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Gallium trichloride-mediated reactions of ‘double’ donor–acceptor cyclopropanes with alkenes and dienes

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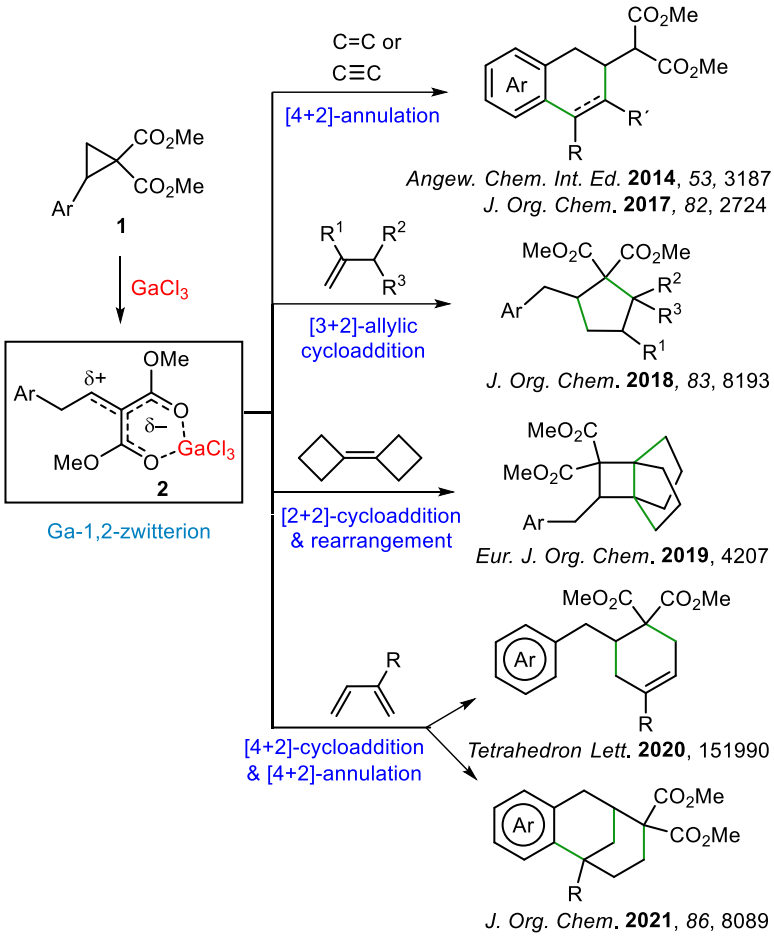
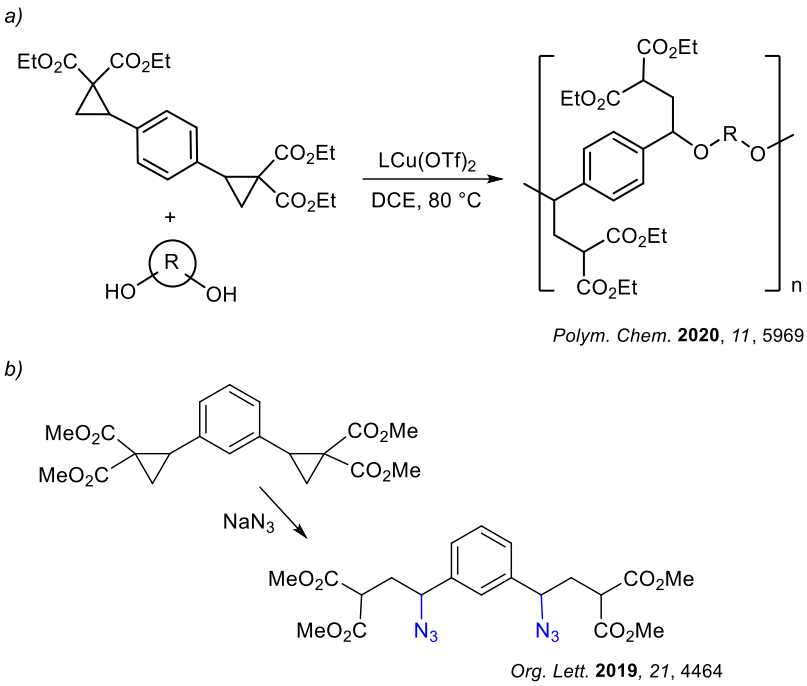
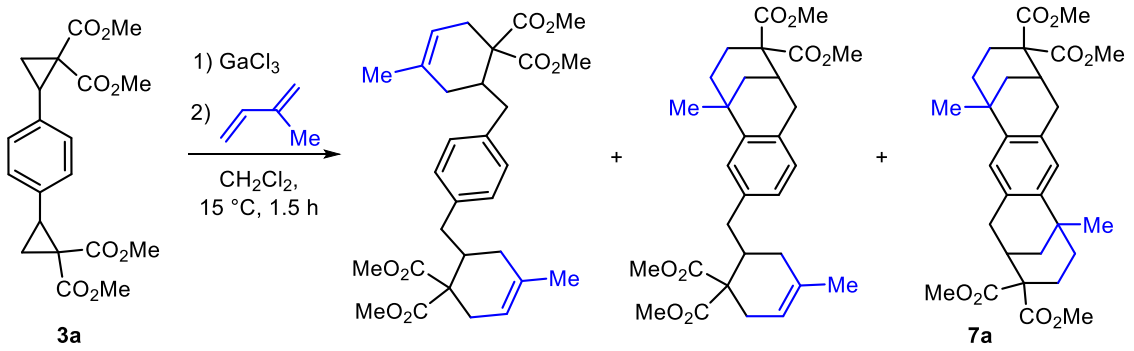


Scheme S1. The reactions of 1,2-zwitterionic gallium complexes **2** with unsaturated substrates that result in the construction of various carbocyclic structures *via* cycloaddition and annulation.



Scheme S2. Known examples of cyclopropane ring opening in tetramethyl 2,2´-(1,3- or 1,4-phenylene)bis(cyclopropane-1,1-dicarboxylates).



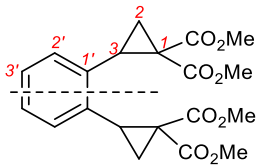
Scheme S3. A mixture of products cycloaddition and annulation in the reaction of 'double' DAC **3a** and $GaCl_3$ with isoprene at 18 °C (from ^1H NMR spectrum).

General Experimental Details. All reagents and solvents were commercial grade chemicals and were used as purchased. All operations with $GaCl_3$ were carried out under dry argon atmosphere. TLC analysis was performed on Silufol chromatographic plates. For preparative chromatography, silica gel 60 (0.040−0.063 mm) was used. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on 400 MHz (400.1 and 100.6 MHz, respectively) and 300 MHz (300.1 and 75.5 MHz, respectively) spectrometers in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. Determinations of the structures and stereochemistry of the obtained compounds and assignments of the ^1H and ^{13}C signals were made with the aid of 2D COSY, NOESY, HSQC, and HMBC spectra. Determinations of the structures were made with the aid of 2D HMBC spectra. High-resolution mass spectra (HRMS TOF) were obtained using simultaneous electospray ionization (ESI).

Synthesis of starting cyclopropanes **3a,b**. Starting cyclopropanes **3a,b** were synthesized from the corresponding aromatic aldehydes through a standard synthetic sequence of Knoevenagel/Corey–Chaykovsky reactions.

Cyclopropane **3c** was synthesized from phthalaldehyde through a synthetic sequence of Wittig reaction/cyclopropanation via dimethyl 2-diazomalonate.

1. General Procedure for synthesis of 1,2-divinylbenzene by the Wittig reaction. To an oven-dried two neck round bottom flask (100 ml) with a magnetic stirring bar was added (methyl)triphenylphosphonium bromide (7.99 g, 22.4 mmol). Under nitrogen atmosphere, dry benzene (60 ml) was added, and the reaction mixture was placed in an ice bath. Potassium *tert*-butoxide (2.93 g, 26.1 mmol) was added. The resulting mixture was allowed to reach room temperature and was stirred for 1.5 h. Then phthalaldehyde (1 g, 7.5 mmol) was added, and the mixture was stirred at room temperature for 12 h. Upon completion, the reaction was filtered through plug with silica gel. The solvent was removed *in vacuo* to afford the title compound in 880 mg yield (90%).

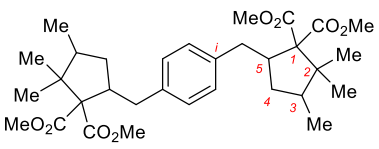


*Tetramethyl 2,2′-benzene-1,2-diyldicyclopropane-1,1-dicarboxylate (**3c**)*

In the air, $Rh_2(esp)_2$ (5 mg, 6.77×10^{-3} mmol, 0.1 mol%) was placed in a 100-ml three-necked flask equipped with a stir bar. The flask was capped and purged with nitrogen (three vacuum/re-filling cycles). Dichloromethane (5 ml) was syringed leading to a pale green homogenous solution. 1,2-Divinylbenzene (0.88 g, 6.76 mmol) was added, and the mixture was then cooled in a water/ice bath. After 5 min, a solution of dimethyl diazomalonate (2.67 g, 16.8 mmol) in CH_2Cl_2 (5 ml) was syringed. The resulting solution was kept in the bath for 10 min and then stirred at room temperature. After 2 h, the mixture was treated with a saturated solution of aqueous thiourea (50 ml) and diluted with CH_2Cl_2 (25 ml). The mixture was stirred for 30 min and then transferred into a separatory funnel. The aqueous layer was extracted with CH_2Cl_2 (3×25 ml). The combined organic layers were washed with brine (100 ml), dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (eluent: petroleum ether – EtOAc, 4:1) to afford the title compound as a colorless thick oil in 590 mg yield (22%). HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{22}O_8Na$ 413.1207; Found, 413.1209.

^{1}H NMR (300.1 MHz, $CDCl_3$) δ 1.78 (dd, 1H, H(2)), ^2J = 9.2 Hz, ^3J = 5.1 Hz), 2.30 (dd, 1H, H(2)), ^2J = 8.2 Hz, ^3J = 5.1 Hz), 3.38 (t, 1H, H(3)), ^2J = ^3J = 9.2 Hz), 3.30 and 3.80 (both s, 2 × 3H, 2 OMe), 7.02–7.07 (m, 1H, C_6H_4, H(2′)), 7.14–7.19 (m, 1H, C_6H_4, H(3′)) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 18.5 (C(2)), 31.2 (C(3)), 36.3 (C(1)), 52.3 and 52.9 (2 OMe), 127.3 (CH(2′)), 127.5 (CH(3′)), 135.5 (CH(1′)),167.1 and 170.1 (2 COO) ppm.

2. Synthetic procedure and spectroscopic data for the reactions of 'double' cyclopropanes 3a,b with unsaturated compounds. Solid $GaCl_3$ (0.85 mmol) in one portion was added at ambient temperature to a solution of cyclopropanes **3a** or **3b** (0.4 mmol) in dry CH_2Cl_2 (4 ml), and the mixture was stirred at the same temperature until for the generation of 1,2-zwitterion **4a,b** (optimal conditions: 25 °C, 30 min). Then a solution of alkene or diene (2.4−8.0 mmol) in dry CH_2Cl_2 (1−2 ml) was added, the mixture was immediately heated to 40 °C and refluxed for 1–1.5 h. An aqueous solution of HCl (10%) was added at room temperature until pH 3 was achieved, and the mixture was twice extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: petroleum ether – EtOAc, 5:1 or dichloromethane – acetone, 40:1) to afford the title compounds.

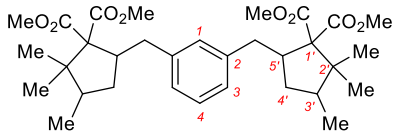


Tetramethyl 5,5′-(1,4-phenylenebis(methylene))bis(2,2,3-trimethylcyclo-pentane-1,1-dicarboxylate) (**5a**)

The title compound was prepared according to the general procedure from DAC **3a** (160 mg, 0.41 mmol), $GaCl_3$ (165 mg, 0.94 mmol), and tetramethylethylene (241 mg, 2.86 mmol) in 120 mg yield (52%) as a mixture of diastereomers in ratio ~2:1. White solid. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{32}H_{46}O_8Na$ 581.3085; Found, 581.3080.

^1H NMR (400.1 MHz, $CDCl_3$) δ 0.71 and 1.16 (both s, 2 × 3H, 2 *trans*-Me at C(2)), 0.79 (d, 3H, *trans*-Me at C(3), ^3J = 7.0 Hz), 0.89 and 1.18 (both s, 2 × 3H, 2 *cis*-Me at C(2)), 1.01 (d, 3H, *cis*-Me at C(3), ^3J = 7.1 Hz), 1.21 – 1.41 (m, 2H, *trans*-H_aC(4), *cis*-H_aC(4)), 1.63 – 1.94 (m, 3H, *trans*-H_bC(4), *cis*-H_bC(4), *cis*-HC(3), *cis*-H_a), 2.01 (t, 1H, *trans*-H_a, ^2J = ^3J = 12.5 Hz), 2.58 – 2.83 (m, 2H, (*trans*-HC(3), *cis*-HC(5)), 2.91 – 3.16 (m, 3H, (*trans*-HC(5), *trans*-H_b, *cis*-H_b), 3.72 and 3.78 (both s, 2 × 3H, 2 *cis*-OMe), 3.73 and 3.80 (both s, 2 × 3H, 2 *trans*-OMe), 7.16 (s, 2H, C_6H_4) ppm.

anti-**5a**: $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ 14.6 (Me at C(3)), 19.7 and 22.3 (2 Me at C(2)), 35.9 (C(4)), 38.4 (CH_2), 40.4 (C(3)), 44.6 (C(5)), 48.3 (C(2)), 51.5 and 51.9 (2 OMe), 72.0 (C(1)), 128.8 (C_6H_4), 139.0 (*i*-C), 170.8 and 171.8 (2 COO).
syn-**5b**: $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ 17.2 (Me at C(3)), 20.4 and 30.9 (2 Me at C(2)), 37.9 (C(4)), 37.9 (CH_2), 42.7 (C(3)), 45.6 (C(5)), 46.6 (C(2)), 51.4 and 51.7 (2 OMe), 71.4 (C(1)), 128.8 (C_6H_4), 138.9 (*i*-C), 170.5 and 171.6 (2 COO).

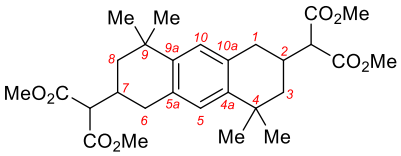


*Tetramethyl 5,5′-(1,3-phenylenebis(methylene))bis(2,2,3-trimethylcyclopentane-1,1-dicarboxylate) (**5b**)*

The title compound was prepared according to the general procedure from DAC **3b** (143 mg, 0.37 mmol), $GaCl_3$ (142 mg, 0.8 mmol), and tetramethylethylene (216 mg, 2.56 mmol) in 104 mg yield (50%) as a mixture of diastereomers in ratio ~1.5:1. White solid. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{32}H_{46}O_8Na$ 581.3085; Found, 581.3088.
^1H NMR (300.1 MHz, $CDCl_3$) δ 0.71, 0.72 and 1.17 (all s, 2 × 3H, 2 *trans*-Me at C(2)), 0.79 (d, 3H, ^3J = 7.0 Hz, *trans*-Me at C(3)), 0.89, 0.90 and 1.18 (all s, 2 × 3H, 2 *cis*-Me at C(2)), 1.01 (d, 3H, *cis*-Me at C(3), ^3J = 7.1 Hz), 1.21 – 1.35 (m, 2H, *trans*-H_aC(4), *cis*-H_aC(4′)), 1.63 – 1.81 (m, 3H, *trans*-H_bC(4), *cis*-H_bC(4), *cis*-HC(3)), 1.88 (t, 1H, *cis*-H_a, ^2J = ^3J = 12.0 Hz), 2.02 (t, 1H, trans-H_a, ^2J = ^3J = 12.0 Hz), 2.61 – 2.83 (m, 2H, (*trans*-HC(3), *cis*-HC(5)), 2.90 – 3.19 (m, 3H, (*trans*-HC(5), *trans*-H_b, *cis*-H_b), 3.73 and 3.78 (both s, 2 × 3H, 2 *cis*-OMe), 3.74 and 3.80 (both s, 2 × 3H, 2 *trans*-OMe), 6.99 – 7.12 (m, 3H, HC(3), HC(1)), 7.15 – 7.23 (m, 1H, HC(4)).

anti-**5b**: $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 14.7 (Me at C(3)), 19.8 and 22.4 (2 Me at C(2)), 35.9, 36.0 (both C(4)), 38.8, 38.9 (both CH_2), 40.5 (C(3)), 44.8 (C(5)), 48.4 (C(2)), 51.7 and 52.0 (2 OMe), 72.2 (C(1)), 126.6 (C(3)), 128.3 (C(4)), 129.8 (C(1)), 141.4 (C(2)), 170.9 and 172.0 (2 COO).
syn-**5b**: $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 17.3 (Me at C(3)), 20.5 and 31.1 (2 Me at C(2)), 38.1 (C(4)), 38.4 (CH_2), 42.9 (C(3)), 45.7, 45.8 (both C(5)), 46.8 (C(2)), 51.5 and 51.9 (2 OMe), 71.5 (C(1)), 126.6

(C(3)), 128.4 (C(4)), 129.6 (C(1)), 141.4 (C(2)), 170.6 and 171.7 (2 COO).

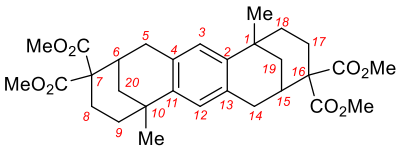


*Tetramethyl 2,2′-(4,4,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydroanthracene-2,6-diyl)dimalonate (**6**)*

The title compound was prepared according to the general procedure but at 0 °C (30 min) from DAC **3a** (184 mg, 0.47 mmol), $GaCl_3$ (182 mg, 1.03 mmol), and isobutylene (~560 mg, 10 mmol) in 82.3 mg yield (35%). Colorless thick oil. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{28}H_{38}O_8Na$ 525.2459; Found, 525.2454.

^1H NMR (300.1 MHz, $CDCl_3$) δ 1.26 and 1.32 (both s, 2 × 6H, 4 Me at C(4) and C(9)), 1.42 – 1.52 (m, 4H) and 1.61 – 1.72 (both m, 2 × 2H, $H_2C(3)$, $H_2C(8)$), 2.57 (dd, J = 14.3, 11.6 Hz, 2H, $H_aC(1)$) 2.58 – 2.86 (m, 4H, $H_bC(1)$, HC(2)), 3.34 (d, *J* = 8.3 Hz, 2H, HC), 3.79 and 3.81 (both s, 2 × 6H, 4 OMe), 6.96 (s, 2H, HC(5), HC(10)).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 31.6 and 31.9 (4 Me), 32.4 (C(2), C(7)), 34.7 (C(1), C(6)), 34.8 (C(4), C(9)), 43.8 (C(3), C(8)), 52.5 and 52.6 (both s, 4 OMe), 57.7 (CH), 126.8 (C(5), C(10), 132.3 (C(5a), C(10a)), 142.3 (C(4a), C(9a)), 169.0 and 169.1 (4 COO).

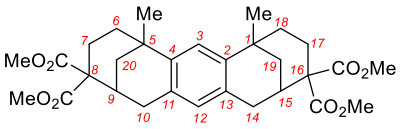


*Tetramethyl 1,8-dimethyl-1,2,3,5,6,8,9,10,12,13-decahydro-1,5:8,12-dimethanobenzo[1,2:4,5]di[8]annulene-4,4,11,11-tetracarboxylate (**7a**)*

The title compound was prepared according to the general procedure from DAC **3a** (65.4 mg, 0.167 mmol), $GaCl_3$ (73,9 mg, 0.42 mmol), and isoprene (45.5 mg, 0.67 mmol) in 60 mg yield (68%) as a mixture of diastereomers in ratio 1:1. White solid. HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{30}H_{38}O_8NH_4$ 527.2905; Found, 572.2901.

^1H NMR (300.1 MHz, $CDCl_3$) δ 1.28 and 1.29 (both s, 2 × 3H, 2 Me at C(1) and C(10)), 1.34 – 1.51 (m, 4H, $H_2C(9)$, $H_2C(18)$), 1.55 – 1.71 and 2.01 – 2.13 (both m, 2 × 2H, $H_2C(8)$, $H_2C(17)$), 1.71 – 1.91 (m, 4H, $H_2C(19)$, $H_2C(20)$), 2.48 and 3.01 – 3.17 (d, *J* = 17.7 Hz, and m, 2 × 2H, $H_2C(5)$, $H_2C(14)$), 2.92 – 3.00 (m, 2H, HC(6), HC(15)), 3.73, 3.74, 3.75, 3.76 (all s, 4 × 3H, 4 OMe), 6.83 and 6.88 (both s, 2 × 1H, HC(3), HC(12)).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 25.0 (C(8), C(17)), 28.2 (2 Me at C(1) and C(10)), 32.5, 32.6 (C(14), C(5)), 32.7, 32.8, 32.8, 32.9 (C(6), C(10), C(9), C(1)), 37.6 (C(19), C(20)), 38.7, 38.9, (C(9), C(18)), 52.7 (4 OMe), 59.5 (C(7), C(16)), 124.0, 124.2 (C(3), C(12)), 133.6, 133.7 (C(4), C(13)), 140.9, 141.1 (C(2), C(11)), 171.5 and 171.9 (4 COO).

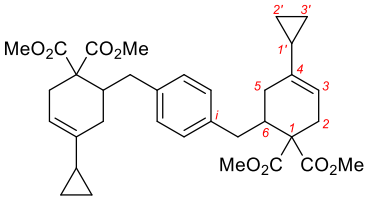


*Tetramethyl 1,13-dimethyl-2,3,6,8,9,11,12,13-octahydro-1,5:9,13-dimethanobenzo[1,2:4,5]di[8]annulene-4,4,10,10(1H,5H)-tetracarboxylate (**7b**)*

The title compound was prepared according to the general procedure from DAC **3b** (78 mg, 0.2 mmol), $GaCl_3$ (81 mg, 0.46 mmol), and isoprene (82 mg, 1.2 mmol) in 50 mg yield (48%) as a mixture of diastereomers in ratio 1:1. White solid. HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{30}H_{38}O_8NH_4$ 527.2905; Found, 572.2896.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 1.31 (s, 6H, 2 Me at C(1) and C(5)), 1.35 – 1.45 (m, 4H, $H_2C(6)$, $H_2C(18)$), 1.50 – 1.69 and 2.06 – 2.18 (both m, 2 × 2H, $H_2C(7)$, $H_2C(17)$), 1.73 – 1.95 (m, 4H, $H_2C(19)$, $H_2C(20)$), 2.48 (d, J = 17.1 Hz, 2H, $H_aC(10)$, $H_aC(14)$), 2.95 – 3.12 (m, 4H, HC(5), HC(9), $H_bC(10)$, $H_bC(14)$) , 3.75 and 3.76 (both s, 2 × 6H, 2 OMe), 6.70 (s, 1H, HC(3)), 7.09 (s, 1H, HC(12)).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 24.9 (C(7), C(17)), 28.3 (2 Me at C(1) and C(10)), 32.3 (C(10), C(14)), 32.8 (C(9), C(15)), 33.0 (C(1), C(5)), 37.7 (C(19), C(20)), 38.8 (C(6), C(18)), 52.8 (4 OMe), 59.5 (C(8), C(16)), 120.8 (C(3)), 127.4 (C(12)), 133.7 (C(3), C(11)), 141.3 (C(2), C(4)), 171.5 and 171.9 (4 COO).

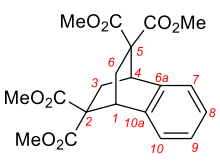


*Tetramethyl 6,6′-(1,4-phenylenebis(methylene))bis(4-cyclopropyl-cyclohex-3-ene-1,1-dicarboxylate) (**8**)*

The title compound was prepared according to the general procedure from DAC **3a** (142 mg, 0.365 mmol), $GaCl_3$ (141 mg, 0.8 mmol) and 2-cyclopropylbuta-1,3-diene (207 mg, 2.2 mmol) in 70 mg yield (35%). Pale yellow thick oil. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{34}H_{42}O_8Na$ 601.2772; Found, 601.2768.

^{1}H NMR (300.1 MHz, $CDCl_3$) δ 0.18 – 0.37 and 0.42 – 0.65 (m, 2 × 2H, $H_2C(2')$, $H_2C(3')$), 1.17 – 1.34 (m, 1H, HC(1')), 1.62 – 1.78 and 1.90 – 2.04 (both m, 2 × 1H, $H_2C(5)$), 2.44 (dd, *J* = 13.5, 11.3 Hz, 1H, H_aC), 2.59 – 2.79 (m, 2H, H_bC, HC(6)), 3.71 and 3.75 (both s, 2 × 3H), 5.27 – 5.56 (m, 1H, HC(3)), 7.10 (s, 2H, C_6H_4).

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 4.6 and 4.7 (C(2′), C(3')), 17.1 (C(1′)), 28.1 (C(2)), 29.3 (C(5)), 36.6 (H_2C), 39.7 (C(6)), 52.6 and 52.8 (4 OMe), 57.6 (C1)), 115.8 (C(3)), 129.3 (C_6H_4), 137.0 (C(4)), 138.4 (*i*-C), 171.3 and 171.9 (4 COO).

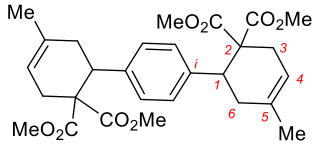


*Tetramethyl 3,4-dihydro-1,4-ethanonaphthalene-2,2,9,9(1H)-tetracarboxylate (**9**).* The title compound was prepared by adding of gallium trichloride to DAC **3c** in dichloromethane at

room temperature. The mixture was stirred for 15 min. After that, an aqueous solution of HCl (10%) was added at room temperature until pH 3 was achieved, and a reaction mixture was twice extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. Then a residue was purified by column chromatography on silica gel (eluent: petroleum ether – EtOAc). HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{22}O_8Na$ 413.1207; Found, 413.1207.

^1H NMR (300.1 MHz, $CDCl_3$) δ 2.35 and 2.67 (dd, J = 14.8, 3.6 Hz, and dd, J = 14.8, 2.2 Hz, 2 × 2H, $H_2C(3)$, H2C(6)), 3.51 and 3.80 (both s, 2 × 3H, 2 OMe), 3.84 (dd, J = 3.5, 2.1 Hz, 2H, HC(1), HC(4)), 7.12 – 7.24 (m, 4H, HC(7), HC(8), HC(9), HC(10),).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 29.7 (C(3), C(6)), 40.0 (C(1), C(4)), 52.8 and 53.0 (4 OMe), 56.9 (C(1), C(4)), 125.2 (C(8), C(9)), 127.2 (C(7), C(10)), 138.8 (C(6a), C(10a)), 170.6 and 171.2 (4 COO).



*Tetramethyl 5,5´´-dimethyl-3,3´´,6,6''-tetrahydro-[1,1':4',1´´-terphenyl]-2,2,2´´,2´´ (1H,1´´H)-tetracarboxylate (**11**)*

The title compound was prepared according to the general procedure but at 10-15 °C from 1,4-phenylenebis(methanylylidene)dimalonate **10** (200 mg, 0.55 mmol), $AlCl_3$ (81.1 mg, 0.61 mmol), and isoprene (150.5 mg, 2.21 mmol) in 163 mg yield (60%). White solid. HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{28}H_{34}O_8NH_4$ 521.2146; Found, 521.2153.

^1H NMR (300.1 MHz, $CDCl_3$) δ 1.71 (s, 3H, Me), 2.12 – 2.27 and 2.83 (m and dd, J = 18.4, 7.4 Hz, 2 × 1H, H2C(5)), 2.39 – 2.70 (m, 2H, H2C(2)), 3.54 and 3.67 (both s, 2 × 3H, 2 OMe), 3.68 – 3.83 (m, 1H, HC(6)), 5.37 – 5.50 (m, 1H), 7.03 (s, 2H, C_6H_4).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 23.4 (Me), 27.1 (C(2)), 34.6 (C(5)), 42.5 (C(6)), 52.2 and 52.7 (2 OMe), 57.4 (C(1)), 118.1 (C(3)), 128.3 (C^{Ar}), 134.5 (C(4)), 141.1 (*i*-C), 170.8 and 171.6 (2 COO).

Table S1. Crystallographic data for **7a** (dk340) and **3c** (nr69_100).

Identification code	**7a** (dk340) (CCDC 2172101)	**3c** (nr69_100) (CCDC 2172102)
Empirical formula	$C_{15}H_{19}O_4$	$C_{20}H_{22}O_8$
Formula weight	263.30	390.37
Temperature/K	100	100
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	Pn
a/Å	11.0167(9)	8.6811(2)
b/Å	5.8484(5)	8.2465(2)
c/Å	20.3245(16)	13.7461(4)
α/°	90	90
β/°	92.414(5)	93.8170(10)
γ/°	90	90
Volume/Å^3	1308.35(19)	981.88(4)
Z	4	2
ρ_{calc} /g cm^{-3}	1.337	1.320
μ/mm^{-1}	0.096	0.103
Crystal size/mm^3	0.13 × 0.12 × 0.1	0.22 × 0.13 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.012 to 52.182	4.94 to 61.074
Index ranges	-12 ≤ h ≤ 13, -7 ≤ k ≤ 7, -25 ≤ l ≤ 25	-12 ≤ h ≤ 12, -11 ≤ k ≤ 11, -19 ≤ l ≤ 13
Reflections collected	12520	13793
Independent reflections	2590 [R_{int} = 0.0744, R_{sigma} = 0.0687]	4956 [R_{int} = 0.0299, R_{sigma} = 0.0351]
Data/restraints/parameters	2590/0/175	4956/2/258
Goodness-of-fit on F^2	1.073	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0653, wR_2 = 0.1611	R_1 = 0.0365, wR_2 = 0.0923
Final R indexes [all data]	R_1 = 0.1030, wR_2 = 0.1831	R_1 = 0.0382, wR_2 = 0.0934
Largest diff. peak/hole / e Å^{-3}	0.55/-0.33	0.29/-0.22
Flack parameter	-	0.3(8)

X-ray diffraction data for **7a** (dk340) (CCDC 2172101) and **3c** (nr69_100) (CCDC 2172102) were collected on an in-lab Bruker QUEST diffractometer (graphite monochromator, φ and ω scan mode). The structures were solved by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogens atoms of methyl, methylene and aromatic fragments were calculated according to those idealized geometry and refined with constraints applied to C-H and N-H bond lengths and equivalent displacement parameters ($U_{eq}(H) = 1.2U_{eq}(X)$, X - cental atom of XH_2 group; $U_{eq}(H) = 1.5U_{eq}(Y)$, Y - central atom of YH_3 group. All structures were solved with the ShelXT[1] program and refined with the ShelXL[2] program. Molecular graphics was drawn using OLEX2[3] program.

CCDC 2172101 and 2172102 contains the supplementary crystallographic data for studied structures. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

References:

1. G. M. Sheldrick, Acta Crystallogr., 2015, **A71**, 3.
2. G. M. Sheldrick, Acta Crystallogr., 2015, **C71**, 3.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, **42**, 339.

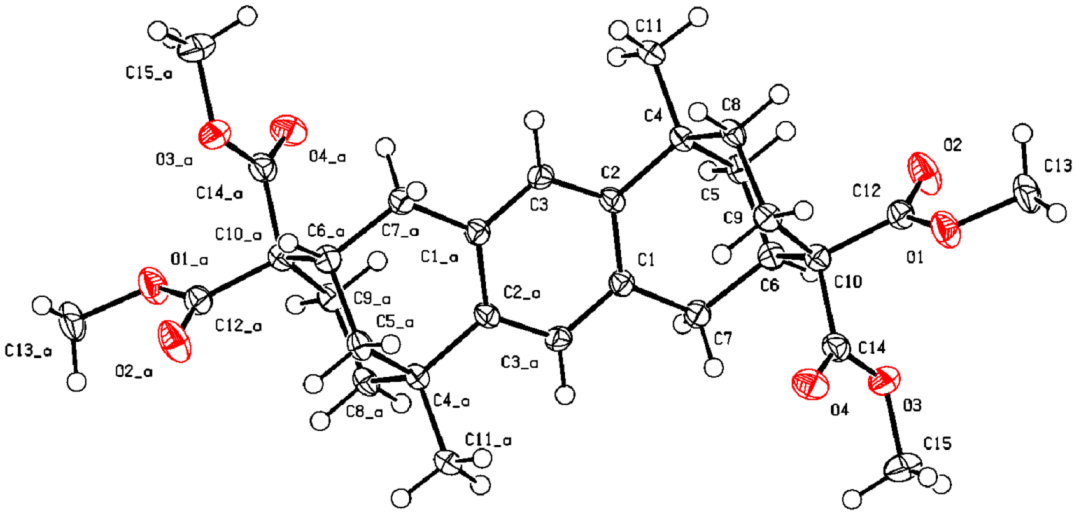


Figure S1. Crystallographic data for **7a** (dk340).

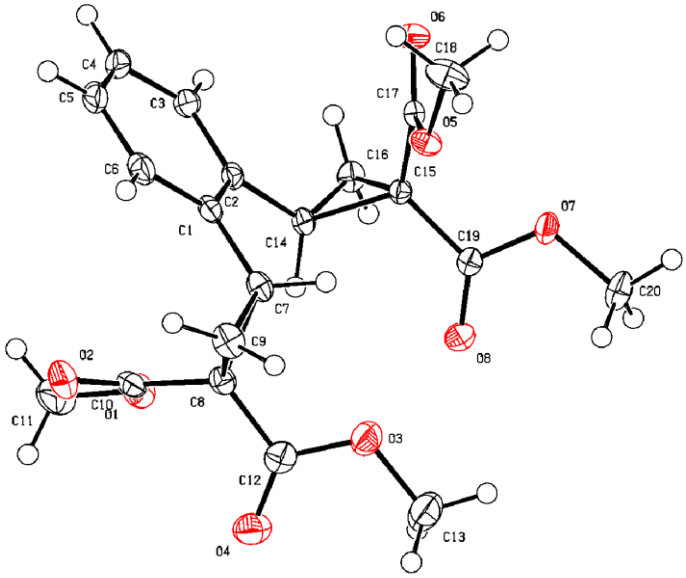
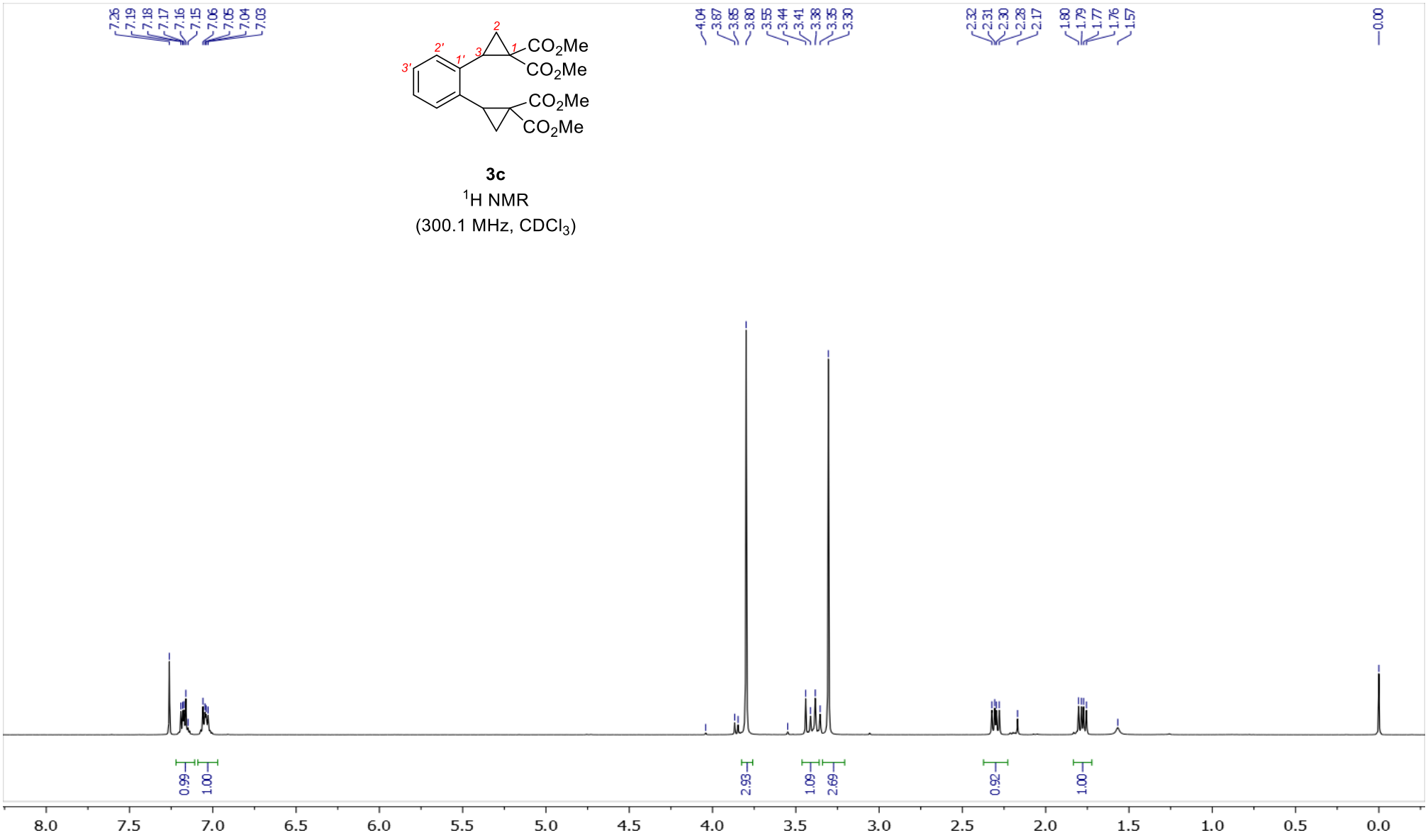


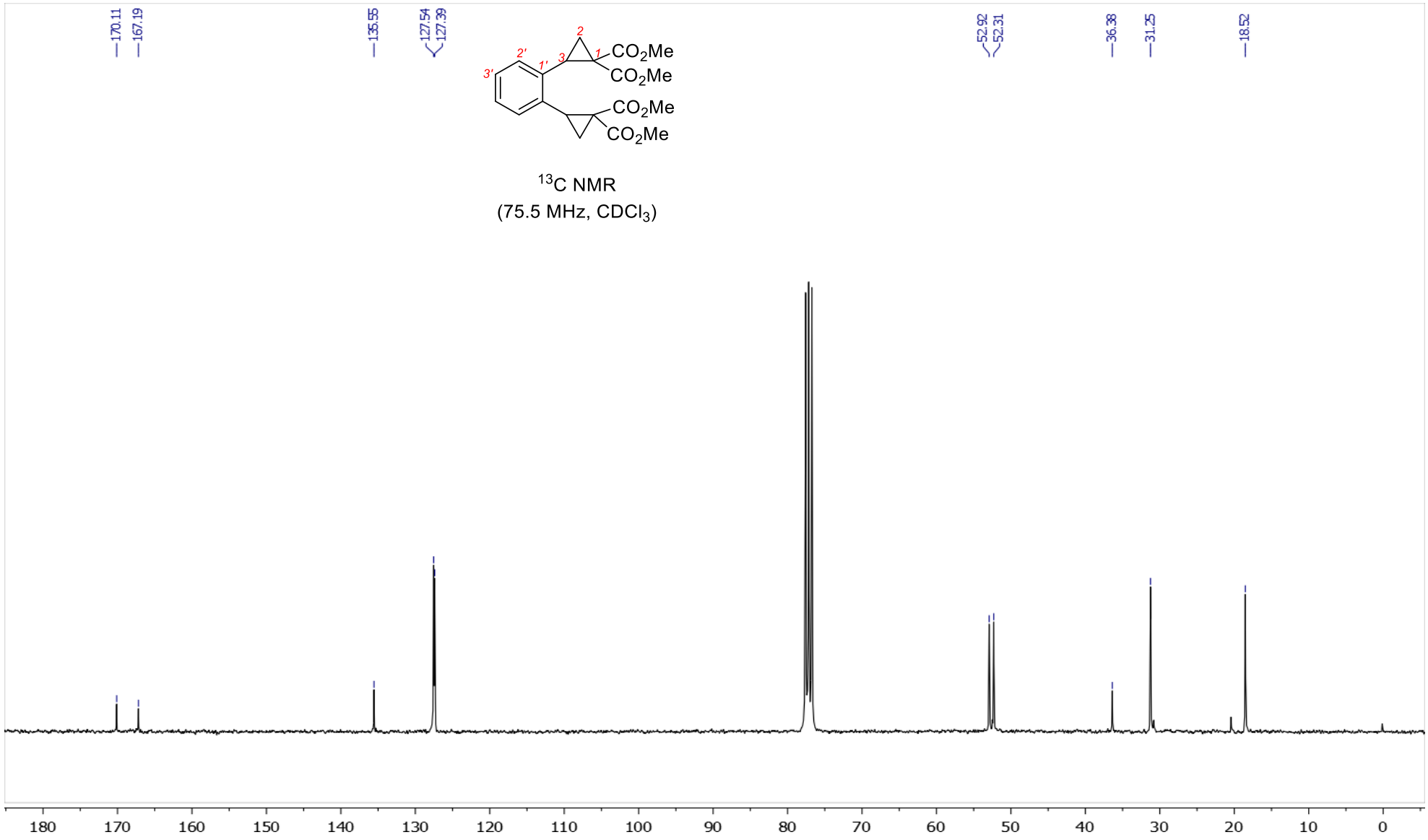
Figure S2. Crystallographic data for **3c** (nr69_100).



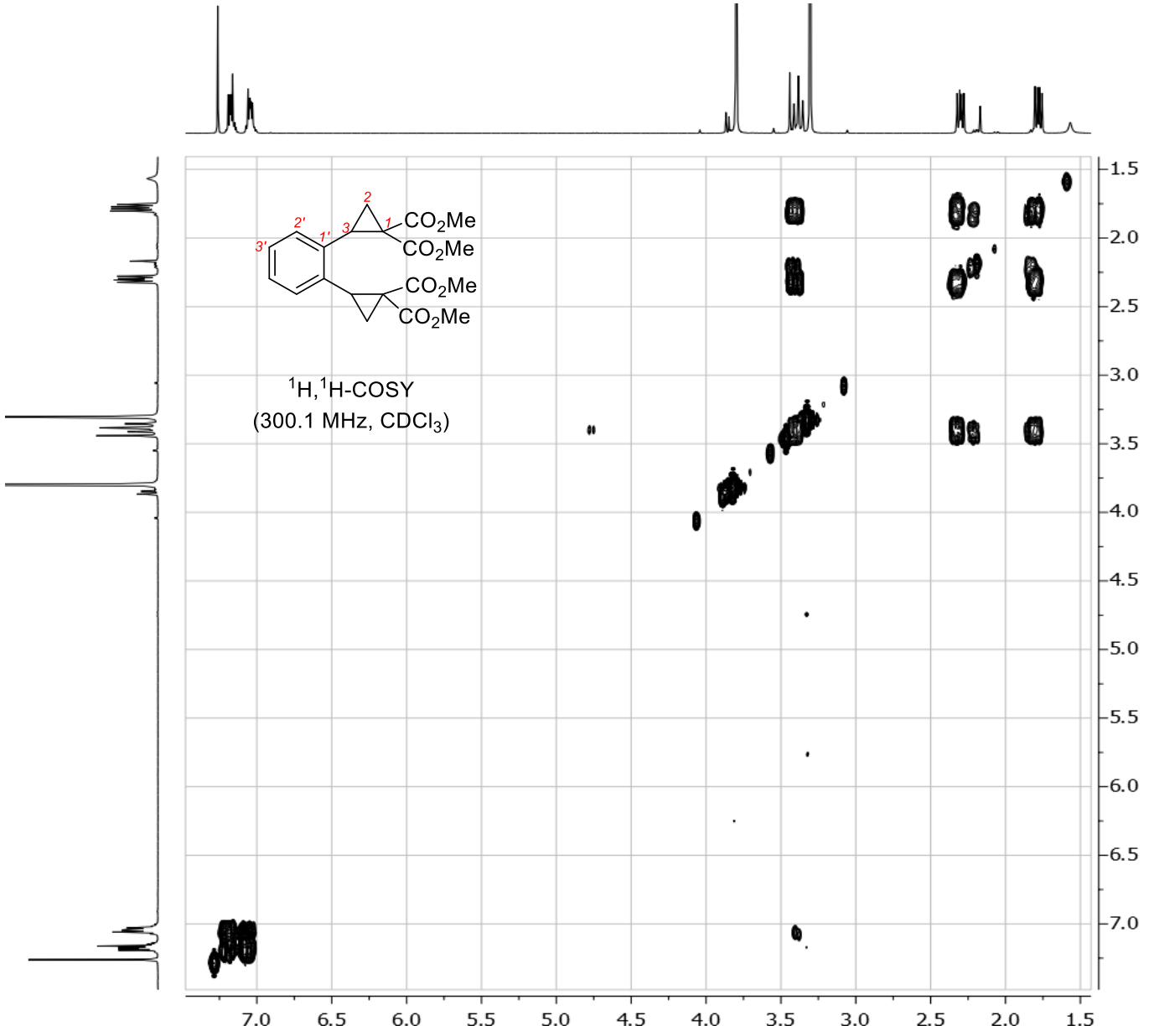
3c

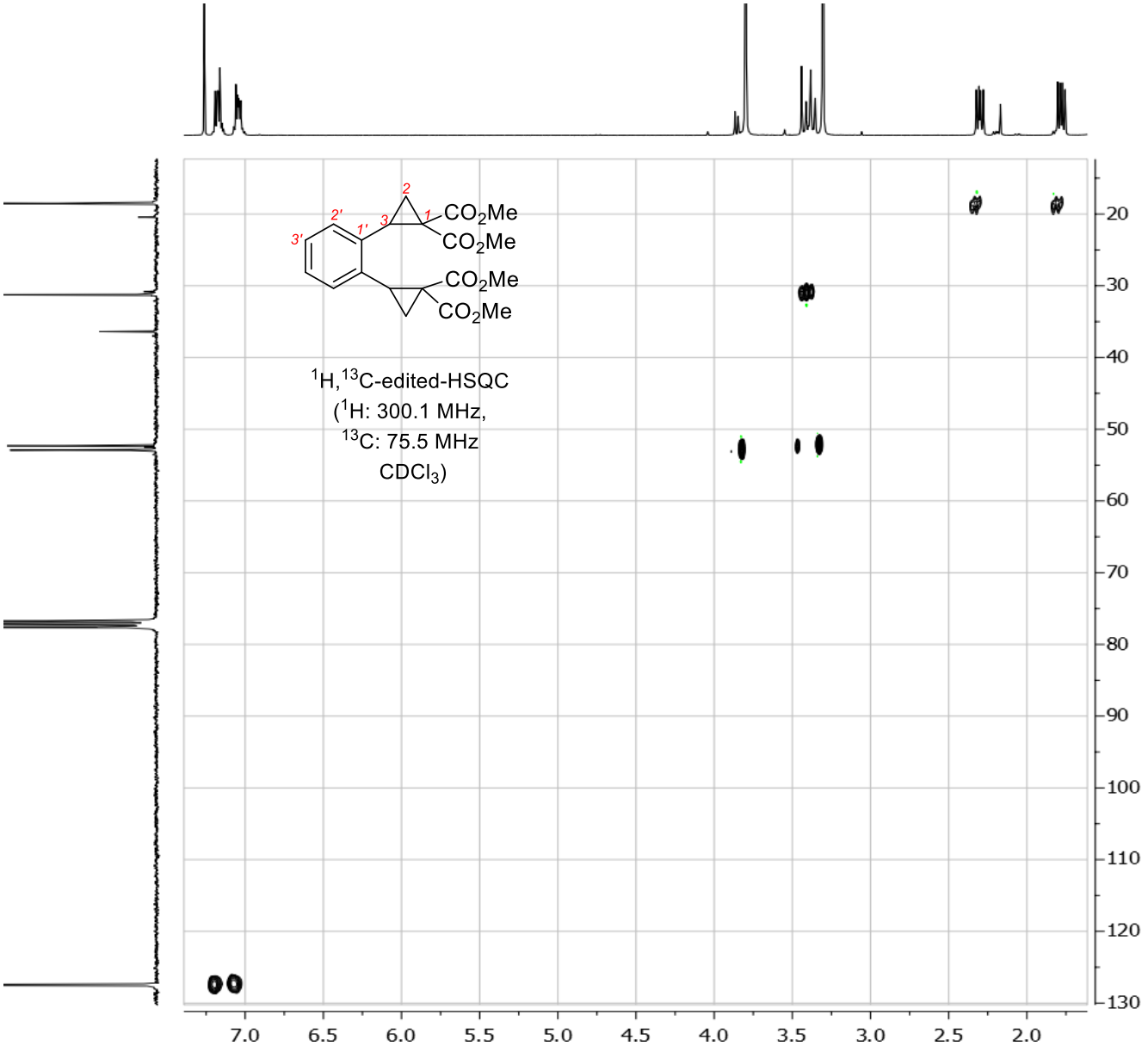
^{1}H NMR

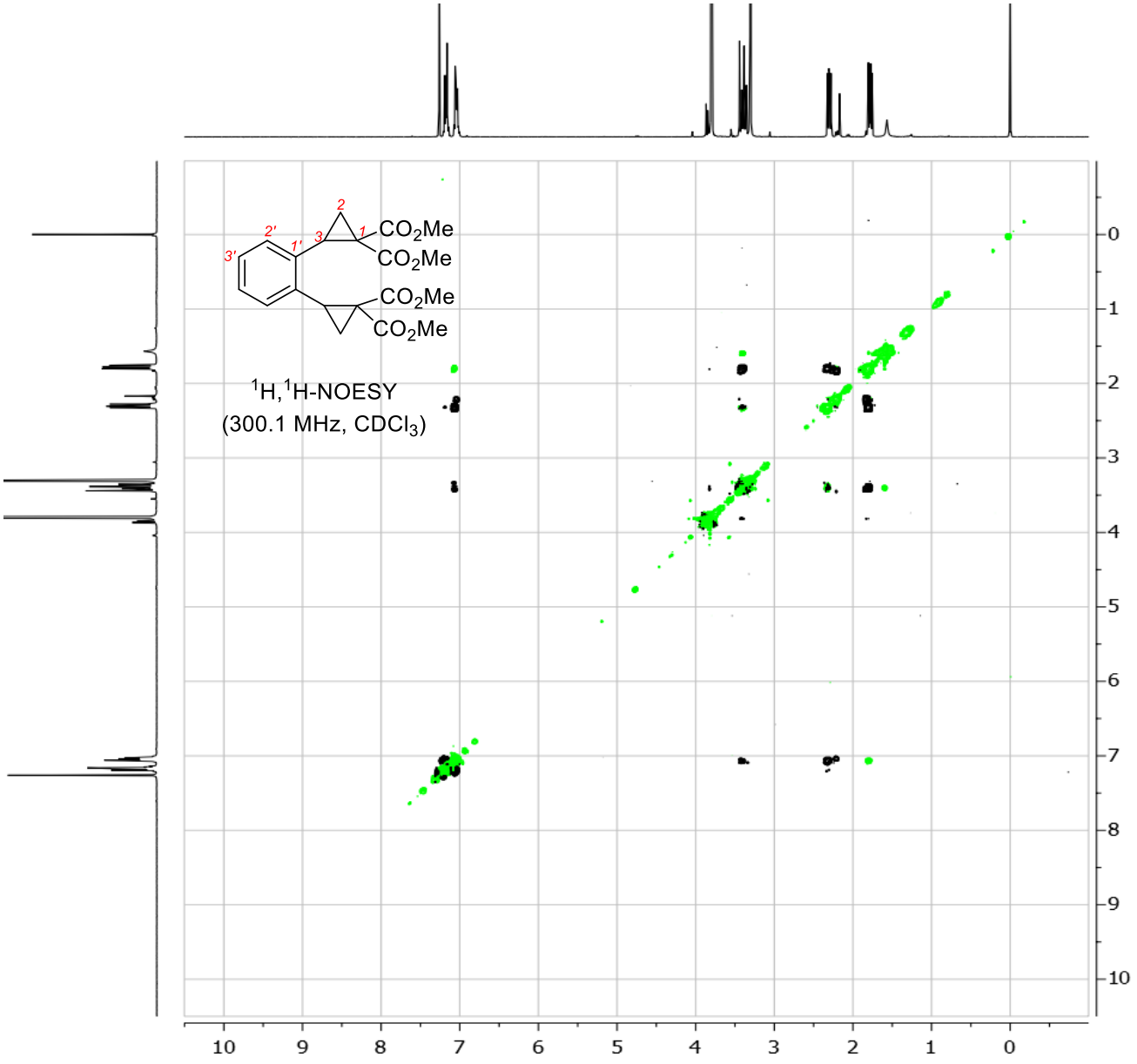
(300.1 MHz, $CDCl_3$)

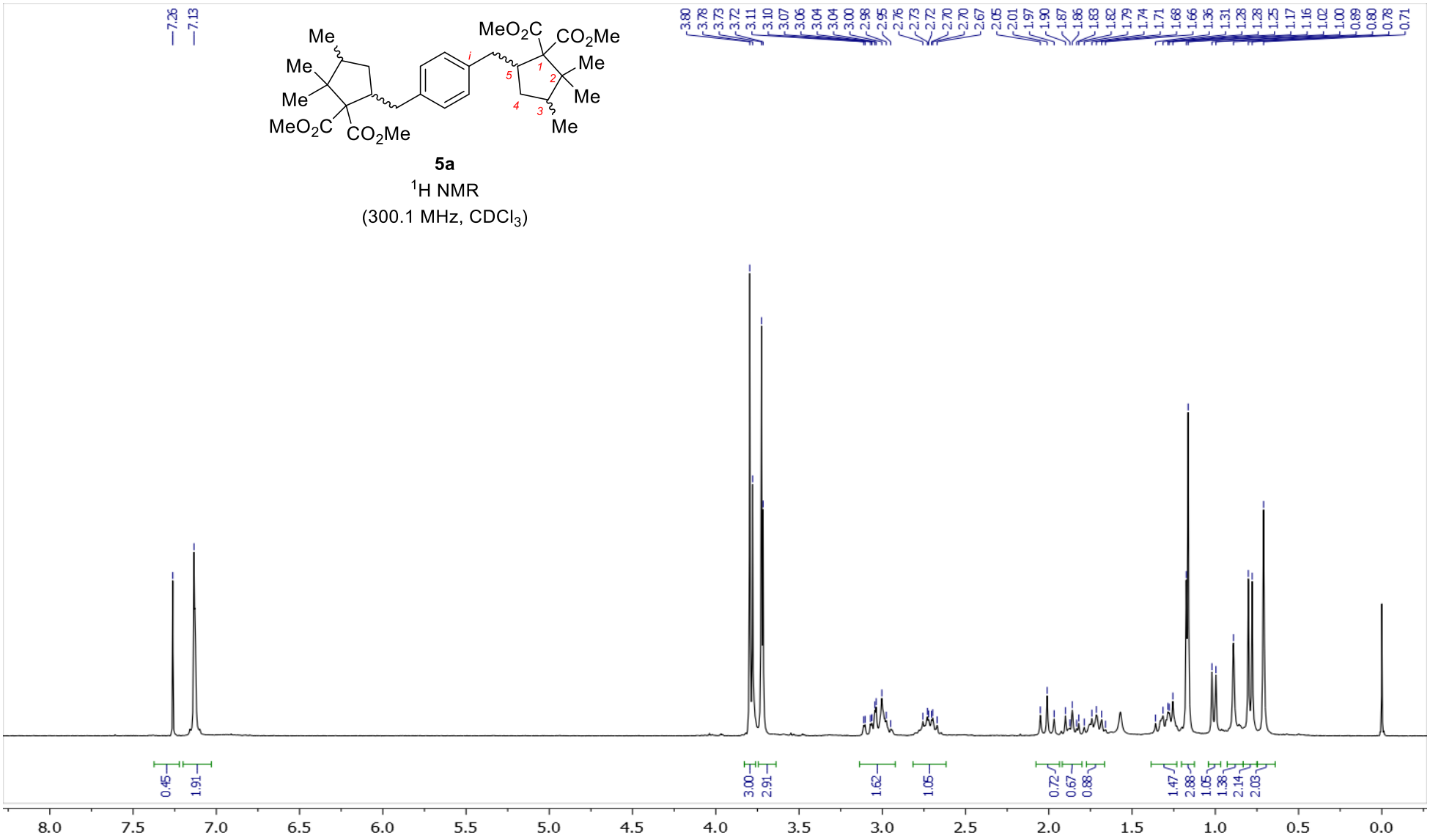


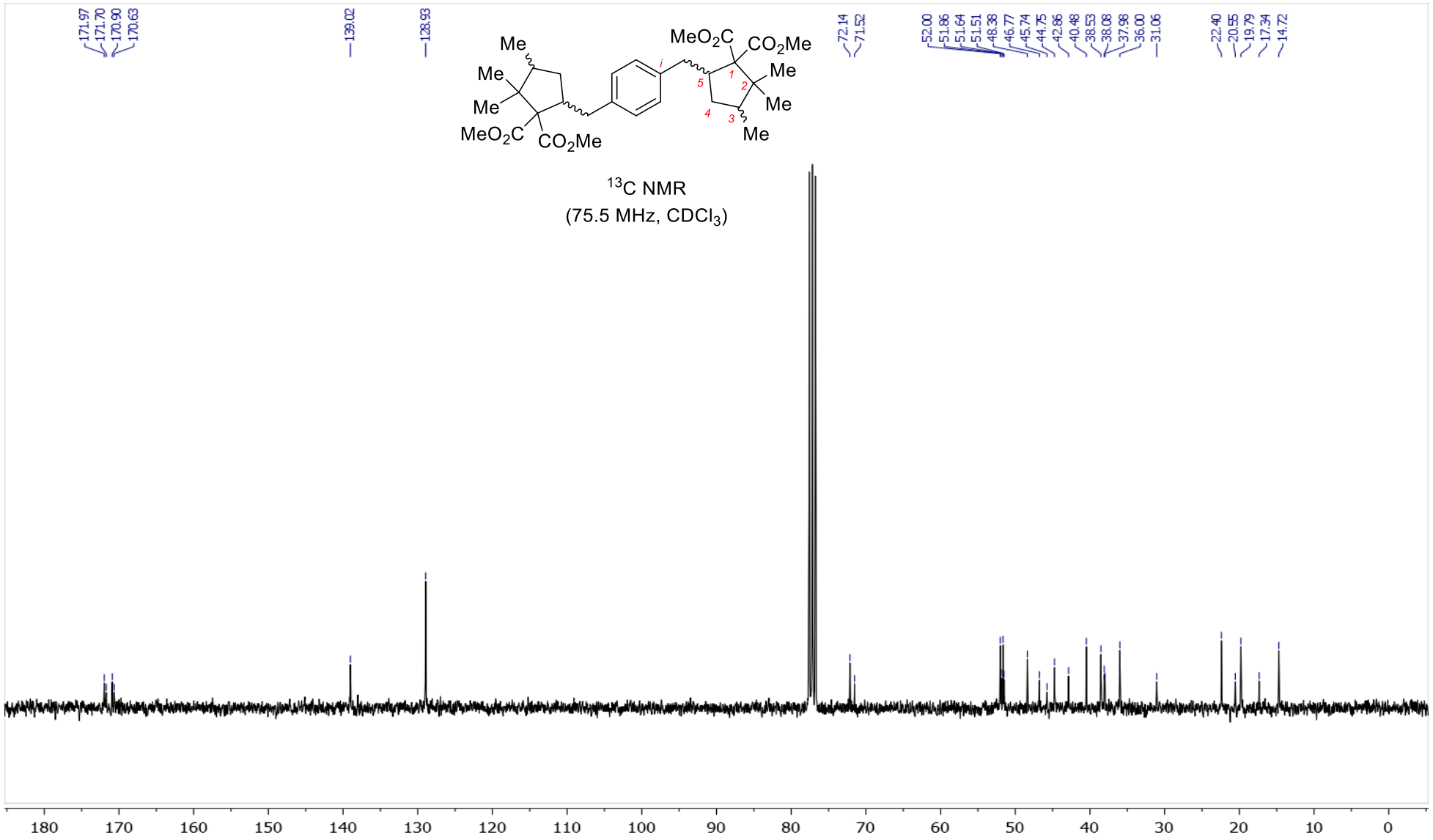
^{13}C NMR
(75.5 MHz, $CDCl_3$)

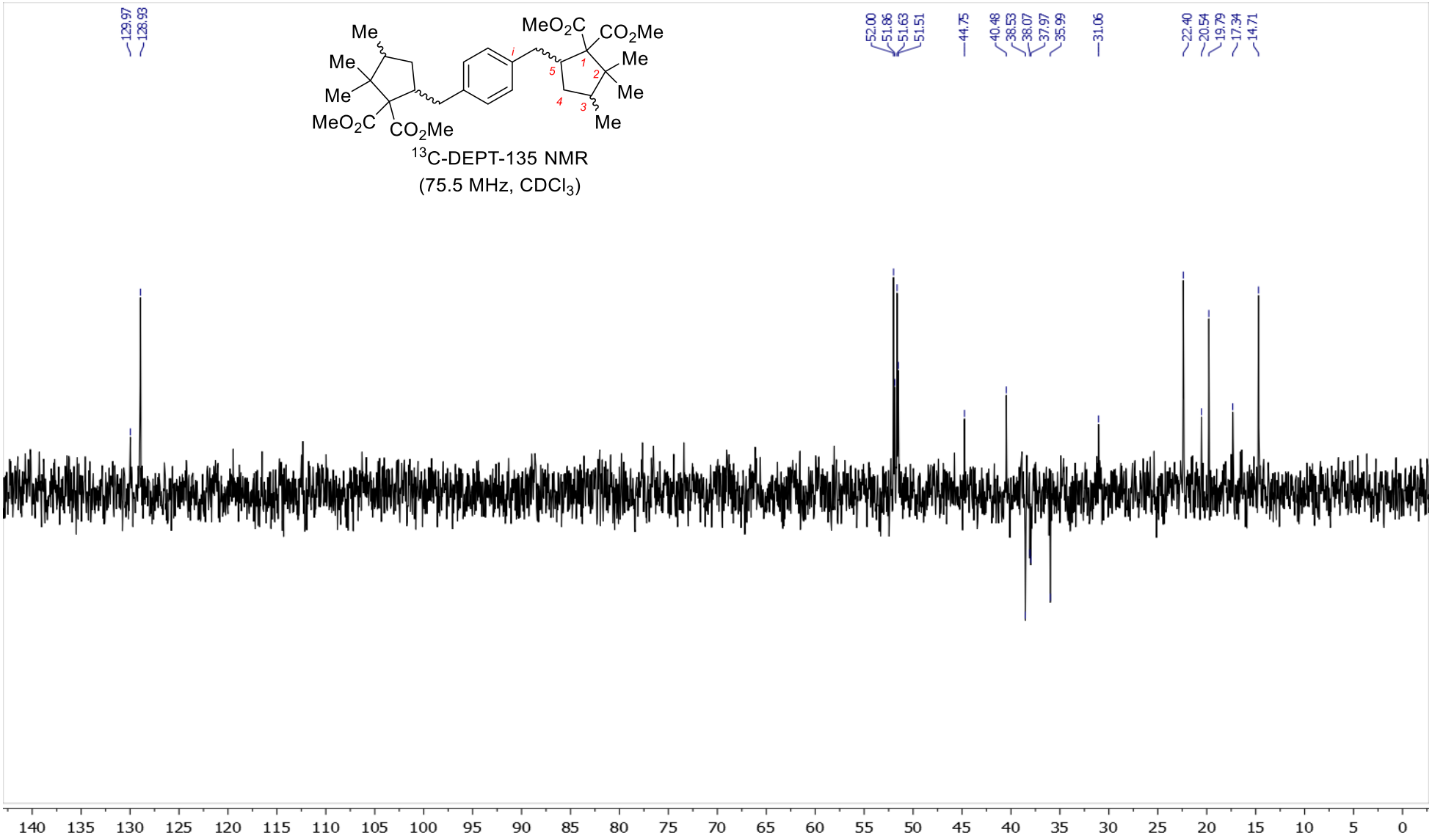

2
2'
3
1
1'
3'
CO_2Me
CO_2Me
CO_2Me
CO_2Me
$^1H,^1H$-COSY
(300.1 MHz, $CDCl_3$)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


2
2'
3
1
1'
3'
CO_2Me
CO_2Me
CO_2Me
CO_2Me
^1H,^{13}C-edited-HSQC
(^1H: 300.1 MHz,
^{13}C: 75.5 MHz
$CDCl_3$)
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

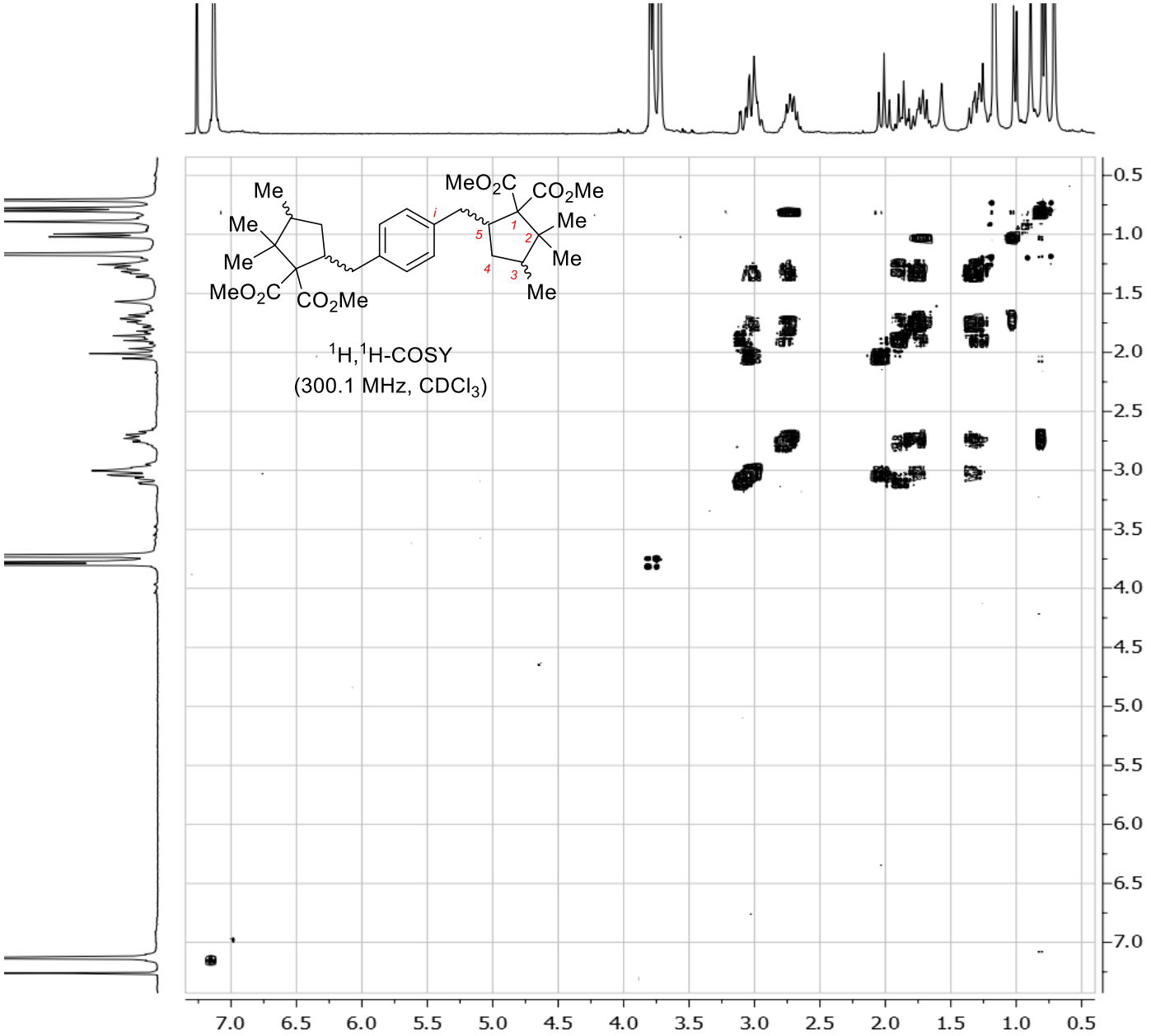

2
2'
1'
3
1
3'
CO2Me
CO2Me
CO2Me
CO2Me
1H,1H-NOESY
(300.1 MHz, CDCl3)
0
1
2
3
4
5
6
7
8
9
10
10
9
8
7
6
5
4
3
2
1
0

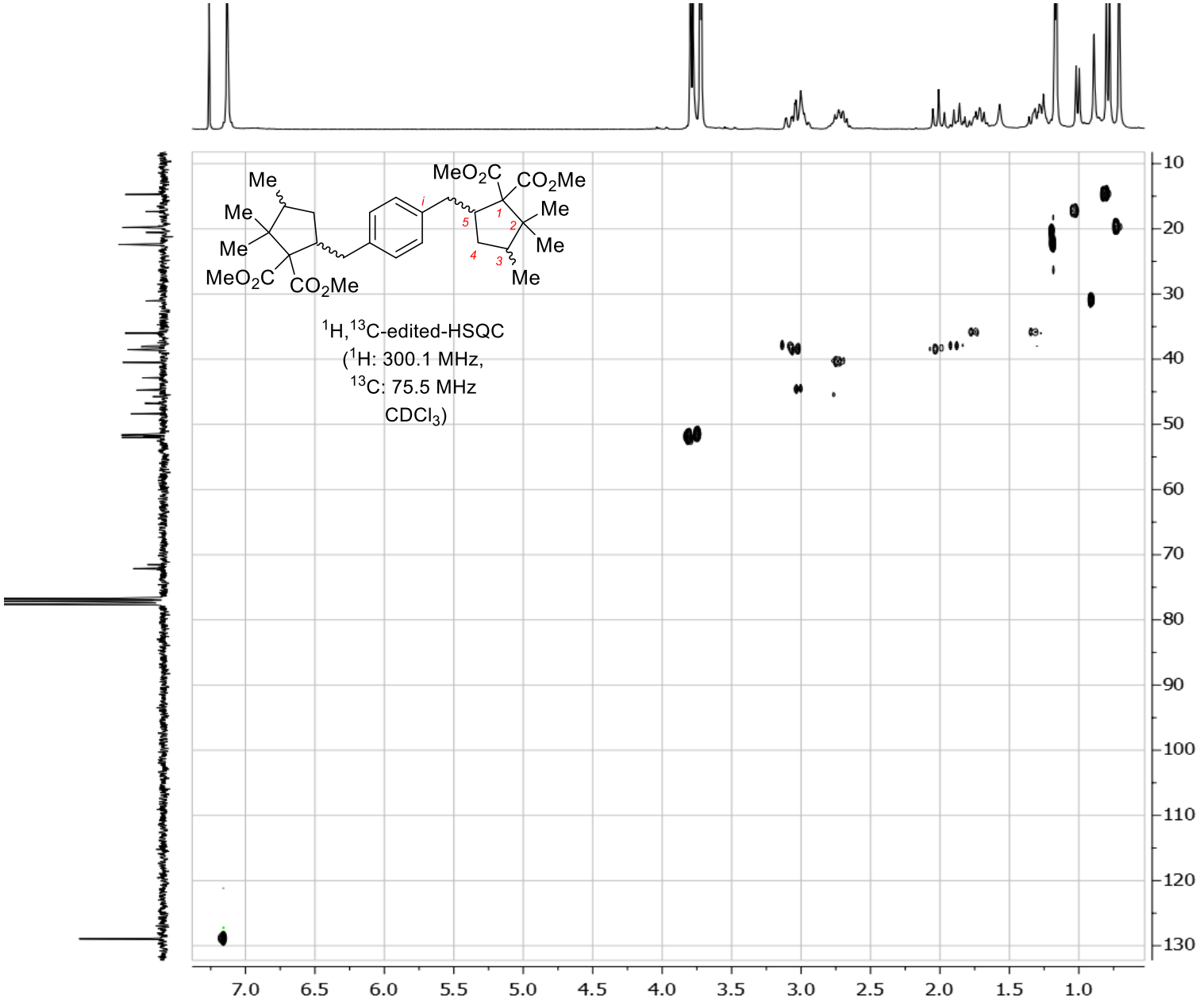

7.26
7.13
Me
Me
Me
MeO2C
CO2Me
MeO2C
CO2Me
Me
Me
Me
i
1
2
3
4
5
5a
1H NMR
(300.1 MHz, CDCl3)
3.80
3.78
3.73
3.72
3.11
3.10
3.07
3.06
3.04
3.04
3.00
2.98
2.95
2.76
2.73
2.72
2.70
2.70
2.67
2.05
2.01
1.97
1.90
1.87
1.86
1.83
1.82
1.79
1.74
1.71
1.68
1.66
1.36
1.31
1.28
1.28
1.25
1.17
1.16
1.02
1.00
0.89
0.80
0.78
0.71
0.45
1.91
3.00
2.91
1.62
1.05
0.72
0.67
0.88
1.47
2.88
1.05
1.38
2.14
2.03
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
1.0
0.5
0.0

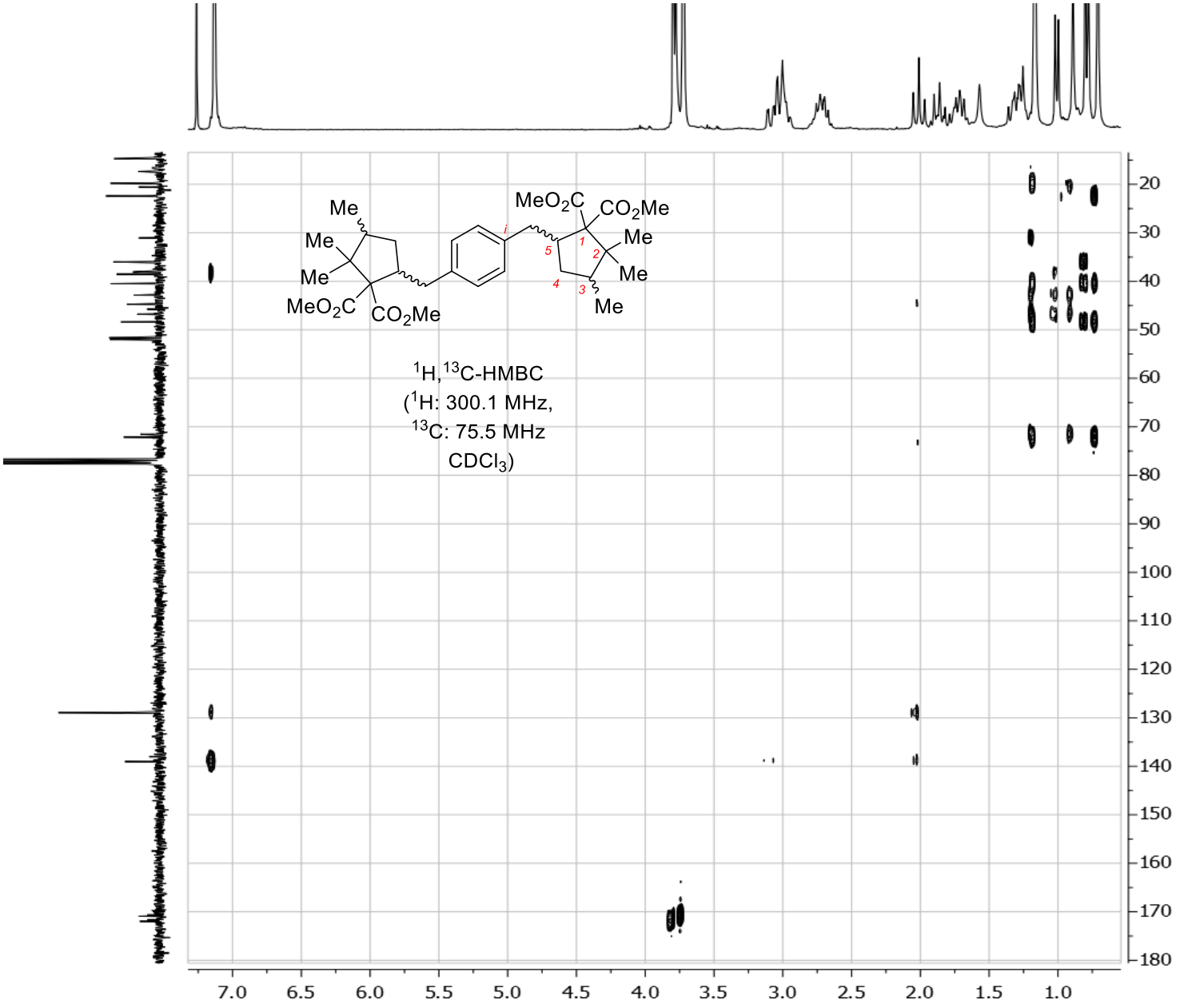

171.97
171.70
170.90
170.63
139.02
128.93
72.14
71.52
52.00
51.86
51.64
51.51
48.38
46.77
45.74
44.75
42.86
40.48
38.53
38.08
37.98
36.00
31.06
22.40
20.55
19.79
17.34
14.72
Me
Me
Me
MeO2C
CO2Me
MeO2C
CO2Me
Me
Me
Me
i
1
2
3
4
5
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

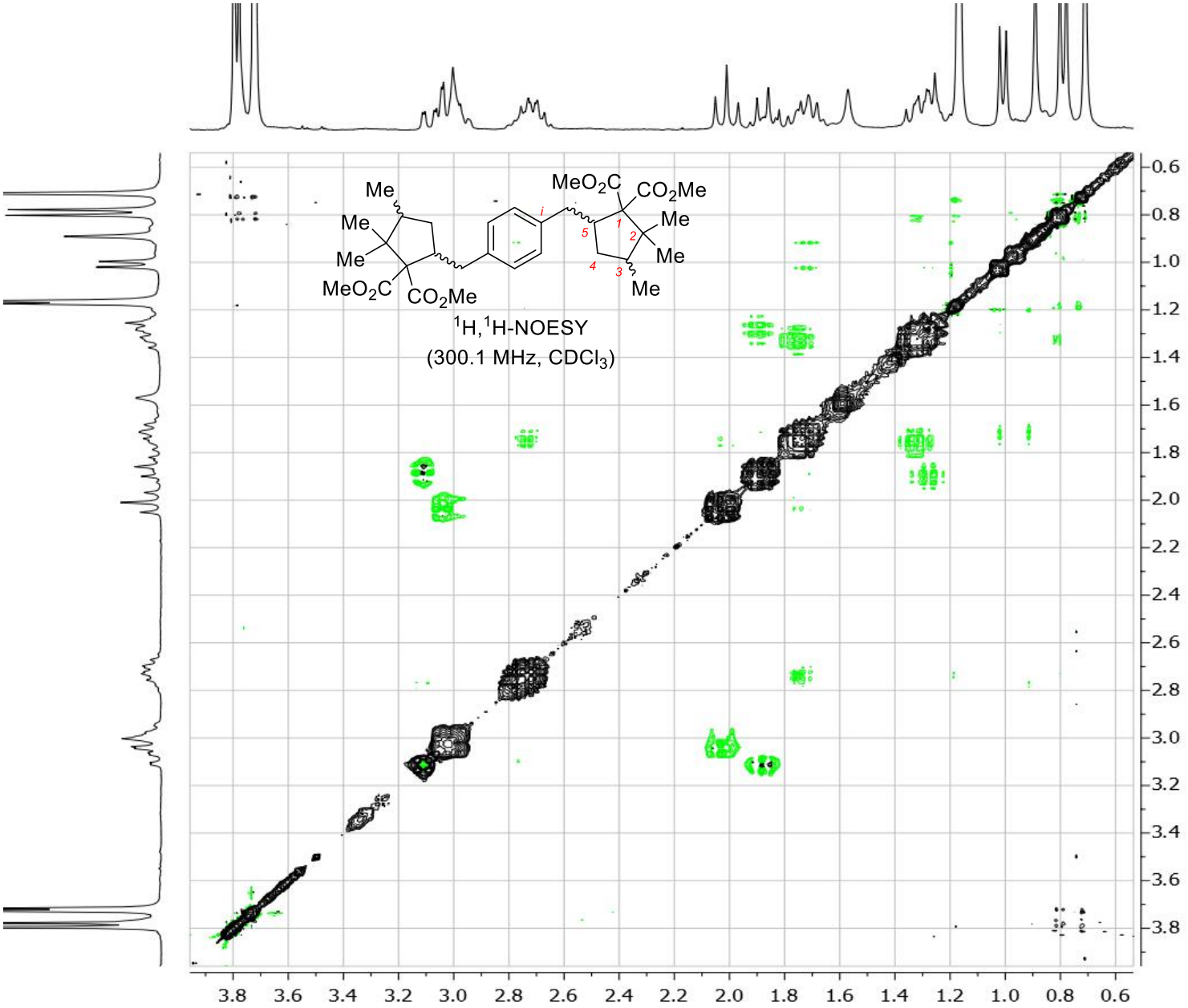


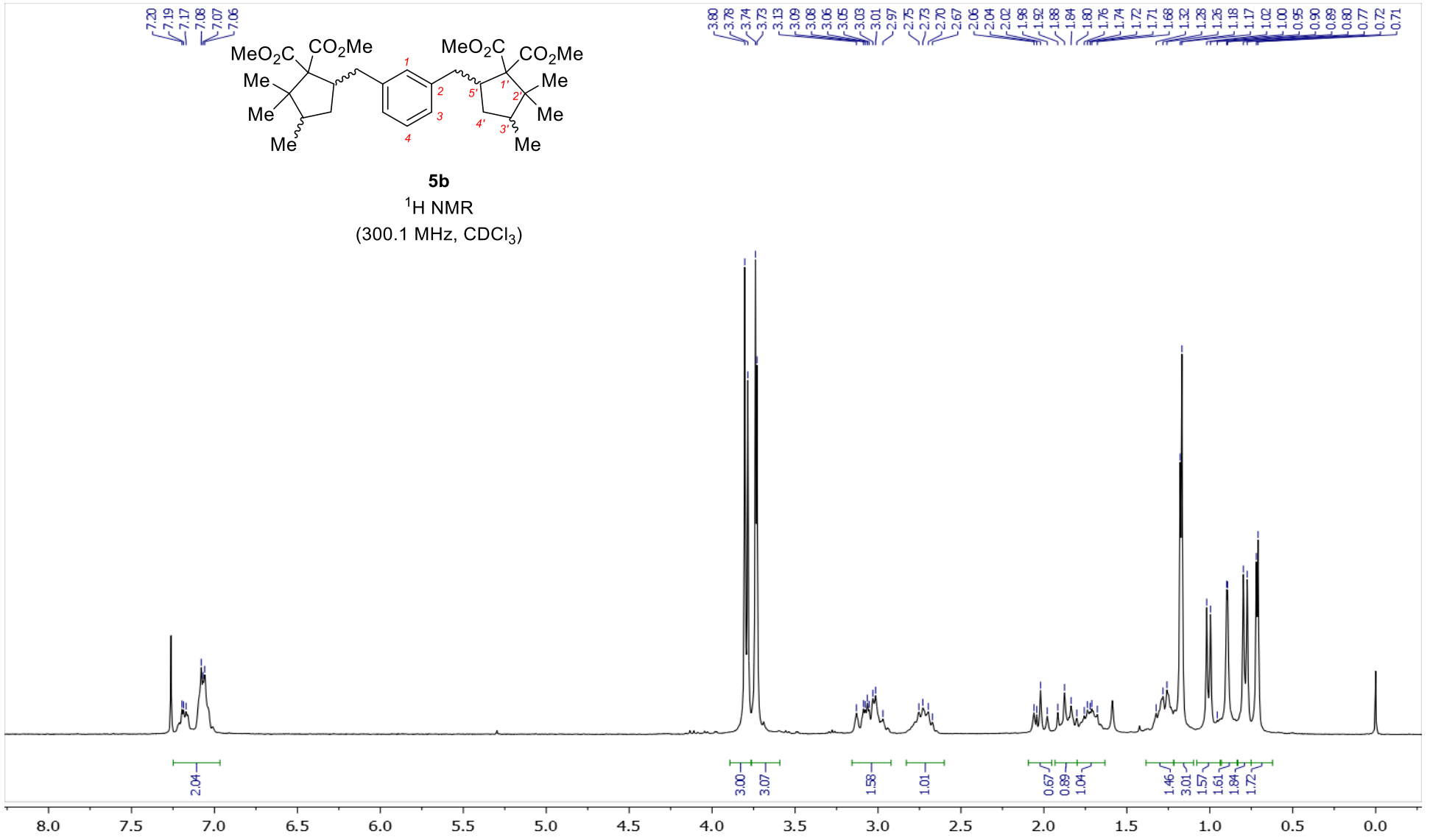
^{13}C-DEPT-135 NMR
(75.5 MHz, $CDCl_3$)

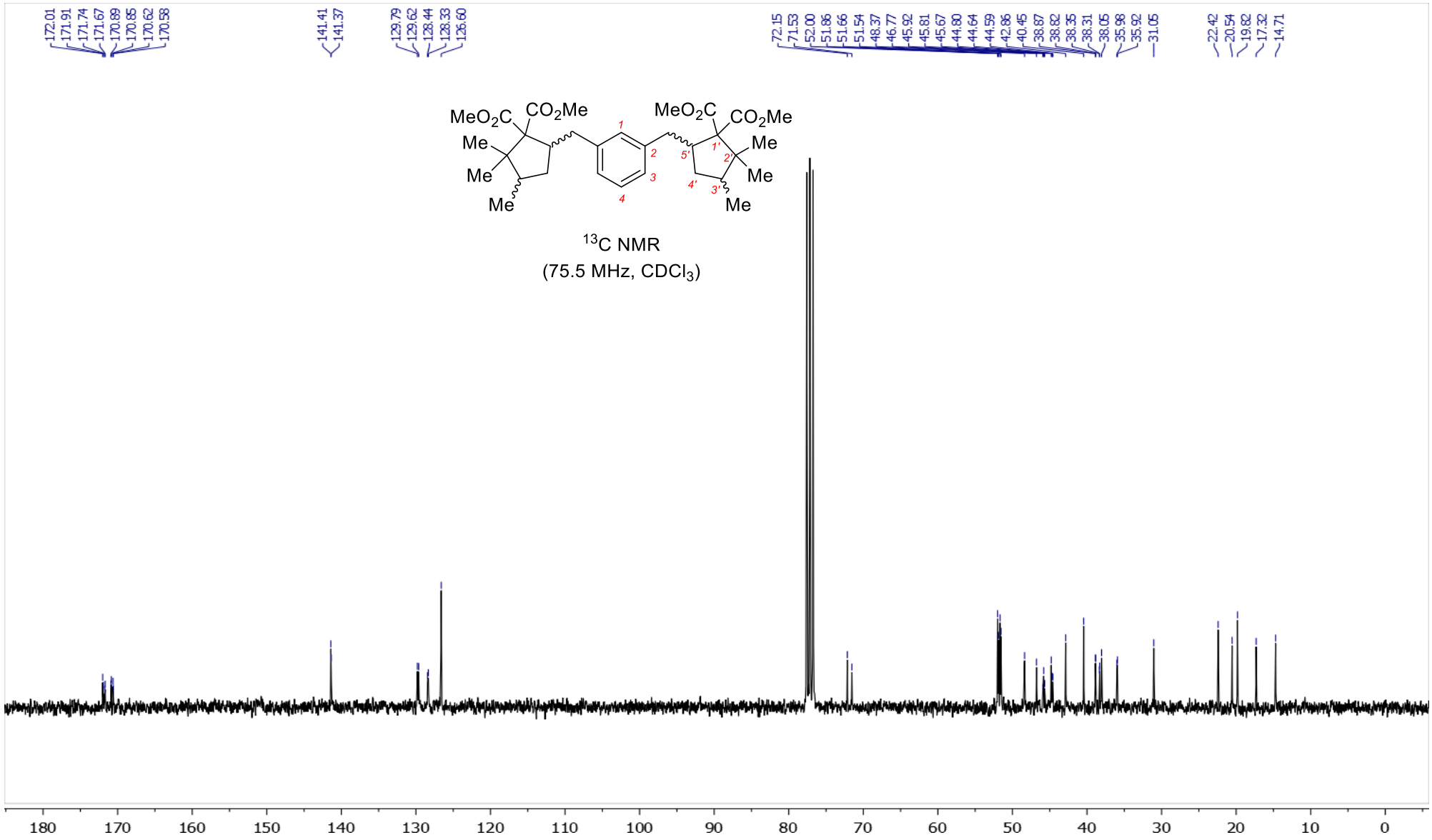

Me
Me
Me
MeO2C
CO2Me
MeO2C
CO2Me
Me
Me
Me
i
1
2
3
4
5
1H,1H-COSY
(300.1 MHz, CDCl3)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

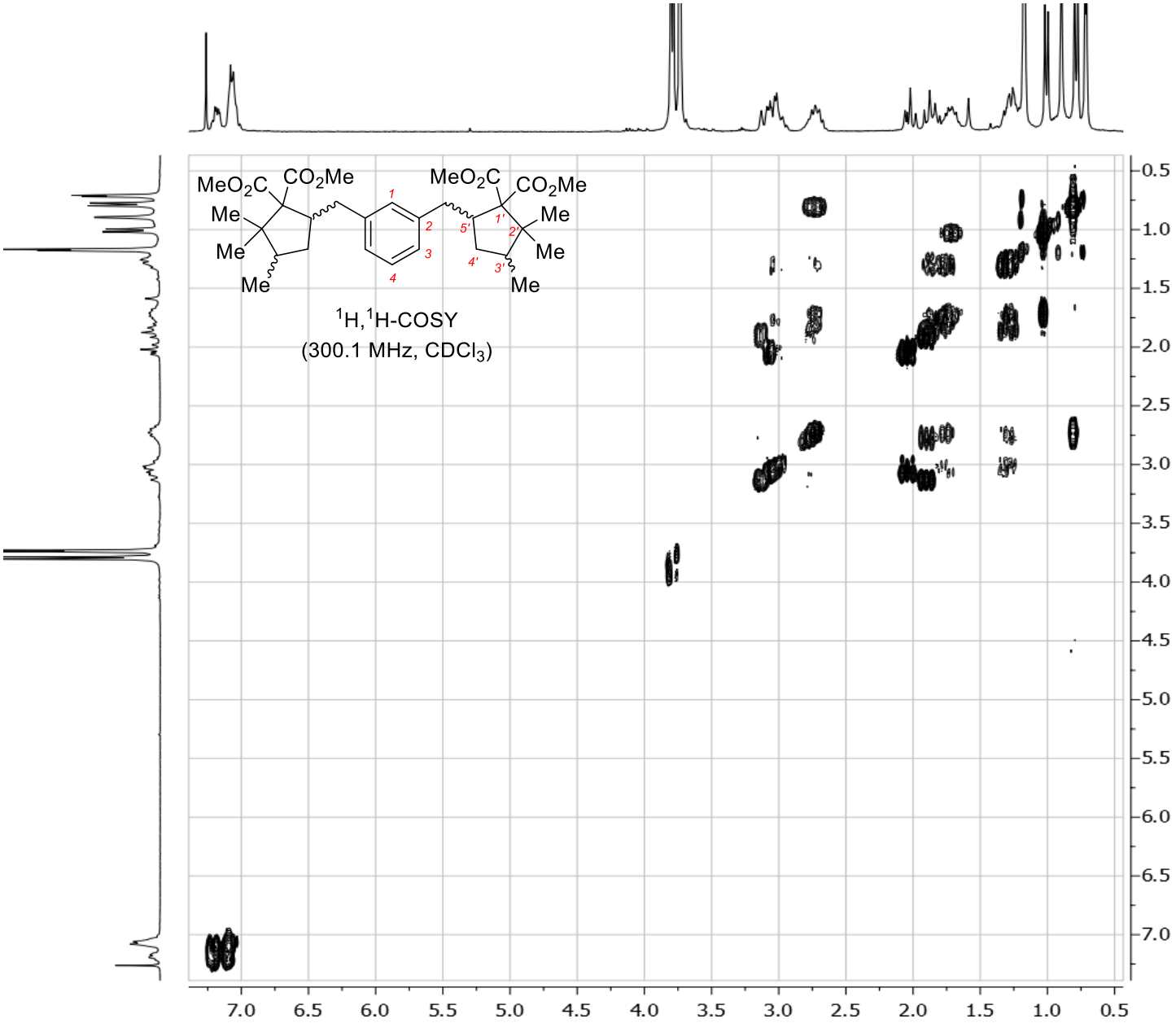

Me
Me
Me
MeO2C
CO2Me
MeO2C
CO2Me
Me
Me
Me
i
1
2
3
4
5
1H,13C-edited-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
10
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

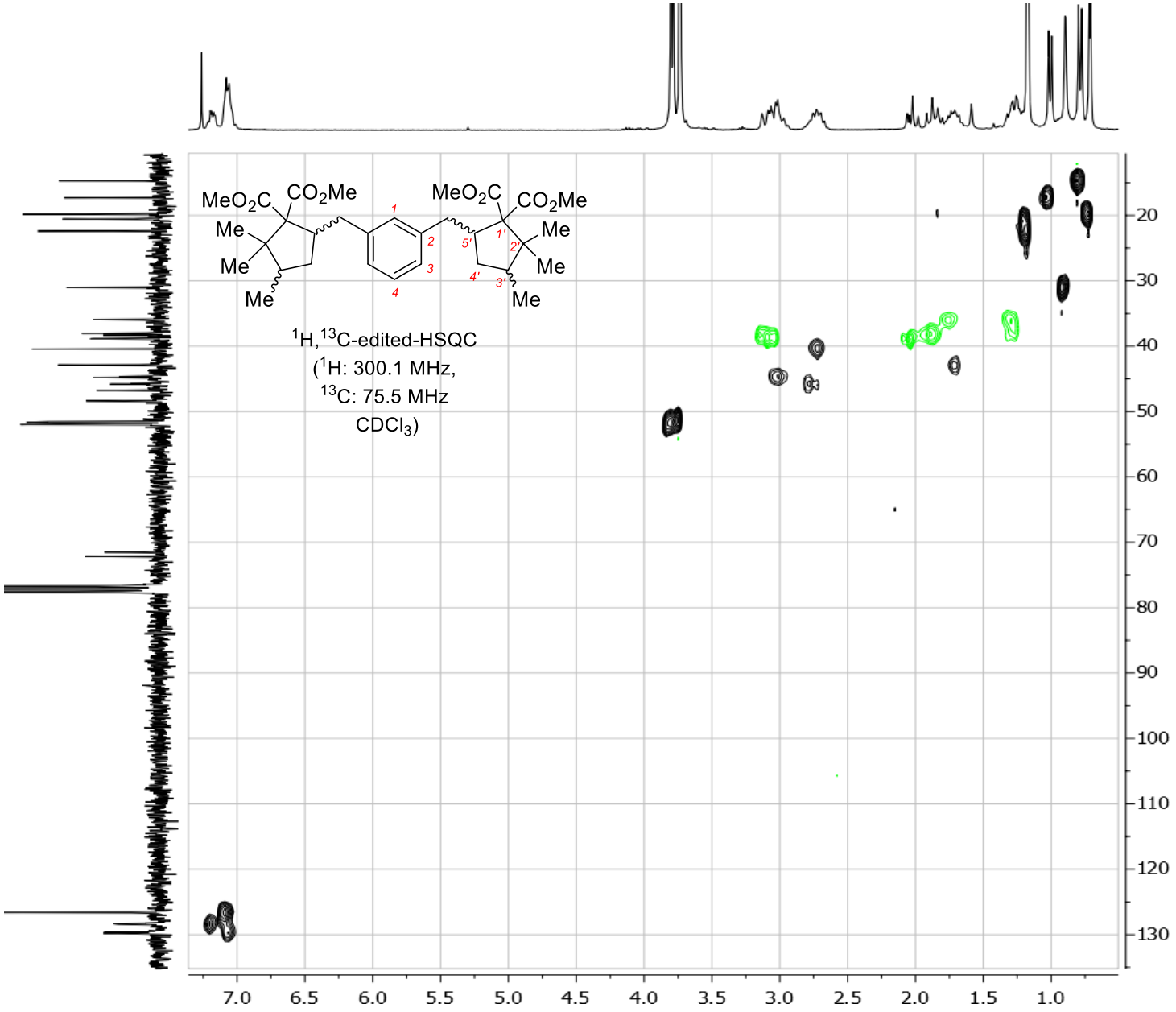

Me
Me
Me
MeO2C
CO2Me
MeO2C
CO2Me
Me
Me
Me
1H,13C-HMBC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

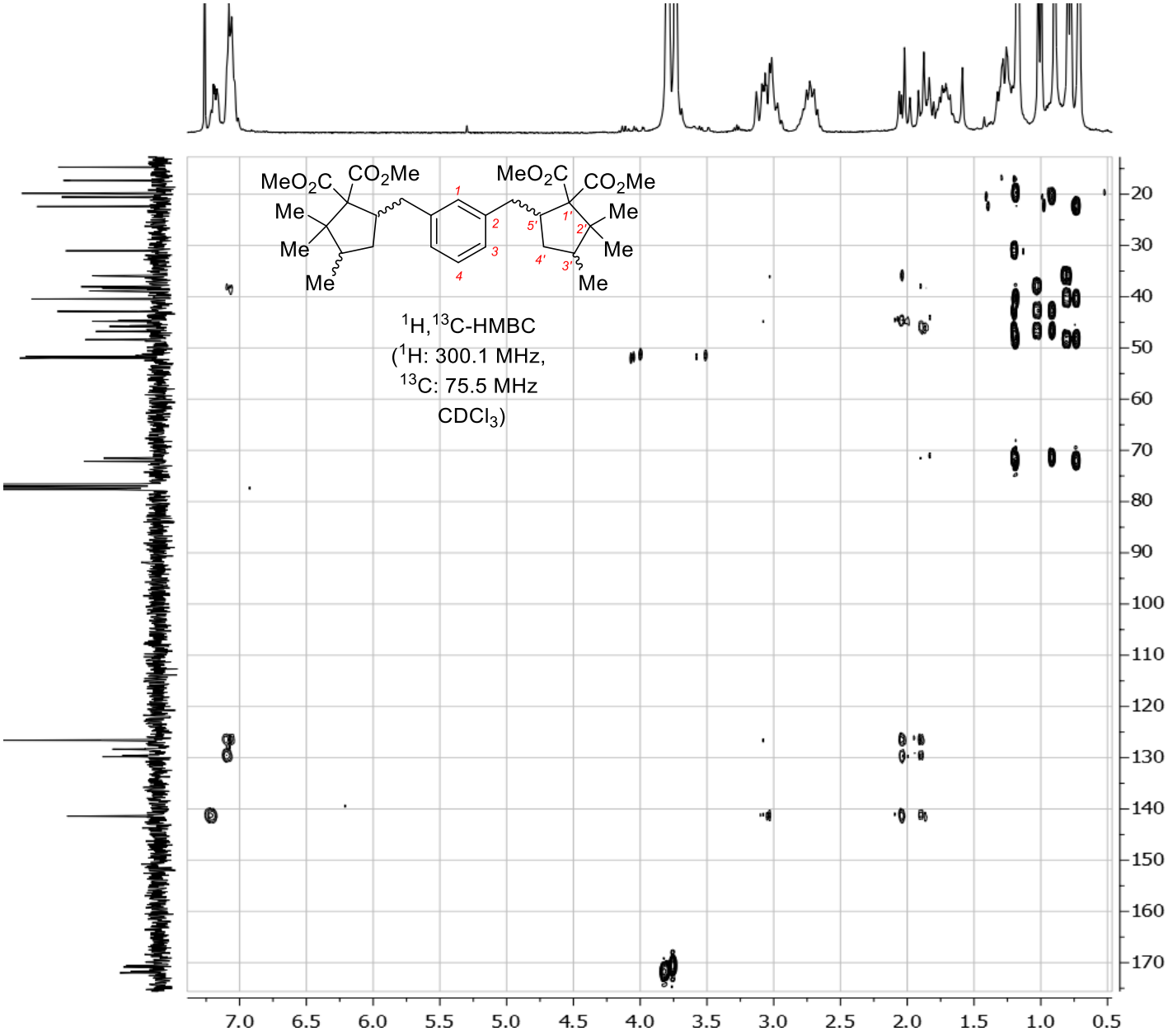

Me
Me
Me
MeO2C
CO2Me
MeO2C
CO2Me
Me
Me
Me
1H,1H-NOESY
(300.1 MHz, CDCl3)
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6

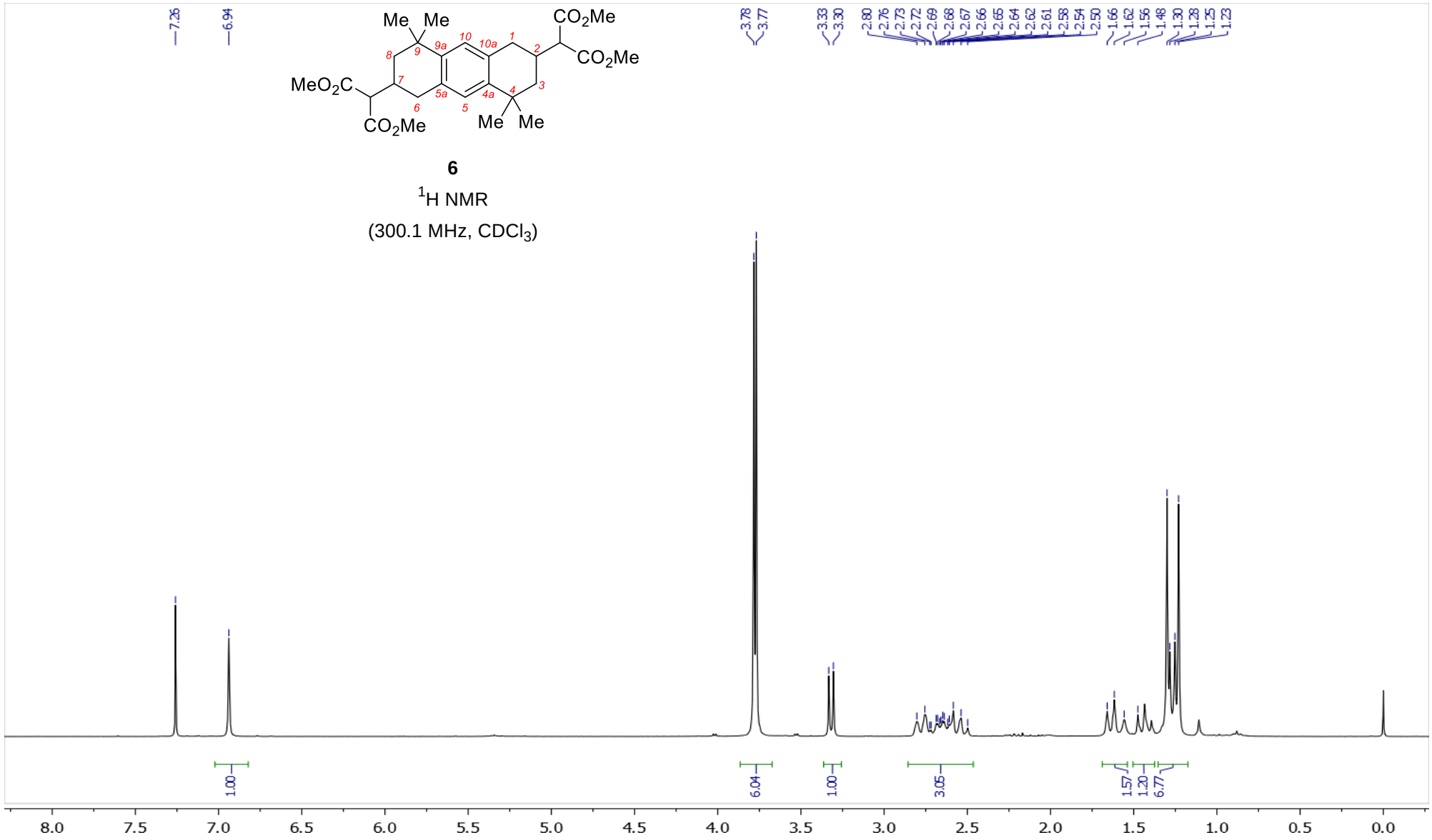

MeO2C
CO2Me
Me
Me
Me
MeO2C
CO2Me
Me
Me
Me
1
2
3
4
5'
1'
2'
4'
3'
5b
1H NMR
(300.1 MHz, CDCl3)
2.04
3.00
3.07
1.58
1.01
0.67
0.89
1.04
1.46
3.01
1.57
1.61
1.84
1.72
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


172.01
171.91
171.74
171.67
170.89
170.85
170.62
170.58
141.41
141.37
129.79
129.62
128.44
128.33
126.60
72.15
71.53
52.00
51.86
51.66
51.54
48.37
46.77
45.92
45.81
45.67
44.80
44.64
44.59
42.86
40.45
38.87
38.82
38.35
38.31
38.05
35.98
35.92
31.05
22.42
20.54
19.82
17.32
14.71
MeO2C
CO2Me
Me
Me
Me
MeO2C
CO2Me
Me
Me
Me
1
2
3
4
1'
2'
3'
4'
5'
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


MeO2C
CO2Me
Me
Me
Me
MeO2C
CO2Me
Me
Me
Me
1
2
3
4
5'
1'
2'
4'
3'
1H,1H-COSY
(300.1 MHz, CDCl3)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


MeO2C
CO2Me
Me
Me
Me
MeO2C
CO2Me
Me
Me
Me
1
2
3
4
5'
1'
2'
3'
4'
1H,13C-edited-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

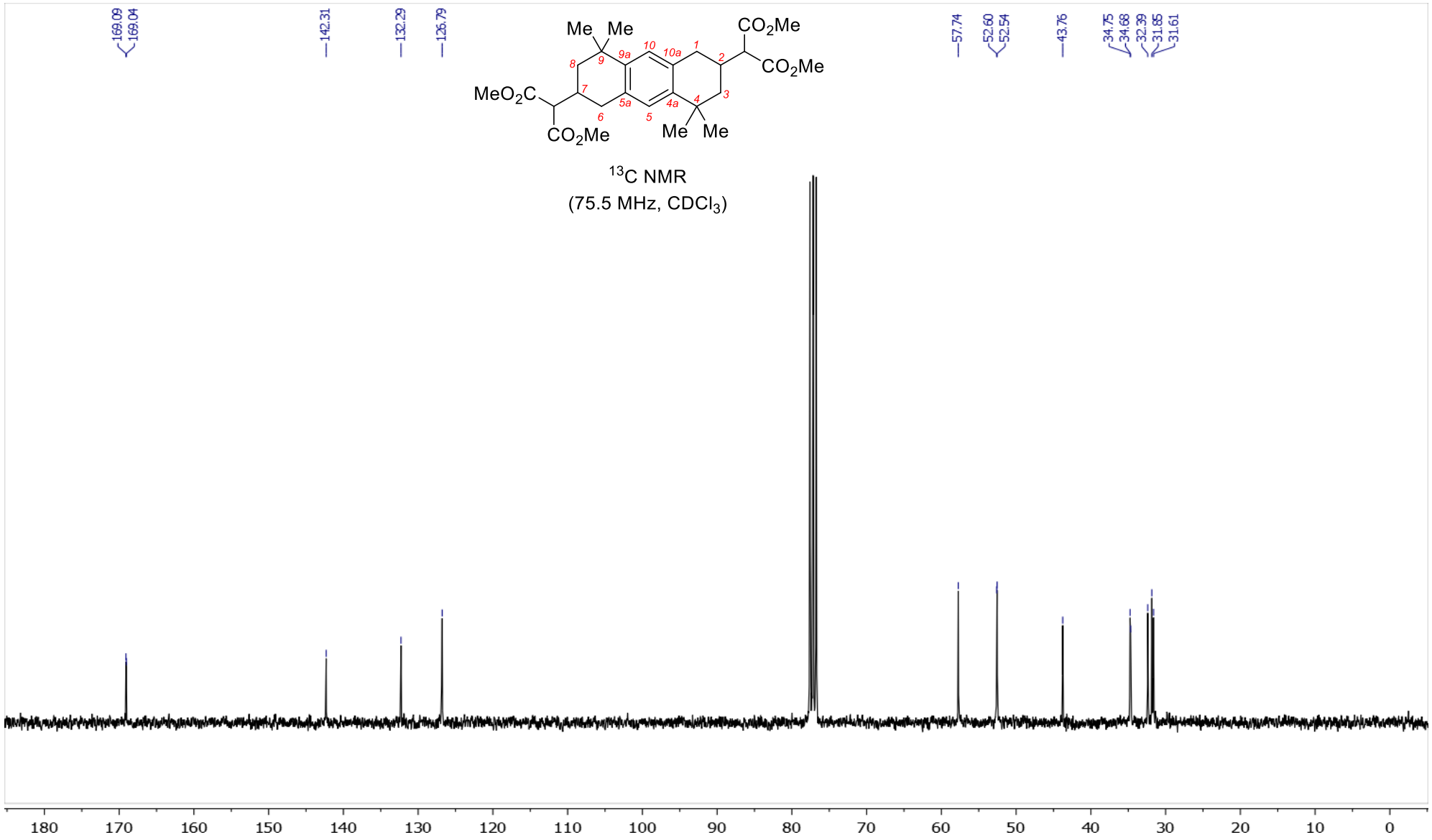

MeO2C
CO2Me
Me
Me
Me
MeO2C
CO2Me
Me
Me
Me
1
2
3
4
1'
2'
3'
4'
5'
1H,13C-HMBC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

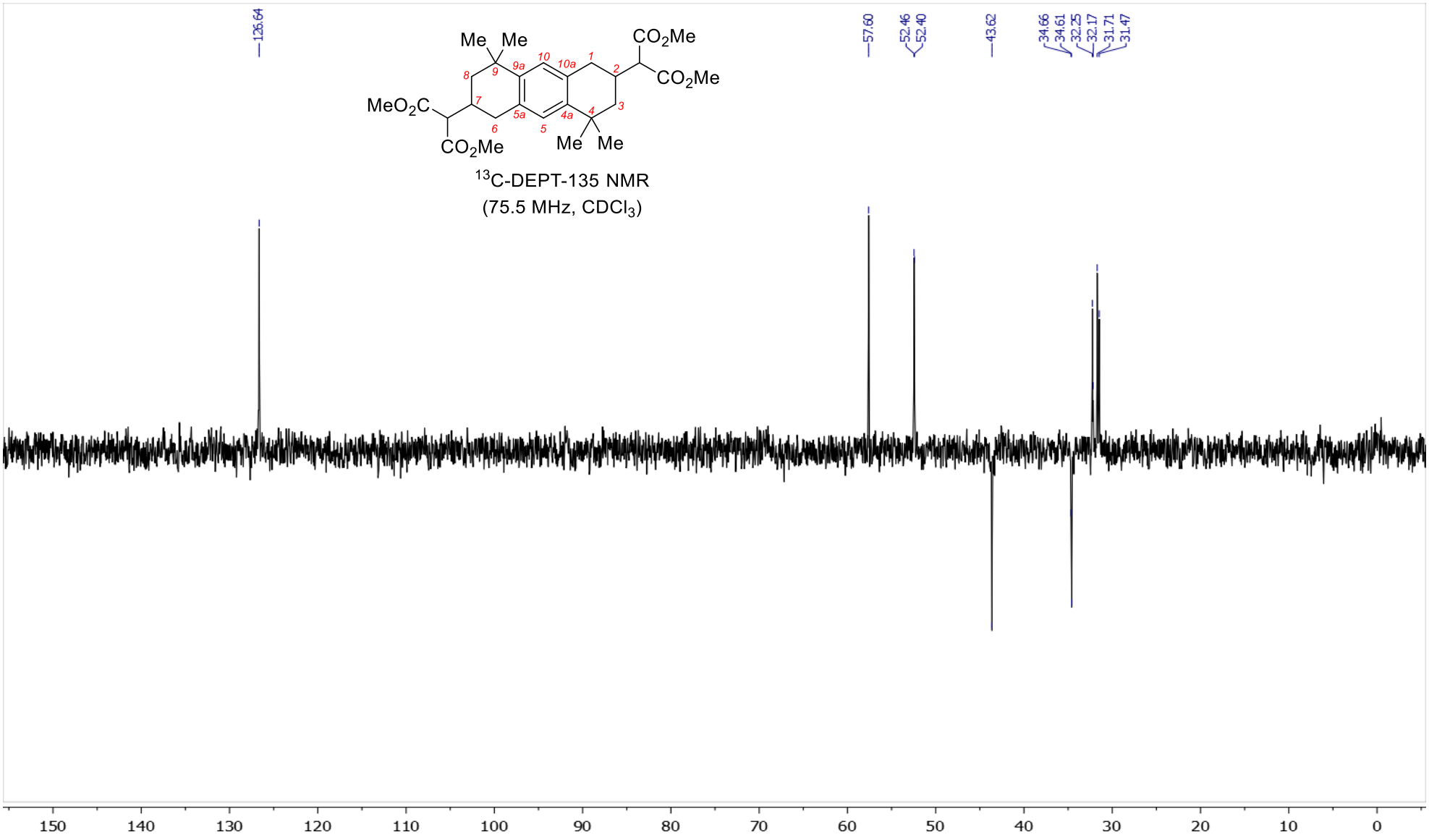


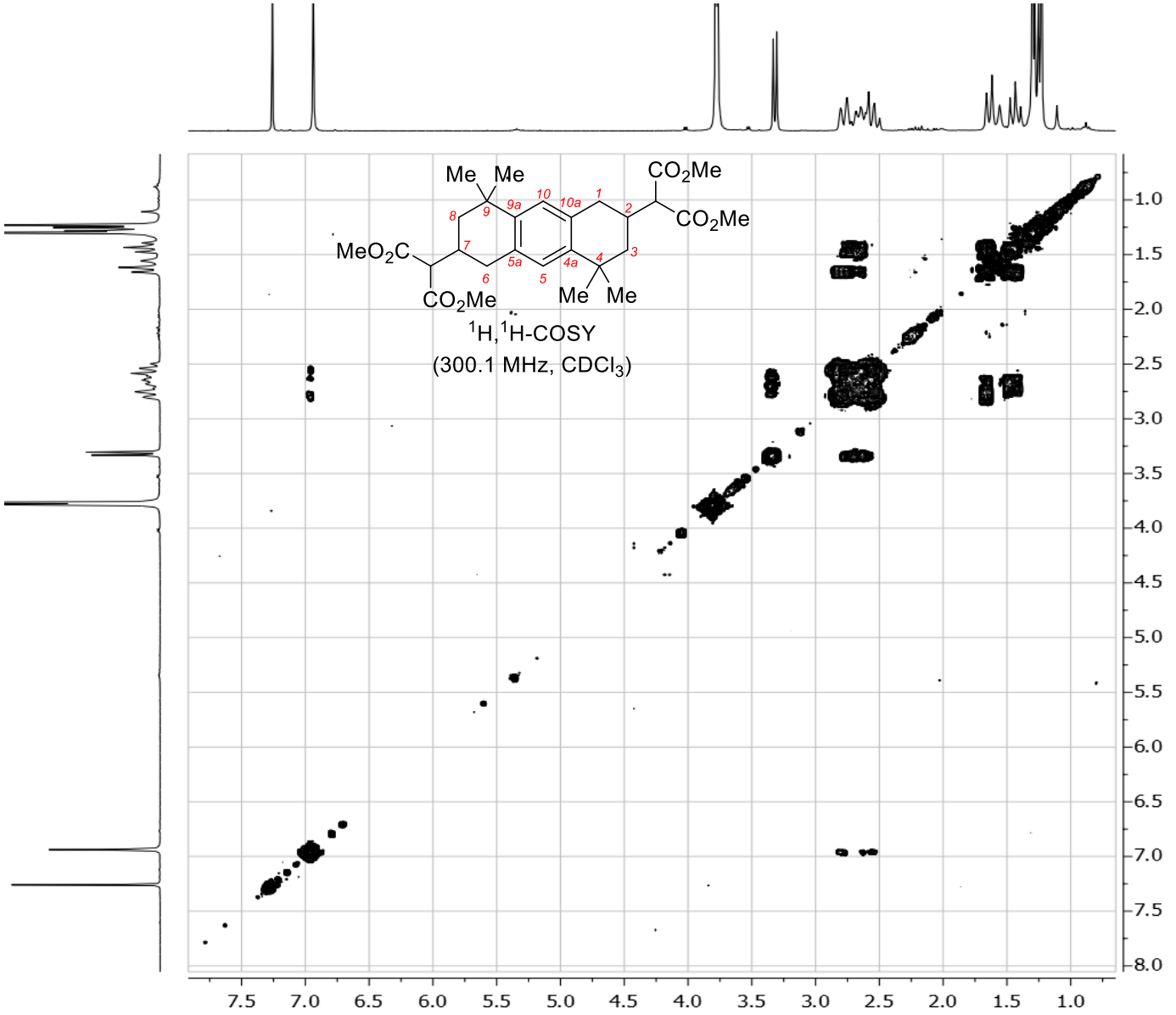
6

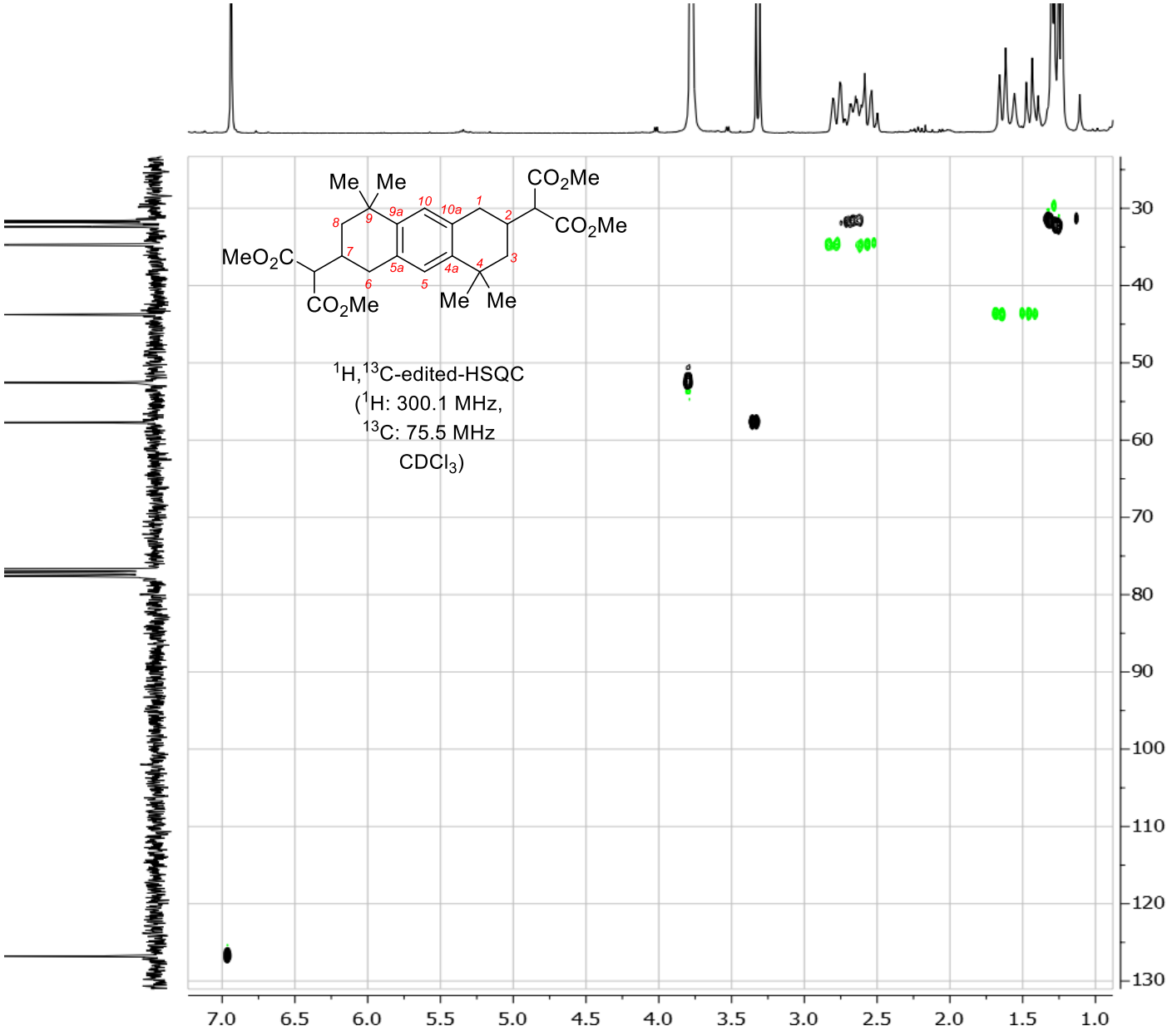
^{1}H NMR

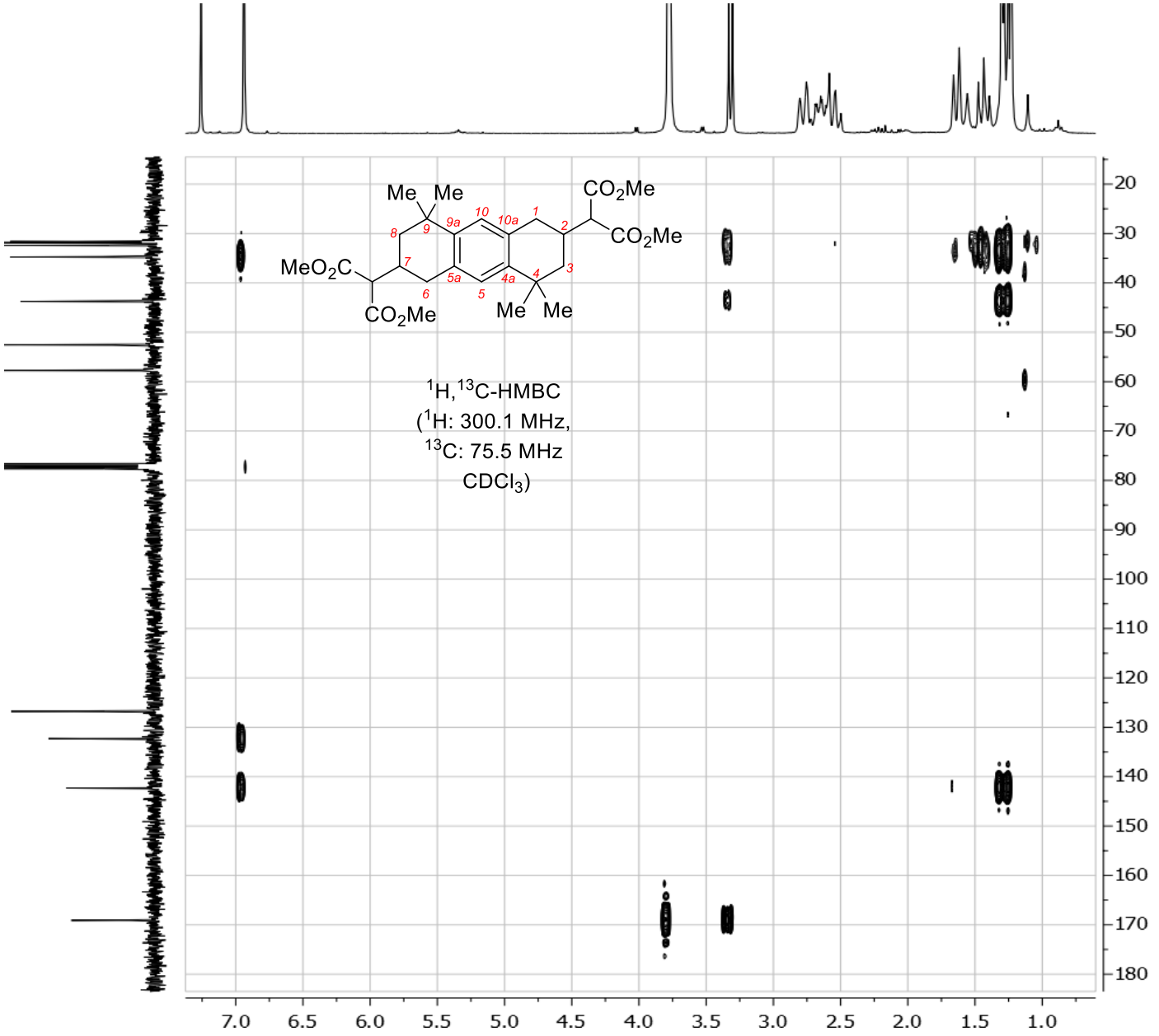
(300.1 MHz, $CDCl_3$)

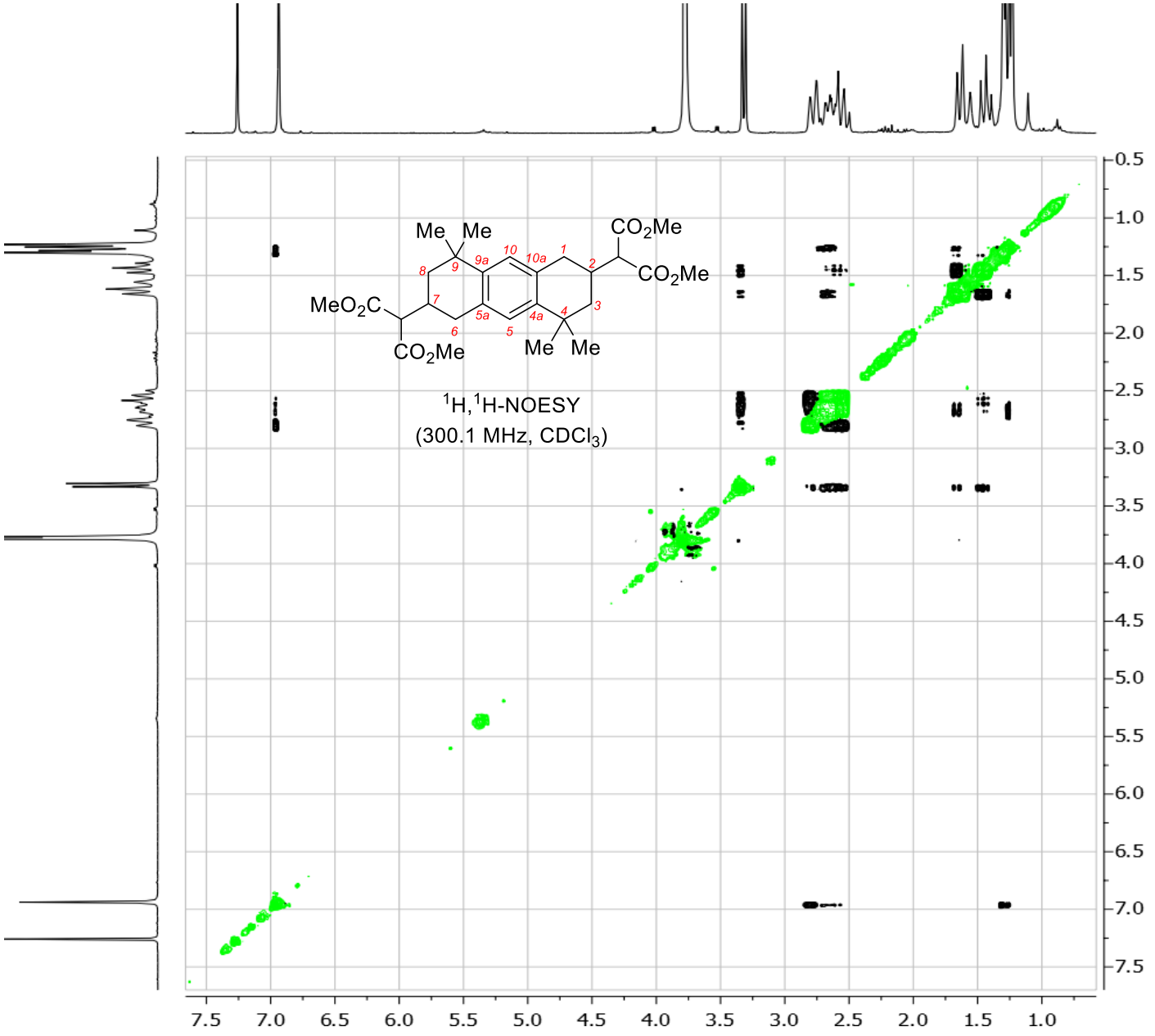

169.09
169.04
142.31
132.29
126.79
57.74
52.60
52.54
43.76
34.75
34.68
32.39
31.85
31.61
Me Me
CO2Me
CO2Me
MeO2C
CO2Me
Me Me
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

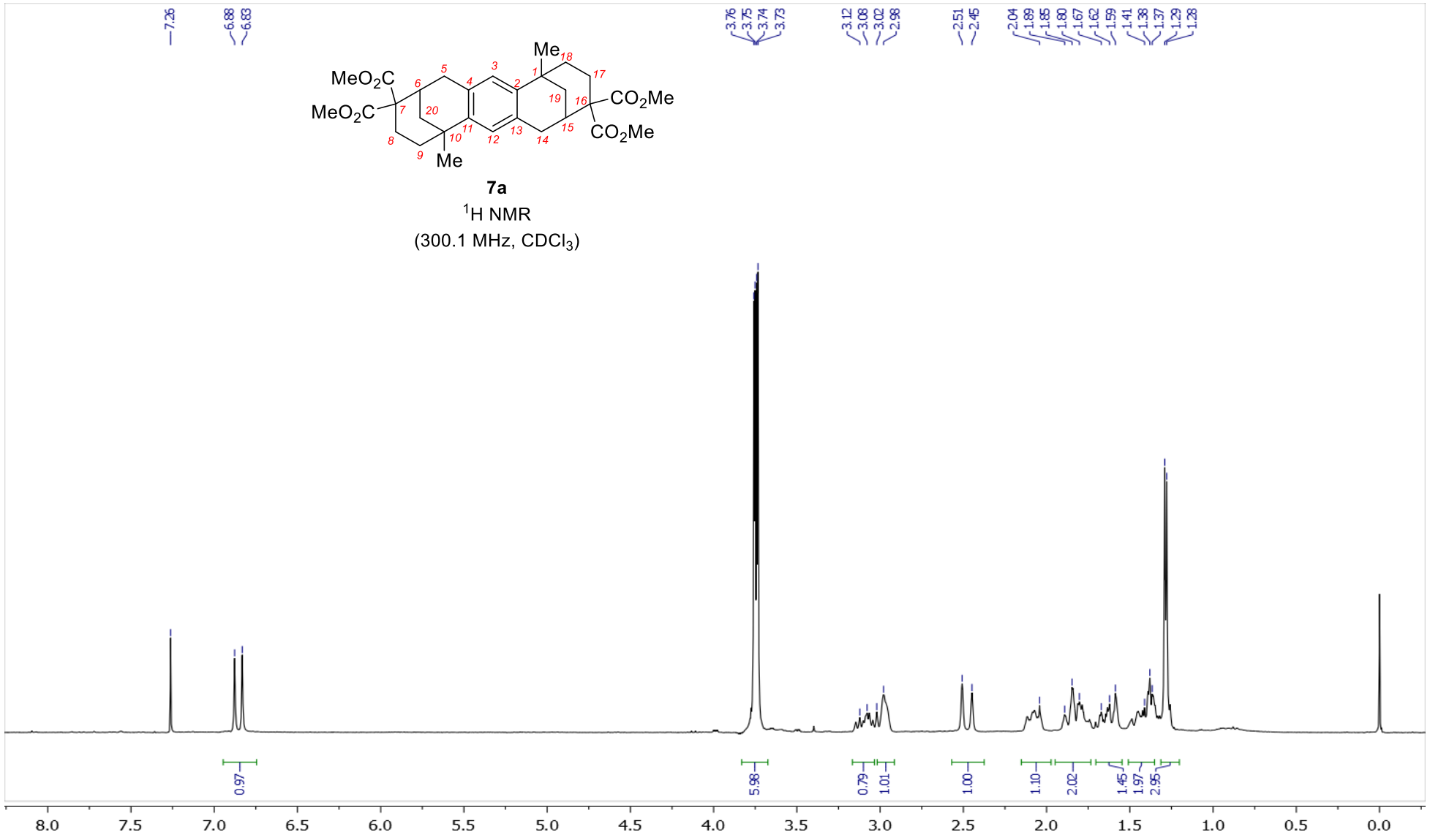

126.64
57.60
52.46
52.40
43.62
34.66
34.61
32.25
32.17
31.71
31.47
Me Me
CO2Me
CO2Me
MeO2C
CO2Me
Me Me
13C-DEPT-135 NMR
(75.5 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Me Me
CO2Me
CO2Me
MeO2C
CO2Me
Me Me
1H,1H-COSY
(300.1 MHz, CDCl3)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
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 1.0


Me Me
CO2Me
CO2Me
MeO2C
CO2Me
Me Me
1H,13C-edited-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


Me Me
CO2Me
CO2Me
MeO2C
CO2Me
Me Me
1H,13C-HMBC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

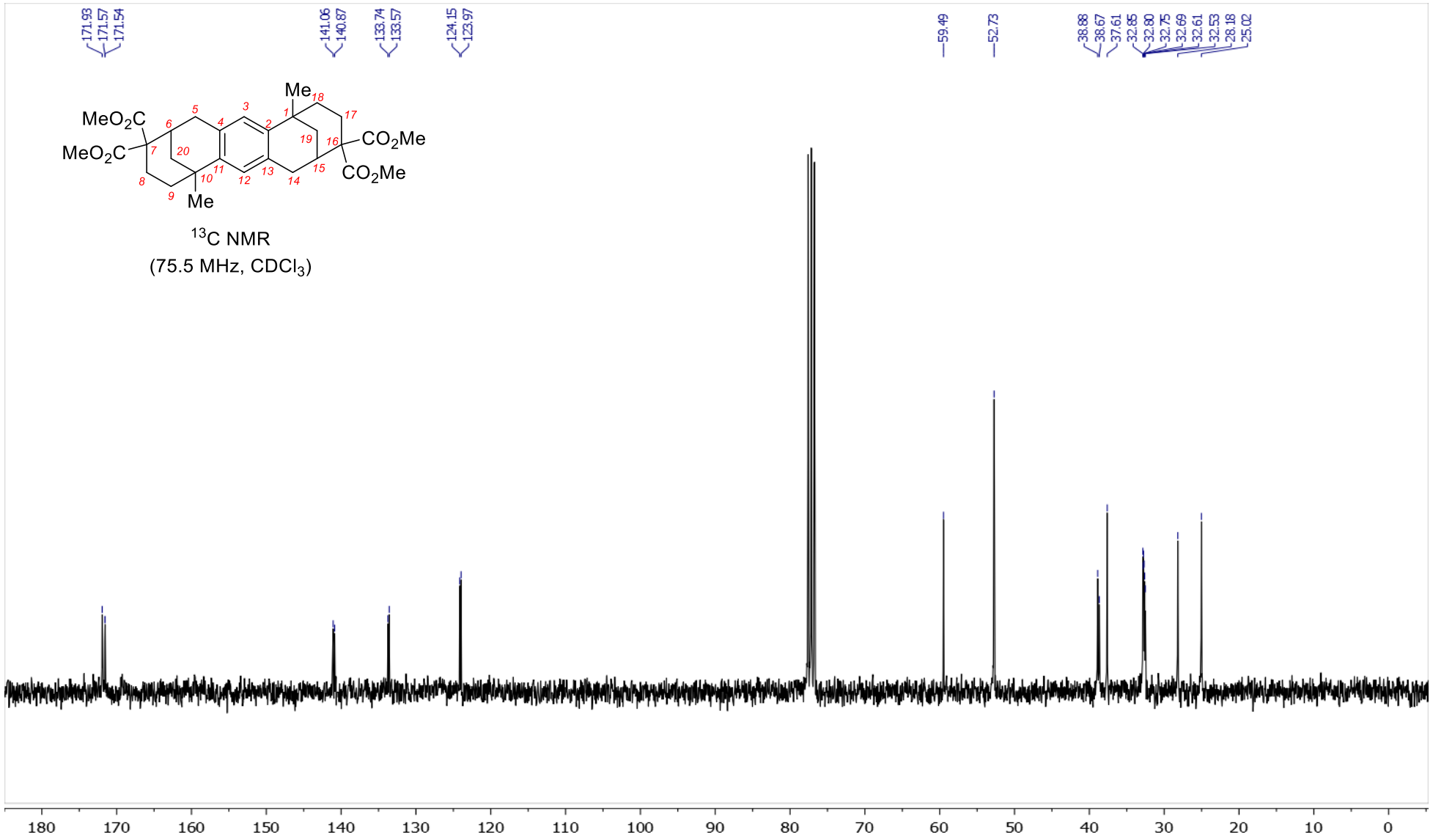

Me Me
CO2Me
CO2Me
MeO2C
CO2Me
Me Me
10
10a
1
2
3
4
4a
5
5a
6
7
8
9
9a
1H,1H-NOESY
(300.1 MHz, CDCl3)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

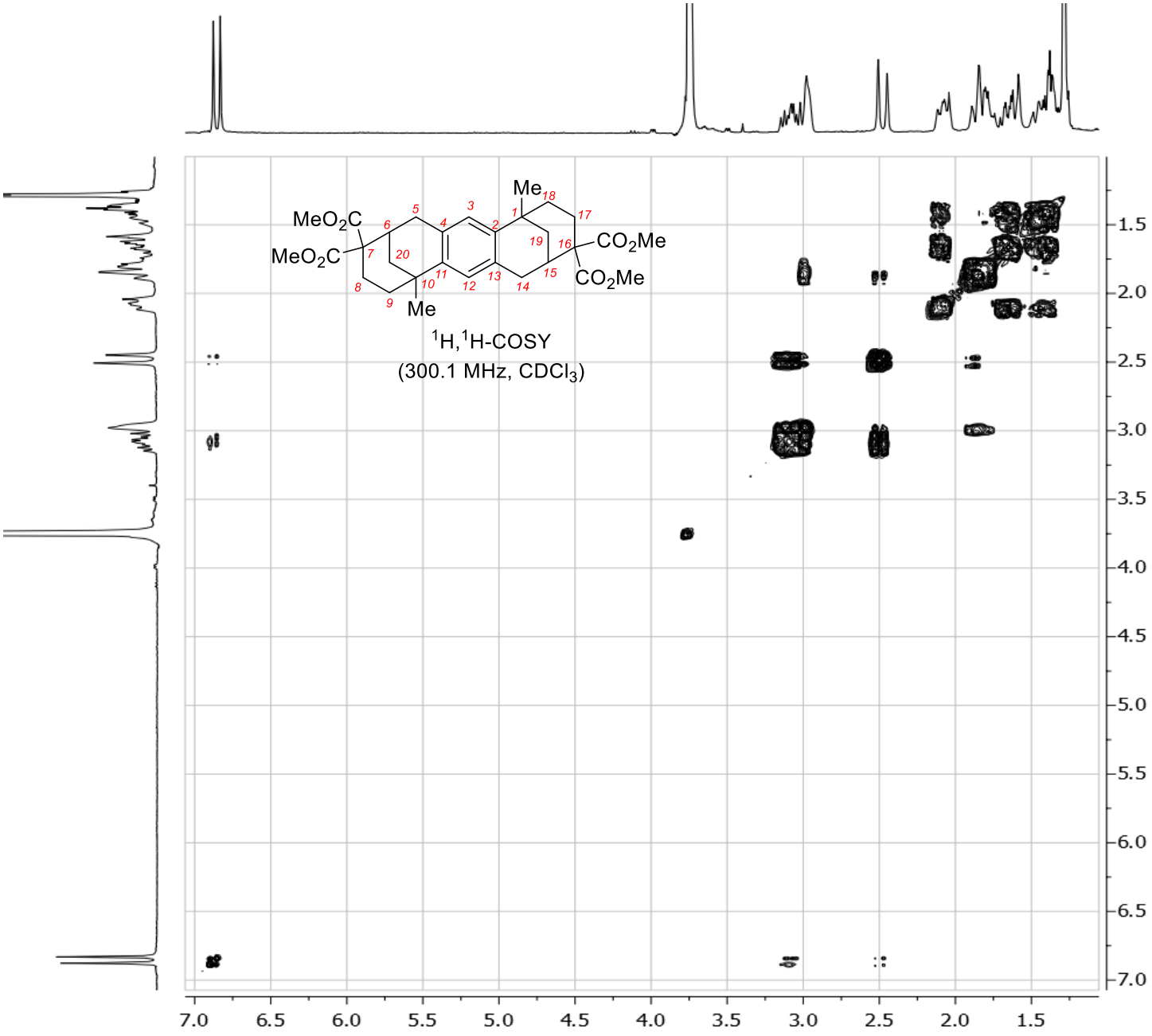


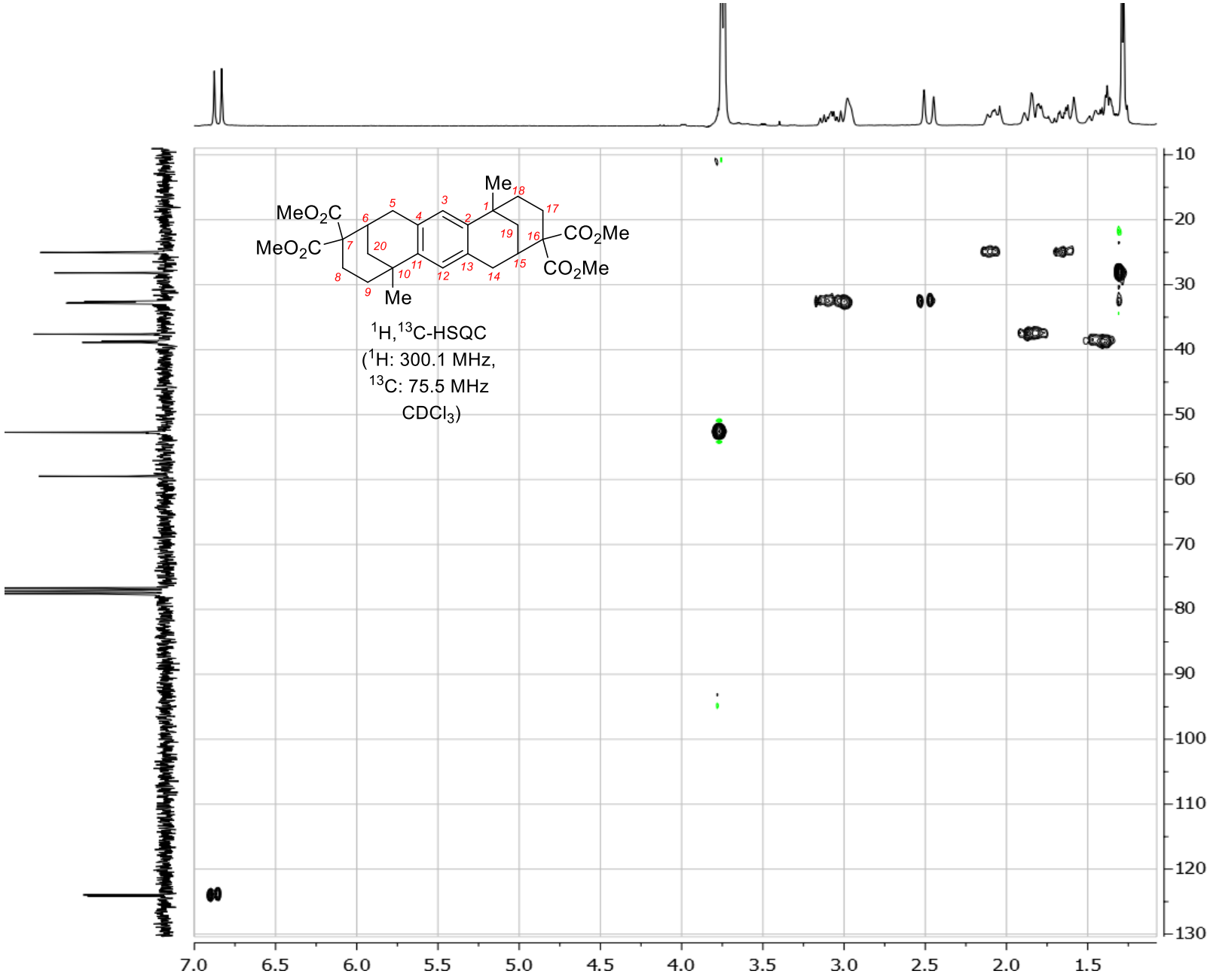
7a

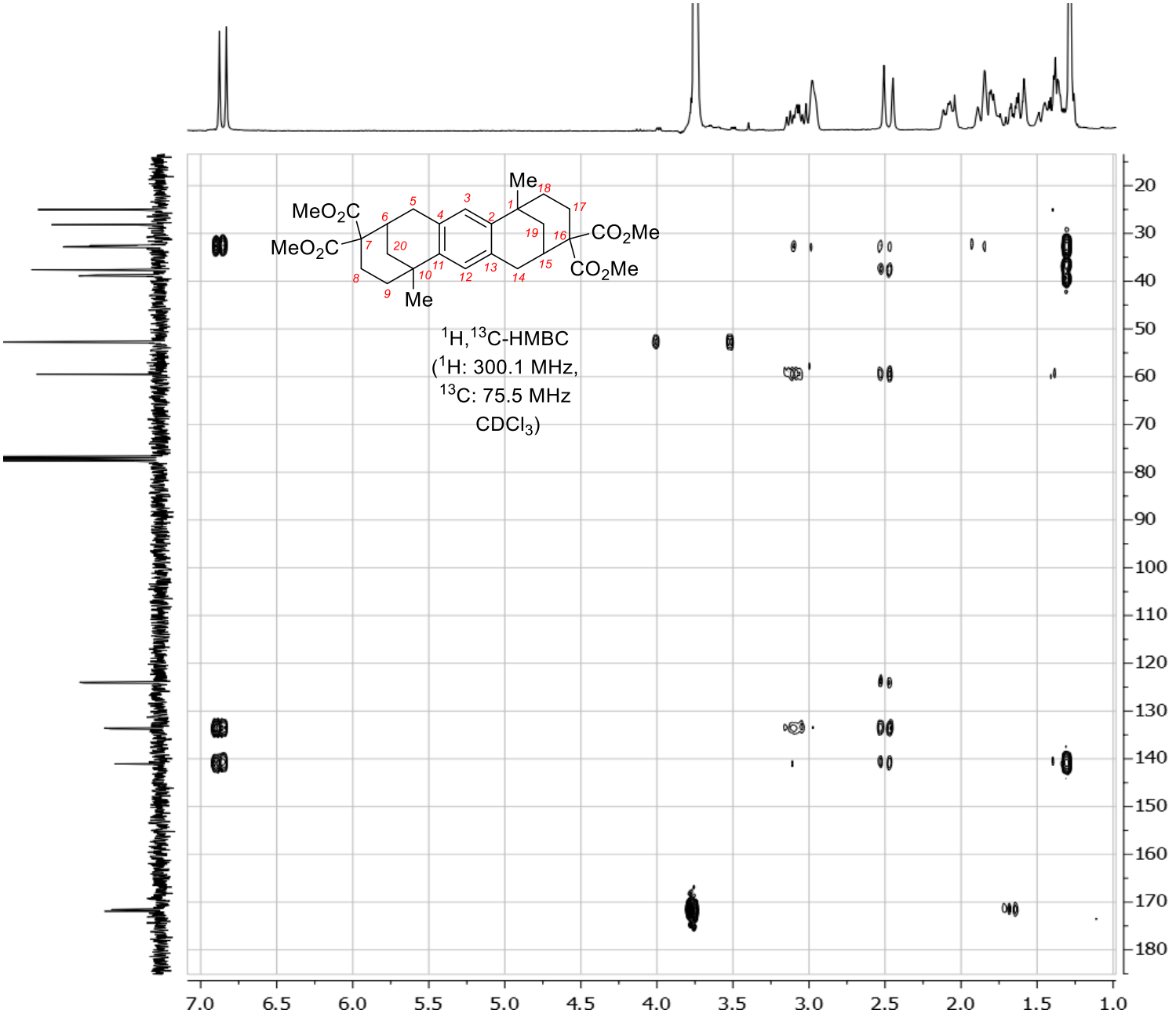
^{1}H NMR

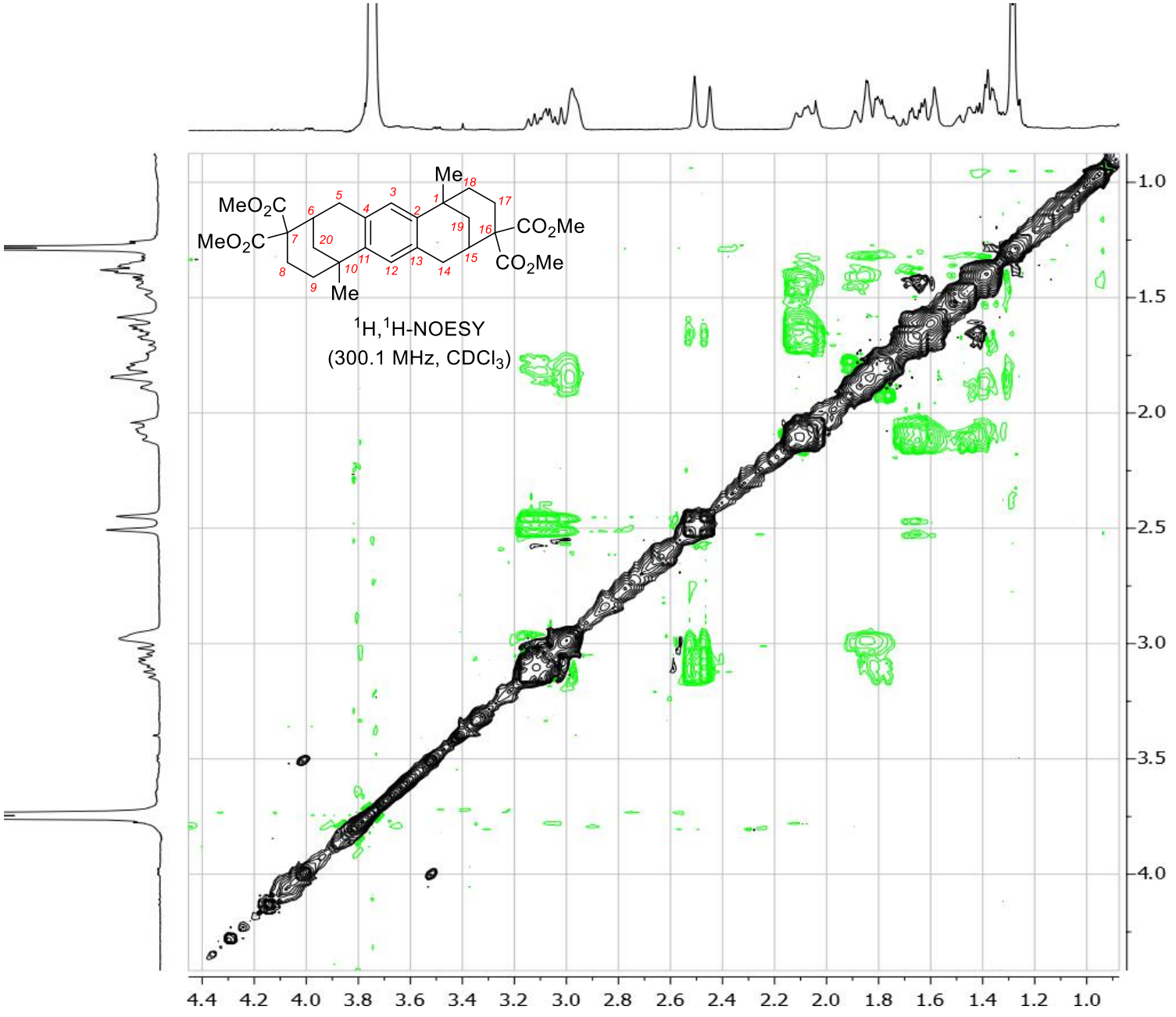
(300.1 MHz, $CDCl_3$)

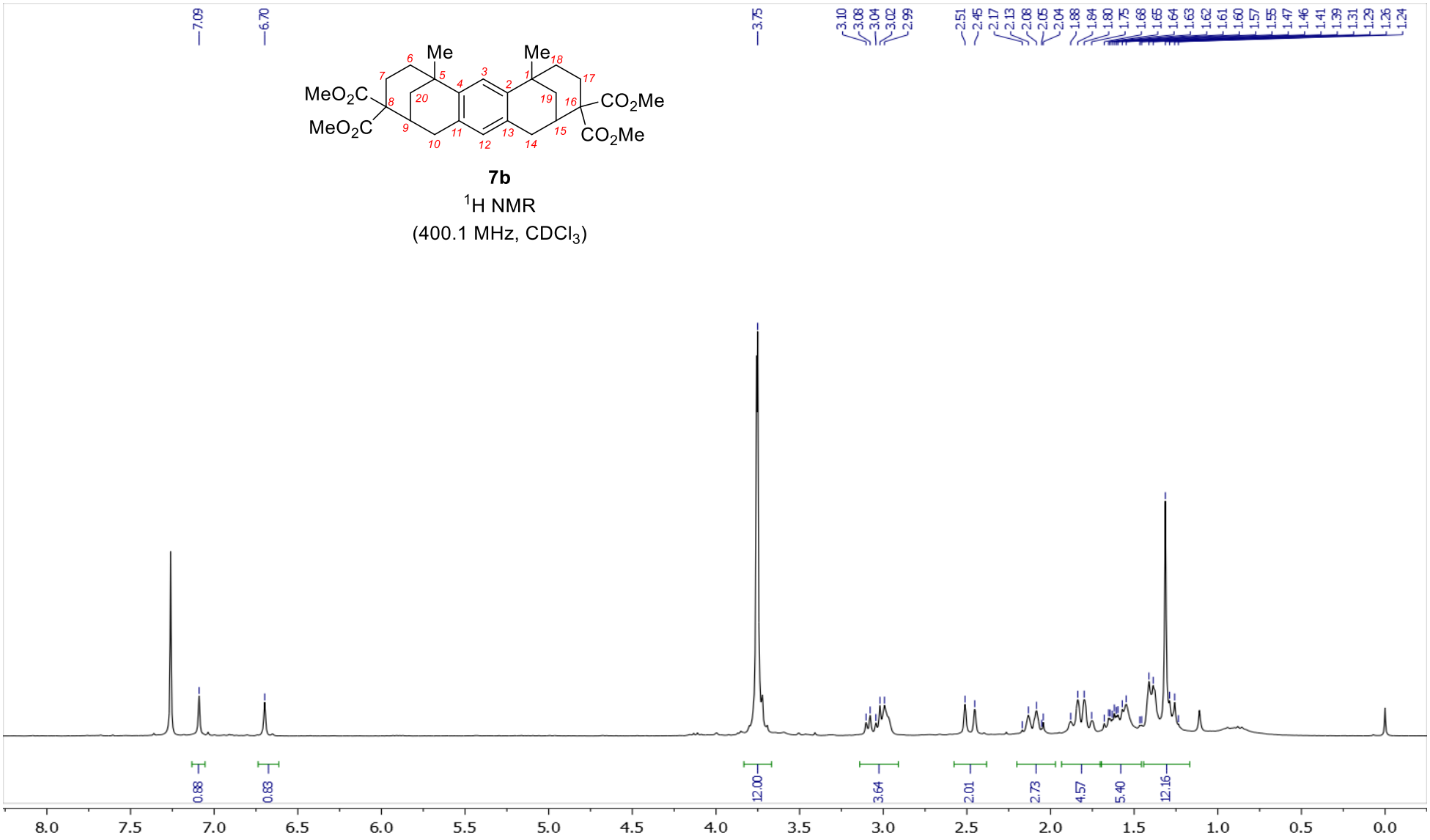

171.93
171.57
171.54
141.06
140.87
133.74
133.57
124.15
123.97
59.49
52.73
38.88
38.67
37.61
32.85
32.80
32.75
32.69
32.61
32.53
28.18
25.02
Me
MeO2C
MeO2C
CO2Me
CO2Me
Me
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Me
18
17
1
2
3
4
5
6
MeO2C
MeO2C
7
20
19
16
CO2Me
CO2Me
8
9
10
11
12
13
14
15
Me
1H,1H-COSY
(300.1 MHz, CDCl3)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


Me
18
17
1
3
5
4
2
6
MeO2C
19
16
CO2Me
7
20
MeO2C
11
15
CO2Me
10
12
13
14
8
9
Me
1H,13C-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
10
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


Me
MeO2C
MeO2C
CO2Me
CO2Me
Me
1H,13C-HMBC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

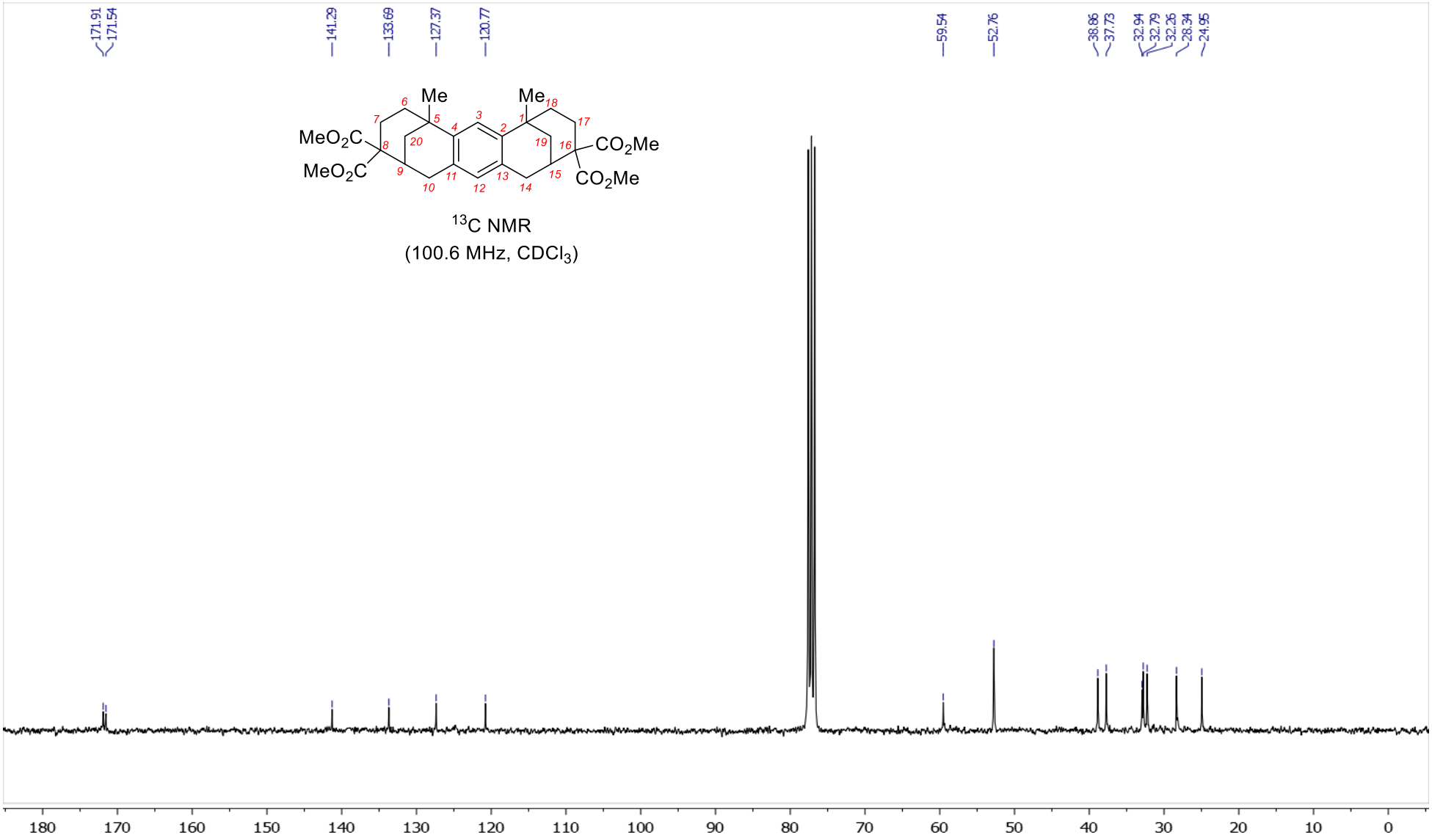

Me
18
MeO2C
MeO2C
CO2Me
CO2Me
Me
1H,1H-NOESY
(300.1 MHz, CDCl3)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0

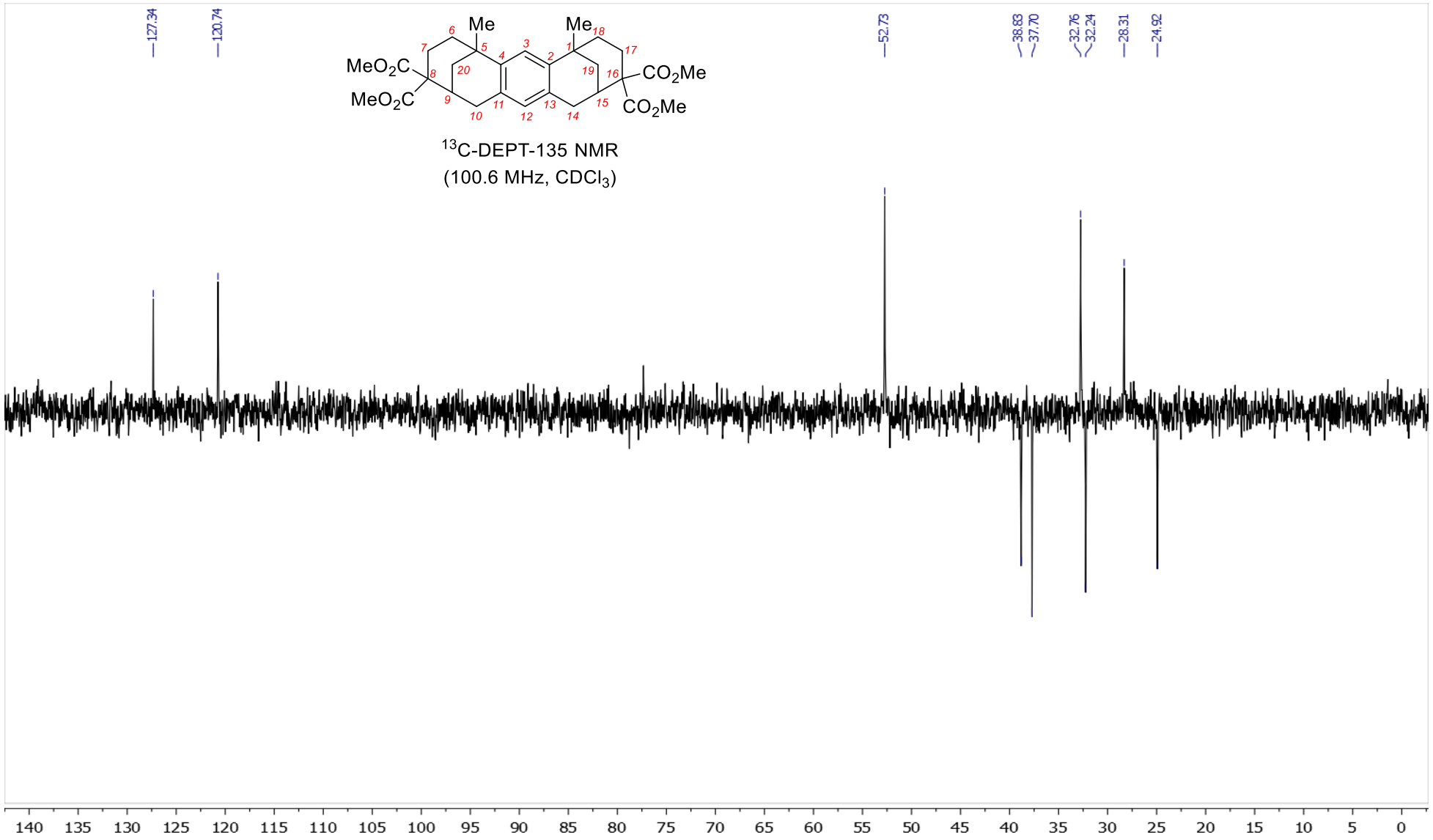


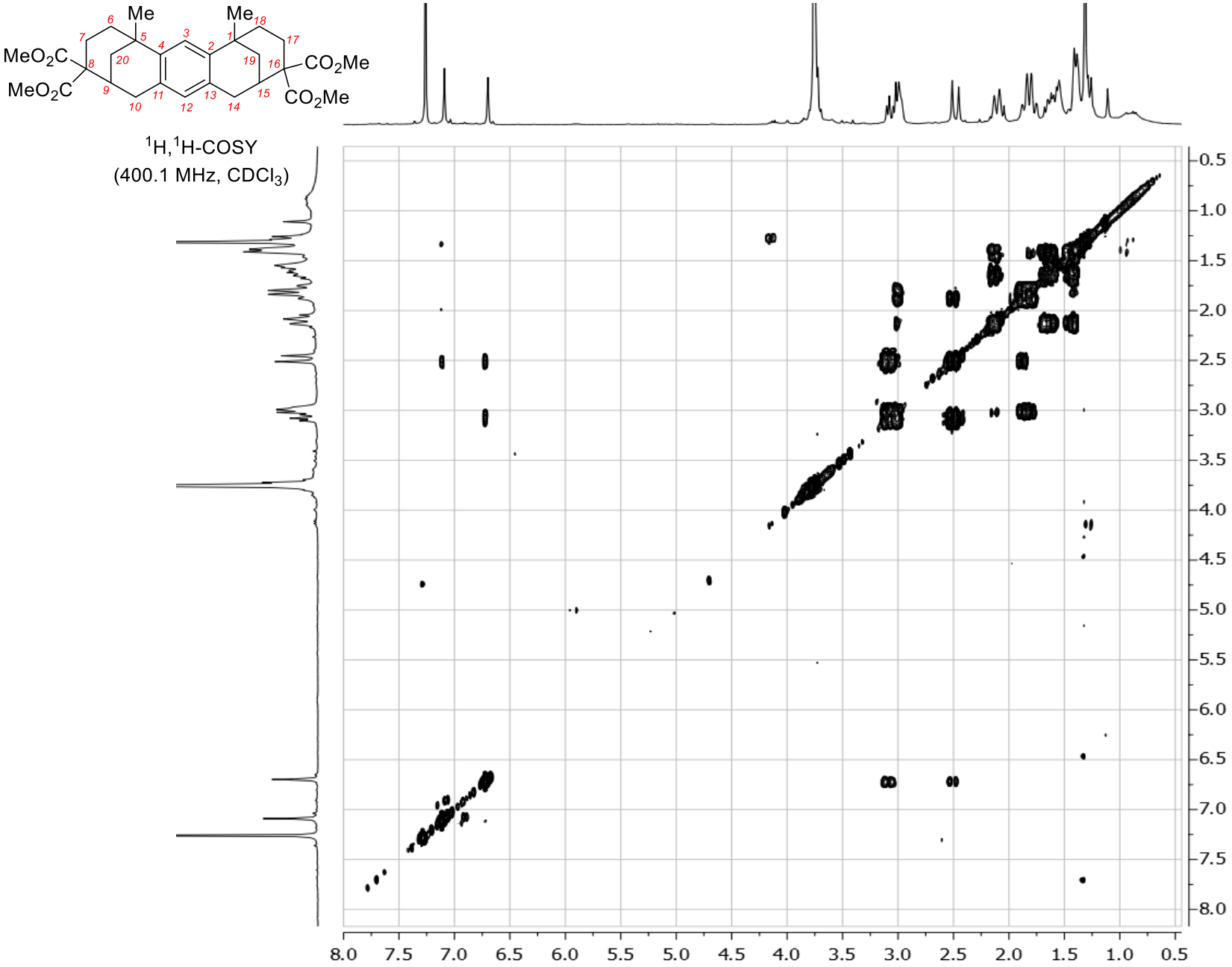
7b

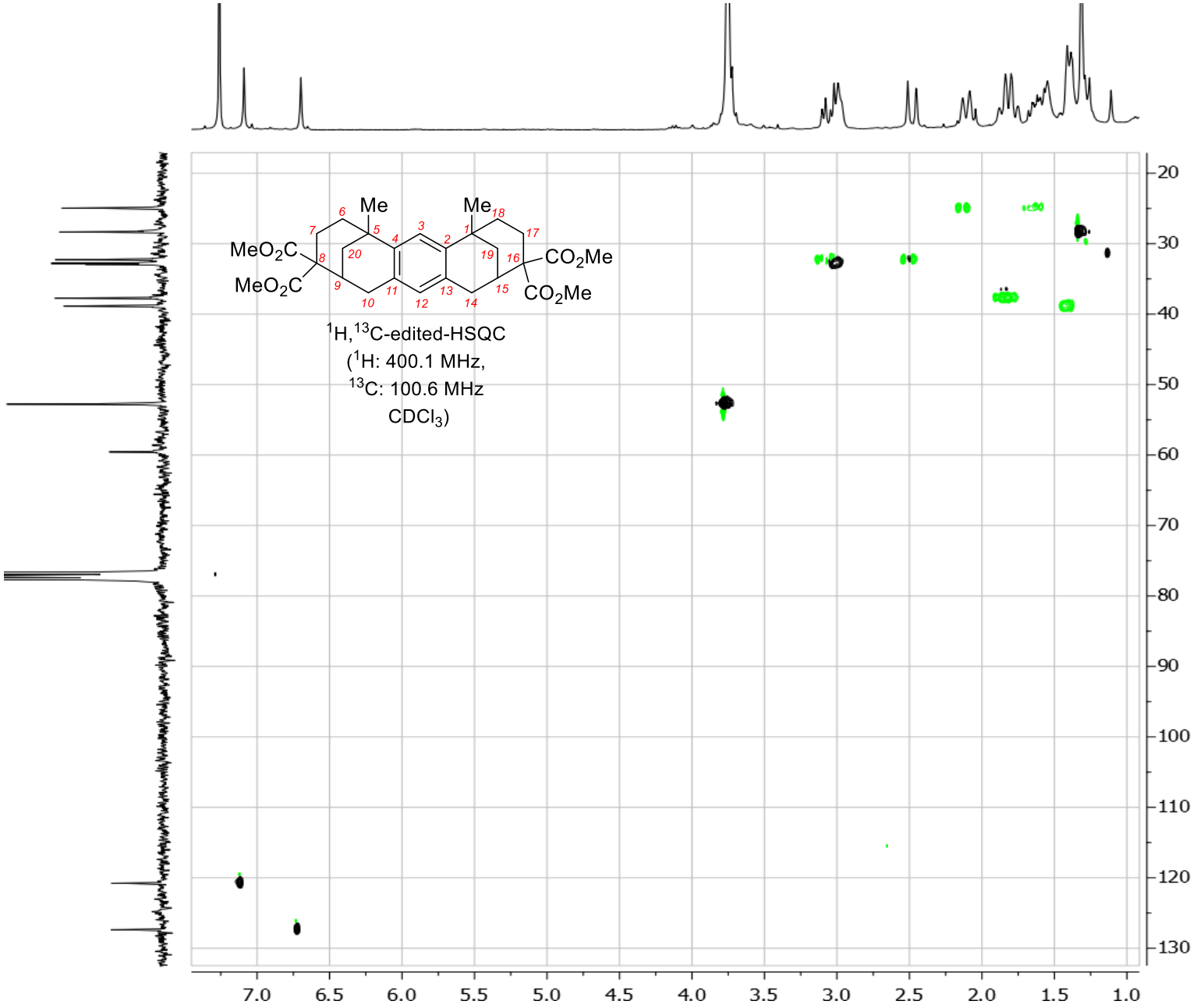
^{1}H NMR

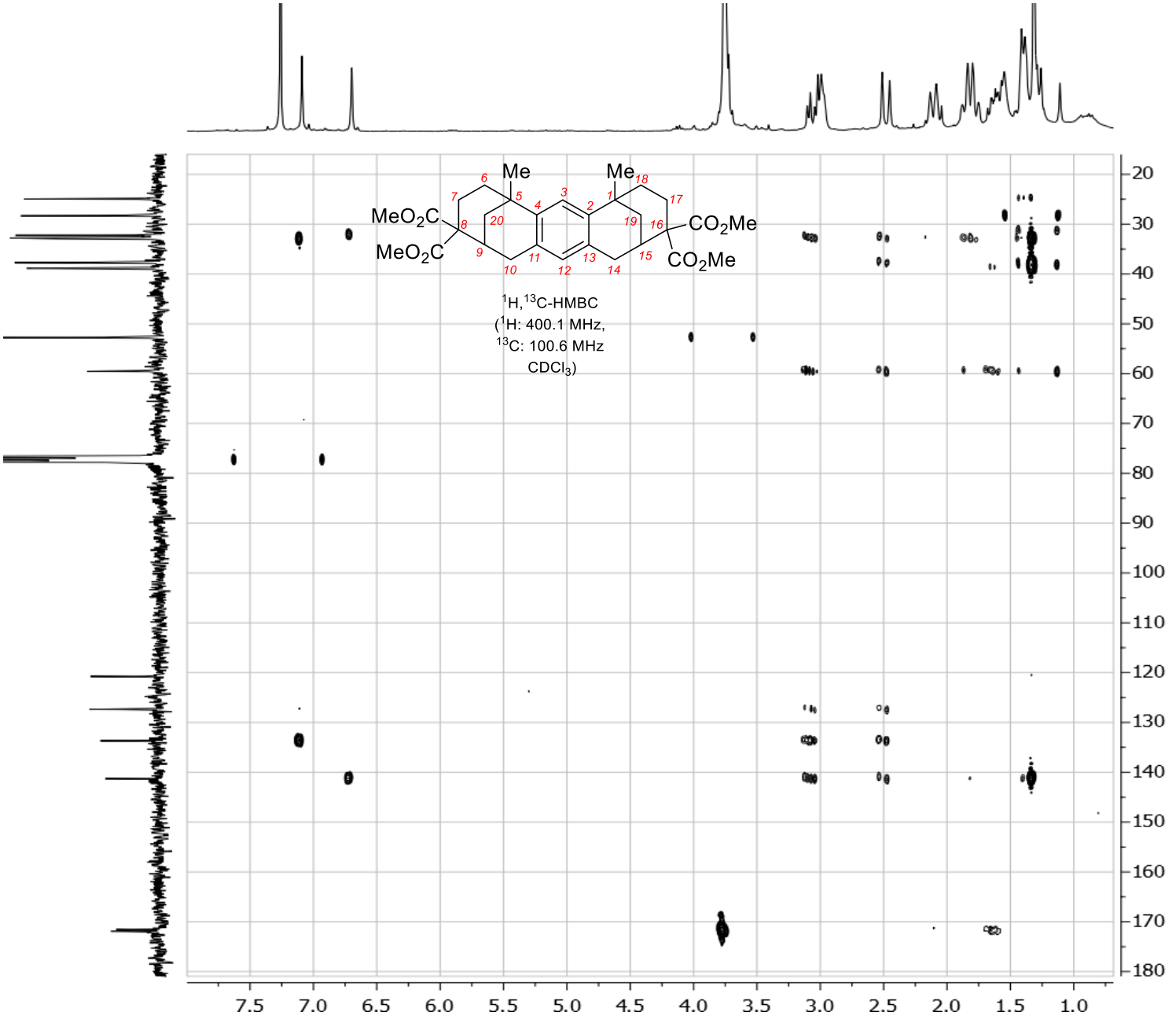
(400.1 MHz, $CDCl_3$)

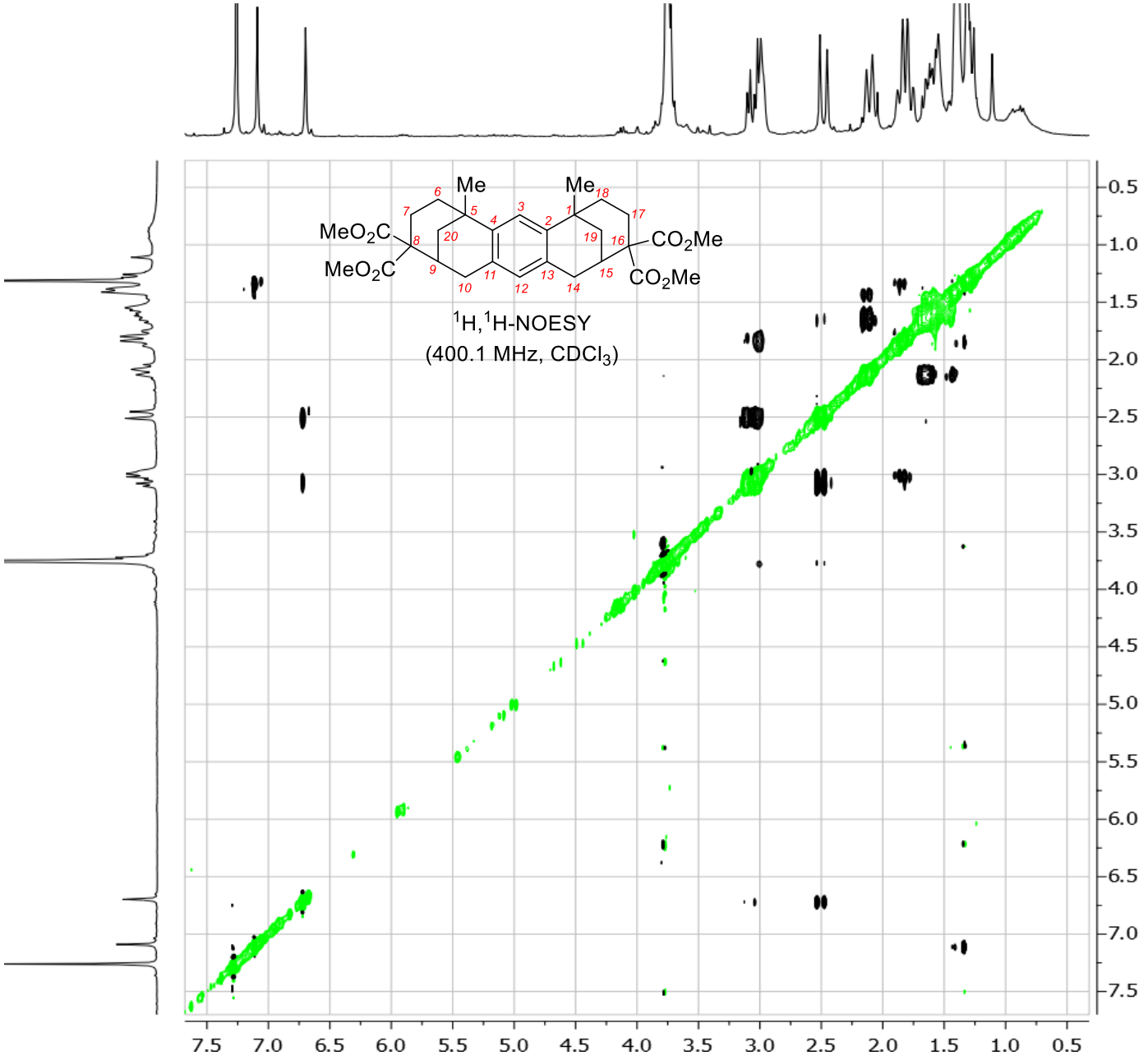

171.91
171.54
141.29
133.69
127.37
120.77
59.54
52.76
38.86
37.73
32.94
32.79
32.26
28.34
24.95
Me
Me
MeO2C
MeO2C
CO2Me
CO2Me
13C NMR
(100.6 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

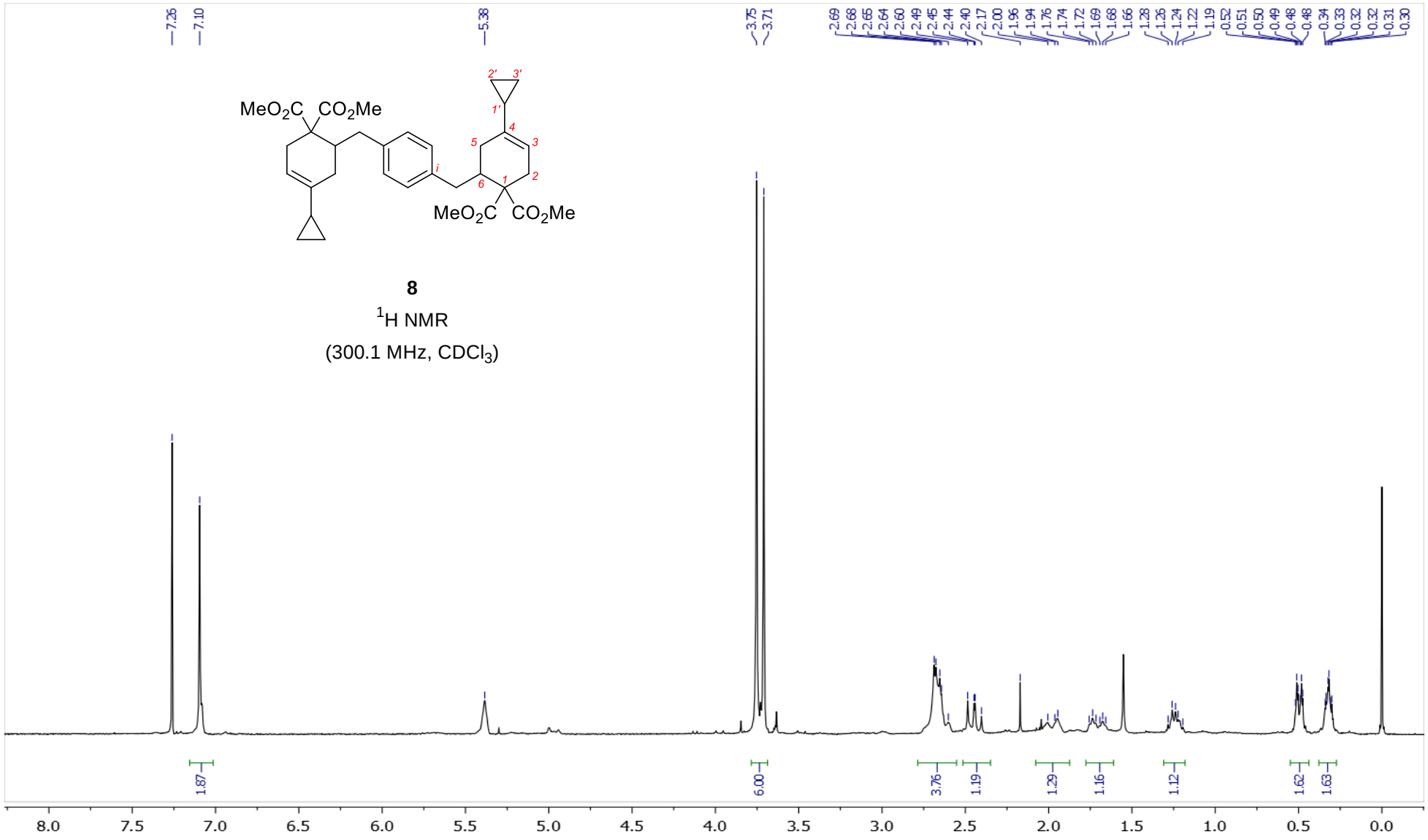

127.34
120.74
52.73
38.83
37.70
32.76
32.24
28.31
24.92
Me
Me
MeO2C
MeO2C
CO2Me
CO2Me
13C-DEPT-135 NMR
(100.6 MHz, CDCl3)
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0


Me
Me
MeO2C
MeO2C
CO2Me
CO2Me
1H,1H-COSY
(400.1 MHz, CDCl3)
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 1.0 0.5
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0


Me
Me
MeO2C
MeO2C
CO2Me
CO2Me
1H,13C-edited-HSQC
(1H: 400.1 MHz,
13C: 100.6 MHz
CDCl3)
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


Me
Me
MeO2C
MeO2C
CO2Me
CO2Me
1H,13C-HMBC
(1H: 400.1 MHz,
13C: 100.6 MHz
CDCl3)
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
1.0
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

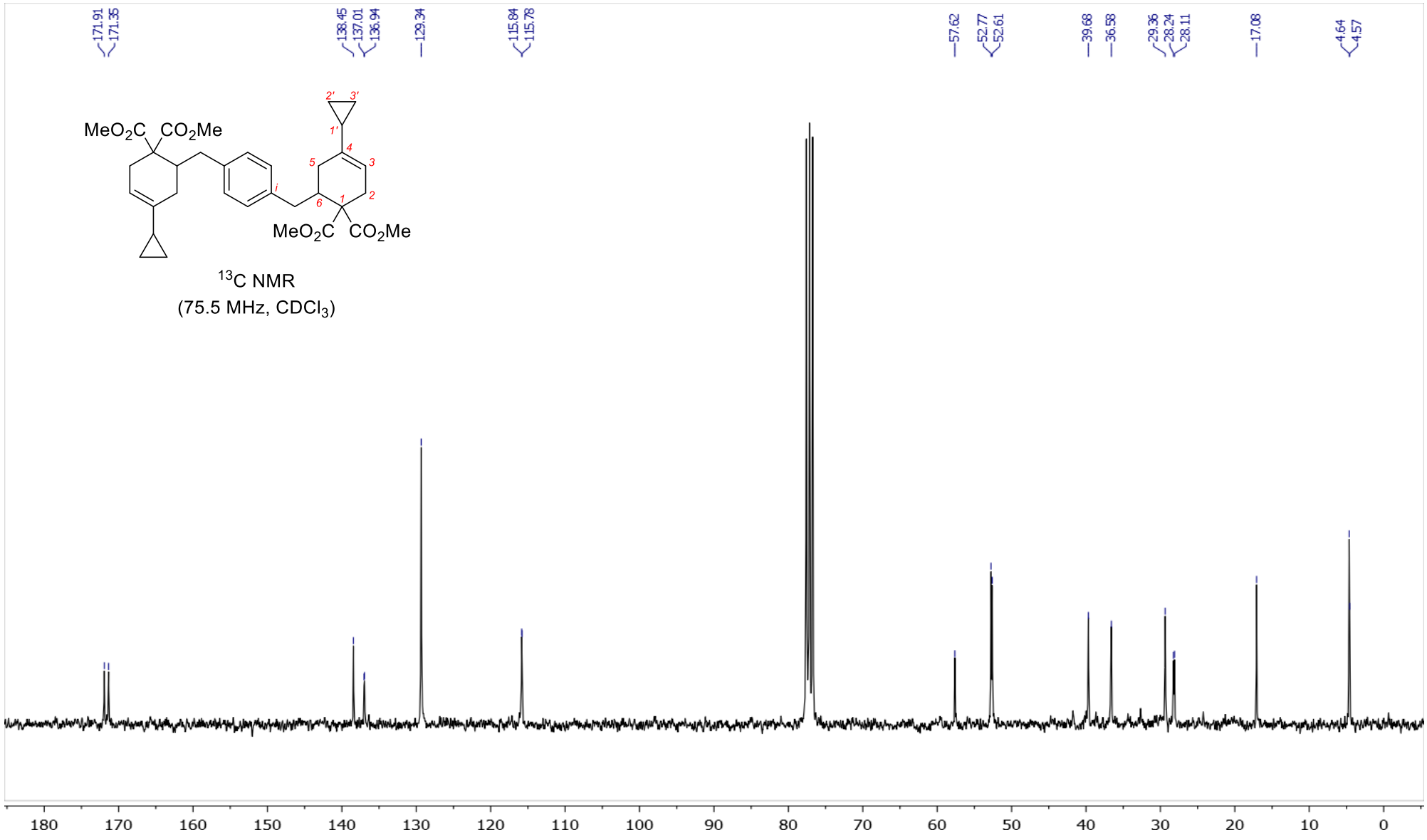

Me
Me
MeO2C
MeO2C
CO2Me
CO2Me
1H,1H-NOESY
(400.1 MHz, CDCl3)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

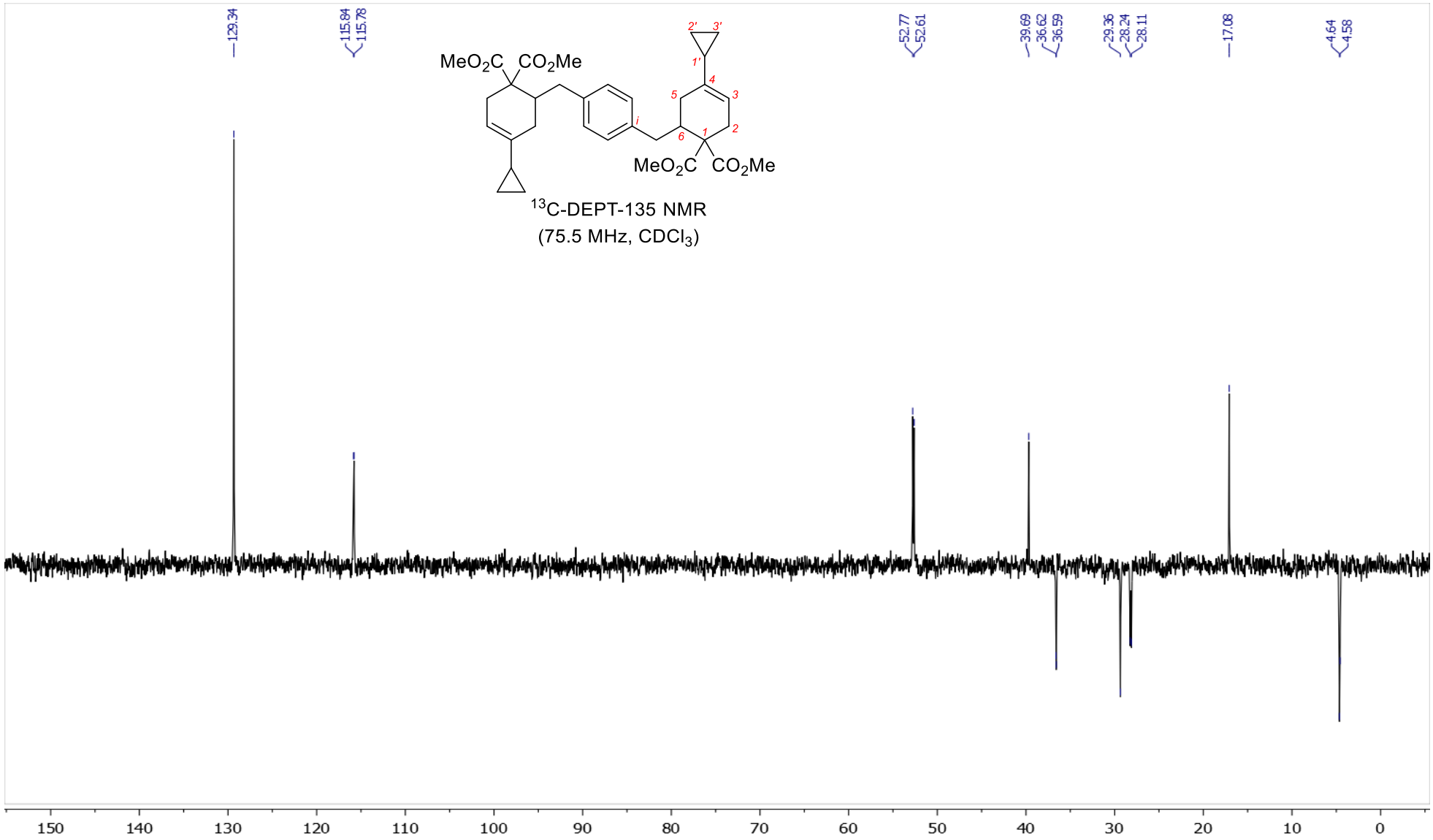


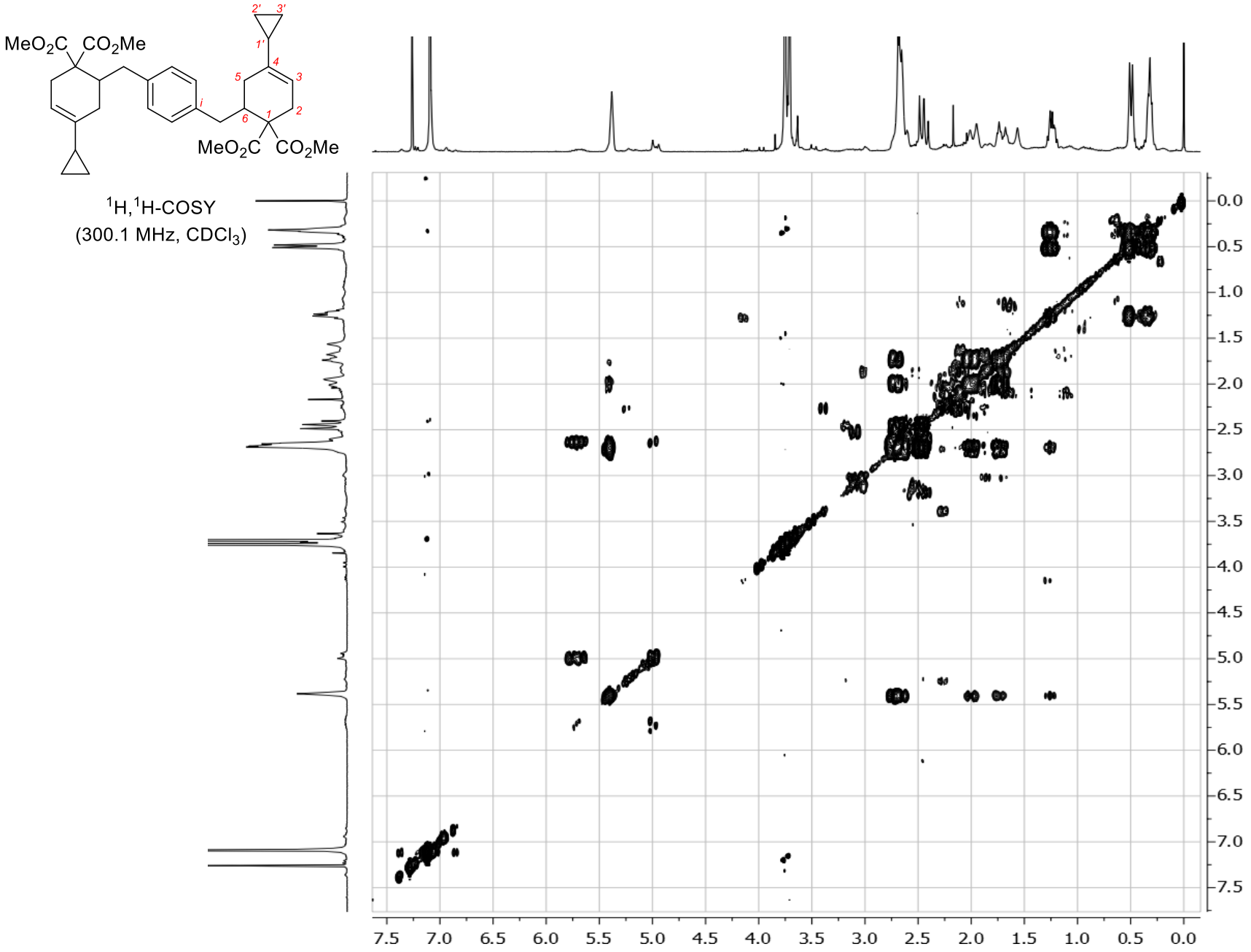
8

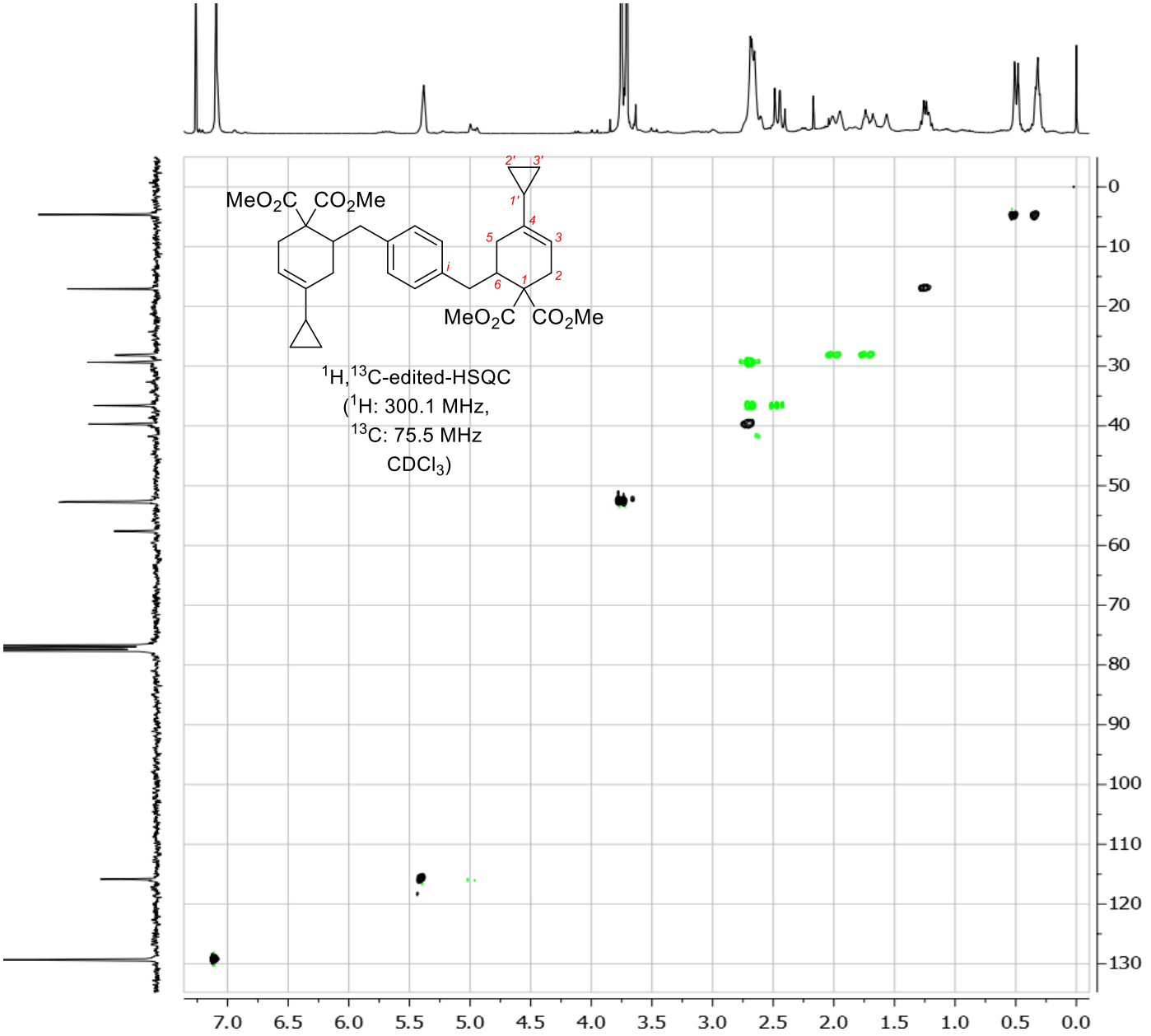
^{1}H NMR

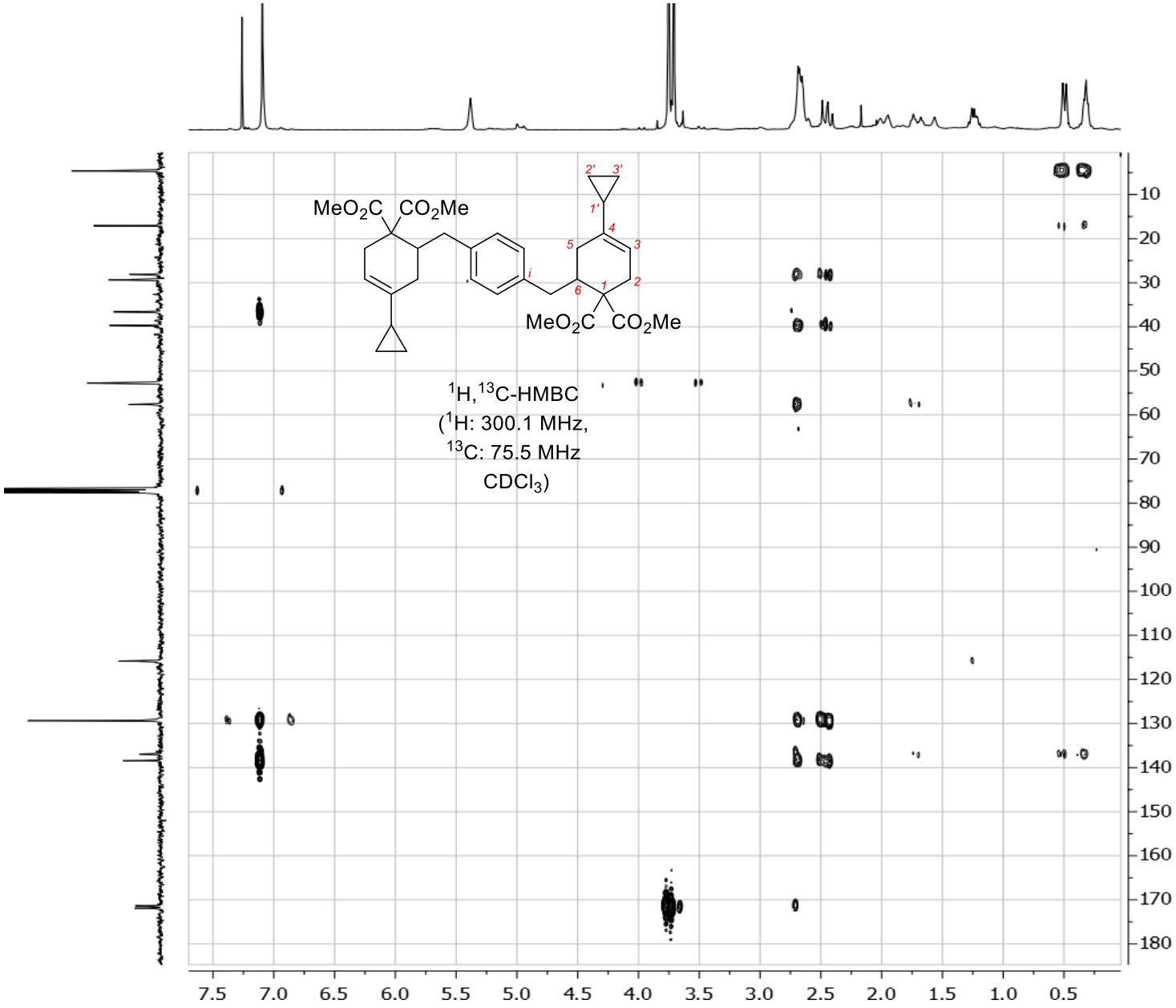
(300.1 MHz, $CDCl_3$)

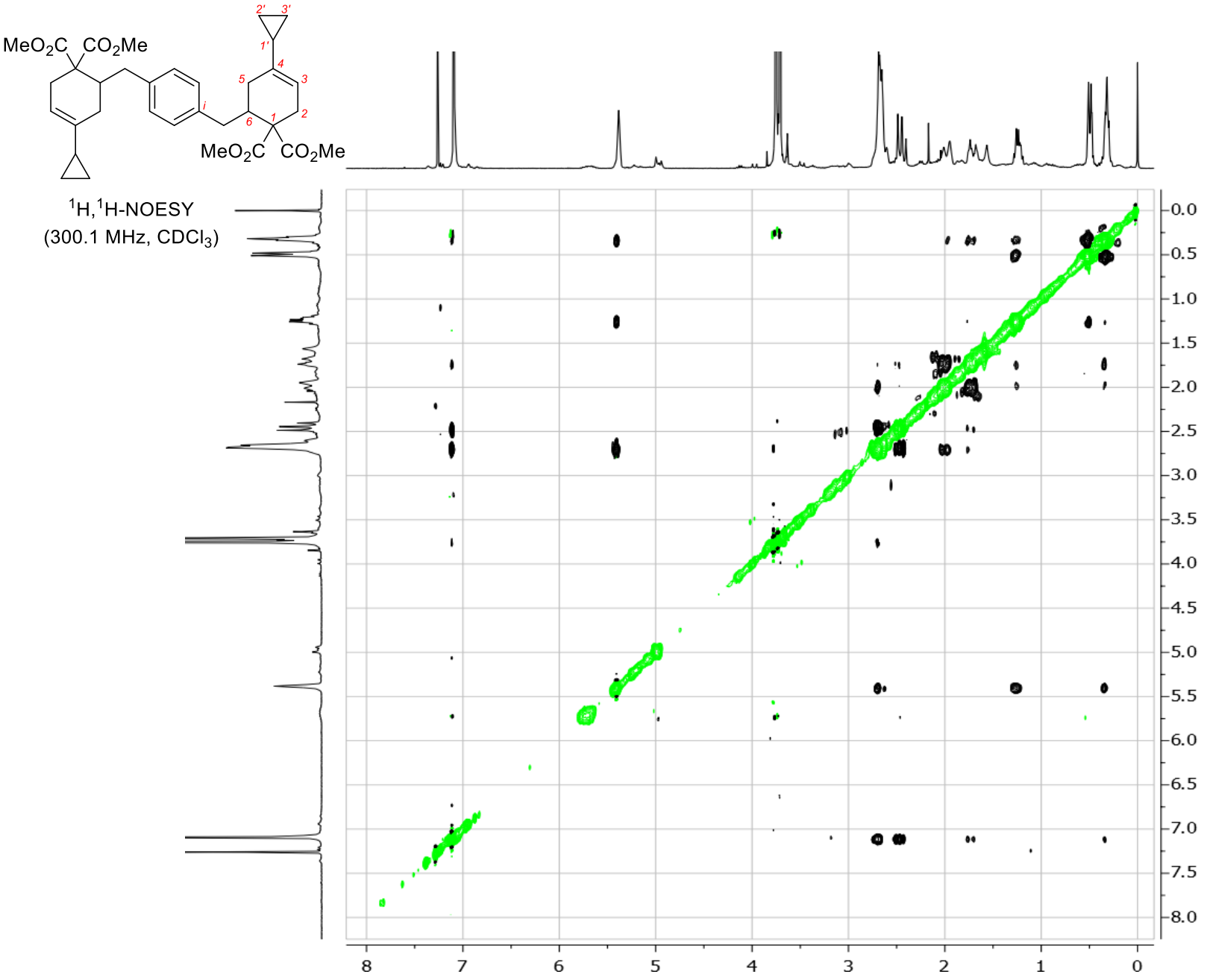

171.91
171.35
138.45
137.01
136.94
129.34
115.84
115.78
57.62
52.77
52.61
39.68
36.58
29.35
28.24
28.11
17.08
4.64
4.57
MeO2C CO2Me
MeO2C CO2Me
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

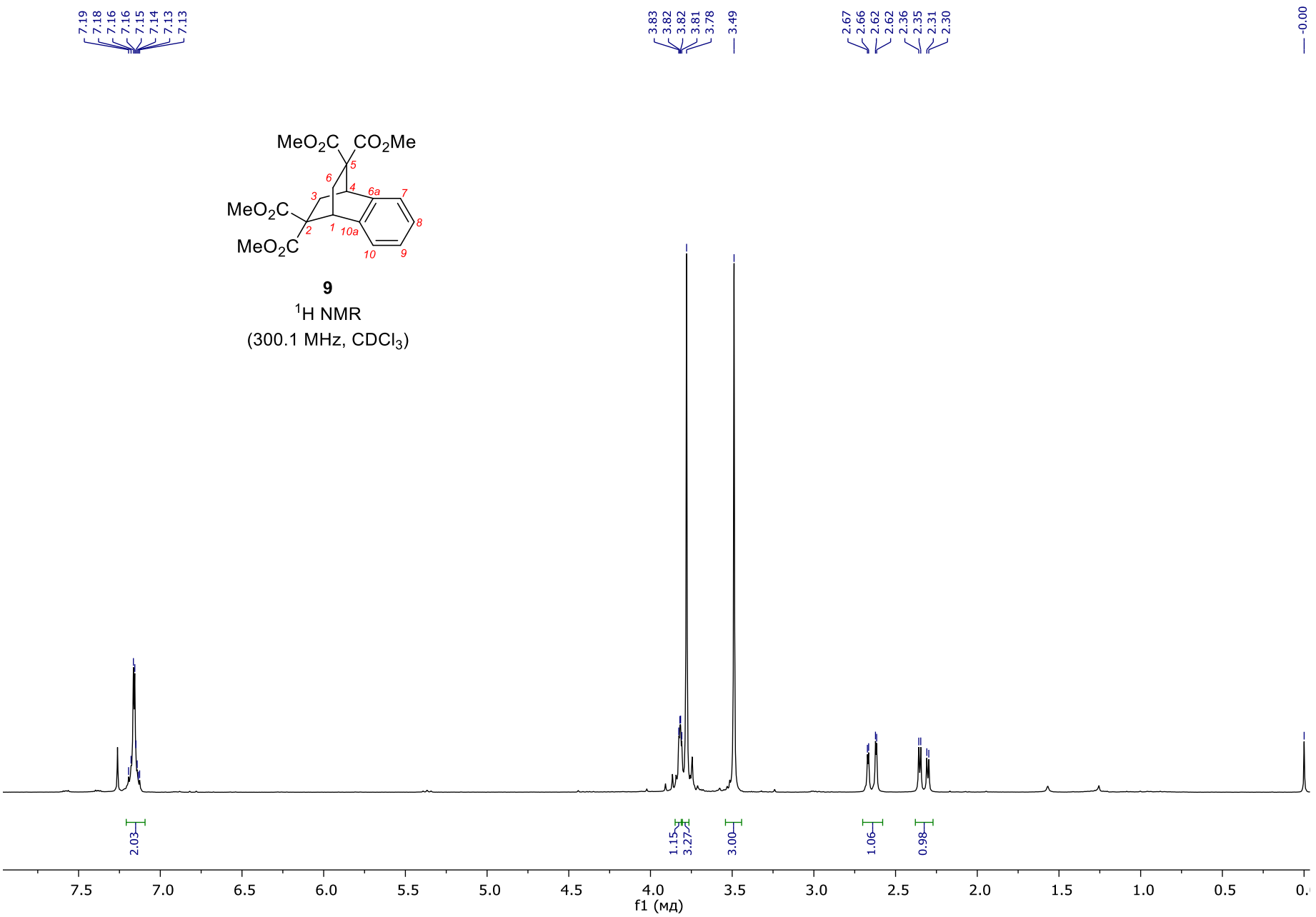

129.34
115.84
115.78
52.77
52.61
39.69
36.62
36.59
29.36
28.24
28.11
17.08
4.64
4.58
MeO2C CO2Me
MeO2C CO2Me
13C-DEPT-135 NMR
(75.5 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


MeO2C CO2Me
MeO2C CO2Me
1H,1H-COSY
(300.1 MHz, CDCl3)
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 1.0 0.5 0.0

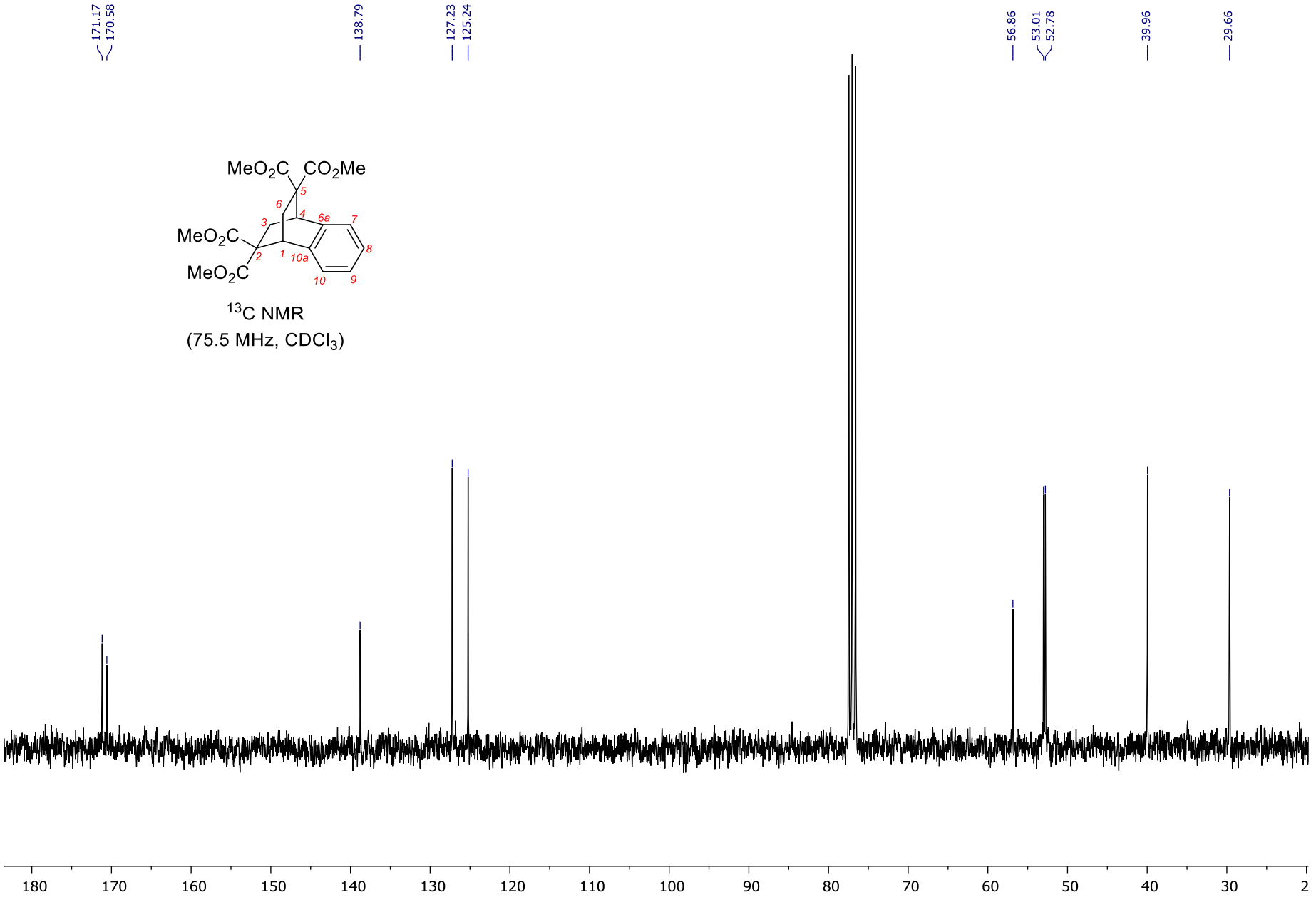

MeO2C CO2Me
MeO2C CO2Me
1H,13C-edited-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

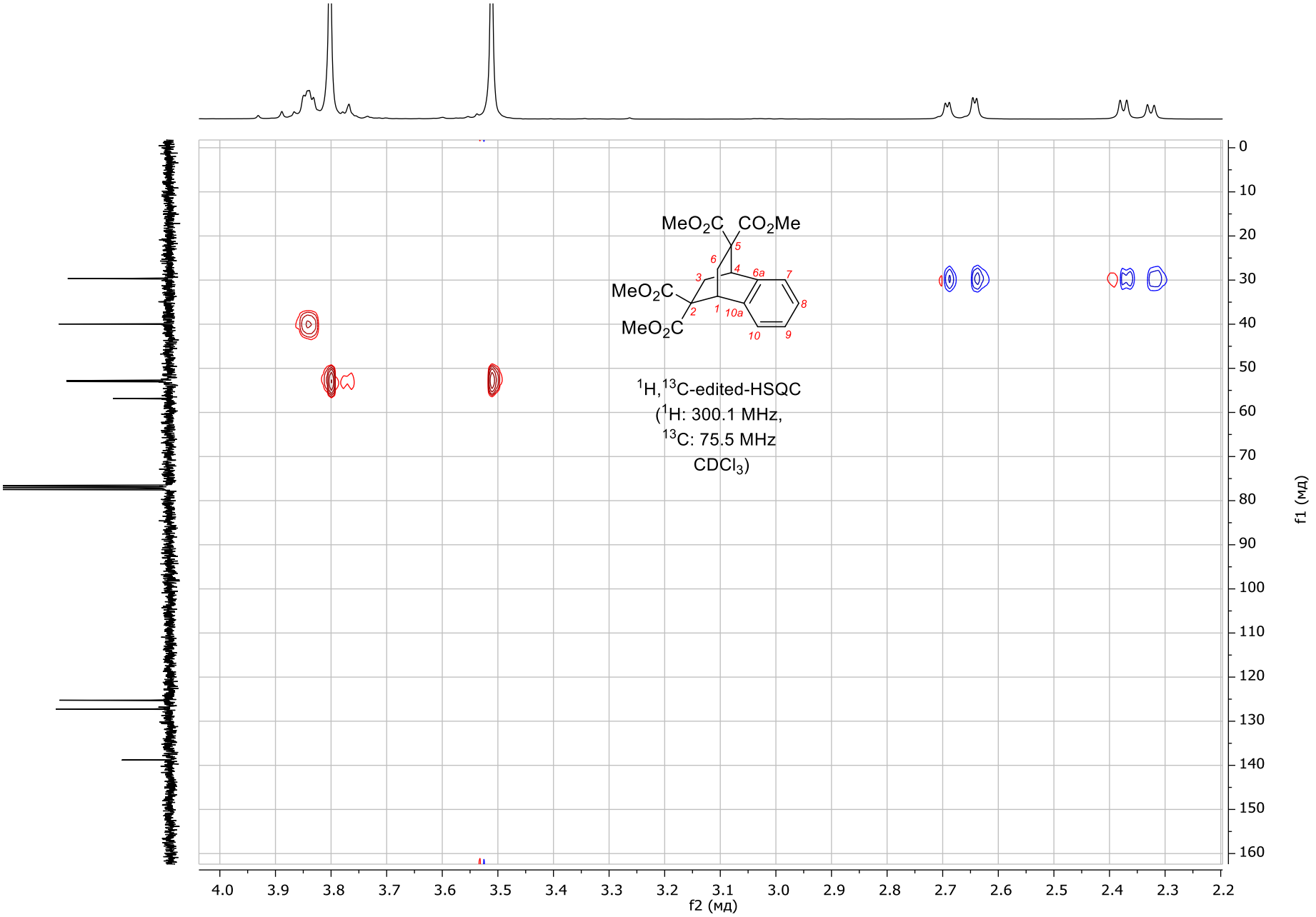

MeO2C CO2Me
MeO2C CO2Me
1H,13C-HMBC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

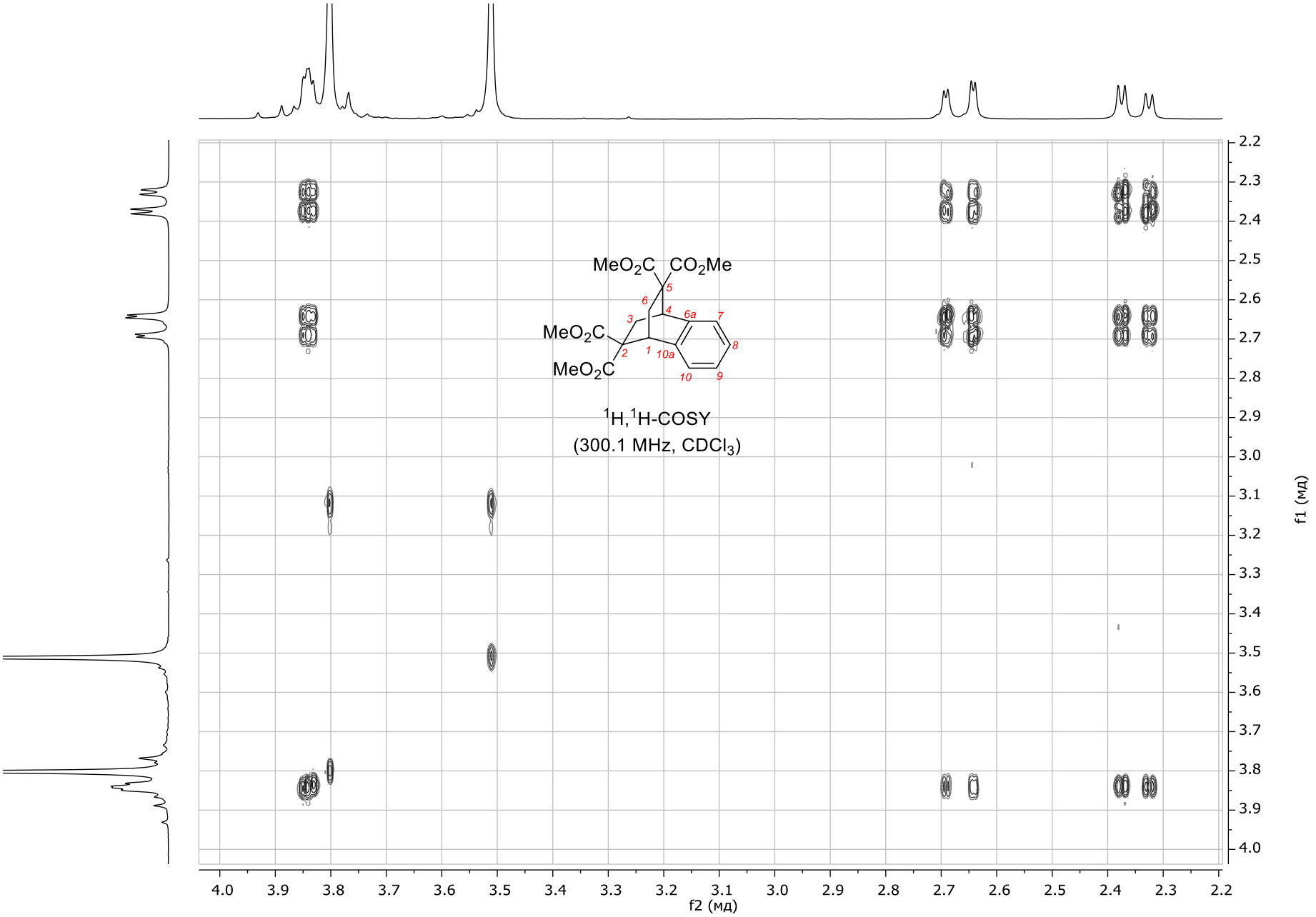

MeO2C CO2Me
MeO2C CO2Me
1H,1H-NOESY
(300.1 MHz, CDCl3)

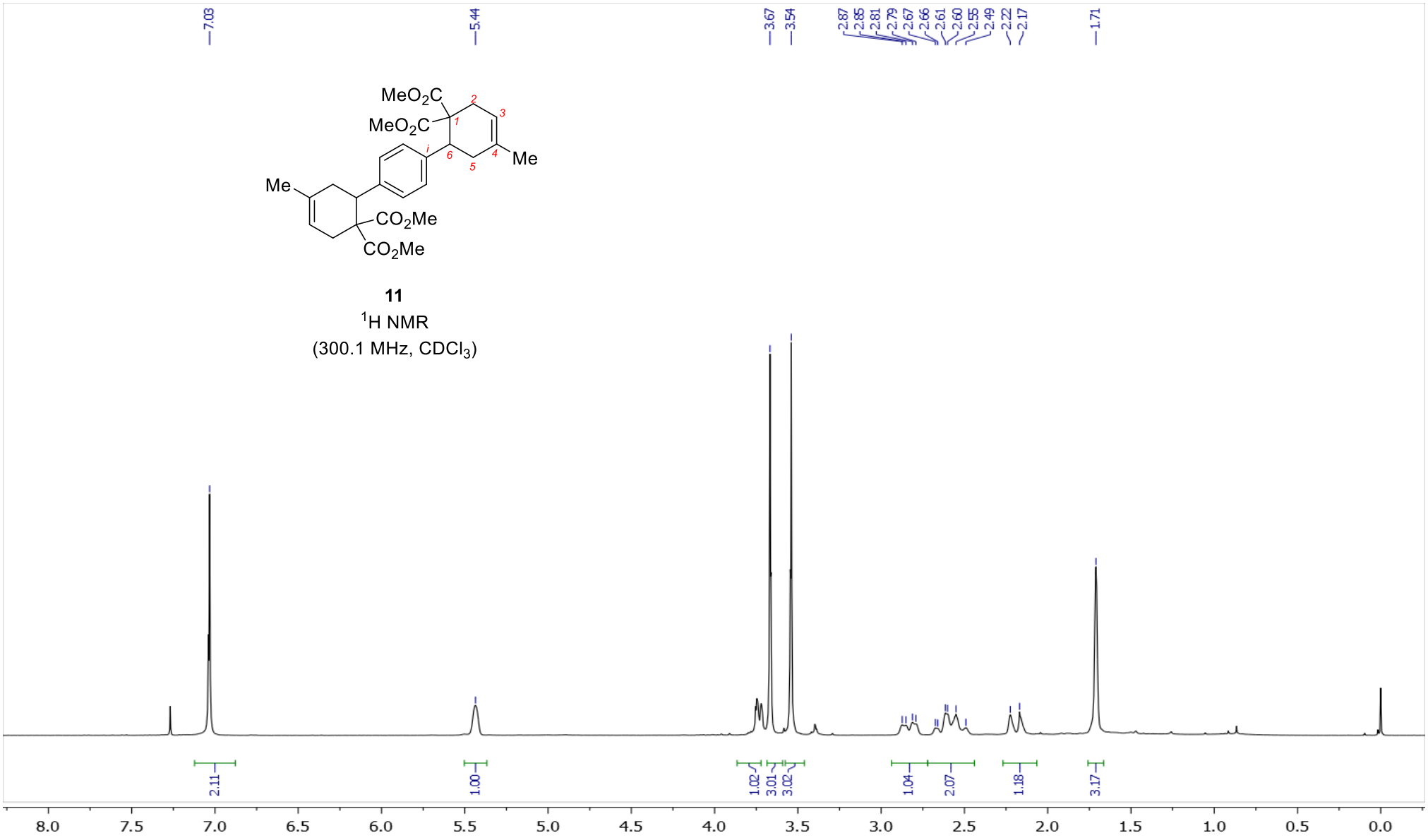

7.19
7.18
7.16
7.16
7.15
7.14
7.13
7.13
3.83
3.82
3.82
3.81
3.78
3.49
2.67
2.66
2.62
2.62
2.36
2.35
2.31
2.30
-0.00
MeO2C
CO2Me
MeO2C
MeO2C
1
2
3
4
5
6
6a
7
8
9
10
10a
9
1H NMR
(300.1 MHz, CDCl3)
2.03
1.15
3.27
3.00
1.06
0.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (мд)

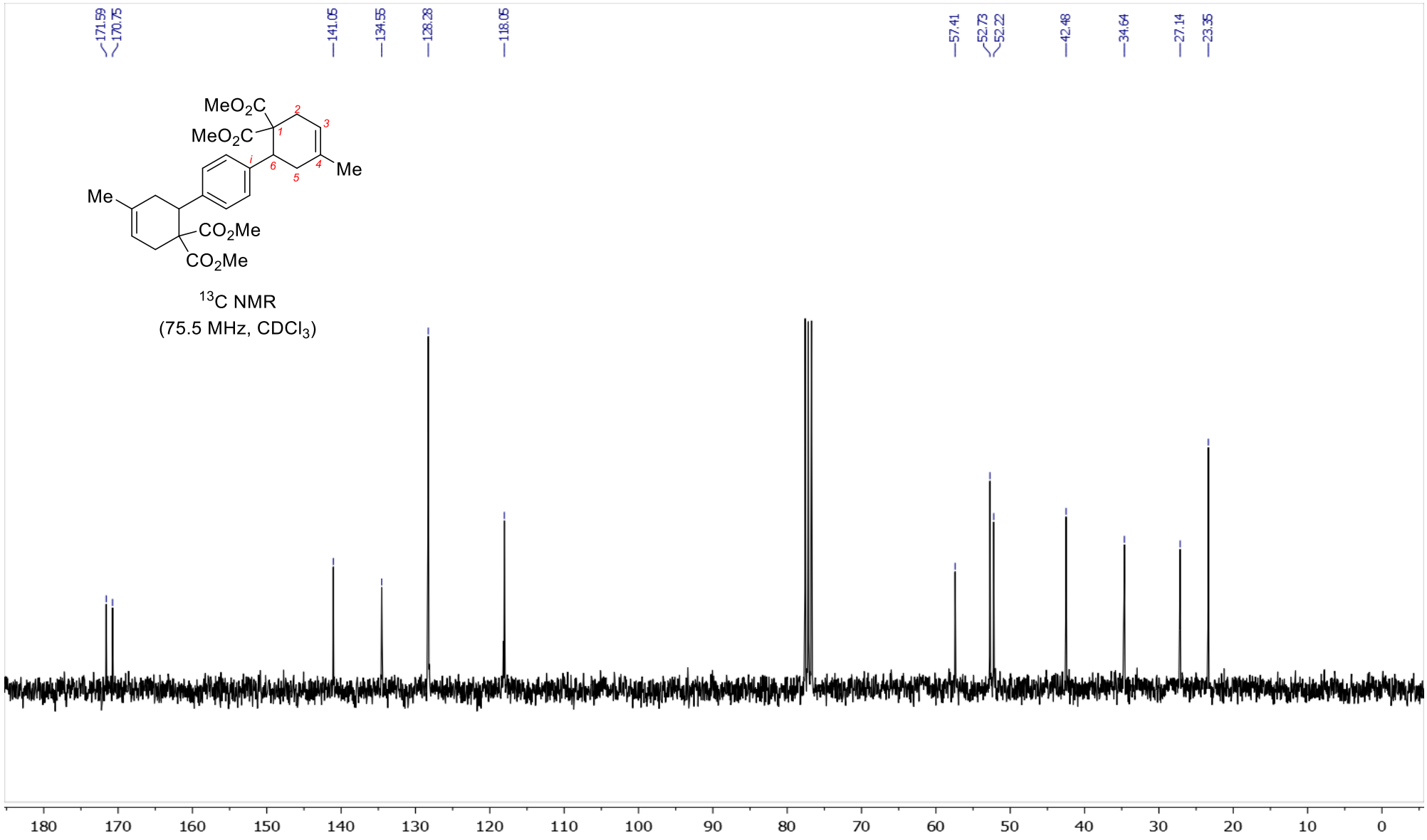
9

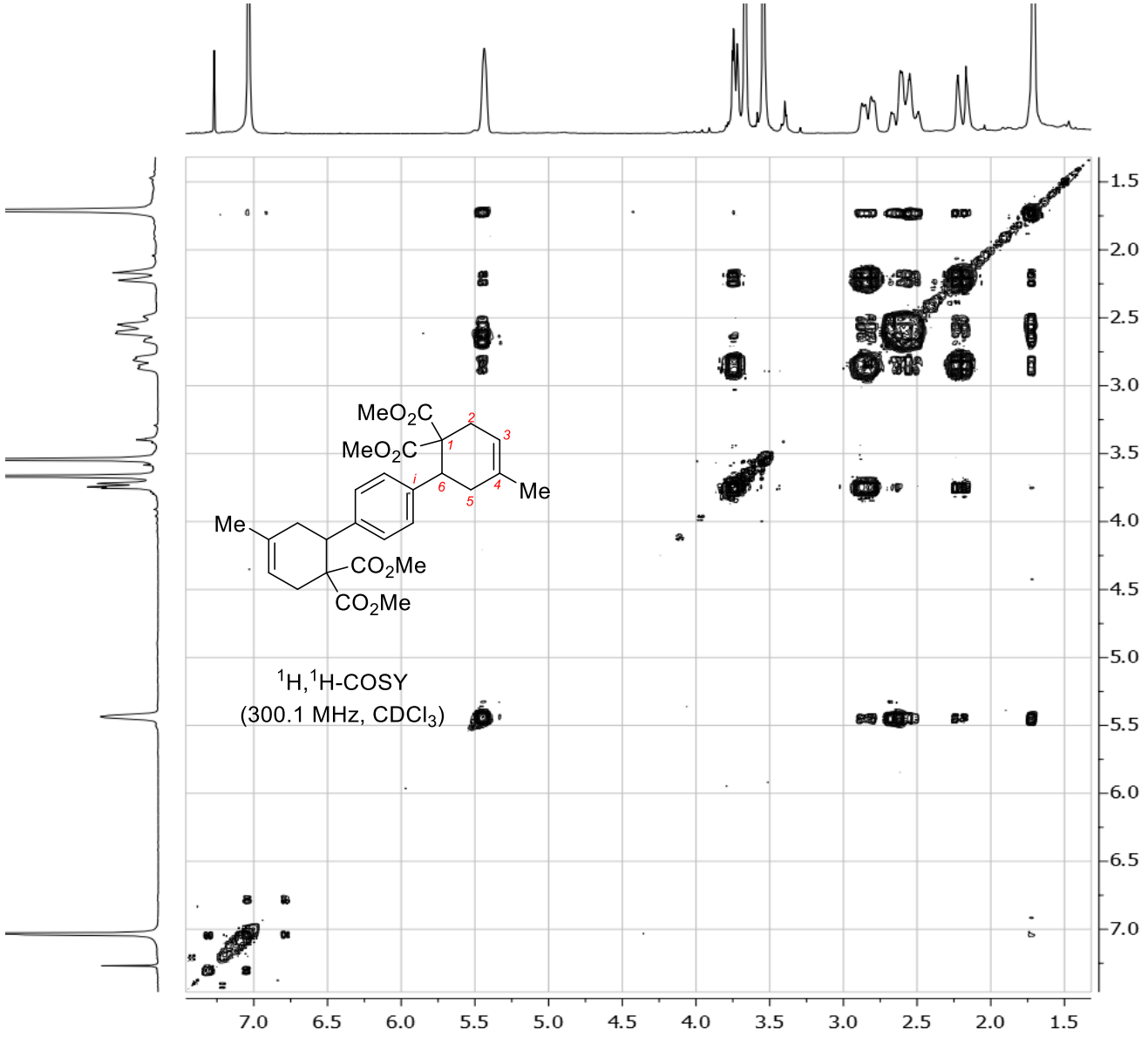

171.17
170.58
138.79
127.23
125.24
56.86
53.01
52.78
39.96
29.66
MeO2C
CO2Me
MeO2C
MeO2C
1
2
3
4
5
6
6a
7
8
9
10
10a
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
2

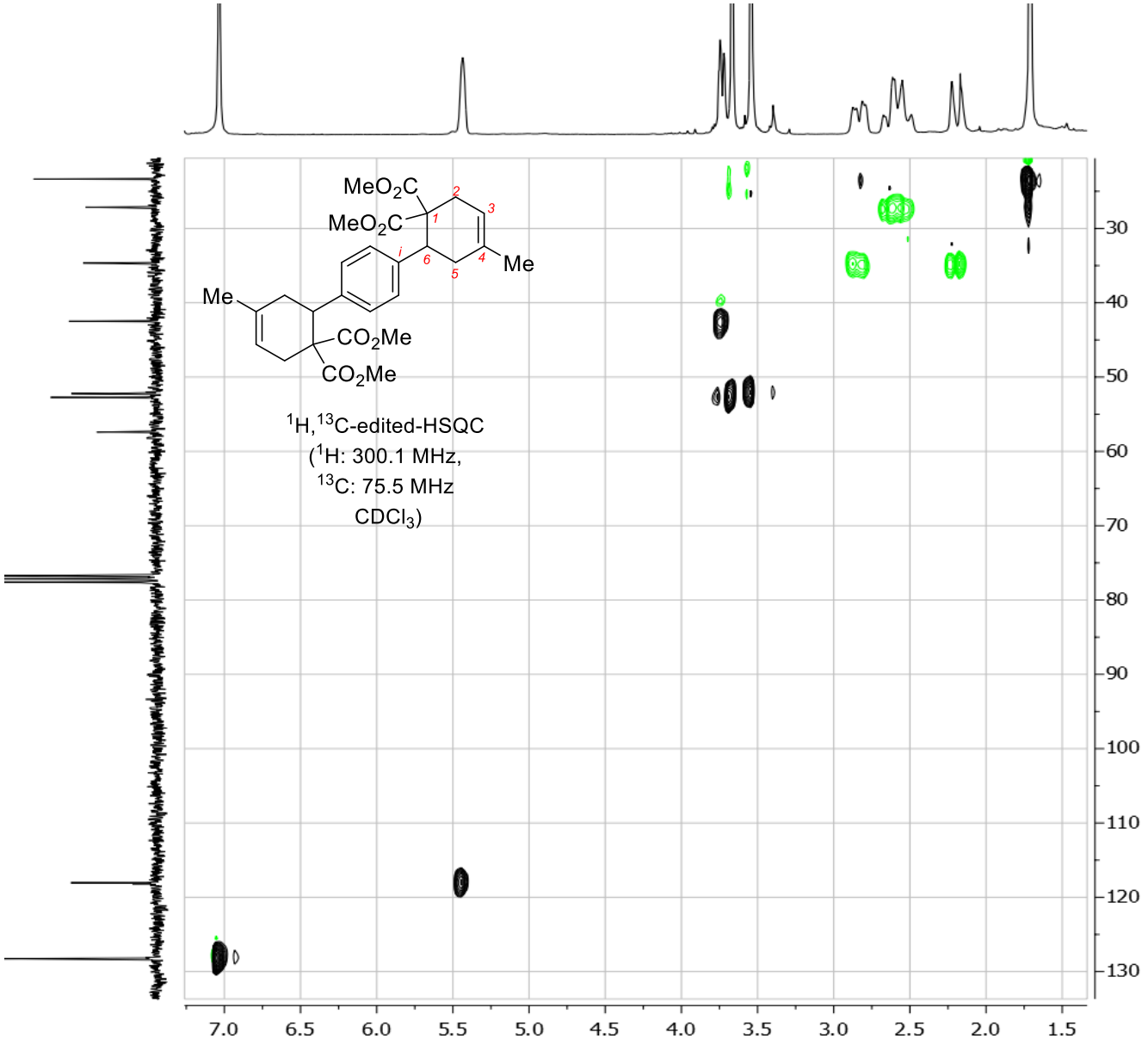

MeO2C CO2Me
MeO2C
MeO2C
1H,13C-edited-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
f2 (мд)
f1 (мд)

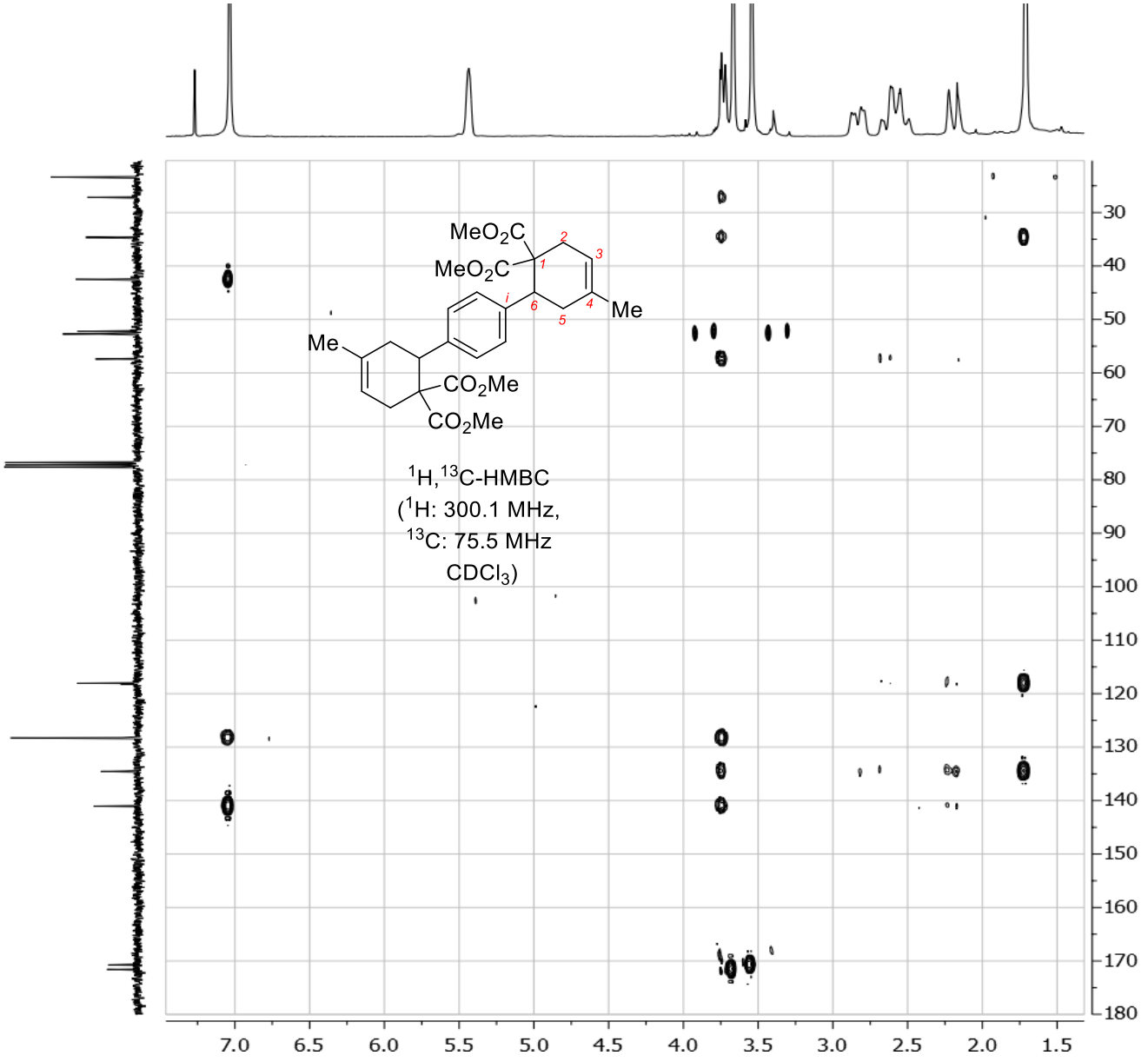

MeO2C CO2Me
MeO2C
MeO2C
1H,1H-COSY
(300.1 MHz, CDCl3)
f2 (мд)
f1 (мд)


7.03
5.44
3.67
3.54
2.87
2.85
2.81
2.79
2.67
2.66
2.61
2.60
2.55
2.49
2.22
2.17
1.71
MeO2C
MeO2C
Me
Me
CO2Me
CO2Me
11
1H NMR
(300.1 MHz, CDCl3)
2.11
1.00
1.02
3.01
3.02
1.04
2.07
1.18
3.17
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
1.0
0.5
0.0


171.59
170.75
141.05
134.55
128.28
118.05
57.41
52.73
52.22
42.48
34.64
27.14
23.35
MeO2C
MeO2C
Me
Me
CO2Me
CO2Me
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


MeO2C
MeO2C
Me
Me
CO2Me
CO2Me
1H,1H-COSY
(300.1 MHz, CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


MeO2C
MeO2C
Me
Me
CO2Me
CO2Me
1H,13C-edited-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
30
40
50
60
70
80
90
100
110
120
130


MeO2C
MeO2C
Me
Me
CO2Me
CO2Me
1H,13C-HMBC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180