Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Brønsted Base-Catalyzed Three-Component Coupling Reaction of α-Ketoesters, Imines, and Diethyl Phosphite Utilizing [1,2]-Phospha-Brook Rearrangement

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General Information

Unless otherwise noted, the reactions were carried out with dried glassware under argon atmosphere. For the title three-component coupling reaction, a 10-mL test tube (16×100 mm) was used. ^{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 ($CDCl_3$). ^{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.

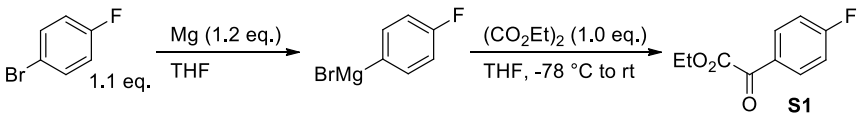
Materials: Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc., and other commercial suppliers and were used without purification. Dichloromethane, tetrahydrofuran and toluene were supplied from Kanto Chemical Co., 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-Ketoesters 1.

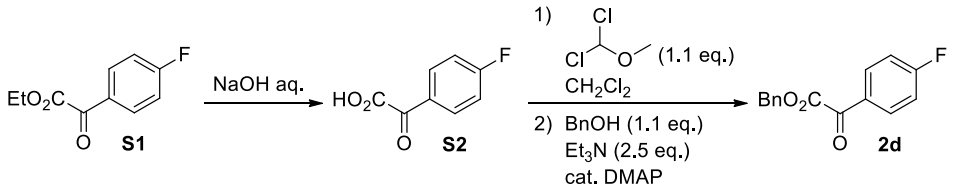
Synthesis of **1d** is representative.

Synthesis of **S1**.



A solution of 1-Bromo-4-fluorobenzene (0.96 g, 5.5 mmol) in THF (5.0 mL) was added dropwise to a mixture of magnesium (0.15 g, 6.0 mmol), dibromoethane (17 μL, 0.20 mmol) and THF (1.0 mL), and the resulting mixture was stirred at room temperature for 1 h. The solution of aryl Grignard reagent in THF thus prepared was then added dropwise to a solution of diethyl oxalate (0.73 g, 5.0 mmol) in THF (10 mL) at –78 °C over 1 h by using a syringe pump. The resulting solution was stirred at that temperature for 2 h and then warmed up to room temperature. After reached room temperature, the reaction was quenched with sat. aq. $NaHCO_3$, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 20:1) to afford **S1** (0.74 g, 3.8 mmol, 76%) as a colorless oil.

Synthesis of **1d**.

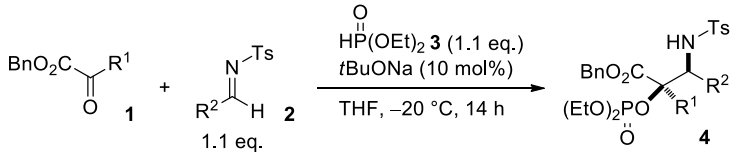


The mixture of **S1** (0.74 g, 3.8 mmol) and aq. NaOH (1.0 *M*, 7.0 mL) was stirred at room temperature for 1 h. The mixture was then carefully acidified with sat. aq. $KHSO_4$. The product was extracted with AcOEt and the combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated to provide **S2** (0.61 g, 3.6 mmol, 95%). This material was used without purification in the next step.

To a solution of **S2** (0.61 g, 3.6 mmol) in CH_2Cl_2 was added dichloromethyl methyl ether (0.46 g, 4.0 mmol) and the mixture was stirred at room temperature for 4 h. The mixture was then cooled to 0 °C, and Et_3N (0.91 g, 9.0 mmol), a catalytic amount of DMAP and benzyl alcohol (0.43 g, 4.0 mmol) were sequentially added. The resulting mixture was allowed to warm to room temperature and stirred for 17 h. The reaction was quenched with H_2O, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 20:1) to afford **2d** (0.87 g, 3.4 mmol, 93%) as a colorless oil.

The NMR spectrum data of all of α-ketoesters **1** were matched with those in the literature.[S1]

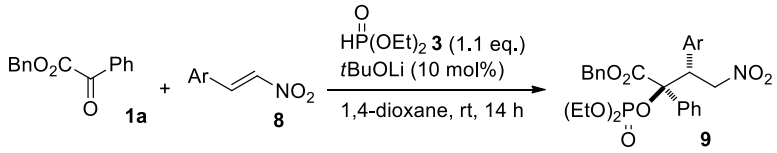
General procedure for three-component coupling reaction of α-ketoesters, imines and diethyl phosphite.



The reaction of **1c**, **2a** and **3** is representative.

To a solution of **1aa** (28 mg, 0.10 mmol), **2c** (29 mg, 0.11 mmol), and diethyl phosphite (**3**, 14 μl, 0.11 mmol) in THF (1.0 mL) was added a solution of *t*BuONa in THF (2.0 M, 5.0 μL, 0.010 mmol) at −20 °C. The resulting mixture was stirred at that temperature for 14 h. The reaction was then 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 purification of the crude mixture by column chromatography (hexane/AcOEt = 1:1) provided a mixture of **4ca** and **5c**. Further purification by using preparative HPLC afforded pure **4ca** (55 mg, 0.082 mmol, 82%) as a colorless oil.

General procedure for three-component coupling reaction of α-ketoesters, β-nitrostyrenes and diethyl phosphite.



The reaction of **1a**, **7a** and **3** is representative.

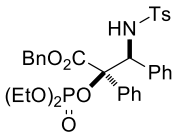
To a solution of **1a** (24 mg, 0.10 mmol), **7a** (30 mg, 0.20 mmol), and diethyl phosphite (**3**, 14 μl, 0.11 mmol) in 1,4-dioxane (1.0 mL) was added a solution of *t*BuOLi in THF (2.0 M, 5.0 μL, 0.010 mmol) at room temperature. The resulting mixture was stirred at that temperature for 14 h. The reaction was then 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 silica-gel column chromatography (hexane/AcOEt = 1:1) to provide a major diastereomer of **8aa** (31 mg, 0.059 mmol, 59%) as a pale yellow solid.

[S1] (a) S.-S. Weng, M.-W. Shen, J.-Q. Kao, Y. S. Munot and C.-T. Chen, *Proc. Natl. Acad. Sci.*, 2006, **103**, 3522-3527; (b) C. J. Roxburgh, C. R. Ganellin and A. J. Thorpe, *Synlett*, 2007, 1211-1214; (c) H.-F. Duan, J.-H. Xie, X.-C. Qiao, L.-X. Wang and Q.-L. Zhou, *Angew. Chem. Int. Ed.*, 2008, **47**, 4351-4353; (d) W. Raimondi, O. Baslé, T. Coustantieux, D. Bonne and J. Rodriguez, *Adv. Synth. Catal.*, 2012, **354**, 563-568; (e) P. Gu, X.-P. Wu, Y. Su, X.-Q. Li, P. Xue and R. Li, *Synlett*, 2014, **25**, 535-538; (f) S. Battula, N. Battini, D. Singh, Q. N. Ahmed, *Org. Biomol. Chem.*, 2015, **13**, 8637-8641.

Analytical Data

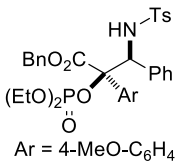
The analytical data of **4aa**, **4ac**, **4ad**, **4ae**, and **5a** were reported in our previous work.[S2] The NMR spectrum data of **6a** were matched with those in the literature.[S3]

Benzyl 2-diethoxyphosphoryloxy-2,3-diphenyl-3-(*N*-tosylamino)propionate (4aa):



diastereomixture. ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.12 (td, *J* = 7.2, 1.2 Hz, 3H), 1.21 (td, *J* = 7.2, 1.2 Hz, 3H), 2.64 (s, 3H), 3.79 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 3.86 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 4.03-4.15 (m, 2H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.33 (d, *J* = 12.0 Hz, 1H), 5.51 (d, *J* = 9.0 Hz, 1H), 6.76 (d, *J* = 7.2 Hz, 2H), 6.85 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.20 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.23-7.40 (m, 10H), 7.66 (d, *J* = 7.8 Hz, 1H); *minor diastereomer*: δ 1.05 (td, *J* = 7.2, 0.60 Hz, 3H), 1.16 (td, *J* = 7.2, 1.2 Hz, 3H), 2.23 (s, 3H), 3.65-3.73 (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* = 10.2 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.90 (dd, *J* = 8.4, 7.2 Hz, 2H), 6.97-7.04 (m, 4H), 7.18-7.40 (m, 9H), 7.61 (d, *J* = 10.2 Hz, 1H), 7.69-7.73 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.8 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 21.3, 63.8 (d, *J* = 7.2 Hz), 64.3, 65.0 (d, *J* = 5.7 Hz), 68.7, 90.9 (d, *J* = 7.2 Hz), 126.4, 126.7, 127.1, 127.3, 128.1, 128.4, 128.5, 128.72, 128.77, 128.85 (2C), 134.0, 134.5, 135.6 (d, *J* = 7.1 Hz), 138.3, 142.3, 168.3; *minor diastereomer*: δ 15.68 (d, *J* = 7.2 Hz), 15.73 (d, *J* = 8.7 Hz), 21.2, 61.7, 64.5 (d, *J* = 5.7 Hz), 64.8 (d, *J* = 5.7 Hz), 67.8, 89.4 (d, *J* = 7.2 Hz), 126.6, 127.56, 127.58, 127.9, 128.1, 128.2, 128.3, 128.4, 128.8, 129.0, 129.2, 134.4 (2C), 135.1, 137.9, 142.2, 167.7 (d, *J* = 10.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.77; *minor diastereomer*: δ −4.83; m.p. *major diastereomer*: 137.0-138.0 °C.

Benzyl 2-diethoxyphosphoryloxy-2-(4-methoxyphenyl)-3-phenyl-3-(*N*-tosylamino)propionate (4ba):

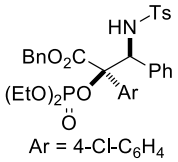


diastereomixture. ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.08 (td, *J* = 7.2, 1.2 Hz, 3H), 1.16 (td, *J* = 7.2, 1.2 Hz, 3H), 2.24 (s, 3H), 3.67-3.83 (m, 2H), 3.83 (s, 3H), 3.91-4.10 (m, 2H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.95 (d, *J* = 12.0 Hz, 1H), 5.57 (d, *J* = 9.6 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.84-7.40 (m, 15H), 7.66 (d, *J* = 9.0 Hz, 2H); *minor diastereomer*: δ 1.09 (td, *J* = 7.2, 1.2 Hz, 3H), 1.20 (td, *J* = 7.2, 1.2 Hz, 3H), 2.27 (s, 3H), 3.67-3.83 (m, 2H), 3.76 (s, 3H), 3.91-4.10 (m, 2H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.31 (d, *J* = 12.0 Hz, 1H), 5.47 (d, *J* = 9.0 Hz, 1H), 6.80 (d, *J* = 7.2 Hz, 2H), 6.84-7.40 (m, 14H), 7.48 (d, *J* = 6.0 Hz, 1H), 7.64 (d, *J* = 10.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 7.2 Hz), 15.8 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 21.26, 21.30, 55.2, 55.3, 61.6, 63.7, 64.2 (d, *J* = 2.9 Hz), 64.5 (d, *J* = 7.2 Hz), 64.8 (d, *J* = 5.9 Hz), 67.8, 68.7, 89.3 (d, *J* = 7.2 Hz), 90.5 (d, *J* = 7.2 Hz), 113.36, 113.38, 126.6, 126.7, 127.1, 127.2, 127.3, 127.37, 127.42, 127.6, 128.1, 128.2, 128.3, 128.4, 128.46, 128.48, 128.76, 128.78, 128.86, 128.91, 129.1, 129.5, 134.2, 134.46, 134.52, 137.9, 138.2, 142.2, 142.3, 159.8, 160.0, 167.9 (d, *J* = 11.4 Hz), 168.6; ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.8; *minor diastereomer*: δ −5.0; IR (ATR): 3144, 3065, 3033, 2983, 2932, 2910, 1758, 1609, 1514, 1456, 1334, 1254, 1183, 1160, 1027 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{38}NO_9PS$ $[M+Na]^+$ 690.1897, Found

[S2] A. Kondoh and M. Terada, *Org. Chem. Front.*, 2015, **2**, 801-805.
[S3] R. Fan, D. Pu, F. Wen and J. Wu, *J. Org. Chem.*, 2007, **72**, 8994-8997.

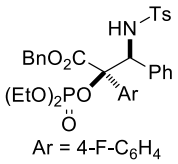
690.1897.

Benzyl 2-(4-chlorophenyl)-2-diethoxyphosphoryloxy-3-phenyl-3-(*N*-tosylamino)propionate (4ca):



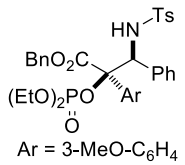
diastereomixture. ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.10 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 2.28 (s, 3H), 3.75-3.88 (m, 2H), 4.00-4.13 (m, 2H), 5.20 (d, *J* = 12.0 Hz, 1H), 5.32 (d, *J* = 12.0 Hz, 1H), 5.40 (d, *J* = 9.0 Hz, 1H), 6.79 (d, *J* = 7.2 Hz, 2H), 6.90 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 9.0 Hz, 2H), 6.98-7.40 (m, 10H), 7.46 (d, *J* = 9.0 Hz, 1H); *minor diastereomer*: δ 1.08 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 2.25 (s, 3H), 3.73-3.88 (m, 1H), 3.92-4.13 (m, 3H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 5.47 (d, *J* = 9.6 Hz, 1H), 6.85-7.38 (m, 17H), 7.64 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.8 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 21.3, 63.9 (d, *J* = 5.9 Hz), 64.3, 64.9 (d, *J* = 5.7 Hz), 68.9, 90.1 (d, *J* = 7.2 Hz), 126.7, 127.3, 127.5, 128.0, 128.2, 128.5, 128.6, 128.7, 128.9, 129.0, 133.9, 134.2, 134.3, 134.9, 138.1, 142.5, 168.0; *minor diastereomer*: δ 15.7 (d, *J* = 7.1 Hz), 15.8 (d, *J* = 7.1 Hz), 21.3, 62.1, 64.5 (d, *J* = 7.2 Hz), 64.9 (d, *J* = 6.4 Hz), 68.1, 89.0 (d, *J* = 5.7 Hz), 126.6, 127.7, 127.8, 128.2, 128.40, 128.44, 128.5, 128.9, 129.0, 129.4, 133.8, 134.2, 134.3, 135.1, 137.6, 142.5, 168.0; ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.81; *minor diastereomer*: δ −4.83; IR (ATR): 3151, 3065, 3033, 2985, 2930, 2909, 1758, 1598, 1494, 1456, 1335, 1243, 1160, 1092, 1027, 984 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{35}ClNO_8PS$ $[M+Na]^+$ 694.1402, Found 694.1401.

Benzyl 2-diethoxyphosphoryloxy-2-(4-fluorophenyl)-3-phenyl-3-(*N*-tosylamino)propionate (4da):



diastereomixture. ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.11 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 2.27 (s, 3H), 3.24-3.88 (m, 2H), 3.92-4.13 (m, 2H), 5.20 (d, *J* = 12.0 Hz, 1H), 5.32 (d, *J* = 12.0 Hz, 1H), 5.42 (d, *J* = 9.0 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 2H), 6.83-7.40 (m, 16H), 7.47 (d, *J* = 9.0 Hz, 1H); *minor diastereomer*: δ 1.08 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 2.24 (s, 3H), 3.24-3.88 (m, 1H), 3.92-4.13 (m, 3H), 4.90 (d, *J* = 12.0 Hz, 1H), 4.96 (d, *J* = 12.0 Hz, 1H), 5.51 (d, *J* = 9.6 Hz, 1H), 6.83-7.40 (m, 16H), 7.47 (d, *J* = 9.6 Hz, 1H), 7.69-7.73 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.8 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 21.3, 63.9 (d, *J* = 5.7 Hz), 64.4, 64.9 (d, *J* = 7.2 Hz), 68.9, 90.2 (d, *J* = 7.2 Hz), 115.0 (d, *J* = 21.6 Hz), 126.7, 127.3, 127.5, 128.5, 128.60 (d, *J* = 7.7 Hz), 128.62, 128.7, 128.9, 129.0, 131.4 (d, *J* = 4.4 Hz), 133.9, 134.3, 138.2, 142.4, 162.7 (d, *J* = 247.1 Hz), 168.2; *minor diastereomer*: δ 15.8 (d, *J* = 5.7 Hz, 2C), 21.3, 61.9, 64.6 (d, *J* = 7.2 Hz), 64.9 (d, *J* = 7.2 Hz), 68.0, 88.9 (d, *J* = 7.2 Hz), 115.0 (d, *J* = 21.6 Hz), 126.6, 127.7, 127.8, 128.3, 128.4, 128.6, 128.8, 129.1, 130.1 (d, *J* = 8.6 Hz), 131.1, 134.2, 134.3, 137.7, 142.4, 162.9 (d, *J* = 248.6 Hz), 167.6 (d, *J* = 11.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.8; *minor diastereomer*: δ −4.9; IR (ATR): 3134, 3066, 3033, 2984, 2931, 1758, 1602, 1509, 1456, 1335, 1240, 1162, 1092, 1031, 987 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{35}FNO_8PS$ $[M+Na]^+$ 678.1697, Found 678.1697.

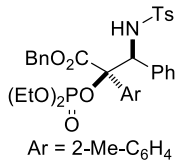
Benzyl 2-diethoxyphosphoryloxy-2-(3-methoxyphenyl)-3-phenyl-3-(*N*-tosylamino)propionate (4ea):



diastereomixture.

^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.13 (td, *J* = 7.2, 0.60 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 2.26 (s, 3H), 3.56 (s, 3H), 3.77-3.91 (m, 2H), 4.05-4.18 (m, 2H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.37 (d, *J* = 12.0 Hz, 1H), 5.48 (d, *J* = 9.0 Hz, 1H), 6.74-7.40 (m, 18H), 7.65 (d, *J* = 9.0 Hz, 1H); *minor diastereomer*: δ 1.08 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 2.23 (s, 3H), 3.70-3.80 (m, 1H), 3.77 (s, 3H), 3.93-4.02 (m, 3H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 5.57 (d, *J* = 10.2 Hz, 1H), 6.74-7.40 (m, 18H), 7.62 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.8 (d, *J* = 7.1 Hz), 15.9 (d, *J* = 8.7 Hz), 21.3, 55.0, 63.9 (d, *J* = 7.2 Hz), 64.4, 65.0 (d, *J* = 5.7 Hz), 68.7, 90.8 (d, *J* = 7.2 Hz), 111.9, 114.7, 118.7, 126.7, 127.1, 127.3, 128.46, 128.49, 128.7, 128.8, 128.9, 129.0, 134.0, 134.5, 137.1 (d, *J* = 8.7 Hz), 138.3, 142.3, 159.1, 168.1; *minor diastereomer*: δ 15.7 (d, *J* = 8.6 Hz), 15.8 (d, *J* = 7.1 Hz), 21.2, 55.4, 61.8, 64.5 (d, *J* = 7.2 Hz), 64.9 (d, *J* = 5.7 Hz), 67.8, 89.4 (d, *J* = 5.9 Hz), 112.9, 115.6, 120.2, 126.6, 127.58, 127.60, 128.2, 128.3, 128.4, 128.8, 129.0, 129.1, 134.40, 134.44, 136.5, 137.8, 142.2, 159.3, 167.6 (d, *J* = 10.2 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.8; *minor diastereomer*: δ −4.9; IR (ATR): 3145, 3065, 3033, 2985, 2940, 2908, 1757, 1601, 1586, 1494, 1455, 1334, 1249, 1159, 1092, 1027, 976 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{38}NO_9PS$ $[M+Na]^+$ 690.1897, Found 690.1897.

Benzyl 2-diethoxyphosphoryloxy-2-(2-methylphenyl)-3-phenyl-3-(*N*-tosylamino)propionate (4fa):



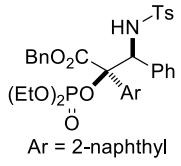
major diastereomer: white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 2.04 (s, 3H), 2.23 (s, 3H), 3.35-3.46 (m, 1H), 3.87-3.95 (m, 1H), 3.98-4.10 (m, 2H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 5.62 (d, *J* = 10.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.91 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.19-7.29 (m, 6H), 7.33-7.37 (m, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.58 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.6 (d, *J* = 7.2 Hz), 15.7 (d, *J* = 7.2 Hz), 20.2, 21.3, 62.2, 64.7 (d, *J* = 7.2 Hz), 65.4 (d, *J* = 5.7 Hz), 67.7, 89.3 (d, *J* = 7.2 Hz), 126.2, 126.6, 127.6 (2C), 128.2, 128.29, 128.33, 128.7, 128.9, 129.1, 129.3, 131.7, 133.9, 134.3, 134.4, 138.1, 138.5, 142.1, 168.1; ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.6; IR (ATR): 3129, 3066, 3032, 2982, 2911, 1766, 1734, 1600, 1456, 1335, 1227, 1159, 1092, 1026 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{38}NO_8PS$ $[M+Na]^+$ 674.1948, Found 674.1948; m.p.: 88.0-90.0 °C.

minor diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.03 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H), 2.14 (s, 3H), 2.29 (s, 3H), 3.47-3.59 (m, 1H), 3.67-3.91 (m, 3H), 5.04 (d, *J* = 12.0 Hz, 1H), 5.17 (d, *J* = 12.0 Hz, 1H), 5.75 (d, *J* = 7.8 Hz, 1H), 6.56 (brs, 1H), 6.90-6.99 (m, 6H), 7.03-7.06 (m, 2H), 7.09-7.14 (m, 3H), 7.16-7.20 (m, 1H), 7.25-7.30 (m, 3H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7 (d, *J* = 8.6 Hz), 15.8 (d, *J* = 8.7 Hz), 20.9, 21.4, 60.8, 63.9 (d, *J* = 5.7 Hz), 64.5 (d, *J* = 5.7 Hz), 68.2, 87.6 (d, *J* = 5.7 Hz), 125.8, 127.0, 127.3, 127.5, 128.4, 128.5, 128.8, 128.9 (2C), 129.0, 129.1, 132.2, 133.3 (d, *J* = 4.4 Hz), 134.1, 134.8, 137.3, 137.9, 142.5, 169.6 (d, *J* = 7.2 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −5.4.

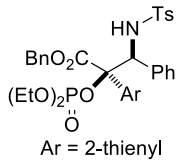
Benzyl 2-diethoxyphosphoryloxy-2-(2-naphthyl)-3-phenyl-3-(*N*-tosylamino)propionate (4ga):



diastereomixture.

^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.11 (td, *J* = 7.2, 1.2 Hz, 3H), 1.20 (td, *J* = 7.2, 1.2 Hz, 3H), 2.24 (s, 3H), 3.76-3.89 (m, 2H), 4.00-4.15 (m, 2H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.38 (d, *J* = 12.0 Hz, 1H), 5.62 (d, *J* = 9.6 Hz, 1H), 6.80-7.86 (m, 22H); *minor diastereomer*: δ 0.95 (td, *J* = 7.2, 1.2 Hz, 3H), 1.17 (td, *J* = 7.2, 1.2 Hz, 3H), 2.21 (s, 3H), 3.60-3.70 (m, 1H), 3.76-4.15 (m, 3H), 4.93 (d, *J* = 12.0 Hz, 1H), 4.96 (d, *J* = 12.0 Hz, 1H), 5.68 (d, *J* = 10.2 Hz, 1H), 6.80-7.86 (m, 21H), 8.33 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.8 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 21.3, 63.9 (d, *J* = 5.7 Hz), 64.3 (d, *J* = 2.9 Hz), 64.9 (d, *J* = 5.7 Hz), 68.8, 90.9 (d, *J* = 7.2 Hz), 123.7, 126.2, 126.3, 126.6, 126.8, 127.2, 127.3, 127.4, 127.7, 128.46, 128.53, 128.6, 128.7, 128.8, 129.0, 132.4, 132.9 (d, *J* = 8.7 Hz), 133.0, 134.2, 134.5, 138.2, 142.3, 168.3; *minor diastereomer*: δ 15.6 (d, *J* = 7.2 Hz), 15.8 (d, *J* = 7.2 Hz), 21.3, 62.0, 64.5 (d, *J* = 7.1 Hz), 64.8 (d, *J* = 5.7 Hz), 68.0, 89.7 (d, *J* = 7.1 Hz), 125.0, 126.2, 126.6, 127.0, 127.3, 127.5, 127.64, 127.65, 127.8, 128.28, 128.34 (2C), 128.8, 128.9, 129.2, 132.5, 132.6, 133.1, 134.3, 134.6, 137.8, 142.3, 167.7 (d, *J* = 10.5 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.71; *minor diastereomer*: δ −4.71; IR (ATR): 3143, 3063, 3033, 2984, 2928, 1757, 1599, 1496, 1455, 1334, 1239, 1160, 1092, 1028, 976 cm^{-1}; HRMS (ESI) Calcd for $C_{37}H_{38}NO_8PS$ $[M+Na]^+$ 710.1948, Found 710.1948.

Benzyl 2-diethoxyphosphoryloxy-3-phenyl-2-(2-thienyl)-3-(*N*-tosylamino)propionate (4ha):



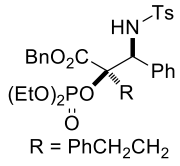
major diastereomer: pale red solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.09 (td, *J* = 7.2, 1.2 Hz, 3H), 1.26 (td, *J* = 7.2, 1.2 Hz, 3H), 2.26 (s, 3H), 3.75 (qd, *J* = 7.2, 7.2 Hz, 1H), 3.82 (qd, *J* = 7.2, 7.2 Hz, 1H), 4.10-4.23 (m, 2H), 5.25 (d, *J* = 12.0 Hz, 1H), 5.40 (d, *J* = 8.4 Hz, 1H), 5.42 (d, *J* = 12.0 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 2H), 6.87-6.90 (m, 3H), 6.92 (d, *J* = 7.2 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 7.09 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.17 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.37-7.41 (m, 3H), 7.46 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 7.2 Hz), 21.3, 64.1 (d, *J* = 7.2 Hz), 65.2 (d, *J* = 7.2 Hz), 66.1 (d, *J* = 2.9 Hz), 69.2, 90.1 (d, *J* = 7.2 Hz), 126.3, 126.7, 126.89, 126.91, 127.2, 127.5, 128.5, 128.57, 128.59, 128.9, 129.1, 133.5, 134.4, 138.3, 139.1 (d, *J* = 8.6 Hz), 142.4, 167.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ −5.9; IR (ATR): 3114, 3066, 3033, 2984, 2909, 1762, 1599, 1456, 1335, 1248, 1161, 1033, 982 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{34}NO_8PS_2$ $[M+Na]^+$ 666.1356, Found 666.1355; m.p.: 109.0-110.2 °C.

minor diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.06 (td, *J* = 7.2, 1.2 Hz, 3H), 1.14 (td, *J* = 7.2, 1.2 Hz, 3H), 2.25 (s, 3H), 3.71-3.93 (m, 4H), 4.99 (d, *J* = 12.0 Hz, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 5.27 (d, *J* = 9.6 Hz, 1H), 6.65 (d, *J* = 10.2 Hz, 1H), 6.85-6.98 (m, 7H), 7.06-7.10 (m, 1H), 7.16-7.18 (m, 1H), 7.22-7.24 (m, 1H), 7.29-7.33 (m, 5H), 7.36 (dd, *J* = 5.4, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.80 (d, *J* = 7.2 Hz), 15.82 (d, *J* = 7.2 Hz), 21.3, 64.29 (d, *J* = 5.7 Hz), 64.31 (d, *J* = 7.2 Hz), 64.4 (d, *J* = 5.7 Hz), 68.5, 86.3 (d, *J* = 7.2 Hz), 125.9, 126.8, 127.7, 127.99, 128.04, 128.5, 128.6, 128.8, 128.9 (2C), 130.3, 134.1, 134.3, 136.2, 137.6, 142.6, 167.3 (d, *J* = 7.2 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.6.

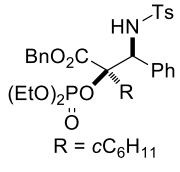
Benzyl 2-diethoxyphosphoryloxy-4-phenyl-2-(*N*-tosylaminobenzyl)butanoate (4ia):



diastereomixture.

^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.14 (td, *J* = 7.2, 1.2 Hz, 3H), 1.34 (td, *J* = 7.2, 1.2 Hz, 3H), 1.91 (ddd, *J* = 13.8, 12.0, 4.8 Hz, 1H), 2.19-2.25 (m, 1H), 2.24 (s, 3H), 2.34 (ddd, *J* = 13.8, 13.2, 4.8 Hz, 1H), 2.62 (ddd, *J* = 13.2, 12.0, 4.8 Hz, 1H), 3.80 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 3.86-3.97 (m, 2H), 4.24-4.34 (m, 1H), 5.02 (d, *J* = 9.6 Hz, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 6.86-7.42 (m, 17H), 7.46-7.49 (m, 2H), 7.88 (d, *J* = 10.2 Hz, 1H); *minor diastereomer*: δ 1.13 (td, *J* = 7.2, 1.2 Hz, 3H), 1.27 (td, *J* = 7.2, 0.6 Hz, 3H), 2.22 (s, 3H), 2.38-2.50 (m, 2H), 2.61-2.70 (m, 1H), 2.81-2.89 (m, 1H), 4.10-4.20 (m, 2H), 4.24-4.35 (m, 2H), 4.99 (d, *J* = 12.0 Hz, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 6.85-7.50 (m, 18H), 7.65 (d, *J* = 10.2 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.8 (d, *J* = 7.2 Hz), 16.1 (d, *J* = 7.2 Hz), 21.3, 29.7, 38.8 (d, *J* = 7.2 Hz), 63.4, 63.8 (d, *J* = 7.2 Hz), 65.2 (d, *J* = 5.7 Hz), 68.5, 91.1 (d, *J* = 10.1 Hz), 126.1, 126.6, 127.69, 127.72, 128.3, 128.4 (2C), 128.6, 128.8, 129.0, 129.2, 134.1, 134.9, 138.3, 140.2, 142.2, 168.9; *minor diastereomer*: δ 15.7 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 5.9 Hz), 21.5, 29.7, 37.4, 62.9, 64.76 (d, *J* = 7.2 Hz), 64.83 (d, *J* = 5.9 Hz), 67.8, 90.6 (d, *J* = 5.7 Hz), 126.4, 126.6, 127.6, 127.8, 128.2, 128.3, 128.6, 128.7, 128.8, 128.9, 129.7, 134.4, 135.2, 138.0, 140.3, 142.4, 168.6 (d, *J* = 13.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.7; *minor diastereomer*: δ −5.0; IR (ATR): 3157, 3064, 3030, 2984, 2934, 1761, 1600, 1496, 1455, 1335, 1242, 1161, 1092, 1029, 982 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{40}NO_8PS$ $[M+Na]^+$ 688.2104, Found 688.2104.

Benzyl 2-cyclohexyl-2-diethoxyphosphoryloxy-3-phenyl-3-(*N*-tosylamino)propionate (4ja):



major diastereomer: colorless oil.

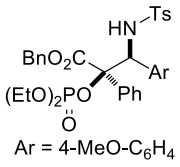
^{1}H NMR (600 MHz, $CDCl_3$) δ 0.70-0.80 (m, 1H), 0.86-1.10 (m, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.24-1.36 (m, 1H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.40-1.80 (m, 5H), 1.90-2.00 (m, 1H), 2.28 (s, 3H), 3.75-3.83 (m, 1H), 3.88-3.96 (m, 1H), 4.21-4.33 (m, 2H), 5.13 (d, *J* = 12.0 Hz, 1H), 5.30 (d, *J* = 9.6 Hz, 1H), 5.42 (d, *J* = 12.0 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 2H), 7.03 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.36 (td, *J* = 7.8, 1.8 Hz, 1H), 7.40 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 8.04 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 8.7 Hz), 16.1 (d, *J* = 5.7 Hz), 21.3, 26.0, 26.1, 26.2, 26.9, 28.6, 44.6 (d, *J* = 7.1 Hz), 60.6, 63.6 (d, *J* = 5.7 Hz), 65.2 (d, *J* = 5.7 Hz), 68.3, 94.9 (d, *J* = 10.1 Hz), 126.5, 127.6, 127.7, 128.5 (2C), 128.7, 128.9, 129.2, 134.8, 134.9, 138.8, 141.9, 168.4; ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.9; IR (ATR): 3141, 3032, 2983, 2931, 2855, 1754, 1599, 1454, 1335, 1245, 1217, 1161, 1031, 981 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{42}NO_8PS$ $[M+Na]^+$ 666.2261, Found 666.2261.

minor diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 0.62-0.72 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 3H), 1.05-1.15 (m, 1H), 1.15-1.28 (m, 1H), 1.30-1.42 (m, 1H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.50-1.60 (m, 1H), 1.66-1.76 (m, 2H), 1.85-1.90 (m, 1H), 2.02-2.10 (m, 1H), 2.22 (s, 3H), 2.29-2.36 (m, 1H), 2.40-2.48 (m, 1H), 3.73-3.82 (m, 2H), 4.13-4.26 (m, 2H), 4.87 (d, *J* = 12.0 Hz, 1H), 5.04 (d, *J* = 12.0 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.87 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.23-7.31 (m, 5H), 8.32 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.5 (d, *J* = 7.2 Hz), 16.1 (d, *J* = 7.2 Hz), 21.3, 26.2 (2C), 26.5, 26.7, 28.4,

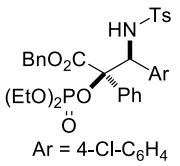
44.0, 60.5, 64.6 (d, *J* = 5.7 Hz), 64.8 (d, *J* = 7.1 Hz), 67.4, 95.3 (d, *J* = 5.7 Hz), 126.6, 127.2, 127.5, 128.4, 128.5, 128.68, 128.72, 129.0, 134.5, 134.6, 138.5, 141.9, 167.7 (d, *J* = 14.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −6.2.

Benzyl 2-diethoxyphosphoryloxy-3-(4-methoxyphenyl)-2-phenyl-3-(*N*-tosylamino)propionate (4ab):



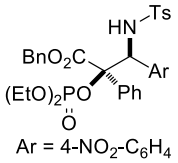
diastereomixture. ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.15 (td, *J* = 7.2, 1.2 Hz, 3H), 1.21 (td, *J* = 7.2, 0.60 Hz, 3H), 2.28 (s, 3H), 3.64 (s, 3H), 3.80-4.16 (m, 4H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.33 (d, *J* = 12.0 Hz, 1H), 5.46 (d, *J* = 9.0 Hz, 1H), 6.38 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 7.20-7.40 (m, 12H), 7.55-7.63 (m, 1H); *minor diastereomer*: δ 1.04 (td, *J* = 7.2, 0.60 Hz, 3H), 1.18 (td, *J* = 7.2, 0.60 Hz, 3H), 2.25 (s, 3H), 3.69 (s, 3H), 3.66-3.72 (m, 1H), 3.80-4.15 (m, 3H), 4.90 (d, *J* = 12.0 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 5.53 (d, *J* = 9.6 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 2H), 6.89 (dd, *J* = 8.4, 7.8 Hz, 2H), 6.99 (d, *J* = 7.2 Hz, 2H), 7.18-7.40 (m, 12H), 7.68-7.73 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.8 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 21.3, 55.0, 63.84, 63.85 (d, *J* = 5.7 Hz), 64.9 (d, *J* = 5.7 Hz), 68.7, 91.0 (d, *J* = 5.7 Hz), 112.5, 126.1, 126.4, 126.7, 128.1, 128.41, 128.44, 128.7, 128.8 (2C), 129.9, 134.5, 135.6 (d, *J* =7.1 Hz), 138.4, 142.2, 158.8, 168.3; *minor diastereomer*: δ 15.7 (d, *J* = 7.2 Hz), 15.8 (d, *J* = 7.2 Hz), 21.2, 61.1, 63.8, 64.5 (d, *J* = 5.7 Hz), 64.8 (d, *J* = 5.7 Hz), 67.7, 89.5 (d, *J* = 7.2 Hz), 112.9, 126.5, 126.7, 127.9, 128.1, 128.29, 128.34, 128.7, 128.8, 129.0, 130.4, 134.4, 135.2, 138.0, 142.1, 159.1, 167.8 (d, *J* = 11.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.7; *minor diastereomer*: δ −4.8; IR (ATR): 3142, 3064, 3033, 2984, 2932, 2909, 1756, 1612, 1514, 1448, 1334, 1246, 1159, 1027, 986 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{38}NO_9PS$ $[M+Na]^+$ 690.1897, Found 690.1897.

Benzyl 3-(4-chlorophenyl)-2-diethoxyphosphoryloxy-2-phenyl-3-(*N*-tosylamino)propionate (4ac):



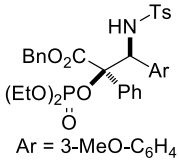
diastereomixture. ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.18 (td, *J* = 7.2, 1.2 Hz, 3H), 1.23 (td, *J* = 7.2, 1.2 Hz, 3H), 2.31 (s, 3H), 3.83-4.18 (m, 4H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.34 (d, *J* = 12.0 Hz, 1H), 5.45 (d, *J* = 9.0 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 7.21 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.24-7.28 (m, 1H), 7.32-7.38 (m, 9H), 7.75 (d, *J* = 6.6 Hz, 1H); *minor diastereomer*: δ 1.06 (td, *J* = 7.2, 1.2 Hz, 3H), 1.18 (td, *J* = 7.2, 1.2 Hz, 3H), 2.29 (s, 3H), 3.65-3.73 (m, 1H), 3.83-4.06 (m, 3H), 4.94 (d, *J* = 12.0 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 5.53 (d, *J* = 9.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 7.22-7.30 (m, 4H), 7.32-7.38 (m, 4H), 7.65-7.70 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.8 (d, *J* = 8.7 Hz), 15.9 (d, *J* = 7.2 Hz), 21.3, 63.8, 64.0 (d, *J* = 5.7 Hz), 65.2 (d, *J* = 7.2 Hz), 68.8, 90.1 (d, *J* = 7.1 Hz), 126.1, 126.7, 127.2, 128.2, 128.5, 128.6, 128.87, 128.90, 128.94, 130.2, 132.7, 133.4, 134.4, 135.3 (d, *J* = 7.2 Hz), 138.2, 142.7, 168.0; *minor diastereomer*: δ 15.7 (d, *J* = 7.2 Hz), 15.8 (d, *J* = 7.2 Hz), 21.3, 61.1, 64.6 (d, *J* = 7.2 Hz), 65.0 (d, *J* = 5.7 Hz), 68.0, 89.1 (d, *J* = 7.2 Hz), 126.7, 127.6, 127.8, 128.2, 128.3, 128.4, 128.5, 128.9, 129.2, 130.7, 132.8, 133.8, 134.2, 134.9, 137.8, 142.7, 167.6 (d, *J* = 10.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.5; *minor diastereomer*: δ −4.7.

Benzyl 2-diethoxyphosphoryloxy-3-(4-nitrophenyl)-2-phenyl-3-(*N*-tosylamino)propionate (4ad):



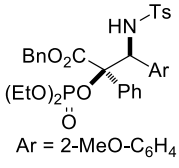
diastereomixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.10 (td, *J* = 7.2, 1.2 Hz, 1.5H), 1.20 (td, *J* = 7.2, 1.2 Hz, 1.5H), 1.23 (td, *J* = 7.2, 1.2 Hz, 1.5H), 1.24 (td, *J* = 7.2, 1.2 Hz, 1.5H), 2.23 (s, 1.5H), 2.29 (s, 1.5H), 3.71-3.73 (m, 0.5H), 3.91-4.06 (m, 2.5H), 4008-4.20 (m, 1.0H), 4.97 (d, *J* = 12.0 Hz, 0.5H), 5.02 (d, *J* = 12.0 Hz, 0.5H), 5.20 (d, *J* = 12.0 Hz, 0.5H), 5.35 (d, *J* = 12.0 Hz, 0.5H), 5.53 (d, *J* = 7.8 Hz, 0.5H), 5.61 (d, *J* = 9.6 Hz, 0.5H), 6.89 (d, *J* = 8.4 Hz, 1.0H), 6.93 (d, *J* = 8.4 Hz, 1.0H), 7.01 (d, *J* = 8.4 Hz, 1.0H), 7.03 (d, *J* = 7.2 Hz, 1.0H), 7.11 (d, *J* = 9.0 Hz, 1.0H), 7.18-7.38 (m, 9.0H), 7.40 (d, *J* = 9.0 Hz, 1.0H), 7.62 (d, *J* = 10.2 Hz, 1.0H), 7.64 (d, *J* = 9.0 Hz, 1.0H), 7.69 (d, *J* = 9.0 Hz, 1.0H), 7.78 (d, *J* = 9.6 Hz, 0.5H), 7.99 (d, *J* = 6.0 Hz, 0.5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7 (d, *J* = 7.2 Hz), 15.8 (d, *J* = 7.2 Hz), 15.92 (d, *J* = 7.2 Hz), 15.95 (d, *J* = 7.2 Hz), 21.2, 21.3, 61.4, 63.9, 64.2 (d, *J* = 5.7 Hz), 64.7 (d, *J* = 7.1 Hz), 65.1 (d, *J* = 5.9 Hz), 65.5 (d, *J* = 5.7 Hz), 68.3, 69.0, 88.6 (d, *J* = 7.2 Hz), 90.1 (d, *J* = 5.7 Hz), 122.1, 122.4, 125.8, 126.6, 126.8, 127.5, 128.4, 128.47 (2C), 128.52, 128.6, 128.69, 128.73, 128.9, 129.0, 129.1, 129.2, 129.4, 129.8, 130.4, 134.0, 134.2, 134.6, 135.1 (d, *J* = 8.6 Hz), 137.7, 138.0, 141.7, 141.9, 143.1, 143.2, 147.0 (2C), 167.5 (d, *J* = 11.6 Hz), 167.7; ^{31}P NMR (243 MHz, $CDCl_3$) δ −3.8, −4.4.

Benzyl 2-diethoxyphosphoryloxy-3-(3-methoxyphenyl)-2-phenyl-3-(*N*-tosylamino)propionate (4ae):



diastereomixture. ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.12 (td, *J* = 7.2, 1.2 Hz, 3H), 1.23 (td, *J* = 7.2, 1.2 Hz, 3H), 2.27 (s, 3H), 3.43 (s, 3H), 3.79 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 3.87 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 4.06-4.19 (m, 2H), 5.23 (d, *J* = 12.0 Hz, 1H), 5.36 (d, *J* = 12.0 Hz, 1H), 5.53 (d, *J* = 9.0 Hz, 1H), 6.28 (s, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 6.53 (dd, *J* = 8.4, 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* = 7.8 Hz, 1H); *minor diastereomer*: δ 1.06 (td, *J* = 7.2, 1.2 Hz, 3H), 1.15 (td, *J* = 7.2, 1.2 Hz, 3H), 2.25 (s, 3H), 3.53 (s, 3H), 3.64-3.74 (m, 1H), 3.90-4.03 (m, 3H), 4.90 (d, *J* = 12.0 Hz, 1H), 4.99 (d, *J* = 12.0 Hz, 1H), 5.59 (d, *J* = 9.6 Hz, 1H), 6.55-6.60 (m, 3H), 6,84 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 7.20-7.43 (m, 8H), 7.66 (d, *J* = 10.2 Hz, 1H), 7.69-7.73 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.7 (d, *J* = 7.1 Hz), 15.9 (d, *J* = 7.2 Hz), 21.2, 54.6, 63.9 (d, *J* = 7.2 Hz), 64.4, 65.0 (d, *J* = 5.7 Hz), 68.8, 91.1 (d, *J* = 7.2 Hz), 113.4, 113.9, 121.2, 126.3, 126.7, 128.0, 128.1, 128.42, 128.45, 128.7, 128.79, 128.83, 134.5, 135.2, 135.7 (d, *J* = 8.6 Hz), 138.4, 142.3, 158.5, 168.2; *minor diastereomer*: δ 15.66 (d, *J* = 5.7 Hz), 15.70 (d, *J* = 5.7 Hz), 21.2, 54.7, 61.6, 64.6 (d, *J* = 5.9 Hz), 64.8 (d, *J* = 5.7 Hz), 67.8, 89.5 (d, *J* = 7.1 Hz), 113.9, 114.1, 121.7, 126.6, 126.7, 127.9, 128.0, 128.27, 128.34, 128.7, 128.8, 129.0, 134.4, 135.1, 135.6, 137.9, 142.3, 158.9, 167.7 (d, *J* = 10.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.8; *minor diastereomer*: δ −4.9.

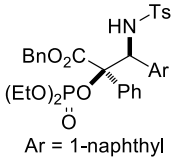
Benzyl 2-diethoxyphosphoryloxy-3-(2-methoxyphenyl)-2-phenyl-3-(*N*-tosylamino)propionate (4af):



diastereomixture. ^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.19 (t, *J* = 7.2 Hz, 6H), 2.23 (s, 3H), 3.26 (s, 3H), 3.94-4.10 (m, 4H), 5.25 (d, *J* = 12.0 Hz, 1H), 5.39 (d, *J* = 12.0 Hz, 1H), 5.88 (d, *J* = 8.4 Hz,

1H), 6.30 (d, *J* = 7.8 Hz, 1H), 6.56 (dd, *J* = 7.8, 7.2 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.95 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.07 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.97-7.40 (m, 11H); *minor diastereomer*: δ 1.10 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 2.20 (s, 3H), 3.19 (s, 3H), 3.83-4.09 (m, 4H), 5.03-5.12 (m, 2H), 5.60-5.74 (brs, 1H), 6.27 (d, *J* = 9.0 Hz, 1H), 6.60 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.63 (d, *J* = 10.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 2H), 6.98-7.40 (m, 14H); ^{13}C NMR (150 MHz, $CDCl_3$) *major diastereomer*: δ 15.9 (d, *J* = 7.2 Hz, 2C), 21.3, 54.5, 64.01, 64.04 (d, *J* = 7.1 Hz), 64.6 (d, *J* = 5.9 Hz), 68.5, 90.7 (d, *J* = 8.7 Hz), 109.4, 119.7, 126.4, 126.8, 127.2, 128.25. 128.29, 128.3, 128.4, 128.6, 128.7, 128.8, 129.7, 134.8, 135.2 (d, *J* = 5.7 Hz), 137.6, 142.2, 156.4, 168.3; *minor diastereomer*: δ 15.79 (d, *J* = 8.3 Hz), 15.82 (d, *J* = 7.2 Hz), 21.2, 57.2, 64.01, 64.04 (d, *J* = 7.1 Hz), 64.4 (d, *J* = 4.2 Hz), 67.9, 88.1, 109.7, 119.9, 122.8, 126.7, 127.3, 128.0, 128.1, 128.3, 128.46, 128.50, 128.8, 129.0, 130.0, 134.9, 135.4, 137.2, 142.4, 156.6, 167.8 (d, *J* = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.6; *minor diastereomer*: δ −4.9; IR (ATR): 3138, 3064, 3033, 2984, 2933, 2908, 1756, 1612, 1514, 1448, 1334, 1246, 1160, 1028, 986 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{38}NO_9PS$ $[M+Na]^+$ 690.1897, Found 690.1896.

Benzyl 2-diethoxyphosphoryloxy-3-(1-naphthyl)-2-phenyl-3-(*N*-tosylamino)propionate (4ag):



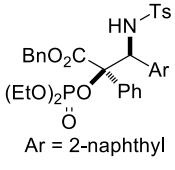
major diastereomer: white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H), 2.12 (s, 3H), 3.53-3.67 (m, 2H), 3.77-3.91 (m, 2H), 5.33 (d, *J* = 12.0 Hz, 1H), 5.38 (d, *J* = 12.0 Hz, 1H), 6.23 (d, *J* = 9.0 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.99 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.02-7.11 (m, 4H), 7.20-7.40 (m, 10H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.6 (d, *J* = 7.2 Hz), 15.8 (d, *J* = 7.2 Hz), 21.1, 57.9, 63.8 (d, *J* = 5.9 Hz), 64.3 (d, *J* = 5.9 Hz), 68.7, 90.3 (d, *J* = 7.2 Hz), 123.0, 124.4, 125.0, 125.7, 126.3, 126.6, 126.8, 127.7, 127.9, 128.2, 128.48, 128.51, 128.56, 128.8, 129.1, 131.2, 132.2, 132.8, 134.5, 134.9 (d, *J* = 4.4 Hz), 137.3, 142.2, 168.7; ^{31}P NMR (243 MHz, $CDCl_3$) δ −5.0; IR (ATR): 3162, 3063, 3033, 2985, 2929, 2910, 1756, 1599, 1449, 1336, 1253, 1160, 1091, 1027, 984 cm^{-1}; HRMS (ESI) Calcd for $C_{37}H_{38}NO_8PS$ $[M+Na]^+$ 710.1948, Found 710.1947 m.p.: 124.4-125.0 °C.

minor diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.03 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 2.04 (s, 3H), 3.70-3.78 (m, 1H), 3.94-4.12 (m, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 6.43 (d, *J* = 10.2 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.08 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.17 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.19-7.24 (m, 2H), 7.29 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.34-7.38 (m, 4H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.78-7.82 (m, 2H), 7.98 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.2 Hz), 21.0, 54.8, 64.5 (d, *J* = 5.9 Hz), 64.9 (d, *J* = 5.7 Hz), 67.6, 88.9 (d, *J* = 7.2 Hz), 123.4, 124.8, 125.2, 126.0, 126.5, 127.2, 127.9, 128.07, 128.13 (3C), 128.15, 128.19, 128.23, 128.5, 129.1, 131.5, 133.1, 134.4, 135.4, 136.9, 142.1, 167.6 (d, *J* = 10.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.8.

Benzyl 2-diethoxyphosphoryloxy-3-(2-naphthyl)-2-phenyl-3-(*N*-tosylamino)propionate (4ah):

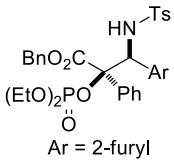


diastereomixture.

^{1}H NMR (600 MHz, $CDCl_3$) *major diastereomer*: δ 1.01 (td, *J* = 7.2, 1.2 Hz, 3H), 1.21 (td, *J* = 7.2, 1.2 Hz, 3H), 1.97 (s, 3H), 3.69-3.76 (m, 1H), 3.81 (ddq, *J* = 9.6, 7.2, 7.2 Hz, 1H), 3.93-4.02

(m, 1H), 4.06-4.18 (m, 1H), 5.27 (d, *J* = 11.4 Hz, 1H), 5.37 (d, *J* = 11.4 Hz, 1H), 5.69 (d, *J* = 9.6 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 9.0 Hz, 1H), 7.18-7.46 (m, 17H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 5.4 Hz, 1H); *minor diastereomer*: δ 1.06 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 1.86 (s, 3H), 3.69-3.76 (m, 1H), 4.02-4.19 (m, 3H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.94 (d, *J* = 12.0 Hz, 1H), 5.72 (d, *J* = 9.6 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 7.10-7.16 (m, 3H), 7.22-7.48 (m, 12H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.72-7.78 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7 (d, *J* = 7.1 Hz), 15.7-15.8 (2C), 15.9 (d, *J* = 7.2 Hz), 20.9, 21.0, 60.3, 63.9 (d, *J* = 5.7 Hz), 64.6, 64.9 (d, *J* = 5.7 Hz), 65.1 (d, *J* = 5.7 Hz), 67.9, 68.9, 89.5 (d, *J* = 5.9 Hz), 91.5 (d, *J* = 7.2 Hz), 125.5, 125.7, 125.9, 126.1, 126.4, 126.46, 126.51, 126.6, 127.1, 127.2, 127.3, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 129.1, 129.3, 131.0, 131.4, 132.3, 132.4, 132.6, 134.3, 134.5, 135.2, 135.5 (d, *J* = 8.6 Hz), 137.7, 138.2, 142.29, 142.33, 167.8 (d, *J* = 10.1 Hz), 168.3; ^{31}P NMR (243 MHz, $CDCl_3$) *major diastereomer*: δ −4.74; *minor diastereomer*: δ −4.72; IR (ATR): 3136, 3061, 3030, 2984, 2931, 2108, 1757, 1599, 1448, 1336, 1241, 1159, 1027, 986 cm^{-1}; HRMS (ESI) Calcd for $C_{37}H_{38}NO_8PS$ $[M+Na]^+$ 710.1948, Found 710.1947.

Benzyl 2-diethoxyphosphoryloxy-3-(2-furyl)-2-phenyl-3-(*N*-tosylamino)propionate (4ai):



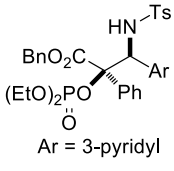
major diastereomer: white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.17 (td, *J* = 7.2, 1.2 Hz, 3H), 1.23 (td, *J* = 7.2, 1.2 Hz, 3H), 2.32 (s, 3H), 3.85-3.95 (m, 2H), 4.05-4.17 (m, 2H), 5.17 (d, *J* = 12.0 Hz, 1H), 5.33 (d, *J* = 12.0 Hz, 1H), 5.67 (d, *J* = 9.6 Hz, 1H), 5.77 (d, *J* = 3.0 Hz, 1H), 5.94 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.89 (d, *J* = 1.2 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.24-7.35 (m, 8H), 7.42-7.45 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.88 (d, *J* = 8.6 Hz), 15.94 (d, *J* = 7.2 Hz), 21.4, 58.2, 63.9 (d, *J* = 5.7 Hz), 64.9 (d, *J* = 5.7 Hz), 68.6, 89.8 (d, *J* = 7.2 Hz), 109.9, 110.1, 126.3, 126.7, 128.2, 128.4 (2C), 128.7, 128.8, 129.0, 134.6, 135.4 (d, *J* = 7.2 Hz), 138.2, 141.8, 142.4, 148.0 167.9; ^{31}P NMR (243 MHz, $CDCl_3$) δ −5.1; IR (ATR): 3117, 3033, 2984, 2913, 1760, 1498, 1449, 1338, 1248, 1161, 1030, 986 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{34}NO_9PS$ $[M+Na]^+$ 650.1584, Found 650.1583; m.p.: 111.7-112.4 °C.

minor diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.12 (td, *J* = 7.2, 1.2 Hz, 3H), 1.17 (td, *J* = 7.2, 1.2 Hz, 3H), 2.31 (s, 3H), 3.78-3.86 (m, 1H), 3.90-4.04 (m, 3H), 5.07 (d, *J* = 12.6 Hz, 1H), 5.11 (d, *J* = 12.6 Hz, 1H), 5.73 (d, *J* = 10.2 Hz, 1H), 5.94 (d, *J* = 3.0 Hz, 1H), 5.97 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.91 (d, *J* = 0.60 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 7.12 (dd, *J* = 7.8, 2.4 Hz, 2H), 7.25-7.35 (m, 6H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.62-7.66 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 7.2 Hz, 2C), 21.4, 56.6, 64.4 (d, *J* = 7.2 Hz), 64.7 (d, *J* = 5.9 Hz), 68.1, 88.9 (d, *J* = 7.2 Hz), 110.1, 110.3, 126.7, 127.4, 128.1, 128.30, 128.34, 128.4, 128.95, 129.05, 134.6, 134.8, 137.9, 141.8, 142.5, 148.5, 167.7 (d, *J* = 10.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −5.3.

Benzyl 2-diethoxyphosphoryloxy-2-phenyl-3-(3-pyridyl)-3-(*N*-tosylamino)propionate (4aj):



major diastereomer: colorless oil.

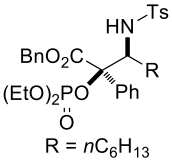
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.22 (td, *J* = 7.2, 1.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 2.29 (s, 3H), 3.94 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 4.01 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 4.09-4.20 (m, 2H),

5.22 (d, *J* = 12.0 Hz, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 5.47 (d, *J* = 8.4 Hz, 1H), 6.80 (dd, *J* = 8.4, 4.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.18-7.23 (m, 3H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.29-7.32 (m, 2H), 7.32-7.35 (m, 5H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 8.22 (dd, *J* = 4.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.91 (d, *J* = 7.2 Hz), 15.94 (d, *J* = 7.2 Hz), 21.4, 62.5, 64.2 (d, *J* = 5.7 Hz), 65.4 (d, *J* = 5.7 Hz), 69.0, 90.5 (d, *J* = 5.7 Hz), 122.1, 125.8, 126.8, 128.4, 128.5, 128.6, 128.9, 129.2 (2C), 130.2, 134.4, 135.2 (d, *J* = 8.6 Hz), 136.0, 138.0, 142.8, 148.5, 150.0, 167.9; ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.0; IR (ATR): 3142, 3064, 3033, 2985, 2930, 2909, 1756, 1598, 1449, 1337, 1247, 1161, 1028, 988 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{35}N_2O_8PS$ $[M+Na]^+$ 661.1744, Found 661.1743.

minor diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.09 (td, *J* = 7.2, 1.2 Hz, 3H), 1.18 (td, *J* = 7.2, 1.2 Hz, 3H), 2.26 (s, 3H), 3.75 (ddq, *J* = 10.2, 9.0, 7.2 Hz, 1H), 3.94-4.06 (m, 3H), 4.95 (d, *J* = 12.0 Hz, 1H), 5.00 (d, *J* = 12.0 Hz, 1H), 5.56 (d, *J* = 9.0 Hz, 1H), 6.79 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.2 Hz, 2H), 7.22-7.42 (m, 9H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 9.6 Hz, 1H), 8.14 (d, *J* = 2.4 Hz, 1H), 8.26 (dd, *J* = 4.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.7 (d, *J* = 7.2 Hz), 15.8 (d, *J* = 7.2 Hz), 21.3, 60.0, 64.7 (d, *J* = 5.7 Hz), 65.1 (d, *J* = 5.7 Hz), 68.2, 89.0 (d, *J* = 7.2 Hz), 122.5, 126.6, 127.6, 128.5 (2C), 128.47, 128.51, 129.1, 129.3, 130.4, 134.1, 134.6, 136.4, 137.7, 142.8, 148.7, 150.4, 167.5 (d, *J* = 11.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.5.

Benzyl 2-diethoxyphosphoryloxy-2-phenyl-3-(*N*-tosylamino)nonanoate (4ak):



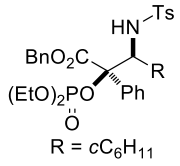
major diastereomer: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 0.77 (t, *J* = 7.2 Hz, 3H), 0.90-1.20 (m, 8H), 1.25-1.35 (m, 1H), 1.28 (td, *J* = 7.2, 0.60 Hz, 3H), 1.32 (td, *J* = 7.2, 1.2 Hz, 3H), 1.37-1.46 (m, 1H), 2.38 (s, 3H), 4.13 (qd, *J* = 7.2, 7.2 Hz, 2H), 4.17-7.27 (m, 2H), 4.62 (td, *J* = 9.6, 3.0 Hz, 1H), 4.73 (d, *J* = 12.6 Hz, 1H), 5.08 (d, *J* = 12.6 Hz, 1H), 7.11-7.16 (m, 2H), 7.21-7.27 (m, 5H), 7.28-7.33 (m, 3H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.52-7.58 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 16.00 (d, *J* = 7.2 Hz), 16.05 (d, *J* = 5.7 Hz), 21.4, 22.4, 26.2, 28.8, 30.9, 31.3, 61.0, 63.9 (d, *J* = 5.7 Hz), 65.1 (d, *J* = 5.7 Hz), 68.0, 92.5 (d, *J* = 7.1 Hz), 125.9, 126.4, 128.17, 128.24, 128.3, 128.4, 128.6, 129.2, 134.8, 136.7 (d, *J* = 8.6 Hz), 140.4, 142.3, 168.3; ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.9; IR (ATR): 3154, 3064, 3033, 2954, 2929, 2859, 1757, 1599, 1448, 1331, 1246, 1159, 1095, 1034, 983 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{44}NO_8PS$ $[M+Na]^+$ 668.2417, Found 688.2417.

minor diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.2 Hz, 3H), 0.95-1.30 (m, 8H), 1.17 (td, *J* = 7.2, 1.2 Hz, 3H), 1.22 (td, *J* = 7.2, 1.2 Hz, 3H), 1.45-1.61 (m, 2H), 2.35 (s, 3H), 3.85-3.93 (m, 1H), 3.96-4.08 (m, 3H), 4.49 (td, *J* = 9.0, 3.0 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 5.66 (d, *J* = 10.2 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.21-7.26 (m, 5H), 7.28-7.32 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.54-7.58 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 15.87 (d, *J* = 7.2 Hz), 15.89 (d, *J* = 7.2 Hz), 21.4, 22.5, 26.6, 28.9, 31.5, 32.8, 60.5 (d, *J* = 2.9 Hz), 64.2 (d, *J* = 7.2 Hz), 64.4 (d, *J* = 5.9 Hz), 68.0, 90.5 (d, *J* = 7.1 Hz), 126.5, 126.8, 128.0, 128.5, 128.6 (3C), 129.2, 134.7, 136.1 (d, *J* = 4.2 Hz), 139.3, 142.4, 168.4 (d, *J* = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −5.4.

Benzyl 3-cyclohexyl-2-diethoxyphosphoryloxy-2-phenyl-3-(*N*-tosylamino)propionate (4al):



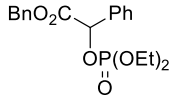
major diastereomer: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 0.85-1.05 (m, 5H), 1.20-1.26 (m, 1H), 1.26 (td, *J* = 7.2, 0.60 Hz, 3H), 1.31 (td, *J* = 7.2, 0.60 Hz, 3H), 1.43-1.55 (m, 3H), 1.57-1.63 (m, 1H), 1.71-1.81 (m, 1H), 2.38 (s, 3H), 4.05-4.24 (m, 4H), 4.49 (dd, *J* = 10.2, 4.8 Hz, 1H), 4.62 (d, *J* = 12.6 Hz, 1H), 5.03 (d, *J* = 12.6 Hz, 1H), 7.07-7.12 (m, 3H), 7.21-7.29 (m, 8H), 7.52-7.56 (m, 2H), 7.72 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.0 (d, *J* = 7.2 Hz, 2C), 21.4, 25.7, 26.1, 26.5, 28.8, 33.0, 39.1, 63.7 (d, *J* = 5.7 Hz), 64.9, 65.0 (d, *J* = 5.7 Hz), 67.9, 92.7 (d, *J* = 7.2 Hz), 126.1, 126.4, 128.16, 128.19, 128.22, 128.27, 128.5, 129.2, 134.7, 136.6 (d, *J* = 8.9 Hz), 140.2, 142.2, 168.4; ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.8; IR (ATR): 3170, 3066, 2983, 2927, 2853, 1756, 1496, 1448, 1329, 1251, 1157, 1094, 1026, 971 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{42}NO_8PS$ $[M+Na]^+$ 666.2261, Found 666.2260.

minor diastereomer:

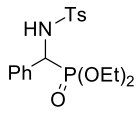
^{1}H NMR (600 MHz, $CDCl_3$) δ 0.85-1.15 (m, 5H), 1.15 (td, *J* = 7.2, 1.2 Hz, 3H), 1.20 (td, *J* = 7.2, 1.2 Hz, 3H), 1.37-1.60 (m, 6H), 2.36 (s, 3H), 3.85-4.05 (m, 4H), 4.20 (d, *J* = 10.2 Hz, 1H), 5.15 (d, *J* = 12.0 Hz, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.40 (d, *J* = 10.2 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.16-7.24 (m, 3H), 7.28-7.35 (m, 5H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 5.7 Hz), 21.4, 25.8, 26.1, 26.6, 28.6, 32.9, 39.9, 64.0 (d, *J* = 6.8 Hz), 64.2 (d, *J* = 5.9 Hz), 64.7 (d, *J* = 4.4 Hz), 68.2, 90.6 (d, *J* = 8.7 Hz), 126.7, 126.9, 127.9, 128.5, 128.58, 128.64, 128.9, 129.2, 134.5, 136.0, 138.9, 142.5, 168.4 (d, *J* = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −5.1.

Benzyl diethoxyphosphoryloxy(phenyl)acetate (5a):



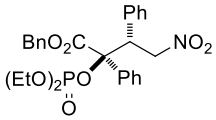
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.16 (td, *J* = 7.2, 1.2 Hz, 3H), 1.30 (td, *J* = 7.2, 1.2 Hz, 3H), 3.89-4.00 (m, 2H), 4.10-4.22 (m, 2H), 5.16 (d, *J* = 12.0 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 5.80 (d, *J* = 8.4 Hz, 1H), 7.18-7.24 (m, 2H), 7.27-7.32 (m, 3H), 7.34-7.39 (m, 3H), 7.43-7.48 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 5.7 Hz), 15.9 (d, *J* = 7.2 Hz), 64.0 (d, *J* = 5.7 Hz), 64.3 (d, *J* = 5.7 Hz), 67.3, 76.7 (d, *J* = 4.4 Hz), 127.2, 128.0, 128.3, 128.4, 128.7, 129.2, 134.9 (d, *J* = 5.9 Hz), 135.0, 168.7 (d, *J* = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −1.4.

Diethyl phenyl(*N*-tosylamino)methylphosphonate (6a):



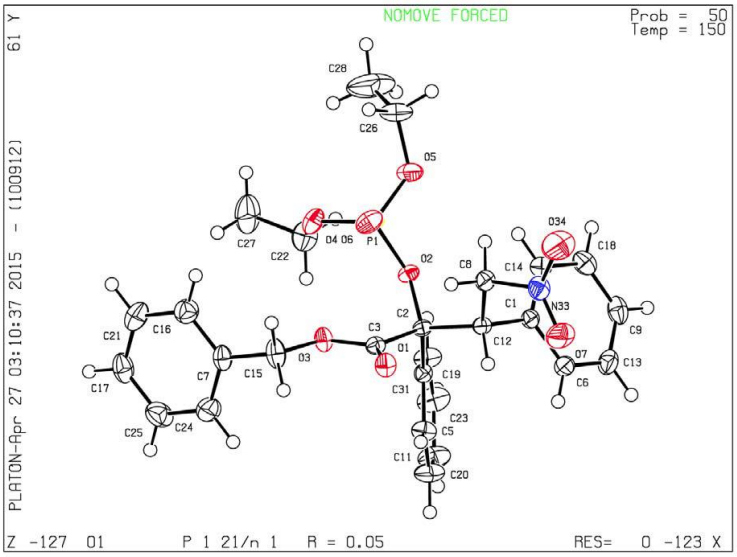
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.03 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 2.28 (s, 3H), 3.55-3.63 (m, 1H), 3.87 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 4.13-4.24 (m, 2H), 4.77 (dd, *J* = 24.0, 9.6 Hz, 1H), 6.34 (brs, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.12 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.10-7.20 (m, 3H), 7.46 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.0 (d, *J* = 5.7 Hz), 16.4 (d, *J* = 5.7 Hz), 21.3, 55.2 (d, *J* = 155.1 Hz), 63.6 (d, *J* = 7.2 Hz), 64.0 (d, *J* = 5.7 Hz), 127.0, 127.8 (d, *J* = 3.9 Hz), 128.12, 128.14, 128.9 (d, *J* = 7.2 Hz), 133.6, 137.8 (d, *J* =12.9 Hz), 142.8 (d, *J* = 14.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.2.

Benzyl 2-diethoxyphosphoryloxy-4-nitro-2,3-diphenylbutanoate (9aa):

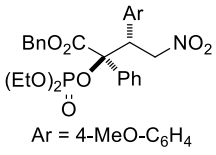


major diastereomer: white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.08 (td, J = 7.2, 1.2 Hz, 3H), 1.21 (td, J = 7.2, 1.2 Hz, 3H), 3.79 (ddq, J = 9.6, 7.2, 7.2 Hz, 1H), 3.85 (ddq, J = 10.8, 7.2, 7.2 Hz, 1H), 3.94 (qd, J = 7.2, 7.2 Hz, 2H), 4.63 (dd, J = 9.6, 4.8 Hz, 1H), 5.04 (dd, J = 13.8, 10.2 Hz, 1H), 5.06 (dd, J = 13.8, 4.8 Hz, 1H), 5.17 (d, J = 12.0 Hz, 1H), 5.33 (d, J = 12.0 Hz, 1H), 7.06-7.18 (m, 5H), 7.19-7.33 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.2 Hz), 15.9 (d, J = 7.2 Hz), 52.3 (d, J = 4.4 Hz), 64.02 (d, J = 5.9 Hz), 64.06 (d, J = 5.7 Hz), 68.4, 76.8, 87.6 (d, J = 7.2 Hz), 125.9, 127.99, 128.02, 128.3, 128.5, 128.6, 128.76, 128.81, 129.7, 133.9, 134.3, 136.5 (d, J = 6.0 Hz), 168.8 (d, J = 3.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.9; IR (ATR): 3064, 3033, 2984, 2908, 1739, 1555, 1496, 1454, 1379, 1269, 1026, 979 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{30}NO_8P$ $[M+Na]^+$ 550.1601, Found 550.1601; m.p.: 97.5-98.2 °C. CCDC1450154.

Figure S1. ORTEP diagram of **9aa**.

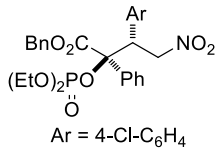


Benzyl 2-diethoxyphosphoryloxy-3-(4-methoxyphenyl)-4-nitro-2-phenylbutanoate (9ab):

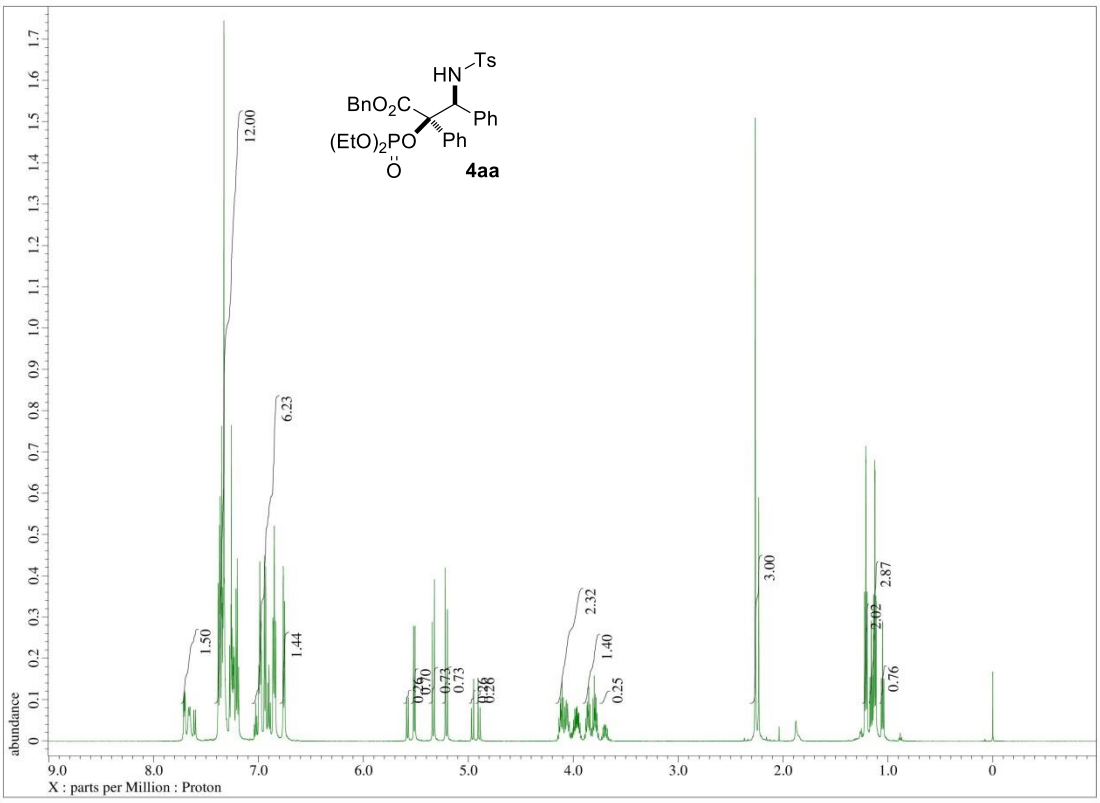


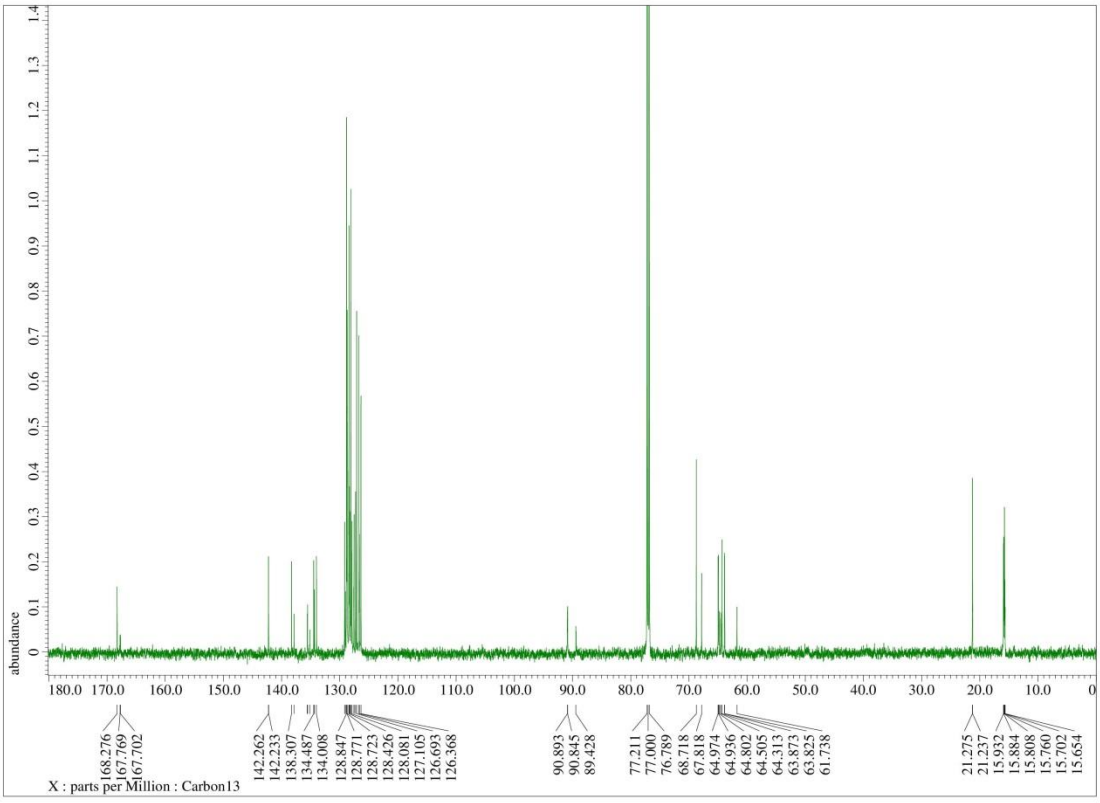
major diastereomer: white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.09 (td, J = 7.2, 1.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 3.72 (s, 3H), 3.81 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 3.87 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 3.96 (qd, J = 7.2, 7.2 Hz, 2H), 4.58 (dd, J = 10.8, 3.6 Hz, 1H), 4.99 (dd, J = 13.8, 11.4 Hz, 1H), 5.03 (dd, J = 13.8, 3.6 Hz, 1H), 5.17 (d, J = 12.0 Hz, 1H), 5.32 (d, J = 12.0 Hz, 1H), 5.65 (d, J = 9.0 Hz, 2H), 5.99 (d, J = 9.0 Hz, 2H), 7.19-7.32 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, J = 7.1 Hz), 15.9 (d, J = 7.2 Hz), 51.6 (d, J = 4.4 Hz), 55.1, 64.03 (d, J = 4.2 Hz), 64.06 (d, J = 5.9 Hz), 68.3, 77.0, 87.8 (d, J = 7.2 Hz), 113.5, 125.6, 125.9, 128.3, 128.5, 128.6, 128.76, 128.78, 130.8, 134.4, 136.5 (d, J = 5.4 Hz), 159.3, 168.8 (d, J = 2.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.9; IR (ATR): 3064, 3034, 2983, 2933, 2912, 2838, 1738, 1612, 1555, 1515, 1449, 1379, 1252, 1183, 1027, 979 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{32}NO_9P$ $[M+Na]^+$ 580.1707, Found 580.1707; m.p.: 106.0-106.6 °C.

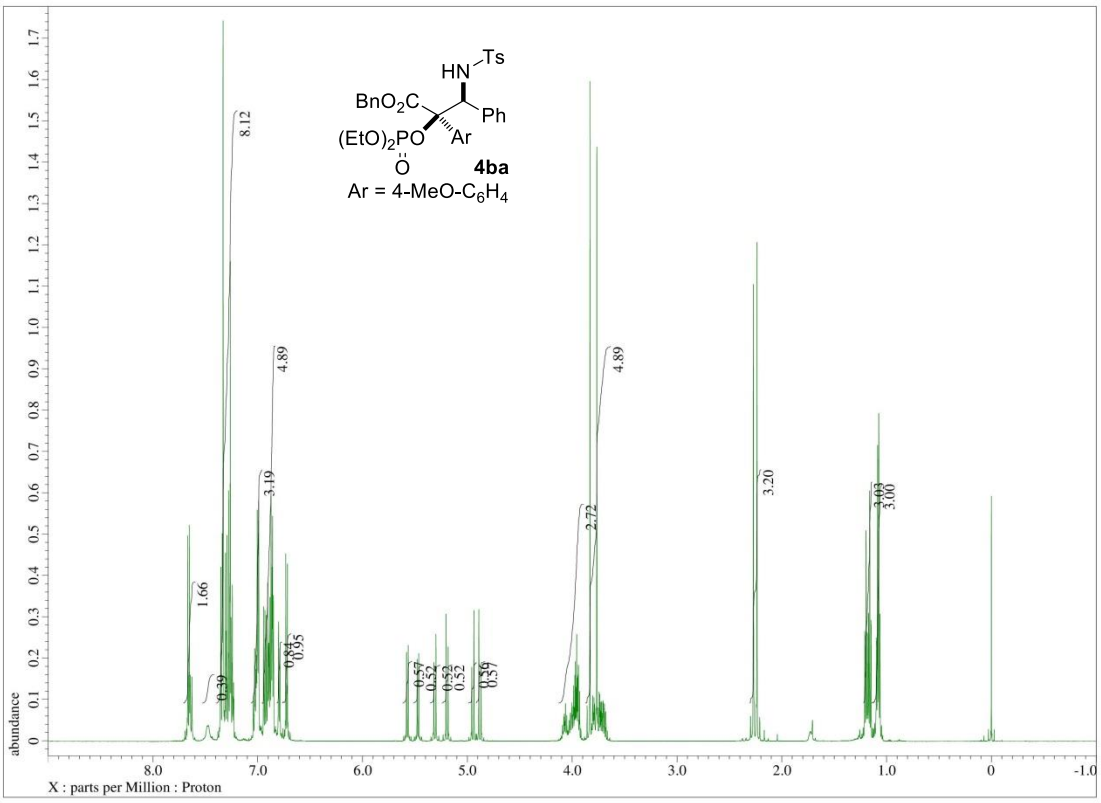
Benzyl 3-(4-chlorophenyl)-2-diethoxyphosphoryloxy-4-nitro-2-phenylbutanoate (9ac):

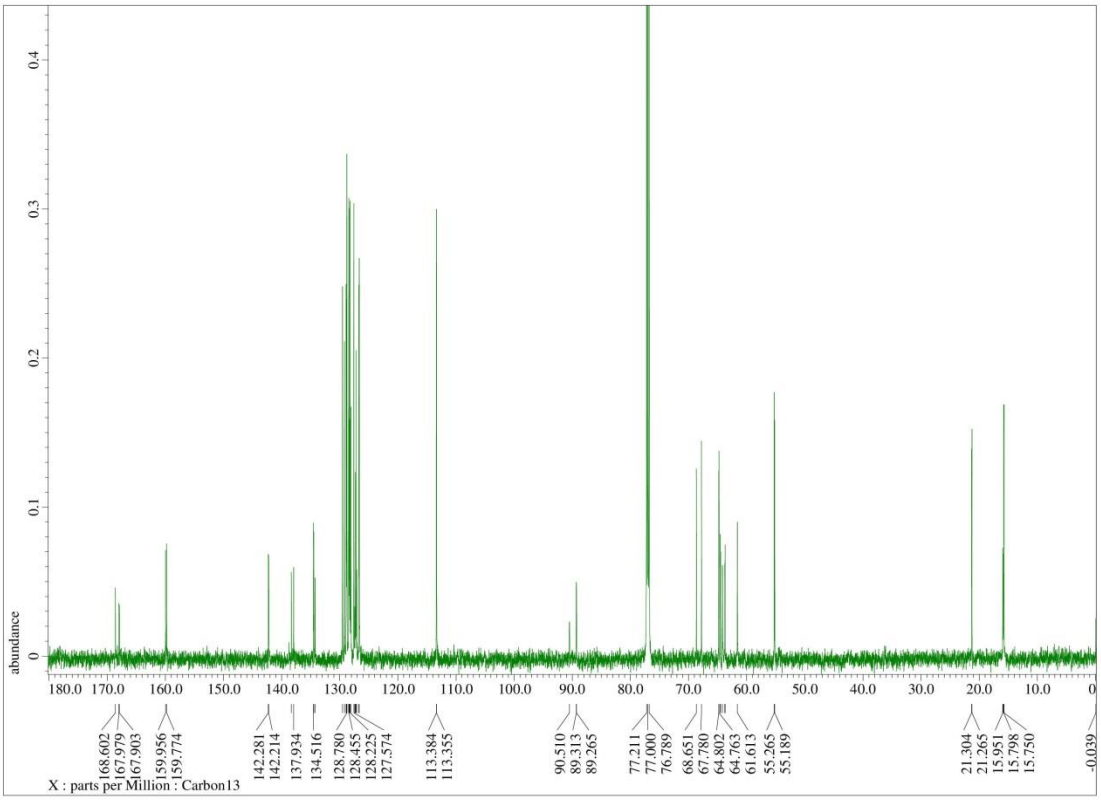


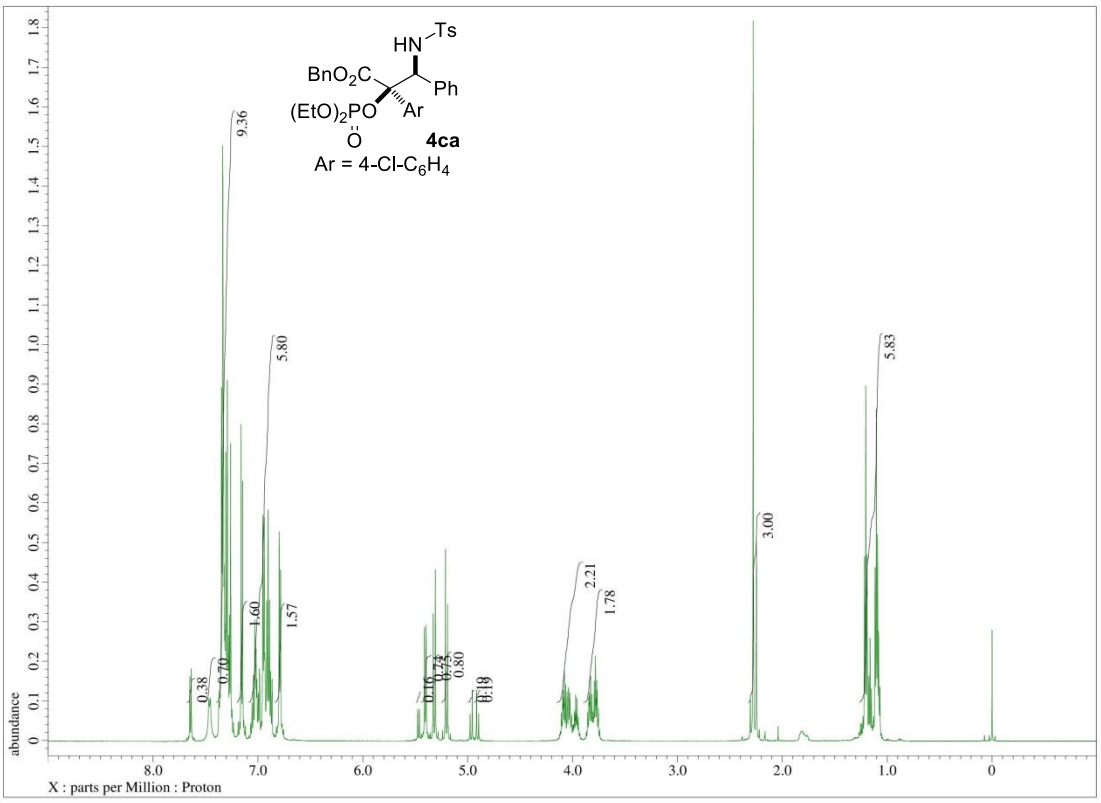
major diastereomer: white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.09 (td, *J* = 7.2, 1.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 3.83 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 3.88 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 1H), 4.01 (qd, *J* = 7.2, 7.2 Hz, 2H), 4.60 (dd, *J* = 11.4, 3.0 Hz, 1H), 4.99 (dd, *J* = 13.8, 11.4 Hz, 1H), 5.13 (dd, *J* = 13.8, 3.0 Hz, 1H), 5.17 (d, *J* = 12.0 Hz, 1H), 5.32 (d, *J* = 12.0 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.17-7.34 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 7.2 Hz), 51.7 (d, *J* = 3.0 Hz), 64.17 (d, *J* = 5.7 Hz), 64.25 (d, *J* = 5.9 Hz), 68.5, 76.7, 87.4 (d, *J* = 5.7 Hz), 125.5, 128.2, 128.4, 128.5, 128.7, 128.8, 128.9, 131.0, 132.5, 134.0, 134.2, 136.4 (d, *J* = 7.1 Hz), 168.6 (d, *J* = 2.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ −4.7; IR (ATR): 3065, 3034, 2984, 2930, 2910, 1739, 1555, 1495, 1449, 1378, 1268, 1025, 979 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{29}ClNO_8P$ $[M+Na]^+$ 584.1212, Found 584.1211; m.p.: 121.5-122.5 °C.

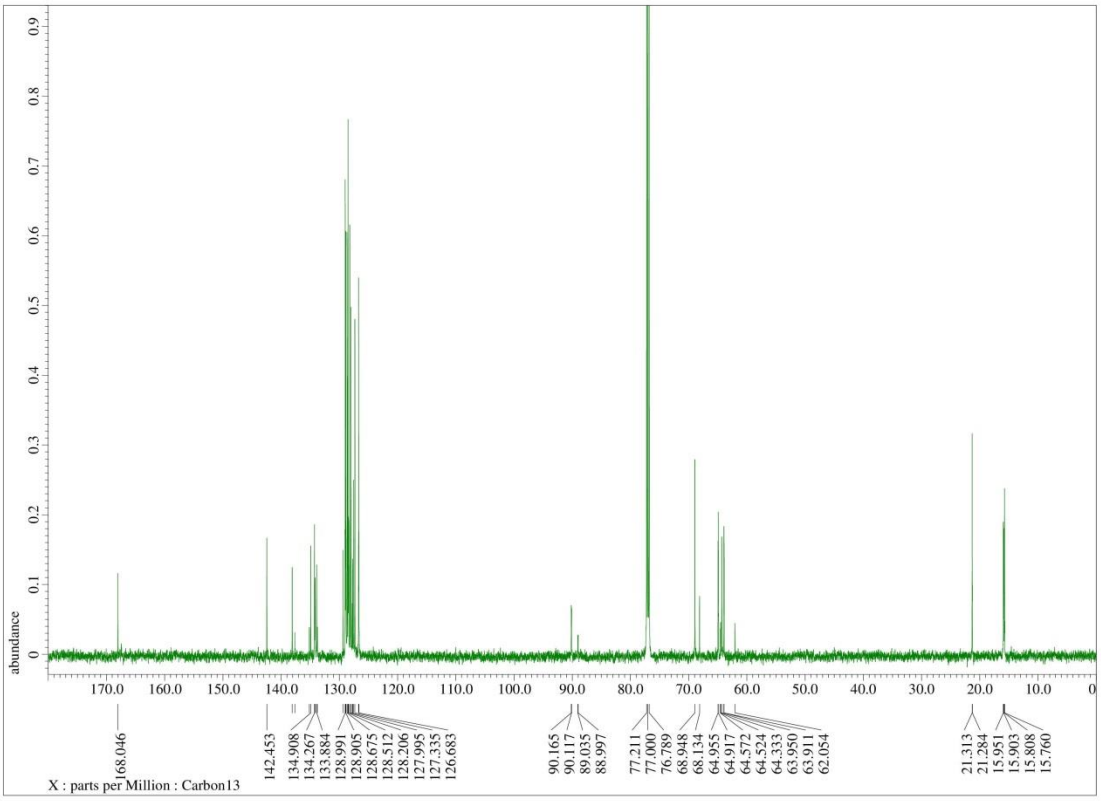

HN
Ts
BnO2C
Ph
(EtO)2PO
Ph
O
4aa
12.00
6.23
1.50
1.44
2.32
1.40
0.25
3.00
2.87
2.02
0.76
abundance
X : parts per Million : Proton

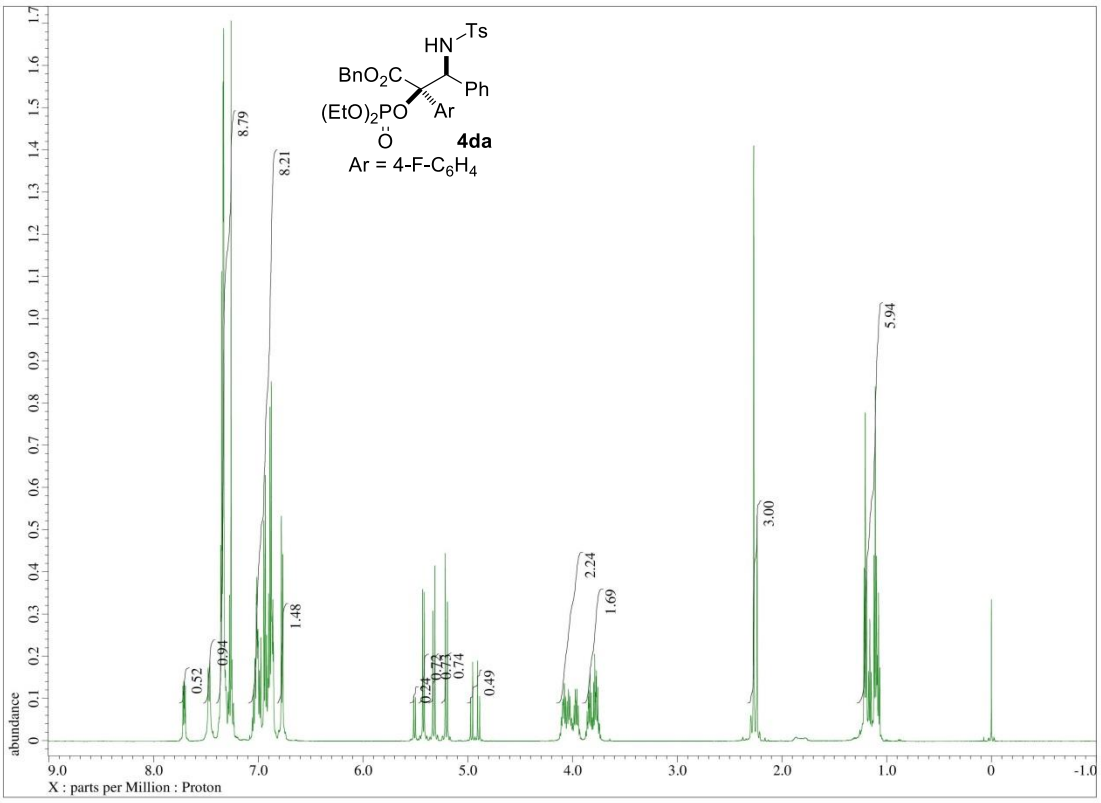

abundance
X : parts per Million : Carbon13

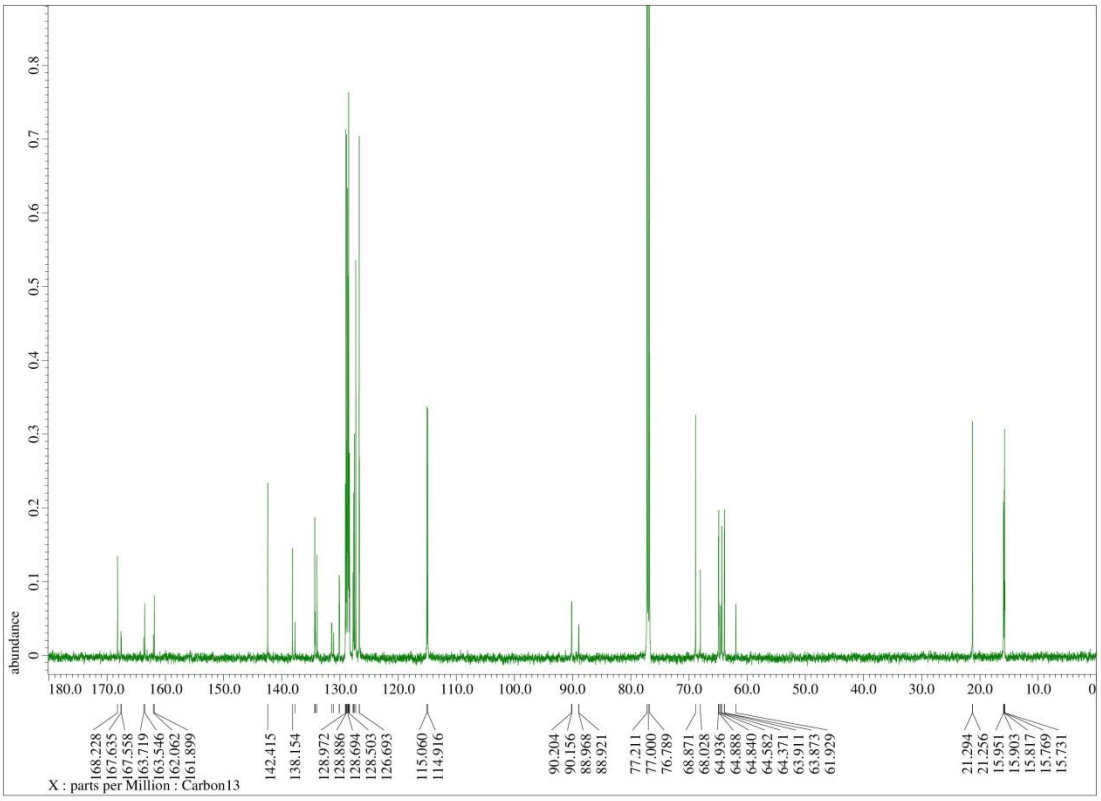

HN
Ts
BnO2C
Ph
(EtO)2PO
Ar
O
4ba
Ar = 4-MeO-C6H4
abundance
X : parts per Million : Proton

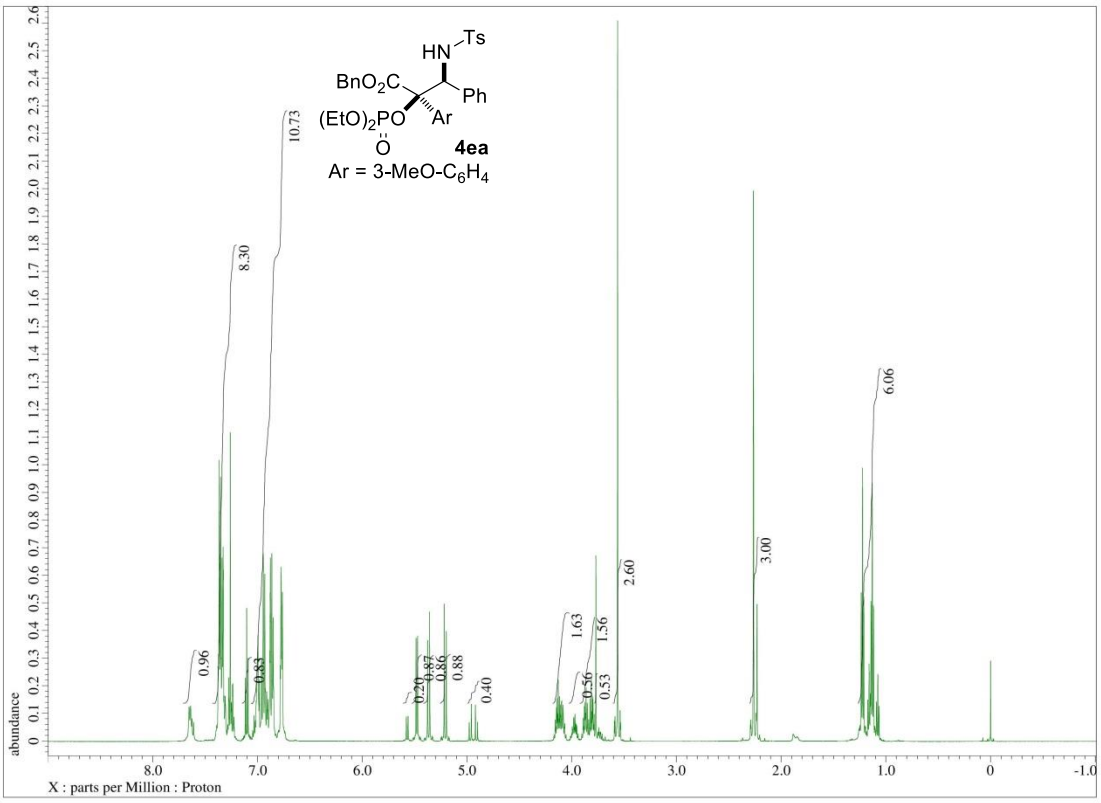

abundance
X : parts per Million : Carbon13

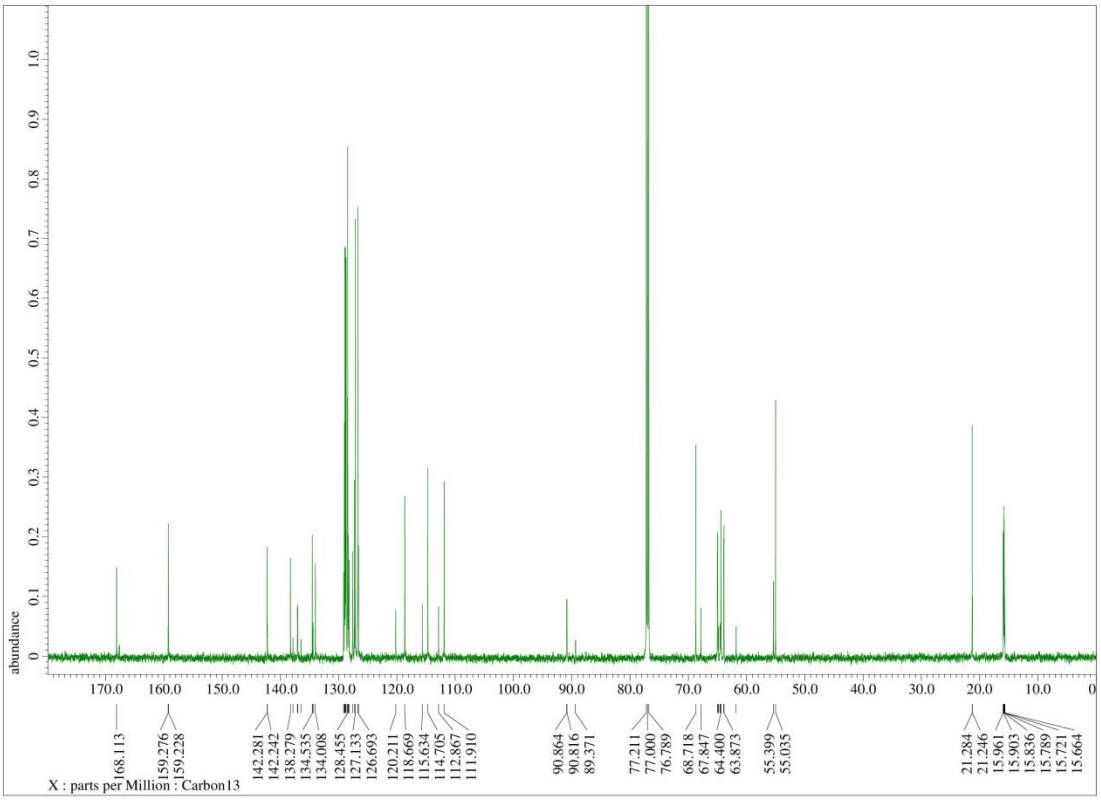

HN
Ts
BnO2C
Ph
(EtO)2PO
Ar
O
4ca
Ar = 4-Cl-C6H4
9.36
5.80
1.60
1.57
0.38
0.70
0.80
2.21
1.78
3.00
5.83
abundance
X : parts per Million : Proton

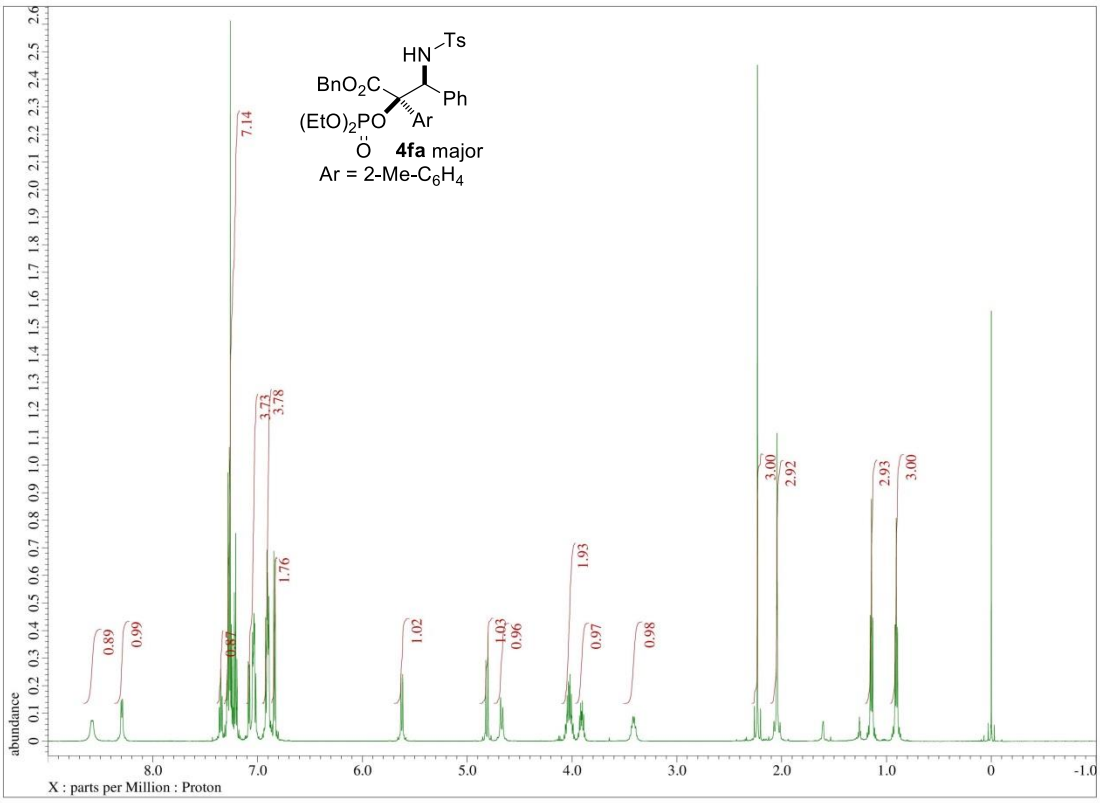

abundance
X : parts per Million : Carbon13
168.046
142.453
134.908
134.267
133.884
128.991
128.905
128.675
128.512
128.206
127.995
127.335
126.683
90.165
90.117
89.035
88.997
77.211
77.000
76.789
68.948
68.134
64.955
64.917
64.572
64.524
64.333
63.950
63.911
62.054
21.313
21.284
15.951
15.903
15.808
15.760

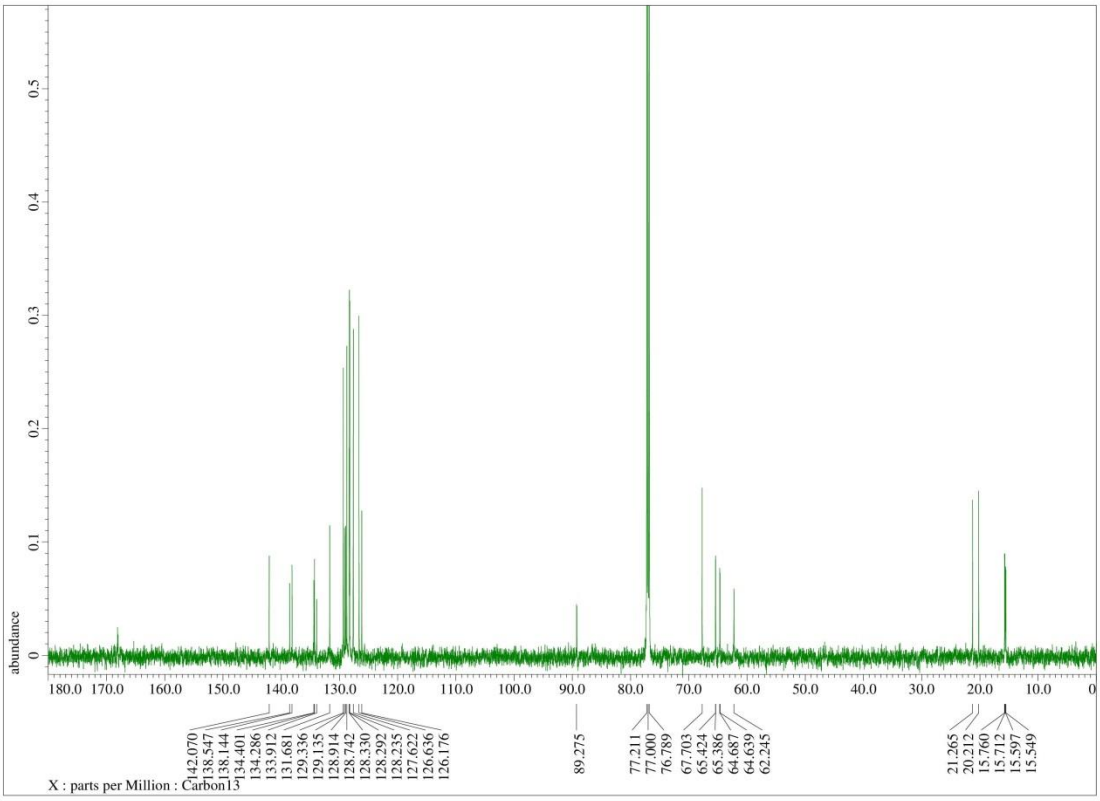

HN
Ts
BnO2C
Ph
(EtO)2PO
Ar
O
4da
Ar = 4-F-C6H4
8.79
8.21
1.48
0.52
0.94
0.24
0.73
0.73
0.74
0.49
2.24
1.69
3.00
5.94
abundance
X : parts per Million : Proton

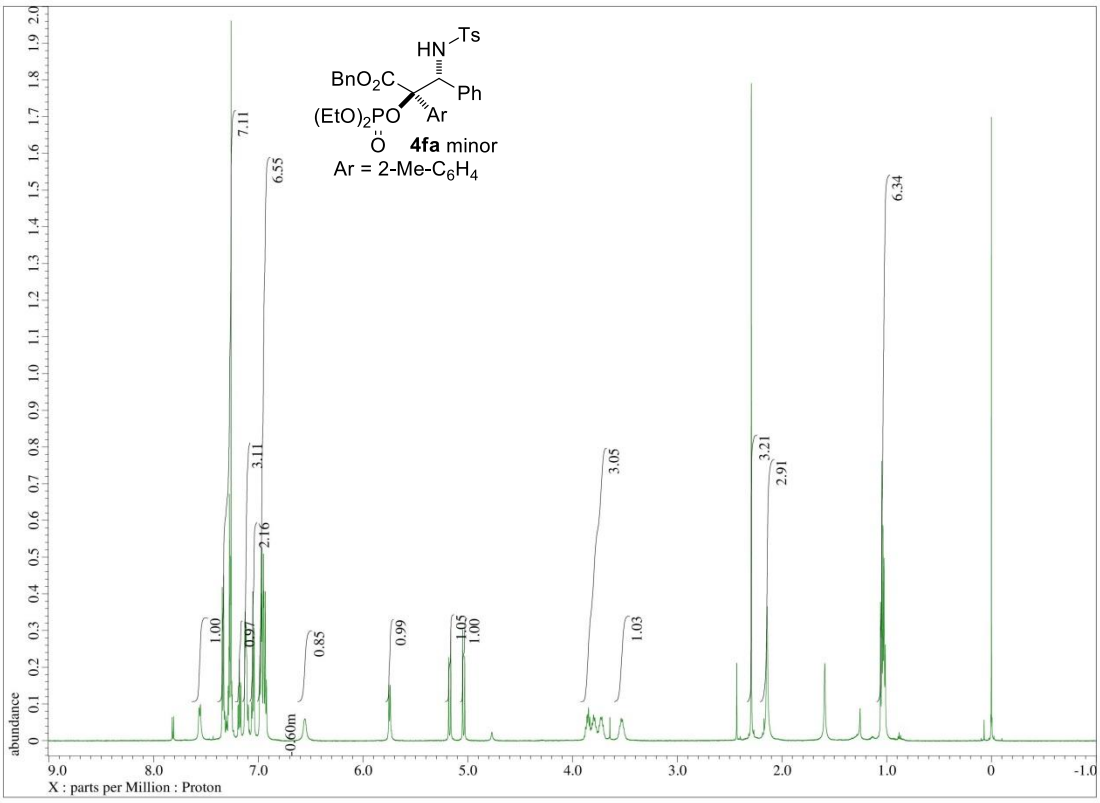

abundance
X : parts per Million : Carbon13
168.228
167.635
167.558
163.719
163.546
162.062
161.899
142.415
138.154
128.972
128.886
128.694
128.503
126.693
115.060
114.916
90.204
90.156
88.968
88.921
77.211
77.000
76.789
68.871
68.028
64.936
64.888
64.840
64.582
64.371
63.911
63.873
61.929
21.294
21.256
15.951
15.903
15.817
15.769
15.731

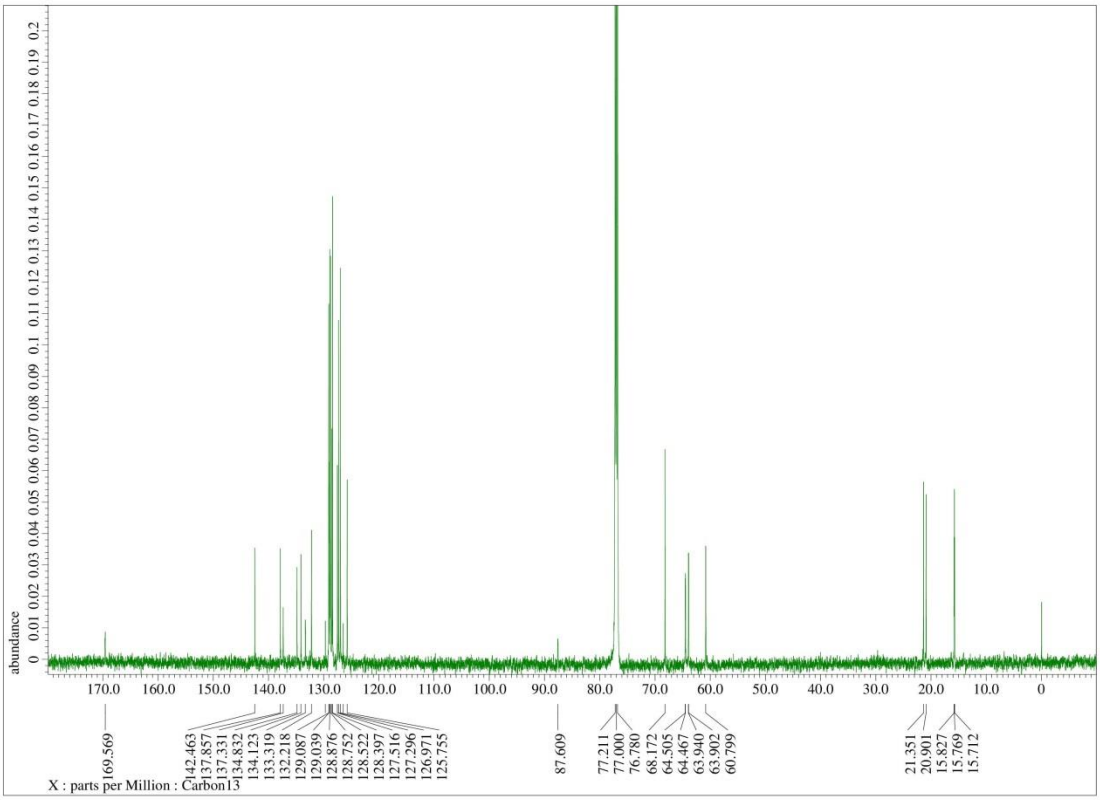

HN
Ts
BnO2C
Ph
(EtO)2PO
Ar
O
4ea
Ar = 3-MeO-C6H4
10.73
8.30
6.06
3.00
2.60
1.63
1.56
0.96
0.93
0.88
0.87
0.86
0.53
0.56
0.20
0.40
abundance
X : parts per Million : Proton

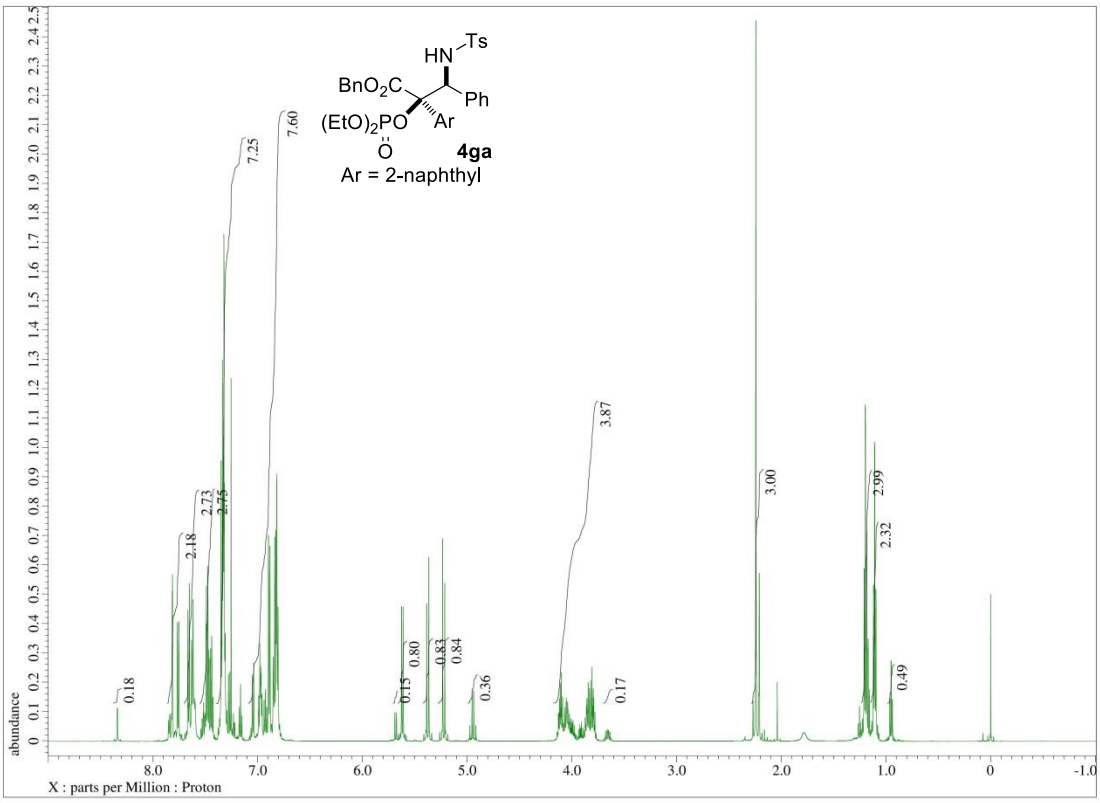

abundance
X : parts per Million : Carbon13
168.113
159.276
159.228
142.281
142.242
138.279
134.535
134.008
128.455
127.133
126.693
120.211
118.669
115.634
114.705
112.867
111.910
90.864
90.816
89.371
77.211
77.000
76.789
68.718
67.847
64.400
63.873
55.399
55.035
21.284
21.246
15.961
15.903
15.836
15.789
15.721
15.664

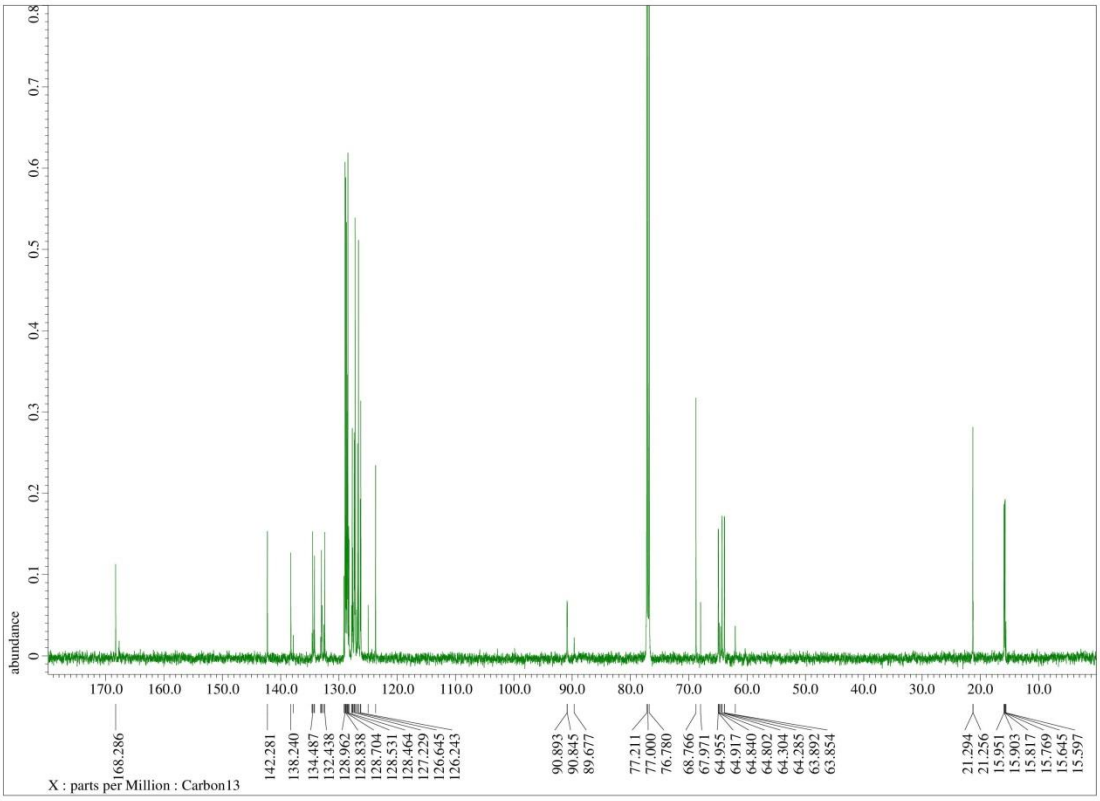

HN
Ts
BnO2C
Ph
(EtO)2PO
Ar
O
4fa major
Ar = 2-Me-C6H4
7.14
3.73
3.78
1.76
0.89
0.99
0.87
1.02
1.03
0.96
1.93
0.97
0.98
3.00
2.92
2.93
3.00
abundance
X : parts per Million : Proton

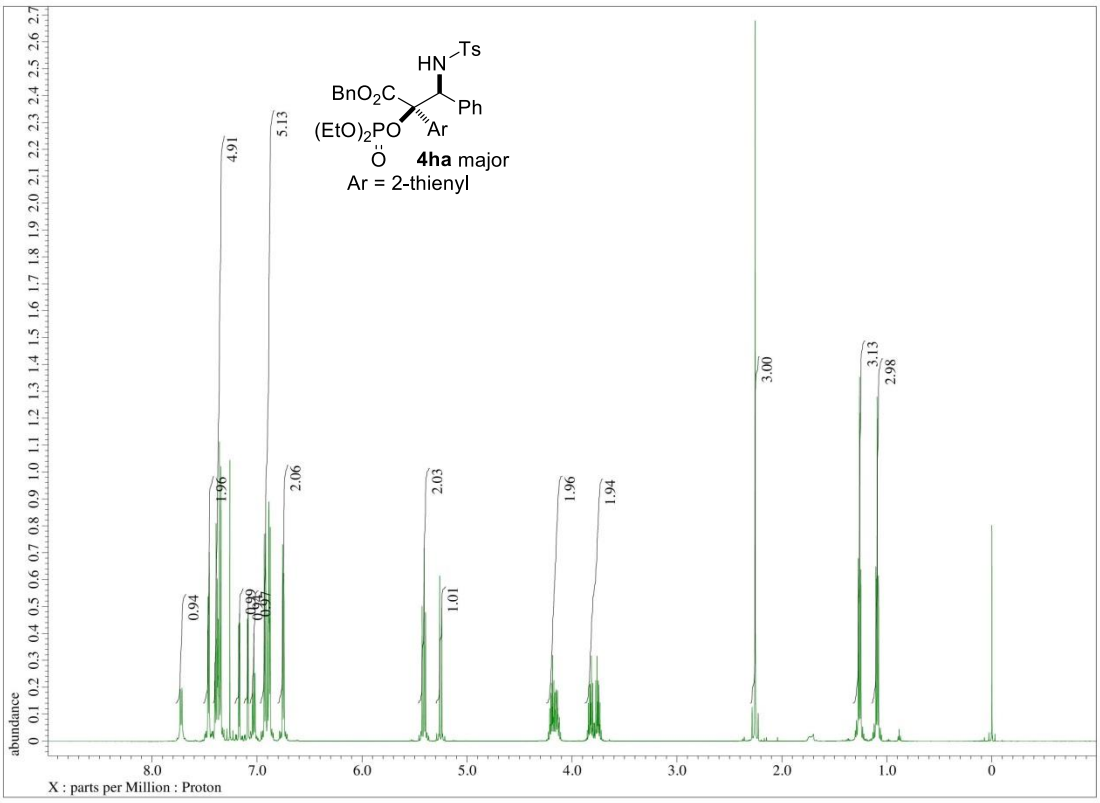

abundance
X : parts per Million : Carbon13
142.070
138.547
138.144
134.401
134.286
133.912
131.681
129.336
129.135
128.914
128.742
128.330
128.292
128.235
127.622
126.636
126.176
89.275
77.211
77.000
76.789
67.703
65.424
65.386
64.687
64.639
62.245
21.265
20.212
15.760
15.712
15.597
15.549

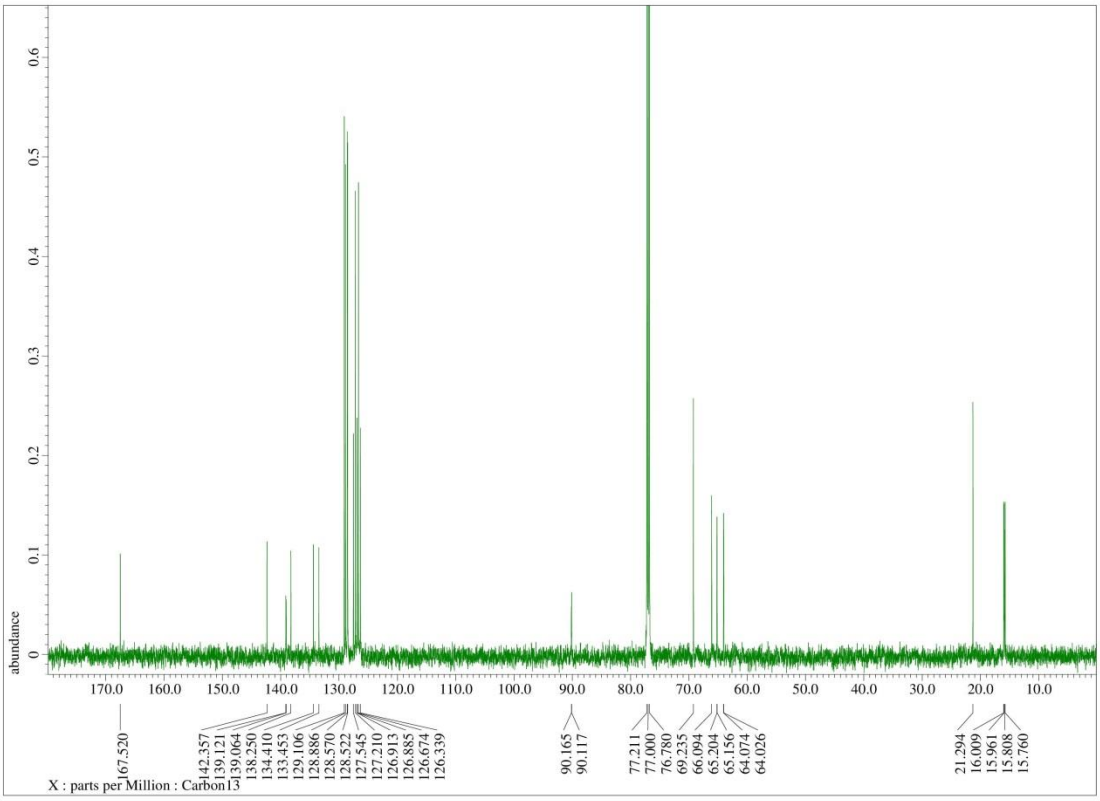

HN
Ts
BnO2C
Ph
(EtO)2PO
Ar
O
4fa minor
Ar = 2-Me-C6H4
7.11
6.55
3.11
2.16
1.00
0.97
0.85
0.99
1.05
1.00
3.05
1.03
3.21
2.91
6.34
abundance
X : parts per Million : Proton

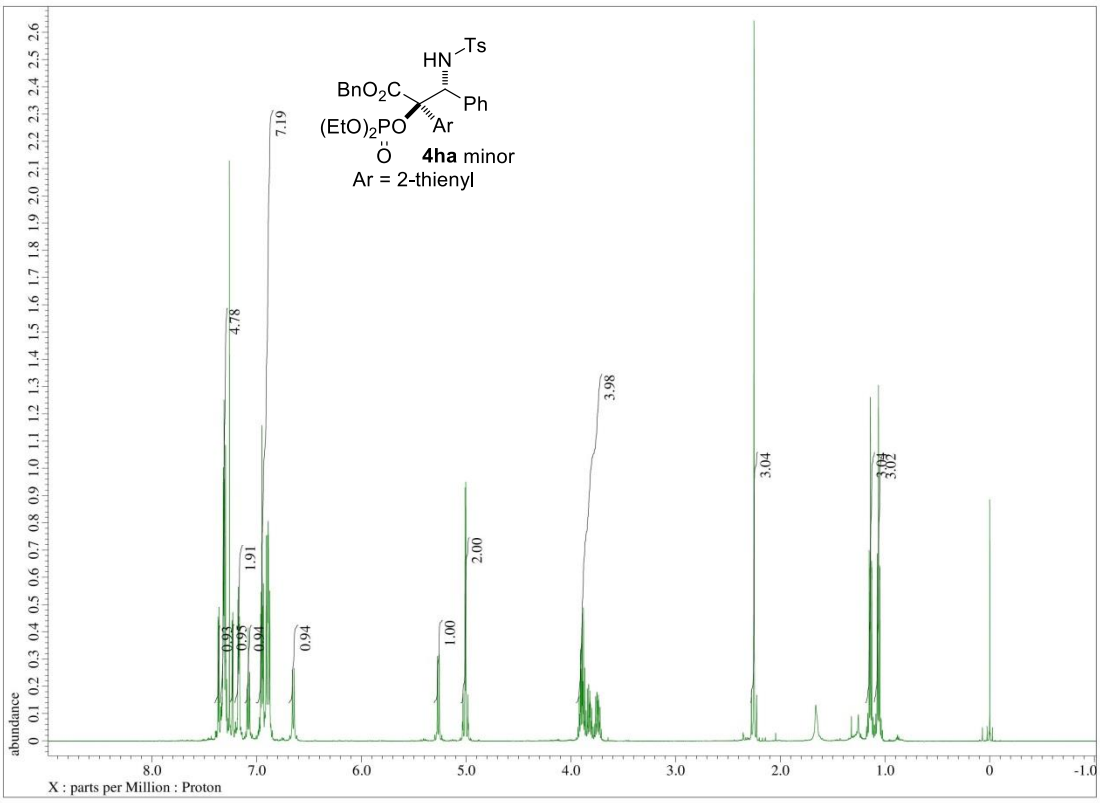

abundance
169.569
142.463
137.857
137.331
134.832
134.123
133.319
132.218
129.087
129.039
128.876
128.752
128.522
128.397
127.516
127.296
126.971
125.755
87.609
77.211
77.000
76.780
68.172
64.505
64.467
63.940
63.902
60.799
21.351
20.901
15.827
15.769
15.712
X : parts per Million : Carbon13

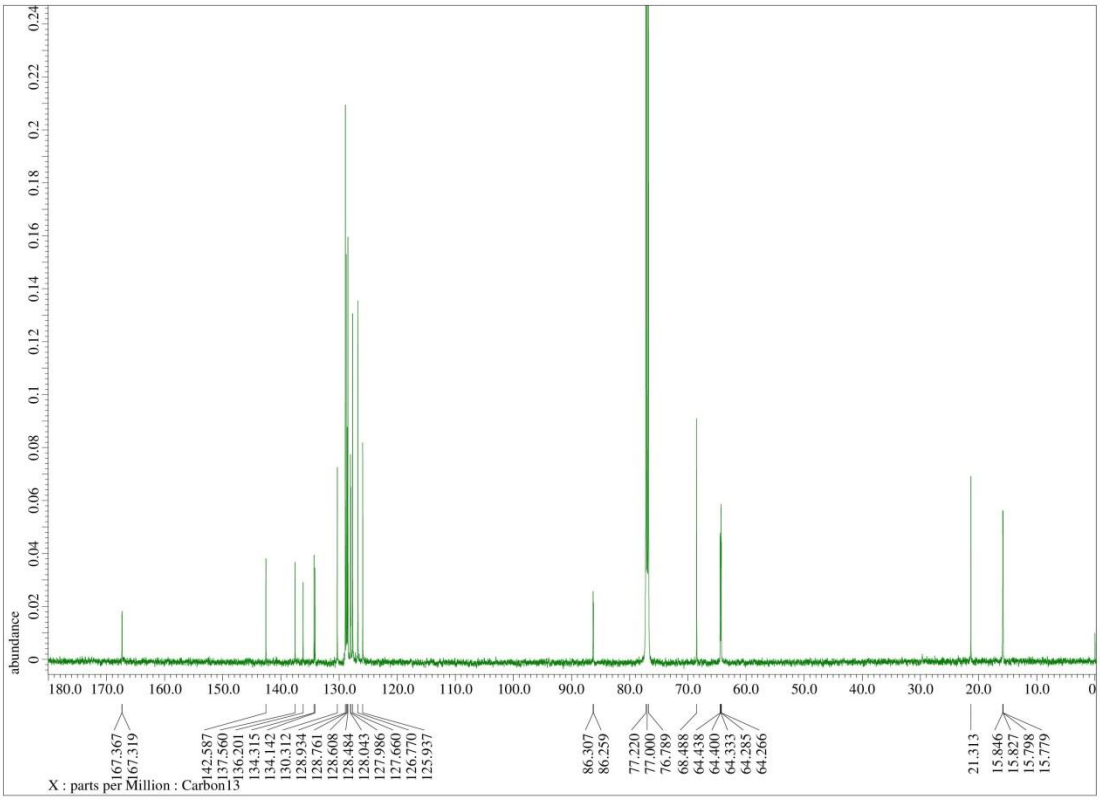

HN
Ts
BnO2C
Ph
(EtO)2PO
Ar
O
4ga
Ar = 2-naphthyl
abundance
X : parts per Million : Proton

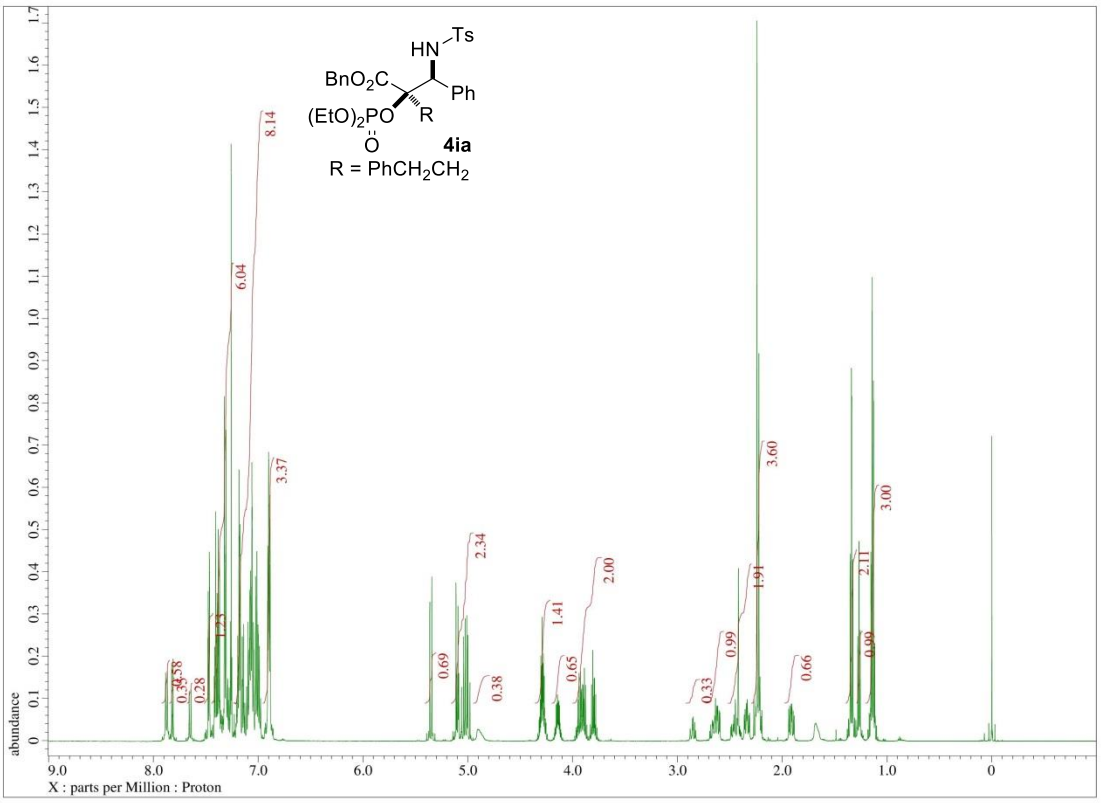

abundance
X : parts per Million : Carbon13

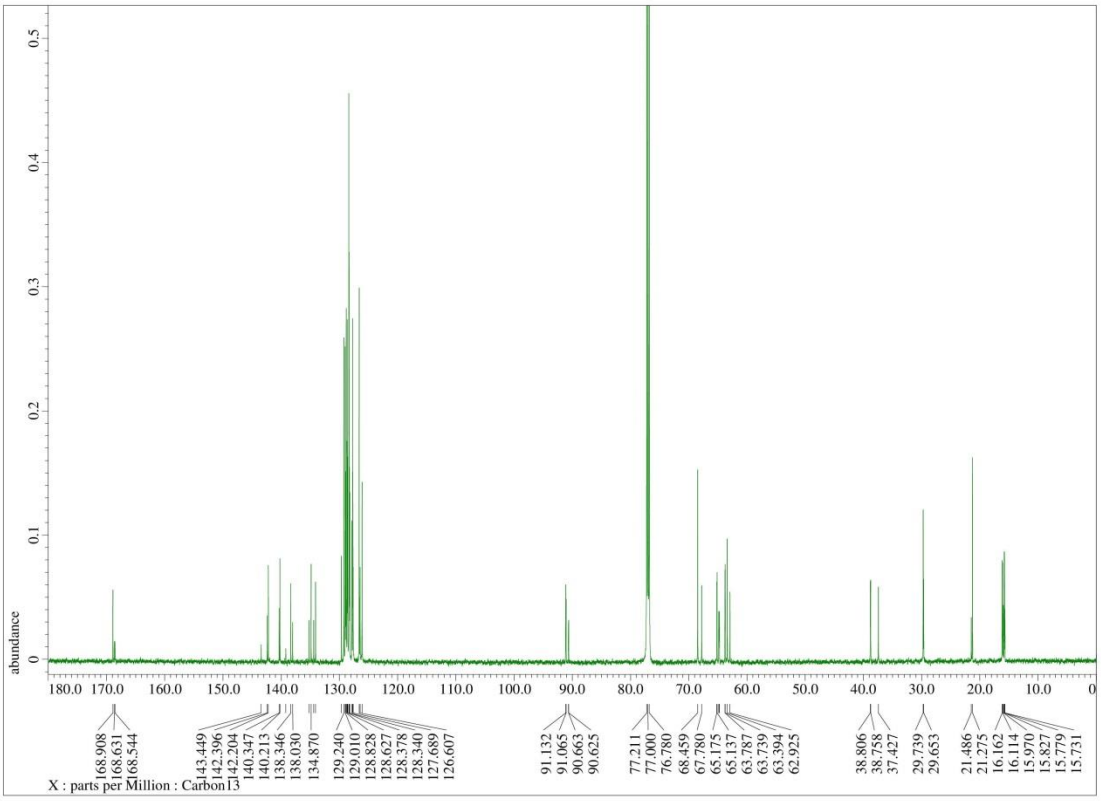

HN
Ts
BnO2C
Ph
(EtO)2PO
Ar
O
4ha major
Ar = 2-thienyl
4.91
5.13
1.96
2.06
2.03
1.01
1.96
1.94
3.00
3.13
2.98
0.94
abundance
X : parts per Million : Proton

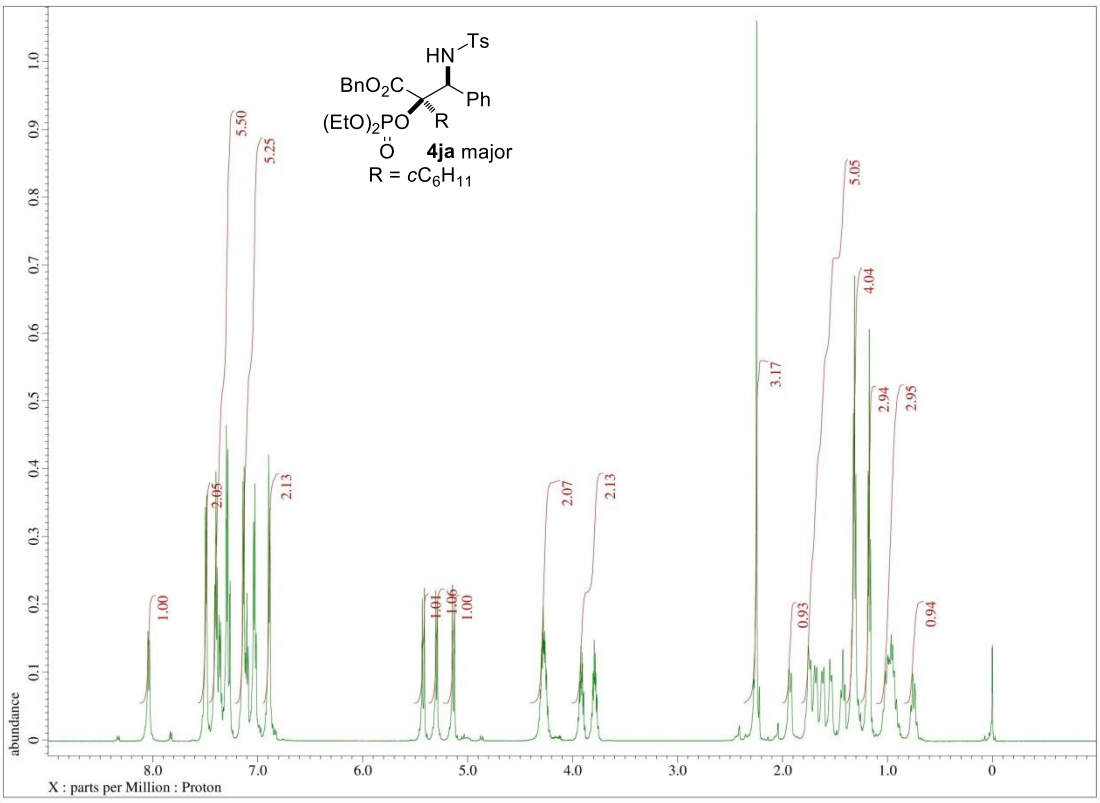

abundance
X : parts per Million : Carbon13
167.520
142.357
139.121
139.064
138.250
134.410
133.453
129.106
128.886
128.570
128.522
127.545
127.210
126.913
126.885
126.674
126.339
90.165
90.117
77.211
77.000
76.780
69.235
66.094
65.204
65.156
64.074
64.026
21.294
16.009
15.961
15.808
15.760

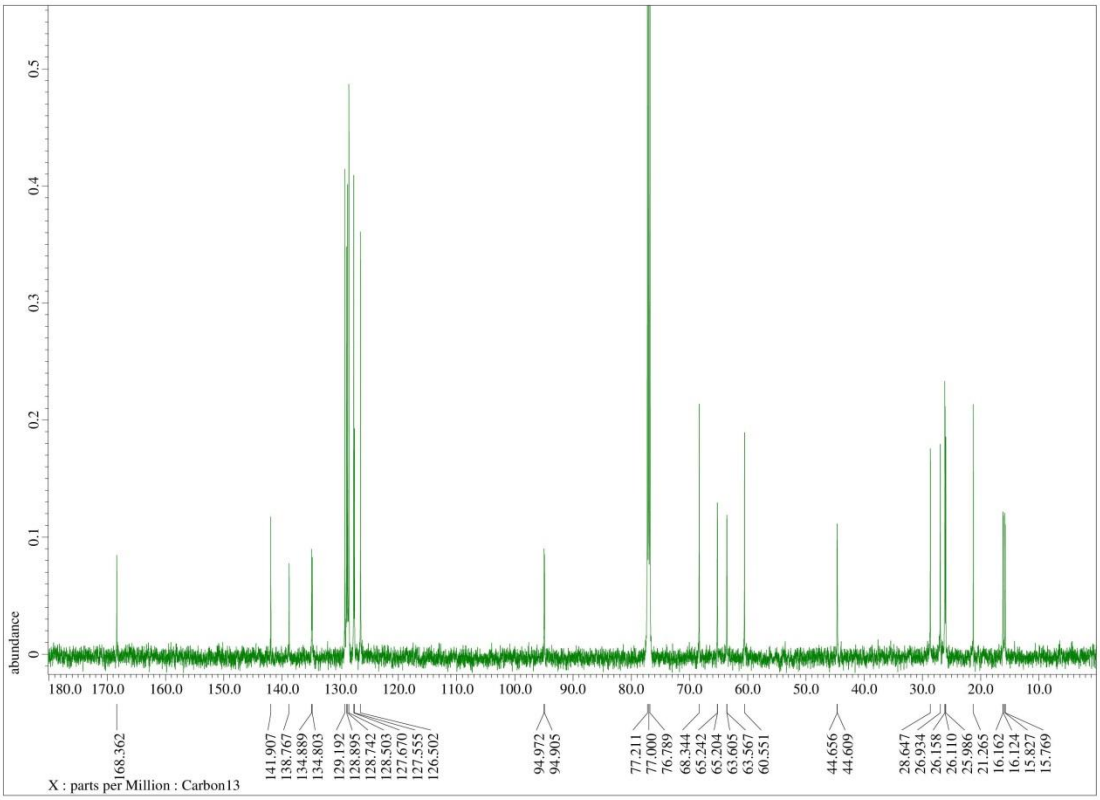

HN
Ts
BnO2C
Ph
(EtO)2PO
Ar
O-
4ha minor
Ar = 2-thienyl
7.19
4.78
3.98
3.04
2.00
1.91
1.00
0.94
0.93
0.95
0.94
3.04
3.02
abundance
X : parts per Million : Proton

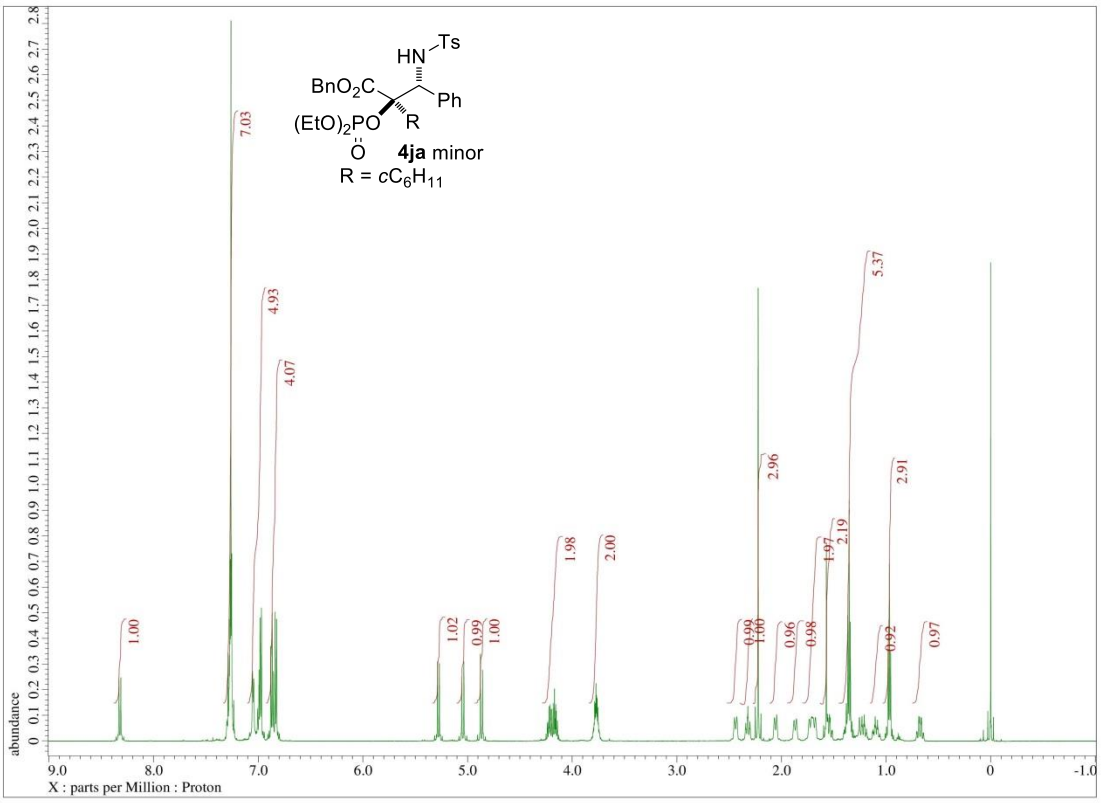

167.367
167.319
142.587
137.560
136.201
134.315
134.142
130.312
128.934
128.761
128.608
128.484
128.043
127.986
127.660
126.770
125.937
86.307
86.259
77.220
77.000
76.789
68.488
64.438
64.400
64.333
64.285
64.266
21.313
15.846
15.827
15.798
15.779
abundance
X : parts per Million : Carbon13

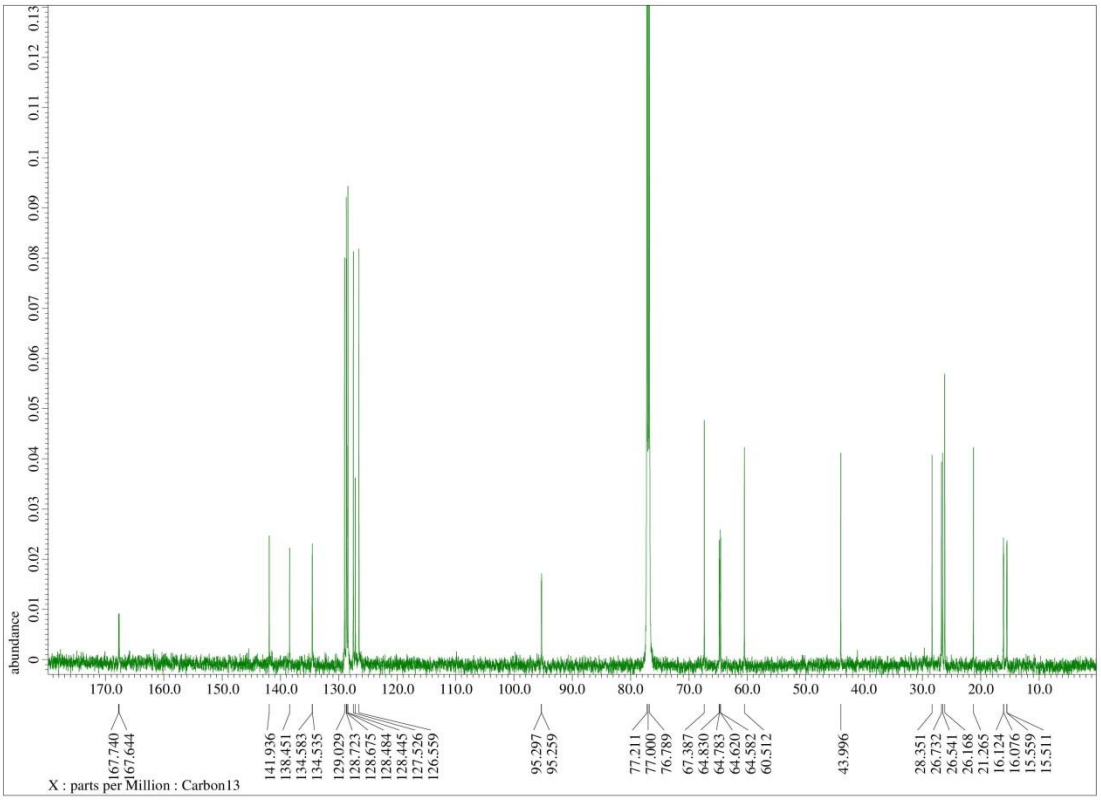

HN
Ts
BnO2C
Ph
(EtO)2PO
R
O
4ia
R = PhCH2CH2
8.14
6.04
3.37
2.34
2.00
1.41
1.23
0.69
0.38
0.65
0.33
0.99
1.91
3.60
0.66
2.11
3.00
0.09
0.58
0.28
abundance
X : parts per Million : Proton

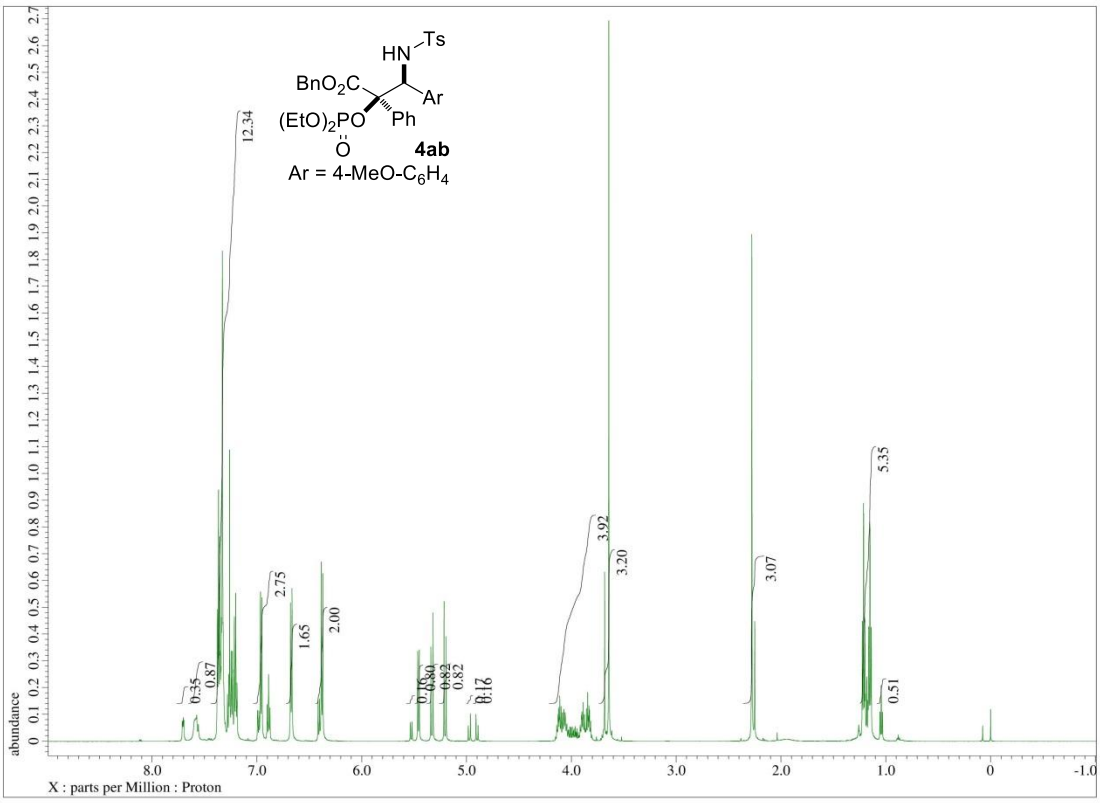

abundance
X : parts per Million : Carbon13
168.908
168.631
168.544
143.449
142.396
142.204
140.347
140.213
138.346
138.030
134.870
129.240
129.010
128.828
128.627
128.378
128.340
127.689
126.607
91.132
91.065
90.663
90.625
77.211
77.000
76.780
68.459
67.780
65.175
65.137
63.787
63.739
63.394
62.925
38.806
38.758
37.427
29.739
29.653
21.486
21.275
16.162
16.114
15.970
15.827
15.779
15.731

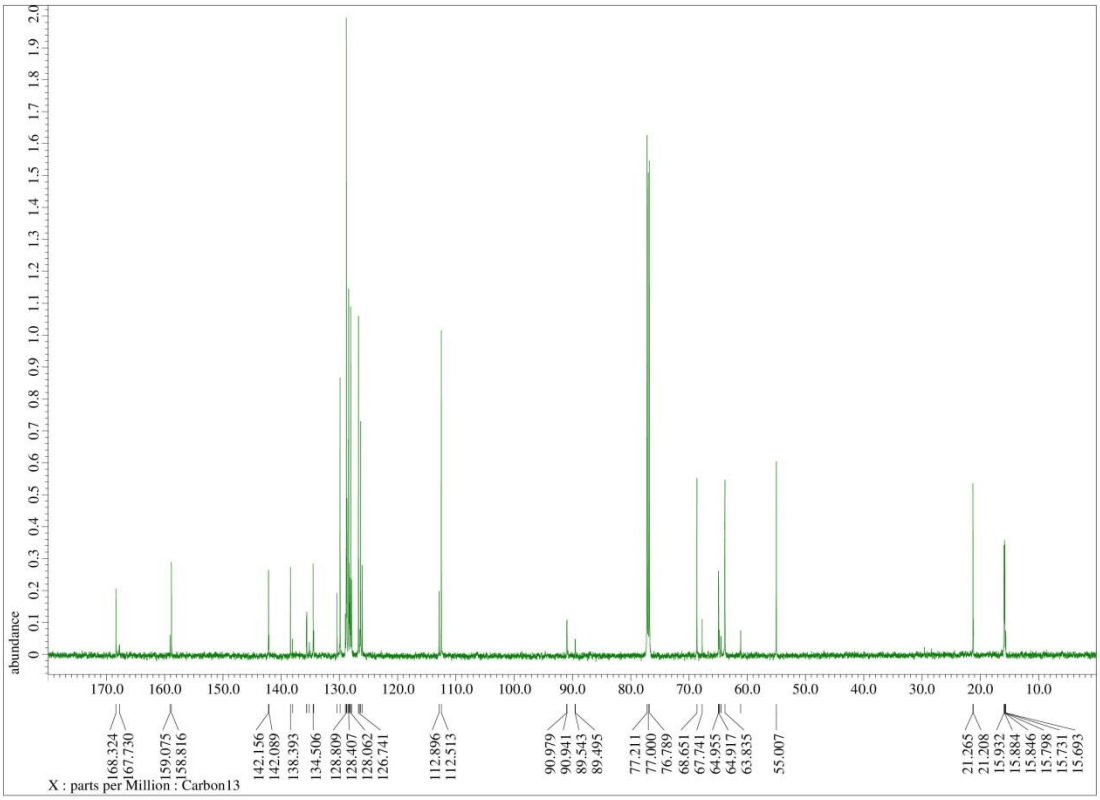

HN
Ts
BnO2C
Ph
(EtO)2PO
R
O
4ja major
R = cC6H11
5.50
5.25
5.05
4.04
3.17
2.94
2.95
2.05
2.13
2.07
2.13
1.00
1.01
1.06
1.00
0.93
0.94
abundance
X : parts per Million : Proton

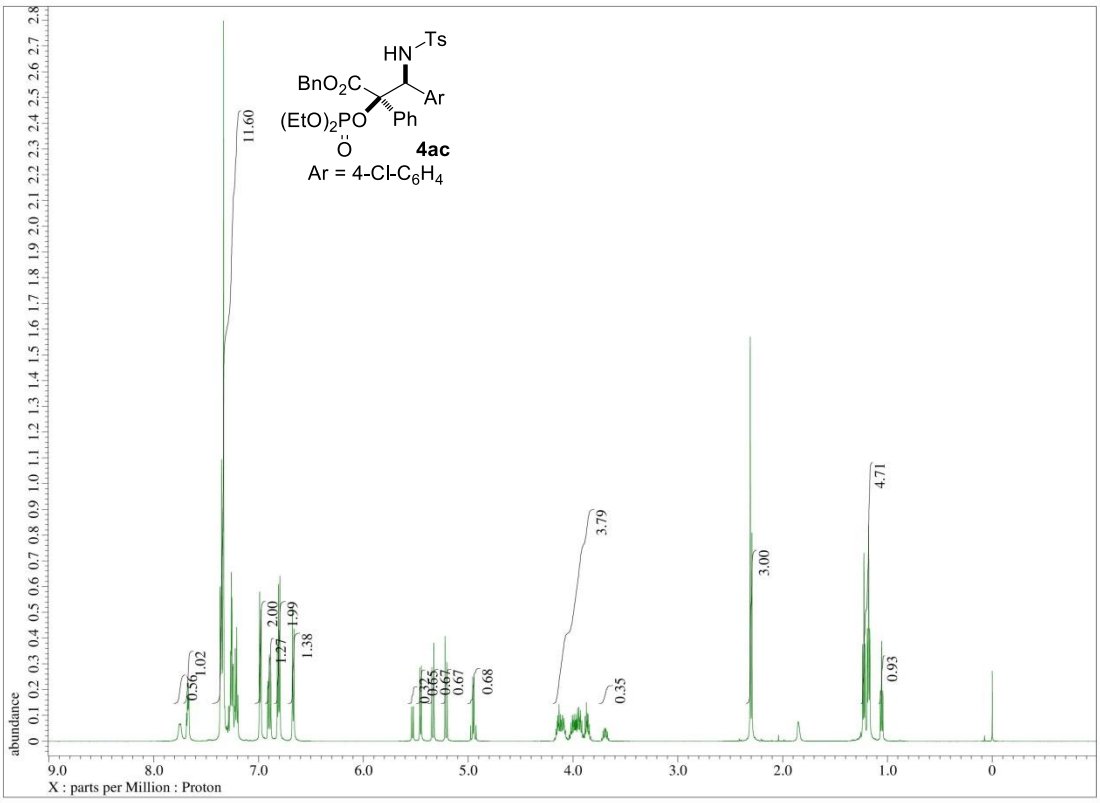

abundance
X : parts per Million : Carbon13
168.362
141.907
138.767
134.889
134.803
129.192
128.895
128.742
128.503
127.670
127.555
126.502
94.972
94.905
77.211
77.000
76.789
68.344
65.242
65.204
63.605
63.567
60.551
44.656
44.609
28.647
26.934
26.158
26.110
25.986
21.265
16.162
16.124
15.827
15.769

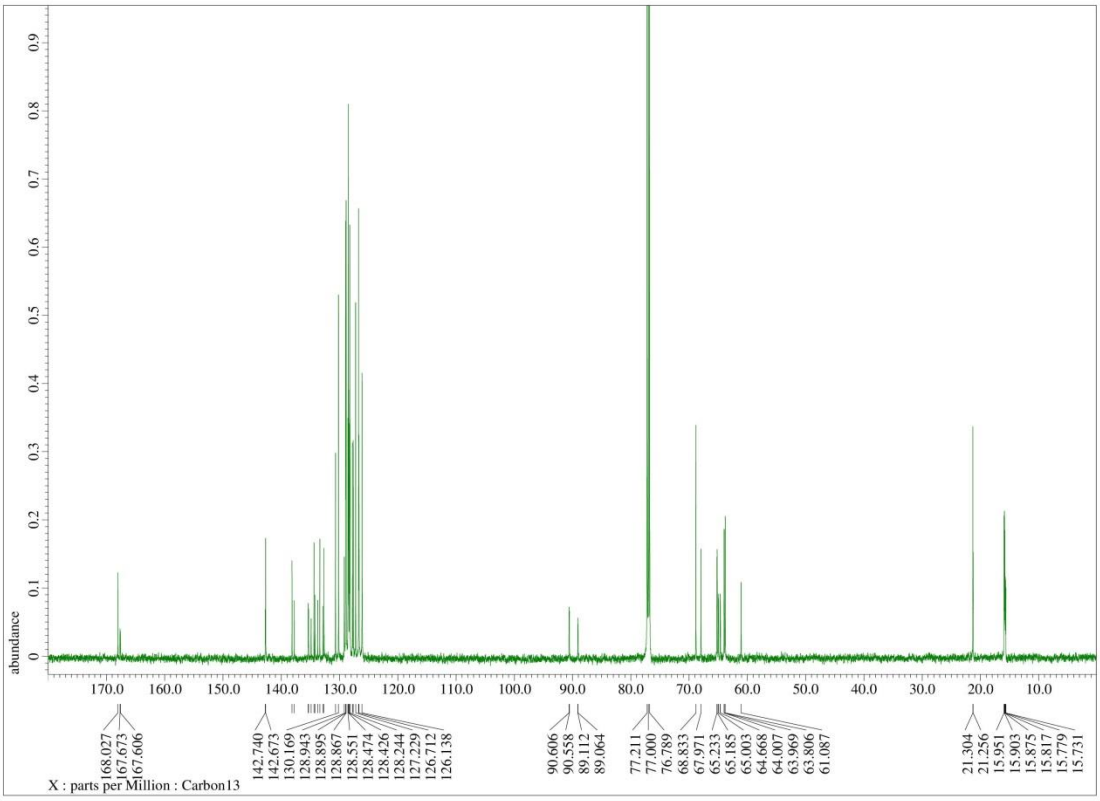

HN
Ts
BnO2C
Ph
(EtO)2PO
R
O
4ja minor
R = cC6H11
abundance
X : parts per Million : Proton

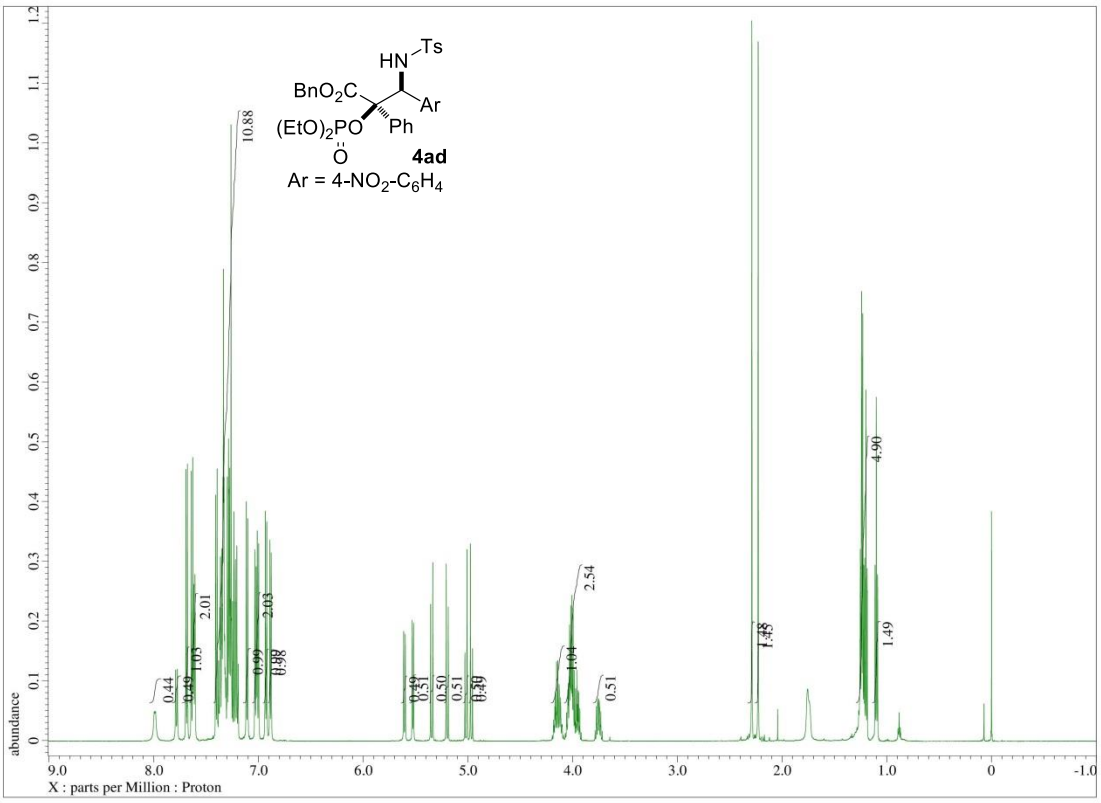

abundance
X : parts per Million : Carbon13

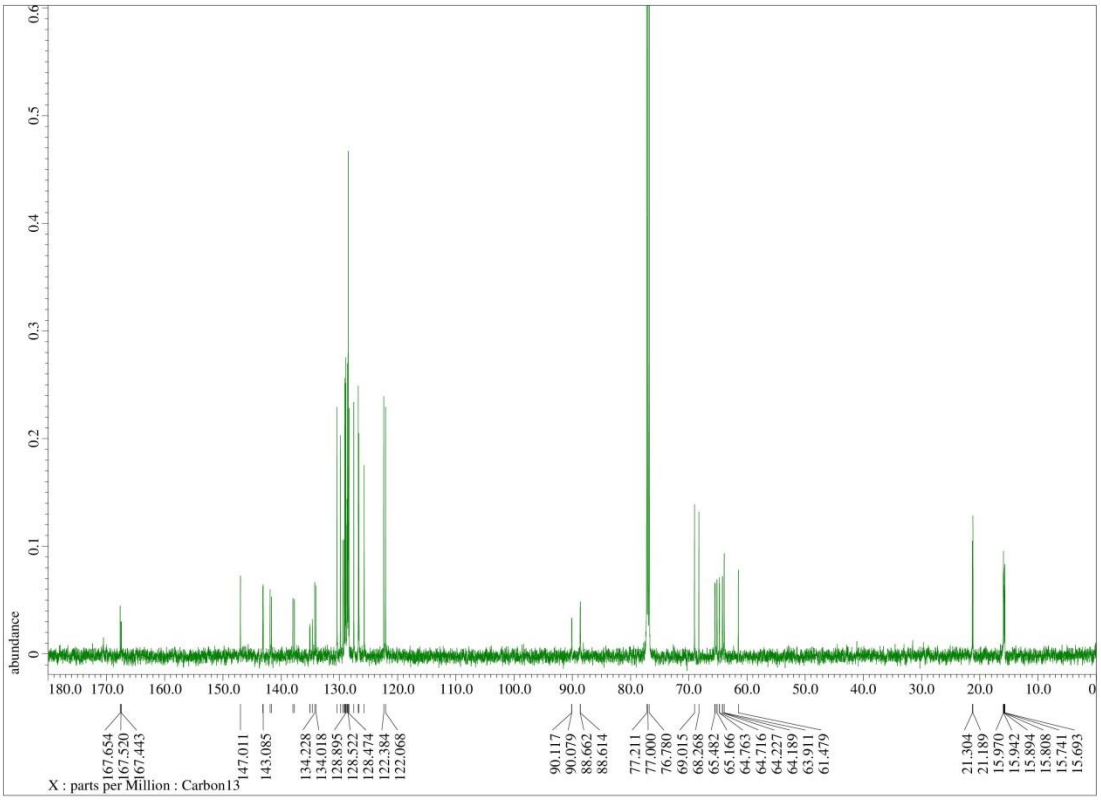

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4ab
Ar = 4-MeO-C6H4
12.34
2.75
1.65
2.00
0.35
0.87
0.16
0.80
0.82
0.82
0.17
0.16
3.92
3.20
3.07
5.35
0.51
abundance
X : parts per Million : Proton

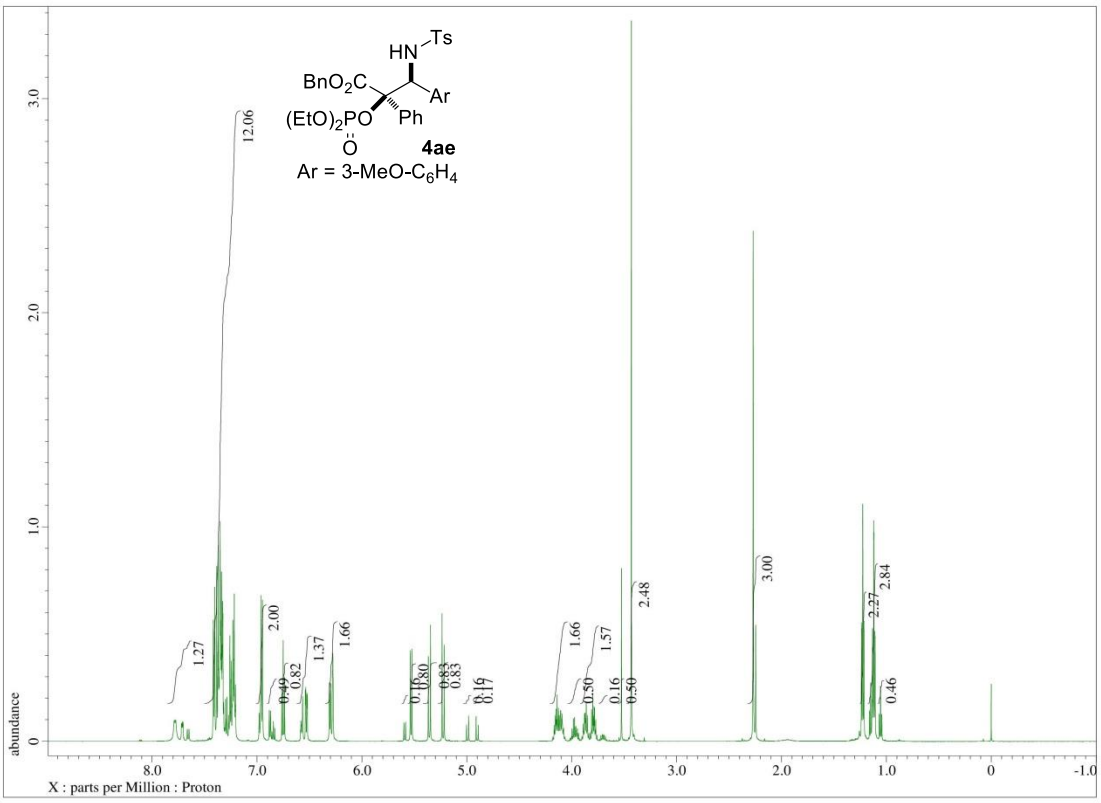

abundance
X : parts per Million : Carbon13
168.324
167.730
159.075
158.816
142.156
142.089
138.393
134.506
128.809
128.407
128.062
126.741
112.896
112.513
90.979
90.941
89.543
89.495
77.211
77.000
76.789
68.651
67.741
64.955
64.917
63.835
55.007
21.265
21.208
15.932
15.884
15.846
15.798
15.731
15.693

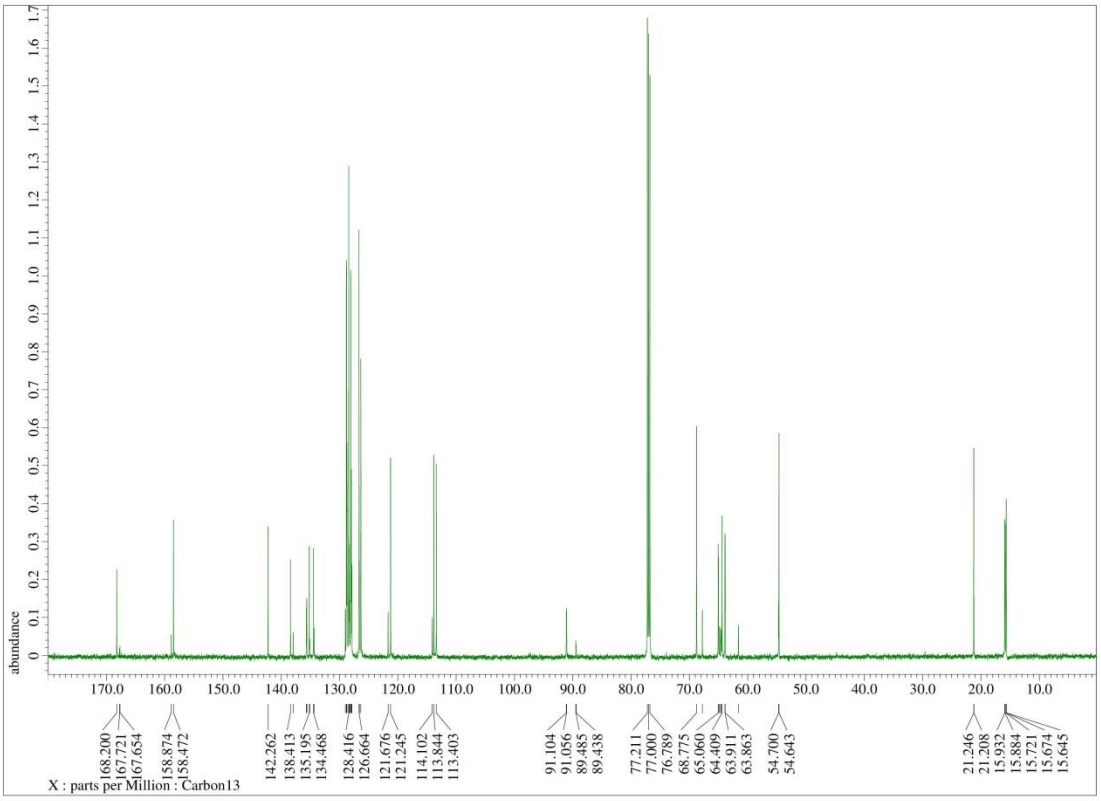

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4ac
Ar = 4-Cl-C6H4
11.60
0.56
1.02
2.00
1.99
1.27
1.38
0.32
0.65
0.67
0.67
0.68
3.79
0.35
3.00
4.71
0.93
abundance
X : parts per Million : Proton

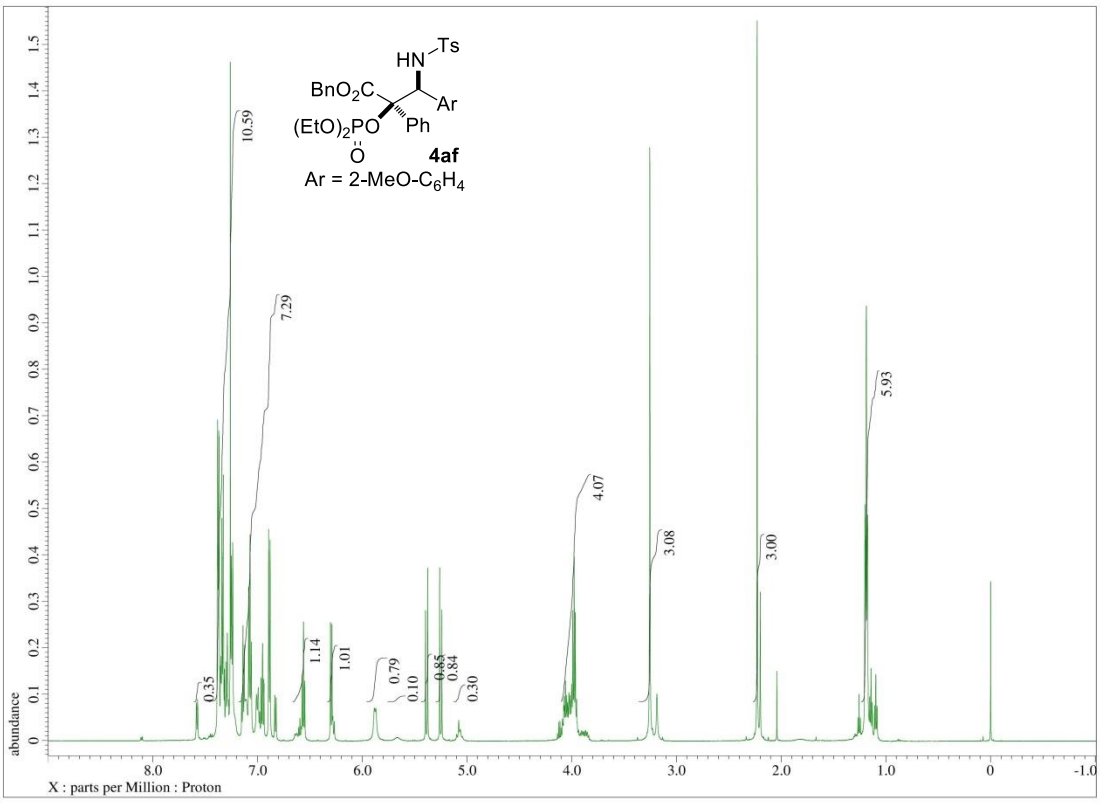

abundance
X : parts per Million : Carbon13
168.027
167.673
167.606
142.740
142.673
130.169
128.943
128.895
128.867
128.551
128.474
128.426
128.244
127.229
126.712
126.138
90.606
90.558
89.112
89.064
77.211
77.000
76.789
68.833
67.971
65.233
65.185
65.003
64.668
64.007
63.969
63.806
61.087
21.304
21.256
15.951
15.903
15.875
15.817
15.779
15.731

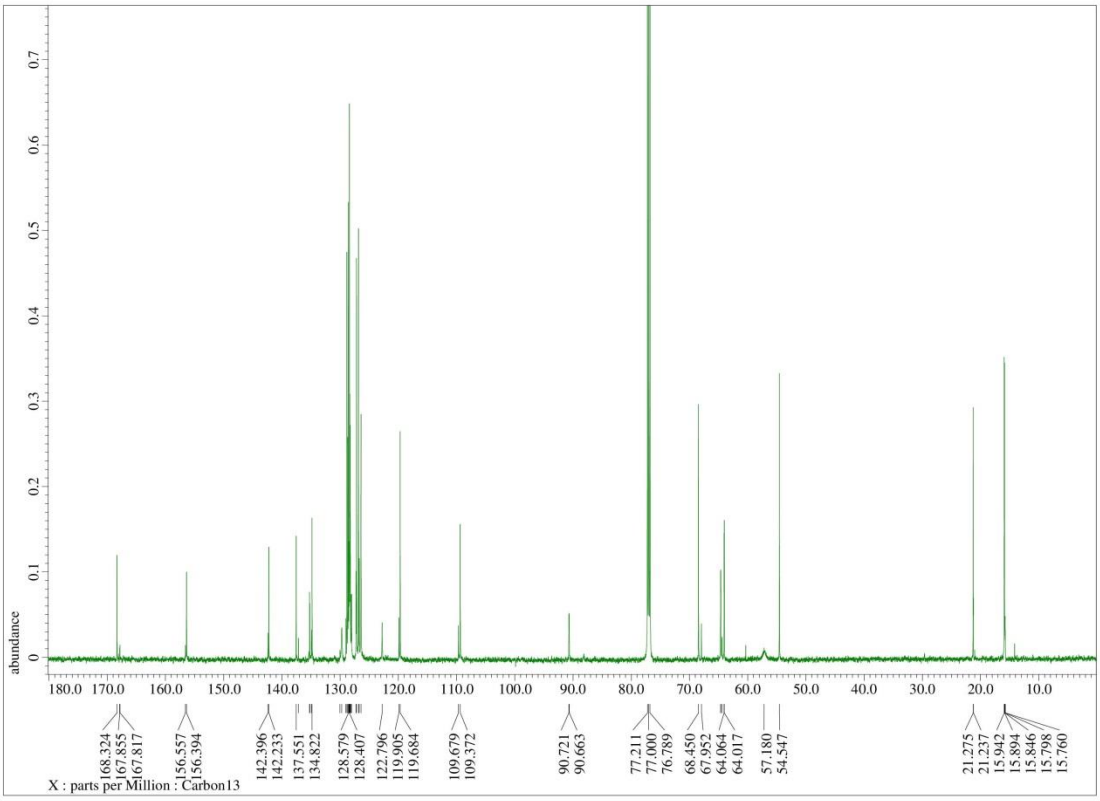

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4ad
Ar = 4-NO2-C6H4
abundance
X : parts per Million : Proton

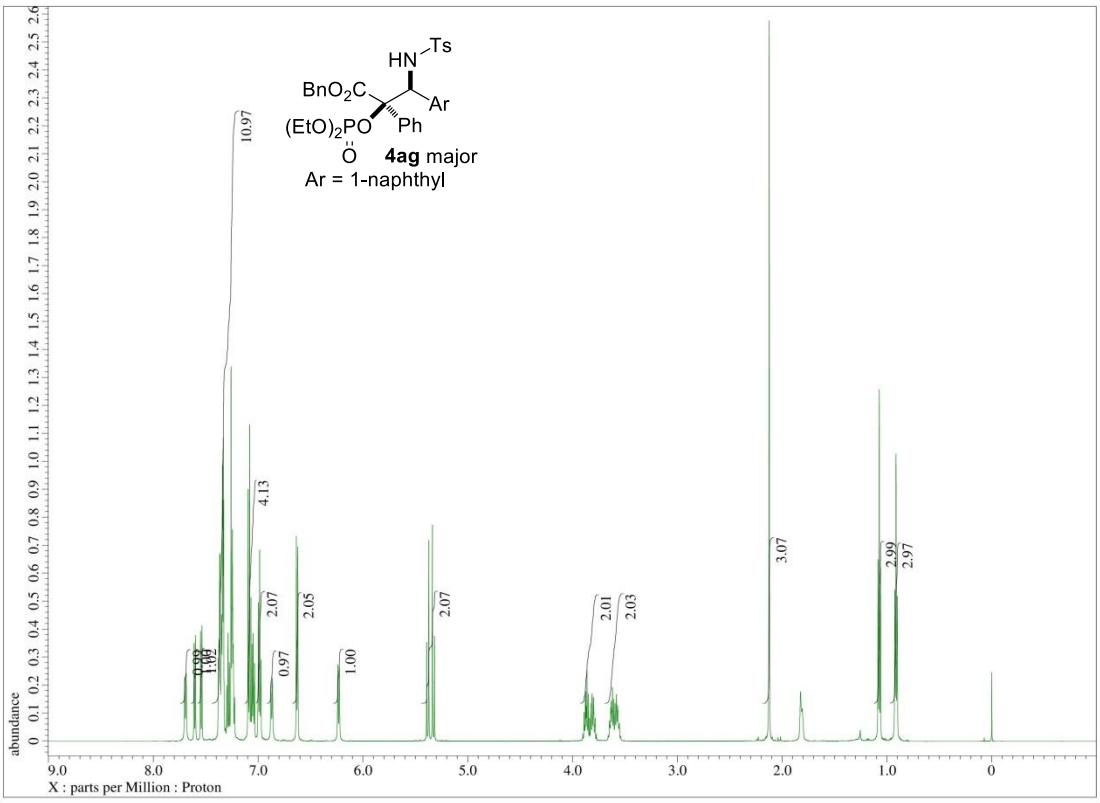

abundance
X : parts per Million : Carbon13

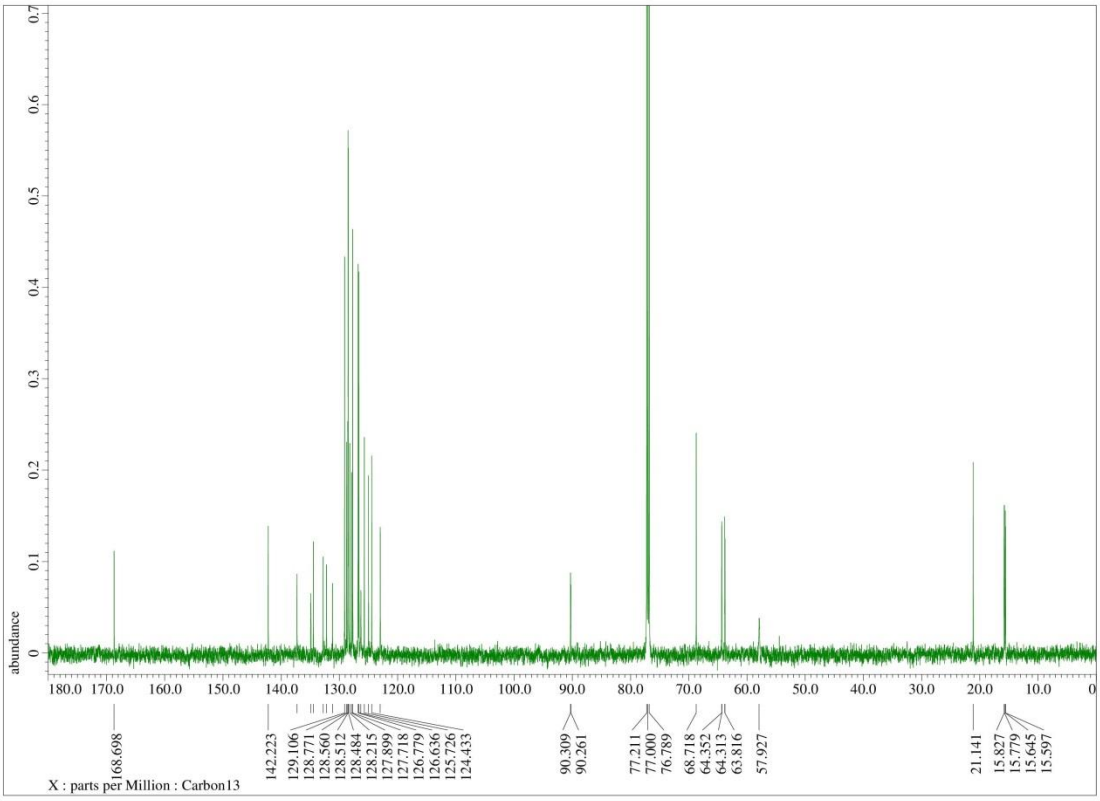

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4ae
Ar = 3-MeO-C6H4
12.06
2.00
1.27
0.49
0.82
1.37
1.66
0.80
0.83
0.16
0.17
1.66
1.57
0.50
0.16
0.50
2.48
3.00
2.27
2.84
0.46
abundance
X : parts per Million : Proton

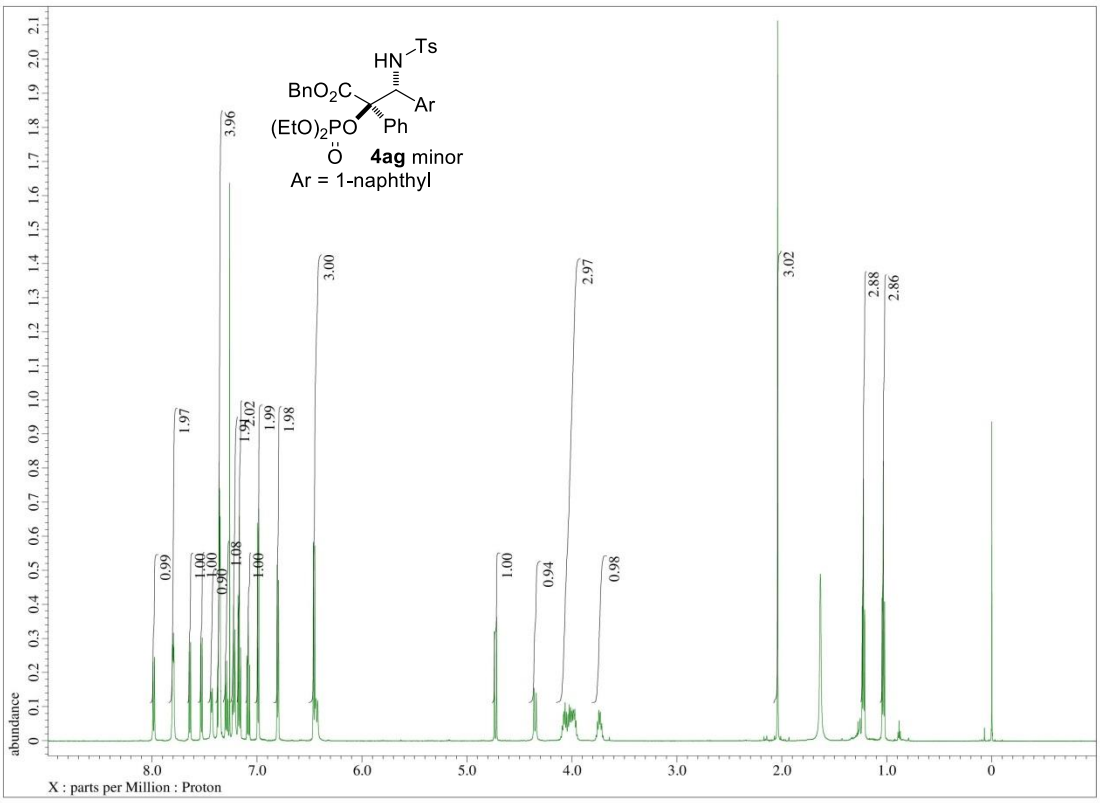

abundance
X : parts per Million : Carbon13
168.200
167.721
167.654
158.874
158.472
142.262
138.413
135.195
134.468
128.416
126.664
121.676
121.245
114.102
113.844
113.403
91.104
91.056
89.485
89.438
77.211
77.000
76.789
68.775
65.060
64.409
63.911
63.863
54.700
54.643
21.246
21.208
15.932
15.884
15.721
15.674
15.645

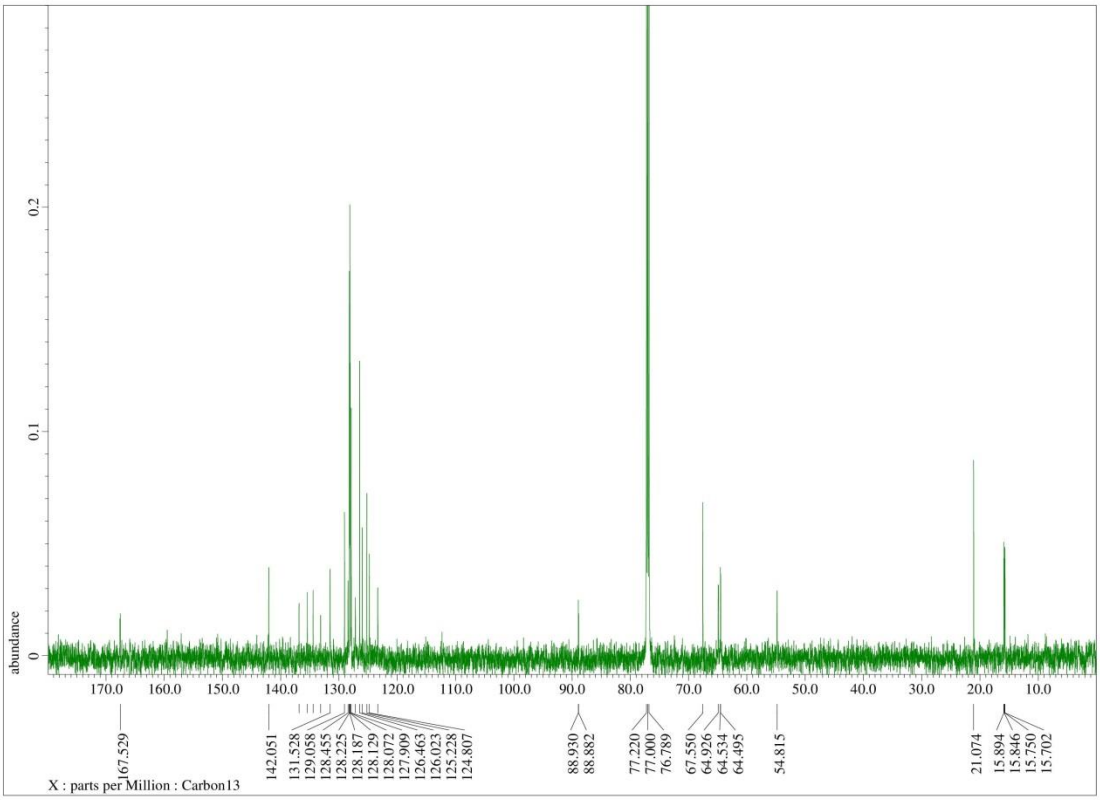

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O-
4af
Ar = 2-MeO-C6H4
10.59
7.29
5.93
4.07
3.08
3.00
1.14
1.01
0.79
0.10
0.85
0.84
0.35
0.30
abundance
X : parts per Million : Proton

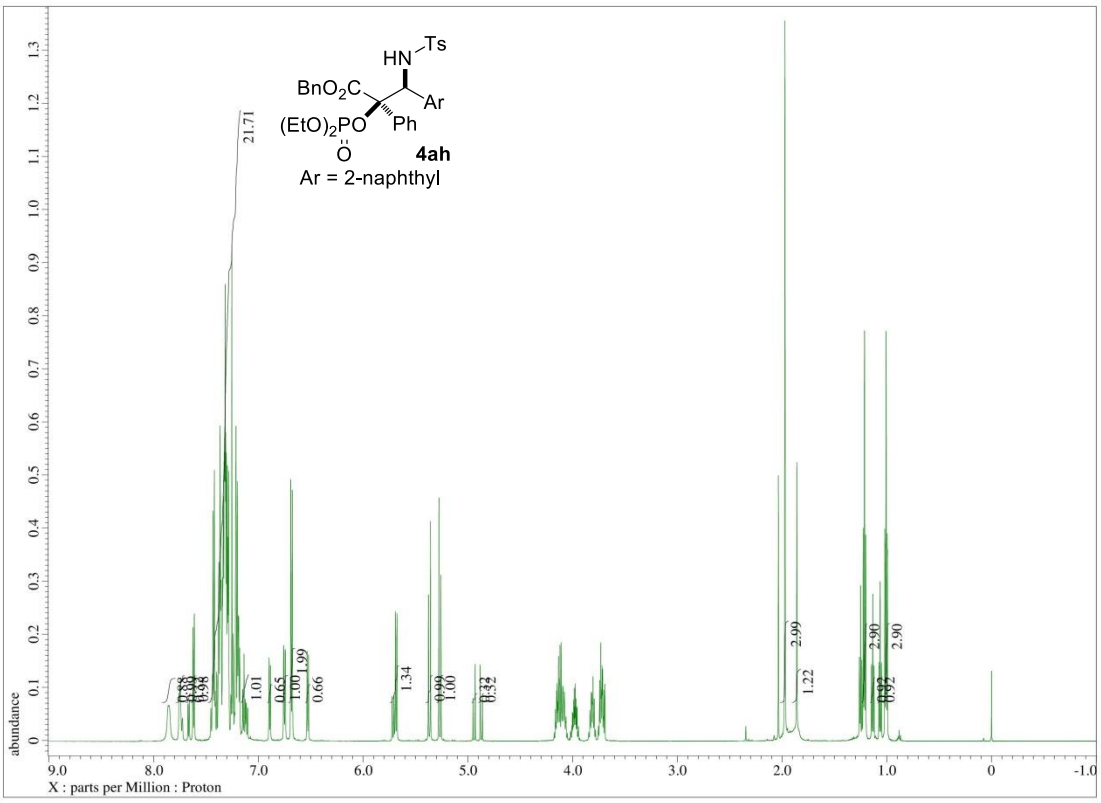

abundance
X : parts per Million : Carbon13
168.324
167.855
167.817
156.557
156.394
142.396
142.233
137.551
134.822
128.579
128.407
122.796
119.905
119.684
109.679
109.372
90.721
90.663
77.211
77.000
76.789
68.450
67.952
64.064
64.017
57.180
54.547
21.275
21.237
15.942
15.894
15.846
15.798
15.760

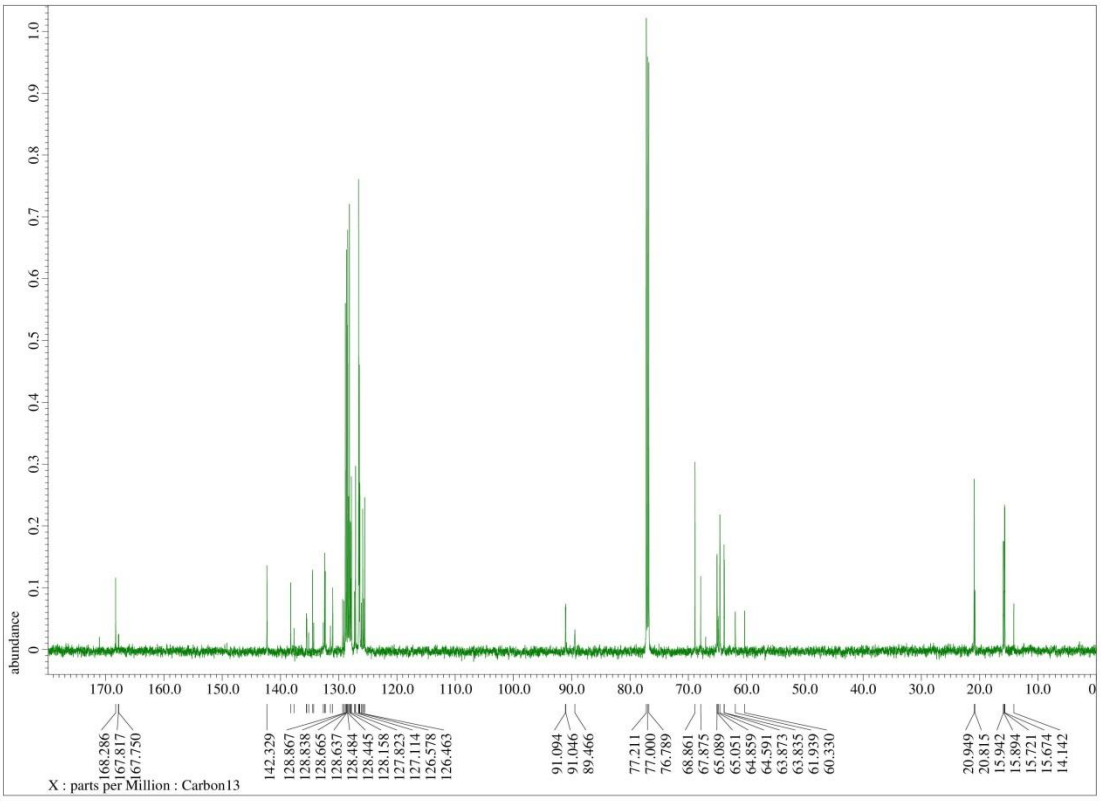

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4ag major
Ar = 1-naphthyl
10.97
4.13
2.07
2.05
0.97
1.00
2.07
2.01
2.03
3.07
2.99
2.97
abundance
X : parts per Million : Proton

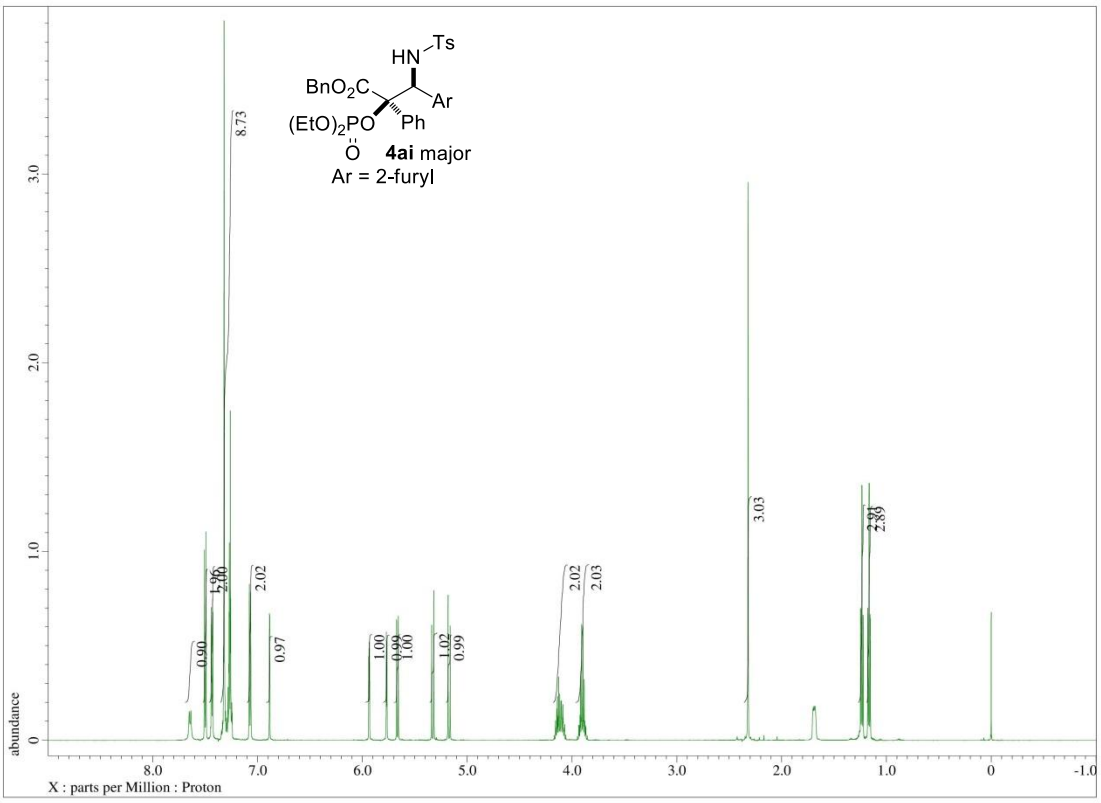

abundance
X : parts per Million : Carbon13
168.698
142.223
129.106
128.771
128.560
128.512
128.484
128.215
127.899
127.718
126.779
126.636
125.726
124.433
90.309
90.261
77.211
77.000
76.789
68.718
64.352
64.313
63.816
57.927
21.141
15.827
15.779
15.645
15.597

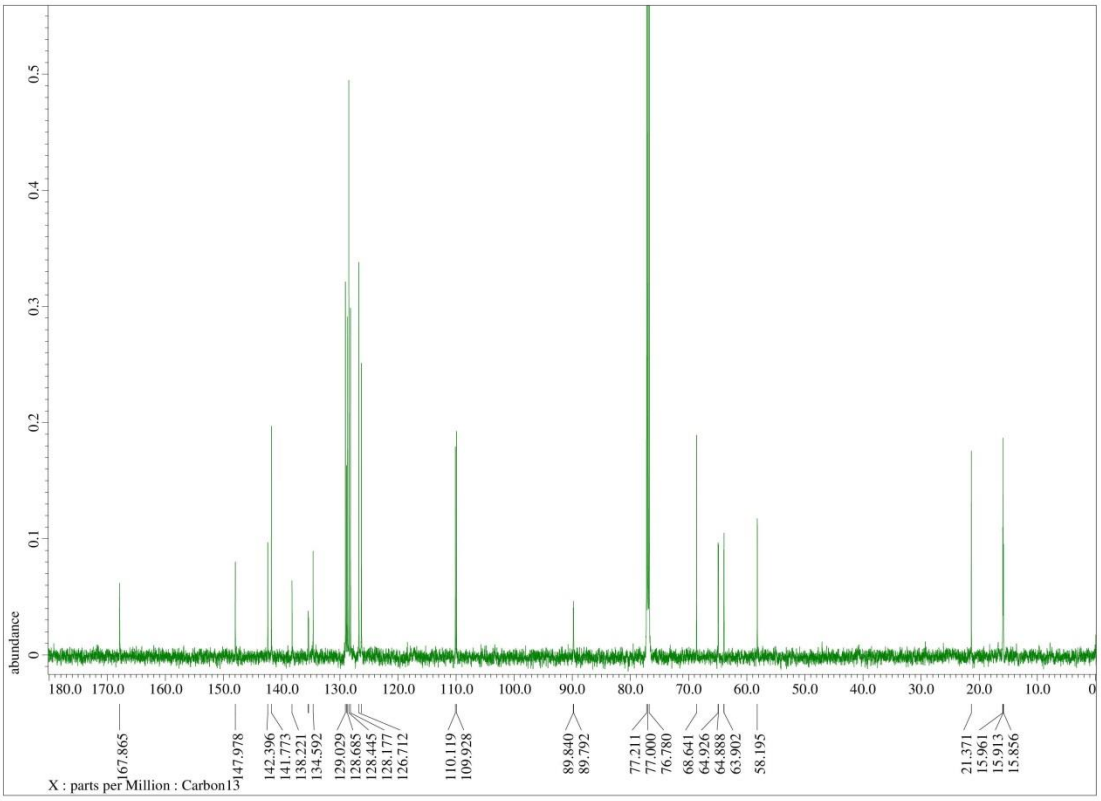

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4ag minor
Ar = 1-naphthyl
abundance
X : parts per Million : Proton

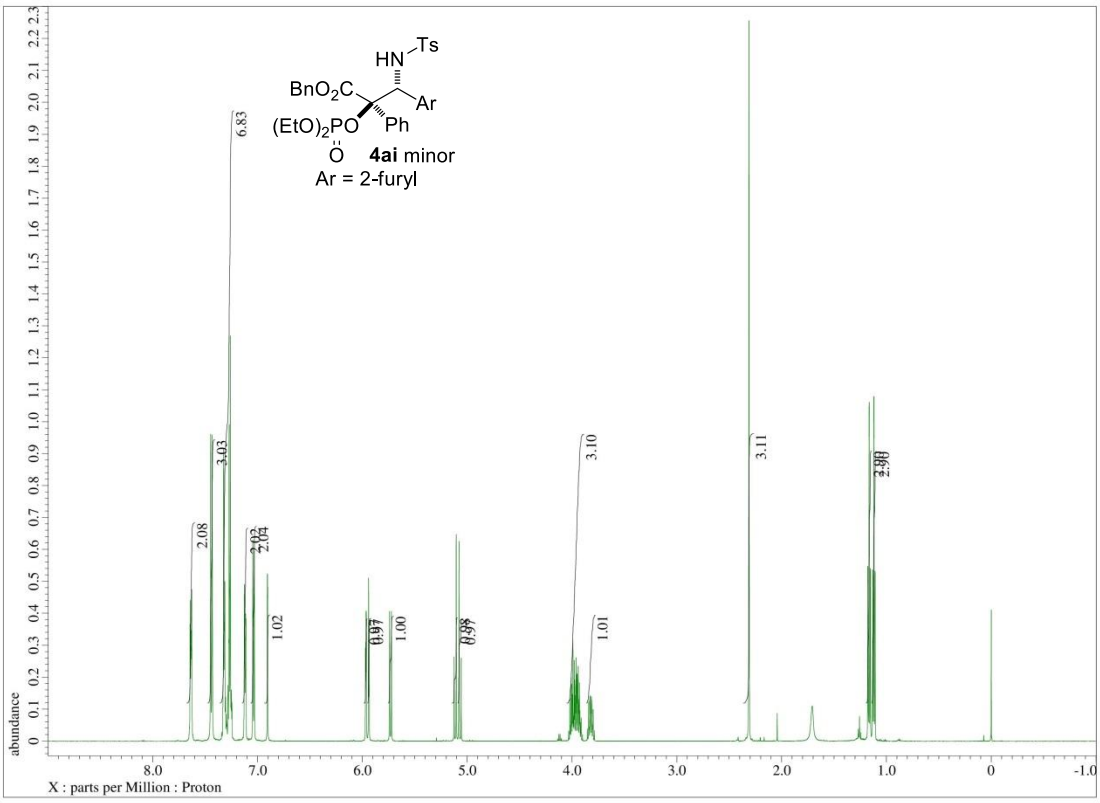

abundance
X : parts per Million : Carbon13

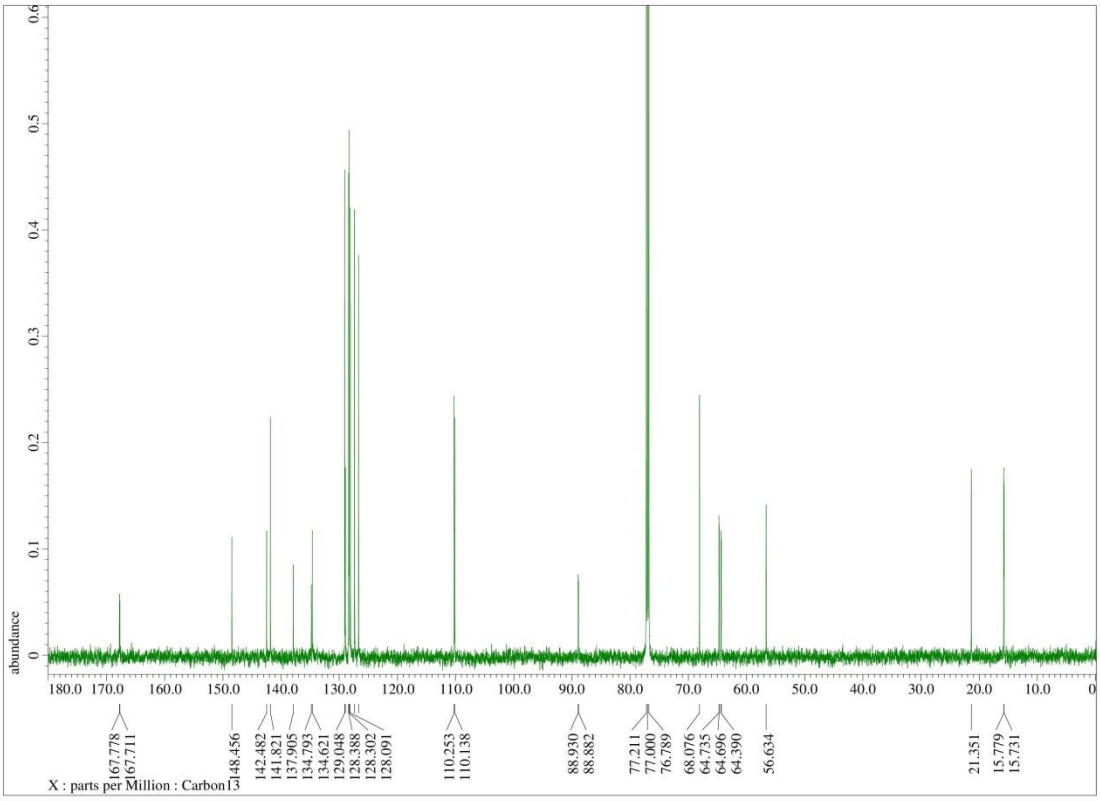

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O-
4ah
Ar = 2-naphthyl
21.71
2.99
1.22
2.90
2.90
2.90
1.34
1.99
1.01
0.66
1.00
0.65
1.00
1.00
0.32
0.32
abundance
X : parts per Million : Proton

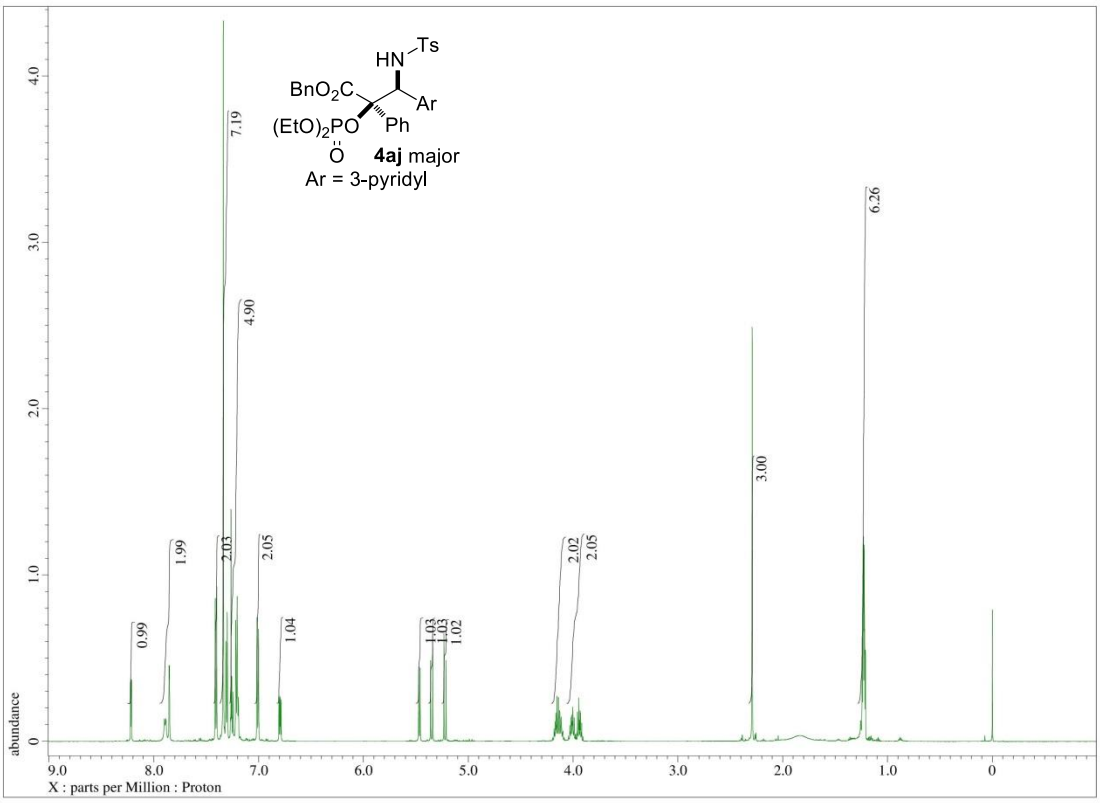

abundance
X : parts per Million : Carbon13
168.286
167.817
167.750
142.329
128.867
128.838
128.665
128.637
128.484
128.445
128.158
127.823
127.114
126.578
126.463
91.094
91.046
89.466
77.211
77.000
76.789
68.861
67.875
65.089
65.051
64.859
64.591
63.873
63.835
61.939
60.330
20.949
20.815
15.942
15.894
15.721
15.674
14.142

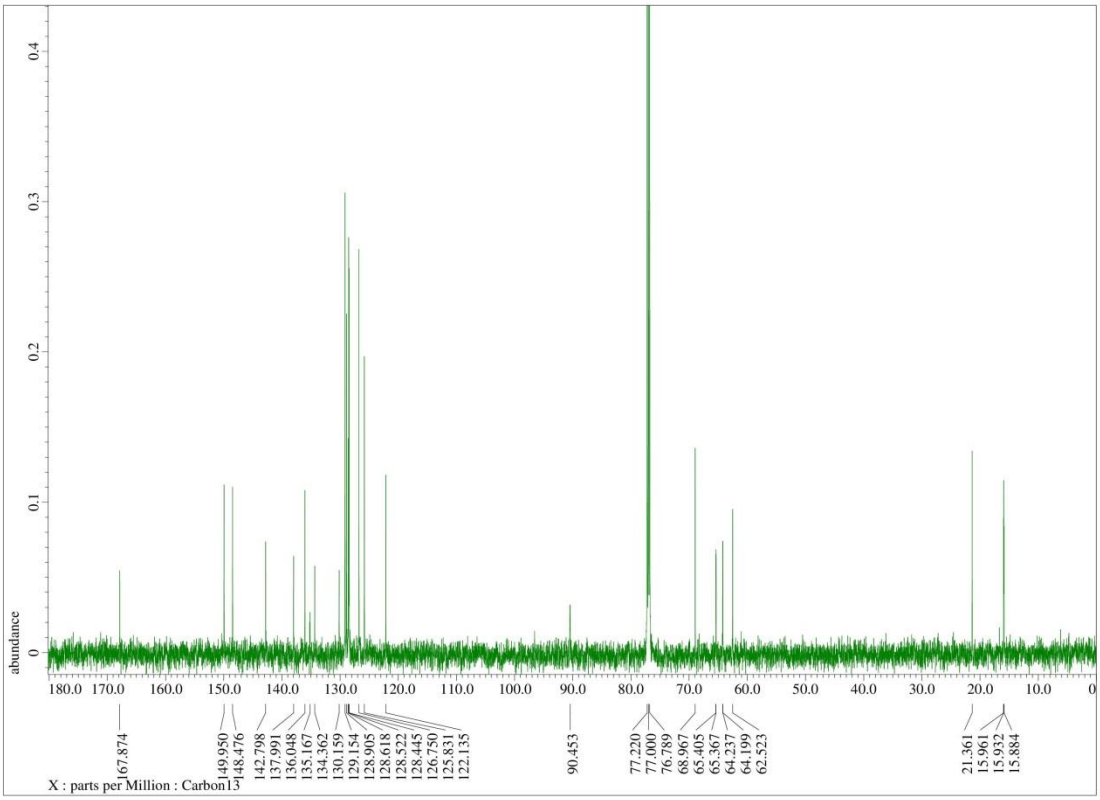

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4ai major
Ar = 2-furyl
8.73
0.90
1.96
1.00
2.02
0.97
1.00
0.99
1.00
1.02
0.99
2.02
2.03
3.03
2.91
2.88
abundance
X : parts per Million : Proton

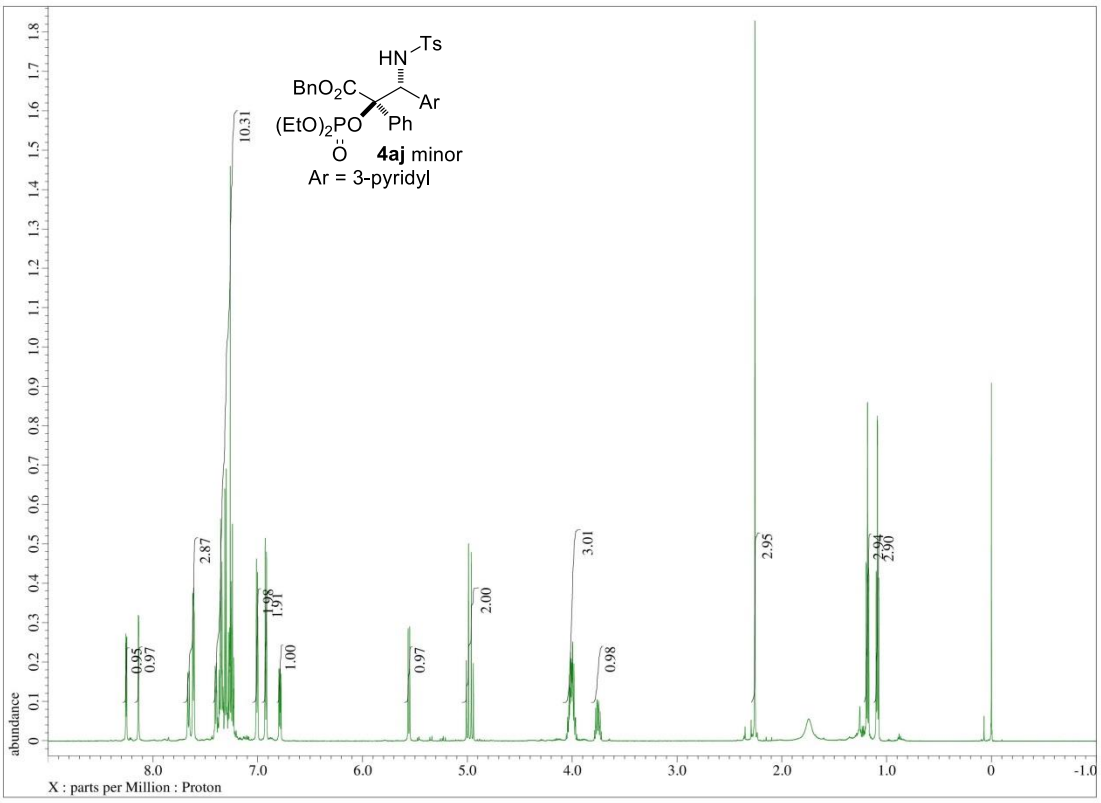

abundance
167.865
147.978
142.396
141.773
138.221
134.592
129.029
128.685
128.445
128.177
126.712
110.119
109.928
89.840
89.792
77.211
77.000
76.780
68.641
64.926
64.888
63.902
58.195
21.371
15.961
15.913
15.856
X : parts per Million : Carbon13

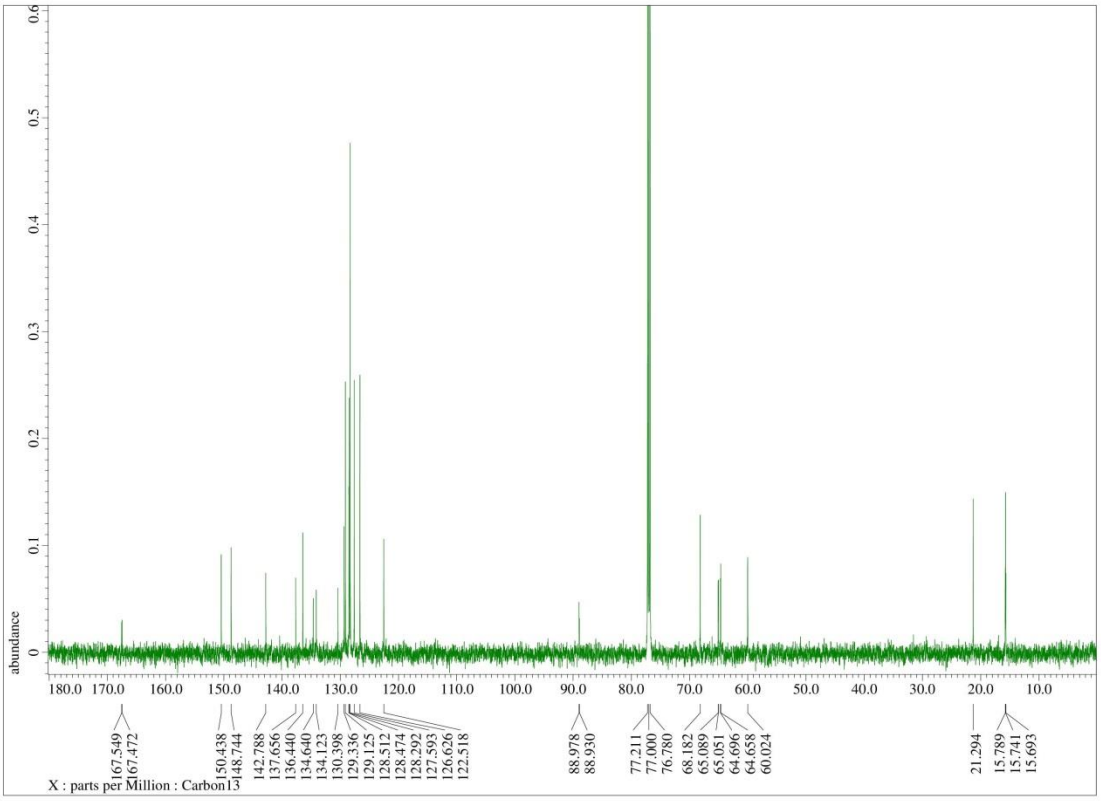

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4ai minor
Ar = 2-furyl
6.83
3.03
2.08
2.02
2.04
1.02
0.97
1.00
0.98
3.10
1.01
3.11
2.30
2.30
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
X : parts per Million : Proton

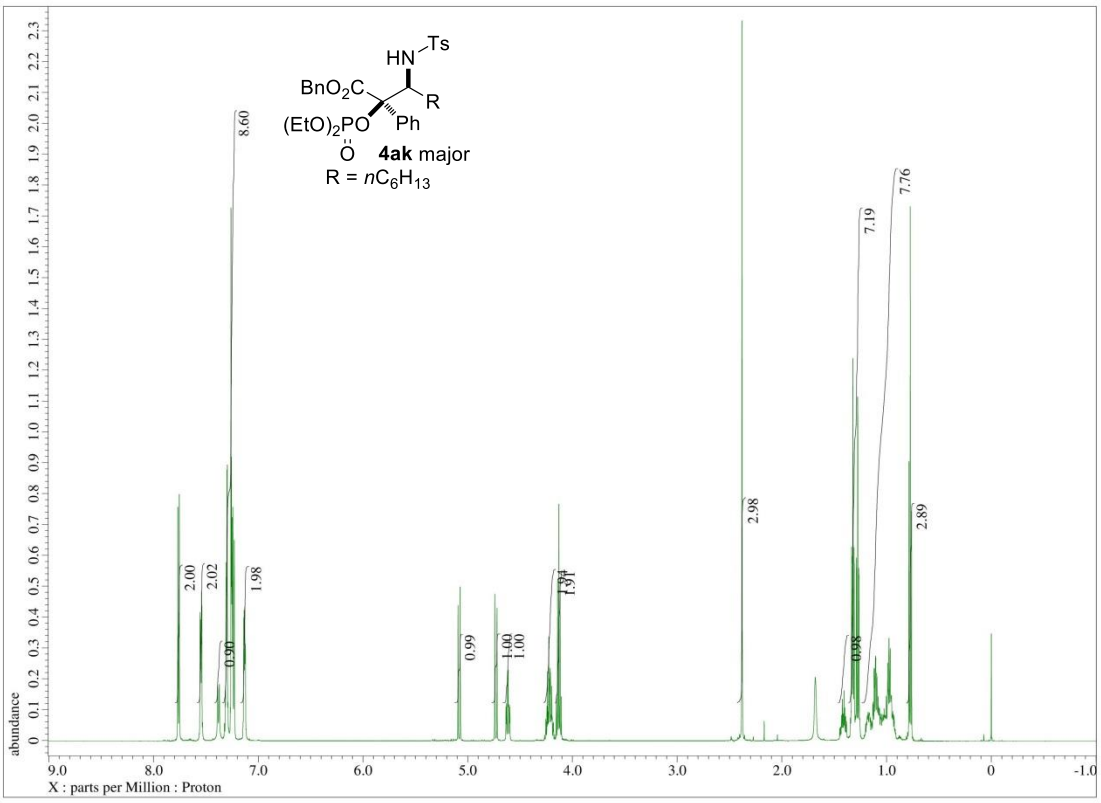

abundance
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.778
167.711
148.456
142.482
141.821
137.905
134.793
134.621
129.048
128.388
128.302
128.091
110.253
110.138
88.930
88.882
77.211
77.000
76.789
68.076
64.735
64.696
64.390
56.634
21.351
15.779
15.731
X : parts per Million : Carbon13

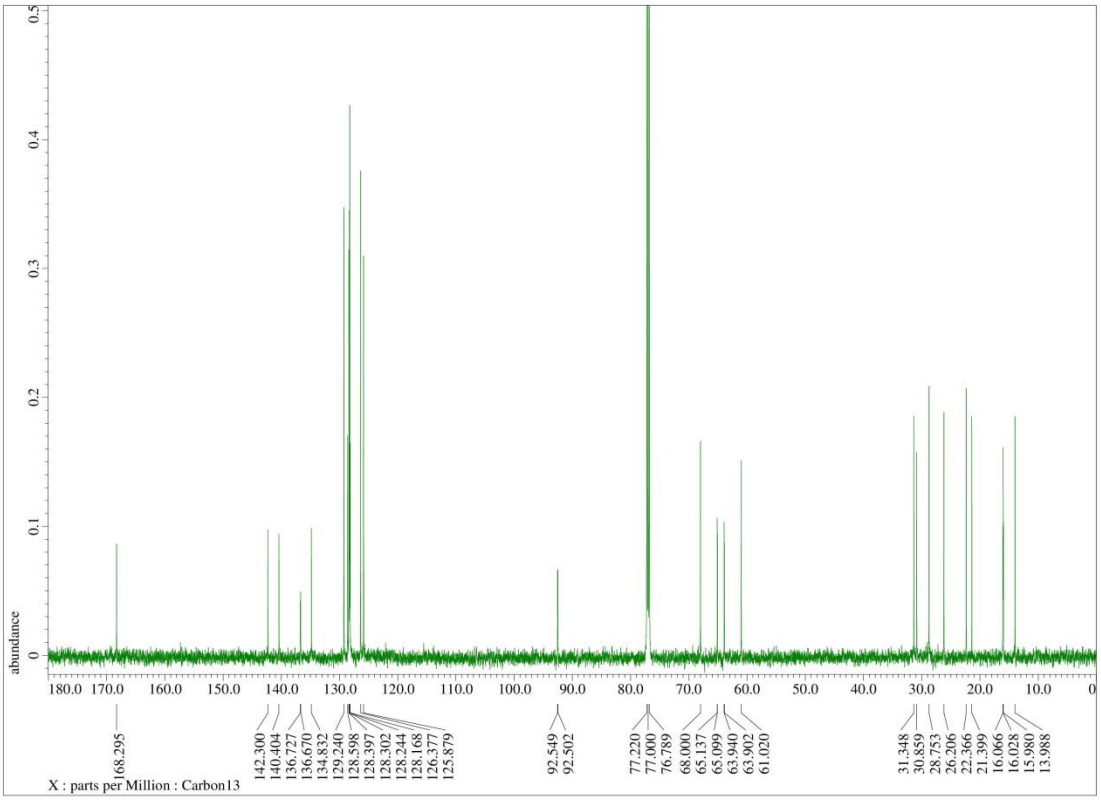

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4aj major
Ar = 3-pyridyl
7.19
4.90
6.26
3.00
1.99
2.03
2.05
1.04
0.99
1.03
1.03
1.02
2.02
2.05
abundance
X : parts per Million : Proton

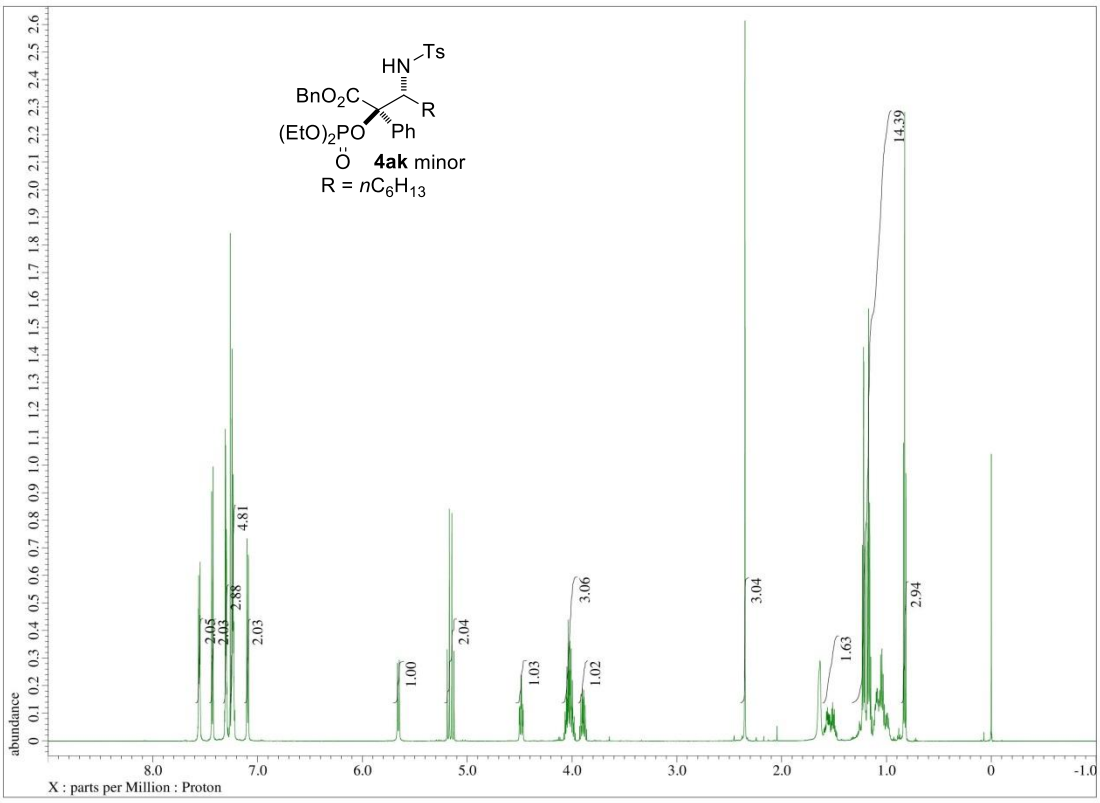

abundance
X : parts per Million : Carbon13
167.874
149.950
148.476
142.798
137.991
136.048
135.167
134.362
130.159
129.154
128.905
128.618
128.522
128.445
126.750
125.831
122.135
90.453
77.220
77.000
76.789
68.967
65.405
65.367
64.237
64.199
62.523
21.361
15.961
15.932
15.884

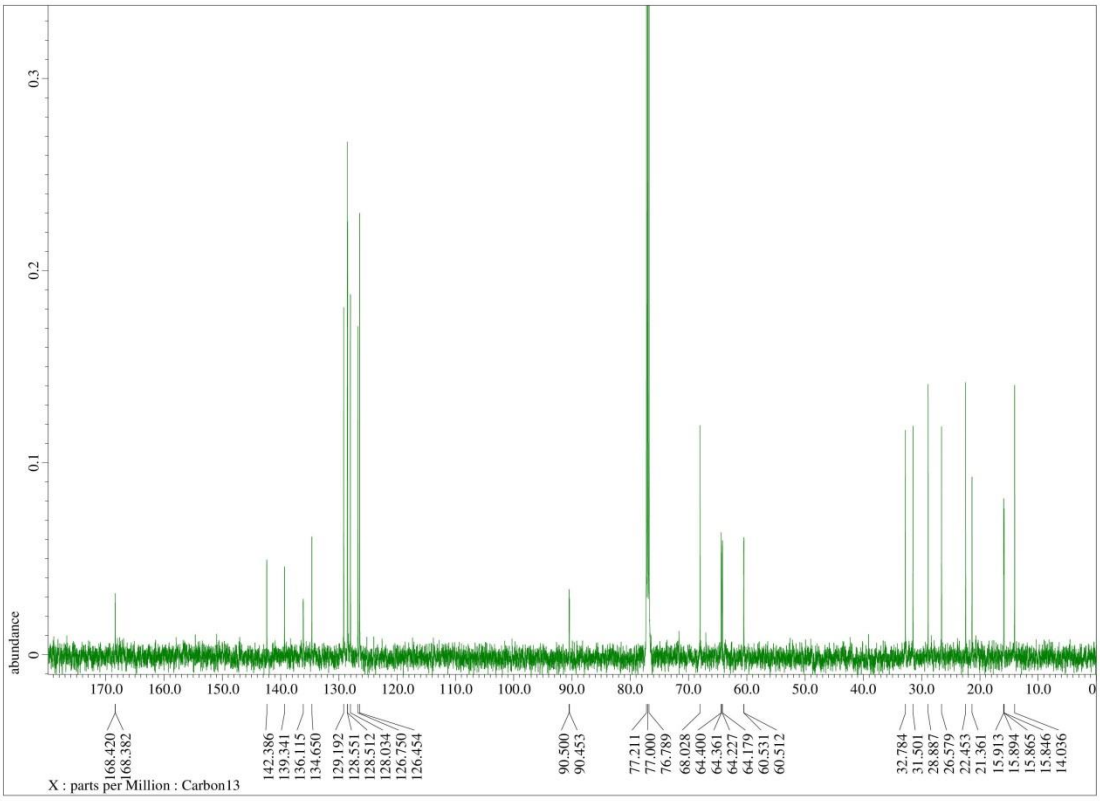

HN
Ts
BnO2C
Ar
(EtO)2PO
Ph
O
4aj minor
Ar = 3-pyridyl
10.31
2.87
1.98
1.91
0.95
0.97
1.00
0.97
2.00
3.01
0.98
2.95
2.94
2.90
abundance
X : parts per Million : Proton

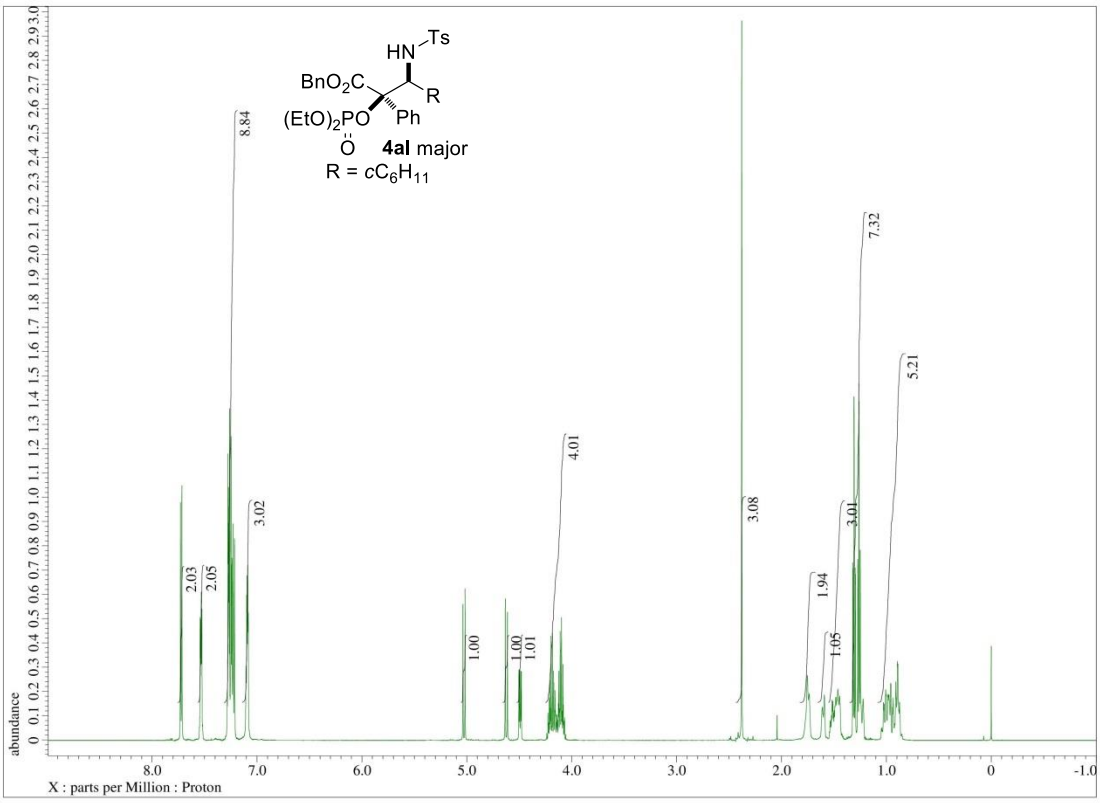

abundance
X : parts per Million : Carbon13
167.549
167.472
150.438
148.744
142.788
137.656
136.440
134.640
134.123
130.398
129.336
129.125
128.512
128.474
128.292
127.593
126.626
122.518
88.978
88.930
77.211
77.000
76.780
68.182
65.089
65.051
64.696
64.658
60.024
21.294
15.789
15.741
15.693

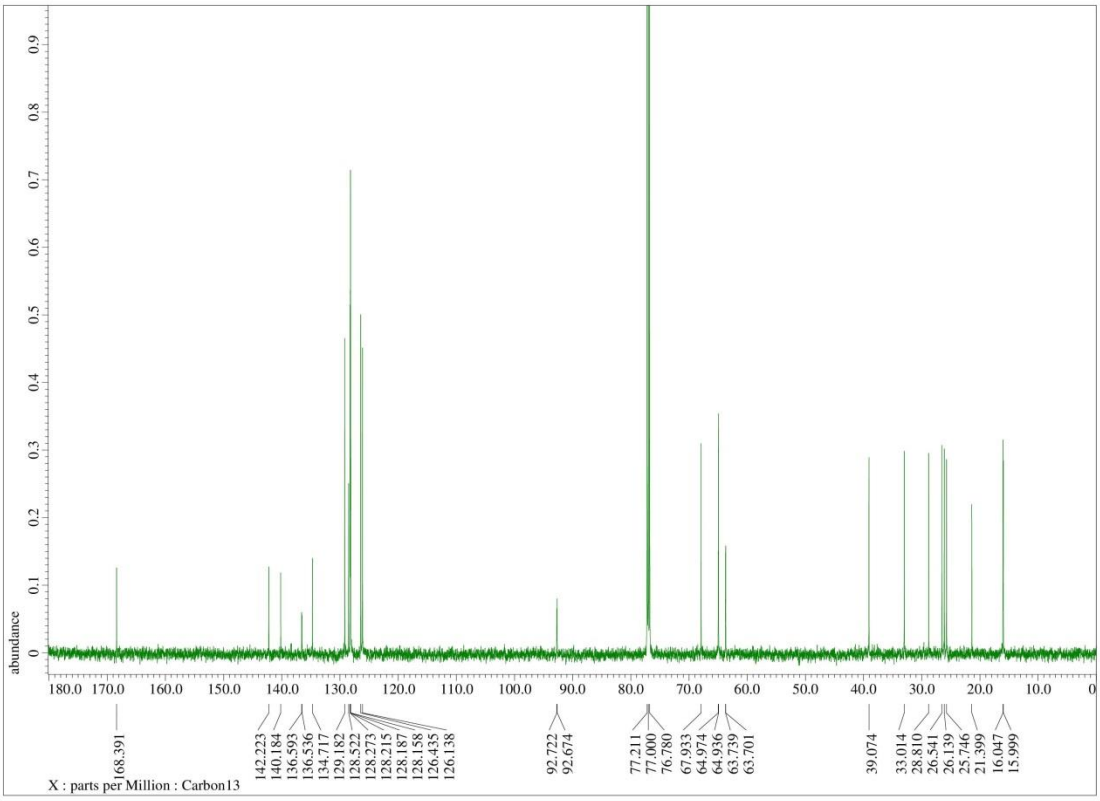

HN
Ts
BnO2C
R
(EtO)2PO
Ph
O
4ak major
R = nC6H13
8.60
2.00
2.02
0.90
1.98
0.99
1.00
1.00
1.94
1.91
2.98
7.19
7.76
0.98
2.89
abundance
X : parts per Million : Proton

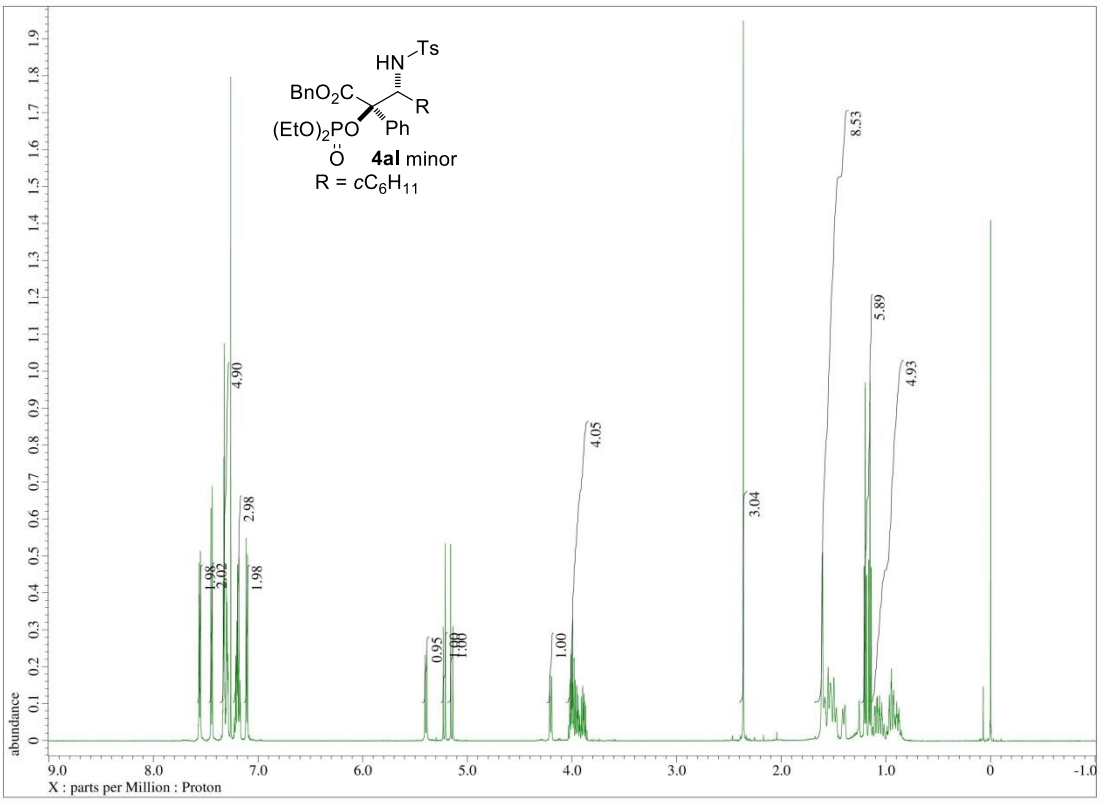

abundance
X : parts per Million : Carbon13
168.295
142.300
140.404
136.727
136.670
134.832
129.240
128.598
128.397
128.302
128.244
128.168
126.377
125.879
92.549
92.502
77.220
77.000
76.789
68.000
65.137
65.099
63.940
63.902
61.020
31.348
30.859
28.753
26.206
22.366
21.399
16.066
16.028
15.980
13.988

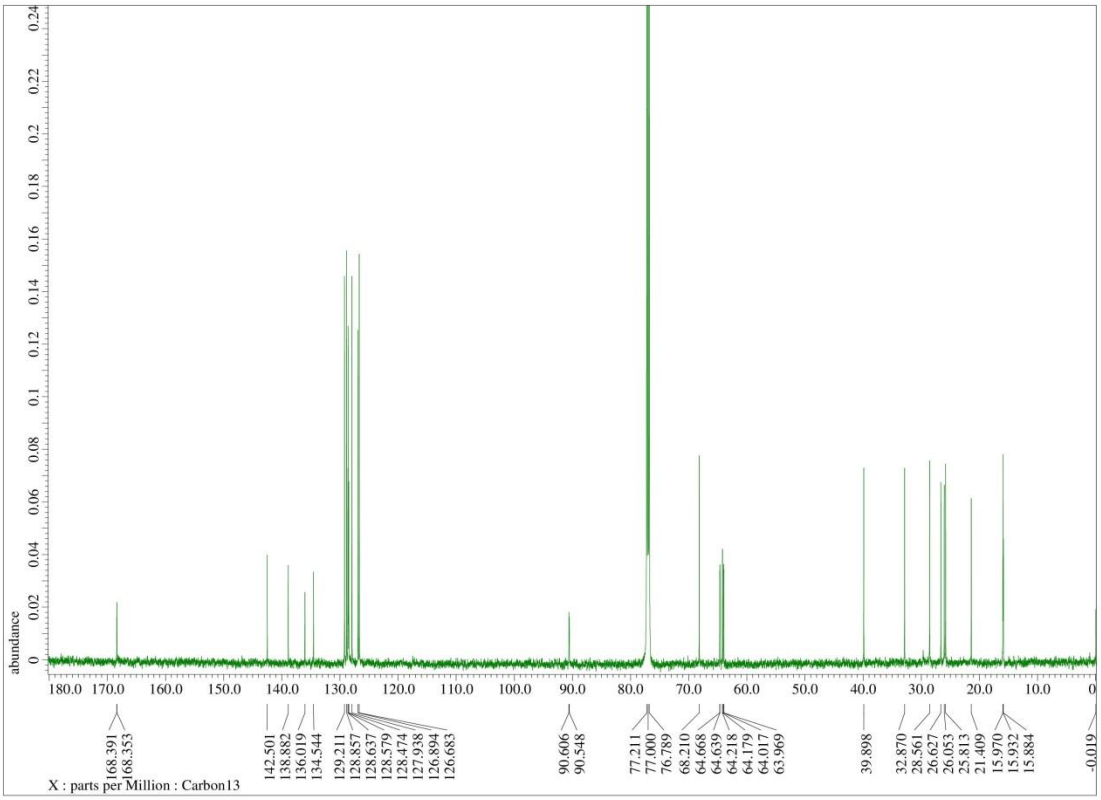

HN
Ts
BnO2C
R
(EtO)2PO
Ph
O
4ak minor
R = nC6H13
abundance
X : parts per Million : Proton
14.39
4.81
3.06
3.04
2.94
2.88
2.05
2.04
2.03
2.03
1.63
1.00
1.03
1.02

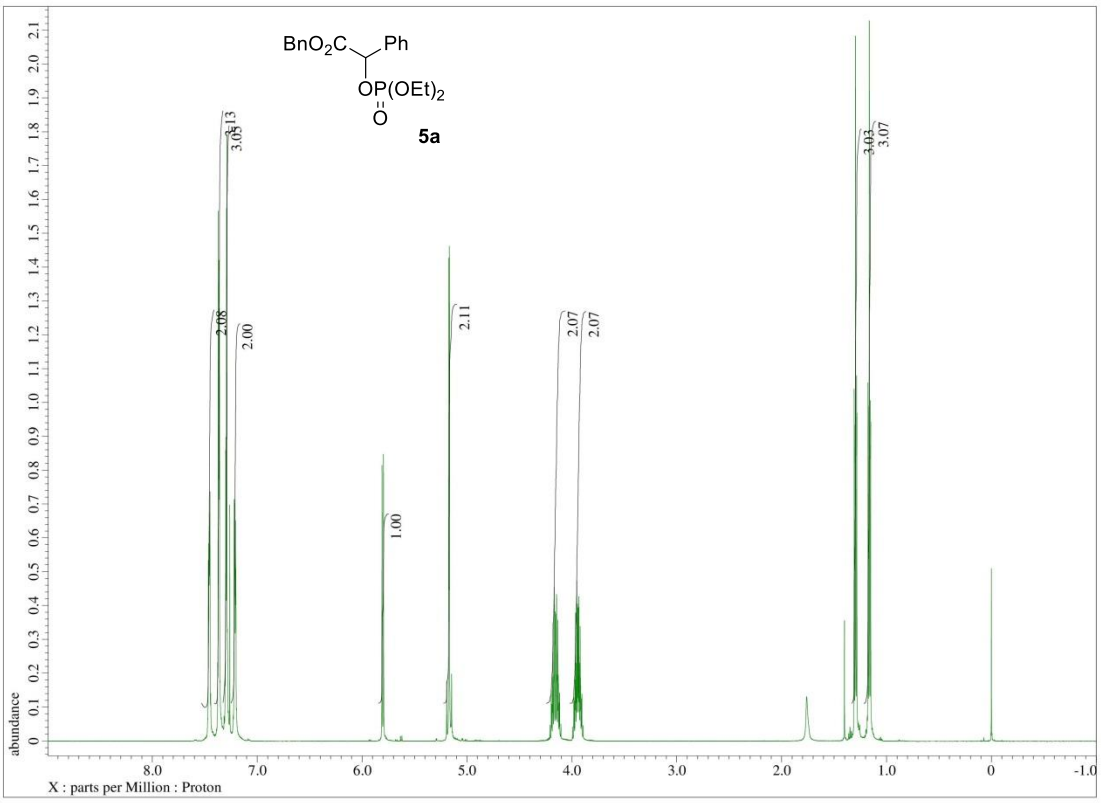

abundance
X : parts per Million : Carbon13
168.420
168.382
142.386
139.341
136.115
134.650
129.192
128.551
128.512
128.034
126.750
126.454
90.500
90.453
77.211
77.000
76.789
68.028
64.400
64.361
64.227
64.179
60.531
60.512
32.784
31.501
28.887
26.579
22.453
21.361
15.913
15.894
15.865
15.846
14.036

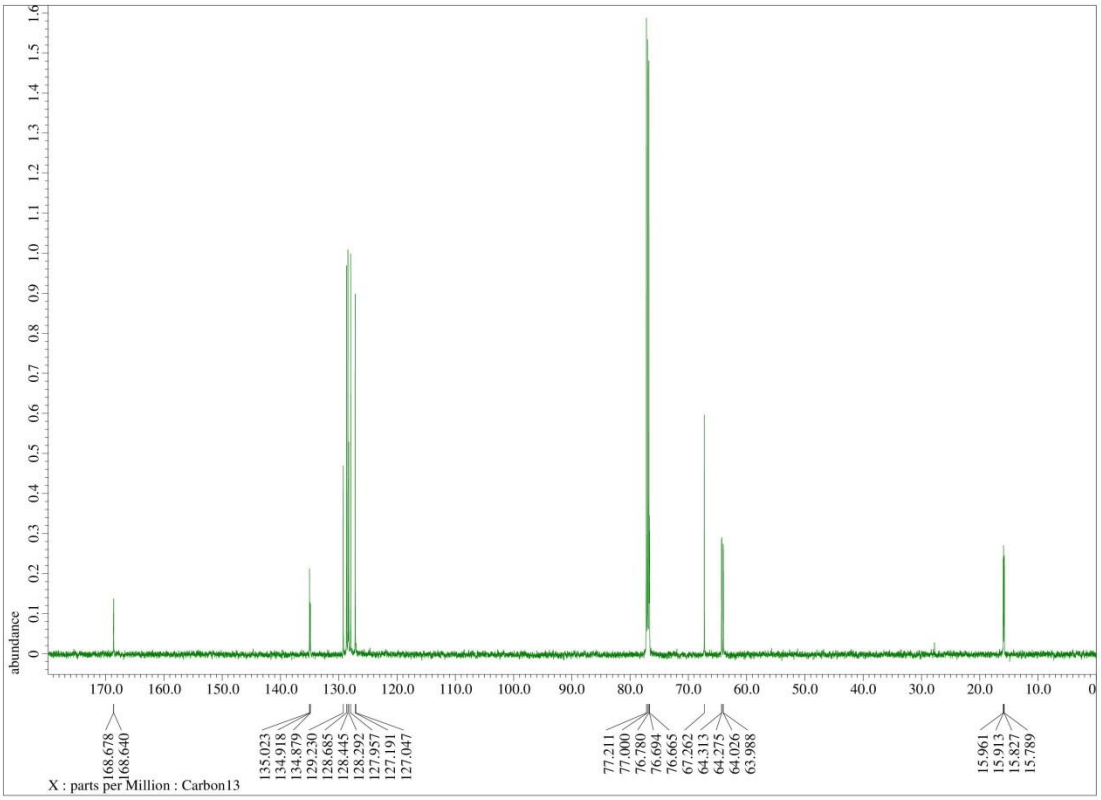

HN
Ts
BnO2C
R
(EtO)2PO
Ph
O
4al major
R = cC6H11
8.84
3.02
2.03
2.05
1.00
1.00
1.01
4.01
3.08
1.94
1.05
3.01
7.32
5.21
abundance
X : parts per Million : Proton

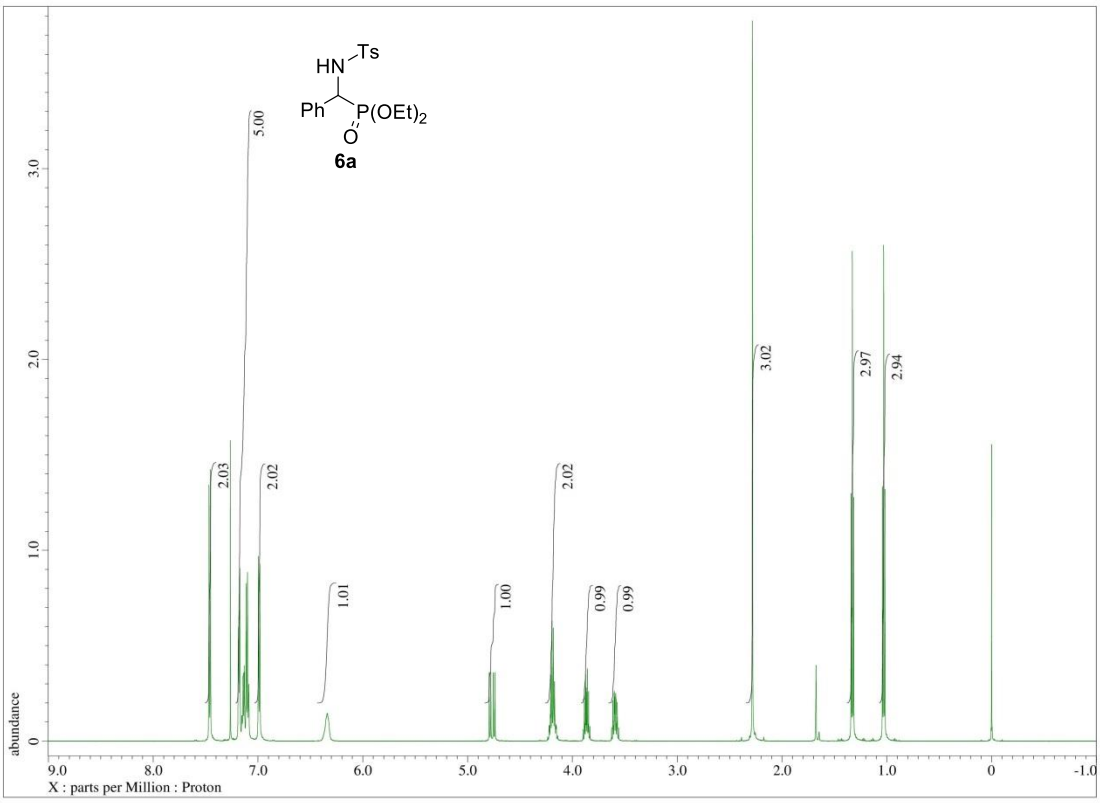

abundance
X : parts per Million : Carbon13
168.391
142.223
140.184
136.593
136.536
134.717
129.182
128.522
128.273
128.215
128.187
128.158
126.435
126.138
92.722
92.674
77.211
77.000
76.780
67.933
64.974
64.936
63.739
63.701
39.074
33.014
28.810
26.541
26.139
25.746
21.399
16.047
15.999

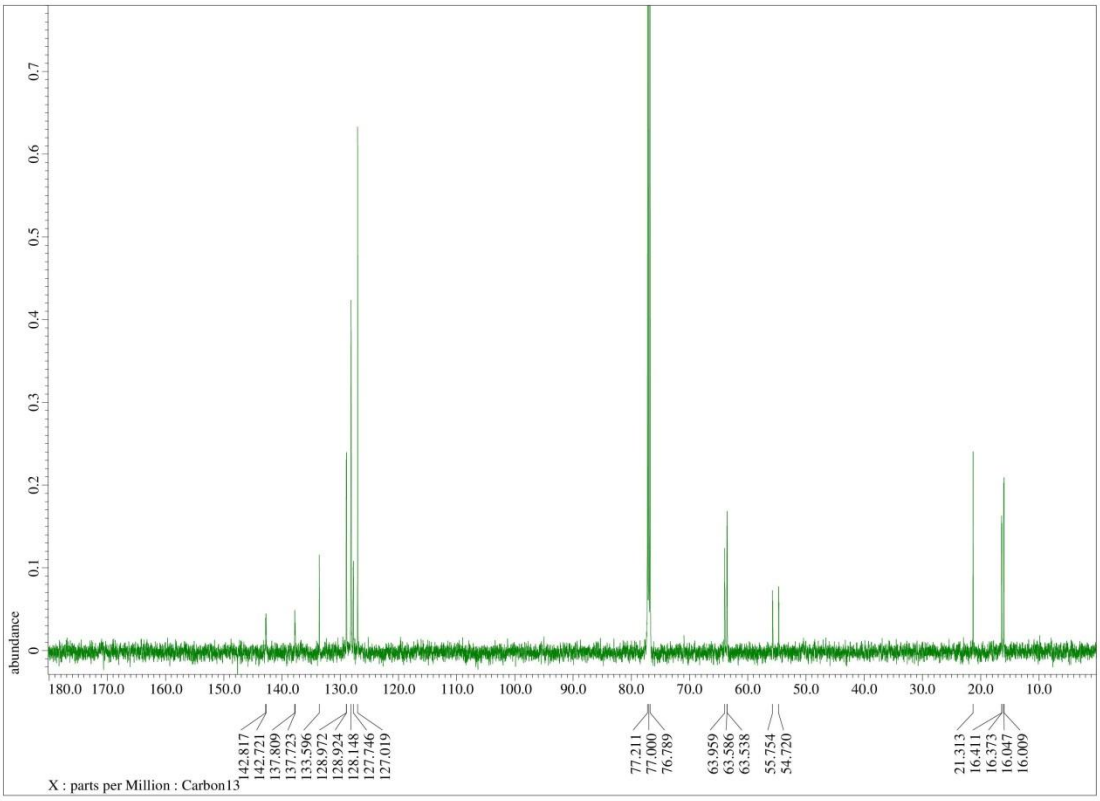

HN
Ts
BnO2C
R
(EtO)2PO
Ph
O
4al minor
R = cC6H11
abundance
X : parts per Million : Proton
1.98
2.02
4.90
2.98
1.98
0.95
1.00
4.05
3.04
8.53
5.89
4.93

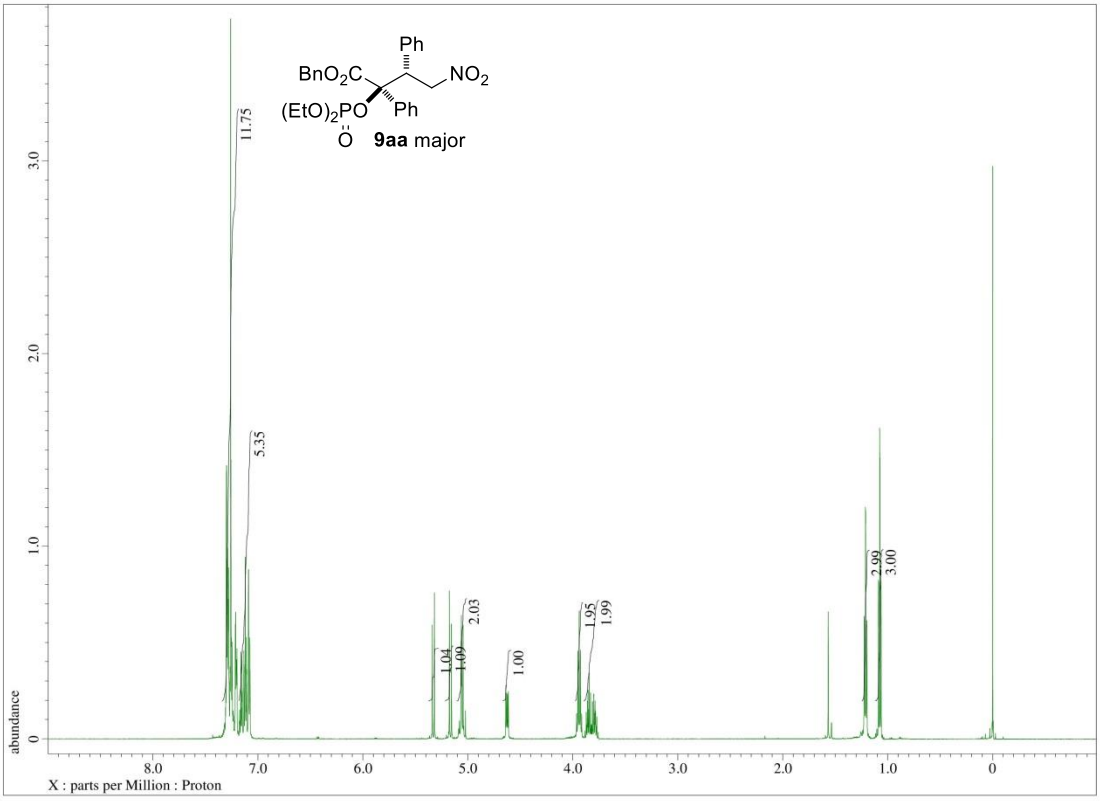

abundance
X : parts per Million : Carbon13
168.391
168.353
142.501
138.882
136.019
134.544
129.211
128.857
128.637
128.579
128.474
127.938
126.894
126.683
90.606
90.548
77.211
77.000
76.789
68.210
64.668
64.639
64.218
64.179
64.017
63.969
39.898
32.870
28.561
26.627
26.053
25.813
21.409
15.970
15.932
15.884

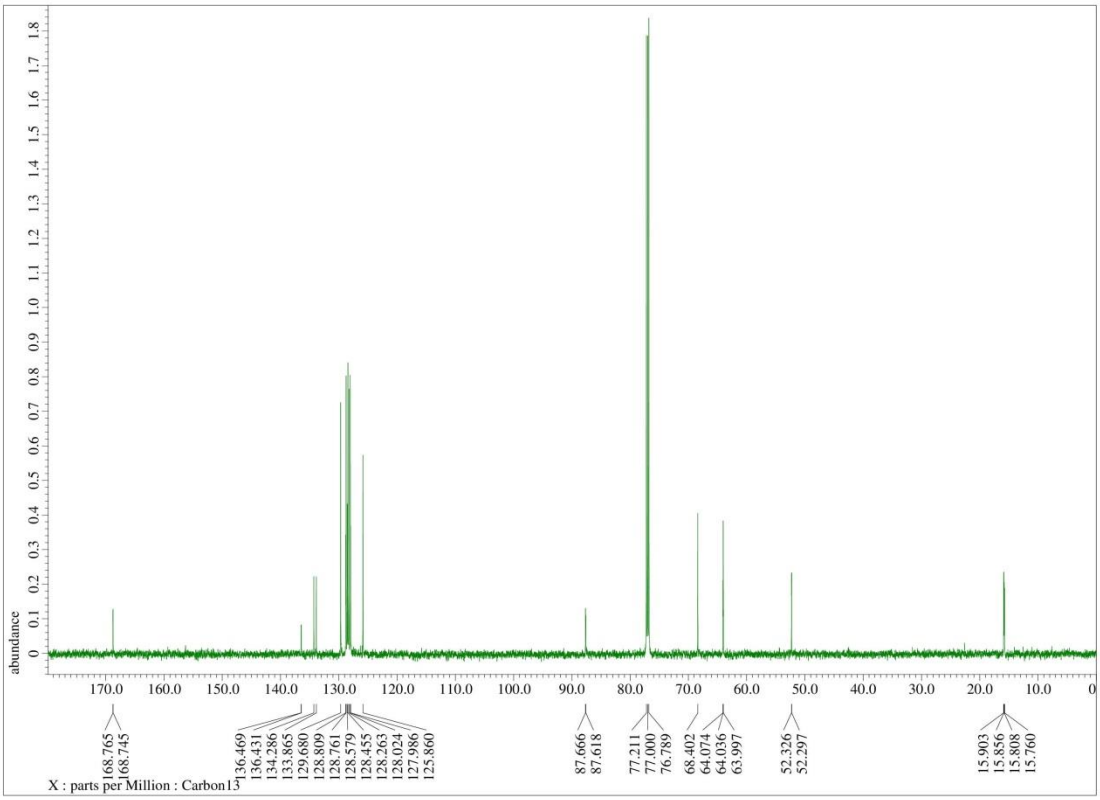

BnO2C
Ph
OP(OEt)2
O
5a
3.13
3.05
2.08
2.00
1.00
2.11
2.07
2.07
3.03
3.07
abundance
X : parts per Million : Proton

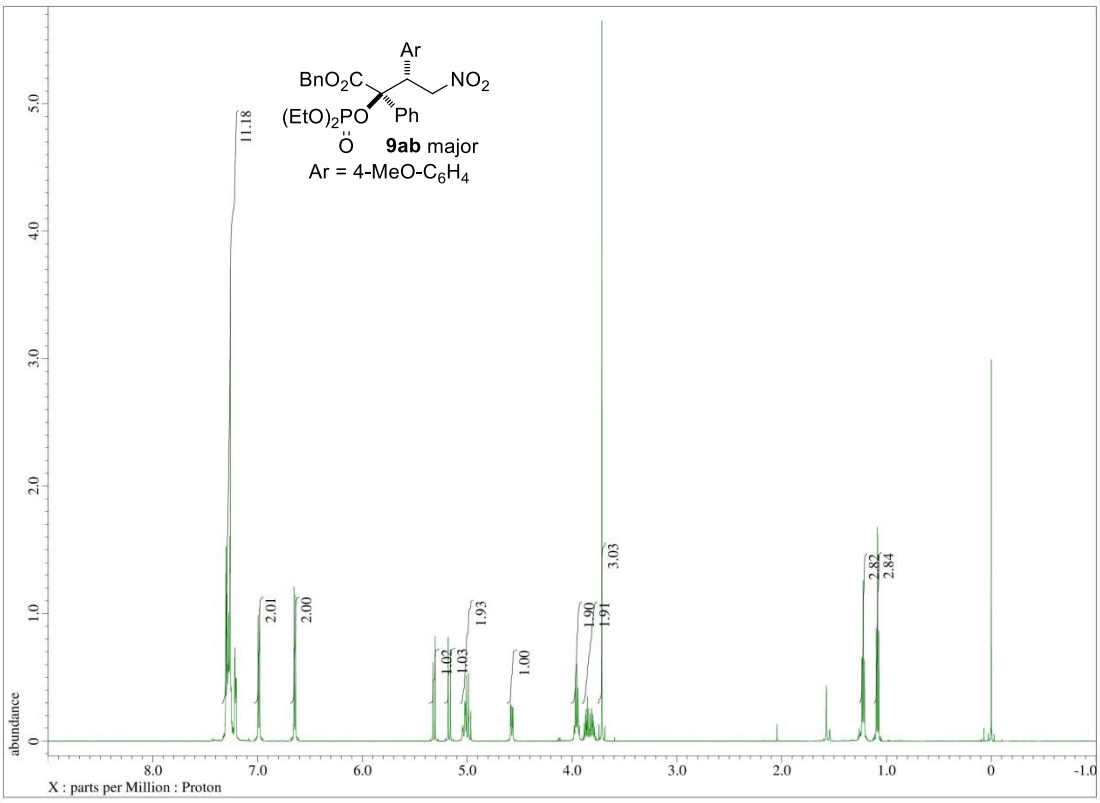

abundance
168.678
168.640
135.023
134.918
134.879
129.230
128.685
128.445
128.292
127.957
127.191
127.047
77.211
77.000
76.780
76.694
76.665
67.262
64.313
64.275
64.026
63.988
15.961
15.913
15.827
15.789
X : parts per Million : Carbon13

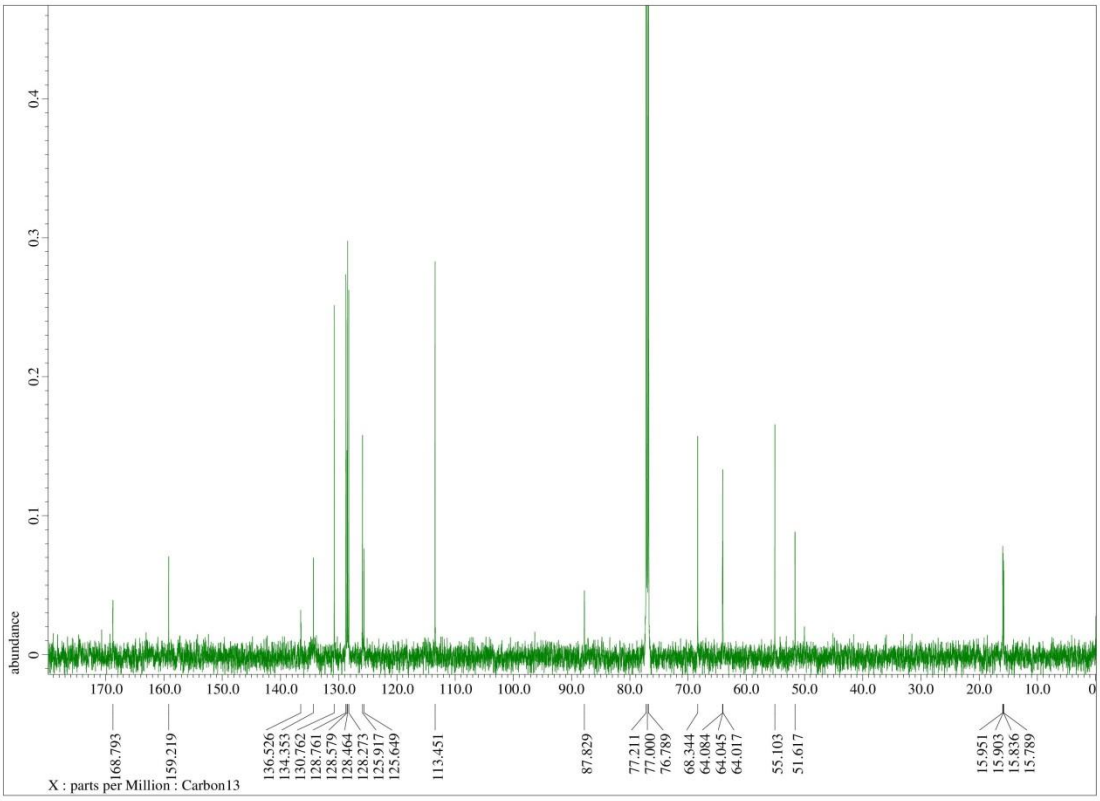

HN
Ts
Ph
P(OEt)2
O
6a
5.00
2.03
2.02
1.01
1.00
2.02
0.99
0.99
3.02
2.97
2.94
abundance
X : parts per Million : Proton

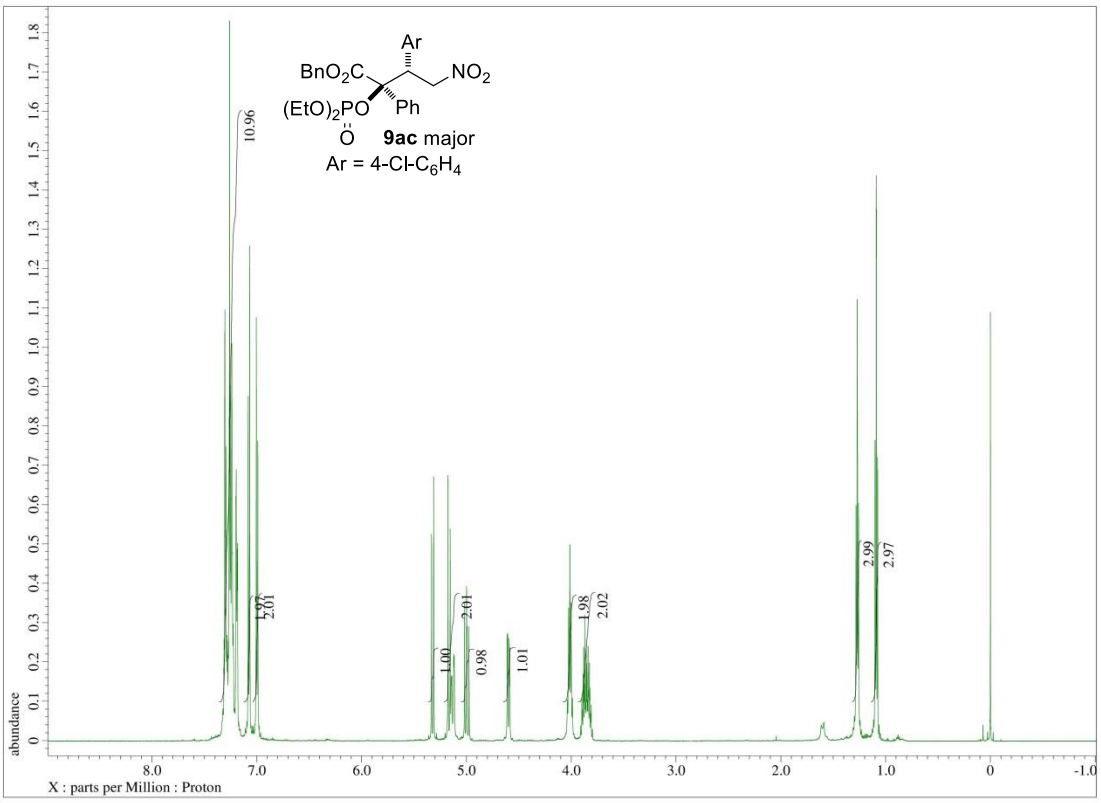

abundance
142.817
142.721
137.809
137.723
133.596
128.972
128.924
128.148
127.746
127.019
77.211
77.000
76.789
63.959
63.586
63.538
55.754
54.720
21.313
16.411
16.373
16.047
16.009
X : parts per Million : Carbon13

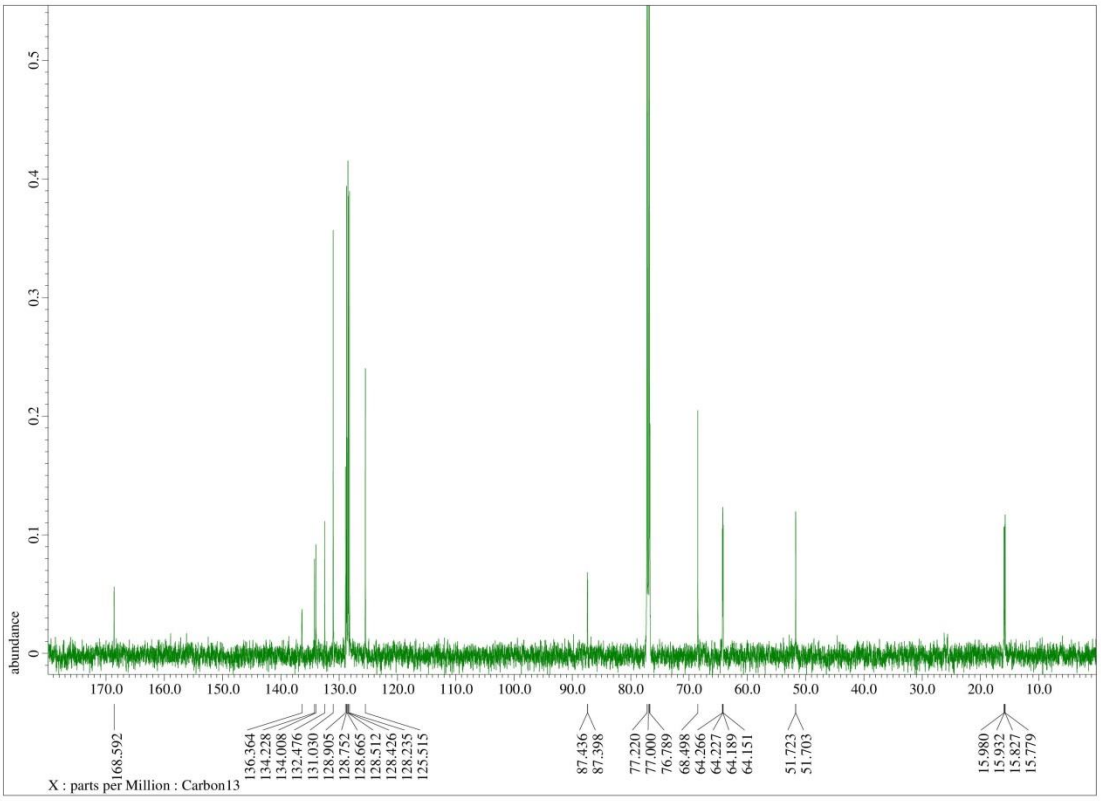

Ph
BnO2C
NO2
(EtO)2PO
Ph
O
9aa major
11.75
5.35
2.03
1.04
1.09
1.00
1.95
1.99
2.99
3.00
abundance
X : parts per Million : Proton


abundance
168.765
168.745
136.469
136.431
134.286
133.865
129.680
128.809
128.761
128.579
128.455
128.263
128.024
127.986
125.860
87.666
87.618
77.211
77.000
76.789
68.402
64.074
64.036
63.997
52.326
52.297
15.903
15.856
15.808
15.760
X : parts per Million : Carbon13


Ar
BnO2C
NO2
(EtO)2PO
Ph
O
9ab major
Ar = 4-MeO-C6H4
11.18
2.01
2.00
1.93
1.02
1.03
1.00
1.90
1.91
3.03
2.82
2.84
abundance
X : parts per Million : Proton


abundance
168.793
159.219
136.526
134.353
130.762
128.761
128.579
128.464
128.273
125.917
125.649
113.451
87.829
77.211
77.000
76.789
68.344
64.084
64.045
64.017
55.103
51.617
15.951
15.903
15.836
15.789
X : parts per Million : Carbon13


Ar
BnO2C
NO2
(EtO)2PO
Ph
O
9ac major
Ar = 4-Cl-C6H4
10.96
1.07
2.01
1.00
2.01
0.98
1.01
1.98
2.02
2.99
2.97
abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13
168.592
136.364
134.228
134.008
132.476
131.030
128.905
128.752
128.665
128.512
128.426
128.235
125.515
87.436
87.398
77.220
77.000
76.789
68.498
64.266
64.227
64.189
64.151
51.723
51.703
15.980
15.932
15.827
15.779