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Reactions of β-styrylmalonates with aromatic aldehydes: the development of a catalytic version using gallium trichloride

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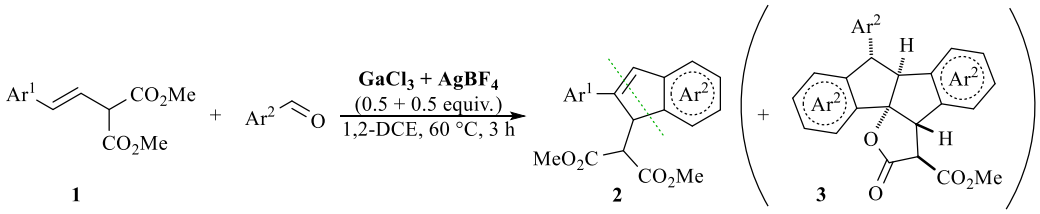
SUPPORTING INFORMATION

Table of contents:

1. General information

All operations with $AgBF_4$ and $GaCl_3$ were carried out under a dry argon atmosphere. 1,2-Dichloroethane as a solvent for reactions was distilled over P_2O_5. All reagents and solvents used for chromatography were commercial-grade chemicals without additional purification. Starting styrylmalonates **1a-e** were synthesized according to the literature from the corresponding D-A cyclopropanes.[S1] ^1H, ^{13}C and 2D NMR spectra were recorded on a 300 MHz (300.1 and 75.5 MHz, respectively) and 400 MHz (400.1 and 101.6 MHz, respectively) spectrometers in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. TLC analysis was performed on Silufol chromatographic plates. For preparative chromatography, silica gel 60 (0.040–0.063 mm) was used. IR spectra were obtained on a Perkin Elmer Spectrum 65 spectrophotometer equipped with a Quest ATR Accessory (Specac), by the attenuated total reflectance (ATR) in the range 400–4000 cm^{-1}. High-resolution mass spectra were obtained with a Bruker micrOTOF Iinstrument (ESI, positive or negative ion modes, capillary voltage 4500 V). X-ray crystallographic data for compound **2l** were obtained on a "Bruker Apex II" diffractometer equipped with CCD detector, MoKα radiation tube and graphite monochromator (ω-scans). A semi-empirical absorption correction using the SADABS program was applied to all compounds.[S2] Using Olex2, the structure was solved with a ShelXS structure solution program using Direct Methods and refined using a ShelXL refinement package with the Least Squares minimization in anisotropic approximation for nonhydrogen atoms.[S3] The H-atoms were added in the calculated positions and refined using the riding model in isotropic approximation. The main crystallography data and refinement details are given in the Table S1. Crystallographic data for the structure **2l** reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary numbers CCDC 2360163. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

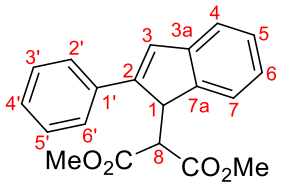
2. General procedure for synthesis of indenes 2a–m and lactones 3a–d and diene 5.



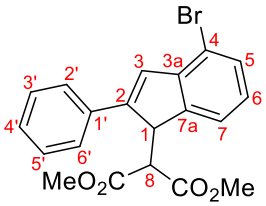
Under an argon atmosphere, a Schlenk flask was charged with 0.25 mmol of $AgBF_4$, a mixture of 0.5 mmol of styrylmalonate **1**, 1.5 mmol of aromatic aldehyde in 3 mL DCE, 0.25 mmol of $GaCl_3$, and a magnetic stir bar. The reaction mixture was heated at 60°C for 3 h, after cooling to ambient temperature, it was diluted with 15 mL CH_2Cl_2 and treated with an aqueous solution of HCl (10 mL, 10%) until pH reached 3. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). A catalytic amount of HBF_4 (50% aq.) and an excess of

ethereal solution of diazomethane* were added to the organic layer, the solution was bubbled with argon and then dried over $MgSO_4$. The solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (benzene to benzene-ethyl acetate, 30:1) to afford the product.

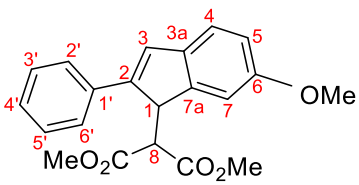
2.1. Characterization data for indenes 2a–m:



Dimethyl 2-(2-phenyl-1*H*-inden-1-yl)malonate (2a). The target compound was prepared from dimethyl 2-styrylmalonate and benzaldehyde, 124 mg (77%) as a colorless oil. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.31 (s, 3H, OMe), 3.70 (s, 3H, OMe), 3.88 (d, 1H, H(8), ^3J = 4.0 Hz), 4.67 (d, 1H, H(1), ^3J = 4.0 Hz), 7.04 (d, 1H, H(3), ^4J = 0.8 Hz), 7.18 (td, 1H, H(6), ^3J = 7.4 Hz, ^4J = 1.2 Hz), 7.24–7.48 (m, 7H, H_{Ar}), 7.54 (d, 1H, H(7),^3J = 7.4 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 47.9 (C(1)), 51.8 and 52.5 (2 OMe), 52.6 (C(8)), 121.2 (C(4)), 124.5 (C(7)), 125.2 (C(6)), 127.0 (C(2′) and C(6′)), 127.6 (C(4′)), 127.7 (C(5)), 128.8 (C(3′) and C(5′)), 129.1 (C(3)), 135.0 (C(1′)), 143.9 (C(7a)), 144.1 (C(3a)), 148.4 (C(2)), 167.2 and 169.4 (2 COO). The data correspond to those previously reported.[S5]



Dimethyl 2-(4-bromo-2-phenyl-1*H*-inden-1-yl)malonate (2b). The target compound was prepared from dimethyl 2-styrylmalonate and 2-bromobenzaldehyde, 138 mg (69%) as a colorless oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 3.33 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.89 (d, 1H, H(8), ^3J = 3.8 Hz), 4.74 (br.d, 1H, H(1), ^3J = 3.8 Hz), 7.04 (dd, 1H, H(6), ^3J = 7.6 and 7.9 Hz), 7.13 (dd, 1H, H(3), J = 1.5 and 0.6 Hz), 7.34–7.53 (m, 7H, H_{Ar}). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 49.2 (C(1)), 52.0 and 52.8 (2 OMe), 52.7 (C(8)), 115.3 (C(4)), 123.6, 126.7, 128.3, 128.4 and 130.9 (C(3), C(5), C(6), C(7) and C(4′)), 127.3 and 129.0 (C(2′), C(6′) and C(3′), C(5′)), 134.5, 144.4, 145.4 and 149.6 (C(1′), C(3a), C(7a) and C(2)), 167.0 and 169.2 (2 COO). The data correspond to those previously reported.[S5]



Dimethyl 2-(6-methoxy-2-phenyl-1*H*-inden-1-yl)malonate (2c). The target compound was prepared from dimethyl 2-styrylmalonate and 4-methoxybenzaldehyde, 79 mg (45%) as a colorless oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 3.34 (s, 3H, OMe), 3.68 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.87 (d, 1H, H(8), ^3J = 4.2 Hz), 4.62 (br.d, 1H, H(1), ^3J = 4.2 Hz), 6.83 (dd, 1H, H(5), ^3J = 8.3 Hz, ^4J = 2.2 Hz), 6.97 (d, 1H, H(3), ^4J = 0.9 Hz), 7.16 (d, 1H, H(7), ^4J = 2.2 Hz), 7.20–7.31 (m, 2H, H_{Ar}), 7.32–7.50 (m, 4H, H_{Ar}). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 48.0 (C(1)), 52.0, 52.7 and 55.7 (3 OMe), 52.9 (C(8)), 111.5 (C(7)), 113.2 (C(5), 121.7 (C(4)), 126.9 and 128.9 (CH(2′), CH(6′) and CH(3′), CH(5′)), 127.5 (C(4′)), 128.8 (C(3)), 135.4, 137.4, 146.0, 146.4 and 158.3 (5 C_{Ar}), 167.3 and 169.5 (2 COO). The data correspond to those previously reported.[S5]

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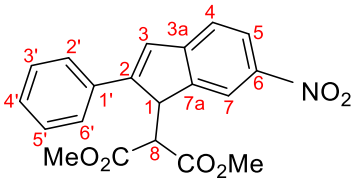
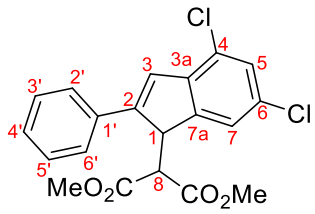
* Previously, partial demethylation of ester groups in the reaction products was observed.[S4] Thus, diazomethane was used to reinstall methyl groups.

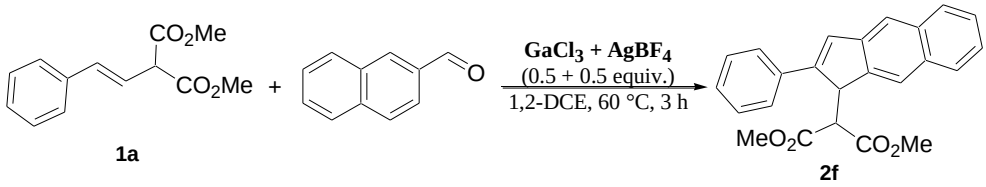


Dimethyl 2-(6-nitro-2-phenyl-1*H*-inden-1-yl)malonate (2d). The target compound was prepared from dimethyl 2-styrylmalonate and 4-nitrobenzaldehyde, 114 mg (62%) as a yellow oil. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.36 and 3.84 (both s, 2×3H, 2 OMe), 4.01 (d, 1H, H(8), ^{3}J = 3.7 Hz), 4.78 (br.d, 1H, H(1), ^{3}J = 3.7 Hz), 7.14 (d, 1H, H(3), ^{4}J = 0.7 Hz), 7.36–7.57 (m, 6H, H_{Ar}), 8.27 (dd, 1H, H(5), ^{3}J = 8.3 Hz, ^{4}J = 2.0 Hz), 8.45 (d, 1H, H(7), ^{4}J = 2.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 48.4 (C(1)), 52.2 (OMe), 52.4 (C(8)), 53.1 (OMe), 120.2, 121.0, 124.2, 127.8 and 129.1 (5 CH_{Ar}), 127.3 and 129.2 (CH(2′), CH(6′) and CH(3′), CH(5′)), 133.9, 144.6, 150.7 and 154.6 (4 C_{Ar}), 145.7 (C(6)), 166.6 and 169.0 (2 COO). The data correspond to those previously reported.[S5]



Dimethyl 2-(4,6-dichloro-2-phenyl-1*H*-inden-1-yl)malonate (2e). The target compound was prepared from dimethyl 2-styrylmalonate and 2,4-dichlorobenzaldehyde, 154 mg (79%) as a yellow solid. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.37 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.91 (d, 1H, H(8), ^{3}J = 3.7 Hz), 4.70 (d, 1H, H(1), ^{3}J = 3.7 Hz), 7.12 (d, 1H, H(3), ^{4}J = 0.8 Hz), 7.28–7.51 (m, 7H, H_{Ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 48.9 (C(1)), 52.1 and 52.9 (2 OMe), 52.3 (C(8)), 123.9, 125.6, 127.8 and 128.4 (C(4′), C(3), C(5) and C(7)), 127.1 and 129.0 (C(3′), C(5′), C(2′) and C(6′)), 131.5, 134.1, 141.1, 141.4, 146.4 and 149.7 (C(1′), C(2), C(3a), C(7a), C(4) and C(6)), 166.7 and 169.1 (2 COO). IR (ATR): $\tilde{\nu}$ 3056, 2987, 2971, 2954, 2900, 2359, 2342, 1787, 1746, 1720, 1588, 1571, 1557, 1494, 1438, 1431, 1404, 1341, 1293, 1279, 1254, 1223, 1206, 1051, 1009, 937, 918, 891, 868, 848, 760, 696 cm^{-1}. HRMS calcd for $C_{20}H_{16}Cl_2O_4$ (*M*): *M*+*H*, 391.0498, *M*+NH_4, 408.0764. Found: *m/z* 391.0487, 408.0756.

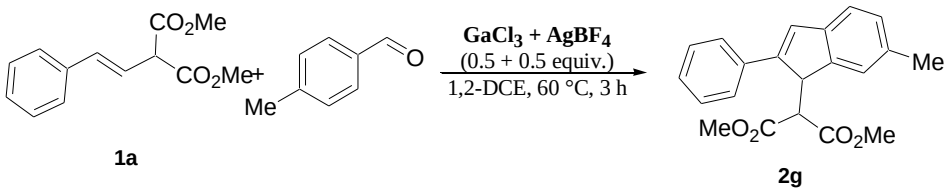
Dimethyl 2-(2-phenyl-1*H*-cyclopenta[*b*]naphthalen-1-yl)malonate (2f).



1a **2f**

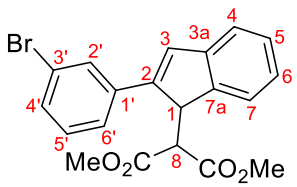
Compound **2f** was formed in the reaction of dimethyl 2-styrylmalonate and 2-naphthaldehyde and observed in an NMR spectrum after work-up in an NMR yield of 47%. The assignment of the product was based on the presence of signals similar to those of other indenes such as **2a** (see Section 4.1). HRMS calcd for $C_{24}H_{20}O_4$ (*M*): *M*+*H*, 373.1434, *M*+NH_4, 390.1700. Found: *m/z* 373.1429, 390.1696.

Dimethyl 2-(6-methyl-2-phenyl-1*H*-inden-1-yl)malonate (2g).

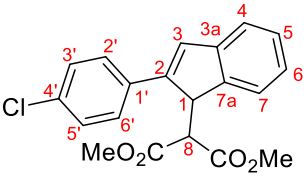


1a **2g**

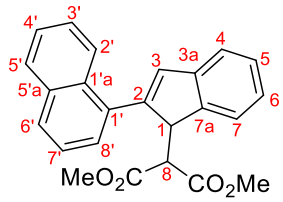
Compound **2g** was formed in the reaction of dimethyl 2-styrylmalonate and 4-methylbenzaldehyde and observed in an NMR spectrum after work-up in an NMR yield of 44%. The assignment of the product was based on the presence of signals similar to those of other indenes such as **2a** (see Section 4.1).



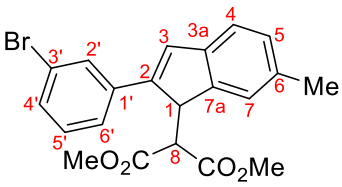
Dimethyl 2-[2-(3-bromophenyl)-1*H*-inden-1-yl]malonate (2h). The target compound was prepared from dimethyl 2-(3-bromostyryl)malonate and benzaldehyde, 160 mg (80%) as a colorless oil. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.37 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.88 (d, 1H, H(8), ^{3}J = 3.9 Hz), 4.66 (br.d, 1H, H(1), ^{3}J = 3.9 Hz), 7.09 (d, 1H, H(3), J = 0.9 Hz), 7.17–7.50 (m, 6H, H_{Ar}), 7.52–7.68 (m, 2H, H_{Ar}). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 47.9 (C(1)), 52.0 and 52.7 (2 OMe), 52.6 (C(8)), 121.5, 124.6, 125.7, 127.8, 129.9, 130.3, 130.5 and 130.6 (C(3), C(4), C(5), C(6), C(7), C(2′), C(4′)), C(5′) and (C(6′)), 123.0 (C(3′)), 137.3, 143.7, 143.9 and 146.8 (C(1′), C(3a), C(7a) and C(2)), 167.1 and 169.1 (2 COO). The data correspond to those previously reported reported.[S5]



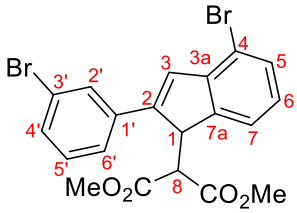
Dimethyl 2-[2-(4-chlorophenyl)-1*H*-inden-1-yl]malonate (2i). The target compound was prepared from dimethyl 2-(4-chlorostyryl)malonate and benzaldehyde, 127 mg (71%) as a yellow oil. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.35 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.87 (d, 1H, H(8), ^{3}J = 4.0 Hz), 4.66 (d, 1H, H(1), ^{3}J = 4.0 Hz), 7.07 (d, 1H, H(3), ^{4}J = 0.9 Hz), 7.17–7.50 (m, 7H, H_{Ar}), 7.57 (d, 1H, H(7), ^{4}J = 7.5 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 47.9 (C(1)), 51.9 and 52.7 (2 OMe), 52.6 (C(8)), 121.4, 124.6, 125.5 and 127.7 (C(4), C(7), C(6) and C(5)), 128.3 and 129.0 (C(3′), C(5′), C(2′) and C(6′)), 129.8 (C(3), 133.6 and 133.6 (C(1′) and C(4′)), 143.8, 143.9 and 147.1 (C(7a), C(3a) and C(2)), 167.1 and 169.2 (2 COO). IR (ATR): $\tilde{\nu}$ 2987, 2953, 2901, 2360, 2342, 1787, 1763, 1736, 1597, 1490, 1459, 1436, 1403, 1339, 1280, 1228, 1151, 1092, 1064, 1015, 831, 813, 754, 715, 700, 614 cm^{-1}. HRMS calcd for $C_{20}H_{17}ClO_4$ (*M*): *M*+*H*, 357.0888, *M*+NH_4, 374.1154. Found: *m/z* 357.0878, 374.1143.



Dimethyl 2-[2-(naphthalen-1-yl)-1*H*-inden-1-yl]malonate (2j). The target compound was prepared from dimethyl (*E*)-2-[2-(naphthalen-1-yl)vinyl]malonate and benzaldehyde. 67 mg (36%) as a yellow oil. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.34 (s, 3H, OMe), 3.49 (s, 3H, OMe), 3.77 (d, 1H, H(8), ^{3}J = 4.9 Hz), 4.86 (d, 1H, H(1), ^{3}J = 4.7 Hz), 7.07 (d, 1H, H(3), ^{4}J = 1.2 Hz), 7.34–7.57 (m, 9H, H_{Ar}), 7.79–7.99 (m, 3H, H_{Ar}), 8.15–8.28 (m, 1H, H(8′)). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 51.0 (C(1)), 52.0 and 52.3 (2 OMe), 52.4 (C(8)), 121.4, 124.3, 125.2,125.3,126.0, 126.0, 126.2, 126.8, 127.7, 128.1, 128.4 and 133.0 (all CH_{Ar}), 132.9, 133.6, 134.0, 143.5 and 144.2 (all C_{Ar}), 167.5 and 168.9 (2 COO). IR (ATR): $\tilde{\nu}$ 2987, 2952, 2900, 2360, 2342, 1732, 1598, 1454, 1434, 1248, 1152, 1057, 1019, 910, 866, 802, 777, 755, 733, 663 cm^{-1}. HRMS calcd for $C_{24}H_{20}O_4$ (*M*): *M*+*H*, 373.1434, *M*+NH_4, 390.1700. Found: *m/z* 373.1435, 390.1703.



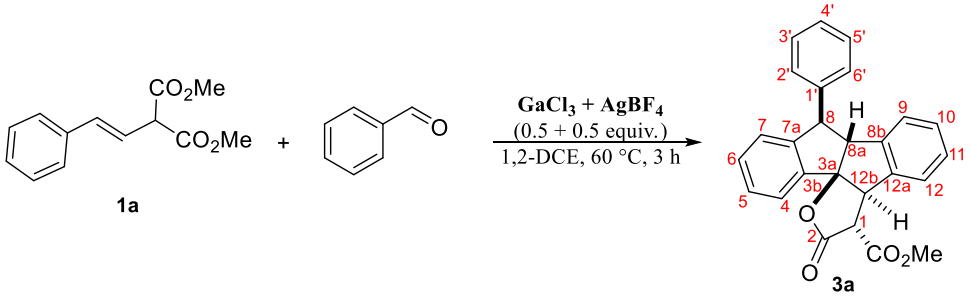
Dimethyl 2-[2-(3-bromophenyl)-6-methyl-1*H*-inden-1-yl]malonate (2k). The target compound was prepared from dimethyl 2-(3-bromostyryl)malonate and 4-methylbenzaldehyde. 141 mg (68%) as a yellow oil. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.42 (s, 3H, Me), 3.39 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.86 (d, 1H, H(8), ^3J = 4.2 Hz), 4.61 (br.d, 1H, H(1), ^3J = 4.1 Hz), 7.05 (d, 1H, H(3), ^3J = 0.8 Hz), 7.14 (d, 1H, H_{Ar}, ^4J = 7.6 Hz), 7.19–7.50 (m, 5H, H_{Ar}), 7.62 (t, 1H, H_{Ar}, ^4J = 1.7 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.8 (Me), 47.7 (C(1)), 52.0 and 52.6 (2 OMe), 52.7 (C(8)), 121.2, 125.4, 125.5, 128.5, 129.8, 130.3, 130.4 and 130.4 (all CH_{Ar}), 122.9, 135.5, 137.5, 141.1, 144.2 and 145.7 (all C_{Ar}), 167.2 and 169.2 (2 COO). IR (ATR): $\tilde{\nu}$ 2972, 2900, 2360, 2342, 1784, 1723, 1591, 1474, 1436, 1334, 1279, 1254, 1224, 1207, 1162, 1074, 1045, 870, 782, 690 cm^{-1}. HRMS calcd for $C_{20}H_{19}BrO_4$ (*M*): *M*+*H*, 415.0539, *M*+Na, 437.0359. Found: *m/z* 415.0528, 437.0348.



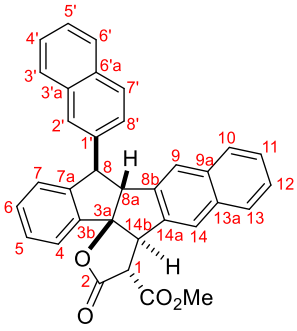
Dimethyl 2-[4-bromo-2-(3-bromophenyl)-1*H*-inden-1-yl]malonate (2l). The target compound was prepared from dimethyl 2-(3-bromostyryl)malonate and 2-brombenzaldehyde. 205 mg (86%) as a yellow solid. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.36 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.86 (d, 1H, H(8), ^3J = 3.9 Hz), 4.70 (br.d, 1H, H(1), ^3J = 3.9 Hz), 7.01–7.17 (m, 2H, H_{Ar}), 7.23–7.53 (m, 5H, H_{Ar}), 7.58–7.66 (m, 1H, H_{Ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 49.0 (C(1)), 52.1 and 52.4 (2 OMe), 52.8 (C(8)), 115.6 (C(4)), 123.1 (C(3′)), 123.6, 125.7, 127.0, 129.6 130.4, 131.0 and 131.1 (C(3), C(5), C(6), C(7), C(4′), C(5′) C(6′) and C(2′)), 136.7, 143.9, 145.3 and 147.8 (C(1′), C(3a), C(7a) and C(2)), 166.8 and 168.9 (2 COO). IR (ATR): $\tilde{\nu}$ 2987, 2972, 2900, 2359, 2342, 1788, 1726, 1585, 1553, 1473, 1433, 1325, 1298, 1248, 1212, 1166, 1057, 1019, 864, 776, 689, 647 cm^{-1}. HRMS calcd for $C_{20}H_{16}Br_2O_4$ (*M*): *M*+*H*, 478.9488, *M*+NH_4, 495.9754. Found: *m/z* 478.9480, 495.9745. Crystal Data for $C_{20}H_{16}Br_2O_4$ see p. *S7*

2.2 Characterization data for indenolactones 3a–d:

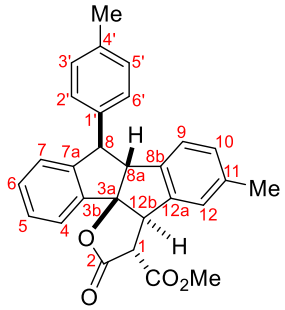
Methyl *rac*-(1*R*,3a*S*,8*R*,8a*R*,12b*R*)-2-oxo-8-phenyl-1,8,8a,12b-tetrahydro-2*H*-indeno[1′,2′:2,3]indeno[2,1-*b*]furan-1-carboxylate (3a).



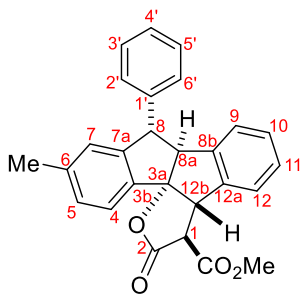
The target compound was formed in the reaction of dimethyl 2-styrylmalonate and benzaldehyde and observed in an NMR spectrum after work-up in an NMR yield of 13%. The assignment of the product was based on the presence of signals corresponding to those previously reported.[S5]



Methyl *rac*-(1*R*,3a*S*,8*R*,8a*R*,14b*R*)-8-(naphthalen-2-yl)-2-oxo-1,8,8a,14b-tetrahydro-2*H*-benzo[5,6]indeno[1′,2′:2,3]indeno[2,1-*b*]-furan-1-carboxylate (3b). The target compound was prepared from dimethyl 2-styrylmalonate and 2-naphthaldehyde. 117 mg (47%) as a light beige solid. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.90 (d, 1H, H(1), ^{3}J = 5.5 Hz), 4.05 (s, 3H, OMe), 4.46 (d, 1H, H(8a), ^{3}J = 4.0 Hz), 4.50 (d, 1H, H(8), ^{3}J = 4.0 Hz), 4.99 (d, 1H, H(14b), ^{3}J = 5.5 Hz), 6.98 (d, 1H, H(7), ^{3}J = 7.7 Hz), 7.21 – 7.60 (m, 7H, H_{Ar}), 7.64 (d, 1H, H_{Ar}, ^{3}J = 7.9 Hz), 7.75 – 7.93 (m, 7H, H_{Ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 53.7 (OMe), 54.1 (C(14b)), 54.1 (C(1)), 58.0 (C(8a)), 66.2 (C(8)), 102.9 (C(3a)), 122.7, 123.5, 124.9, 125.9, 126.1, 126.1, 126.2, 126.4, 126.6, 127.5, 127.8, 128.7, 129.1 and 129.2 (15 CH_{Ar}), 129.7 (1 C_{Ar}), 130.5 and 130.8 (2 CH_{Ar}), 132.6, 133.5, 133.8, 135.8, 140.7, 140.8, 141.8 and 146.2 (8 C_{Ar}), 168.9 (COO), 171.0 (C(2)). IR (ATR): $\tilde{\nu}$ 3060, 2987, 2971, 2954, 2900, 2360, 2342, 1773, 1728, 1585, 1553, 1473, 1451, 1434, 1324, 1298, 1276, 1266, 1248, 1213, 1166, 1057, 1019, 865, 776, 753, 690, 648 cm^{-1}. HRMS calcd for $C_{34}H_{24}O_4$ (M): M+H, 497.1747, M+NH_4, 514.2013. Found: m/z 497.1747, 514.2014.



Methyl *rac*-(1*R*,3a*S*,8*R*,8a*R*,12b*R*)-11-methyl-2-oxo-8-(*p*-tolyl)-1,8,8a,12b-tetrahydro-2*H*-indeno[1′,2′:2,3]indeno[2,1-*b*]furan-1-carboxylate (3c). The target compound was prepared from dimethyl 2-styrylmalonate and 4-methylbenzaldehyde. 104 mg (49%) as a white solid. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.34 (s, 3H, Me), 2.36 (s, 3H, Me), 3.77 (d, 1H, H(1), ^{3}J = 5.4 Hz), 3.96 (s, 3H, OMe), 4.12 (d, 1H, H(8a), ^{3}J = 4.2 Hz), 4.22 (d, 1H, H(8), ^{3}J = 4.2 Hz), 4.45 (d, 1H, H(12b), ^{3}J = 5.4 Hz), 6.96 (d, 1H, H(7), ^{3}J = 7.6 Hz), 7.03 (s, 1H, H_{Ar}), 7.07 – 7.43 (m, 8H, H_{Ar}), 7.62 (d, 1H, H(4), ^{3}J = 7.1 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.1 and 21.3 (2 Me), 53.5 (OMe), 54.5 (C(12b)), 54.9 (C(1)), 57.5 (C(8)), 65.3 (C(8a)), 103.3 (C(3a)), 124.7 (C(4)), 125.0 and 125.4 (2 CH_{Ar}), 125.8(C(7)), 128.0 and 129.6 (C(3′), C(5′), C(2′) and C(6′)), 128.3, 130.1 and 130.6 (3 CH_{Ar}), 136.6, 138.7, 140.4, 140.6, 141.3 and 141.5 (6 C_{Ar}), 146.5 (C(7a)), 168.5 (COO)), 171.0 (C(2)). IR (ATR): $\tilde{\nu}$ 2987, 2972, 2921, 2900, 2359, 2342, 1793, 1736, 1512, 1451, 1436, 1406, 1393, 1257, 1225, 1183, 1163, 1149, 1074, 1056, 1029, 1006, 891, 878, 865, 825, 754, 740, 697, 642 cm^{-1}. HRMS calcd for $C_{28}H_{24}O_4$ (M): M+H, 425.1747, M+NH_4, 442.2013. Found: m/z 425.1738, 442.2004.

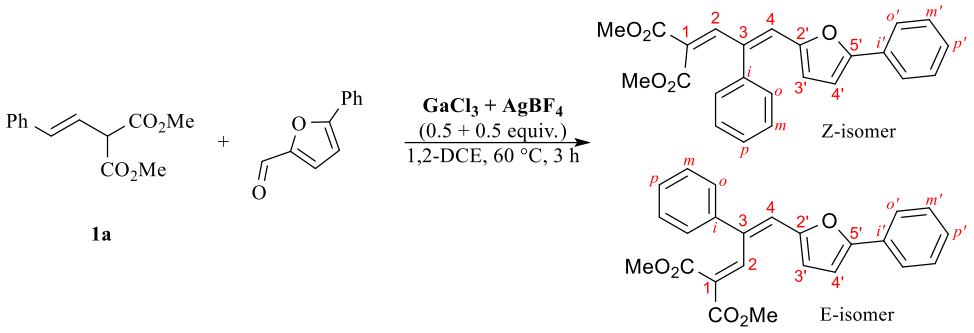


Methyl *rac*-(1*R*,3a*S*,8*R*,8a*R*,12b*R*)-6-methyl-2-oxo-8-phenyl-1,8,8a,12b-tetrahydro-2*H*-indeno[1′,2′:2,3]indeno[2,1-*b*]furan-1-carboxylate (3d). The target compound was prepared from dimethyl 2-(methylstyryl)malonate and benzaldehyde. 123 mg (60%) as a yellow oil. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.30 (s, 3H, Me), 3.80 (d, 1H, H(1), ^{3}J = 5.6 Hz), 3.98 (s, 3H, OMe), 4.21 (d, 1H, H(8a), ^{3}J = 4.1 Hz), 4.27 (d, 1H, H(8), ^{3}J = 4.1 Hz), 4.52 (d, 1H, H(12b), ^{3}J = 5.3 Hz),

6.80 (br.s, 1H, H(7)), 7.17 – 7.44 (m, 10H, H_{Ar}), 7.54 (d, 1H, H(4), ^{3}J = 7.9 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.5 (Me), 53.5 (OMe), 54.6 (C(12b)), 54.9 (C(1)), 57.7 (C(8)), 65.6 (C(8a)),102.9 (C(3a)), 124.4, 125.0, 125.3, 126.1 and 127.0 (5 CH_{Ar}), 128.1 and 129.0 (C(3′), C(5′), C(2′) and C(6′)), 128.7, 129.2 and 129.50 (3 CH_{Ar}), 137.5, 140.9, 141.2, 143.6, 144.5 and 146.5 (6 C_{Ar}), 168.4 (COO)), 170.9 (C(2)). IR (ATR): $\tilde{\nu}$ 2987, 2971, 2901, 2360, 2342, 1778, 1736, 1495, 1453, 1436, 1160, 1075, 1028, 1010, 820, 752, 699 cm^{-1}. HRMS calcd for $C_{27}H_{22}O_4$ (M): M+H, 411.1591, M+NH_4, 428.1856. Found: m/z 411.1584, 428.1846.

2.3 Characterization data for diene 5.

Dimethyl 2-[2-phenyl-3-(5-phenylfuran-2-yl)allylidene]malonate (5).



5

The target compound was prepared from dimethyl 2-styrylmalonate and 5-phenylfuran-2-carbaldehyde. Both isomers 128 mg (66%) as a brown oil. Major E-isomer: ^{1}H NMR (300.1 MHz, $CDCl_3$): *δ* 3.12 (s, 3H, OMe), 3.93 (s, 3H, OMe), 6.66 (d, 1H, H(3′), ^{3}J = 3.6 Hz), 6.71 (br.s, 1H, H(4)), 6.82 (d, 1H, H(4′), ^{3}J = 3.6 Hz), 7.26–7.50 (m, 8H, H_{Ar}), 7.75–7.82 (m, 2H, H_{Ar}), 8.70 (d, 1H, H(2), ^{3}J = 1.0 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): *δ* 51.6 and 52.6 (2 OMe), 107.7 (C(4′)), 117.6 (C(3′)), 124.6 (C(4)), 124.3, 127.0, 127.9, 128.2, 128.3, 128.9, 128.9 and 129.9 (C(1), C(*i*′) and 10 CH_{Ar}), 133.2 (C(*i*)), 139.9 (C(3)), 143.1 (C(2)), 151.9 (C(2′)), 156.0 (C(5′)), 165.1 and 165.5 (2 COO). Minor Z-isomer: ^{1}H NMR (300.1 MHz, $CDCl_3$): *δ* 3.15 (s, 3H, OMe), 3.80 (s, 3H, OMe), 5.87 (d, 1H, H(3′), ^{3}J = 3.6 Hz), 6.54 (d, 1H, H(4′), ^{3}J = 3.6 Hz), 6.97 (s, 1H, H(4)), 7.17–7.55 (m, 10H, H_{Ar}), 7.67 (s, 1H, H(2)). ^{13}C NMR (75.5 MHz, $CDCl_3$): *δ* 51.8 and 52.5 (2 OMe), 107.8 (C(4′)), 117.3 (C(3′)), 123.8, 124.1, 125.0, 128.0, 128.1, 128.6, 128.7, 128.9, 129.7, 129.8, 134.6 (C(1), C(*i*), C(*i*′) and 10 CH_{Ar}), 129.7 (C(4)), 136.1 (C(3)), 144.8 (C(2)), 150.9 (C(2′))155.5 (C(5′)), 165.2 and 165.9 (2 COO). IR (ATR): $\tilde{\nu}$ 2987, 2952, 2923, 2901, 2360, 2342, 1718, 1603, 1582, 1473, 1449, 1435, 1227, 1179, 1072, 1026, 924, 795, 760, 700 cm^{-1}. HRMS calcd for $C_{24}H_{20}O_5$ (*M*): *M+H*, 389.1384, *M+Na*, 411.1203. Found: *m/z* 389.1376, 411.1199.

2.4. Crystal data for indene 2l

Table S1. Crystal data and structure refinement for **2l**

Identification code	**2l**
Empirical formula	$C_{20}H_{16}Br_2O_4$
Formula weight	480.15
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.546(2)
b/Å	8.0371(14)
c/Å	17.920(3)
α/°	90
β/°	107.182(7)
γ/°	90
Volume/Å^3	1863.9(6)
Z	4
ρ_{calc}g/cm^3	1.711
μ/mm^{-1}	4.372
F(000)	952.0
Crystal size/mm^3	0.2 × 0.2 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.758 to 51.992
Index ranges	$-16 \leq h \leq 16$, $-9 \leq k \leq 9$, $-21 \leq l \leq 22$
Reflections collected	14198
Independent reflections	3634 [R_{int} = 0.1248, R_{sigma} = 0.0794]
Data/restraints/parameters	3634/0/237
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0600, wR_2 = 0.1553
Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1634
Largest diff. peak/hole / e Å^{-3}	0.66/-1.01

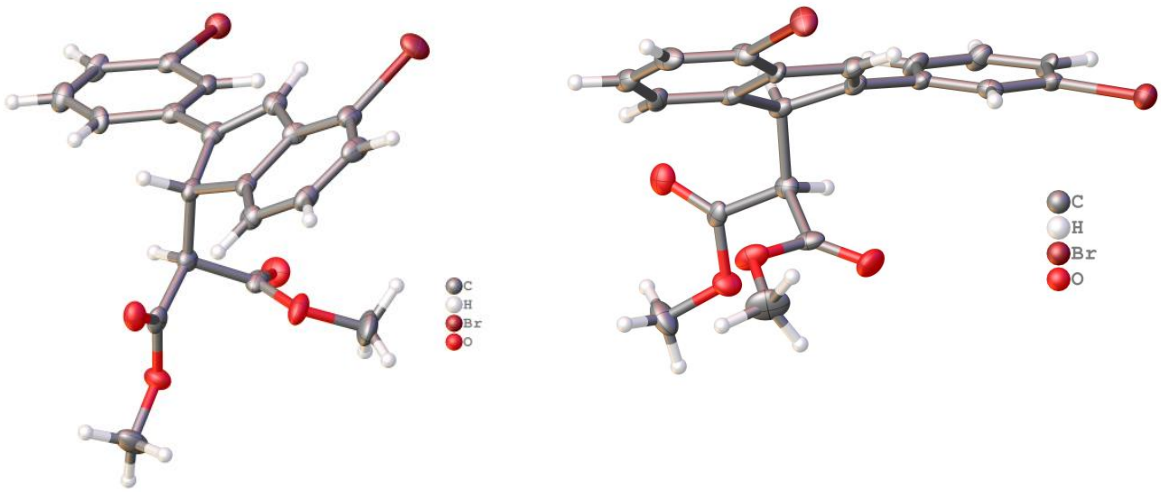


Figure S1. Crystallographic structure for **2l**.

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2l**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
Br2	9186.7(5)	-2339.5(8)	860.9(3)	24.2(2)
Br1	7626.2(5)	220.5(8)	4617.5(3)	28.7(2)
O1	7214(3)	7771(6)	2171(2)	27.2(10)
O2	6161(3)	6945(6)	1012(2)	26.8(9)
O4	5643(3)	4262(6)	2007(2)	28.9(10)
O3	6121(3)	2580(6)	1173(3)	31.2(11)
C12	9344(4)	-77(7)	1191(3)	19.3(12)
C13	9958(4)	978(8)	915(3)	21.3(13)
C17	6878(4)	6704(8)	1698(3)	20.3(12)
C2	8379(4)	2703(8)	2499(3)	20.6(12)
C10	8900(4)	2122(8)	1930(3)	18.8(11)
C19	6275(4)	3783(8)	1589(3)	22.7(13)
C9	7647(4)	4414(8)	3262(3)	19.4(12)
C11	8814(4)	465(7)	1694(3)	19.0(12)
C4	7740(4)	2775(7)	3540(3)	18.0(11)
C1	8024(4)	4453(8)	2542(3)	18.6(12)
C3	8169(4)	1722(8)	3053(3)	21.5(12)
C7	7087(4)	5255(8)	4342(3)	23.6(13)
C14	10030(5)	2623(8)	1132(4)	26.1(14)
C16	7212(4)	4886(7)	1763(3)	19.7(12)
C8	7323(4)	5666(8)	3661(3)	21.0(12)
C6	7152(4)	3678(9)	4621(3)	26.6(14)
C5	7482(4)	2416(8)	4220(3)	23.7(13)
C15	9513(4)	3224(8)	1639(3)	21.6(12)
C18	5740(5)	8627(9)	872(4)	35.5(17)
C20	4754(5)	3249(11)	1920(4)	43.4(19)

Table S3. Bond Lengths for **2l**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Br2	C12	1.904(6)		C2	C3	1.362(8)
Br1	C5	1.891(6)		C10	C11	1.392(8)
O1	C17	1.197(7)		C10	C15	1.415(8)
O2	C17	1.337(7)		C19	C16	1.503(8)
O2	C18	1.460(8)		C9	C4	1.401(8)
O4	C19	1.349(7)		C9	C1	1.522(7)
O4	C20	1.423(7)		C9	C8	1.379(8)
O3	C19	1.201(7)		C4	C3	1.454(8)
C12	C13	1.378(8)		C4	C5	1.393(7)
C12	C11	1.378(7)		C1	C16	1.540(7)
C13	C14	1.373(9)		C7	C8	1.389(8)
C17	C16	1.523(8)		C7	C6	1.356(9)
C2	C10	1.477(7)		C14	C15	1.388(8)
C2	C1	1.496(8)		C6	C5	1.390(9)

Table S4. Bond Angles for **2l**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C17	O2	C18	115.7(5)		C8	C9	C1	131.5(6)
C19	O4	C20	115.6(5)		C12	C11	C10	119.2(5)
C13	C12	Br2	120.0(4)		C9	C4	C3	110.0(5)
C13	C12	C11	121.8(6)		C5	C4	C9	119.1(5)
C11	C12	Br2	118.2(4)		C5	C4	C3	130.7(6)

C14	C13	C12	119.4(5)		C2	C1	C9	102.5(5)
O1	C17	O2	124.6(6)		C2	C1	C16	108.7(5)
O1	C17	C16	126.2(6)		C9	C1	C16	116.4(4)
O2	C17	C16	109.1(5)		C2	C3	C4	107.9(6)
C10	C2	C1	124.0(5)		C6	C7	C8	122.7(6)
C3	C2	C10	124.5(6)		C13	C14	C15	120.9(6)
C3	C2	C1	111.6(5)		C17	C16	C1	113.7(5)
C11	C10	C2	119.9(5)		C19	C16	C17	109.7(5)
C11	C10	C15	119.5(5)		C19	C16	C1	112.8(5)
C15	C10	C2	120.6(5)		C9	C8	C7	118.2(6)
O4	C19	C16	110.6(5)		C7	C6	C5	119.1(5)
O3	C19	O4	123.5(5)		C4	C5	Br1	119.8(4)
O3	C19	C16	125.8(5)		C6	C5	Br1	120.0(4)
C4	C9	C1	107.7(5)		C6	C5	C4	120.2(6)
C8	C9	C4	120.7(5)		C14	C15	C10	119.2(6)

Table S5. Torsion Angles for **2l**.

A	**B**	**C**	**D**	**Angle/°**		**A**	**B**	**C**	**D**	**Angle/°**
Br2	C12	C13	C14	177.3(4)		C4	C9	C1	C16	115.3(6)
Br2	C12	C11	C10	-178.7(4)		C4	C9	C8	C7	-0.3(8)
O1	C17	C16	C19	130.3(5)		C1	C2	C10	C11	-152.5(5)
O1	C17	C16	C1	2.9(8)		C1	C2	C10	C15	29.4(8)
O2	C17	C16	C19	-51.4(6)		C1	C2	C3	C4	-4.6(6)
O2	C17	C16	C1	-178.8(4)		C1	C9	C4	C3	0.7(6)
O4	C19	C16	C17	-49.5(6)		C1	C9	C4	C5	177.4(5)
O4	C19	C16	C1	78.4(6)		C1	C9	C8	C7	-175.6(5)
O3	C19	C16	C17	134.4(6)		C3	C2	C10	C11	28.1(8)
O3	C19	C16	C1	-97.7(7)		C3	C2	C10	C15	-150.0(6)
C12	C13	C14	C15	1.5(9)		C3	C2	C1	C9	4.8(6)
C13	C12	C11	C10	-0.1(8)		C3	C2	C1	C16	-118.9(5)
C13	C14	C15	C10	-0.4(9)		C3	C4	C5	Br1	-2.8(9)
C2	C10	C11	C12	-176.9(5)		C3	C4	C5	C6	175.0(6)
C2	C10	C15	C14	177.2(5)		C7	C6	C5	Br1	177.7(4)
C2	C1	C16	C17	-173.5(4)		C7	C6	C5	C4	-0.1(9)
C2	C1	C16	C19	60.8(6)		C8	C9	C4	C3	-175.6(5)
C10	C2	C1	C9	-174.7(5)		C8	C9	C4	C5	1.1(8)
C10	C2	C1	C16	61.6(7)		C8	C9	C1	C2	172.6(6)
C10	C2	C3	C4	174.9(5)		C8	C9	C1	C16	-69.0(8)
C9	C4	C3	C2	2.4(6)		C8	C7	C6	C5	1.0(9)
C9	C4	C5	Br1	-178.8(4)		C6	C7	C8	C9	-0.8(8)
C9	C4	C5	C6	-0.9(8)		C5	C4	C3	C2	-173.8(6)
C9	C1	C16	C17	71.5(6)		C15	C10	C11	C12	1.2(8)
C9	C1	C16	C19	-54.2(7)		C18	O2	C17	O1	-3.5(8)
C11	C12	C13	C14	-1.2(9)		C18	O2	C17	C16	178.2(4)
C11	C10	C15	C14	-1.0(8)		C20	O4	C19	O3	-0.6(9)
C4	C9	C1	C2	-3.2(6)		C20	O4	C19	C16	-176.7(5)

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2l**.

Atom	***x***	***y***	***z***	**U(eq)**
H13	10327.47	571.91	577.24	26
H11	8393.63	-283.87	1876.42	23
H1	8625.68	5228.76	2632.61	22
H3	8281.87	556.22	3111.18	26
H7	6871.69	6114	4622.77	28
H14	10439.39	3358.79	932.62	31

H16	7543.58	4683.75	1341.35	24
H8	7263.42	6779.45	3475.25	25
H6	6974.11	3438.27	5084.07	32
H15	9570.76	4361.44	1789.65	26
H18A	5291.97	8716.12	332.73	53
H18B	6307.08	9429.26	956.65	53
H18C	5337.08	8865.15	1232.77	53
H20A	4451.98	2958.38	1368.69	65
H20B	4244.91	3859.83	2104.58	65
H20C	4953.73	2230.03	2228.76	65

3. References

S1 (*a*) R. A. Novikov, A. V. Tarasova, V. A. Korolev, V. P. Timofeev and Y. V. Tomilov, *Angew. Chem., Int. Ed.*, 2014, **53**, 3187; https://doi.org/10.1002/anie.201306186; (*b*) D. D. Borisov, G. R. Chermashentsev, R. A. Novikov and Y. V. Tomilov, *Synthesis*, 2021, **53**, 2253.

S2 R. H. Blessing, *Acta Crystallogr.*, 1995, **A51**, 33; https://doi.org/10.1107/S0108767394005726.

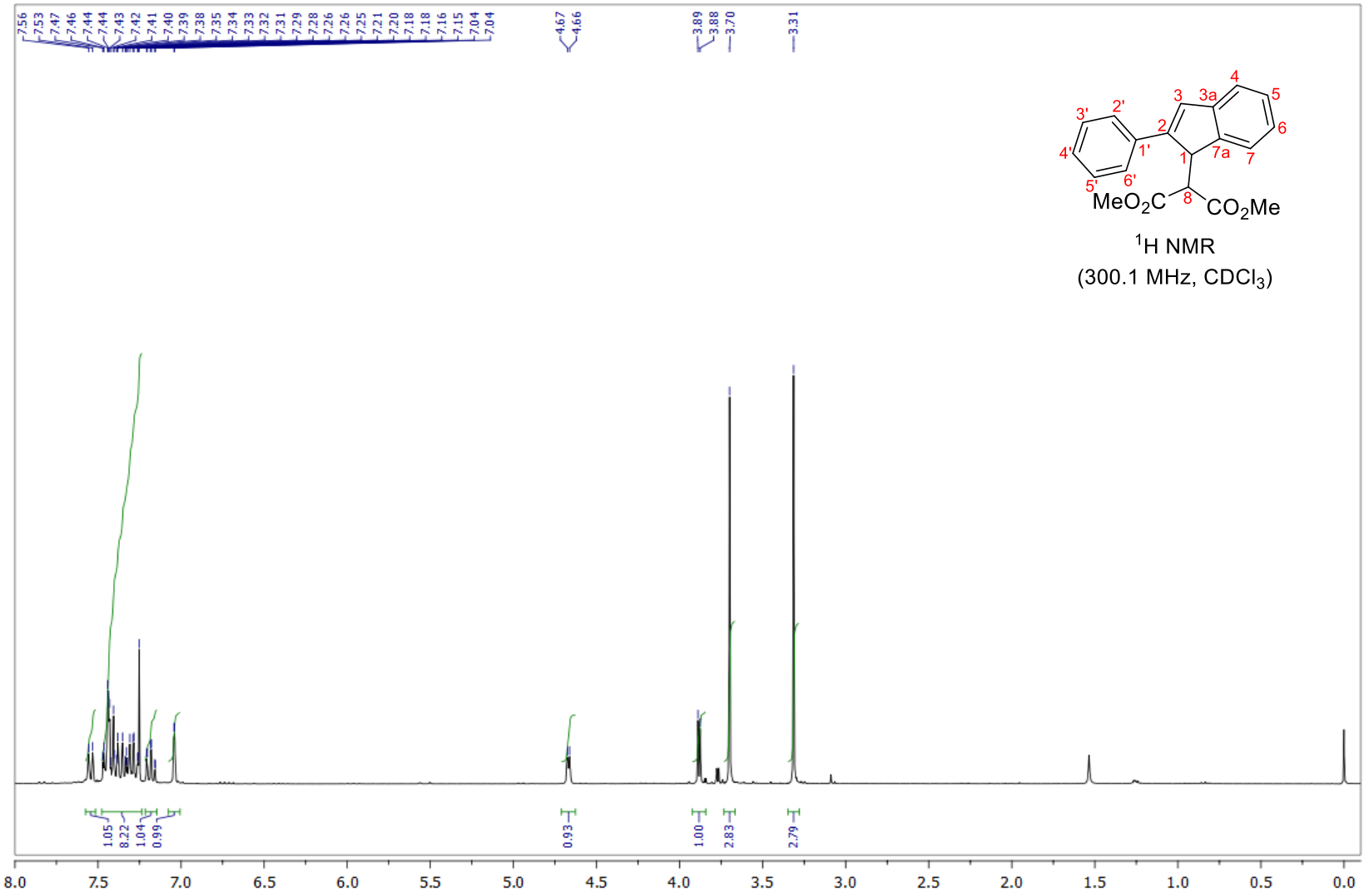
S3 (*a*) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339; https://doi.org/10.1107/S0021889808042726; (*b*) G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3; https://doi.org/10.1107/S2053229614024218.

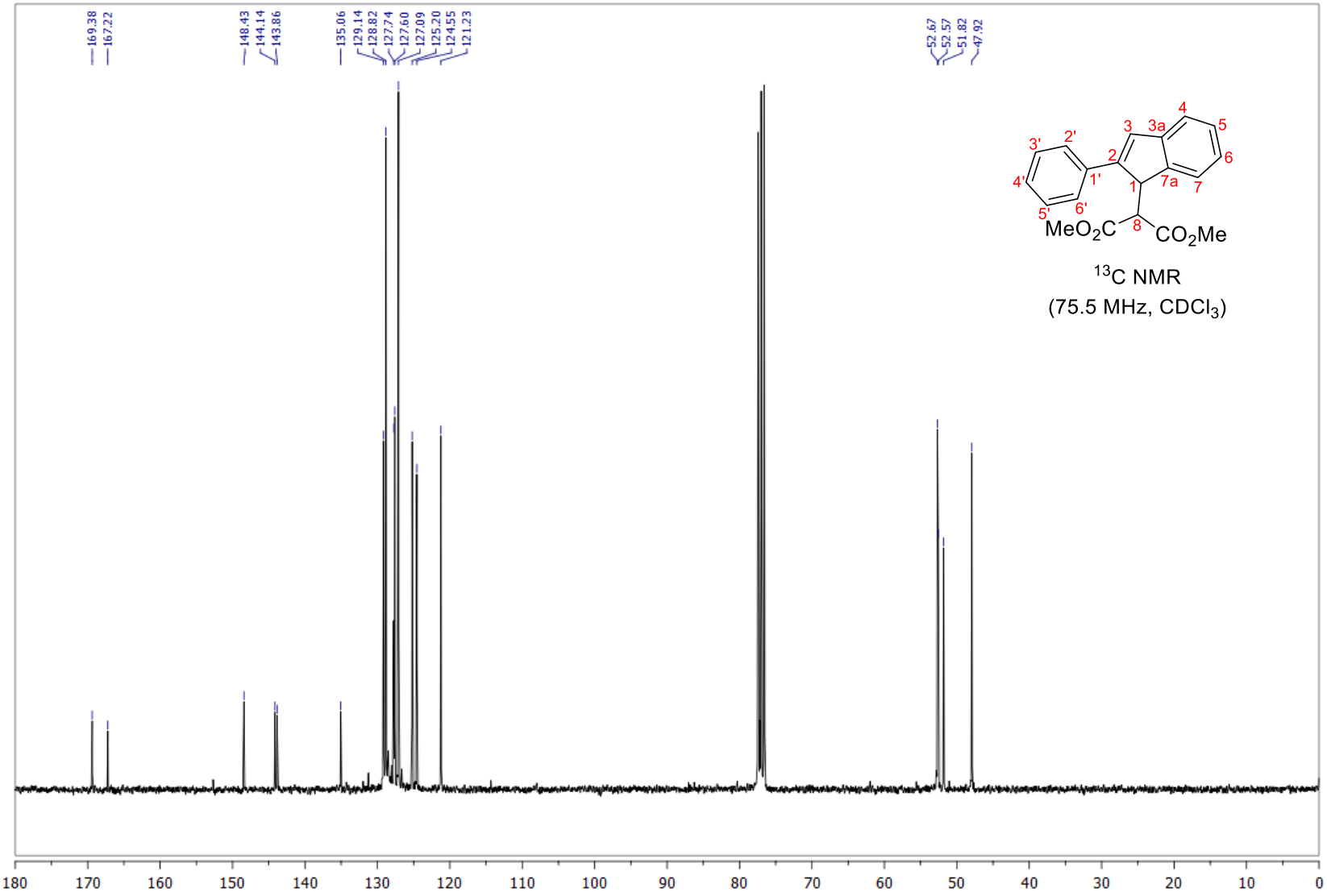
S4 D. D. Borisov, R. A. Novikov and Yu. V. Tomilov, *J. Org. Chem.*, 2021, **86**, 4457; https://doi.org/10.1021/acs.joc.0c02891.

S5 D. D. Borisov, R. A. Novikov and Y. V. Tomilov, *Angew. Chem., Int. Ed.*, 2016, **55**, 12233; https://doi.org/10.1002/anie.201603927.

4. NMR Spectrum Copies:

4.1 NMR spectra for indenes **2a–l**:

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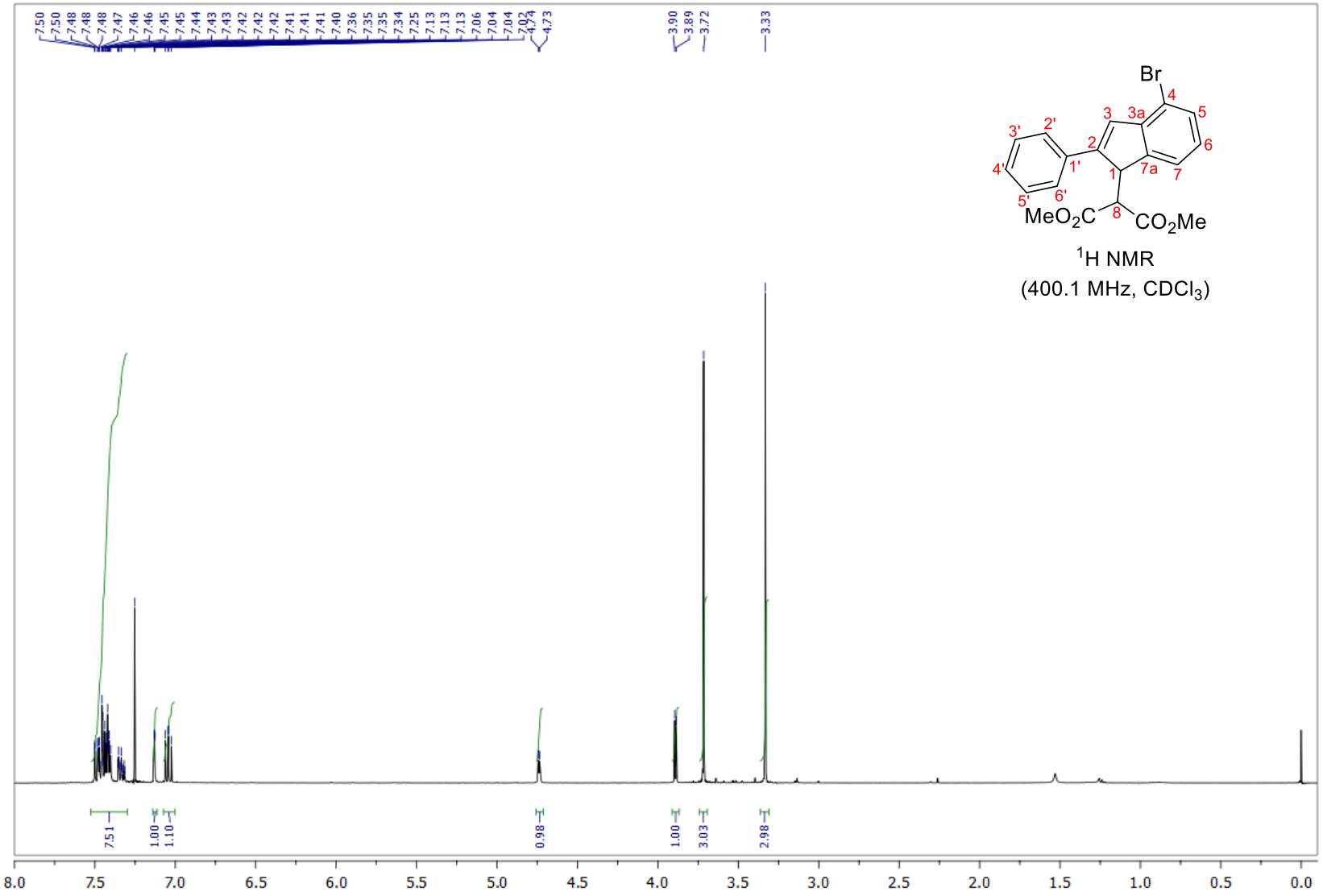
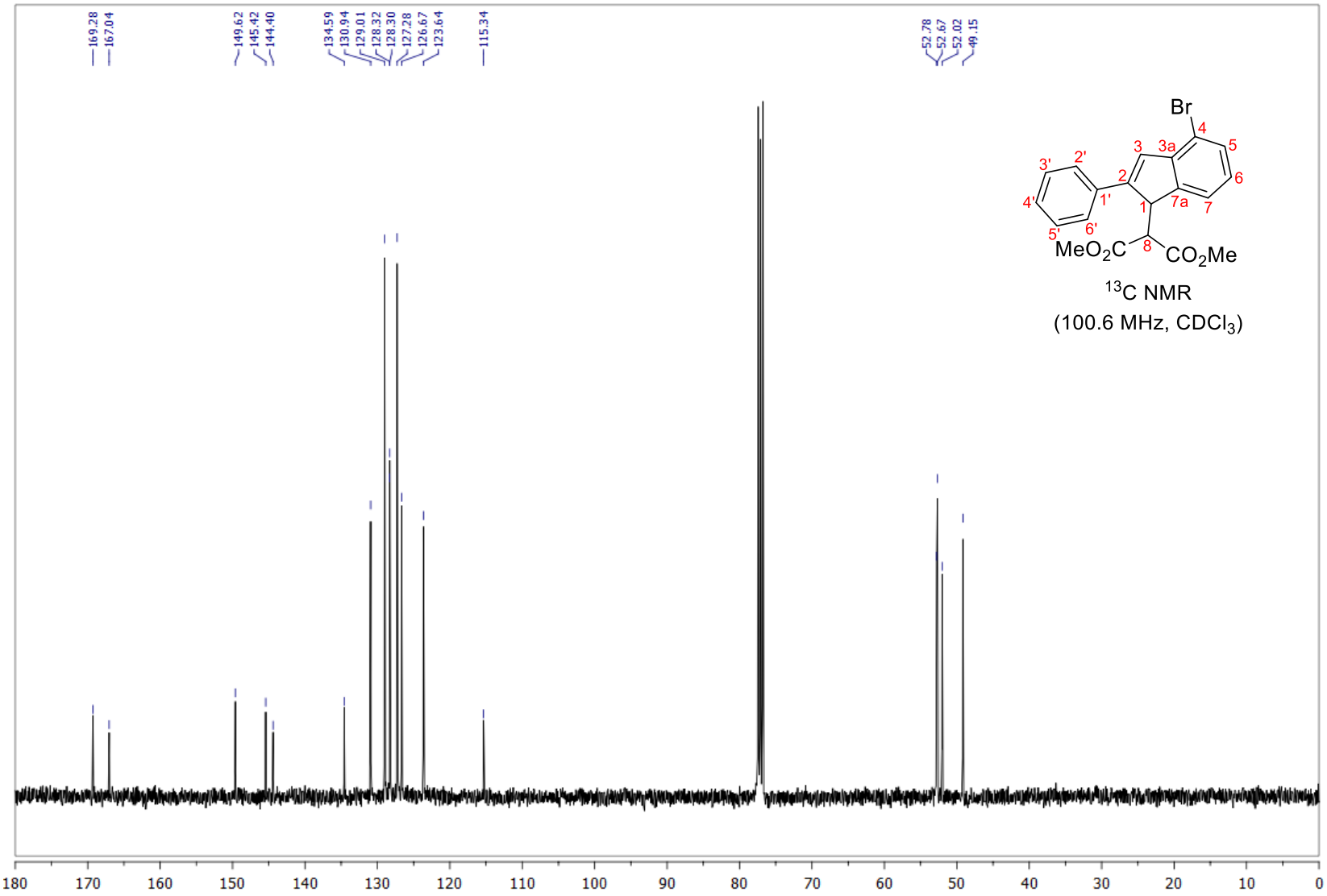
167.22
148.43
144.14
143.86
135.06
129.14
128.82
127.74
127.60
127.09
125.20
124.55
121.23
52.67
52.57
51.82
47.92
4
3
3a
5
6
7
7a
1
2
1'
2'
3'
4'
5'
6'
8
MeO2C
CO2Me
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Br
4
5
6
7
7a
3a
3
2
1
1'
2'
3'
4'
5'
6'
8
MeO2C
CO2Me
1H NMR
(400.1 MHz, CDCl3)
7.50
7.50
7.48
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.36
7.35
7.35
7.34
7.25
7.13
7.13
7.13
7.06
7.04
7.04
7.02
4.74
4.73
3.90
3.89
3.72
3.33
7.51
1.00
1.10
0.98
1.00
3.03
2.98
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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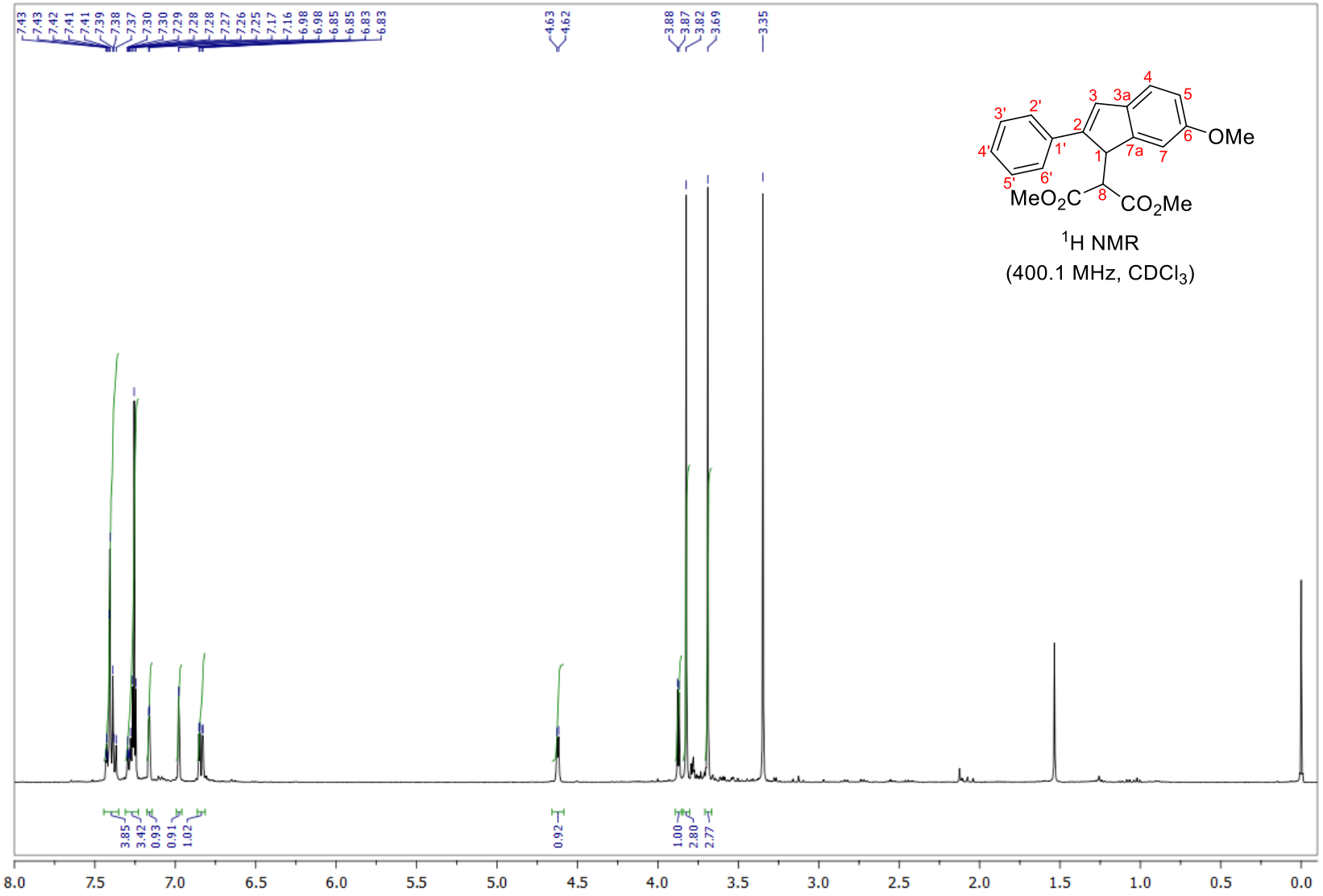
167.04
149.62
145.42
144.40
134.59
130.94
129.01
128.32
128.30
127.28
126.67
123.64
115.34
52.78
52.67
52.02
49.15
Br
MeO2C
CO2Me
13C NMR
(100.6 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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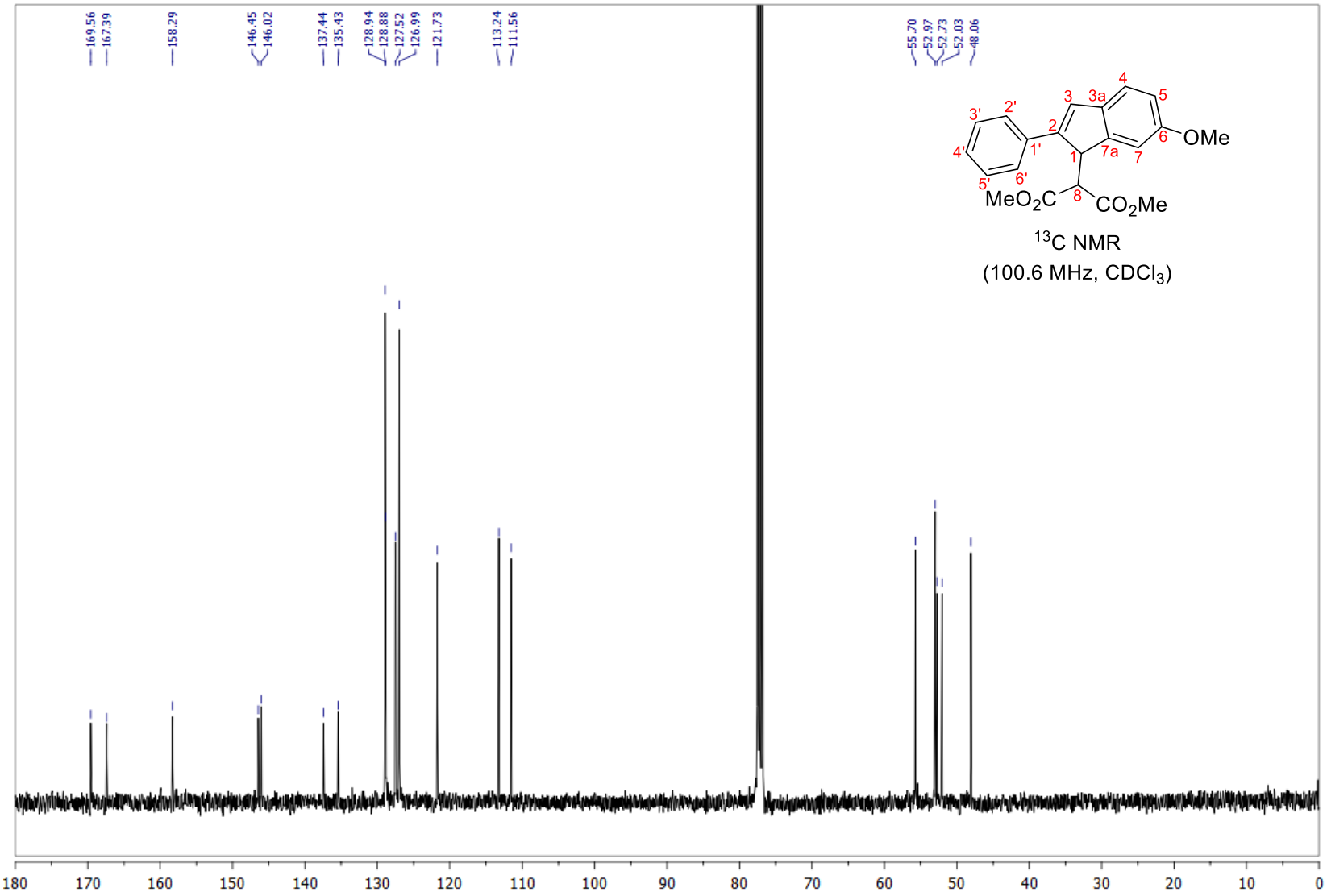
7.43
7.42
7.41
7.41
7.39
7.38
7.37
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.25
7.17
7.16
6.98
6.98
6.85
6.85
6.83
6.83
4.63
4.62
3.88
3.87
3.82
3.69
3.35
4
3
3a
5
2'
3'
2
6
OMe
4'
1'
1
7a
7
6'
5'
8
MeO2C
CO2Me
1H NMR
(400.1 MHz, CDCl3)
3.85
3.42
0.93
0.91
1.02
0.92
1.00
2.80
2.77
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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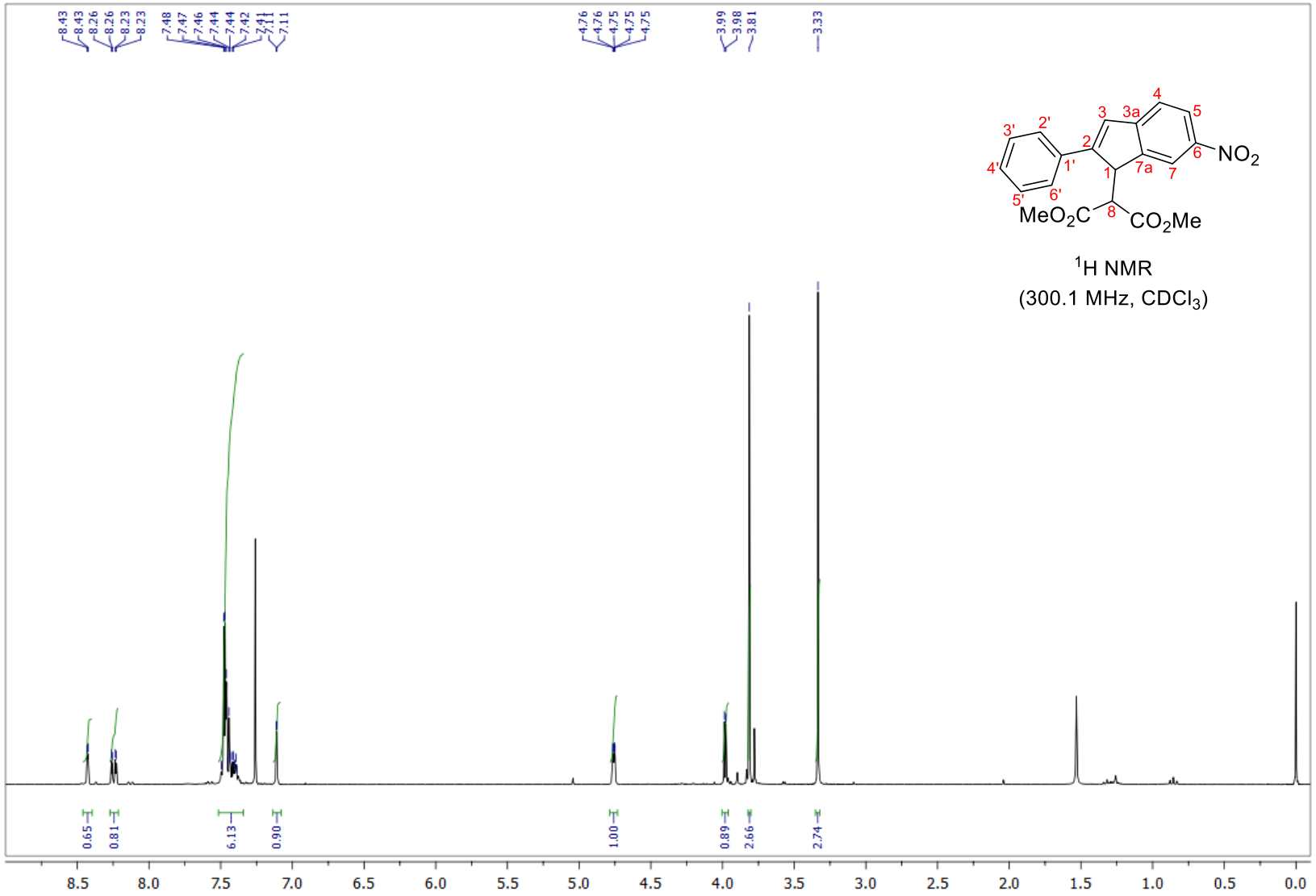
158.29
146.45
146.02
137.44
135.43
128.94
128.88
127.52
126.99
121.73
113.24
111.56
55.70
52.97
52.73
52.03
48.06
OMe
MeO2C
CO2Me
13C NMR
(100.6 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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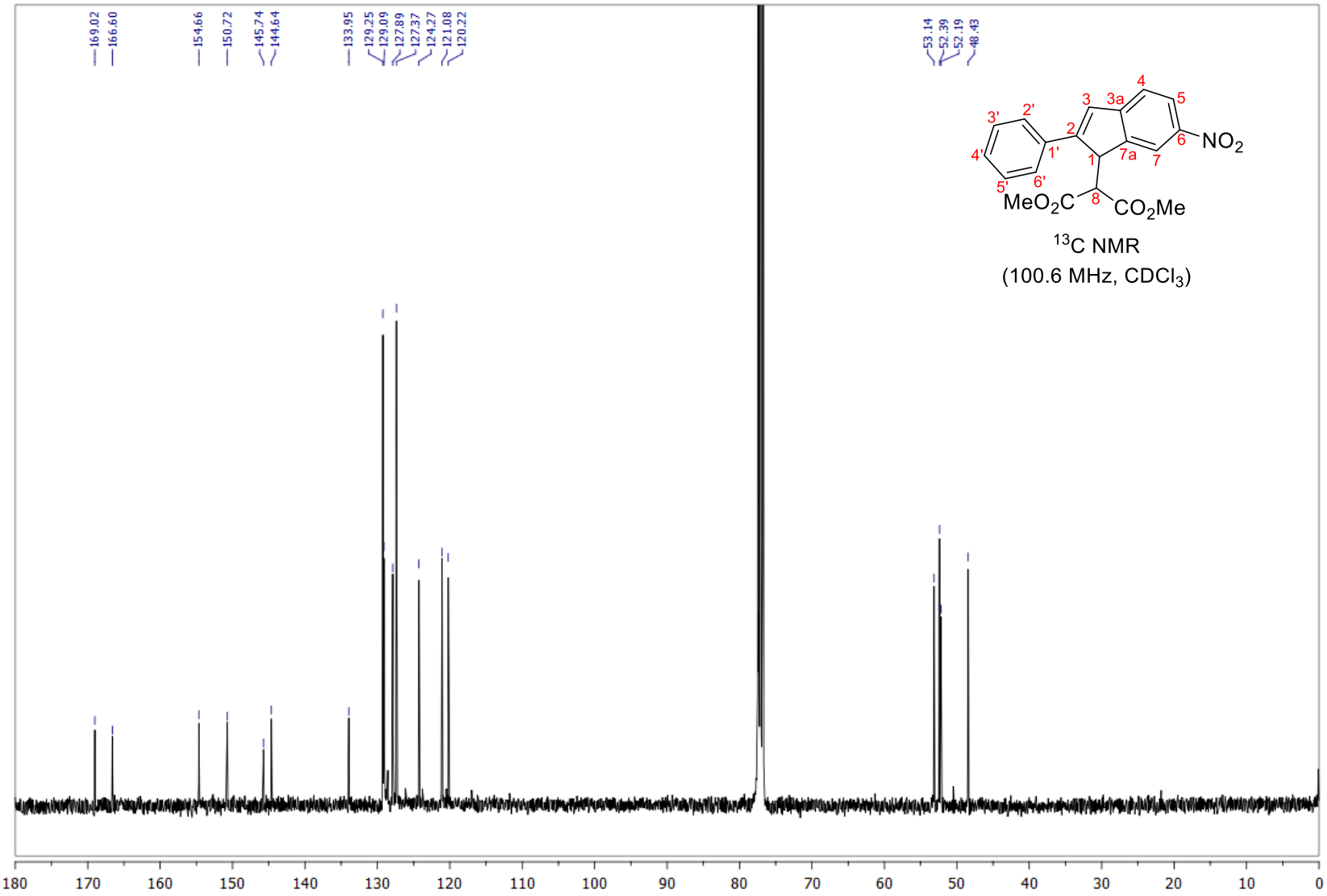
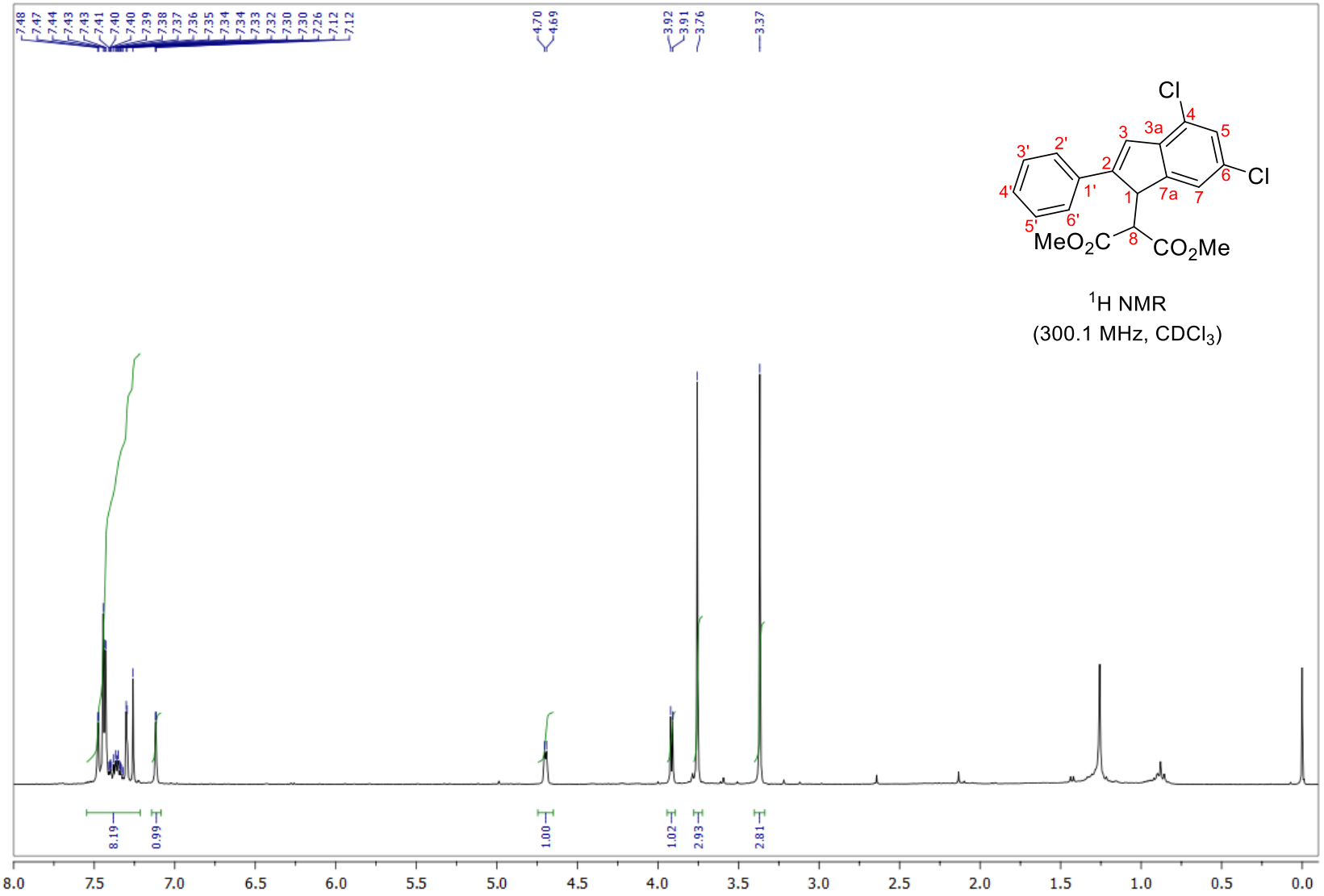
8.43
8.26
8.26
8.23
8.23
7.48
7.47
7.46
7.44
7.44
7.42
7.11
7.11
4.76
4.76
4.75
4.75
4.75
4.75
3.99
3.98
3.81
3.33
4
3
3a
5
3'
2'
2
6
NO2
4'
1'
1
7a
7
5'
6'
MeO2C
8
CO2Me
1H NMR
(300.1 MHz, CDCl3)
0.65
0.81
6.13
0.90
1.00
0.89
2.66
2.74
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


169.02
166.60
154.66
150.72
145.74
144.64
133.95
129.25
129.09
127.89
127.37
124.27
121.08
120.22
53.14
52.39
52.19
48.43
4
3
3a
5
2'
3'
2
6
NO2
4'
1'
1
7a
7
6'
5'
MeO2C
8
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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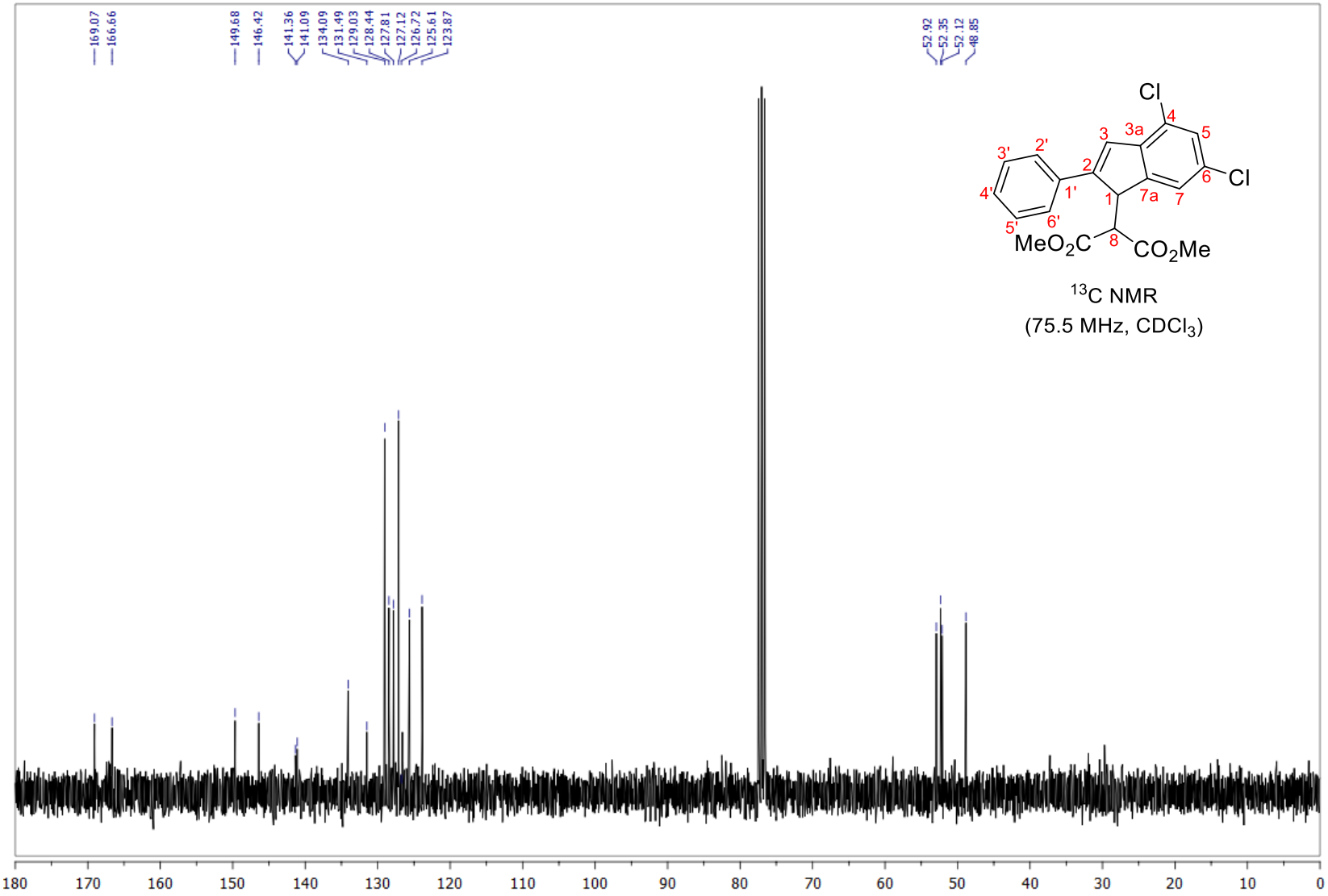
7.47
7.44
7.43
7.43
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.30
7.30
7.26
7.12
7.12
4.70
4.69
3.92
3.91
3.76
3.37
Cl
4
3
3a
5
2'
3'
2
6
Cl
4'
1'
1
7a
7
6'
5'
8
MeO2C
CO2Me
1H NMR
(300.1 MHz, CDCl3)
8.19
0.99
1.00
1.02
2.93
2.81
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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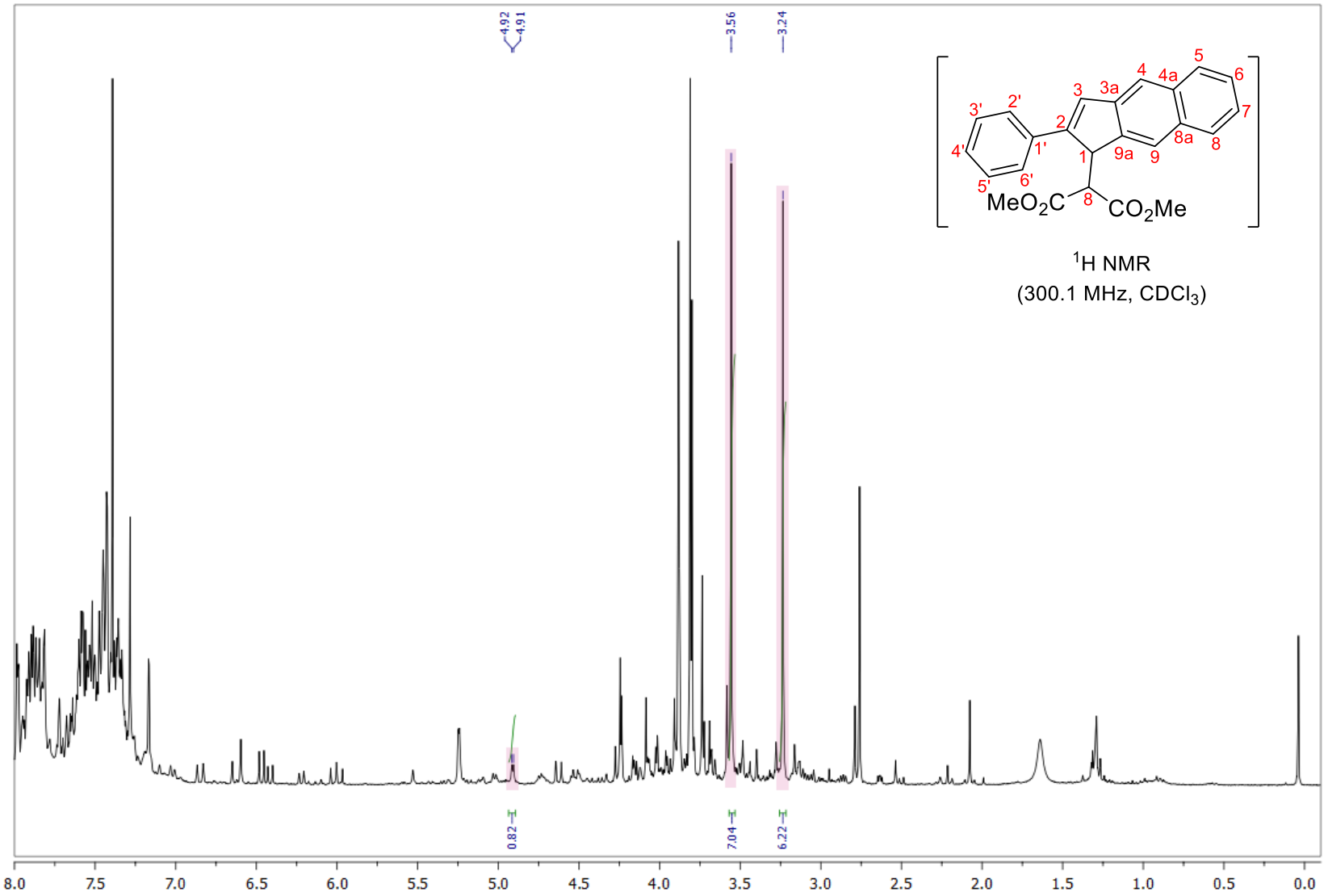
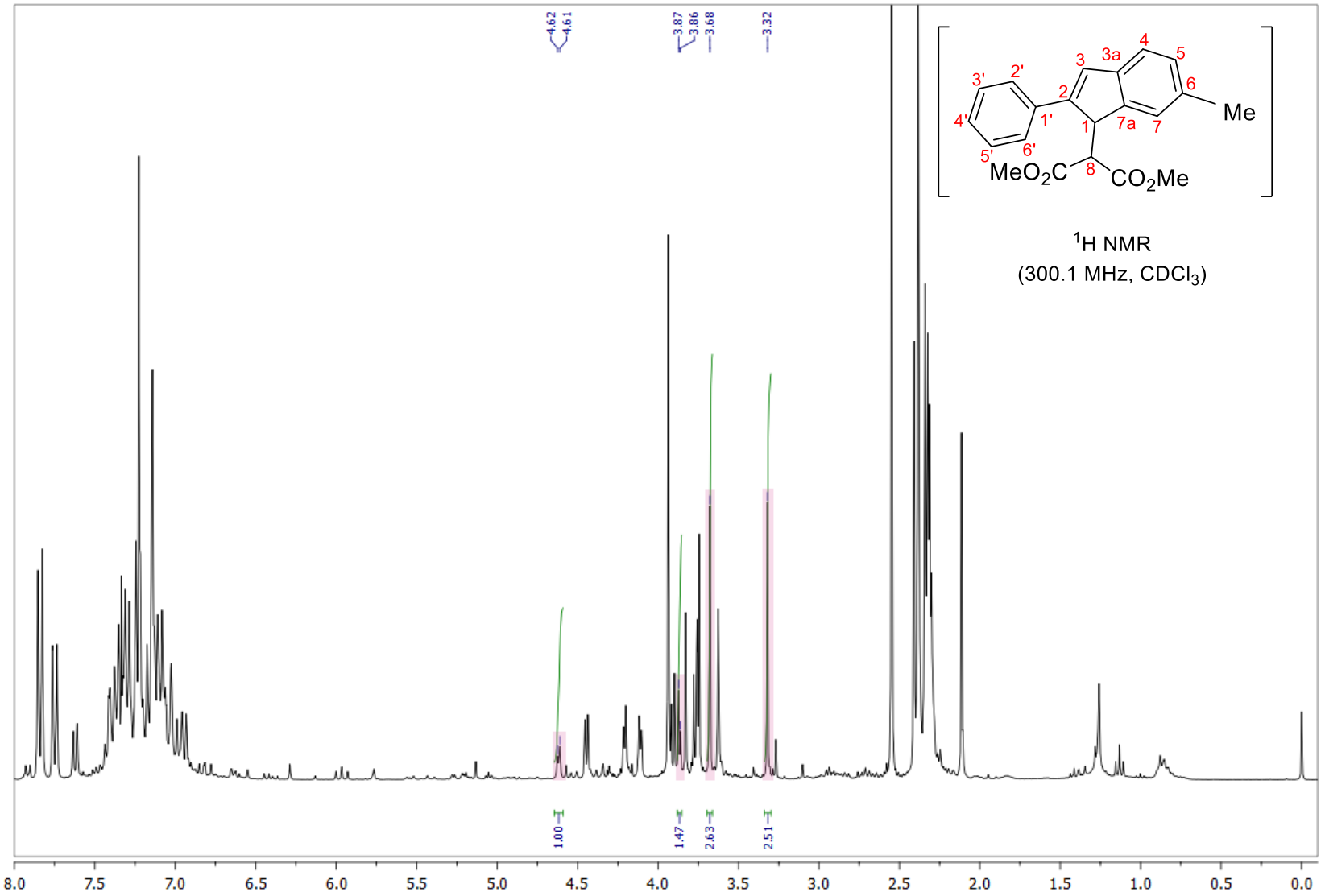
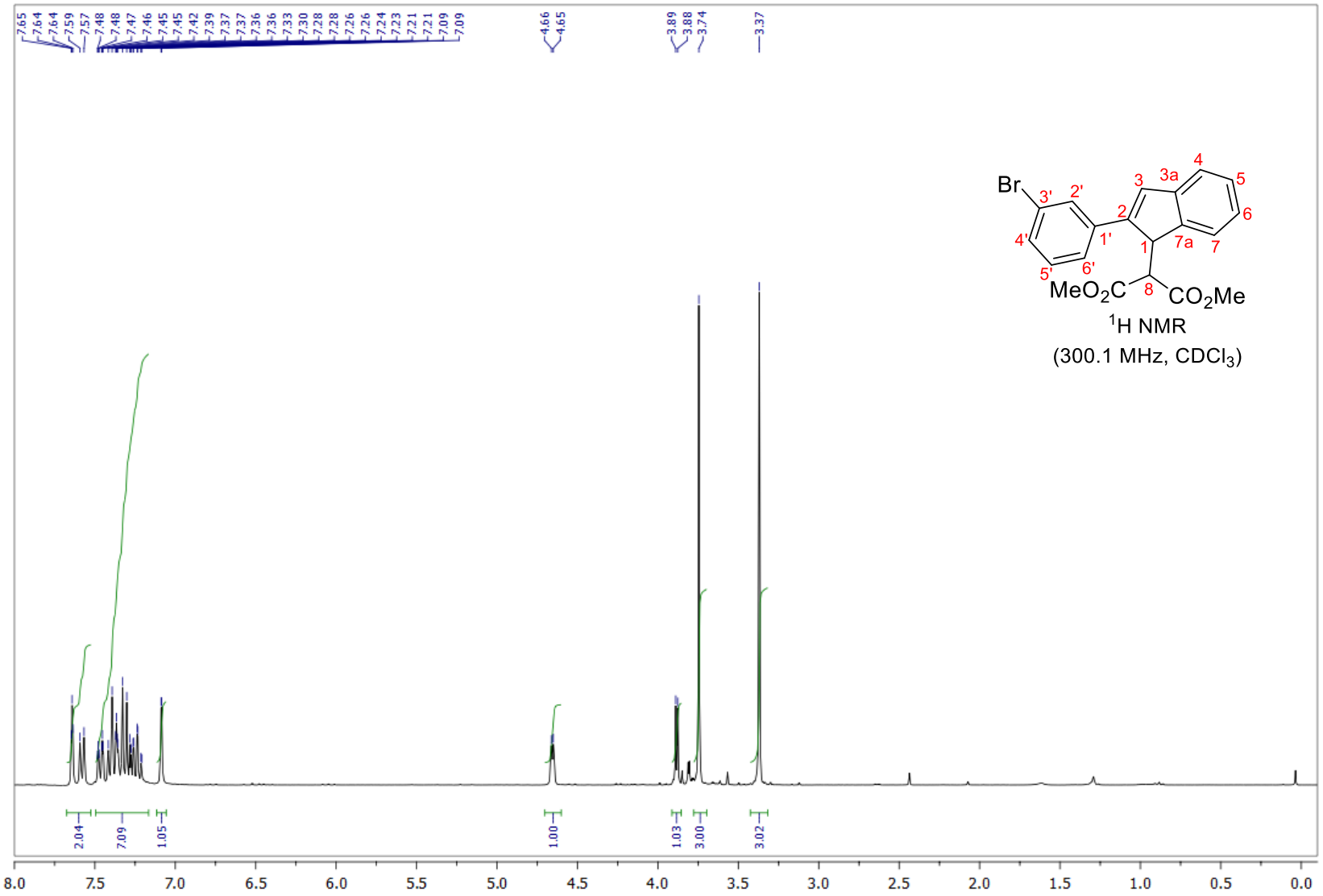
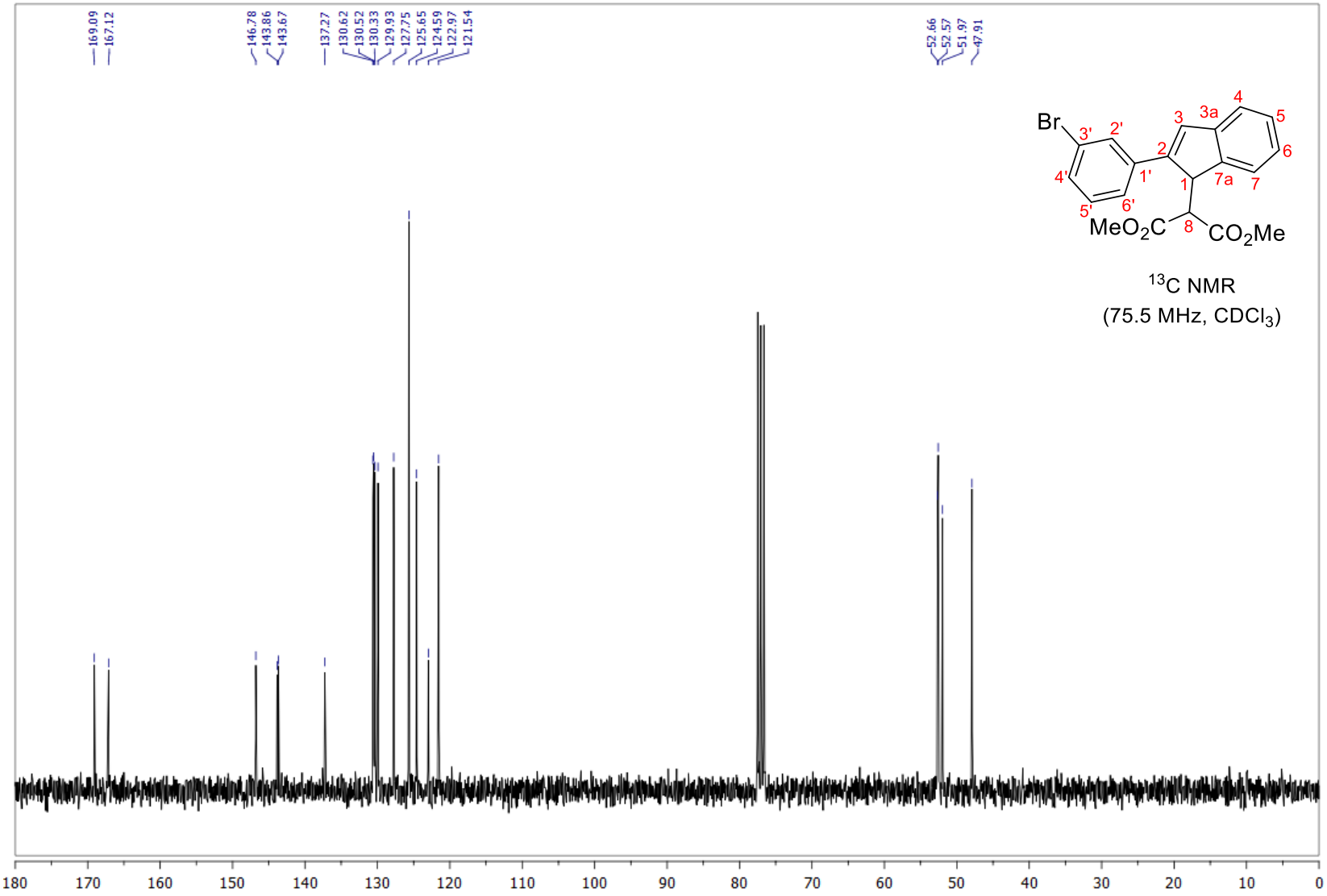
166.66
149.68
146.42
141.36
141.09
134.09
131.49
129.03
128.44
127.81
127.12
126.72
125.61
123.87
52.92
52.35
52.12
48.85
Cl
Cl
MeO2C
CO2Me
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


4.92
4.91
3.56
3.24
0.82
7.04
6.22
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
MeO2C
CO2Me
1H NMR
(300.1 MHz, CDCl3)


4.62
4.61
3.87
3.86
3.68
3.32
1.00
1.47
2.63
2.51
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
Me
MeO2C
CO2Me
1H NMR
(300.1 MHz, CDCl3)


7.65
7.64
7.64
7.59
7.57
7.48
7.48
7.47
7.46
7.45
7.45
7.42
7.39
7.37
7.37
7.36
7.36
7.33
7.30
7.28
7.28
7.26
7.26
7.24
7.23
7.21
7.21
7.09
7.09
4.66
4.65
3.89
3.88
3.74
3.37
Br
3'
2'
3
3a
4
5
6
2
4'
1'
1
7a
7
6'
5'
8
MeO2C
CO2Me
1H NMR
(300.1 MHz, CDCl3)
2.04
7.09
1.05
1.00
1.03
3.00
3.02
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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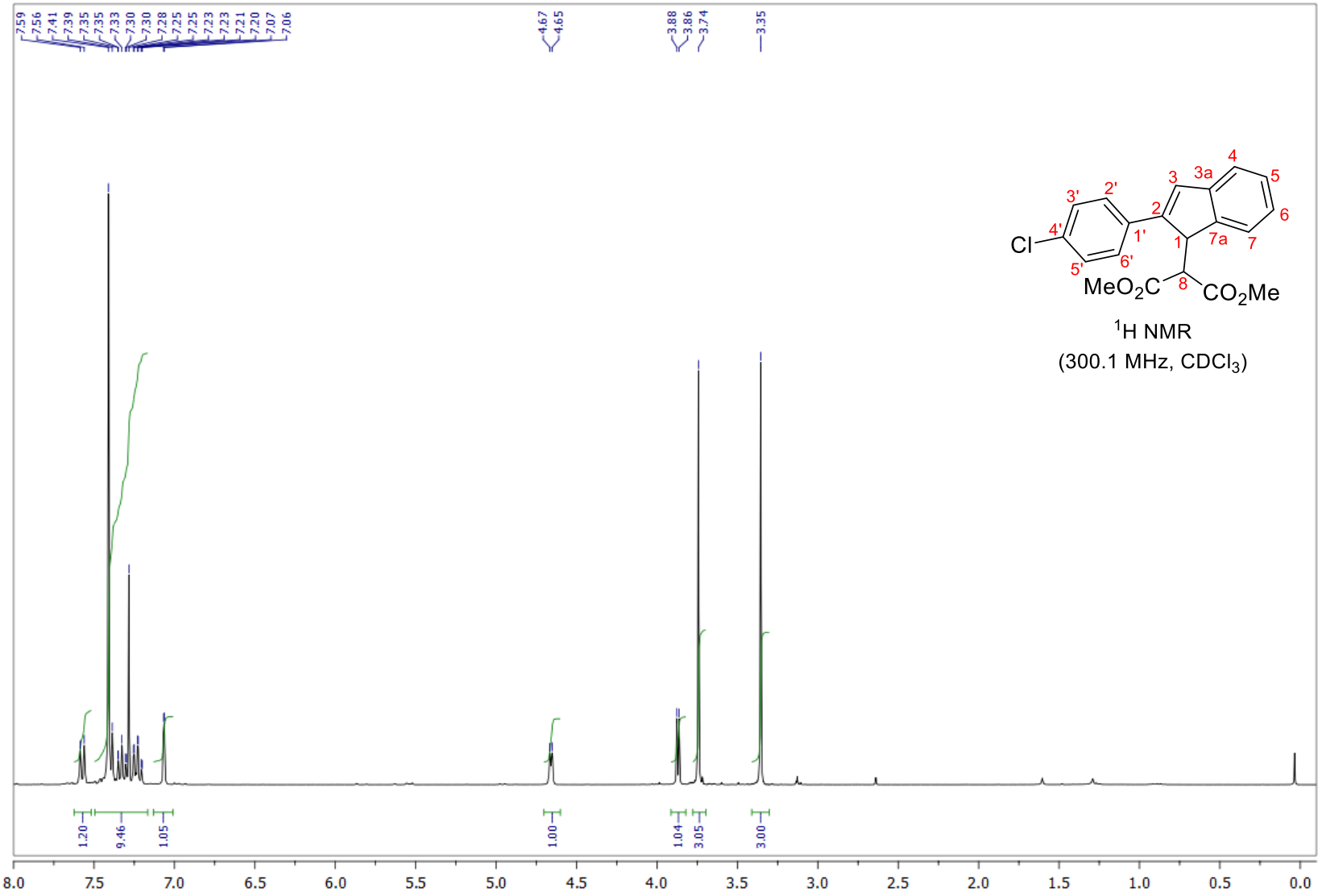
167.12
146.78
143.86
143.67
137.27
130.62
130.52
130.33
129.93
127.75
125.65
124.59
122.97
121.54
52.66
52.57
51.97
47.91
Br
3'
2'
3
3a
4
5
6
2
4'
1'
1
7a
7
5'
6'
MeO2C
8
CO2Me
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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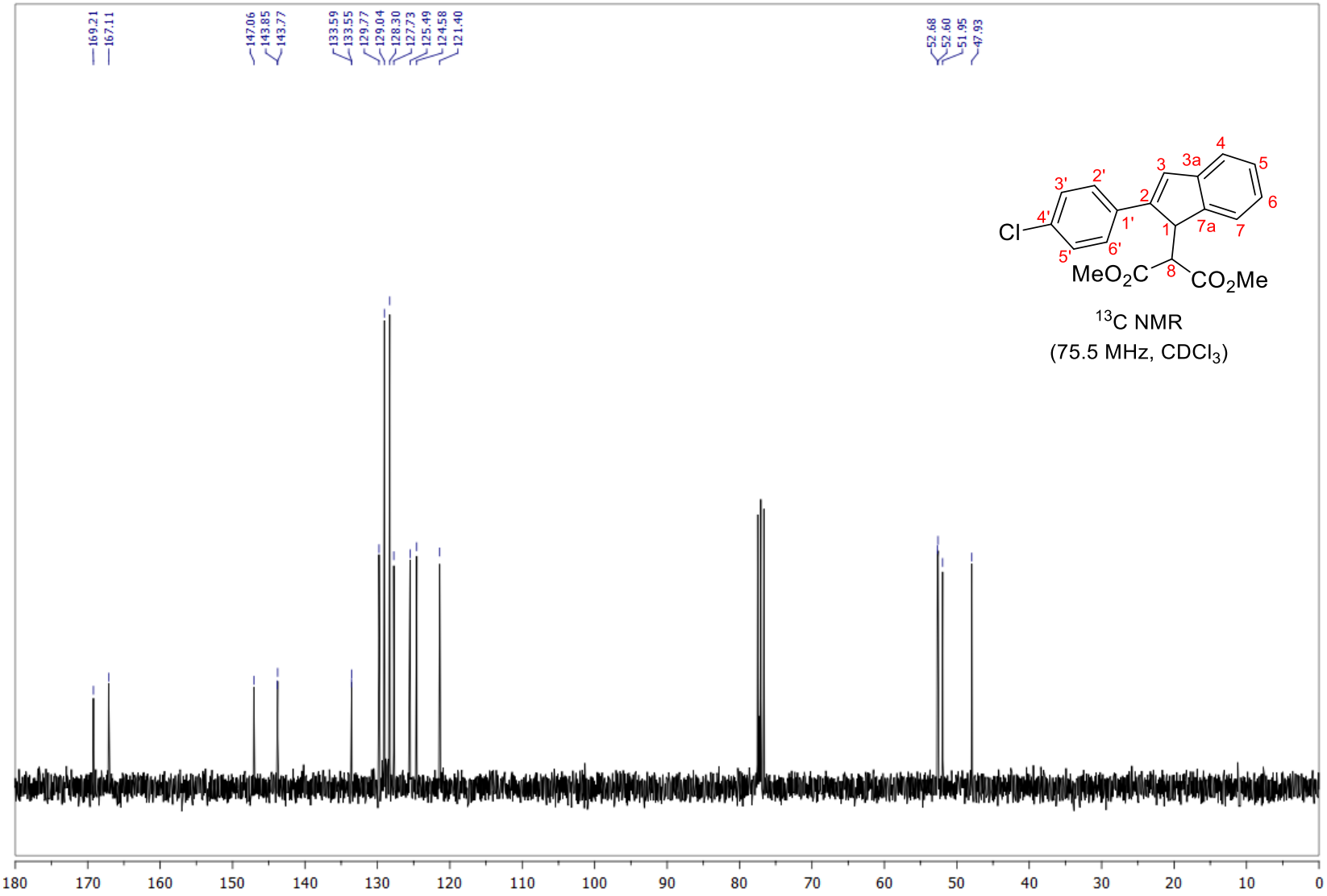
7.56
7.41
7.39
7.35
7.35
7.33
7.30
7.30
7.28
7.25
7.25
7.23
7.23
7.21
7.20
7.07
7.06
4.67
4.65
3.88
3.86
3.74
3.35
1.20
9.46
1.05
1.00
1.04
3.05
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Cl
MeO2C
CO2Me
1H NMR
(300.1 MHz, CDCl3)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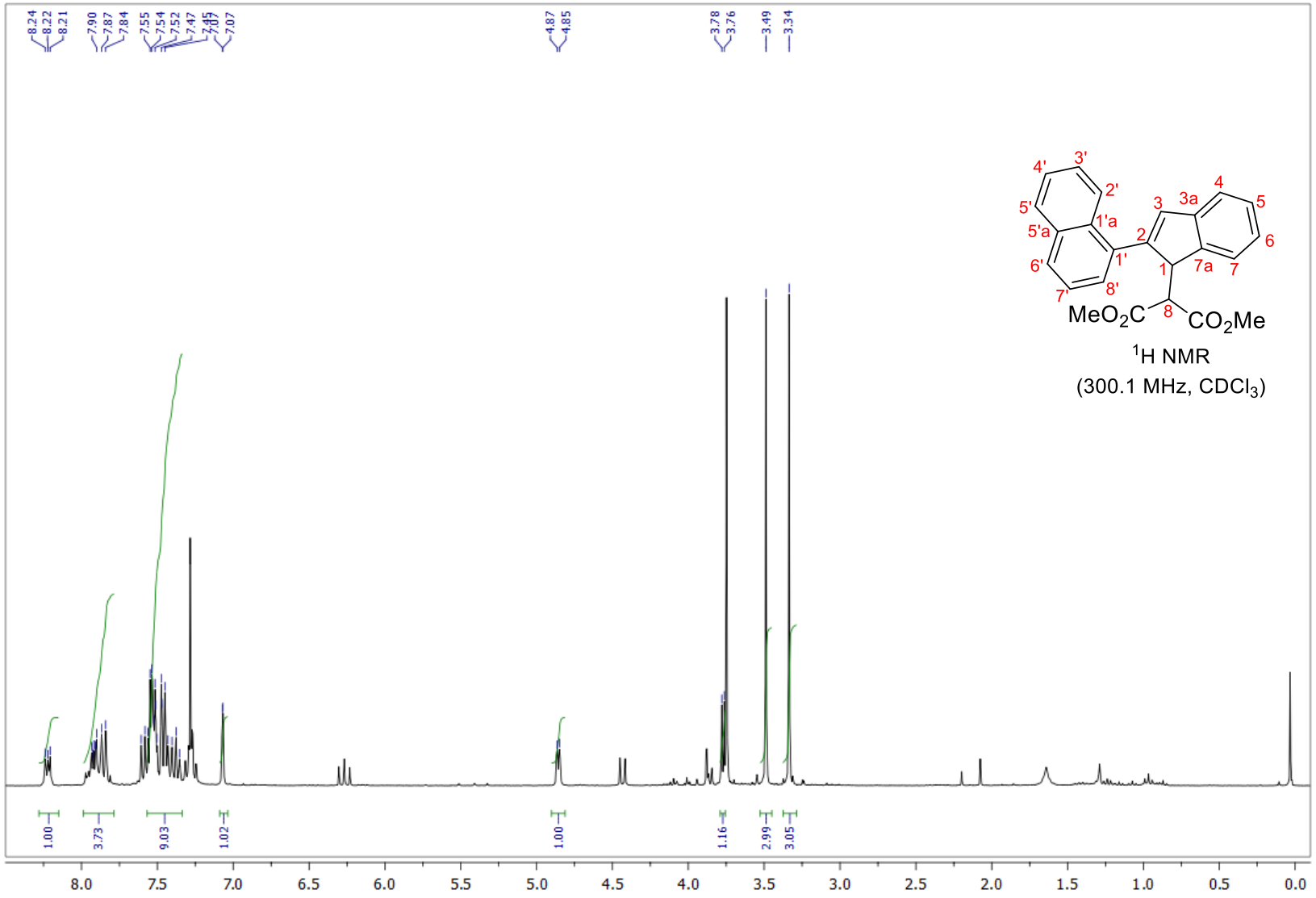
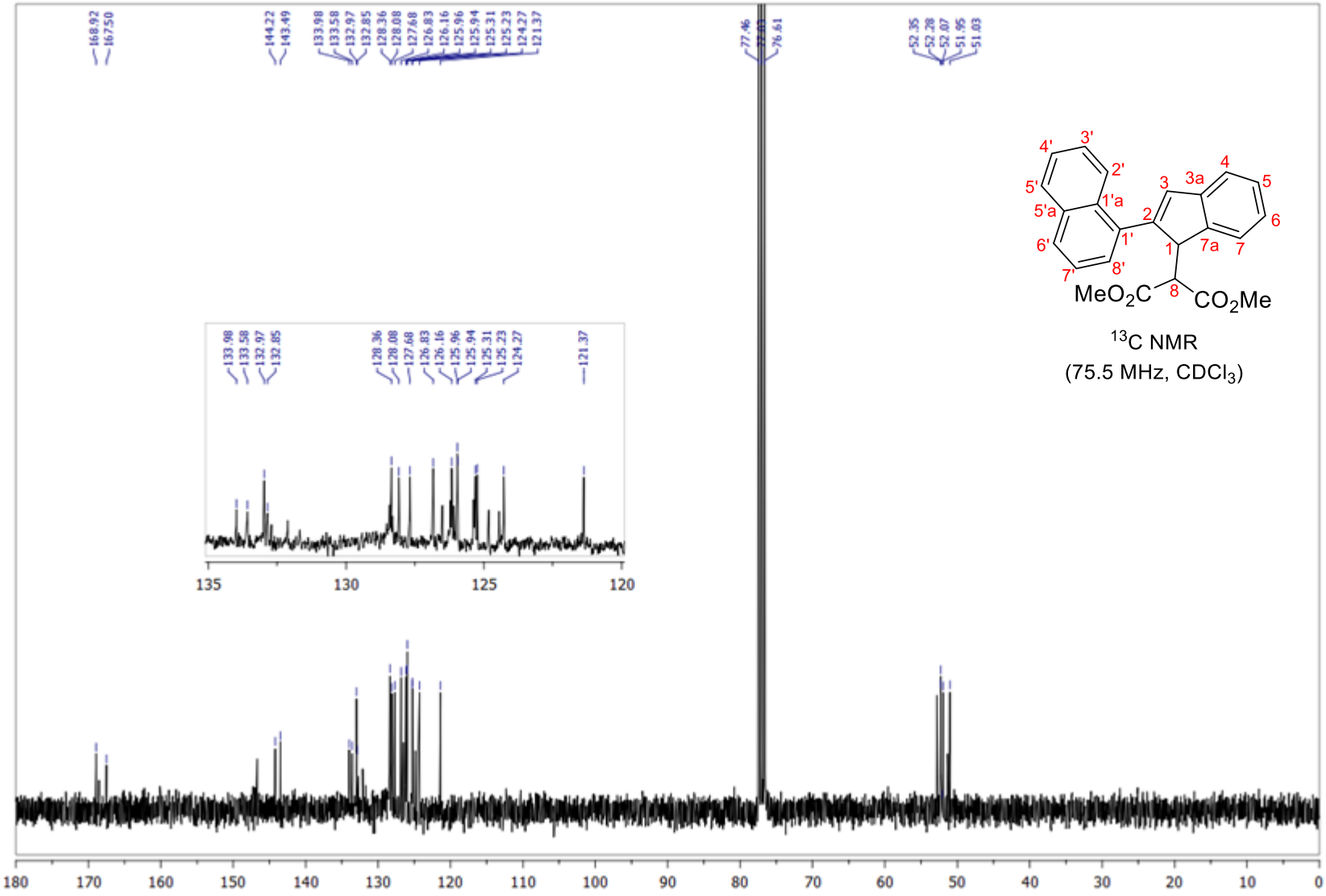
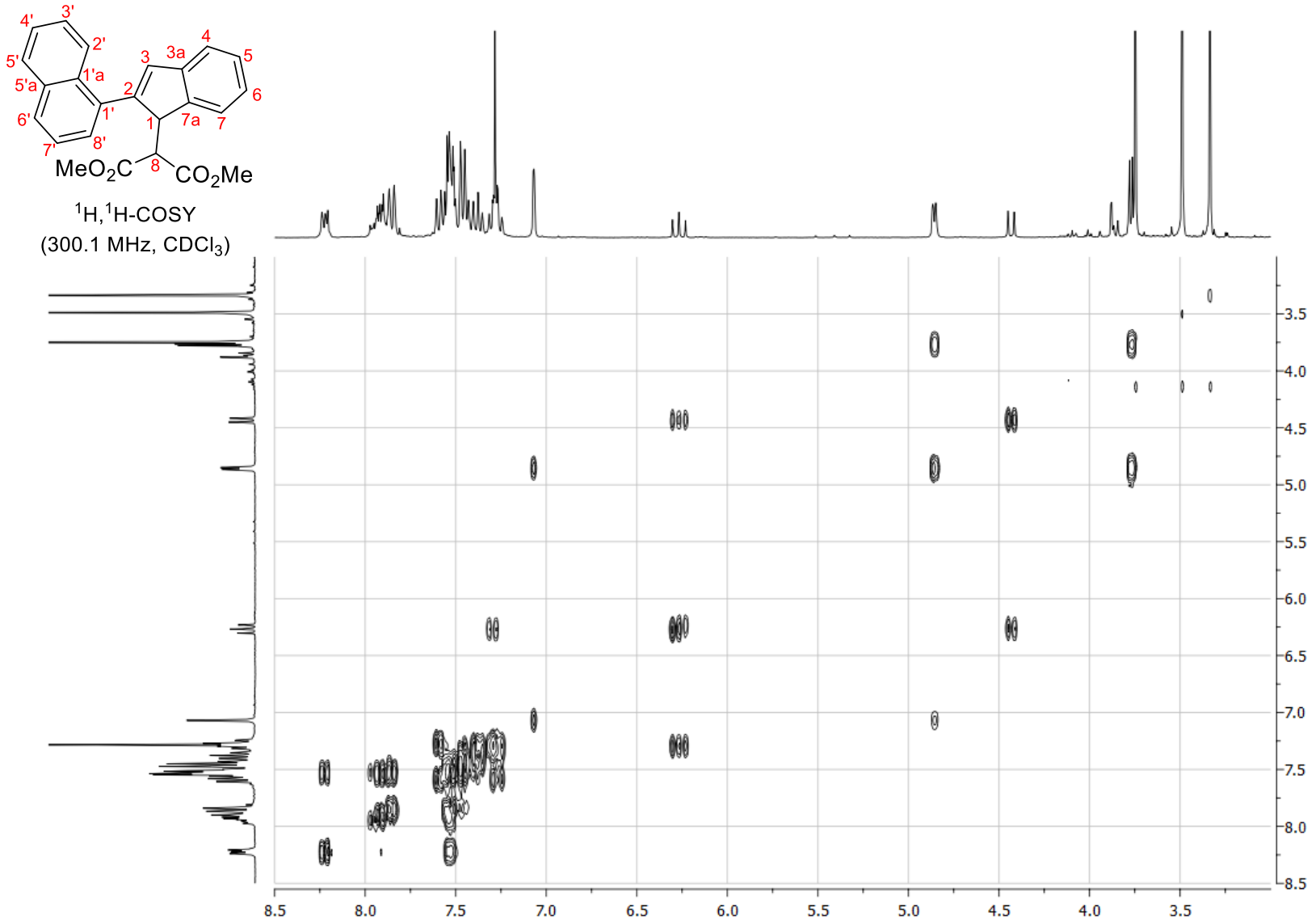
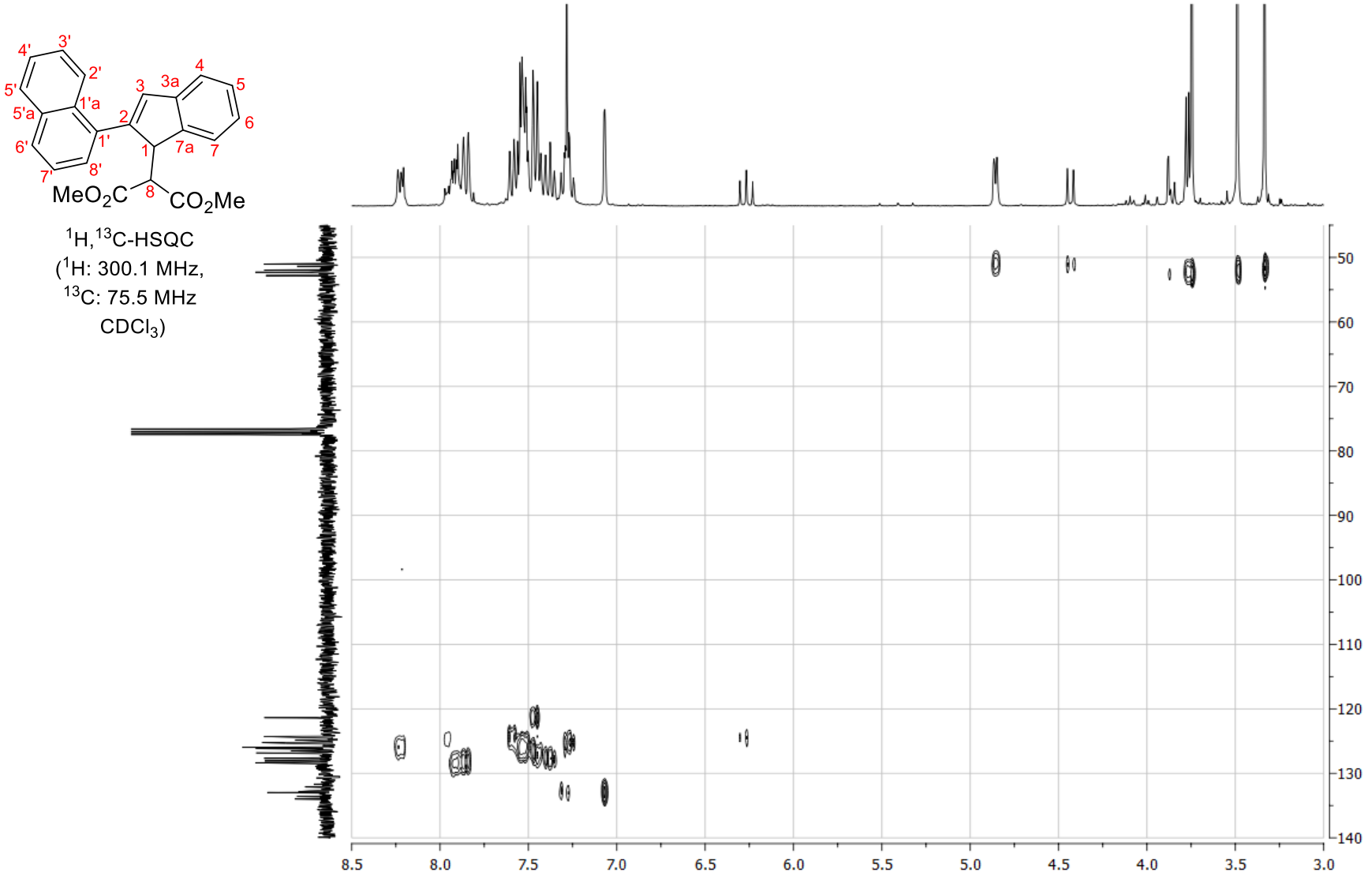
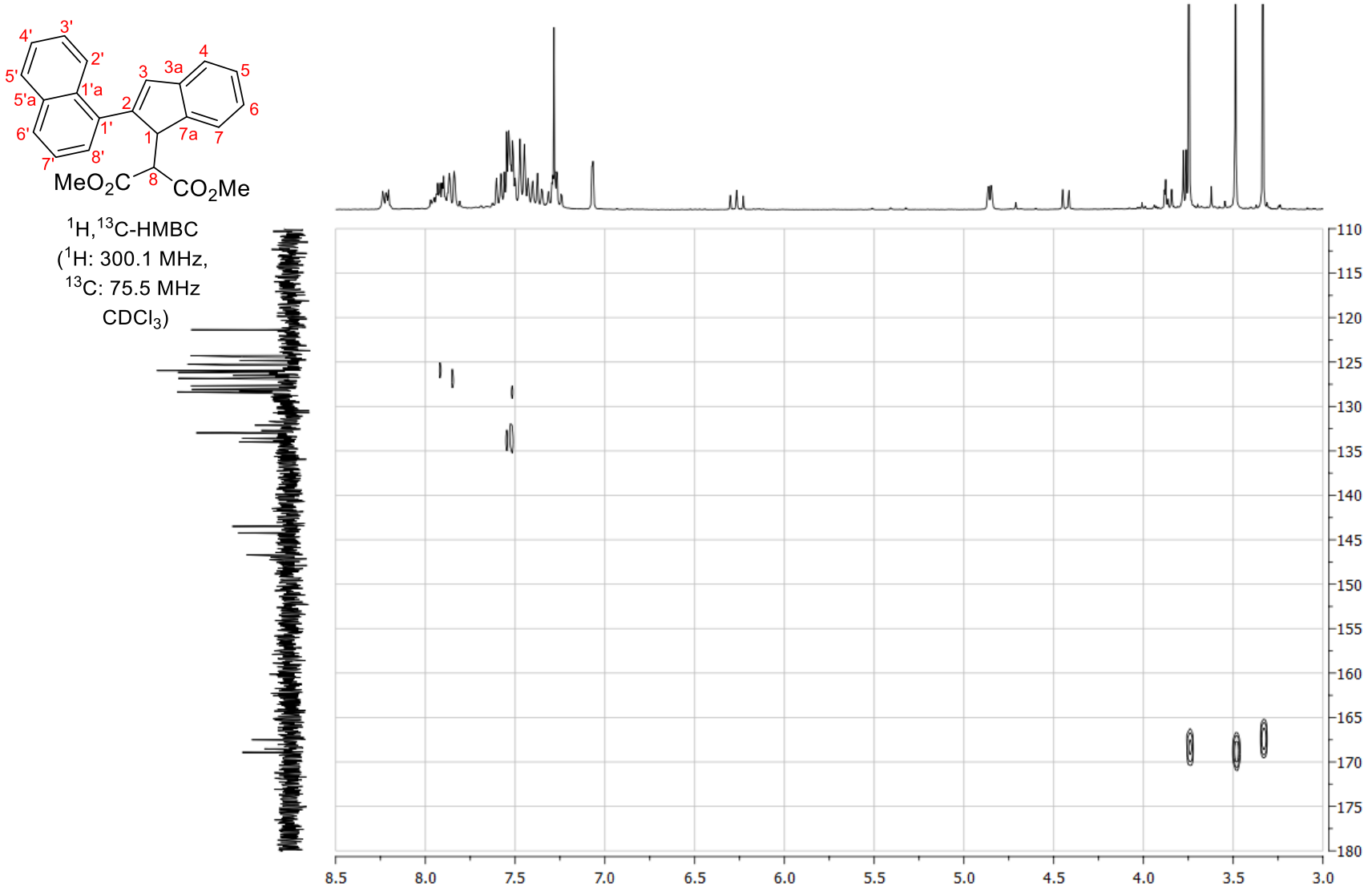
147.06
143.85
143.77
133.59
133.55
129.77
129.04
128.30
127.73
125.49
124.58
121.40
52.68
52.60
51.95
47.93
Cl
MeO2C
CO2Me
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

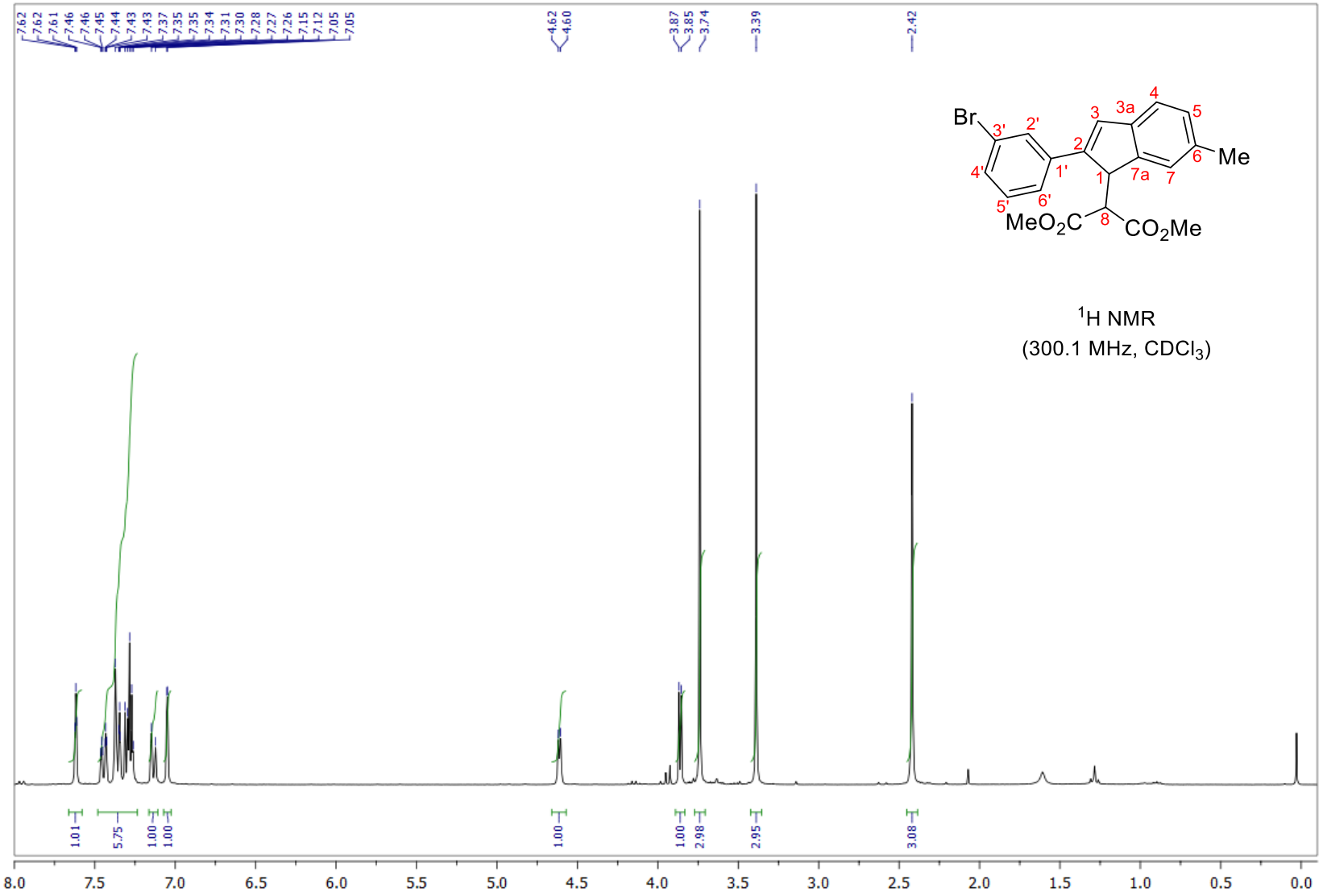

8.24
8.22
8.21
7.90
7.87
7.84
7.55
7.54
7.52
7.47
7.07
4.87
4.85
3.78
3.76
3.49
3.34
1.00
3.73
9.03
1.02
1.00
1.16
2.99
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4'
3'
2'
5'
1'a
3
3a
4
5
5'a
2
6
6'
1'
1
7a
7
7'
8'
8
MeO2C
CO2Me
1H NMR
(300.1 MHz, CDCl3)

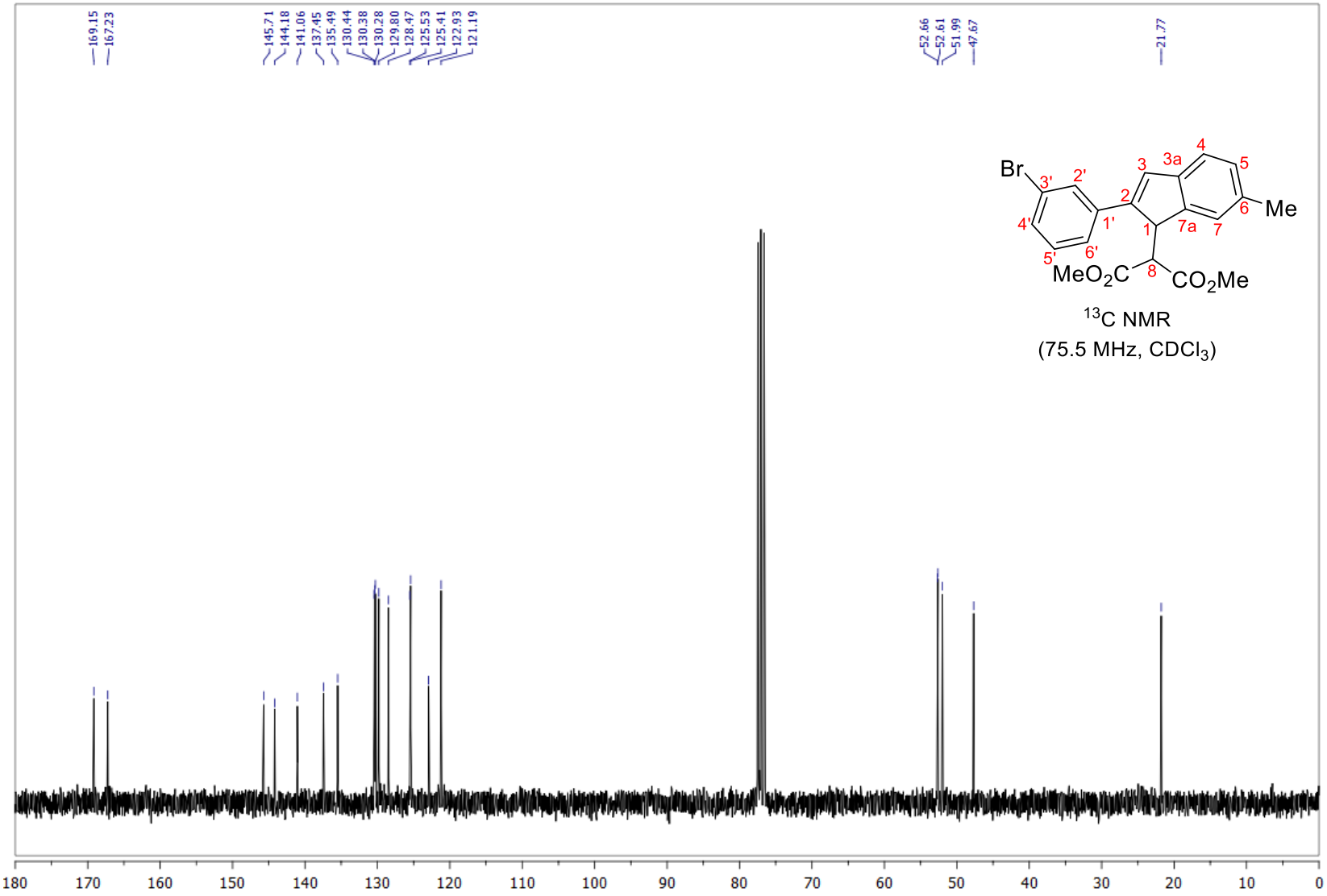

168.92
167.50
144.22
143.49
133.98
133.58
132.97
132.85
128.36
128.08
127.68
126.83
126.16
125.96
125.94
125.31
125.23
124.27
121.37
77.46
77.03
76.61
52.35
52.28
52.07
51.95
51.03
4'
3'
2'
3
3a
4
5
5'
1'a
5'a
2
6
6'
1'
1
7a
7
7'
8'
MeO2C
8
CO2Me
13C NMR
(75.5 MHz, CDCl3)
135
130
125
120
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

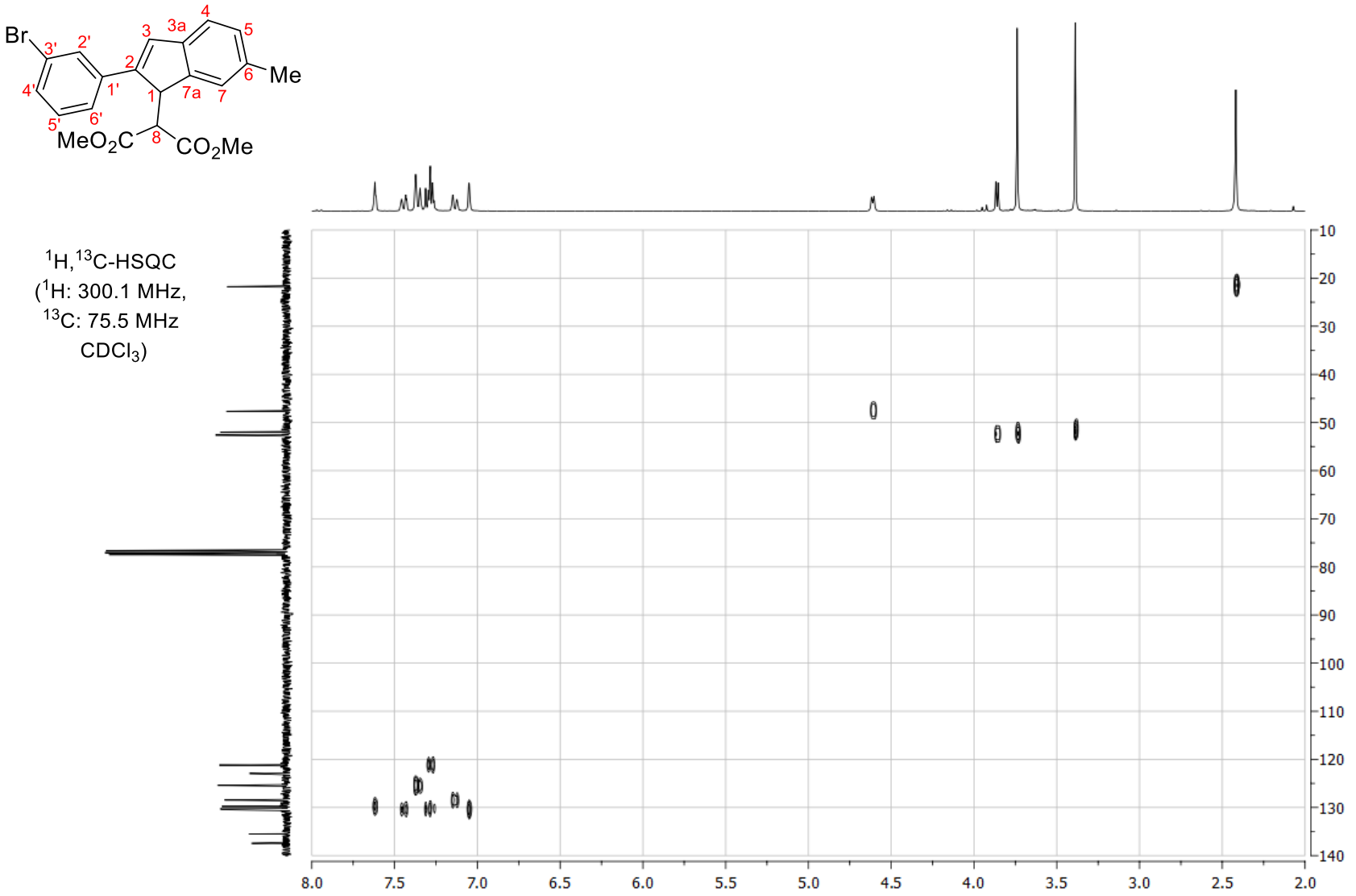

4'
3'
2'
5'
1'a
3
3a
4
5
5'a
2
6
6'
1'
1
7a
7
7'
8'
MeO2C
8
CO2Me
1H,1H-COSY
(300.1 MHz, CDCl3)
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

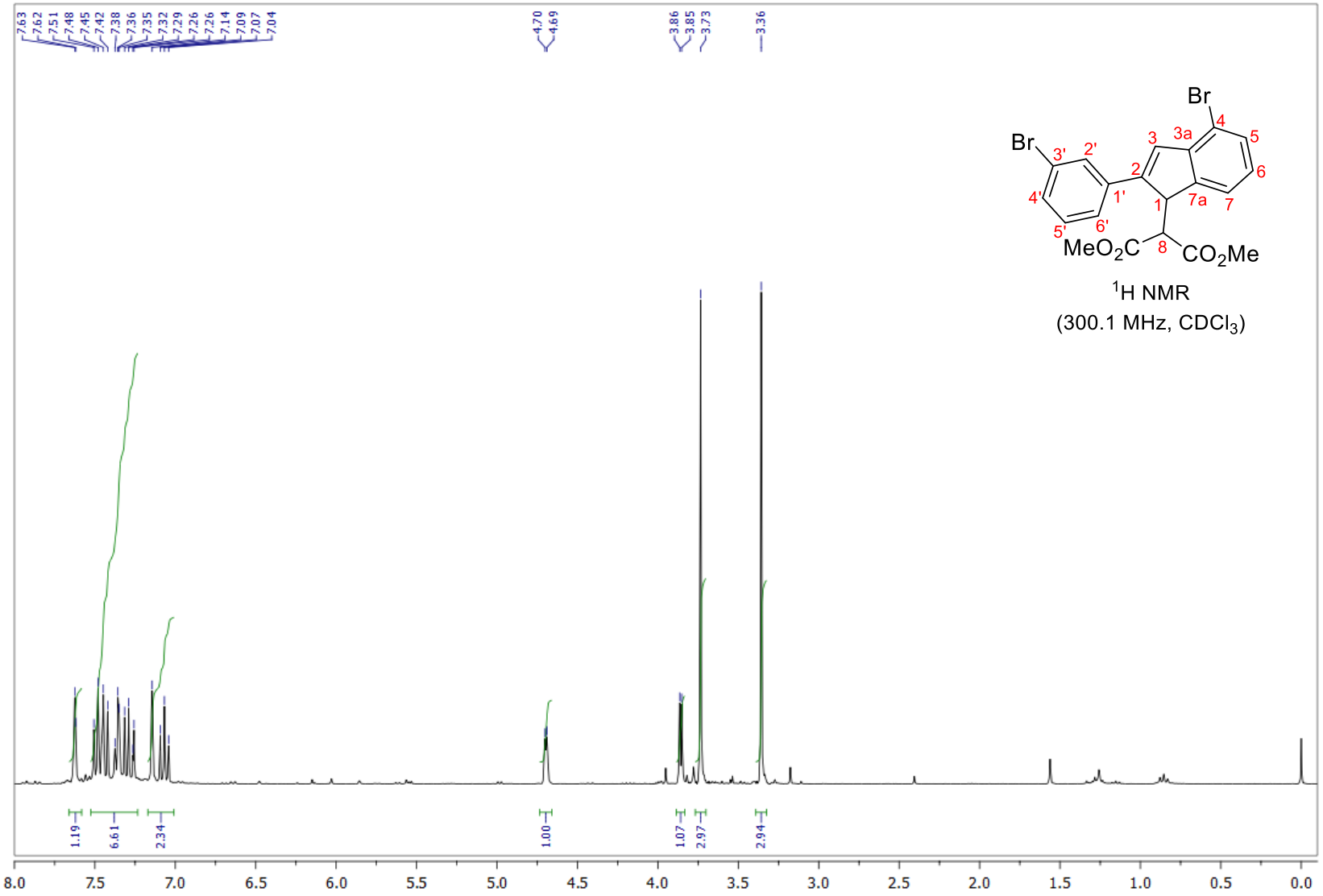

4'
3'
2'
5'
3
3a
4
5
1'a
5'a
2
6
6'
1'
1
7a
7
7'
8'
8
MeO2C
CO2Me
1H,13C-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
50
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

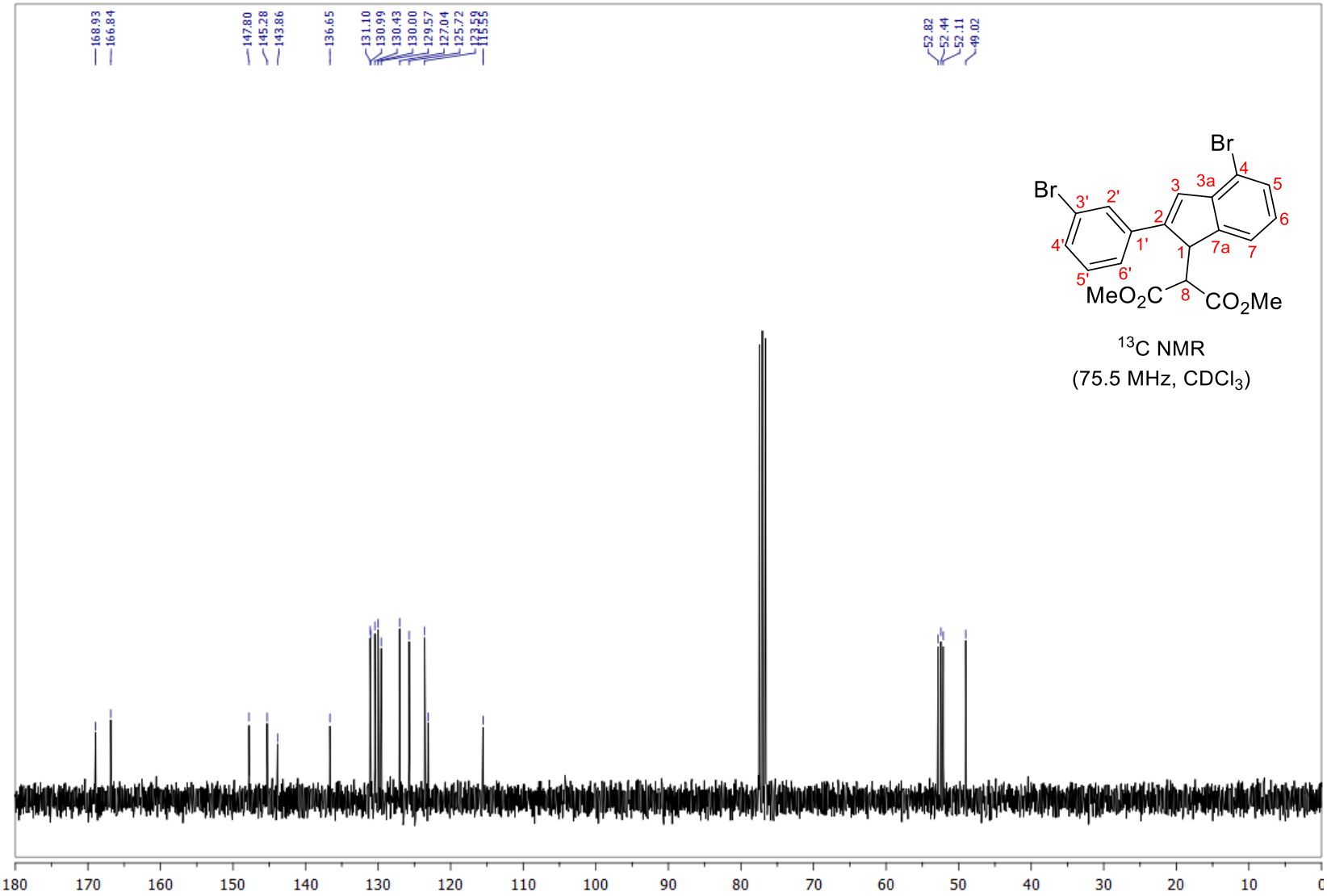

4'
3'
2'
5'
1'a
3
3a
4
5
5'a
2
6
1'
6'
1
7a
7
8'
7'
8
MeO2C
CO2Me
1H,13C-HMBC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0


7.62
7.62
7.61
7.46
7.46
7.45
7.44
7.43
7.43
7.37
7.35
7.35
7.34
7.31
7.30
7.28
7.27
7.26
7.15
7.12
7.05
7.05
4.62
4.60
3.87
3.85
3.74
3.39
2.42
Br
3'
2'
3
3a
4
5
2
6
Me
4'
1'
1
7a
7
6'
5'
MeO2C
8
CO2Me
1H NMR
(300.1 MHz, CDCl3)
1.01
5.75
1.00
1.00
1.00
2.98
2.95
3.08
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

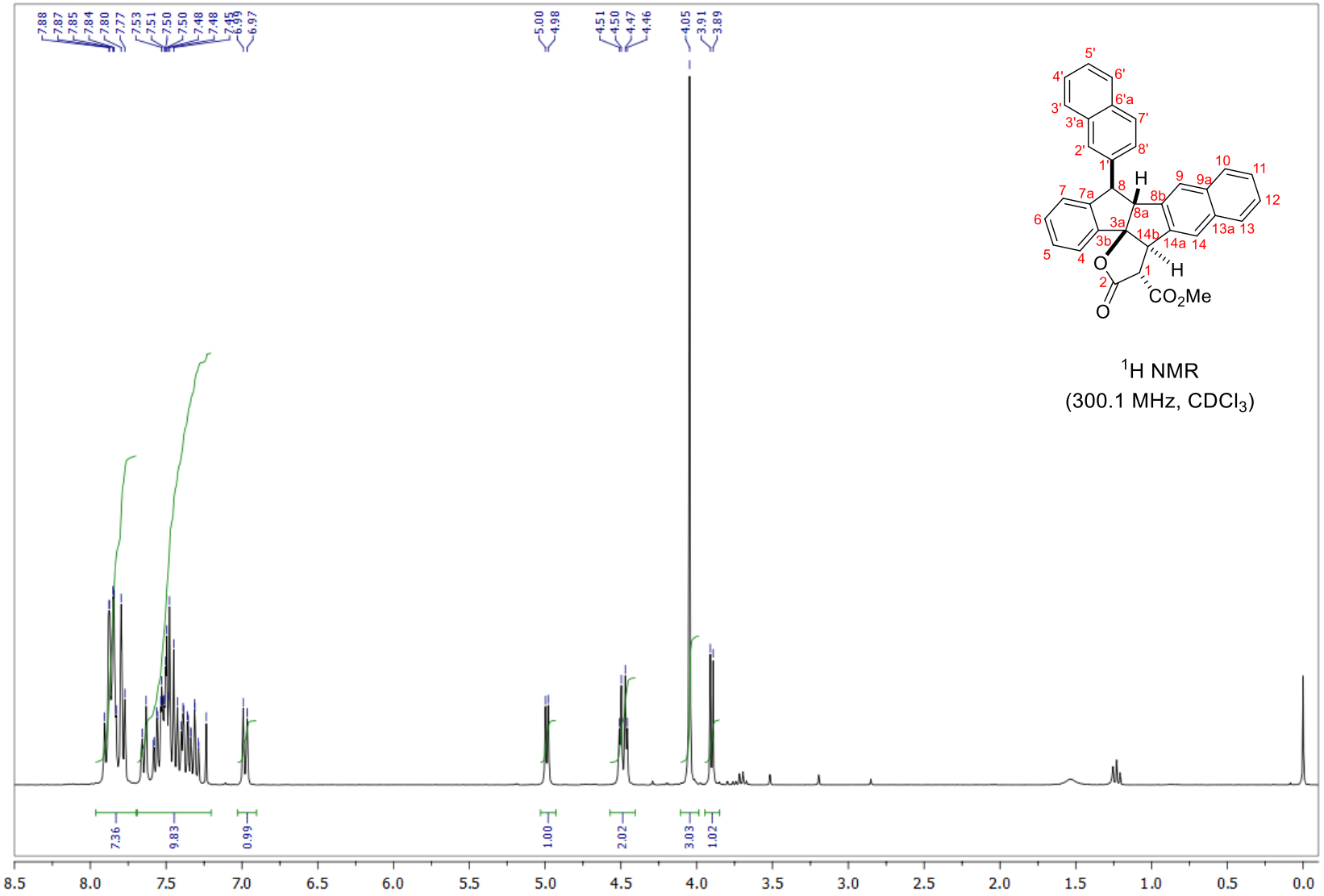

169.15
167.23
145.71
144.18
141.06
137.45
135.49
130.44
130.38
130.28
129.80
128.47
125.53
125.41
122.93
121.19
52.66
52.61
51.99
47.67
21.77
Br
Me
MeO2C
CO2Me
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

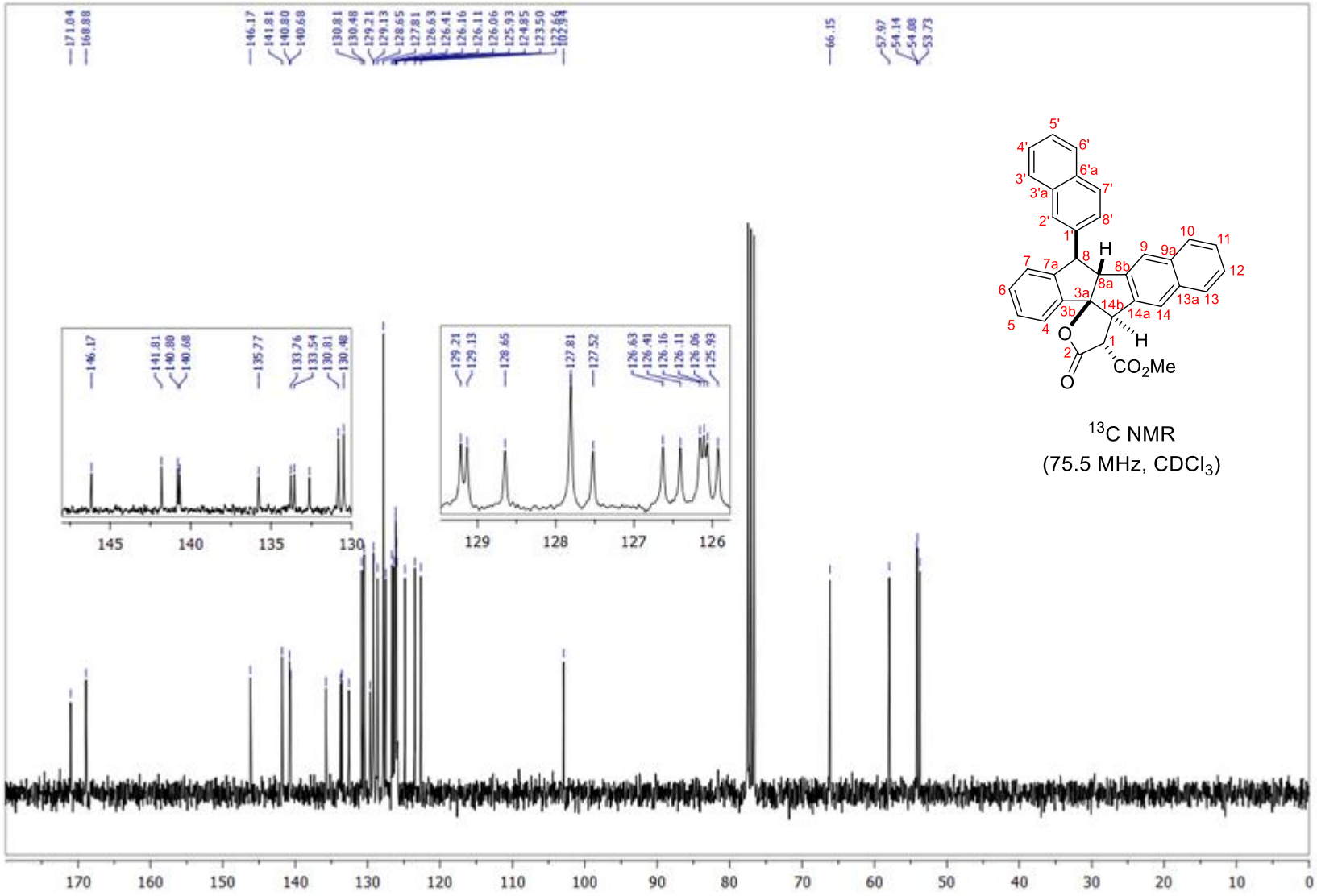

Br
3'
2'
3
3a
4
5
2
6
Me
4'
1'
1
7a
7
5'
6'
MeO2C
8
CO2Me
1H,13C-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
10
20
30
40
50
60
70
80
90
100
110
120
130
140

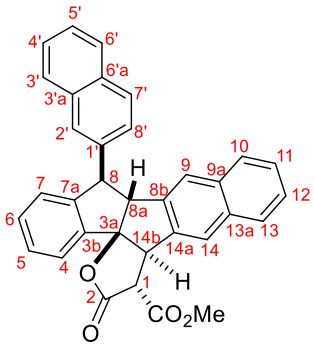

7.63
7.62
7.51
7.48
7.45
7.42
7.38
7.36
7.35
7.32
7.29
7.26
7.26
7.14
7.09
7.07
7.04
4.70
4.69
3.86
3.85
3.73
3.36
Br
Br
4
5
6
7
7a
3a
3
2
1
1'
2'
3'
4'
5'
6'
8
MeO2C
CO2Me
1H NMR
(300.1 MHz, CDCl3)
1.19
6.61
2.34
1.00
1.07
2.97
2.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


168.93
166.84
147.80
145.28
143.86
136.65
131.10
130.99
130.43
130.00
129.57
127.04
125.72
123.58
115.55
52.82
52.44
52.11
49.02
Br
Br
4
5
6
7
7a
3
3a
2
1
1'
2'
3'
4'
5'
6'
8
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

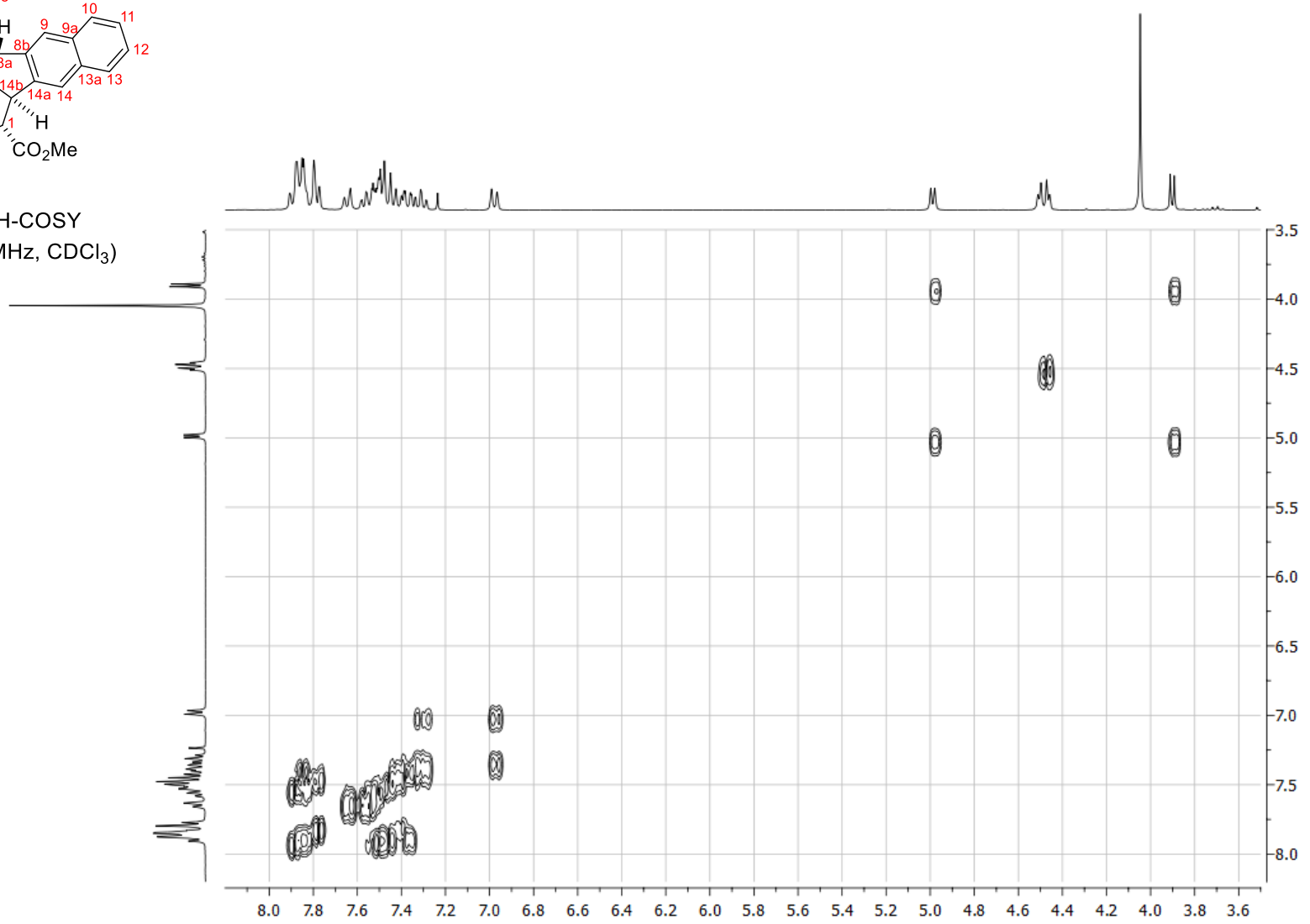
4.2 NMR spectra for the lactones **3a–d**:

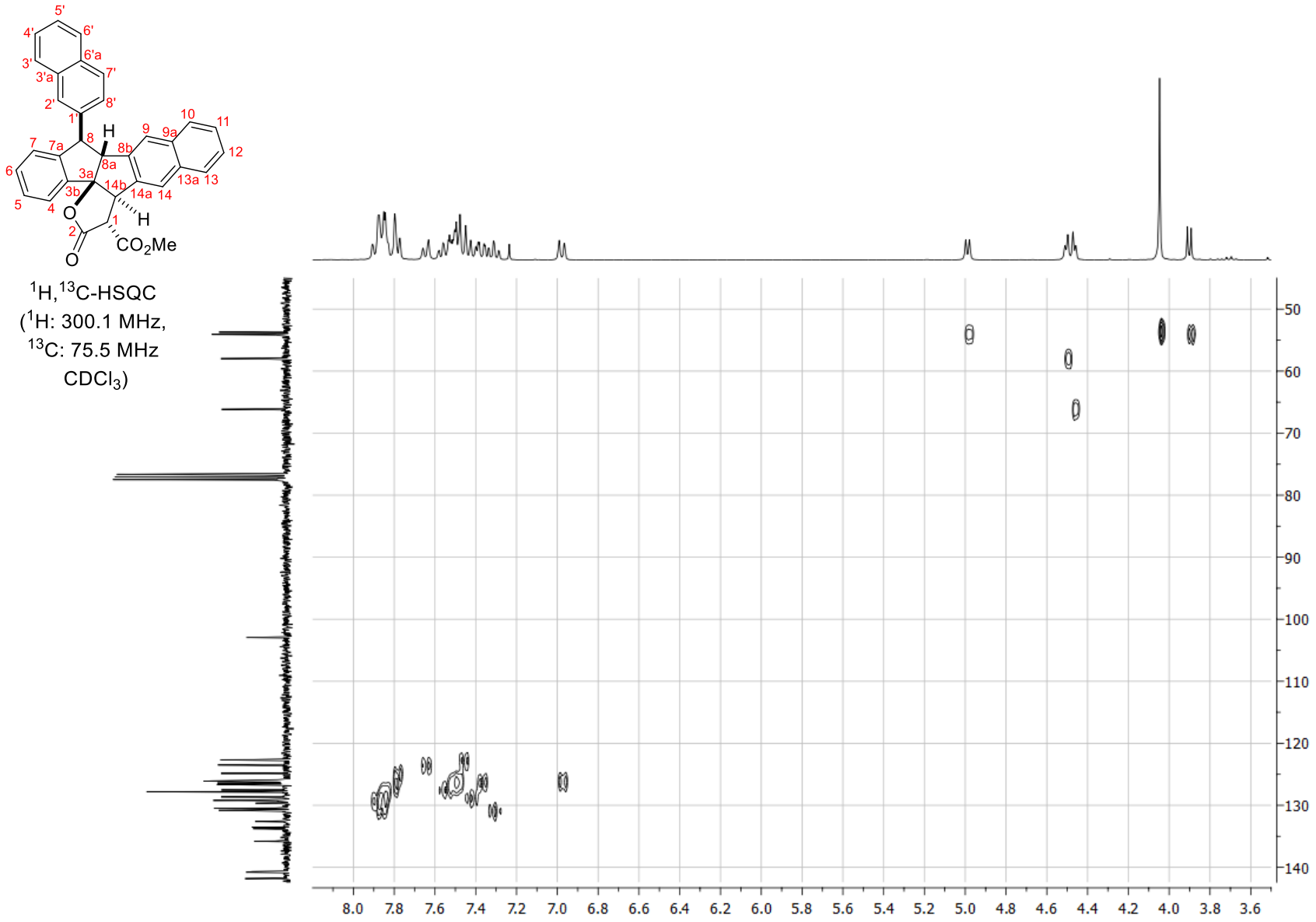


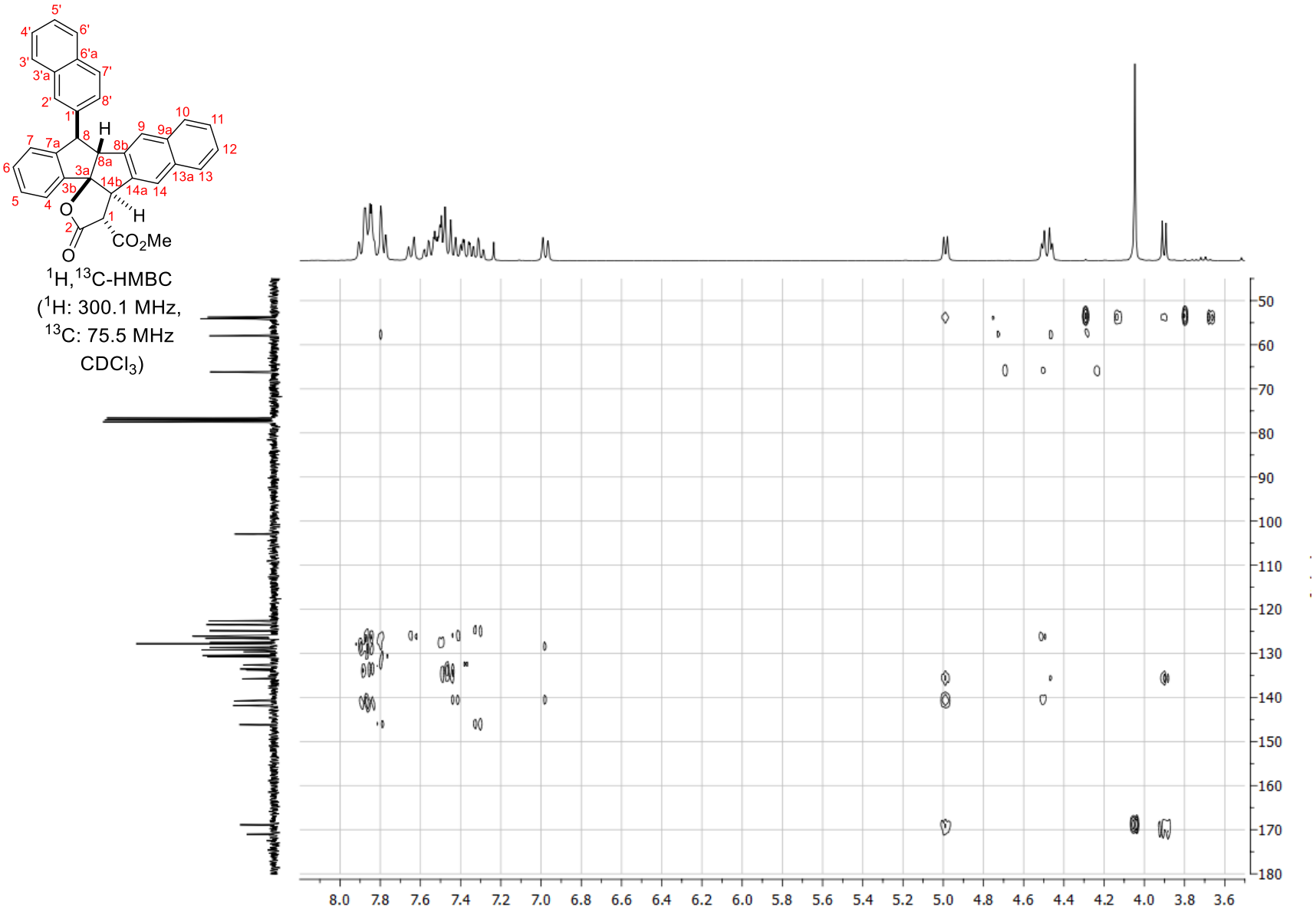

171.04
168.88
146.17
141.81
140.80
140.68
130.81
130.48
129.21
129.13
128.65
127.81
126.63
126.41
126.16
126.11
126.06
125.93
124.85
123.50
66.15
57.97
54.14
54.08
53.73
5'
4'
6'
6'a
3'
3'a
7'
2'
8'
1'
8
H
10
11
9
9a
12
7
7a
8b
8a
6
3a
13a
13
14b
14a
14
5
4
3b
O
1
H
2
CO2Me
O
13C NMR
(75.5 MHz, CDCl3)
145
140
135
130
129
128
127
126
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

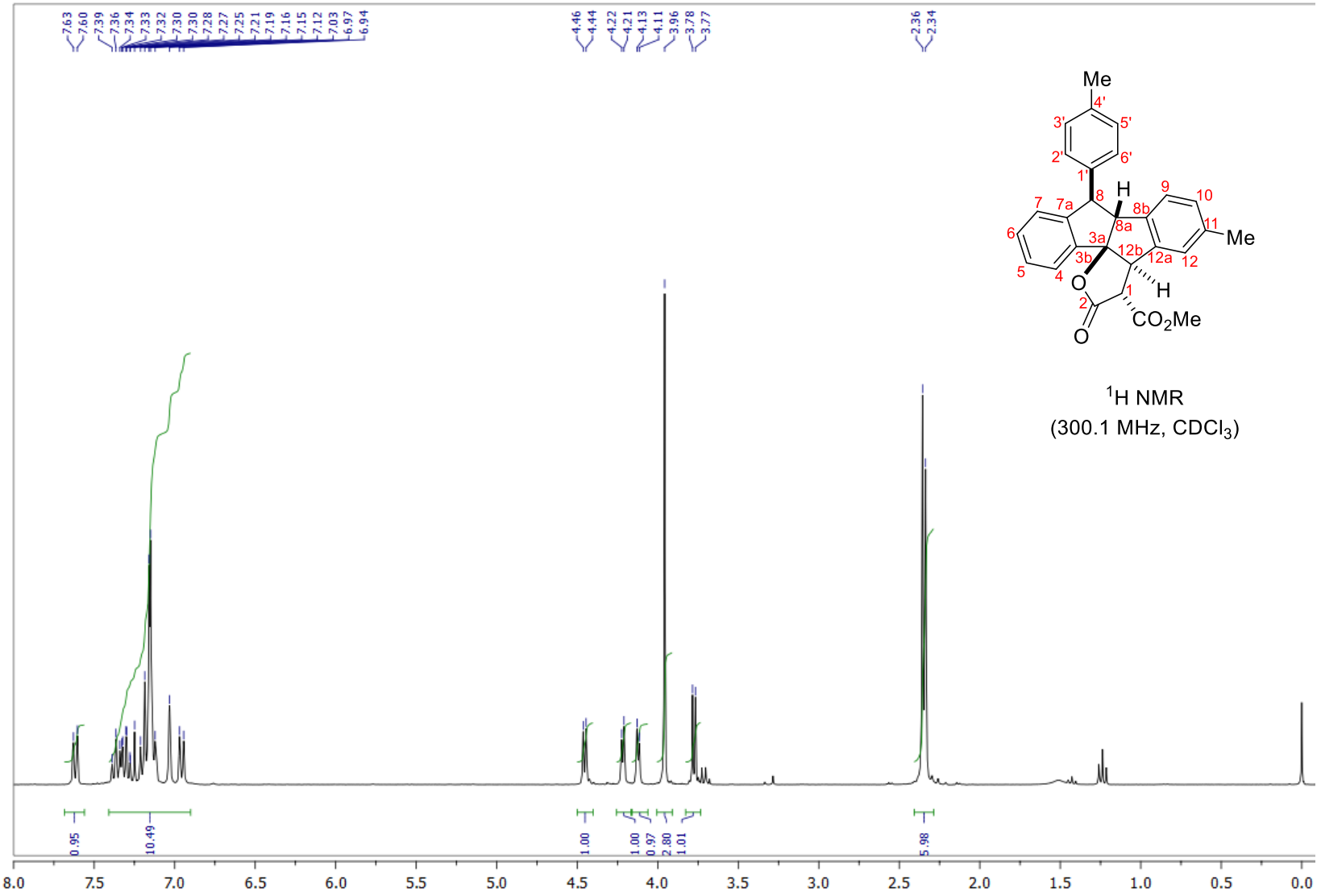


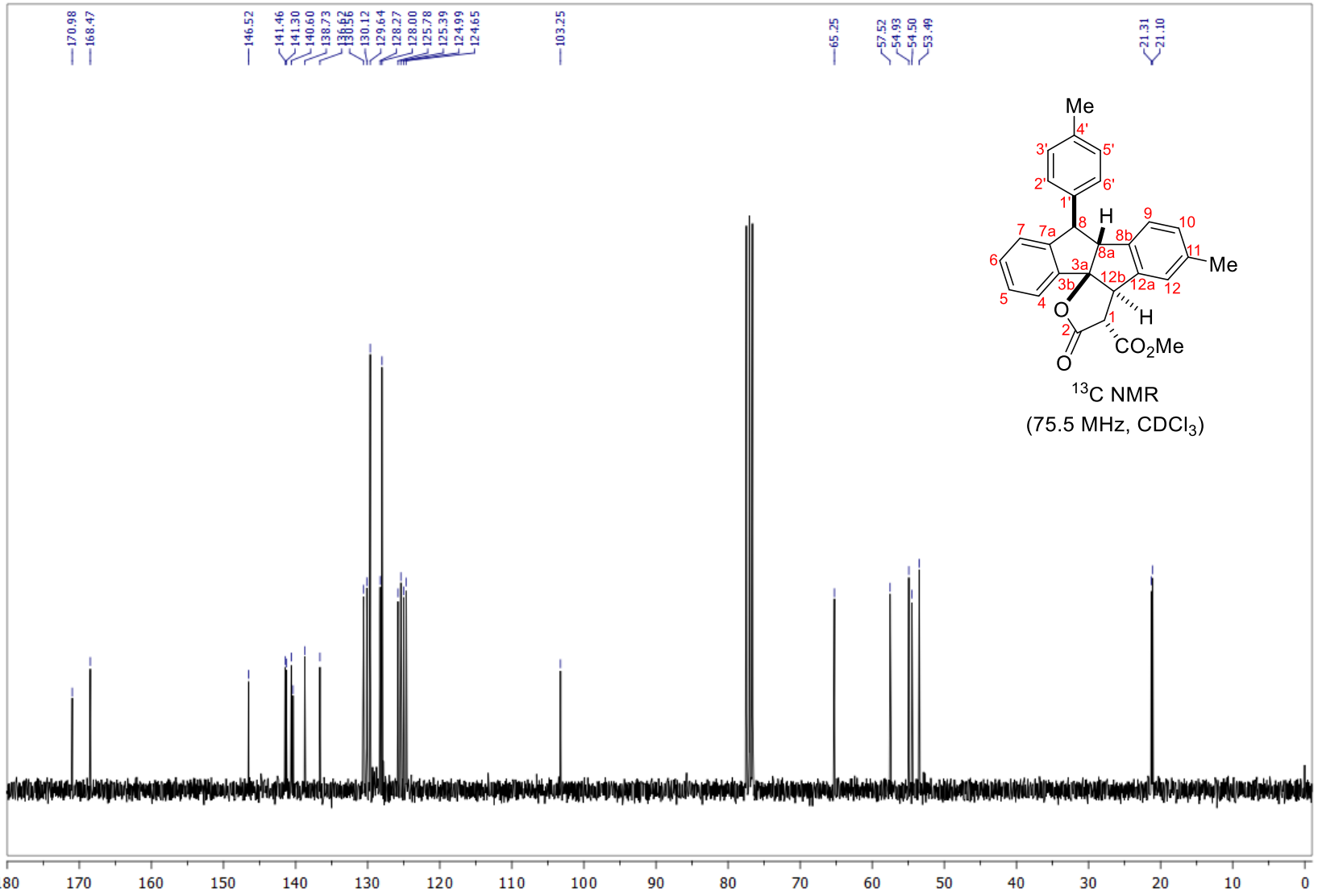
^{1}H,^{1}H-COSY
(300.1 MHz, $CDCl_3$)

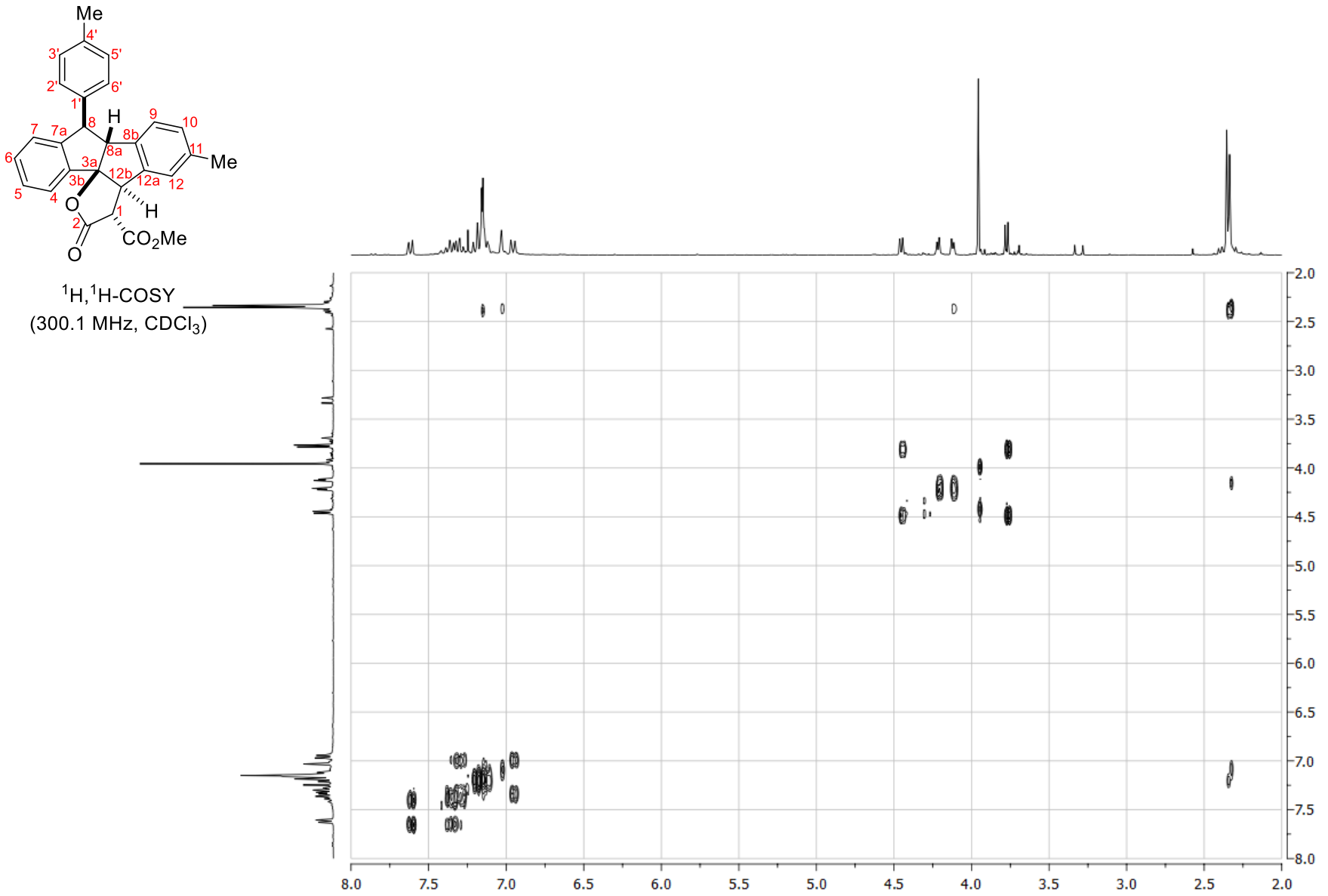


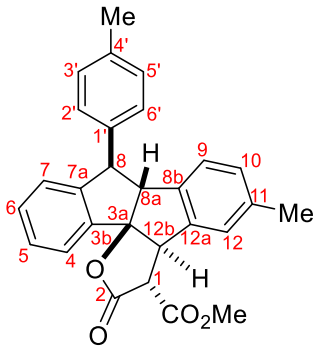

5'
4'
6'
3'
6'a
3'a
7'
2'
8'
1'
H
8
9
9a
10
11
12
7
7a
8b
6
3a
8a
13a
13
5
3b
14b
14a
14
4
O
1
H
2
CO2Me
O
1H,13C-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
50
60
70
80
90
100
110
120
130
140
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6


^{1}H,^{13}C-HMBC
(^{1}H: 300.1 MHz,
^{13}C: 75.5 MHz
$CDCl_3$)
CO_2Me

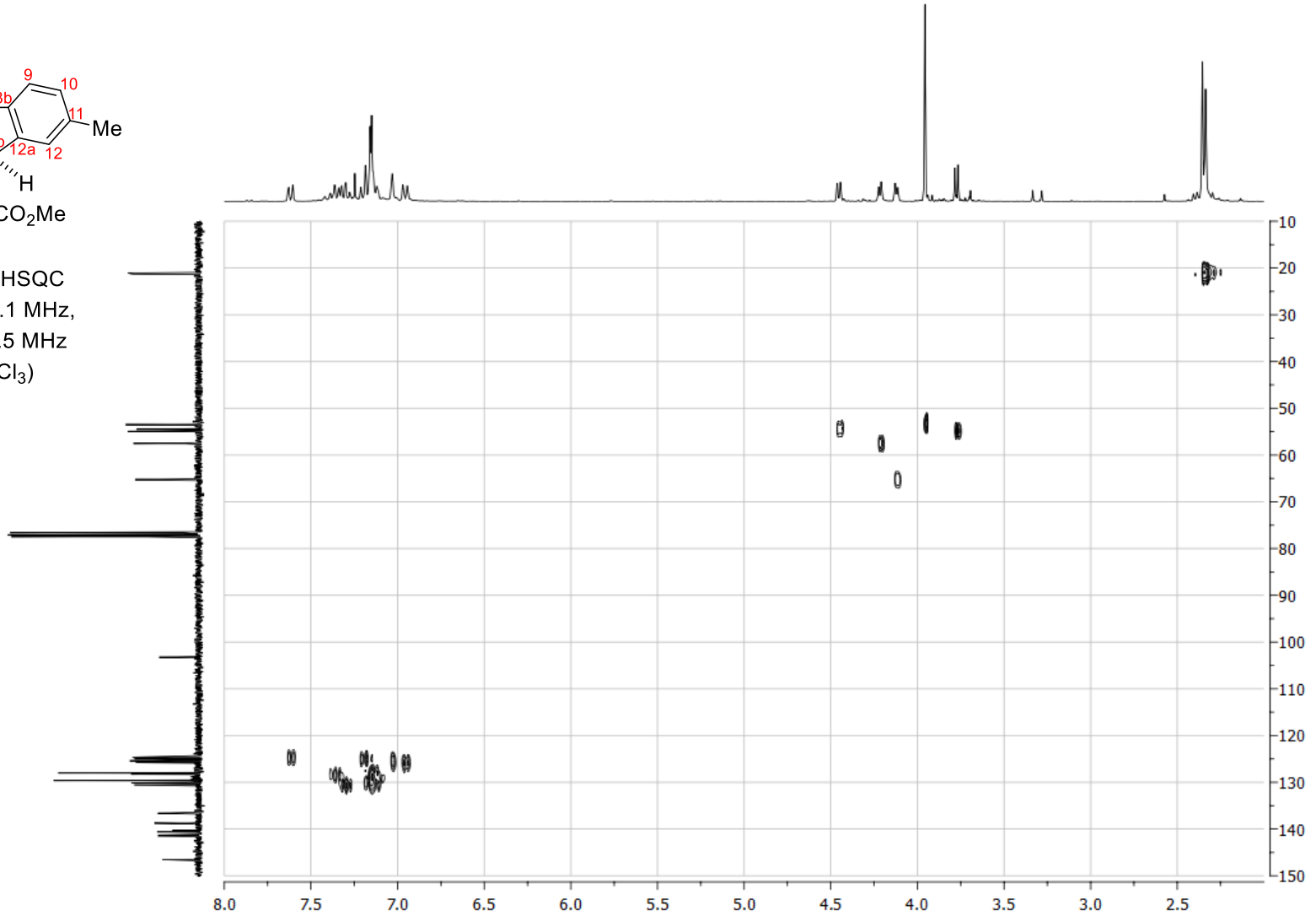

7.63
7.60
7.39
7.36
7.34
7.33
7.32
7.30
7.30
7.28
7.27
7.25
7.21
7.19
7.16
7.15
7.12
7.03
6.97
6.94
4.46
4.44
4.22
4.21
4.13
4.11
3.96
3.78
3.77
2.36
2.34
Me
4'
3'
5'
2'
6'
1'
8
H
9
10
7
7a
8b
11
6
8a
Me
3a
12b
12a
12
3b
5
4
O
1
H
2
CO2Me
O
1H NMR
(300.1 MHz, CDCl3)
0.95
10.49
1.00
1.00
0.97
2.80
1.01
5.98
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

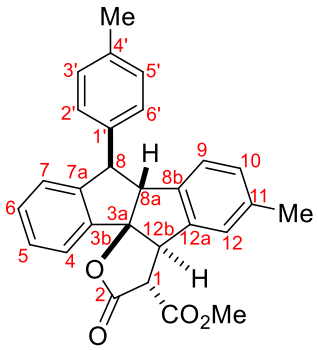

170.98
168.47
146.52
141.46
141.30
140.60
138.73
130.12
129.64
128.27
128.00
125.78
125.39
124.99
124.65
103.25
65.25
57.52
54.93
54.50
53.49
21.31
21.10
Me
4'
3'
5'
2'
6'
1'
H
8
9
10
7
7a
8b
8a
11
Me
6
3a
12b
3b
12a
12
5
4
O
1
H
2
CO2Me
O
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Me
4'
3'
5'
2'
6'
1'
8
H
9
10
7
7a
8b
11
Me
6
8a
3a
12b
12a
12
3b
5
4
O
1
H
2
CO2Me
O
1H,1H-COSY
(300.1 MHz, CDCl3)
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
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

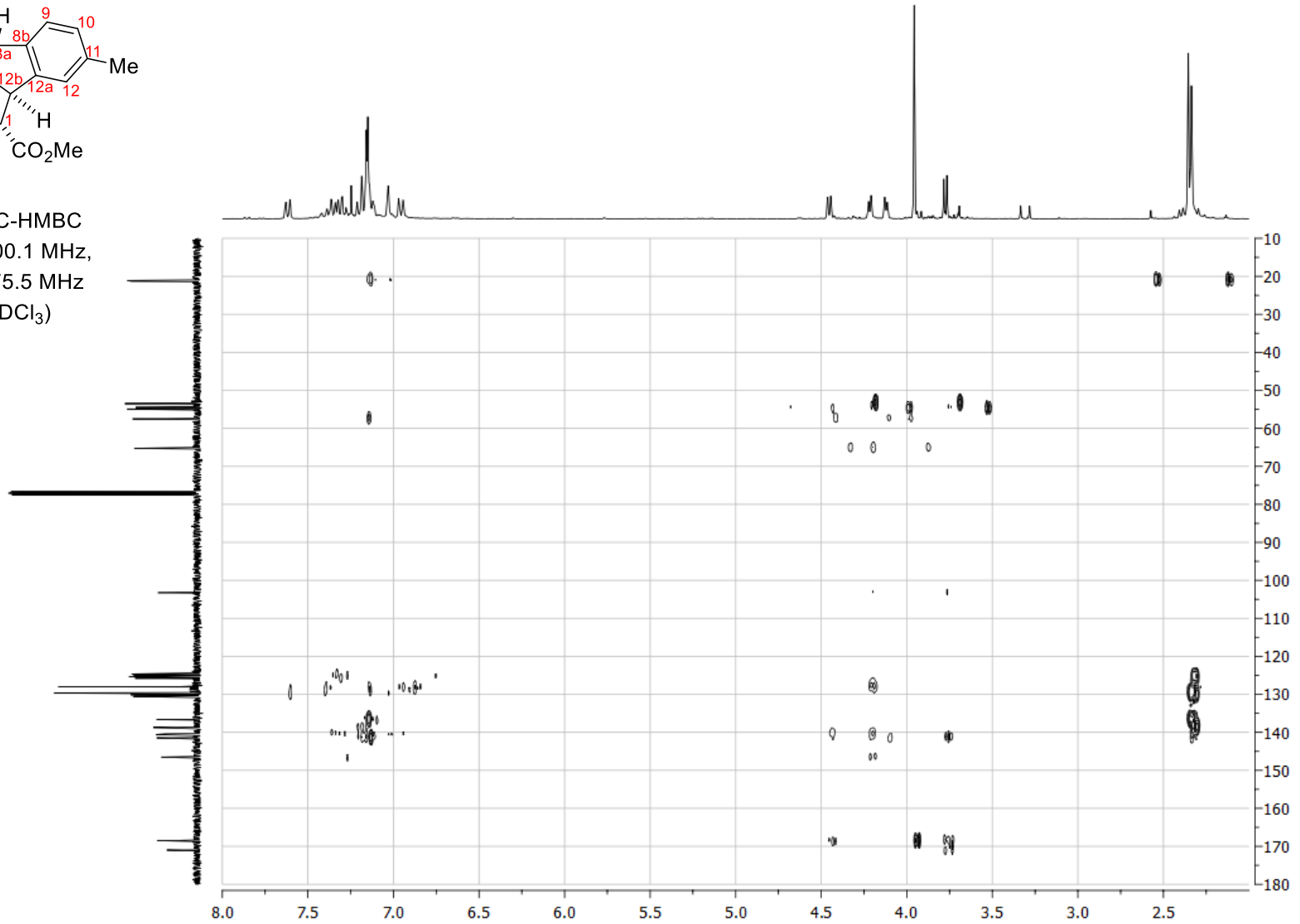


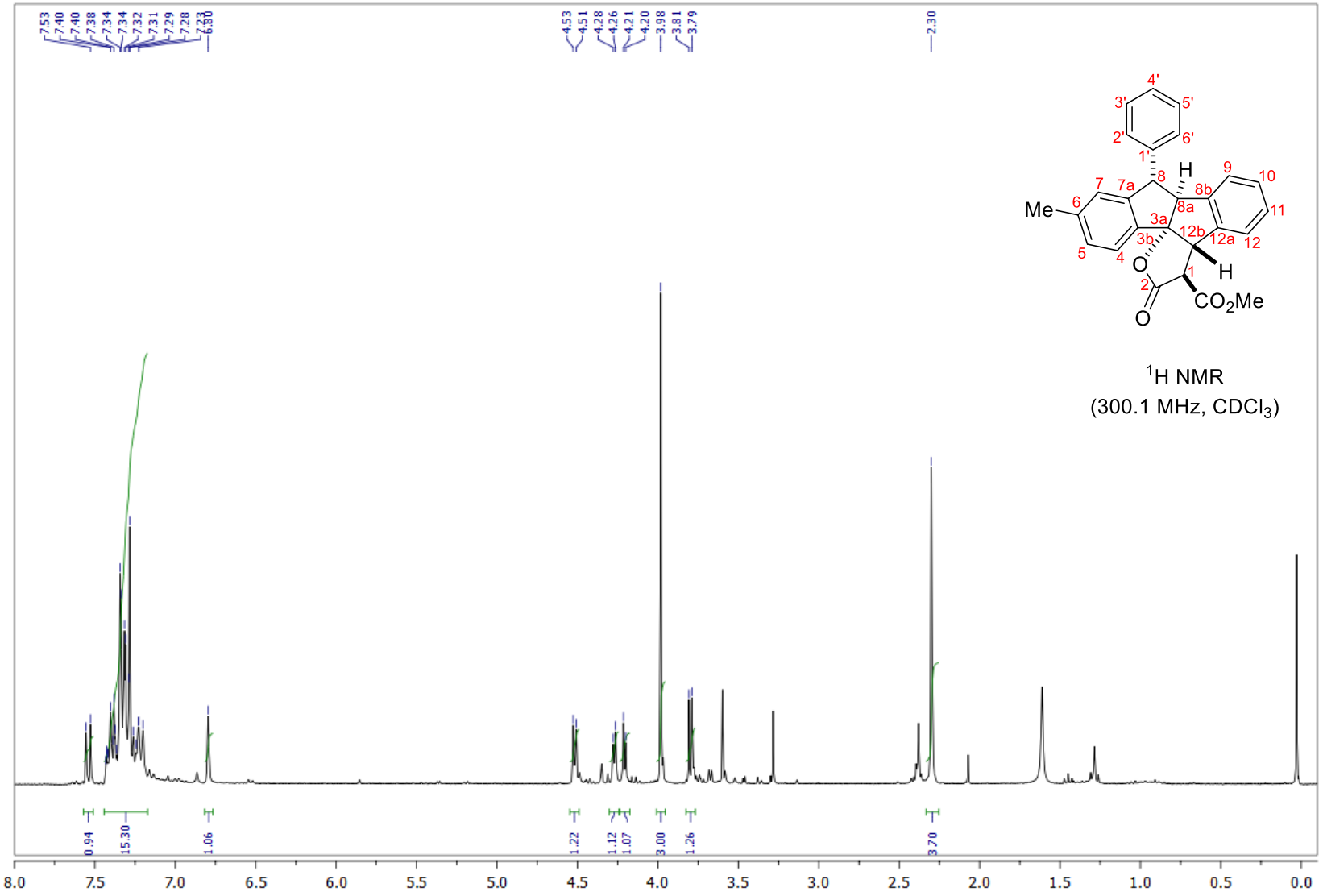
$^{1}H,^{13}C$-HSQC
(^{1}H: 300.1 MHz,
^{13}C: 75.5 MHz
$CDCl_3$)

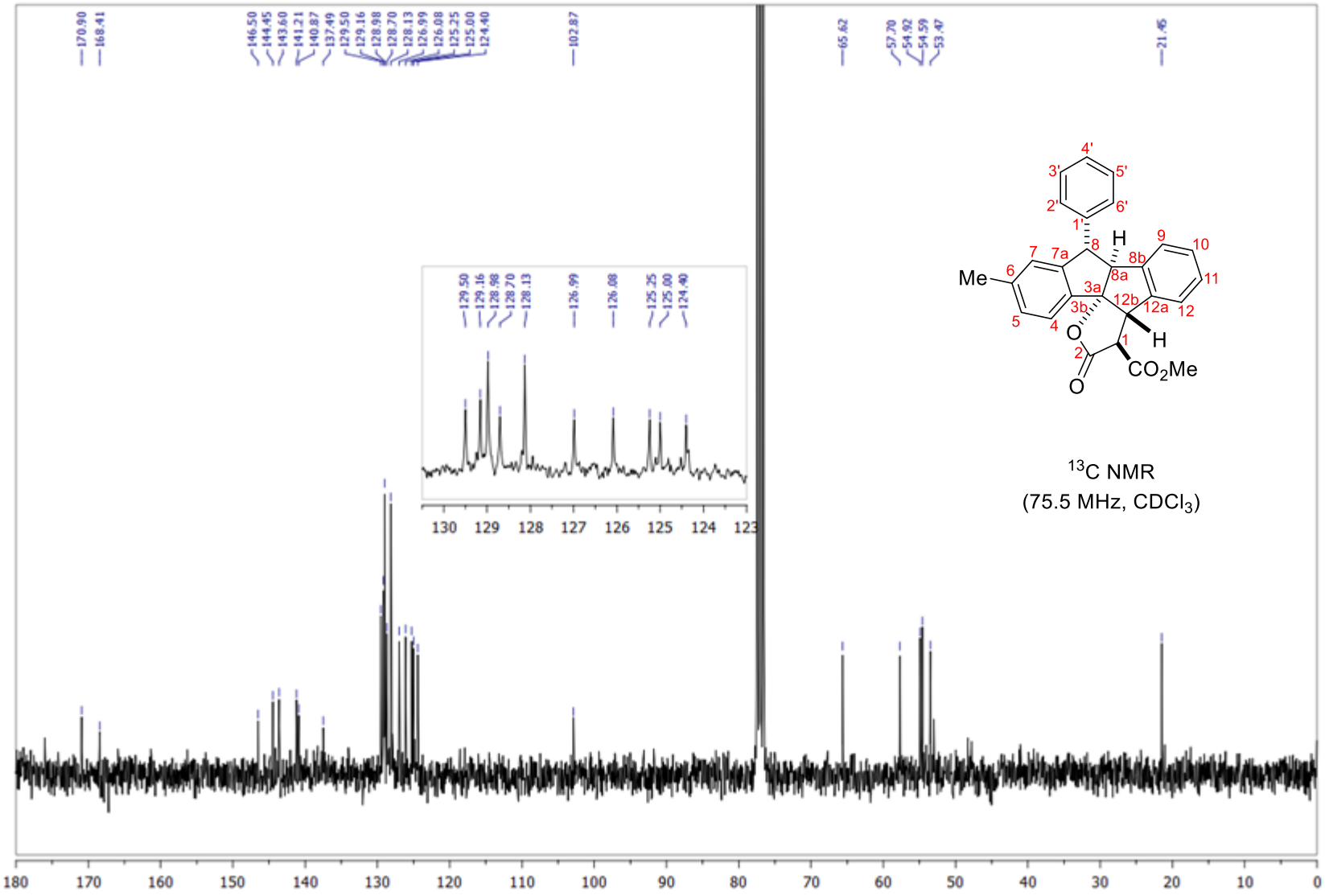


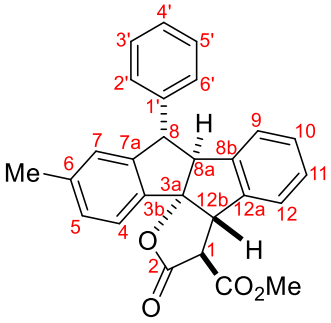


$^{1}H,^{13}C$-HMBC
(^{1}H: 300.1 MHz,
^{13}C: 75.5 MHz
$CDCl_3$)

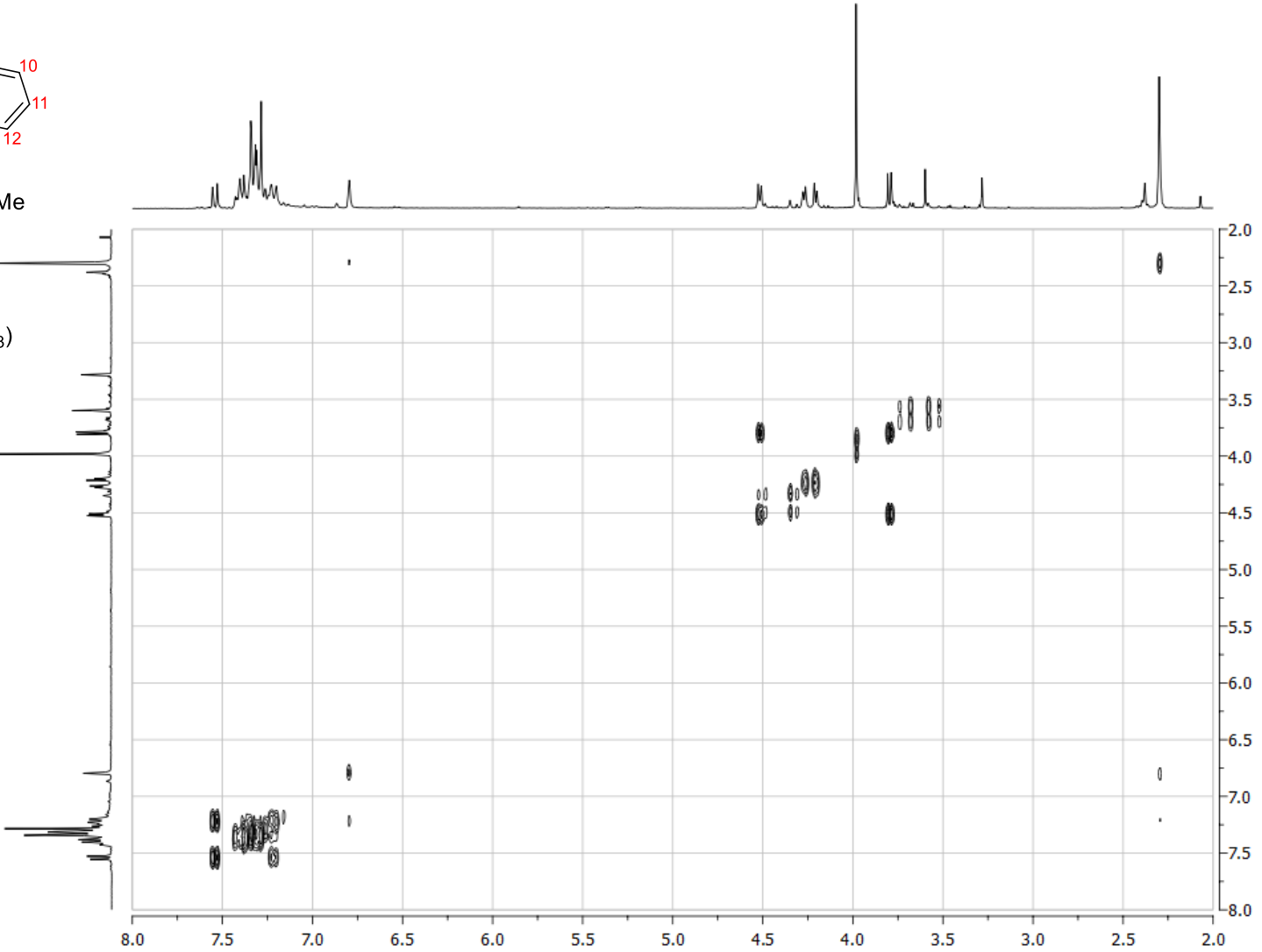



7.53
7.40
7.40
7.38
7.34
7.34
7.32
7.31
7.29
7.28
7.23
6.80
4.53
4.51
4.28
4.26
4.21
4.20
3.98
3.81
3.79
2.30
0.94
15.30
1.06
1.22
1.12
1.07
3.00
1.26
3.70
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Me
H
H
O
O
CO_2Me
^1H NMR
(300.1 MHz, $CDCl_3$)

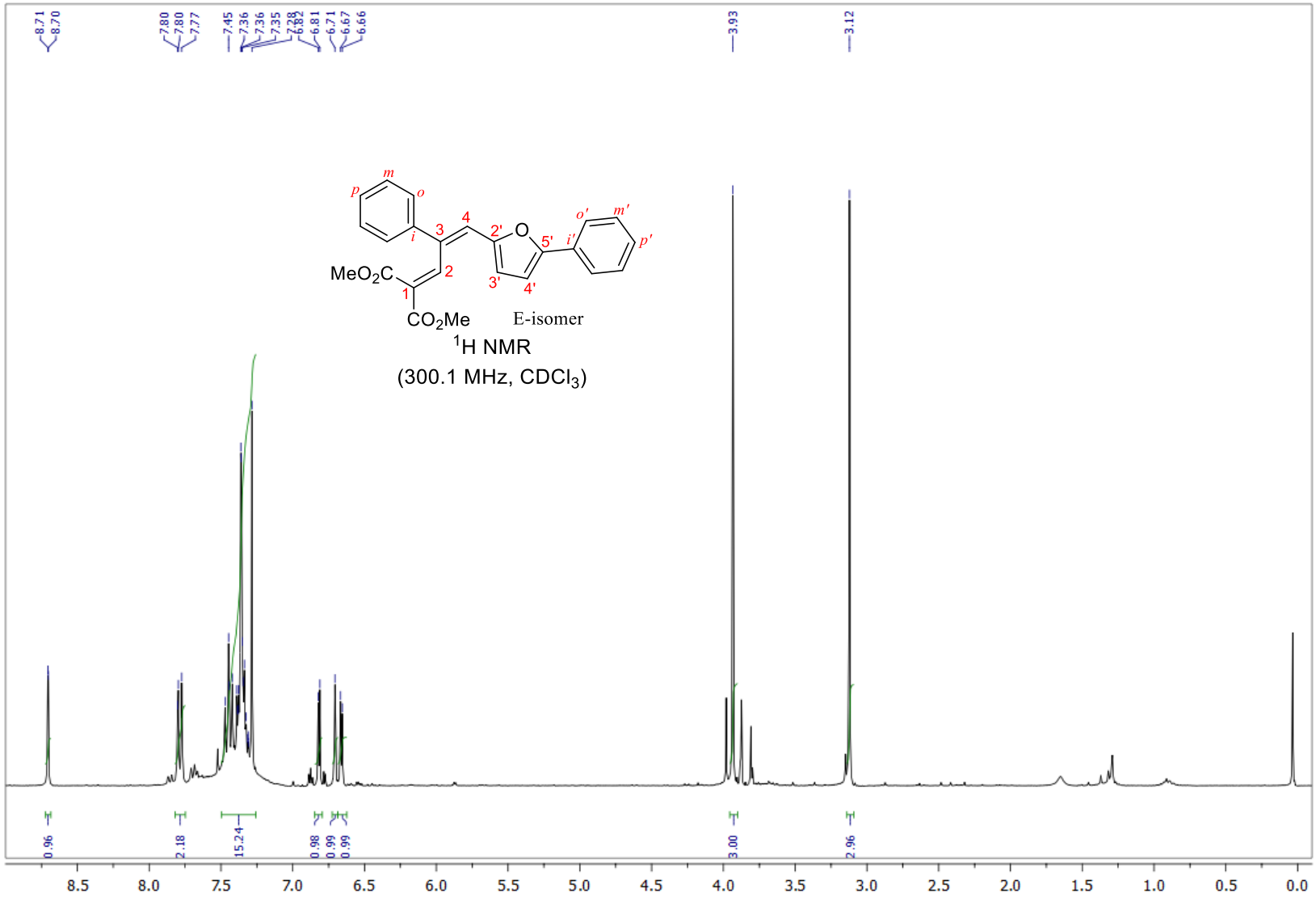

170.90
168.41
146.50
144.45
143.60
141.21
140.87
137.49
129.50
129.16
128.98
128.70
128.13
126.99
126.08
125.25
125.00
124.40
102.87
65.62
57.70
54.92
54.59
53.47
21.46
Me
H
H
O
O
CO2Me
13C NMR
(75.5 MHz, CDCl3)

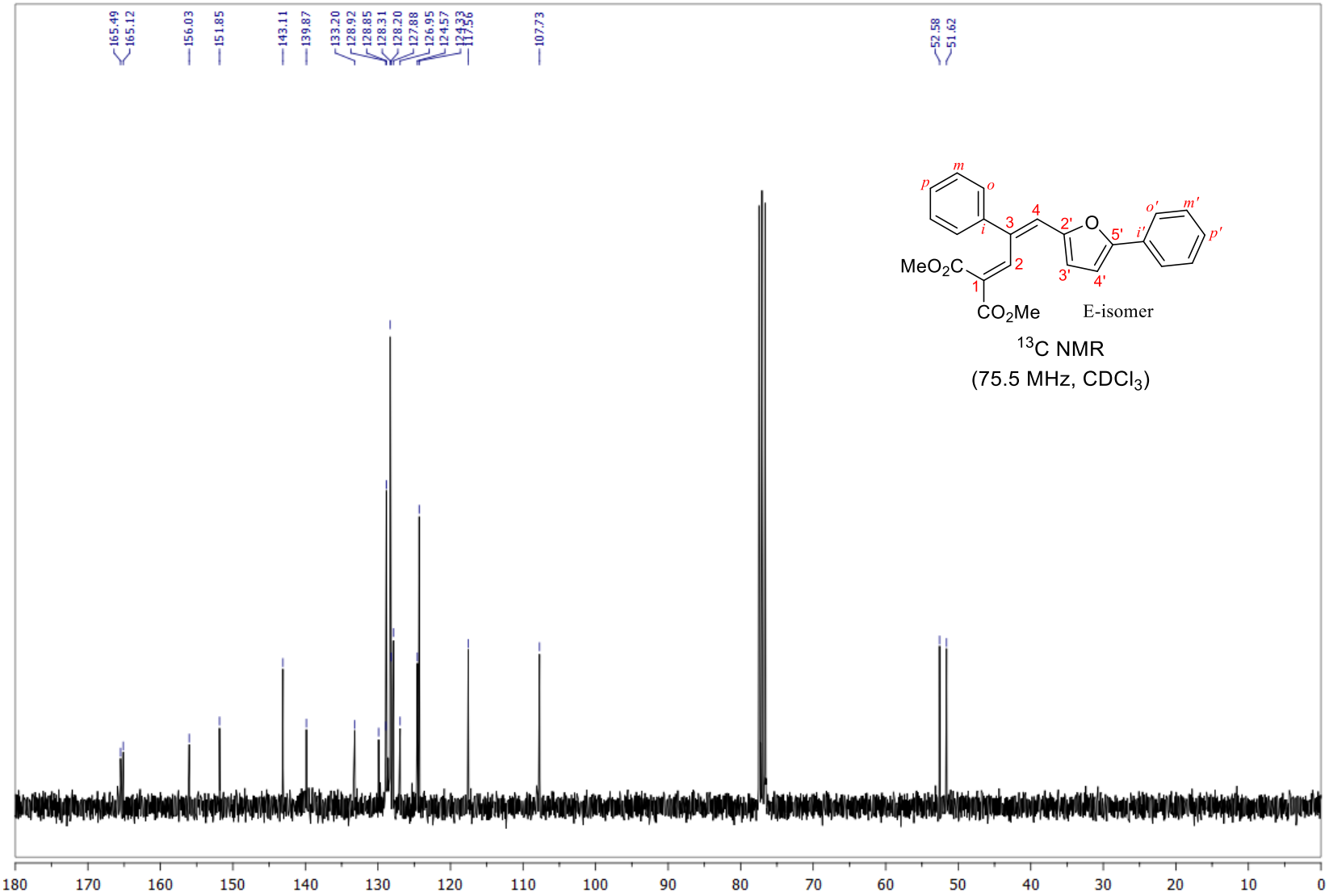


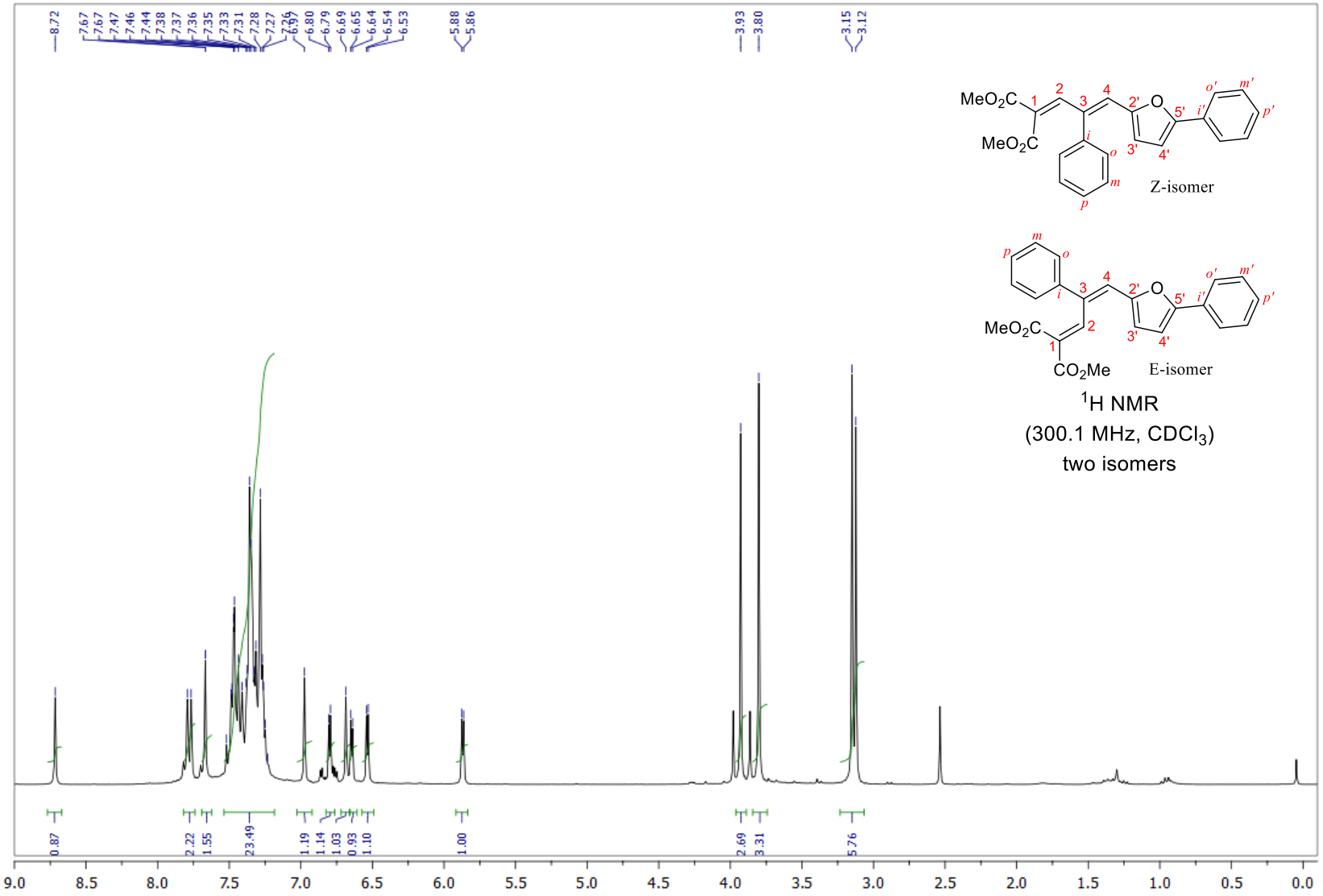
$^{1}H,^{1}H$-COSY
(300.1 MHz, $CDCl_3$)

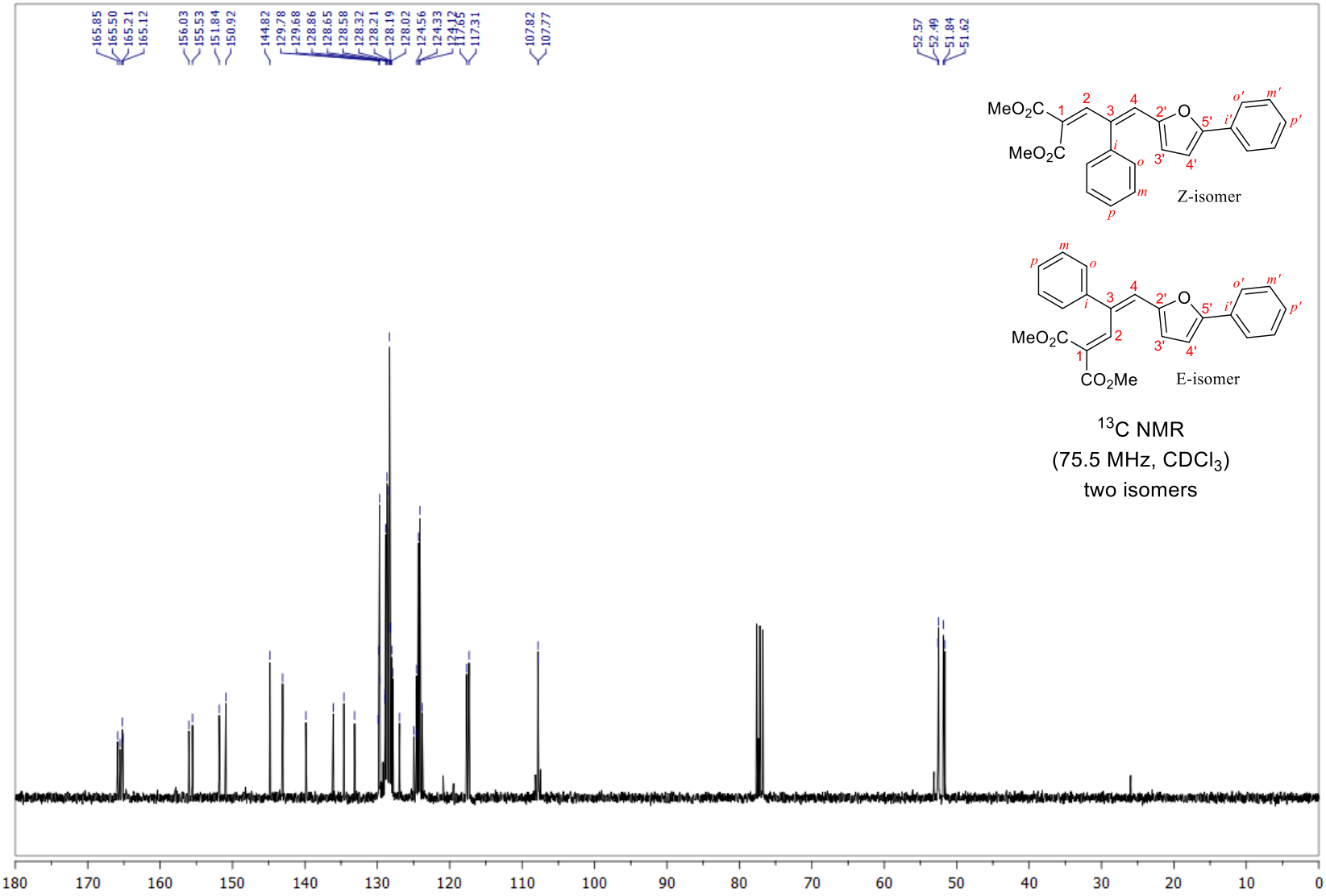


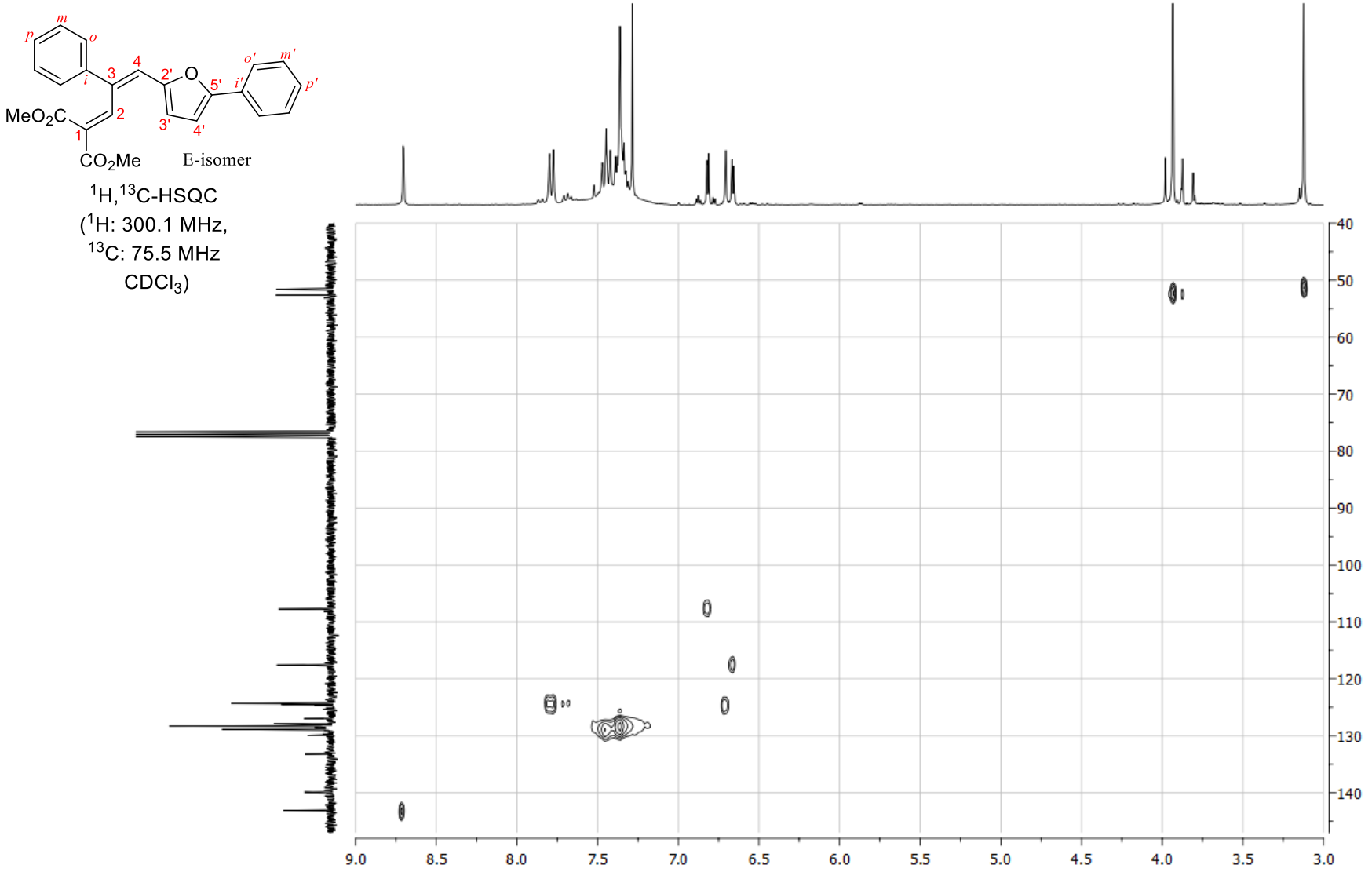
4.3 NMR spectra for the diene **5**:

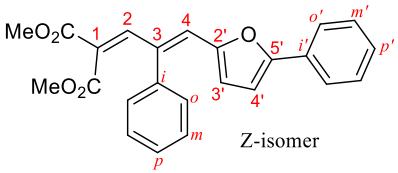


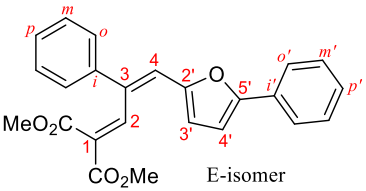

165.49
165.12
156.03
151.85
143.11
139.87
133.20
128.92
128.85
128.31
128.20
127.88
126.95
124.57
124.33
117.56
107.73
52.58
51.62
m
p
o
i
3
4
2'
O
5'
i'
o'
m'
p'
MeO2C
2
1
3'
4'
CO2Me
E-isomer
13C NMR
(75.5 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.72
7.67
7.67
7.47
7.46
7.44
7.38
7.37
7.36
7.35
7.33
7.31
7.28
7.27
7.26
6.97
6.80
6.79
6.69
6.65
6.64
6.54
6.53
5.88
5.86
3.93
3.80
3.15
3.12
0.87
2.22
1.55
23.49
1.19
1.14
1.03
0.93
1.10
1.00
2.69
3.31
5.76
9.0
8.5
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
0.5
0.0
MeO2C
MeO2C
Z-isomer
CO2Me
E-isomer
1H NMR
(300.1 MHz, CDCl3)
two isomers

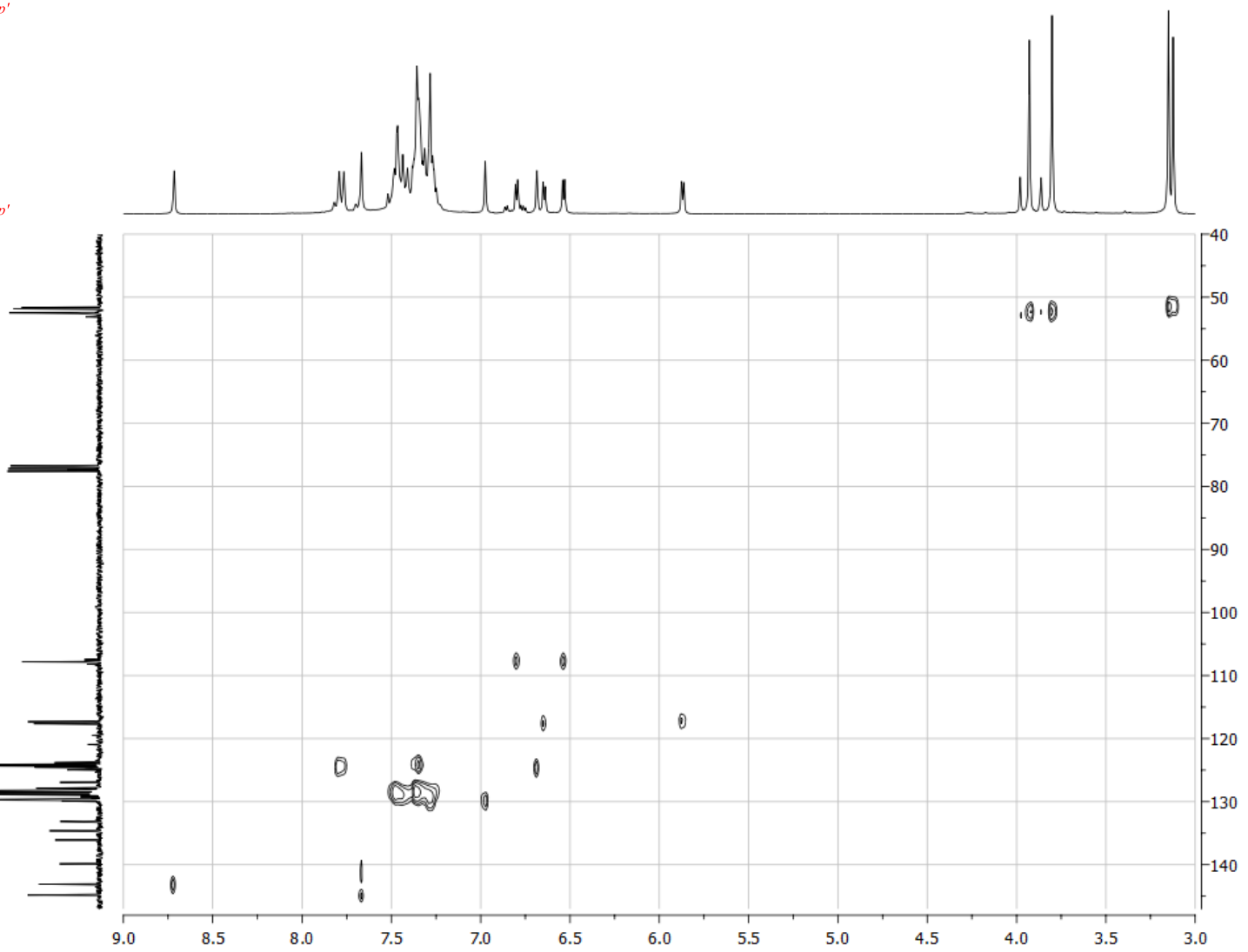

165.85
165.50
165.21
165.12
156.03
155.53
151.84
150.92
144.82
129.78
129.68
128.86
128.65
128.58
128.32
128.21
128.19
128.02
124.56
124.33
117.65
117.31
107.82
107.77
52.57
52.49
51.84
51.62
MeO2C
MeO2C
Z-isomer
MeO2C
CO2Me
E-isomer
13C NMR
(75.5 MHz, CDCl3)
two isomers
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

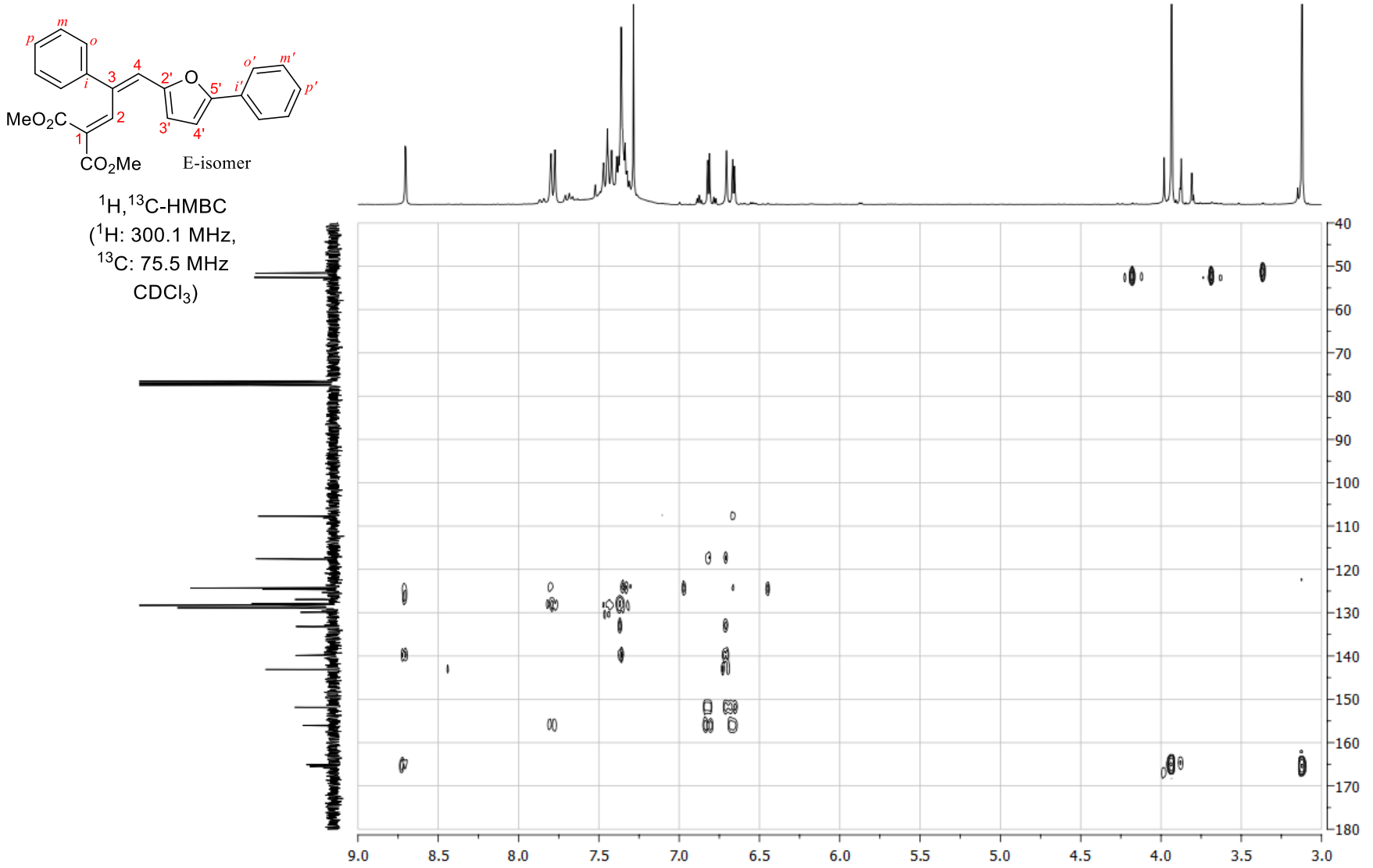

MeO2C
CO2Me
E-isomer
1H,13C-HSQC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
40
50
60
70
80
90
100
110
120
130
140

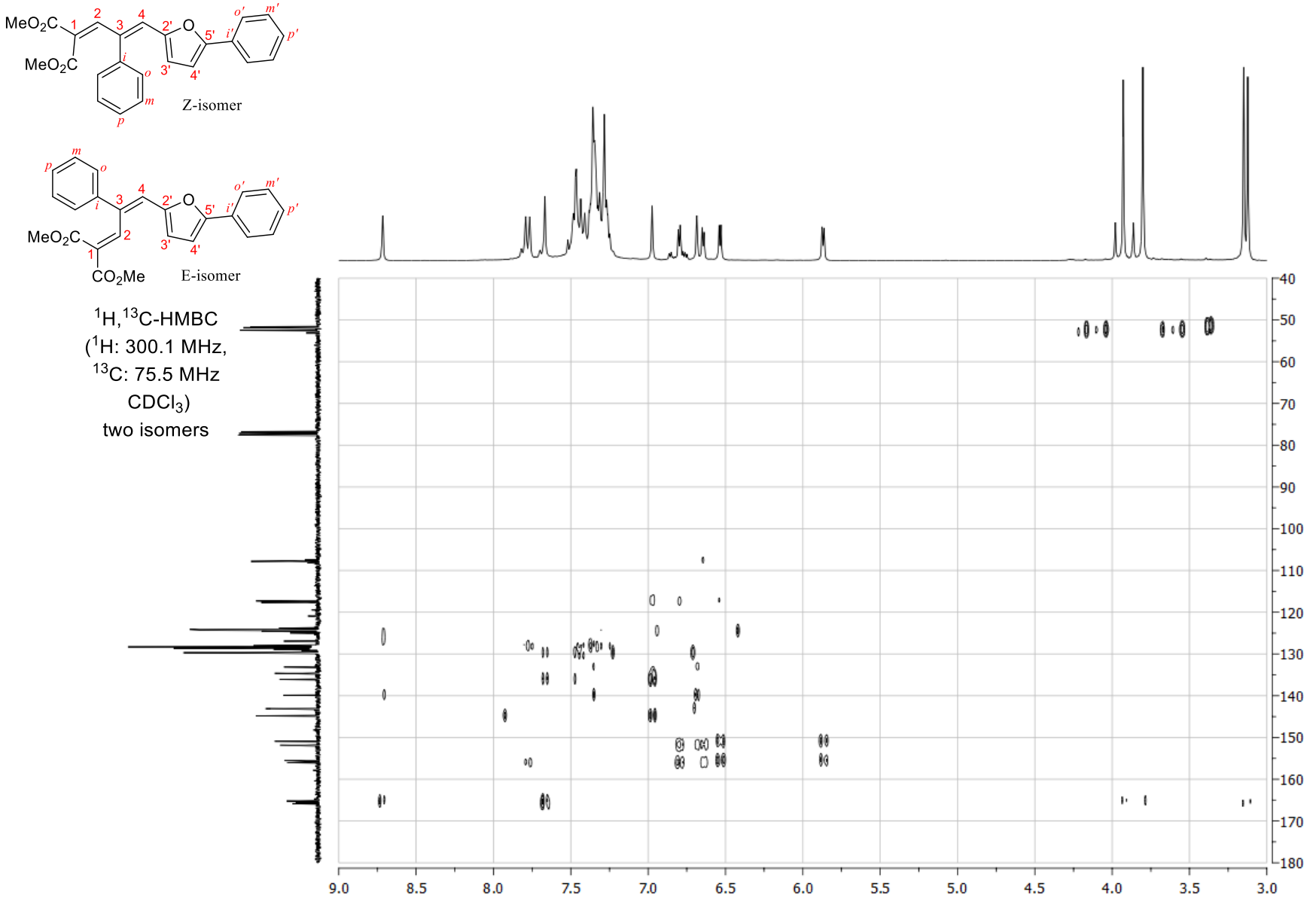




$^{1}H,^{13}C$-HSQC
(^{1}H: 300.1 MHz,
^{13}C: 75.5 MHz
$CDCl_3$)
two isomers




MeO2C
CO2Me
E-isomer
1H,13C-HMBC
(1H: 300.1 MHz,
13C: 75.5 MHz
CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


Z-isomer
E-isomer
^{1}H,^{13}C-HMBC
(^{1}H: 300.1 MHz,
^{13}C: 75.5 MHz
$CDCl_3$)
two isomers