

# Supporting Information

for

## A new and convenient synthetic way to 2-substituted thieno[2,3-*b*]indoles

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### Analytical data and copies of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the new compounds

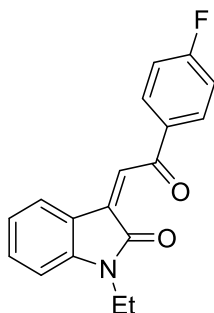
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### 3-(2-Oxo-2-(hetero)arylethylidene)indolin-2-ones 10

Compounds synthesized by method A:

#### 1-Ethyl-3-(2-(4-fluorophenyl)-2-oxoethylidene)indolin-2-one (10b).



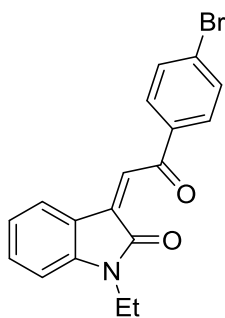
Red crystals; Yield 575 mg (65%); Mp 108 – 109 °C.

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.19 – 8.11 (m, 2H), 7.99 (d,  $J$  = 7.6 Hz, 1H), 7.76 (s, 1H), 7.45 – 7.37 (m, 3H), 7.11 (d,  $J$  = 7.8 Hz, 1H), 7.04 – 6.97 (m, 1H), 3.77 (q,  $J$  = 7.2 Hz, 2H), 1.18 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  189.9, 166.3, 165.5 (d,  $J_{\text{CF}}$  = 253.5 Hz), 144.8, 135.3, 133.6 (d,  $J_{\text{CF}}$  = 2.7 Hz), 132.8, 131.8 (d,  $J_{\text{CF}}$  = 9.8 Hz), 126.5, 126.4, 122.2, 119.3, 116.2 (d,  $J_{\text{CF}}$  = 22.1 Hz), 109.2, 34.3, 12.5.

IR(DRA): 479, 489, 549, 574, 590, 607, 671, 712, 750, 784, 816, 845, 863, 883, 891, 950, 989, 1006, 1029, 1066, 1085, 1110, 1129, 1159, 1170, 1221, 1287, 1307, 1354, 1392, 1410, 1465, 1480, 1505, 1599, 1619, 1656, 1706, 1779, 2977, 3075, 3110  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{18}\text{H}_{14}\text{FNO}_2$ : C, 73.21; H, 4.78; N, 4.74. Found: C, 73.19; H, 4.56; N, 4.76.

#### 3-(2-(4-Bromophenyl)-2-oxoethylidene)-1-ethylindolin-2-one (10c).



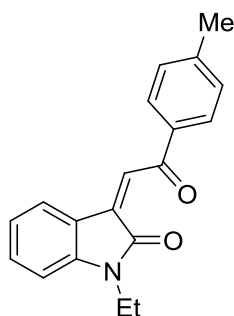
Red crystals; Yield 740 mg (69%); Mp 154 – 155 °C.

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.07 – 7.98 (m, 3H), 7.82 (d,  $J$  = 8.6 Hz, 2H), 7.76 (s, 1H), 7.44 (td,  $J$  = 7.8, 1.0 Hz, 1H), 7.13 (d,  $J$  = 7.8 Hz, 1H), 7.03 (td,  $J$  = 7.7, 0.6 Hz, 1H), 3.78 (q,  $J$  = 7.2 Hz, 2H), 1.19 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  190.4, 166.3, 144.9, 135.9, 135.6, 133.0, 132.2, 130.6, 128.3, 126.5, 126.2, 122.2, 119.3, 109.3, 34.3, 12.5.

IR(DRA): 462, 490, 504, 548, 575, 603, 626, 645, 669, 697, 750, 784, 795, 826, 844, 866, 898, 936, 948, 1001, 1015, 1031, 1067, 1085, 1104, 1152, 1224, 1286, 1349, 1363, 1384, 1400, 1449, 1463, 1518, 1595, 1657, 1708, 1921, 2875, 2937, 2977, 3094, 3123, 3406  $\text{cm}^{-1}$ .

Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>BrNO<sub>2</sub>: C, 60.69; H, 3.96; N, 3.93. Found: C, 60.47; H, 3.87; N, 3.89.

**1-Ethyl-3-(2-oxo-2-(*p*-tolyl)ethylidene)indolin-2-one (10d).**



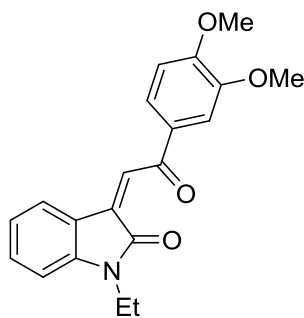
Red crystals; Yield 500 mg, (57%); Mp 99 – 100 °C.

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.99 – 7.96 (m, 3H), 7.77 (s, 1H), 7.44 – 7.39 (m, 3H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.01 (td, *J* = 7.7, 0.7 Hz, 1H), 3.78 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 190.9, 166.3, 144.9, 144.7, 134.9, 134.4, 132.6, 129.7, 128.7, 127.2, 126.3, 122.1, 119.4, 109.2, 34.3, 21.3, 12.5.

IR(DRA): 467, 492, 549, 573, 606, 675, 711, 745, 780, 835, 852, 880, 889, 941, 964, 993, 1010, 1024, 1071, 1085, 1111, 1131, 1153, 1177, 1211, 1232, 1299, 1350, 1388, 1408, 1448, 1479, 1603, 1619, 1652, 1709, 1777, 1795, 1828, 1946, 2607, 2738, 2874, 2938, 2981, 3042, 3113, 3402 cm<sup>-1</sup>.

Anal. Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>2</sub>: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.00; H, 5.89; N, 4.77.

**3-(2-(3,4-Dimethoxyphenyl)-2-oxoethylidene)-1-ethylindolin-2-one (10g).**



Orange powder; Yield 750 mg, (74%); Mp 143 – 144 °C.

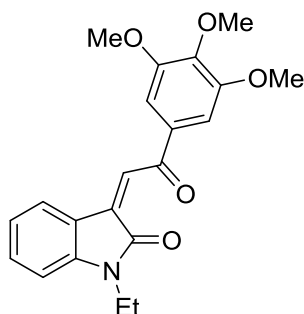
<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.78 (s, 1H), 7.74 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.41 (td, *J* = 7.9, 0.9 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.03 – 6.98 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.78 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 189.6, 166.4, 154.1, 149.1, 144.6, 134.5, 132.4, 129.8, 127.4, 126.3, 124.2, 122.1, 119.5, 111.1, 110.0, 109.1, 55.9, 55.5, 34.2, 12.5.

IR(DRA): 484, 551, 565, 583, 623, 673, 691, 751, 765, 784, 800, 844, 868, 920, 939, 959, 992, 1018, 1033, 1086, 1111, 1146, 1173, 1192, 1209, 1224, 1264, 1287, 1305, 1360, 1390, 1421,

1448, 1470, 1515, 1576, 1600, 1615, 1649, 1708, 1753, 1822, 2850, 2878, 2941, 2987, 3022, 3083  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{20}\text{H}_{19}\text{NO}_4$ : C, 71.20; H, 5.62; N, 4.15. Found: C, 71.20; H, 5.62; N, 4.08.

**1-Ethyl-3-(2-oxo-2-(3,4,5-trimethoxyphenyl)ethylidene)indolin-2-one (10h).**



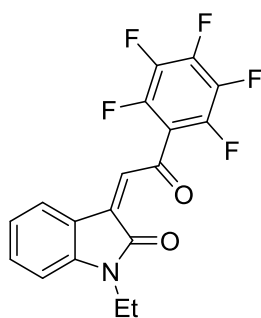
Red powder; Yield 1g (91%); Mp 122 – 123 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.01 (d,  $J = 7.6$  Hz, 1H), 7.81 (s, 1H), 7.45 – 7.39 (m, 1H), 7.36 (s, 2H), 7.11 (d,  $J = 7.9$  Hz, 1H), 7.04 – 6.98 (m, 1H), 3.88 (s, 6H), 3.81 – 3.74 (m, 5H), 1.19 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ )  $\delta$  190.1, 166.4, 153.0, 144.7, 142.8, 135.3, 132.7, 132.2, 127.1, 126.4, 122.1, 119.4, 109.2, 106.2, 60.2, 56.1, 34.3, 12.5.

IR(DRA): 473, 490, 548, 567, 584, 642, 675, 690, 746, 778, 846, 897, 932, 1002, 1058, 1080, 1128, 1164, 1187, 1224, 1285, 1324, 1348, 1391, 1414, 1464, 1485, 1502, 1584, 1608, 1629, 1653, 1709, 1780, 2648, 2837, 2939, 3021, 3402  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{21}\text{H}_{11}\text{NO}_5$ : C, 68.65; H, 5.76; N, 3.81. Found: C, 68.41; H, 5.73; N, 3.80.

**1-Ethyl-3-(2-oxo-2-(perfluorophenyl)ethylidene)indolin-2-one (10i).**



Dark-red powder; Yield 365 mg (33%); Mp 118 – 119 °C.

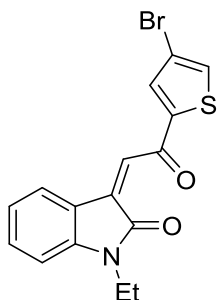
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.46 (d,  $J = 7.5$  Hz, 1H), 7.53 (td,  $J = 7.8, 1.0$  Hz, 1H), 7.35 (t,  $J = 2.3$  Hz, 1H), 7.15 (d,  $J = 7.9$  Hz, 1H), 7.13 – 7.07 (m, 1H), 3.77 (q,  $J = 7.2$  Hz, 2H), 1.19 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ )  $\delta$  182.9, 166.3, 145.9, 144.6 (dm\*,  $J_{\text{CF}} = 244.8$  Hz), 142.5 (dm\*,  $J_{\text{CF}} = 242.9$  Hz), 137.7, 137.2 (dm\*,  $J_{\text{CF}} = 248.2$  Hz), 134.6, 127.5, 126.0, 122.4, 119.1, 114.9 (t,  $J_{\text{CF}} = 16.4$  Hz), 109.4, 34.4, 12.4.

\*dm = doublet of multiplets.

IR(DRA): 480, 547, 569, 615, 641, 700, 723, 756, 767, 783, 801, 831, 862, 896, 920, 950, 988, 1034, 1049, 1087, 1106, 1161, 1227, 1290, 1314, 1349, 1363, 1388, 1409, 1468, 1498, 1519, 1596, 1618, 1650, 1674, 1712, 2882, 2939, 2979, 3037, 3127  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{18}\text{H}_{10}\text{F}_5\text{NO}_2$ : C, 58.86; H, 2.74; N, 3.81. Found: C, 58.85; H, 2.81; N, 3.90.

### 3-(2-(4-Bromothiophen-2-yl)-2-oxoethylidene)-1-ethylindolin-2-one (10j).



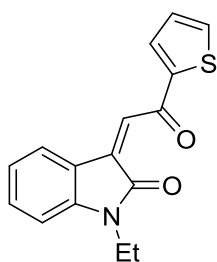
Red powder; Yield 825 mg (76%); Mp 160 – 161  $^{\circ}\text{C}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.35 (d,  $J = 7.7$  Hz, 1H), 8.27 (d,  $J = 1.0$  Hz, 1H), 8.24 (d,  $J = 1.0$  Hz, 1H), 7.70 (s, 1H), 7.52 – 7.42 (m, 1H), 7.12 (d,  $J = 7.9$  Hz, 1H), 7.09 – 7.01 (m, 1H), 3.78 (q,  $J = 7.1$  Hz, 2H), 1.19 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  181.9, 166.3, 145.4, 145.3, 136.8, 136.0, 134.1, 133.5, 127.6, 124.3, 122.2, 119.4, 110.6, 109.2, 34.3, 12.5.

IR(DRA): 472, 492, 549, 569, 595, 642, 707, 732, 753, 785, 815, 848, 875, 889, 948, 976, 1031, 1087, 1107, 1156, 1195, 1227, 1291, 1307, 1356, 1401, 1466, 1482, 1509, 1598, 1619, 1650, 1706, 1925, 2873, 2932, 2976, 3096  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{16}\text{H}_{12}\text{BrNO}_2\text{S}$ : C, 53.05; H, 3.34; N, 3.87. Found: C, 52.89; H, 3.29; N, 3.82.

### 1-Ethyl-3-(2-oxo-2-(thiophen-2-yl)ethylidene)indolin-2-one (10k).

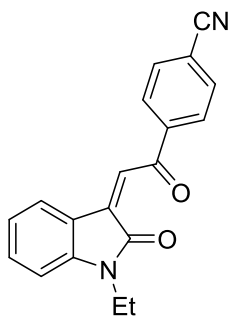


Red crystals; Yield 645 mg (76%); Mp 147 – 148  $^{\circ}\text{C}$ .

Indolin-2-one **10k** was previously described in the literature and its analytical data are identical to the reported data [1].

**Compounds synthesized by method B:**

**3-(2-(4-Cyanophenyl)-2-oxoethylidene)-1-ethylindolin-2-one (10e).**



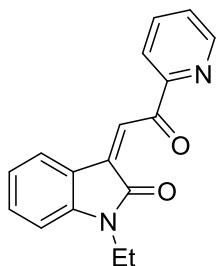
Dark-red crystals; Yield 680 mg (75%); Mp 176 – 177 °C.

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.21 (d,  $J = 8.5$  Hz, 2H), 8.12 (d,  $J = 7.5$  Hz, 1H), 8.06 (d,  $J = 8.5$  Hz, 2H), 7.77 (s, 1H), 7.45 (td,  $J = 7.8, 1.1$  Hz, 1H), 7.13 (d,  $J = 7.9$  Hz, 1H), 7.03 (td,  $J = 7.7, 0.8$  Hz, 1H), 3.78 (q,  $J = 7.2$  Hz, 2H), 1.18 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  190.3, 166.3, 145.2, 140.2, 136.4, 133.4, 133.1, 129.2, 126.8, 125.5, 122.3, 119.3, 118.1, 115.7, 109.3, 34.3, 12.5.

IR(DRA): 487,553, 565, 604, 643, 674, 718, 755, 783, 847, 887, 941, 991, 1022, 1070, 1087, 1111, 1134, 1159, 1177, 1226, 1291, 1358, 1390, 1406, 1467, 1605, 1619, 1656, 1705, 1929, 2229, 2877, 2938, 2978, 3097, 3116, 3402  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_2$ : C, 75.48; H, 4.67; N, 9.27. Found: C, 75.36; H, 4.48; N, 9.16.

**1-Ethyl-3-(2-oxo-2-(pyridin-2-yl)ethylidene)indolin-2-one (10l).**



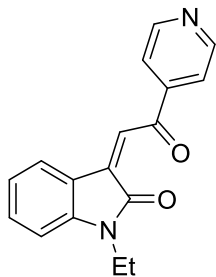
Red crystals; Yield 550 mg (66%); Mp 142 – 143 °C.

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.83 (ddd,  $J = 4.7, 1.5, 0.9$  Hz, 1H), 8.54 (d,  $J = 7.2$  Hz, 1H), 8.45 (s, 1H), 8.18 (dd,  $J = 6.9, 0.9$  Hz, 1H), 8.11 (td,  $J = 7.7, 1.7$  Hz, 1H), 7.75 (ddd,  $J = 7.5, 4.7, 1.2$  Hz, 1H), 7.48 (td,  $J = 7.7, 1.1$  Hz, 1H), 7.14 (d,  $J = 7.8$  Hz, 1H), 7.10 (td,  $J = 7.7, 0.9$  Hz, 1H), 3.79 (q,  $J = 7.2$  Hz, 2H), 1.20 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  190.1, 166.7, 153.4, 149.3, 145.4, 137.9, 136.7, 133.4, 128.1, 127.6, 124.7, 122.5, 122.2, 119.7, 109.1, 34.3, 12.5.

IR(DRA): 491, 547, 573, 603, 616, 640, 697, 745, 784, 807, 819, 859, 885, 911, 940, 996, 1016, 1083, 1104, 1132, 1156, 1227, 1294, 1351, 1387, 1433, 1481, 1580, 1597, 1619, 1669, 1705, 1919, 2934, 2973, 3049, 3116  $\text{cm}^{-1}$ .

Anal. Calcd. for  $C_{17}H_{14}N_2O_2$ : C, 73.37; H, 5.07; N, 10.07. Found: C, 73.13; H, 5.03; N, 10.08.

**1-Ethyl-3-(2-oxo-2-(pyridin-4-yl)ethylidene)indolin-2-one (10m).**



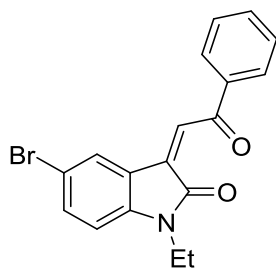
Dark-red crystals; Yield 560 mg (67%); Mp 144 – 145 °C.

$^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.88 (dd,  $J = 4.4, 1.6$  Hz, 2H), 8.23 (d,  $J = 7.7$  Hz, 1H), 7.94 (dd,  $J = 4.4, 1.6$  Hz, 2H), 7.75 (s, 1H), 7.53 – 7.44 (m, 1H), 7.14 (d,  $J = 7.9$  Hz, 1H), 7.10 – 7.03 (m, 1H), 3.79 (q,  $J = 7.2$  Hz, 2H), 1.19 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  190.7, 166.3, 151.0, 145.3, 143.0, 136.9, 133.6, 127.0, 124.7, 122.3, 121.4, 119.3, 109.3, 34.3, 12.5.

IR(DRA): 469, 490, 548, 574, 602, 630, 664, 692, 728, 746, 783, 835, 869, 887, 947, 993, 1027, 1072, 1110, 1135, 1160, 1230, 1293, 1354, 1406, 1469, 1482, 1554, 1598, 1620, 1665, 1709, 1949, 2979, 3046  $cm^{-1}$ .

Anal. Calcd. for  $C_{17}H_{14}N_2O_2$ : C, 73.37; H, 5.07; N, 10.07. Found: C, 73.15; H, 5.03; N, 10.10.

**5-Bromo-1-ethyl-3-(2-oxo-2-phenylethylidene)indolin-2-one (10n).**



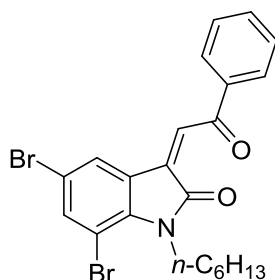
Red crystals; Yield 560 mg (52%); Mp 118 – 119 °C.

$^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.25 (d,  $J = 1.9$  Hz, 1H), 8.09 (d,  $J = 7.3$  Hz, 2H), 7.86 (s, 1H), 7.76 – 7.73 (m, 1H), 7.67 – 7.59 (m, 3H), 7.12 (d,  $J = 8.4$  Hz, 1H), 3.78 (q,  $J = 7.2$  Hz, 2H), 1.18 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  190.9, 166.0, 144.1, 136.8, 135.0, 134.6, 134.3, 129.1, 128.9, 128.7, 127.8, 121.3, 113.8, 111.2, 34.5, 12.4.

IR(DRA): 472, 533, 587, 612, 683, 726, 788, 811, 893, 907, 938, 1007, 1073, 1089, 1114, 1140, 1185, 1230, 1272, 1290, 1342, 1365, 1446, 1458, 1468, 1578, 1598, 1615, 1666, 1706, 1809, 1840, 1864, 1896, 1958, 1977, 2350, 2728, 2875, 2946, 2970, 3039, 3066, 3115, 3392  $cm^{-1}$ .

Anal. Calcd. for  $C_{18}H_{14}BrNO_2$ : C, 60.69; H, 3.96; N, 3.93. Found: C, 60.49; H, 3.78; N, 3.92.

**5,7-Dibromo-1-hexyl-3-(2-oxo-2-phenylethylidene)indolin-2-one (10o).**



Orange powder; Yield 780 mg (64%); Mp 100 – 101 °C.

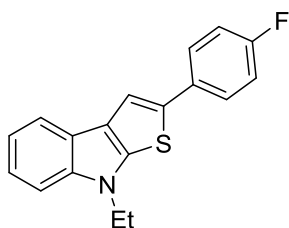
$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.14 (d,  $J = 1.9$  Hz, 1H), 8.08 (dd,  $J = 8.3, 1.1$  Hz, 2H), 7.93 (s, 1H), 7.85 (d,  $J = 1.9$  Hz, 1H), 7.78 – 7.72 (m, 1H), 7.66 – 7.59 (m, 1H), 4.09 – 4.02 (m, 1H), 1.71 – 1.57 (m, 2H), 1.41 – 1.24 (m, 6H), 0.86 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  191.3, 167.0, 141.4, 138.8, 136.5, 134.5, 132.4, 130.2, 129.2, 128.8, 127.7, 124.2, 114.1, 102.8, 41.1, 30.8, 29.1, 25.5, 21.9, 13.8.

IR(DRA): 455, 500, 553, 567, 584, 617, 627, 660, 689, 699, 735, 753, 789, 829, 893, 960, 976, 999, 1039, 1053, 1066, 1091, 1149, 1192, 1218, 1248, 1281, 1302, 1342, 1365, 1403, 1421, 1440, 1467, 1495, 1523, 1572, 1595, 1658, 1744, 1797, 1874, 1933, 1952, 2852, 2928, 2953, 3021, 3076  $\text{cm}^{-1}$ ;

Anal. Calcd. for  $\text{C}_{22}\text{H}_{21}\text{Br}_2\text{NO}_2$ : C, 53.79; H, 4.31; N, 2.85. Found: C, 53.61; H, 4.10; N, 2.81.

**Thieno[2,3-*b*]indoles 12**

**8-Ethyl-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole (12b).**



White needles; Yield 590 mg (90%); Mp 110 – 111 °C.

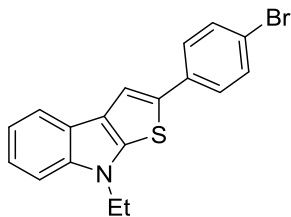
$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.88 (s, 1H), 7.82 (d,  $J = 7.7$  Hz, 1H), 7.74 – 7.65 (m, 2H), 7.59 (d,  $J = 8.3$  Hz, 1H), 7.30 – 7.23 (m, 3H), 7.20 – 7.13 (m, 1H), 4.33 (q,  $J = 7.2$  Hz, 2H), 1.40 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  161.1 (d,  $J_{\text{CF}} = 244.1$  Hz), 141.5, 140.7, 133.7, 131.6 (d,  $J_{\text{CF}} = 3.1$  Hz), 126.4 (d,  $J_{\text{CF}} = 8.0$  Hz), 123.4, 122.0, 121.5, 119.4, 119.1, 116.0 (d,  $J_{\text{CF}} = 21.8$  Hz), 114.9, 109.9, 40.3, 13.6.

IR(DRA): 457, 498, 531, 549, 624, 667, 684, 745, 776, 802, 823, 837, 854, 927, 939, 1010, 1054, 1080, 1097, 1132, 1162, 1225, 1252, 1282, 1298, 1334, 1379, 1395, 1417, 1453, 1480, 1529, 1592, 1612, 1672, 1773, 1879, 1924, 2877, 2941, 2987, 3038, 3071  $\text{cm}^{-1}$ .

MS (+APCI): Calcd. for  $\text{C}_{18}\text{H}_{14}\text{FNS}$   $m/z$  296.0904 (M+H), found  $m/z$  296.0902 (M+H).



**2-(4-Bromophenyl)-8-ethyl-8H-thieno[2,3-b]indole (12c).**



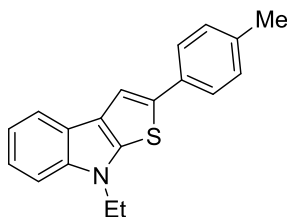
Pale yellow needles; Yield 670 mg (94%); Mp 142 – 143 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.99 (s, 1H), 7.82 (d,  $J = 7.6$  Hz, 1H), 7.68 – 7.56 (m, 5H), 7.28 (ddd,  $J = 8.3, 7.2, 1.2$  Hz, 1H), 7.17 (td,  $J = 7.6, 0.9$  Hz, 1H), 4.35 (q,  $J = 7.2$  Hz, 2H), 1.41 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  141.8, 140.8, 134.3, 133.3, 131.9, 126.3, 123.5, 122.2, 121.5, 119.5, 119.2, 119.2, 115.6, 110.0, 40.4, 13.6.

IR(DRA): 478, 548, 582, 663, 683, 702, 744, 777, 814, 850, 926, 941, 1002, 1015, 1055, 1070, 1098, 1112, 1131, 1162, 1183, 1203, 1251, 1278, 1334, 1378, 1393, 1414, 1455, 1473, 1523, 1557, 1573, 1647, 1770, 1886, 1924, 2875, 2937, 2984, 3021, 3055  $\text{cm}^{-1}$ .

MS (+APCI): Calcd. for  $\text{C}_{18}\text{H}_{14}\text{BrNS}$   $m/z$  356.0103 (M+H), found  $m/z$  356.0100 (M+H).

**8-Ethyl-2-(*p*-tolyl)-8H-thieno[2,3-b]indole (12d).**



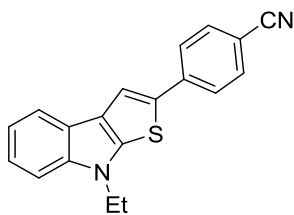
White needles; Yield 560 mg (79%); Mp 102 – 103 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.85 (s, 1H), 7.81 (d,  $J = 7.7$  Hz, 1H), 7.59 (d,  $J = 8.3$  Hz, 1H), 7.56 (d,  $J = 8.0$  Hz, 2H), 7.28 – 7.24 (m, 1H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.19 – 7.12 (m, 1H), 4.33 (q,  $J = 7.2$  Hz, 2H), 2.31 (s, 3H), 1.40 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  141.2, 140.7, 136.0, 135.1, 132.3, 129.7, 124.4, 123.4, 121.9, 121.5, 119.3, 119.1, 114.1, 109.9, 40.3, 20.7, 13.6.

IR(DRA): 484, 533, 552, 611, 627, 683, 739, 750, 779, 810, 833, 853, 922, 943, 1014, 1031, 1055, 1086, 1120, 1132, 1162, 1184, 1204, 1253, 1282, 1335, 1380, 1396, 1419, 1440, 1466, 1481, 1507, 1531, 1565, 1596, 1644, 1762, 1797, 1841, 1874, 1893, 1910, 2731, 2876, 2937, 2981, 3018  $\text{cm}^{-1}$ .

MS (+APCI): Calcd. for  $\text{C}_{19}\text{H}_{17}\text{NS}$   $m/z$  292.1154 (M+H), found  $m/z$  292.1153 (M+H).

**2-(4-Cyanophenyl)-8-ethyl-8H-thieno[2,3-b]indole (12e).**



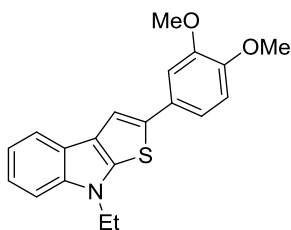
Yellow needles; Yield 555 mg (92%); Mp 150 – 151 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.19 (s, 1H), 7.86 – 7.79 (m, 5H), 7.62 (d,  $J = 8.3$  Hz, 1H), 7.34 – 7.27 (m, 1H), 7.23 – 7.17 (m, 1H), 4.36 (q,  $J = 7.2$  Hz, 2H), 1.41 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  143.2, 141.1, 139.6, 133.0, 132.5, 124.5, 123.9, 122.6, 121.5, 119.8, 119.3, 119.0, 117.8, 110.1, 108.0, 40.4, 13.5.

IR(DRA): 501, 528, 556, 640, 668, 687, 749, 777, 813, 830, 851, 942, 961, 1017, 1053, 1084, 1109, 1131, 1178, 1203, 1254, 1278, 1330, 1353, 1401, 1418, 1453, 1469, 1504, 1525, 1553, 1573, 1600, 1657, 1883, 2168, 2220, 2417, 2574, 2730, 2879, 2942, 2981, 3057, 3077, 3197, 3396, 3819  $\text{cm}^{-1}$ .

MS (+ESI): Calcd. for  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{S}$   $m/z$  627,1648 (2M+Na), found  $m/z$  627.1653 (2M+Na).

**2-(3,4-Dimethoxyphenyl)-8-ethyl-8H-thieno[2,3-b]indole (12g).**



White powder; Yield 375 mg (56%); Mp 108 – 109 °C.

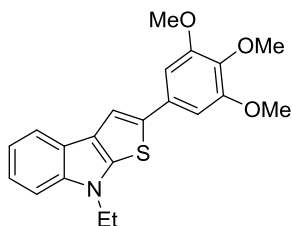
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.83 (s, 1H), 7.80 (d,  $J = 7.8$  Hz, 1H), 7.58 (d,  $J = 8.3$  Hz, 1H), 7.35 – 7.22 (m, 2H), 7.20 – 7.11 (m, 2H), 6.97 (d,  $J = 8.3$  Hz, 1H), 4.33 (q,  $J = 7.2$  Hz, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 1.41 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR\* (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  149.2, 148.0, 141.0, 140.6, 135.3, 128.0, 123.3, 121.8, 121.5, 119.3, 119.0, 116.9, 113.7, 112.3, 109.9, 108.6, 55.6, 40.3, 13.6.

\*The signals from non-equivalent carbon atoms of MeO-groups have substantially identical chemical shift and appear as a single peak at 55.6 ppm.

IR(DRA): 497, 521, 552, 568, 624, 637, 668, 687, 737, 763, 777, 797, 806, 822, 848, 883, 919, 950, 1001, 1023, 1054, 1082, 1146, 1165, 1187, 1203, 1258, 1288, 1336, 1383, 1396, 1416, 1445, 1483, 1508, 1532, 1583, 1604, 1641, 1752, 1826, 1875, 1915, 2019, 2580, 2834, 2932, 2978, 3002, 3050, 3081  $\text{cm}^{-1}$ .

MS (+APCI): Calcd. for  $\text{C}_{20}\text{H}_{19}\text{NO}_2\text{S}$   $m/z$  338.1209 (M+H), found  $m/z$  338.1211 (M+H).

**8-Ethyl-2-(3,4,5-trimethoxyphenyl)-8H-thieno[2,3-b]indole (12h).**



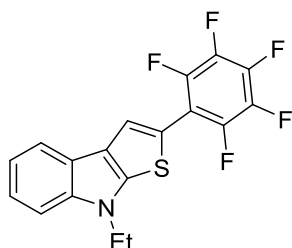
White powder; Yield 515 mg (70%); Mp 104 – 105 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.93 (s, 1H), 7.81 (d,  $J = 7.7$  Hz, 1H), 7.60 (d,  $J = 8.2$  Hz, 1H), 7.30 – 7.23 (m, 1H), 7.20 – 7.13 (m, 1H), 6.95 (s, 2H), 4.35 (q,  $J = 7.2$  Hz, 2H), 3.88 (s, 6H), 3.69 (s, 3H), 1.42 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  153.3, 141.4, 140.7, 136.6, 135.0, 130.8, 123.3, 121.9, 121.5, 119.4, 119.0, 114.8, 109.9, 102.1, 60.1, 56.0, 40.3, 13.6.

IR(DRA): 502, 531, 579, 629, 648, 665, 697, 733, 752, 777, 802, 813, 919, 1002, 1013, 1025, 1053, 1081, 1128, 1205, 1162, 1245, 1318, 1275, 1337, 1378, 1423, 1464, 1484, 1507, 1529, 1579, 1996, 2833, 2940, 2973, 3056  $\text{cm}^{-1}$ ;

MS (+APCI): Calcd. for  $\text{C}_{21}\text{H}_{21}\text{NO}_3\text{S}$   $m/z$  368.1315 (M+H), found  $m/z$  368.1317 (M+H).

**8-Ethyl-2-(perfluorophenyl)-8H-thieno[2,3-b]indole (12i).**



White needles; Yield 565 mg (77%); Mp 176 – 177 °C.

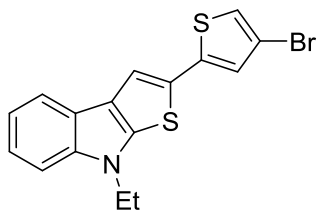
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.02 (s, 1H), 7.94 (d,  $J = 7.7$  Hz, 1H), 7.65 (d,  $J = 8.3$  Hz, 1H), 7.35 – 7.30 (m, 1H), 7.24 – 7.17 (m, 1H), 4.40 (q,  $J = 7.2$  Hz, 2H), 1.42 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  144.1, 143.2 (dm\*,  $J_{\text{CF}} = 247.3$  Hz), 141.1, 138.4 (dm\*,  $J_{\text{CF}} = 250.6$  Hz), 137.4 (dm\*,  $J_{\text{CF}} = 250.5$  Hz), 122.7, 122.4, 122.1 – 121.8 (m), 121.1, 119.5, 119.2, 115.5, 110.6 – 110.2 (m), 109.7, 40.3, 13.1.

\*dm = doublet of multiplets.

IR(DRA): 509, 550, 564, 636, 679, 745, 780, 796, 840, 880, 926, 980, 1015, 1032, 1058, 1087, 1128, 1142, 1166, 1213, 1255, 1280, 1330, 1355, 1380, 1402, 1429, 1478, 1497, 1525, 1610, 1680, 1886, 1924, 2946, 2989, 3055, 3120  $\text{cm}^{-1}$ .

MS (+APCI): Calcd. for  $\text{C}_{18}\text{H}_{10}\text{F}_5\text{NS}$   $m/z$  367.0449 (M), found  $m/z$  367.0449 (M).

**2-(4-Bromothiophen-2-yl)-8-ethyl-8H-thieno[2,3-*b*]indole (12j).**



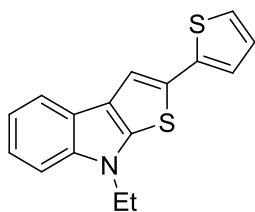
Yellow powder; Yield 545 mg (75%); Mp 114 – 115 °C.

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.83 (d,  $J = 7.7$  Hz, 1H), 7.79 (s, 1H), 7.61 (d,  $J = 8.3$  Hz, 1H), 7.57 (d,  $J = 1.4$  Hz, 1H), 7.33 – 7.25 (m, 2H), 7.21 – 7.13 (m, 1H), 4.35 (q,  $J = 7.2$  Hz, 2H), 1.40 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  141.6, 140.9, 139.7, 126.3, 124.1, 123.1, 122.3, 121.3, 121.2, 119.6, 119.3, 116.2, 110.0, 109.5, 40.4, 13.5.

IR(DRA): 486, 542, 561, 586, 650, 675, 695, 725, 750, 777, 786, 807, 822, 833, 847, 863, 908, 926, 946, 1017, 1050, 1081, 1130, 1138, 1161, 1172, 1192, 1217, 1253, 1278, 1334, 1357, 1380, 1398, 1429, 1442, 1464, 1475, 1503, 1547, 1570, 1599, 1662, 1774, 1811, 1855, 1891, 1929, 2867, 2930, 2974, 3047, 3069, 3114  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{16}\text{H}_{12}\text{BrNS}_2$ : C, 53.04; H, 3.34; N, 3.87. Found: C, 52.93; H, 3.21; N, 3.70.

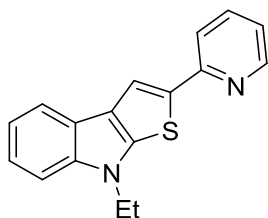
**8-Ethyl-2-(thiophen-2-yl)-8H-thieno[2,3-*b*]indole (12k).**



Cream powder; Yield 420 mg (74%); Mp 85 – 86 °C.

Analytical data of thieno[2,3-*b*]indole **12k** are identical to the reported data [2].

**8-Ethyl-2-(pyridin-2-yl)-8H-thieno[2,3-*b*]indole (12l).**



Pale yellow powder; Yield 340 mg (61%); Mp 83 – 84 °C.

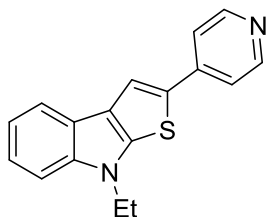
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.47 (d,  $J = 4.2$  Hz, 1H), 8.22 (s, 1H), 7.94 (d,  $J = 8.1$  Hz, 1H), 7.85 – 7.77 (m, 2H), 7.61 (d,  $J = 8.2$  Hz, 1H), 7.31 – 7.25 (m, 1H), 7.22 – 7.14 (m, 2H), 4.37 (q,  $J = 7.2$  Hz, 2H), 1.43 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  153.0,

149.0, 144.2, 141.0, 136.8, 136.5, 123.5, 122.2, 121.7, 121.2, 119.6, 119.1, 117.6, 116.7, 110.0, 40.3, 13.5.

IR(DRA): 475, 550, 573, 602, 619, 670, 705, 740, 775, 809, 842, 853, 876, 890, 945, 959, 991, 1016, 1050, 1087, 1131, 1154, 1207, 1251, 1281, 1292, 1331, 1383, 1412, 1430, 1455, 1479, 1494, 1527, 1583, 1609, 1675, 1764, 1849, 1884, 1920, 1970, 2875, 2933, 2971, 3048  $\text{cm}^{-1}$ .

MS (+ESI): Calcd. for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{S}$   $m/z$  279.0950 (M+H), found  $m/z$  279.0949 (M+H).

### 8-Ethyl-2-(pyridin-4-yl)-8H-thieno[2,3-b]indole (12m).



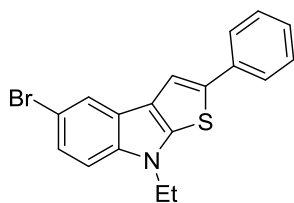
Pale yellow powder; Yield 335 mg (60%); Mp 140 – 141 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.53 (dd,  $J = 4.7, 1.5$  Hz, 2H), 8.29 (s, 1H), 7.86 (d,  $J = 7.7$  Hz, 1H), 7.68 – 7.54 (m, 3H), 7.36 – 7.26 (m, 1H), 7.25 – 7.16 (m, 1H), 4.39 (q,  $J = 7.2$  Hz, 2H), 1.43 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  150.2, 143.1, 142.0, 141.2, 131.4, 123.7, 122.6, 121.4, 119.8, 119.3, 118.3, 118.1, 110.2, 40.5, 13.5.

IR(DRA): 479, 550, 563, 661, 682, 694, 729, 774, 809, 844, 854, 867, 924, 941, 967, 991, 1018, 1052, 1077, 1133, 1163, 1219, 1254, 1280, 1325, 1348, 1378, 1406, 1454, 1466, 1481, 1496, 1521, 1538, 1573, 1593, 1668, 1930, 2934, 2980, 3054  $\text{cm}^{-1}$ .

MS (+ESI): Calcd. for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{S}$   $m/z$  279.0950 (M+H), found  $m/z$  279.0953 (M+H).

### 5-Bromo-8-ethyl-2-phenyl-8H-thieno[2,3-b]indole (12n).



White needles; Yield 600 mg (84%); Mp 140 – 141 °C.

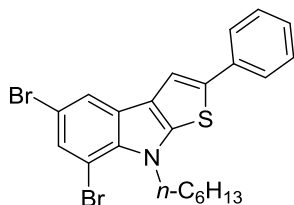
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.05 (d,  $J = 2.0$  Hz, 1H), 7.92 (s, 1H), 7.69 – 7.62 (m, 2H), 7.60 (d,  $J = 8.7$  Hz, 1H), 7.47 – 7.41 (m, 2H), 7.38 (dd,  $J = 8.7, 2.0$  Hz, 1H), 7.32 – 7.25 (m, 1H), 4.35 (q,  $J = 7.2$  Hz, 2H), 1.40 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  142.7, 139.5, 135.5, 134.8, 129.2, 126.9, 124.6, 124.3, 123.0, 122.7, 121.5, 114.7, 112.0, 111.8, 40.6, 13.6.

IR(DRA): 473, 555, 578, 584, 621, 692, 740, 754, 779, 798, 827, 836, 860, 872, 904, 937, 962, 978, 1042, 1059, 1082, 1101, 1138, 1159, 1187, 1205, 1247, 1260, 1313, 1332, 1345, 1378,

1400, 1438, 1455, 1478, 1496, 1524, 1561, 1574, 1593, 1659, 1716, 1805, 1851, 1936, 1955, 2874, 2932, 2977, 3023, 3074  $\text{cm}^{-1}$ .

MS (+APCI): Calcd. for  $\text{C}_{18}\text{H}_{14}\text{BrNS}$   $m/z$  355.0025 (M), found  $m/z$  355.0022 (M).

### 5,7-Dibromo-8-hexyl-2-phenyl-8H-thieno[2,3-b]indole (12o).



White needles; Yield 775 mg (79%); Mp 104 – 105 °C.

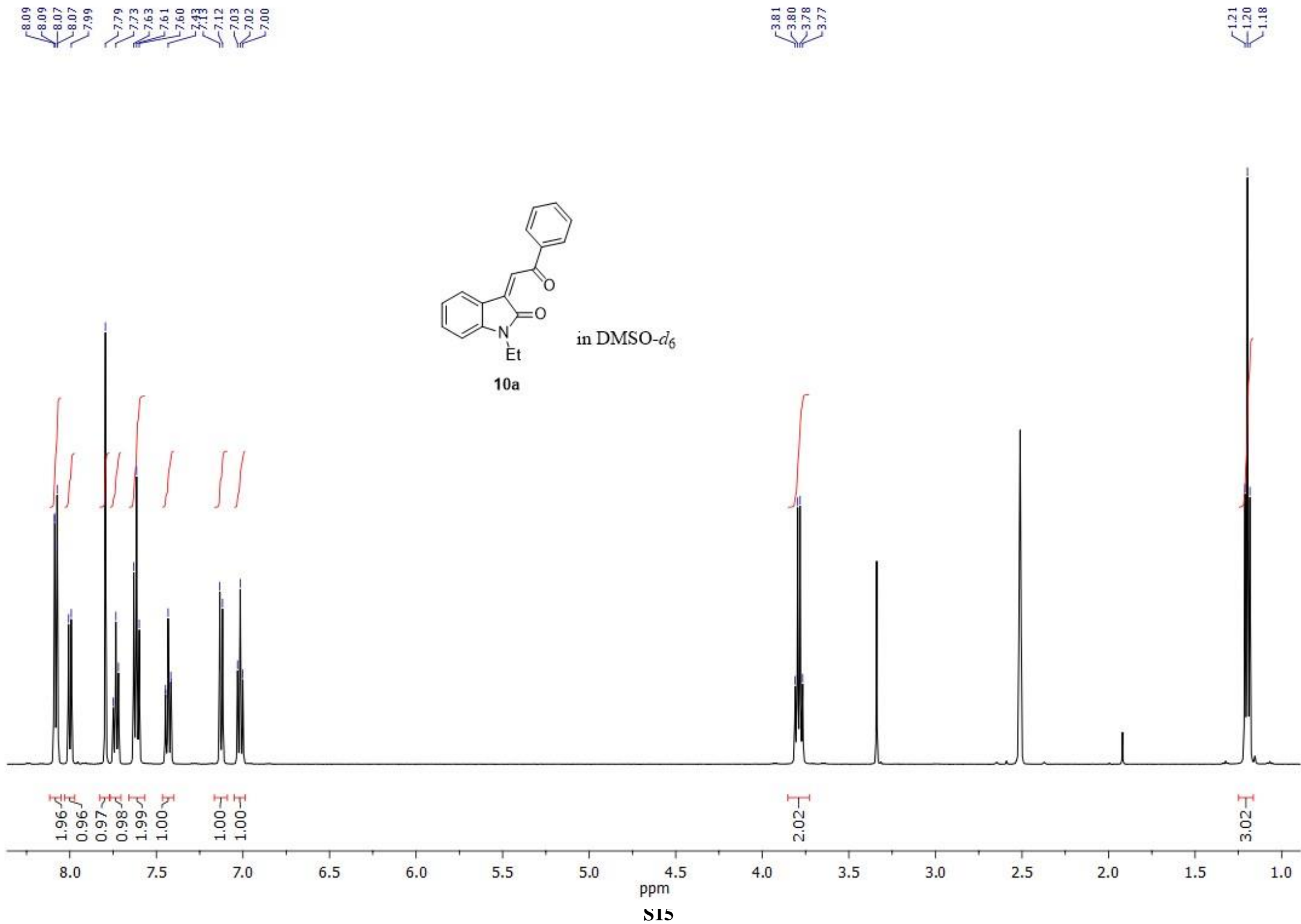
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.11 (d,  $J = 1.8$  Hz, 1H), 7.93 (s, 1H), 7.66 (d,  $J = 7.3$  Hz, 2H), 7.61 (d,  $J = 1.8$  Hz, 1H), 7.50 – 7.41 (m, 2H), 7.35 – 7.28 (m, 1H), 4.60 (t,  $J = 7.4$  Hz, 2H), 1.90 – 1.79 (m, 2H), 1.36 – 1.23 (m, 6H), 0.83 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ )  $\delta$  145.9, 136.5, 135.6, 134.4, 129.3, 128.4, 127.3, 125.9, 124.7, 122.2, 121.4, 114.5, 111.9, 103.6, 48.2, 30.7, 30.1, 25.6, 21.9, 13.8.

IR(DRA): 455, 465, 500, 553, 567, 584, 617, 627, 660, 677, 689, 699, 735, 753, 789, 829, 875, 893, 960, 976, 999, 1039, 1053, 1066, 1091, 1122, 1149, 1192, 1218, 1248, 1281, 1302, 1331, 1342, 1365, 1403, 1421, 1440, 1467, 1485, 1495, 1523, 1544, 1572, 1595, 1658, 1744, 1797, 1874, 1933, 1952, 2852, 2928, 2953, 3021, 3076  $\text{cm}^{-1}$ .

MS (+ESI): Calcd. for  $\text{C}_{22}\text{H}_{21}\text{Br}_2\text{NS}$   $m/z$  489.9834 (M+H), found  $m/z$  489.9838 (M+H).

## References

1. Metwally, S. A.; Younes, M. I.; Abbas, H. H. *Acta Chim. Hungarica* **1989**, *126*, 591–598.
2. Irgashev, R. A.; Karmatsky, A. A.; Kozyukhin, S. A.; Ivanov, V. K.; Sadovnikov, A.; Kozik, V. V.; Grinberg, V. A.; Emets, V. V.; Rusinov, G. L.; Charushin, V. N. *Synth. Met.* **2015**, *199*, 152–158.



—191.3

—166.3

—144.8

—136.8

—135.2

—134.1

—132.8

—129.1

—128.6

—126.8

—126.4

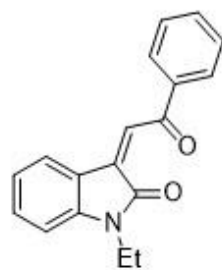
—122.1

—119.4

—109.2

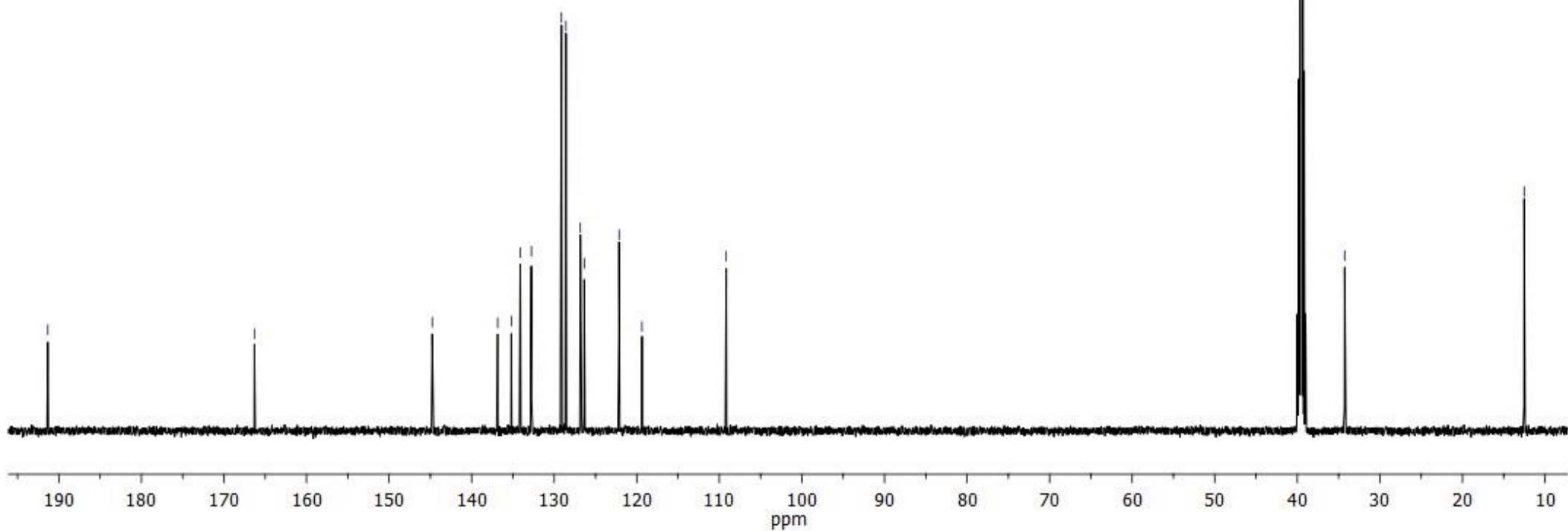
—34.3

—12.5



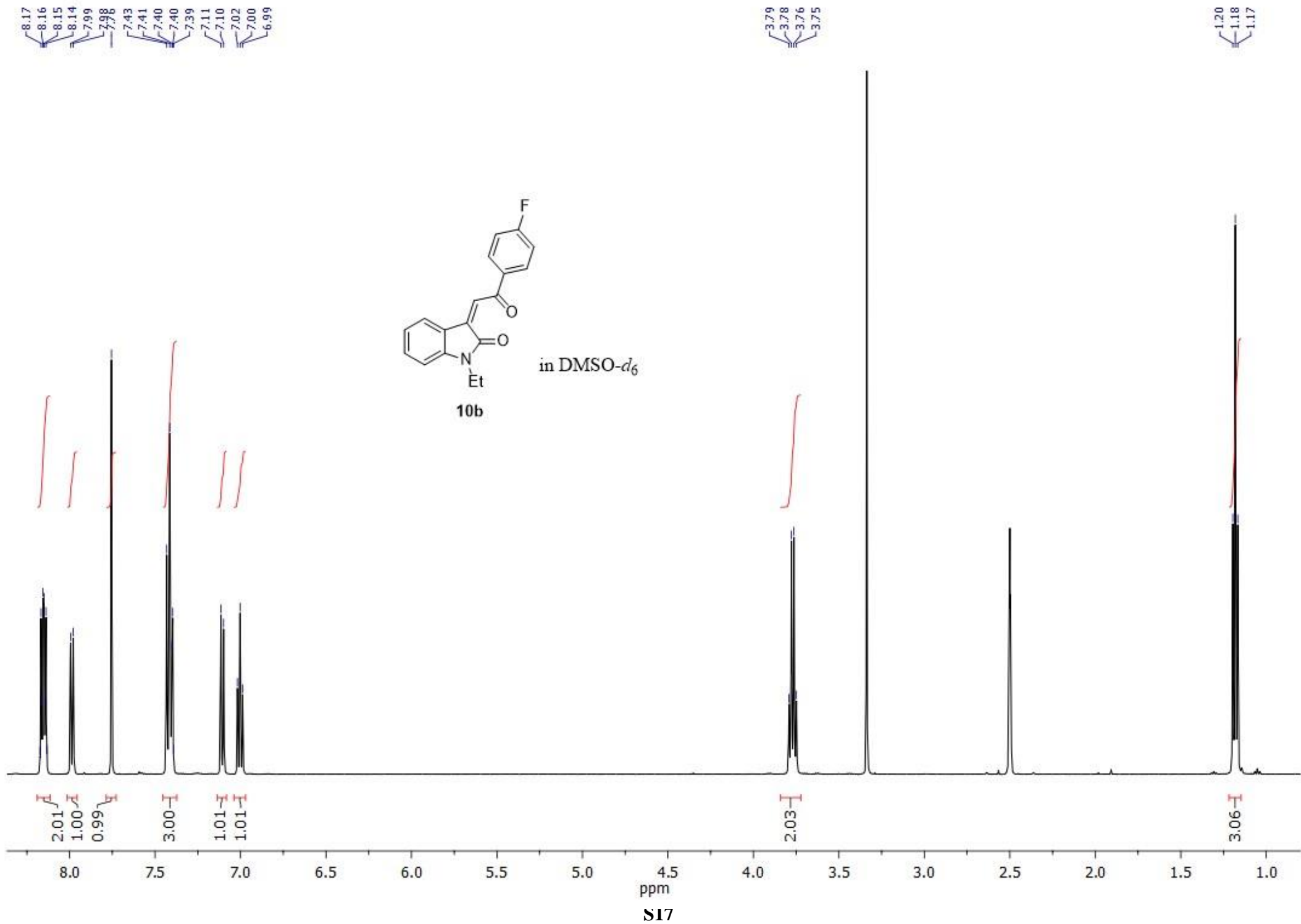
in DMSO-*d*<sub>6</sub>

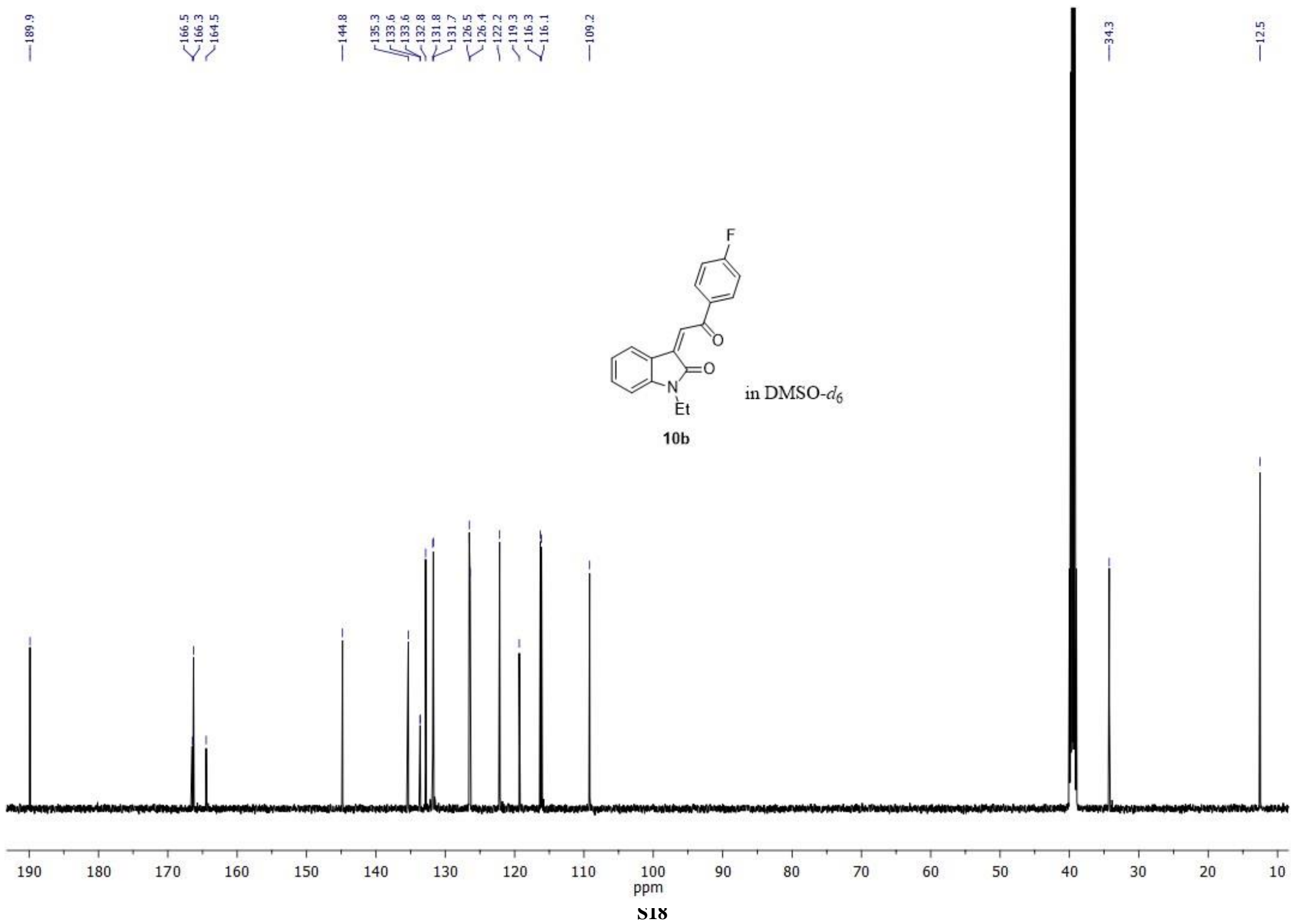
**10a**

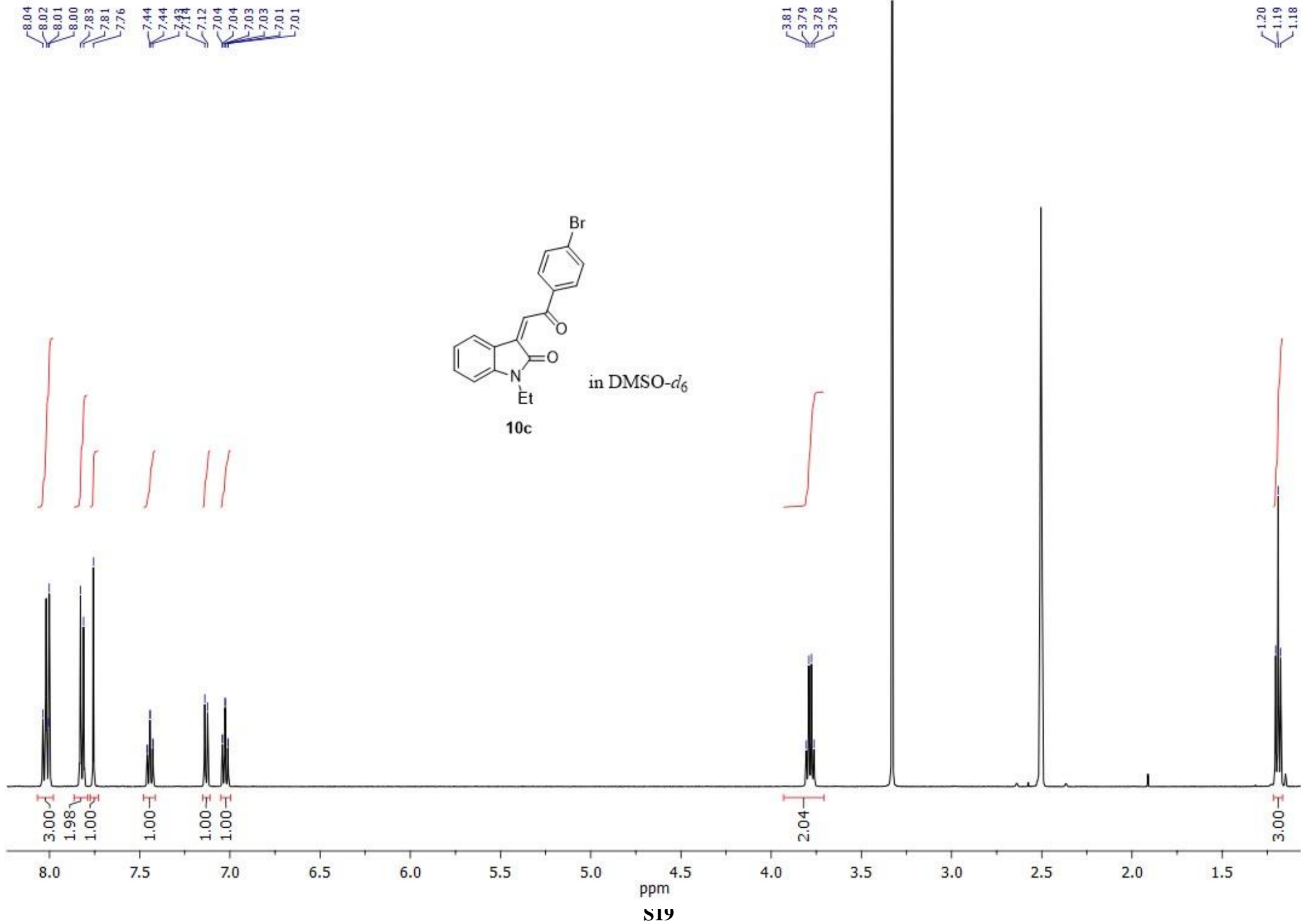


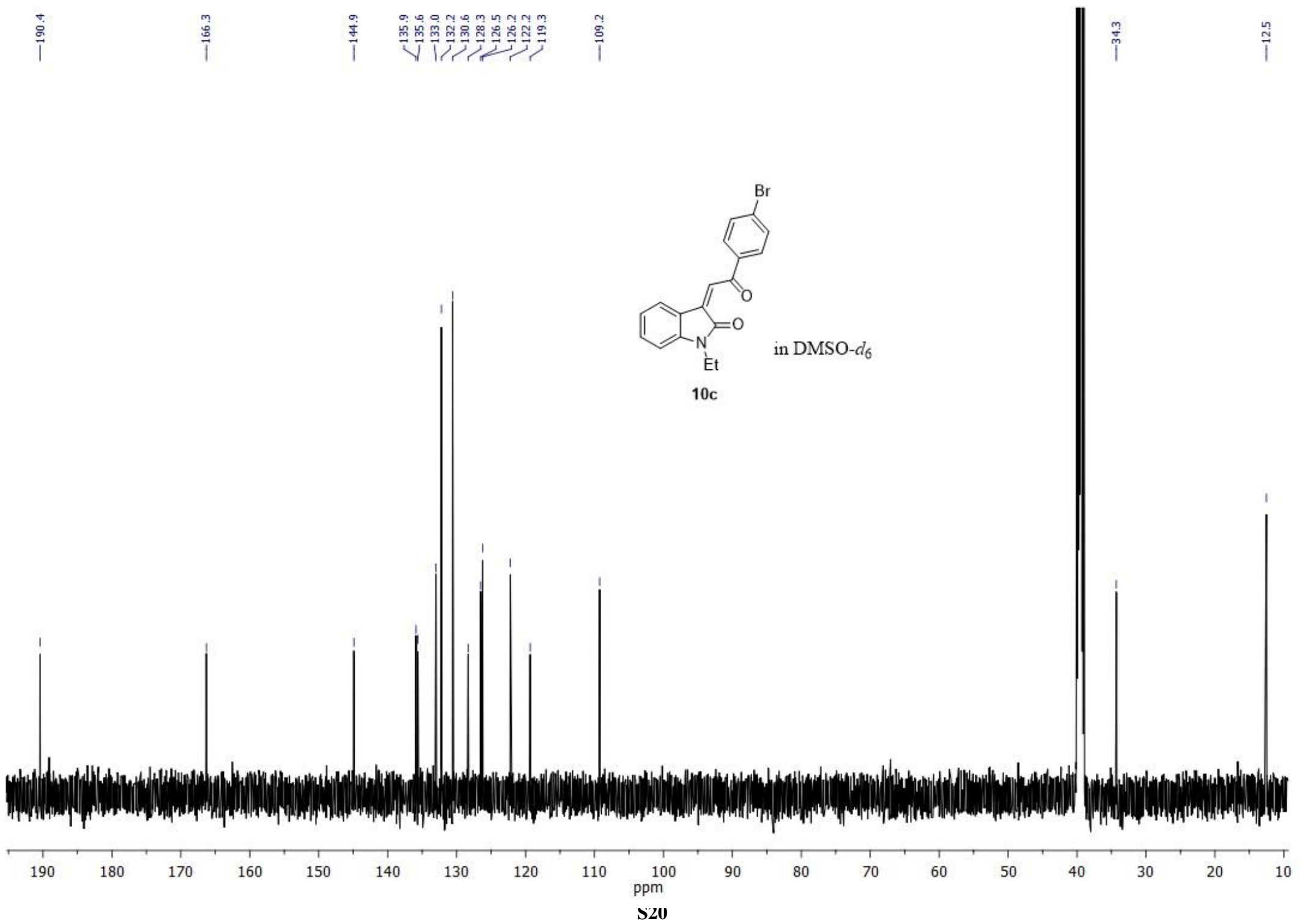
**S16**











—190.4

—166.3

—144.9

—135.9

—135.6

—133.0

—132.2

—130.6

—128.3

—126.5

—126.2

—122.2

—119.3

—109.2

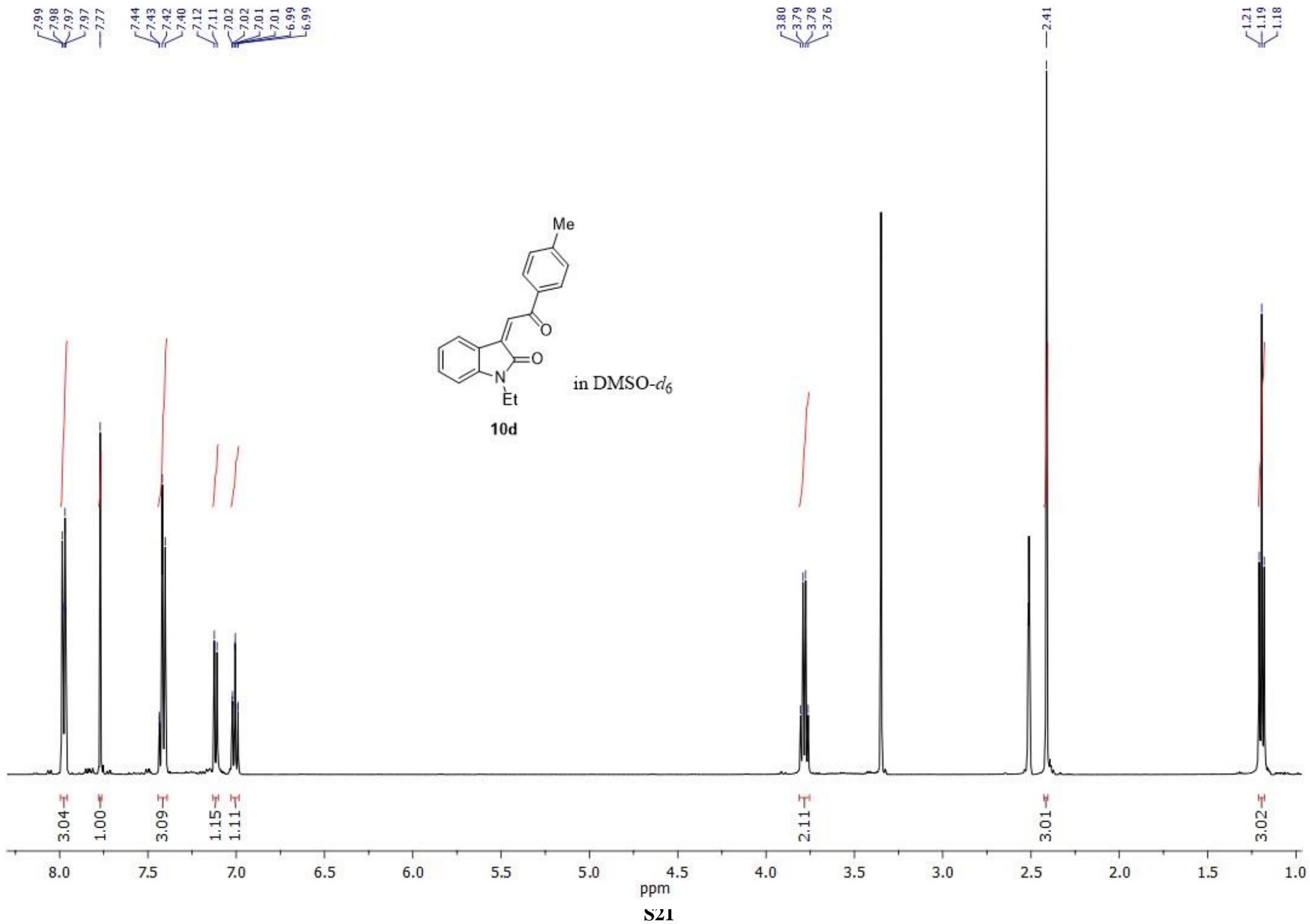
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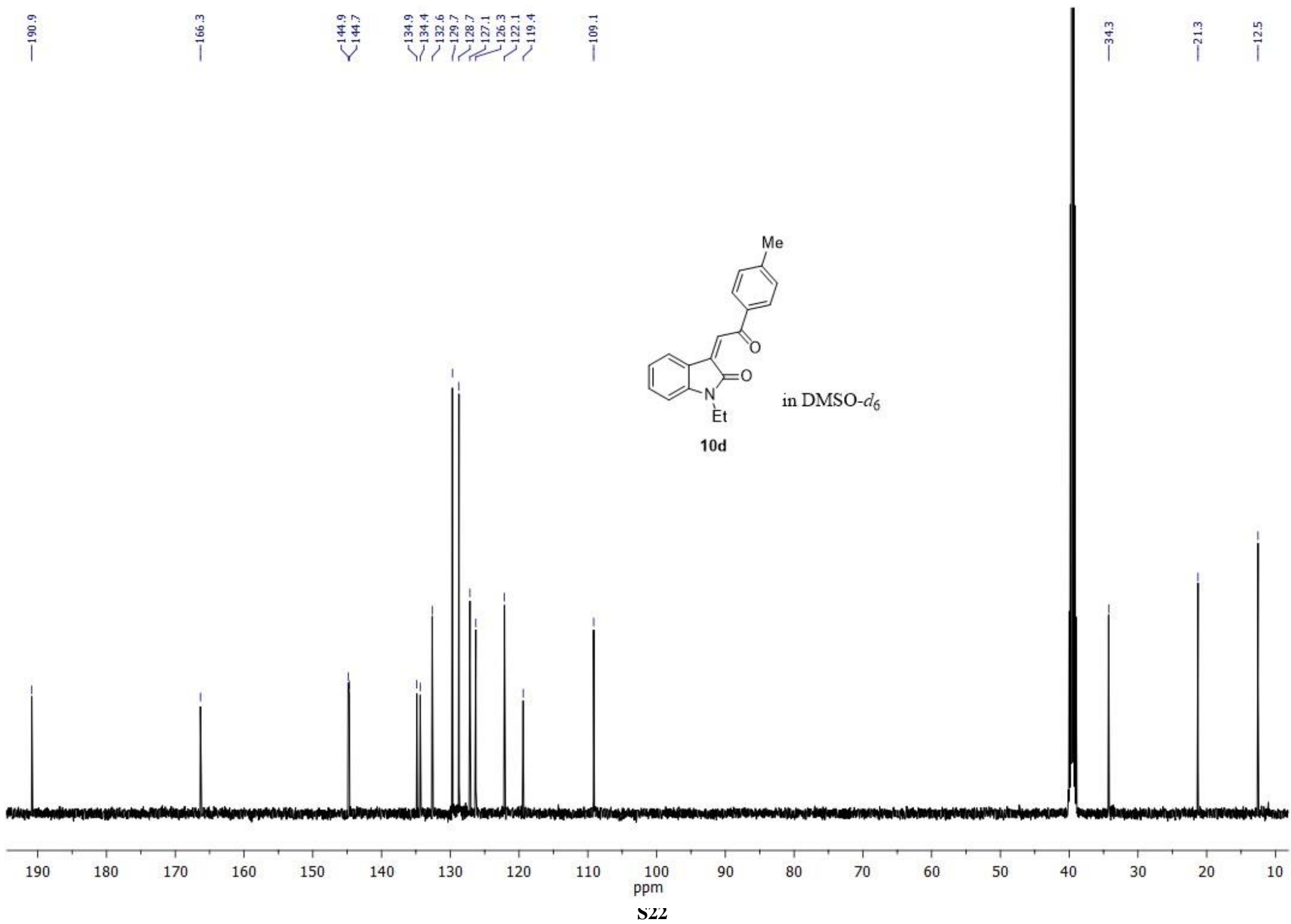
—12.5

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

ppm

S20



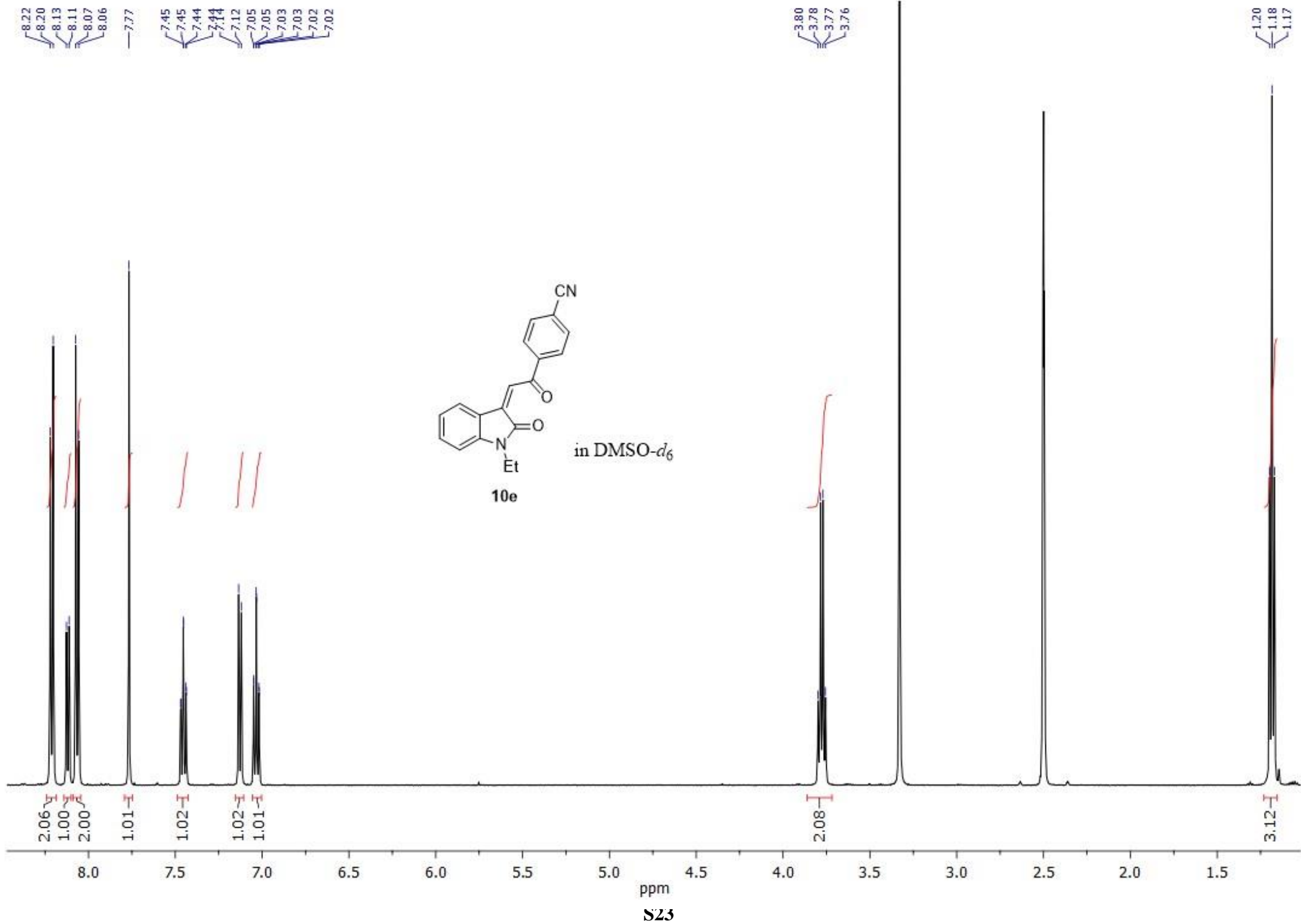


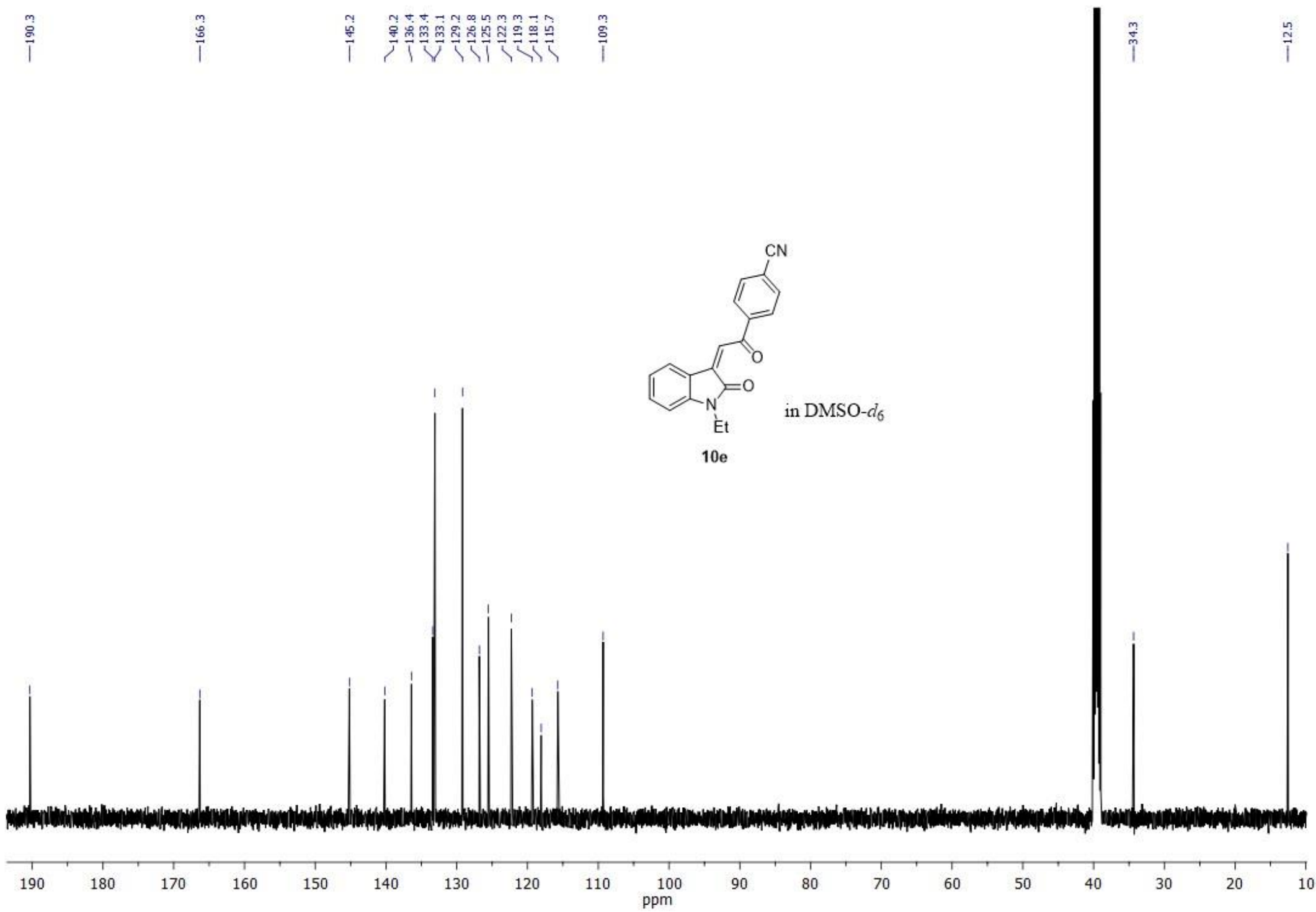
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166.3  
144.9  
144.7  
134.9  
134.4  
132.6  
129.7  
128.7  
127.1  
126.3  
122.1  
119.4  
109.1

34.3  
21.3  
12.5

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

S22





—190.3

—166.3

—145.2

—140.2

—136.4

—133.4

—133.1

—129.2

—126.8

—125.5

—122.3

—119.3

—118.1

—115.7

—109.3

—34.3

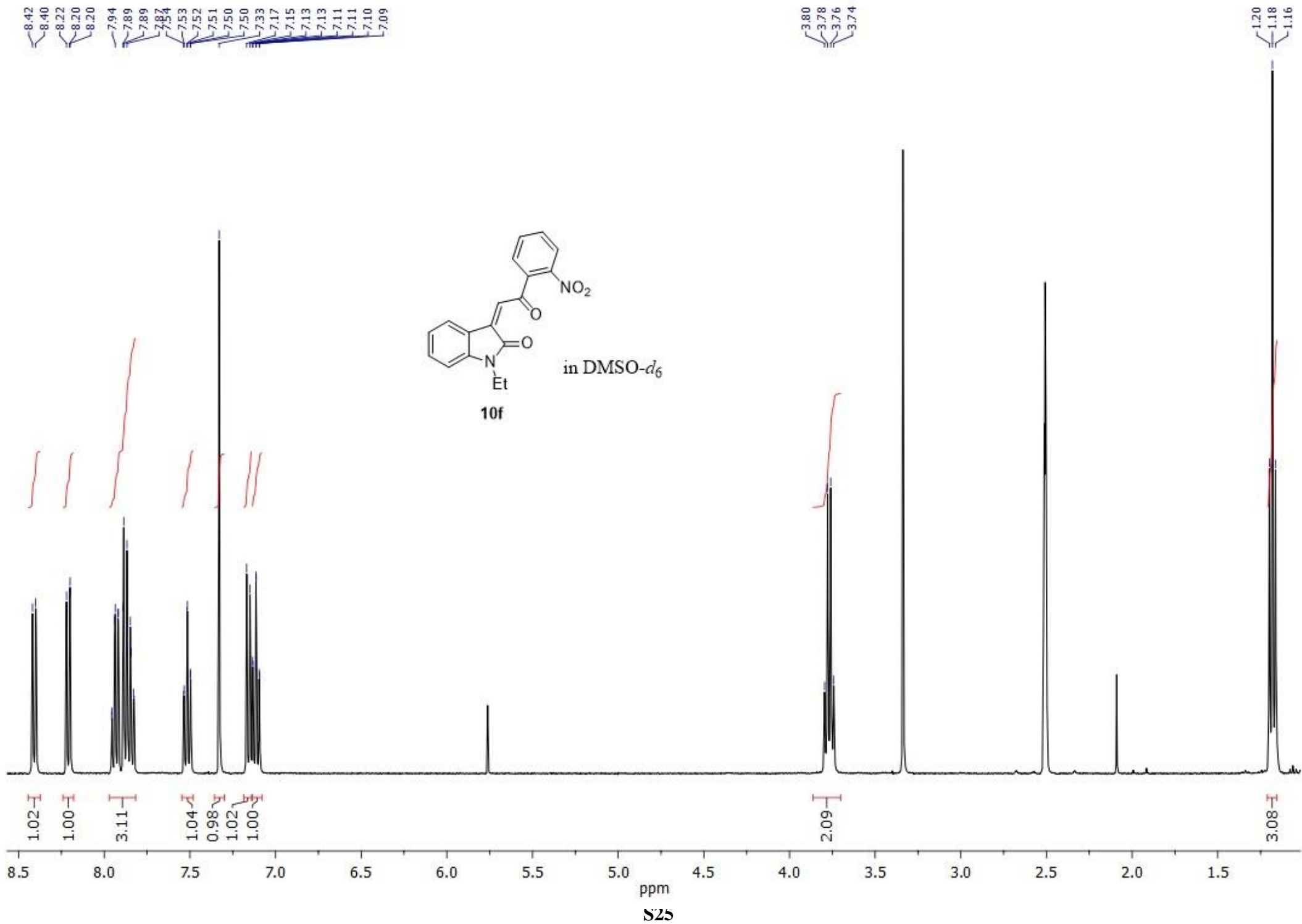
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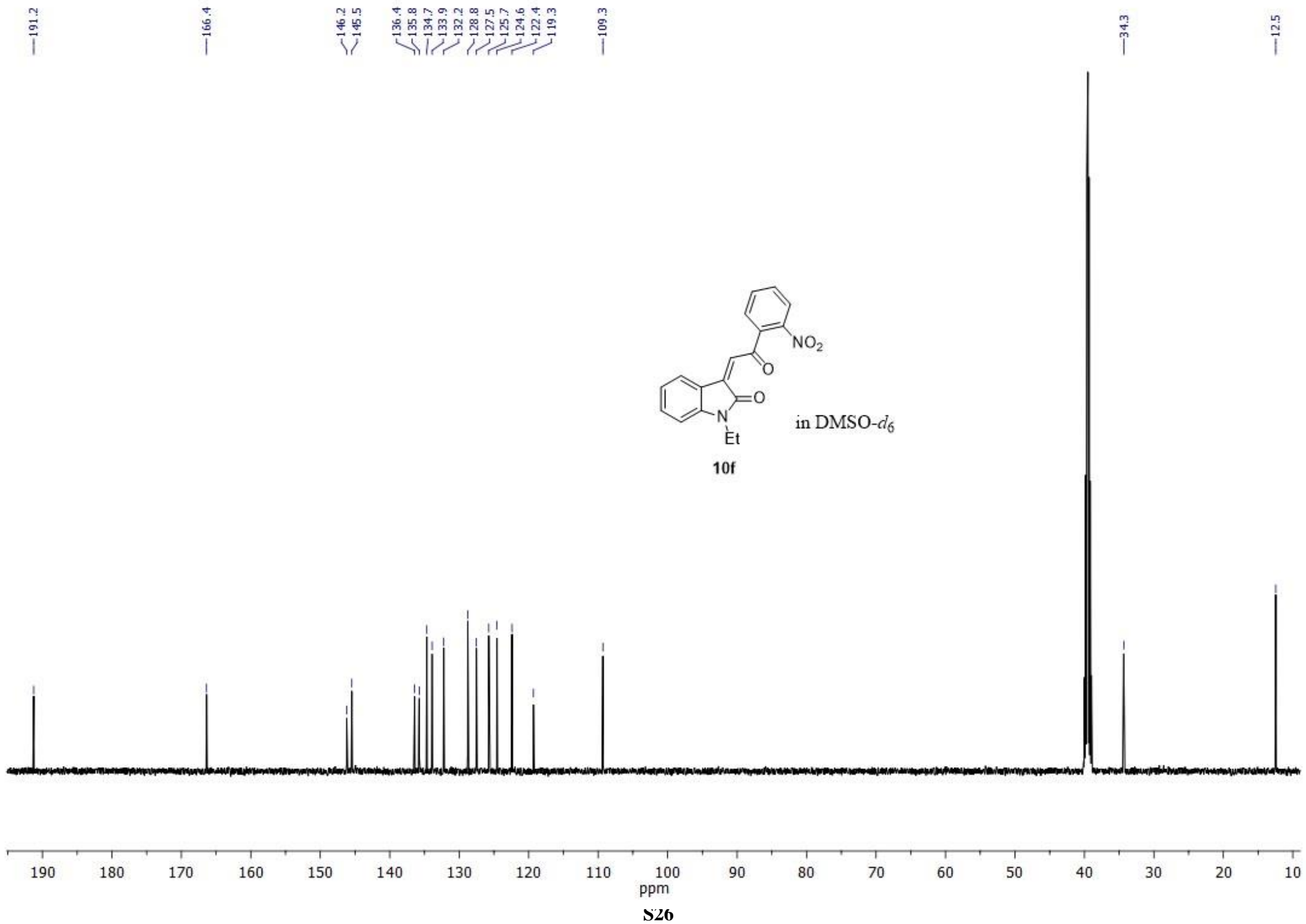
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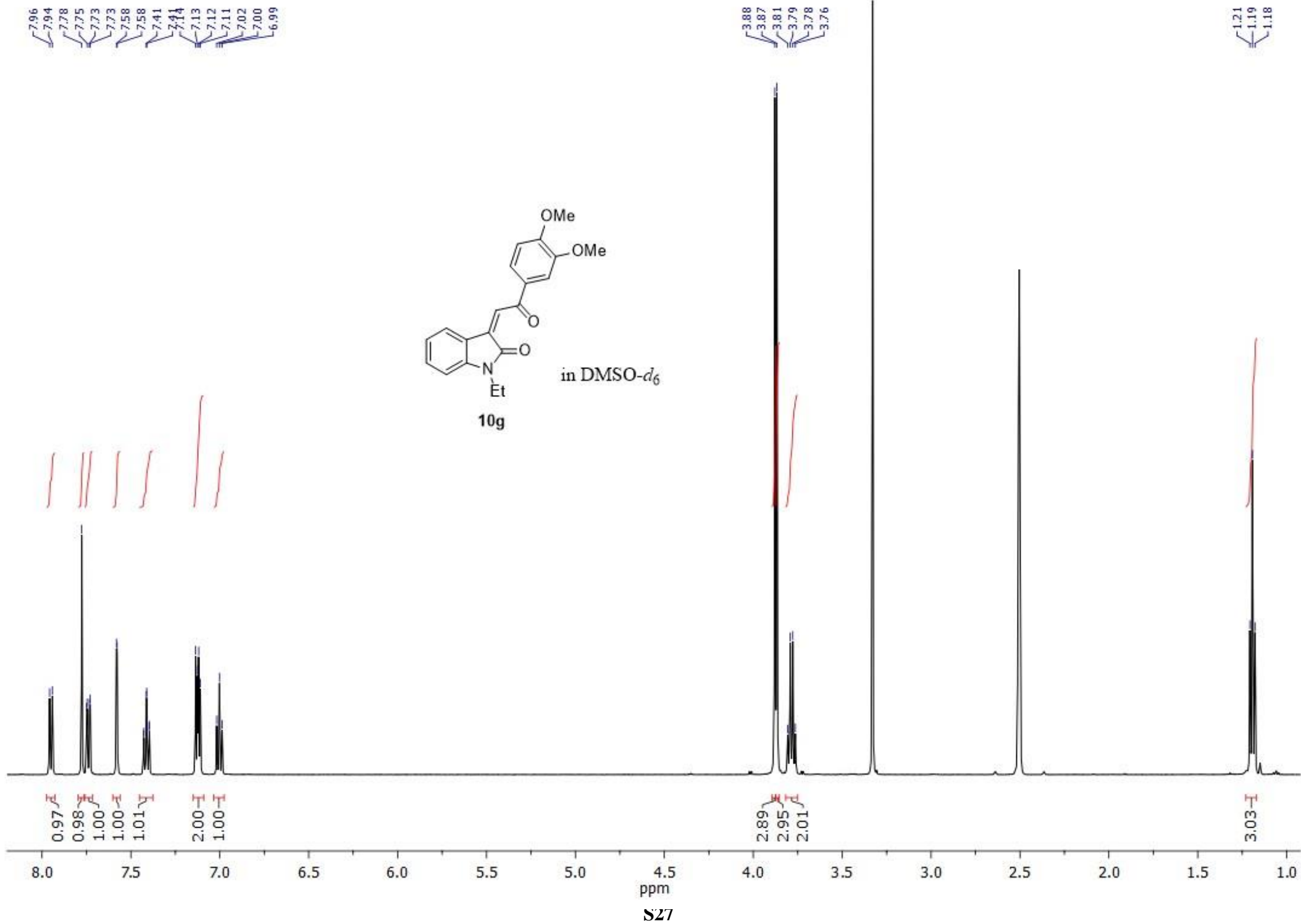
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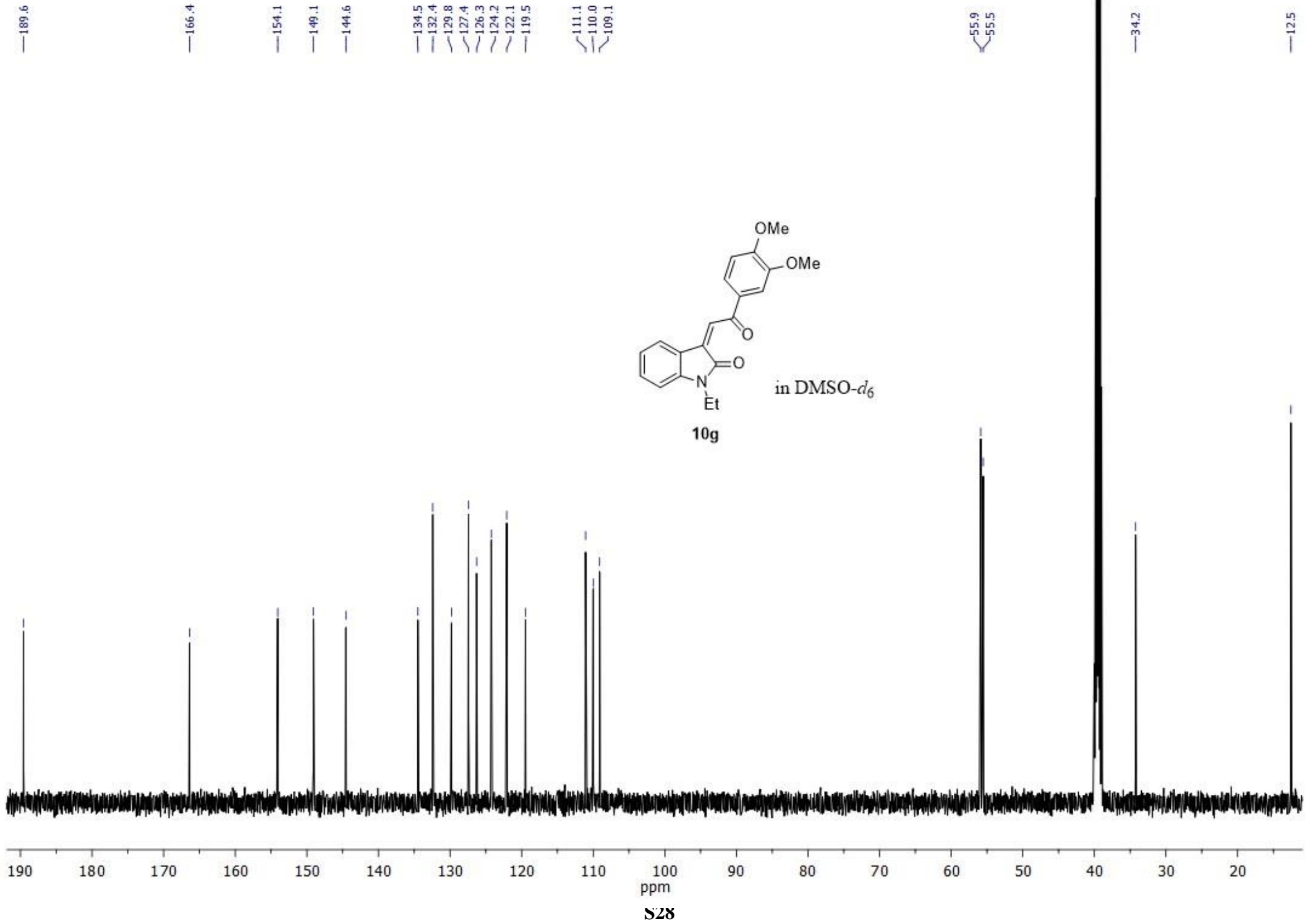
S24

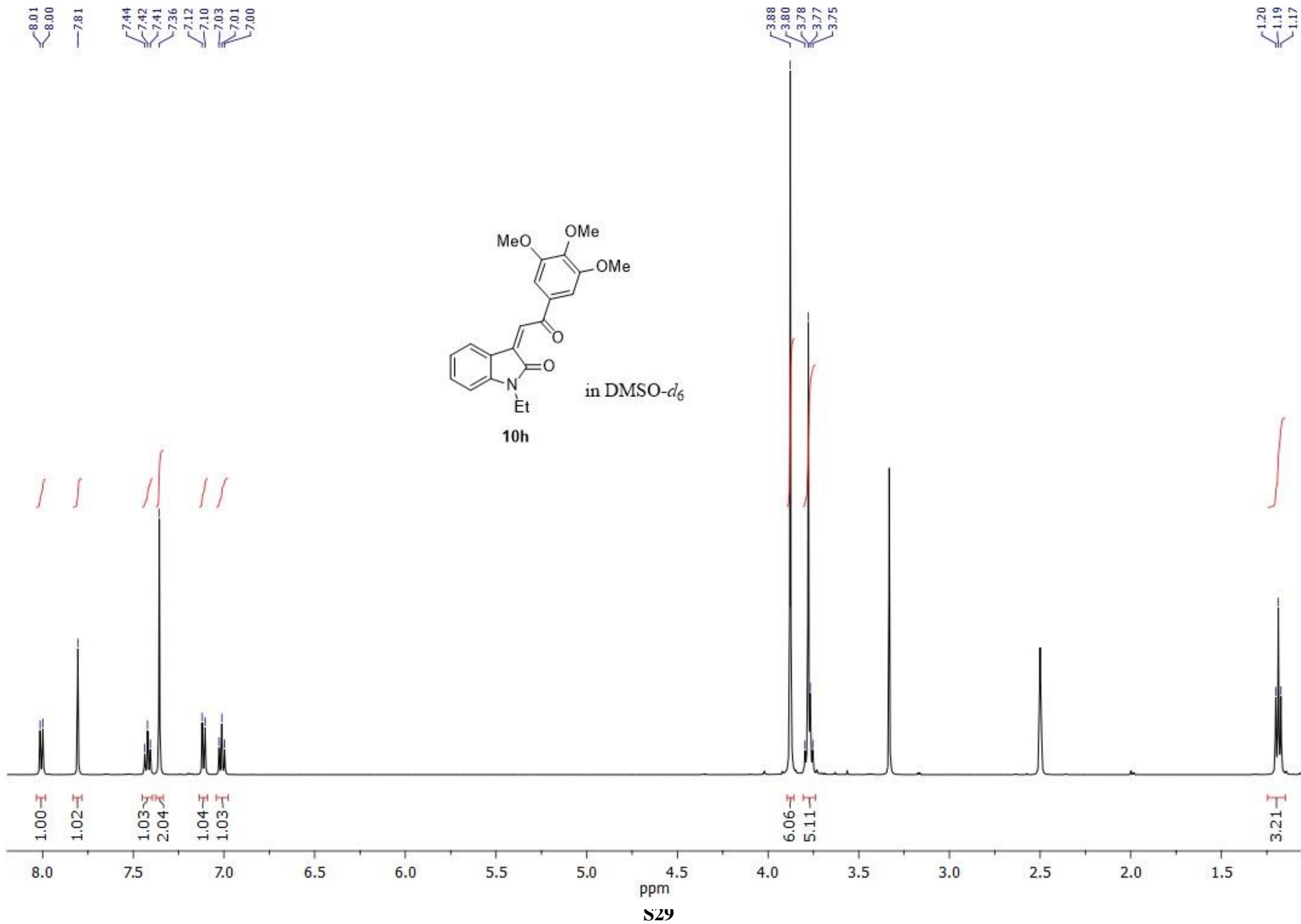


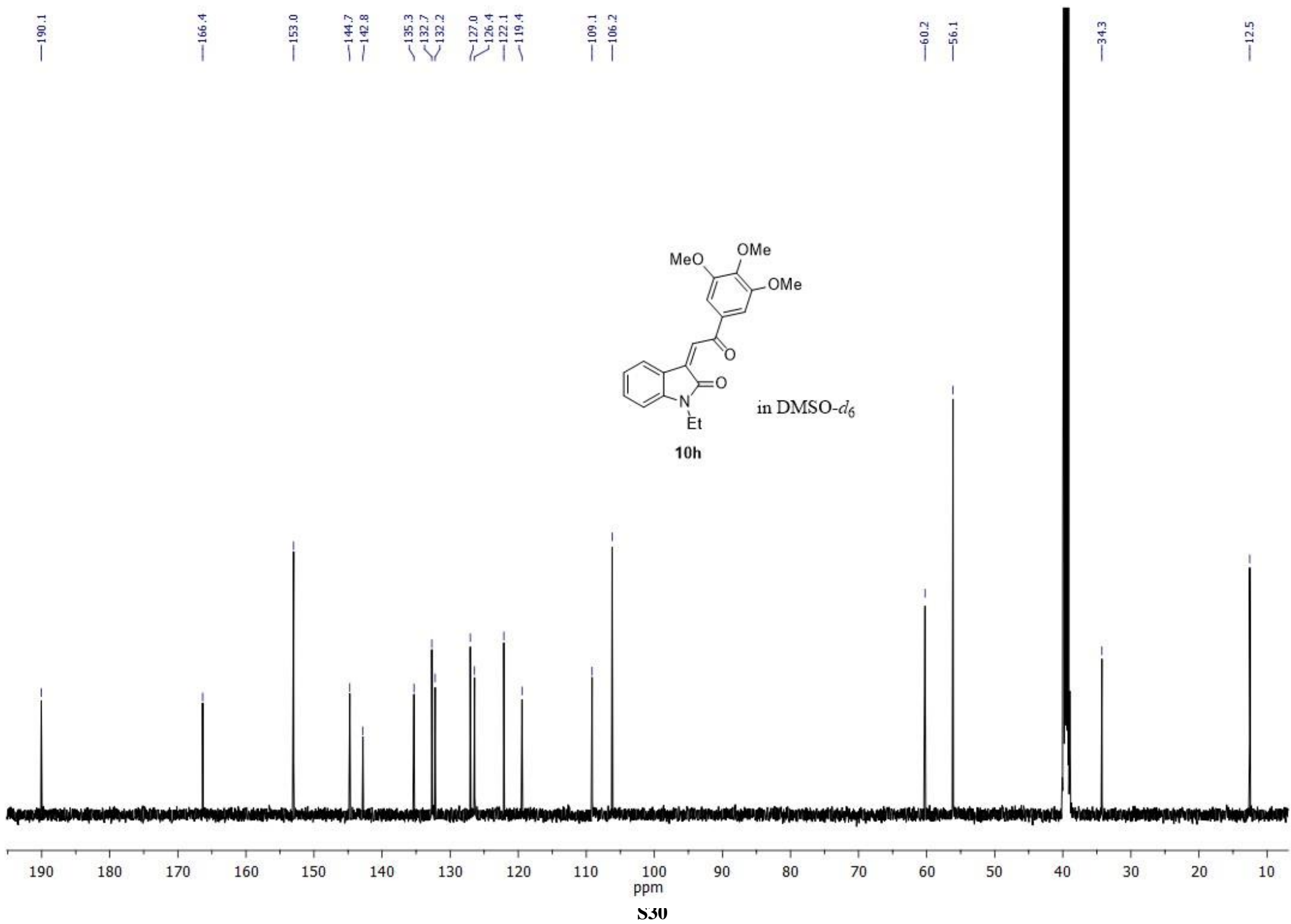


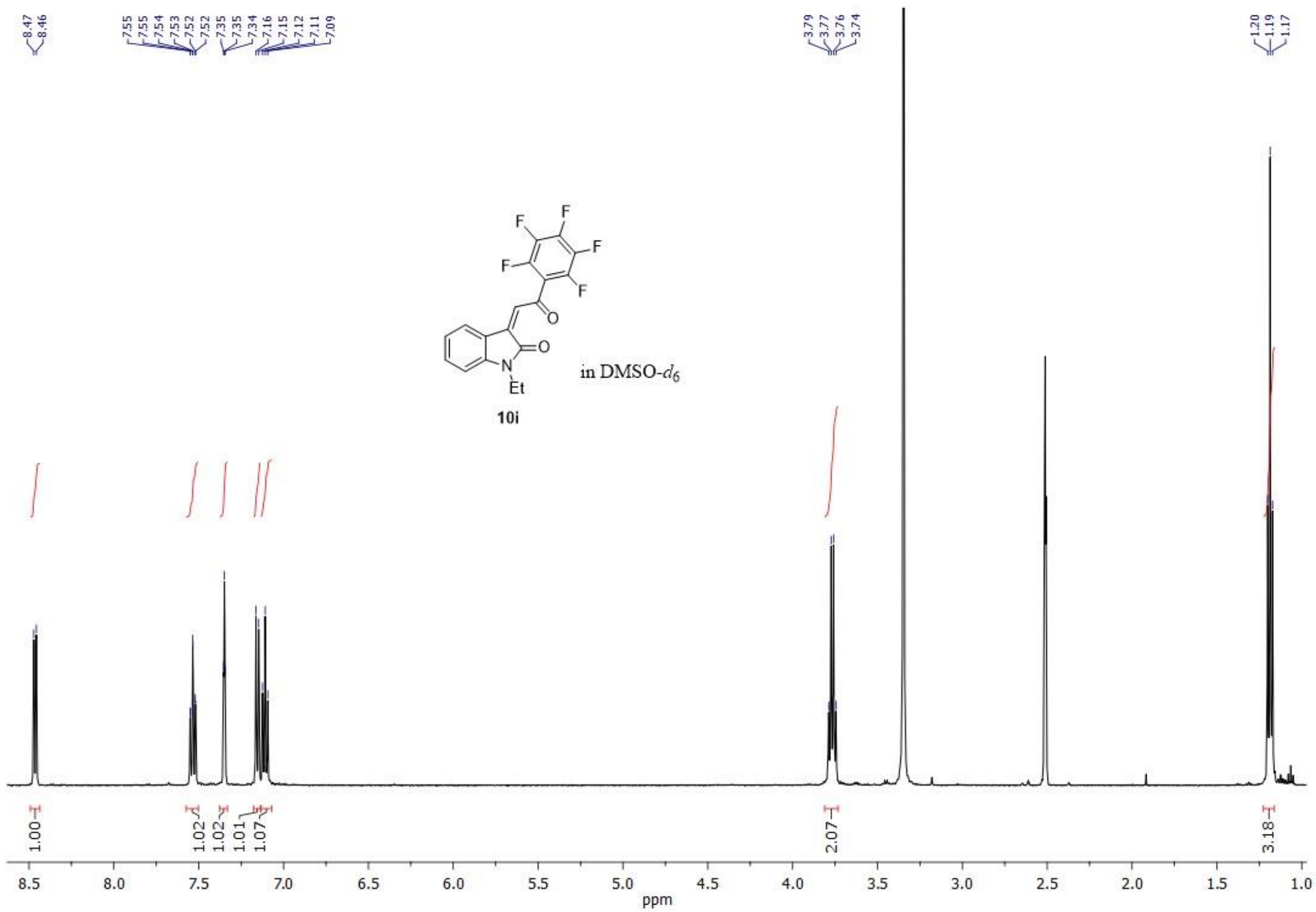


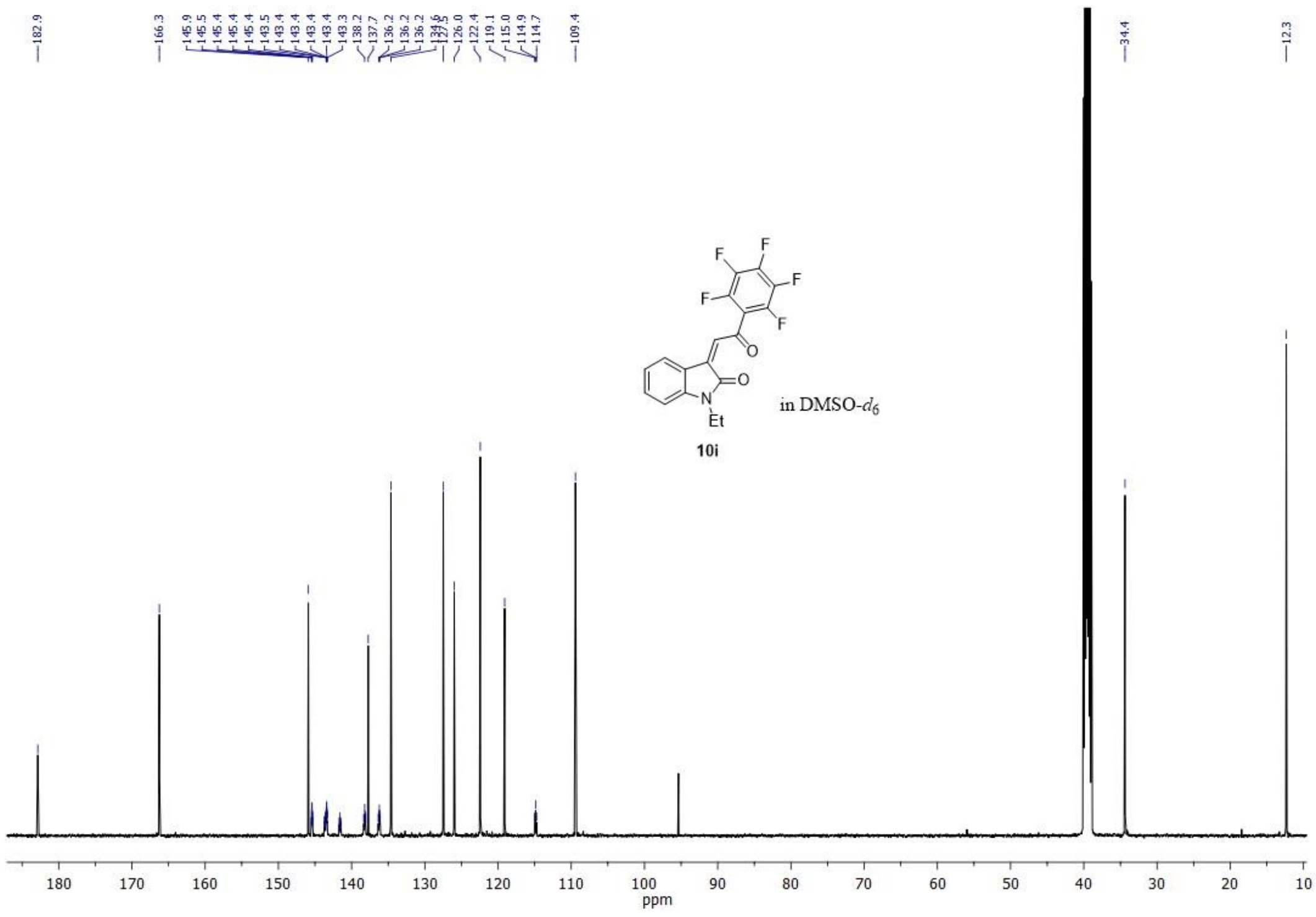














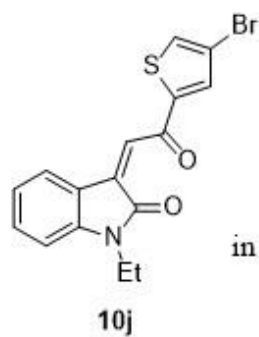
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8.24  
8.24

7.70

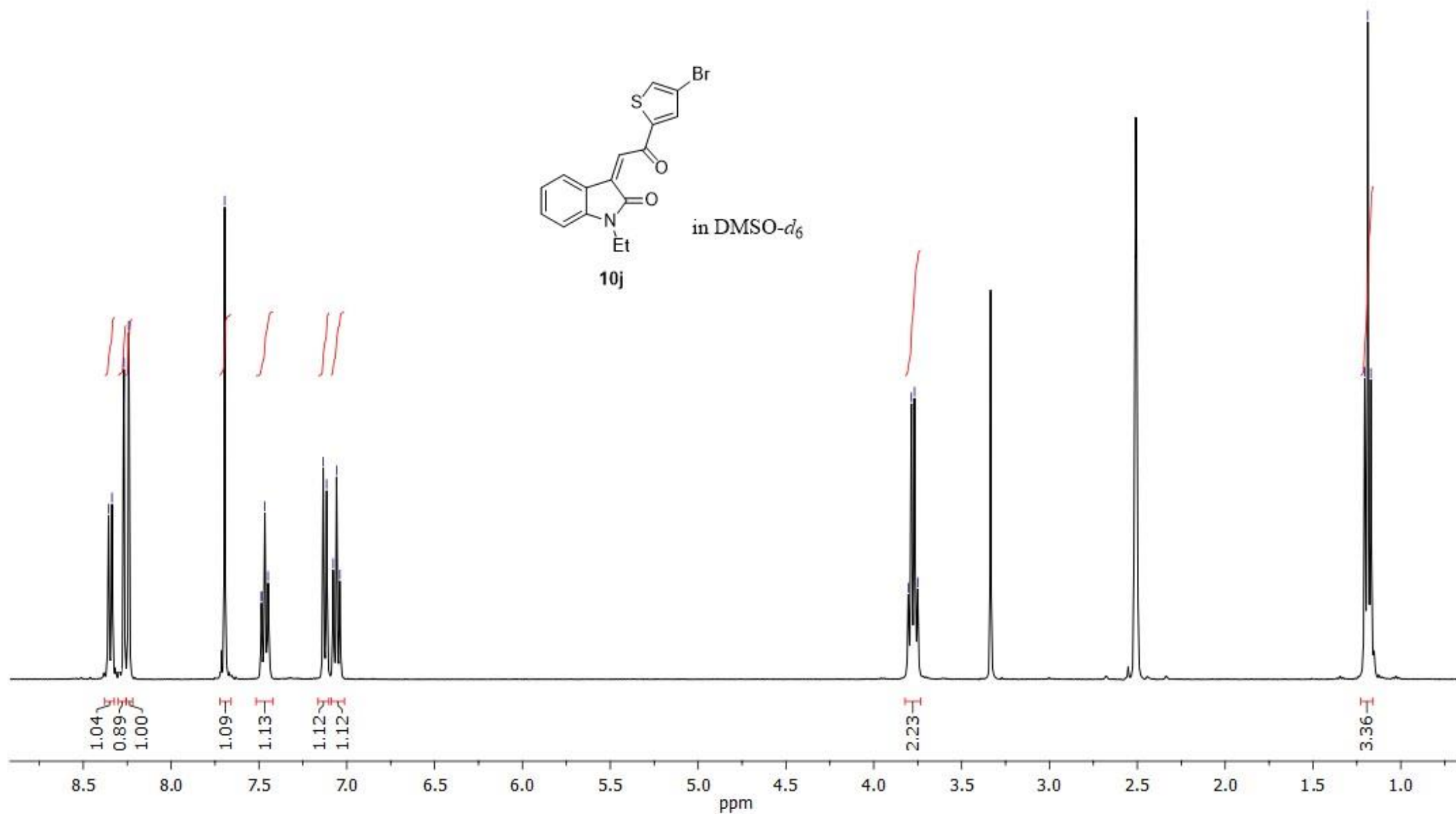
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7.47  
7.45  
7.43  
7.11  
7.08  
7.06  
7.04

3.80  
3.79  
3.77  
3.75

1.21  
1.19  
1.17

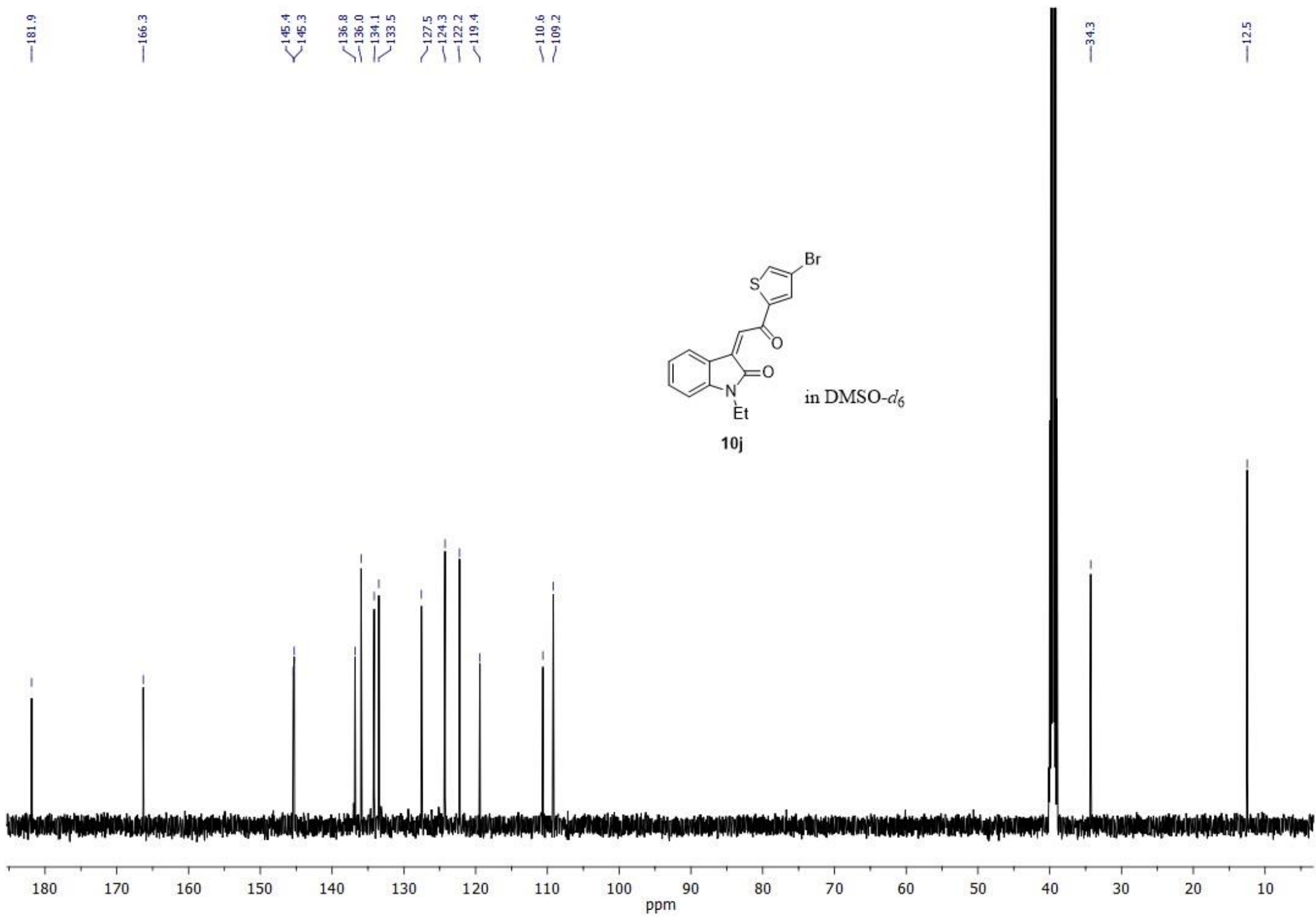


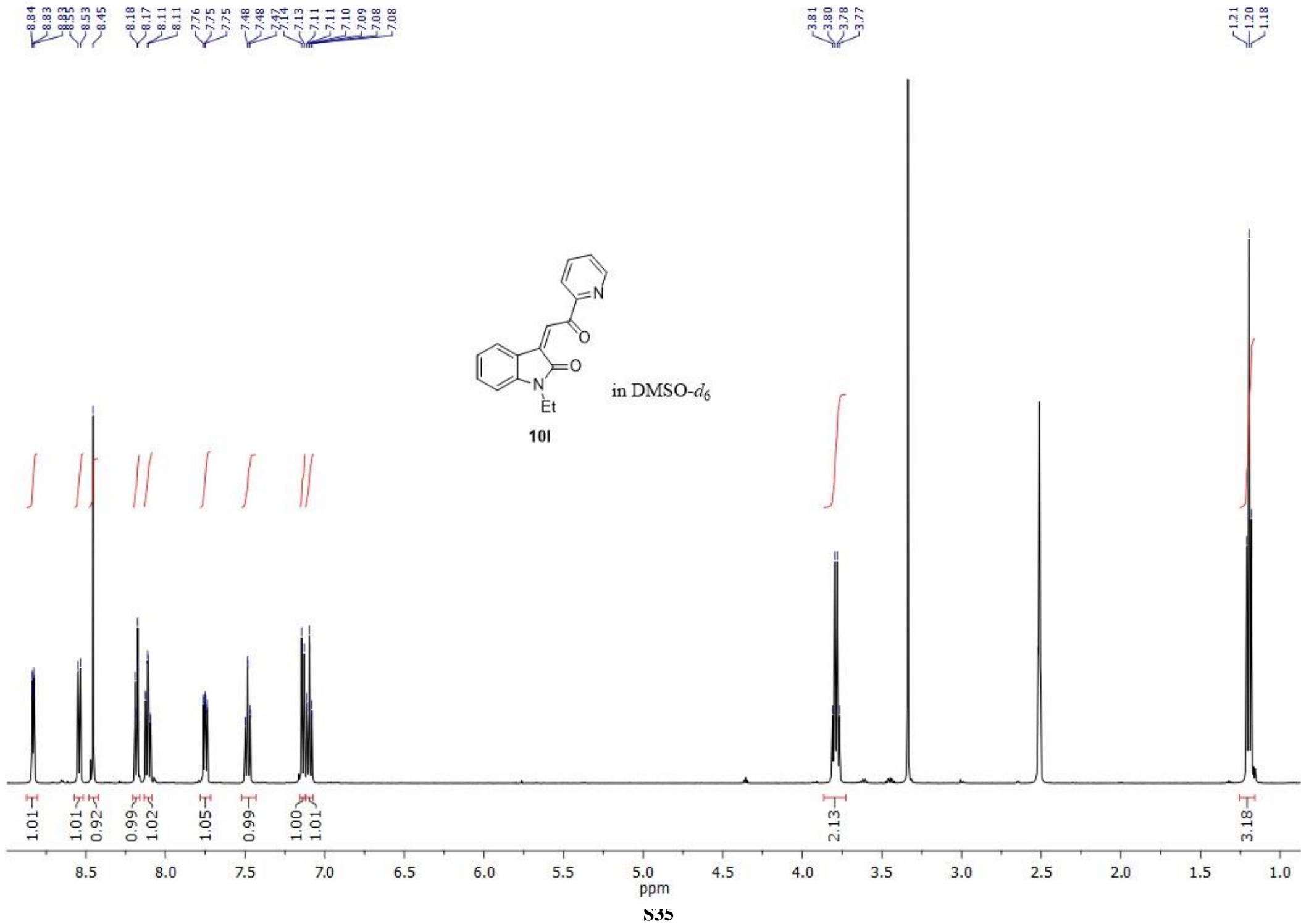
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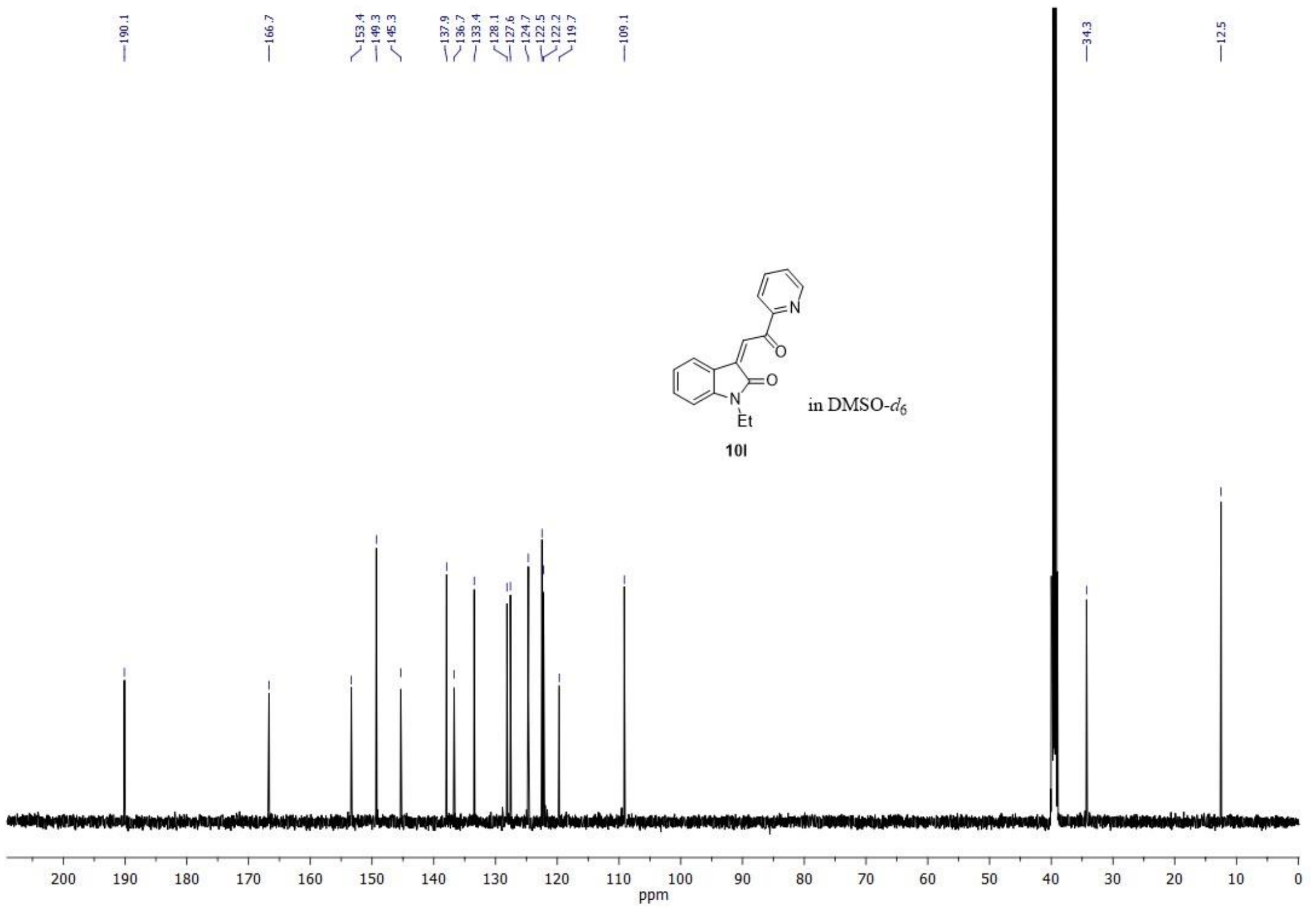


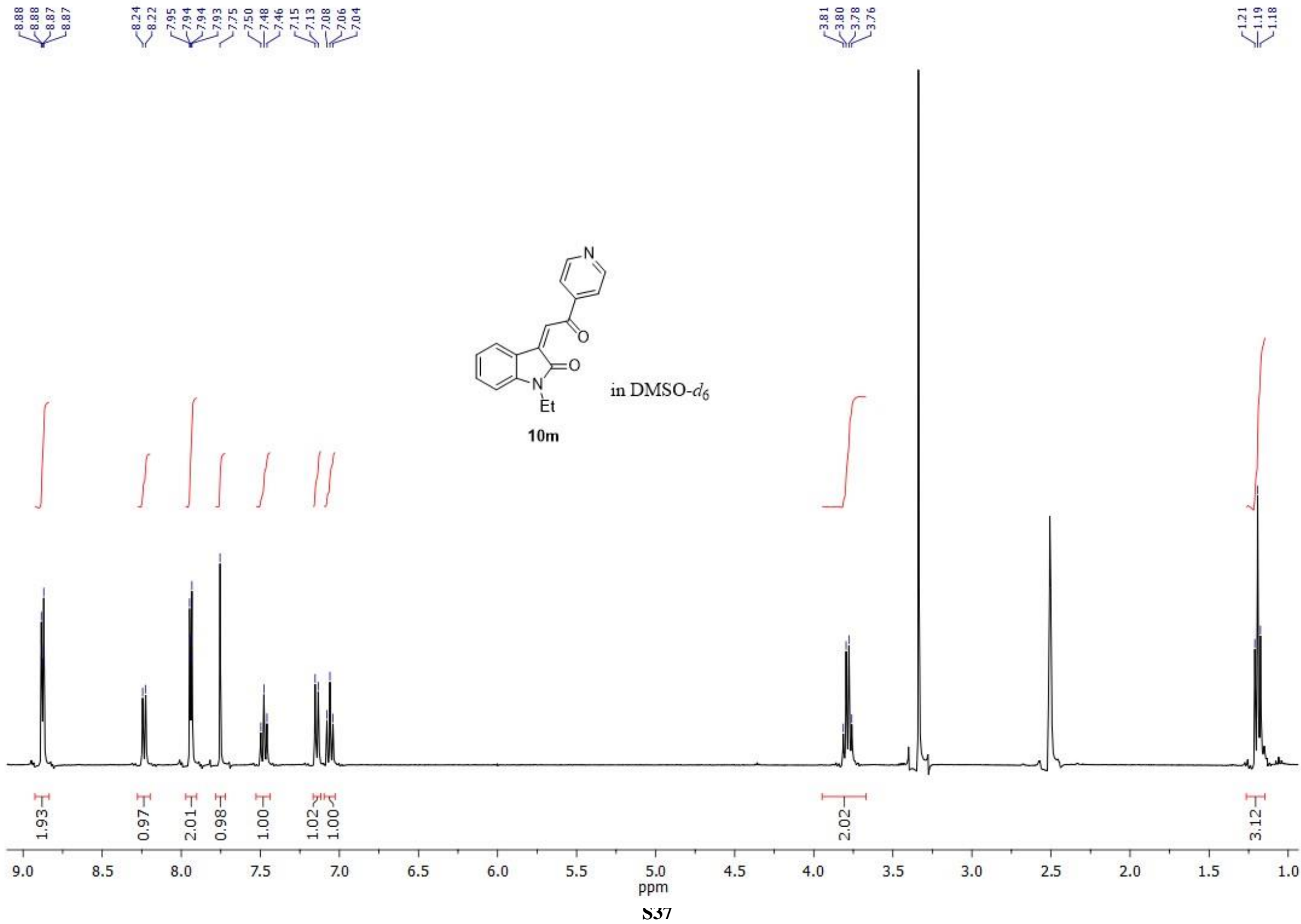
ppm

S33

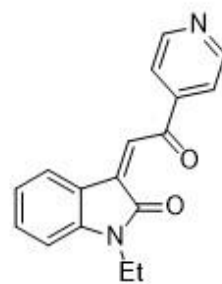








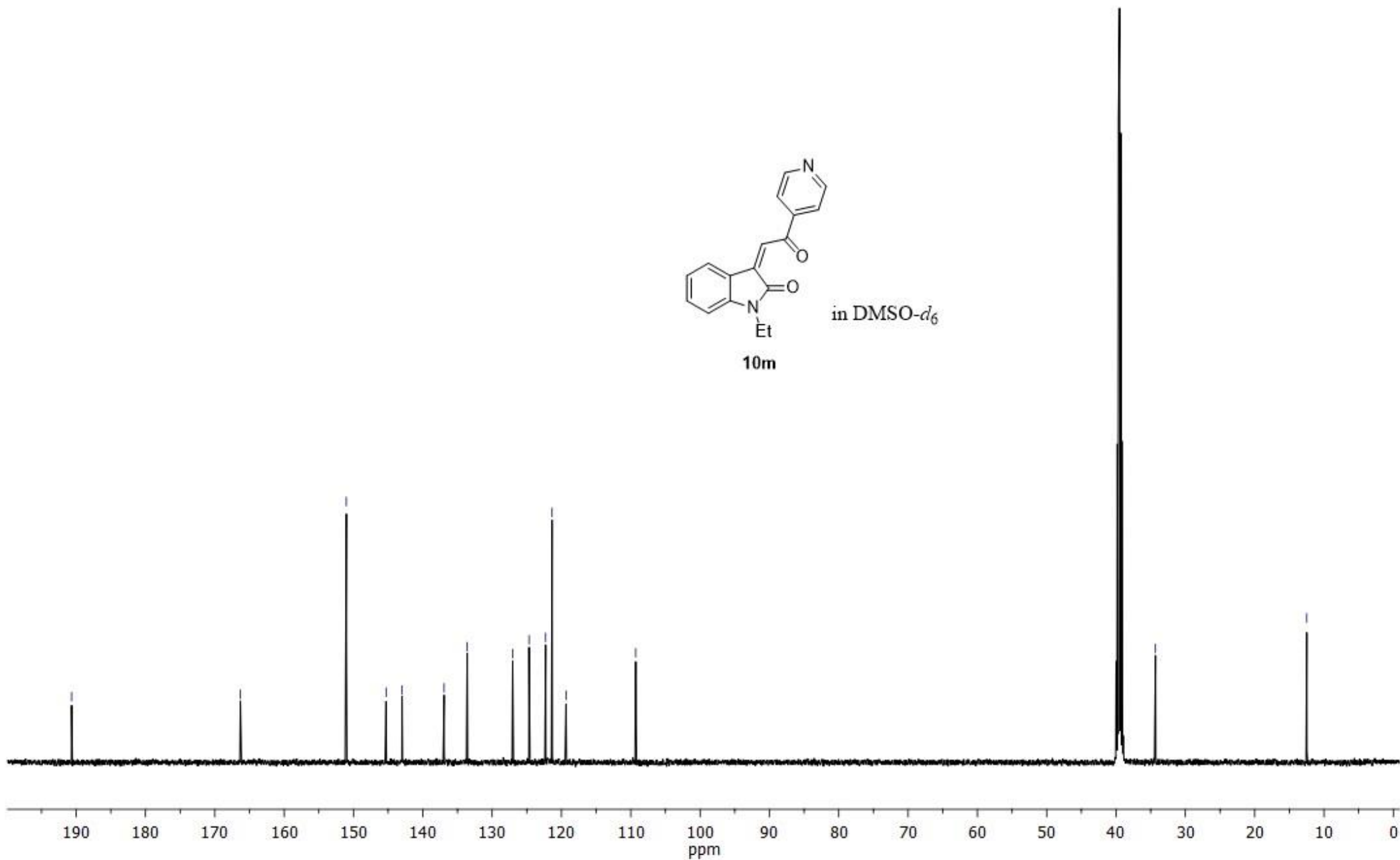
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145.3  
143.0  
136.9  
133.6  
127.0  
124.7  
122.3  
121.3  
119.3  
109.3



in DMSO-*d*<sub>6</sub>

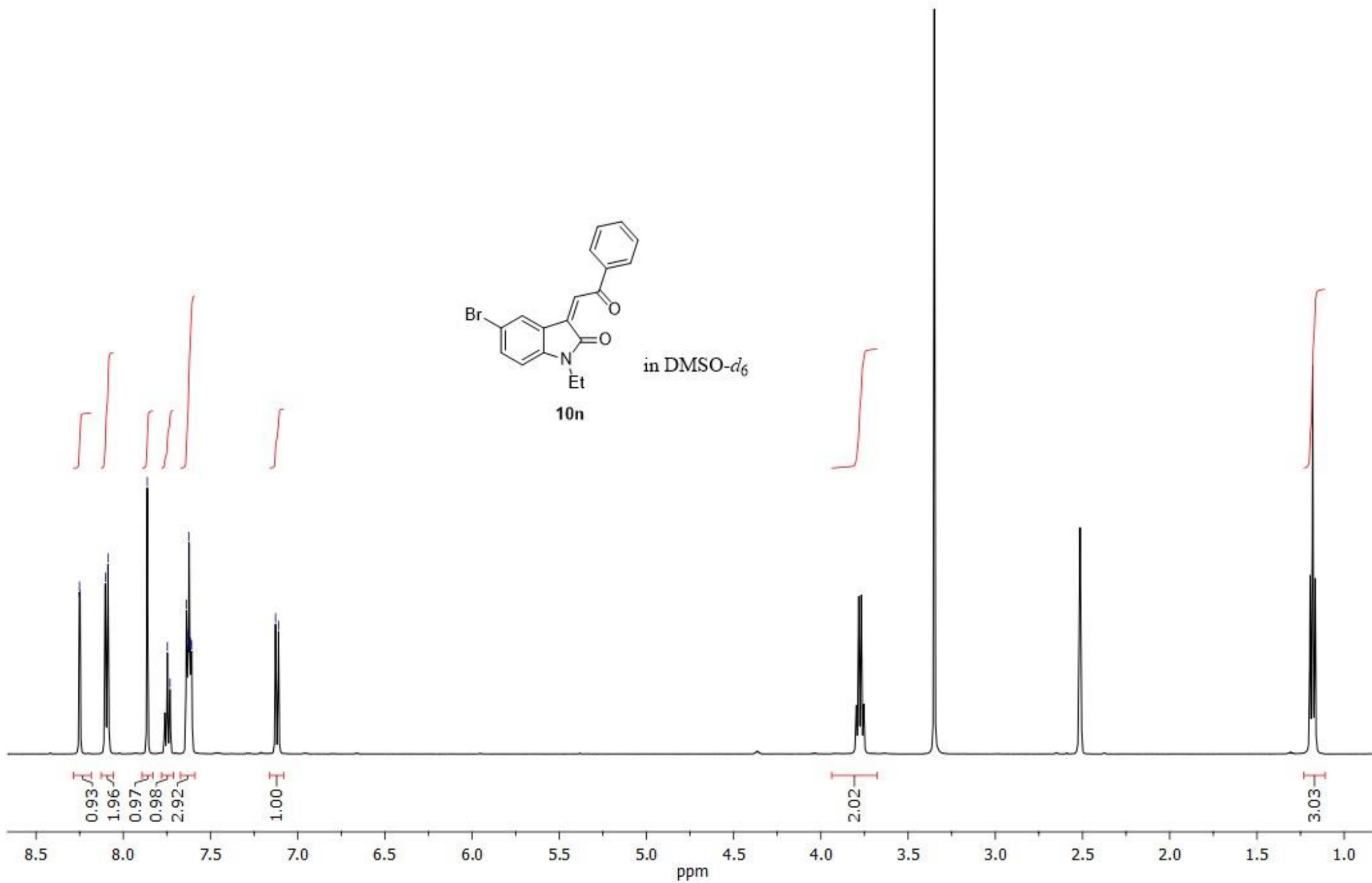
10m

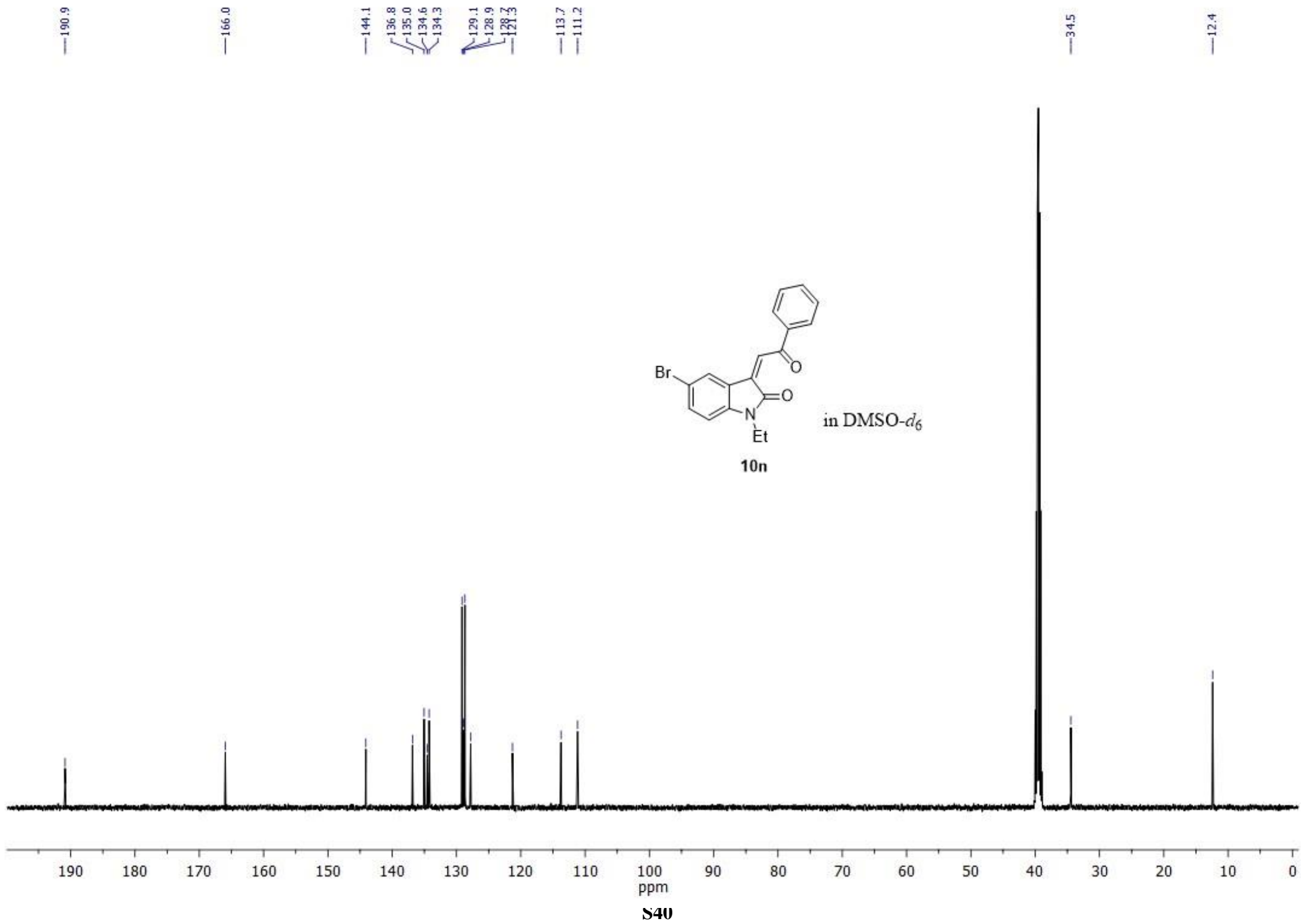
34.3  
12.5



S38

8.25  
8.25  
8.10  
8.09  
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7.75  
7.64  
7.63  
7.62  
7.61  
7.53  
7.11



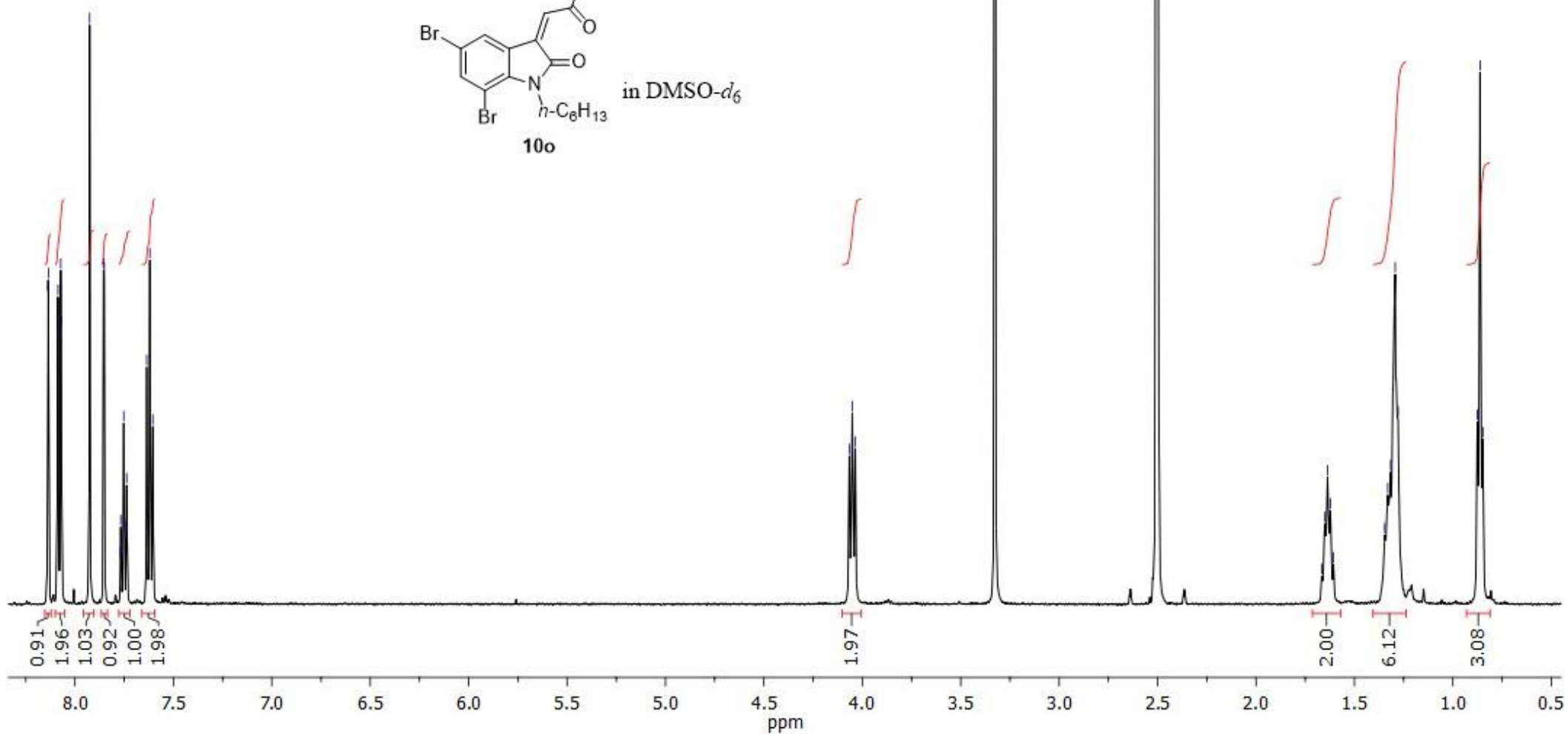
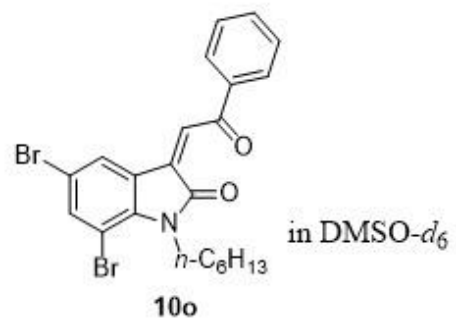


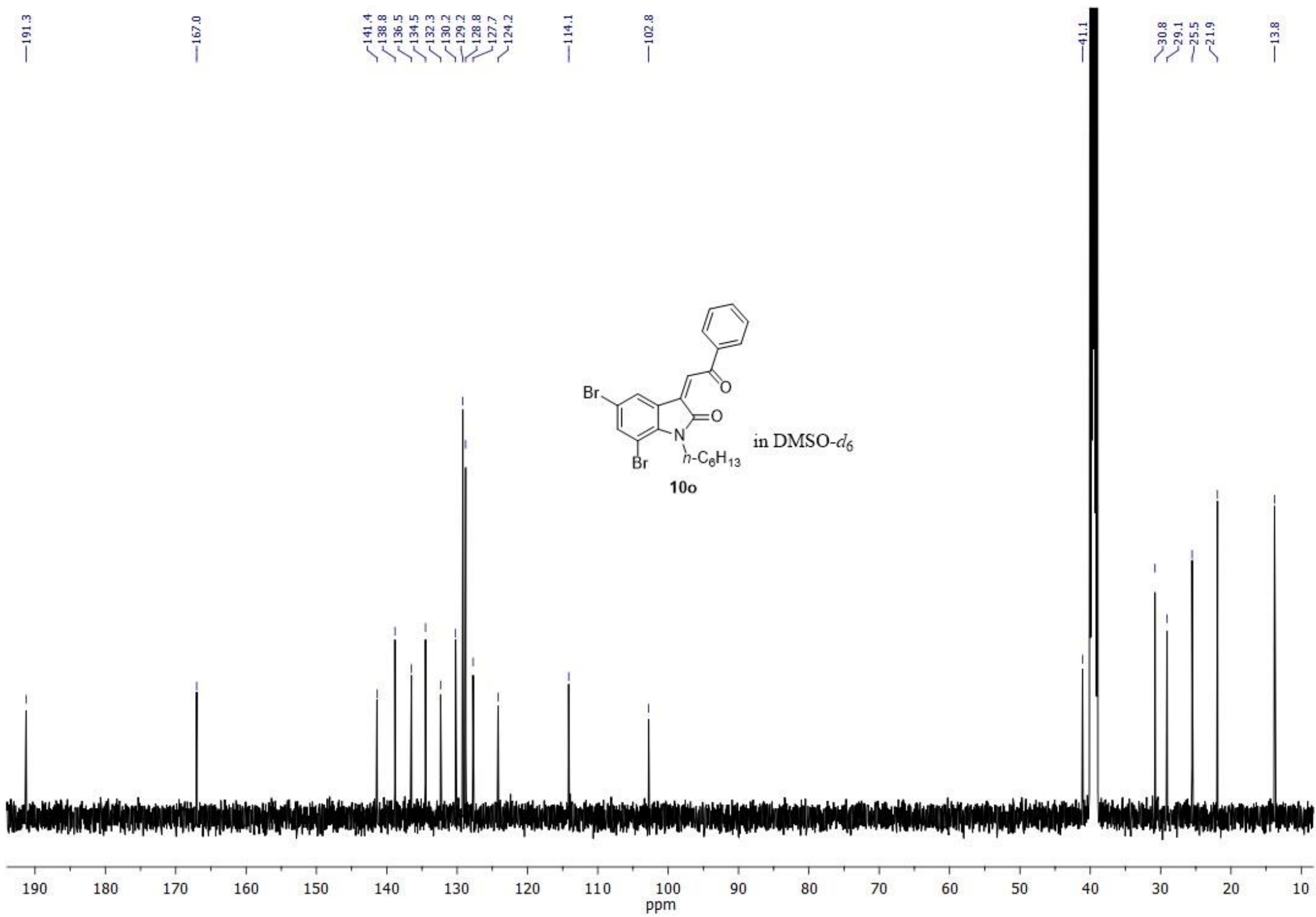


8.14  
8.13  
8.09  
8.09  
8.07  
8.07  
7.93  
7.85  
7.85  
7.77  
7.77  
7.76  
7.75  
7.74  
7.74  
7.74  
7.64  
7.62  
7.61  
7.60

4.07  
4.05  
4.04

1.67  
1.65  
1.64  
1.62  
1.61  
1.33  
1.32  
1.30  
1.29  
1.28  
0.88  
0.86  
0.85





—191.3

—167.0

141.4  
138.8  
136.5  
134.5  
132.3  
130.2  
129.2  
128.8  
127.7  
124.2

—114.1

—102.8

—41.1

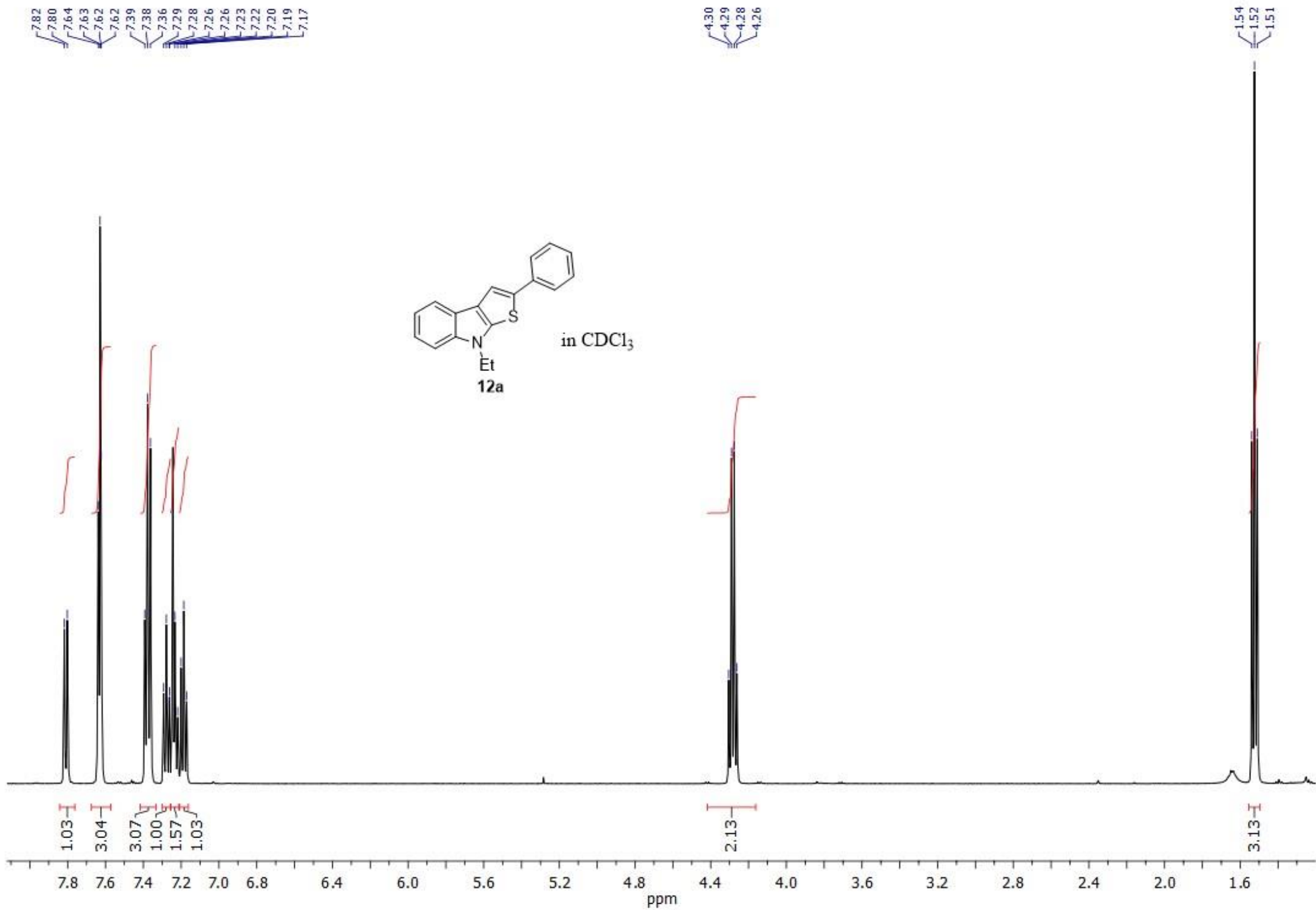
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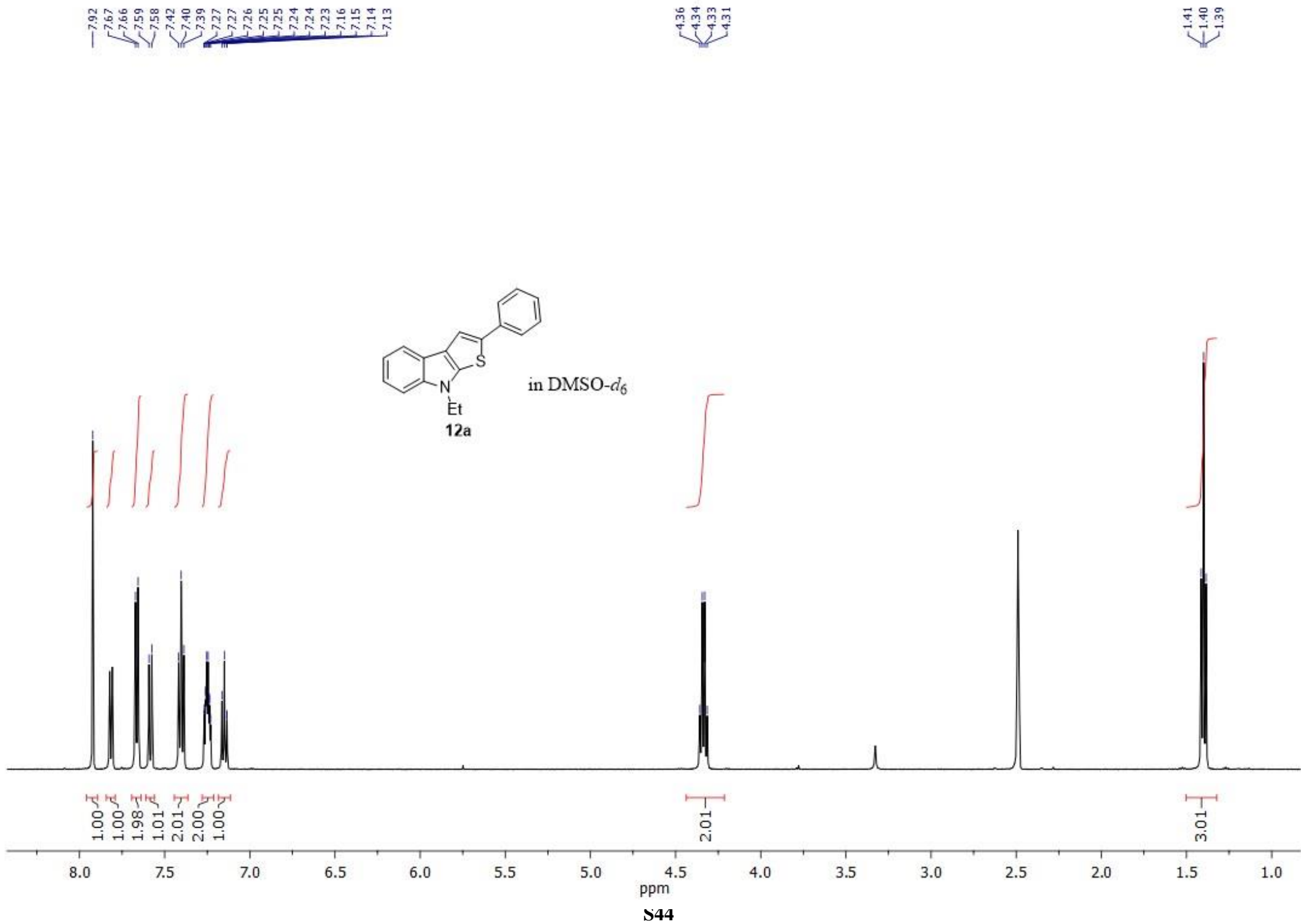
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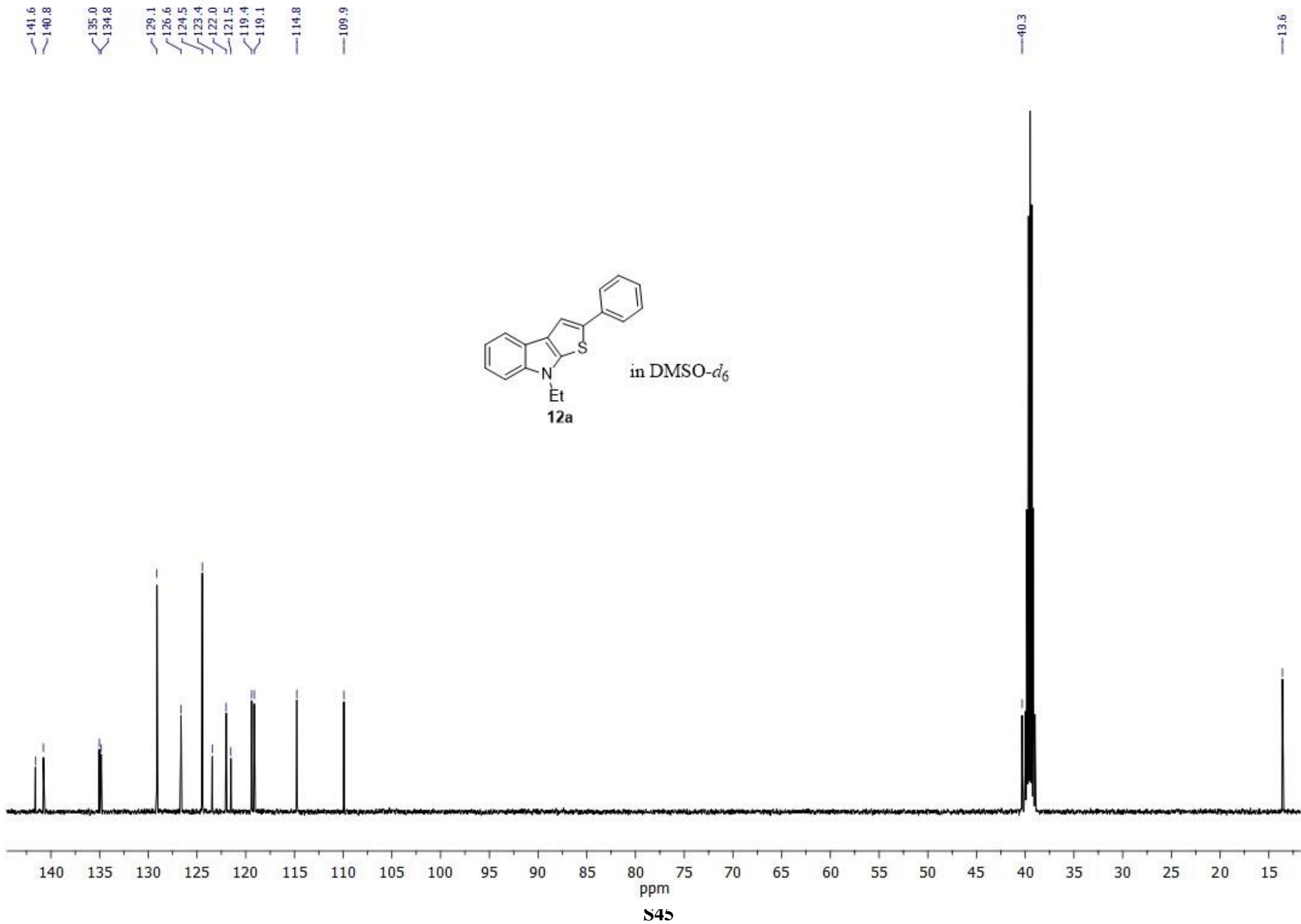
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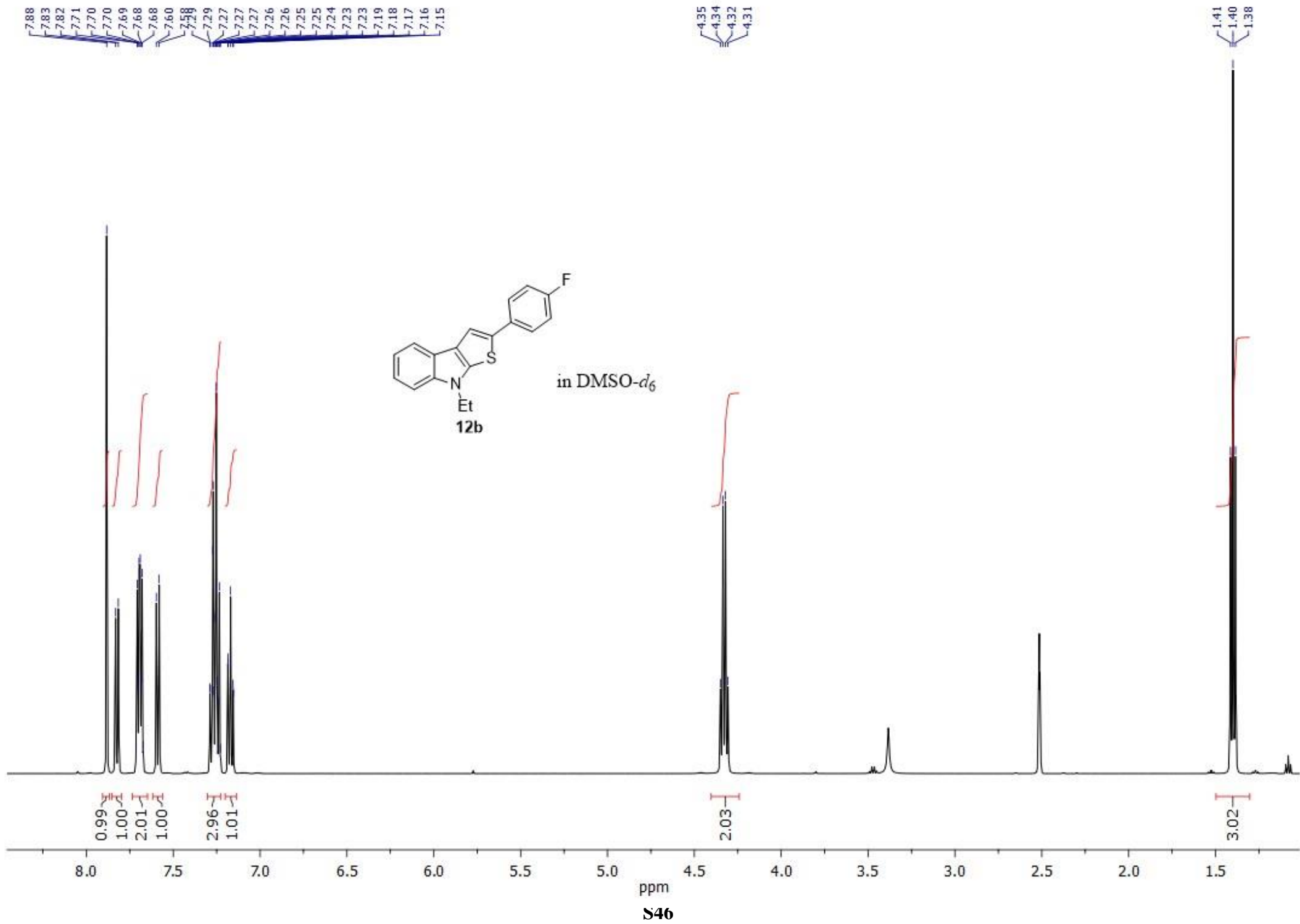
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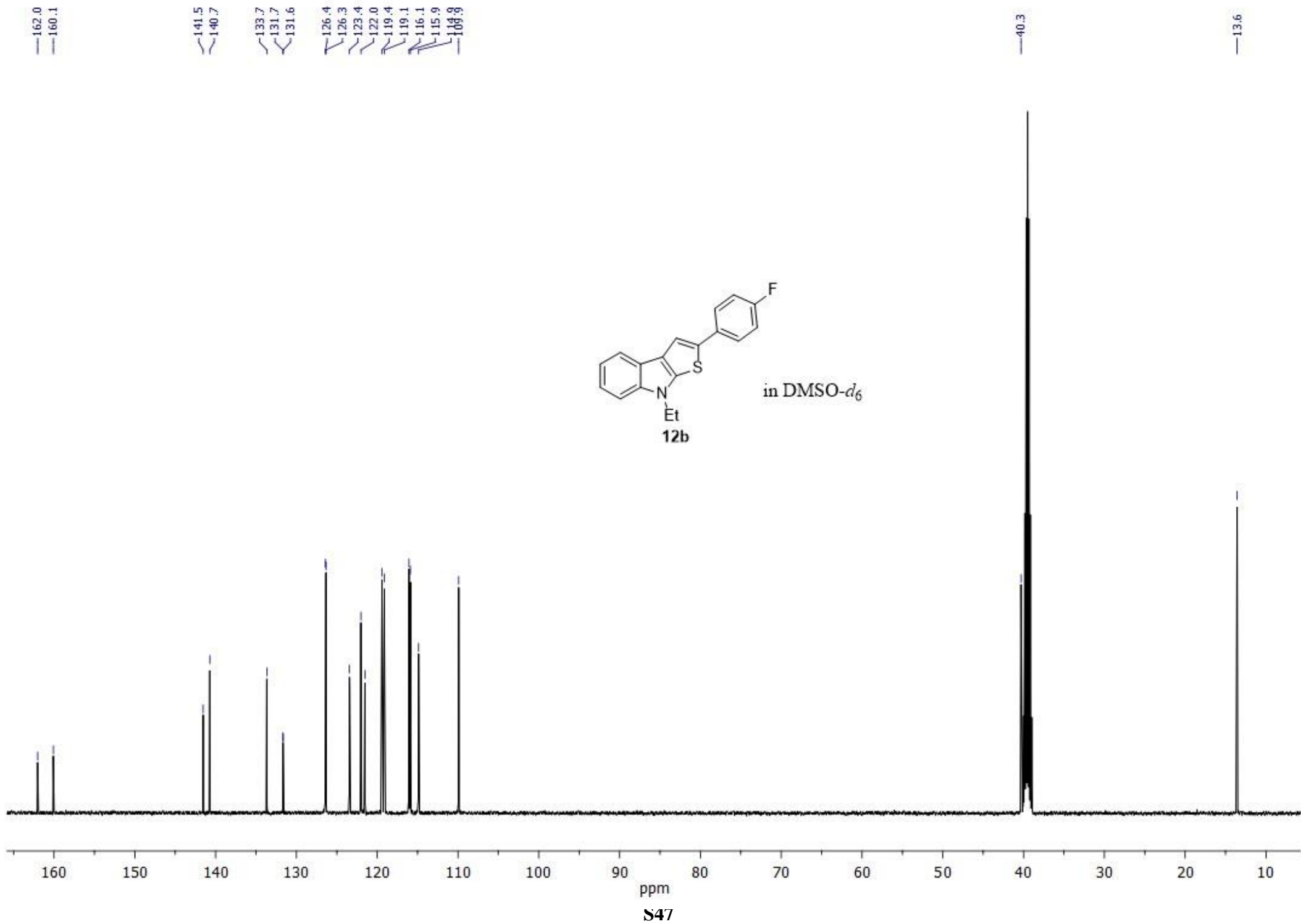
S42

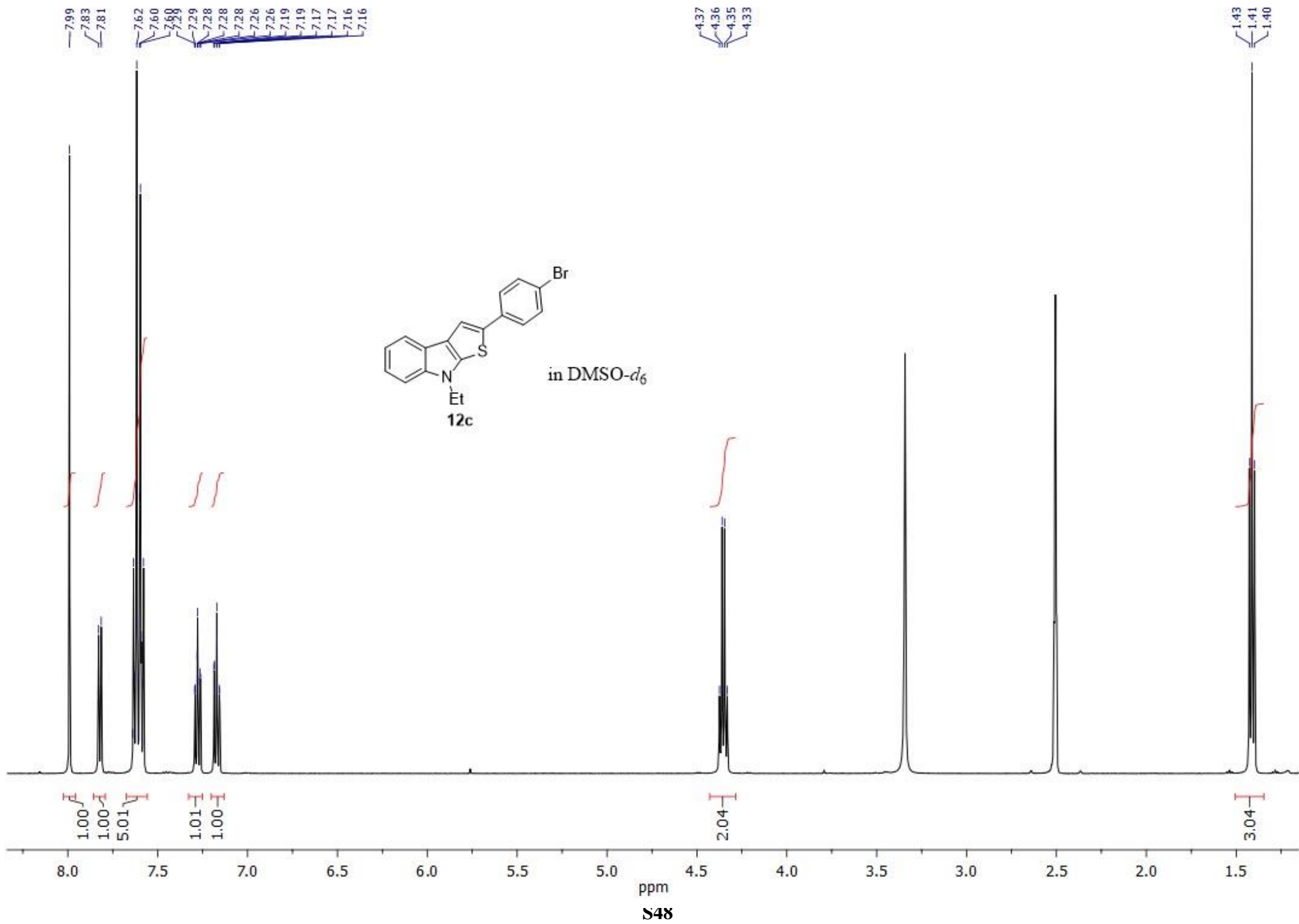






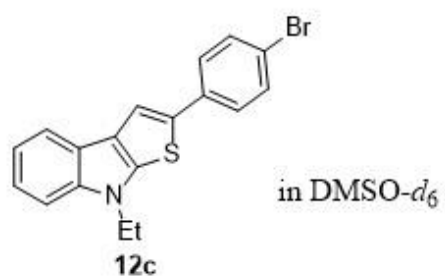






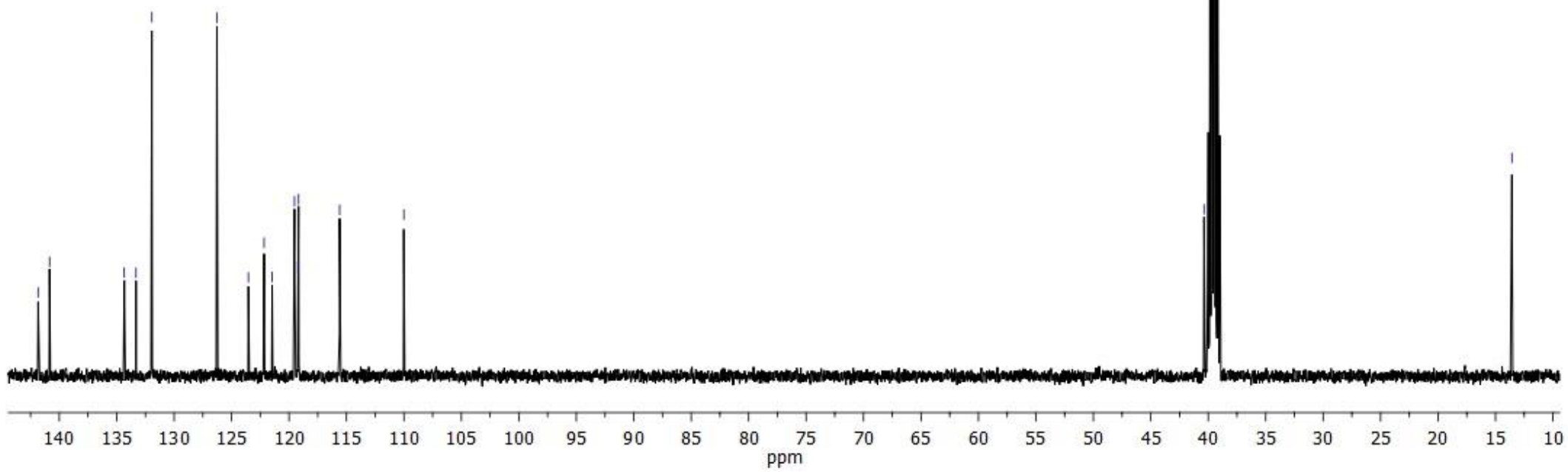


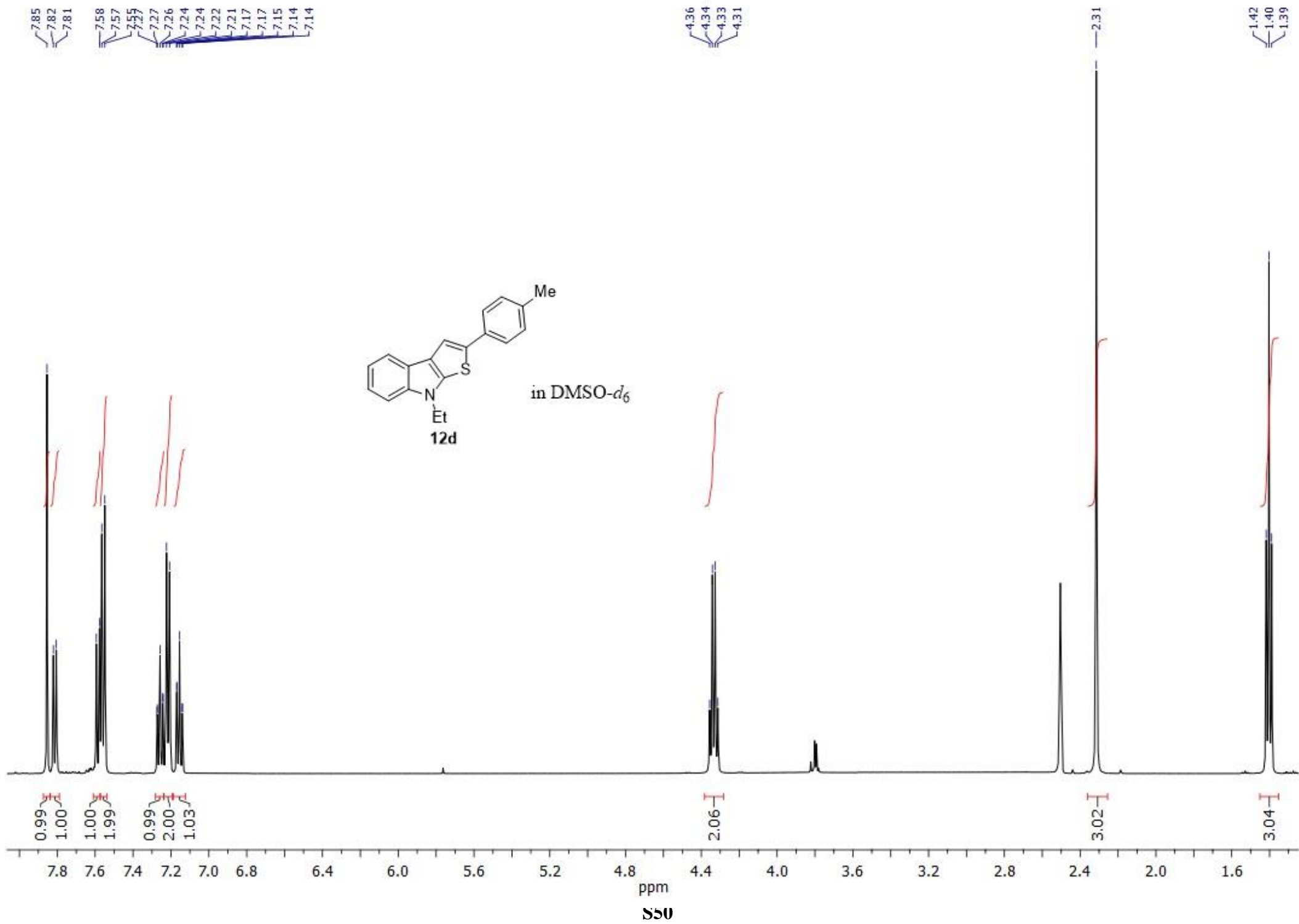
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140.8  
134.3  
133.3  
131.9  
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123.5  
122.2  
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119.2  
119.2  
115.6  
110.0

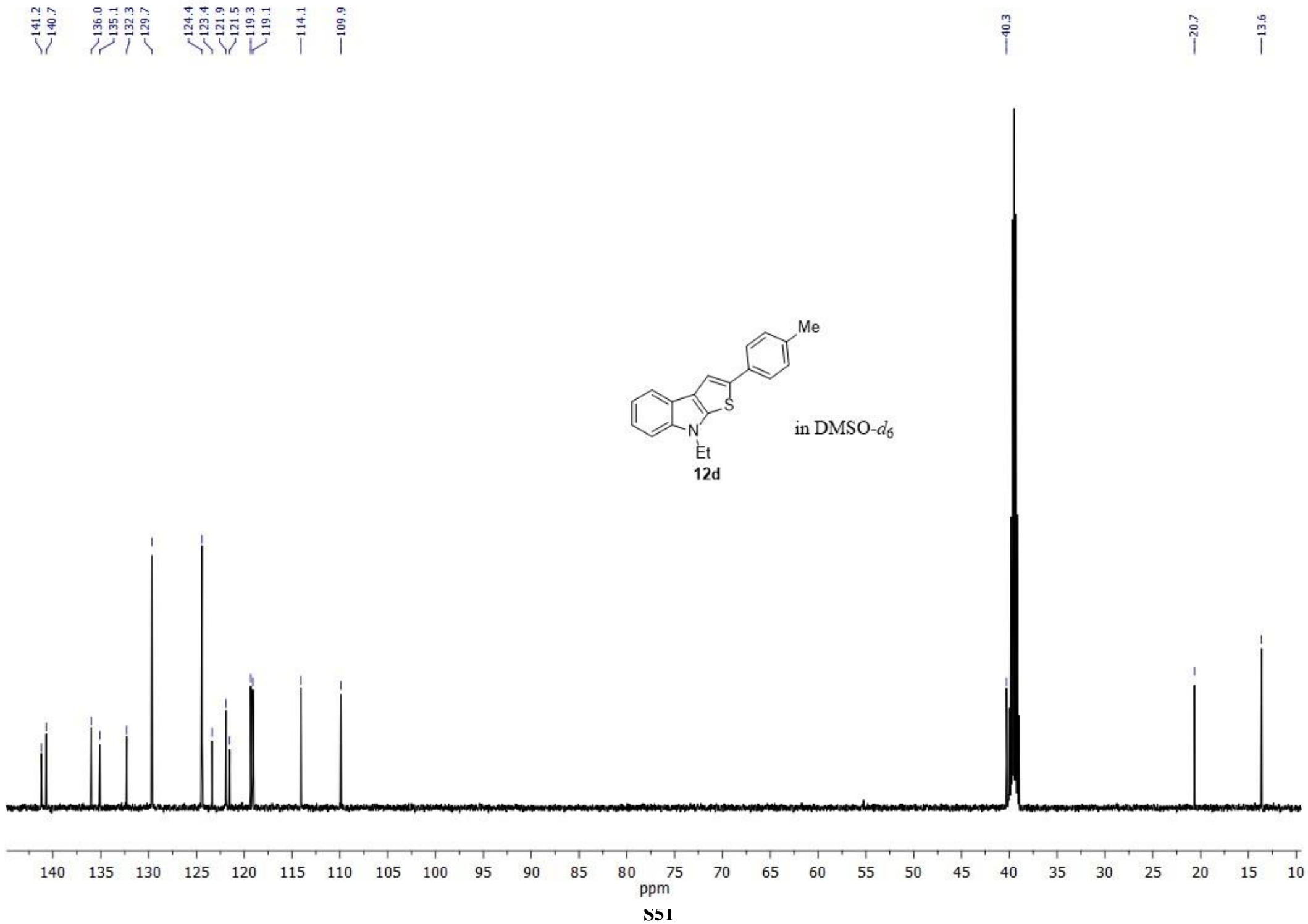


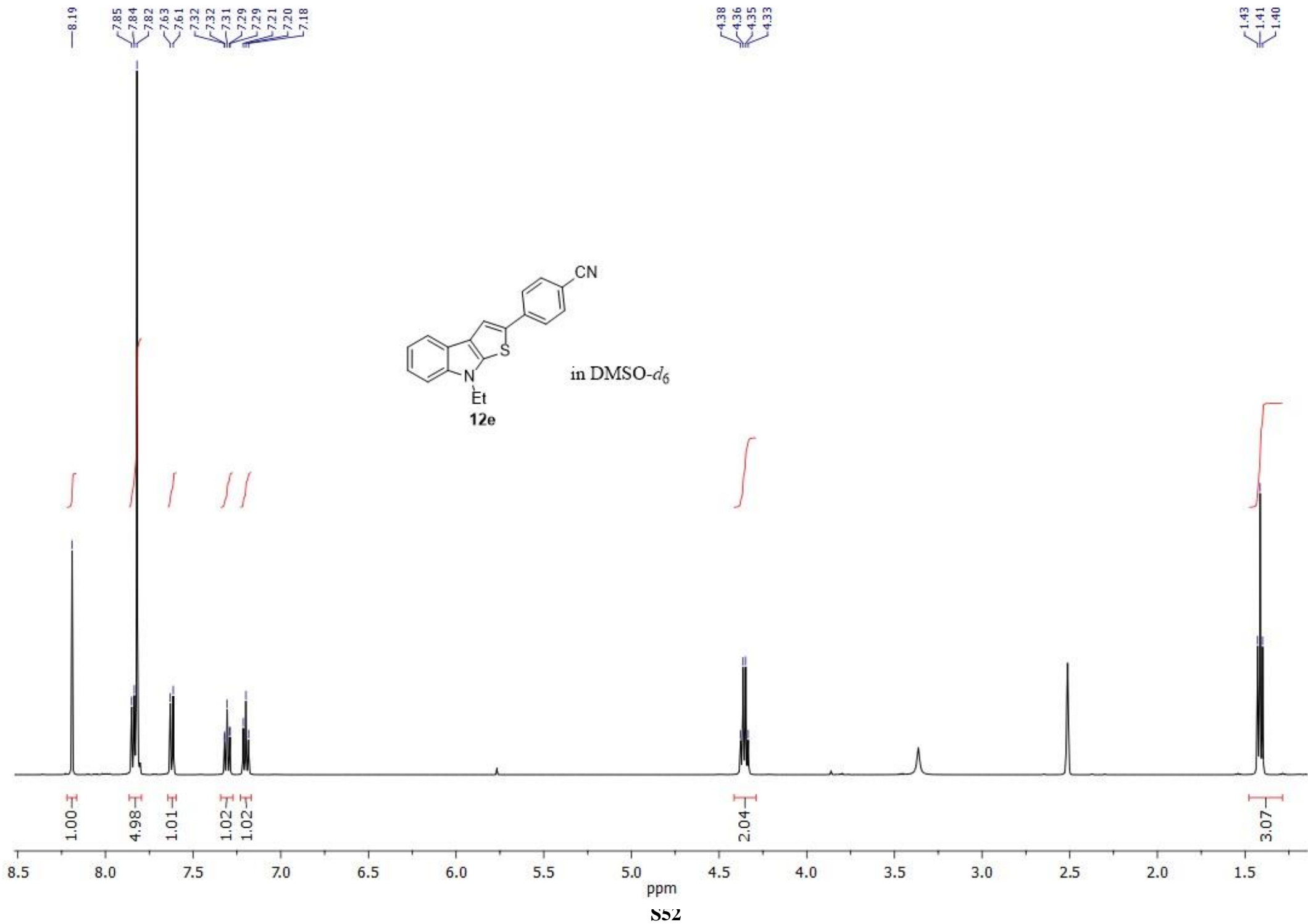
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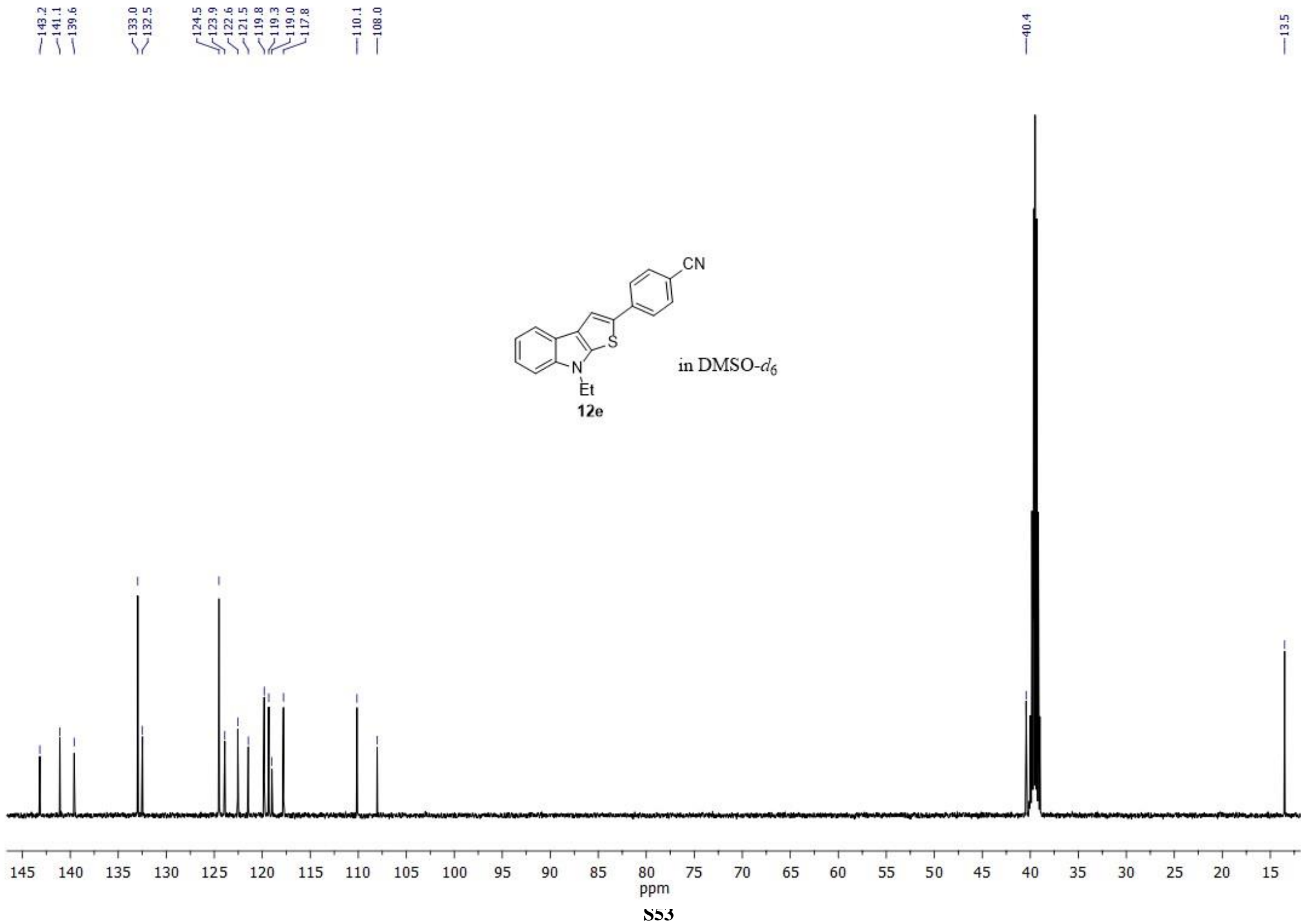
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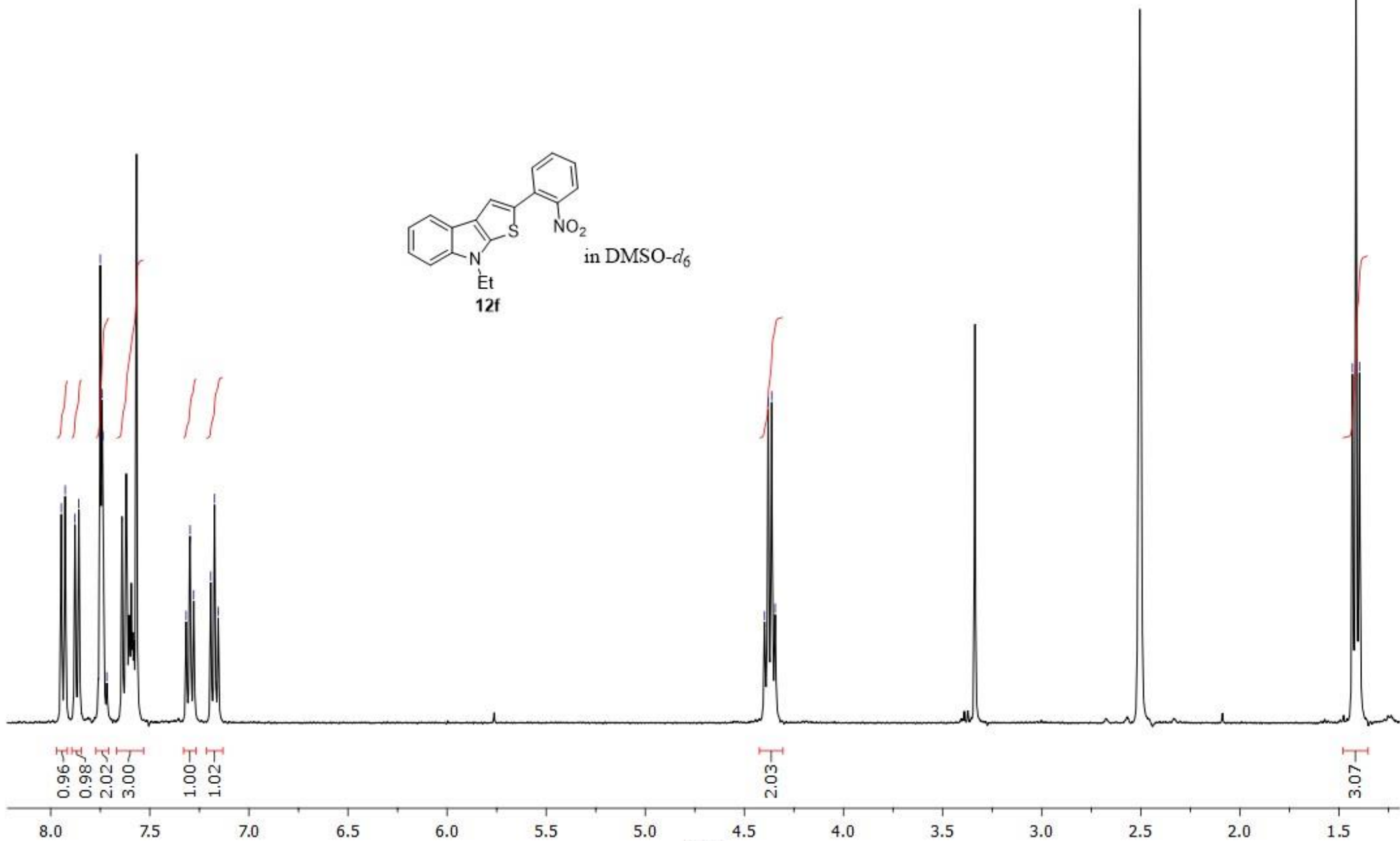
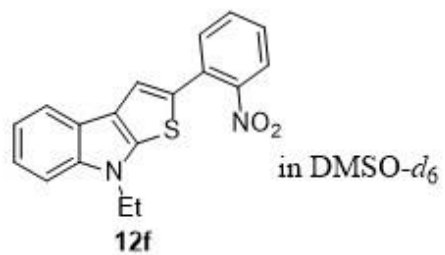




7.95  
7.93  
7.88  
7.86  
7.75  
7.74  
7.74  
7.72  
7.32  
7.30  
7.28  
7.19  
7.17  
7.16

4.40  
4.38  
4.36  
4.34

1.43  
1.41  
1.40



ppm

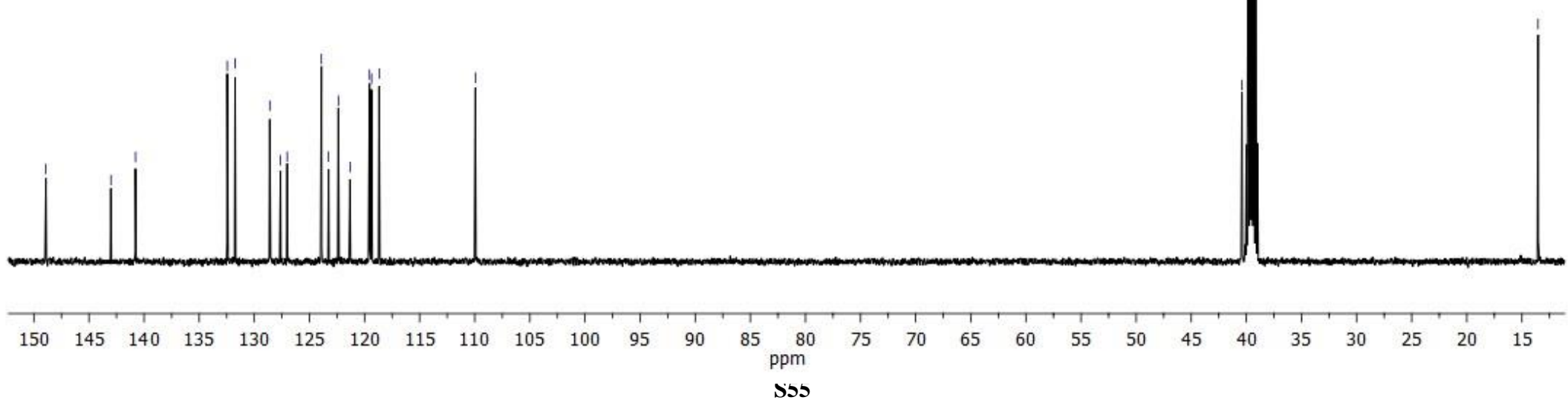
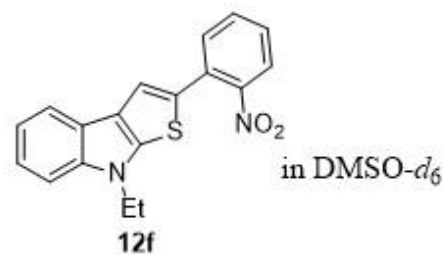
S54

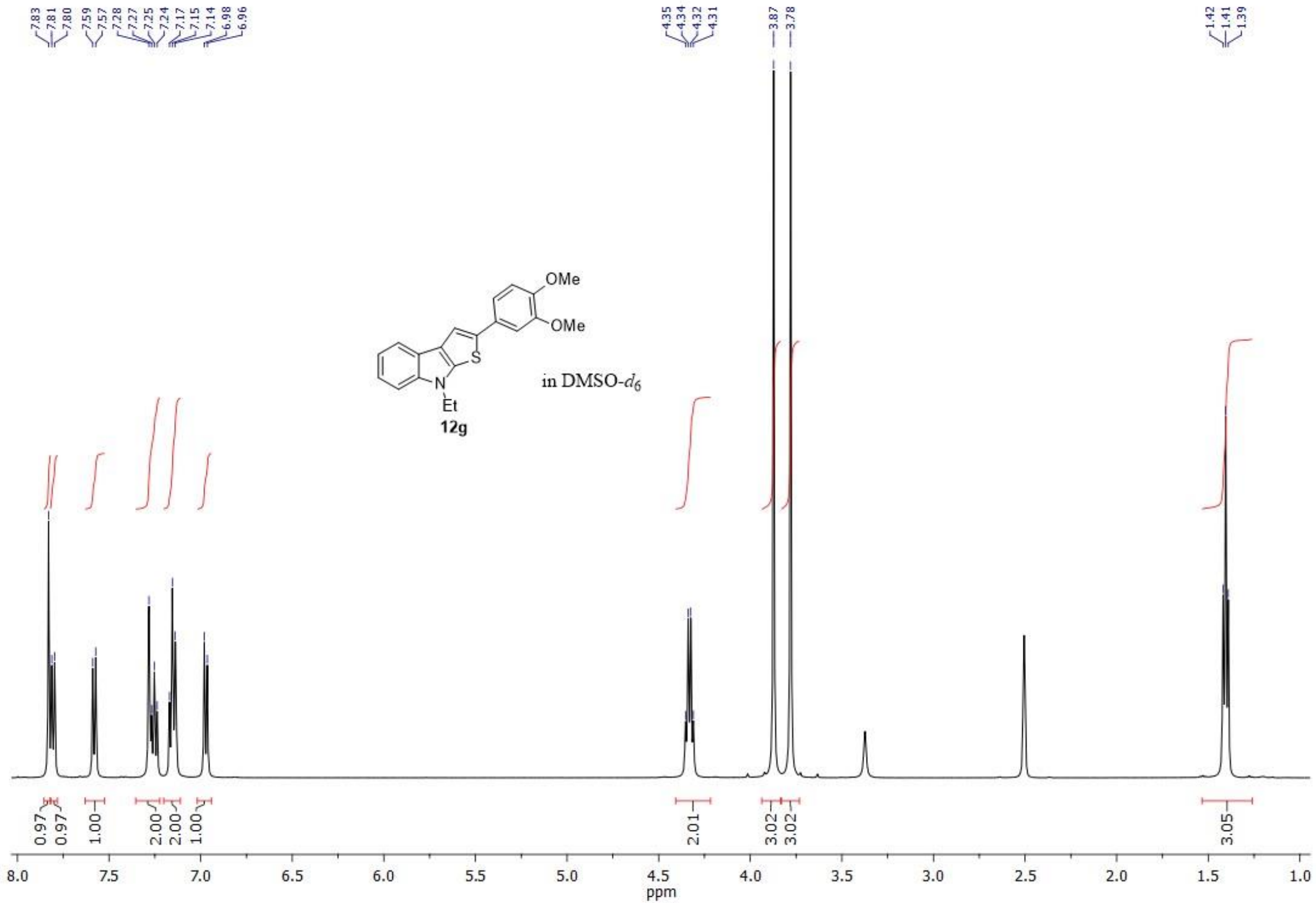
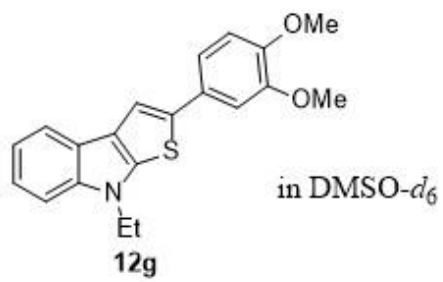
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—140.8  
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131.7  
128.6  
127.6  
127.0  
123.9  
123.3  
122.4  
121.3  
119.6  
118.7

—109.9

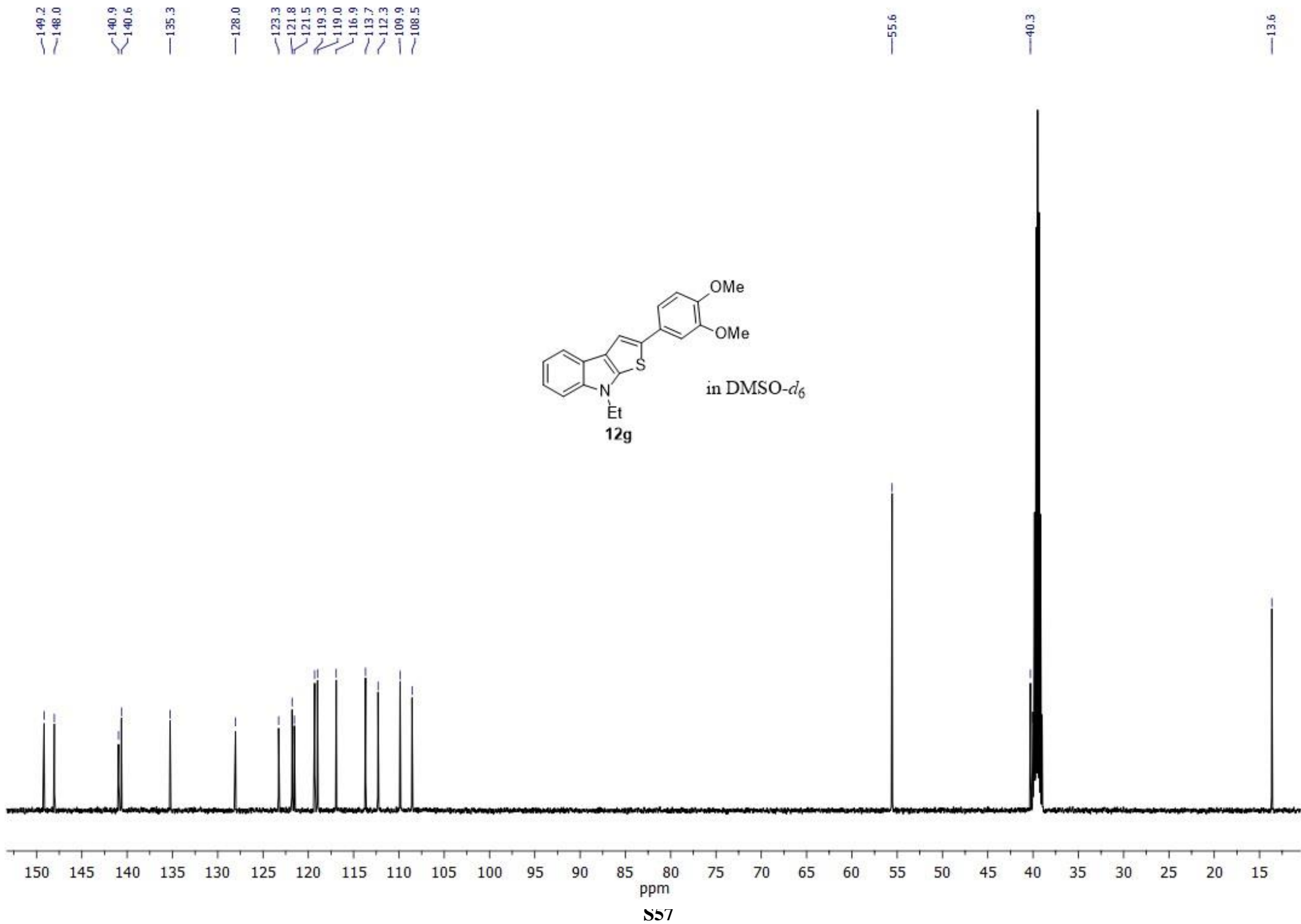
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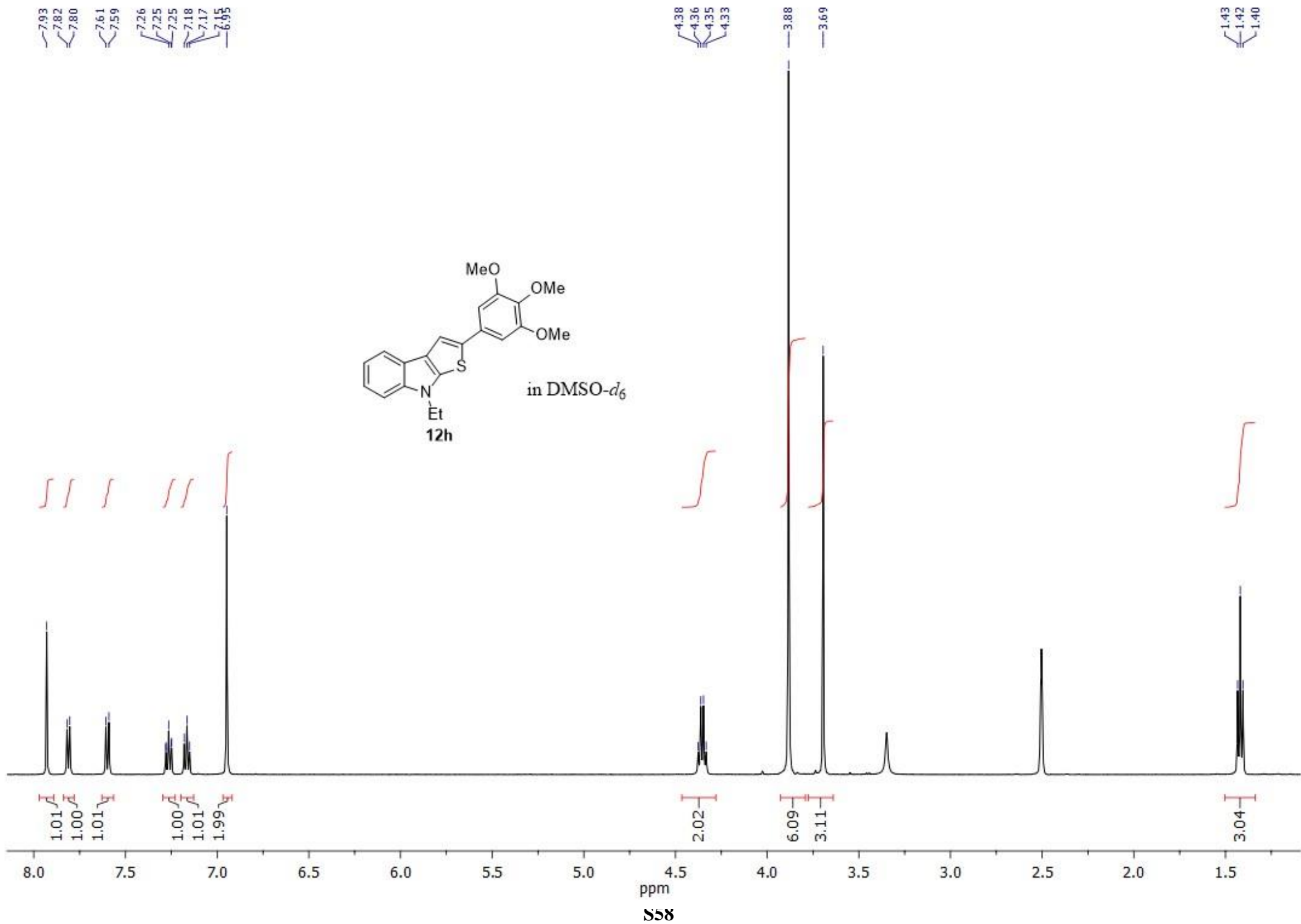
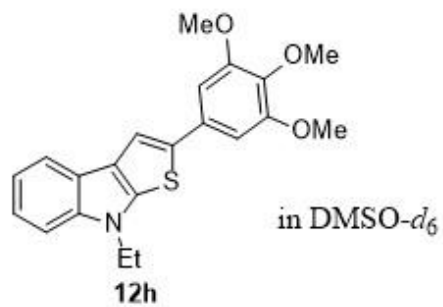
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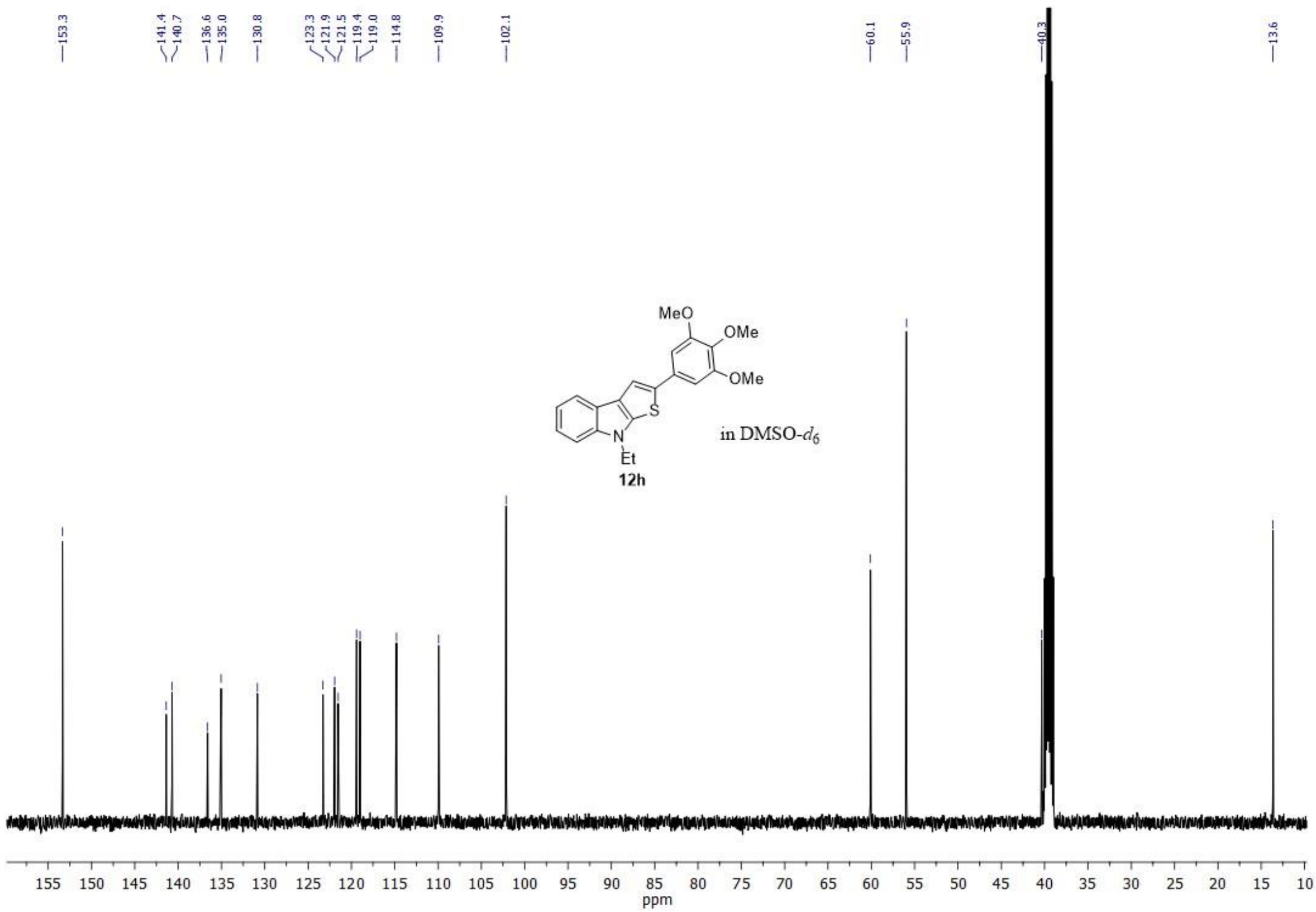


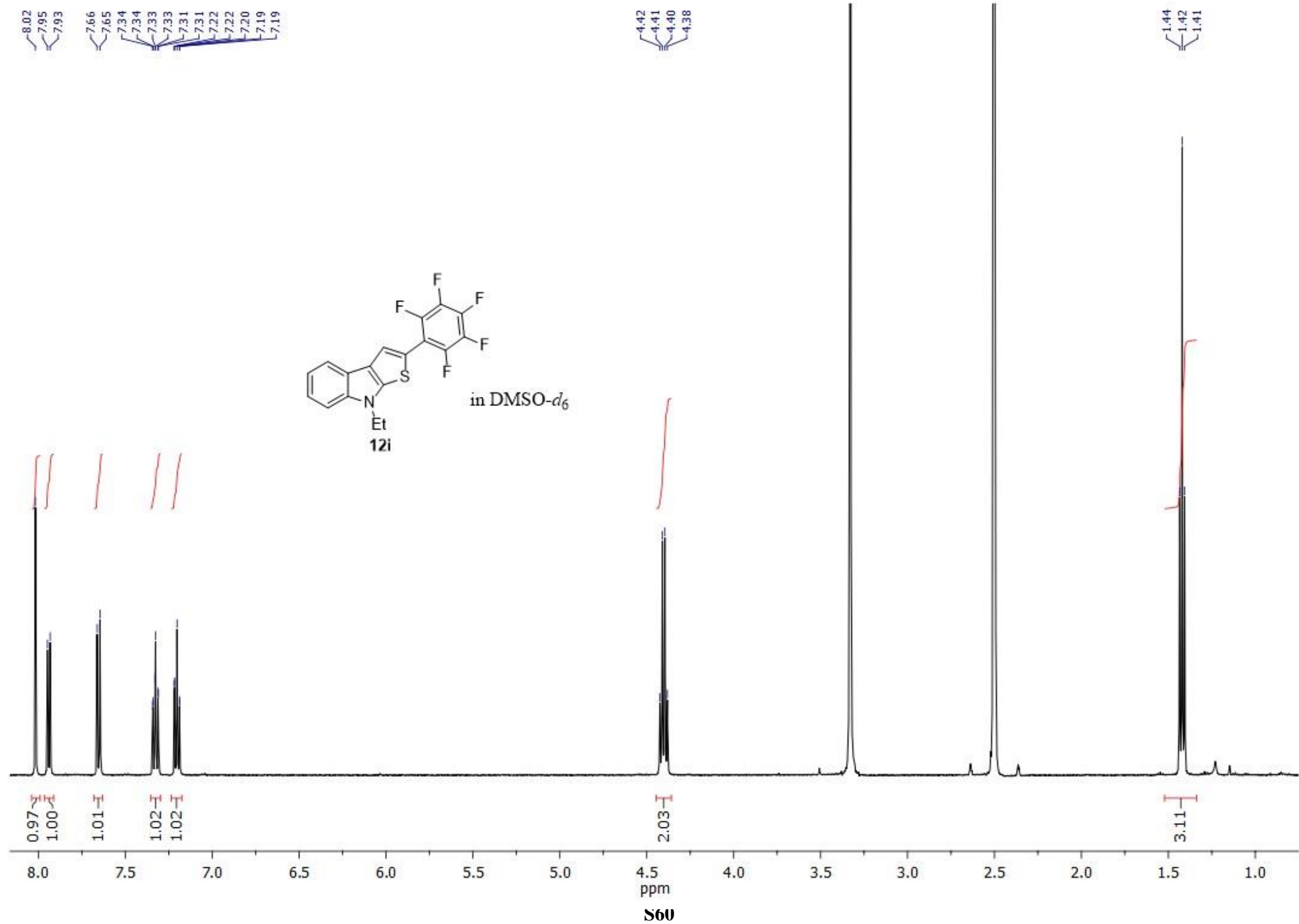










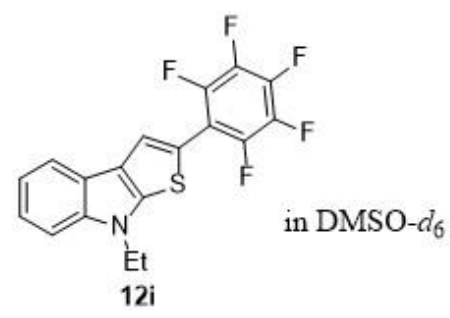
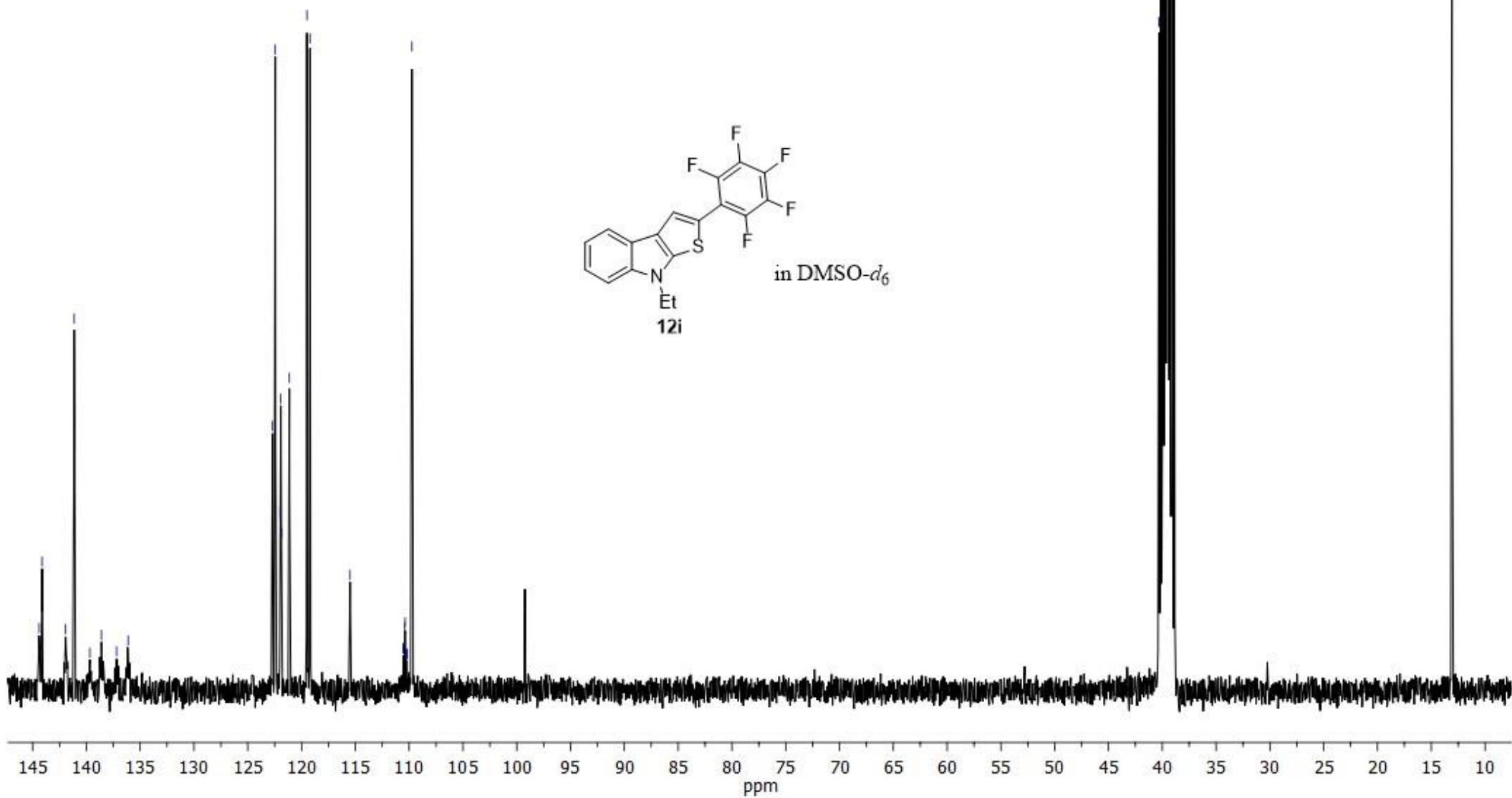


144.4  
144.1  
141.9  
141.1  
139.7  
138.6  
137.2  
136.1

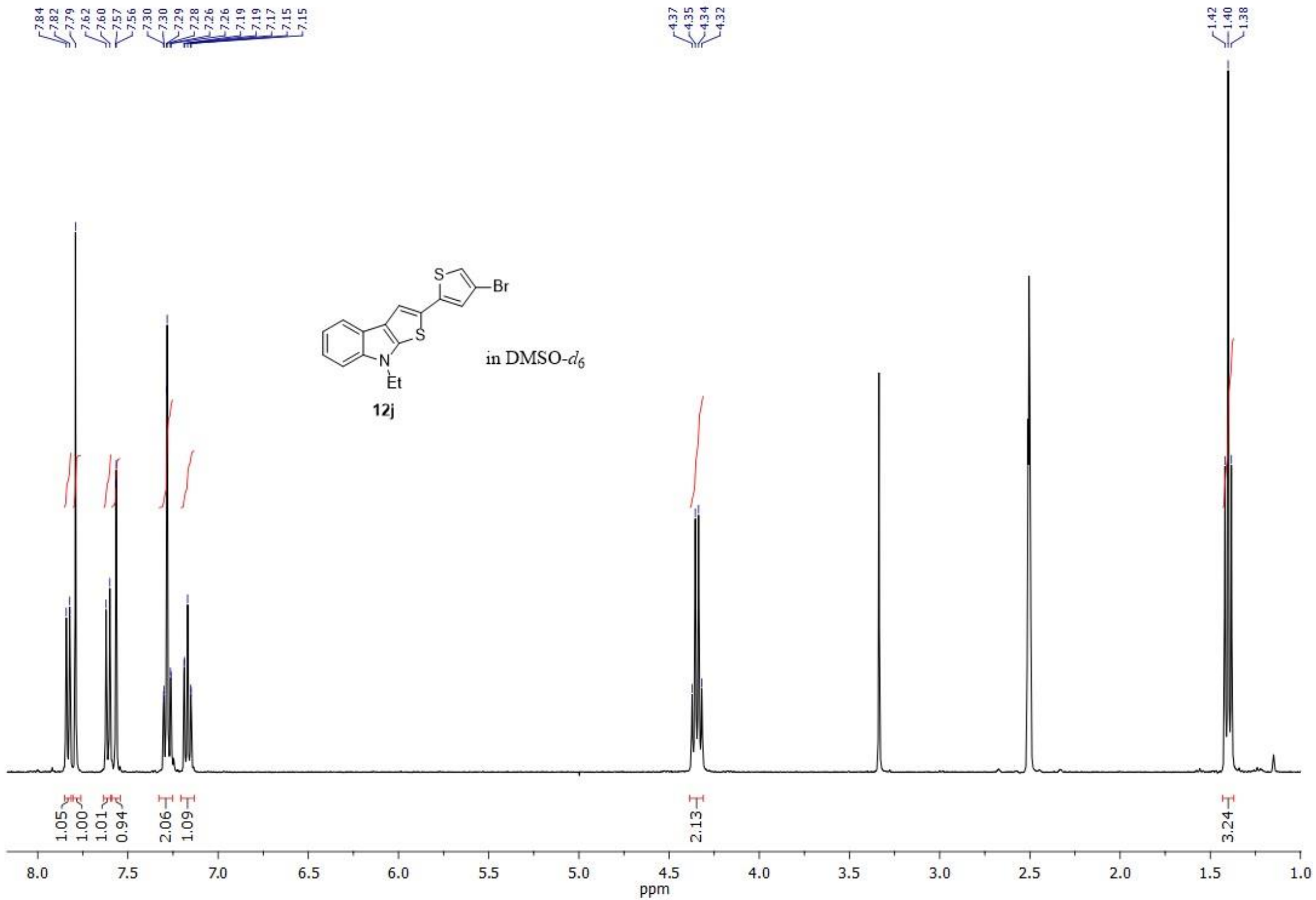
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122.4  
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121.9  
121.9  
121.1  
119.5  
119.2  
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110.5  
110.4  
110.4  
110.3  
110.2  
110.2  
109.7

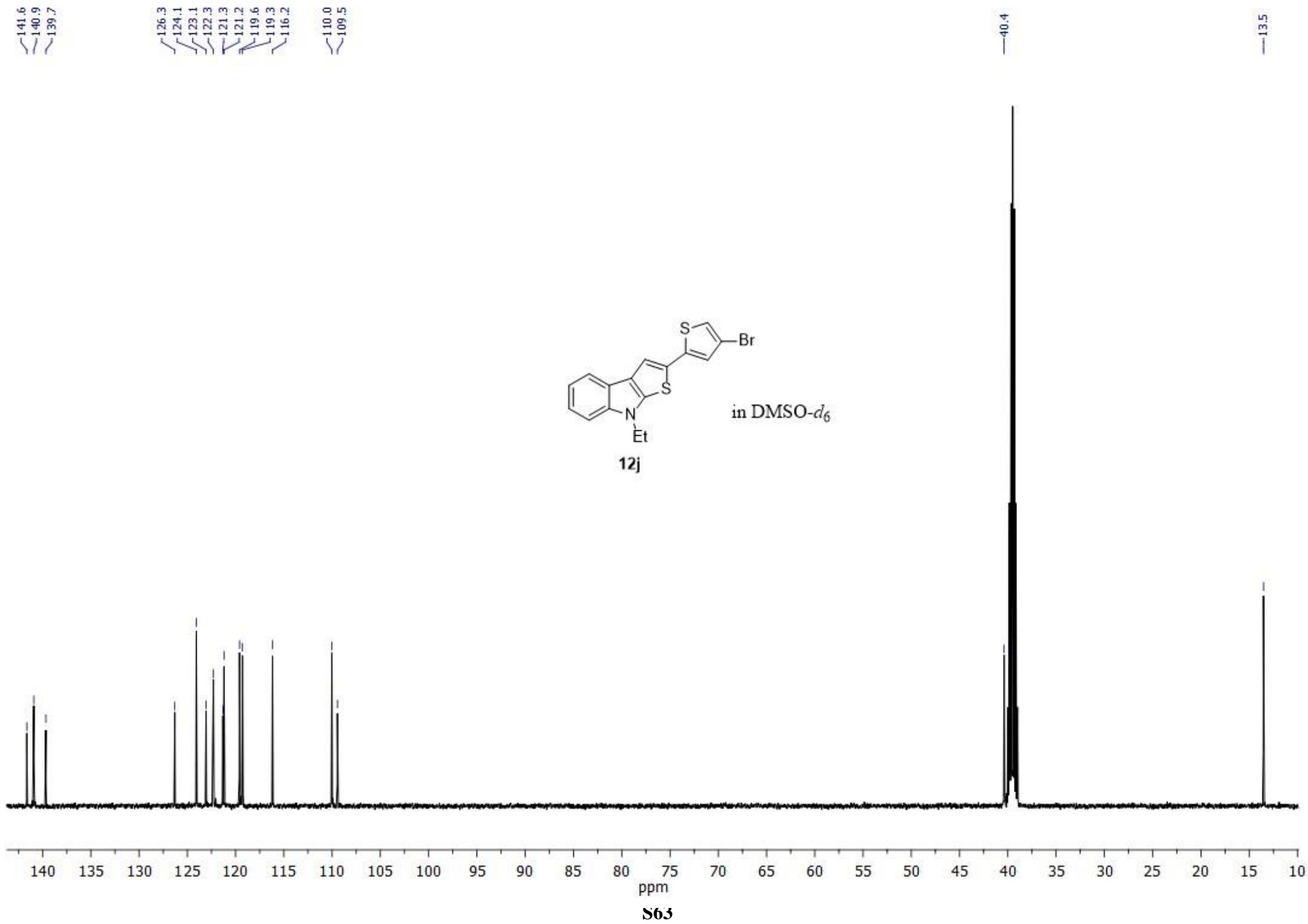
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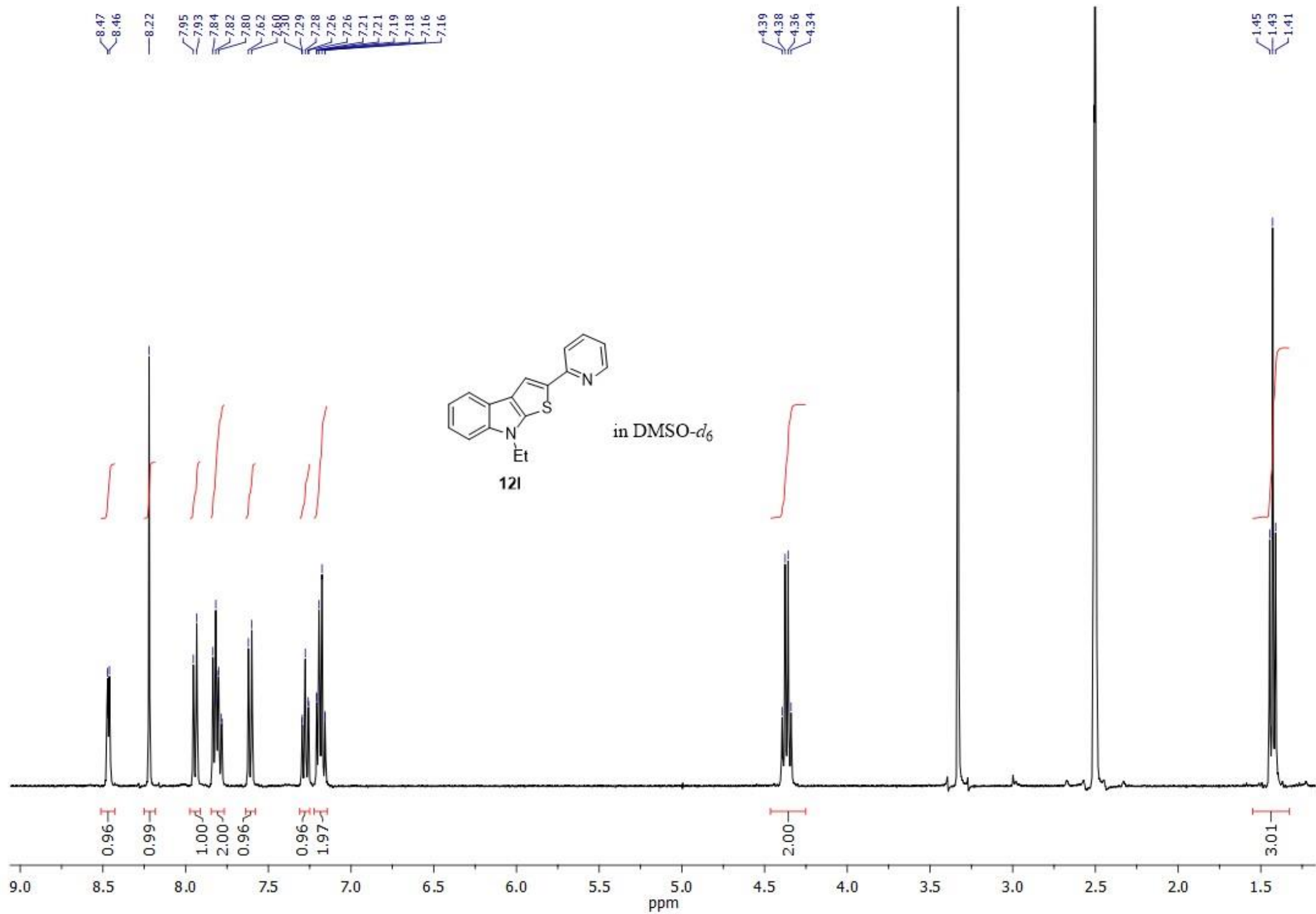
13.1



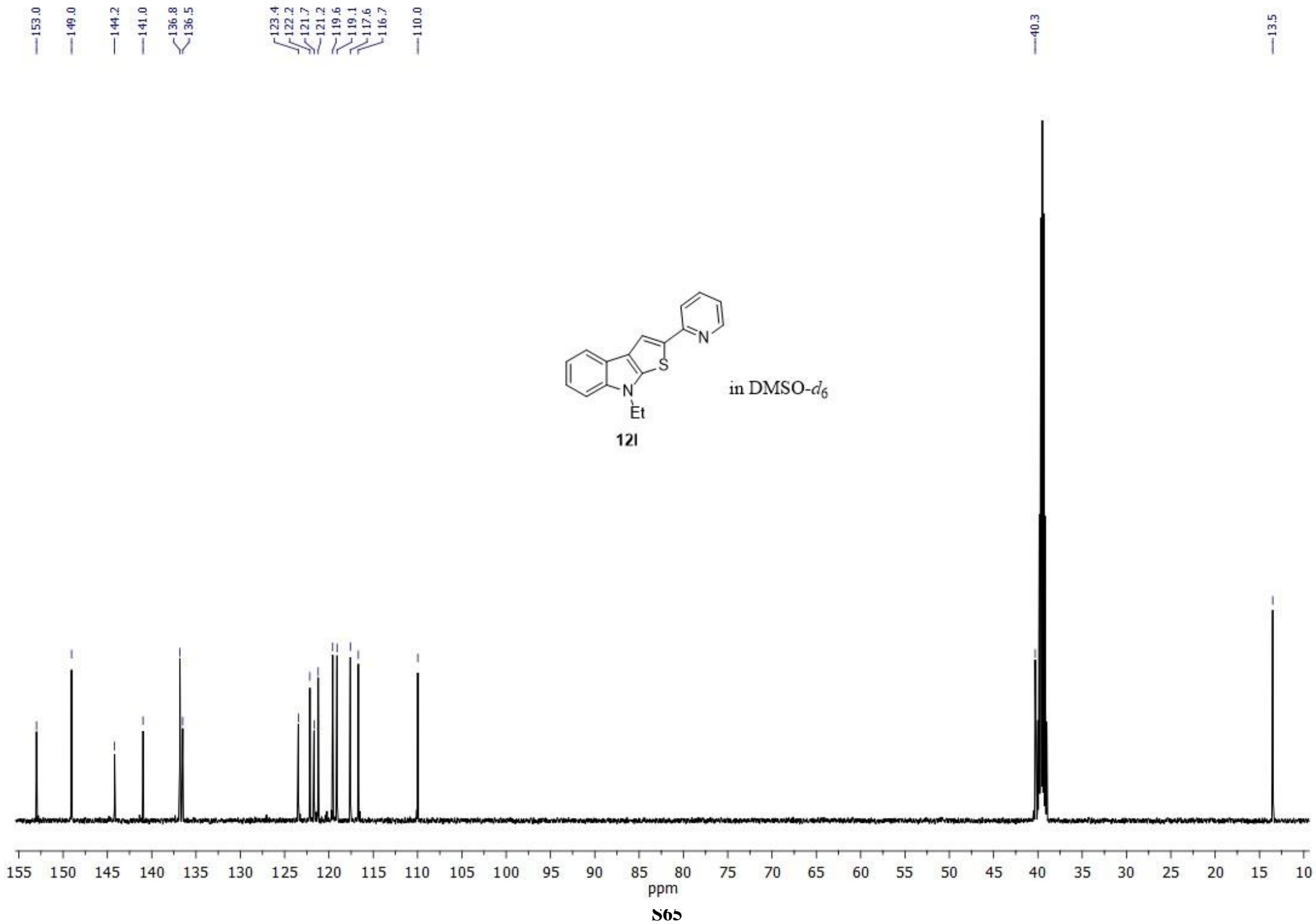
S01

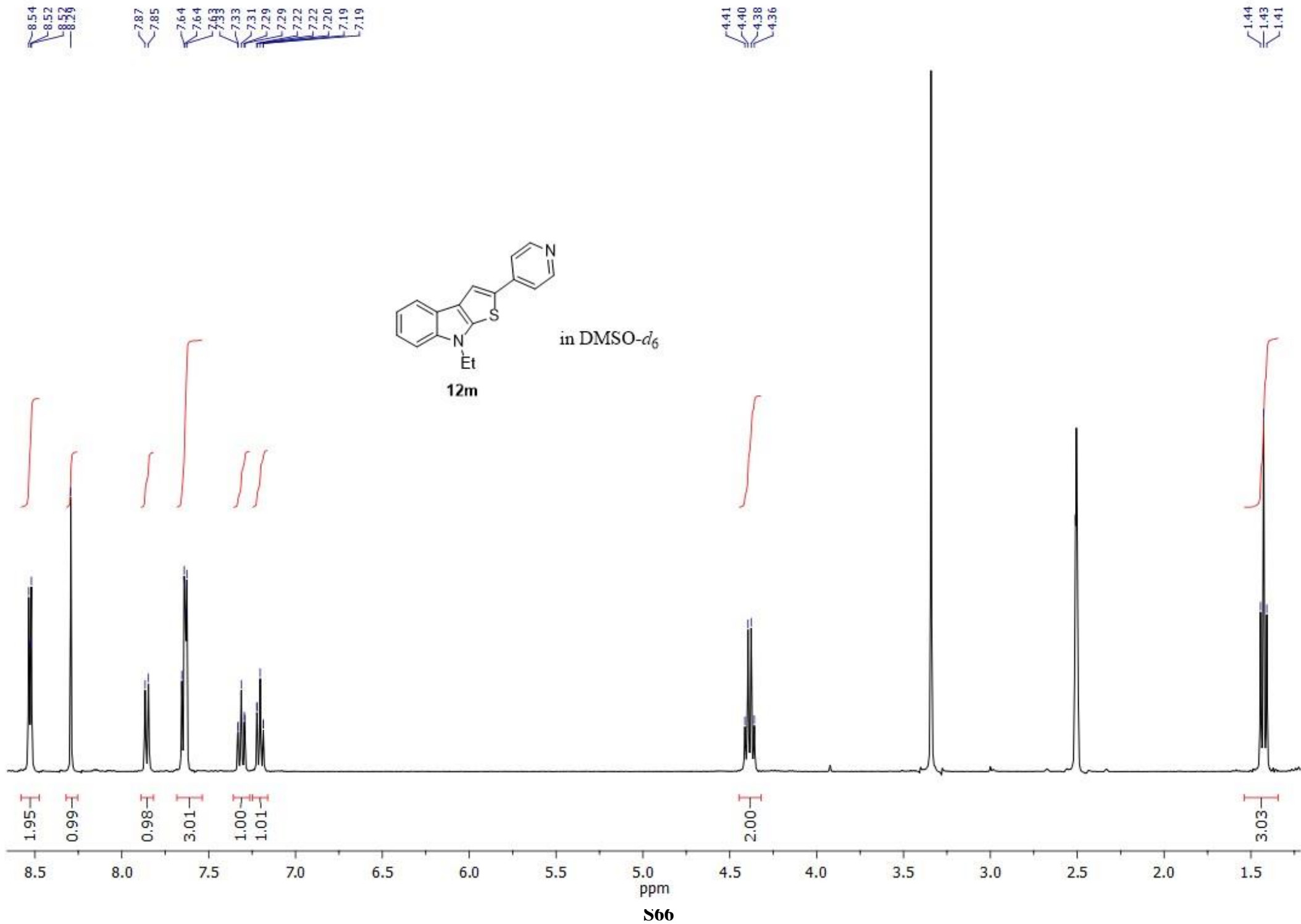


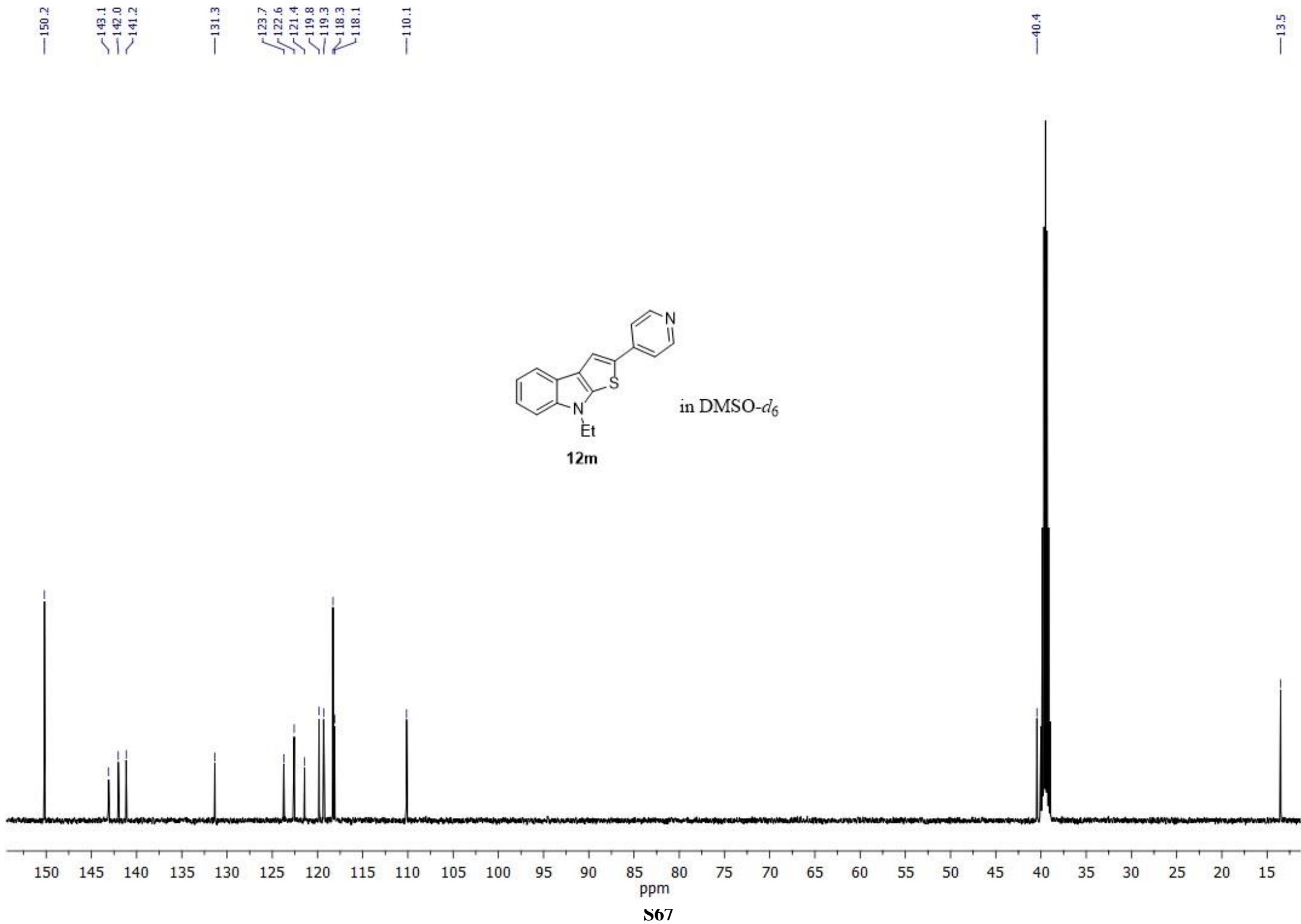


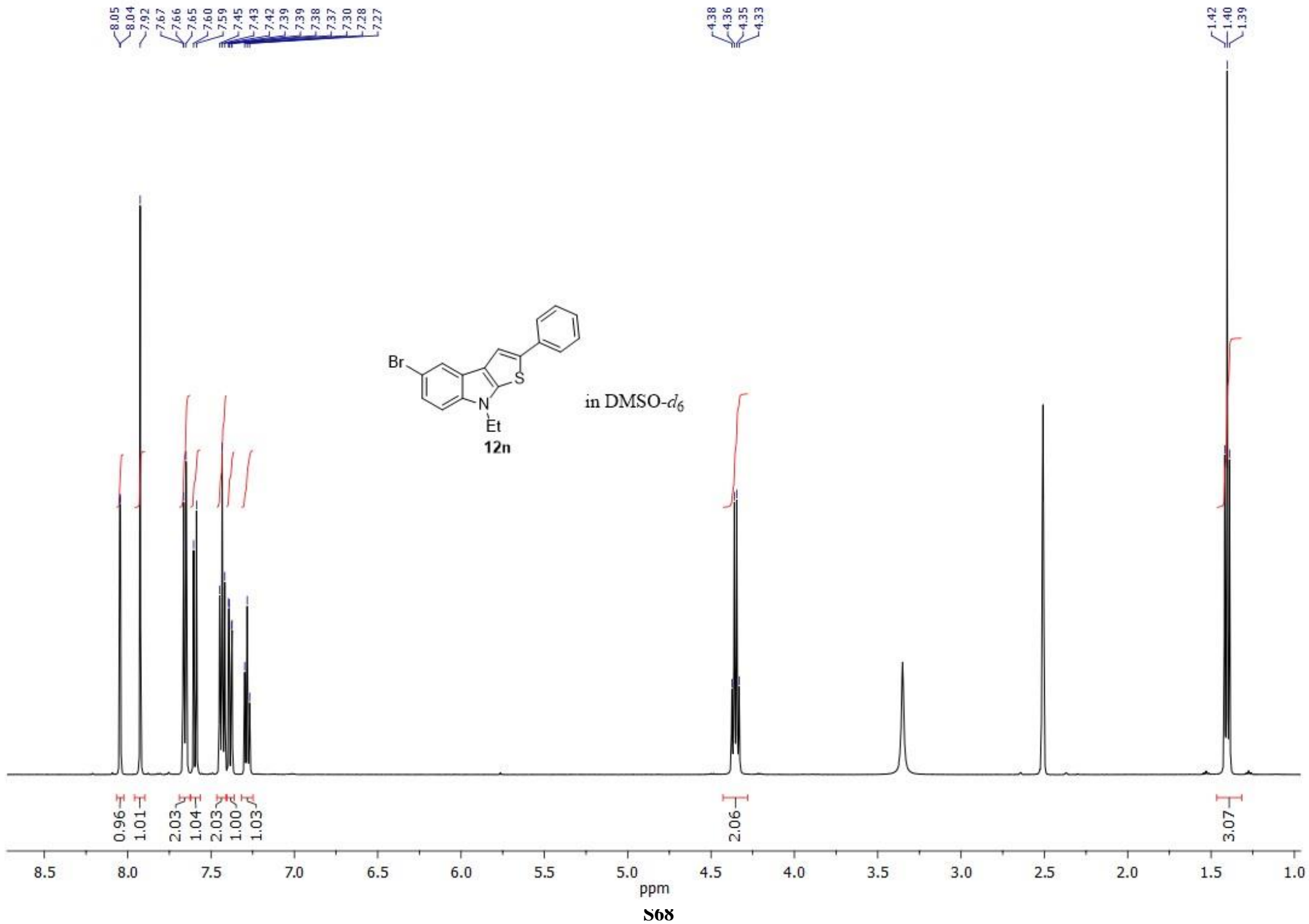




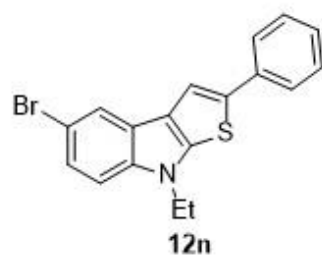








—142.7  
—139.5  
—135.5  
—134.8  
—129.2  
—126.9  
—124.6  
—124.3  
—123.0  
—122.7  
—121.5  
—114.7  
—111.9  
—111.8



in DMSO-*d*<sub>6</sub>

—40.6

—13.6

