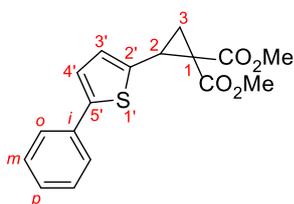


## Gallium(III)-mediated dimerization routes for (5-phenyl-2-thienyl)cyclopropane-1,1-dicarboxylate

Denis D. Borisov, Roman A. Novikov and Yury V. Tomilov

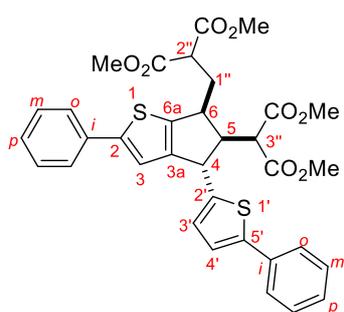
### Dimethyl 2-(5-phenylthiophen-2-yl)cyclopropane-1,1-dicarboxylate (**5**)



The title compound was obtained according to known method in yield 73% (2.54 g) as red thick oil. The compound was recrystallized from ethanol for additionally purification, yellow crystals, m.p. = 51–53 °C. IR (CHCl<sub>3</sub>):  $\tilde{\nu}$  3048, 3002, 2955, 2849, 1723 br (C=O), 1599, 1502, 1439, 1372, 1335, 1284, 1248, 1181, 1133 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  1.84 (dd, 1H, H(3), <sup>2</sup>J = 5.2 Hz, <sup>3</sup>J = 8.5 Hz), 2.16 (dd, 1H, H(3), <sup>2</sup>J = 5.2 Hz, <sup>3</sup>J = 8.5 Hz), 3.29 (t, 1H, H(2), <sup>3</sup>J = 8.5 Hz), 3.52 (s, 3H, CO<sub>2</sub>Me), 3.79 (s, 3H, CO<sub>2</sub>Me), 6.80 (dd, 1H, H(3'), <sup>3</sup>J = 3.7 Hz, <sup>4</sup>J = 0.7 Hz), 7.11 (d, 1H, H(4'), <sup>3</sup>J = 3.7 Hz), 7.26 (br t, 1H, H(p), <sup>3</sup>J = 7.4 Hz), 7.35 (t, 2H, 2 H(m), <sup>3</sup>J = 7.4 Hz), 7.54 (br d, 2H, 2 H(o), <sup>3</sup>J = 7.4 Hz) ppm. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  20.9 (C(3)), 27.6 (C(2)), 37.9 (C(1)), 52.6 and 52.9 (2 OMe), 122.5 (C(4')), 125.5 (2 C(o)), 127.1 (C(3')), 127.5 (C(p)), 128.8 (2 C(m)), 134.1 (C(i)), 137.4 (C(2')), 143.9 (C(5')), 166.7 and 169.7 (2 COO). HRMS calcd for C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>S (M): M+Na, 339.0662. Found: m/z 339.0657.

### Dimethyl 2-(((4SR,5SR,6SR)-5-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-2-phenyl-4-(5-phenylthiophen-2-yl)-5,6-dihydro-4H-cyclopenta[b]thiophen-6-yl)methyl)malonate (**7**)

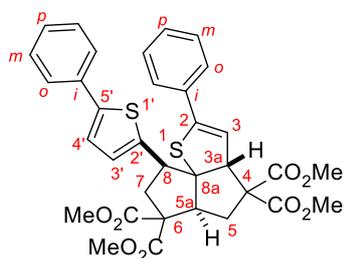
All operations were performed under dry argon atmosphere. A solution of Ga(NTf<sub>2</sub>)<sub>3</sub> (0.1 mmol, 0.05 eq.) and HNTf<sub>2</sub> (0.02 mmol, 0.01 eq.) in dry chlorobenzene (PhCl, 7 ml) was added to a solution of D–A cyclopropane **5** (1.9 mmol, 1.0 eq.) with molecular molecular sieves 4 Å in dry PhCl (20 ml) at room temperature, and the resulting mixture was stirred at 130 °C for 1 hour. Then a saturated solution of NaHCO<sub>3</sub> was added at room temperature, and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 ml). The organic layer was dried over MgSO<sub>4</sub>, and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (benzene to benzene–EtOAc, 25:1) to afford title dimeric compound **7** as colorless crystals in yield 68% (345 mg), and in yield 57% (290 mg) after recrystallization from EtOH.



Colorless crystals, m.p. = 175-177°C (EtOH). IR (CHCl<sub>3</sub>):  $\tilde{\nu}$  3057, 3002, 2955, 2925, 2850, 1760 and 1734 br (C=O), 1598, 1499, 1463, 1437, 1355, 1326, 1293, 1234, 1198, 1178, 1150 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  1.86 (td, 1H, H(1''), <sup>2</sup>J = 12.7 Hz, <sup>3</sup>J = 3.4 Hz), 2.15 (td, 1H, H(1''), <sup>2</sup>J = 12.7 Hz, <sup>3</sup>J = 3.4 Hz), 3.27 (s, 3H, CO<sub>2</sub>Me), 3.50–3.62 (m, 1H, H(6)), 3.65-3.97 (m, 12H, 3 CO<sub>2</sub>Me, H(5), H(2'') and H(3'')), 4.55 (d, 1H, H(4), <sup>3</sup>J = 9.1 Hz), 6.86 (br s, 1H, H(3)), 6.89 (d, 1H, H(3'), <sup>3</sup>J = 3.5 Hz), 7.13 (d, 1H, H(4'), <sup>3</sup>J = 3.5 Hz), 7.17-7.38 (m, 6H, 4 H(*m*) and 2 H(*p*)), 7.45–7.60 (m, 4H, 4 H(*o*)) ppm. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  29.7 (C(1'')), 41.7 (C(6)), 45.3 (C(4)), 49.6 (C(2'')), 52.2, 52.5, 52.7 and 52.8 (4 OMe and C(3'')), 56.0 (C(5)), 118.2 (C(3)), 122.0 (C(4')), 125.5 (4 C(*o*)), 127.2 (C(3')), 127.3 and 127.5 (2 C(*p*)), 128.8 and 128.9 (4 C(*m*)), 134.3 and 134.6 (2 C(*i*)), 141.2 (C(6a)), 143.6 (C(5')), 145.0 (C(2')), 147.9 (C(2)), 148.8 (C(3a)), 167.9, 168.2, 169.1 and 169.2 (4 COO). HRMS calcd for C<sub>34</sub>H<sub>32</sub>O<sub>8</sub>S<sub>2</sub> (*M*): *M*+Na, 655.1431. Found: *m/z* 655.1420.

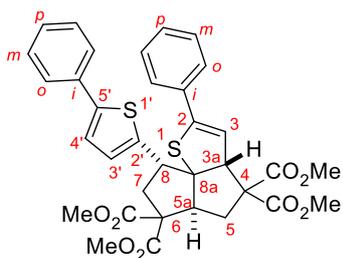
**Tetramethyl 2-phenyl-8-(5-phenylthiophen-2-yl)-5,5a,7,8-tetrahydro-6H-pentaleno[6a,1-b]thiophene-4,4,6,6(3aH)-tetracarboxylate (6)**

All operations were performed under dry argon atmosphere. A solution of GaCl<sub>3</sub> (2M in dry CH<sub>2</sub>Cl<sub>2</sub>, 0.7 mmol, 1.2 eq.) was added to a solution of D–A cyclopropane **5** (0.6 mmol, 1 eq.) in dry CH<sub>2</sub>Cl<sub>2</sub> (3 ml) at –10 °C, and the resulting mixture was stirred at this temperature for 15 min. Then an aqueous solution of HCl (10%) was added without warming up to room temperature, and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 ml). The organic layer was dried over MgSO<sub>4</sub> and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (benzene to benzene–EtOAc, 30:1 to 20:1) to afford title dimeric compound **6** as a mixture of 2 diastereomers in ratio 1.5:1 in yield 73% (140 mg), which can be separated to a large extent later using PTLC (SiO<sub>2</sub>, Merck plates) and the same eluting systems. Red thick oil. IR (CHCl<sub>3</sub>):  $\tilde{\nu}$  3047, 3002, 2955, 2846, 1733 br (C=O), 1599, 1497, 1437, 1267, 1182, 1072 cm<sup>-1</sup>. HRMS calcd for C<sub>34</sub>H<sub>32</sub>O<sub>8</sub>S<sub>2</sub> (*M*): *M*+H, 633.1611, *M*+Na, 655.1431. Found: *m/z* 633.1618, 655.1429.



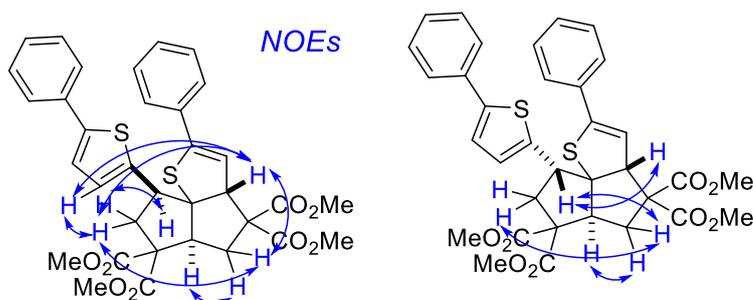
**(3aRS,5aSR,8SR)-diastereomer.** <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  1.54 (dd, 1H, H(5), <sup>2</sup>J = 13.1 Hz, <sup>3</sup>J = 10.9 Hz), 2.44–2.64 (m, 2H, H(5) and H(7)), 2.73 (t, 1H, H(7), <sup>2</sup>J = <sup>3</sup>J = 14.0 Hz), 3.55 (s, 3H, CO<sub>2</sub>Me), 3.65–3.87 (m, 10H, 3 CO<sub>2</sub>Me and H(8)), 3.98 (d, 1H, H(3a), <sup>3</sup>J = 3.6 Hz), 4.20 (br. t, 1H, H(5a), <sup>3</sup>J = 10.9 Hz), 5.46 (d, 1H,

H(3),  $^3J = 3.6$  Hz), 6.93 (d, 1H, H(3'),  $^3J = 3.6$  Hz), 7.10 (d, 1H, H(4'),  $^3J = 3.6$  Hz), 7.15–7.59 (m, 10H, 10 H<sub>Ar</sub>) ppm.  $^{13}\text{C}$  NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  35.8 (C(7)), 36.7 (C(5)), 52.2 (C(8)), 52.6, 52.8, 52.9 and 53.2 (4 OMe), 56.4 (C(5a)), 61.5 (C(6)), 63.7 (C(3a)), 66.3 (C(4)), 73.4 (C(8a)), 115.8 (C(3)), 122.5 (C(4')), 125.6 (2 C(*o*)), 125.8 (C(3')), 126.6 (2 C(*o*)), 127.2 (C(*p*)), 128.3 (2 C(*m*) and C(*p*)), 128.7 (2 C(*m*)), 133.9 and 134.3 (2 C(*i*)), 139.1 (C(2')), 142.8 (C(2)), 143.3 (C(5')), 169.6, 170.4, 170.9 and 171.5 (4 COO).

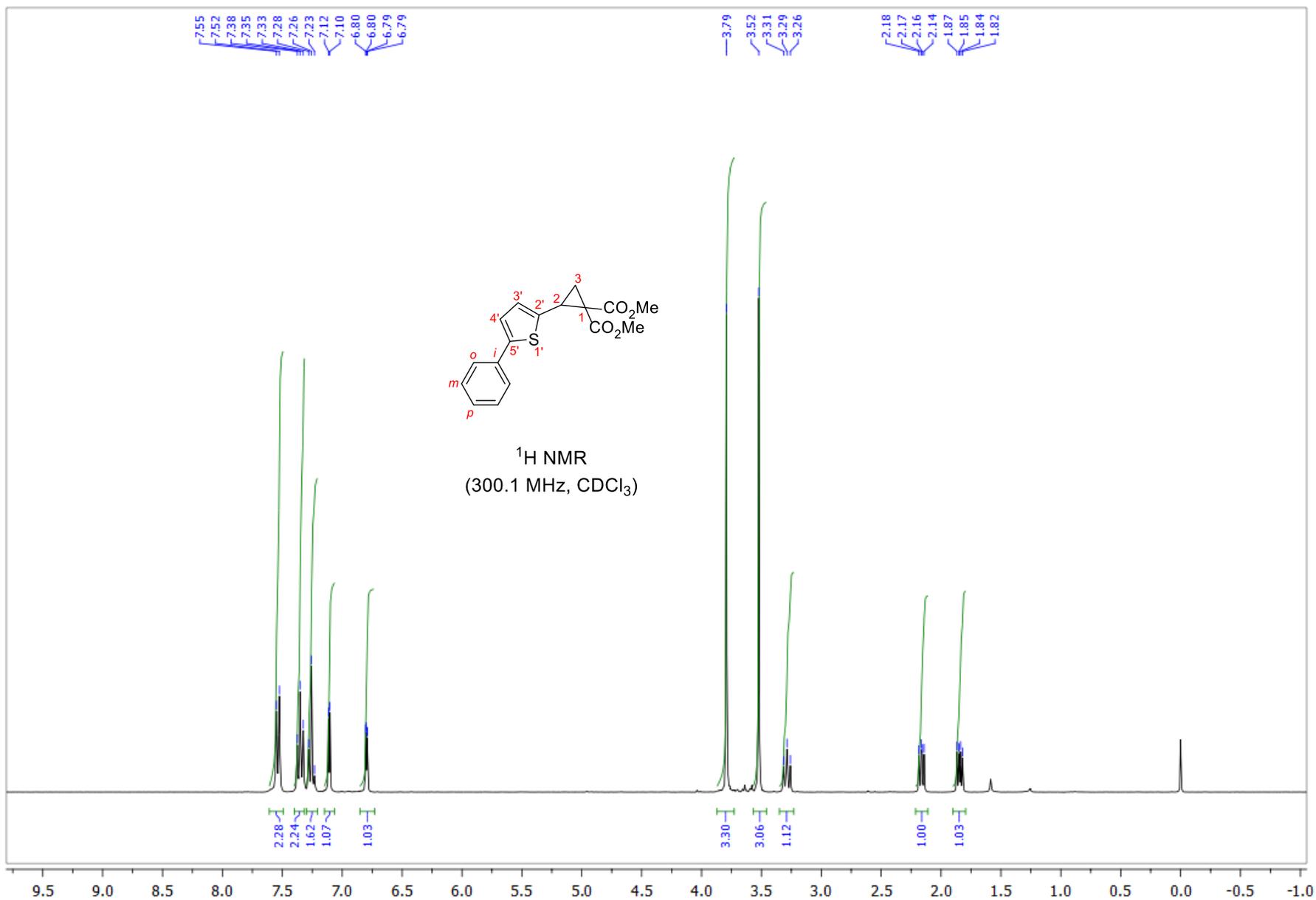


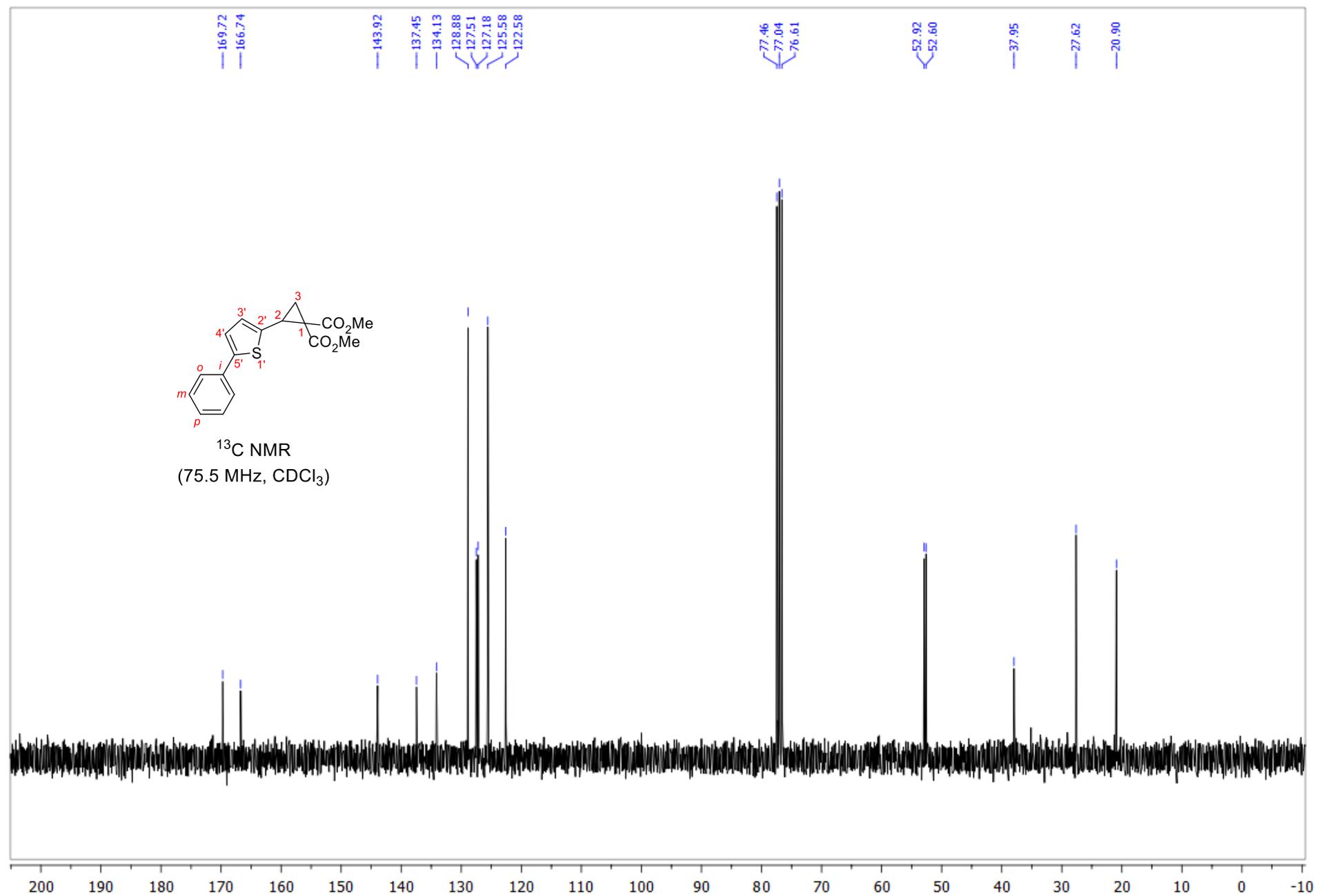
**(3a*RS*,5a*SR*,8*RS*)-diastereomer.**  $^1\text{H}$  NMR (300.1 MHz, CDCl<sub>3</sub>):

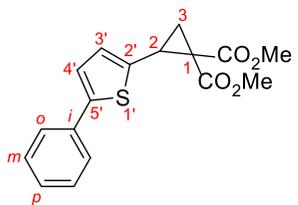
$\delta$  1.68 (t, 1H, H(5),  $^2J = ^3J = 12.7$  Hz), 2.32 (t, 1H, H(7),  $^2J = ^3J = 13.3$  Hz), 2.71 (dd, 1H, H(5),  $^2J = 12.7$  Hz,  $^3J = 7.7$  Hz), 3.12 (dd, 1H, H(7),  $^2J = 13.3$  Hz,  $^3J = 5.7$  Hz), 3.67 (s, 3H, CO<sub>2</sub>Me), 3.70-3.89 (m, 10H, 3 CO<sub>2</sub>Me and H(8)), 4.49 (d, 1H, H(3a),  $^3J = 3.3$  Hz), 4.60 (dd, 1H, H(5a),  $^3J = 12.7$  Hz,  $^3J = 7.7$  Hz), 5.68 (d, 1H, H(3),  $^3J = 3.3$  Hz), 6.92 (d, 1H, H(3'),  $^3J = 3.6$  Hz), 7.11 (d, 1H, H(4'),  $^3J = 3.6$  Hz), 7.15-7.61 (m, 10H, 10 H<sub>Ar</sub>) ppm.  $^{13}\text{C}$  NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  36.9 (C(5)), 43.9 (C(7)), 52.0 (C(8)), 52.5, 52.6, 53.1 and 53.2 (4 OMe), 59.7 (C(5a) and C(6)), 64.7 (C(3a)), 68.2 (C(4)), 77.4 (C(8a)), 114.9 (C(3)), 122.2 (C(4')), 125.6 (2 C(*o*)), 126.6 (2 C(*o*) and C(3')), 127.1 (C(*p*)), 128.2 and 128.4 (2 C(*m*) and C(*p*)), 128.7 (2 C(*m*)), 133.7 and 134.5 (2 C(*i*)), 140.0 (C(2')), 142.5 (C(2)), 143.3 (C(5')), 169.9, 170.9, 171.2 and 171.3 (4 COO).



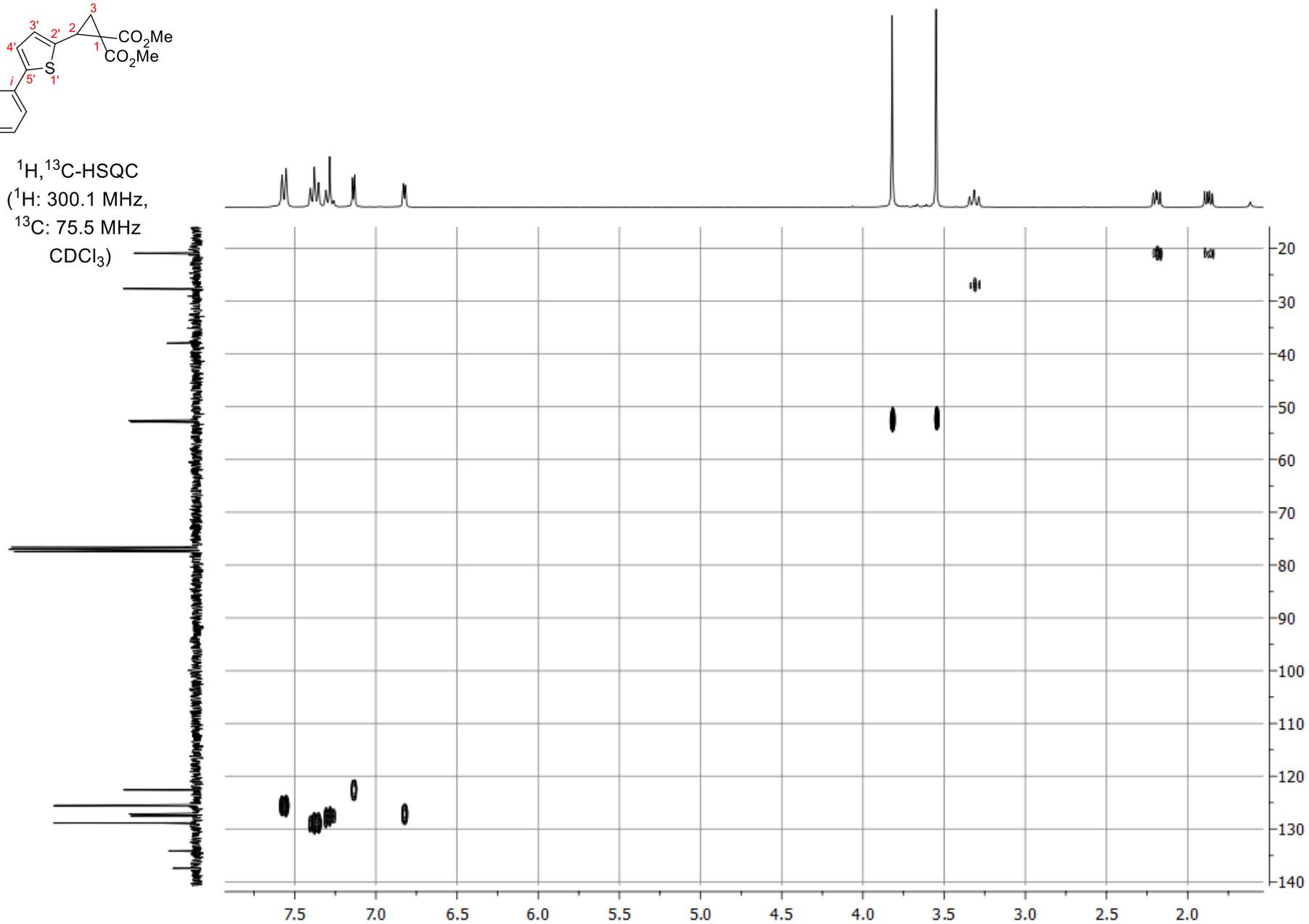
### 3. NMR spectra for the new compounds:

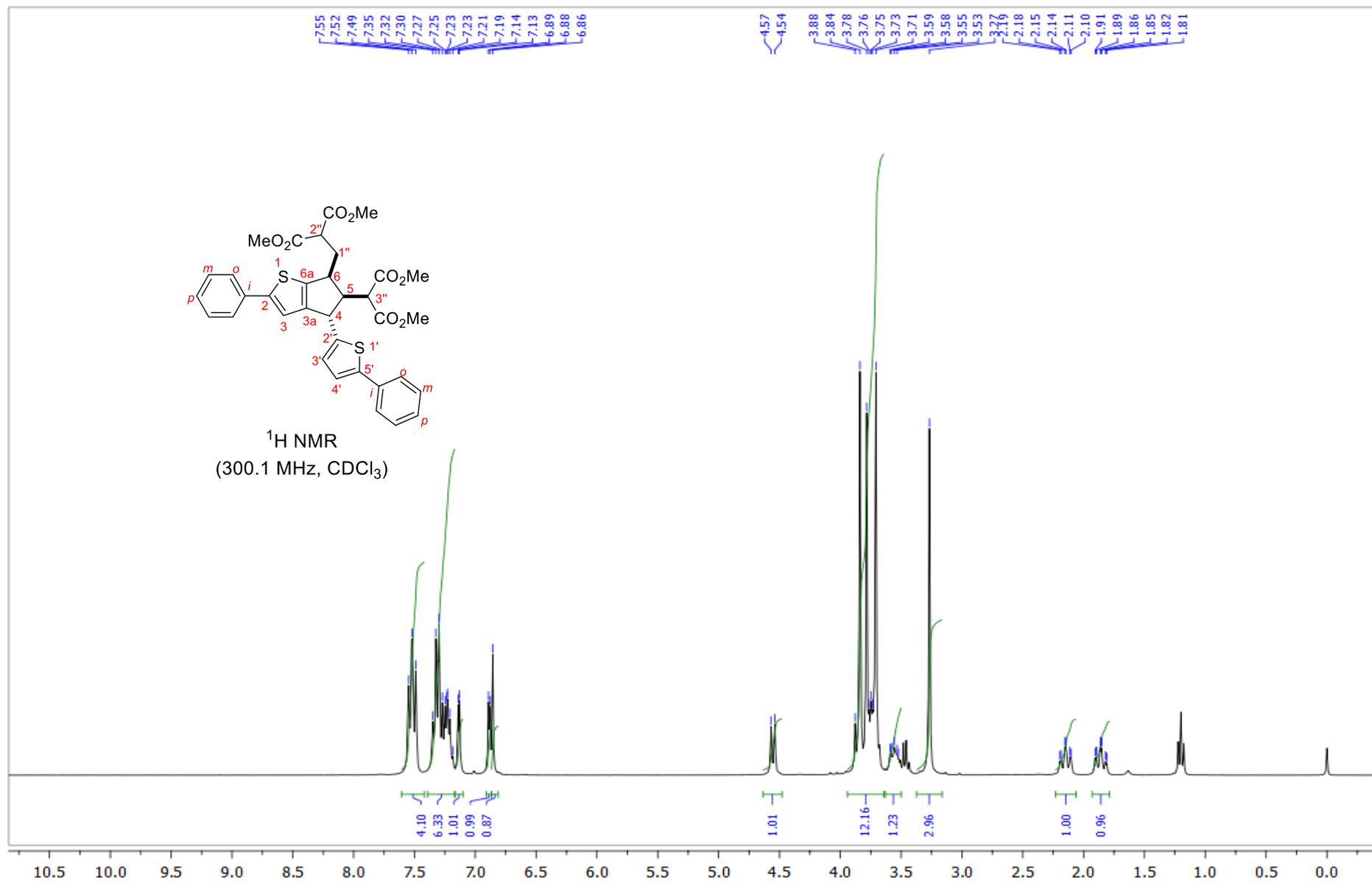


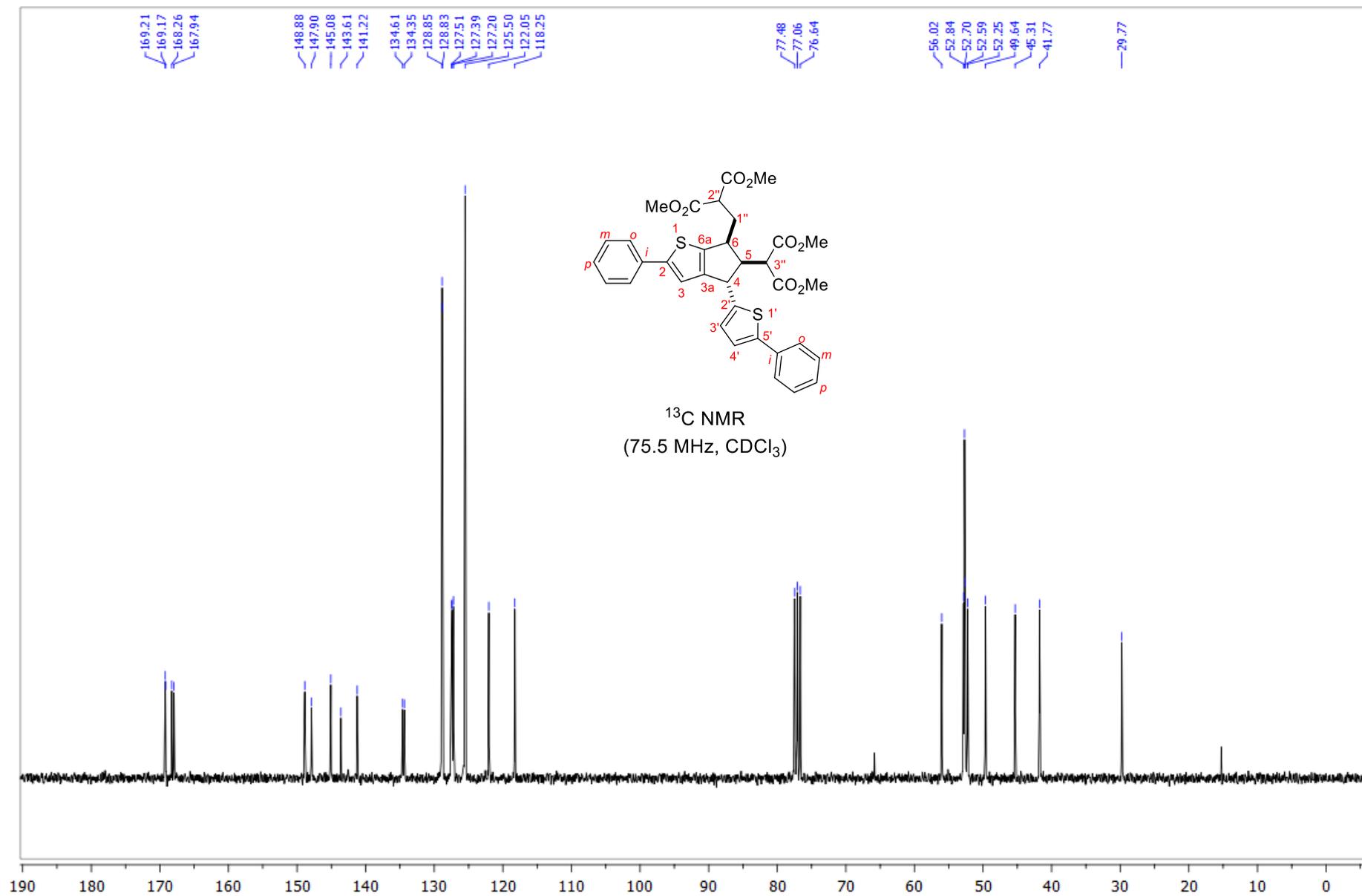


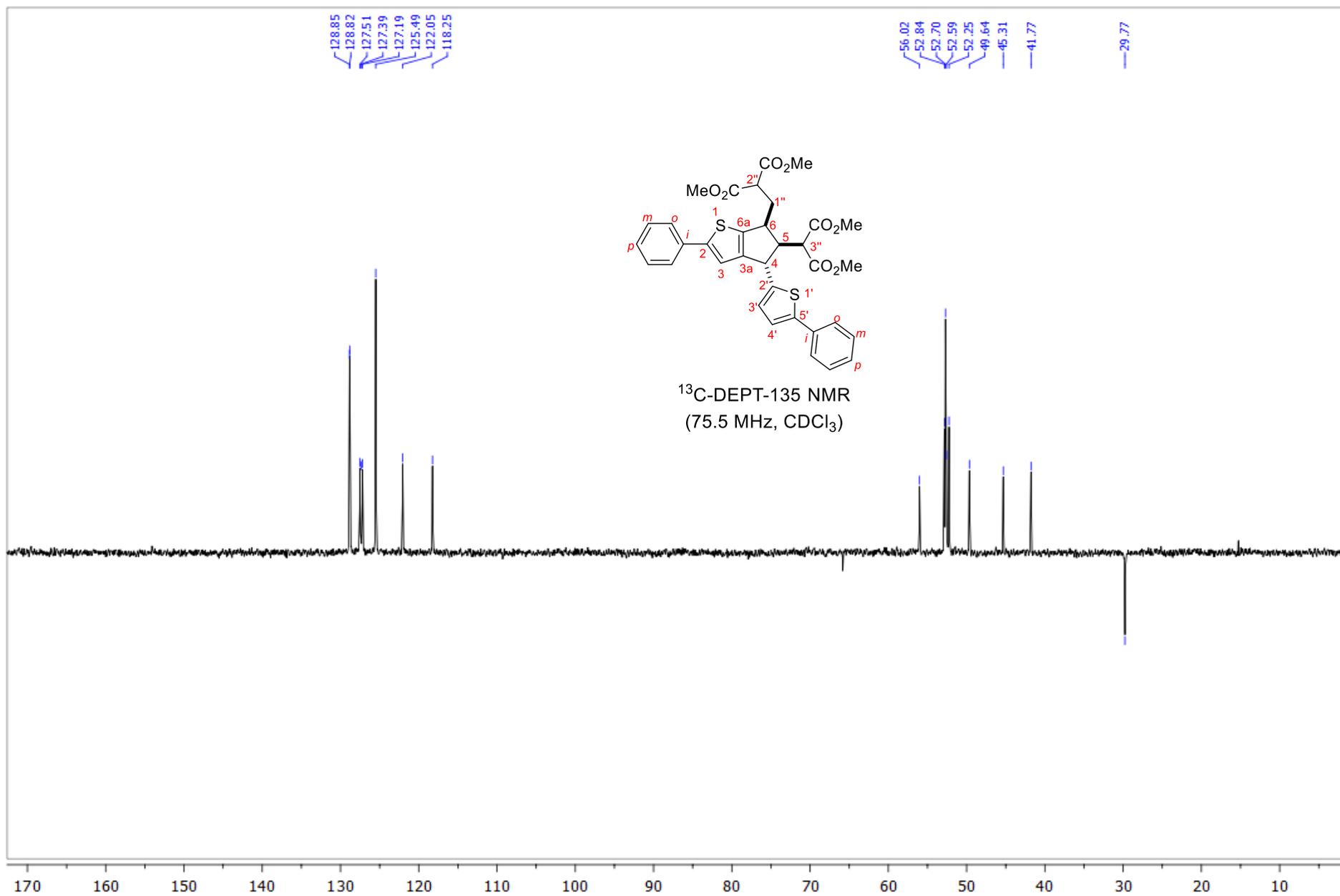


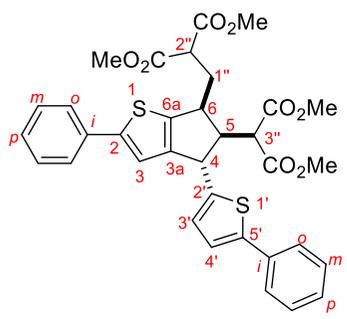
$^1\text{H}, ^{13}\text{C}$ -HSQC  
( $^1\text{H}$ : 300.1 MHz,  
 $^{13}\text{C}$ : 75.5 MHz  
 $\text{CDCl}_3$ )



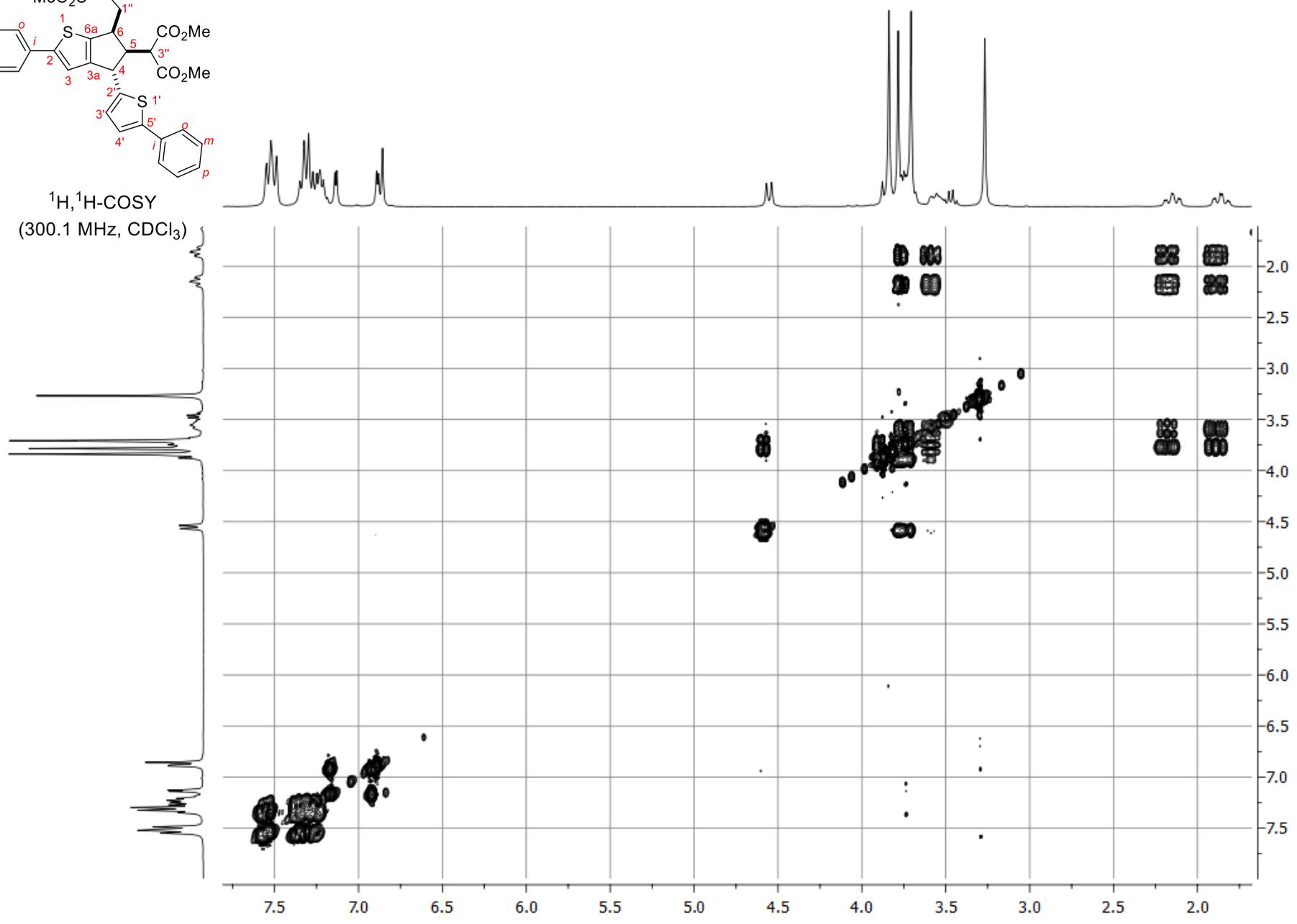


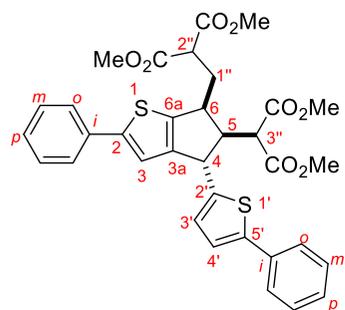




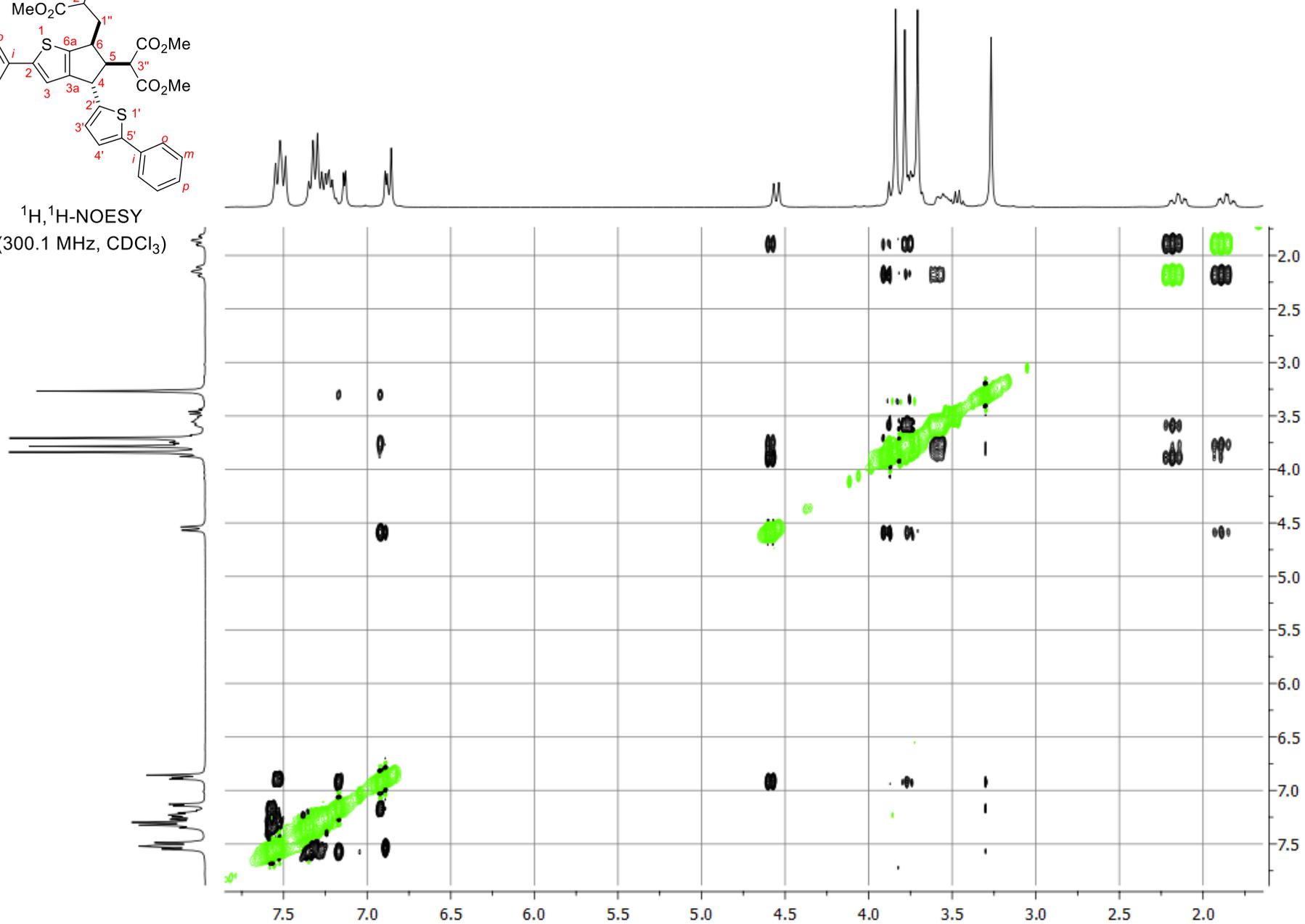


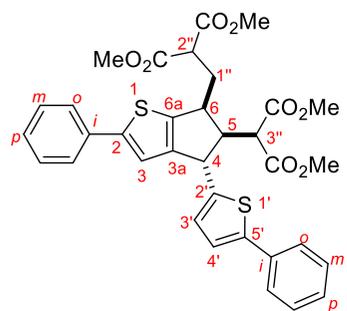
$^1\text{H}, ^1\text{H}$ -COSY  
(300.1 MHz,  $\text{CDCl}_3$ )



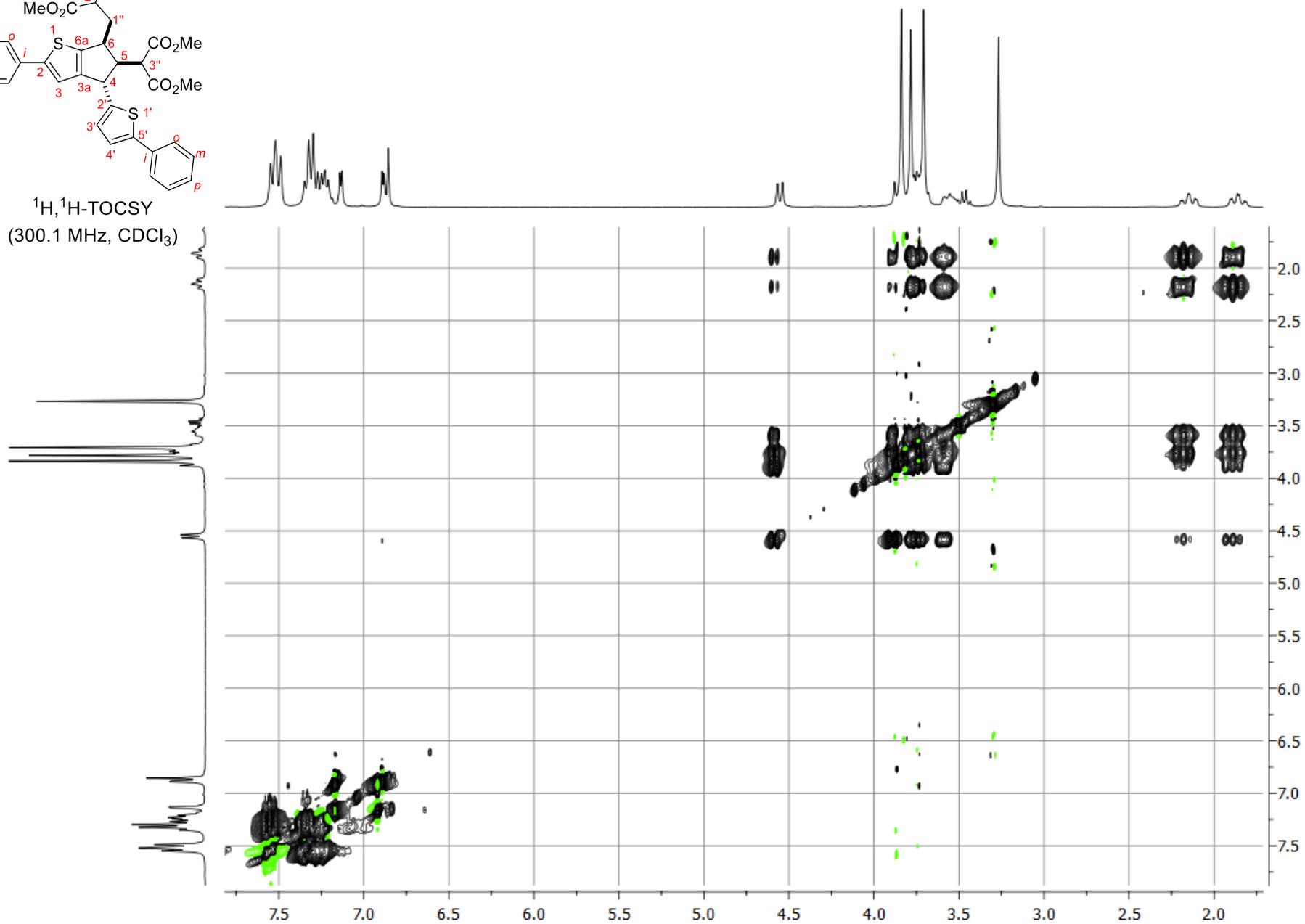


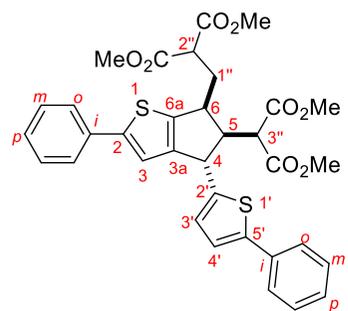
$^1\text{H}, ^1\text{H}$ -NOESY  
(300.1 MHz,  $\text{CDCl}_3$ )



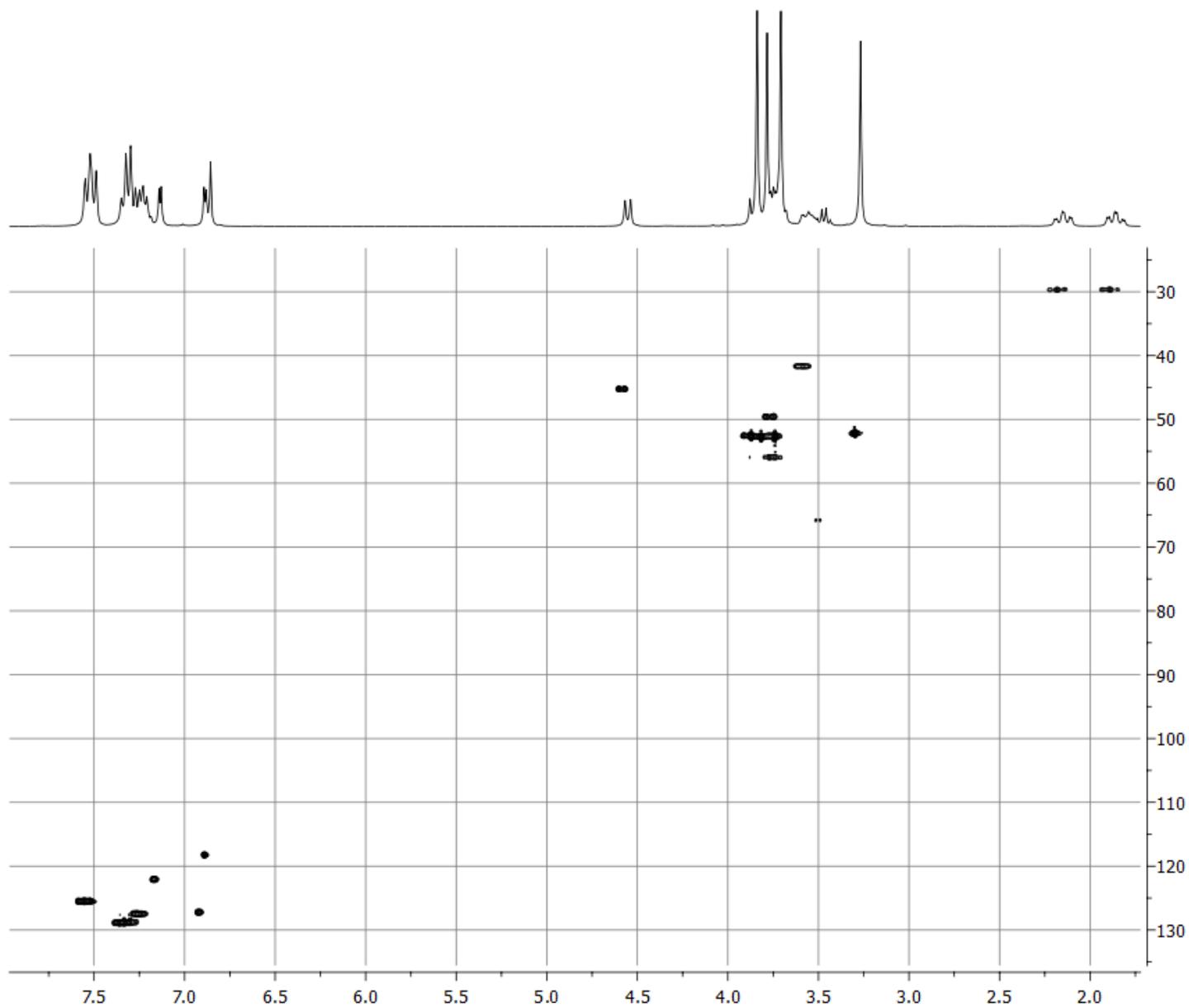


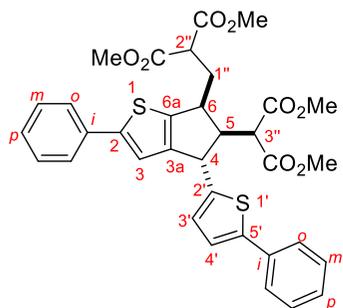
$^1\text{H}, ^1\text{H}$ -TOCSY  
(300.1 MHz,  $\text{CDCl}_3$ )



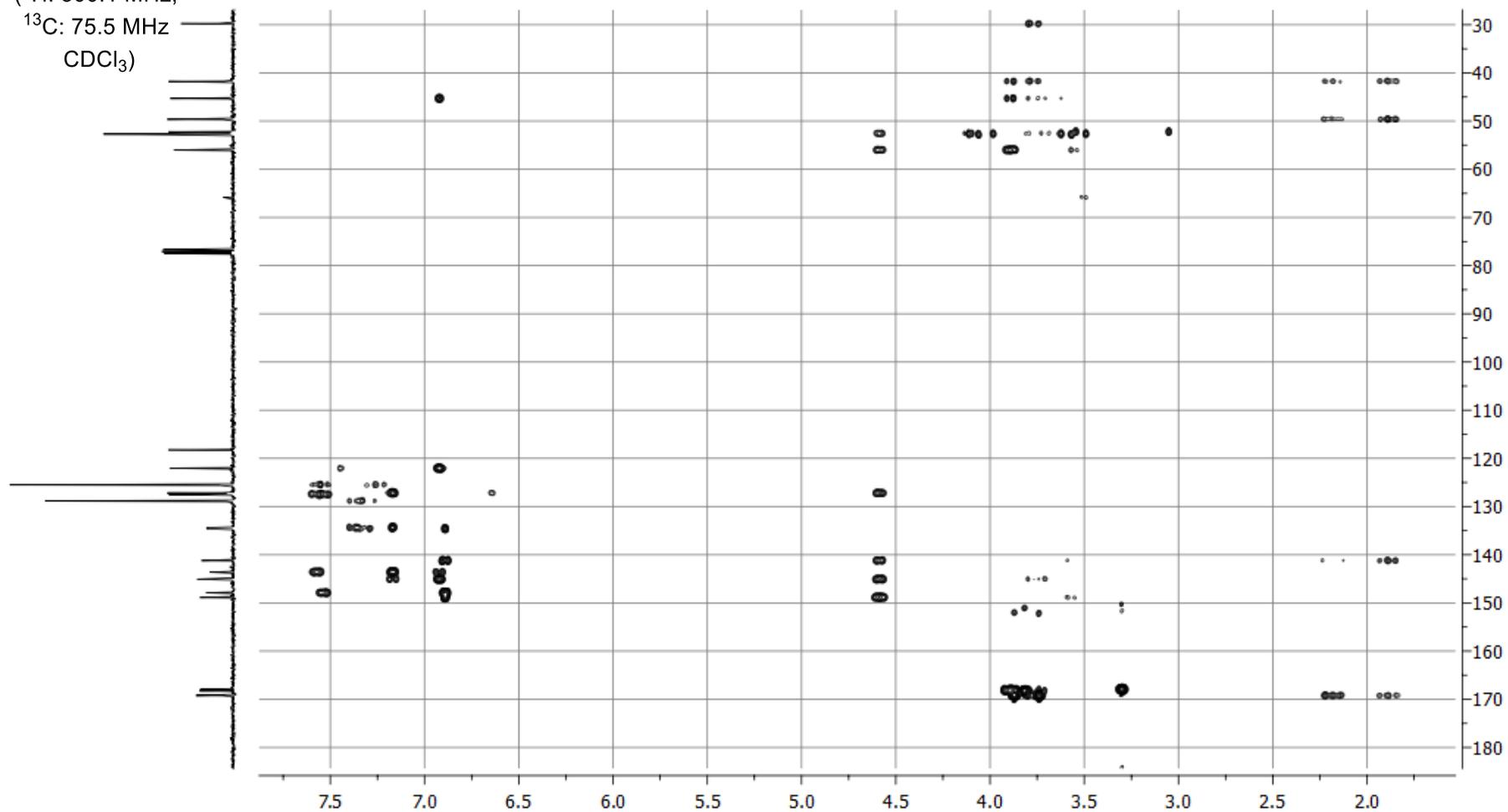


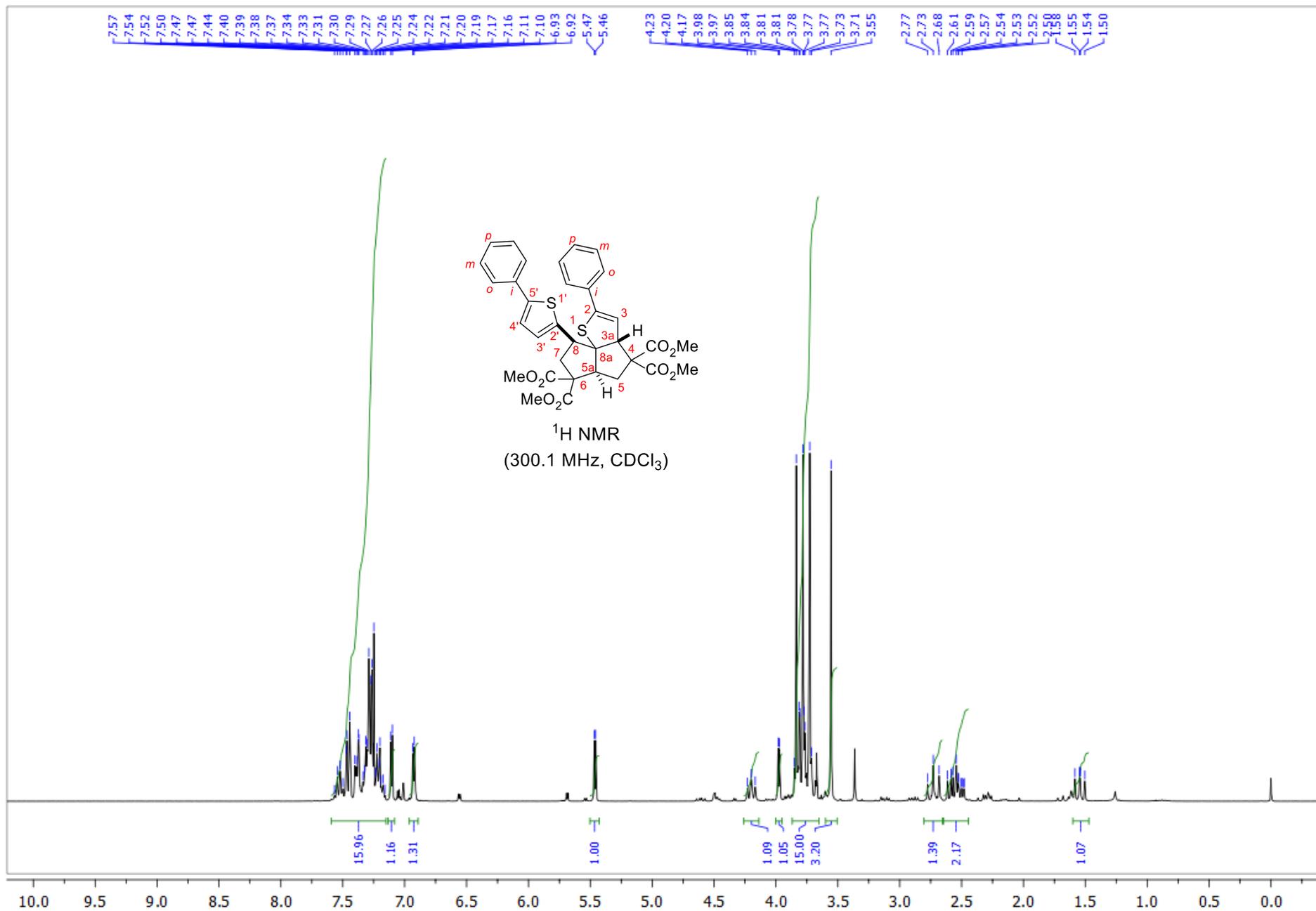
$^1\text{H}, ^{13}\text{C}$ -HSQC  
 ( $^1\text{H}$ : 300.1 MHz,  
 $^{13}\text{C}$ : 75.5 MHz  
 $\text{CDCl}_3$ )

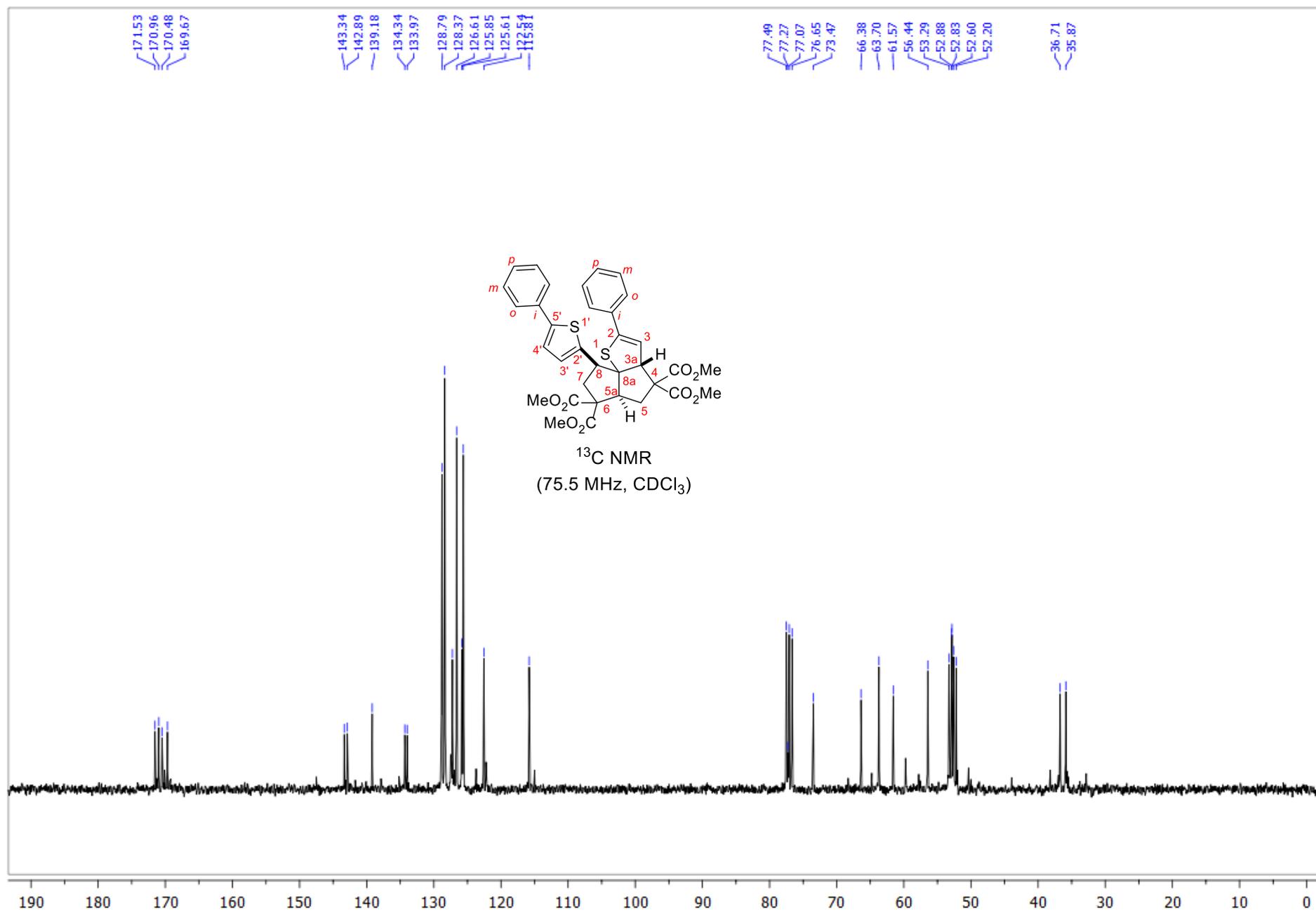


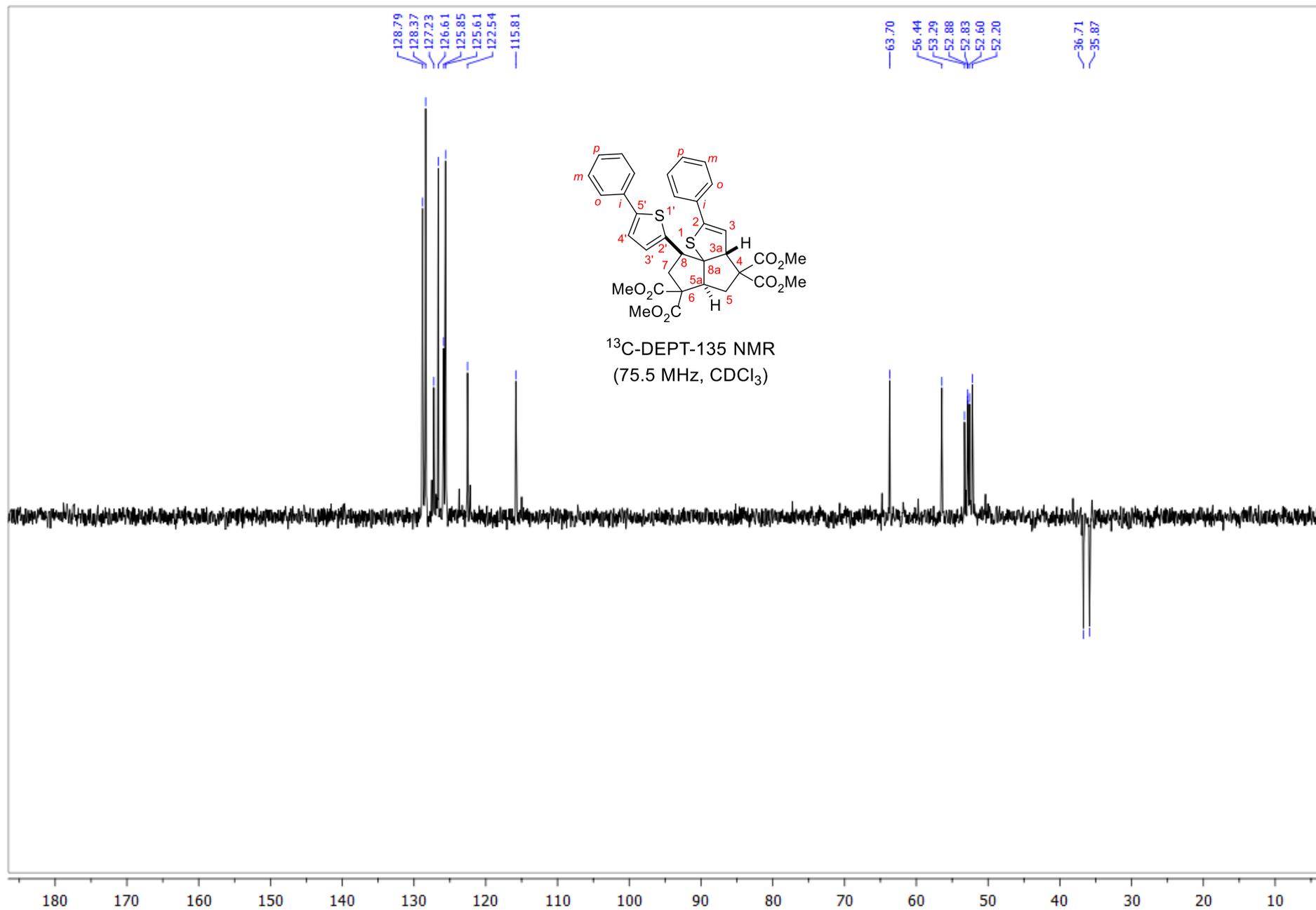


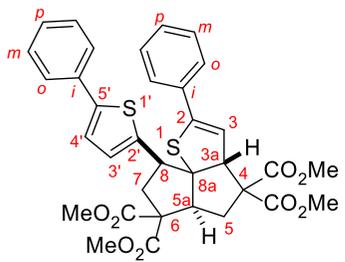
<sup>1</sup>H, <sup>13</sup>C-HMBC  
 (1H: 300.1 MHz,  
 13C: 75.5 MHz  
 CDCl<sub>3</sub>)



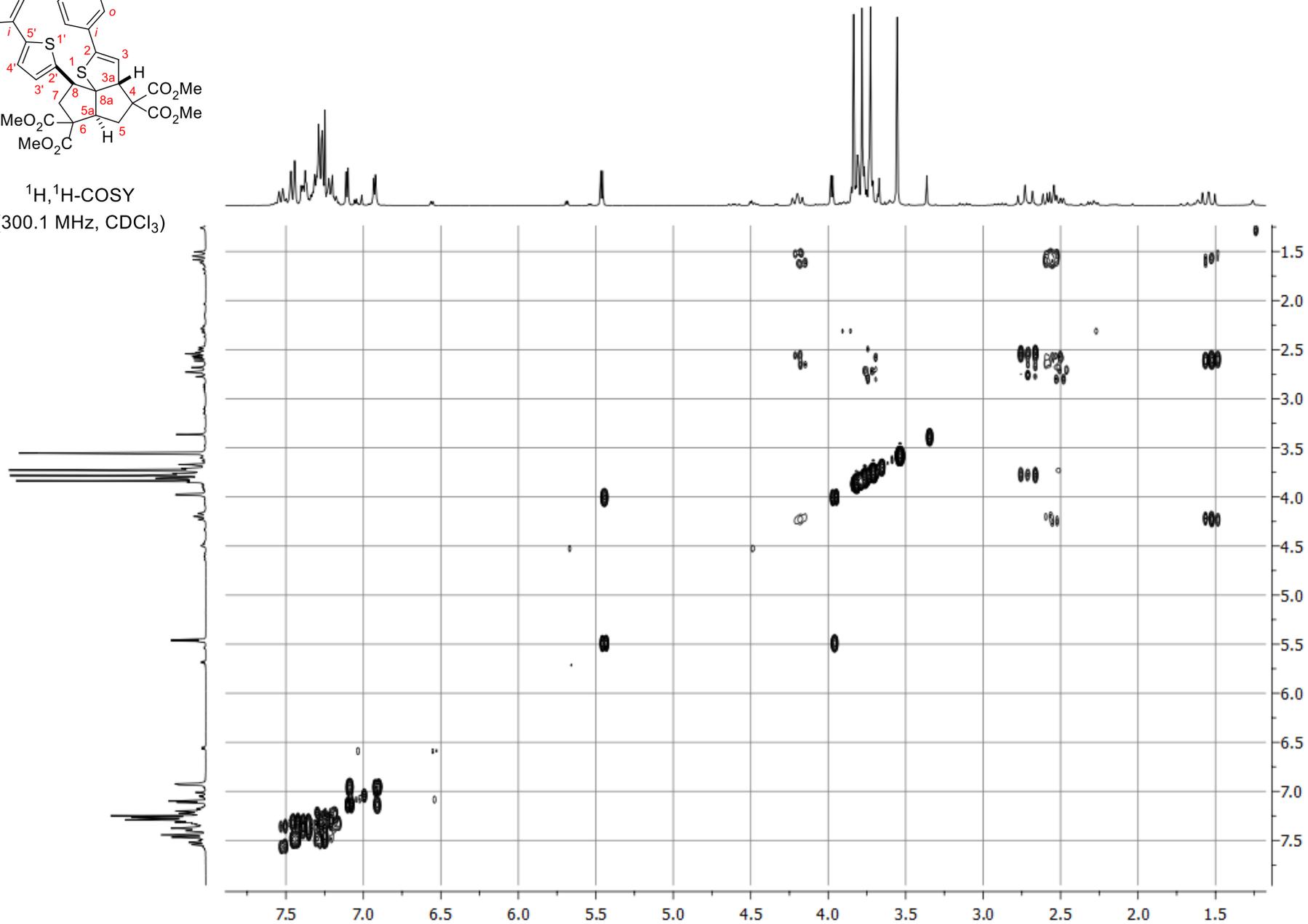


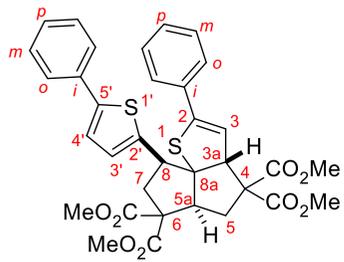




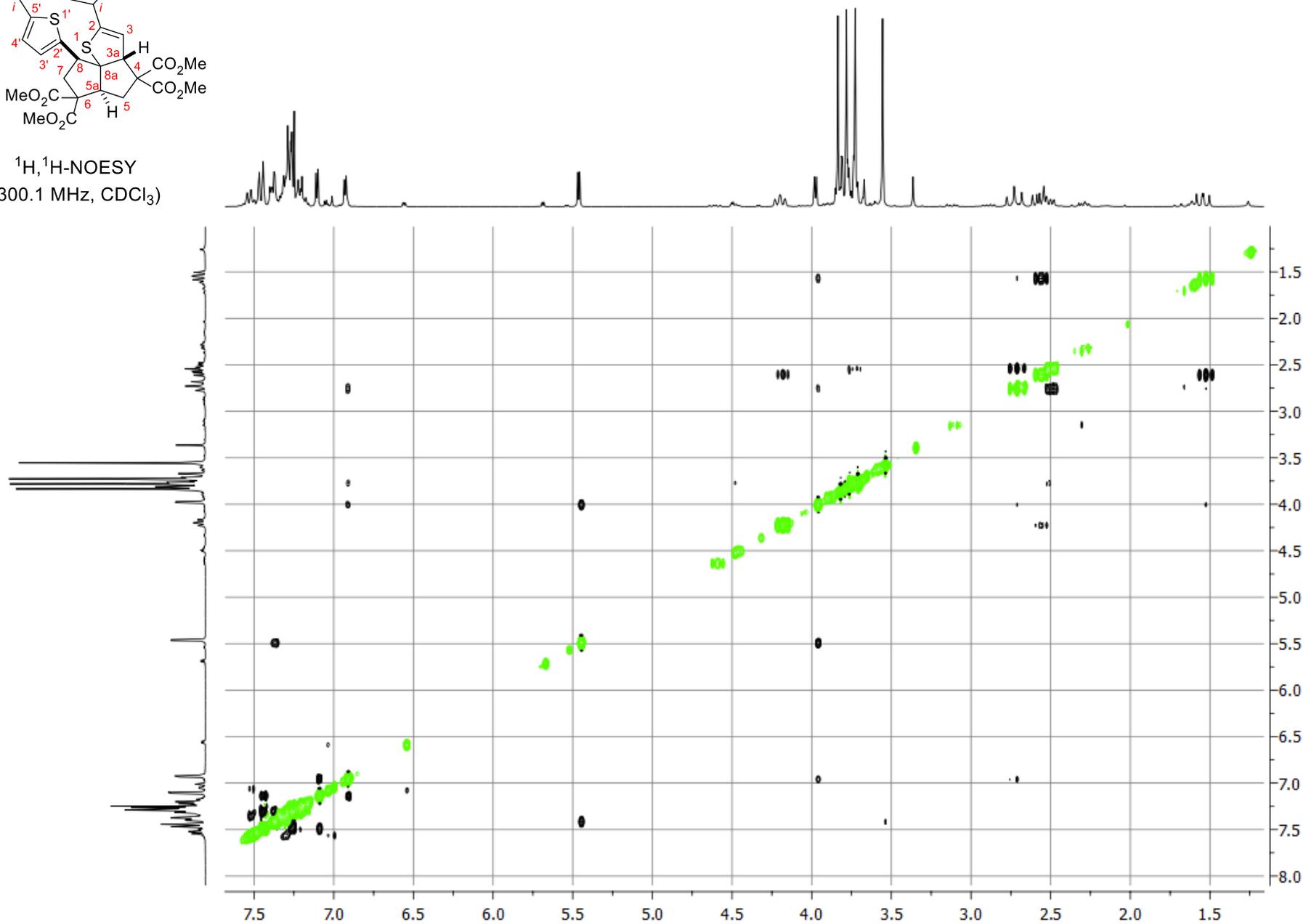


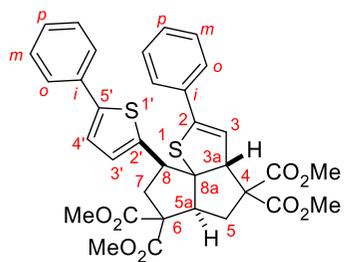
$^1\text{H}, ^1\text{H}$ -COSY  
(300.1 MHz,  $\text{CDCl}_3$ )



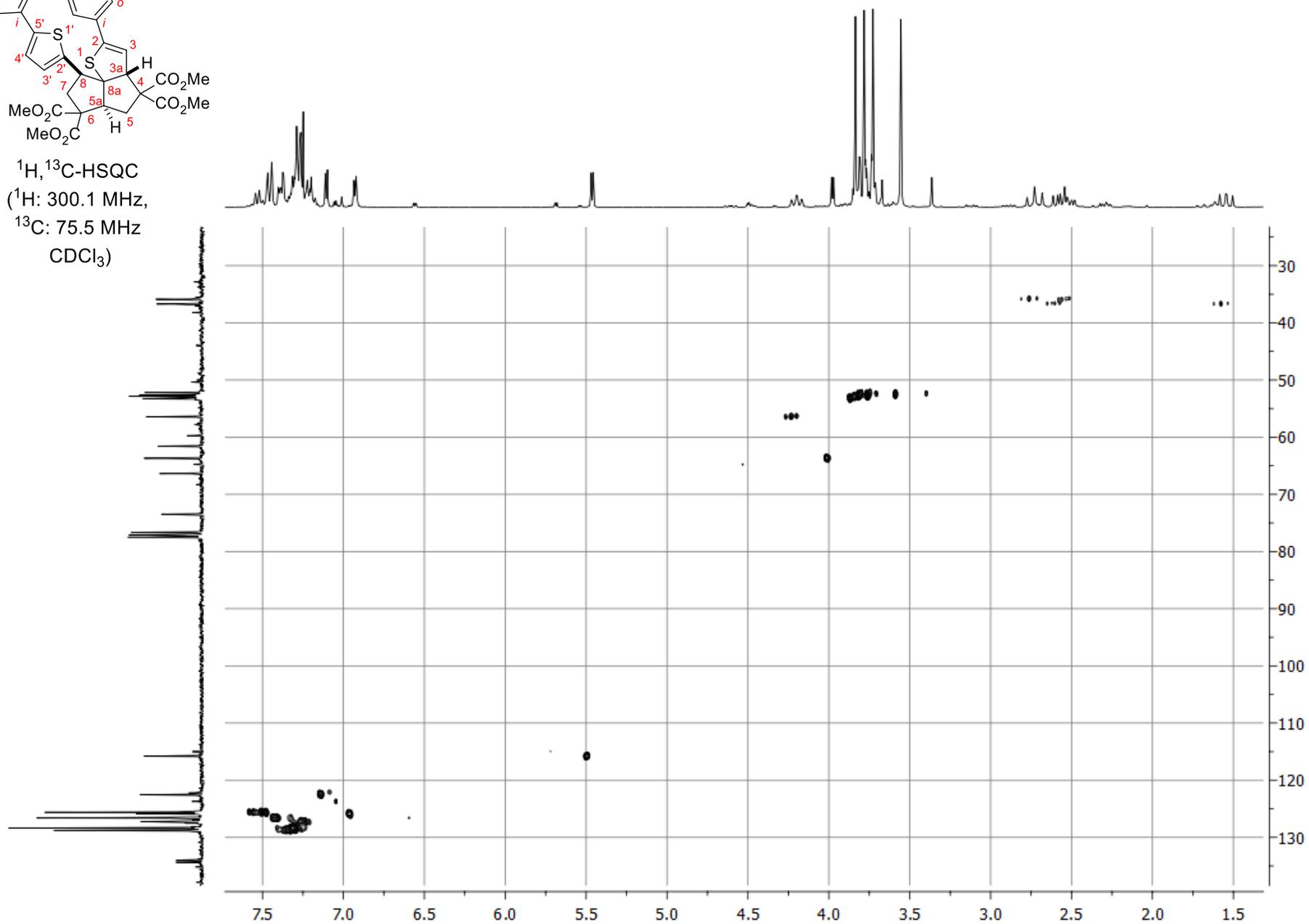


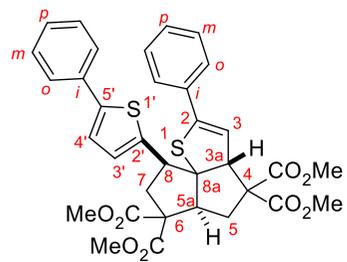
$^1\text{H}, ^1\text{H}$ -NOESY  
(300.1 MHz,  $\text{CDCl}_3$ )



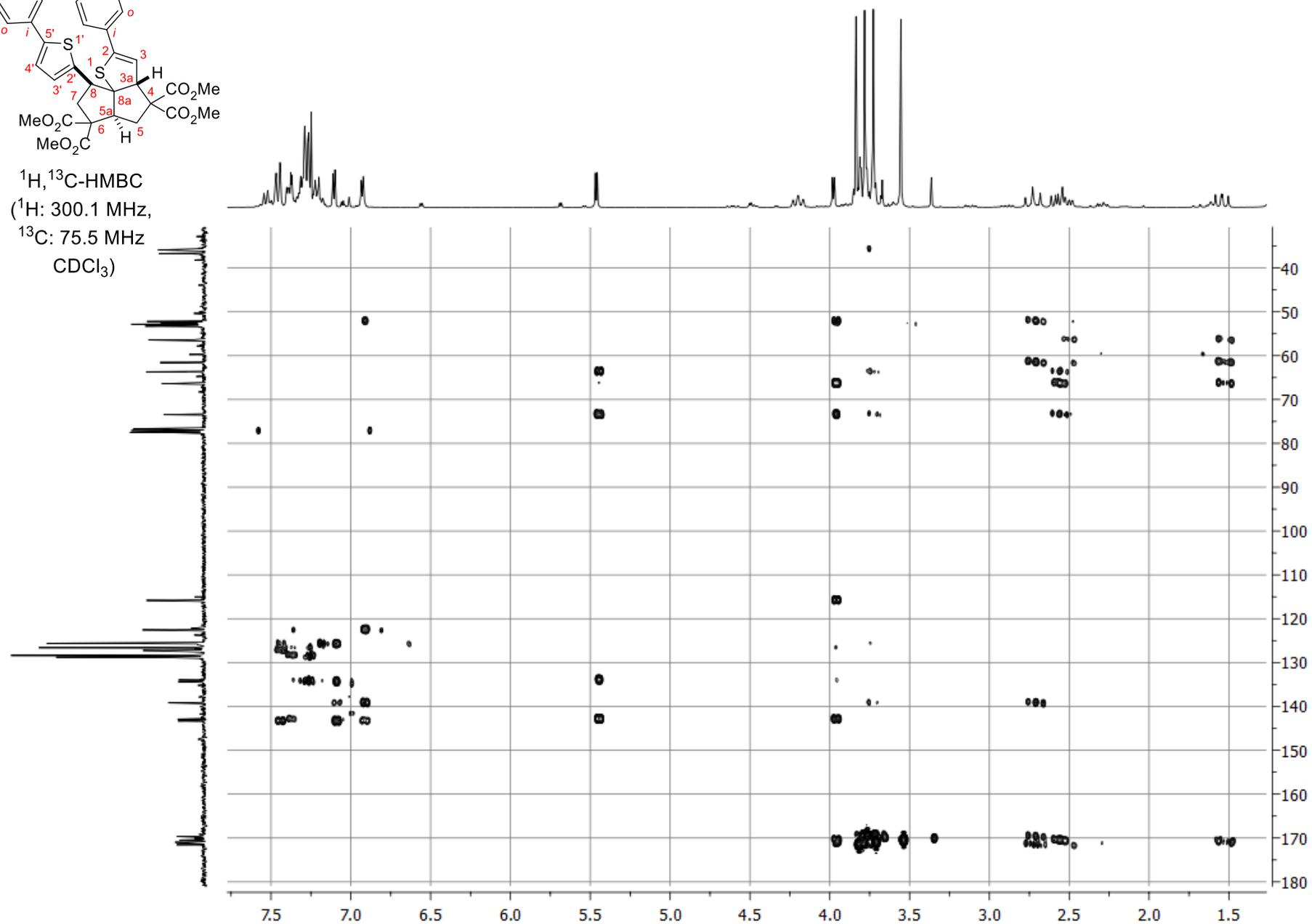


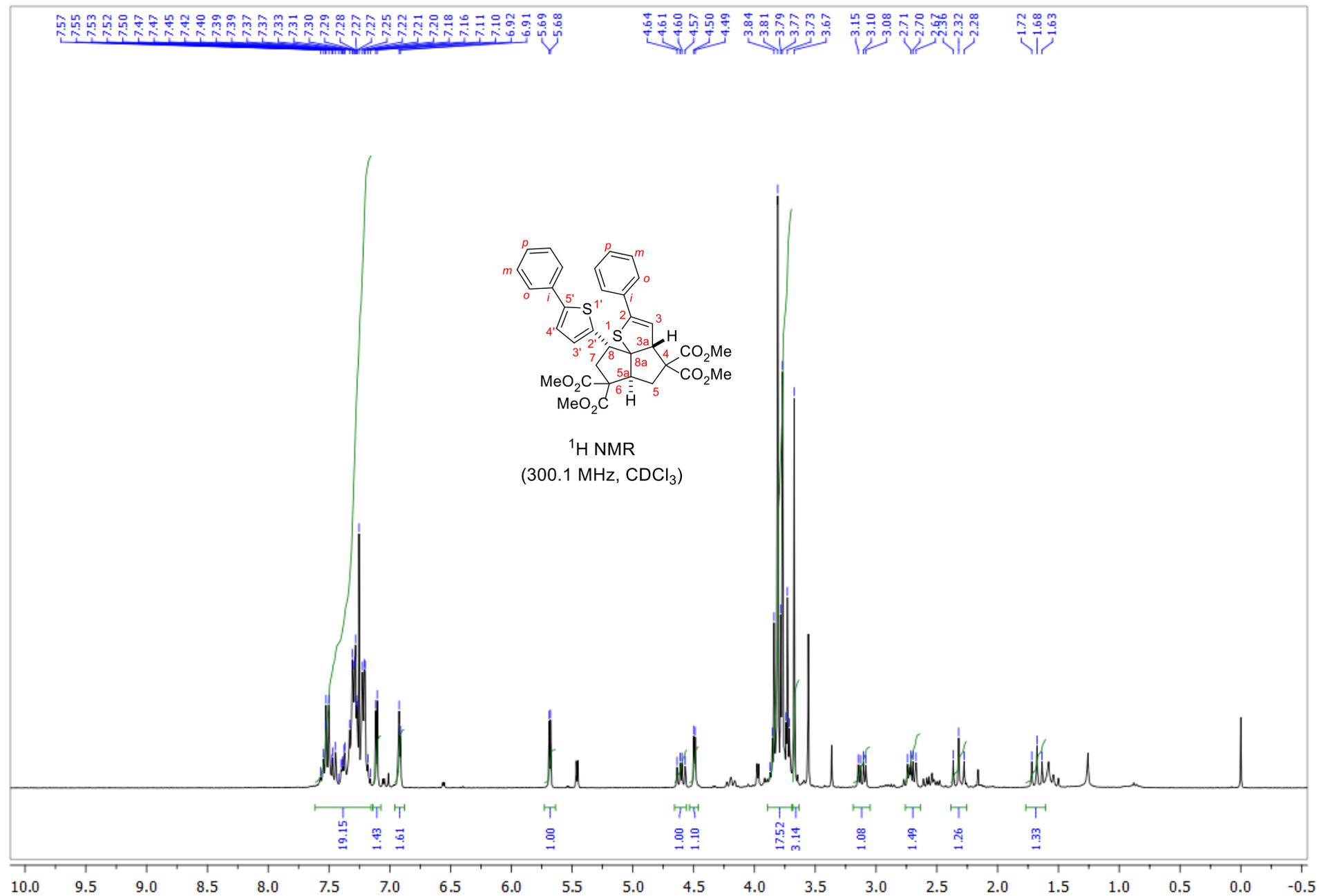
$^1\text{H}, ^{13}\text{C}$ -HSQC  
 ( $^1\text{H}$ : 300.1 MHz,  
 $^{13}\text{C}$ : 75.5 MHz  
 $\text{CDCl}_3$ )

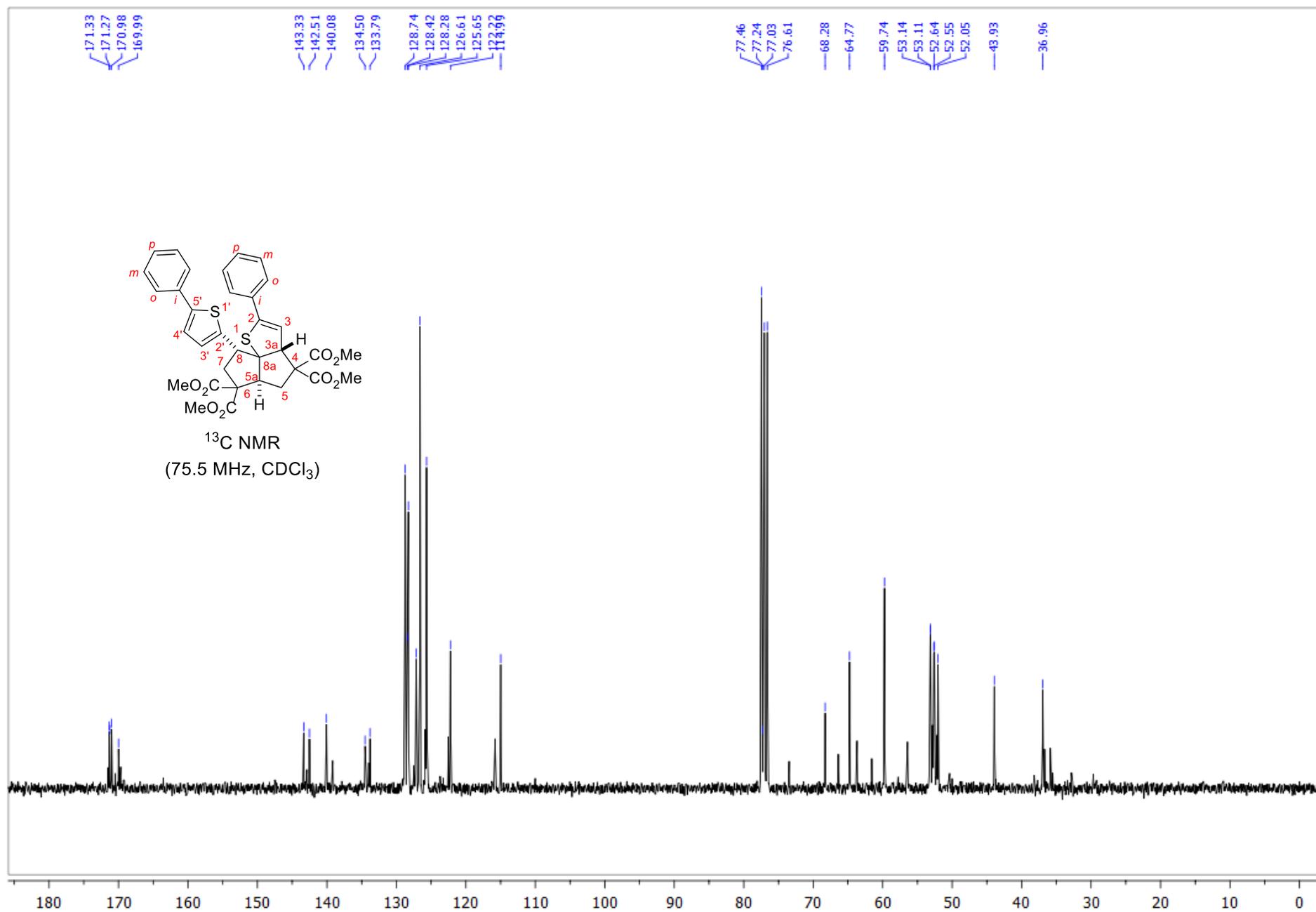


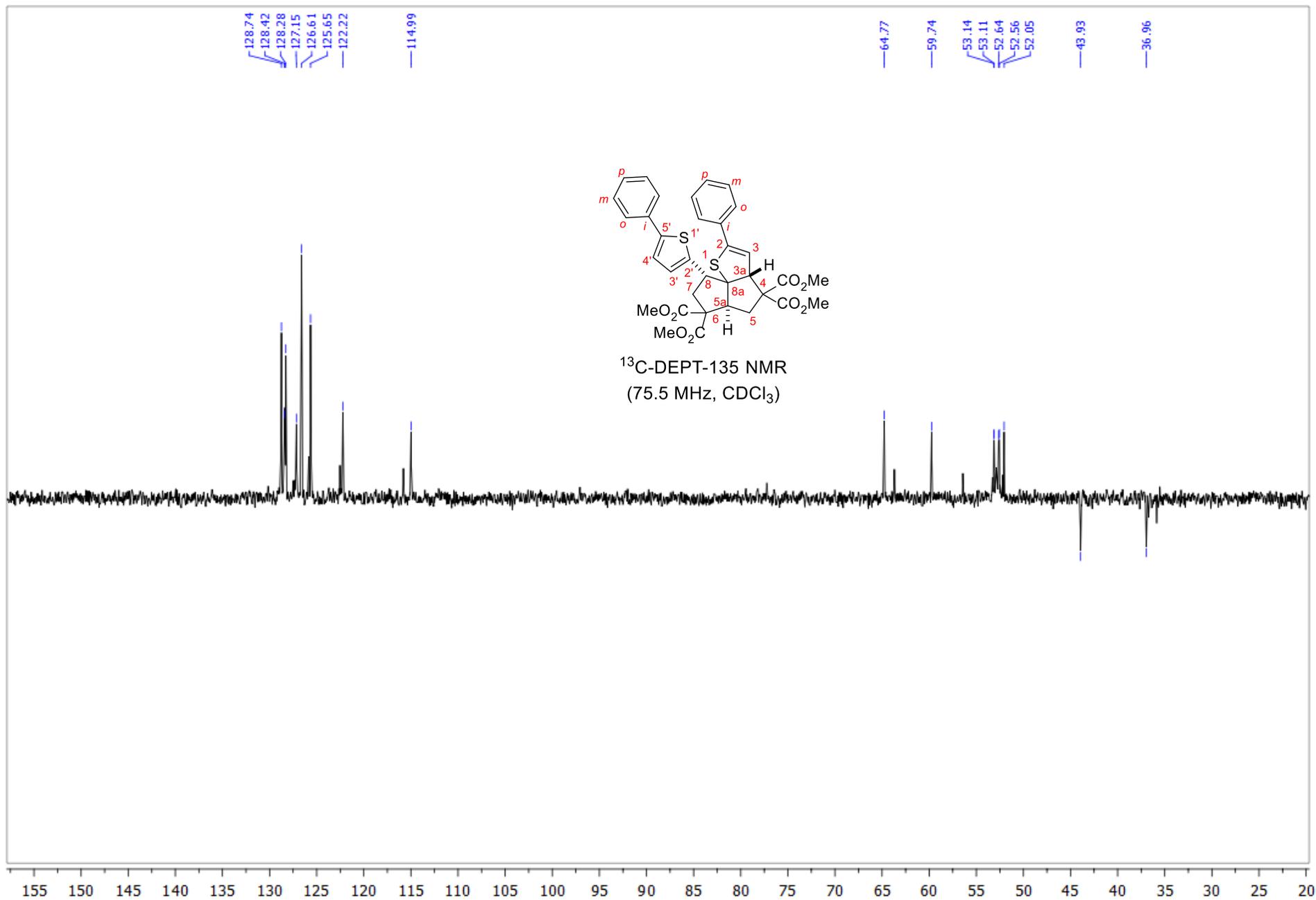


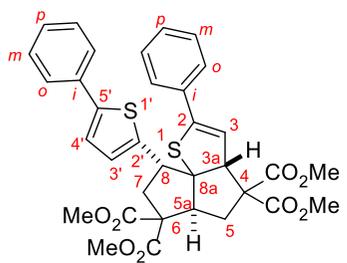
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 ( $^1\text{H}$ : 300.1 MHz,  
 $^{13}\text{C}$ : 75.5 MHz  
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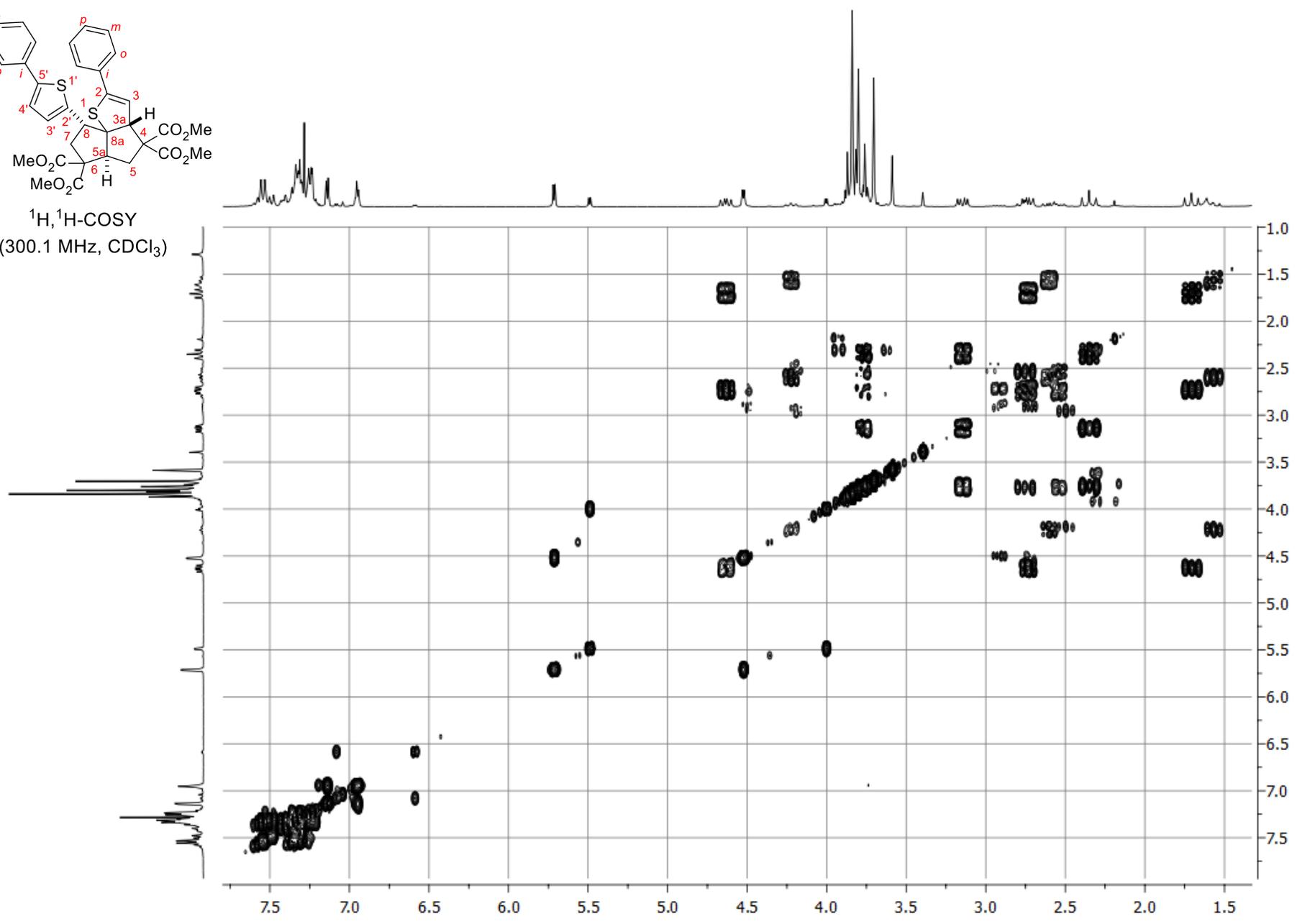


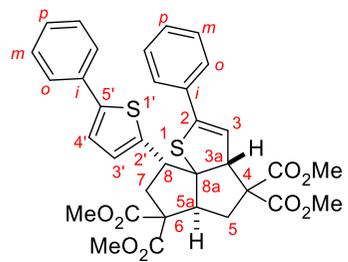




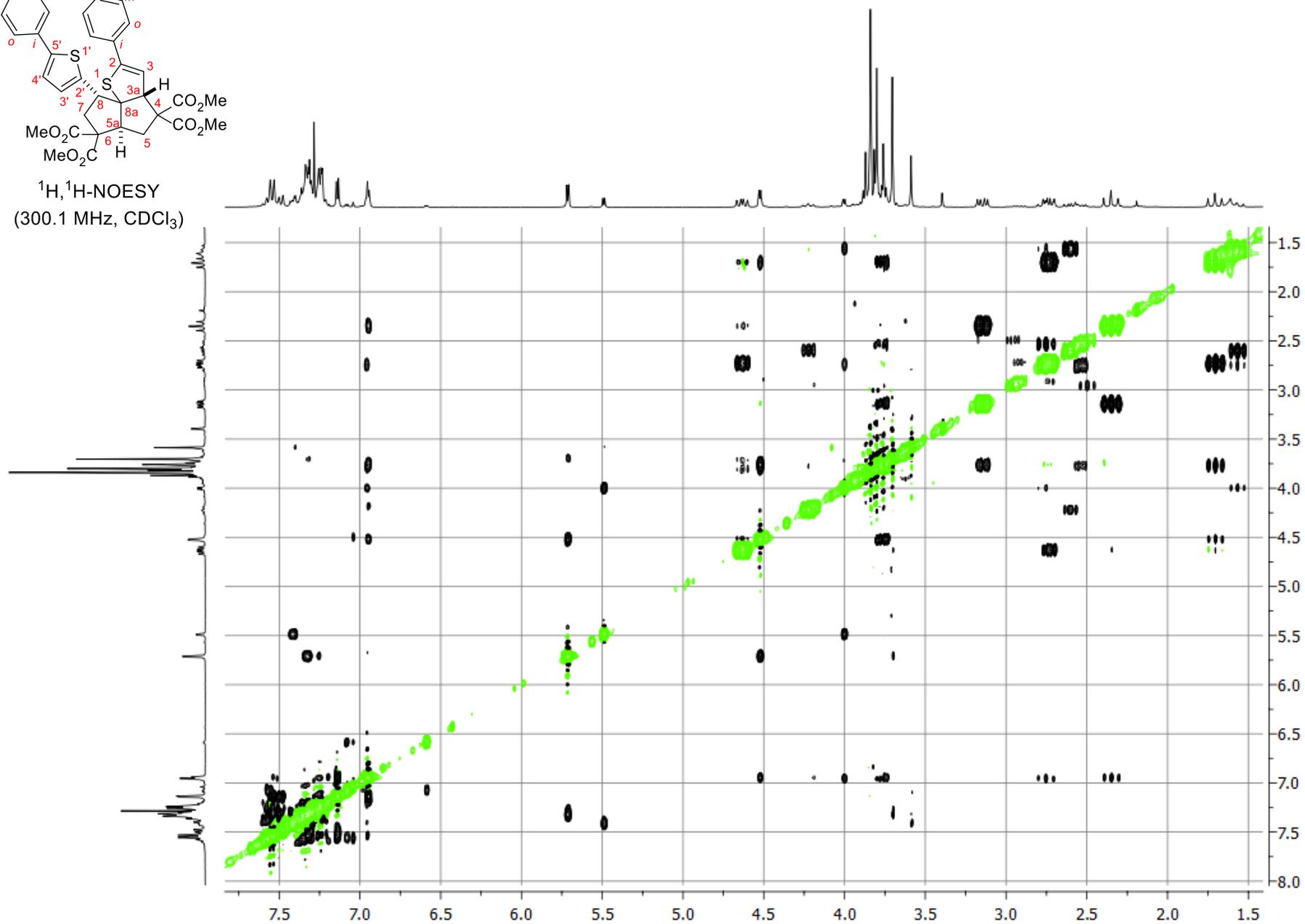


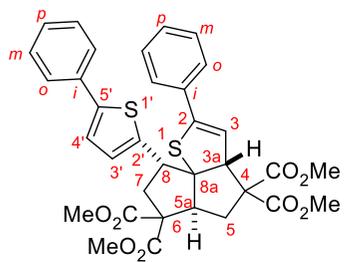
$^1\text{H}, ^1\text{H}$ -COSY  
(300.1 MHz,  $\text{CDCl}_3$ )



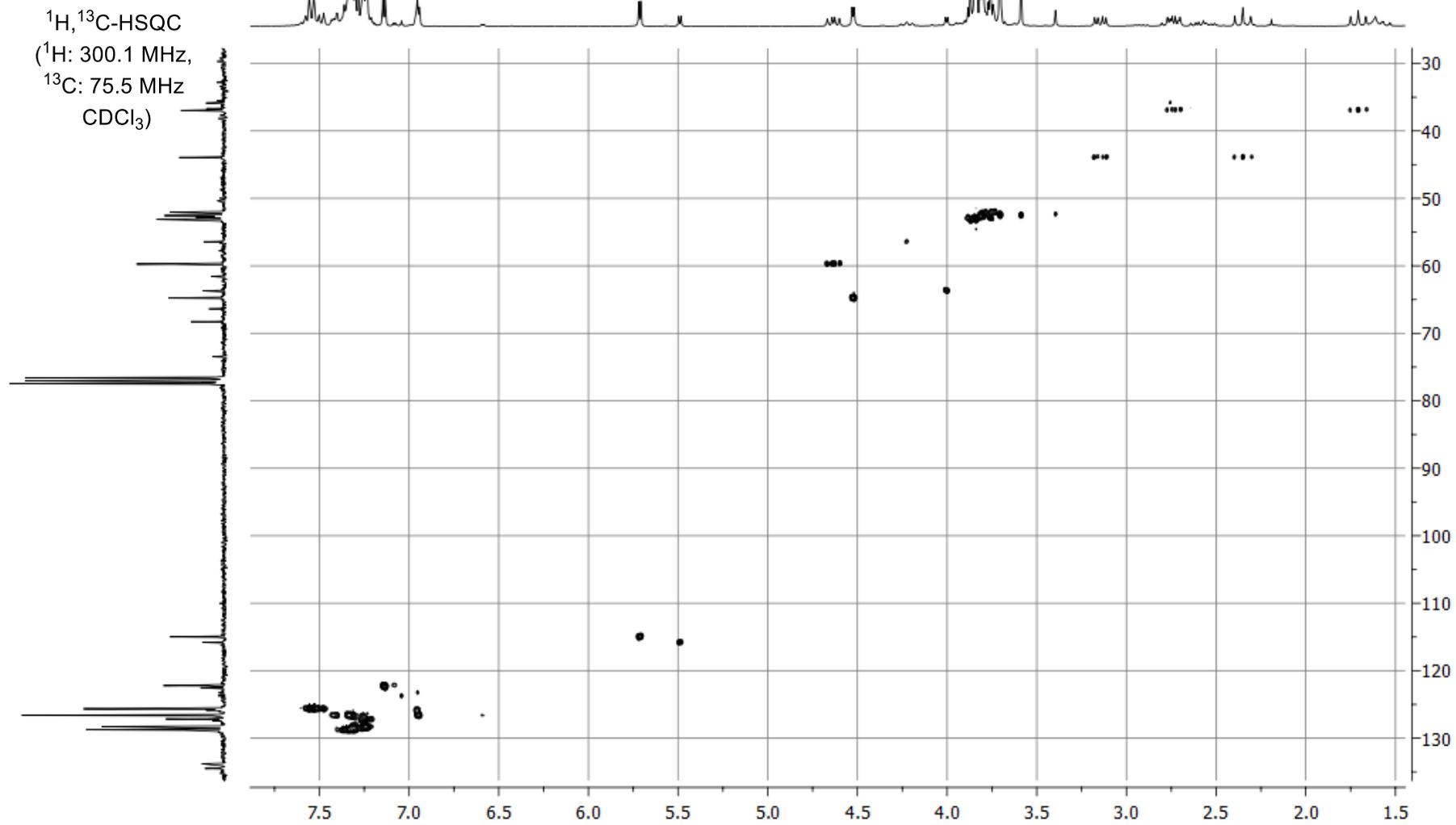


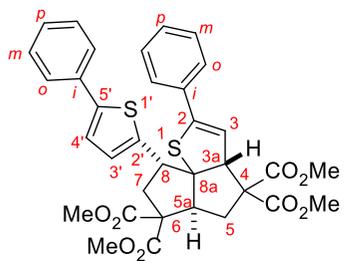
$^1\text{H}, ^1\text{H}$ -NOESY  
(300.1 MHz,  $\text{CDCl}_3$ )





$^1\text{H}, ^{13}\text{C}$ -HSQC  
 ( $^1\text{H}$ : 300.1 MHz,  
 $^{13}\text{C}$ : 75.5 MHz  
 $\text{CDCl}_3$ )





<sup>1</sup>H, <sup>13</sup>C-HMBC  
 (<sup>1</sup>H: 300.1 MHz,  
<sup>13</sup>C: 75.5 MHz  
 CDCl<sub>3</sub>)

