

Supporting Information

The Cope rearrangement of *gem*-dimethyl substituted divinylcyclopropanes

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General Information

All reagents were purchased from commercial sources and were used without further purification.

Unless otherwise stated, all procedures were carried out under an atmosphere of argon. Where necessary, solvents were dried on an MBraun SPS solvent purification system. Anhydrous THF was obtained by distillation over sodium benzophenone. Hexane refers to n-hexane and pet. ether refers to light petroleum ether, bp 40–60 °C.

Flash column chromatography was performed using Fluka silica gel 60 under positive pressure. Analytical thin layer chromatography was performed on aluminium sheets pre-coated with Merck silica gel 60 F₂₅₄ and visualised with ultraviolet light (254 nm), aqueous potassium permanganate or anisaldehyde solutions where appropriate.

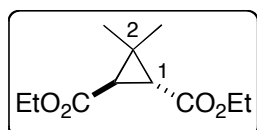
^1H NMR spectra were recorded on a JEOL ECX 400 (400 MHz) instrument. The chemical shift data is reported in parts per million (ppm) on the delta (δ) scale relative to tetramethylsilane (TMS) where $\delta_{\text{TMS}} = 0.00$ ppm. The number of protons (n) for a given resonance is indicated by $n\text{H}$. The multiplicity of each signal is indicated by: s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The coupling constants (J) are quoted to the nearest 0.5 Hz. The residual protic solvent (CHCl_3) ($\delta_{\text{H}}=7.26$ ppm) was used as an internal reference. ^{13}C NMR spectra were recorded on a JEOL ECX 400 instrument at 100 MHz. The central signal of CDCl_3 ($\delta_{\text{C}}=77.0$ ppm) was used as an internal reference. ^{13}C spectra were verified using DEPT experiments and COSY and HSQC experiments were used for assignment purposes where necessary. Chemical shifts are reported to the nearest 0.01 ppm for ^1H NMR and to the nearest 0.1 ppm for ^{13}C NMR.

Infrared spectra were carried out on a ThermoNicolet IR100 spectrometer and are recorded as a thin film between NaCl discs. Absorption maxima are reported in wavenumbers (cm^{-1}) and only selected absorbances are reported. Mass spectra and accurate mass measurements were obtained through the University of York mass spectrometry service and were recorded on a Bruker Daltonics, Micro-tof spectrometer. All melting points were taken on a Gallenkamp instrument.

All numbering of structures is for characterisation purposes only and does not conform to IUPAC rules.

Compounds **3**¹, **4a**¹ and **27**² were made using literature procedures.

Diethyl (\pm)-(1*R*,2*R*)-3,3-dimethylcyclopropane-1,2-dicarboxylate (**7**)³



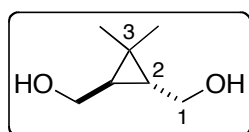
To a stirred solution of NaH (920 mg, 23.0 mmol, 60% dispersion in mineral oil) in DMF (150 mL) at 0 °C was added triisopropylsulfoxonium tetrafluoroborate (6.08 g, 23.0 mmol).

This solution was allowed to stir for 5 mins before the drop-wise addition of a solution of diethyl fumarate (3.31 g, 19.2 mmol) in DMF (35 mL). The reaction mixture was allowed to stir at 0 °C for 5 mins before being warmed to RT and stirred

for a further 2 h. It was diluted with Et₂O (115 mL), washed with sat. NH₄Cl (aq.) (100 mL), the organic layer separated and the aqueous layer extracted with further portions of Et₂O (2 x 150 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether: Et₂O (7: 1 → 4: 1) to afford the title compound **7** as a colourless oil (3.01 g, 73%).

R_f (3: 1 pet. ether: EtOAc) 0.59; ν_{\max} (thin film)/cm⁻¹ 2982, 1723; ¹H NMR (400 MHz; CDCl₃) δ 4.20–4.08 (4H, m, CH₃CH₂O), 2.21 (2H, s, H-1), 1.29 (6H, s, CH₃), 1.27 (6H, t, *J* 7.1, CH₃CH₂O); *m/z* (ESI): 215 [MH⁺]; HRMS (ESI): calcd. for C₁₁H₁₉O₄, 215.1278. Found: [MH⁺], 215.1283 (2.3 ppm error). Data in agreement with those reported in the literature.³

(±)-((1*R*,2*R*)-3,3-Dimethylcyclopropane-1,2-diyl)dimethanol (8**)**

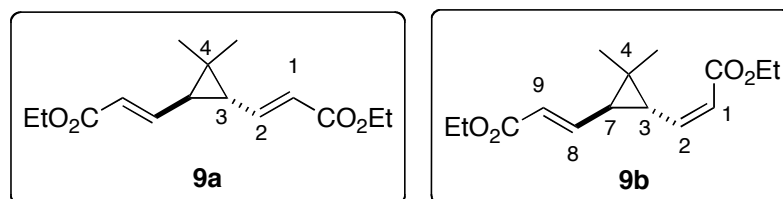


To a stirred solution of LiAlH₄ (963 mg, 25.4 mmol) in THF (25 mL) at 0 °C was added a solution of **7** (3.63 g, 16.9 mmol) in THF (9 mL), over a period of 1 h *via* a dropping syringe. The reaction mixture was then refluxed at 70 °C for 2 h, before being cooled to RT and stirred for 18 h. After being cooled to 0 °C the mixture was diluted with EtOAc (6 mL), washed cautiously with sat. NH₄Cl (aq.) (6 mL). The resulting suspension was filtered, and the insoluble salts were washed with further portions of EtOAc (2 x 10 mL). The filtrate was concentrated under reduced pressure, and the residue taken up in EtOAc (10 mL). The solution was then dried (MgSO₄), filtered and concentrated under reduced pressure to afford the title compound **8** as a colourless oil. (1.89 g, 86%).

R_f (EtOAc) 0.23; ν_{\max} (thin film)/cm⁻¹ 3337, 2926, 2874; ¹H NMR (400 MHz; CDCl₃) δ 3.77–3.69 (2H, m, H-1a), 3.59–3.50 (2H, m, H-1b), 2.23 (2H, broad s, OH), 1.13 (6H, s, H-4 & H-5), 0.85–0.79 (2H, m, H-2); ¹³C NMR (101 MHz; CDCl₃) δ 63.1 (C-1), 32.1 (C-2), 21.9 (C-4 & C-5), 20.8 (C-3); *m/z* (ESI): 153

[MNa⁺]; HRMS (ESI): calcd. for C₇H₁₄NaO₂, 153.0886. Found: [MNa⁺], 153.0888 (−1.5 ppm error).

Diethyl (±)-(2*E*,2'*E*)-3,3'-[(1*R*,2*R*)-3,3-dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (9a**) & Diethyl (±)-(2*Z*,2'*E*)-3,3'-[(1*R*,2*R*)-3,3-dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (**9b**)**



To a stirred solution of **8** (934 mg, 7.17 mmol) in CHCl₃ (70 mL) was added

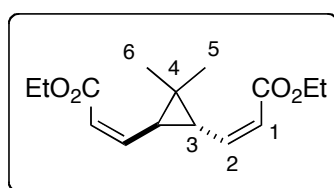
manganese (IV) dioxide (12.4 g, 143 mmol) and (carbethoxymethylene) triphenyl phosphorane (5.99 g, 17.2 mmol). The resulting suspension was stirred vigorously with heating to maintain gentle reflux for 18 h. After cooling to room temperature, the suspension was filtered through Celite, and washed with CHCl₃ (25 mL). The filtrate was concentrated under reduced pressure to give the crude product. This was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (20:1) to afford the title compound **9a** as a white solid (1.31 g, 69%), and **9b** as a colourless oil (85 mg, 4%).

9a R_f (1:1 pet. ether:Et₂O) 0.38; mp 49–52 °C; ν_{max} (thin film)/cm^{−1} 2934, 1687, 1616; ¹H NMR (400 MHz; CDCl₃) δ: 6.73–6.63 (2H, m, H-2), 5.91 (2H, d, *J* 15.5, H-1), 4.17 (4H, q, *J* 7.0, CH₃CH₂O), 1.77–1.72 (2H, m, H-3), 1.27 (6H, t, *J* 7.0, CH₃CH₂O), 1.23 (6H, s, H-5 & H-6); ¹³C NMR (101 MHz; CDCl₃) δ 166.4 (C=O), 147.5 (C-2), 121.5 (C-1), 60.3 (CH₃CH₂O), 38.5 (C-3), 30.3 (C-4), 22.4 (C-5 & C-6), 14.4 (CH₃CH₂O); m/z (ESI): 267 [MH⁺]; HRMS: calcd. for C₁₅H₂₃O₄, 267.1591. Found: [MH⁺], 267.1581 (3.6 ppm error).

9b R_f (1:1 pet. ether:Et₂O) 0.39; ν_{max} (thin film)/cm^{−1} 2934, 1688, 1615; ¹H NMR (400 MHz; CDCl₃) δ 6.74 (1H, dd, *J* 15.5, 10.0, H-8), 5.91 (1H, d, *J* 15.5, H-9), 5.87–5.77 (2H, m, H-2 & H-1), 4.21–4.14 (4H, m, CH₃CH₂O), 3.08 (1H, dd, *J* 10.0, 5.0, H-3), 1.65 (1H, dd, *J* 10.0, 5.0, H-7), 1.31–1.27 (6H, m, CH₃CH₂O), 1.26 (3H, s,

H-5), 1.21 (3H, s, H-6); ^{13}C NMR (101 MHz; CDCl_3) δ 166.8 ($\text{C}=\text{O}$), 166.5 ($\text{C}=\text{O}$), 148.3 (C-8 or C-2), 148.1 (C-8 or C-2), 121.2 (C-9 or C-1), 119.9 (C-9 or C-1), 60.3 ($\text{CH}_3\text{CH}_2\text{O}$), 60.0 ($\text{CH}_3\text{CH}_2\text{O}$), 39.7 (C-7), 35.6 (C-3), 30.6 (C-4), 22.6 (C-5), 22.3 (C-6), 14.5 ($\text{CH}_3\text{CH}_2\text{O}$), 14.4 ($\text{CH}_3\text{CH}_2\text{O}$); m/z (ESI): 267 [MH^+]; HRMS: calcd. for $\text{C}_{15}\text{H}_{23}\text{O}_4$, 267.1591. Found: [MH^+], 267.1587 (1.1 ppm error).

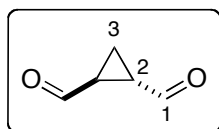
(2Z,2'Z)-Diethyl (\pm)-3,3'-((1R,2R)-3,3-dimethylcyclopropane-1,2-diyl)diprop-2-enoate (9c)



To a stirred solution of **8** (1.80 g, 13.8 mmol) in CHCl_3 (150 mL) was added manganese (IV) dioxide (24.0 g, 276 mmol). The suspension was refluxed gently and after 16 h, the suspension was filtered through Celite, and washed with CHCl_3 (250 mL). The filtrate was concentrated under reduced pressure to give (1.25 g, 72%) of dialdehyde. (195 mg, 1.55 mmol) of the resulting dialdehyde was diluted with THF (8 mL). This was added, *via* cannula, to a solution of ethyl [bis(2,2,2-trifluoroethoxy)phosphoryl]acetate (1.33 mg, 4.00 mmol), 18-crown-6 (2.34 g, 9.02 mmol) and KHMDS (5.80 mL, 0.7 M in toluene, 3.45 mmol) at -78°C . After 2 h the reaction was quenched with sat. NH_4Cl (aq.) (15 mL), Et_2O (25 mL) added and the organic layer separated. The aqueous layer was extracted with further portions of Et_2O (2×25 mL) and the combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (10:1) to afford the title compound **9c** as a colourless oil (144 mg, 35%).

R_f (1:1 pet. ether: Et_2O) 0.41; ν_{max} (thin film)/ cm^{-1} 2934, 1688, 1604; ^1H NMR (400 MHz; CDCl_3) δ 5.98–5.90 (2H, m, H-2), 5.80 (2H, d, J 11.5, H-1), 4.17 (4H, q, J 7.0, $\text{CH}_3\text{CH}_2\text{O}$), 3.04–3.00 (2H, m, H-3), 1.27 (6H, t, J 7.0, $\text{CH}_3\text{CH}_2\text{O}$), 1.23 (6H, s, H-5 & H-6); ^{13}C NMR (101 MHz; CDCl_3) δ 167.0 ($\text{C}=\text{O}$), 149.3 (C-2), 119.3 (C-1), 59.9 ($\text{CH}_3\text{CH}_2\text{O}$), 37.0 (C-3), 30.9 (C-4), 22.5 (C-5 & C-6), 14.4 ($\text{CH}_3\text{CH}_2\text{O}$); m/z (ESI): 267 [MH^+]; HRMS: calcd. for $\text{C}_{15}\text{H}_{23}\text{O}_4$, 267.1591. Found: [MH^+], 267.1583 (2.8 ppm error).

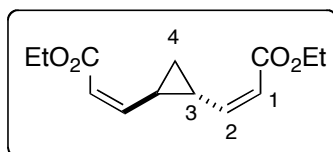
(±)-(1*S*,2*S*)-Cyclopropane-1,2-dicarbaldehyde (SI-1)⁴



To a stirred solution of **3** (2.00 g, 19.6 mmol) in CHCl₃ (150 mL) was added manganese (IV) dioxide (34.1 g, 392 mmol). The suspension was refluxed gently and after 16 h, the suspension was filtered through Celite, and washed with CHCl₃ (250 mL). The filtrate was concentrated under reduced pressure to afford the title compound **SI-1** as a colourless oil (205 mg, 11%), which was used in the next step without further purification.

R_f (1:1 pet. ether:EtOAc) 0.54; ¹H NMR (400 MHz; CDCl₃) δ 9.34–9.32 (2H, m, H-1), 2.57–2.49 (2H, m, H-2), 1.71–1.65 (2H, m, H-3). Data in agreement with those reported in the literature.⁴

Diethyl (±)-(2'*Z*)-3,3'-(1*R*,2*R*)-cyclopropane-1,2-diylbisprop-2-enoate (4c**)**

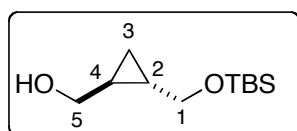


To a solution of ethyl [bis(2,2,2-trifluoroethoxy)phosphoryl]acetate (1.32 mg, 3.98 mmol) in THF (15 mL) was added 18-crown-6 (2.30 g, 8.87 mmol). The solution was cooled to 0 °C and KHMDS (5.70 mL, 0.7 M in toluene, 3.98 mmol) was added cautiously. After 15 min the solution was cooled to –78 °C and **SI-1** (150 mg, 1.53 mmol) in THF (8 mL) was added *via* cannula. After 2 h the reaction was quenched with sat. NH₄Cl (aq.) (15 mL), Et₂O (25 mL) added and the organic layer separated. The aqueous layer was extracted with further portions of Et₂O (2 × 25 mL) and the combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (10:1) to afford the title compound **4c** as a colourless oil (192 mg, 63%).

R_f (10:1 pet. ether:EtOAc) 0.37; ν_{max} (thin film)/cm^{–1} 2935, 2885, 1691, 1612; ¹H NMR (400 MHz; CDCl₃) δ 5.73 (2H, d, *J* 11.5, H-1), 5.60–5.53 (2H, m, H-2), 4.17 (4H, q, *J* 7.0, CH₃CH₂O), 3.18–3.10 (2H, m, H-3), 1.28 (6H, t, *J* 7.0, CH₃CH₂O), 1.20 (2H, t, *J* 7.0, H-4); ¹³C NMR (101 MHz; CDCl₃) δ 167.0 (CH₃CH₂OC=O), 151.4 (C-

2), 118.4 (C-1), 60.0 (OCH₂CH₃), 23.4 (C-3), 18.3 (C-4), 14.4 (OCH₂CH₃); m/z (ESI) 239 [MH⁺]; HRMS: calcd. for C₁₃H₁₉O₄, 239.1278. Found: [MH⁺], 239.1285 (−3.2 ppm error).

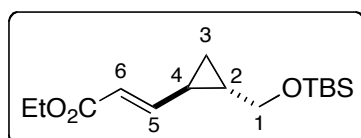
(±)-[(1*S*,2*S*)-2-({*tert*-Butyl(dimethyl)silyl}oxy)methyl]cyclopropyl]methanol (16**)**



To a stirred solution of **3** (1.00 g, 9.80 mmol) in THF (20 mL) at 0 °C was added NaH (472 mg, 11.8 mmol, 60% dispersion in mineral oil). After 45 mins, by which time a large amount of white precipitate had formed, TBSCl (1.48 g, 9.80 mmol) was added. The reaction mixture was warmed to RT and allowed to stir for a further 1 h before dilution with Et₂O (25 mL). It was then washed with sat. NH₄Cl (aq.) (20 mL) and brine (10 mL), the organic layer separated and the aqueous layer extracted with further portions of Et₂O (2 × 20 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (20:1 → 4:1) to afford the title compound **16** as a colourless oil (1.46 g, 69%).

R_f (EtOAc) 0.89; ν_{max} (thin film)/cm^{−1} 3315, 2909, 2884, 2842; ¹H NMR (400 MHz; CDCl₃) δ 3.59 (1H, dd, *J* 10.5, 6.0) and 3.51–3.42 (3H, m, H-1 & H-5), 1.06–0.90 (2H, m, H-4 & H-2), 0.89 (9H, s, SiC(CH₃)₃), 0.53–0.40 (2H, m, H-3), 0.05 (6H, s, SiCH₃); ¹³C NMR (101 MHz; CDCl₃) δ 66.6 (C-1 or C-5), 65.9 (C-1 or C-5), 26.0 (SiC(CH₃)₃), 19.5 (C-2 or C-4), 19.4 (C-2 or C-4), 18.4 (SiC(CH₃)₃), 7.9 (C-3), −5.1 (SiCH₃); m/z (ESI) 217 [MH⁺]; HRMS: calcd. for C₁₁H₂₅O₂Si, 217.1618. Found: [MH⁺], 217.1622 (−2.3 ppm error).

Ethyl (±)-(2*E*)-3-[(1*R*,2*S*)-2-({*tert*-butyl(dimethyl)silyl}oxy)methyl]cyclopropyl]prop-2-enoate (17**)**

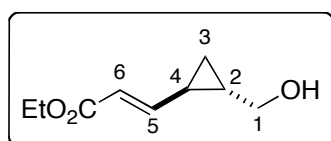


To a stirred solution of **16** (1.46 g, 6.75 mmol) in CHCl₃ (70 mL) was added manganese (IV) dioxide

(5.87 g, 67.5 mmol) and (carbethoxymethylene) triphenyl phosphorane (2.82 g, 8.10 mmol). The resulting suspension was stirred vigorously with heating to maintain gentle reflux for 18 h. After cooling to room temperature, the suspension was filtered through Celite, and washed with CHCl_3 (100 mL). The filtrate was concentrated under reduced pressure to give the crude product. This was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (40:1 \rightarrow 10:1) to afford the title compound **17** as a colourless oil (1.63 g, 85%).

R_f (10:1 pet. ether:EtOAc) 0.24; ν_{\max} (thin film)/ cm^{-1} 2909, 2886, 2814, 1691, 1621; ^1H NMR (400 MHz; CDCl_3) δ 6.48 (1H, dd, J 15.5, 10.0, H-5), 5.85 (1H, d, J 15.5), 4.17 (2H, q, J 7.0, $\text{CH}_3\text{CH}_2\text{O}$), 3.65–3.54 (2H, m, H-1), 1.54–1.47 (1H, m, H-4), 1.33–1.25 (1H, m, H-2), 1.27 (3H, t, J 7.0 $\text{CH}_3\text{CH}_2\text{O}$), 0.96–0.90 (1H, m, H-3a), 0.88 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.84–0.79 (1H, m H-3b), 0.04 (6H, s, SiCH_3); ^{13}C NMR (101 MHz; CDCl_3) δ 166.9 ($\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 152.8 (C-5), 118.4 (C-6), 64.6 (C-1), 60.2 (OCH_2CH_3), 26.1 ($\text{SiC}(\text{CH}_3)_3$), 24.8 (C-2 or C-4), 19.6 (C-2 or C-4), 18.5 ($\text{SiC}(\text{CH}_3)_3$), 14.5 (OCH_2CH_3), 13.1 (C-3), -5.1 (SiCH_3); m/z (ESI) 285 [MH^+]; HRMS: calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Si}$, 285.1880. Found: [MH^+], 285.1877 (1.2 ppm error).

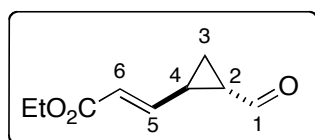
Ethyl (\pm)-(2*E*)-3-[(1*R*,2*S*)-2-(hydroxymethyl)cyclopropyl]prop-2-enoate (**18**)



To a solution of **17** (1.60 g, 5.40 mmol) in THF (50 mL) at 0 °C was added TBAF (6.48 mL, 1 M in THF, 6.48 mmol). After 17 h the reaction mixture was diluted with Et_2O (50 mL) and washed with sat. NH_4Cl (aq.) (50 mL), the organic layer separated and the aqueous layer extracted with further portions of Et_2O (2×50 mL). The combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure to give the crude product. This was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (2:1) to afford the title compound **18** as a colourless oil (704 mg, 77%).

R_f (1:1 pet. ether:EtOAc) 0.59; ν_{\max} (thin film)/ cm^{-1} 3374, 2938, 2893, 2830, 1687, 1670; ^1H NMR (400 MHz; CDCl_3) δ 6.47 (1H, dd, J 15.5, 10.0, H-5), 5.88 (1H, d, J 15.5, H-6), 4.17 (2H, q, J 7.0, $\text{CH}_3\text{CH}_2\text{O}$), 3.60 (1H, dd, J 11.5, 6.5, H-1a), 3.53 (1H, dd, J 11.5, 7.0, H-1b), 1.57–1.49 (1H, m, H-2 or H-4), 1.43–1.35 (1H, m, H-2 or H-4), 1.27 (3H, t, J 7.0 $\text{CH}_3\text{CH}_2\text{O}$), 0.96–0.86 (2H, m, H-3); ^{13}C NMR (101 MHz; CDCl_3) δ 166.8 ($\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 152.0 (C-5), 118.9 (C-6), 65.6 (C-1), 60.3 (OCH_2CH_3), 24.8 (C-2 or C-4), 20.0 (C-2 or C-4), 14.4 (OCH_2CH_3), 13.4 (C-3); m/z (ESI) 171 [MH^+]; HRMS: calcd. for $\text{C}_9\text{H}_{15}\text{O}_3$, 171.1016. Found: [MH^+], 171.1010 (3.8 ppm error).

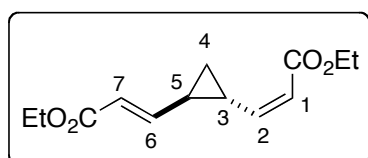
Ethyl (\pm)-(2*E*)-3-[(1*R*,2*S*)-2-formylcyclopropyl]prop-2-enoate (SI-2)



To a stirred solution of **18** (704 mg, 4.14 mmol) in CHCl_3 (40 mL) was added manganese (IV) dioxide (3.60 g, 41.4 mmol) and 4Å molecular sieves (3.60 g). After 20 h the suspension was filtered through Celite, and washed with CHCl_3 (100 mL). The filtrate was concentrated under reduced pressure to afford the title compound **SI-2** as a colourless oil (468 mg, 67%).

R_f (1:1 pet. ether:EtOAc) 0.72; ν_{\max} (thin film)/ cm^{-1} 2937, 2893, 2796, 1681, 1624; ^1H NMR (400 MHz; CDCl_3) δ 9.31 (1H, d, J 4.0, H-1), 6.42 (1H, dd, J 15.5, 9.5, H-5), 5.97 (1H, d, J 15.5, H-6), 4.17 (2H, q, J 7.0, $\text{CH}_3\text{CH}_2\text{O}$), 2.28–2.20 (1H, m, H-4), 2.17–2.10 (1H, m, H-2), 1.68–1.63 (1H, m, H-3a), 1.35–1.29 (1H, m, H-3b), 1.27 (3H, t, J 7.0 $\text{CH}_3\text{CH}_2\text{O}$); ^{13}C NMR (101 MHz; CDCl_3) δ 198.7 (C-1), 166.2 ($\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 147.4 (C-5), 121.7 (C-6), 60.6 (OCH_2CH_3), 31.8 (C-2), 24.8 (C-4), 16.3 (C-3), 14.4 (OCH_2CH_3); m/z (ESI) 169 [MH^+]; HRMS: calcd. for $\text{C}_9\text{H}_{13}\text{O}_3$, 169.0859. Found: [MH^+], 169.0861 (−0.9 ppm error).

Diethyl (\pm)-(2'*E*)-3,3'-(1*R*,2*R*)-cyclopropane-1,2-diylbisprop-2-enoate (4b)

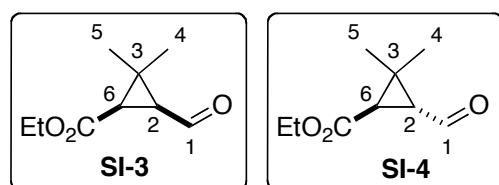


To a solution of ethyl [bis(2,2,2-trifluoroethoxy)phosphoryl]acetate (257 mg, 0.774

mmol) in THF (6 mL) was added 18-Crown-6 (457 mg, 1.73 mmol). The solution was cooled to 0 °C and KHMDS (1.10 mL, 0.7 M in toluene, 0.774 mmol) was added cautiously. After 15 min the solution was cooled to -78 °C and **SI-2** (100 mg, 0.595 mmol) in THF (3 mL) was added *via* cannula. After 2 h the reaction was quenched with sat. NH₄Cl (aq.) (10 mL), Et₂O (20 mL) added and the organic layer separated. The aqueous layer was extracted with further portions of Et₂O (2 × 20 mL) and the combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (20:1) to afford the title compound **4b** as a colourless oil (65 mg, 46%).

R_f (1:1 pet. ether:Et₂O) 0.56; ν_{\max} (thin film)/cm⁻¹ 2938, 2893, 2862, 1688, 1618; ¹H NMR (400 MHz; CDCl₃) δ 6.50 (1H, dd, *J* 15.5, 10.0, H-6), 5.88 (1H, d, *J* 15.5, H-7), 5.73 (1H, d, *J* 11.0, H-1), 5.50 (1H, dd, *J* 11.0, 11.0, H-2), 4.17 (2H, q, *J* 7.0, CH₃CH₂O), 4.15 c 3.24–3.13 (1H, m, H-3), 1.78–1.68 (1H, m, H-5), 1.31–1.26 (1H, m, H-4a), 1.28 (3H, t, *J* 7.0 CH₃CH₂O), 1.26 (3H, t, *J* 7.0 CH₃CH₂O), 1.18–1.09 (1H, m, H-4b); ¹³C NMR (101 MHz; CDCl₃) δ 166.8 (CH₃CH₂OC=O), 166.4 (CH₃CH₂OC=O), 150.7 (C-2), 150.0 (C-6), 119.8 (C-7), 118.8 (C-1), 60.3 (OCH₂CH₃), 60.1 (OCH₂CH₃), 25.5 (C-5), 23.0 (C-3), 18.0 (C-4), 14.4 (OCH₂CH₃); *m/z* (ESI) 239 [MH⁺]; HRMS: calcd. for C₁₃H₁₉O₄, 239.1278. Found: [MH⁺], 239.1276 (0.5 ppm error).

Ethyl (±)-(1*S*,3*R*)-3-formyl-2,2-dimethylcyclopropanecarboxylate (SI-3) & Ethyl (±)-(1*R*,3*R*)-3-formyl-2,2-dimethylcyclopropanecarboxylate (SI-4)⁵

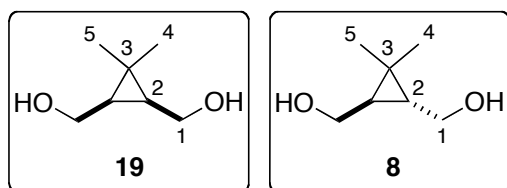


Oxygen was bubbled through a solution of ethyl chrysanthemate (10.0 g, 0.0510 mmol) in CH₂Cl₂ (500 mL) at -78 °C for 5 min. Ozone was then bubbled through the solution until a sky blue colour could be seen (55 min), after which time oxygen was bubbled through the solution for a further 5 min. DMS (37.4 mL, 0.510 mmol) was next added to the solution, which was then allowed to stir at RT overnight. The

solution was concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (10:1) to afford the title compound as a mixture of diastereomers (**SI-3**:**SI-4** *cis:trans* 2:3) and as a colourless oil (8.23 g, 97%).

R_f (20:1 pet. ether:EtOAc) 0.21; ^1H NMR (400 MHz; CDCl_3) **SI-3** δ 9.70 (1H, d, J 6.5, H-1), 4.08–4.16 (2H, m, $\text{CH}_3\text{CH}_2\text{O}$), 2.08 (1H, d, J 8.5, H-2 or H-6), 1.79 (1H, dd, J 6.5, 6.5, H-2 or H-6), 1.56 (3H, s, H-4), 1.24 (3H t, J 7.0, $\text{CH}_3\text{CH}_2\text{O}$), 1.23 (3H, s, H-5); **SI-4** δ 9.53 (1H, d, J 3.5, H-1), 4.08–4.16 (2H, m, $\text{CH}_3\text{CH}_2\text{O}$), 2.35–2.45 (2H, m, H-2 & H-6), 1.30 (3H, s, H-4), 1.26 (3H, s, H-5), 1.23 (3H, t J 7.0, $\text{CH}_3\text{CH}_2\text{O}$). Data in agreement with those reported in the literature.⁵

(±)-[(1*R*,2*R*)-3,3-Dimethylcyclopropane-1,2-diyl]dimethanol (19**) & [(1*R*,2*S*)-3,3-Dimethylcyclopropane-1,2-diyl]dimethanol (**8**)**



To a stirred suspension of LiAlH_4 (7.30 g, 192 mmol) in THF (500 mL) at 0 °C was added **SI-3/SI-4** (16.4 g, 96.3 mmol) in THF (500 mL) *via* cannula. The reaction

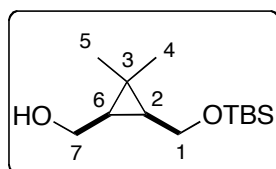
was warmed to RT and stirred for 10 min. The reaction was cooled to 0 °C and water (7.3 mL) was added cautiously, followed by NaOH (aq. 15%) (7.3 mL) and water (21.9 mL). The aluminium salts were removed by filtration and washed with EtOAc (500 mL). The filtrate was concentrated under reduced pressure to give the crude product. This was purified by flash column chromatography on silica gel, eluting with EtOAc to afford the title compound **19** as a colourless oil (3.93 g, 31%) and **8** as a colourless oil (6.22 g, 49%).

19 R_f (EtOAc) 0.34; ν_{max} (thin film)/ cm^{-1} 3342, 2987, 2929, 2887; ^1H NMR (400 MHz; CDCl_3) δ 3.97 (2H, dd, J 11.5, 5.5, H-1a), 3.50–3.46 (2H, m, H-1b), 2.83 (2H, broad s, OH), 1.10–1.05 (2H, m, H-2), 1.07 (3H, s, H-4), 1.05 (3H, s, H-5); ^{13}C NMR (101 MHz; CDCl_3) δ 59.7 (C-1), 29.2 (C-4), 29.1 (C-5), 20.2 (C-3), 15.6 (C-

2); m/z (ESI): 153 [MNa^+]; HRMS (ESI): calcd. for $C_7H_{14}NaO_2$, 153.0886. Found: [MNa^+], 153.0884 (1.3 ppm error).

8 R_f (EtOAc) 0.23; ν_{max} (thin film)/ cm^{-1} 3337, 2926, 2874; 1H NMR (400 MHz; $CDCl_3$) δ 3.77–3.69 (2H, m, H-1a), 3.59–3.50 (2H, m, H-1b), 2.23 (2H, broad s, OH), 1.13 (6H, s, H-4 & H-5), 0.85–0.79 (2H, m, H-2); ^{13}C NMR (101 MHz; $CDCl_3$) δ 63.1 (C-1), 32.1 (C-2), 21.9 (C-4 & C-5), 20.8 (C-3); m/z (ESI): 153 [MNa^+]; HRMS (ESI): calcd. for $C_7H_{14}NaO_2$, 153.0886. Found: [MNa^+], 153.0888 (–1.5 ppm error).

(±)-[(1*S*,3*R*)-3-({*tert*-Butyl(dimethyl)silyl}oxy)methyl]-2,2-dimethylcyclopropylmethanol (20**)**

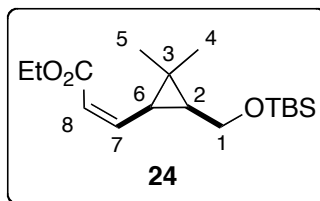
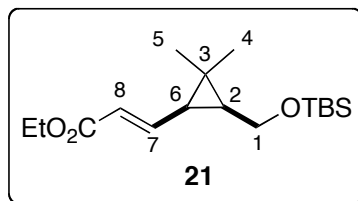


To a stirred solution of **19** (276 mg, 2.12 mmol) in THF (4 mL) at 0 °C was added NaH (102 mg, 2.54 mmol, 60% dispersion in mineral oil). After 45 mins, by which time a large amount of white precipitate had formed, TBSCl (319 mg, 2.12 mmol) was added. The reaction mixture was warmed to RT and allowed to stir for a further 1 h before dilution with Et_2O (15 mL). It was then washed with sat. NH_4Cl (aq.) (10 mL) and brine (10 mL), the organic layer separated and the aqueous layer extracted with further portions of Et_2O (2×20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (20:1 \rightarrow 10:1) to afford the title compound **20** as a colourless oil (506 mg, 84%).

R_f (1:1 pet. ether:EtOAc) 0.48; ν_{max} (thin film)/ cm^{-1} 3346, 2885, 2842, 22816; 1H NMR (400 MHz; $CDCl_3$) δ 4.07–3.98 (1H, m, H-1a or H-7a), 3.89–3.80 (1H, m, H-1a or H-7a), 3.57–3.45 (2H, m, H-1b & H-7b), 2.97 (1H, br s, OH), 1.16–1.08 (1H, m, H-2 or H-6), 1.06 (3H, s, H-4), 1.04 (3H, s, H-5), 1.03–0.93 (1H, m, H-2 or H-6), 0.90 (9H, s, $SiC(CH_3)_3$), 0.10 (3H, s, $SiCH_3$), 0.08 (3H, s, $SiCH_3$); ^{13}C NMR (101 MHz; $CDCl_3$) δ 60.6 (C-1 or C-7), 59.7 (C-1 or C-7), 29.9 (C-4), 29.2 (C-2 or C-6), 29.0 (C-2 or C-6), 26.0 ($SiC(CH_3)_3$), 20.3 (C-3), 18.3 ($SiC(CH_3)_3$), 15.7 (C-5) –5.1

(SiCH₃), -5.3 (SiCH₃); m/z (ESI) 267 [MNa⁺]; HRMS: calcd. for C₁₃H₂₈NaO₂Si, 267.1751. Found: [MNa⁺], 267.1742 (3.1 ppm error).

Ethyl (±)-(2*E*)-3-[(1*S*,3*R*)-3-({*tert*-butyl(dimethyl)silyl}oxy)methyl)-2,2-dimethylcyclopropyl]prop-2-enoate (21**) & Ethyl (±)-(2*Z*)-3-[(1*S*,3*R*)-3-({*tert*-butyl(dimethyl)silyl}oxy)methyl)-2,2-dimethylcyclopropyl]prop-2-enoate (**24**)**



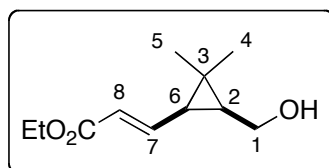
To a stirred solution of **20** (18.0 g, 73.5 mmol) in CHCl₃ (300 mL) was added manganese (IV) dioxide (63.9

g, 735 mmol) and (carbethoxymethylene) triphenyl phosphorane (30.7 g, 88.2 mmol). The resulting suspension was stirred vigorously with heating to maintain gentle reflux for 18 h. After cooling to room temperature, the suspension was filtered through Celite, and washed with CHCl₃ (500 mL). The filtrate was concentrated under reduced pressure to give the crude product. This was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (20:1) to afford the title compound as an inseparable mixture of *E/Z* **21/24** isomers in a ratio of 1:0.2 and as a colourless oil (17.94 g, 78%).

R_f (20:1 pet. ether:EtOAc) 0.31; ν_{max} (thin film)/cm⁻¹ 2910, 2884, 2813, 1690; ¹H NMR (400 MHz; CDCl₃) **21** δ 6.75 (1H, dd, *J* 15.0, 11.0, H-7), 5.93 (1H, d, *J* 15.0, H-8), 4.19–4.13 (2H, m, OCH₂CH₃), 3.77 (1H, dd, *J* 11.0, 7.5, H1a), 3.72 (1H, dd, *J* 11.0, 7.0, H-1b), 1.51 (1H, dd, *J* 11.0, 9.0, H-6), 1.39–1.32 (1H, m, H-2), 1.27 (3H, t, *J* 7.0, OCH₂CH₃), 1.16 (3H, s, H-4), 1.15 (3H, s, H-5), 0.87 (9H, s, SiC(CH₃)₃), 0.05 (3H, s, SiCH₃), 0.04 (3H, s, SiCH₃); **24** δ 5.98 (1H, dd, *J* 11.5, 11.5, H-7), 5.79 (1H, d, *J* 11.5, H-8), 4.19–4.13 (2H, m, OCH₂CH₃), 3.75–3.69 (1H, m, H-1a), 2.75 (1H, dd, *J* 11.0, 9.0, H-1b), 1.71–1.66 (1H, m, H-6 or H-2), 1.39–1.32 (1H, m, H-6 or H-2), 1.28 (3H, t, *J* 7.0, OCH₂CH₃), 1.16 (3H, s, H-4), 1.15 (3H, s, H-5), 0.87 (9H, s, SiC(CH₃)₃), 0.05 (3H, s, SiCH₃), 0.04 (3H, s, SiCH₃); ¹³C NMR (101 MHz; CDCl₃) **21** δ 166.6 (CH₃CH₂OC=O), 147.7 (C-7), 121.3 (C-8), 60.1 (C-1), 60.1 (CH₃CH₂O), 35.6 (C-6 or C-2), 31.2 (C-4), 28.9 (C-6 or C-2), 26.0 (SiC(CH₃)₃), 25.4 (C-3), 18.4

(SiC(CH₃)₃), 15.9 (C-5), 14.5 (CH₃CH₂O), -5.0 (SiCH₃), -5.1 (SiCH₃); m/z (ESI) 335 [MNa⁺]; HRMS: calcd. for C₁₇H₃₂NaO₃Si, 335.2013. Found: [MNa⁺], 335.2014 (-0.9 ppm error).

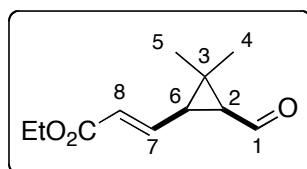
Ethyl (±)-(2E)-3-[(1S,3R)-3-(hydroxymethyl)-2,2-dimethylcyclopropyl]prop-2-enoate (22)



To a stirred solution of **21/24** (2.06 g, 6.59 mmol) in MeCN (65 mL) in a plastic container was added HF (0.41 mL, 48 wt % in water, 9.9 mmol). This was stirred at RT for 16 h before the addition of sat. NaHCO₃ (aq.) (50 mL). The solution was diluted with CH₂Cl₂ (200mL), the organic layer was separated and the aqueous layer extracted with further portions of CH₂Cl₂ (2 × 200 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (2:1) to afford the title compound **22** as a colourless oil (1.22 g, 93%).

R_f (5:1 pet. ether:EtOAc) 0.14; ν_{max} (thin film)/cm⁻¹ 3372, 2938, 2910, 1683, 1613; ¹H NMR (400 MHz; CDCl₃) δ; 6.76 (1H, dd, *J* 15.0, 11.0, H-7), 5.97 (2H, d, *J* 15.0, H-8), 4.17 (4H, q, *J* 7.0, CH₃CH₂O), 3.83 (1H, dd, *J* 11.5, 7.5, H-1a), 3.75 (1H, dd, *J* 11.5, 8.0, H-1b), 1.57 (1H, dd, *J* 11.0, 8.5, H-6), 1.50 (1H, br. s, OH), 1.42 (1H, dd, *J* 11.0, 8.0, H-2), 1.27 (6H, t, *J* 7.0, CH₃CH₂O), 1.19 (3H, s, H-5), 1.17 (3H, s, H-4); ¹³C NMR (101 MHz; CDCl₃) δ 166.6 (C=O), 146.7 (C-7), 122.0 (C-8), 60.3 (CH₃CH₂O), 60.0 (C-1) 35.5 (C-2), 31.1 (C-6), 28.9 (C-5), 25.5 (C-3), 15.9 (C-4), 14.5, (CH₃CH₂O); m/z (ESI): 221 [MNa⁺]; HRMS: calcd. for C₁₁H₁₈NaO₃, 221.1148. Found: [MNa⁺], 221.1150 (-1.0 ppm error).

Ethyl (±)-(2E)-3-[(1S,3R)-3-formyl-2,2-dimethylcyclopropyl]prop-2-enoate (23)

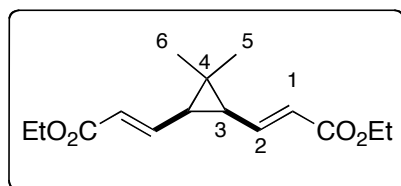


To a stirred solution of **22** (259 mg, 1.31 mmol) in CHCl₃ (13 mL) was added manganese (IV) dioxide (1.13 g, 13.1

mmol) and 4Å molecular sieves (1.13 g). After 16 h the suspension was filtered through Celite, and washed with CHCl₃ (50 mL). The filtrate was concentrated under reduced pressure to give the crude product. This was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (5:1) to afford the title compound **23** as a colourless oil (117 mg, 46%).

R_f (5:1 pet. ether:EtOAc) 0.19; ν_{max} (thin film)/cm⁻¹ 2935, 2915, 2888, 1688, 1617; ¹H NMR (400 MHz; CDCl₃) δ 9.62 (1H, d, *J* 5.0, H-1), 7.19 (1H, dd, *J* 15.5, 10.5, H-7), 5.99 (1H, d, *J* 15.5, H-8), 4.17 (2H, q, *J* 7.0, OCH₂CH₃), 2.14 (1H, dd, *J* 10.5, 8.5, H-6), 2.07 (1H, dd, *J* 8.5, 5.0, H-2), 1.40 (3H, s, H-4), 1.26 (3H, t, *J* 7.0, OCH₂CH₃), 1.25 (3H, s, H-5); ¹³C NMR (101 MHz; CDCl₃) δ 199.5 (C-1), 166.0 (CH₃CH₂OC=O), 142.9 (C-7), 123.6 (C-8), 60.4 (CH₃CH₂O), 43.2 (C-2), 38.7 (C-6), 32.4 (C-3), 28.6 (C-5), 15.7 (C-4), 14.4 (CH₃CH₂O); *m/z* (ESI) 219 [MNa⁺]; HRMS: calcd. for C₁₁H₁₆NaO₃, 219.0992. Found: [MNa⁺], 219.0991 (0.5 ppm error).

Diethyl (2*E*,2'*E*)-3,3'-[(1*R*,2*S*)-3,3-dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (9d**)**

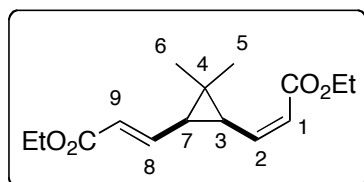


To a stirred solution of **23** (83 mg, 0.423 mmol) in CHCl₃ (10 mL) at RT was added (carbethoxymethylene)triphenylphosphorane (177 mg, 0.508 mmol). After 16 h the solution was concentrated under reduced pressure and the crude product purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (10:1) to afford the title compound **9d** as a colourless oil (53 mg, 47%).

R_f (1:1 pet. ether:EtOAc) 0.62; ν_{max} (thin film)/cm⁻¹ 2936, 2876, 1691, 1613; ¹H NMR (400 MHz; CDCl₃) δ 6.90–6.76 (2H, m, H-2), 5.95 (2H, d, *J* 15.0, H-1), 4.17 (4H, q, *J* 7.0, OCH₂CH₃), 1.91–1.85 (2H, m, H-3), 1.28 (6H, t, *J* 7.0, OCH₂CH₃), 1.25 (3H, s, H-5), 1.21, (3H, s, H-6); ¹³C NMR (101 MHz; CDCl₃) δ 166.2 (CH₃CH₂OC=O), 145.4 (C-2), 123.0 (C-1), 60.3 (CH₃CH₂O), 36.6 (C-3), 29.6 (C-4),

28.6 (C-5), 16.7 (C-6), 14.4 ($\text{CH}_3\text{CH}_2\text{O}$); m/z (ESI) 289 [MNa^+]; HRMS: calcd. for $\text{C}_{15}\text{H}_{22}\text{NaO}_4$, 289.1410. Found: [MNa^+], 289.1403 (2.3 ppm error).

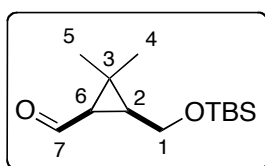
Diethyl (\pm)-(2*Z*,2'*E*)-3,3'-[(1*R*,2*S*)-3,3-Dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (9e**)**



To a solution of ethyl [bis(2,2,2-trifluoroethoxy)phosphoryl]acetate (82 mg, 0.246 mmol) in THF (2 mL) was added 18-crown-6 (145 mg, 0.548 mmol). The solution was cooled to 0 °C and KHMDS (351 μL , 0.7 M in toluene, 0.246 mmol) was added cautiously. After 15 min the solution was cooled to -78 °C and **23** (37 mg, 0.189 mmol) in THF (1 mL) was added *via* cannula. After 1 h the reaction was quenched with sat. NH_4Cl (aq.) (5 mL), Et_2O (10 mL) added and the organic layer separated. The aqueous layer was extracted with further portions of Et_2O (2×10 mL) and the combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (20:1) to afford the title compound **9e** as a colourless oil (26 mg, 52%).

R_f (15:1 pet. ether:EtOAc) 0.41; ν_{max} (thin film)/ cm^{-1} 2936, 2913, 2881, 1688, 1612; ^1H NMR (400 MHz; CDCl_3) δ 6.82 (1H, dd, J 15.0, 11.0, H-8), 6.10 (1H, dd, J 11.5, 11.5, H-2), 5.95 (1H, d, J 15.0, H-9), 5.87 (1H, d, J 11.5, H-1), 4.17 (2H, q, J 7.0, OCH_2CH_3), 4.16 (2H, q, J 7.0, OCH_2CH_3), 3.17 (1H, dd, J 11.5, 9.0, H-3), 1.94 (1H, dd, J 11.0, 9.0, H-7), 1.28 (3H, t, J 7.0, OCH_2CH_3), 1.27 (3H, t, J 7.0, OCH_2CH_3), 1.24 (3H, s, H-5), 1.23, (3H, s, H-6); ^{13}C NMR (101 MHz; CDCl_3) δ 166.7 ($\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 166.4 ($\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 146.0 (C-2 or C-8), 145.9 (C-2 or C-8), 122.6 (C-0), 121.1 (C-1), 60.3 (OCH_2CH_3), 60.0 (OCH_2CH_3), 36.7 (C-7), 33.7 (C-3), 29.9 (C-4), 28.6 (C-5), 16.5 (C-6), 14.4 (OCH_2CH_3), 14.4 (OCH_2CH_3); m/z (ESI) 289 [MNa^+]; HRMS: calcd. for $\text{C}_{15}\text{H}_{22}\text{NaO}_4$, 289.1410. Found: [MNa^+], 289.1406 (1.0 ppm error).

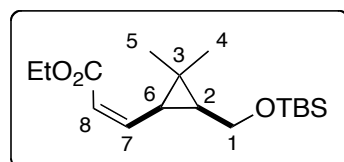
(±)-(1*S*,3*R*)-3-([*tert*-Butyl(dimethyl)silyl]oxy)methyl)-2,2-dimethylcyclopropanecarbaldehyde (SI-5)



To a stirred solution of **20** (304 mg, 1.24 mmol) in CH₂Cl₂ (10 mL) was added manganese (IV) dioxide (1.08 g, 12.4 mmol) and 4Å molecular sieves (1.08 g). After 16 h the suspension was filtered through Celite, and washed with CHCl₃ (50 mL). The filtrate was concentrated under reduced pressure to give the crude product. This was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (15:1) to afford the title compound **SI-5** as a colourless oil (166 mg, 55%).

R_f (15:1 pet. ether:EtOAc) 0.17; ν_{max} (thin film)/cm⁻¹ 2909, 2885, 2841, 1676; ¹H NMR (400 MHz; CDCl₃) δ 9.50 (1H, d, *J* 5.5, H-7), 4.06 (1H, dd, *J* 11.5, 7.5, H-1a), 3.90 (1H, dd, *J* 11.5, 7.0, H-1b), 1.74–1.62 (2H, m, H-6 & H-2), 1.36 (3H, s, H-5), 1.20 (3H, s, H-4), 0.88 (9H, s, SiC(CH₃)₃), 0.05 (3H, s, SiCH₃), 0.05 (3H, s, SiCH₃); ¹³C NMR (101 MHz; CDCl₃) δ 201.3 (C-7), 58.6 (C-1), 39.0 (C-2 or C-6), 38.8 (C-2 or C-6), 29.8 (C-3), 29.1 (C-4), 26.0 (SiC(CH₃)₃), 18.4 (SiC(CH₃)₃), 15.3 (C-5), -5.1 (SiCH₃); m/z (ESI) 265 [MNa⁺]; HRMS: calcd. for C₁₃H₂₆NaO₂Si, 265.1594. Found: [MNa⁺], 265.1593 (0.1 ppm error).

Ethyl (±)-(2*Z*)-3-[(1*S*,3*R*)-3-([*tert*-butyl(dimethyl)silyl]oxy)methyl)-2,2-dimethylcyclopropyl]prop-2-enoate (24**)**

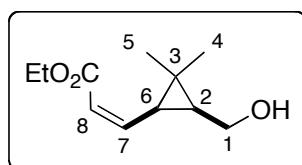


To a solution of ethyl [bis(2,2,2-trifluoroethoxy)phosphoryl]acetate (285 mg, 0.859 mmol) in THF (6 mL) was added 18-crown-6 (507 mg, 1.92 mmol). The solution was cooled to 0 °C and KHMDS (1.23 mL, 0.7 M in toluene, 0.859 mmol) was added cautiously. After 15 min the solution was cooled to -78 °C and **SI-5** (160 mg, 0.661 mmol) in THF (3 mL) was added *via* cannula. After 30 min the reaction was quenched with sat. NH₄Cl (aq.) (5 mL), Et₂O (10 mL) added and the organic layer separated. The aqueous layer was extracted with further portions of Et₂O (2 × 10 mL) and the combined organic

extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (40:1) to afford the title compound **24** as a colourless oil (109 mg, 53%).

R_f (10:1 pet. ether:EtOAc) 0.57; ν_{\max} (thin film)/cm⁻¹ 2909, 2883, 2814, 1690, 1601; ¹H NMR (400 MHz; CDCl₃) δ 5.98 (1H, dd *J* 11.5, 11.5, H-7), 5.79 (1H, d, *J* 11.5, H-8), 4.16 (2H, q, *J* 7.0, OCH₂CH₃), 3.74–3.71 (1H, m, H-1), 2.75 (1H, dd, *J* 11.5, 9.0, H-6), 1.40–1.34 (1H, m, H-2), 1.28 (3H, t, *J* 7.0, OCH₂CH₃), 1.18 (3H, s, H-4), 1.12 (3H, s, H-5), 0.87 (9H, s, SiC(CH₃)₃), 0.04 (6H, s, SiCH₃); ¹³C NMR (101 MHz; CDCl₃) δ 167.1 (CH₃CH₂OC=O), 148.1 (C-7), 119.5 (C-8), 60.0 (C-1), 59.8 (OCH₂CH₃), 35.6 (C-2), 29.0 (C-4), 28.1 (C-3), 26.0 (SiC(CH₃)₃), 25.6 (C-6), 18.4 (SiC(CH₃)₃), 15.6 (C-5), 14.5 (OCH₂CH₃), –5.0 (SiCH₃), –5.0 (SiCH₃); *m/z* (ESI) 335 [MNa⁺]; HRMS: calcd. for C₁₇H₃₂NaO₃Si, 335.2013. Found: [MNa⁺], 335.2006 (1.4 ppm error).

Ethyl (±)-(2*Z*)-3-[(1*S*,3*R*)-3-(hydroxymethyl)-2,2-dimethylcyclopropyl]prop-2-enoate (25**)**

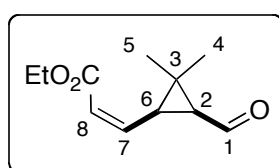


To a stirred solution of **24** (136 mg, 0.435 mmol) in MeCN (10 mL) in a plastic container was added HF (2 drops, 48 wt % in water). This was stirred at RT for 16 h before the addition of sat. NaHCO₃ (aq.) (5 mL). The solution was diluted with CH₂Cl₂ (10 mL), the organic layer was separated and the aqueous layer extracted with further portions of CH₂Cl₂ (2 × 10 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (2:1) to afford the title compound **25** as a colourless oil (73 mg, 85%).

R_f (1:1 pet. ether:EtOAc) 0.38; ν_{\max} (thin film)/cm⁻¹ 3372, 2939, 2883, 2827, 1689, 1601; ¹H NMR (400 MHz; CDCl₃) δ 6.02 (1H, dd, *J* 11.5 10.5, H-7), 5.85 (1H, d, *J* 11.5, H-8), 4.17 (2H, q, *J* 7.0, OCH₂CH₃), 3.79 (1H, dd, *J* 11.5, 7.5, H-1a), 3.65 (1H,

dd, J 11.5, 8.0, H-1b), 2.73–2.68 (1H, m, H-6), 1.47–1.39 (1H, m, H-2), 1.28 (3H, t, J 7.0, OCH_2CH_3), 1.19 (3H, s, H-4), 1.14 (3H, s, H-5); ^{13}C NMR (101 MHz; CDCl_3) δ 167.1 ($\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 147.0 (C-7), 120.5 (C-8), 60.0 (C-1), 60.0 (OCH_2CH_3), 35.5 (C-2), 28.8 (C-6), 28.0 (C-5), 25.4 (C-3), 15.6 (C-4), 14.4 (OCH_2CH_3); m/z (ESI) 221 [MNa^+]; HRMS: calcd. for $\text{C}_{11}\text{H}_{18}\text{NaO}_3$, 221.1148. Found: [MNa^+], 221.1140 (3.5 ppm error).

Ethyl (\pm)-(2Z)-3-[(1S,3R)-3-formyl-2,2-dimethylcyclopropyl]prop-2-enoate (SI-6)

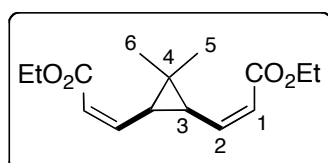


To a stirred solution of **25** (73 mg, 0.368 mmol) in CHCl_3 (5 mL) was added manganese (IV) dioxide (320 mg, 3.68 mmol) and 4 Å molecular sieves (320 mg). After 12 h the suspension was filtered through Celite, and washed with CHCl_3 (25 mL).

The filtrate was concentrated under reduced pressure to give the crude product. This was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (5:1) to afford the title compound **SI-6** as a colourless oil (38 mg, 53%).

R_f (5:1 pet. ether:EtOAc) 0.34; ν_{max} (thin film)/ cm^{-1} 2911, 2876, 1689, 1610; ^1H NMR (400 MHz; CDCl_3) δ 9.72 (1H, d, J 4.0, H-1), 6.55 (1H, dd, J 11.5, 10.5, H-7), 5.88 (1H, d, J 11.5, H-8), 4.16 (2H, q, J 7.0, OCH_2CH_3), 3.49–3.44 (1H, m, H-6), 2.21 (1H, dd, J 8.5, 4.0, H-2), 1.34 (3H, s, H-4), 1.30 (3H, s, H-5), 1.28 (3H, t, J 7.0, OCH_2CH_3); ^{13}C NMR (101 MHz; CDCl_3) δ 199.9 (C-1), 166.7 ($\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 143.7 (C-7), 121.3 (C-8), 60.1 (OCH_2CH_3), 43.1 (C-2), 36.2 (C-6), 33.3 (C-3), 28.8 (C-4), 15.1 (C-5), 14.4 (OCH_2CH_3); m/z (ESI) 197 [MH^+]; HRMS: calcd. for $\text{C}_{11}\text{H}_{17}\text{O}_3$, 197.1172. Found: [MH^+], 197.1167 (2.8 ppm error).

Diethyl (2Z,2'Z)-3,3'-[(1R,2S)-3,3-dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (9f)

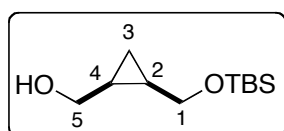


To a solution of ethyl [bis(2,2,2-trifluoroethoxy)phosphoryl]acetate (80 mg, 0.246 mmol) in THF (3 mL) was added 18-crown-6 (145 mg, 0.548

mmol). The solution was cooled to 0 °C and KHMDS (350 µL, 0.7 M in toluene, 0.246 mmol) was added cautiously. After 15 min the solution was cooled to –78 °C and **SI-6** (37 mg, 0.189 mmol) in THF (2 mL) was added *via* cannula. After 1 h the reaction was quenched with sat. NH₄Cl (aq.) (5 mL), Et₂O (10 mL) added and the organic layer separated. The aqueous layer was extracted with further portions of Et₂O (2 × 10 mL) and the combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (20:1) to afford the title compound **9f** as a colourless oil (28 mg, 56%).

R_f (1:1 pet. ether:Et₂O) 0.71; ν_{max} (thin film)/cm^{–1} 2935, 2913, 2874, 1691, 1627; ¹H NMR (400 MHz; CDCl₃) δ 6.08–6.01 (2H, m, H-2), 5.85 (2H, d, *J* 12.0, H-1), 4.16 (4H, q, *J* 7.0, OCH₂CH₃), 3.17–3.11 (2H, m, H-3), 1.28 (3H, s, H-5), 1.28 (3H, t, *J* 7.0, OCH₂CH₃), 1.17 (3H, s, H-6); ¹³C NMR (101 MHz; CDCl₃) δ 166.7 (CH₃CH₂OC=O), 146.0 (C-2), 121.0 (C-1), 60.0 (OCH₂CH₃), 33.7 (C-3), 30.2 (C-4), 28.8 (C-5), 16.3 (C-6), 14.4 (OCH₂CH₃); *m/z* (ESI) 267 [MH⁺]; HRMS: calcd. for C₁₅H₂₃O₄, 267.1591. Found: [MH⁺], 267.1587 (1.1 ppm error).

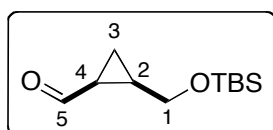
(±)-[(1*R*,2*S*)-2-({*tert*-Butyl(dimethyl)silyl}oxy)methyl]cyclopropyl]methanol (**28**)⁵



To a stirred solution of **27** (720 mg, 7.06 mmol) in THF (14 mL) at 0 °C was added NaH (339 mg, 8.47 mmol, 60% dispersion in mineral oil). After 45 mins, by which time a large amount of white precipitate had formed, TBSCl (1.06 g, 7.06 mmol) was added. The reaction mixture was warmed to RT and allowed to stir for a further 1 h before dilution with Et₂O (25 mL). It was then washed with sat. NH₄Cl (aq.) (20 mL) and brine (10 mL), the organic layer separated and the aqueous layer extracted with further portions of Et₂O (2 × 20 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure to afford the title compound **28** as a colourless oil (1.53 g, 100%), which was used in the next step without further purification.

R_f (EtOAc) 0.81; ^1H NMR (400 MHz; CDCl_3) δ 4.15 (1H, dd, J 11.5, 5.5, H-1a or H-5a), 3.97 (1H, dd, J 12.0, 5.5, H-1a or H-5a), 3.26–3.20 (2H, m, H-1 & H-5) 1.43–1.30 (1H, m, H-4 or H-2), 1.30–1.18 (1H, m, H-4 or H-2), 0.92 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.80–0.71 (1H, m, H-3a), 0.23–0.16 (1H, m, H-3b), 0.12 (3H, s, SiCH_3), 0.10 (3H, s, SiCH_3). Data in agreement with those reported in the literature.⁵

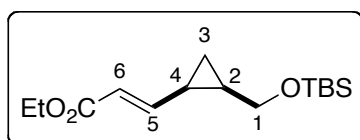
(±)-(1*R*,2*S*)-2-([*tert*-Butyl(dimethyl)silyl]oxy)methyl)cyclopropanecarbaldehyde (SI-7)⁵



To a stirred solution of **28** (1.61 g, 7.44 mmol) in CHCl_3 (75 mL) was added manganese (IV) dioxide (6.47 g, 74.4 mmol) and 4 Å molecular sieves (6.47 g). After 16 h the suspension was filtered through Celite, and washed with CHCl_3 (150 mL). The filtrate was concentrated under reduced pressure to afford the title compound **SI-7** as a colourless oil (1.20 g, 75%), which was used in the next step without further purification.

R_f (1:1 pet. ether:EtOAc) 0.86; ^1H NMR (400 MHz; CDCl_3) δ 9.41 (1H, d, J 5.0, H-5), 3.97 (1H, dd, J 11.0, 5.5, H-1a), 3.62 (1H, dd, J 11.0, 7.5, H-1b), 2.02–1.91 (1H, m, H-4 or H-2), 1.82–1.73 (1H, m, H-4 or H-2), 1.37–1.32 (1H, m, H-3a), 1.25–1.20 (1H, m, H-3b), 0.87 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.04 (3H, s, SiCH_3), 0.03 (3H, s, SiCH_3). Data in agreement with those reported in the literature.⁵

Ethyl (±)-(2*E*)-3-[(1*S*,2*S*)-2-([*tert*-butyl(dimethyl)silyl]oxy)methyl]cyclopropyl]prop-2-enoate (29)⁵

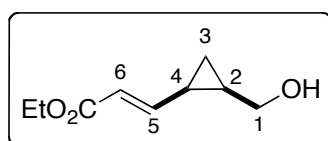


To a stirred solution of **SI-7** (534 mg, 2.50 mmol) in CHCl_3 (25 mL) at RT was added (carbethoxymethylene) triphenyl phosphorane (1.04 g, 3.00 mmol). After 16 h the solution was concentrated under reduced pressure and the crude product purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (40:1) to afford the title compound **29** as a colourless oil (471 mg, 63%).

R_f (20:1 pet. ether:EtOAc) 0.31; ^1H NMR (400 MHz; CDCl_3) δ 6.72 (1H, dd, J 15.5,

10.5, H-5), 5.92 (1H, d, J 15.5, H-6), 4.17 (2H, q, J 7.0, CH₃CH₂O), 3.82 (1H, dd, J 11.0, 5.6, H-1a), (1H, dd, J 11.0 7.5, H-1b), 1.67–1.78 (1H, m, H-4 or H-2), 1.49–1.58 (1H, m, H-4 or H-2), 1.28 (3H, t, J 7.1, CH₃CH₂O), 1.09–1.16 (1H, m, H-3a), 0.89 (9H, s, SiC(CH₃)₃), 0.68–0.75 (1H, m, H-3b), 0.06 (3H, s, SiCH₃), 0.05 (3H, s, SiCH₃). Data in agreement with those reported in the literature.⁵

Ethyl (±)-(2*E*)-3-[(1*S*,2*S*)-2-(hydroxymethyl)cyclopropyl]prop-2-enoate (30**)⁶**

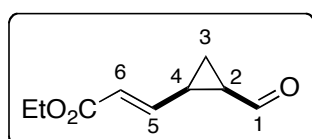


To a stirred solution of **29** (471 mg, 1.59 mmol) in MeCN (15 mL) in a plastic container was added HF (130 μL, 48 wt % in water, 3.18 mmol). This was stirred at RT for 16

h before the addition of sat. NaHCO₃ (aq.) (15 mL). The solution was diluted with CH₂Cl₂ (10 mL), the organic layer was separated and the aqueous layer extracted with further portions of CH₂Cl₂ (2 × 20 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure to afford the title compound **30** as a colourless oil (254 mg, 94%), which was used in the next step without further purification.

R_f (1:1 pet. ether: EtOAc) 0.42; ¹H NMR (400 MHz; CDCl₃) δ 6.69 (1H, dd, J 15.5, 10.0, H-5), 5.95 (1H, d, J 15.5, H-6), 4.19–4.11 (2H, m, CH₃CH₂O), 3.82 (1H, ddd, J 11.5, 6.0, 1.5 H-1a), 3.50 (1H, dd, J 11.5, 8.5, H-1b), 1.98 (1H, br s, OH), 1.81–1.70 (1H, m, H-4 or H-2), 1.63–1.52 (1H, m, H-4 or H-2), 1.25 (3H, t, J 7.0, CH₃CH₂O), 1.20–1.13 (1H, m, H-3a), 0.72–0.65 (1H, m, H-3b). Data in agreement with those reported in the literature.⁶

Ethyl (±)-(2*E*)-3-[(1*S*,2*S*)-2-formylcyclopropyl]prop-2-enoate (31**)⁶**



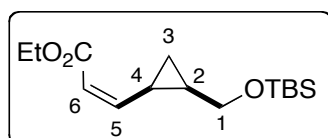
To a stirred solution of **30** (281 mg, 1.65 mmol) in CHCl₃ (15 mL) was added manganese (IV) dioxide (1.43 g, 16.5 mmol) and 4Å molecular sieves (1.43 g). After 16 h the

suspension was filtered through Celite, and washed with CHCl₃ (50 mL). The filtrate was concentrated under reduced pressure to afford the title compound **31** as a

colourless oil (224 mg, 81%), which was used in the next step without further purification.

R_f (1:1 pet. ether: EtOAc) 0.57; ^1H NMR (400 MHz; CDCl_3) δ 9.47 (1H, d, J 4.5, H-1), 6.82 (1H, dd, J 15.5, 9.5, H-5), 6.02 (1H, d, J 15.5, H-6), 4.18 (1H, q, J 7.0, $\text{CH}_3\text{CH}_a\text{H}_b\text{O}$), 4.17 (1H, q, J 7.0, $\text{CH}_3\text{CH}_a\text{H}_b\text{O}$), 2.37–2.21 (2H, m, H-4 & H-2), 1.68–1.63 (1H, m, H-3a), 1.60–1.53 (1H, m, H-3b), 1.28 (3H, t, J 7.0, $\text{CH}_3\text{CH}_2\text{O}$). Data in agreement with those reported in the literature.⁶

Ethyl (\pm)-(2Z)-3-[(1S,2S)-2-([*tert*-butyl(dimethyl)silyl]oxy)methyl)cyclopropyl]prop-2-enoate (32**)**



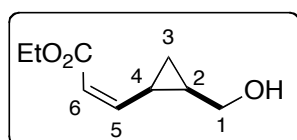
To a solution of ethyl [bis(2,2,2-trifluoroethoxy)phosphoryl]acetate (1.31 g, 4.04 mmol) in THF (40 mL) was added 18-crown-6 (2.38 g, 9.02 mmol).

The solution was cooled to 0 °C and KHMDS (5.80 mL, 0.7 M in toluene, 4.04 mmol) was added cautiously. After 15 min the solution was cooled to –78 °C and **SI-7** (665 mg, 3.11 mmol) in THF (40 mL) was added *via* cannula. After 2 h the reaction was quenched with sat. NH_4Cl (aq.) (50 mL), Et_2O (50 mL) added and the organic layer separated. The aqueous layer was extracted with further portions of Et_2O (2 \times 50 mL) and the combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (50:1) to afford the title compound **32** as a colourless oil (883 mg, 40%).

R_f (50:1 pet. ether:EtOAc) 0.18; ν_{max} (thin film)/ cm^{-1} 2910, 2886, 2814, 1690, 1608; ^1H NMR (400 MHz; CDCl_3) δ 5.91 (1H, dd, J 11.5, 11.5, H-5), 5.75 (1H, d, J 11.5, H-6), 4.17 (2H, q, J 7.0, OCH_2CH_3), 3.78 (1H, dd, J 11.0, 6.0, H-1a), 3.69 (1H, dd, J 11.0, 7.0, H-1b), 3.04–2.95 (1H, m, H-4), 1.59–1.49 (1H, m, H-2), 1.29 (3H, t, J 7.0, $\text{CH}_3\text{CH}_2\text{O}$), 1.24–1.15 (1H, m, H-3a), 0.88 (9H, s, $(\text{SiC}(\text{CH}_3)_3)$), 0.70–0.63 (1H, m, H-3b), 0.05 (6H, s, SiCH_3); ^{13}C NMR (101 MHz; CDCl_3) δ 167.2 ($\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 151.3 (C-5), 118.7 (C-6), 62.6 (C-1), 59.8 (OCH_2CH_3), 26.1 ($\text{SiC}(\text{CH}_3)_3$), 23.7 (C-2),

18.5 (SiC(CH₃)₃), 17.0 (C-4), 14.5 (OCH₂CH₃), 14.4 (C-3), -5.1 (SiCH₃), -5.1 (SiCH₃); m/z (ESI) 285 [MH⁺]; HRMS: calcd. for C₁₅H₂₉O₃Si, 285.1880. Found: [MH⁺], 285.1880 (0.0 ppm error).

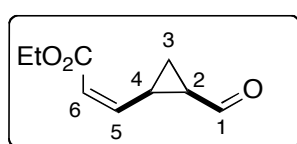
Ethyl (±)-(2Z)-3-[(1S,2S)-2-(hydroxymethyl)cyclopropyl]prop-2-enoate (**33**)



To a stirred solution of **32** (339 mg, 1.14 mmol) in MeCN (10 mL) in a plastic container was added HF (90 μL, 48 wt % in water, 2.28 mmol). This was stirred at RT for 16 h before the addition of sat. NaHCO₃ (aq.) (15 mL). The solution was diluted with CH₂Cl₂ (15 mL), the organic layer was separated and the aqueous layer extracted with further portions of CH₂Cl₂ (2 × 20 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure to afford the title compound **33** as a colourless oil (188 mg, 97%), which was used in the next step without further purification.

R_f (1:1 pet. ether: EtOAc) 0.43; ν_{max} (thin film)/cm⁻¹ 3365, 2937, 2912, 2874, 1687, 1607; ¹H NMR (400 MHz; CDCl₃) δ 5.89 (1H, dd, *J* 11.5, 10.0, H-5), 5.83 (1H, d, *J* 11.5, H-6), 4.19 (2H, q, *J* 7.0, OCH₂CH₃), 3.85 (1H, dd, *J* 11.5, 6.0, H-1a), 3.55 (1H, dd, *J* 11.5, 8.5, H-1b), 3.03–2.95 (1H, m, H-4), 1.69–1.39 (1H, m, H-2), 1.29 (3H, t, *J* 7.0, CH₃CH₂O), 1.28–1.23 (1H, m, H-3a), 0.67–0.62 (1H, m, H-3b); ¹³C NMR (101 MHz; CDCl₃) δ 167.0 (CH₃CH₂OC=O), 149.8 (C-5), 120.0 (C-6), 63.1 (C-1), 60.0 (OCH₂CH₃), 23.8 (C-2), 16.5 (C-4), 14.5 (C-3), 14.4 (OCH₂CH₃); m/z (ESI) 193 [MNa⁺]; HRMS: calcd. for C₉H₁₄NaO₃, 193.0835. Found: [MNa⁺], 193.0833 (0.6 ppm error).

Ethyl (±)-(2Z)-3-[(1S,2S)-2-formylcyclopropyl]prop-2-enoate (**SI-8**)

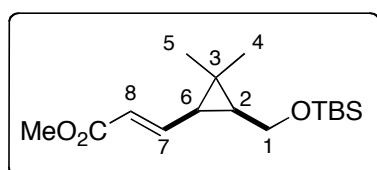


To a stirred solution of **33** (185 mg, 1.09 mmol) in CHCl₃ (10 mL) was added manganese (IV) dioxide (948 mg, 10.9 mmol) and 4Å molecular sieves (948 mg). After 16 h the suspension was filtered through Celite, and washed with CHCl₃ (50 mL). The filtrate

was concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (20:1) to afford the title compound **SI-8** as a colourless oil (97 mg, 53%).

R_f (20:1 pet. ether:EtOAc) 0.18; ν_{\max} (thin film)/ cm^{-1} 2938, 2894, 2861, 2803, 2699, 1685, 1613; ^1H NMR (400 MHz; CDCl_3) δ 9.67 (1H, d, J 3.5, H-1), 6.09 (1H, dd, J 11.5, 10.5, H-5), 5.83 (1H, d, J 11.5, H-6), 4.18 (2H, q, J 7.0, OCH_2CH_3), 3.67–3.56 (1H, m, H-4), 2.50–2.42 (1H, m, H-2), 1.60–1.52 (2H, m, H-3), 1.29 (3H, t, J 7.0, $\text{CH}_3\text{CH}_2\text{O}$); ^{13}C NMR (101 MHz; CDCl_3) δ 200.0 (C-1), 166.7 ($\text{CH}_3\text{CH}_2\text{OC}=\text{O}$), 146.0 (C-5), 121.1 (C-6), 60.2 (OCH_2CH_3), 31.1 (C-2), 23.9 (C-4), 17.3 (C-3), 14.4 (OCH_2CH_3); m/z (ESI) 191 [MNa^+]; HRMS: calcd. for $\text{C}_9\text{H}_{12}\text{NaO}_3$, 191.0679. Found: [MNa^+], 191.0676 (0.3 ppm error).

Methyl (\pm)-(E)-3-((1*R*,3*S*)-3-((*tert*-butyldimethylsilyloxy)methyl)-2,2-dimethylcyclopropyl)prop-2-enoate (34**)**

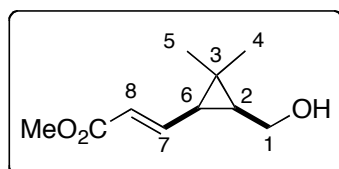


To a stirred solution of **20** (200 mg, 0.818 mmol) in CHCl_3 (8 mL) was added manganese (IV) dioxide (711 mg, 8.18 mmol) and (methoxycarbonylmethylen)-triphenylphosphorane (328 mg, 0.982 mmol). The resulting suspension was stirred vigorously with heating to maintain gentle reflux for 48 h. After cooling to room temperature, the suspension was filtered through Celite, and washed with CHCl_3 (20 mL). The filtrate was concentrated under reduced pressure to give the crude product. This was purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (50:1) to afford the title compound **34** as a mixture of *E/Z* isomers in a ratio of 1:0.16 and as a colourless oil (118 mg, 48%).

R_f (10:1 pet.ether:EtOAc) 0.56; ν_{\max} (thin film)/ cm^{-1} 2908, 2814, 1696, 1242, 1066; ^1H NMR (400 MHz; CDCl_3) *E* δ 6.76 (1H, dd, J 15.0, 11.0, H-7), 5.93 (1H, d, J 15.0, H-8), 3.81–3.69 (2H, m, H-1), 3.71 (3H, s, OCH_3), 1.57–1.48 (1H, m, H-6), 1.39–1.32 (1H, m, H-2), 1.16 (3H, s, H-4), 1.15 (3H, s, H-5), 0.87 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.05 (3H, s, SiCH_3), 0.04 (3H, s, SiCH_3) *Z* δ 5.99 (1H, dd, J 11.5, 11.5, H-7), 5.80

(1H, d, J 11.5, H-8), 4.00–3.86 (2H, m, H-1), 3.71 (3H, s, OCH₃), 1.50–1.44 (2H, m, H-6 & H-2), 1.20 (3H, s, H-4), 1.19 (3H, s, H-5), 0.89 (9H, s, SiC(CH₃)₃), 0.06 (6H, s, SiCH₃); ¹³C NMR (101 MHz; CDCl₃) E δ 167.0 (CH₃OC=O), 148.1 (C-7), 120.8 (C-8), 60.1 (C-1), 51.4 (CH₃O), 35.7 (C-6 or C-2), 31.2 (C-4), 28.9 (C-6 or C-2), 26.0 (SiC(CH₃)₃), 25.6 (C-3), 18.4 (SiC(CH₃)₃), 15.9 (C-5), –5.1 (SiCH₃), –5.1 (SiCH₃); m/z (ESI): 321 [MNa⁺]; HRMS: calcd. for C₁₆H₃₀NaO₃Si, 321.1856. Found: [MNa⁺], 321.1852 (1.1 ppm error).

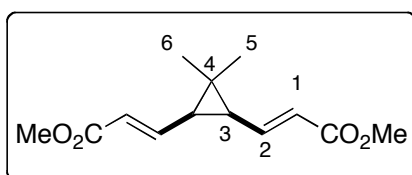
Methyl (±)-(E)-3-((1R,3S)-3-(hydroxymethyl)-2,2-dimethylcyclopropyl)prop-2-enoate (35)



To a stirred solution of **34** (100 mg, 0.335 mmol) in MeCN (4 mL) in a plastic container was added HF (23 μ L, 48 wt % in water, 0.531 mmol). This was stirred at RT for 16 h before the addition of sat. NaHCO₃ (aq.) (5 mL). The solution was diluted with CH₂Cl₂ (10 mL), the organic layer was separated and the aqueous layer extracted with further portions of CH₂Cl₂ (2 \times 10 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure to afford the title compound **35** as a colourless oil (50 mg, 81%), which was used in the next step without further purification.

R_f (1:1 pet.ether:EtOAc) 0.47; ν_{\max} (thin film)/cm⁻¹ 3373, 2907, 1690, 1416; ¹H NMR (400 MHz; CDCl₃) E δ 6.78 (1H, dd, J 15.0, 11.0, H-7), 5.98 (1H, d, J 15.0, H-8), 3.87–3.73 (2H, m, H-1), 3.71 (3H, s, OCH₃), 1.58 (1H, dd, J 11.0, 9.0, H-6), 1.43 (1H, dd, J 9.0, 7.5, H-2), 1.19 (3H, s, H-4), 1.18 (3H, s, H-5); Z δ 6.78 (1H, dd, J 11.5, 10.5, H-7), 5.87 (1H, d, J 11.5, H-8), 3.87–3.73 (2H, m, H-1), 3.72 (3H, s, OCH₃), 1.60–1.39 (2H, m, H-6 & H-2), 1.19 (3H, s, H-4), 1.18 (3H, s, H-5); ¹³C NMR (101 MHz; CDCl₃) δ 167.0 (CH₃OC=O), 147.1 (C-7), 121.5 (C-8), 59.9 (C-1), 51.5 (CH₃O), 35.5 (C-6 or C-2), 31.1 (C-4), 28.9 (C-6 or C-2), 25.7 (C-3), 15.9 (C-5); m/z (ESI): 207 [MNa⁺]; HRMS: calcd. for C₁₀H₁₆NaO₃, 207.0992. Found: [MNa⁺], 207.0989 (1.0 ppm error).

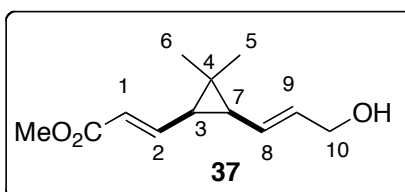
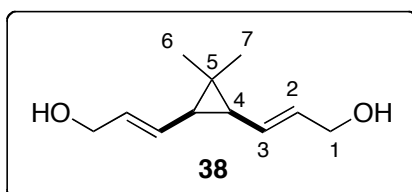
Dimethyl (2*E*,2'*E*)-3,3'-((1*R*,2*S*)-3,3-dimethylcyclopropane-1,2-diyl)diprop-2-enoate (36**)**



To a stirred solution of **35** (50 mg, 0.272 mmol) in CHCl_3 (3 mL) at RT was added (methoxycarbonylmethylen)-triphenylphosphorane (109 mg, 0.326 mmol). After 16 h the solution was concentrated under reduced pressure and the crude product purified by flash column chromatography on silica gel, eluting with pet. ether:EtOAc (20:1) to afford the title compound **36** as a colourless oil (32 mg, 49%).

R_f (20:1 pet.ether:EtOAc) 0.18; ν_{\max} (thin film)/ cm^{-1} 2908, 2873, 1689, 1610, 1413; ^1H NMR (400 MHz; CDCl_3) δ 6.89–6.78 (2H, m, H-2), 5.96 (2H, d, J 15.5, H-1), 3.72 (6H, s, OCH_3), 1.93–1.86 (2H, m, H-3), 1.26 (3H, s, H-5), 1.21, (3H, s, H-6); ^{13}C NMR (101 MHz; CDCl_3) δ 166.6 ($\text{CH}_3\text{OC}=\text{O}$), 145.7 (C-2), 122.5 (C-1), 51.6 (CH_3O), 36.7 (C-3), 29.7 (C-4), 28.5 (C-5), 16.7 (C-6); m/z (ESI): 261 [MNa^+]; HRMS: calcd. for $\text{C}_{10}\text{H}_{16}\text{NaO}_3$, 261.1097. Found: [MNa^+], 261.1096 (0.4 ppm error).

(2*E*,2'*E*)-3,3'-((1*R*,2*S*)-3,3-Dimethylcyclopropane-1,2-diyl)diprop-2-en-1-ol (38**) & Methyl (\pm)-(*E*)-3-((1*R*,3*S*)-3-((*E*)-3-hydroxyprop-1-enyl)-2,2-dimethylcyclopropyl)prop-2-enoate (**37**)**



To a stirred solution of **36** (250 mg, 1.06 mmol) in CH_2Cl_2

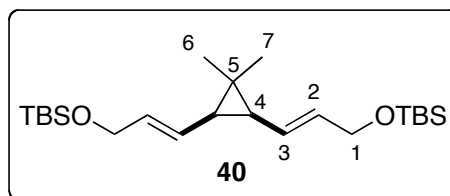
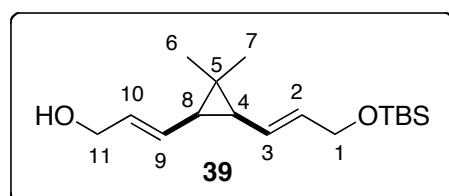
(10 mL) at -78°C was added DIBAL (2.10 mL, 2.10 mmol, 1M in hexanes). After 30 mins, MeOH (1 mL) was added and the reaction was warmed to RT, sat. aq. Rochelle's salt (5 mL) was added and the mixture was stirred overnight. The organic layer was separated and the aqueous layer extracted with further portions of CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure to afford the crude compound, which was purified by flash column chromatography on silica gel, eluting with pet. ether: EtOAc

(2: 1) to afford **38** as a colourless oil (64 mg, 33%) and **37** as a colourless oil (21 mg, 9%).

38 R_f (2:1 pet.ether:EtOAc) 0.18; ν_{\max} (thin film)/ cm^{-1} 3284, 2954, 2899, 2821, 1356; ^1H NMR (400 MHz; CDCl_3) δ 5.79 (2H, dt, J 15.0, 6.0, H-3), 5.56–5.48 (2H, m, H-2), 4.10 (4H, dd, J 6.0, 1.5, H-1), 1.58–1.52 (2H, m, H-4), 1.12 (3H, s, H-5), 1.09 (3H, s, H-6); ^{13}C NMR (101 MHz; CDCl_3) δ 130.7 (C-3), 129.5 (C-2), 63.9 (C-1), 33.4 (C-4), 28.6 (C-7), 24.4 (C-5), 16.3 (C-6); m/z (ESI): 205 [MNa^+]; HRMS: calcd. for $\text{C}_{11}\text{H}_{18}\text{NaO}_2$, 205.1199. Found: [MNa^+], 205.1192 (3.0 ppm error).

37 R_f (2:1 pet.ether:EtOAc) 0.55; ν_{\max} (thin film)/ cm^{-1} 3357, 2906, 2876, 1689, 1610; ^1H NMR (400 MHz; CDCl_3) δ 6.81 (1H, dd, J 15.0, 11.0, H-2), 5.94 (1H, d, J 15.0, H-1), 5.83 (1H, dt, J 15.0, 6.0, H-9), 5.60 (1H, ddt, J 15.0, 9.5, 1.5, H-8), 4.13 (2H, dd, J 6.0, 1.5, H-10), 3.72 (3H, s, OCH_3), 1.81 (1H, dd, J 9.5, 8.5, H-7), 1.68 (1H, dd, J 11.0, 8.5, H-3), 1.19 (3H, s, H-5), 1.17 (3H, s, H-6); ^{13}C NMR (101 MHz; CDCl_3) δ 167.0 ($\text{CH}_3\text{OC}=\text{O}$), 147.7 (C-2), 132.0 (C-1), 128.2 (C-9), 121.3 (C-8), 63.8 (C-10), 51.5 (CH_3O), 36.5 (C-7), 34.4 (C-3), 28.6 (C-5), 27.6 (C-4), 16.6 (C-6); m/z (ESI): 233 [MNa^+]; HRMS: calcd. for $\text{C}_{12}\text{H}_{18}\text{NaO}_3$, 233.1148. Found: [MNa^+], 233.1143 (2.1 ppm error).

(±)-(*E*)-3-((1*R*,3*S*)-3-((*E*)-3-(*tert*-butyldimethylsilyloxy)prop-1-enyl)-2,2-dimethylcyclopropyl)prop-2-en-1-ol (**39**) & (2*E*,2'*E*)-3,3'-((1*R*,2*S*)-3,3-Dimethylcyclopropane-1,2-diyl)bis(prop-2-ene-3,1-diyl)bis(oxy)bis(*tert*-butyldimethylsilane) (**40**)



To a stirred solution of diol **38** (122 mg,

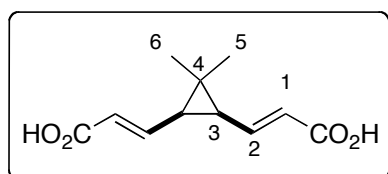
0.669 mmol) in CH_2Cl_2 (10 mL) was added TBSCl (150 mg, 1.00 mmol) and imidazole (68 mg, 1.00 mmol). After 2 h aq. HCl (10 mL) was added. The organic layer was separated and the aqueous layer extracted with further portions of CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried (MgSO_4), filtered and

concentrated under reduced pressure to afford the crude compound, which was purified by flash column chromatography on silica gel, eluting with pet. ether: Et₂O (10: 1) to afford **39** as a colourless oil (40 mg, 20%) and **40** as a colourless oil (96 mg, 35%).

39 R_f (10:1 pet.ether:Et₂O) 0.28; ν_{\max} (thin film)/cm⁻¹ 3346, 2882, 2813, 1441; ¹H NMR (400 MHz; CDCl₃) δ 5.78 (1H, dt, *J* 15.0, 6.0, H-2 or H-10), 5.69 (1H, dt, *J* 15.0, 5.0, H-2 or H-10), 5.56–5.43 (2H, m, H-3 & H-9), 4.15 (2H, br d, *J* 5.0, H-1 or H-11), 4.09 (2H, br d, *J* 6.0, H-1 or H-11), 1.58–1.50 (1H, m, H-4 or H-8), 1.11 (3H, s, H-5), 1.09 (3H, s, H-6), 0.94–0.85 (1H, m H-4 or H-8), 0.905 (9H, s, SiC(CH₃)₃), 0.06 (6H, s, SiCH₃); ¹³C NMR (101 MHz; CDCl₃) δ 131.0 (C-2 or C-10), 130.5 (C-2 or C-10), 130.1 (C-3 or C-9), 127.4 (C-3 or C-9), 64.1 (C-1 or C-11), 64.1 (C-1 or C-11), 33.4 (C-4 or C-8), 33.3 (C-4 or C-8), 28.7 (C-7), 26.1 (SiC(CH₃)₃), 24.3 (C-5), 18.6 (SiC(CH₃)₃), 16.3 (C-6), –5.0 (SiCH₃) m/z (ESI): 319 [MNa⁺]; HRMS: calcd. for C₁₇H₃₂NaO₂Si, 319.2064. Found: [MNa⁺], 319.2047 (4.9 ppm error).

40 R_f (10:1 pet.ether:Et₂O) 0.75; ν_{\max} (thin film)/cm⁻¹ 2909, 2885, 2813; ¹H NMR (400 MHz; CDCl₃) δ 5.68 (2H, dt, *J* 15.0, 5.5, H-3), 5.53–5.42 (2H, m, H-2), 4.18–4.08 (4H, m, H-1), 1.58–1.52 (2H, m, H-4), 1.12 (3H, s, H-5), 1.09 (3H, s, H-6), 0.90 (18H, s, SiC(CH₃)₃), 0.06 (12H, s, SiCH₃); ¹³C NMR (101 MHz; CDCl₃) δ 130.8 (C-3), 127.8 (C-2), 64.2 (C-1), 33.3 (C-4), 28.7 (C-7), 26.1 (SiC(CH₃)₃), 24.0 (C-5), 18.6 (SiC(CH₃)₃), 16.4 (C-6), –5.0 (SiCH₃); m/z (ESI): 433 [MNa⁺]; HRMS: calcd. for C₂₃H₄₆NaO₂Si₂, 433.2929. Found: [MNa⁺], 433.2916 (3.2 ppm error).

(2*E*,2'*E*)-3,3'-((1*R*,2*S*)-3,3-dimethylcyclopropane-1,2-diyl)diprop-2-enoic acid (41)



To a solution of **36** (71 mg, 0.298 mmol) in THF:H₂O 1:1 (6 mL) was added NaOH (83 mg, 2.09 mmol). This was stirred at RT for 16 h before the addition of Et₂O (10 mL). The Et₂O layer was

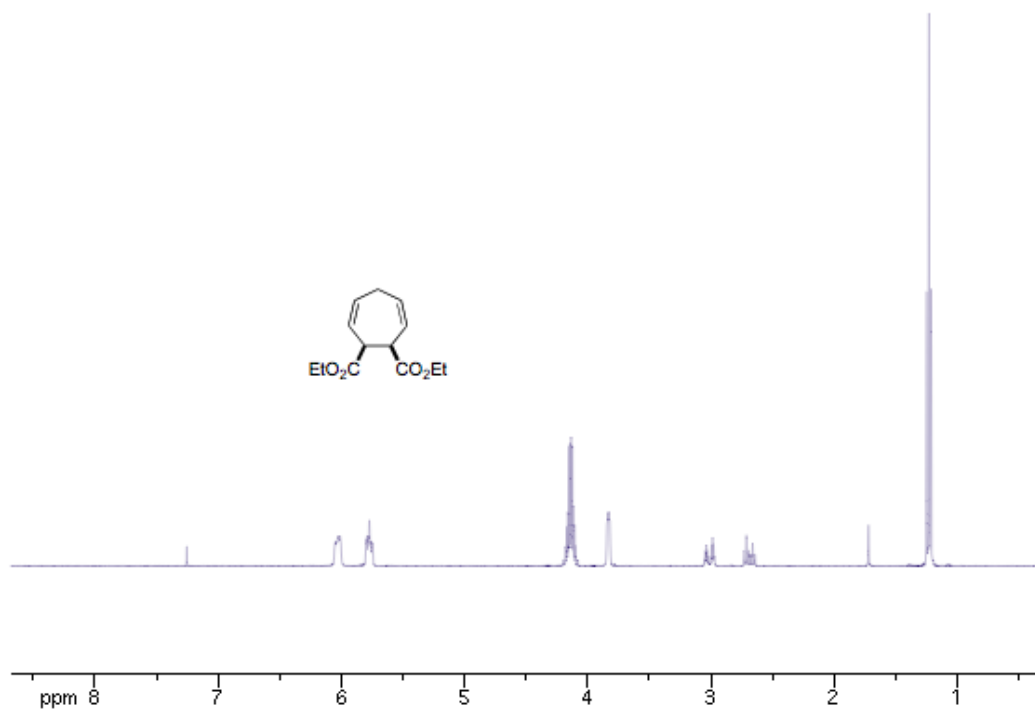
removed and the aq. layer was acidified with 10% aq. HCl (20 mL). The aqueous layer was extracted with of EtOAc (2 x 20 mL) and the combined organic extracts

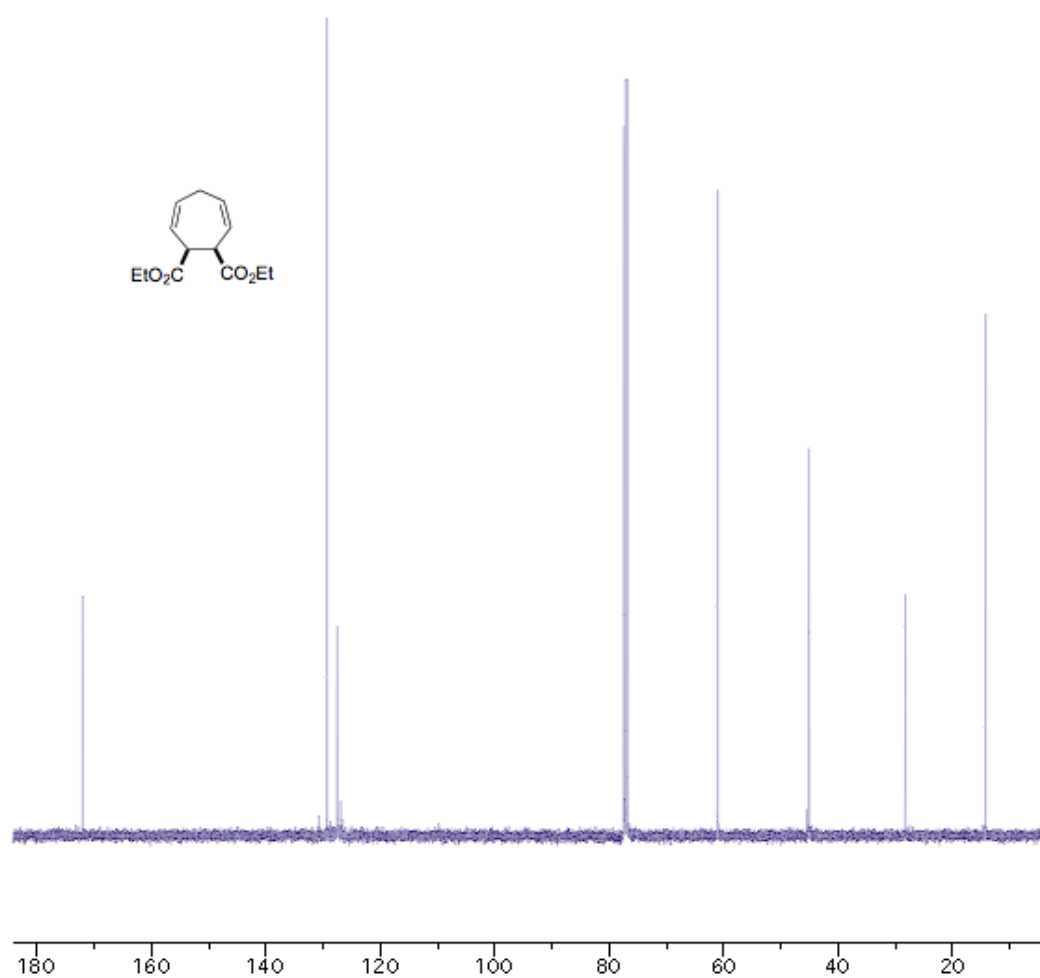
were dried (MgSO_4), filtered and concentrated under reduced pressure to afford title compound **41**, without further purification as a light brown solid (62 mg, 100%).

ν_{max} (thin film)/ cm^{-1} 2879, 2600 (br), 1679, 1627, 1421; ^1H NMR (400 MHz; DMSO) δ 5.93–5.85 (2H, m, H-2), 5.10 (2H, d, J 15.0, H-1), 1.21–1.14 (2H, m, H-3), 0.34 (3H, s, H-5), 0.30 (3H, s, H-6) ^{13}C NMR (101 MHz; DMSO) δ 167.1 ($\text{C}=\text{O}$), 146.0 (C-2), 123.8 (C-1), 36.3 (C-3), 29.8 (C-5), 28.4 (C-4), 16.8 (C-6); m/z (ESI): 433 [MNa^+]; HRMS: calcd. for $\text{C}_{23}\text{H}_{46}\text{NaO}_2\text{Si}_2$, 433.2929. Found: [MNa^+], 433.2916 (3.2 ppm error).

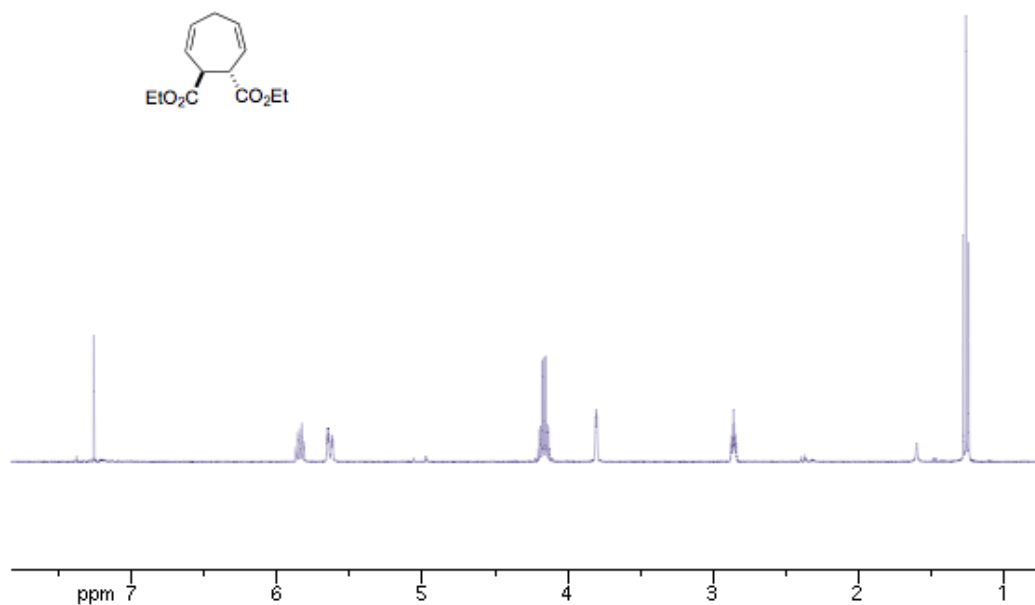
***¹H and ¹³C NMR spectra corresponding to characterisation data
and experimental procedures in the manuscript***

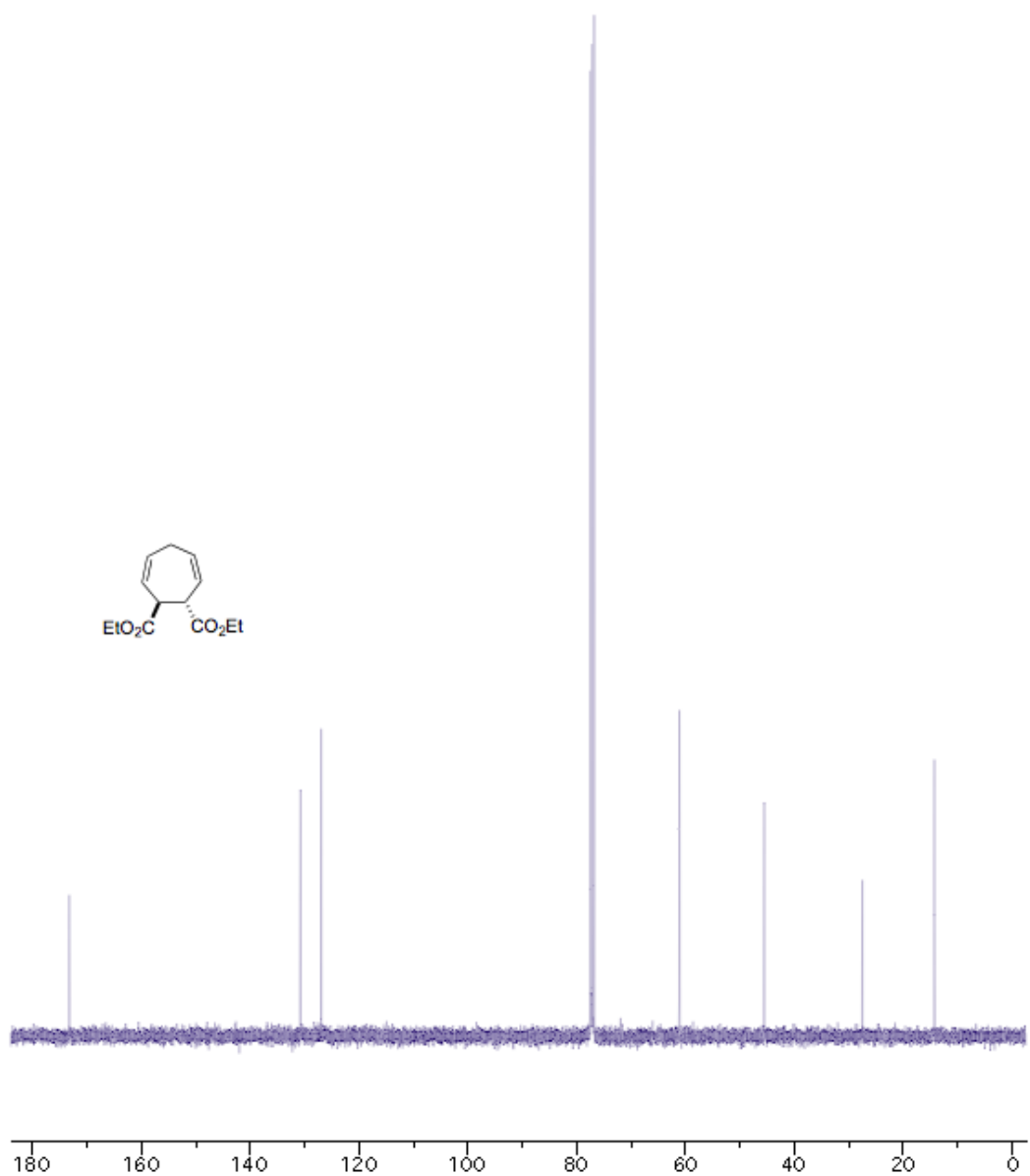
Diethyl (1*R*,2*S*)-cyclohepta-3,6-diene-1,2-dicarboxylate (5a)



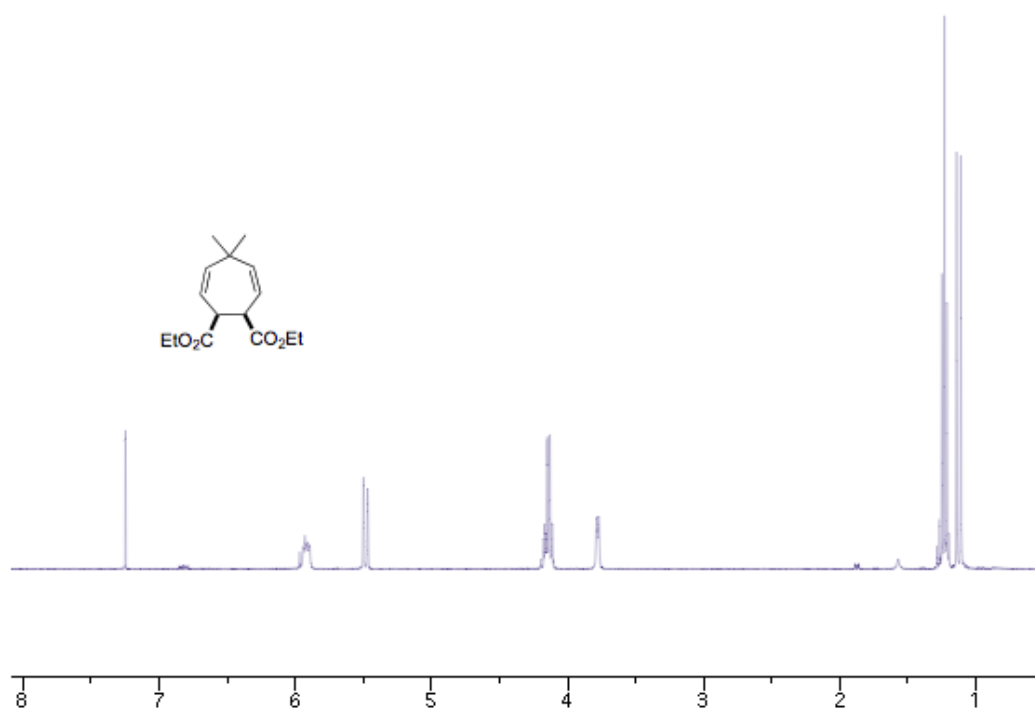


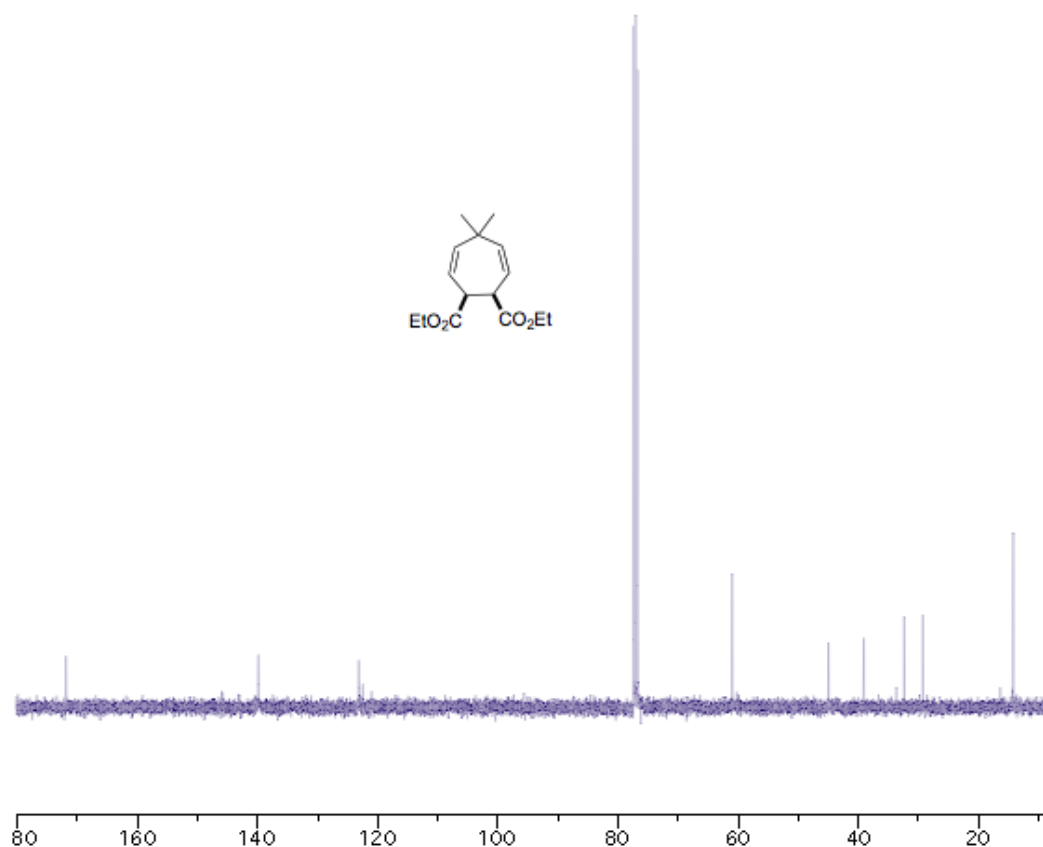
Diethyl (±)-(1*S*,2*S*)-cyclohepta-3,6-diene-1,2-dicarboxylate (5b)



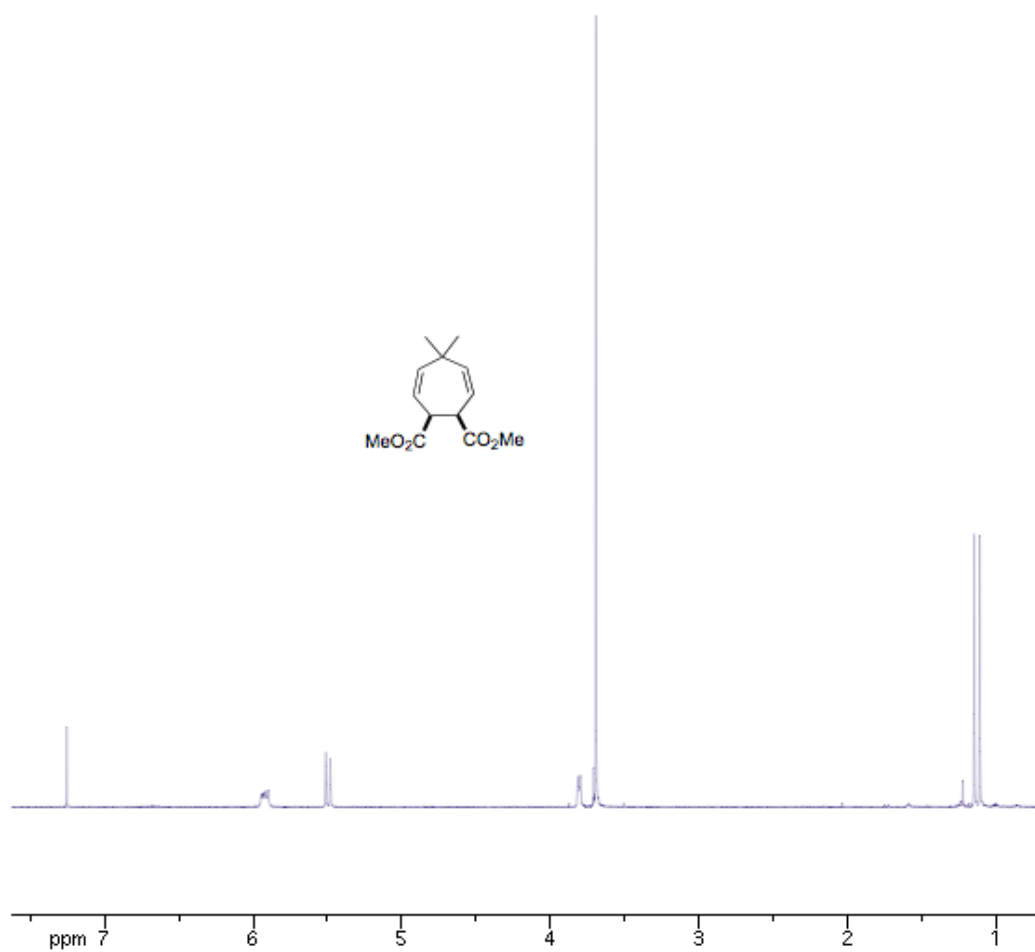


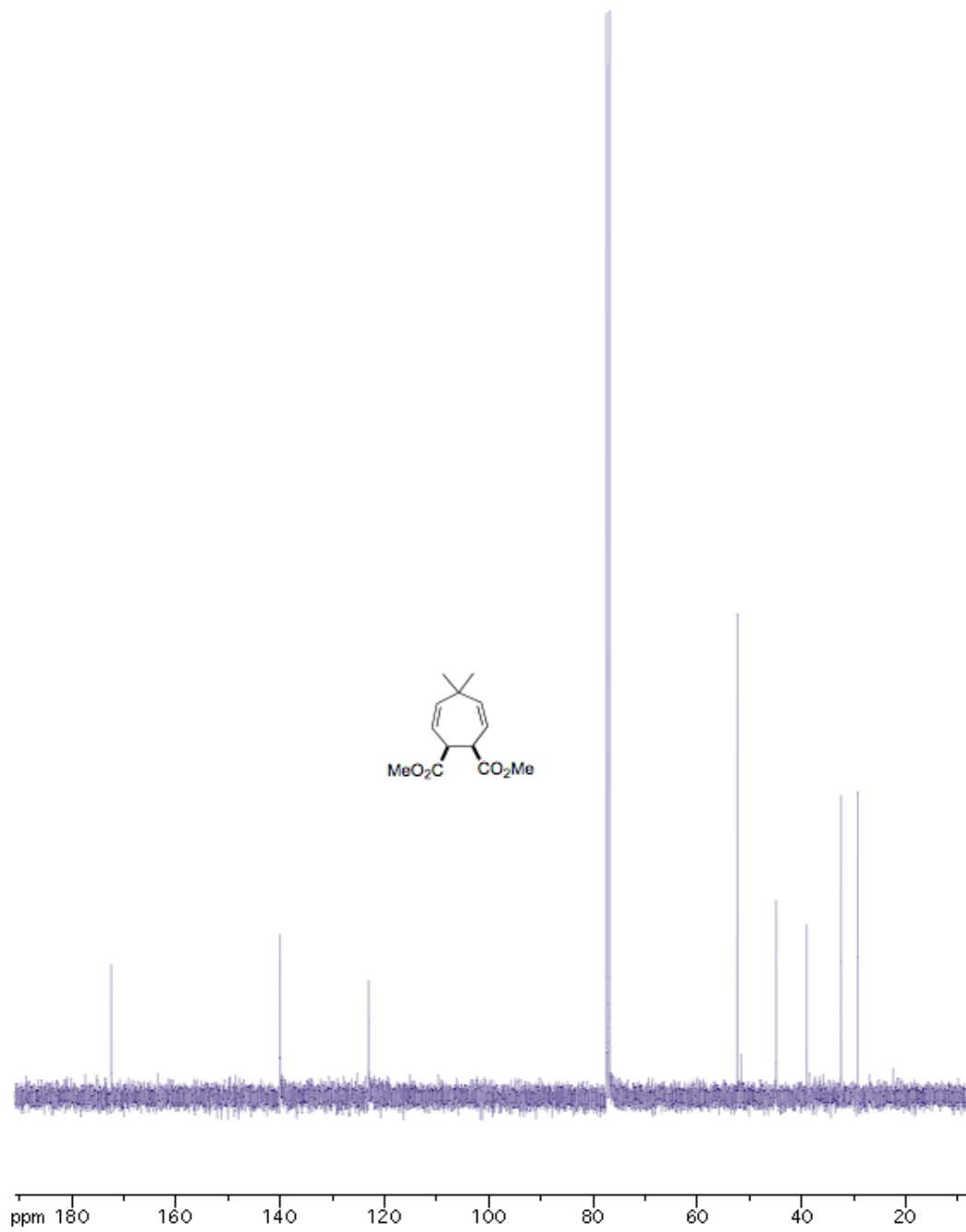
Diethyl (1*R*,2*S*)-5,5-dimethylcyclohepta-3,6-diene-1,2-dicarboxylate (10a)



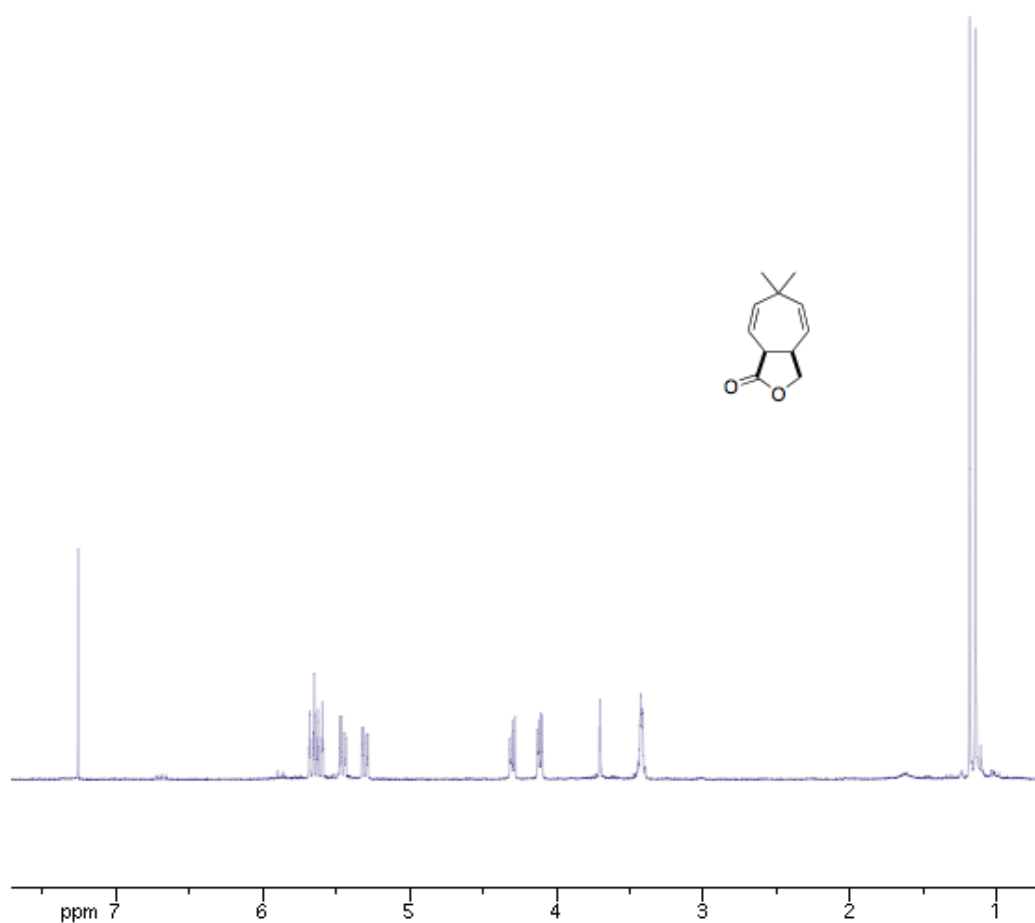


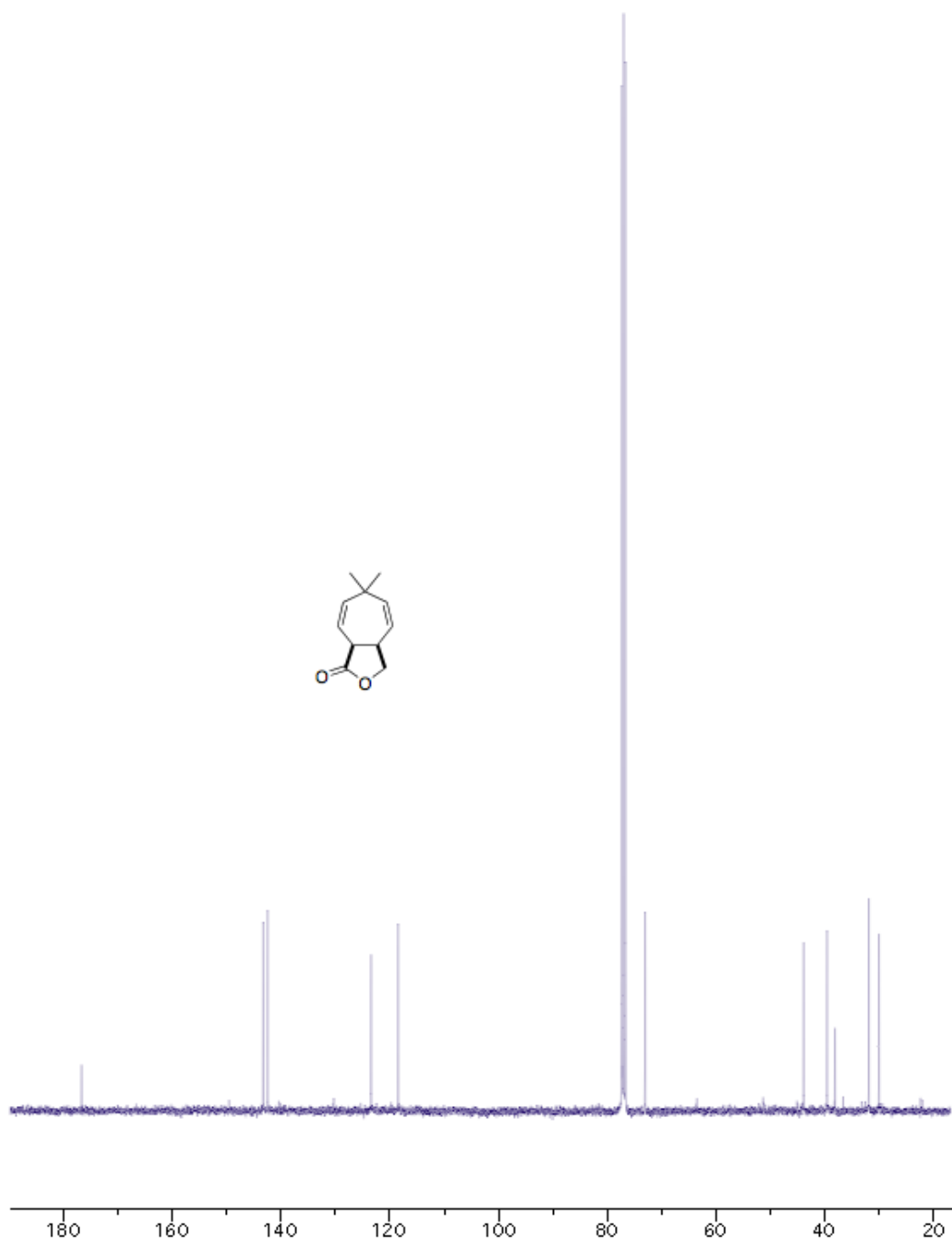
Dimethyl (1*R*,2*S*)-5,5-dimethylcyclohepta-3,6-diene-1,2-dicarboxylate (42)



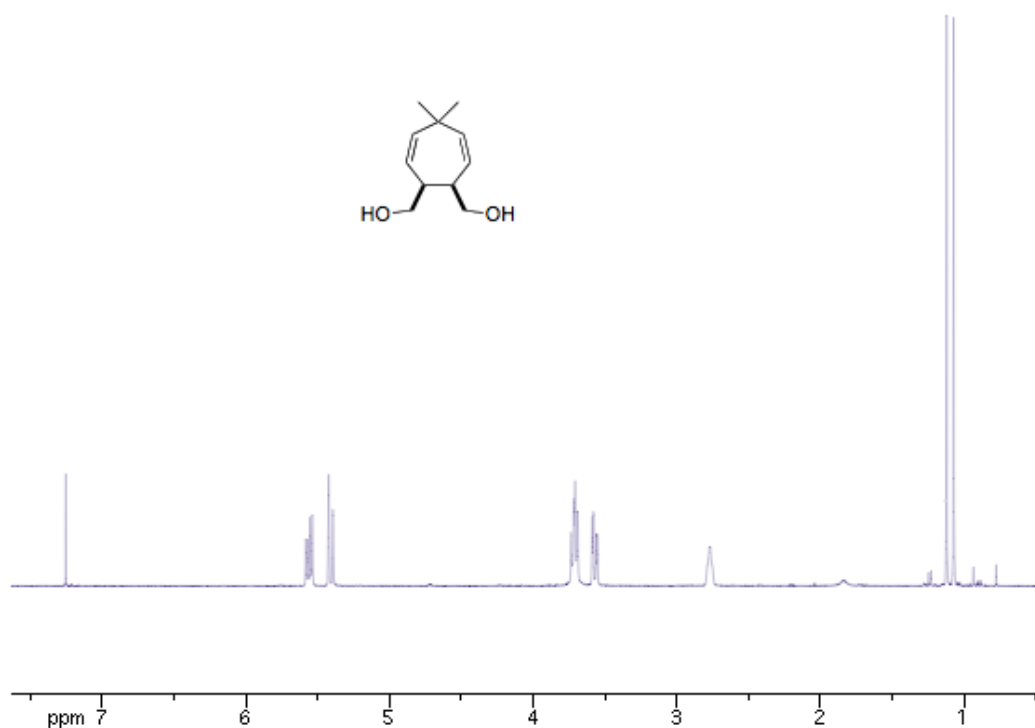


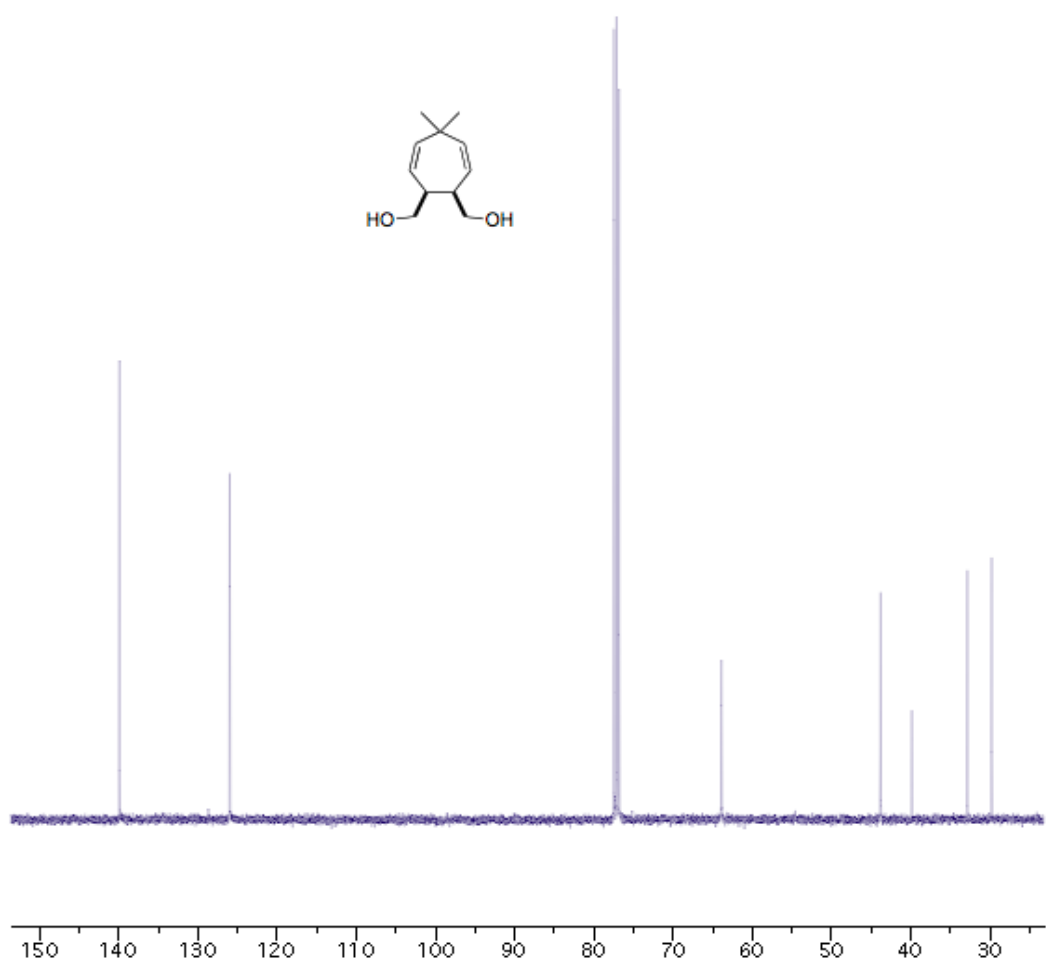
(±)-(3a*R*,8a*S*)-6,6-Dimethyl-3,3a,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-1-one
(43)



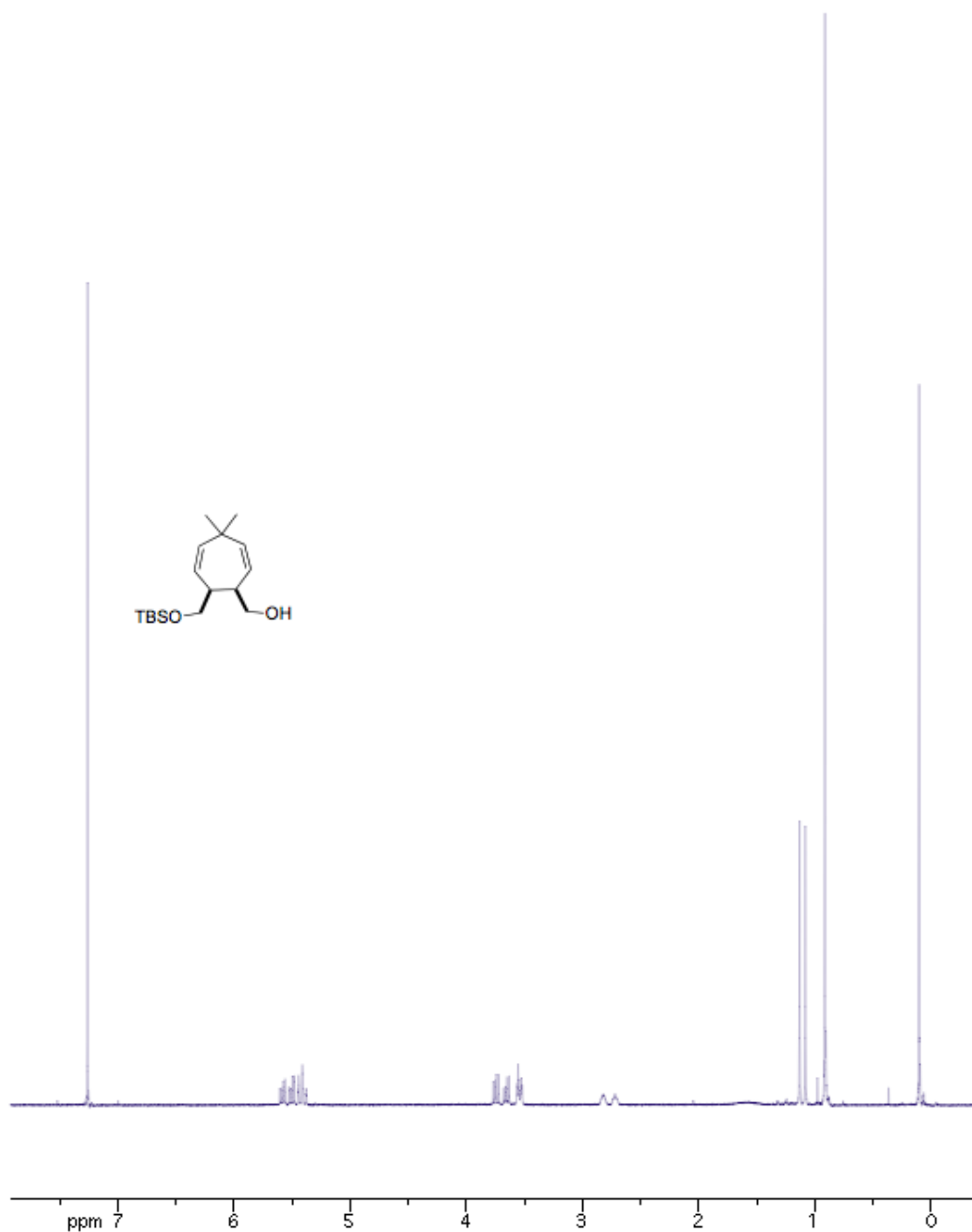


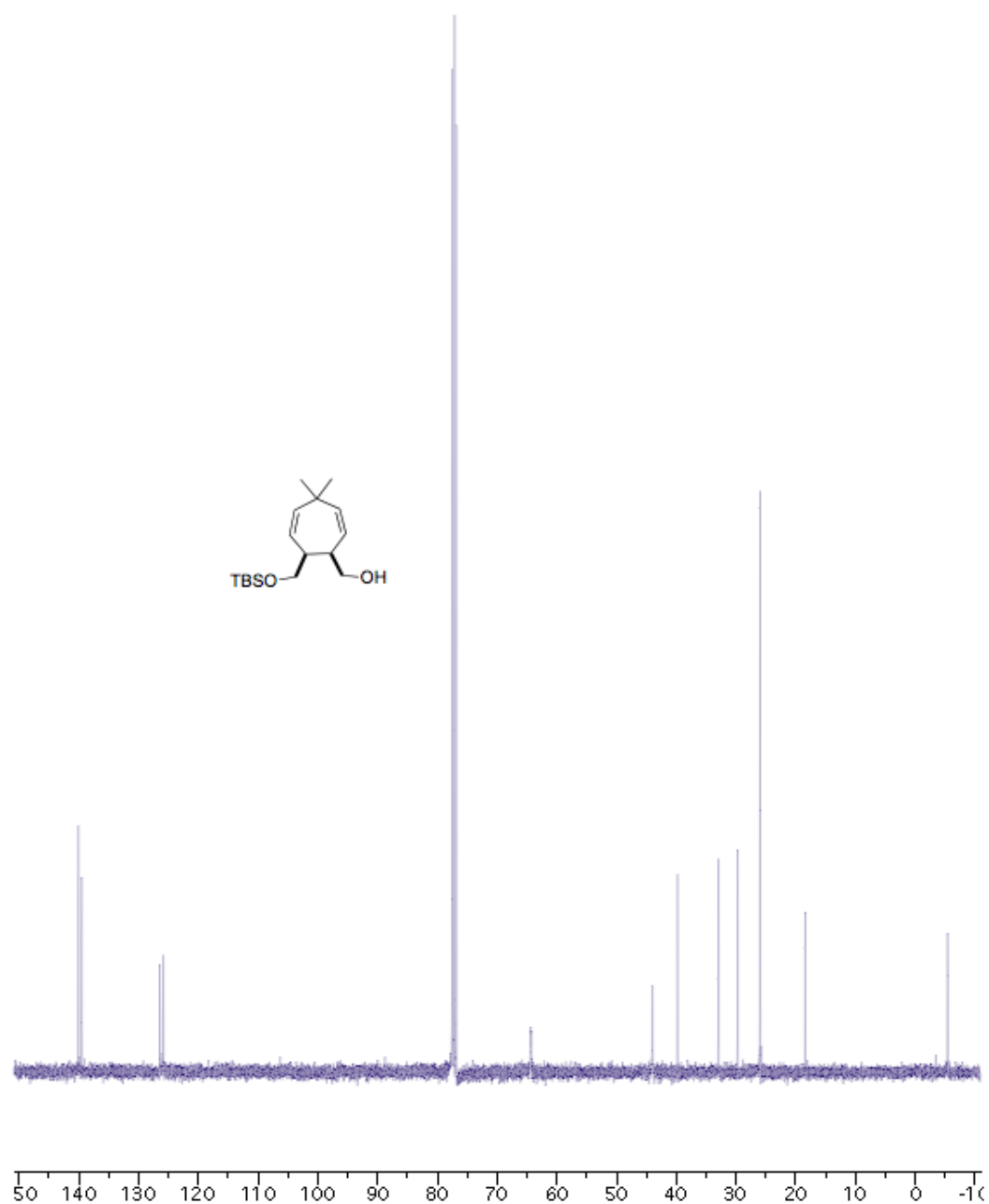
((1*R*,2*S*)-5,5-Dimethylcyclohepta-3,6-diene-1,2-diyl)dimethanol (44)



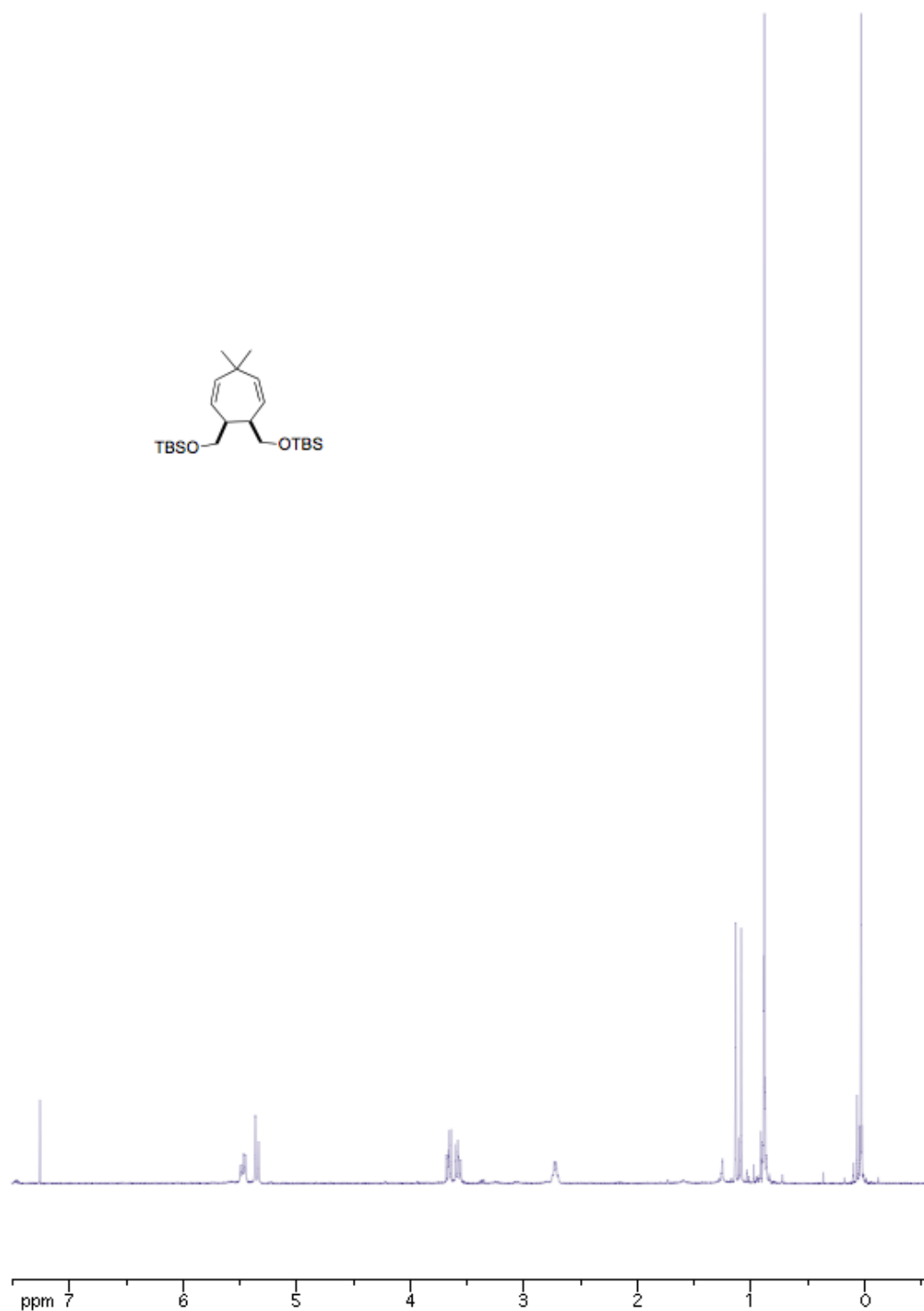


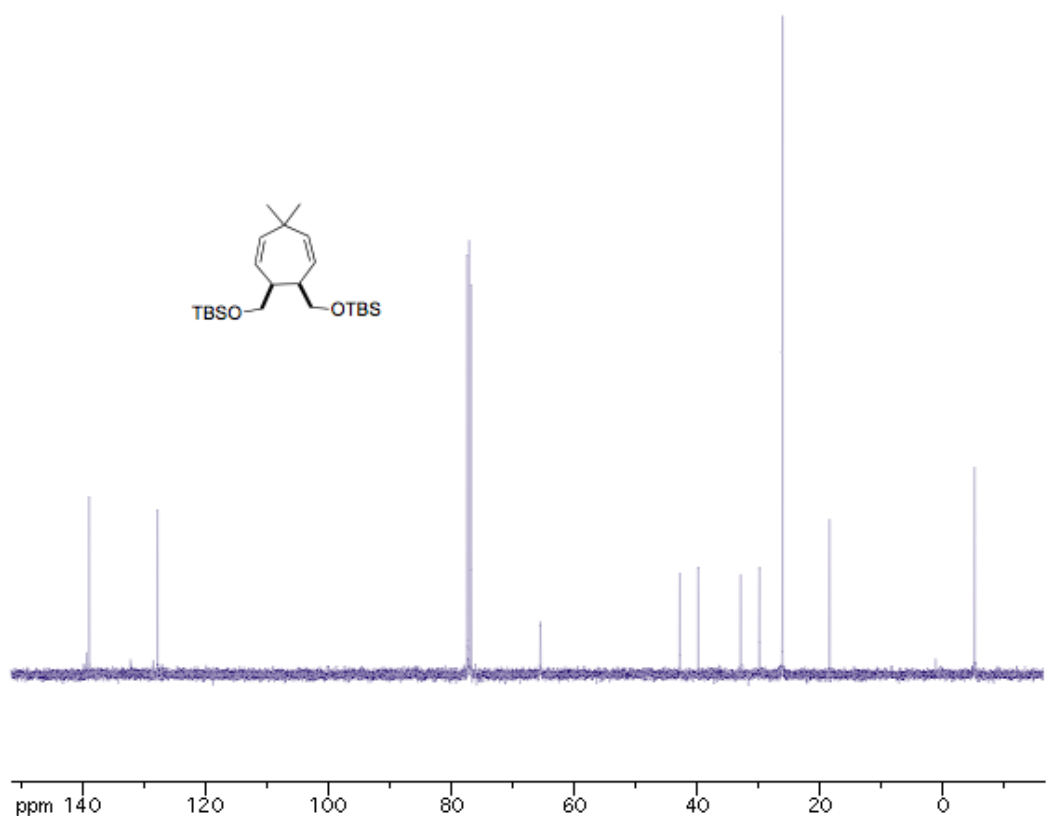
(±)-((1*R*,7*S*)-7-((*tert*-Butyldimethylsilyloxy)methyl)-4,4-dimethylcyclohepta-2,5-dienyl)methanol (45)



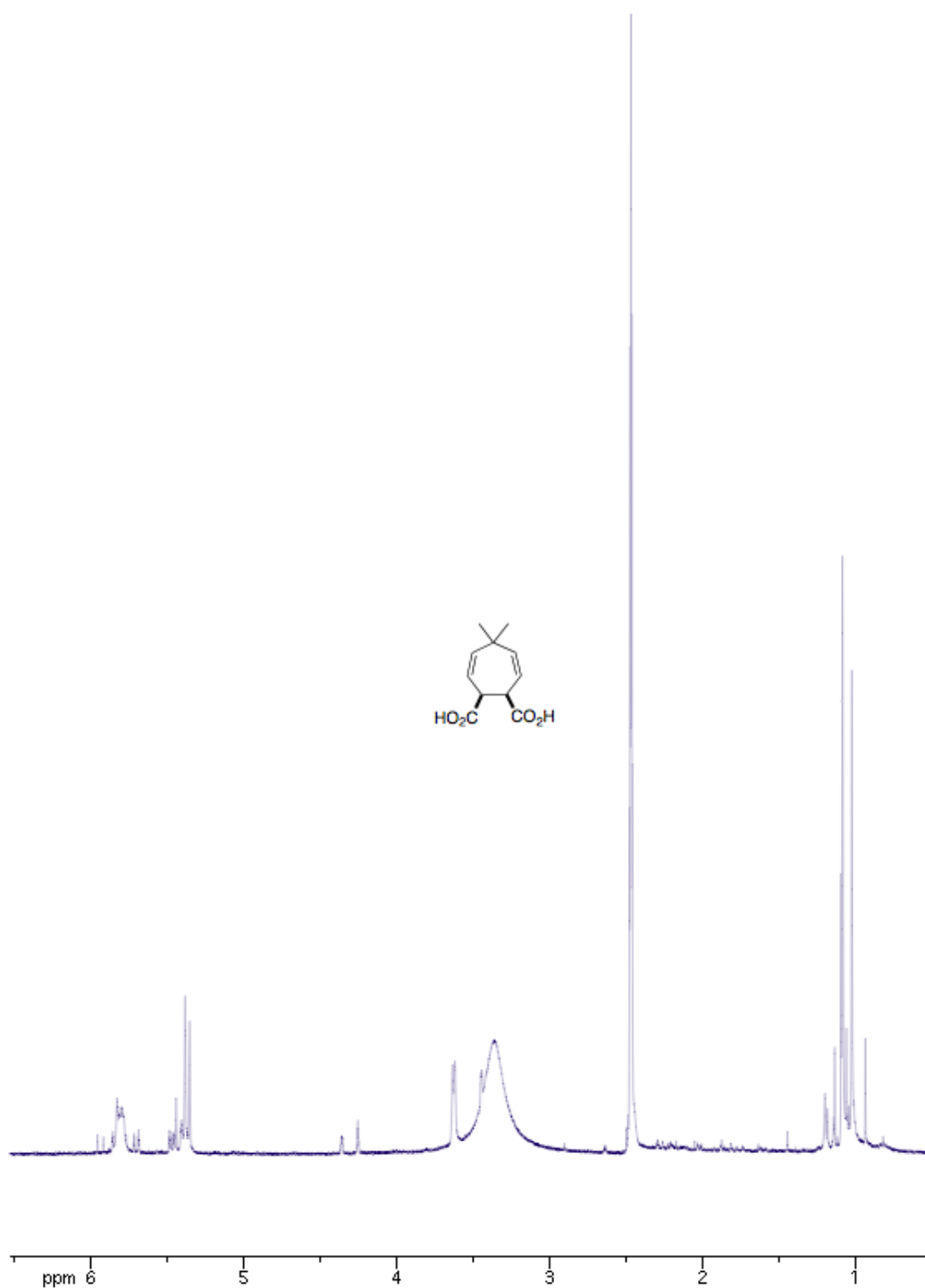


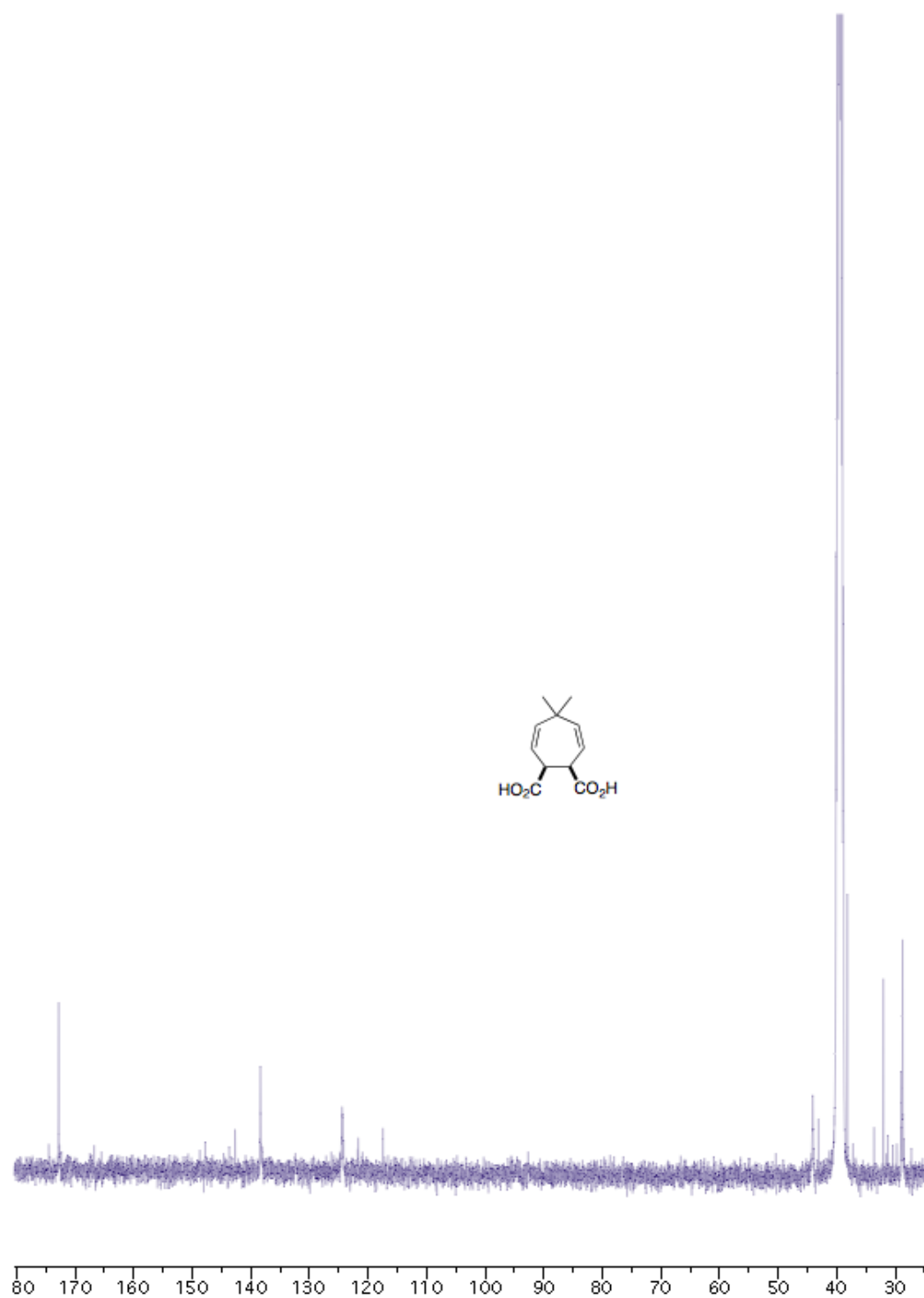
((1*R*,2*S*)-5,5-Dimethylcyclohepta-3,6-diene-1,2-diyl)bis(methylene)bis(oxy)bis(*tert*-butyldimethylsilane) (46)





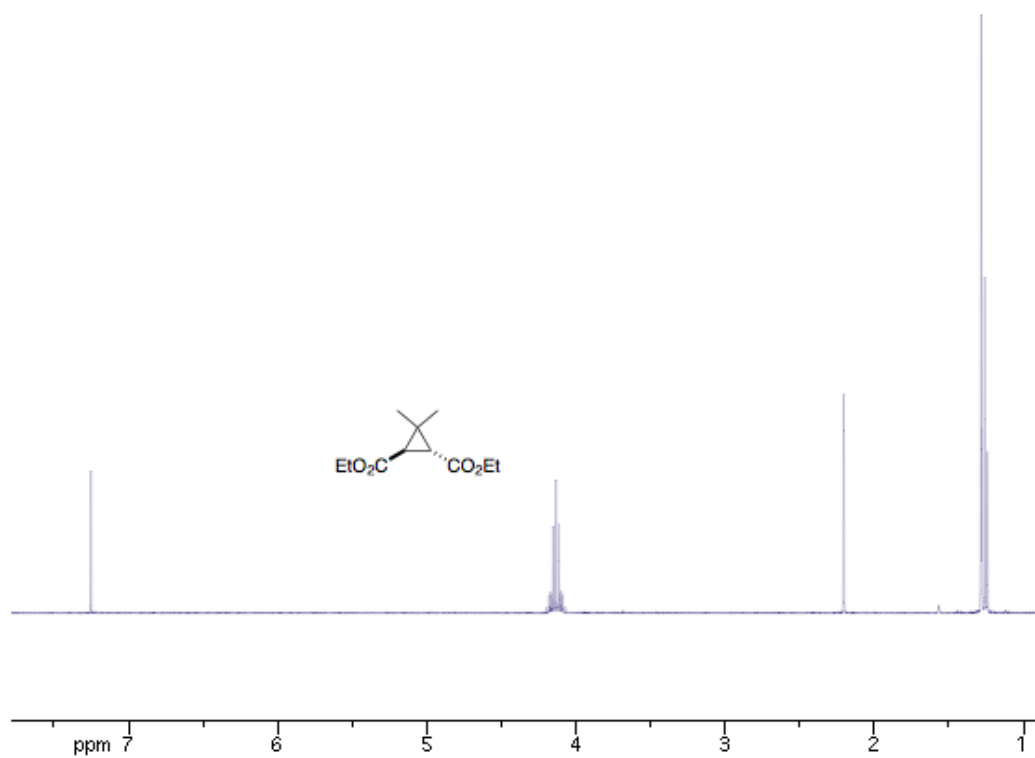
(1*R*,2*S*)-5,5-Dimethylcyclohepta-3,6-diene-1,2-dicarboxylic acid (47)



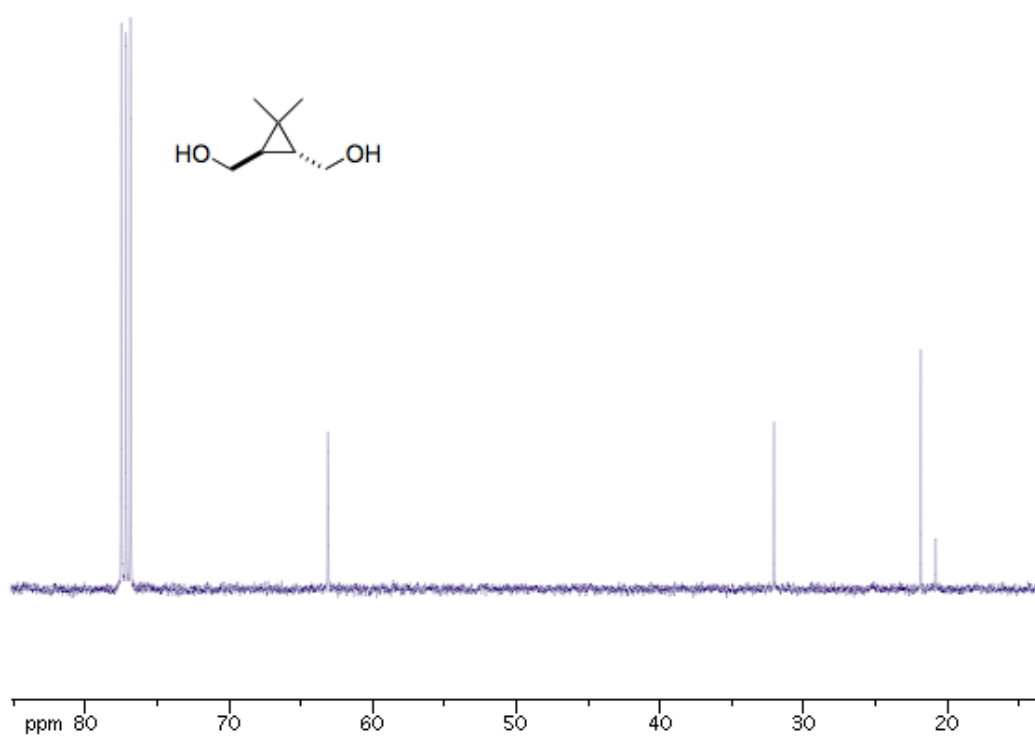
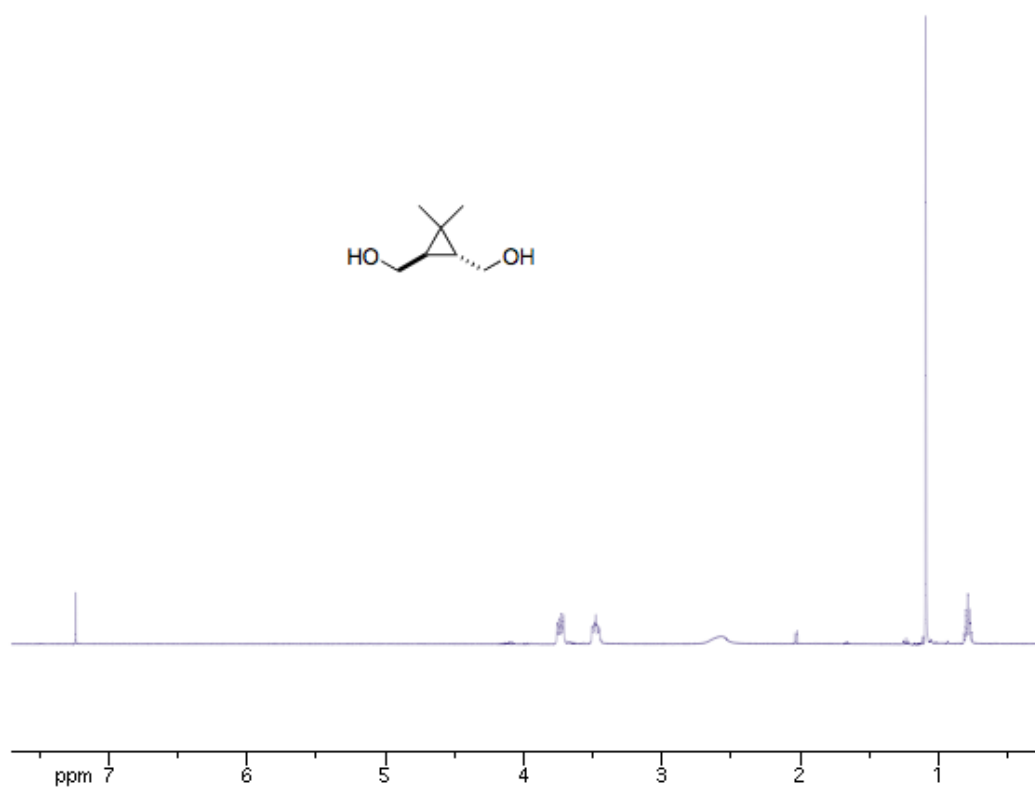


***¹H and ¹³C NMR spectra corresponding to characterisation data
and experimental procedures in the SI***

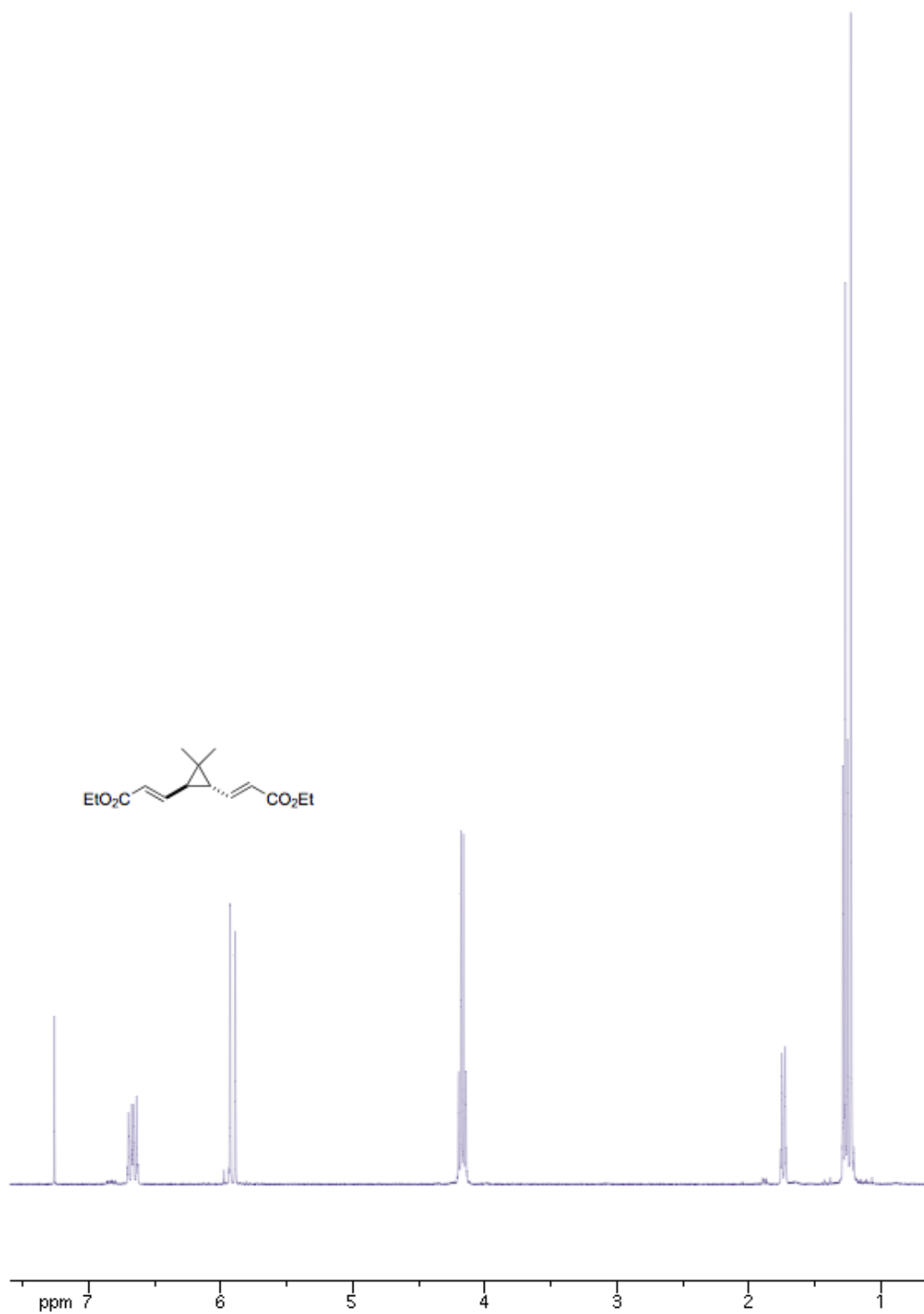
Diethyl (±)-(1*R*,2*R*)-3,3-dimethylcyclopropane-1,2-dicarboxylate (7)

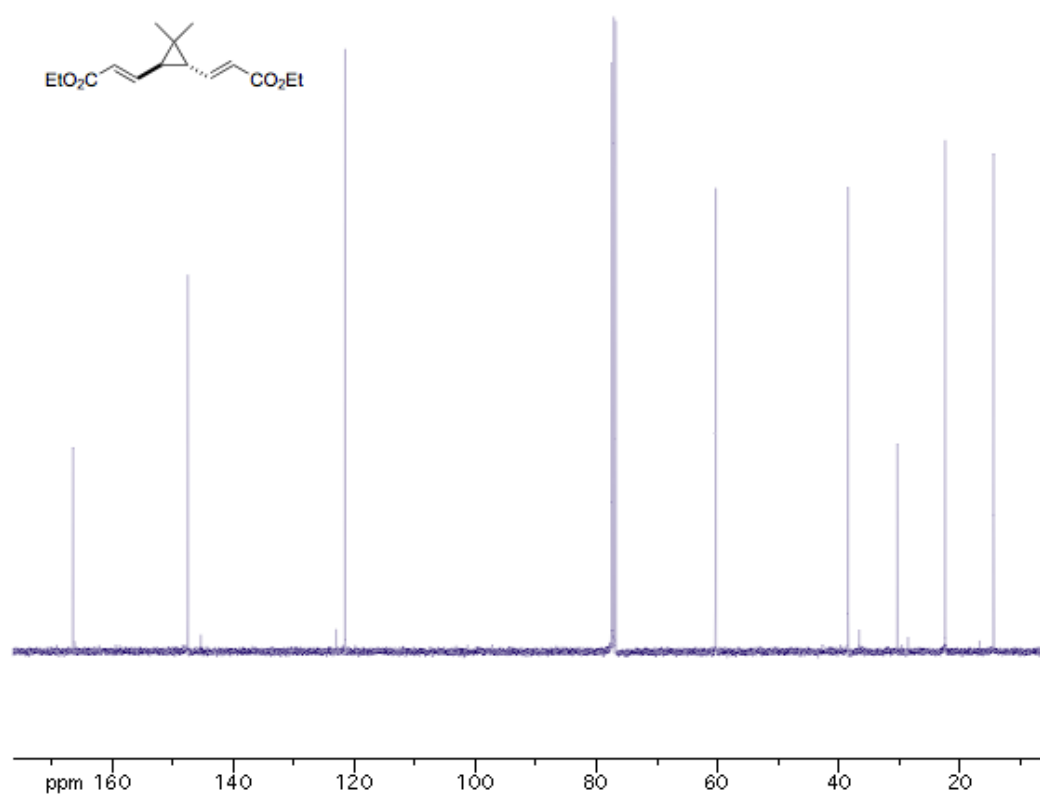


(±)-((1*R*,2*R*)-3,3-Dimethylcyclopropane-1,2-diyl)dimethanol (8)

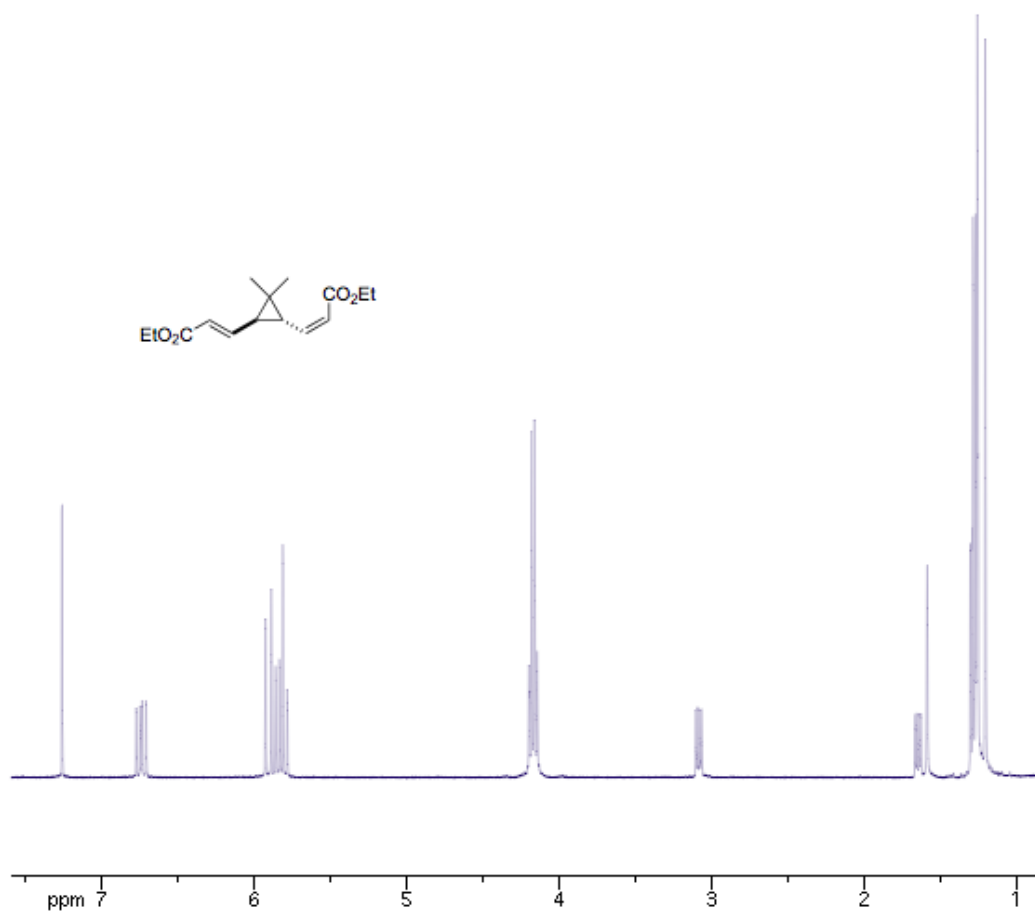


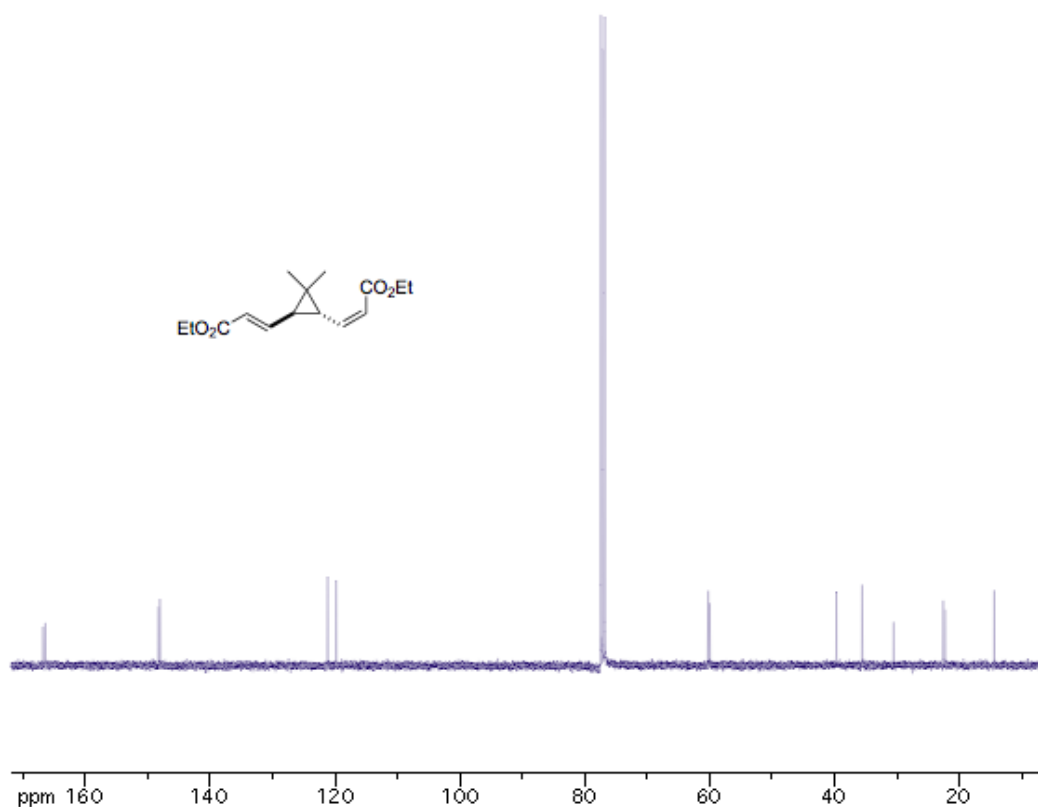
Diethyl (±)-(2*E*,2'*E*)-3,3'-[(1*R*,2*R*)-3,3-dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (9a)



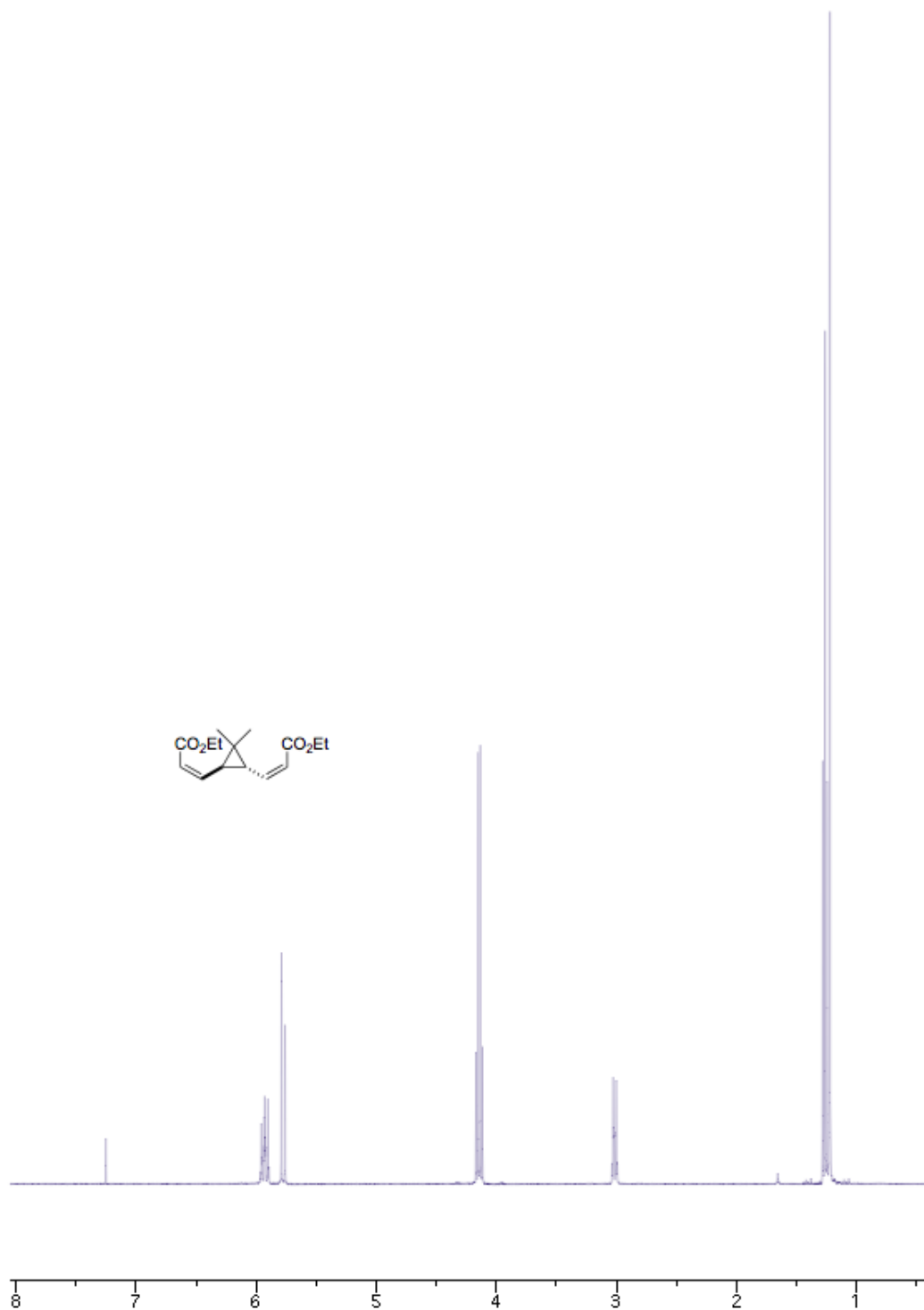


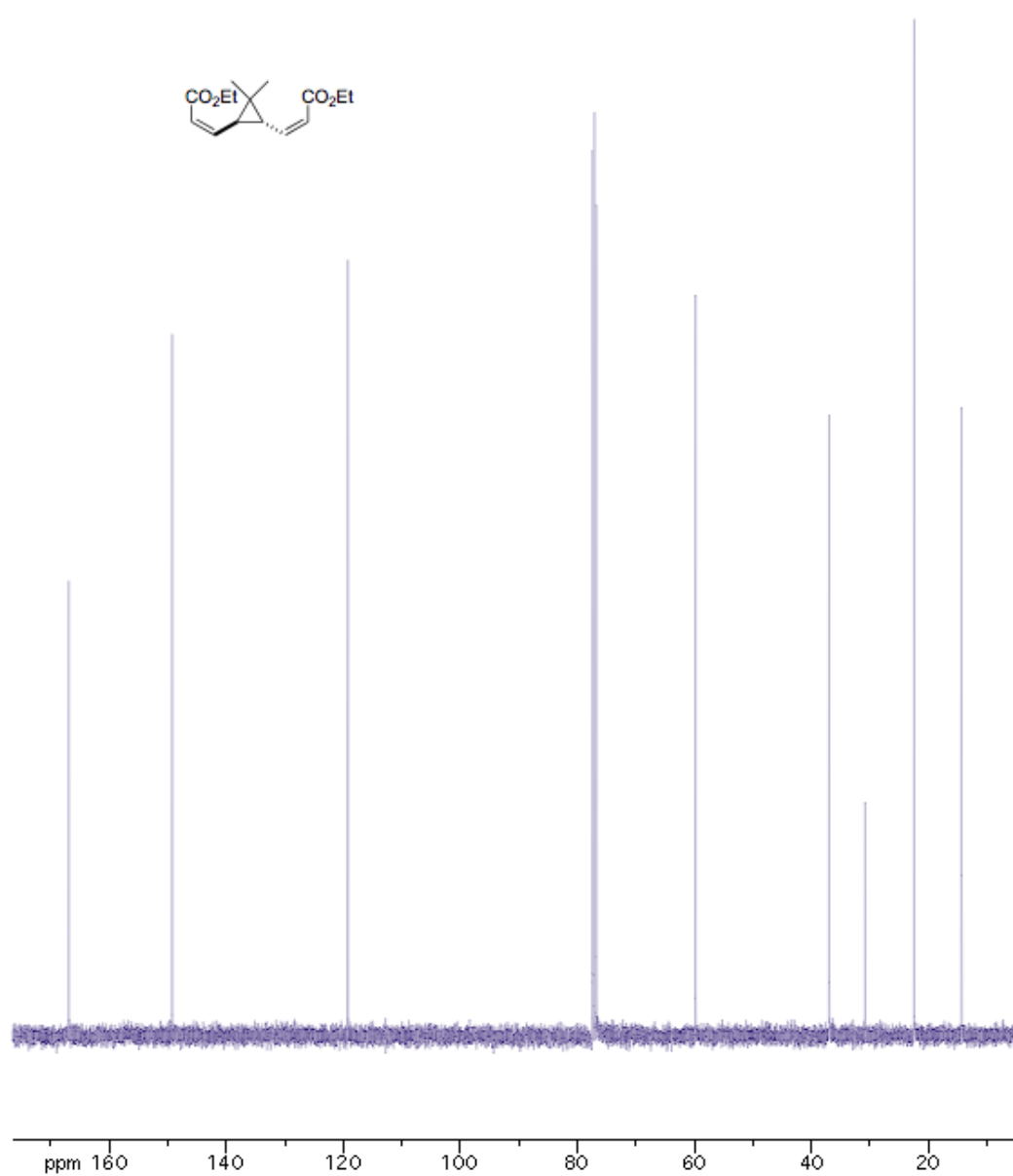
Diethyl (±)-(2*Z*,2'*E*)-3,3'-[(1*R*,2*R*)-3,3-dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (9b)



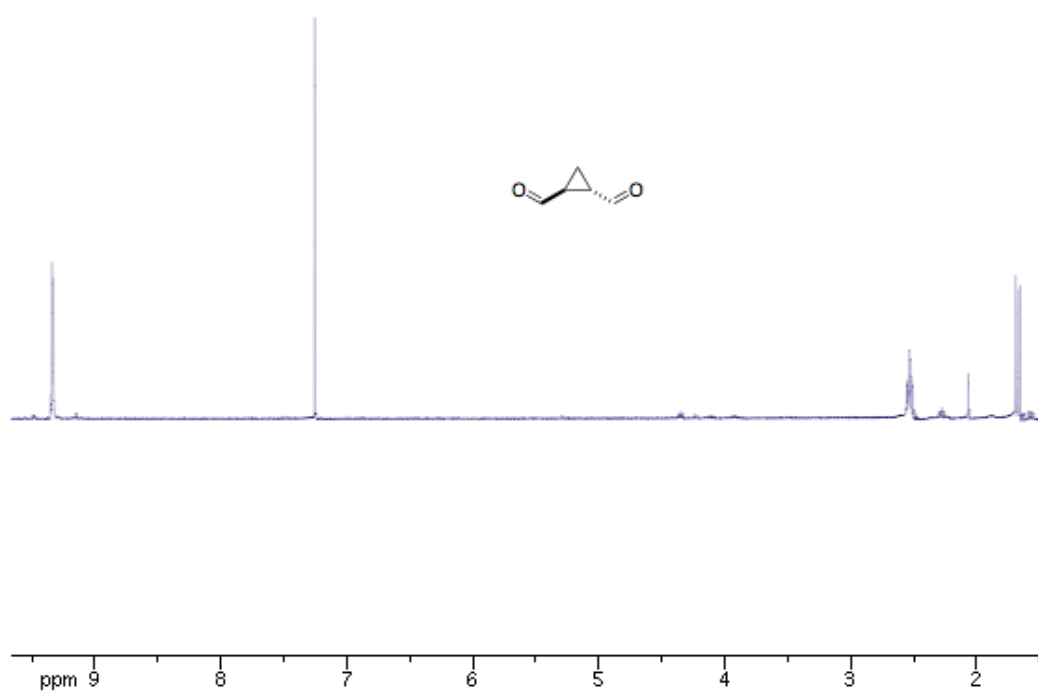


(2Z,2'Z)-Diethyl (±)-3,3'-((1R,2R)-3,3-dimethylcyclopropane-1,2-diyl)diprop-2-enoate (9c)

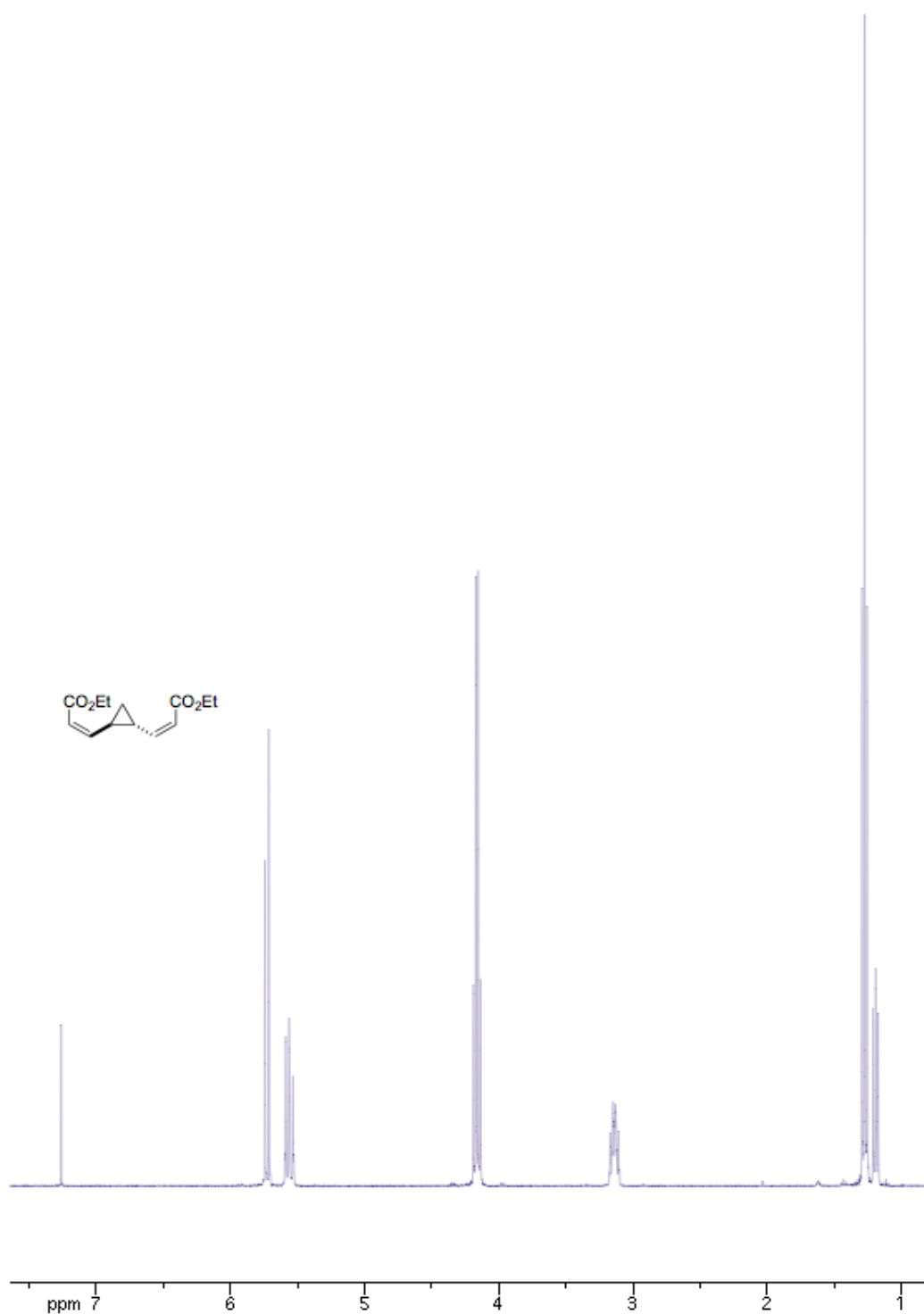


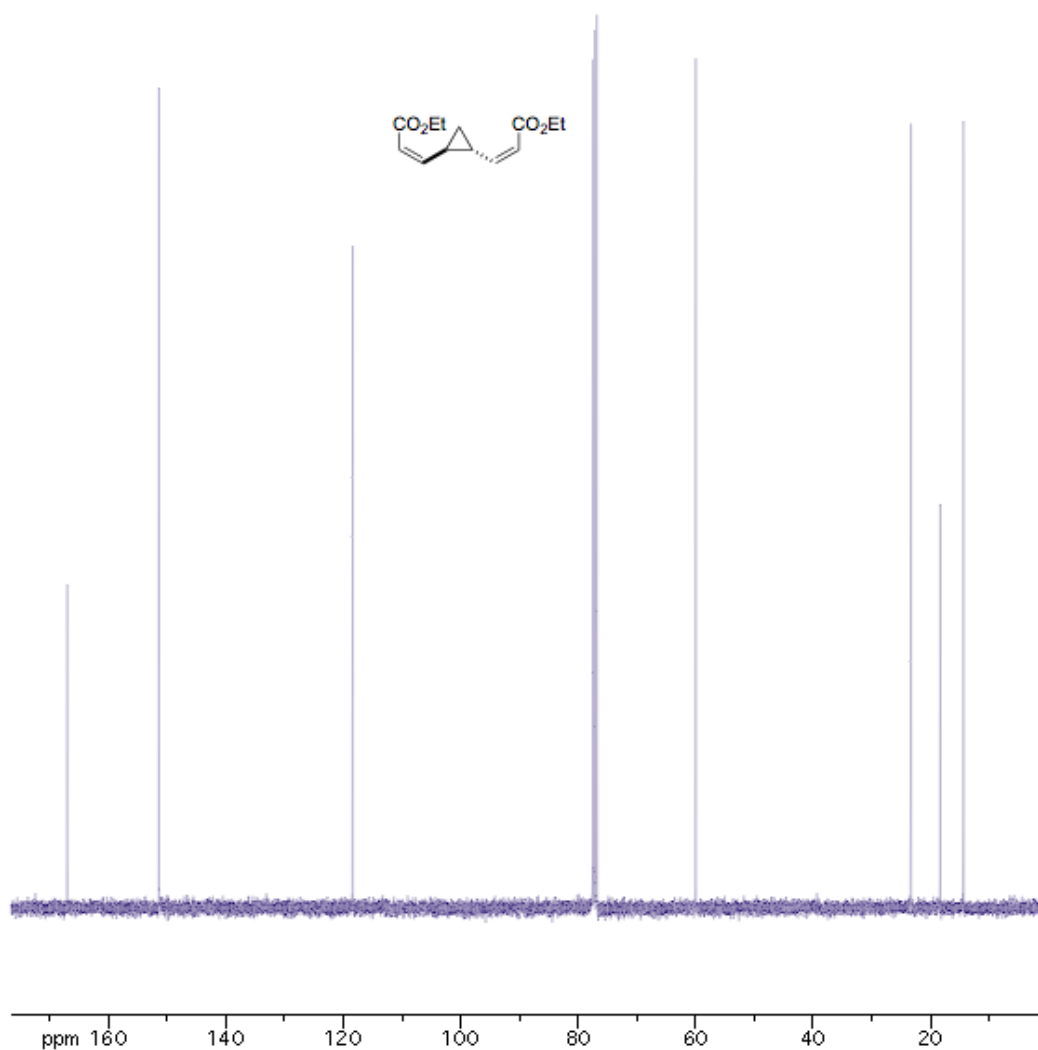


(±)-(1*S*,2*S*)-Cyclopropane-1,2-dicarbaldehyde (SI-1)

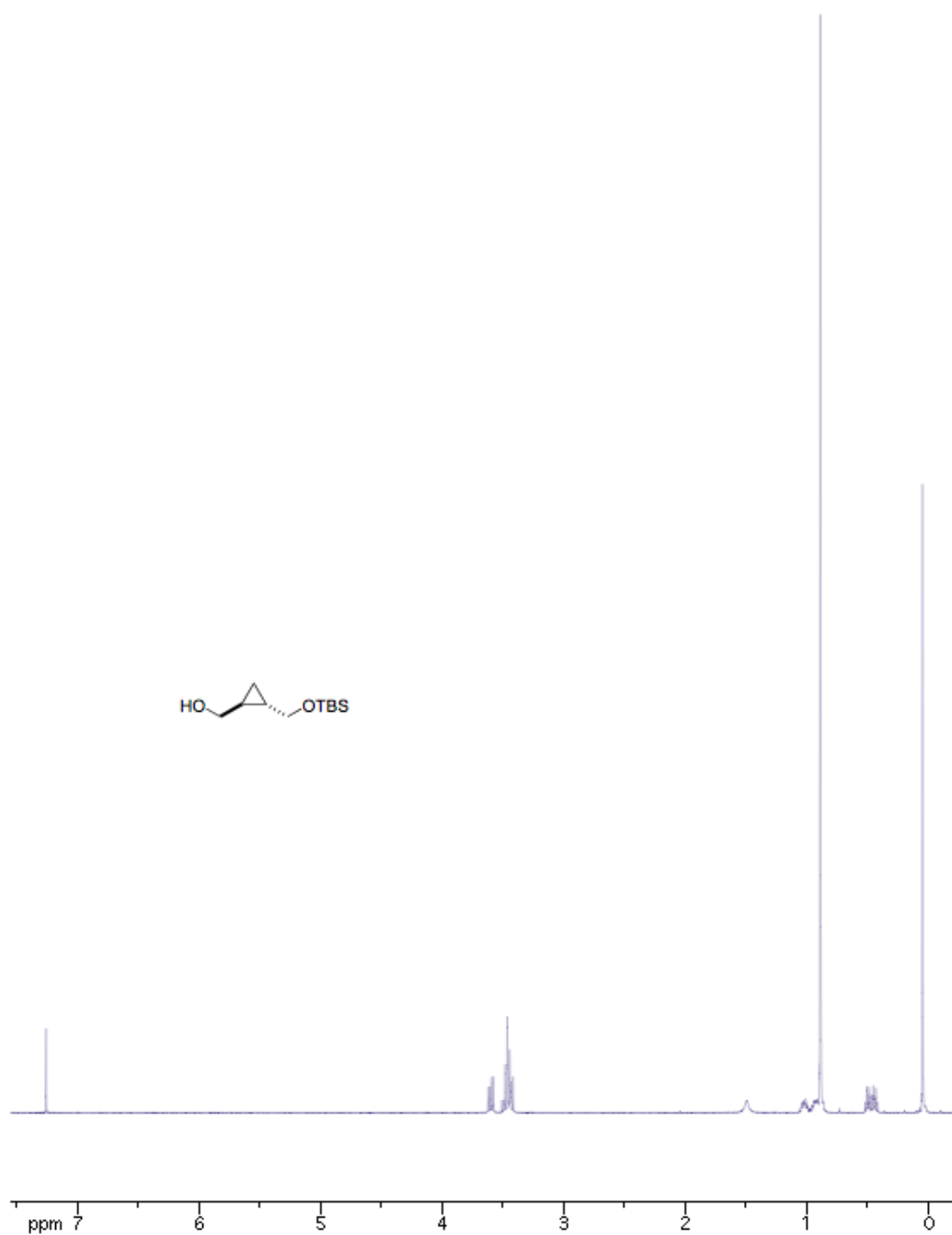


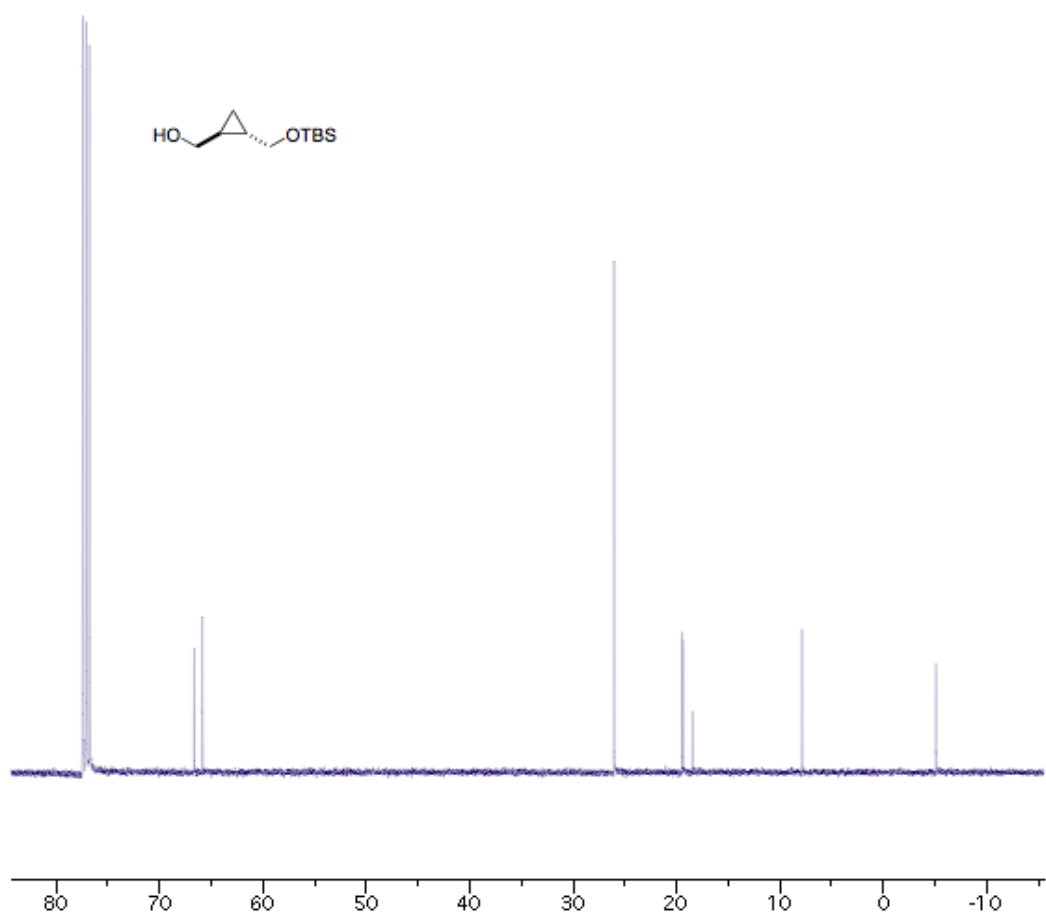
Diethyl (±)-(2'*Z*)-3,3'-(1*R*,2*R*)-cyclopropane-1,2-diylbisprop-2-enoate (4c)



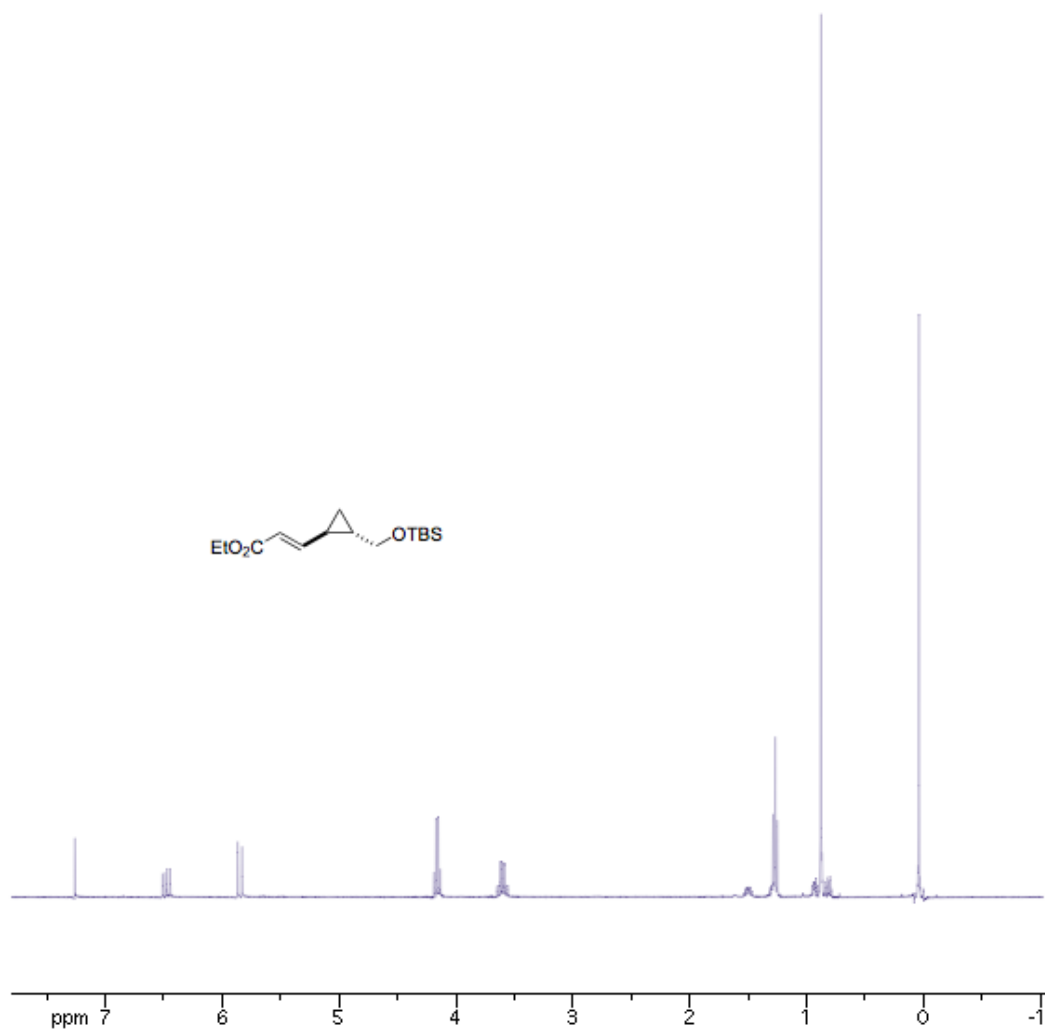


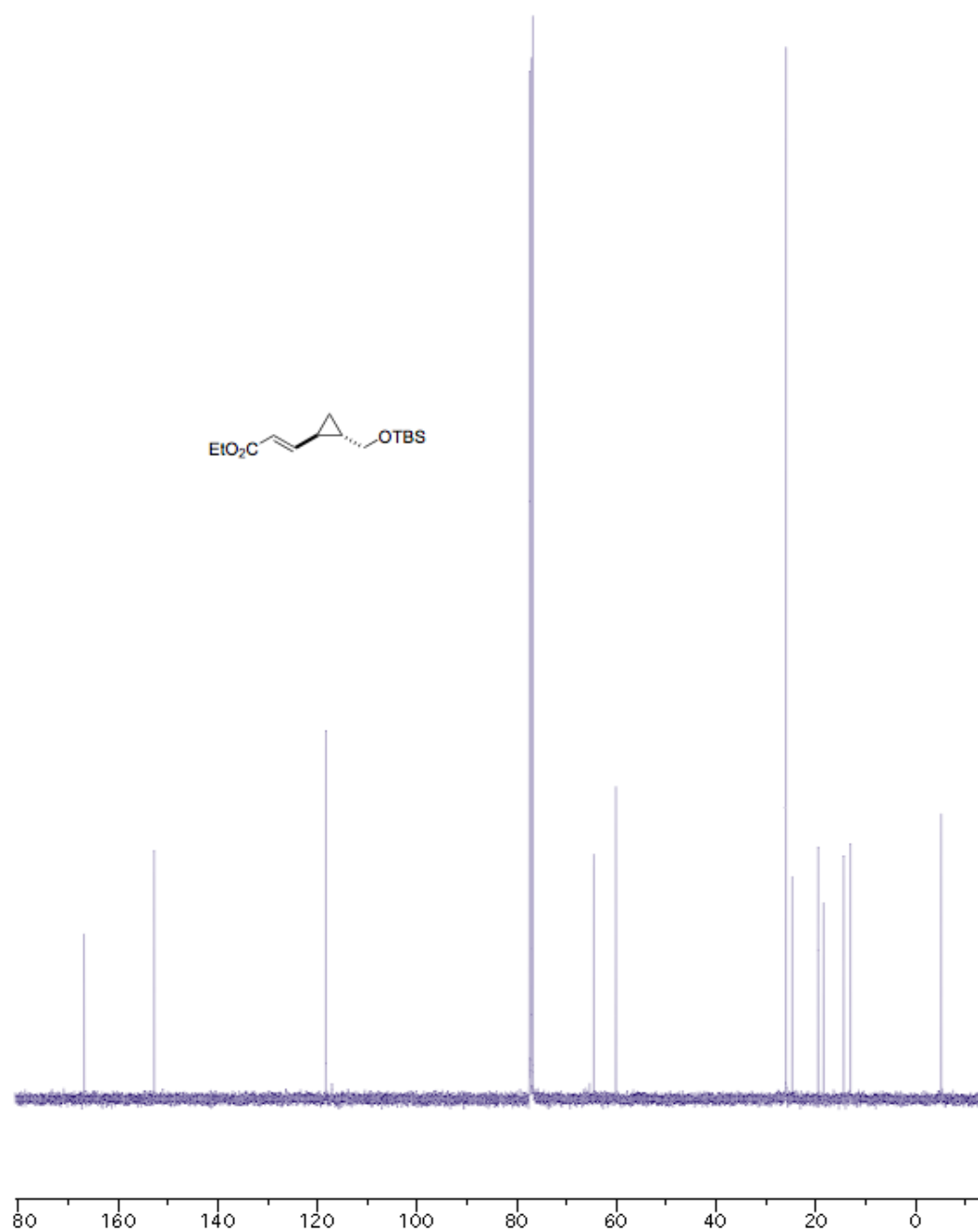
(±)-[(1*S*,2*S*)-2-({*tert*-Butyl(dimethyl)silyl}oxy)methyl]cyclopropyl]methanol (16)



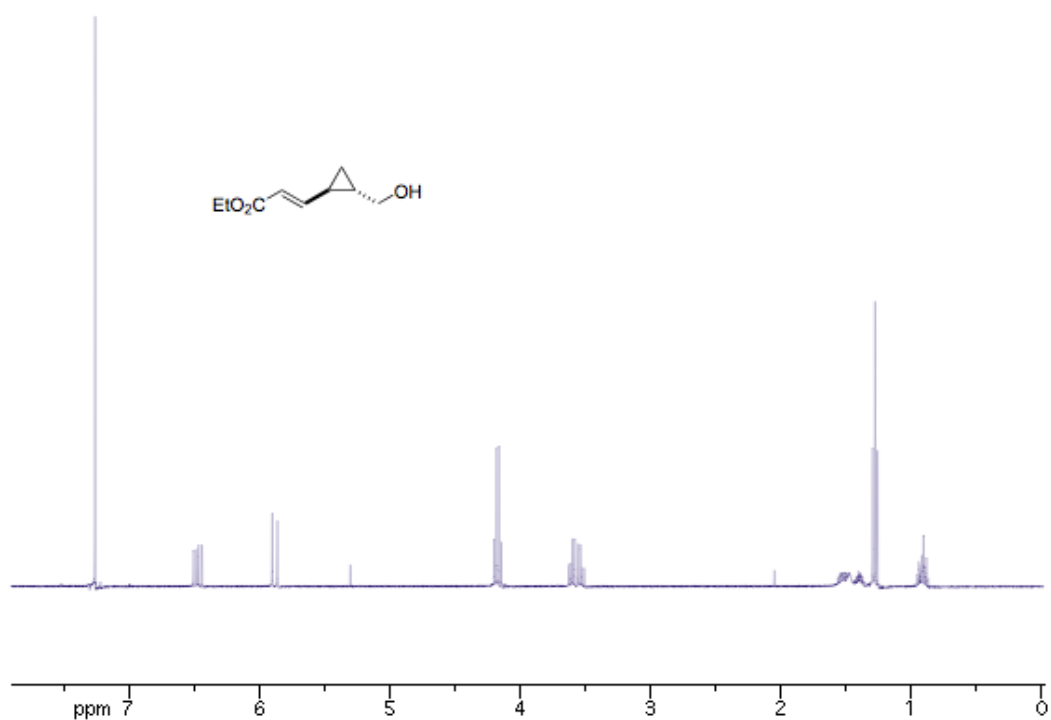


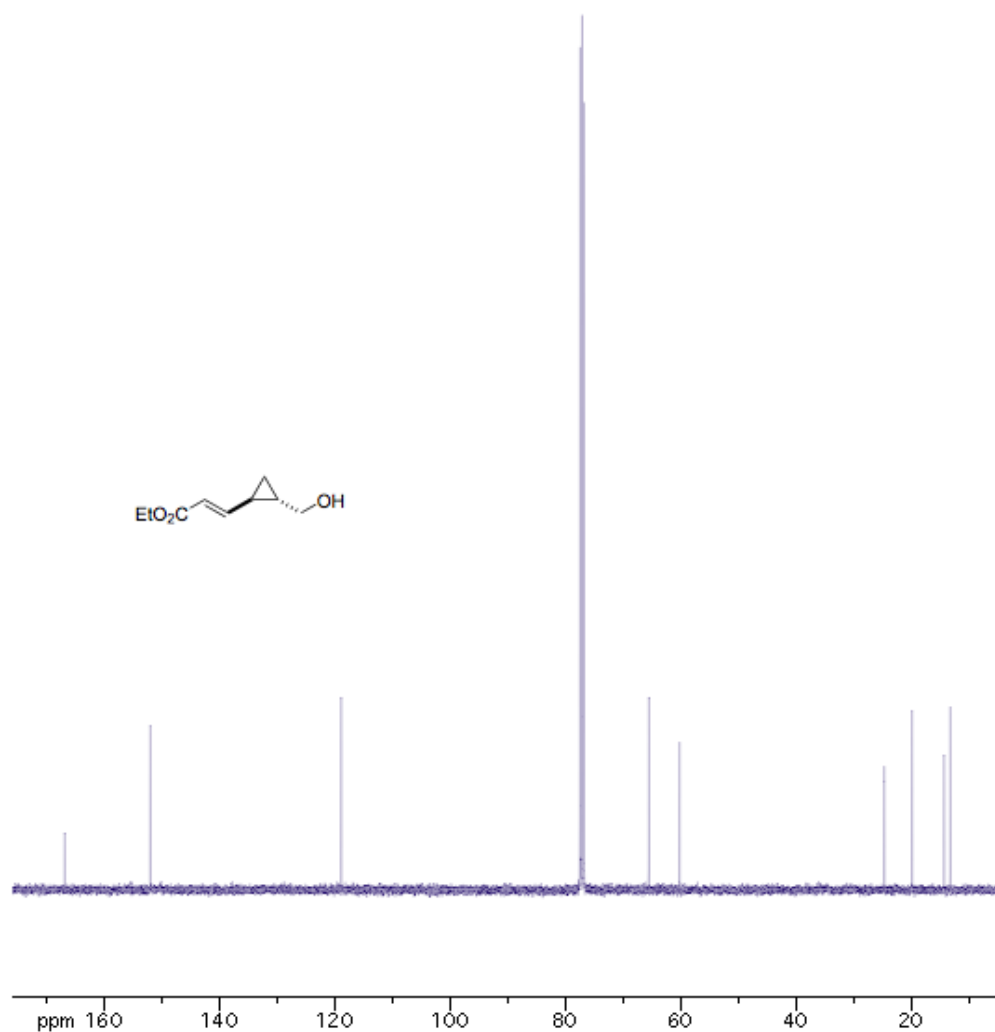
**Ethyl (±)-(2*E*)-3-[(1*R*,2*S*)-2-([*tert*-
butyl(dimethyl)silyl]oxy)methyl]cyclopropyl]prop-2-enoate (17)**



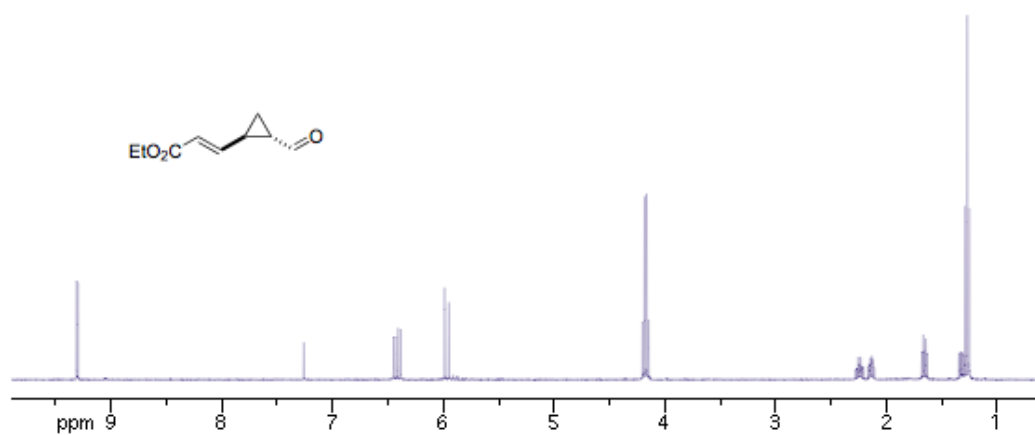


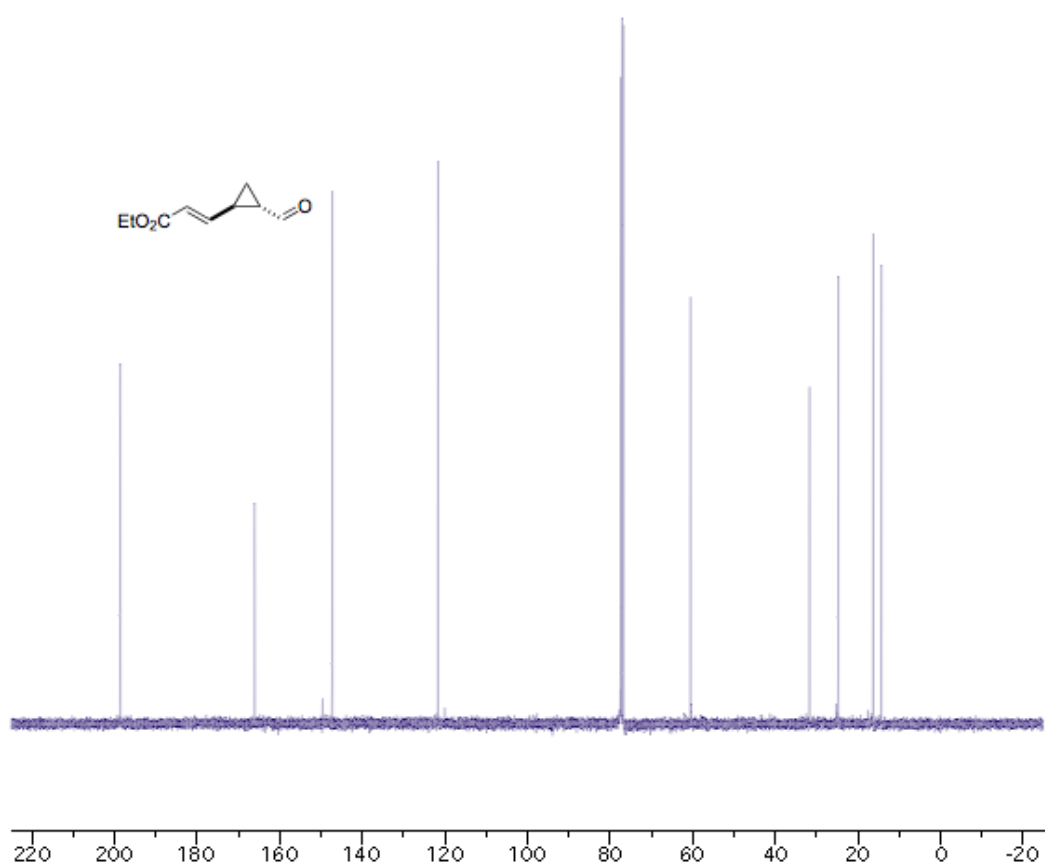
Ethyl (±)-(2*E*)-3-[(1*R*,2*S*)-2-(hydroxymethyl)cyclopropyl]prop-2-enoate (18)





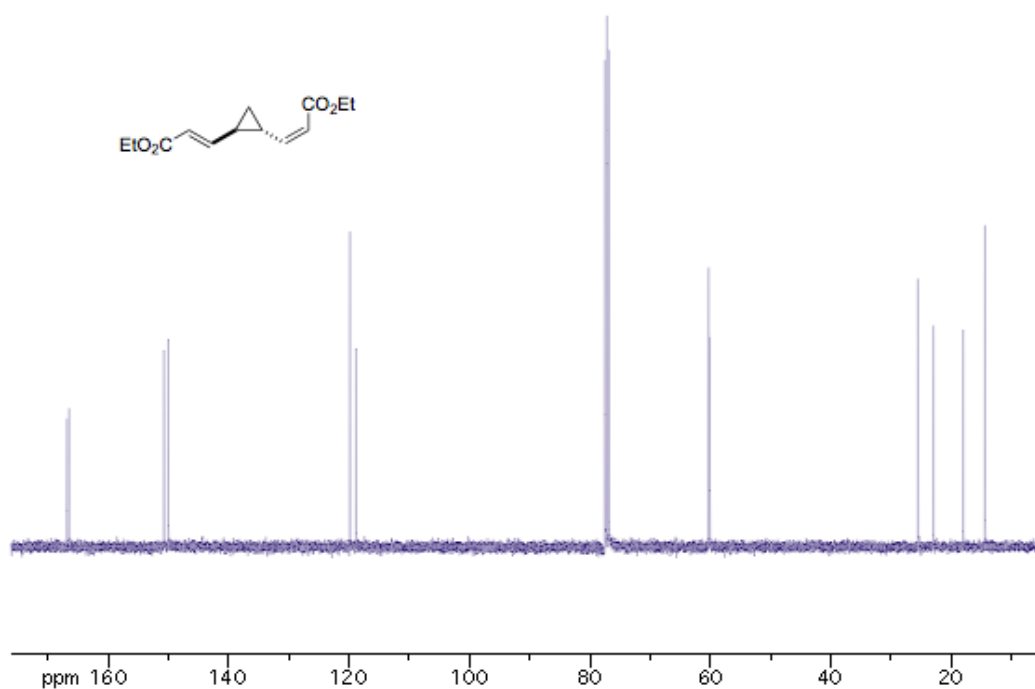
Ethyl (±)-(2*E*)-3-[(1*R*,2*S*)-2-formylcyclopropyl]prop-2-enoate (SI-2)



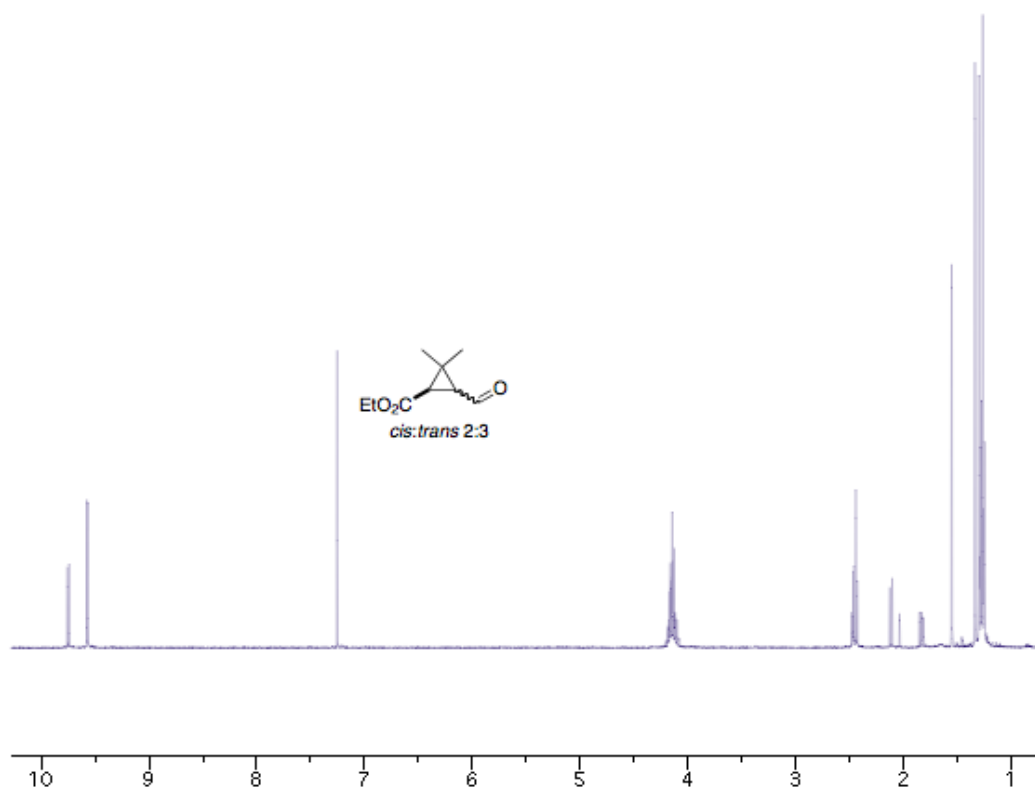


Diethyl (±)-(2'*E*)-3,3'-(1*R*,2*R*)-cyclopropane-1,2-diylbisprop-2-enoate (4b)

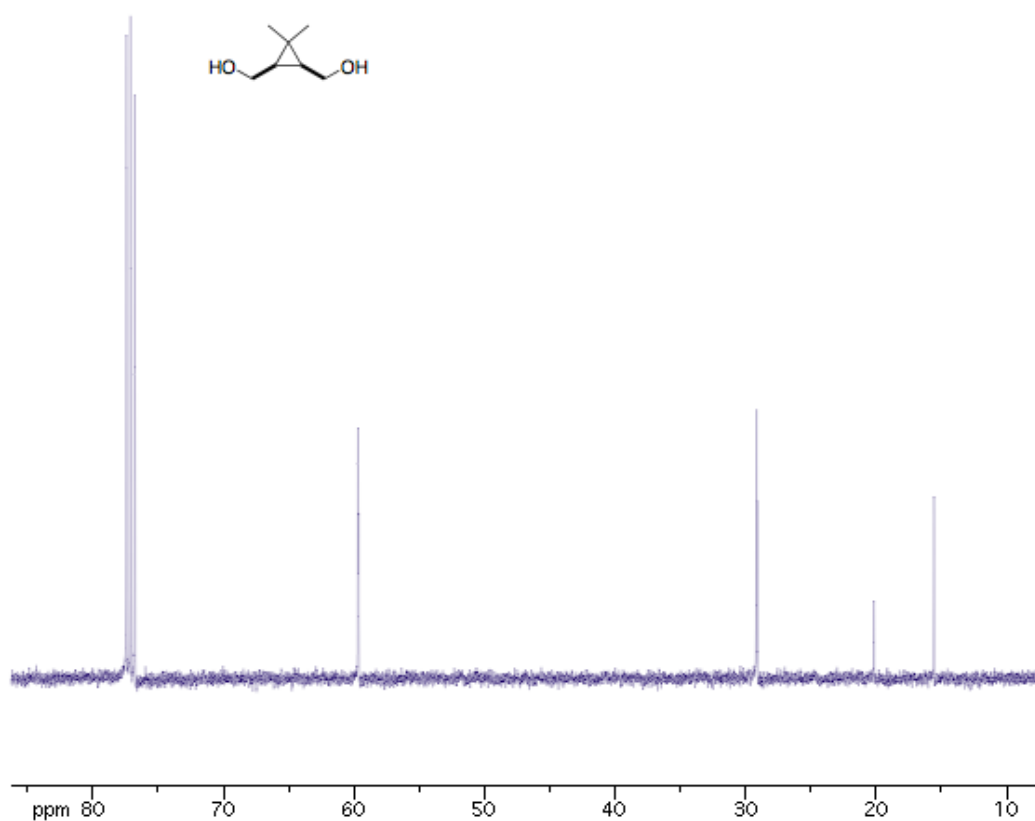


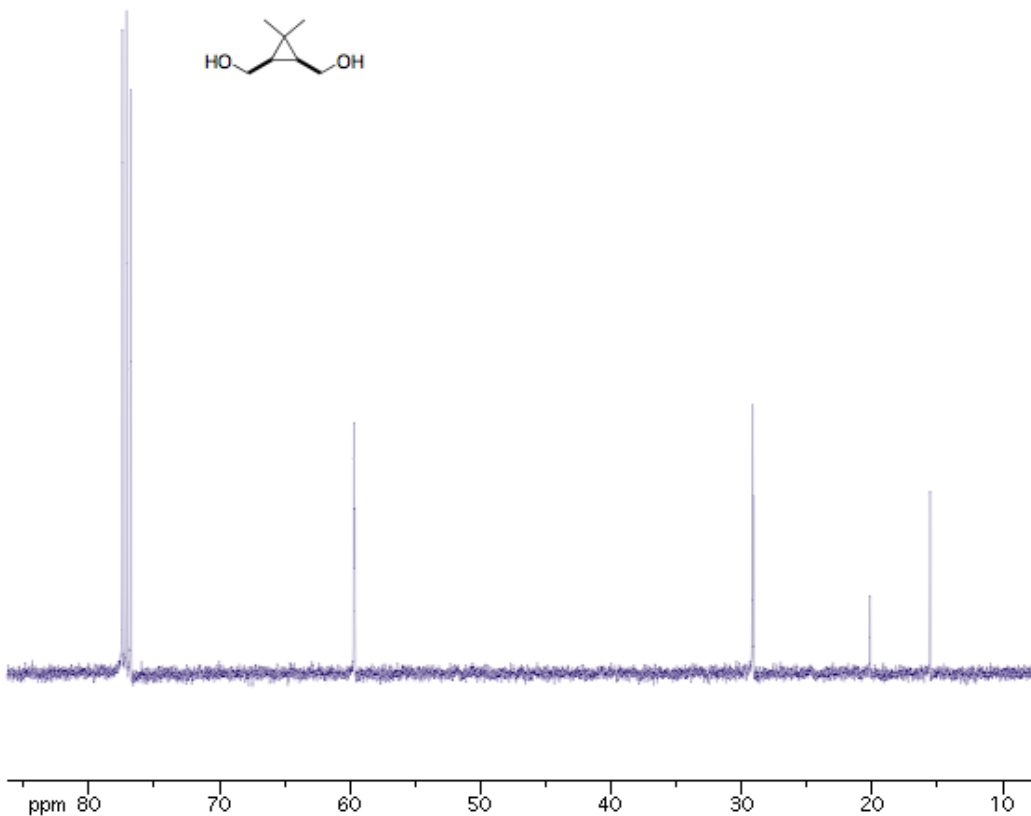


Ethyl (±)-(1*S*,3*R*)-3-formyl-2,2-dimethylcyclopropanecarboxylate (SI-3) & Ethyl (±)-(1*R*,3*R*)-3-formyl-2,2-dimethylcyclopropanecarboxylate (SI-4)

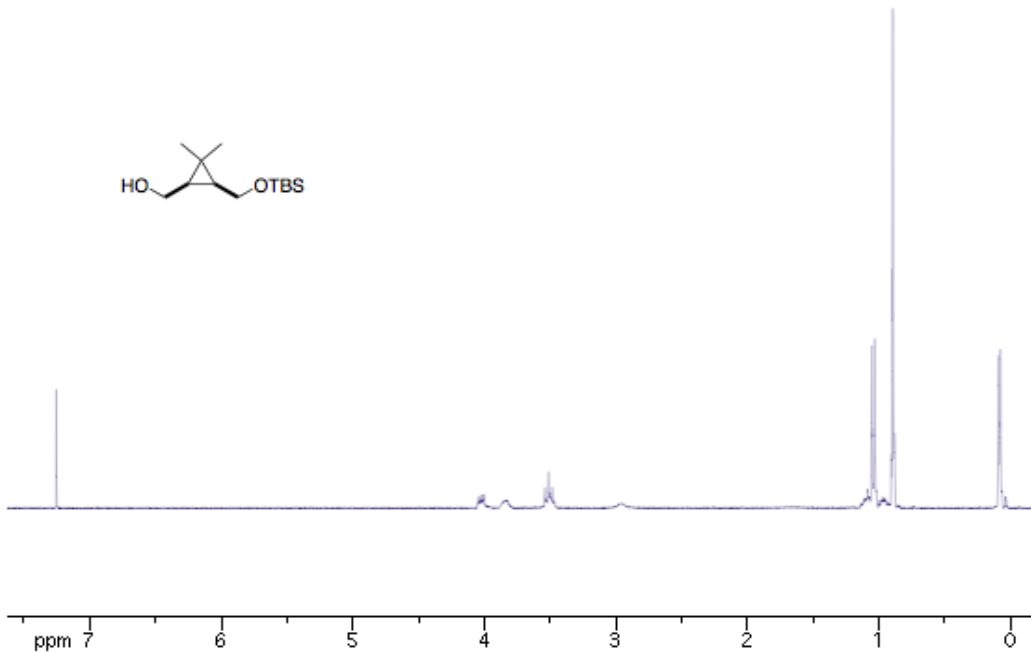


(±)-[(1*R*,2*R*)-3,3-Dimethylcyclopropane-1,2-diyl]dimethanol (19)



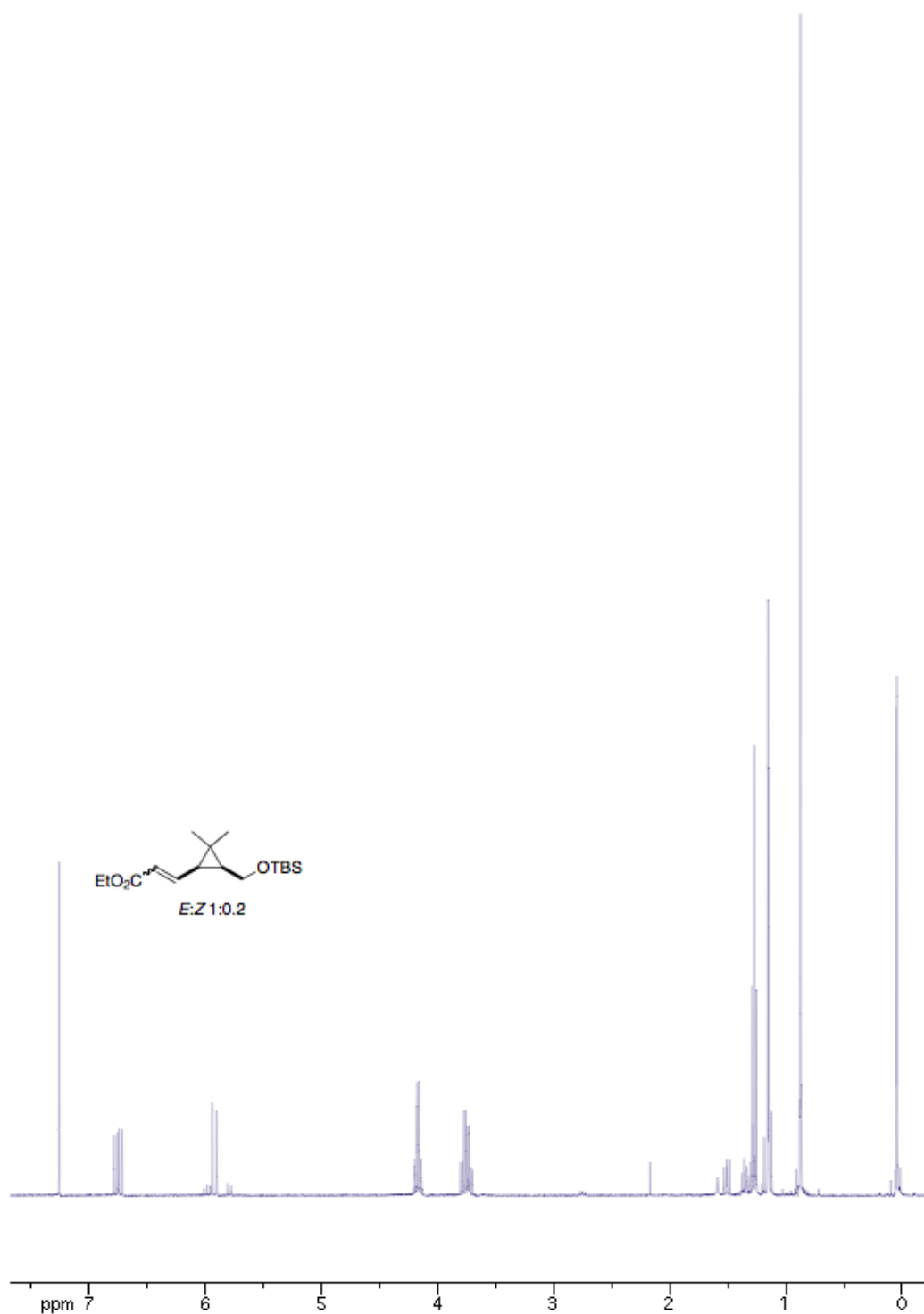


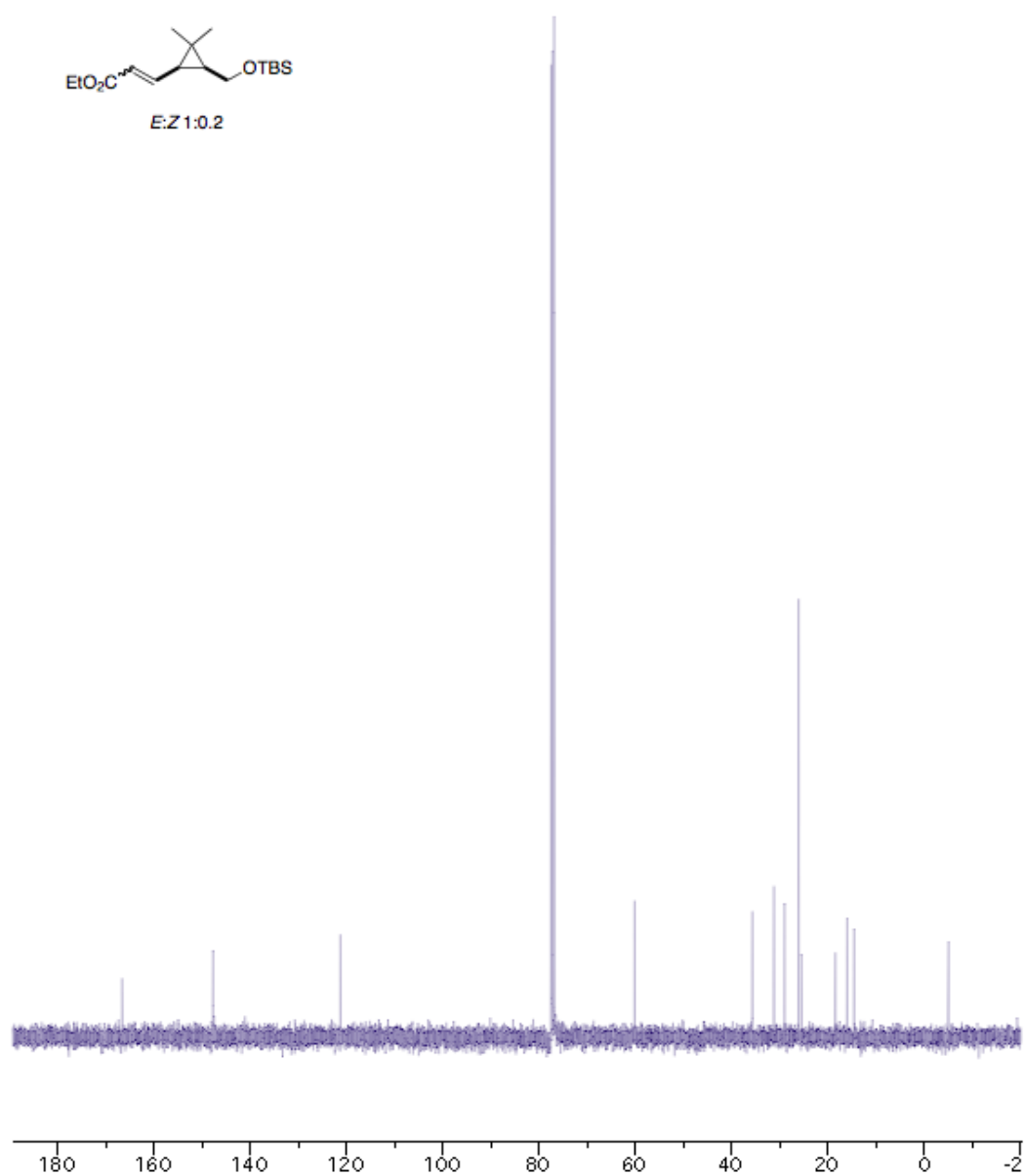
(±)-[(1*S*,3*R*)-3-([*tert*-Butyl(dimethyl)silyl]oxy)methyl)-2,2-dimethylcyclopropyl]methanol (20)



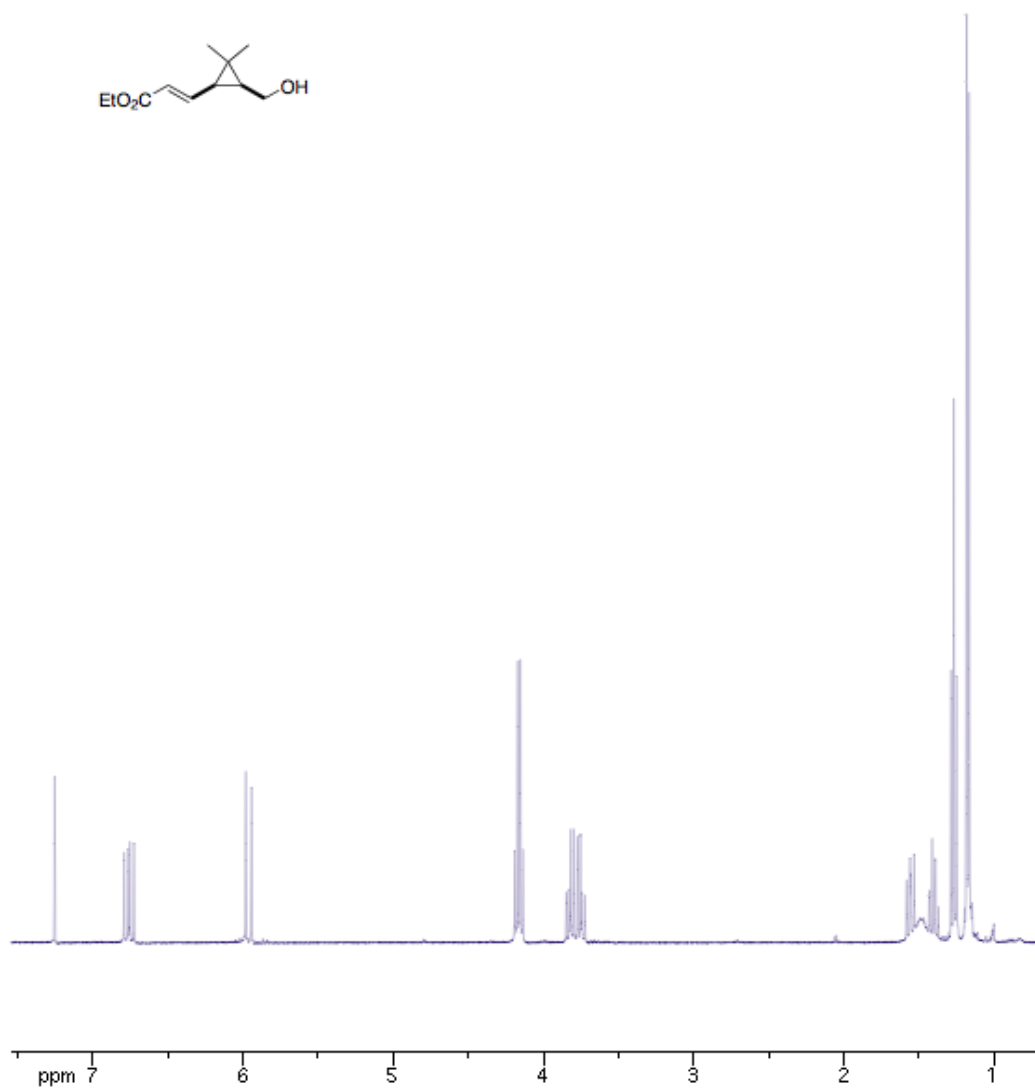


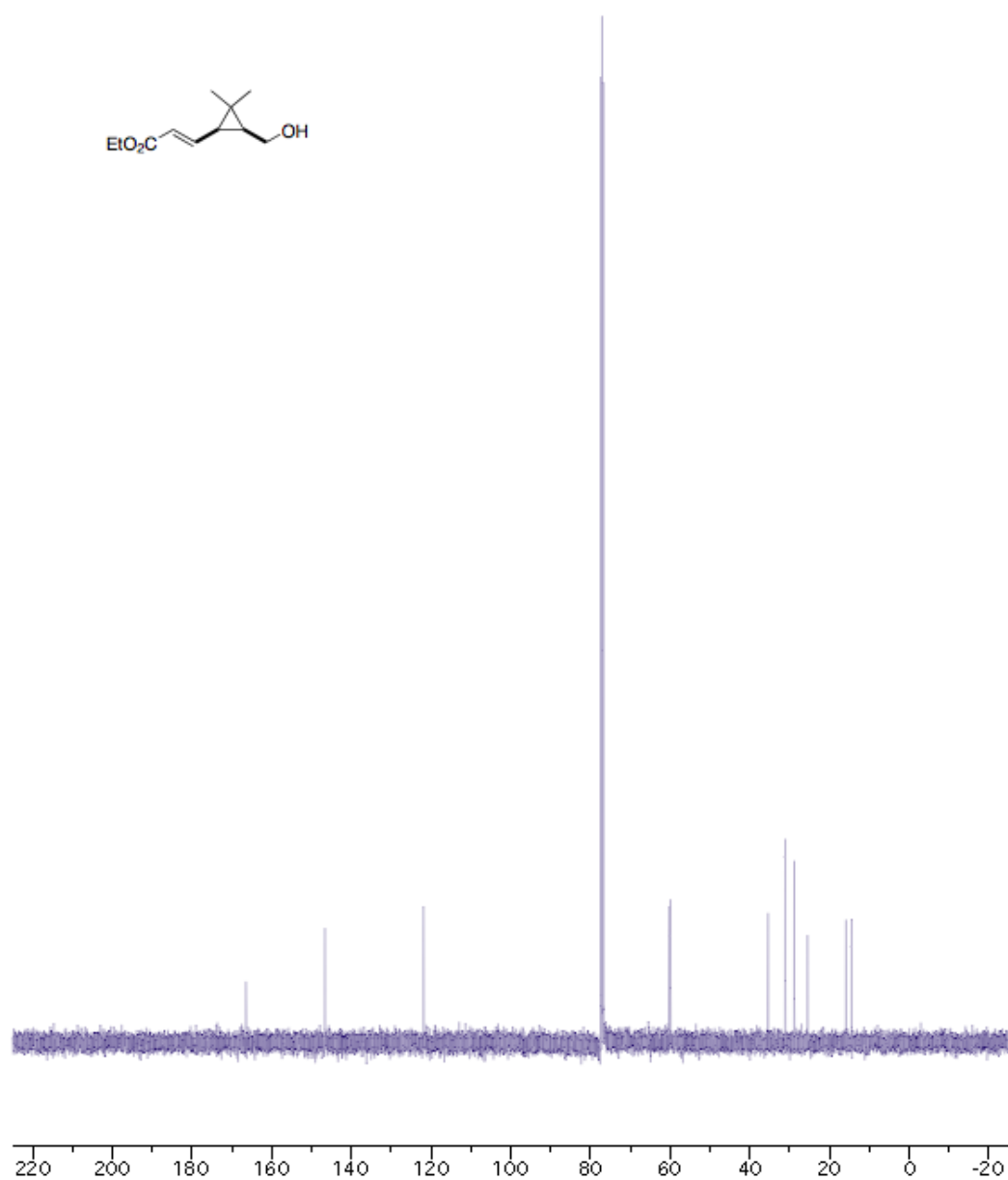
Ethyl (±)-(2*E*)-3-[(1*S*,3*R*)-3-([*tert*-butyl(dimethyl)silyl]oxy)methyl)-2,2-dimethylcyclopropyl]prop-2-enoate (21) & Ethyl (±)-(2*Z*)-3-[(1*S*,3*R*)-3-([*tert*-butyl(dimethyl)silyl]oxy)methyl)-2,2-dimethylcyclopropyl]prop-2-enoate (24)



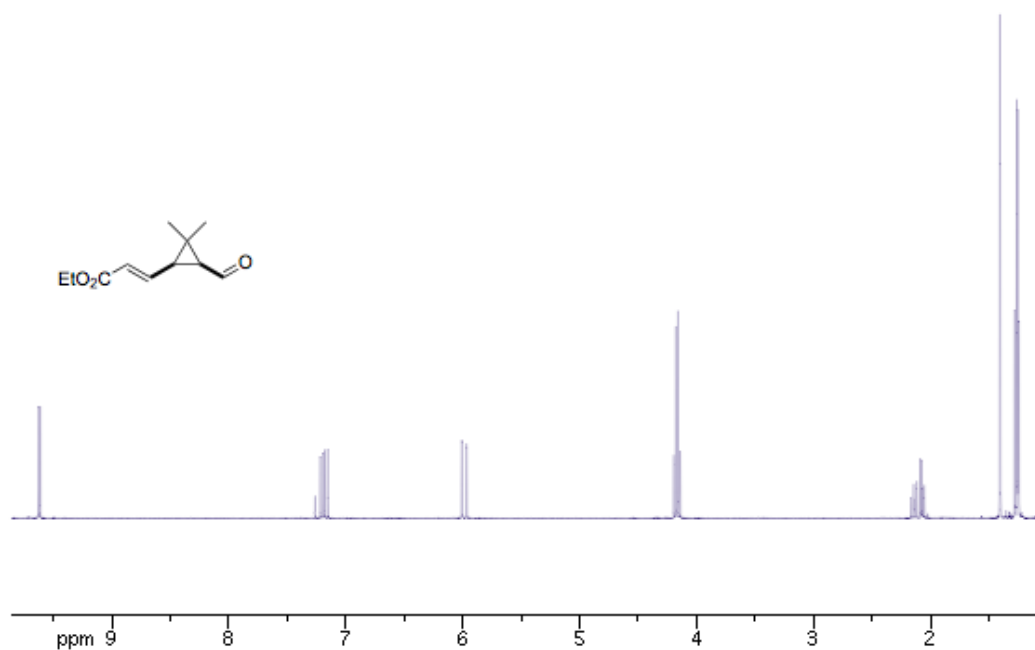


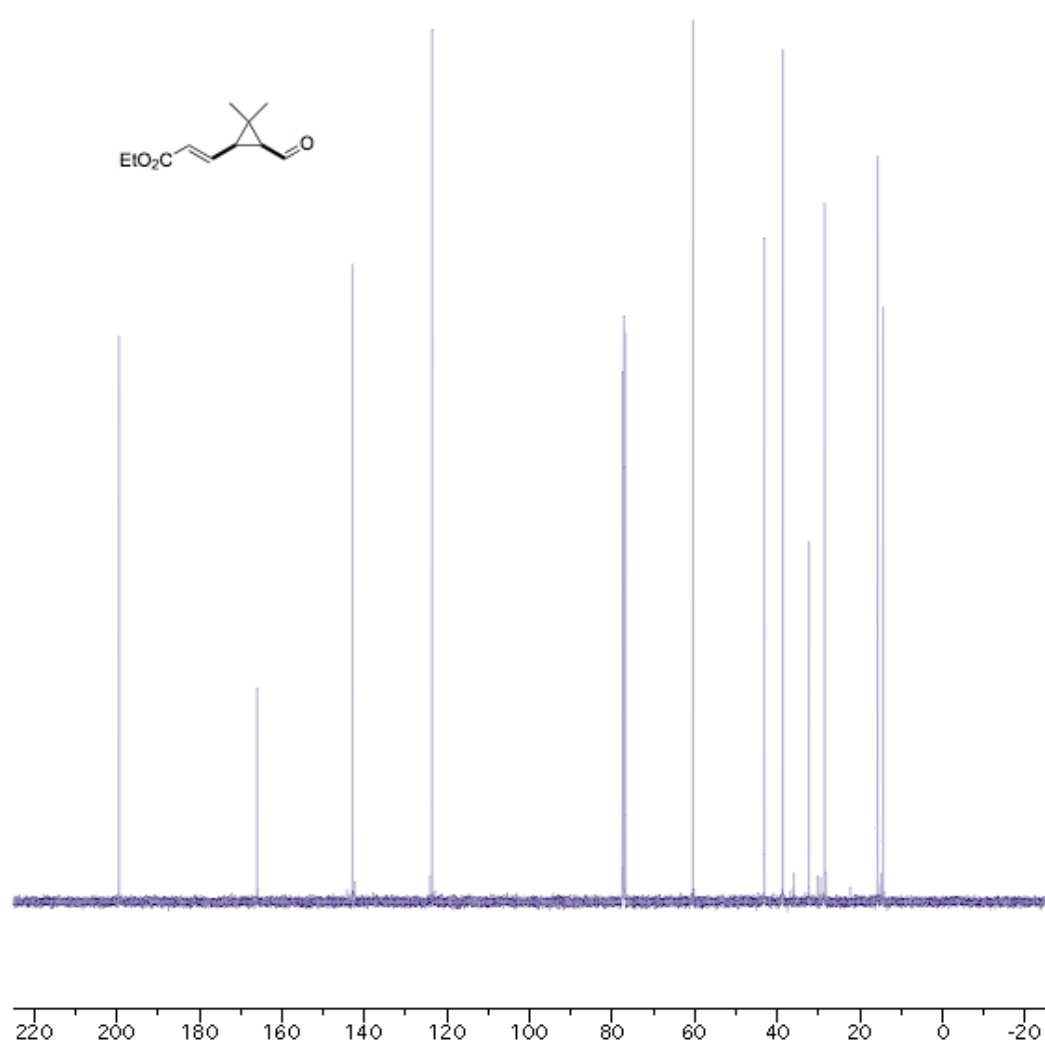
Ethyl (±)-(2*E*)-3-[(1*S*,3*R*)-3-(hydroxymethyl)-2,2-dimethylcyclopropyl]prop-2-enoate (22)



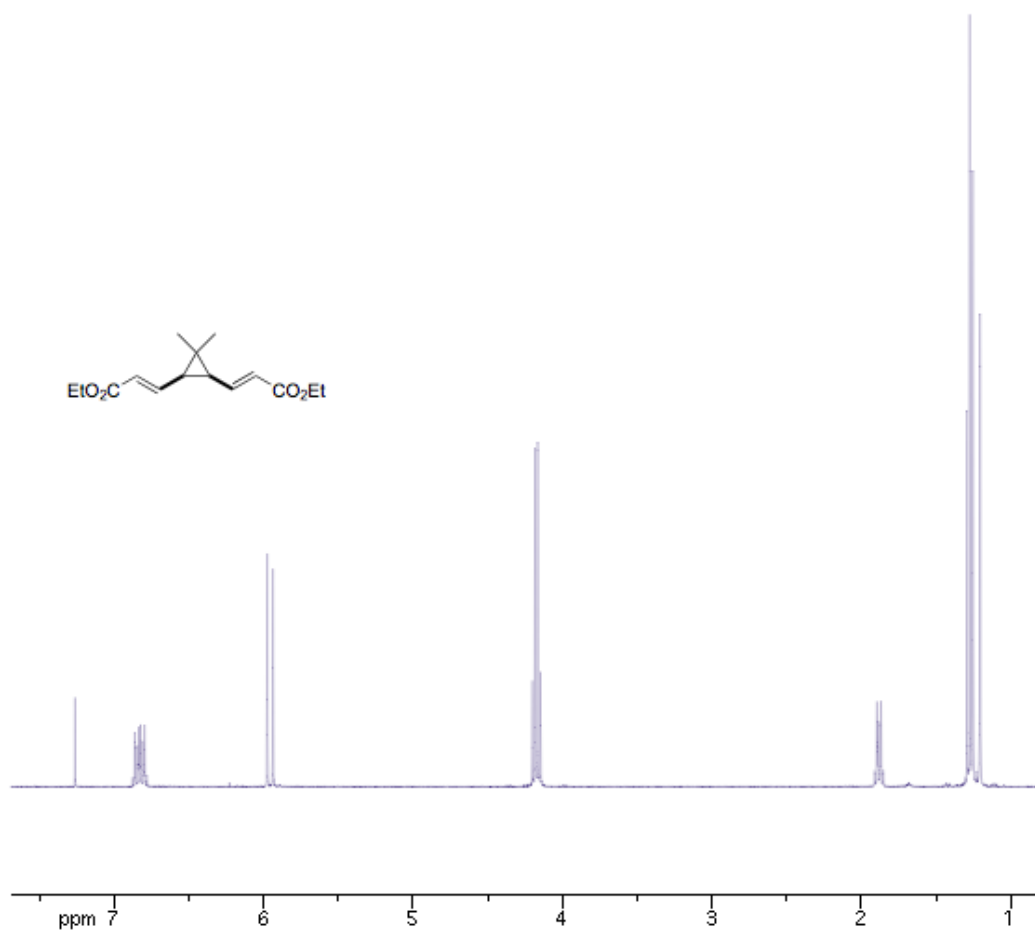


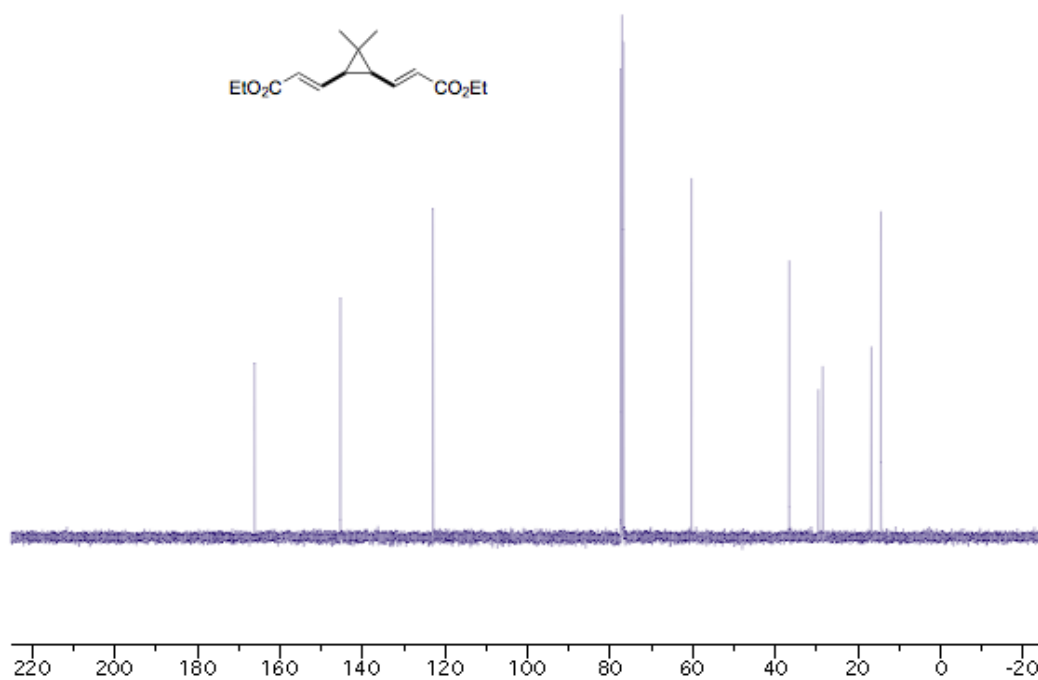
Ethyl (±)-(2*E*)-3-[(1*S*,3*R*)-3-formyl-2,2-dimethylcyclopropyl]prop-2-enoate (23)



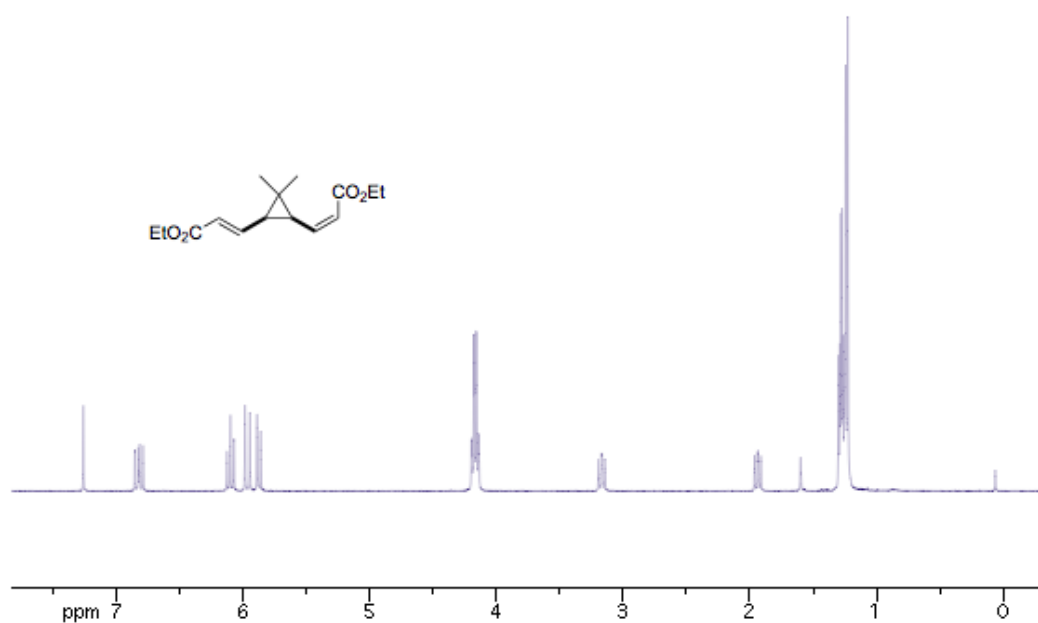


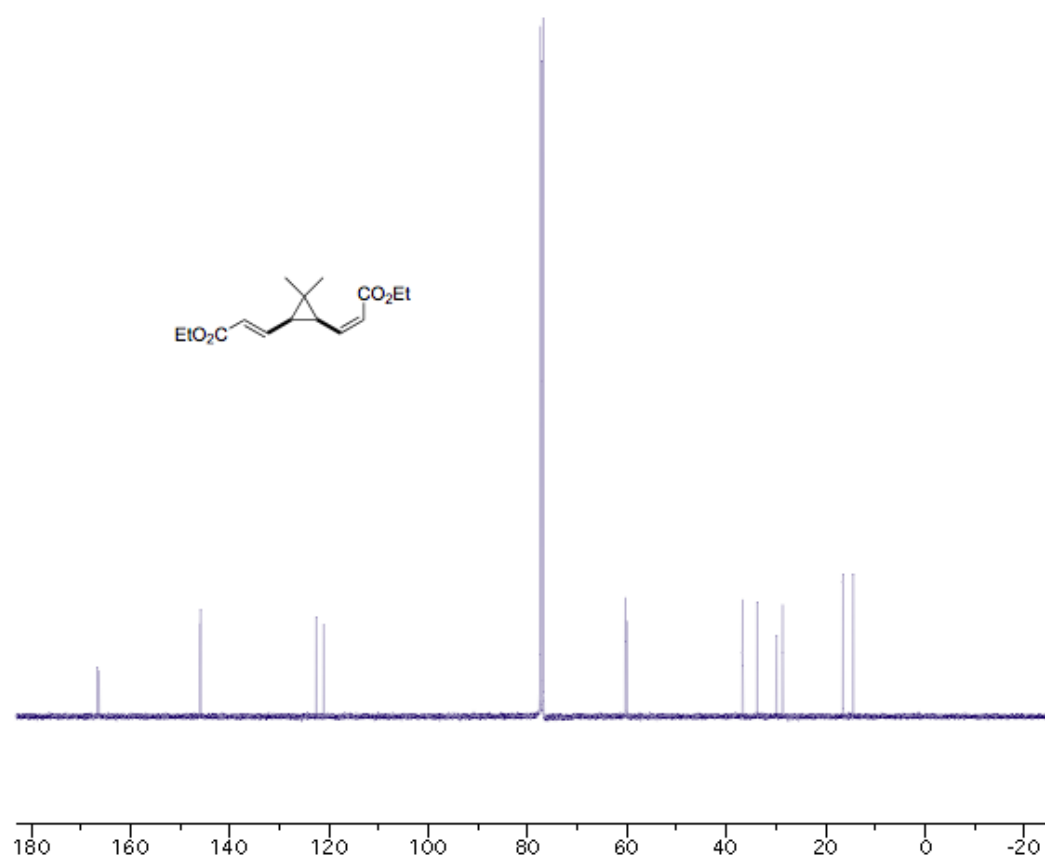
Diethyl (2*E*,2'*E*)-3,3'-[(1*R*,2*S*)-3,3-dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (9d)



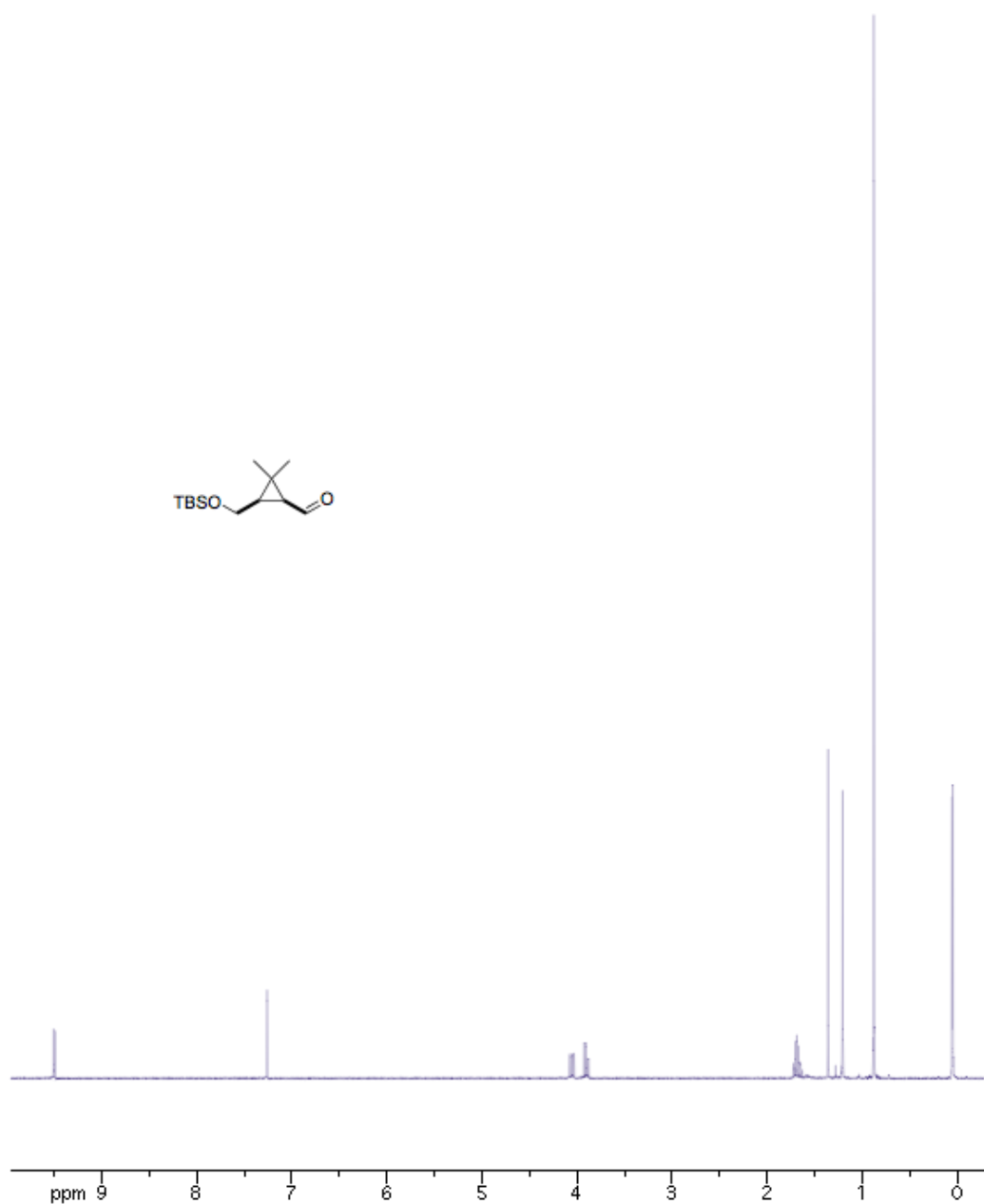


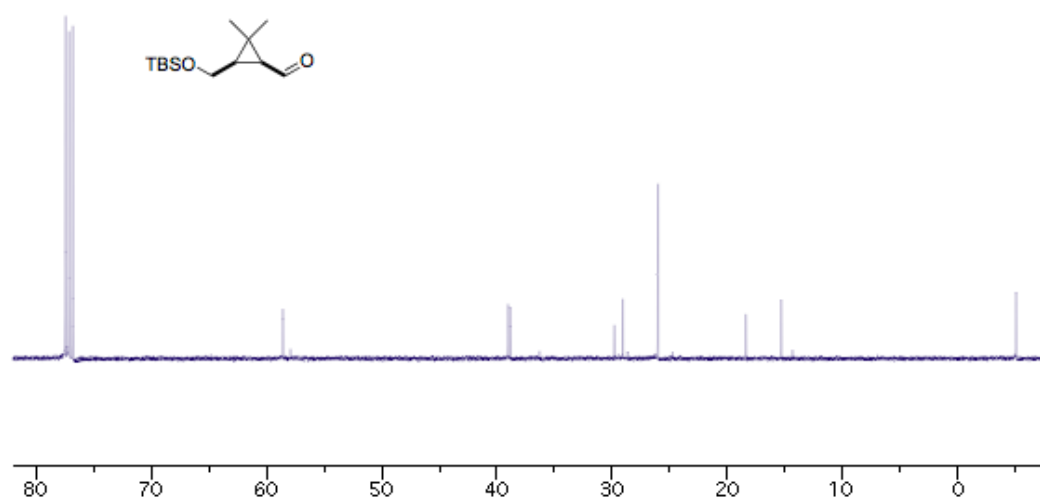
Diethyl (±)-(2Z,2'E)-3,3'-[(1R,2S)-3,3-Dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (9e)



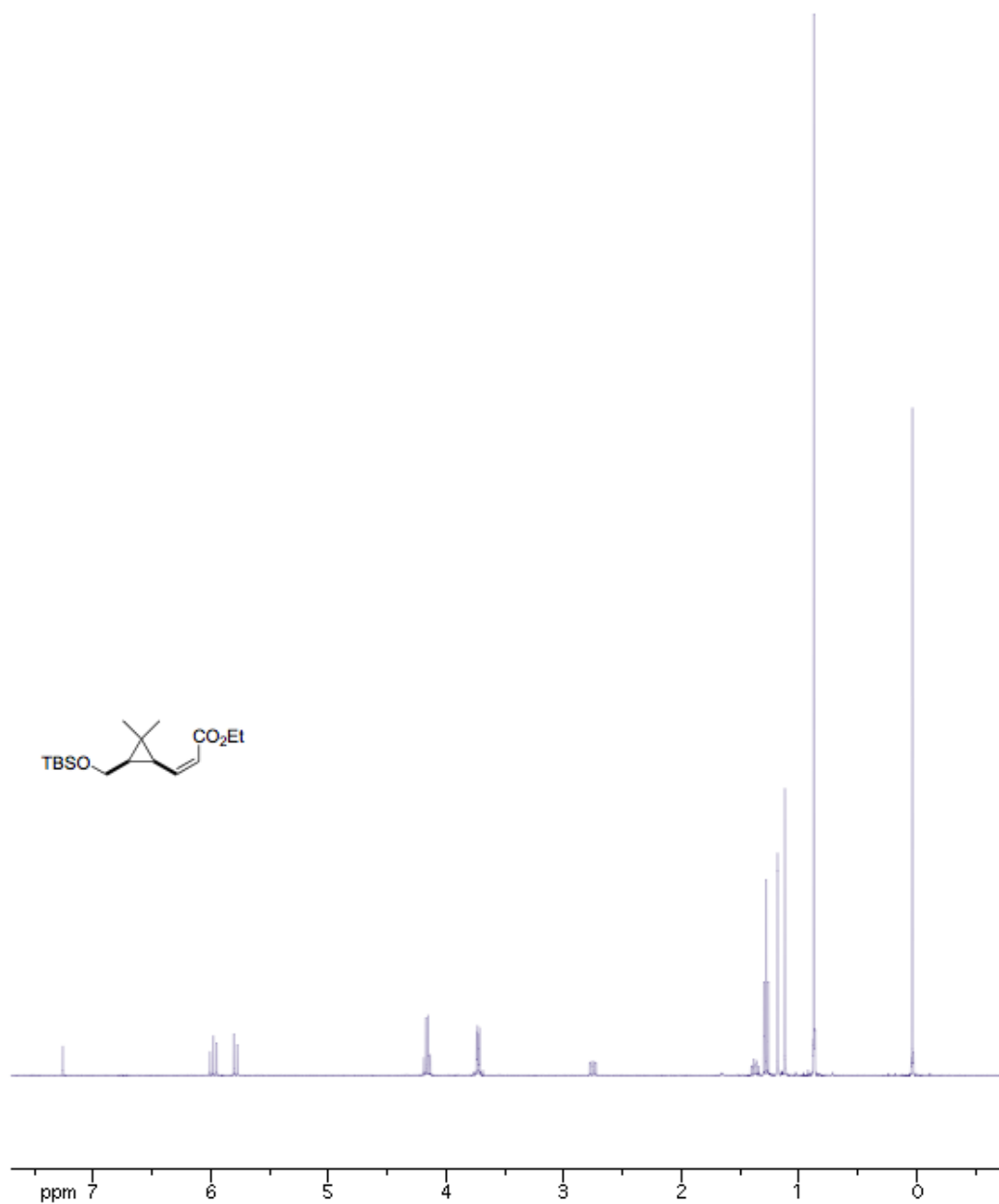


(±)-(1*S*,3*R*)-3-({*tert*-Butyl(dimethyl)silyl}oxy)methyl)-2,2-dimethylcyclopropanecarbaldehyde (SI-5)

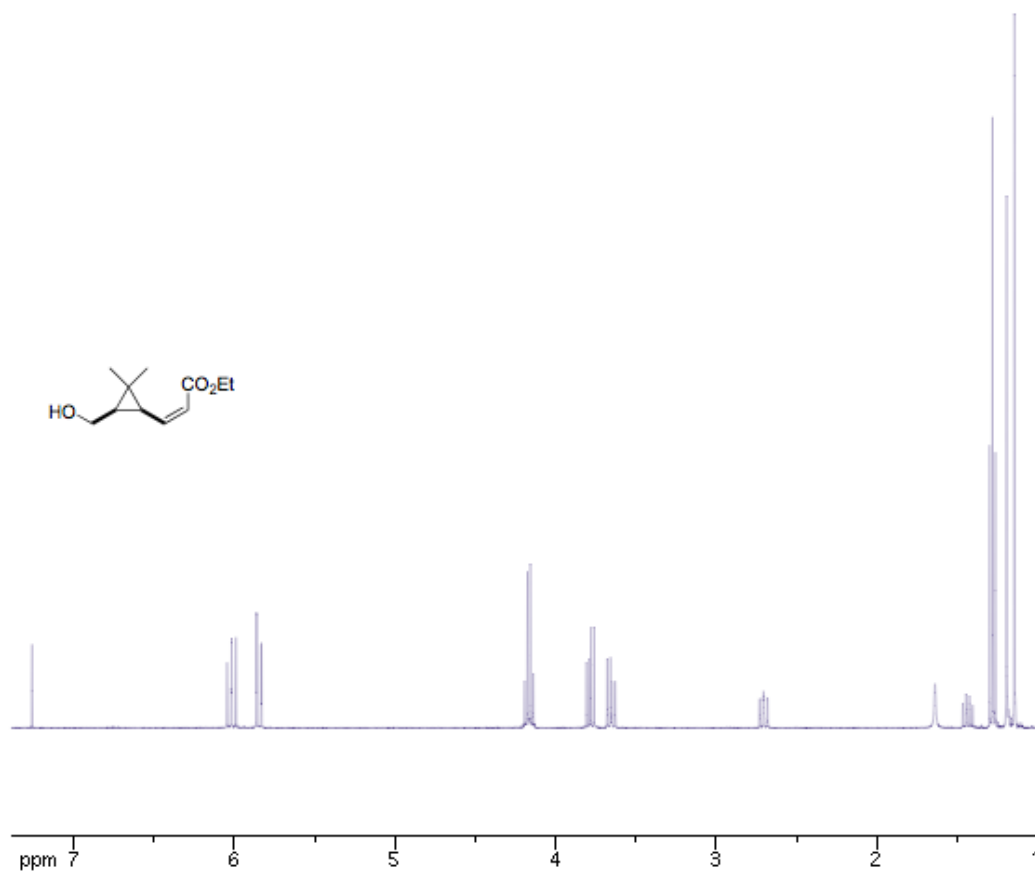


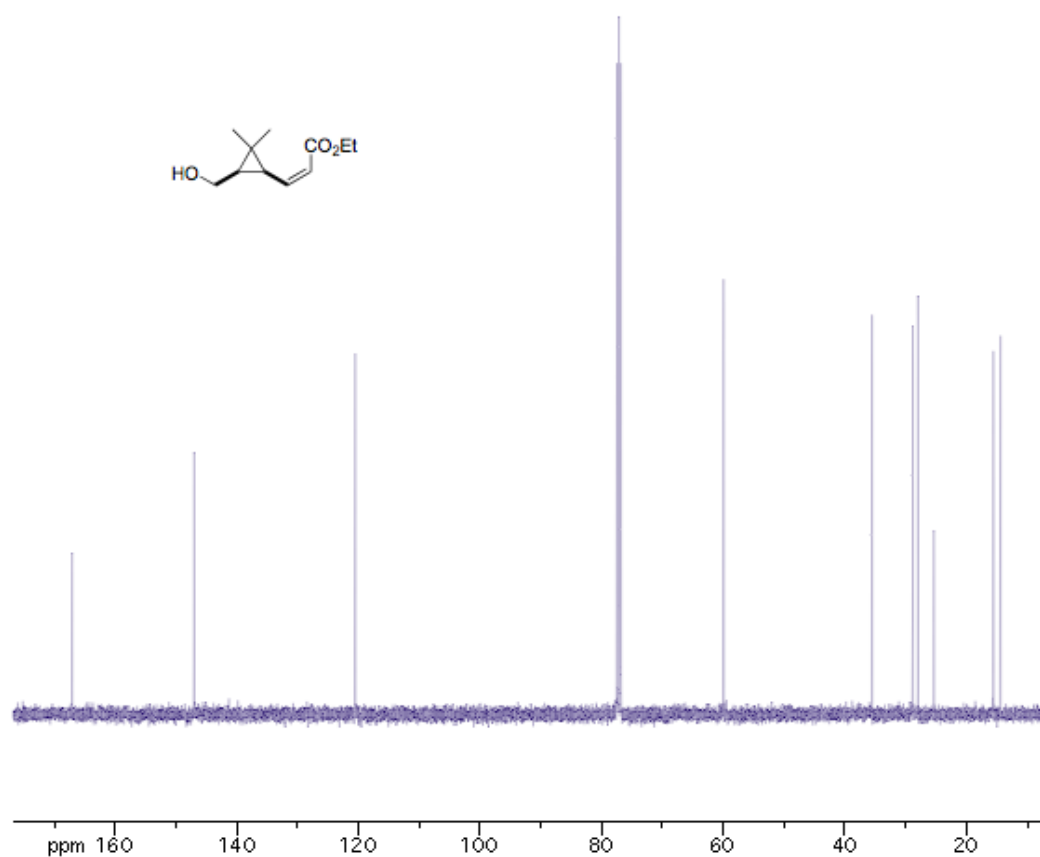


Ethyl (±)-(2*Z*)-3-[(1*S*,3*R*)-3-([*tert*-butyl(dimethyl)silyl]oxy)methyl]-2,2-dimethylcyclopropyl]prop-2-enoate (24)

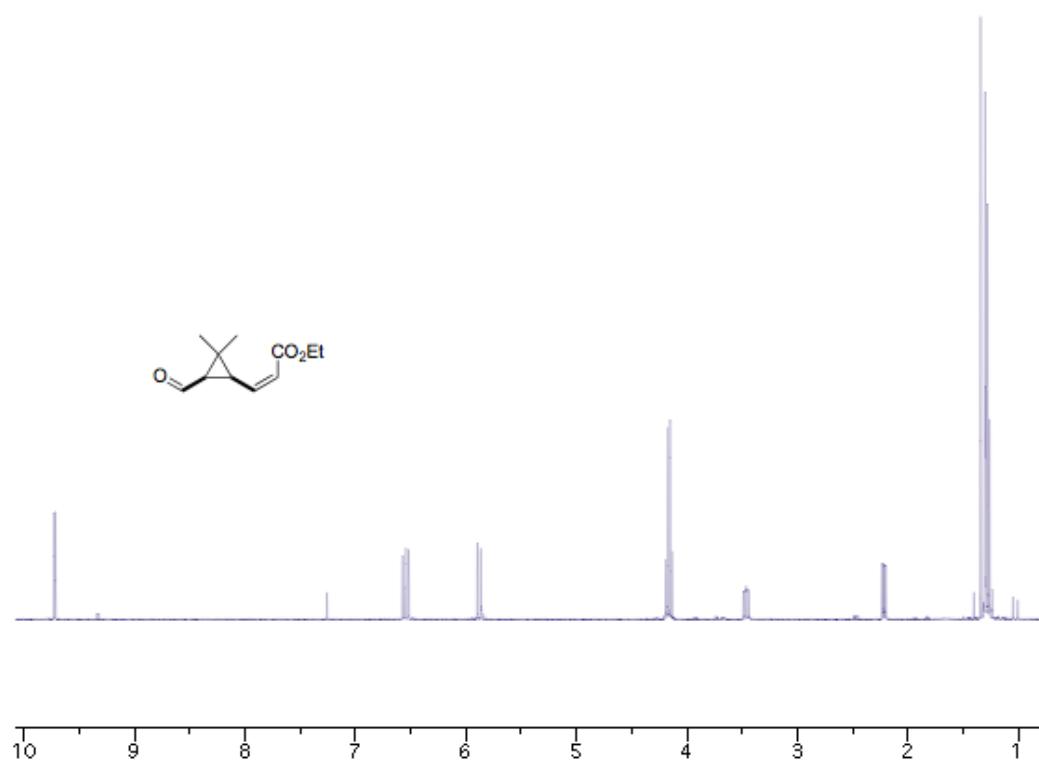


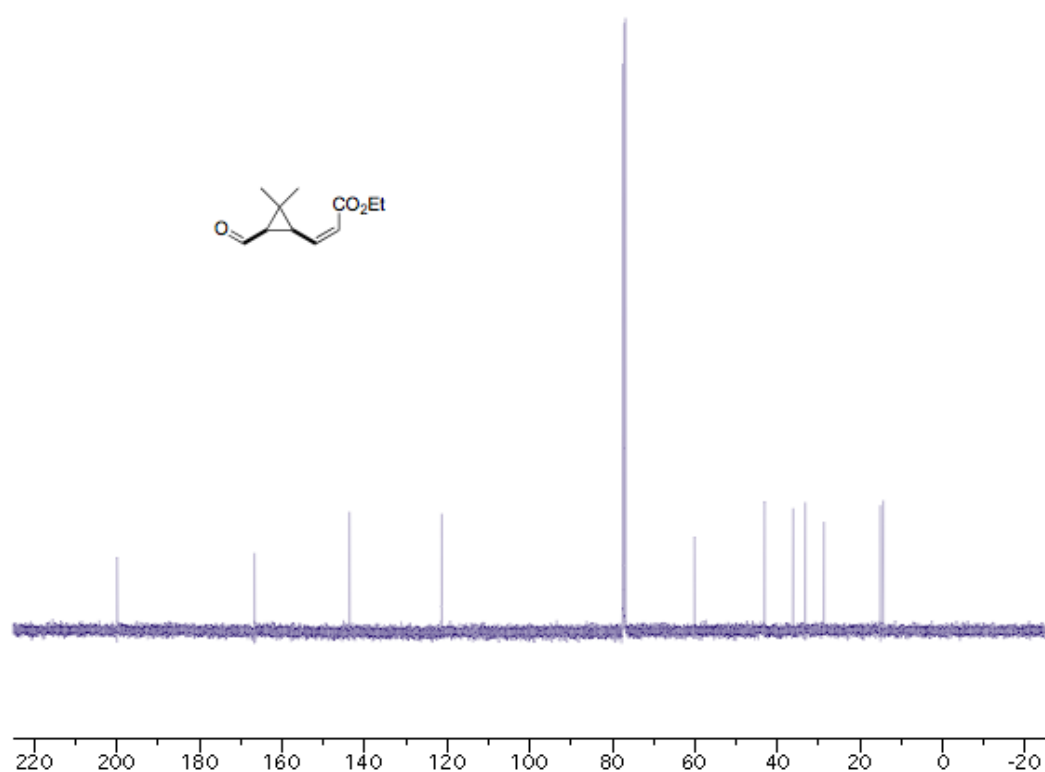
Ethyl (±)-(2Z)-3-[(1S,3R)-3-(hydroxymethyl)-2,2-dimethylcyclopropyl]prop-2-enoate (25)



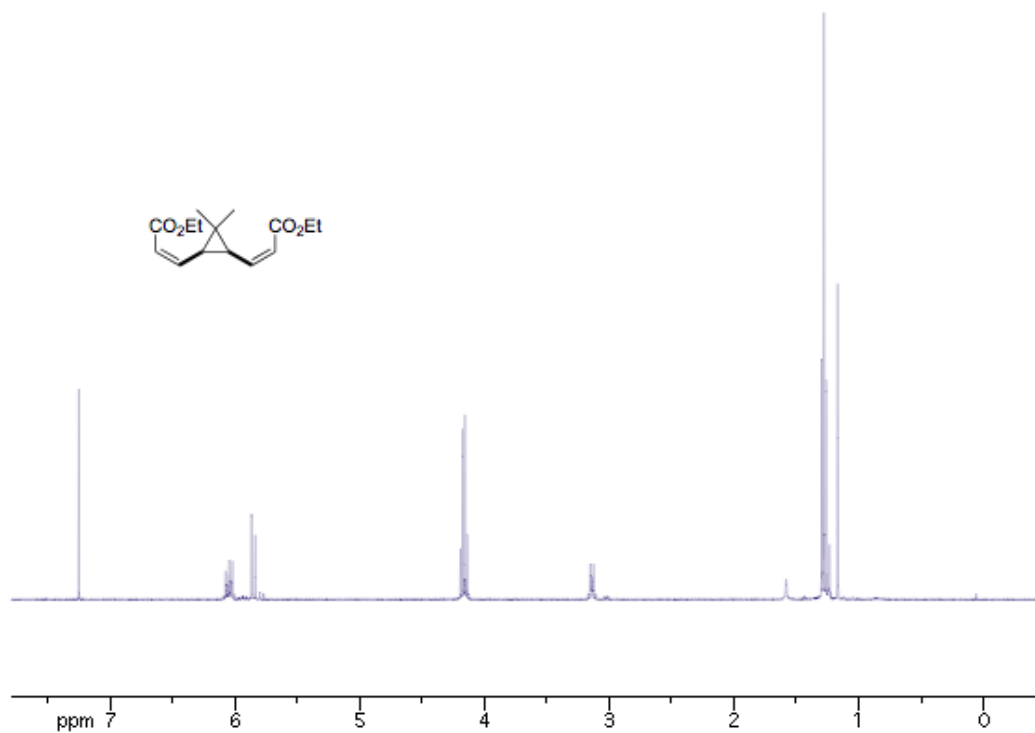


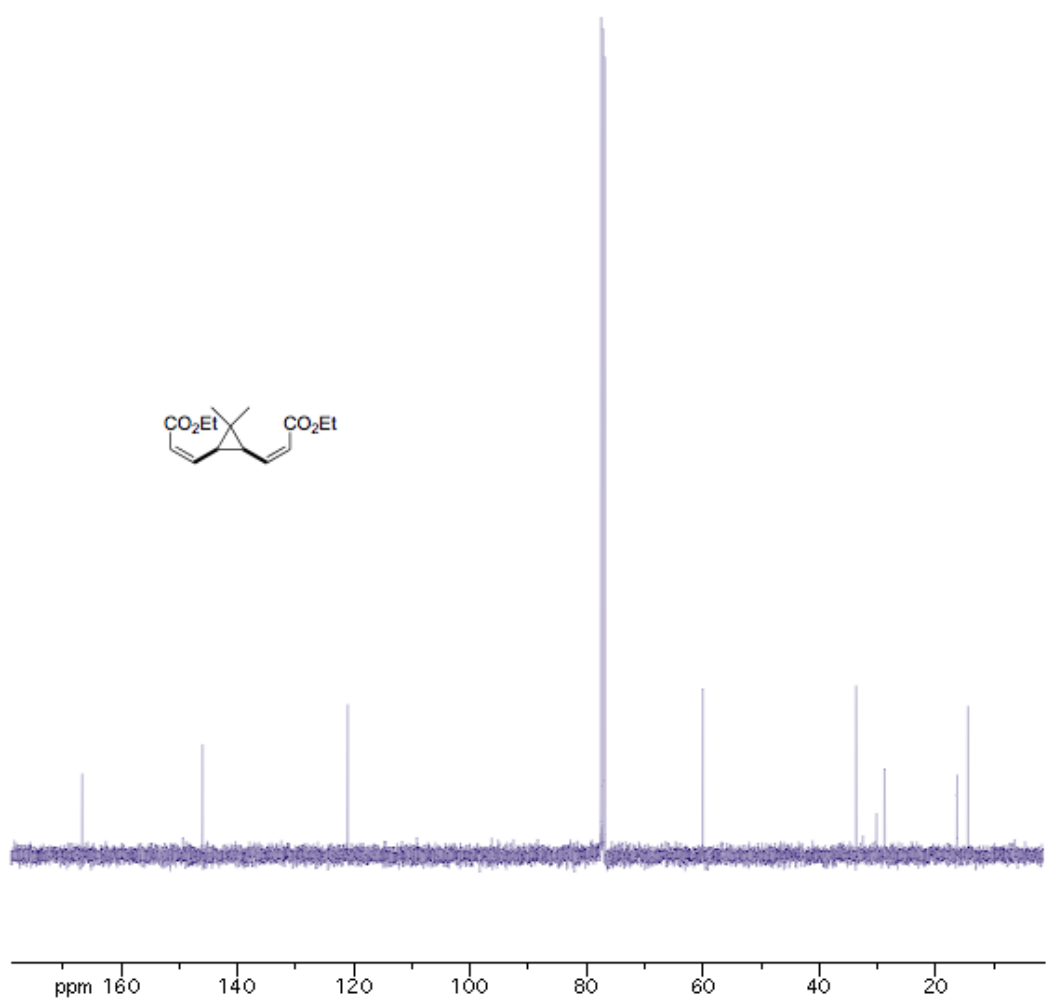
Ethyl (±)-(2Z)-3-[(1S,3R)-3-formyl-2,2-dimethylcyclopropyl]prop-2-enoate (SI-6)



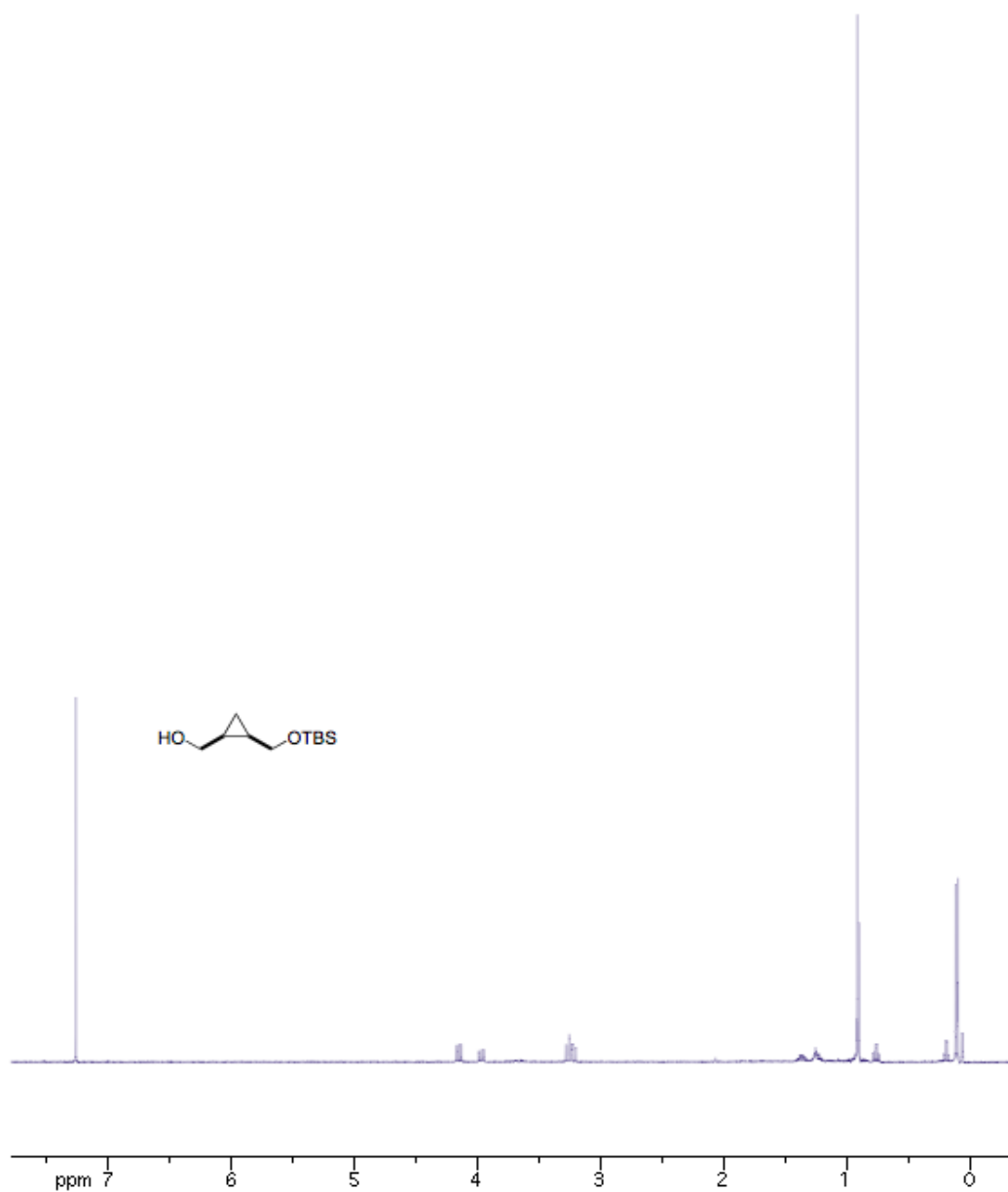


Diethyl (2Z,2'Z)-3,3'-[(1R,2S)-3,3-dimethylcyclopropane-1,2-diyl]bisprop-2-enoate (9f)

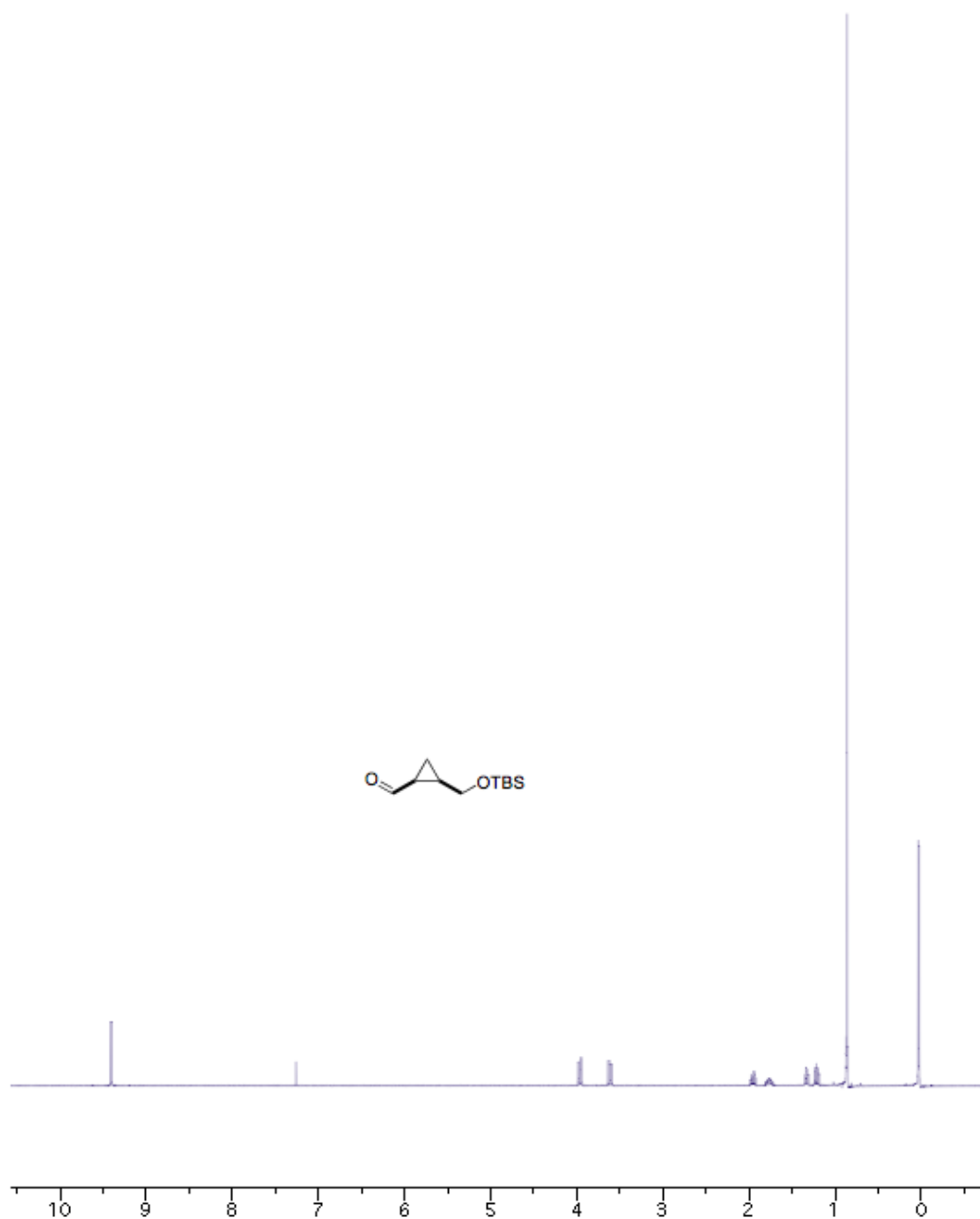




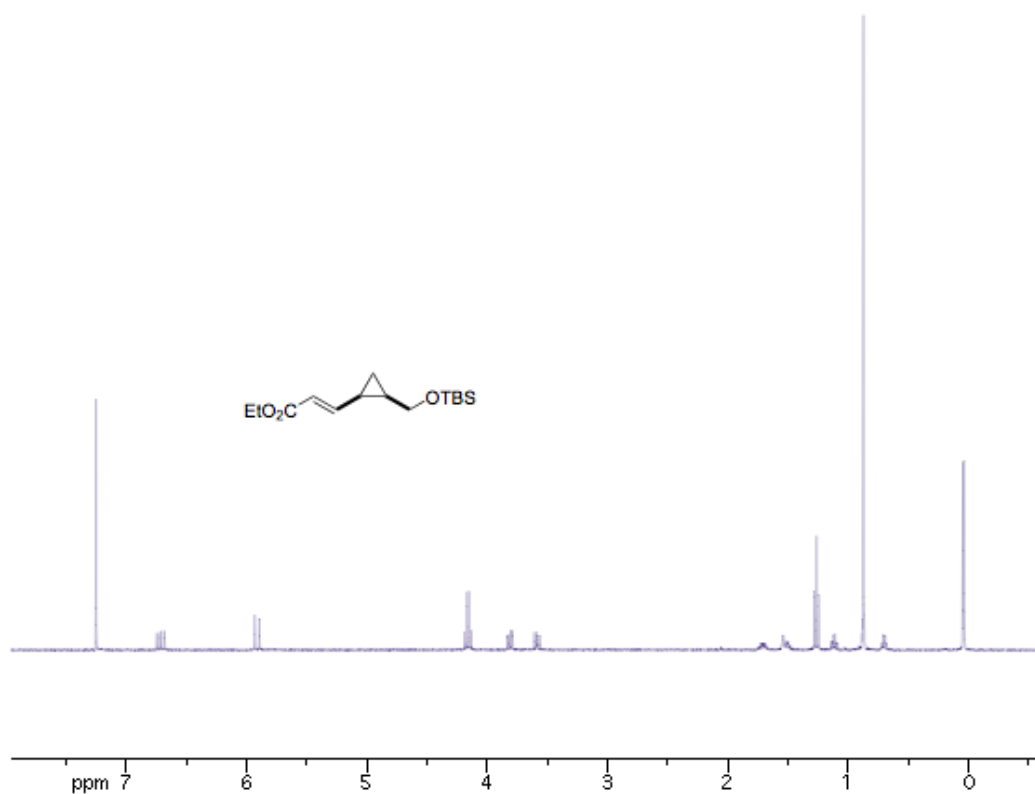
(±)-[(1*R*,2*S*)-2-({*tert*-Butyl(dimethyl)silyl}oxy)methyl]cyclopropyl]methanol (28)



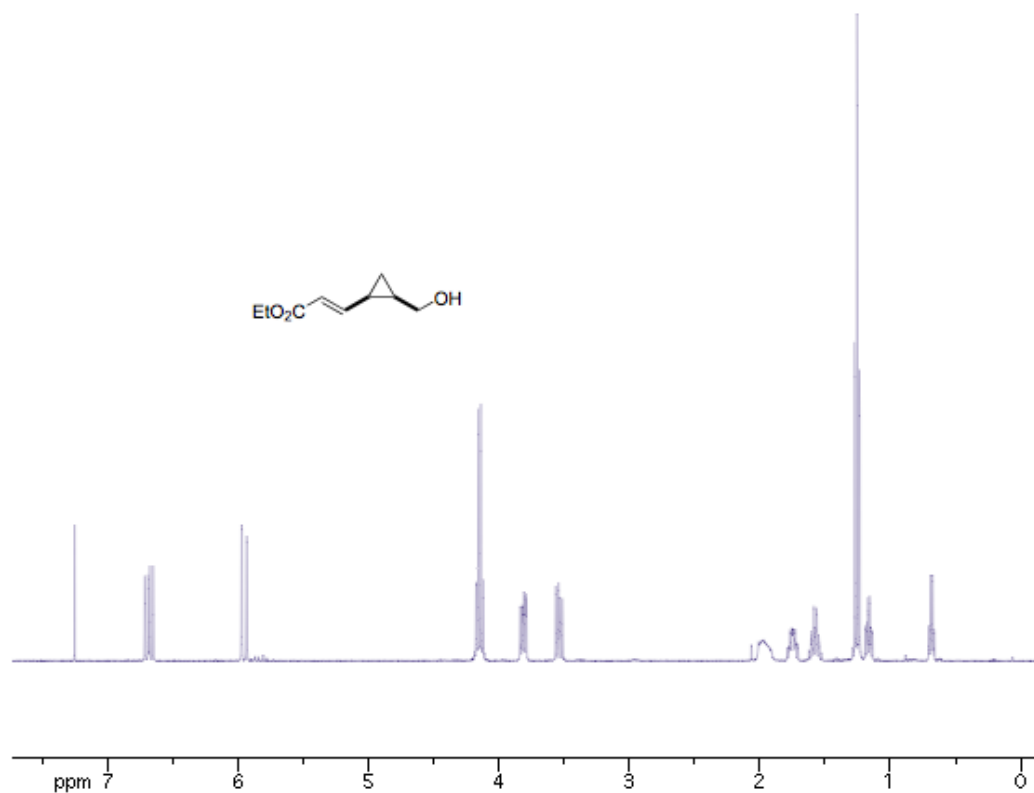
**(±)-(1*R*,2*S*)-2-([*tert*-Butyl(dimethyl)silyl]oxy)methyl)cyclopropanecarbaldehyde
(SI-7)**



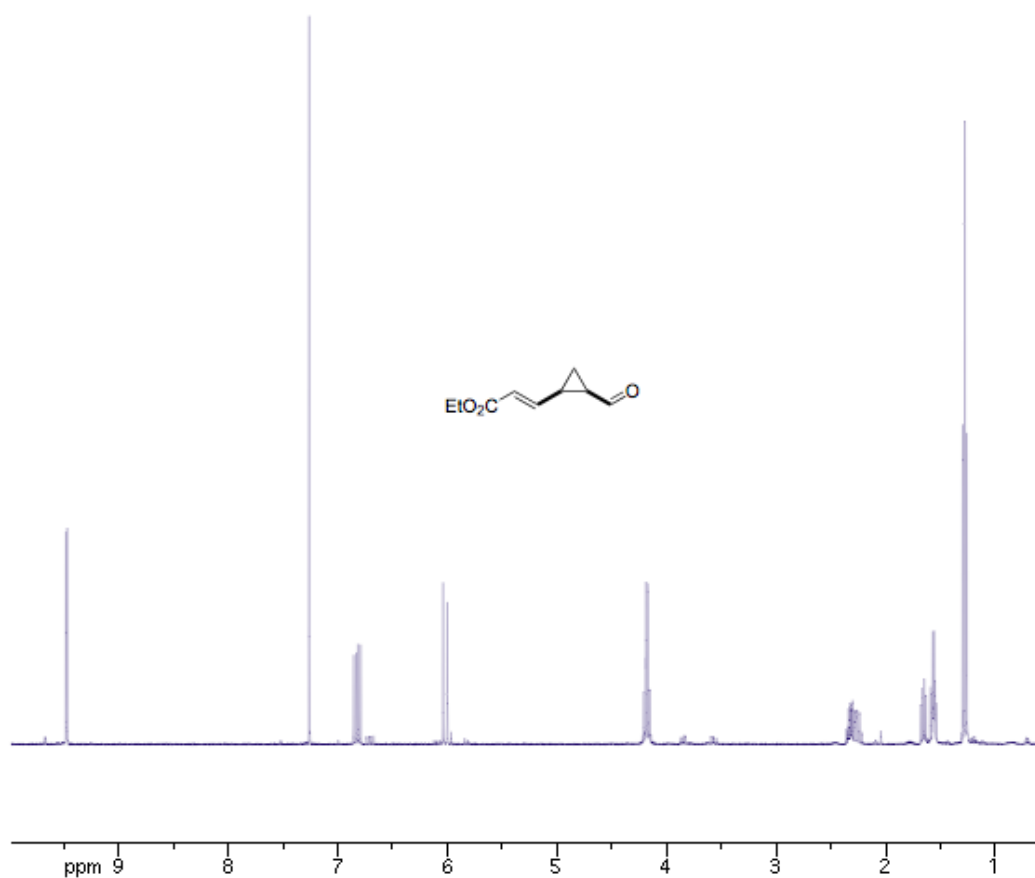
**Ethyl (±)-(2*E*)-3-[(1*S*,2*S*)-2-([*tert*-
 butyl(dimethyl)silyl]oxy)methyl)cyclopropyl]prop-2-enoate (29)**



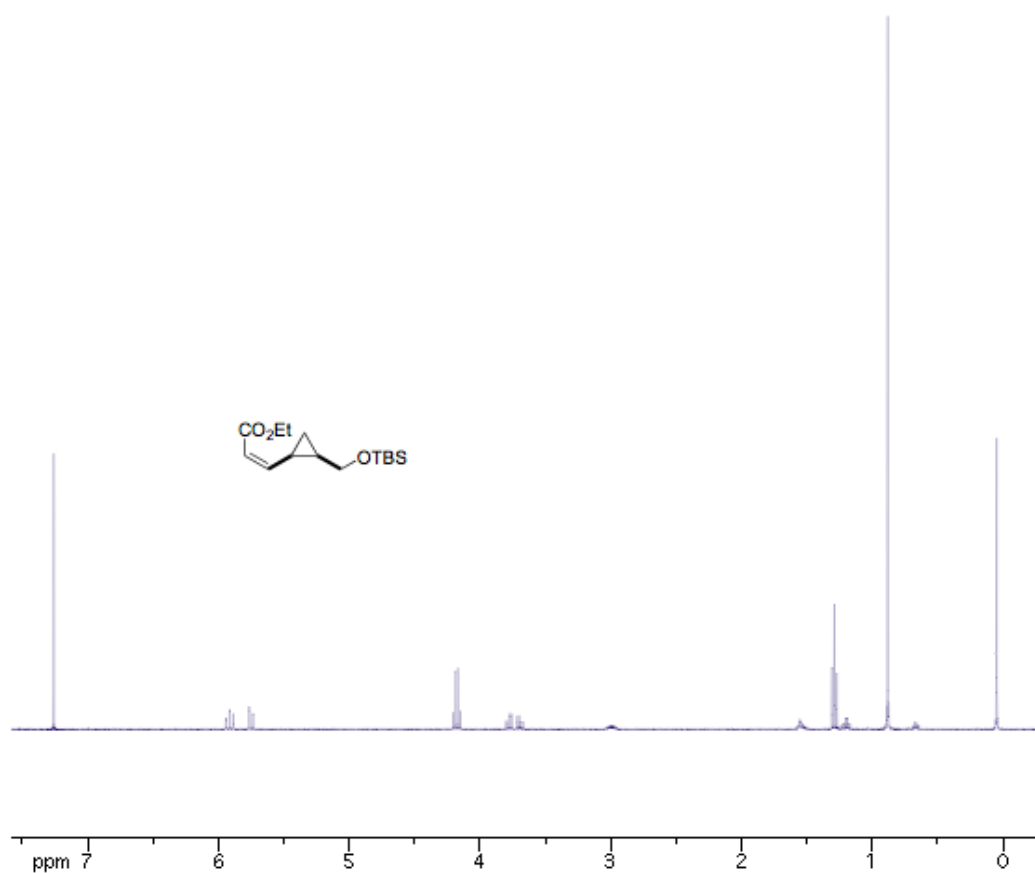
Ethyl (±)-(2*E*)-3-[(1*S*,2*S*)-2-(hydroxymethyl)cyclopropyl]prop-2-enoate (30)

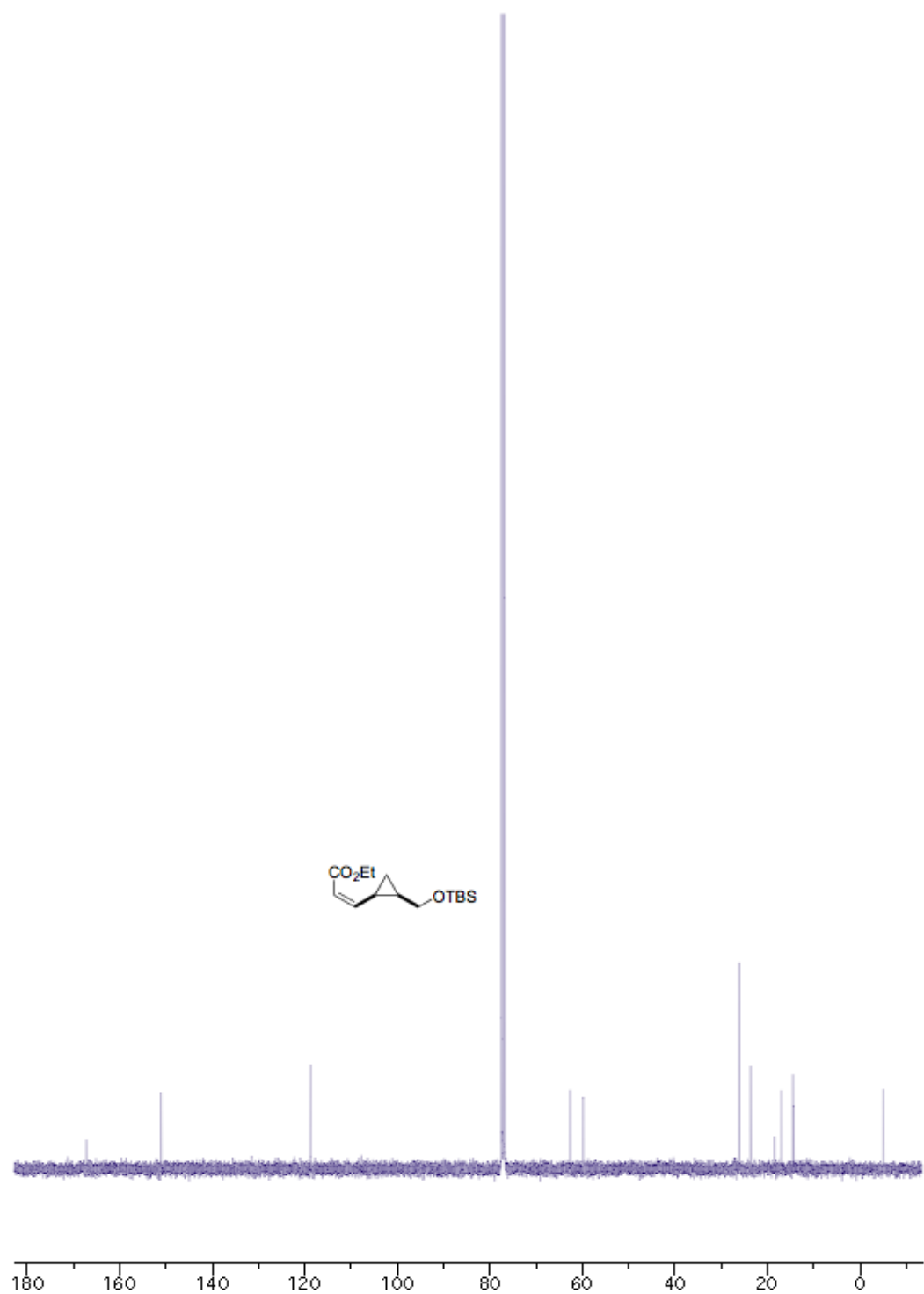


Ethyl (±)-(2*E*)-3-[(1*S*,2*S*)-2-formylcyclopropyl]prop-2-enoate (31)

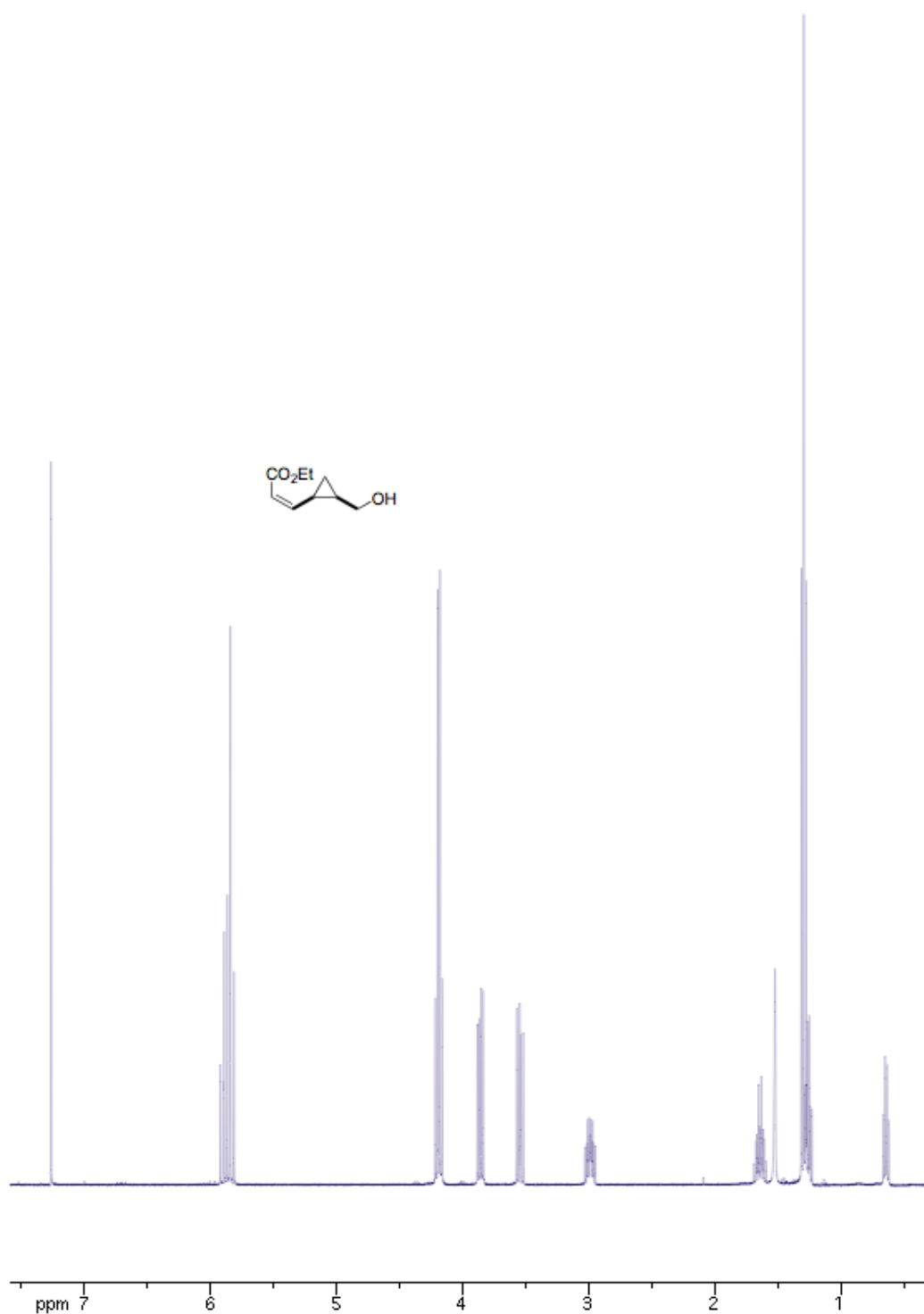


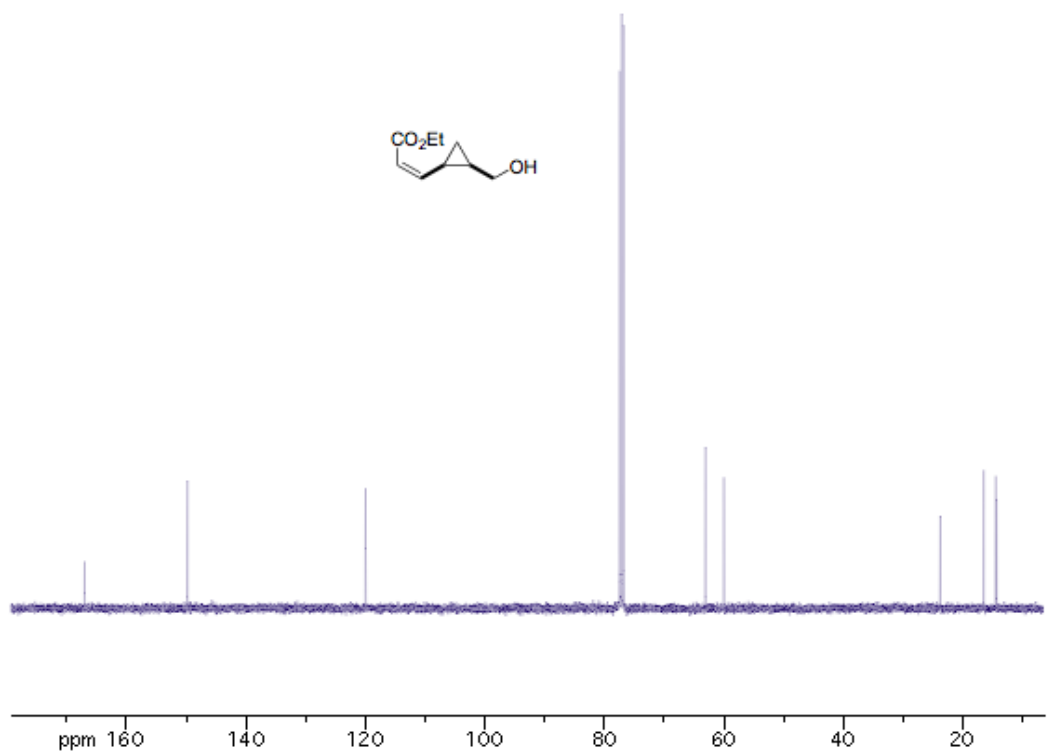
Ethyl (±)-(2Z)-3-[(1S,2S)-2-({*tert*-butyl(dimethyl)silyl}oxy)methyl]cyclopropyl]prop-2-enoate (32)



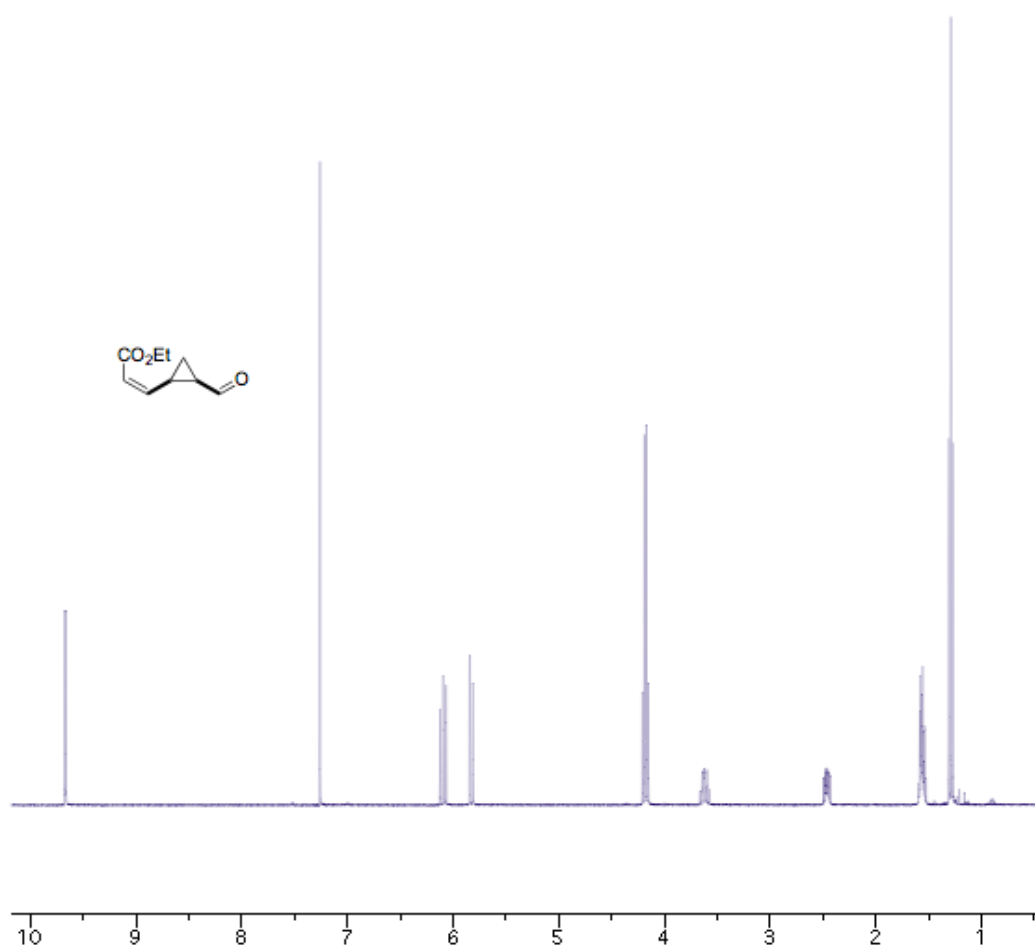


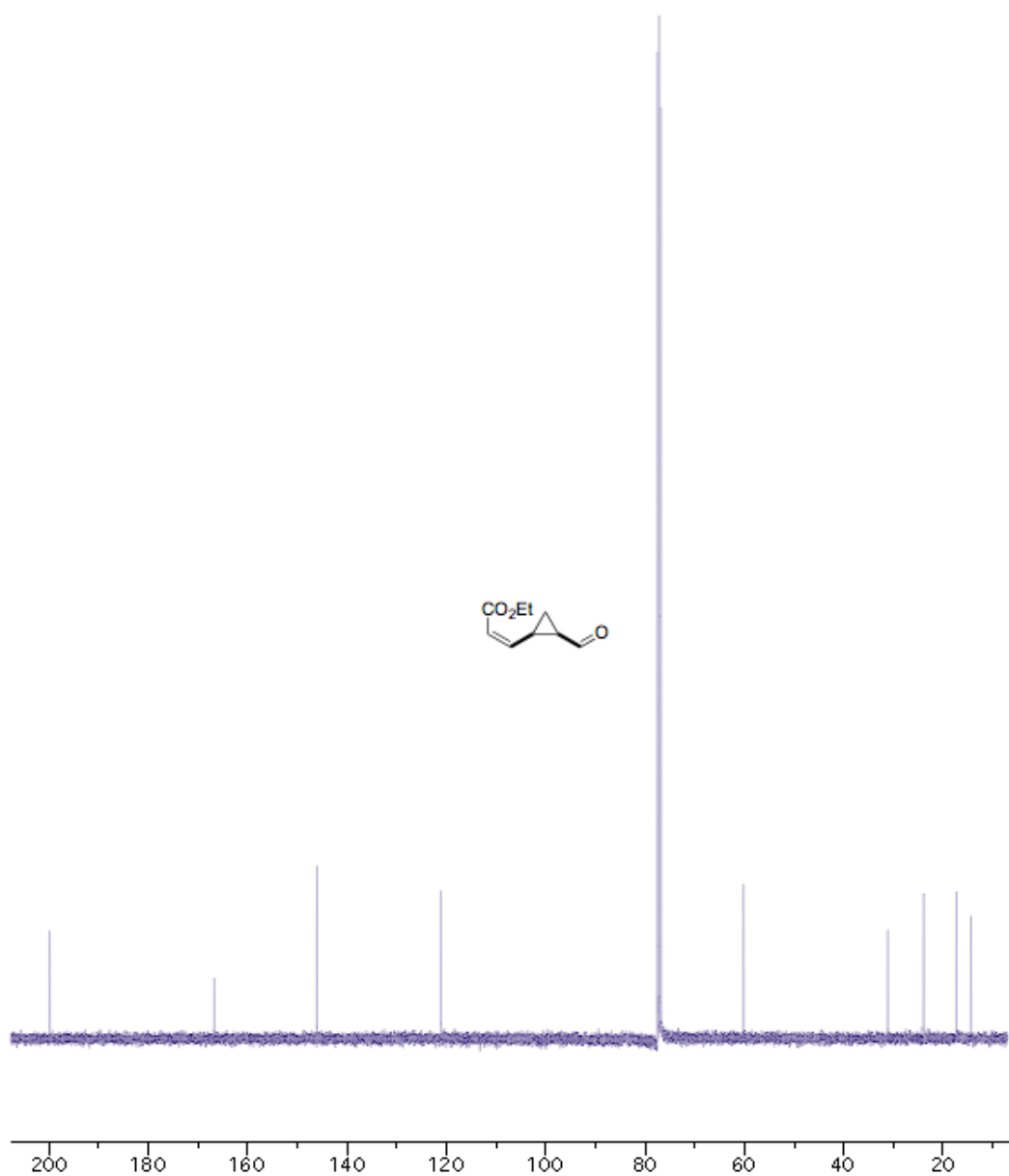
Ethyl (±)-(2Z)-3-[(1S,2S)-2-(hydroxymethyl)cyclopropyl]prop-2-enoate (33)



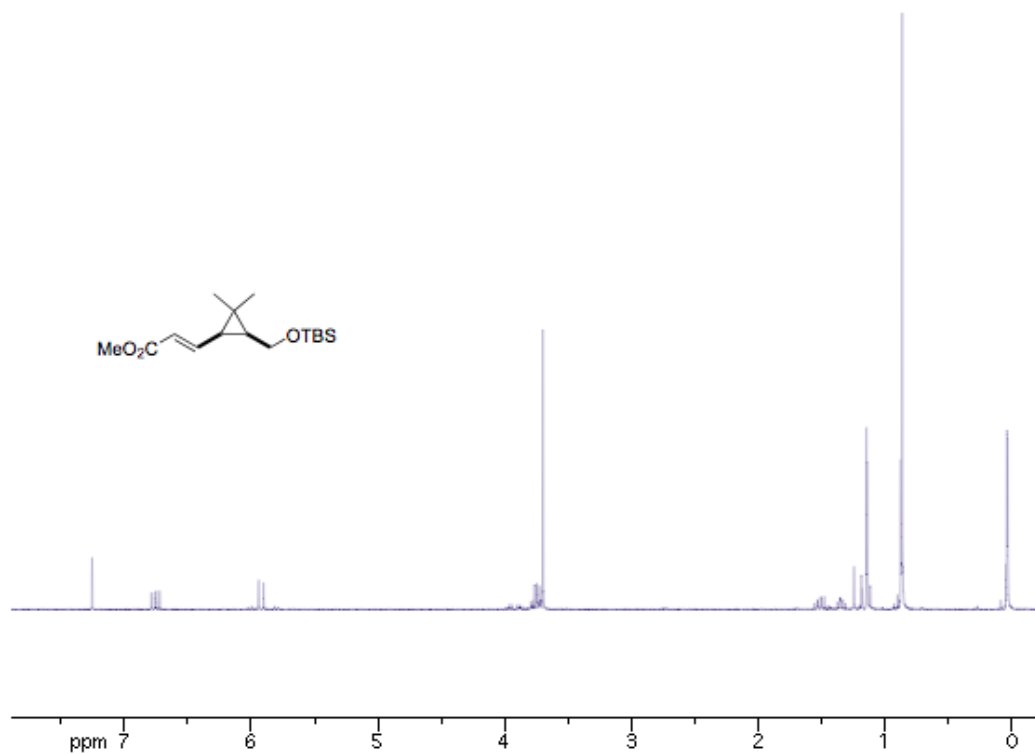


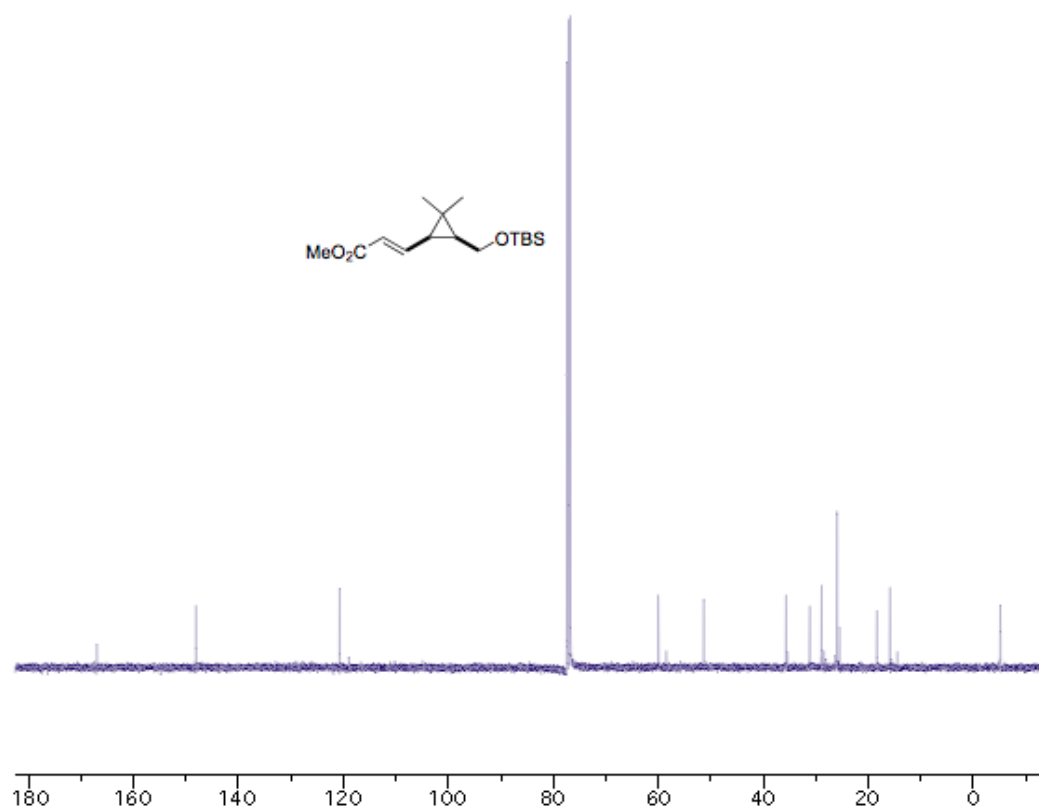
Ethyl (±)-(2Z)-3-[(1S,2S)-2-formylcyclopropyl]prop-2-enoate (SI-8)



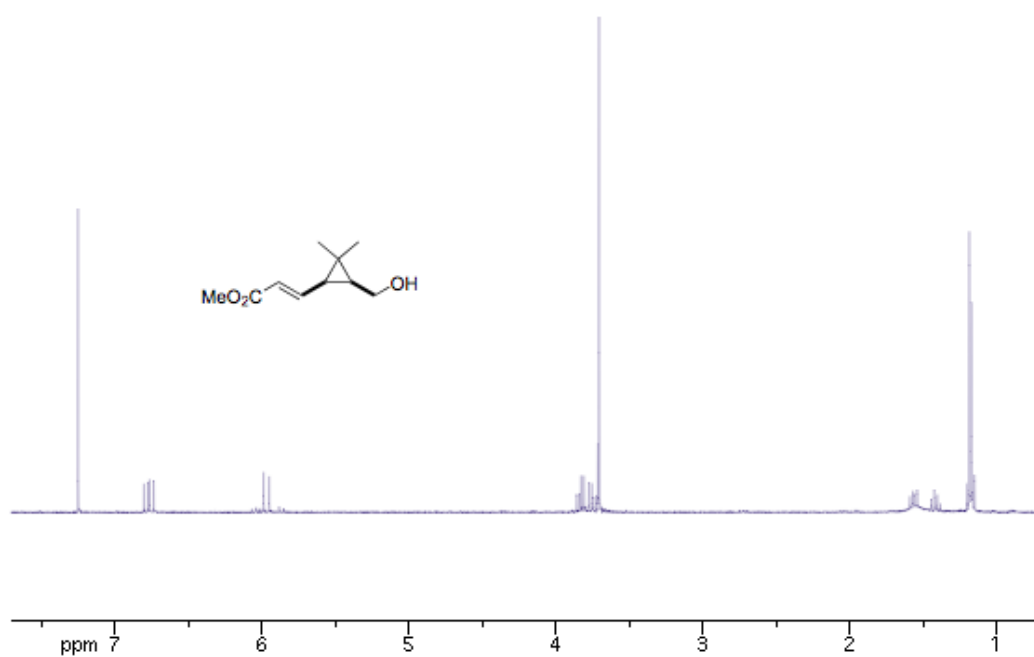


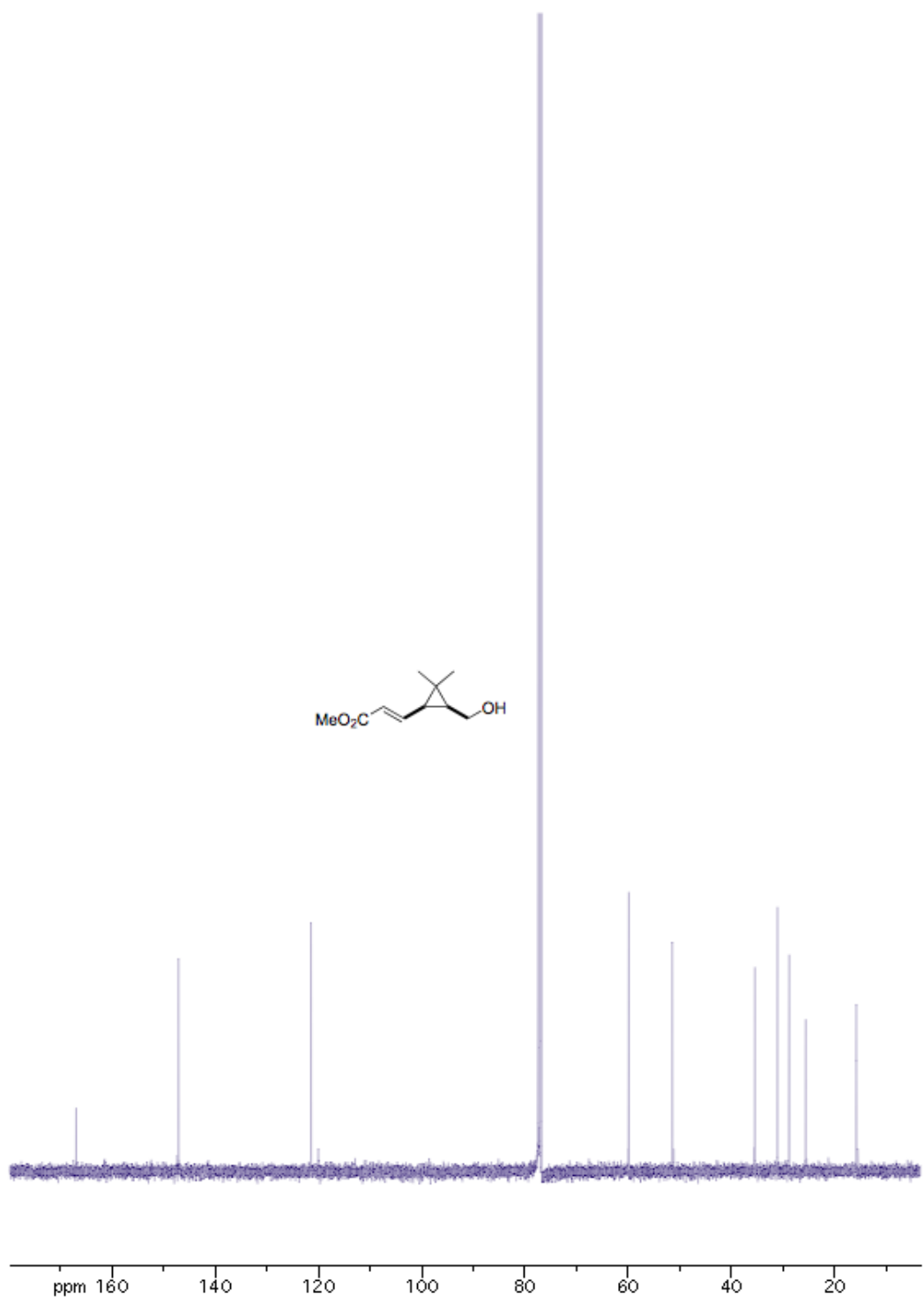
Methyl (±)-(*E*)-3-((1*R*,3*S*)-3-((*tert*-butyldimethylsilyloxy)methyl)-2,2-dimethylcyclopropyl)prop-2-enoate (34)



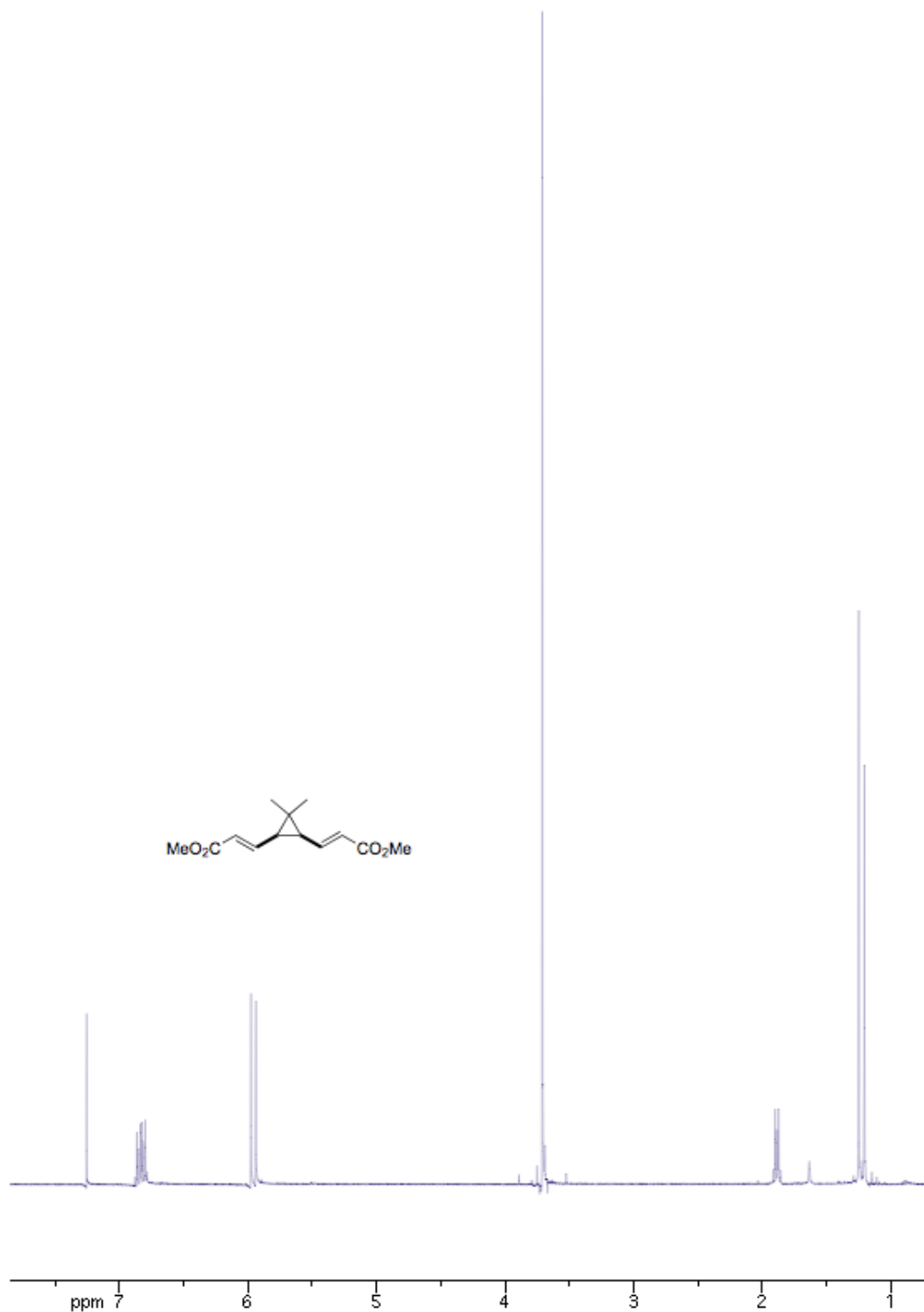


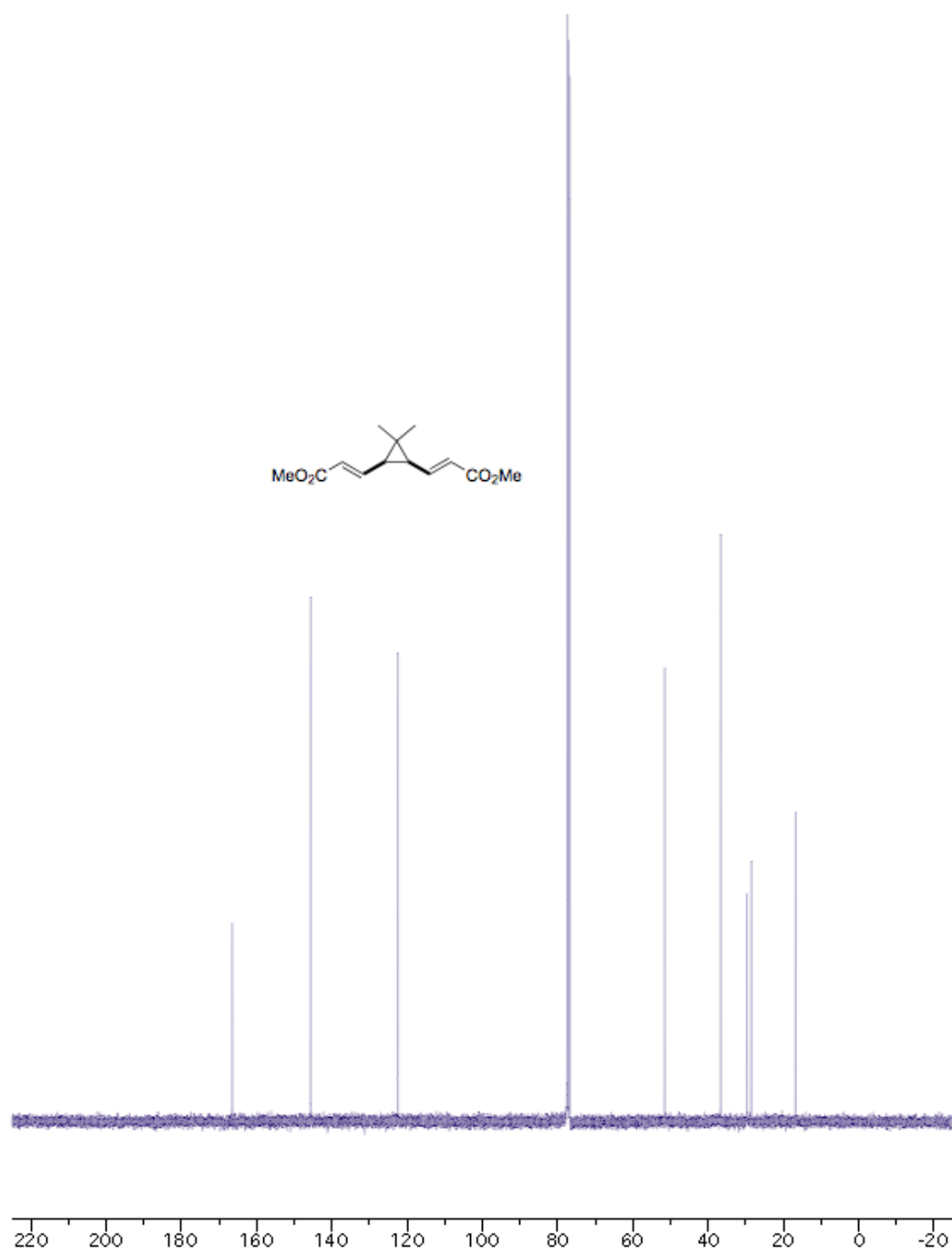
Methyl (±)-(*E*)-3-((1*R*,3*S*)-3-(hydroxymethyl)-2,2-dimethylcyclopropyl)prop-2-enoate (35)



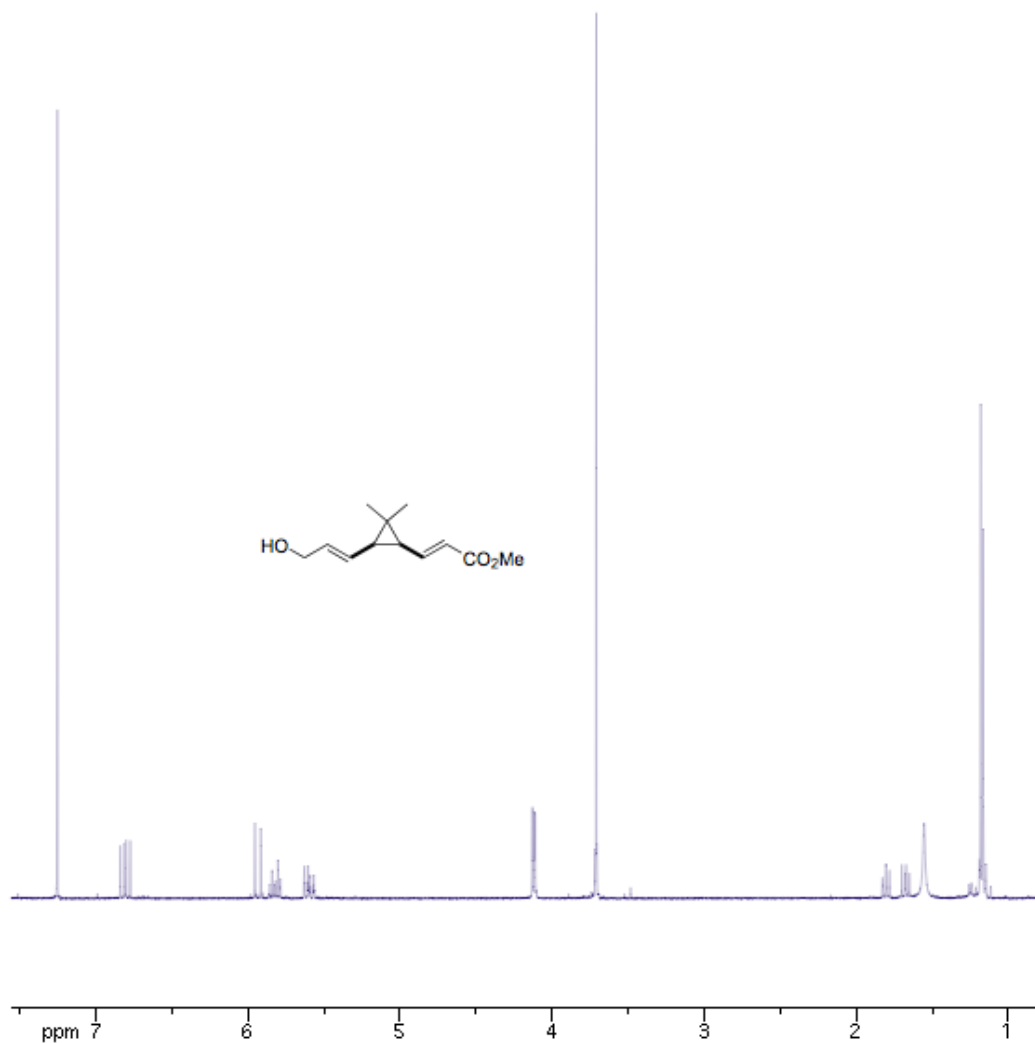


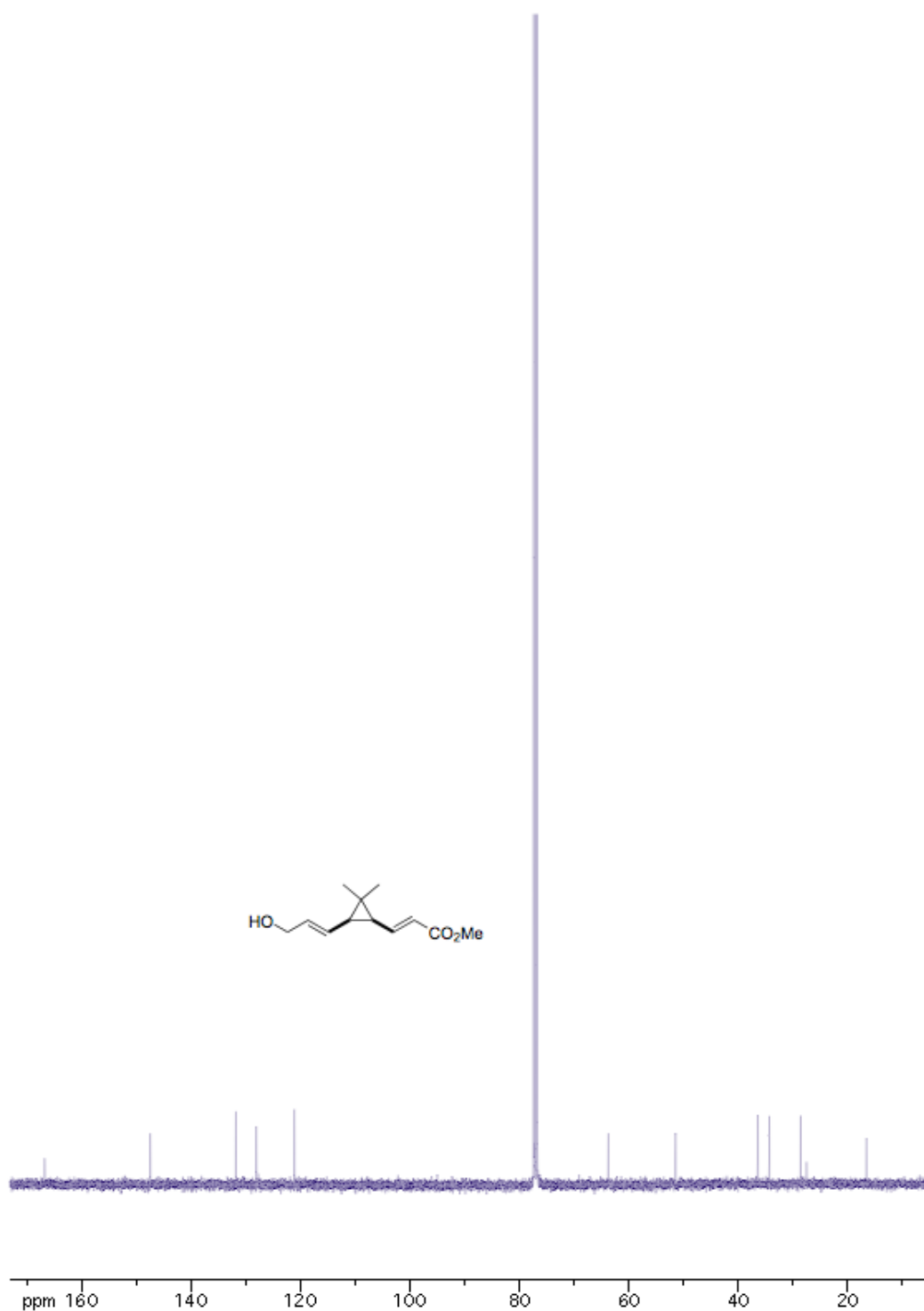
Dimethyl (2*E*,2'*E*)-3,3'-((1*R*,2*S*)-3,3-dimethylcyclopropane-1,2-diyl)diprop-2-enoate (36)



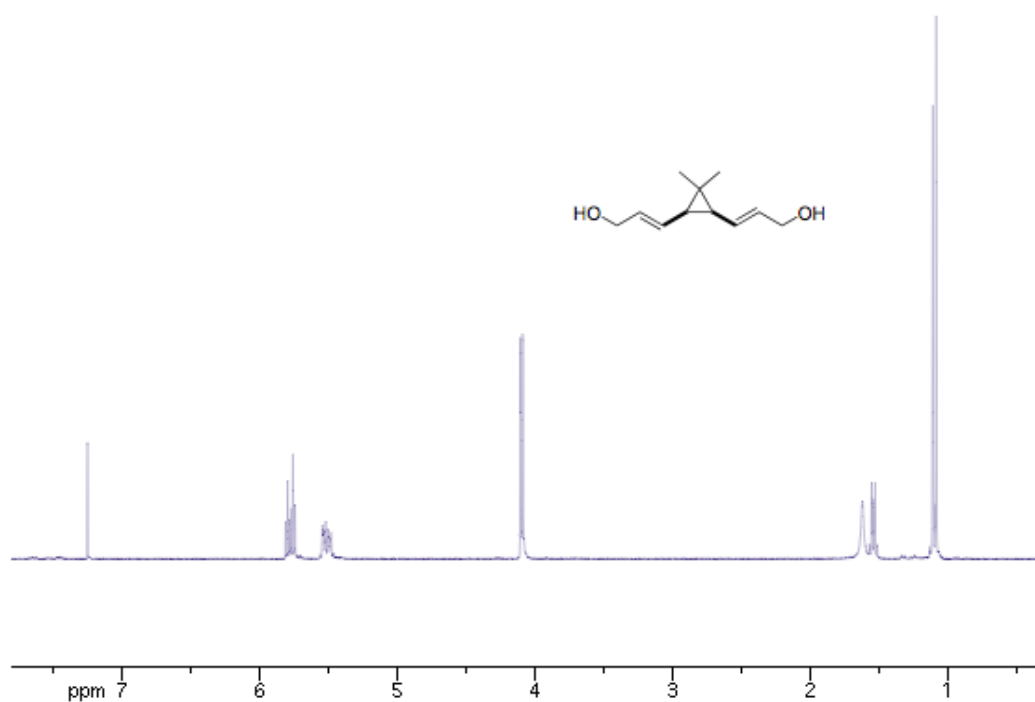


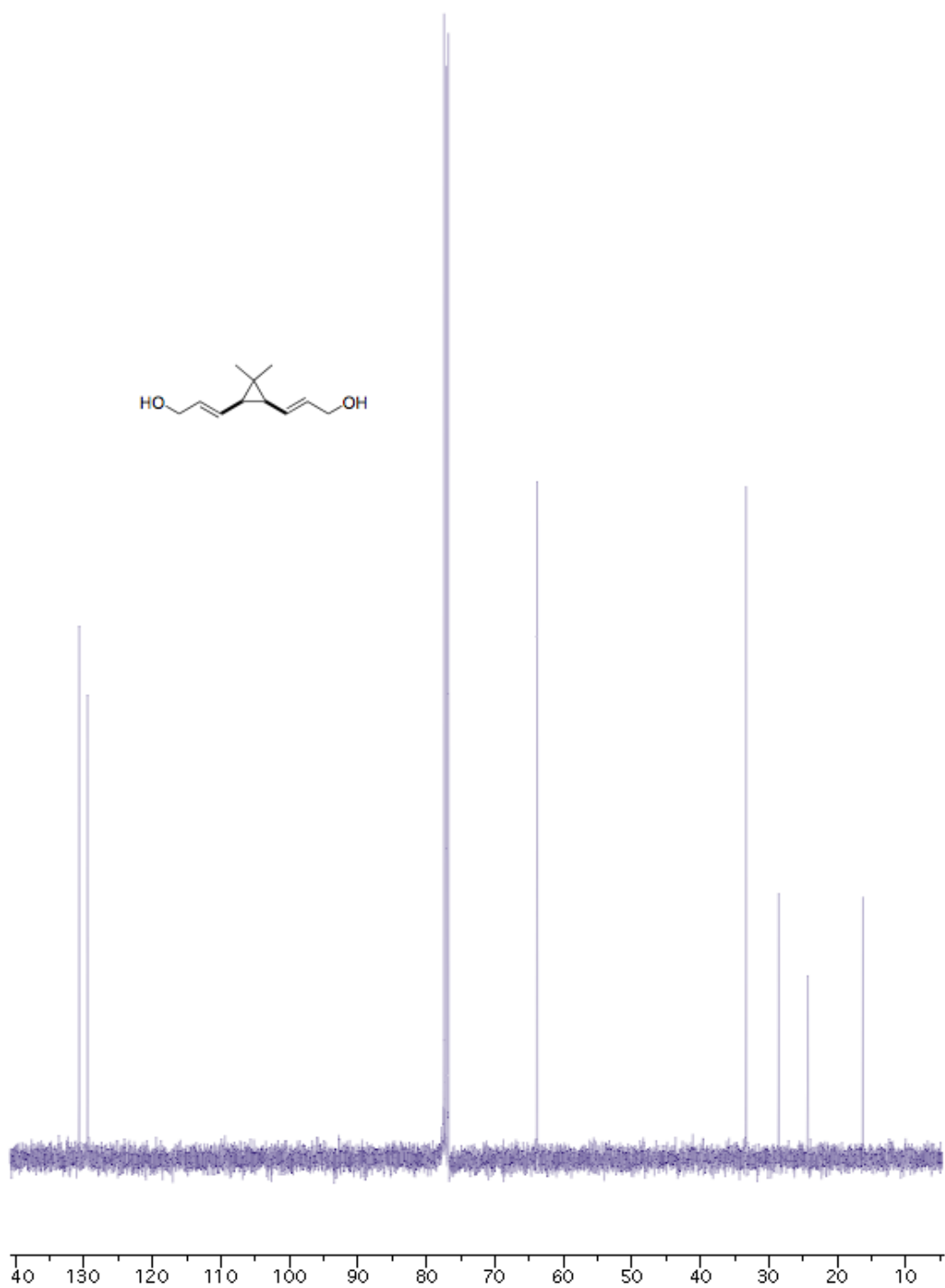
Methyl (±)-(E)-3-((1*R*,3*S*)-3-((*E*)-3-hydroxyprop-1-enyl)-2,2-dimethylcyclopropyl)prop-2-enoate (37)



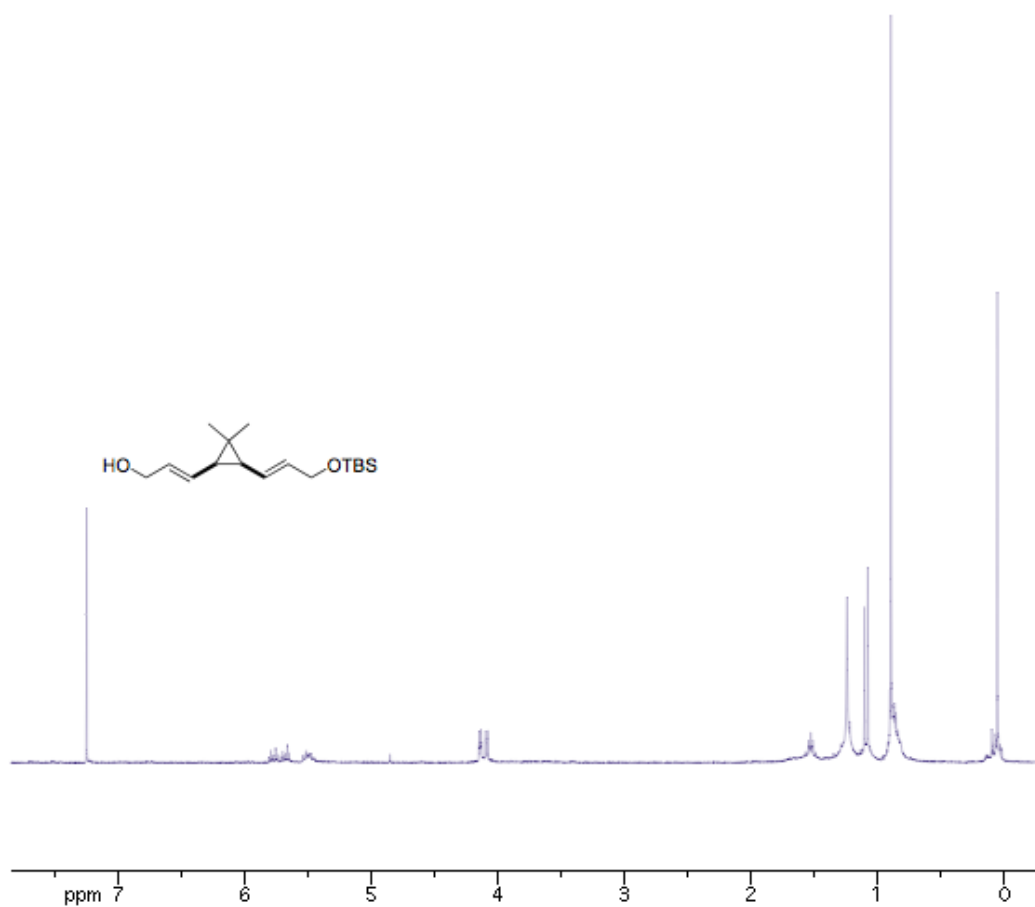


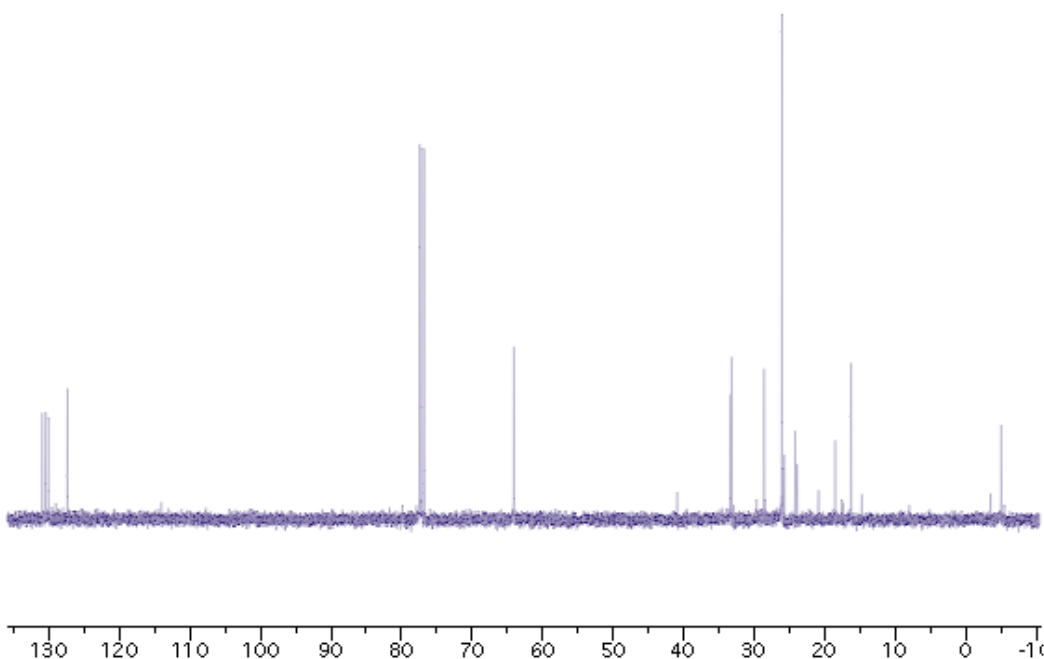
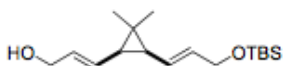
(2*E*,2'*E*)-3,3'-((1*R*,2*S*)-3,3-Dimethylcyclopropane-1,2-diyl)diprop-2-en-1-ol (38)



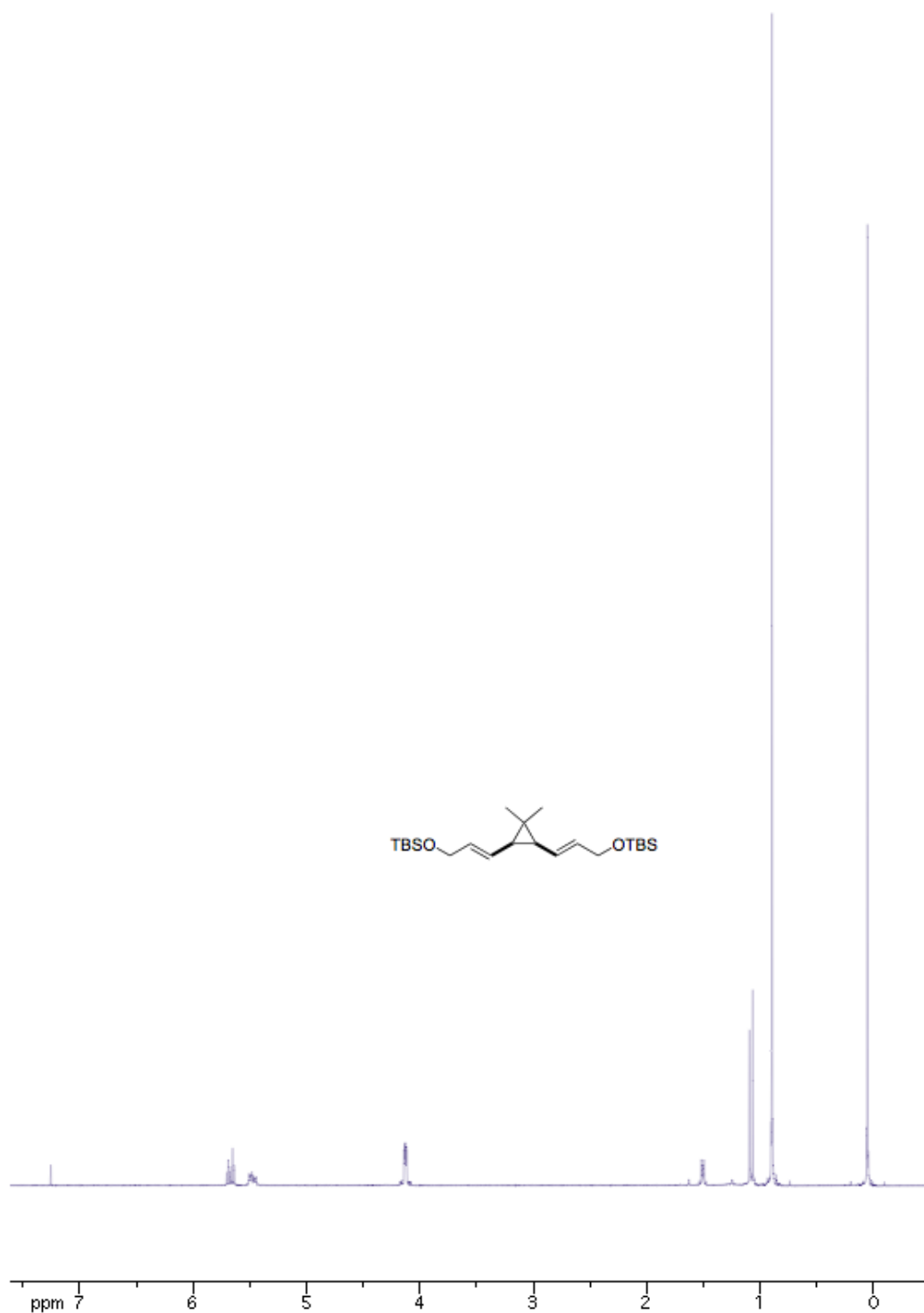


(±)-(E)-3-((1*R*,3*S*)-3-((*E*)-3-(*tert*-butyldimethylsilyloxy)prop-1-enyl)-2,2-dimethylcyclopropyl)prop-2-en-1-ol (39)

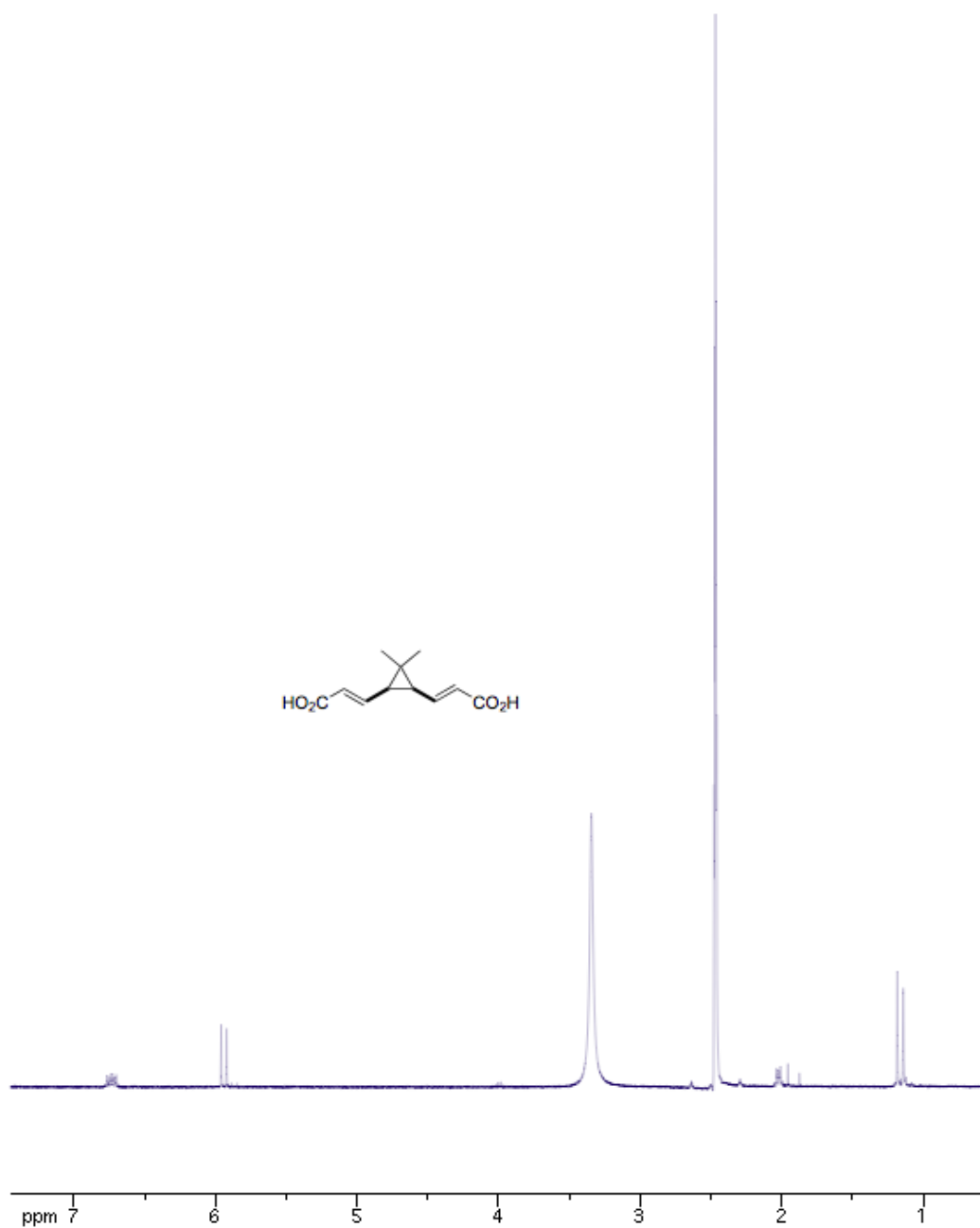


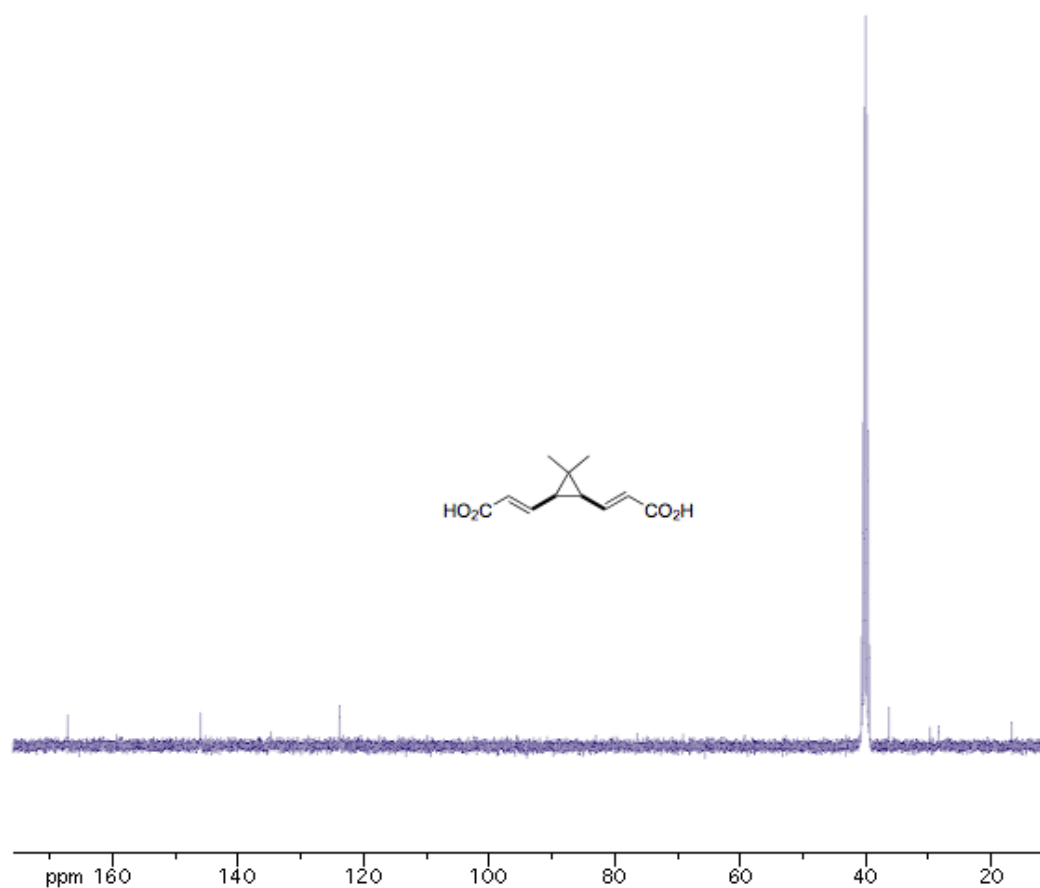


(2*E*,2'*E*)-3,3'-((1*R*,2*S*)-3,3-Dimethylcyclopropane-1,2-diyl)bis(prop-2-ene-3,1-diyl)bis(oxy)bis(*tert*-butyldimethylsilane) (40)



**(2*E*,2'*E*)-3,3'-((1*R*,2*S*)-3,3-dimethylcyclopropane-1,2-diyl)diprop-2-enoic acid
(41)**





References

- 1) L. Blackburn, M. Lautens, G. D. McAllister and R. J. K. Taylor, *Org. Synth*, 2008, **85**, 15–26.
- 2) I. Masato, A. Osaku, A. Shiibashi and T. Ikariya, *Org. Lett.*, 2007, **9**, 1821–1824.
- 3) I. J. Jakovac, H. B. Goodbrand, P. K. Lok and J. B. Jones, *J. Am. Chem. Soc.*, 1982, **104**, 4659–4665.
- 4) J. E. Baldwin and S. J. Cianciosi, *J. Am. Chem. Soc.*, 1992, **114**, 9401–9408.
- 5) P. A. Wender and A. J. Dyckman, *Org. Lett.*, 1999, **1**, 2089–2092.
- 6) C. Hertweck and W. Boland, *J. Org. Chem.*, 2000, **65**, 2458–2463.