Supporting Information for:
Tin-Free Radical Cyclization Reactions Initiated by Visible Light Photoredox Catalysis

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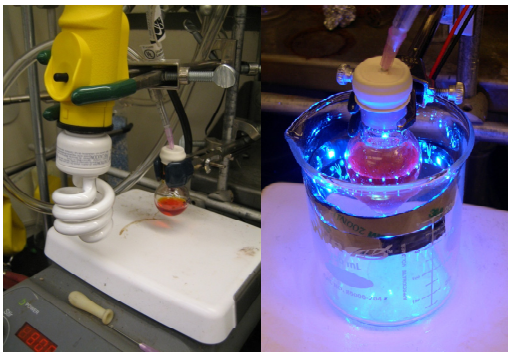
General Information:

Chemicals were either used as received or purified according to *Purification of Common Laboratory Chemicals*. Glassware was dried in an oven at 150°C or flame dried and cooled under a dry atmosphere prior to use. All reactions were performed using common dry, inert atmosphere techniques. Reactions were monitored by TLC and visualized by a dual short wave/long wave UV lamp and stained with an ethanolic solution of potassium permanganate or p-anisaldehyde. Column flash chromatography was performed using 230-400 mesh silica gel. NMR spectra were recorded on Varian Mercury 300, Varian Unity Plus 400, and Varian Mercury 400 spectrometers. Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CHCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm. Proton and carbon assignments were established using spectral data of similar compounds. The abbreviations s, br. s, d, dd, br. d, ddd, t, q, br. q, m, and br. m stand for the resonance multiplicity singlet, broad singlet, doublet, doublet of doublets, broad doublet, doublet of doublet of doublets, triplet, quartet, broad quartet, multiplet and broad multiplet, respectively. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. Mass spectra were recorded at the Mass Spectrometry Facility at the Department of Chemistry of the Boston University in Boston, MA on a Waters Q-Tof API-US with ESI high resolution mass spectrometer. Concentration refers to removal of solvent under reduced pressure (house vacuum at ca. 20 mmHg).

Reaction Apparatus:

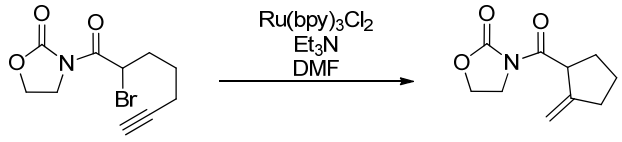
$Ir(ppy)_2(dtbbpy)PF_6$ catalyzed reactions were carried out under visible light irradiation by a 14W household compact fluorescent lamp (CFL) clamped ~15 cm from the reaction vessel. $Ru(bpy)_3Cl_2$ catalyzed reaction were carried out under irradiation by a 15 cm blue LED strip (available from http://www.creativelightings.com/, λ_{max} = 435 nm) surrounding the reaction vessel. The $Ru(bpy)_3Cl_2$ photoredox system is also active under irradiation by the CFL.

Ir Apparatus **Ru Apparatus**



General Procedure A: Photoredox Cyclization Reaction

A flame dried 10 mL round bottom flask is equipped with a rubber septum and magnetic stir bar and is charged with photoredox catalyst (1.0 μmol, 0.010 equiv), the corresponding halide (0.10 mmol, 1.0 equiv), Et_3N (0.20 mmol, 2.0 equiv) and DMF (5.0 mL). The mixture is degassed by the freeze-pump-thaw procedure, and placed in the respective irradiation apparatus. After the reaction is complete (as judged by TLC analysis), the mixture is poured into a separatory funnel containing 25 mL of Et_2O and 25 mL of H_2O. The layers are separated and the aqueous layer is extracted with Et_2O (2 X 50 mL). The combined organic layers are dried (Na_2SO_4) and concentrated. The residue is purified by chromatography on silica gel, using the solvent system indicated, to afford the desired cyclized product.



1 **2**

3-(2-methylenecyclopentanecarbonyl)oxazolidin-2-one, **2** *(Scheme 1)*: According to General Procedure A, **1** (32 mg, 0.12 mmol), Et_3N (32 μL, 0.23 mmol) and tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate (0.90 mg, 1.2 μmol) in dry DMF (6.0 mL) afforded **2** (19 mg, 85%) as a colorless oil after purification by chromatography on SiO_2 (15:85, AcOEt:hexane) (12 h reaction time).

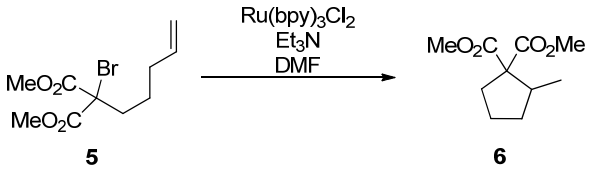
R_f (AcOEt/hexane 30:70) 0.28;

IR (neat): 3363, 2958, 2922, 2355, 1776, 1697, 1479, 1386, 1222, 1106, 1041, 761 cm^{-1};

^1H NMR ($CDCl_3$, 500 MHz) δ 5.04 (dd, J = 4.2, 2.0 Hz, 1 H), 4.90 (dd, J = 4.2, 2.0 Hz, 1 H), 4.70 – 4.74 (m, 1 H), 4.21 (t, J = 8.0 Hz, 2 H), 4.05 (dt, J = 8.0, 1.5 Hz, 2 H), 2.37 – 2.49 (m, 2 H), 1.99 – 2.09 (m, 2 H), 1.86 – 1. 73 (m, 1 H), 1.64 – 1.73 (m, 1 H);

^{13}C NMR ($CDCl_3$, 300 MHz) δ 174.9, 153.4, 151.0, 108.1, 61.8, 47.1, 43.0, 33.8, 31.0, 25.1;

HRMS (ESI) *m/z* calculated for $C_{10}H_{14}NO_3^+$ ($[M+1]^+$) 196.0974, found 196.1053.



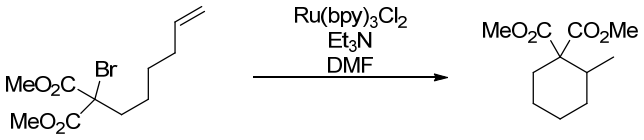
5 **6**

Dimethyl 2-methylcyclopentane-1,1-dicarboxylate[1], **6** *(Table 1, Entry 1)*: According to General Procedure A, **5** (30 mg, 0.11 mmol), Et_3N (31 μL, 0.22 mmol) and tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate (0.80 mg, 1.1 μmol) in dry DMF (5.5 mL) afforded **6** (17 mg, 77%) as a colorless oil after purification by chromatography on SiO_2 (95:5, hexanes/EtOAc) (12 h reaction time).

R_f (AcOEt/hexane 10:90) 0.31;

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.71 (s, 3 H), 3.70 (s, 3 H), 2.63 – 2.71 (m, 1 H), 2.40 – 2.46 (m, 1 H), 1.99 – 2.04 (m, 1 H), 1.88 – 1.94 (m, 1 H), 1.78 – 1.86 (m, 1 H), 1.51 – 1.59 (m, 1 H), 1.35 – 1.43 (m, 1 H), 0.97 (d, J = 7.0 Hz, 3 H).

[1] L. H. Powell, P. H. Docherty, D. G. Hulcoop, P. D. Kemmitt, J. W. Burton, *Chem. Commun.* 2008, 2559.



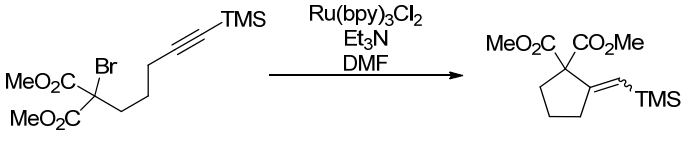
7 **8**

Dimethyl 2-methylcyclohexane-1,1-dicarboxylate[2], **8** *(Table 1, Entry 2)*: According to General Procedure A, **7** (89 mg, 0.30 mmol), Et_3N (84 μL, 0.61 mmol) and tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate (2.2 mg, 3.0 μmol) in dry DMF (15 mL) afforded **8** (45 mg, 69%) as a colorless oil after purification by chromatography on SiO_2 (50:50, DCM:Petroleum Ether) (12 h reaction time).

R_f (AcOEt/hexane 15:85) 0.39;

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.73 (s, 3 H), 3.72 (s, 3 H), 2.29 – 2.35 (m, 1 H), 2.09 – 2.17 (m, 2 H), 1.89 – 1.97 (m, 1 H), 1.34 – 1.60 (br. m, 4 H), 1.01 (d, J = 7.2 Hz, 3 H).

[2] P. Canonne and J. Plamondon, *Can. J. Chem.*, 1980, **67**, 555.



9 **10**

Dimethyl 2-((trimethylsilyl)methylene)cyclopentane-1,1-dicarboxylate, **10** *(Table 1, Entry 3)*: According to General Procedure A, **9** (42 mg, 0.12 mmol), Et_3N (33 μL, 0.24 mmol) and tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate (0.90 mg, 1.2 μmol) in dry DMF (6.0 mL) afforded **10** (32 mg, quant.) as a colorless oil consisting of a 3:1 mixture of diastereoisomers after purification by chromatography on SiO_2 (99:1, Petroleum Ether:Et_2O) (12 h reaction time).

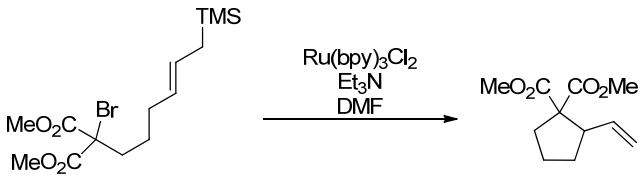
Data for major diastereoisomer:
R_f (AcOEt/hexane 5:95) 0.28;

IR (neat): 3077, 2954, 2861, 1747, 1436, 1255, 1133, 993, 915, 714 cm^{-1};

^1H NMR ($CDCl_3$, 500 MHz) δ 5.76 (t, J = 2.0 Hz, 1 H), 3.74 (s, 3 H), 3.73 (s, 3 H), 2.73 (t, J = 7.5 Hz, 1 H), 2.56 (td, J = 7.5, 2.0 Hz, 1 H), 2.48 (t, J = 7.0 Hz, 1 H) 2.39 (t, J = 7.0 Hz, 1 H), 1.69 – 1.76 (m, 2 H), 0.05 (s, 9 H);

^{13}C NMR ($CDCl_3$, 500 MHz) δ 171.4, 171.2, 170.2, 170.1, 154.7, 150.9, 133.9, 128.2, 125.8, 65.0, 63.3, 52.8, 52.6, 41.7, 41.0, 39.8, 39.7, 35.6, 32.9, 24.3, 24.0, 0.1, -0.3;

HRMS (ESI) *m/z* calculated for $C_{13}H_{22}NaO_4Si^+$ ($[M+Na]^+$) 293.1185, found 293.1217.



11 **12**

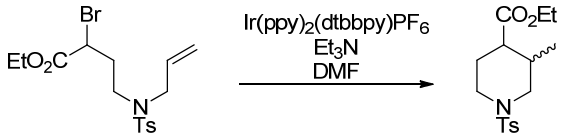
Dimethyl 2-vinylcyclopentane-1,1-dicarboxylate, **12** *(Table 1, Entry 4)*: According to General Procedure A, **11** (40 mg, 0.11 mmol), Et_3N (30 μL, 0.22 mmol) and tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate (0.80 mg, 1.1 μmol) in dry DMF (5.5 mL) afforded **12** (21 mg, 92%) as a colorless oil after purification by chromatography on SiO_2 (99:1, Petroleum Ether:Et_2O) (12 h reaction time).

R_f (AcOEt/hexane 5:95) 0.37;

IR (neat): 2887, 2861, 1747, 1443, 1255, 1223, 1082, 993, 876, 743, 682 cm^{-1};

^1H NMR ($CDCl_3$, 300 MHz) δ 5.72 – 5.84 (m, 1 H), 4.99 – 5.12 (m, 2 H), 3.73 (s, 3 H), 3.65 (s, 3 H), 3.24 (dt, J = 8.1, 7.5 Hz, 1 H), 2.41 – 2.51 (m, 1 H), 2.04 – 2.13 (m, 1 H), 1.80 – 2.00 (m, 2 H), 1.60 – 1.73 (m, 2 H);

^{13}C NMR ($CDCl_3$, 300 MHz) δ 172.6, 171.2, 137.6, 115.9, 64.3, 52.5, 52.1, 50.0, 33.9, 30.7, 23.1;



13 **14**

Ethyl 3-methyl-1-tosylpiperidine-4-carboxylate, **14** *(Table 1, Entry 5)*: According to General Procedure A, **13** (42.0 mg, 0.10 mmol), Et_3N (29 μL, 0.20 mmol) and bis(2,2′-phenylpyridyl)(4,4'-ditertbutyl-2,2'-bipyridyl)iridium(III) hexafluorophosphate (0.90 mg, 1.0 μmol) in dry DMF (5.0 mL) afforded **14** (29 mg, 85%) as a colorless oil containing an inseparable mixture of diastereomers (1:1) after purification by chromatography on SiO_2 (80:20, Hexanes:EtOAc) (20 h reaction time).

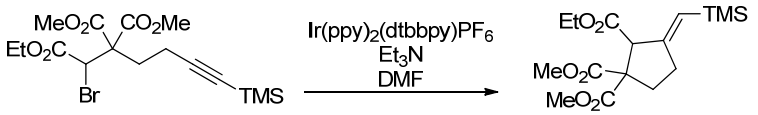
R_f (AcOEt/hexane 80:20) 0.21;

IR (neat): 2982, 2910, 1732, 1598, 1343, 1160, 1093, 757, 667 cm^{-1};

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, *J* = 8.0 Hz, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 4.08 – 4.17 (m, 4 H), 3.80 (br. d, *J* = 10.4 Hz, 1 H), 3.72 (ddd, *J* = 11.6, 4.0, 2.4 Hz, 1 H), 3.54 (dd, *J* = 11.6, 5.6 Hz, 1 H), 3.34 (dd, *J* = 10.4, 5.6 Hz, 1 H), 2.51 (dd, *J* = 11.2, 3.2 Hz, 1 H), 2.59 – 2.65 (m, 1 H), 2.47 (s, 3 H), 2.45 (s, 3 H), 2.25 – 2.31 (m, 1 H), 1.79 – 2.07 (m, 5 H), 1.23 – 1.29 (m, 10 H), 1.04 (d, *J* = 6.8 Hz, 3 H), 0.93 (d, *J* = 6.0 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 300 MHz): δ 174.2, 173.4, 143.7, 143.6, 133.4, 133.2, 129.8, 129.7, 127.8, 127.7, 127.1, 60.7, 60.5, 51.9, 51.1, 48.7, 45.5, 44.9, 43.5, 32.8, 31.0, 29.8, 28.3, 23.4, 21.7, 17.2, 14.3, 13.9;

HRMS (ESI) *m/z* calculated for $C_{16}H_{23}NaNO_4S^+$ ($[M+Na]^+$) 348.1245, found 348.1235.



15 **16**

Dimethyl 2-vinylcyclopentane-1,1-dicarboxylate, **16** *(Table 1, Entry 6)*: According to General Procedure A, **15** (82 mg, 0.19 mmol), Et_3N (54 μL, 0.39 mmol) and bis(2,2′-phenylpyridyl)(4,4'-ditertbutyl-2,2'-bipyridyl)iridium(III) hexafluorophosphate (1.7 mg, 2.0 μmol) in dry DMF (10 mL) afforded **16** (48 mg, 74%) as a colorless oil after purification by chromatography on SiO_2 (95:5, Petroleum Ether:Et_2O) (12 h reaction time).

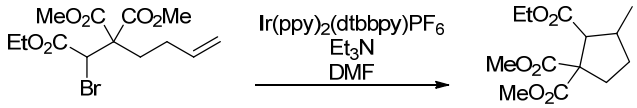
R_f (AcOEt/hexane 10:90) 0.25;

IR (neat): 2954, 2360, 1736, 1628, 1434, 1246, 1220, 1152, 1110, 1029, 863, 842, 756 693 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 5.53 (s, 1 H), 4.06 – 4.15 (m, 3 H), 3.72 (s, 3 H), 3.70 (s, 3 H), 2.64 – 2.78 (m, 2 H), 2.33 – 2.45 (m, 2 H), 1.26 (t, J = 7.2 Hz, 3 H), 0.13 (s, 9 H);

^{13}C NMR ($CDCl_3$, 400 MHz): δ 171.0, 170.7, 169.9, 154.7, 126.3, 64.1, 61.1, 55.3, 53.1, 52.7, 33.6, 30.3, 14.0, -0.47;

HRMS (ESI) *m/z* calculated for $C_{16}H_{27}O_6Si^+$ ($[M+1]^+$) 343.1577, found 343.1583.



17 **18**

2-ethyl 1,1-dimethyl 3-methylcyclopentane-1,1,2-tricarboxylate, **18** *(Table 1, Entry 7)*: According to General Procedure A, **17** (60 mg, 0.17 mmol), Et_3N (48 μL, 0.34 mmol) and bis(2,2′-phenylpyridyl)(4,4'-ditertbutyl-2,2'-bipyridyl)iridium(III) hexafluorophosphate (1.6 mg, 2.0 μmol) in dry DMF (10 mL) afforded **18** (36 mg, 76 %) as a colorless oil containing an inseparable mixture of diastereomers (1:1) after purification by chromatography on SiO_2 (90:10), Hexanes:EtOAc) (4 h reaction time).

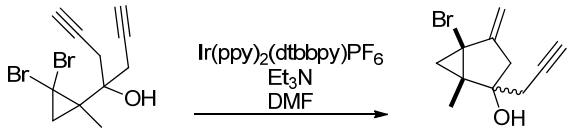
R_f (AcOEt/hexane 10:90) 0.24;

IR (neat): 2982, 2955, 2909, 1736, 1642, 1436, 1374, 1275, 1201, 1030, 921, 720 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 4.09 – 4.16 (m, 4 H), 3.75 (s, 3 H), 3.72 (s, 3 H), 3.69 (s, 3 H), 3.67 (s, 3 H), 3.50 – 3.52 (d, J = 8 Hz, 1 H), 3.10 – 3.13 (d, J = 12 Hz, 1 H), 2.76 – 2.83 (m, 1 H), 2.43 – 2.55 (m, 2 H) 2.29 – 2.41 (m, 1 H), 2.13 – 2.21 (m, 2 H), 1.94 – 2.04 (m, 1 H), 1.83 – 1.91 (m, 1 H), 1.57 – 1.68 (m, 1 H), 1.22 – 1.27 (m, 8 H), 1.11 – 1.13 (d, J = 8 Hz, 3 H), 0.97 – 0.99 (d, J = 8 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 400 MHz): δ 172.7, 172.0, 170.7, 63.8, 60.6, 57.7, 52.9, 52.5, 38.1, 34.5, 32.3, 19.4, 14.1.

HRMS (ESI) *m/z* calculated for $C_{13}H_{20}NaO_6^+$ ($[M+Na]^+$) 295.1158, found 295.1167.



19 **20**

5-bromo-1-methyl-4-methylene-2-(prop-2-yn-1-yl)bicyclo[3.1.0]hexan-2-ol[3], **20** *(Table 1, Entry 8)*: According to General Procedure A, **19** (68 mg, 0.12 mmol), Et_3N (33 μL, 0.24 mmol) and bis(2,2′-phenylpyridyl)(4,4'-ditertbutyl-2,2'-bipyridyl)iridium(III) hexafluorophosphate (2.4 mg, 2.4 μmol) in dry DMF (6.0 mL) afforded **20** (25 mg, 89 %) as a colorless oil containing a 1:1 mixture of diastereoisomers after purification by chromatography on SiO_2 (95:5, Petroleum Ether:Et_2O) (12 h reaction time).

Diastereoisomer 1:
R_f (AcOEt/hexane 10:90) 0.29;

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.15 (d, J = 2.5 Hz, 1 H), 4.91 (d, J – 2.5 Hz, 1 H), 2.67 (t, J = 15.5 Hz, 2 H), 2.31 (dd, J = 16.5, 2.5 Hz, 1 H), 2.09 – 2.17 (m, 3 H), 1.74 (d, J = 6.0 Hz, 1 H), 1.34 (s, 3 H), 1.13 (d, J = 6.0 Hz, 1 H);

Diastereoisomer 2:
R_f (AcOEt/hexane 10:90) 0.25;

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.29 (s, 1 H), 5.01 (s, 1 H), 2.62 (dt, J = 17.0, 2.5 Hz, 1 H), 2.45 (dt, J = 17.0, 2.5 Hz, 1 H), 2.36 (s, 2 H), 2.07 (s, 1 H), 1.96 (s, 1 H), 1.45 (d, J = 6.5 Hz, 1 H), 1.39 (s, 3 H), 1.19 (d, J = 6.5 Hz, 1 H);

[3] Y. Tanabe, Y. Nishii and K. Wakimura, *Chem. Lett.* 1994, 1757.

21 **22**

2-allyl-5-bromo-1,4-dimethylbicyclo[3.1.0]hexan-2-ol[4], **22** *(Table 1, Entry 9)*: According to General Procedure A, **21** (56 mg, 0.17 mmol), Et_3N (49 μL, 0.35 mmol) and bis(2,2′-phenylpyridyl)(4,4'-ditertbutyl-2,2'-bipyridyl)iridium(III) hexafluorophosphate (3.5 mg, 1.7 μmol) in dry DMF (8.5 mL) afforded **22** (34 mg, 81 %) as a colorless oil after purification by chromatography on SiO_2 (99:1, Petroleum Ether:Et_2O) (12 h reaction time).

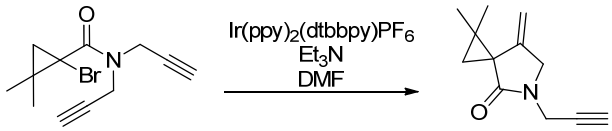
Diastereoisomer 1:
R_f (AcOEt/hexane 5:95): 0.25;

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.76 – 5.90 (m, 1 H), 5.11 – 5.15 (m, 2 H), 2.65 – 2.78 (m, 1 H), 2.38 (dd, J = 13.0, 7.4 Hz, 1 H), 2.18 (dd, J = 13.0, 7.4 Hz. 1 H) 1.58 – 1.66 (m, 2 H), 1.31 (s, 3 H), 1.07 (d, J = 6.3 Hz, 3 H), 0.86 – 1.00 (m, 3 H), 0.69 (d, J = 6.6 Hz, 1 H).

Diastereoisomer 2:
R_f (AcOEt/hexane 5:95): 0.19;

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.80 – 5.88 (m, 1 H), 5.14 – 5.18 (m, 2 H), 2.46 (dd, J = 14.0, 7.0 Hz, 1 H), 2.35 – 2.41 (m, 1 H), 2.30 (dd, J = 14.0, 7.0 Hz, 1 H); 1.85 (dd, J = 14.0, 8.0 Hz, 1 H), 1.47 (s, 1 H), 1.29 – 1.31 (m, 4 H), 1.05 (d, J = 6.5 Hz, 3 H), 0.85 (t, J = 12.0 Hz, 1 H), 0.64 (d, J = 6.0 Hz, 1 H).

[4] Y. Tanabe, Y. Nishii and K. Wakimura, *Chem. Lett.* 1994, 1757.



23 **24**

1,1-dimethyl-7-methylene-5-(prop-2-yn-1-yl)-5-azaspiro[2.4]heptan-4-one, 24 *(Table 1, Entry 10)*: According to General Procedure A, **23** (0.13 g, 0.47 mmol), Et_3N (0.13 mL, 0.94 mmol) and bis(2,2′-phenylpyridyl)(4,4'-ditertbutyl-2,2'-bipyridyl)iridium(III) hexafluorophosphate (4.5 mg, 5.0 μmol) in dry DMF (15 mL) afforded **24** (65 mg, 73%) as a colorless oil after purification by chromatography on SiO_2 (90:10, Petroleum Ether:Et_2O) (12 h reaction time).

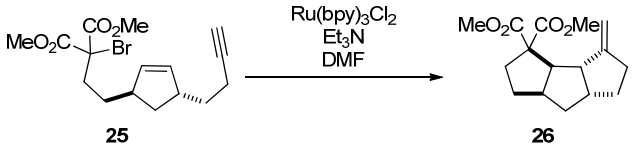
R_f (AcOEt/hexane 20:80) 0.39;

IR (neat): 3301, 3236, 2924, 2872, 1691, 1659, 1428, 1247, 1108, 881, 639 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 5.00 (s, 1 H), 4.59, (s, 1 H), 4.19 (br s, 2 H), 4.12 (dt, J = 13.2, 2.4 Hz, 1 H), 4.00 (d, J = 13.2 Hz, 1 H), 2.23 (t, J = 2.4 Hz, 1 H), 1.49 (d, J = 4.8 Hz, 1 H), 1.35 (s, 3 H), 1.13 (s, 3 H), 0.99 (d, J = 4.8 Hz, 1 H);

^{13}C NMR ($CDCl_3$, 300 MHz): δ 173.2, 141.0, 104.8, 77.8, 72.2, 50.6, 37.7, 31.8, 31.4, 26.2, 20.4, 20.1;

HRMS (ESI) *m/z* calculated for $C_{12}H_{16}NO^+$ ($[M+1]^+$) 190.1232, found 190.1241.



25 **26**

Dimethyl 4-methyleneoctahydro-1H-cyclopenta[a]pentalene-3,3(2H)-dicarboxylate, 26: According to General Procedure A, **25** (64 mg, 0.18 mmol), Et_3N (50 μL, 0.36 mmol) and tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate (1.4 mg, 1.8 μmol) in dry DMF (8.0 mL) afforded **26** (35 mg, 69%) as a colorless oil after purification by chromatography on SiO_2 (95:5, Petroleum Ether:Et_2O) (4 h reaction time).

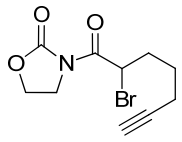
R_f (AcOEt/hexane 10:90) 0.53;

IR (neat): 2949, 1732, 1650, 1434, 1272, 1244, 1142, 1079, 912, 736 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 4.88 (s, 1 H), 4.81 (s, 1 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.10 (dd, J = 7.2, 3.6 Hz, 1 H), 2.80 – 2.88 (m, 1 H), 2.51 – 2.59 (m, 1 H), 2.24 – 2.49 (m, 4 H), 2.07 (dd, J = 12.8, 6.8 Hz, 1 H), 1.65 – 1.76 (m, 2 H), 1.36 – 1.56 (m, 4 H);

^{13}C NMR ($CDCl_3$, 300 MHz): δ 172.6, 171.4, 157.2, 106.2, 65.9, 57.4, 52.6, 52.2, 52.1, 45.5, 44.9, 38.8, 33.5, 31.7, 30.3, 28.8;

HRMS (ESI) *m/z* calculated for $C_{12}H_{23}O_4^+$ ($[M+1]^+$) 279.1596, found 279.1586.



1

3-(2-bromohept-6-ynoyl)oxazolidin-2-one, 1: A flame dried 100 mL round bottom flask is equipped with a rubber septum and magnetic stir bar and is charged with a solution of 3-(hept-6-ynoyl)oxazolidin-2-one[5] (0.75 g, 3.8 mmol) in THF (40 mL) and cooled to -78 ºC. A 1M solution of NaHMDS in THF (4.2 mL, 1.1 equiv) is added dropwise and the mixture allowed to stir at -78 ºC for 30 min. NBS (0.75 g, 1.1 equiv) is then added and the mixture stirred at -78 ºC until the reaction is complete (as judged by TLC analysis), the mixture is poured into a separatory funnel containing 50 mL of Et_2O and 50 mL of H_2O. The layers are separated and the aqueous layer is extracted with Et_2O (2 X 75 mL). The combined organic layers are dried (Na_2SO_4) and concentrated to afford **1** (0.20 g, 20%) as a yellow oil after purification by chromatography on SiO_2 (30:70, AcOEt:hexane) (5.5 h reaction time).

R_f (AcOEt/hexane 30:60) 0.25;

IR (neat): 3381, 3295, 2923, 2853, 2359, 1776, 1700, 1389, 1364, 1305, 1221, 1115, 1040, 908, 731, 631 cm^{-1};

^1H NMR ($CDCl_3$, 300 MHz): δ 5.64 (dd, J = 8.1, 6.6 Hz, 1 H), 4.47 (t, J = 8.2 Hz, 2 H), 4.08 (t, J = 8.2 Hz, 2 H) 2.12 – 2.30 (m, 4 H), 1.98 (t, J = 3.0 Hz, 1 H), 1.55 – 1.83 (m, 2 H);

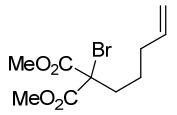
^{13}C NMR ($CDCl_3$, 300 MHz): δ 169.1, 152.5, 83.2, 69.1, 62.1, 43.0, 42.8, 32.8, 26.0, 17.8;

HRMS (ESI) *m/z* calculated for $C_{10}H_{12}BrNaNO_3^+$ ($[M+Na]^+$) 295.9898, found 295.9990.

[5] J. R. Falck, S. Gao, R. N. Prasad, and S. R. Koduru, *Cioorg. Med. Chem. Lett.* 2008, **18**, 1768.

General Procedure B: Bromination of Dimethyl Malonates

A flame dried 25 mL round bottom flask, equipped with a rubber septum and magnetic stir bar, is charged with the corresponding malonate (0.50 mmol, 1.0 equiv), and anhydrous THF (5 mL) and cooled to -78 °C. A 1.0 M solution of NaHMDS in THF (0.55 mL, 1.1 equiv.) is then added dropwise and the mixture allowed to stir for 15 min. NBS (0.55 mmol, 1.1 equiv) is then added and the mixture allowed to slowly warm to 0 °C over 4 h. After the reaction is complete (as judged by TLC analysis), the mixture is poured into a separatory funnel containing 25 mL of Et_2O and 25 mL of H_2O. The layers are separated and the aqueous layer is extracted with Et_2O (2 X 50 mL). The combined organic layers are dried (Na_2SO_4) and concentrated. The residue is purified by chromatography on silica gel, using the solvent system indicated, to afford the desired reduced product.



5

Dimethyl 2-bromo-2-(pent-4-en-1-yl)malonate, 5: According to General Procedure B, dimethyl 2-(pent-4-en-1-yl)malonate[6] (1.9 g, 9.5 mmol), 1 M NaHMDS solution (10 mL, 10 mmol) and NBS (1.9 g, 10 mmol) in dry THF (95 mL) afforded **5** (2.5 g, 93%) as a colorless oil after purification by chromatography on SiO_2 (95:5, hexane:AcOEt) (7.5 h reaction time).

R_f (AcOEt/hexane 5:95): 0.21;

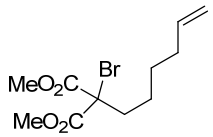
IR (neat): 3457, 2956, 1743, 1641, 1436, 1255, 1132, 1101, 997, 925, 737 cm^{-1};

^1H NMR ($CDCl_3$, 300 MHz): δ 5.71 – 5.84 (m, 1 H), 4.97 – 5.06 (m, 2 H), 3.82 (s, 6 H), 2.28 (t, J = 7.8 Hz, 2 H), 2.11 (q, J = 6.6 Hz, 2 H), 1.46 – 1.56 (m, 2 H);

^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.0, 137.2, 115.1, 62.3, 53.5, 37.4, 32.7, 24.2;

HRMS (ESI) *m/z* calculated for $C_{10}H_{16}BrO_4^+$ ($[M+1]^+$) 279.0232, found 279.0234.

[6] C. Kammerer, G. Prestat, T. Gaillard, D. Madec, and G. Poli, *Org. Lett.,* 2008, **10**, 405.



7

Dimethyl 2-bromo-2-(hex-5-en-1-yl)malonate, 7: According to General Procedure B, dimethyl 2-(pent-4-en-1-yl)malonate[7] (1.0 g, 4.7 mmol), 1 M NaHMDS solution (5.1 mL, 5.1 mmol) and NBS (0.91 g, 5.1 mmol) in dry THF (47 mL) afforded **7** (1.3 g, 96%) as a colorless oil after purification by chromatography on SiO_2 (95:5, hexane:AcOEt) (7.5 h reaction time).

R_f (AcOEt/hexane 15:85) 0.43;

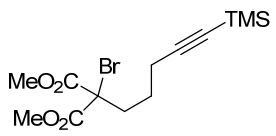
IR (neat): 3077, 2931, 2859, 1744, 1640, 1436, 1251, 1133, 1102, 993, 913 cm^{-1};

^1H NMR ($CDCl_3$, 300 MHz): δ 5.71 – 5.85 (m, 1 H), 4.93 – 5.04 (m, 2 H), 3.82 (s, 6 H), 2.24 – 2.95 (m, 2 H), 2.04 – 2. 08 (m, 2 H), 1.39 – 1.47 (m, 4 H);

^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.3, 138.1, 114.7, 62.6, 53.8, 38.0, 33.2, 28.2, 24.6;

HRMS (ESI) *m/z* calculated for $C_{11}H_{18}BrO_4^+$ ($[M+1]^+$) 293.0388, found 293.0396.

[7] K. Osamau, F. Hiroki, S. Takashi, T. Taguchi, and M. Shiro, *J. Org. Chem.*, 2000, **65**, 6819.



9

Dimethyl 2-bromo-2-(5-(trimethylsilyl)pent-4-yn-1-yl)malonate, 9: According to General Procedure B, dimethyl 2-(5-(trimethylsilyl)pent-4-yn-1-yl)malonate[8] (0.34 g, 1.3 mmol), 1 M NaHMDS solution (1.4 mL, 1.4 mmol) and NBS (0.25 g, 1.4 mmol) in dry THF (20 mL) afforded **9** (0.39 g, 89%) as a colorless oil after purification by chromatography on SiO_2 (95:5, hexane:AcOEt) (7.5 h reaction time).

R_f (AcOEt/hexane 5:95): 0.25;

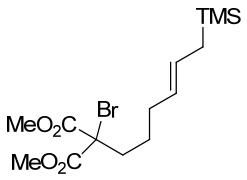
IR (neat): 2956, 2899, 2174, 1745, 1436, 1249, 1168, 840, 759, 639 cm^{-1};

^1H NMR ($CDCl_3$, 300 MHz): δ 3.83 (s, 6 H), 2.35 – 2.40 (m, 2 H), 2.28 (t, J = 6.9 Hz, 2 H), 1.59 – 1.70 (m, 2 H), 0.15 (s, 9 H);

^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.0, 105.7, 85.3, 62.1, 53.7, 37.3, 24.6, 19.3, -0.1;

HRMS (ESI) *m/z* calculated for $C_{13}H_{22}BrO_4Si^+$ ($[M+1]^+$) 349.0471, found 349.0477.

[8] G. Fournet, G. Balme, and J. Gore, *Tetrahedron*, 1991, **47**, 6293.



11

(E)-dimethyl 2-bromo-2-(6-(trimethylsilyl)hex-4-en-1-yl)malonate, 11: A flame dried 10 mL round bottom flask is equipped with a reflux condenser and magnetic stir bar and is charged with Gubbs II catalysts (42.0 mg, 50 μmol). A solution of **4** (0.28 mg, 0.99 mmol) and allyl TMS (0.47 mL, 3.0 mmol) in degassed DCM (5 mL) is then added and the mixture heated to reflux. The reaction is cooled to rt and ethylvinylether is added and stirred for 30 min. The solvent is evaporated and the residue purified by chromatography on SiO_2 (99:1, hexane:AcOEt) to afford **11** (0.13 mg, 35%) as a colorless oil.

R_f (AcOEt/hexane 5:95): 0.36;

IR (neat): 3003, 2955, 1747, 1436, 1248, 1143, 912, 856, 736 cm^{-1};

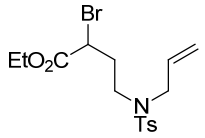
^1H NMR ($CDCl_3$, 300 MHz): δ 5.36 – 5.48 (m, 1 H), 5.15 – 5.26 (m, 1 H), 3.82 (s, 6 H), 2.23 – 2.29 (m, 2 H), 2.04 (t, J = 6.6 Hz, 2 H), 139 – 1.50 (m, 4 H), -0.01 (s, 9 H);

^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.5, 127.5, 127.3, 62.8, 53.8, 37.8 32.1, 25.5, 22.7, -1.9;

HRMS (ESI) *m/z* calculated for $C_{14}H_{26}BrO_4Si^+$ ($[M+1]^+$) 365.0784, found 365.0785.

General Procedure C: α-Bromination of Esters

A flame dried 25 mL round bottom flask, equipped with a rubber septum and magnetic stir bar, is charged with the corresponding ester (0.50 mmol, 1.0 equiv), and anhydrous THF (5 mL) and cooled to -78 °C. A 1.0 M solution of NaHMDS in THF (0.55 mL, 1.1 equiv.) is then added dropwise and the mixture allowed to stir for 30 min. TMSCl (0.55 mmol, 1.1 equiv) is then added and the mixture allowed to stir for 1 h. NBS (0.55 mmol, 1.1 equiv) is then added and the reaction allowed to stir at -78 °C. After the reaction is complete (as judged by TLC analysis), the mixture is poured into a separatory funnel containing 25 mL of Et_2O and 25 mL of H_2O. The layers are separated and the aqueous layer is extracted with Et_2O (2 X 50 mL). The combined organic layers are dried (Na_2SO_4) and concentrated. The residue is purified by chromatography on silica gel, using the solvent system indicated, to afford the desired reduced product.



13

Ethyl 4-(N-allyl-4-methylphenylsulfonamido)-2-bromobutanoate, 13: According to General Procedure C, ethyl 4-(N-allyl-4-methylphenylsulfonamido)butanoate (0.50 g, 1.5 mmol), NaHMDS (1.7 mL, 1.7 mmol), TMSCl (0.21 mL, 1.7 mmol) and NBS (0.30 g, 1.7 mmol) in dry THF (16 mL) afforded **13** (0.42 g, 62%) as a light yellow oil after purification by chromatography on SiO_2 (90:10, hexanes:AcOEt) (8 h reaction time).

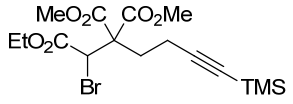
R_f (AcOEt/hexane 20:80): 0.29;

IR (neat): 3083, 2983, 2873, 1735, 1598, 1494, 1372, 1155, 1092, 1019, 754, 662 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 5.57 – 5.67 (m, 1 H), 5.16 – 5.22 (m, 2 H), 4.35 (dd, J = 6.0, 8.0 Hz, 1 H), 4.26 (q, J = 7.0 Hz, 2 H), 3.81 (d, J = 6.4 Hz, 2 H), 3.18 – 3.32 (m, 2 H), 2.46 (s, 3 H), 2.37 – 2.45 (m, 1 H), 2.18 – 2.27 (m, 1 H), 1.35 (t, J = 7.0 Hz, 3 H);

^{13}C NMR ($CDCl_3$, 300 MHz): δ 169.3, 143.5, 136.3, 132.7, 129.8, 127.2, 119.6, 62.1, 51.6, 45.2, 42.8, 33.8, 21.5, 13.9;

HRMS (ESI) *m/z* calculated for $C_{16}H_{23}BrNO_4S^+$ ($[M+1]^+$) 404.0531, found 404.0518.



15

1-ethyl 2,2-dimethyl 1-bromo-6-(trimethylsilyl)hex-5-yne-1,2,2-tricarboxylate, **15**: A flame dried 50 mL round bottom flask, equipped with a rubber septum and magnetic stir bar, is charged with 1-ethyl 2,2-dimethyl hex-5-yne-1,2,2-tricarboxylate (1.0 g, 3.8 mmol), and anhydrous THF (40 mL) and cooled to -78 °C. A 1.0 M solution of NaHMDS in THF (7.9 mL, 7.9 mmol) is then added dropwise and the mixture allowed to stir for 30 min. TMSCl (1.0 mL, 7.9 mmol) is then added and the mixture allowed to stir for 2 h. NBS (0.67 g, 3.8 mmol) is then added and the reaction allowed to stir at -78 °C. After the reaction is complete (as judged by TLC analysis), the mixture is poured into a separatory funnel containing 50 mL of Et_2O and 50 mL of H_2O. The layers are separated and the aqueous layer is extracted with Et_2O (2 X 75 mL). The combined organic layers are dried (Na_2SO_4) and concentrated. The residue is purified by chromatography on SiO_2 (90:10, hexanes:AcOEt) to afford **15** (0.91 g, 69%) as a colorless oil.

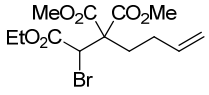
R_f (AcOEt/hexane 10:90): 0.23 ;

IR (neat): 2957, 2177, 1736, 1435, 1370, 1249, 1206, 1180, 1067, 1027, 842 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 4.81 (s, 1 H), 4.23 (q, J = 7.2 Hz, 2 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 2.32 – 2.54 (m, 4 H), 1.29 (t, J = 7.2 Hz, 3 H) 0.1 (s, 9 H);

^{13}C NMR ($CDCl_3$, 400 MHz): δ 168.4, 168.3, 167.3, 105.2, 85.3, 62.5, 60.1, 53.0, 53.0, 47.4, 32.7, 16.1, 13.8, 0.0;

HRMS (ESI) *m/z* calculated for $C_{16}H_{26}BrO_6Si^+$ ($[M+1]^+$) 421.0682, found 421.0673.



17

1-ethyl 2,2-dimethyl 1-bromohex-5-ene-1,2,2-tricarboxylate, 17: According to General Procedure C, 1-ethyl 2,2-dimethyl hex-5-ene-1,2,2-tricarboxylate (1.0 g, 3.7 mmol), NaHMDS (4.0 mL, 4.0 mmol), TMSCl (0.51 mL, 4.0 mmol) and NBS (0.72 g, 4.0 mmol) in dry THF (40 mL) afforded **17** (0.68 g, 53%) as a light yellow oil after purification by chromatography on SiO_2 (95:5, hexanes:AcOEt) (12 h reaction time).

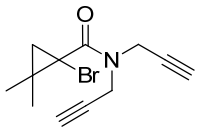
R_f (AcOEt/hexane 20:80) 0.24;

IR (neat): 3075, 2982, 2955, 1743, 1642, 1435, 1337, 1264, 1212, 1154, 1027, 763 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 5.73 – 5.83 (m, 1 H), 4.98 – 5.08 (m, 2 H), 4.80 (s, 1 H), 4.25 (q, J = 7.2 Hz, 2 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 2.90 – 2.35 (m, 1 H), 2.13 – 2.24 (m, 3 H), 1.33 (t, J = 7.2, 3 H);

^{13}C NMR ($CDCl_3$, 500 MHz): δ 168.8, 168.7, 167.5, 137.0, 115.5, 62.5, 60.3, 53.0, 52.9, 47.7, 33.5, 29.0, 13.9;

HRMS (ESI) *m/z* calculated for $C_{13}H_{19}BrNaO_6^+$ ($[M+Na]^+$) 373.0263, found 373.0254.



23

1-bromo-2,2-dimethyl-N,N-di(prop-2-yn-1-yl)cyclopropanecarboxamide (23): A flame dried 25 mL round bottom flask, equipped with a rubber septum and magnetic stir bar, is charged with 1-bromo-2,2-dimethylcyclopropanecarboxylic acid[9] (10 mmol, 1.0 equiv) and DCM (12 mL) and cooled to 0 °C. Oxalyl chloride (15 mmol, 1.5 equiv), and DMF (5 drops) are then added and the mixture allowed to warm to rt. After stirring for 2.5 h, the solvent was removed and the crude acid choride was used immediately. A separate flame dried 100 mL round bottom flask, equipped with a rubber septum and magnetic stir bar is charged with dipropargyl ammonium trifluoroacetate[10] (15 mmol, 1.5 equiv), DMF (30 mL), and Et_3N (31 mmol, 3.0 equiv). The crude acid chloride in DMF (10 mL) is then added and the mixture is allowed to stir at rt. After 12 h, the mixture is poured into a separatory funnel containing 25 mL of Et_2O and 25 mL of H_2O. The layers are separated and the aqueous layer is extracted with Et_2O (2 X 50 mL). The combined organic layers are dried (Na_2SO_4) and concentrated. The residue is purified by chromatography on SiO_2 (95:5 to 90:10, hexanes:AcOEt) to afford **23** (2.0 g, 70%) as a pale yellow oil.

R_f (AcOEt/hexane 15:85) 0.36;

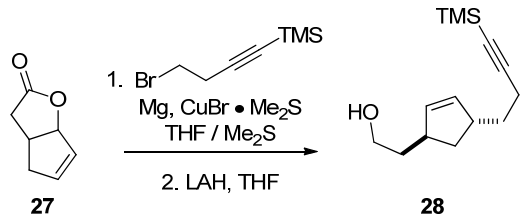
IR (neat): 3295, 2956, 2928, 2121, 1651, 1414, 1337, 1234, 1180, 1022, 953, 656 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 4.38 – 4.46 (m, 2 H), 4.27 – 4. 34 (m, 2 H), 2.35 (t, *J*, = 2.4 Hz, 1 H), 2.21 (t, *J* = 2.4 Hz, 1 H), 1.61 (d, *J* = 6.6 Hz, 1 H), 1.44 (s, 3 H), 1.12 (s, 3 H), 1.02 (d, *J* = 6.6 Hz, 1 H);

^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.9, 77.6, 77.2, 73.6, 72.1, 39.4, 37.2, 33.3, 27.0, 24.3, 23.6, 21.0;

HRMS (ESI) *m/z* calculated for $C_{12}H_{15}BrNO^+$ ($[M+1]^+$) 268.0337, found 268.0342.

[9] H. M. R. Hoffmann, J. M. Wulff, A. Kuetz, and W. Rudolf, *Angew. Chem*., 1982, **94**, 79.
[10] T. C. Krasia, and J. H. G. Steinke, *Chem. Commun*., **2002**, 22.



27 **28**

2-(4-(4-(trimethylsilyl)but-3-yn-1-yl)cyclopent-2-en-1-yl)ethanol, 28: A flame dried 50 mL round bottom flask, equipped with a rubber septum and magnetic stir bar, is charged with Mg (0.39 g, 2.0 equiv), THF (15 mL), I_2 (60 mg), and dibromoethane (45 μL). (4-bromobut-1-yn-1-yl)trimethylsilane (2.5 g, 1.5 equiv) in THF (25 mL) is added over 1 h. The mixture is then allowed to stir at rt for 2 h. A separate flame dried 250 mL round bottom flask, equipped with a rubber septum and magnetic stir bar, is charged with CuBr•Me_2S (3.3 g, 2.0 equiv), THF (20 mL), and Me_2S (20 mL) and cooled to -10 °C. The Grignard solution is then added and the slurry and is allowed to stir at -10 °C for 20 min. **27**[11] (0.99 g, 8.0 mmol) in THF (5.0 mL) is added and the reaction allowed to stir at -10 °C for 4 h. The reaction mixture is partitioned between 1 N aq. HCl (50 mL) and Et_2O (50 mL). The layers are separated and the aqueous layer is extracted with Et_2O (2 X 50 mL). The combined organic layers are dried (Na_2SO_4) and concentrated. The residue is passed through a silca gel pad using 70:28:2 hexane:EtOAc:AcOH as the elutent affording the cyclopentenyl acetic acid which was used without further purification (1.6 g, 79% yield).
A flame dried 50 mL round bottom flask, equipped with a rubber septum and magnetic stir bar, is charged with the crude acid residue and THF (25 mL) and cooled to 0 °C. A 1.5 M solution of LAH in THF (6.4 mL, 1.5 equiv) is added dropwise and the reaction allowed to stir at 0 °C for 2 h. The reaction is then quenched by the slow addition of H_2O (10 mL) The rxn is partitioned between 1 N aq. NaOH (50 mL) and Et_2O (50 mL) The layers are separated and the aqueous layer is extracted with Et_2O (2 X 50 mL). The combined organic layers are dried (Na_2SO_4) and concentrated. The residue is purified by chromatography on SiO_2 (90:10, hexanes:AcOEt) to afford **28** (1.3 g 85%) as a pale yellow oil.

R_f (AcOEt/hexane 10:90) 0.13;

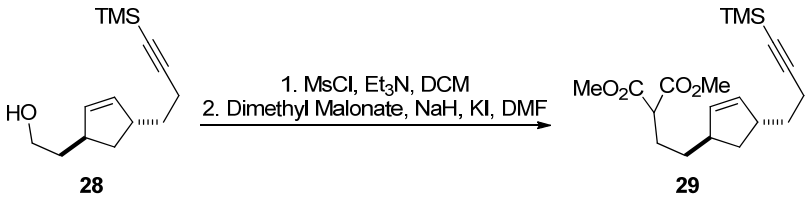
IR (neat): 3354, 2930, 2174, 1710, 1248, 1049, 839, 758, 736 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 5.70 (br s, 2 H), 3.64 – 3.72 (m, 2 H), 2.78 – 2.82 (m, 2 H), 2.21 – 2.26 (m, 2 H), 1.47 – 1.70 (m, 6 H), 0.14 (s, 9 H);

^{13}C NMR ($CDCl_3$, 400 MHz): δ 134.6, 134.2, 107.4, 84.3, 61.5, 43.9, 41.2, 38.6, 36.0, 34.5, 18.2, 0.06.

HRMS (ESI) *m/z* calculated for $C_{19}H_{30}BrNO^+$ ($[M+1]^+$) 268.0337, found 268.0342.

[11] T. Mitsudome, T. Umetani, N. Nosaka, K. Mori, T. Mizugaki, K. Ebitani, and K. Kaneda, *Agnew. Chem., Int. Ed.*, 2006, **45**, 481.



28 **29**

Dimethyl 2-(2-(4-(4-(trimethylsilyl)but-3-yn-1-yl)cyclopent-2-en-1-yl)ethyl)malonate (29): A flame dried 25 mL round bottom flask, equipped with a magnetic stir bar and rubber septum, is charged with **28** (0.74 g, 3.2 mmol), and DCM (11 mL) and cooled to 0 °C. The mixture is then treated with Et_3N (1.3 mL, 3.0 equiv) and MsCl (0.27 mL, 1.1 equiv). After 2 h at 0 °C the reaction is partitioned between sat. aq. NH_4Cl (50 mL) and Et_2O (50 mL). The layers are separated and the aqueous layer is extracted with Et_2O (2 x 50 mL). The combined organic layers are washed with H_2O and brine, dried (Na_2SO_4), and concentrated. The crude mesylate is used without further purification.
A flame dried 25 ml round bottom flask, equipped with a rubber septum and a magnetic stir bar, is charged with a 60% dispersion of NaH in mineral oil (0.14 g, 1.1 equiv) and a 1:1 THF:DMF mixture (10 mL) and cooled to 0 °C. The slurry is then treated with KI (53 mg, 0.1 equiv) and dimethyl malonate (0.39 mL, 1.1 equiv). The mixture is then allowed to warm to rt and treated with the crude mesylate in 1:1 THF:DMF (5 mL) and heated to 70 °C. After 16 h the reaction is partitioned between H_2O (50 mL) and Et_2O (50 mL). The layers are separated and the aqueous layers are extracted with Et_2O (2 x 50 mL). The combined organic layers are washed with H_2O and brine, dried (Na_2SO_4) and concentrated. The residue is purified by chromatography on SiO_2 (95:5 hexane:EtOAc) to afford **29** (0.72 g, 65%) as a pale yellow oil.

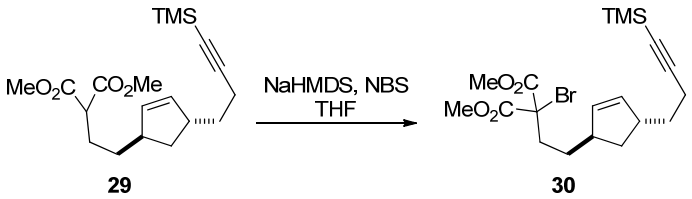
R_f (AcOEt/hexane 15:85) 0.37;

IR (neat): 2954, 2857, 2173, 1736, 1435, 1248, 1148, 840, 759 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 5.67 – 5.69 (m, 1 H), 5.64 – 5.66 (m, 1 H), 3.73 (s, 6 H), 3.34 (t, J = 7.6 Hz, 1 H), 2.75 – 2.78 (m, 1 H), 2.66 – 2.69 (m, 1 H), 2.22 (td, J = 7.6, 2.0 Hz, 2 H), 1.87 – 1.94 (m, 2 H), 1.55 – 1.65 (m, 3 H), 1.46 – 1.52 (m, 1 H), 1.34 – 1.43 (m, 1 H), 1.22 – 1.31 (m, 1 H), 0.14 (s, 9 H);

^{13}C NMR ($CDCl_3$, 400 MHz): δ 169.5, 134.3, 134.2, 107.2, 84.1, 52.2, 51.6, 44.2, 43.8, 35.7, 34.5, 33.3, 26.9, 18.1, -0.06;

HRMS (ESI) *m/z* calculated for $C_{14}H_{25}OSi^+$ ($[M+1]^+$) 237.1675, found 237.1774.



29 **30**

Dimethyl 2-bromo-2-(2-(4-(4-(trimethylsilyl)but-3-yn-1-yl)cyclopent-2-en-1-yl)ethyl)malonate (30): According to General Procedure B, **29** (0.70 g, 2.0 mmol), 1 M NaHMDS solution (2.2 mL, 2.2 mmol) and NBS (0.39 mg, 2.2 mmol) in dry THF (25 mL) afforded **30** (0.61 g, 71%) as a pale yellow oil after purification by chromatography on SiO_2 (95:5, hexane:AcOEt) (6 h reaction time).

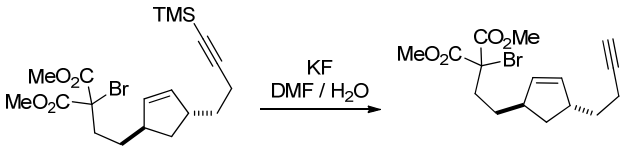
R_f (AcOEt/hexane 5:95): 0.34;

IR (neat): 2955, 2173, 1745, 1436, 1249, 912, 840, 733 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz): δ 5.69 – 5.71 (m, 1 H), 5.63 – 5.65 (m, 1 H), 3.82 (s, 6 H), 2.77 – 2.80 (m, 1 H), 2.69 – 2.73 (m, 1 H), 2.21 – 2.30 (m, 4 H), 1.45 – 1.68 (m, 5 H), 1.31 – 1.39 (m, 1 H), 0.14 (s, 9 H);

^{13}C NMR ($CDCl_3$, 400 MHz): δ 167.3, 134.7, 134.0, 107.3, 84.3, 62.6, 53.7, 44.1, 44.0, 36.4, 35.7, 34.5, 31.1, 18.2, 0.06.

HRMS (ESI) *m/z* calculated for $C_{19}H_{30}BrO_4Si^+$ ($[M+1]^+$) 429.1097, found 429.1078.



30 **25**

Dimethyl 2-bromo-2-(2-(4-(but-3-yn-1-yl)cyclopent-2-en-1-yl)ethyl)malonate (25): A 10 mL round bottom flask, equipped with a magnetic stir bar and rubber septum, is charged with **30** (0.20 g, 0.46 mmol), and DMF (4 mL). The mixture is then treated with KF (40 mg, 1.5 equiv) and H_2O (0.10 mL). After 12 h at rt the reaction is partitioned between H_2O (50 mL) and Et_2O (50 mL). The layers are separated and the aqueous layer is extracted with Et_2O (2 x 50 mL). The combined organic layers are washed with H_2O and brine, dried (Na_2SO_4), and concentrated. The residue is purified by chromatography on SiO_2 (95:5 hexane:EtOAc) to afford **30** (0.16 mg, 99%) as a pale yellow oil.

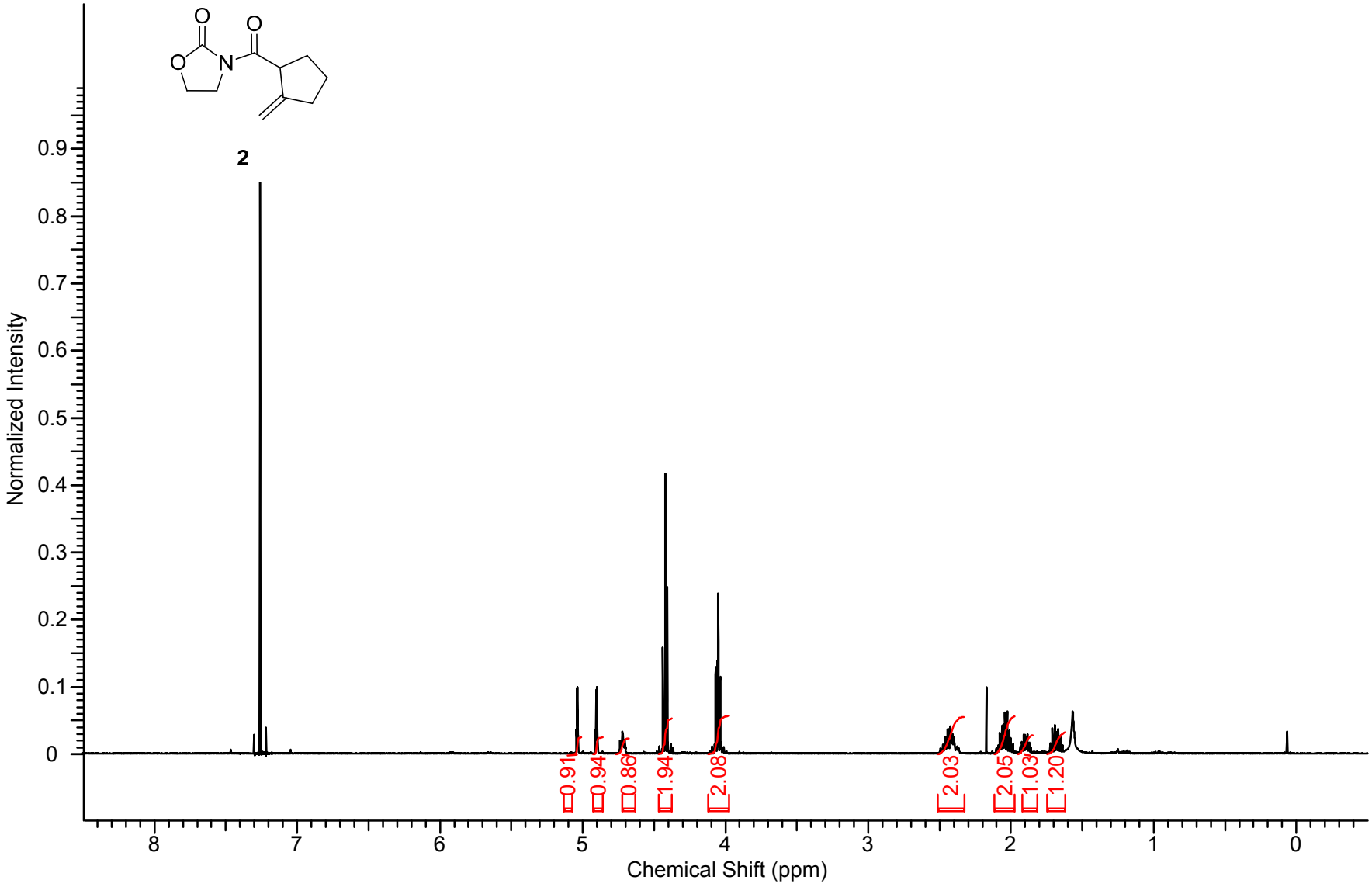
R_f (AcOEt/hexane 10:90): 0.33;

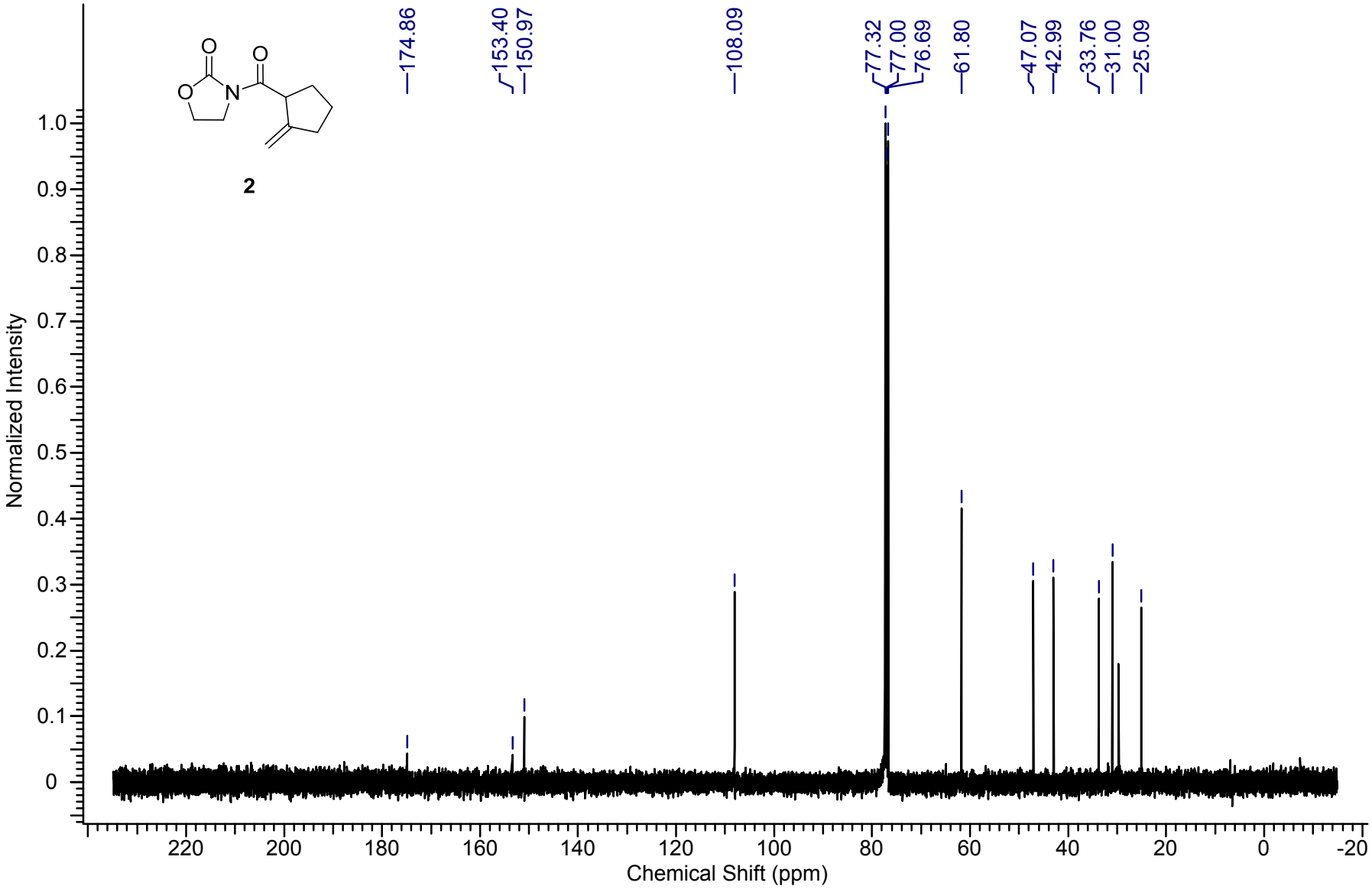
IR (neat): 3294, 3043, 2930, 2858, 1744, 1436, 1258 cm^{-1};

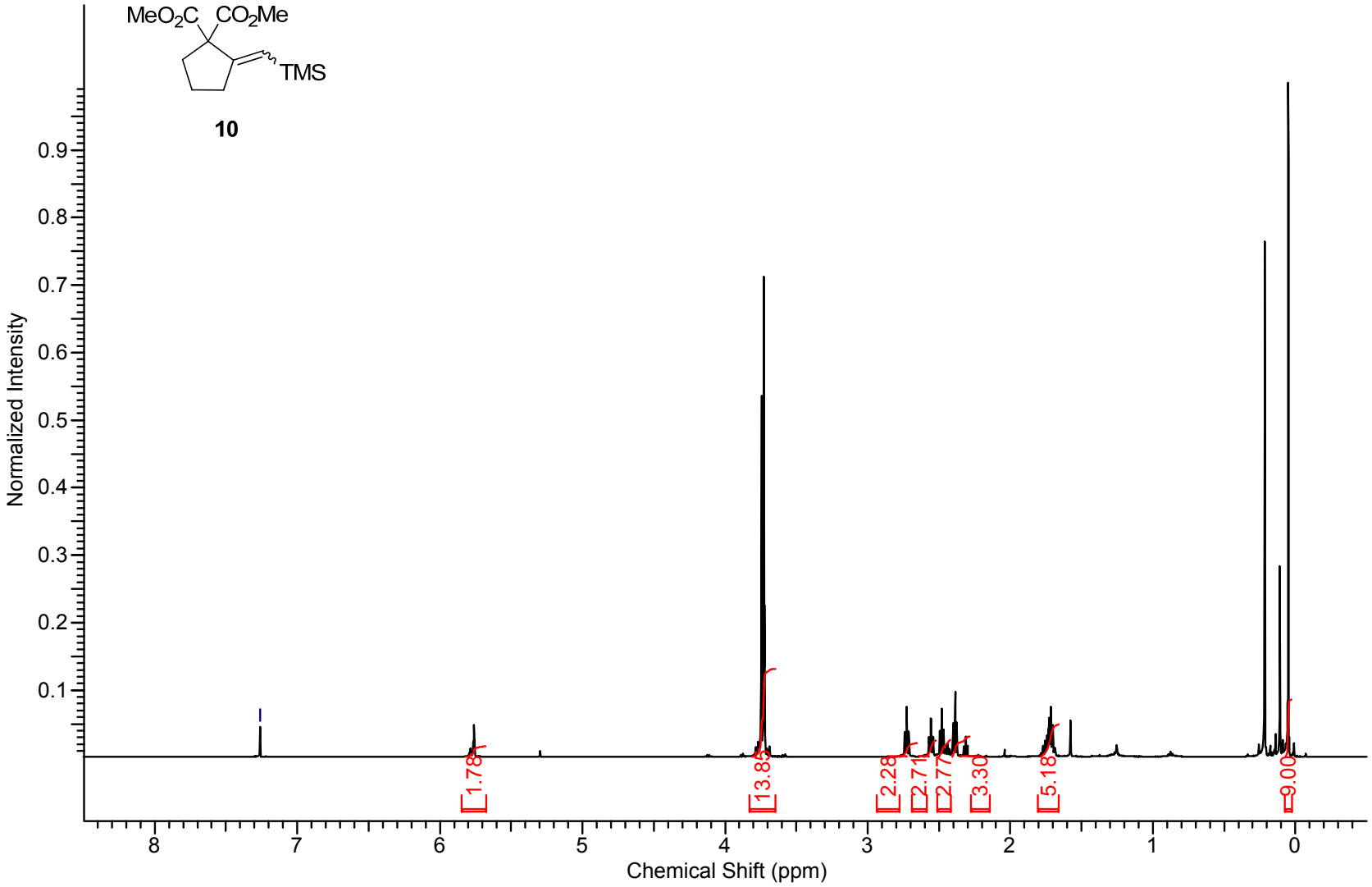
^1H NMR ($CDCl_3$, 500 MHz): δ 5.70 – 5.72 (m, 1 H), 5.66 – 5.68 (m, 1 H), 3.84 (s, 6 H), 2.82 – 2.88 (m, 1 H), 2.71 – 2.77 (m, 1 H),. 2.30 (ddd, J = 2.5, 2.5, 2.5 Hz, 1 H), 2.20 – 2.25 (m, 1 H), 1.97 (t, J = 2.5 Hz, 1 H), 1.70 (t, J = 6.5 Hz, 1 H), 1.60 – 1.67 (m, 1 H), 1.49 – 1.55 (m, 1 H), 1.36 – 1.44 (m, 1 H);

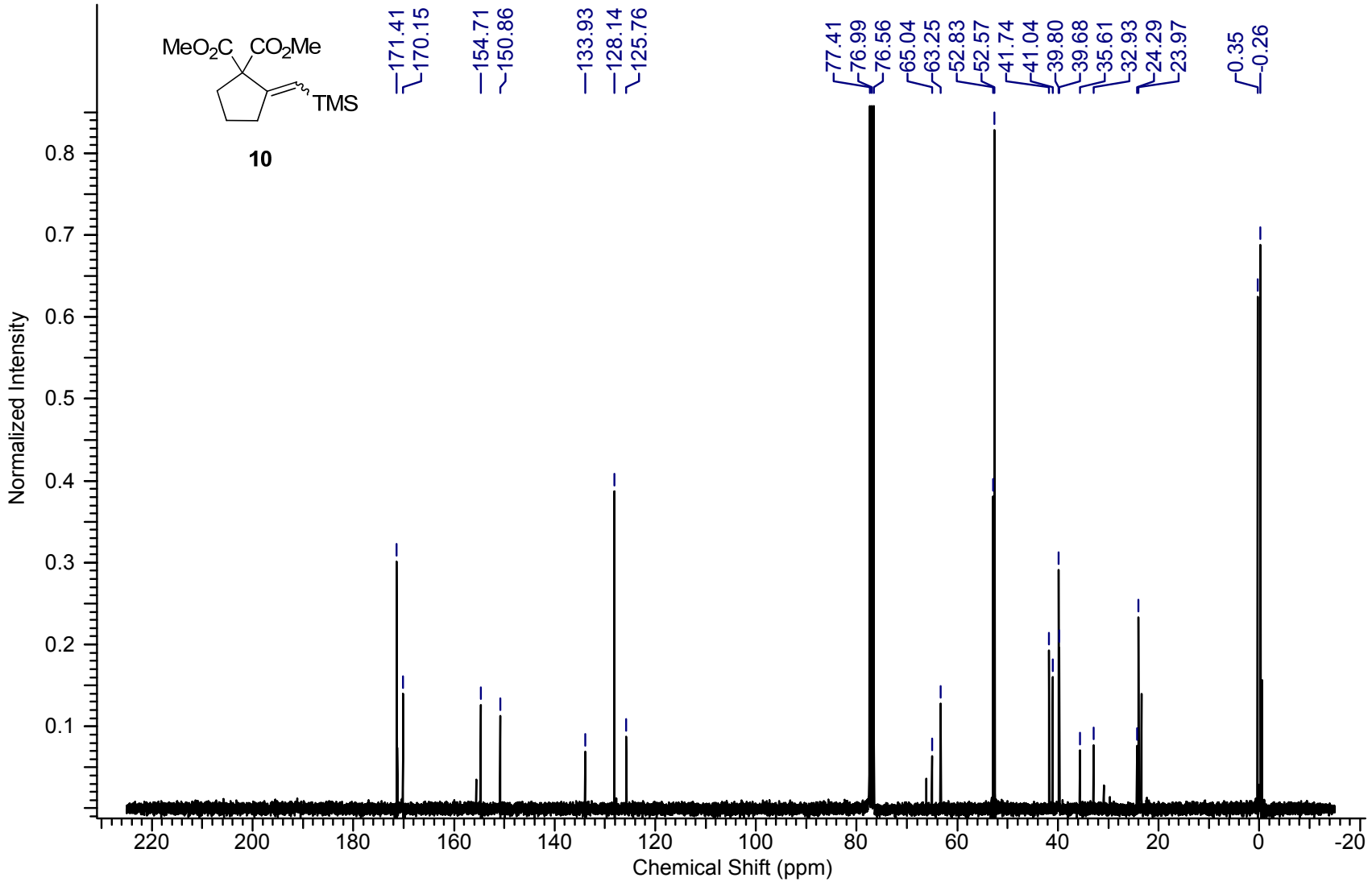
^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.3, 134.5, 134.1, 84.4, 68.2, 62.6, 53.8, 44.1, 43.8, 36.5, 35.7, 34.4, 31.1, 16.7;

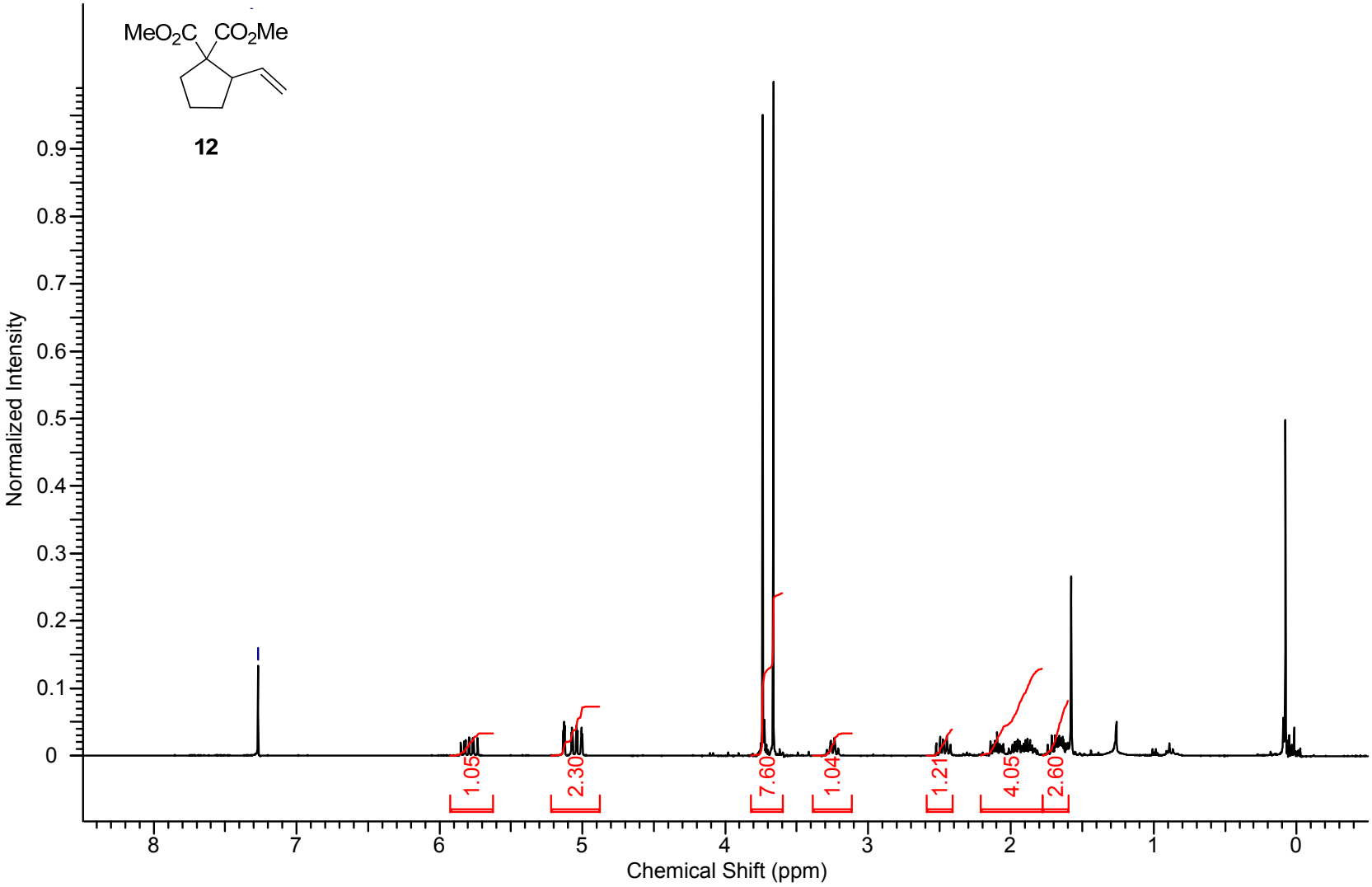
HRMS (ESI) *m/z* calculated for $C_{16}H_{22}BrO_4^+$ ($[M+1]^+$) 357.0701, found 357.2697.

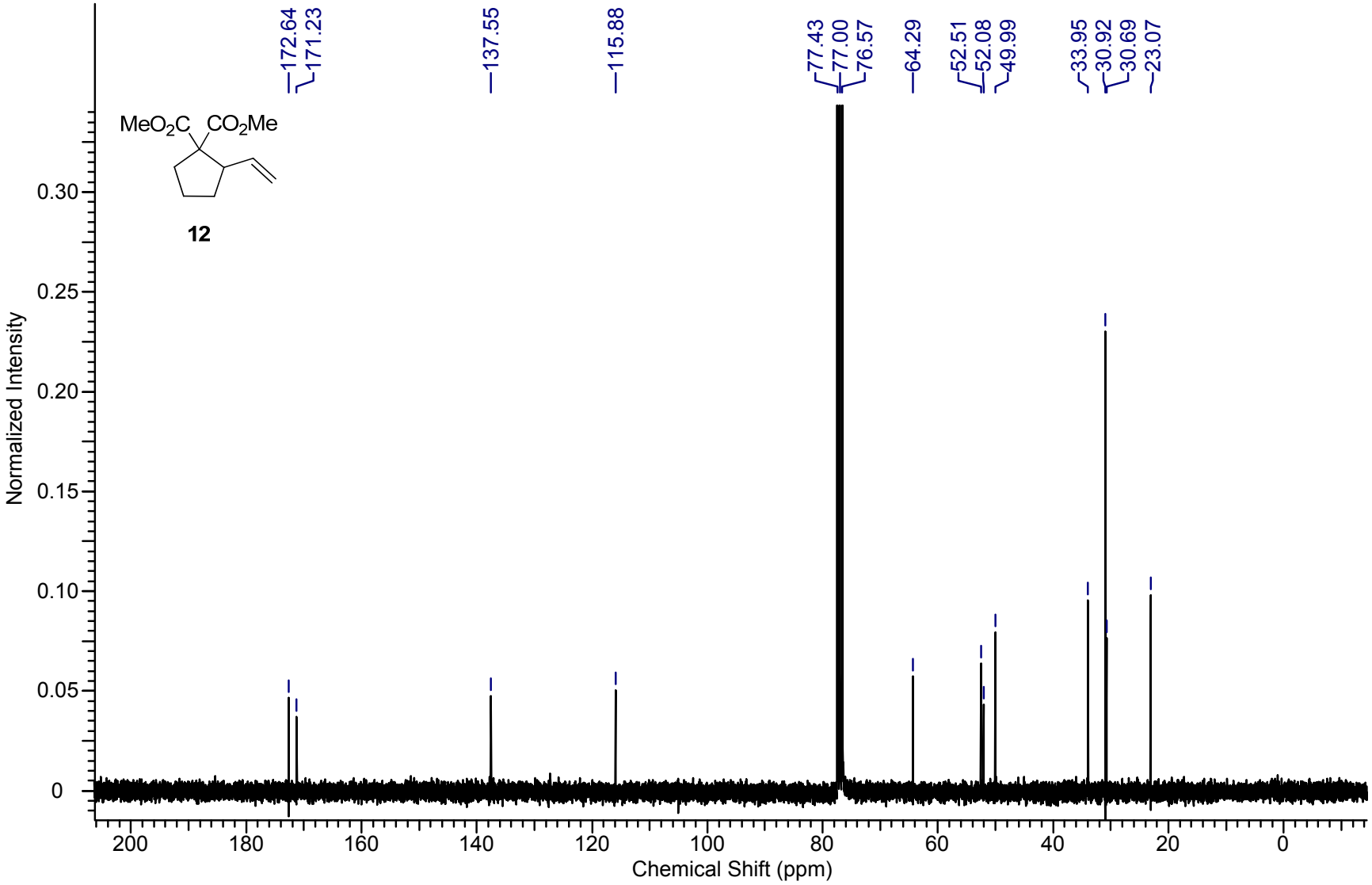

O
O
O
N
2
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.91
0.94
0.86
1.94
2.08
2.03
2.05
1.03
1.20
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

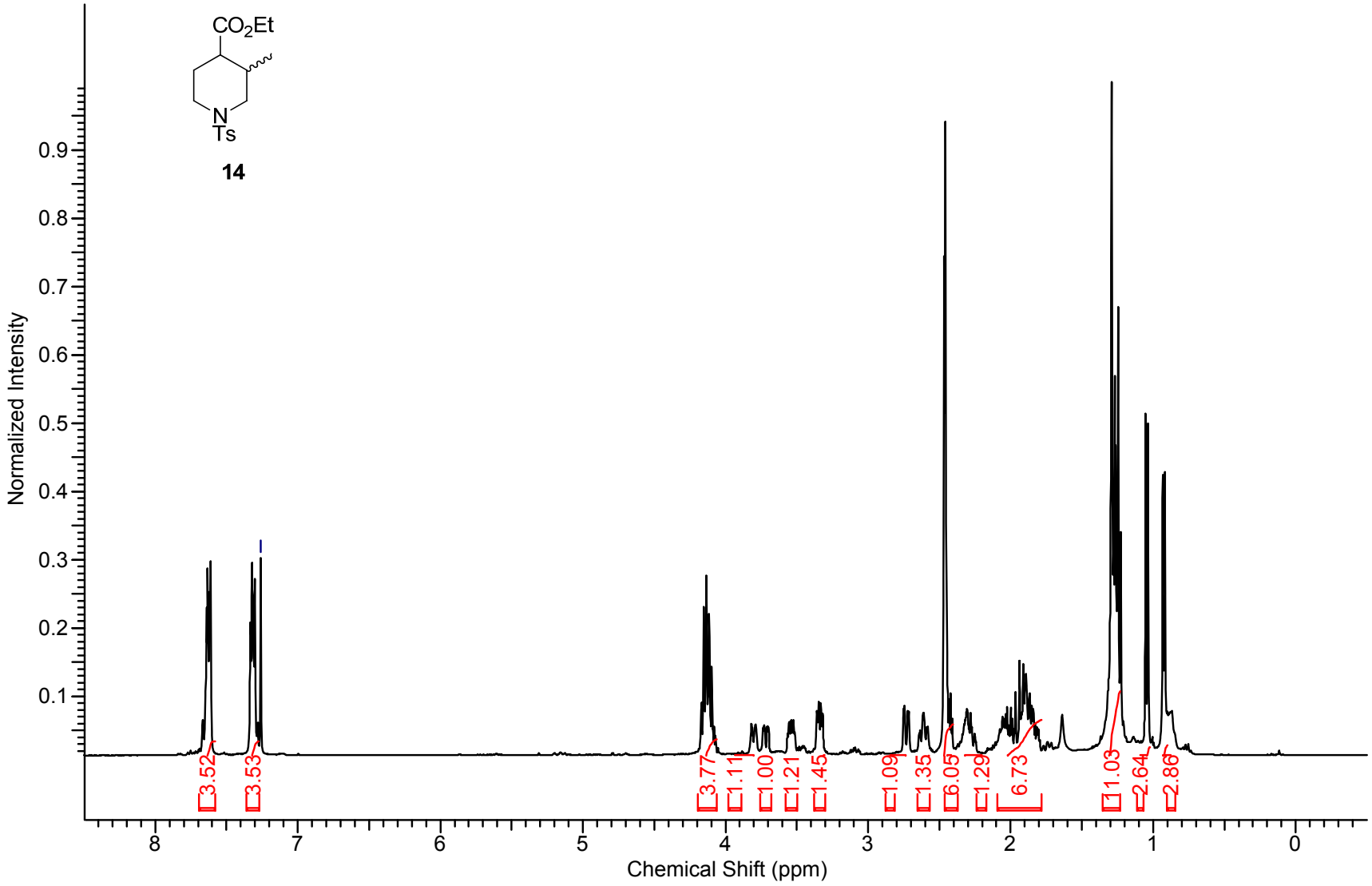

174.86
153.40
150.97
108.09
77.32
77.00
76.69
61.80
47.07
42.99
33.76
31.00
25.09
2
Normalized Intensity
Chemical Shift (ppm)


MeO2C CO2Me
TMS
10
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1.78
13.85
2.28
2.71
2.77
3.30
5.18
9.00
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


MeO2C CO2Me
TMS
10
171.41
170.15
154.71
150.86
133.93
128.14
125.76
77.41
76.99
76.56
65.04
63.25
52.83
52.57
41.74
41.04
39.80
39.68
35.61
32.93
24.29
23.97
0.35
-0.26
Normalized Intensity
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


MeO2C CO2Me
12
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.05
2.30
7.60
1.04
1.21
4.05
2.60
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


172.64
171.23
137.55
115.88
77.43
77.00
76.57
64.29
52.51
52.08
49.99
33.95
30.92
30.69
23.07
MeO2C CO2Me
12
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CO2Et
N
Ts
14
Normalized Intensity
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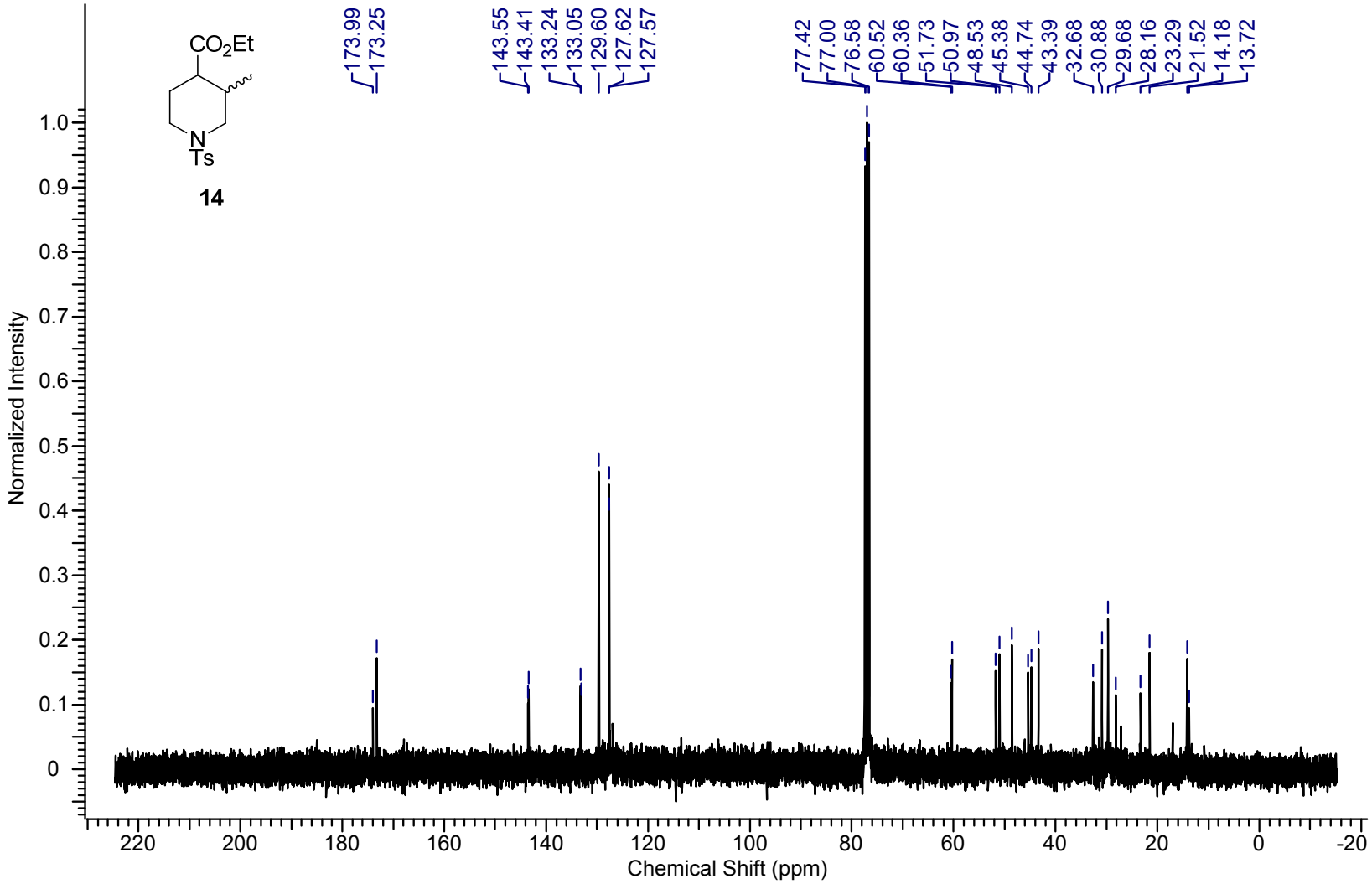
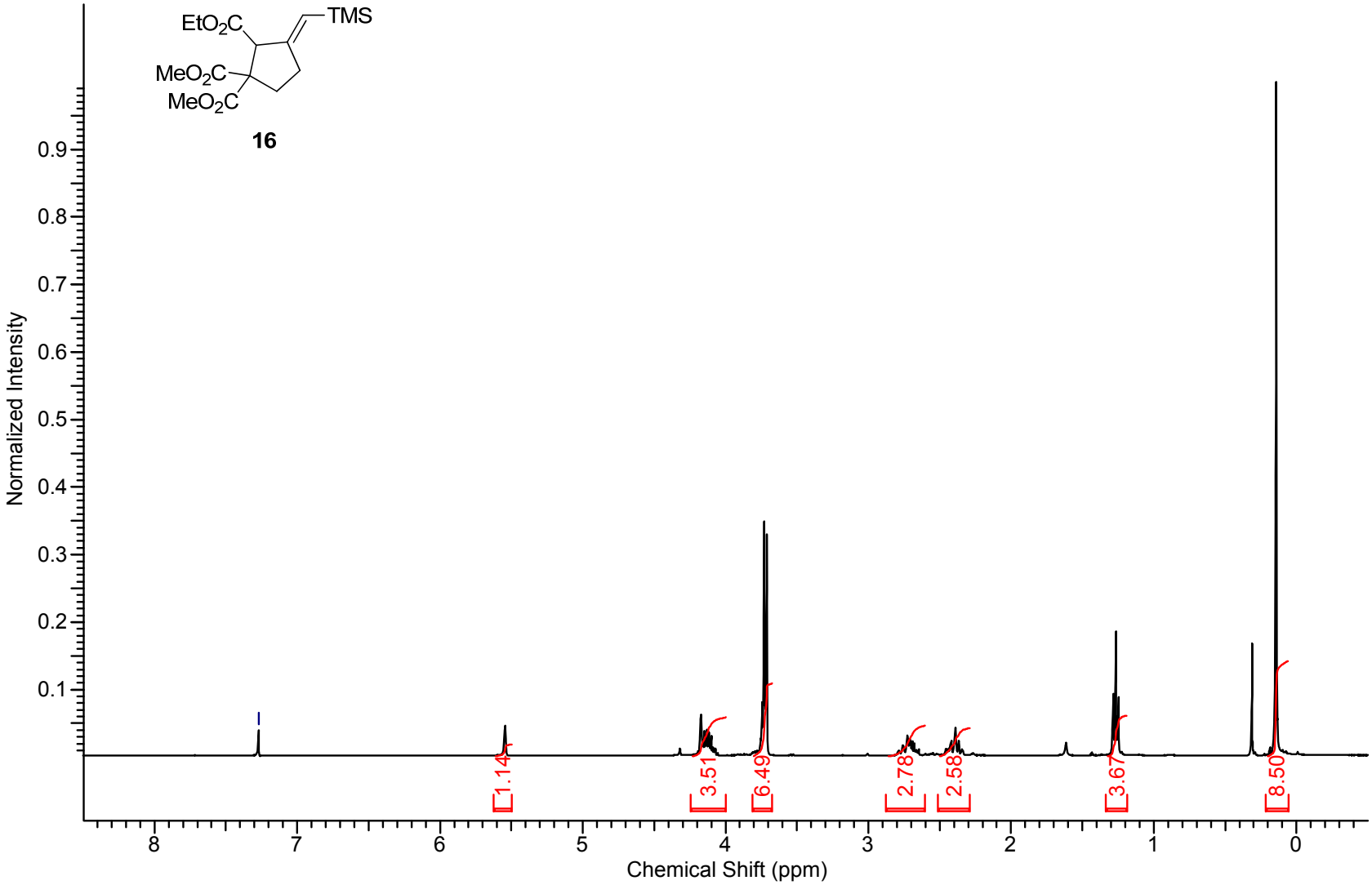
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
3.52
3.53
3.77
1.11
1.00
1.21
1.45
1.09
1.35
6.05
1.29
6.73
11.03
2.64
2.86
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CO2Et
N
Ts
14
173.99
173.25
143.55
143.41
133.24
133.05
129.60
127.62
127.57
77.42
77.00
76.58
60.52
60.36
51.73
50.97
48.53
45.38
44.74
43.39
32.68
30.88
29.68
28.16
23.29
21.52
14.18
13.72
Normalized Intensity
Chemical Shift (ppm)


EtO2C
TMS
MeO2C
MeO2C
16
Normalized Intensity
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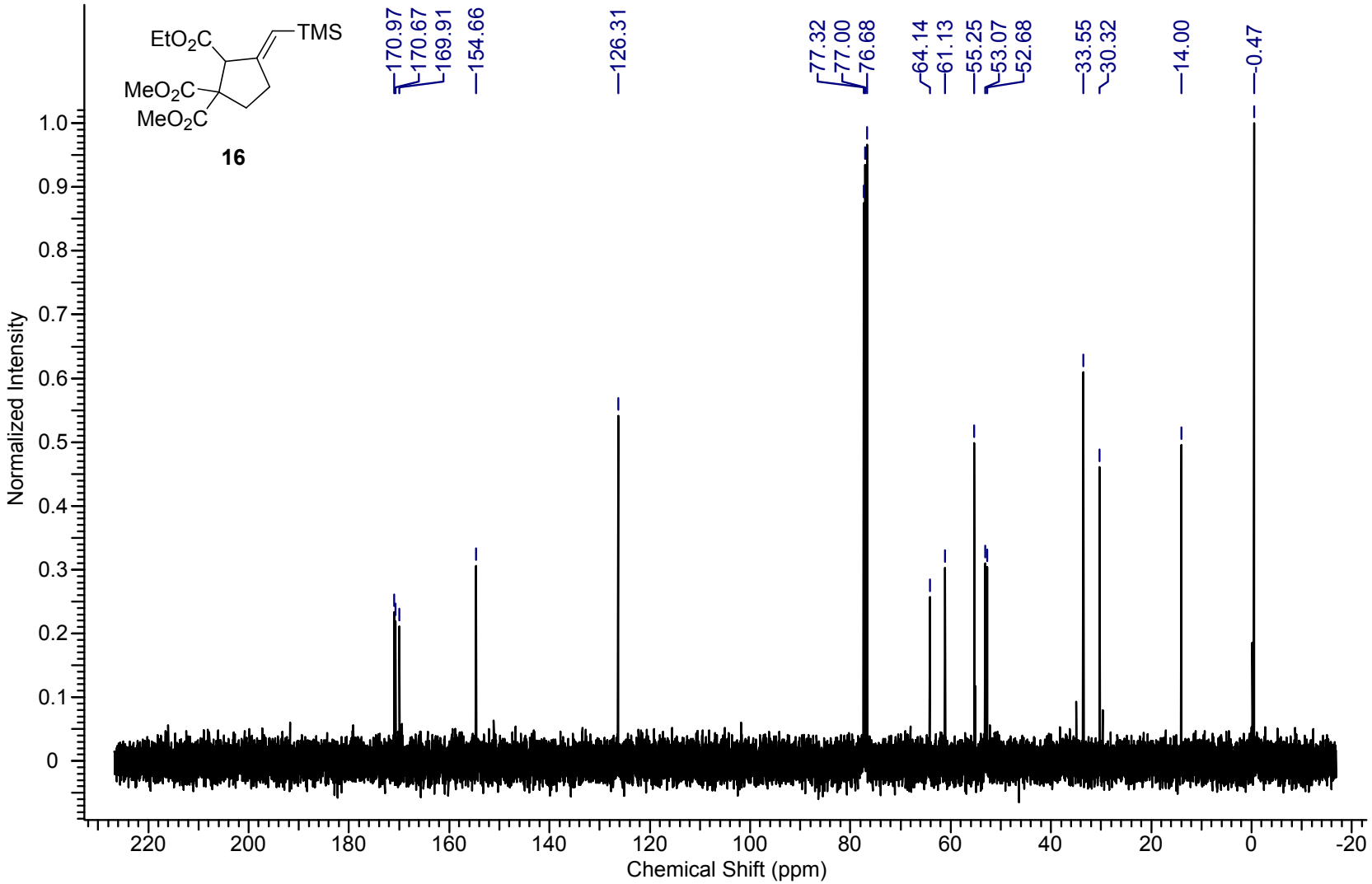
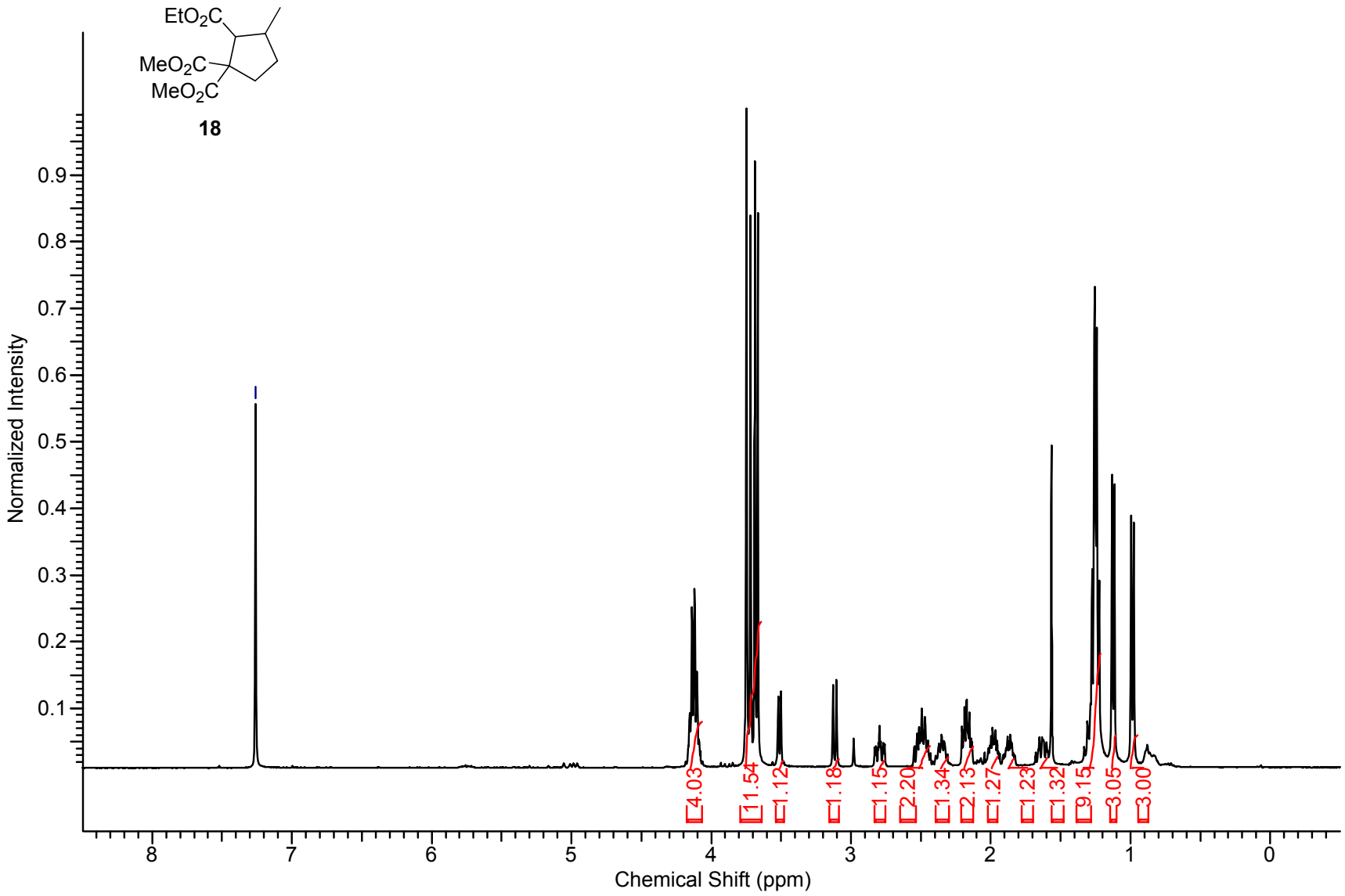
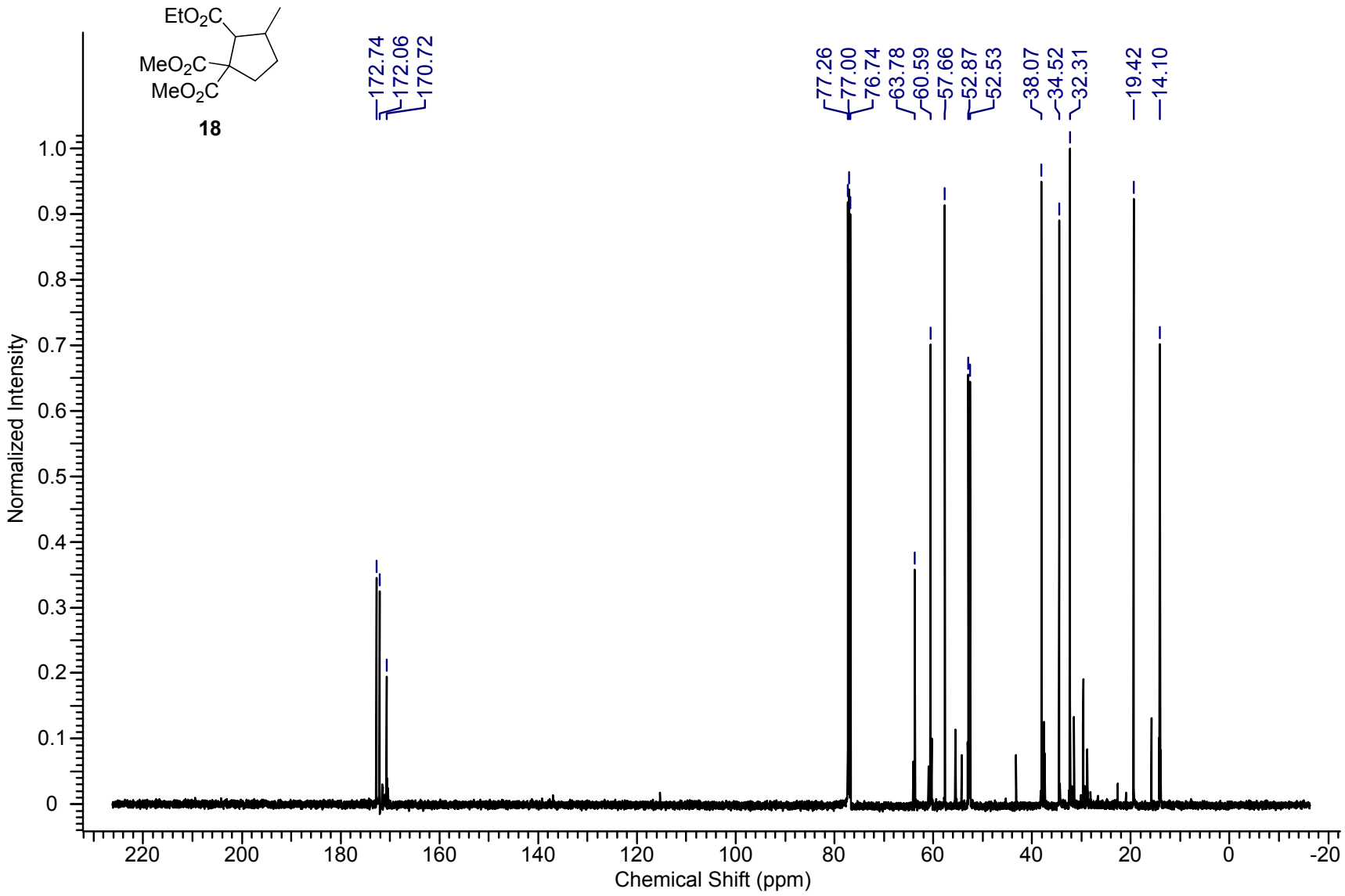
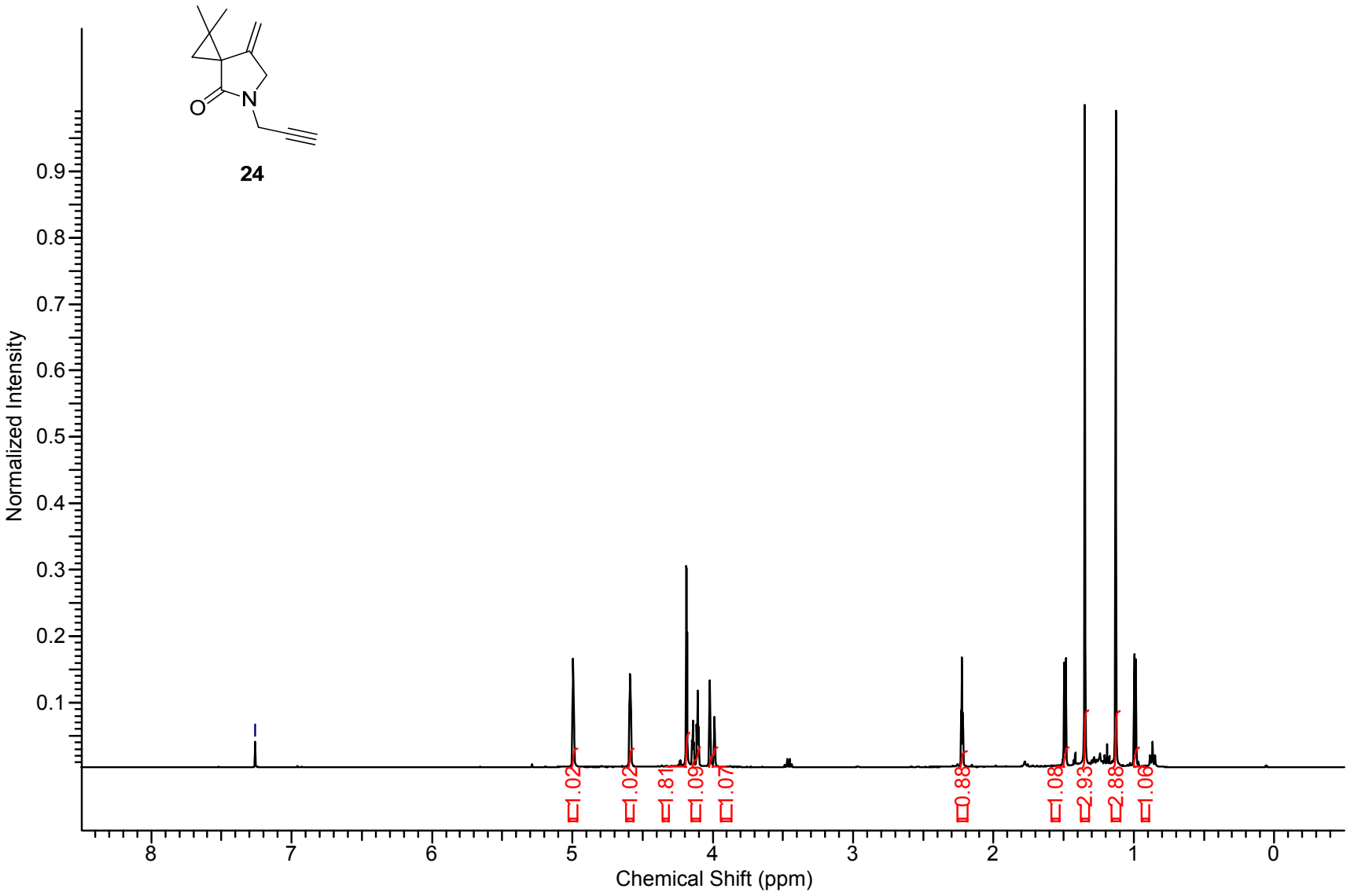
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1.14
3.51
6.49
2.78
2.58
3.67
8.50
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


EtO2C
TMS
MeO2C
MeO2C
16
170.97
170.67
169.91
154.66
126.31
77.32
77.00
76.68
64.14
61.13
55.25
53.07
52.68
33.55
30.32
14.00
0.47
Normalized Intensity
Chemical Shift (ppm)


EtO2C
MeO2C
MeO2C
18
Normalized Intensity
Chemical Shift (ppm)
4.03
11.54
1.12
1.18
1.15
2.20
1.34
2.13
1.27
1.23
1.32
9.15
3.05
3.00


EtO2C
MeO2C
MeO2C
18
172.74
172.06
170.72
77.26
77.00
76.74
63.78
60.59
57.66
52.87
52.53
38.07
34.52
32.31
19.42
14.10
Normalized Intensity
Chemical Shift (ppm)


O
N
24
Normalized Intensity
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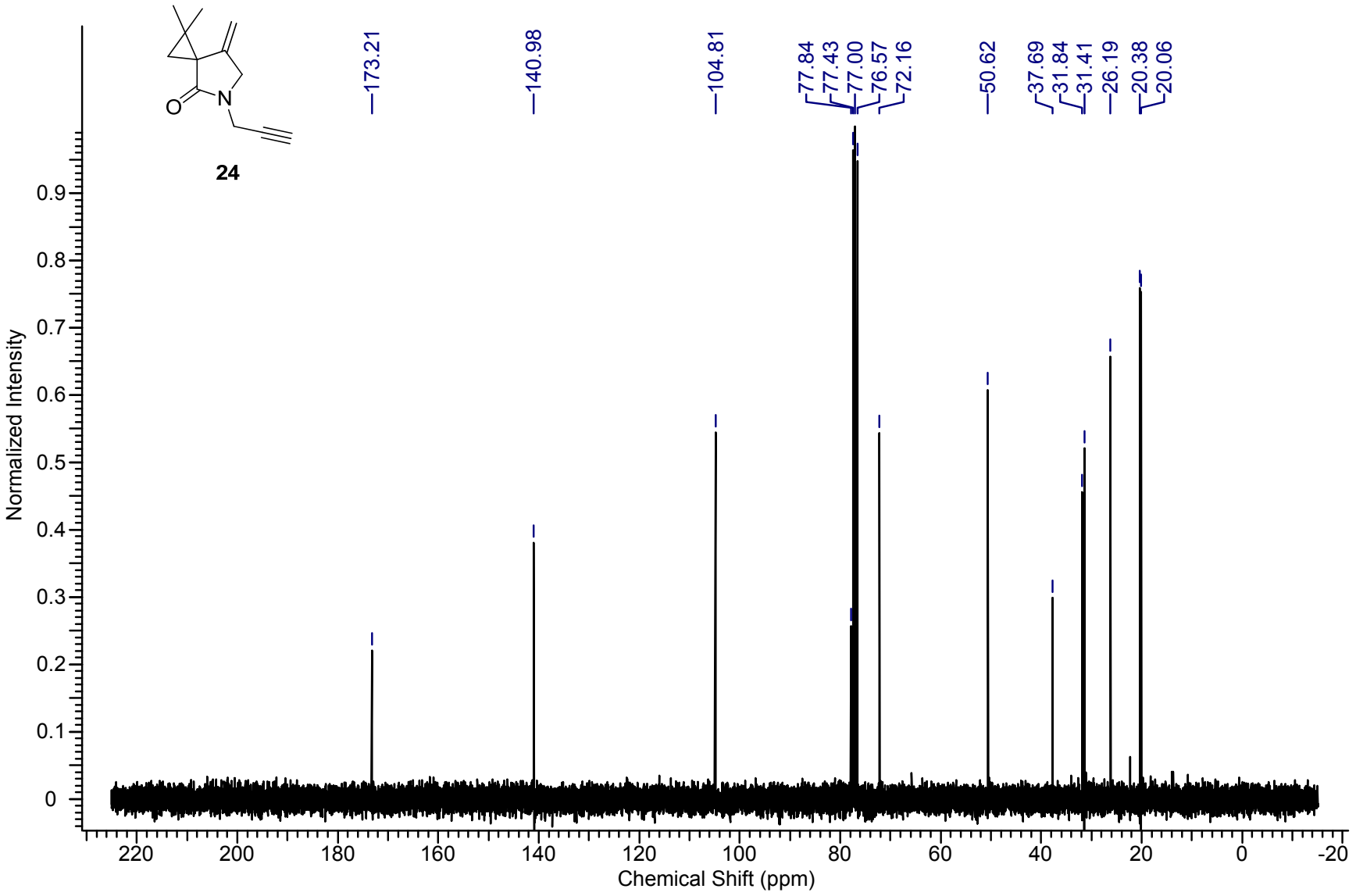
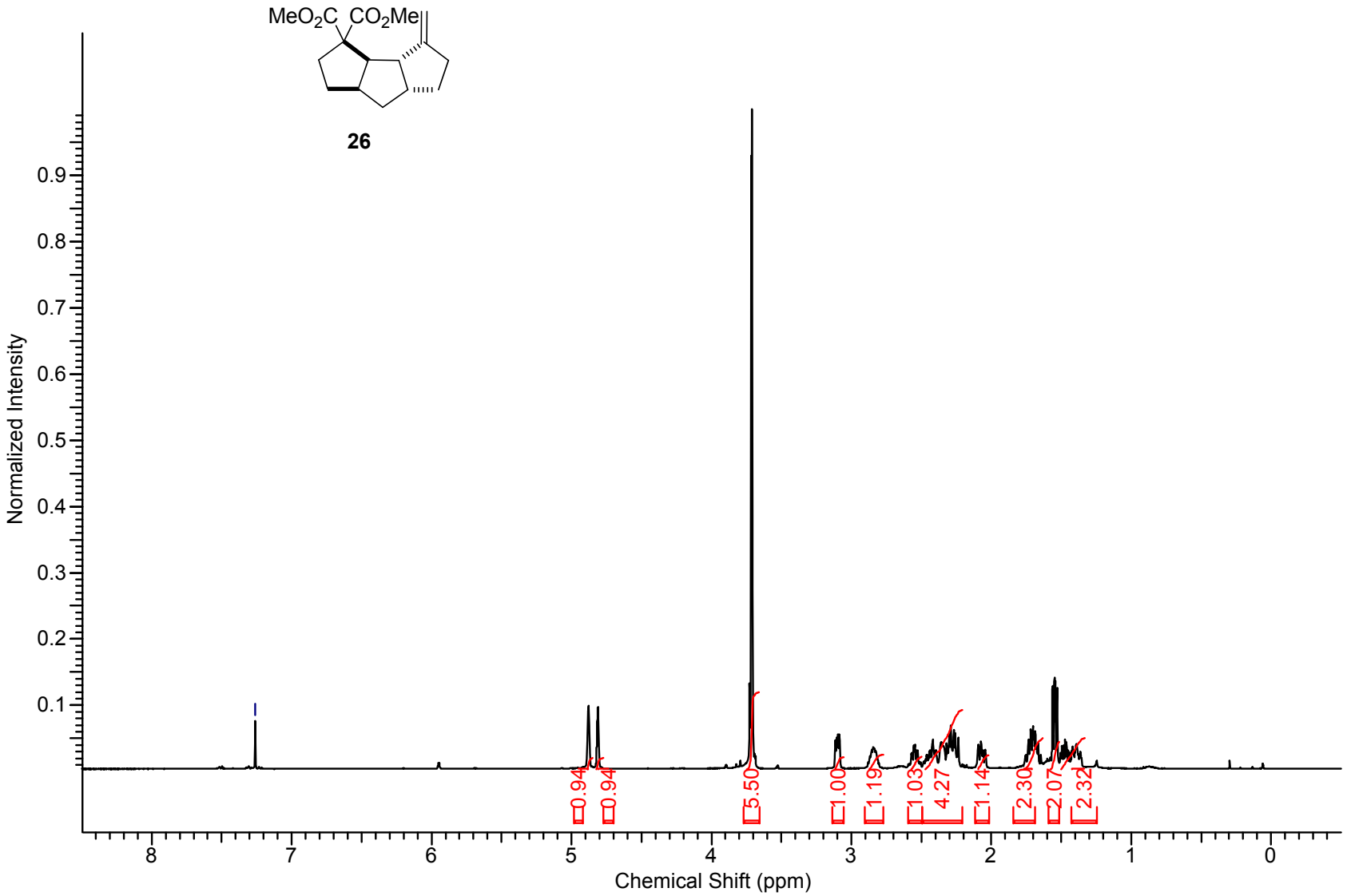
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
1.02
1.02
1.81
1.09
1.07
0.88
1.08
2.93
2.88
1.06


O
N
24
173.21
140.98
104.81
77.84
77.43
77.00
76.57
72.16
50.62
37.69
31.84
31.41
26.19
20.38
20.06
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


MeO2C CO2Me
26
Normalized Intensity
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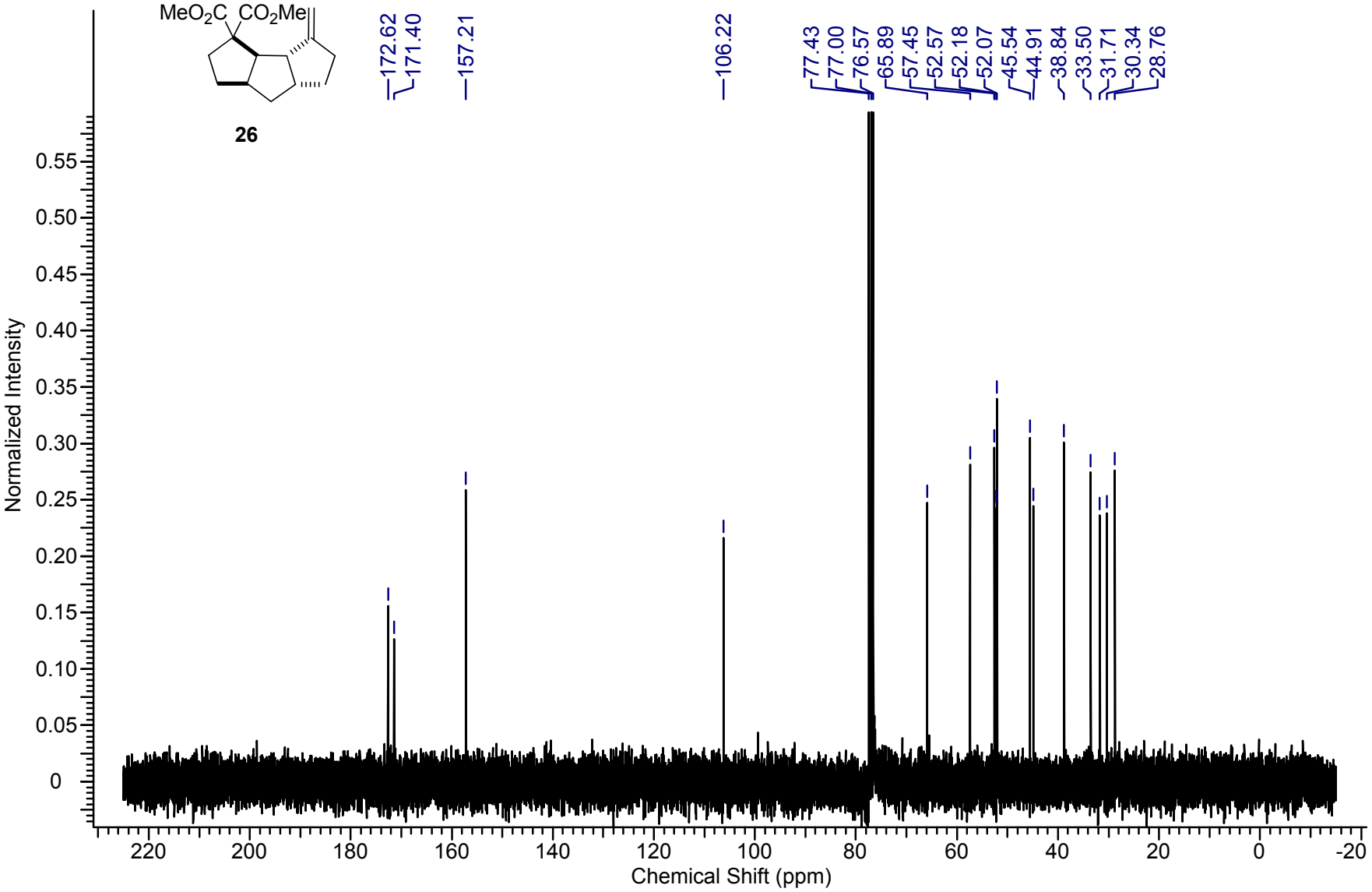
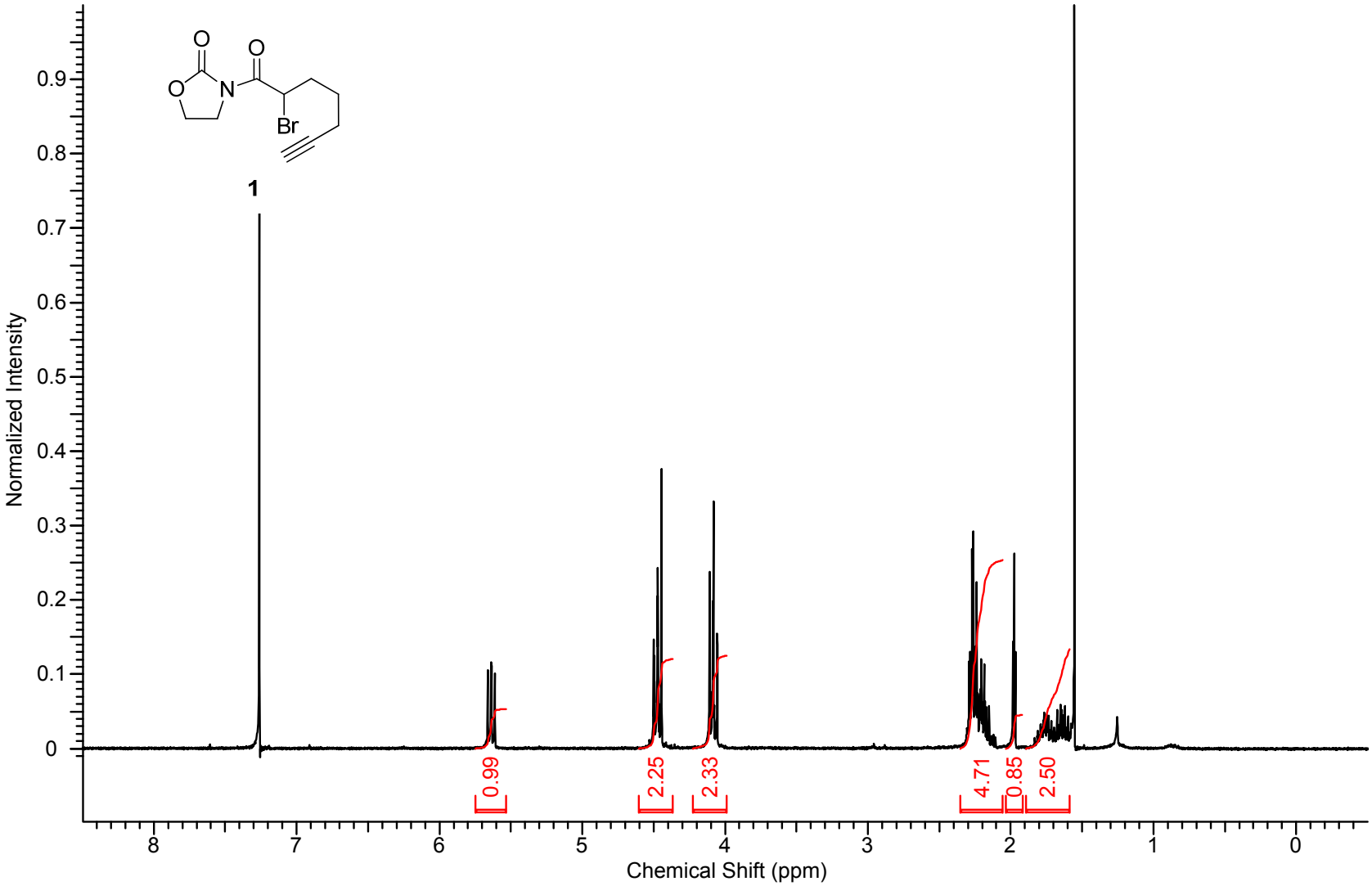
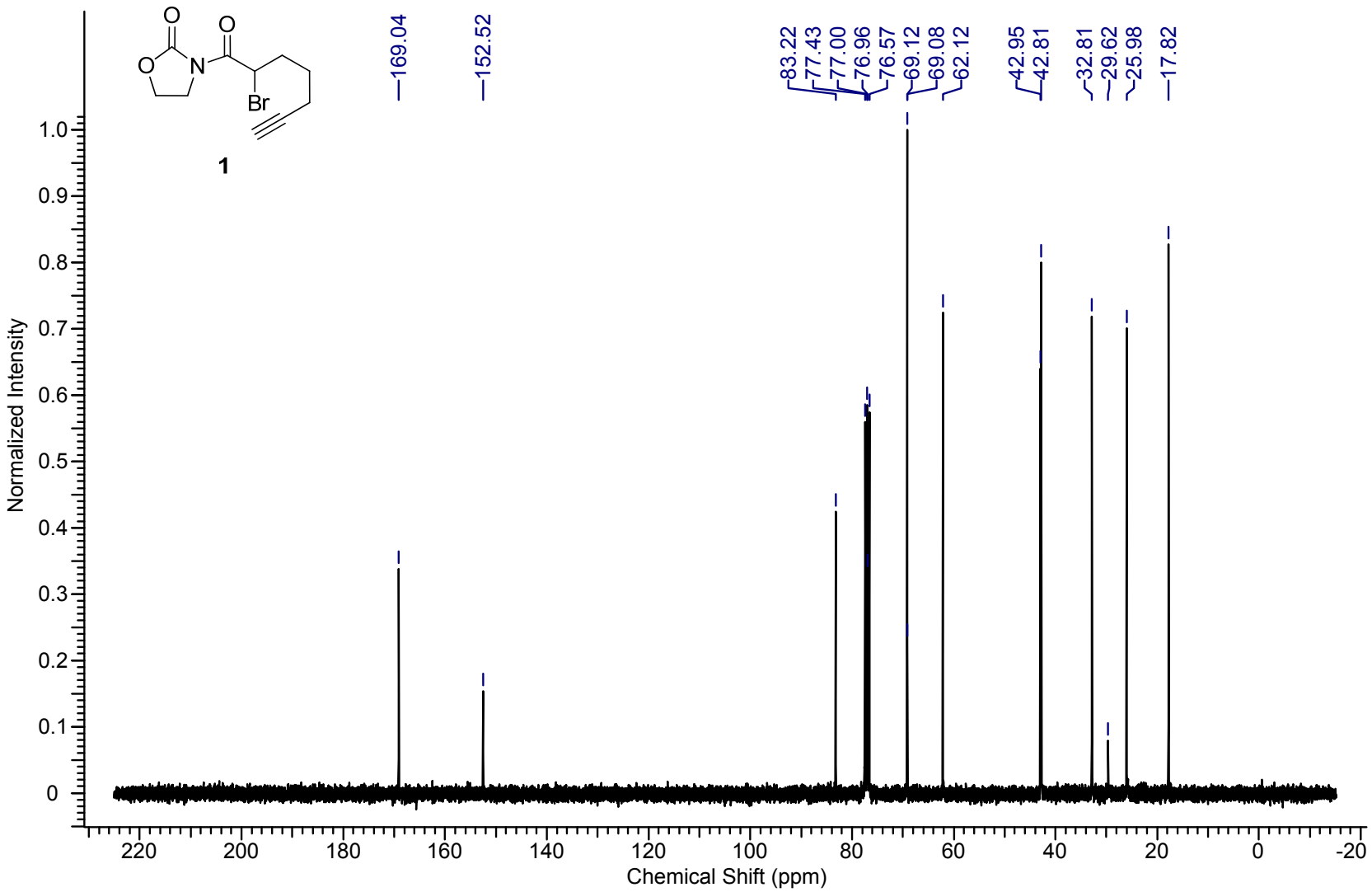
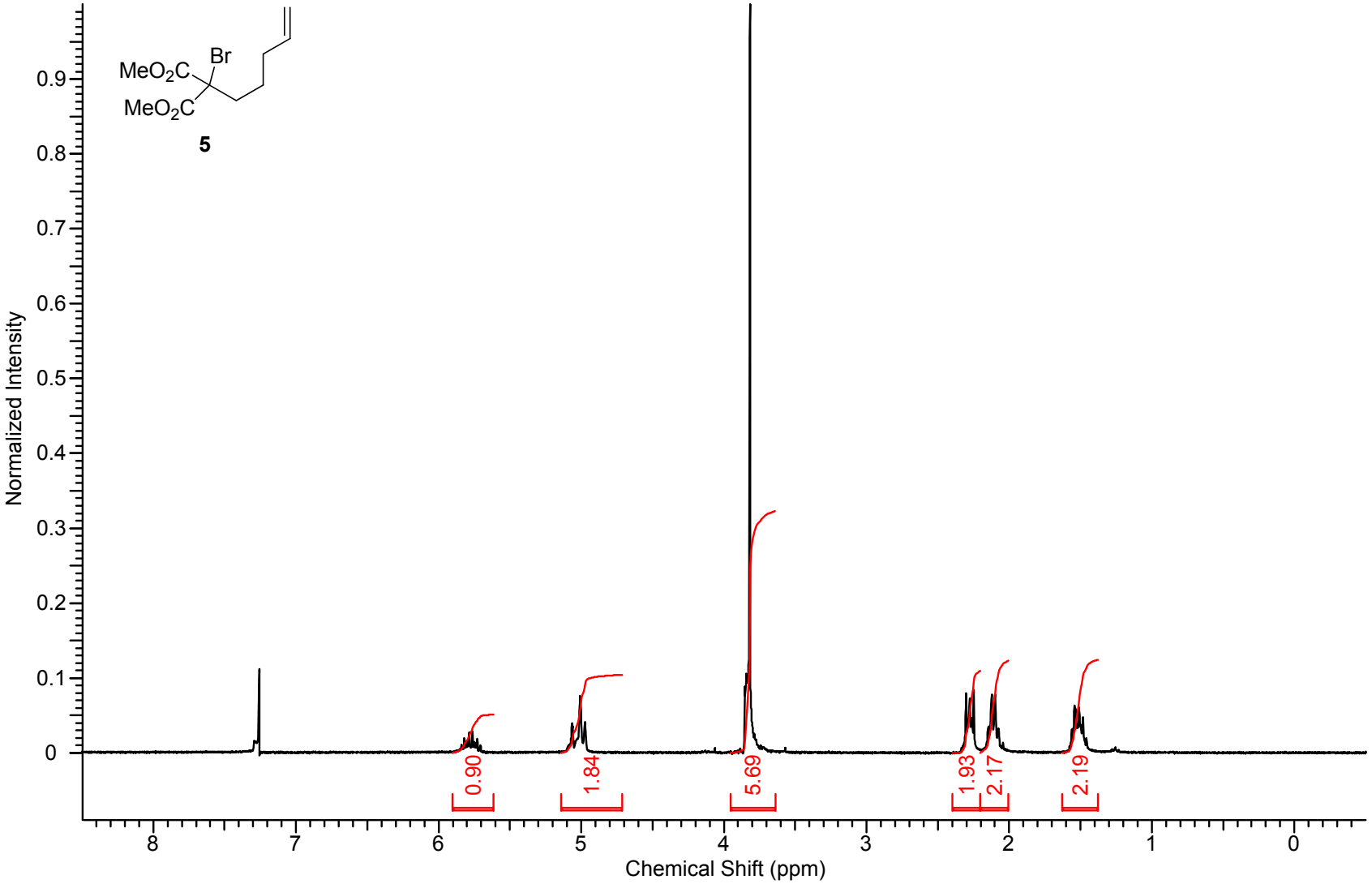
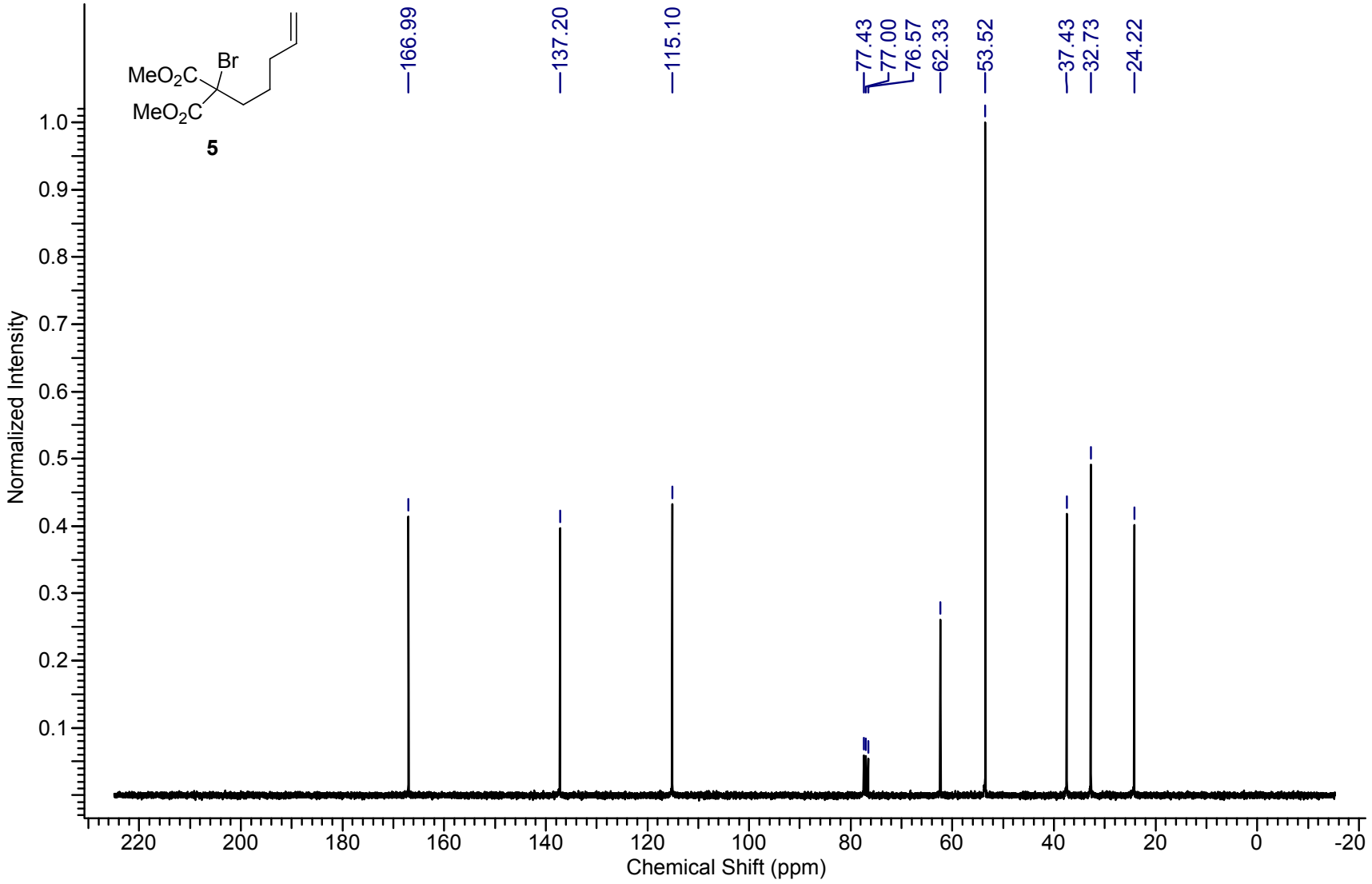
0.6
0.5
0.4
0.3
0.2
0.1
0.94
0.94
5.50
1.00
1.19
1.03
4.27
1.14
2.30
2.07
2.32
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

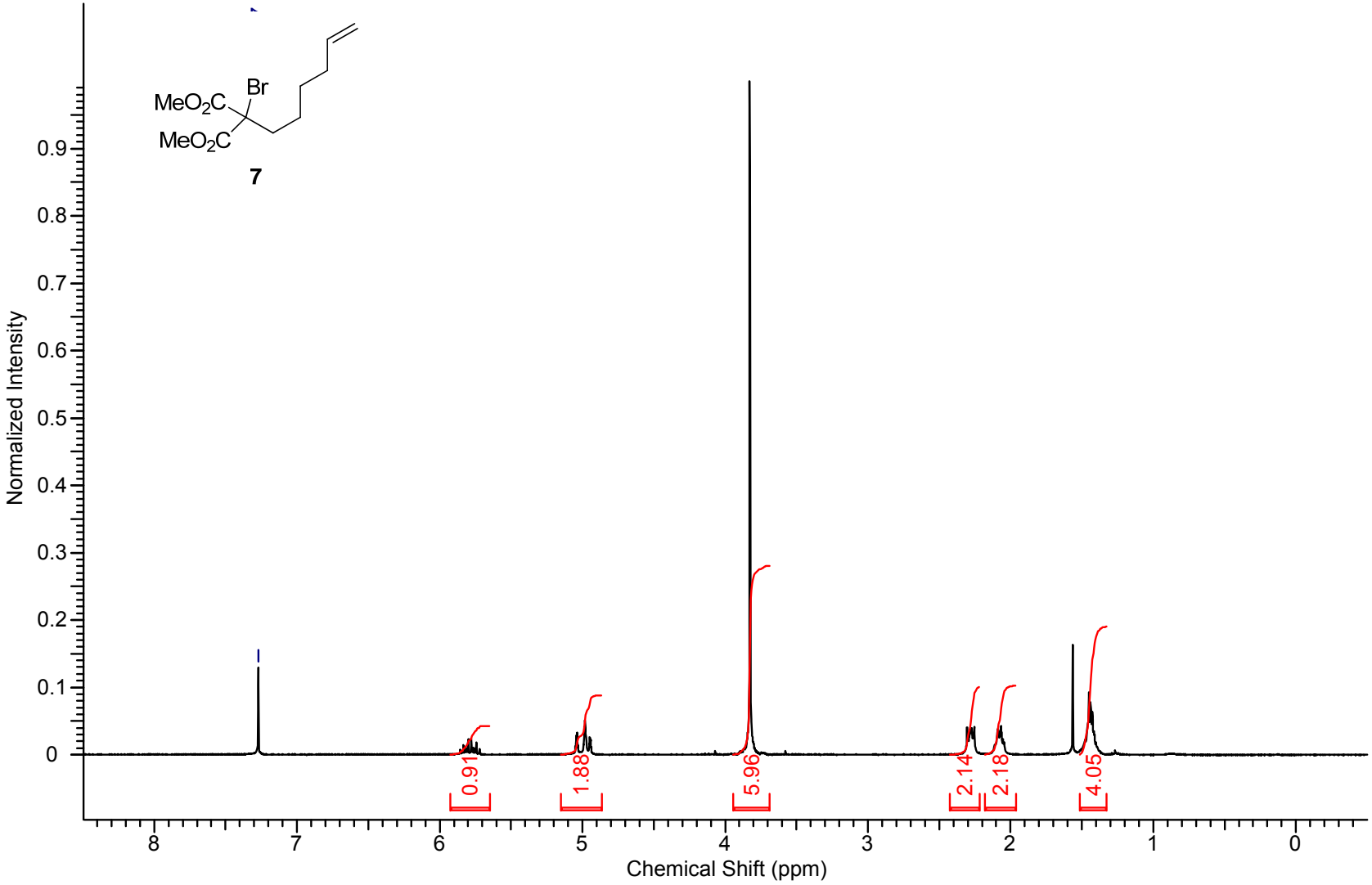

MeO2C CO2Me
26
172.62
171.40
157.21
106.22
77.43
77.00
76.57
65.89
57.45
52.57
52.18
52.07
45.54
44.91
38.84
33.50
31.71
30.34
28.76
Normalized Intensity
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

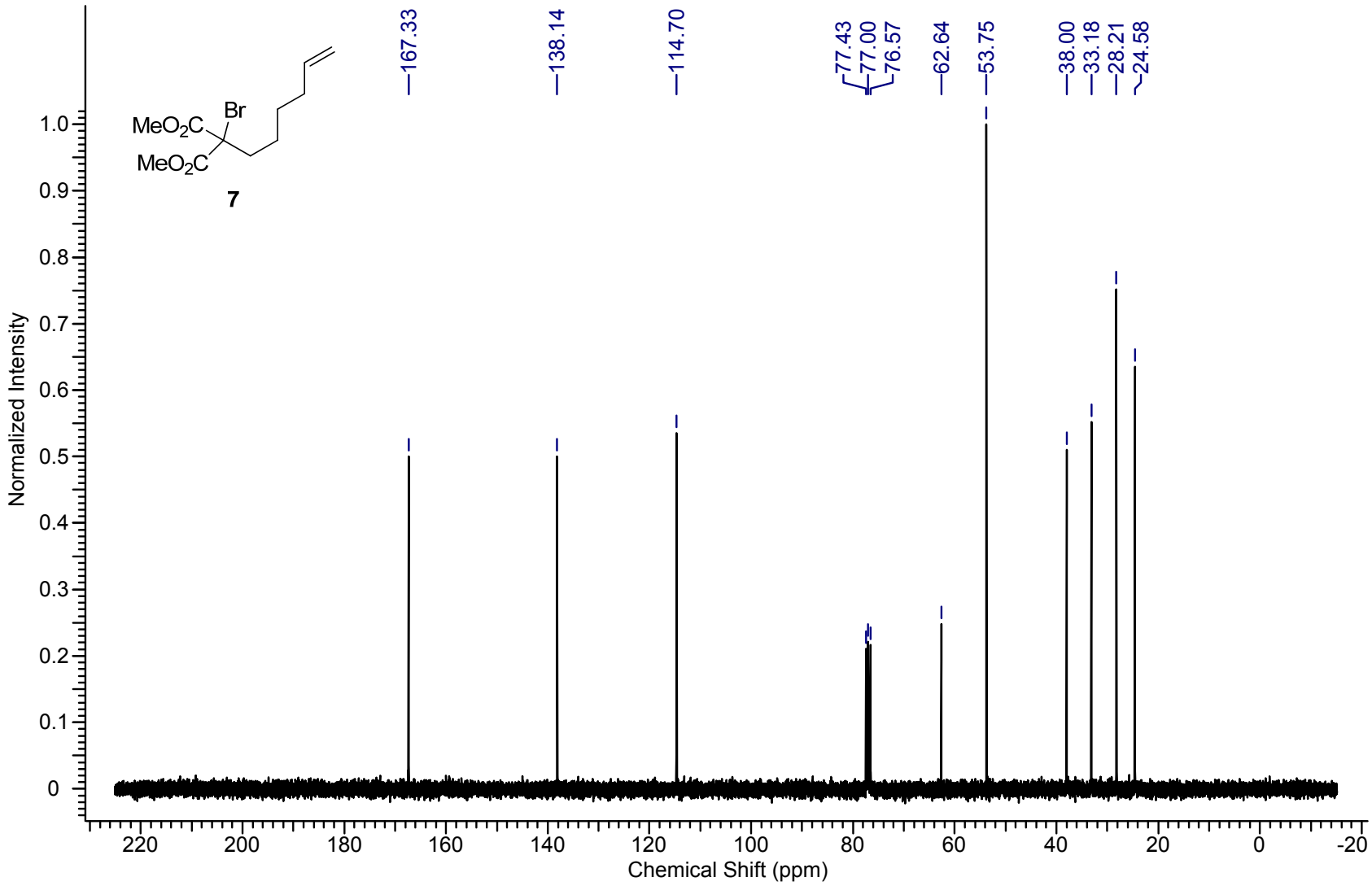

O
O
O
N
Br
1
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.99
2.25
2.33
4.71
0.85
2.50
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

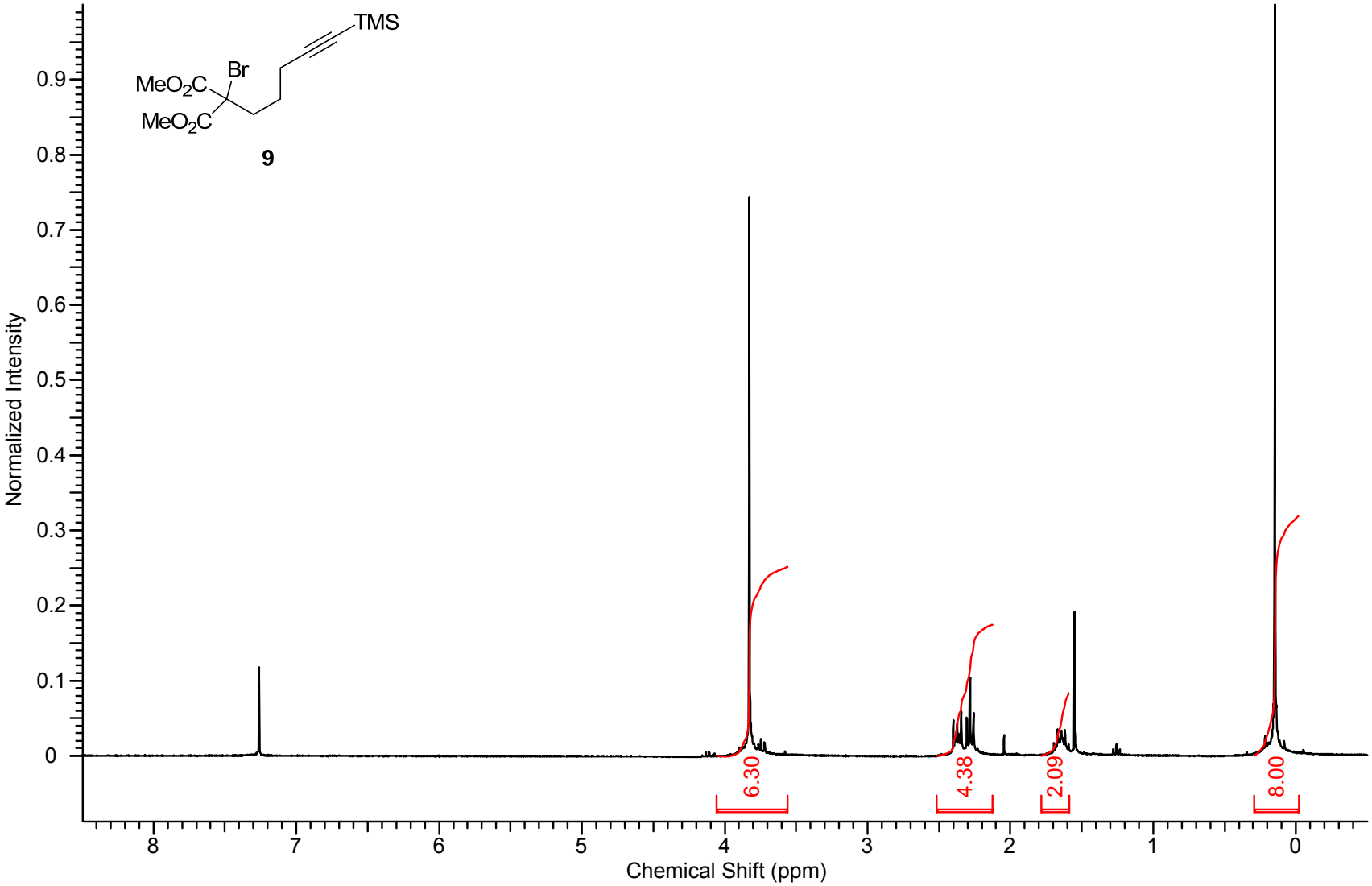

O
O
O
N
Br
1
169.04
152.52
83.22
77.43
77.00
76.96
76.57
69.12
69.08
62.12
42.95
42.81
32.81
29.62
25.98
17.82
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

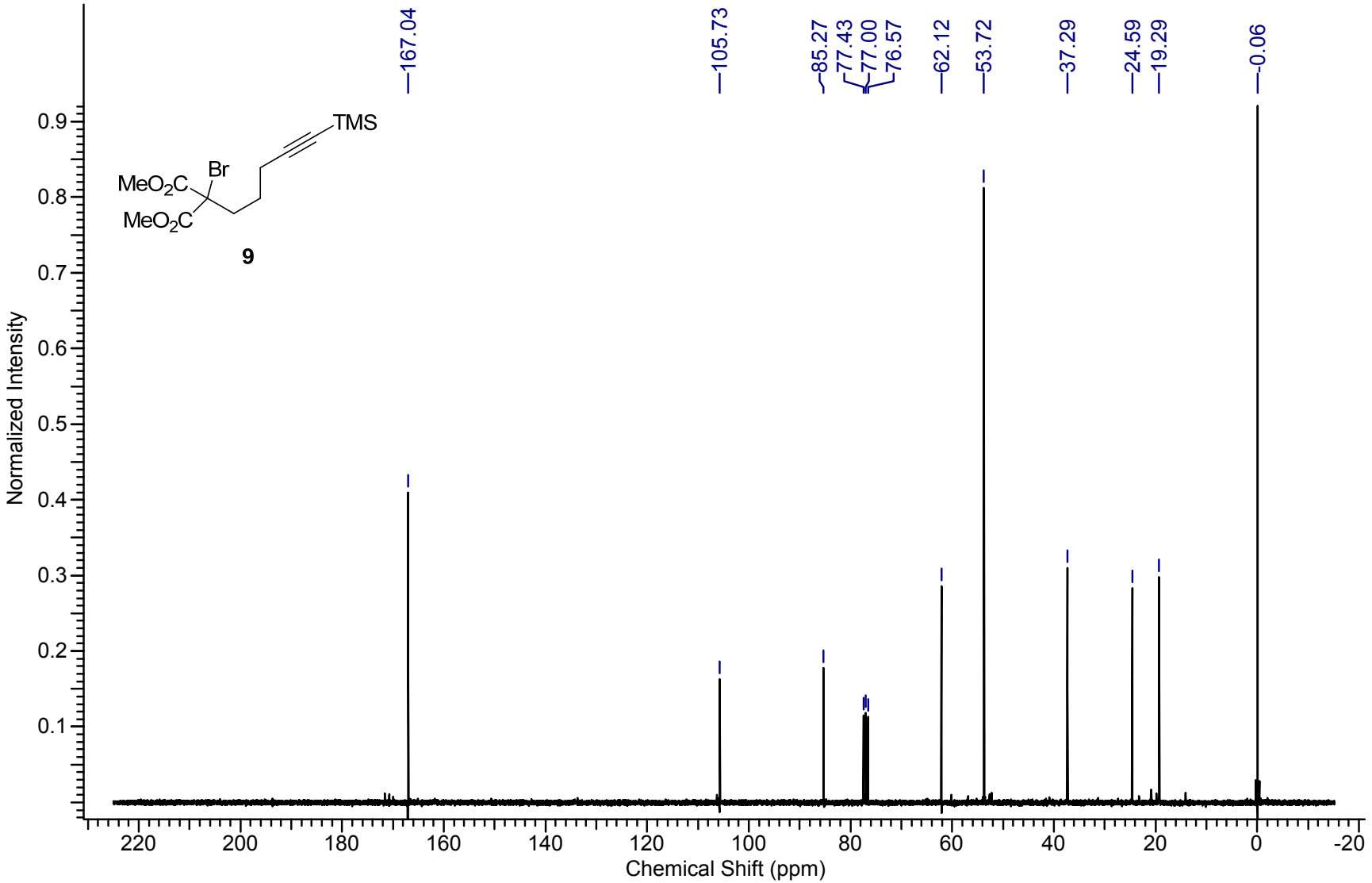

MeO2C
Br
MeO2C
5
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
0.90
1.84
5.69
1.93
2.17
2.19
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

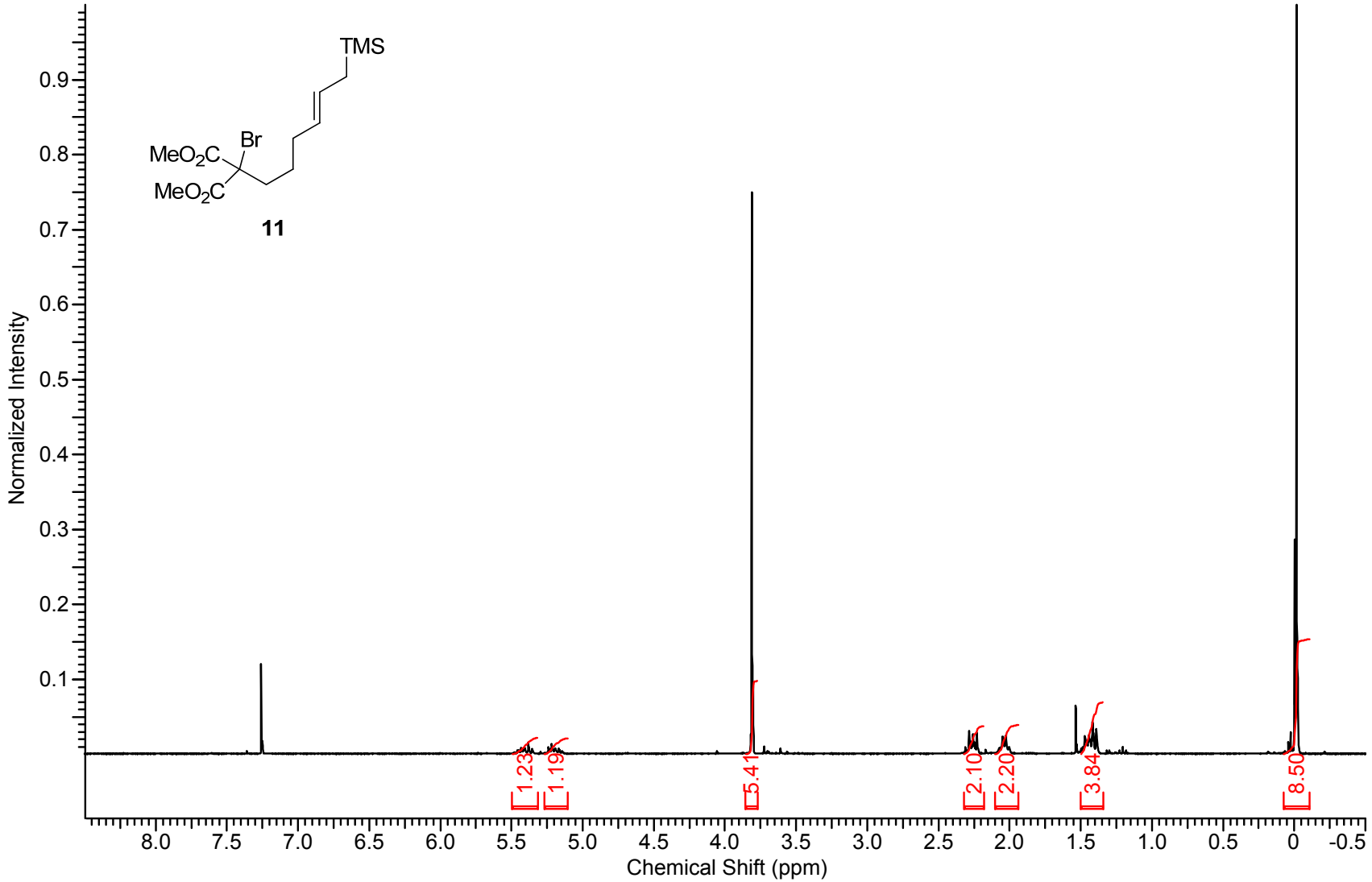

MeO2C
Br
MeO2C
5
166.99
137.20
115.10
77.43
77.00
76.57
62.33
53.52
37.43
32.73
24.22
Normalized Intensity
Chemical Shift (ppm)

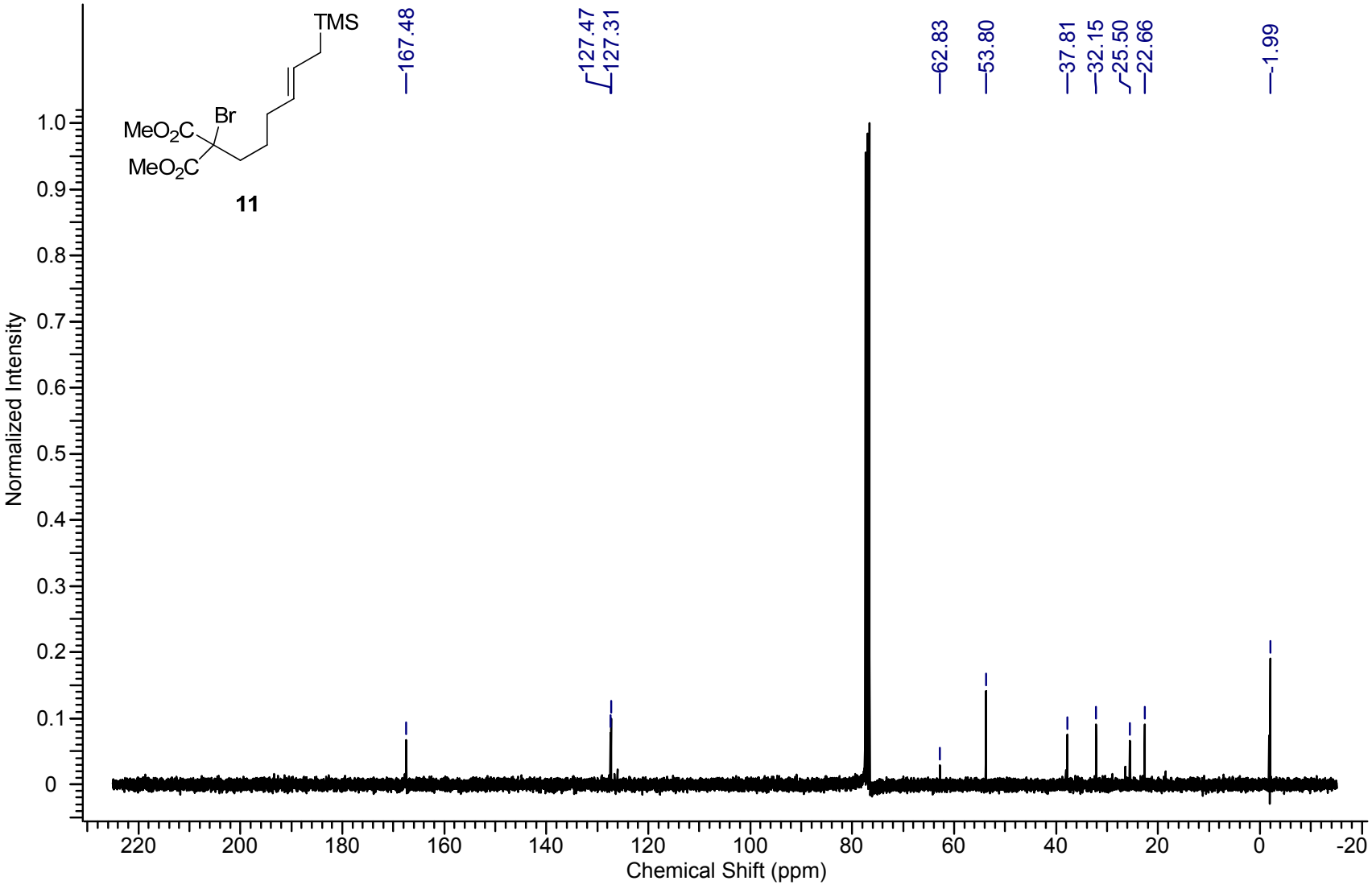

Br
MeO2C
MeO2C
7
Normalized Intensity
Chemical Shift (ppm)
0.91
1.88
5.96
2.14
2.18
4.05

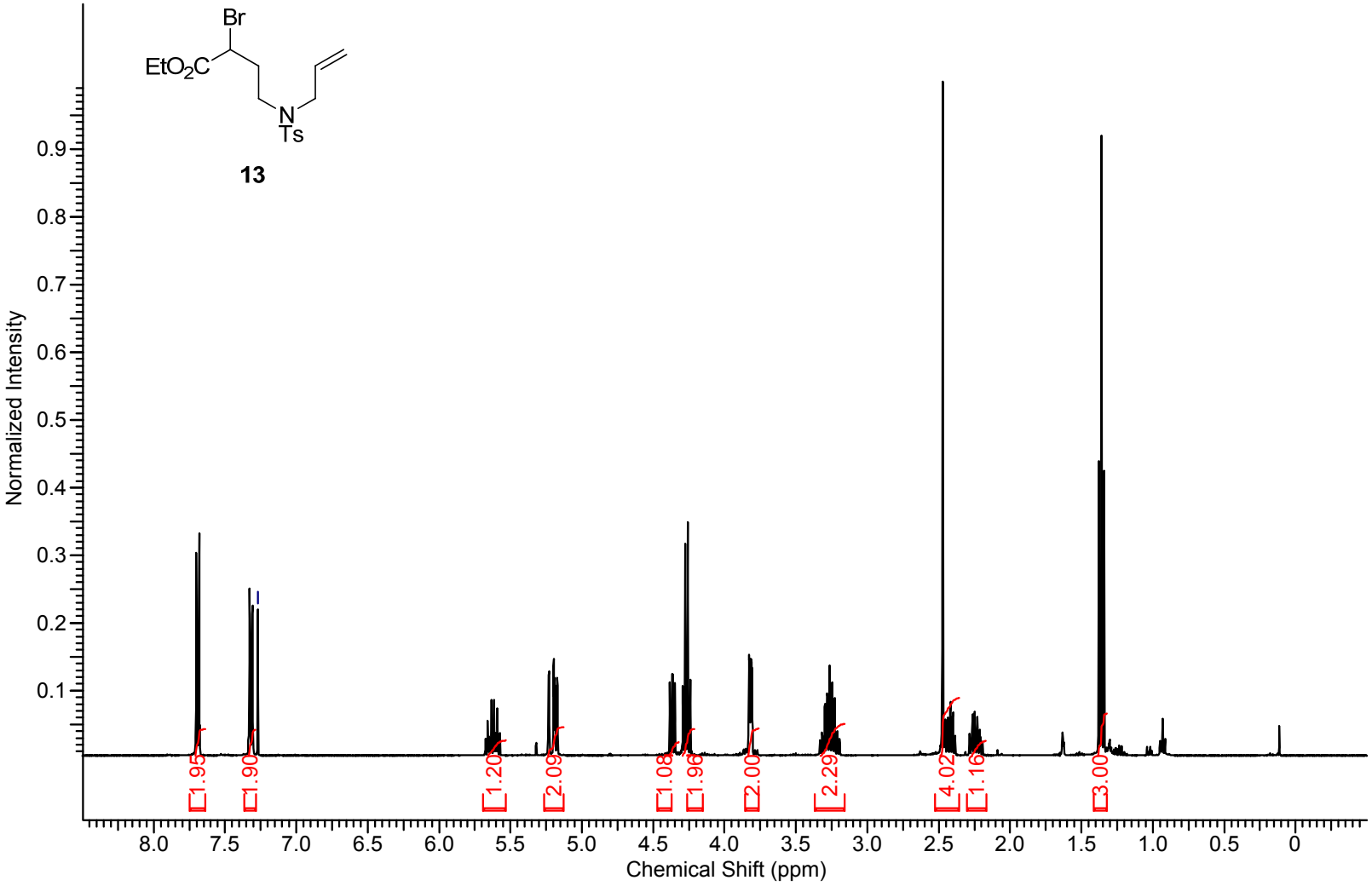

167.33
138.14
114.70
77.43
77.00
76.57
62.64
53.75
38.00
33.18
28.21
24.58
MeO2C
Br
MeO2C
7
Normalized Intensity
Chemical Shift (ppm)

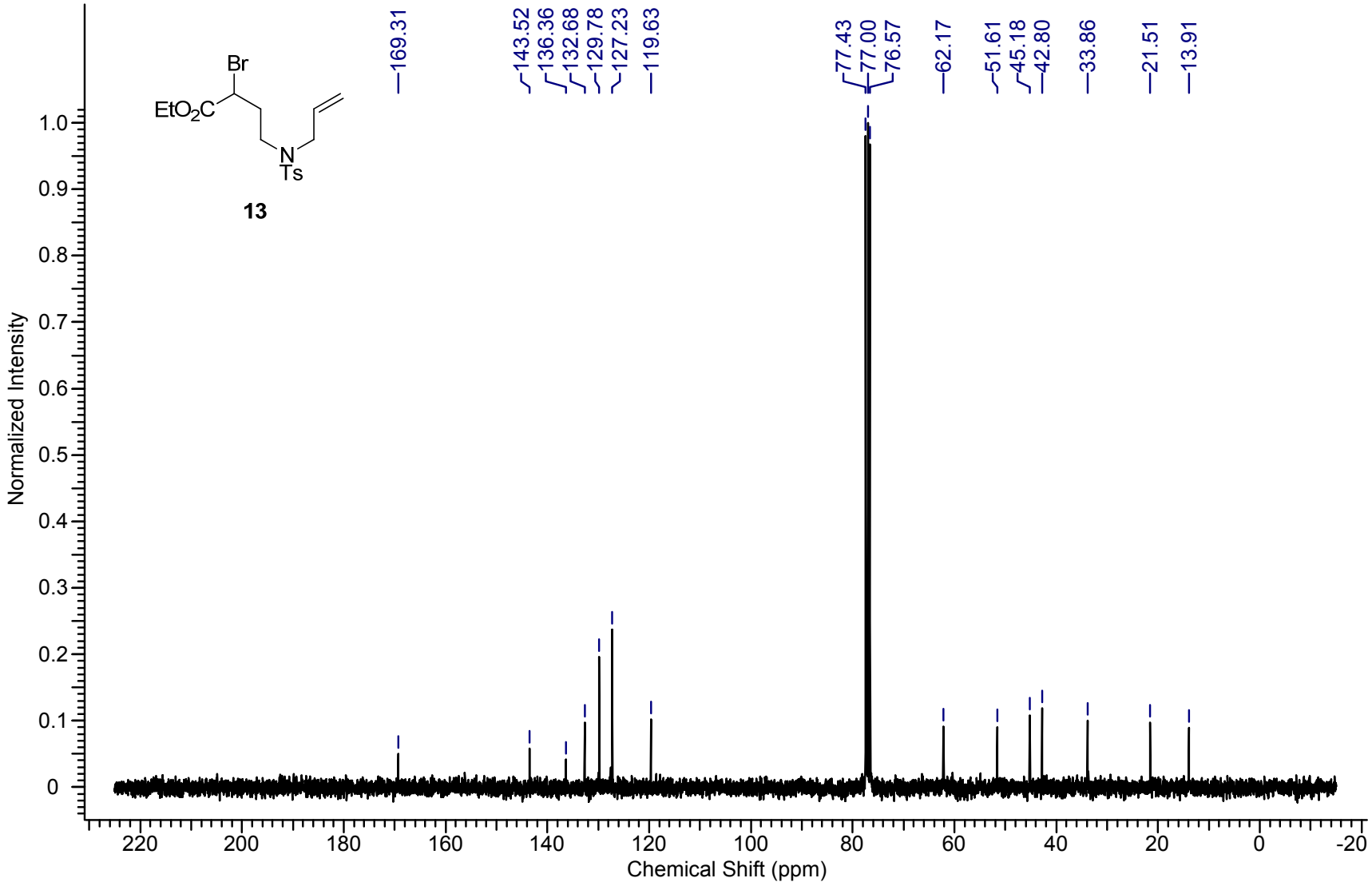

TMS
Br
MeO2C
MeO2C
9
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
6.30
4.38
2.09
8.00
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

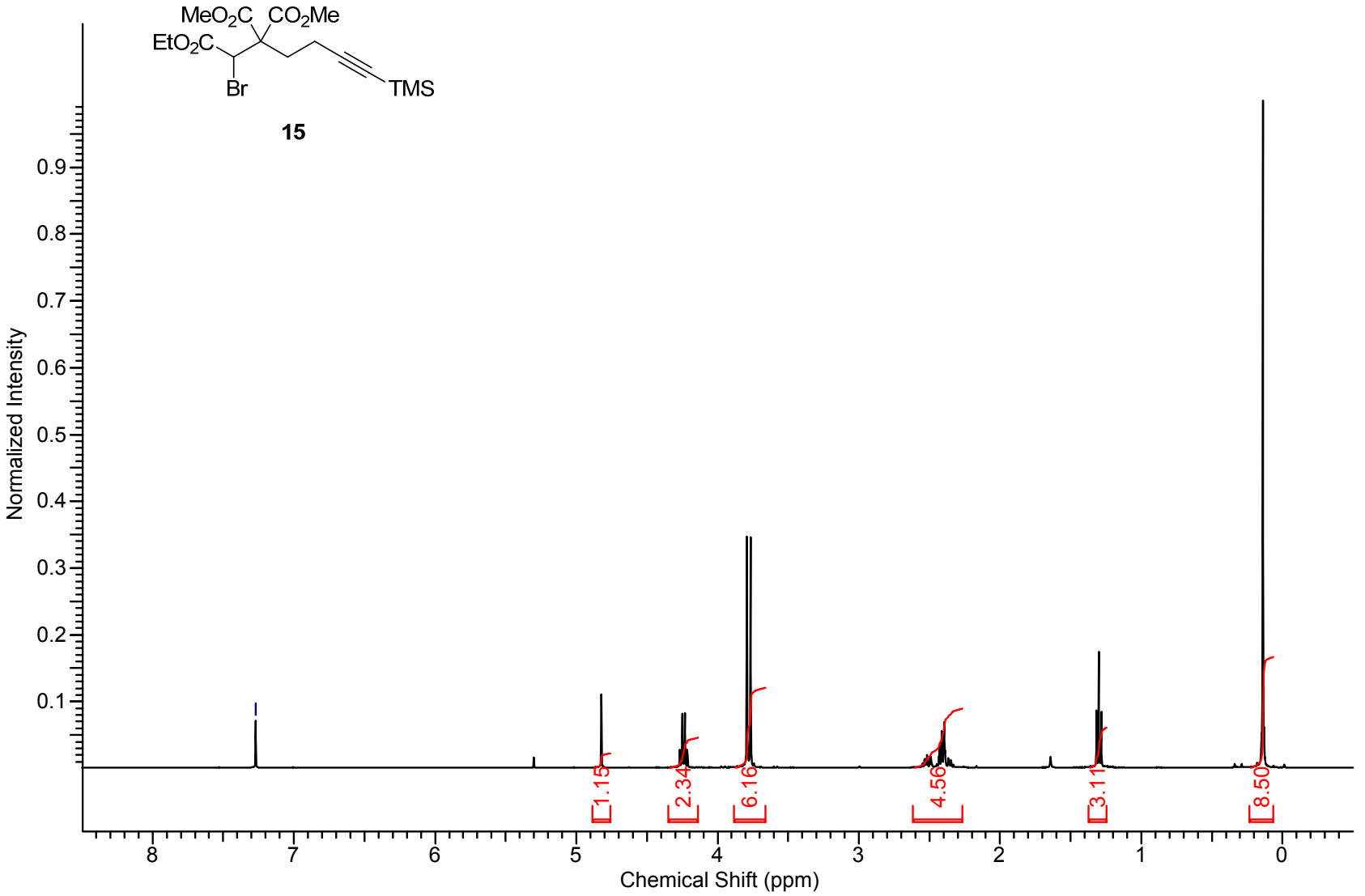

167.04
105.73
85.27
77.43
77.00
76.57
62.12
53.72
37.29
24.59
19.29
0.06
TMS
Br
MeO2C
MeO2C
9
Normalized Intensity
Chemical Shift (ppm)

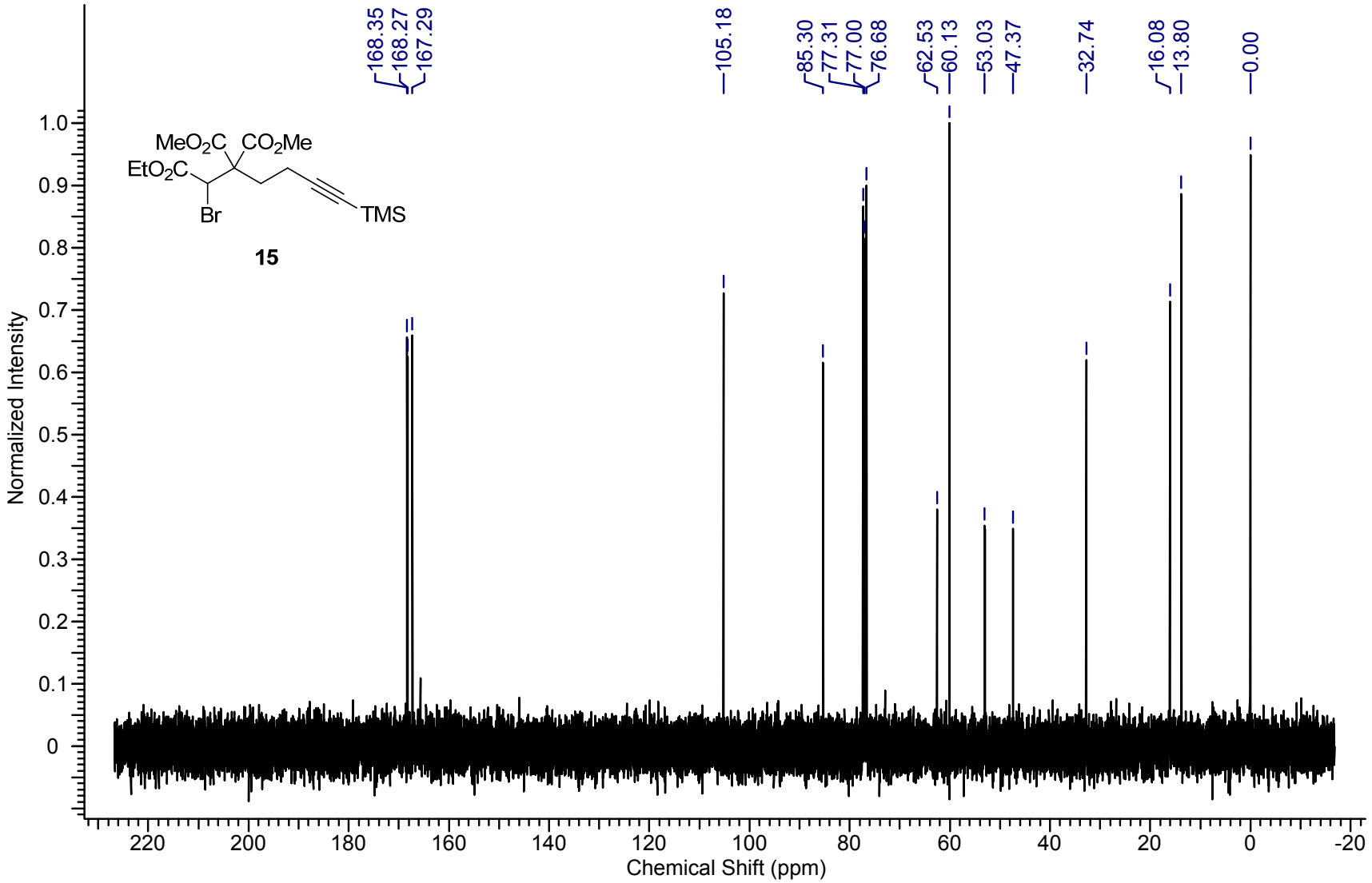

TMS
Br
MeO2C
MeO2C
11
Normalized Intensity
Chemical Shift (ppm)
1.23
1.19
5.41
2.10
2.20
3.84
8.50

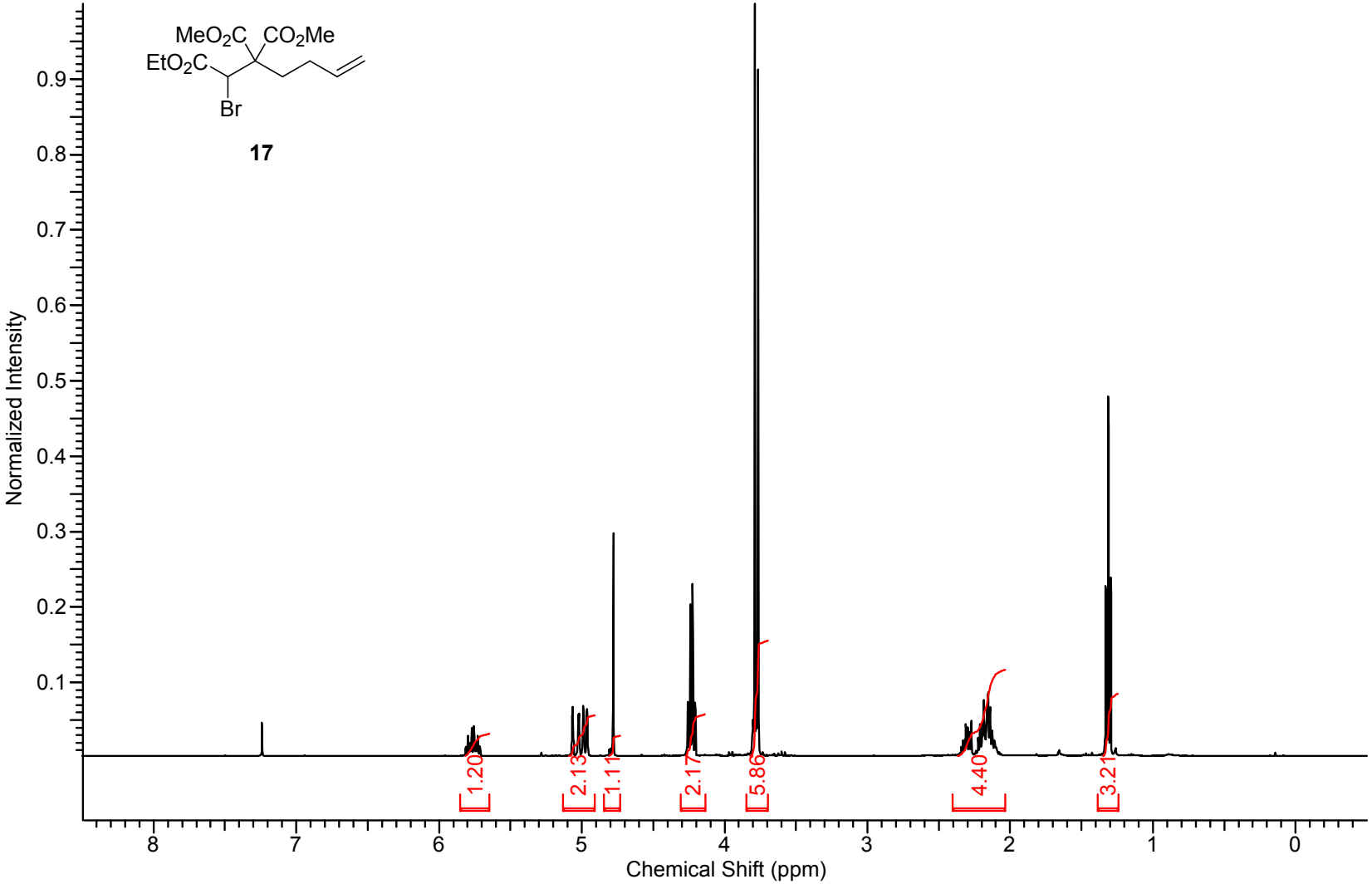

TMS
Br
MeO2C
MeO2C
11
167.48
127.47
127.31
62.83
53.80
37.81
32.15
25.50
22.66
1.99
Normalized Intensity
Chemical Shift (ppm)

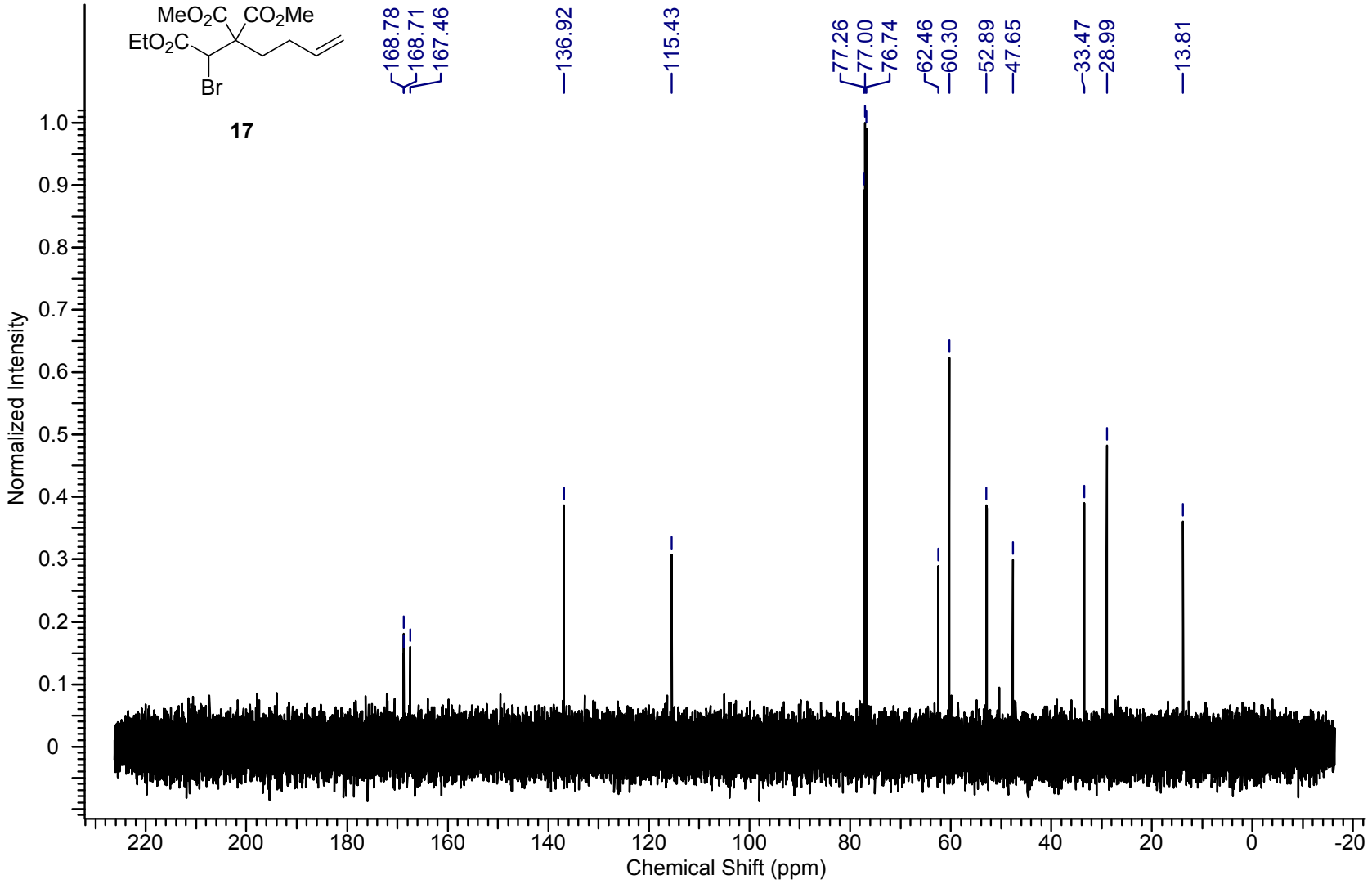

Br
EtO2C
N
Ts
13
Normalized Intensity
Chemical Shift (ppm)
1.95
1.90
1.20
2.09
1.08
1.96
2.00
2.29
4.02
1.16
3.00

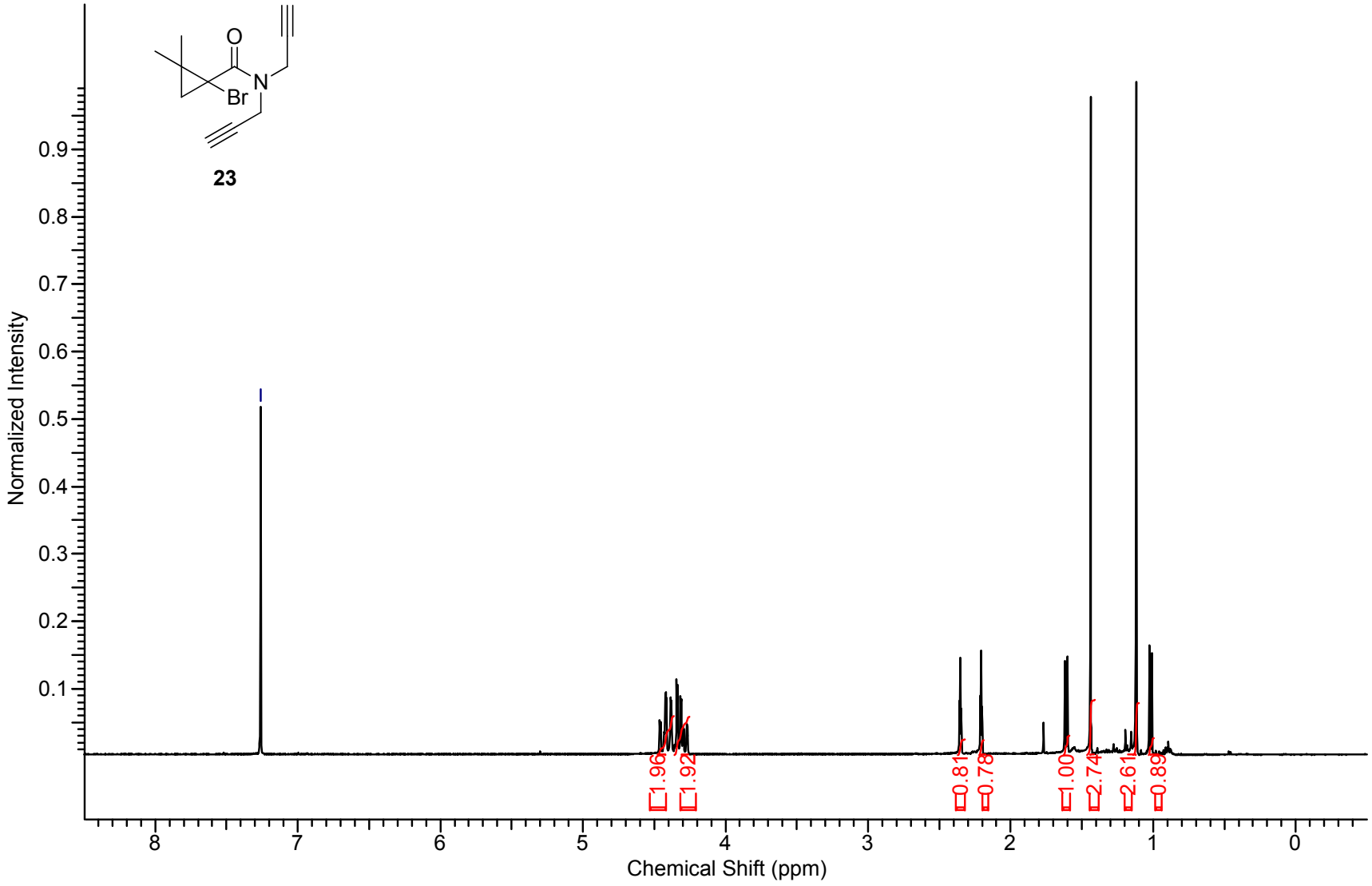

Br
EtO2C
N
Ts
13
169.31
143.52
136.36
132.68
129.78
127.23
119.63
77.43
77.00
76.57
62.17
51.61
45.18
42.80
33.86
21.51
13.91
Normalized Intensity
Chemical Shift (ppm)

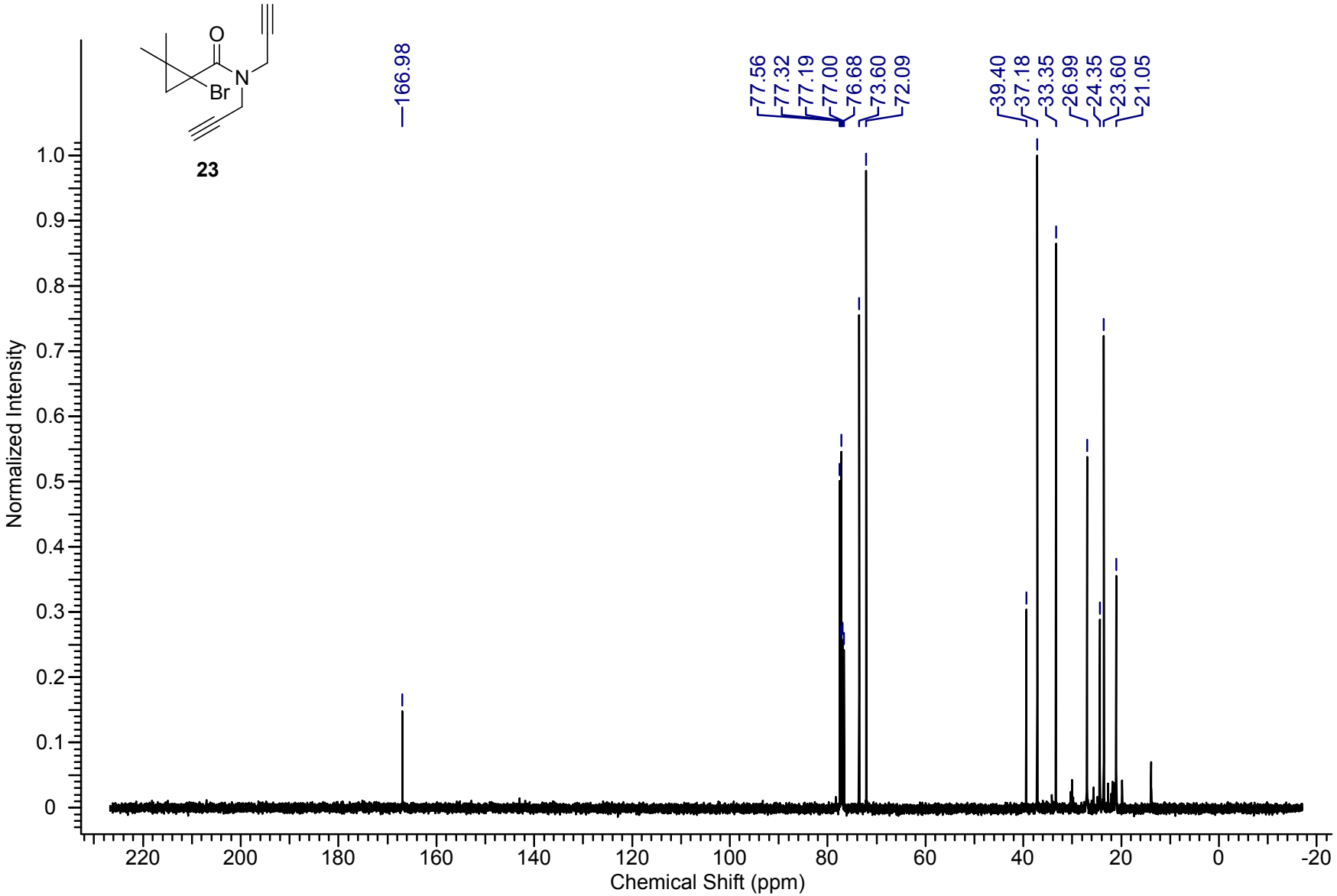

MeO2C CO2Me
EtO2C
Br
TMS
15
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1.15
2.34
6.16
4.56
3.11
8.50
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

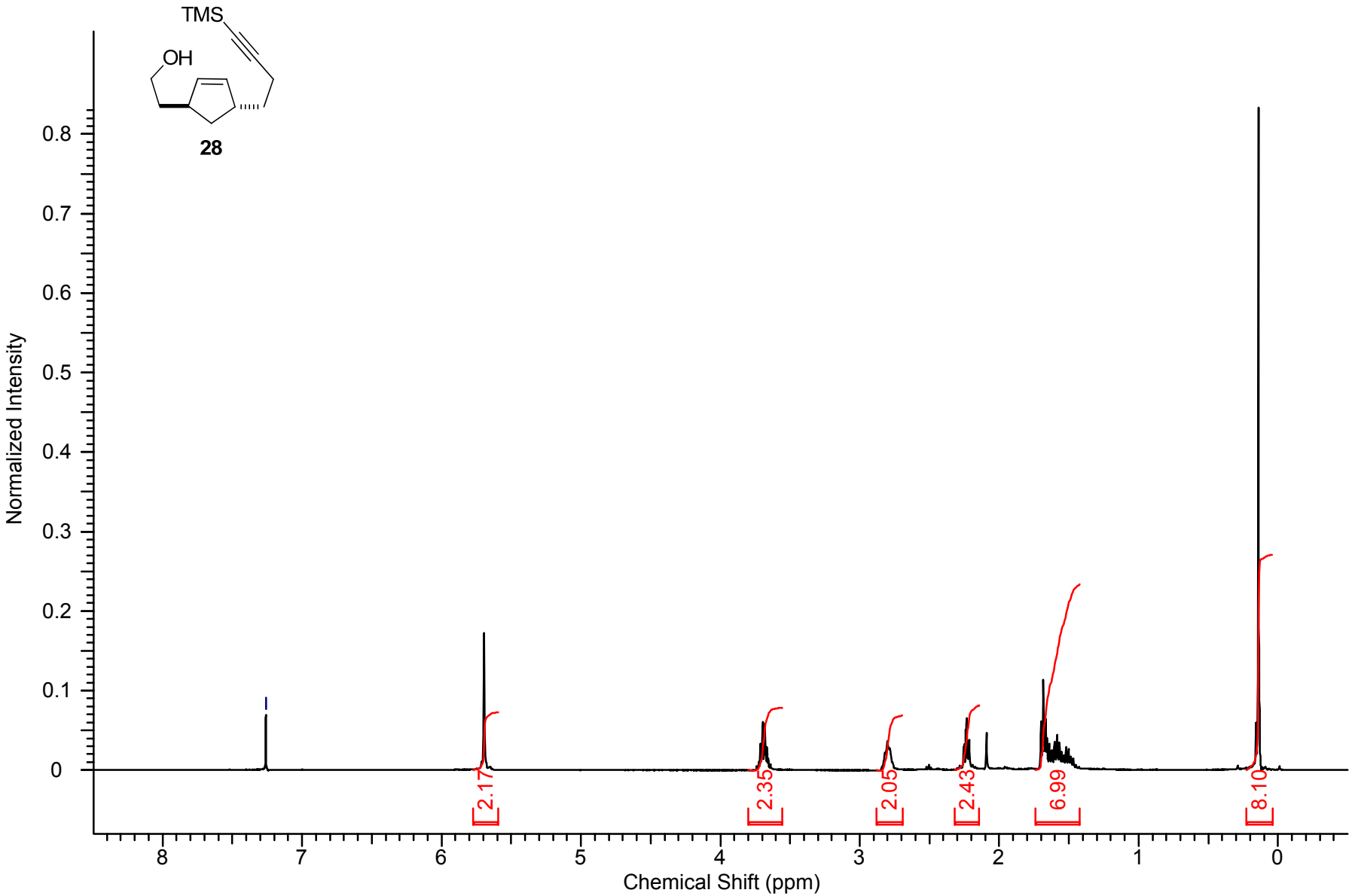

168.35
168.27
167.29
105.18
85.30
77.31
77.00
76.68
62.53
60.13
53.03
47.37
32.74
16.08
13.80
0.00
MeO2C
CO2Me
EtO2C
Br
TMS
15
Normalized Intensity
Chemical Shift (ppm)

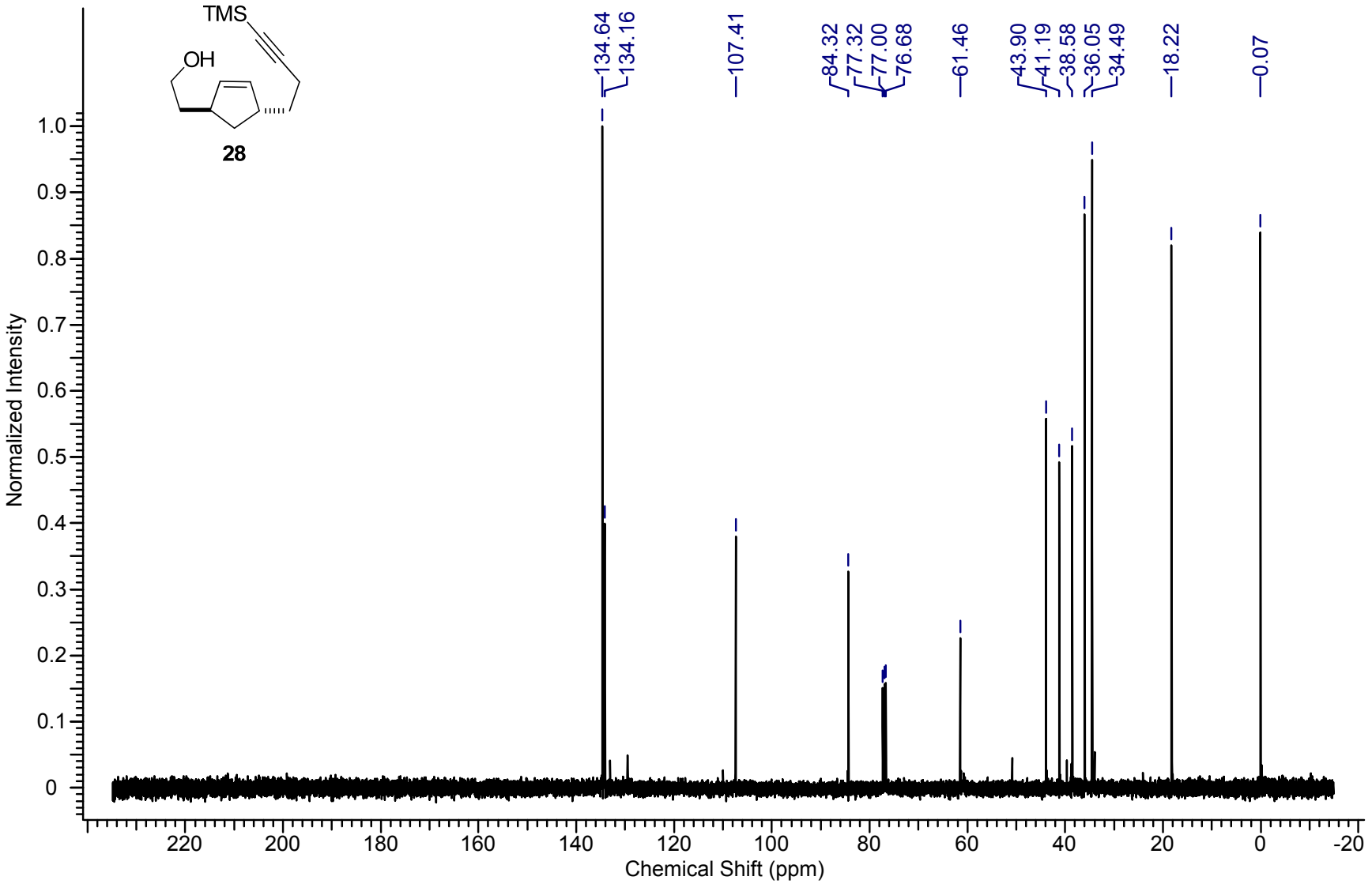

MeO2C CO2Me
EtO2C
Br
17
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1.20
2.13
1.11
2.17
5.86
4.40
3.21
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

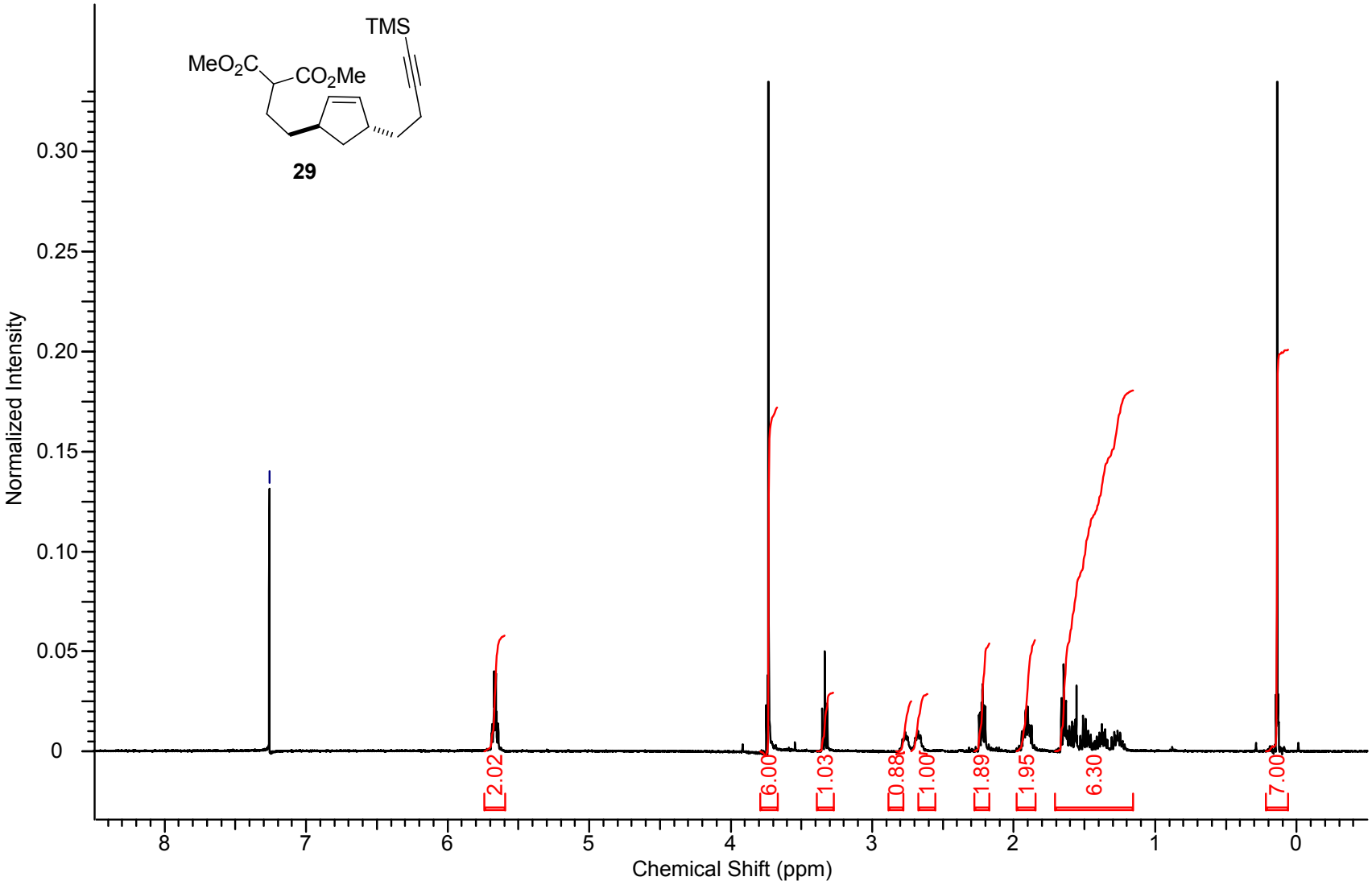

MeO2C CO2Me
EtO2C
Br
17
168.78
168.71
167.46
136.92
115.43
77.26
77.00
76.74
62.46
60.30
52.89
47.65
33.47
28.99
13.81
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

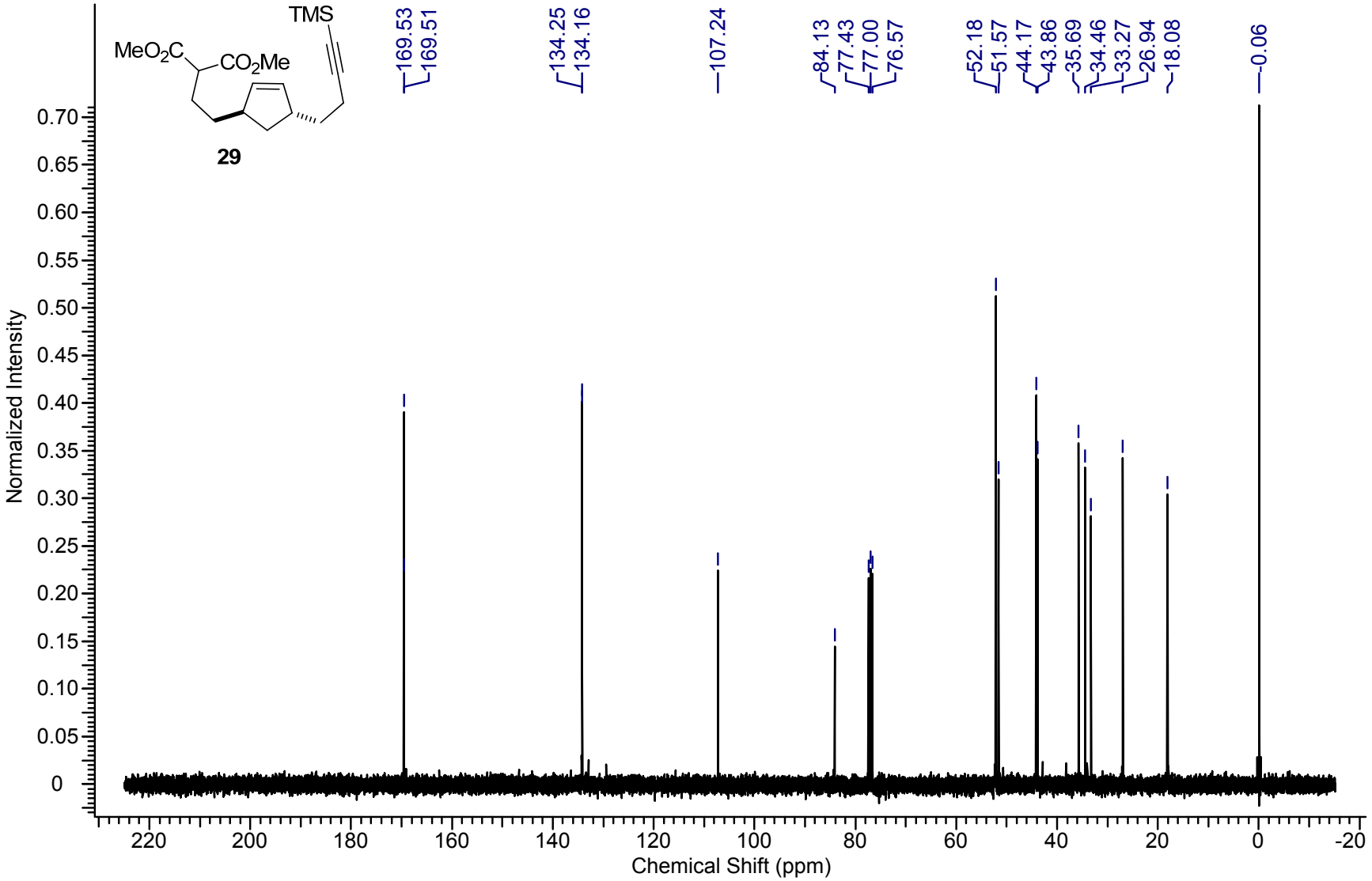

O
N
Br
23
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1.96
1.92
0.81
0.78
1.00
2.74
2.61
0.89
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

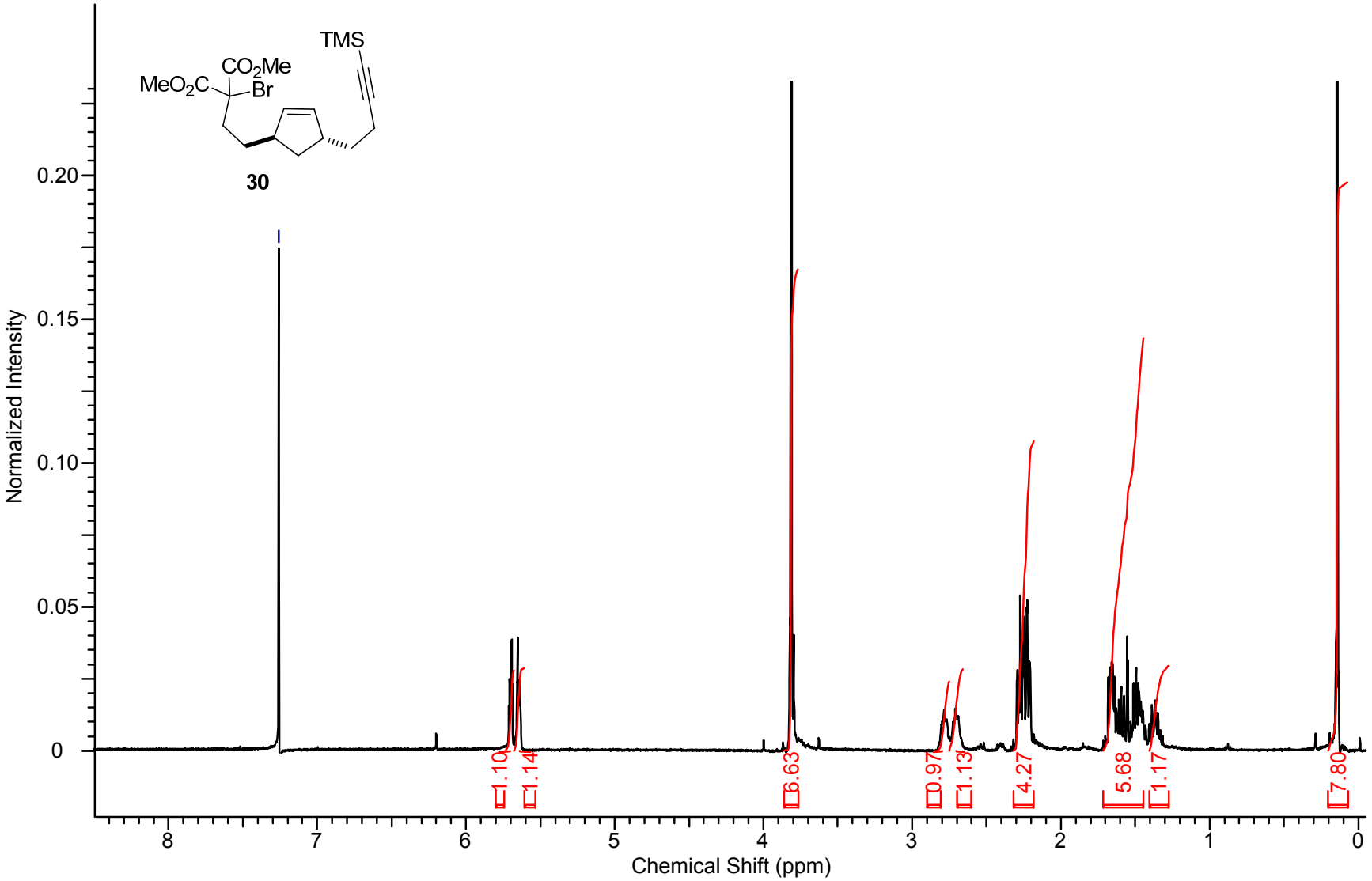

O
N
Br
23
166.98
77.56
77.32
77.19
77.00
76.68
73.60
72.09
39.40
37.18
33.35
26.99
24.35
23.60
21.05
Normalized Intensity
Chemical Shift (ppm)

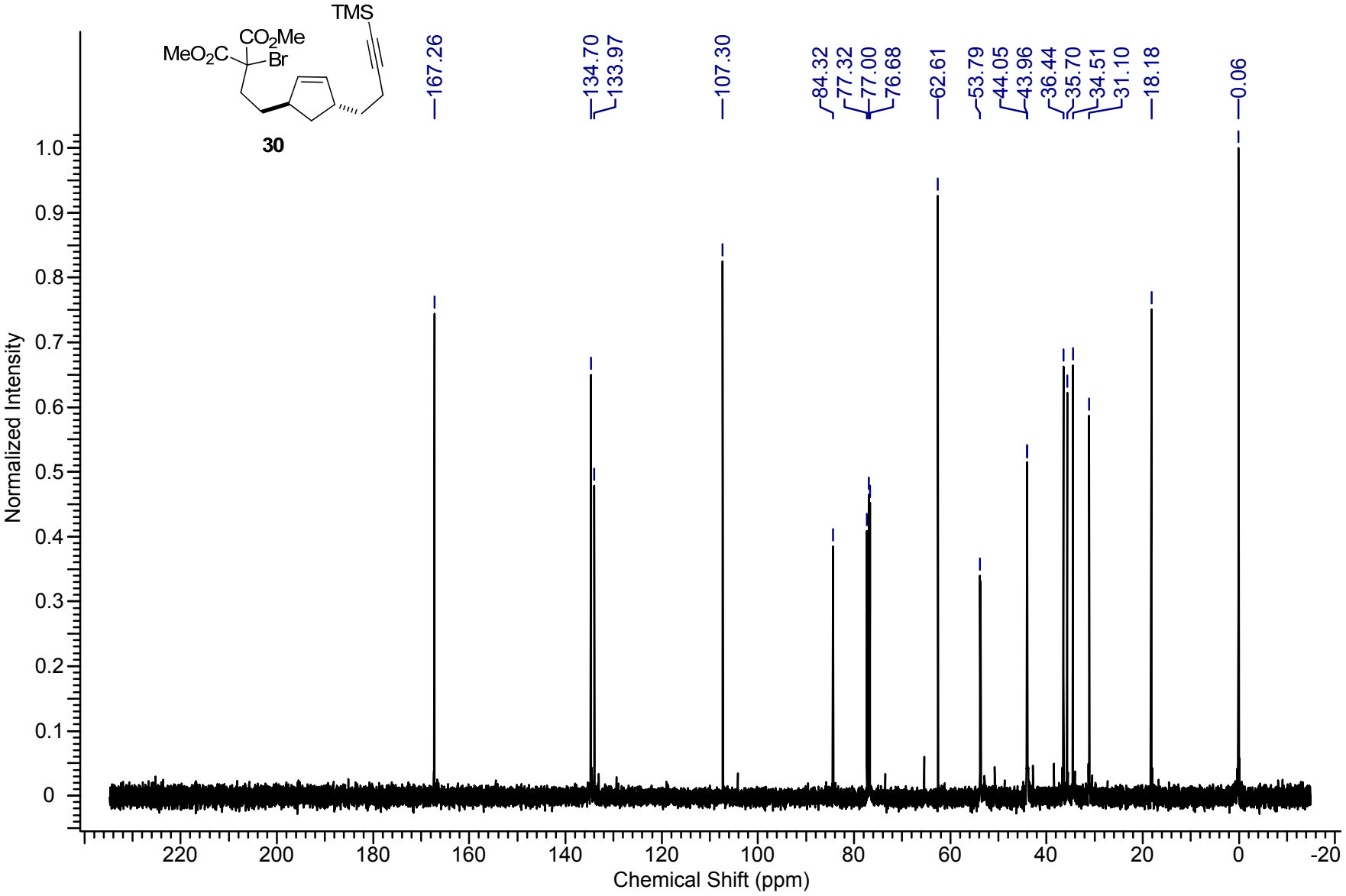

TMS
OH
28
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
2.17
2.35
2.05
2.43
6.99
8.10
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

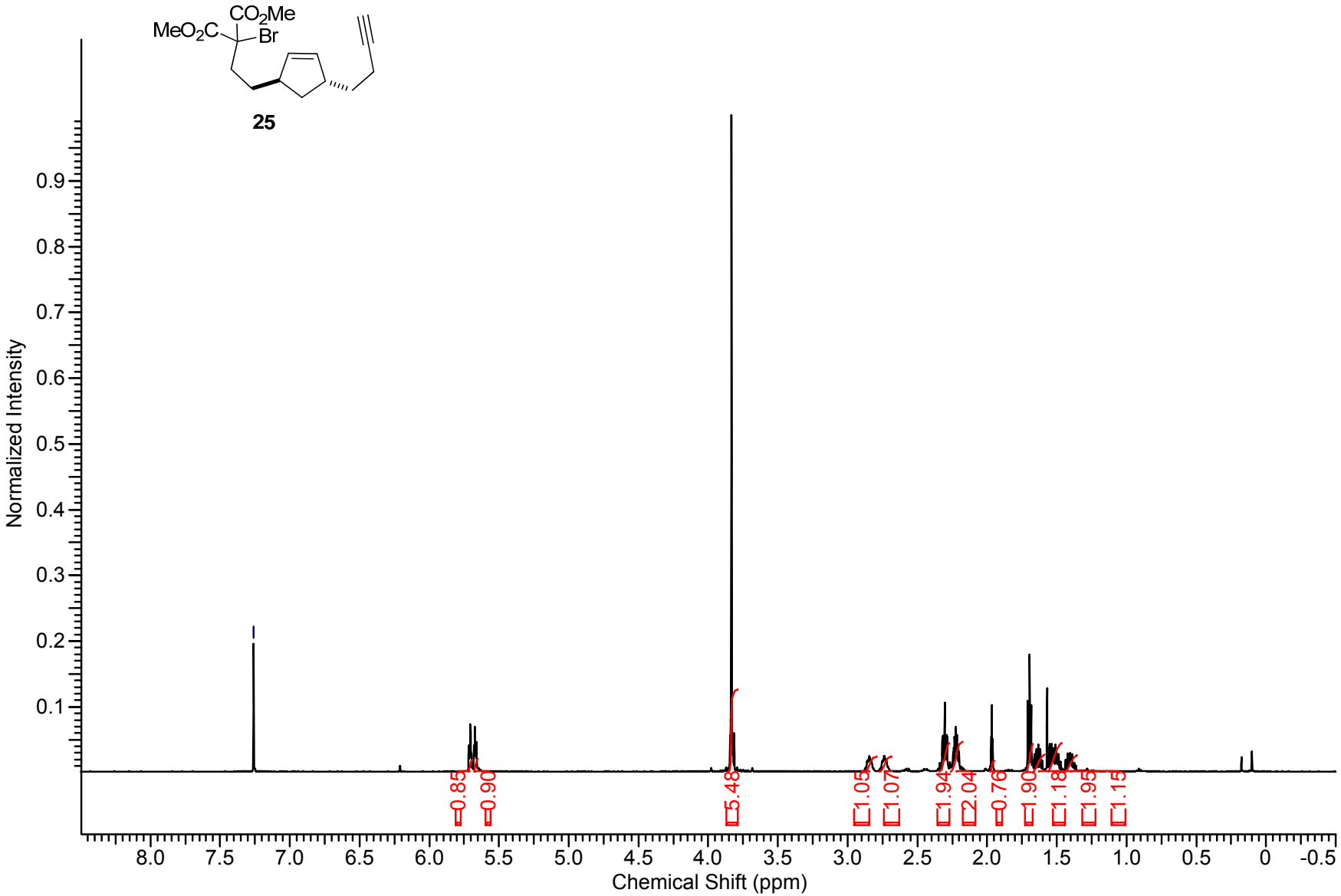

TMS
OH
28
134.64
134.16
107.41
84.32
77.32
77.00
76.68
61.46
43.90
41.19
38.58
36.05
34.49
18.22
0.07
Normalized Intensity
Chemical Shift (ppm)

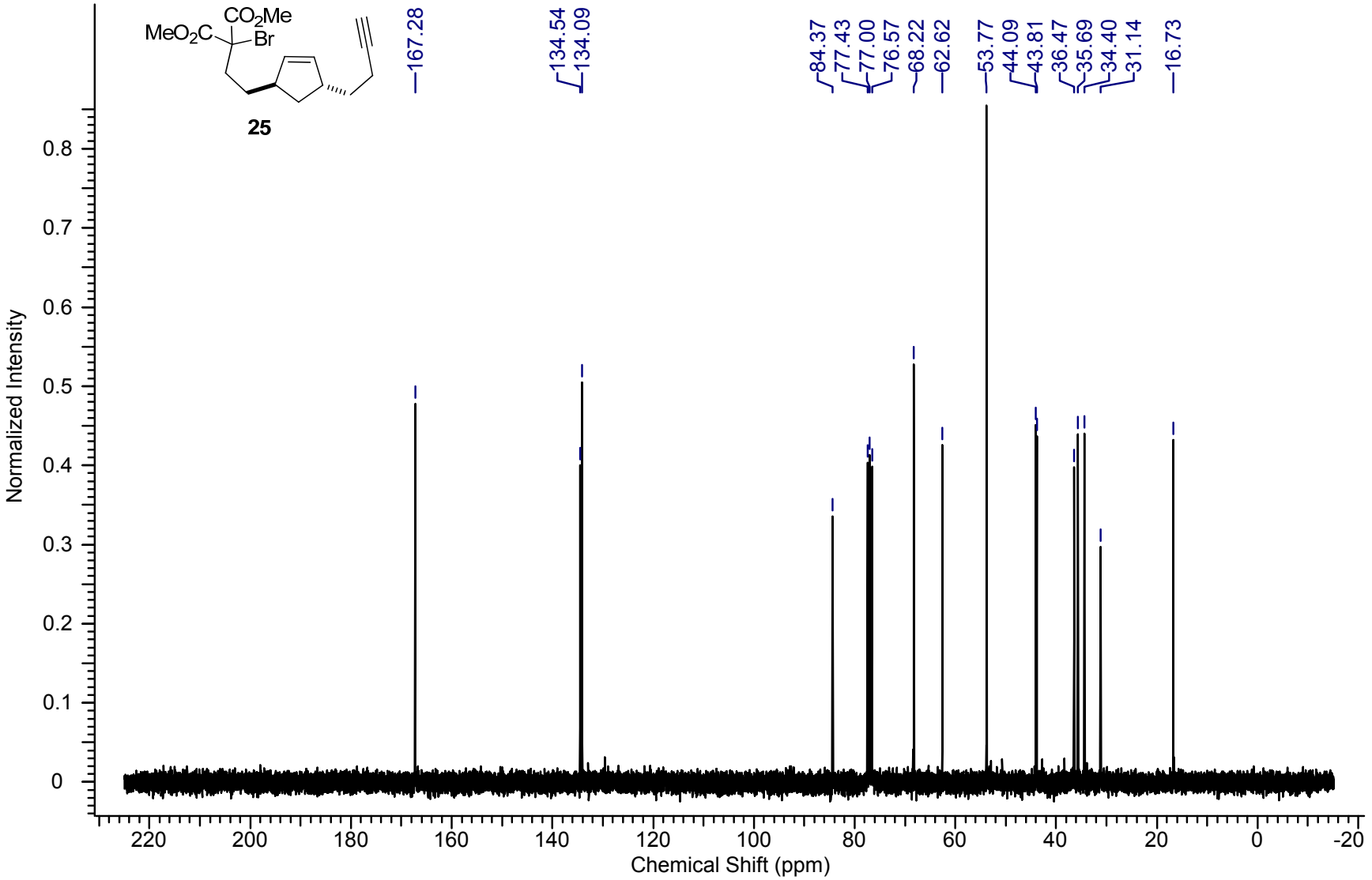

TMS
MeO2C
CO2Me
29
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
2.02
6.00
1.03
0.88
1.00
1.89
1.95
6.30
7.00
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


TMS
MeO2C
CO2Me
29
169.53
169.51
134.25
134.16
107.24
84.13
77.43
77.00
76.57
52.18
51.57
44.17
43.86
35.69
34.46
33.27
26.94
18.08
0.06
Normalized Intensity
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


TMS
CO2Me
MeO2C
Br
30
Normalized Intensity
0.20
0.15
0.10
0.05
0
1.10
1.14
6.63
0.97
1.13
4.27
5.68
1.17
7.80
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


TMS
CO2Me
MeO2C
Br
30
167.26
134.70
133.97
107.30
84.32
77.32
77.00
76.68
62.61
53.79
44.05
43.96
36.44
35.70
34.51
31.10
18.18
0.06
Normalized Intensity
Chemical Shift (ppm)


CO2Me
MeO2C
Br
25
Normalized Intensity
Chemical Shift (ppm)
0.85
0.90
5.48
1.05
1.07
1.94
2.04
0.76
1.90
1.18
1.95
1.15


CO2Me
MeO2C
Br
25
167.28
134.54
134.09
84.37
77.43
77.00
76.57
68.22
62.62
53.77
44.09
43.81
36.47
35.69
34.40
31.14
16.73
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)