Supporting Information For:

Functionalized α,α-Dibromoesters Through Claisen Rearrangements of Dibromoketene Acetals

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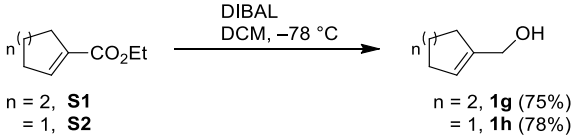
General Information

All reactions were performed under Ar atmospheres with dry solvents and anhydrous conditions, unless otherwise noted. THF, toluene, and benzene were distilled over Na/benzophenone ketyl; CH_2Cl_2 was distilled from CaH_2. Reactions were monitored using thin layer chromatography (TLC) on 0.25-mm SiliCycle silica gel plates (60F-254) and visualized under UV light or through iodine or permanganate staining. Flash column chromatography (FCC) was performed using SiliCycle silica gel 60 (230–400 mesh) and compressed air. IR spectra were recorded using a PerkinElmer pargon 1400 FTIR spectrometer. NMR spectra were recorded using Bruker AV-300, AV-400, and AV-500 instruments, as indicated, and calibrated using residual $CHCl_3$ as the internal reference (7.26 ppm for ^{1}H NMR; 77.00 ppm for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. The following abbreviations are used for the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; qt = quintet; sex = sextet; hep = heptet; oct = octet; m = multiplet; br = broad; app = apparent. An Agilent 6890-5975 GC-MS was used to acquire mass spectra. High-resolution mass spectrometry (HRMS) was performed using a Waters LCT Premier XE time-of-flight instrument controlled by Mass Lynx 4.1 software.

Materials

The allylic alcohols **1a**–**c**, **1f**, and **1o** were purchased from Sigma–Aldrich. Tribromoacetaldehyde (bromal) was purchased from TCI-America. Reagents were used as received from commercial sources.

Preparation of Novel Compounds



The ethyl esters **S2** and **S3** were synthesized using the method described by Chang and coworkers.[1] **S2** (5.1 g, 90%) was isolated as a liquid. The spectral data matched those reported in the literature.[2]

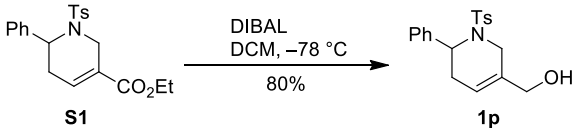
The reductions of **S1** and **S2** were performed as described below.

[1] Kim, J.; Chang, S. *Angew. Chem. Int. Ed*. **2014**, *53*, 2203 –2207
[2] Beagley, B.; Larsen, D. S.; Pritchard, R. G.; Stoodley, R. J.; Whiting, A. *J. Chem. Soc. Perkin Trans. 1* **1989**, 1127–1137.

Cyclohex-1-en-1-ylmethanol (1g) was isolated as a liquid (3.2 g, 75%). Its spectral data matched those reported in the literature.[3]

Cyclopent-1-en-1-ylmethanol (1h) was isolated as a liquid (0.5 g, 78%). Its spectral data matched those reported in the literature.[4]

Synthesis of Allylic Alcohols:

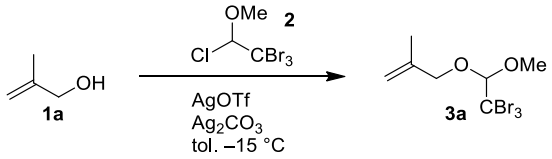


S1 **1p**

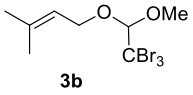
(6-Phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)methanol (1p): The ester **S3**[5] (5.78 g, 10.0 mmol) was dissolved in CH_2Cl_2 (50 ml) and placed in a dry ice/acetone bath. Once cooled, 1.0 M DIBAL in hexane (25.0 mL, 25.0 mmol, 2.5 equiv) was added dropwise and then the mixture was stirred for 2 h. A saturated aqueous solution of sodium/potassium tartrate (25.0 mL) was added and then the mixture was warmed to ambient temperature. EtOAc (100 mL) was added and then the two-phase solution was stirred vigorously overnight. The organic phase was separated and then the aqueous phase was extracted with EtOAc (2 × 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated, and then the residue was chromatographed (SiO_2; EtOAc/hexanes, 40:60; R_f = 0.3) to give the allylic alcohol **1p** as a solid (2.77 g, 80%). M.p.: 102 °C; IR (CH_2Cl_2) ν_{max} 3511, 2961, 1587, 1332, 1151 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.37–7.24 (m, 7H), 5.79 (s, 1H), 5.38–5.33 (m, 1H), 4.22 (d, *J* = 18.1 Hz, 1H), 4.05–3.91 (m, 2H), 3.37 (d, *J* = 18.1 Hz, 1H), 2.52–2.41 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 139.0, 137.5, 134.6, 129.5, 128.4, 127.5, 127.3, 127.1, 120.1, 64.7, 52.8, 41.0, 26.2, 21.5; HRMS (ESI) calcd for $C_{19}H_{22}NO_3S$ $[M + H]^+$ *m*/*z* 344.1320, found 344.1337.

[3] Hanessian, S.; Szychowski, J.; Maianti, J. P. *Org. Lett*. **2009**, *11*, 429–432.
[4] Giuliano M. W.; Maynard, S. J.; Almeida, A. M.; Reidenbach, L. G.; Guo, L.; Ulrich, E. C.; Guzei, I. A.; Gellman, S. H. *J. Org. Chem.* **2013**, *78*, 12351–12361.
[5] Zhu, X-F..; Lan, J.; Kwon, O. *J. Am. Chem. Soc*. **2003**, *125*, 4716–4717

Mixed Acetal Formation:

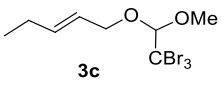


2-Methyl-3-(2,2,2-tribromo-1-methoxyethoxy)prop-1-ene (3a): The alcohol **1a** (1.0 mmol), AgOTf (330 mg, 1.3 mmol), and Ag_2CO_3 (550 mg, 2.0 mmol) were placed in a round-bottom flask, covered in aluminum foil, containing a magnetic stirrer bar. Toluene (5 mL) was added and the mixture was cooled in an ice/salt bath. The ether **2** (500 mg, 1.5 mmol) was added slowly to the vigorously stirred solution and then stirring was continued for 1 h. Saturated $Na_2S_2O_3$ was added (0.3 mL) and then the mixture was removed from the cooling bath and stirred for 30 min. The suspension was filtered through a silica plug and washed with EtOAc (25 mL). The solvent was evaporated and the residue chromatographed (SiO_2; EtOAc/hexanes, 5:95; R_f = 0.5) to give **3a** as an oil (261 mg, 71%). IR (CH_2Cl_2) ν_{max} 1652, 1480, 1117, 1091 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.01 (s, 1H), 5.00 (s, 1H), 4.52 (s, 1H), 4.29 (s, 1H), 3.74 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 114.1, 107.7, 74.3, 59.3, 46.5, 19.7; GCMS (EI+) calcd for $C_6H_8Br_3O$ $[M - CH_3O]^+$ *m*/*z* 332.8, found 332.8.



3b

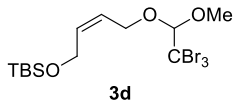
3-Methyl-1-(2,2,2-tribromo-1-methoxyethoxy)but-2-ene (3b): The alcohol **1b** was subjected to the conditions described above to yield the mixed acetal **3b** (4.72 g, 62%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 5:95; R_f = 0.45). IR (CH_2Cl_2) ν_{max} 2366, 1452, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.52–5.47 (m, 1H), 4.56 (s, 1H), 4.48 (d, *J* = 6.9 Hz, 2H), 3.74 (s, 3H), 1.83 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 119.6, 107.5, 67.7, 58.5, 46.9, 25.9, 18.3; GCMS (EI+) calcd for $[C_8H_{14}Br_3O_2]^+$ *m*/*z* 377.8, found 377.8.



3c

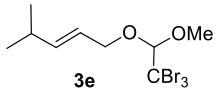
(*E*)-1-(2,2,2-Tribromo-1-methoxyethoxy)pent-2-ene (3c): The alcohol **1c** was subjected to the conditions described above to yield the mixed acetal **3c** (316 mg, 83%) as an oil after chromatography

(SiO_2; EtOAc/hexanes, 5:95; R_f = 0.5). IR (CH_2Cl_2) ν_{max} 2832, 2954, 1670, 1109 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.89–5.82 (m, 1H), 5.68–5.60 (m, 1H), 4.53 (s, 1H), 4.37 (dd, *J* = 6.4, 1.0 Hz, 2H), 3.69 (s, 3H), 2.15–2.07 (m, 2H), 1.02 (t, *J* = 7.46 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 123.8, 107.4, 72.1, 58.6, 46.8, 25.3, 13.2; GCMS (EI+) calcd for $[C_8H_{13}Br_3O_2]^+$ *m*/*z* 377.8, found 377.8.



3d

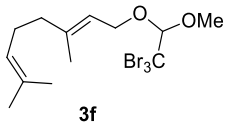
(*Z*)-10,10,11,11-Tetramethyl-3-(tribromomethyl)-2,4,9-trioxa-10-siladodec-6-ene (3d): The alcohol **1d**[6] was subjected to the conditions described above to yield the mixed acetal **3d** (447 mg, 90%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.2). IR (CH_2Cl_2) ν_{max} 2935, 2889, 1453, 1067 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.82–5.75 (m, 2H), 4.58–4.55 (m, 3H), 4.34–4.31 (m, 2H), 3.76 (s, 3H), 0.94 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.6, 125.4, 107.9, 66.8, 59.6, 58.8, 46.4, 25.9, 18.3, –5.16, –5.17; GCMS (EI+) calcd for $[C_{13}H_{25}Br_3O_3Si]^+$ *m*/*z* 497.9, found 480.0



3e

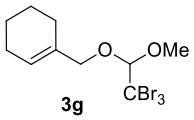
(*E*)-4-Methyl-1-(2,2,2-tribromo-1-methoxyethoxy)pent-2-ene (3e): The alcohol **1e**[7] was subjected to the conditions described above to yield the mixed acetal **3e** (225 mg, 62%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 5:95; R_f = 0.55). IR (CH_2Cl_2) ν_{max} 2960, 2927, 1455, 1137 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.77 (dd, *J* = 15.5, 6.4 Hz, 1H), 5.63–5.57 (m, 1H), 4.52 (s, 1H), 4.37 (d, *J* = 6.3 Hz, 2H), 3.69 (s, 3H), 2.35 (oct, *J* = 6.8 Hz, 1H), 1.02 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 121.9, 107.4, 72.3, 58.5, 46.8, 30.2, 22.1, 22.0; GCMS (EI+) calcd for $C_9H_{15}Br_2O_2$ [M – Br]$^+$ *m*/*z* 314.9, found 314.9.

[6] Marshall, J.A.; Garofalo, A. W. *J. Org. Chem.***1996**, *61*, 8732–8738.
[7] Ghosh, A. K.; Lee, H. Y.; Thompson, W. J.; Culberson, C.; Holloway, M. K.; Mckee, S. P.; Munson, P. M.; Duong, T. T.; Smith, A. M.; Darke, P. L.; Zugay, J. A.; Emini, E. A.; Schleif, W.A.; Huff, J. R.; Anderson, P. S. *J. Med. Chem.* **1994**, *37*, 1177–1188.



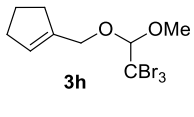
3f

(*E*)-3,7-Dimethyl-1-(2,2,2-tribromo-1-methoxyethoxy)octa-2,6-diene (3f): The alcohol **1f** was subjected to the conditions described above to yield the mixed acetal **3f** (341 mg, 76%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 5:95; R_f = 0.6). IR (CH_2Cl_2) ν_{max} 2972, 2733, 1671, 1436, 1407 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.49 (dt, *J* = 7.0, 1.2 Hz, 1H), 5.15–5.10 (m, 1H), 4.57 (s, 1H), 4.50 (d, *J* = 6.9 Hz, 2H), 3.75 (s, 1H), 2.20–2.11 (m, 4H), 1.76 (s, 3H), 1.72 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 131.9, 123.7, 119.4, 107.4, 67.5, 58.6, 47.0,39.6, 26.2, 25.7, 17.7, 16.7; GCMS (EI+) calcd for $C_{12}H_{21}Br_2O_2$ $[M - Br]^+$ *m*/*z* 354.9, found 354.9.



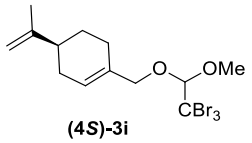
3g

1-[(2,2,2-Tribromo-1-methoxyethoxy)methyl]cyclohex-1-ene (3g): The alcohol **1g** was subjected to the conditions described above to yield the mixed acetal **3g** (3.09 g, 76%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.5). IR (CH_2Cl_2) ν_{max} 2887, 2834, 1454, 1260 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.80 (s, 1H), 4.50 (s, 1H), 4.24 (app s, 2H), 3.73 (s, 1H), 2.13–2.07 (m, 4H), 1.67–1.59 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.8, 127.2, 107.3, 75.5, 59.2, 46.9, 26.1, 25.1, 22.4, 22.2; GCMS (EI+) calcd for $C_{10}H_{15}Br_2O_2$ $[M - Br]^+$ *m*/*z* 326.9, found 327.0.



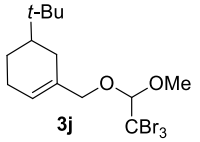
3h

1-[(2,2,2-Tribromo-1-methoxyethoxy)methyl]cyclopent-1-ene (3h): The alcohol **1h** was subjected to the conditions described above to yield the mixed acetal **3h** (255 mg, 65%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.48). IR (CH_2Cl_2) ν_{max} 2919, 2843, 1457, 1099 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.78–5.76 (m, 1H), 4.52 (s, 1H), 4.44 (s, 2H), 3.73 (s, 3H), 2.41–2.36 (m, 4H), (qt, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 129.8, 107.5, 69.3, 59.1, 46.7, 33.1, 32.4, 23.4; GCMS (EI+) calcd for $[C_9H_{13}Br_3O_2]^+$ *m*/*z* 391.8, found 391.8.



(4*S*)-3i

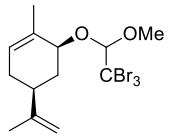
(4*S*)-4-(Prop-1-en-2-yl)-1-[(2,2,2-tribromo-1-methoxyethoxy)methyl]cyclohex-1-ene (3i): The alcohol **1i**[8] was subjected to the conditions described above to yield the mixed acetal **3i** (434 mg, 91%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 5:95; R_f = 0.5). The acetal **3i** was isolated as a 1:1 mixture of inseparable diastereoisomers. NMR spectroscopic data is provided for both isomers. IR (CH_2Cl_2) ν_{max} 2962, 2883, 1641, 1451, 1088 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.84–5.79 (m, 1+1H), 4.78–7.73 (m, 2+2H), 4.52–4.50 (s, 1+1H), 4.31–4.22 (m, 2+2H), 3.75 (s, 3H), 3.73 (s, 3H), 2.30–2.14 (m, 4+4H), 2.08–1.99 (m, 1+1H), 1.91–1.84 (m, 1+1H), 1.75 (s, 3+3H), 1.53–1.42 (m, 1+1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 149.5, 133.5, 133.4, 126.7, 126.5, 108.84, 108.82, 107.5, 107.2, 75.2, 74.6, 59.3, 59.1, 46.8, 46.7, 40.9, 40.8, 30.6, 30.5, 27.4, 27.3, 26.6, 26.5, 20.8, 20.7; GCMS (EI+) calcd for $[C_{13}H_{19}Br_3O_2]^+$ *m*/*z* 445.9, found 445.9.



3j

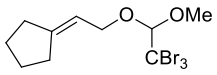
5-(*tert*-Butyl)-1-[(2,2,2-tribromo-1-methoxyethoxy)methyl]cyclohex-1-ene (3i): The alcohol **1j**[9] was subjected to the conditions described above to yield the mixed acetal **3j** (301 mg, 65%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.5). The acetal **3j** was isolated as a 1:1 mixture of inseparable diastereoisomers. NMR spectroscopic data is provided for both isomers. IR (CH_2Cl_2) ν_{max} 2947, 2857, 1529, 1066 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.82–5.76 (app br s, 1+1H), 4.51 (s, 1H), 4.49 (s, 1H), 4.33–4.18 (m, 2+2H), 3.76 (s, 3H), 3.72 (s, 3H), 2.33–2.00 (m, 3+3H), 1.97–1.77 (2+2H), 1.38–1.26 (m, 1+1H), 1.20–1.05 (m, 1+1H), 0.88 (s, 9H), 0.87 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.0, 133.9, 127.4, 127.1, 107.2, 106.9, 75.5, 74.7, 59.5, 59.1, 46.9, 46.8, 44.1, 44.0, 32.3, 27.9, 27.7, 27.3, 27.2, 26.5, 26.4, 23.6, 23.5; GCMS (EI+) calcd for $[C_{14}H_{25}Br_3O_2]^+$ *m*/*z* 461.9, found 461.9.

[8] Hui, Z.; Zhang, M.; Cong, L.; Xia, M.; Dong, J. *Molecules* **2014**, *19*, 6671–6682.
[9] Paquette, L. A.; Maynard, G. D. *J. Am. Chem. Soc.* **1992**, *114*, 5018–5027.



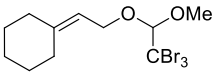
(4*S*, 6*S*)-3k

(4*S*,6*S*)-1-Methyl-4-(prop-1-en-2-yl)-6-(2,2,2-tribromo-1-methoxyethoxy)cyclohex-1-ene (3k): The alcohol **1j**[10] was subjected to the conditions described above to yield the mixed acetal **3k** (393 mg, 88%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.6). The acetal **3k** was isolated as a 1:1 mixture of inseparable diastereoisomers. NMR spectroscopic data is provided for both isomers. IR (CH_2Cl_2) ν_{max} 2361, 2336, 1444, 1314, 1092 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.65–5.57 (app br s, 1+1H), 4.82–4.77 (m, 2+2H), 4.75 (s, 1H), 4.69 (s, 1H), 4.59–4.40 (m, 1+1H), 3.90 (s, 3H), 3.80 (s, 3H), 2.37–2.67 (m, 2+2H), 2.17–2.00 (m, 2+2H), 1.92–1.90 (m, 3H), 1.87–1.86 (m, 3H), 1.79 (s, 3+3H), 1.75–1.68 (m, 1+1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 148.6, 134.4, 134.3, 125.4, 125.2, 109.4, 107.7, 106.2, 80.3, 76.4, 60.8, 58.6, 47.9, 47.3, 40.6, 40.5, 35.9, 33.5, 30.8, 20.4, 20.1, 19.5; GCMS (EI+) calcd for $C_{13}H_{19}Br_2O_2$ $[M - Br]^+$ *m*/*z* 366.9, found 366.9.



3l

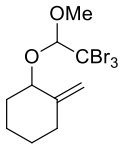
[2-(2,2,2-Tribromo-1-methoxyethoxy)ethylidene]cyclopentane (3l): The alcohol **1l**[11] was subjected to the conditions described above to yield the mixed acetal **3l** (289 mg, 71%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 5:95; R_f = 0.5). IR (CH_2Cl_2) ν_{max} 2955, 2866, 1508, 1128 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.39 (tt, *J* = 7.2, 1.0 Hz, 1H), 4.58 (s, 1H), 4.45 (d, *J* = 7.2 Hz, 2H), 3.69 (s, 3H), 2.23–2.15 (m, 4H), 1.59–1.53 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 115.1, 107.6, 69.5, 58.4, 47.0, 33.8, 29.1, 26.3, 26.0; GCMS (EI+) calcd for $[C_{10}H_{15}Br_3O_2]^+$ *m*/*z* 405.9, found 405.9.



3m

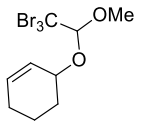
[10] Elamparuthi, E.; Fellay, C.; Neuburger, M.; Gademann, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 4071–4073.
[11] Comito, R. J.; Finelli, F. G.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2013**, *135*, 9358–9361.

[2-(2,2,2-Tribromo-1-methoxyethoxy)ethylidene]cyclohexane (3m): The alcohol **1m**[11] was subjected to the conditions described above to yield the mixed acetal **3m** (316 mg, 75%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.5). IR (CH_2Cl_2) ν_{max} 2930, 2854, 2662, 1444, 1078 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.64–5.58 (m, 1H), 4.58 (s, 1H), 4.47 (dt, *J* = 7.1, 1.1 Hz, 2H), 3.76 (s, 1H), 2.36 (app q, *J* = 7.3 Hz, 4H), 1.79–1.64 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 116.3, 107.4, 66.9, 58.4, 47.0, 37.1, 29.2, 28.3, 27.8, 26.6; GCMS (EI+) calcd for $[C_{11}H_{17}Br_3O_2]^+$ *m/z* 419.9, found 419.9.



3n

1-Methylene-2-(2,2,2-tribromo-1-methoxyethoxy)cyclohexane (3n): The alcohol **1n**[12] was subjected to the conditions described above to yield the mixed acetal **3n** (325 mg, 80%) as an oil after chromatography (SiO2; EtOAc/hexanes, 5:95; R_f = 0.5). The acetal **3n** was isolated as a 1:1 mixture of inseparable diastereoisomers. NMR spectroscopic data is provided for both isomers. IR (CH_2Cl_2) ν_{max} 2934, 2841, 1445, 1107 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.06–5.01 (m, 1+2H), 4.92 (app br s, 1H), 4.56 (s, 1H), 4.54 (s, 1H), 4.34 (t, *J* = 3.8 Hz, 1H), 4.30 (t, *J* = 3.8 Hz, 1H), 3.83 (s, 3H), 3.67 (s, 3H), 2.60–244 (m, 1+1H), 2.24–2.13 (m, 1+1H), 2.11–1.98 (m, 1+1H), 1.96–1.67 (m, 3+3H), 1.58–1.38 (m, 2+2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 146.5, 112.1, 110.0, 107.5, 105.3, 82.0, 77.5, 60.1, 58.7, 48.3, 47.6, 33.8, 33.1, 31.9, 31.7, 27.7, 27.6, 21.6, 21.1; GCMS (EI+) calcd for $C_{10}H_{15}Br_2O_2$ $[M - Br]^+$ *m/z* 326.9, found 326.9.

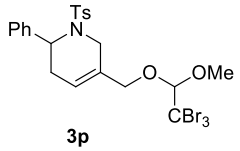


3o

3-(2,2,2-Tribromo-1-methoxyethoxy)cyclohex-1-ene (3o): The alcohol **1o** was subjected to the conditions described above to yield the mixed acetal **3o** (282 mg, 72%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.5). The acetal **3o** was isolated as a 1:1 mixture of inseparable

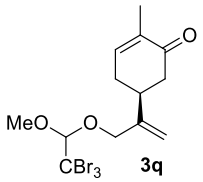
[12] Alcaraz, L; Cridland, A.; Kinchin, E. *Org. Lett.* **2001**, *3*, 4051–4053.

diastereoisomers. NMR spectroscopic data is provided for both isomers. IR (CH_2Cl_2) ν_{max} 2930, 1440, 1313, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.99–5.83 (m, 2H), 4.66 (s, 1H), 4.47–4.41 (m, 1H), 3.74 (s, 3H), 2.15–2.05 (m, 1H), 2.04–1.80 (m, 4H), 1.67–1.57 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.5, 132.3, 126.6, 126.2, 107.3, 106.8, 74.5, 73.5, 58.5, 58.2, 48.0, 47.7, 29.7, 28.2, 25.1, 25.0, 19.0, 18.8; GCMS (EI+) calcd for $C_{13}H_{19}Br_2O_2$ $[M - Br]^+$ *m*/*z* 312.9, found 312.9.



3p

2-Phenyl-1-tosyl-5-[(2,2,2-tribromo-1-methoxyethoxy)methyl]-1,2,3,6-tetrahydropyridine (3p): The alcohol **1p** was subjected to the conditions described above to yield the mixed acetal **3p** (1.8 g, 94%) as an amorphous solid after chromatography (SiO_2; EtOAc/hexanes, 20:80; R_f = 0.6). The acetal **3p** was isolated as a 1:1 mixture of inseparable diastereoisomers. NMR spectroscopic data is provided for both isomers. M.p.: 124 °C; IR (CH_2Cl_2) ν_{max} 1597, 1332, 1155, 1152 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74–7.69 (m, 2+2H), 7.34–7.22 (m, 7+7H), 5.86 (d, *J* = 3.3 Hz, 1H), 5.82 (d, *J* = 4.2 Hz, 1H), 5.35 (s, 1H), 5.33 (s, 1H), 4.44–4.29 (m, 2+2H), 4.25–4.05 (m, 2+2H), 3.67 (s, 3H), 3.64 (s, 3H), 3.50–3.35 (m, 1+1H), 2.55–2.39 (m, 5+5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.24, 143.21, 138.8, 138.7, 137.5, 137.4, 131.1, 130.9, 129.6, 128.54, 128.5, 127.7, 127.6, 127.3, 127.2, 127.1, 123.9, 123.6, 107.5, 107.3, 71.7, 71.2, 59.7, 59.6, 52.6, 46.1, 45.8, 41.5, 41.4, 28.426.1, 21.56, 21.55; HRMS (ESI) calcd for $C_{22}H_{24}Br_3NNaO_4S$ $[M + Na]^+$ *m*/*z* 659.8854, found 659.8880.



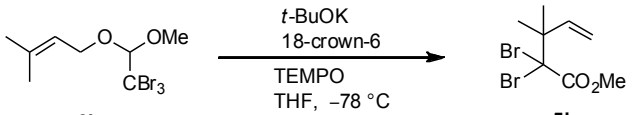
3q

(5*S*)-2-Methyl-5-[3-(2,2,2-tribromo-1-methoxyethoxy)prop-1-en-2-yl]cyclohex-2-enone (3q): The alcohol **1q**[13] was subjected to the conditions described above with the following modifications: (I) The alcohol **1q** and the chloroether **2** were added as a solution in toluene (1 mL) to the silver salts in toluene (5 mL); (II) the reaction was conducted at room temperature. The mixed acetal **3q** (332 mg, 72%) was

[13] Xuan, M.; Paterson, I.; Dalby, S. M. *Org. Lett.* **2012**, *14*, 5492–5495.

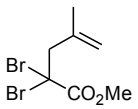
isolated as a heavy oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.35). The acetal **3q** was isolated as a 1:1 mixture of inseparable diastereoisomers. NMR spectroscopic data is provided for both isomers. IR (CH_2Cl_2) ν_{max} 2976, 2919, 1745, 1418, 1248 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.77 (app br s., 1+1H), 5.28 (s, 1+1H), 5.11 (s, 1+1H), 4.56 (s, 1H), 4.55 (s, 1H), 4.47–4.34 (m, 2+2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.09–2.91 (m, 1+1H), 2.74–2.59 (m, 2+2H), 2.54–2.36 (m, 2+2H), 1.82–1.80 (m, 3+3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 46.9, 132.7, 132.6, 127.3, 127.1, 108.9, 108.7, 102.2, 101.9, 98.4, 97.8, 67.8, 67.7, 59.2, 58.9, 48.3, 48.2, 37.9, 37.8, 37.6, 36.3, 32.4, 32.2, 17.3, 16.7; GCMS (EI+) calcd for $C_{13}H_{17}Br_2O_3$ $[M - Br]^+$ *m*/*z* 380.9, found 381.0.

Rearrangement reaction:



3b **5b**

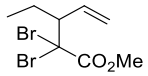
Methyl 2,2-Dibromo-3,3-dimethylpent-4-enoate (5b): THF (10 mL) was added to the acetal **3b** (3.81 g, 10.0 mmol), [18]crown-6 (280 mg, 1.05 mmol, 2.1 equiv), and TEMPO (27.0 mg, 0.175 mmol, 35 mol%) in a round-bottom flask and then the mixture was placed in a dry ice/acetone bath. Once cooled, 1 M *t*-BuOK in THF (1.00 mL, 1.00 mmol, 2 equiv) was added slowly. After stirring for 2 h,sat. NH_4Cl (1 mL) was added. The mixture was warmed to room temperature and partitioned between EtOAc (10 mL) and water (10 mL). The aqueous phase was washed with EtOAc (3 × 5 mL). The combined organic phases were washed with sat. NaCl (5 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.5) to yield **5b** (2.37 g, 79%) as an oil. IR (CH_2Cl_2) ν_{max} 2991, 1749, 1178 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.24 (dd, *J* = 17.1, 11.0 Hz, 1H), 5.24 (s, 1H), 5.19 (dd, *J* = 7.5, 0.6 Hz, 1H), 3.87 (s, 3H), 1.50 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 141.4, 115.1, 73.5, 54.2, 48.3, 24.8; GCMS (EI+) calcd for $[C_8H_{12}Br_2O_2]^+$ *m*/*z* 297.9, found 297.9.



5a

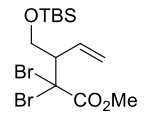
Methyl 2,2-Dibromo-4-methylpent-4-enoate (5a): The mixed acetal **3a** was subjected to the conditions described above with the following modifications: (1) the reaction was run at –90 °C using a liquid N_2/hexanes cooling bath; (2) the reaction was stirred for 3 h before being quenched. The α,α-dibromoester

5a (106 mg, 76%) was isolated as an oil after chromatography (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.55). IR (CH_2Cl_2) ν_{max} 2915, 1717, 1564, 1143 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.02 (t, J = 1.4 Hz, 1H), 4.90 (s, 1H), 3.88 (s, 3H), 3.43 (s, 2H), 1.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 140.1, 117.6, 57.4, 54.5, 54.1, 23.4; GCMS (EI+) calcd for $[C_7H_{10}Br_2O_2]^+$ m/z 258.9, found 258.9.



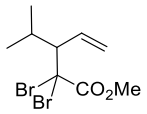
5c

Methyl 2,2-Dibromo-3-ethylpent-4-enoate (5c): The mixed acetal **3c** was subjected to the conditions described above with the following modifications: (1) the reaction was run at –90 °C using a liquid N_2/hexanes cooling bath; (2) the reaction was stirred for 3 h before being quenched. The α,α-dibromoester **5c** (125 mg, 83%) was isolated as an oil after chromatography (SiO_2; EtOAc/hexanes, 1:9; R_f = 0.5). IR (CH_2Cl_2) ν_{max} 2885, 1730, 1438, 1253 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.63 (ddd, J = 16.9, 10.4, 9.0 Hz, 1H), 5.31 (dd, J = 10.4, 1.7 Hz, 1H), 5.21 (dq, J = 16.9, 0.7 Hz, 1H), 3.86 (s, 3H), 2.82–2.76 (m, 1H), 1.89–1.76 (m, 1H), 1.55–1.47 (m, 1H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 135.4, 120.9, 66.9, 58.2, 54.4, 25.0, 11.7; GCMS (EI+) calcd for $[C_8H_{12}Br_2O_2]^+$ m/z 297.9, found 297.9.



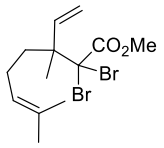
5d

Methyl 2,2-Dibromo-3-{[(*tert*-Butyldimethylsilyl)oxy]methyl}pent-4-enoate (5d): The mixed acetal **3d** was subjected to the rearrangement conditions described above to yield **5d** (156 mg, 75%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 5:95; R_f = 0.6). IR (CH_2Cl_2) ν_{max} 2851, 1759, 1475, 1107 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.79 (ddd, J = 16.9, 10.2, 8.8 Hz, 1H), 5.39–5.31 (m, 2H), 3.93–3.88 (m, 4H), 3.76–3.70 (m, 1H), 3.37 (q, J = 7.0 Hz, 1H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 134.1, 121.2, 65.2, 64.5, 57.2, 54.3, 25.9, 18.5, –5.5; GCMS (EI+) calcd for $C_{13}H_{24}BrO_3S$ $[M - Br]^+$ m/z 335.1, found 335.1.



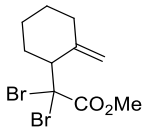
5e

Methyl 2,2-Dibromo-3-isopropylpent-4-enoate (5e): The mixed acetal **3e** was subjected to the rearrangement conditions described above to yield **5e** (107 mg, 68%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.6). IR (CH_2Cl_2) ν_{max} 2901, 1756, 1455, 1234 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.75 (dt, *J* = 16.9, 8.5 Hz, 1H), 5.31 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.17 (dd, 16.9, 1.4 Hz, 1H), 3.85 (s, 3H), 2.87 (dd, *J* = 9.5, 3.8 Hz, 1H), 2.06–1.96 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 134.3, 120.9, 66.5, 61.1, 54.4, 31.3, 22.7, 19.6; GCMS (EI+) calcd for $C_9H_{13}BrO_2$ $[M - HBr]^+$ *m*/*z* 232.0, found 232.1.



5f

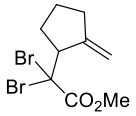
Methyl 2,2-Dibromo-3,7-dimethyl-3-vinyloct-6-enoate (5f): The mixed acetal **3f** was subjected to the rearrangement conditions described above to yield **5f** (180 mg, 98%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.6). IR (CH_2Cl_2) ν_{max} 2897, 1730, 1515, 1443, 1272 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.07 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.35 (dd, *J* = 10.8, 0.9 Hz, 1H), 5.21–5.09 (m, 2H), 3.87 (s, 3H), 1.97–1.81 (m, 4H), 1.72 (s, 3H), 1.62 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 139.3, 132.0, 123.8, 117.2, 74.8, 54.2, 51.1, 36.5, 25.7, 23.9, 19.0, 17.7; GCMS (EI+) calcd for $C_{13}H_{20}BrO_2$ $[M - Br]^+$ *m*/*z* 287.1, found 286.9.



5g

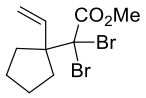
Methyl 2,2-Dibromo-2-(2-methylenecyclohexyl)acetate (5g): The mixed acetal **3g** was subjected to the rearrangement conditions described above to yield **5g** (1.6 g, 98%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.5). IR (CH_2Cl_2) ν_{max} 2947, 2847, 1749, 1447, 1245 cm^{-1}; ^1H NMR

(300 MHz, $CDCl_3$) δ 4.89 (s, 1H), 4.69 (s, 1H), 3.90 (s, 3H), 3.06–3.00 (m, 1H), 2.49–2.29 (m, 2H), 2.13–1.96 (m, 2H), 1.90–1.60 (m, 3H), 1.55–1.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 146.5, 138.2, 65.1, 55.3, 54.6, 37.8, 31.9, 28.3, 25.8; GCMS (EI+) calcd for $C_{10}H_{14}BrO_2$ $[M - Br]^+$ *m*/*z* 245.0.0, found 245.0.



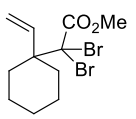
5h

Methyl 2,2-Dibromo-2-(2-methylenecyclopentyl)acetate (5h): The mixed acetal **3h** was subjected to the rearrangement conditions described above to yield **5h** (106 mg, 68%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.5). IR (CH_2Cl_2) ν_{max} 2353, 1745, 1428, 1159 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.13 (s, 1H), 4.90 (s, 1H), 3.95 (s, 3H), 3.76–3.69 (m, 1H), 2.61–2.29 (m, 3H), 2.07–1.88 (m, 2H), 1.63–1.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 150.9, 110.2, 66.9, 54.7, 54.5, 36.2, 32.7, 24.7; GCMS (EI+) calcd for $C_9H_{12}BrO_2$ $[M - Br]^+$ *m*/*z* 231.0, found 231.0.



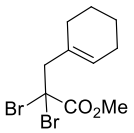
5l

Methyl 2,2-Dibromo-2-(1-vinylcyclopentyl)acetate (5l): The mixed acetal **3i** was subjected to the rearrangement conditions described above to yield **5i** (122 mg, 75%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.55). IR (CH_2Cl_2) ν_{max} 2847, 1738, 1632, 1004 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.99 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.25 (dd, *J* = 17.3, 10.7 Hz, 2H), 3.82 (s, 3H), 2.26–2.19 (m, 2H), 2.04–1.98 (m, 2H), 1.77–1.70 (m, 2H), 1.67–1.62 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 139.1, 116.9, 72.9, 60.1, 54.2, 35.9, 24.6; GCMS (EI+) calcd for $C_{10}H_{14}BrO_2$ $[M - Br]^+$ *m*/*z* 245.1, found 245.0.



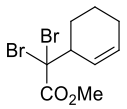
5m

Methyl 2,2-Dibromo-2-(1-vinylcyclohexyl)acetate (5m): The mixed acetal **3m** was subjected to the rearrangement conditions described above to yield **5m** (119 mg, 70%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.5). IR (CH_2Cl_2) ν_{max} 2456, 1741, 1443, 1240, 999 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.53 (dd, *J* = 17.6, 1 Hz, 1H), 5.24 (dd, *J* = 17.6, 1 Hz, 1H), 3.85 (s, 3H), 2.23 (br d, *J* = 13.3, 2H), 1.88 (dt, *J* = 13.3, 3.3 Hz, 2H), 1.70–1.60 (m, 3H), 1.52–1.34 (m, 2H), 1.22–1.01 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 137.4, 120.4, 76.6, 54.2, 50.8, 32.0, 25.7, 22.7; GCMS (EI+) calcd for $[C_{11}H_{16}Br_2O_2]^+$ *m*/*z* 339.9, found 339.9.



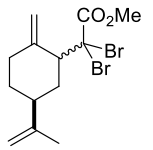
5n

Methyl 2,2-Dibromo-3-(cyclohex-1-en-1-yl)propanoate (5n): The mixed acetal **3n** was subjected to the rearrangement conditions described above to yield **5n** (139 mg, 85%) as an oil after chromatography (SiO+; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.55). IR (CH_2Cl_2) ν_{max} 2840, 1749, 1432 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.63 (br s, 1H), 3.88 (s, 3H), 3.34 (s, 2H), 2.04–2.00 (m, 4H), 1.63–1.51 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167, 132.9, 129.4, 59.0, 66.0, 65.5, 29.2, 25.5, 22.8, 21.8; GCMS (EI+) calcd for $[C_{10}H_{14}Br_2O_2]^+$ *m*/*z* 325.9, found 325.9.



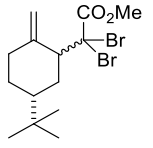
5o

Methyl 2,2-Dibromo-2-(cyclohex-2-en-1-yl)acetate (5o): The mixed acetal **3o** was subjected to the rearrangement conditions described above to yield **5o** (151 mg, 97%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.55). IR (CH_2Cl_2) ν_{max} 2924, 1738, 1436 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.97–5.92 (m, 1H), 5.63 (dqt, *J* = 10.2, 2.0 Hz, 1H), 3.90 (s, 3H), 3.26–3.20 (m, 1H), 2.05–1.98 (m, 3H), 1.92–1.85 (m, 1H), 1.61–1.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 131.3, 126.1, 67.6, 54.6, 48.8, 26.7, 24.8, 21.4; GCMS (EI+) calcd for $[C_9H_{12}Br_2O_2]^+$ *m*/*z* 309.9, found 310.0.



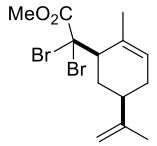
(5*S*)-5i

Methyl 2,2-Dibromo-2-[(5*S*)-2-methylene-5-(prop-1-en-2-yl)cyclohexyl]acetate (5i): The mixed acetal **3i** was subjected to the rearrangement conditions described above to yield **5i** (110 mg, 60%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0..65). The dibromoester **5i** was isolated as a 1:2 mixture of inseparable diastereoisomers. NMR spectroscopic data is provided for both isomers. IR (CH_2Cl_2) ν_{max} 2940, 2853, 1752, 1744, 1450, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.96–4.71 (m, $4H_{minor}$+$4H_{major}$), 3.91 (s, $3H_{minor}$), 3.89 (s, $3H_{major}$), 3.40 (t, J = 6.1 Hz, $1H_{major}$), 3.13–3.08 (m, $1H_{minor}$), 2.88–2.79 (m, $1H_{major}$), 2.55–2.12 (m, $5H_{minor}$+$4H_{major}$), 1.96–1.88 (m, $1H_{major}$), 1.83 (s, $3H_{major}$), 1.81 (s, $3H_{minor}$), 1.73–1.61 (m, $1H_{minor}$+$1H_{major}$), 1.48–1.32 (m, $1H_{minor}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 166.7, 148.7, 147.3, 146.0, 145.7, 111.8, 110.5, 109.5, 108.4, 65.9, 64.7, 54.6, 54.5, 51.5, 44.9, 38.8, 37.4, 36.6 34.0, 33.3 33.1, 30.9, 21.8, 20.8; GCMS (EI+) calcd for $[C_{13}H_{17}BrO_2]^+$ *m*/*z* 365.9, found 366.0.



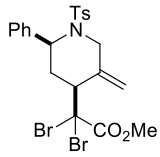
5j

Methyl 2,2-Dibromo-2-(5-*tert*-butyl-2-methylenecyclohexyl)acetate (5j): The mixed acetal **3j** was subjected to the rearrangement conditions described above to yield **5j** (187 mg, 98%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.55). The dibromoester **5j** was isolated as a 1:2 mixture of inseparable diastereoisomers. NMR spectroscopic data is provided for both isomers. IR (CH_2Cl_2) ν_{max} 2936, 2853, 1720, 1446 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.07 (m, $1H_{major}$), 4.90 (s, $1H_{minor}$+$1H_{major}$), 4.67 (s, $1H_{minor}$), 3.91 (s, $1H_{major}$), 3.90 (s, $1H_{minor}$), 3.49–3.44 (m, $1H_{major}$), 2.99–2.92 (m, $1H_{minor}$), 2.55–2.46 (m, $1H_{minor}$+$1H_{major}$), 2.36–2.19 (m, $2H_{minor}$+$2H_{major}$), 2.05–1.87 (m, $2H_{minor}$+$2H_{major}$), 1.84–1.63 (m, $1H_{minor}$+$1H_{major}$), 0.92 (s, $9H_{minor}$+$9H_{major}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 166.5, 146.5, 116.3, 108.1, 66.6, 55.2, 54.6, 54.4, 51.9, 50.0, 47.7, 39.1, 33.5, 33.0, 32.4, 31.5, 28.4, 27.4, 27.3, 27.5, 26.8, 22.0; GCMS (EI+) calcd for $C_{14}H_{23}BrO_2$ [M – HBr]$^+$ *m*/*z* 302.1, found 302.1.



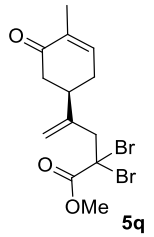
(1*R*, 5*R*)-5k

Methyl 2,2-Dibromo-2-[(1*R*,5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl]acetate (5k): The mixed acetal **3k** was subjected to the rearrangement conditions described above to yield **5k** (55 mg, 30%) as an oil after chromatography (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.65). IR (CH_2Cl_2) ν_{max} 2969, 1750, 1642, 1438 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.75–5.68 (m, 1H), 4.83 (s, 2H), 3.95 (s, 3H), 3.52–3.43 (m, 1H), 2.53–2.44 (m, 1H), 2.36–2.25 (m, 1H), 2.19–2.09 (m, 1H), 2.05–1.93 (m, 1H), 1.82 (s, 3H), 1.75–1.69 (m, 1H), 1.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 148.9, 131.8, 129.2, 109.4, 69.2, 54.6, 50.9, 41.2, 34.4, 31.2, 21.9, 20.7; GCMS (EI+) calcd for $C_{13}H_{18}BrO_2$ $[M - Br]^+$ *m*/*z* 287.1, found 287.1.



5p

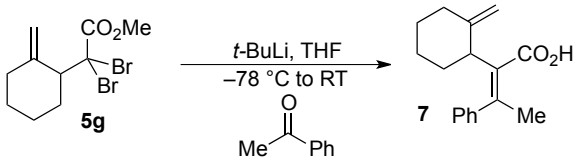
Methyl 2,2-Dibromo-2-(5-methylene-2-phenyl-1-tosylpiperidin-4-yl)acetate (5p): The mixed acetal **3p** was subjected to the rearrangement conditions described above to yield **5p** (346 mg, 62%) as a thick oil after chromatography (SiO_2; EtOAc/hexanes, 15:85; R_f = 0.4). The dibromoester **5p** was isolated as a 1:10 mixture of inseparable diastereoisomers. NMR spectroscopic data is reported only for the major isomer. IR (CH_2Cl_2) ν_{max} 2953, 1758, 1594, 1160 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.54–7.33 (m, 7H), 5.37 (app s, 1H), 5.15 (s, 1H), 4.76 (s, 1H), 4.26 (d, *J* = 14.4 Hz, 1H), 3.82 (s, 3H), 3.74 (d, *J* = 14.4 Hz, 1H), 3.21–3.12 (m, 1H), 2.85–2.78 (m, 1H), 2.45 (s, 3H), 1.88 (ddd, *J* = 13.7, 12.3, 5.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 143.6, 138.2, 137.9, 136.8, 129.8, 129.7, 128.9, 127.6, 126.5, 114.8, 64.0, 55.1, 54.7, 49.7, 47.6, 30.9, 21.5; HRMS (ESI) calcd for $C_{22}H_{24}Br_2NO_4S$ $[M + H]^+$ *m*/*z* 557.9774, found 557.9791.



5q

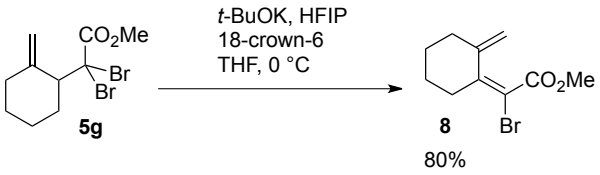
(*R*)-Methyl 2,2-Dibromo-4-(4-methyl-5-oxocyclohex-3-en-1-yl)pent-4-enoate (5q): The mixed acetal **3q** was subjected to the rearrangement conditions described above to yield **5q** (144 mg, 76%) as a heavy oil after chromatography (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.4). IR (CH_2Cl_2) ν_{max} 2955, 2888, 1738, 1669, 1440, 1235 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.79–5.76 (m, 1H), 4.82–4.78 (m, 2H), 4.33–4.22 (m, 2H), 3.77 (s, 3H), 2.97–2.91 (m, 1H), 2.48 (dhep, *J* = 18.3, 2.7 Hz, 1H), 2.25 (ddd, *J* = 11.5, 3.9, 0.9 Hz, 1H), 2.07 (dd, *J* = 11.5, 0.9 Hz, 1H), 2.00–1.94 (m, 1H), 1.86–1.84 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 146.4, 131.9, 126.6, 109.1, 102.4, 67.6, 65.9, 57.9, 37.4, 34.2, 32.5, 16.5; GCMS (EI+) calcd for $[C_{13}H_{16}Br_2O_3]^+$ *m*/*z* 379.9, found 379.9.

Functionalization of Dibromoesters:

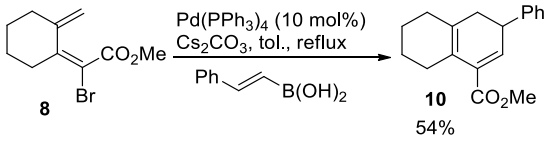


(*E*)-2-(2-Methylenecyclohexyl)-3-phenylbut-2-enoic acid (7): *t*-BuLi (4.9 equiv) was added slowly to a solution of the dibromoester **5g** (97.8 mg, 0.3 mmol, 1.2 equiv) in THF (3 mL) cooled in a dry ice/acetone bath. The mixture was stirred for 3 h at –78 °C, then warmed to 0 °C and stirred at that temperature for 30 min, then warmed to room temperature and stirred for 30 min. A solution of acetophenone (30 mg, 0.25 mmol, 1 equiv) in THF (0.5 mL) was added and then the mixture was stirred for 30 min. After partitioning between 1 N NaOH (2 mL) and EtOAc (5 mL), the organic phase was extracted with 1 N NaOH (3 × 5 mL). The combined aqueous phases were acidified to pH 3 with concentrated HCl and then extracted with EtOAc (5 × 3 mL). The combined organic extracts were washed with water (3 × 5 mL) and brine (5 mL), dried (Na_2SO_4), and concentrated to give **7** as a heavy oil (55.6 mg, 87%). The carboxylic acid **7** was isolated as a 5.6:1 mixture of E/Z isomers. NMR spectroscopic data is reported only for the major isomer. IR (CH_2Cl_2) ν_{max} 3062, 2925, 1687, 1489, 1296 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41–7.30 (m, 3H), 7.26–7.21 (m, 2H), 5.00–4.97 (m, 1H), 4.90–4.88 (m, 1H), 2.89 (br d, *J* = 13.7 Hz, 1H), 2.37 (br d, *J* = 13.7 Hz, 1H), 2.27 (s, 3H), 1.90–1.57 (m, 6H), 1.42–1.30 (m, 1H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 174.2, 150.2, 144.1, 142.3, 131.4, 127.3, 126.5, 108.6, 46.1, 35.8, 31.9, 27.1, 26.1, 23.7; HRMS (ESI) calcd for $C_{17}H_{19}O_2$ [M – H] *m*/*z* 255.1385, found 255.1373.

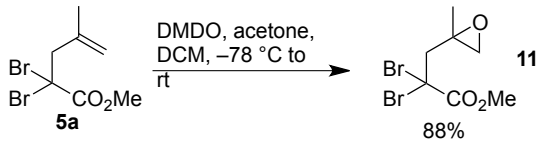


(*E*)-Methyl 2-Bromo-2-(2-methylenecyclohexylidene)acetate (8): 1 M *t*-BuOK in THF (15.0 mL, 15.0 mmol, 5 equiv) was added slowly to a solution of hexafluoroisopropanol (15.0 mmol, 5.5 equiv) and [18]crown-6 (4.22 g, 16.5 mmol, 5.5 equiv) in THF (85 mL) at 0 °C under argon and then the solution was stirred at 0 °C for 20 min. A solution of the α,α-dibromoester **5g** (0.978 g, 3 mmol) in THF (5 mL) was added slowly. The mixture was stirred for 30 min, at which point sat. NH_4Cl (50 mL) was added. The mixture was warmed to room temperature and partitioned between EtOAc (100 mL) and water (50 mL). The aqueous phase was extracted with EtOAc (2 × 50 mL) and then the combined organic phases were washed with sat. NaCl (100 mL) and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.4) to give **8** as a liquid (0.59 g, 80%). The vinyl bromide **8** was isolated as a 10:1 mixture of E/Z isomers. NMR spectroscopic data, including the NOESY, is reported only for the major isomer. IR (CH_2Cl_2) ν_{max} 2947, 1778, 1436, 913 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.87 (s, 1H), 4.82 (s, 1H), 3.76 (s, 3H), 2.58–2.48 (m, 2H), 2.39–2.32 (m, 2H), 1.78–1.72 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 148.8, 147.8, 111.5, 105.5, 52.7, 35.8, 34.9, 27.2, 26.3; GCMS (EI+) calcd for $[C_{10}H_{13}BrO_3]^+$ *m*/*z* 244.0, found 244.0.

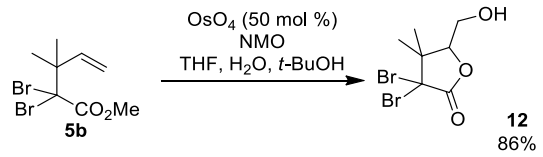


Methyl 3-Phenyl-3,4,5,6,7,8-hexahydronaphthalene-1-carboxylate (10): Toluene (1 mL) was added to the vinyl bromide **8** (23.7 mg, 97.0 μmol), Cs_2CO_3 (95.0 mg, 0.291 mmol, 3 equiv), and β-styrene boronic acid (21.0 mg, 0.145 mmol, 1.5 equiv) in a dry 4-mL vial and then the mixture was deoxygenated by bubbling Ar through the solution for 15 min. $Pd(PPh_3)_4$ (11.0 mg, 9.70 μmol, 10 mol%) was added. The headspace was purged with Ar and the vial was then sealed and heated at 100 °C for 18 h. After cooling, the mixture was loaded directly onto a silica gel column and chromatographed (EtOAc/hexanes, 0:100 to

5:95; R_f = 0.6) to give **10** as a film (14.2 mg, 54%). IR (CH_2Cl_2) ν_{max} 2894, 1734, 1544, 1491 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51–7.30 (m, 5H), 6.14–6.11 (m, 1H), 3.85–3.78 (m, 1H), 3.74 (s, 1H), 3.21–3.08 (m, 1H), 2.98–2.86 (m, 1H), 2.15–1.66 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 140.6, 136.9, 129.3, 128.4, 127.5, 125.3, 123.1, 119.4, 52.2, 49.8, 33.9, 30.1, 28.2, 23.1, 22.8; GCMS (EI+) calcd for $[C_{18}H_{20}O_2]$ *m*/*z* 269.1, found 269.1.



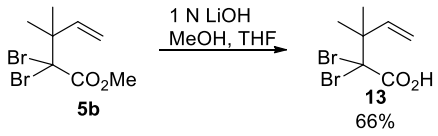
Methyl 2,2-Dibromo-3-(2-methyloxiran-2-yl)propanoate (11): A solution of the dibromoester **5a** (286 mg, 1.00 mmol) in CH_2Cl_2 (10 mL) was cooled in a dry ice/acetone bath and then a freshly prepared solution of DMDO in acetone (ca. 60–65 mM, 25.0 mL, ca. 1.50 mmol, ca. 1.5 equiv) was added.[14] The mixture was warmed slowly to room temperature overnight. The solvent was evaporated and the residue chromatographed (SiO_2; EtOAc/hexanes, 10:90; R_f = 0.3) to give **11** as an oil (266 mg, 88%). IR (CH_2Cl_2) ν_{max} 2986, 1736, 1282, 1254 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.93 (s, 3H), 3.33 (dd, *J* = 15, 0.9 Hz, 1H), 2.87 (dd, *J* = 9.8, 5.1 Hz, 1H), 2.66 (dd, *J* = 4.7, 0.8 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 55.6, 54.7, 54.6, 54.2, 52.6, 22.0; GCMS (EI+) calcd for $[C_7H_{10}Br_2O_3]^+$ *m*/*z* 299.9, found 299.9.



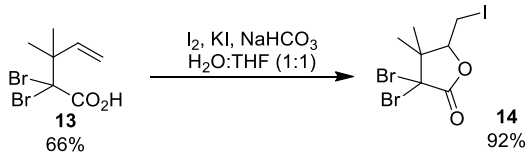
3,3-Dibromo-5-(hydroxymethyl)-4,4-dimethyldihydrofuran-2(3*H*)-one (12): 2 wt/% OsO_4 (0.30 mL, 25 μmol, 50 mol%) was added carefully to a solution of the dibromoester **5b** (15 mg, 50 μmol) and NMO (12 mg, 100 μmol, 2 equiv) in THF (0.5 mL) and *t*-BuOH (0.1 mL) at room temperature. The mixture was stirred for 12 h at which point the reaction was quenched with corn oil (0.6 mL) and then the mixture was stirred for 30 min. Sat. $KHSO_4$(2 mL) and EtOAc (5 mL) were added. The aqueous phase was washed with EtOAc (2 × 5 mL) and the combined organic phases were dried (Na_2SO_4) and concentrated. The residue was chromatographed (SiO_2; EtOAc/hexanes, 40:60; R_f = 0.2) to give **12** (13 mg, 86%) as a

[14] Taber, D. F.; Dematteo, P. W.; Hassan, R. A.*Org. Synth.* **2013**, *90*, 350–357.

thick oil. IR (CH_2Cl_2) ν_{max} 3572, 2880, 1787, 1482, 1266 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.98 (dd, *J* = 7.5, 3.7 Hz, 1H), 3.98–3.83 (m, 2H), 2.08 (br s, 1H), 1.44 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 85.5, 66.2, 60.9, 49.1, 21.1, 20.4; GCMS (EI+) calcd for $[C_{17}H_{10}BrO_3]^+$ *m*/*z* 299.9, found 300.0.

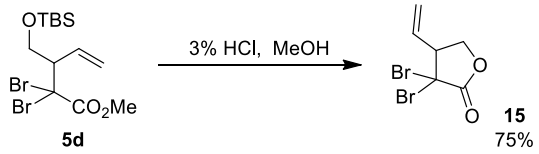


2,2-Dibromo-3,3-dimethylpent-4-enoic acid (13): The dibromoester **5b** (300 mg, 1.00 mmol) was dissolved in THF (1.5 mL), MeOH (1 mL), and 2 N LiOH (1.5 mL, 3 mmol, 3 equiv). The mixture was stirred for 12 h, at which point it was partitioned between 1 N NaOH (5 mL) and EtOAc (10 mL). The organic phase was extracted with 1 N NaOH (3 × 5 mL). The combined aqueous phases were acidified to pH 3 with concentrated HCl and then extracted with EtOAc (10 × 3 mL). The combined organic phases were washed with water (2 × 10 mL) and brine (5 mL), dried (Na_2SO_4), and concentrated to give **13** (189 mg, 66%) as a solid. M.p.: 148 °C (decomp.); IR (CH_2Cl_2) ν_{max} 3114, 2794, 1715, 1470, 1265 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.26 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.25 (dd, *J* = 13.8, 3.0 Hz, 2H), 1.53 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 140.9, 115.6, 72.9, 48.1, 24.9; HRMS (ESI) calcd for $C_7H_9Br_2O_2$ $[M - H]^-$ *m*/*z* 284.8954, found 284.9001.



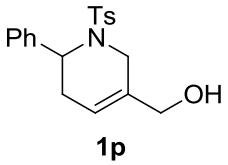
3,3-Dibromo-5-(iodomethyl)-4,4-dimethyldihydrofuran-2(3*H*)-one (14): I_2 (25 mg, 0.1 mmol, 1.1 equiv), KI (16 mg, 0.1 mmol, 1.1 equiv), and $NaHCO_3$ (25 mg, 0.3 mmol, 3 equiv) were added to a solution of the carboxylic acid **13** (26 mg, 90 μmol) in THF (0.5 mL) and water (0.5 mL). The mixture was stirred for 12 h, at which point sat. $Na_2S_2O_3$ (1 mL) was added. The mixture was washed with EtOAc (3 × 5 mL), dried (Na_2SO_4), and concentrated. The residue was passed through a plug of silica, eluting with Et_2O (25 mL). The solvent was evaporated to give **14** (34 mg, 92%) as a white solid. M.p.: 111 °C; IR (CH_2Cl_2) ν_{max} 2866, 1788, 1454, 1170 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.74 (t, *J* = 6.7 Hz, 1H),

3.32–3.30 (m, 2H), 1.60 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 85.5, 66.1, 60.9, 49.1, 21.1, 20.4; GCMS (EI+) calcd for $[C_7H_9Br_2IO_2]^+$ *m*/*z* 413.8, found 413.8.



3,3-Dibromo-4-vinyldihydrofuran-2(3*H*)-one (15): AcCl (3 μL) was added to a solution of the dibromoester **5d** (41 mg, 0.1 mmol) in MeOH (1 mL) and then the mixture was stirred for 12 h at room temperature, at which point sat. $NaHCO_3$ (0.5 mL) was added. After partitioning between EtOAc (5 mL) and water (5 mL), the aqueous phase was extracted with EtOAc (3 × 5 mL). The combined organic phase was dried (Na_2SO_4) and concentrated. The residue was chromatographed (SiO_2; EtOAc/hexanes, 0:100 to 5:95; R_f = 0.5) to give **15** (20 mg, 75%) as an oil. IR (CH_2Cl_2) ν_{max} 2836, 1791, 1638 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97–5.85 (m, 1H), 5.52 (dd, *J* = 26.0, 13.7 Hz, 1H), 4.41 (dd, *J* = 9.1, 7.2 Hz, 1H), 4.20 (t, *J* = 9.1 Hz, 1H), 3.55–3.47 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 129.7, 123.0, 69.4, 57.1, 54.9; GCMS (EI+) calcd for $C_6H_7BrO_3$ $[M - HBr]^+$ *m*/*z* 187.9, found 188.0.

Spectral Data:



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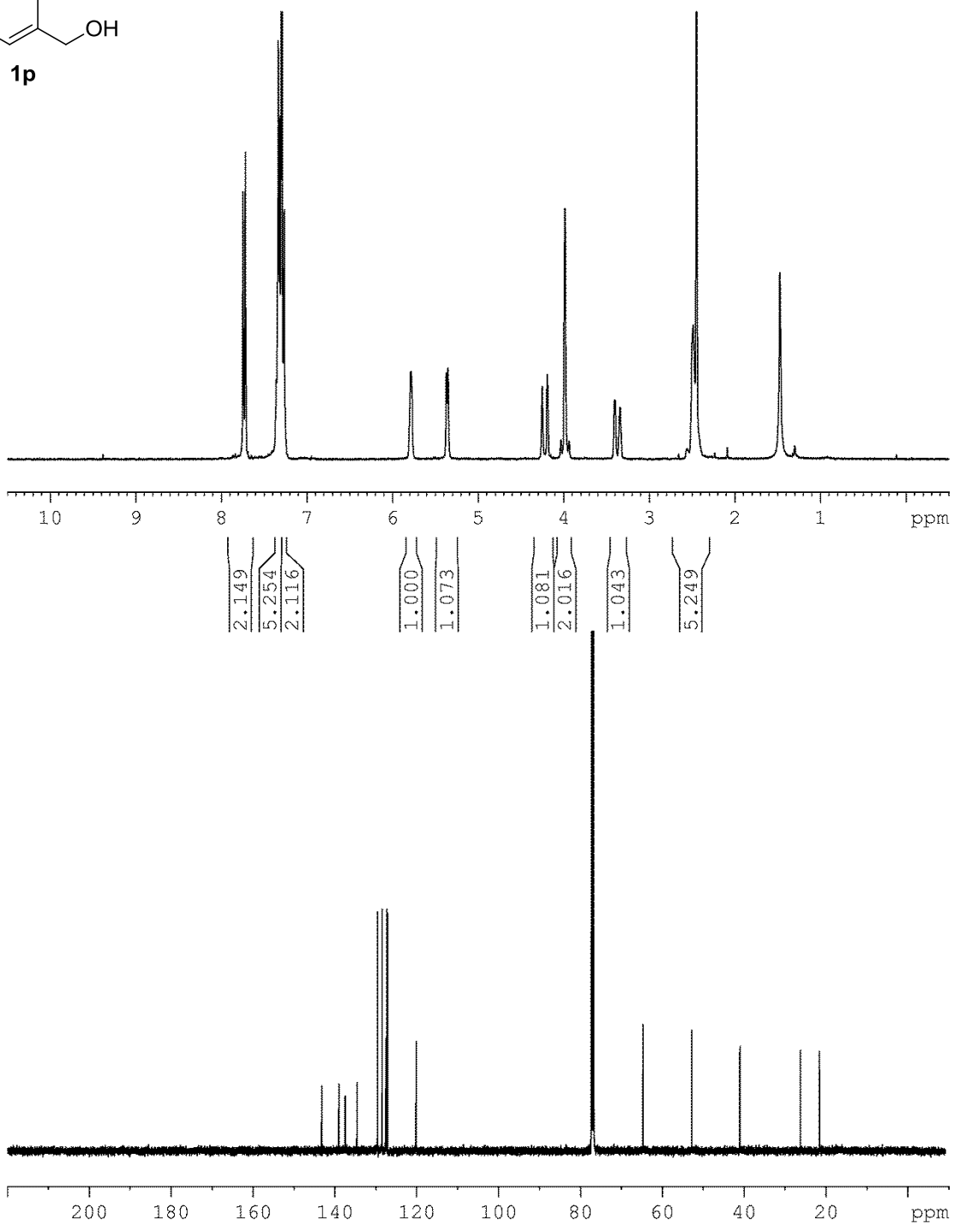

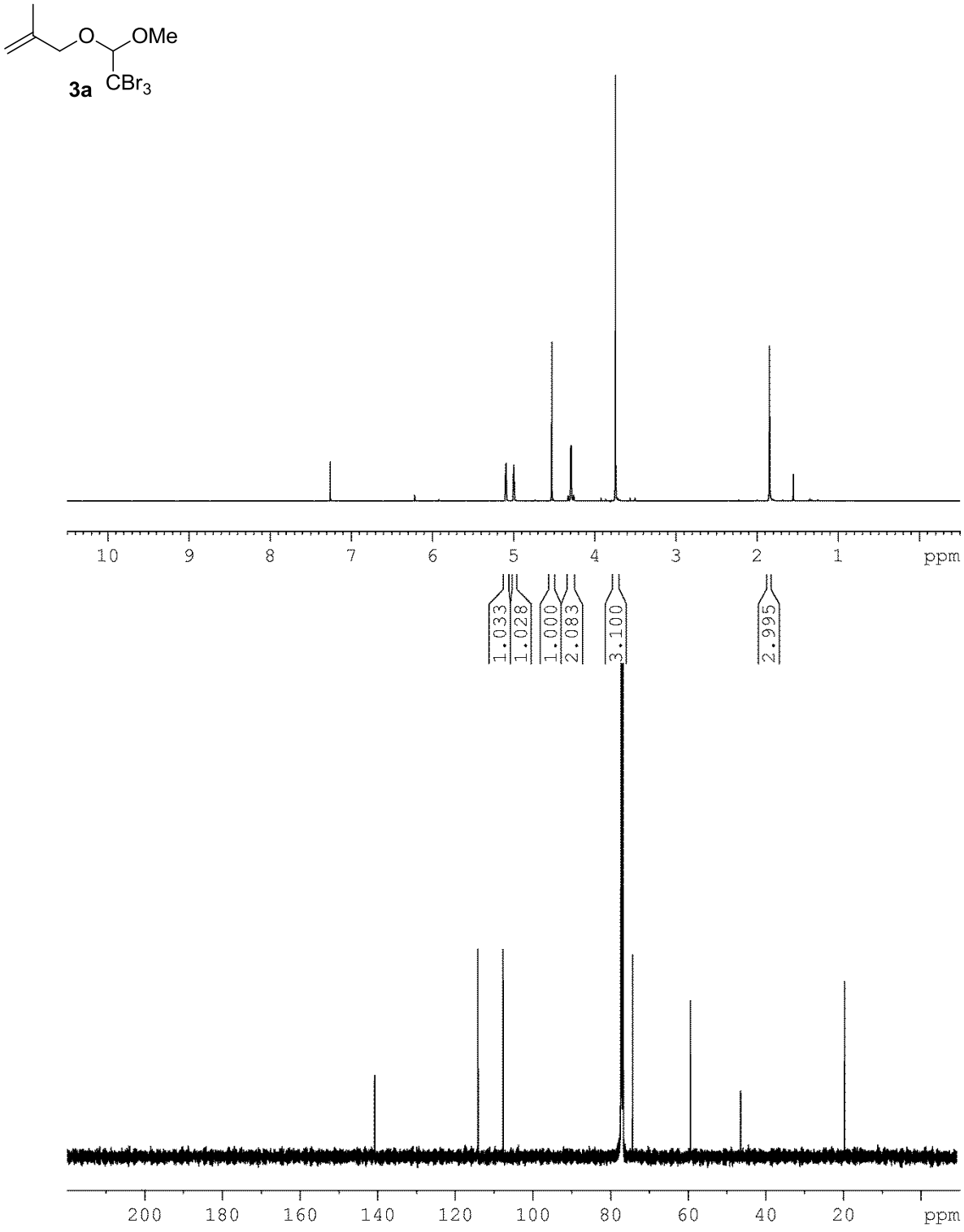
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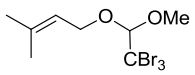
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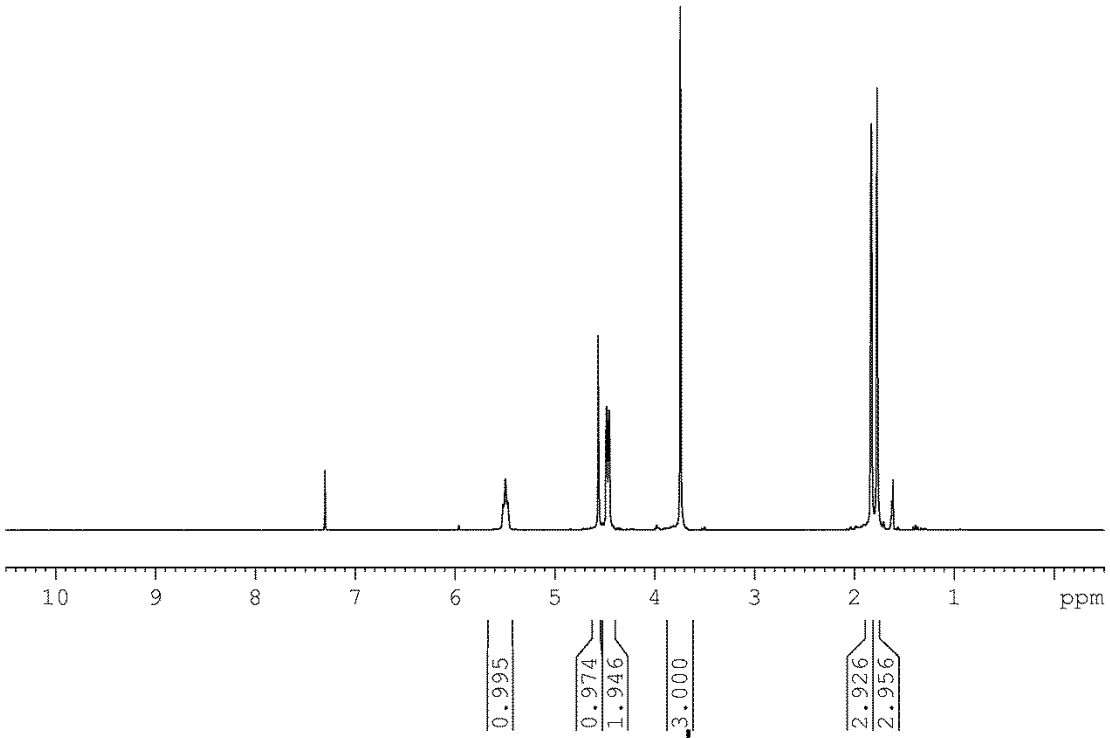
CBr3

3b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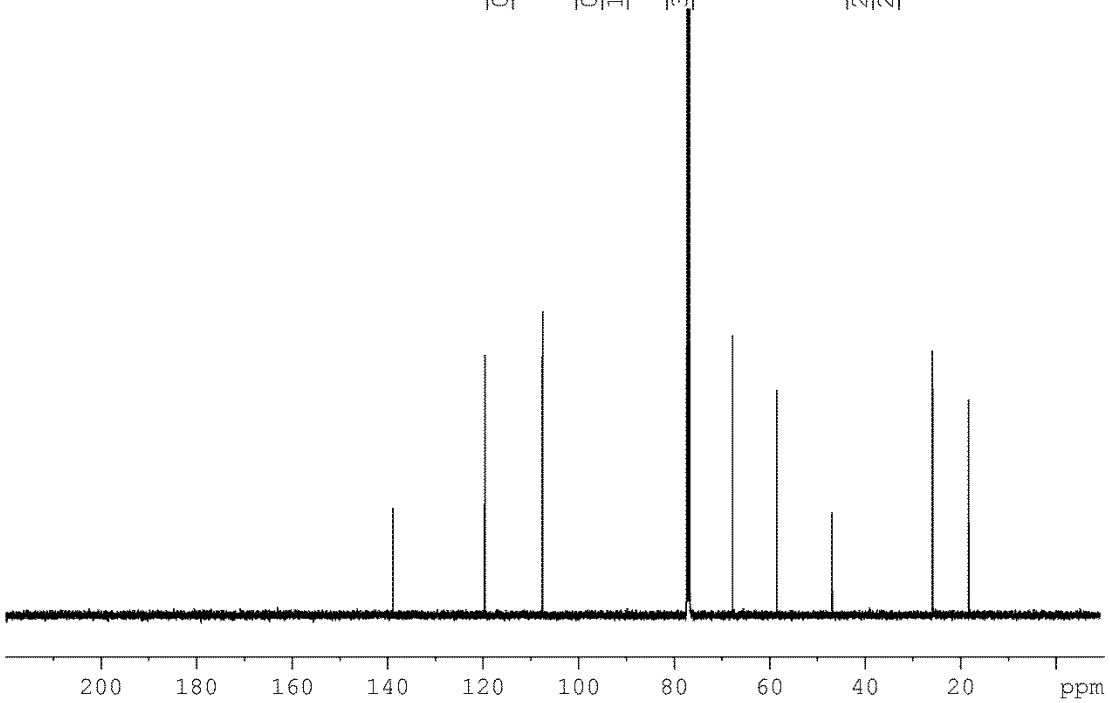
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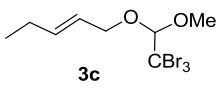
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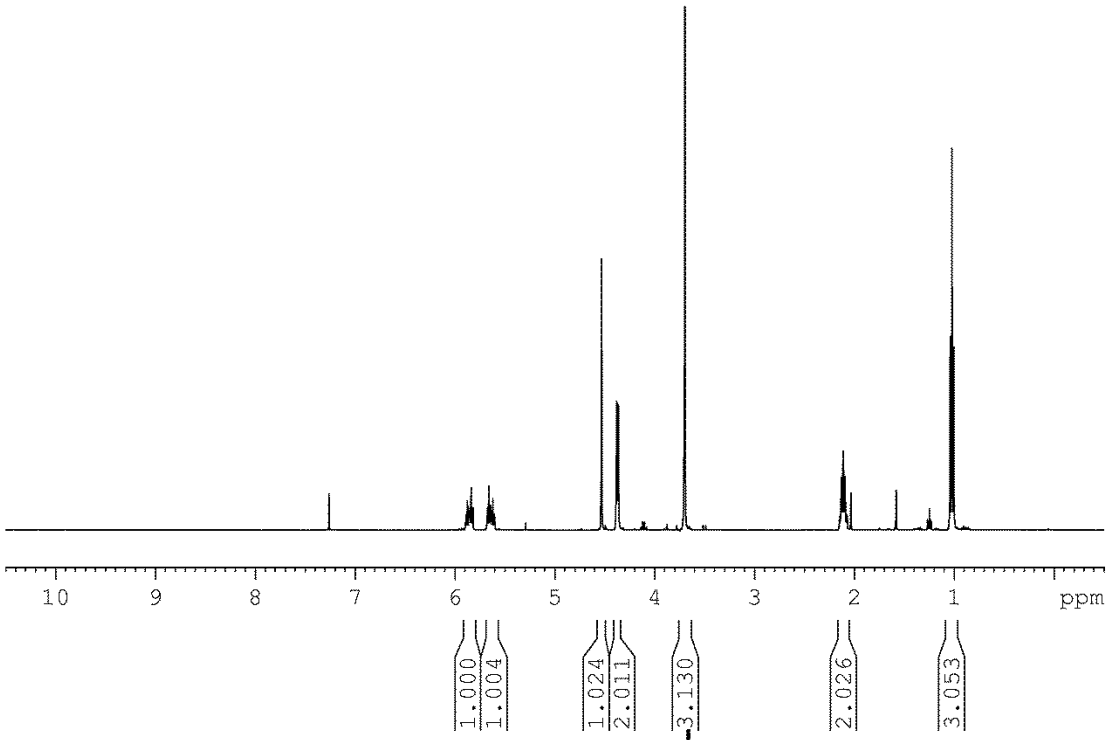
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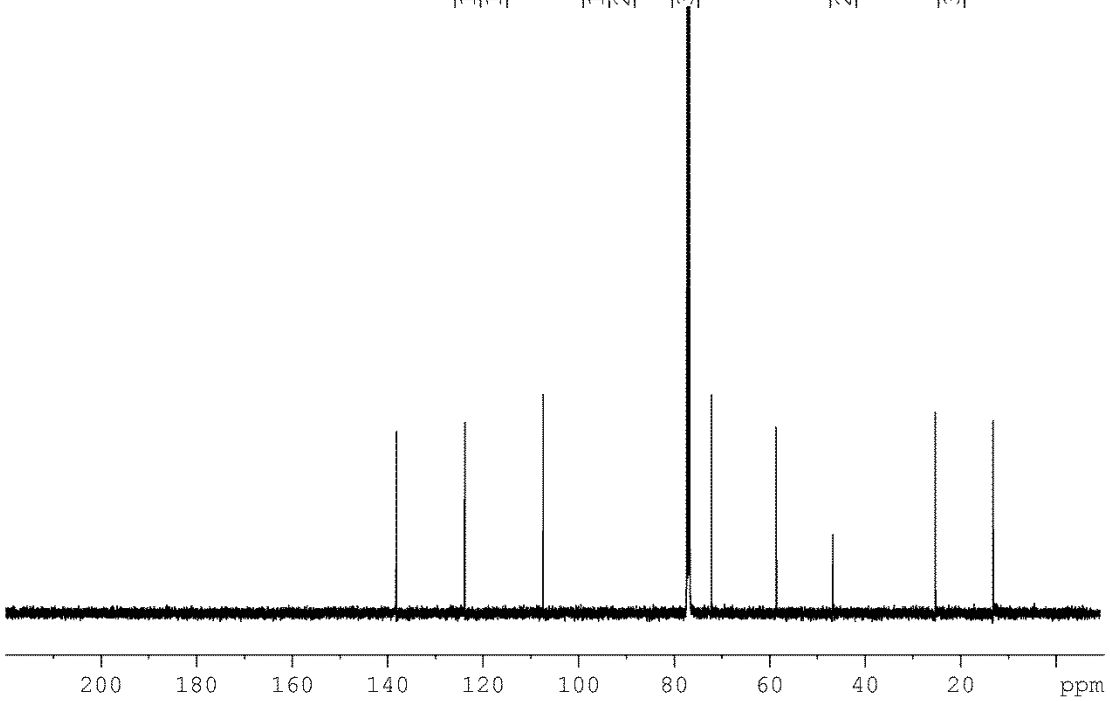
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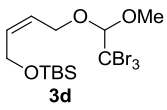
ppm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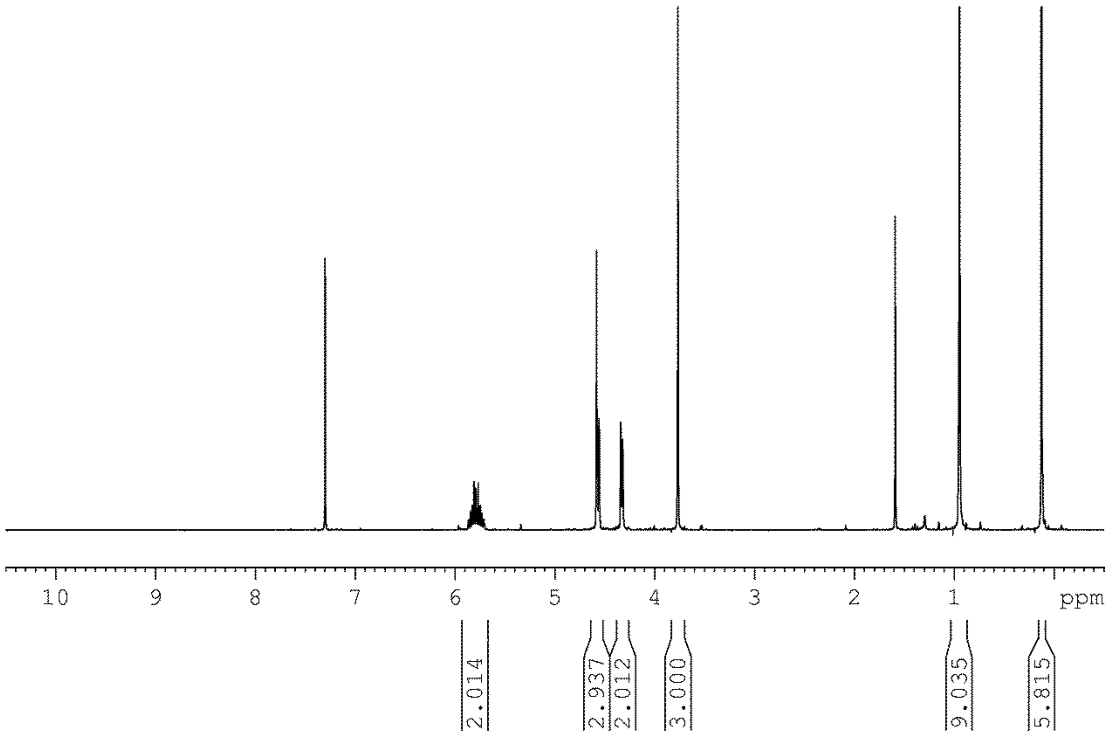
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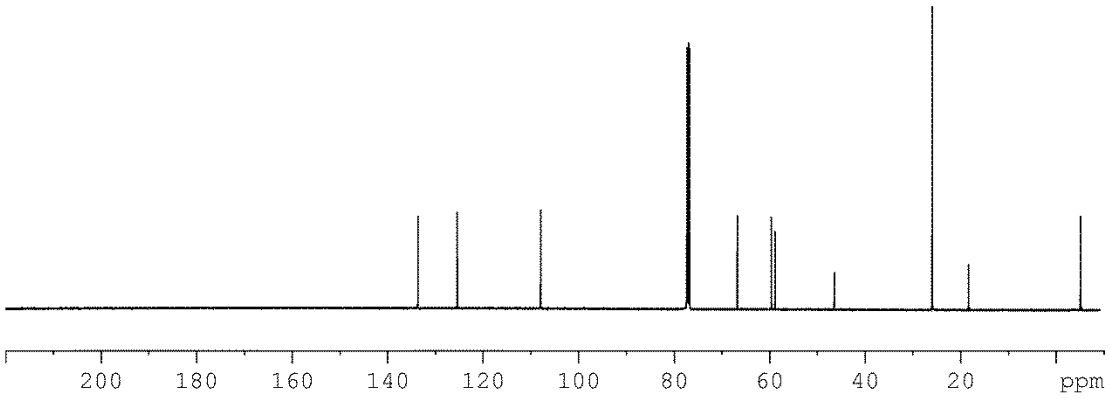
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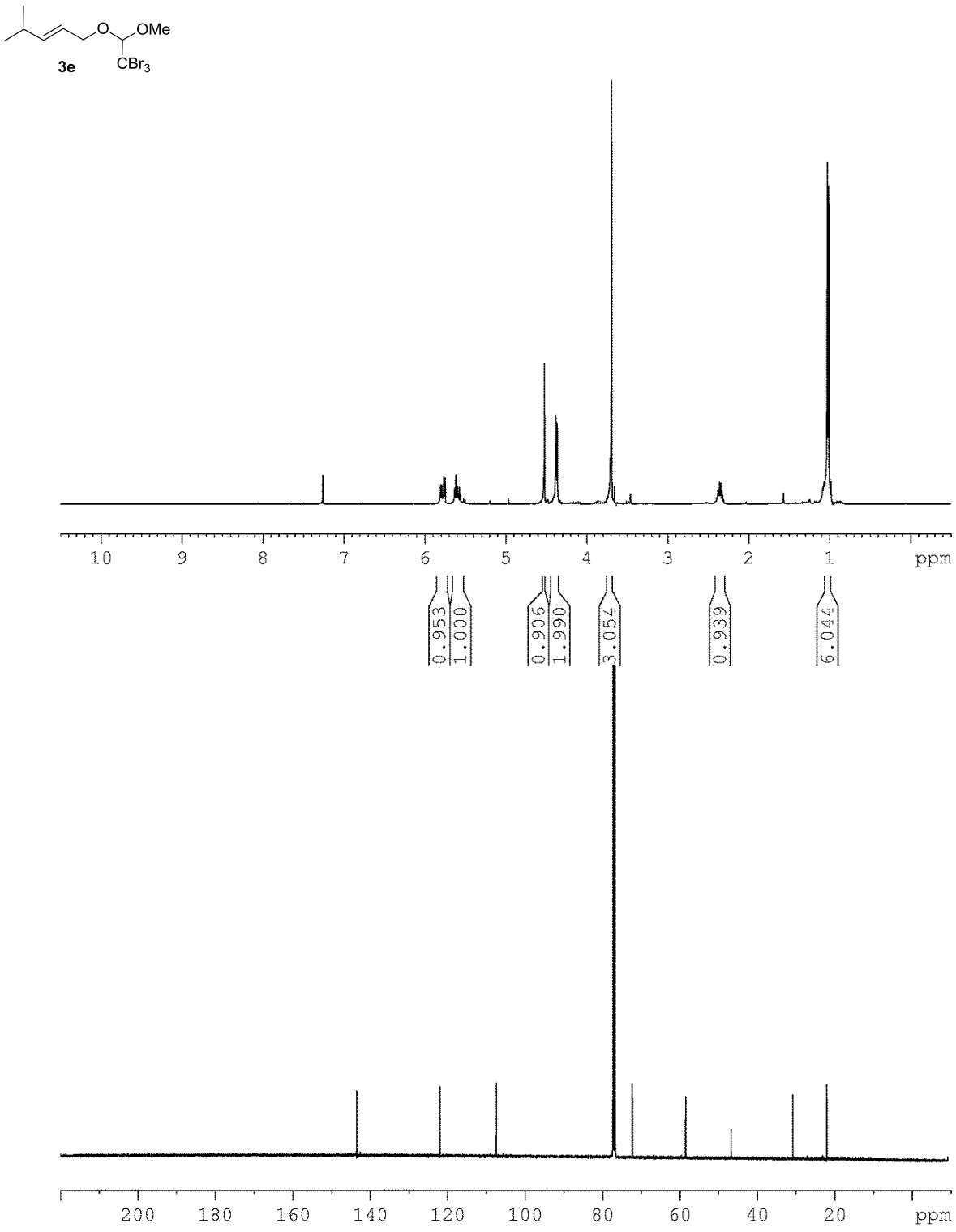
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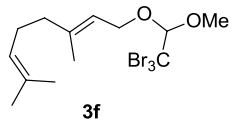
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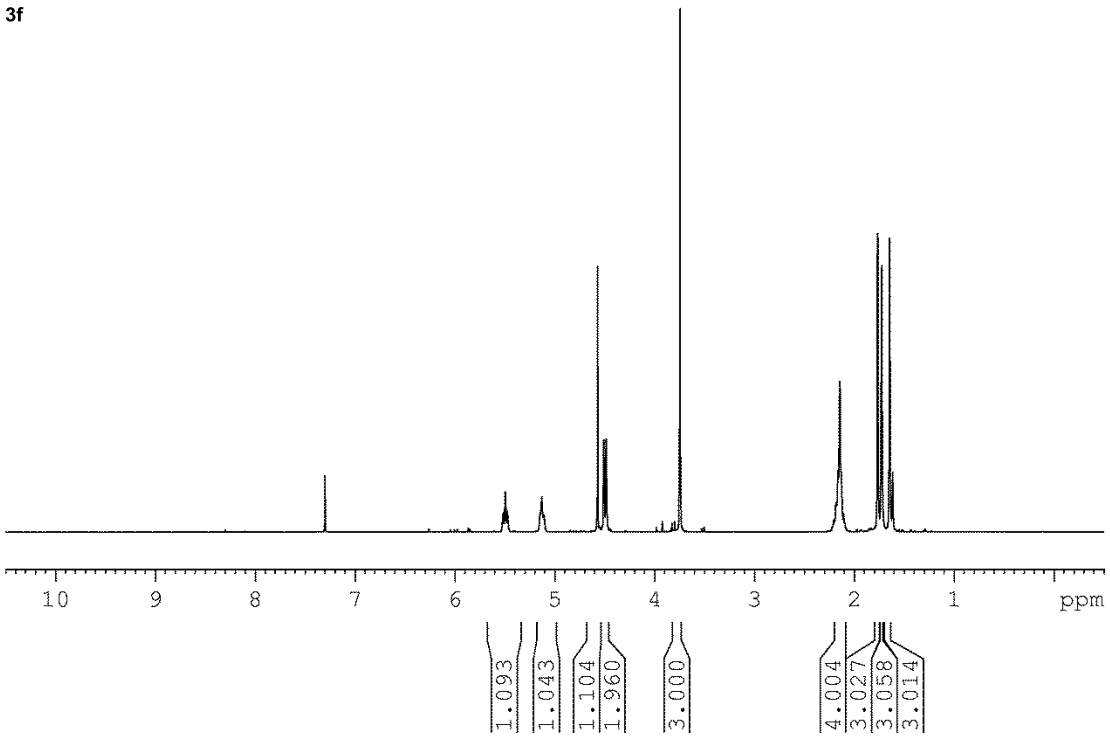
3f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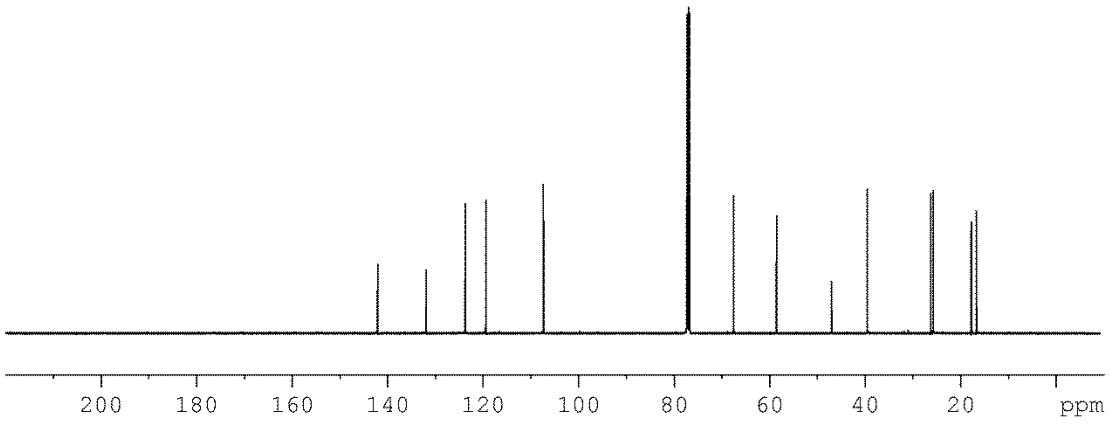
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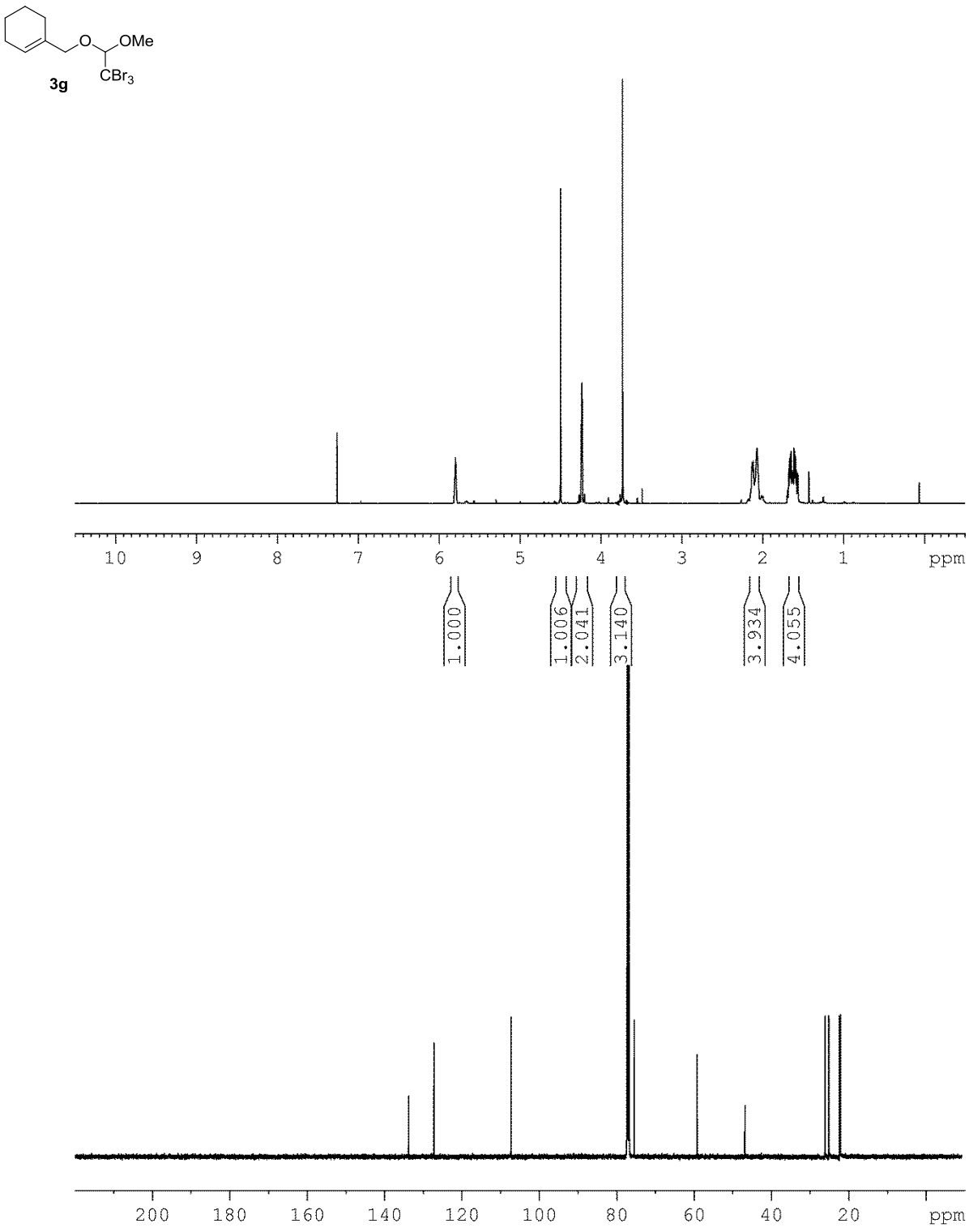
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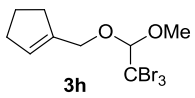
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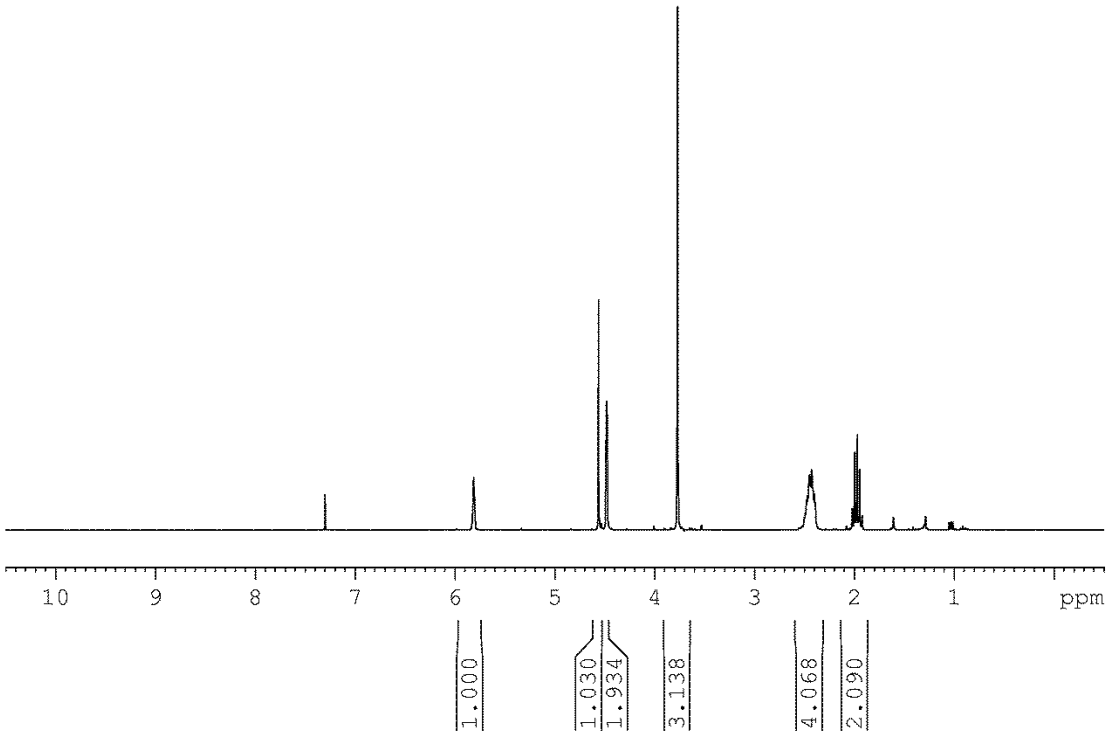
CBr3

3h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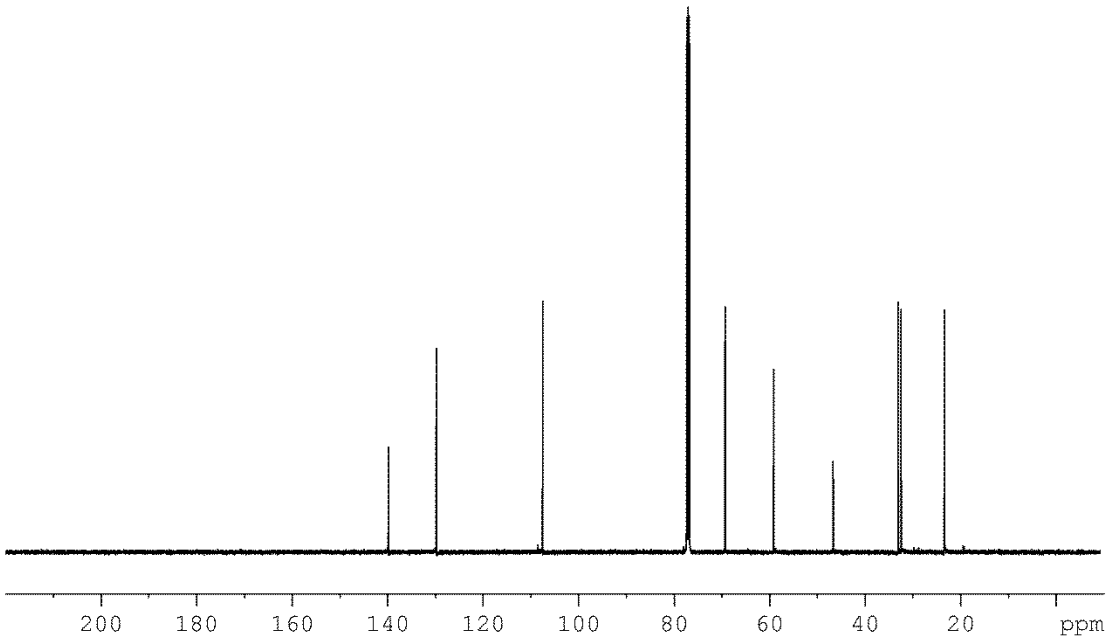
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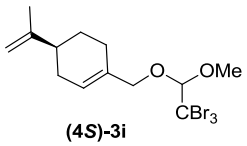
O
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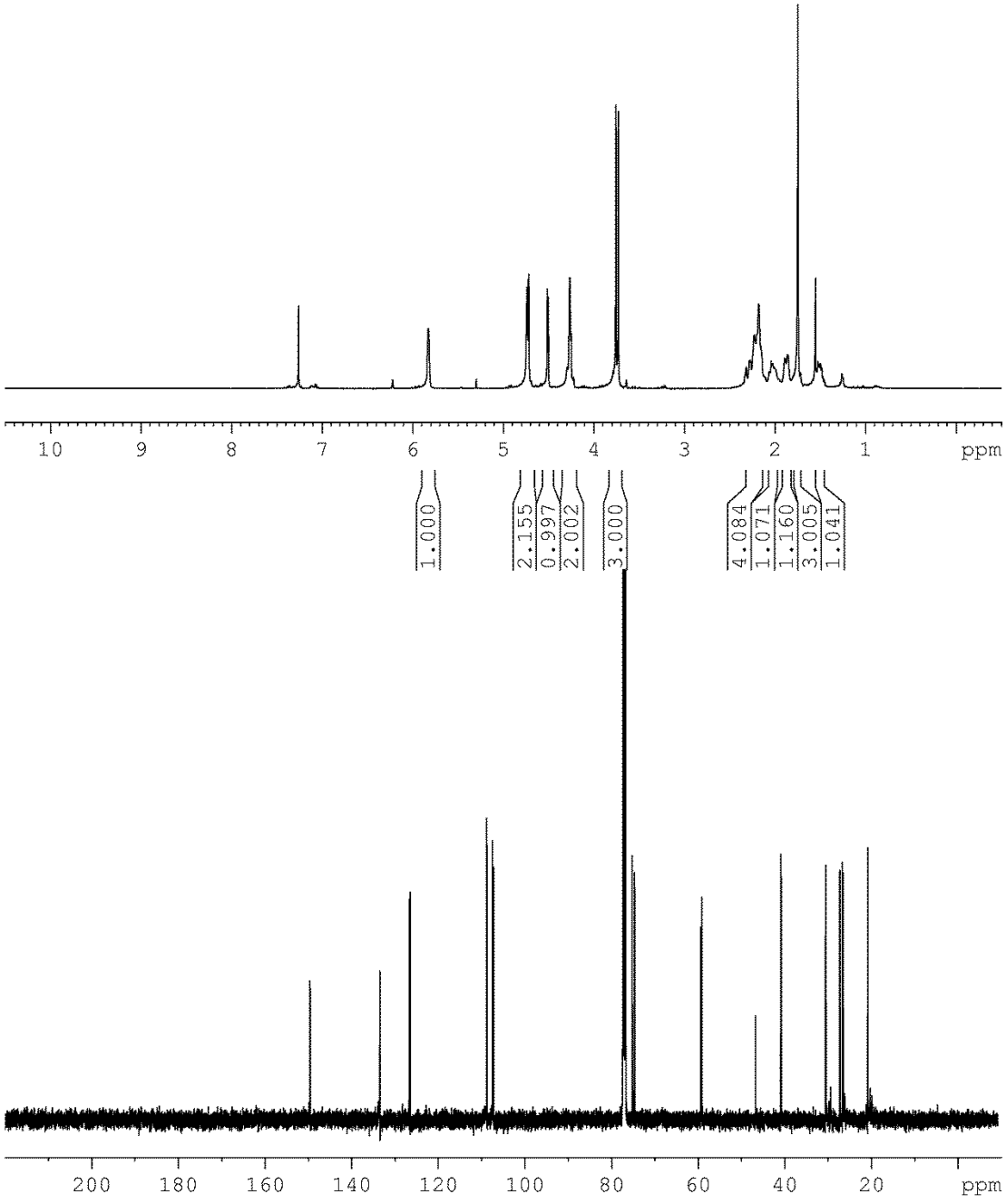
CBr3

(4*S*)-3i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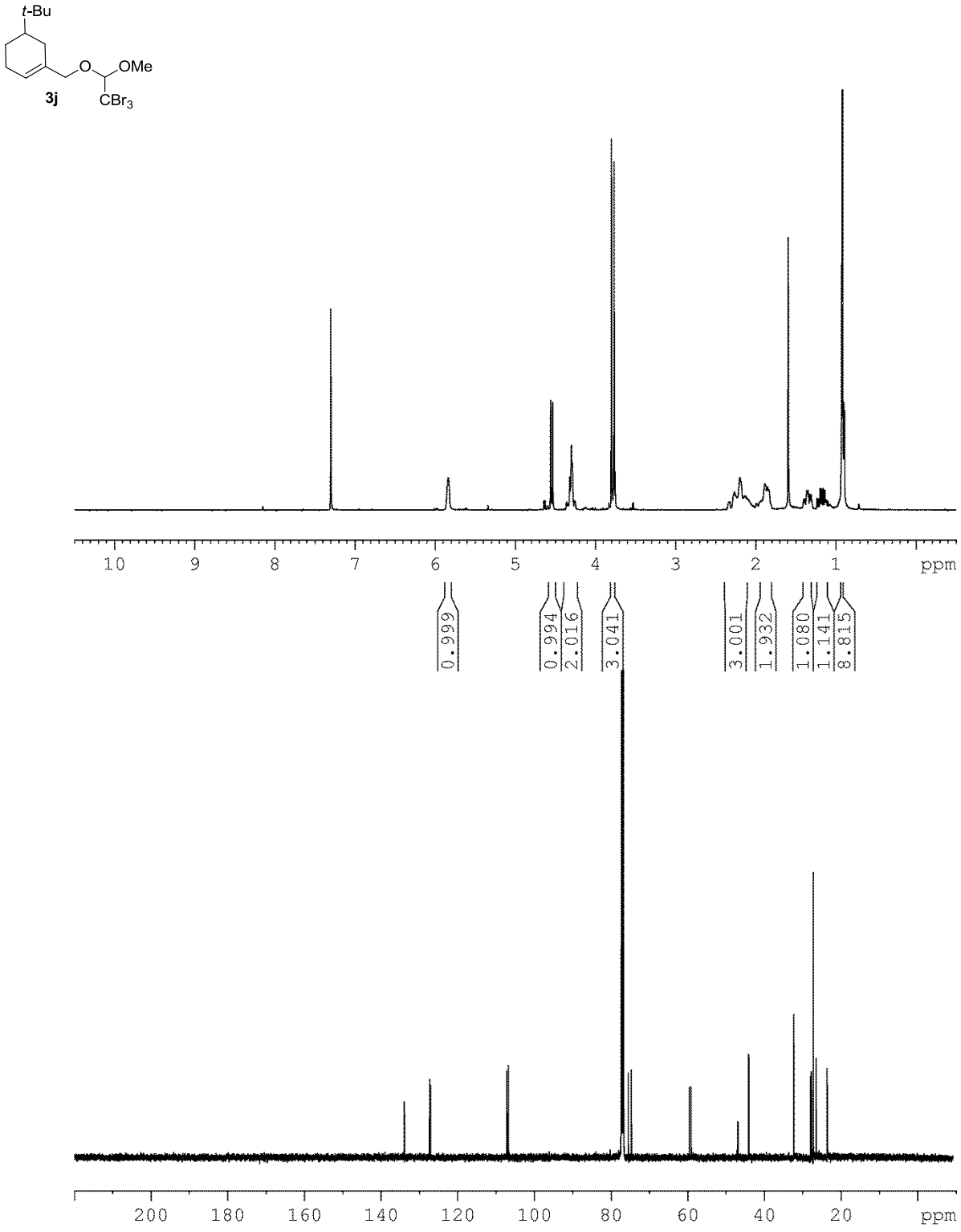
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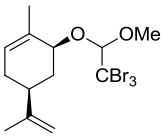
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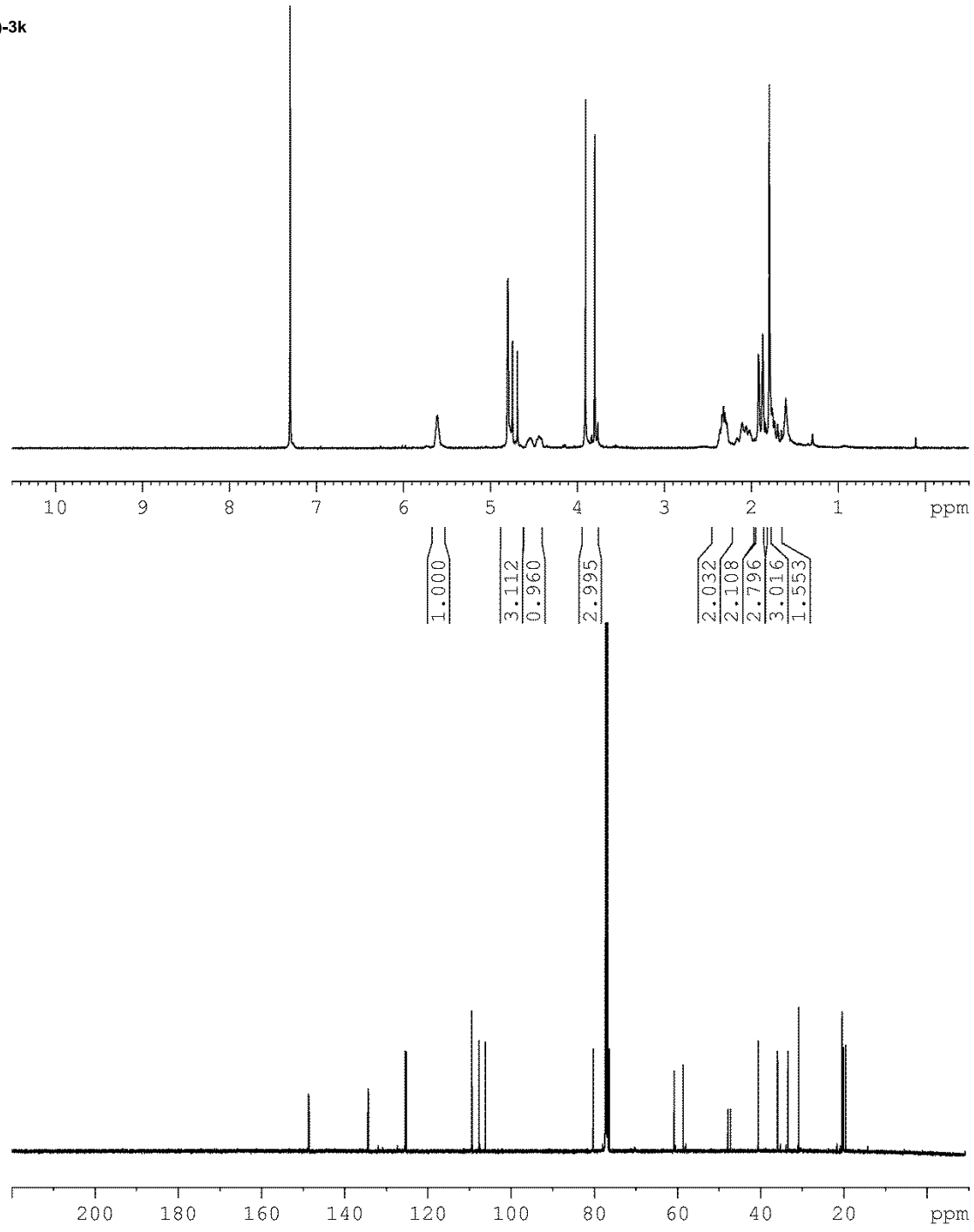
CBr3

(4*S*, 6*S*)-3k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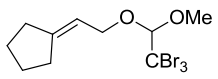
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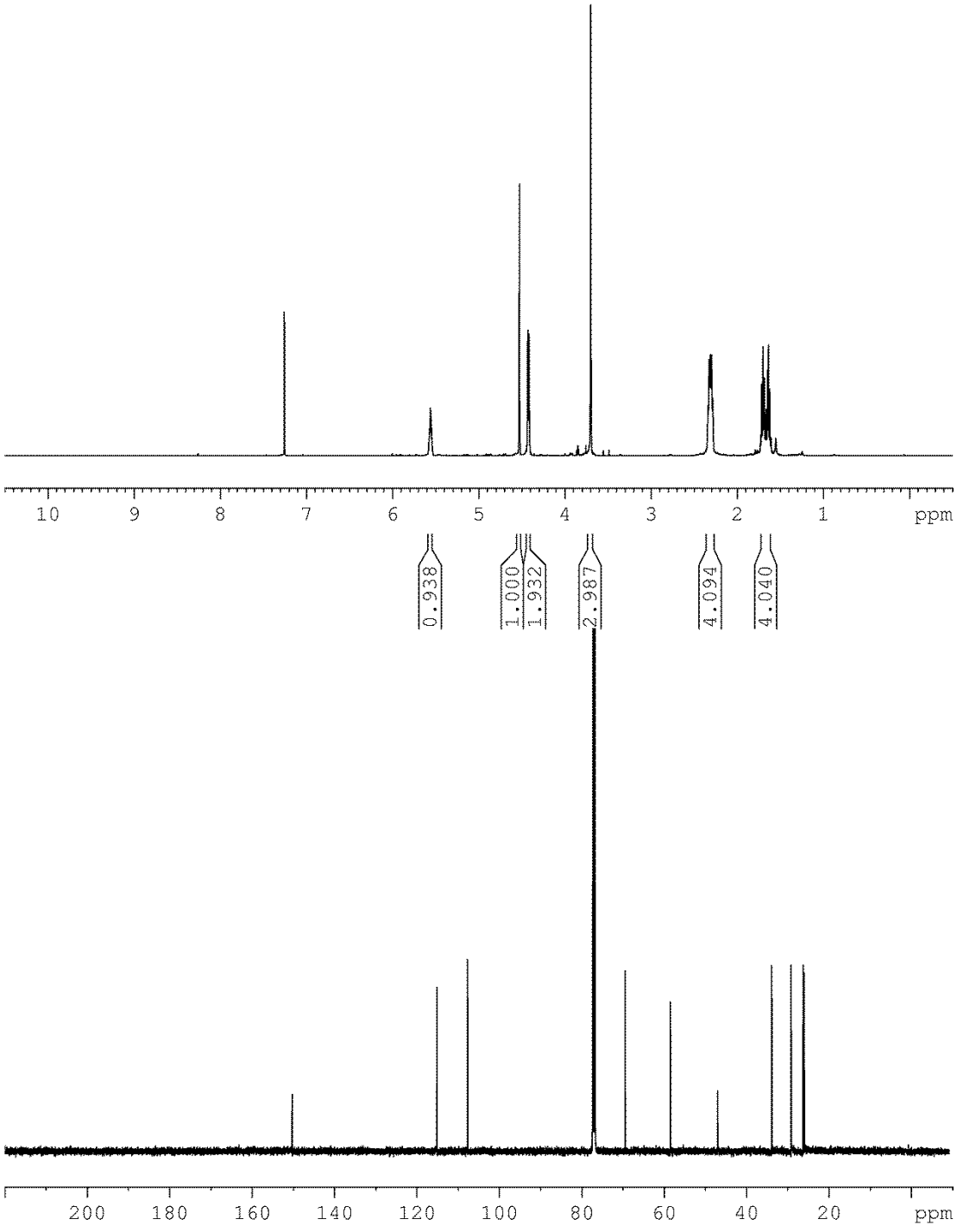
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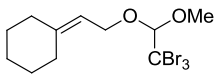
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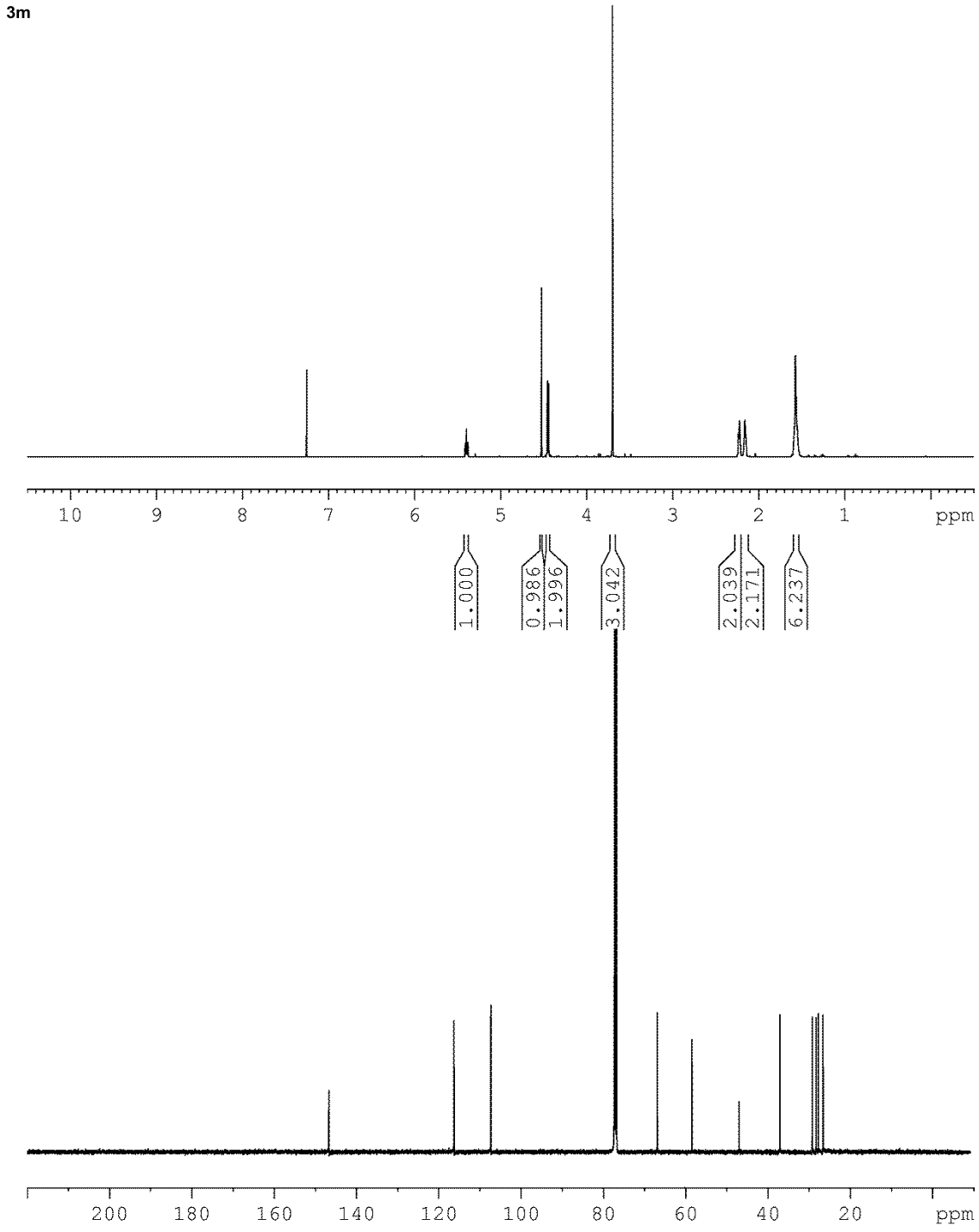
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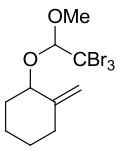
OMe
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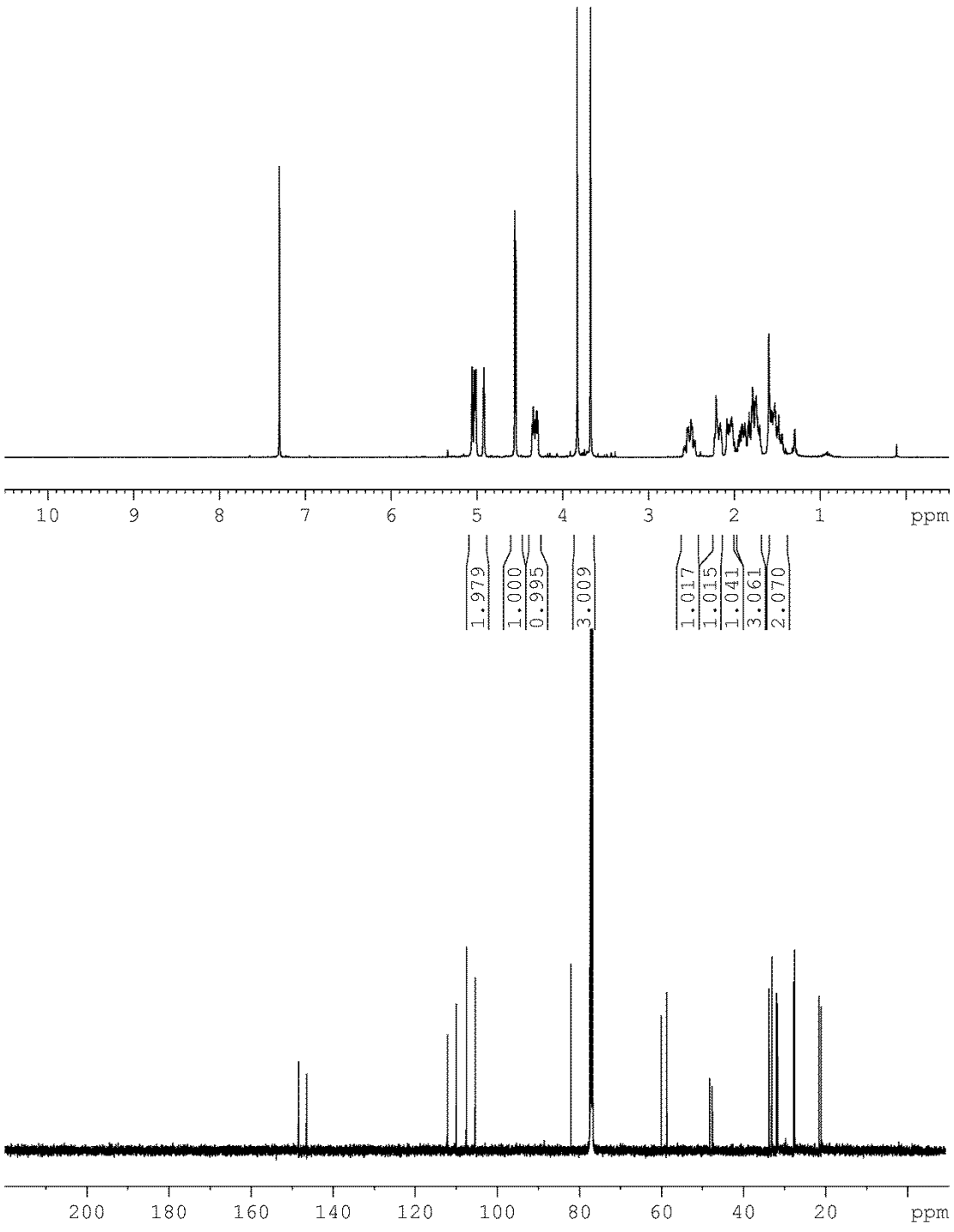
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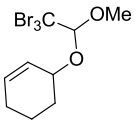
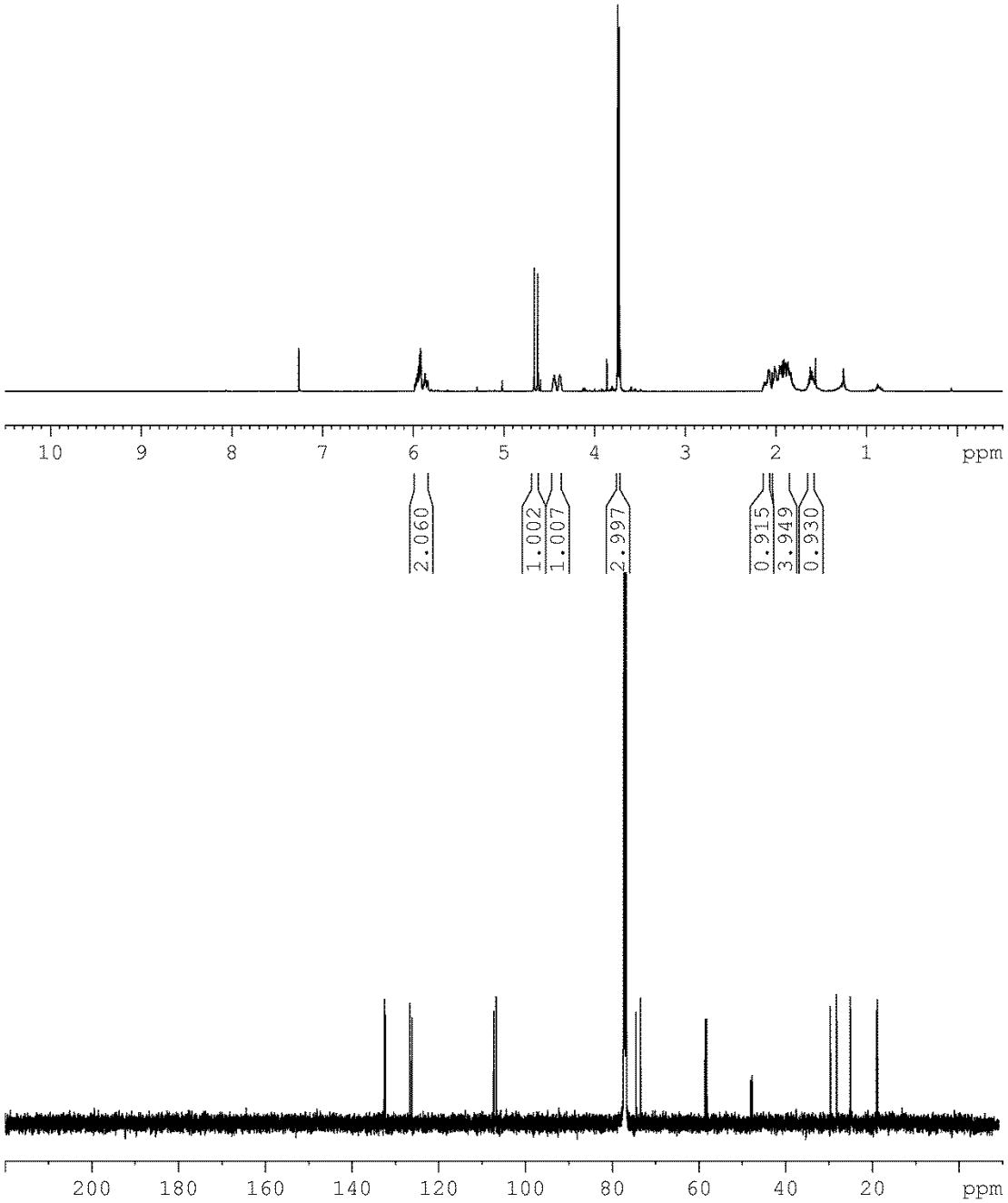

Br3C
OMe
O

3o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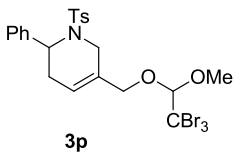
Ts
Ph
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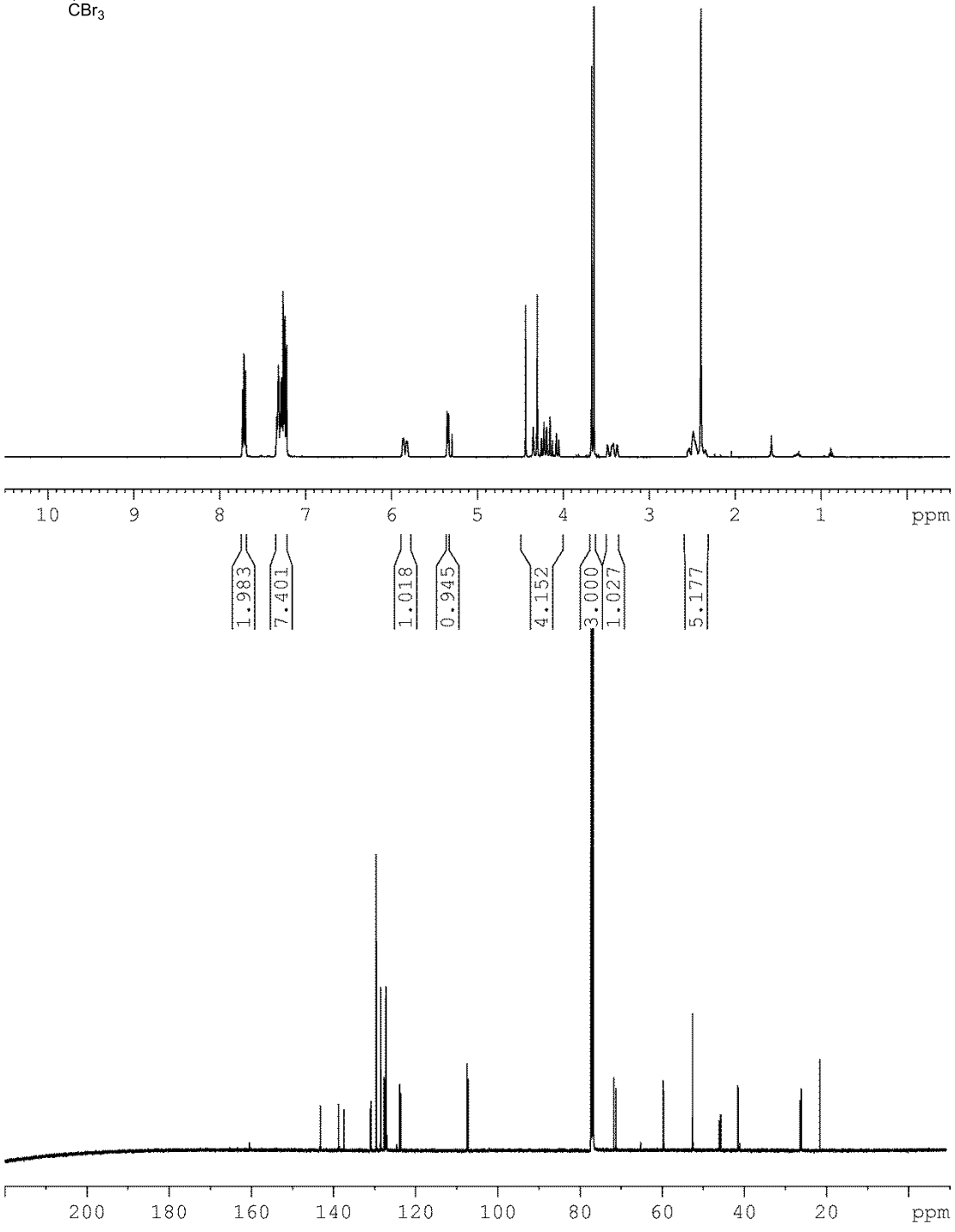
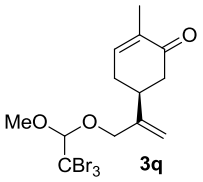
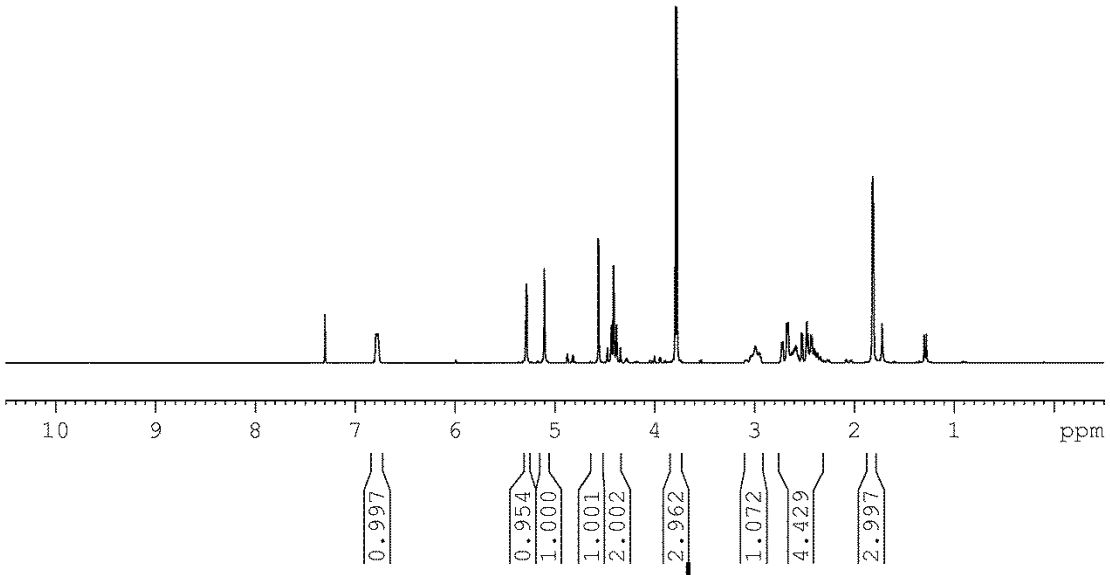
OMe
CBr3

3p


10
9
8
7
6
5
4
3
2
1
ppm
1.983
7.401
1.018
0.945
4.152
3.000
1.027
5.177
200
180
160
140
120
100
80
60
40
20
ppm


O
MeO
O
CBr3

3q


10
9
8
7
6
5
4
3
2
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ppm
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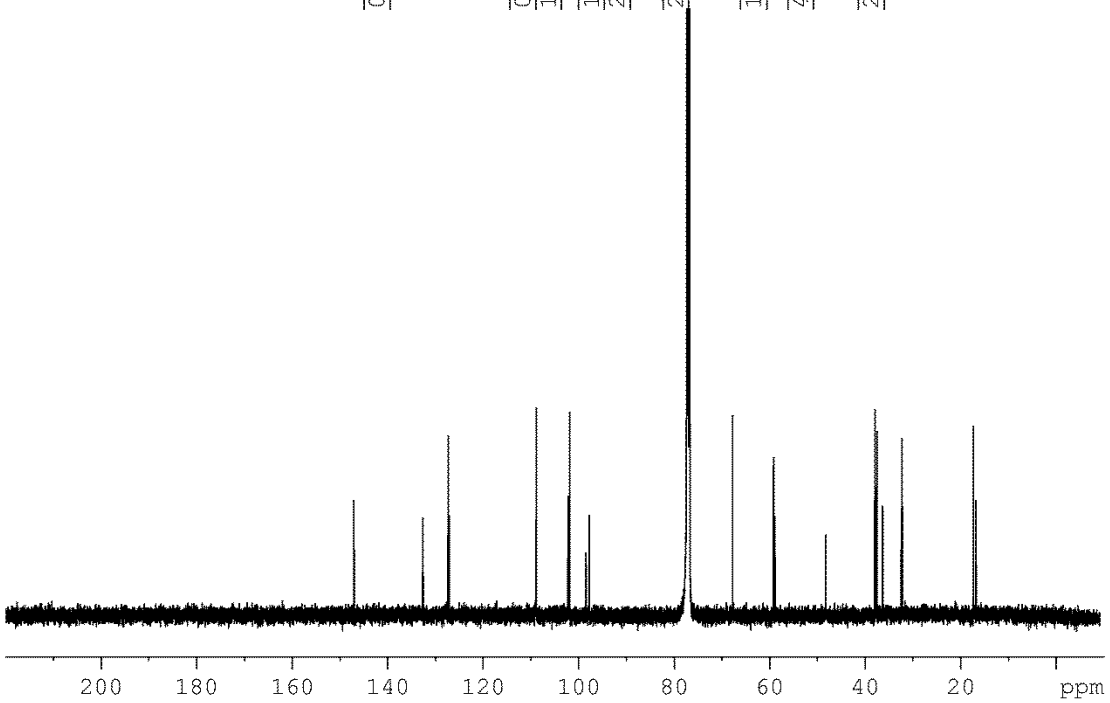
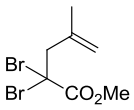
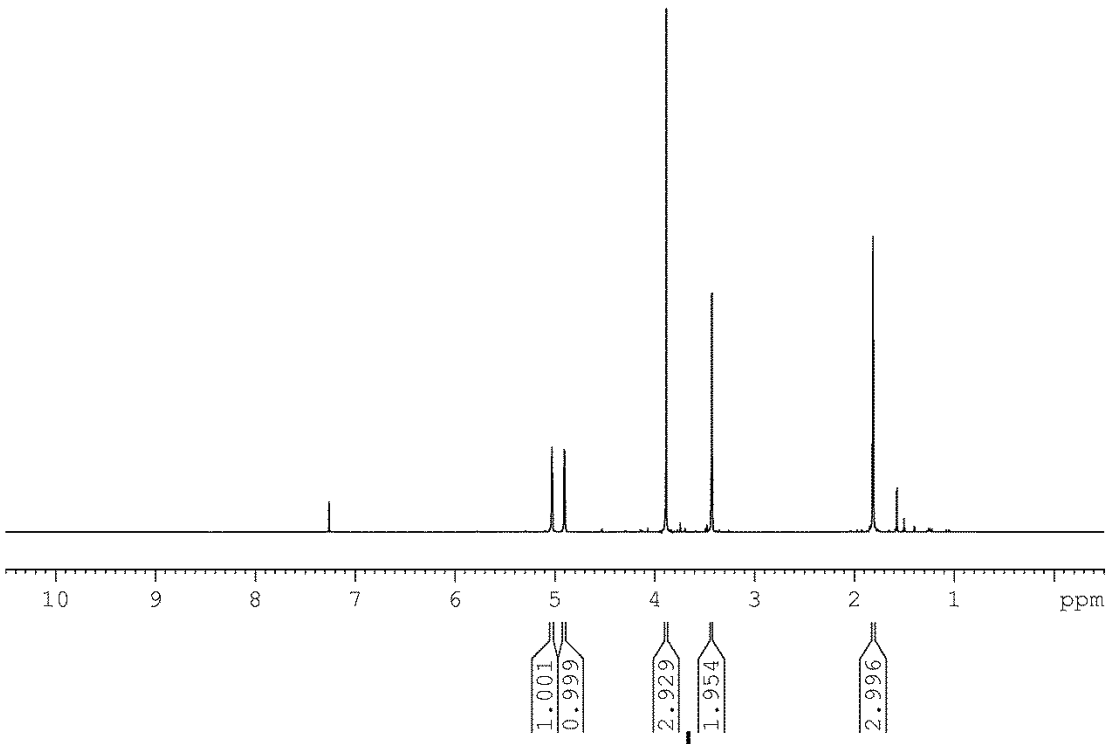
0.954
1.000
1.001
2.002
2.962
1.072
4.429
2.997


200
180
160
140
120
100
80
60
40
20
ppm


Br
Br
CO2Me

5a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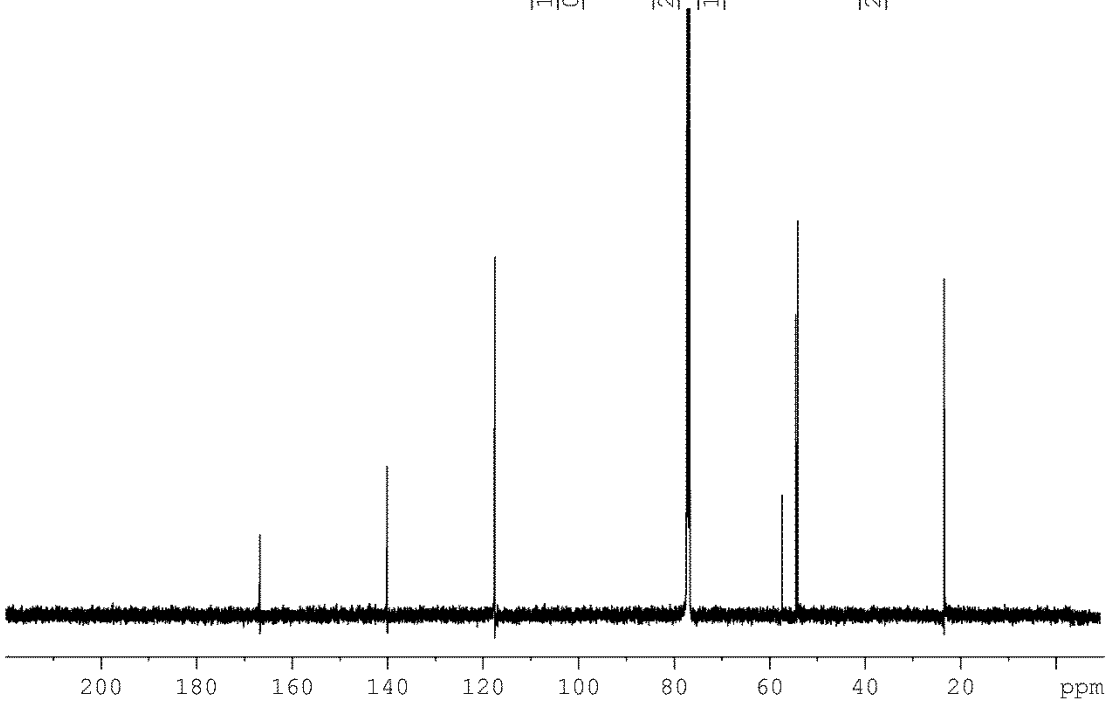
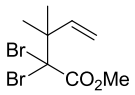
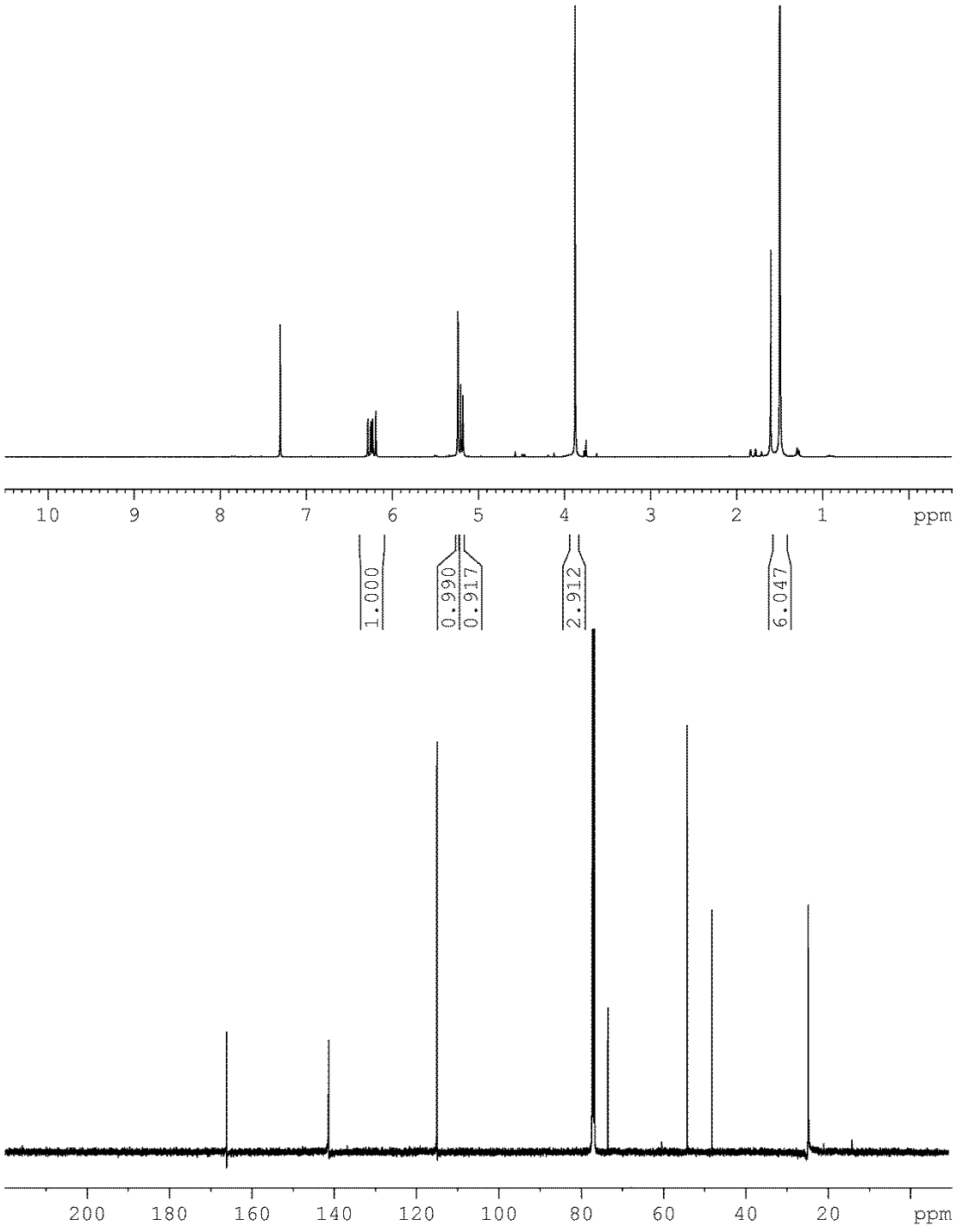
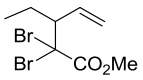
9
8
7
6
5
4
3
2
1
ppm
1.001
0.999
2.929
1.954
2.996


200
180
160
140
120
100
80
60
40
20
ppm

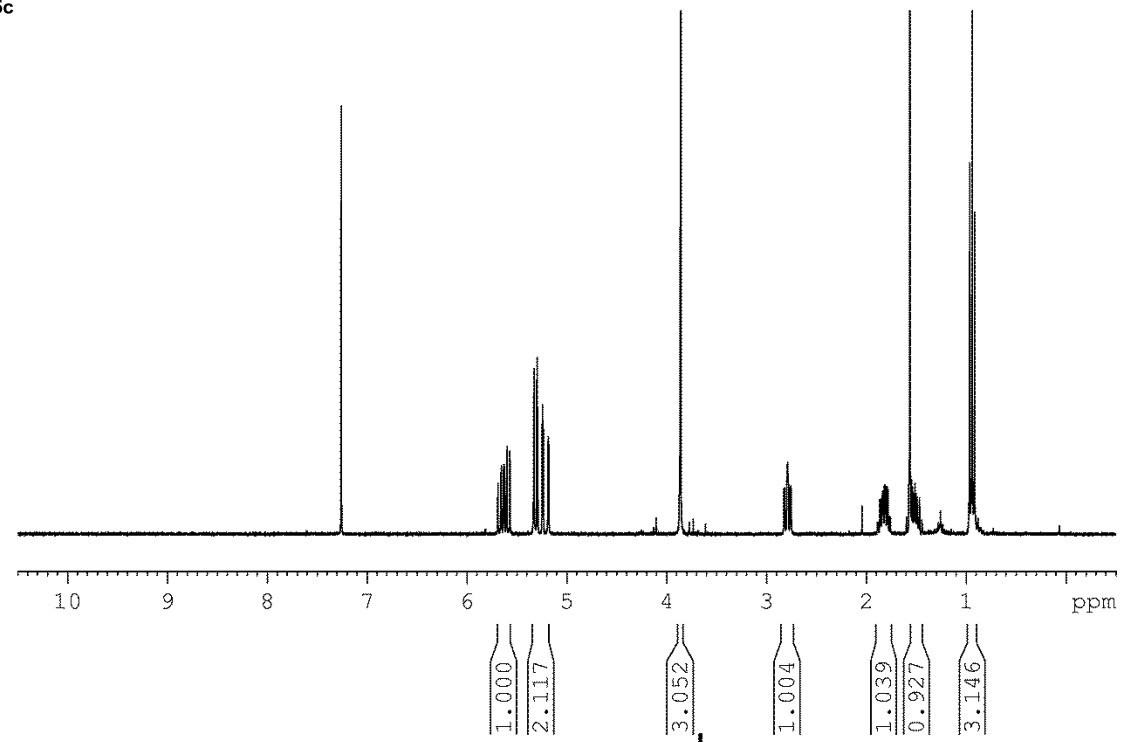

Br
Br
CO2Me

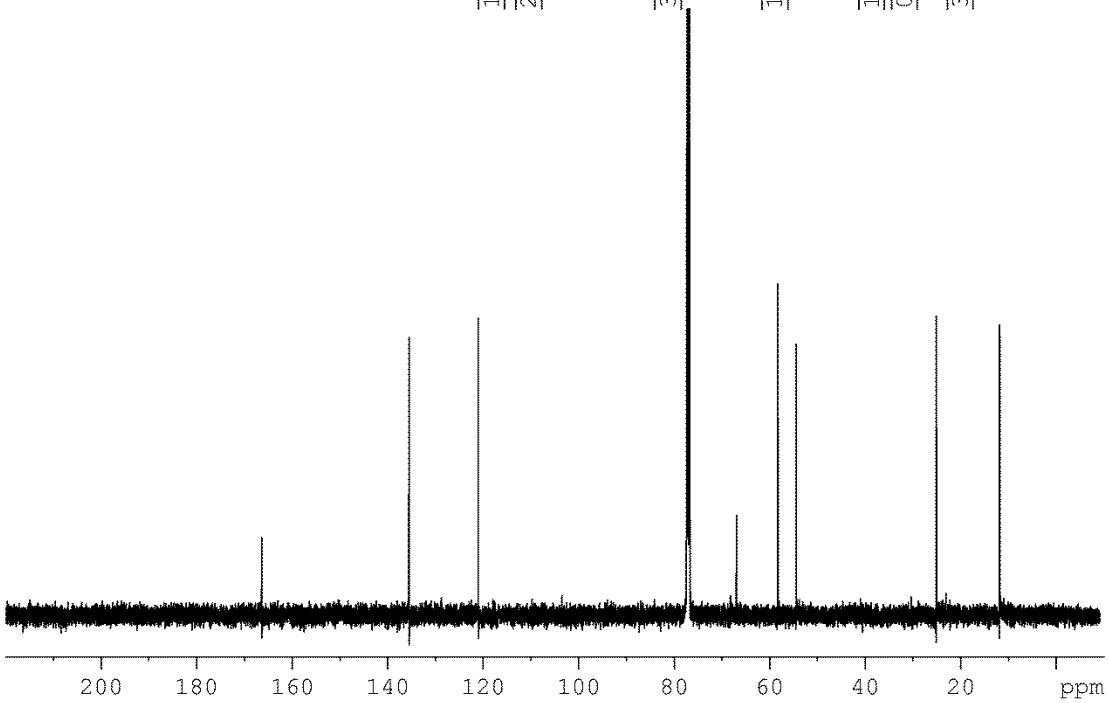
5b

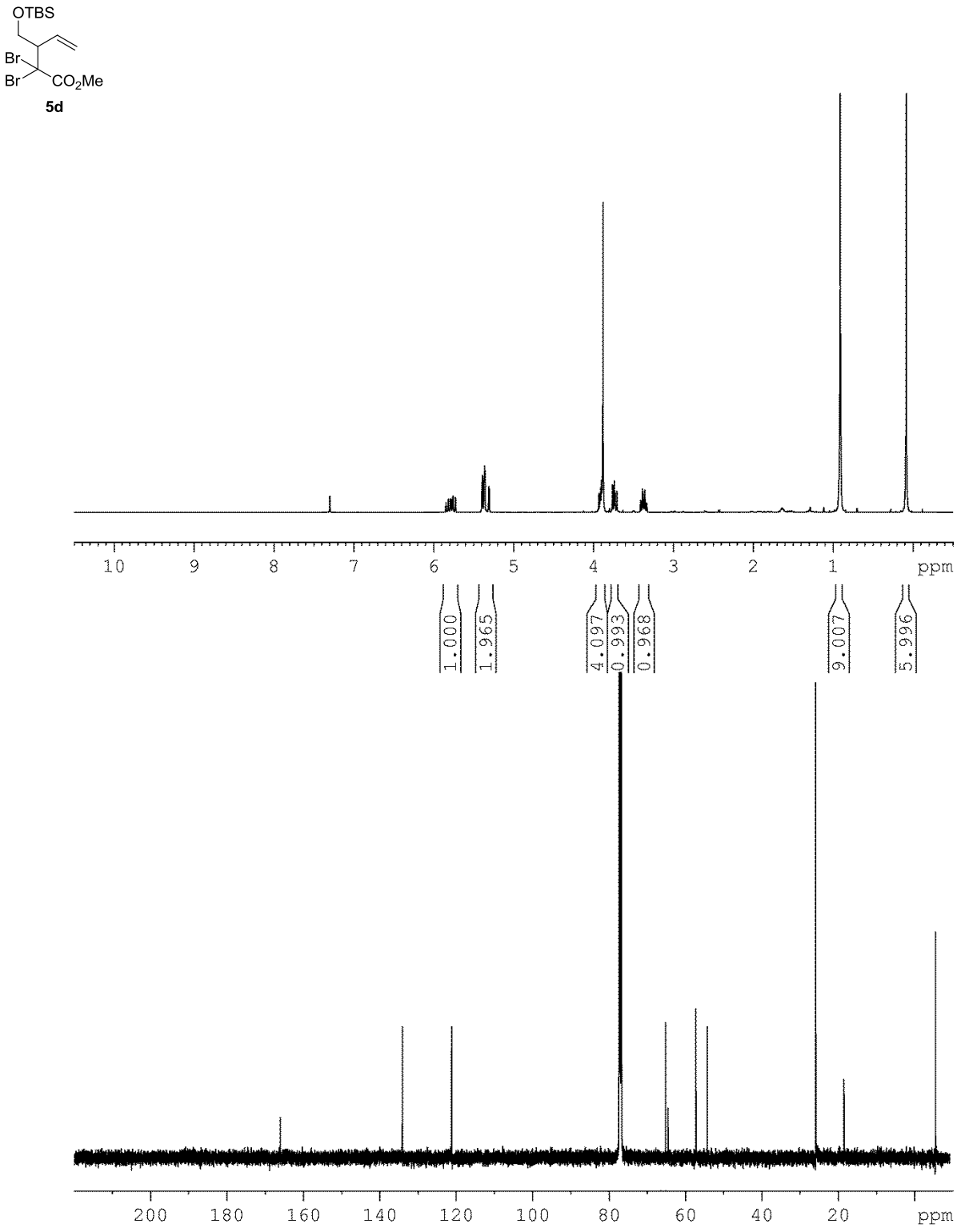

10
9
8
7
6
5
4
3
2
1
ppm
1.000
0.990
0.917
2.912
6.047
200
180
160
140
120
100
80
60
40
20
ppm

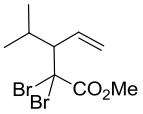

Br
Br
CO2Me

5c

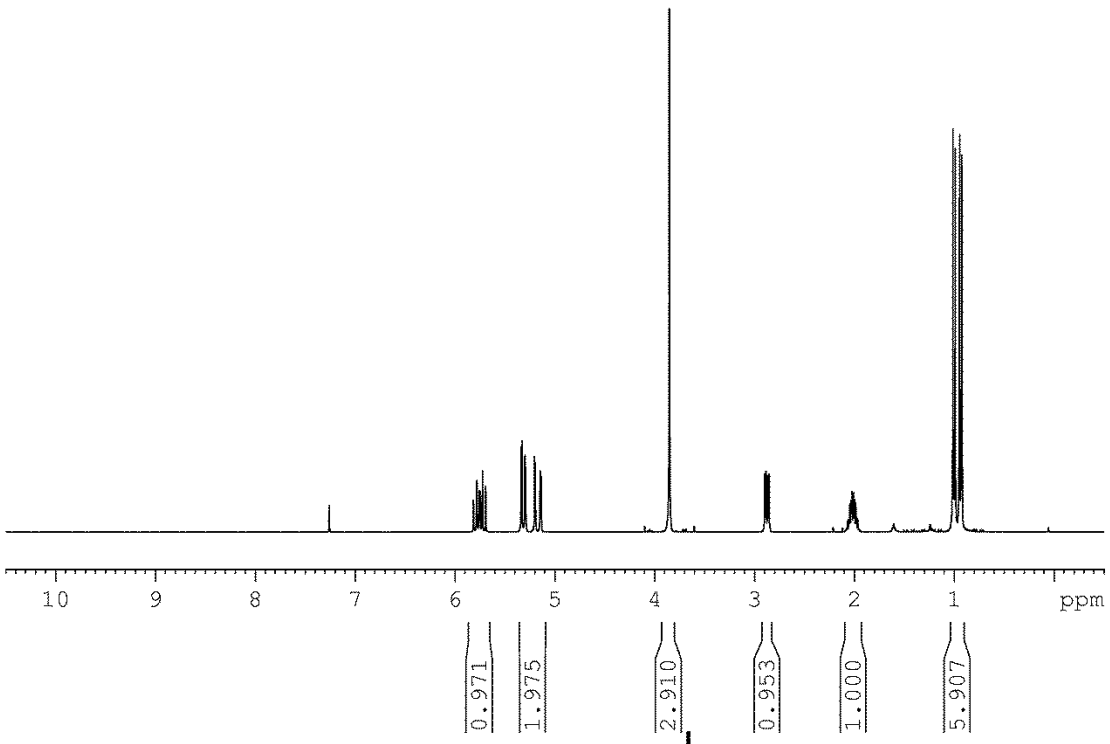

10
9
8
7
6
5
4
3
2
1
ppm
1.000
2.117
3.052
1.004
1.039
0.927
3.146


200
180
160
140
120
100
80
60
40
20
ppm


OTBS
Br
Br
CO2Me
5d
10
9
8
7
6
5
4
3
2
1
ppm
1.000
1.965
4.097
0.993
0.968
9.007
5.996
200
180
160
140
120
100
80
60
40
20
ppm


Br
Br
CO2Me

5e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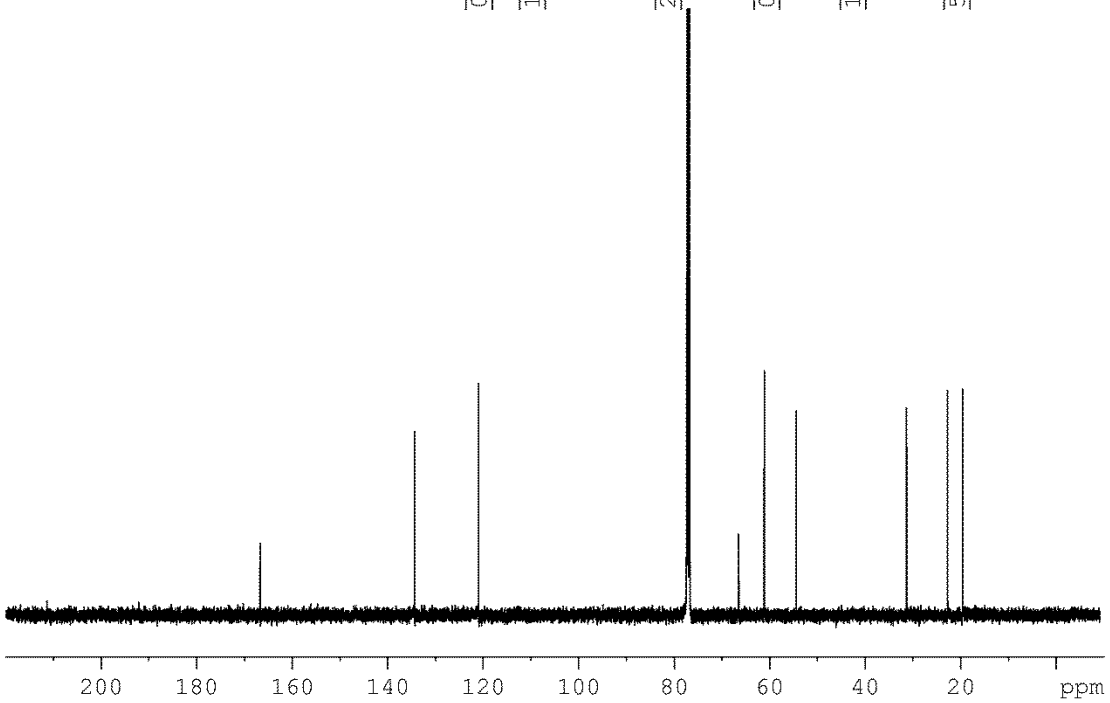
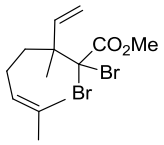
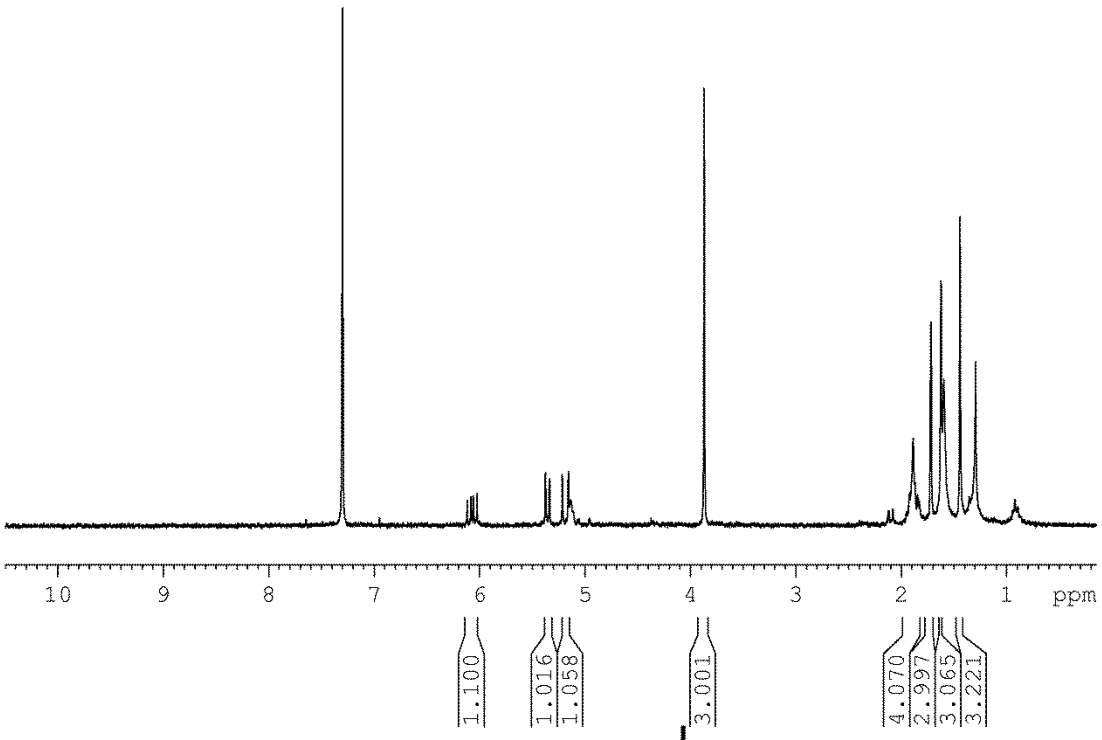
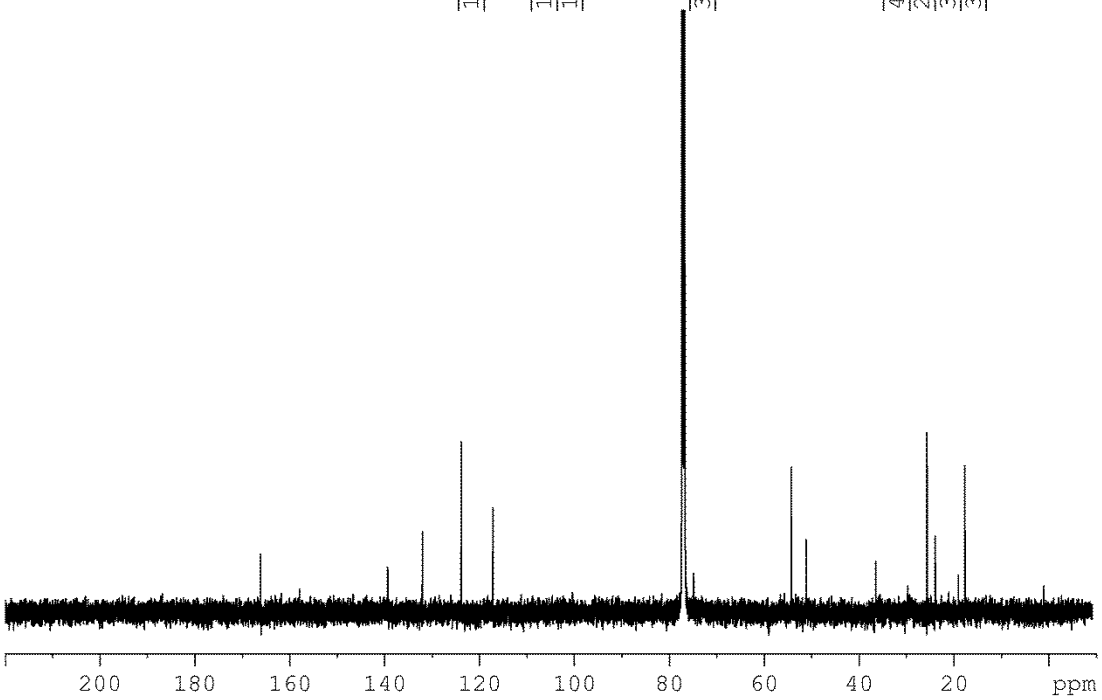
8
7
6
5
4
3
2
1
ppm
0.971
1.975
2.910
0.953
1.000
5.907

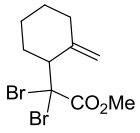

200
180
160
140
120
100
80
60
40
20
ppm


CO2Me
Br
Br

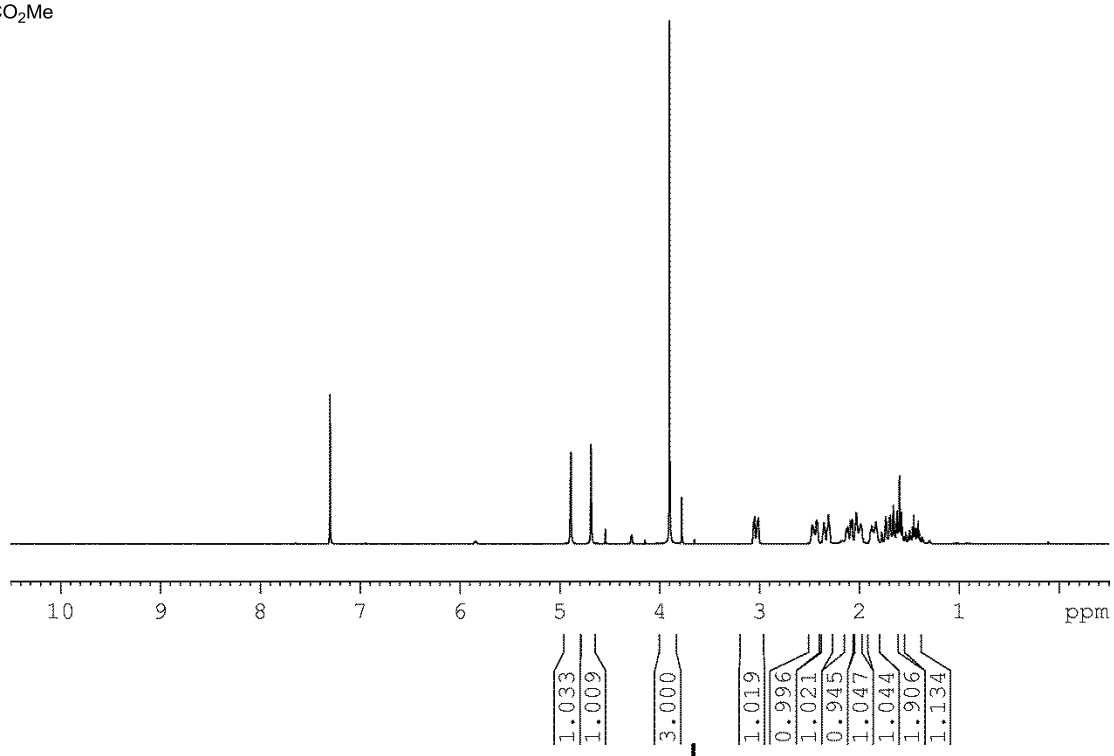
5f

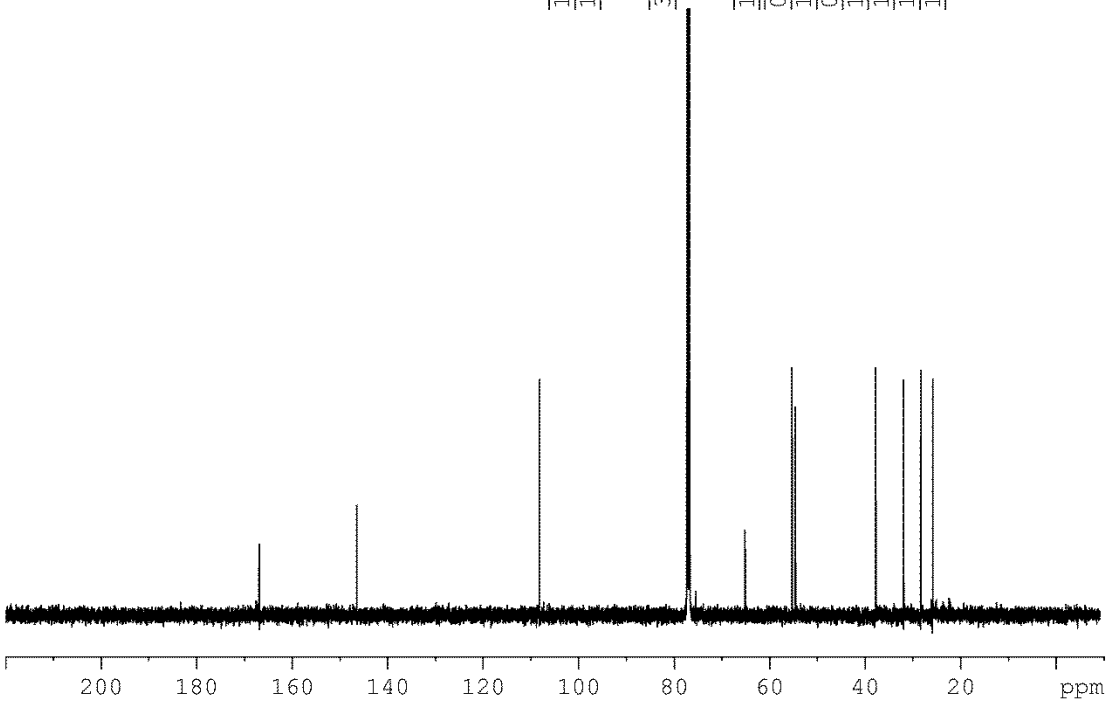

10
9
8
7
6
5
4
3
2
1
ppm
1.100
1.016
1.058
3.001
4.070
2.997
3.065
3.221

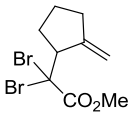

200
180
160
140
120
100
80
60
40
20
ppm


Br
CO2Me
Br

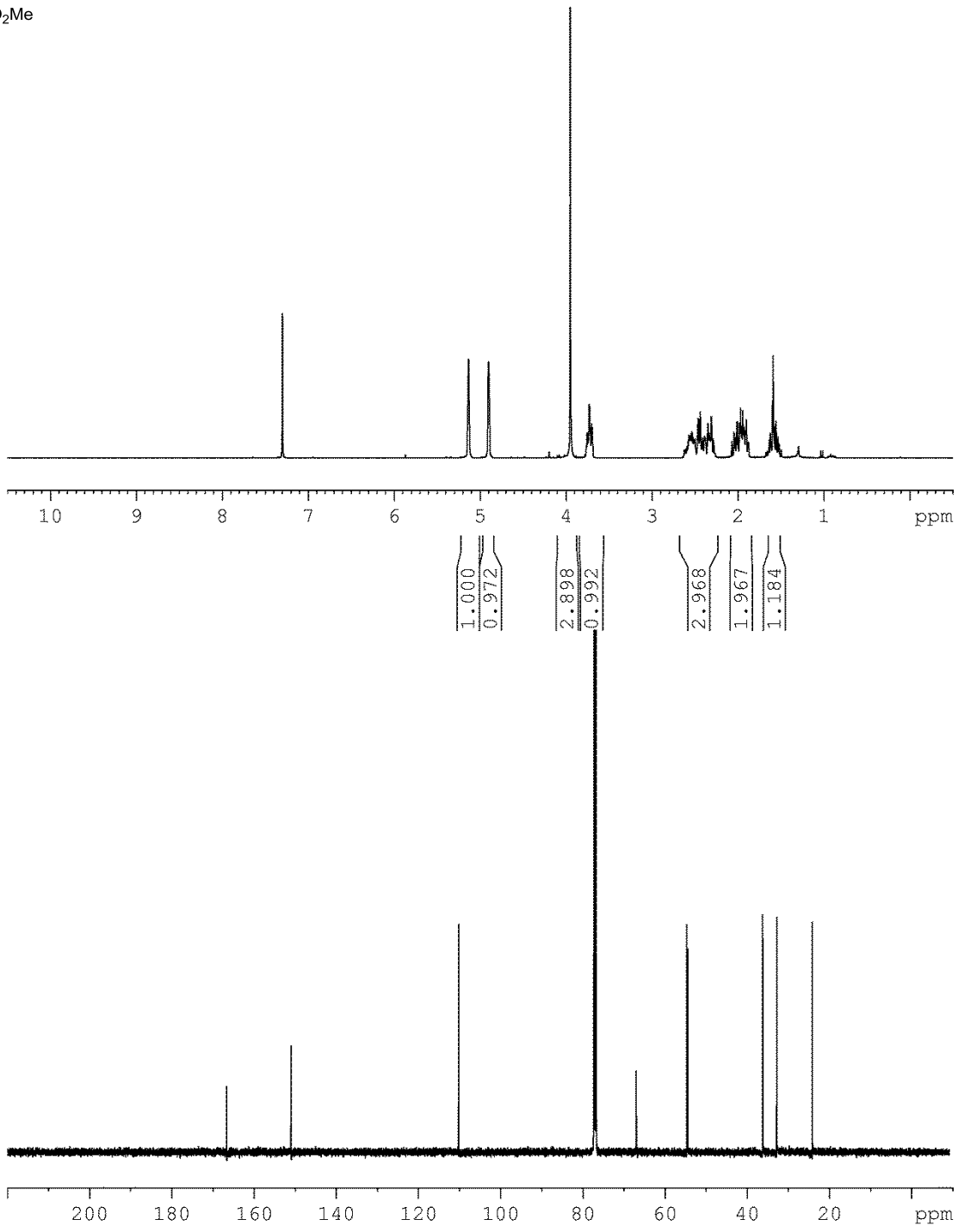
5g

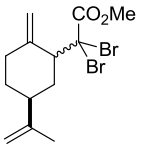

10
9
8
7
6
5
4
3
2
1
ppm
1.033
1.009
3.000
1.019
0.996
1.021
0.945
1.047
1.044
1.906
1.134


200
180
160
140
120
100
80
60
40
20
ppm

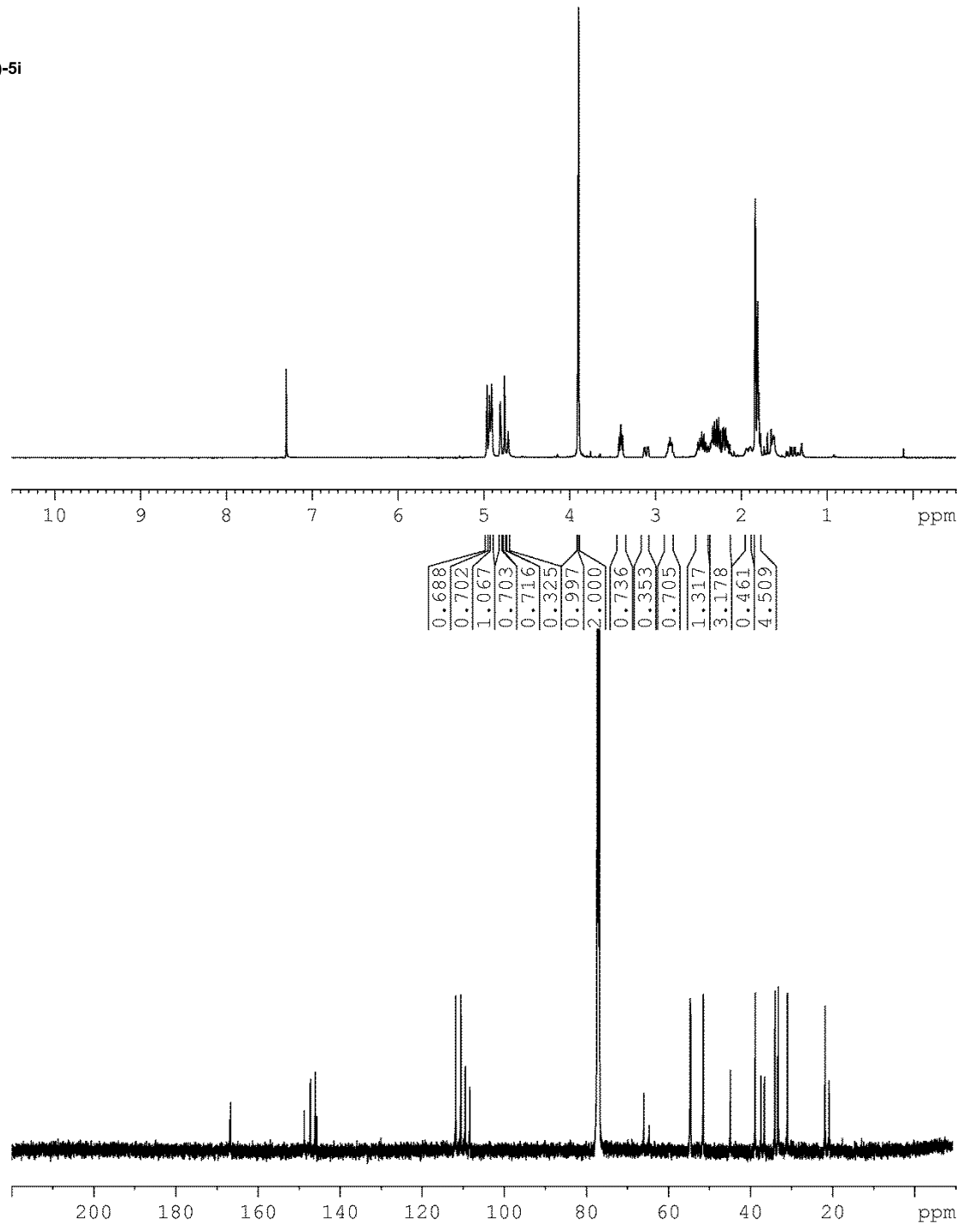

Br
Br
CO2Me

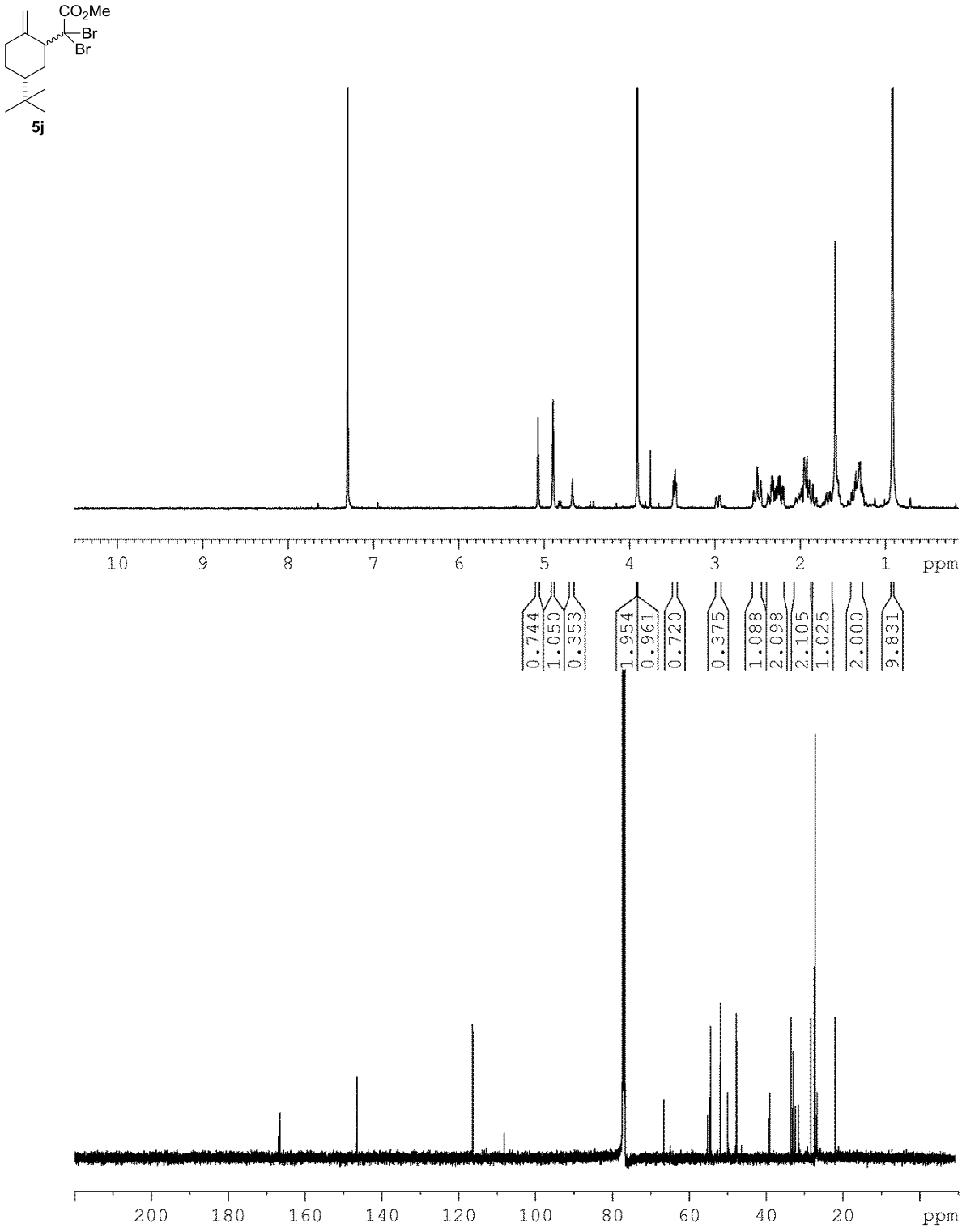
5h

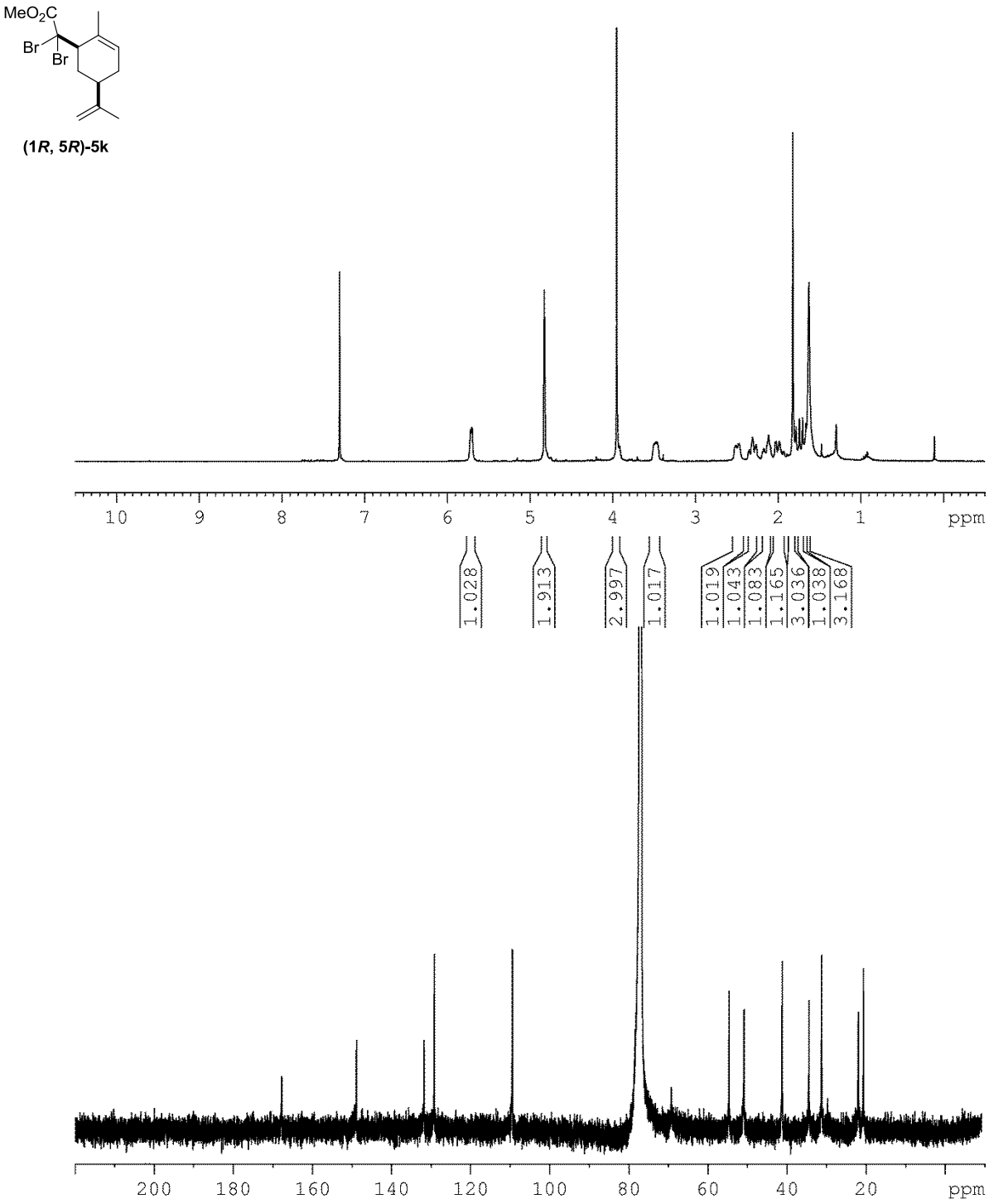

10
9
8
7
6
5
4
3
2
1
ppm
1.000
0.972
2.898
0.992
2.968
1.967
1.184
200
180
160
140
120
100
80
60
40
20
ppm


CO2Me
Br
Br

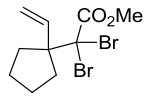
(5*S*)-5i


10
9
8
7
6
5
4
3
2
1
ppm
0.688
0.702
1.067
0.703
0.716
0.325
0.997
2.000
0.736
0.353
0.705
1.317
3.178
0.461
4.509
200
180
160
140
120
100
80
60
40
20
ppm

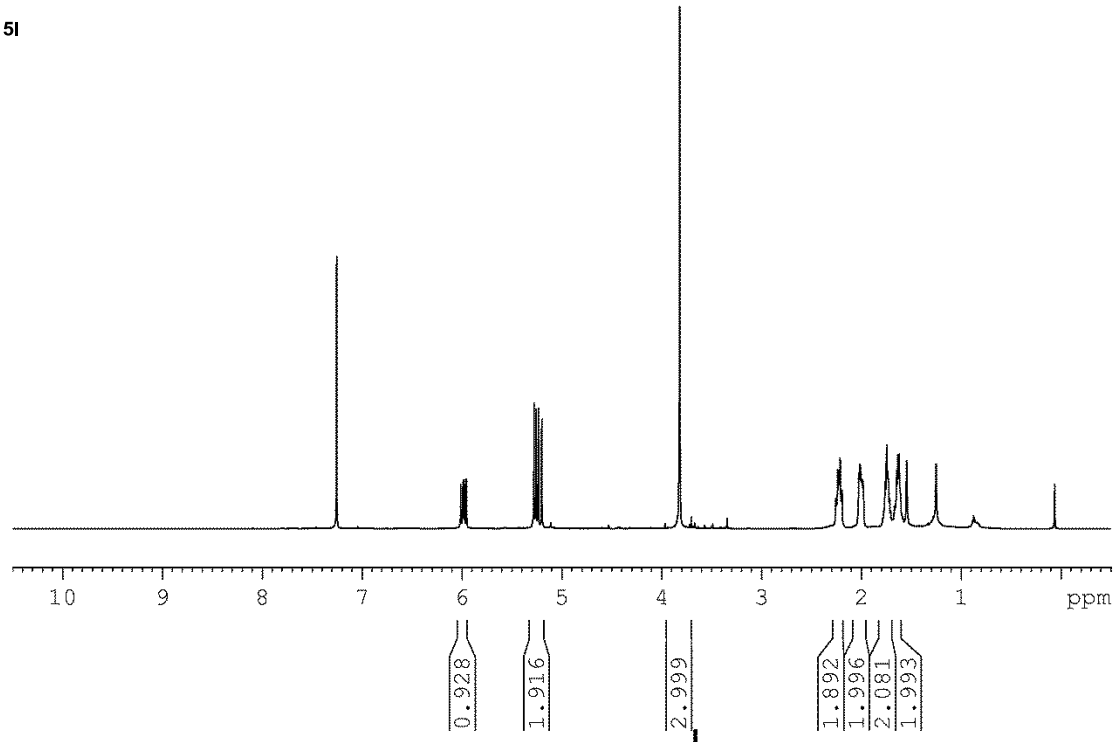

CO2Me
Br
Br
5j
10
9
8
7
6
5
4
3
2
1
ppm
0.744
1.050
0.353
1.954
0.961
0.720
0.375
1.088
2.098
2.105
1.025
2.000
9.831
200
180
160
140
120
100
80
60
40
20
ppm

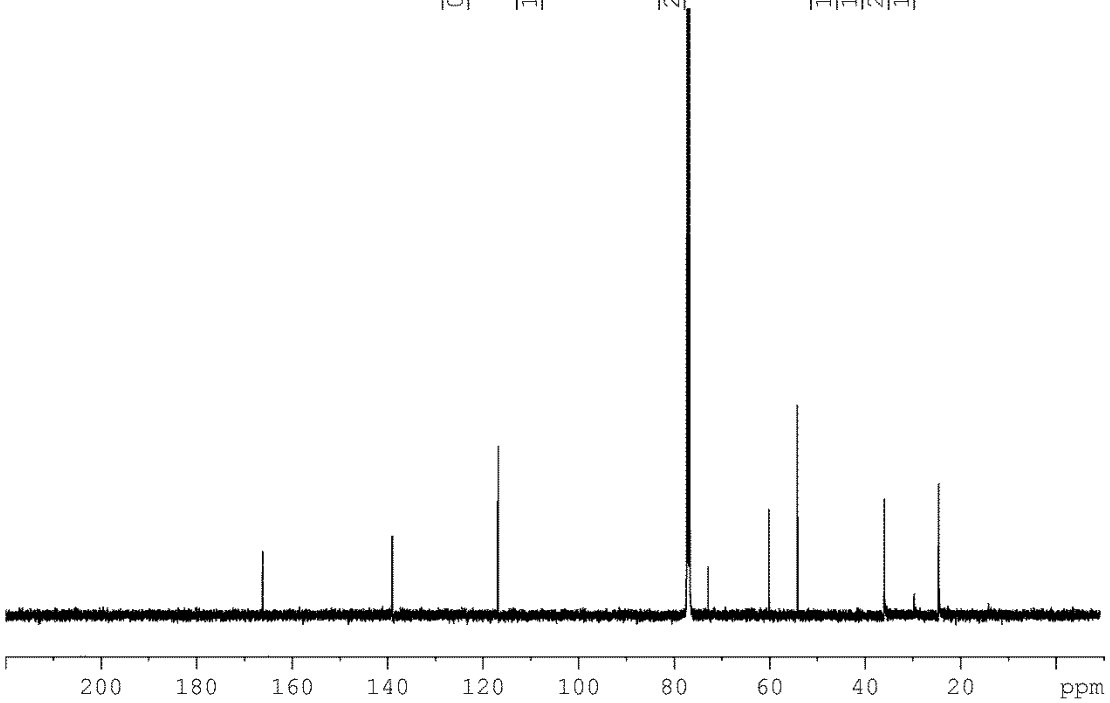

MeO2C
Br
Br
10
9
8
7
6
5
4
3
2
1
ppm
1.028
1.913
2.997
1.017
1.019
1.043
1.083
1.165
3.036
1.038
3.168
200
180
160
140
120
100
80
60
40
20
ppm

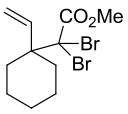
(1*R*, 5*R*)-5k


CO2Me
Br
Br

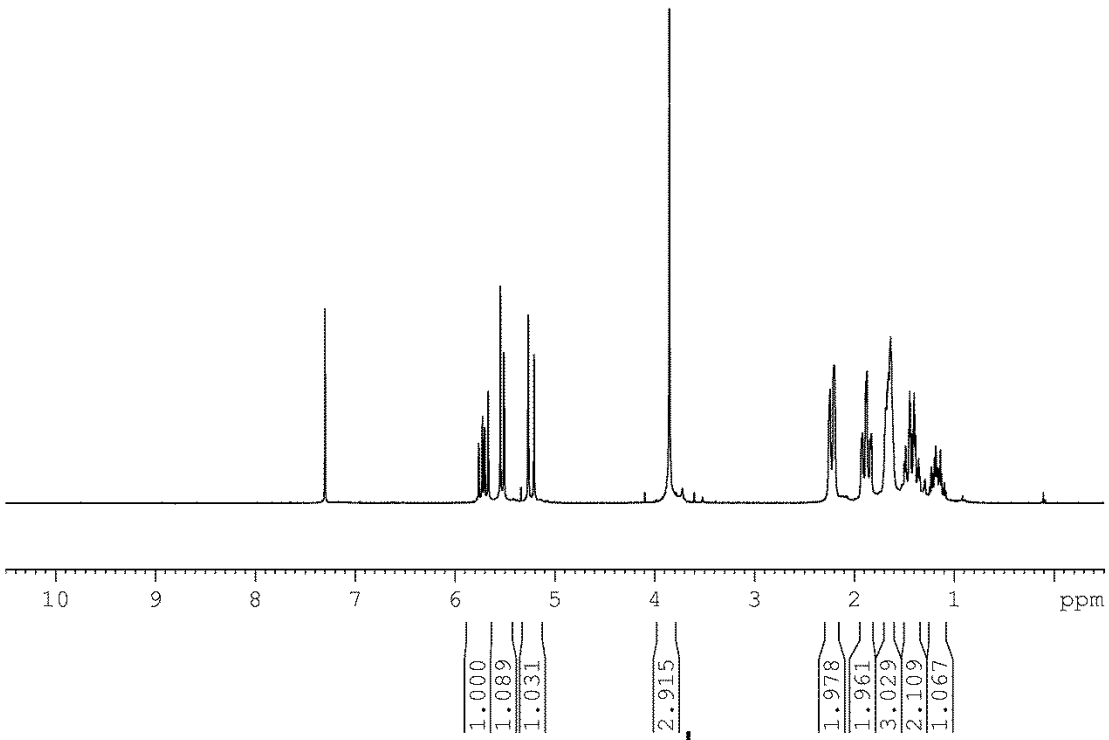
5l

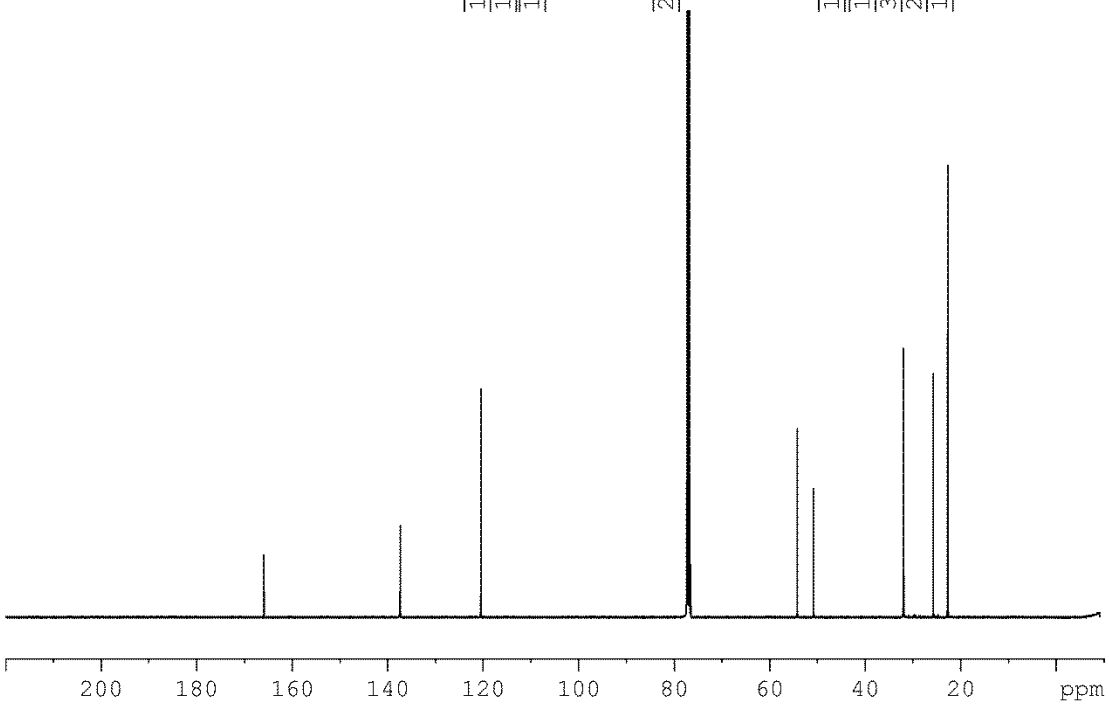

10
9
8
7
6
5
4
3
2
1
ppm
0.928
1.916
2.999
1.892
1.996
2.081
1.993

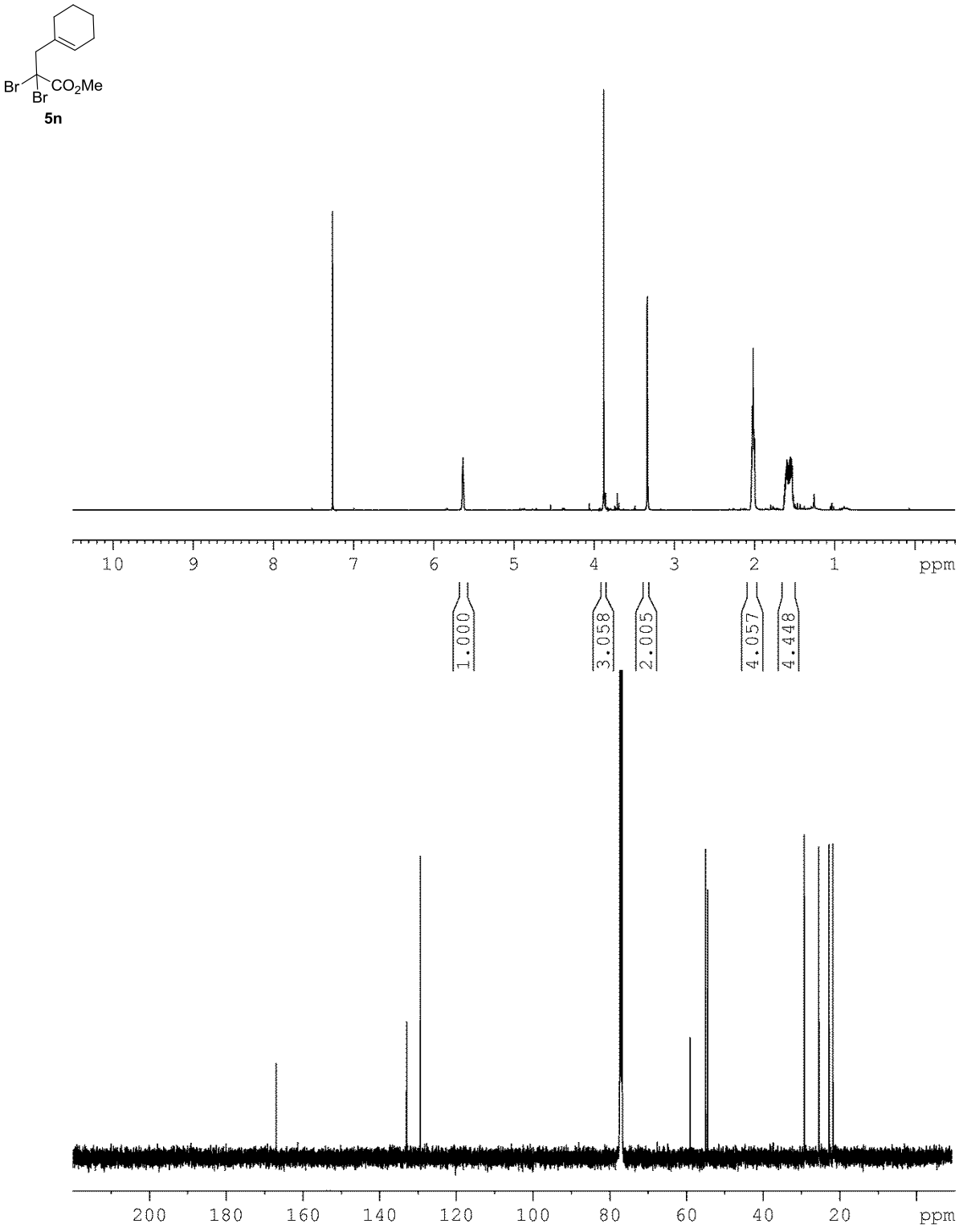

200
180
160
140
120
100
80
60
40
20
ppm

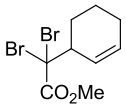

CO2Me
Br
Br

5m

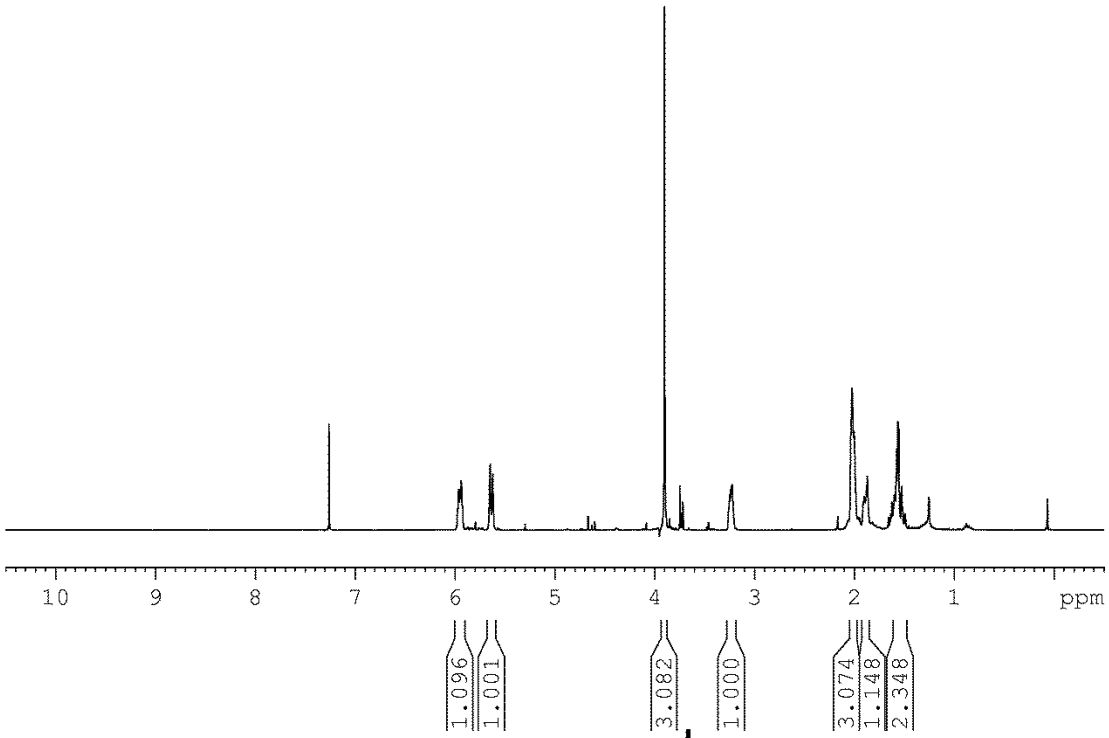

10
9
8
7
6
5
4
3
2
1
ppm
1.000
1.089
1.031
2.915
1.978
1.961
3.029
2.109
1.067

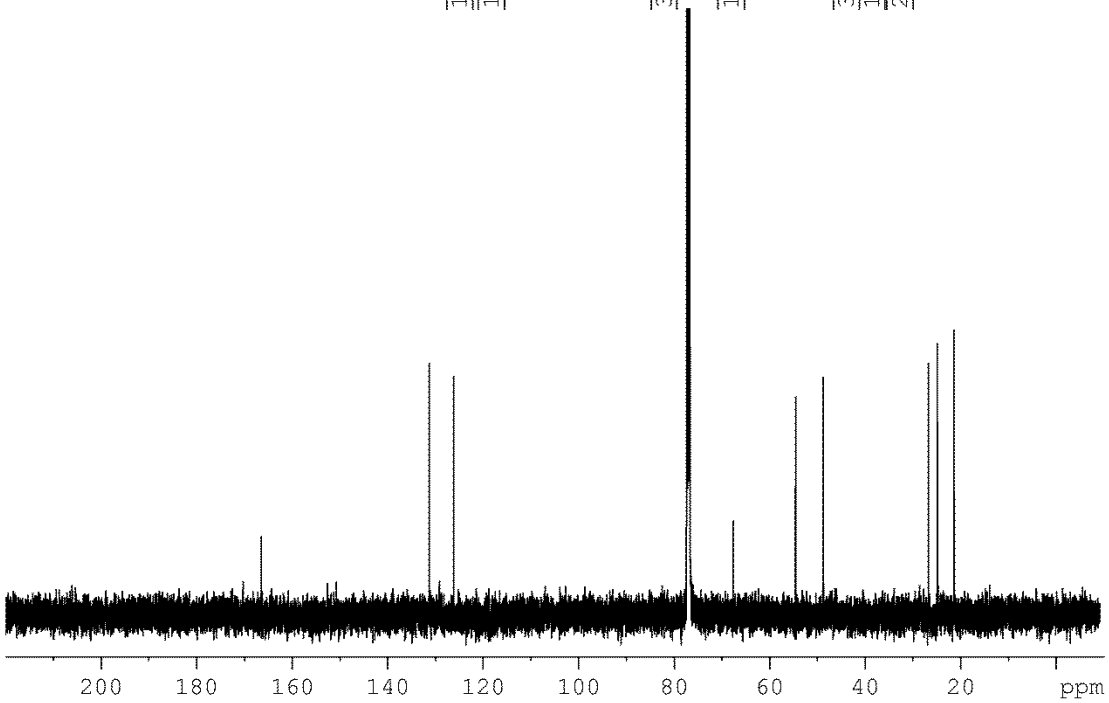

200
180
160
140
120
100
80
60
40
20
ppm

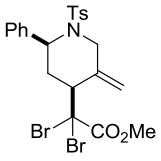

Br
Br
CO2Me
5n
10
9
8
7
6
5
4
3
2
1
ppm
1.000
3.058
2.005
4.057
4.448
200
180
160
140
120
100
80
60
40
20
ppm


Br
Br
CO2Me

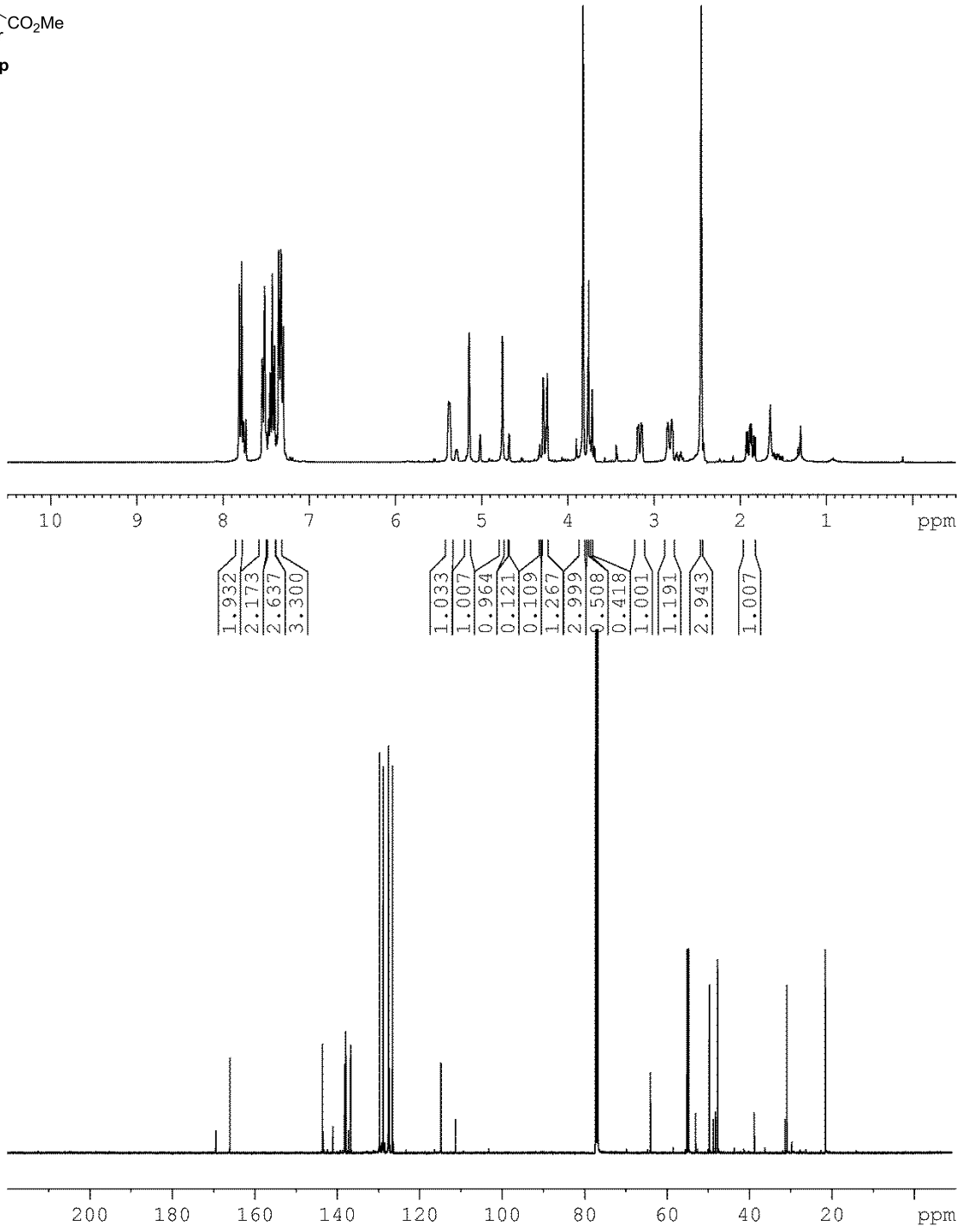
5o

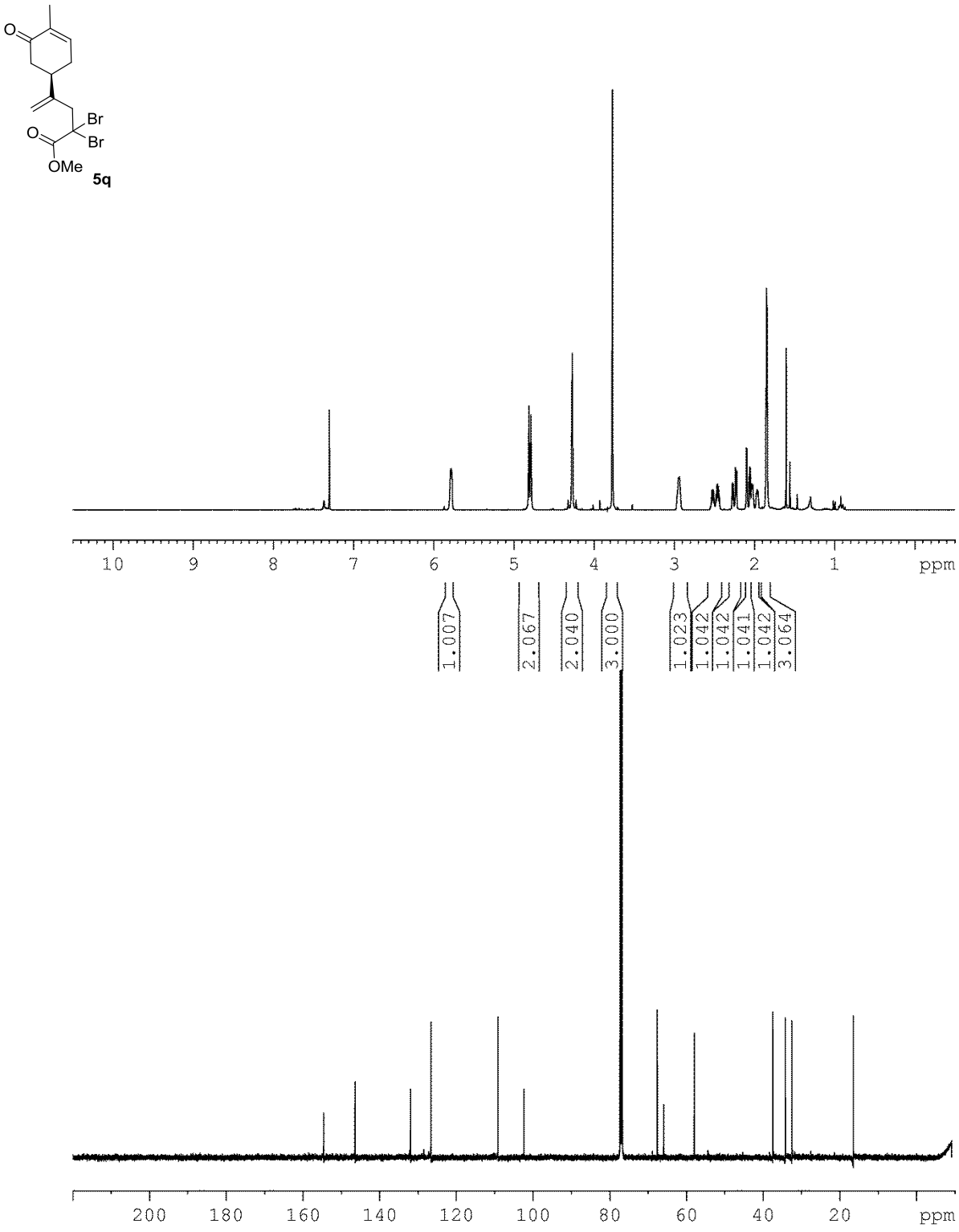

10
9
8
7
6
5
4
3
2
1
ppm
1.096
1.001
3.082
1.000
3.074
1.148
2.348

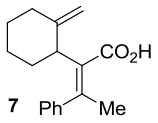

200
180
160
140
120
100
80
60
40
20
ppm


Ts
N
Ph
Br
Br
CO2Me

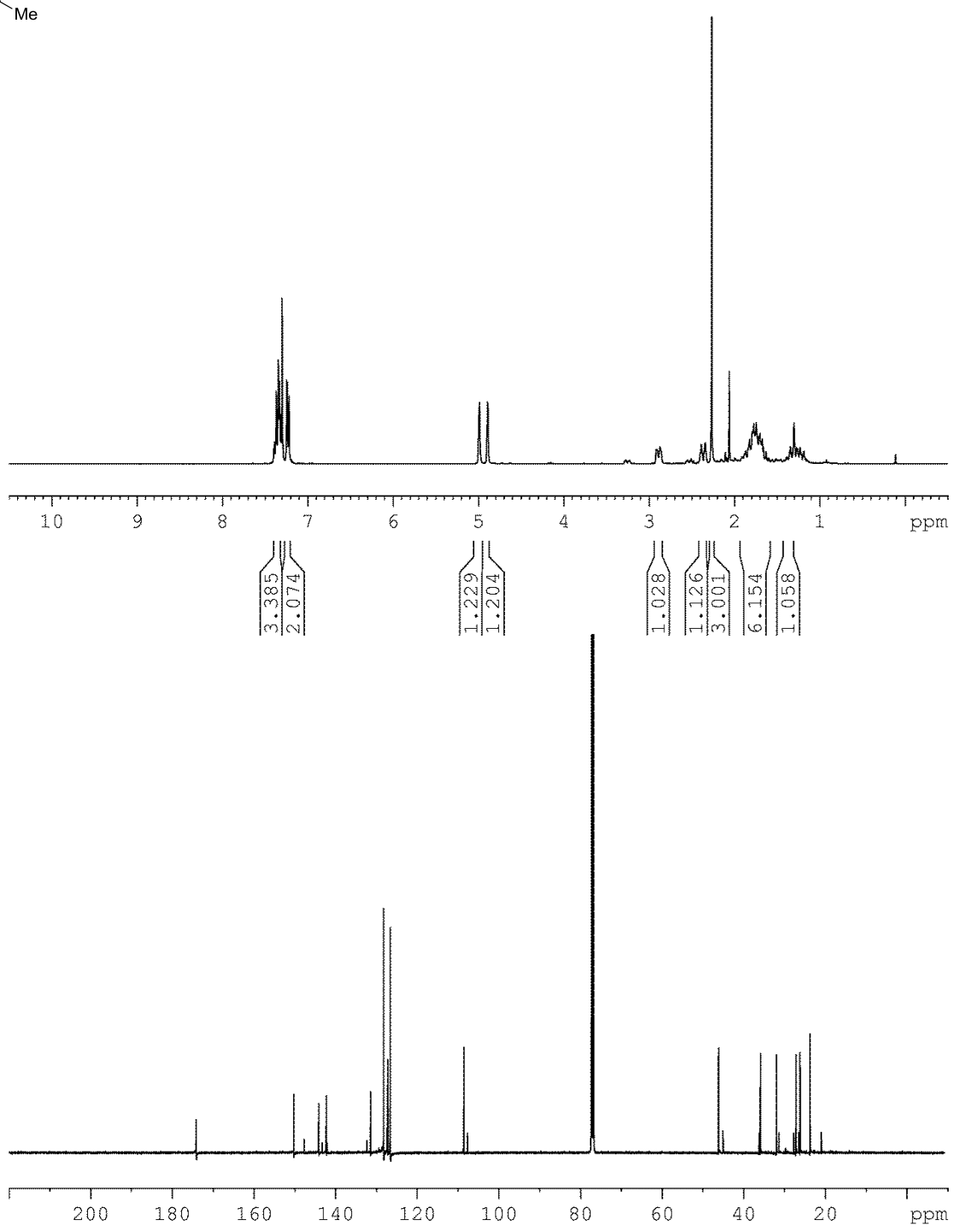
5p

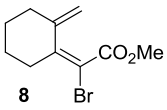

10
9
8
7
6
5
4
3
2
1
ppm
1.932
2.173
2.637
3.300
1.033
1.007
0.964
0.121
0.109
1.267
2.999
0.508
0.418
1.001
1.191
2.943
1.007
200
180
160
140
120
100
80
60
40
20
ppm


O
Br
O
Br
OMe
5q
10
9
8
7
6
5
4
3
2
1
ppm
1.007
2.067
2.040
3.000
1.023
1.042
1.042
1.041
1.042
3.064
200
180
160
140
120
100
80
60
40
20
ppm

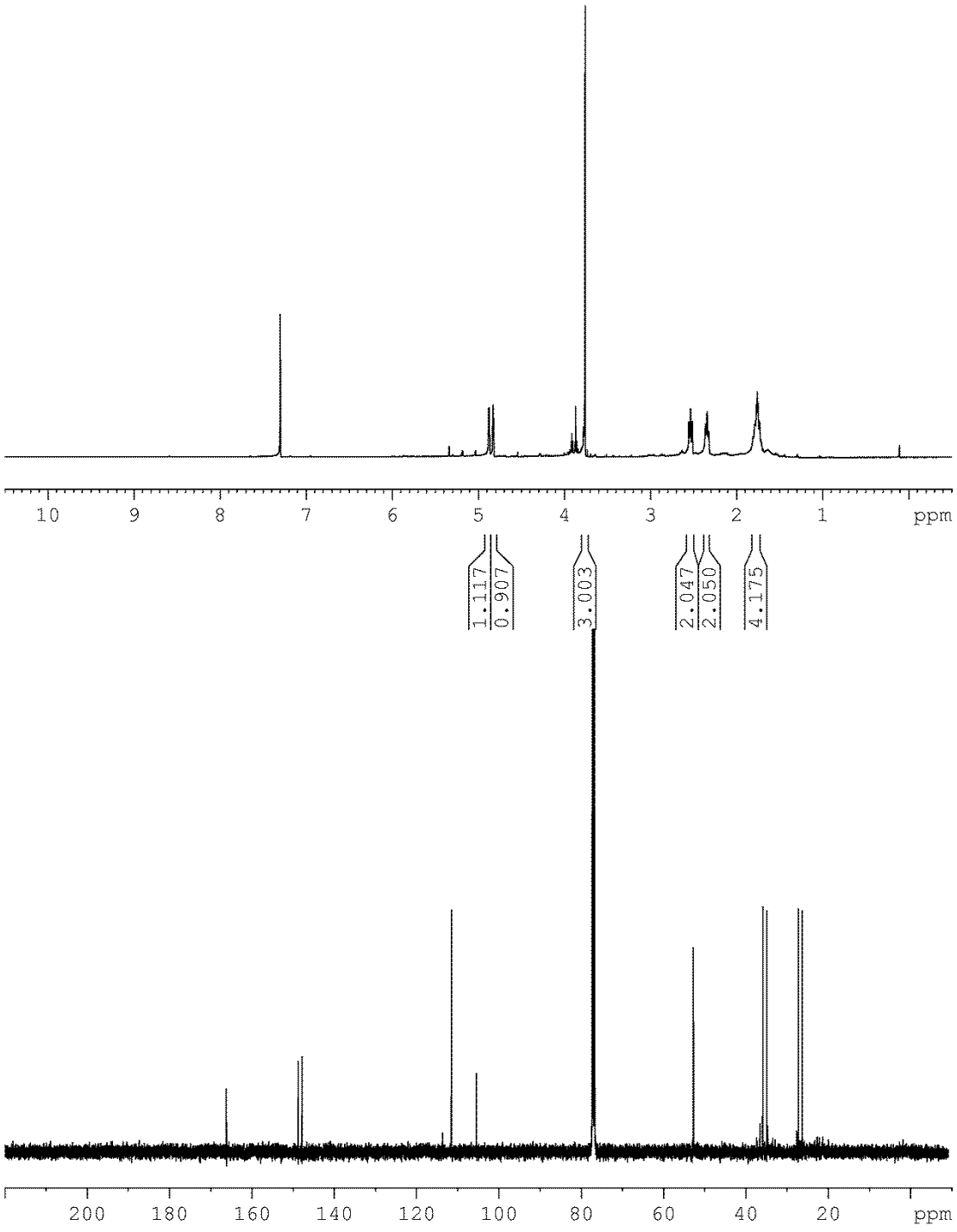

CO2H
Ph
Me

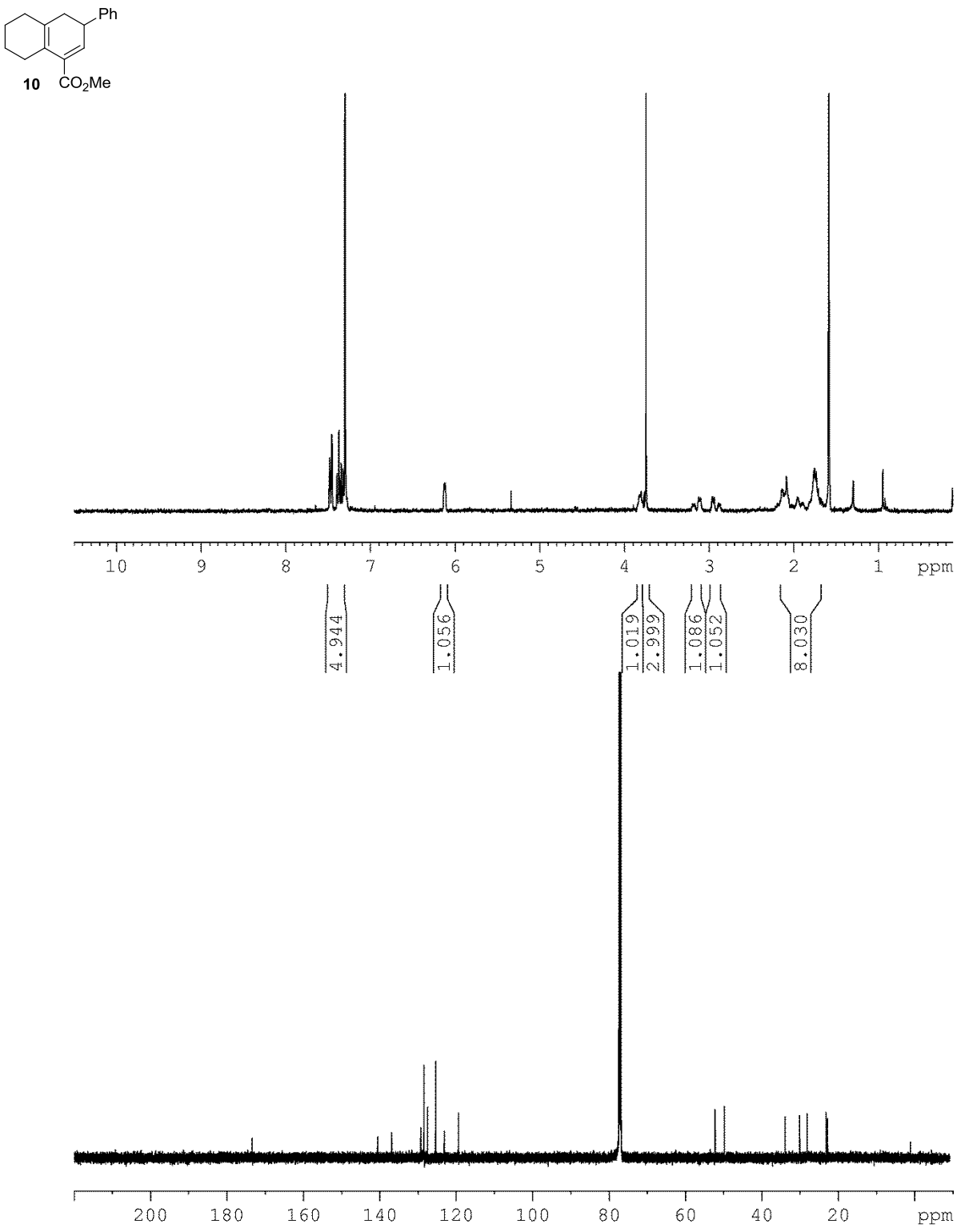
7

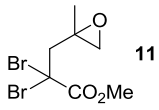

10
9
8
7
6
5
4
3
2
1
ppm
3.385
2.074
1.229
1.204
1.028
1.126
3.001
6.154
1.058
200
180
160
140
120
100
80
60
40
20
ppm


CO2Me
Br

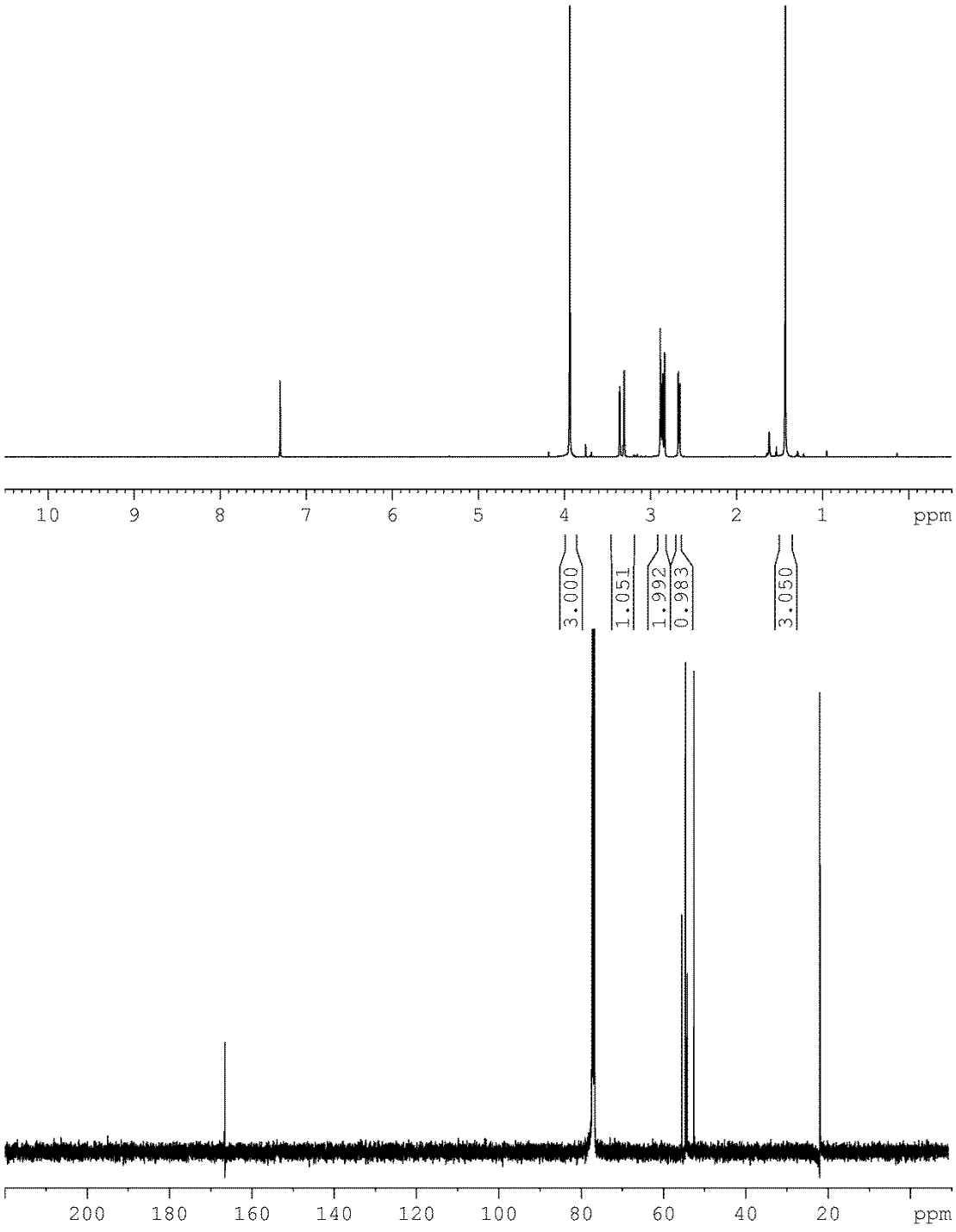
8

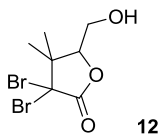

10
9
8
7
6
5
4
3
2
1
ppm
1.117
0.907
3.003
2.047
2.050
4.175
200
180
160
140
120
100
80
60
40
20
ppm


Ph
10
CO2Me
10 9 8 7 6 5 4 3 2 1 ppm
4.944
1.056
1.019
2.999
1.086
1.052
8.030
200 180 160 140 120 100 80 60 40 20 ppm

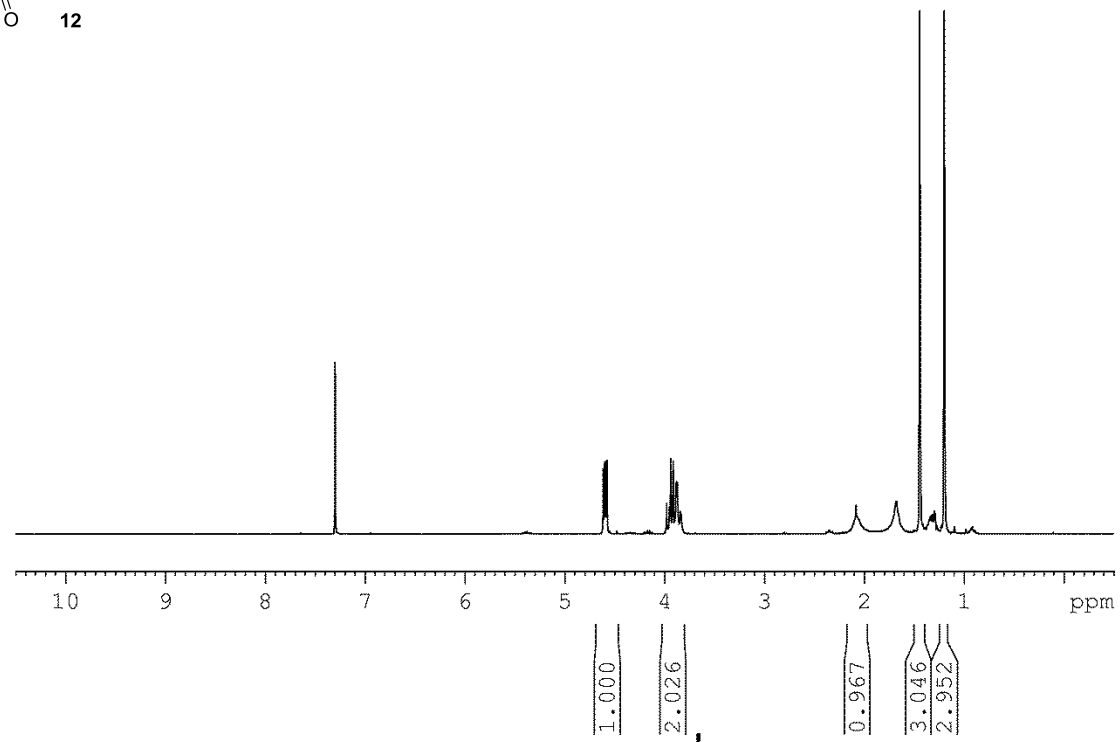

O
Br
Br
CO2Me

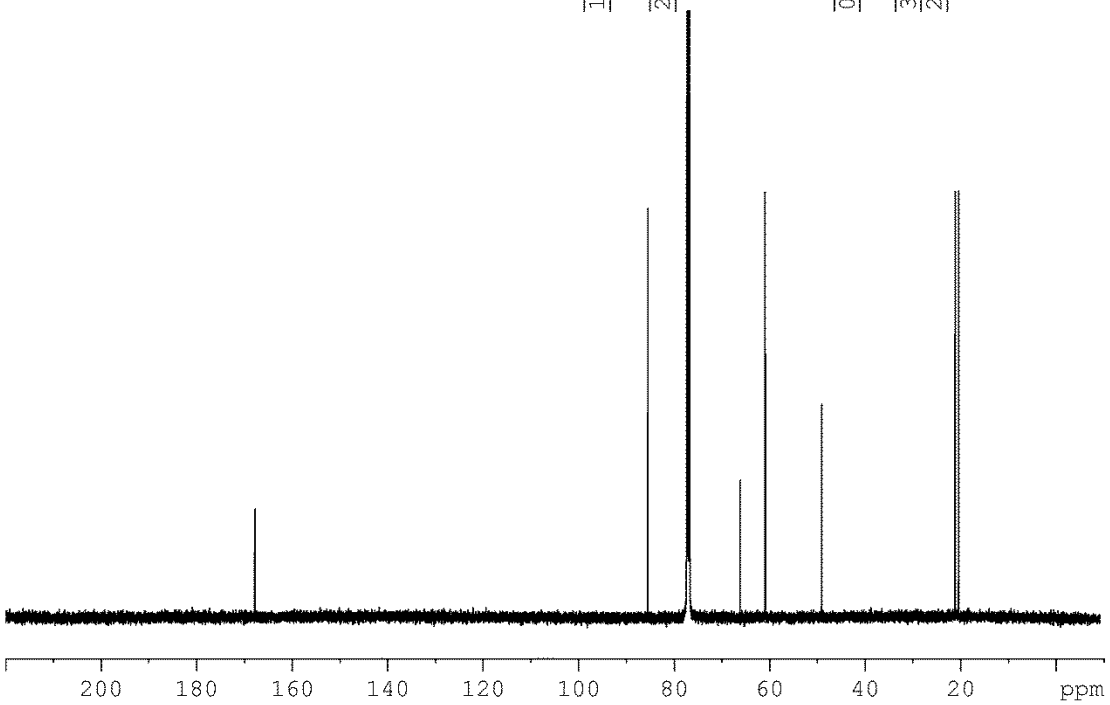
11

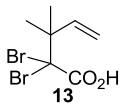

10
9
8
7
6
5
4
3
2
1
ppm
3.000
1.051
1.992
0.983
3.050
200
180
160
140
120
100
80
60
40
20
ppm


OH
Br
Br
O
O

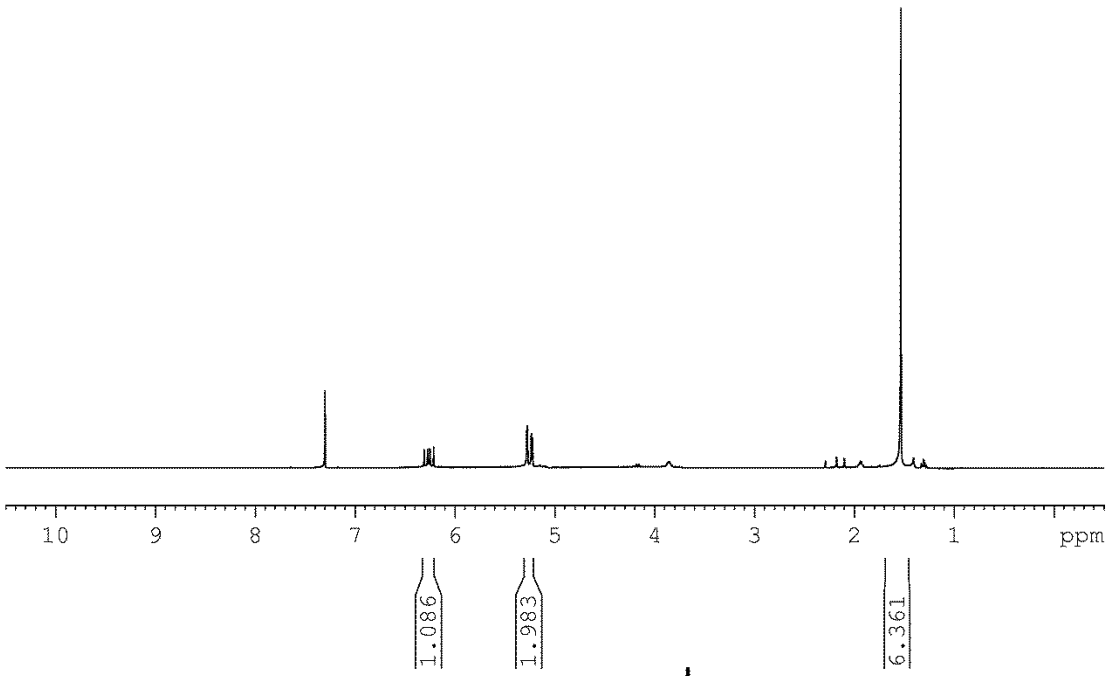
12

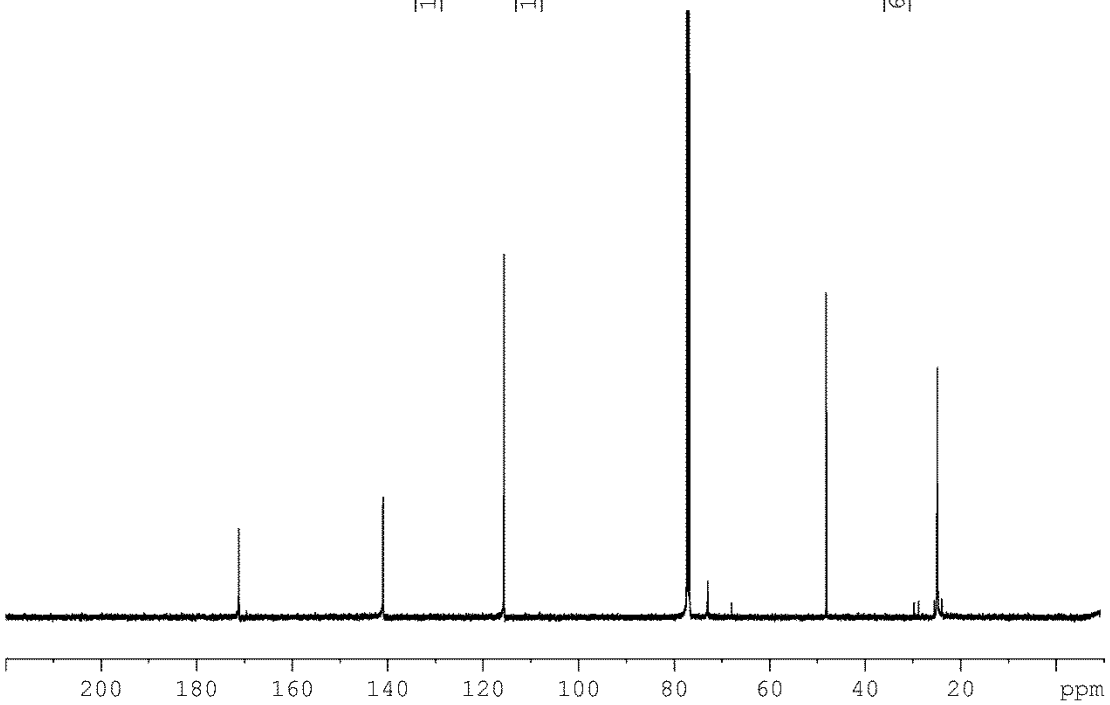

10
9
8
7
6
5
4
3
2
1
ppm
1.000
2.026
0.967
3.046
2.952

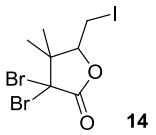

200
180
160
140
120
100
80
60
40
20
ppm


Br
Br
CO2H

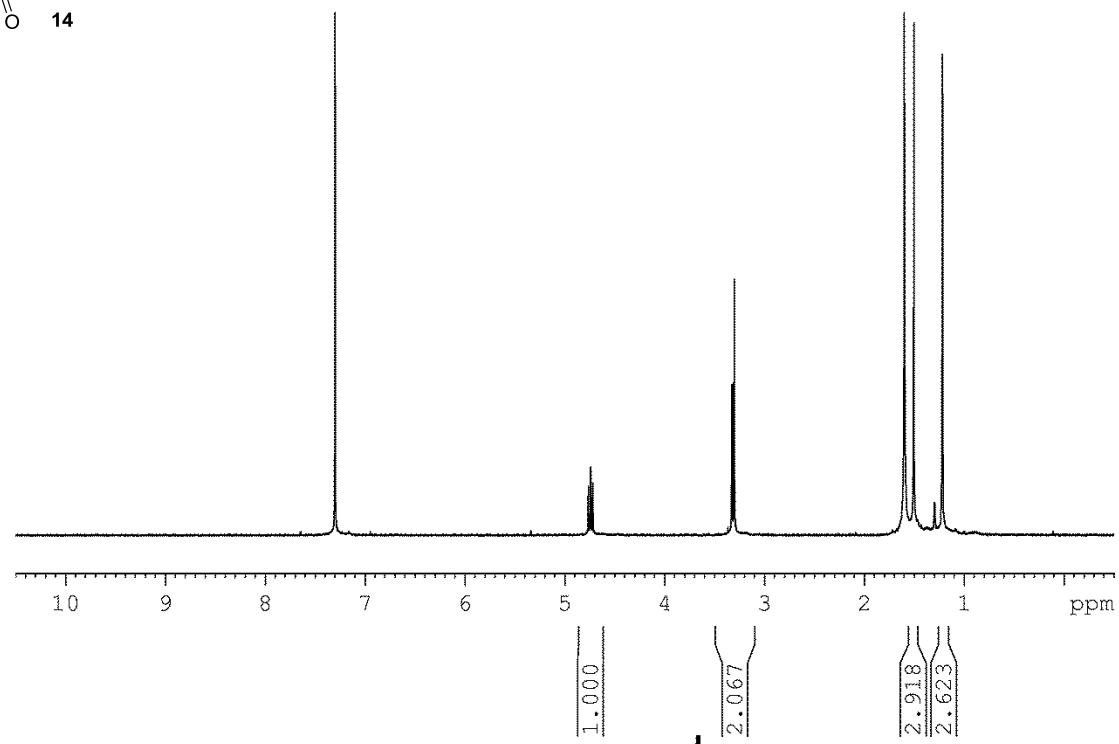
13

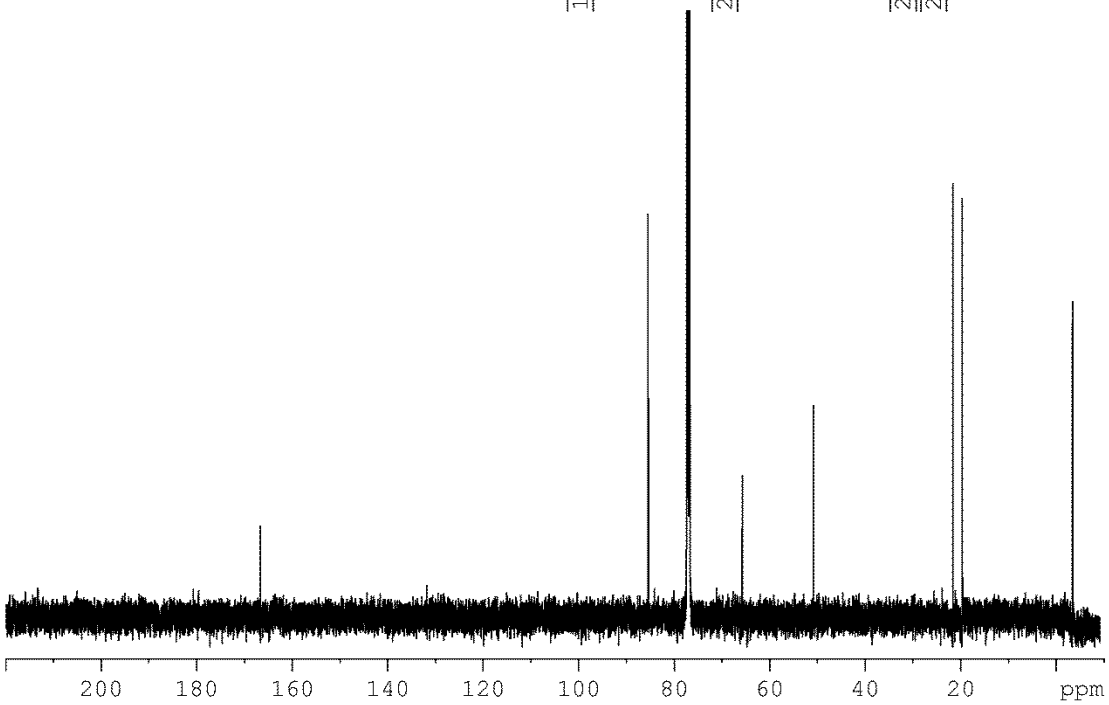

10
9
8
7
6
5
4
3
2
1
ppm
1.086
1.983
6.361

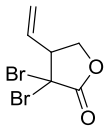

200
180
160
140
120
100
80
60
40
20
ppm


I
Br
Br
O
O

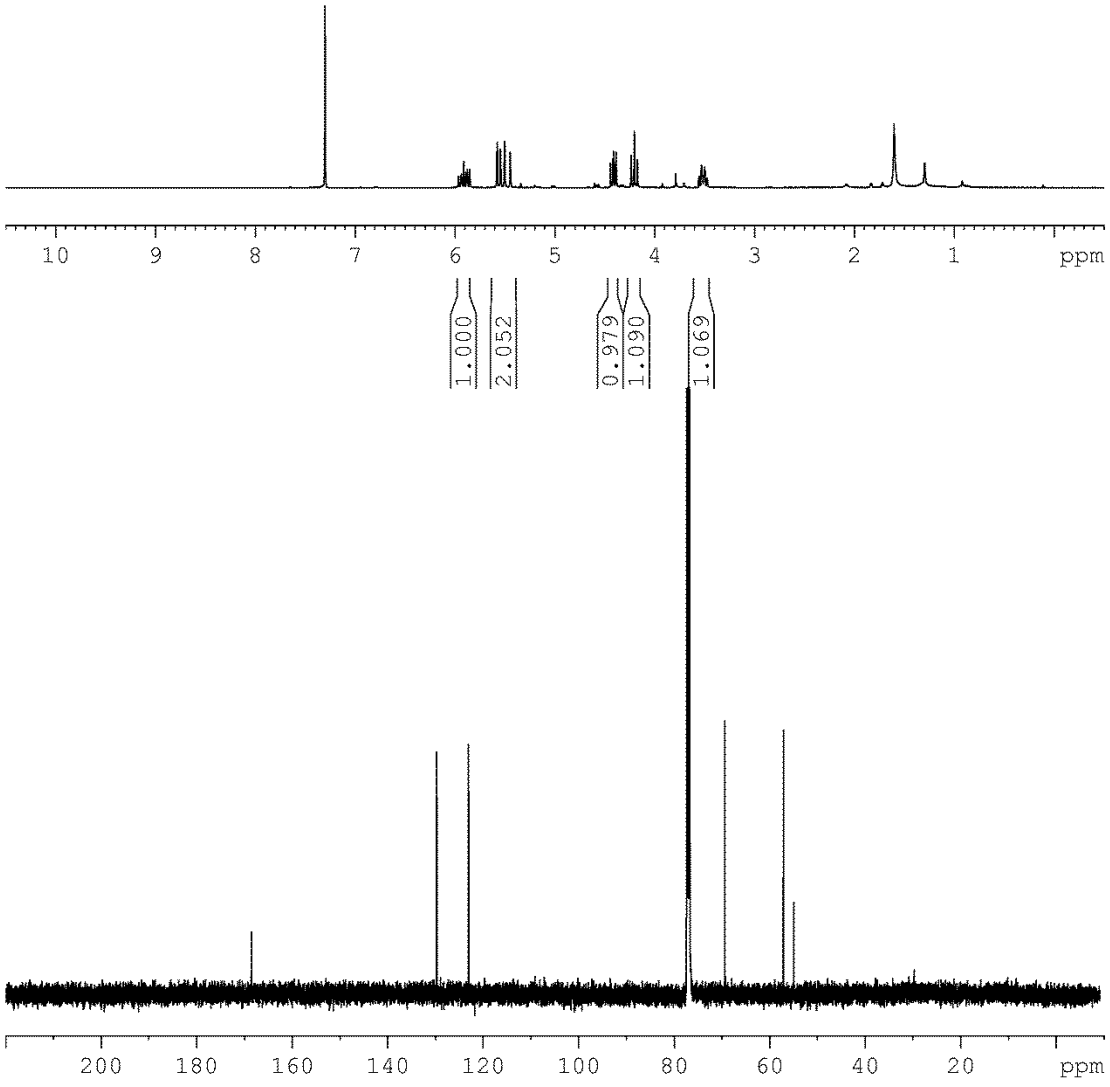
14


10
9
8
7
6
5
4
3
2
1
ppm
1.000
2.067
2.918
2.623

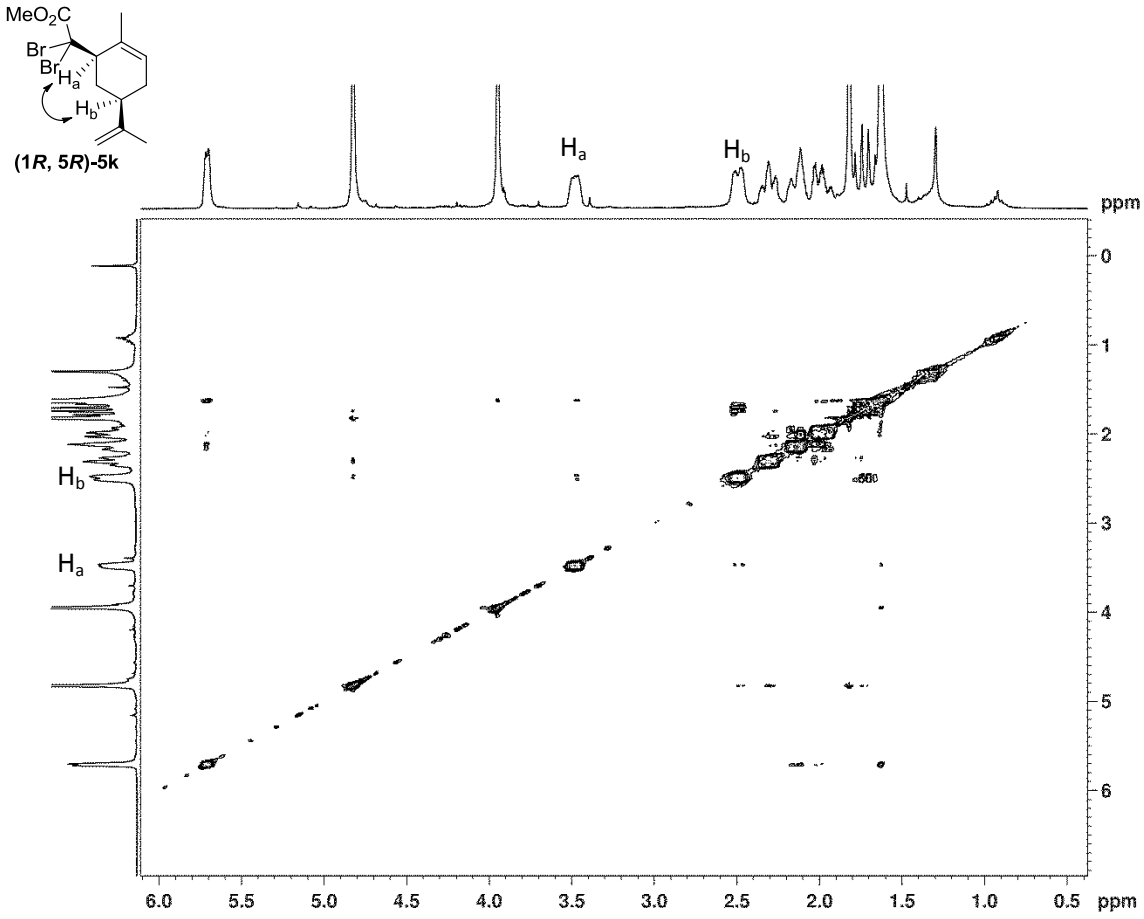

200
180
160
140
120
100
80
60
40
20
ppm

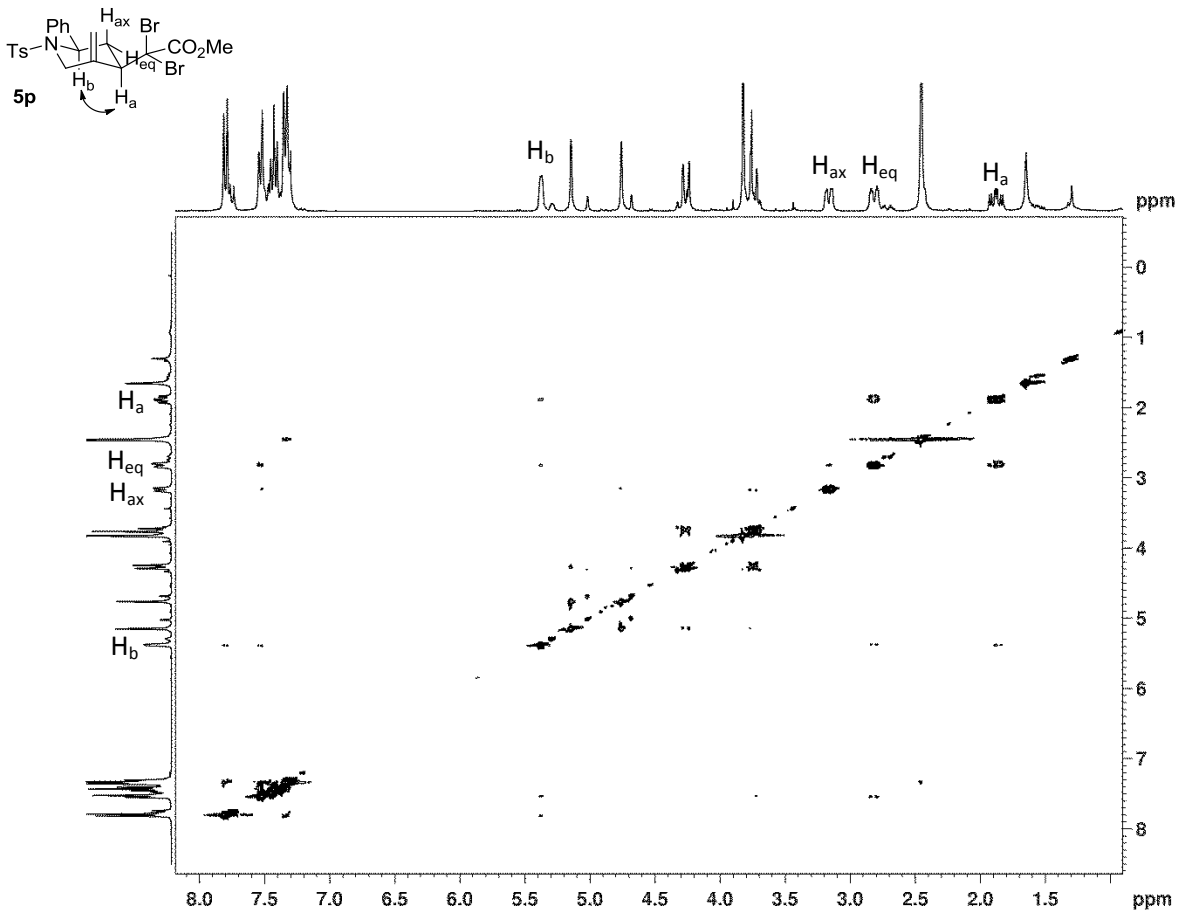

Br
Br
O
O

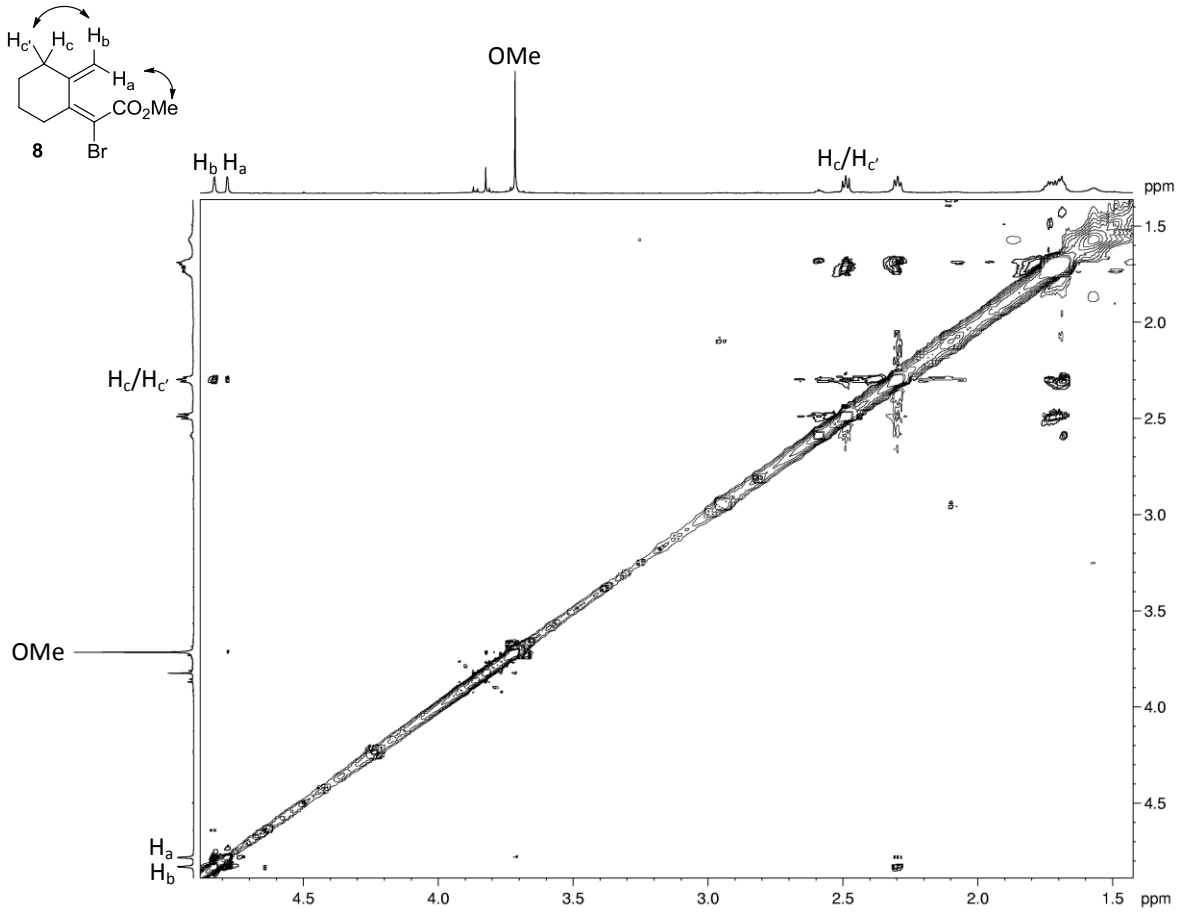
15


10
9
8
7
6
5
4
3
2
1
ppm
1.000
2.052
0.979
1.090
1.069
200
180
160
140
120
100
80
60
40
20
ppm

NOE Data:


MeO2C
Br
Br
Ha
Hb
(1R, 5R)-5k
Ha
Hb
ppm
0
1
2
3
4
5
6
Hb
Ha
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


Ph
Hax
Br
Ts
N
CO2Me
Heq
Br
Hb
Ha
5p
Hb
Hax
Heq
Ha
ppm
Ha
Heq
Hax
Hb
0
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


Hc' Hc Hb
Ha
CO2Me
Br
8
OMe
Hb Ha
Hc/Hc'
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Hc/Hc'
OMe
Ha
Hb
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm