

*Electronic Supplementary Information for*

**Organocatalytic asymmetric desymmetrization: efficient construction  
of spirocyclic oxindoles bearing a unique all-carbon quaternary  
stereogenic center *via* sulfa-Michael addition**

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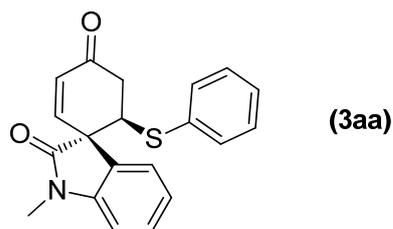
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## I. General Remarks

$^1\text{H}$  NMR spectra were recorded on a VARIAN Mercury 300 MHz or Bruker 400 MHz spectrometer in  $\text{CDCl}_3$ . Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quarte, m = multiple or unresolved, brs = broad single, coupling constant(s) in Hz, integration).  $^{13}\text{C}$  NMR spectra were recorded on a VARIAN Mercury 75 MHz or Bruker 100 MHz spectrometer in  $\text{CDCl}_3$  or in  $\text{DMSO}-d_6$ . Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm and with the internal hexadeuterodimethyl sulfoxide signal at 39.5 ppm as a standard. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Enantiomeric ratios were determined by HPLC, using a chiralpak AS-H column and chiralpak IC column with hexane and *i*-PrOH as solvents. Catalysts **I-VI** were prepared according to our previous report<sup>1</sup>. The spiro cyclohexadienone oxindoles<sup>2</sup> were prepared according to the literature procedure. The racemic adducts were attained by using DABCO as the catalyst. The absolute configuration of **3aj** was determined unequivocally according to the X-ray diffraction analysis of the derived oximes **4E**, and those of other adducts were deduced on the basis of these results.

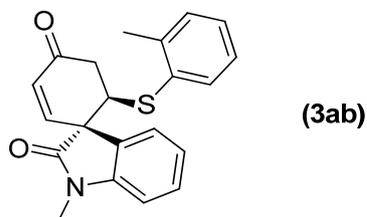
## II. General Procedure for Asymmetric *sulfa*-Michael Addition of Thiols to Spiro Cyclohexadienone Oxindoles Catalyzed by Organocatalysts (**I-d**)

Under argon atmosphere, spiro cyclohexadienone oxindole (0.020 mmol) and the catalyst **I-d** (8.1 mg, 0.012 mmol) were dissolved in 0.5 mL  $\text{CHCl}_3$ . After the mixture was cooled to  $-20\text{ }^\circ\text{C}$ , thiol (0.22 mmol) was added. The mixture was stirred at this temperature until the consumption of **1** (monitored by TLC analysis). Then, the solvent was removed and the residue was purified by flash chromatography on silica gel to give the corresponding product, which was then directly analyzed by HPLC to determine the enantiomeric excess.



**(1R,6R)-1'-methyl-6-(phenylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

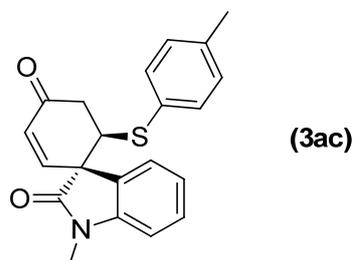
Yield (92%); Yellow solid; m.p. 47 °C;  $[\alpha]_D^{25} = +86$  (*c* 0.23, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.44 (t, *J* = 7.8 Hz, 1H), 7.29-7.21 (m, 6H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 10.2 Hz, 1H), 6.25 (d, *J* = 10.2 Hz, 1H), 4.22-4.15 (m, 1H), 3.28 (s, 3H), 3.02-2.98 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 196.6, 176.1, 146.3, 144.3, 133.3, 132.3, 130.1, 129.0, 128.1, 125.3, 125.0, 123.0, 108.9, 54.8, 49.9, 42.0, 26.7; IR (KBr) ν 3068, 3017, 1675, 1568, 1315, 1128, 819 765, 696; HRMS Calcd. For C<sub>20</sub>H<sub>17</sub>NO<sub>2</sub>S + H<sup>+</sup>: 336.1061, found: 336.1053. The product was analyzed by HPLC to determine the enantiomeric excess: 84% ee (Chiralpak AS-H, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min, λ = 230 nm); t<sub>r</sub> = 9.97 and 13.20 min.



**(1R,6R)-1'-methyl-6-(o-tolylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

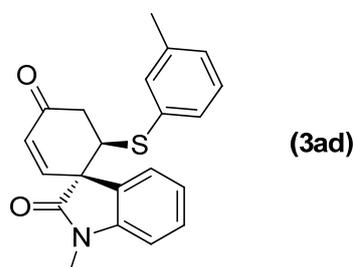
Yield (85%); Light yellow solid; m.p. 53 °C;  $[\alpha]_D^{25} = +105.7$  (*c* 0.49, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.44 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.16-7.11 (m, 4H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 9.9 Hz, 1H), 6.23 (d, *J* = 9.9 Hz, 1H), 4.11 (dd, *J*<sub>1</sub> = 4.8 Hz and *J*<sub>2</sub> = 13.2 Hz, 1H), 3.23 (s, 3H), 3.10-2.90 (m, 2H), 2.30 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 196.5, 175.9, 146.4, 144.1, 141.1, 130.4, 130.0, 128.5, 126.4, 125.3, 125.0, 123.0, 108.9, 54.6, 48.9, 41.8, 26.5, 20.8; IR (KBr) ν 3030, 2945, 1608, 1473, 1428, 1337, 1129, 818, 756, 699; HRMS Calcd. For C<sub>21</sub>H<sub>19</sub>NO<sub>2</sub>S + H<sup>+</sup>: 350.1218, found: 350.1209. The product was analyzed by HPLC to determine the enantiomeric excess: 83% ee

(Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 9.48$  and 14.13 min.



**(1R,6R)-1'-methyl-6-(p-tolylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

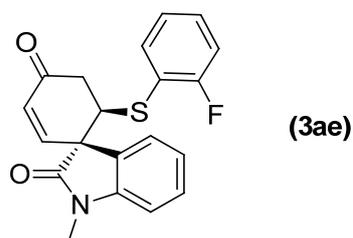
Yield (85%); Light yellow solid; m.p. 72 °C;  $[\alpha]_D^{25} = +113.4$  (*c* 0.52, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz)  $\delta$  7.43 (t, *J* = 7.8 Hz, 1H), 7.22-7.16 (m, 3H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.56 (d, *J* = 10.2 Hz, 1H), 6.23 (d, *J* = 10.2 Hz, 1H), 4.14-4.10 (m, 1H), 3.28 (s, 3H), 2.99-2.95 (m, 2H), 2.29 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz)  $\delta$  196.5, 176.0, 146.2, 144.1, 138.2, 133.7, 130.0, 129.9, 129.6, 128.4, 125.2, 124.9, 122.8, 108.8, 54.7, 50.0, 41.7, 26.5, 21.0; IR (KBr)  $\nu$  3068, 3013, 1702, 1601, 1319, 1120, 825, 778, 712; HRMS Calcd. For C<sub>21</sub>H<sub>19</sub>NO<sub>2</sub>S + H<sup>+</sup>: 350.1218, found: 350.1209. The product was analyzed by HPLC to determine the enantiomeric excess: 82% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 10.81$  and 17.16 min.



**(1R,6R)-1'-methyl-6-(m-tolylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

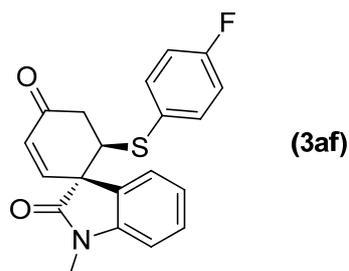
Yield (83%); White solid; m.p. 126 °C;  $[\alpha]_D^{25} = +109.7$  (*c* 0.55, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz)  $\delta$  7.43 (t, *J* = 7.2 Hz, 1H), 7.21-7.10 (m, 6H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.56 (d, *J* = 9.9 Hz, 1H), 6.23 (d, *J* = 9.9 Hz, 1H), 4.17 (t, *J* = 8.1 Hz,

1H), 3.27 (s, 3H), 2.99-2.96 (m, 2H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta$  196.6, 176.0, 146.2, 144.2, 138.7, 133.8, 131.6, 130.0, 129.9, 128.9, 128.7, 125.2, 125.0, 122.9, 108.8, 107.1, 54.7, 49.5, 41.8, 26.6, 21.1; IR (KBr)  $\nu$  3072, 3031, 1698, 1574, 1332, 1173, 809, 747, 687; HRMS Calcd. For  $\text{C}_{21}\text{H}_{19}\text{NO}_2\text{S} + \text{H}^+$ : 350.1219, found: 350.1209. The product was analyzed by HPLC to determine the enantiomeric excess: 82% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min,  $\lambda$  = 254 nm);  $t_r$  = 10.17 and 14.56 min.



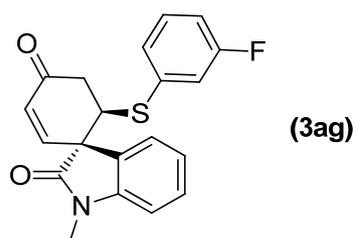
**(1R,6R)-6-((2-fluorophenyl)thio)-1'-methylspiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

Yield (77%); White solid; m.p. 51 °C;  $[\alpha]_D^{25} = +132.4$  (*c* 0.54,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta$  7.44 (t,  $J = 7.8$  Hz, 1H), 7.27-7.21 (m, 3H), 7.14-6.96 (m, 4H), 6.56 (d,  $J = 9.9$  Hz, 1H), 6.24 (d,  $J = 9.9$  Hz, 1H), 4.21 (t,  $J = 9.3$  Hz, 1H), 3.25 (s, 3H), 3.03 (d,  $J = 9.6$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 100 MHz)  $\delta$  196.3, 175.7, 162.3 (d,  $J = 24.6$  Hz), 146.3, 144.2, 135.8, 132.4, 130.6 (d,  $J = 8.0$  Hz), 127.8, 125.0, 124.5 (d,  $J = 3.9$  Hz), 123.2, 123.0, 119.4, 119.2, 160.0 (d,  $J = 22.9$  Hz), 108.9, 54.8, 49.1, 41.8, 26.6; IR (KBr)  $\nu$  3032, 3013, 1701, 1568, 1437, 1255, 1214, 1108, 818, 754, 699; HRMS Calcd. For  $\text{C}_{20}\text{H}_{16}\text{NO}_2\text{FS} + \text{H}^+$ : 354.0970, found: 354.0958. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min,  $\lambda$  = 254 nm);  $t_r$  = 10.54 and 21.55 min.



**(1R,6R)-6-((4-fluorophenyl)thio)-1'-methylspiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

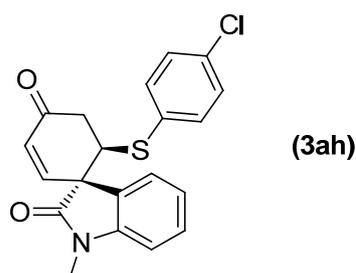
Yield (85%); White solid; m.p. 42 °C;  $[\alpha]_D^{25} = +115.5$  (*c* 0.54, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.44 (t, *J* = 7.5 Hz, 1H), 7.27-7.19 (m, 3H), 7.13-7.08 (m, 1H), 7.00-6.91 (m, 3H), 6.57 (d, *J* = 9.9 Hz, 1H), 6.24 (d, *J* = 9.9 Hz, 1H), 4.09 (dd, *J*<sub>1</sub> = 6.9 Hz and *J*<sub>2</sub> = 11.7 Hz, 1H), 3.30 (m, 3H), 3.00-2.95 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 125 MHz) δ 196.3, 176.1, 162.8 (d, *J* = 247.6 Hz), 146.2, 144.2, 136.0 (d, *J* = 8.5 Hz), 130.1, 127.2 (d, *J* = 2.6 Hz), 125.2, 125.0, 116.1 (d, *J* = 21.9 Hz), 109.0, 54.8, 50.4, 41.8, 26.6; IR (KBr) ν 3057, 3007, 1687, 1591, 1487, 1136, 1074, 827, 765, 694; HRMS Calcd. For C<sub>20</sub>H<sub>16</sub>NO<sub>2</sub>FS + H<sup>+</sup>: 354.0968, found: 354.0958. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm); t<sub>r</sub> = 9.04 and 12.45 min.



**(1R,6R)-6-((3-fluorophenyl)thio)-1'-methylspiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

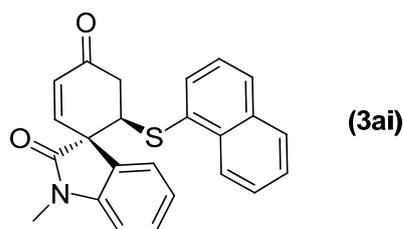
Yield (84%); Yellow solid; m.p. 46 °C;  $[\alpha]_D^{25} = +112$  (*c* 0.21, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.45 (t, *J* = 7.8 Hz, 1H), 7.23-7.20 (m, 2H), 7.14-7.09 (m, 2H), 7.00-6.92 (m, 3H), 6.59 (d, *J* = 9.9 Hz, 1H), 6.26 (d, *J* = 10.2 Hz, 1H), 4.25-4.19 (m, 1H), 3.28 (s, 3H), 3.03-2.99 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 125 MHz) δ 196.2, 176.0, 162.4 (d, *J* = 248.1 Hz), 146.2, 144.3, 134.5, 134.4, 130.2, 128.5, 125.1, 125.0,

123.1, 119.7 (d,  $J = 21.9$  Hz), 115.2 (d,  $J = 20.6$  Hz), 109.0, 54.7, 49.7, 41.9, 26.7; IR (KBr)  $\nu$  3046, 2981, 1693, 1582, 1502, 1227, 1216, 1113, 830, 767, 685; HRMS Calcd. For  $C_{20}H_{16}NO_2FS + H^+$ : 354.0966, found: 354.0958. The product was analyzed by HPLC to determine the enantiomeric excess: 85% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 9.82$  and 11.53 min.



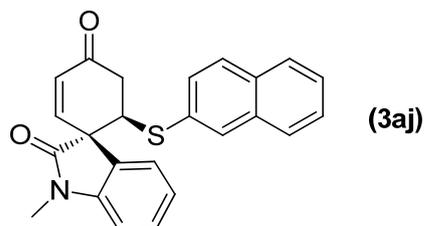
**(1*R*,6*R*)-6-((4-chlorophenyl)thio)-1'-methylspiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

Yield (95%); White solid; m.p. 51 °C;  $[\alpha]_D^{25} = +140.3$  ( $c$  0.80,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz)  $\delta$  7.45 (t,  $J = 7.8$  Hz, 1H), 7.22 (m, 5H), 7.11 (t,  $J = 7.5$  Hz, 1H), 6.98 (d,  $J = 8.7$  Hz, 1H), 6.58 (d,  $J = 9.9$  Hz, 1H), 6.25 (d,  $J = 9.9$  Hz, 1H), 4.14 (dd,  $J_1 = 6.6$  Hz and  $J_2 = 12.3$  Hz, 1H), 3.28 (s, 3H), 3.00-2.96 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , TMS, 75 MHz)  $\delta$  196.2, 176.0, 146.2, 144.2, 134.7, 134.4, 130.7, 130.1, 129.2, 125.2, 125.1, 123.1, 109.0, 54.8, 50.0, 41.8, 26.7; IR (KBr)  $\nu$  3048, 2940, 1617, 1484, 1472, 1254, 1103, 1054, 823, 751, 695; HRMS Calcd. For  $C_{20}H_{16}NO_2SCL + H^+$ : 370.0670, found: 370.0670. The product was analyzed by HPLC to determine the enantiomeric excess: 86% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 10.78$  and 14.50 min.



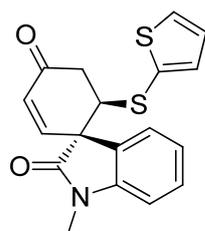
**(1*R*,6*R*)-1'-methyl-6-(naphthalen-1-ylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

Yield (86%); White solid; m.p. 70 °C;  $[\alpha]_D^{25} = +87.1$  (*c* 0.77, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 8.23 (d, *J* = 8.1 Hz, 1H), 7.81-7.79 (m, 2H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.55-7.25 (m, 6H), 7.18-7.13 (m, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 9.9 Hz, 1H), 6.21 (d, *J* = 9.9 Hz, 1H), 4.26 (dd, *J*<sub>1</sub> = 4.8 Hz and *J*<sub>2</sub> = 13.5 Hz, 1H), 3.16 (s, 3H), 3.06-2.85 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 196.3, 175.8, 146.4, 144.1, 134.2, 134.1, 133.9, 129.9, 129.6, 129.0, 128.4, 126.8, 126.2, 125.5, 125.4, 125.3, 125.0, 122.9, 109.0, 54.6, 49.5, 41.6, 26.4; IR (KBr) ν 3057, 3016, 1698, 1591, 1482, 1351, 1137, 817, 750, 685; HRMS Calcd. For C<sub>24</sub>H<sub>19</sub>NO<sub>2</sub>S + H<sup>+</sup>: 386.1218, found: 386.1209. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm); t<sub>r</sub> = 11.73 and 17.38 min.



**(1R,6R)-1'-methyl-6-(naphthalen-2-ylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

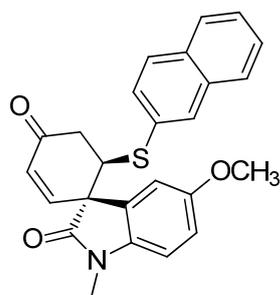
Yield (89%); White solid; m.p. 61 °C;  $[\alpha]_D^{25} = +152.9$  (*c* 0.77, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.79-7.72 (m, 4H), 7.49-7.47 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.26-7.22 (m, 1H), 7.15-7.10 (m, 1H), 6.99 (d, *J* = 6.9 Hz, 1H), 6.59 (d, *J* = 9.9 Hz, 1H), 6.25 (d, *J* = 9.9 Hz, 1H), 4.32 (t, *J* = 9.6 Hz, 1H) 3.25 (s, 3H), 3.04-3.01 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 196.4, 176.1, 146.3, 144.2, 133.2, 132.6, 130.2, 130.1, 130.0, 129.2, 128.7, 127.6, 127.5, 126.6, 125.3, 125.1, 123.0, 109.0, 54.8, 49.3, 41.8, 26.6; IR (KBr) ν 3054, 3018, 1710, 1580, 1472, 1352, 1140, 823, 756, 691; HRMS Calcd. For C<sub>24</sub>H<sub>19</sub>NO<sub>2</sub>S + H<sup>+</sup>: 386.1217, found: 386.1209. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm); t<sub>r</sub> = 13.66 and 18.92 min.



(3ak)

**(1*R*,6*R*)-1'-methyl-6-(thiophen-2-ylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

Yield (83%); Yellow solid; m.p. 53 °C;  $[\alpha]_D^{25} = +99$  (*c* 0.18, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.44 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 4.5 Hz, 1H), 7.18-7.06 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.90-6.86 (m, 2H), 6.56 (d, *J* = 9.9 Hz, 1H), 6.24 (d, *J* = 9.9 Hz, 1H), 4.02 (dd, *J*<sub>1</sub> = 5.7 Hz and *J*<sub>2</sub> = 12.6 Hz, 1H), 3.34 (s, 3H), 3.10-2.92 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 196.4, 175.9, 146.1, 144.3, 136.1, 131.1, 130.1, 129.6, 127.6, 125.2, 124.9, 123.0, 109.0, 54.6, 51.6, 41.3, 26.7; IR (KBr) ν 3034, 3087, 1614, 1527, 1432, 1325, 1134, 864, 826, 743, 690; HRMS Calcd. For C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>S<sub>2</sub> + H<sup>+</sup>: 342.0624, found: 342.0617. The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm); t<sub>r</sub> = 12.98 and 18.15 min.

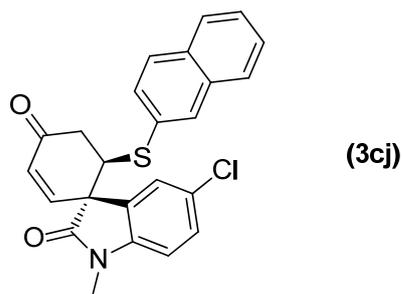


(3bj)

**(1*R*,6*R*)-5'-methoxy-1'-methyl-6-(naphthalen-2-ylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

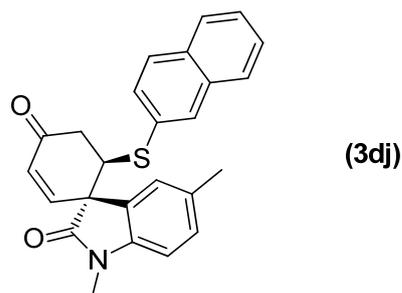
Yield (85%); White solid; m.p. 86 °C;  $[\alpha]_D^{25} = +201.9$  (*c* 0.84, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.79-7.72 (m, 4H), 7.49-7.46 (m, 2H), 7.39-7.36 (m, 1H), 6.97-6.88 (m, 2H), 6.79 (s, 1H), 6.59 (d, *J* = 9.6 Hz, 1H), 6.25 (d, *J* = 9.9 Hz, 1H), 4.30 (t, *J* = 9.3 Hz, 1H), 3.75 (s, 3H), 3.22 (s, 3H), 3.01 (d, *J* = 10.2 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 196.3, 175.5, 155.9, 146.3, 137.5, 133.1, 132.5,

130.2, 129.9, 129.1, 128.5, 127.5, 127.4, 126.4, 113.8, 112.6, 109.1, 55.6, 55.1, 49.0, 41.6, 26.6; IR (KBr)  $\nu$  3064, 3012, 1702, 1611, 1452, 1375, 1127, 1070, 820, 743, 690; HRMS Calcd. For  $C_{25}H_{21}NO_3S + H^+$ : 416.1325, found: 416.1315. The product was analyzed by HPLC to determine the enantiomeric excess: 84% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min,  $\lambda$  = 254 nm);  $t_r$  = 17.12 and 25.34 min.



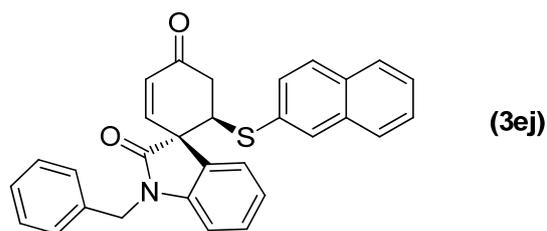
**(1R,6R)-5'-chloro-1'-methyl-6-(naphthalen-2-ylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

Yield (80%); White solid; m.p. 98 °C;  $[\alpha]_D^{25} = +223.7$  (*c* 0.66,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz)  $\delta$  7.81-7.71 (m, 4H), 7.50-7.47 (m, 2H), 7.44-7.41 (m, 1H), 7.38-7.35 (m, 1H), 7.19-7.18 (m, 1H), 6.91 (d,  $J$  = 8.1 Hz, 1H), 6.55 (d,  $J$  = 9.9 Hz, 1H), 6.27 (d,  $J$  = 9.9 Hz, 1H), 4.32-4.26 (m, 1H), 3.21 (s, 3H), 3.02-2.98 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , TMS, 75 MHz)  $\delta$  195.9, 175.6, 145.3, 142.8, 133.2, 132.6, 130.5, 130.1, 129.9, 128.7, 128.3, 127.6, 127.4, 127.0, 126.6, 125.5, 109.8, 54.9, 49.0, 41.6, 26.7; IR (KBr)  $\nu$  3030, 3014, 1698, 1589, 1491, 1472, 1324, 1132, 1084, 817, 745, 696; HRMS Calcd. For  $C_{24}H_{18}NO_2SCl + Na^+$ : 442.0647, found: 442.0639. The product was analyzed by HPLC to determine the enantiomeric excess: 84% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min,  $\lambda$  = 254 nm);  $t_r$  = 12.54 and 17.21 min.



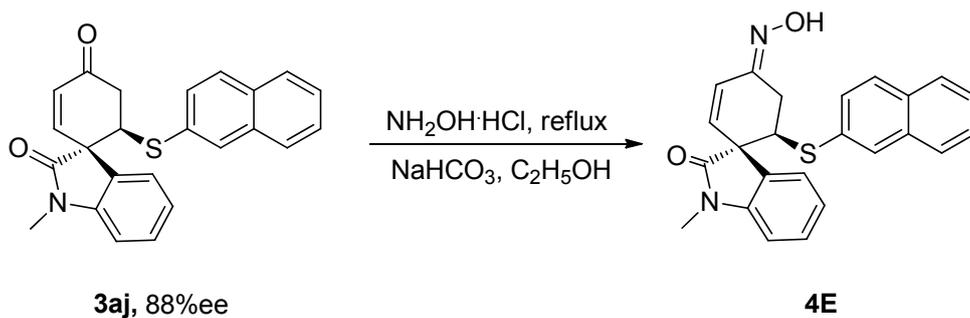
**(1*R*,6*R*)-1',5'-dimethyl-6-(naphthalen-2-ylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

Yield (81%); White solid; m.p. 72 °C;  $[\alpha]_D^{25} = +191.6$  (*c* 0.43, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.79-7.71 (m, 4H), 7.48-7.47 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.26-7.23 (m, 1H), 6.99 (s, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 9.9 Hz, 1H), 6.24 (d, *J* = 9.9 Hz, 1H), 4.33-4.27 (m, 1H), 3.24 (s, 3H), 3.05-3.01 (m, 2H), 2.30 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 196.6, 176.0, 146.6, 141.8, 133.2, 132.6, 130.3, 130.0, 129.1, 128.5, 127.5, 127.4, 126.5, 125.8, 125.1, 108.7, 54.9, 49.1, 41.7, 26.6, 21.0; IR (KBr) ν 3043, 1702, 1596, 1483, 1459, 1231, 1145, 821, 752, 689; HRMS Calcd. For C<sub>25</sub>H<sub>21</sub>NO<sub>2</sub>S + H<sup>+</sup>: 400.1373, found: 400.1366. The product was analyzed by HPLC to determine the enantiomeric excess: 82% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm); t<sub>r</sub> = 14.25 and 21.62 min.



**(1*R*,6*R*)-1'-benzyl-6-(naphthalen-2-ylthio)spiro[cyclohex[2]ene-1,3'-indoline]-2',4-dione:**

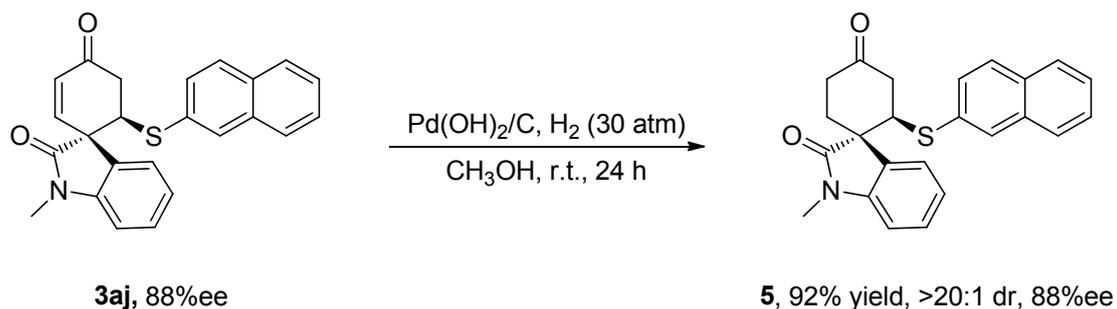
Yield (82%); White solid; m.p. 75 °C;  $[\alpha]_D^{25} = +177.2$  (*c* 0.89, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.79-7.72 (m, 4H), 7.49-7.38 (m, 5H), 7.30-7.23 (m, 3H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 9.9 Hz, 1H), 6.27 (d, *J* = 10.2 Hz, 1H), 5.15 (d, *J* = 15.9 Hz, 1H), 4.85 (d, *J* = 15.9 Hz, 1H), 4.36 (dd, *J*<sub>1</sub> = 5.4 Hz, *J*<sub>2</sub> = 12.6 Hz, 1H), 3.16-3.07 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 196.4, 176.4, 146.2, 143.3, 135.0, 133.3, 132.5, 130.1, 130.0, 129.3, 128.7, 127.7, 127.6, 127.5, 127.3, 126.5, 125.3, 125.1, 123.0, 110.1, 54.8, 49.3, 44.3, 42.1; IR (KBr) ν 3074, 3021, 1715, 1587, 1485, 1457, 1252, 1234, 814, 748, 685; HRMS Calcd. For C<sub>30</sub>H<sub>23</sub>NO<sub>2</sub>S + H<sup>+</sup>: 462.1527, found: 462.1522. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm); t<sub>r</sub> = 11.16 and 14.19 min.



Under argon atmosphere, **3aj** (77 mg, 0.2 mmol, 88% ee) and NaHCO<sub>3</sub> were dissolved in 2 mL C<sub>2</sub>H<sub>5</sub>OH, and hydroxylammonium chloride (16.8 mg, 0.24 mmol) was added, the mixture was refluxed for 2 h. Then, the solvent was evaporated and the residue was purified by column chromatography followed by recrystallization (in CH<sub>3</sub>OH/DCM) to give **(1R,6R)-4E** in 36% yield, which was then directly analyzed by HPLC to determine the enantiomeric excess.

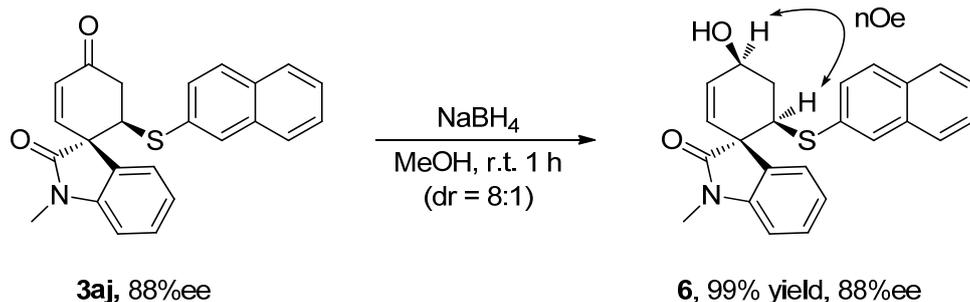
**(1R,6R,E)-4-(hydroxyimino)-1'-methyl-6-(naphthalen-2-ylthio)spiro[cyclohex[2]ene-1,3'-indolin]-2'-one:** White solid; m.p. 193 °C;  $[\alpha]_D^{25} = +103.1$  (*c* 0.37, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.78-7.72 (m, 4H), 7.45-7.42 (m, 4H), 7.18-7.10 (m, 2H), 6.97-6.94 (m, 1H), 6.41 (d, *J* = 9.6 Hz, 1H), 5.92 (d, *J* = 9. Hz, 1H), 4.06-4.02 (m, 1H), 3.68-3.62 (m, 1H), 3.24 (s, 3H), 2.79 (t, *J* = 16.5Hz, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, TMS, 75 MHz) δ 176.4, 151.6, 144.0, 133.1, 131.9, 131.7, 130.7, 130.0, 129.3, 129.0, 128.6, 127.6, 127.5, 127.3, 126.8, 126.4, 126.1, 124.7, 122.6, 109.0, 54.1, 48.2, 27.1, 26.4; IR (KBr) ν 3407, 3034, 2935, 1701, 1684, 1611, 1482, 1452, 1341, 1129, 813, 742, 685; The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm); *t*<sub>r</sub> = 17.50 and 25.10 min.

### III. Synthetic Application of the Michael Adduct **3aj**.



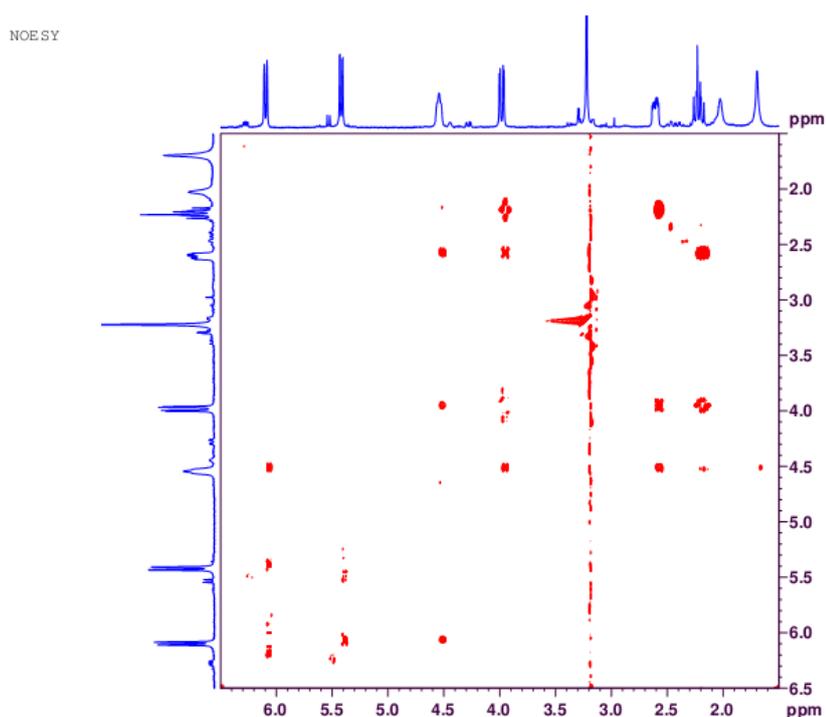
To a solution of **3aj** (77 mg, 0.2 mmol, 88% ee) in 2 mL CH<sub>3</sub>OH was added Pd(OH)<sub>2</sub>/C (7.7 mg, 10% w/w). The mixture was stirred under H<sub>2</sub> (30 atm) at room temperature for 24 h. Then, the solvent was evaporated and the residue was purified by column chromatography to give **5** in 92% yield, which was then directly analyzed by HPLC to determine the enantiomeric excess.

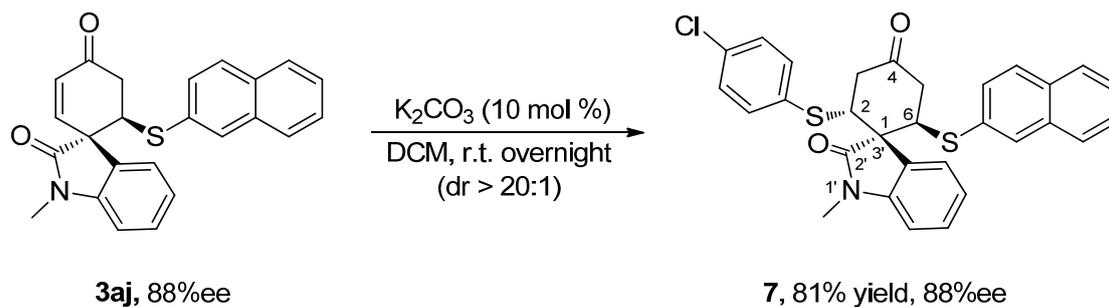
**(1R,2R)-1'-methyl-2-(naphthalen-2-ylthio)spiro[cyclohexane-1,3'-indoline]-2',4-dione**: White solid; m.p. 61 °C;  $[\alpha]_D^{25} = +43.7$  (*c* 0.35, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.79-7.69 (m, 4H), 7.49-7.43 (m, 4H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 3.97 (dd, *J*<sub>1</sub> = 6.9 Hz, *J*<sub>2</sub> = 11.4 Hz 1H), 3.27 (s, 3H), 3.01-2.97 (m, 2H), 2.85-2.74 (m, 1H), 2.61-2.56 (m, 1H), 2.43-2.32 (m, 1H), 2.01-1.95 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 206.9, 177.7, 144.0, 133.3, 132.6, 130.3, 129.6, 129.2, 128.9, 128.6, 127.6, 127.5, 126.5, 124.6, 122.5, 108.9, 51.5, 51.3, 45.7, 36.8, 32.8, 26.6; IR (KBr) ν 3057, 1721, 1603, 1583, 1317, 1115, 819, 736, 678; HRMS Calcd. For C<sub>24</sub>H<sub>21</sub>NO<sub>2</sub>S + H<sup>+</sup>: 388.1379, found: 388.1366. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak IC, *i*-propanol/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm); t<sub>r</sub> = 13.93 and 21.18 min.



To a solution of **3aj** (77 mg, 0.2 mmol, 88% ee) in 2 mL MeOH was added NaBH<sub>4</sub> (8.4 mg, 1.1 eq.), the mixture was stirred at this temperature for 1 h. Then, the solvent was evaporated and the residue was purified by column chromatography to give **6** in 99% yield, which was then directly analyzed by HPLC to determine the enantiomeric excess.

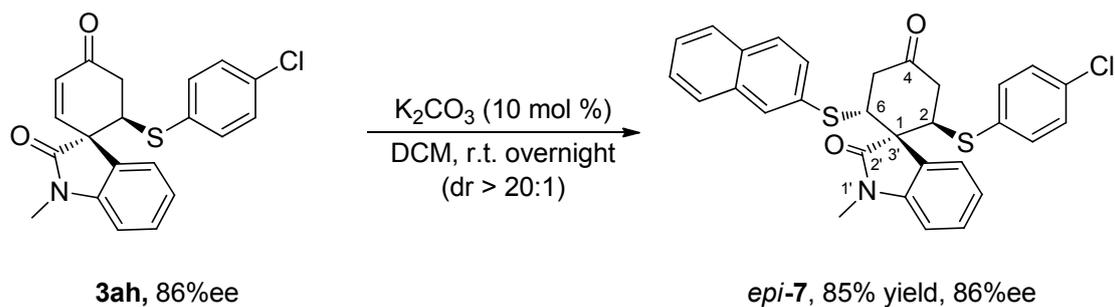
**(1R,4S,6R)-4-hydroxy-1'-methyl-6-(naphthalen-2-ylthio)spiro[cyclohex[2]ene-1,3'-indolin]-2'-one**: White solid; m.p. 78 °C;  $[\alpha]_D^{25} = +95.1$  (*c* 0.84, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) δ 7.74-7.71 (m, 4H), 7.48-7.39 (m, 5H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.05 (d, *J* = 9.9 Hz, 1H), 5.37 (d, *J* = 9.9 Hz, 1H), 4.49 (s, 1H), 3.93 (d, *J* = 12.6 Hz, 1H), 3.17 (s, 3H), 2.58-2.53 (m, 1H), 2.16 (q, *J* = 13.2 Hz, 1H), 1.93 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) δ 177.9, 143.5, 134.4, 133.1, 132.2, 131.4, 130.6, 129.9, 128.9, 128.8, 128.3, 127.4, 127.2, 126.3, 126.1, 125.9, 125.3, 122.6, 108.2, 66.2, 54.3, 48.8, 36.3, 26.3; IR (KBr) ν 3407, 3052, 2930, 1695, 1609, 1491, 1469, 1351, 1132, 816, 747, 695; HRMS Calcd. For C<sub>24</sub>H<sub>21</sub>NO<sub>2</sub>S + Na<sup>+</sup>: 410.1192, found: 410.11852. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak IC, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); *t*<sub>r</sub> = 32.63 and 42.00 min.





Under argon atmosphere, **3aj** (77.1 mg, 0.2 mmol, 88% ee) and  $K_2CO_3$  (2.7 mg, 0.02 mmol) were dissolved in 2 mL DCM, and 4-Chlorothiophenol (31.8 mg, 0.22 mmol) was added, the mixture was stirred at room temperature overnight. Then, the solvent was evaporated and the residue was purified by column chromatography to give **7** in 81% yield, which was then directly analyzed by HPLC to determine the enantiomeric excess.

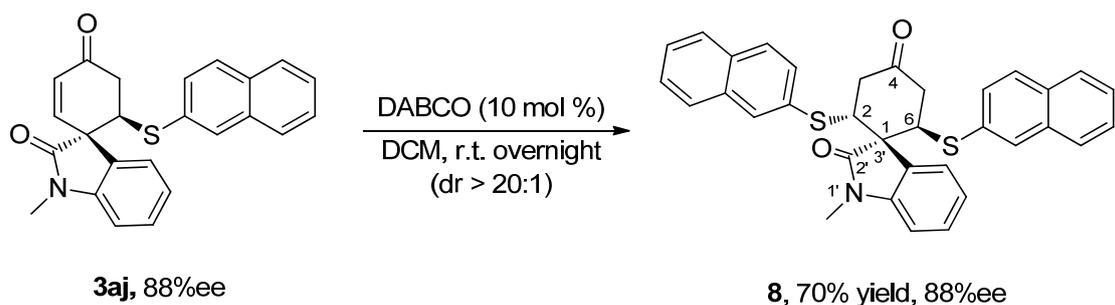
**(1R,2R,6R)-2-((4-chlorophenyl)thio)-1'-methyl-6-(naphthalen-2-ylthio)spiro[cyclohexane-1,3'-indoline]-2',4-dione**: White solid; m.p. 83 °C;  $[\alpha]_D^{25} = +10.5$  ( $c$  0.44,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz)  $\delta$  7.76-7.69 (m, 4H), 7.48-7.34 (m, 4H), 7.26-7.24 (m, 1H), 7.11 (d,  $J = 8.4$  Hz, 2H), 6.96-6.91 (m, 4H), 4.02 (dd,  $J_1 = 5.1$  Hz and  $J_2 = 12.6$  Hz, 1H), 3.85 (t,  $J = 5.1$  Hz, 1H), 3.57 (dd,  $J_1 = 4.2$  Hz and  $J_2 = 15.6$  Hz, 1H), 3.46-3.36 (m, 1H), 3.28 (s, 3H), 2.88 (dd,  $J_1 = 4.5$  Hz and  $J_2 = 15.9$  Hz, 1H), 2.63 (dd,  $J_1 = 5.1$  Hz and  $J_2 = 15.9$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , TMS, 75 MHz)  $\delta$  205.9, 175.3, 143.9, 134.8, 134.3, 133.4, 132.8, 132.6, 131.7, 130.0, 129.2, 129.0, 128.9, 128.5, 127.6, 127.5, 126.7, 126.5, 122.2, 108.2, 54.8, 51.1, 50.5, 44.3, 42.1, 26.4; IR (KBr)  $\nu$  3046, 1711, 1618, 1482, 1347, 1123, 827, 745, 697; HRMS Calcd. For  $C_{30}H_{24}NO_2S_2Cl + Na^+$ : 552.0842, found: 552.0829. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak IC, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 17.50$  and 25.10 min.



Under argon atmosphere, **3ah** (73.8 mg, 0.2 mmol, 88% ee) and  $K_2CO_3$  (2.7 mg, 0.02 mmol) were dissolved in 2 mL DCM, and 4-Chlorothiophenol (31.8 mg, 0.22 mmol) was added, the mixture was stirred at room temperature overnight. Then, the solvent was evaporated and the residue was purified by column chromatography to give *epi-7* in 85% yield, which was then directly analyzed by HPLC to determine the enantiomeric excess.

**(1*S*,2*R*,6*R*)-2-((4-chlorophenyl)thio)-1'-methyl-6-(naphthalen-2-ylthio)spiro[cyclohexane-1,3'-indoline]-2',4-dione**: White solid; m.p. 81 °C;  $[\alpha]_D^{25} = +11.2$  (*c* 0.37,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz)  $\delta$  7.77-7.75 (m, 1H), 7.65-7.62 (m, 2H), 7.48-7.43 (m, 3H), 7.32-7.26 (m, 2H), 7.20-7.14 (m, 5H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.79-6.75 (m, 1H), 4.08-4.04 (m, 1H), 3.74 (m, 1H), 3.59-3.40 (m, 2H), 3.34 (s, 3H), 2.95- 2.90 (m, 1H), 2.60-2.54 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , TMS, 75 MHz)  $\delta$  206.1, 134.8, 133.2, 132.6, 130.3, 129.4, 128.6, 127.6, 126.6, 126.4, 122.1, 108.3, 51.5, 50.0, 44.5, 42.1, 26.5, 14.2; IR (KBr)  $\nu$  3061, 2935, 1715, 1514, 1472, 1341, 1126, 817, 750, 691; The product was analyzed by HPLC to determine the enantiomeric excess: 86% ee (Chiralpak IC, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda$  = 254 nm);  $t_r$  = 19.78 and 32.49 min.

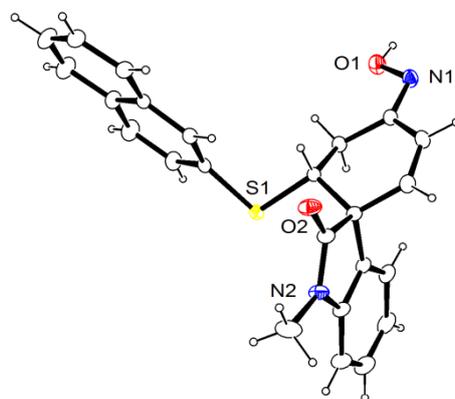
**Scheme S1.** Control experiment verifying 2,6-*trans* configuration in double SMA.



Under argon atmosphere, **3aj** (77 mg, 0.2 mmol, 88% ee) and DABCO (2.2 mg, 0.02 mmol) were dissolved in 2 mL DCM, and 2-Naphthalenethiol (35.3 mg, 0.22 mmol) was added, the mixture was stirred at room temperature overnight. Then, the solvent was evaporated and the residue was purified by column chromatography to give **8** in 70% yield, which was then directly analyzed by HPLC to determine the enantiomeric excess. This control experiment demonstrates that the two substituted groups at 2,6-position in the cyclohexanone are in *trans* configuration, otherwise *meso*-compound should be generated.

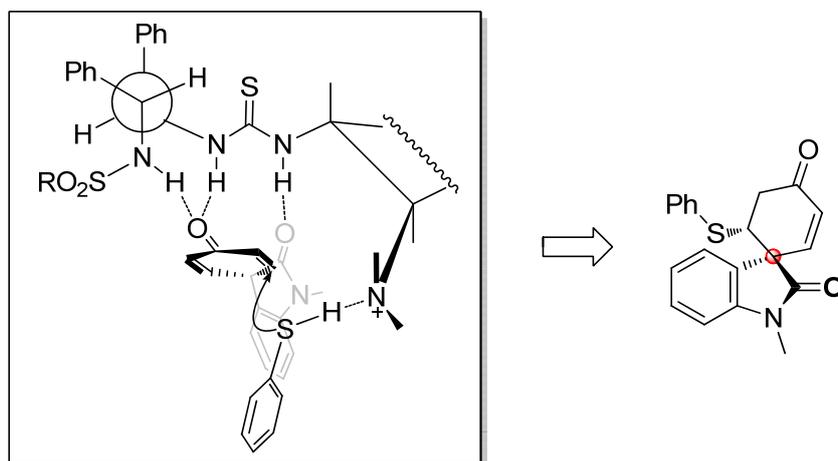
**(2*R*,6*R*)-1'-methyl-2,6-bis(naphthalen-2-ylthio)spiro[cyclohexane-1,3'-indoline]-2',4-dione**: White solid; mp 79 °C;  $[\alpha]_D^{25} = +10$  ( $c$  0.27, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz)  $\delta$  7.76-7.64 (m, 6H), 7.46-7.27 (m, 9H), 7.17 (d,  $J = 8.1$  Hz, 1H), 6.95 (d,  $J = 6.6$  Hz, 1H), 6.80 (t,  $J = 7.2$  Hz, 1H), 4.15-4.11 (m, 1H), 3.89 (m, 1H), 3.61-3.44 (m, 2H), 3.32 (s, 3H), 2.97-2.92 (m, 1H), 2.67-2.61 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz)  $\delta$  206.3, 175.5, 144.0, 133.1, 132.7, 132.5, 130.3, 130.0, 129.3, 129.1, 128.8, 128.5, 127.6, 126.6, 126.4, 122.1, 108.2, 54.8, 51.1, 50.0, 44.6, 42.1, 26.4; IR (KBr)  $\nu$  3057, 1696, 1607, 1484, 1312, 1023, 857, 762, 662; HRMS Calcd. For C<sub>34</sub>H<sub>27</sub>NO<sub>2</sub>S<sub>2</sub> + Na<sup>+</sup>: 568.1370, found: 568.1375. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak IC, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 22.00$  and 38.87 min.

#### IV. X-ray Crystal Structures of (1*R*,6*R*)-4*E*



Crystal data for **(1R,6R)-4E**:  $C_{24}H_{20}N_2O_2S$ ,  $M_r = 400.48$ ,  $T = 296$  K, Orthorhombic, space group  $P2_12_12_1$ ,  $a = 8.8678(9)$ ,  $b = 9.3161(9)$ ,  $c = 24.972(3)$  Å,  $V = 2063.0(4)$  Å<sup>3</sup>,  $Z = 4$ , 4277 reflections measured, 3493 unique ( $R_{int} = 0.0363$ ) which were used in all calculations. The final  $wR_2 = 0.0851$  (all data), Flack  $\chi = 0.02(7)$ . CCDC 932106 contains the supplementary crystallographic data, which can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

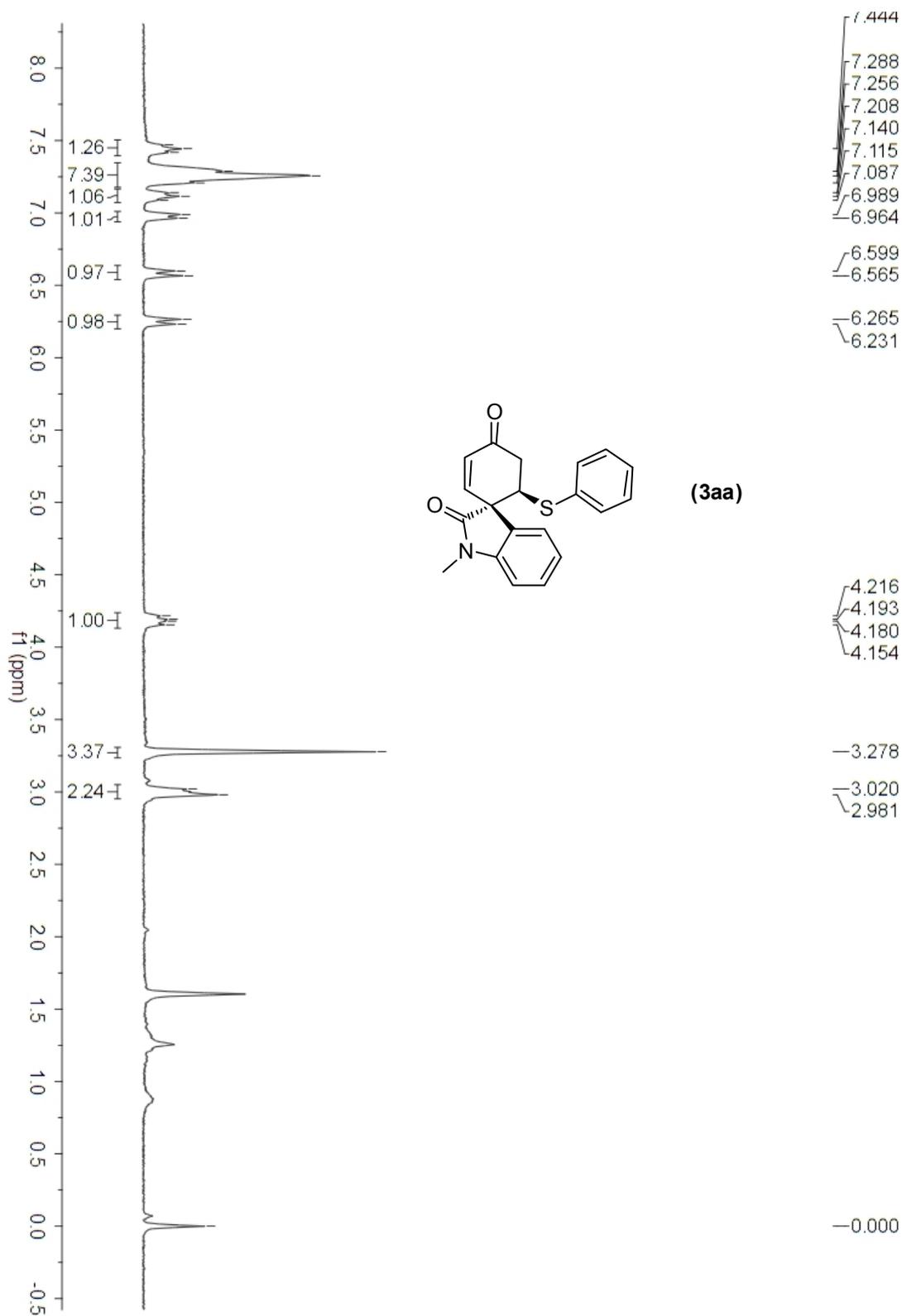
## V. Proposed transition-state model for our catalytic system

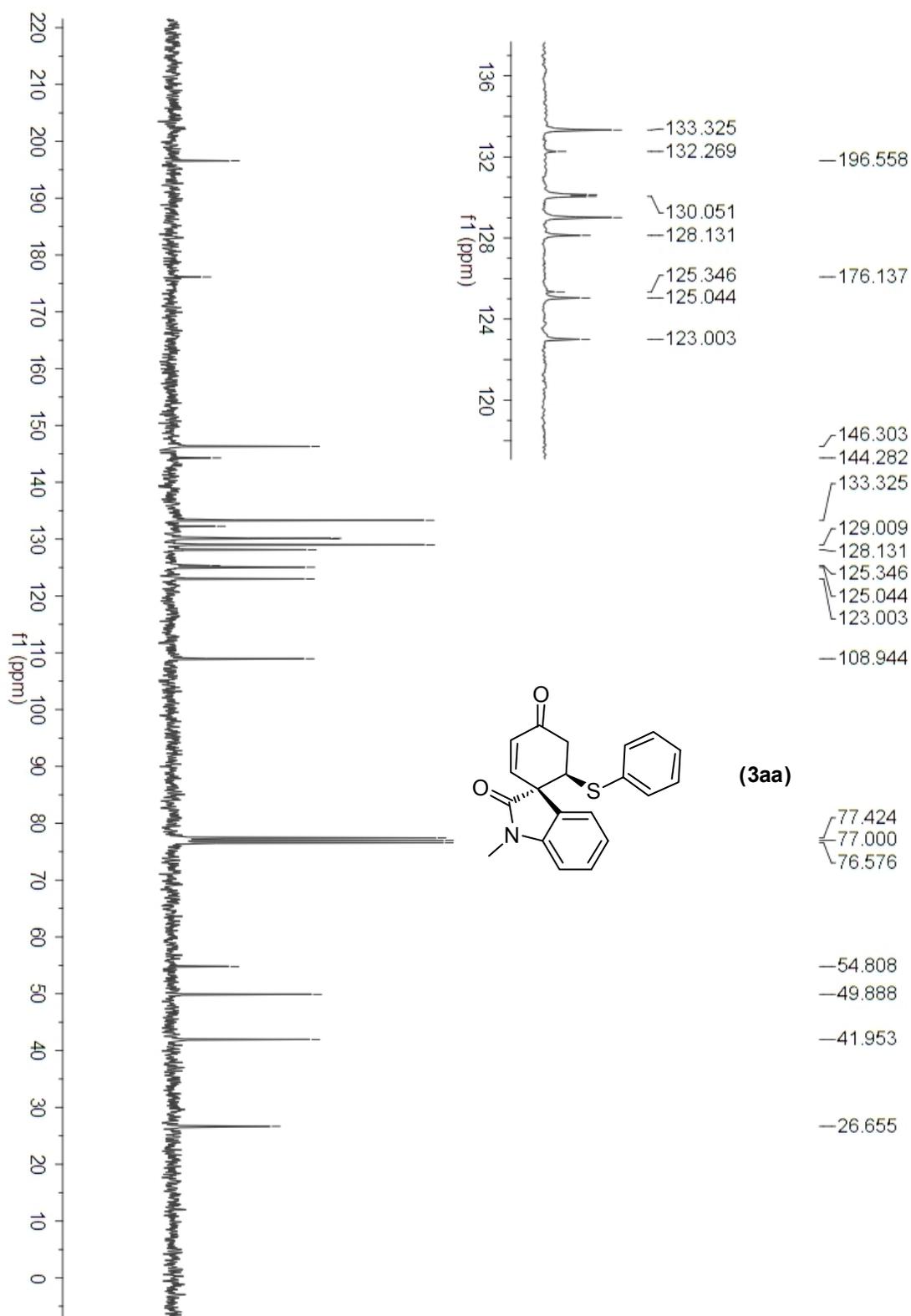


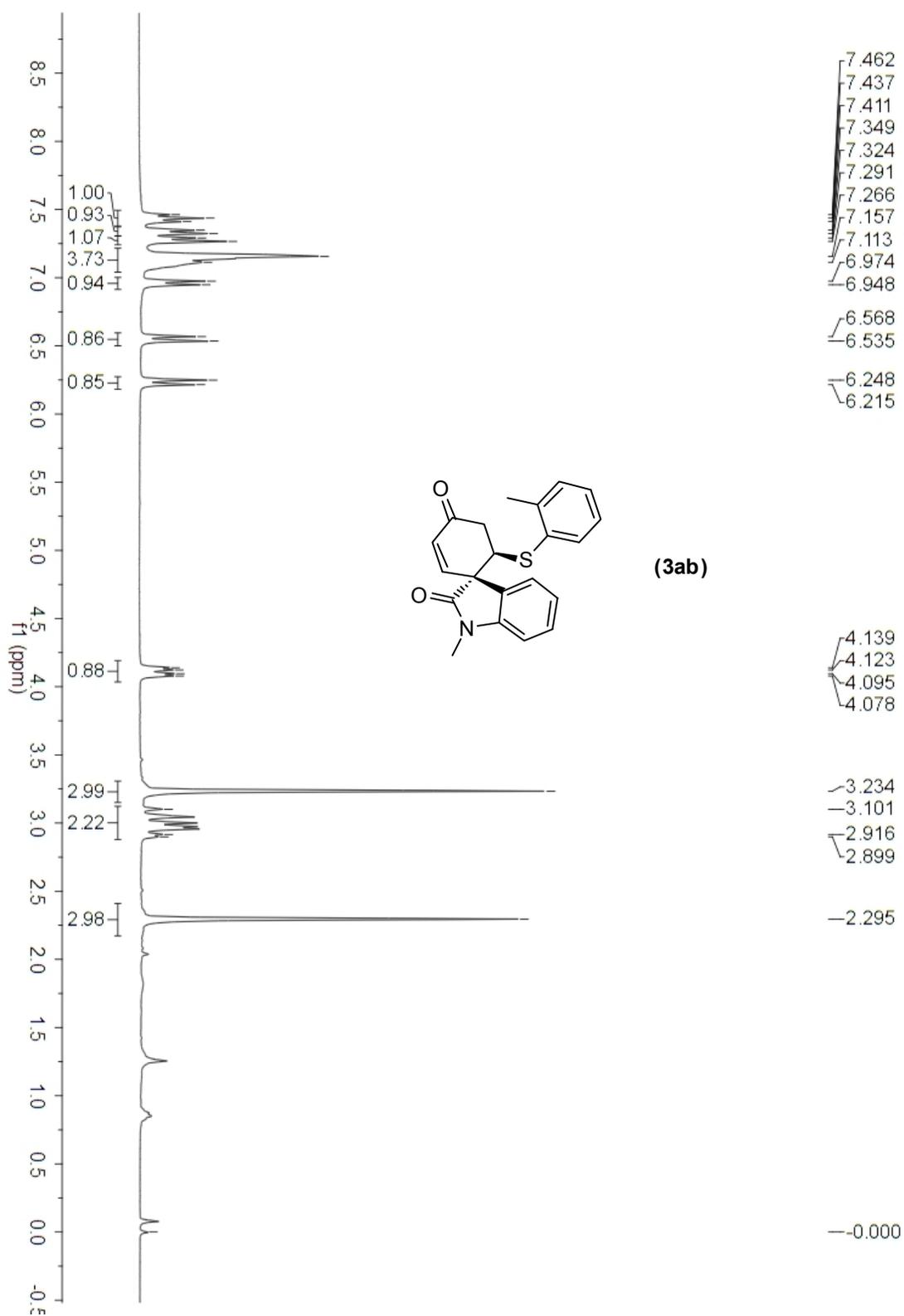
## VI. Reference

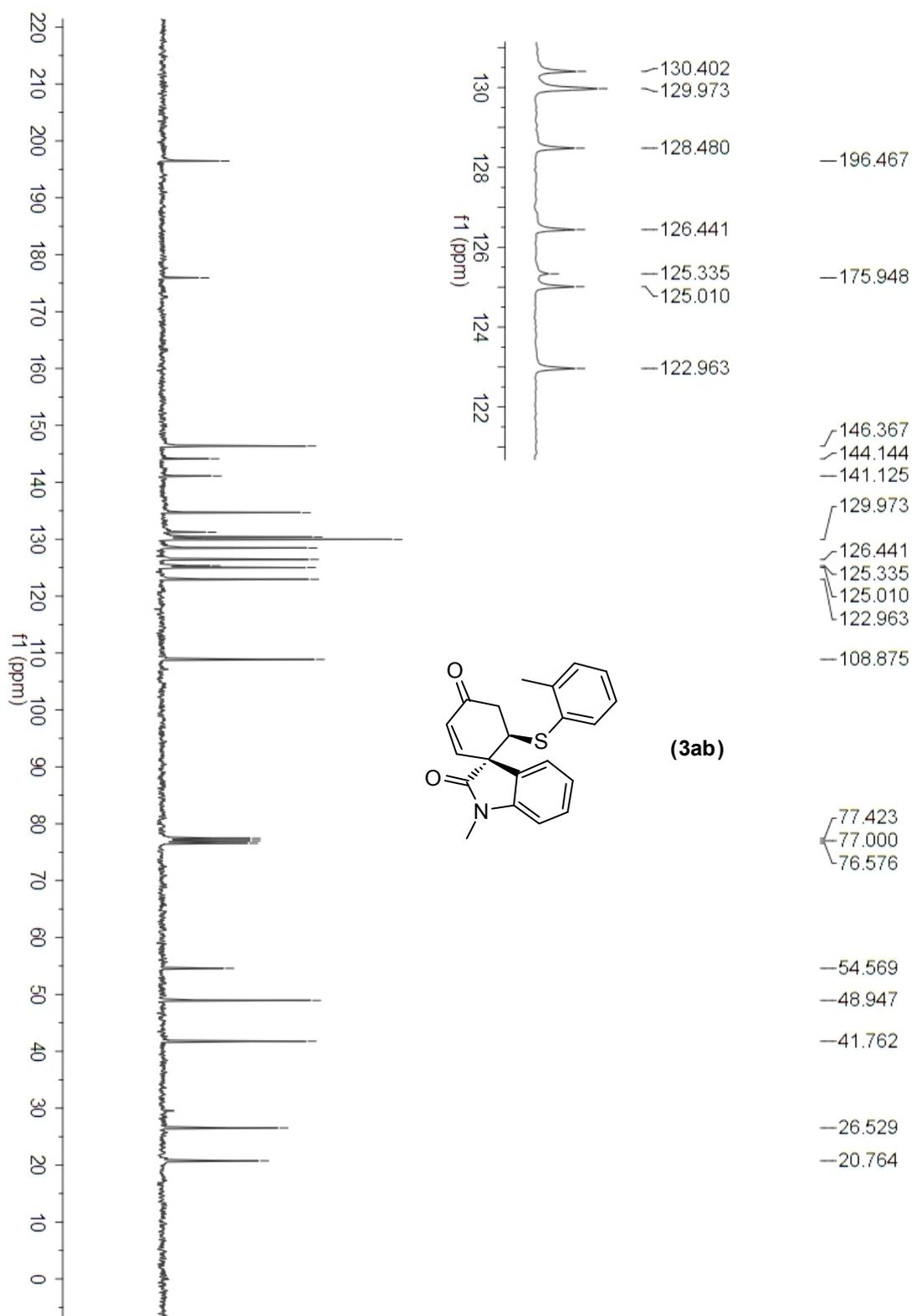
- [1] a) T. Okino, Y. Hoashi, Y. Takemoto, *J. Am. Chem. Soc.* **2003**, *125*, 12672; b) B. Vakulya, S. Varga, A. Csampai, T. Soos, *Org. Lett.* **2005**, *7*, 1967; c) T. Marcelli, J. H. van Maarseveen, H. Hiemstra, *Angew. Chem. Int. Ed.* **2006**, *45*, 7496; d) S. J. Connon, *Chem. Commun.* **2008**, 2499; e) C. J. Wang, Z. H. Zhang, X. Q. Dong, X. J. Wu, *Chem. Commun.* **2008**, *0*, 1431.
- [2] a) G. O'Mahony, A. K. Pitts, *Org. Lett.* **2010**, *12*, 2024; b) W. Yu, Z. Yu, X. Ju, J. Wang, *Synthesis* **2011**, *2011*, 860.

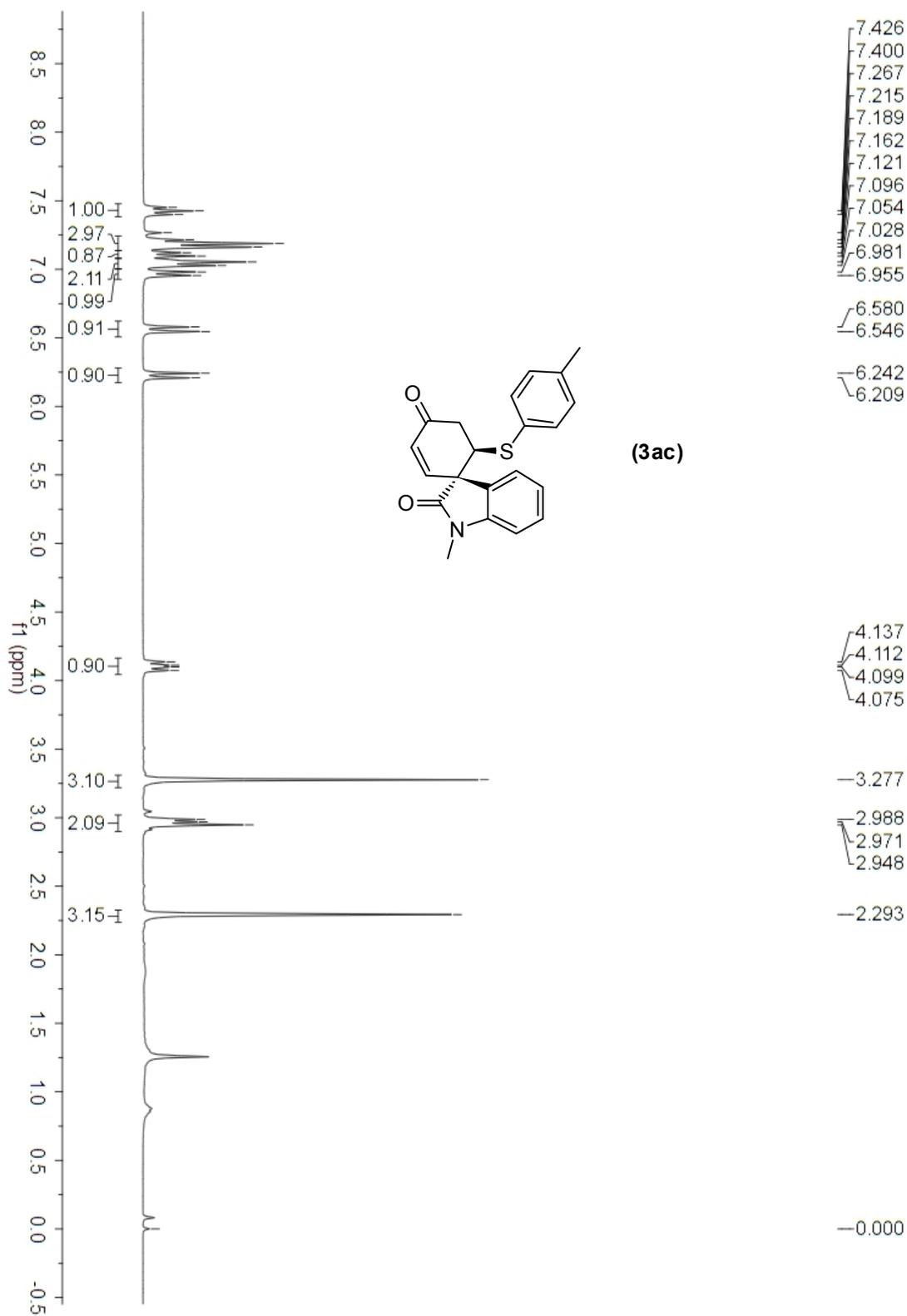
## VII. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

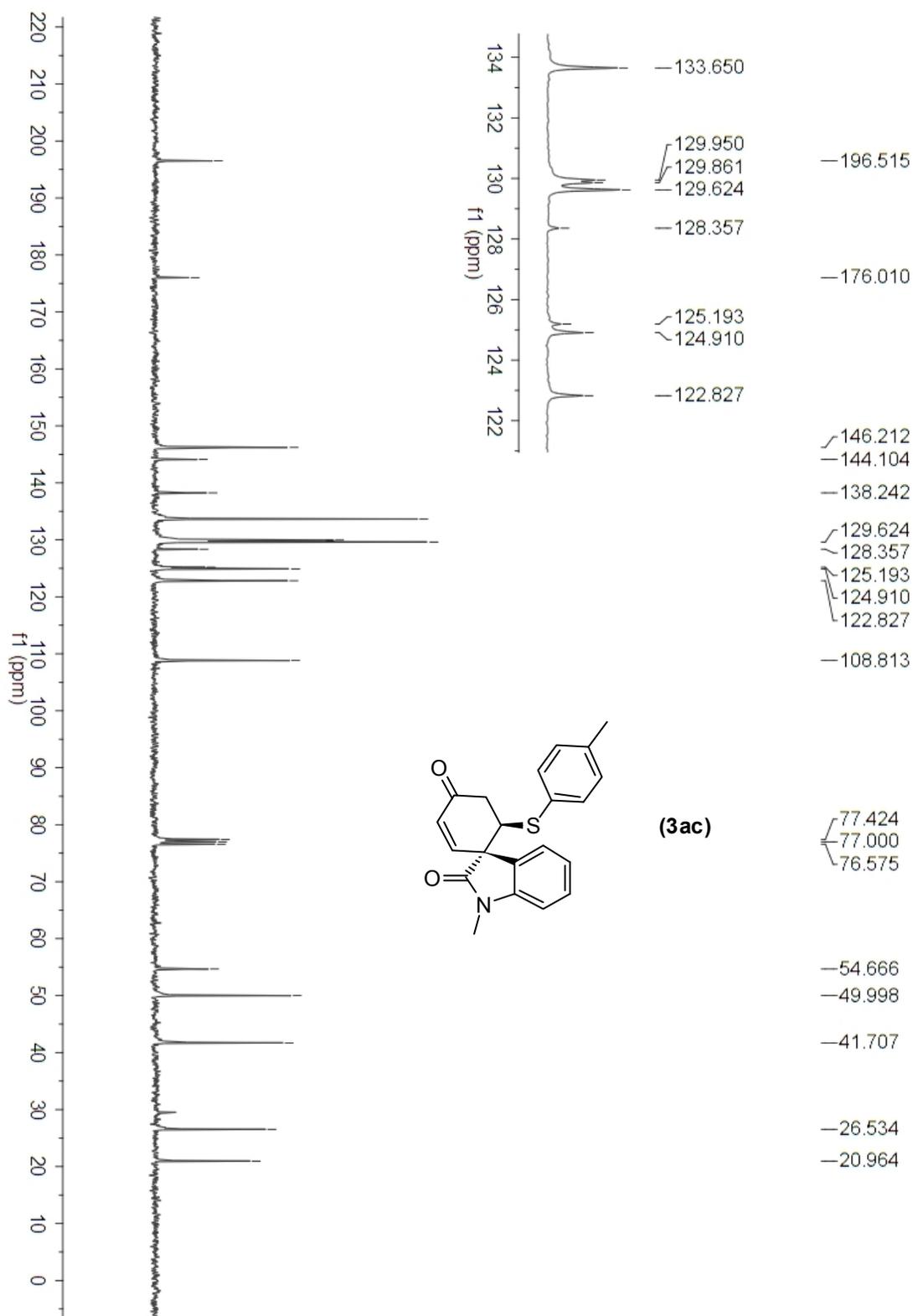


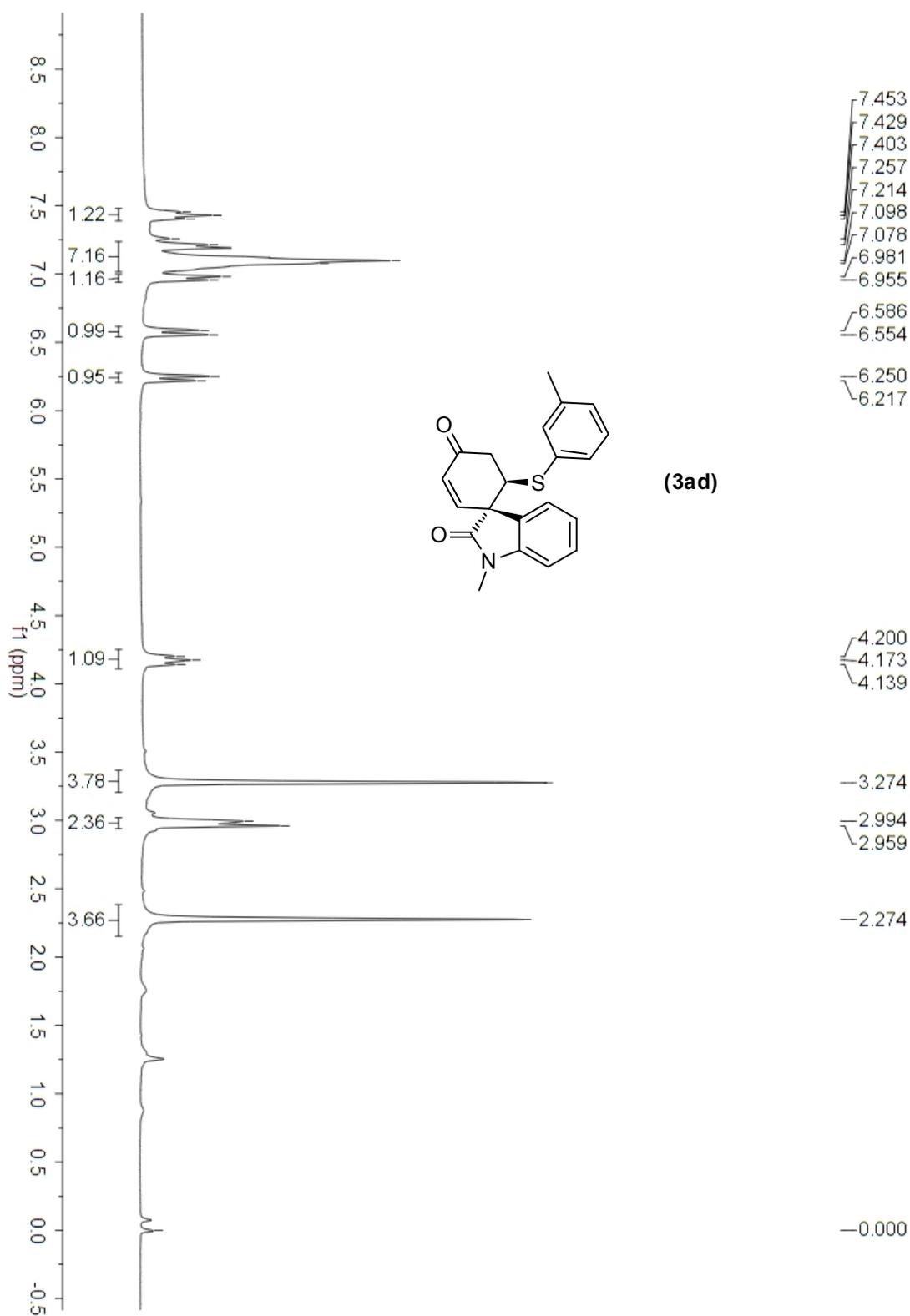


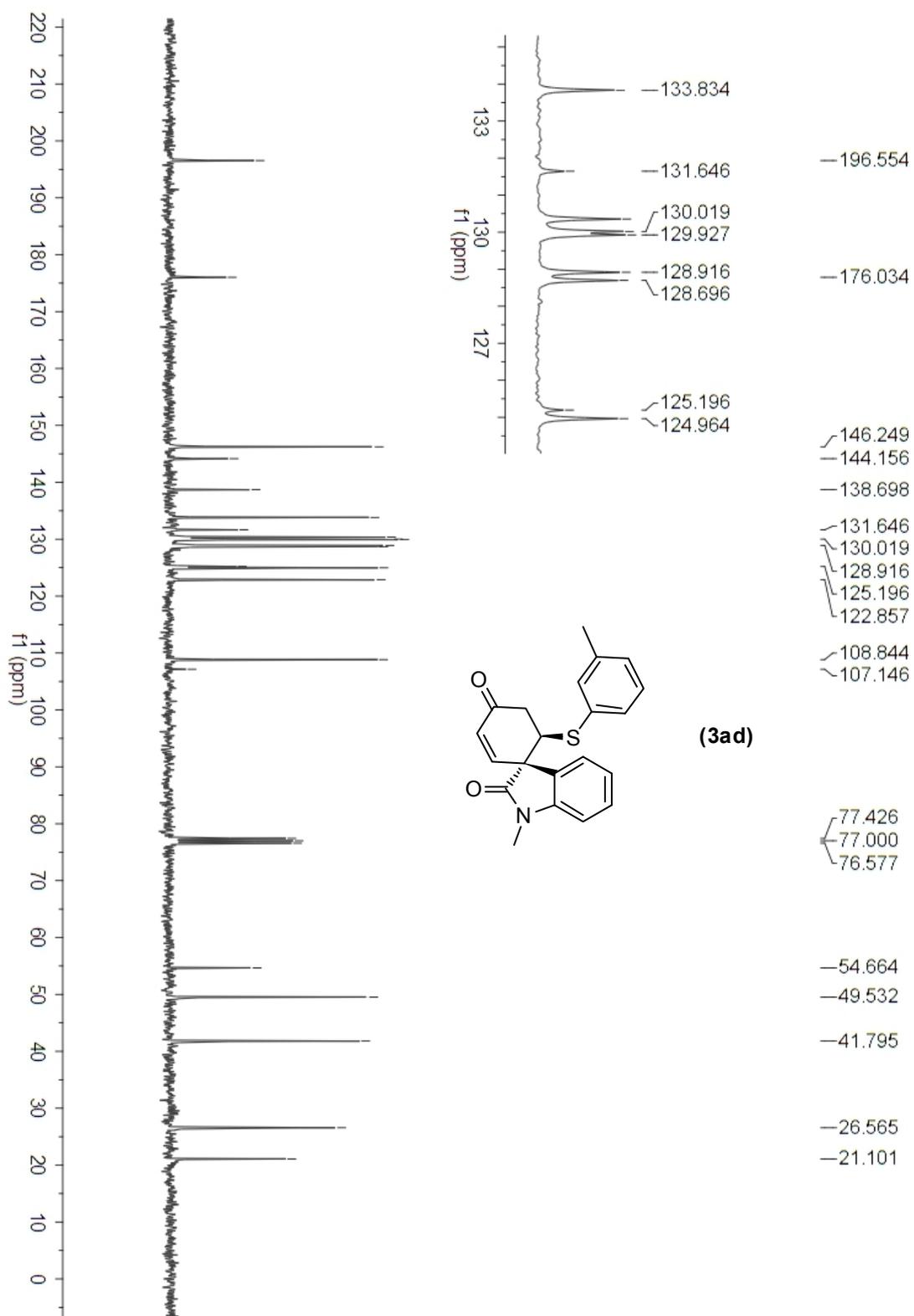


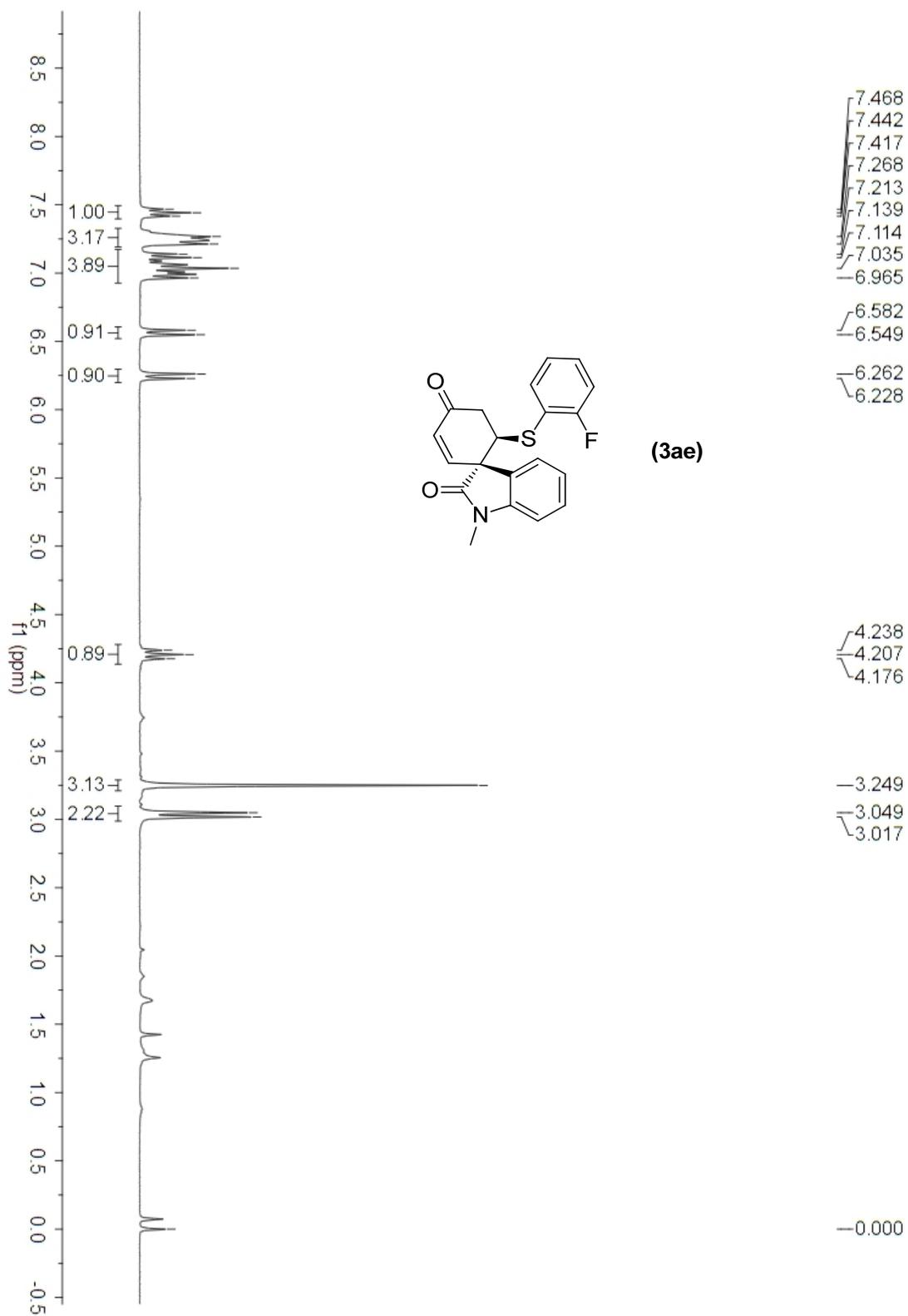


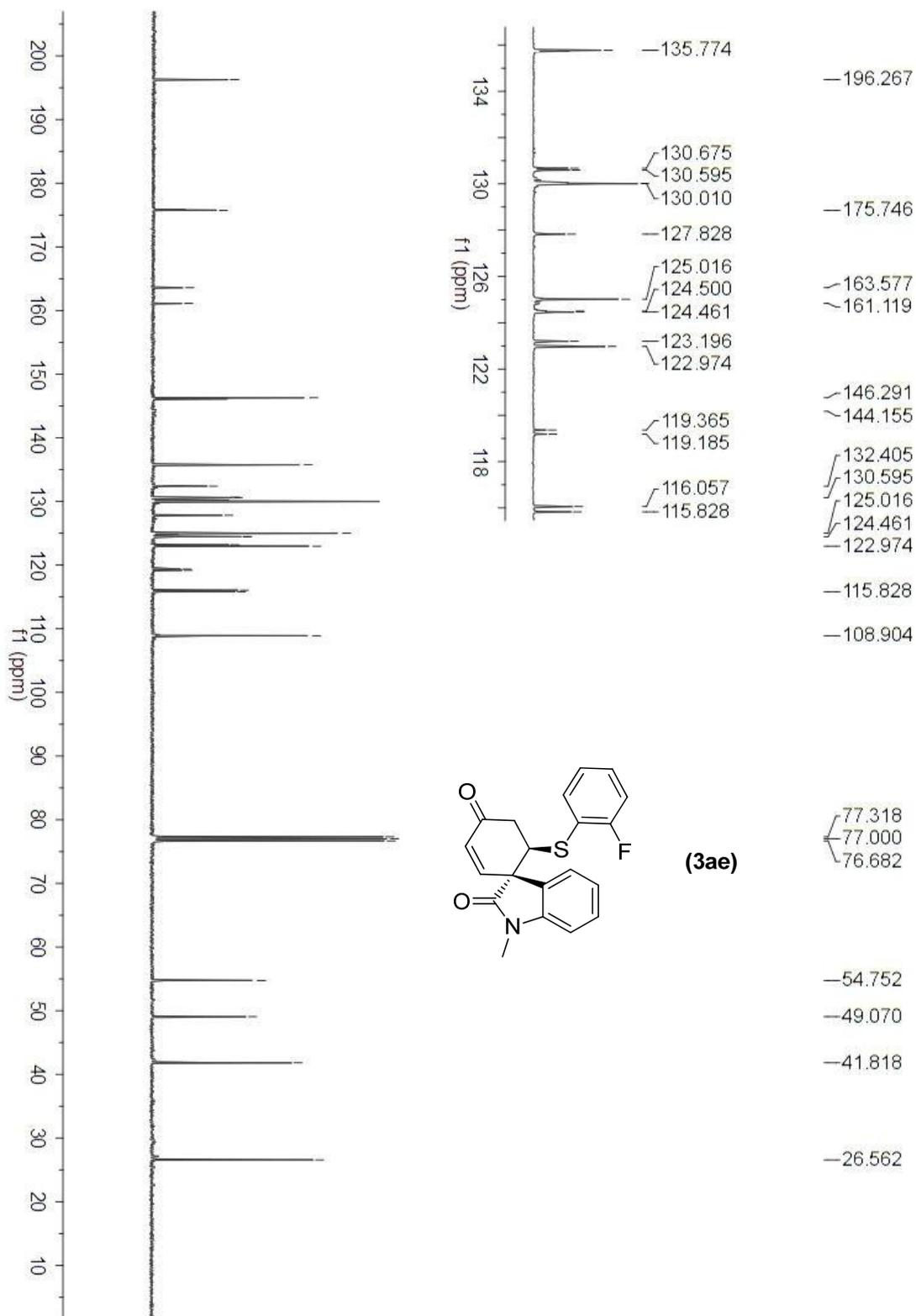


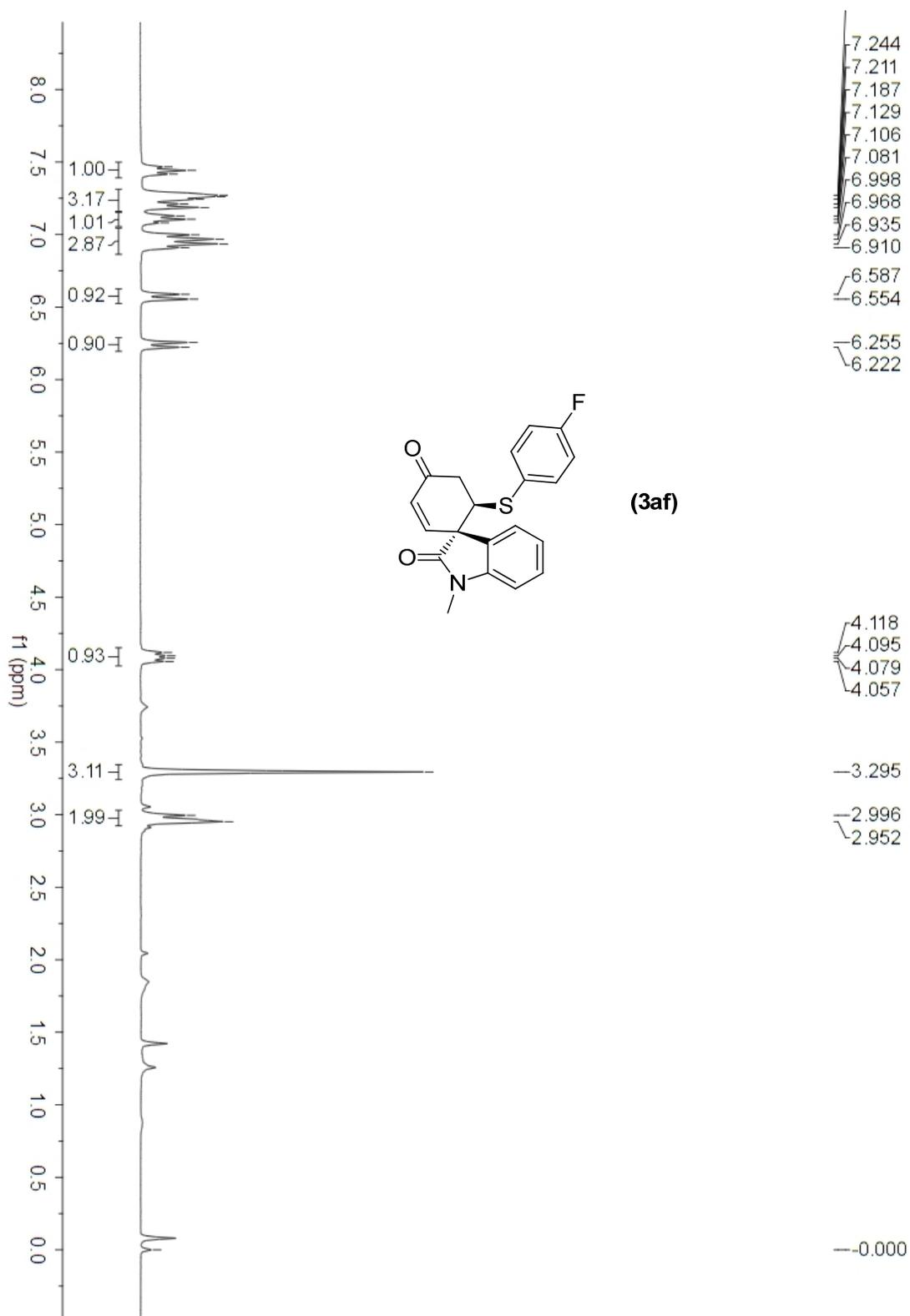


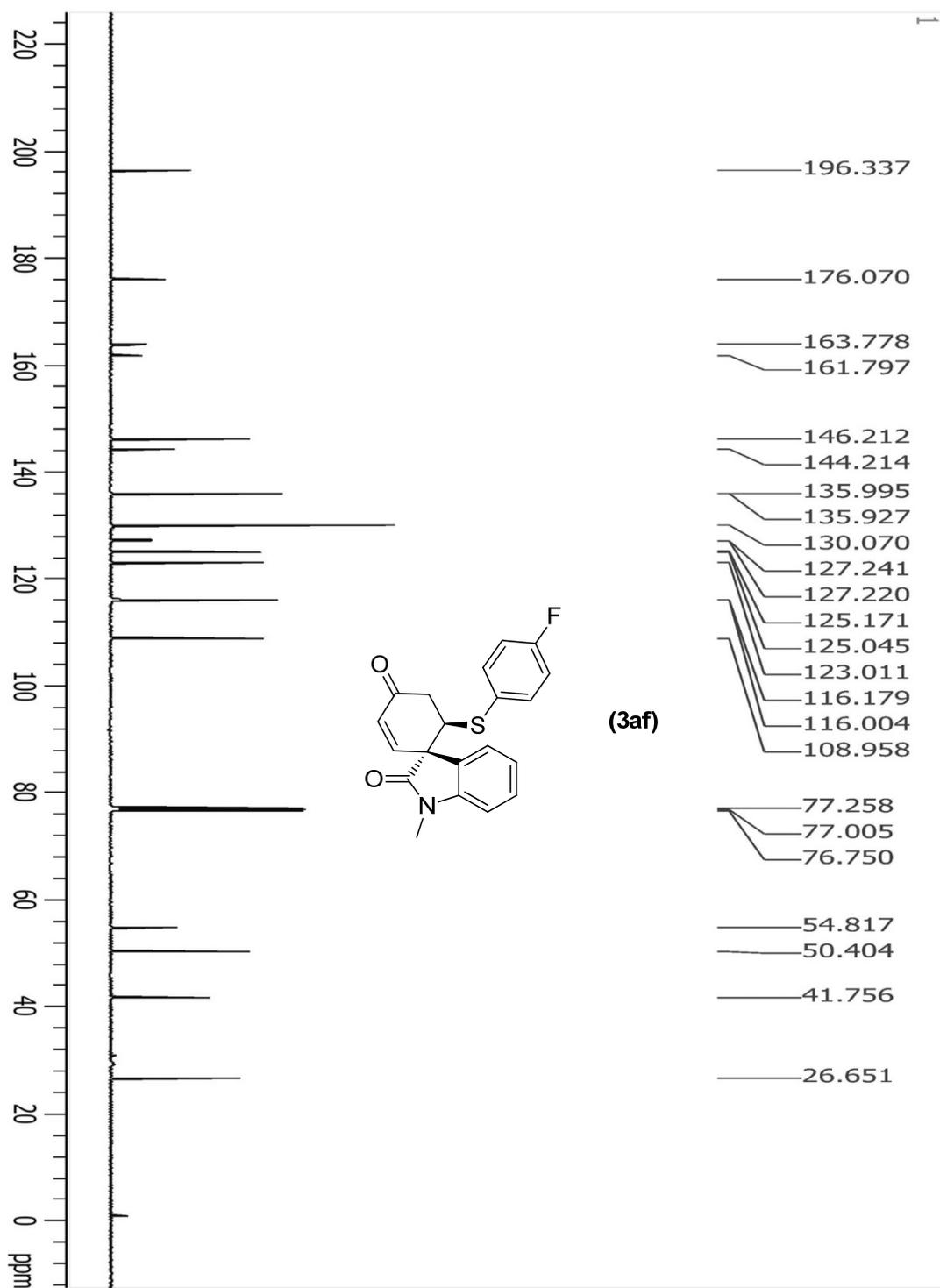


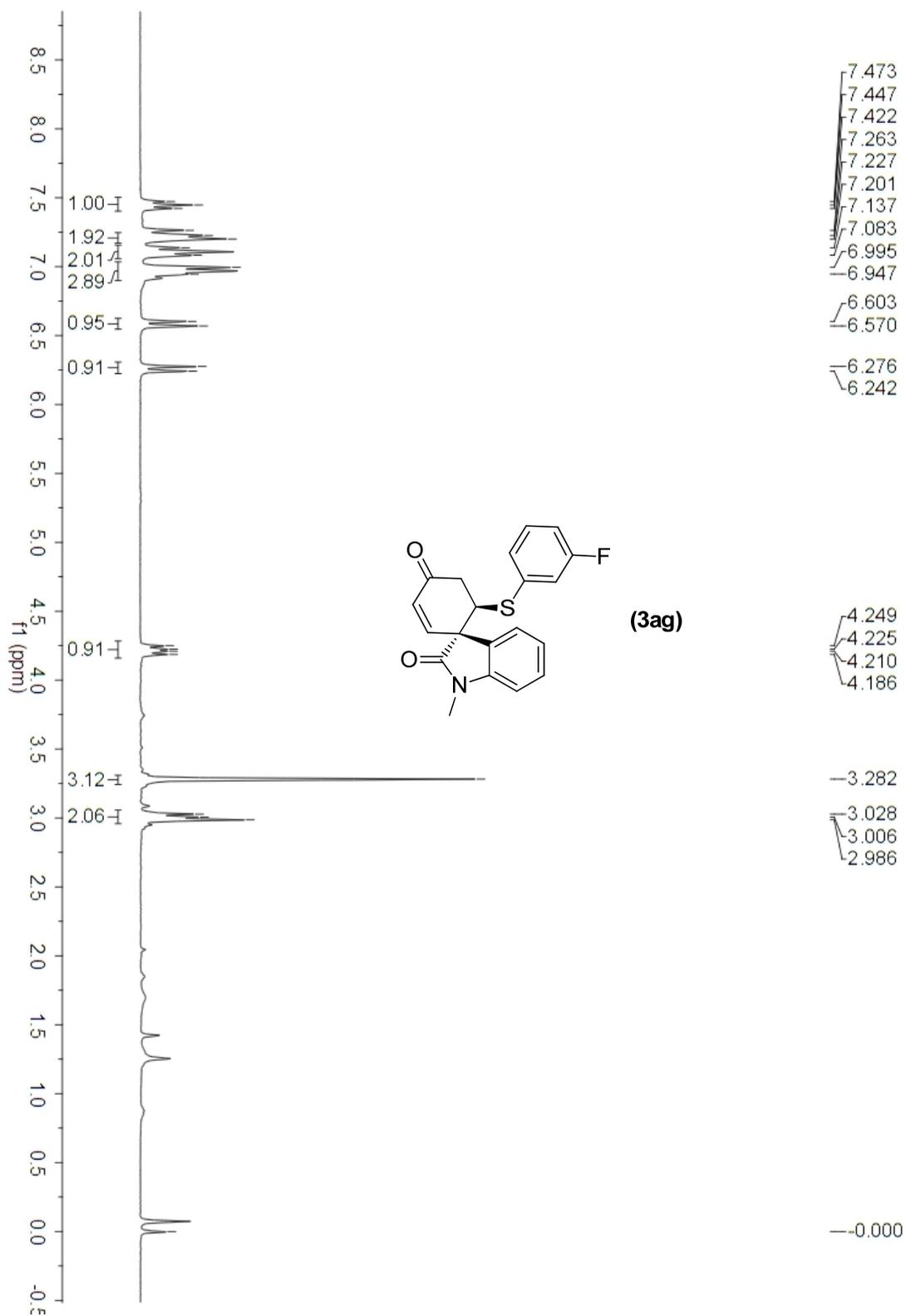


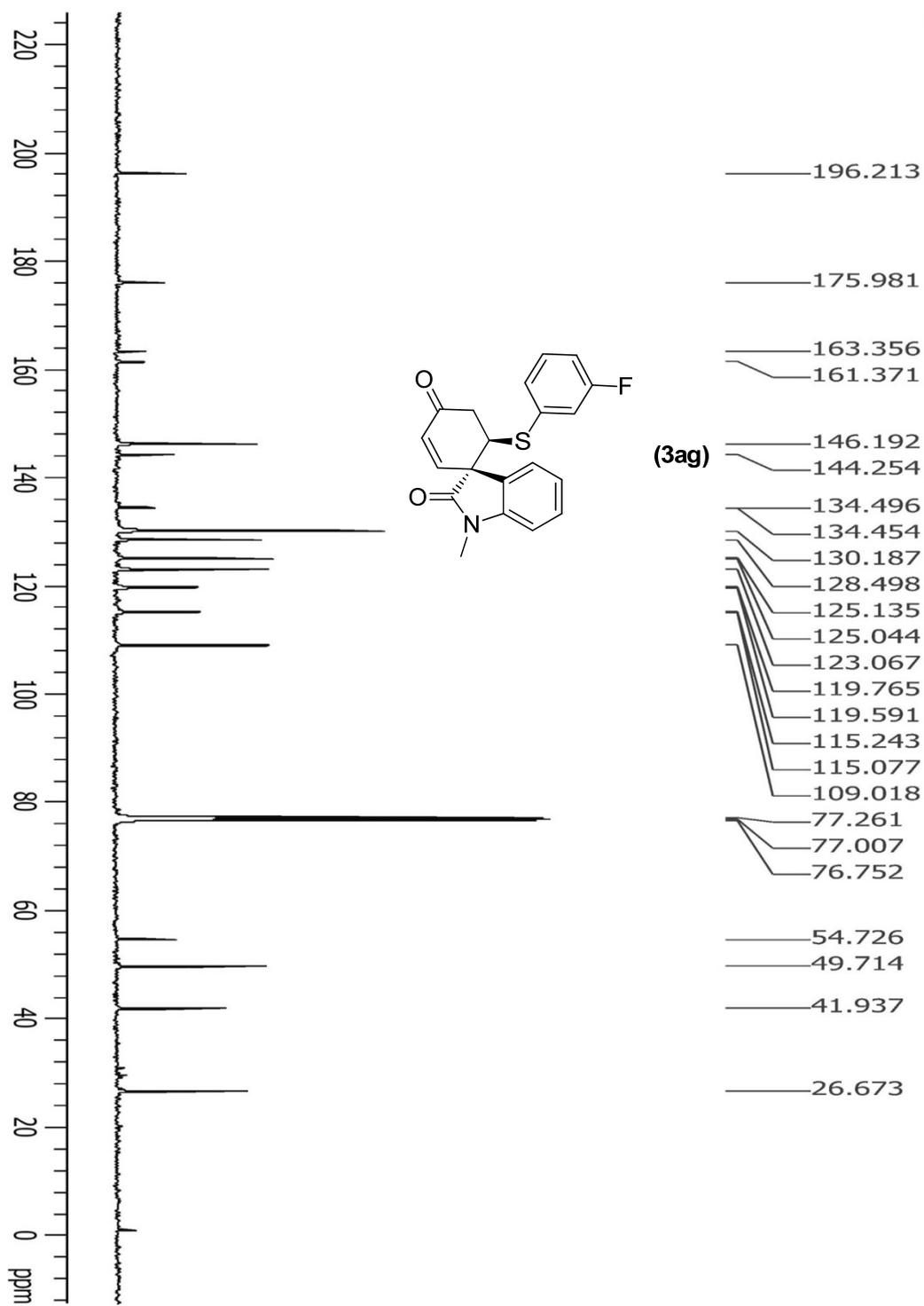


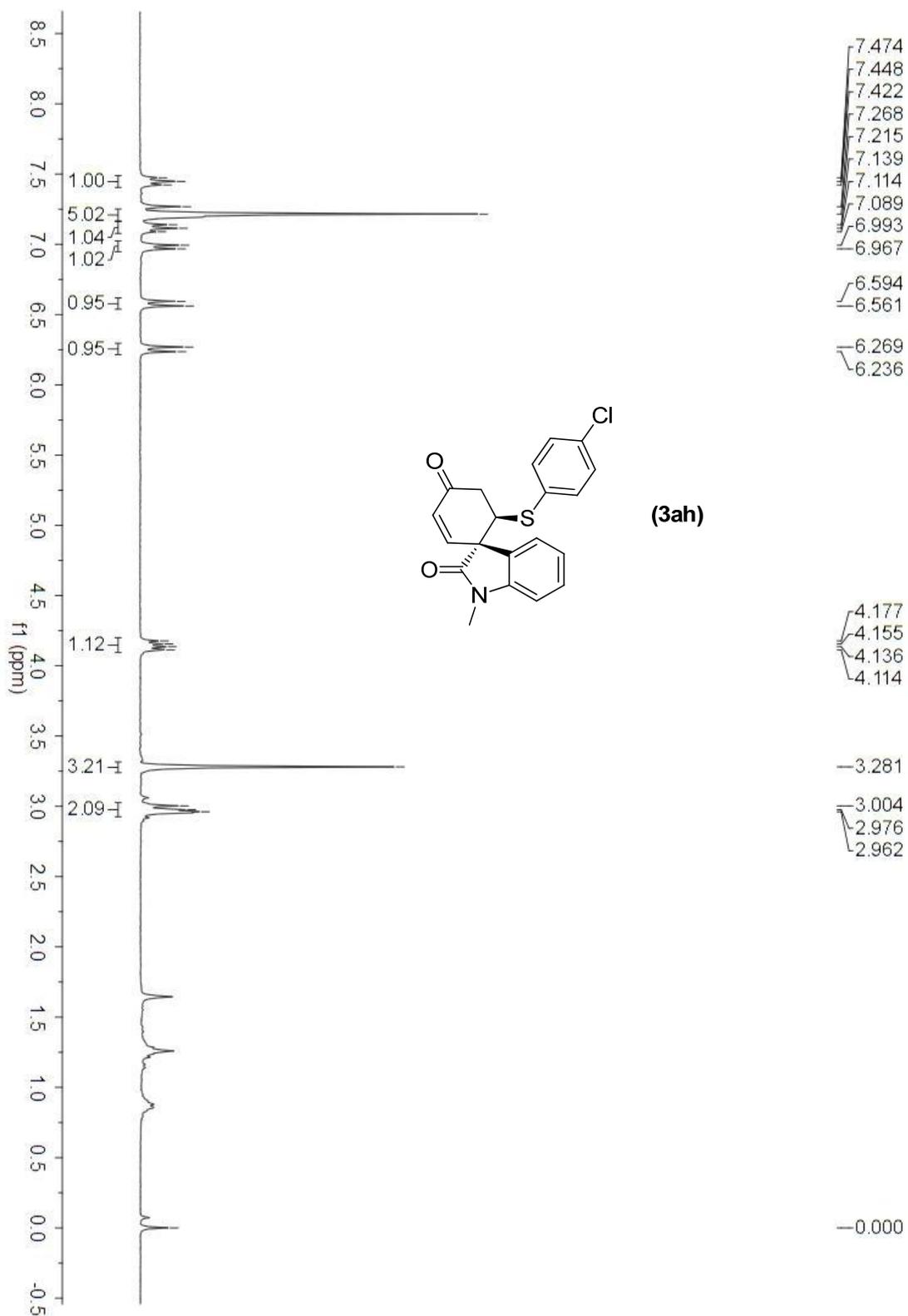


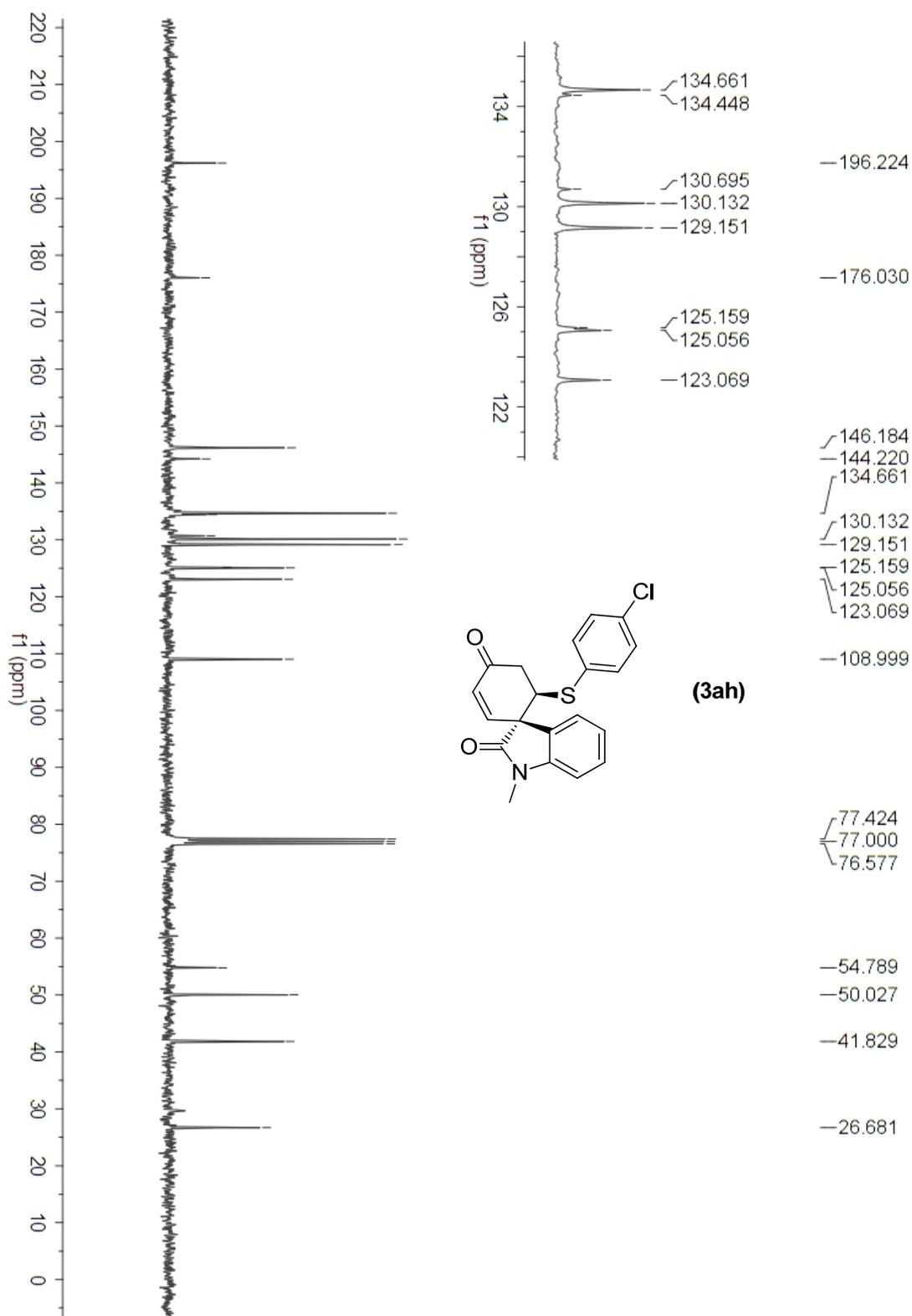


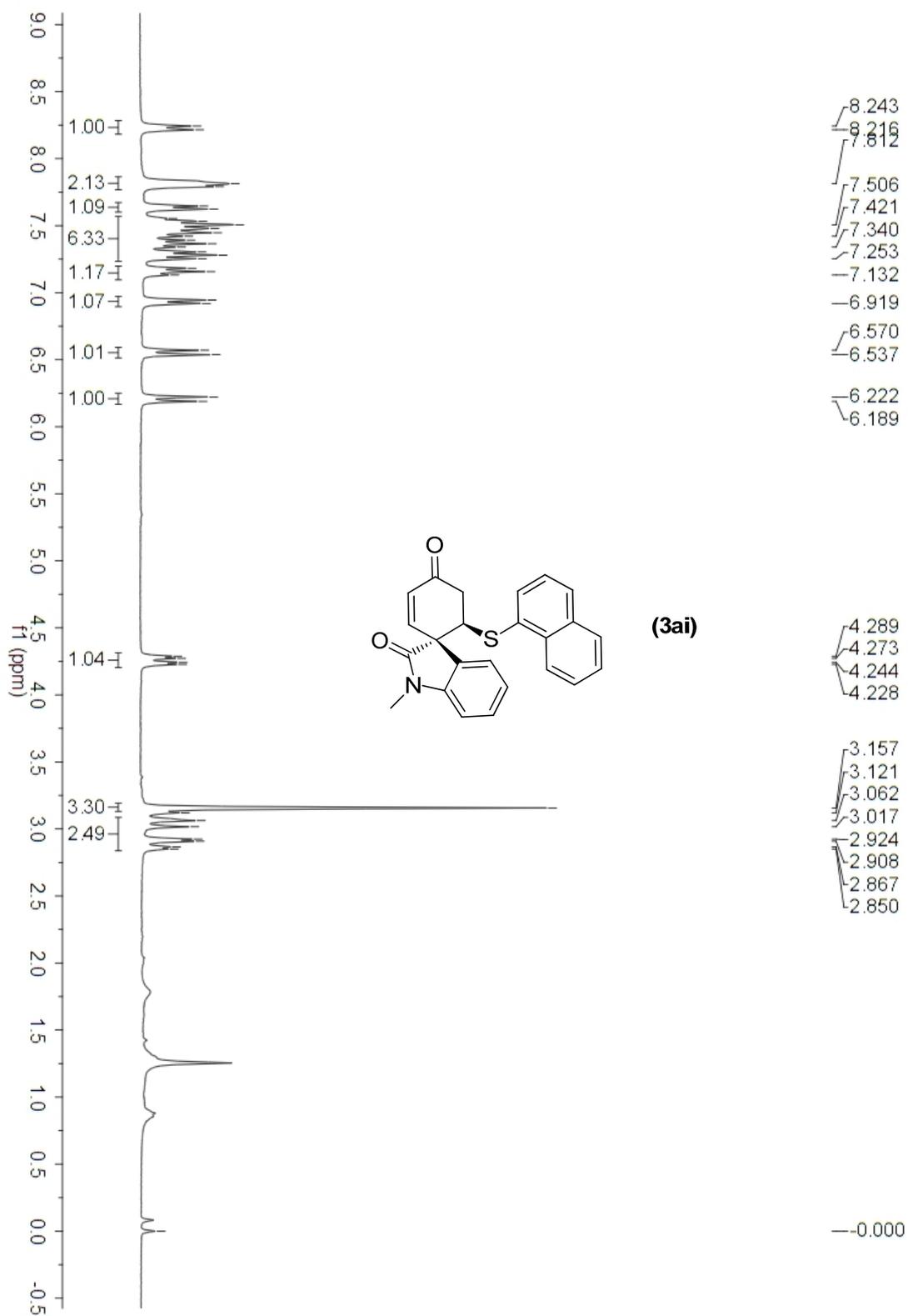


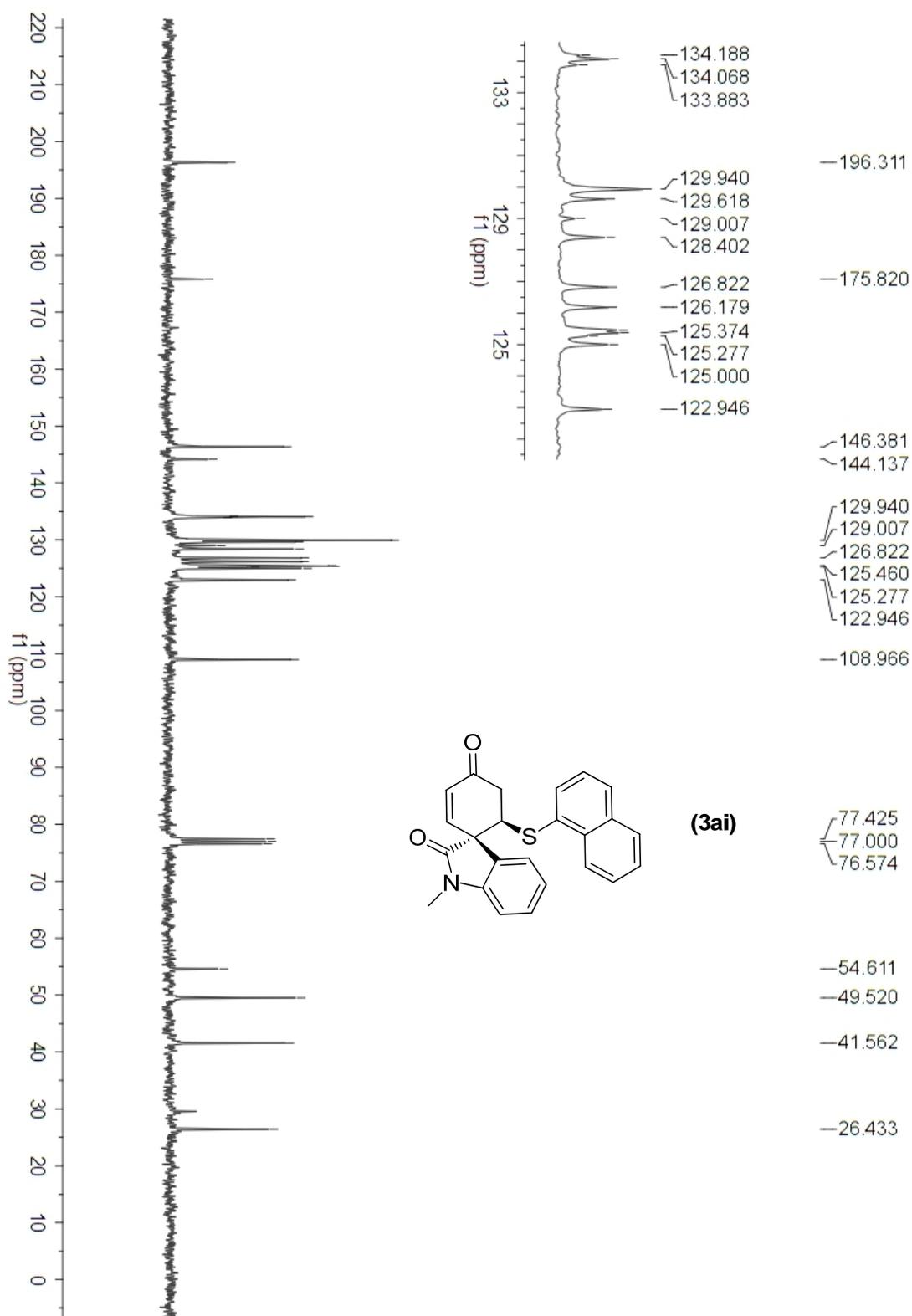


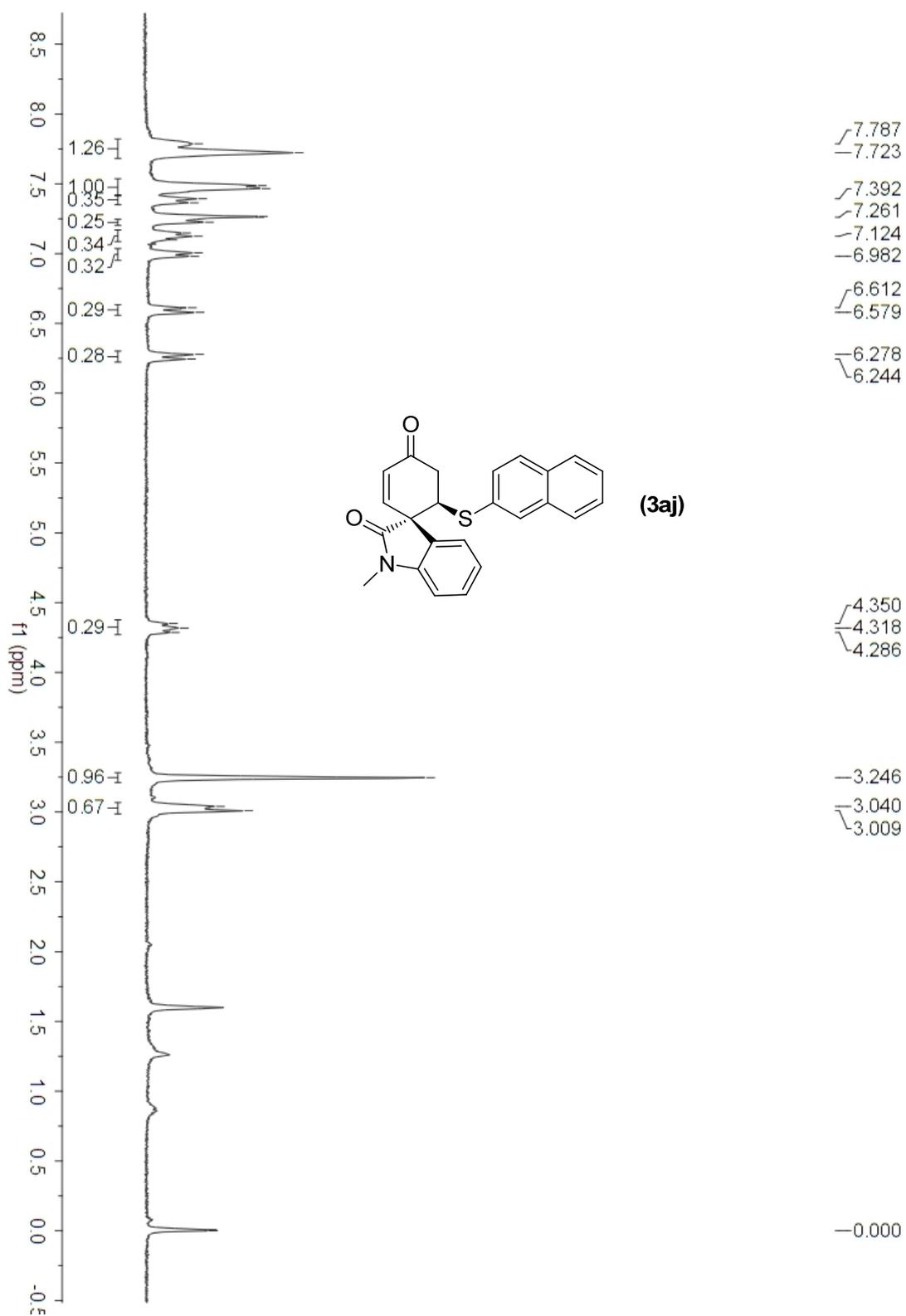


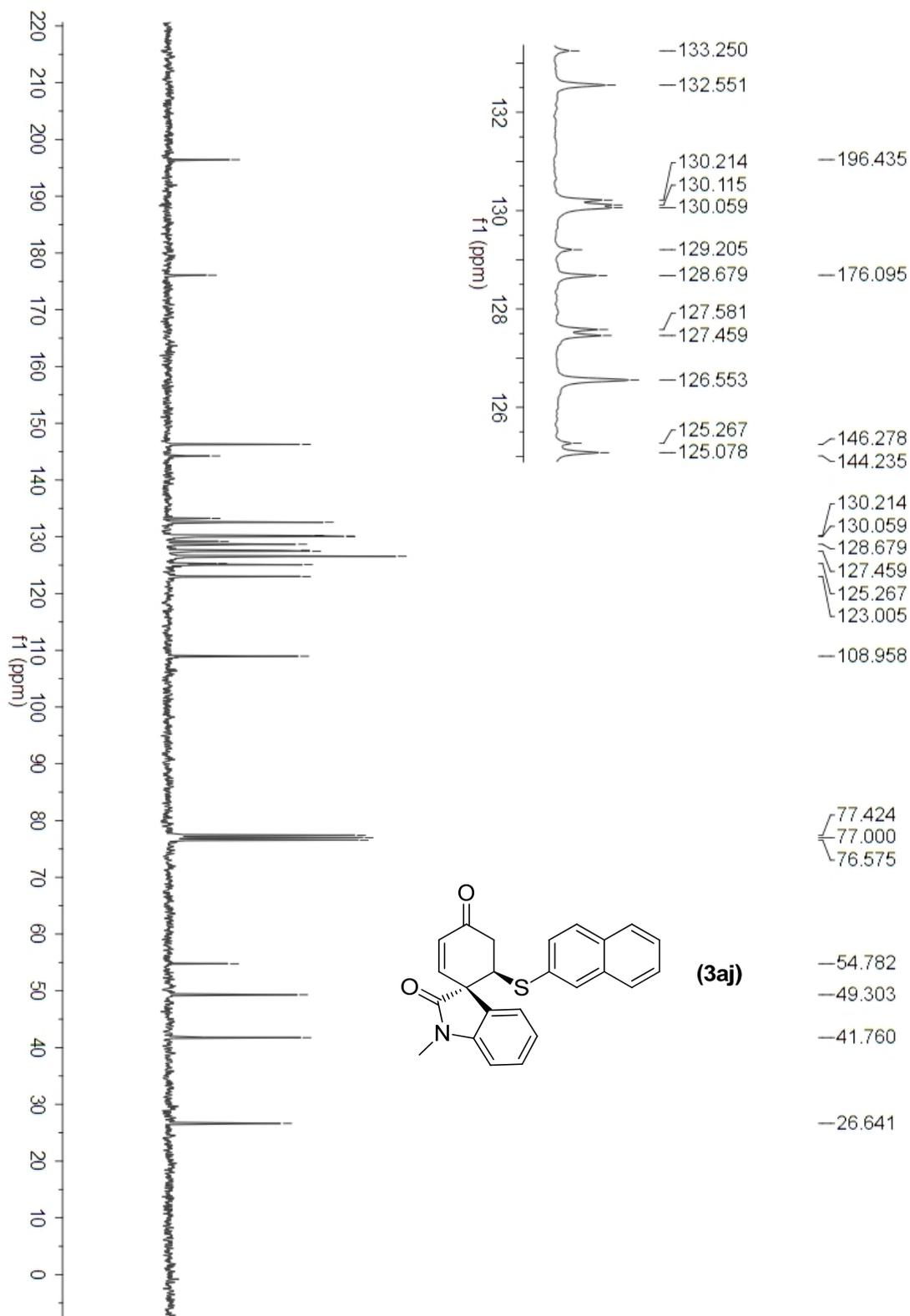


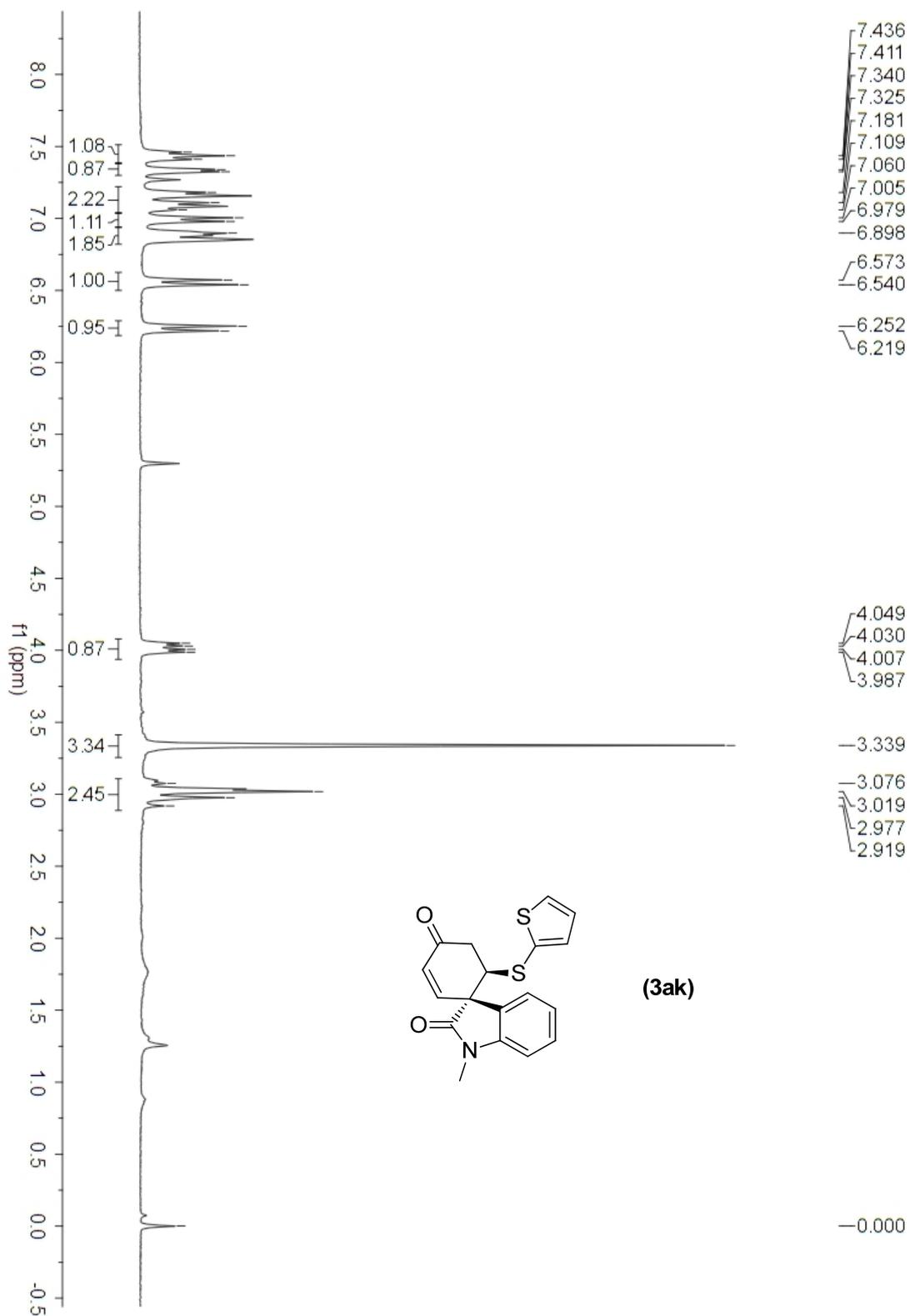


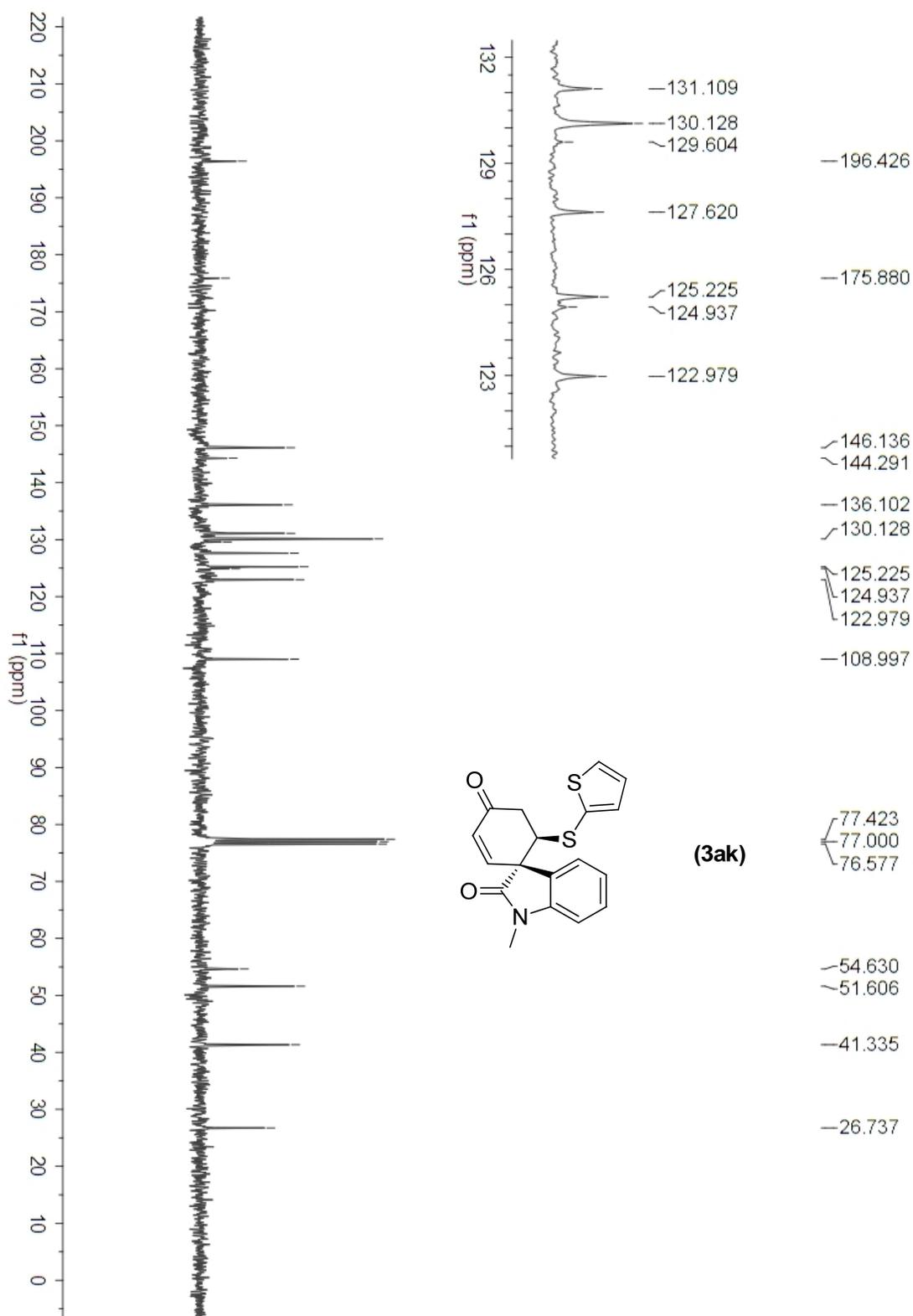


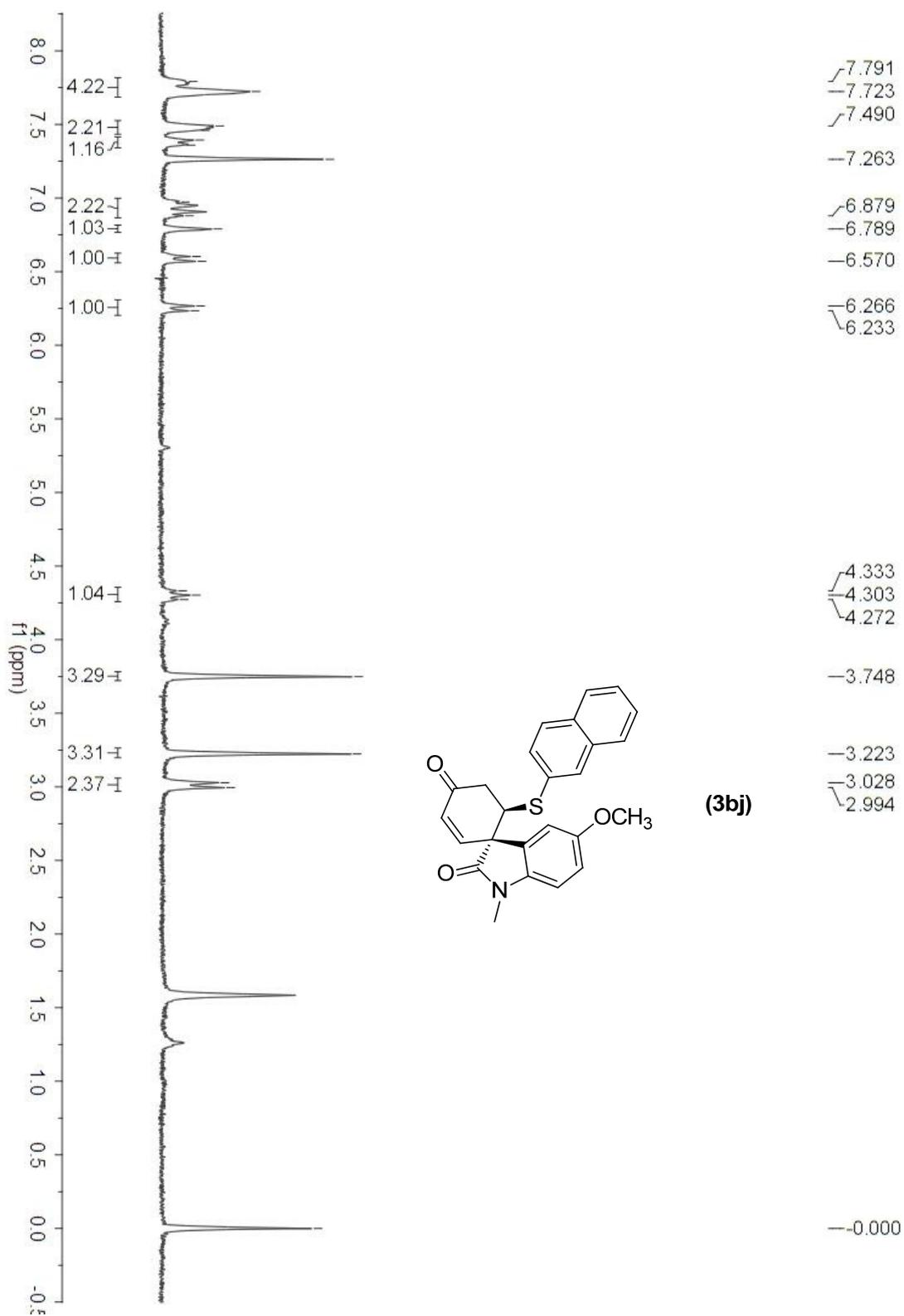


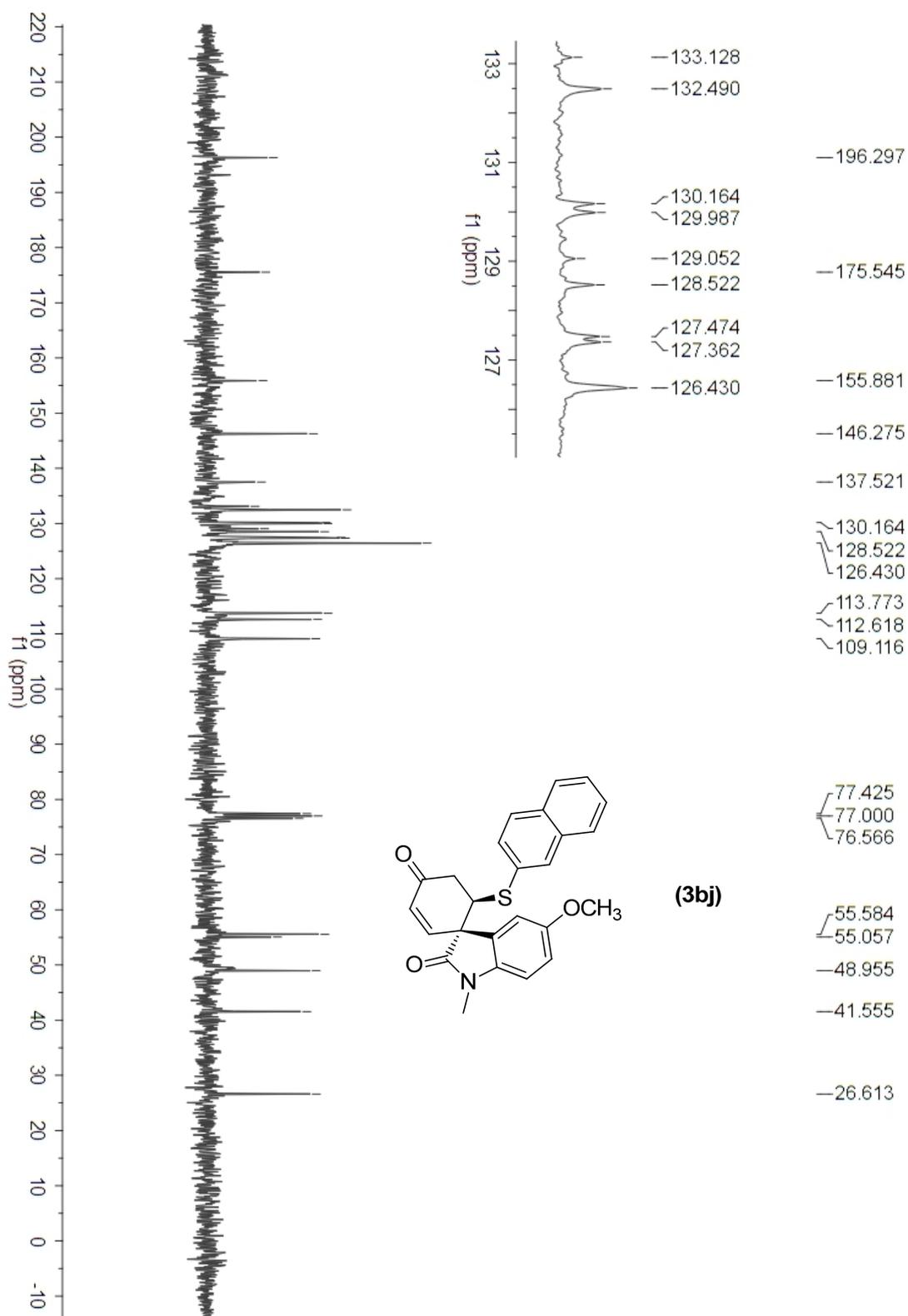


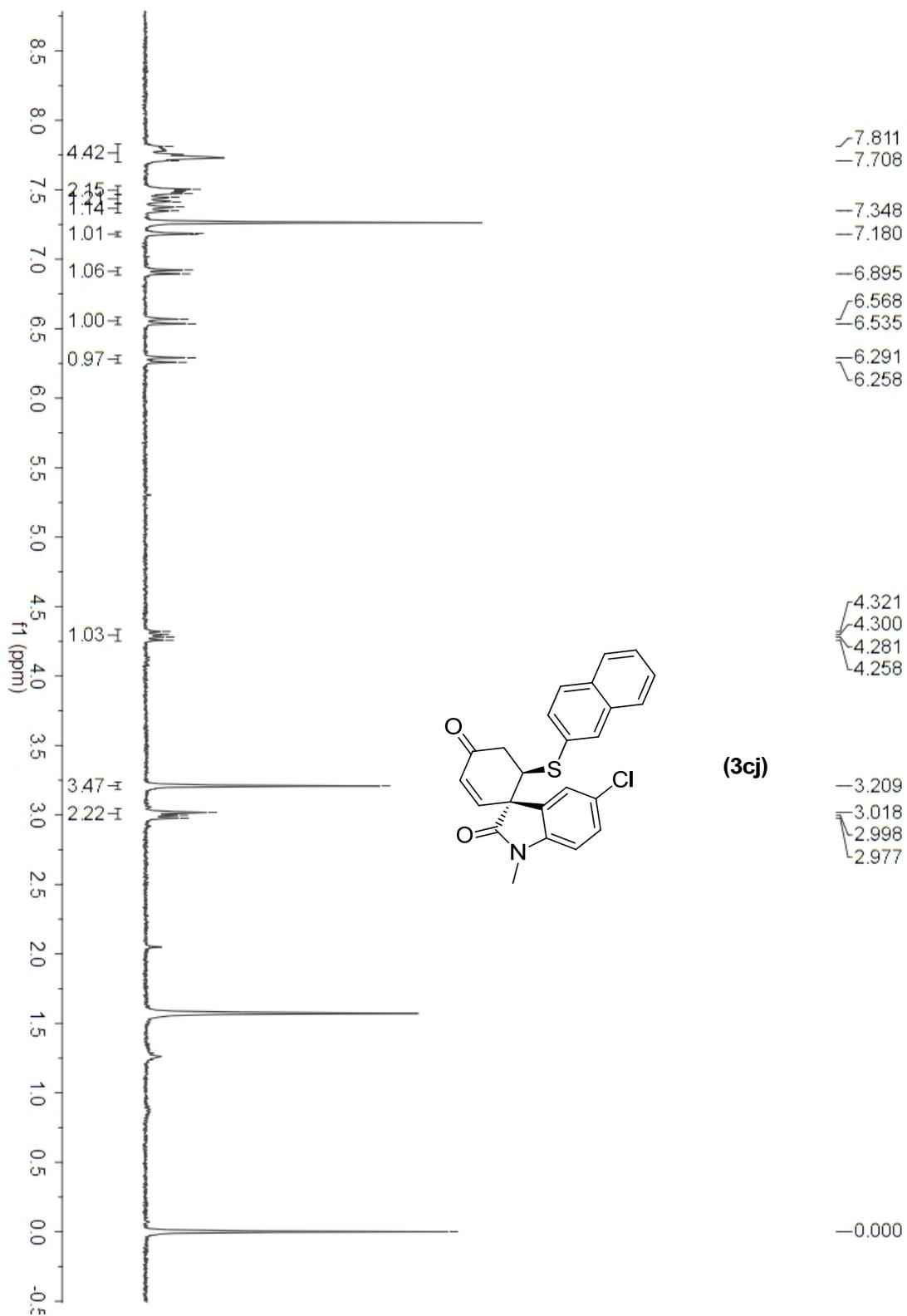


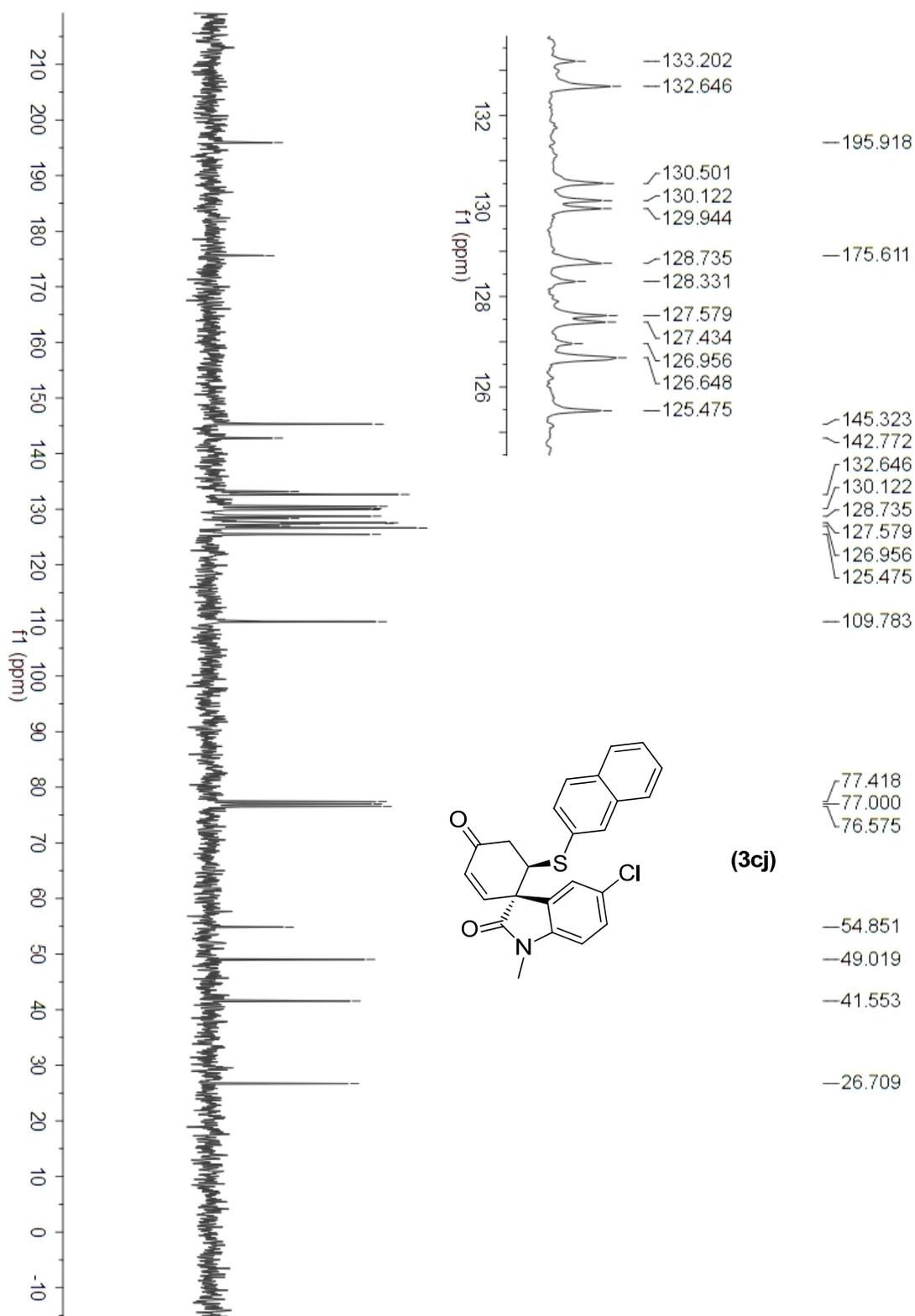


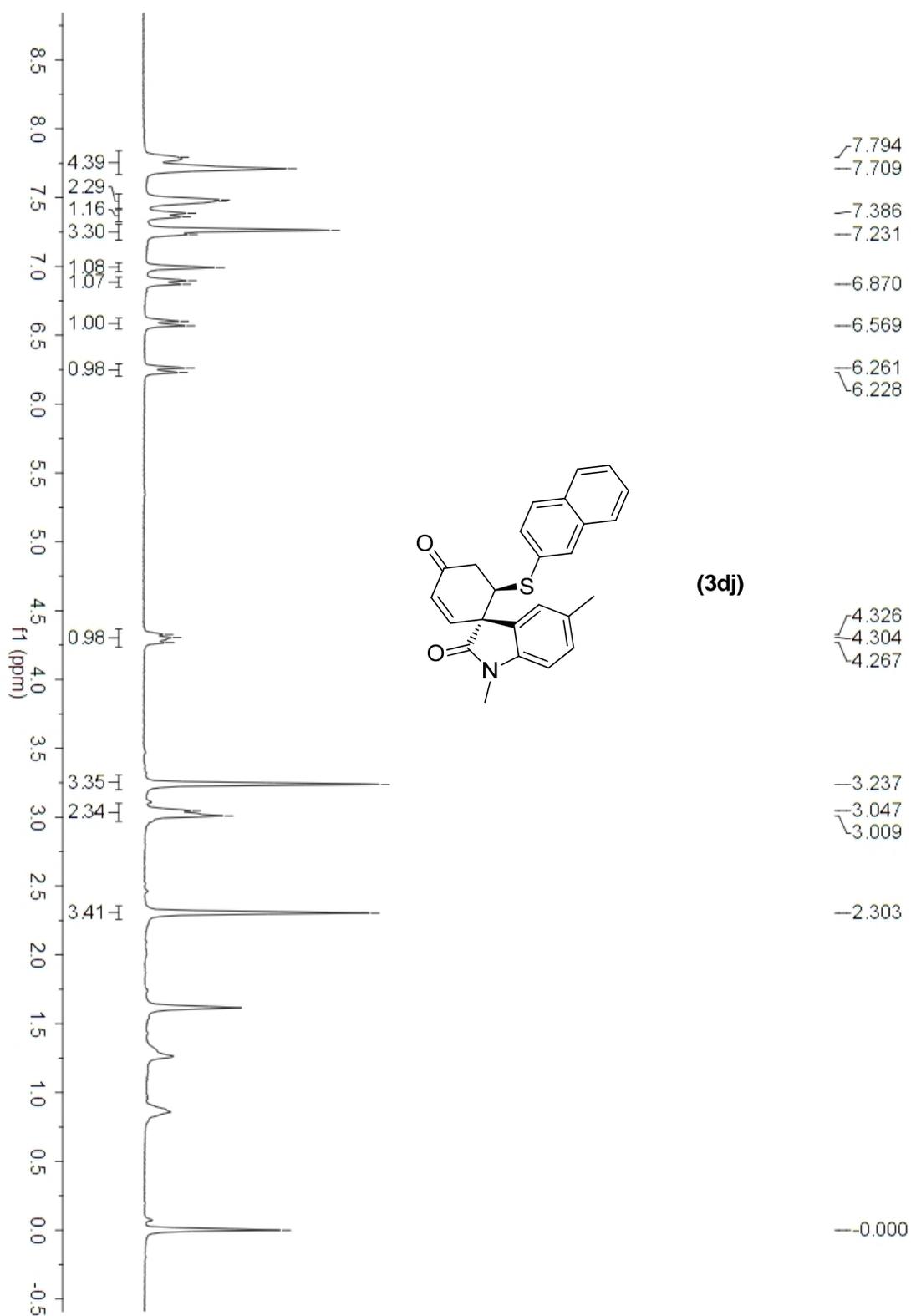


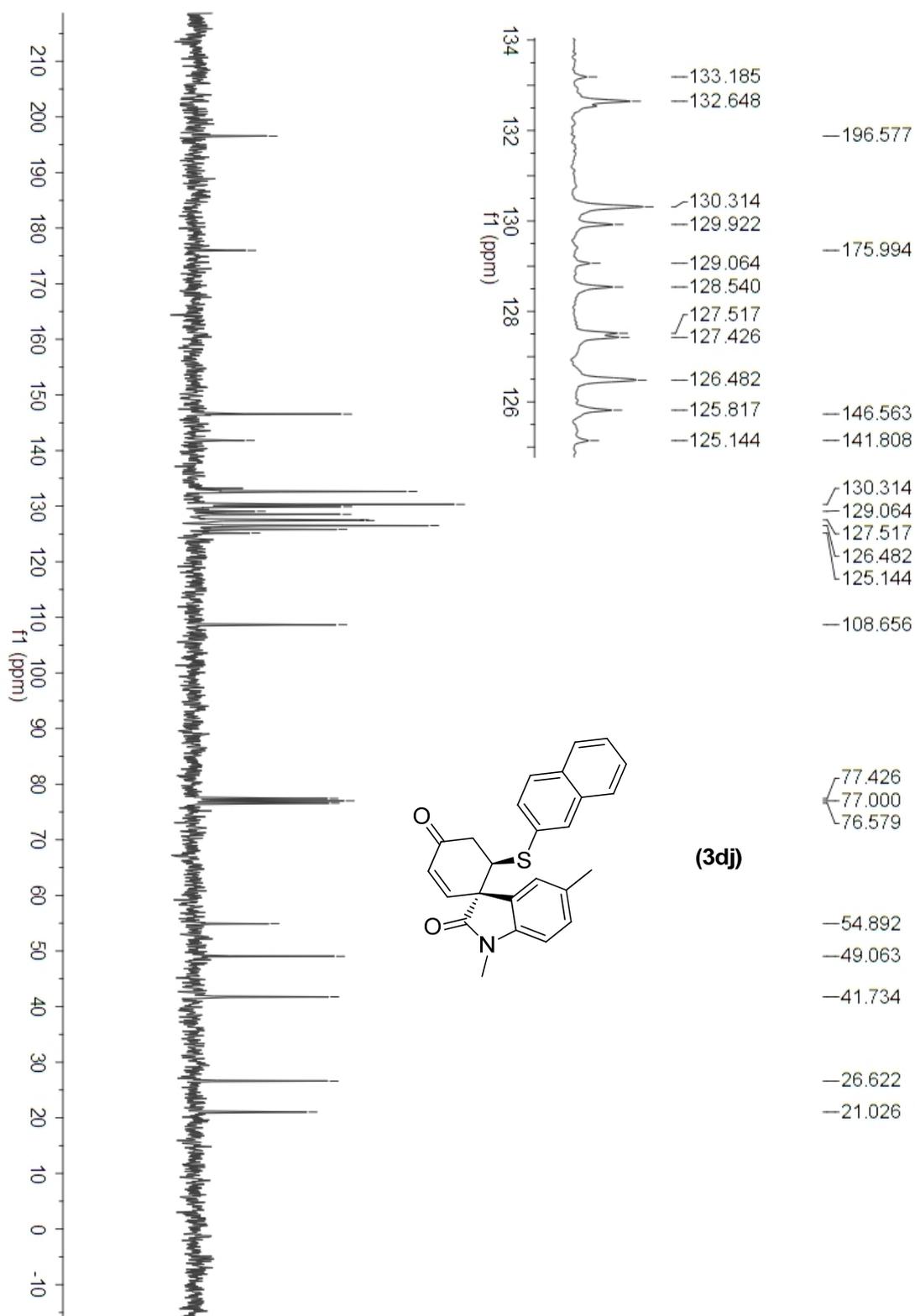




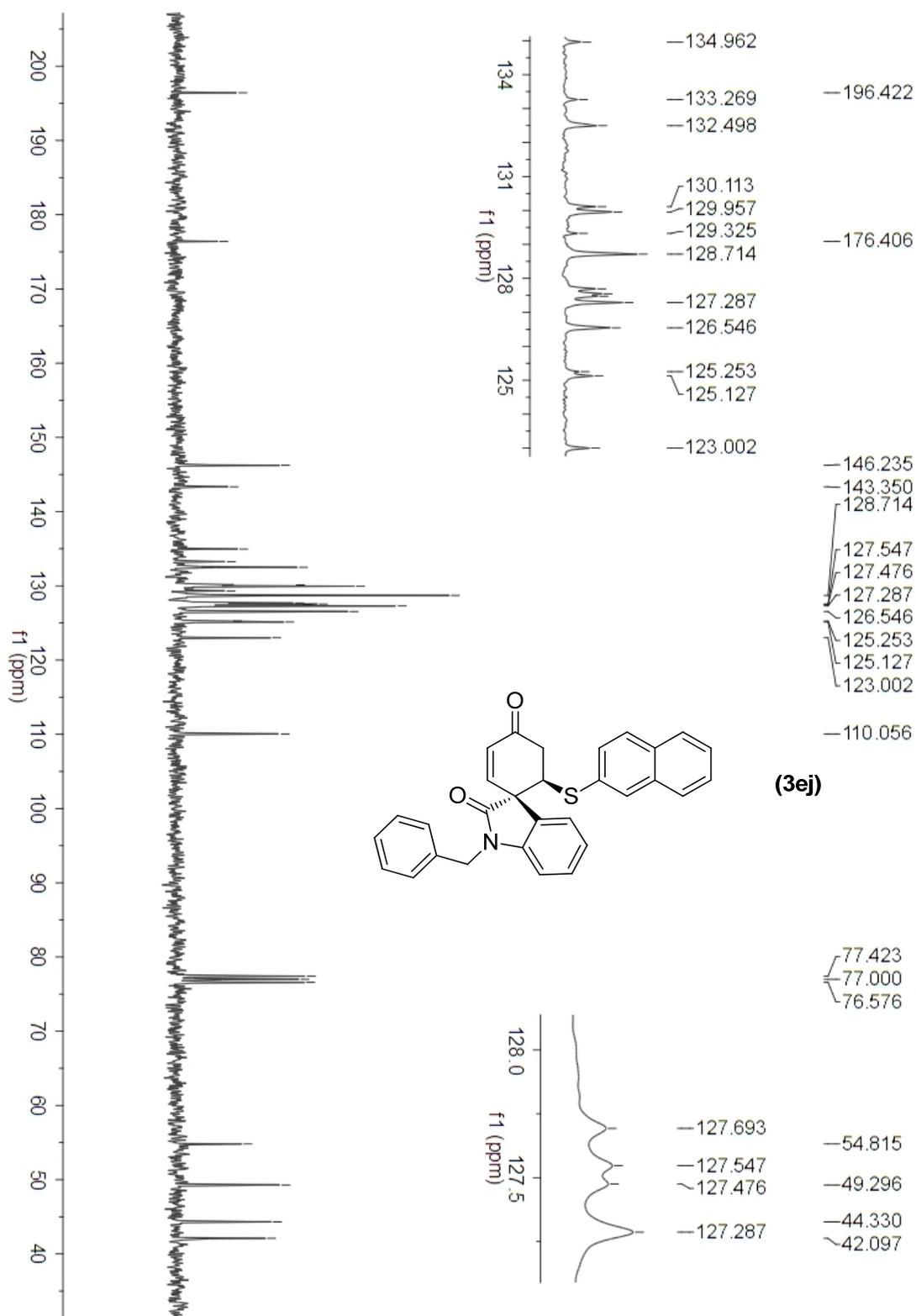


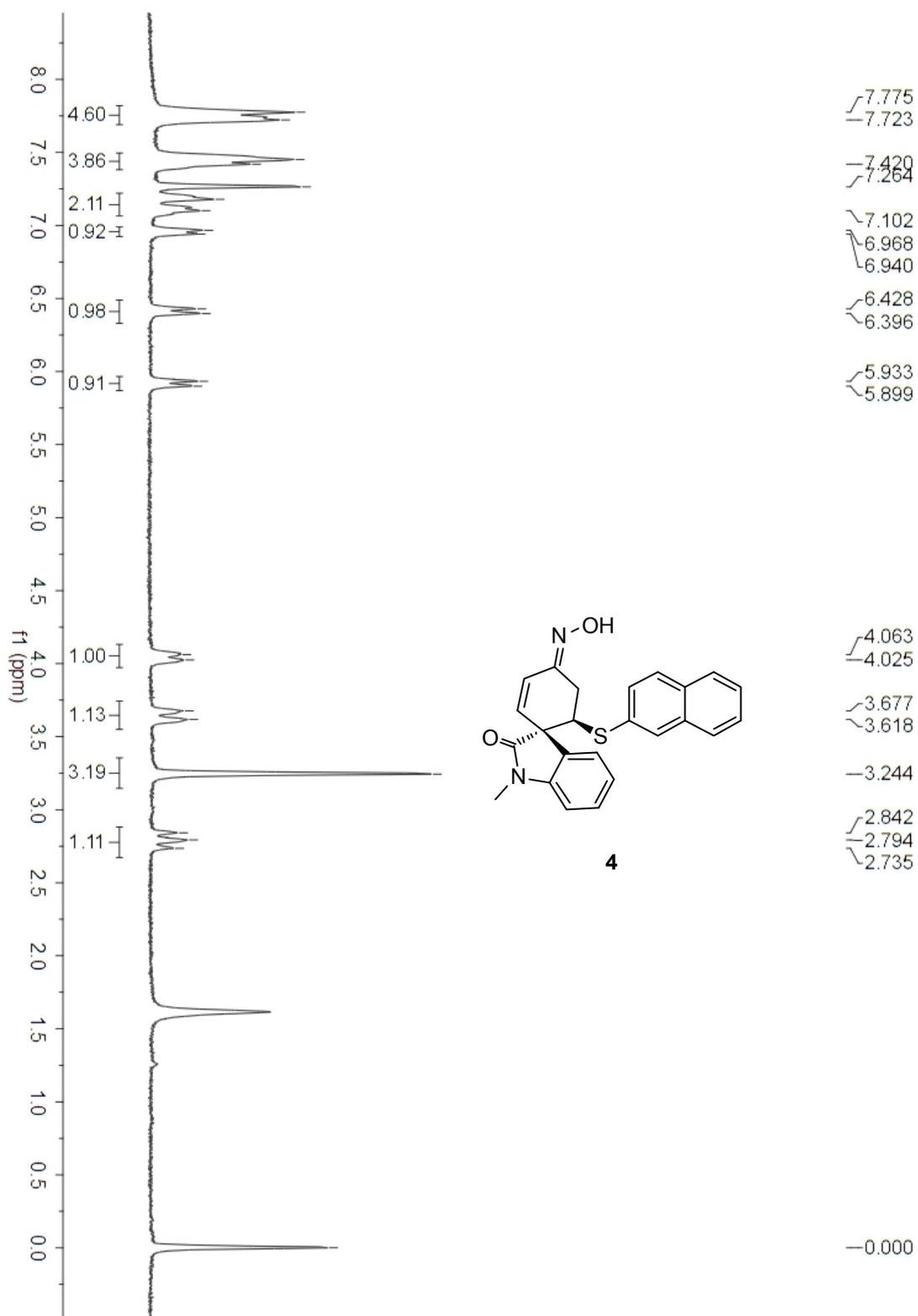


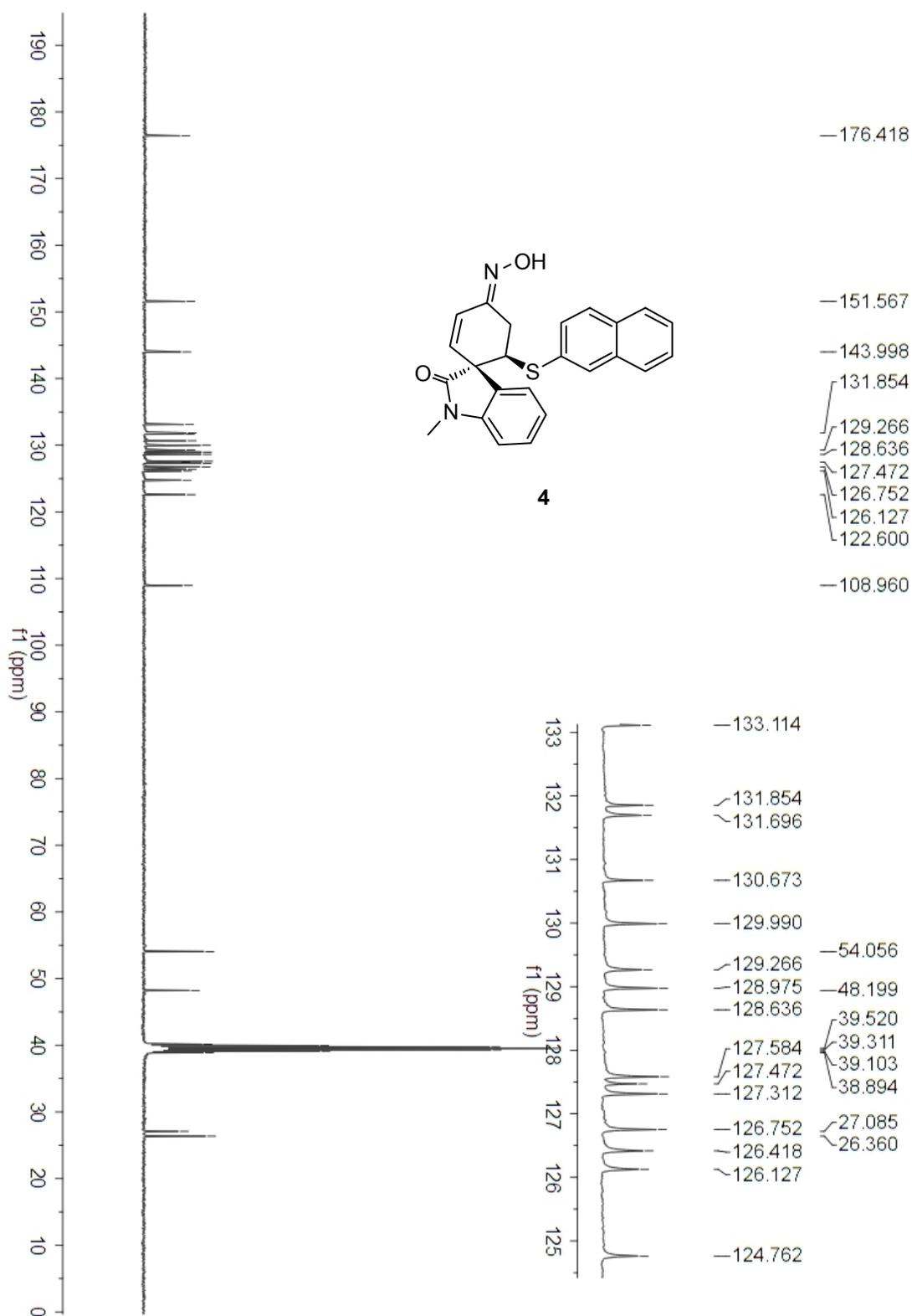


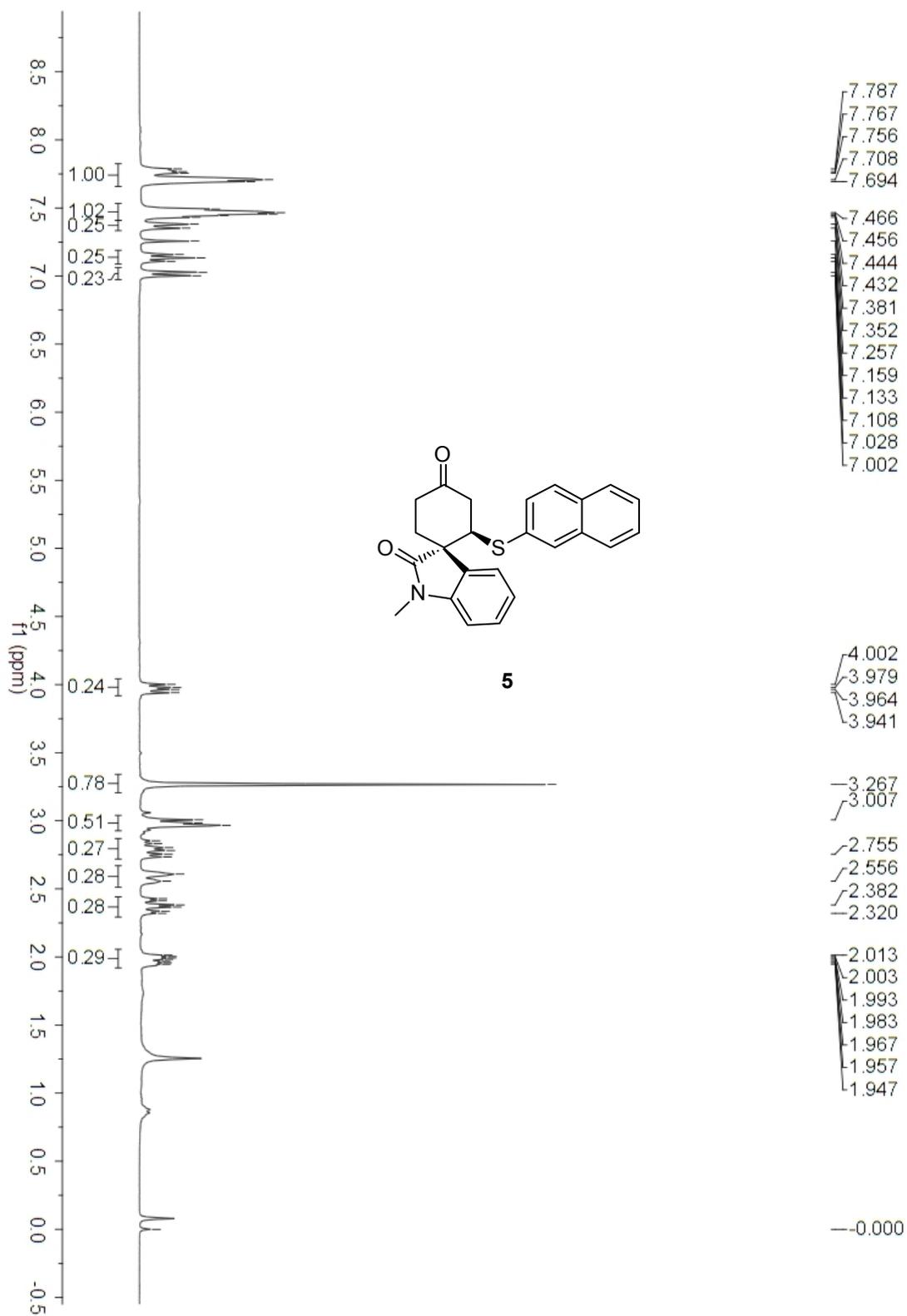


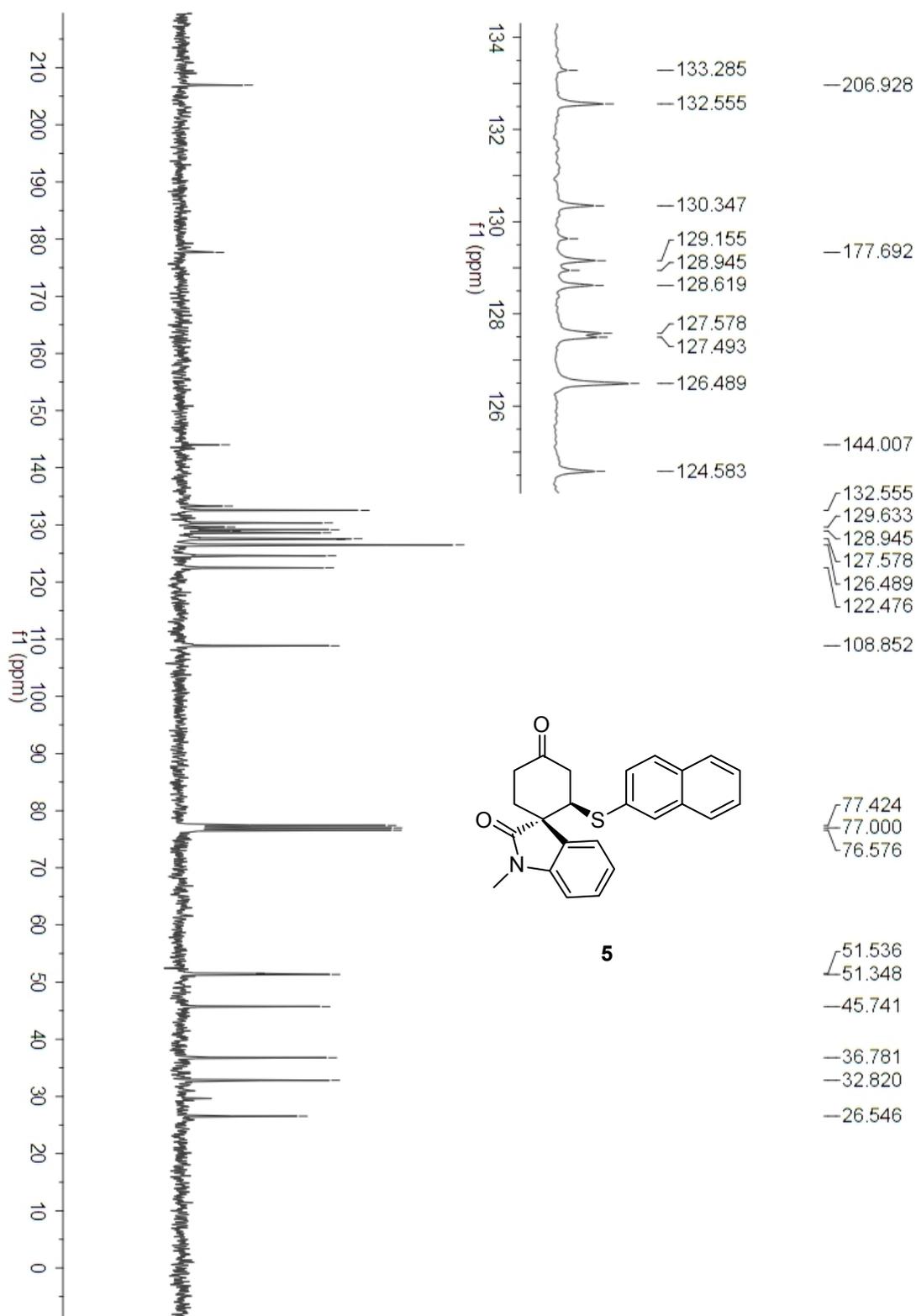


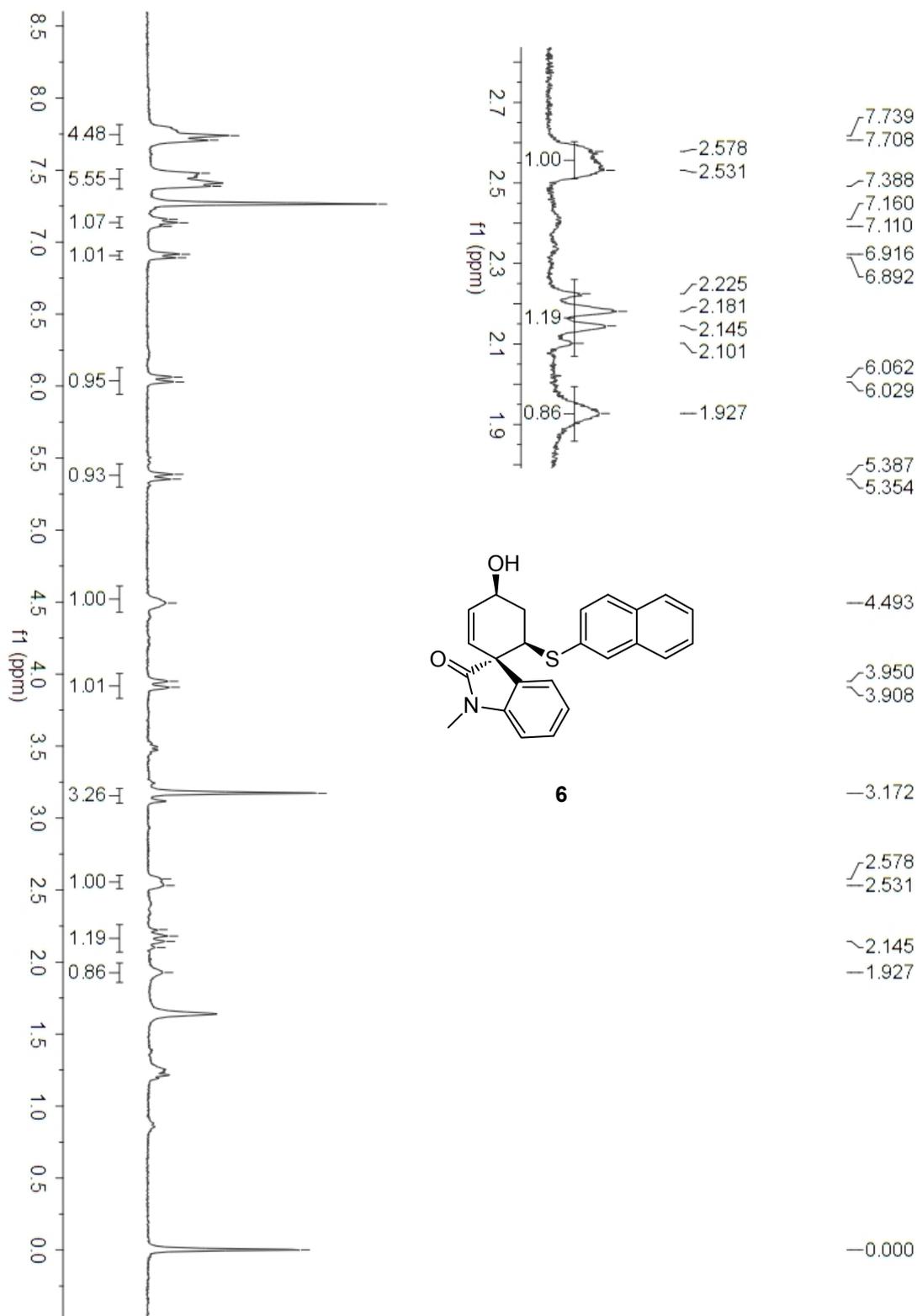


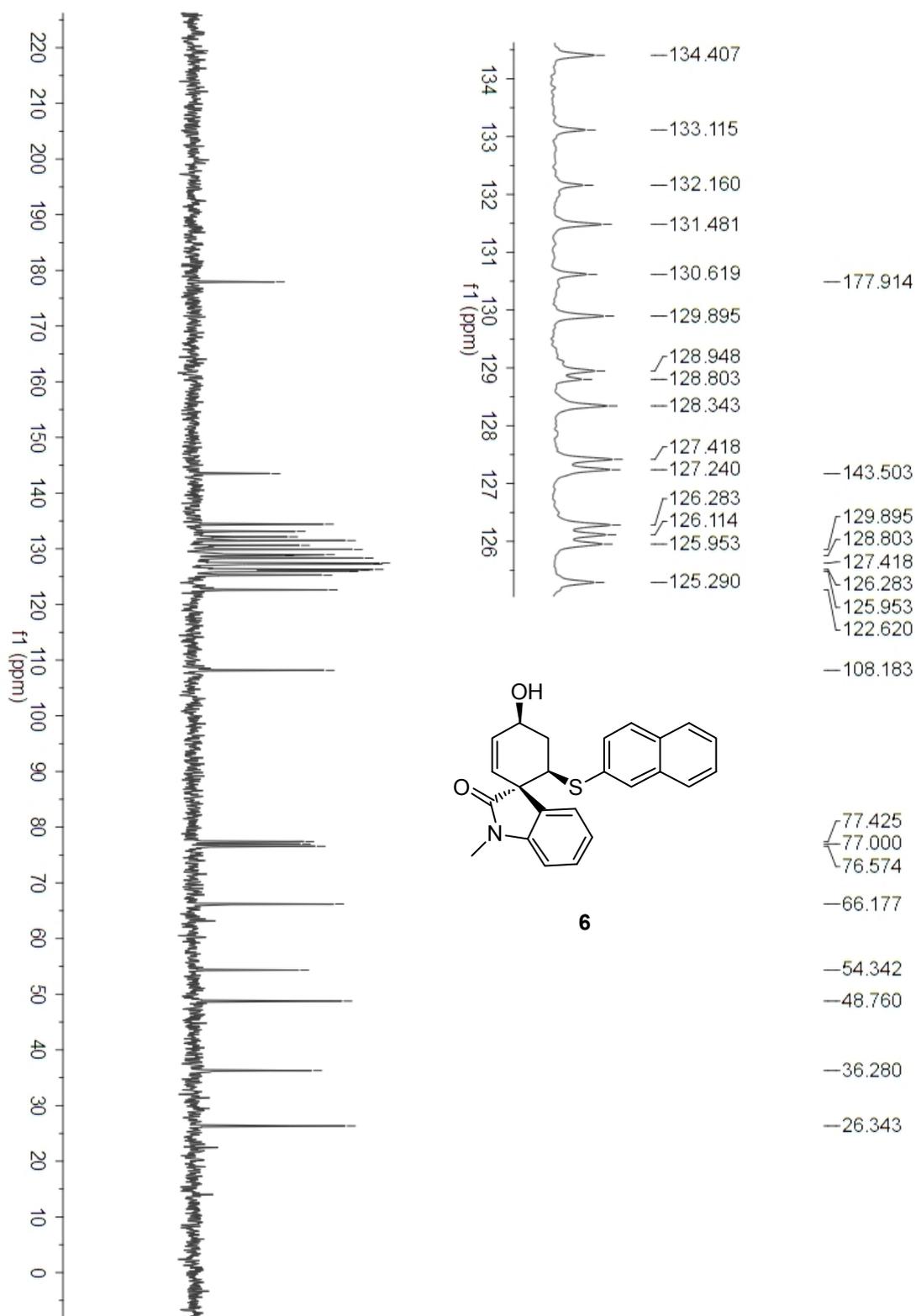


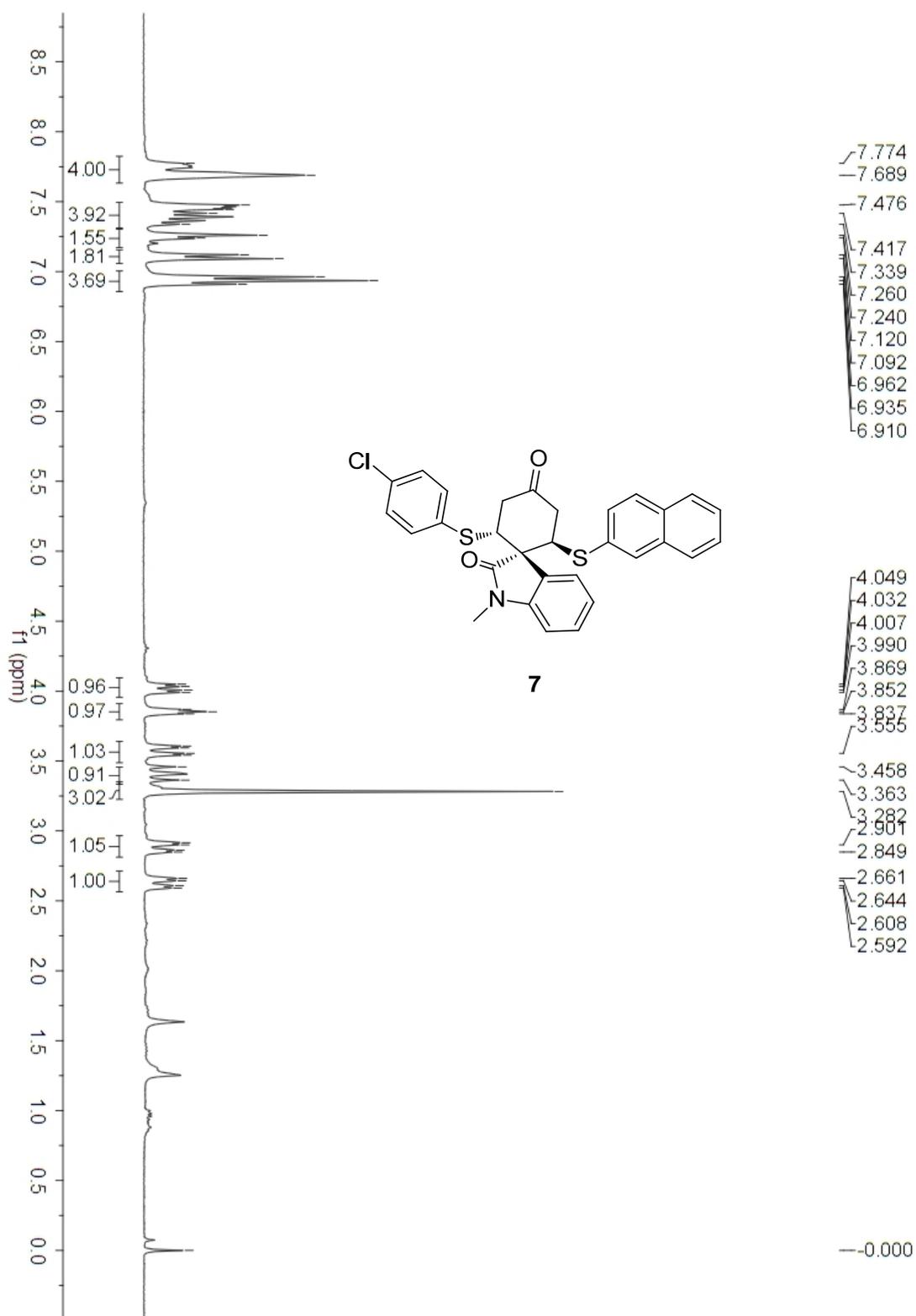


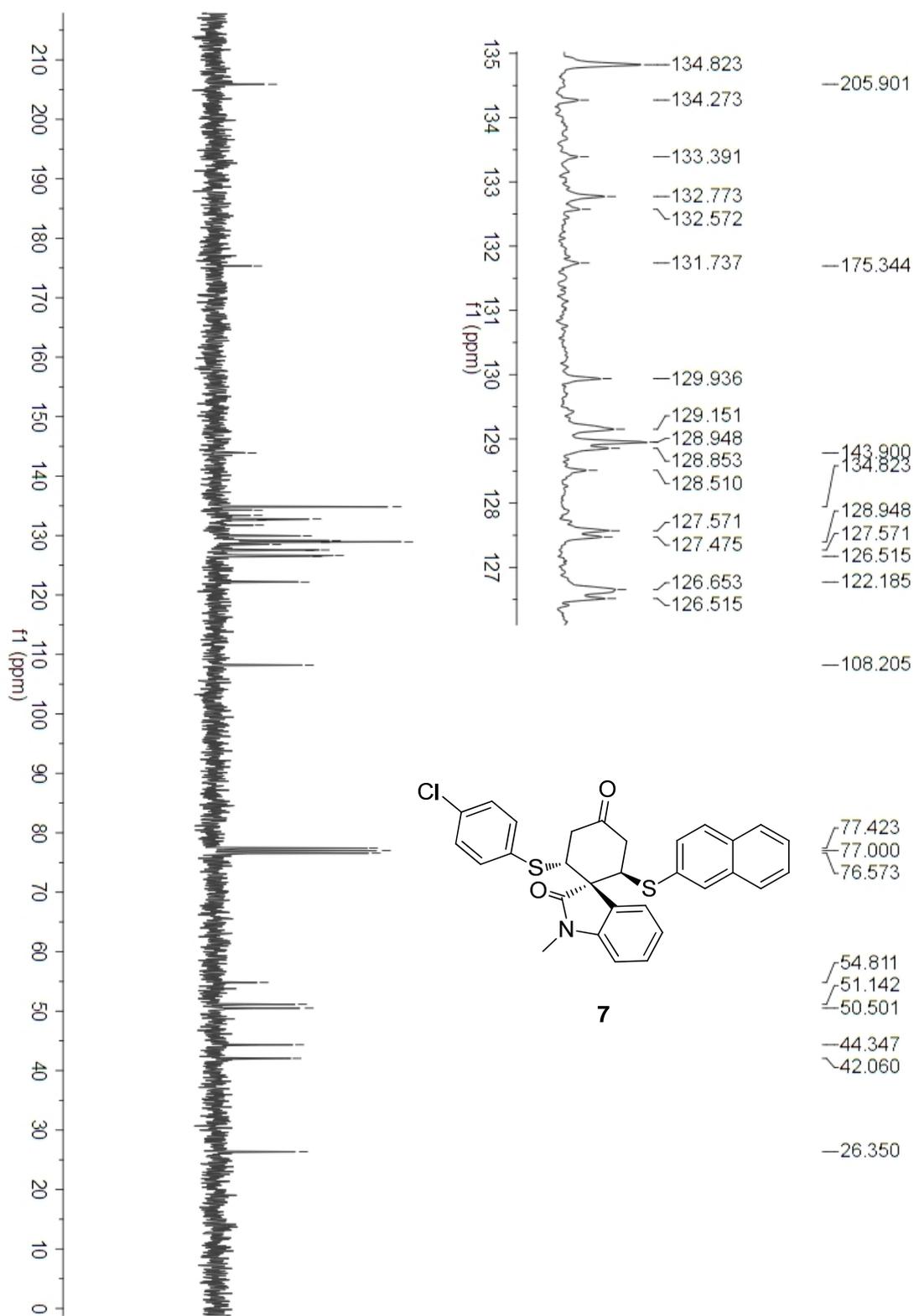


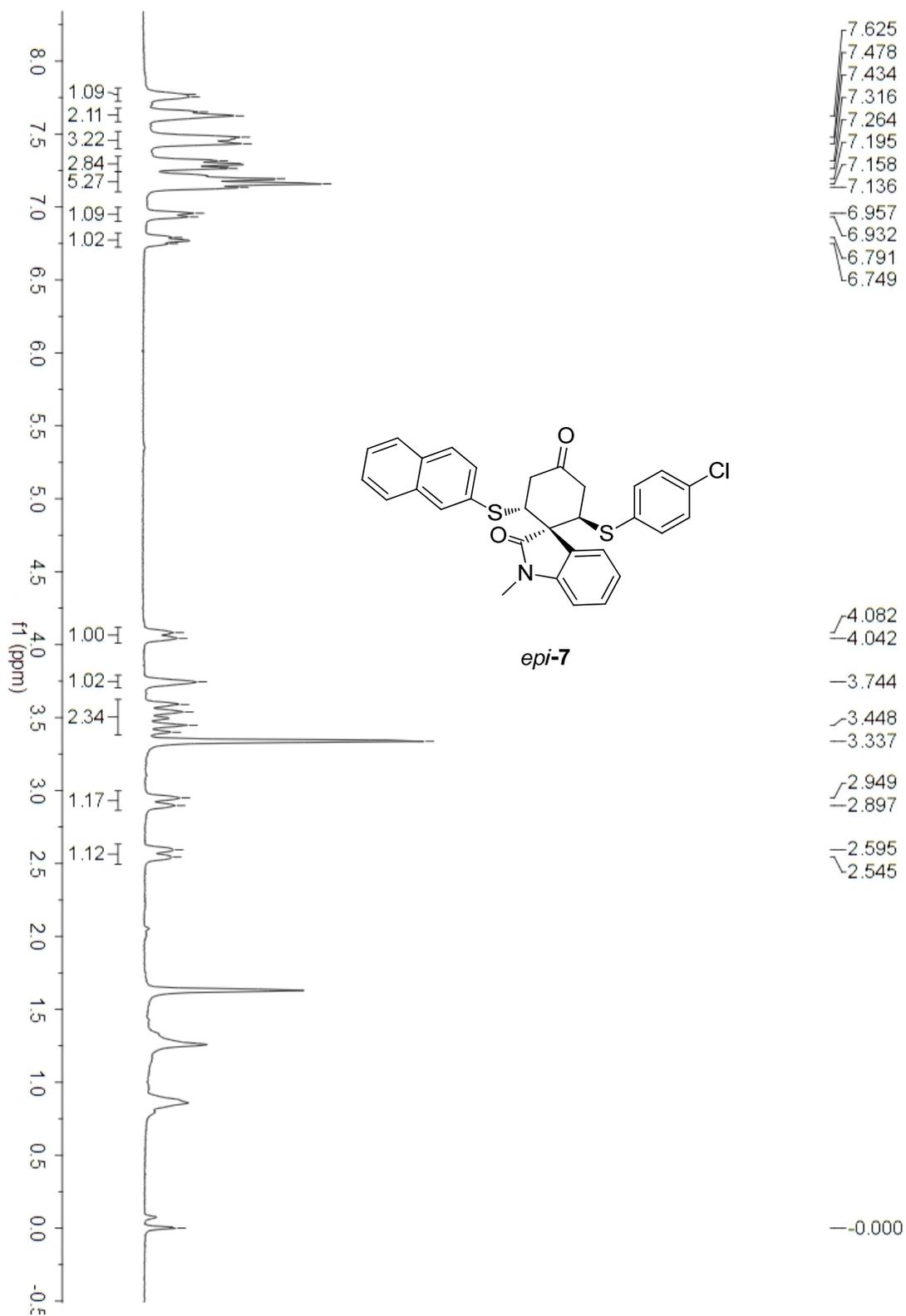


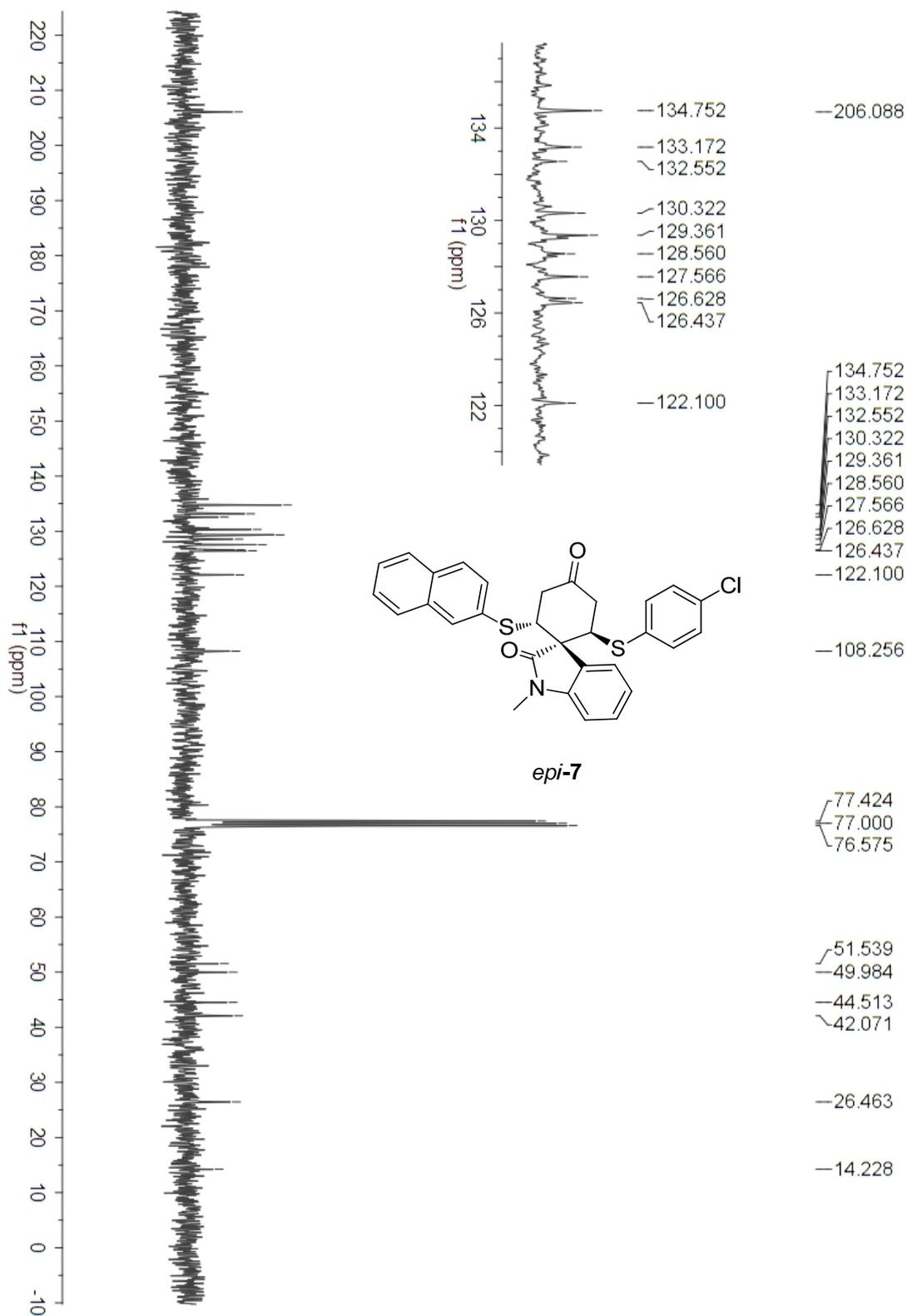


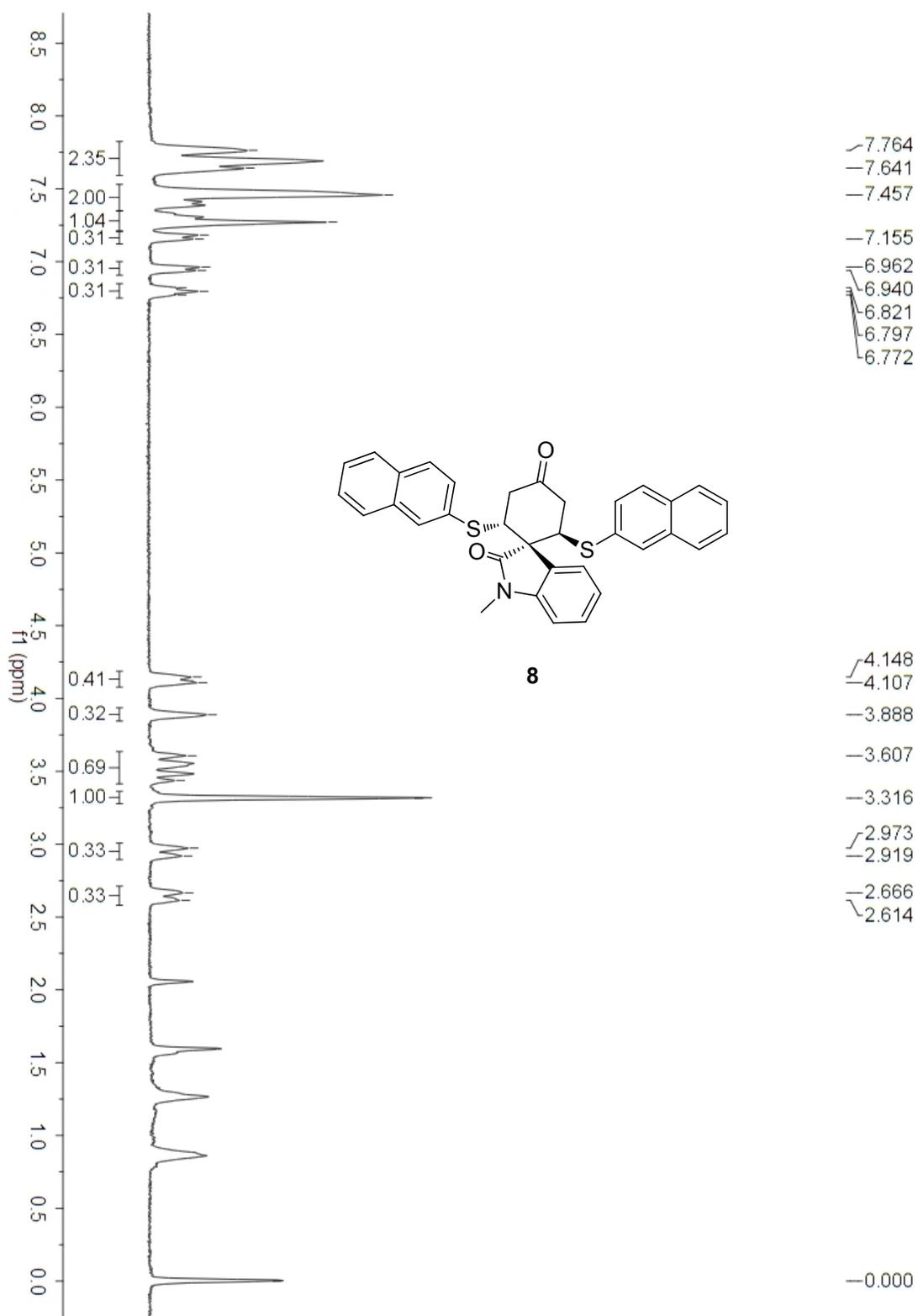


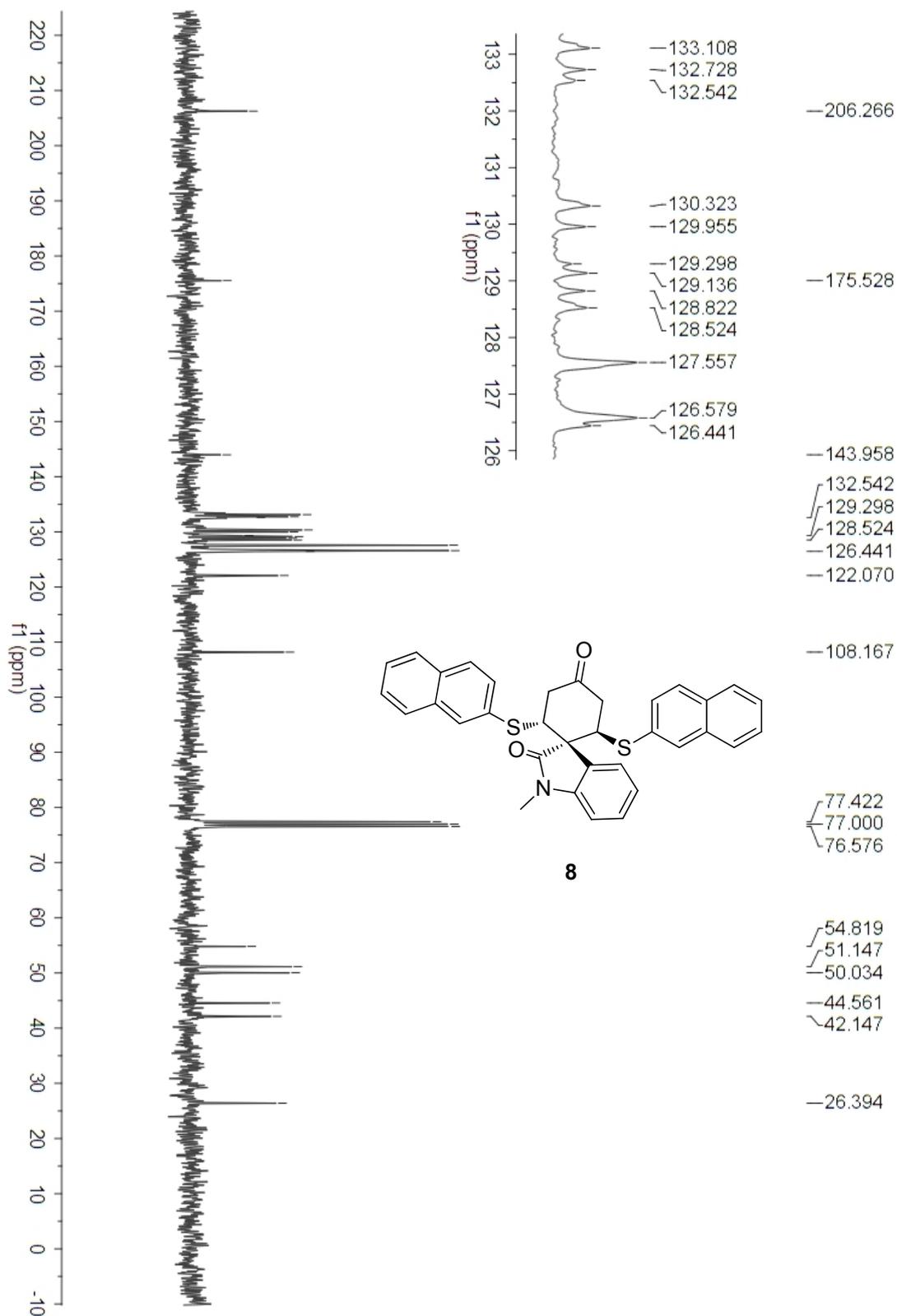








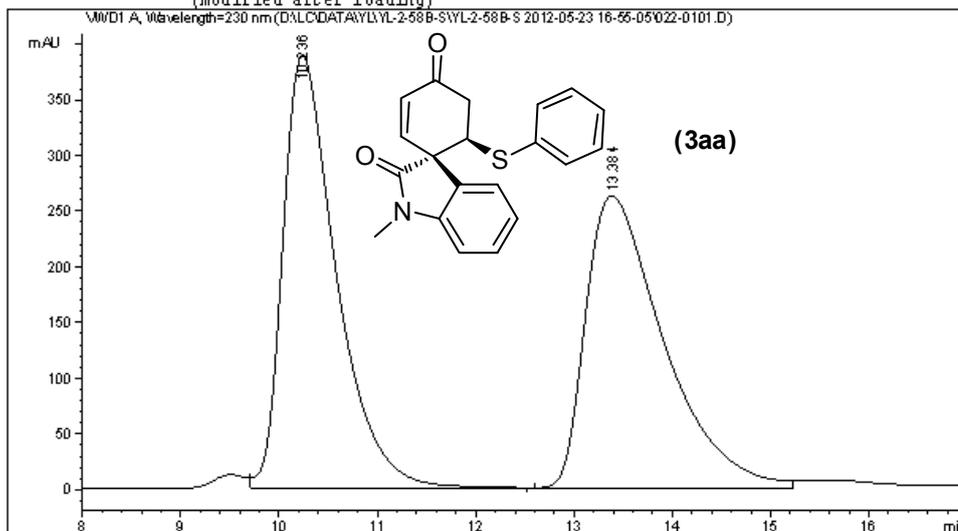




## VIII. HPLC Chromatograms

Data File D:\LC\DATA\YL\YL-2-58B-S\YL-2-58B-S 2012-05-23 16-55-05\022-0101.D  
Sample Name: YL-2-58B-S

```
=====
Acq. Operator   : THL                               Seq. Line :    1
Acq. Instrument : Instrument 1                       Location  : Vial 22
Injection Date  : 5/23/2012 4:57:07 PM              Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\DATA\YL\YL-2-58B-S\YL-2-58B-S 2012-05-23 16-55-05\ASH-50-50-1ML-
                230NM.M
Last changed    : 5/23/2012 4:54:08 PM by THL
Analysis Method : D:\LC\DATA\YL\YL-2-58B-S\YL-2-58B-S 2012-05-23 16-55-05\022-0101.D\D.A.M (
                ASH-50-50-1ML-230NM.M)
Last changed    : 1/30/2013 9:56:22 AM by FX
                (modified after loading)
=====
```



### Area Percent Report

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: WVD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	10.236	VB	0.5690	1.46745e4	388.35678	50.3719
2	13.384	BB	0.8274	1.44578e4	262.54214	49.6281

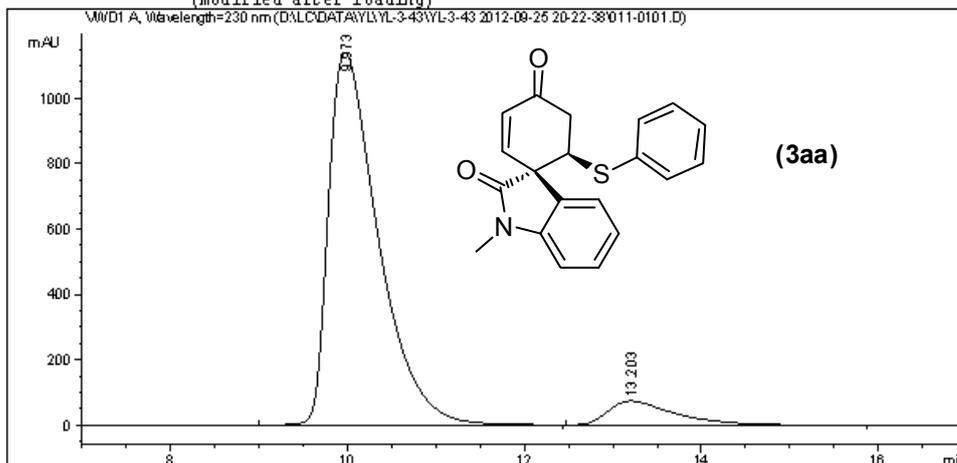
Totals : 2.91323e4 650.89893

Instrument 1 1/30/2013 9:56:43 AM FX

Page 1 of 1

Data File D:\LC\DATA\YL\YL-3-43\YL-3-43 2012-09-25 20-22-38\011-0101.D  
Sample Name: YL-3-43

```
=====
Acq. Operator   : YL                      Seq. Line :    1
Acq. Instrument : Instrument 1             Location  : Vial 11
Injection Date  : 9/25/2012 8:23:52 PM    Inj       :    1
                                           Inj Volume: 5 µl
Acq. Method     : D:\LC\DATA\YL\YL-3-43\YL-3-43 2012-09-25 20-22-38\ASH-50-50-1ML-230NM-
20MIN.M
Last changed    : 5/23/2012 8:48:56 PM by THL
Analysis Method : D:\LC\DATA\YL\YL-3-43\YL-3-43 2012-09-25 20-22-38\011-0101.D\DA.M (ASH-50-
50-1ML-230NM-20MIN.M)
Last changed    : 1/29/2013 7:57:57 PM by FX
                 (modified after loading)
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VMD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	9.973	BB	0.5938	4.46753e4	1140.58459	91.8316
2	13.203	BB	0.7807	3973.87573	74.18596	8.1684

Totals : 4.86492e4 1214.77055

=====  
\*\*\* End of Report \*\*\*

Instrument 1 1/29/2013 7:58:46 PM FX

Page 1 of 1











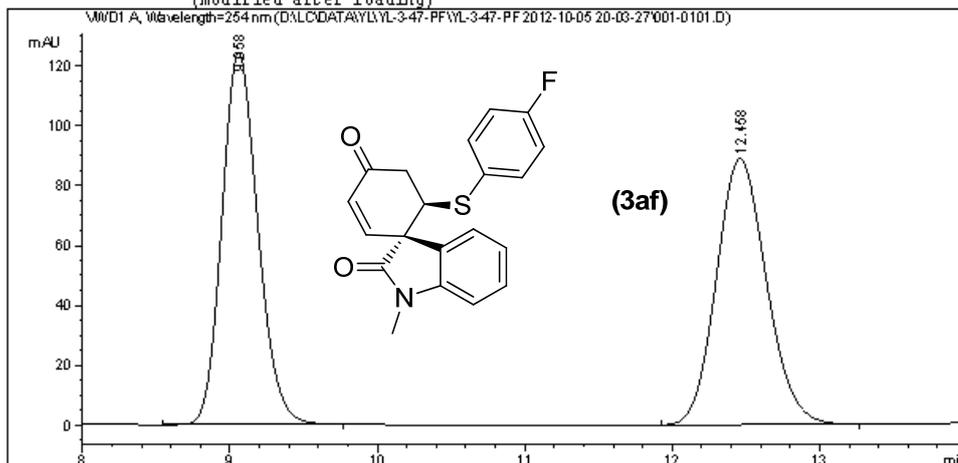






Data File D:\LC\DATA\YL\YL-3-47-PF\YL-3-47-PF 2012-10-05 20-03-27\001-0101.D  
Sample Name: YL-3-47-PF

```
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Acq. Instrument : Instrument 1             Location  : Vial 1
Injection Date  : 10/5/2012 8:04:48 PM    Inj       :    1
                                           Inj Volume: 5 µl
Acq. Method     : D:\LC\DATA\YL\YL-3-47-PF\YL-3-47-PF 2012-10-05 20-03-27\ICH-50-50ML-254NM.M
                                           M
Last changed    : 9/28/2012 7:27:35 PM by YL
Analysis Method : D:\LC\DATA\YL\YL-3-47-PF\YL-3-47-PF 2012-10-05 20-03-27\001-0101.D\DA.M (
                                           ICH-50-50ML-254NM.M)
Last changed    : 1/29/2013 8:28:31 PM by FX
                                           (modified after loading)
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	9.058	VB	0.2617	2108.23682	50.1061	124.42626	50.1061
2	12.458	BB	0.3670	2099.30688	49.8939	88.98952	49.8939

Totals : 4207.54370 213.41578

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\*\*\* End of Report \*\*\*

Instrument 1 1/29/2013 8:28:37 PM FX

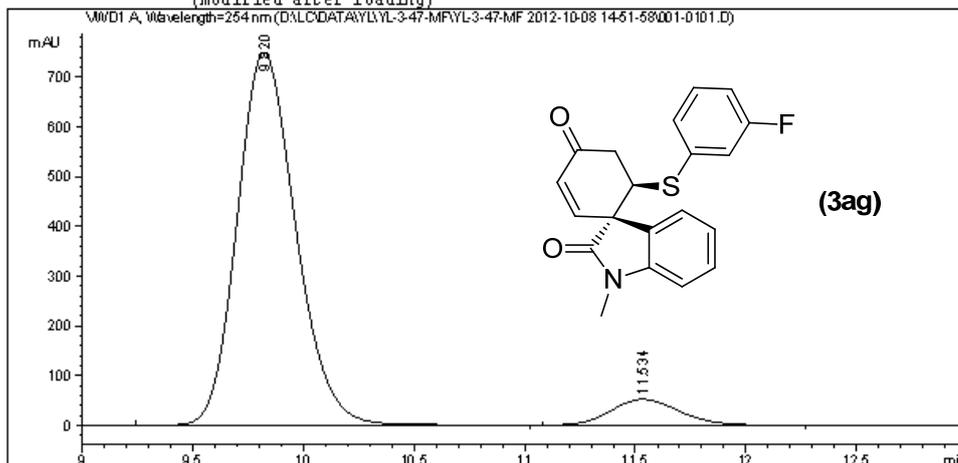
Page 1 of 1





Data File D:\LC\DATA\YL\YL-3-47-MF\YL-3-47-MF 2012-10-08 14-51-58\001-0101.D  
Sample Name: YL-3-47-MF

```
=====
Acq. Operator   : FX                               Seq. Line :    1
Acq. Instrument : Instrument 1                     Location  : Vial 1
Injection Date  : 10/8/2012 2:53:26 PM           Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\DATA\YL\YL-3-47-MF\YL-3-47-MF 2012-10-08 14-51-58\ICH-50-50ML-254NM-
20MIN.M
Last changed    : 10/8/2012 2:44:55 PM by YL
Analysis Method : D:\LC\DATA\YL\YL-3-47-MF\YL-3-47-MF 2012-10-08 14-51-58\001-0101.D\A.M (
ICH-50-50ML-254NM-20MIN.M)
Last changed    : 1/29/2013 9:05:32 PM by FX
(modified after loading)
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: WWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	9.820	VB	0.2843	1.37896e4	750.30682	92.3717
2	11.534	BB	0.3386	1138.78308	52.26485	7.6283

Totals : 1.49284e4 802.57167

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\*\*\* End of Report \*\*\*

Instrument 1 1/29/2013 9:05:37 PM FX

Page 1 of 1











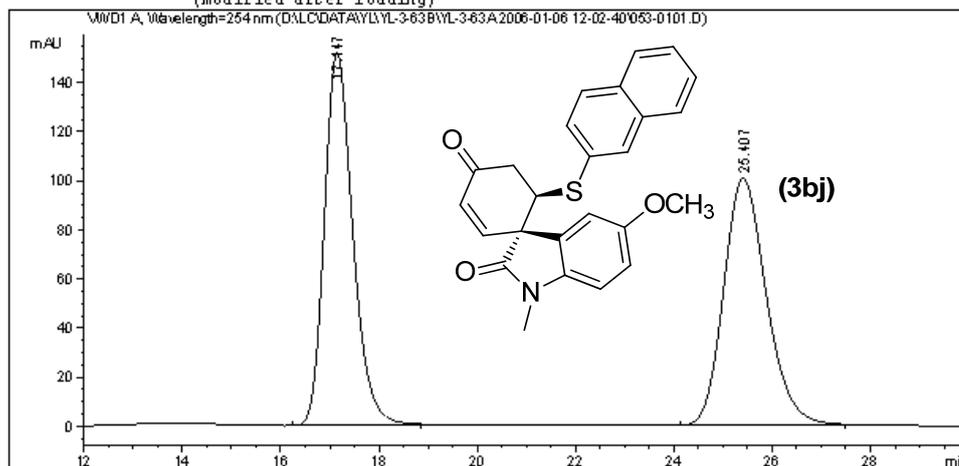






Data File D:\LC\DATA\YL\YL-3-63B\YL-3-63A 2006-01-06 12-02-40\053-0101.D  
Sample Name: YL-3-63A

```
=====
Acq. Operator   : THL                               Seq. Line :    1
Acq. Instrument : Instrument 1                       Location  : Vial 53
Injection Date  : 1/6/2006 12:04:21 PM              Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\DATA\YL\YL-3-63B\YL-3-63A 2006-01-06 12-02-40\ICH-50-50ML-254NM.M
Last changed    : 9/28/2012 7:27:35 PM by YL
Analysis Method : D:\LC\DATA\YL\YL-3-63B\YL-3-63A 2006-01-06 12-02-40\053-0101.D\DA.M (ICH-
50-50ML-254NM.M)
Last changed    : 1/29/2013 8:37:14 PM by FX
                  (modified after loading)
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	17.147	BB	0.6178	6080.92090	50.1486	151.65036	50.1486
2	25.407	BB	0.9220	6044.88525	49.8514	100.65038	49.8514

Totals : 1.21258e4 252.30074

=====  
\*\*\* End of Report \*\*\*

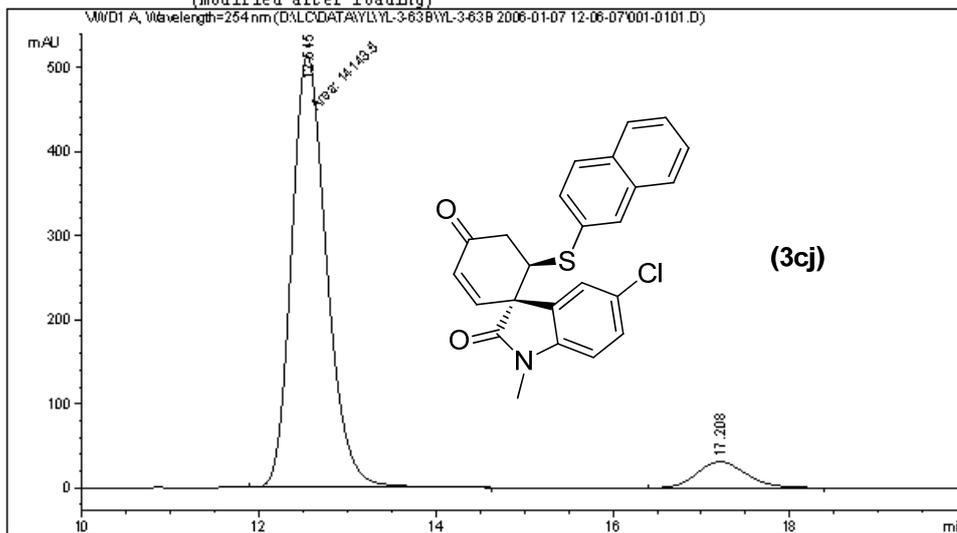




Data File D:\LC\DATA\YL\YL-3-63B\YL-3-63B 2006-01-07 12-06-07\001-0101.D  
 Sample Name: YL-3-63b

```

=====
Acq. Operator   : LQH                               Seq. Line :    1
Acq. Instrument : Instrument 1                       Location  : Vial 1
Injection Date  : 1/ 7/2006 12:07:22 PM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\DATA\YL\YL-3-63B\YL-3-63B 2006-01-07 12-06-07\ICH-50-50ML-254NM-
                25MIN.M
Last changed    : 10/6/2012 3:15:19 PM by YL
Analysis Method : D:\LC\DATA\YL\YL-3-63B\YL-3-63B 2006-01-07 12-06-07\001-0101.D\DA.M (ICH-
                50-50ML-254NM-25MIN.M)
Last changed    : 1/29/2013 9:22:57 PM by FX
                (modified after loading)
    
```



=====  
 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
    
```

Signal 1: VMD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	12.545	MM	0.4587	1.41435e4	513.91882	92.1190
2	17.208	BB	0.6006	1210.00098	31.12719	7.8810

Totals :                    1.53535e4    545.04601

Instrument 1 1/29/2013 9:23:04 PM FX

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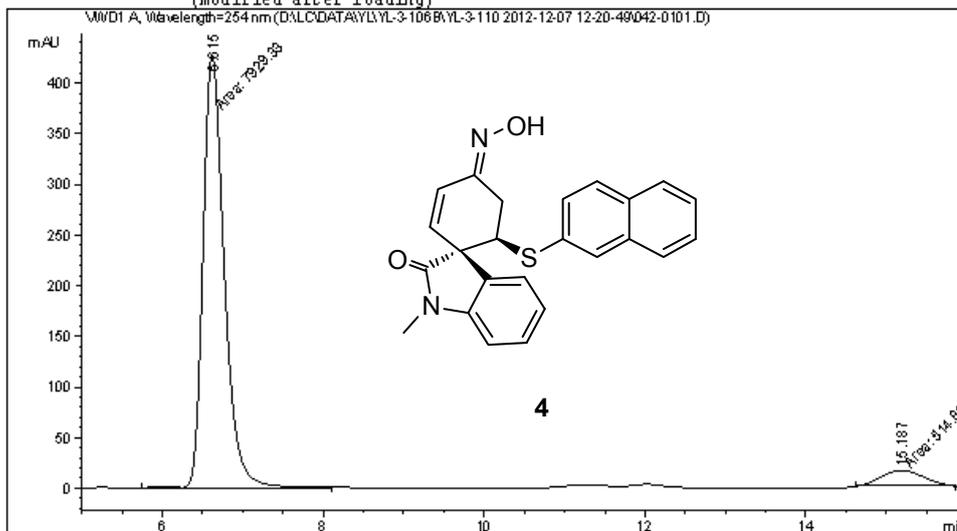




Data File D:\LC\DATA\YL\YL-3-106B\YL-3-110 2012-12-07 12-20-49\042-0101.D  
 Sample Name: YL-3-110A

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=====
Acq. Operator   : hzl                               Seq. Line :    1
Acq. Instrument : Instrument 1                       Location  : Vial 42
Injection Date  : 12/7/2012 12:22:37 PM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\DATA\YL\YL-3-106B\YL-3-110 2012-12-07 12-20-49\ICH-50-50ML-254MM-
25MIN.M
Last changed    : 10/6/2012 3:15:19 PM by YL
Analysis Method : D:\LC\DATA\YL\YL-3-106B\YL-3-110 2012-12-07 12-20-49\042-0101.D\DA.M (ICH-
50-50ML-254MM-25MIN.M)
Last changed    : 4/8/2013 5:30:53 PM by TMC
                (modified after loading)
    
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=====  
 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
    
```

Signal 1: VMD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.615	MM	0.3090	7929.32568	427.64563	93.9024
2	15.187	MM	0.5797	514.89221	14.80229	6.0976

Totals :                      8444.21790   442.44792

Instrument 1 4/8/2013 5:31:06 PM TMC

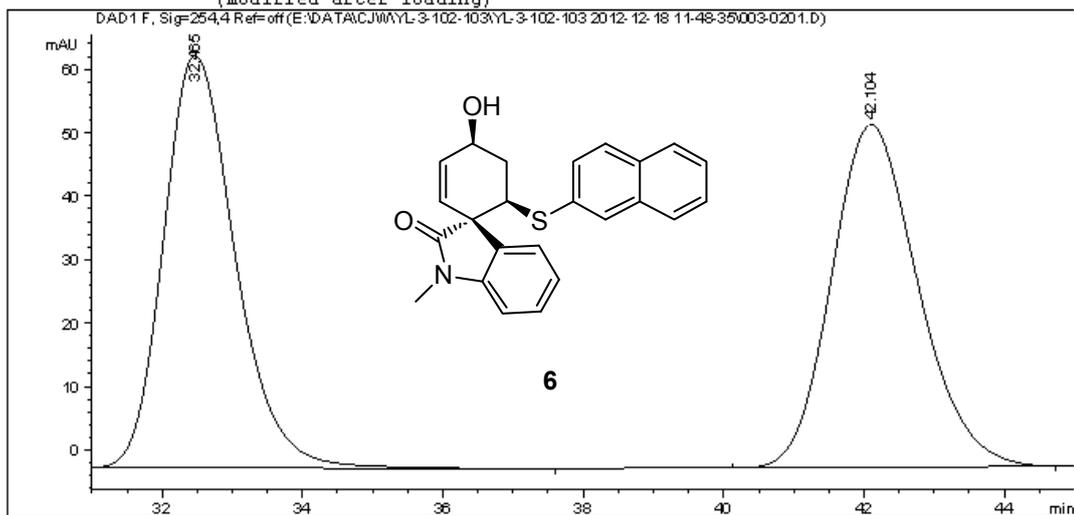
Page 1 of 1





Data File E:\DATA\CJW\YL-3-102-103\YL-3-102-103 2012-12-18 11-48-35\003-0201.D  
Sample Name: YL-3-102

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Acq. Operator   : SYSTEM                      Seq. Line :    2
Acq. Instrument : 1260HPLC-DAD                Location  : Vial 3
Injection Date  : 12/18/2012 12:00:29 PM      Inj       :    1
                                           Inj Volume: 5.000 µl
Acq. Method     : E:\DATA\CJW\YL-3-102-103\YL-3-102-103 2012-12-18 11-48-35\DAD-ICH-10-90-
LML-60MIN.M
Last changed    : 12/18/2012 11:48:35 AM by SYSTEM
Analysis Method : E:\DATA\CJW\YL-3-102-103\YL-3-102-103 2012-12-18 11-48-35\DAD-ICH-10-90-
LML-60MIN.M (Sequence Method)
Last changed    : 1/30/2013 12:55:03 PM by SYSTEM
                (modified after loading)
=====
```



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 F, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.465	BB	1.0756	4600.70313	65.00924	49.9965
2	42.104	BB	1.2908	4601.35107	53.96385	50.0035

Totals : 9202.05420 118.97309

=====  
\*\*\* End of Report \*\*\*

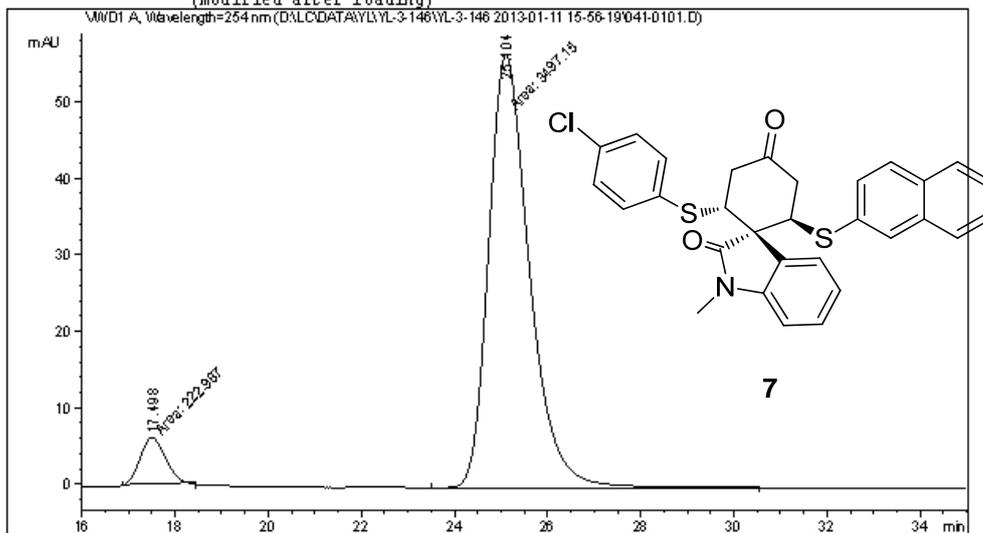




Data File D:\LC\DATA\YL\YL-3-146\YL-3-146 2013-01-11 15-56-19\041-0101.D  
 Sample Name: YL-3-146

```

=====
Acq. Operator   : FX                               Seq. Line :    1
Acq. Instrument : Instrument 1                     Location  : Vial 41
Injection Date  : 1/11/2013 3:57:34 PM           Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\DATA\YL\YL-3-146\YL-3-146 2013-01-11 15-56-19\ICH-30-70ML-254NM-
35MIN.M
Last changed    : 1/10/2013 11:09:12 AM by FX
Analysis Method : D:\LC\DATA\YL\YL-3-146\YL-3-146 2013-01-11 15-56-19\041-0101.D\DA.M (ICH-
30-70ML-254NM-35MIN.M)
Last changed    : 4/8/2013 5:17:10 PM by TMC
                (modified after loading)
    
```



=====  
 Area Percent Report  
 =====

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
    
```

Signal 1: VMD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	17.498	MM	0.6174	222.98653	6.01981	5.9940
2	25.104	MM	1.0285	3497.15308	56.66911	94.0060

Totals :                    3720.13960    62.68892

Instrument 1 4/8/2013 5:17:23 PM TMC

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