γ-C (sp^3)-H bond functionalisation by nucleophilic phenylation and alkylation of α,β-unsaturated amides through an umpolung strategy

Erika Futaki,[a] *Norihiko Takeda*,*[a] *Motohiro Yasui*,[a] *Tetsuro Shinada*,[b] *Okiko Miyata*,[a,b] *Masafumi Ueda**[a]

[a]*Kobe pharmaceutical University*, *Motoyamakita*, *Higashinada*, *Kobe 658-8558*, *Japan*
[b] *Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi, Osaka, 558-8585, Japan*

E-mail: masa-u@kobepharma-u.ac.jp (MU); n-takeda@kobepharma-u.ac.jp (NT)

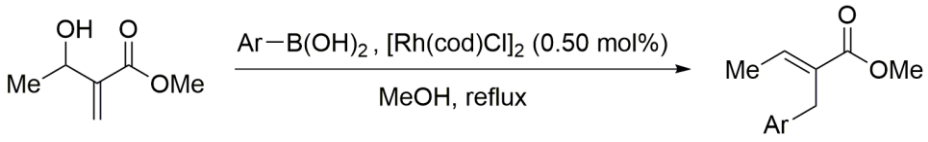
Table of contents

I. General Information

All reactions were carried out under an argon with dry solvents under anhydrous conditions, unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Flash column chromatography were performed using Silicycle silica gel (SiliaFlash® F60, 40-63 μm) or performed on Biotage Automated Liquid Chromatography System Isorera One using Biotage SNAP KP-Sil 50g silica gel cartridges. NMR spectra were recorded at 300 MHz/75 MHz (^{1}H NMR/^{13}C NMR), 500 MHz/125 MHz (^{1}H NMR/^{13}C NMR) or 600 MHz/150 MHz (^{1}H NMR/^{13}C NMR) using Varian MERCURY plus 300 (300 MHz),Varian NMR system AS 500 (500 MHz), or Bruker Avance III HD (600 MHz) spectrometers. Chemical shifts are reported in ppm with the solvent resonance or TMS as the internal standard. Multiplicities are indicated by (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets, qd = quartet of doublets, qt = quartet of triplets, qq = quartet of quartets, septd = septet of doublets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet, br = broad). Infrared (IR) spectra were recorded on a Perkin-Elmer SpectrumOne A spectrometer. The high-resolution mass spectra (HRMS) were obtained using Thermo Fischer Scientific Exactive Orbitrap mass spectrometer by ESI technique. Melting points (uncorrected) were determined on BÜCHI M-565 apparatus. Ph_3Al (1.0 M in *n*-Bu_2O), Me_3Al (2.0 M in toluene), and *i*-Bu_3Al (1.0 M in *n*-hexane) were purchased from Aldrich. Et_3Al (1.0 M in *n*-hexane) was purchased from Kanto Chemical Co., Inc. Isoxazolidine hydrochloride[1] was prepared by the reported procedure. (2*E*/*Z*)-2-(1-Methylethyl)-2-butenoic acid[2], (2*E*)-2-(2-propen-1-yl)-2-butenoic acid[3], (2*E*)-2-phenyl-2-butenoic acid[4], and (2*Z*)-2-bromo-2-butenoic acid[5] were prepared by the reported procedure.

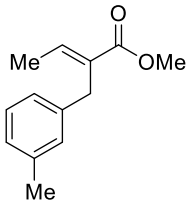
II. Experimental Section

General procedure for preparation of α,β-unsaturated carboxylic acid methyl esters[6]



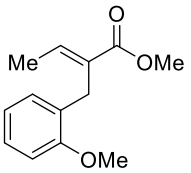
To a solution of 3-hydroxy-2-methylene-butanoic acid methyl ester (0.61 mL, 5.0 mmol) in MeOH (20 mL) were added arylboronic acid (20 mmol) and $[Rh(cod)Cl]_2$ (12.0 mg, 0.50 mol%) at room temperature. After being stirred at reflux for 16-24 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexane : EtOAc = 10 : 1) to give α,β-unsaturated carboxylic acid methyl ester **S1-S3** in the yields as described below.

(2*E*)-2-[(3-Methylphenyl)methyl]-2-butenoic acid methyl ester (S1)



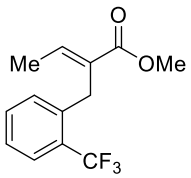
87% yield. A colorless oil; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 1717, 1650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.17-6.97 (m, 5H), 3.69 (s, 3H), 3.66 (s, 2H), 2.31 (s, 3H), 1.89 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.0, 139.4, 138.8, 137.8, 131.9, 128.9, 128.1, 126.7, 125.1, 51.6, 31.8, 21.4, 14.6; HRMS (ESI) calcd for $C_{13}H_{16}O_2Na$ [M+Na^+] 227.1043, found 227.1040.

(2*E*)-2-[(2-Methoxyphenyl)methyl]-2-butenoic acid methyl ester (S2)



88% yield. A pale yellow oil; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 1716, 1649 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.16 (br t, *J* = 7.8 Hz, 1H), 7.08-7.01 (m, 2H), 6.87-6.82 (m, 2H), 3.83 (s, 3H), 3.69 (s, 3H), 3.67 (s, 2H), 1.82 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.3, 157.2, 139.3, 131.1, 128.7, 127.5, 127.0, 120.2, 109.9, 55.2, 51.6, 26.2, 14.5; HRMS (ESI) calcd for $C_{13}H_{16}O_3Na$ [M+Na^+] 243.0992, found 243.0987.

(2*E*)-2-[[2-(Trifluoromethyl)phenyl]methyl]-2-butenoic acid methyl ester (S3)



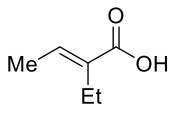
68% yield. A colorless oil; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 1717, 1650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.30-7.18 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 3.90 (s, 2H), 3.69 (s, 3H), 1.80 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.9, 141.0, 137.9, 131.8, 130.3, 128.4 (q, *J* = 29.6 Hz), 128.2, 126.0, 125.9 (q, *J* = 5.9 Hz), 124.6 (q, *J* = 272.1 Hz), 51.8, 28.1, 14.5; HRMS (ESI) calcd for $C_{13}H_{13}O_2F_3Na$ [M+Na^+] 281.0760, found 281.0758.

General procedure for preparation of α,β-unsaturated carboxylic acids

To a solution of α,β-unsaturated ester (1.0 equiv) in EtOH/H_2O (v/v = 4:3, 0.14 M) was added LiOH·H_2O (3.0 equiv) at room temperature. After being stirred at 100 °C for12-24 h, this reaction mixture was diluted with $CHCl_3$ and water. The water layer was washed with $CHCl_3$. Subsequently, the water layer was acidified with an 1 M HCl until pH = 1 and the resulting suspension was extracted

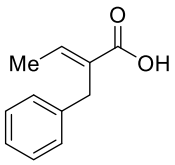
with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexane : EtOAc = 1 : 2) to give α,β-unsaturated carboxylic acid **S4-S17** in the yields as described below.

(2*E*/*Z*)-2-Ethyl-2-butenoic acid (S4)



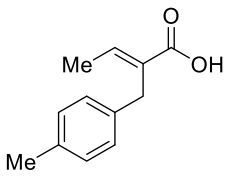
99% yield. A pale yellow oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 4/1; IR (neat) ν_{max} 2972, 1687, 1642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 6.98 (q, *J* = 7.2 Hz, 4/5 H), 6.17 (br q, *J* = 7.2 Hz, 1/5 H), 2.37-2.25 (m, 2H), 2.04 (br d, *J* = 7.5 Hz, 3/5 H), 1.84 (d, *J* = 7.2 Hz, 12/5 H), 1.06 (t, *J* = 7.5 Hz, 3/5 H), 1.03 (t, *J* = 7.5 Hz, 12/5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.0 (*Z*), 173.5, 139.6, 139.0 (*Z*), 134.3, 133.6 (*Z*), 27.3 (*Z*), 19.3, 16.0 (*Z*), 14.2, 13.7 (*Z*), 13.4; HRMS (ESI) calcd for $C_6H_9O_2$ [M-H^+] 113.0608, found 113.0598.

(2*E*)-2-(Phenylmethyl)-2-butenoic acid (S5)



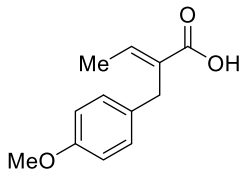
94% yield. White solid; Mp: 100-101 ℃; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 3012, 1691, 1642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.29-7.15 (m, 6H), 3.69 (s, 2H), 1.92 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.4, 141.8, 139.3, 131.4, 128.3, 128.1, 126.0, 31.5, 14.9; HRMS (ESI) calcd for $C_{11}H_{12}O_2Na$ [M+Na^+] 199.0730, found 199.0726.

(2*E*)-2-[(4-Methylphenyl)methyl]-2-butenoic acid (S6)



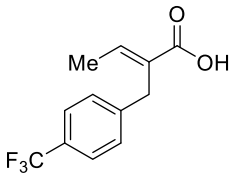
99% yield. White solid; Mp: 110-111 ℃; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 3011, 1690, 1642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.16 (q, *J* = 6.9 Hz, 1H), 7.07 (m, 4H), 3.64 (s, 2H), 2.30 (s, 3H), 1.91 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.9, 141.4, 136.2, 135.5, 131.6, 129.1, 128.1, 31.1, 21.0, 14.9; HRMS (ESI) calcd for $C_{12}H_{14}O_2Na$ [M+Na^+] 213.0886, found 213.0887.

(2*E*)-2-[(4-Methoxyphenyl)methyl]-2-butenoic acid (S7)



77% yield. White solid; Mp: 111-112 ℃; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 3012, 1688, 1642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.18-7.08 (m, 3H), 6.80 (br d, *J* = 8.7 Hz, 2H), 3.77 (s, 3H), 3.62 (s, 2H), 1.92 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.2, 157.8, 141.3, 131.8, 131.4, 129.1, 113.7, 55.1, 30.6, 14.8; HRMS (ESI) calcd for $C_{12}H_{14}O_3Na$ [M+Na^+] 229.0835, found 229.0836.

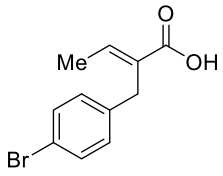
(2*E*)-2-[[4-(Trifluoromethyl)phenyl]methyl]-2-butenoic acid (S8)



84% yield. White solid; Mp: 69-70 ℃; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 2944, 1687, 1643 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.1 Hz, 2H), 7.31-7.20 (m, 3H), 3.73 (s, 2H), 1.92 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 172.4, 143.4, 142.5, 130.6, 128.47, 128.51 (q, *J* = 32.0 Hz), 125.3 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 270.2 Hz), 31.5, 15.0; HRMS (ESI) calcd for

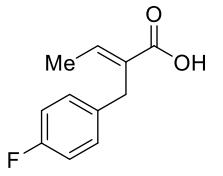
$C_{12}H_{10}O_2F_3$ [M-H$^+$] 243.0638, found 243.0638.

(2*E*)-2-[(4-Bromophenyl)methyl]-2-butenoic acid (S9)



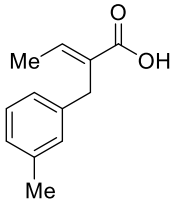
84% yield. White solid; Mp: 131-132 ℃; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 3014, 1687, 1643 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 8.4 Hz, 2H), 7.18 (q, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 3.63 (s, 2H), 1.91 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.0, 142.1, 138.3, 131.4, 131.0, 129.9, 119.8, 31.0, 15.0; HRMS (ESI) calcd for $C_{11}H_{10}O_2{}^{79}Br$ [M-H$^+$] 252.9870, found 252.9872.

(2*E*)-2-[(4-Fluoropheny)methyl]-2-butenoic acid (S10)



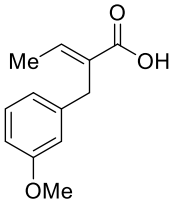
92% yield. White solid; Mp: 93-94 ℃; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 16/1; IR ($CHCl_3$) ν_{max} 2940, 1691, 1642 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.21-7.11 (m, 3H), 6.98-6.90 (m, 2H), 3.64 (s, 32/17H), 3.55 (s, 2/17H), 2.07 (d, *J* = 7.2 Hz, 3/17 H), 1.92 (d, *J* = 7.2 Hz, 48/17 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 172.6, 161.4 (d, *J* = 240.0 Hz), 142.3 (*Z*), 141.8, 134.9, 131.4, 131.2 (*Z*), 130.4 (*Z*) (d, *J* = 7.8 Hz), 129.6 (d, *J* = 7.8 Hz), 115.1 (d, *J* = 21 Hz), 39.2 (*Z*), 30.8, 16.1 (*Z*), 14.9; HRMS (ESI) calcd for $C_{11}H_{10}O_2F$ [M-H$^+$] 193.0670, found 193.0665.

(2*E*)-2-[(3-Methylphenyl)methyl]-2-butenoic acid (S11)



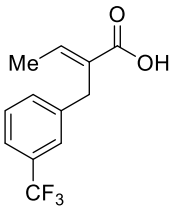
79% yield. White solid; Mp: 115-116 ℃; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 3012, 1687, 1642 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.22-7.12 (m, 2H), 6.99-6.98 (m, 3H), 3.65 (s, 2H), 2.31 (s, 3H), 1.91 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.3, 141.7, 139.2, 137.9, 131.4, 128.9, 128.2, 126.8, 125.1, 31.4, 21.4, 14.9; HRMS (ESI) calcd for $C_{12}H_{14}O_2Na$ [M+Na$^+$] 213.0886, found 213.0886.

(2*E*)-2-[(3-Methoxyphenyl)methyl]-2-butenoic acid (S12)



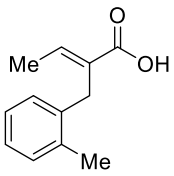
99% yield. White solid; Mp: 92-93 ℃; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 3011, 1687, 1642 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.22-7.15 (m, 2H), 6.79-6.70 (m, 3H), 3.77 (s, 3H), 3.66 (s, 2H), 1.91 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.1, 159.6, 141.9, 140.9, 131.2, 129.3, 120.5, 114.1, 111.2, 55.1, 31.5, 14.9; HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{14}O_3Na$ [M+Na$^+$] 229.0835, found 229.0835.

(2*E*)-2-[[3-(Trifluoromethyl)phenyl]methyl]-2-butenoic acid (S13)



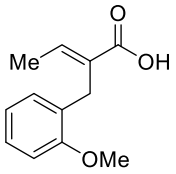
98% yield. White solid; Mp: 106-107 ℃; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 17/1; IR ($CHCl_3$) ν_{max} 3032, 1688, 1644 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46-7.36 (m, 3H), 7.27-7.20 (m, 2H), 3.74 (s, 34/18H), 3.64 (s, 2/18H), 2.10 (d, *J* = 7.5 Hz, 3/18H), 1.94 (d, *J* = 7.2 Hz, 51/18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 172.6, 142.5, 140.3, 131.6, 130.8 (q, *J* = 31.8 Hz), 130.6, 128.8, 124.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 270.3 Hz), 123.0 (q, *J* = 4.0 Hz), 31.4, 15.0; HRMS (ESI) calcd for $C_{12}H_{10}O_2F_3$ [M-H$^+$] 243.0638, found 243.0637.

(2*E*)-2-[(2-Methylphenyl)methyl]-2-butenoic acid (S14)



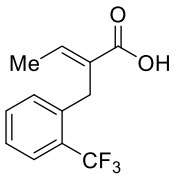
94% yield. White solid; Mp: 119-120 °C; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 3012, 1688, 1643 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.30-7.25 (m, 1H), 7.17-7.08 (m, 3H), 6.97-6.94 (m, 1H), 3.62 (s, 2H), 2.35 (s, 3H), 1.84 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.9, 142.3, 136.9, 136.2, 130.7, 130.3, 126.6, 126.0, 125.9, 28.7, 19.8, 14.9; HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{13}O_2$ [M-H^+] 189.0921, found 189.0918.

(2*E*)-2-[(2-Methoxyphenyl)methyl]-2-butenoic acid (S15)



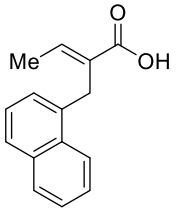
94% yield. White solid; Mp: 118-121 °C; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 3011, 1691, 1642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.22-7.14 (m, 2H), 7.08 (br d, *J* = 7.2 Hz, 1H), 6.87-6.82 (m, 2H), 3.82 (s, 3H), 3.65 (s, 2H), 1.85 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.6, 157.2, 142.0, 130.7, 128.7, 127.2, 127.1, 120.3, 109.9, 55.1, 25.8, 14.7; HRMS (ESI) calcd for $C_{12}H_{14}O_3Na$ [M+Na^+] 229.0835, found 229.0832.

(2*E*)-2-[[2-(Trifluoromethyl)phenyl]methyl]-2-butenoic acid (S16)



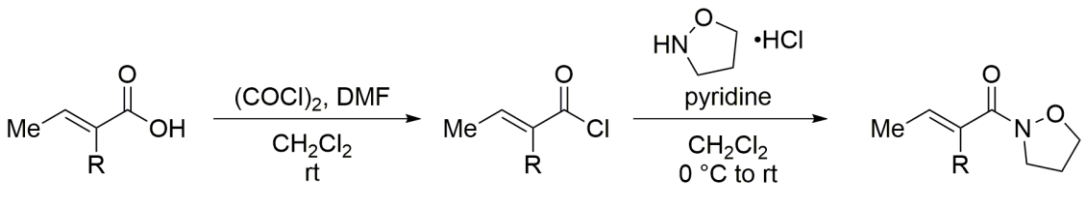
86% yield. White solid; Mp: 100-101 °C; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 2990, 1691, 1645 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.8 Hz, 1H), 7.44-7.26 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 3.90 (s, 2H), 1.80 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 172.8, 143.9, 137.6, 131.9, 129.8, 128.5 (q, *J* = 29.6 Hz), 128.1, 126.1, 126.0 (q, *J* = 6.2 Hz), 124.6 (q, *J* = 272.3 Hz), 27.7, 14.8; HRMS (ESI) calcd for $C_{12}H_{10}O_2F_3$ [M-H^+] 243.0638, found 243.0638.

(2*E*)-2-[(1-Naphthalenyl)methyl]-2-butenoic acid (S17)



93% yield. White solid; Mp: 140-141 °C; *E*/*Z* = >20/1; IR ($CHCl_3$) ν_{max} 3012, 1687, 1643 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.11 (br d, *J* = 8.1 Hz, 1H), 7.86 (br d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.56-7.47 (m, 2H), 7.41-7.33 (m, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 4.13 (s, 2H), 1.83 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.4, 143.2, 134.2, 133.7, 131.9, 130.3, 128.7, 126.7, 125.9, 125.50, 125.46, 123.6, 123.2, 28.2, 14.9; HRMS (ESI) calcd for $C_{15}H_{13}O_2$ [M-H^+] 225.0921, found 225.0918.

General procedure for preparation of α,β-unsaturated *N*-alkoxyamides 3a-3s

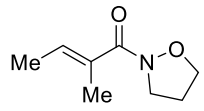


3a-3s

To a solution of α,β-unsaturated carboxylic acid (2.0 mmol) in CH_2Cl_2 (0.70 mL) were added oxalyl chloride (0.2 mL, 2.4 mmol) and a few drops of DMF under an argon atmosphere at room temperature. After being stirred for 2 h at the same temperature, the solvent and excess of oxalyl chloride were removed under reduced pressure to give crude product (acyl chloride) which was used without further purification.

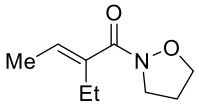
Subsequently, to the solution of the acyl chloride in CH_2Cl_2 (4.3 mL) were added isoxazolidine hydrochloride[1] (0.22 g, 2.0 mmol) and pyridine (0.34 mL, 4.2 mmol) at 0 °C. After being stirred for 16-24 h at room temperature, the reaction mixture was diluted with EtOAc. The mixture was washed with 1 M HCl, saturated $NaHCO_3$, and saturated NaCl. The organic phase was dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-hexane : EtOAc = 1 : 1) to afford α,β-unsaturated *N*-alkoxyamide **3a-3s** in the yields as described below.

(2*E*)-1-(2-Isoxazolidinyl)-2-methyl-2-buten-1-one (3a)



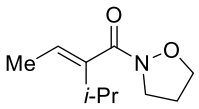
49% yield. A pale yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1659, 1623 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 6.17 (qq, *J* = 6.9, 1.5 Hz, 1H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.76-3.71 (m, 2H), 2.28 (br quint, *J* = 6.9 Hz, 2H), 1.87 (br s, 3H), 1.75 (dq, *J* = 6.9, 1.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171,8, 131.1, 130.9, 68.8, 44.7, 27.3, 13.6, 13.5; HRMS (ESI) calcd for $C_8H_{13}O_2NNa$ [M+Na^+] 178.0839, found 178.0840.

(2*E*)-2-Ethyl-1-(2-isoxazolidinyl)-2-buten-1-one (3b)



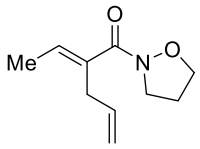
64% yield. A yellow oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 10/1; IR (neat) ν_{max} 1660, 1630 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 6.04 (qt, *J* = 6.9, 0.9 Hz, 10/11H), 5.55 (qt, *J* = 6.9,1.5 Hz, 1/11H), 3.94 (t, *J* = 6.9 Hz, 2H), 3.78-3.74 (m, 2H), 2.38 (br q, *J* = 7.5 Hz, 2H), 2.28 (br quint, *J* = 6.9 Hz, 2H), 1.76 (dt, *J* = 6.9, 0.6 Hz, 30/11H), 1.69 (dt, *J* = 6.9, 1.5 Hz, 3/11H), 1.09-0.98 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.0, 137.7 (*Z*), 137.5, 129.8, 68.8, 44.7, 27.2, 27.0 (*Z*), 20.6, 14.7 (*Z*), 13.2, 12.8, 12.1 (*Z*); HRMS (ESI) calcd for $C_9H_{15}O_2NNa$ [M+Na^+] 192.0995, found 192.0994.

(2*E*/*Z*)-1-(2-Isoxazolidinyl)-2-(1-methylethyl)-2-buten-1-one (3c)



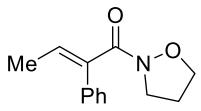
56% yield. A pale yellow oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 9/1; IR (neat) ν_{max} 1661, 1634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.72 (qd, *J* = 7.2, 0.9 Hz, 9/10H), 5.52 (qd, *J* = 6.9, 1.5 Hz, 1/10H), 3.95 (t, *J* = 7.2 Hz, 2H), 3.77-3.72 (m, 2H), 2.87 (septd, *J* = 6.9, 0.9 Hz, 9/10H), 2.60 (sept, *J* = 6.9 Hz, 1/10H), 2.40-2.24 (m, 2H), 1.75 (d, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 54/10H), 1.07 (d, *J* = 6.9 Hz, 6/10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 178.3 (Z), 170.71, 142.3 (*Z*), 141.3, 126.8, 68.8, 44.5, 43.0 (*Z*), 27.7, 27.4, 21.1 (*Z*), 21.0, 14.8 (*Z*), 13.8 (*Z*), 13.0; HRMS (ESI) calcd for $C_{10}H_{17}O_2NNa$ [M+Na^+] 206.1152, found 206.1150.

(2*E*)-1-(2-Isoxazolidinyl)-2-(2-propen-1-yl)-4-butene-1-one (3d)



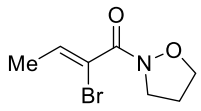
36% yield. A yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1661, 1635 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 6.23 (qt, *J* = 7.2, 0.9 Hz, 1H), 5.80 (ddt, *J* = 17.1, 9.9, 6.3 Hz, 1H), 5.11-4.98 (m, 2H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.78-3.73 (m, 2H), 3.13 (br d, *J* = 6.3 Hz, 2H), 2.26 (br quint, *J* = 6.9 Hz, 2H), 1.78 (dt, *J* = 7.2, 0.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.9, 135.0, 133.5, 132.5, 115.5, 69.1, 44.7, 31.8, 27.4, 13.7; HRMS (ESI) calcd for $C_{10}H_{15}O_2NNa$ [M+Na^+] 204.0995, found 204.0997.

(2*E*)-1-(2-Isoxazolidinyl)-2-phenyl-2-buten-1-one (3e)



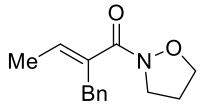
99% yield. White solid; *E*/*Z* = >20/1; Mp 57-58 °C; IR ($CHCl_3$) ν_{max} 1646, 1619 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.37-7.24 (m, 5H), 6.40 (q, *J* = 7.2 Hz, 1H), 3.72 (t, *J* = 6.9 Hz, 2H), 3.63-3.58 (m, 2H), 2.20 (br quint, *J* = 6.9 Hz, 2H), 1.80 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.2, 137.0, 135.1, 131.8, 128.6, 127.7, 126.9, 68.6, 44.5, 27.5, 14.8; HRMS (ESI) calcd for $C_{13}H_{15}O_2NNa$ [M+Na^+] 240.0995, found 240.0994.

(2*Z*)-2-Bromo-1-(2-isoxazolidinyl)-2-buten-1-one (3f)



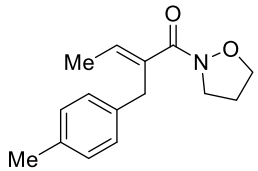
47% yield. A pale yellow oil; *E*/*Z* = 1/>20; IR (neat) ν_{max} 1634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 6.63 (q, *J* = 6.6 Hz, 1H), 4.02 (t, *J* = 6.9 Hz, 2H), 3.81-3.76 (m, 2H), 2.36 (br quint, *J* = 6.9 Hz, 2H), 1.90 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.5, 134.4, 116.5, 69.4, 45.0, 27.4, 17.2; HRMS (ESI) calcd for $C_7H_{10}O_2N^{79}BrNa$ [M+Na^+] 241.9787, found 241.9788.

(2*E*)-1-(2-Isoxazolidinyl)-2-(phenylmethyl)-2-buten-1-one (3g)



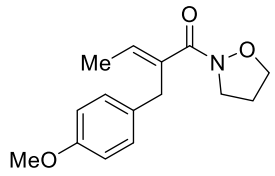
86% yield. A pale yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1663, 1630 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.28-7.13 (m, 5H), 6.20 (br q, *J* = 6.9 Hz, 1H), 3.74 (s, 2H), 3.66 (t, *J* = 6.9 Hz, 2H), 3.58-3.53 (m, 2H), 2.00 (br quint, *J* = 6.9 Hz, 2H), 1.88 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.6, 138.8, 134.7, 130.9, 128.2, 128.0, 125.7, 68.8, 44.9, 33.4, 27.2, 14.1; HRMS (ESI) calcd for $C_{14}H_{17}O_2NNa$ [M+Na^+] 254.1152, found 254.1147.

(2*E*)-1-(2-Isoxazolidinyl)-2-[(4-methylphenyl)methyl]-2-buten-1-one (3h)



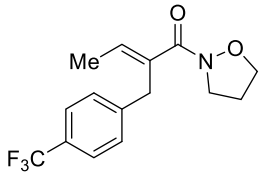
99% yield. A yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1662, 1633 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.10-7.04 (m, 4H), 6.18 (q, *J* = 6.9 Hz, 1H), 3.72-3.67 (m, 4H), 3.58-3.53 (m, 2H), 2.29 (s, 3H), 2.01 (br quint, *J* = 7.2 Hz, 2H), 1.86 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.9, 135.8, 135.2, 135.0, 130.8, 128.8, 128.1, 68.7, 44.7, 32.6, 27.0, 20.7, 13.7; HRMS (ESI) calcd for $C_{15}H_{19}O_2NNa$ [M+Na^+] 268.1308, found 268.1305.

(2*E*)-1-(2-Isoxazolidinyl)-2-[(4-methoxyphenyl)methyl]-2-buten-1-one (3i)



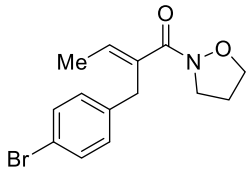
98% yield. A pale yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1664, 1635 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.12 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.16 (br q, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 3.71-3.66 (m, 4H), 3.58-3.53 (m, 2H), 2.02 (br quint, *J* = 7.2 Hz, 2H), 1.87 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.1, 157.8, 135.3, 131.1, 130.7, 129.4, 113.6, 68.9, 55.1, 44.8, 32.3, 27.1, 13.8; HRMS (ESI) calcd for $C_{15}H_{19}O_3NNa$ [M+Na^+] 284.1257, found 284.1254.

(2*E*)-1-(2-Isoxazolidinyl)-2-[[4-(trifluoromethyl)phenyl]methyl]-2-buten-1-one (3j)



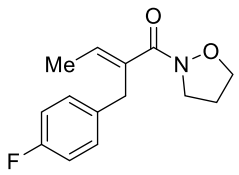
80% yield. A colorless oil; IR (neat) ν_{max} 1661, 1618 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.35 (q, *J* = 6.9 Hz, 1H), 3.80 (s, 2H), 3.73 (t, *J* = 7.2 Hz, 2H), 3.65-3.60 (m, 2H), 2.11 (br quint, *J* = 7.2 Hz, 2H), 1.86 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ_c 171.3, 143.6, 133.8, 133.2, 128.7, 128.5 (q, *J* = 32.1 Hz), 125.3 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 270.1 Hz), 69.2, 44.5, 33.2, 27.2, 14.1; HRMS (ESI) calcd for $C_{15}H_{16}O_2NF_3Na$ [M+Na^+] 322.1025, found 322.1023.

(2*E*)-2-[(4-Bromophenyl)methyl]-1-(2-isoxazolidinyl)-2-buten-1-one (3k)



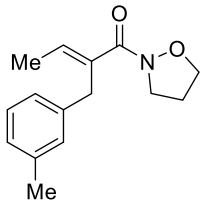
79% yield. A colorless oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1661, 1622 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.37 (br d, *J* = 8.1 Hz, 2H), 7.08 (br d, *J* = 8.1 Hz, 2H), 6.27 (br q, *J* = 7.2 Hz, 1H), 3.72 (t, *J* = 6.9 Hz, 2H), 3.68 (s, 2H), 3.63-3.58 (m, 2H), 2.10 (br quint, *J* = 6.9 Hz, 2H), 1.85 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.4, 138.3, 134.2, 132.4, 131.3, 130.1, 119.7, 69.1, 44.5, 32.7, 27.2, 14.0; HRMS (ESI) calcd for $C_{14}H_{16}O_2N^{79}BrNa$ [M+Na^+] 332.0257, found 332.0259.

(2*E*)-2-[(4-Fluoropheny)methyl]-1-(2-isoxazolidinyl)-2-buten-1-one (3l)



74% yield. A colorless oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1663, 1627 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ: 7.17-7.15 (m, 2H), 6.95-6.92 (m, 2H), 6.23 (q, *J* = 7.2 Hz, 1H), 3.71-3.69 (m, 4H), 3.60-3.58 (m, 2H), 2.07 (br quint, *J* = 7.2 Hz, 2H), 1.86 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 171.8, 161.4 (d, *J* = 242.7 Hz), 134.9 (d, *J* = 3.2 Hz), 134.8, 131.8, 129.9 (d, *J* = 7.7 Hz), 115.1 (d, *J* = 21.0 Hz), 69.0, 44.6, 32.5, 27.2, 13.9; HRMS (ESI) calcd for $C_{14}H_{16}O_2NFNa$ [M+Na^+] 272.1057, found 272.1059.

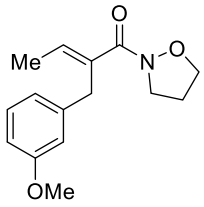
(2*E*)-1-(2-Isoxazolidinyl)-2-[(3-methylphenyl)methyl]-2-buten-1-one (3m)



85% yield. A colorless oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1662, 1634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.14 (t, *J* = 7.5 Hz, 1H), 7.01-6.96 (m, 3H), 6.18 (br q, *J* = 6.9 Hz, 1H), 3.70-3.65 (m, 4H), 3.58-3.53 (m, 2H), 2.30 (s, 3H), 2.00 (br quint, *J* = 6.9 Hz, 2H), 1.87 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.2,

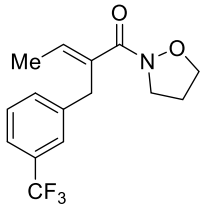
139.1, 137.8, 135.0, 131.1, 129.2, 128.2, 126.7, 125.4, 68.9, 44.8, 33.2, 27.1, 21.3, 13.9; HRMS (ESI) calcd for $C_{15}H_{19}O_2NNa$ [M+Na$^+$] 268.1308, found 268.1307.

(2*E*)-1-(2-Isoxazolidinyl)-2-[(3-methoxyphenyl)methyl]-2-buten-1-one (3n)



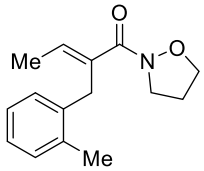
65% yield. A yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1662, 1632 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.17 (t, *J* = 7.8 Hz, 1H), 6.81-6.70 (m, 3H), 6.21 (br q, *J* = 6.9 Hz Hz, 1H), 3.77 (s, 3H), 3.73-3.69 (m, 4H), 3.60-3.55 (m, 2H), 2.04 (br quint, *J* = 6.9 Hz, 2H), 1.87 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$,) δ: 172.0, 159.6, 140.8, 134.7, 131.6, 129.2, 120.8, 114.1, 111.4, 68.9, 55.0, 44.8, 33.3, 27.2, 13.9; HRMS (ESI) calcd for $C_{15}H_{19}O_3NNa$ [M+Na$^+$] 284.1257, found 284.1252.

(2*E*)-1-(2-Isoxazolidinyl)-2-[[3-(trifluoromethyl)phenyl]methyl]-2-buten-1-one (3o)



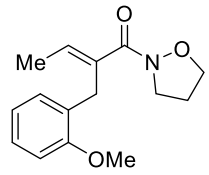
75% yield. A pale yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1662, 1627 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.49-7.36 (m, 4H), 6.34 (br q, *J* = 7.2 Hz, 1H), 3.80 (s, 2H), 3.70 (t, *J* = 7.2 Hz, 2H), 3.63-3.61 (m, 2H), 2.09 (br quint, *J* = 7.2 Hz, 2H), 1.87 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ_c 171.4, 140.4, 133.7, 133.2, 132.1, 130.6 (q, *J* = 31.9 Hz), 128.8, 124.9 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.4 Hz), 122.9 (q, *J* = 3.8 Hz), 69.1, 44.5, 33.0, 27.2, 14.1; HRMS (ESI) calcd for $C_{15}H_{16}O_2NF_3Na$ [M+Na$^+$] 322.1025, found 322.1018.

(2*E*)-1-(2-Isoxazolidinyl)-2-[(2-methylphenyl)methyl]-2-buten-1-one (3p)



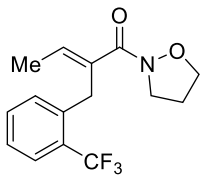
76% yield. A colorless oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1663, 1635 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.18-7.07 (m, 4H), 6.19 (br q, *J* = 6.9 Hz, 1H), 3.69 (s, 2H), 3.61 (t, *J* = 7.2 Hz, 2H), 3.56-3.51 (m, 2H), 2.33 (s, 3H), 1.96 (br quint, *J* = 7.2 Hz, 2H), 1.85 (br d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.9, 136.7, 136.2, 134.1, 130.8, 129.8, 128.6, 126.0, 125.7, 68.8, 44.3, 30.6, 27.0, 19.4, 13.7; HRMS (ESI) calcd for $C_{15}H_{19}O_2NNa$ [M+Na$^+$] 268.1308, found 268.1303.

(2*E*)-1-(2-Isoxazolidinyl)-2-[(2-methoxyphenyl)methyl]-2-buten-1-one (3q)



93% yield. A yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1664, 1630 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.19-7.13 (m, 2H), 6.87-6.81 (m, 2H), 6.13 (br q, *J* = 6.9 Hz, 1H), 3.82 (s, 3H), 3.71-3.66 (m, 4H), 3.56-3.51 (m, 2H), 1.96 (br quint, *J* = 6.9 Hz, 2H), 1.84 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.4, 157.2, 134.3, 131.3, 129.8, 127.3, 127.2, 120.2, 109.9, 68.7, 55.1, 45.1, 27.8, 27.1, 13.7; HRMS (ESI) calcd for $C_{15}H_{19}O_3NNa$ [M+Na$^+$] 284.1257, found 284.1252.

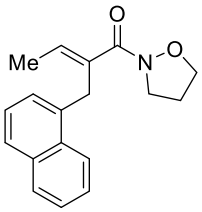
(2*E*)-1-(2-Isoxazolidinyl)-2-[[2-(trifluoromethyl)phenyl]methyl]-2-buten-1-one (3r)



78% yield. A pale yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1661, 1624 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 7.8 Hz, 1H), 7.44-7.39 (m, 2H), 7.29-7.26 (m. 1H), 6.44 (q, *J* = 7.2 Hz, 1H), 3.95 (s, 2H), 3.79 (t, *J* = 7.2 Hz, 2H), 3.67-3.65 (m, 2H), 2.14 (br quint, *J* = 7.2 Hz, 2H), 1.76 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR

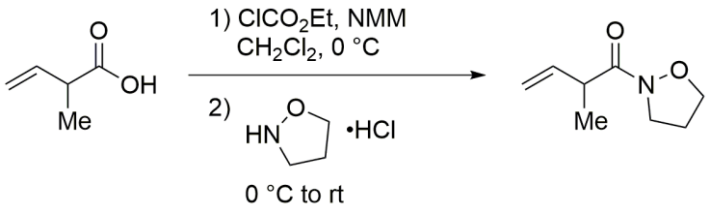
(150 MHz, $CDCl_3$) δ: 171.0, 137.8, 134.6, 133.2, 131.8, 129.9, 128.4 (q, *J* = 29.7 Hz), 126.0, 125.8 (q, *J* = 5.8 Hz), 124.6 (q, *J* = 272.2 Hz), 69.2, 44.3, 29.7, 27.2, 14.0; HRMS (ESI) calcd for $C_{15}H_{16}O_2NF_3Na$ [M+Na^+] 322.1025, found 322.1021.

(2*E*)-1-(2-Isoxazolidinyl)-2-[(1-naphthalenyl)methyl]-2-buten-1-one (3s)



80% yield. A pale orange oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 1662, 1626 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.07 (br d, *J* = 8.4 Hz, 1H), 7.85-7.82 (m, 1H), 7.70 (dd, *J* = 6.9, 2.7 Hz, 1H), 7.55-7.34 (m, 4H), 6.26 (q, *J* = 6.9 Hz, 1H), 4.18 (s, 2H), 3.47 (t, *J* = 6.9 Hz, 2H), 3.43-3.38 (m, 2H), 1.92 (d, *J* = 6.6 Hz, 3H), 1.77 (br quint, *J* = 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.8, 134.7, 134.4, 133.6, 131.8, 131.7, 128.5, 126.8, 126.2, 125.8, 125.5, 125.4, 123.6, 68.8, 44.6, 30.4, 26.9, 14.0; HRMS (ESI) calcd for $C_{18}H_{19}O_2NNa$ [M+Na^+] 304.1308, found 304.1301.

Preparation of β,γ-unsaturated *N*-alkoxyamide 6



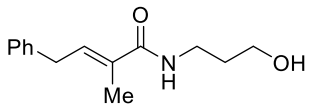
To a solution of 2-methyl-3-butenoic acid (200 mg, 2.0 mmol) in CH_2Cl_2 (6.0 mL) was added 4-methylmorpholine (0.44 mL, 4.0 mmol) at 0 °C. After 15 min, ethyl chloroformate (0.19 mL, 2.0 mmol) was added dropwise and stirring at 0 °C for 15 min. Subsequently, isoxazolidine hydrochloride[1] (219 mg, 2.0 mmol) was added at 0 °C and this solution was gradually warmed to room temperature. After being stirred at the same temperature for 12 h, the reaction mixture was diluted with EtOAc. The mixture was washed with 1 M HCl, saturated $NaHCO_3$, and saturated NaCl. The organic phase was dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane : AcOEt = 1 : 1) to give 1-(2-isoxazolidinyl)-2-methyl-3-buten-1-one (**6**) (122 mg, 0.79 mmol, 40%) as a colorless oil; IR (neat) ν_{max} 1651, 1634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.93 (ddd, *J* = 17.4, 10.2, 7.7 Hz, 1H), 5.17-5.07 (m, 2H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.79-3.61 (m, 3H), 2.31 (br quint, *J* = 6.9 Hz, 2H), 1.25 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.6, 137.8, 115.4, 69.3, 43.1, 40.8, 27.4, 16.6; HRMS (ESI) calcd for $C_8H_{13}O_2NNa$ [M+Na^+] 178.0839, found 178.0840.

General procedure for preparation of γ-phenyl α,β-unsaturated amides 4aa-4ae from α,β-unsaturated *N*-alkoxyamide 3a (Table 1, entries 1-4)

To a solution of α,β-unsaturated *N*-alkoxyamide **3a** (0.35 mmol) in CH_2Cl_2 (1.25 mL) were added silylating agent (0.74 mmol), *i*-Pr_2NEt (0.24 mL, 1.40 mmol), and Ph_3Al (1.0 M in *n*-dibutyl ether,

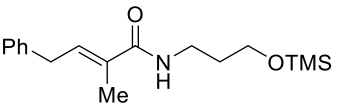
1.05mL, 1.05 mmol) dropwise at room temperature under an argon atmosphere. After being stirred at the same temperature for several hours, this reaction mixture was quenched with an aqueous Rochelle's salt (1.3 M). The resulting suspension was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage Isorera One using Biotage SNAP KP-Sil 50g silica gel cartridges) (*n*-hexane : AcOEt = 4 : 1 to EtOAc) to give γ-phenyl α,β-unsaturated amide **4aa**-**4ae** as shown in Table 1, entries 1-4.

(2*E*)-*N*-(3-Hydroxypropyl)-2-methyl-4-phenyl-2-butenamide (4aa)



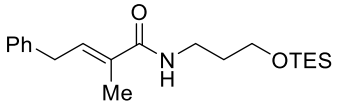
A pale yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 3331, 1659, 1615 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.33-7.17 (m, 5H), 6.49 (br t, *J* = 7.2 Hz, 1H), 6.18 (br s, 1H), 3.63 (br t, *J* = 5.4 Hz, 2H), 3.51-3.45 (m, 4H), 3.33 (br s, 1H), 1.97 (s, 3H), 1.70 (quint, *J* = 5.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.5, 139.2, 134.4, 131.4, 128.6, 128.4, 126.4, 59.3, 36.5, 34.5, 32.3, 12.9; HRMS (ESI) calcd for $C_{14}H_{19}O_2NNa$ [M+Na^+] 256.1308, found 256.1308.

(2*E*)-2-Methyl-4-phenyl- *N*-[3-[(trimethylsilyl)oxy]propyl]-2-butenamide (4ab)



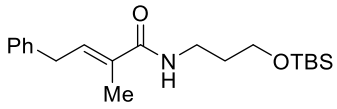
A pale yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 3323, 1661, 1621 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ: 7.32-7.17 (m, 5H), 6.49 (br s, 1H), 6.40 (br t, *J* = 7.5 Hz, 1H), 3.70 (t, *J* = 5.7 Hz, 2H), 3.48 (d, *J* = 7.5 Hz, 2H), 3.37 (q, *J* = 5.7 Hz, 2H), 1.93 (s, 3H), 1.72 (quint, *J* = 5.7 Hz, 2H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.6, 139.8, 133.2, 132.0, 128.6, 128.5, 126.3, 62.1, 38.8, 34.5, 31.4, 12.7, -0.9; HRMS (ESI) calcd for $C_{17}H_{27}O_2NNaSi$ [M+Na^+] 328.1703, found 328.1697.

(2*E*)-2-Methyl-4-phenyl-*N*-[3-(triethylsilyl)oxy]propyl]-2-butenamide (4ac)



A pale yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 3322, 1661, 1620 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ: 7.33-7.17 (m, 5H), 6.48 (br s, 1H), 6.37 (br t, *J* = 7.5 Hz, 1H), 3.73 (t, *J* = 5.4 Hz, 2H), 3.48 (d, *J* = 7.2 Hz, 2H), 3.38 (q, *J* = 5.4 Hz, 2H), 1.93 (s, 3H), 1.73 (quint, *J* = 5.7 Hz, 2H), 0.93 (t, *J* = 7.8 Hz, 9H), 0.58 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.8, 139.8, 133.0, 132.3, 128.6, 128.5, 126.2, 62.4, 38.8, 34.5, 31.6, 12.8, 6.6, 4.2; HRMS (ESI) calcd for $C_{20}H_{33}O_2NNaSi$ [M+Na^+] 370.2173, found 370.2166.

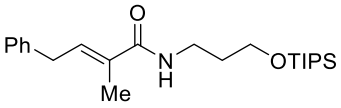
(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-methyl-4-phenyl-2-butenamide (4ad)



A yellow oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 10/1; IR (neat) ν_{max} 3321, 1661, 1620 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ: 7.57-7.16 (m, 5H), 6.41-6.38 (m, 2H), 3.74 (t, *J* = 6.0 Hz, 20/11H), 3.61 (t, *J* = 6.0 Hz, 2/11H), 3.52 (d, *J* = 6.0 Hz, 2/11H), 3.48 (d, *J* = 7.2 Hz, 20/11H), 3.43 (q, *J* = 6.0

Hz, 20/11H), 3.34 (q, *J* = 6.0 Hz, 2/11H), 1.98 (s, 3/11H), 1.96 (s, 30/11H), 1.74 (br quint, *J* = 6.0 Hz, 20/11H), 1.64 (br quint, *J* = 6.0 Hz, 2/11H), 0.87 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 169.3, 169.1 (*Z*), 139.4, 139.3 (*Z*), 133.1, 133.0 (*Z*), 132.4 (*Z*), 132.3, 128.9 (*Z*), 128.7 (*Z*), 128.6, 128.5, 126.3, 126.2 (*Z*), 62.83 (*Z*), 62.78, 38.72 (*Z*), 38.67, 34.5, 34.1 (*Z*), 31.54 (*Z*), 31.48, 25.92, 25.88 (*Z*), 18.4, 13.04 (*Z*), 13.00, -5.4, -5.5 (*Z*); HRMS (ESI) calcd for $C_{20}H_{33}O_2NNaSi$ [M+Na$^+$] 370.2173, found 370.2172.

(2*E*)-2-Methyl-4-phenyl-*N*-[3-[[tris(1-methylethyl)silyl]oxy]propyl]-2-butenamide (4ae)

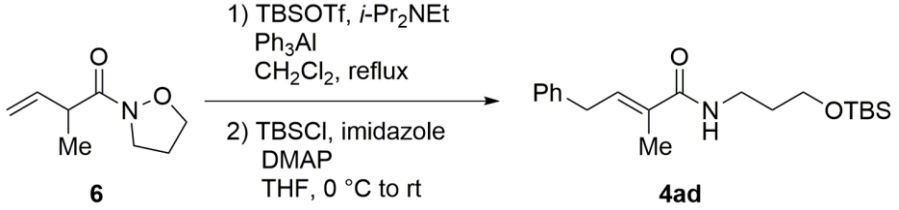


A pale yellow oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 9/1; IR (neat) ν_{max} 3323, 1660, 1620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32-7.15 (m, 5H), 6.43 (br s, 1H), 6.36 (br t, *J* = 7.2 Hz, 1H), 3.82 (t, *J* = 5.4 Hz, 18/10H), 3.70 (t, *J* = 5.4 Hz, 2/10H), 3.48-3.43 (m, 4H), 1.96 (s, 3H), 1.77 (br quint, *J* = 5.4 Hz, 2H), 1.08-1.02 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.5, 139.4, 133.3, 132.5, 128.6, 128.4, 126.3, 63.0, 38.7, 34.5, 31.5, 17.9, 13.0, 11.8; HRMS (ESI) calcd for $C_{23}H_{39}O_2NNaSi$ [M+Na$^+$] 412.2642, found 412.2640.

Sequential nucleophilic phenylation/silylation of vinylketene *N*,*O*-acetal generated from α,β-unsaturated *N*-alkoxyamide 3a (Table 1, entry 10)

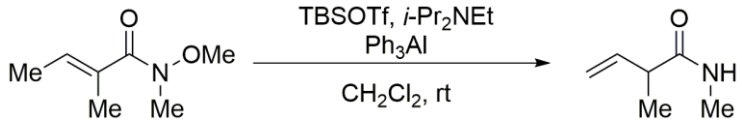
To a solution of α,β-unsaturated *N*-alkoxyamide **3a** (54.3 mg, 0.35 mmol) in CH_2Cl_2 (1.25 mL) were added TBSOTf (0.17 mL, 0.74 mmol), *i*-Pr_2NEt (0.24 mL, 1.40 mmol), and Ph_3Al (1.0 M in *n*-dibutyl ether, 1.05 mL, 1.05 mmol) dropwise at room temperature under argon atmosphere. After being stirred at 40 ℃ for 5.5 h, this reaction mixture was quenched with an aqueous Rochelle's salt (1.3 M). The resulting suspension was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. To a solution of crude product in THF (2.5 mL) were added imidazole (88.5 mg, 1.3 mmol), DMAP (13.4 mg, 0.11 mmol), and TBSCl (180 mg, 1.2 mmol) at 0 °C. After being stirred at room temperature for 16 h, the reaction mixture was quenched with saturated $NaHCO_3$. The mixture was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage Isorera One using Biotage SNAP KP-Sil 50g silica gel cartridges) (*n*-hexane : AcOEt = 4 : 1) to give γ-phenyl α,β-unsaturated amide **4ad** (80.5 mg, 66%, *E*/*Z* = 10/1).

Sequential nucleophilic phenylation/silylation of vinylketene *N*,*O*-acetal generated from β,γ-unsaturated *N*-alkoxyamide 6



To a solution of β,γ-unsaturated *N*-alkoxyamide **6** (54.3 mg, 0.35 mmol) in CH_2Cl_2 (1.25 mL) were added TBSOTf (0.17 mL, 0.74 mmol), *i*-Pr_2NEt (0.24 mL, 1.4 mmol), and Ph_3Al (1.0 M in *n*-dibutyl ether, 1.05 mL, 1.05 mmol) dropwise at room temperature under an argon atmosphere. After being stirred at 40 ℃ for 4 h, this reaction mixture was quenched with an aqueous Rochelle's salt (1.3 M). The resulting suspension was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. To a solution of crude product in THF (2.5 mL) were added imidazole (88.5 mg, 1.3 mmol), DMAP (13.4 mg, 0.11 mmol), and TBSCl (180 mg, 1.2 mmol) at 0 °C. After being stirred at room temperature for 16 h, the reaction mixture was quenched with saturated $NaHCO_3$. The mixture was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage Isorera One using Biotage SNAP KP-Sil 50g silica gel cartridges) (*n*-hexane : AcOEt = 4 : 1) to give γ-phenyl α,β-unsaturated amide **4ad** (72.0 mg, 59%, *E*/*Z* = 5/1).

Reaction of α,β-unsaturated *N*-alkoxy amide 8 with TBSOTf, *i*-Pr_2NEt, and Ph_3Al



8 **9**

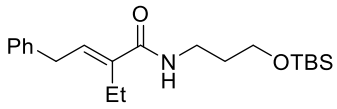
To a solution of α,β-unsaturated *N*-alkoxyamide **8** (28.6 mg, 0.20 mmol) in CH_2Cl_2 (0.71 mL) were added TBSOTf (0.10 mL, 0.42 mmol), *i*-Pr_2NEt (0.13 mL, 0.80 mmol), and Ph_3Al (1.0 M in *n*-dibutyl ether, 0.60 mL, 0.60 mmol) dropwise at room temperature under an argon atmosphere. After being stirred at the same temperature for 7.5 h, this reaction mixture was quenched with an aqueous Rochelle's salt (1.3 M). The resulting suspension was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative TLC ($CHCl_3$: MeOH = 10 : 1) to give *N*,2-dimehyl-3-butenamide (**9**) (4.8 mg, 21%) as a colorless oil; IR (neat) ν_{max} 3300, 1654, 1637 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.90 (ddd, *J* = 17.4, 10.2, 7.8 Hz, 1H), 5.64 (br s, 1H), 5.23-5.16 (m, 2H), 2.99 (quint, *J* = 7.2 Hz, 1H), 2.80 (d, *J* = 5.1 Hz, 3H), 1.28 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.3, 138.4, 116.9, 45.4, 26.4, 16.8; HRMS (ESI) calcd for $C_6H_{11}ONNa$ $[M+Na^+]$ 136.0733, found 136.0732.

General procedure for preparation of γ-phenyl and γ-alkyl α,β-unsaturated amides (Table 2)

To a solution of α,β-unsaturated *N*-alkoxyamide (0.35 mmol) in CH_2Cl_2 (1.25 mL) were added TBSOTf (0.17 mL, 0.74 mmol), *i*-Pr_2NEt (0.24 mL, 1.40 mmol), and organoaluminium reagent (1.05 mmol) dropwise at room temperature under an argon atmosphere. After being stirred at 40 °C for several hours, this reaction mixture was quenched with an aqueous Rochelle's salt (1.3 M). The resulting suspension was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. To a solution of crude product in THF (2.5 mL) were added

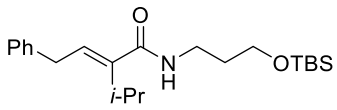
imidazole (88.5 mg, 1.3 mmol), DMAP (13.4 mg, 0.11 mmol), and TBSCl (180 mg, 1.2 mmol) at 0 °C. After being stirred at room temperature for 16-24 h, the reaction mixture was quenched with saturated $NaHCO_3$. The mixture was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Biotage Isorera One using Biotage SNAP KP-Sil 50g silica gel cartridges) (*n*-hexane : EtOAc = 4:1) to give γ-phenyl α,β-unsaturated amide **4bd-4sd** and γ-alkyl α,β-unsaturated amide **10gd-12gd**.

(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-ethyl-4-phenyl-2-butenamide (4bd)



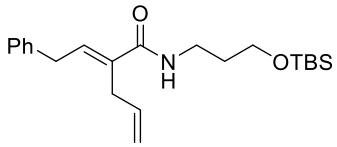
54% yield. A pale yellow oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 3/1; IR (neat) ν_{max} 3317, 1658, 1620 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.58-7.16 (m, 5H), 6.42-6.39 (m, 1H), 6.23-6.17 (m, 1H), 3.75-3.72 (m, 2H), 3.52 (d, *J* = 7.5 Hz, 2/4H), 3.47 (d, *J* = 7.5 Hz, 6/4H), 3.44-3.41 (m, 2H), 2.50-2.43 (m, 2H), 2.32 (br q, *J* = 7.5 Hz, 2/4H), 1.78-1.72 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3/4H), 1.06 (t, *J* = 7.5 Hz, 9/4H), 0.90 (s, 9/4H), 0.87 (s, 27/4H), 0.07 (s, 6/4H), 0.02 (s, 18/4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.4, 139.5, 139.4, 131.4, 131.2 (*Z*), 128.9 (*Z*), 128.7 (*Z*), 128.6, 128.4, 126.3, 62.7, 38.5, 38.4 (*Z*), 34.1, 31.5, 25.9, 20.6, 20.5 (*Z*), 18.3, 13.6, -5.4 (*Z*), -5.5; HRMS (ESI) calcd for $C_{21}H_{35}O_2NNaSi$ [M+Na^+] 384.2329, found 384.2334.

(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-(1-methylethyl)-4-phenyl-2-butenamide (4cd)



14% yield. A pale yellow oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 1/1; IR (neat) ν_{max} 3301, 1655, 1627 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.64-7.16 (m, 5H), 6.42-6.18 (m, 1H), 5.83 (t, *J* = 7.5 Hz, 1/2H), 5.52 (td, *J* = 7.5, 1.5 Hz, 1/2H), 3.72 (q, *J* = 5.7 Hz, 2H), 3.52-3.34 (m, 4H), 2.94 (sept, *J* = 6.9 Hz, 1/2H), 2.60 (br sept, *J* = 6.9 Hz, 1/2H), 1.80-1.67 (m, 2H), 1.23 (d, *J* = 6.9 Hz, 6/2H), 1.08 (d, *J* = 6.9 Hz, 6/2H), 0.89 (s, 9/2H), 0.86 (s, 9/2H), 0.05 (s, 6/2H), 0.01 (s, 6/2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.7, 170.2, 145.3, 144.8, 140.3, 139.7, 128.9, 128.6, 128.5, 128.4, 128.3, 126.2, 126.1, 124.8, 62.54, 62.46, 38.03, 38.00, 35.4, 33.6, 32.1, 31.7, 31.6, 28.1, 25.90, 25.87, 25.86, 21.4, 21.3, 18.2, -5.5; HRMS (ESI) calcd for $C_{22}H_{37}O_2NNaSi$ [M+Na^+] 398.2486, found 398.2483.

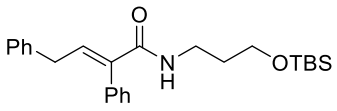
(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-(2-propen-1-yl)-4-phenyl-2-butenamide (4dd)



55% yield. A colorless oil; An inseparable mixture of *E*/*Z* isomers. Ratio of *E*/*Z* isomer could not be calculated due to overlap signals of (*E*)-allylic protons with (*Z*)-allylic protons; IR (neat) ν_{max} 3315, 1656, 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.59-7.16 (m, 5H), 6.42 (t, *J* = 7.5 Hz, 1H), 6.34 (br s, 1H), 5.94-5.80 (m, 1H), 5.16-5.06 (m, 2H), 3.71 (t, *J* = 6.0 Hz, 2H), 3.54-

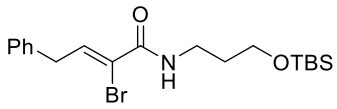
3.47 (m, 2H), 3.41 (q, *J* = 6.0 Hz, 2H), 3.20 (t, *J* = 5.7 Hz, 2H), 1.72 (quint, *J* = 6.0 Hz, 2H), 0.86 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.9, 139.4, 139.1, 135.2, 134.5, 134.3, 129.0, 128.7, 128.6, 128.5, 126.4, 115.9, 62.3, 38.3, 34.3, 34.0, 31.6, 31.4, 25.9, 25.6, 18.3, -5.4; HRMS (ESI) calcd for $C_{22}H_{35}O_2NNaSi$ [M+Na$^+$] 396.2329, found 396.2324.

(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2,4-diphenyl-2-butenamide (4ed)



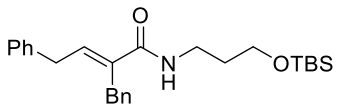
44% yield. A yellow oil; An inseparable mixture of *E/Z* isomers. Ratio of *E/Z* isomer could not be calculated due to overlap signals of olefinic protons with Ph protons; IR (neat) ν_{max} 3313, 1662, 1626 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57-7.03 (m, 11H), 5.57 (br s, 1H), 3.58 (t, *J* = 6.3 Hz, 2H), 3.41-3.34 (m, 2H), 3.32 (d, *J* = 8.1 Hz, 2H), 1.72-1.64 (m, 2H), 0.84 (s, 9H), -0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.6, 139.1, 138.4, 136.5, 135.6, 135.5, 129.79, 129.76, 129.0, 128.9, 128.5, 128.4, 128.2, 128.0, 126.2, 60.8, 37.1, 35.3, 32.0, 25.9, 25.5, 18.3, -5.5; HRMS (ESI) calcd for $C_{25}H_{35}O_2NNaSi$ [M+Na$^+$] 432.2329, found 432.2333.

(2*E*/*Z*)-2-Bromo-*N*-[3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]propyl]-4-phenyl-2-butenamide (4fd)



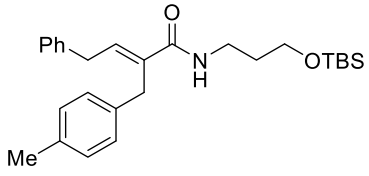
35% yield. A yellow oil; An inseparable mixture of *E/Z* isomers. Ratio of *E/Z* isomer could not be calculated due to overlap signals of (*Z*)-allylic protons with (*E*)-allylic protons; IR (neat) ν_{max} 3333, 1656, 1625 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.56-7.18 (m, 6H), 7.06 (br s, 1H), 3.74 (t, *J* = 5.7 Hz, 2H), 3.64 (t, *J* = 7.2 Hz, 2H), 3.46 (q, *J* = 5.7 Hz, 2H), 1.78 (quint, *J* = 5.7 Hz, 2H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.3, 139.5, 139.3, 137.2, 136.5, 128.9, 128.8, 128.5, 128.4, 126.5, 118.6, 62.1, 39.1, 38.9, 38.2, 31.6, 29.9, 26.2, 18.7, -5.0; HRMS (ESI) calcd for $C_{19}H_{30}O_2N^{79}BrNaSi$ [M+Na$^+$] 434.1121, found 434.1121.

(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-4-phenyl-2-(phenylmethyl)-2-butenamide (4gd)



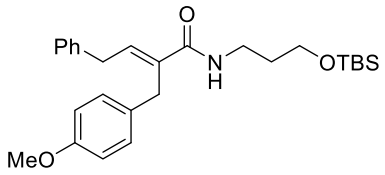
72% yield. A pale yellow oil; An inseparable mixture of *E/Z* isomers. *E*/*Z* = 12:1; IR (neat) ν_{max} 3313, 1658, 1622 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.63-7.19 (m, 10H), 6.51 (t, *J* = 7.8 Hz, 1H), 6.26 (br s, 1H), 3.90 (s, 2/13H), 3.88 (s, 24/13H), 3.65 (t, *J* = 6.0 Hz, 2H), 3.61 (d, *J* = 7.8 Hz, 2H), 3.40 (q, *J* = 6.0 Hz, 2H), 1.68 (quint, *J* = 6.0 Hz, 2H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 169.0, 139.04, 139.00, 136.1, 134.0, 133.8 (*Z*), 128.62, 128.58, 128.53, 128.51 (*Z*), 128.3, 126.4, 126.3, 126.2 (*Z*), 62.14, 62.09, 38.20, 38.15, 34.6, 33.0, 31.5, 25.91, 25.88, 18.3, -5.5; HRMS (ESI) calcd for $C_{26}H_{37}O_2NNaSi$ [M+Na$^+$] 446.2486, found 446.2482.

(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-[(4-methylphenyl)methyl]-4-phenyl-2-butenamide (4hd)



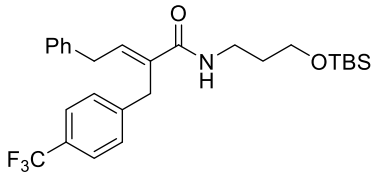
71% yield. A pale yellow oil; An inseparable mixture of *E/Z* isomers. Ratio of *E/Z* isomer could not be calculated due to overlap signals of allylic protons with C*H*$_2$OTBS protons; IR (neat) ν_{max} 3319, 1658, 1622 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58-7.07 (m, 9H), 6.47 (t, *J* = 7.5 Hz, 1H), 6.15 (br s, 1H), 3.78 (br s, 2H), 3.62-3.56 (m, 4H), 3.35 (q, *J* = 6.0 Hz, 2H), 2.33 (s, 3H), 1.64 (quint, *J* = 6.0 Hz, 2H), 0.86 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.6, 138.8, 135.9, 135.8, 135.5, 135.4, 133.7, 133.5, 129.0, 128.7, 128.4, 128.3, 128.2, 127.8, 127.1, 126.7, 126.1, 61.9, 38.1, 34.6, 34.3, 32.6, 31.6, 26.0, 21.1, 18.4, -5.2; HRMS (ESI) calcd for $C_{27}H_{39}O_2NNaSi$ [M+Na$^+$] 460.2642, found 460.2637.

(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-[(4-methoxyphenyl)methyl]-4-phenyl-2-butenamide (4id)



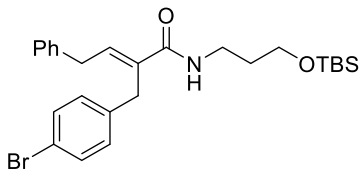
55% yield. A pale yellow oil; An inseparable mixture of *E/Z* isomers. Ratio of *E/Z* isomer could not be calculated due to overlap signals of allylic protons with C*H*$_2$OTBS protons; IR (neat) ν_{max} 3322, 1655, 1616 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58-7.12 (m, 7H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.45 (t, *J* = 7.5 Hz, 1H), 6.19 (br s, 1H), 3.78 (s, 3H), 3.75 (s, 2H), 3.62-3.55 (m, 4H), 3.33 (q, *J* = 5.4 Hz, 2H), 1.63 (quint, *J* = 5.4 Hz, 2H), 0.84 (s, 9H), -0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.0, 158.1, 139.1, 136.4, 136.3, 133.8, 133.6, 130.9, 129.2, 128.9, 128.7, 128.6, 128.5, 126.4, 114.0, 62.0, 55.2, 38.1, 34.5, 34.2, 32.0, 31.5, 25.9, 18.2, -5.5; HRMS (ESI) calcd for $C_{27}H_{39}O_3NNaSi$ [M+Na$^+$] 476.2591, found 476.2582.

(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-4-phenyl-2-[[4-(trifluoromethyl)-phenyl]methyl]-2-butenamide (4jd)



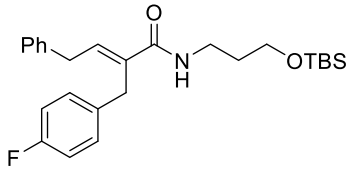
52% yield. A pale yellow oil; An inseparable mixture of *E/Z* isomers. *E*/*Z* = 7/1; IR (neat) ν_{max} 3316, 1658, 1618 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.57-7.18 (m, 7H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.42-6.36 (m, 2H), 3.90 (s, 2/8H), 3.88 (s, 14/8H), 3.65 (t, *J* = 5.4 Hz, 2H), 3.59 (d, *J* = 7.2 Hz, 2/8H), 3.54 (q, *J* = 7.8 Hz, 14/8H), 3.37 (q, *J* = 5.4 Hz, 2H), 1.67 (quint, *J* = 5.4 Hz, 2H), 0.83 (s, 9H), -0.02 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$,) δ: 168.8, 143.5, 138.7, 136.2, 136.1, 133.7, 133.6, 128.8 (q, *J* = 30.8 Hz), 128.73, 128.67, 128.4, 125.4 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 270.0 Hz), 126.6, 62.6, 38.74 (*Z*), 38.68, 34.7, 34.3 (*Z*), 32.9, 31.3, 25.9, 18.2, -5.5; HRMS (ESI) calcd for $C_{27}H_{36}O_2NF_3NaSi$ [M+Na$^+$] 514.2360, found 514.2357.

(2*E*/*Z*)-2-[(4-Bromophenyl)methyl]-*N*-[3-[[(1,1-dimethylethyl)dimethylsilyl]oxy]propyl]-4-phenyl-2-butenamide (4kd)



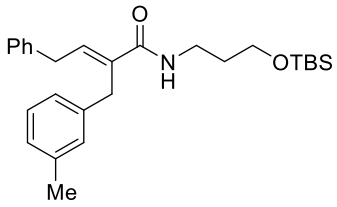
65% yield. A pale yellow oil; An inseparable mixture of *E/Z* isomers. Ratio of *E/Z* isomer could not be calculated due to overlap signals of (*E*)-allylic protons with (*Z*)-allylic protons; IR (neat) ν_{max} 3316, 1656, 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.58-7.09 (m, 9H), 6.39-6.32 (m, 2H), 3.78 (br s, 2H), 3.65 (t, *J* = 5.4 Hz, 2H), 3.54 (d, *J* = 7.2 Hz, 2H), 3.37 (q, *J* = 5.4 Hz, 2H), 1.67 (quint, *J* = 5.4 Hz, 2H), 0.85 (s, 9), 0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.4, 138.5, 137.9, 136.0, 135.9, 133.4, 131.3, 129.9, 128.5, 128.4, 128.2, 126.3, 119.8, 62.4, 38.6, 34.7, 32.5, 31.5, 26.0, 18.4, -5.2; HRMS (ESI) calcd for $C_{26}H_{36}O_2N^{79}BrNaSi$ [M+Na^+] 524.1591, found 524.1595.

(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-[(4-fluorophenyl)methyl]-4-phenyl-2-butenamide (4ld)



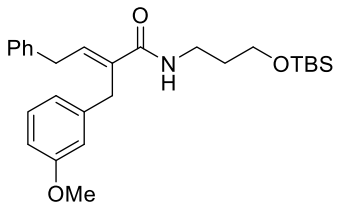
57% yield. A pale yellow oil; An inseparable mixture of *E/Z* isomers. Ratio of *E/Z* isomer could not be calculated due to overlap signals of olefinic protons with N*H* proton; IR (neat) ν_{max} 3317, 1654, 1622 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.69-7.01 (m, 9H), 6.47 (t, *J* = 7.2, 1H), 6.39 (br s, 1H), 3.87 (s, 2H), 3.71 (t, *J* = 5.7 Hz, 2H), 3.63 (d, *J* = 7.2 Hz, 2H), 3.44 (q, *J* = 5.7 Hz, 2H), 1.73 (quint, *J* = 5.7 Hz, 2H), 0.92 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ_c 168.93, 168.89, 161.5 (d, *J* = 242.6 Hz), 138.9, 136.5, 134.8 (d, *J* = 3.3 Hz), 133.6, 129.8 (d, *J* = 7.7 Hz), 128.7, 128.5, 126.5, 115.3 (d, *J* = 21.3 Hz), 62.4, 38.4, 34.6, 32.2, 31.4, 25.9, 18.3, -5.5; HRMS (ESI) calcd for $C_{26}H_{36}O_2NFNaSi$ [M+Na^+] 464.2392, found 464.2383.

(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-[(3-methylphenyl)methyl]-4-phenyl-2-butenamide (4md)



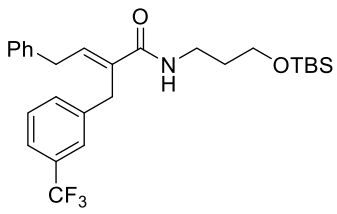
50% yield. A colorless oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 3317, 1656, 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.32-7.00 (m, 9H), 6.49 (t, *J* = 7.2 Hz, 1H), 6.19 (br s, 1H), 3.78 (s, 2H), 3.61-3.55 (m, 4H), 3.34 (q, *J* = 6.0 Hz, 2H), 2.30 (s, 3H), 1.63 (quint, *J* = 6.0 Hz, 2H), 0.84 (s, 9H), -0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.0, 139.1, 138.8, 138.2, 135.9, 134.2, 129.0, 128.62, 128.55, 128.49, 127.1, 126.4, 125.2, 62.0, 38.1, 34.6, 32.9, 31.5, 25.9, 21.4, 18.3, -5.5; HRMS (ESI) calcd for $C_{27}H_{39}O_2NNaSi$ [M+Na^+] 460.2642, found 460.2637.

(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-[(3-methoxyphenyl)methyl]-4-phenyl-2-butenamide (4nd)



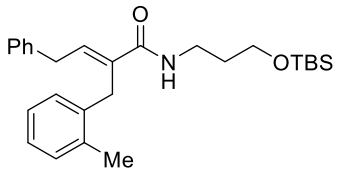
42% yield. A pale yellow oil; An inseparable mixture of *E*/*Z* isomers. Ratio of *E*/*Z* isomer could not be calculated due to overlap signals of (*E*)-allylic protons with (*Z*)-allylic protons; IR (neat) ν_{max} 3321, 1657, 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.63-7.19 (m, 6H), 6.87-6.79 (m, 3H), 6.53 (t, *J* = 7.5 Hz, 1H), 6.26 (br s, 1H), 3.84 (br s, 2H), 3.80 (s, 3H), 3.67-3.60 (m, 4H), 3.39 (q, *J* = 5.7 Hz, 2H), 1.69 (quint, *J* = 5.7 Hz, 2H), 0.89 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.0, 159.8, 140.5, 139.0, 135.8, 134.3, 129.6, 128.6, 128.5, 126.4, 120.6, 113.8, 111.9, 62.0, 55.1, 38.1, 36.4, 33.0, 31.5, 25.9, 18.3, -5.5; HRMS (ESI) calcd for $C_{27}H_{39}O_3NNaSi$ [M+Na^+] 476.2591, found 476.2586.

(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-4-phenyl-2-[[3-(trifluoromethyl)-phenyl]methyl]-2-butenamide (4od)



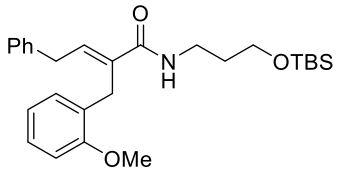
49% yield. A pale yellow oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 10/1; IR (neat) ν_{max} 3319, 1658, 1622 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ: 7.57-7.17 (m, 8H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.41-6.36 (m, 2H), 3.91 (s, 2/11H), 3.88 (s, 20/11H), 3.65 (t, *J* = 5.4 Hz, 2H), 3.55 (d, *J* = 7.2 Hz, 2H), 3.37 (q, *J* = 5.4 Hz, 2H), 1.66 (quint, *J* = 6.0 Hz, 2H), 0.83 (s, 9H), -0.03 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ: 168.8, 140.2, 138.7, 136.2, 136.1, 133.8, 133.6, 131.9, 130.8 (q, *J* = 31.9 Hz), 128.9, 128.7, 128.5, 126.6, 124.9 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 270.7 Hz), 123.1 (q, *J* = 3.8 Hz), 62.6, 38.6, 34.7, 32.8, 31.3, 25.8, 18.2, -5.5; HRMS (ESI) calcd for $C_{27}H_{36}O_2NF_3NaSi$ [M+Na^+] 514.2360, found 514.2357.

(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-[(2-methylphenyl)methyl]-4-phenyl-2-butenamide (4pd)



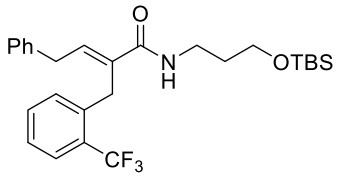
51% yield. A pale yellow oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 17:1; IR (neat) ν_{max} 3315, 1655, 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.56-7.11 (m, 9H), 6.53 (t, *J* = 7.2 Hz, 1H), 6.22 (br s, 1H), 3.78-3.76 (br s, 2H), 3.60 (t, *J* = 5.7 Hz, 2H), 3.49 (d, *J* = 7.2 Hz, 2H), 3.39 (q, *J* = 6.0 Hz, 2H), 2.38-2.37 (br s, 3H), 1.63 (quint, *J* = 5.7 Hz, 2H), 0.85 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.1, 139.0, 136.7, 136.3, 136.2 (*Z*), 135.5, 134.7, 130.3 (*Z*), 130.2, 128.72 (*Z*), 127.68 (*Z*), 128.61, 128.5, 127.5, 126.4, 126.3, 126.1, 62.1, 38.1, 34.6, 31.5, 30.2, 25.9, 25.6 (*Z*), 19.8, 18.3, -5.5; HRMS (ESI) calcd for $C_{27}H_{39}O_2NNaSi$ [M+Na^+] 460.2642, found 460.2637.

(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-[(2-methoxyphenyl)methyl]-4-phenyl-2-butenamide (4qd)



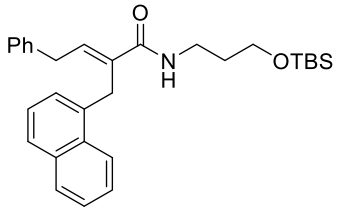
53% yield. A colorless oil; An inseparable mixture of *E/Z* isomers. *E/Z* = 16:1; IR (neat) ν_{max} 3318, 1658, 1622 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.31-7.12 (m, 7H), 6.91-6.81 (m, 2H), 6.62 (t, *J* = 7.5 Hz, 16/17H), 6.34-6.31 (m, 1H), 5.64 (br t, *J* = 7.8 Hz, 1/17H), 3.85 (br s, 3H), 3.78 (s, 2H), 3.61-3.56 (m, 4H), 3.31 (q, *J* = 6.6 Hz, 2H), 1.64 (quint, *J* = 6.6 Hz, 2H), 0.85 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.7, 156.8, 139.3, 135.2, 134.9, 129.4, 128.51, 128.49, 128.4 (*Z*), 127.5, 127.0, 126.2, 120.7, 120.6 (*Z*), 110.10, 110.05, 61.6, 55.2, 37.7, 34.5, 31.7, 31.5 (*Z*), 26.4, 25.8, 18.2, -5.5; HRMS (ESI) calcd for $C_{27}H_{39}O_3NNaSi$ [M+Na^+] 476.2591, found 476.2588.

(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-4-phenyl-2-[[2-(trifluoromethyl)-phenyl]methyl]-2-butenamide (4rd)



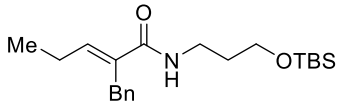
56% yield. A pale yellow oil; An inseparable mixture of *E/Z* isomers. *E/Z* = 7:1; IR (neat) ν_{max} 3314, 1657, 1622 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ: 7.67-7.10 (m, 9H), 6.64 (t, *J* = 7.8 Hz, 1H), 6.24 (br s, 1H), 4.03 (s, 2/8H), 4.00 (s, 14/8H), 3.61 (t, *J* = 6.0 Hz, 2H), 3.49 (d, *J* = 7.2 Hz, 2/8 Hz), 3.45 (d, *J* = 7.8 Hz, 14/8H), 3.36 (q, *J* = 6.0 Hz, 2H), 1.64 (quint, *J* = 6.0 Hz, 2H), 0.85 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 168.4, 138.7, 137.5, 136.4, 134.2, 132.0, 129.5, 128.9 (q, *J* = 30.6 Hz), 128.7, 128.5, 126.50 (*Z*), 126.46, 126.36, 126.0 (q, *J* = 5.6 Hz), 124.7 (q, *J* = 271.9 Hz), 62.14, 62.08 (*Z*), 38.31 (*Z*), 38.25, 34.7, 31.5, 29.1, 25.9, 18.3, -5.5; HRMS (ESI) calcd for $C_{27}H_{36}O_2NF_3NaSi$ [M+Na^+] 514.2360, found 514.2358.

(2*E*/*Z*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-[(1-naphthalenyl)methyl]-4-phenyl-2-butenamide (4sd)



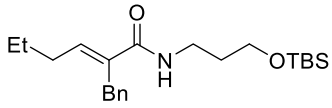
53% yield. A pale yellow oil; An inseparable mixture of *E/Z* isomers. Ratio of *E/Z* isomer could not be calculated due to overlap signals of allylic protons with C*H*$_2$OTBS protons; IR (neat) ν_{max} 3314, 1655, 1619 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.15-8.11 (m, 1H), 7.89-7.86 (m, 1H), 7.76-7.73 (d, *J* = 8.1 Hz, 1H), 7.58-7.13 (m, 9H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.22 (br s, 1H), 4.26 (br s, 2H), 3.57-3.51 (m, 4H), 3.33 (q, *J* = 6.0 Hz, 2H), 1.63-1.55 (m, 2H), 0.80 (s, 9H), -0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.1, 138.9, 135.5, 135.3, 135.2, 134.3, 133.8, 132.0, 128.8, 128.7, 128.62, 128.55, 127.1, 126.4, 126.1, 125.7, 125.5, 125.1, 123.4, 61.9, 38.1, 34.7, 31.5, 29.8, 25.8, 18.2, -5.5; HRMS (ESI) calcd for $C_{30}H_{39}O_2NNaSi$ [M+Na^+] 496.2642, found 496.2632.

(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-(phenylmethyl)-2-pentenamide (10gd)



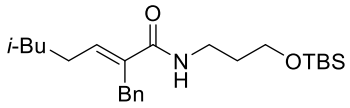
Me_3Al (2.0 M in toluene, 0.53 mL, 1.05 mmol) was used. 44% yield. A pale yellow oil; *E*/*Z* = >20:1; IR (neat) ν_{max} 3317, 1658, 1621 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.31-7.20 (m, 5H), 6.37 (t, *J* = 7.5 Hz, 1H), 6.20 (br s, 1H), 3.71 (s, 2H), 3.63 (t, *J* = 5.7 Hz, 2H), 3.37 (q, *J* = 5.7 Hz, 2H), 2.26 (quint, *J* = 7.5 Hz, 2H), 1.67 (quint, *J* = 5.7 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.2, 139.2, 137.7, 134.6, 128.5, 128.2, 126.1, 62.1, 38.1, 32.8, 31.5, 25.9, 21.7, 18.3, 13.5, -5.4; HRMS (ESI) calcd for $C_{21}H_{35}O_2NNaSi$ [M+Na^+] 384.2329, found 384.2326.

(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2-(phenylmethyl)-2-hexenamide (11gd)



Et_3Al (1.0 M in *n*-hexane, 1.05 mL, 1.05 mmol) was used. 31% yield. A colorless oil; An inseparable mixture of *E*/*Z* isomers. *E*/*Z* = 13:1; IR (neat) ν_{max} 3314, 1656, 1619 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.31-7.18 (m, 5H), 6.40 (t, *J* = 7.5 Hz, 1H), 6.17 (br s, 13/14H), 5.47 (t, *J* = 7.5 Hz, 1/14H), 3.72 (s, 2H), 3.62 (t, *J* = 5.7 Hz, 2H), 3.36 (q, *J* = 6.0 Hz, 2H), 2.22 (q, *J* = 7.5 Hz, 2H), 1.65 (quint, *J* = 6.0 Hz, 2H), 1.49 (sext, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.1, 139.2, 136.3, 135.2, 128.5, 128.4, 128.2, 126.3, 126.2, 62.0, 38.0, 32.8, 31.6, 30.5, 25.9, 22.2, 18.3, 14.0, -5.4; HRMS (ESI) calcd for $C_{22}H_{37}O_2NNaSi$ [M+Na^+] 398.2486, found 398.2480.

(2*E*)-*N*-[3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-6-methyl-(2-phenylmethyl)-2-heptenamide (12gd)



i-Bu_3Al (1.0 M in *n*-hexane, 1.05 mL, 1.05 mmol) was used. 38% yield. A yellow oil; *E*/*Z* = >20/1; IR (neat) ν_{max} 3315, 1658, 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.29-7.16 (m, 5H), 6.36 (t, *J* = 7.5 Hz, 1H), 6.14 (br s, 1H), 3.69 (s, 2H), 3.60 (t, *J* = 6.0 Hz, 2H), 3.33 (q, *J* = 6.0 Hz, 2H), 2.21 (q, *J* = 7.5 Hz, 2H), 1.67-1.53 (m, 3H), 1.34-1.25 (m, 2H), 0.89-0.86 (m, 15H), 0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.2, 139.2, 136.6, 134.9, 128.5, 128.1, 126.1, 62.0, 38.0, 32.8, 31.5, 27.7, 26.3, 25.9, 25.5, 22.4, 18.3, -5.4; HRMS (ESI) calcd for $C_{24}H_{41}O_2NNaSi$ [M+Na^+] 426.2799, found 426.2796.

Ⅲ. References

(1) T. L. Cupps, R. H. Boutin, H. Rapoport, *J. Org. Chem*. **1985**, *50*, 3972-3979.

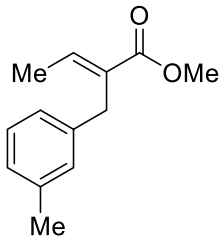
(2) a) T. J. Senter, O. O. Fadeyi, C. W. Lindsley, *Org. Lett.* **2012**, *14*, 1869-1871; b) D. Zargarian, H. Alper, *Organometallics* **1993**, *12*, 712-724.

(3) a) T. Janecki, E. Błaszczyk, K, Studzian, M. Różalski, U. Krajewska, A. Janecka, *J. Med. Chem*. **2002**, *45*, 1142-1145; b) C. te Grotenhuis, N. van den Heuvel, J. I. van der Vlugt, B. de Bruin, *Angew. Chem. Int. Ed.* **2018**, *57*, 140-145; c) Y. Li, A. Goeke, R. Wang, Q. Wang, G. Fráter, *Tetrahedron* **2007**, *63*, 9605-9613.

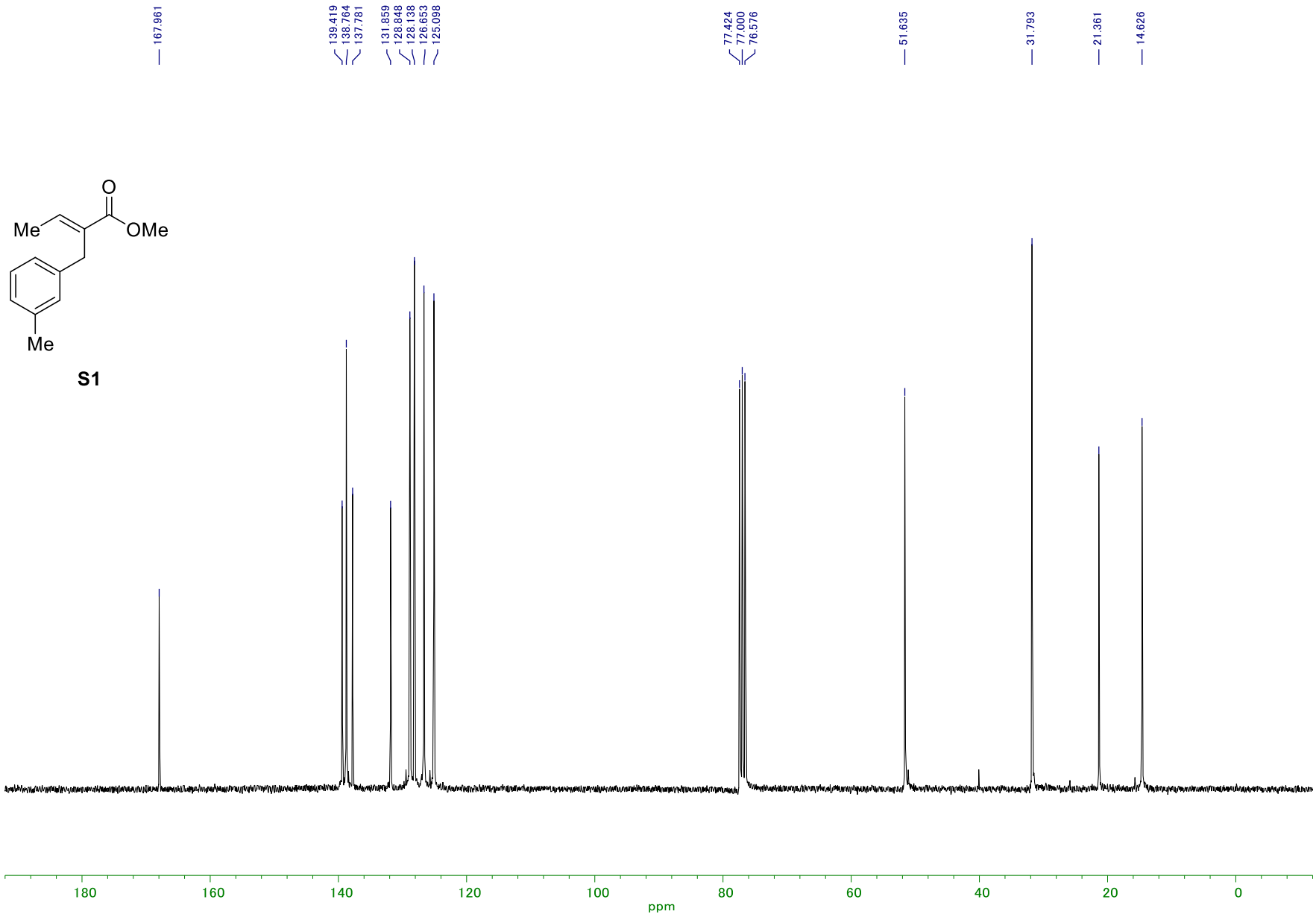
(4) a) H. Nakatsuji, H. Nishikado, K. Ueno, Y. Tanabe, *Org. Lett.* **2009**, *11*, 4258-4261; b) H. Nishikado, H. Nakatsuji, K. Ueno, R. Nagase, Y. Tanabe, *Synlett* **2010**, *14*, 2087-2092; c) F. N. Palmer, F. Lach, C. Poriel, A. G. Pepper, M. C. Bagley, A. M. Z. Slawin, C. J. Moody, *Org. Biomol. Chem.* **2005**, *3*, 3805-3811.

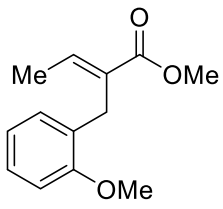
(5) a) E. Brenna, F. G. Gatti, A. Manfredi, D. Monti, F. Parmeggiani, *Org. Process. Res. Dev*. **2012**, *16*, 262-268; b) P. M. Holstein, D. Dailler, J. Vantourout, J. Shaya, A. Millet, O. Baudoin, *Angew. Chem. Int. Ed*. **2016**, *55*, 2805-2809.

(6) L. Navarre, S. Darses, J.-P. Genet, *Chem. Commun*. **2004**, 1108-1109.

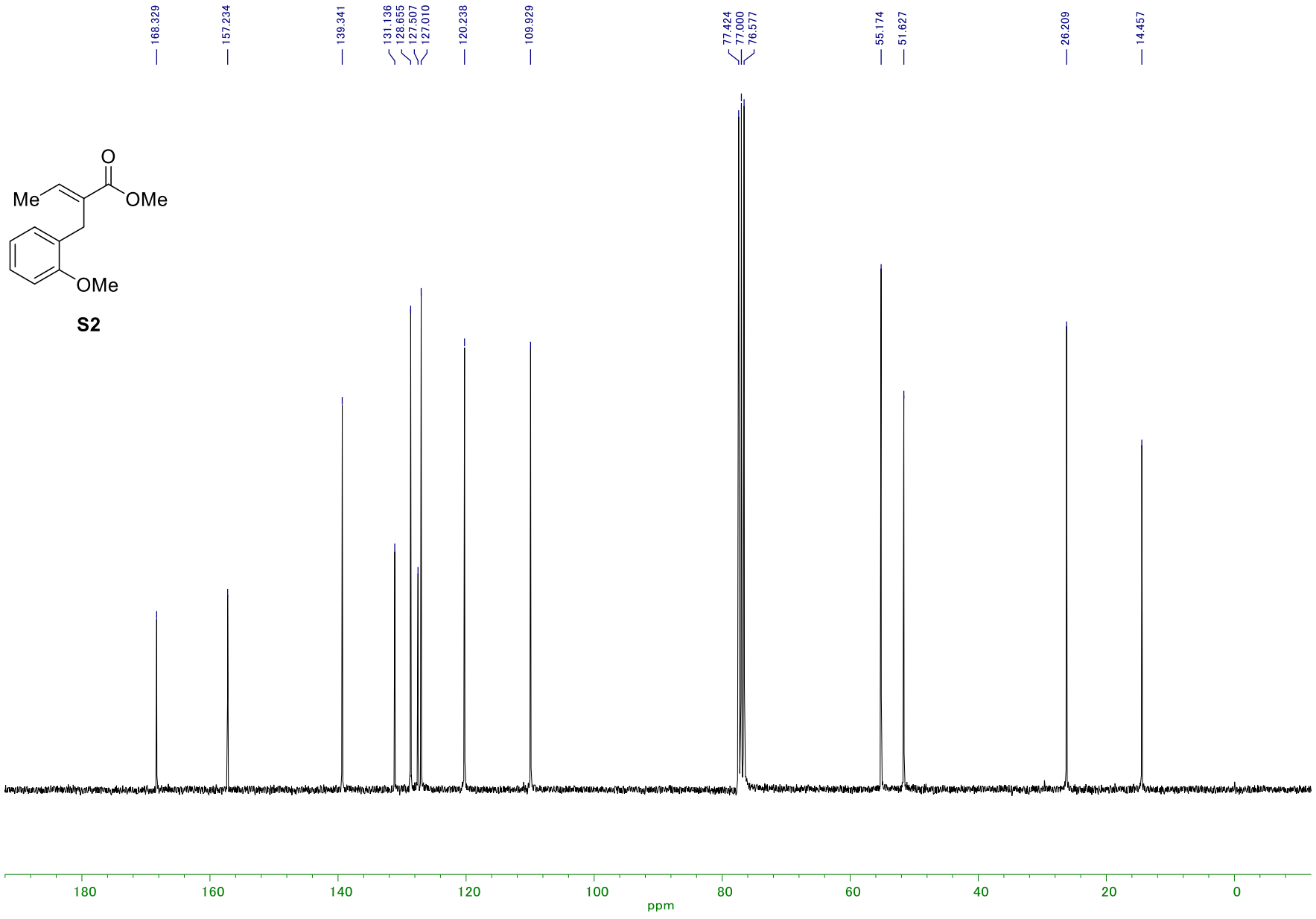


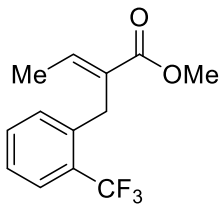
S1


167.961
139.419
138.764
137.781
131.859
128.848
128.138
126.653
125.098
77.424
77.000
76.576
51.635
31.793
21.361
14.626
O
Me
OMe
Me
S1
180
160
140
120
100
80
60
40
20
0
ppm

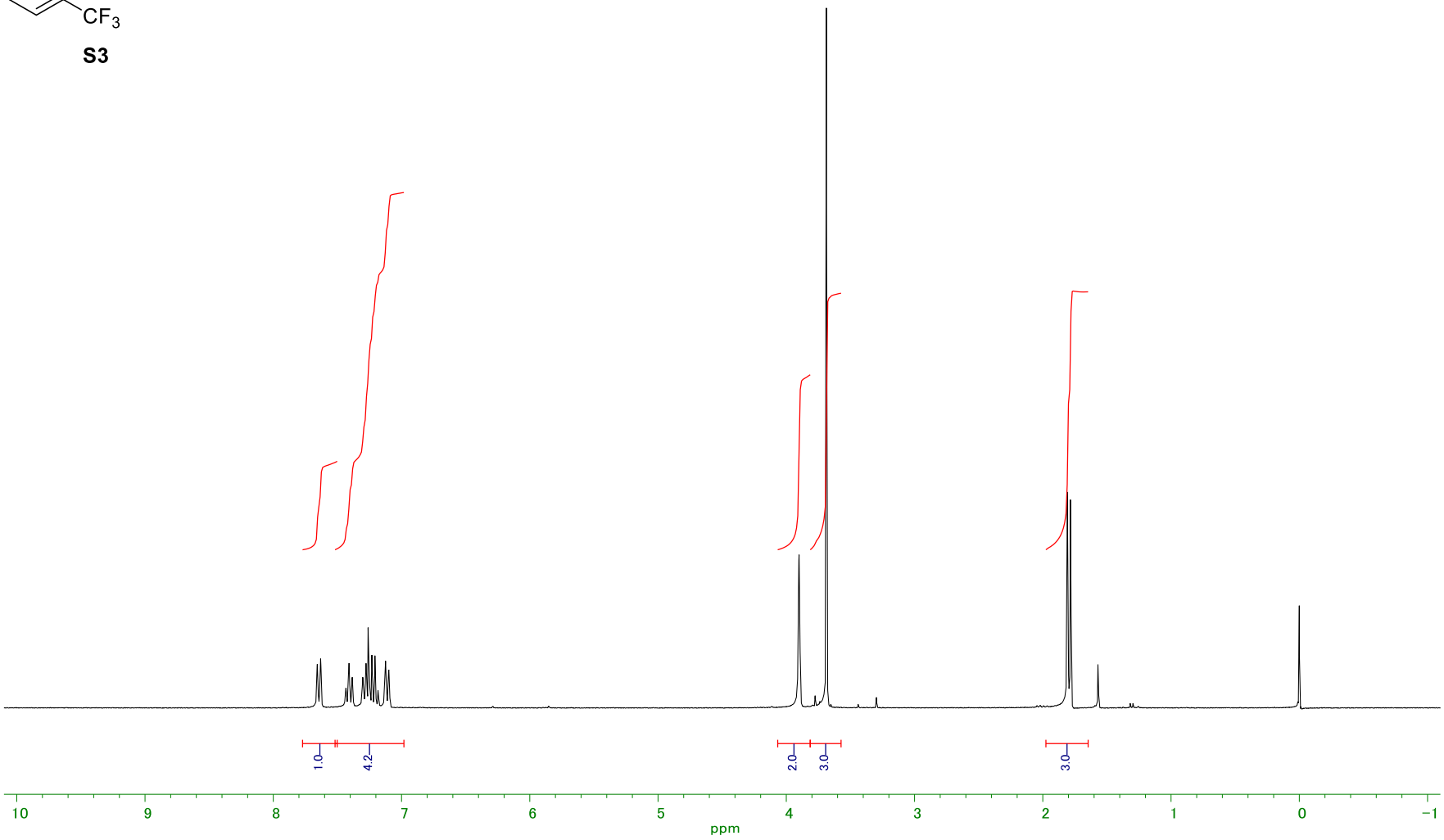


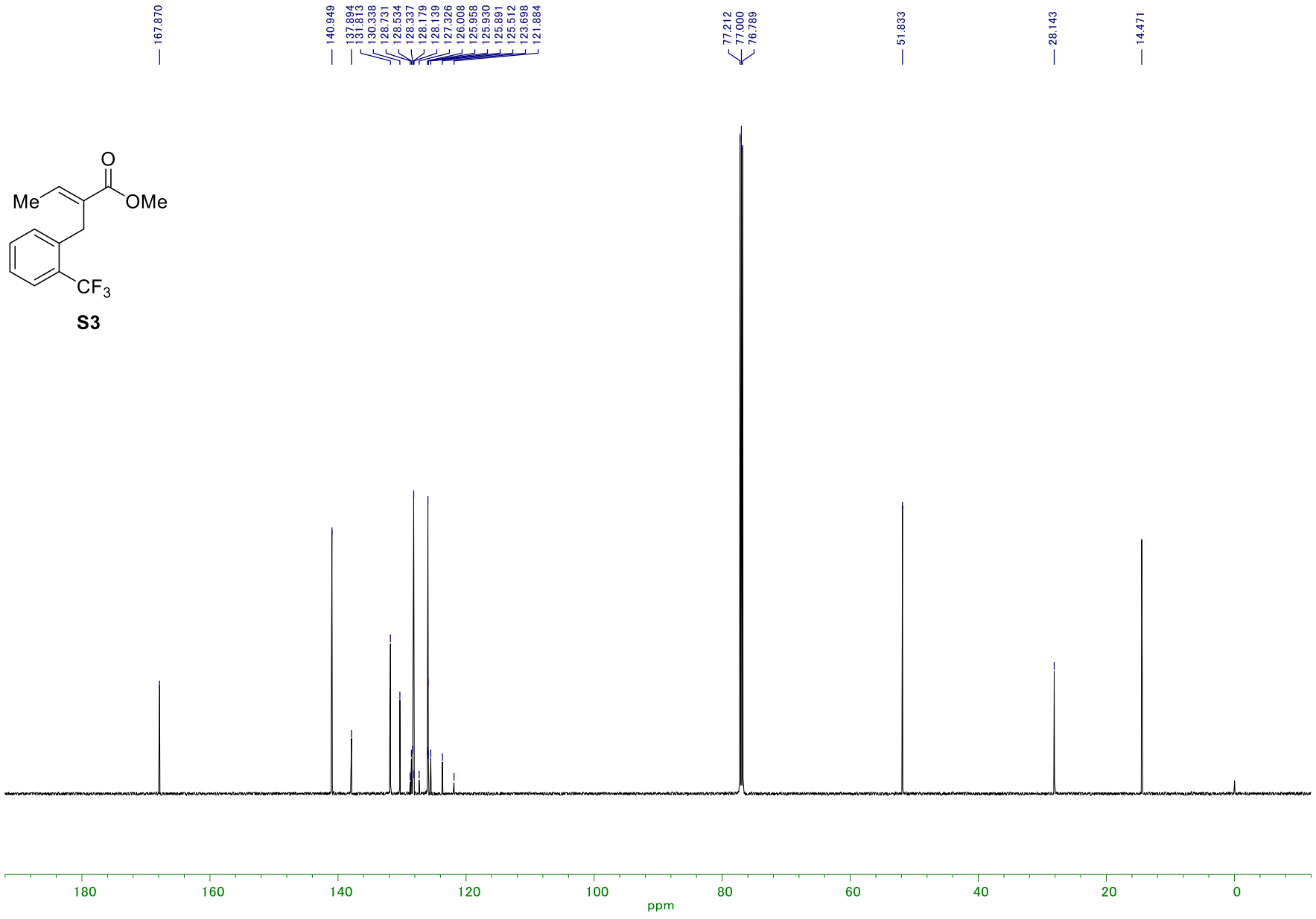
S2

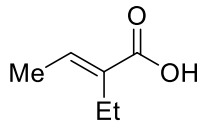

168.329
157.234
139.341
131.136
128.655
127.507
127.010
120.238
109.929
77.424
77.000
76.577
55.174
51.627
26.209
14.457
O
Me
OMe
OMe
S2
180
160
140
120
100
80
60
40
20
0
ppm



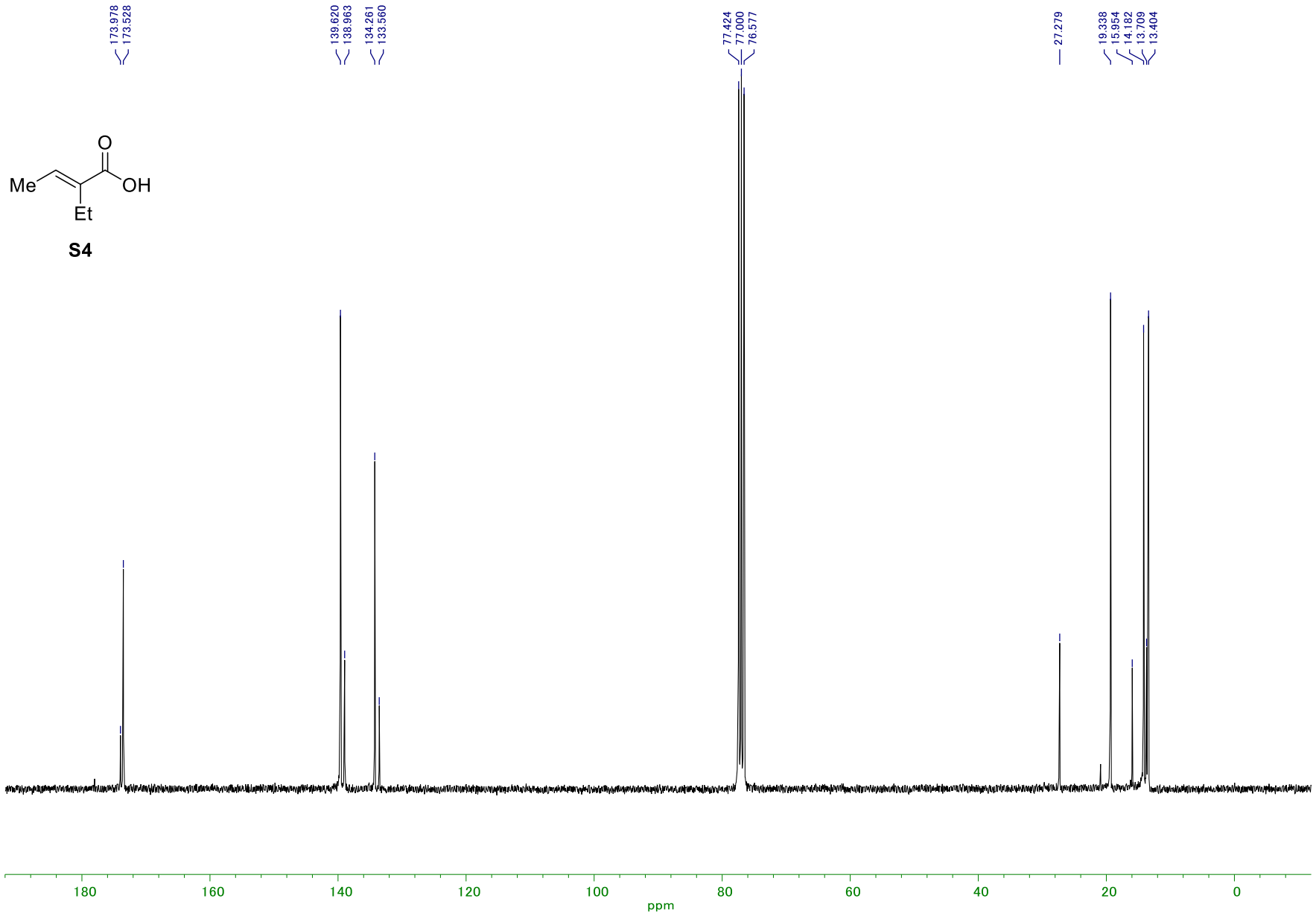
S3



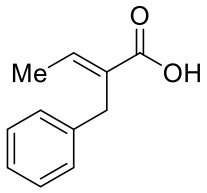

167.870
140.949
137.894
131.813
130.338
128.731
128.534
128.337
128.179
128.139
127.326
126.008
125.958
125.930
125.891
125.512
123.698
121.884
77.212
77.000
76.789
51.833
28.143
14.471
O
Me
OMe
CF3
S3
180
160
140
120
100
80
60
40
20
0
ppm



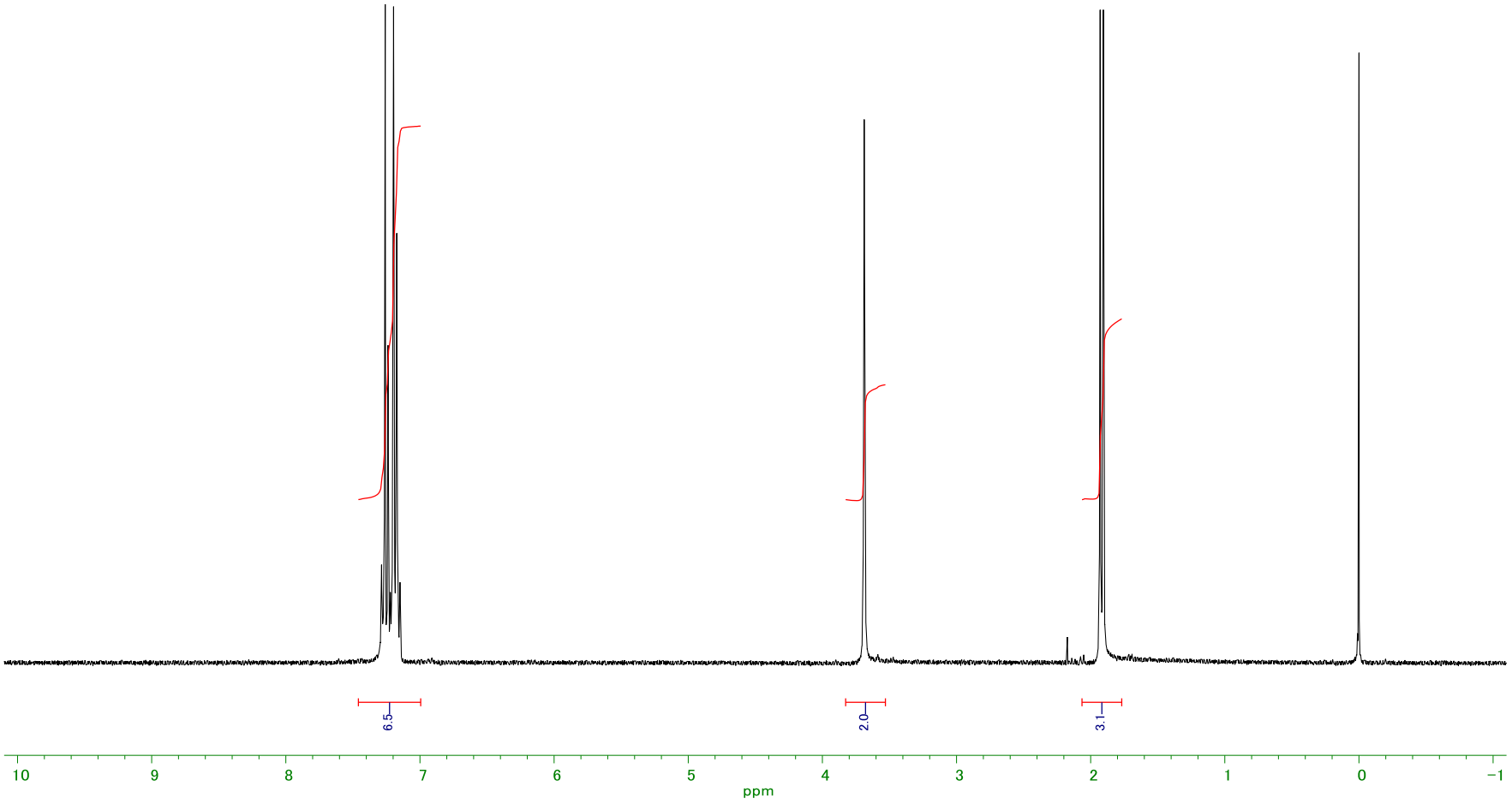
S4

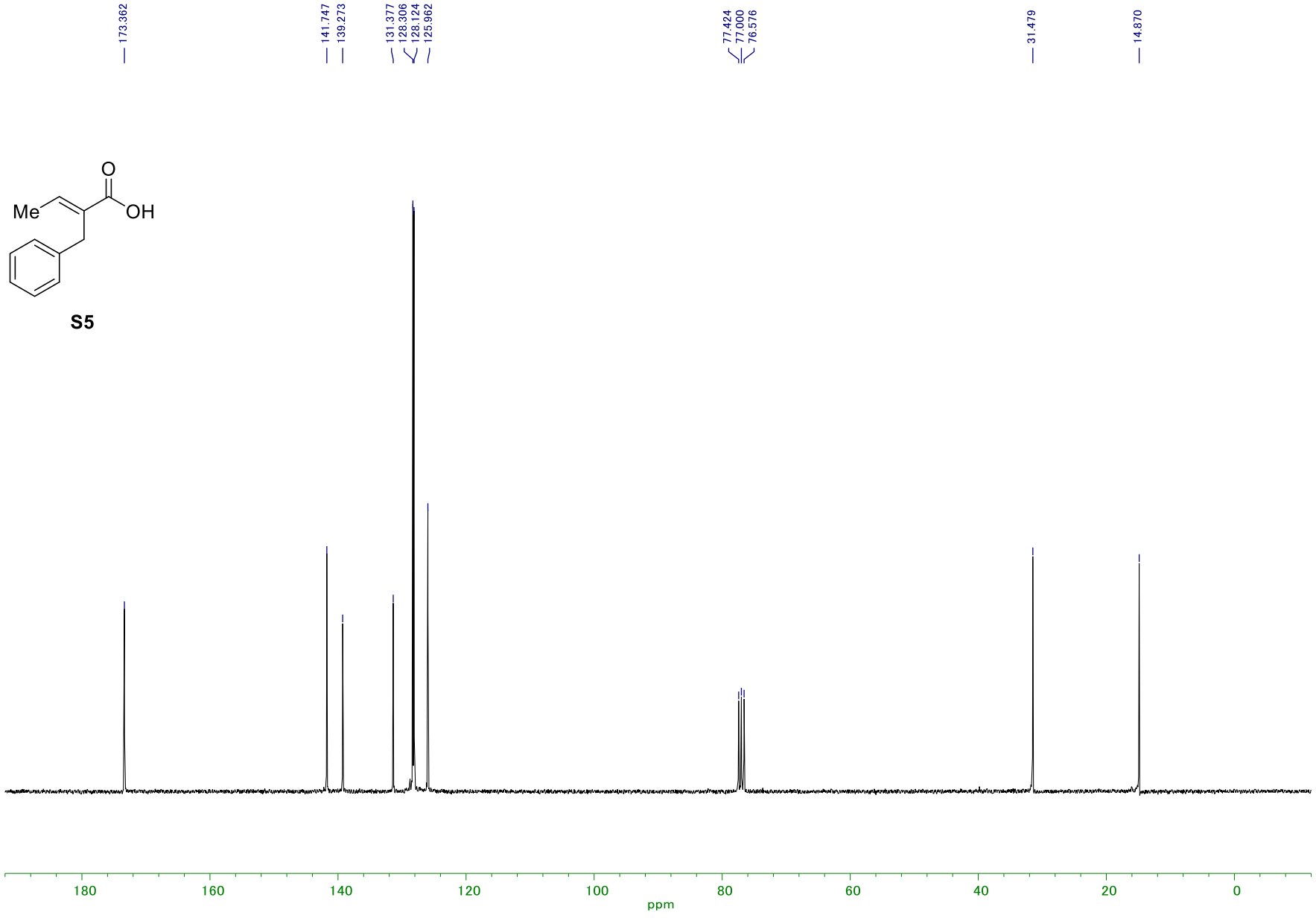

173.978
173.528
139.620
138.963
134.261
133.560
77.424
77.000
76.577
27.279
19.338
15.954
14.182
13.709
13.404
O
Me
OH
Et
180
160
140
120
100
80
60
40
20
0
ppm

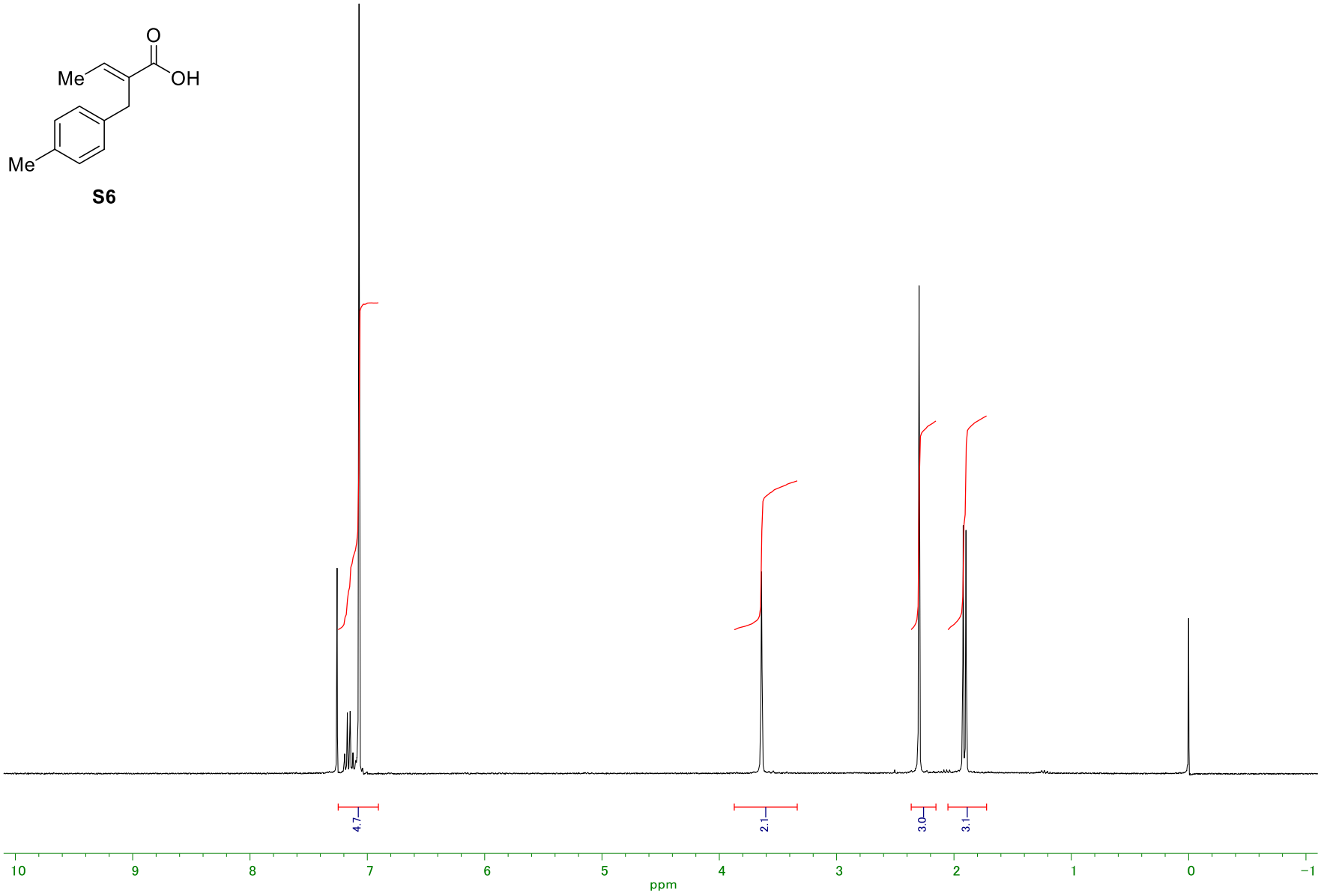
S4



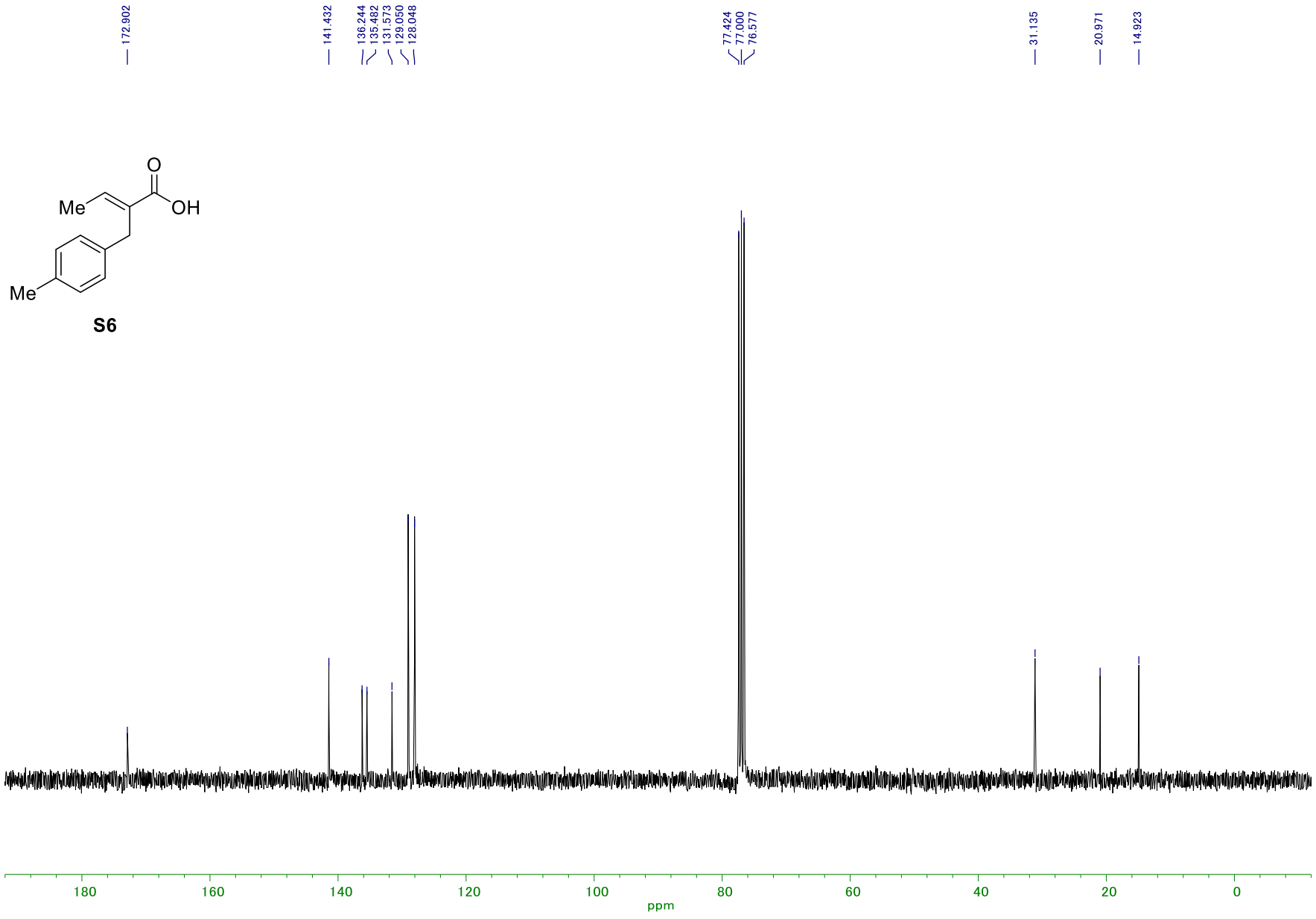
S5



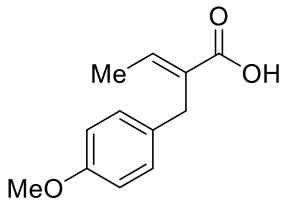

173.362
141.747
139.273
131.377
128.306
128.124
125.962
77.424
77.000
76.576
31.479
14.870
O
Me
OH
S5
180
160
140
120
100
80
60
40
20
0
ppm



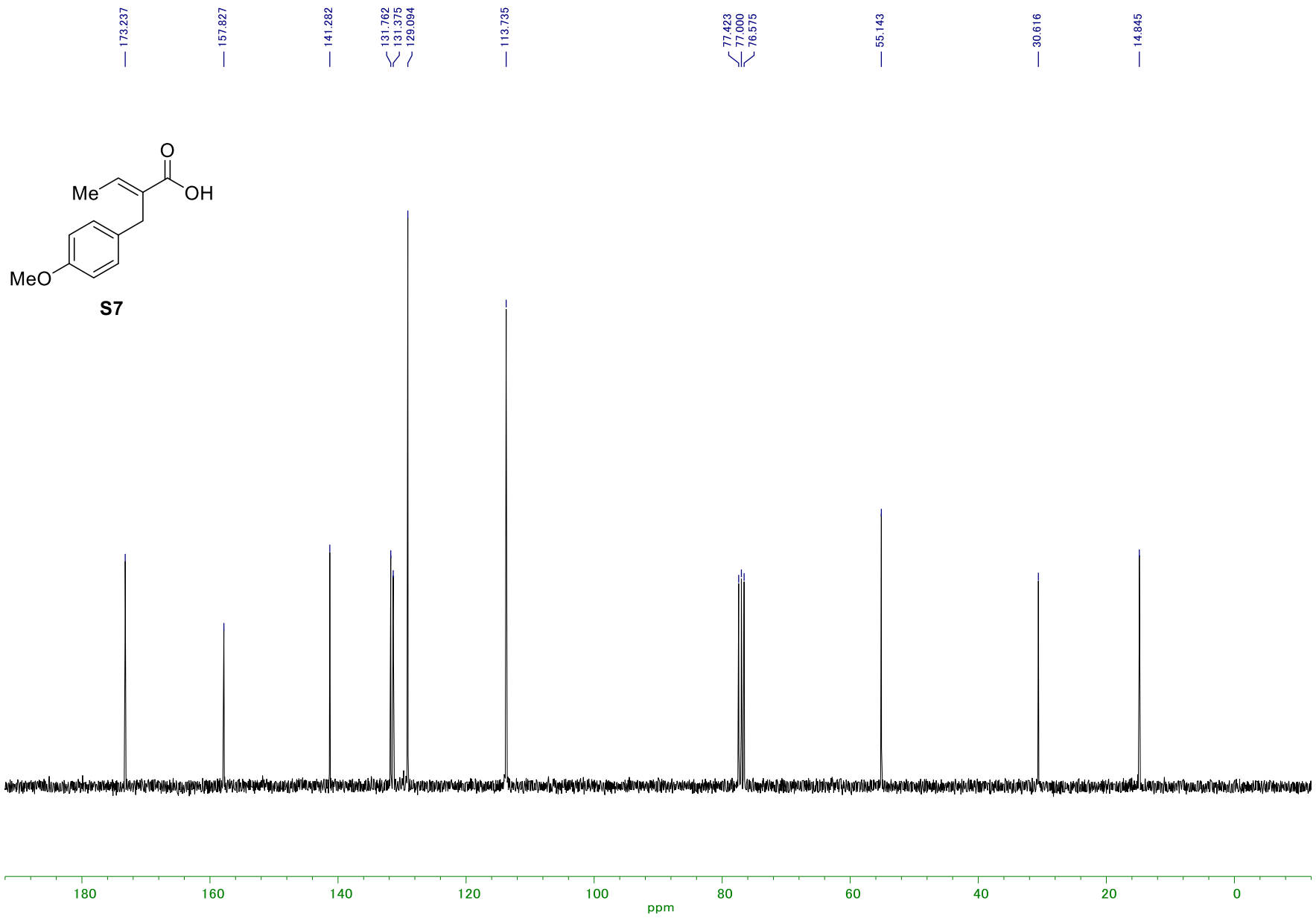
S6

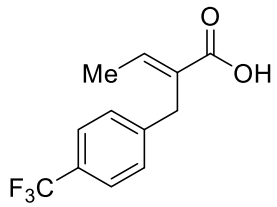

172.902
141.432
136.244
135.482
131.573
129.050
128.048
77.424
77.000
76.577
31.135
20.971
14.923
O
OH
Me
Me
180
160
140
120
100
80
60
40
20
0
ppm

S6

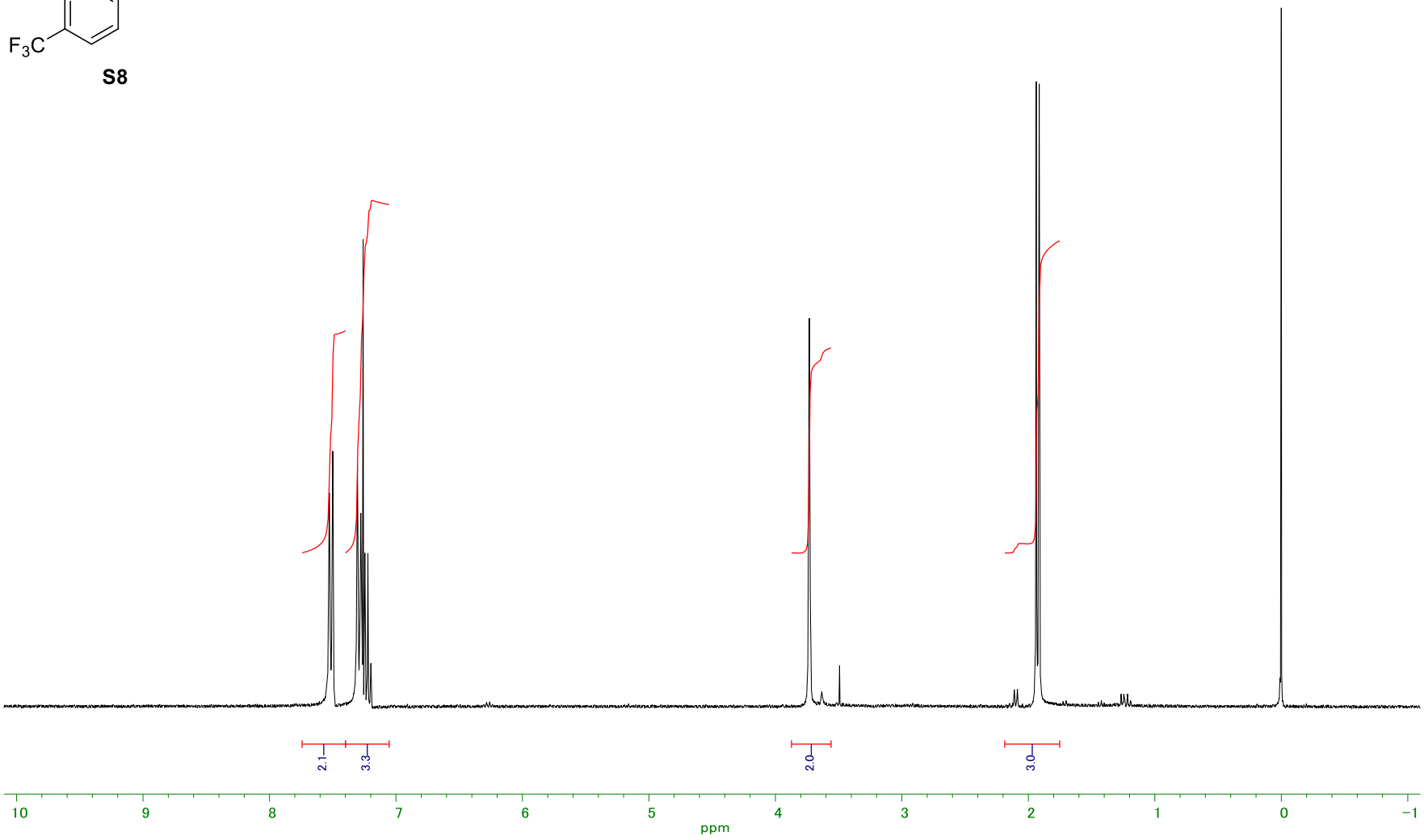


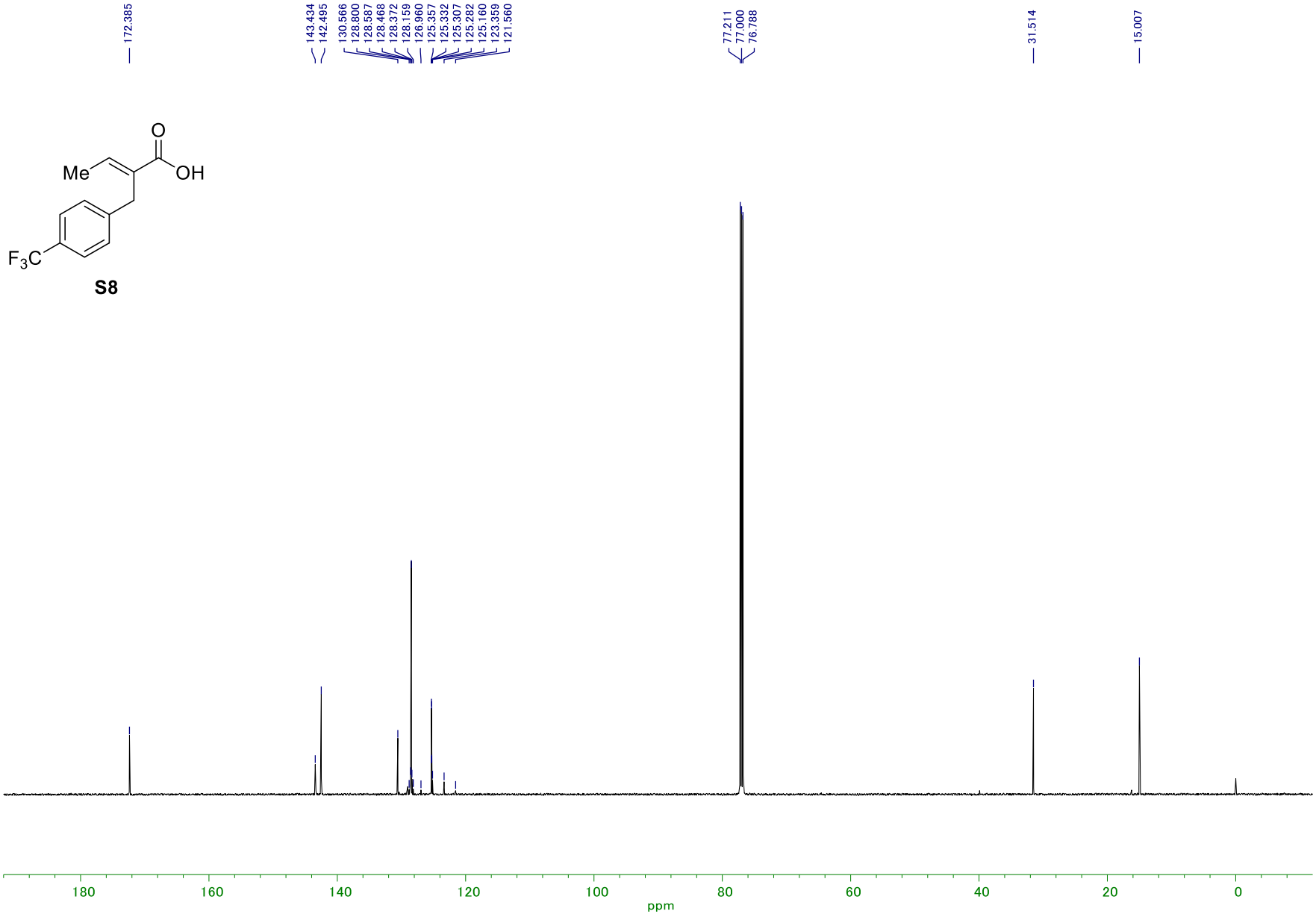
S7

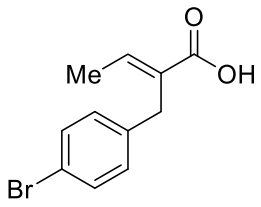

173.237
157.827
141.282
131.762
131.375
129.094
113.735
77.423
77.000
76.575
55.143
30.616
14.845
O
Me
OH
MeO
S7
180
160
140
120
100
80
60
40
20
0
ppm



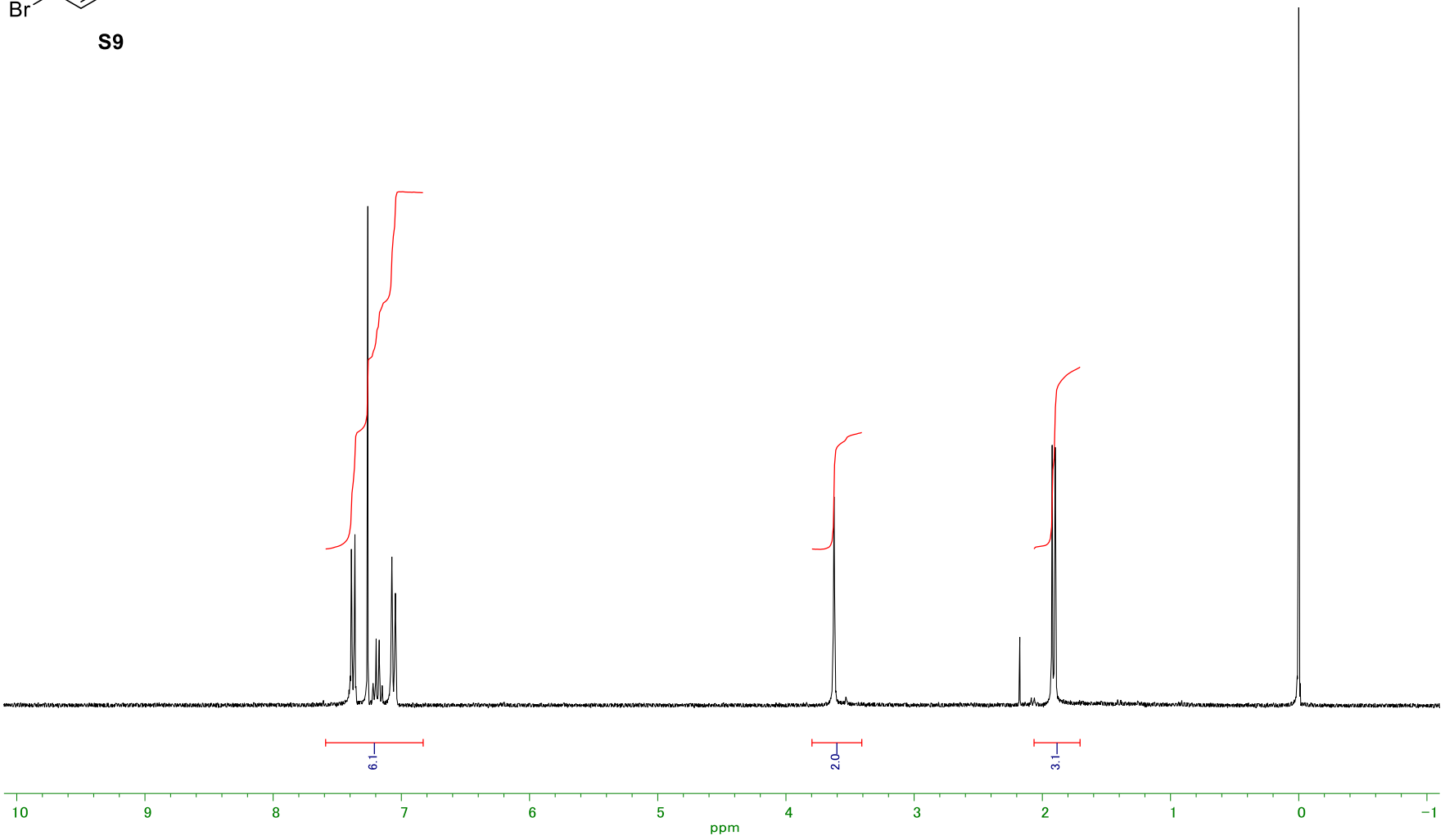
S8

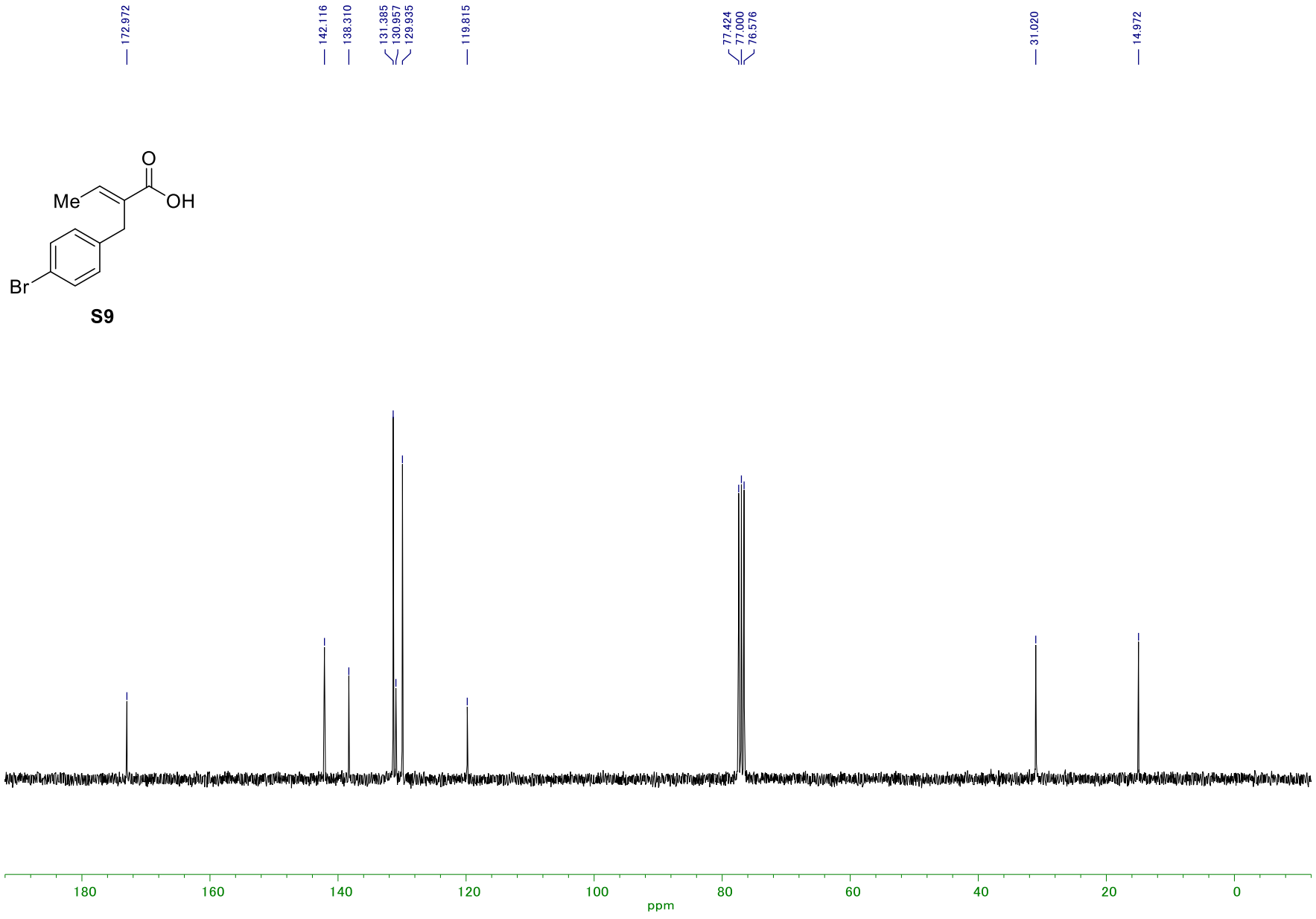



172.385
143.434
142.495
130.566
128.800
128.587
128.468
128.372
128.159
126.960
125.357
125.332
125.307
125.282
125.160
123.359
121.560
77.211
77.000
76.788
31.514
15.007
O
Me
OH
F3C
S8
180
160
140
120
100
80
60
40
20
0
ppm

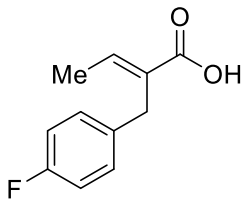


S9

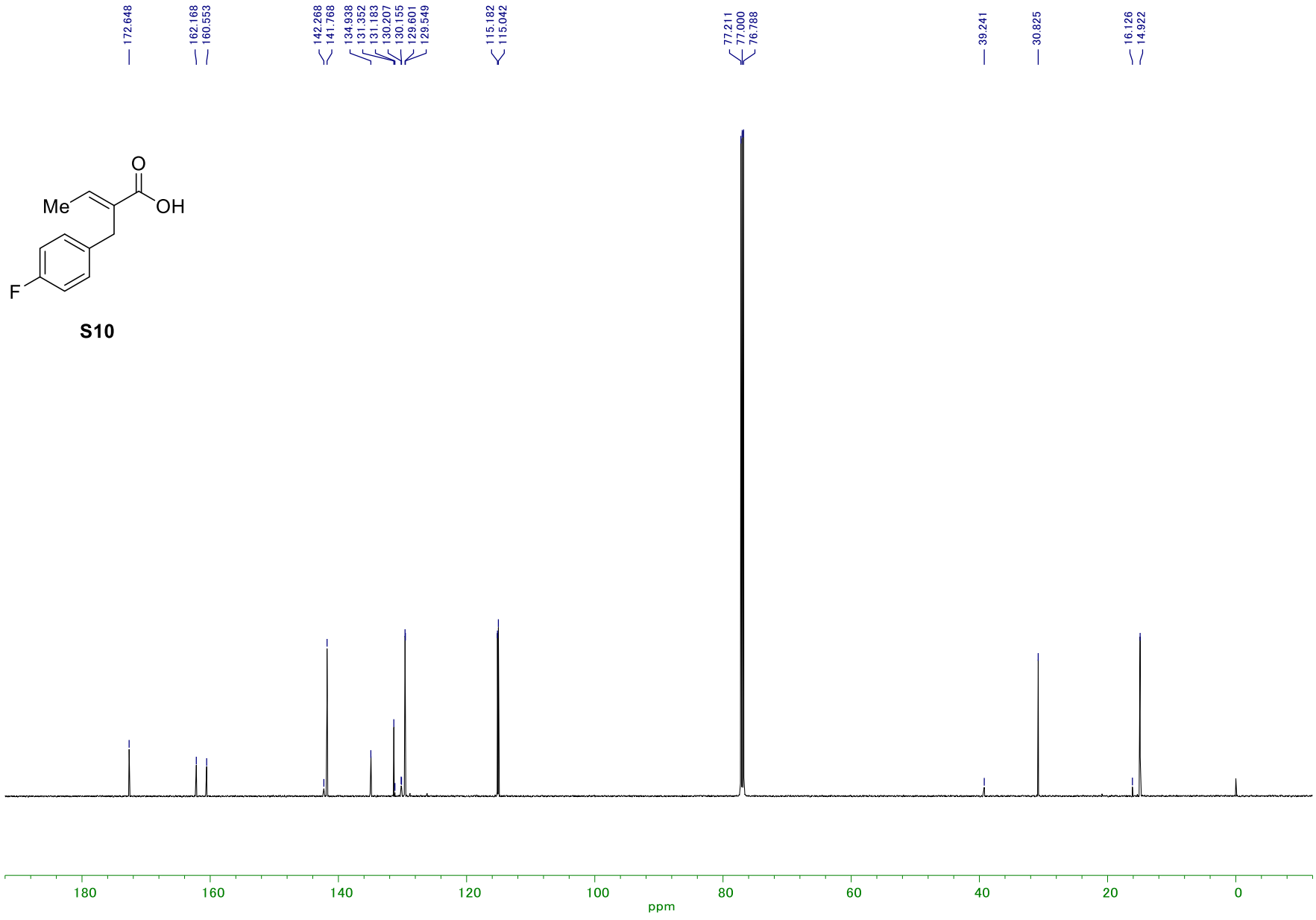



172.972
142.116
138.310
131.385
130.957
129.935
119.815
77.424
77.000
76.576
31.020
14.972
O
Me
OH
Br
180
160
140
120
100
80
60
40
20
0
ppm

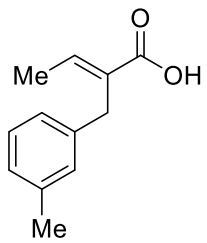
S9



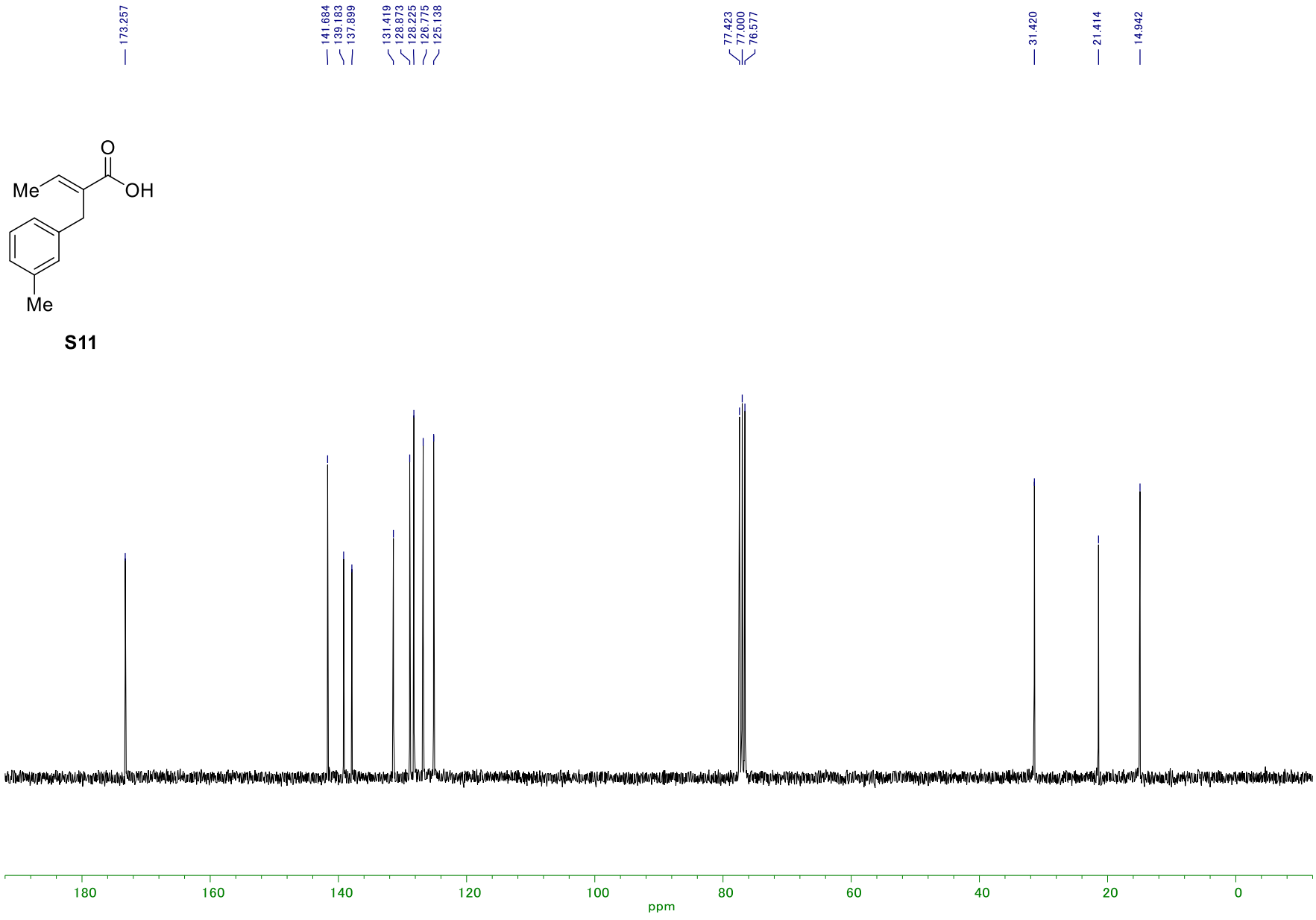
S10


172.648
162.168
160.553
142.268
141.768
134.938
131.352
131.183
130.207
130.155
129.601
129.549
115.182
115.042
77.211
77.000
76.788
39.241
30.825
16.126
14.922
O
Me
OH
F
180
160
140
120
100
80
60
40
20
0
ppm

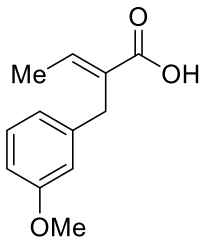
S10



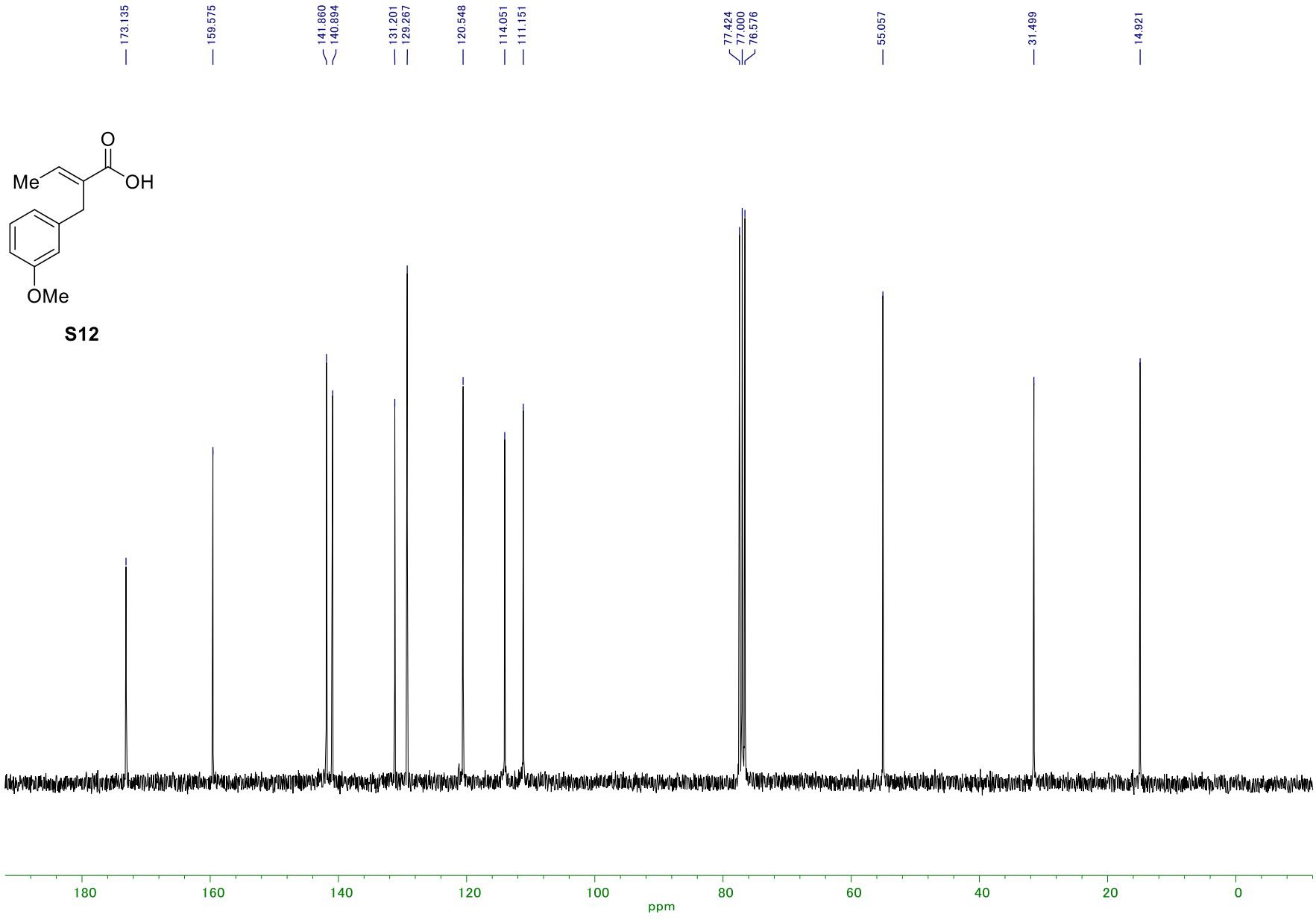
S11

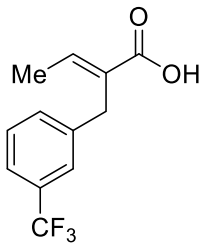

173.257
141.684
139.183
137.899
131.419
128.873
128.225
126.775
125.138
77.423
77.000
76.577
31.420
21.414
14.942
O
OH
Me
Me
180
160
140
120
100
80
60
40
20
0
ppm

S11

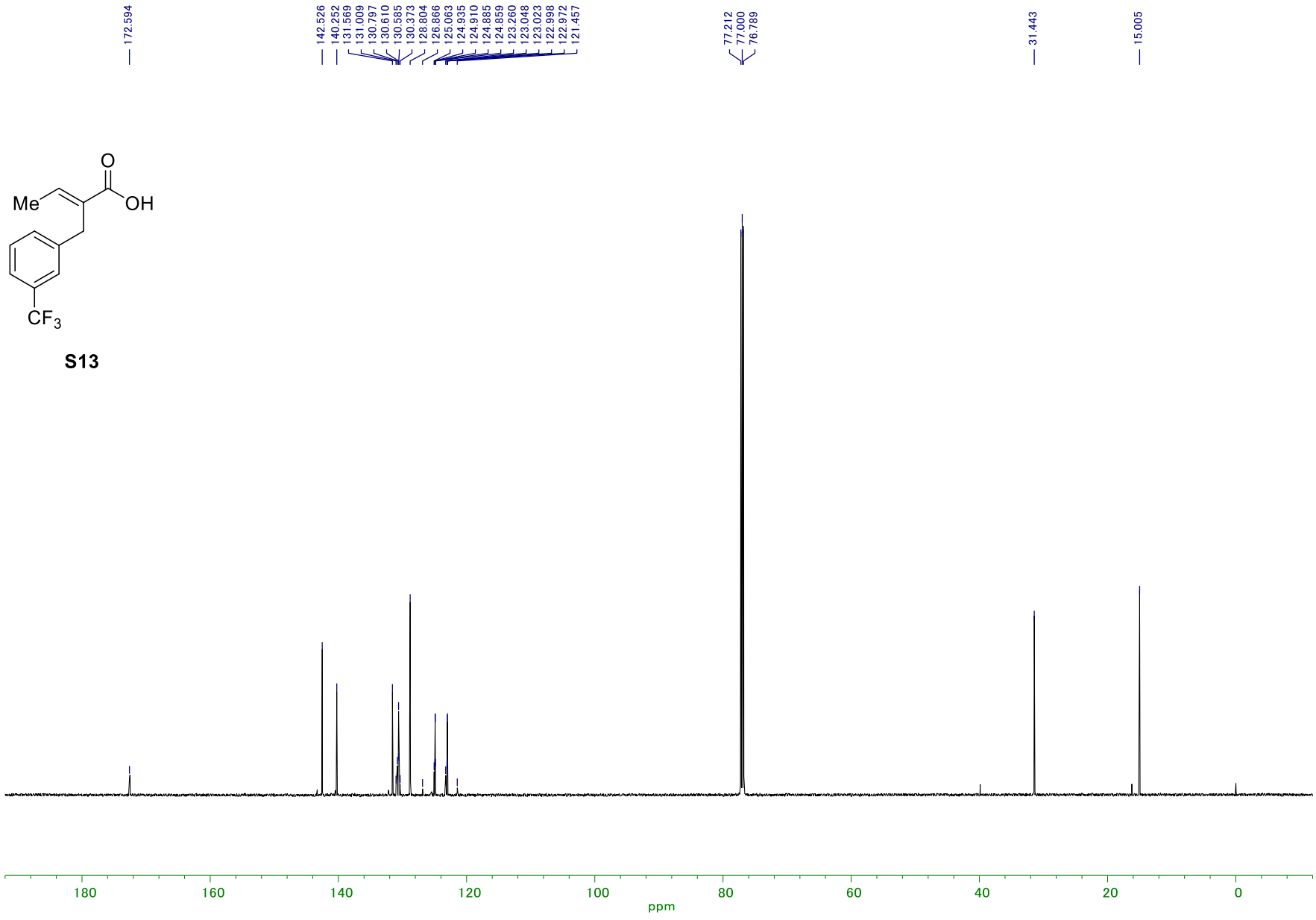


S12

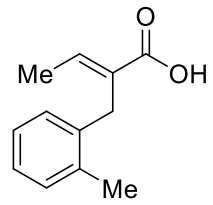

173.135
159.575
141.860
140.894
131.201
129.267
120.548
114.051
111.151
77.424
77.000
76.576
55.057
31.499
14.921
O
Me
OH
OMe
S12
180
160
140
120
100
80
60
40
20
0
ppm



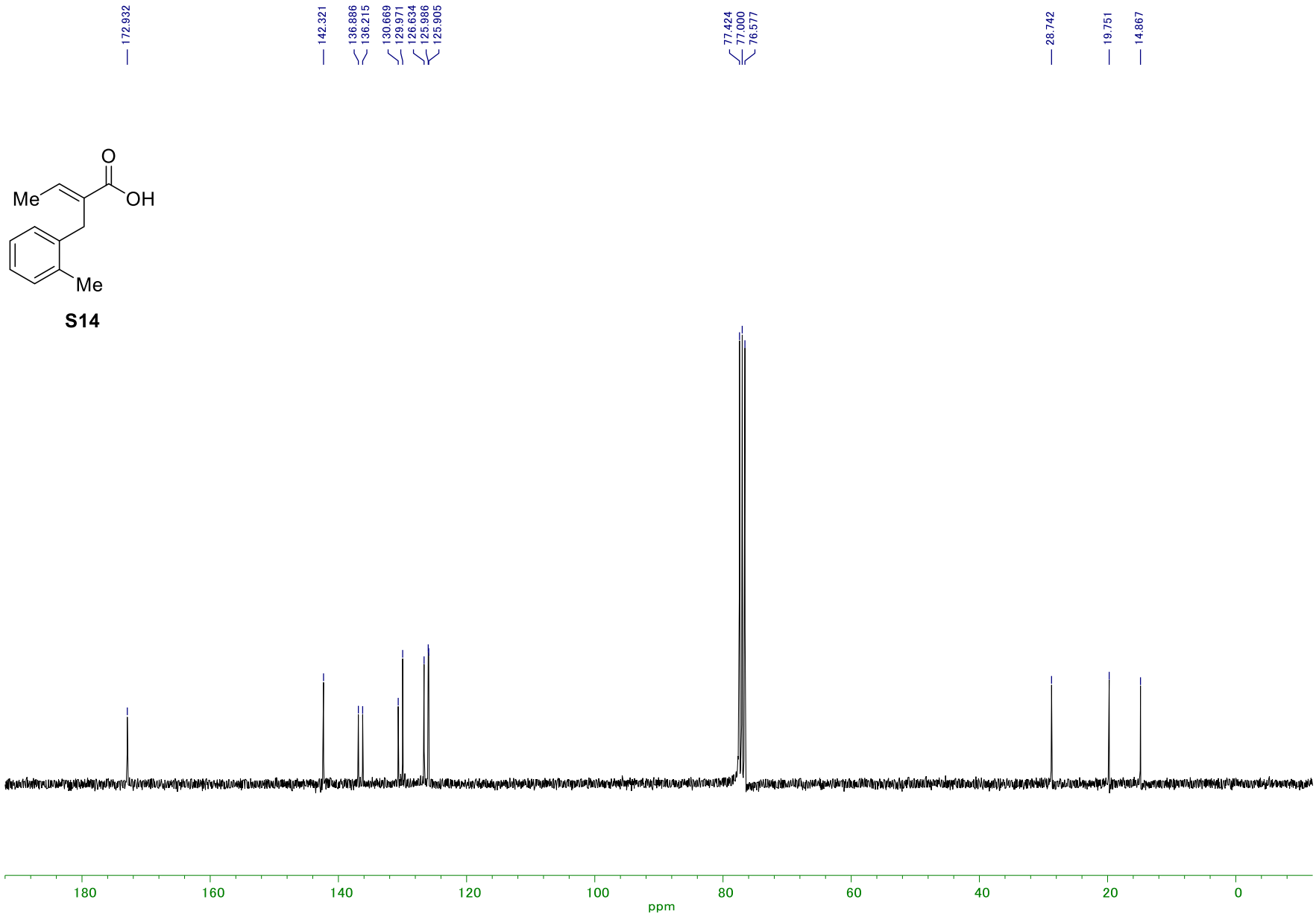
S13


172.594
142.526
140.252
131.569
131.009
130.797
130.610
130.585
130.373
128.804
126.866
125.063
124.935
124.910
124.885
124.859
123.260
123.048
123.023
122.998
122.972
121.457
77.212
77.000
76.789
31.443
15.005
O
Me
OH
CF3
180
160
140
120
100
80
60
40
20
0
ppm

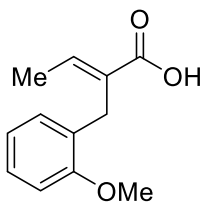
S13



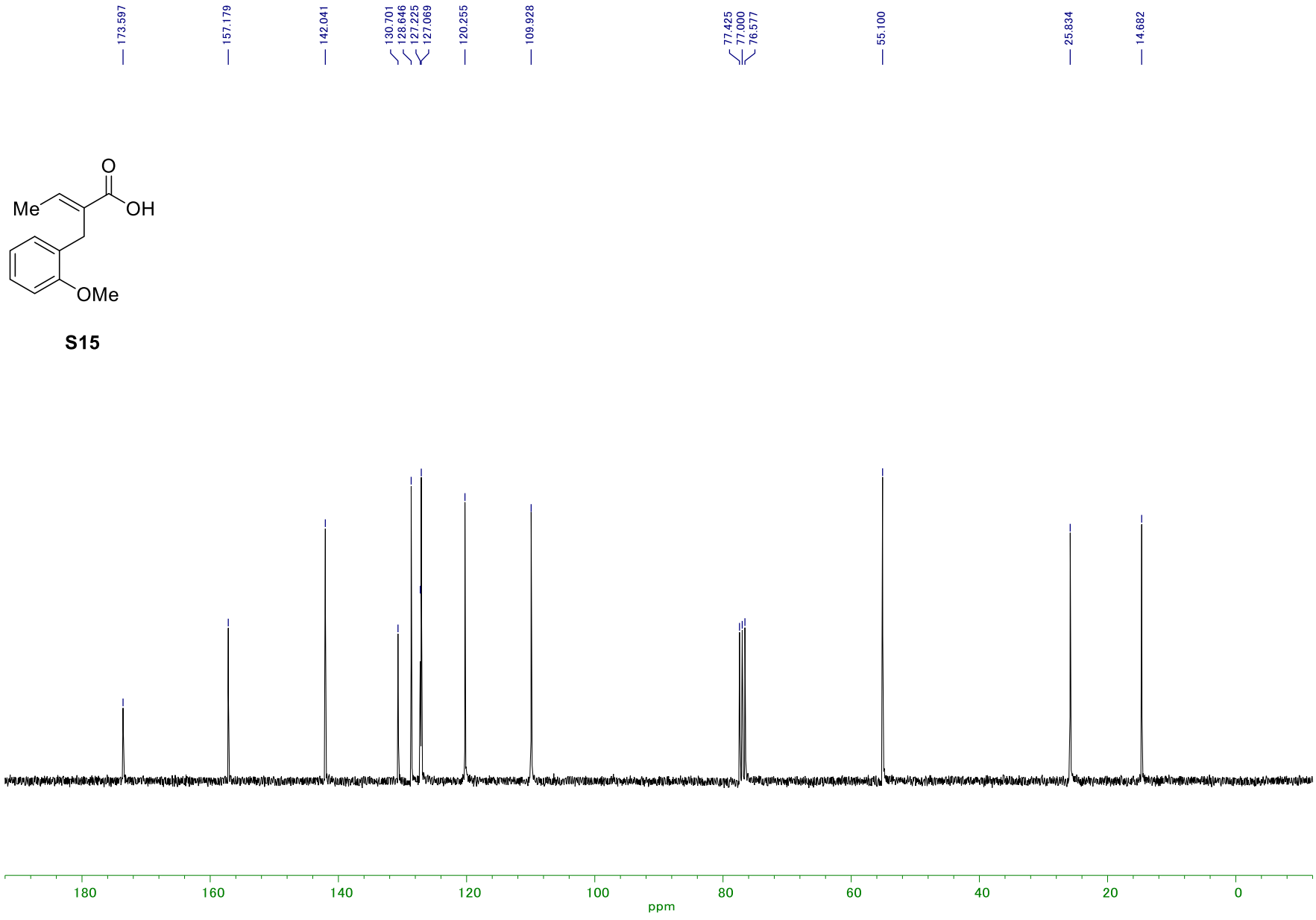
S14


172.932
142.321
136.886
136.215
130.669
129.971
126.634
125.986
125.905
77.424
77.000
76.577
28.742
19.751
14.867
O
OH
Me
Me
180
160
140
120
100
80
60
40
20
0
ppm

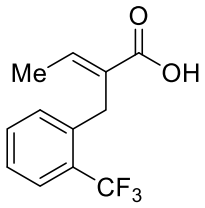
S14



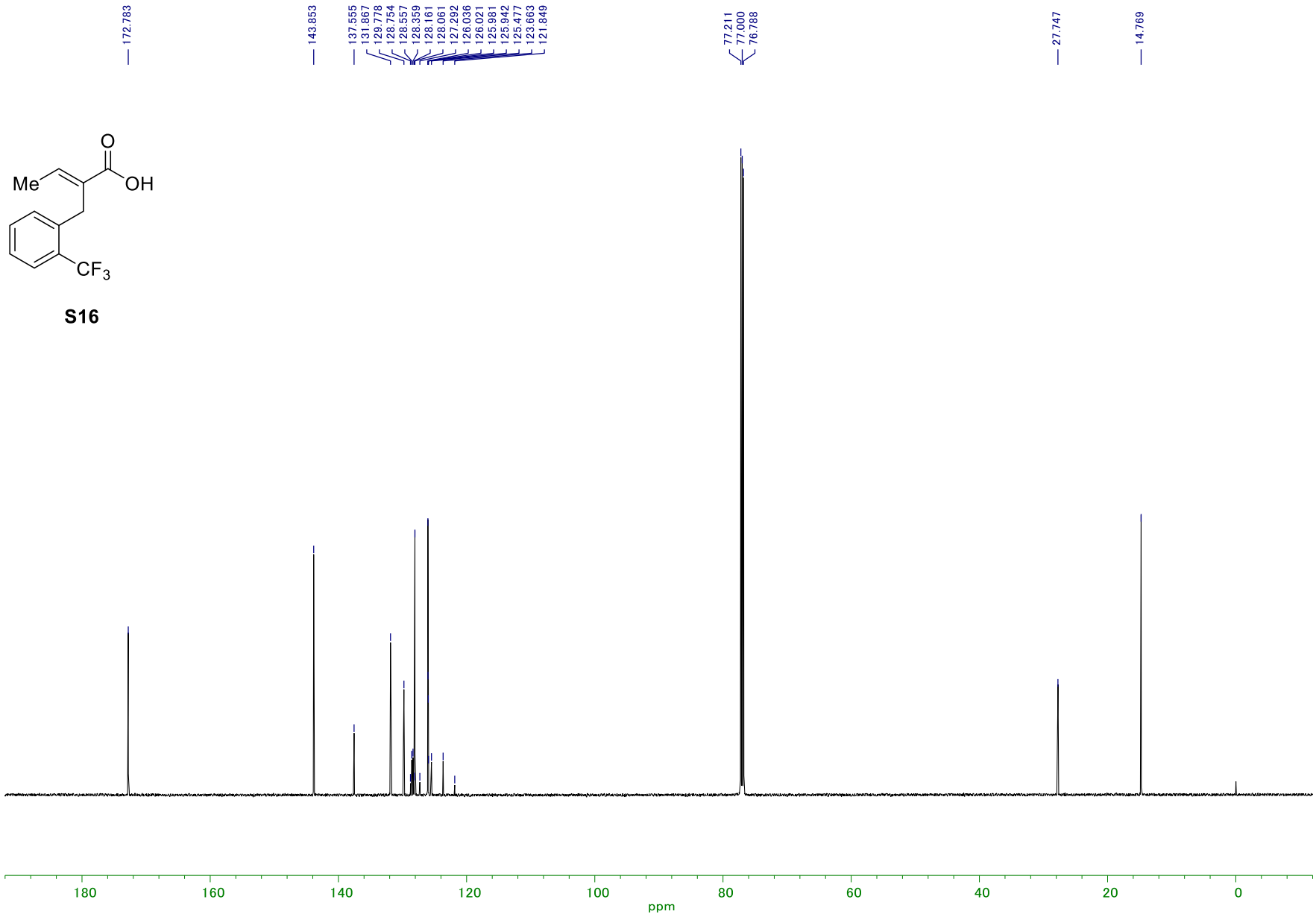
S15


173.597
157.179
142.041
130.701
128.646
127.225
127.069
120.255
109.928
77.425
77.000
76.577
55.100
25.834
14.682
O
Me
OH
OMe
180
160
140
120
100
80
60
40
20
0
ppm

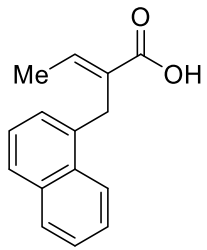
S15



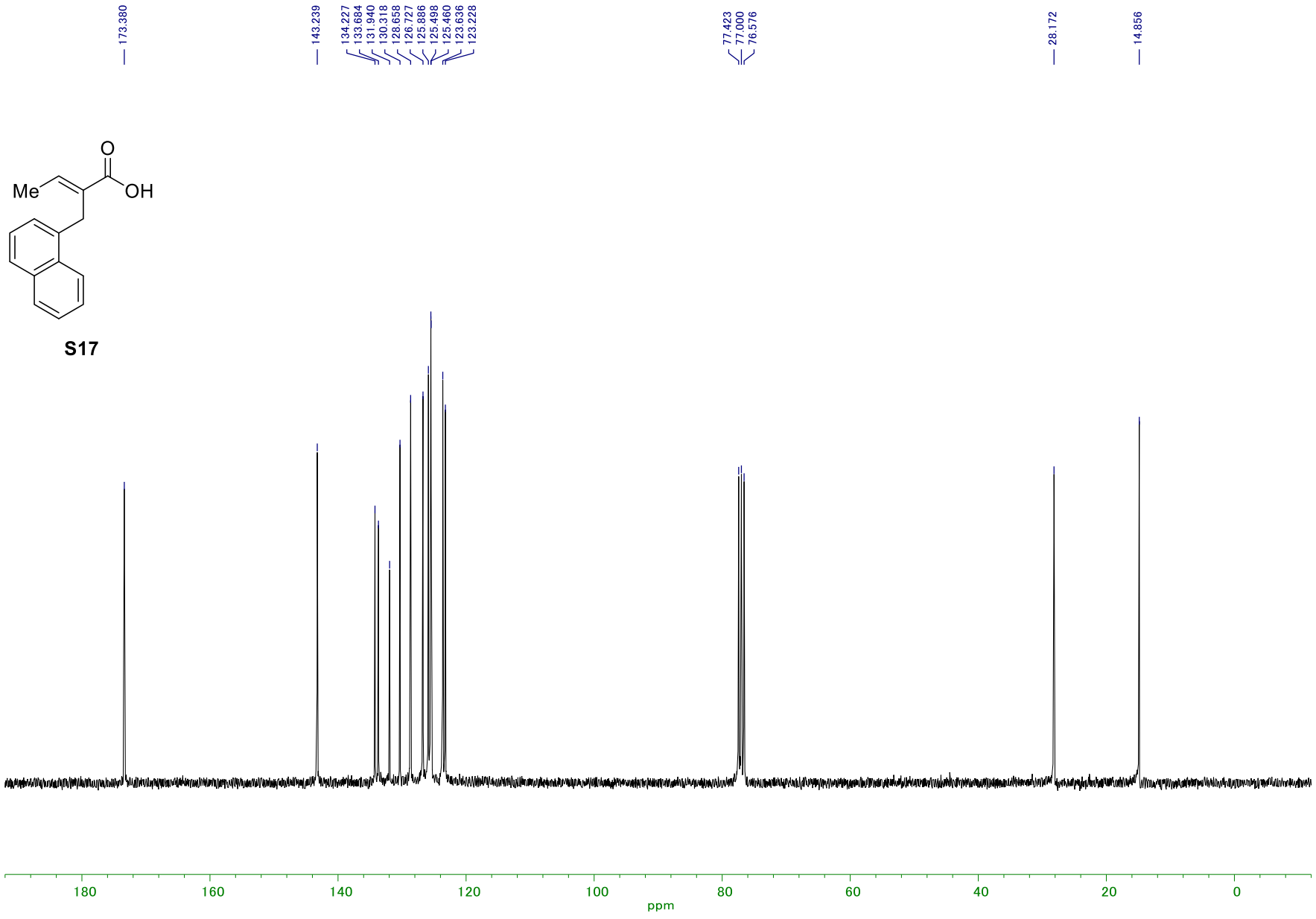
S16


172.783
143.853
137.555
131.867
129.778
128.754
128.557
128.359
128.161
128.061
127.292
126.036
126.021
125.981
125.942
125.477
123.663
121.849
77.211
77.000
76.788
27.747
14.769
O
OH
Me
CF3
180
160
140
120
100
80
60
40
20
0
ppm

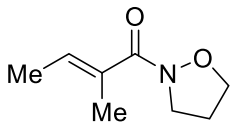
S16



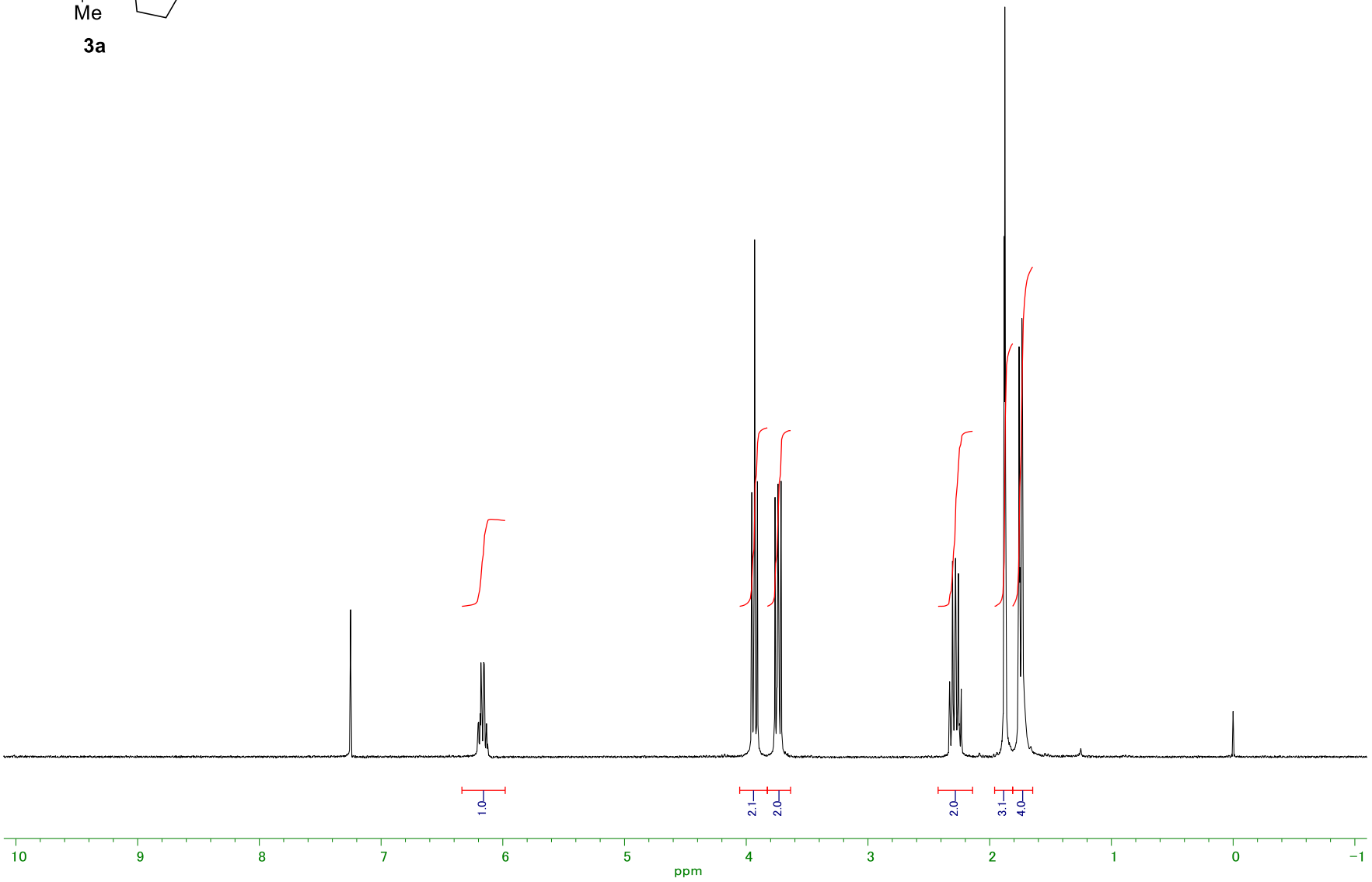
S17

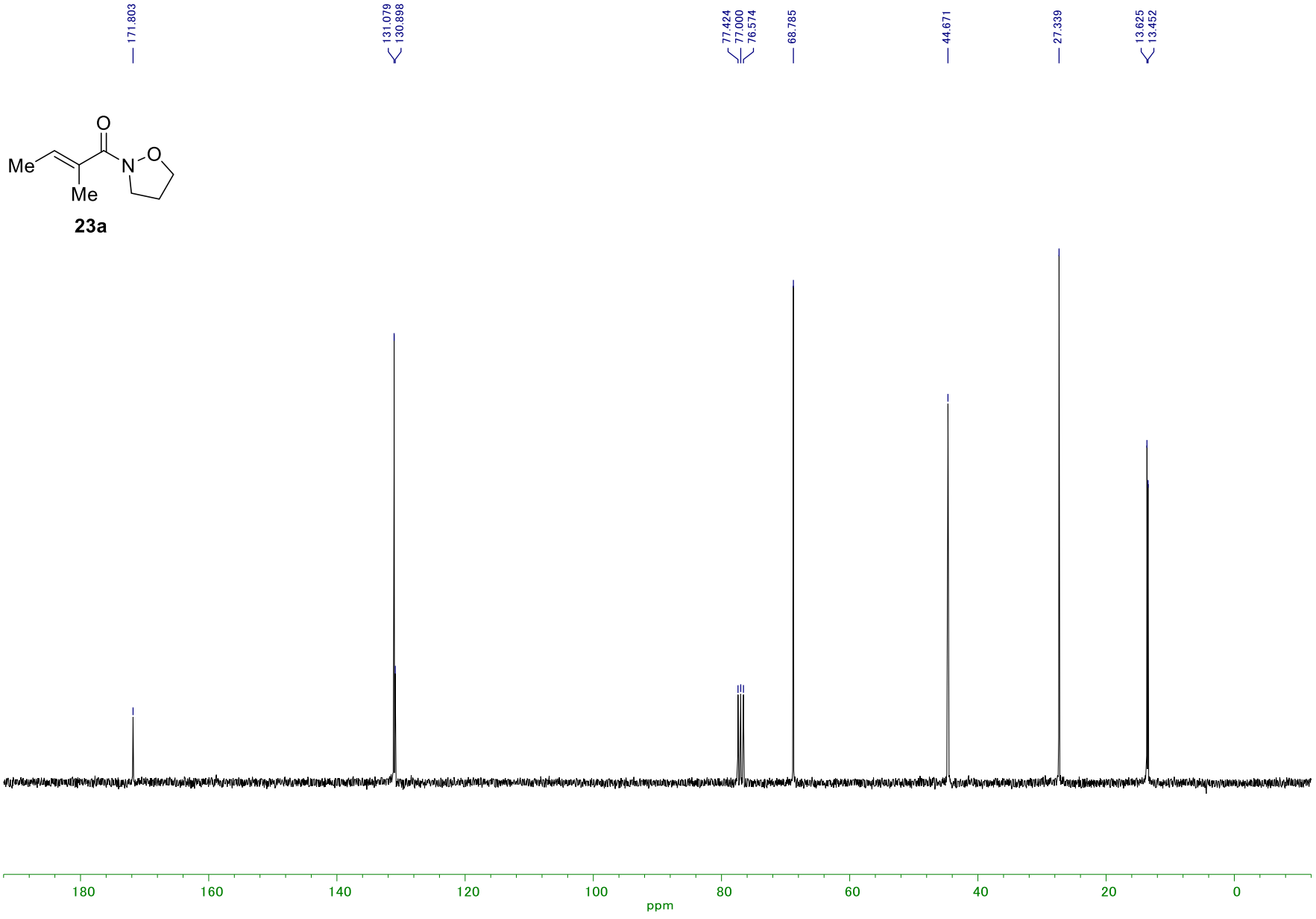

173.380
143.239
134.227
133.684
131.940
130.318
128.658
126.727
125.886
125.498
125.460
123.636
123.228
77.423
77.000
76.576
28.172
14.856
O
Me
OH
180
160
140
120
100
80
60
40
20
0
ppm

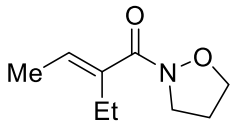
S17



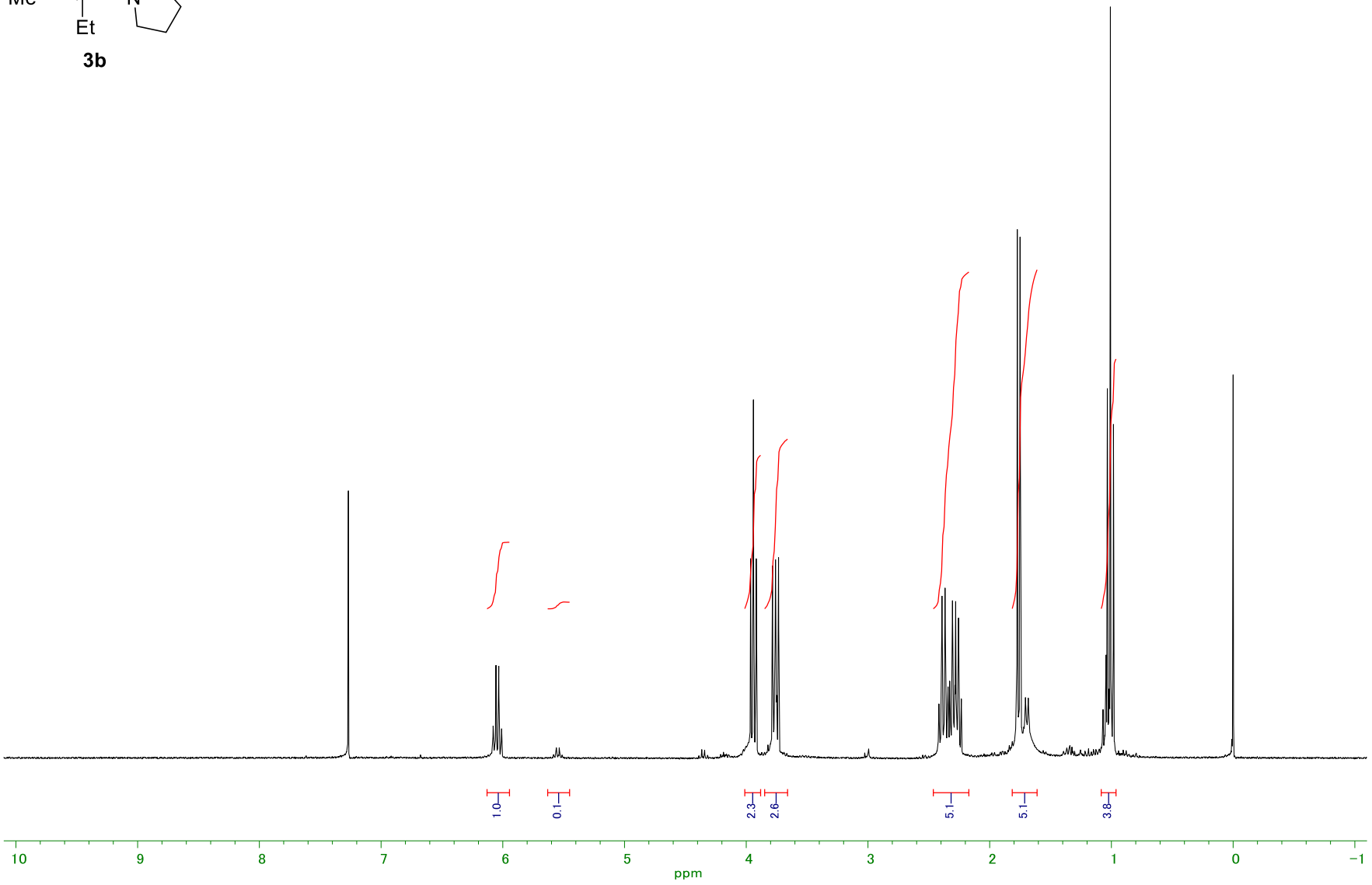
3a

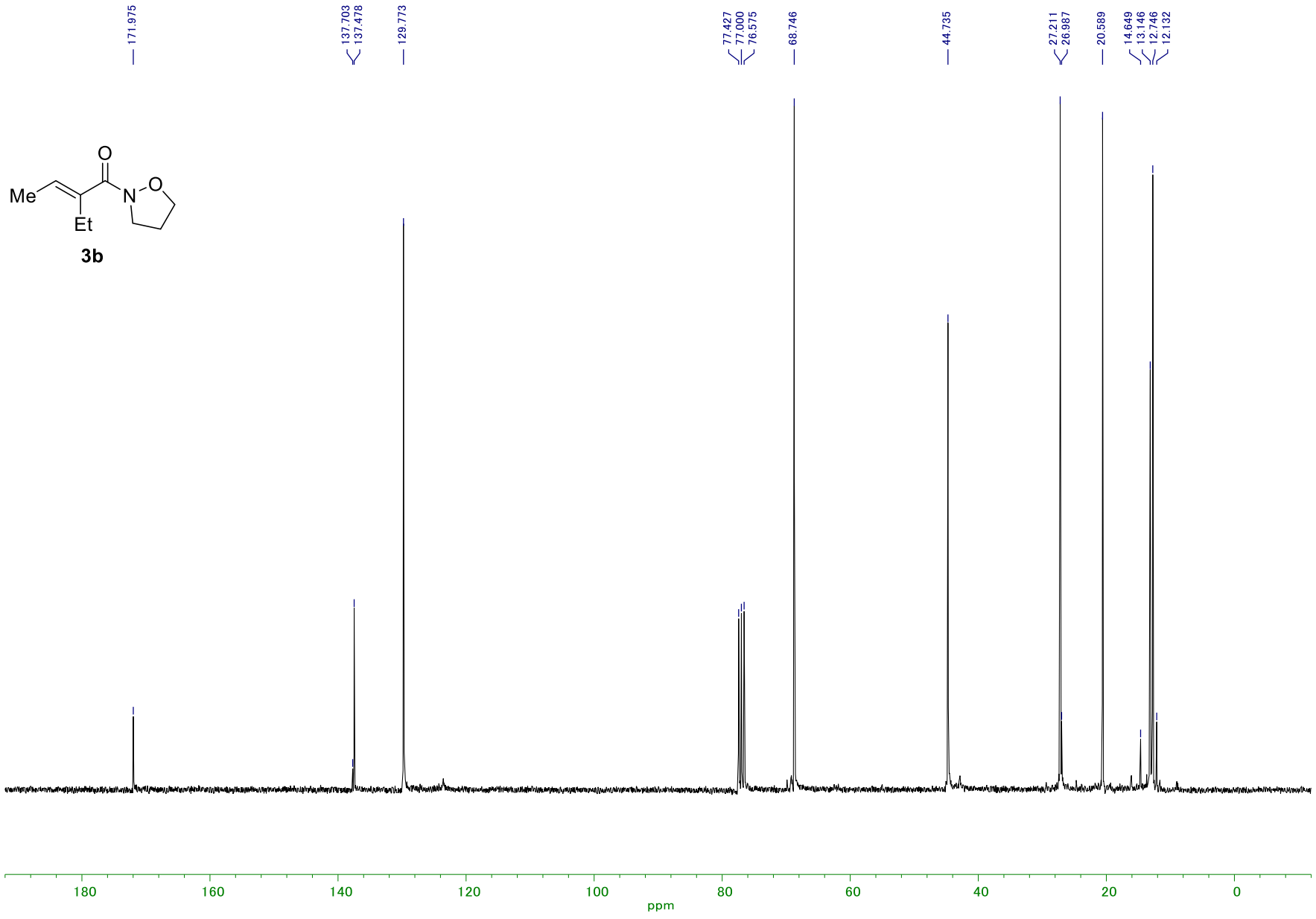


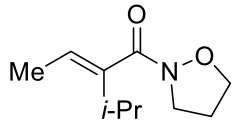

171.803
131.079
130.898
77.424
77.000
76.574
68.785
44.671
27.339
13.625
13.452
O
Me
N
O
Me
23a
180
160
140
120
100
80
60
40
20
0
ppm



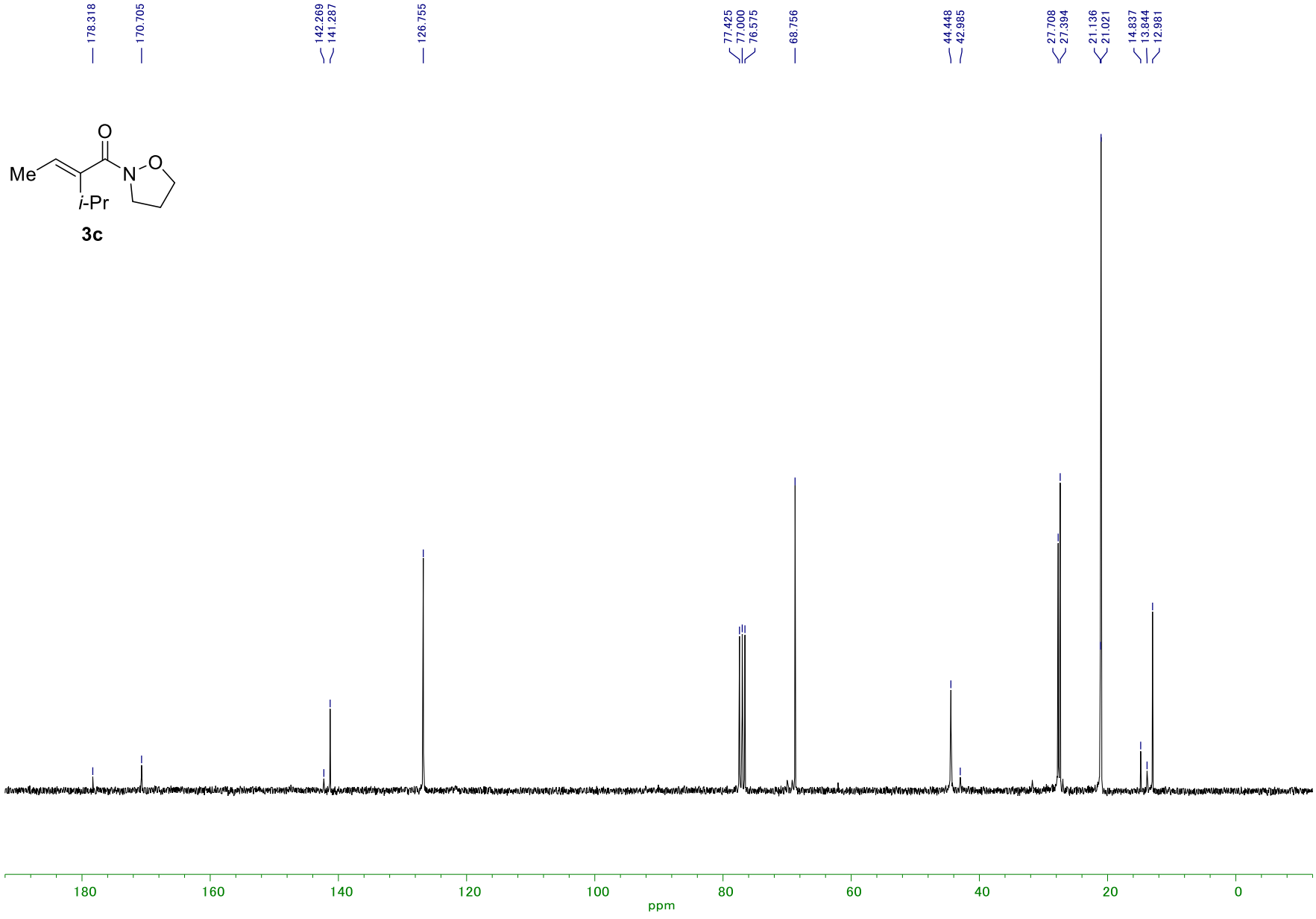
3b

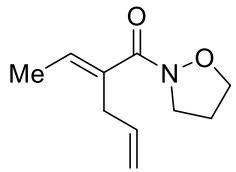



171.975
137.703
137.478
129.773
77.427
77.000
76.575
68.746
44.735
27.211
26.987
20.589
14.649
13.146
12.746
12.132
O
Me
N
O
Et
3b
180
160
140
120
100
80
60
40
20
0
ppm

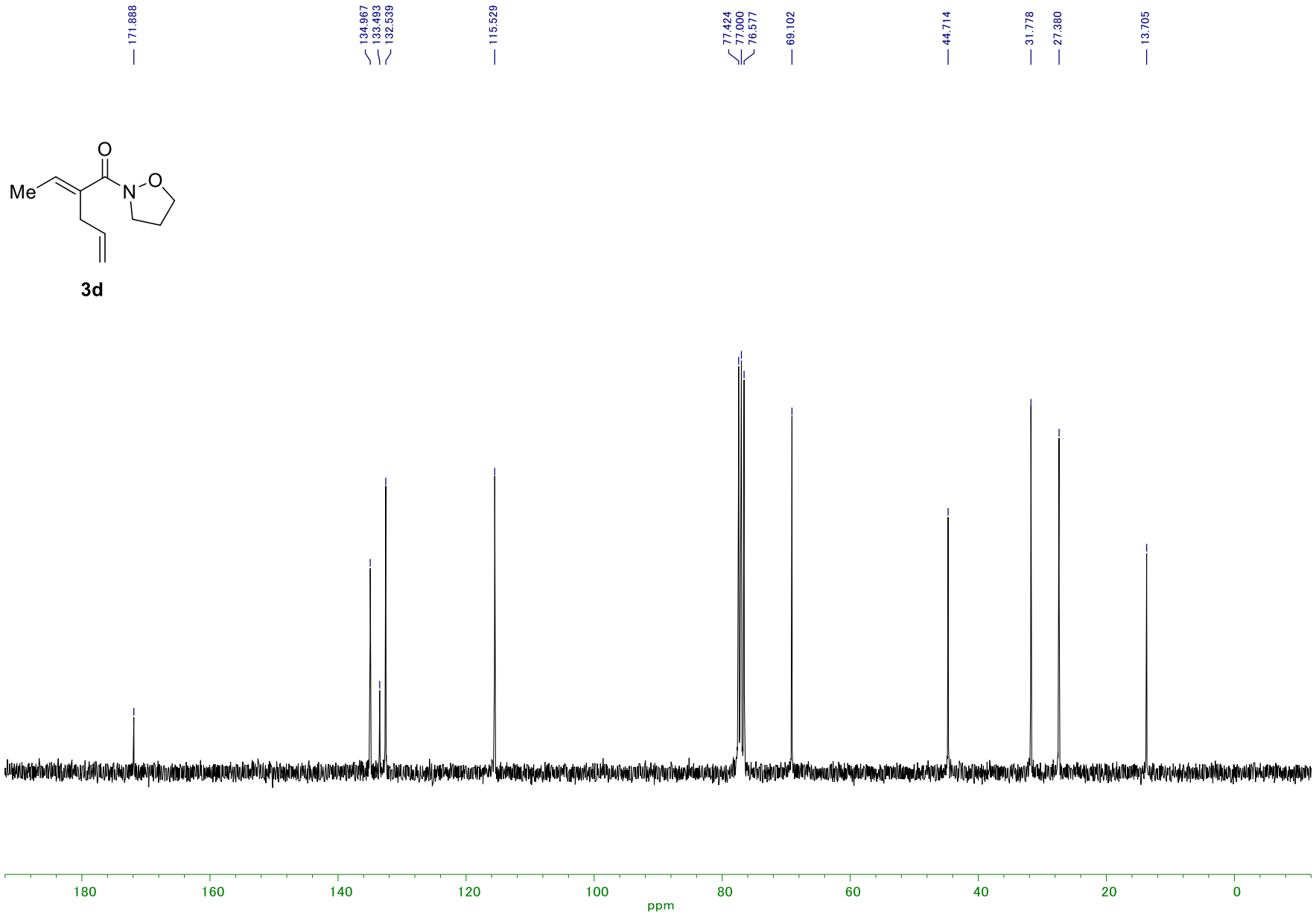


3c

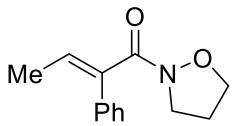

178.318
170.705
142.269
141.287
126.755
77.425
77.000
76.575
68.756
44.448
42.985
27.708
27.394
21.136
21.021
14.837
13.844
12.981
O
Me
N
O
i-Pr
3c
180
160
140
120
100
80
60
40
20
0
ppm



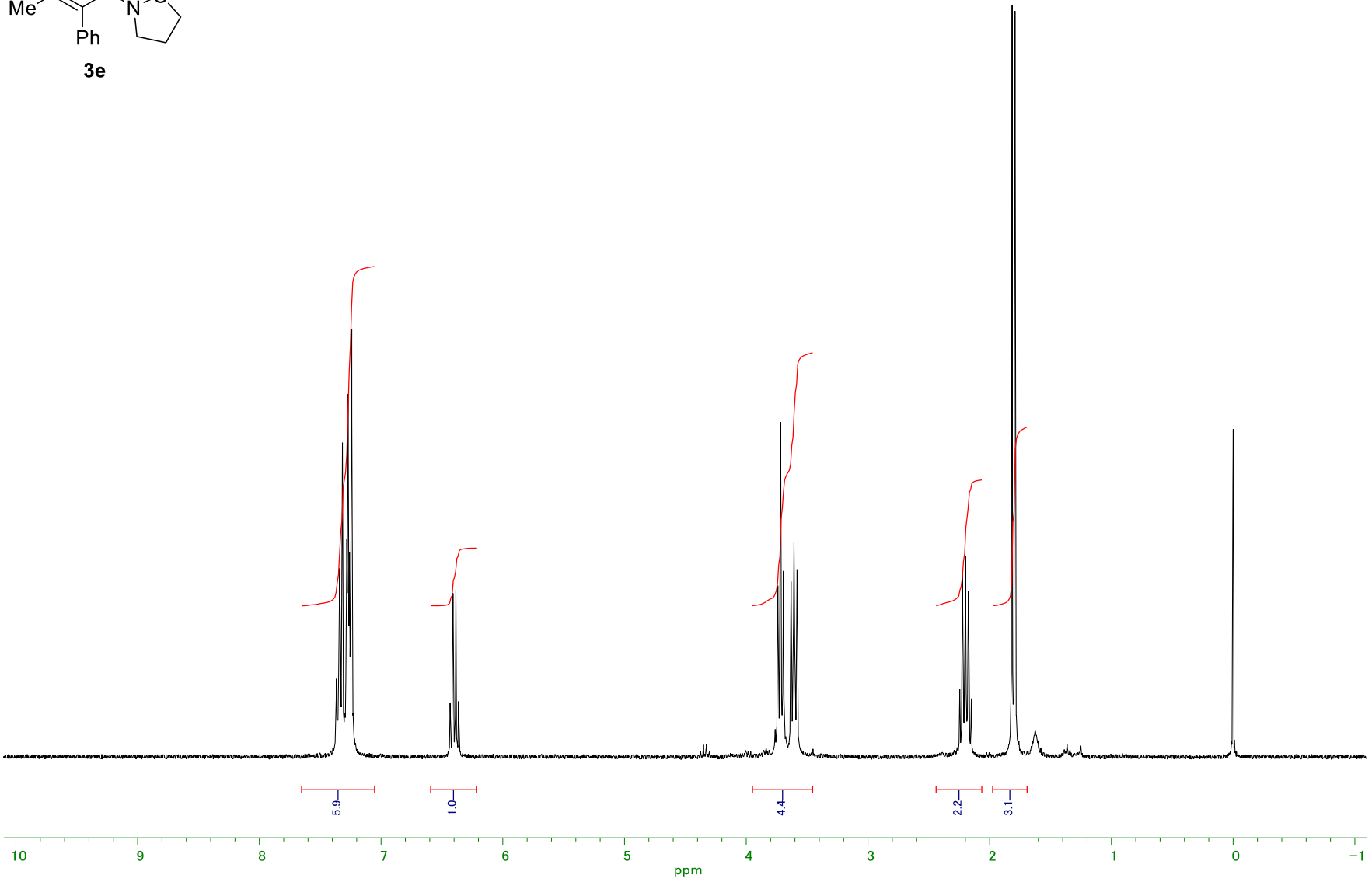
3d

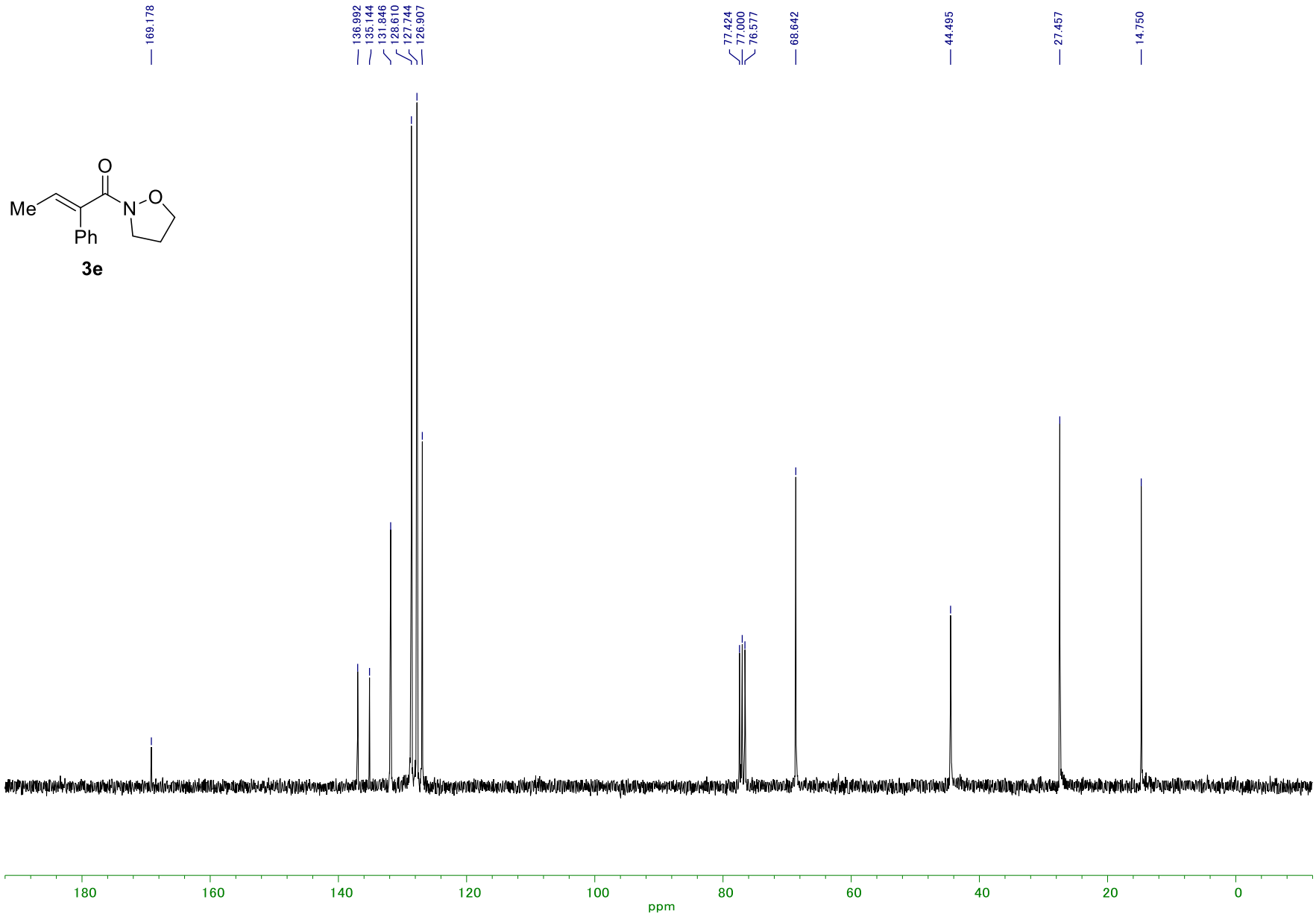

171.888
134.967
133.493
132.539
115.529
77.424
77.000
76.577
69.102
44.714
31.778
27.380
13.705
O
Me
N
O
180
160
140
120
100
80
60
40
20
0
ppm

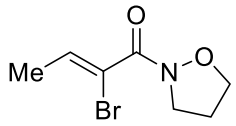
3d



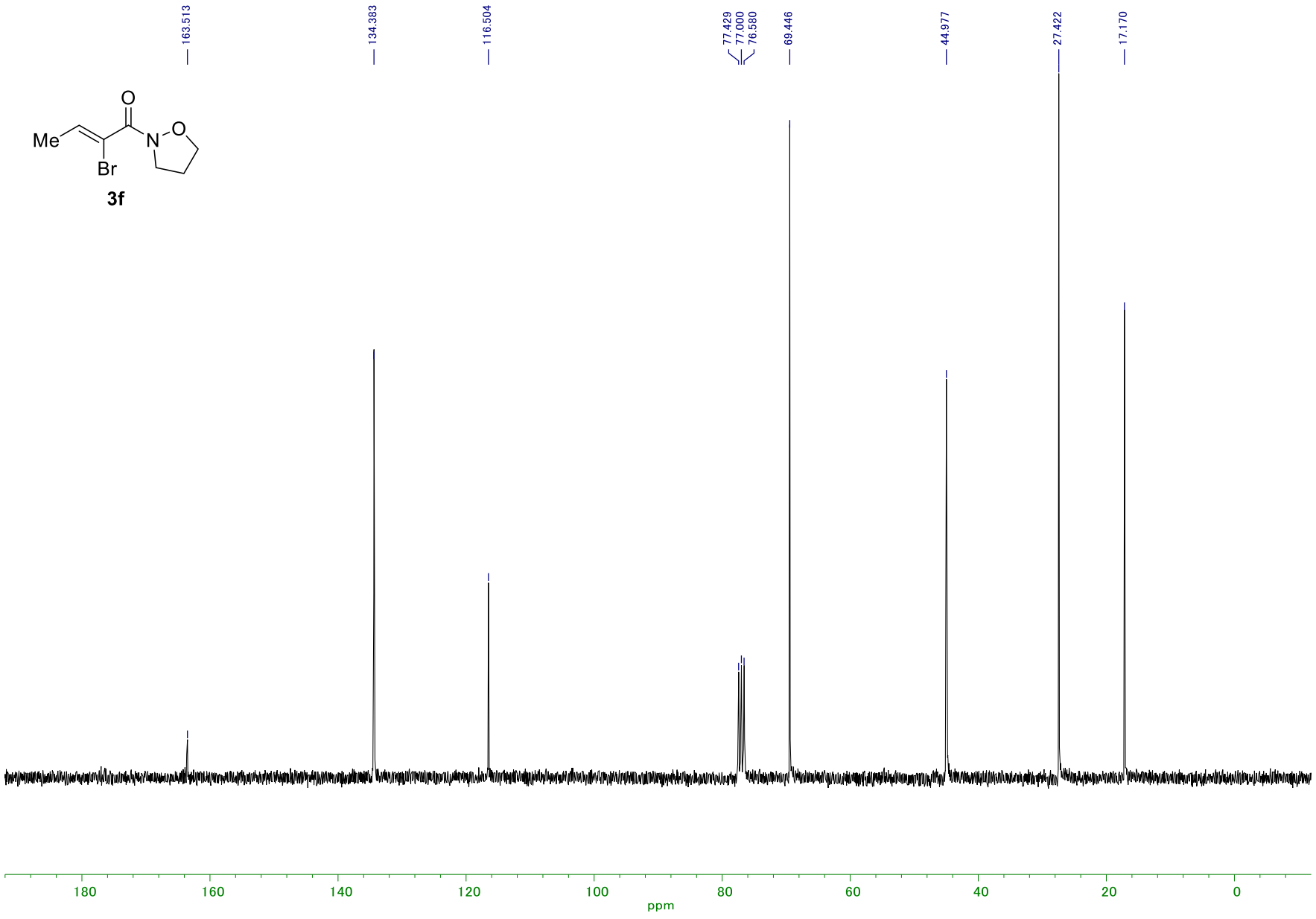
3e

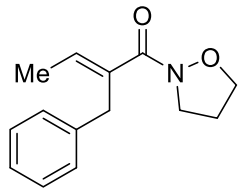



169.178
136.992
135.144
131.846
128.610
127.744
126.907
77.424
77.000
76.577
68.642
44.495
27.457
14.750
O
Me
N
O
Ph
3e
180
160
140
120
100
80
60
40
20
0
ppm

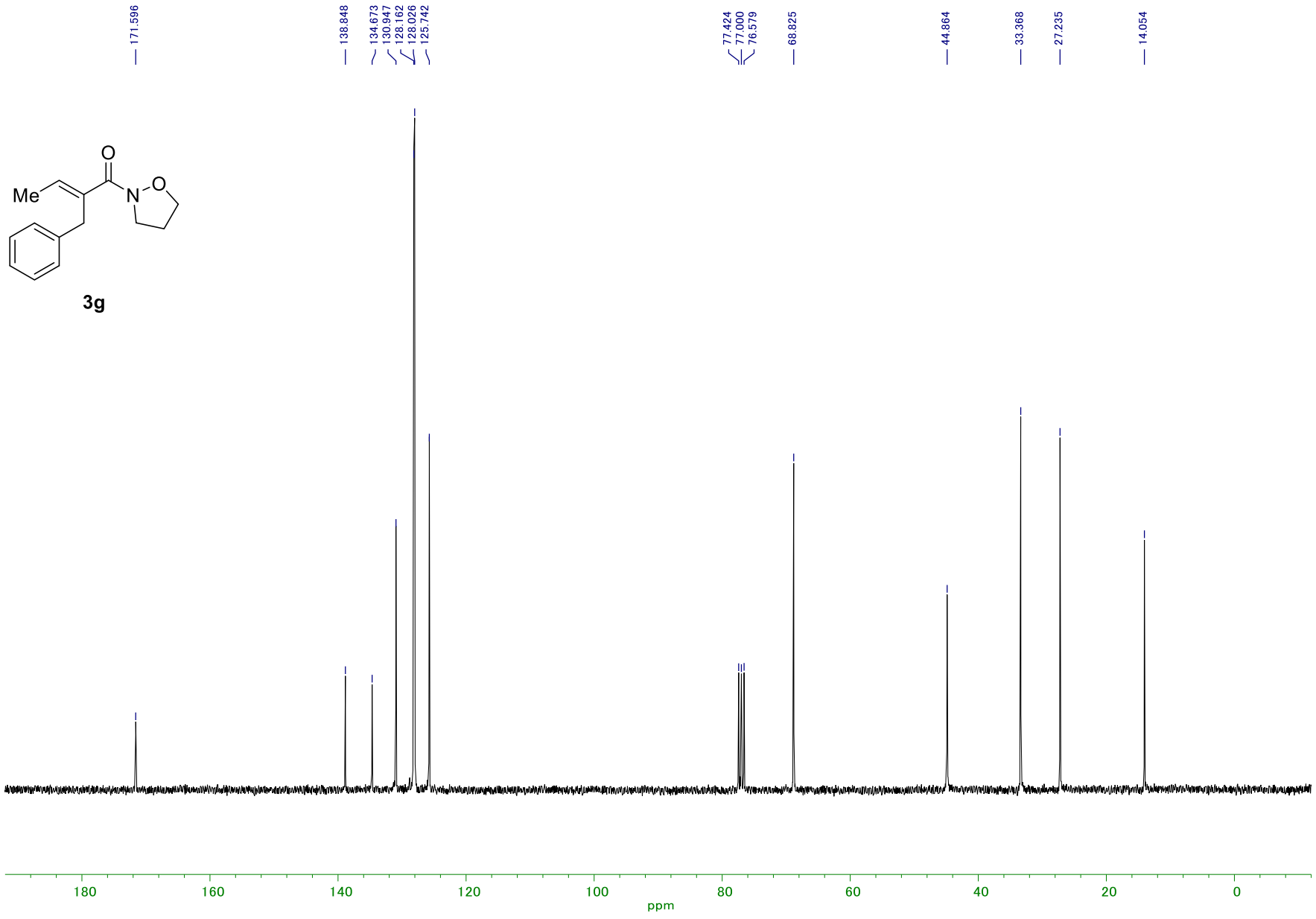


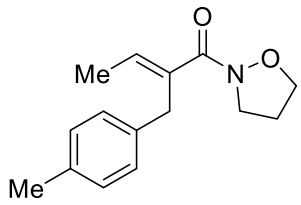
3f


163.513
134.383
116.504
77.429
77.000
76.580
69.446
44.977
27.422
17.170
O
Me
N
O
Br
3f
180
160
140
120
100
80
60
40
20
0
ppm

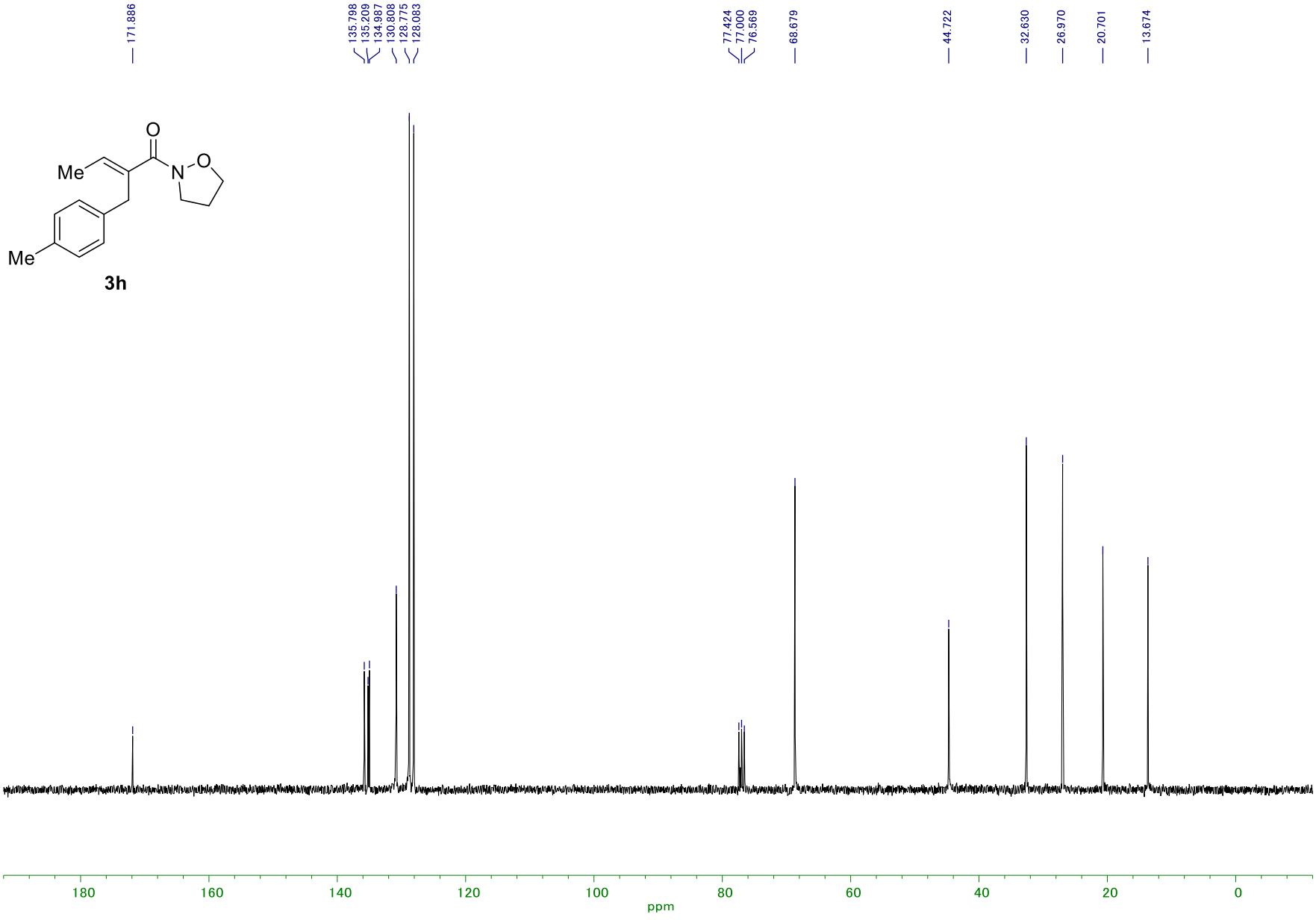


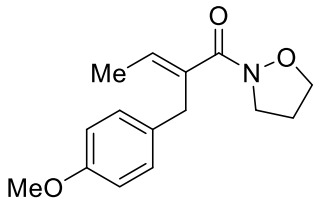
3g


171.596
138.848
134.673
130.947
128.162
128.026
125.742
77.424
77.000
76.579
68.825
44.864
33.368
27.235
14.054
O
Me
N
O
3g
180
160
140
120
100
80
60
40
20
0
ppm

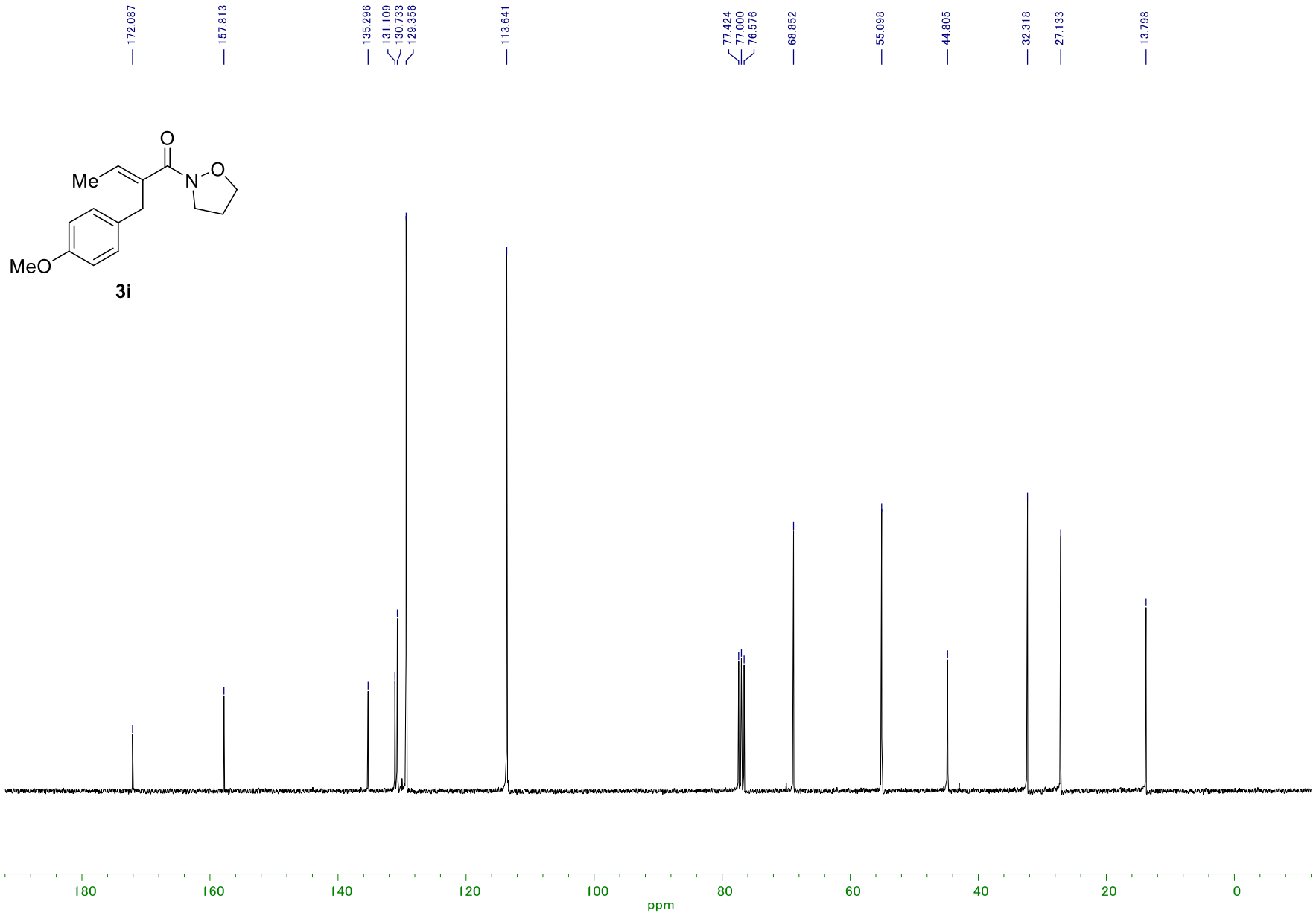


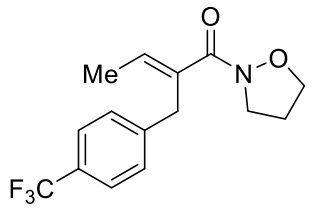
3h


171.886
135.798
135.209
134.987
130.808
128.775
128.083
77.424
77.000
76.569
68.679
44.722
32.630
26.970
20.701
13.674
O
Me
N
O
Me
3h
180
160
140
120
100
80
60
40
20
0
ppm

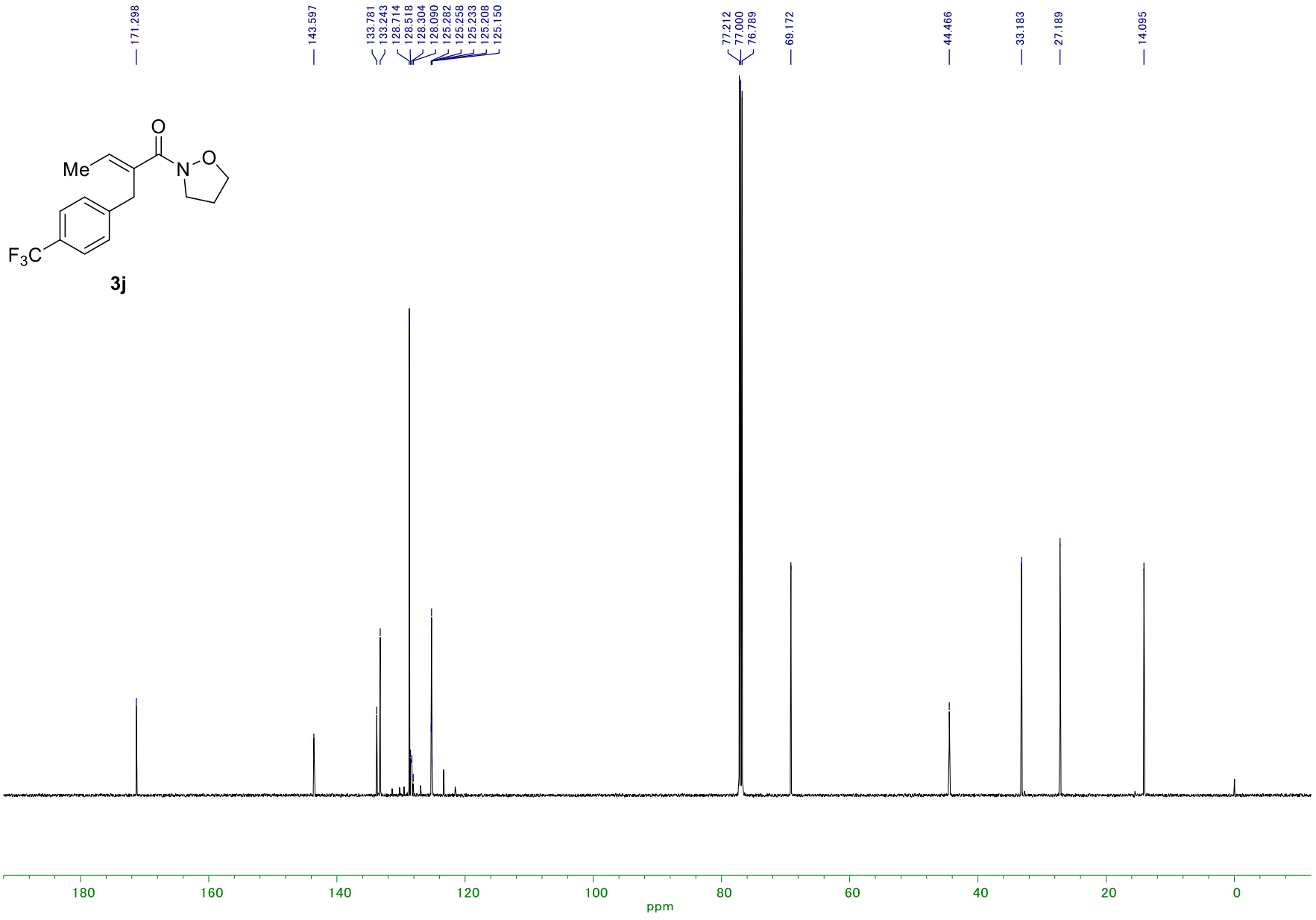


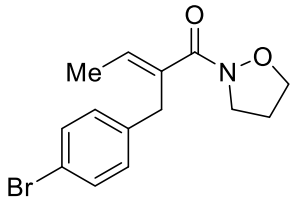
3i


172.087
157.813
135.296
131.109
130.733
129.356
113.641
77.424
77.000
76.576
68.852
55.098
44.805
32.318
27.133
13.798
O
Me
N
O
MeO
3i
180
160
140
120
100
80
60
40
20
0
ppm

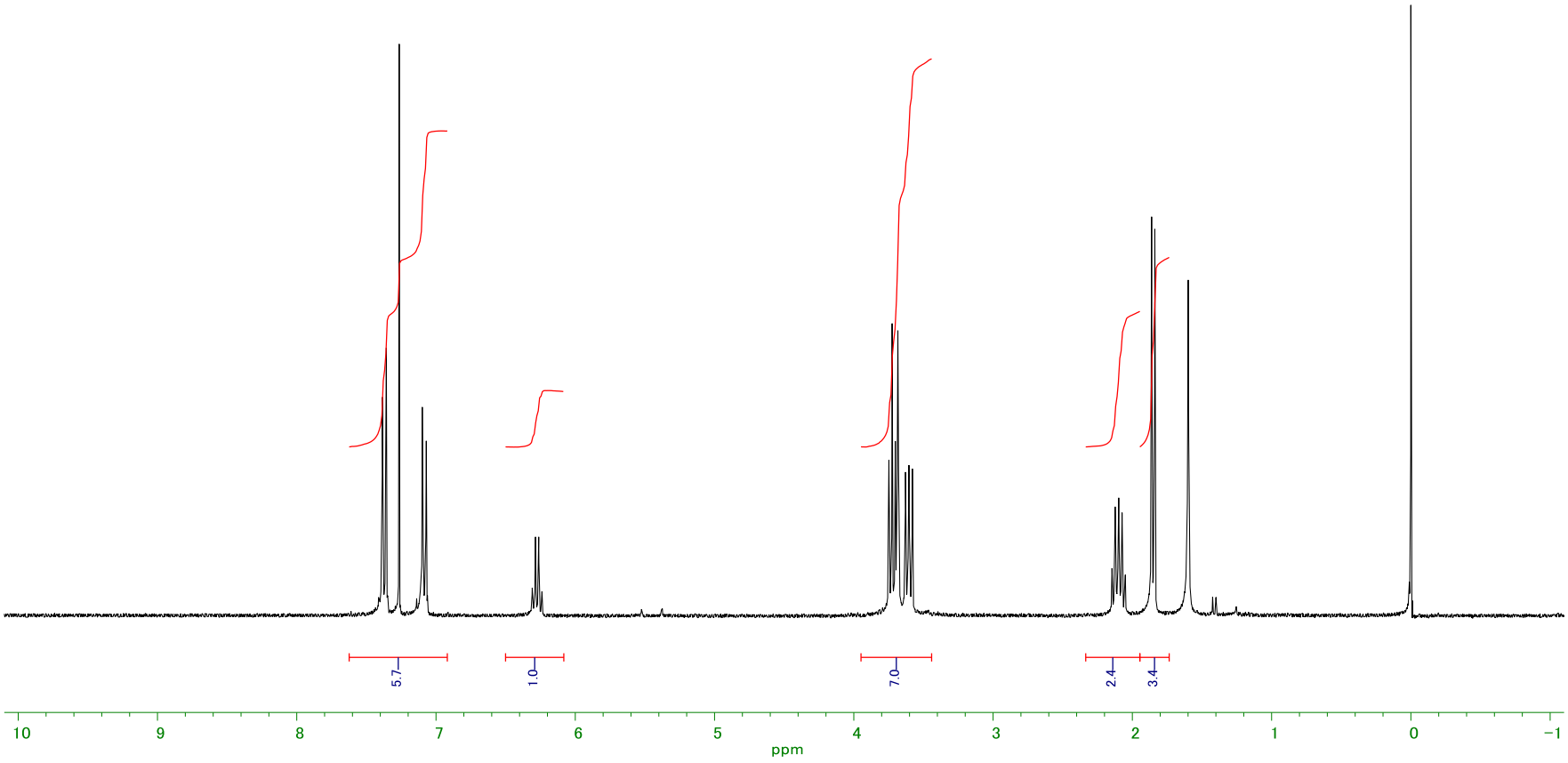


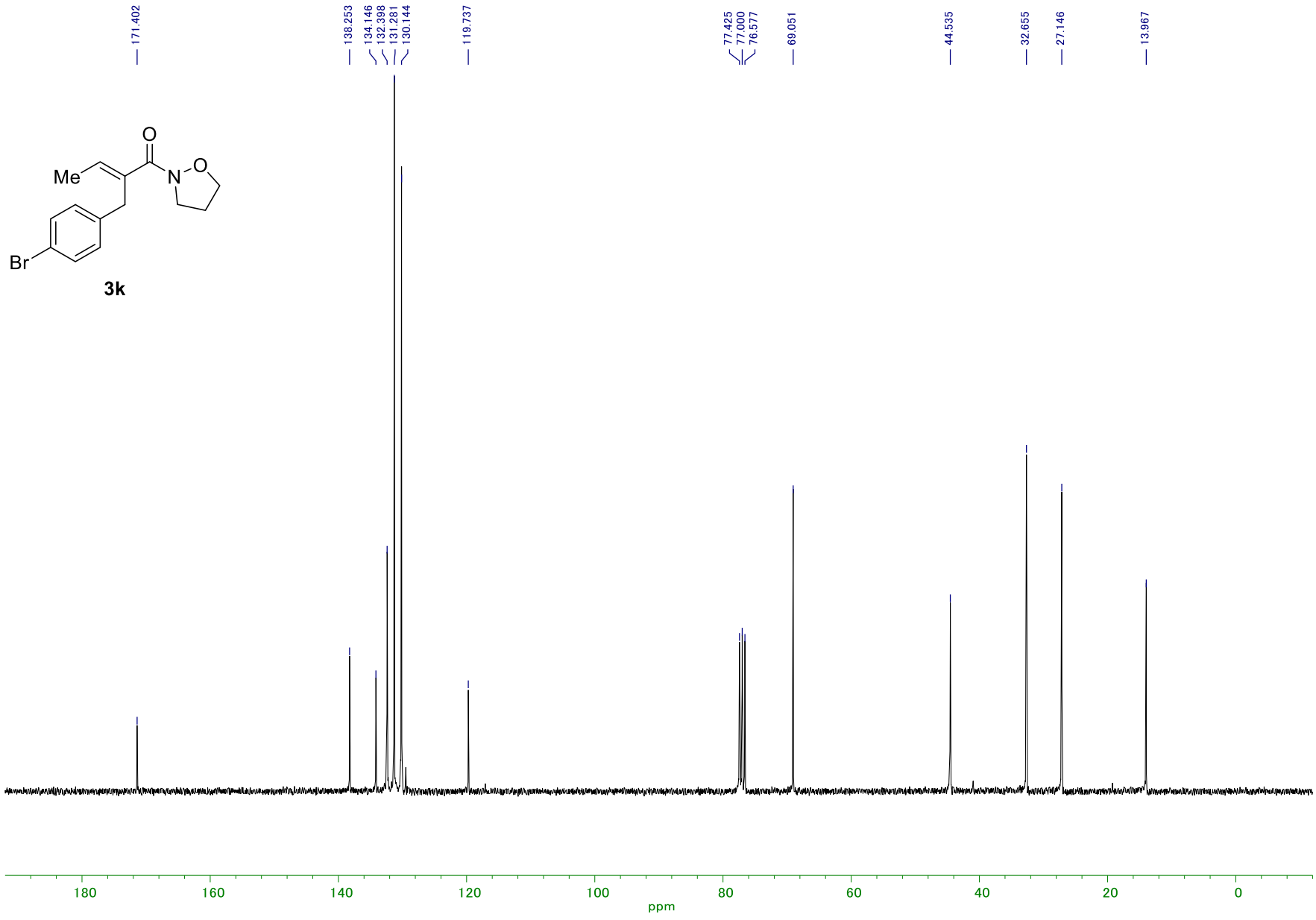
3j

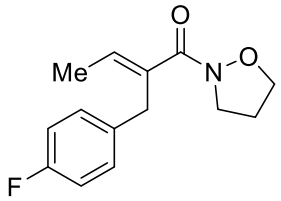

171.298
143.597
133.781
133.243
128.714
128.518
128.304
128.090
125.282
125.258
125.233
125.208
125.150
77.212
77.000
76.789
69.172
44.466
33.183
27.189
14.095
O
Me
N
O
F3C
3j
180
160
140
120
100
80
60
40
20
0
ppm



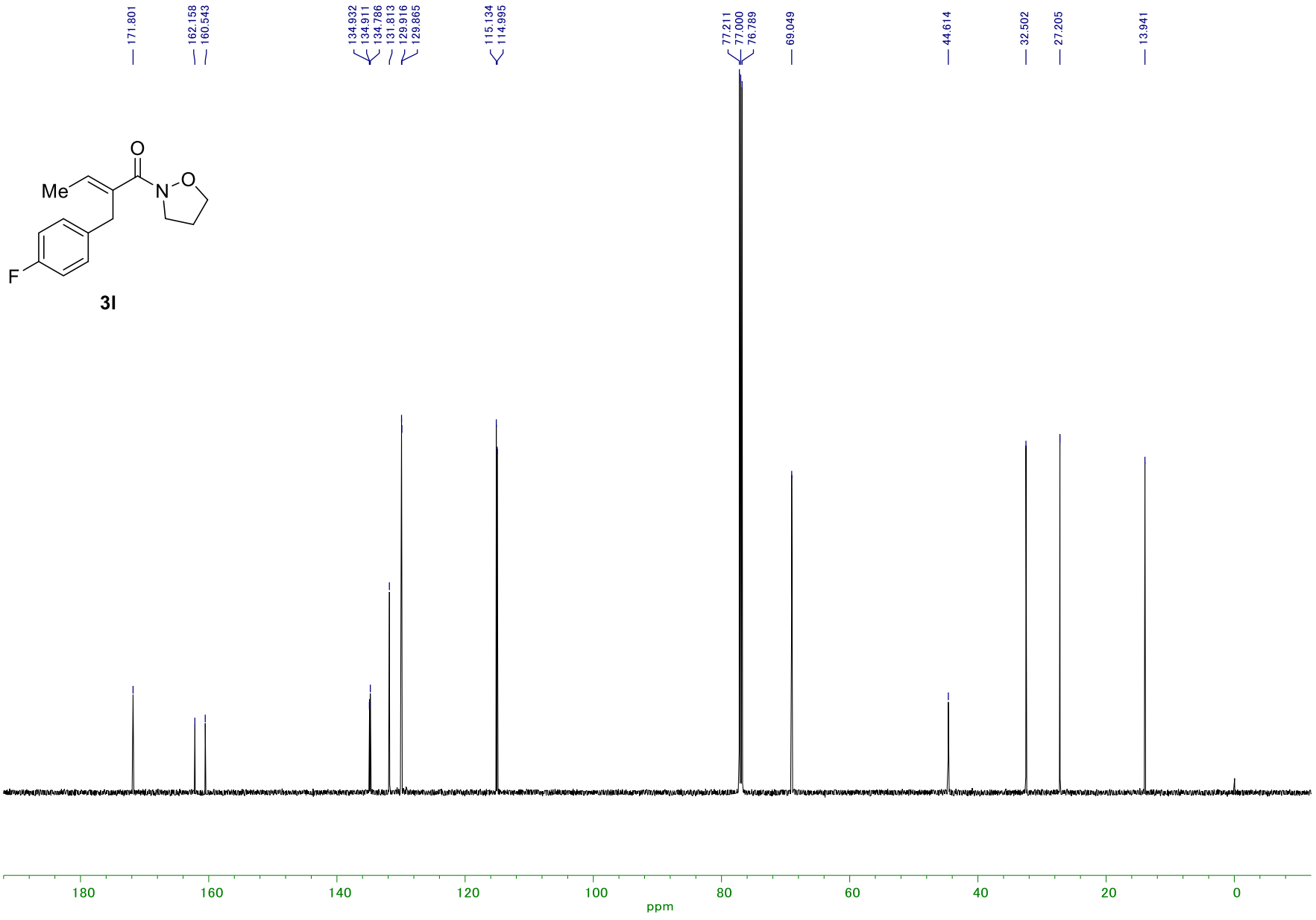
3k



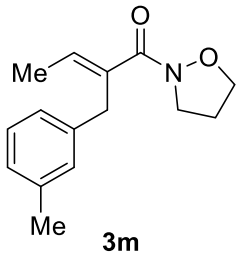

171.402
138.253
134.146
132.398
131.281
130.144
119.737
77.425
77.000
76.577
69.051
44.535
32.655
27.146
13.967
O
Me
N
O
Br
3k
180
160
140
120
100
80
60
40
20
0
ppm



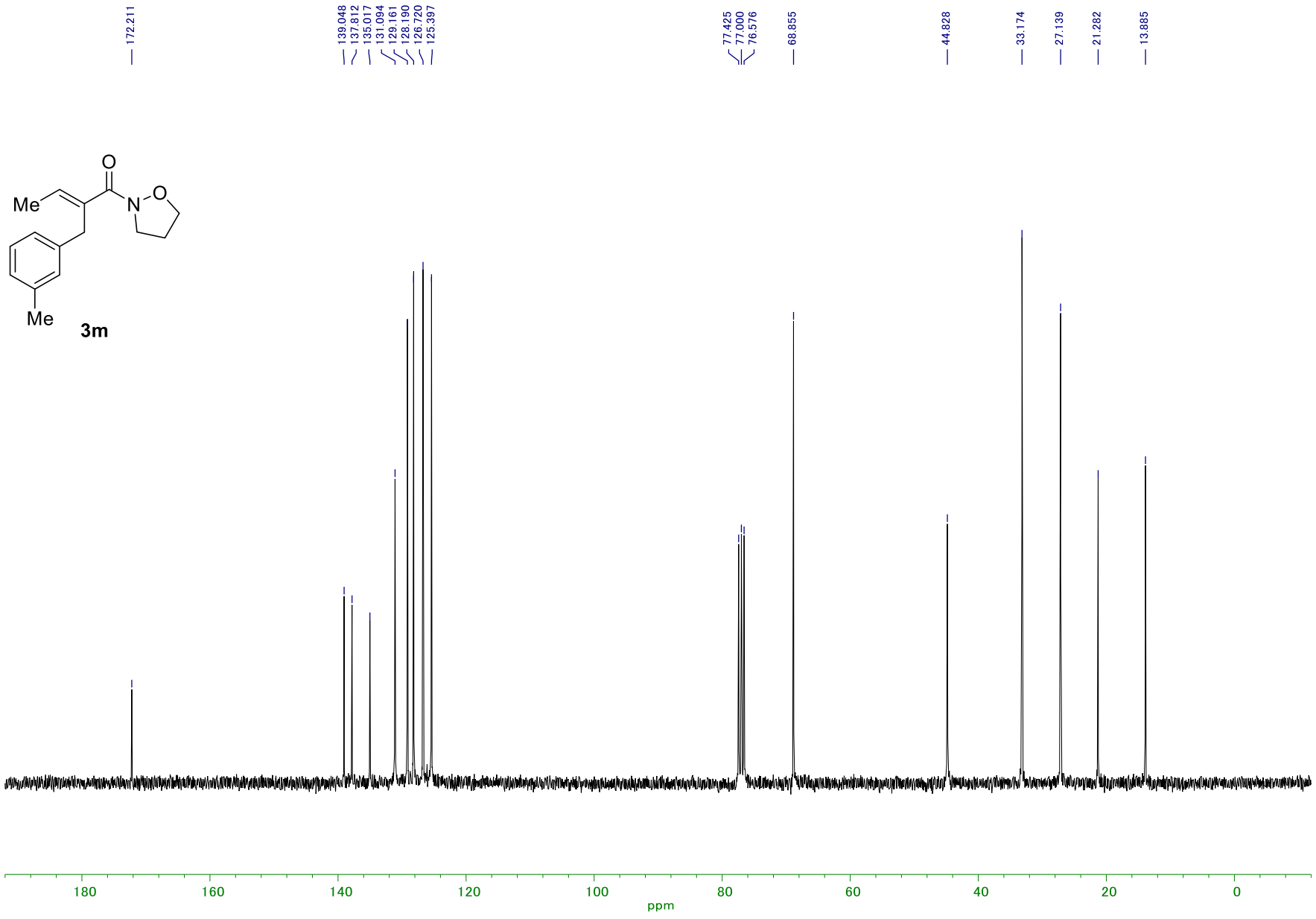
3l

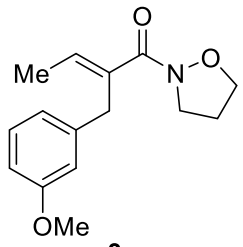

171.801
162.158
160.543
134.932
134.911
134.786
131.813
129.916
129.865
115.134
114.995
77.211
77.000
76.789
69.049
44.614
32.502
27.205
13.941
O
Me
N
O
F
180
160
140
120
100
80
60
40
20
0
ppm

3l

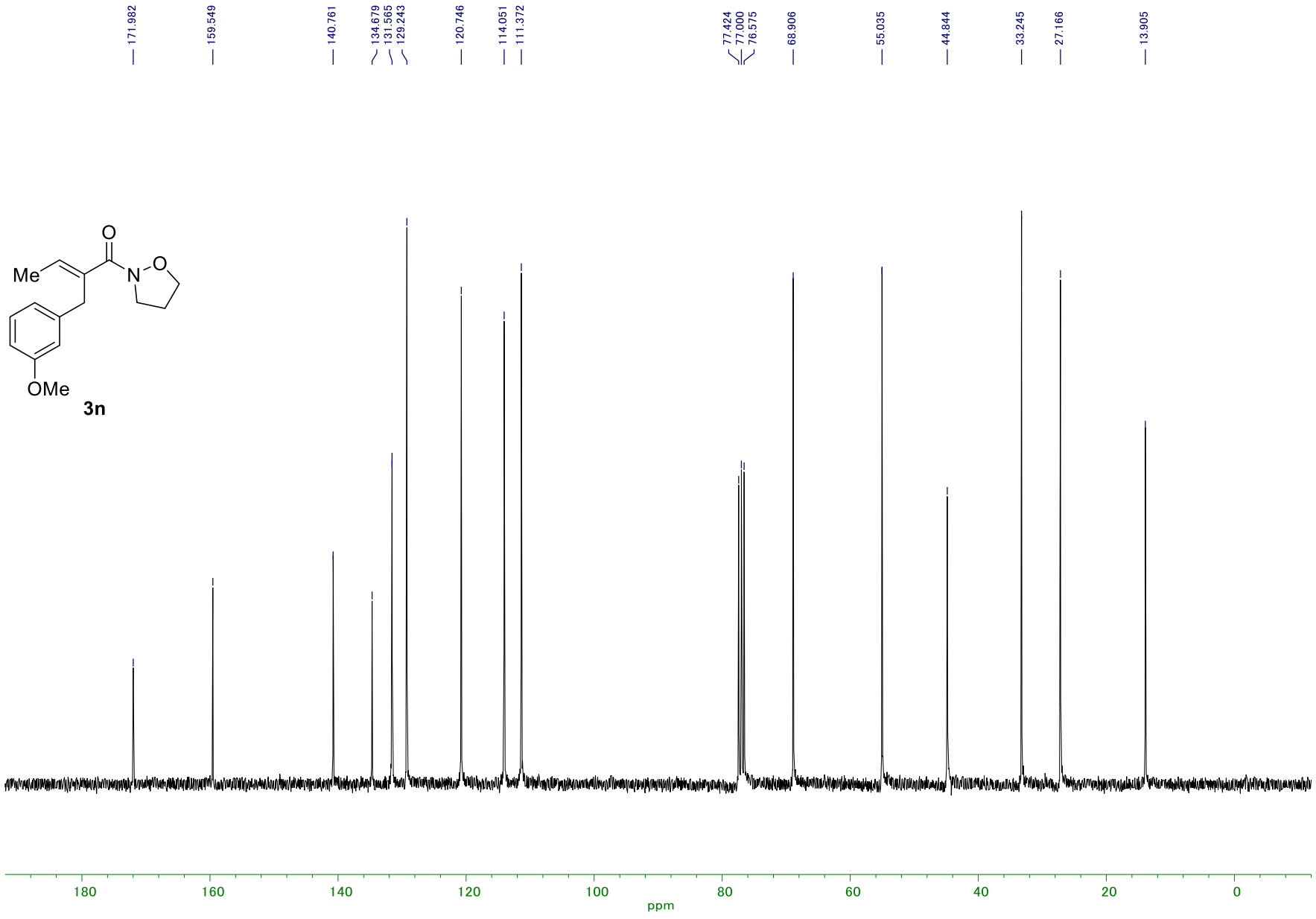


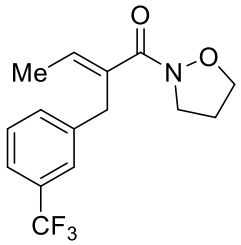
3m


172.211
139.048
137.812
135.017
131.094
129.161
128.190
126.720
125.397
77.425
77.000
76.576
68.855
44.828
33.174
27.139
21.282
13.885
O
Me
N
O
Me
3m
180
160
140
120
100
80
60
40
20
0
ppm

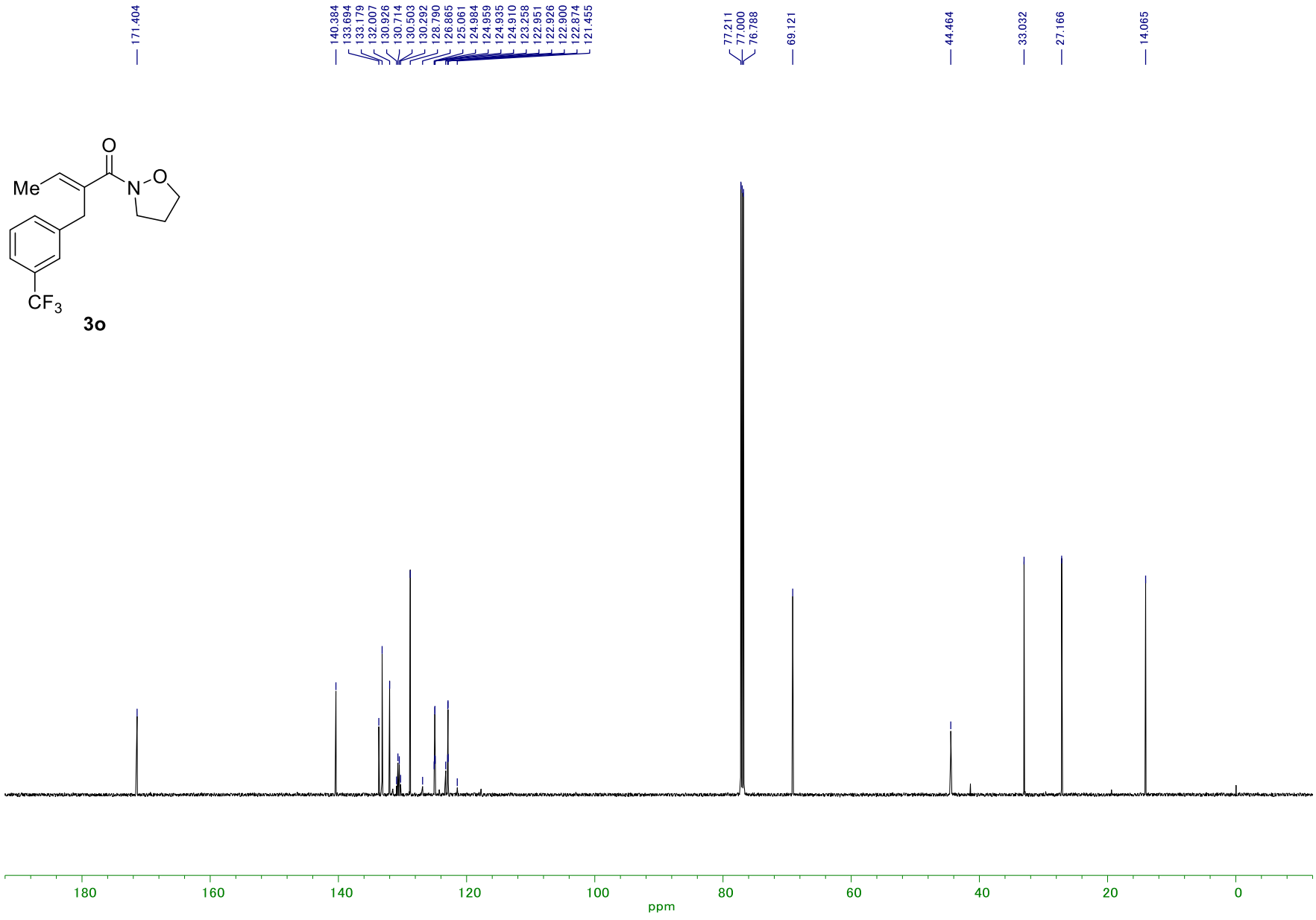


3n

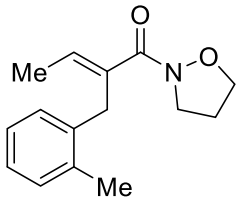

171.982
159.549
140.761
134.679
131.565
129.243
120.746
114.051
111.372
77.424
77.000
76.575
68.906
55.035
44.844
33.245
27.166
13.905
O
Me
N
O
OMe
3n
180
160
140
120
100
80
60
40
20
0
ppm



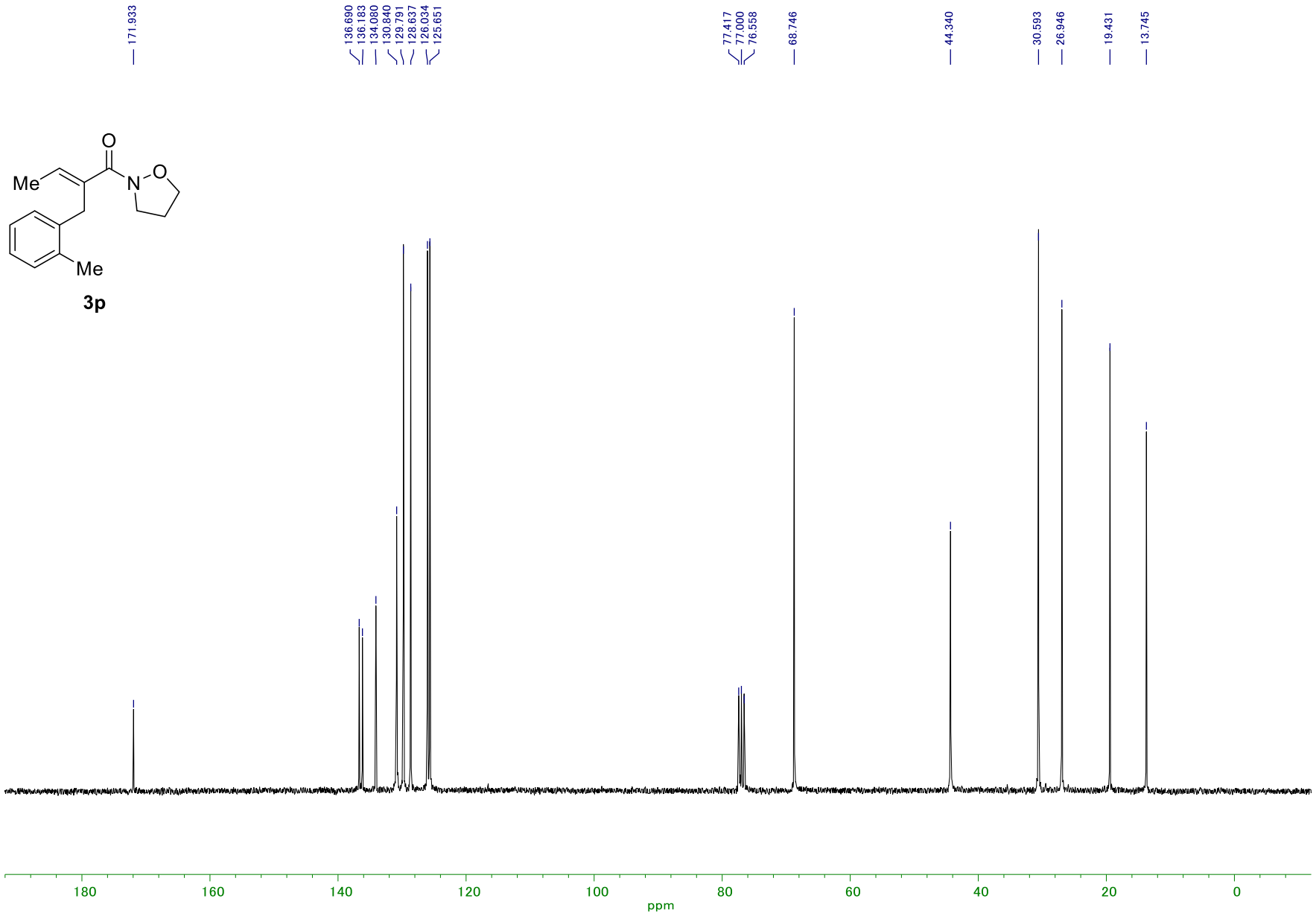
3o

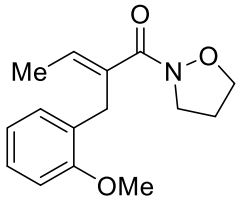

171.404
140.384
133.694
133.179
132.007
130.926
130.714
130.503
130.292
128.790
126.865
125.061
124.984
124.959
124.935
124.910
123.258
122.951
122.926
122.900
122.874
121.455
77.211
77.000
76.788
69.121
44.464
33.032
27.166
14.065
O
Me
N
O
CF3
180
160
140
120
100
80
60
40
20
0
ppm

3o

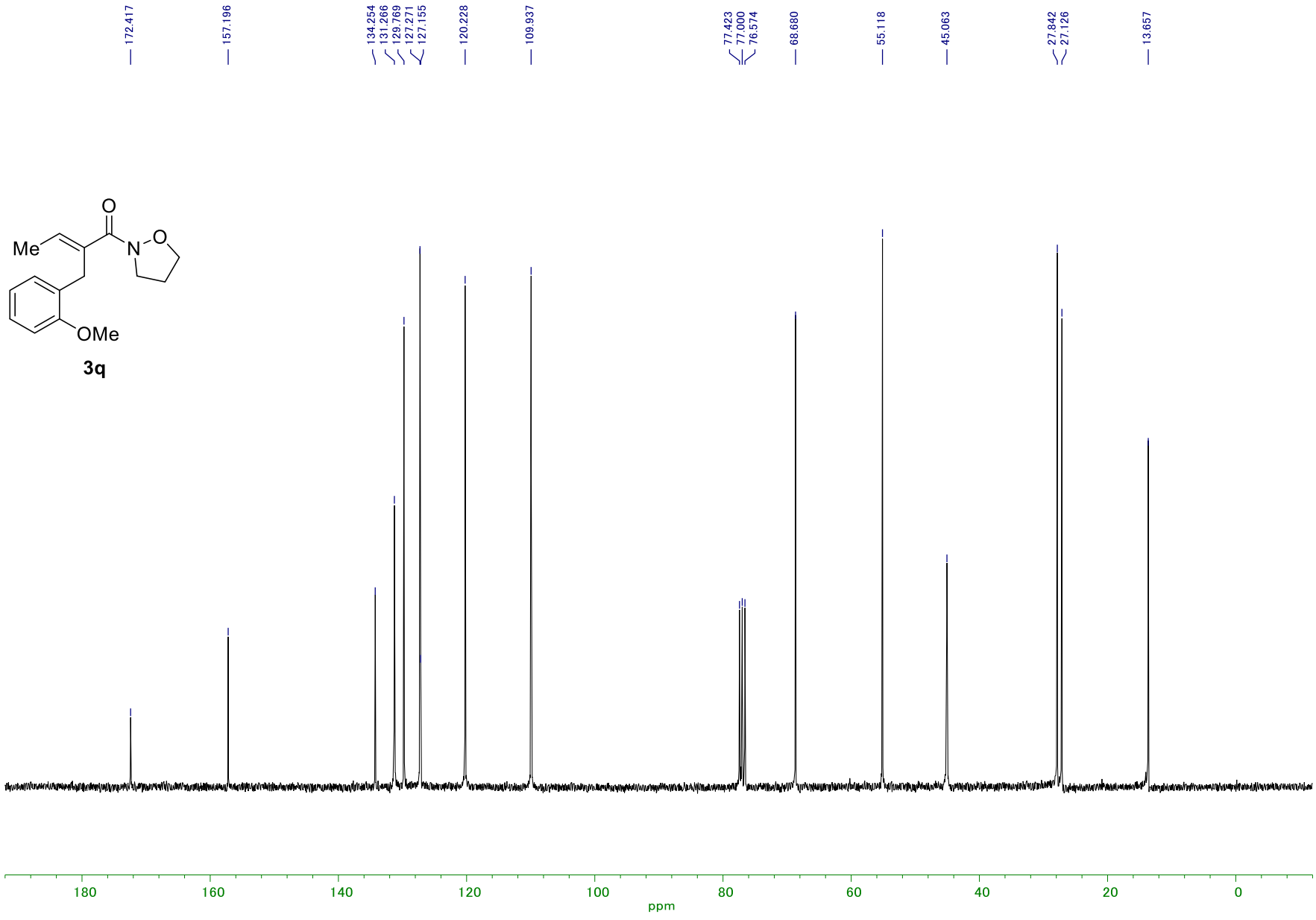


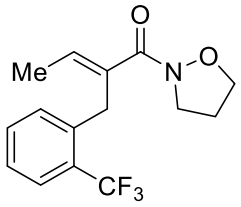
3p


171.933
136.690
136.183
134.080
130.840
129.791
128.637
126.034
125.651
77.417
77.000
76.558
68.746
44.340
30.593
26.946
19.431
13.745
O
Me
N
O
Me
3p
180
160
140
120
100
80
60
40
20
0
ppm

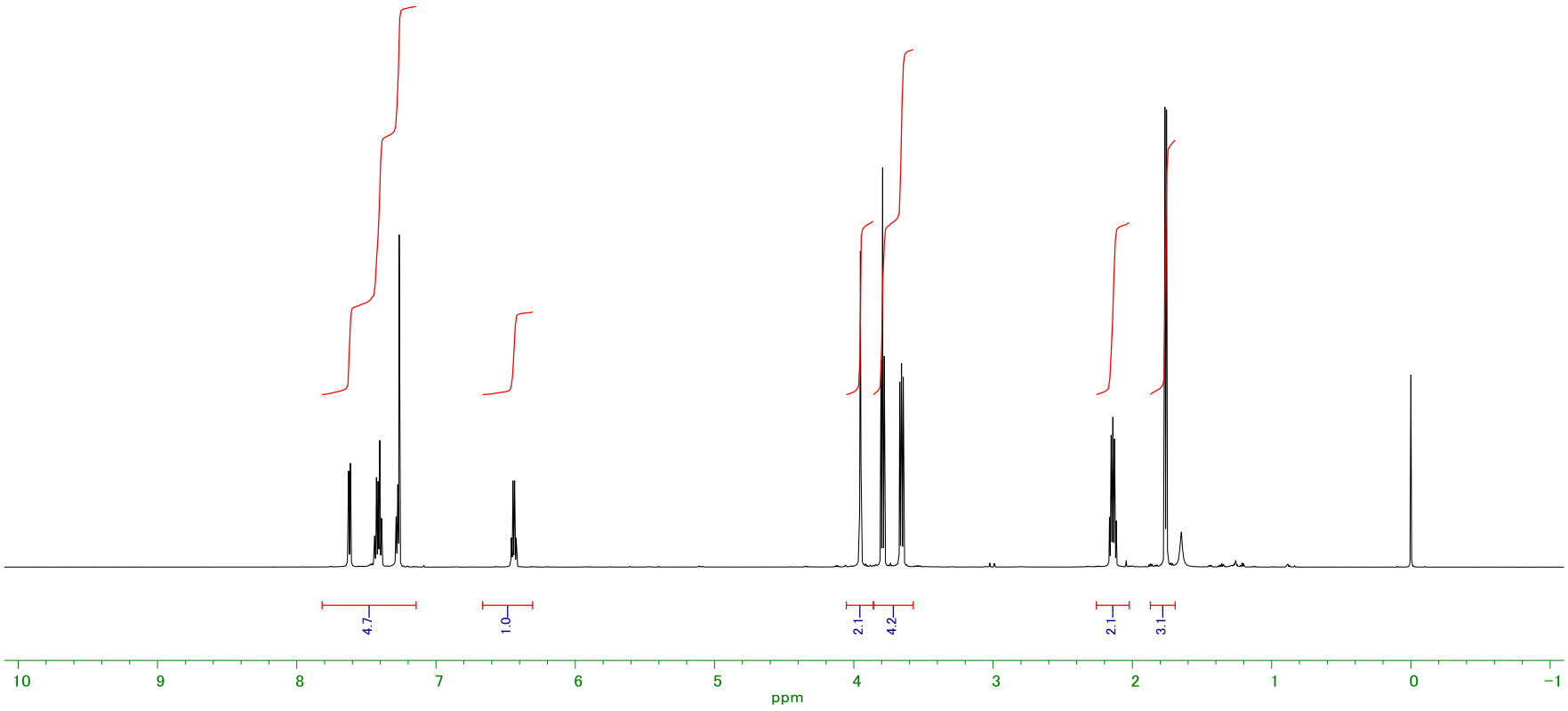


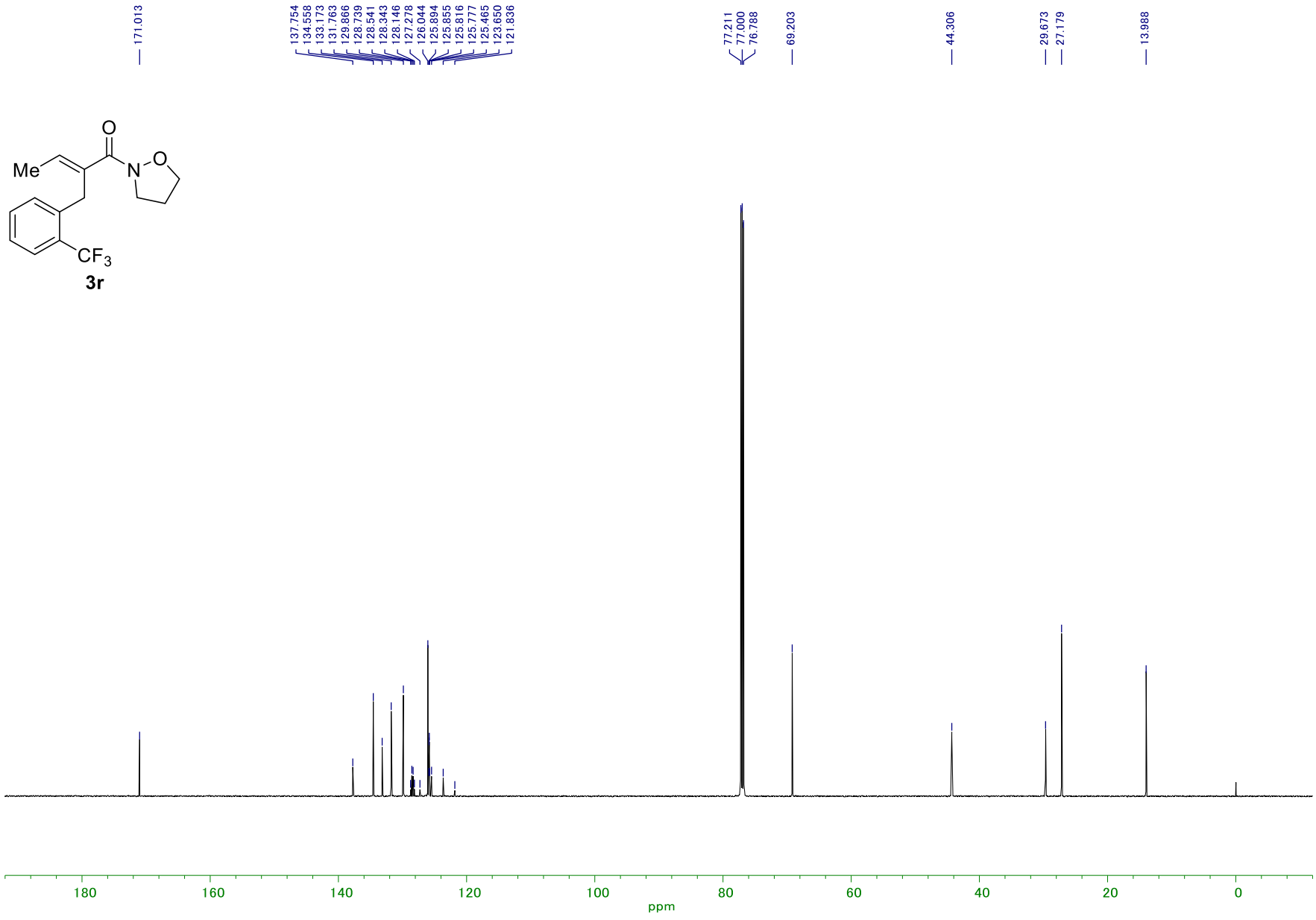
3q

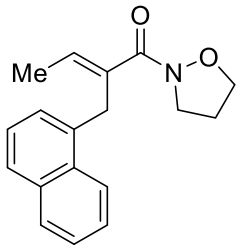

172.417
157.196
134.254
131.266
129.769
127.271
127.155
120.228
109.937
77.423
77.000
76.574
68.680
55.118
45.063
27.842
27.126
13.657
O
Me
N
O
OMe
3q
180
160
140
120
100
80
60
40
20
0
ppm



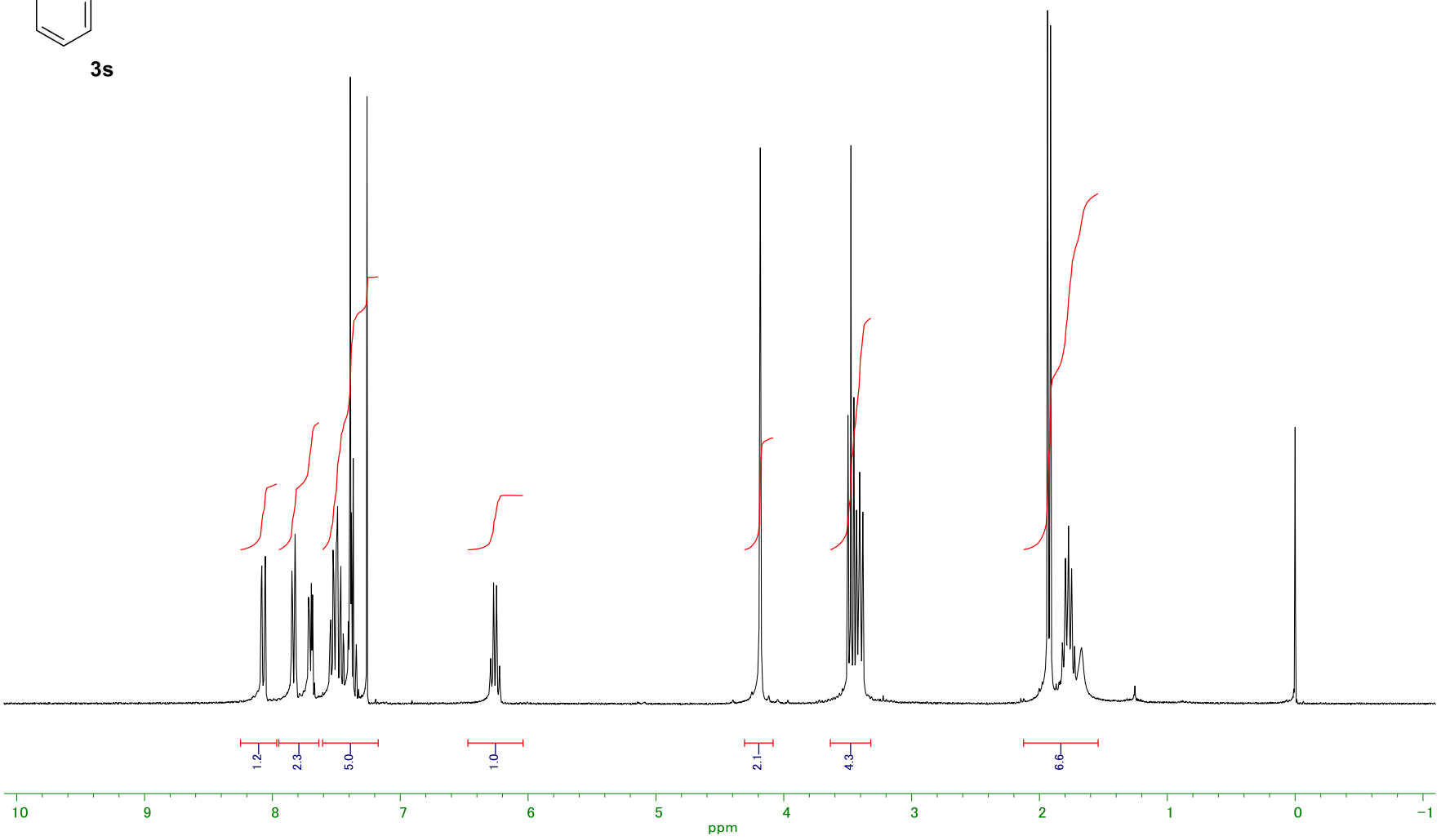
3r

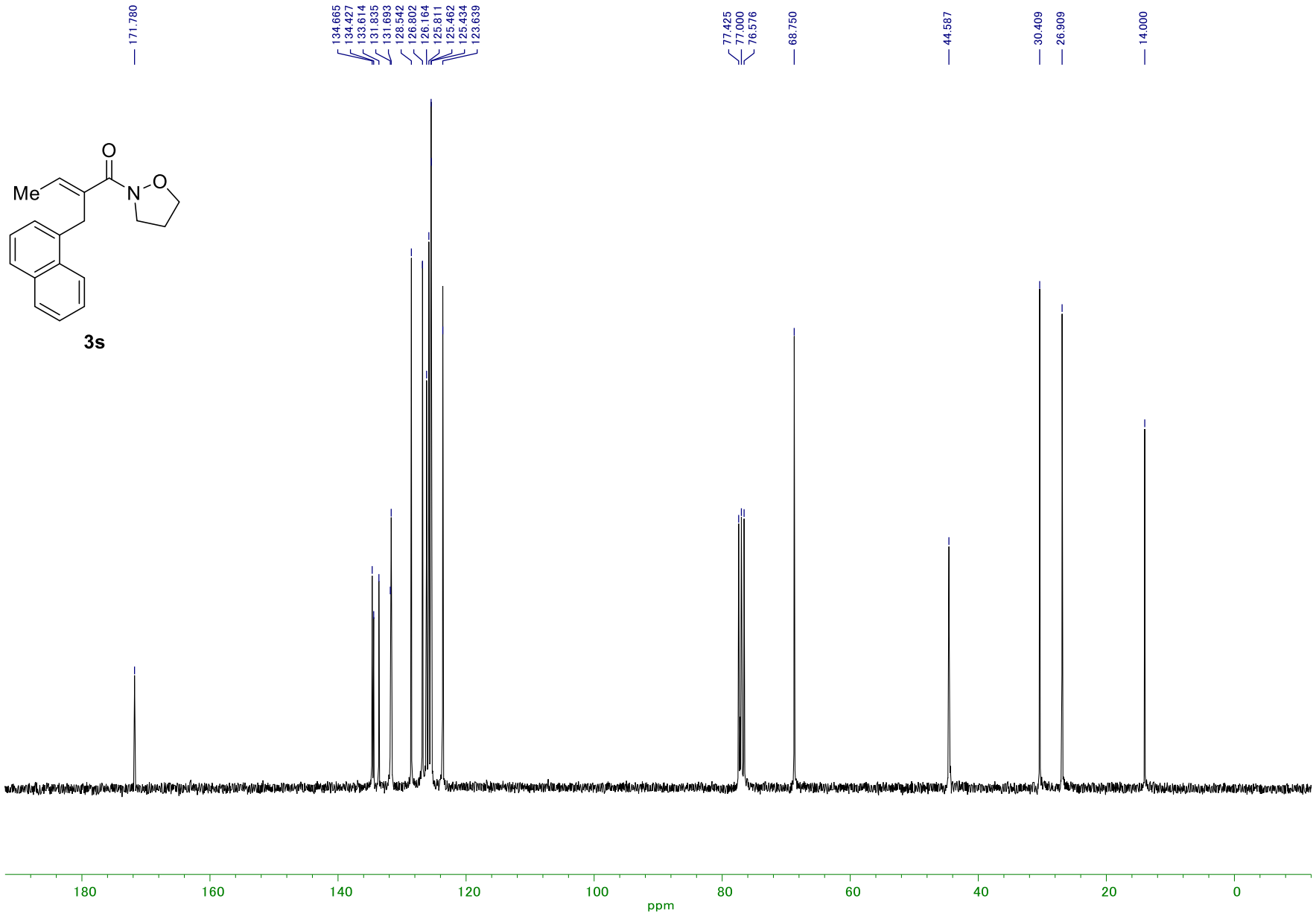


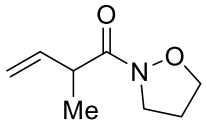

171.013
137.754
134.558
133.173
131.763
129.866
128.739
128.541
128.343
128.146
127.278
126.044
125.894
125.855
125.816
125.777
125.465
123.650
121.836
77.211
77.000
76.788
69.203
44.306
29.673
27.179
13.988
O
Me
N
O
CF3
3r
180
160
140
120
100
80
60
40
20
0
ppm



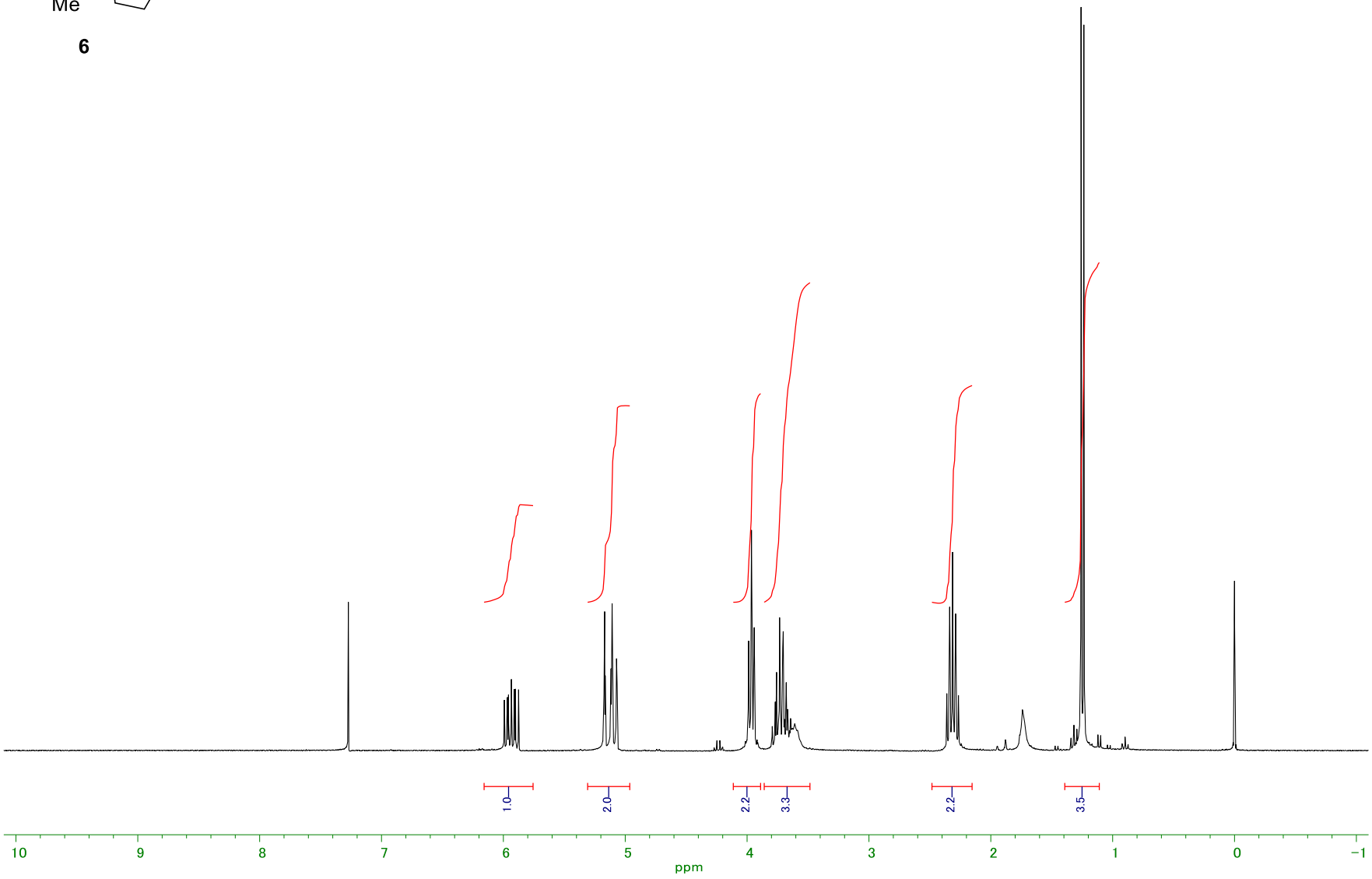
3s

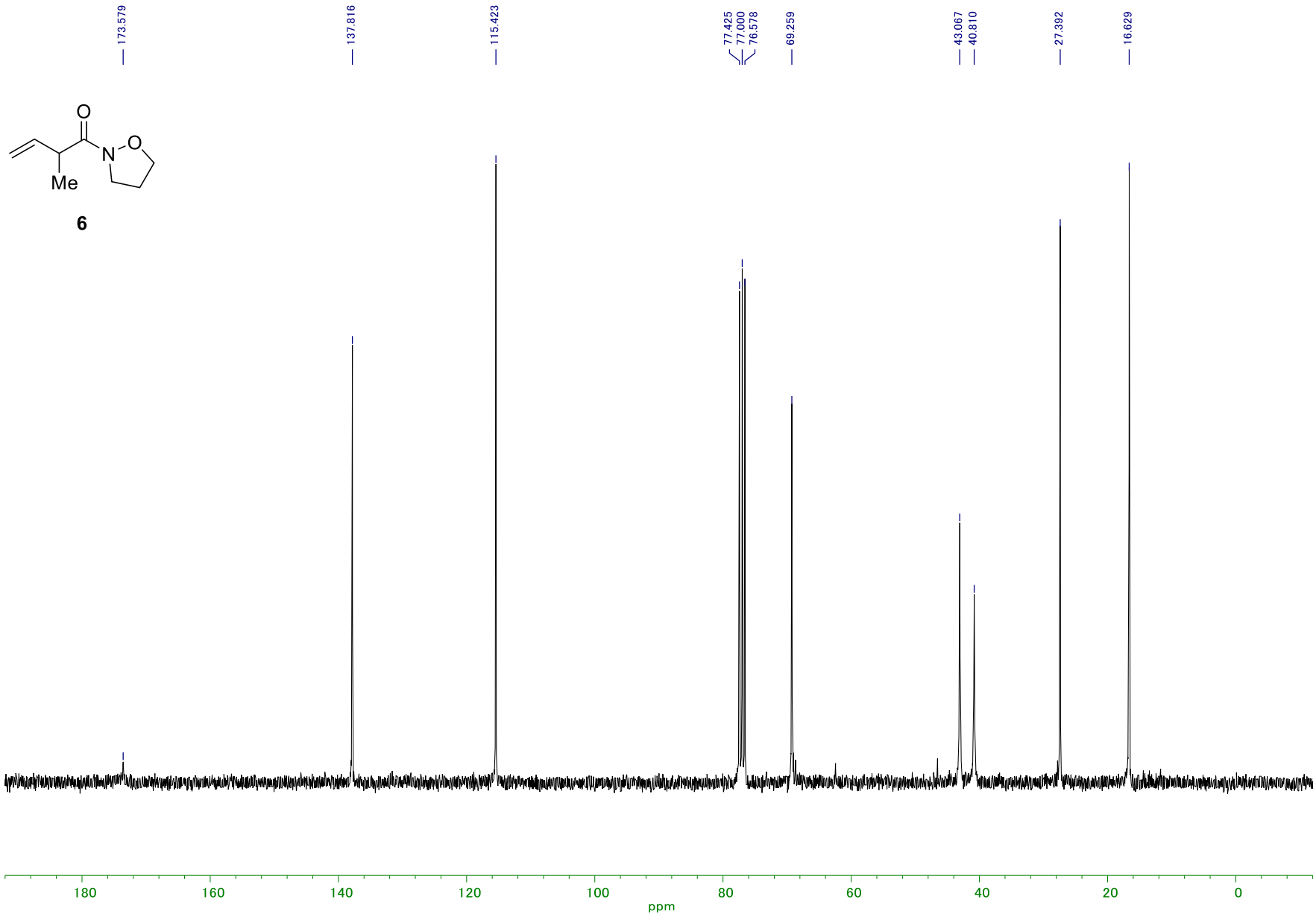


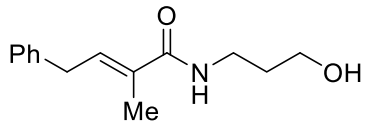

171.780
134.665
134.427
133.614
131.835
131.693
128.542
126.802
126.164
125.811
125.462
125.434
123.639
77.425
77.000
76.576
68.750
44.587
30.409
26.909
14.000
O
Me
N
O
3s
180
160
140
120
100
80
60
40
20
0
ppm



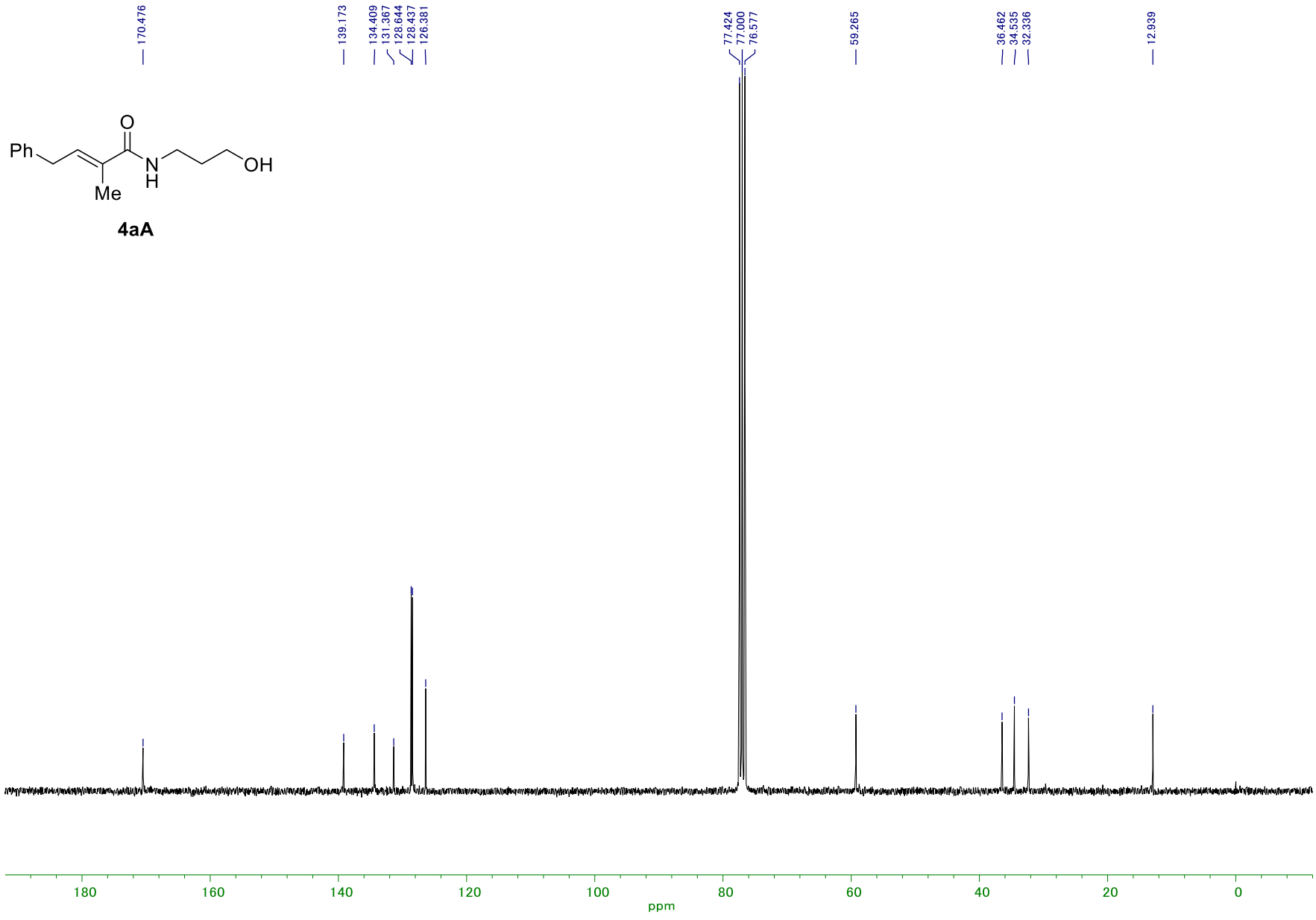
6

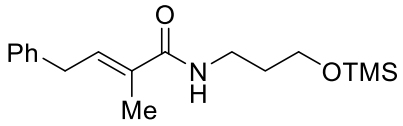



173.579
137.816
115.423
77.425
77.000
76.578
69.259
43.067
40.810
27.392
16.629
O
N
O
Me
6
180
160
140
120
100
80
60
40
20
0
ppm

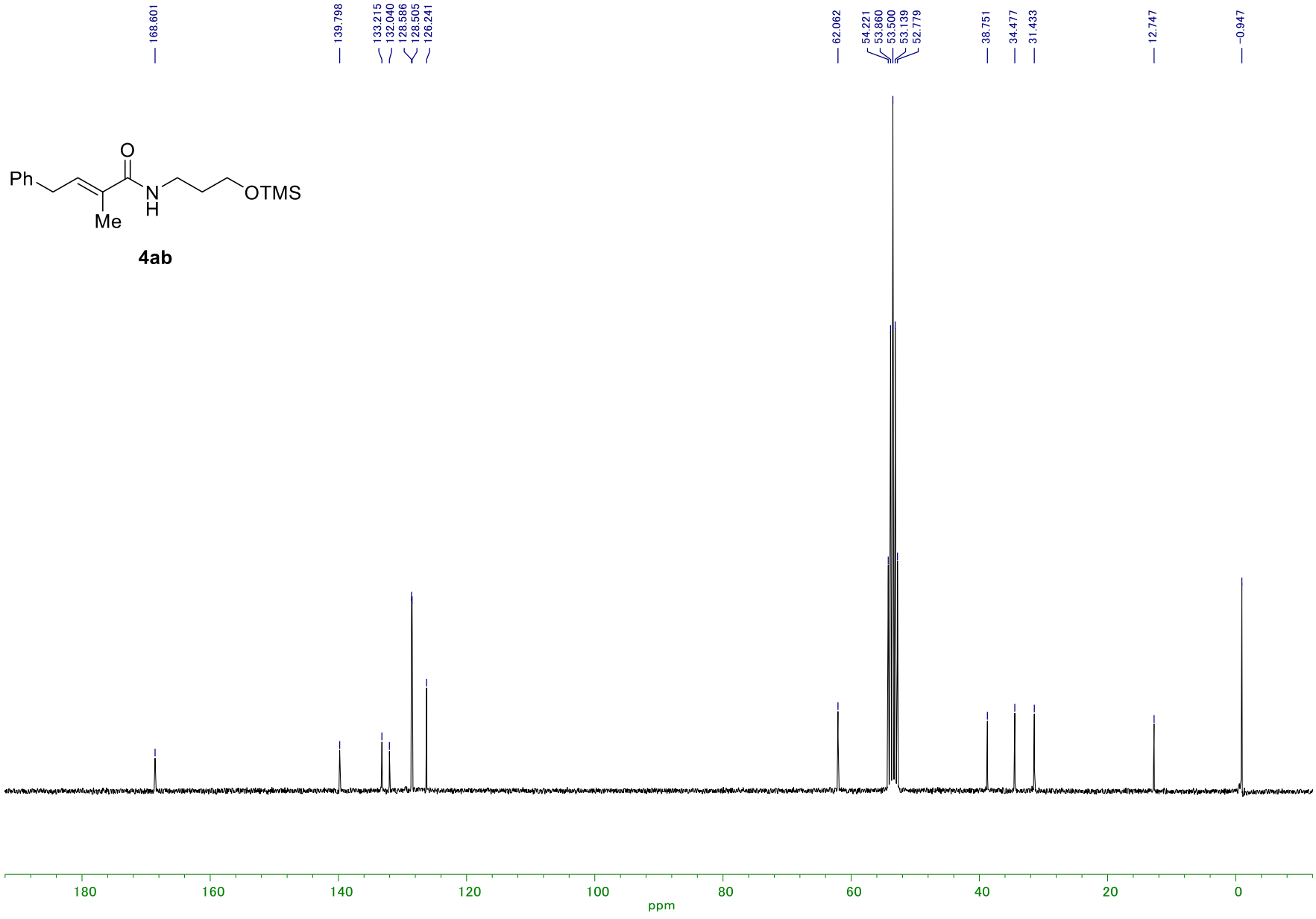


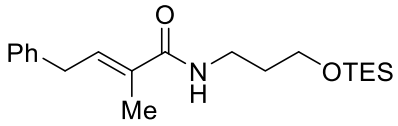
4aA


170.476
139.173
134.409
131.367
128.644
128.437
126.381
77.424
77.000
76.577
59.265
36.462
34.535
32.336
12.939
Ph
O
N
H
OH
Me
4aA
180
160
140
120
100
80
60
40
20
0
ppm

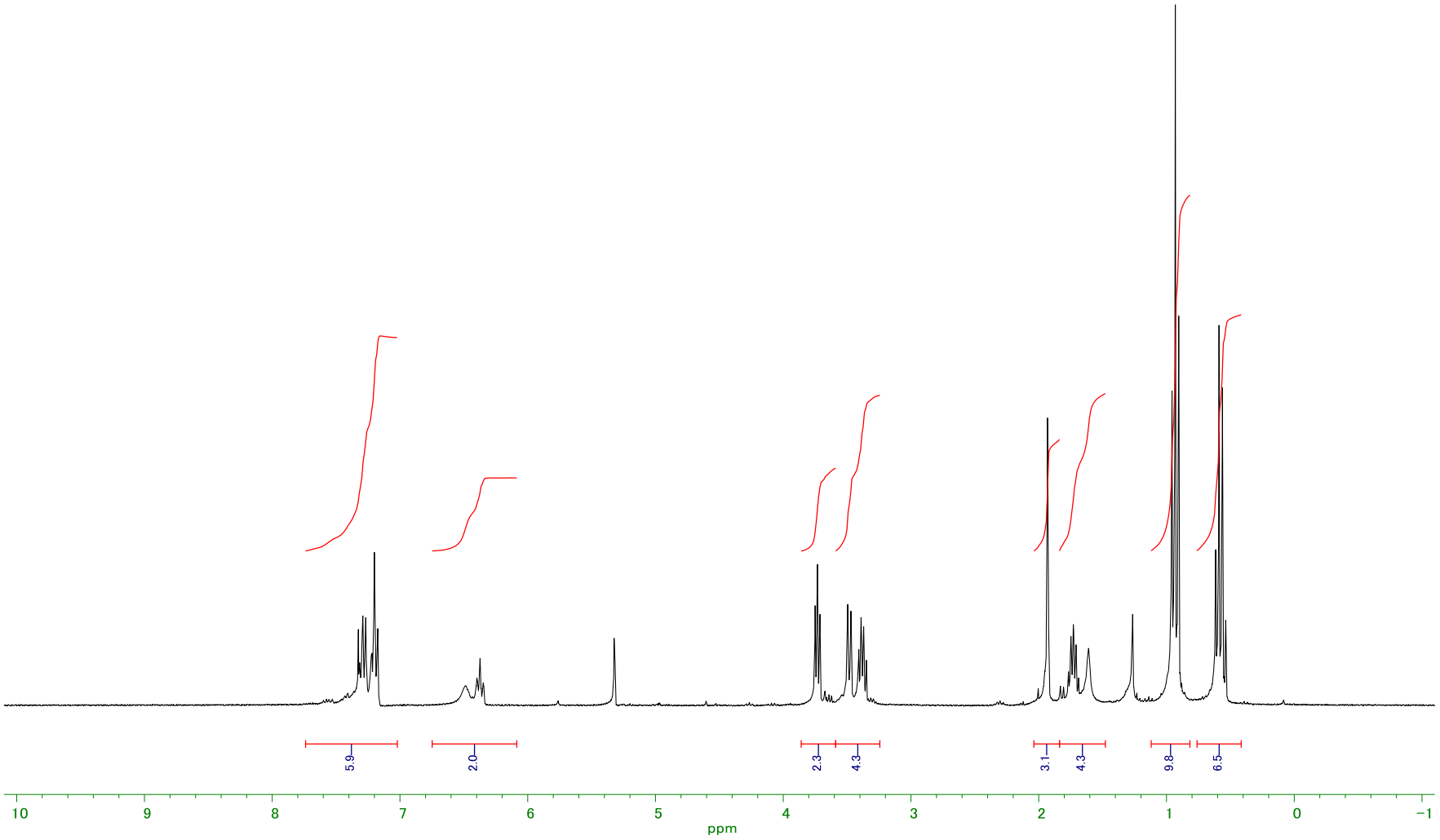


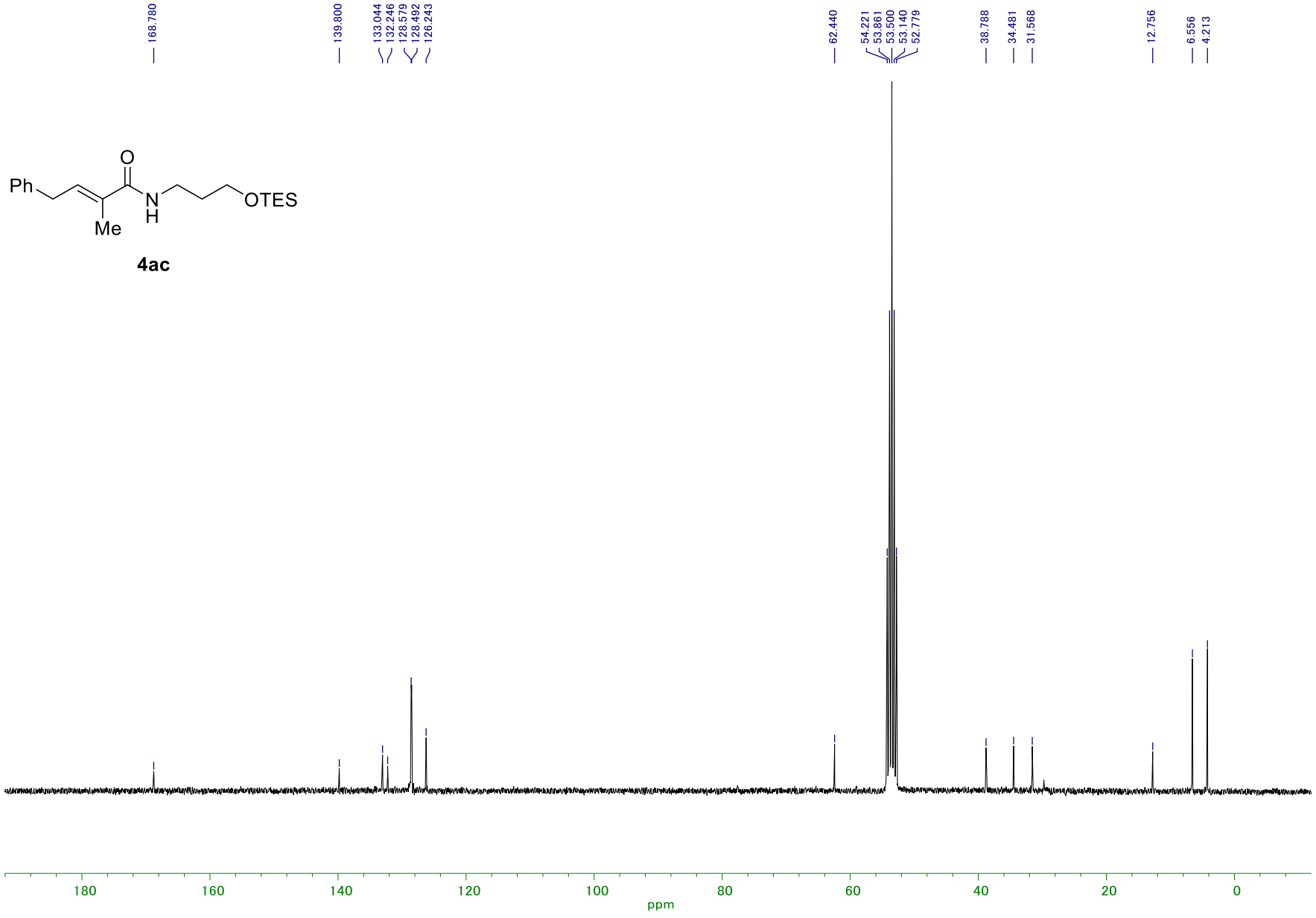
4ab


168.601
139.798
133.215
132.040
128.586
128.505
126.241
62.062
54.221
53.860
53.500
53.139
52.779
38.751
34.477
31.433
12.747
-0.947
O
Ph
N
H
OTMS
Me
4ab
180
160
140
120
100
80
60
40
20
0
ppm

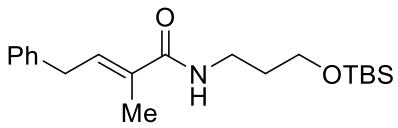


4ac

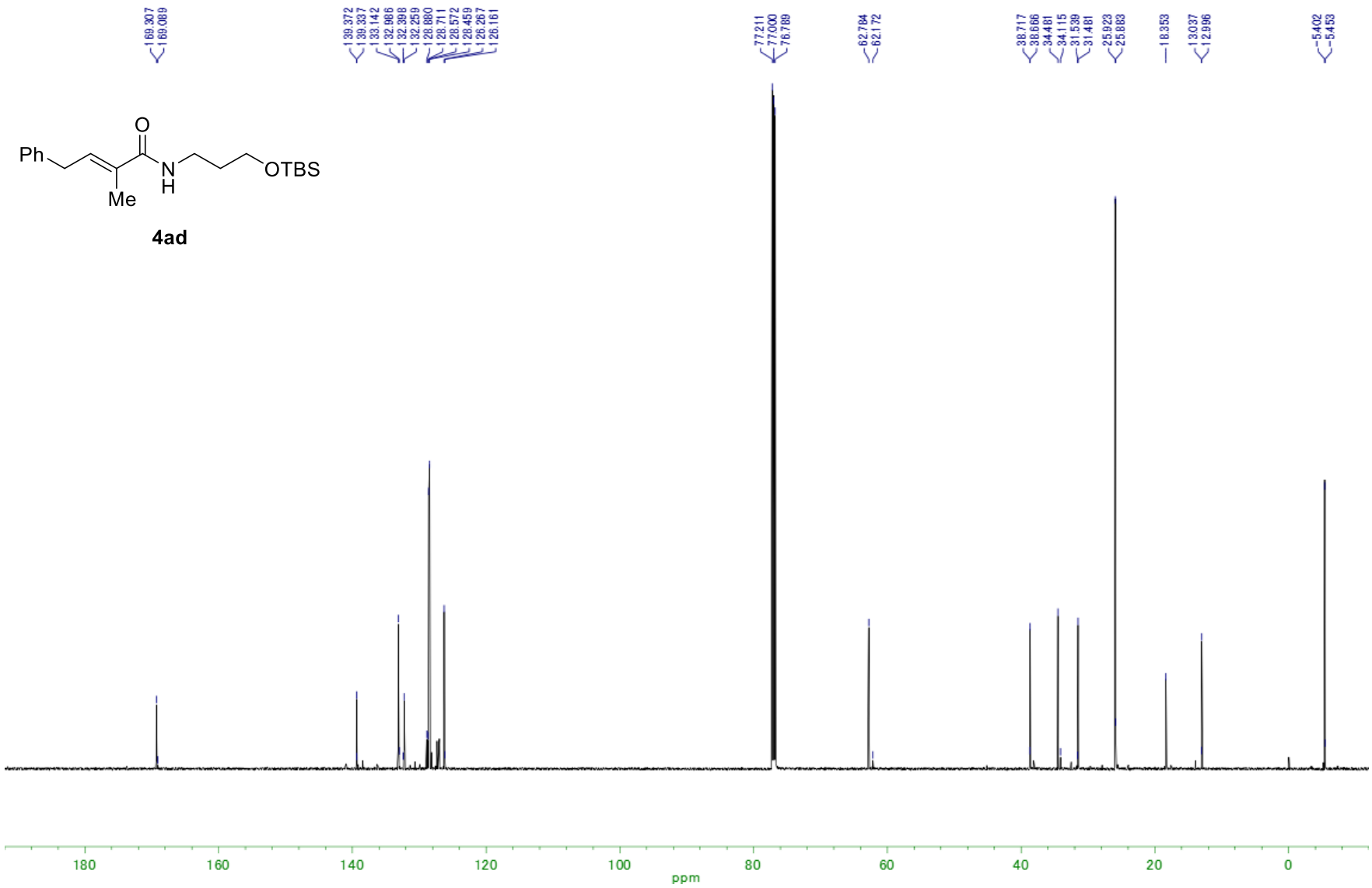



168.780
139.800
133.044
132.246
128.579
128.492
126.243
62.440
54.221
53.861
53.500
53.140
52.779
38.788
34.481
31.568
12.756
6.556
4.213
Ph
O
N
H
Me
OTES
180
160
140
120
100
80
60
40
20
0
ppm

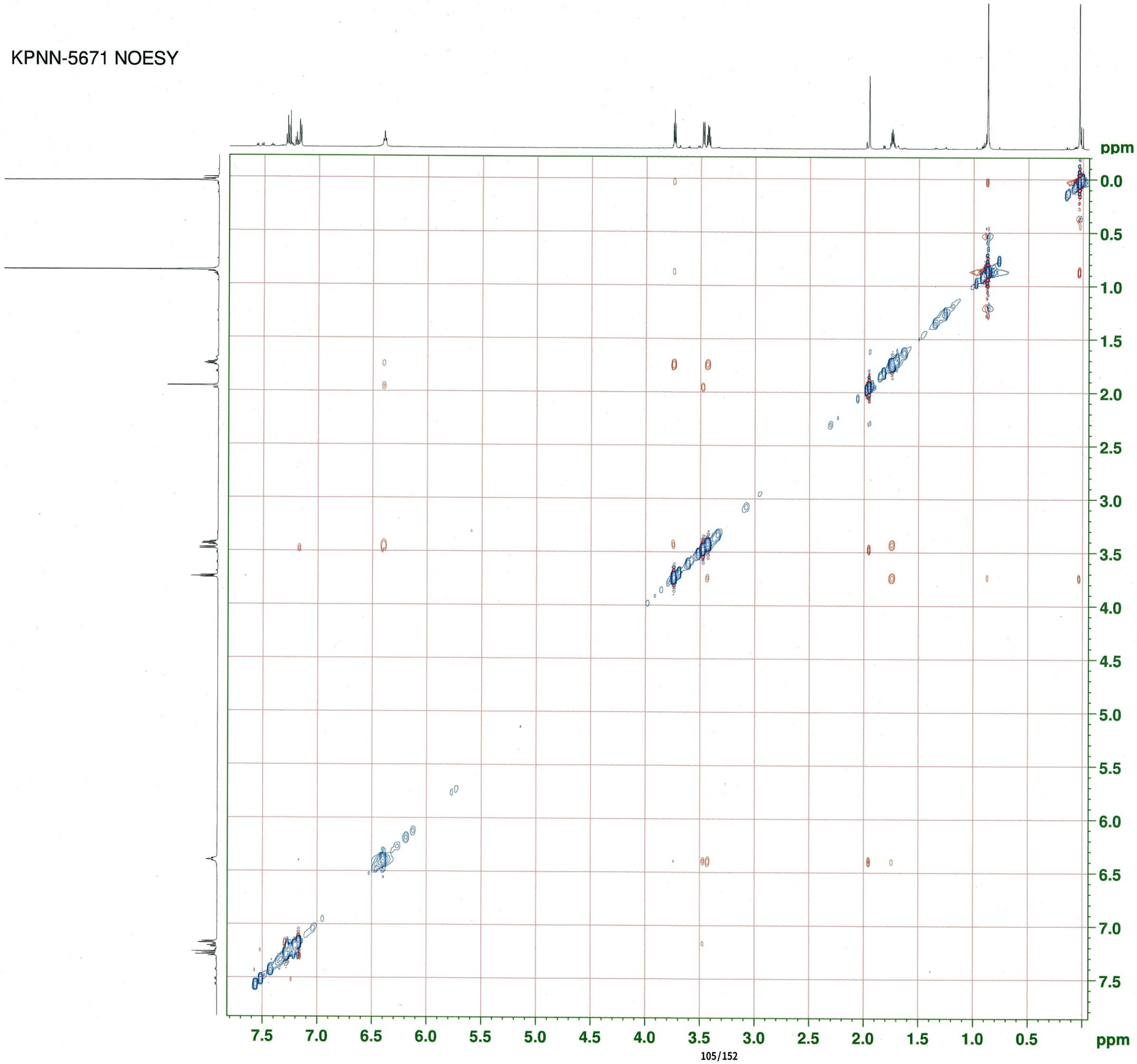
4ac



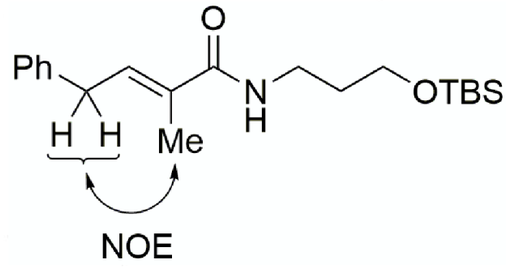
4ad


169.307
169.089
139.372
139.337
133.142
132.986
132.398
132.259
128.880
128.711
128.572
128.459
126.267
126.161
77.211
77.000
76.789
62.784
62.172
38.717
38.666
34.481
34.115
31.539
31.481
25.923
25.883
18.353
13.037
12.996
5.402
5.453
O
Ph
N
H
OTBS
Me
4ad
180
160
140
120
100
80
60
40
20
0
ppm

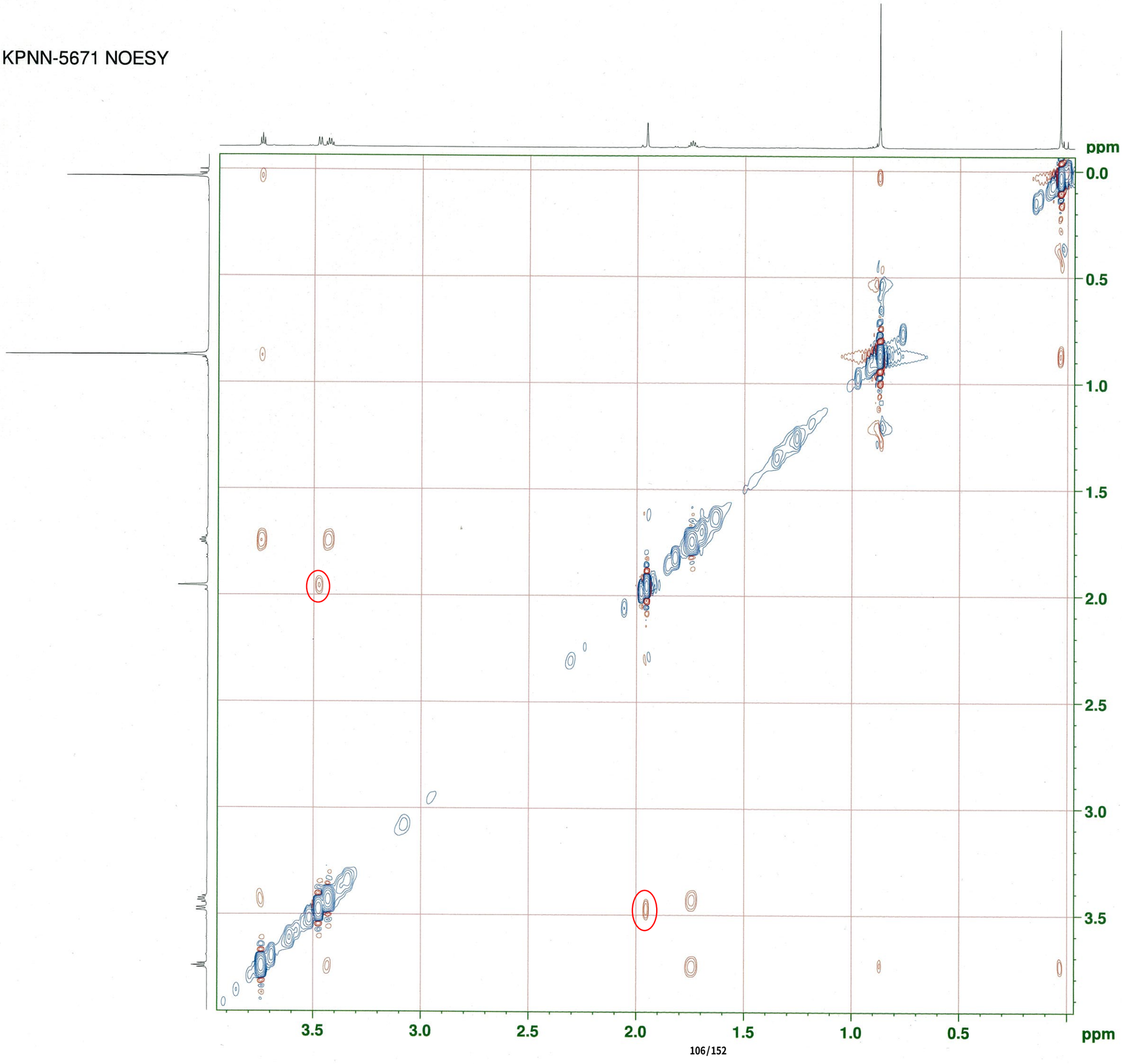
KPNN-5671 NOESY



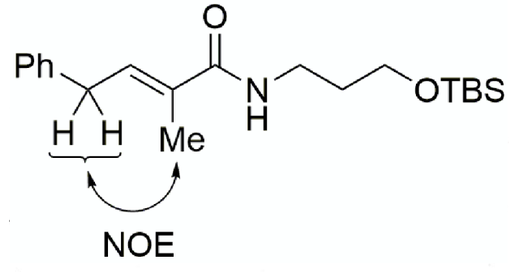

```
Current Data Parameters
NAME            KPNN-5671
EXPNO                  40
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190508
Time               21.01 h
INSTRUM              spect
PROBHD   Z114607_0202 (
PULPROG  noesygpphzskuri
TD                   2048
SOLVENT              CDCl3
NS                      8
DS                     16
SWH              9009.009 Hz
FIDRES           8.797860 Hz
AQ               0.1136640 sec
RG                  31.12
DW                 55.500 usec
DE                 11.13 usec
TE                 298.1 K
D0               0.00004277 sec
D1               2.00000000 sec
D8               0.69999999 sec
D16              0.00020000 sec
IN0              0.00011100 sec
TDav                    1
SFO1          600.5342037 MHz
NUC1                   1H
P1                 10.00 usec
P32             20000.00 usec
PLW1          24.00600052 W
SPNAM[29 Crp60,20,20.10
SPOAL29             0.500
SPOFFS29 0 Hz
SPW29          0.09169600 W
GPZ0                10.00 %
GPNAM[1]       SMSQ10.100
GPZ1                40.00 %
P31               5000.00 usec

F1 - Acquisition parameters
TD                     256
SFO1             600.5342 MHz
FIDRES          70.382881 Hz
SW                15.002 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                    4096
SF            600.5300155 MHz
WDW                 QSINE
SSB                     2
LB         0 Hz
GB         0
PC                  1.00

F1 - Processing parameters
SI                    4096
MC2          States-TPPI
SF            600.5300145 MHz
WDW                 QSINE
SSB                     2
LB         0 Hz
GB         0
```

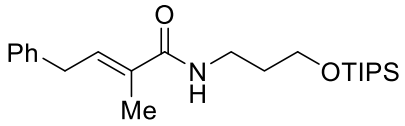


KPNN-5671 NOESY

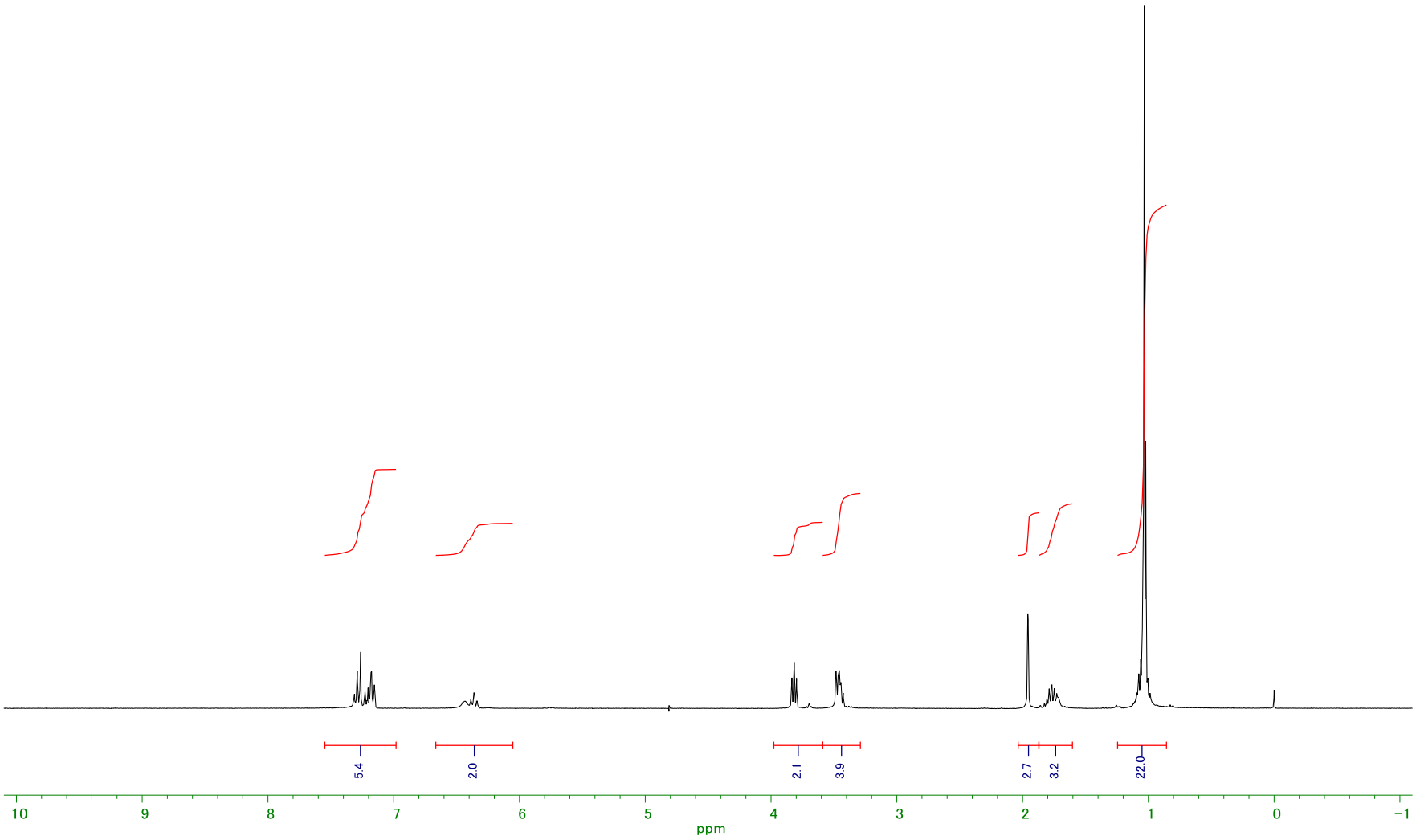


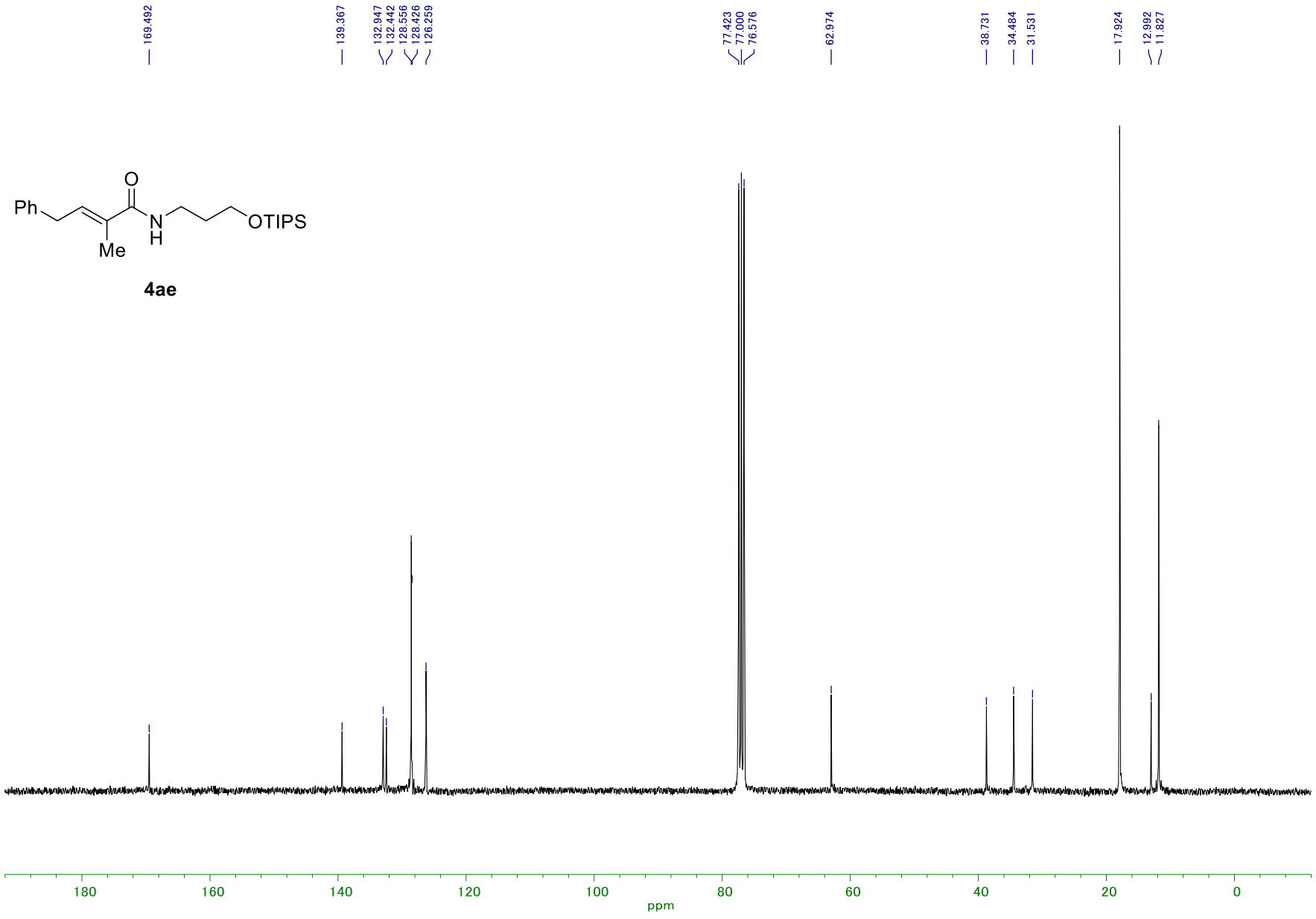

```
Current Data Parameters
NAME            KPNN-5671
EXPNO                  40
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190508
Time               21.01 h
INSTRUM             spect
PROBHD    Z114607_0202 (
PULPROG   noesygpphzskuri
TD                   2048
SOLVENT              CDCl3
NS                      8
DS                     16
SWH             9009.009 Hz
FIDRES          8.797860 Hz
AQ              0.1136640 sec
RG                  31.12
DW                55.500 usec
DE                11.13 usec
TE                298.1 K
D0              0.00004277 sec
D1              2.00000000 sec
D8              0.69999999 sec
D16             0.00020000 sec
IN0             0.00011100 sec
TDav                    1
SFO1          600.5342037 MHz
NUC1                   1H
P1                 10.00 usec
P32             20000.00 usec
PLW1          24.00600052 W
SPNAM[29 Crp60,20,20.10
SPOAL29             0.500
SPOFFS29 0 Hz
SPW29          0.09169600 W
GPZ0              10.00 %
GPNAM[1]       SMSQ10.100
GPZ1              40.00 %
P31             5000.00 usec

F1 - Acquisition parameters
TD                     256
SFO1            600.5342 MHz
FIDRES         70.382881 Hz
SW                15.002 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                    4096
SF           600.5300155 MHz
WDW                 QSINE
SSB                     2
LB         0 Hz
GB         0
PC                   1.00

F1 - Processing parameters
SI                    4096
MC2          States-TPPI
SF           600.5300145 MHz
WDW                 QSINE
SSB                     2
LB         0 Hz
GB         0
```

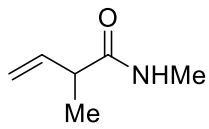




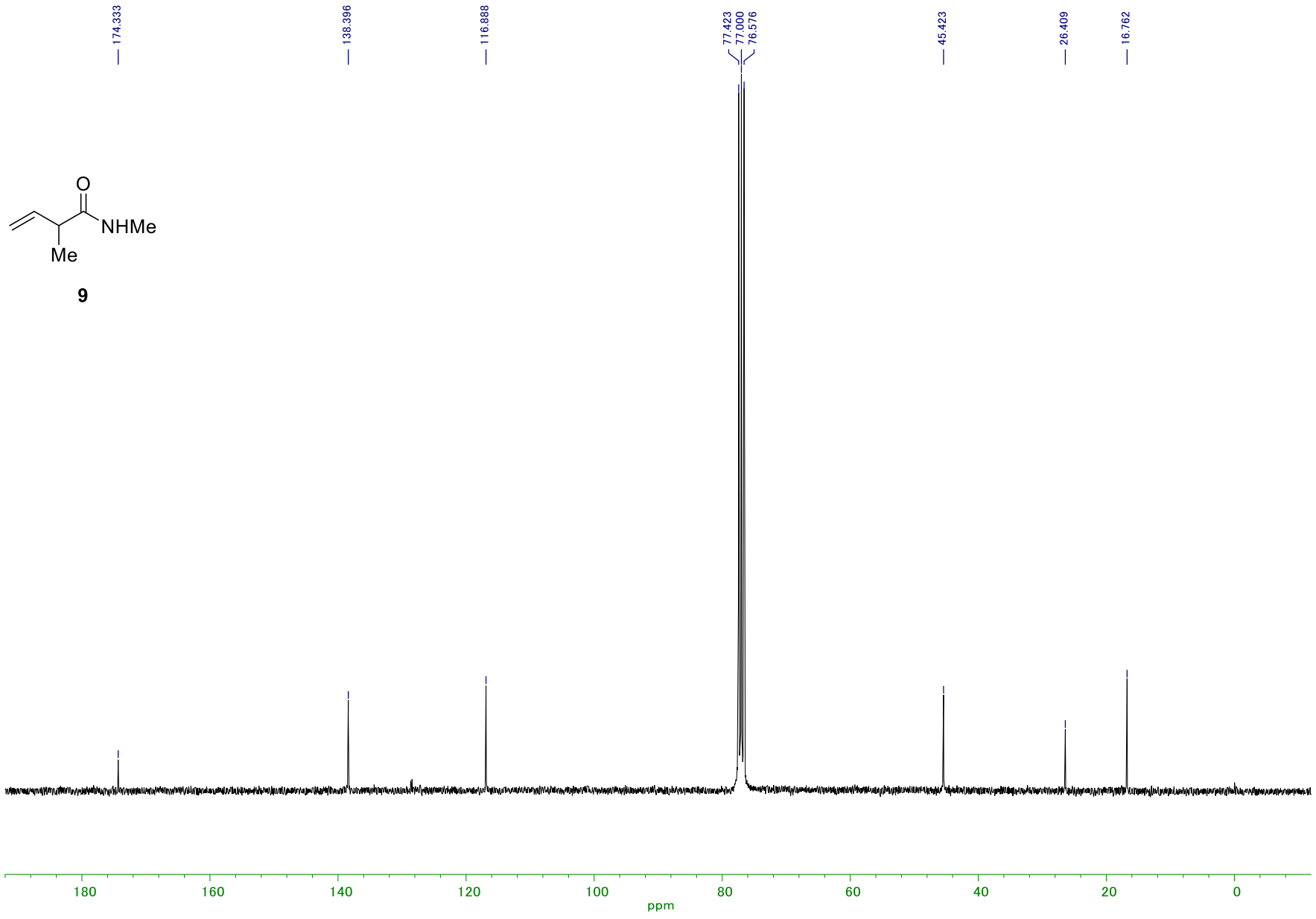
4ae

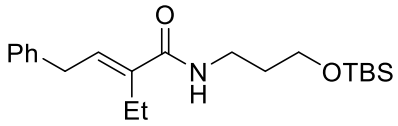



169.492
139.367
132.947
132.442
128.556
128.426
126.259
77.423
77.000
76.576
62.974
38.731
34.484
31.531
17.924
12.992
11.827
Ph
O
N
H
OTIPS
Me
4ae
180
160
140
120
100
80
60
40
20
0
ppm

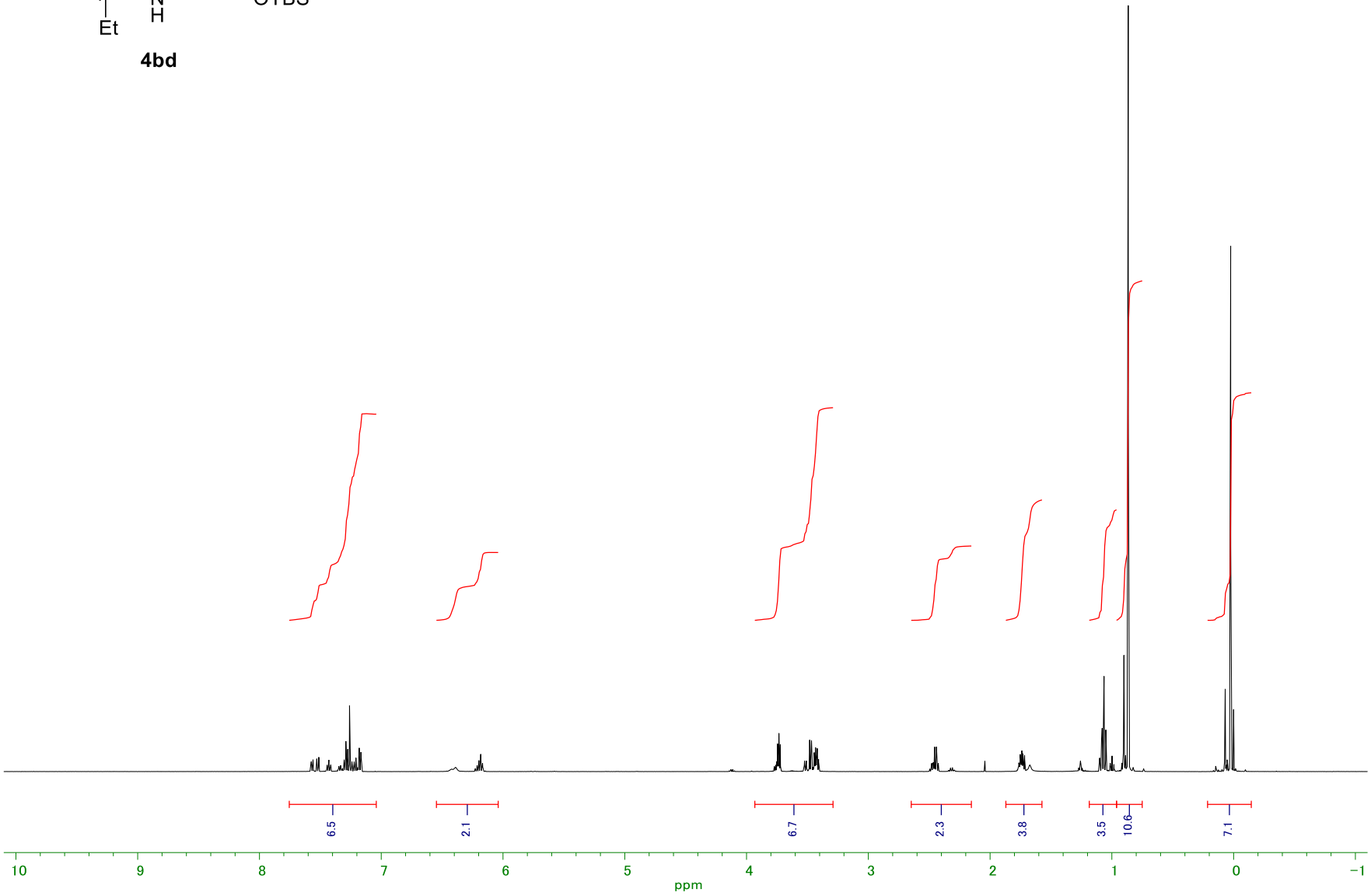


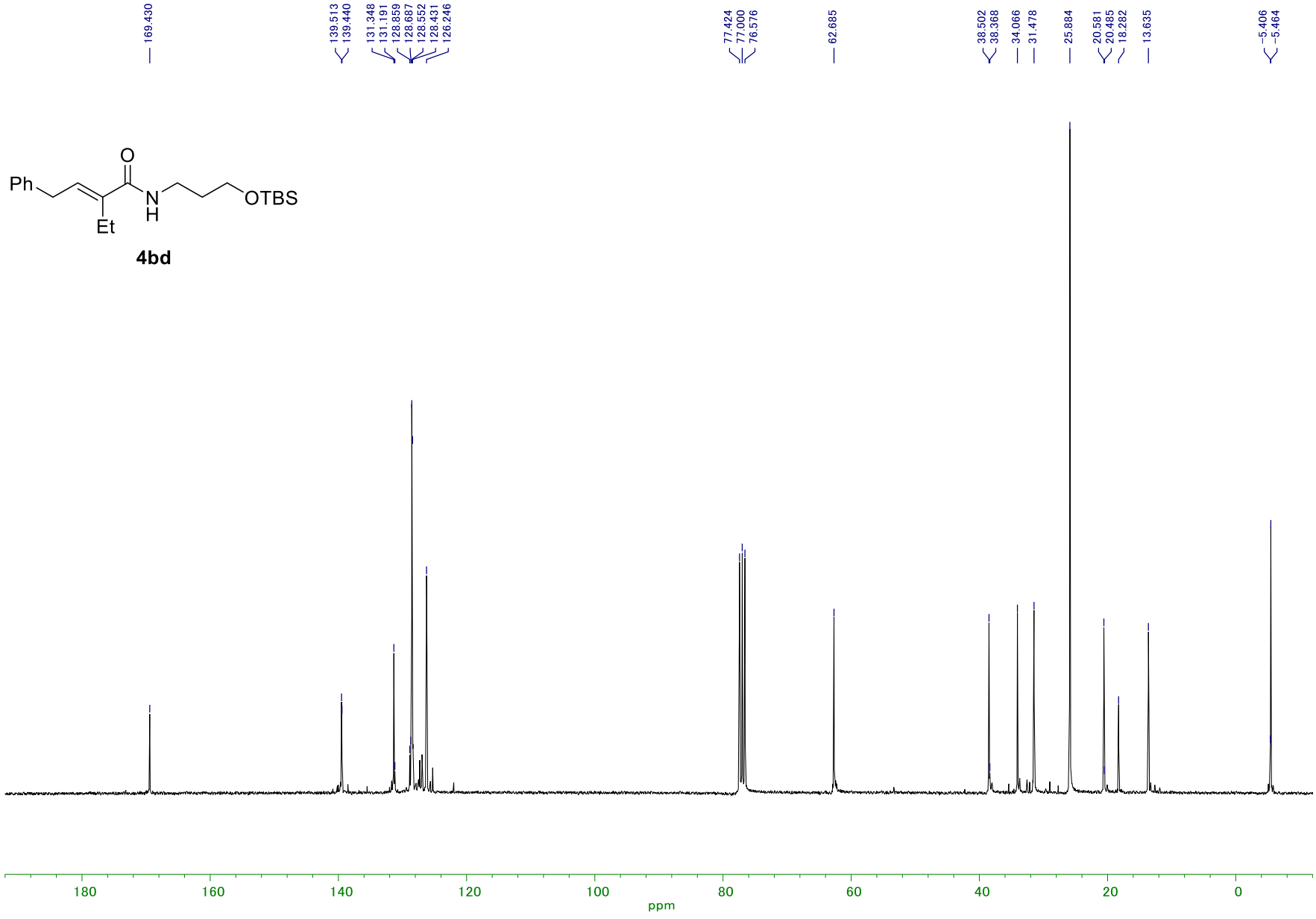
9

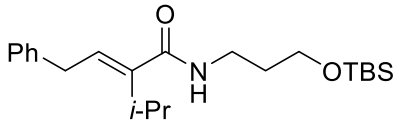

174.333
138.396
116.888
77.423
77.000
76.576
45.423
26.409
16.762
O
NHMe
Me
9
180
160
140
120
100
80
60
40
20
0
ppm



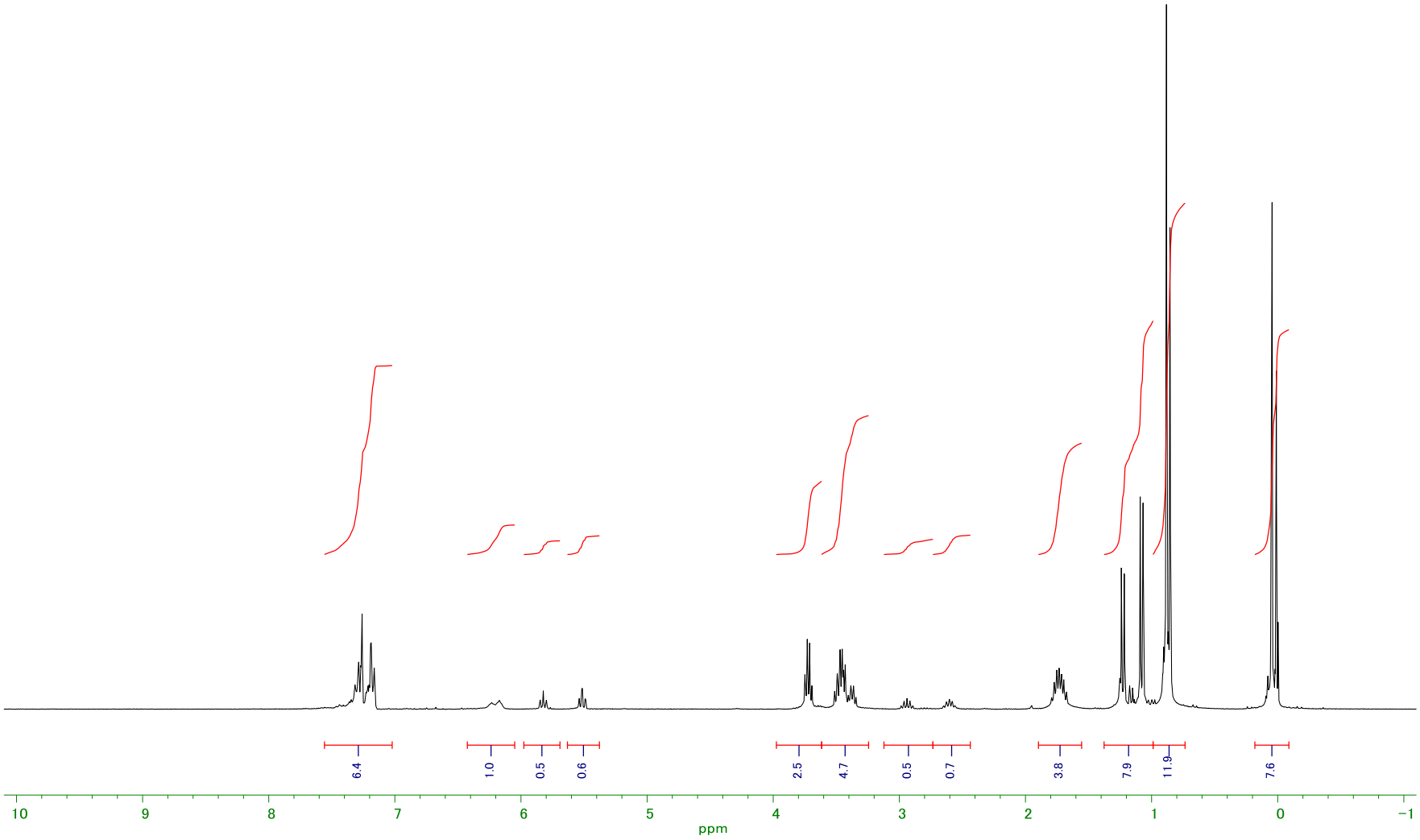
4bd

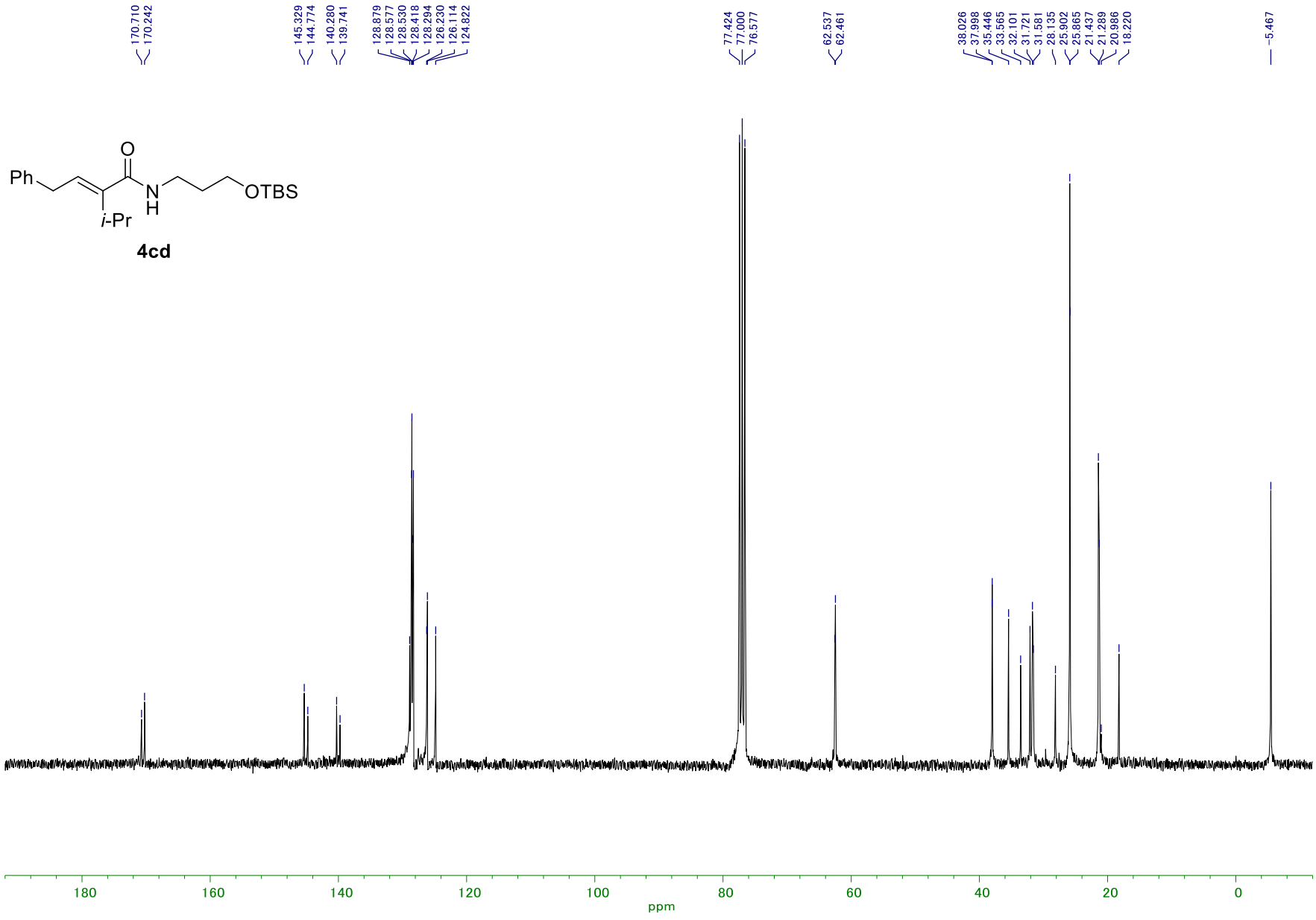


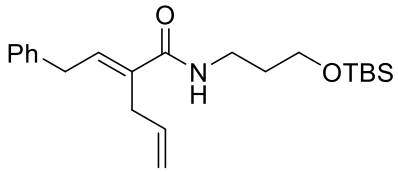

169.430
139.513
139.440
131.348
131.191
128.859
128.687
128.552
128.431
126.246
77.424
77.000
76.576
62.685
38.502
38.368
34.066
31.478
25.884
20.581
20.485
18.282
13.635
-5.406
-5.464
Ph
O
N
H
OTBS
Et
4bd
180
160
140
120
100
80
60
40
20
0
ppm


Ph
O
N
H
OTBS
i-Pr

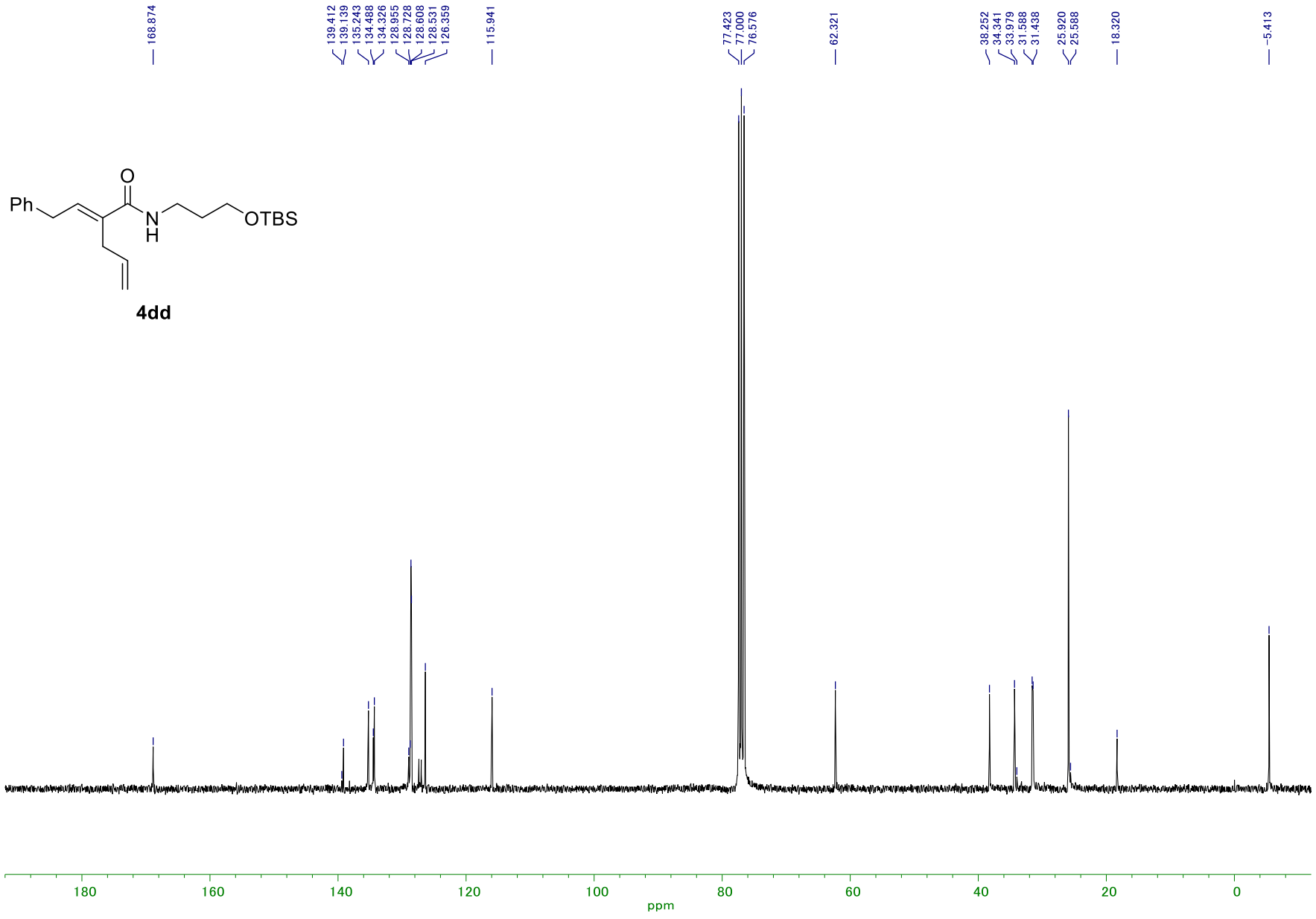
4cd

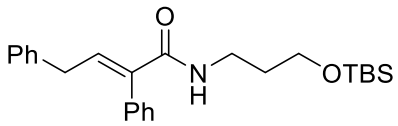

6.4
1.0
0.5
0.6
2.5
4.7
0.5
0.7
3.8
7.9
11.9
7.6
10
9
8
7
6
5
4
3
2
1
0
−1
ppm


170.710
170.242
145.329
144.774
140.280
139.741
128.879
128.577
128.530
128.418
128.294
126.230
126.114
124.822
77.424
77.000
76.577
62.537
62.461
38.026
37.998
35.446
33.565
32.101
31.721
31.581
28.135
25.902
25.865
21.437
21.289
20.986
18.220
-5.467
Ph
O
N
H
OTBS
i-Pr
4cd
180
160
140
120
100
80
60
40
20
0
ppm

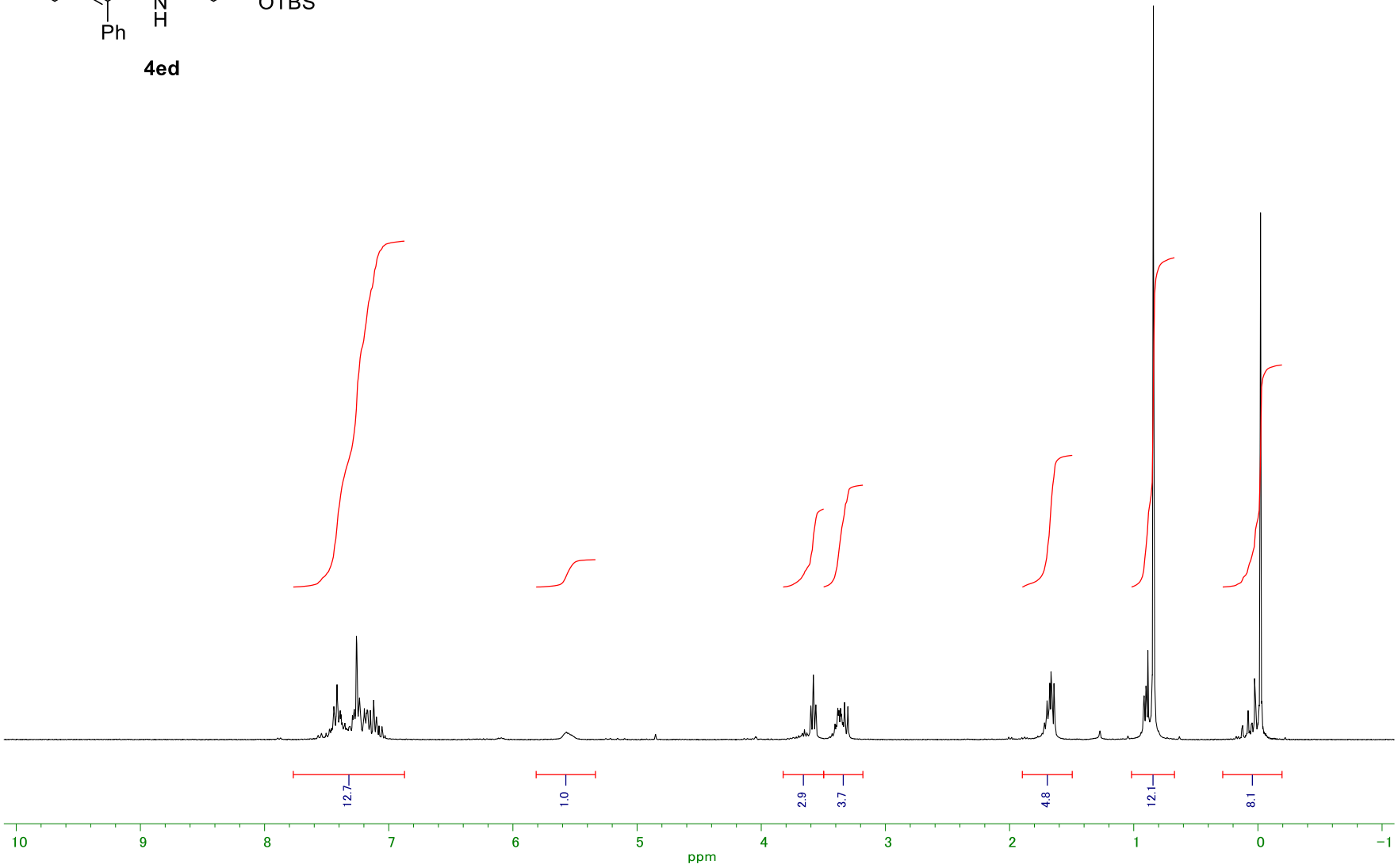


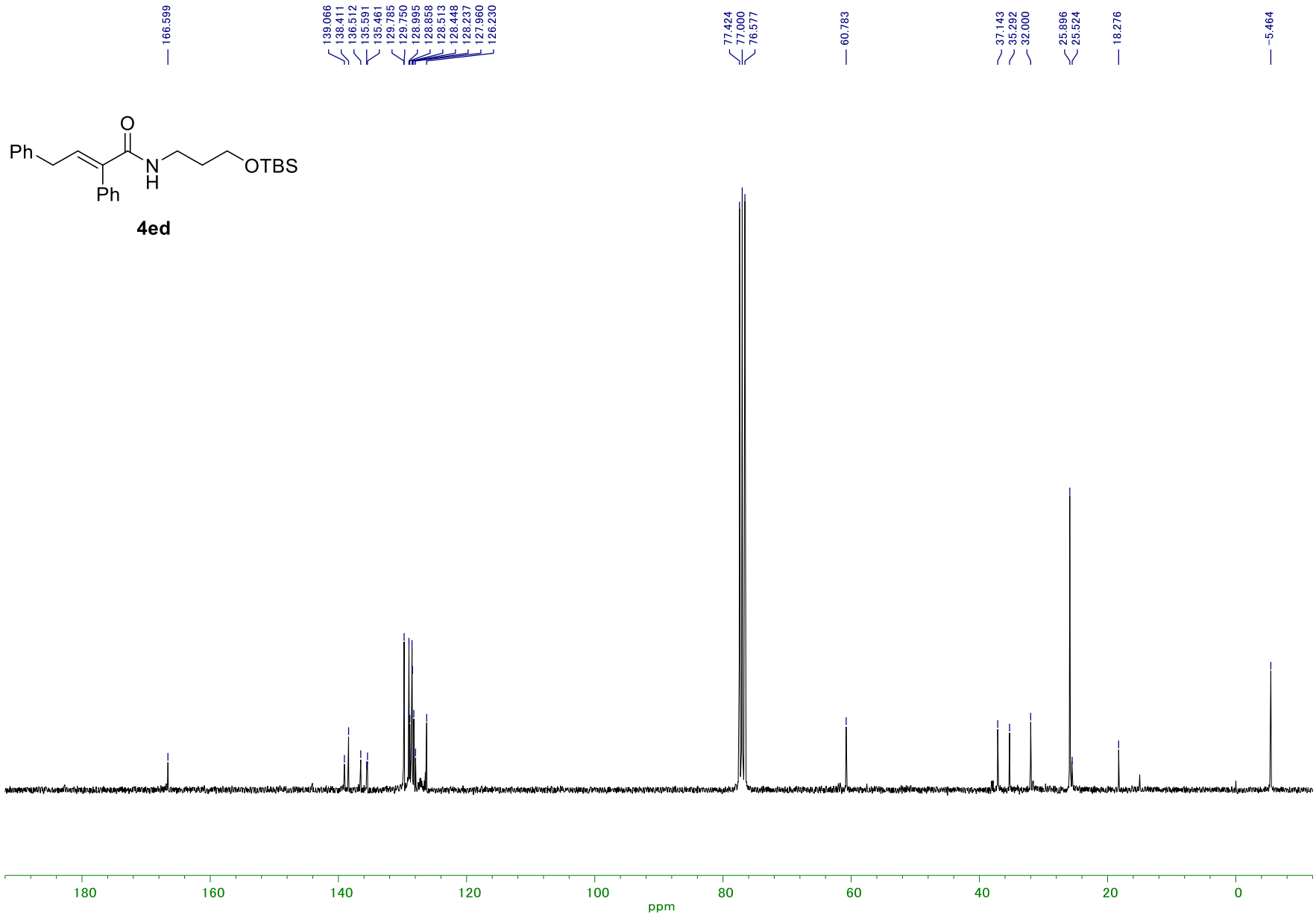
4dd

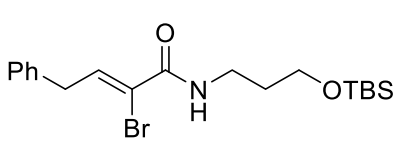

168.874
139.412
139.139
135.243
134.488
134.326
128.955
128.728
128.608
128.531
126.359
115.941
77.423
77.000
76.576
62.321
38.252
34.341
33.979
31.588
31.438
25.920
25.588
18.320
-5.413
Ph
O
N
H
OTBS
4dd
180
160
140
120
100
80
60
40
20
0
ppm



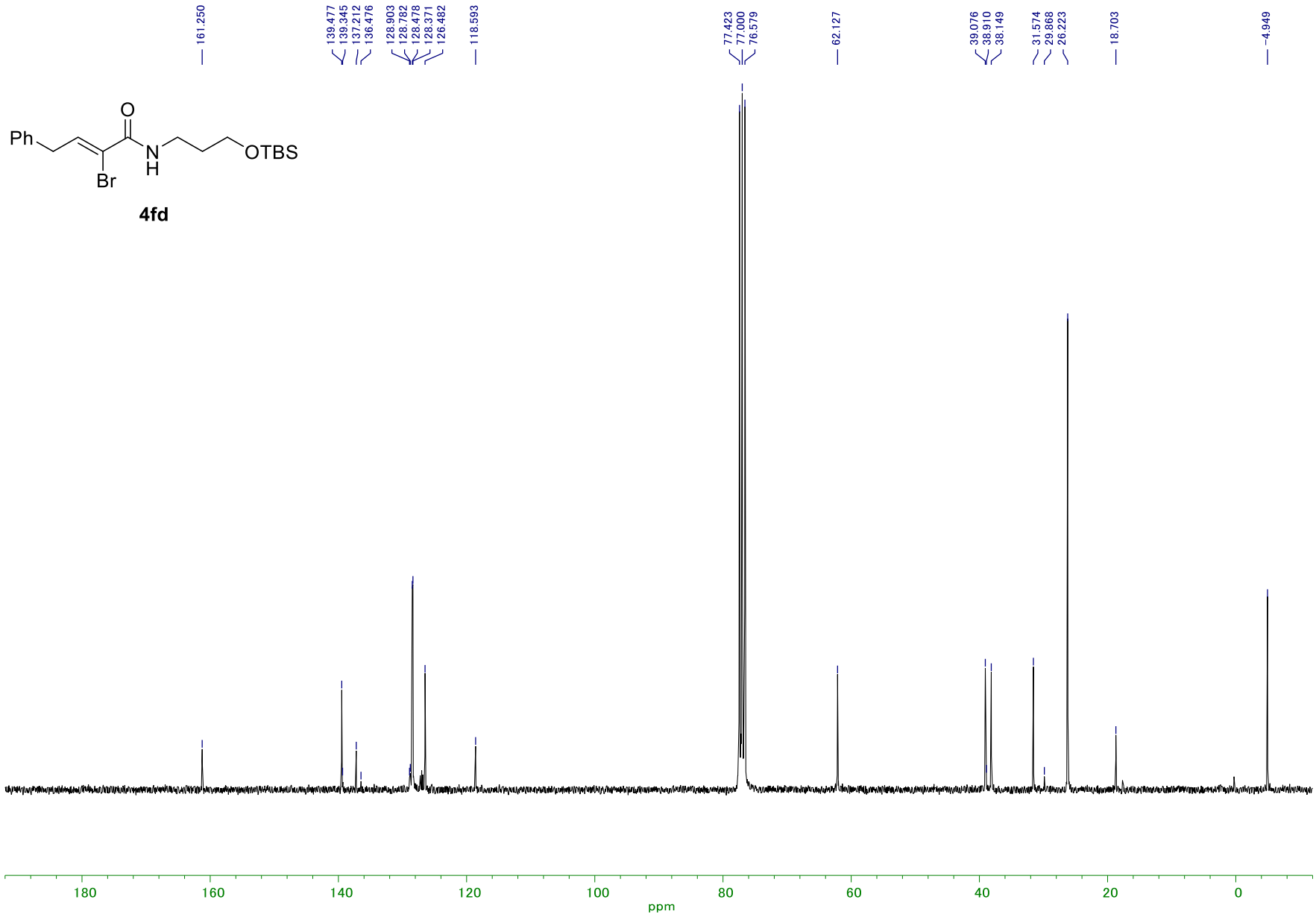
4ed

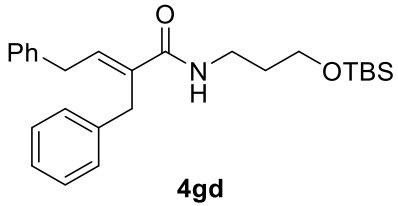



166.599
139.066
138.411
136.512
135.591
135.461
129.785
129.750
128.995
128.858
128.513
128.448
128.237
127.960
126.230
77.424
77.000
76.577
60.783
37.143
35.292
32.000
25.896
25.524
18.276
-5.464
Ph
O
N
H
OTBS
Ph
4ed
180
160
140
120
100
80
60
40
20
0
ppm

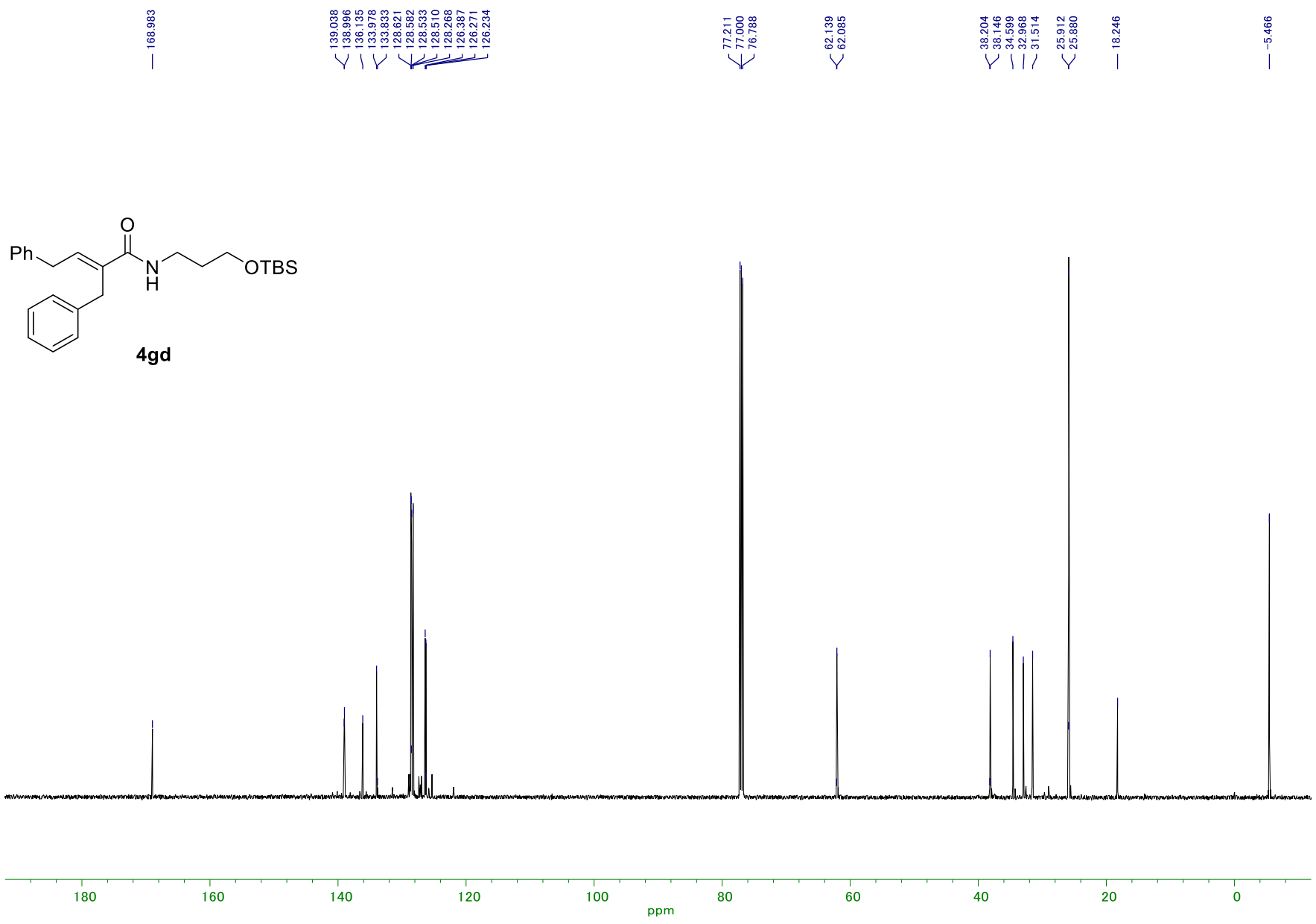


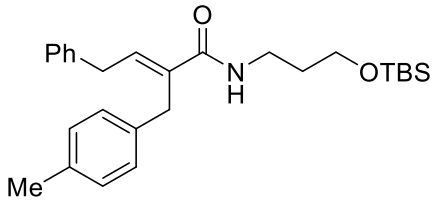
4fd


161.250
139.477
139.345
137.212
136.476
128.903
128.782
128.478
128.371
126.482
118.593
77.423
77.000
76.579
62.127
39.076
38.910
38.149
31.574
29.868
26.223
18.703
-4.949
O
Ph
N
H
OTBS
Br
4fd
180
160
140
120
100
80
60
40
20
0
ppm

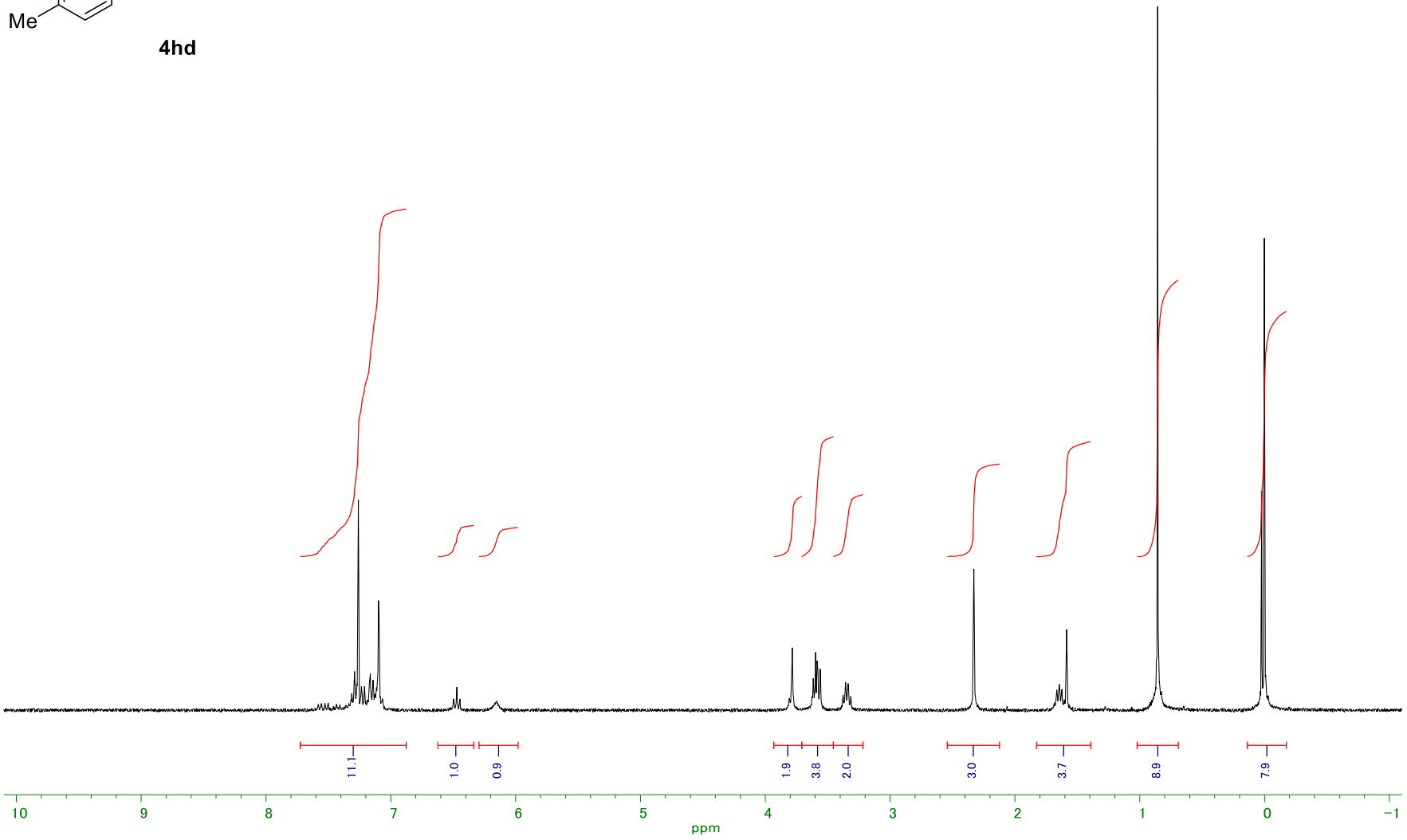


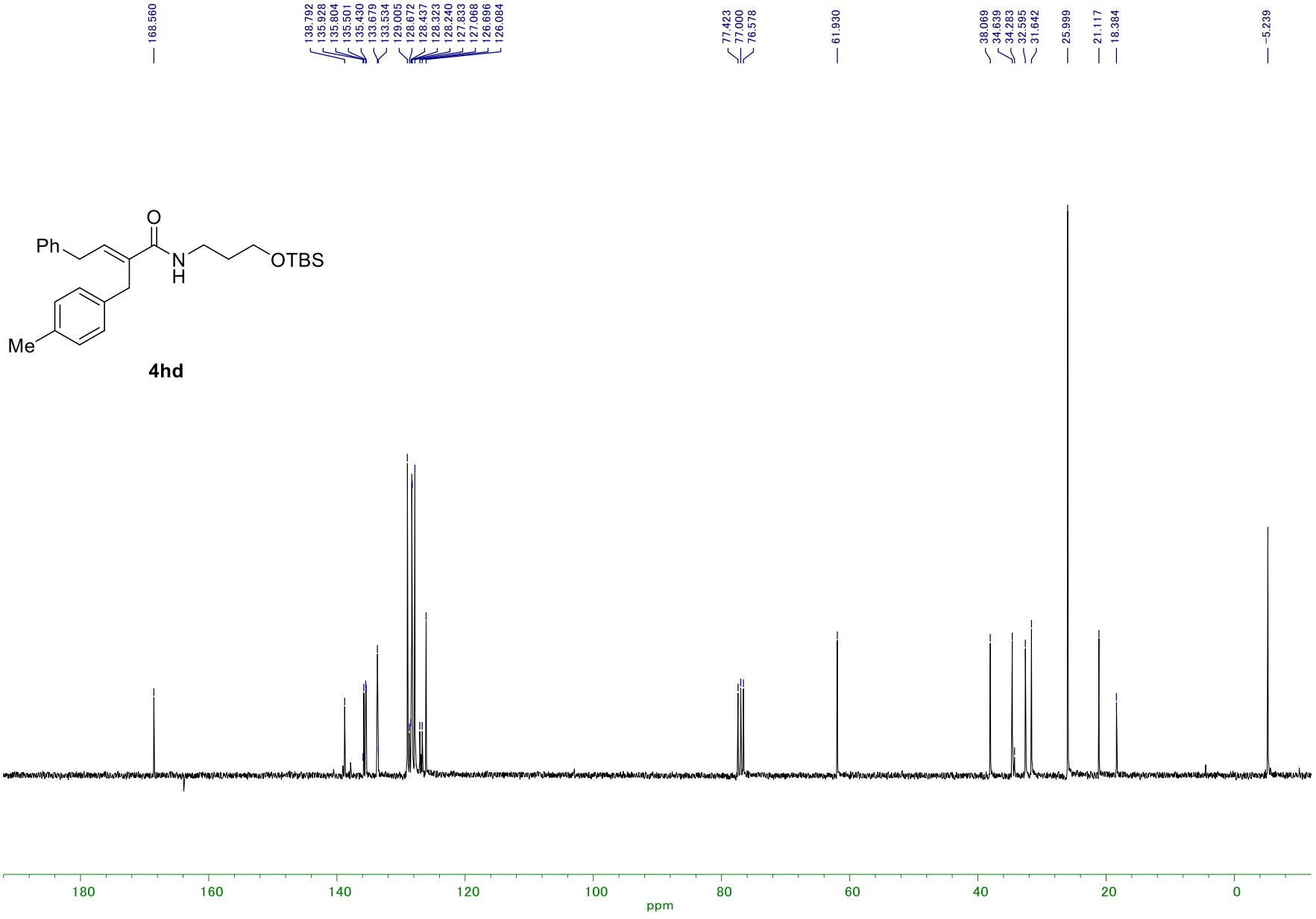
4gd

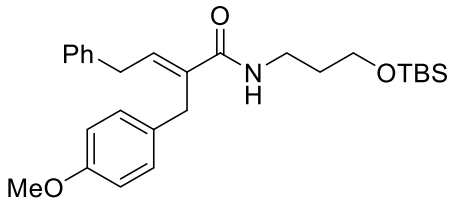

168.983
139.038
138.996
136.135
133.978
133.833
128.621
128.582
128.533
128.510
128.268
126.387
126.271
126.234
77.211
77.000
76.788
62.139
62.085
38.204
38.146
34.599
32.968
31.514
25.912
25.880
18.246
-5.466
O
Ph
N
H
OTBS
4gd
180
160
140
120
100
80
60
40
20
0
ppm



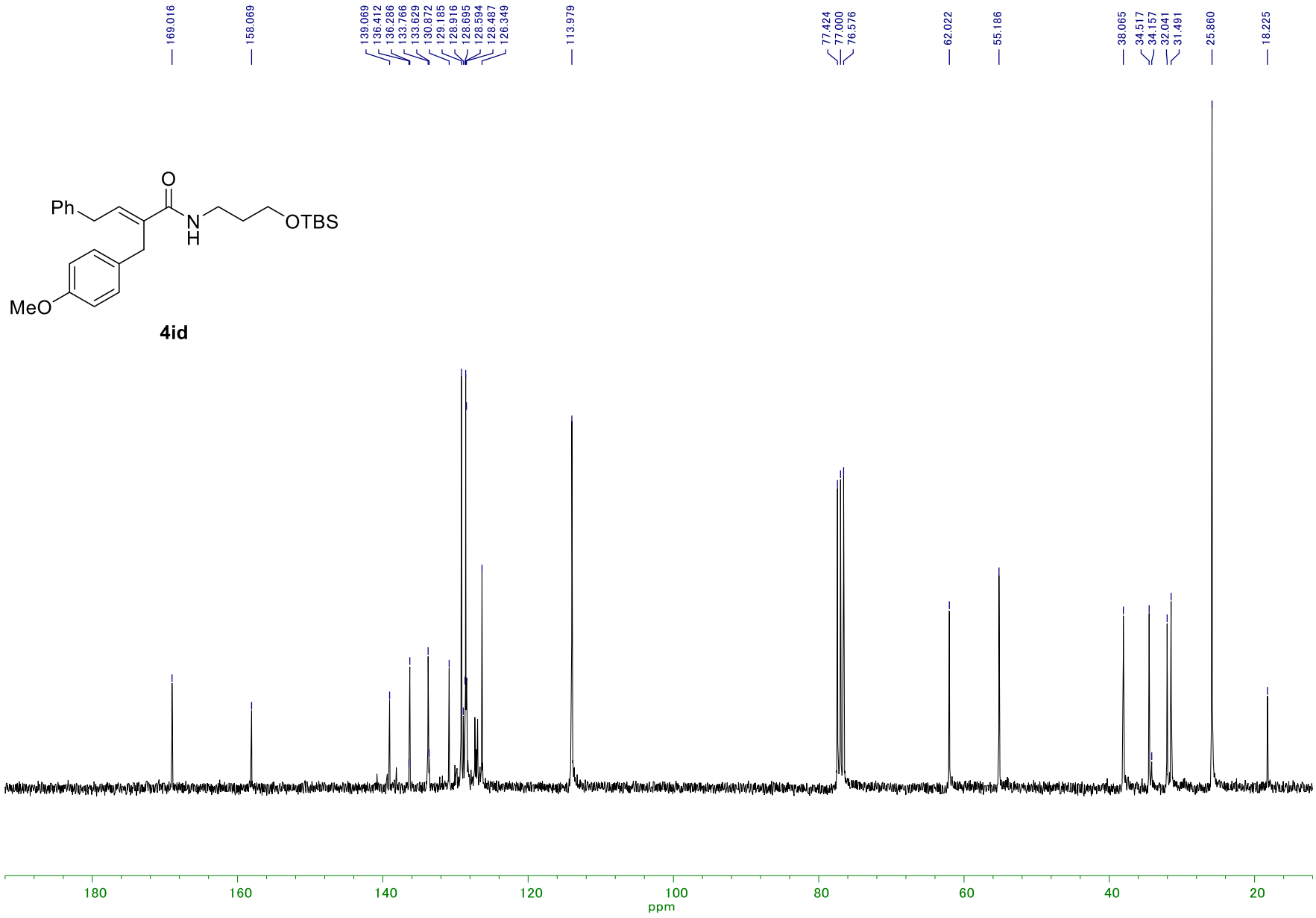
4hd

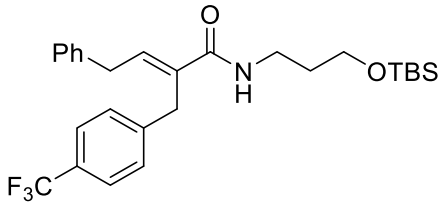



168.560
138.792
135.928
135.804
135.501
135.430
133.679
133.534
129.005
128.672
128.437
128.323
128.240
127.833
127.068
126.696
126.084
77.423
77.000
76.578
61.930
38.069
34.639
34.283
32.595
31.642
25.999
21.117
18.384
-5.239
O
Ph
N
H
OTBS
Me
4hd
180
160
140
120
100
80
60
40
20
0
ppm

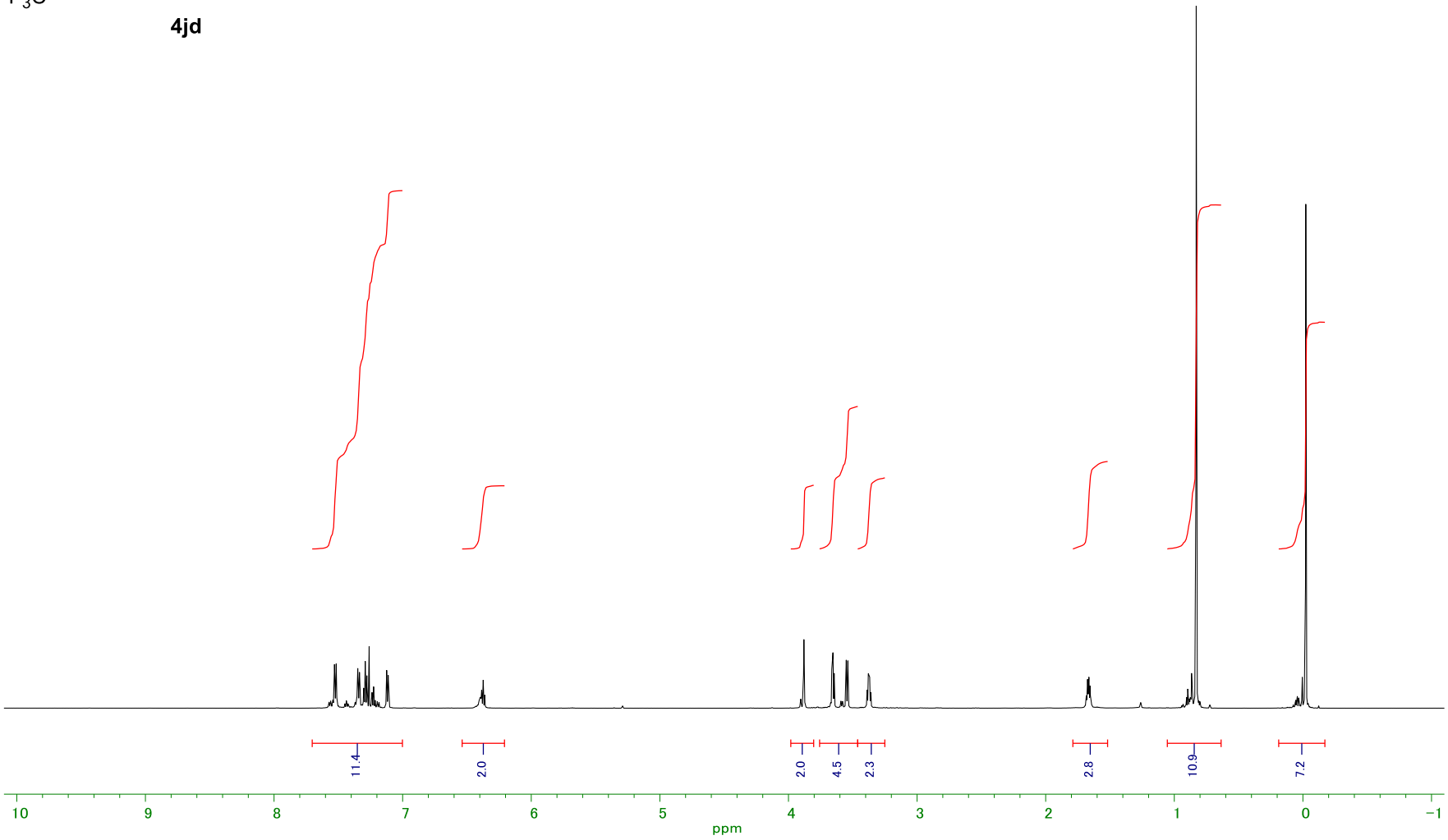


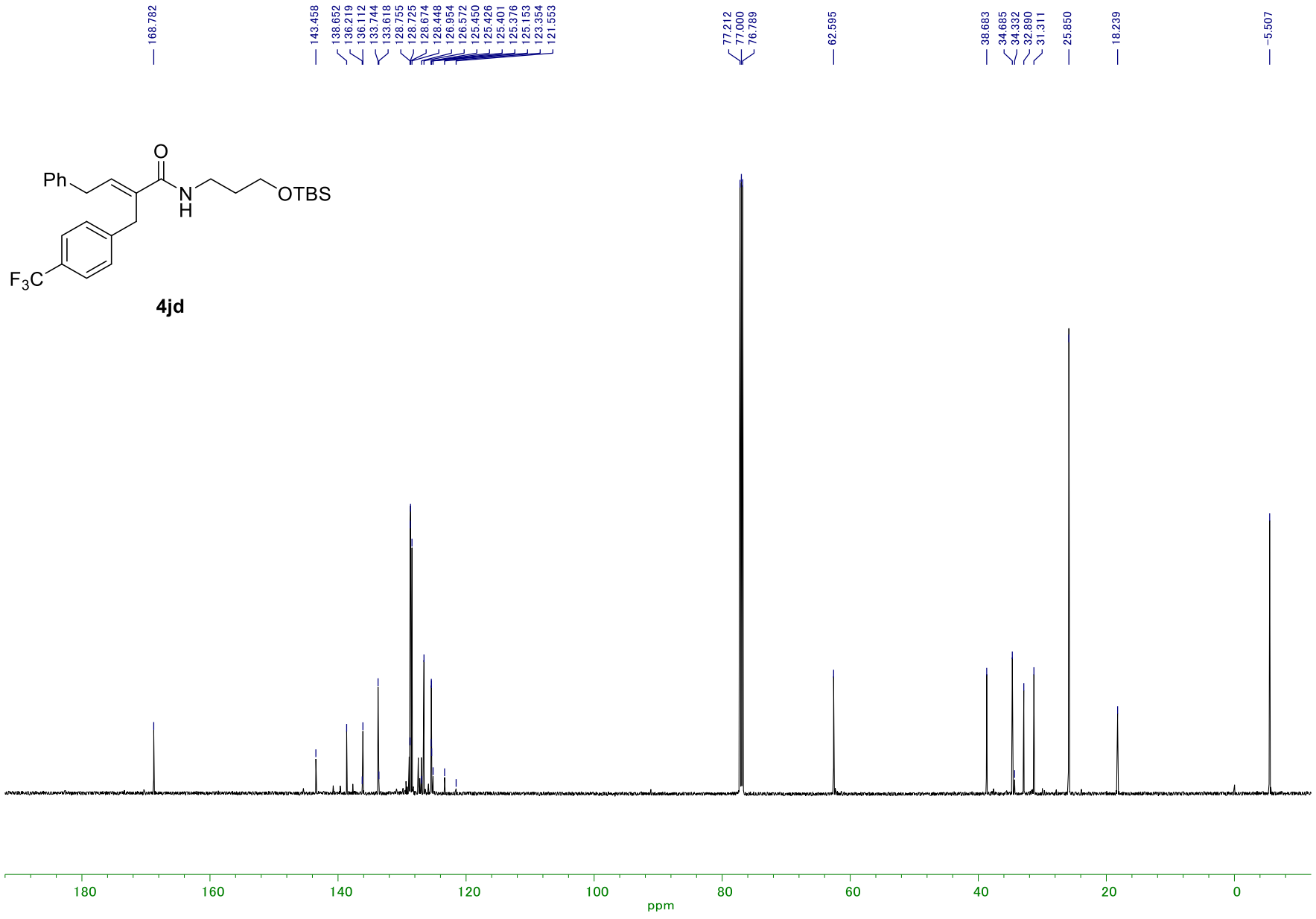
4id

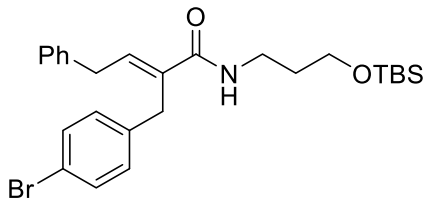

169.016
158.069
139.069
136.412
136.286
133.766
133.629
130.872
129.185
128.916
128.695
128.594
128.487
126.349
113.979
77.424
77.000
76.576
62.022
55.186
38.065
34.517
34.157
32.041
31.491
25.860
18.225
Ph
O
N
H
OTBS
MeO
4id
180
160
140
120
100
80
60
40
20
ppm



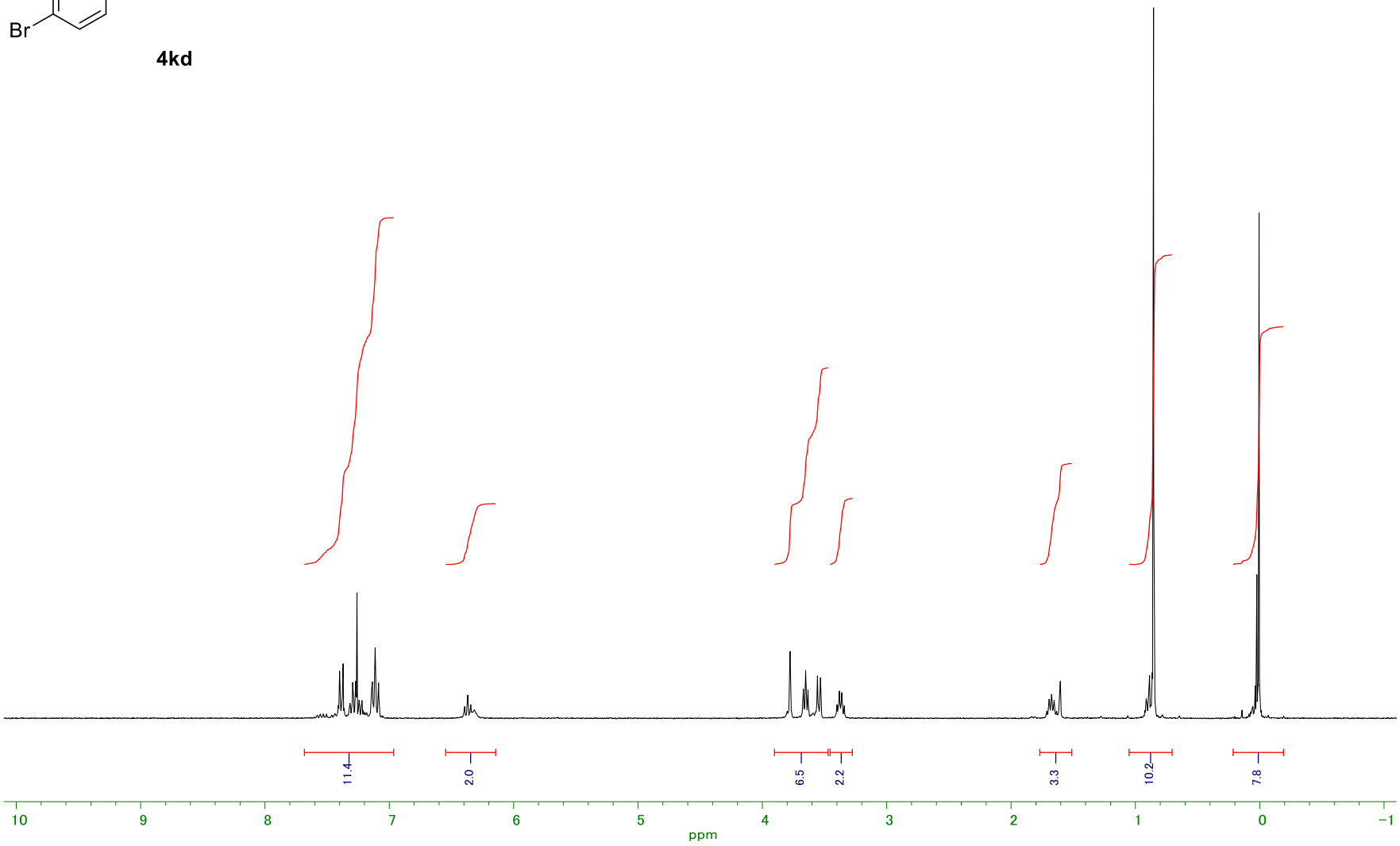
4jd

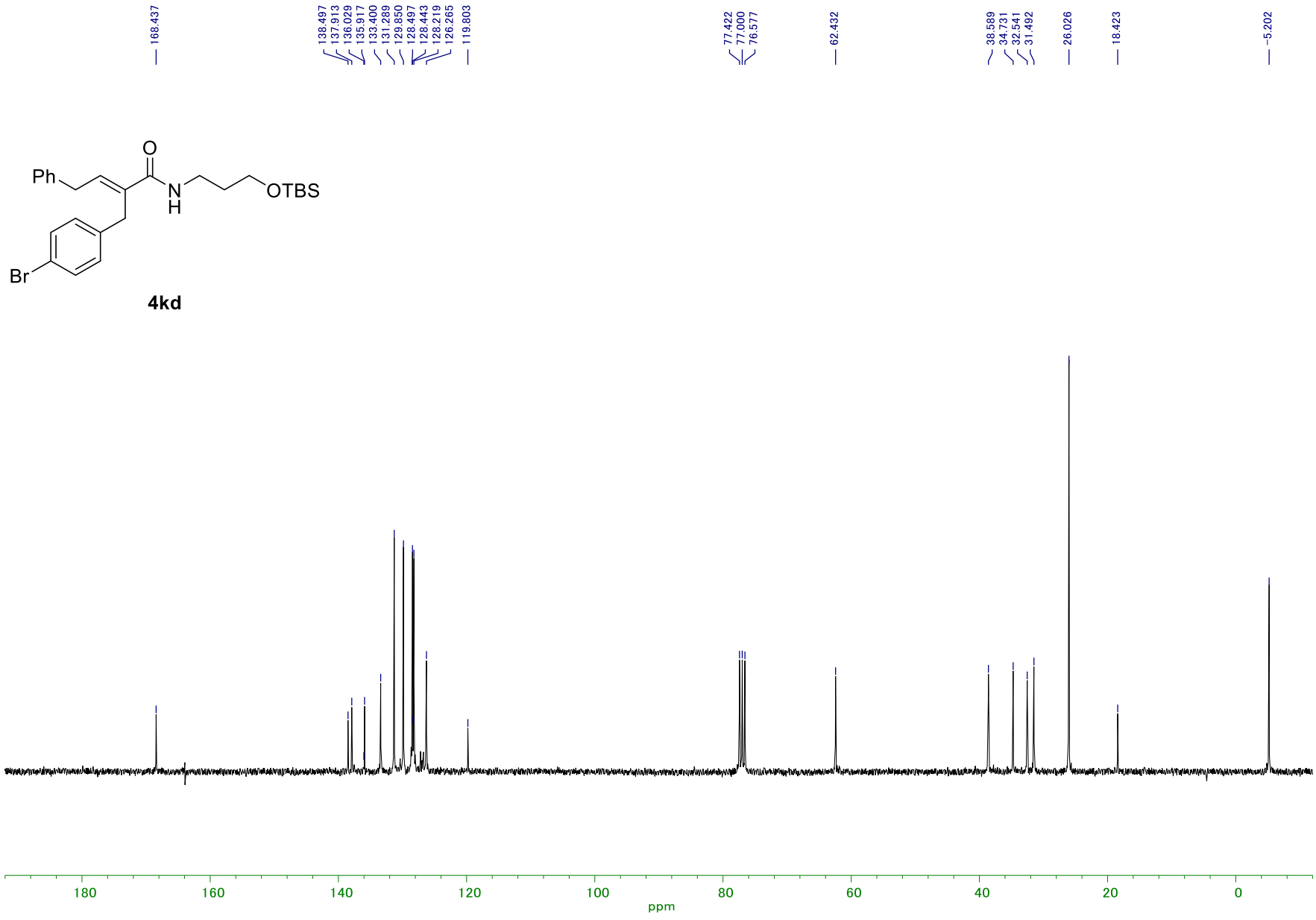


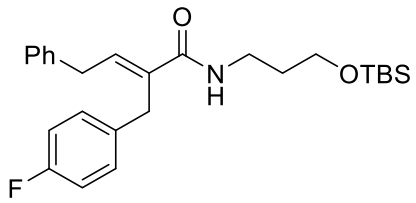

168.782
143.458
138.652
136.219
136.112
133.744
133.618
128.755
128.725
128.674
128.448
126.954
126.572
125.450
125.426
125.401
125.376
125.153
123.354
121.553
77.212
77.000
76.789
62.595
38.683
34.685
34.332
32.890
31.311
25.850
18.239
-5.507
Ph
O
N
H
OTBS
F3C
4jd
180
160
140
120
100
80
60
40
20
0
ppm



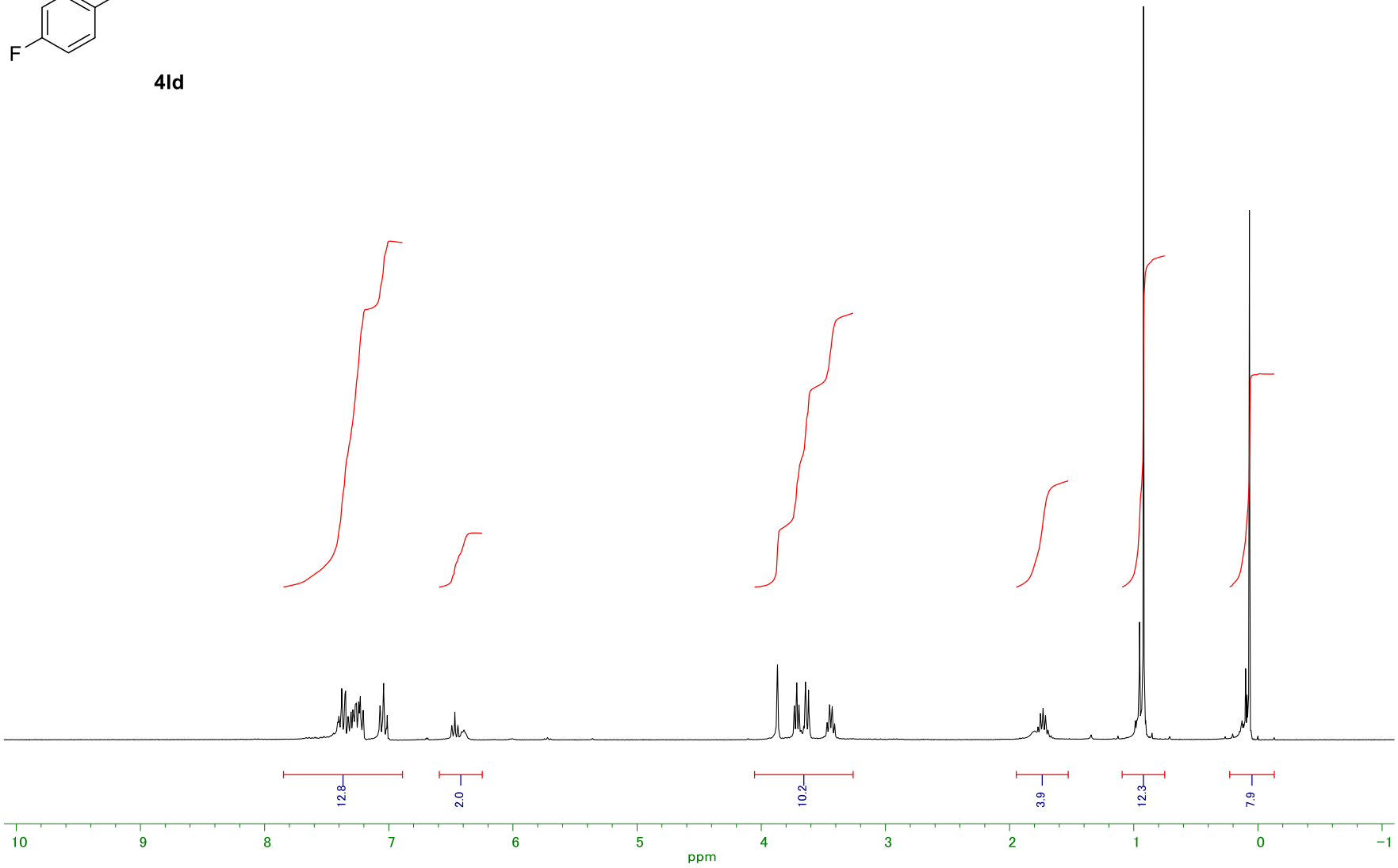
4kd

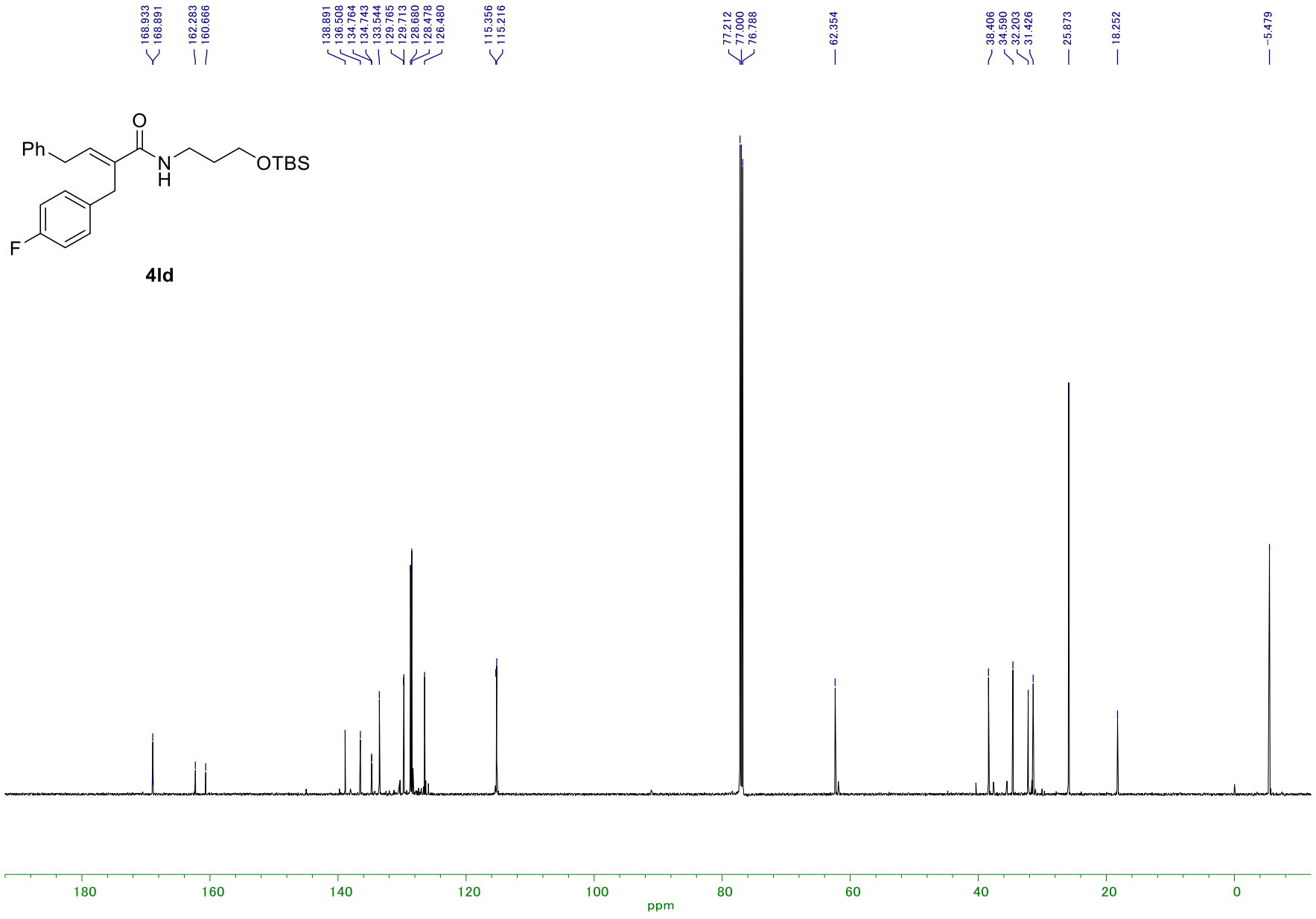


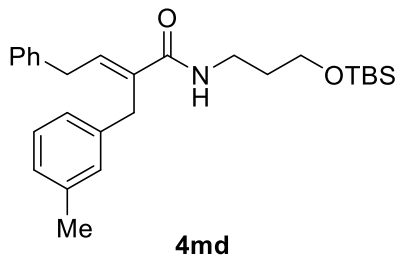

168.437
138.497
137.913
136.029
135.917
133.400
131.289
129.850
128.497
128.443
128.219
126.265
119.803
77.422
77.000
76.577
62.432
38.589
34.731
32.541
31.492
26.026
18.423
-5.202
O
Ph
N
H
OTBS
Br
4kd
180
160
140
120
100
80
60
40
20
0
ppm



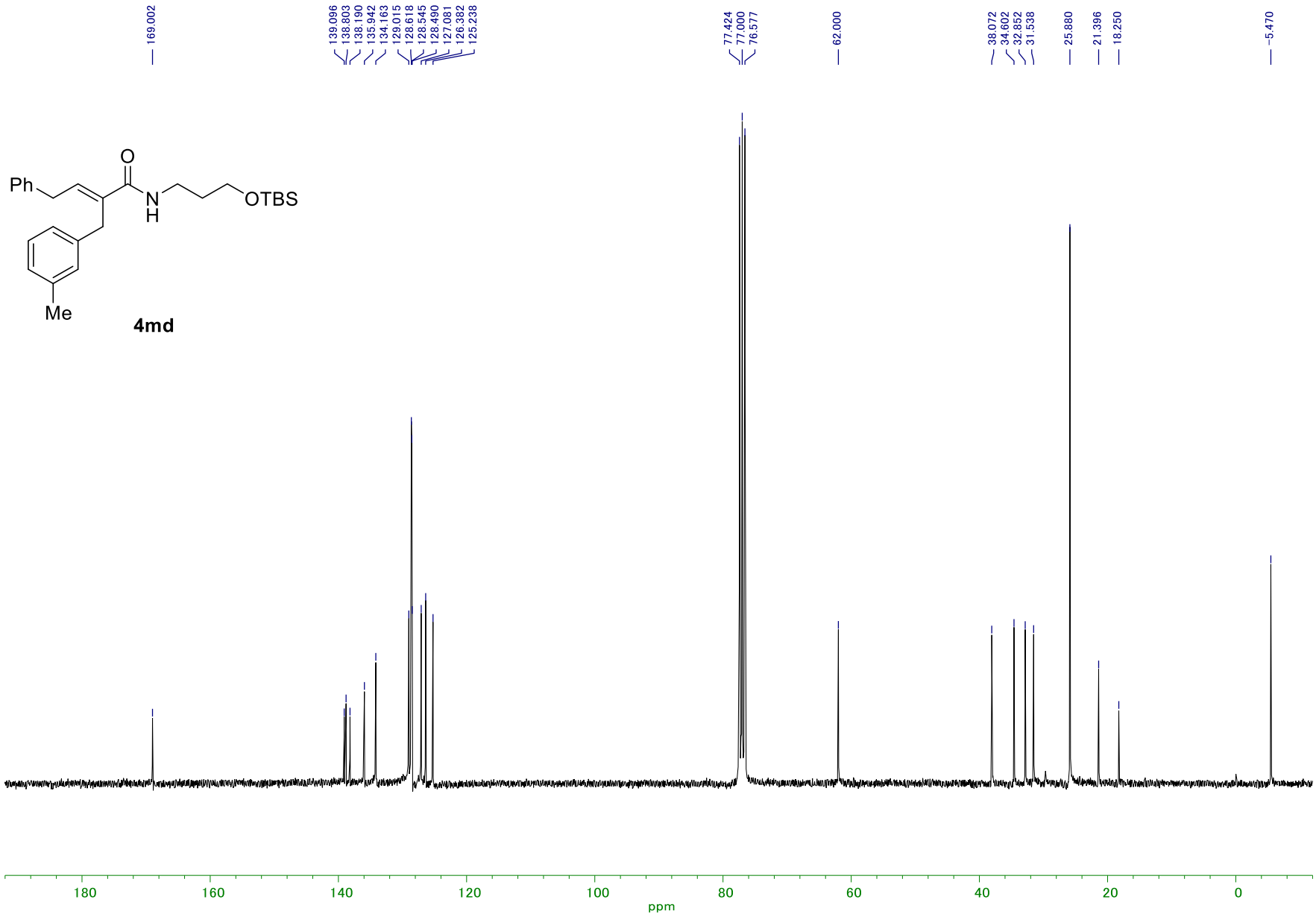
4ld

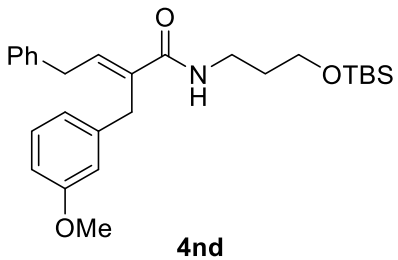



168.933
168.891
162.283
160.666
138.891
136.508
134.764
134.743
133.544
129.765
129.713
128.680
128.478
126.480
115.356
115.216
77.212
77.000
76.788
62.354
38.406
34.590
32.203
31.426
25.873
18.252
-5.479
Ph
O
N
H
OTBS
F
4Id
180
160
140
120
100
80
60
40
20
0
ppm

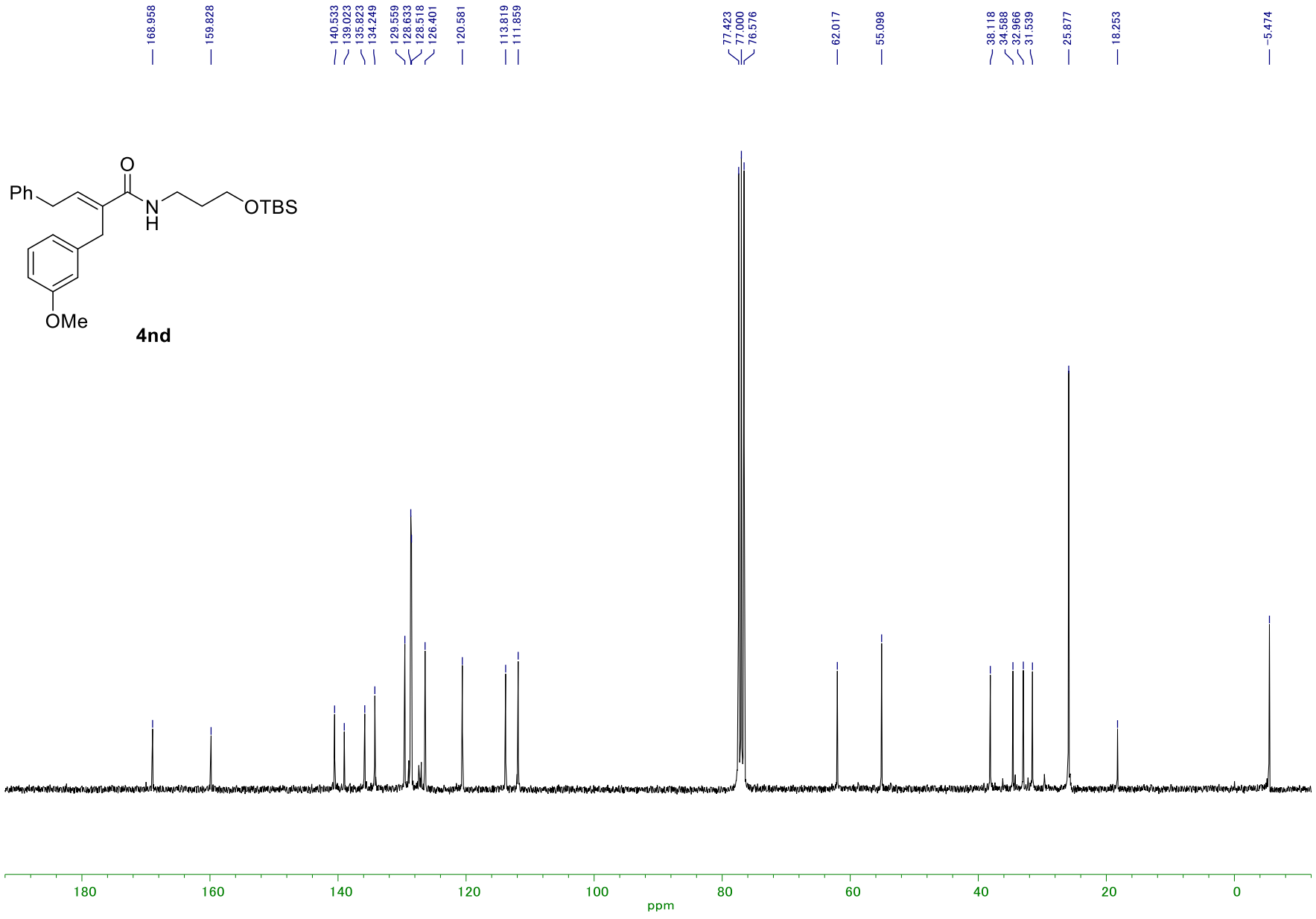


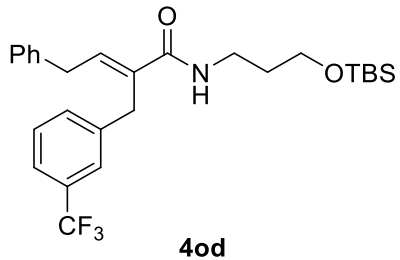
4md


169.002
139.096
138.803
138.190
135.942
134.163
129.015
128.618
128.545
128.490
127.081
126.382
125.238
77.424
77.000
76.577
62.000
38.072
34.602
32.852
31.538
25.880
21.396
18.250
-5.470
Ph
O
N
H
OTBS
Me
4md
180
160
140
120
100
80
60
40
20
0
ppm

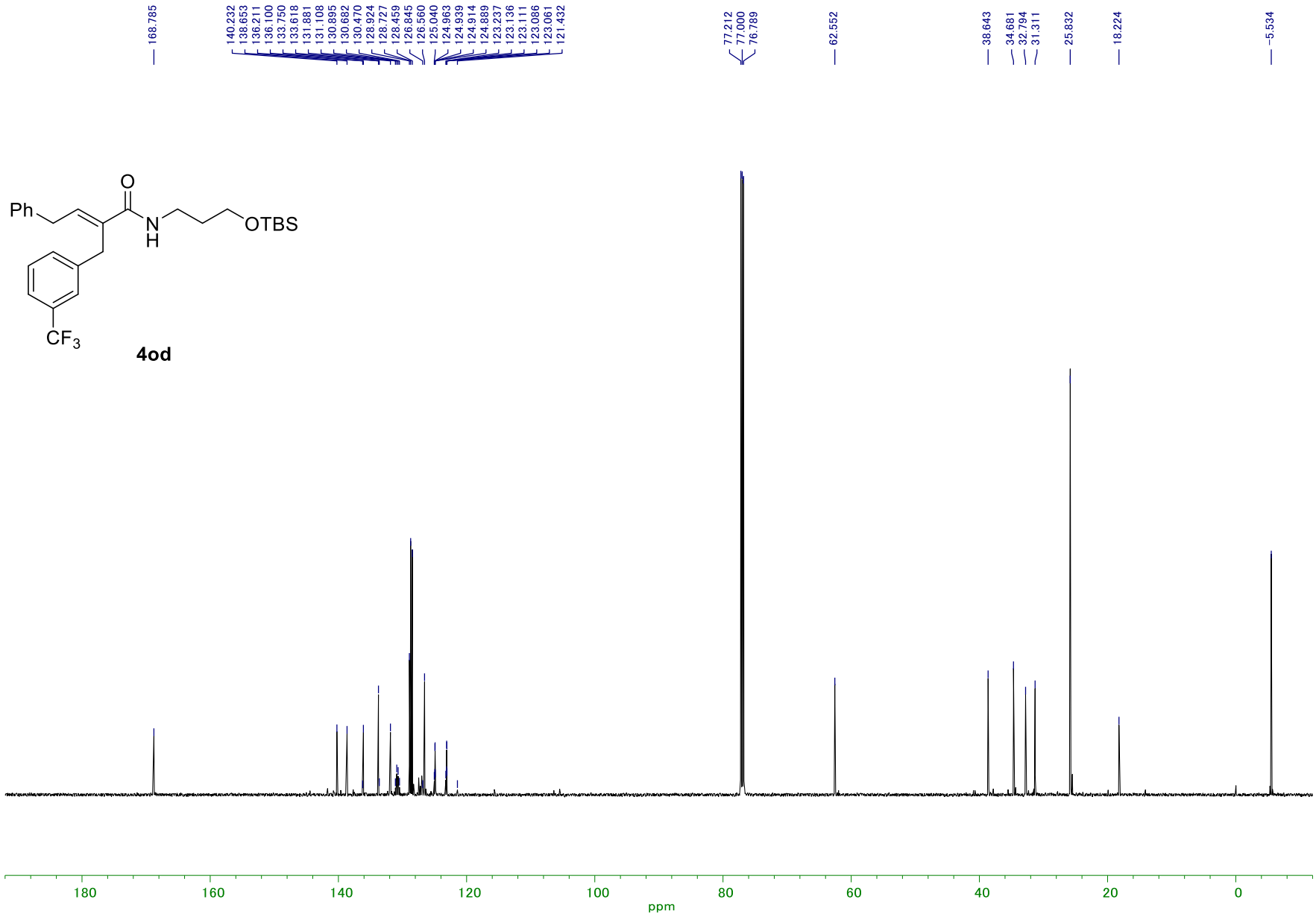


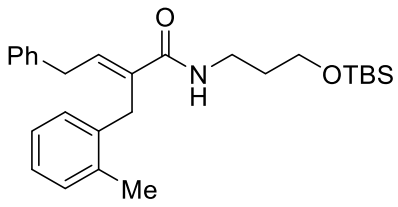
4nd


168.958
159.828
140.533
139.023
135.823
134.249
129.559
128.633
128.518
126.401
120.581
113.819
111.859
77.423
77.000
76.576
62.017
55.098
38.118
34.588
32.966
31.539
25.877
18.253
-5.474
Ph
O
N
H
OTBS
OMe
4nd
180
160
140
120
100
80
60
40
20
0
ppm

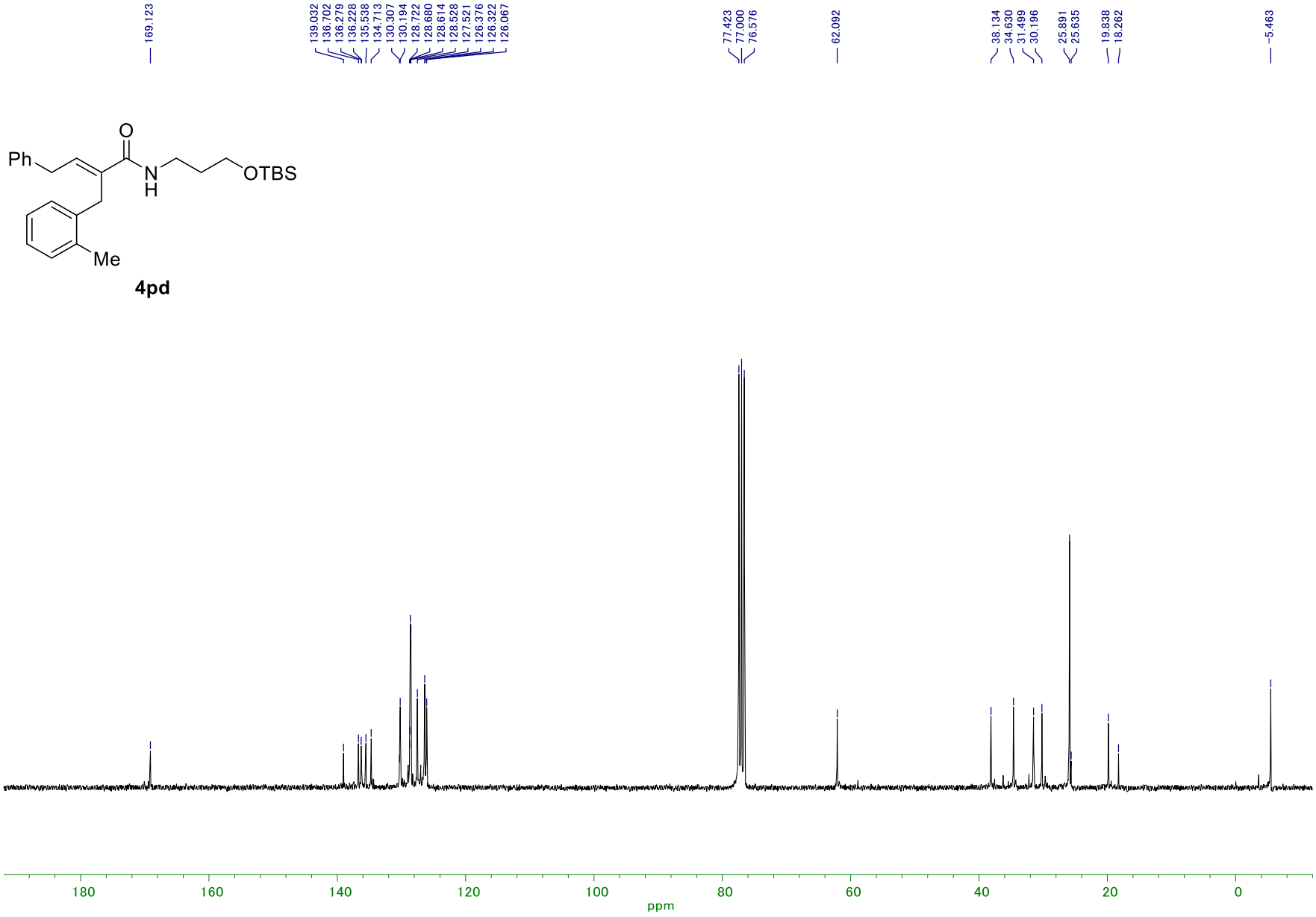


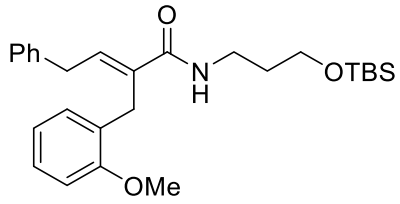
4od


168.785
140.232
138.653
136.211
136.100
133.750
133.618
131.881
131.108
130.895
130.682
130.470
128.924
128.727
128.459
126.845
126.560
125.040
124.963
124.939
124.914
124.889
123.237
123.136
123.111
123.086
123.061
121.432
77.212
77.000
76.789
62.552
38.643
34.681
32.794
31.311
25.832
18.224
-5.534
Ph
O
N
H
OTBS
CF3
4od
180
160
140
120
100
80
60
40
20
0
ppm



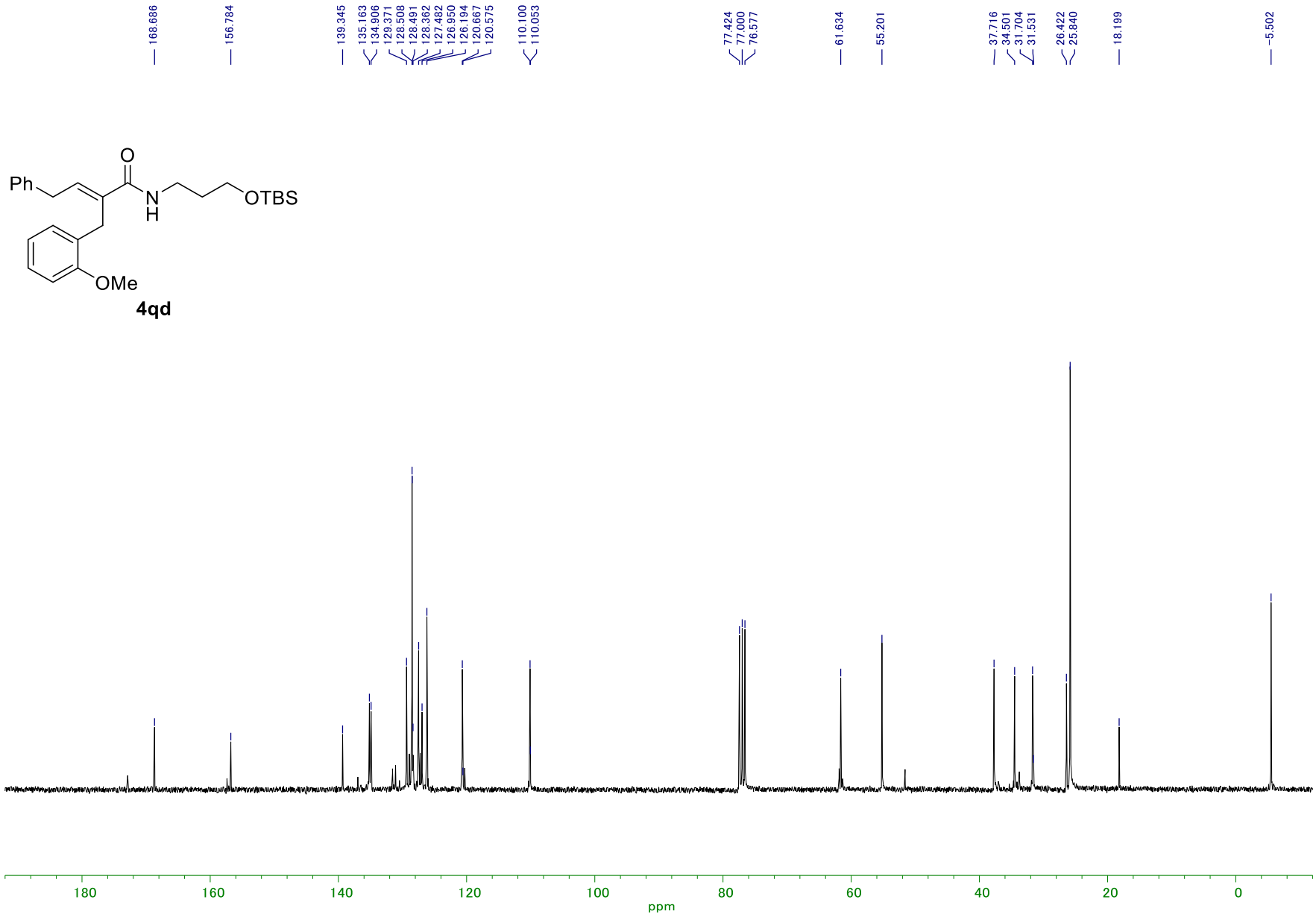
4pd

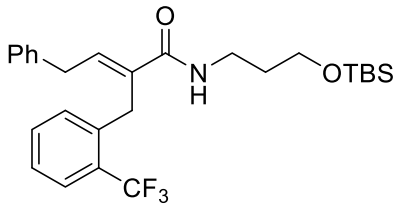

169.123
139.032
136.702
136.279
136.228
135.538
134.713
130.307
130.194
128.722
128.680
128.614
128.528
127.521
126.376
126.322
126.067
77.423
77.000
76.576
62.092
38.134
34.630
31.499
30.196
25.891
25.635
19.838
18.262
-5.463
O
Ph
N
H
OTBS
Me
4pd
180
160
140
120
100
80
60
40
20
0
ppm


O
Ph
N
H
OTBS
OMe

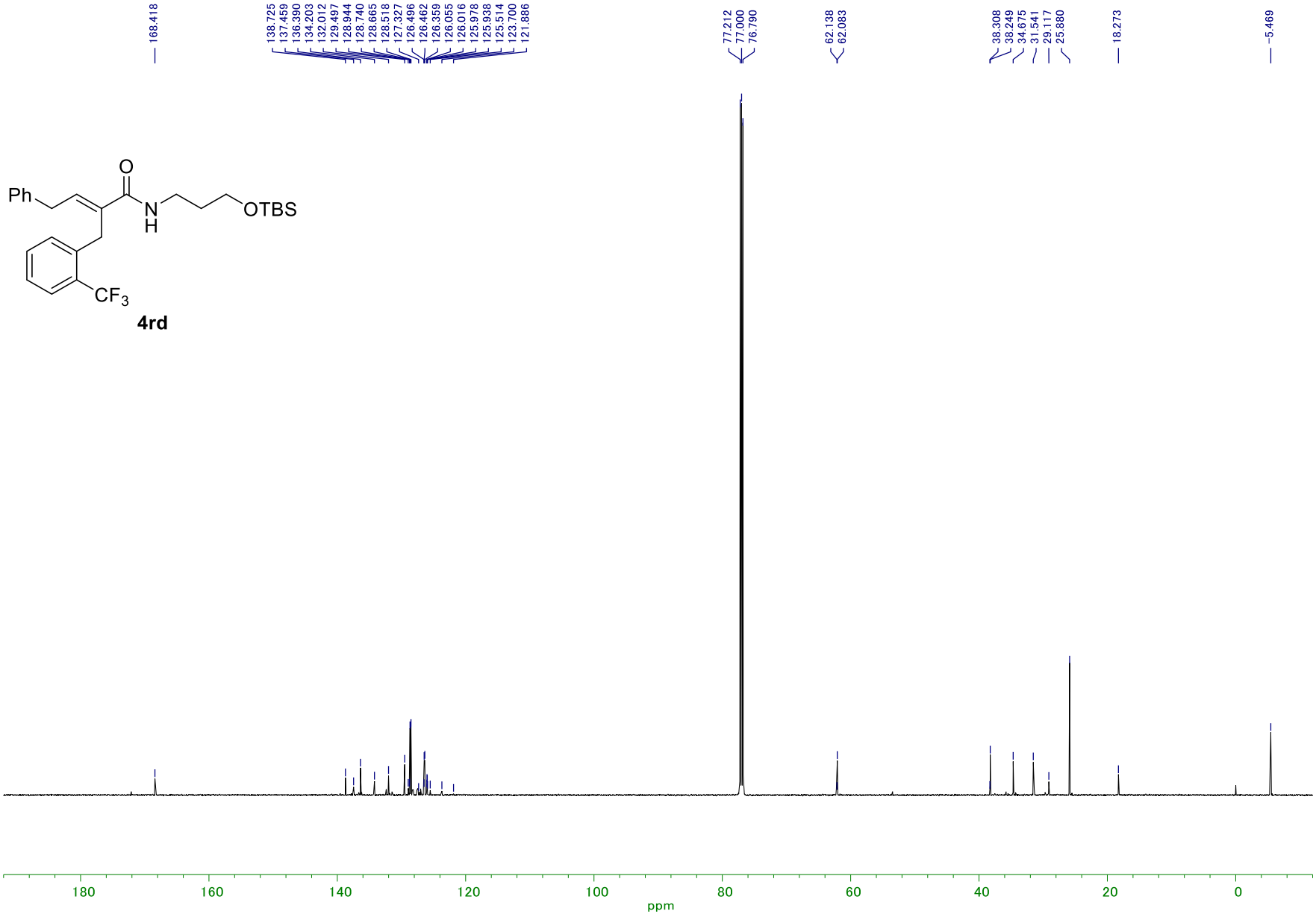
4qd

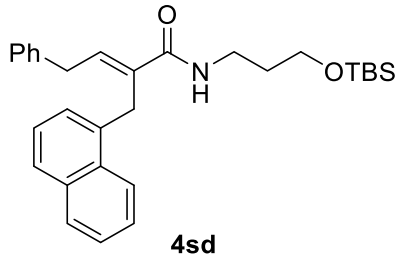
10.2
2.7
1.0
1.4
0.1
6.3
5.3
3.3
2.9
12.7
8.3
10
9
8
7
6
5
4
3
2
1
0
−1
ppm


168.686
156.784
139.345
135.163
134.906
129.371
128.508
128.491
128.362
127.482
126.950
126.194
120.667
120.575
110.100
110.053
77.424
77.000
76.577
61.634
55.201
37.716
34.501
31.704
31.531
26.422
25.840
18.199
-5.502
Ph
O
N
H
OTBS
OMe
4qd
180
160
140
120
100
80
60
40
20
0
ppm

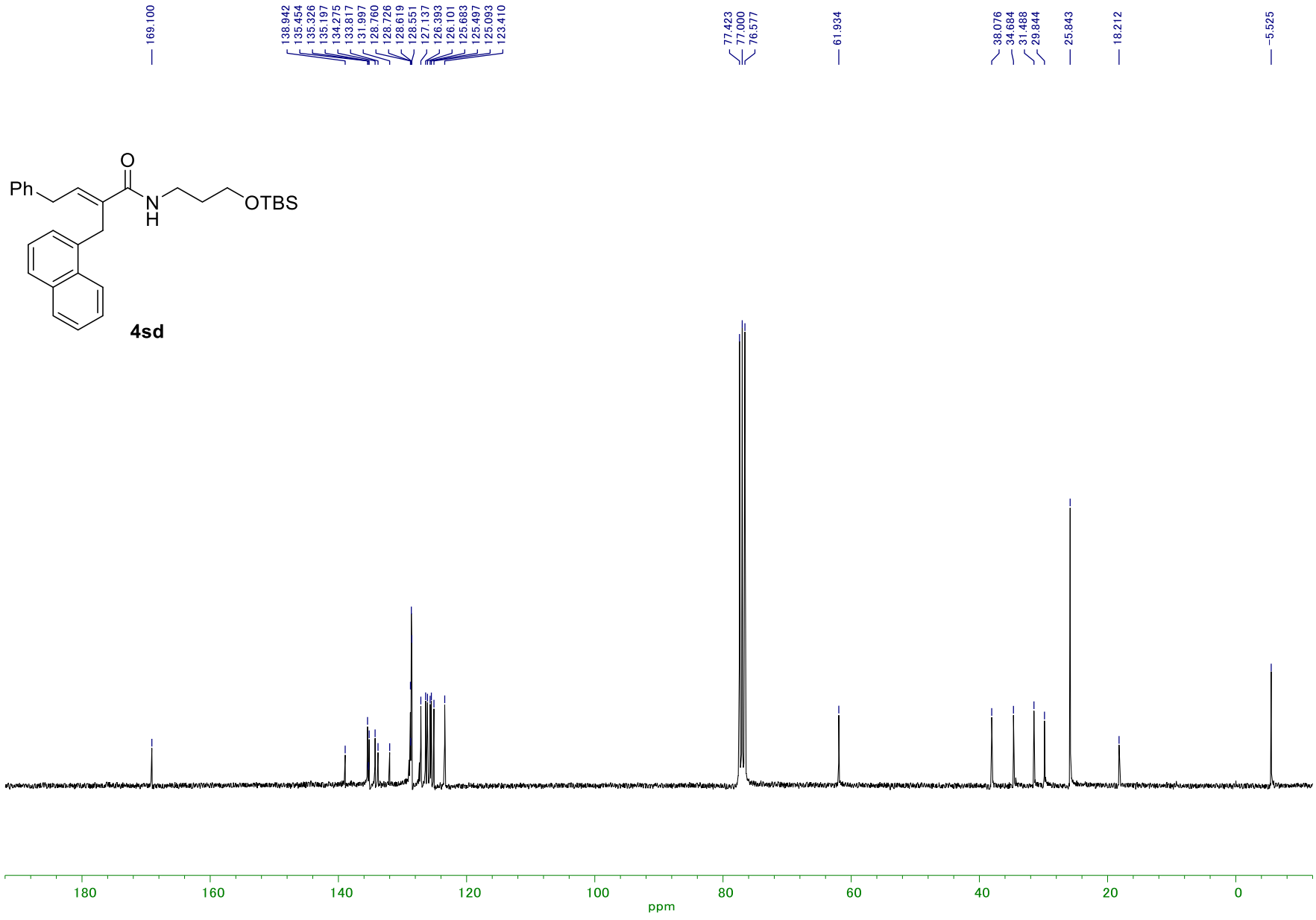


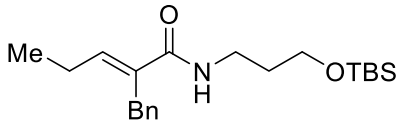
4rd


168.418
138.725
137.459
136.390
134.203
132.012
129.497
128.944
128.740
128.665
128.518
127.327
126.496
126.462
126.359
126.055
126.016
125.978
125.938
125.514
123.700
121.886
77.212
77.000
76.790
62.138
62.083
38.308
38.249
34.675
31.541
29.117
25.880
18.273
-5.469
Ph
O
N
H
OTBS
CF3
4rd
180
160
140
120
100
80
60
40
20
0
ppm

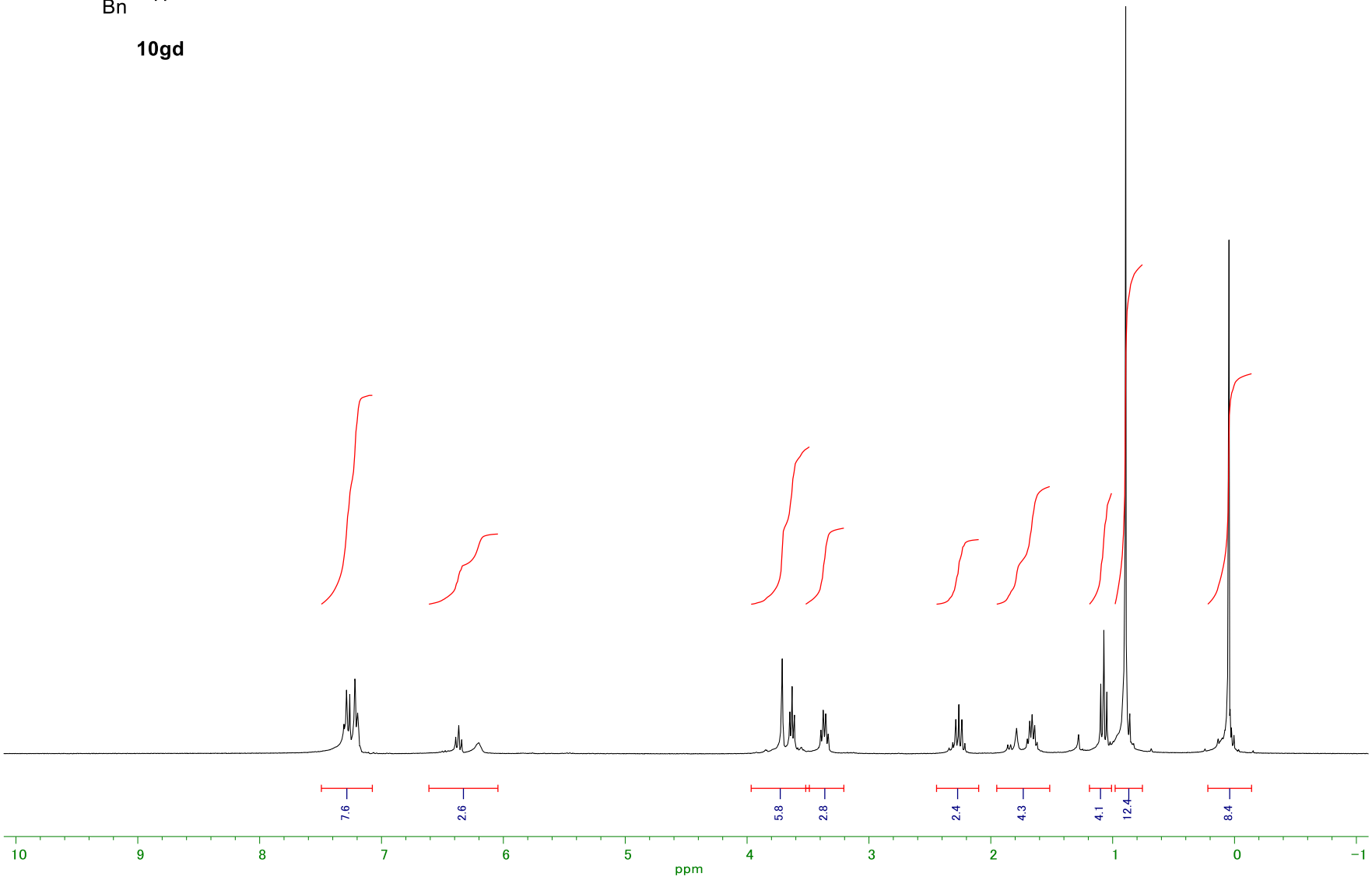


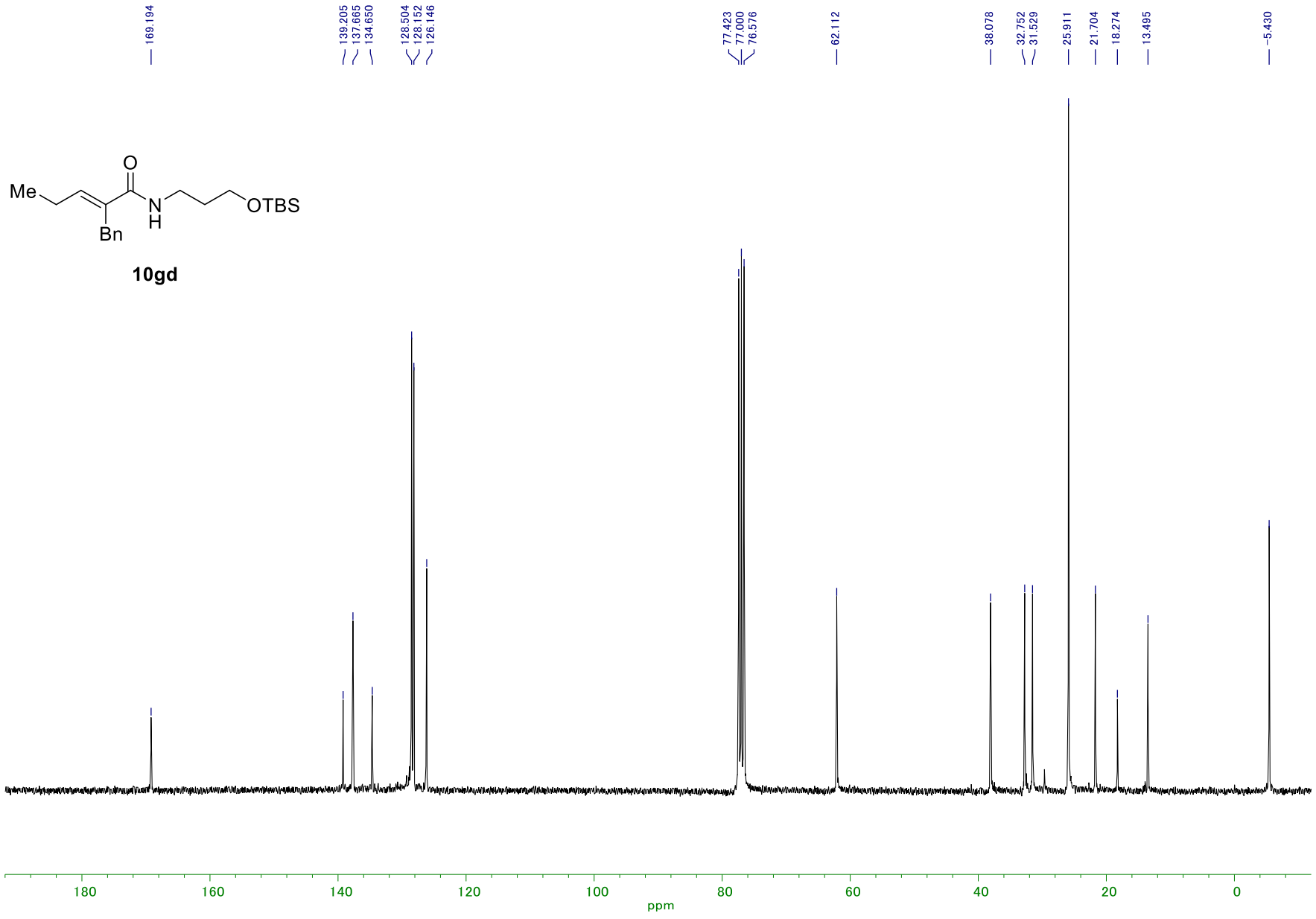
4sd

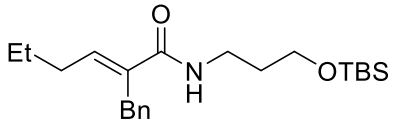

169.100
138.942
135.454
135.326
135.197
134.275
133.817
131.997
128.760
128.726
128.619
128.551
127.137
126.393
126.101
125.683
125.497
125.093
123.410
77.423
77.000
76.577
61.934
38.076
34.684
31.488
29.844
25.843
18.212
-5.525
Ph
O
N
H
OTBS
4sd
180
160
140
120
100
80
60
40
20
0
ppm



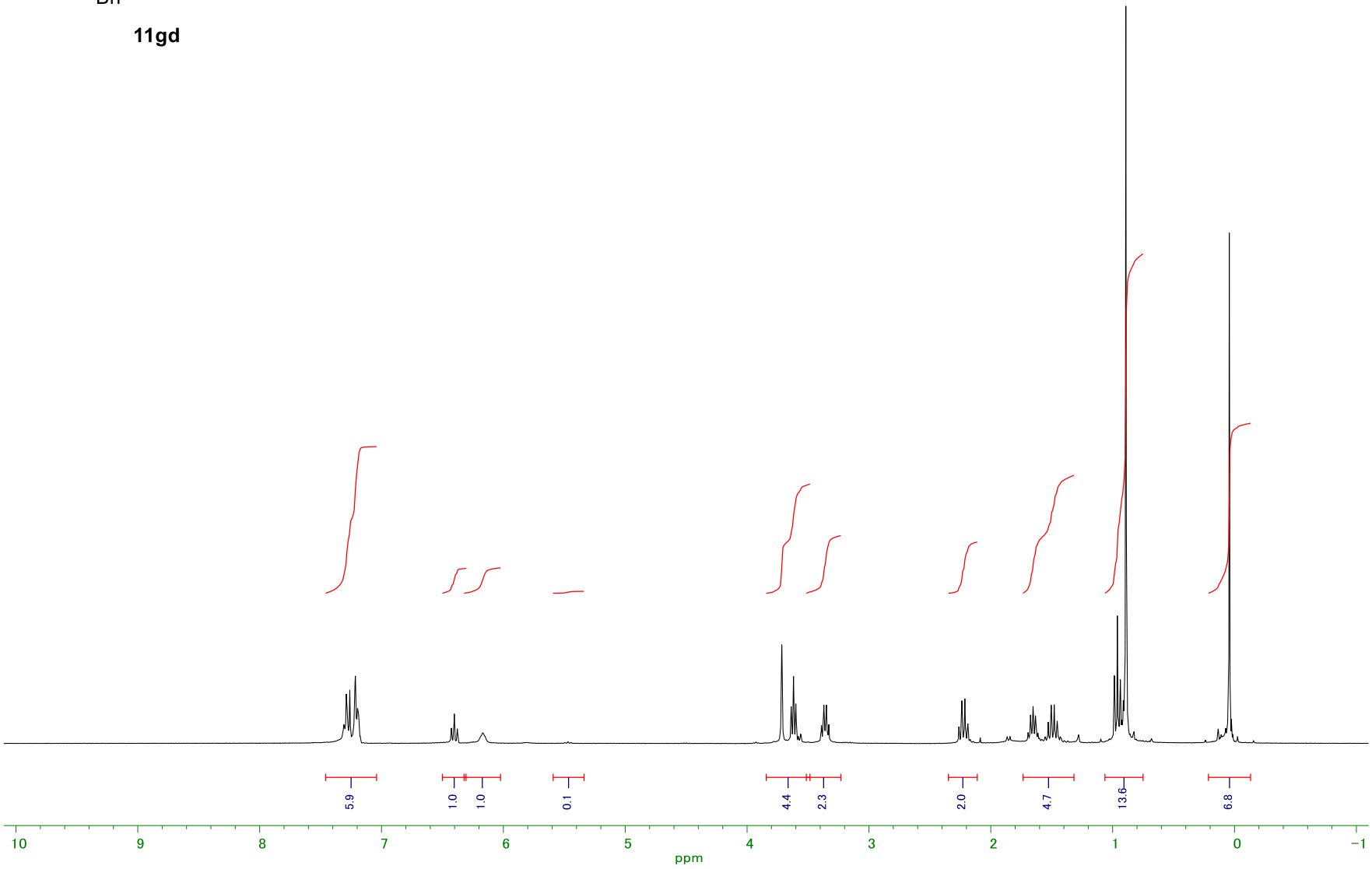
10gd

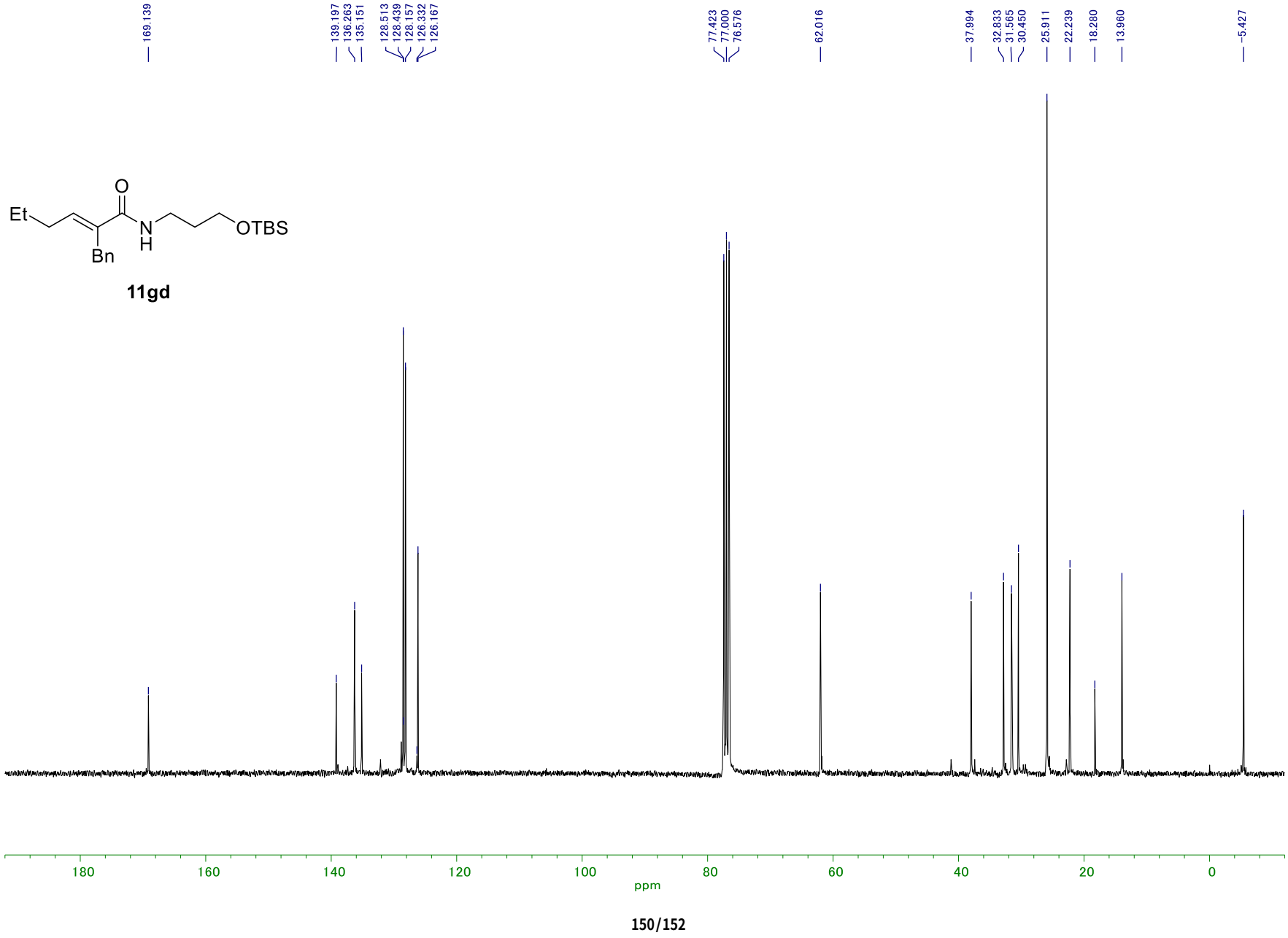


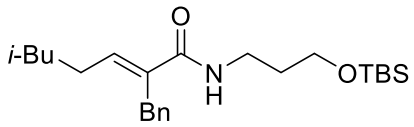

169.194
139.205
137.665
134.650
128.504
128.152
126.146
77.423
77.000
76.576
62.112
38.078
32.752
31.529
25.911
21.704
18.274
13.495
-5.430
Me
O
N
H
OTBS
Bn
10gd
180
160
140
120
100
80
60
40
20
0
ppm



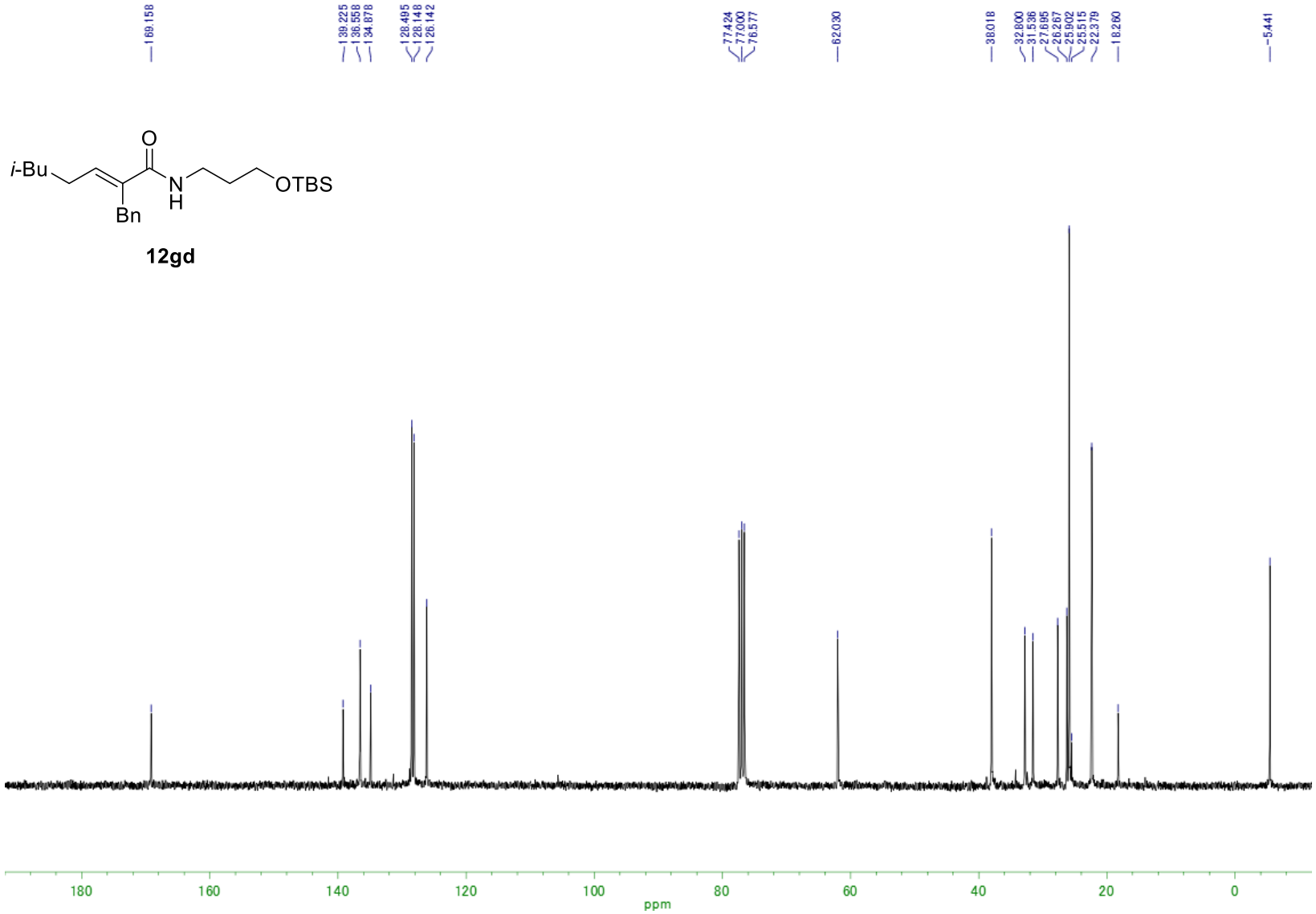
11gd




169.139
139.197
136.263
135.151
128.513
128.439
128.157
126.332
126.167
77.423
77.000
76.576
62.016
37.994
32.833
31.565
30.450
25.911
22.239
18.280
13.960
-5.427
O
Et
N
H
OTBS
Bn
11gd
180
160
140
120
100
80
60
40
20
0
ppm



12gd


169.158
139.225
136.558
134.878
128.495
128.148
126.142
77.424
77.000
76.577
62.030
38.018
32.800
31.536
27.695
26.267
25.902
25.515
22.379
18.260
-5.441
O
i-Bu
N
H
OTBS
Bn
12gd
180
160
140
120
100
80
60
40
20
0
ppm