Electronic Supplementary Information

Phosphazene-Catalyzed Intramolecular Cyclization of Nitrogen-Tethered Alkynyl Esters

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Contents

General Information

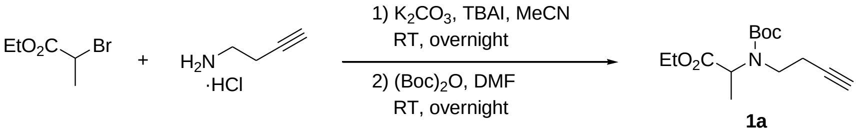
Unless otherwise noted, the reactions were carried out with dried glassware under argon atmosphere. ^{1}H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm, C_6D_6: 7.15 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet), 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). 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. 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

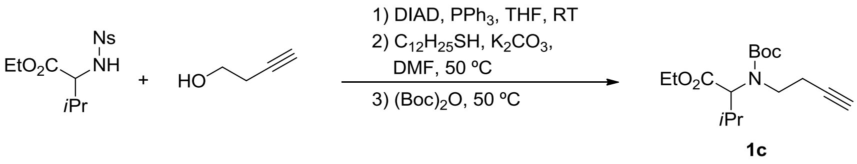
1. Preparation of Alkynyl Esters

Representative Procedure for Preparation of Alkynyl Esters 1a, 1d, 1f and 3a



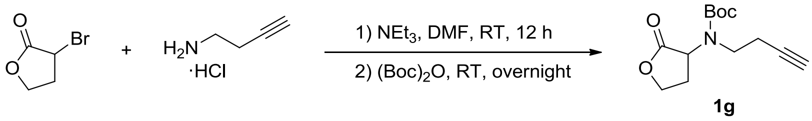
To a suspension of 3-butynylamine hydrochloride[1] (528 mg, 5 mmol), K_2CO_3 (1.38 g, 10 mmol) and TBAI (554 mg, 1.5 mmol) in MeCN (20 mL) was added 2-bromo propionic acid ethyl ester (905 mg, 5 mmol). After the resulting slurry was stirred overnight at 40 °C, the resulting mixture was extracted with AcOEt. The organic phase was extracted with 1 *N* aqueous HCl and washed with DCM. The aqueous phase was basified by using 3 *N* aqueous NaOH and extracted with DCM. The combined organic phase was dried over Na_2SO_4, filtered and concentrated. The residual oil was dissolved in DMF (10 mL) and $(Boc)_2O$ (2.18 g, 10 mmol) was added to the solution. The mixture was stirred overnight at 40 °C. The resulting mixture was quenched with 1 *N* aqueous HCl and extracted with AcOEt. The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (hexane/AcOEt = 8/1 as eluent) to afford **1a** (986 mg, 3.66 mmol, 73%) as colorless oil.

Procedure for Preparation of Alkynyl Esters 1b and 1c



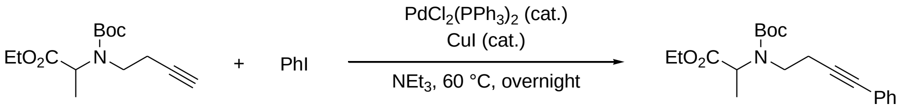
To a solution of *N*-(2-nitrobenzenesulfonyl)-(L)-valine ethyl ester[2] (1.23 g, 3.7 mmol), 3-butyn-1-ol (393 mg, 5.6 mmol) and PPh_3 (1.47 g, 5.6 mmol) in THF (18.5 mL) was added DIAD (1.10 mL, 5.6 mmol) at 0 °C. The reaction mixture was stirred for 24 h at room temperature and then concentrated. The residual oil was purified by flash column chromatography (hexane/AcOEt = 2/1 as eluent). To the solution of the product in DMF (14 mL) was added K_2CO_3 (1.99 g, 14.4 mmol) and $C_{12}H_{25}SH$ (1.82 g, 9.0 mmol) under N_2 atmosphere. After stirred overnight at 50 °C, $(Boc)_2O$ (1.96 g, 9.0 mmol) was added to the mixture. The resulting mixture was further stirred overnight and then quenched with 1 *N* aqueous HCl. The product was extracted with AcOEt. The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (hexane/AcOEt = 10/1 as eluent) to afford **1c** (723 mg, 2.4 mmol, 66%) as white solid.

Representative Procedure for Preparation of 1g, 1h, 1j and 3b



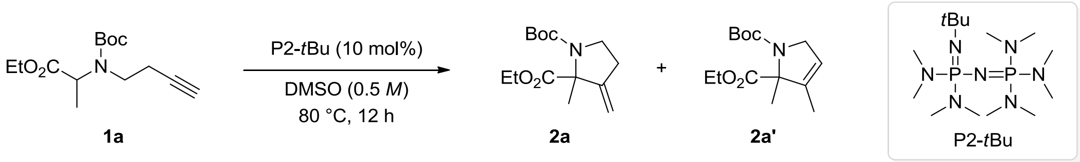
To a solution of 3-butynylamine hydrochloride[1] (2.11 g, 20 mmol) in DMF (40 mL) was added NEt_3 (2.71 g, 40 mmol) followed after 30 min by 3-bromodihydrofuran-2(3*H*)-one (3.30 g, 20 mmol). After the resulting slurry was stirred for 12 h at room temperature, $(Boc)_2O$ (8.73 g, 40 mmol) was added to the mixture and stirred overnight. The reaction mixture was quenched with 1 *N* aqueous HCl and extracted with AcOEt. The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (hexane/AcOEt = 2/1 as eluent) to afford **1g** (2.32 g, 46%) as white solid.

Preparation of Alkynyl Ester 1e and 1i



To a mixture of $PdCl_2(PPh_3)_2$ (21.1 mg, 0.03 mmol) and CuI (5.7 mg, 0.03 mmol) in NEt_3 (2 mL) was added **1a** (269 mg, 1.0 mmol) and iodobenzene (224 mg, 2.2 mmol) under N_2 atmosphere. After stirred overnight at room temperature, the resulting mixture was extracted with AcOEt. The organic phase was dried over Na_2SO_4 and filtered. After being concentrated, the residue was purified by flash column chromatography (hexane/AcOEt = 10/1 as eluent) to afford **1e** (334 mg, 0.967 mmol, 97%) as colorless oil.

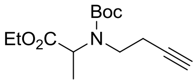
2. Representative Procedure for Intramolecular Cyclization of Alkynyl Eaters and Lactones Catalyzed by Phosphazene Bases (Table 1, Entry 10)



To a solution of **1a** (53.9 mg, 0.20 mmol) in DMSO (0.4 mL) was added phosphazene base P2-*t*Bu solution (2.0 M in THF, 10 μL, 0.020 mmol). After the resulting mixture was stirred for 12 h at 80 °C, the reaction was quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The organic phase was dried over Na_2SO_4 and filtered. After removal of solvents, the residue was purified by flash column chromatography (hexane/AcOEt = 10/1 as eluent) to afford a mixture of cyclization products **2a** and **2a’** (51.5 mg, 96%, **2a**/**2a’** = 90/10).

Analytical Data

Ethyl 2-{But-3-yn-1-yl(*tert*-butoxycarbonyl)amino}propanoate (1a):

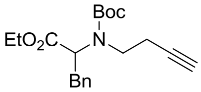


73% yield; colorless oil.

Rotamers were observed, and the ratio was 50:50 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.25-1.29 (3.0H, m), 1.42-1.48 (12.0H, m), 1.97-1.99 (1.0H, m), 2.42-2.55 (2.0H, m), 3.21-3.26 (0.5H, m), 3.35-3.39 (0.5H, m), 3.44-3.55 (1.0H, m), 4.11-4.19 (2.5H, m), 4.51 (0.5H, q, J = 7.2 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 13.9, 15.3, 15.9, 18.6, 19.3, 28.1, 28.1, 44.9, 46.2, 54.9, 56.2, 60.8, 69.4, 69.5, 80.2, 80.3, 81.5, 81.8, 154.4, 154.9, 171.9, 172.0; IR (ATR): 3290, 2979, 2939, 1739, 1694, 1366, 1299, 1161, 1071 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 292.1525, Found 292.1519.

Ethyl 2-{But-3-yn-1-yl(*tert*-butoxycarbonyl)amino}-3-phenylpropanoate (1b):

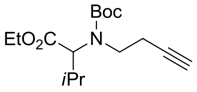


29% yield; white solid.

Rotamers were observed, and the ratio was 55:45 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.24-1.31 (3.0H, m), 1.44 (9.0H, s), 1.85 (0.55H, brs), 1.91 (0.45H, brs), 2.14-2.31 (2.0H, m), 2.72-2.77 (0.55H, m), 2.85-2.90 (0.45H, m), 3.12-3.42 (3.0H, m), 4.06-4.29 (2.0H, m), 7.16-7.31 (5.0H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 14.0, 17.7, 18.4, 28.2, 28.2, 35.3, 36.2, 47.5, 48.1, 61.0, 61.1, 62.5, 63.3, 69.2, 69.3, 80.2, 80.7, 81.6, 81.8, 126.4, 126.6, 128.3, 128.5, 129.1, 129.1, 137.9, 154.2, 154.6, 170.8, 170.8; IR (ATR): 3294, 2978, 2935, 1739, 1695, 1416, 1366, 1224, 1160, 1030 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 368.1838, Found 368.1832.

Ethyl 2-{But-3-yn-1-yl(*tert*-butoxycarbonyl)amino}-3-methylbutanoate (1c):

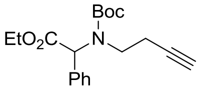


66% yield; colorless, oil.

Rotamers were observed, and the ratio was 50:50 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 0.90 (3.0H, brs), 0.98-1.00 (3.0H, m), 1.27 (3.0H, brs), 1.44-1.48 (9.0H, m), 1.96 (1.0H, brs), 2.23-2.52 (3.0H, m), 3.32-3.39 (1.5H, m), 3.54-3.59 (0.5H, m), 3.75-3.76 (0.5H, m), 4.16-4.23 (2.5H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 14.0, 18.0, 18.9, 19.1, 19.8, 20.7, 28.2, 28.5, 44.3, 46.1, 60.6, 64.0, 66.1, 69.3, 69.4, 80.3, 80.4, 81.5, 81.7, 154.7, 155.4, 170.8, 171.2; IR (ATR): 3311, 2974, 2934, 2875, 1737, 1695, 1457, 1366, 1296, 1160, 1028 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 320.1838, Found 320.1832.

Ethyl 2-{But-3-yn-1-yl(*tert*-butoxycarbonyl)amino}-2-phenylacetate (1d):

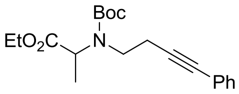


45% yield; colorless oil.

Rotamers were observed, and the ratio was 65:35 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.26 (3.0H, brs), 1.50 (9.0H, s), 1.83-2.08 (2.0H, m), 2.28-2.37 (1.0H, m), 3.16-3.26 (1.0H, m), 3.33-3.38 (1.0H, m), 4.25 (2.0H, q, J = 6.6 Hz), 5.57 (0.35H, s), 5.89 (0.65H, s), 7.27-7.29 (2.0H, m), 7.35-7.40 (3.0H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 13.8, 18.1, 18.7, 28.0, 43.8, 44.2, 60.9, 62.0, 63.4, 69.0, 80.4, 81.2, 128.3, 128.5, 128.8, 134.2, 134.7, 154.4, 155.4, 170.6; IR (ATR): 3309, 2979, 2934, 1742, 1694, 1366, 1299, 1156, 1030 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 354.1681, Found 354.1676.

Ethyl 2-{*tert*-Butoxycarbonyl(4-phenylbut-3-yn-1-yl)amino}propanoate (1e):

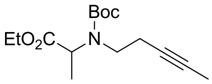


97% yield; colorless oil.

Rotamers were observed, and the ratio was 50:50 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.25-1.28 (3.0H, m), 1.43-1.53 (12.0H, m), 2.62-2.76 (2.0H, m), 3.29-3.34 (0.5H, m), 3.43-3.48 (0.5H, m), 3.52-3.62 (1.0H, m), 4.15-4.18 (2.5H, m), 4.54 (0.5H, q, J = 7.2 Hz), 7.27-7.29 (3.0H, m), 7.36-7.39 (2.0H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 14.2, 15.6, 16.2, 19.9, 20.5, 28.3, 28.4, 45.4, 46.7, 55.1, 56.5, 61.1, 80.4, 80.6, 81.7, 81.8, 87.3, 87.7, 123.5, 123.7, 127.7, 127.8, 128.2, 131.5, 154.7, 155.3, 172.2, 172.4; IR (ATR): 2979, 2936, 1739, 1696, 1366, 1299, 1214, 1161, 1070 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 368.1838, Found 368.1833.

Ethyl 2-{*tert*-Butoxycarbonyl(pent-3-yn-1-yl)amino}propanoate (1f):

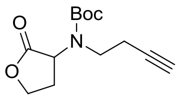


87% yield; colorless oil.

Rotamers were observed, and the ratio was 50:50 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.20-1.28 (3.0H, m), 1.36-1.50 (12.0H, m), 1.72-1.78 (3.0H, m), 2.27-2.46 (2.0H, m), 3.09-3.20 (0.5H, m), 3.26-3.35 (0.5H, m), 3.35-3.49 (1.0H, m), 4.05-4.20 (2.5H, m), 4.43-4.51 (0.5H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 3.5, 14.2, 15.6, 16.2, 19.2, 19.9, 28.4, 28.5, 45.7, 47.1, 55.1, 56.5, 61.8, 76.3, 76.8, 80.3, 80.5, 154.7, 155.4, 172.3, 172.4; IR (ATR): 2979, 2939, 1739, 1696, 1366, 1162, 1071 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 306.1681, Found 306.1675.

tert-Butyl But-3-yn-1-yl(2-oxotetrahydrofuran-3-yl)carbamate (1g):

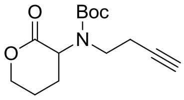


46% yield; white solid.

Rotamers were observed, and the ratio was 50:50 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.46 (4.5H, s), 1.48 (4.5H, s), 2.00 (1.0H, brs), 2.46-2.62 (4.0H, m), 3.35-3.43 (1.0H, m), 3.47-3.52 (0.50H, m), 3.63-3.67 (0.50H, m), 4.09 (0.50H, dd, J = 10.2, 10.2 Hz), 4.20-4.25 (1.5H, m), 4.41-4.44 (0.50H, m), 4.51 (0.50H, dd, J = 8.4, 8.4 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 18.8, 19.3, 26.9, 27.7, 28.0, 28.2, 47.9, 48.5, 57.4, 57.6, 64.9, 65.4, 69.8, 70.0, 81.2, 81.3, 81.6, 81.9, 153.4, 154.2, 174.2, 174.3; IR (ATR): 3267, 2977, 2933, 1778, 1691, 1366, 1253, 1159, 1024 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 276.1212, Found 276.1206.

tert-Butyl But-3-yn-1-yl(2-oxotetrahydro-2*H*-pyran-3-yl)carbamate (1h):



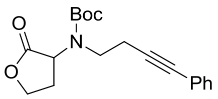
3-Bromotetrahydro-2*H*-pyran-2-one was prepared according to the literature procedure[3] and used instead of 3-bromodihydrofuran-2(3*H*)-one.

30% yield; white solid.

Rotamers were observed, and the ratio was 55:45 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.47 (4.0H, s), 1.48 (5.0H, s), 1.91-1.99 (3.0H, m), 2.20-2.31 (2.0H, m), 2.45-2.58 (2.0H, m), 3.35-3.40 (0.55H, m), 3.45-3.55 (1.45H, m), 3.84 (0.45H, dd, J = 10.8, 7.2 Hz), 4.08-4.11 (0.55H, m), 4.29 (0.45H, ddd, *J* = 10.8, 10.8, 3.6 Hz), 4.34-4.42 (1.55H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.7, 19.3, 22.8, 23.1, 25.8, 27.2, 28.2, 28.3, 47.8, 48.5, 57.8, 58.8, 69.0, 69.5, 69.6, 69.7, 80.8, 81.5, 81.6, 82.0, 154.0, 154.7, 169.5, 169.9; IR (ATR): 3263, 2975, 2934, 1740, 1690, 1366, 1253, 1155, 1082, 963 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 290.1368, Found 290.1363.

***tert*-Butyl 2-Oxotetrahydrofuran-3-yl(4-phenylbut-3-yn-1-yl)carbamate (1i):**

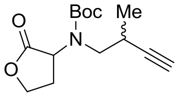


95% yield; white solid.

Rotamers were observed, and the ratio was 50:50 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.47 (4.5H, s), 1.48 (4.5H, s), 2.48-2.79 (4.0H, m), 3.43-3.47 (1.0H, m), 3.56-3.60 (0.50H, m), 3.73-3.78 (0.50H, m), 4.13-4.23 (1.5H, m), 4.29 (0.50H, dd, *J* = 9.6, 9.6 Hz), 4.41 (0.50H, dd, *J* = 8.4, 8.4 Hz), 4.50 (0.50H, dd, *J* = 8.4, 8.4 Hz), 7.29 (3.0H, brs), 7.38 (2.0H, brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.8, 20.3, 26.9, 27.7, 28.0, 28.2, 48.2, 48.7, 57.5, 57.7, 65.0, 65.4, 81.2, 81.8, 81.9, 82.0, 86.8, 87.2, 123.2, 123.3, 127.8, 127.9, 128.2, 131.4, 153.5, 154.3, 174.2, 174.3; IR (ATR): 2976, 2932, 1780, 1693, 1417, 1366, 1252, 1158, 1024, 949 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 352.1525, Found 352.1518.

***tert*-Butyl 2-Methylbut-3-yn-1-yl(2-oxotetrahydrofuran-3-yl)carbamate (1j):**

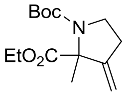


30% yield; dr = 60:40; white solid.

Rotamers were observed, and the ratios were 50:50 for both diastereomers in ^{1}H NMR analysis.

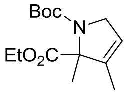
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.20-1.23 (3.0H, m), 1.46 (9.0H, s), 2.09-2.11 (1.0H, m), 2.46-2.79 (3.0H, m), 3.05 (0.20H, dd, *J* = 13.8, 9.0 Hz), 3.17 (0.20H, dd, *J* = 13.8, 7.8 Hz), 3.37 (0.30H, dd, *J* = 13.8, 6.0 Hz), 3.41-3.46 (0.90H, m), 3.61 (0.20H, dd, *J* = 14.4, 6.0 Hz), 3.80 (0.20H, dd, *J* = 13.8, 5.4 Hz), 4.01 (0.20H, dd, *J* = 9.6, 9.6 Hz), 4.06-4.15 (0.80H, m), 4.19-4.24 (1.0H, m), 4.40-4.44 (0.50H, m), 4.41-4.54 (0.50H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.0, 18.1, 18.2, 26.1, 26.4, 26.8, 26.9, 27.2, 27.5, 28.0, 28.2, 28.4, 53.7, 53.9, 55.9, 56.1, 57.2, 57.3, 58.8, 64.9, 65.0, 65.5, 69.7, 69.8, 69.9, 70.0, 81.2, 81.9, 82.1, 86.2, 86.5, 86.7, 87.3, 153.7, 154.0, 154.1, 154.5, 174.2, 174.4; IR (ATR): 3297, 2978, 2942, 1760, 1699, 1455, 1429, 1365, 1254, 1152, 1024, 1004 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 290.1368, Found 290.1362.

1-*tert*-Butyl 2-Ethyl 2-Methyl-3-methylenepyrrolidine-1,2-dicarboxylate (2a),
1-*tert*-Butyl 2-Ethyl 2,3-Dimethyl-1*H*-pyrrole-1,2(2*H*,5*H*)-dicarboxylate (2a’):



2a

+



2a'

96% yield (**2a**/**2a’** = 90/10) for using P2-*t*Bu as a base catalyst.

89% yield (**2a**/**2a’** = 5/>95) for using P4-*t*Bu as a base catalyst.

2a: colorless oil.

Rotamers were observed, and the ratio was 65:35 (in $CDCl_3$) and 56:44 (in C_6D_6) in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.20-1.26 (3.0H, m), 1.43 (5.85H, s), 1.46 (3.15H, s), 1.61 (1.95H, s), 1.66 (1.05H, s), 2.57-2.70 (2.0H, m), 3.47-3.52 (1.0H, m), 3.59 (0.35H, dd, *J* = 8.4, 8.4 Hz), 3.68 (0.65H, dd, *J* = 8.4, 8.4 Hz), 4.06-4.23 (2.0H, m), 5.01-5.03 (1.65H, m), 5.06-5.07 (0.35H, m); ^{1}H NMR (600 MHz, C_6D_6) δ 0.94 (1.68H, t, *J* = 7.2 Hz), 0.97 (1.32H, t, *J* = 7.2 Hz), 1.43 (4.95H, s), 1.45 (4.05H, s), 1.74 (1.68H, s), 1.93 (1.32H, s), 2.03-2.09 (0.56H, m), 2.10-2.17 (0.44H, m), 2.22-2.34 (1H, m), 3.28 (0.44H, ddd, *J* = 10.2, 8.4, 5.4 Hz), 3.41 (0.56H, ddd, *J*

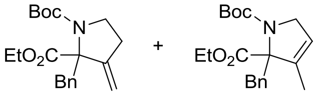
= 10.8, 8.4, 6.0 Hz), 3.51 (0.44H, ddd, *J* = 10.2, 8.4, 8.4 Hz), 3.73 (0.56H, ddd, *J* = 10.8, 9.0, 7.2 Hz), 3.84-4.01 (1.56H, m), 4.13 (0.44H, *J* = 10.8, 7.2 Hz), 4.69 (0.56H, dd, *J* = 1.8, 1.8 Hz), 4.74 (0.44H, dd, *J* = 1.8, 1.8 Hz), 4.99 (0.56H, dd, *J* = 1.8, 1.8 Hz), 5.09 (0.44H, dd, *J* = 1.8, 1.8 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 14.0, 23.1, 23.9, 28.3, 28.4, 30.1, 30.7, 45.5, 46.0, 61.1, 61.2, 67.6, 67.9, 79.7, 80.2, 107.6, 107.7, 151.3, 152.1, 153.8, 154.0, 172.5, 172.6; IR (ATR): 2978, 2938, 1739, 1698, 1456, 1382, 1365, 1249, 1168, 1115, 1063, 899, 861 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 292.1525, Found 292.1519.

2a': colorless oil.

Rotamers were observed, and the ratio was 65:35 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.21-1.26 (3.0H, m), 1.44 (5.85H, s), 1.46 (3.15H, s), 1.57 (1.95H, s), 1.63-1.65 (4.05H, m), 4.03-4.25 (4.0H, m), 5.47 (0.35H, brs), 5.53 (0.65H, brs); ^{13}C NMR (150 MHz, CDCl$_3$) δ 12.1, 12.3, 14.1, 20.0, 20.8, 28.3, 28.4, 52.9, 53.1, 61.0, 61.1, 73.1, 73.4, 79.5, 80.0, 121.0, 121.0, 138.6, 138.8, 153.4, 153.5, 172.0, 172.1; IR (ATR): 2978, 2939, 2865, 1738, 1701, 1669, 1447, 1387, 1365, 1257, 1227, 1165, 1150, 1116, 1066, 1012 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 292.1525, Found 292.1519.

1-*tert*-Butyl 2-Ethyl 2-Benzyl-3-methylenepyrrolidine-1,2-dicarboxylate (2b),
1-*tert*-Butyl 2-Ethyl 2-Benzyl-3-methyl-1*H*-pyrrole-1,2(2*H*,5*H*)-dicarboxylate (2b'):



2b **2b'**

94% yield (**2b**/**2b'** = 95/5) for using P2-*t*Bu as a base catalyst.

90% yield (**2b**/**2b'** = 58/42) for using P4-*t*Bu as a base catalyst.

2b: colorless oil.

Rotamers were observed, and the ratio was 60:40 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.23-1.29 (3.0H, m), 1.51 (3.6H, s), 1.53 (5.4H, s), 1.58-1.66 (0.6H, m), 1.71-1.76 (0.4H, m), 2.30-2.37 (1.0H, m), 2.83 (0.4H, td, *J* = 9.6, 4.8 Hz), 2.93 (0.6H, td, *J* = 9.6, 4.8 Hz), 3.22-3.25 (1.0H, m), 3.34 (0.4H, d, *J* = 9.6, 7.8 Hz), 3.42 (0.6H, d, *J* = 9.6, 7.8 Hz), 3.65 (0.6H, d, *J* = 13.2 Hz), 3.85 (0.4H, d, *J* = 13.2 Hz), 4.08-4.15 (1.0H, m), 4.19-4.25 (0.6H, m), 4.26-4.32 (0.4H, m), 5.10 (0.6H, t, *J* = 2.4 Hz), 5.12 (0.4H, t, *J* = 2.4 Hz), 5.18 (0.6H, t, *J* = 2.4 Hz), 5.25 (0.4H, t, *J* = 2.4 Hz), 7.09-7.13 (2.0H, m), 7.19-7.24 (3.0H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 13.9, 14.0, 28.4, 28.4, 30.1, 31.0, 40.1, 41.1, 46.0, 46.1, 61.2, 61.4, 71.9, 72.0, 79.6, 80.6, 108.3, 126.3, 126.5, 127.7, 127.9, 130.7, 136.5, 137.1, 149.5, 150.3, 153.6, 154.0, 172.1, 172.3; IR (ATR): 3031, 2978, 2884, 1738, 1697, 1454, 1387, 1365, 1243, 1167, 1130, 1068, 1032, 900 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 368.1838, Found 368.1833.

2b': colorless oil.

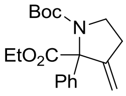
Rotamers were observed, and the ratio was 60:40 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.25-1.30 (3.0H, m), 1.49 (3.6H, s), 1.53 (5.4H, s), 1.73 (1.8H, brs), 1.77 (1.2H, brs), 3.17 (0.4H, d, *J* = 15.6 Hz), 3.20-3.25 (1.0H, m), 3.32 (0.6H, dt, *J* = 14.4, 1.8 Hz), 3.53 (0.6H, d, *J* = 14.4 Hz), 3.73 (0.4H, d, *J* = 14.4 Hz), 3.93 (0.4H, dt, *J* = 14.4, 2.4 Hz), 4.05 (0.6H, dt, *J* = 14.4, 2.4 Hz), 4.10-4.19 (1.0H, m), 4.21-4.26(0.6H, m), 4.31-4.36 (0.4H, m), 5.36 (0.4H, brs), 5.39 (0.6H, brs), 7.05-7.08 (2.0H, m), 7.17-7.23 (3.0H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 12.8, 12.9, 14.2, 14.2, 28.4, 28.5, 35.8, 36.8, 53.3, 61.2, 61.3, 77.2, 77.3, 79.5, 80.5, 123.6, 123.7, 126.2, 126.4, 127.6, 127.9, 129.9, 130.1, 135.5, 135.6, 136.3, 136.8, 153.0, 153.2, 171.6, 171.8; IR (ATR): 2978, 2863, 1737, 1700, 1668, 1453, 1391, 1366, 1255, 1231, 1174, 1134, 1069, 1047, 1034, 987 cm^{-1};

HRMS (ESI) Calcd for $[M+Na]^+$ 368.1838, Found 368.1832.

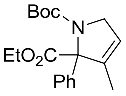
1-*tert*-Butyl 2-Ethyl 3-Methylene-2-phenylpyrrolidine-1,2-dicarboxylate (2d),
1-*tert*-Butyl 2-Ethyl 3-Methyl-2-phenyl-1*H*-pyrrole-1,2(2*H*,5*H*)-dicarboxylate (2d'):

99% yield (**2d**/**2d'** = >95/5) for using P2-*t*Bu as a base catalyst.



2d

+



2d'

95% yield (**2d**/**2d'** = 5/>95) for using P4-*t*Bu as a base catalyst.

2d: colorless oil.

Rotamers were observed, and the ratio was 70:30 in ^{1}H NMR analysis.

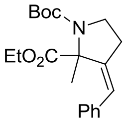
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.20 (6.3H, s), 1.25 (0.9H, t, *J* = 7.2 Hz), 1.30 (2.1H, t, *J* = 7.2 Hz), 1.47 (2.7H, s), 2.59-2.69 (2.0H, m), 3.65-3.77 (1.3H, m), 3.82 (0.7H, ddd, *J* = 10.2, 9.0, 4.8 Hz), 4.14-4.29 (2.0H, m), 5.04 (0.7H, t, *J* = 1.8 Hz), 5.08 (0.3H, brs), 5.09 (0.7H, d, *J* = 1.8 Hz), 5.15 (0.3H, brs), 7.23-7.26 (1.0H, m), 7.29-7.32 (2.0H, m), 7.58-7.62 (2.0H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 27.9, 28.3, 30.2, 31.3, 46.1, 46.5, 61.4, 61.4, 73.2, 73.6, 79.9, 80.3, 108.9, 109.4, 126.9, 127.0, 127.2, 127.4, 139.4, 140.7, 150.7, 151.8, 153.8, 154.0, 170.7, 170.7; IR (ATR): 2978, 2933, 2885, 1741, 1698, 1446, 1382, 1365, 1234, 1159, 1137, 1029, 952, 905, 861 cm^{-1}; HRMS (ESI) Calcd for $[M+Na]^+$ 354.1681, Found 354.1676.

2d': colorless oil.

Rotamers were observed, and the ratio was 70:30 in ^{1}H NMR analysis.

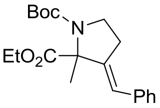
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.18 (6.3H, s), 1.28 (0.9H, t, *J* = 7.2 Hz), 1.31 (2.1H, t, *J* = 7.2 Hz), 1.41 (2.7H, s), 1.55-1.56 (2.1H, m), 1.60-1.61 (0.9H, m), 4.17-4.35 (4.0H, m), 5.70-5.72 (1.0H, m), 7.23-7.26 (1.0H, m), 7.28-7.33 (2.0H, m), 7.51-7.56 (2.0H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.9, 13.0, 14.1, 14.2, 28.0, 28.3, 53.2, 53.5, 61.2, 78.5, 78.8, 79.5, 80.0, 122.3, 123.0, 127.1, 127.1, 127.4, 127.5, 127.6, 128.1, 138.0, 138.6, 139.2, 139.3, 153.0, 153.4, 169.5, 169.7; IR (ATR): 2978, 2930, 2862, 1737, 1702, 1666, 1447, 1388, 1365, 1247, 1140, 1030, 949 cm^{-1}; HRMS (ESI) Calcd for $[M+Na]^+$ 354.1681, Found 354.1676.

(*Z*)-1-*tert*-Butyl 2-Ethyl 3-Benzylidene-2-methylpyrrolidine-1,2-dicarboxylate ((*Z*)-2e),
(*E*)-1-*tert*-Butyl 2-Ethyl 3-Benzylidene-2-methylpyrrolidine-1,2-dicarboxylate ((*E*)-2e),
1-*tert*-Butyl 2-Ethyl 3-Benzyl-2-methyl-1*H*-pyrrole-1,2(2*H*,5*H*)-dicarboxylate (2e'):



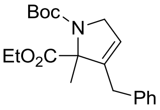
(*Z*)-**2e**

+



(*E*)-**2e**

+



2e'

83% yield (**2e**/**2e'** = 66/34, (*Z*)-**2e**/(*E*)-**2e** = 43/57) for using P2-*t*Bu as a base catalyst.

96% yield (**2e**/**2e'** = 29/71, (*Z*)-**2e**/(*E*)-**2e** = >95/5) for using P4-*t*Bu as a base catalyst.

(*Z*)-**2e**: colorless oil.

Rotamers were observed, and the ratio was 70:30 in ^{1}H NMR analysis.

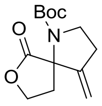
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.08-1.13 (3.0H, m), 1.37 (6.3H, s), 1.43 (2.7H, s), 1.56-1.58 (3.0H, m), 2.72-2.83 (2.0H, m), 3.48-3.57 (1.0H, m), 3.61-3.68 (1.0H, m), 3.78-3.83 (0.7H, m), 3.85-3.90 (1.3H, m), 6.55 (1.0H, s), 7.13-7.17 (2.0H, m), 7.22-7.25 (1.0H, m), 7.28-7.30 (2.0H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 21.6, 22.6, 28.2, 28.4, 33.4, 34.3, 45.0, 45.4, 60.9, 61.1, 66.4, 66.8, 79.7, 80.4, 124.7, 124.7, 127.0, 127.1, 127.8, 128.9, 135.7, 135.8, 143.5, 144.4, 153.3, 153.4, 171.8; IR (ATR): 2978, 2938, 1742, 1697, 1389, 1366, 1249, 1232, 1163, 1114, 1056 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 368.1838, Found 368.1832.

(*E*)-**2e** and **2e'**: colorless oil.

Rotamers were observed for both of (*E*)-**2e** and **2e'**, and the ratios were 67:33 for (*E*)-**2e** and 57:43 for **2e'**.

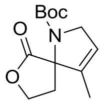
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.18-1.26 (3.0H, m), 1.43-1.48 (9.0H, m), 1.63 (1.2H, s), 1.69 (0.6H, s), 1.72 (0.6H, s), 1.78 (0.3H, s), 2.87-2.97 (0.6H, m), 3.14-3.20 (0.7H, m), 3.31-3.34 (0.7H, m), 3.56-3.60 (0.3H, m), 3.66 (0.1H, q, J = 8.4 Hz), 3.75 (0.2H, q, J = 7.8 Hz), 3.96-4.25 (3.4H, m), 5.24 (0.3H, s), 5.32 (0.4H, s), 6.41 (0.2H, s), 6.46 (0.1H, s), 7.14-7.15 (1.4H, m), 7.20-7.24 (0.6H, m), 7.26-7.30 (2.4H, m), 7.33-7.36 (0.6H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 14.1, 14.1, 20.4, 21.3, 23.5, 24.2, 28.2, 28.3, 28.3, 28.9, 33.0, 33.2, 46.1, 46.6, 52.9, 53.1, 61.0, 61.1, 61.1, 61.2, 68.7, 69.1, 72.8, 73.2, 79.6, 79.7, 80.1, 80.3, 122.4, 122.5, 122.7, 122.8, 126.3, 126.4, 127.0, 127.1, 128.3, 128.3, 128.5, 129.1, 136.6, 136.7, 137.6, 137.8, 142.7, 142.9, 143.9, 144.8, 153.3, 153.4, 153.7, 154.0, 171.9, 172.0, 172.7; IR (ATR): 2979, 2937, 2903, 1738, 1701, 1455, 1387, 1366, 1255, 1172, 1115, 1061, 1029 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 368.1838, Found 368.1832.

***tert*-Butyl 4-Methylene-6-oxo-7-oxa-1-azaspiro[4.4]nonane-1-carboxylate (2g),**
***tert*-Butyl 4-Methyl-6-oxo-7-oxa-1-azaspiro[4.4]non-3-ene-1-carboxylate (2g'):**



2g

+



2g'

98% yield (**2g**/**2g'** = >95/5) for using P2-*t*Bu as a base catalyst.

96% yield (**2g**/**2g'** = 5/>95) for using P4-*t*Bu as a base catalyst.

2g: white solid.

Rotamers were observed, and the ratio was 55:45 in ^{1}H NMR analysis.

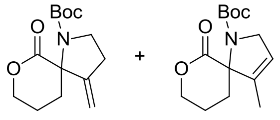
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.47 (9.0H, s), 2.25 (0.45H, ddd, J = 12.6, 9.6, 3.0 Hz), 2.30 (0.55H, ddd, J = 13.2, 7.8, 2.4 Hz), 2.61-2.68 (1.0H, m), 2.72-2.79 (1.0H, m), 2.91 (0.55H, ddd, J = 13.2, 10.8, 10.8 Hz), 3.04 (0.45H, ddd, J = 12.6, 9.6, 9.6 Hz), 3.48-3.54 (1.0H, m), 3.67 (0.45H, ddd, J = 8.4, 8.4, 8.4 Hz), 3.75 (0.55H, ddd, J = 10.2, 10.2, 10.2 Hz), 4.31-4.36 (1.0H, m), 4.49 (0.55H, ddd, J = 10.8, 10.8, 2.4 Hz), 4.60 (0.45H, ddd, J = 9.6, 9.6, 3.0 Hz), 5.00 (0.55H, brs), 5.04 (0.45H, brs), 5.14 (1.0H, brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.9, 28.2, 30.6, 31.3, 33.3, 34.4, 45.6, 46.0, 64.8, 65.2, 67.2, 67.3, 80.5, 81.3, 107.7, 150.2, 150.9, 152.6, 153.5, 175.5, 175.6; IR (ATR): 2977, 2919, 1778, 1694, 1387, 1367, 1166, 1104, 1072, 1029, 977, 962 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 276.1212, Found 276.1206.

2g': white solid.

Rotamers were observed, and the ratio was 55:45 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.47 (4.0H, s), 1.48 (5.0H, s), 1.75-1.76 (3.0H, m), 2.32-2.40 (1.0H, m), 2.79 (0.55H, ddd, J = 13.2, 10.2, 8.4 Hz), 2.85 (0.45H, ddd, J = 13.2, 9.6, 7.2 Hz), 4.03-4.10 (1.0H, m), 4.25-4.28 (0.45H, m), 4.29-4.37 (1.55H, m), 4.48 (0.55H, ddd, J = 10.2, 10.2, 3.6 Hz), 4.63 (0.45H, ddd, J = 9.6, 9.6, 4.2 Hz), 5.58 (0.45H, brs), 5.63 (0.55H, brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.0, 12.1, 28.1, 28.3, 30.4, 31.4, 53.1, 53.2, 64.9, 65.5, 72.8, 73.0, 80.5, 81.5, 122.4, 122.6, 136.4, 152.4, 153.3, 175.4, 175.5; IR (ATR): 2979, 2922, 1778, 1698, 1668, 1454, 1392, 1368, 1175, 1076, 1030 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 276.1212, Found 276.1206.

***tert*-Butyl 4-Methylene-6-oxo-7-oxa-1-azaspiro[4.5]decane-1-carboxylate (2h),**
***tert*-Butyl 4-Methyl-6-oxo-7-oxa-1-azaspiro[4.5]dec-3-ene-1-carboxylate (2h'):**



2h **2h'**

98% yield (**2h**/**2h'** = >95/5) for using P2-*t*Bu as a base catalyst.

88% yield (**2h**/**2h'** = 33/67) for using P4-*t*Bu as a base catalyst.

2h: white solid.

Rotamers were observed, and the ratio was 50:50 in ^{1}H NMR analysis.

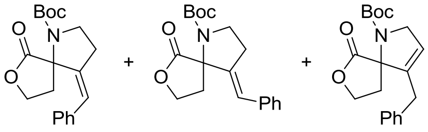
^{1}H NMR (600 MHz, CDCl$_3$) δ 1.47 (4.5H, s), 1.49 (4.5H, s), 1.79-1.88 (2.0H, m), 2.16-2.23 (1.0H, m), 2.44-2.49 (0.50H, m), 2.55-2.62 (1.5H, m), 2.65-2.74 (1.0H, m), 3.53-3.63 (1.50H, m), 3.66-3.69 (0.50H, m), 4.35-4.39 (0.50H, m), 4.43-4.50 (1.0H, m), 4.52-4.57 (0.50H, m), 5.05 (0.5H, s), 5.08 (0.5H, s), 5.10 (0.5H, s), 5.11 (0.5H, s); ^{13}C NMR (150 MHz, CDCl$_3$) δ 20.9, 21.3, 28.3, 28.4, 30.4, 31.5, 32.8, 33.2, 46.2, 46.6, 67.0, 67.2, 70.0, 70.1, 80.3, 81.3, 108.3, 108.9, 151.5, 151.6, 153.2, 154.1, 171.0, 171.4; IR (ATR): 2974, 2934, 1740, 1689, 1385, 1366, 1269, 1252, 1153, 1116, 1076, 1003, 965 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 290.1368, Found 290.1362.

2h and **2h'**: white solid.

Rotamers were observed for both of **2h** and **2h'**, and the ratios were 50:50 for **2h** and 64:36 for **2h'**.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.46 (5.4H, s), 1.49 (1.35H, s), 1.51 (2.25H, s), 1.79-1.88 (2.7H, m), 1.99-2.23 (2.4H, m), 2.44-2.49 (0.40H, m), 2.52-2.62 (0.9H, m), 2.65-2.74 (0.3H, m), 3.53-3.63 (0.45H, m), 3.66-3.69 (0.15H, m), 4.03 (0.45H, d, *J* = 14.4 Hz), 4.07 (0.25H, d, *J* =15.0 Hz), 4.23 (0.45H, d, *J* =14.4 Hz), 4.32 (0.25H, d, *J* = 15.0 Hz), 4.35-4.51 (1.4H, m), 4.52-4.57 (0.15H, m), 4.64 (0.45H, td, *J* = 10.2, 2.4 Hz), 5.05 (0.15H, s), 5.08 (0.15H, s), 5.10 (0.15H, s), 5.11 (0.15H, s), 5.51 (0.45H, brs), 5.58 (0.25H, brs); ^{13}C NMR (150 MHz, CDCl$_3$) δ 13.8, 14.5, 21.0, 21.4, 22.6, 23.1, 28.4, 28.5, 28.5, 28.5, 30.5, 31.6, 32.9, 33.3, 33.8, 46.3, 46.6, 53.1, 53.2, 67.1, 67.2, 69.8, 69.9, 70.0, 70.1, 71.5, 71.7, 80.3, 80.4, 81.4, 81.7, 108.4, 109.0, 122.1, 122.4, 139.5, 139.7, 151.6, 151.7, 152.9, 153.3, 153.9, 154.2, 171.0, 171.2, 171.4, 171.7; IR (ATR): 2975, 2932, 1739, 1691, 1667, 1476, 1454, 1389, 1366, 1261, 1151, 1078, 1001, 967 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 290.1368, Found 290.1363.

(*Z*)-*tert*-Butyl 4-Benzylidene-6-oxo-7-oxa-1-azaspiro[4.4]nonane-1-carboxylate ((Z)-2i),
(*E*)-*tert*-Butyl 4-Benzylidene-6-oxo-7-oxa-1-azaspiro[4.4]nonane-1-carboxylate ((*E*)-2i),
***tert*-Butyl 4-Benzyl-6-oxo-7-oxa-1-azaspiro[4.4]non-3-ene-1-carboxylate (2i'):**



(*Z*)-**2i** (*E*)-**2i** **2i'**

97% yield (**2i**/**2i'** = 64/36, (*Z*)-**2i**/(*E*)-**2i** = 19/81) for using P2-*t*Bu as a base catalyst.

92% yield (**2i**/**2i'** = 28/72, (*Z*)-**2i**/(*E*)-**2i** = >95/5) for using P4-*t*Bu as a base catalyst.

(*Z*)-**2i**: white solid.

Rotamers were observed, and the ratio was 50:50 in ^{1}H NMR analysis.

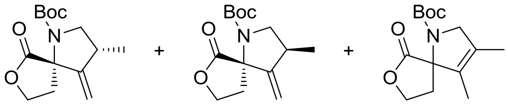
^{1}H NMR (600 MHz, CDCl$_3$) δ 1.43 (4.5H, s), 1.45 (4.5H, s), 2.28-2.45 (2.0H, m), 2.72-2.77 (1.0H, m), 2.94-3.05 (1.5H, m), 3.21-3.26 (0.50H, m), 3.42-3.49 (1.0H, m), 3.74 (0.50H, ddd, *J* = 9.6, 9.6, 4.8 Hz), 3.85 (0.5H, ddd, *J* = 9.6, 9.6, 4.8 Hz), 4.04 (0.50H, ddd, *J* = 9.6, 9.6, 4.8 Hz), 4.29 (0.50H, ddd, *J* = 9.6, 9.0, 5.4 Hz), 6.70 (1.0H, brs), 7.17 (2.0H, d, *J* = 7.2 Hz), 7.29 (1.0H, t, *J* = 7.2 Hz), 7.34 (2.0H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 28.0, 28.3, 33.1, 33.7, 34.0, 35.2, 45.0, 45.1, 64.8, 65.7, 65.8, 66.0, 80.6, 81.8, 125.1, 125.2, 127.4, 127.5, 128.2, 128.3, 128.6, 128.7, 135.5, 135.7, 144.3, 145.8, 152.6, 153.6, 176.8, 177.0; IR (ATR): 2975, 2926, 1766, 1693, 1477, 1444, 1389, 1366, 1165, 1153, 1090, 1071, 1032 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 352.1525, Found 352.1519.

(*E*)-**2i** and **2i'**: white solid.

Rotamers were observed for both of (*E*)-**2i** and **2i'**, and the ratios were 55:45 for (*E*)-**2i** and 50:50 for **2i'**.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.46-1.49 (9.0H, m), 2.34-2.47 (1.0H, m), 2.77 (0.33H, ddd, *J* = 13.2, 10.2, 8.4 Hz), 2.84 (0.33H, ddd, *J* = 13.2, 10.2, 7.2 Hz), 2.88-2.93 (0.25H, m), 3.00-3.04 (0.47H, m), 3.12 (0.11H, ddd, *J* = 12.6, 9.6, 9.6 Hz), 3.27-3.34 (1.33H, m), 3.56-3.58 (0.25H, m), 3.70 (0.11H, ddd, *J* = 9.6, 8.4, 6.6 Hz), 3.79 (0.14H, ddd, *J* = 10.2, 8.4, 6.6 Hz), 4.02-4.09 (0.75H, m), 4.23-4.36 (1.5H, m), 4.41-4.47 (0.58H, m), 4.54 (0.14H, ddd, *J* = 9.0, 9.0, 3.0 Hz), 4.60-4.68 (0.44H, m), 5.31 (0.33H, dd, *J* =1.8, 1.8), 5.39 (0.33H, dd, *J* = 1.8, 1.8 Hz), 6.38 (0.14H, brs), 6.42 (0.11H, brs), 7.20-7.21 (2.0H, m), 7.24-7.37 (3.0H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 28.4, 29.1, 30.7, 31.5, 31.8, 33.1, 33.2, 33.7, 34.0, 35.1, 46.2, 46.5, 53.1, 53.2, 64.9, 65.4, 65.6, 68.6, 68.8, 72.6. 72.9, 80.7, 80.8, 81.6, 81.7, 122.8, 122.9, 123.8, 124.0, 126.8, 126.9, 127.5, 127.6, 128.4, 128.5, 128.6, 128.7, 129.1, 129.2, 135.8, 135.9, 136.5, 136.8, 140.9, 141.0, 143.3, 144.1, 152,4, 152.8, 153.3, 153.8, 175.4, 175.5, 175.9; IR (ATR): 2978, 2930, 1775, 1697, 1389, 1367, 1256, 1166, 1071, 1029, 971 cm^{-1}; (ESI) Calcd for [M+Na]$^+$ 352.1525, Found 352.1519.

***tert*-Butyl 3-Methyl-4-methylene-6-oxo-7-oxa-1-azaspiro[4.4]nonane-1-carboxylate (2j), *tert*-Butyl 3,4-Dimethyl-6-oxo-7-oxa-1-azaspiro[4.4]non-3-ene-1-carboxylate (2j'):**



major-**2j** *minor*-**2j** **2j'**

97% yield (**2j**/**2j'** = >95/5, *major*/*minor* = 89/11) for using P2-*t*Bu as a base catalyst.

93% yield (**2j**/**2j'** = 15/85, *major*/*minor* = >95/5) for using P4-*t*Bu as a base catalyst.

major-**2j**: white solid.

Rotamers were observed, and the ratio was 55:45 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.15-1.16 (3.0H, m), 1.47 (9.0H, s), 2.36 (0.45H, ddd, *J* = 13.2, 9.0, 3.6 Hz), 2.43 (0.55H, ddd, *J* = 13.2, 8.4, 3.0 Hz), 2.90-2.96 (1.55H, m), 2.98-3.08 (1.45H, m), 3.93 (0.45H, dd, *J* = 9.6, 8.4 Hz), 4.05 (0.55H, dd, *J* = 9.6, 8.4 Hz), 4.36-4.42 (1.0H, m), 4.49 (0.55H, ddd, *J* = 10.8, 9.6, 3.0 Hz), 4.62 (0.45H, ddd, *J* = 10.2, 9.0, 3.6 Hz), 5.06-5.08 (1.55H, m), 5.11-5.12 (0.45H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 14.9, 15.1, 27.9, 28.2, 33.1, 34.2, 36.0, 36.5, 52.3, 52.8, 65.1, 65.5, 67.3, 67.4, 80.4, 81.3, 106.3, 106.4, 152.5, 153.4, 155.6, 156.5, 175.5, 175.6; IR (ATR): 2973, 2931, 2875, 1771, 1691, 1390, 1366, 1163, 1099, 1068, 1029, 963, 907 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 290.1368, Found 290.1362; CCDC No. 945901.

minor-**2j**: white solid.

Rotamers were observed, and the ratio was 55:45 in ^{1}H NMR analysis.

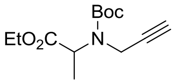
^{1}H NMR (600 MHz, CDCl$_3$) δ 1.18-1.20 (3.0H, m), 1.46 (9.0H, s), 2.11-2.19 (1.0H, m), 2.82-2.93 (1.55H, m), 3.05 (0.45H, ddd, *J* = 12.6, 9.6, 9.6 Hz), 3.10-3.17 (1.0H, m), 3.75-3.82 (1.0H, m), 4.26-4.30 (1.0H, m), 4.47 (0.55H, ddd, *J* = 9.6, 9.6, 1.8 Hz), 4.57 (0.45H, ddd, *J* = 9.6, 9.6, 2.4 Hz), 4.94 (0.55H, brs), 4.99 (0.45H, brs), 5.01 (1.0H, brs); ^{13}C NMR (150 MHz, CDCl$_3$) δ 14.1, 14.2, 28.1, 28.4, 34.3, 35.3, 35.4, 36.3, 53.1, 53.6, 64.7, 65.1, 68.7, 68.8, 80.7, 81.5, 105.8, 105.9, 152.7, 153.5, 154.6, 155.0, 175.6, 175.8; IR (ATR): 2974, 2932, 2875, 1779, 1694, 1389, 1366, 1165, 1144, 1069, 1025, 984, 962 cm^{-1}; HRMS (ESI) Calcd for $[M+Na]^+$ 290.1368, Found 290.1363.

2j'; white solid.

Rotamers were observed, and the ratio was 55:45 in ^1H NMR analysis.

^1H NMR (600 MHz, $CDCl_3$) δ 1.47 (4.0H, s), 1.48 (5.0H, s), 1.64 (3.0H, brs), 1.70 (1.35H, brs), 1.71 (1.65H, brs), 2.29-2.38 (1.0H, m), 2.75 (0.55H, ddd, *J* = 13.8, 10.2, 8.4 Hz), 2.81 (0.45H, ddd, *J* = 13.8, 10.8, 7.8 Hz), 3.97-4.02 (1.0H, m), 4.21 (0.45H, d, *J* = 14.4 Hz), 4.27-4.35 (1.55H, m), 4.46 (0.55H, ddd, *J* = 10.2, 9.0, 3.6 Hz), 4.61 (0.45H, ddd, *J* = 10.2, 8.4, 4.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 9.1, 9.2, 11.4, 28.1, 28.4, 30.5, 31.5, 57.1, 57.2, 65.0, 65.5, 73.8, 74.0, 80.4, 81.4, 128.2, 128.3, 130.0, 130.2, 152.3, 153.2, 176.0, 176.1; IR (ATR): 2979, 2919, 2861, 1770, 1703, 1686, 1394, 1367, 1176, 1155, 1072, 1031 cm^{-1}; HRMS (ESI) Calcd for $[M+Na]^+$ 290.1368, Found 290.1363.

Ethyl 2-{*tert*-Butoxycarbonyl(prop-2-yn-1yl)amino}propanoate (3a):

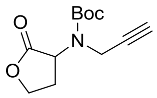


67% yield; colorless oil.

Rotamers were observed, and the ratio was 55:45 in ^1H NMR analysis.

^1H NMR (600 MHz, $CDCl_3$) δ 1.27 (3.0H, brs), 1.44-1.52 (12.0H, m), 2.17-2.22 (1.0H, m), 3.90-3.94 (0.45H, m), 4.10-4.28 (4.1H, m), 4.67-4.71 (0.45H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 15.0, 15.5, 27.9, 34.5, 35.5, 53.6, 54.7, 60.6, 70.6, 71.5, 79.4, 80.1, 80.5, 154.0, 154.2, 171.6; IR (ATR): 3265, 2979, 2938, 1739, 1697, 1367, 1251, 1163, 1067, 861 cm^{-1}; HRMS (ESI) Calcd for $[M+Na]^+$ 278.1368, Found 278.1363.

***tert*-Butyl 2-Oxotetrahydrofuran-3-yl(prop-2-yn-1-yl)carbamate (3b):**



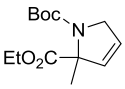
59% yield; colorless oil.

Rotamers were observed in ^{13}C NMR analysis.

^1H NMR (600 MHz, $CDCl_3$) δ 1.48 (9H, brs), 2.29 (1H, brs), 2.59-2.65 (2H, m), 4.05-4.27 (3H, m), 4.44-4.51 (2H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 26.5, 27.3, 28.1, 37.1, 37.5, 55.8, 65.2, 65.6, 72.3, 72.9, 79.0, 79.4, 81.9, 82.6, 153.3, 153.9, 174.1; IR (ATR): 3273, 2979, 2934, 1779, 1698, 1368, 1250, 1146, 1021, 951 cm^{-1}; HRMS (ESI) Calcd for $[M+Na]^+$ 262.1055, Found 262.1049.

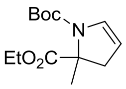
1-*tert*-Butyl 2-Ethyl 2-Methyl-1*H*-pyrrole-1,2(2*H*,5*H*)-dicarboxylate (4a),

1-*tert*-Butyl 2-Ethyl 2-Methyl-2,3-dihydro-1*H*-pyrrole-1,2-dicarboxylate (4a'):



4a

+



4a'

47% yield (**4a**/**4a'** = 50/50) for using P2-*t*Bu as a base catalyst.

76% yield (**4a**/**4a'** = 14/86) for using P4-*t*Bu as a base catalyst.

4a: colorless oil.

Rotamers were observed, and the ratio was 65:35 in ^1H NMR analysis.

^1H NMR (600 MHz, $CDCl_3$) δ 1.22-1.27 (3.0H, m), 1.44 (5.85H, s), 1.47 (3.15H, s), 1.61 (1.95H, s), 1.67 (1.05H, s) 4.05-4.36 (4.0H, m), 5.57 (0.65H, dt, *J* = 6.0, 1.8 Hz), 5.61 (0.35H, dt, *J* = 6.0, 1.8 Hz), 5.85 (0.35H, dt, *J* = 6.0, 1.8 Hz), 5.90 (0.65H, dt, *J* = 6.0, 1.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.2, 14.2, 21.9, 22.8, 28.4, 28.5, 54.4, 54.5, 61.2, 61.3, 71.7, 72.1, 79.7, 80.2, 126.9, 127.0, 131.6, 131.7, 153.5, 172.3, 172.5; IR (ATR): 2979, 2937, 2868, 1739, 1699, 1385, 1366, 1256, 1218, 1173, 1106, 1047 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 278.1368, Found 278.1363.

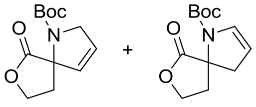
4a': colorless oil.

Rotamers were observed, and the ratio was 60:40 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.25 (1.2H, t, J = 7.2 Hz), 1.29 (1.8H, t, J = 7.2 Hz), 1.44 (5.4H, s), 1,47 (3.6H, s), 1.57 (1.8H, s), 1.63 (1.2H, s), 2.52 (0.4H, ddd, J = 16.8, 1.8, 1.8 Hz), 2.58 (0.6H, ddd, J = 16.8, 1.8, 1.8 Hz), 2.94 (0.4H, ddd, J = 16.8, 1.8, 1.8 Hz), 3.01 (0.6H, ddd, J = 16.8, 1.8, 1.8 Hz), 4.12-4.18 (1.0H, m), 4.21-4.30 (1.0H, m), 4.82-4.84 (0.4H, m), 4.89-4.91 (0.6H, m), 6.46-6.47 (0.4H, m), 6.60-6.61 (0.6H, m); ^{13}C NMR (150 MHz, CDCl$_3$) δ 14.1, 14.1, 22.3, 23.1, 28.2, 28.3, 44.1, 45.4, 61.2, 61.2, 65.2, 65.3, 80.5, 80.8, 103.3, 103.4, 129.7, 129.8, 150.8, 151.2, 173.2, 173.3; IR (ATR): 2979, 2936, 1742, 1699, 1627, 1386, 1367, 1340, 1328, 1298, 1279, 1186, 1157, 1116, 1051 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 278.1368, Found 278.1362.

***tert*-Butyl 6-Oxo-7-oxa-1-azaspiro[4.4]non-3-ene-1-carboxylate (4b),**

***tert*-Butyl 6-Oxo-7-oxa-1-azaspiro[4.4]non-2-ene-1-carboxylate (4b'):**



4b **4b'**

93% yield (**4b**/**4b'** = >95/5) for using P2-*t*Bu as a base catalyst.

87% yield (**4b**/**4b'** = >95/5) for using P4-*t*Bu as a base catalyst.

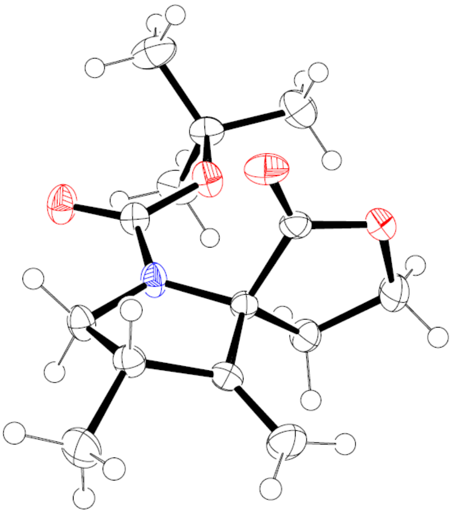
4b: colorless oil.

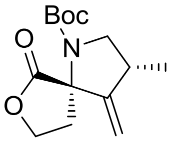
Rotamers were observed, and the ratio was 55:45 in ^{1}H NMR analysis.

^{1}H NMR (600 MHz, CDCl$_3$) δ 1.47 (5.0H, s), 1.48 (4.0H, s), 2.21-2.29 (1.0H, m), 2.90 (0.55H, ddd, J = 13.2, 9.6, 9.6 Hz), 3.00 (0.45H, ddd, J = 13.2, 9.6, 8.4 Hz), 4.12-4.19 (1.0H, m), 4.28-4.33 (1.0H, m), 4.38 (0.45H, ddd, J = 15.6, 2.4, 2.4 Hz), 4.45-4.49 (1.10H, m), 5.60 (0.45H, ddd, J = 9.0, 9.0, 3.6 Hz), 5.71-5.73 (1.0H, m), 6.01 (0.45H, ddd, J = 6.0, 2.4, 2.4 Hz), 6.06 (0.55H, ddd, J = 6.6, 1.8, 1.8 Hz); ^{13}C NMR (150 MHz, CDCl$_3$) δ 28.1, 28.3, 31.9, 32.9, 54.0, 54.1, 64.6, 65.2, 71.3, 71.5, 80.7, 81.6, 127.4, 127.8, 128.2, 128.4, 152.5, 153.2, 175.0, 175.1; IR (ATR): 2977, 2927, 2871, 1781, 1696, 1390, 1367, 1172, 1112, 1064, 1025, 964 cm^{-1}; HRMS (ESI) Calcd for [M+Na]$^+$ 262.1055, Found 262.1050.

X-ray crystallographic data of *major* diastereomer of 2j

major-**2j** was recrystallized from hexane/AcOEt solvents system. Relative configuration of *major* diastereomer of **2j** was determined by X-ray crystallographic analysis.





major-**2j**

Figure S1. ORTEP Drawing of major diastereomer of **2j**

Experimental

Data Collection

A colorless block crystal of $C_{14}H_{21}NO_{4}$ having approximate dimensions of 0.400 x 0.400 x 0.200 mm was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB mini diffractometer using graphite monochromated Mo-Kα radiation.

The crystal-to-detector distance was 50.00 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 15.235(3) Å
b = 6.156(1) Å β = 109.641(8)^{o}
c = 15.923(3) Å
V = 1406.4(5) Å^{3}

For Z = 4 and F.W. = 267.32, the calculated density is 1.262 g/cm^{3}. The reflection conditions of:

h0l: h+l = 2n
0k0: k = 2n

uniquely determine the space group to be:

P2$_{1}$/n (#14)

The data were collected at a temperature of -123 ± 1^{o}C to a maximum 2θ value of 55.0^{o}. A total of 570 oscillation images were collected. A sweep of data was done using ω oscillations from -70.0 to 120.0^{o} in 1.0^{o} steps. The exposure rate was 16.0 [sec./^{o}]. The detector swing angle was 30.00^{o}. A second sweep was performed using ω oscillations from -70.0 to 120.0^{o} in 1.0^{o} steps. The exposure rate was 16.0 [sec./^{o}]. The detector swing angle was

30.00°. Another sweep was performed using ω oscillations from -70.0 to 120.0° in 1.0° steps. The exposure rate was 16.0 [sec./°]. The detector swing angle was 30.00°. Another sweep was performed using ω oscillations from -70.0 to 120.0° in 1.0° steps. The exposure rate was 16.0 [sec./°]. The detector swing angle was 30.00°. Another sweep was performed using ω oscillations from -70.0 to 120.0° in 1.0° steps. The exposure rate was 16.0 [sec./°]. The detector swing angle was 30.00°. Another sweep was performed using ω oscillations from -70.0 to 120.0° in 1.0° steps. The exposure rate was 16.0 [sec./°]. The detector swing angle was 30.00°. The crystal-to-detector distance was 50.00 mm. Readout was performed in the 0.146 mm pixel mode.

Data Reduction

Of the 15000 reflections that were collected, 3211 were unique (R_{int} = 0.0200); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).

The linear absorption coefficient, μ, for Mo-Kα radiation is 0.919 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.907 to 0.982. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 3211 observed reflections and 172 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0366$

$wR2 = [\, \Sigma \, (w \, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, w(Fo^2)^2]^{1/2} = 0.0964$

The standard deviation of an observation of unit weight[4] was 1.05. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and -0.19 e$^-$/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the CrystalStructure[9] crystallographic software package except for refinement, which was performed using SHELXL-97[10].

References

(1) CrystalClear: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000.J.W.Pflugrath (1999) Acta Cryst. D55, 1718-1725.

(2) SIR2008: M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna (2007)

(3) Least Squares function minimized: (SHELXL97)

$\Sigma w(F_o^2 - F_c^2)^2$ where w = Least Squares weights.

(4) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$

where: N_o = number of observations

N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).
(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
(9) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.
(10) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{14}H_{21}NO_4$
Formula Weight	267.32
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.400 X 0.400 X 0.200 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 15.235(3) Å
b = 6.156(1) Å	
c = 15.923(3) Å	
β = 109.641(8) ^{o}	
V = 1406.4(5) Å^{3}	
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.262 g/cm^{3}
F_{000}	576.00
μ(MoKα)	0.919 cm^{-1}

B. Intensity Measurements

Diffractometer	XtaLAB mini
Radiation	MoKα (λ = 0.71075 Å)
graphite monochromated	
Voltage, Current	50kV, 12mA
Temperature	-123.0^{o}C
Detector Aperture	75 mm (diameter)
Data Images	570 exposures
ω oscillation Range	-70.0 - 120.0^{o}
Exposure Rate	16.0 sec./^{o}
Detector Swing Angle	30.00^{o}
ω oscillation Range	-70.0 - 120.0^{o}

Exposure Rate	16.0 sec./^{o}
Detector Swing Angle	30.00^{o}
ω oscillation Range	-70.0 - 120.0^{o}
Exposure Rate	16.0 sec./^{o}
Detector Swing Angle	30.00^{o}
ω oscillation Range	-70.0 - 120.0^{o}
Exposure Rate	16.0 sec./^{o}
Detector Swing Angle	30.00^{o}
ω oscillation Range	-70.0 - 120.0^{o}
Exposure Rate	16.0 sec./^{o}
Detector Swing Angle	30.00^{o}
ω oscillation Range	-70.0 - 120.0^{o}
Exposure Rate	16.0 sec./^{o}
Detector Swing Angle	30.00^{o}
Detector Position	50.00 mm
Pixel Size	0.146 mm
$2\theta_{max}$	55.0^{o}
No. of Reflections Measured	Total: 15000
Unique: 3211 (R_{int} = 0.0200)	
Corrections	Lorentz-polarization
Absorption	
(trans. factors: 0.907 - 0.982)	

C. Structure Solution and Refinement

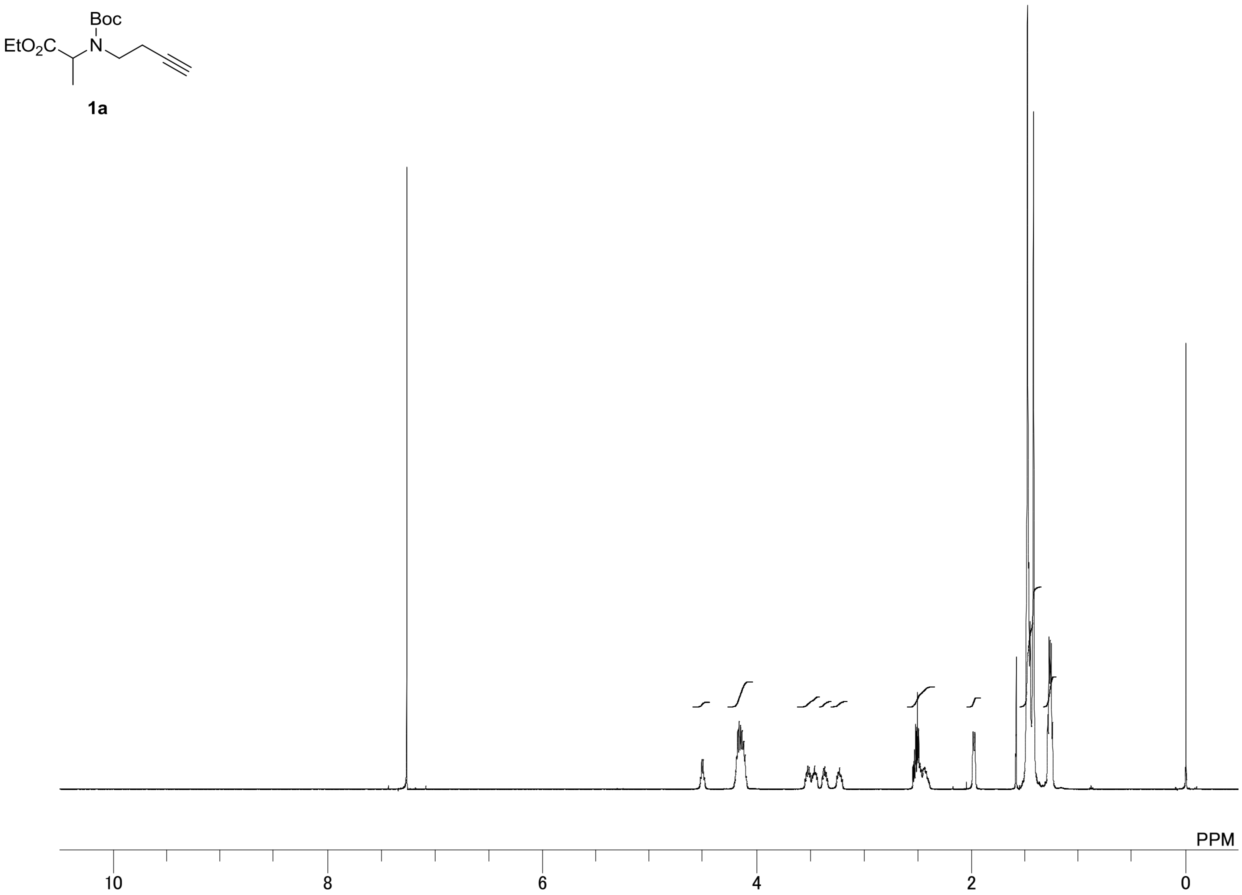
Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	w = 1/ [$\sigma^2(Fo^2)$ + $(0.0459 \cdot P)^2$
+ 0.4616 · P]	
where P = (Max(Fo^2,0) + 2Fc^2)/3	
$2\theta_{max}$ cutoff	55.0^{o}
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3211
No. Variables	172
Reflection/Parameter Ratio	18.67
Residuals: R1 (I>2.00σ(I))	0.0366
Residuals: R (All reflections)	0.0406
Residuals: wR2 (All reflections)	0.0964
Goodness of Fit Indicator	1.051
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.35 e^-/Å^3
Minimum peak in Final Diff. Map	-0.19 e^-/Å

References

1 Y. Karibe, H. Kusama and N. Iwasawa, *Angew. Chem., Int. Ed.*, 2012, **51**, 6214.

2 D. Albanese, D. Landini, V. Lupi and M. Penso, *Eur. J. Org. Chem.*, 2000, 1443.

3 B. Baskar, P.-Y. Dakas and K. Kumar, *Org. Lett.* 2011, **13**, 1988.



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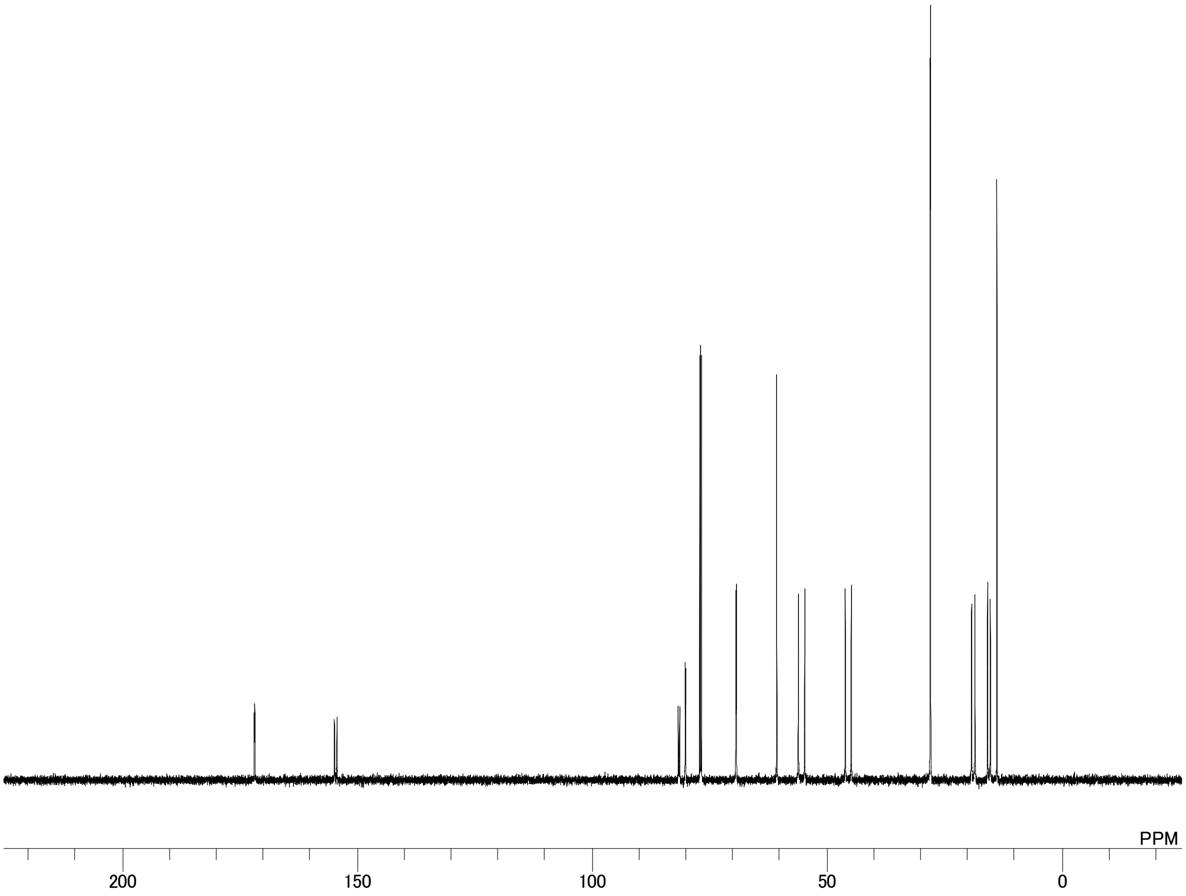

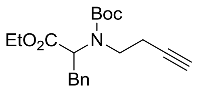

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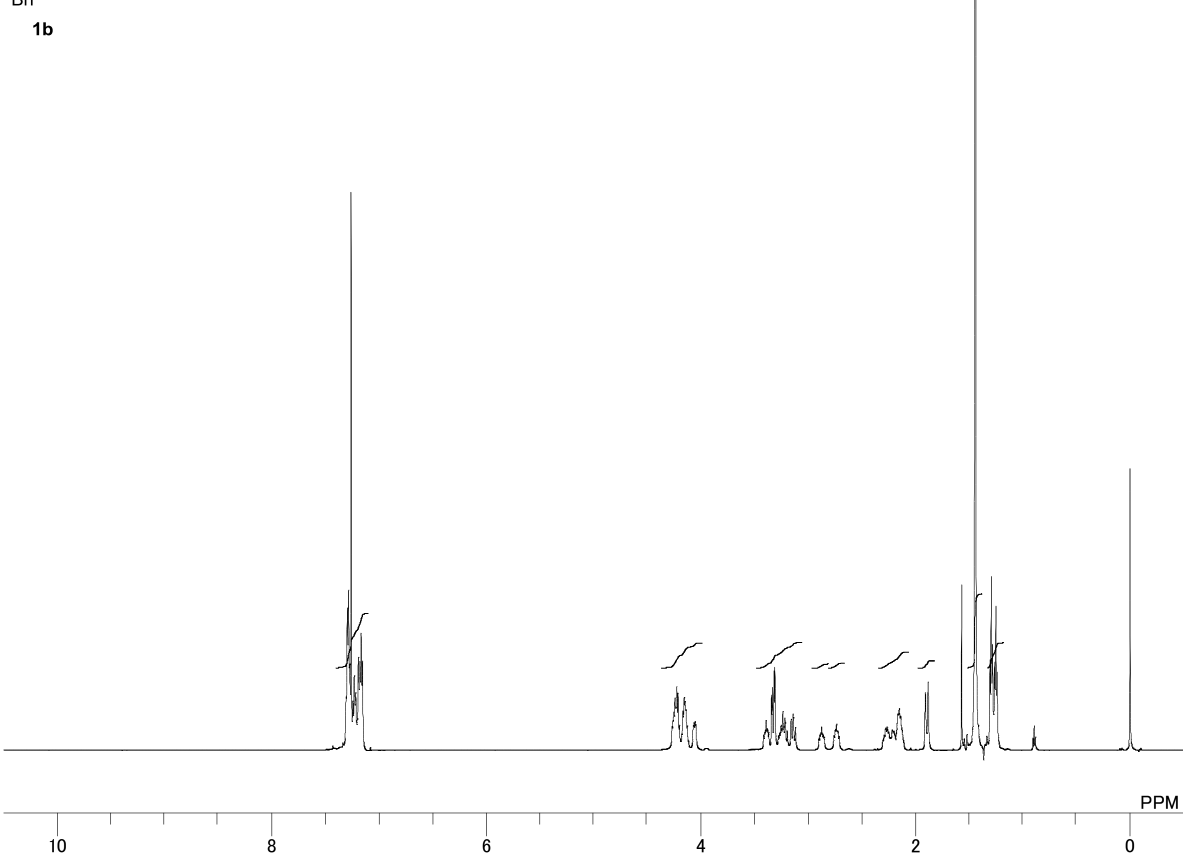

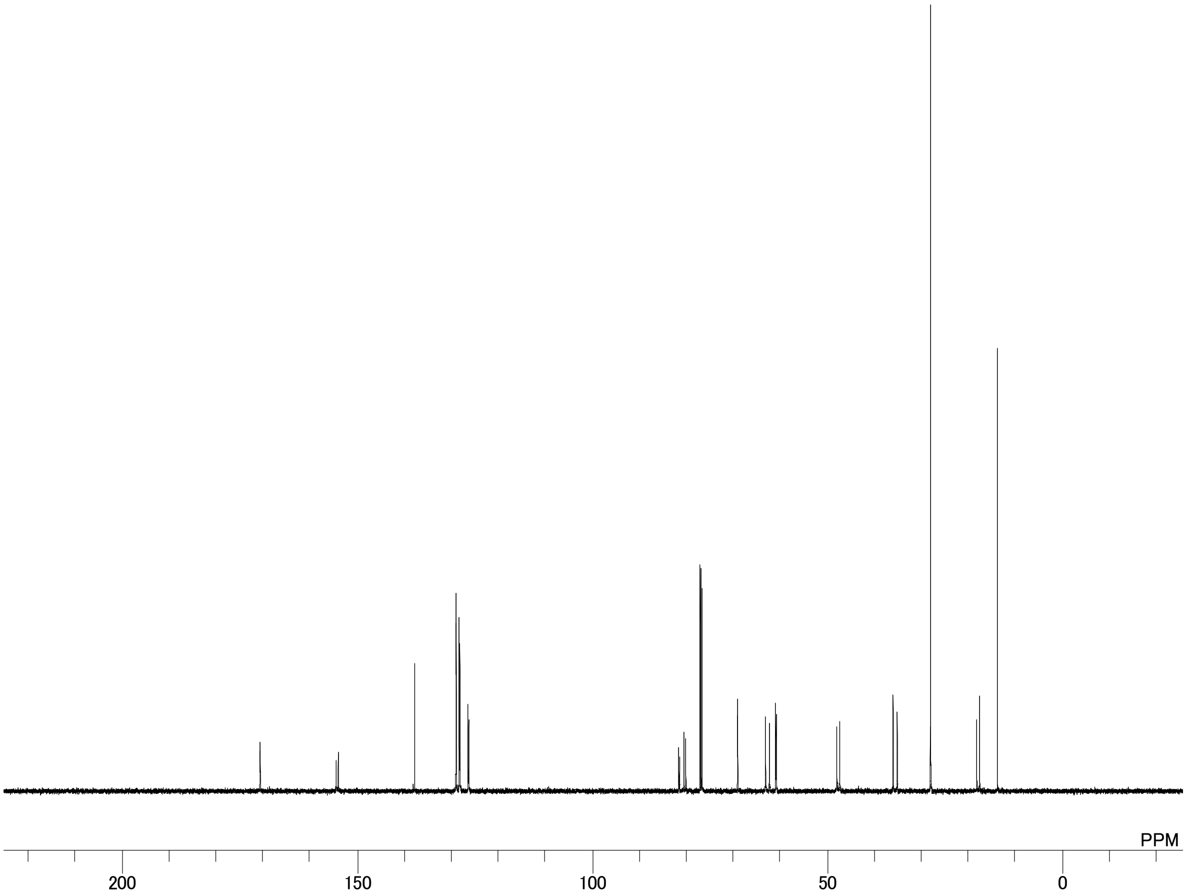

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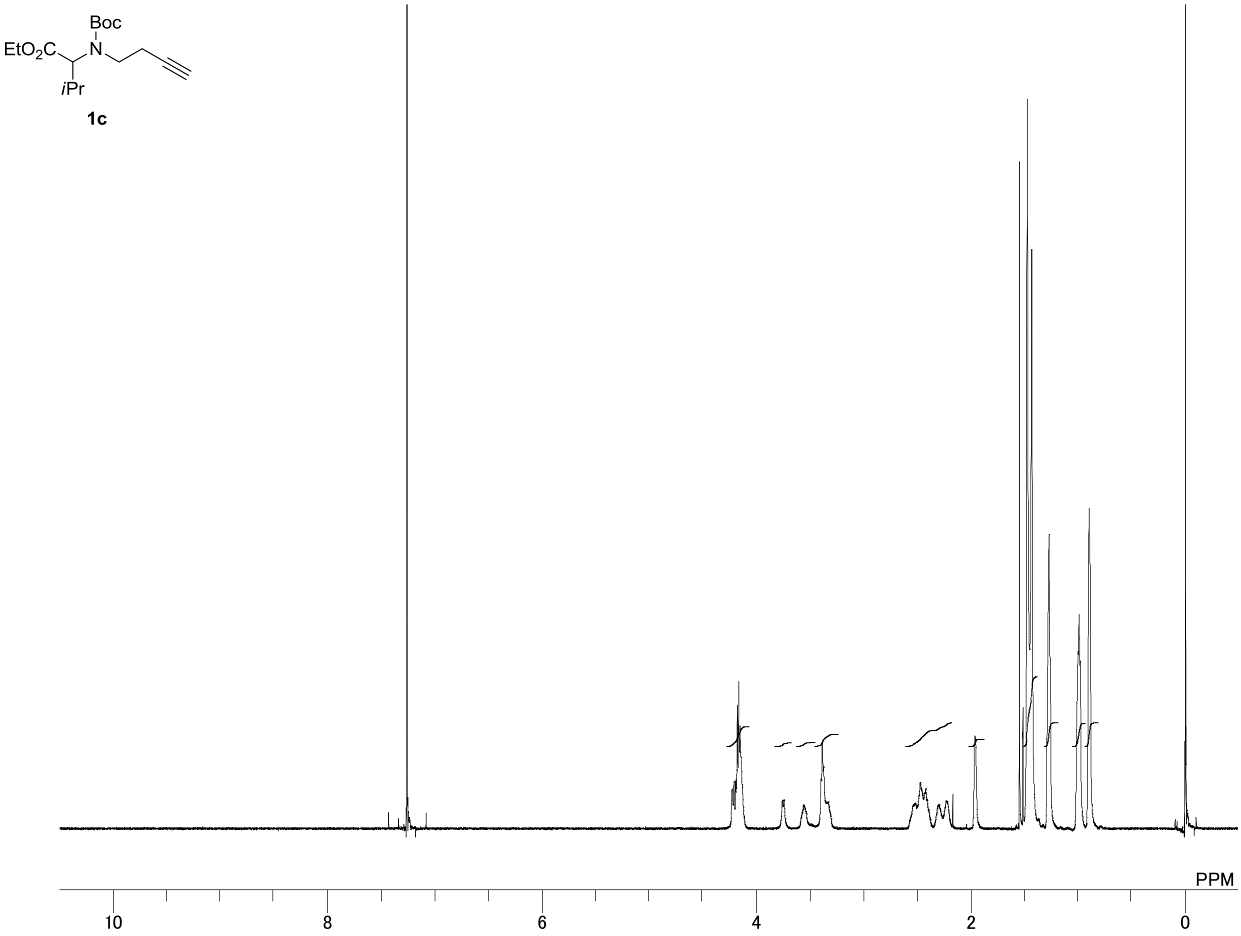

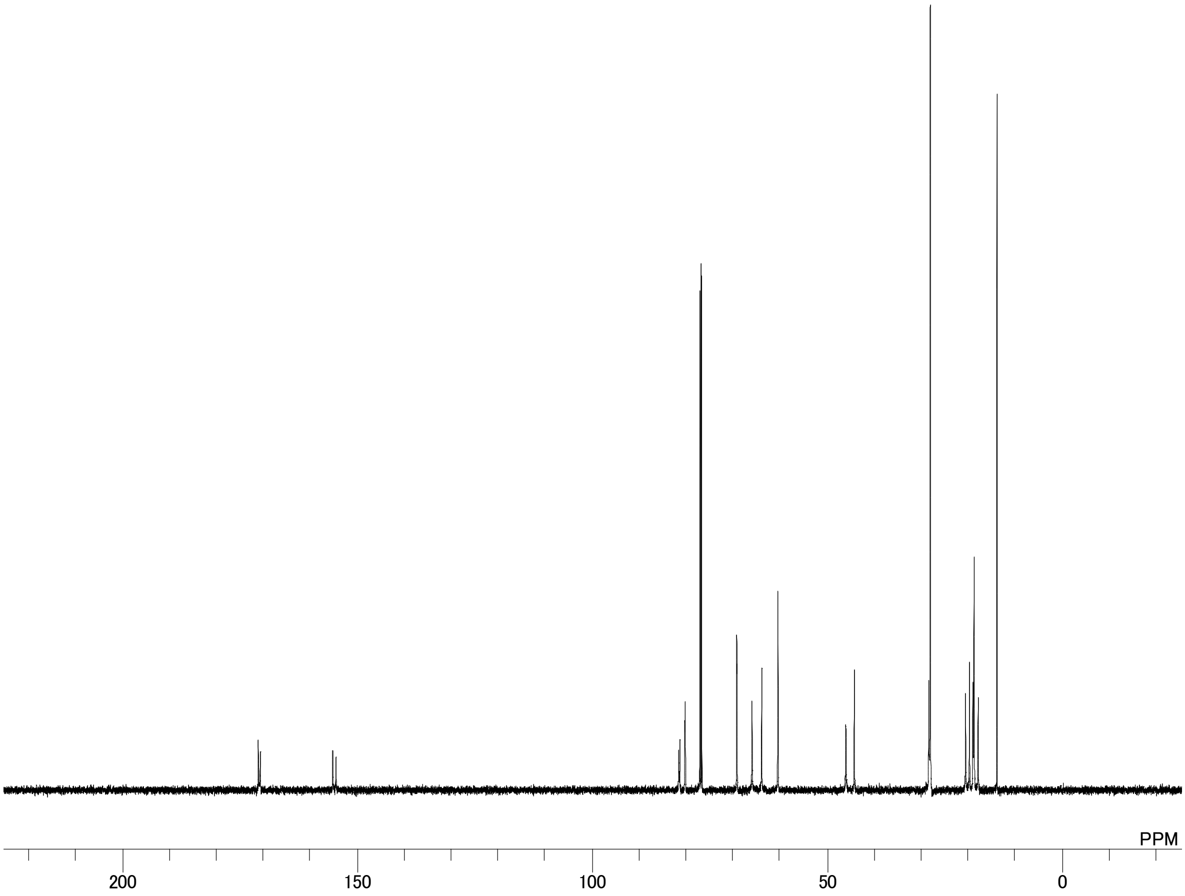

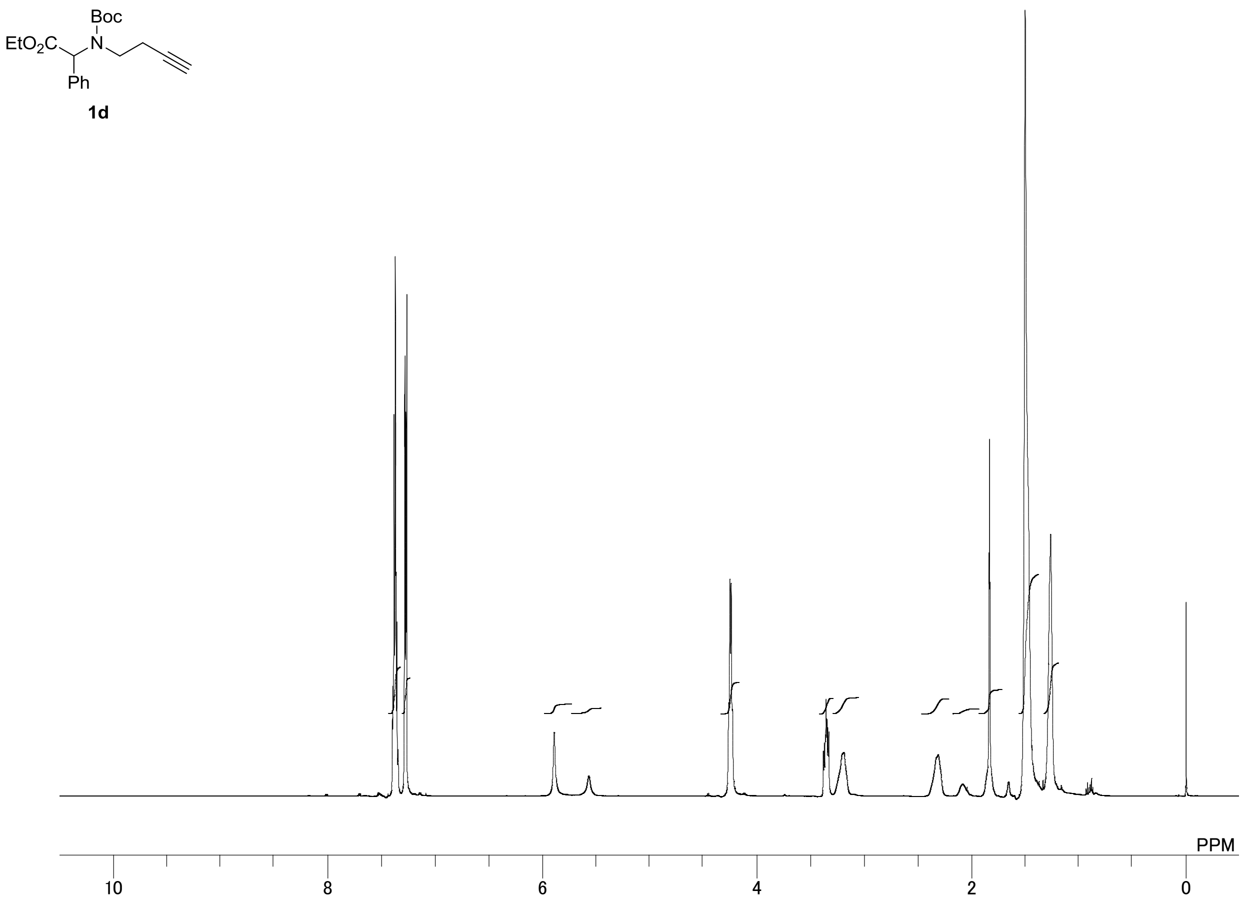
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PPM
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6
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2
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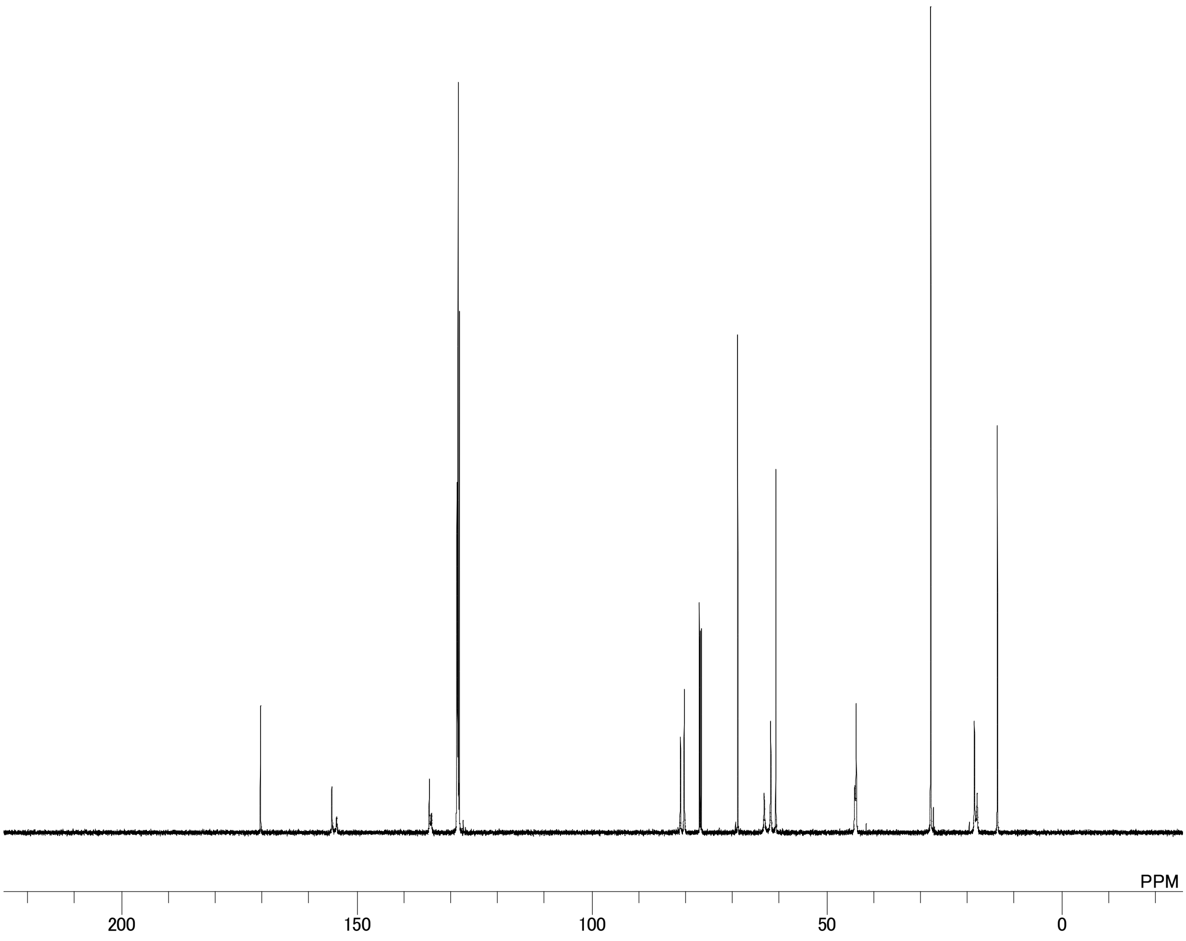
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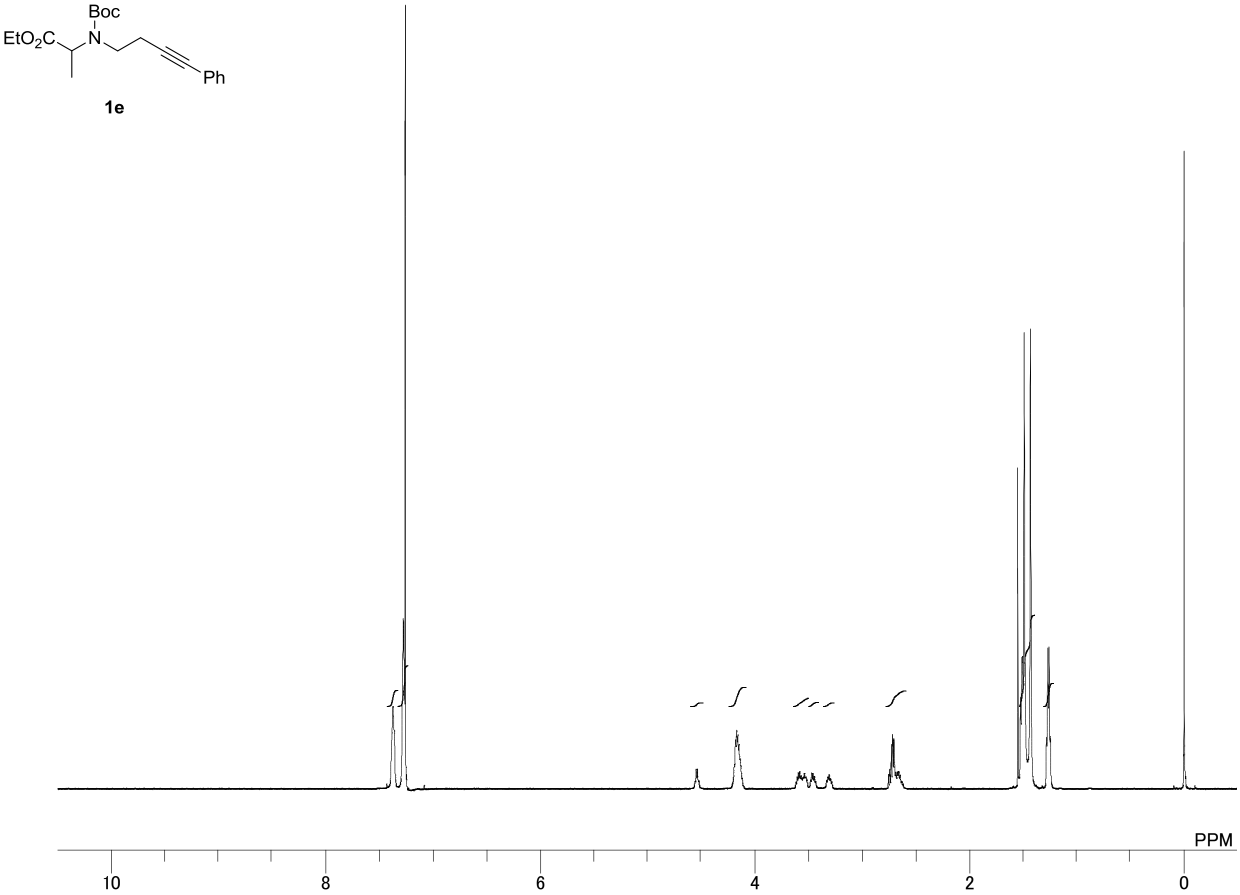

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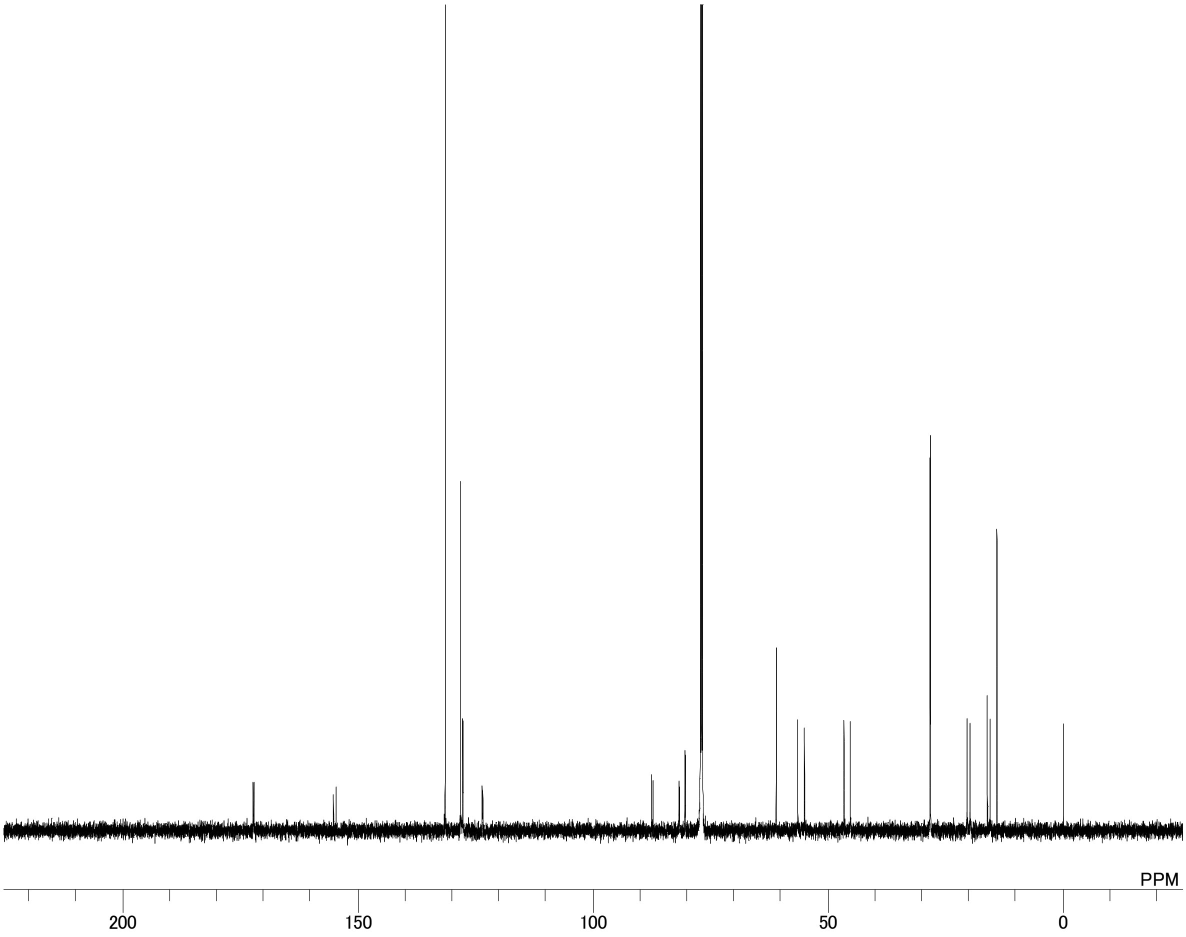

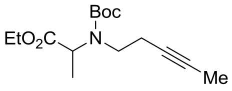

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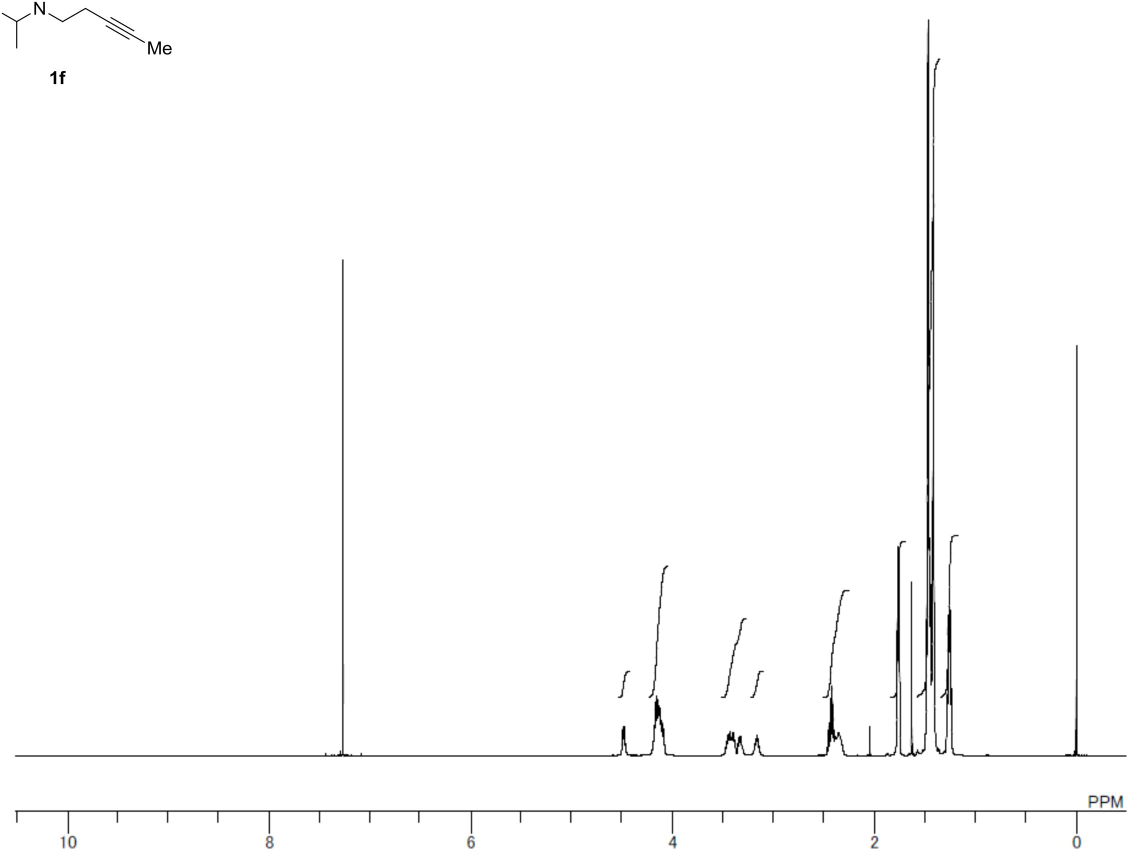

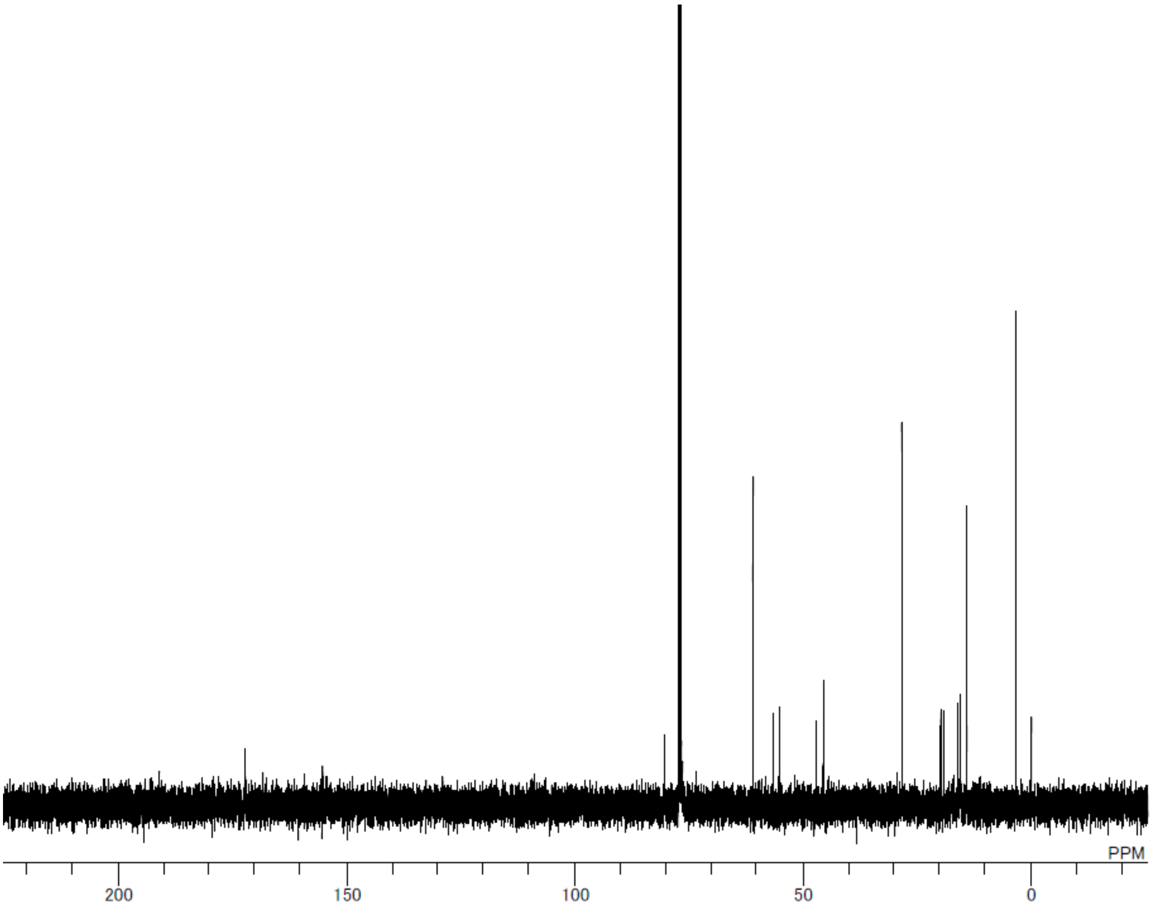

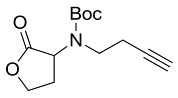

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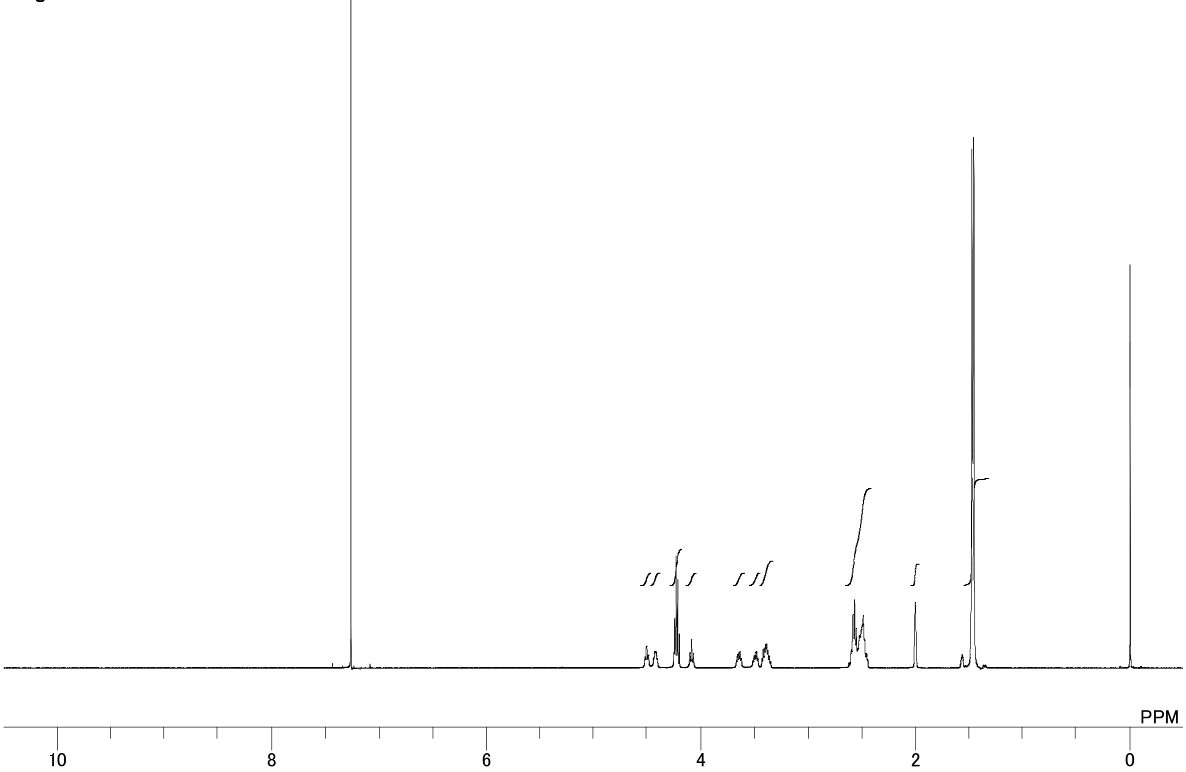

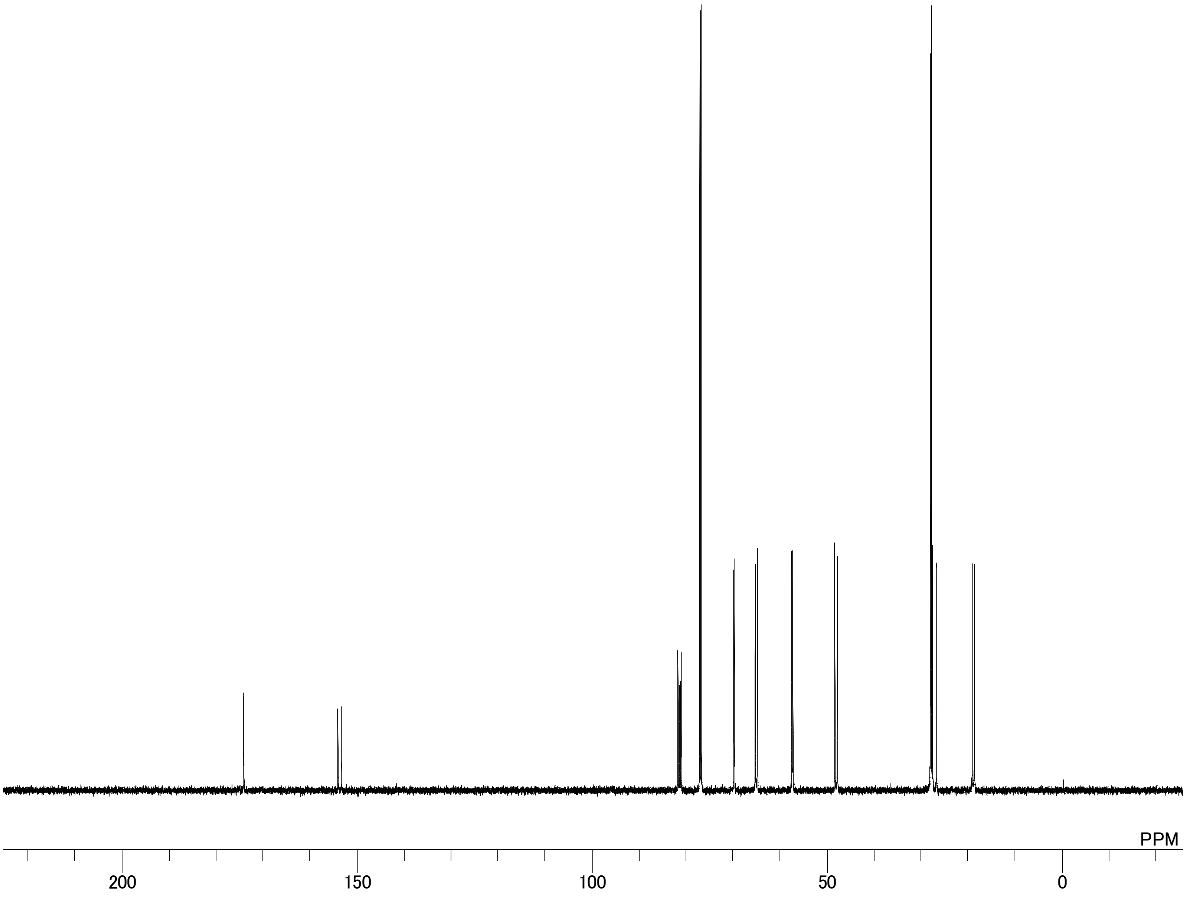

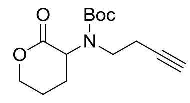

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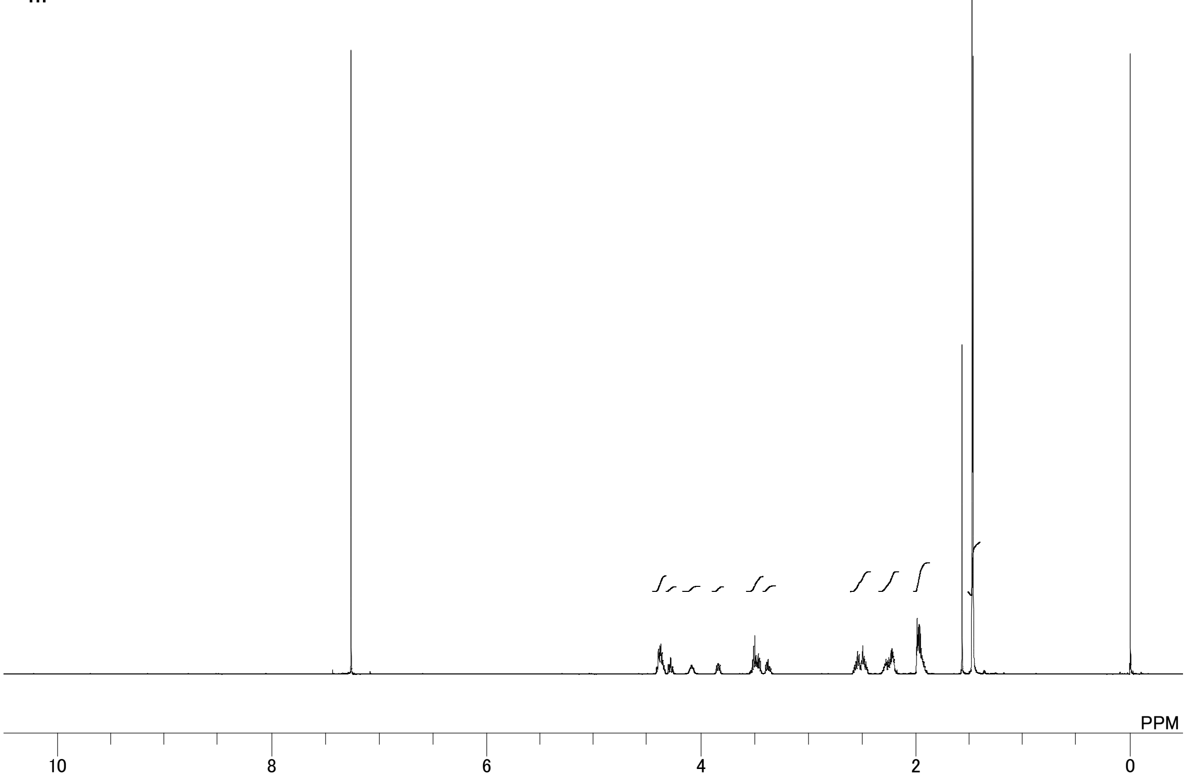

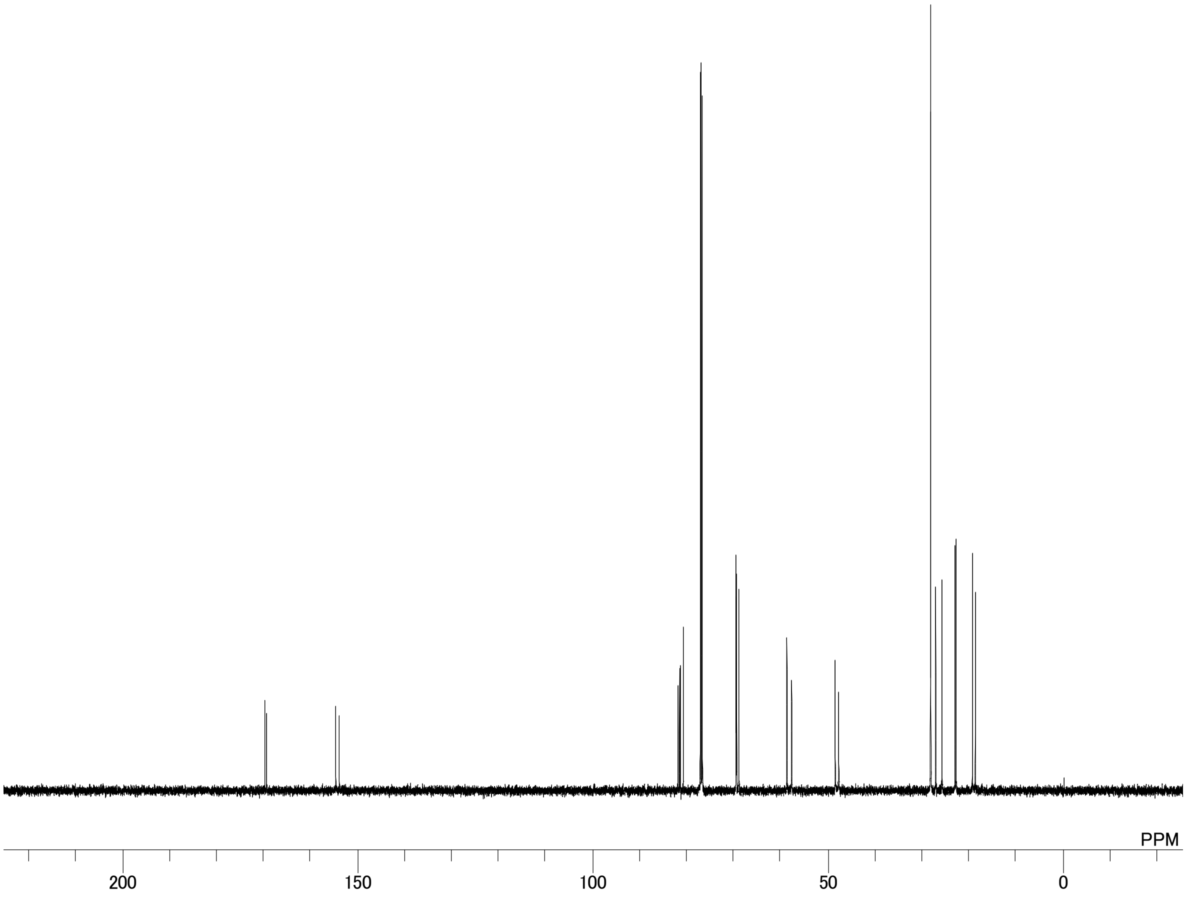

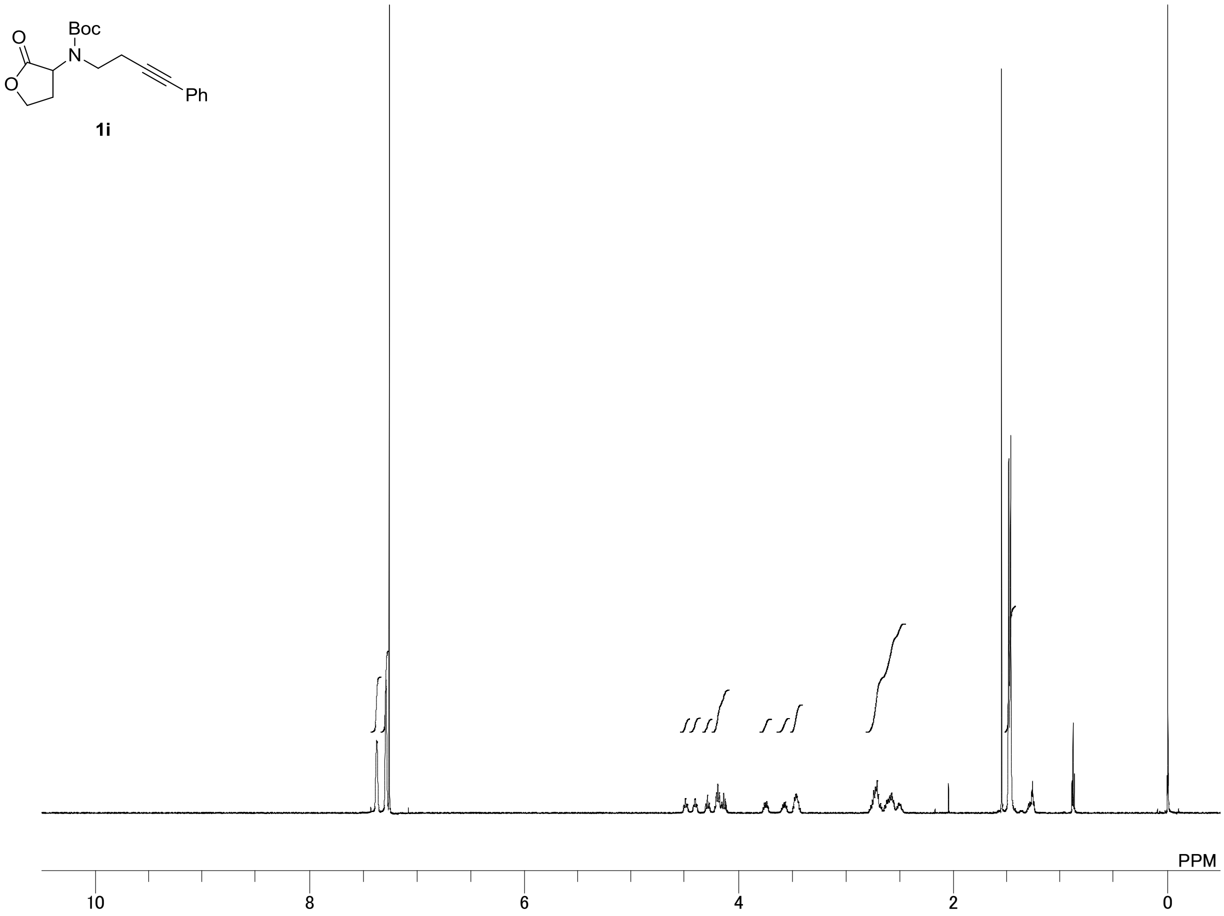

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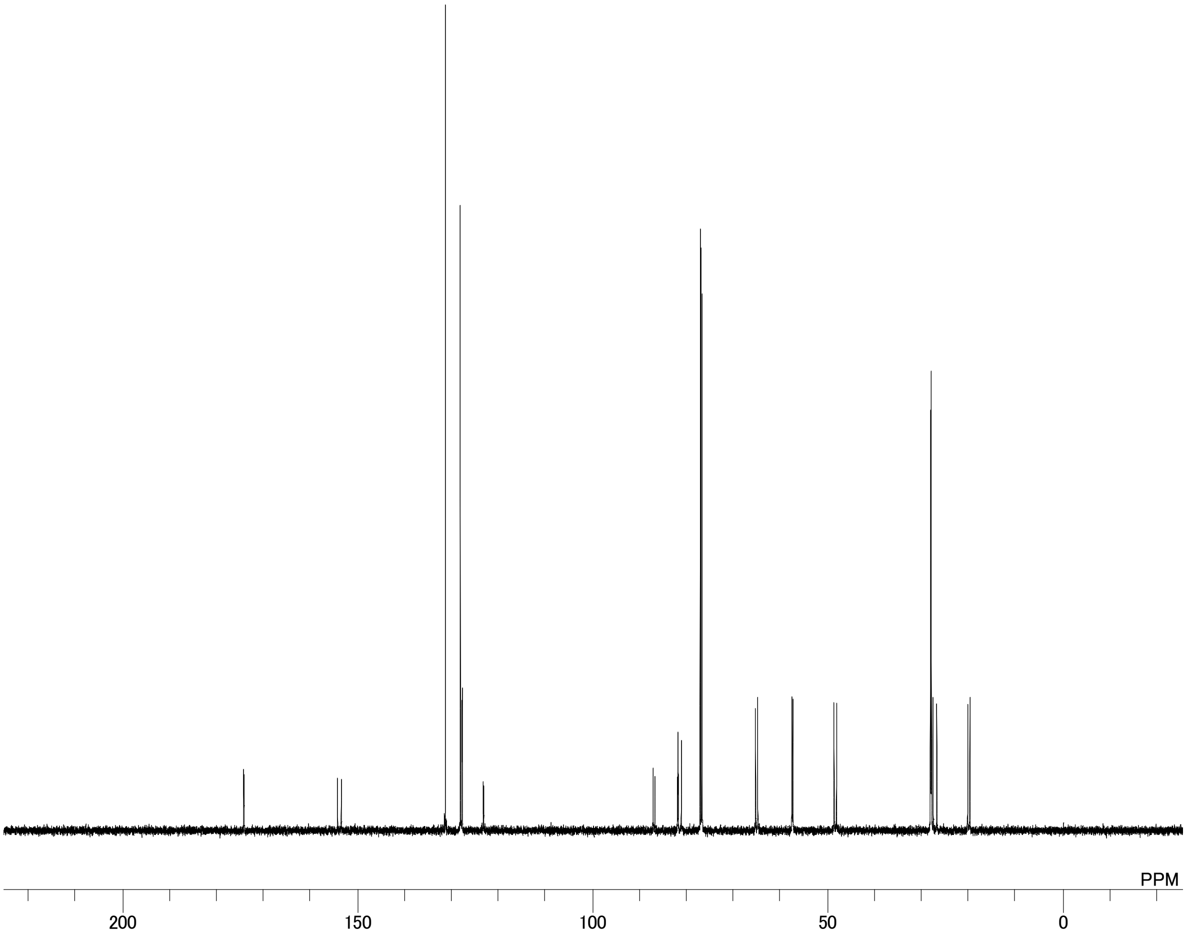

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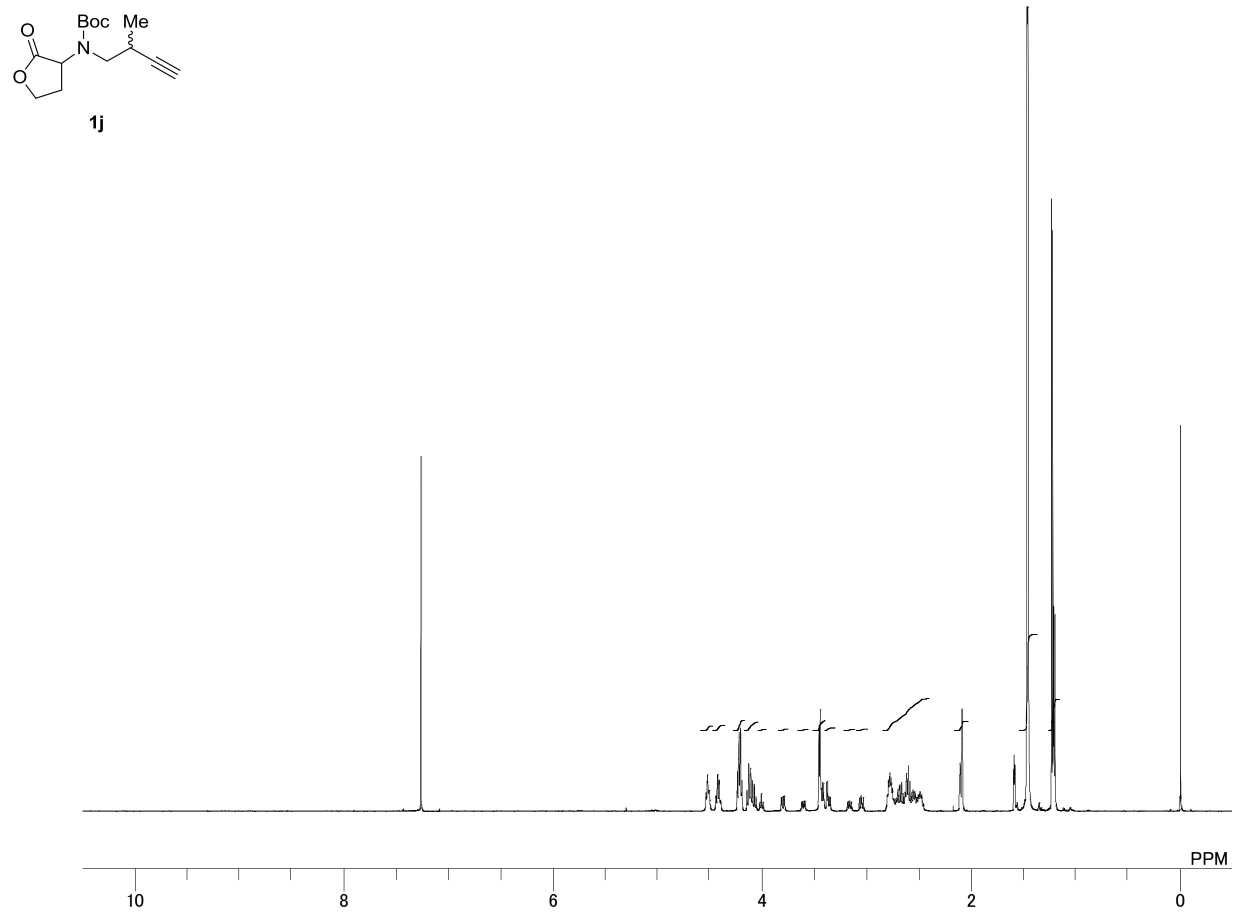
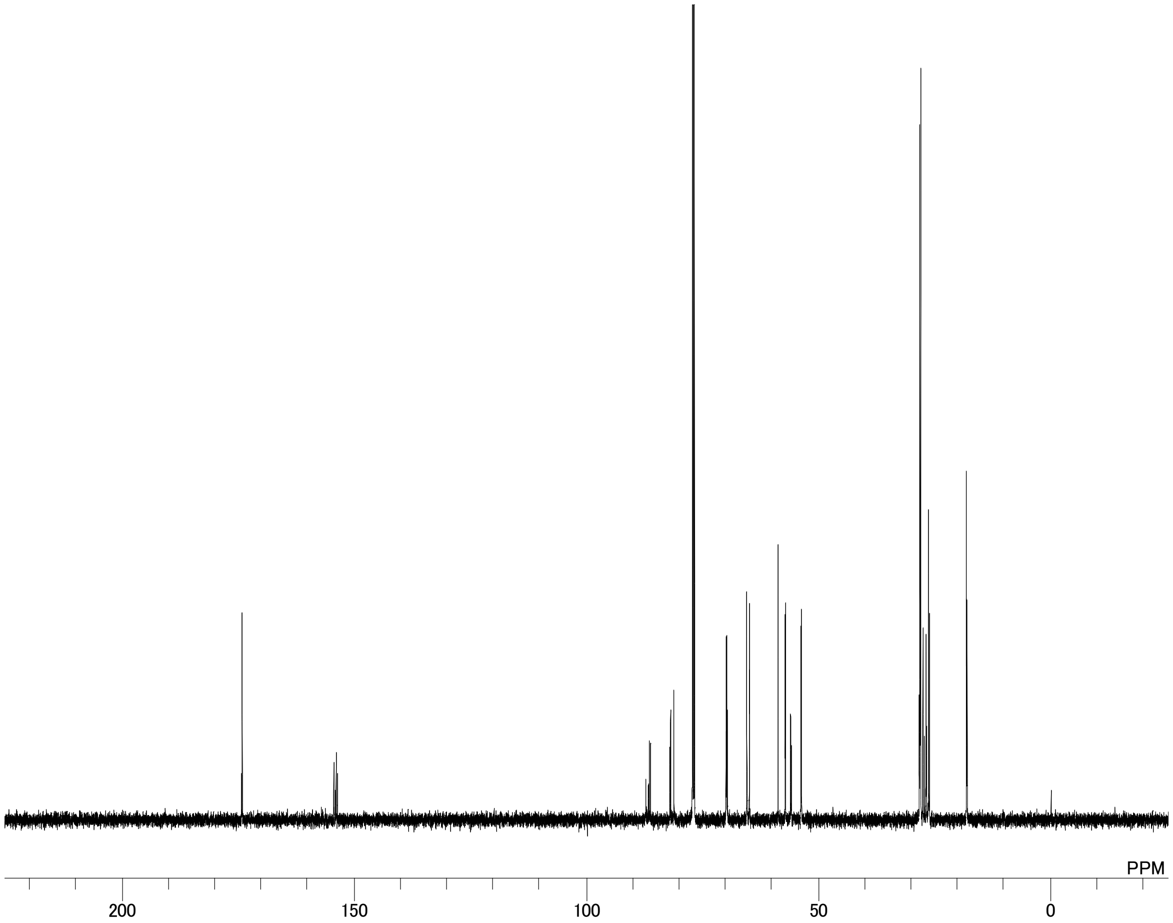
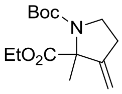
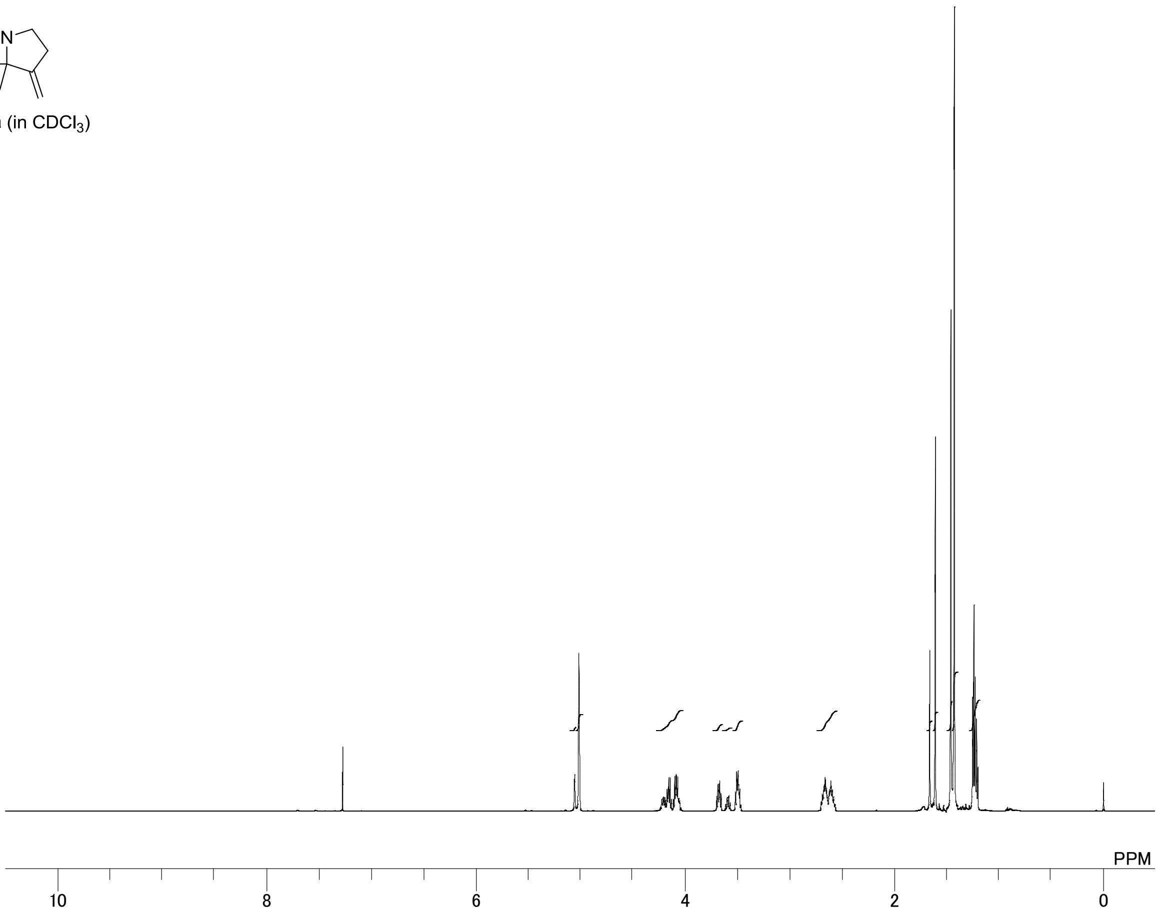
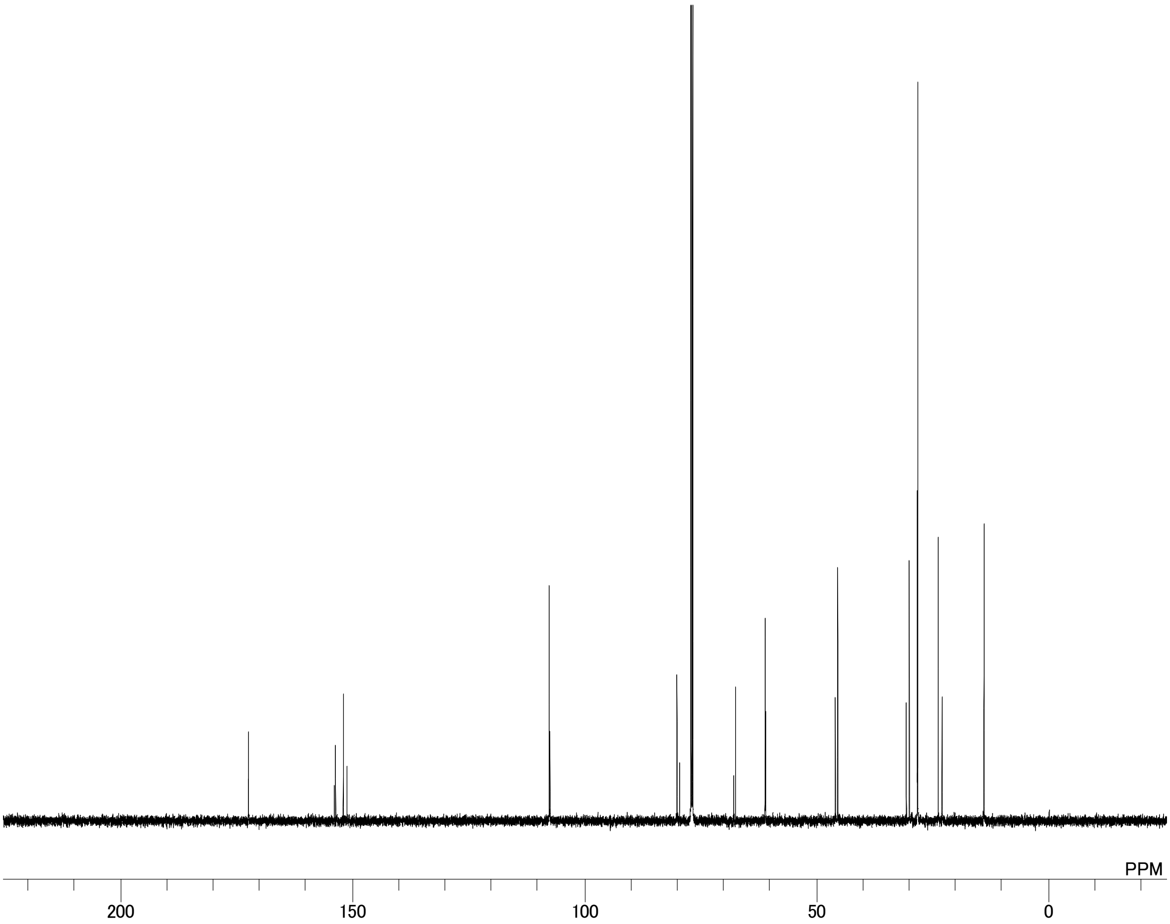


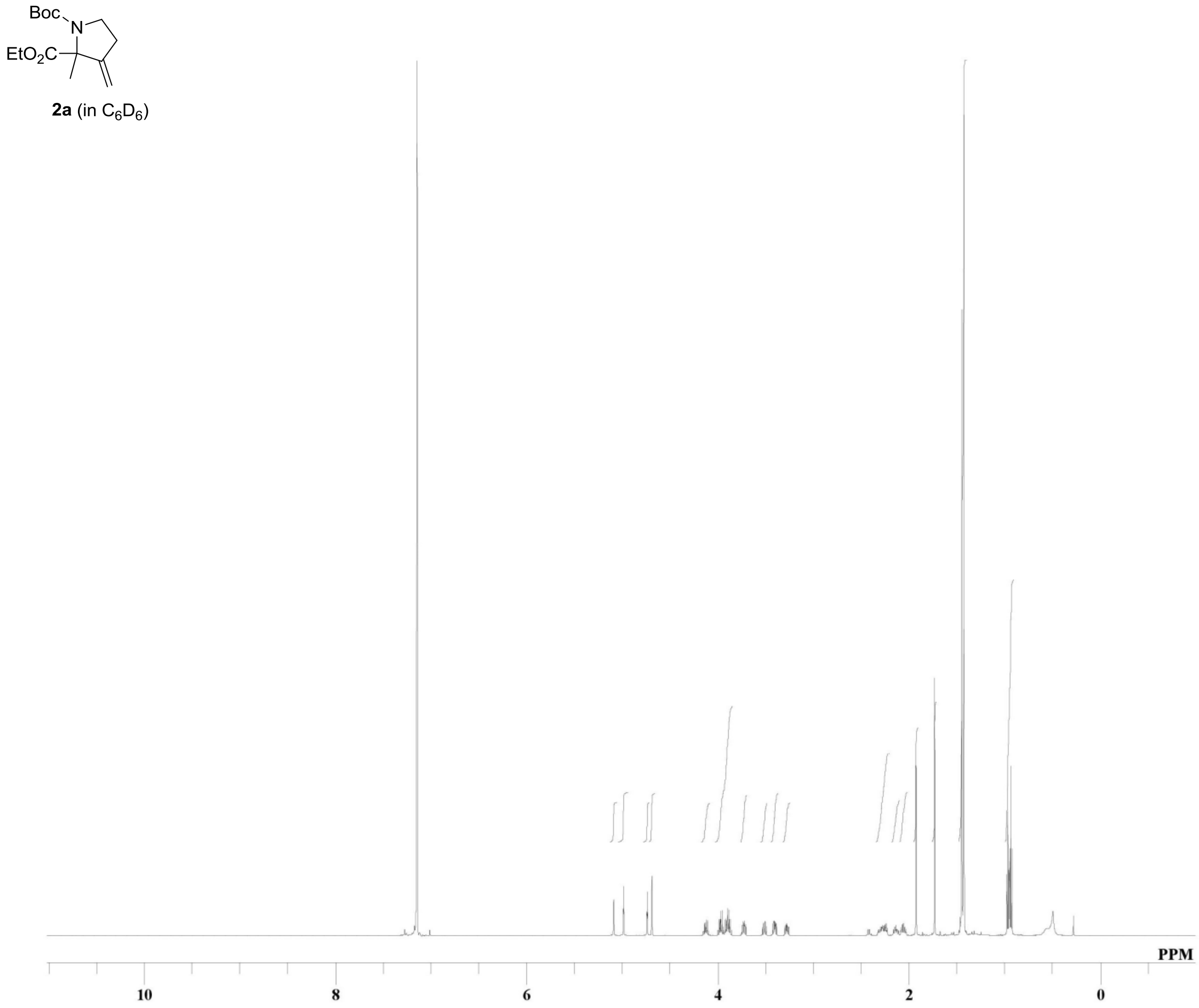




2a (in $CDCl_3$)







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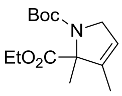

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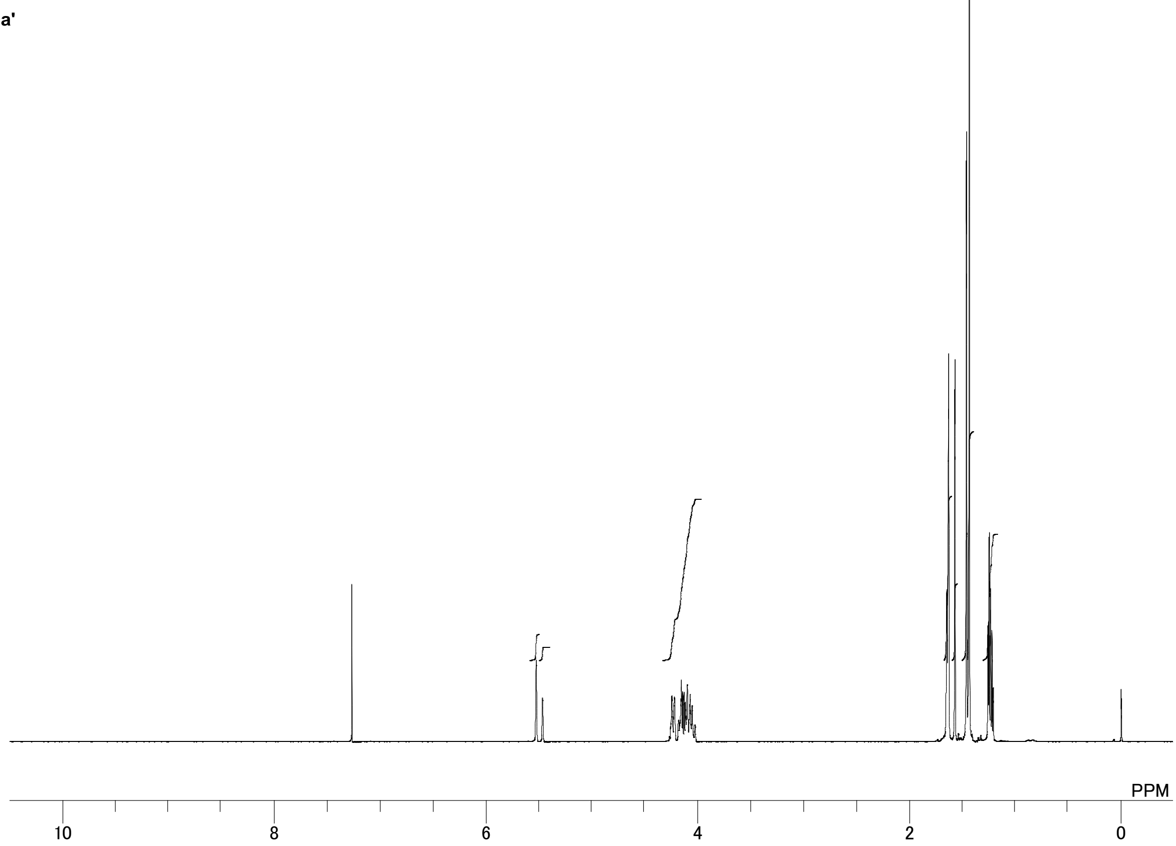

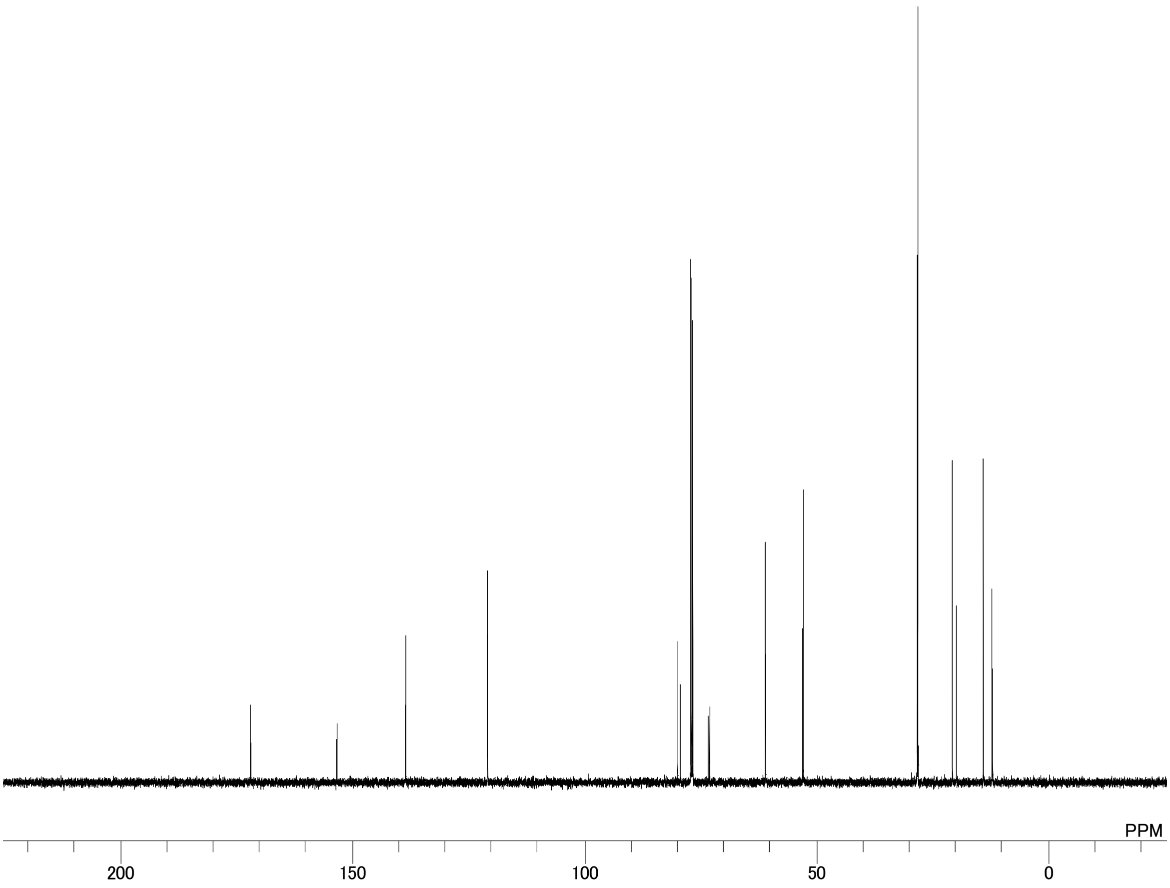

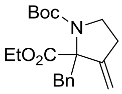

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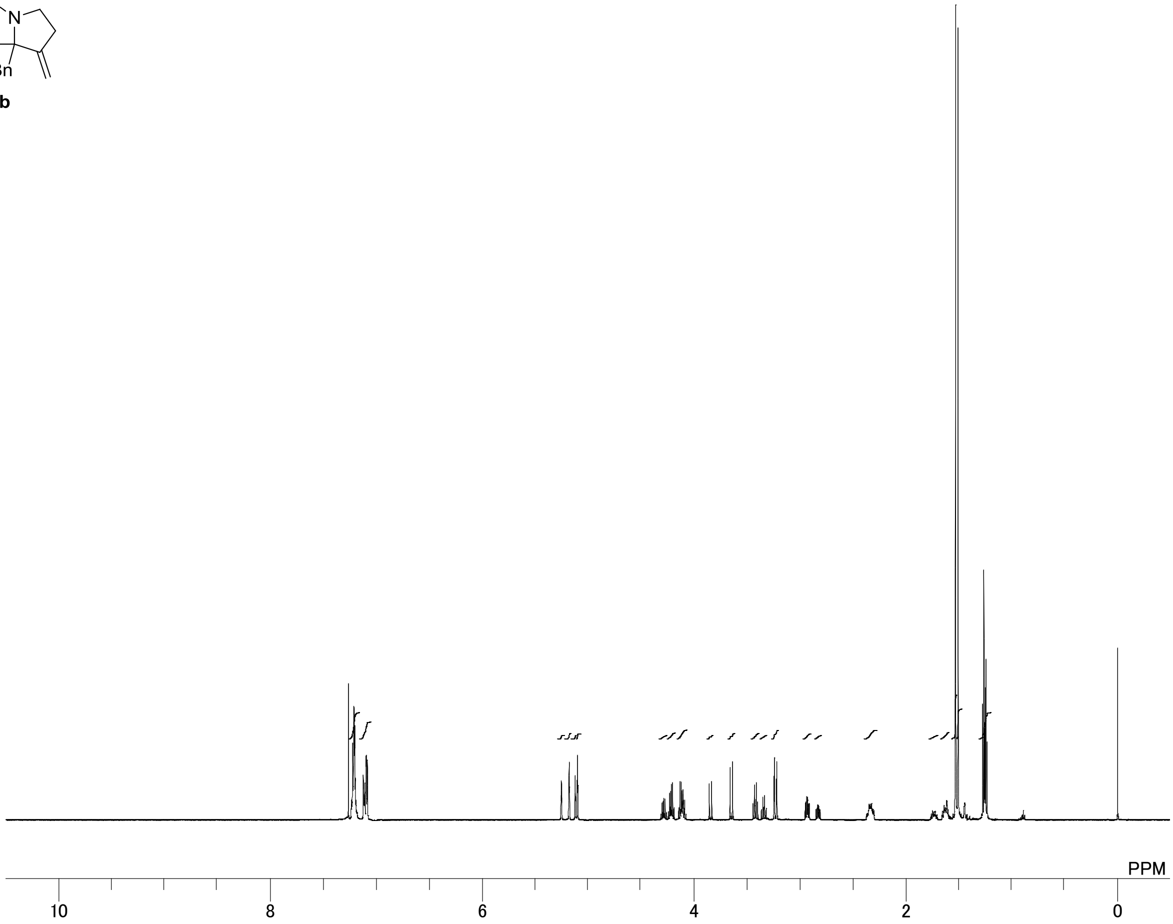

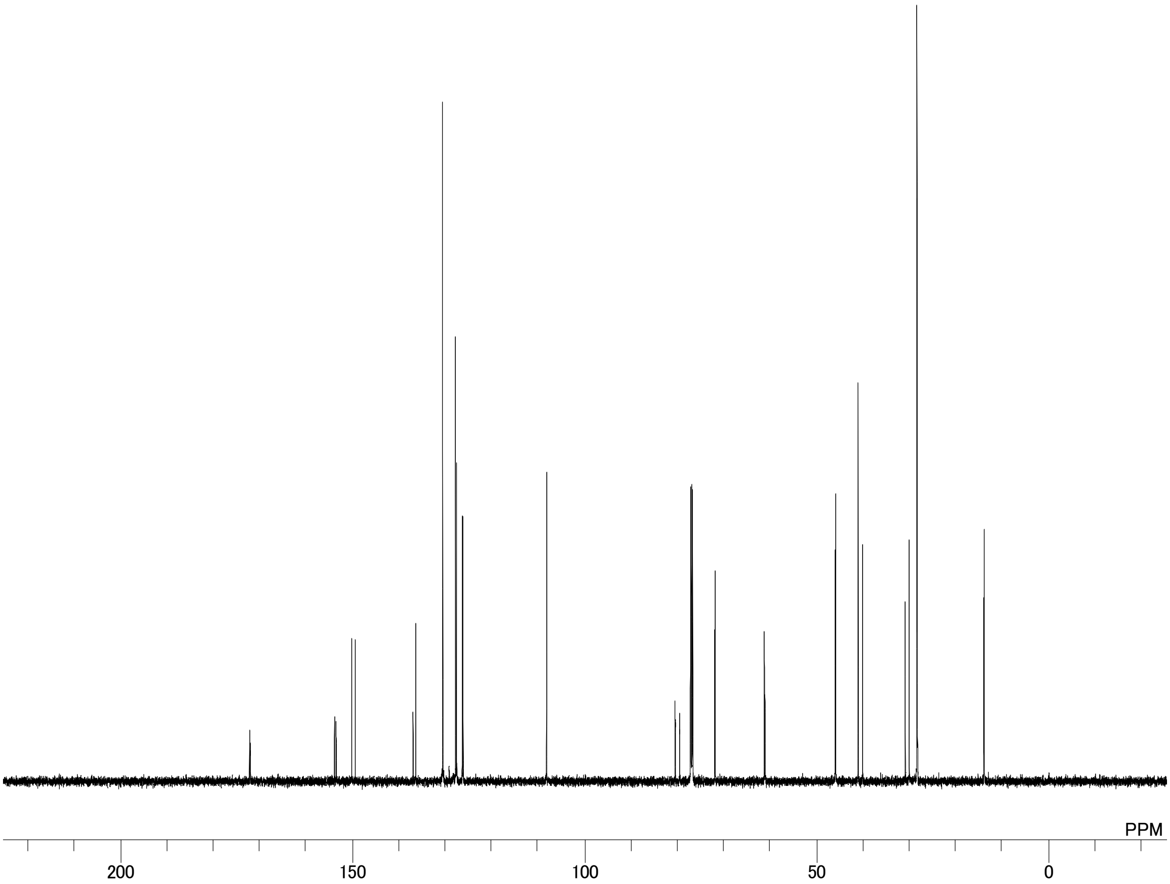

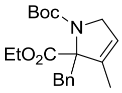

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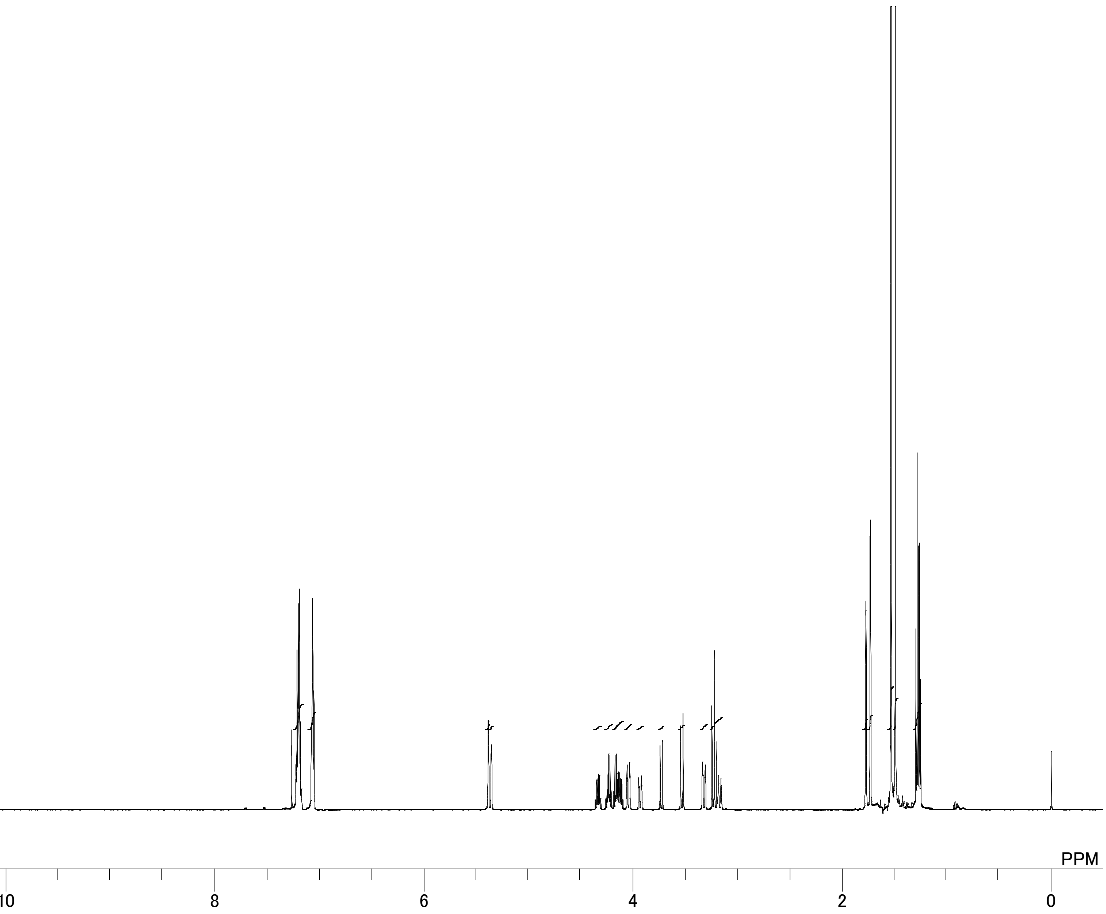

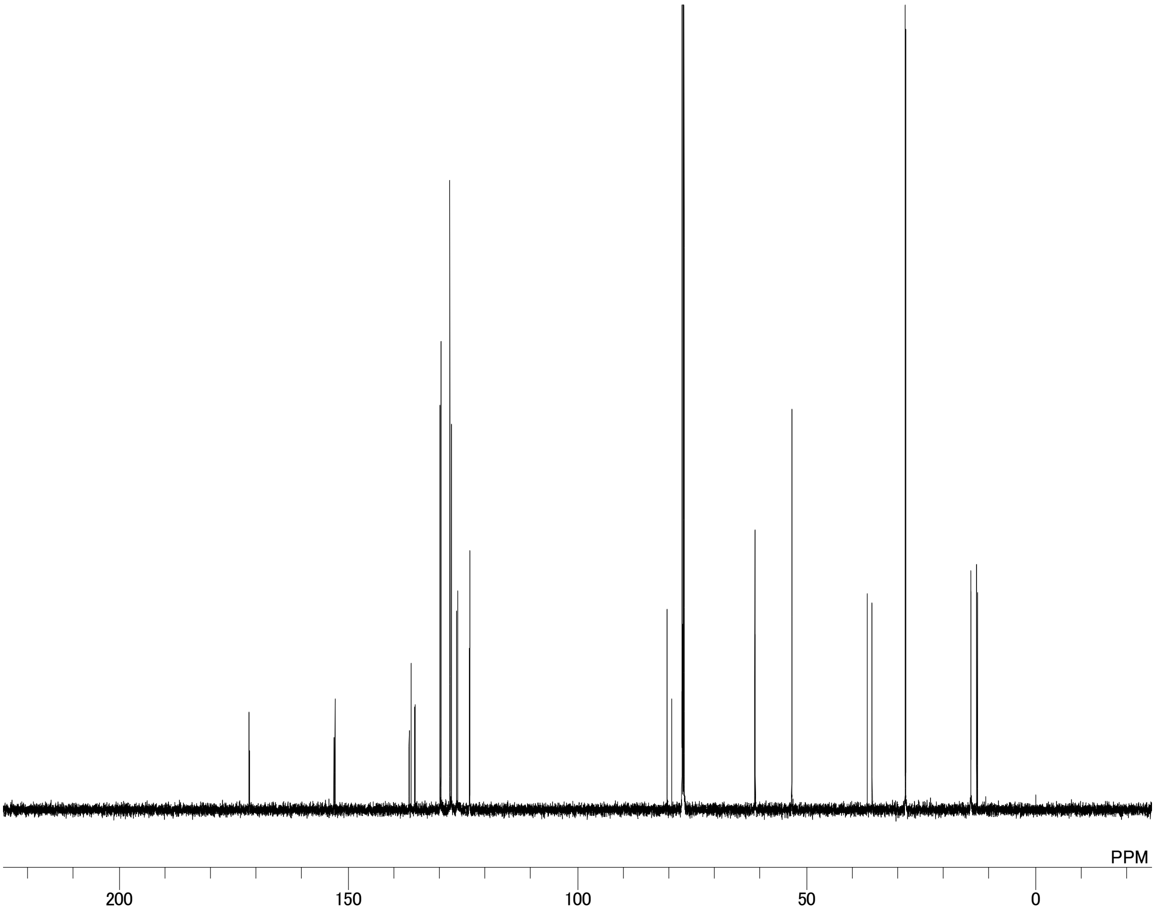

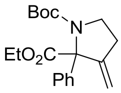

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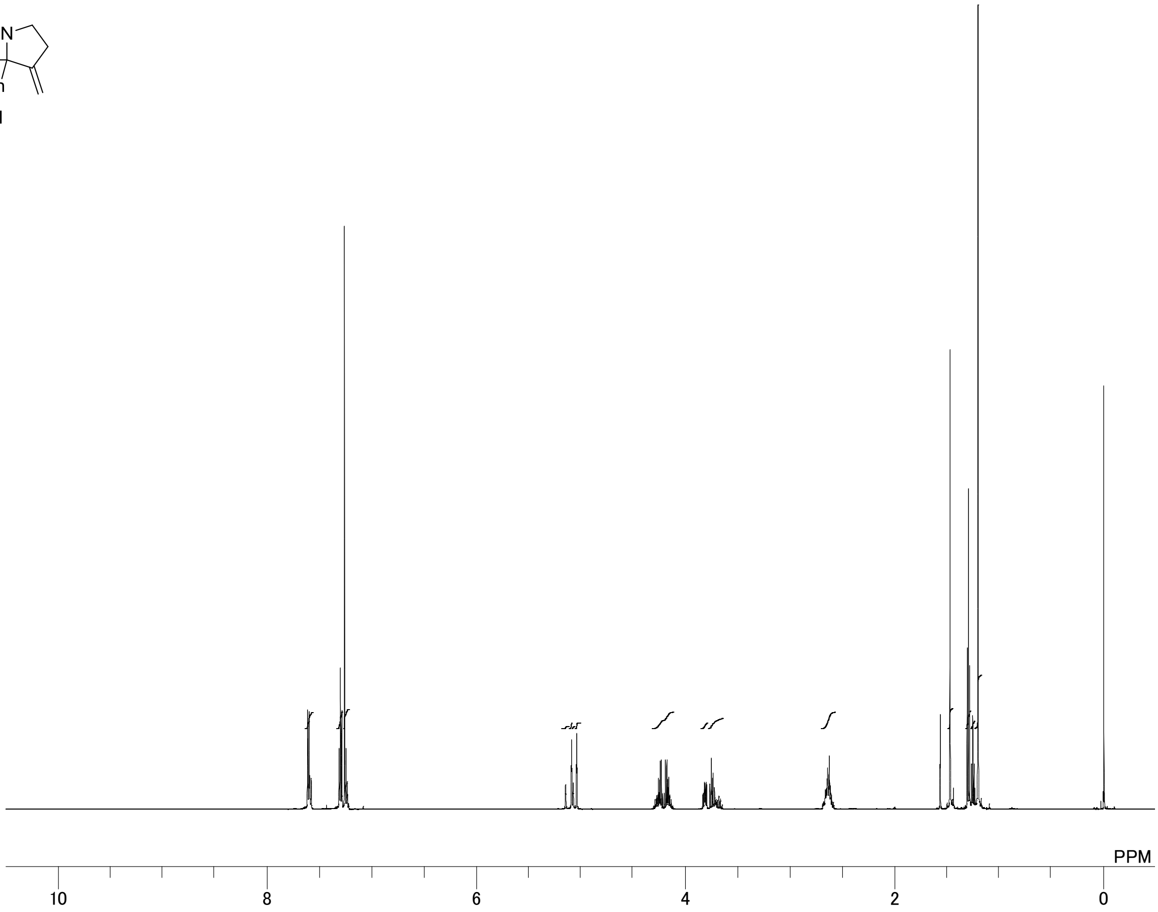

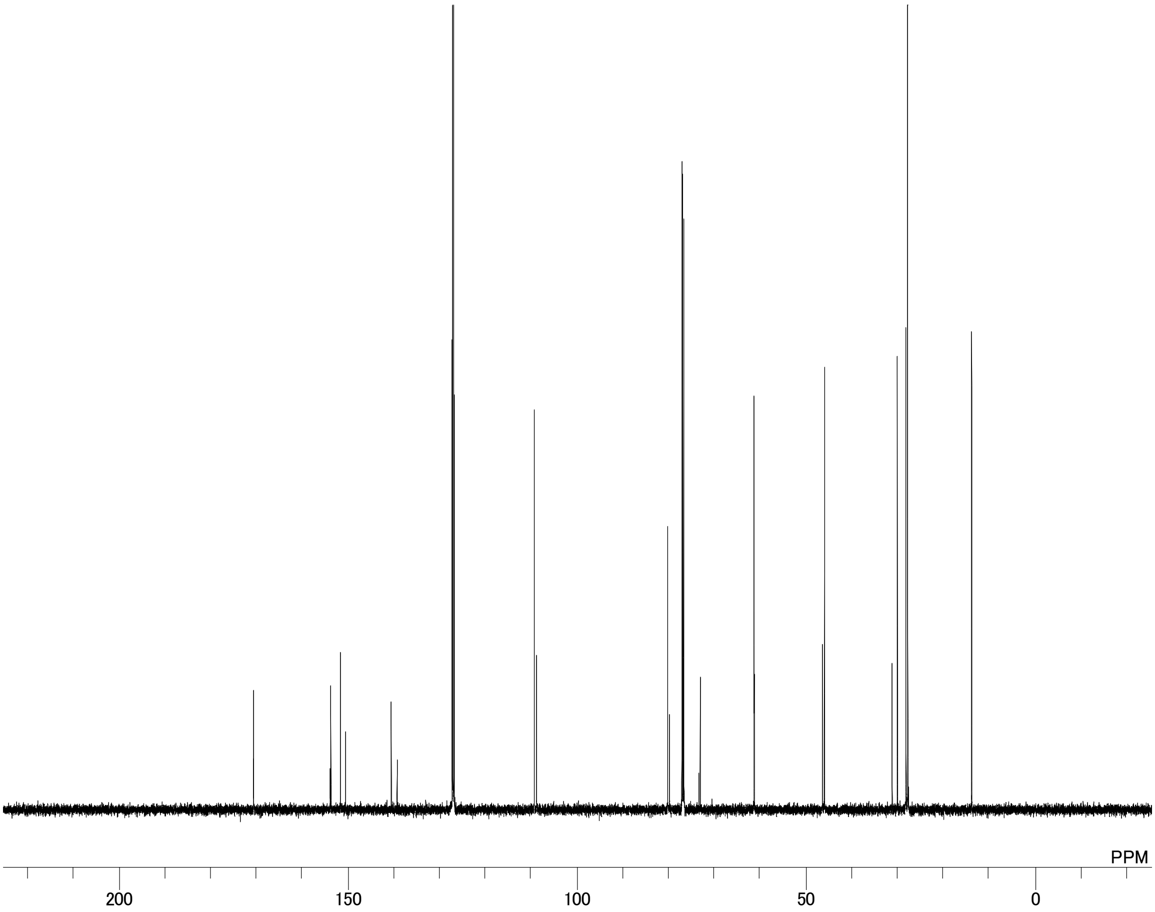

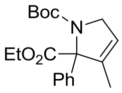

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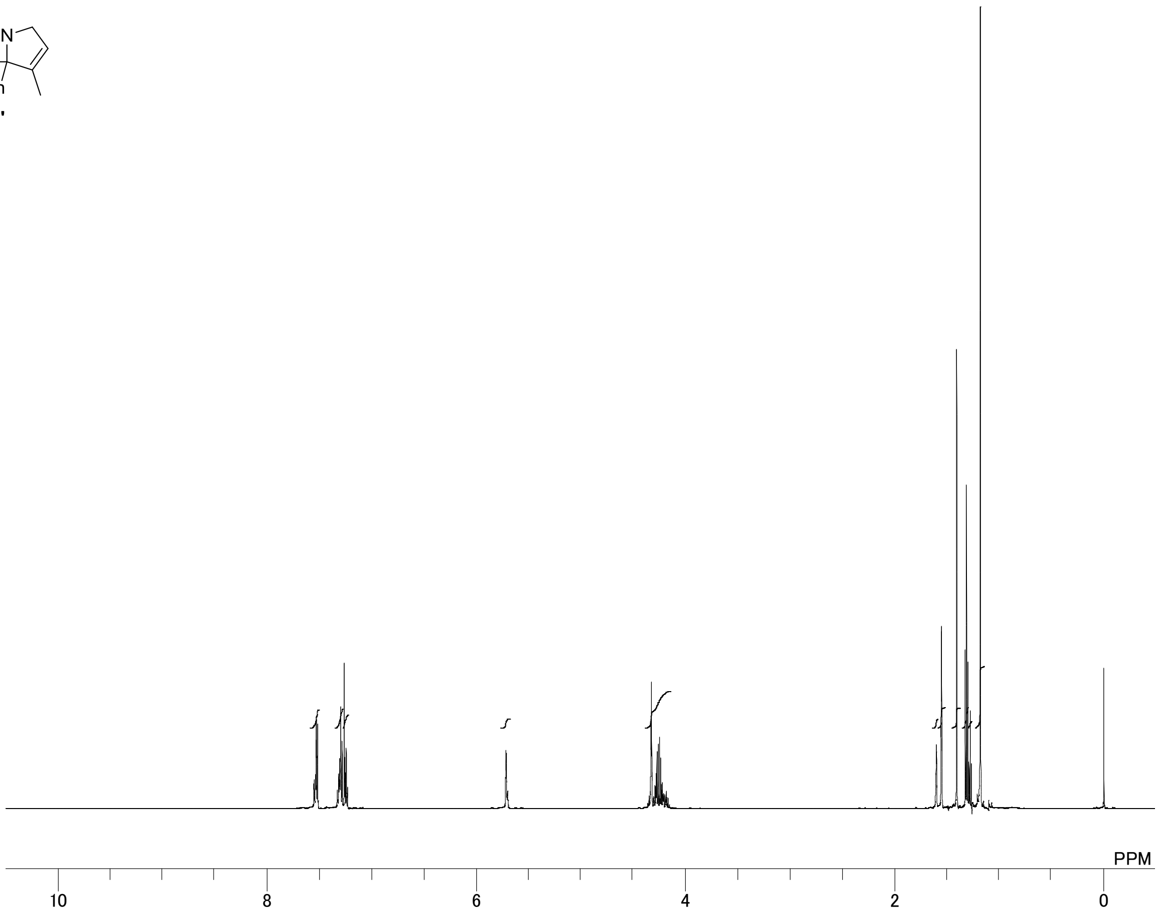
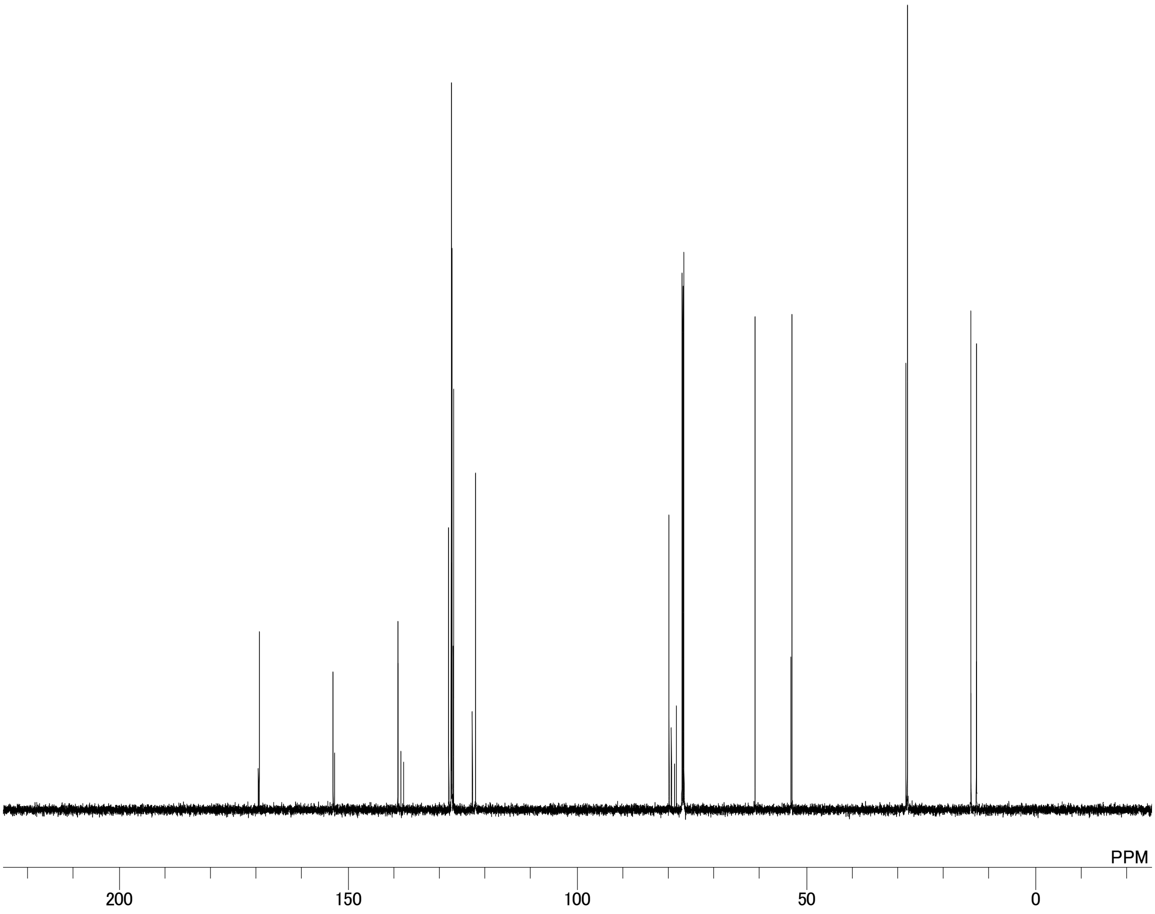
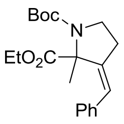
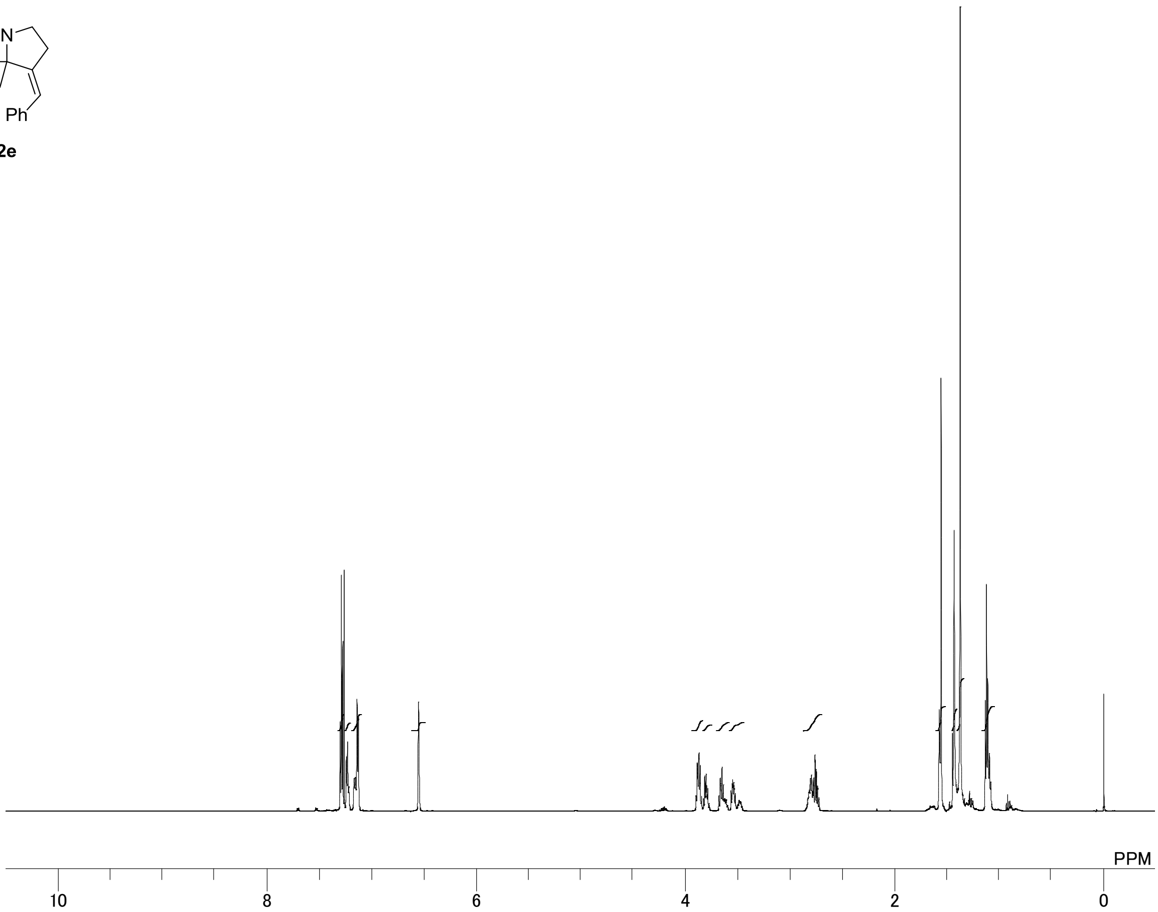
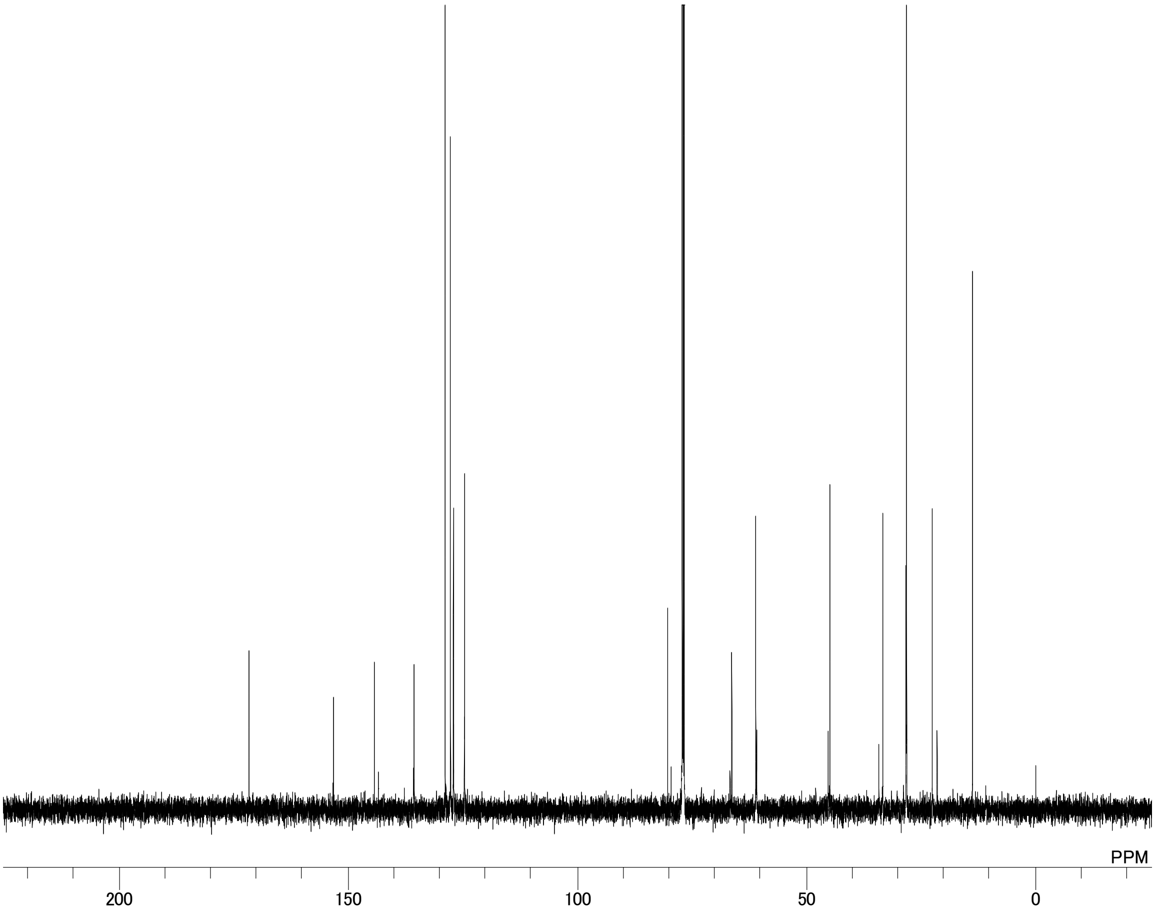


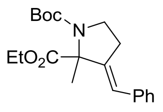




(*Z*)-**2e**







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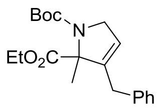

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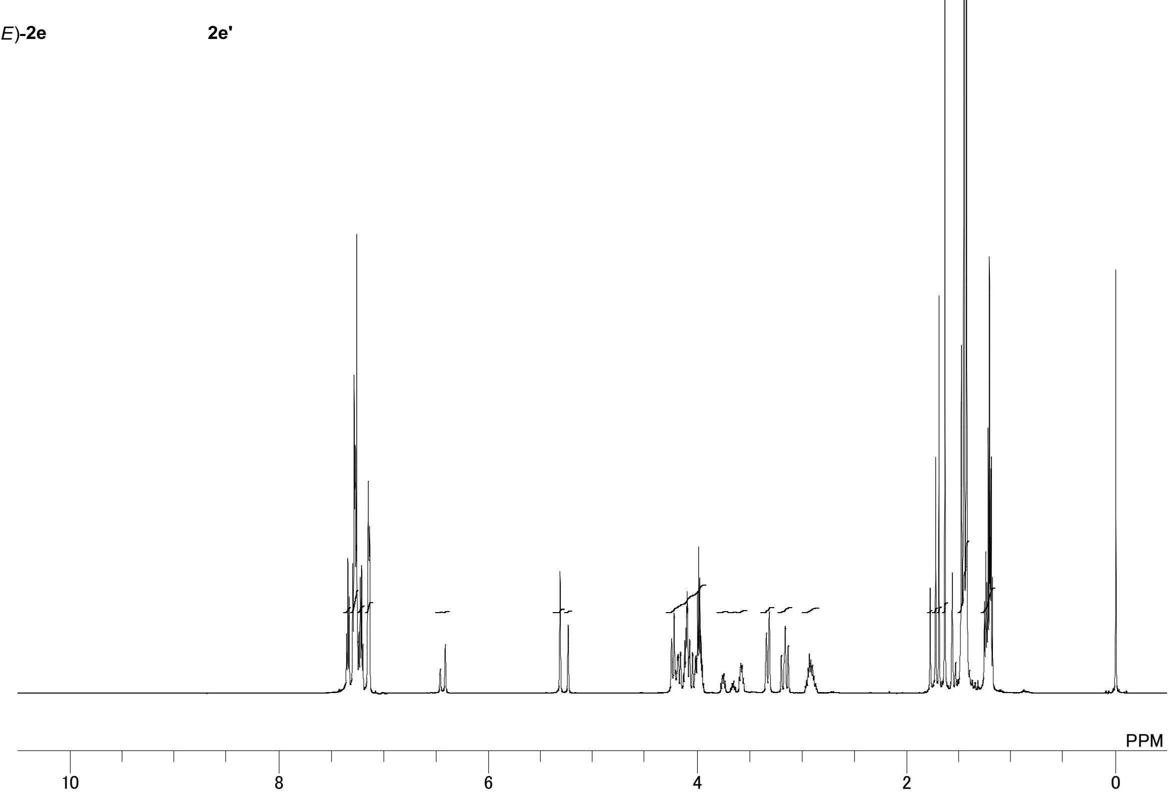

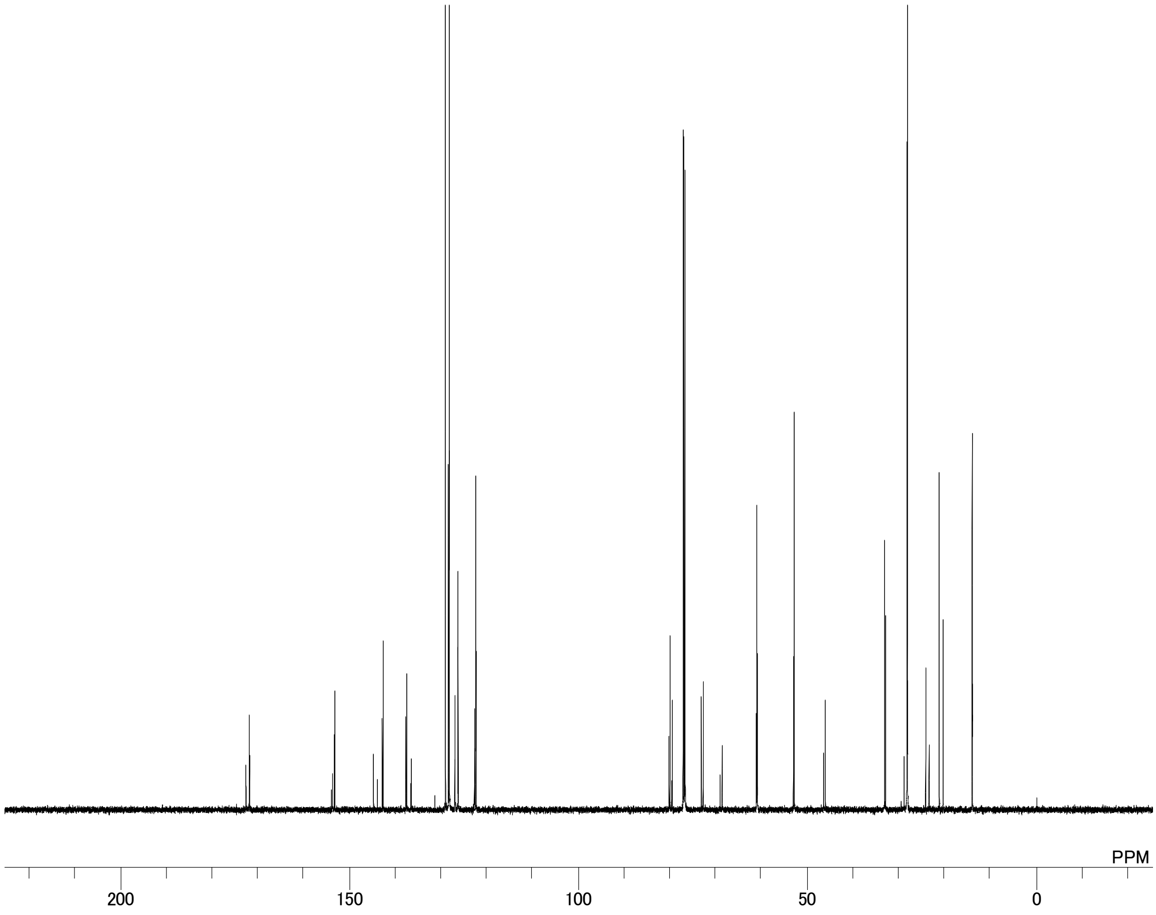

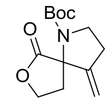

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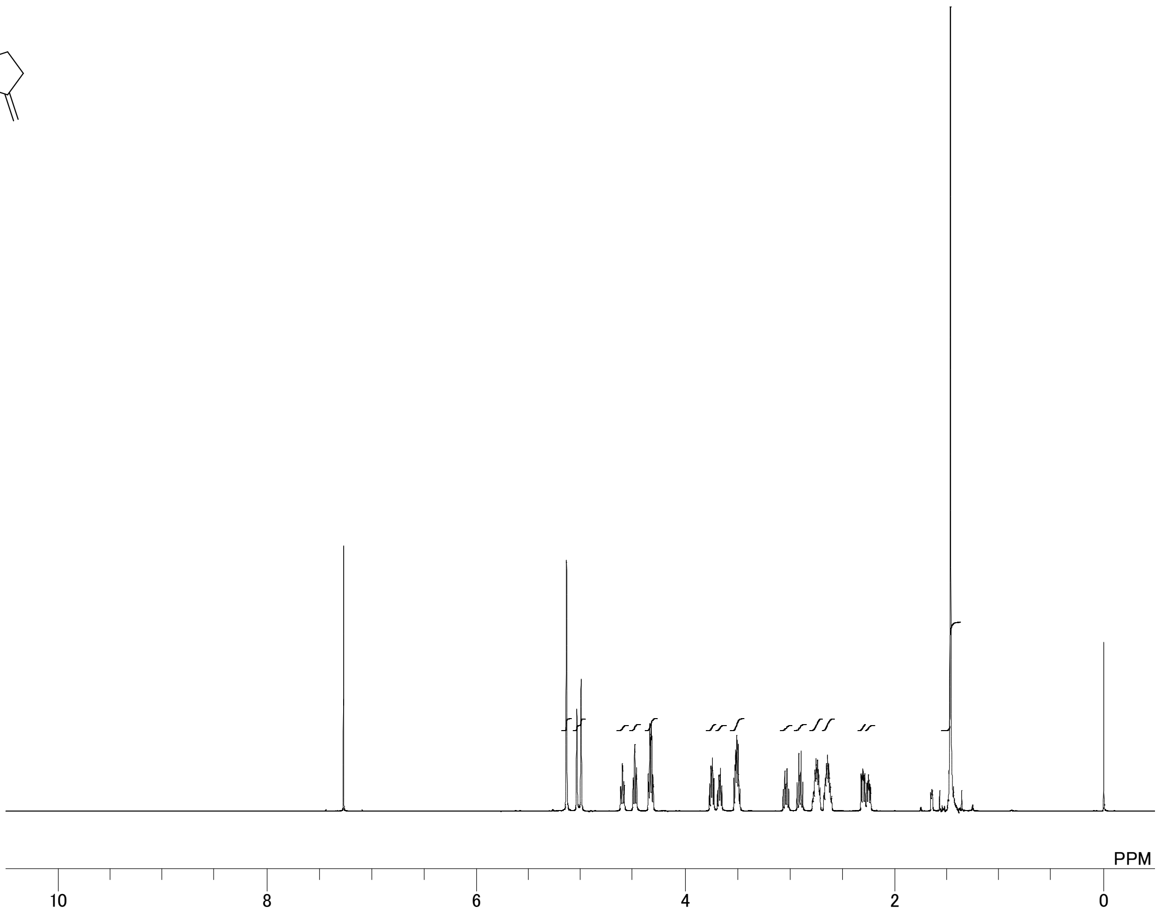

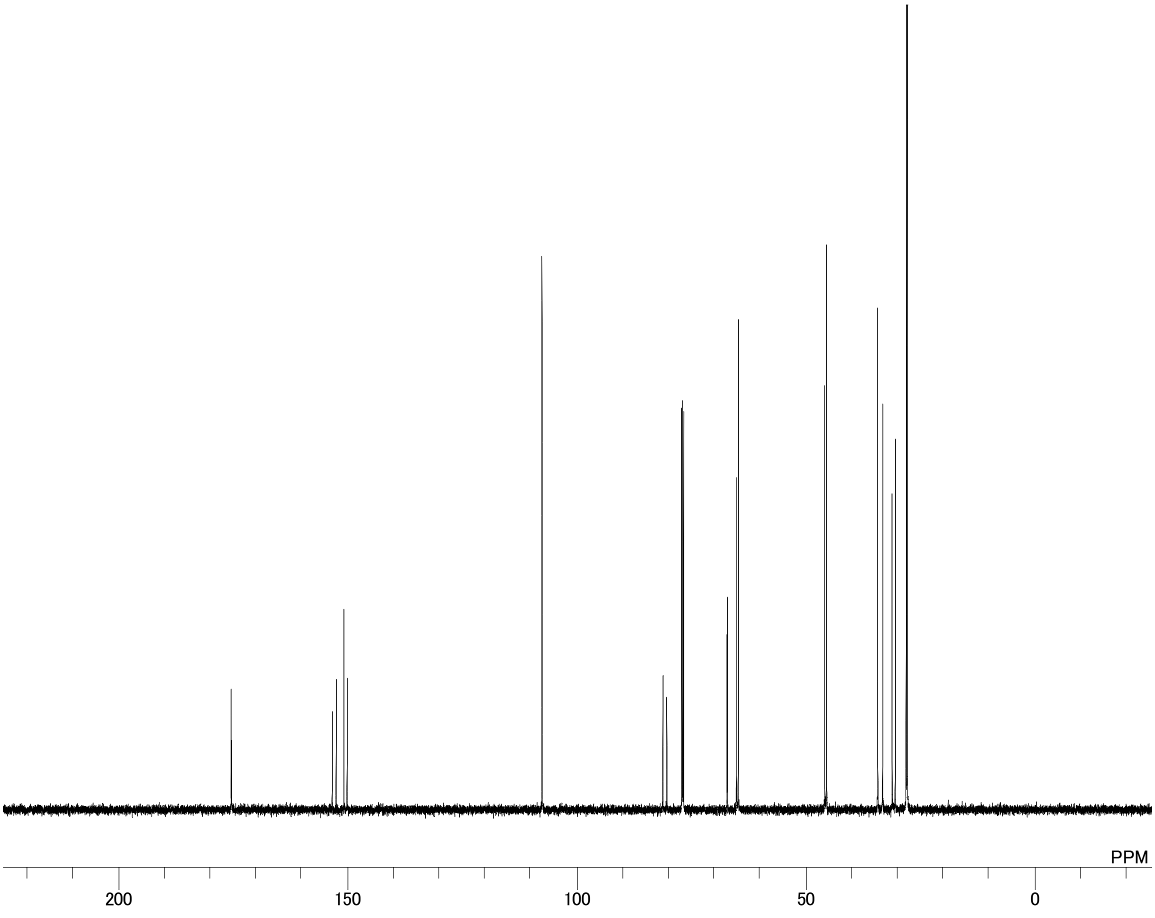

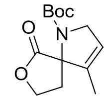

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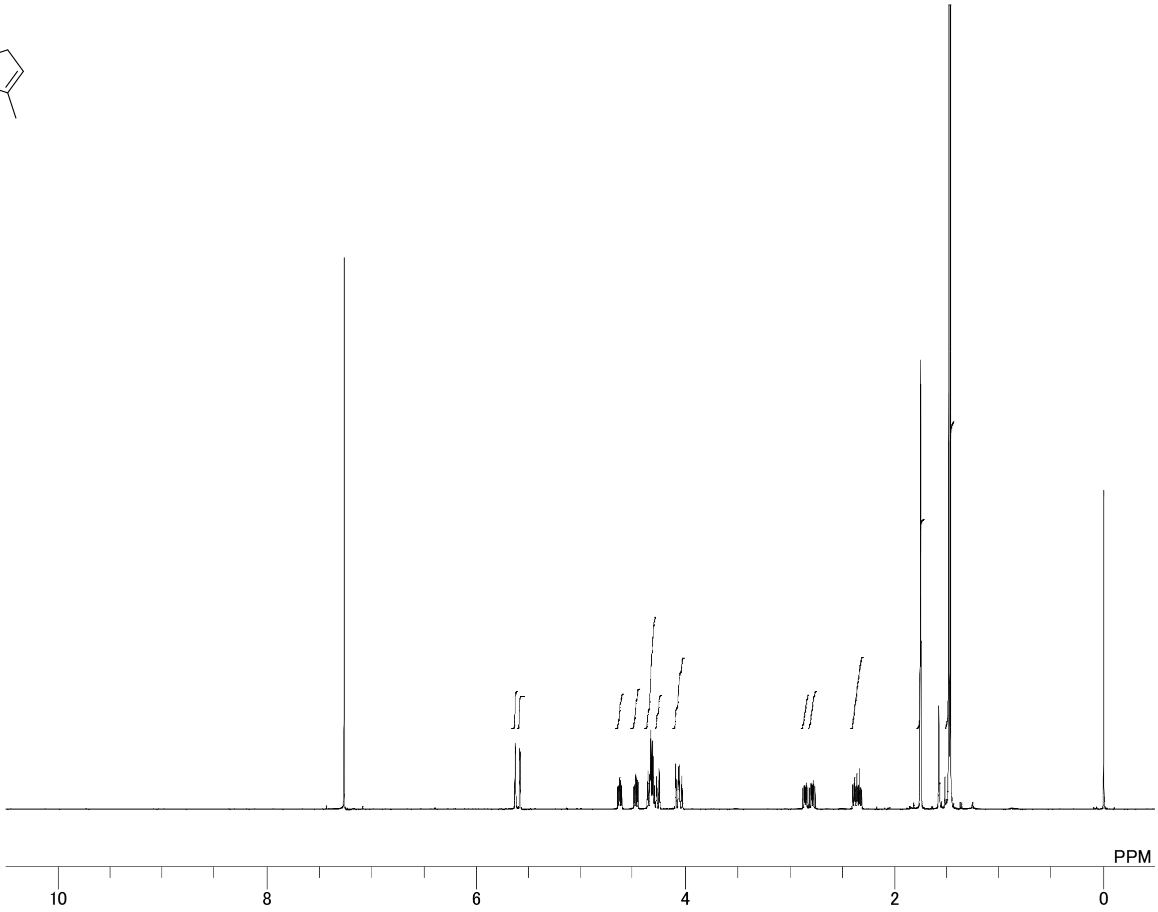
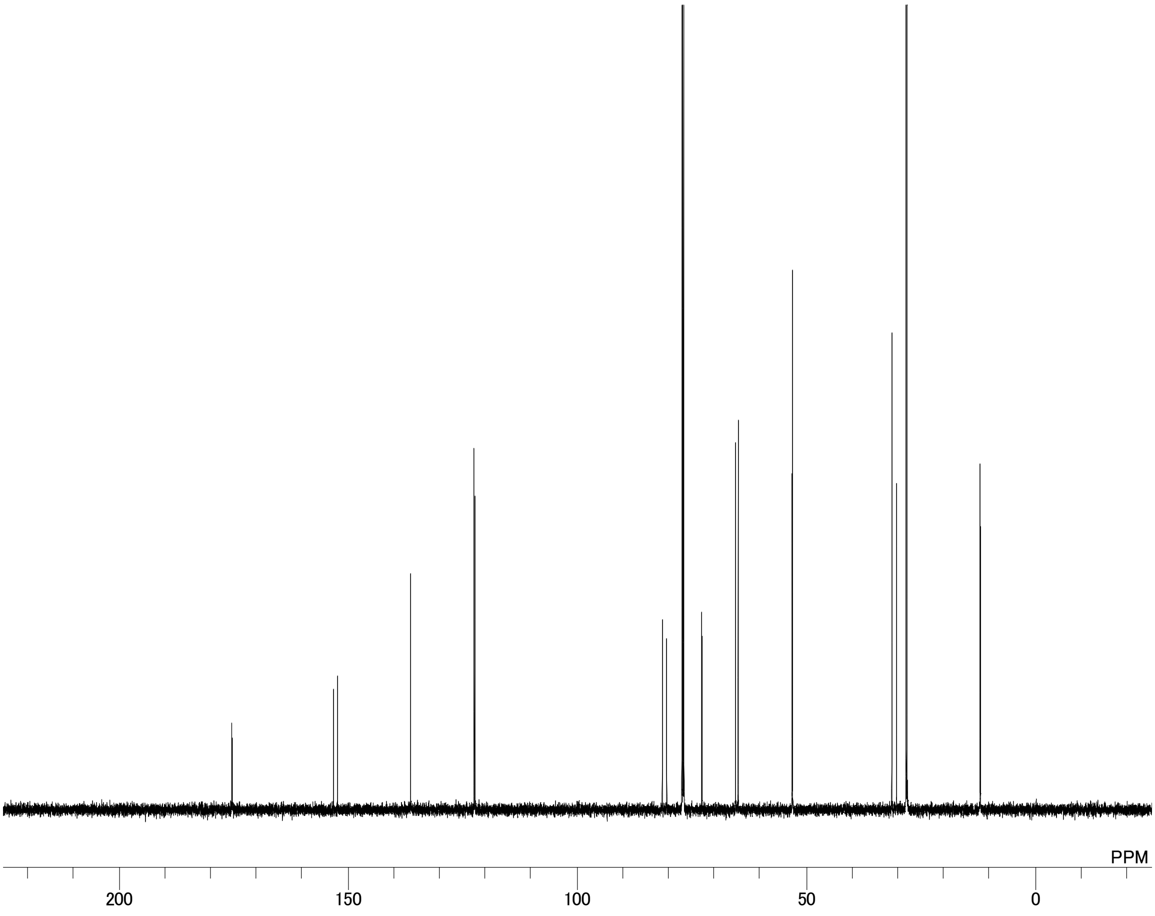
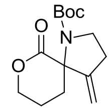
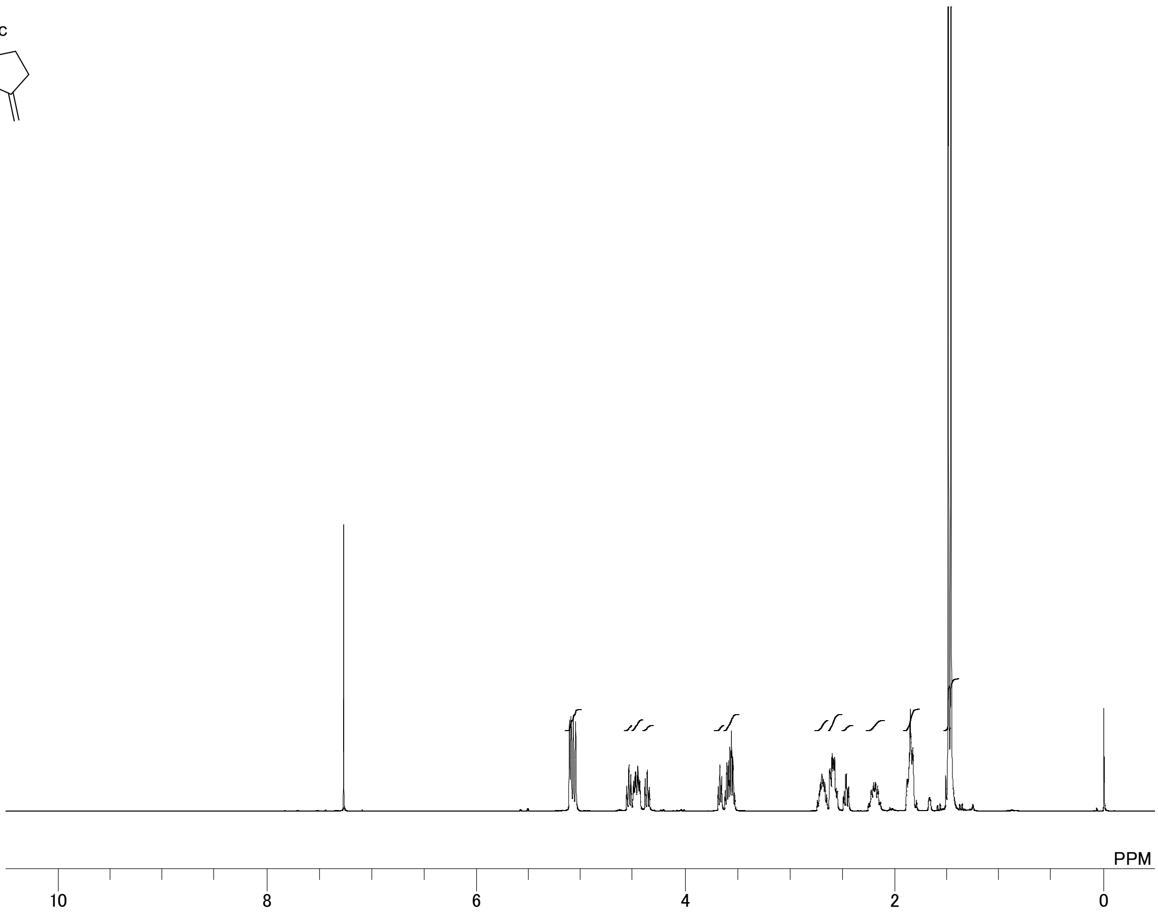
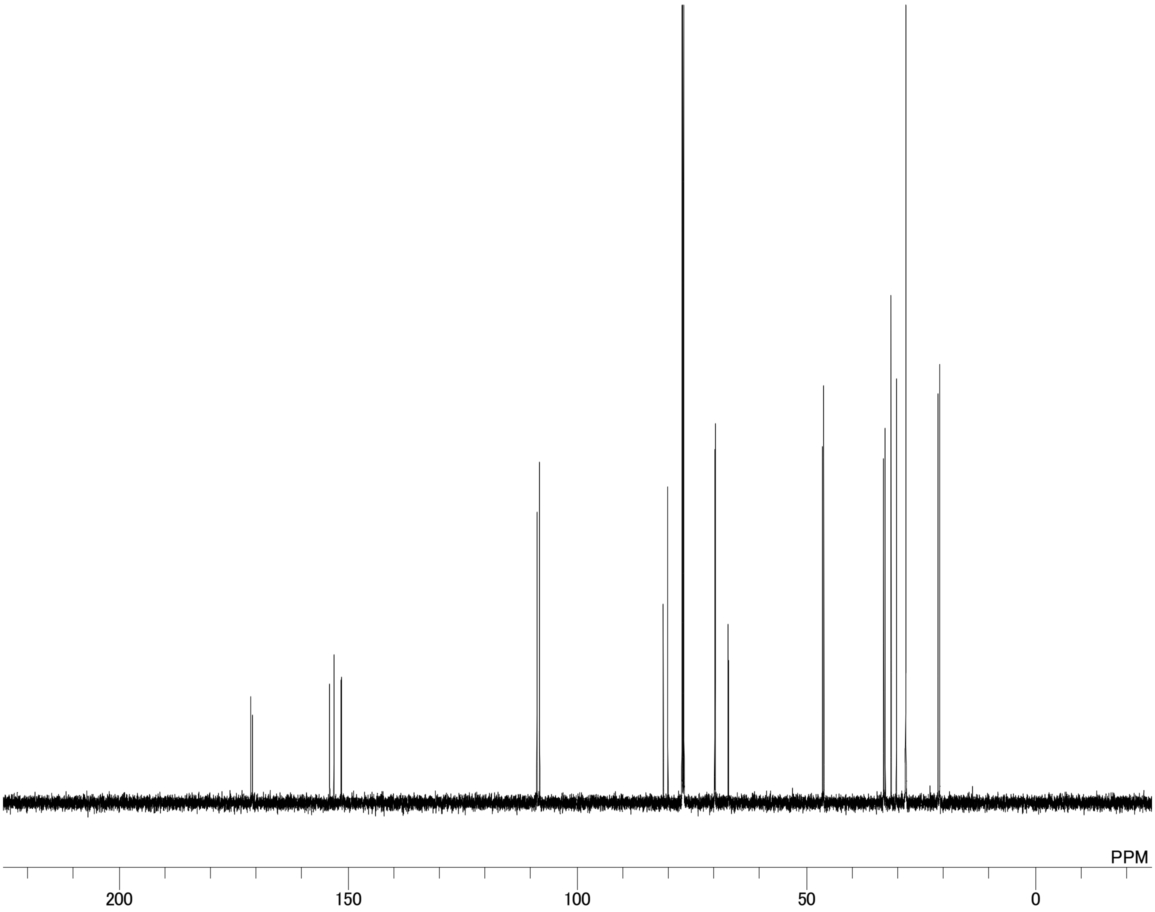


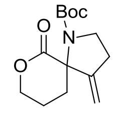




2h







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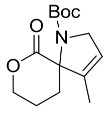

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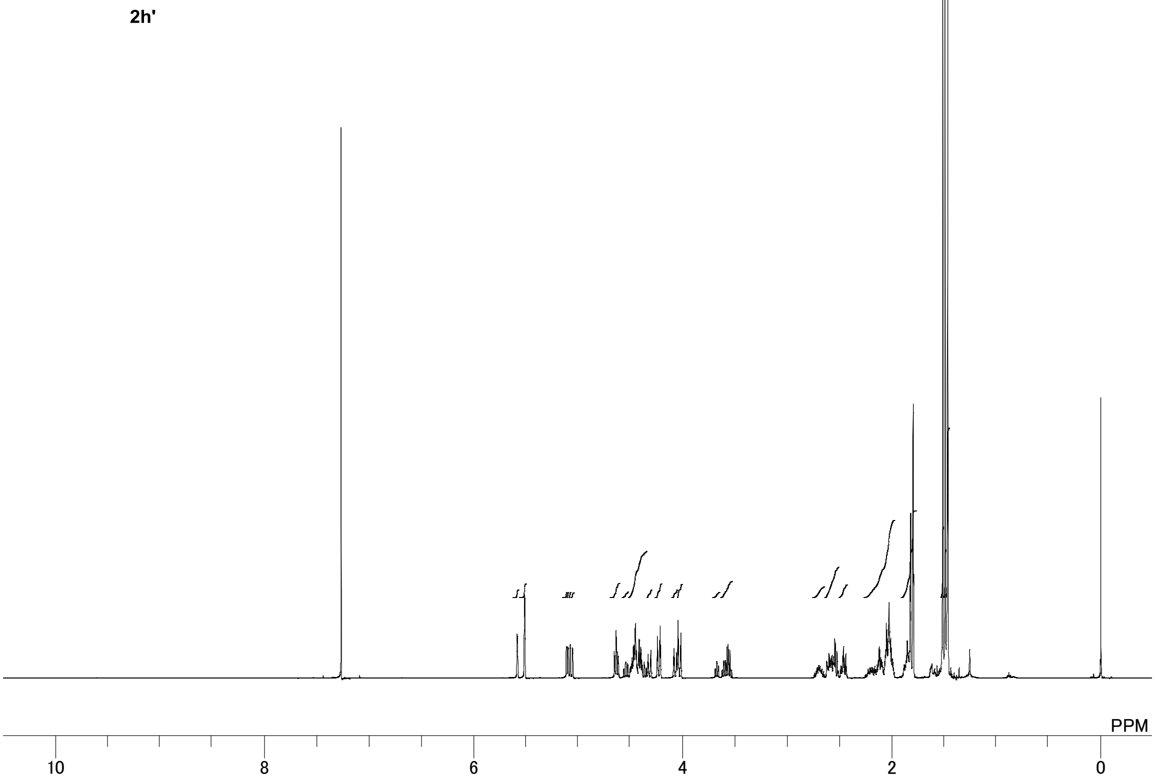
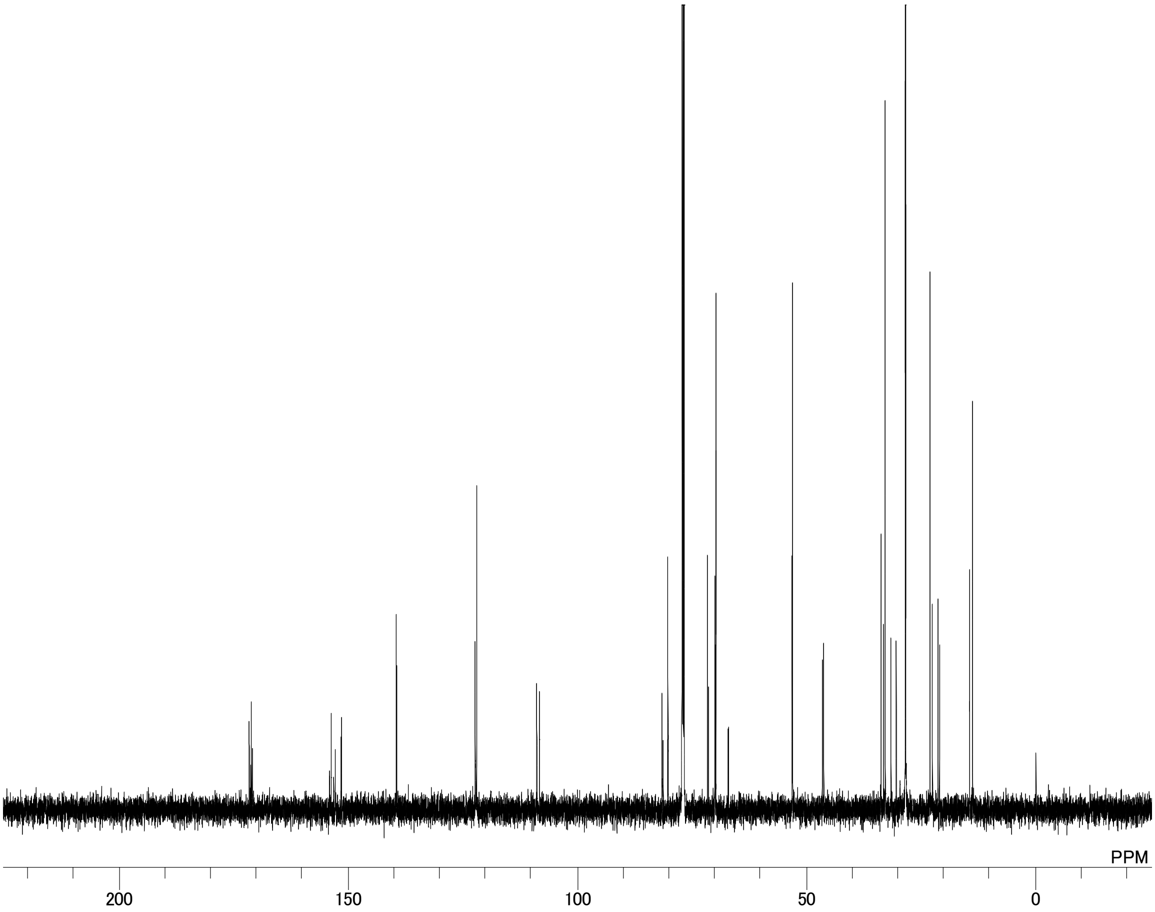
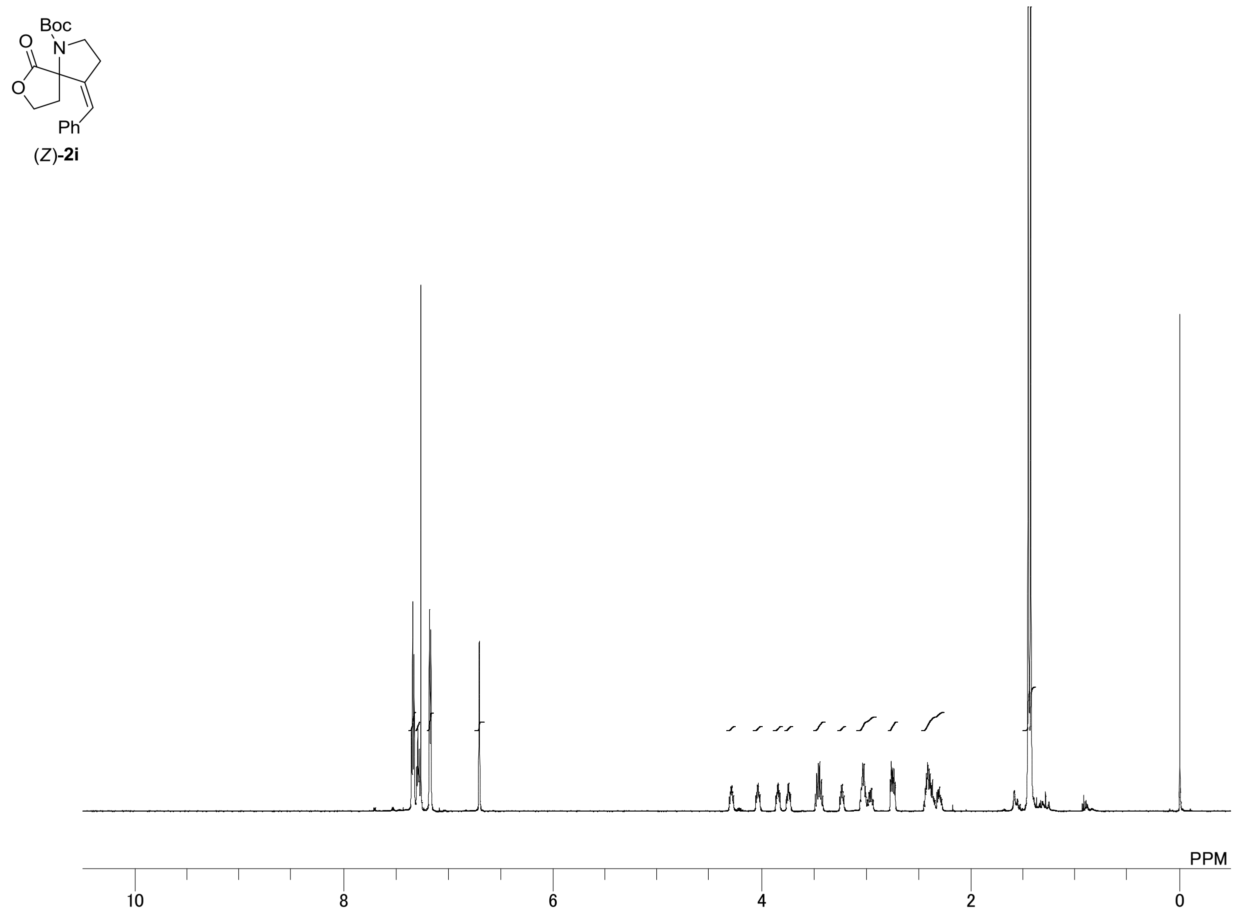
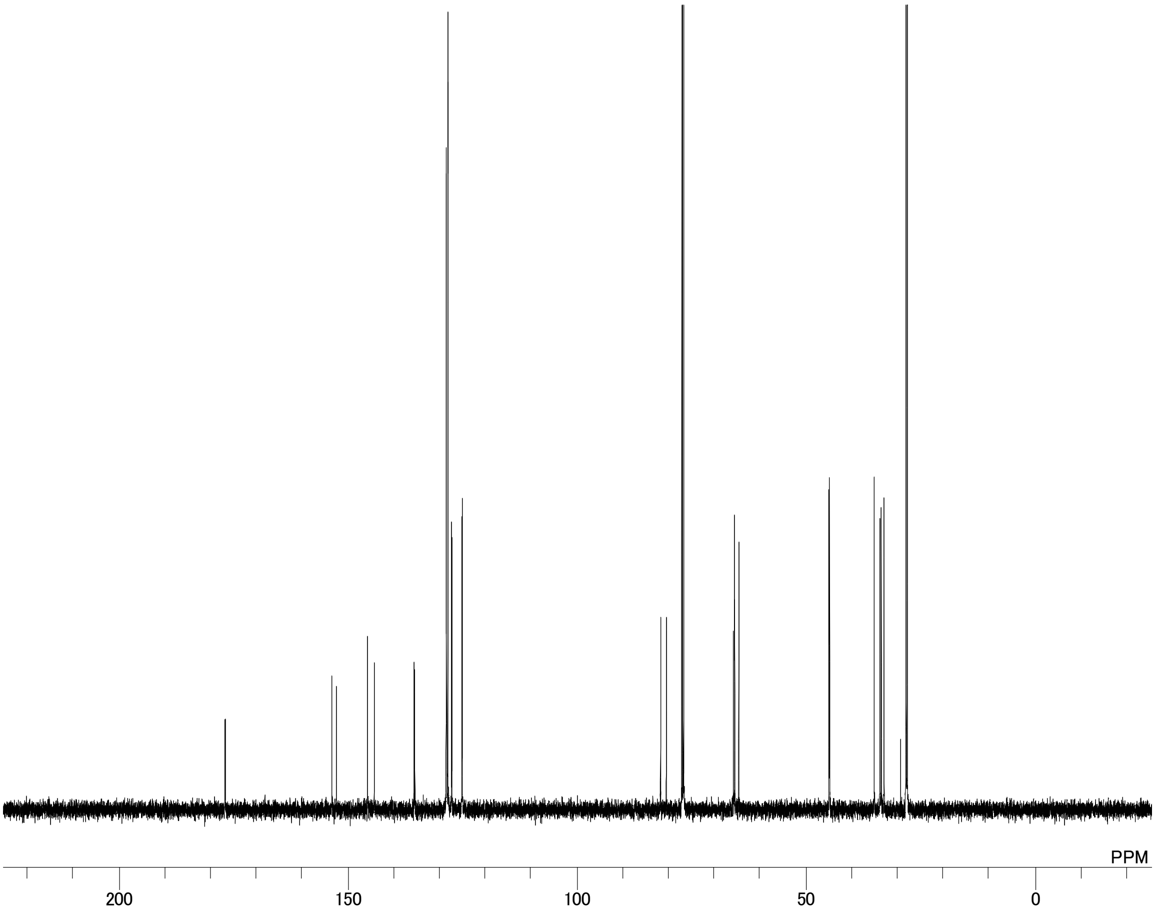


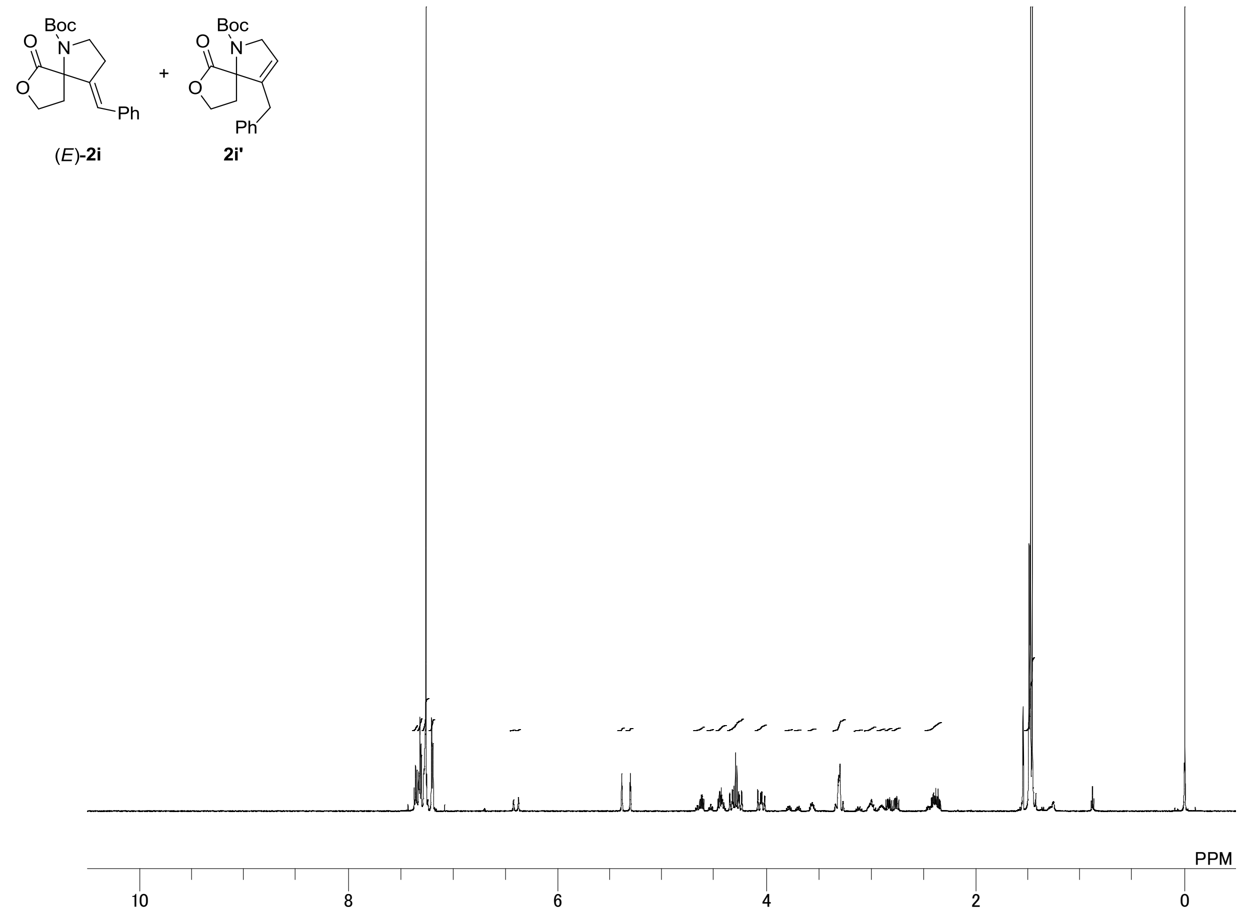


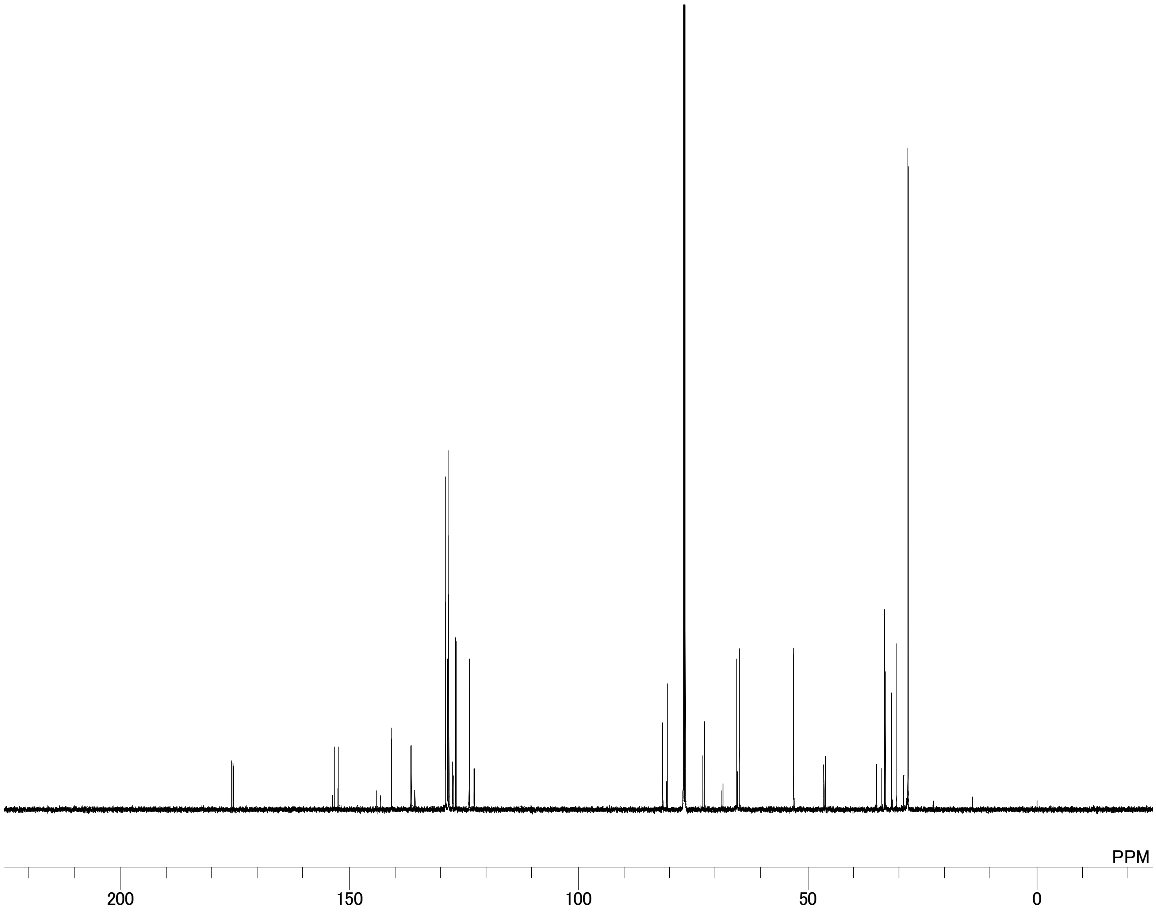


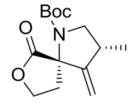
(*Z*)-**2i**



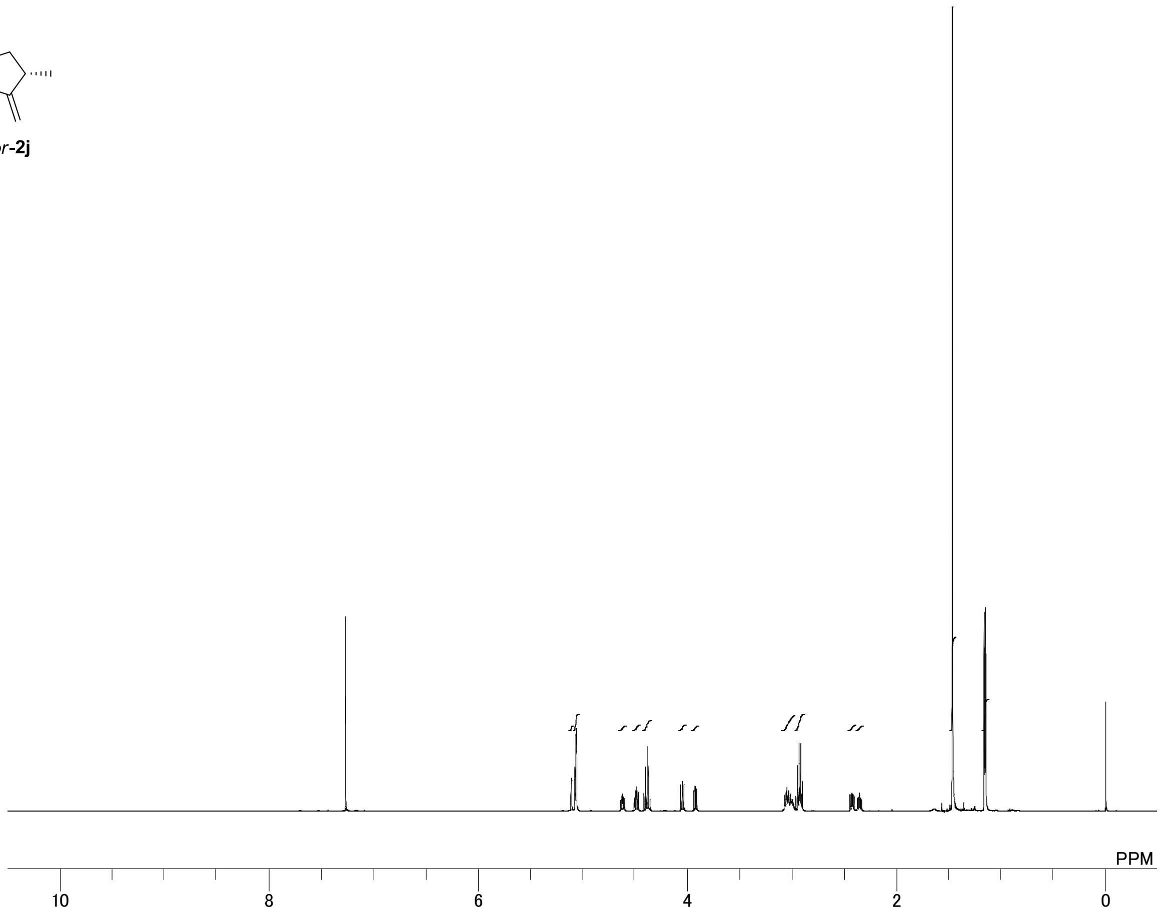
(*E*)-**2i** **2i'**

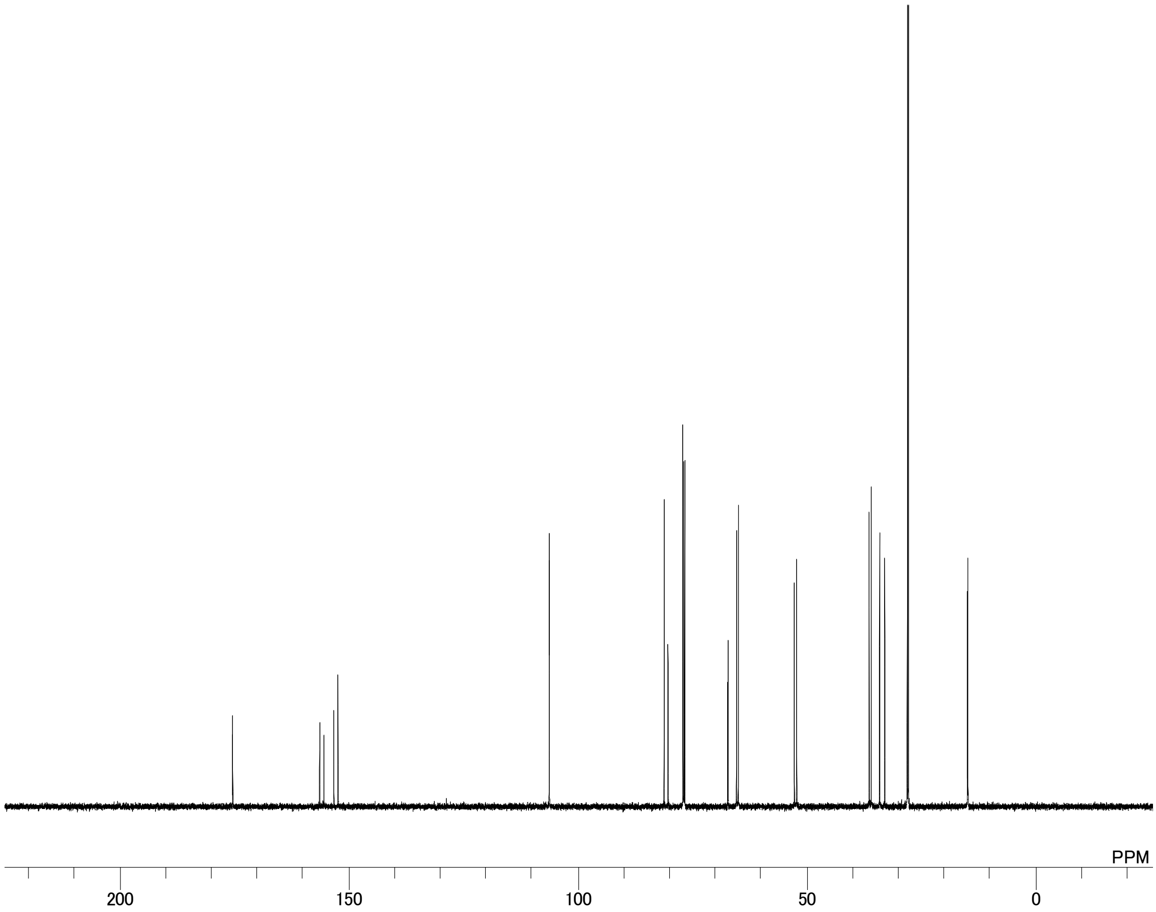


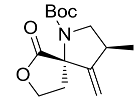




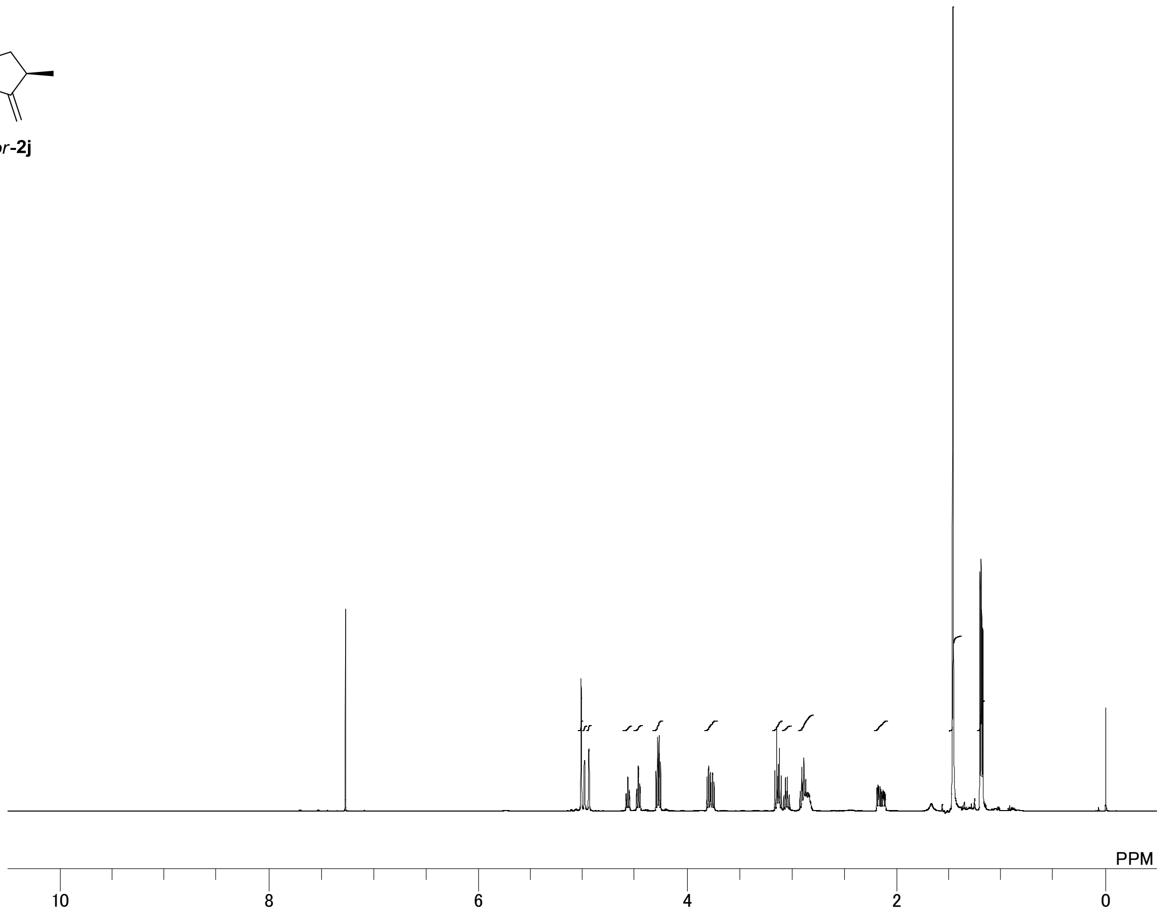
major-**2j**

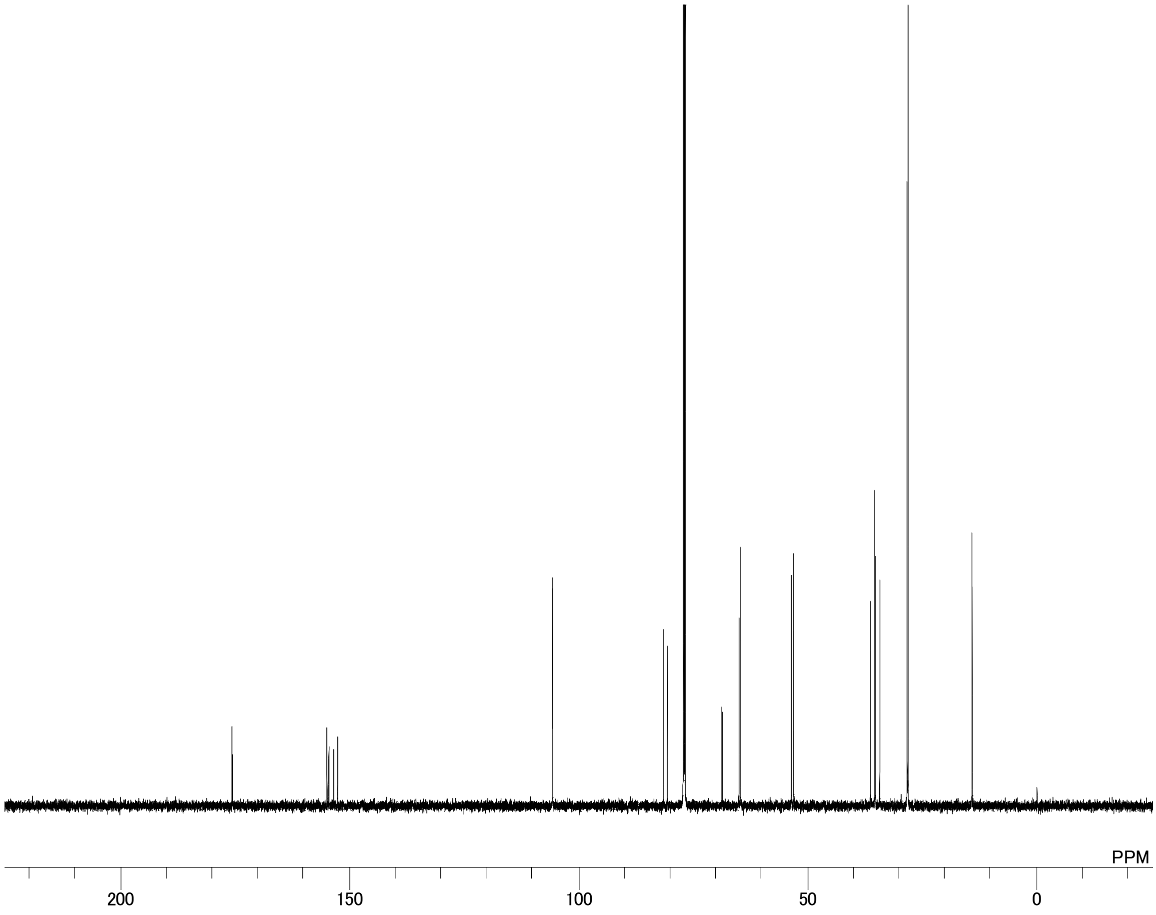


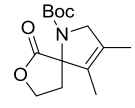




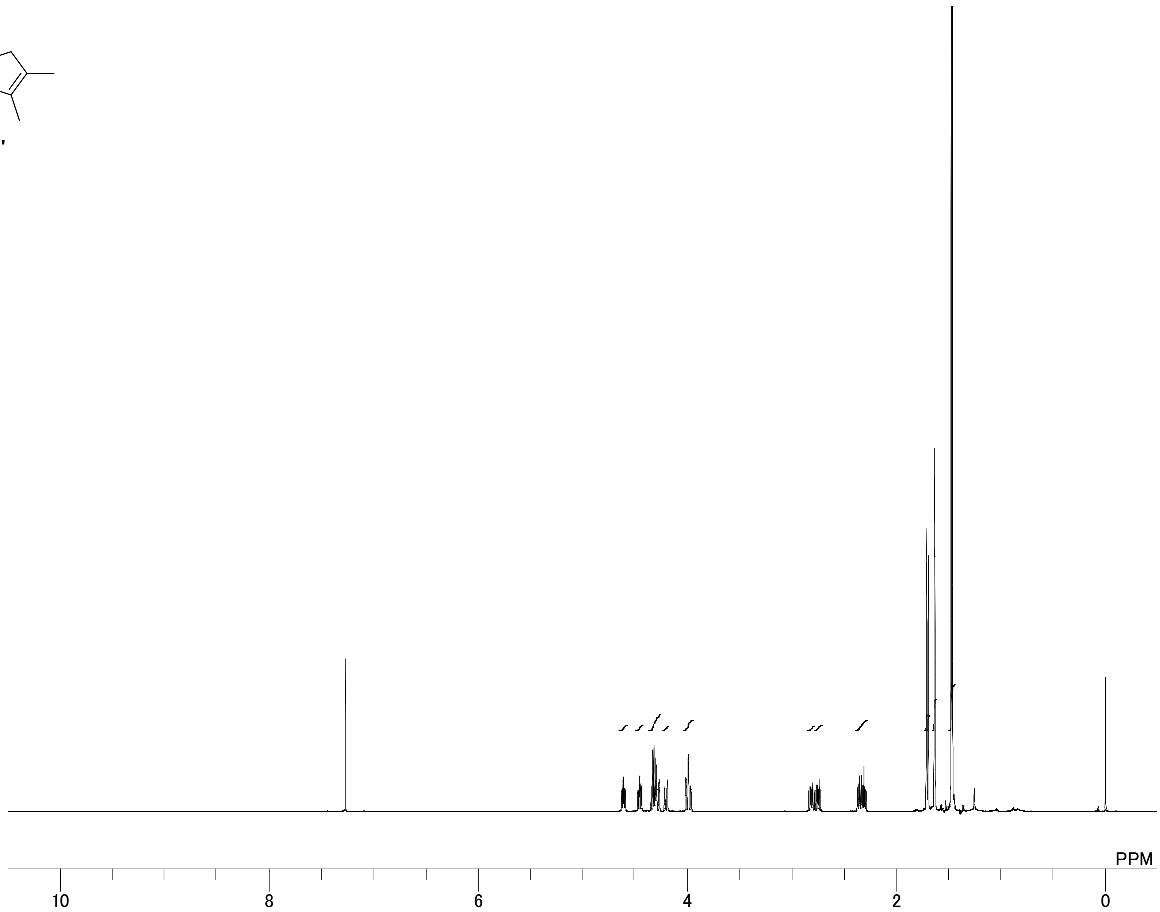
minor-**2j**

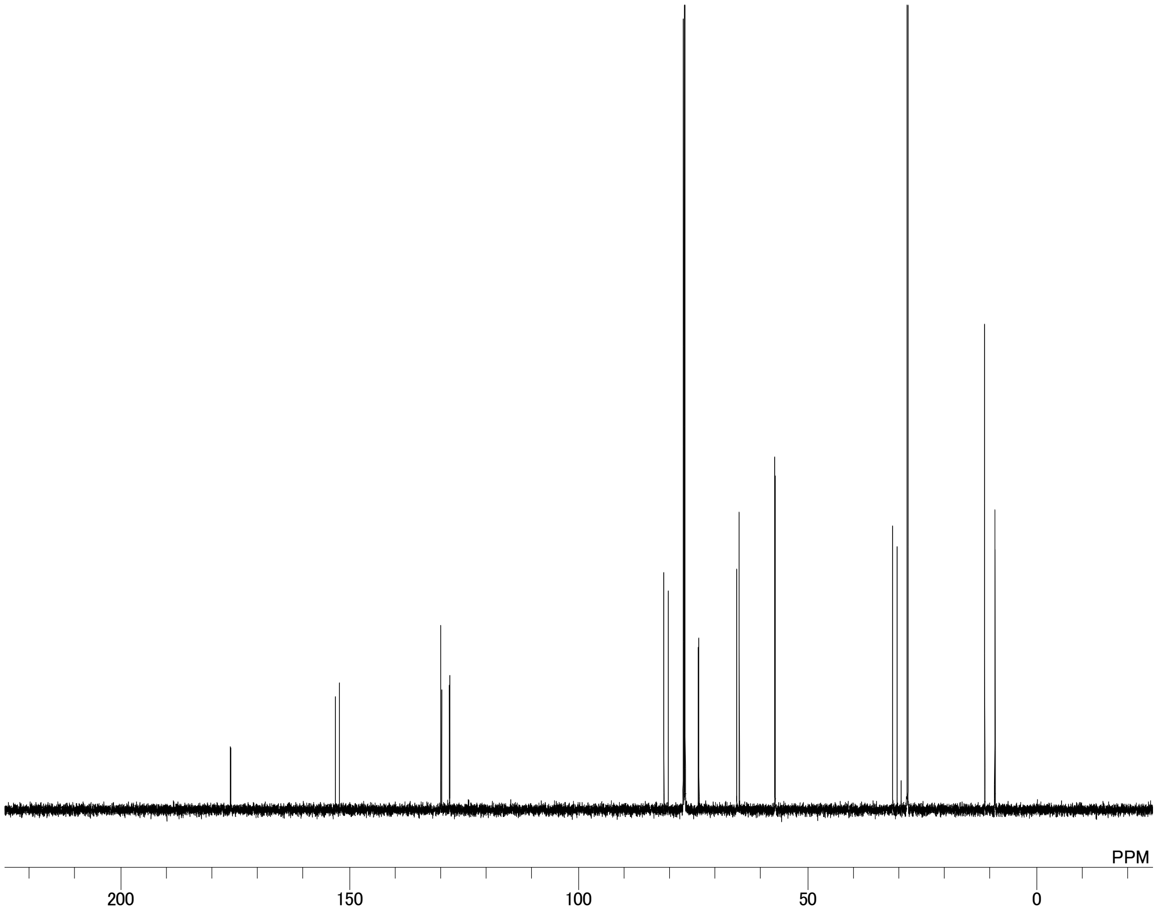


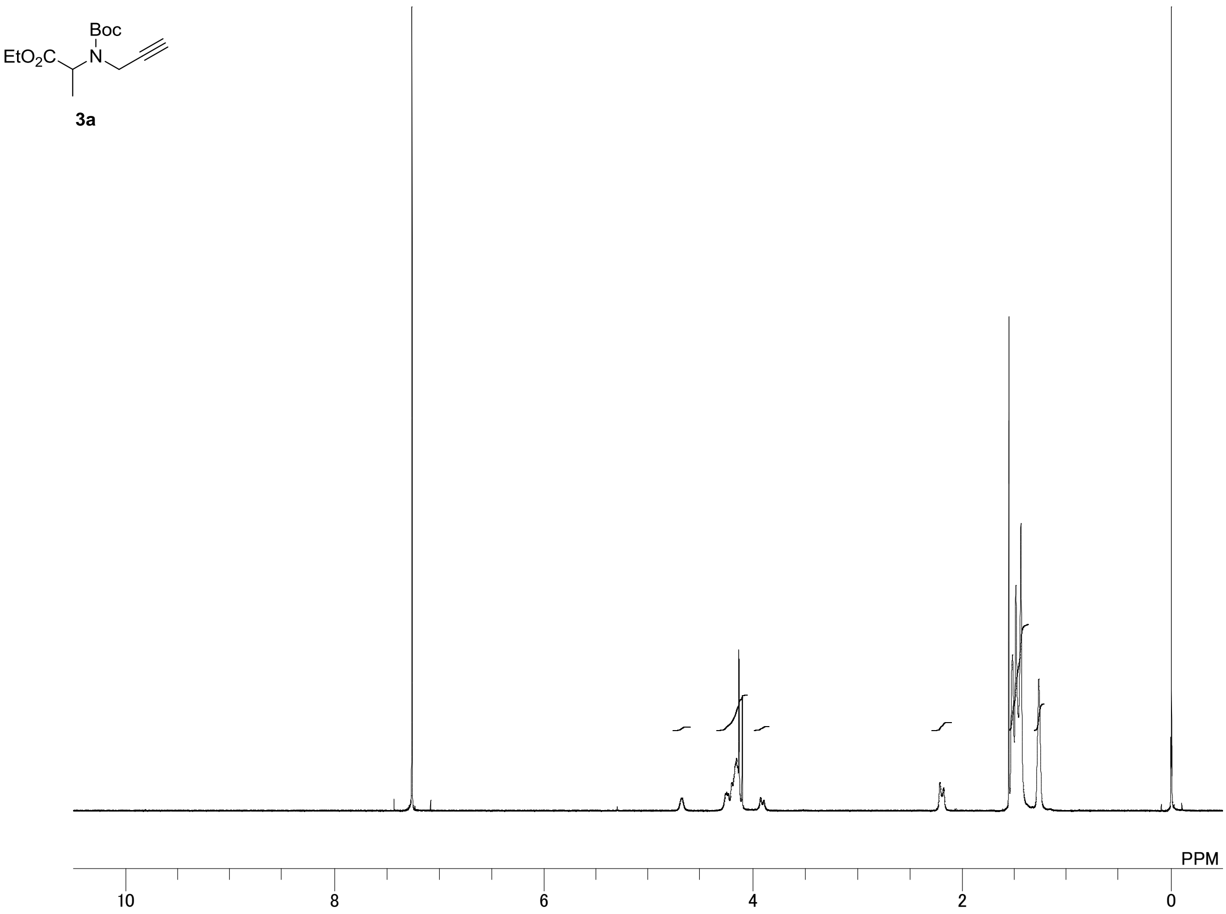




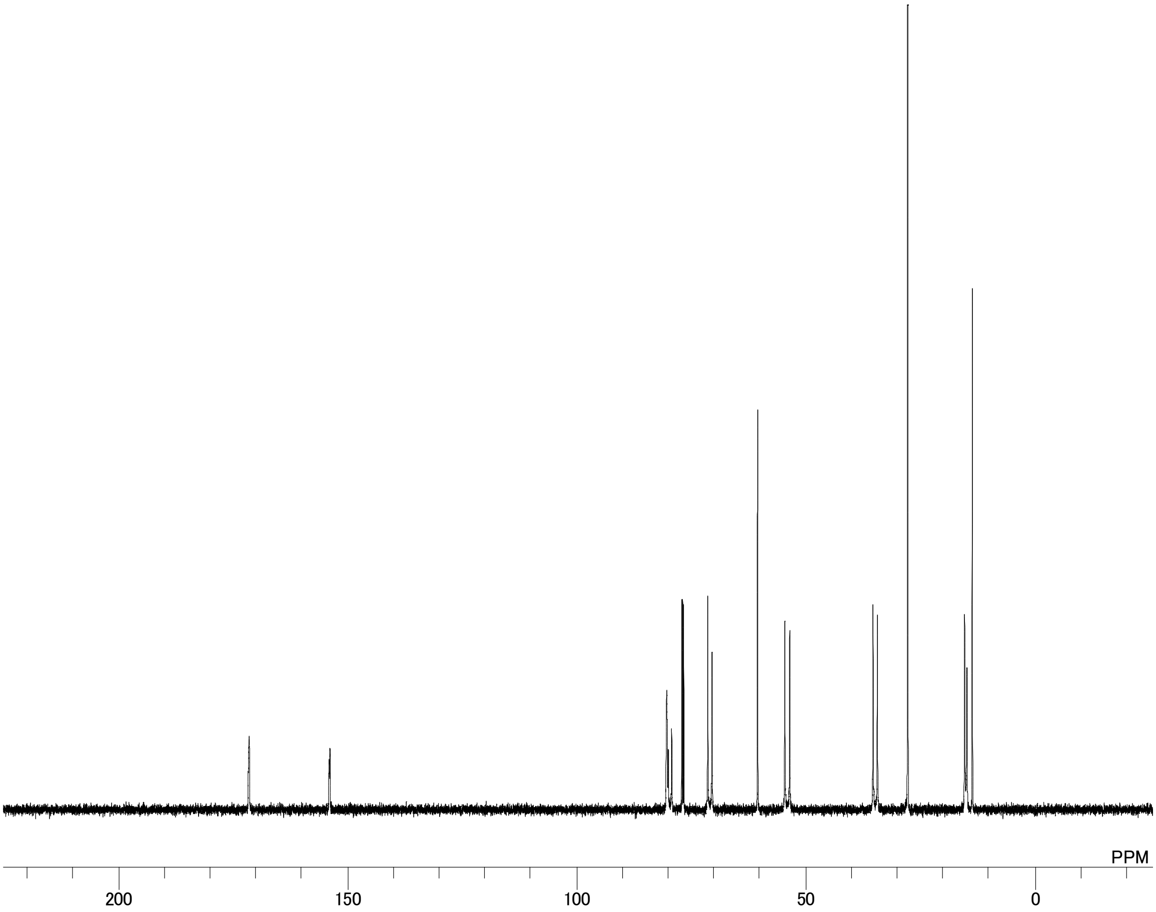
2j'

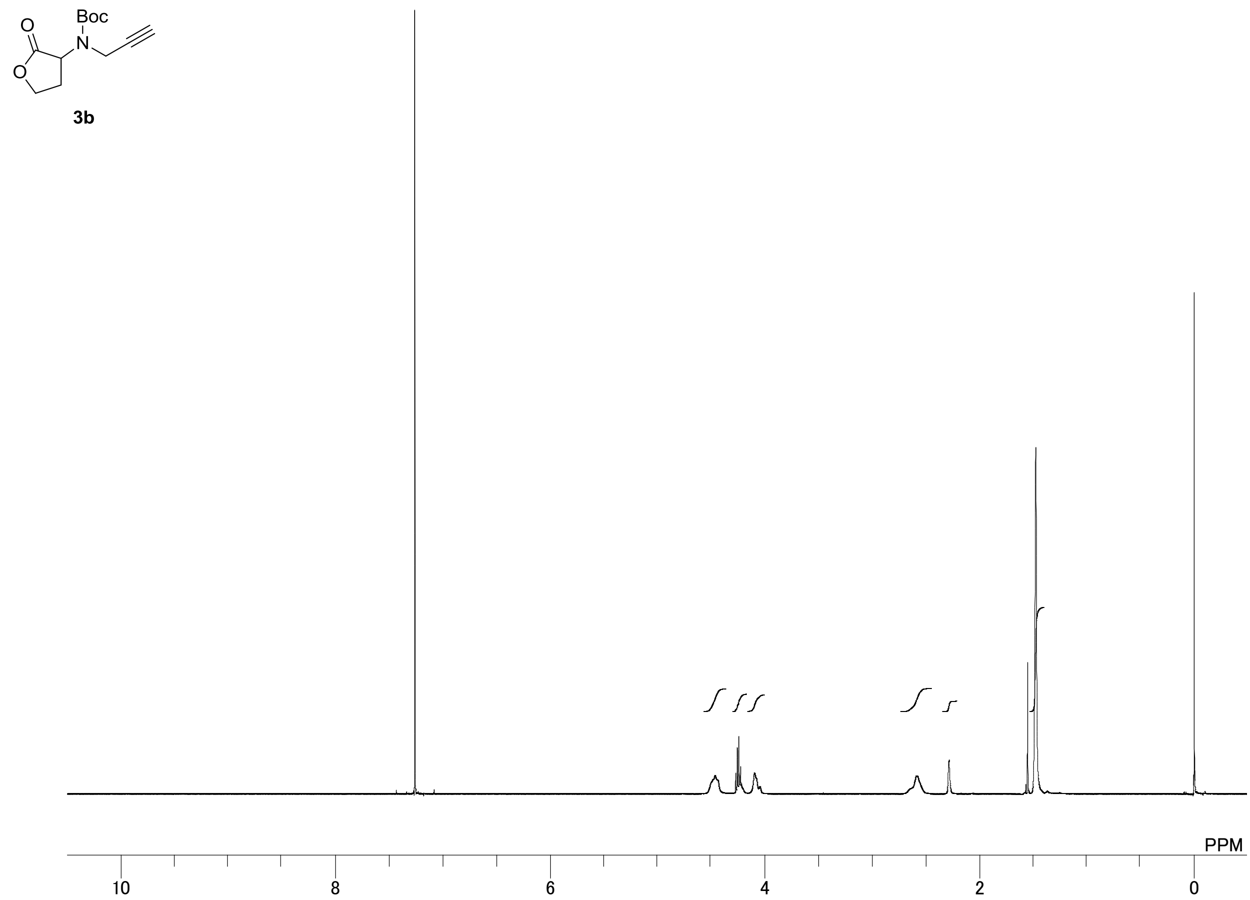






3a





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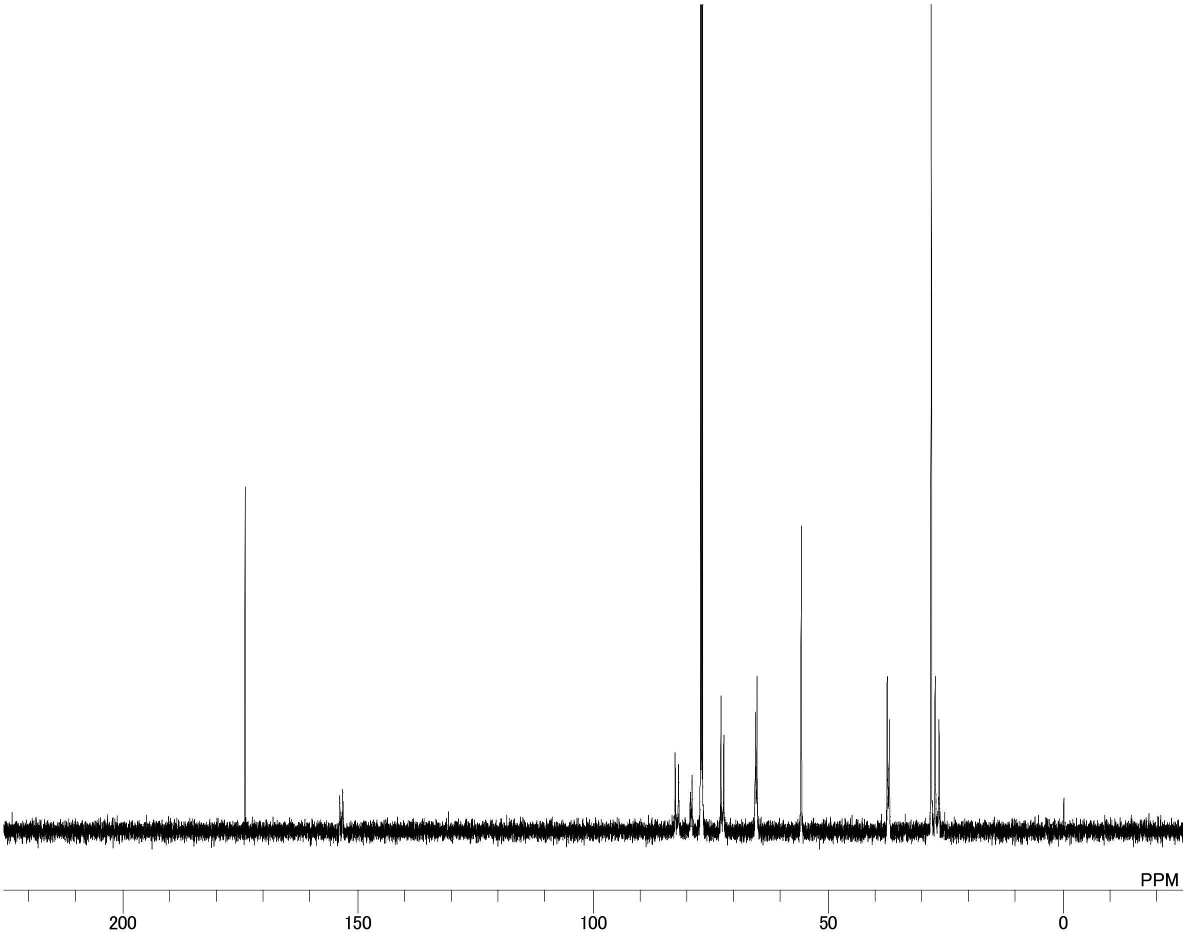

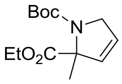

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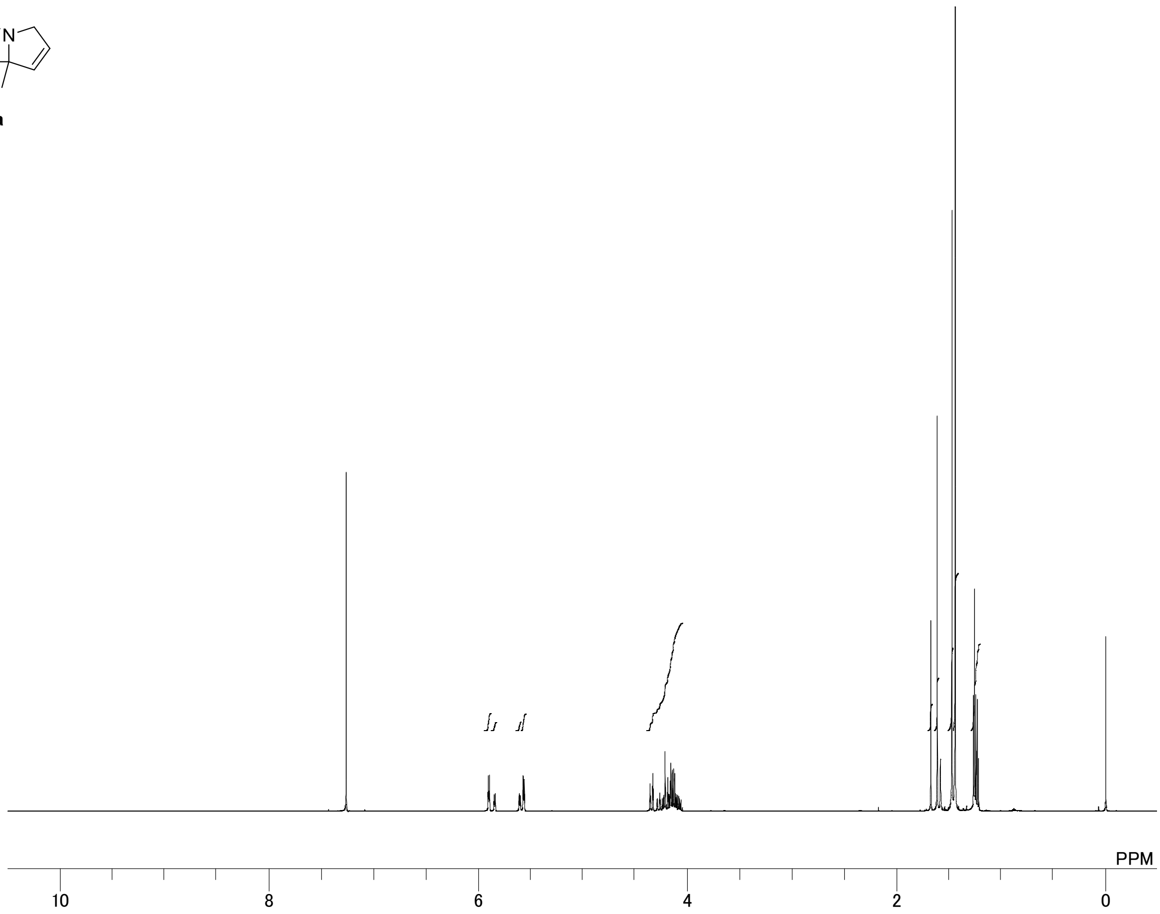

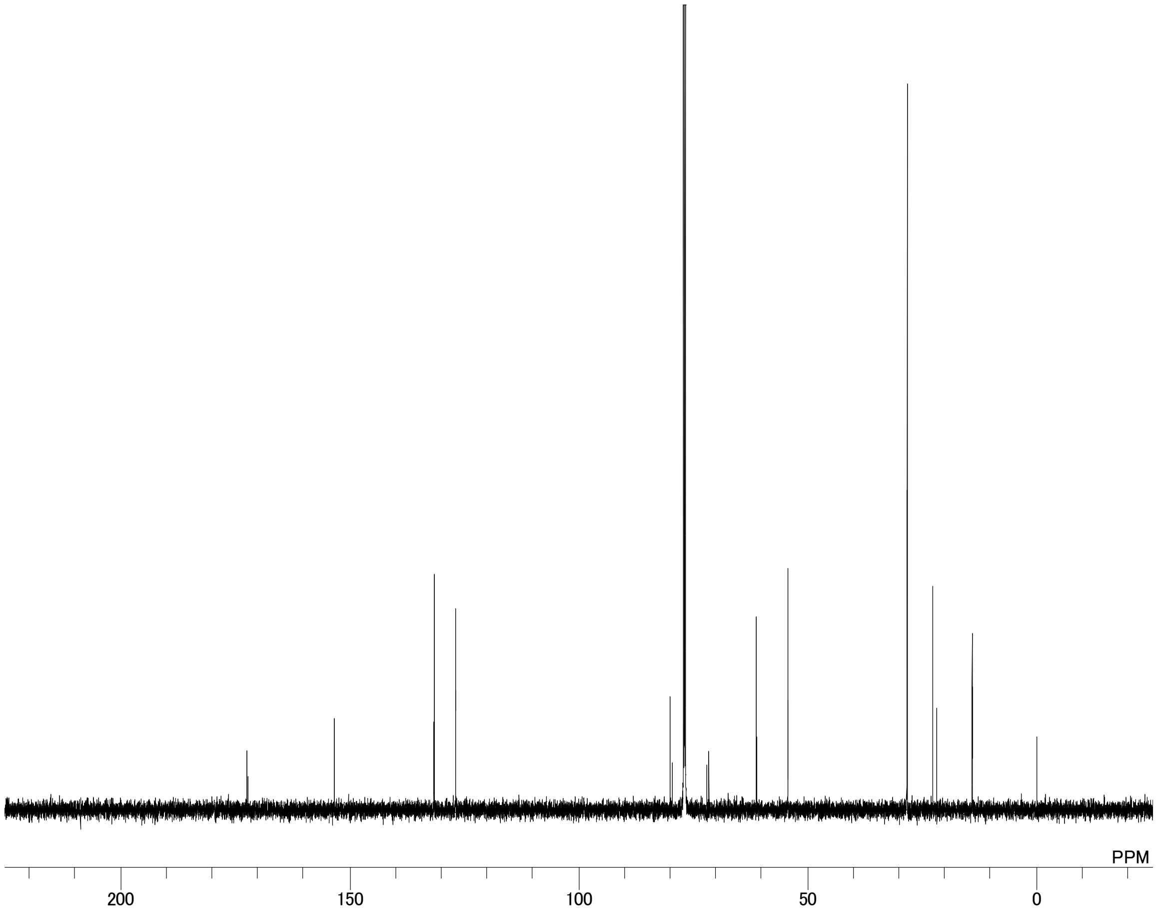

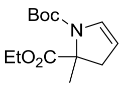

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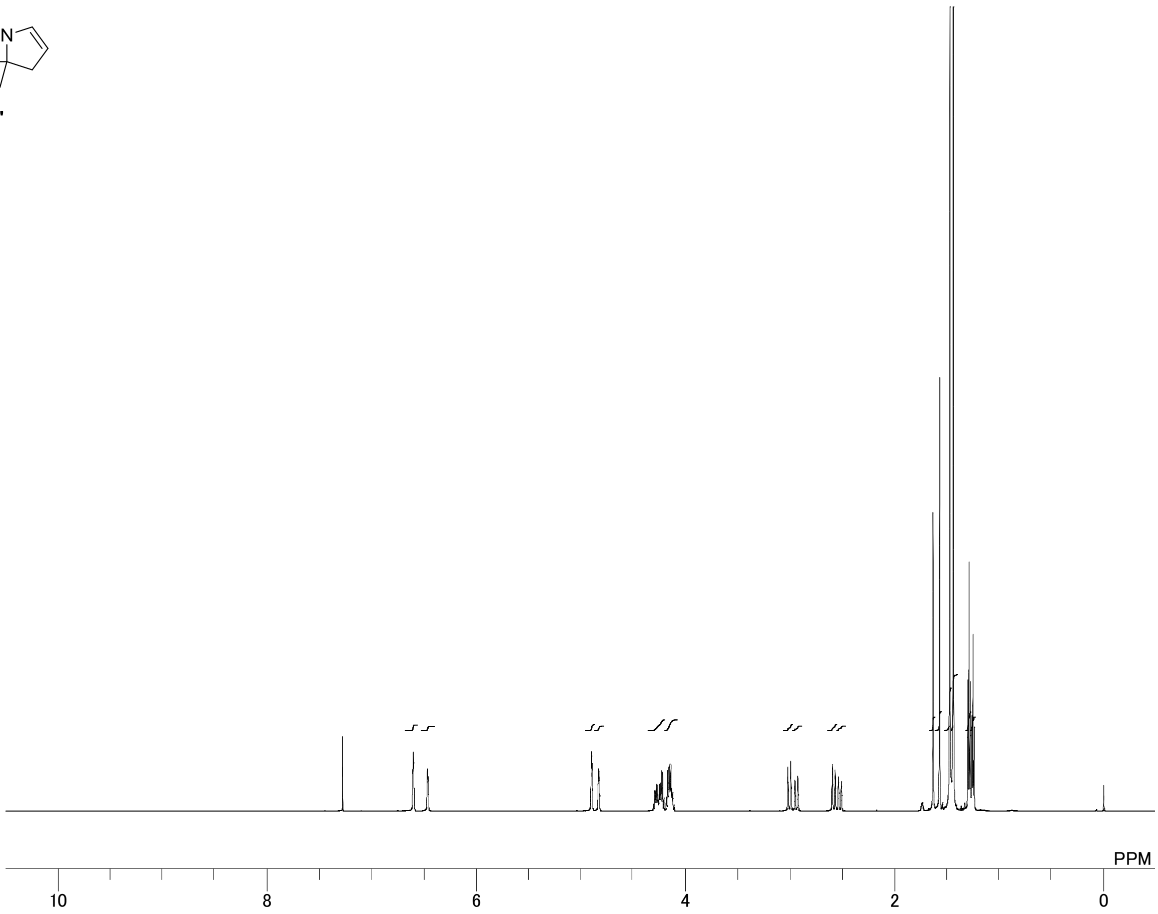

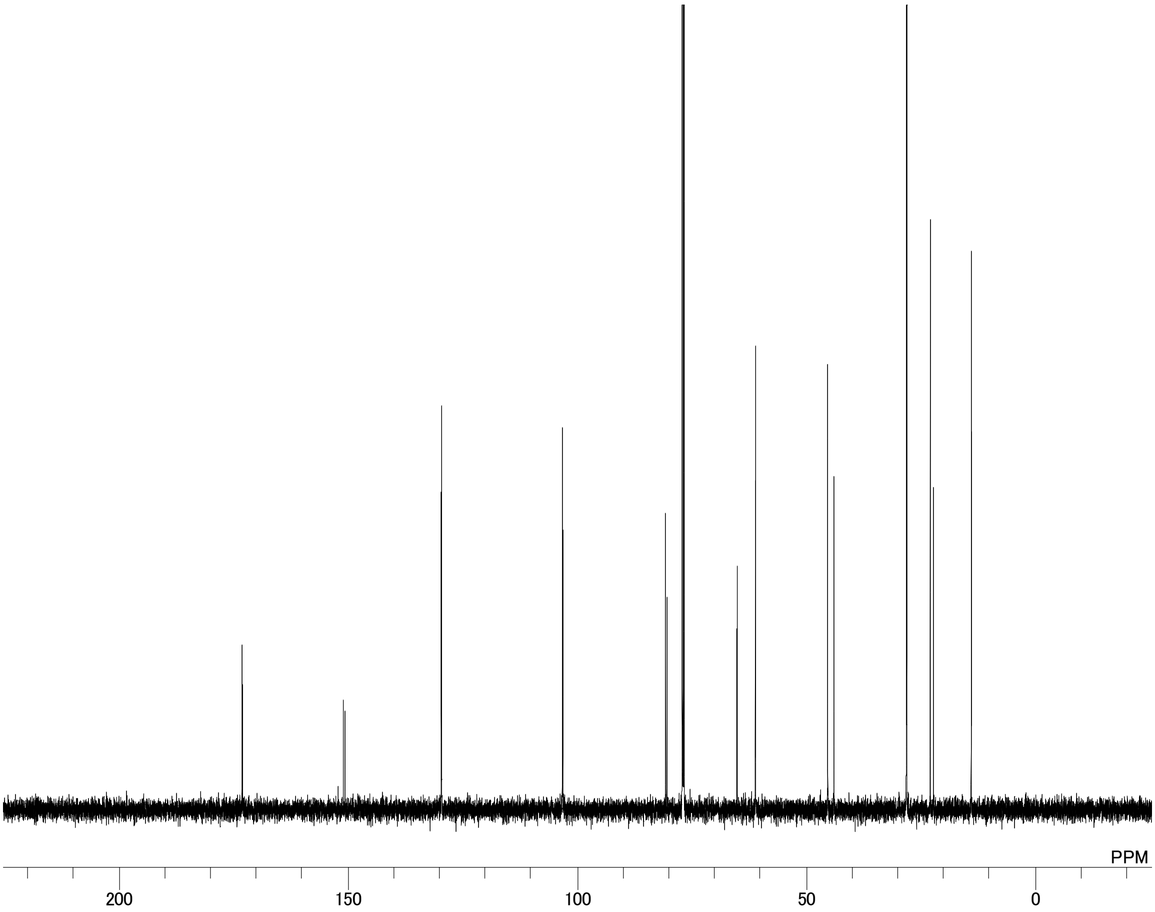

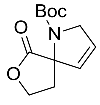

4b