Electronic Supplementary Information

Enantioselective hydrophosphinylation of 1-alkenylphosphine oxides catalyzed by chiral strong Brønsted base

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Contents

1. General Information

Unless otherwise noted, the reactions were carried out with dried glassware under argon or nitrogen 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, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants (Hz). ^{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.). Optically rotations were measured on a Jasco P-1020 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]^{T^{\circ}C}{}_{D}$ (c = g/100 mL, solvent). HPLC was performed on JASCO HPLC systems consisting of the following: pump, PU-2080 plus; degasser, DG-2080-53; mixer, MX-2080-32; UV/Vis detector, UV2077 plus; CD detector, CD-2095; Oven, CO-2067 plus. SFC was performed on JASCO SFC systems consisting of the following: HPLC pump, PU-2080 plus; CO_2 delivery pump, PU-2080-CO_2 plus; solvent selection unit, LV-2080-03; Back Pressure Regulators, BP-2080 and BP-2080 plus; Photodiode detector, MD-2018 plus; Oven, CO-4065. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. High resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T FT-ICR-MS spectrometer and a JEOL JMS-T100GCV Time-of-Flight Mass Spectrometer at Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

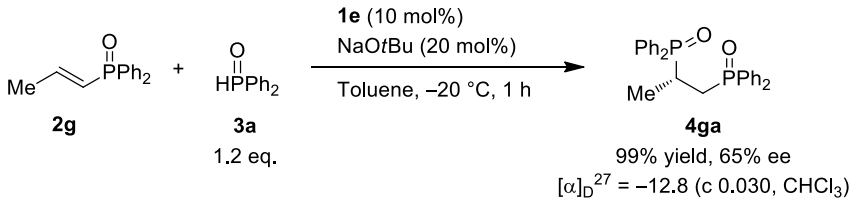
Materials: Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc., and other commercial suppliers and were used without purification. Dichloromethane, tetrahydrofuran, diethyl ether and toluene were supplied from Kanto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

2. Additional Experimental Results

Determination of Absolute Configuration of Diphosphine Dioxides 4

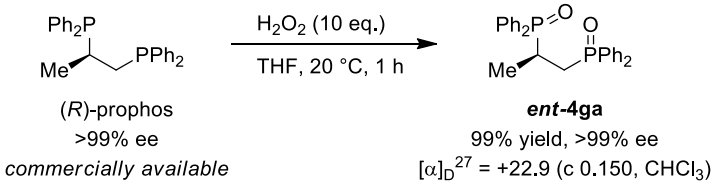
The reaction of **2g** with **3a** under the optimized reaction conditions provided diphosphine dioxide **4ga**, which is the dioxide of prophos, with 67% ee (Scheme S1).

Scheme S1



On the other hand, the authentic sample of dioxide of (*R*)-prophos was synthesized by the oxidation of commercially available (*R*)-prophos (Scheme S2).

Scheme S2

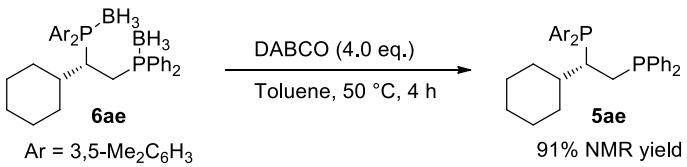


The comparison of the SFC chart and the optical rotation of **4ga** synthesized by our method with those of the authentic sample determined the absolute configuration of **4** as (*S*).

Transformation of Phosphine-Borane Complex 6ae to of 1,2-Diphosphinoalkane 5ae

1,2-Diphosphinoalkane **5ae** is air-sensitive and easily oxidized under air. Although the isolation of **5ae** from a crude mixture obtained by the direct reduction of **4ae** was unsuccessful, **5ae** was isolated in a relatively pure form through the decomplexation of phosphine-borane complex **6ae** with DABCO (Scheme S3). The experimental procedure and the NMR data are provided in the following sections.

Scheme S3

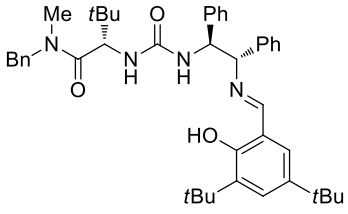


3. Experimental Procedure and Analytical Data

Preparation of Chiral Urea 1

Chiral ureas **1b-1e** were synthesized according to the procedure reported in our previous work.[1]

Urea 1e:

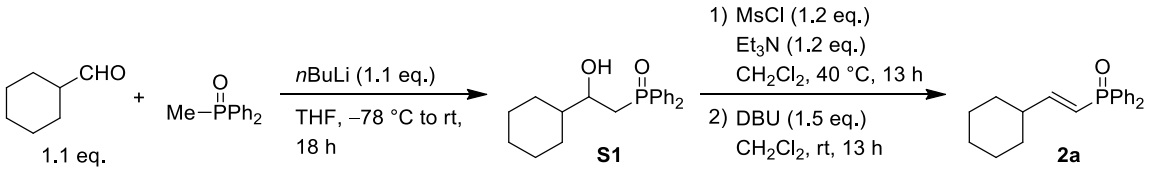


Ratio of rotamers = 76:24

Yellow powder; Optical rotation $[\alpha]_D^{26}$ = -22.6 (c 0.175, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.76 (s, 2.16H), 0.79 (s, 6.84H), 1.267 (s, 6.84H), 1.269 (s, 2.16H), 1.47 (s, 9H), 2.81 (s, 0.72H), 2.97 (s, 2.28H), 4.32 (d, *J* = 15.0 Hz, 0.76H), 4.33 (d, *J* = 15.0 Hz, 0.24H), 4.60 (d, *J* = 5.4 Hz, 0.24H), 4.61 (d, *J* = 5.4 Hz, 0.76H), 4.69 (d, *J* = 9.6 Hz, 0.76H), 4.75 (d, *J* = 14.4 Hz, 0.76H), 4.82 (d, *J* = 9.6 Hz, 0.24H), 4.84 (d, *J* = 14.4 Hz, 0.24H), 5.06 (d, *J* = 6.6 Hz, 0.24H), 5.09 (d, *J* = 6.6 Hz, 0.76H), 5.15 (d, *J* = 9.6 Hz, 0.24H), 5.18 (d, *J* = 9.6 Hz, 0.76H), 5.23 (br, 0.24H), 5.26 (br, 0.76H), 6.95 (d, *J* = 8.4 Hz, 0.76H), 6.96 (d, *J* = 8.4 Hz, 0.24H), 7.10-7.31 (m, 15H), 7.393 (d, *J* = 2.4 Hz, 0.76H), 7.395 (d, *J* = 2.4 Hz, 0.24H), 8.20 (s, 0.76H), 8.23 (s, 0.24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 26.4, 26.44, 29.5, 31.4, 33.5, 34.1, 35.1, 35.67, 35.69, 35.9, 51.1, 54.3, 55.3, 60.4, 78.11, 78.15, 117.7, 126.4, 127.37, 127.43, 127.5, 127.56, 127.64, 127.7, 127.8, 128.0, 128.2, 128.3, 128.6, 128.7, 136.1, 136.7, 136.8, 139.47, 139.50, 140.2, 156.6, 156.9, 157.9, 167.9, 172.7, 172.9; IR (ATR): 3371, 3062, 3030, 3002, 2957, 2870, 1679, 1626, 1591, 1539, 1495, 1478, 1454, 1441, 1414, 1393, 1362, 1273, 1250, 1214, 1173, 1090, 1029, 755, 699 cm^{-1}; HRMS (ESI) Calcd for $C_{44}H_{56}N_4O_3$ $[M+Na]^+$ 711.4245, Found 711.4244; mp. 142.0-145.0 °C.

Preparation of 1-Alkenylphosphine Oxides 2

Method A



Synthesis of **2a** is representative.

*Synthesis of **S1***

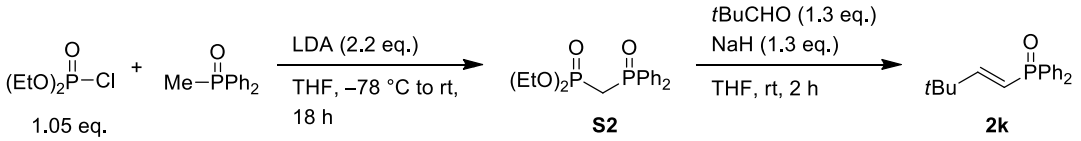
To a solution of methyl(diphenyl)phosphine oxide (1.1 g, 5.0 mmol) in THF (20 mL) was added *n*BuLi (1.6 M in hexane, 3.8 mL, 6.0 mmol) dropwise at -78 °C. After stirring for 15 min, cyclohexanecarboxaldehyde (0.70 mL, 5.5 mmol) was added dropwise to the mixture at the same temperature. The resulting mixture was then warmed up to room temperature and stirred for 18 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by reprecipitation from CH_2Cl_2 and hexane to afford **S1** (1.1 g, 3.4 mmol, 67%) as a white powder.

*Synthesis of **2a** from **S1***

To a solution of **S1** (1.1 g, 3.4 mmol) and triethylamine (0.56 mL, 4.0 mmol) in CH_2Cl_2 (15 mL) was added a solution of methanesulfonyl chloride (0.31 mL, 4.0 mmol) in CH_2Cl_2 (5.0 mL) dropwise at 0 °C. The mixture was heated at 40 °C for 13 h. After cooled to room temperature, the reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was used in the next step without purification.

The crude mixture was dissolved in CH_2Cl_2 (10 mL), and DBU (0.75 mL, 5.0 mmol) was added to the solution at 0 °C. The mixture was stirred at room temperature for 13 h. The reaction was then quenched with sat. aq. NH_4Cl, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 30:1) followed by recrystallization from a hexane/AcOEt mixture to afford **2a** (0.65 g, 2.1 mmol, 63% yield, over 2 steps) as a white powder.

Method B



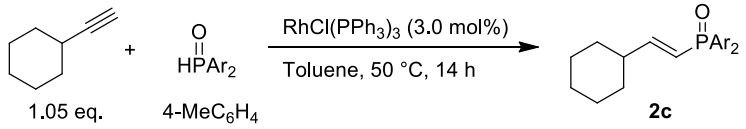
*Synthesis of **S2***

To a solution of ethyl(diisopropyl)amine (1.6 mL, 11.0 mmol) in THF (10 mL) was added *n*BuLi (1.6 M in hexane, 6.9 mL, 11.0 mmol) dropwise at -78 °C, and the mixture was stirred for 15 min. A solution of methyl(diphenyl)phosphine oxide (1.1 g, 5.0 mmol) in THF (10 mL) was then added dropwise at -78 °C. After stirred for 10 min, a solution of diethyl chlorophosphate (0.76 mL, 5.3 mmol) in THF (5.0 mL) was added dropwise at the same temperature. The resulting mixture was warmed up to room temperature and stirred for 18 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 20:1) to afford **S2** (1.6 g, 4.6 mmol, 92%) as a white powder.

*Synthesis of **2k** from **S2***

To a suspension of sodium hydride (52 mg, 1.3 mmol) in THF (3.0 mL) was added **S2** (0.35 g, 1.0 mmol) at 0 °C and the mixture was stirred for 10 min. Pivalaldehyde (0.14 mL, 1.3 mmol) was then added dropwise to the mixture at 0 °C. After stirring at room temperature for 2 h, the reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 30:1) followed by recrystallization from a hexane/AcOEt mixture to afford **2k** (0.20 g, 0.69 mmol, 69% yield) as a white powder.

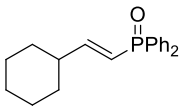
Method C[2]



Synthesis of **2c** is representative.

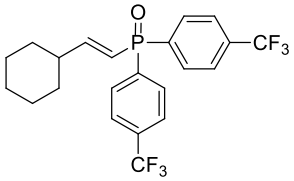
To a solution of di(*para*-tolyl)phosphine oxide (0.16 g, 0.70 mmol) and cyclohexyl acetylene (96 μL, 0.74 mmol) in toluene (1.8 mL) was added $RhCl(PPh_3)_3$ (19 mg, 0.021 mmol) at room temprature. The mixture was heated at 50 °C for 14 h. After cooled to room temperature, the resulting solution was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 50:1) followed by reprecipitation from CH_2Cl_2 and hexane to afford **2c** (0.16 g, 0.49 mmol, 69% yield) as a white powder.

(*E*)-2-Cyclohexyl-1-(diphenylphosphoryl)ethene (2a):



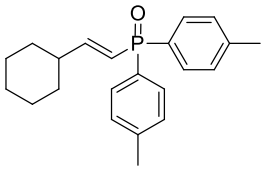
42% yield (Method A, over 3 steps); White powder; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.12-1.22 (m, 3H), 1.24-1.34 (m, 2H), 1.64-1.70 (m, 1H), 1.73-1.79 (m, 2H), 1.79-1.85 (m, 2H), 2.17-2.26 (m, 1H), 6.16 (ddd, *J* = 24.6, 17.4, 1.2 Hz, 1H), 6.71 (ddd, *J* = 19.8, 17.4, 6.6 Hz, 1H), 7.41-7.48 (m, 4H), 7.51 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 2H), 7.69 (ddd, *J* = 12.0, 8.4, 1.2 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.7, 25.9, 31.6, 42.3 (d, *J* = 15.8 Hz), 119.0 (d, *J* = 103.4 Hz), 128.4 (d, *J* = 12.9 Hz), 131.3 (d, *J* = 8.7 Hz), 131.6 (d, *J* = 2.9 Hz), 133.4 (d, *J* = 103.4 Hz), 157.6; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.4; IR (ATR): 3429, 3073, 3054, 2925, 2850, 1617, 1438, 1219, 1183, 1120, 1109, 1071, 1003, 818, 772, 749, 719, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{23}OP$ $[M+Na]^+$ 333.1379, Found 333.1378; mp. 129.0-131.0 °C.

(*E*)-1-Bis(4-(trifluoromethyl)phenyl)phosphoryl-2-cyclohexylethene (2b):



59% yield (Method C); Yellow powder; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.13-1.24 (m, 3H), 1.26-1.36 (m, 2H), 1.66-1.73 (m, 1H), 1.74-1.80 (m, 2H), 1.80-1.86 (m, 2H), 2.20-2.30 (m, 1H), 6.17 (ddd, *J* = 26.4, 16.8, 1.8 Hz, 1H), 6.82 (ddd, *J* = 20.4, 16.8, 6.6 Hz, 1H), 7.74 (dd, *J* = 8.4, 2.4 Hz, 4H), 7.82 (dd, *J* = 11.4, 8.4 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.6, 25.8, 31.5, 42.5 (d, *J* = 15.8 Hz), 117.3 (d, *J* = 104.9 Hz), 123.5 (q, *J* = 271.5 Hz), 125.6 (dq, *J* = 11.4, 4.4 Hz), 131.7 (d, *J* = 10.1 Hz), 133.8 (q, *J* = 33.0 Hz), 137.2 (d, *J* = 102.0 Hz), 159.9; ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.1; IR (ATR): 3420, 3043, 2993, 2927, 2903, 2853, 1611, 1450, 1399, 1324, 1189, 1167, 1130, 1102, 1063, 1018, 997, 836, 818, 771, 710, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{21}F_6OP$ $[M+Na]^+$ 469.1126, Found 469.1126; mp. 189.0-191.0 °C.

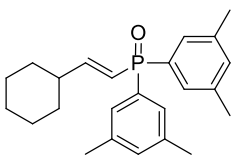
(*E*)-2-Cyclohexyl-1-(di-*para*-tolylphosphoryl)ethene (2c):



69% yield (Method C); White powder; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.11-1.21 (m, 3H), 1.24-1.33 (m, 2H), 1.64-1.70 (m, 1H), 1.72-1.78 (m, 2H), 1.78-1.83 (m, 2H), 2.15-2.23 (m, 1H), 2.39 (s, 6H), 6.13 (ddd, *J* = 24.6, 16.8, 1.8 Hz, 1H), 6.66 (ddd, *J* = 19.8, 16.8, 6.0 Hz, 1H), 7.25 (dd, *J* = 7.8, 2.4 Hz, 4H), 7.55 (dd, *J* = 12.0, 7.8 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 25.8, 25.9, 31.7, 42.3 (d, *J* = 14.4 Hz), 119.4 (d, *J* = 103.4 Hz), 129.2 (d, *J* = 11.4 Hz), 130.2 (d, *J* = 106.4 Hz), 131.3 (d, *J* = 10.1 Hz), 141.9 (d, *J* = 3.0 Hz), 157.0; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.8; IR

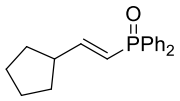
(ATR): 3385, 3053, 3034, 3020, 2983, 2923, 2898, 2849, 1641, 1626, 1603, 1501, 1447, 1398, 1179, 1117, 1110, 1009, 811, 714, 654, 630 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{27}OP$ $[M+Na]^+$ 361.1692, Found 361.1691; mp. 154.0-155.0 ℃.

(*E*)-1-Bis(3,5-dimethylphenyl)phosphoryl-2-cyclohexylethene (2d):



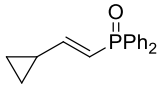
46% yield (Method C); Yellow-brown powder; ^1H NMR (600 MHz, $CDCl_3$) δ 1.13-1.23 (m, 3H), 1.24-1.34 (m, 2H), 1.62-1.70 (m, 1H), 1.72-1.79 (m, 2H), 1.79-1.85 (m, 2H), 2.17-2.25 (m, 1H), 2.33 (s, 12H), 6.14 (ddd, *J* = 24.6, 16.8, 1.2 Hz, 1H), 6.70 (ddd, *J* = 19.2, 16.8, 6.0 Hz, 1H), 7.12 (s, 2H), 7.29 (d, *J* = 12.6 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.2, 25.7, 25.9, 31.7, 42.3 (d, *J* = 15.9 Hz), 119.3 (d, *J* = 101.9 Hz), 128.8 (d, *J* = 10.1 Hz), 133.2 (d, *J* = 2.9 Hz), 133.3 (d, *J* = 102.0 Hz), 138.0 (d, *J* = 12.9 Hz), 156.9; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.5; IR (ATR): 3440, 3031, 2997, 2923, 2851, 1630, 1601, 1448, 1418, 1274, 1182, 1128, 991, 872, 851, 810, 692 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{31}OP$ $[M+Na]^+$ 389.2005, Found 389.2004; mp. 151.0-153.0 ℃.

(*E*)-2-Cyclopentyl-1-(diphenylphosphoryl)ethane (2e):



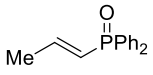
60% yield (Method C); White powder; ^1H NMR (600 MHz, $CDCl_3$) δ 1.39-1.48 (m, 2H), 1.56-1.73 (m, 4H), 1.82-1.90 (m, 2H), 2.65-2.74 (m, 1H), 6.18 (ddd, *J* = 24.6, 16.8, 1.2 Hz, 1H), 6.74 (ddd, *J* = 19.8, 16.8, 7.8 Hz, 1H), 7.42-7.48 (m, 4H), 7.49-7.54 (m, 2H), 7.70 (ddd, *J* = 12.0, 7.8, 1.2 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.2, 32.2, 44.9 (d, *J* = 15.8 Hz), 119.4 (d, *J* = 103.4 Hz), 128.4 (d, *J* = 11.6 Hz), 131.3 (d, *J* = 10.1 Hz), 131.6 (d, *J* = 2.9 Hz), 133.4 (d, *J* = 103.4 Hz), 156.8; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.1; IR (ATR): 3457, 3075, 3052, 3008, 2963, 2915, 2865, 1632, 1604, 1485, 1439, 1178, 1118, 1104, 1073, 1007, 809, 772, 752, 714, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{21}OP$ $[M+Na]^+$ 319.1222, Found 319.1222; mp. 112.0-114.0 ℃.

(*E*)-2-Cyclopropyl-1-(diphenylphosphoryl)ethene (2f):



50% yield (Method C); White powder; ^1H NMR (600 MHz, $CDCl_3$) δ 0.60-0.69 (m, 2H), 0.88-0.97 (m, 2H), 1.64-1.71 (m, 1H), 6.18 (ddd, *J* = 19.2, 16.8, 7,8 Hz, 1H), 6.26 (dd, *J* = 24.0, 16.8 Hz, 1H), 7.42-7.48 (m, 4H), 7.48-7.53 (m, 2H), 7.70 (ddd, *J* = 12.0, 8.4, 1.2 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 8.5, 16.4 (d, *J* = 21.6 Hz), 117.7 (d, *J* = 104.9 Hz), 128.4 (d, *J* = 12.9 Hz), 131.2 (d, *J* = 10.1 Hz), 131.5 (d, *J* = 2.9 Hz), 133.6 (d, *J* = 104.9 Hz), 156.6 (d, *J* = 2.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.7; IR (ATR): 3432, 3074, 3057, 3007, 2972, 2936, 2874, 1621, 1438, 1182, 1120, 1104, 998, 955, 794, 771, 752, 720, 697 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}OP$ $[M+Na]^+$ 291.0909, Found 291.0909; mp. 131.0-133.0 ℃.

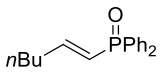
(*E*)-1-(Diphenyphosphoryl)prop-1-ene (2g):



42% yield (Method A, over 3 steps); White powder; ^1H NMR (600 MHz, $CDCl_3$) δ 1.99 (ddd, *J* = 6.6, 2.4, 1.8 Hz, 3H), 6.27 (ddq, *J* = 24.0, 16.8, 1.8 Hz, 1H), 6.71 (ddq, *J* = 19.2, 16.8, 6.6 Hz, 1H), 7.43-7.49 (m, 4H), 7.49-7.54 (m, 2H), 7.70 (ddd, *J* = 12.0, 8.4, 1.8 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.4 (d, *J* = 18.6 Hz), 123.5 (d, *J* = 103.5 Hz), 128.5 (d, *J* = 11.6 Hz), 131.3 (d, *J* = 10.1 Hz), 131.6 (d, *J* = 2.9 Hz), 133.2 (d, *J* = 104.9 Hz), 147.9 (d, *J* = 2.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.8; IR (ATR): 3403, 3058, 2993, 2966, 2940, 1631, 1591, 1560, 1485, 1439, 1220, 1181, 1120, 1106, 1071, 1027, 996, 791, 773, 751, 718, 698 cm^{-1}; HRMS

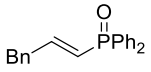
(ESI) Calcd for $C_{15}H_{15}OP$ $[M+Na]^+$ 265.0753, Found 265.0752; mp. 128.0-130.0 ℃.

(*E*)-1-(Diphenylphosphoryl)hex-1-ene (2h):



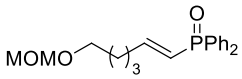
78% yield (Method C); White powder; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.35 (qt, *J* = 7.2, 7.2 Hz, 2H), 1.47 (tt, *J* = 7.8, 7.2 Hz, 2H), 2.27-2.34 (m, 2H), 6.23 (ddt, *J* = 24.6, 16.8, 1.8 Hz, 1H), 6.73 (ddt, *J* = 19.8, 16.8, 6.6 Hz, 1H), 7.41-7.49 (m, 4H), 7.49-7.54 (m, 2H), 7.69 (ddd, *J* = 12.0, 8.4, 1.8 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.7, 22.1, 29.9, 34.1 (d, *J* = 17.3 Hz), 121.6 (d, *J* = 102.0 Hz), 128.4 (d, *J* = 11.6 Hz), 131.2 (d, *J* = 8.6 Hz), 131.5 (d, *J* = 2.9 Hz), 133.2 (d, *J* = 104.9 Hz), 152.8; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.0; IR (ATR): 3439, 3055, 2957, 2928, 2871, 1630, 1591, 1484, 1465, 1437, 1379, 1308, 1183, 1119, 1105, 1070, 1028, 998, 930, 815, 746, 719, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{21}OP$ $[M+Na]^+$ 307.1222, Found 307.1222; mp. 73.0-75.0 ℃.

(*E*)-1-(Diphenylphosphoryl)-3-phenylprop-1-ene (2i):



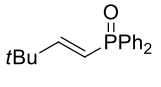
53% yield (Method C); White powder; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.62 (ddd, *J* = 6.0, 2.4, 1.8 Hz, 2H), 6.21 (ddt, *J* = 24.0, 16.8, 1.8 Hz, 1H), 6.88 (ddt, *J* = 18.6, 16.8, 6.0 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.31 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.45 (ddd, *J* = 7.8, 7.2, 3.0 Hz, 4H), 7.52 (td, *J* = 7.2, 1.2 Hz, 2 H), 7.67 (ddd, *J* = 12.0, 7.8, 1.2 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 40.6 (d, *J* = 17.1 Hz), 123.3 (d, *J* = 102.0 Hz), 126.7, 128.5 (d, *J* = 11.6 Hz), 128.7, 128.9, 131.3 (d, *J* = 8.7 Hz), 131.7, 133.0 (d, *J* = 104.9 Hz), 137.5, 150.7 (d, *J* = 2.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.0; IR (ATR): 3410, 3055, 3025, 2993, 2967, 2937, 1632, 1618, 1601, 1495, 1485, 1454, 1439, 1180, 1120, 1108, 1072, 1001, 852, 776, 745, 720, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{19}OP$ $[M+Na]^+$ 341.1066, Found 341.1065; mp. 125.0-127.0 ℃.

(*E*)-1-(Diphenylphosphoryl)-6-(methoxymethyl)oxyhex-1-ene (2j):



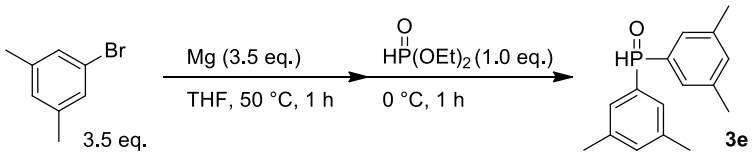
46% yield (Method C); White powder; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.55-1.67 (m, 4H), 2.31-2.38 (m, 2H), 3.34 (s, 3H), 3.53 (t, *J* = 6.6 Hz, 2H), 4.60 (s, 2H), 6.25 (ddt, *J* = 24.6, 16.8, 1.2 Hz, 1H), 6.74 (ddt, *J* = 19.2, 16.8, 6.6 Hz, 1H), 7.42-7.49 (m, 4H), 7.49-7.55 (m, 2H), 7.69 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.6, 29.2, 34.1 (d, *J* = 15.8 Hz), 55.1, 67.2, 96.3, 122.0 (d, *J* = 102.0 Hz), 128.4 (d, *J* = 11.4 Hz), 131.2 (d, *J* = 10.1 Hz), 131.6 (d, *J* = 2.9 Hz), 133.2 (d, *J* = 104.9 Hz), 152.2; ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.9; IR (ATR): 3435, 3056, 2990, 2937, 2877, 2832, 1631, 1438, 1187, 1146, 1119, 1107, 1071, 1041, 998, 917, 809, 748, 720, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{25}O_3P$ $[M+Na]^+$ 367.1434, Found 367.1433; mp. 59.0-61.0 ℃.

(*E*)-1-(Diphenylphosphoryl)-3,3-dimethylbut-1-ene (2k):



69% yield (Method B); White powder; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.11 (s, 9H), 6.11 (dd, *J* = 24.0, 16.8 Hz, 1H), 6.77 (dd, *J* = 19.8, 16.8 Hz, 1H), 7.44-7.49 (m, 4H), 7.50-7.55 (m, 2H), 7.68 (ddd, *J* = 12.0, 8.4, 1.2 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.6, 35.2 (d, *J* = 15.9 Hz), 116.3 (d, *J* = 103.5 Hz), 128.5 (d, *J* = 11.4 Hz), 131.2 (d, *J* = 10.1 Hz), 133.3 (d, *J* = 104.9 Hz), 162.3; ^{31}P NMR (243 MHz, $CDCl_3$) δ 24.1; IR (ATR): 3341, 3054, 3018, 2964, 2929, 2900, 2867, 1644, 1605, 1486, 1439, 1270, 1245, 1180, 1119, 1105, 1073, 1033, 1006, 828, 820, 745, 721, 711, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{21}OP$ $[M+Na]^+$ 307.1222, Found 307.1222; mp. 163.0-165.0 ℃.

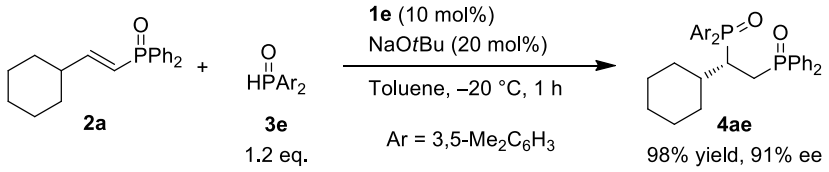
Preparation of Diarylphosphine Oxides 3[3]



Synthesis of **3e** is representative.

To a mixture of magnesium (0.43 g, 17.5 mmol) and THF (10 mL) was added a solution of 1-bromo-3,5-dimethylbenzene (2.4 mL, 17.5 mmol) in THF (10 mL) dropwise with a dropping funnel at 50 °C and the resulting mixture was stirred for 1 h. After cooled to 0 °C, a solution of diethyl phosphite (0.65 mL, 5.0 mmol) in THF (10 mL) was added dropwise with a dropping funnel at 0 °C. After stirring at 0 °C for 1 h, the reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 1:1) followed by recrystallization from a hexane/AcOEt mixture to afford **3e** (0.82 g, 3.2 mmol, 64%) as a white powder.

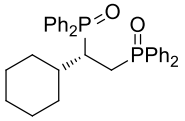
General Procedure for Hydrophosphinylation of 1-Alkenylphosphine Oxides Catalyzed By a Chiral Ureate



The reaction of **2a** with **3e** is representative (Scheme 2).

To a solution of urea **1e** (6.9 mg, 0.010 mmol) in toluene (1.0 mL) was added a solution of NaO*t*Bu in THF (2.0 M, 10 μL, 0.020 mmol) at room temperature. The mixture was cooled to -20 °C and stirred for 10 min. Then, diarylphosphine oxide **3e** (31 mg, 0.12 mmol) was added at -20 °C. After stirring for 5 min, (*E*)-1-alkenyl(diphenyl)phosphine oxide **2a** (31 mg, 0.10 mmol) was added at -20 °C, and the reaction mixture was stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 50:1) to afford **4ae** (56 mg, 0.098 mmol, 98% yield, 91% ee) as a white powder. Recrystallization from a mixture of hexane and methanol improved the enantiomeric purity of **4ae** (> 99% ee, 24 mg from 32 mg of **4ae** with 91% ee).

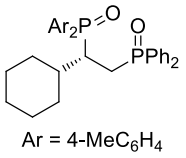
(*S*)-1-Cyclohexyl-1,2-bis(diphenylphosphoryl)ethane (4aa):



43 mg, 84% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 5.4 (minor), 7.1 (major) min; 76% ee; Optical rotation $[\alpha]_D^{28}$ = +7.6 (c 0.165, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.71-0.96 (m, 4H), 1.31-1.43 (m, 2H), 1.44-1.54 (m, 2H), 1.54-1.60 (m, 1H), 1.62-1.77 (m, 2H), 2.55-2.73 (m, 2H), 2.98-3.07 (m, 1H), 7.29 (ddd, *J* = 7.8, 7.2, 3.0 Hz, 2H), 7.33-7.40 (m, 4H), 7.40-7.45 (m, 4H), 7.45-7.53 (m, 4H), 7.72 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H), 7.76-7.83 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.9 (d, *J* = 68.9 Hz), 25.8, 26.7, 26.8, 30.7,

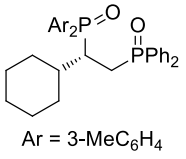
31.8 (d, *J* = 11.6 Hz), 36.7 (dd, *J* = 68.9, 4.4 Hz), 38.3, 128.47 (d, *J* = 11.4 Hz), 128.49 (d, *J* = 11.4 Hz), 128.60 (d, *J* = 11.6 Hz), 128.64 (d, *J* = 10.1 Hz), 130.6 (d, *J* = 10.1 Hz), 130.7 (d, *J* = 8.6 Hz), 130.9 (d, *J* = 8.6 Hz), 131.1 (d, *J* = 8.6 Hz), 131.4 (2C), 131.5 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 93.5 Hz), 133.0 (d, *J* = 93.3 Hz), 133.3 (d, *J* = 97.7 Hz), 133.7 (d, *J* = 97.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.4 (d, *J* = 42.8 Hz), 37.4 (d, *J* = 42.8 Hz); IR (ATR): 3425, 3095, 3054, 3024, 2987, 2925, 2850, 1591, 1486, 1438, 1410, 1343, 1182, 1117, 1100, 1071, 999, 818, 750, 718, 697, 662, 612 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{34}O_2P_2$ $[M+Na]^+$ 535.1926, Found 535.1926; mp. 246.0-248.0 ℃.

(*S*)-1-Cyclohexyl-2-(diphenylphosphoryl)-1-(di-*para*-tolyl)phosphorylethane (4ab):



47 mg, 86% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 6.2 (minor), 9.3 (major) min; 55% ee; Optical rotation $[\alpha]_D^{28}$ = +4.9 (c 0.170, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.77-0.99 (m, 4H), 1.29-1.43 (m, 2H), 1.47-1.54 (m, 2H), 1.54-1.60 (m, 1H), 1.66-1.77 (m, 2H), 2.32 (s, 3H), 2.36 (s, 3H), 2.59-2.69 (m, 2H), 2.93-3.02 (m, 1H), 7.13 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.22 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.28 (ddd, *J* = 7.8, 7.8, 3.0 Hz, 2H), 7.36 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H), 7.42 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.43-7.47 (m, 2H), 7.48-7.52 (m, 1H), 7.63 (dd, *J* = 10.2, 7.8 Hz, 2H), 7.66 (dd, *J* = 10.8, 7.8 Hz, 2H), 7.71 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.46, 21.50, 24.8 (d, *J* = 69.0 Hz), 25.8, 26.7, 26.9, 30.6, 31.9 (d, *J* = 10.1 Hz), 36.8 (dd, *J* = 67.5, 4.2 Hz), 38.3, 128.4 (d, *J* = 11.4 Hz), 128.6 (d, *J* = 11.6 Hz), 129.2 (d, *J* = 12.9 Hz), 129.3 (d, *J* = 12.9 Hz), 129.6 (d, *J* = 96.2 Hz), 129.9 (d, *J* = 97.7 Hz), 130.64 (d, *J* = 10.1 Hz), 130.70 (d, *J* = 8.6 Hz), 130.9 (d, *J* = 8.6 Hz), 131.0 (d, *J* = 8.6 Hz), 131.3(d, *J* = 2.9 Hz), 131.6 (d, *J* = 2.9 Hz), 133.4 (d, *J* = 99.2 Hz), 134.0 (d, *J* = 97.7 Hz), 141.6 (d, *J* = 2.9 Hz), 141.8; ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.4 (d, *J* = 39.6 Hz), 37.8 (d, *J* = 39.6 Hz); IR (ATR): 3426, 3055, 3023, 2966, 2925, 2852, 1602, 1499, 1484, 1450, 1438, 1400, 1374, 1312, 1262, 1178, 1114, 1099, 1070, 1020, 998, 893, 808, 745, 722, 695, 658, 634 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{38}O_2P_2$ $[M+Na]^+$ 563.2239, Found 563.2239; mp. 235.0-238.0 ℃.

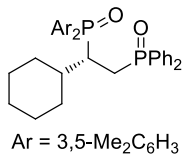
(*S*)-1-Cyclohexyl-2-(diphenylphosphoryl)-1-(di-*meta*-tolyl)phosphorylethane (4ad):



41 mg, 76% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 5.0 (minor), 6.6 (major) min; 90% ee; Optical rotation $[\alpha]_D^{27}$ = +15.7 (c 0.130, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.75-0.97 (m, 4H), 1.22-1.43 (m, 2H), 1.46-1.58 (m, 3H), 1.65-1.77 (m, 2H), 2.32 (s, 3H), 2.36 (s, 3H), 2.58-2.70 (m, 2H), 2.95-3.05 (m, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.23-7.33 (m, 5H), 7.35 (ddd, *J* = 10.8, 9.0, 1.2 Hz, 2H), 7.41 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.43-7.48 (m, 2H), 7.50 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.52-7.57 (m, 2H), 7.66 (d, *J* = 11.4 Hz, 2H), 7.71 (ddd, *J* = 11.4, 8.4, 1.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.4, 24.8 (d, *J* = 68.9 Hz), 25.8, 26.7, 26.9, 30.6, 32.0 (d, *J* = 10.1 Hz), 36.7 (dd, *J* = 67.5, 2.9 Hz), 38.2, 127.9 (d, *J* = 8.6 Hz), 128.0 (d, *J* = 8.7 Hz), 128.3 (d, *J* = 10.1 Hz), 128.4 (d, *J* = 11.6 Hz), 128.56 (d, *J* = 11.4 Hz), 128.59 (d, *J* = 11.4 Hz), 130.6 (d, *J* = 8.6 Hz), 130.7 (d, *J* = 8.7 Hz), 131.4 (d, *J* = 2.9 Hz), 131.56 (d, *J* = 8.7 Hz), 131.64 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 7.2 Hz), 132.2 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 2.9 Hz), 132.7 (d, *J* = 93.5 Hz), 132.9 (d, *J* = 93.3 Hz), 133.5 (d, *J* = 97.7 Hz), 133.9 (d, *J* = 97.7 Hz), 138.4 (d, *J* = 11.6 Hz), 138.5 (d, *J* = 11.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.3 (d, *J* = 42.8 Hz), 37.9 (d, *J* = 42.8 Hz); IR (ATR): 3437, 3054, 2926, 2852, 1593, 1483, 1450, 1438, 1408, 1317,

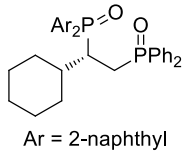
1262, 1182, 1117, 1088, 1068, 998, 870, 819, 788, 745, 733, 721, 699 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{38}O_2P_2$ $[M+Na]^+$ 563.2239, Found 563.2239; mp. 213.0-216.0 ℃.

(*S*)-1-(Bis(3,5-dimethylphenyl)phosphoryl)-1-cyclohexyl-2-(diphenylphosphoryl)ethane (4ae):



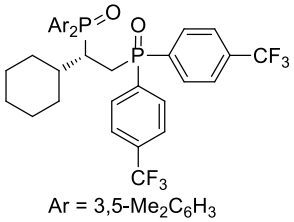
56 mg, 98% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 4.0 (minor), 4.9 (major) min; 91% ee; Optical rotation $[\alpha]_D^{27}$ = +12.0 (c 0.190, $CHCl_3$), $[\alpha]_D^{27}$ = +10.8 (c 0.05, $CHCl_3$) after enhancement of enantiomeric purity (>99% ee); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.75-0.97 (m, 4H), 1.22-1.33 (m, 1H), 1.35-1.43 (m, 1H), 1.46-1.80 (m, 5H), 2.28 (s, 6H), 2.32 (s, 6H), 2.58-2.72 (m, 2H), 2.96-3.05 (m, 1H), 7.00 (s, 1H), 7.08 (s, 1H), 7.27 (ddd, *J* = 8.4, 7.2, 3.0 Hz, 2H), 7.33 (ddd, *J* = 10.8, 8.4, 1.8 Hz, 2H), 7.38-7.42 (m, 1H), 7.41 (d, *J* = 12.0 Hz, 2H), 7.44 (d, *J* = 10.2 Hz, 2H), 7.43-7.48 (m, 2H), 7.48-7.52 (m, 1H), 7.71 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.3, 24.7 (d, *J* = 67.5 Hz), 25.9, 26.7, 26.9, 30.4, 32.2 (d, *J* = 11.4 Hz), 36.6 (dd, *J* = 67.5, 4.4 Hz), 38.1, 128.3 (d, *J* = 11.4 Hz), 128.5 (d, *J* = 8.7 Hz), 128.6 (d, *J* = 11.6 Hz), 128.7 (d, *J* = 8.7 Hz), 130.4 (d, *J* = 8.6 Hz), 130.8 (d, *J* = 10.1 Hz), 131.3, 131.6 (d, *J* = 2.9 Hz), 132.66 (d, *J* = 93.3 Hz), 132.72 (d, *J* = 94.8 Hz), 133.2 (d, *J* = 3.0 Hz), 133.3, 133.7 (d, *J* = 99.2 Hz), 134.0 (d, *J* = 97.7 Hz), 138.2 (d, *J* = 11.4 Hz), 138.3 (d, *J* = 11.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.2 (d, *J* = 42.8 Hz), 38.4 (d, *J* = 42.8 Hz); IR (ATR): 3427, 3055, 3025, 2925, 2853, 1600, 1485, 1453, 1438, 1418, 1378, 1273, 1182, 1121, 1102, 1071, 1044, 997, 870, 850, 818, 749, 735, 721, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{36}H_{42}O_2P_2$ $[M+Na]^+$ 591.2552, Found 591.2552; mp. 256.0-258.0 ℃.

(*S*)-1-Cyclohexyl-1-(di(2-naphthyl)phosphoryl)-2-(diphenylphosphoryl)ethane (4af):



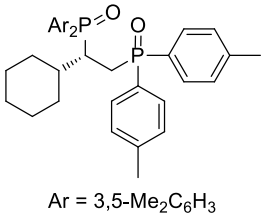
45 mg, 74% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 20.4 (minor), 33.9 (major) min; 25% ee; Optical rotation $[\alpha]_D^{27}$ = +12.0 (c 0.090, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.74-0.91 (m, 3H), 0.94-1.05 (m, 1H), 1.32-1.41 (m, 2H), 1.44-1.55 (m, 2H), 1.65-1.71 (m, 1H), 1.76-1.88 (m, 2H), 2.69-2.83 (m, 2H), 3.29-3.38 (m, 1H), 6.98 (ddd, *J* = 7.8, 7.8, 3.0 Hz, 2H), 7.18 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.22 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H), 7.42-7.46 (m, 2H), 7.47-7.58 (m, 5H), 7.70 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H), 7.75-7.82 (m, 4H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.87-7.91 (m, 2H), 7.93 (d, *J* = 7.8 Hz, 1H), 8.49 (d, *J* = 12.0 Hz, 1H), 8.52 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.8 (d, *J* = 67.5 Hz), 25.8, 26.6, 26.8, 30.6, 32.0 (d, *J* = 10.1 Hz), 36.4 (dd, *J* = 67.5, 4.2 Hz), 38.6, 125.7 (d, *J* = 11.6 Hz), 125.8 (d, *J* = 10.1 Hz), 126.7, 126.9, 127.7, 127.8, 127.96, 128.03, 128.2 (d, *J* = 11.4 Hz), 128.4 (d, *J* = 10.1 Hz), 128.59 (d, *J* = 11.4 Hz), 128.63 (d, *J* = 11.4 Hz), 128.9, 129.0, 129.9 (d, *J* = 94.8 Hz), 130.2 (d, *J* = 94.8 Hz), 130.3 (d, *J* = 8.6 Hz), 130.7 (d, *J* = 10.1 Hz), 131.2 (d, *J* = 2.9 Hz), 131.7, 132.5 (d, *J* = 12.9 Hz), 132.6 (d, *J* = 12.9 Hz), 132.7, 132.99 (d, *J* = 7.1 Hz), 133.01 (d, *J* = 99.2 Hz), 133.2 (d, *J* = 7.1 Hz), 133.8 (d, *J* = 97.7 Hz), 134.5 (d, *J* = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.3 (d, *J* = 39.6 Hz), 37.8 (d, *J* = 39.6 Hz); IR (ATR): 3426, 3055, 2964, 2927, 2852, 1627, 1591, 1500, 1450, 1438, 1341, 1271, 1181, 1134, 1118, 1086, 859, 820, 745, 718, 696, 658, 615 cm^{-1}; HRMS (ESI) Calcd for $C_{40}H_{38}O_2P_2$ $[M+Na]^+$ 635.2239, Found 635.2239; mp. 254.0-256.0 ℃.

(*S*)-1-(Bis(3,5-dimethylphenyl)phosphoryl)-2-(bis(4-trifluoromethylphenyl)phosphoryl)-1-cyclohexylethane (4be):



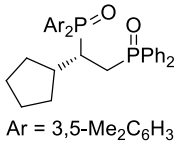
42 mg, 60% yield; White powder; SFC analysis DAICEL Chiralpak IA-3/SFC 4.6×150 mm (CO_2/MeOH = 95/5, 3.0 mL/min, 220 nm, 40 °C) 3.2 (major), 4.9 (minor) min; 93% ee; Optical rotation $[\alpha]_D^{28}$ = +17.2 (c 0.135, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.81-1.05 (m, 4H), 1.18-1.29 (m, 1H), 1.42-1.51 (m, 1H), 1.58-1.76 (m, 4H), 1.82-1.89 (m, 1H), 2.21 (s, 6H), 2.33 (s, 6H), 2.55-2.65 (m, 1H), 2.84-2.95 (m, 1H), 2.98-3.07 (m, 1H), 6.88 (s, 1H), 7.10 (s, 1H), 7.34 (d, *J* = 10.2 Hz, 2H), 7.39 (d, *J* = 10.8 Hz, 2H), 7.49-7.54 (m, 4H), 7.72 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.82 (dd, *J* = 10.8, 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ21.1, 21.3, 23.7 (d, *J* = 70.4 Hz), 25.8, 26.3, 26.7, 29.7, 32.4 (d, *J* = 11.6 Hz), 36.4 (dd, *J* = 67.5, 4.4 Hz), 38.3, 123.4 (qd, *J* = 271.5, 2.9 Hz), 125.1 (dq, *J* = 11.6, 4.4 Hz), 125.7 (dq, *J* = 11.6, 4.4 Hz), 128.5 (d, *J* = 7.2 Hz), 130.7 (d, *J* = 8.6 Hz), 130.8 (d, *J* = 8.7 Hz), 131.9 (d, *J* = 94.8 Hz), 132.2 (d, *J* = 93.3 Hz), 133.2 (q, *J* = 33.0 Hz), 133.4, 133.5 (d, *J* = 2.9 Hz), 133.8 (qd, *J* = 33.2, 2.9 Hz), 136.9 (d, *J* = 94.8 Hz), 138.26, 138.35, 138.6 (d, *J* = 92.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ28.3 (d, *J* = 33.0 Hz), 37.4 (d, *J* = 33.0 Hz); IR (ATR): 3435, 3038, 2990, 2926, 2854, 1602, 1450, 1400, 1320, 1273, 1168, 1127, 1101, 1062, 1017, 871, 848, 819, 788, 755, 722, 707, 696, 665, 627, 605 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{40}F_6O_2P_2$ $[M+Na]^+$ 727.2300, Found 727.2300; mp. 246.0-248.0 ℃.

(*S*)-1-(Bis(3,5-dimethylphenyl)phosphoryl)-1-cyclohexyl-2-(di-*para*-tolylphosphoryl)ethane (4ce):



78% yield (NMR); White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 4.3 (minor), 5.7 (major) min; 89% ee; Optical rotation $[\alpha]_D^{27}$ = +24.9 (c 0.150, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.76-0.99 (m, 4H), 1.27-1.42 (m, 2H), 1.47-1.58 (m, 3H), 1.68-1.76 (m, 2H), 2.28 (s, 6H), 2.32 (s, 6H), 2.33 (s, 3H), 2.38 (s, 3H), 2.53-2.68 (m, 2H), 2.93-3.02 (m, 1H), 7.01 (s, 1H), 7.06 (dd, *J* = 7.8, 2.4 Hz, 2H), 7.08 (s, 1H), 7.19 (dd, *J* = 10.8, 7.8 Hz, 2H), 7.25 (dd, *J* = 7.8, 2.4 Hz, 2H), 7.40 (d, *J* = 11.4 Hz, 2H), 7.42 (d, *J* = 10.8 Hz, 2H), 7.57 (dd *J* = 10.8, 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ21.26, 21.28, 21.4, 21.5, 24.7 (d, *J* = 68.9 Hz), 25.9, 26.7, 26.9, 30.4, 32.1 (d, *J* = 10.1 Hz), 36.6 (dd, *J* = 67.5, 4.4 Hz), 38.1, 128.5 (d, *J* = 8.7 Hz), 128.7 (d, *J* = 10.1 Hz), 129.0 (d, *J* = 11.4 Hz), 129.2 (d, *J* = 12.9 Hz), 130.4 (d, *J* = 100.1 Hz), 130.5 (d, *J* = 10.1 Hz), 130.7 (d, *J* = 10.1 Hz), 130.8 (d, *J* = 103.5 Hz), 132.6 (d, *J* = 93.5 Hz), 132.7 (d, *J* = 93.3 Hz), 133.0, 133.2 (d, *J* = 2.9 Hz), 138.1 (d, *J* = 11.4 Hz), 138.2 (d, *J* = 11.6 Hz), 141.5 (d, *J* = 2.9 Hz), 141.9 (d, *J* = 3.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ30.7 (d, *J* = 42.8 Hz), 38.5 (d, *J* = 42.8 Hz); IR (ATR): 3436, 3038, 2980, 2924, 2853, 1652, 1602, 1449, 1418, 1272, 1183, 1118, 1100, 888, 871, 850, 809, 742, 728, 705, 651 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{46}O_2P_2$ $[M+Na]^+$ 619.2865, Found 619.2865; mp. 242.0-244.0 ℃.

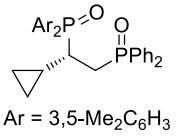
(*S*)-1-(Bis(3,5-dimethylphenyl)phosphoryl)-1-cyclopentyl-2-(diphenylphosphoryl)ethane (4ee):



46 mg, 83% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 3.8 (minor), 5.3 (major) min; 95% ee; Optical rotation $[\alpha]_D^{28}$ = -5.3 (c 0.170, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.13-1.41 (m, 6H), 1.48-1.56 (m, 1H), 2.11-2.19 (m, 1H), 2.22 (s, 6H), 2.33 (s, 6H), 2.41-2.49 (m, 1H), 2.76-2.87 (m, 1H), 3.35-3.44 (m, 1H), 6.90 (s, 1H), 7.08 (s, 1H), 7.19-7.26 (m, 4H), 7.36 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.44 (d,

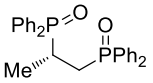
J = 11.4 Hz, 2H), 7.46 (d, *J* = 12.6 Hz, 2H), 7.41-7.50 (m, 3H), 7.68 (ddd, *J* = 11.4, 7.2, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.2, 21.3, 24.6, 24.9, 25.4 (d, *J* = 68.9 Hz), 29.5 (d, *J* = 4.2 Hz), 31.6, 33.9 (dd, *J* = 69.0, 4.4 Hz), 39.6, 128.2 (d, *J* = 11.4 Hz), 128.3 (d, *J* = 8.6 Hz), 128.6 (d, *J* = 11.4 Hz), 128.7 (d, *J* = 8.7 Hz), 130.2 (d, *J* = 8.7 Hz), 130.5 (d, *J* = 8.6 Hz), 131.1 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 2.9 Hz), 132.4 (d, *J* = 93.3 Hz), 132.9 (d, *J* = 93.3 Hz), 133.2 (d, *J* = 2.9 Hz), 133.3, 133.8 (d, *J* = 99.0 Hz), 134.3 (d, *J* = 97.7 Hz), 138.2 (d, *J* = 11.4 Hz), 138.3 (d, *J* = 11.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.8 (d, *J* = 32.8 Hz), 37.8 (d, *J* = 32.8 Hz); IR (ATR): 3435, 3055, 3024, 2956, 2919, 2868, 1633, 1601, 1482, 1452, 1438, 1418, 1378, 1308, 1273, 1179, 1120, 1104, 1070, 1040, 997, 943, 872, 851, 802, 747, 732, 696, 665, 621 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{40}O_2P_2$ $[M+Na]^+$ 577.2396, Found 577.2395; mp. 143.0-146.0 ℃.

(*S*)-1-(Bis(3,5-dimethylphenyl)phosphoryl)-1-cyclopropyl-2-(diphenylphosphoryl)ethane (4fe):



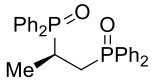
52 mg, 99% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 85/15, 3.0 mL/min, 220 nm, 40 °C) 5.2 (minor), 6.0 (major) min; 87% ee; Optical rotation $[\alpha]_D^{26}$ = -2.3 (c 0.160, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ -0.48--0.97 (m, 1H), -0.36--0.29 (m, 1H), -0.04--0.03 (m, 1H), 0.09-0.16 (m, 1H), 0.78-0.87 (m, 1H), 2.30 (s, 6H), 2.34 (s, 6H), 2.44-2.54 (m, 1H), 2.64-2.81 (m, 2H), 7.08 (s, 1H), 7.11 (s, 1H), 7.31 (ddd, *J* = 7.8, 7.2, 3.0 Hz, 2H), 7.39 (d, *J* = 11.4 Hz, 2H), 7.38-7.42 (m, 1H), 7.43-7.52 (m, 5H), 7.52 (d, *J* = 9.6 Hz, 2H), 7.85 (ddd, *J* = 12.0, 9.0, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 6.0 (d, *J* = 14.3 Hz), 6.6, 10.7, 21.16, 21.22, 29.8 (d, *J* = 69.0 Hz), 36.9 (dd, *J* = 68.9, 4.4 Hz), 128.38 (d, *J* = 11.6 Hz), 128.44 (d, *J* = 11.6 Hz), 128.6 (d, *J* = 8.6 Hz), 128.8 (d, *J* = 8.6 Hz), 130.1 (d, *J* = 10.1 Hz), 130.9 (d, *J* = 8.7 Hz), 131.3, 131.5 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 93.5 Hz), 132.4 (d, *J* = 94.8 Hz), 133.2 (d, *J* = 2.9 Hz), 133.4 (d, *J* = 97.7 Hz), 133.5, 134.7 (d, *J* = 99.2 Hz), 137.8 (d, *J* = 11.4 Hz), 138.5 (d, *J* = 11.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.7 (d, *J* = 42.8 Hz), 38.2 (d, *J* = 42.8 Hz); IR (ATR): 3429, 3080, 3056, 3008, 2976, 2965, 2919, 2863, 1743, 1658, 1601, 1489, 1438, 1368, 1273, 1219, 1178, 1121, 1029, 850, 738, 710, 697 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{36}O_2P_2$ $[M+Na]^+$ 549.2083, Found 549.2082; mp. 163.0-166.0 ℃.

(*S*)-1,2-Bis(diphenylphosphoryl)propane (4ga):



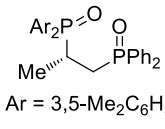
44 mg, 99% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 6.1 (minor), 7.8 (major) min; 65% ee; Optical rotation $[\alpha]_D^{27}$ = -12.8 (c 0.030, $CHCl_3$);^{1}H NMR (600 MHz, $CDCl_3$) δ 1.20 (dd, *J* = 17.4, 7.2 Hz, 2H), 2.44-2.62 (m, 2H), 2.92-3.03 (m, 1H), 7.38-7.47 (m, 8H), 7.47-7.57 (m, 6H), 7.68-7.76 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.6 (d, *J* = 2.9 Hz), 26.8 (dd, *J* = 70.4, 4.4 Hz), 28.7 (d, *J* = 67.5 Hz), 128.59 (d, *J* = 10.5 Hz), 128.67 (d, *J* = 11.6 Hz), 128.71 (d, *J* = 11.6 Hz), 128.9 (d, *J* = 11.6 Hz), 130.5 (d, *J* = 10.1 Hz), 130.7 (d, *J* = 10.1 Hz), 131.0 (d, *J* = 8.7 Hz, 2C), 131.03 (d, *J* = 95.4 Hz), 131.1 (d, *J* = 94.8 Hz), 131.76, 131.77 (d, *J* = 3.0 Hz), 131.8, 131.9 (d, *J* = 2.9 Hz), 132.6 (d, *J* = 99.1 Hz), 133.3 (d, *J* = 97.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.8 (d, *J* = 49.3 Hz), 38.2 (d, *J* = 49.3 Hz); IR (ATR): 3430, 3078, 3057, 2976, 2940, 2904, 1653, 1590, 1484, 1438, 1404, 1311, 1179, 1119, 1102, 1072, 1028, 998, 805, 745, 723, 695, 677 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{26}O_2P_2$ $[M+Na]^+$ 467.1300, Found 467.1300; mp. 169.0-171.0 ℃.

(*R*)-1,2-Bis(diphenylphosphoryl)propane (*ent*-4ga):



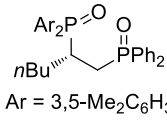
Prepared from commercially available (*R*)-prophos, 44 mg, 99% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 5.1 (major), 7.2 (major) min; >99% ee; Optical rotation $[\alpha]_D^{27}$ = +22.9 (c 0.150, $CHCl_3$).

(*S*)-2-(Bis(3,5-dimethylphenyl)phosphoryl)-1-(diphenylphosphoryl)propane (4ge):



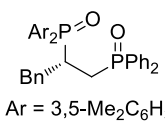
50 mg, 99% yield; White sticky oil; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 3.8 (minor), 4.3 (major) min; 94% ee; Optical rotation $[\alpha]_D^{28}$ = -8.6 (c 0.115, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.17 (dd, *J* = 16.8, 7.2 Hz, 3H), 2.31 (s, 12H), 2.43-2.52 (m, 1H), 2.54-2.63 (m, 1H), 2.91-3.02 (m, 1H), 7.09 (s, 1H), 7.12 (s, 1H), 7.34 (d, *J* = 11.4 Hz, 2H), 7.37 (d, *J* = 11.4 Hz, 2H), 7.39 (ddd, *J* = 7.8, 7.2, 2.4 Hz, 2H), 7.42-7.46 (m, 2H), 7.47-7.51 (m, 2H), 7.53 (ddd, *J* = 10.8, 7.8, 1.8 Hz, 2H), 7.71 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.7, 21.2, 21.3, 26.8 (dd, *J* = 68.9, 4.4 Hz), 28.7 (d, *J* = 68.9 Hz), 128.46 (d, *J* = 8.7 Hz), 128.51 (d, *J* = 8.4 Hz), 128.60 (d, *J* = 11.6 Hz), 128.61 (d, *J* = 11.6 Hz), 130.6 (d, *J* = 8.6 Hz, 2C), 131.0 (d, *J* = 94.8 Hz), 131.2 (d, *J* = 94.7 Hz), 131.6 (d, *J* = 2.9 Hz), 131.7, 133.0 (d, *J* = 104.9 Hz), 133.4 (d, *J* = 3.0 Hz), 133.5, 133.6 (d, *J* = 103.5 Hz), 138.3 (d, *J* = 11.6 Hz), 138.5 (d, *J* = 11.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.2 (d, *J* = 42.8 Hz), 38.4 (d, *J* = 42.8 Hz); IR (ATR): 3445, 3054, 3023, 2972, 2919, 2857, 1747, 1601, 1438, 1274, 1181, 1122, 1104, 1072, 1038, 996, 873, 851, 805, 745, 721, 711, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{34}O_2P_2$ $[M+Na]^+$ 523.1926, Found 523.1926.

(*S*)-2-(Bis(3,5-dimethylphenyl)phosphoryl)-1-(diphenylphosphoryl)hexane (4he):



54 mg, 99% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 90/10, 3.0 mL/min, 220 nm, 40 °C) 11.7 (minor), 14.4 (major) min; 96% ee; Optical rotation $[\alpha]_D^{28}$ = +19.8 (c 0.300, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.53 (t, *J* = 7.2 Hz, 3H), 0.77-0.87 (m, 2H), 0.89-0.99 (m, 1H), 1.19-1.28 (m, 1H), 1.39-1.49 (m, 1H), 1.63-1.77 (m, 1H), 2.31 (s, 12H), 2.56-2.63 (m, 2H), 2.94-3.04 (m, 1H), 7.08 (s, 2H), 7.35 (ddd, *J* = 8.4, 7.8, 3.0 Hz, 2H), 7.37 (d, *J* = 12.0 Hz, 2H), 7.42-7.52 (m, 8H), 7.74 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.3, 21.17, 21.25, 22.5, 27.5 (d, *J* = 69.0 Hz), 27.9, 29.0 (d, *J* = 4.2 Hz), 31.1 (dd, *J* = 68.9, 2.9 Hz), 128.45 (d, *J* = 10.1 Hz), 128.53 (d, *J* = 8.4 Hz), 128.6 (d, *J* = 8.6 Hz), 130.4 (d, *J* = 8.7 Hz), 130.7 (d, *J* = 8.7 Hz), 131.5, 131.7 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 93.5 Hz, 2C), 133.18 (d, *J* = 2.9 Hz), 133.35 (d, *J* = 2.9 Hz), 133.50 (d, *J* = 99.0 Hz), 133.51 (d, *J* = 96.2 Hz), 138.1 (d, *J* = 11.4 Hz), 138.4 (d, *J* = 12.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.7 (d, *J* = 46.2 Hz), 38.4 (d, *J* = 46.2 Hz); IR (ATR): 3436, 3055, 3023, 2955, 2932, 2862, 1601, 1485, 1465, 1438, 1416, 1379, 1311, 1273, 1181, 1120, 1071, 997, 872, 850, 812, 743, 716, 697 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{40}O_2P_2$ $[M+Na]^+$ 565.2396, Found 565.2396; mp. 172.0-174.0 ℃.

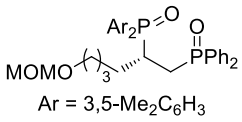
(*S*)-2-(Bis(3,5-dimethylphenyl)phosphoryl)-1-(diphenylphosphoryl)-3-phenylpropane (4ie):



52 mg, 90% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 80/20, 3.0 mL/min, 220 nm, 40 °C) 6.5 (minor), 7.7 (major) min; 95% ee; Optical rotation $[\alpha]_D^{27}$ = +14.2 (c 0.195, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.16 (s, 6H), 2.25 (s, 6H), 2.53-2.68 (m, 2H), 3.01-3.17 (m, 2H), 3.39-3.49 (m, 1H), 6.90 (s, 1 H), 6.90-6.96 (m, 5H), 7.00 (s, 1H), 7.15 (d, *J* = 11.4 Hz, 2H), 7.28-7.47 (m, 8H), 7.38 (d, *J* = 11.4 Hz, 2H), 7.55 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H); ^{13}C NMR (150

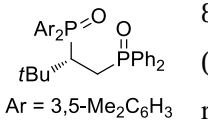
MHz $CDCl_3$) δ 21.1, 21.2, 28.0 (d, *J* = 67.5 Hz), 33.2 (dd, *J* = 67.5, 4.2 Hz), 34.5, 125.8, 127.6, 128.37 (d, *J* = 8.6 Hz), 128.40 (d, *J* = 11.6 Hz), 128.42 (d, *J* = 8.6 Hz), 128.5 (d, *J* = 11.6 Hz), 129.2, 130.4 (d, *J* = 10.1 Hz, 2C), 131.48 (d, *J* = 94.8 Hz), 131.4, 131.5, 132.0 (d, *J* = 94.8 Hz), 133.1 (d, *J* = 2.9 Hz), 133.3 (d, *J* = 2.9 Hz), 133.36 (d, *J* = 99.2 Hz), 133.8 (d, *J* = 99.2 Hz), 137.8 (d, *J* = 11.4 Hz), 138.3 (d, *J* = 11.6 Hz), 138.9 (d, *J* = 4.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.3 (d, *J* = 39.4 Hz), 36.9 (d, *J* = 39.4 Hz); IR (ATR): 3429, 3057, 3028, 2981, 2952, 2918, 2860, 1602, 1485, 1456, 1438, 1415, 1273, 1182, 1121, 1106, 1072, 1038, 1030, 997, 873, 850, 739, 718, 697 cm^{-1}; HRMS (ESI) Calcd for $C_{37}H_{38}O_2P_2$ $[M+Na]^+$ 599.2239, Found 599.2238; mp.82.0-84.0 ℃.

(*S*)-2-(Bis(3,5-dimethylphenyl)phosphoryl)-1-(diphenylphosphoryl)-6-(methoxymethyl)oxyhexane (4je):



60 mg, 99% yield; White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 90/10, 3.0 mL/min, 220 nm, 40 °C) 14.0 (minor), 15.4 (major) min; 97% ee; Optical rotation $[\alpha]_D^{27}$ = +16.7 (c 0.220, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.00-1.09 (m, 1H), 1.10-1.17 (m, 2H), 1.30-1.40 (m, 1H), 1.44-1.55 (m, 1H), 1.70-1.82 (m, 1H), 2.30 (s, 6H), 2.31 (s, 6H), 2.55-2.65 (m, 2H), 2.93-3.04 (m, 1H), 3.10-3.18 (m, 2H), 3.26 (s, 3H), 4.45 (s, 2H), 7.08 (s, 2H), 7.35 (ddd, *J* = 7.8, 7.8, 2.4 Hz, 2H), 7.37 (d, *J* = 10.8 Hz, 2H), 7.42 (d, *J* = 10.8 Hz, 2H), 7.43-7.53 (m, 6H), 7.73 (ddd, *J* = 11.4, 8.4, 1.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.18, 21.25, 23.6 (d, *J* = 4.2 Hz), 27.4 (d, *J* = 69.0 Hz), 28.2, 29.5, 31.2 (dd, *J* = 69.0, 4.4 Hz), 54.9, 67.2, 96.1, 128.3 (d, *J* = 10.1 Hz), 128.5 (d, *J* = 11.4 Hz), 128.56 (d, *J* = 10.1 Hz), 128.58 (d, *J* = 11.7 Hz), 130.4 (d, *J* = 8.6 Hz), 130.6 (d, *J* = 10.1 Hz), 131.5, 131.67 (d, *J* = 93.3 Hz), 131.71, 131.71 (d, *J* = 94.8 Hz), 133.31 (d, *J* = 97.7 Hz), 133.35 (d, *J* = 3.0 Hz), 133.40, 133.51 (d, *J* = 97.7 Hz), 138.2 (d, *J* = 11.4 Hz), 138.4 (d, *J* = 11.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.7 (d, *J* = 45.9 Hz), 38.1 (d, *J* = 45.9 Hz); IR (ATR): 3428, 3055, 2990, 2945, 2923, 2866, 2821, 1637, 1601, 1460, 1438, 1419, 1379, 1273, 1181, 1146, 1117, 1074, 1039, 998, 918, 872, 850, 817, 741, 716, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{36}H_{44}O_4P_2$ $[M+Na]^+$ 625.2607, Found 625.2606; mp. 139.0-142.0 ℃.

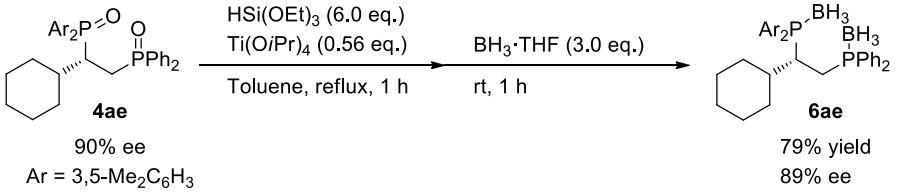
(*S*)-2-(Bis(3,5-dimethylphenyl)phosphoryl)-1-(diphenylphosphoryl)-3,3-dimethylbutane (4ke):



88% yield (NMR); White powder; SFC analysis DAICEL Chiralpak ID-3/SFC 4.6×150 mm (CO_2/MeOH = 85/15, 3.0 mL/min, 220 nm, 40 °C) 3.5 (minor), 4.2 (major) min; 49% ee; Optical rotation $[\alpha]_D^{28}$ = +8.8 (c 0.125, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.88 (s, 9H), 2.11 (s, 6H), 2.22 (s, 6H), 2.45 (dddd, *J* = 16.8, 9.0, 6.0, 6.0 Hz, 1H), 2.88 (dddd, *J* = 23.4, 16.8, 12.0, 3.6 Hz, 1H), 3.43 (dddd, *J* = 22.8, 6.0, 6.0, 3.6 Hz, 1H), 6.57 (s, 1H), 7.06 (s, 1H), 7.16-7.22 (m, 4H), 7.30-7.35 (m, 1H), 7.37-7.46 (m, 3H), 7.48 (d, *J* = 10.8 Hz, 2H), 7.61 (d, *J* = 11.4 Hz, 2H), 7.64 (ddd, *J* = 11.4, 8.4, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.2, 21.3, 25.8 (d, *J* = 67.5 Hz), 30.2 (d, *J* = 7.1 Hz), 35.4, 40.6 (dd, *J* = 67.5, 4.4 Hz), 127.9 (d, *J* = 11.6 Hz), 128.3 (d, *J* = 8.6 Hz), 128.5 (d, *J* = 11.6 Hz), 128.6 (d, *J* = 8.6 Hz), 129.6 (d, *J* = 10.1 Hz), 130.2 (d, *J* = 8.6 Hz), 130.8, 131.2 (d, *J* = 2.9 Hz), 132.7, 133.0, 133.5 (d, *J* = 94.8 Hz), 134.7 (d, *J* = 99.0 Hz), 135.3 (d, *J* = 91.8 Hz), 135.4 (d, *J* = 97.7 Hz), 138.0 (d, *J* = 11.6 Hz), 138.1 (d, *J* = 10.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.7 (d, *J* = 26.5 Hz), 36.7 (d, *J* = 26.5 Hz); IR (ATR): 3437, 3055, 2960, 2916, 2871, 1601, 1470, 1438, 1371, 1271, 1182, 1119, 1107, 1071, 1041, 997, 869, 849, 824, 750, 729, 699, 665 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{40}O_2P_2$ $[M+Na]^+$ 565.2396, Found 565.2396; mp. 221.0-224.0 ℃.

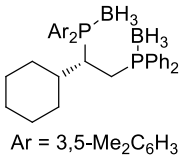
Procedure for Transformation of Diphosphine Dioxides 4

Transformation of 4ae into 6ae (Scheme 4)[4]



To a solution of **4ae** (28 mg, 0.049 mmol, 90% ee) in toluene (1.5 mL) were sequentially added triethoxysilane (54 μL, 0.30 mmol) and Ti(O*i*Pr)$_4$ (8.2 μL, 0.028 mmol) at room temperature. The mixture was heated at 120 °C for 1 h. After cooled to room temperature, BH_3·THF (0.16 mL, 0.15 mmol) was added. After stirring for 1 h, the resulting solution was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 2:1) to afford **6ae** (22 mg, 0.039 mmol, 79% yield, 89% ee) as a white powder.

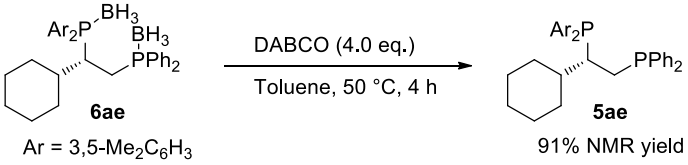
(*S*)-1-(Bis(3,5-dimethylphenyl)phosphino)-1-cyclohexyl-2-(diphenylphosphino)ethane borane complex (6ae)



30 mg, 57% yield; White powder; HPLC analysis DAICEL Chiralcel OD-3 4.6×250 mm (hexane/*i*PrOH = 90/10, 0.8 mL/min, 220 nm, 40 °C) 5.2 (major), 5.6 (minor) min; 89% ee; Optical rotation $[\alpha]_D^{27}$ = +49.3 (c 0.105, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.34-0.51 (m, 3H), 0.69-0.80 (m, 1H), 1.02-1.11 (m, 1H), 0.70-1.30 (br, 6H), 1.23-1.57 (m, 6H), 2.20 (dddd, *J* = 15.6, 15.6, 11.4, 1.2 Hz, 1H), 2.32 (s, 6H), 2.35 (s, 6H), 2.77-2.86 (m, 1H), 3.37-3.48 (m, 1H), 7.077 (s, 1H), 7.083 (s, 1H), 7.14 (ddd, *J* = 10.8, 8.4, 1.2 Hz, 2H), 7.25 (ddd, *J* = 7.8, 7.8, 2.4 Hz, 2H), 7.33-7.38 (m, 1H), 7.41 (d, *J* = 10.8 Hz, 2H), 7.47-7.51 (m, 2H), 7.52-7.54 (m, 1H), 7.54 (d, *J* = 10.8 Hz, 2H), 7.81 (ddd, *J* = 10.8, 8.4, 1.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.3, 21.4, 23.9 (dd, *J* = 31.5, 5.7 Hz), 25.7, 26.6 (2C), 30.9, 31.9 (d, *J* = 8.7 Hz), 34.8 (d, *J* = 31.5 Hz), 38.9, 128.6 (d, *J* = 10.1 Hz), 128.77 (d, *J* = 51.2 Hz), 128.80 (d, *J* = 10.1 Hz), 128.88 (d, *J* = 53.1 Hz), 128.95 (d, *J* = 51.8 Hz), 130.2 (d, *J* = 8.6 Hz), 130.4 (d, *J* = 8.6 Hz), 130.6, 131.1 (d, *J* = 57.5 Hz), 131.2 (d, *J* = 8.6 Hz), 131.7, 132.9, 133.1, 133.2 (d, *J* = 8.6 Hz), 138.2 (d, *J* = 10.1 Hz), 138.6 (d, *J* = 10.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.2, 22.9; IR (ATR): 3412, 3055, 3006, 2924, 2853, 2384, 2346, 2256, 1602, 1589, 1482, 1450, 1437, 1130, 1107, 1058, 1030, 996, 849, 823, 751, 737, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{36}H_{48}B_2P_2$ $[M+Na]^+$ 587.3310, Found 587.3310; mp. 171.0-174.0 °C.

Transformation of 6ae into 5ae (Scheme S3)

Scheme S3



A solution of **6ae** (28 mg, 0.050 mmol) in toluene (1.0 mL) and DABCO (22 mg, 0.20 mmol) was heated at 50 °C for 4 h. After cooled to room temperature, the resulting mixture was passed through a short pad of florisil® with toluene as an eluent under nitrogen stream, and the following evaporation provided **5ae** in 91% NMR yield

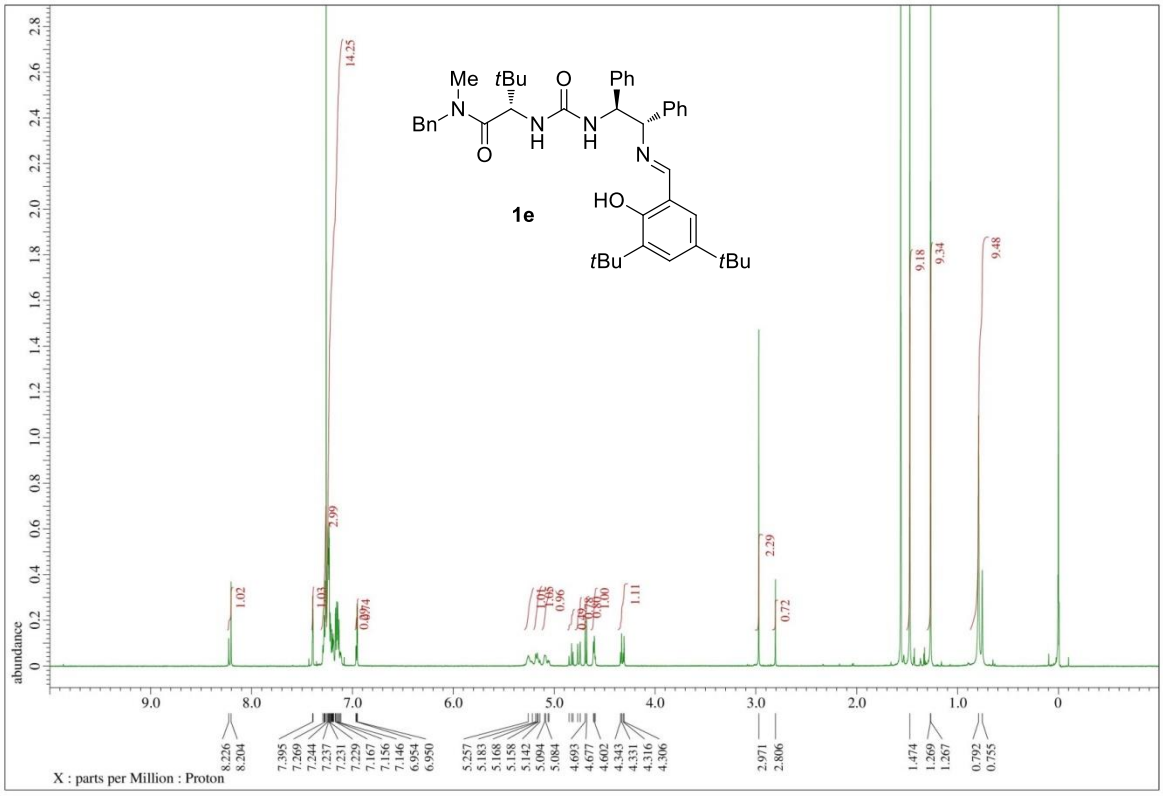
(trimethyl phosphate was used as an internal standard) as a white solid.

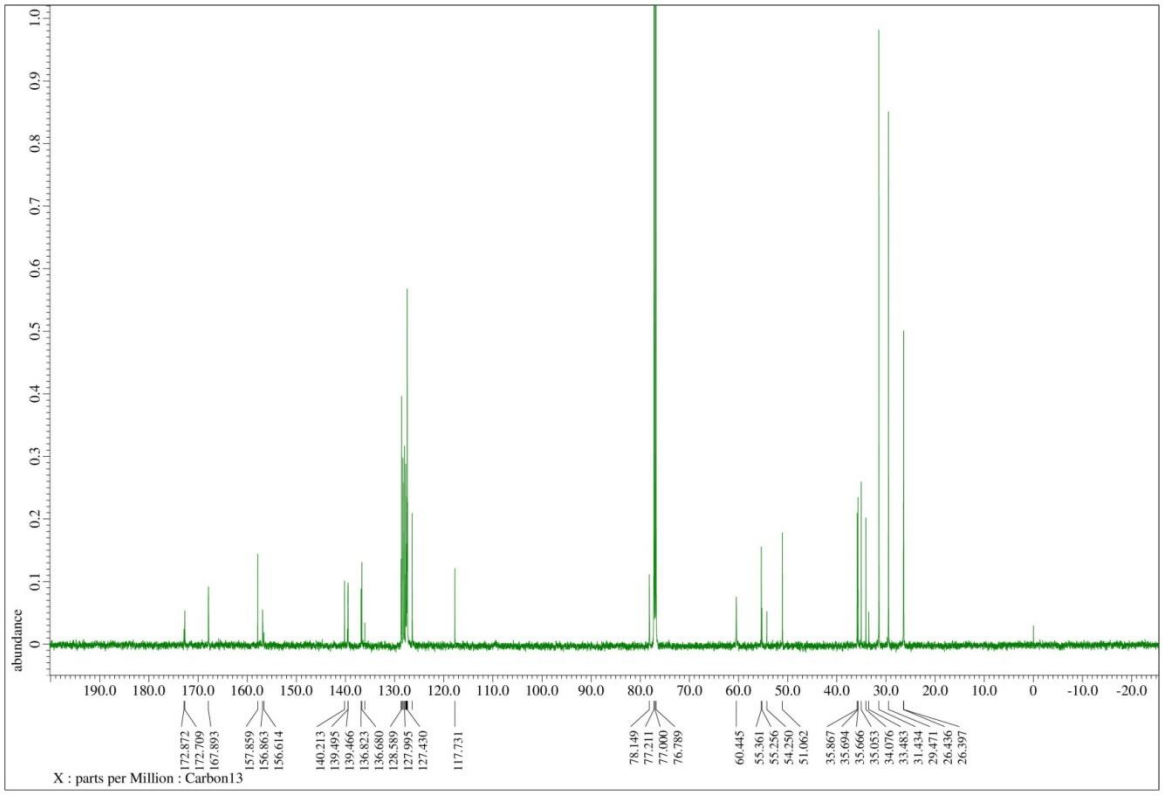
(*S*)-1-(Bis(3,5-dimethylphenyl)phosphino)-1-cyclohexyl-2-(diphenylphosphino)ethane (5ae)

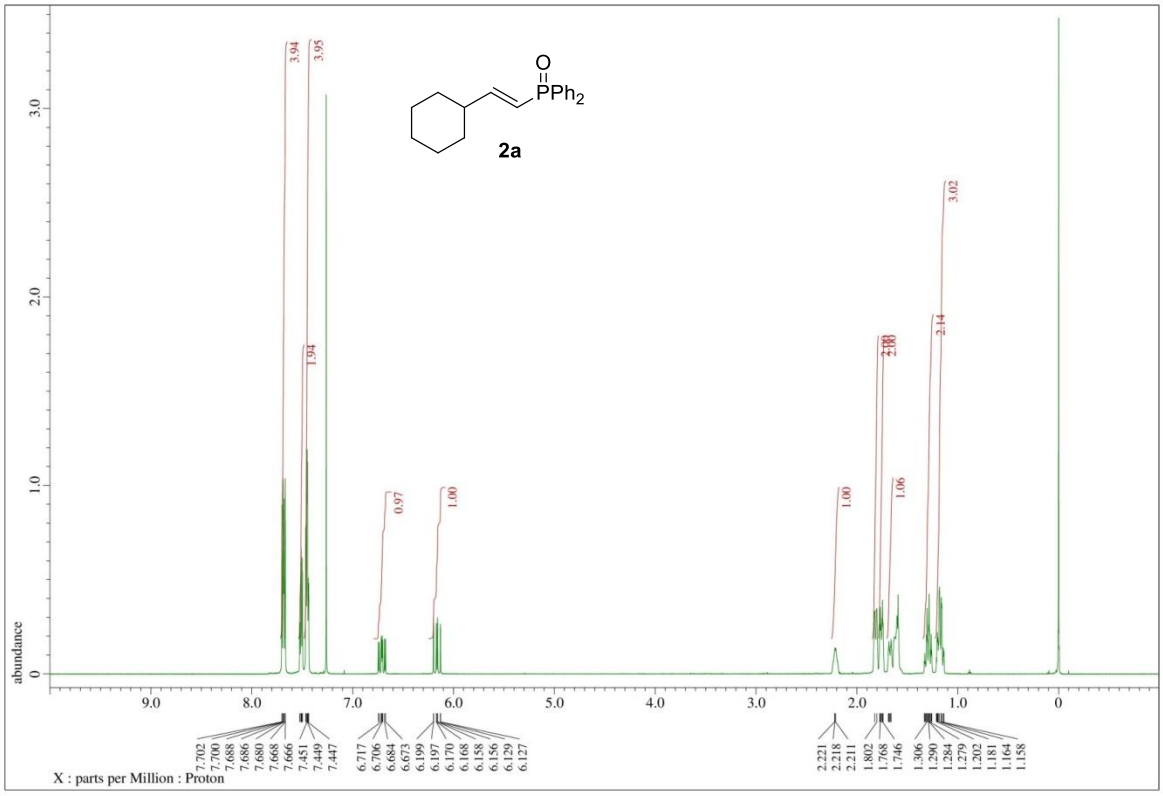
91% NMR yield; White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.02-1.17 (m, 3H), 1.29-1.39 (m, 1H), 1.52-1.73 (m, 6H), 1.79-1.89 (m, 1H), 2.01-2.15 (m, 2H), 2.22 (s, 6H), 2.25 (s, 6H), 2.23-2.30 (m, 1H), 6.89 (s, 1H), 6.93 (s, 1H), 6.95 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 7.20 (ddd, *J* = 7.2, 6.6, 1.2 Hz, 2H), 7.24-7.28 (m, 7H), 7.32 (td, *J* = 7.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.3, 26.5, 26.8, 27.1, 28.1 (dd, *J* = 14.0, 14.0 Hz), 30.9 (d, *J* = 8.6 Hz), 32.0 (dd, *J* = 10.1, 4.2 Hz), 38.1 (dd, *J* = 17.3, 10.1 Hz), 40.3 (dd, *J* = 14.4, 5.9 Hz), 128.1, 128.2 (d, *J* = 5.7 Hz), 128.3 (d, *J* = 7.1 Hz), 128.6, 130.1, 130.6, 130.8 (d, *J* = 18.8 Hz), 132.3 (d, *J* = 17.3 Hz), 132.5 (d, *J* = 21.6 Hz), 133.4 (d, *J* = 18.6 Hz), 137.0 (d, *J* = 14.4 Hz), 137.39 (d, *J* = 17.2 Hz), 137.43 (d, *J* = 15.9 Hz), 137.7 (d, *J* = 12.9 Hz), 138.4 (d, *J* = 14.4 Hz), 139.8 (d, *J* = 14.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ -4.7 (d, *J* = 16.3 Hz), -17.1 (d, *J* = 16.3 Hz).

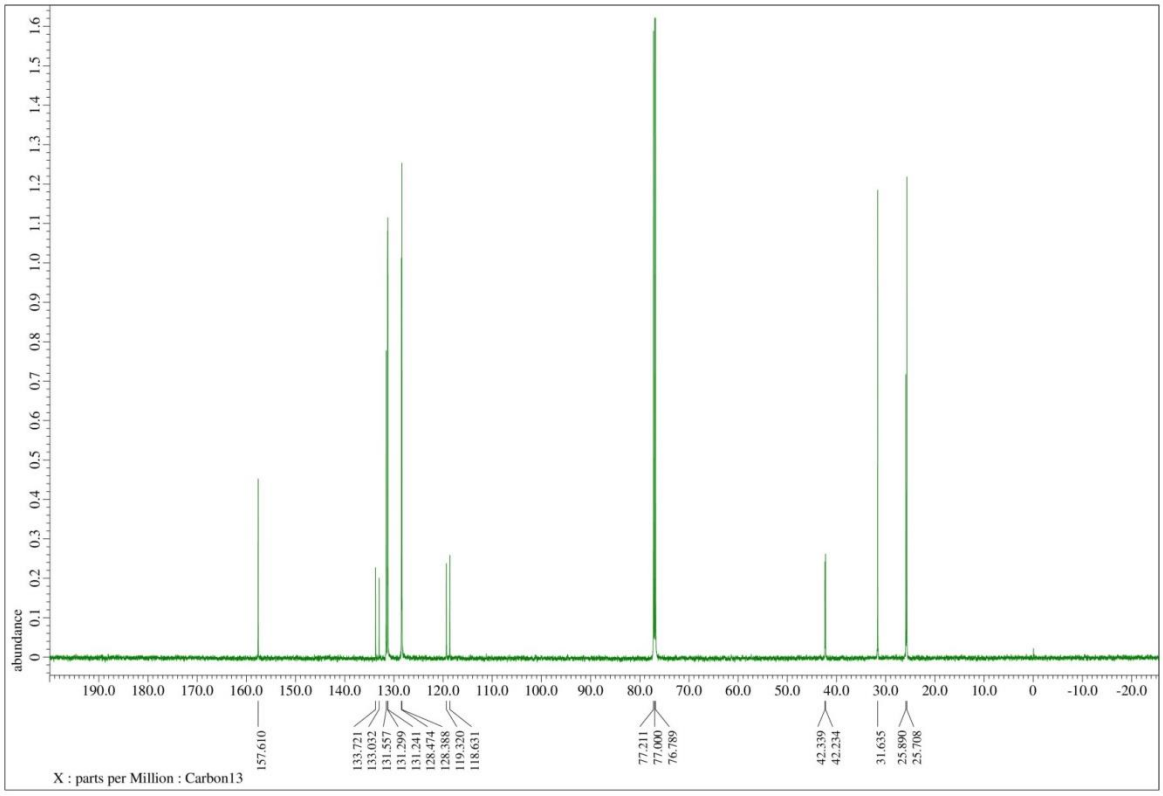
4. References

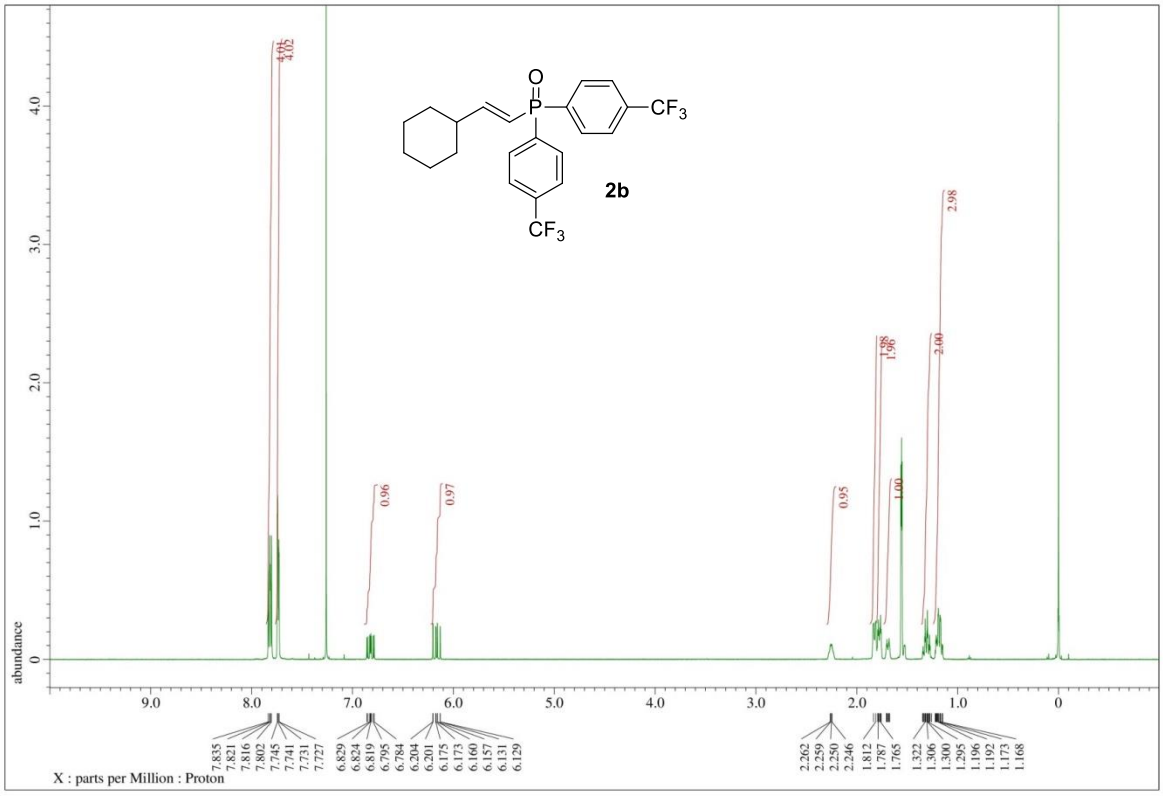
1. A. Kondoh, S. Ishikawa and M. Terada, *J. Am. Chem. Soc.*, 2020, **142**, 3724– 3728
2. V. Hornillos, C. Vila, E. Otten and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2015, **54**, 7867-7871.
3. M. Jin and M. Nakamura, *Chem. Lett.*, 2013, **42**, 1035-1037
4. A. Allen, Jr., L. Ma and W. Lin, *Tetrahedron Lett.*, 2002, **43**, 3707-3710.

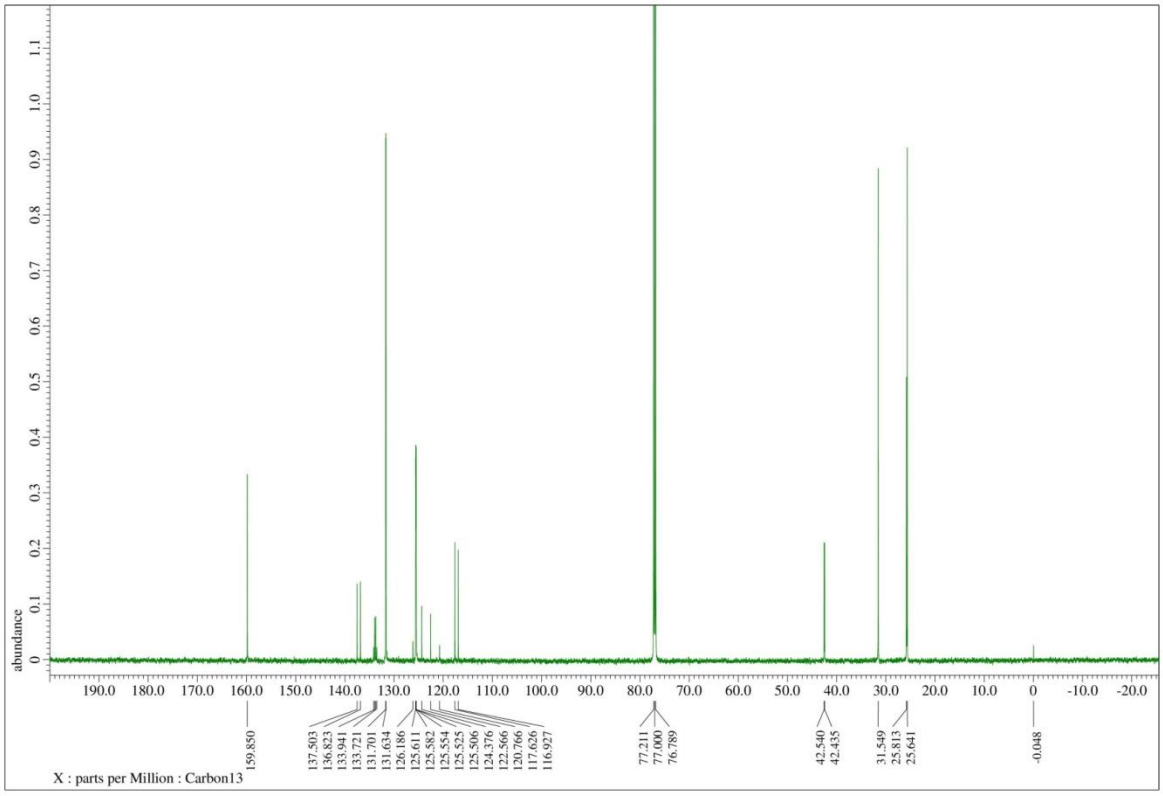

Me tBu O Ph
Bn N N N Ph
O H H N
HO
tBu tBu
1e
14.25
2.99
1.02
2.29
0.72
9.18
9.34
9.48
1.11
abundance
X : parts per Million : Proton

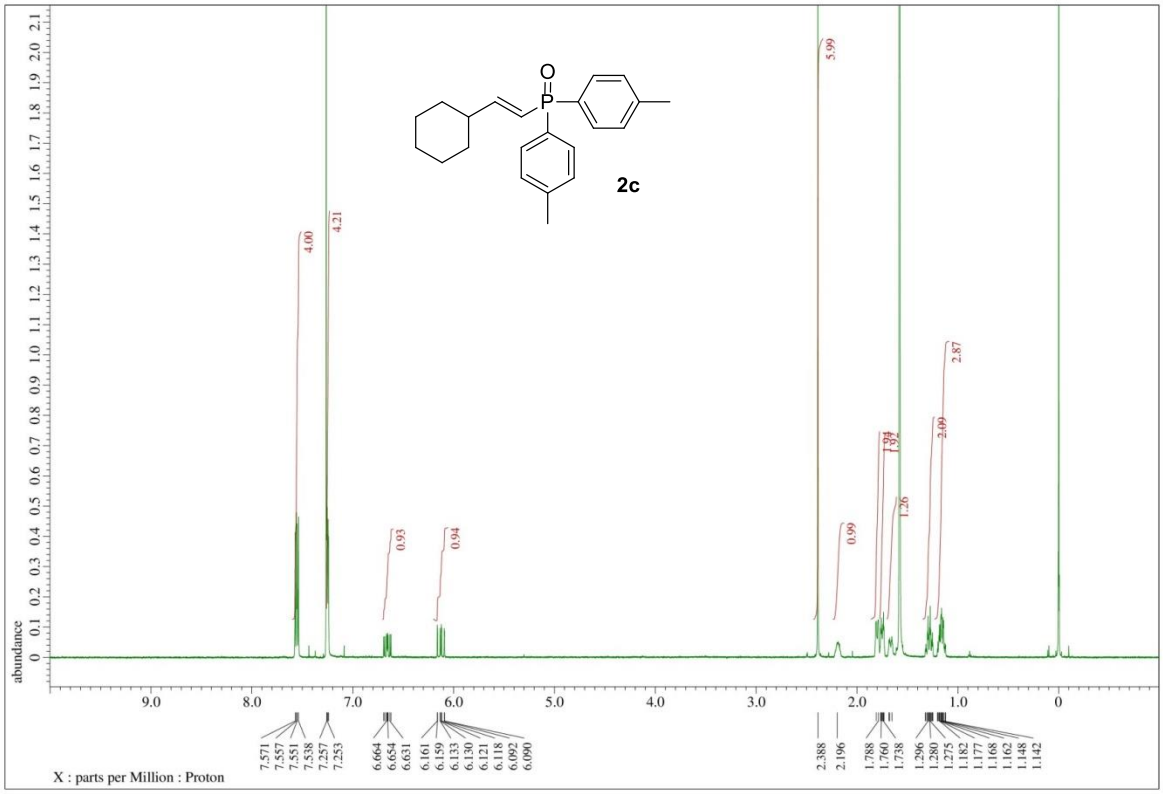

abundance
X : parts per Million : Carbon13

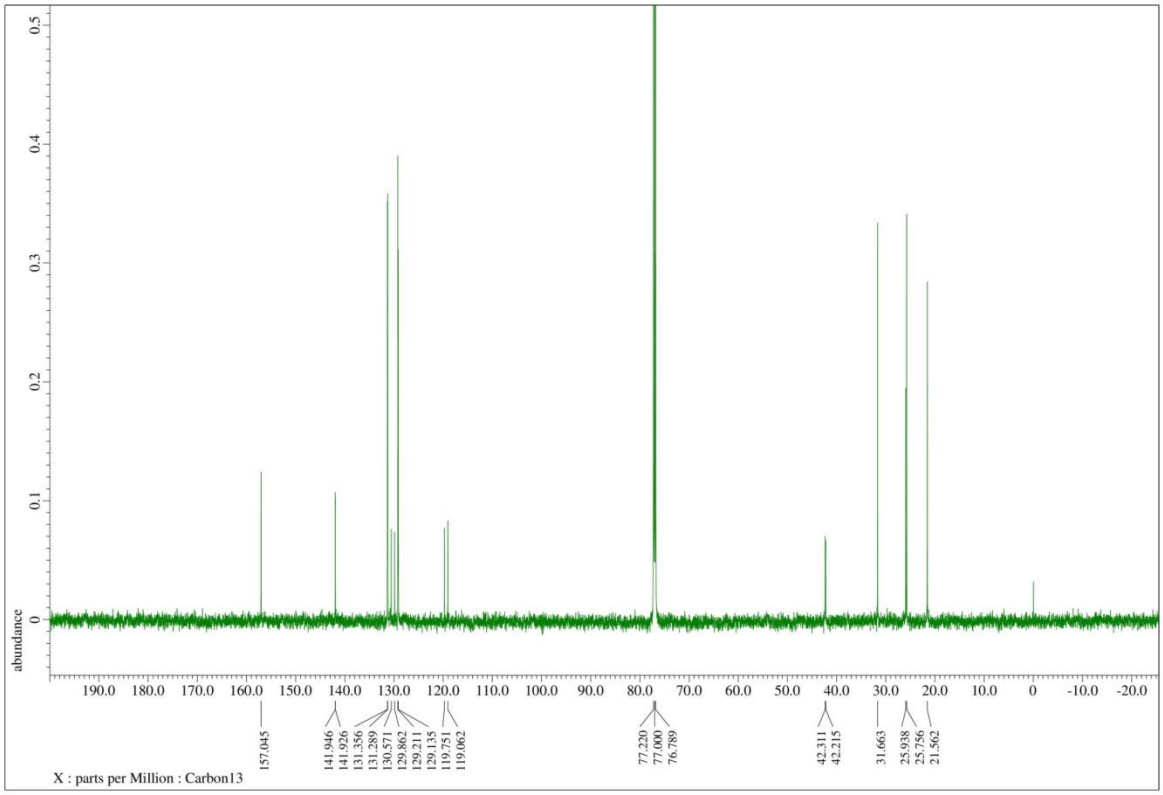

O
PPh2
2a
abundance
X : parts per Million : Proton

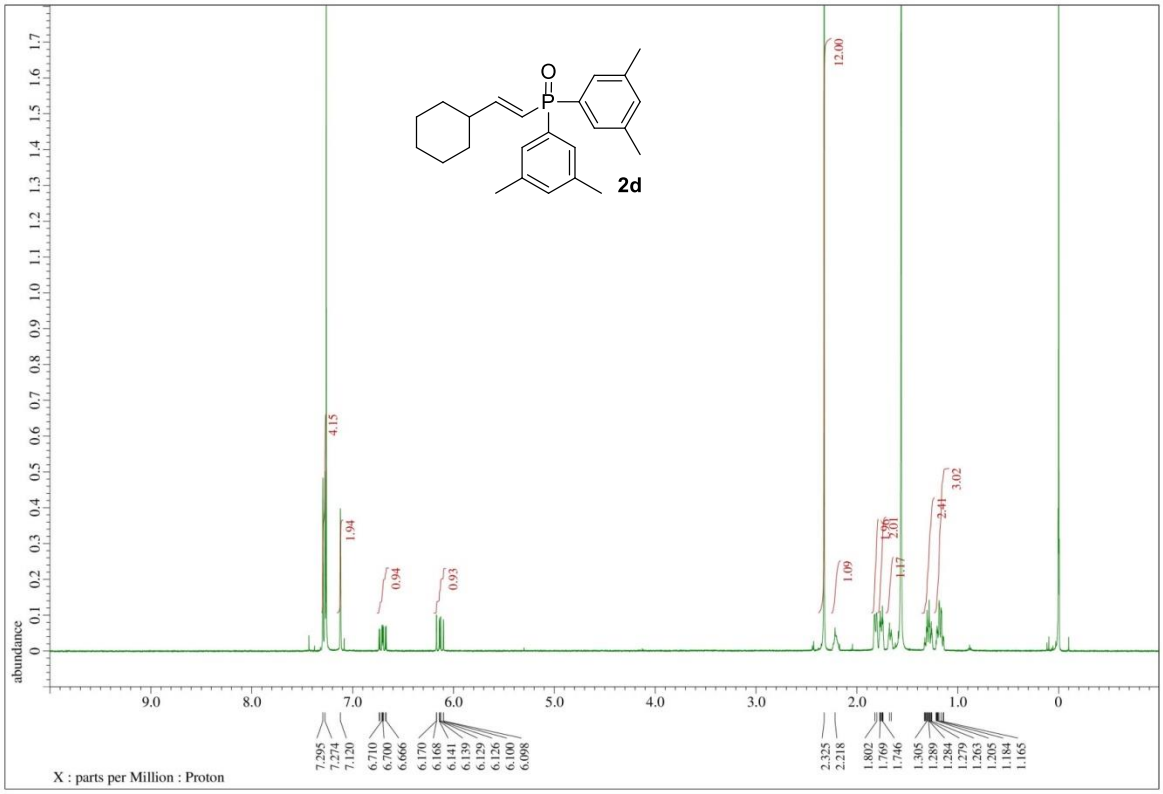

abundance
X : parts per Million : Carbon13

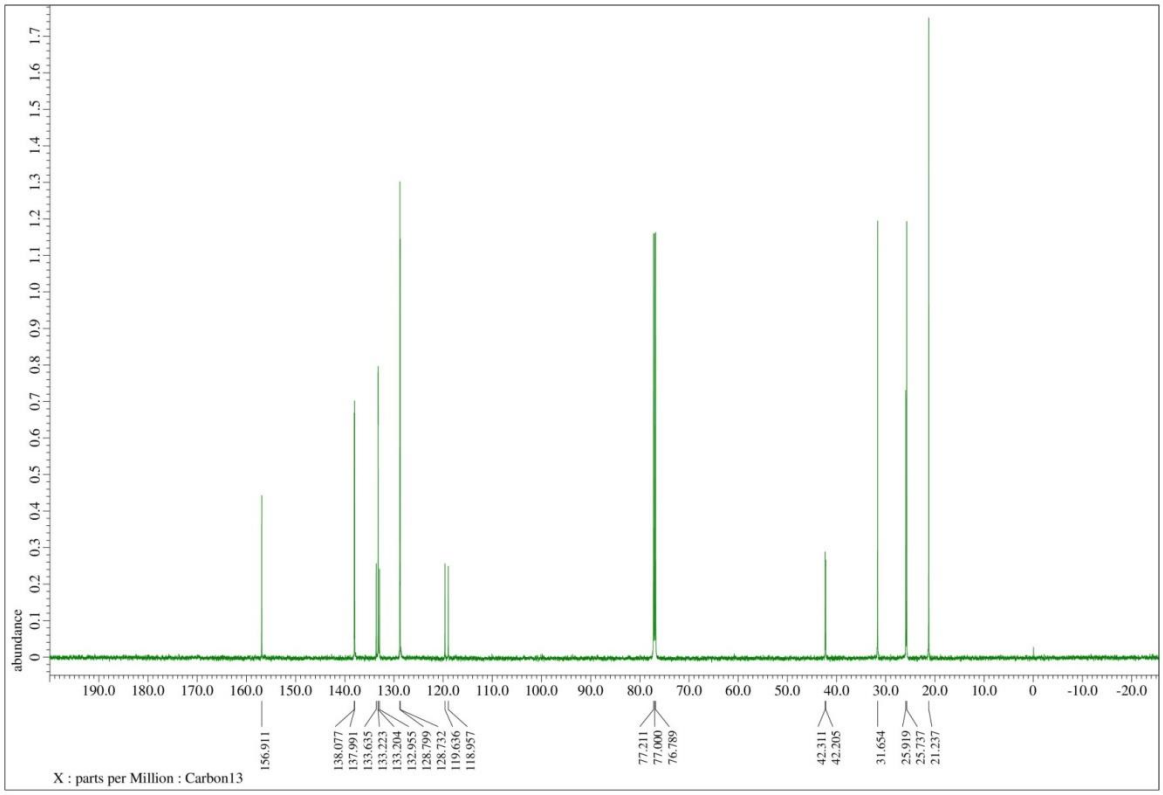

O
P
CF3
CF3
2b
abundance
X : parts per Million : Proton

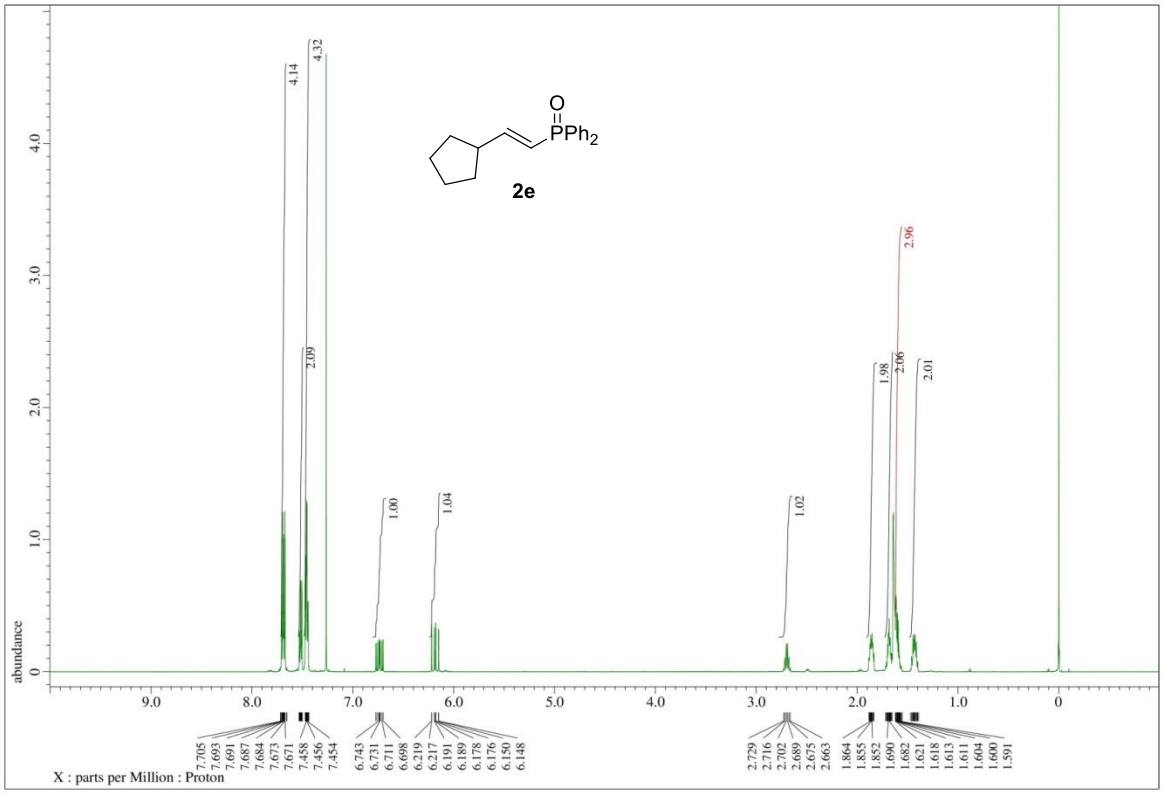

abundance
X : parts per Million : Carbon13

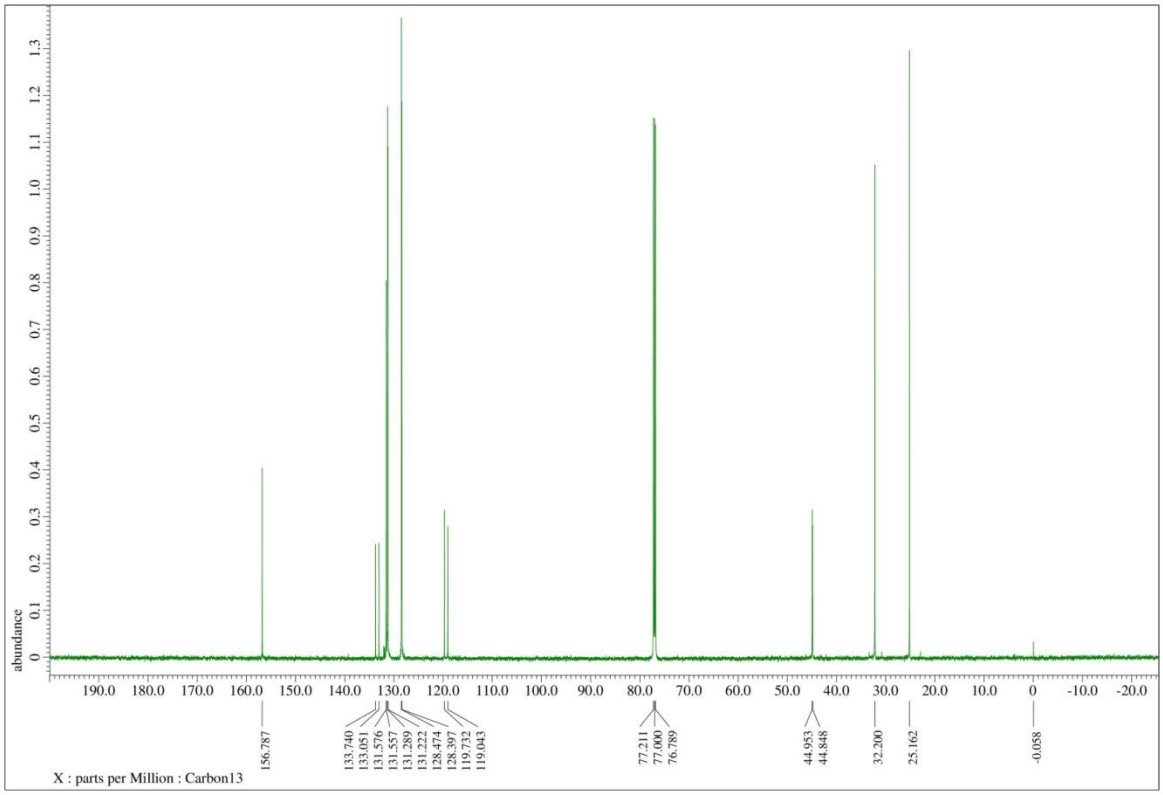

2c
abundance
X : parts per Million : Proton

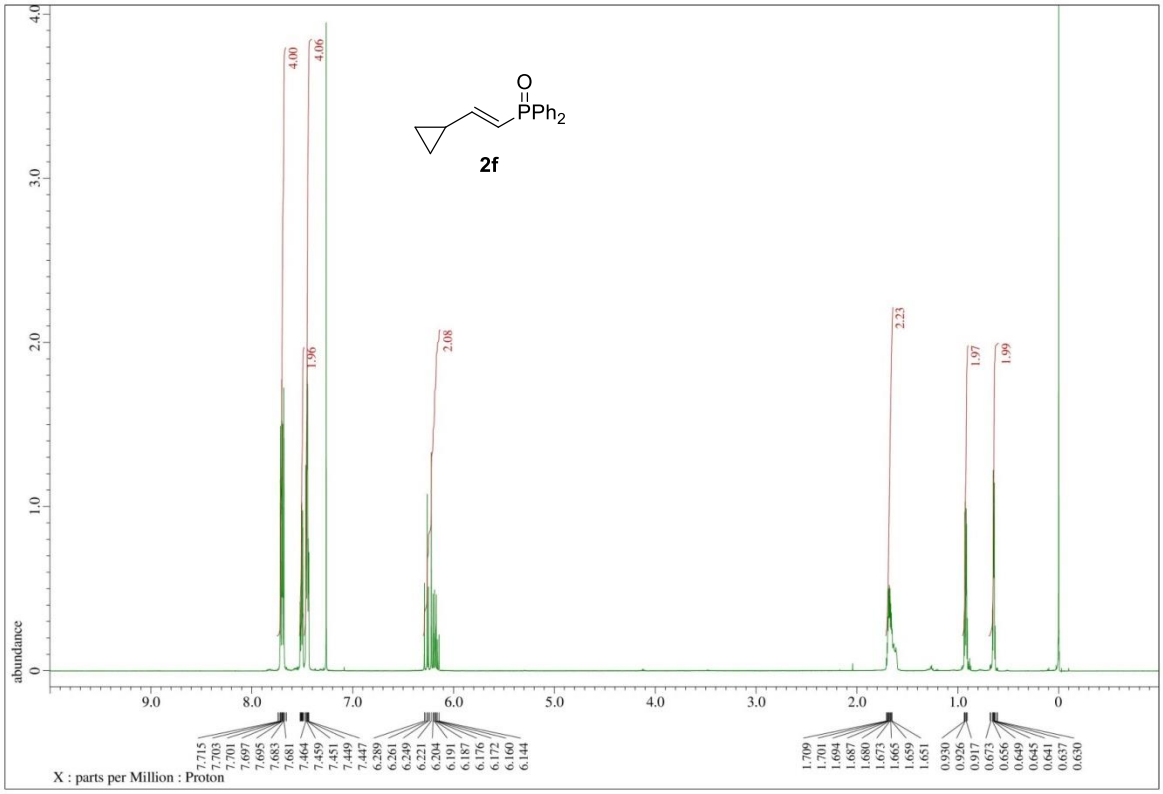

abundance
X : parts per Million : Carbon13

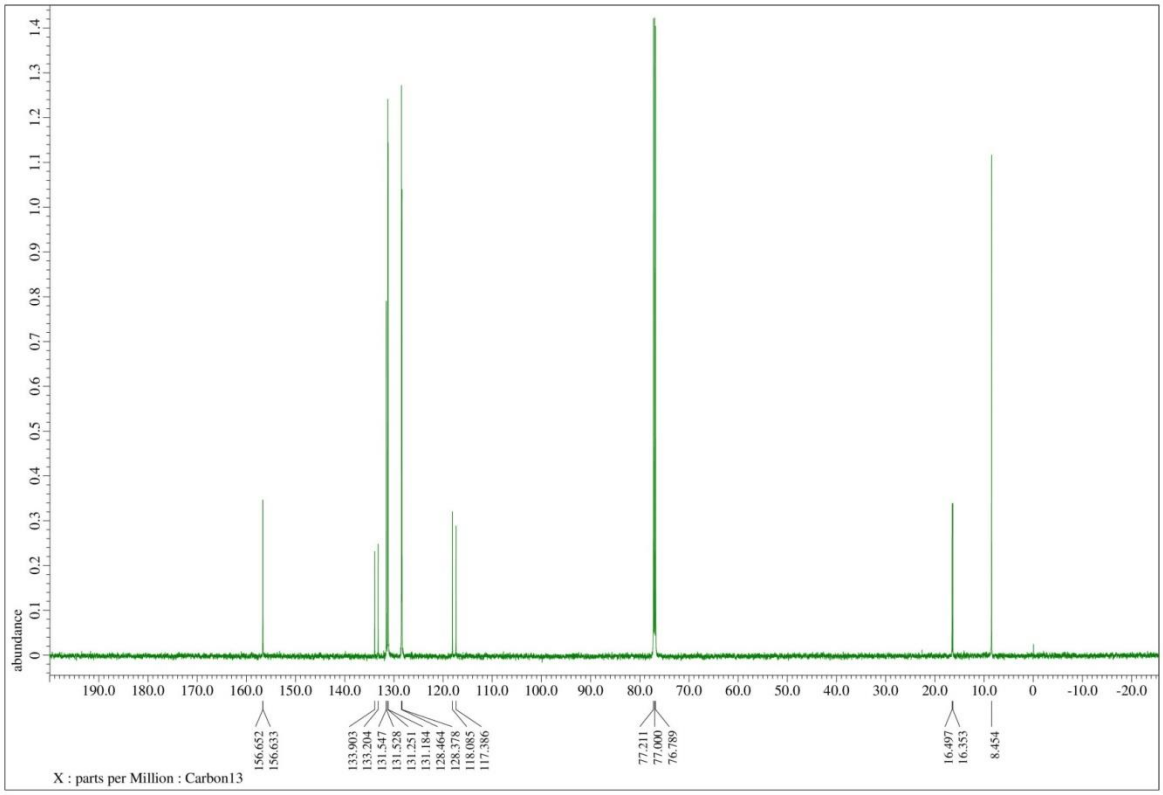

2d
abundance
X : parts per Million : Proton

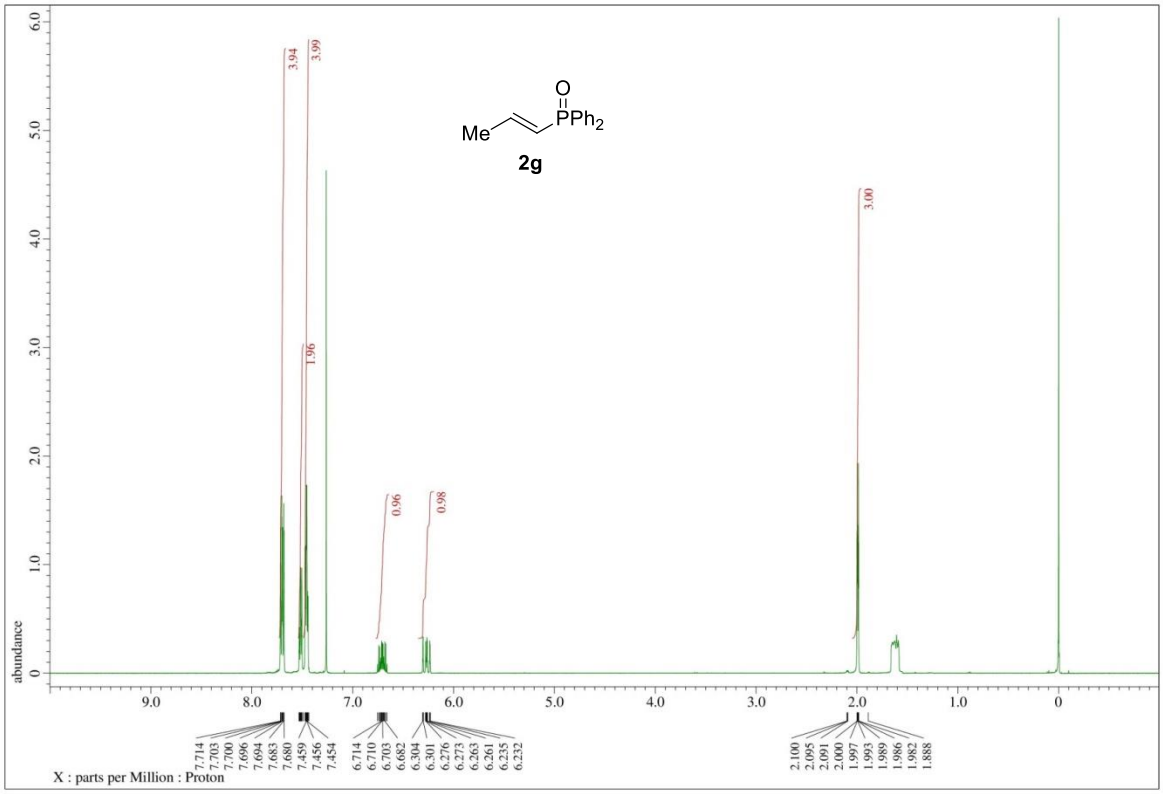

abundance
X : parts per Million : Carbon13

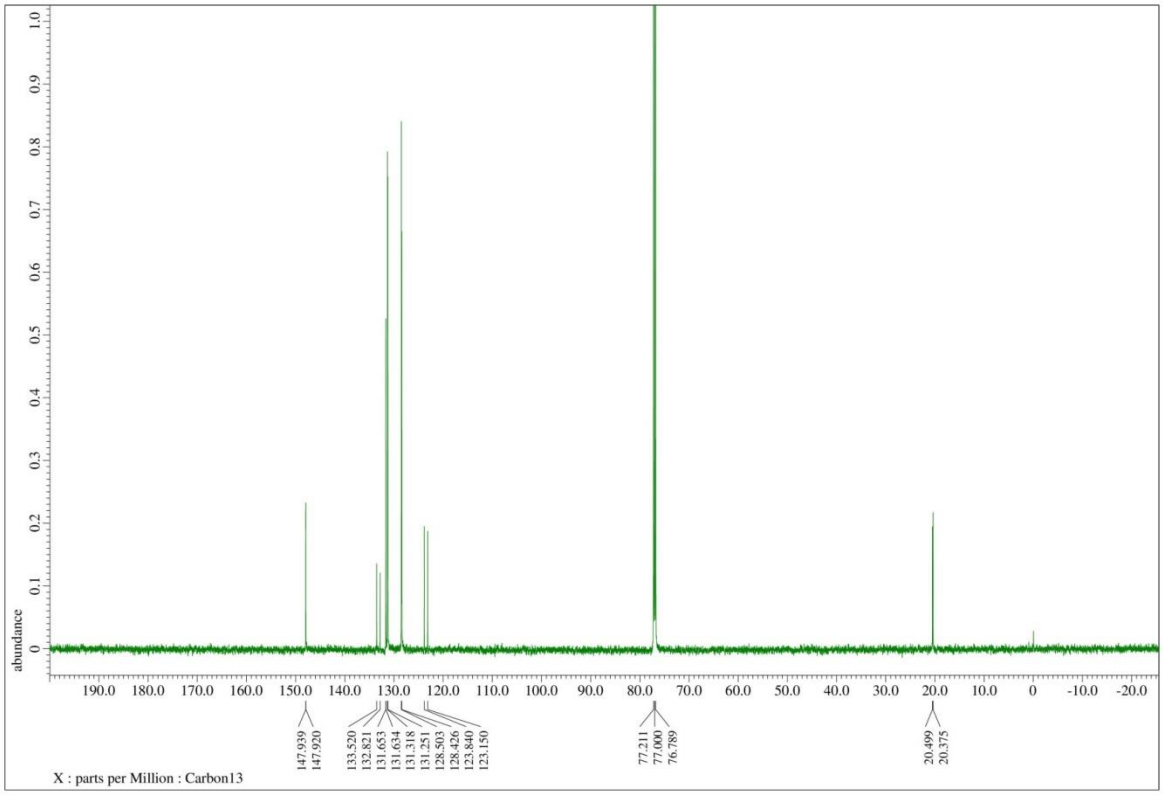

O
PPh2
2e
abundance
X : parts per Million : Proton

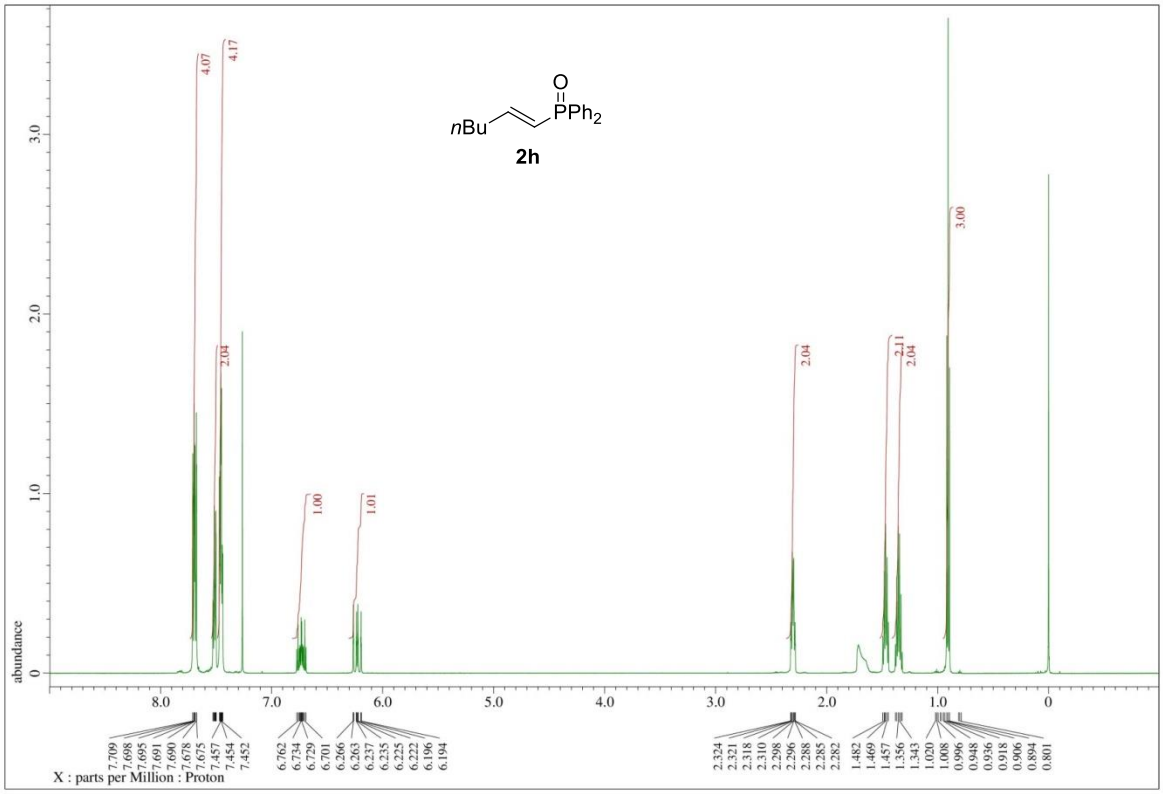

abundance
X : parts per Million : Carbon13

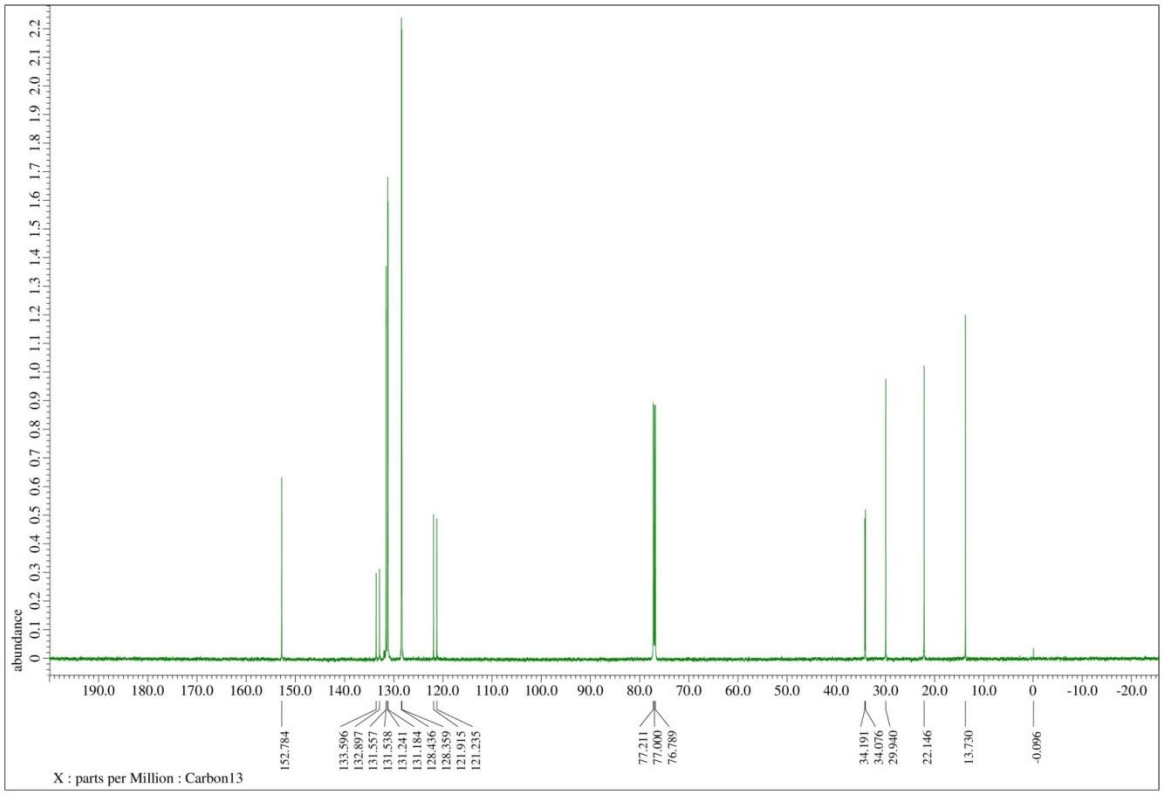

O
PPh2
2f
4.00
4.06
1.96
2.08
2.23
1.97
1.99
abundance
X : parts per Million : Proton

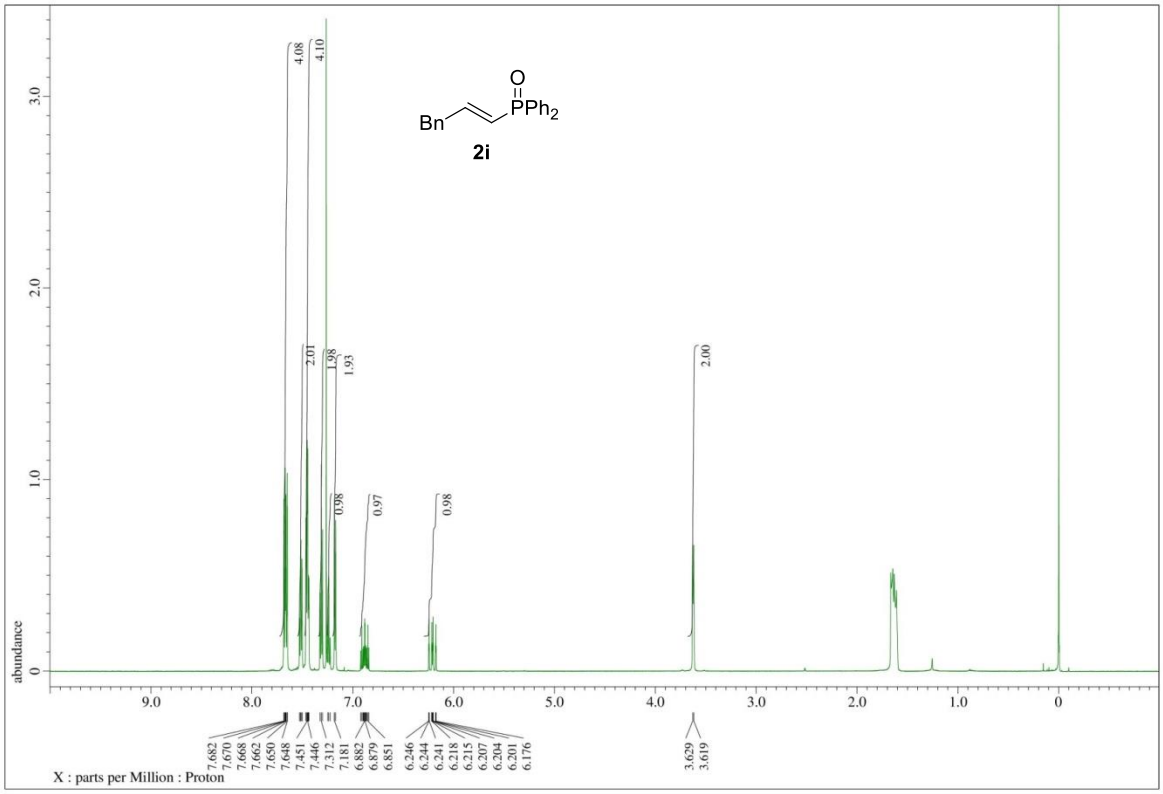

abundance
156.652
156.633
133.903
133.204
131.547
131.528
131.251
131.184
128.464
128.378
118.085
117.386
77.211
77.000
76.789
16.497
16.353
8.454
X : parts per Million : Carbon13

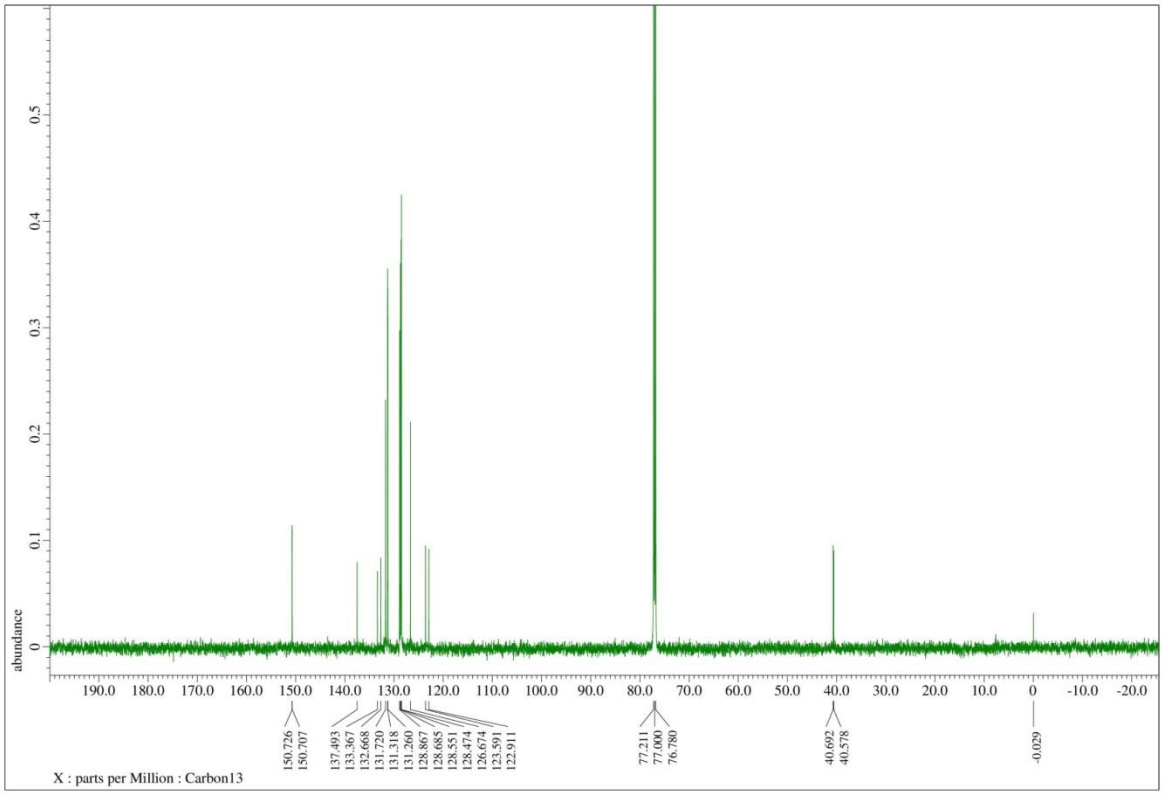

O
PPh2
Me
2g
3.94
3.99
1.96
0.96
0.98
3.00
abundance
X : parts per Million : Proton

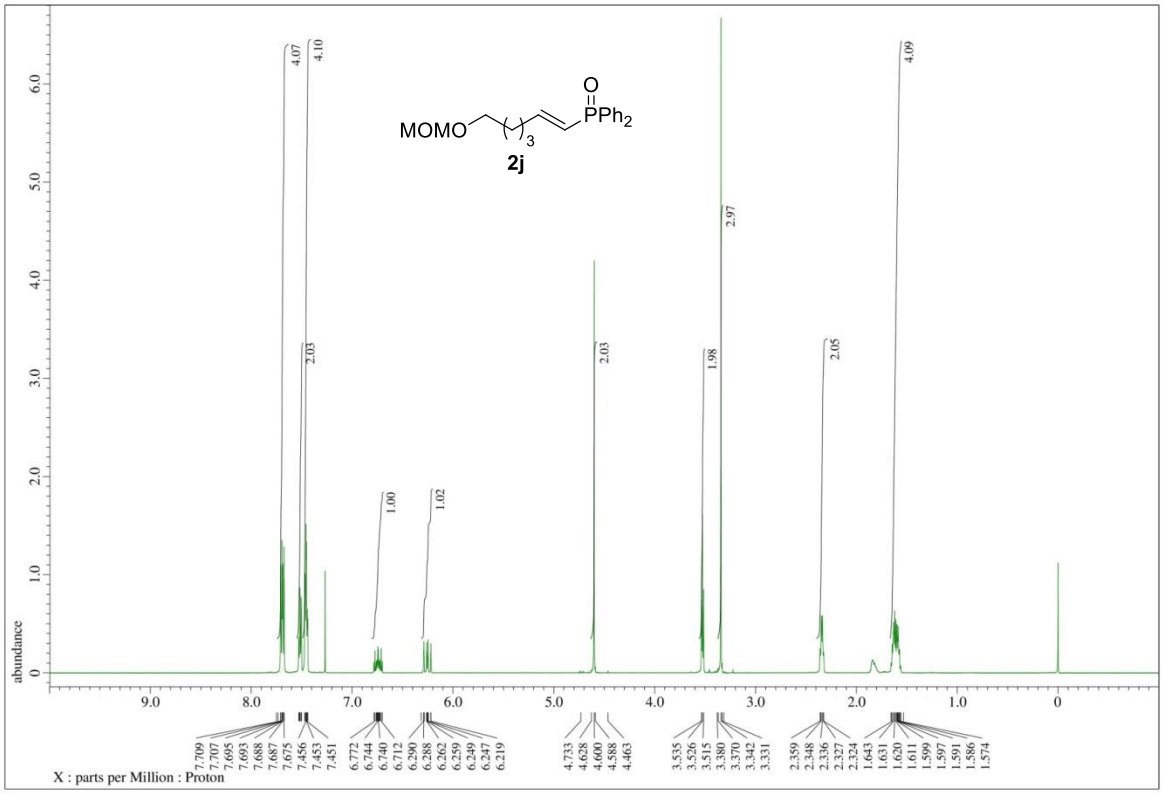

abundance
X : parts per Million : Carbon13

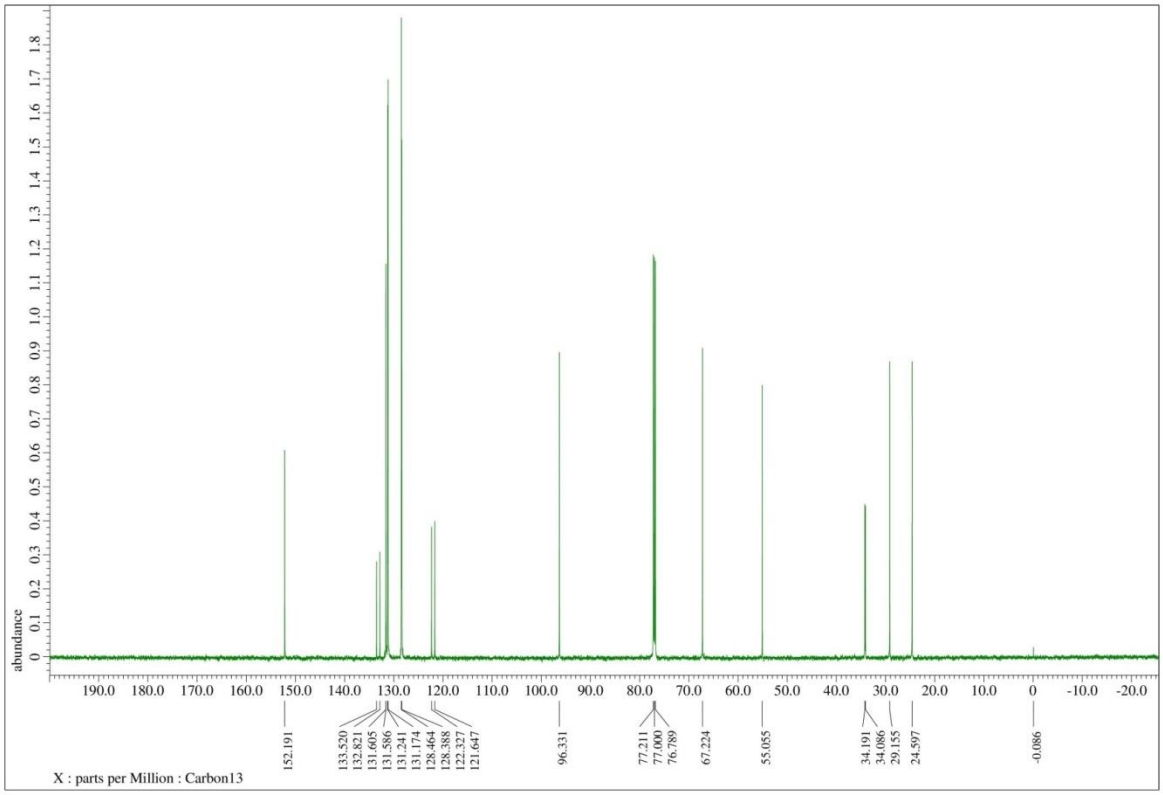

nBu
O
PPh2
2h
4.07
4.17
2.04
1.00
1.01
2.04
2.11
2.04
3.00
abundance
X : parts per Million : Proton

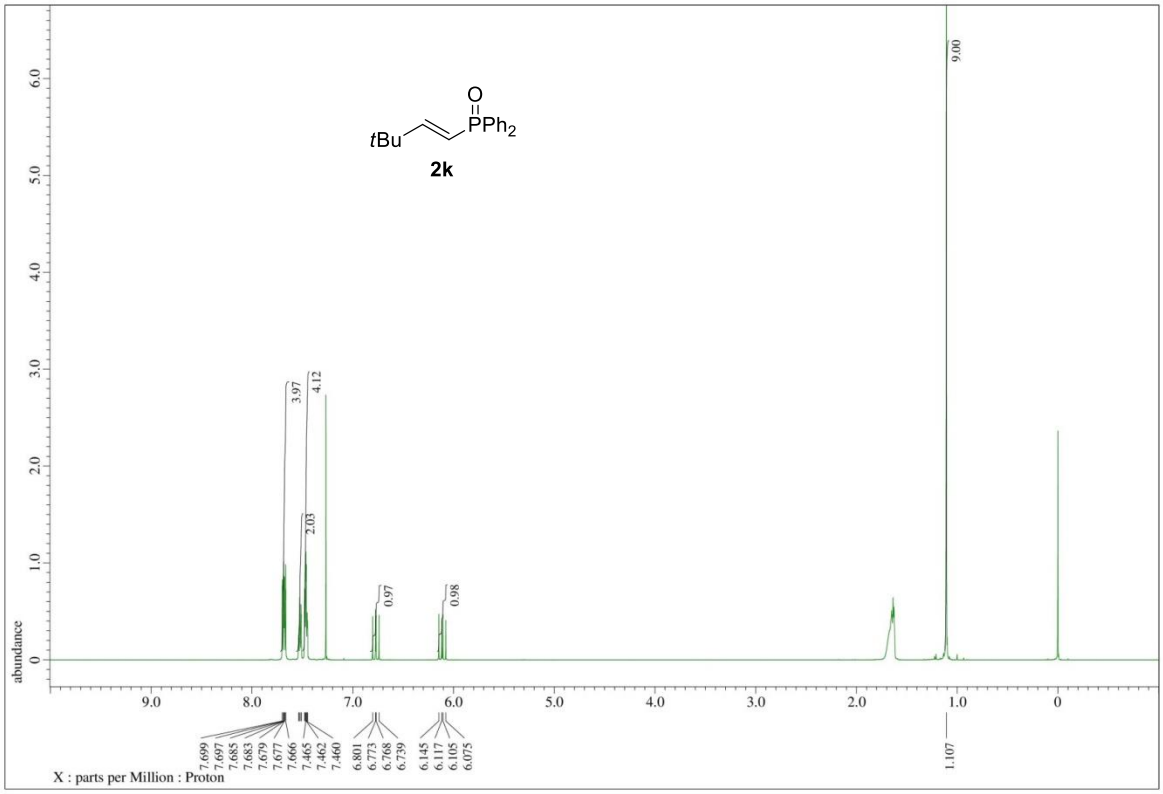

abundance
152.784
133.596
132.897
131.557
131.538
131.241
131.184
128.436
128.359
121.915
121.235
77.211
77.000
76.789
34.191
34.076
29.940
22.146
13.730
-0.096
X : parts per Million : Carbon13

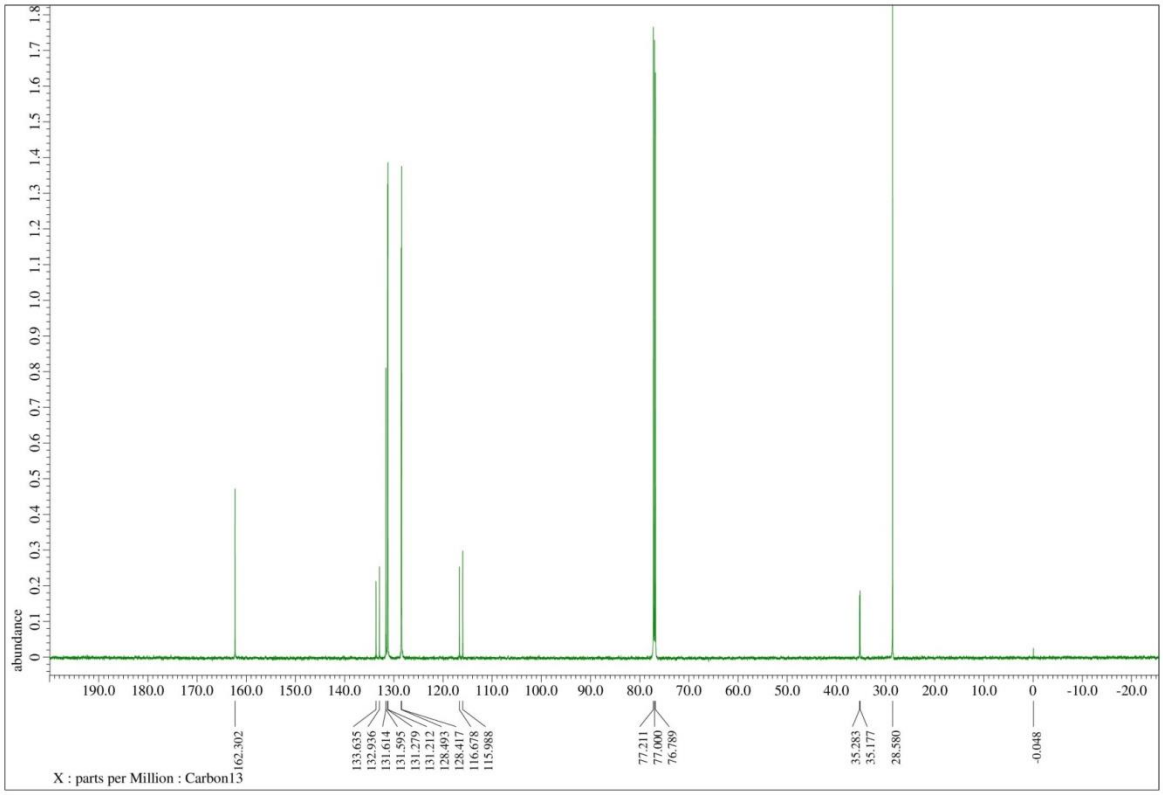

Bn
O
PPh2
2i
4.08
4.10
2.01
1.98
1.93
0.98
0.97
0.98
2.00
abundance
X : parts per Million : Proton

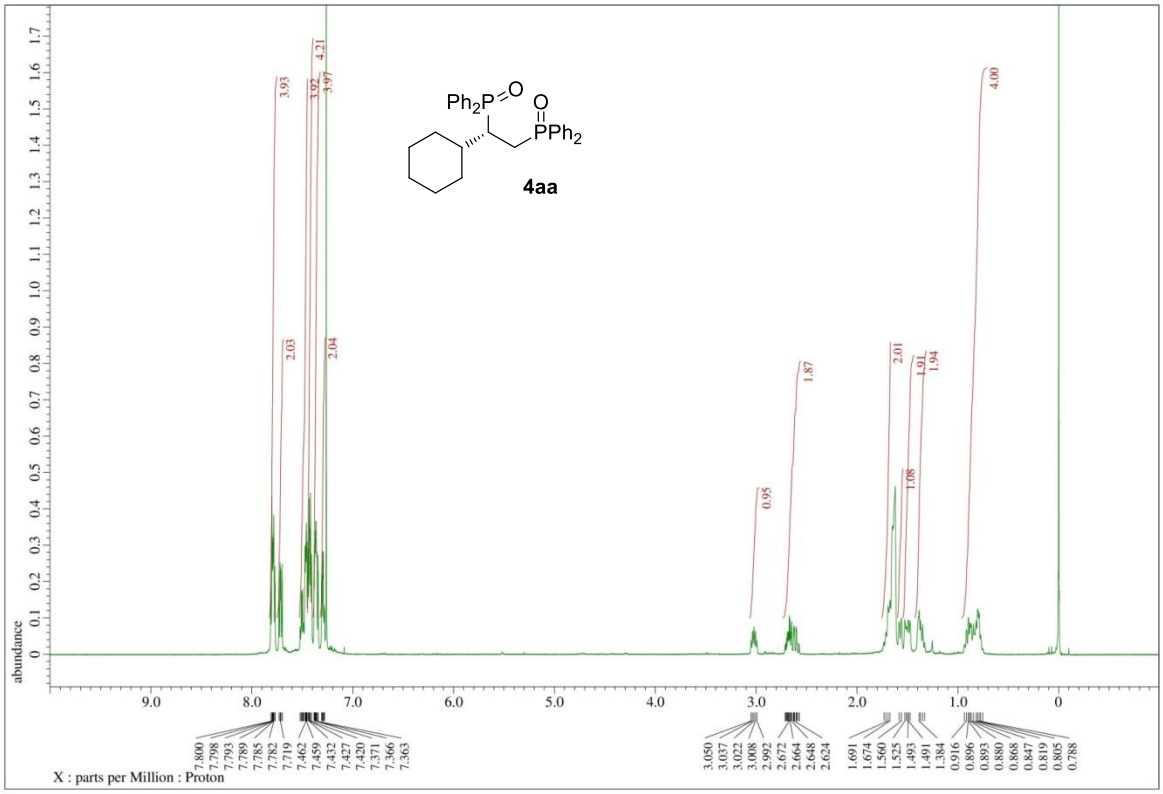

abundance
X : parts per Million : Carbon13

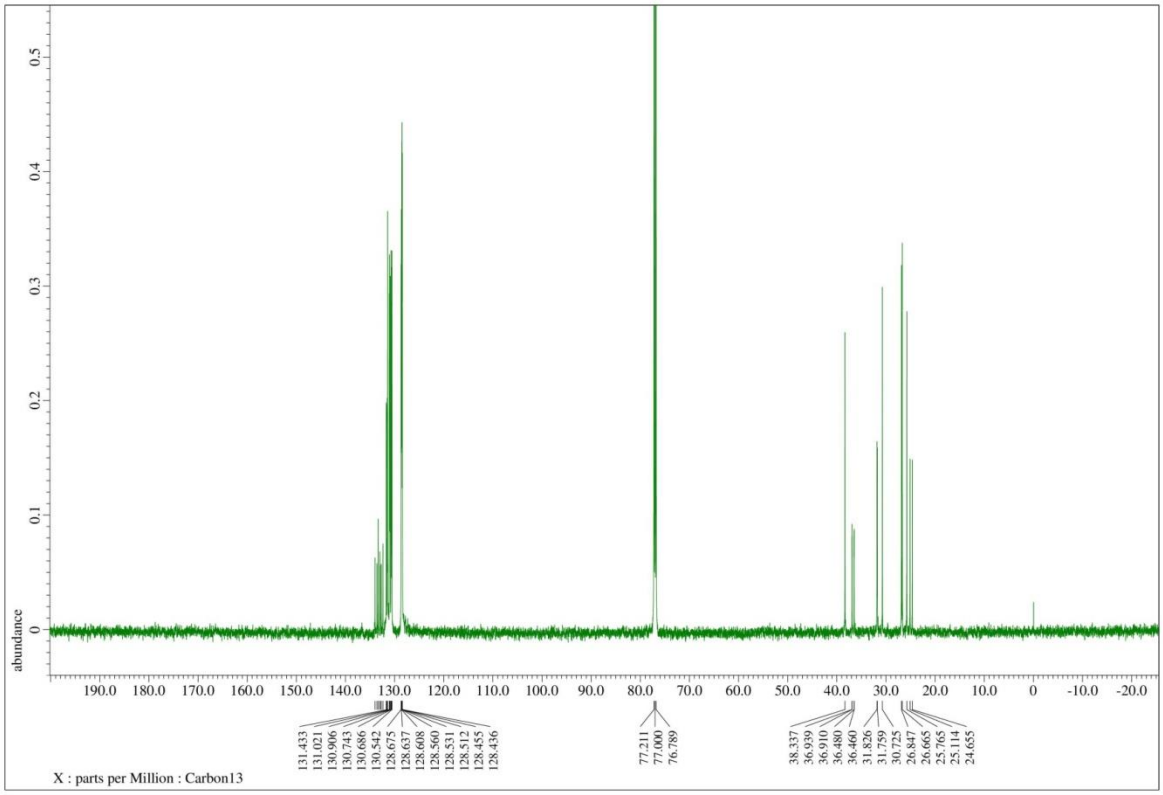

MOMO
O
PPh2
3
2j
abundance
X : parts per Million : Proton

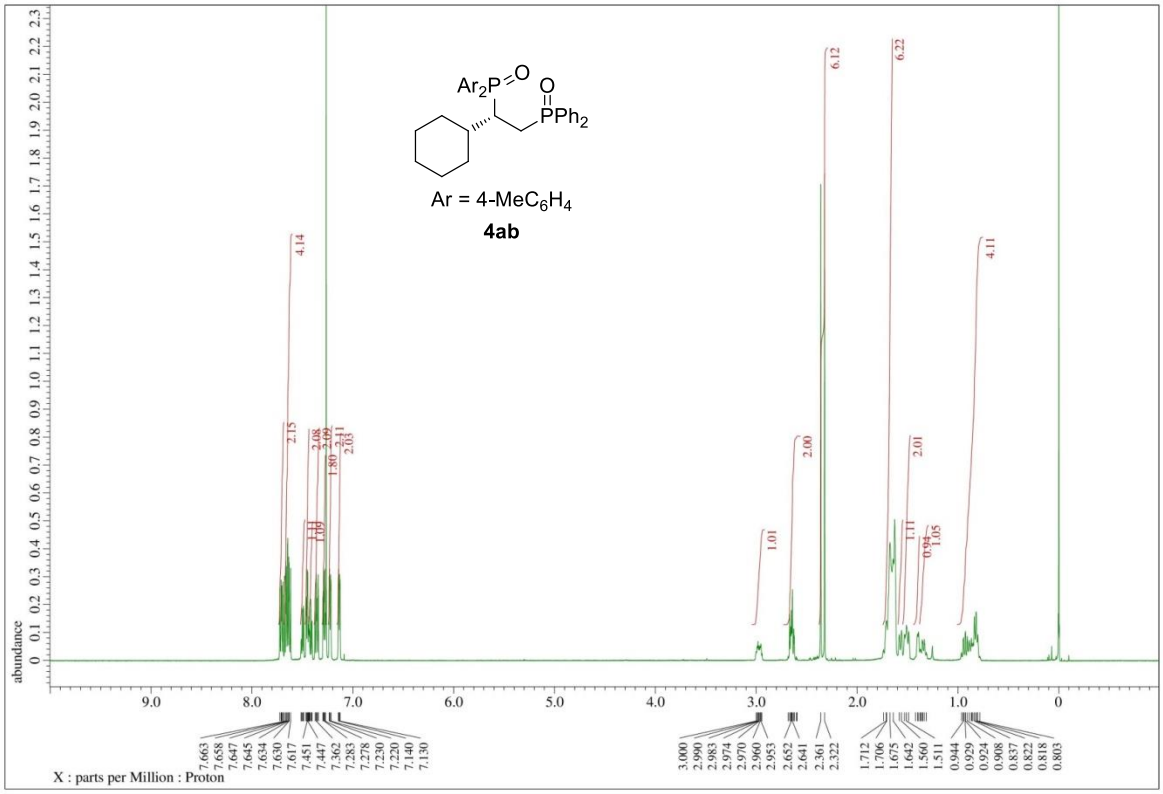

abundance
X : parts per Million : Carbon13

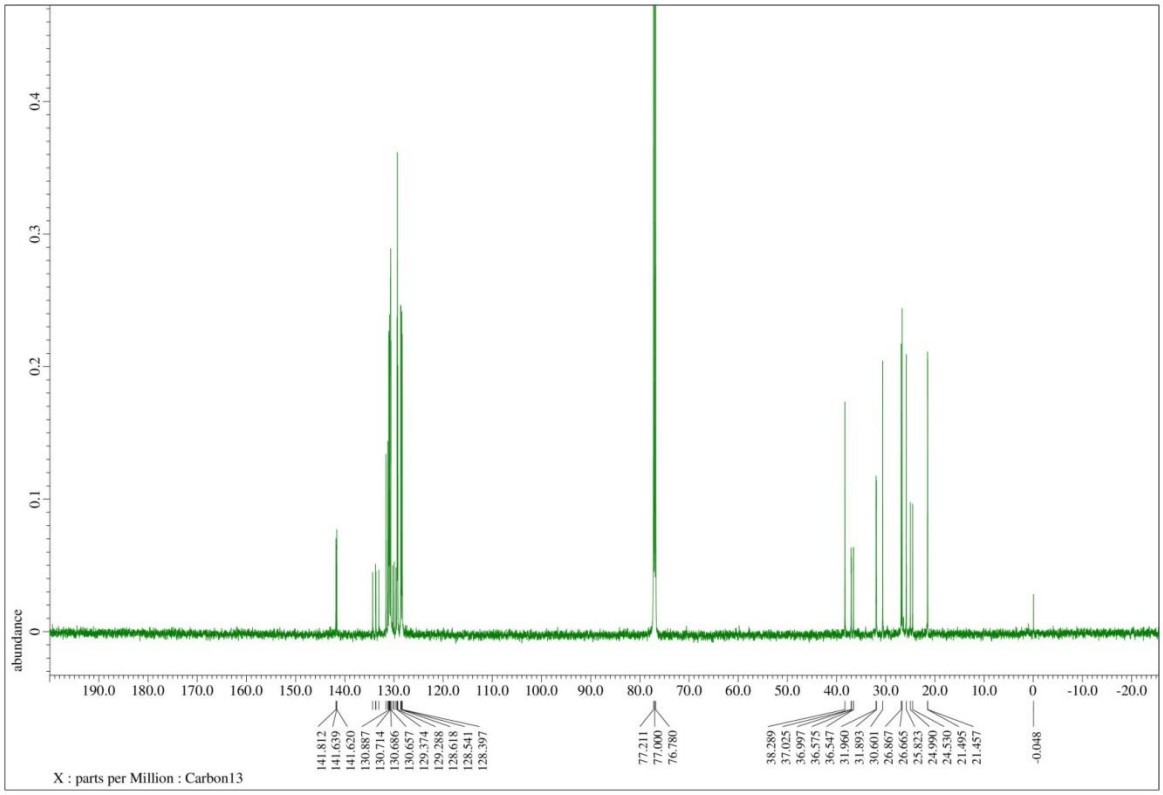

tBu
PPh2
O
2k
abundance
X : parts per Million : Proton
9.00
4.12
3.97
2.03
0.97
0.98
1.107

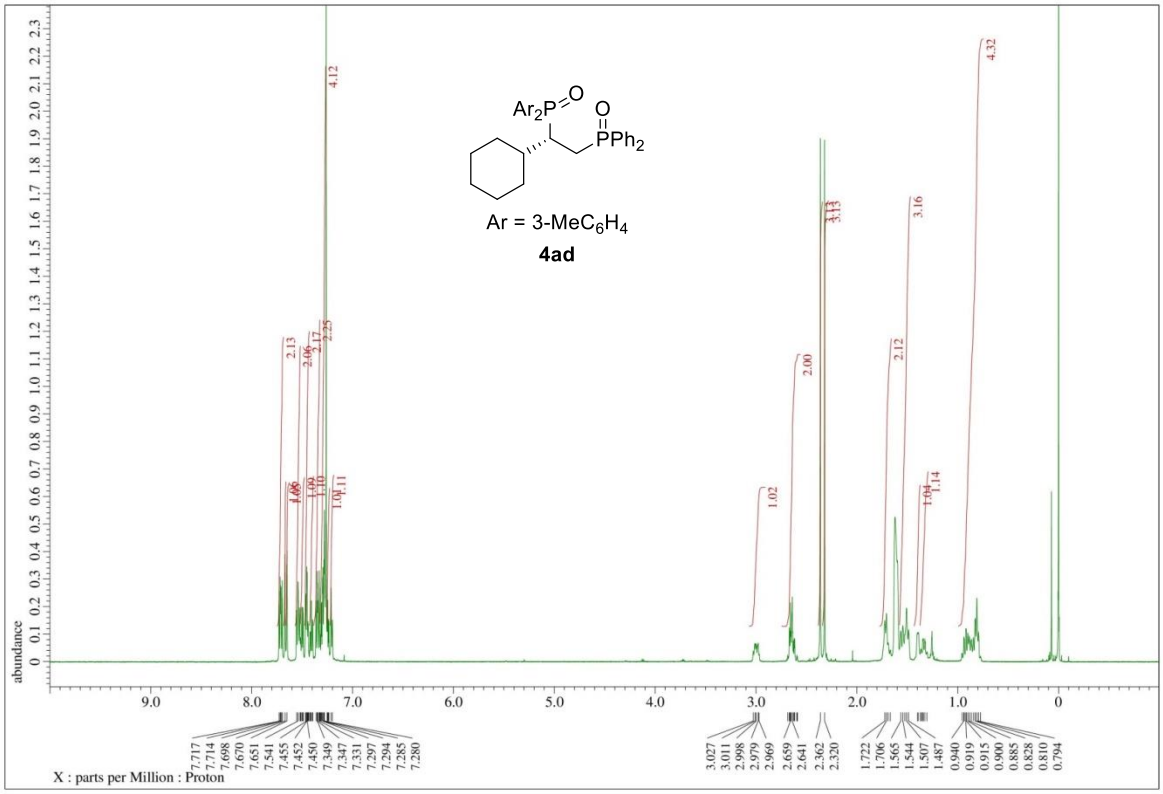

abundance
X : parts per Million : Carbon13
162.302
133.635
132.936
131.614
131.595
131.279
131.212
128.493
128.417
116.678
115.988
77.211
77.000
76.789
35.283
35.177
28.580
-0.048

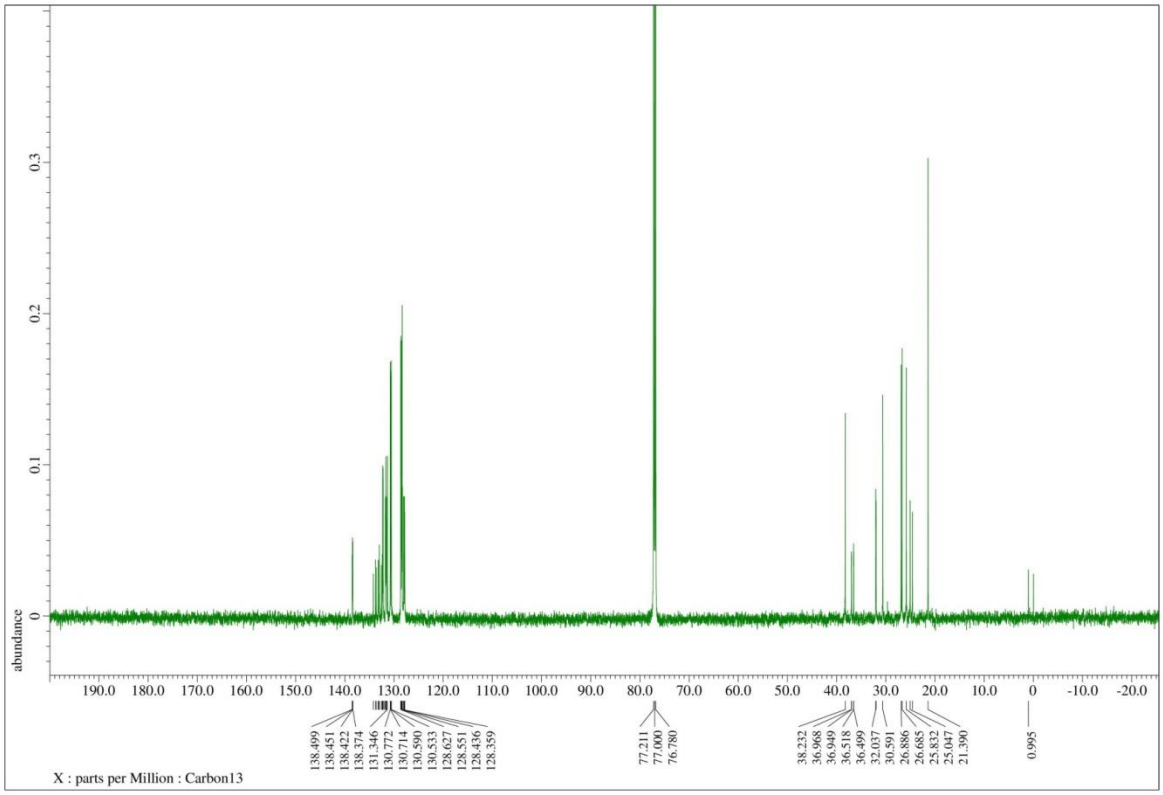

Ph2P
O
O
PPh2
4aa
abundance
X : parts per Million : Proton

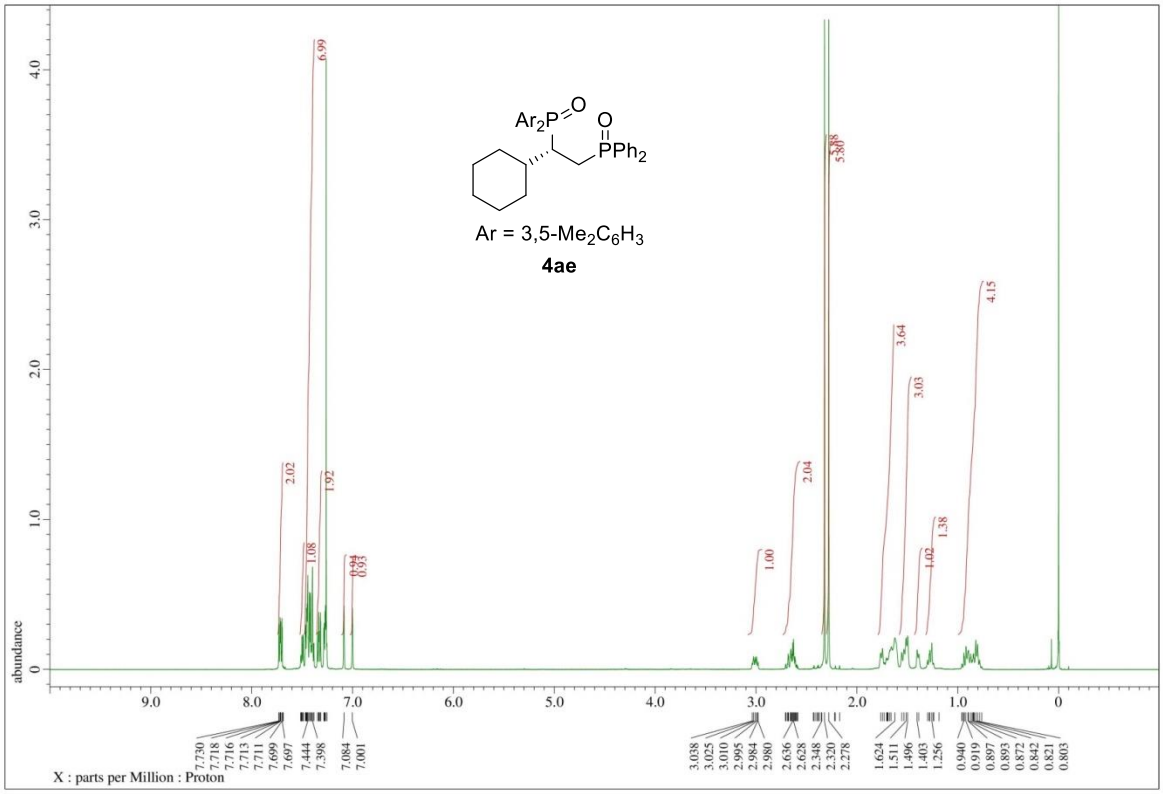

abundance
X : parts per Million : Carbon13

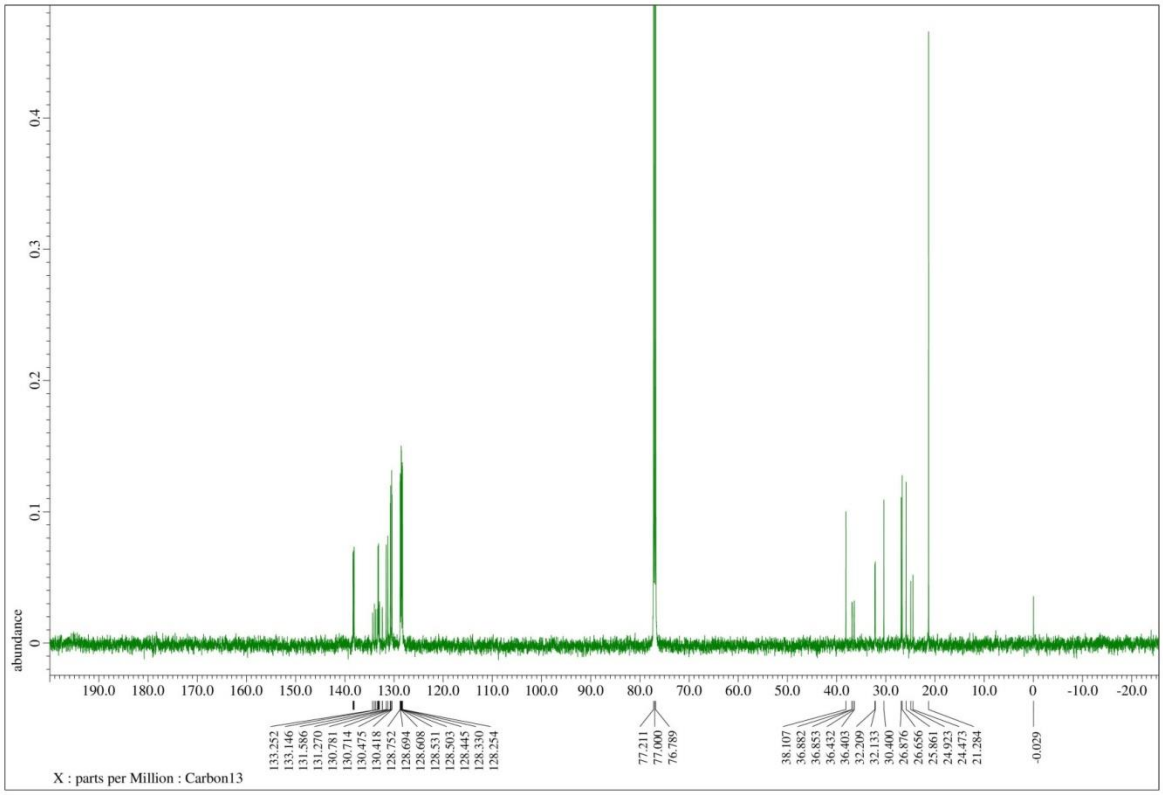

Ar = 4-MeC6H4
4ab
abundance
X : parts per Million : Proton

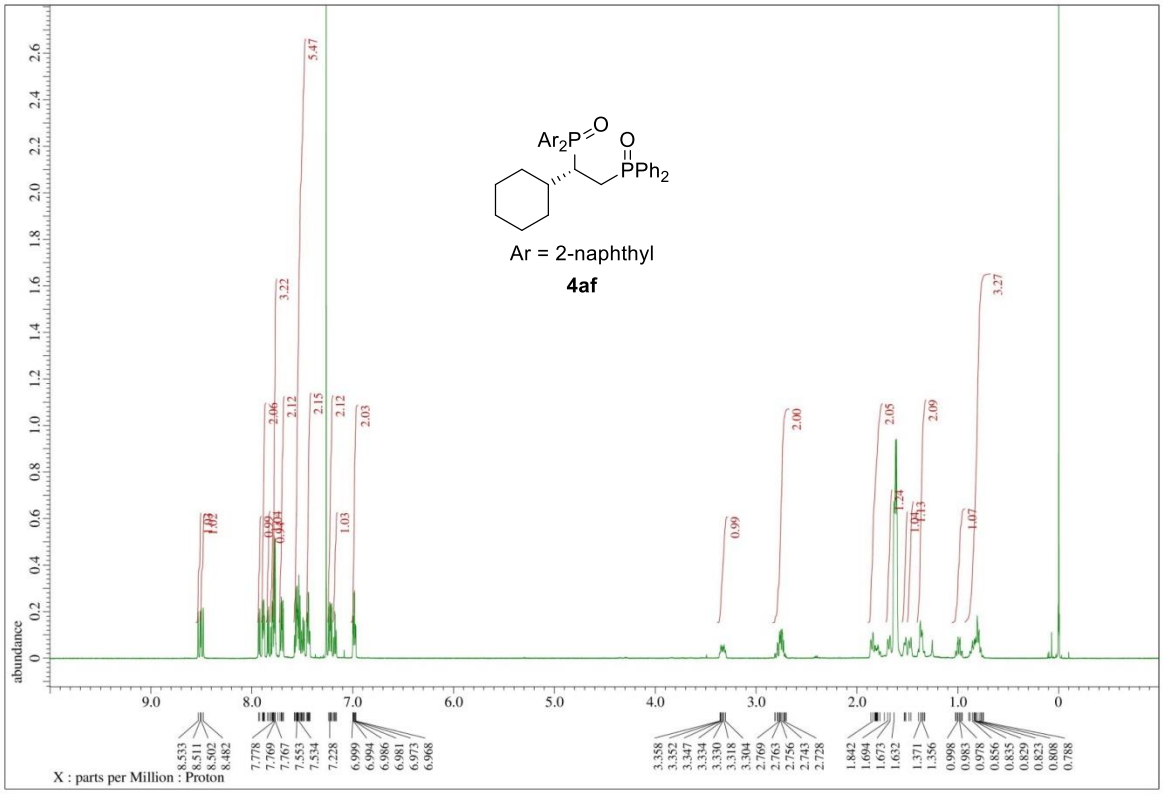

abundance
X : parts per Million : Carbon13

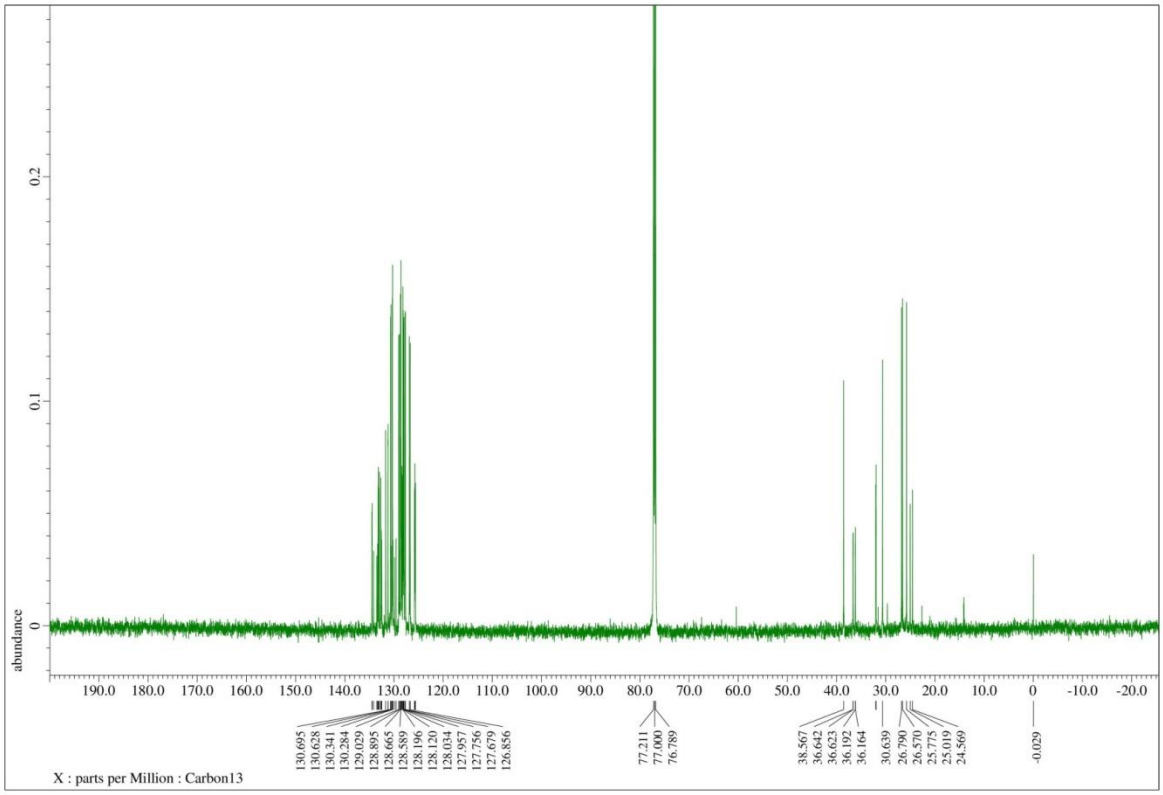

Ar = 3-MeC6H4
4ad
abundance
X : parts per Million : Proton

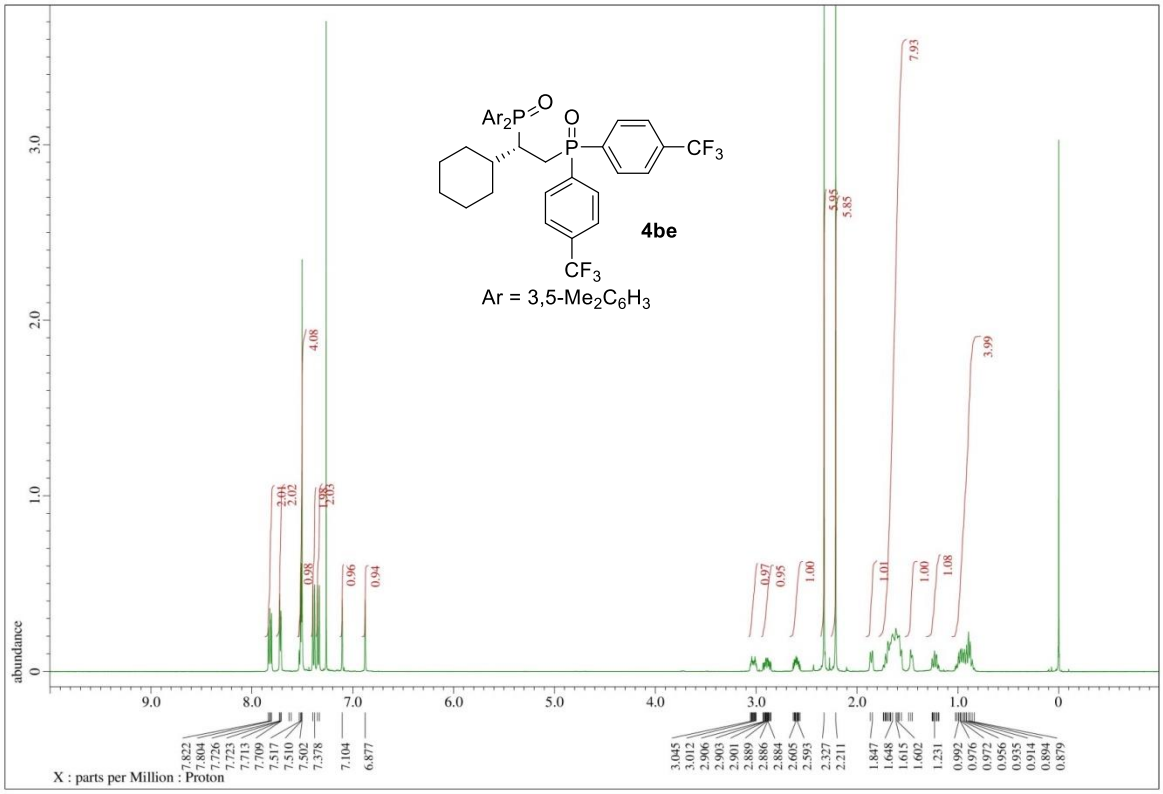

abundance
X : parts per Million : Carbon13

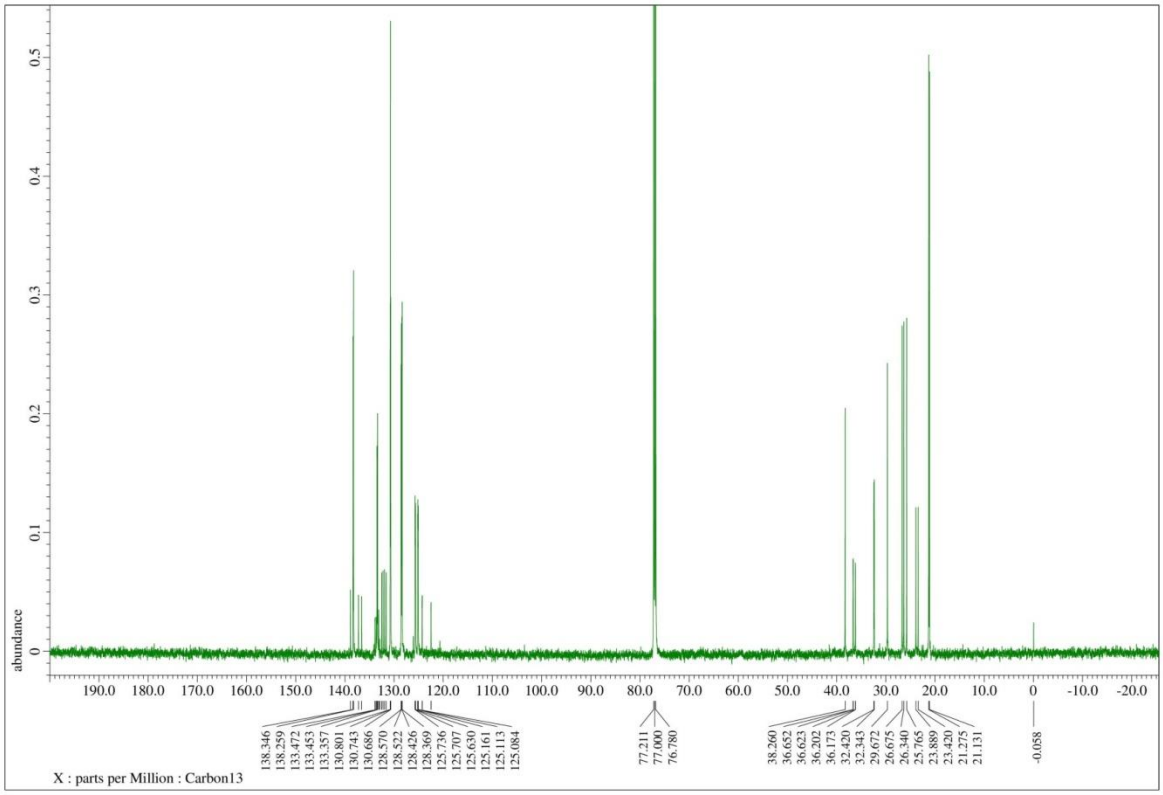

Ar = 3,5-Me2C6H3
4ae
abundance
X : parts per Million : Proton

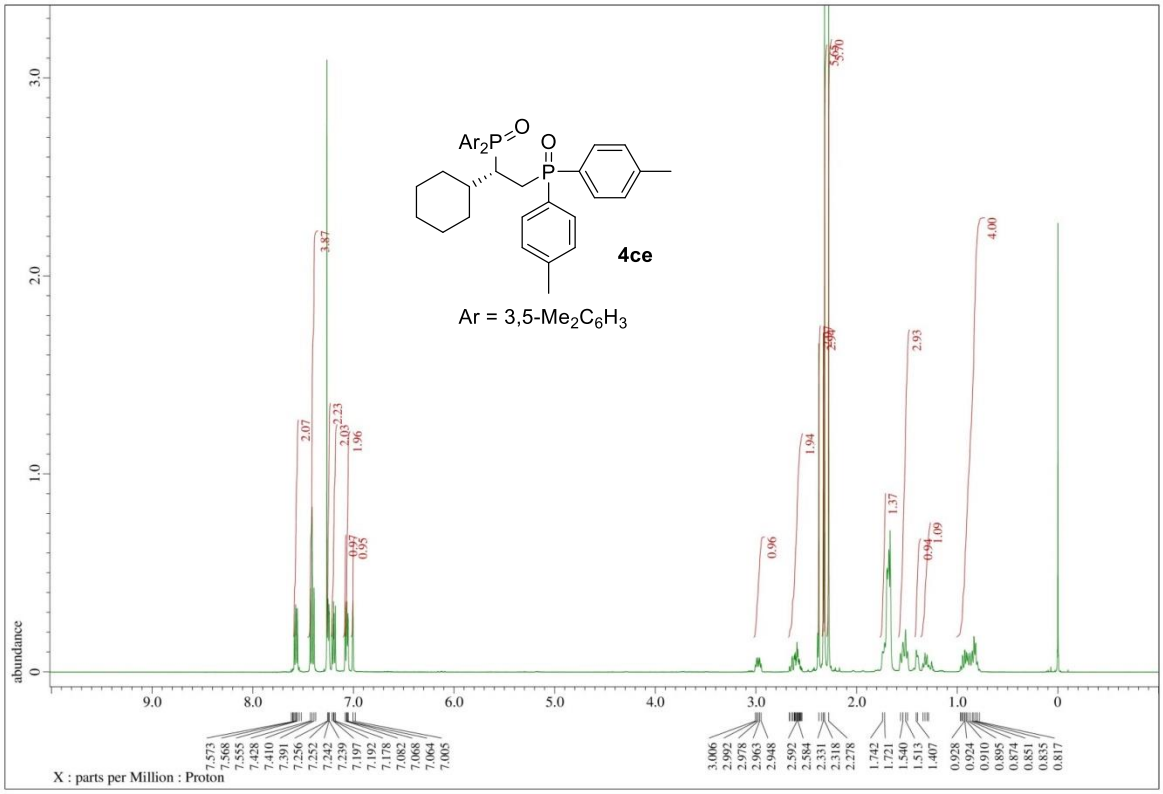

abundance
X : parts per Million : Carbon13

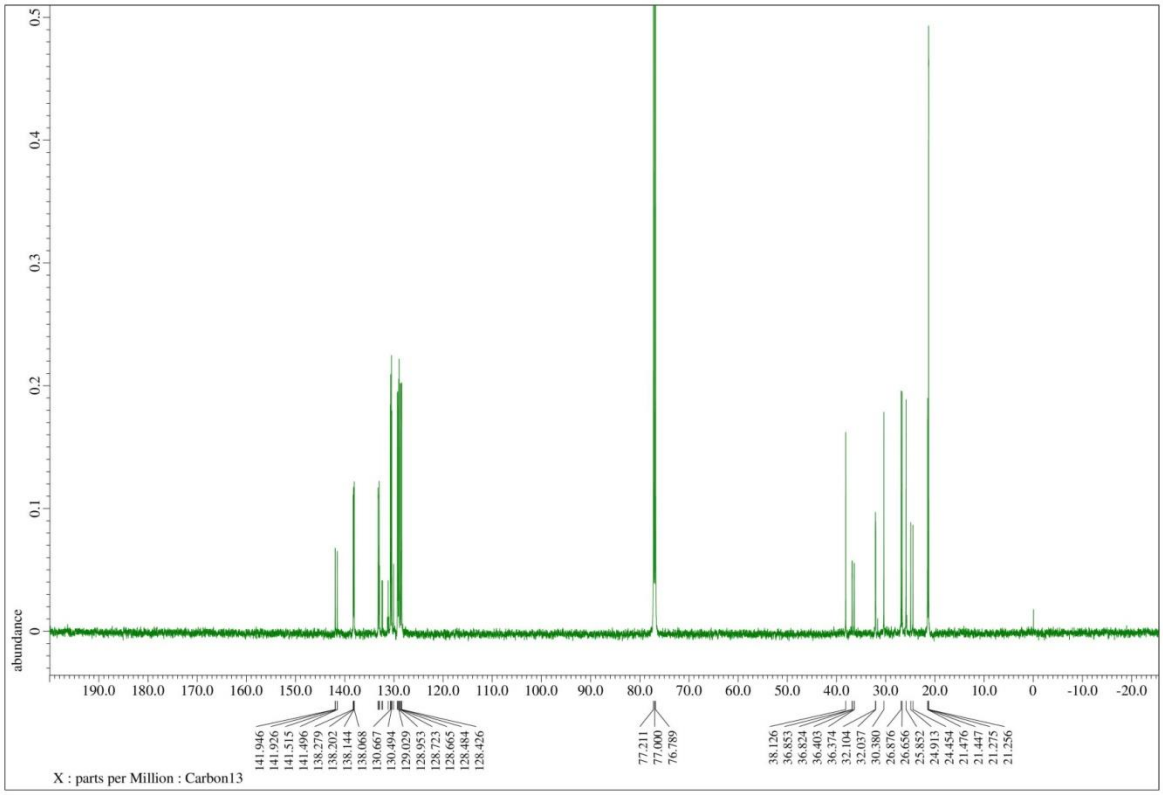

Ar = 2-naphthyl
4af
abundance
X : parts per Million : Proton

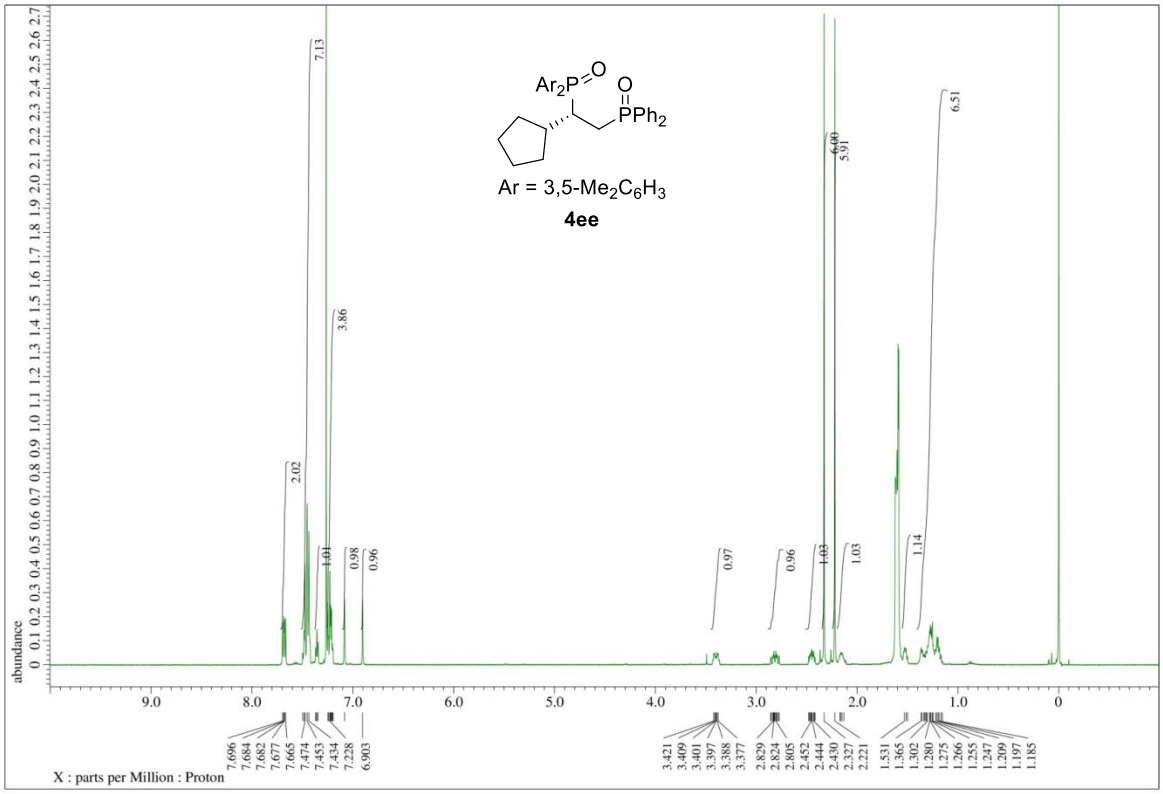

abundance
X : parts per Million : Carbon13

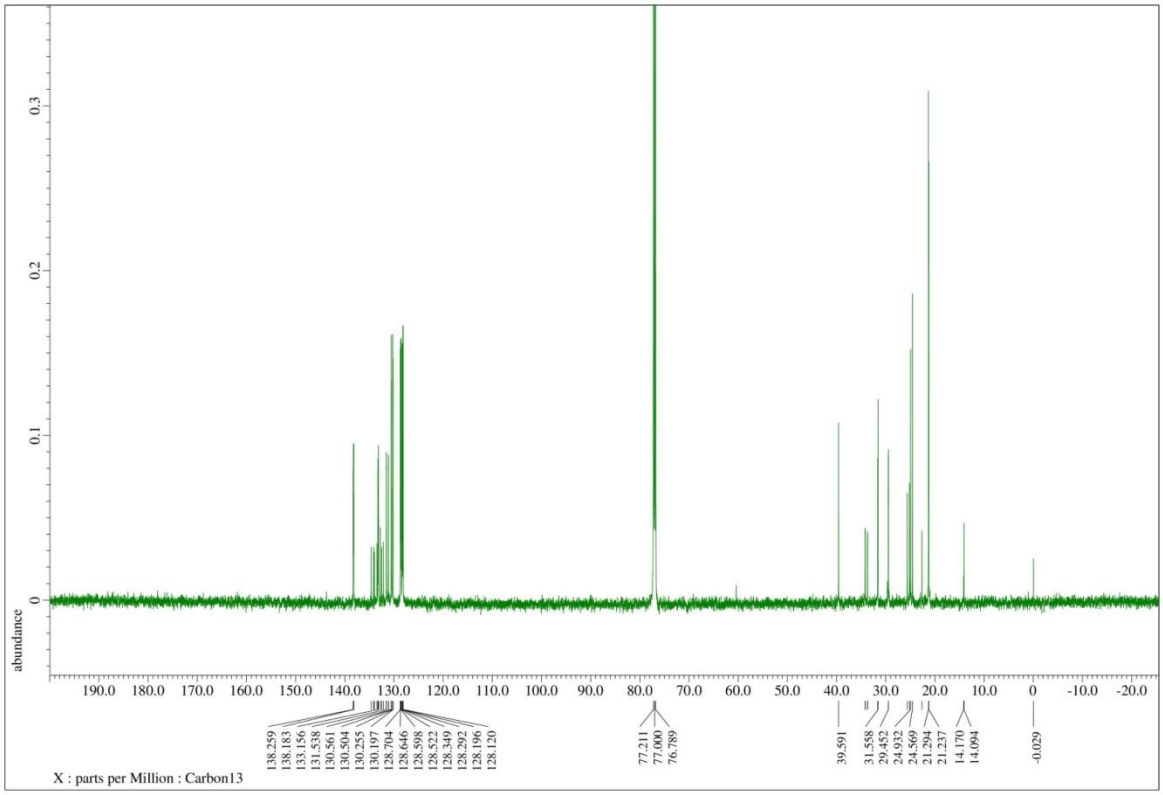

Ar2P
O
P
O
CF3
CF3
4be
Ar = 3,5-Me2C6H3
abundance
X : parts per Million : Proton

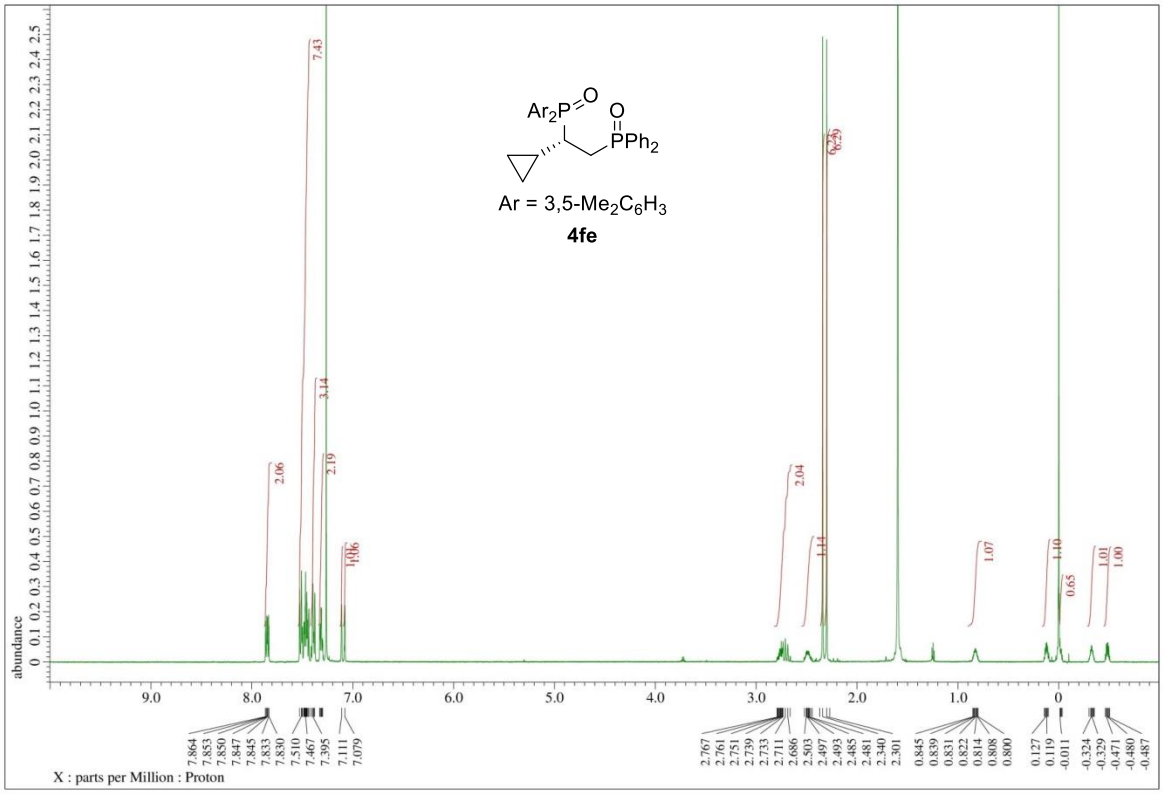

abundance
X : parts per Million : Carbon13

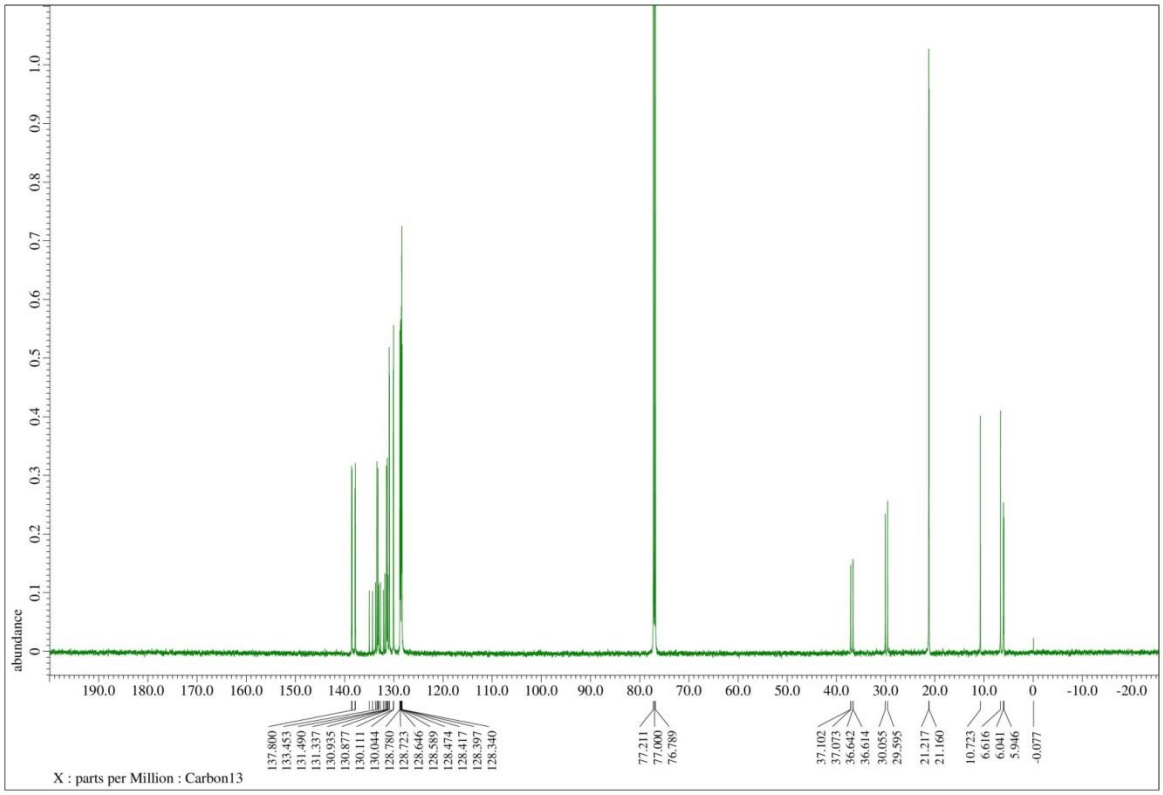

Ar2P
O
O
P
4ce
Ar = 3,5-Me2C6H3
abundance
X : parts per Million : Proton

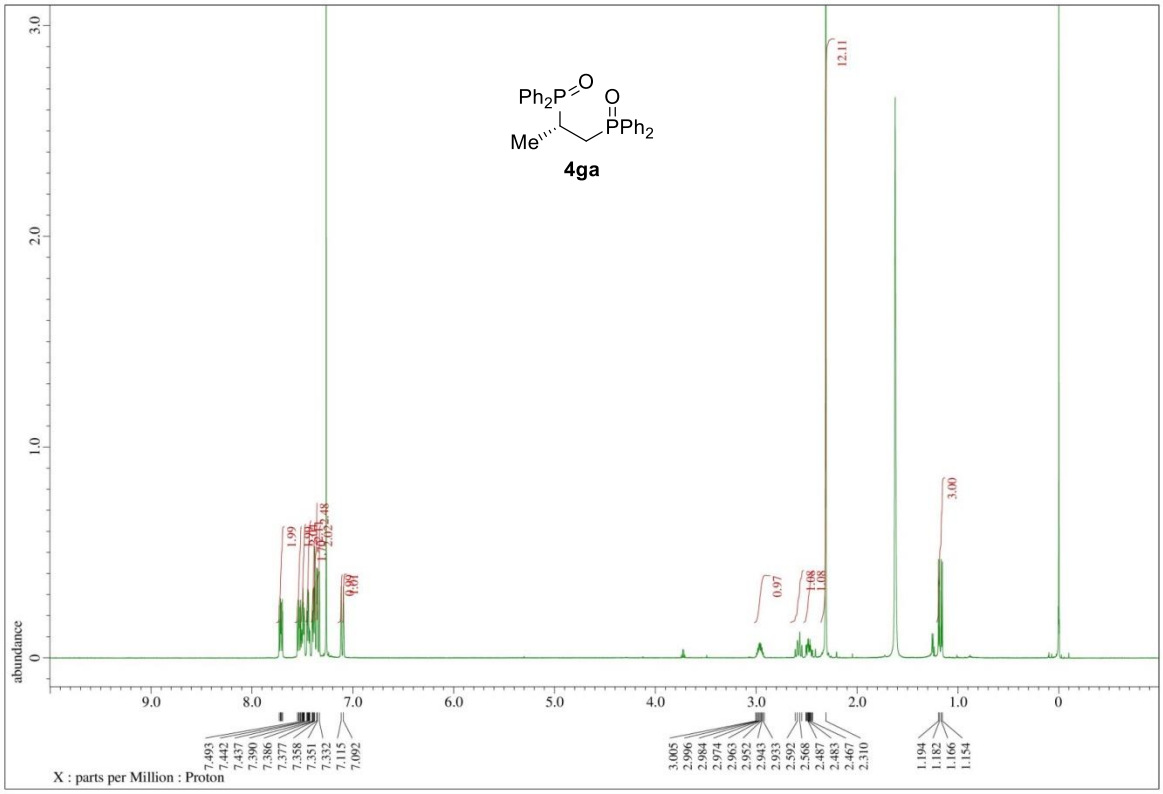

abundance
X : parts per Million : Carbon13

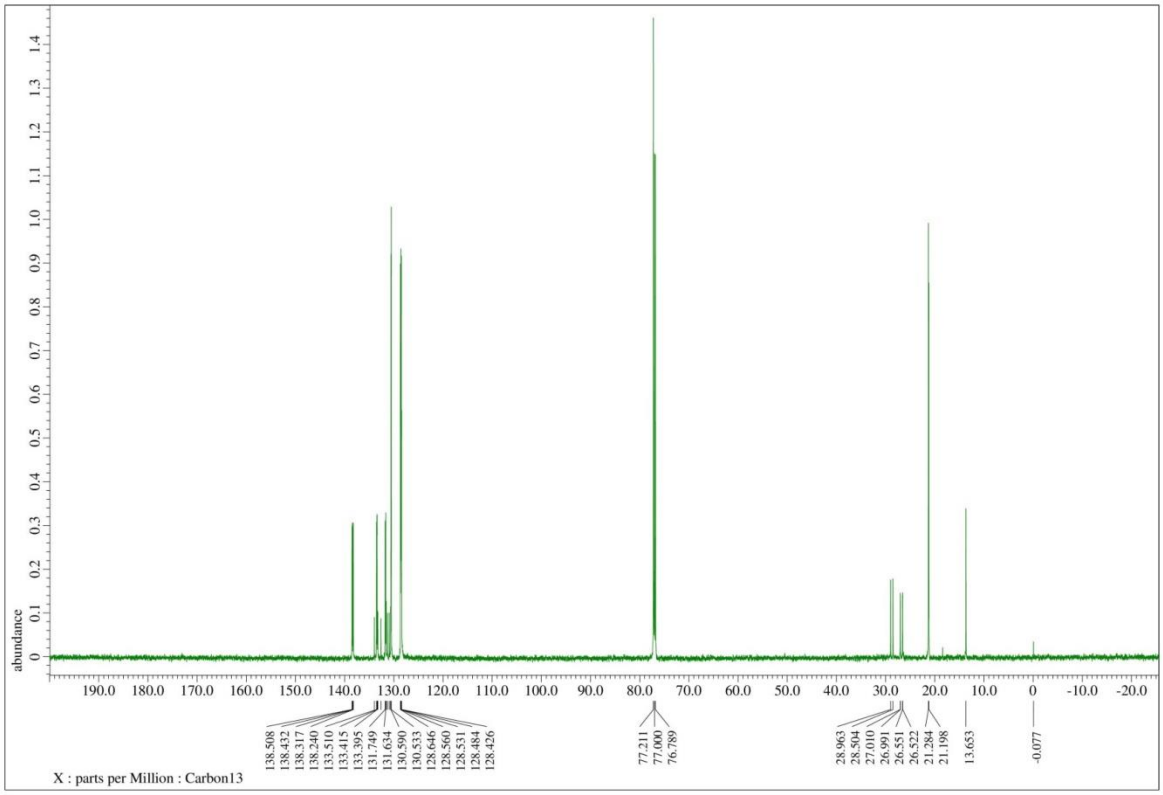

Ar = 3,5-Me2C6H3
4ee
abundance
X : parts per Million : Proton

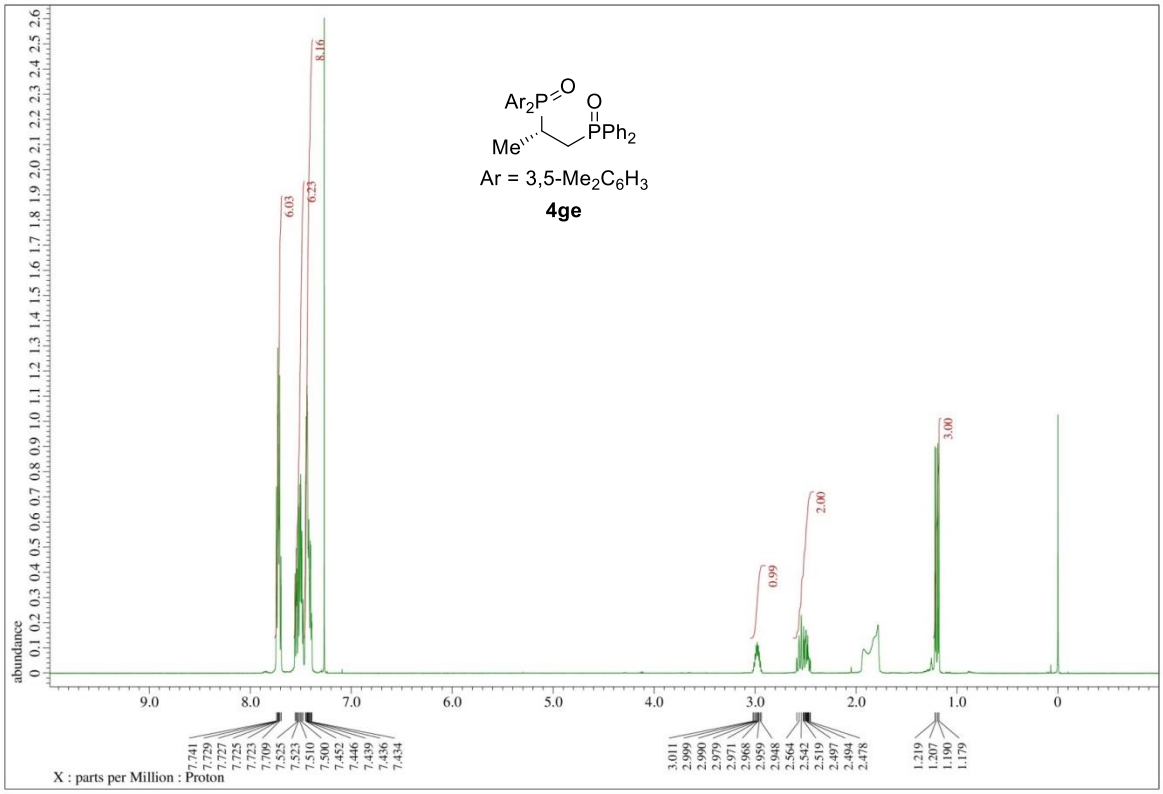

abundance
X : parts per Million : Carbon13

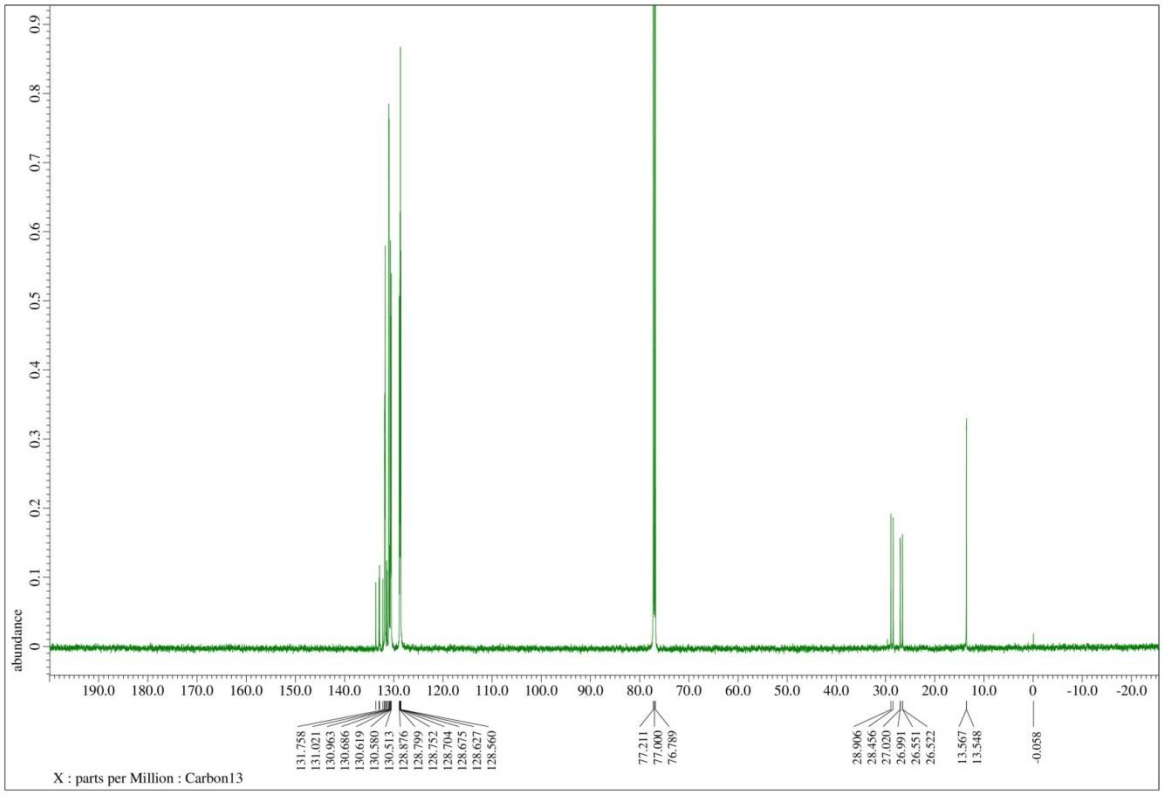

Ar = 3,5-Me2C6H3
4fe
X : parts per Million : Proton

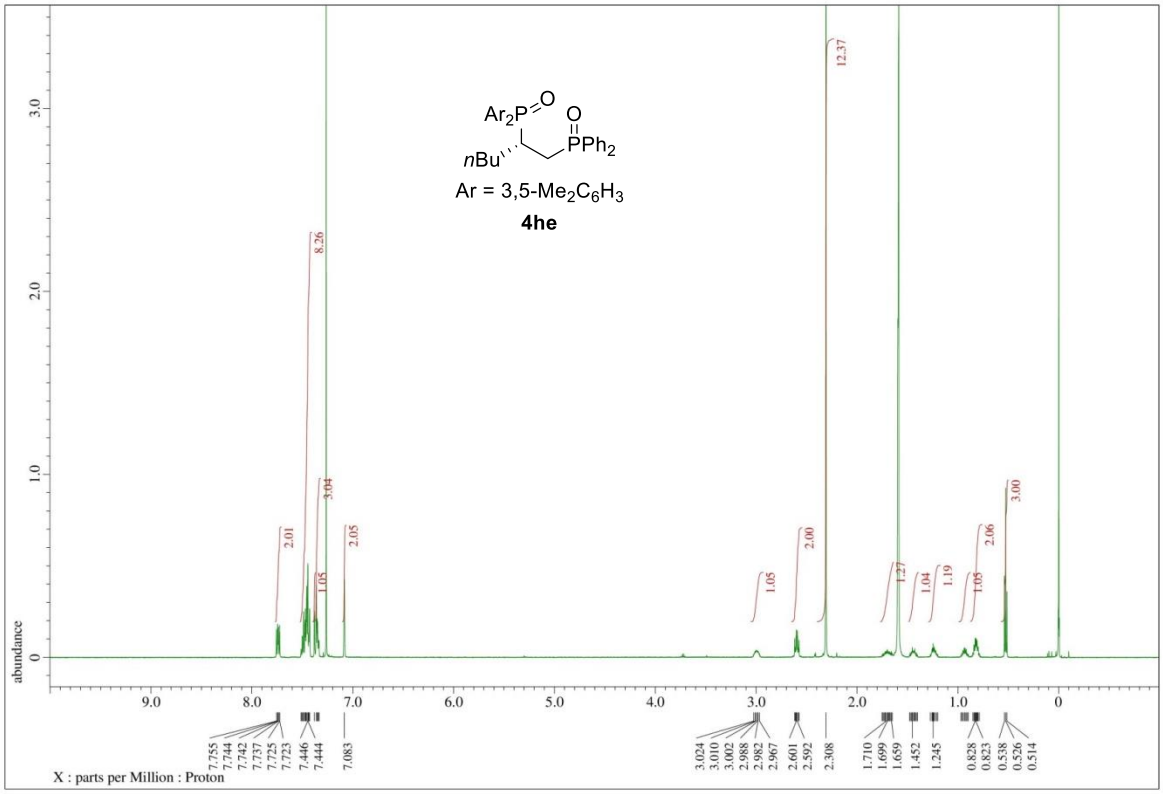

X : parts per Million : Carbon13

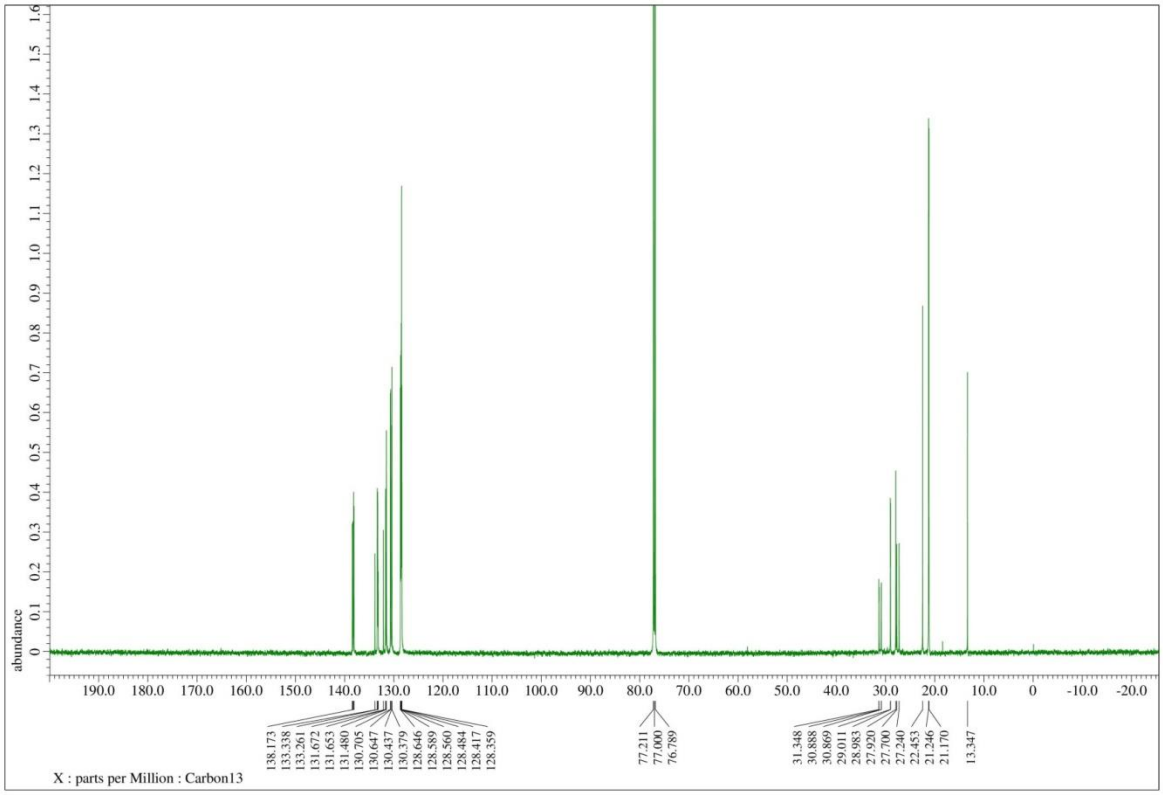

Ph2P
O
O
PPh2
Me
4ga
12.11
3.00
0.97
1.99
abundance
X : parts per Million : Proton

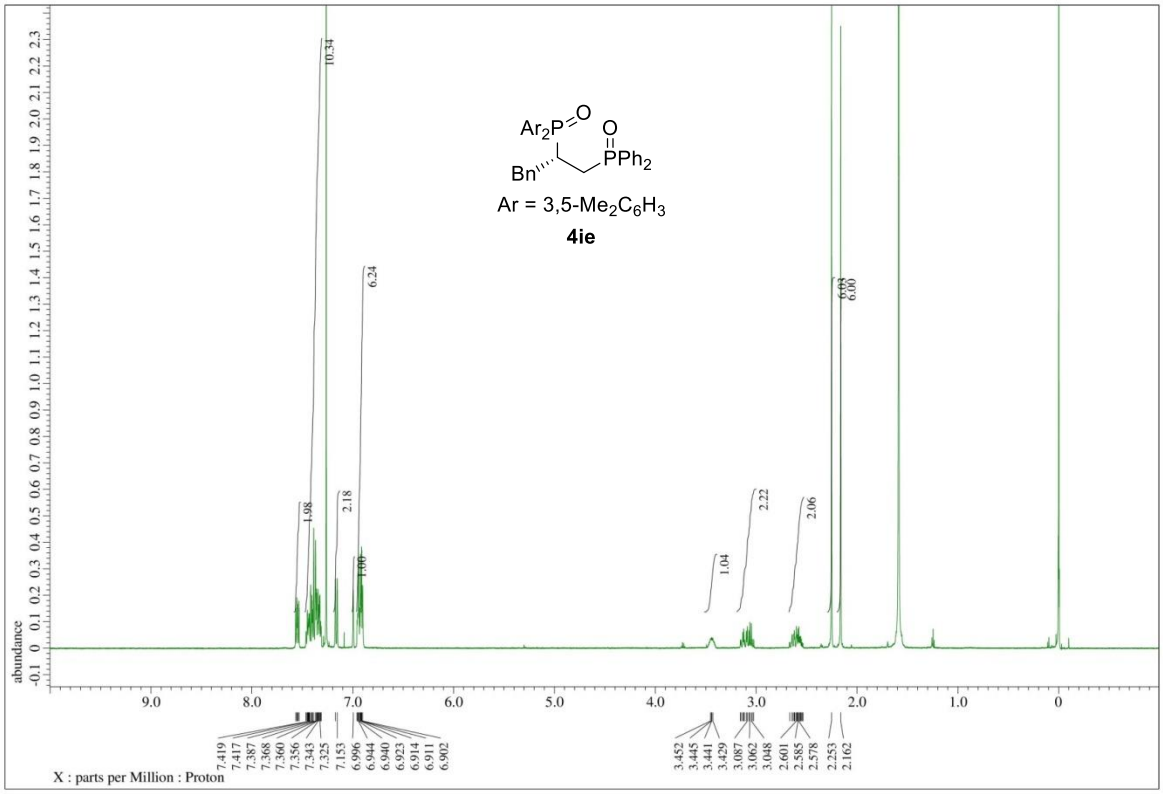

abundance
X : parts per Million : Carbon13

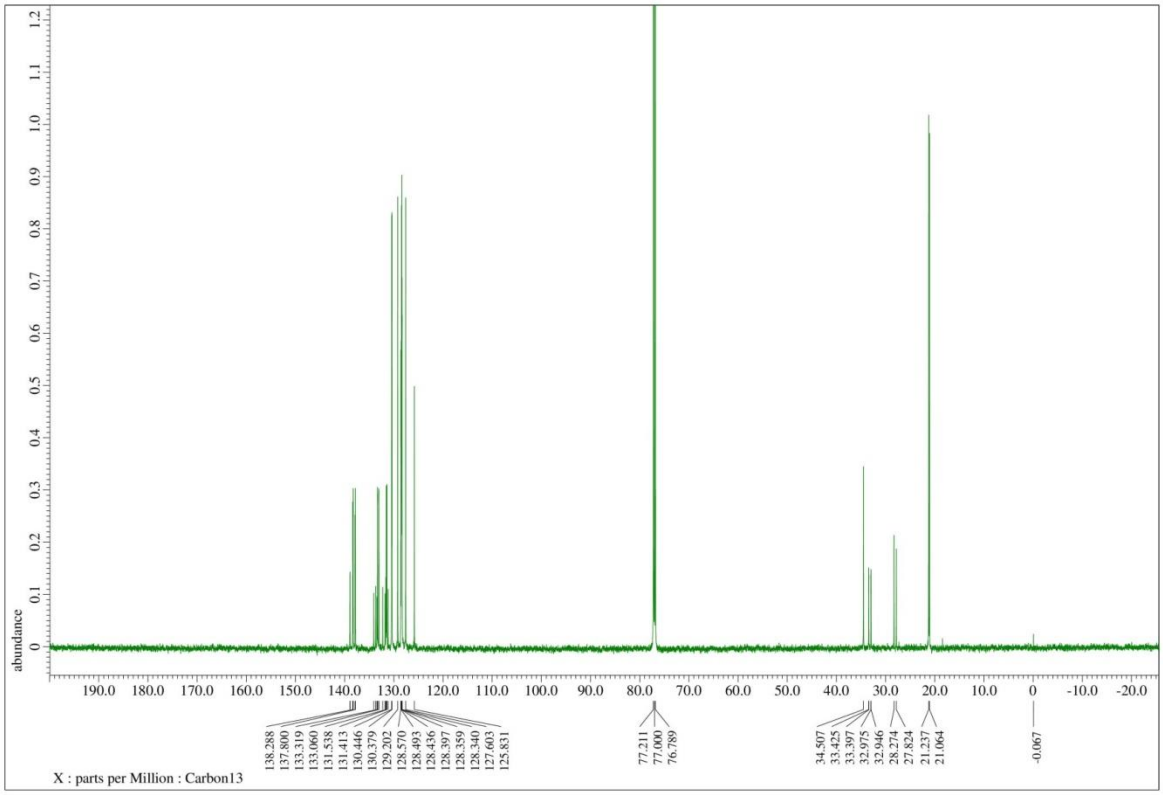

Ar = 3,5-Me2C6H3
4ge
abundance
X : parts per Million : Proton

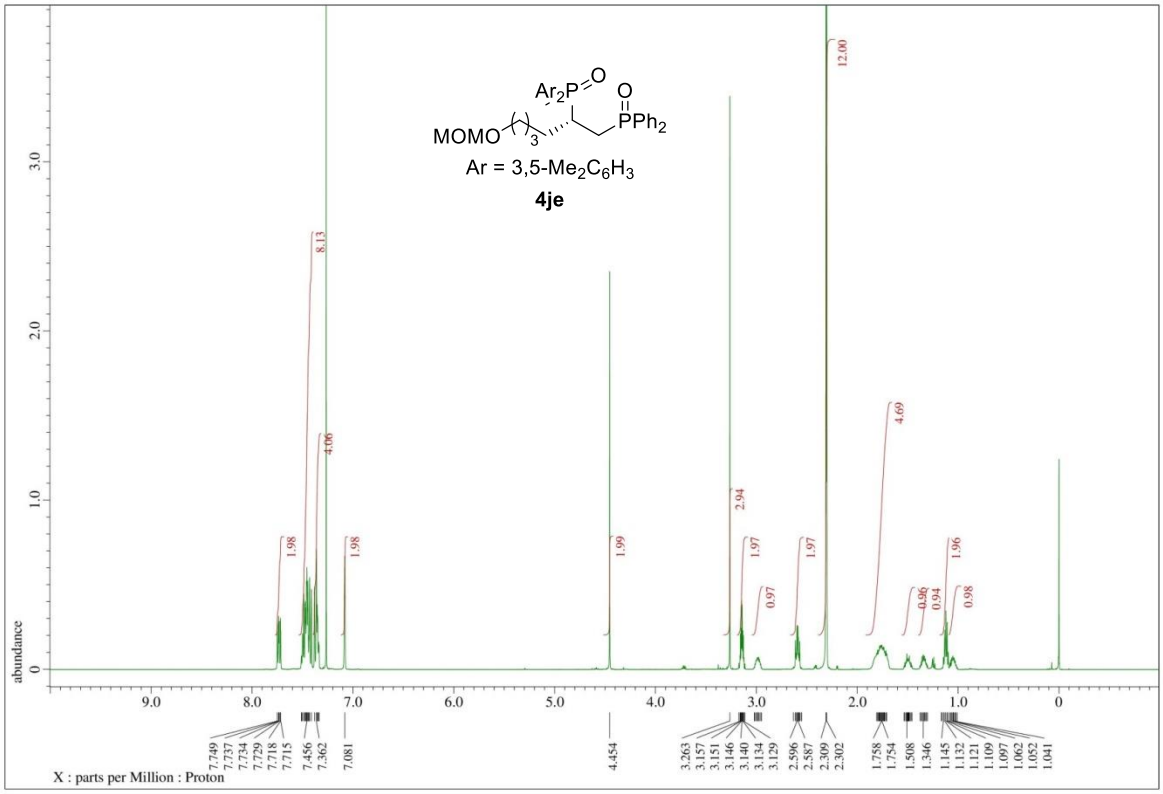

abundance
X : parts per Million : Carbon13

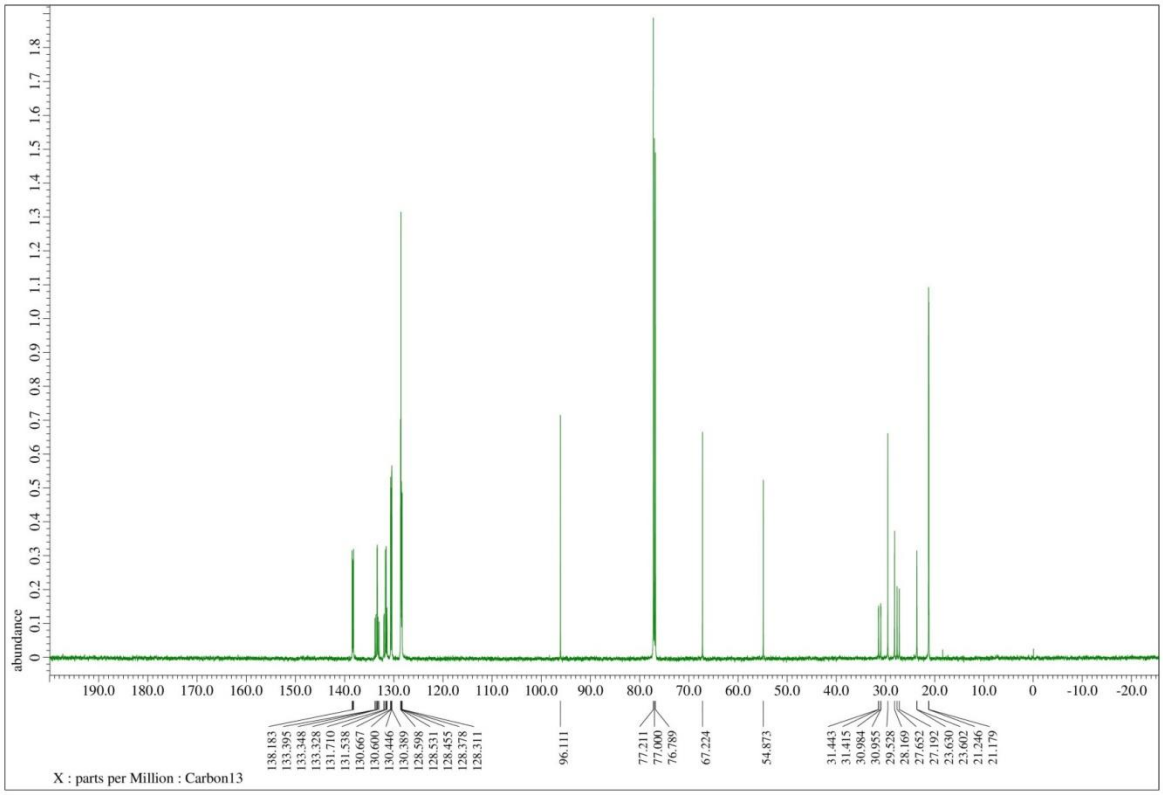

Ar = 3,5-Me2C6H3
4he
abundance
X : parts per Million : Proton

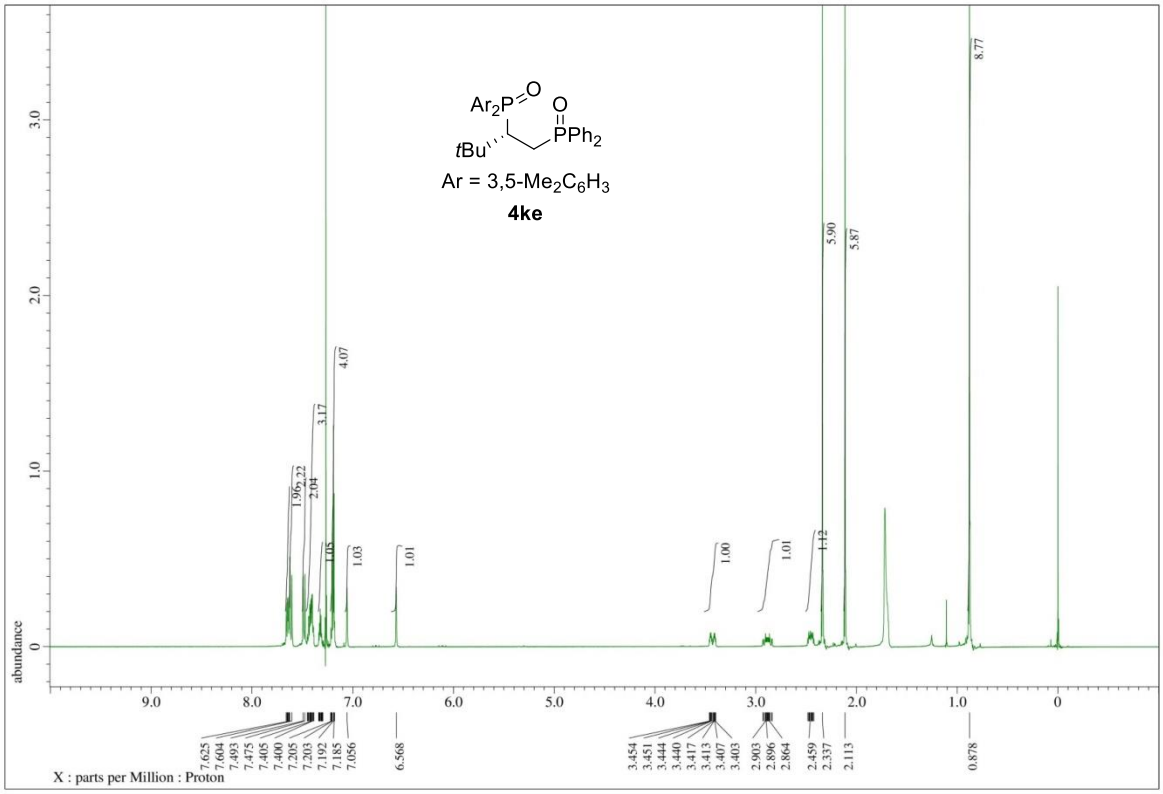

abundance
X : parts per Million : Carbon13

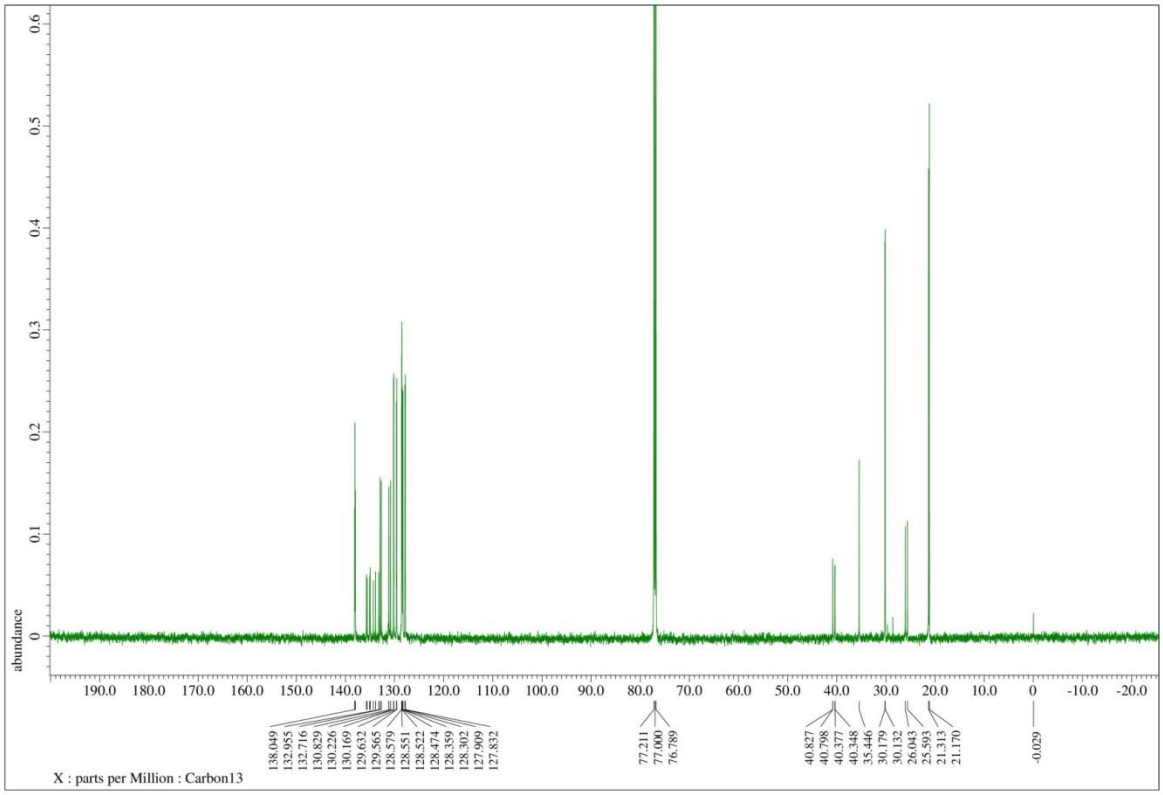

Ar = 3,5-Me2C6H3
4ie
abundance
X : parts per Million : Proton

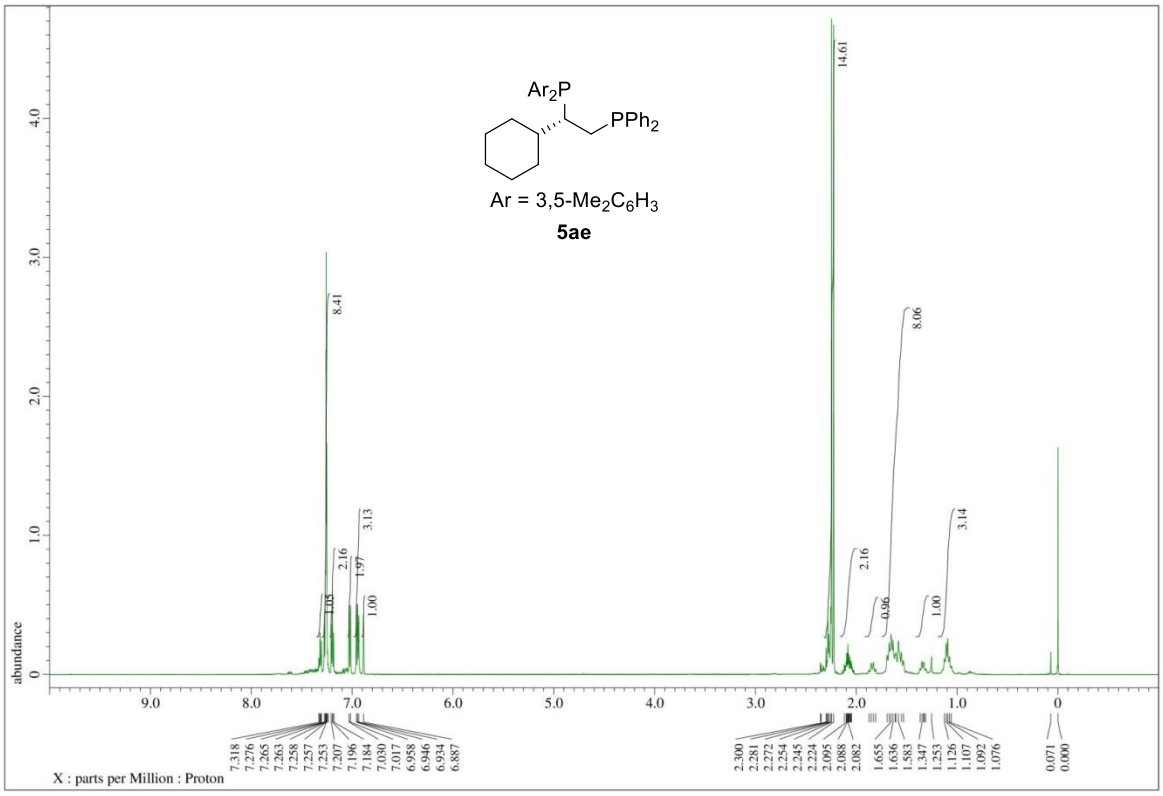

abundance
X : parts per Million : Carbon13

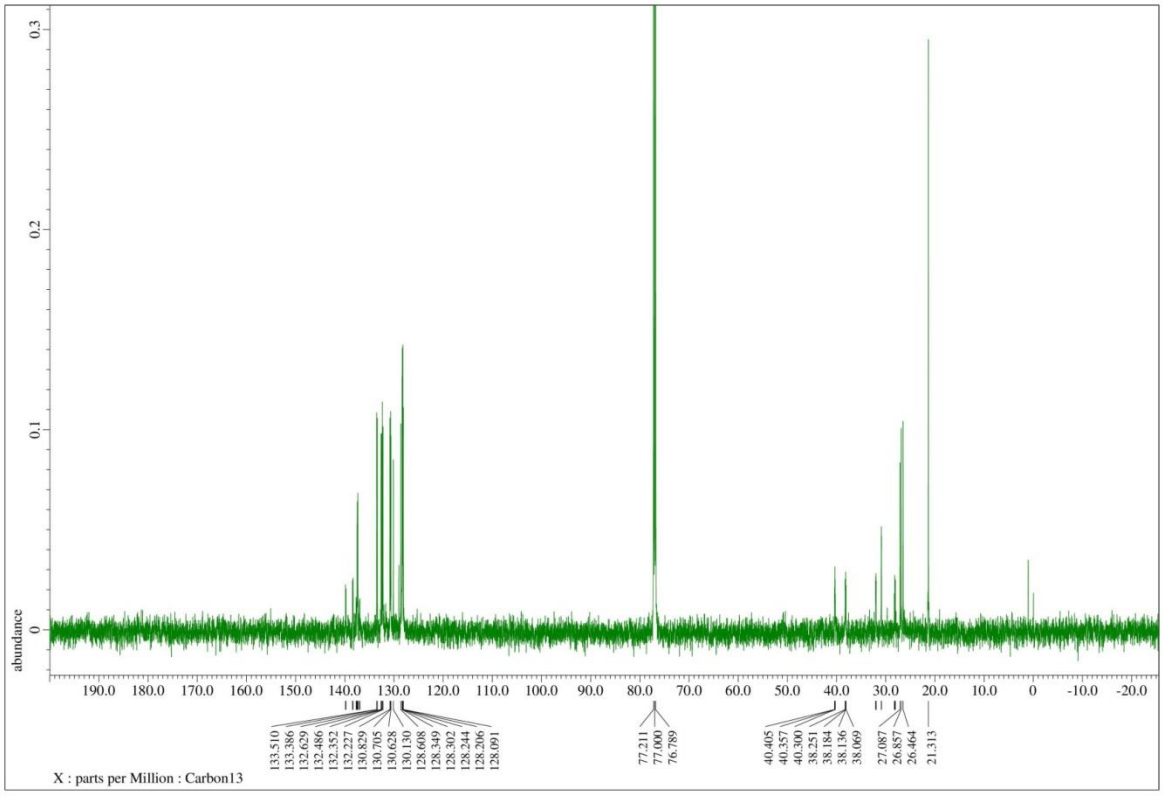

Ar = 3,5-Me2C6H3
4je
X : parts per Million : Proton

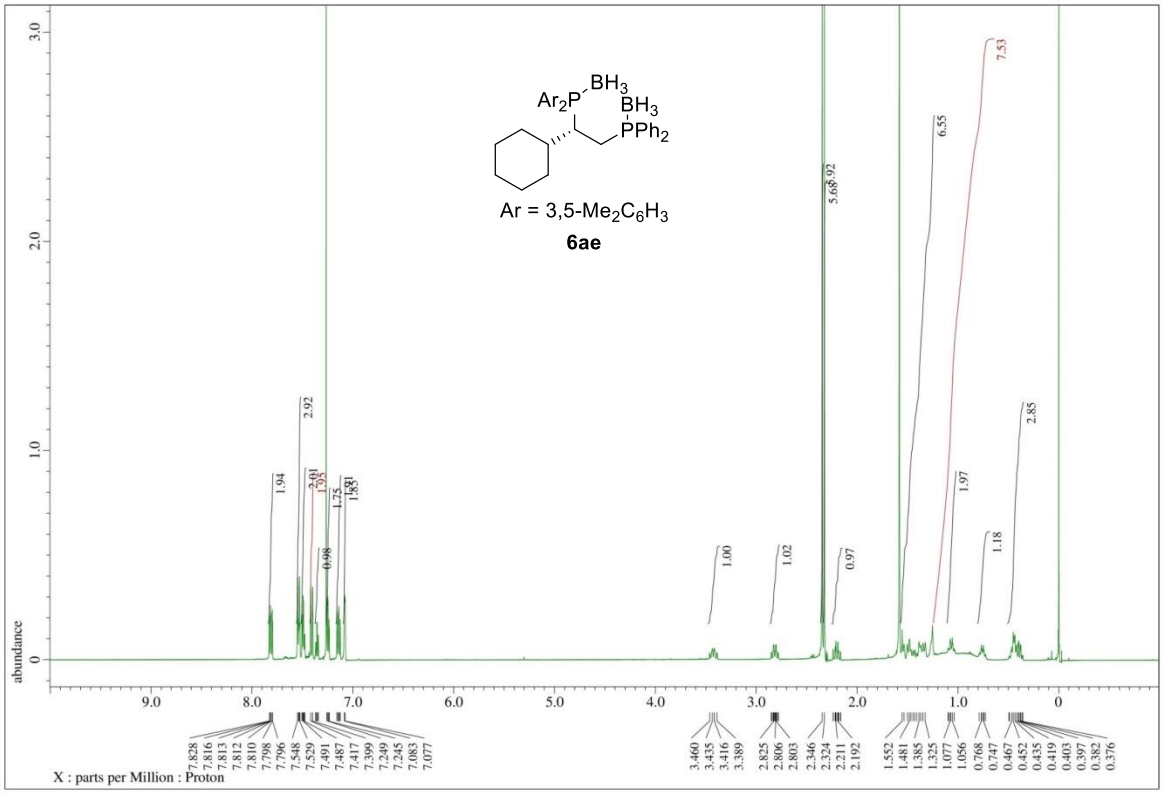

X : parts per Million : Carbon13

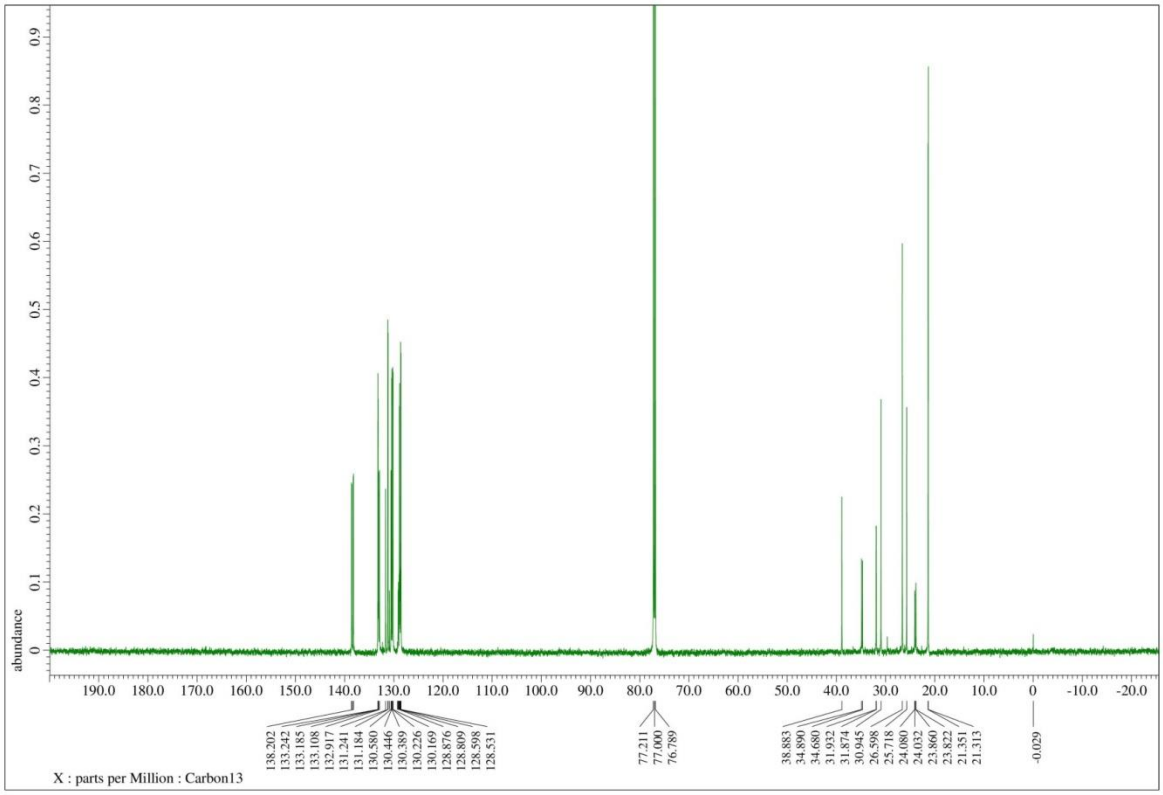

Ar = 3,5-Me2C6H3
4ke
abundance
X : parts per Million : Proton

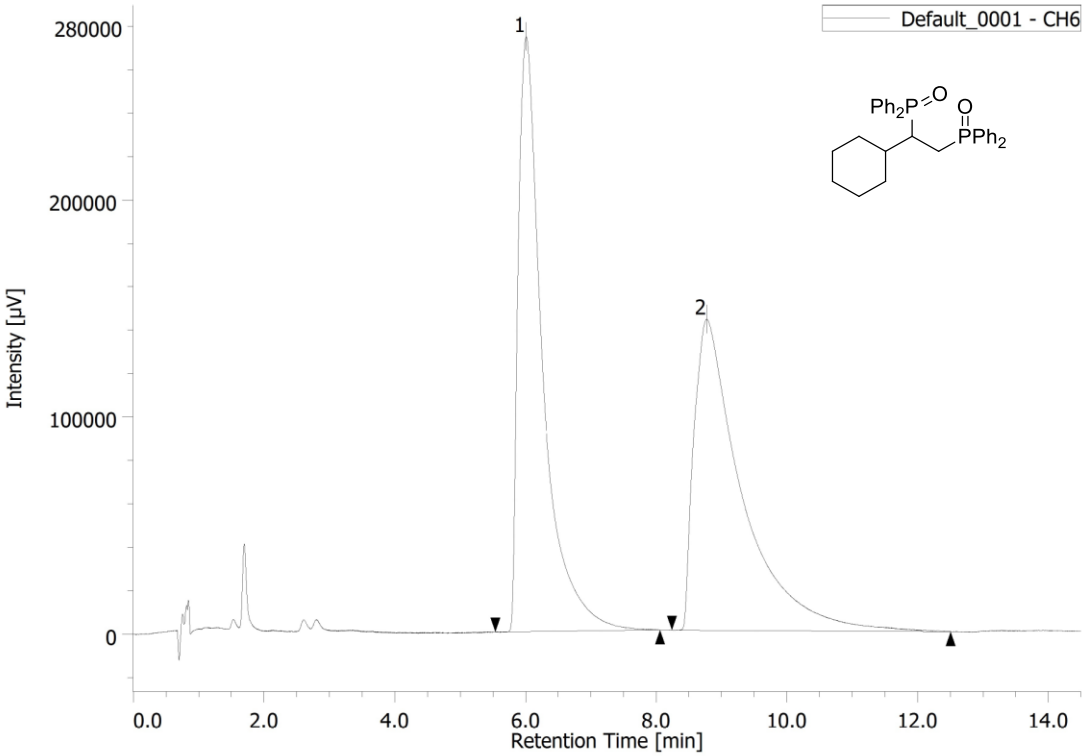

abundance
X : parts per Million : Carbon13

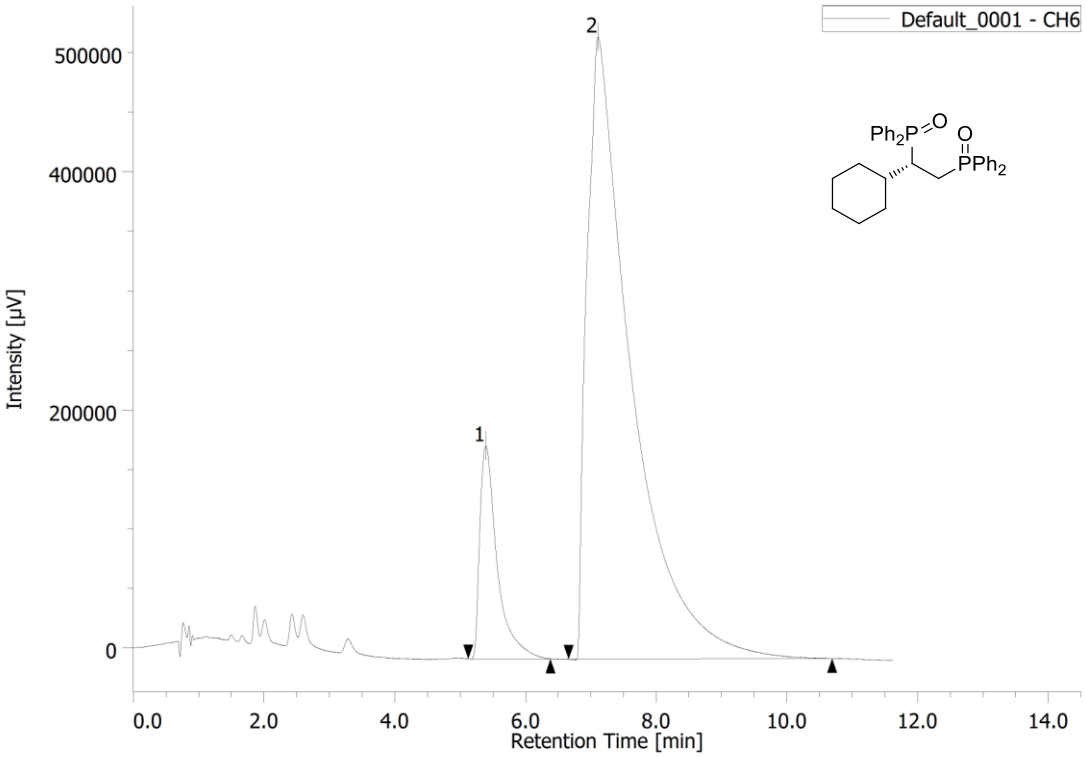

Ar2P
PPh2
Ar = 3,5-Me2C6H3
5ae
abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13


Ar = 3,5-Me2C6H3
6ae
abundance
X : parts per Million : Proton

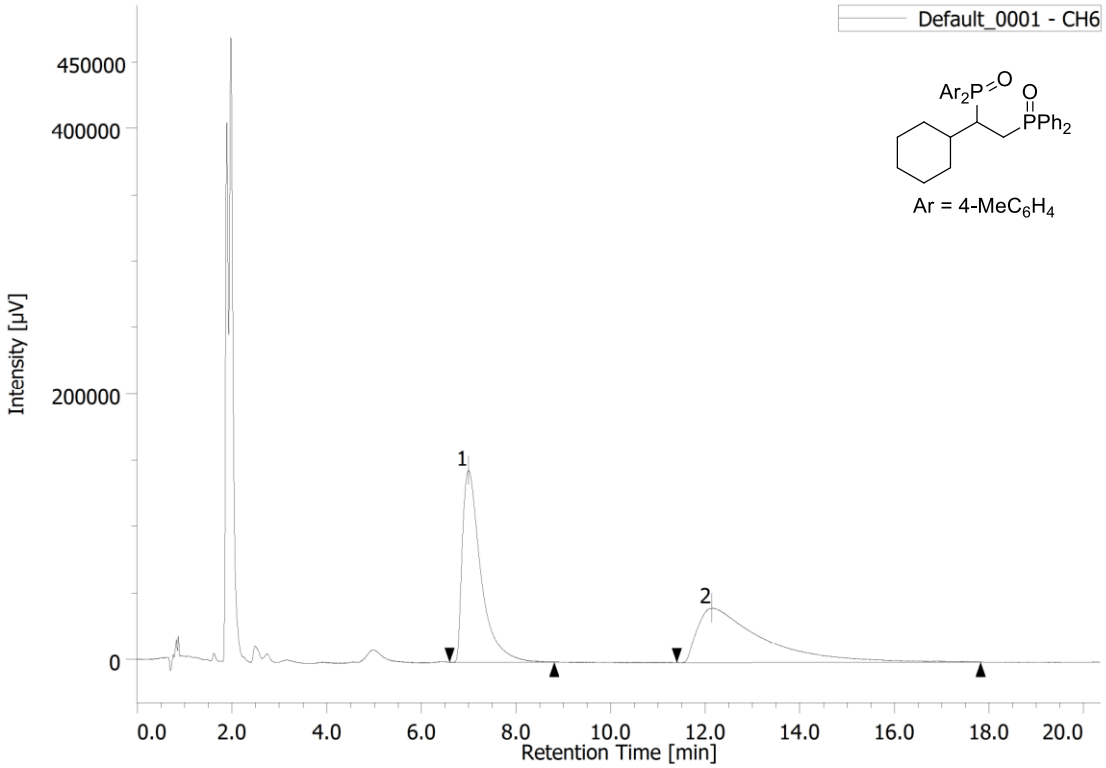

abundance
X : parts per Million : Carbon13

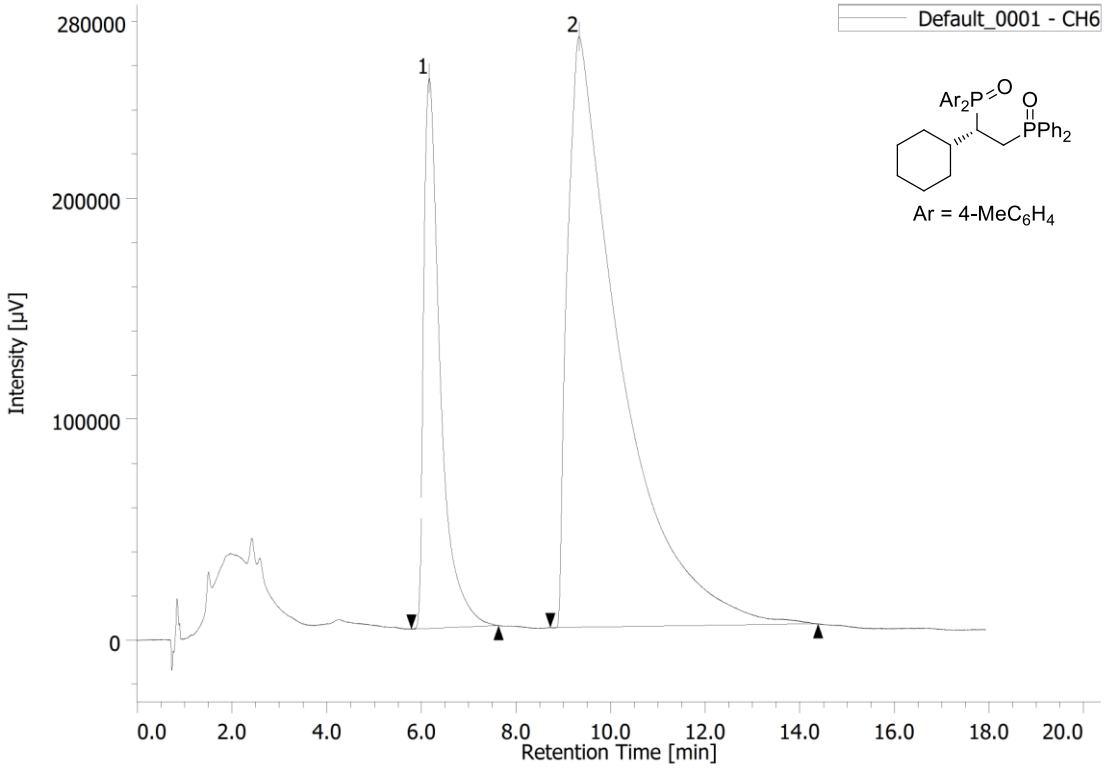




4aa

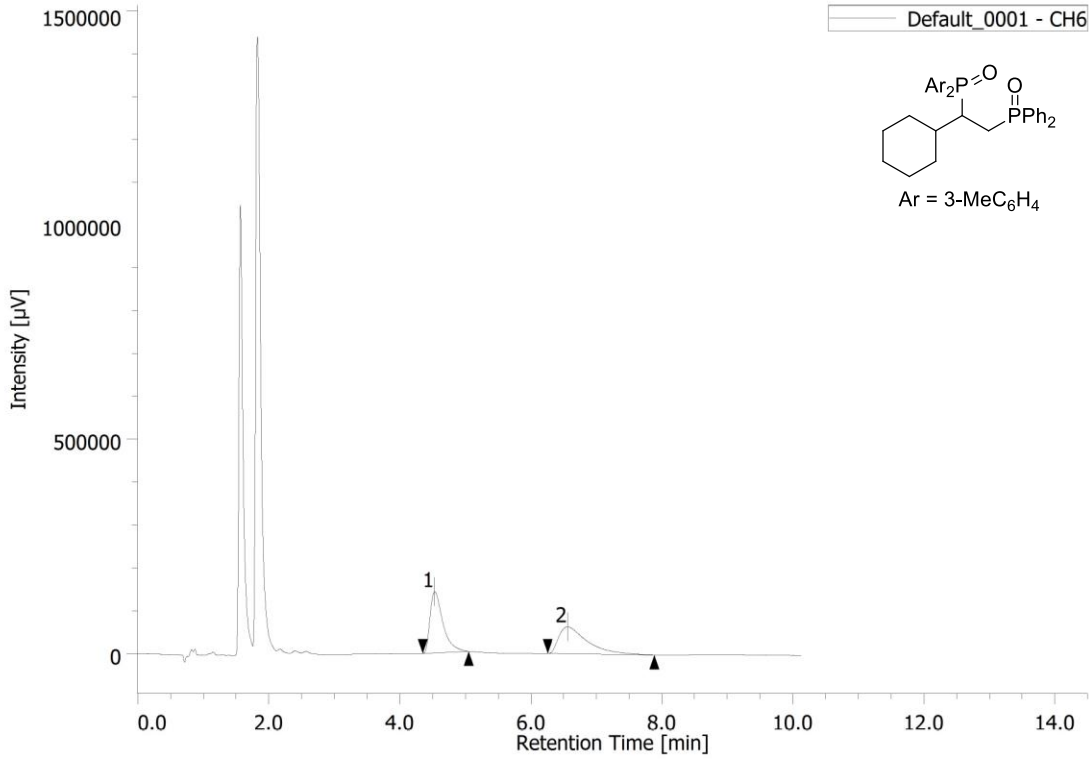
Peak	1	2
Retention Time (min)	5.4	7.1
Area (%)	11.8	88.2

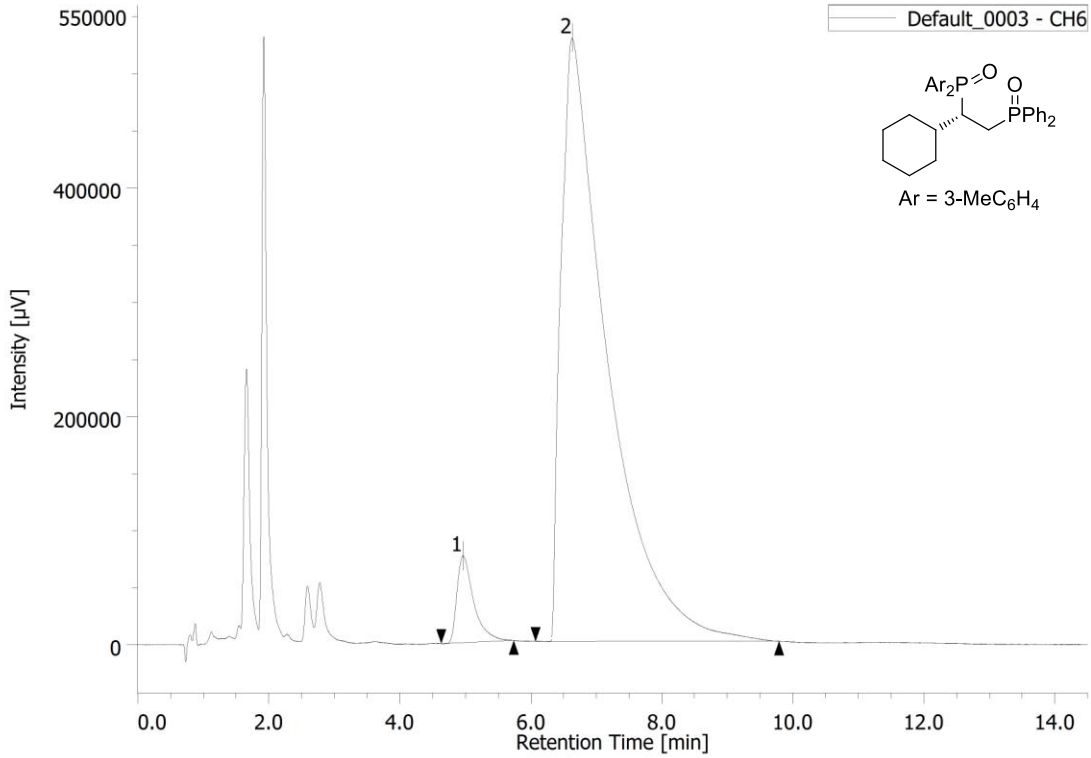




4ab

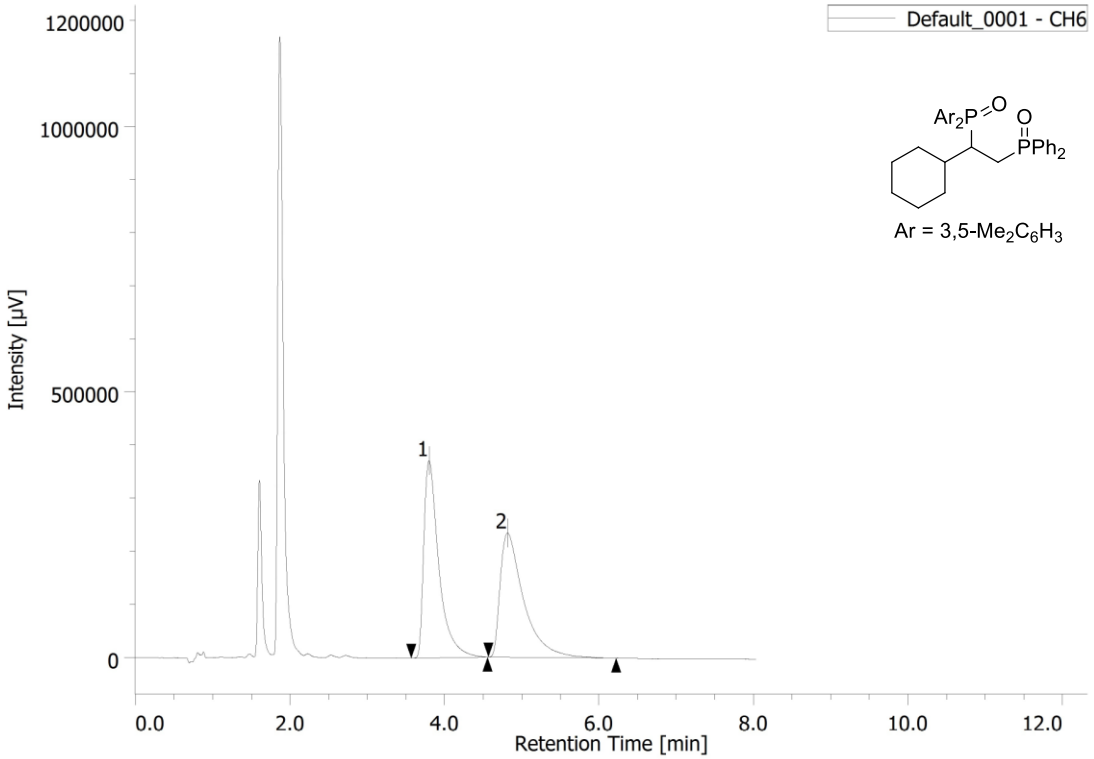
Peak	1	2
Retention Time (min)	6.2	9.3
Area (%)	22.7	77.3

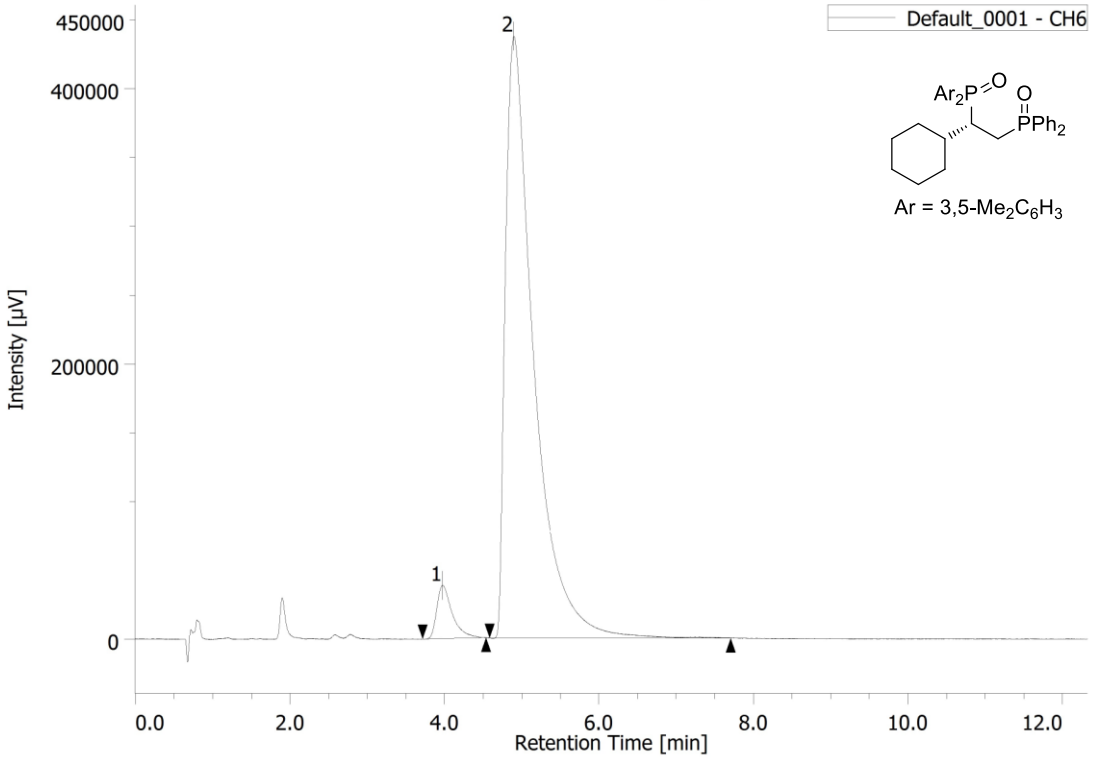




4ad

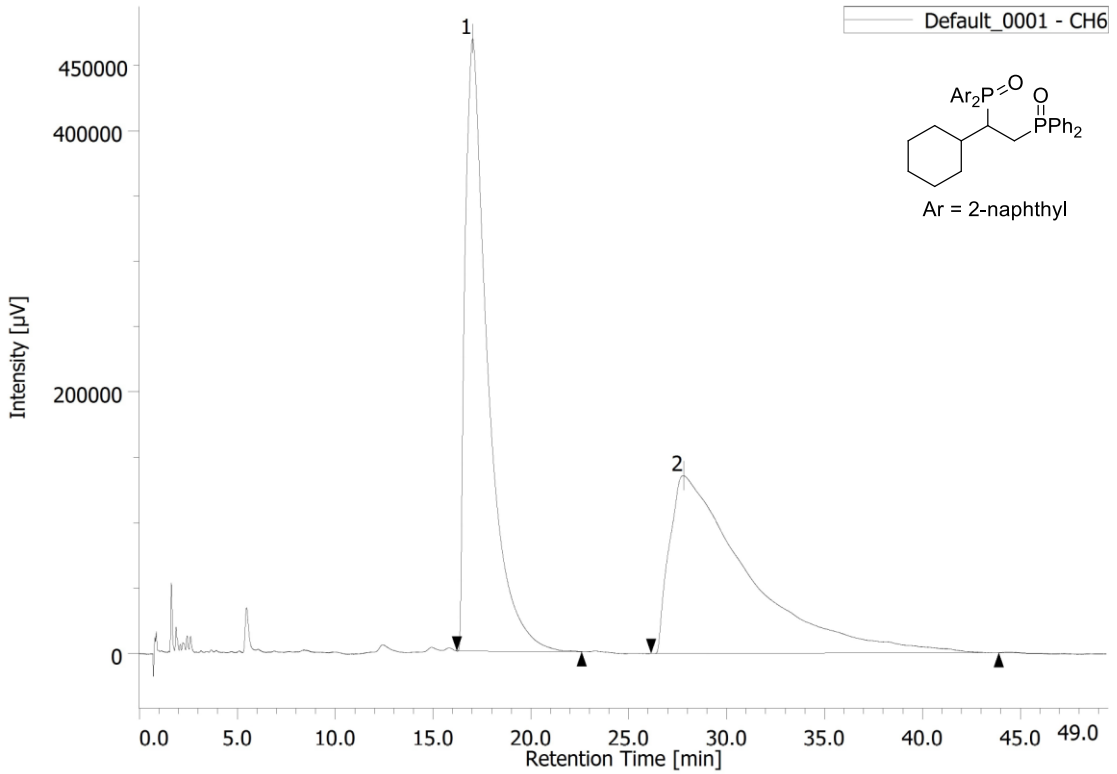
Peak	1	2
Retention Time (min)	5.0	4.9
Area (%)	22.7	95.1

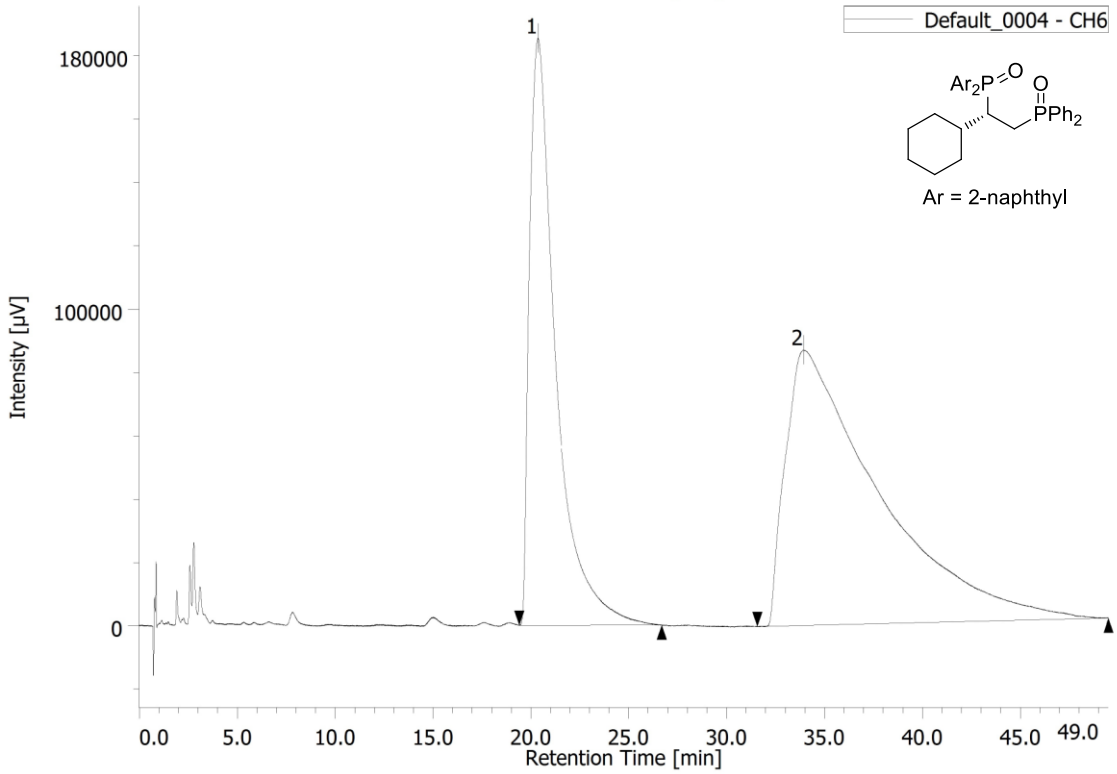




4ae

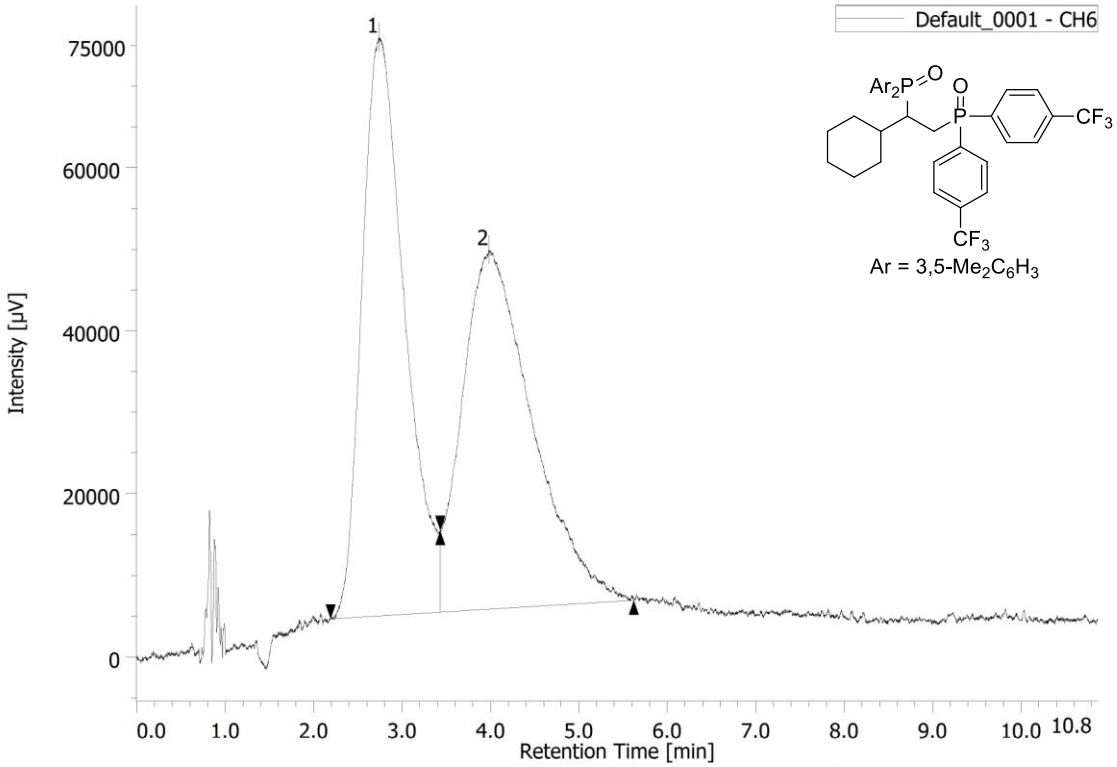
Peak	1	2
Retention Time (min)	4.0	4.9
Area (%)	4.6	95.4

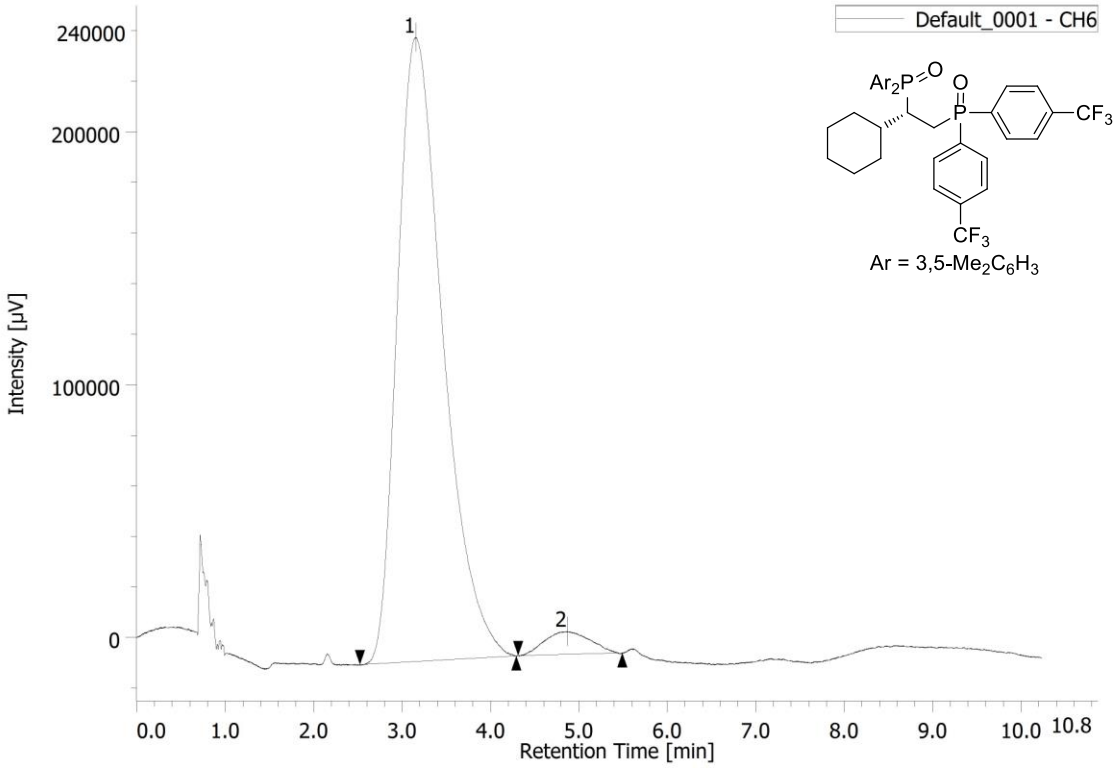




4af

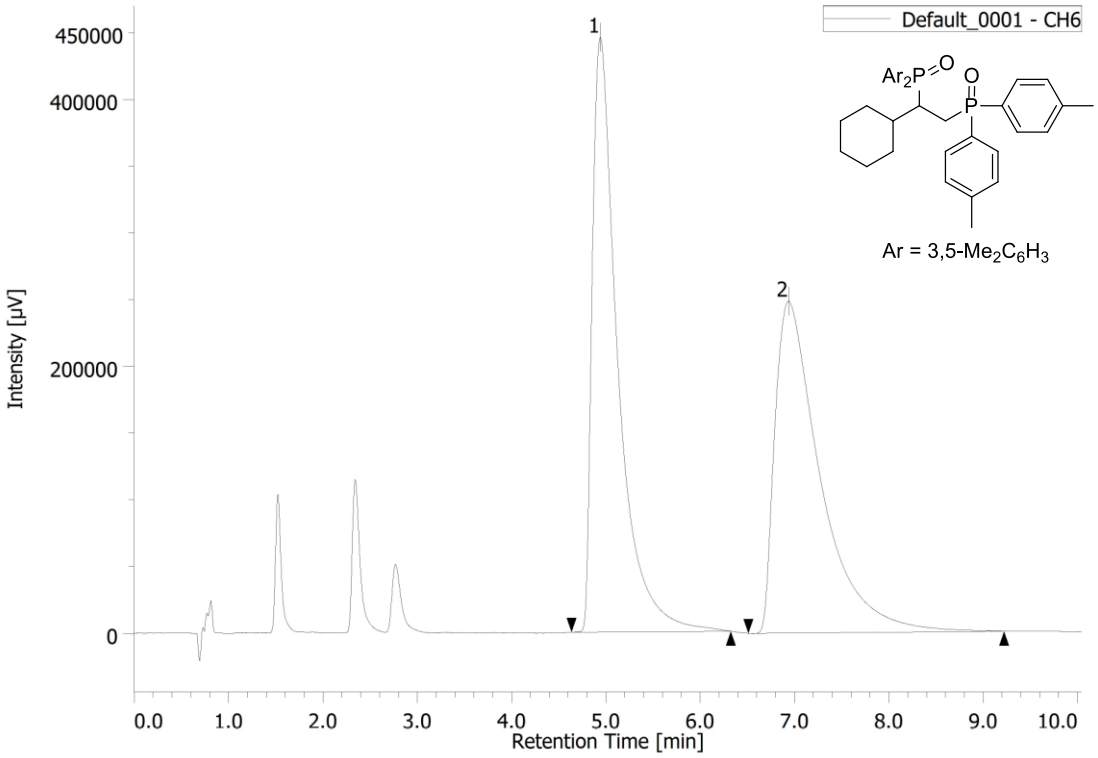
Peak	1	2
Retention Time (min)	20.4	33.9
Area (%)	37.6	62.4

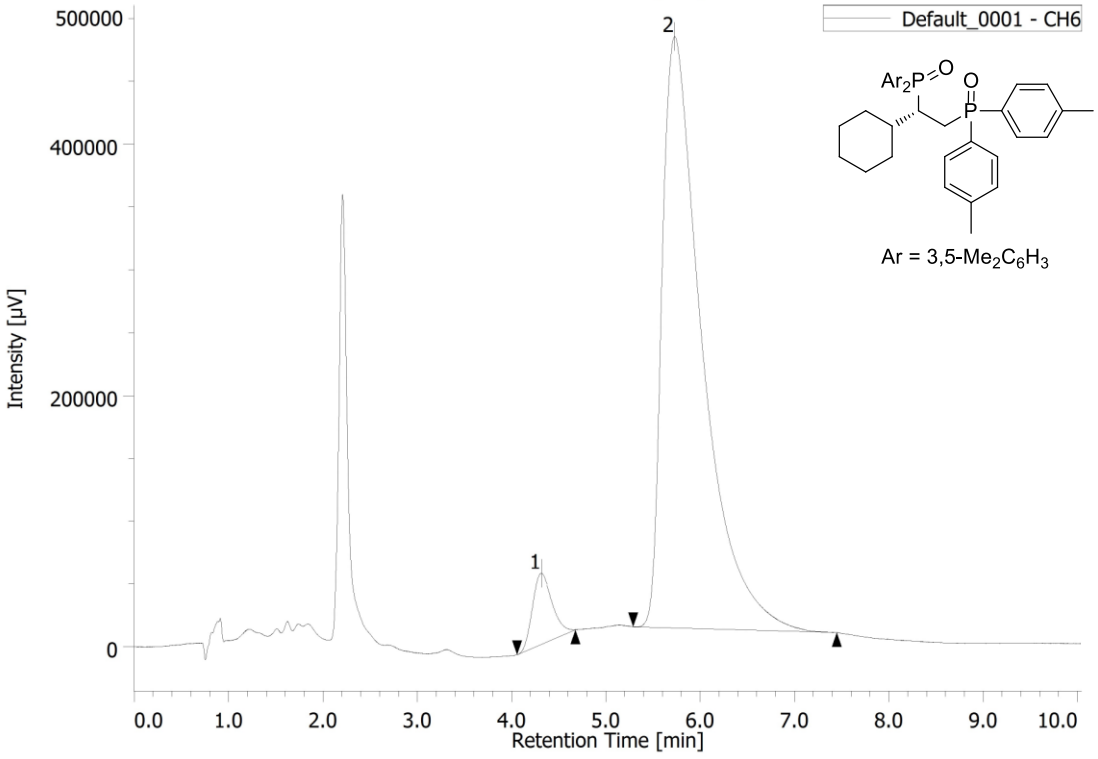




4be

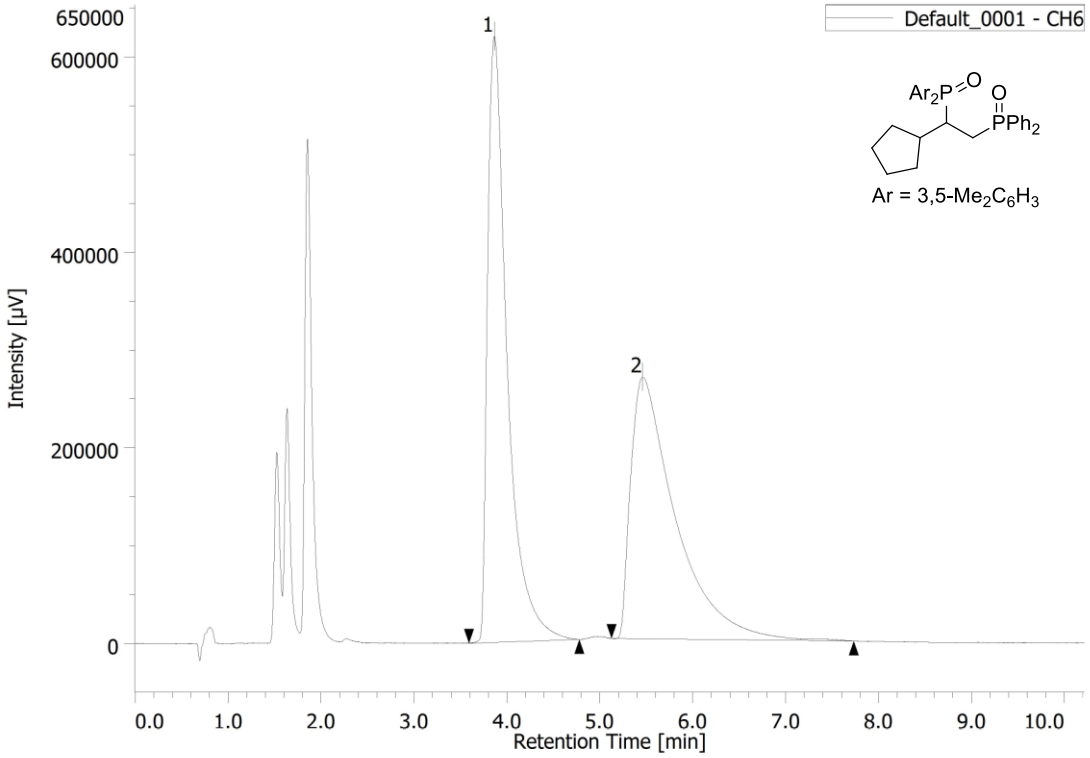
Peak	1	2
Retention Time (min)	3.2	4.9
Area (%)	96.5	3.5

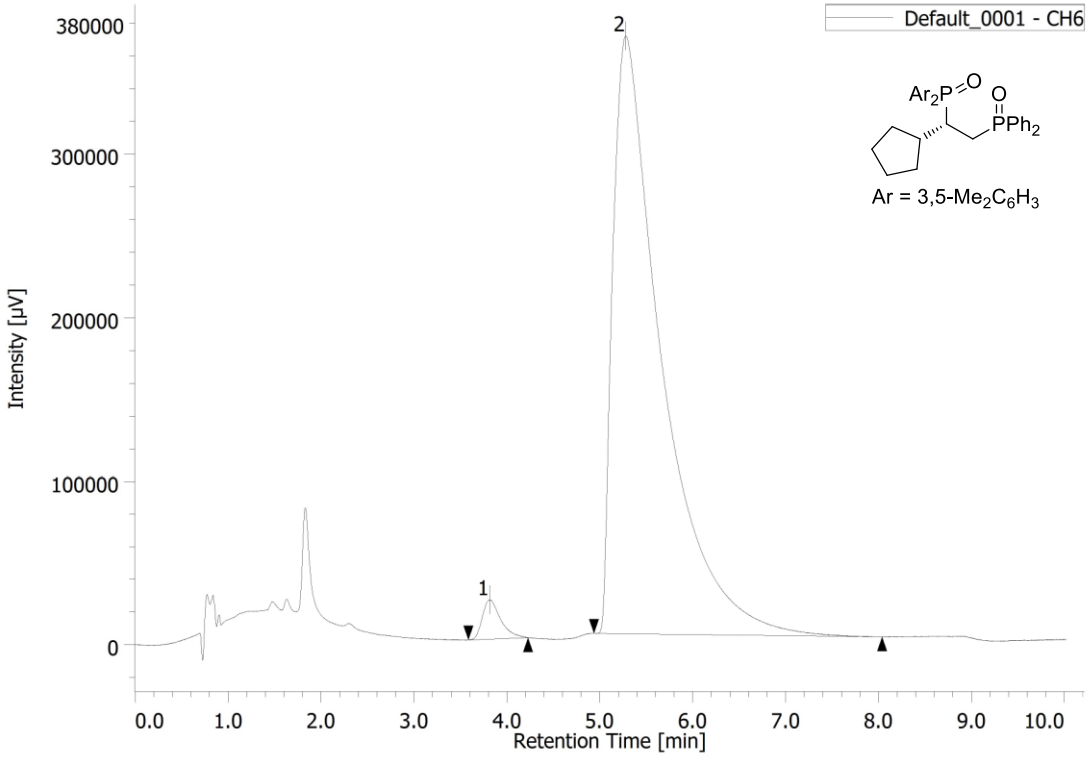




4ce

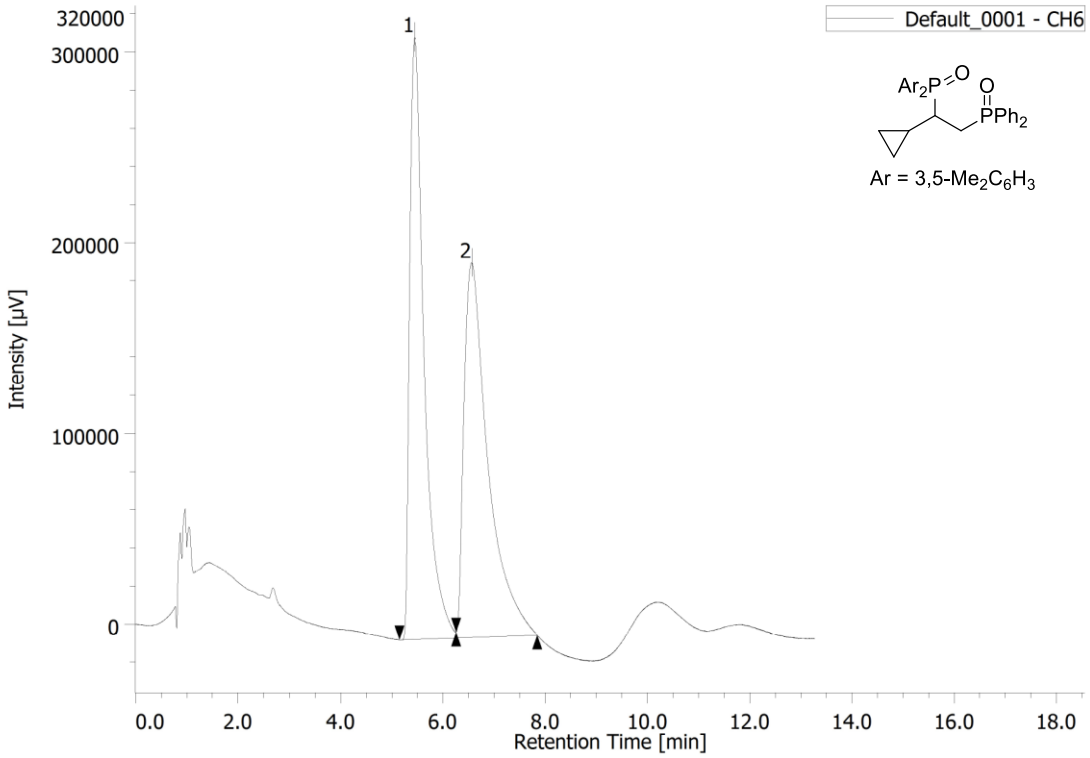
Peak	1	2
Retention Time (min)	4.3	5.7
Area (%)	5.6	94.4

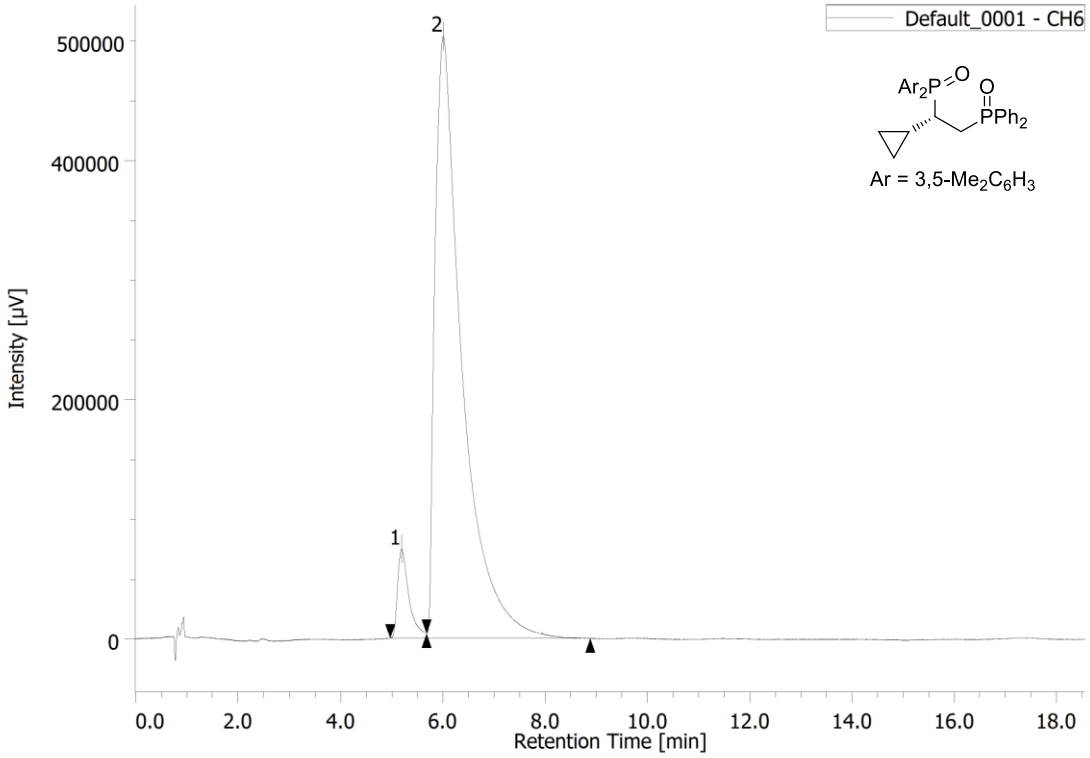




4ee

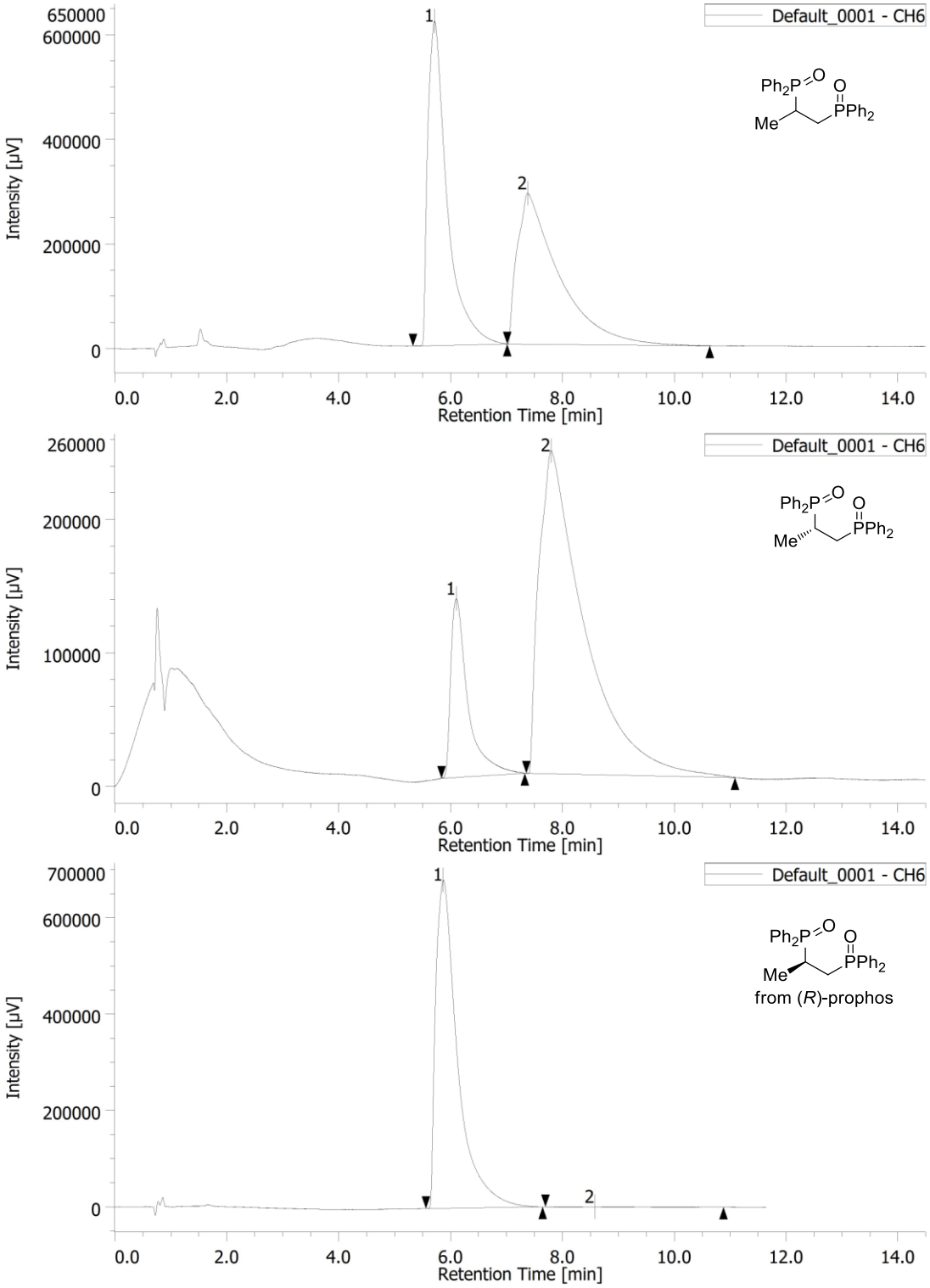
Peak	1	2
Retention Time (min)	3.8	5.3
Area (%)	2.4	97.6





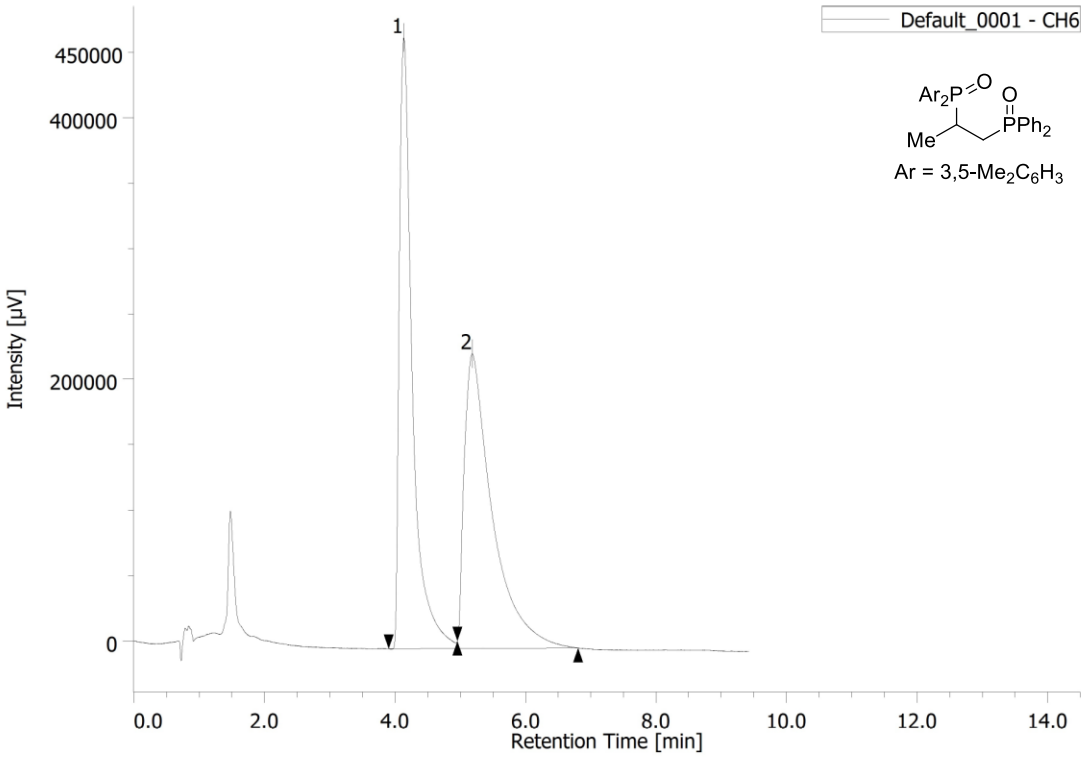
4fe

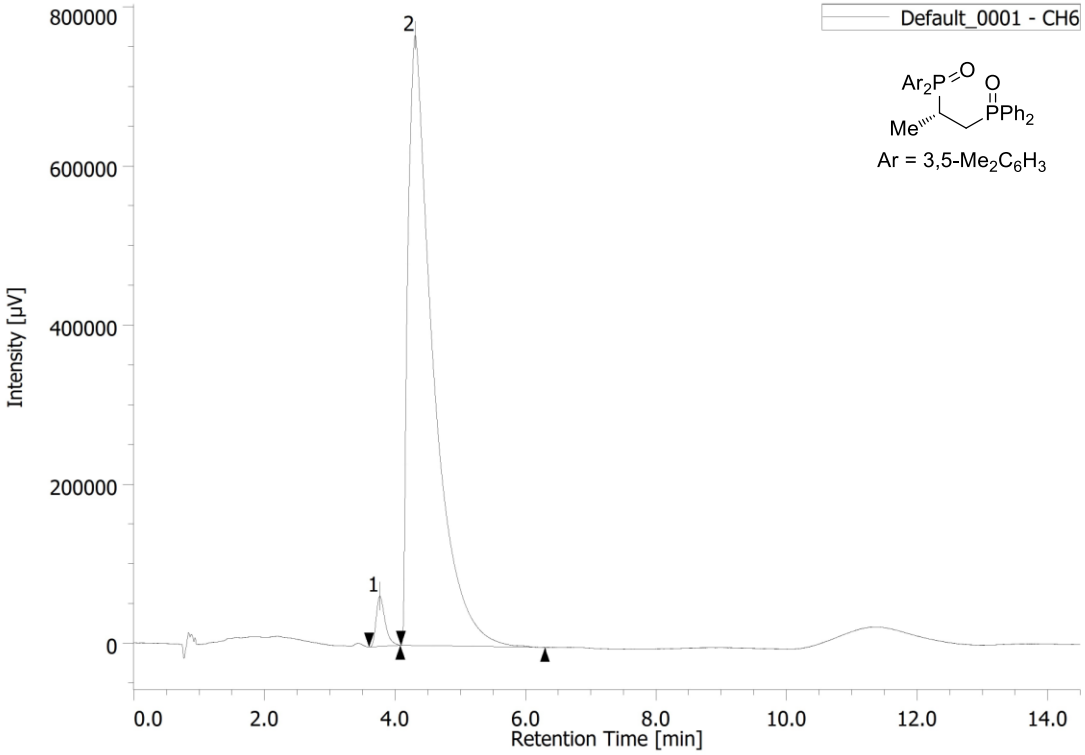
Peak	1	2
Retention Time (min)	5.2	6.0
Area (%)	6.0	94.0



4ga

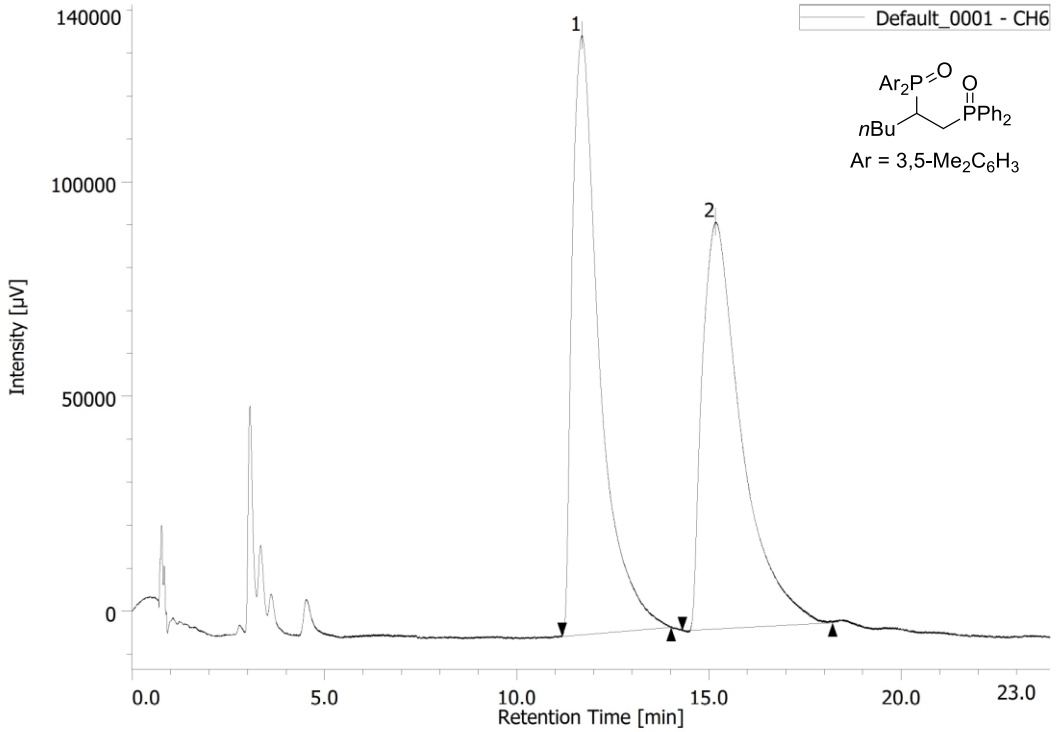
Peak	1	2
Retention Time (min)	6.1	7.8
Area (%)	17.4	82.6

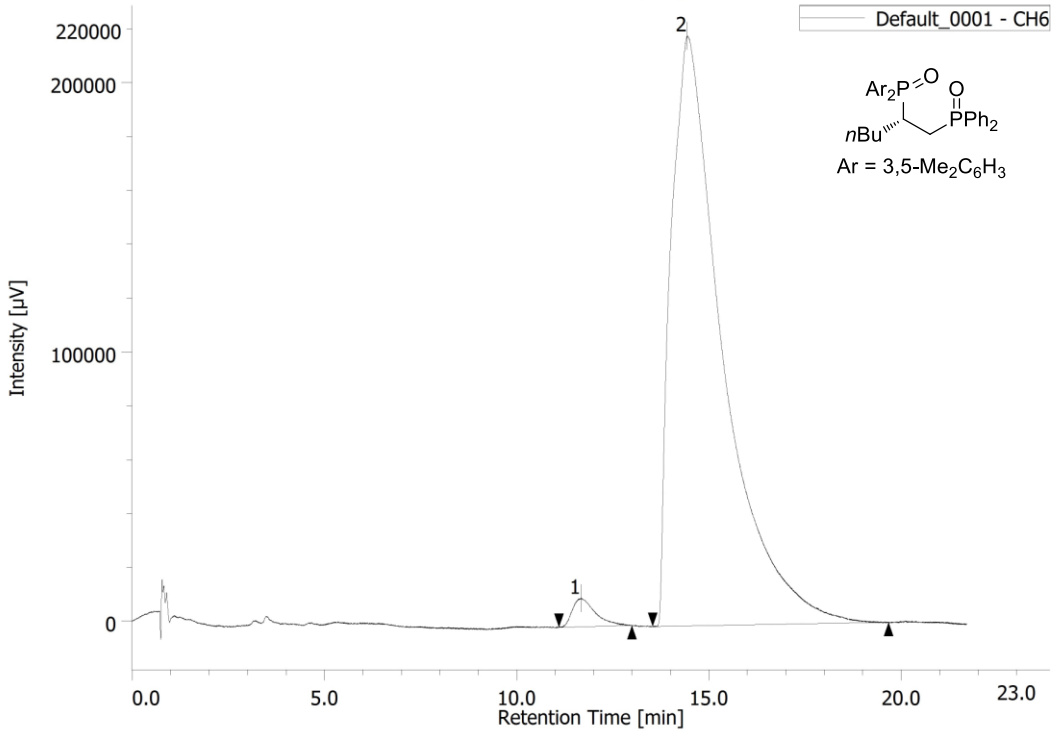




4ge

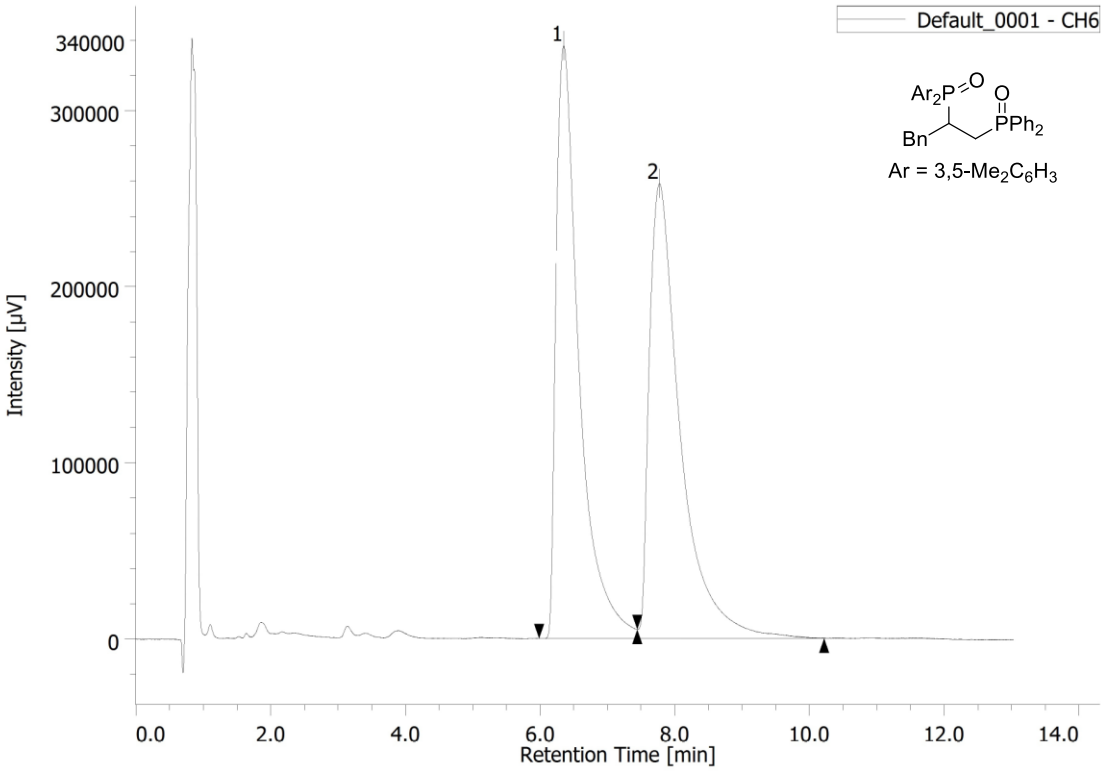
Peak	1	2
Retention Time (min)	3.8	4.3
Area (%)	2.8	97.2

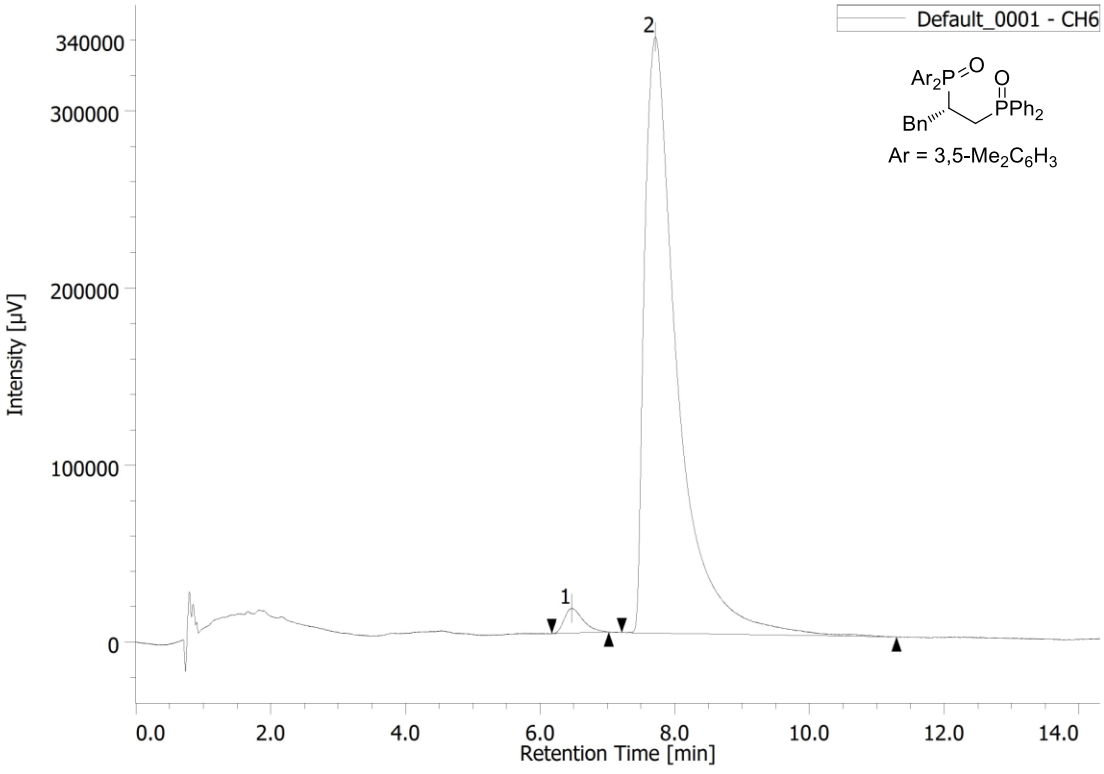




4he

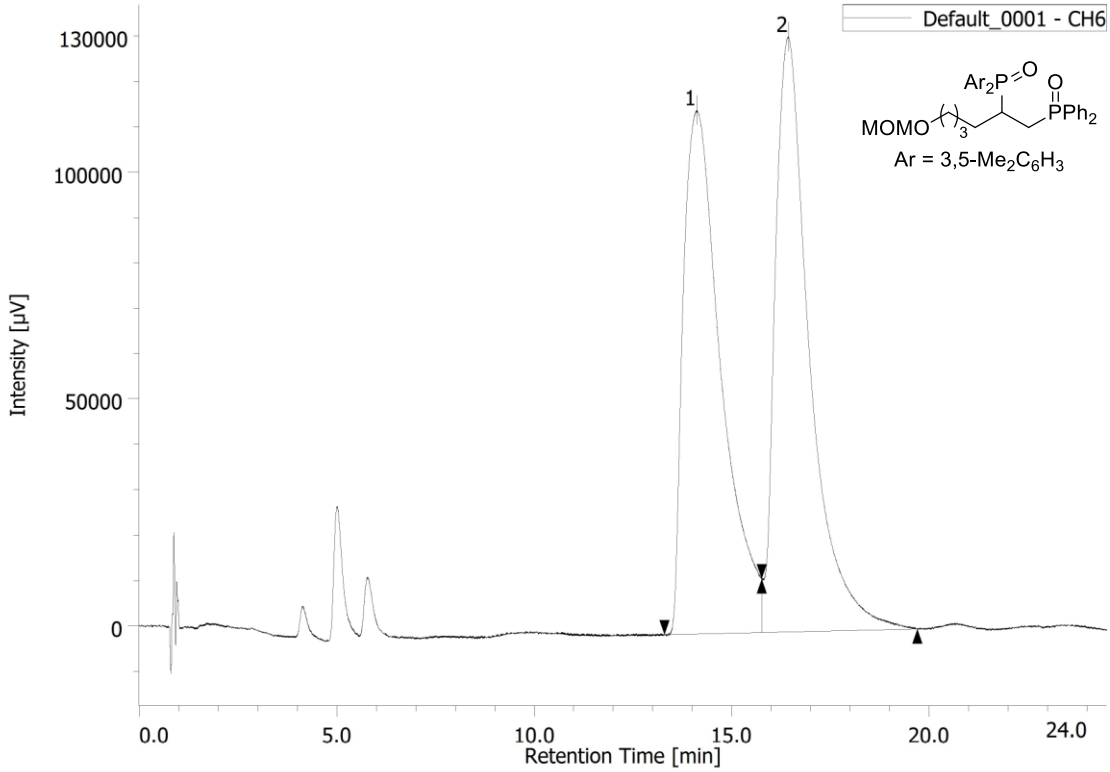
Peak	1	2
Retention Time (min)	11.7	14.4
Area (%)	2.1	97.9

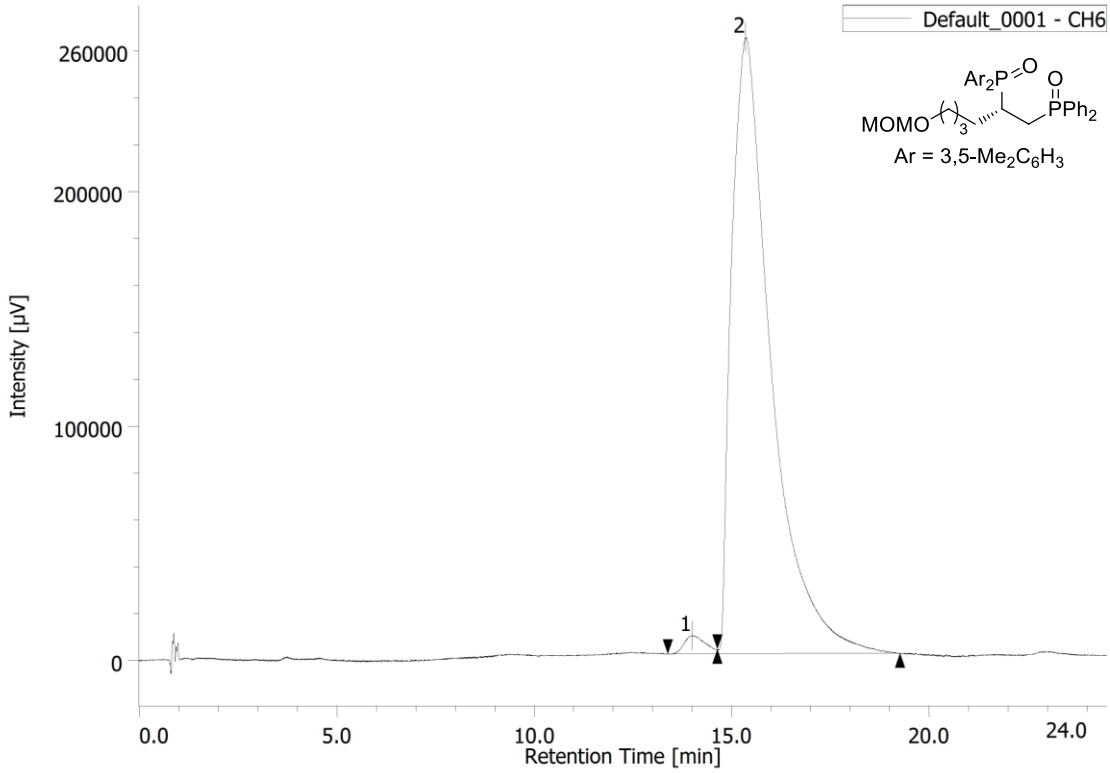




4ie

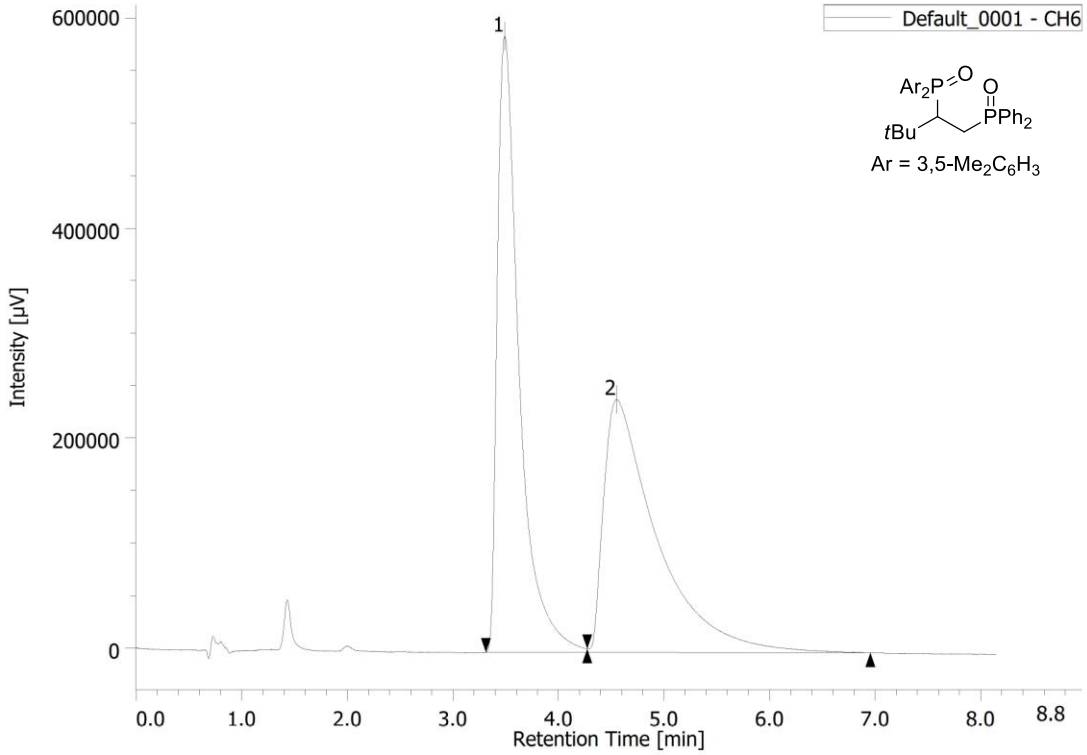
Peak	1	2
Retention Time (min)	6.5	7.7
Area (%)	2.3	97.7

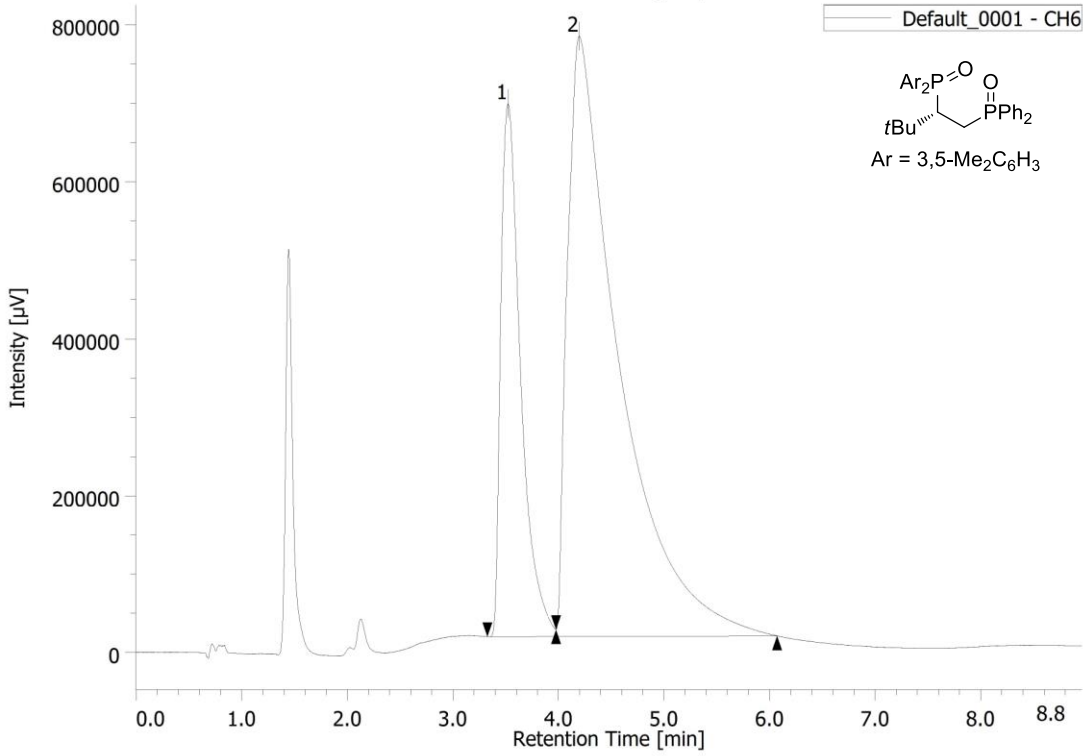




4je

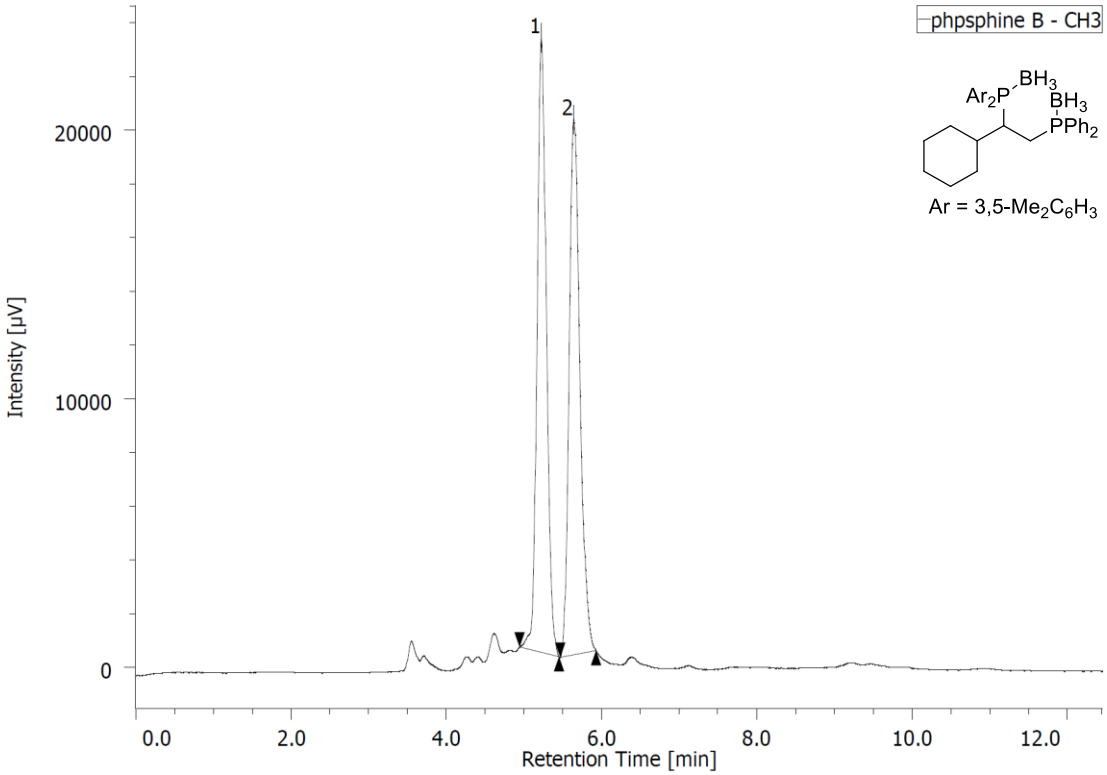
Peak	1	2
Retention Time (min)	14.0	15.4
Area (%)	1.6	98.4

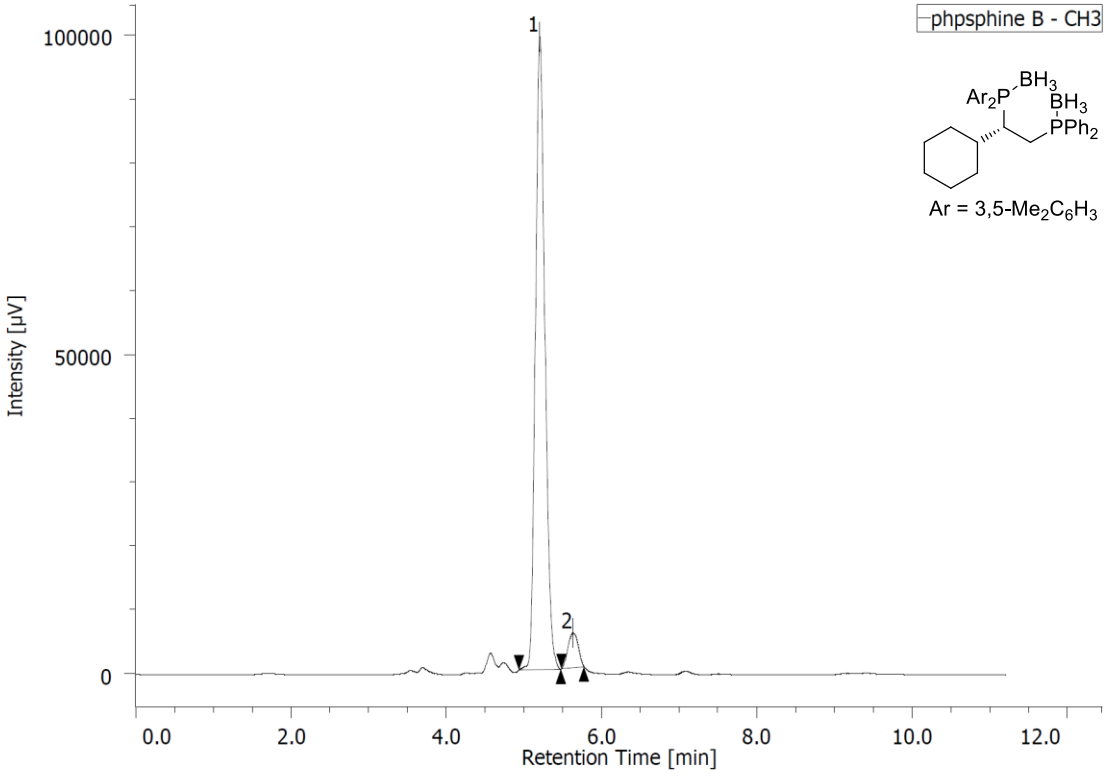




4ke

Peak	1	2
Retention Time (min)	3.5	4.2
Area (%)	25.6	74.4





6ae

Peak	1	2
Retention Time (min)	5.2	5.6
Area (%)	94.4	5.6