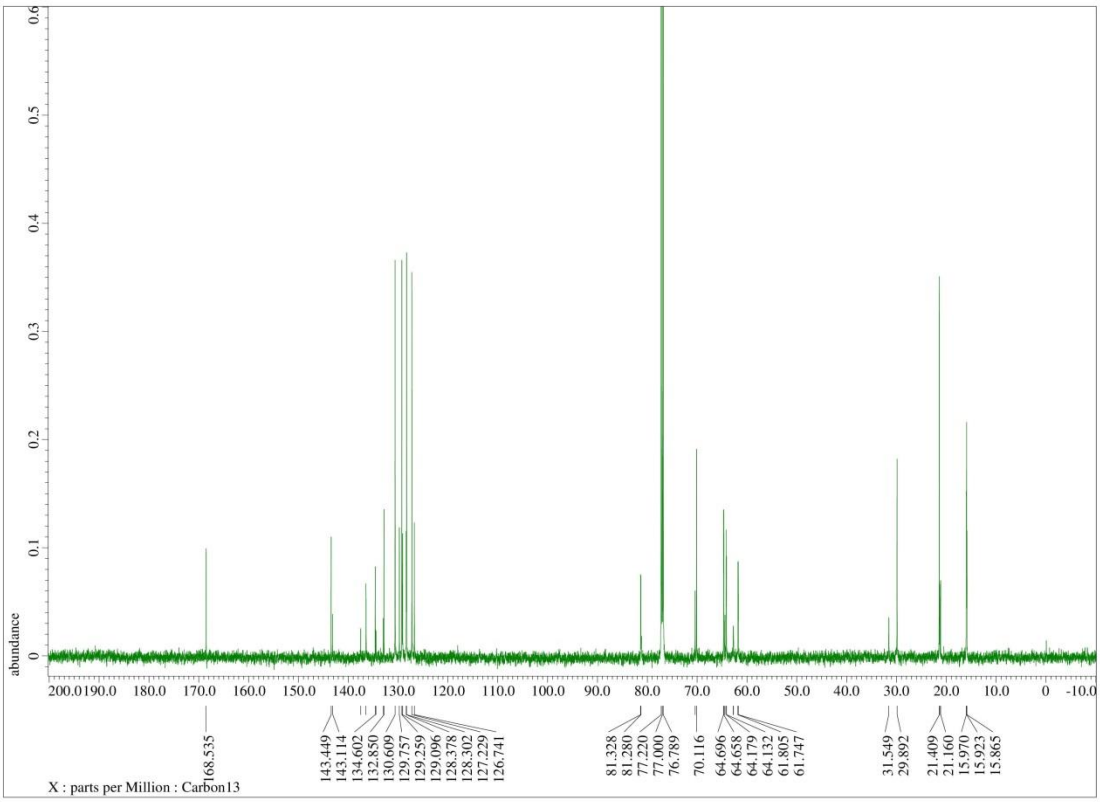

HN
Ts
EtO2C
Ph
Ph
OP(OEt)2
O
4da
major
6.52
0.92
1.97
1.92
0.92
1.87
1.92
1.88
1.00
1.95
1.94
1.96
2.99
2.88
2.90
2.88
abundance
X : parts per Million : Proton

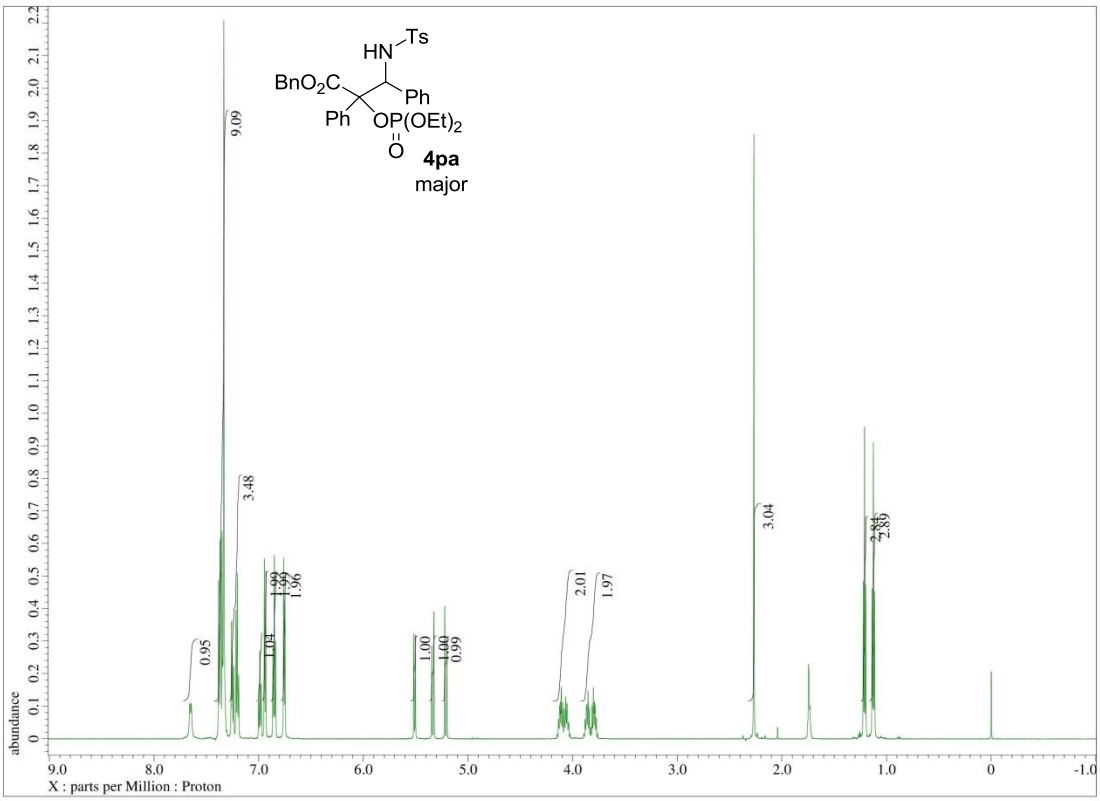

abundance
168.276
142.233
138.460
133.932
128.838
128.771
128.158
127.258
127.076
126.674
126.243
91.219
77.211
77.000
76.789
65.118
64.591
63.892
63.854
63.260
21.304
16.076
15.913
15.856
13.950
X : parts per Million : Carbon13

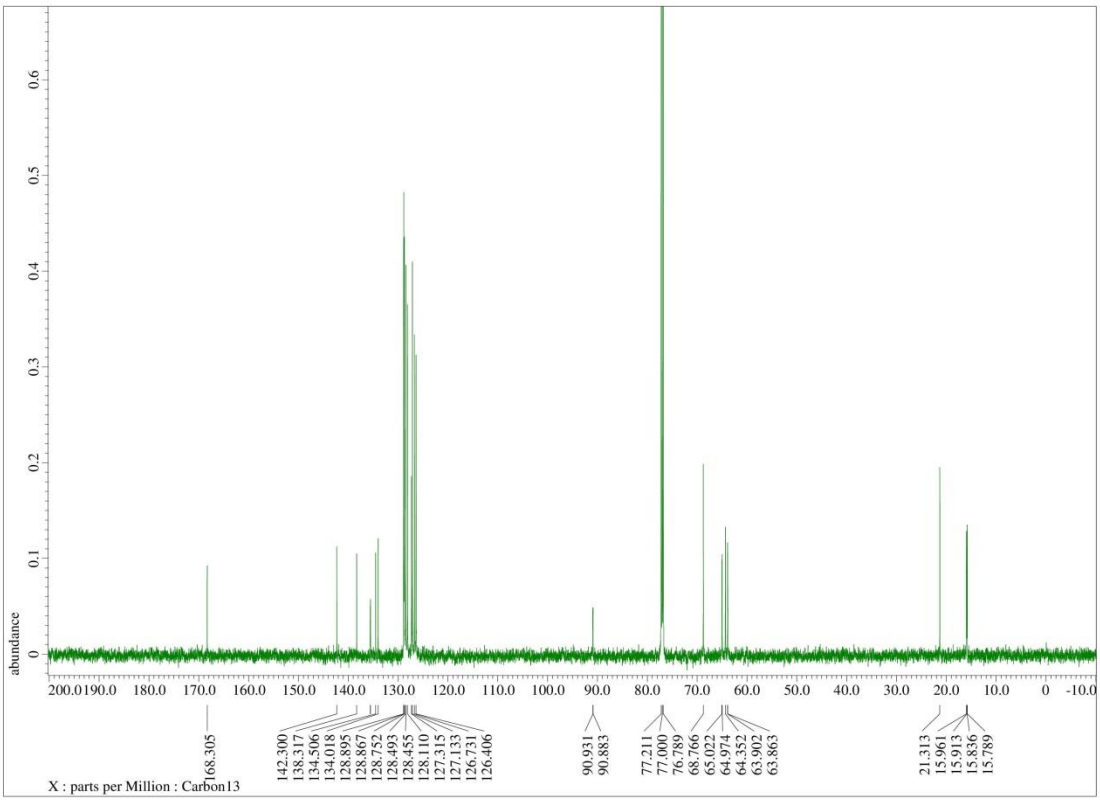

HN
Ts
EtO2C
Ph
Ph
OP(OEt)2
O
4da
minor
abundance
X : parts per Million : Proton
1.95
0.97
2.93
2.43
2.87
1.95
1.97
1.00
4.82
0.96
2.93
2.91
5.63

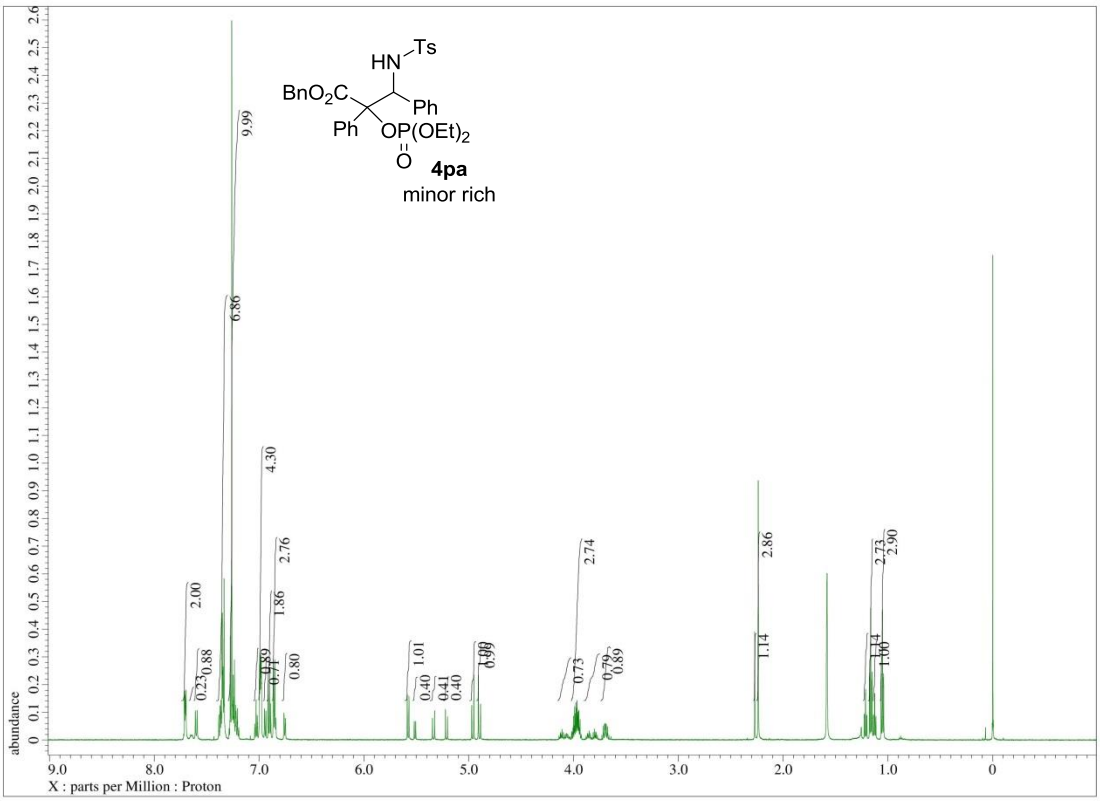

abundance
X : parts per Million : Carbon13
167.970
167.903
142.281
137.896
135.368
134.583
129.240
128.981
128.819
128.062
127.794
127.641
127.526
127.066
126.683
126.233
89.313
89.275
77.211
77.000
76.789
64.830
64.792
64.505
64.457
62.331
62.054
31.558
21.275
15.894
15.846
15.789
15.741
13.596
-0.039

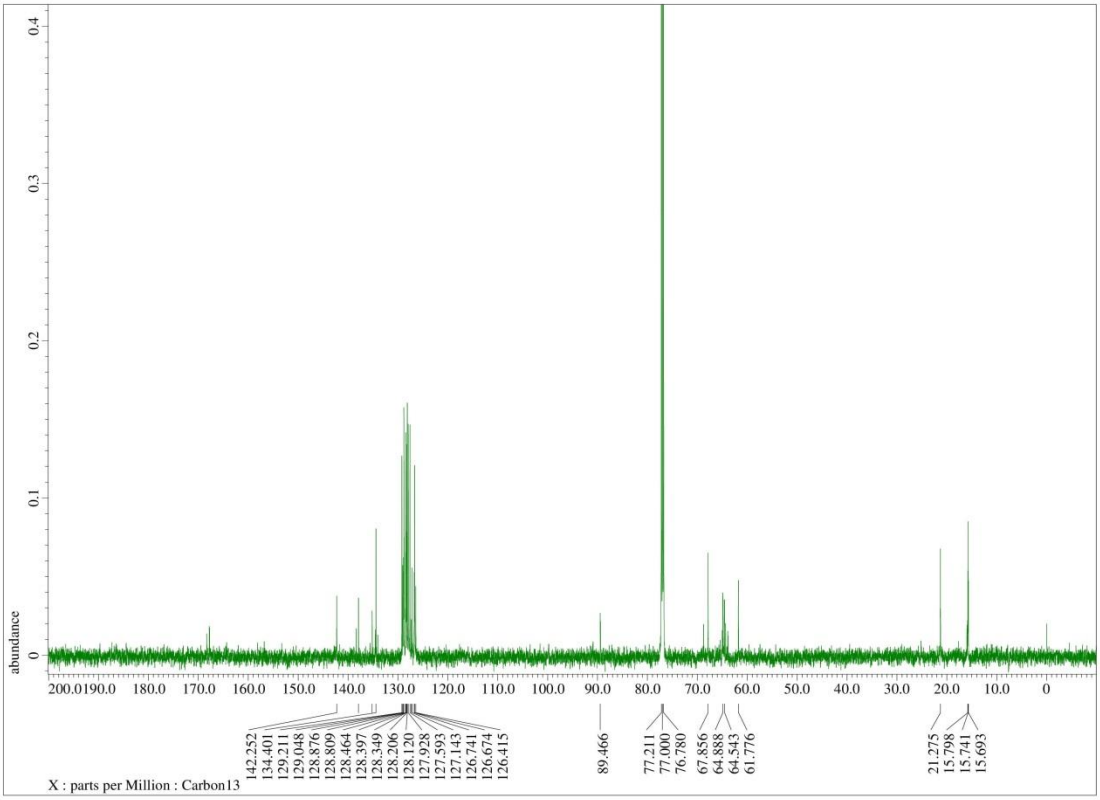

O
HN
Ts
O
Ar
OP(OEt)2
O
4ob
Ar = 4-Cl-C6H4
diastereomixture
abundance
X : parts per Million : Proton
6.08
2.01
0.63
0.31
0.98
0.31
1.00
1.33
4.67
1.97
3.01
0.48
0.96
0.94
0.98
1.26
2.43
0.32
4.87
3.03

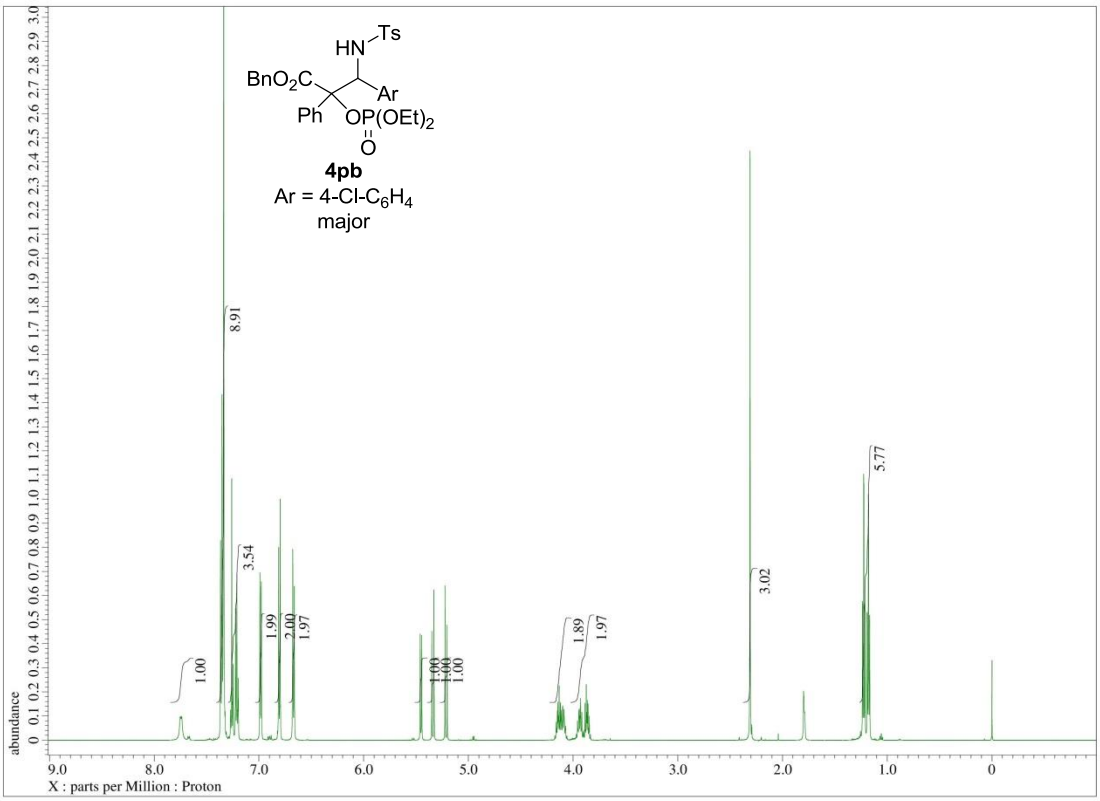

abundance
X : parts per Million : Carbon13
168.535
143.449
143.114
134.602
132.850
130.609
129.757
129.259
129.096
128.378
128.302
127.229
126.741
81.328
81.280
77.220
77.000
76.789
70.116
64.696
64.658
64.179
64.132
61.805
61.747
31.549
29.892
21.409
21.160
15.970
15.923
15.865

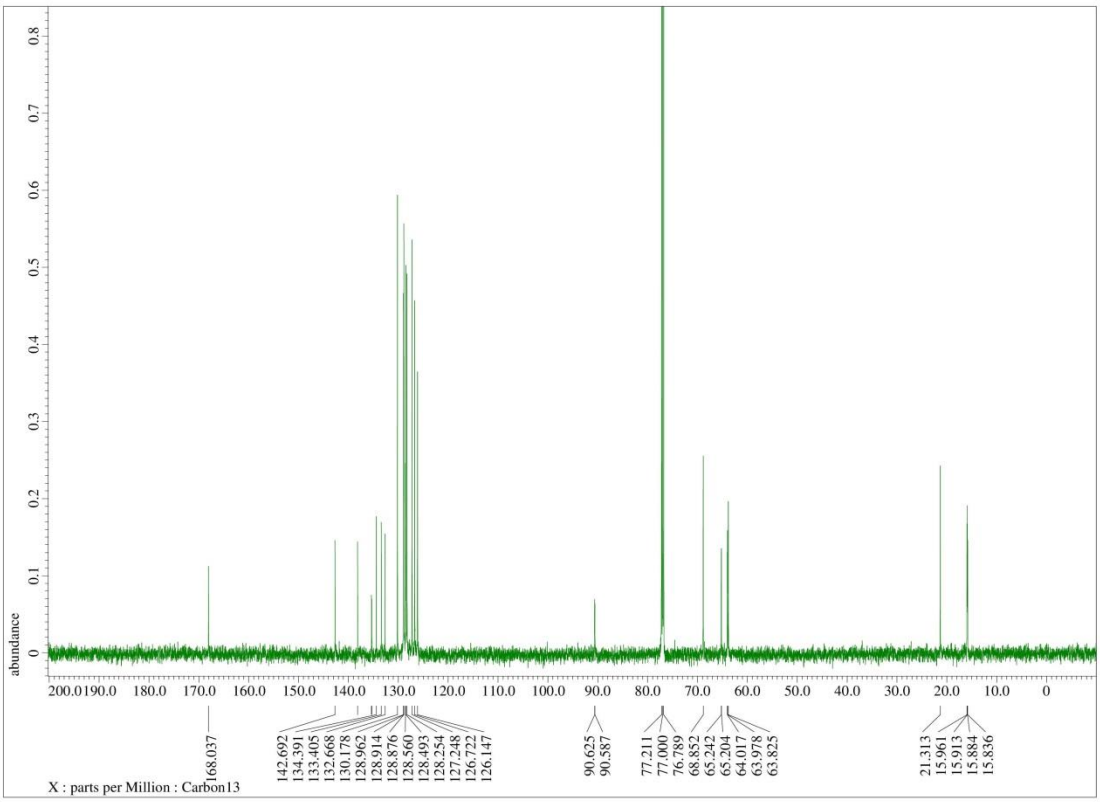

HN
Ts
BnO2C
Ph
Ph
OP(OEt)2
O
4pa
major
abundance
X : parts per Million : Proton

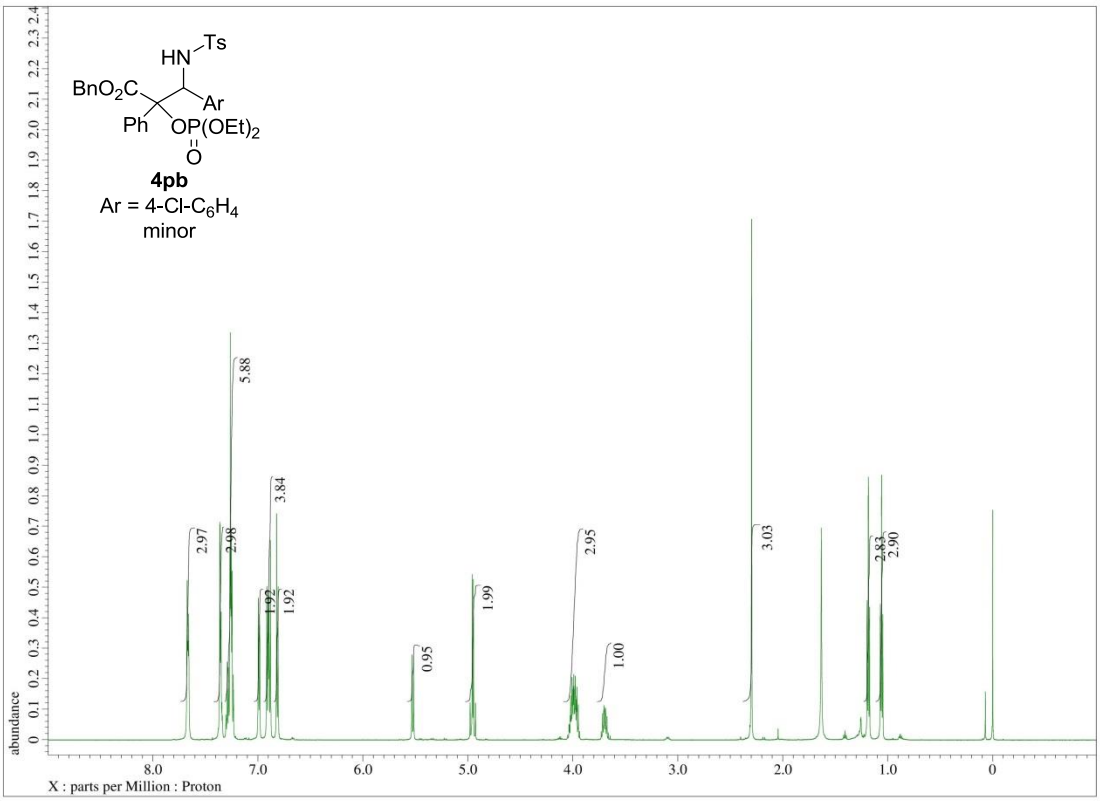

abundance
X : parts per Million : Carbon13

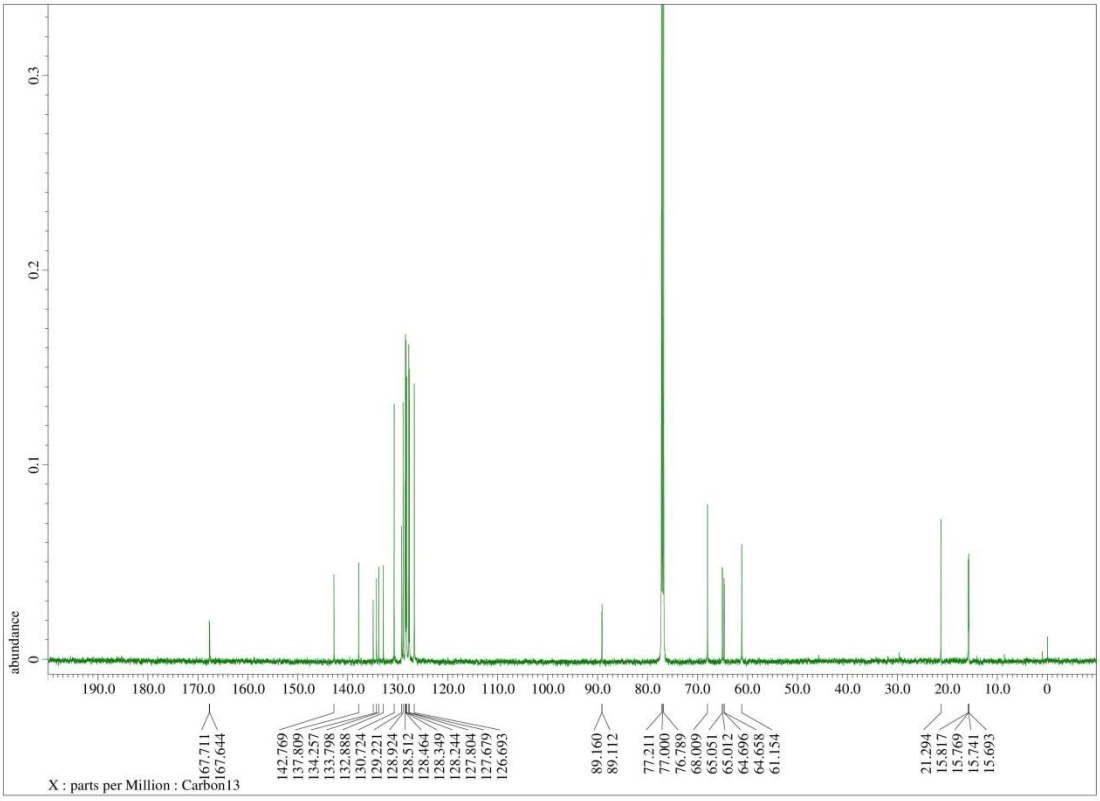

HN
Ts
BnO2C
Ph
Ph
OP(OEt)2
O
4pa
minor rich
abundance
X : parts per Million : Proton

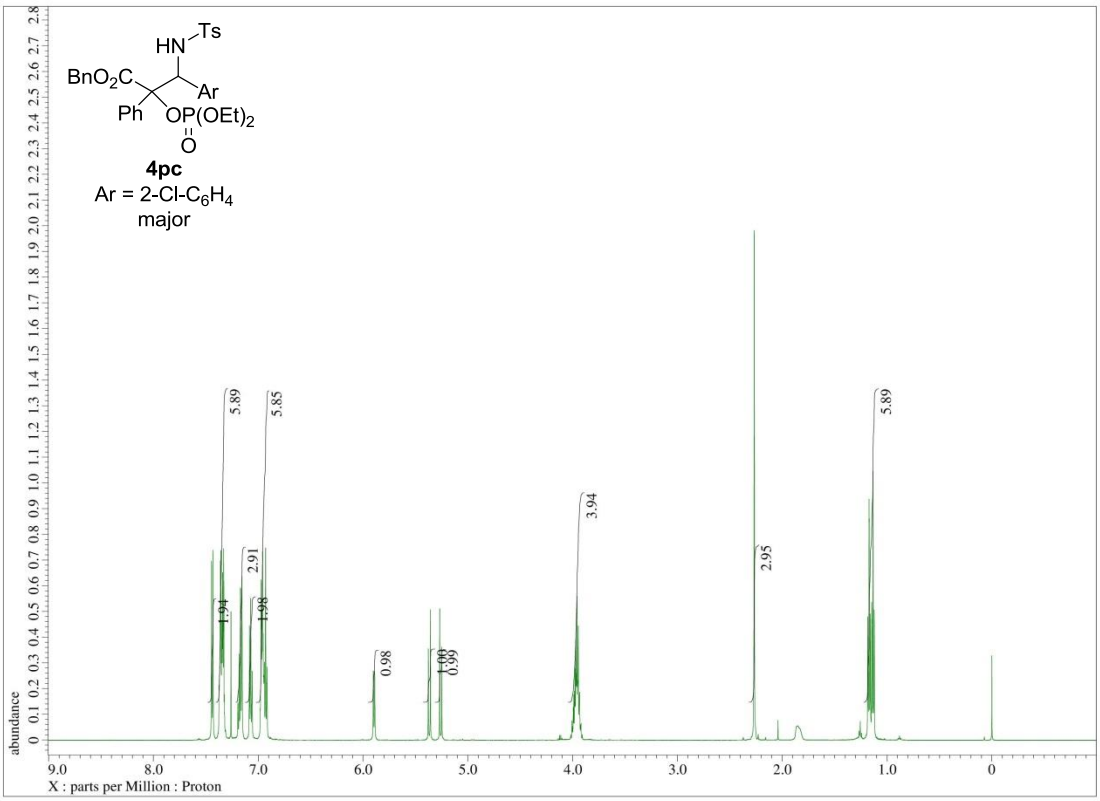

abundance
X : parts per Million : Carbon13

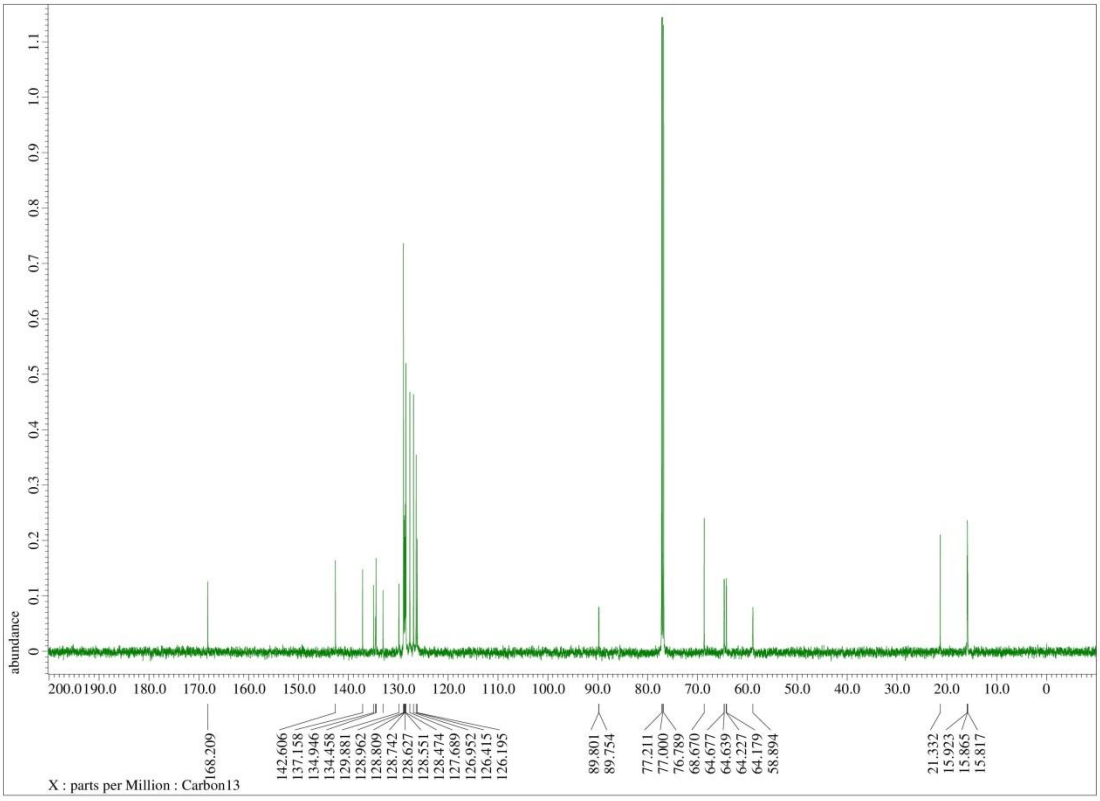

HN
Ts
BnO2C
Ar
Ph
OP(OEt)2
O
4pb
Ar = 4-Cl-C6H4
major
abundance
X : parts per Million : Proton
8.91
3.54
1.99
2.00
1.97
1.00
1.00
1.00
1.00
1.89
1.97
3.02
5.77

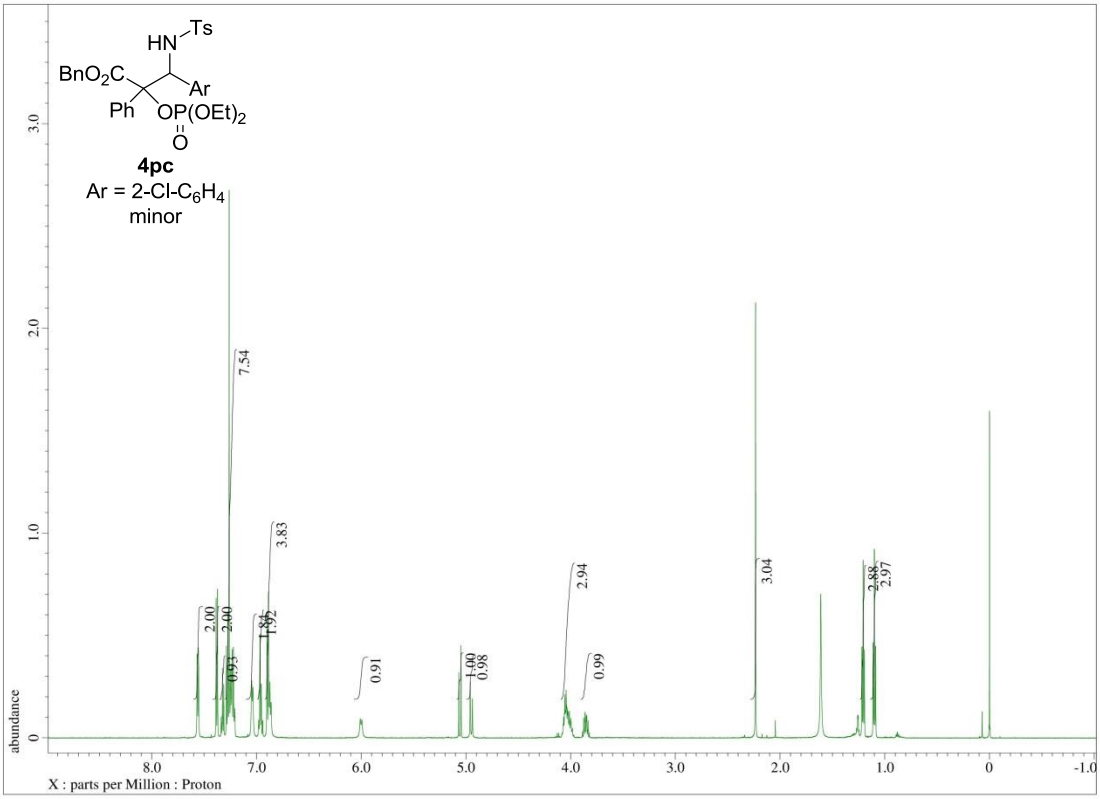

abundance
X : parts per Million : Carbon13
168.037
142.692
134.391
133.405
132.668
130.178
128.962
128.914
128.876
128.560
128.493
128.254
127.248
126.722
126.147
90.625
90.587
77.211
77.000
76.789
68.852
65.242
65.204
64.017
63.978
63.825
21.313
15.961
15.913
15.884
15.836

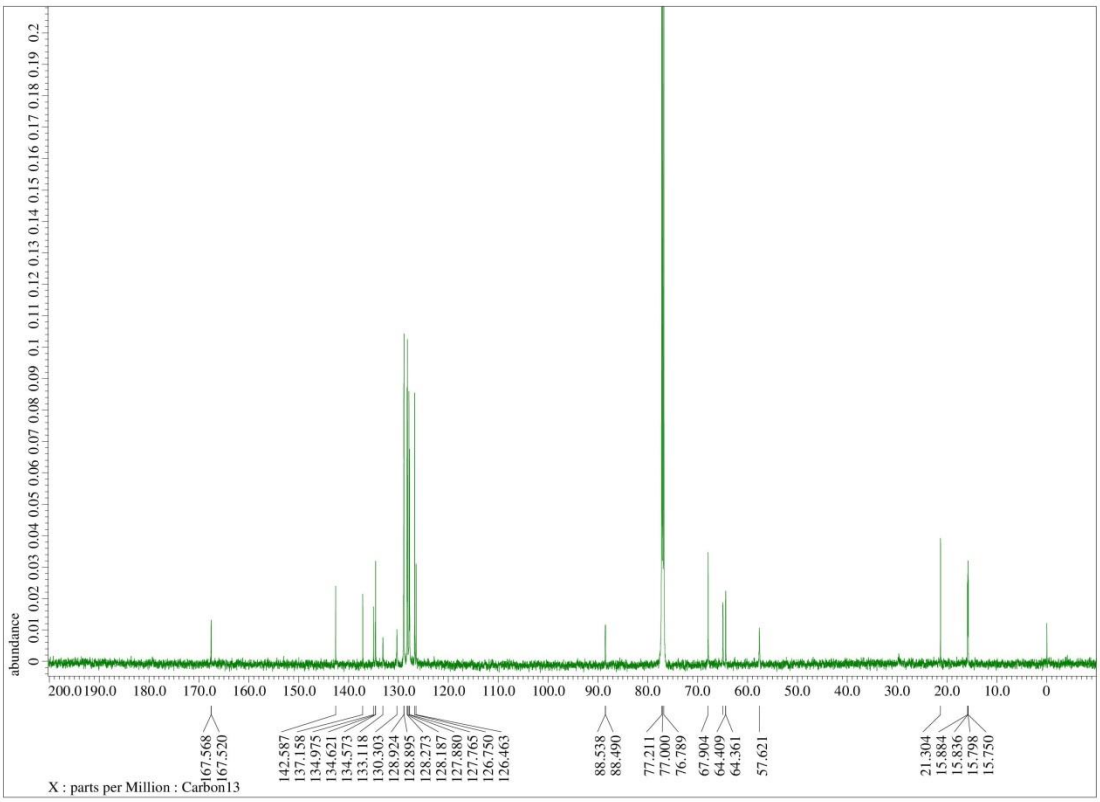

HN
Ts
BnO2C
Ar
Ph
OP(OEt)2
O
4pb
Ar = 4-Cl-C6H4
minor
abundance
X : parts per Million : Proton
2.97
2.98
5.88
3.84
1.92
1.92
0.95
1.99
2.95
1.00
3.03
2.83
2.90

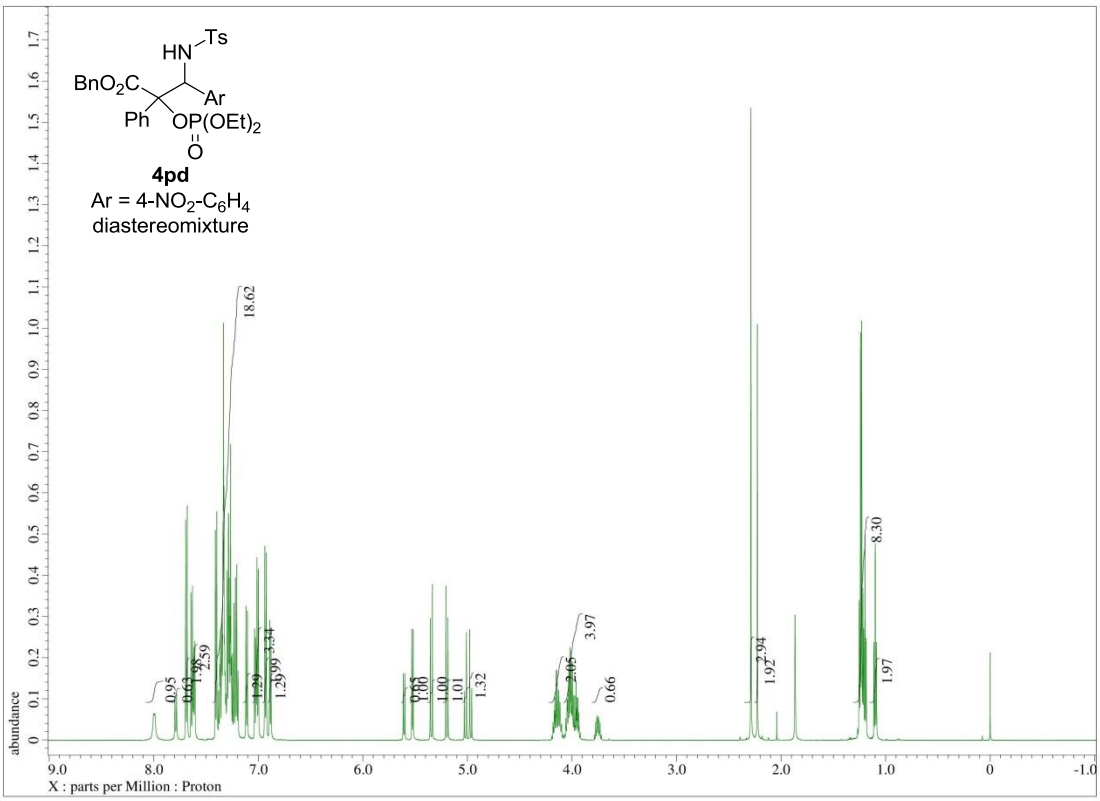

abundance
X : parts per Million : Carbon13
167.711
167.644
142.769
137.809
134.257
133.798
132.888
130.724
129.221
128.924
128.512
128.464
128.349
128.244
127.804
127.679
126.693
89.160
89.112
77.211
77.000
76.789
68.009
65.051
65.012
64.696
64.658
61.154
21.294
15.817
15.769
15.741
15.693

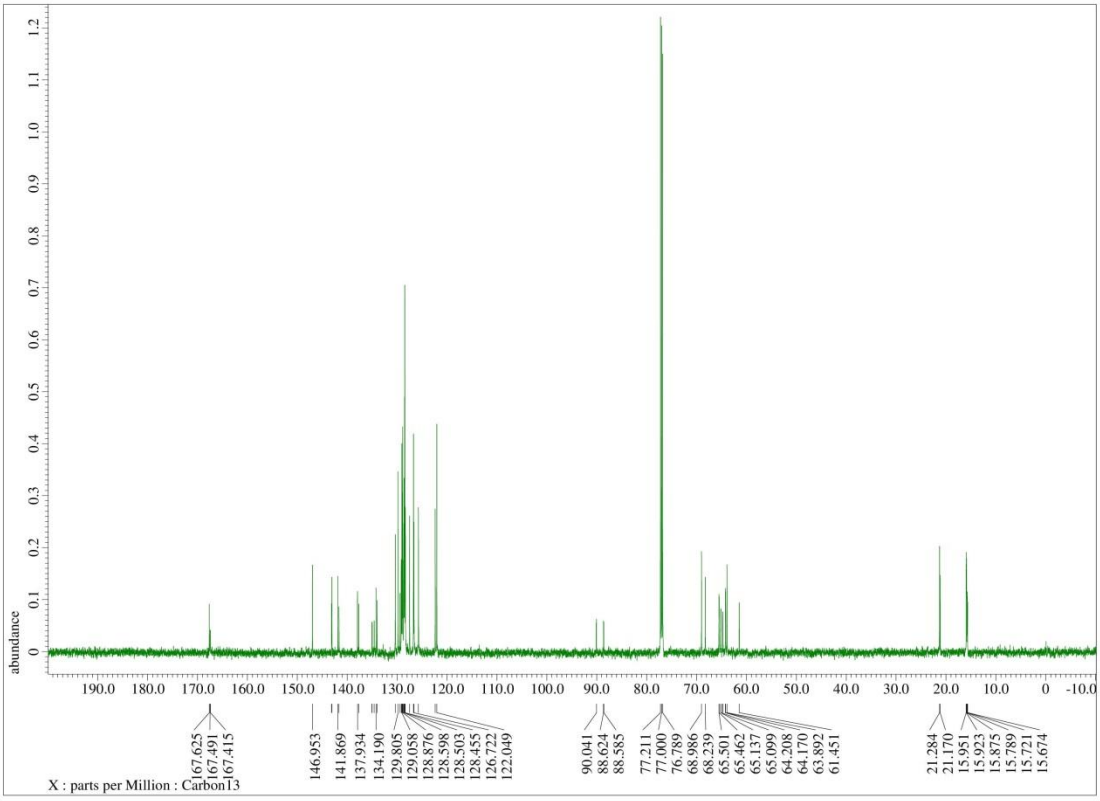

HN
Ts
BnO2C
Ar
Ph
OP(OEt)2
O
4pc
Ar = 2-Cl-C6H4
major
abundance
X : parts per Million : Proton
5.89
5.85
2.91
1.94
1.98
0.98
1.00
0.99
3.94
2.95
5.89

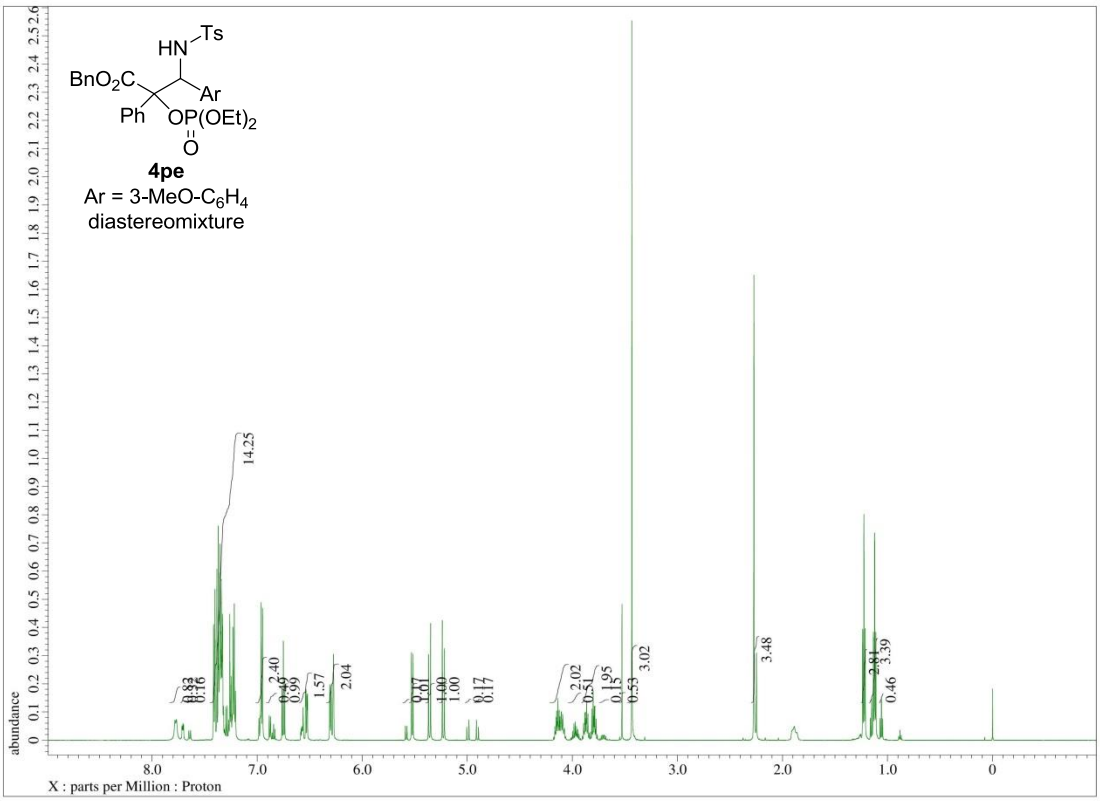

abundance
X : parts per Million : Carbon13
168.209
142.606
137.158
134.946
134.458
129.881
128.962
128.809
128.742
128.627
128.551
128.474
127.689
126.952
126.415
126.195
89.801
89.754
77.211
77.000
76.789
68.670
64.677
64.639
64.227
64.179
58.894
21.332
15.923
15.865
15.817

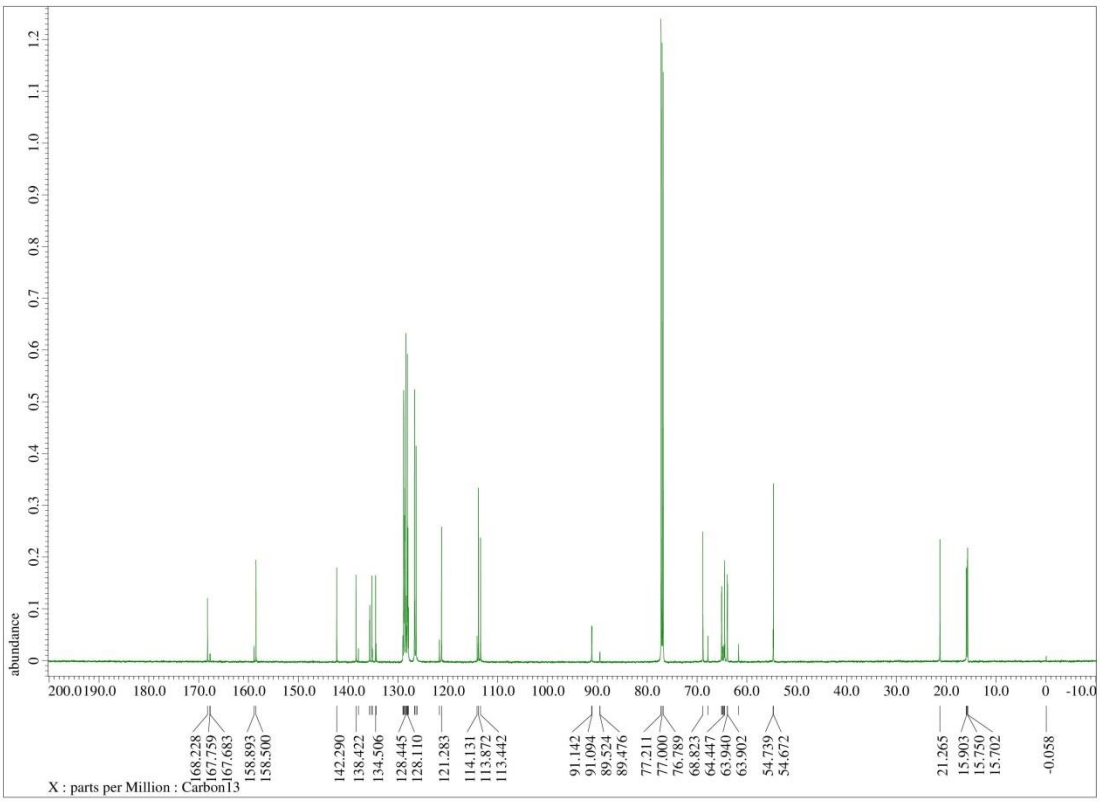

HN
Ts
BnO2C
Ar
Ph
OP(OEt)2
O
4pc
Ar = 2-Cl-C6H4
minor
abundance
X : parts per Million : Proton

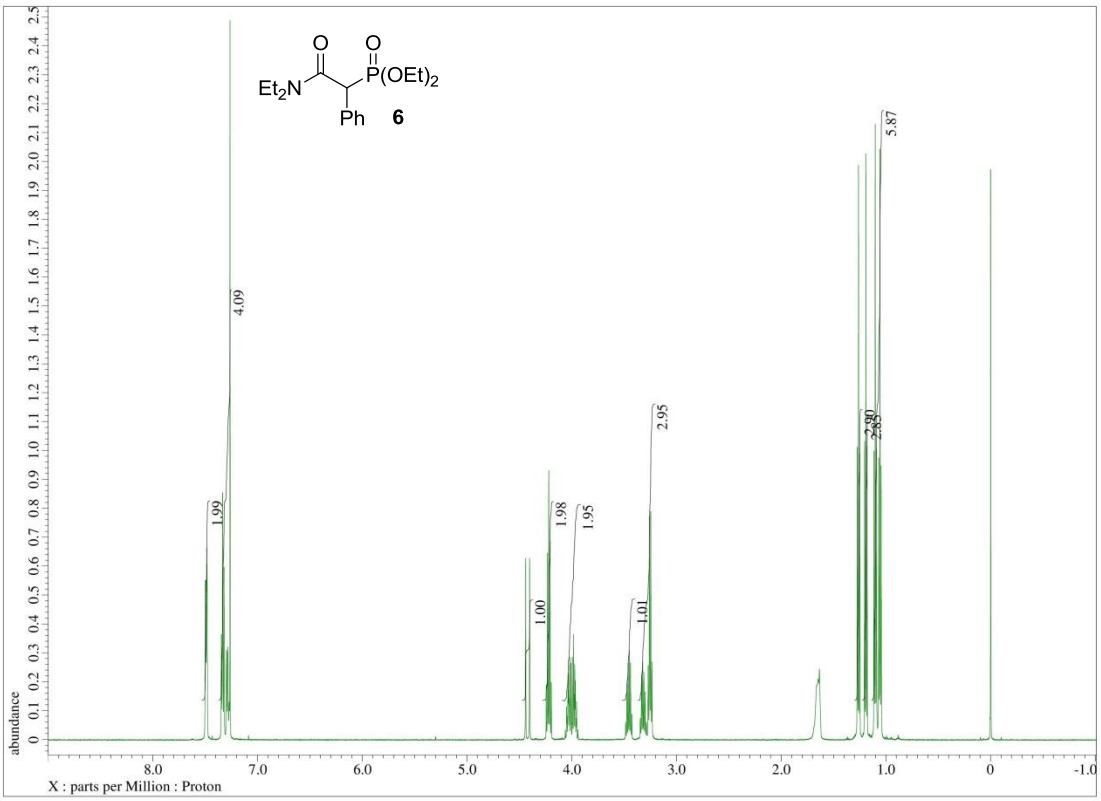

abundance
X : parts per Million : Carbon13

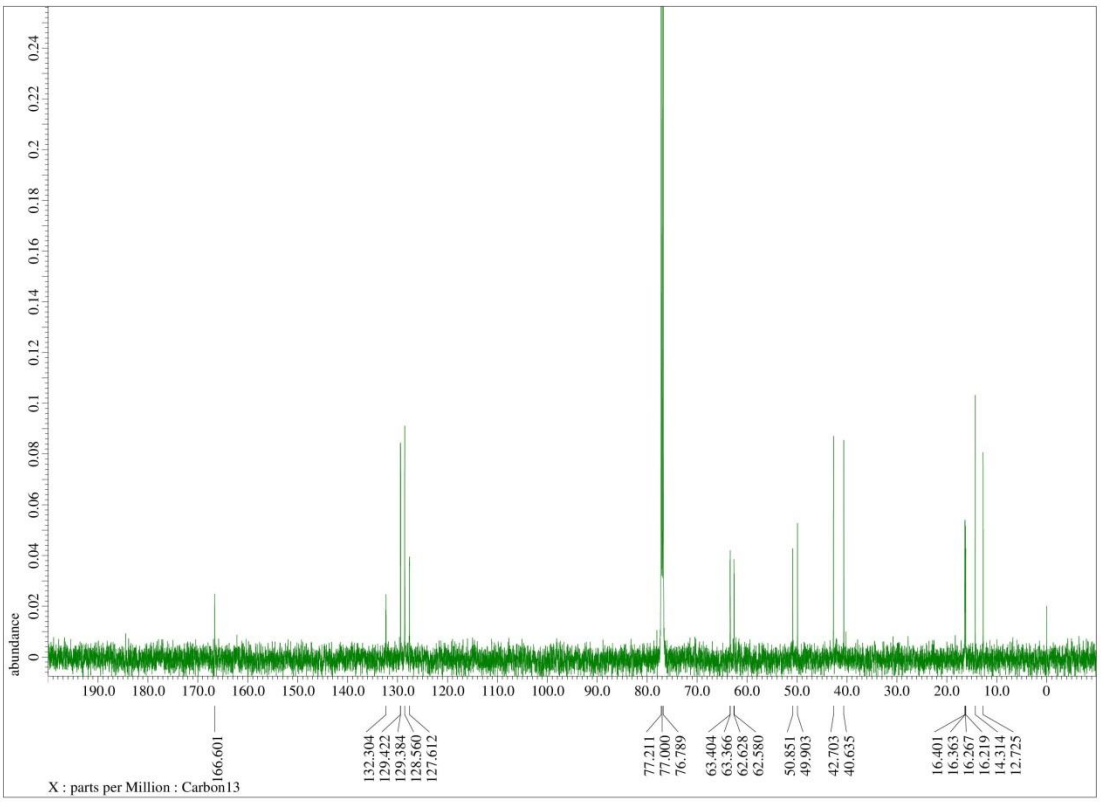

HN
Ts
BnO2C
Ar
Ph
OP(OEt)2
O
4pd
Ar = 4-NO2-C6H4
diastereomixture
abundance
X : parts per Million : Proton

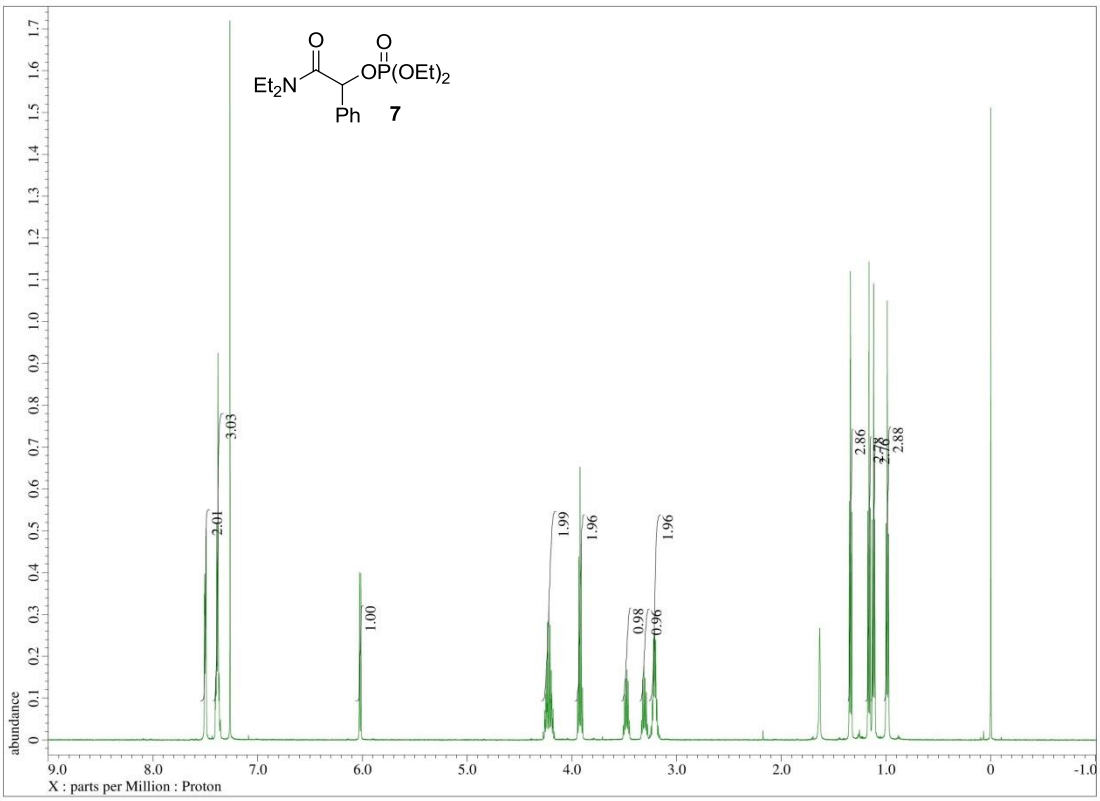

abundance
X : parts per Million : Carbon13

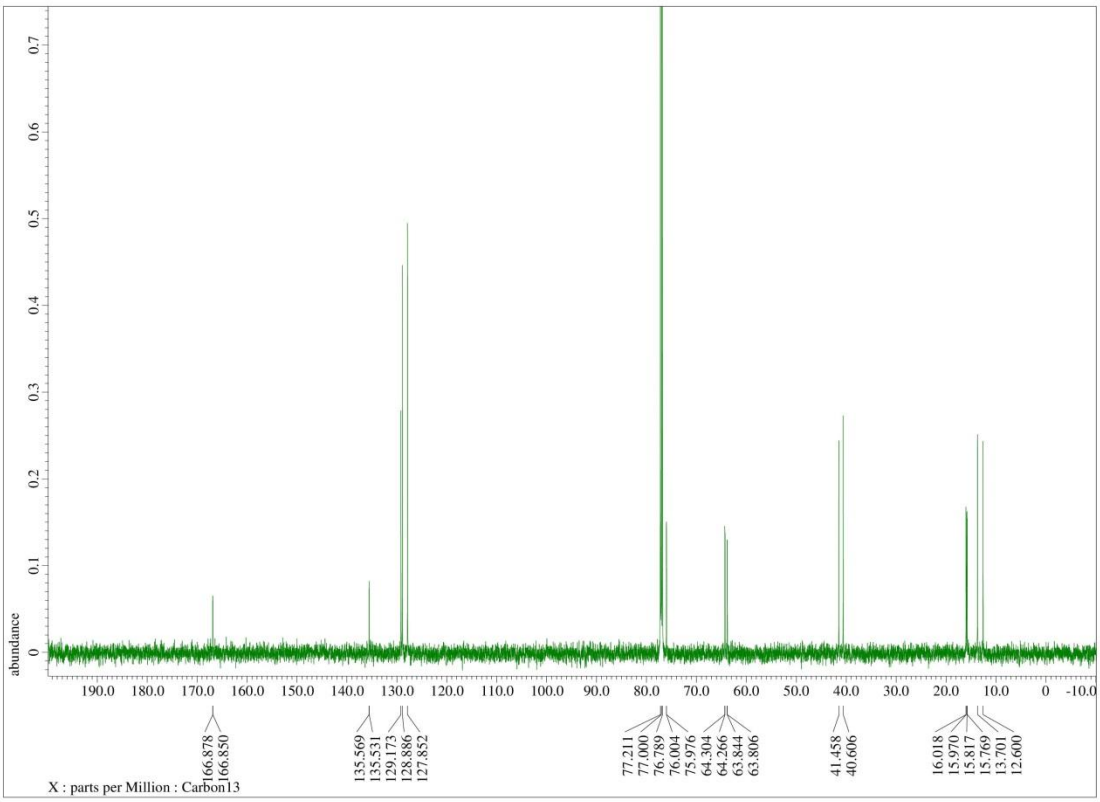

HN
Ts
BnO2C
Ar
Ph
OP(OEt)2
O
4pe
Ar = 3-MeO-C6H4
diastereomixture
abundance
X : parts per Million : Proton

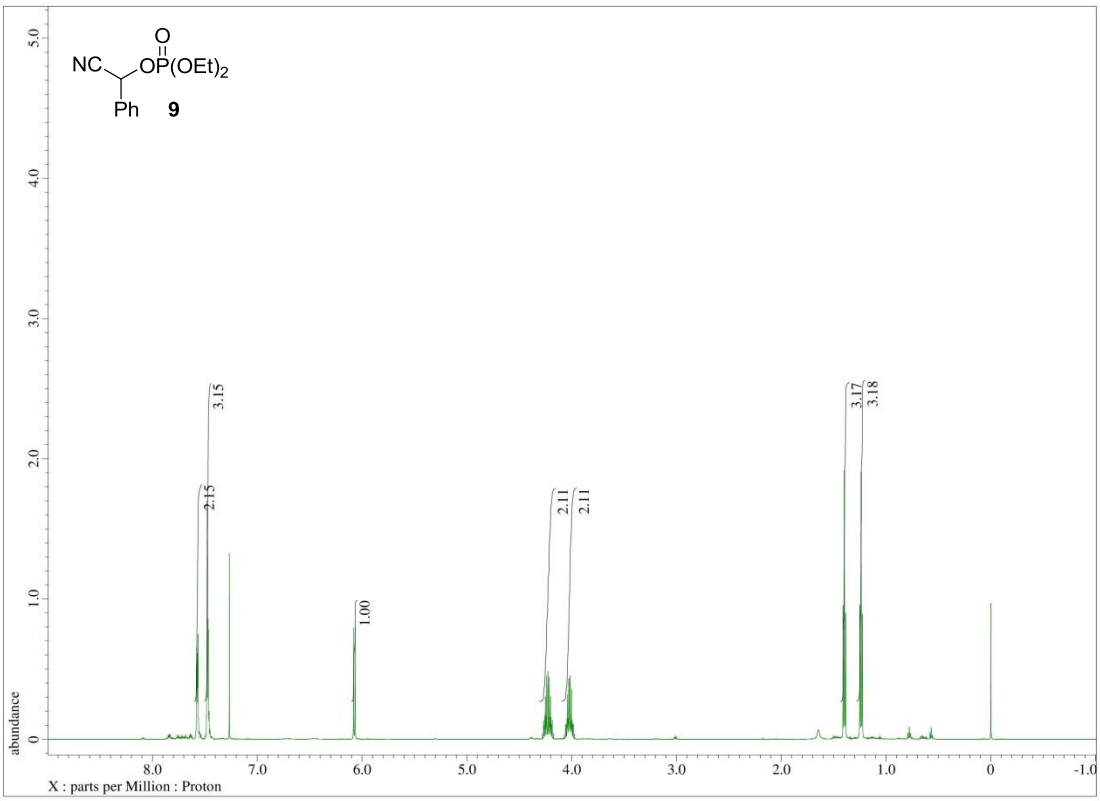

abundance
X : parts per Million : Carbon13

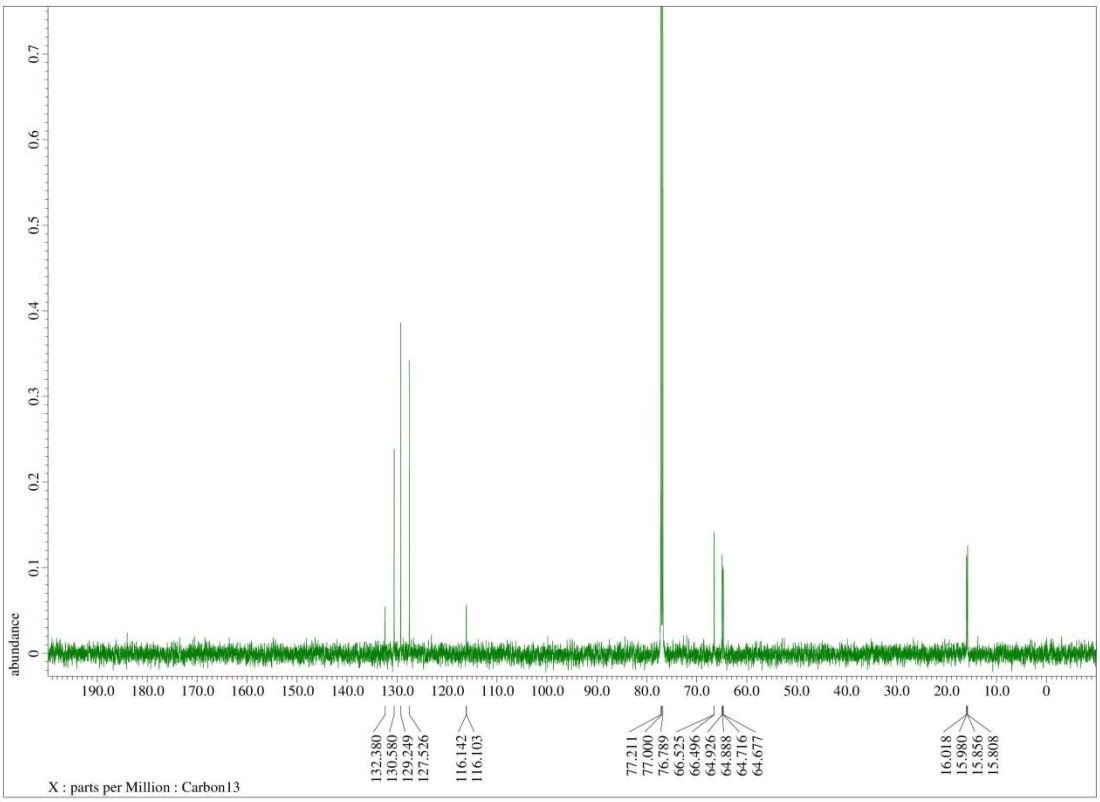

Et2N
O
O
P(OEt)2
Ph
6
abundance
X : parts per Million : Proton
1.99
4.09
1.00
1.98
1.95
1.01
2.95
2.90
2.85
5.87

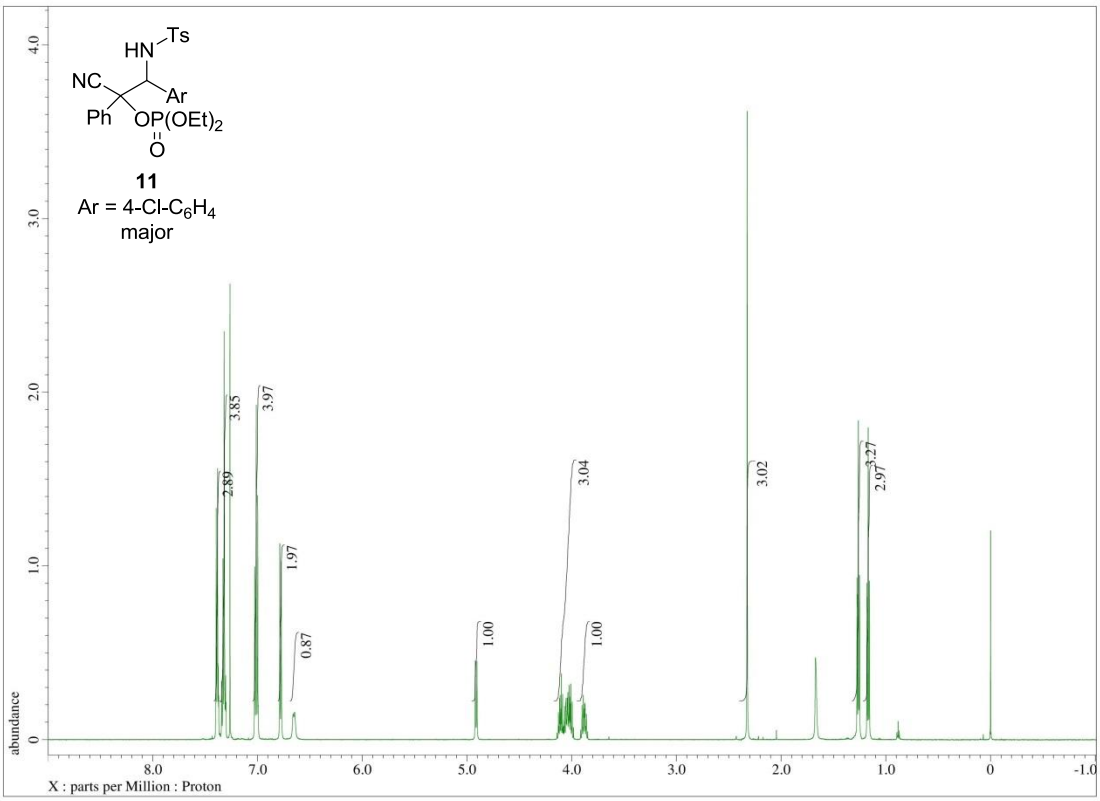

abundance
X : parts per Million : Carbon13
166.601
132.304
129.422
129.384
128.560
127.612
77.211
77.000
76.789
63.404
63.366
62.628
62.580
50.851
49.903
42.703
40.635
16.401
16.363
16.267
16.219
14.314
12.725

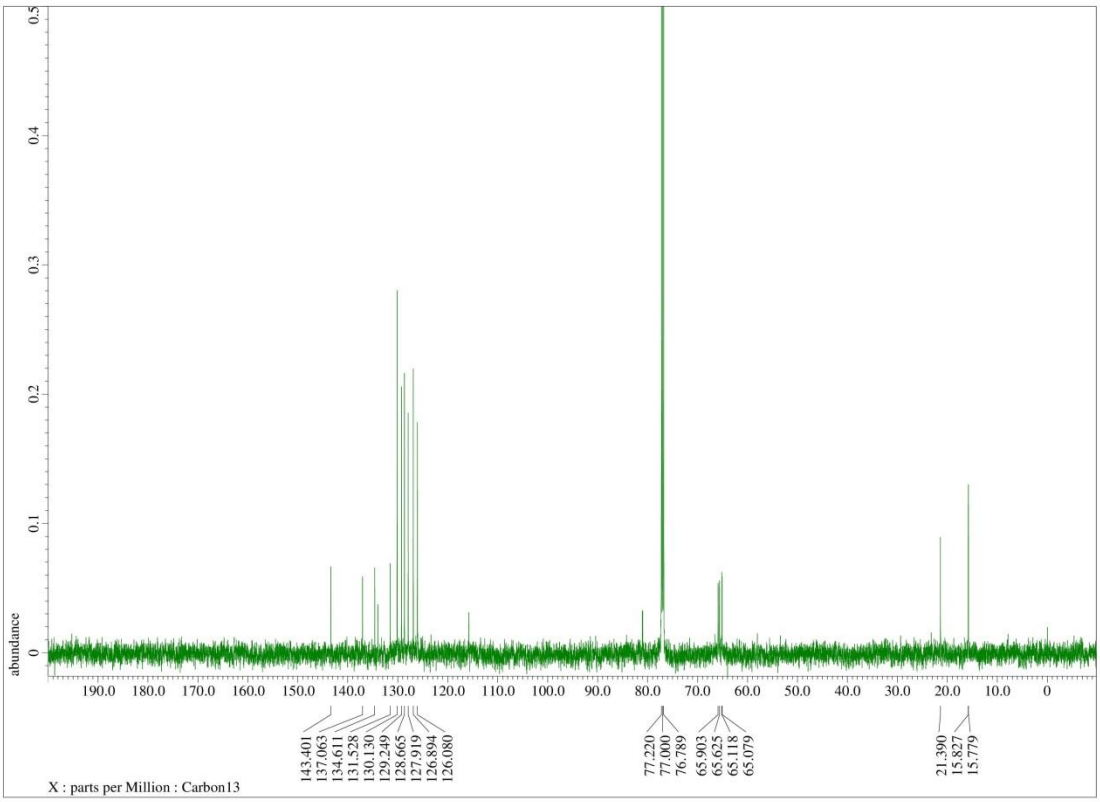

Et2N
O
O
OP(OEt)2
Ph
7
abundance
X : parts per Million : Proton
3.03
2.01
1.00
1.99
1.96
1.96
0.98
0.96
2.86
2.78
2.88

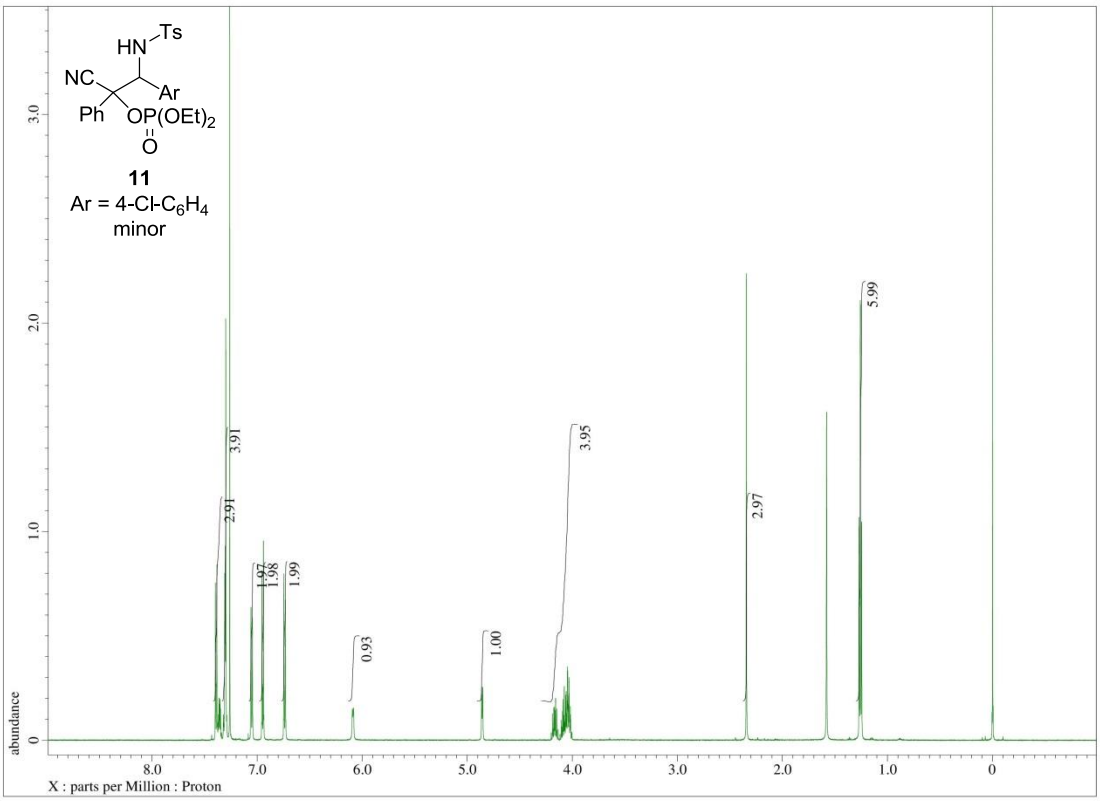

abundance
X : parts per Million : Carbon13
166.878
166.850
135.569
135.531
129.173
128.886
127.852
77.211
77.000
76.789
76.004
75.976
64.304
64.266
63.844
63.806
41.458
40.606
16.018
15.970
15.817
15.769
13.701
12.600

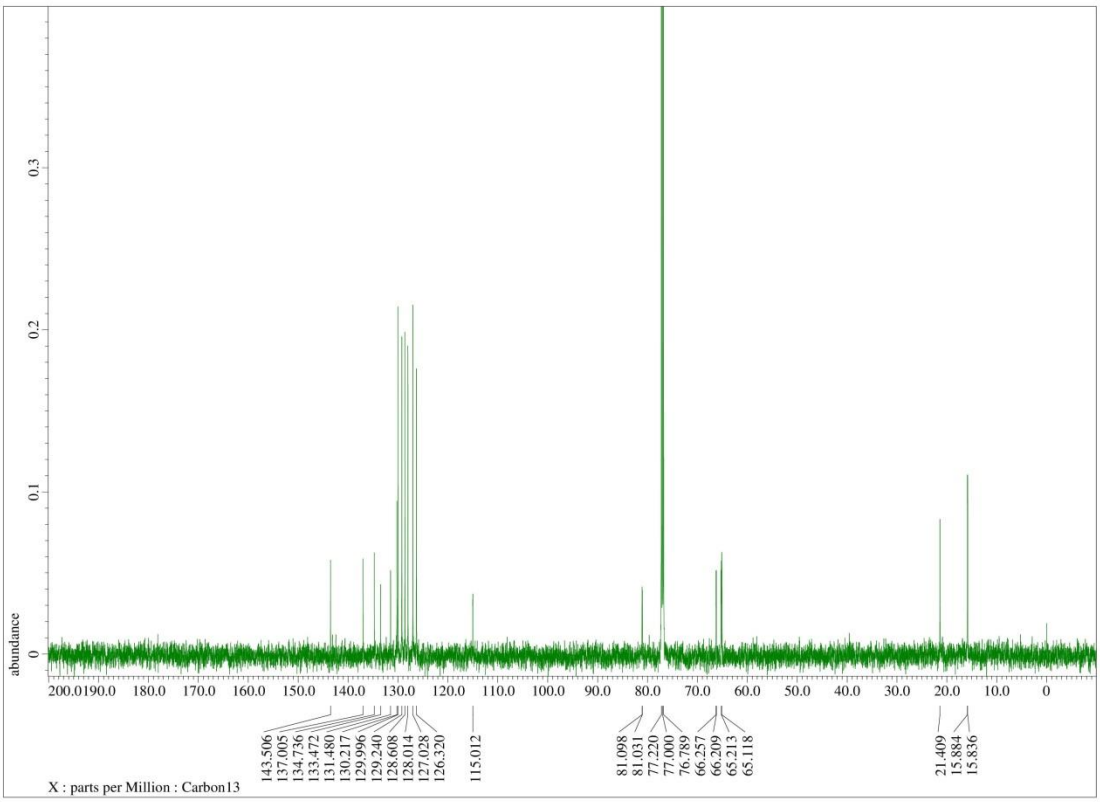

NC
O
OP(OEt)2
Ph
9
abundance
X : parts per Million : Proton
3.15
2.15
1.00
2.11
2.11
3.17
3.18

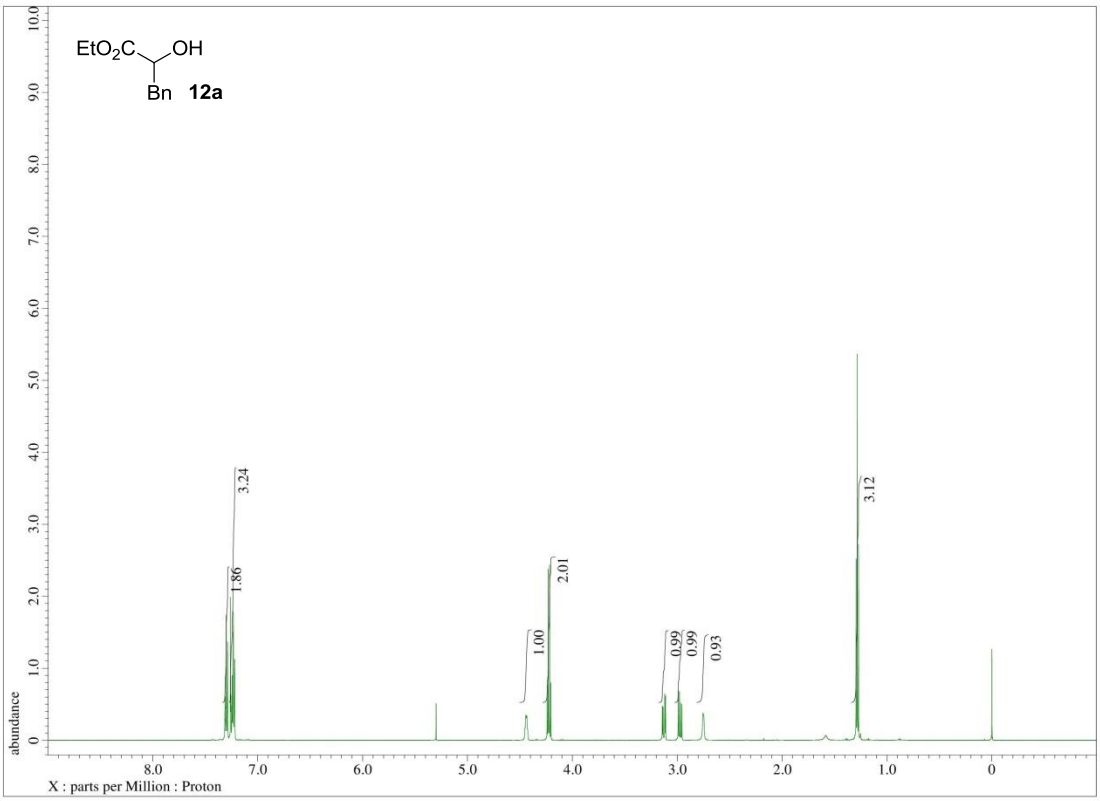

abundance
X : parts per Million : Carbon13
132.380
130.580
129.249
127.526
116.142
116.103
77.211
77.000
76.789
66.525
66.496
64.926
64.888
64.716
64.677
16.018
15.980
15.856
15.808

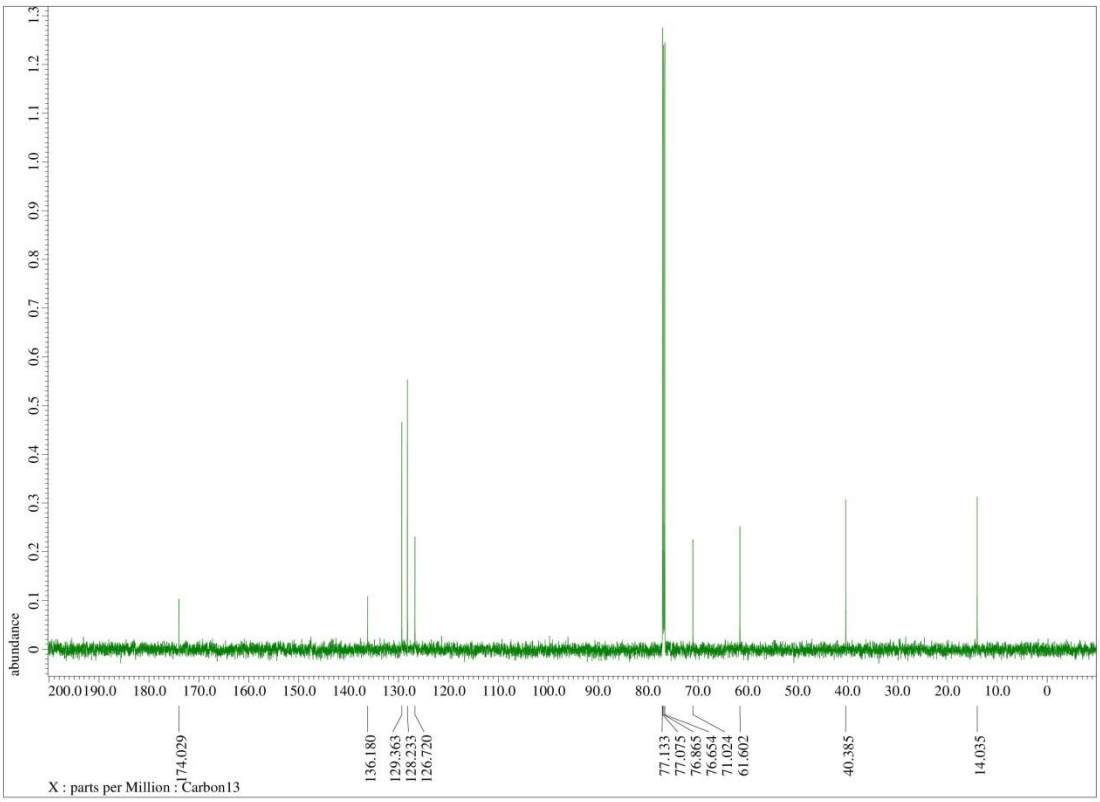

HN
Ts
NC
Ar
Ph
OP(OEt)2
O
11
Ar = 4-Cl-C6H4
major
abundance
2.89
3.85
3.97
1.97
0.87
1.00
3.04
1.00
3.02
3.27
2.97
X : parts per Million : Proton

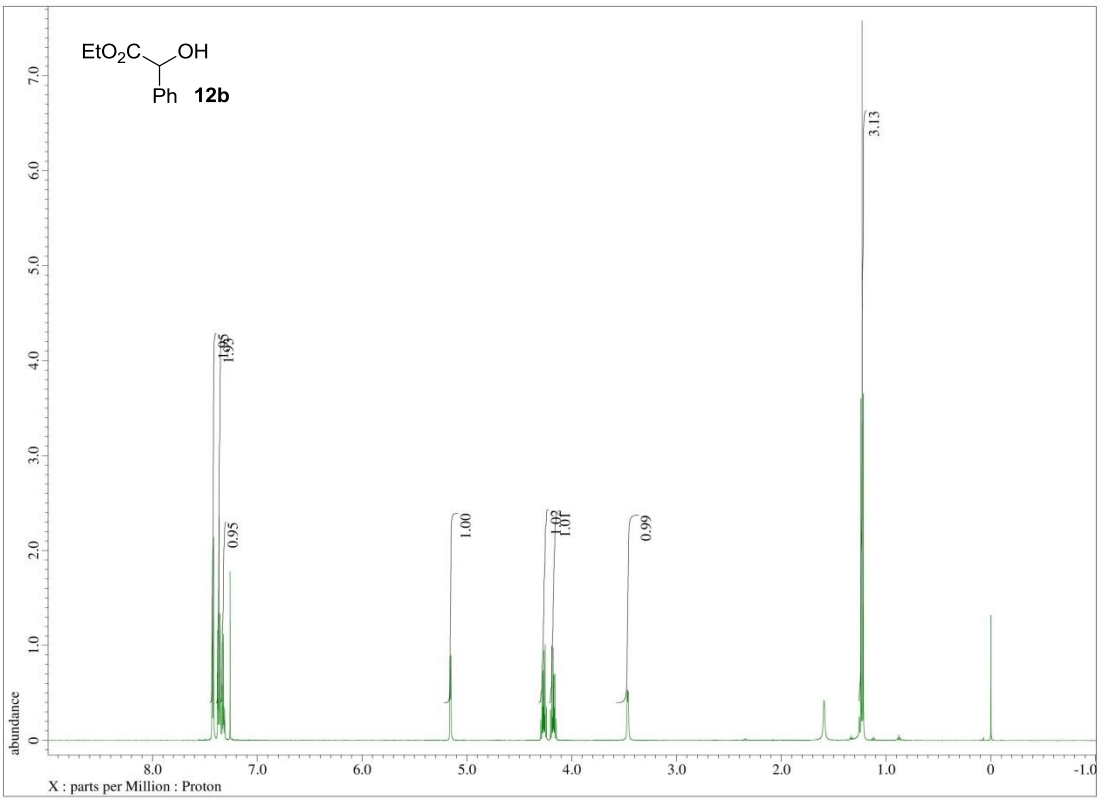

abundance
143.401
137.063
134.611
131.528
130.130
129.249
128.665
127.919
126.894
126.080
77.220
77.000
76.789
65.903
65.625
65.118
65.079
21.390
15.827
15.779
X : parts per Million : Carbon13

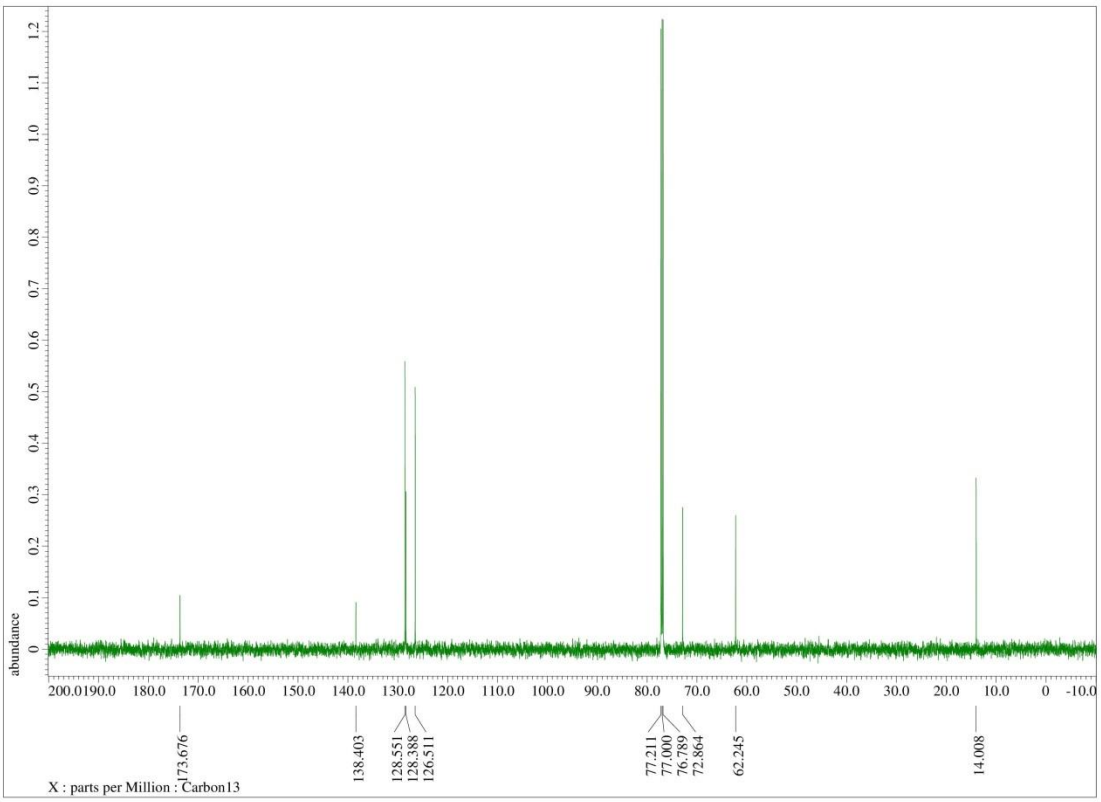

HN
Ts
NC
Ar
Ph
OP(OEt)2
O
11
Ar = 4-Cl-C6H4
minor
abundance
X : parts per Million : Proton
3.91
2.91
1.97
1.98
1.99
0.93
1.00
3.95
2.97
5.99

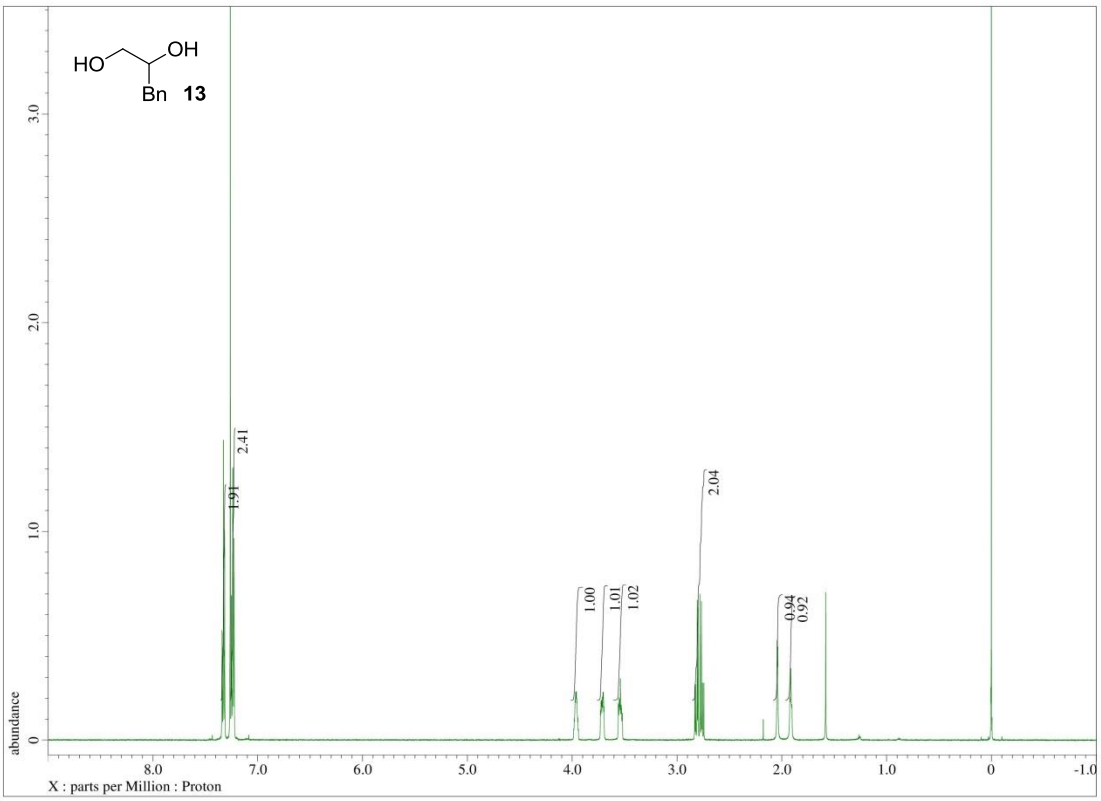

abundance
X : parts per Million : Carbon13
143.506
137.005
134.736
133.472
131.480
130.217
129.996
129.240
128.608
128.014
127.028
126.320
115.012
81.098
81.031
77.220
77.000
76.789
66.257
66.209
65.213
65.118
21.409
15.884
15.836

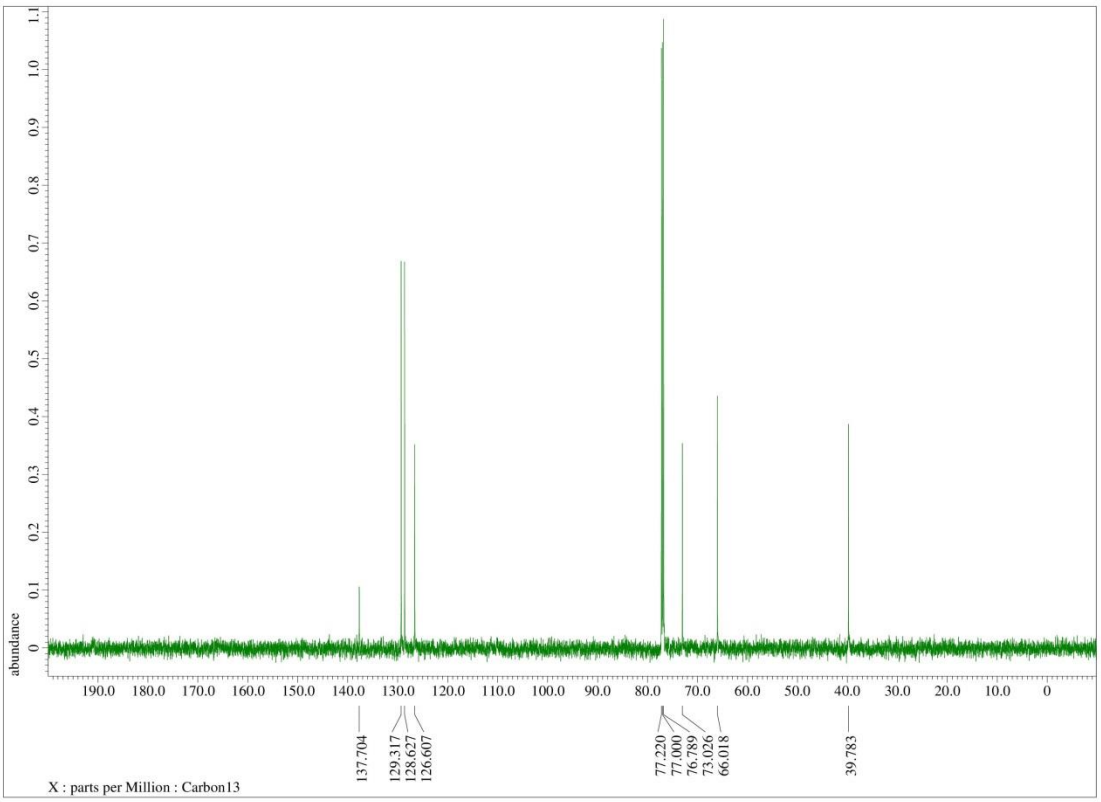

EtO2C
OH
Bn
12a
abundance
X : parts per Million : Proton
3.24
1.86
1.00
2.01
0.99
0.99
0.93
3.12

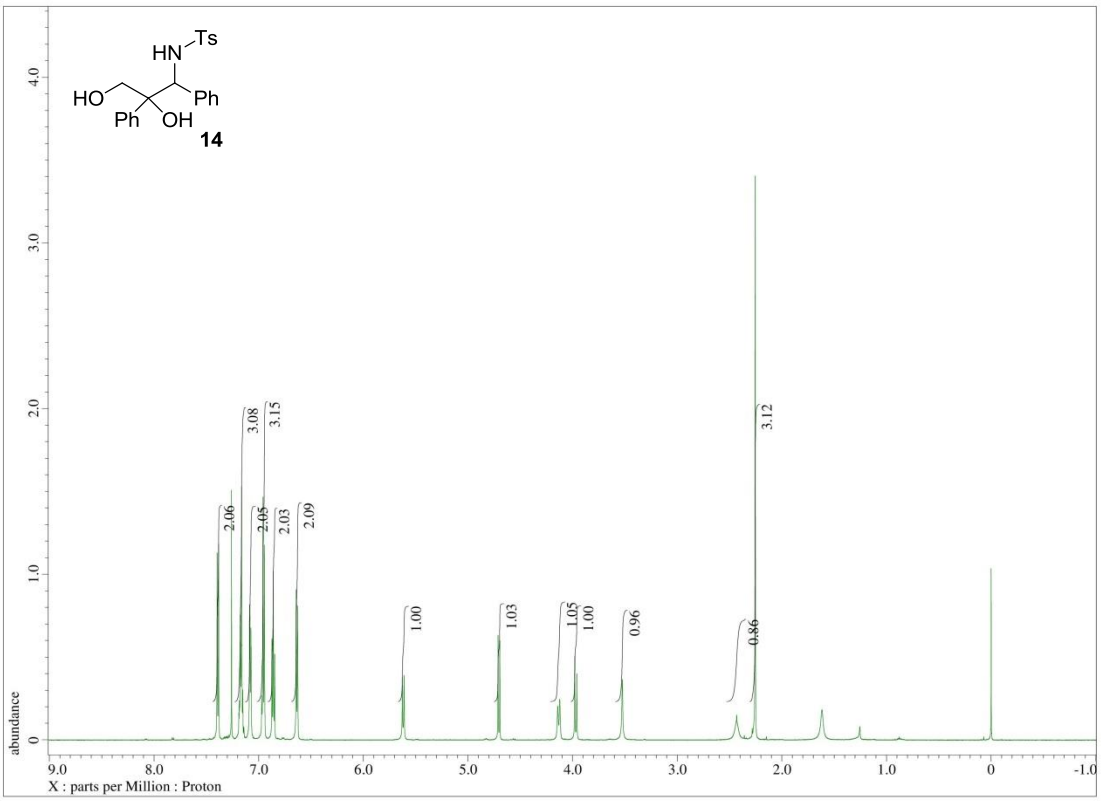

abundance
X : parts per Million : Carbon13
174.029
136.180
129.363
128.233
126.720
77.133
77.075
76.865
76.654
71.024
61.602
40.385
14.035

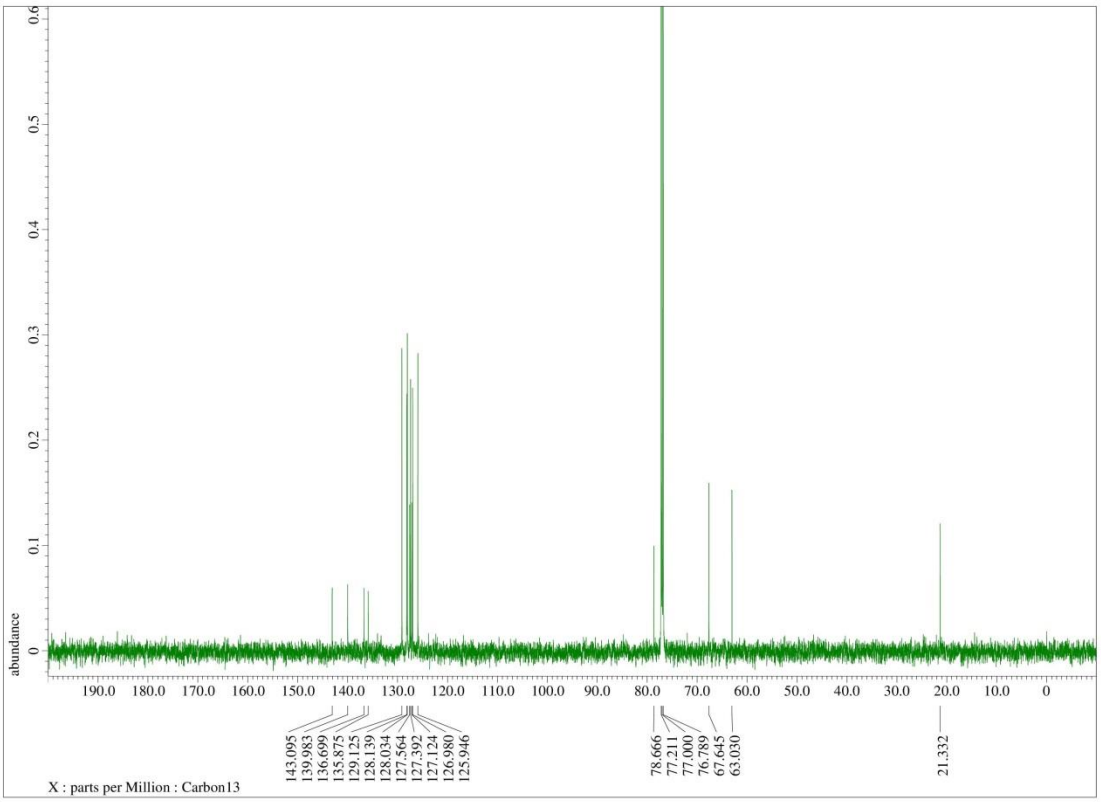

EtO2C
OH
Ph 12b
3.13
1.00
0.99
0.95
abundance
X : parts per Million : Proton


173.676
138.403
128.551
128.388
126.511
77.211
77.000
76.789
72.864
62.245
14.008
abundance
X : parts per Million : Carbon13


HO
OH
Bn 13
abundance
X : parts per Million : Proton
1.91
2.41
1.00
1.01
1.02
2.04
0.94
0.92


abundance
X : parts per Million : Carbon13
137.704
129.317
128.627
126.607
77.220
77.000
76.789
73.026
66.018
39.783


HN
Ts
HO
Ph
Ph
OH
14
abundance
X : parts per Million : Proton
2.06
3.08
3.15
2.05
2.03
2.09
1.00
1.03
1.05
1.00
0.96
0.86
3.12


abundance
X : parts per Million : Carbon13
143.095
139.983
136.699
135.875
129.125
128.139
128.034
127.564
127.392
127.124
126.980
125.946
78.666
77.211
77.000
76.789
67.645
63.030
21.332