

## Organocatalytic C-C Bond Activation of Cyclopropenones for Ring-Opening Formal [3+2] Cycloaddition with Isatins

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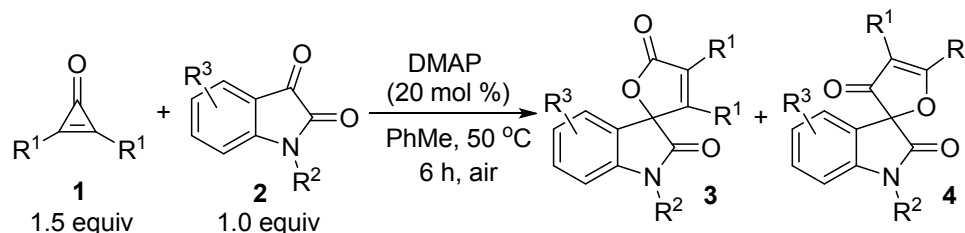
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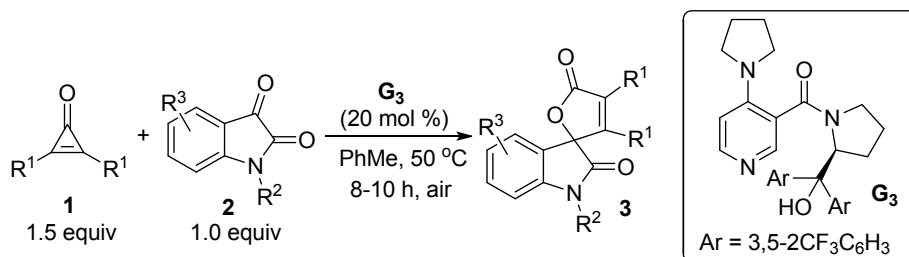
**General Methods and Materials.** All reactions were carried out in dry glassware, and were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Cyclopropenones **1** are commercially available or prepared according to known procedures.<sup>[1]</sup> Purification of the products was accomplished by flash chromatography using silica gel (200-300 mesh). All NMR spectra were recorded on Bruker spectrometers, running at 300 MHz or 500 MHz for <sup>1</sup>H and 75 MHz or 125 MHz for <sup>13</sup>C respectively. Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) are reported in ppm and Hz respectively. The solvent signals were used as references (residual CHCl<sub>3</sub> in CDCl<sub>3</sub>:  $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.0$  ppm). The following abbreviations are used to indicate the multiplicity in NMR spectra: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). High resolution mass spectrometry (HRMS) was recorded on TOF perimer for ESI<sup>+</sup>. The e.e. value was determined via chiral HPLC analysis (Chiral pack IB, *n*-hexane and *iso*-propanol as the mobile phase).

**General procedure for DMAP-catalyzed ring-opening [3+2] cycloaddition of cyclopropenones **1** with isatins **2**.**



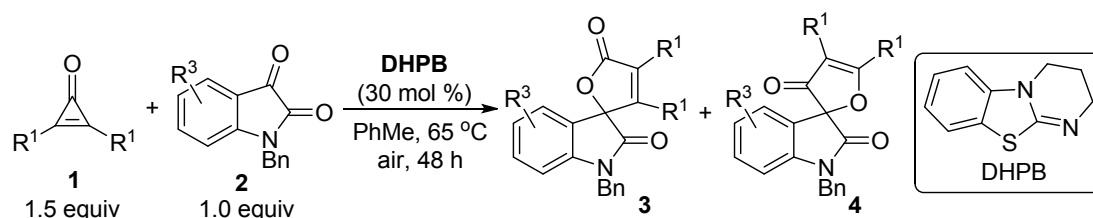
To an oven-dried 25 mL round-bottom flask was charged with cyclopropenones **1** (0.3 mmol), isatins **2** (0.2 mmol) and DMAP (5 mg, 0.04 mmol). Then anhydrous PhMe (4 mL) was added to the flask and the resulting mixture was heated at 50 °C in air for a period time (usually 6 h) until the completion of the reaction as monitored by TLC. The mixture was cooled to room temperature and was concentrated under reduced pressure. The residue was purified by chromatography on silica gel using hexane/EtOAc (15:1) as the eluent to afford products **3** or **4**.

**General procedure for preliminary enantioselective studies on ring-opening [3+2] cycloaddition of cyclopropenones **1** with isatins **2**.**



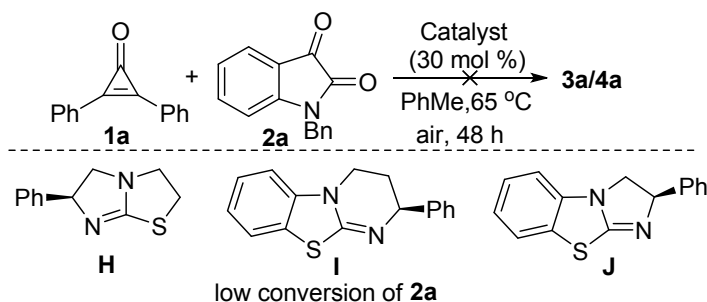
To an oven-dried 25 mL round-bottom flask was charged with cyclopropenones **1** (0.3 mmol), isatins **2** (0.2 mmol) and **H<sub>2</sub>** (28 mg, 0.04 mmol). Then anhydrous PhMe (4 mL) was added to the flask and the resulting mixture was heated at 50 °C in air for a period time (usually 8-10 h) until the completion of the reaction as monitored by TLC. The mixture was cooled to room temperature and was concentrated under reduced pressure. The residue was purified by chromatography on silica gel using hexane/EtOAc (15:1) as the eluent to afford products **3**.

**General procedure for DHPB-promoted ring-opening [3+2] annulation of cyclopropenones **1** with isatins **2**.**



To an oven-dried 25 mL round-bottom flask was charged with cyclopropenones **1** (0.3 mmol), isatins **2** (0.2 mmol) and DHPB (11 mg, 0.06 mmol). Then anhydrous PhMe (4 mL) was added to the flask and the resulting mixture was heated at 65 °C in air for 48 h. The mixture was cooled to room temperature and was concentrated under reduced pressure. The residue was purified by chromatography on silica gel using hexane/EtOAc (15:1) as the eluent to afford products **3** and/or **4**.

**A preliminary enantioselective study of the cycloaddition of 1a with 2a promoted by several chiral isothioureia catalysts**



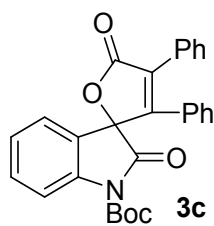
To an oven-dried 25 mL round-bottom flask was charged with cyclopropenones **1** (0.3 mmol), isatins **2** (0.2 mmol) and a chiral isothioureia catalyst (0.06 mmol). Then anhydrous PhMe (4 mL) was added to the flask and the resulting mixture was heated at 65 °C in air for 48 h. No desired products were detected as monitored by TLC.

**Characterization of products 3 and 4.**

1'-Benzyl-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3a**). White solid, mp: 196-198 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.50-7.60 (m, 2H), 7.27-7.43 (m, 6H), 7.08-7.24 (m, 6H), 6.81-6.87 (m, 4H), 6.66 (d, *J* = 8.1 Hz, 1H), 5.13 and 4.56 (d×2, *J* = 15.9 Hz, 2H). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ 171.4, 170.3, 156.5, 143.8, 134.4, 131.6, 130.3, 129.8, 129.4, 129.1, 129.0, 128.9, 128.8, 128.4, 128.1, 127.6, 126.8, 124.9, 123.7, 122.9, 114.6, 110.3, 86.3, 44.3. HRMS (ESI) calcd for C<sub>30</sub>H<sub>22</sub>NO<sub>3</sub> (M+H)<sup>+</sup>: 444.1594, found 444.1591.

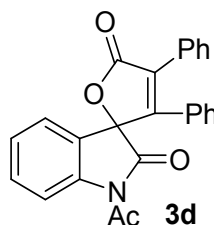
1'-Methyl-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3b**). White solid, mp: 202-204 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.48-7.50 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 3H), 7.21-7.31 (m, 5H), 7.10-7.17 (m, 3H), 6.82-6.89 (m, 3H), 3.16 (s, 3H). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ 171.4, 170.1, 156.4, 144.6, 131.6, 130.2, 129.7, 129.4, 129.0, 128.8, 128.3, 127.7, 124.8, 123.7, 123.0, 86.2, 26.8. HRMS (ESI) calcd for C<sub>24</sub>H<sub>18</sub>NO<sub>3</sub> (M+H)<sup>+</sup>: 368.1281, found 368.1277.

*tert*-Butyl 2',5-dioxo-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-1'-carboxylate (**3c**).



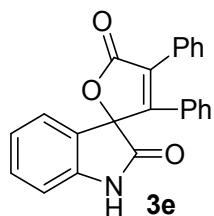
White solid, mp: 153-154 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 6.4 Hz, 2H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.39-7.33 (m, 4H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 7.4 Hz, 2H), 1.63 (s, 9H). <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ 170.9, 168.4, 155.9, 148.3, 141.0, 131.9, 129.9, 129.4, 129.2, 129.0, 128.91, 128.85, 128.4, 127.8, 125.4, 124.7, 122.0, 116.0, 85.9, 85.3, 27.9. HRMS (ESI) calcd for C<sub>28</sub>H<sub>24</sub>NO<sub>5</sub> (M+H)<sup>+</sup>: 454.1649, found 454.1649.

1'-Acetyl-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3d**). White solid,



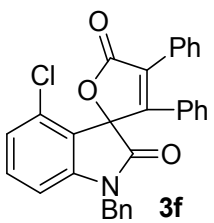
mp: 211-213 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.47-7.53 (m, 3H), 7.27-7.43 (m, 6H), 7.18 (t, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 2.60 (s, 3H). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ 171.3, 170.8, 169.8, 155.7, 141.3, 132.1, 130.2, 129.7, 129.4, 129.3, 129.0, 128.7, 128.5, 127.7, 126.2, 124.6, 122.2, 117.4, 86.0, 26.3. HRMS (ESI) calcd for C<sub>25</sub>H<sub>18</sub>NO<sub>4</sub> (M+H)<sup>+</sup>: 396.1230, found 396.1230.

3,4-Diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3e**). White solid, mp: 198-



200 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.60 (brs, 1H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.36-7.28 (m, 5H), 7.27-7.23 (m, 1H), 7.15 (t, *J* = 7.7 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.94-6.89 (m, 3H). <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ 172.12, 171.5, 156.3, 141.7, 131.7, 130.1, 129.9, 129.4, 129.2, 129.1, 128.9, 128.4, 127.8, 125.3, 123.8, 123.4, 111.2, 86.5. HRMS (ESI) calcd for C<sub>25</sub>H<sub>16</sub>NO<sub>3</sub> (M+H)<sup>+</sup>: 354.1125, found 354.1124.

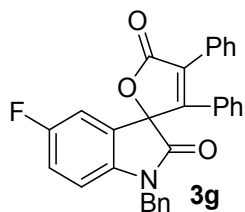
1'-Benzyl-4'-chloro-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3f**).



White solid, mp: 193-195 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.52 (d, *J* = 5.7 Hz, 2H), 7.35-7.30 (m, 4H), 7.23-7.16 (m, 6H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.87 (d, *J* = 7.1 Hz, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 5.11 and 4.59 (d×2, *J* = 15.8 Hz, 2H). <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>): δ 171.1, 169.7, 154.6, 145.4, 134.0, 132.7, 132.6, 130.5, 130.2, 129.8, 129.3, 129.1, 129.1, 128.96, 128.9, 128.4, 127.83, 127.80, 126.8, 124.5,

119.8, 108.6, 86.0, 44.5. HRMS (ESI) calcd for C<sub>30</sub>H<sub>21</sub>ClNO<sub>3</sub> (M+H)<sup>+</sup>: 478.1204, found 478.1207.

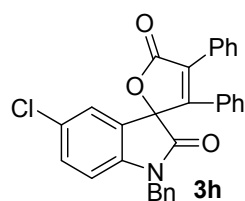
1'-Benzyl-5'-fluoro-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3g**). White



solid, mp: 191-192 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.51-7.52 (m, 2H), 7.29-7.35 (m, 4H), 7.23 (m, 1H), 7.16-7.20 (m, 4H), 7.12 (dd, *J* = 7.0, 2.5 Hz, 1H), 6.99 (td, *J* = 8.8, 2.4 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 2H), 6.85 (d, *J* = 7.4 Hz, 2H), 6.60 (dd, *J* = 8.6,

3.9 Hz, 1H), 5.12 and 4.56 (d×2, *J* = 15.8 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 171.1, 170.1, 159.5 (d, *J* = 243.0 Hz, 1C), 156.0, 139.8, 134.1, 130.0, 129.9, 129.4, 129.3, 129.02, 128.9, 128.7, 128.4, 128.0, 127.8, 126.8, 124.6 (d, *J* = 7.9 Hz, 1C), 118.1 (d, *J* = 23.3 Hz, 1C), 112.9 (d, *J* = 24.8 Hz, 1C), 111.15 (d, *J* = 7.9 Hz, 1C), 86.1, 44.5. HRMS (ESI) calcd for C<sub>30</sub>H<sub>21</sub>FNO<sub>3</sub> (M+H)<sup>+</sup>: 462.1487, found 462.1494.

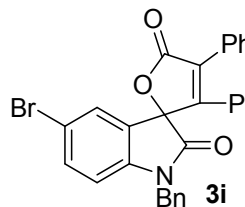
1'-Benzyl-5'-chloro-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3h**).



White solid, mp: 192-193 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.51 (d, *J* = 6.4 Hz, 2H), 7.36-7.29 (m, 5H), 7.27-7.20 (m, 2H), 7.15-7.19 (m, 4H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 7.3 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 1H), 5.10 and 4.55 (d×2, *J* = 15.8 Hz,

2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 171.0, 169.9, 155.8, 142.3, 134.0, 131.6, 130.0, 129.9, 129.38, 129.30, 129.27, 129.1, 128.9, 128.7, 128.4, 128.0, 127.9, 126.8, 125.3, 124.7, 111.3, 85.8, 44.5. HRMS (ESI) calcd for C<sub>30</sub>H<sub>21</sub>ClNO<sub>3</sub> (M+H)<sup>+</sup>: 478.1204, found 478.1201.

1'-Benzyl-5'-bromo-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3i**).

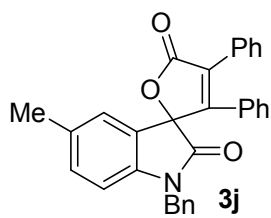


White solid, mp: 195-197 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.48 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.36-7.29 (m, 4H), 7.23 (m, 1H), 7.19-7.16 (m, 4H), 6.89 (d, *J* = 7.9 Hz, 2H), 6.83 (d, *J* = 7.4 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 1H),

5.11 and 4.55 (d×2, *J* = 15.8 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 171.0, 169.8, 155.8, 142.8, 134.5, 133.9, 129.99, 129.97, 129.38, 129.31, 129.1, 128.9, 128.7, 128.4, 128.0, 127.9, 126.8, 125.1, 116.3, 111.8, 85.8, 44.5. HRMS (ESI) calcd for

$C_{30}H_{21}BrNO_3$  (M+H)<sup>+</sup>: 522.0699, found 522.0698.

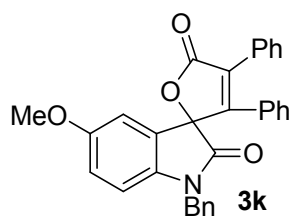
1'-Benzyl-5'-methyl-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (3j).



White solid, mp: 198-200 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.53 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.34-7.29 (m, 4H), 7.23 -7.12 (m, 6H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.3 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.10 and

4.54 (d×2, *J* = 15.8 Hz, 2H), 2.33 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 171.5, 170.2, 156.6, 141.4, 134.6, 133.6, 131.9, 130.3, 129.8, 129.4, 129.1, 128.9, 128.74, 128.69, 128.4, 128.1, 127.6, 126.9, 125.5, 122.9, 110.1, 86.5, 44.3, 20.97. HRMS (ESI) calcd for C<sub>31</sub>H<sub>24</sub>NO<sub>3</sub> (M+H)<sup>+</sup>: 458.1751, found 458.1752.

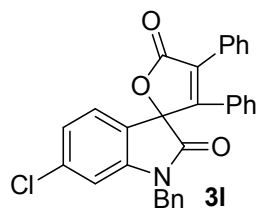
1'-Benzyl-5'-methoxy-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (3k).



White solid, mp: 172-173 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.52 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.36-7.28 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.18-7.14 (m, 4H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 2H), 6.83-6.80 (m, 3H), 6.57 (d, *J* = 8.6 Hz, 1H), 5.11 and 4.52 (d×2, *J* = 15.8 Hz, 2H), 3.77 (s, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 171.4, 167.0, 156.7, 156.5, 137.1, 134.5, 130.2, 129.8, 129.4, 129.1, 129.0, 128.9, 128.74, 128.71, 128.4, 128.1, 127.6, 126.8, 124.1, 116.5, 111.5, 110.9, 86.6, 55.9, 44.4. HRMS (ESI) calcd for C<sub>31</sub>H<sub>24</sub>NO<sub>4</sub> (M+H)<sup>+</sup>: 474.1700, found 474.1700.

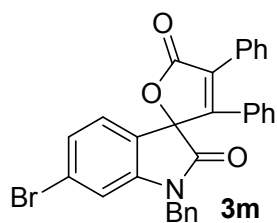
1'-Benzyl-6'-chloro-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (3l).



White solid, mp: 166-167 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.50 (d, *J* = 6.4 Hz, 2H), 7.35-7.27 (m, 5H), 7.23-7.14 (m, 5H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.86 (dd, *J* = 12.7, 7.6 Hz, 4H), 6.67 (s, 1H), 5.09 and 4.54 (d×2, *J* = 15.8 Hz, 2H). <sup>13</sup>C NMR (125 MHz,

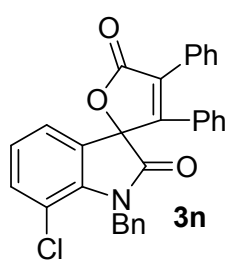
CDCl<sub>3</sub>): δ 171.1, 170.3, 155.9, 145.0, 137.5, 133.9, 130.1, 129.9, 129.4, 129.3, 129.05, 129.0, 128.9, 128.8, 128.4, 127.98, 127.90, 126.8, 125.9, 123.8, 121.4, 110.9, 85.7, 44.5. HRMS (ESI) calcd for, found. HRMS (ESI) calcd for C<sub>30</sub>H<sub>21</sub>ClNO<sub>3</sub> (M+H)<sup>+</sup>: 478.1204,, found 478.1199.

1'-Benzyl-6'-bromo-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3m**).

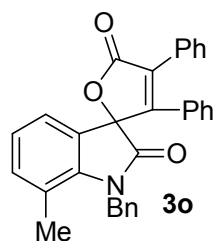


White solid, mp: 195-197 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.51 (d, *J* = 6.4 Hz, 2H), 7.35-7.28 (m, 5H), 7.24-7.156 (m, 6H), 6.89-6.83 (m, 5H), 5.10 and 4.55 (d×2, *J* = 15.9 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 171.1, 170.2, 155.9, 145.1, 133.9, 130.1, 129.9, 129.4, 129.3, 129.1, 129.0, 128.9, 128.8, 128.4, 128.0, 127.9, 126.8, 126.7, 126.2, 125.4, 121.95, 113.7, 85.7, 44.5. HRMS (ESI) calcd for, found.

1'-Benzyl-7'-chloro-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3n**).



White solid, mp: 178-179 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.50 (d, *J* = 6.5 Hz, 2H), 7.39-7.27 (m, 6H), 7.23-7.12 (m, 5H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 7.3 Hz, 2H), 5.31 and 5.26 (d×2, *J* = 6.5 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 171.1, 170.8, 156.0, 140.1, 136.2, 134.2, 130.02, 129.98, 129.4, 129.3, 129.1, 128.7, 128.6, 128.4, 128.0, 127.2, 126.1, 125.8, 124.6, 123.7, 116.5, 85.3, 45.5. HRMS (ESI) calcd for C<sub>30</sub>H<sub>21</sub>ClNO<sub>3</sub> (M+H)<sup>+</sup>: 478.1204,, found 478.1200.

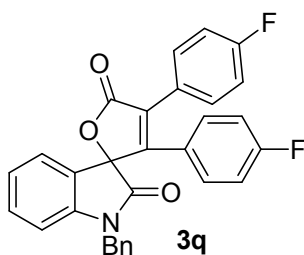


1'-Benzyl-7'-methyl-3,4-diphenyl-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3o**). White solid, mp: 196-197 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.52 (d, *J* = 6.1 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.31-7.28 (m, 3H), 7.26 (m, 1H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 2H), 7.10-7.05 (m, 2H), 6.91 (d, *J* = 7.7 Hz, 2H), 6.66 (d, *J* = 7.4 Hz, 2H), 5.28 and 4.92 (d×2, *J* = 17.0 Hz, 1H), 2.19 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 171.5, 171.2, 156.7, 142.0, 136.4, 135.6, 130.5, 129.8, 129.4, 129.1, 129.0, 128.8, 128.34, 128.27, 127.2, 125.3, 123.8, 123.4, 123.0, 121.1, 85.9, 45.6, 18.5. HRMS (ESI) calcd for C<sub>31</sub>H<sub>24</sub>NO<sub>3</sub> (M+H)<sup>+</sup>: 458.1751, found 458.1747.

1'-Benzyl-3,4-bis(4-fluorophenyl)-5*H*-spiro[furan-2,3'-indoline]-2',5-dione (**3q**).

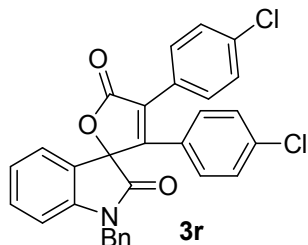
White solid, mp: 190-191 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.50 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.87-6.79 (m,





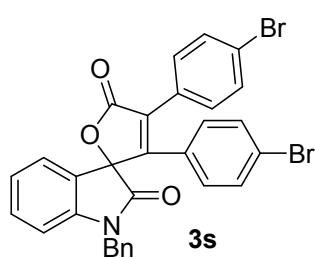
6H), 6.73 (d,  $J = 7.9$  Hz, 1H), 5.12 and 4.55 (d $\times$ 2,  $J = 15.7$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.2, 170.1, 163.5 (d,  $J = 249.9$  Hz, 1C), 163.1 (d,  $J = 249.0$  Hz, 1C), 155.2, 143.8, 134.4, 131.8, 131.4 (d,  $J = 8.5$  Hz, 1C), 130.2 (d,  $J = 8.3$  Hz, 1C), 128.8, 128.0, 127.9, 126.9, 126.1 (d,  $J = 3.2$  Hz, 1C), 124.9, 124.8 (d,  $J = 3.3$  Hz, 1C), 123.9, 122.6, 116.4 (d,  $J = 21.5$  Hz, 1C), 115.7 (d,  $J = 21.6$  Hz, 1C), 110.4, 86.3, 44.4. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{20}\text{F}_2\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 480.1406, found 480.1406.

1'-Benzyl-3,4-bis(4-chlorophenyl)-5H-spiro[furan-2,3'-indoline]-2',5-dione (**3r**).



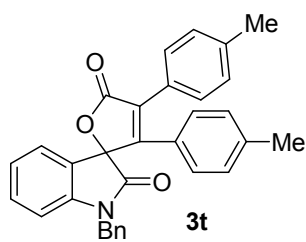
White solid, mp: 213-214 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 (d,  $J = 8.5$  Hz, 2H), 7.36-7.31 (m, 2H), 7.30 (d,  $J = 8.5$  Hz, 2H), 7.26-7.22 (m, 1H), 7.20 (t,  $J = 7.3$  Hz, 2H), 7.16-7.11 (m 3H), 6.82 (d,  $J = 7.3$  Hz, 2H), 6.73 (t,  $J = 8.8$  Hz, 3H), 5.12 and 4.52 (d $\times$ 2,  $J = 15.7$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.8, 169.9, 155.5, 143.8, 136.4, 135.6, 134.3, 131.9, 130.6, 129.5, 129.4, 128.9, 128.8, 128.4, 128.1, 127.9, 127.1, 126.9, 124.9, 123.9, 122.3, 110.4, 86.2, 44.4. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{20}\text{Cl}_2\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 512.0815, found 512.0811.

1'-Benzyl-3,4-bis(4-bromophenyl)-5H-spiro[furan-2,3'-indoline]-2',5-dione (**3s**).



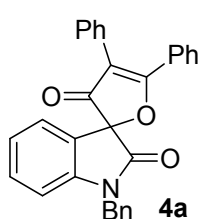
White solid, mp: 219-220 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (d,  $J = 8.5$  Hz, 2H), 7.40-7.31 (m, 4H), 7.29-7.24 (m, 3H), 7.21 (t,  $J = 7.2$  Hz, 2H), 7.15 (t,  $J = 7.5$  Hz, 1H), 6.82 (d,  $J = 7.3$  Hz, 2H), 6.72 (d,  $J = 7.9$  Hz, 1H), 6.67 (d,  $J = 8.4$  Hz, 2H), 5.13 and 4.52 (d $\times$ 2,  $J = 15.7$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.8, 169.9, 155.6, 143.8, 134.3, 132.4, 131.9, 131.9, 130.9, 129.6, 128.8, 128.2, 127.9, 127.5, 126.9, 124.9, 124.7, 123.95, 123.91, 122.3, 110.5, 86.2, 44.4. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{20}\text{Br}_2\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 599.9804, found 599.9802.

1'-Benzyl-3,4-di-p-tolyl-5H-spiro[furan-2,3'-indoline]-2',5-dione (**3t**). White solid, mp: 204-205 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43 (d,  $J = 8.2$  Hz, 2H), 7.36-7.29



(m, 2H), 7.25-7.06 (m, 6H), 6.99-6.86 (m, 4H), 6.75 (d,  $J = 8.1$  Hz, 2H), 6.68 (d,  $J = 7.9$  Hz, 1H), 5.12 and 4.56 (d $\times$ 2,  $J = 15.8$  Hz, 2H), 2.33 (s, 3H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.8, 170.5, 155.8, 143.8, 139.8, 139.1, 134.5, 131.5, 129.6, 129.2, 129.1, 128.8, 128.6, 127.9, 127.6, 127.4, 126.9, 126.2, 124.9, 123.7, 123.2, 110.2, 86.2, 44.3, 21.37. HRMS (ESI) calcd for  $\text{C}_{32}\text{H}_{26}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 472.1907, found 472.1902.

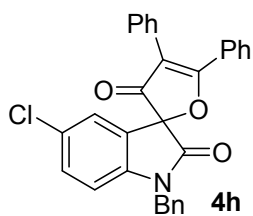
1'-Benzyl-4,5-diphenyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (**4a**). White solid,



mp: 193-194 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76-7.79 (m, 2H), 7.52 (t,  $J = 7.5$  Hz, 1H), 7.24-7.41 (m, 14H), 7.06 (t,  $J = 7.5$  Hz, 1H), 6.77 (d,  $J = 7.8$  Hz, 1H), 5.13 and 4.84 (2 $\times$ d,  $J = 15.9$  Hz, 2H).  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  196.1, 182.3, 169.2, 144.4, 134.7,

132.5, 131.1, 129.7, 129.0, 128.95, 128.91, 128.8, 128.7, 128.5, 128.1, 127.8, 127.1, 124.2, 123.9, 123.4, 115.5, 110.3, 87.9, 44.3. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{22}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 444.1594, found 444.1597.

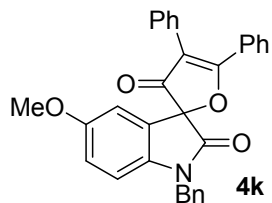
1'-Benzyl-5'-chloro-4,5-diphenyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (**4h**).



White solid, mp: 238-239 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (d,  $J = 7.5$  Hz, 2H), 7.55 (t,  $J = 7.2$  Hz, 1H), 7.44-7.38 (m, 11H), 7.35-7.27 (m, 3H), 6.71 (d,  $J = 9.0$  Hz, 1H), 5.14 and 4.83 (2 $\times$ d,  $J = 15.9$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$

195.5, 182.4, 168.8, 142.9, 134.2, 132.7, 130.9, 129.7, 129.0, 128.84, 128.83, 128.76, 128.68, 128.59, 128.3, 127.9, 127.1, 125.6, 124.3, 115.4, 111.3, 87.5, 44.4. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{21}\text{ClNO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 478.1204, found 478.1210.

1'-Benzyl-5'-methoxy-4,5-diphenyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (**4k**).

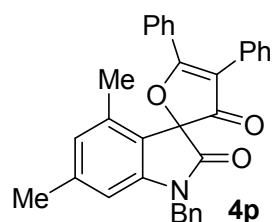


White solid, mp: 229-230 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 7.4$  Hz, 2H), 7.52 (t,  $J = 7.5$  Hz, 1H), 7.44-7.33 (m, 11H), 7.28 (t,  $J = 7.1$  Hz, 1H), 6.84 (d,  $J = 2.4$  Hz, 1H), 6.80 (dd,  $J = 8.6, 2.5$  Hz, 1H), 6.66 (d,  $J = 8.6$  Hz, 1H), 5.10 and

4.80 (2 $\times$ d,  $J = 15.9$  Hz, 2H), 3.73 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.1, 182.2,

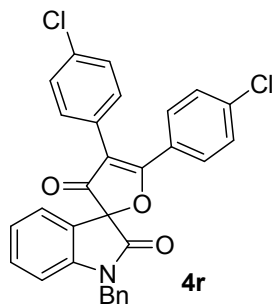
168.9, 156.4, 137.5, 134.7, 132.5, 129.6, 128.92, 128.89, 128.85, 128.7, 128.6, 128.5, 128.1, 127.7, 127.1, 125.1, 115.6, 110.9, 110.8, 88.2, 55.8, 44.3. HRMS (ESI) calcd for  $C_{31}H_{24}NO_4$  ( $M+H$ )<sup>+</sup>: 474.1700, found 474.1709.

1'-Benzyl-4',6'-dimethyl-4,5-diphenyl-3*H*-spiro[furan-2,3'-indoline]-2',3-dione (**4p**).



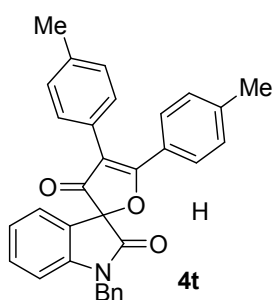
White solid, mp: 176-178 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.1 Hz, 1H), 7.43-7.33 (m, 11H), 7.28 (d, *J* = 6.5 Hz, 1H), 6.68 (s, 1H), 6.43 (s, 1H), 5.06 and 4.81 (2×d, *J* = 15.9 Hz, 2H), 2.26 (s, 3H), 2.16 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 196.3, 181.3, 169.4, 144.8, 141.5, 135.9, 135.0, 132.4, 129.7, 129.2, 129.1, 128.9, 128.8, 128.6, 128.1, 127.7, 127.0, 126.03, 126.02, 119.5, 116.8, 108.6, 88.5, 44.2, 21.9, 17.5. HRMS (ESI) calcd for  $C_{32}H_{26}NO_3$  ( $M+H$ )<sup>+</sup>: 472.1907, found 472.1910.

1'-Benzyl-4,5-bis(4-chlorophenyl)-3*H*-spiro[furan-2,3'-indoline]-2',3-dione (**4r**).



White solid, mp: 251-252 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.71 (d, *J* = 8.7 Hz, 2H), 7.41-7.22 (m, 13H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.10 and 4.83 (2×d, *J* = 15.9 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 195.6, 181.1, 168.9, 144.4, 139.2, 134.6, 134.4, 131.3, 130.9, 129.9, 129.2, 129.1, 128.9, 127.9, 127.15, 127.13, 127.10, 124.0, 123.8, 123.5, 114.6, 110.4, 88.2, 44.4. HRMS (ESI) calcd for  $C_{30}H_{20}Cl_2NO_3$  ( $M+H$ )<sup>+</sup>: 512.0815, found 512.0815.

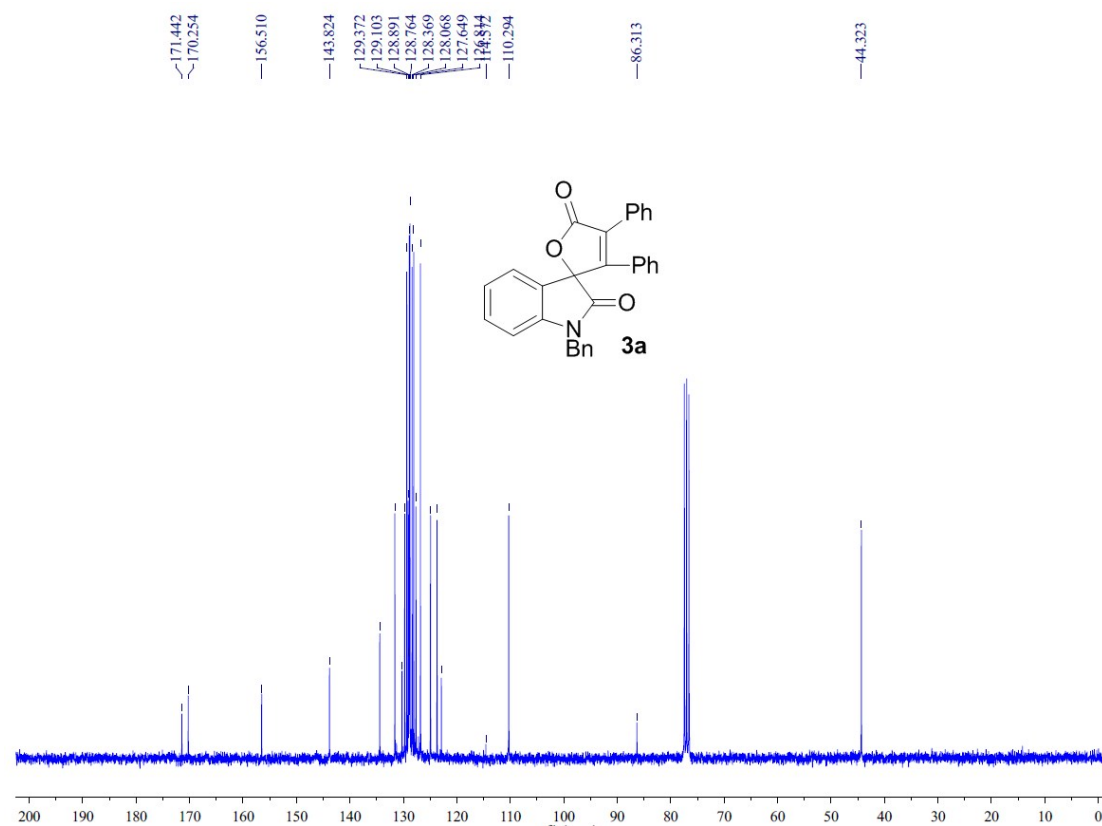
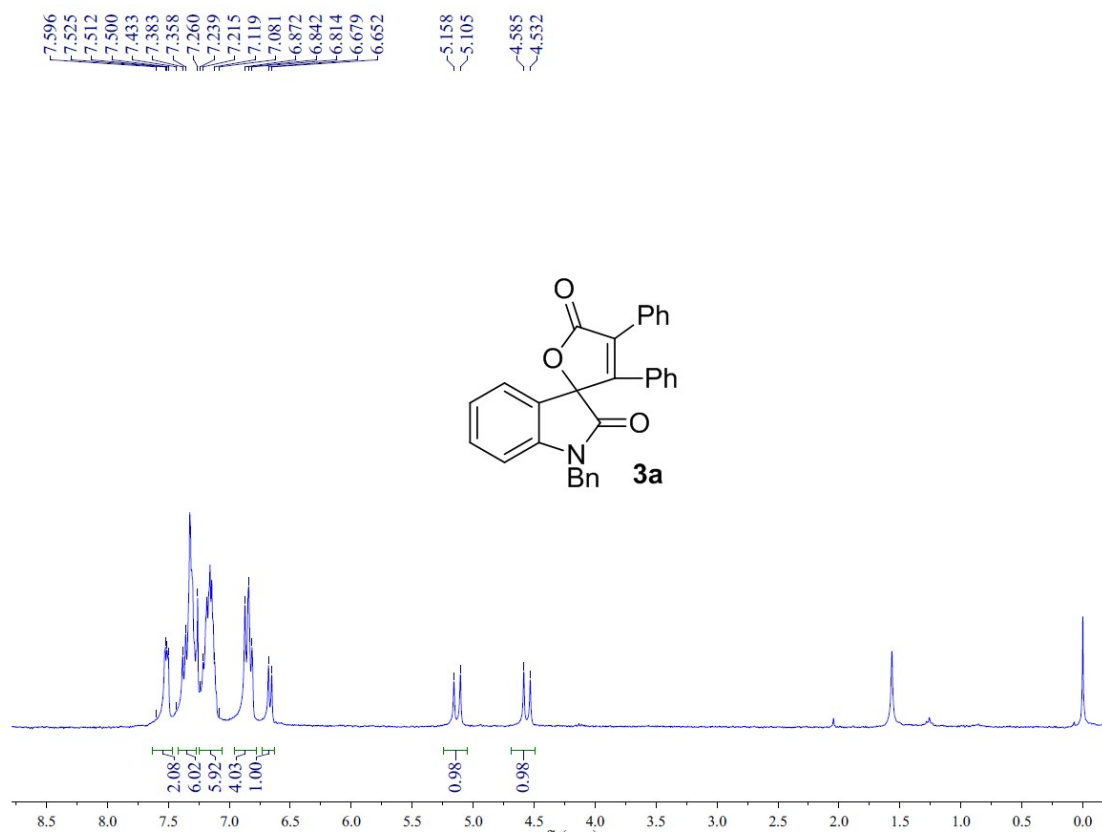
1'-Benzyl-4,5-di-*p*-tolyl-3*H*-spiro[furan-2,3'-indoline]-2',3-dione (**4t**). White solid,

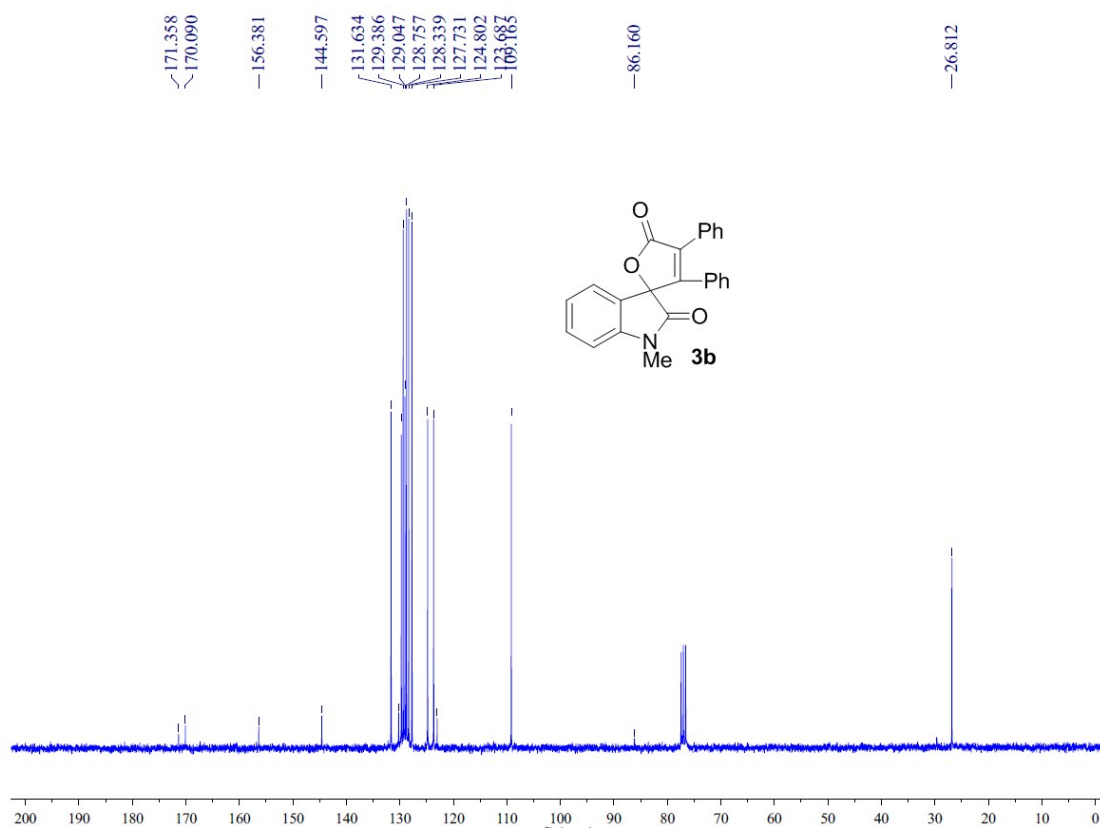
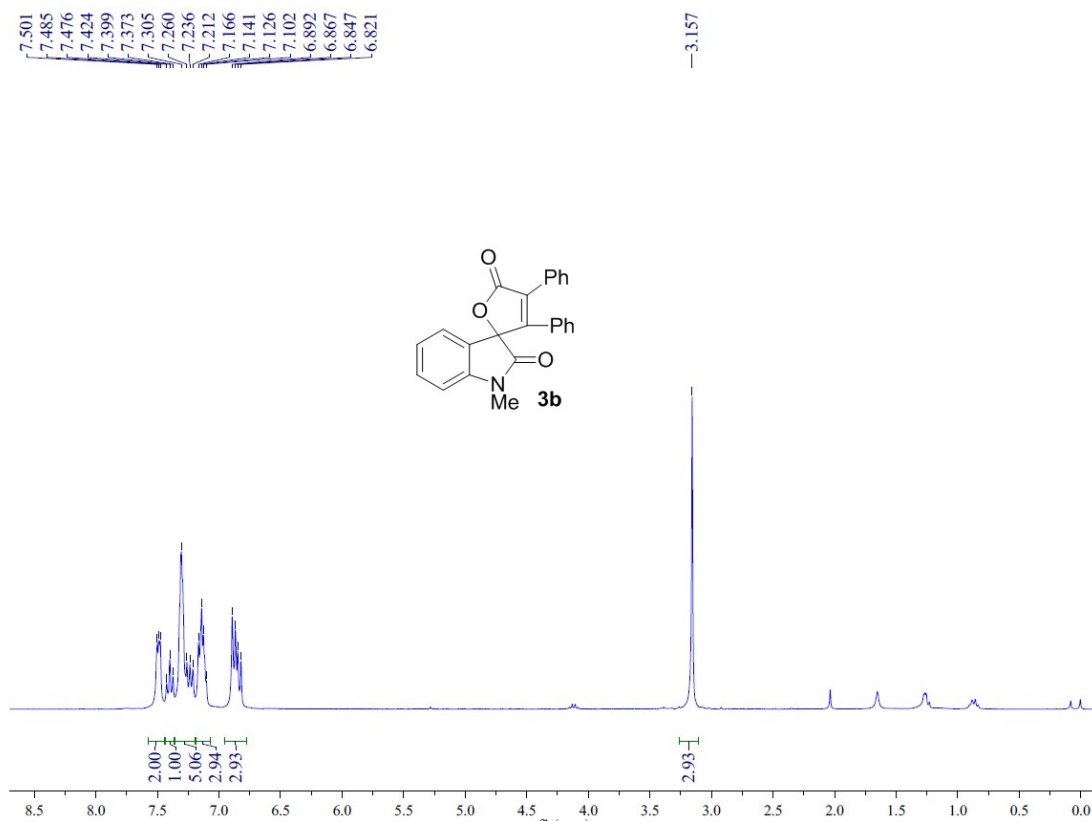


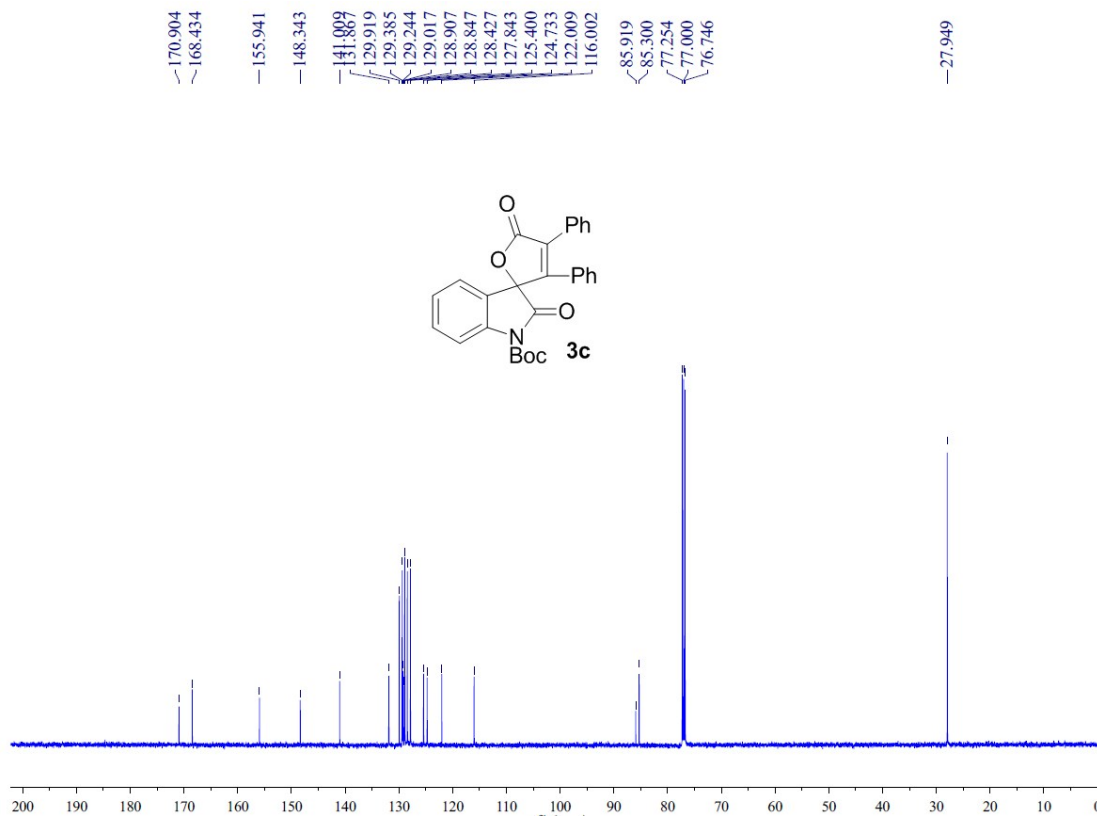
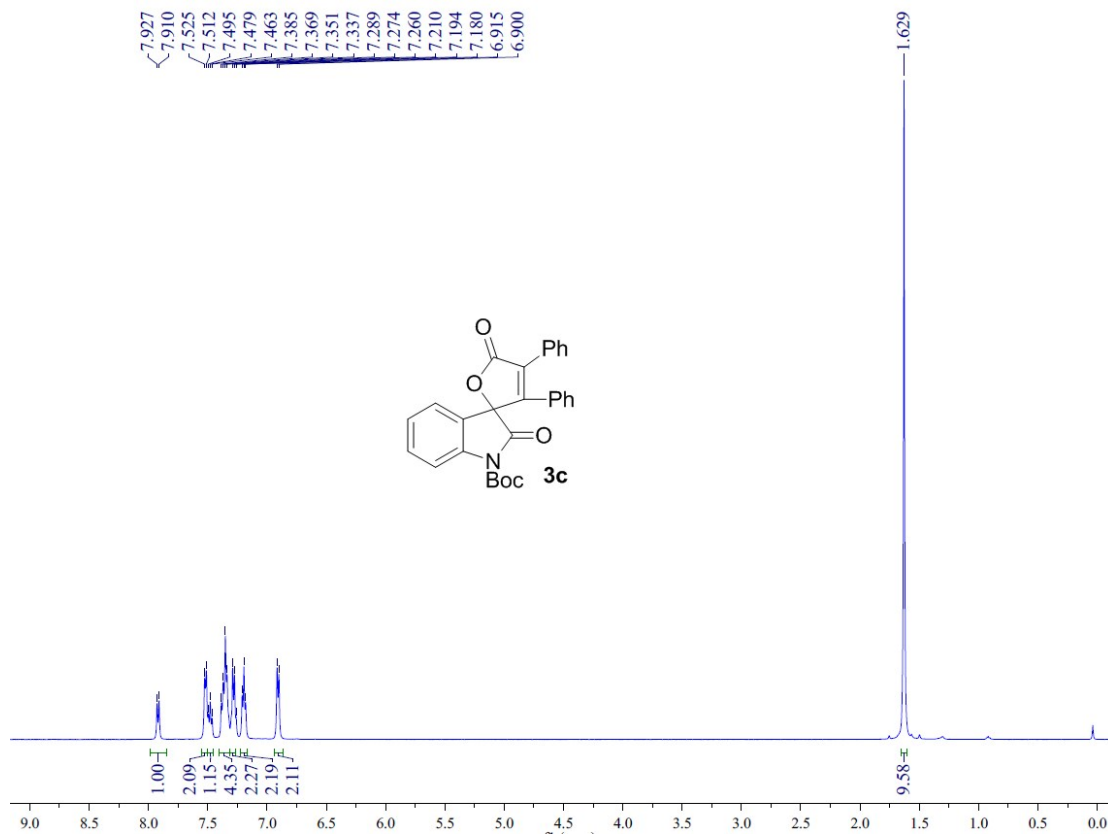
mp: 202-203 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.40-7.16 (m, 13H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 5.10 and 4.81 (2×d, *J* = 15.9 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 196.2, 182.1, 169.4, 144.3, 143.3, 137.8, 134.7, 130.9, 129.54, 129.47, 129.2, 128.9, 128.6, 127.7, 127.1, 126.3, 126.1, 124.4, 123.8, 123.3, 114.8, 110.2, 87.8, 44.2, 21.7, 21.3. HRMS (ESI) calcd for  $C_{32}H_{26}NO_3$  ( $M+H$ )<sup>+</sup>: 472.1907, found 472.1914.

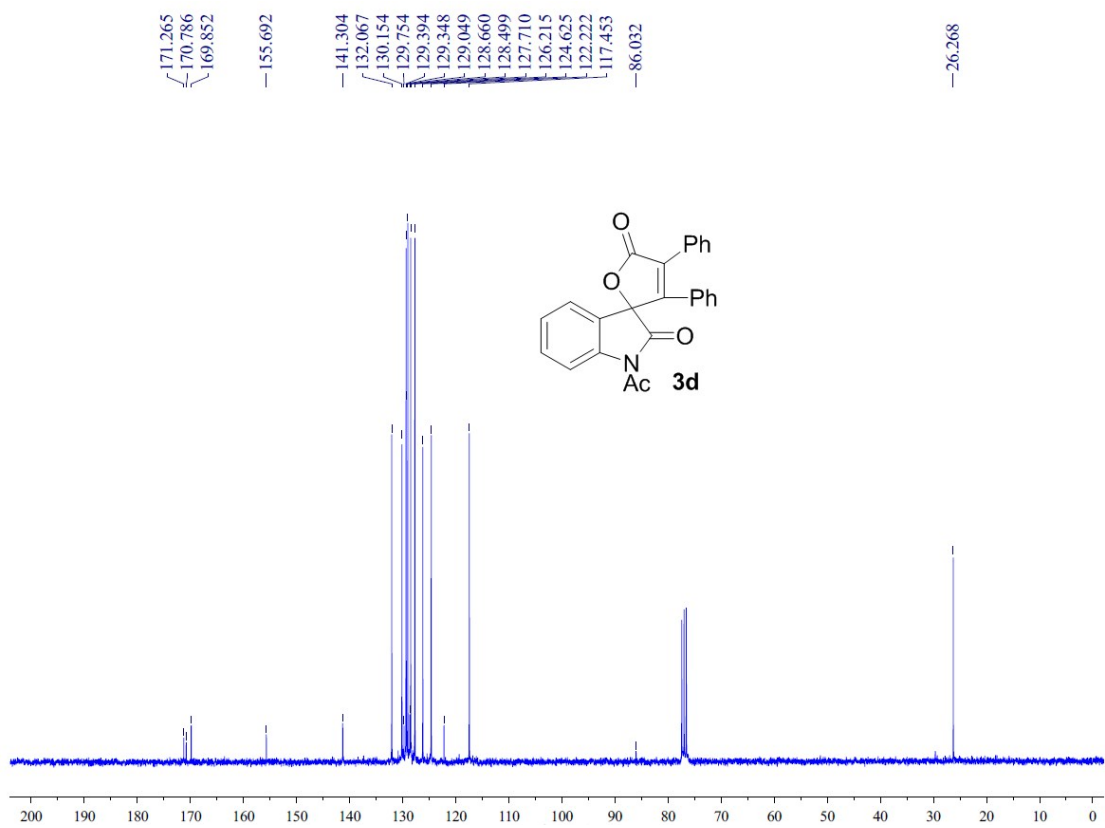
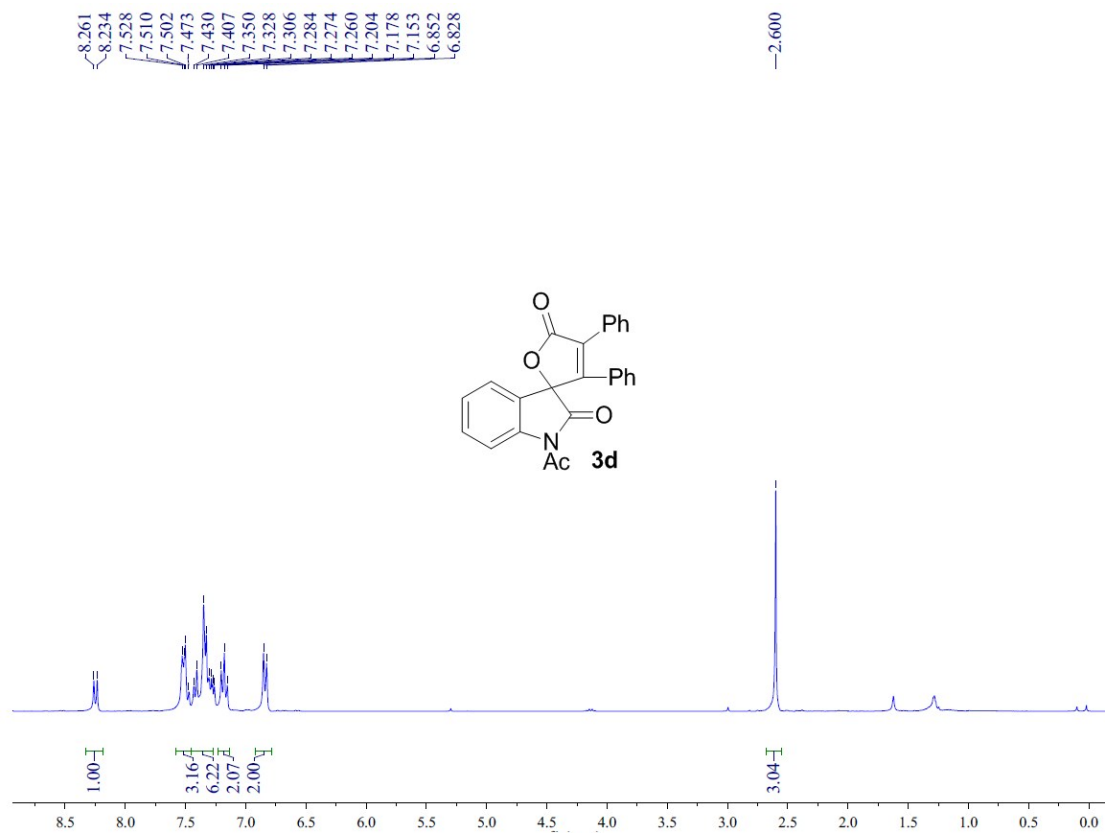
**Reference:**

- [1] C. M. Vanos, T. H. Lambert, *Angew. Chem. Int. Ed.* **2011**, *50*, 12222.

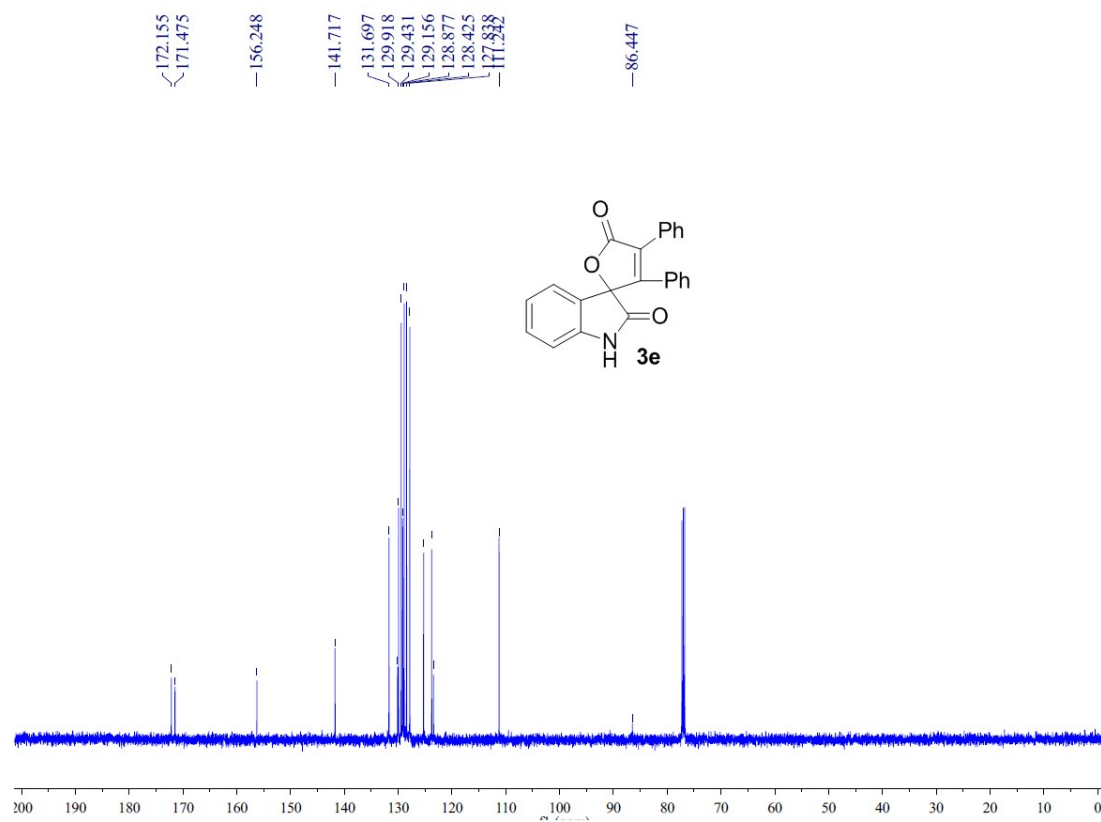
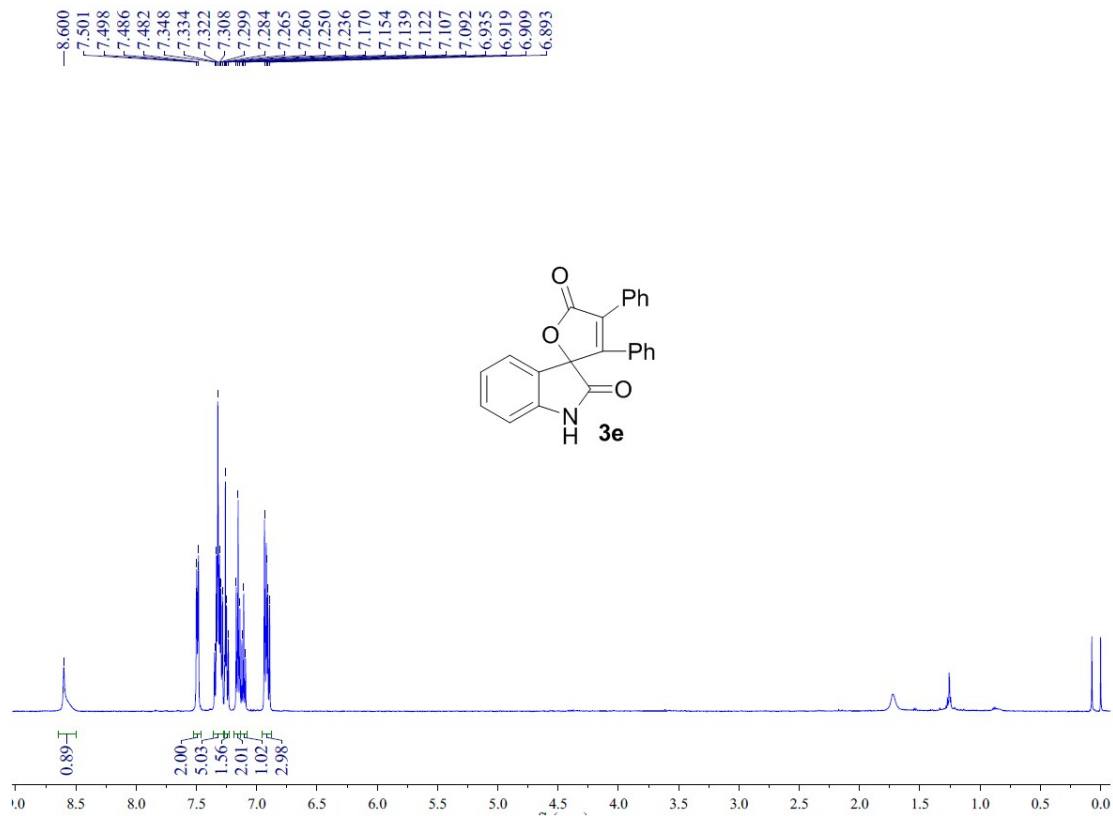


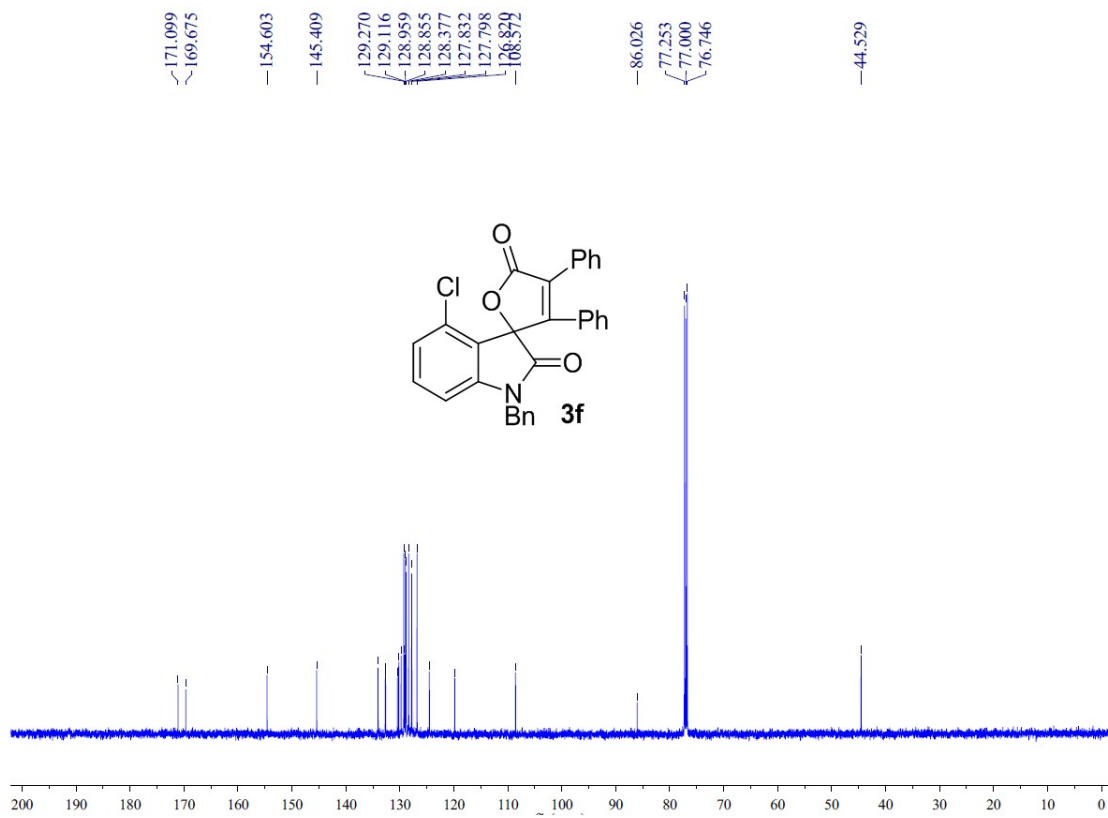
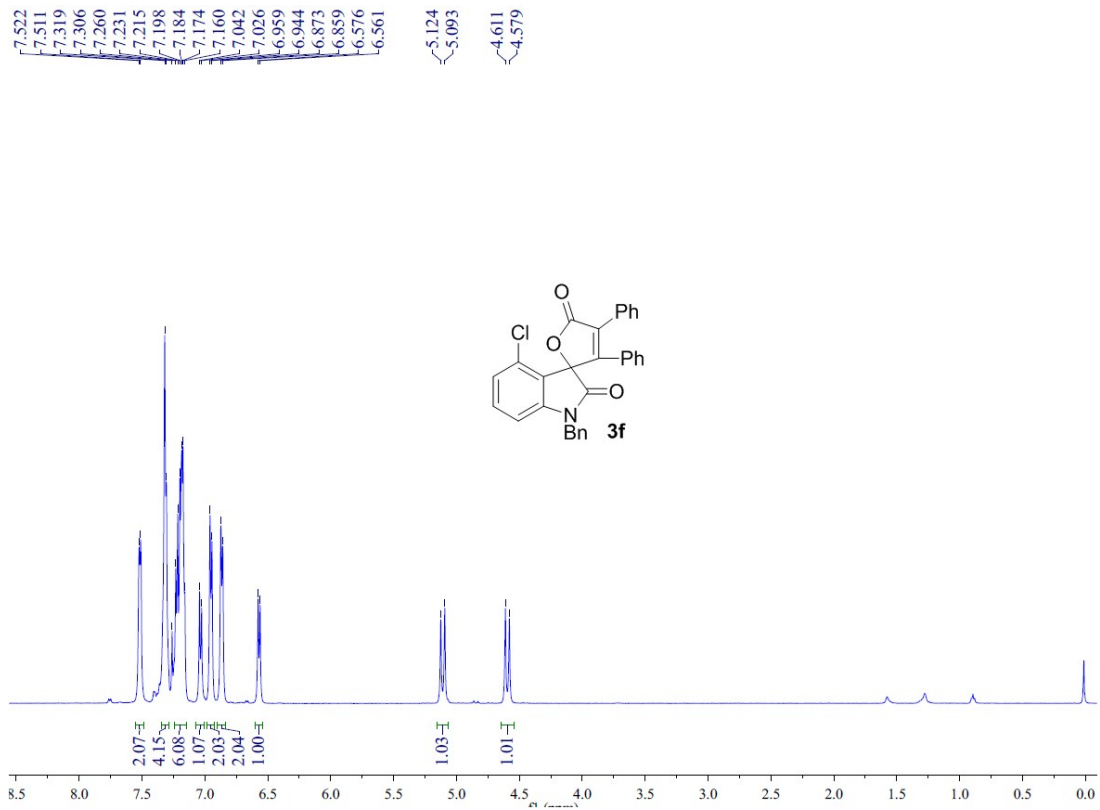


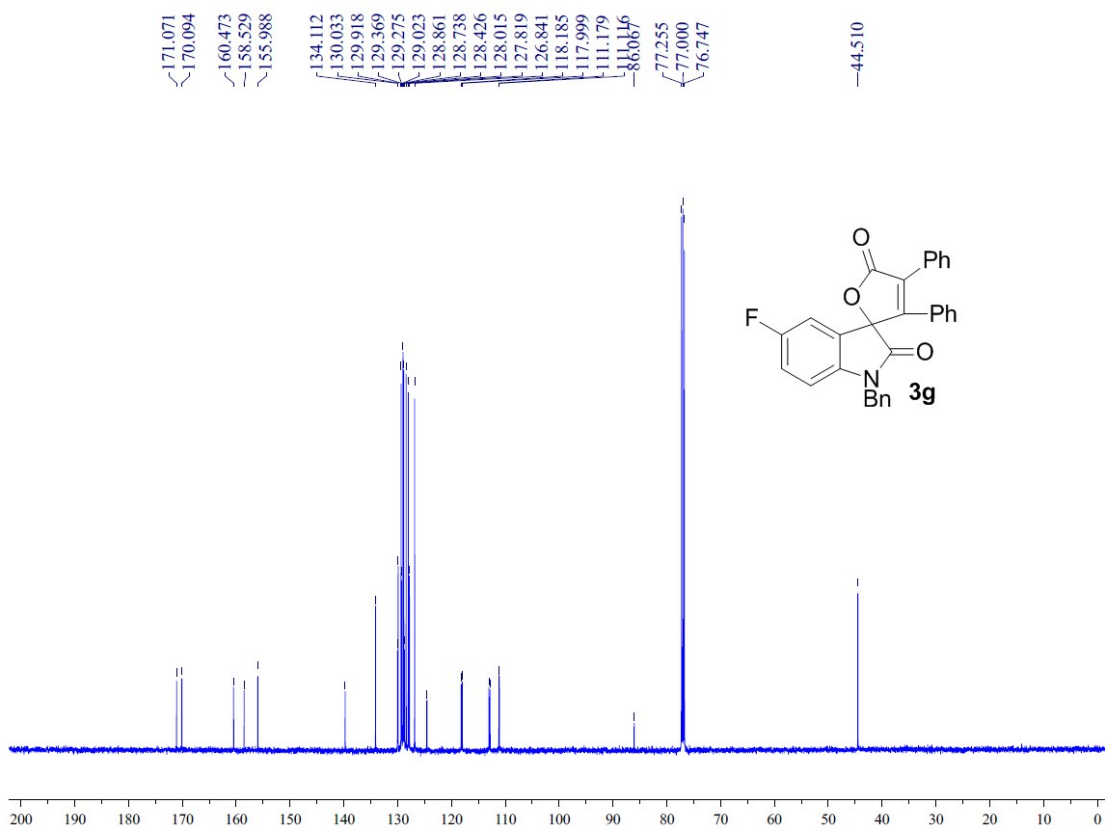
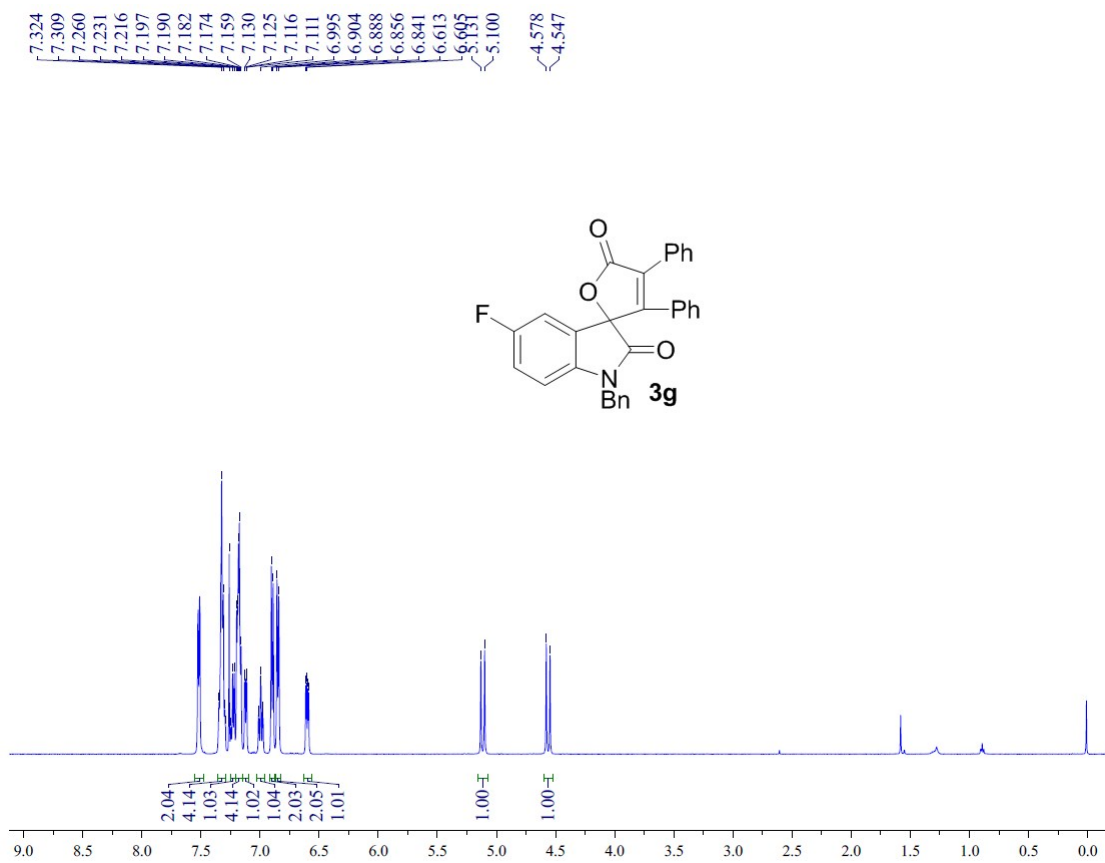


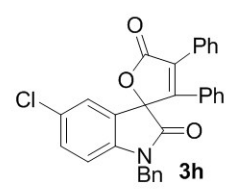
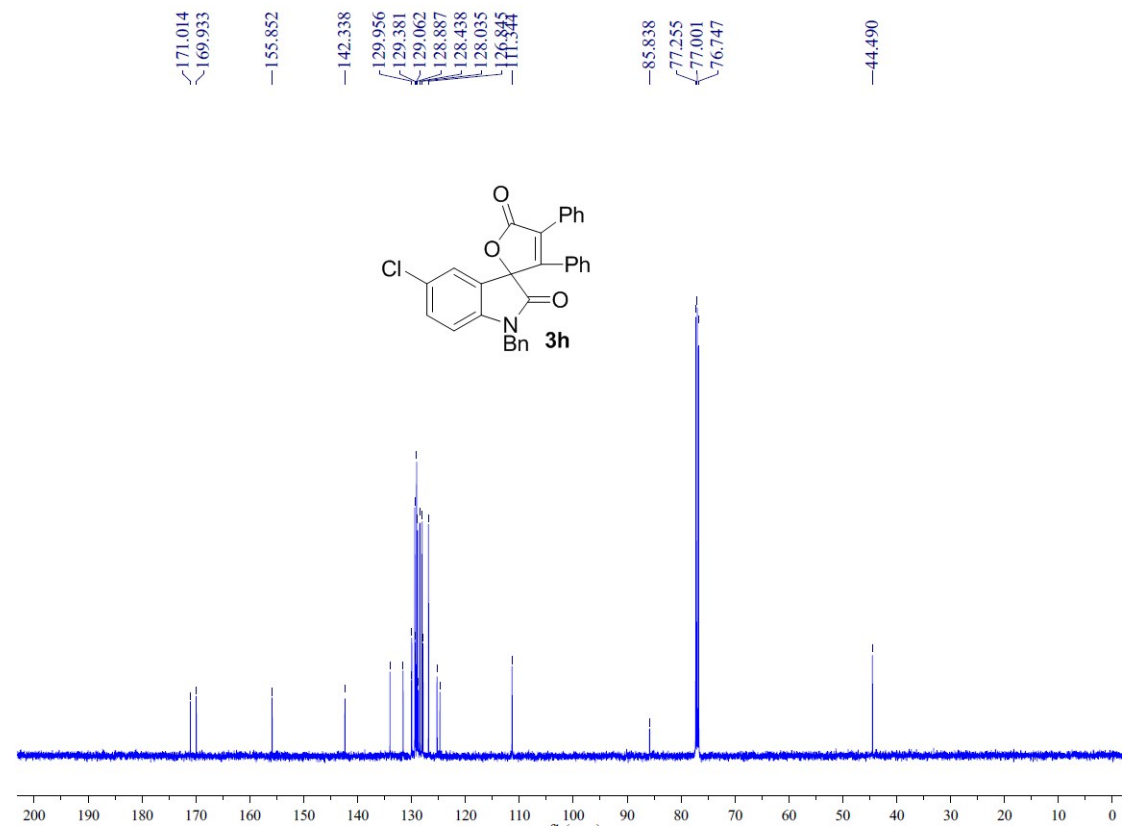
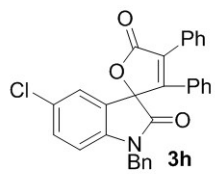
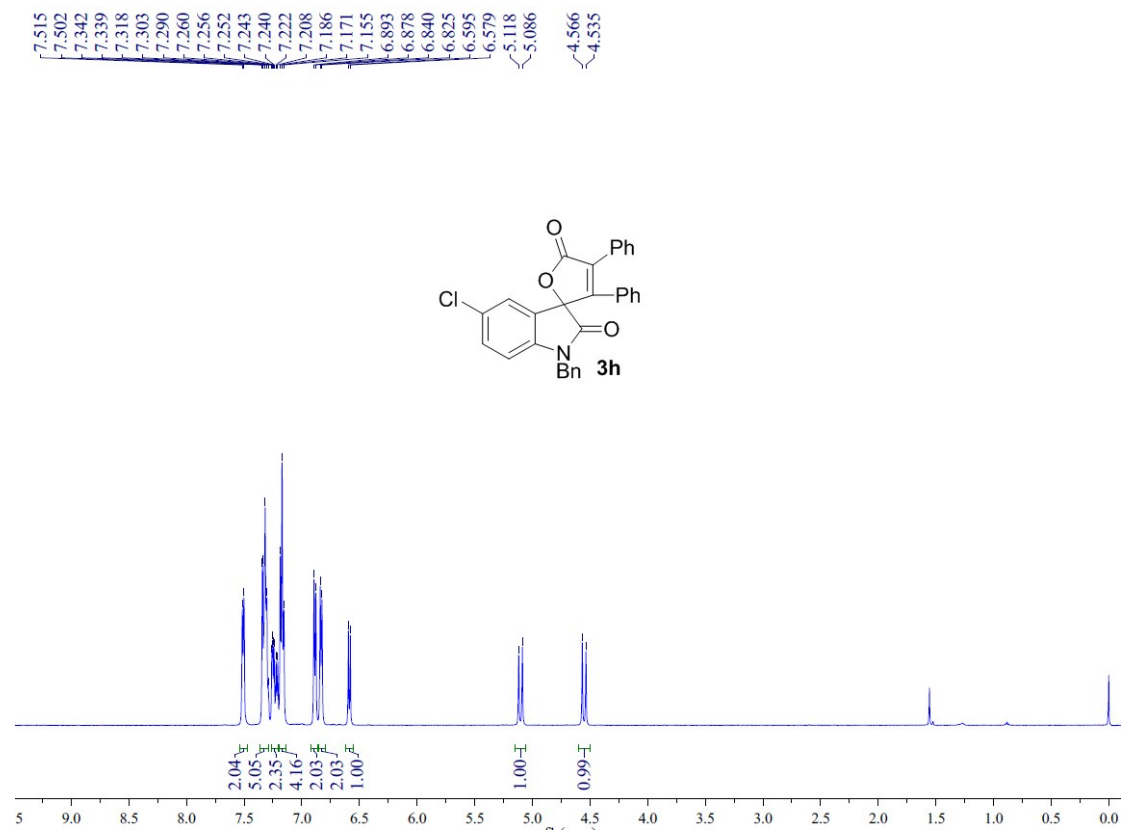


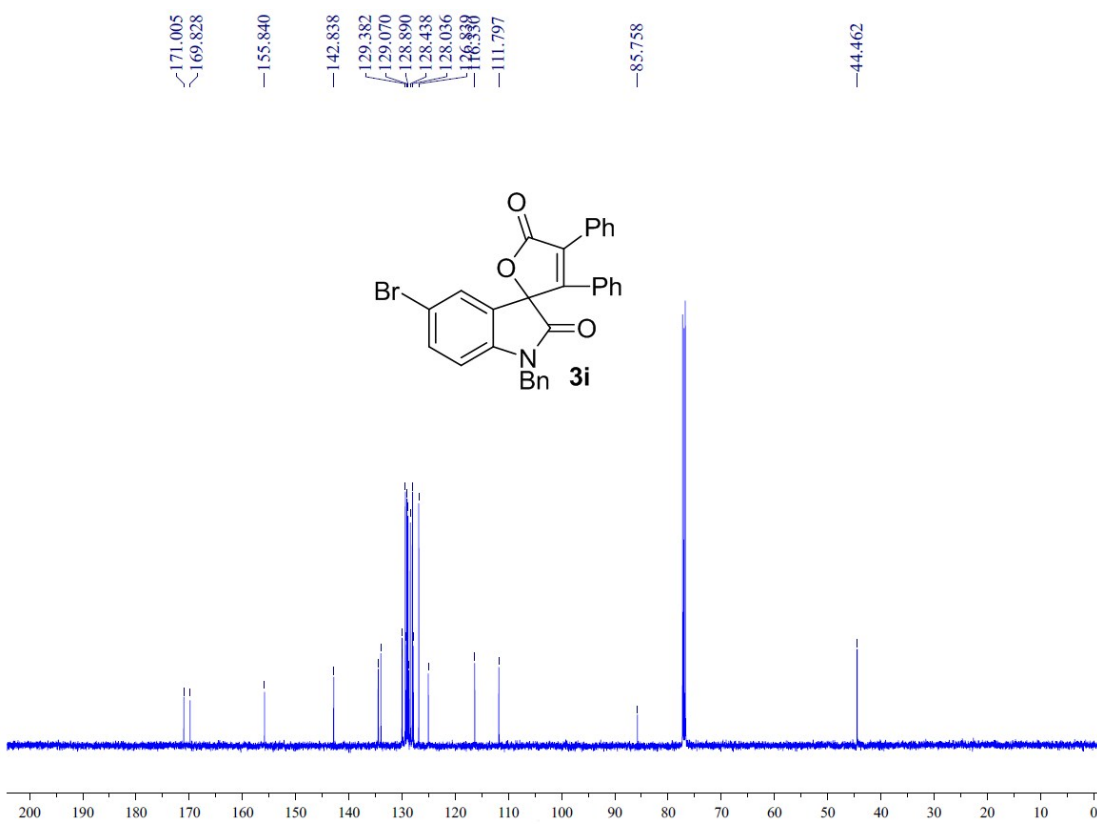
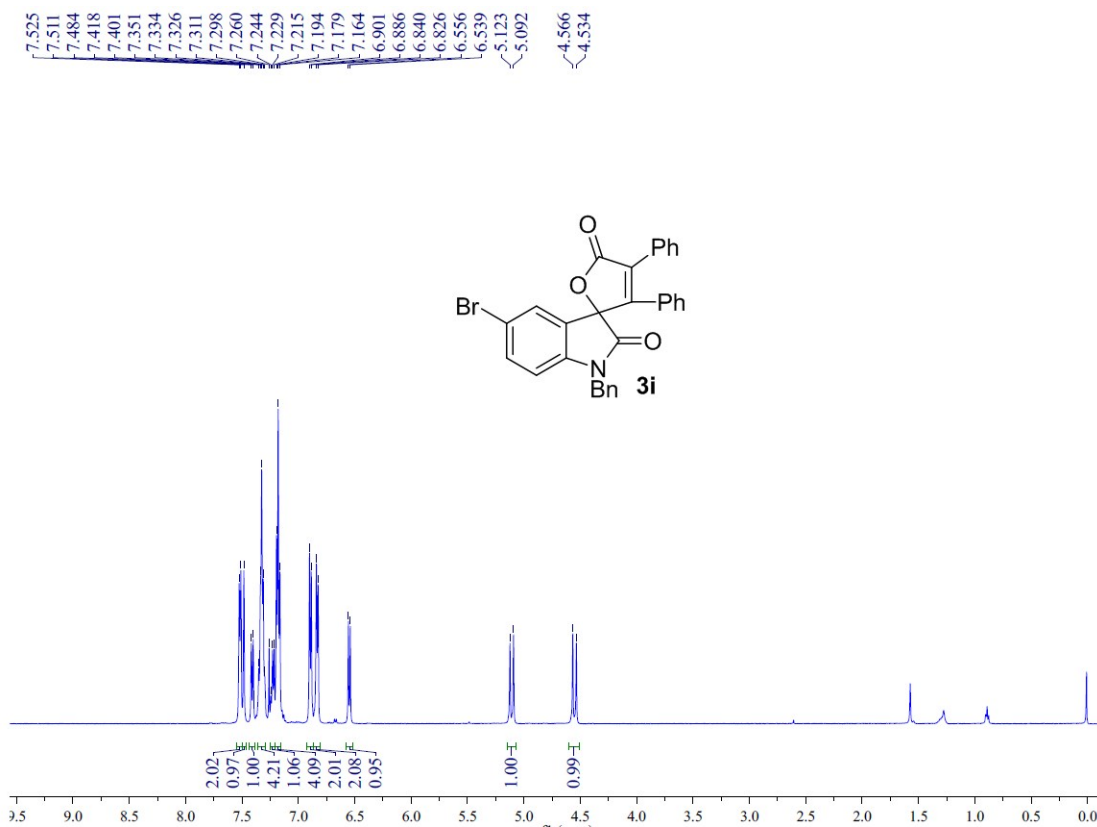


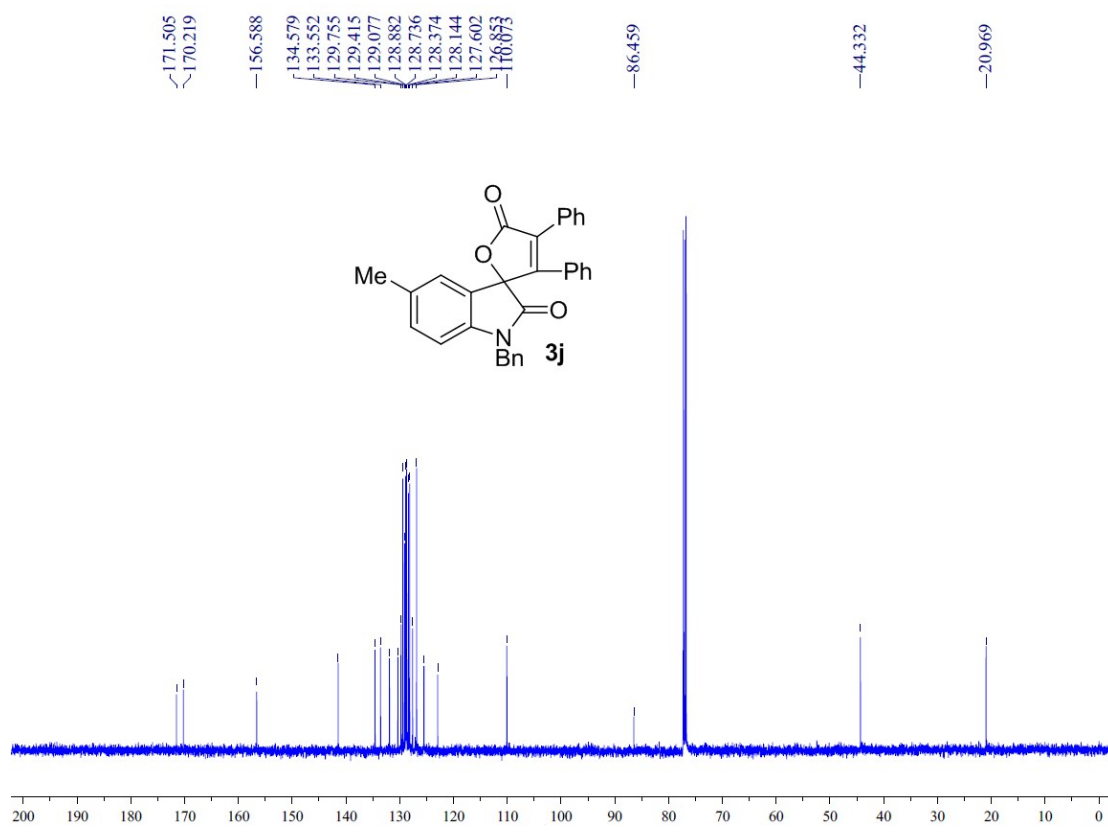
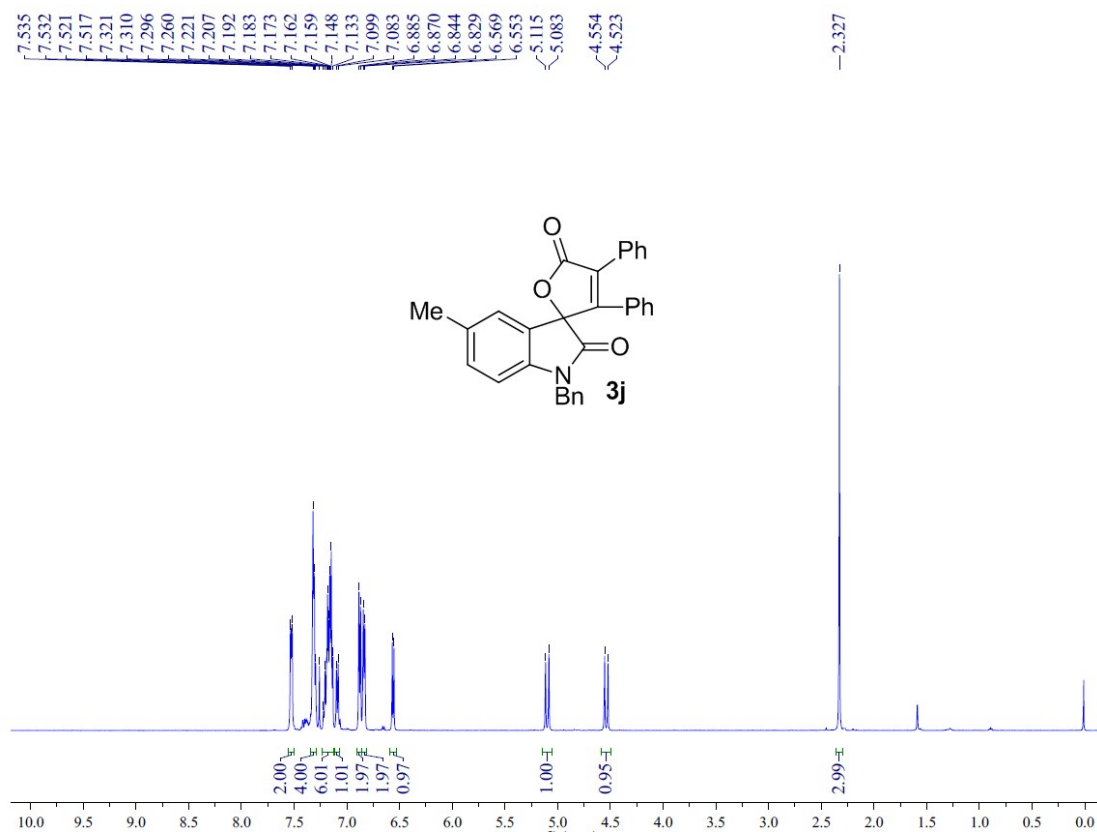


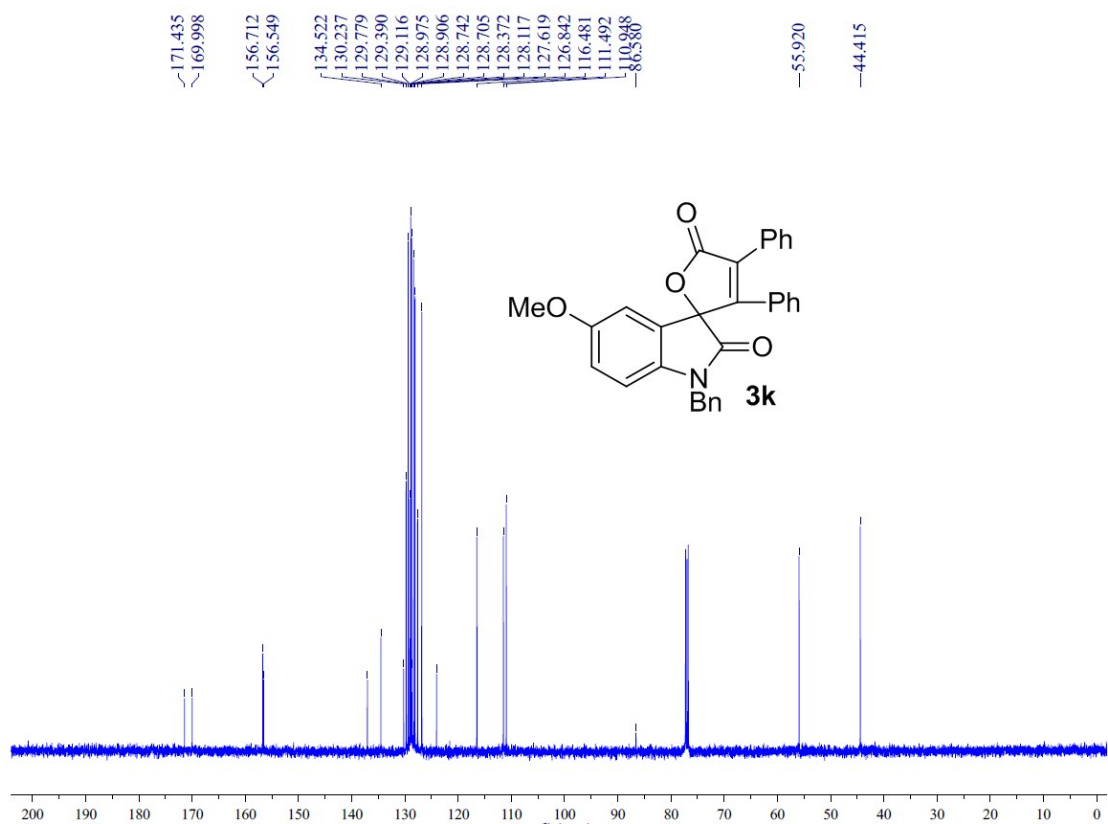
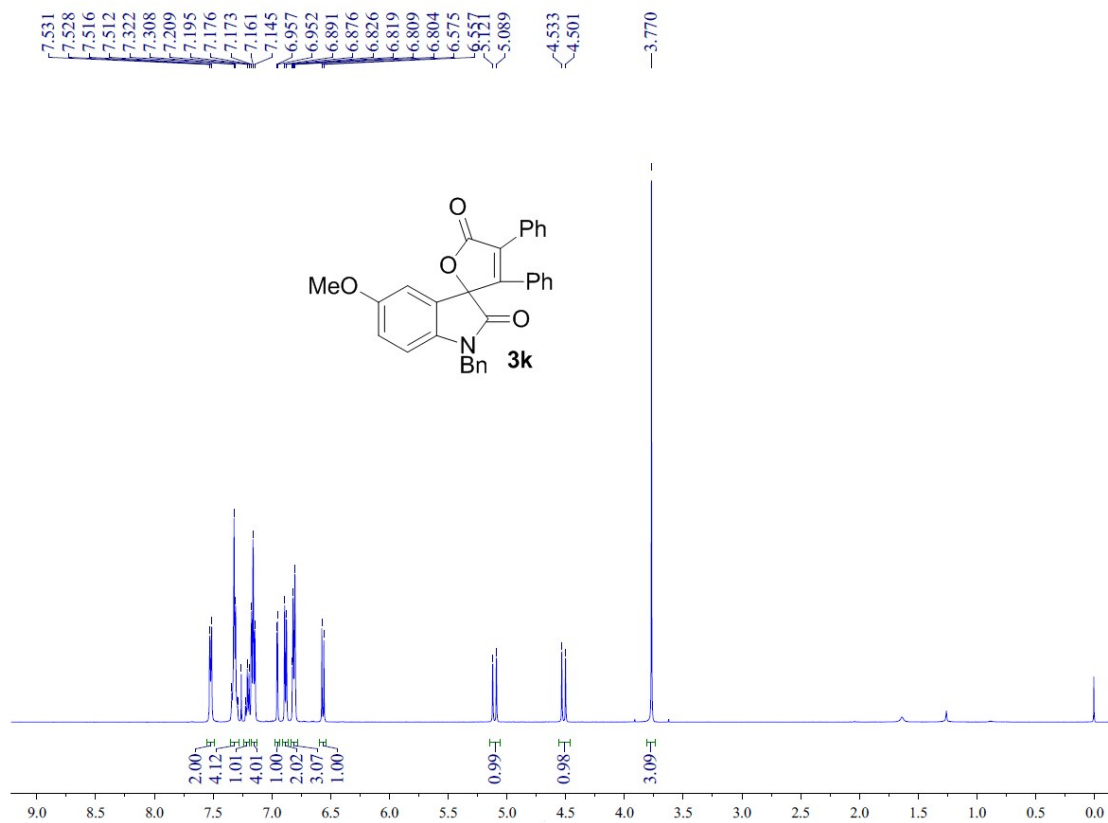






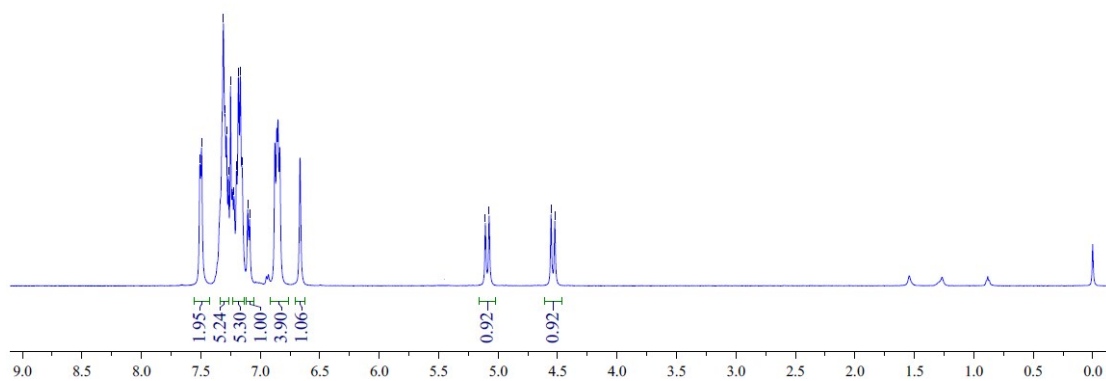
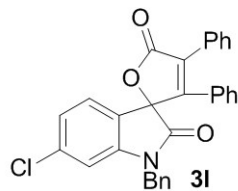






7.507  
7.494  
7.310  
7.297  
7.284  
7.268  
7.250  
7.220  
7.200  
7.184  
7.167  
7.155  
7.105  
7.090

5.107  
5.075  
4.555  
4.523



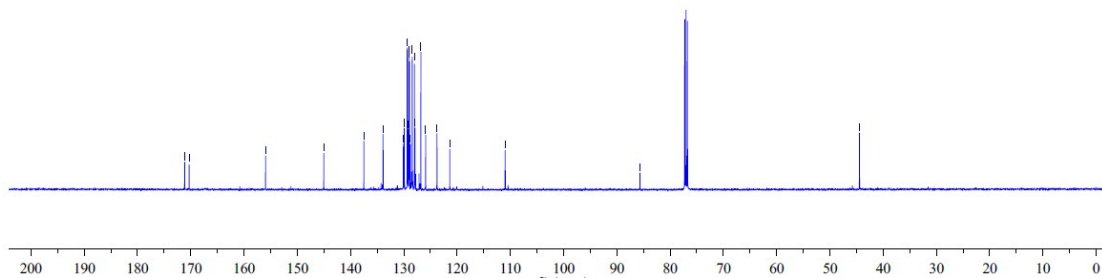
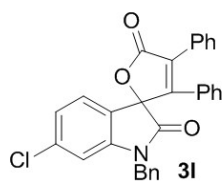
171.124  
170.286

155.947

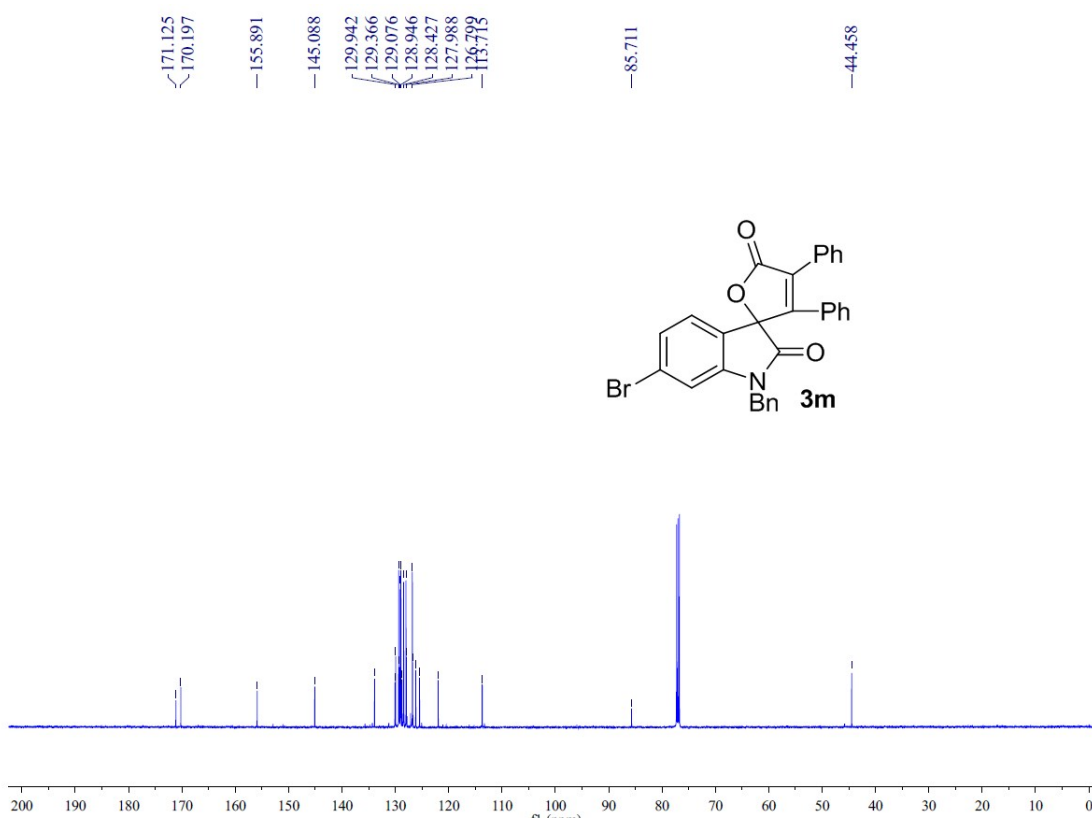
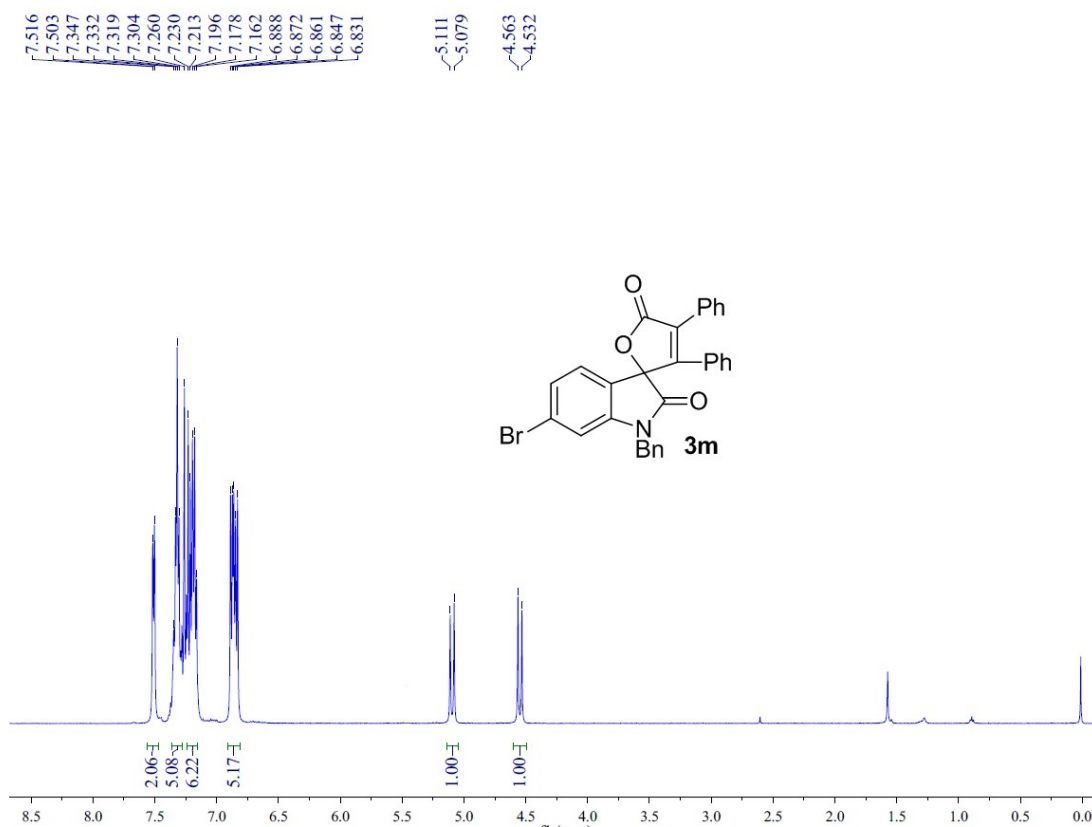
129.918  
129.351  
129.250  
129.049  
128.928  
128.411  
127.979  
127.903  
126.792  
123.558  
120.364

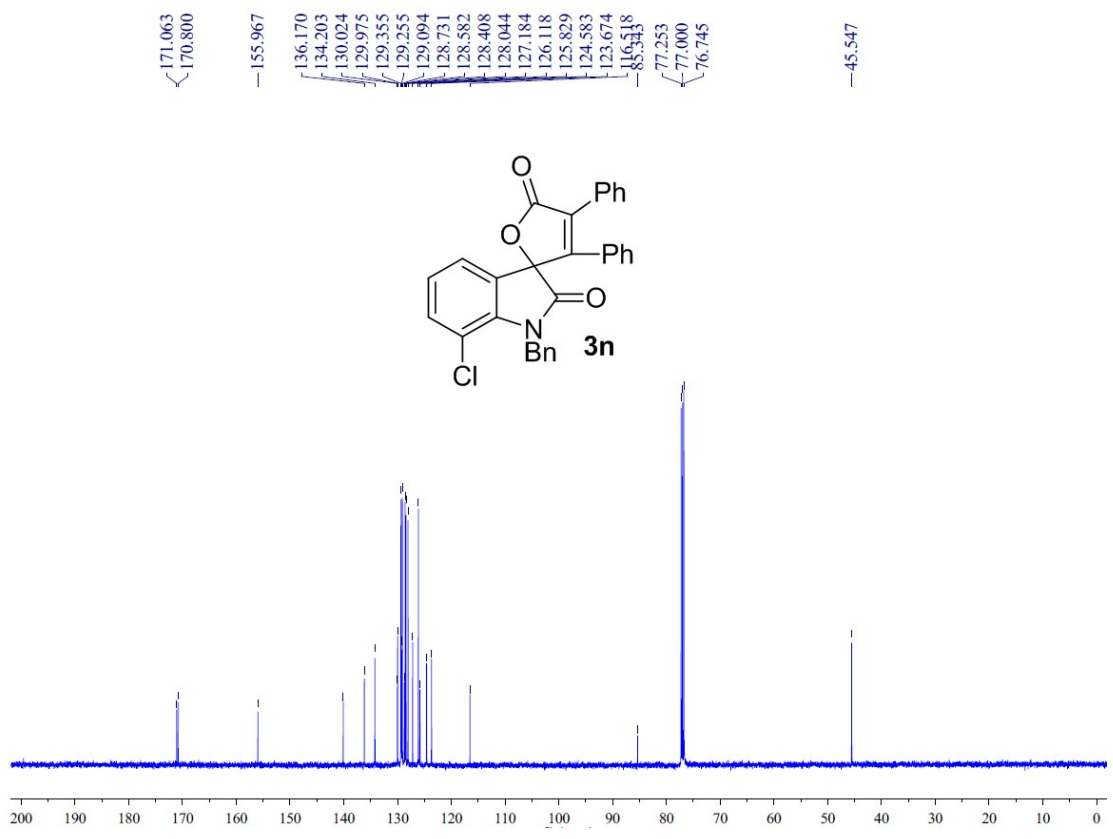
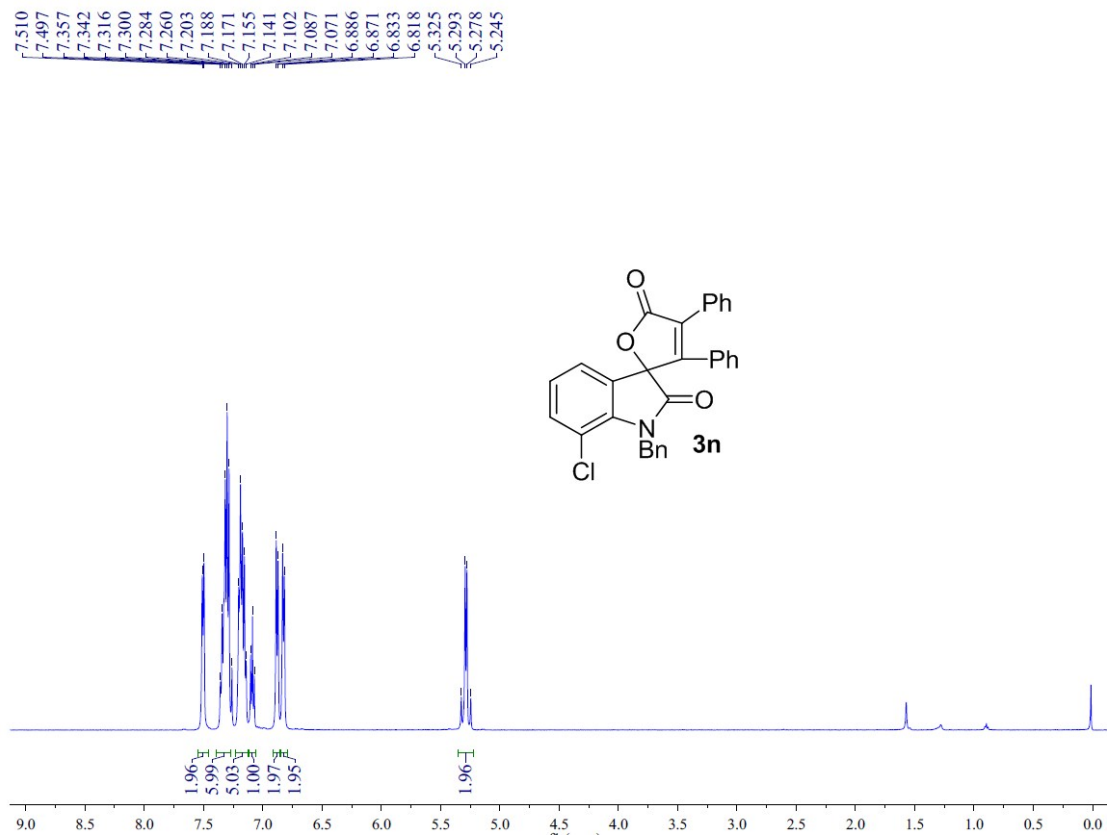
85.665

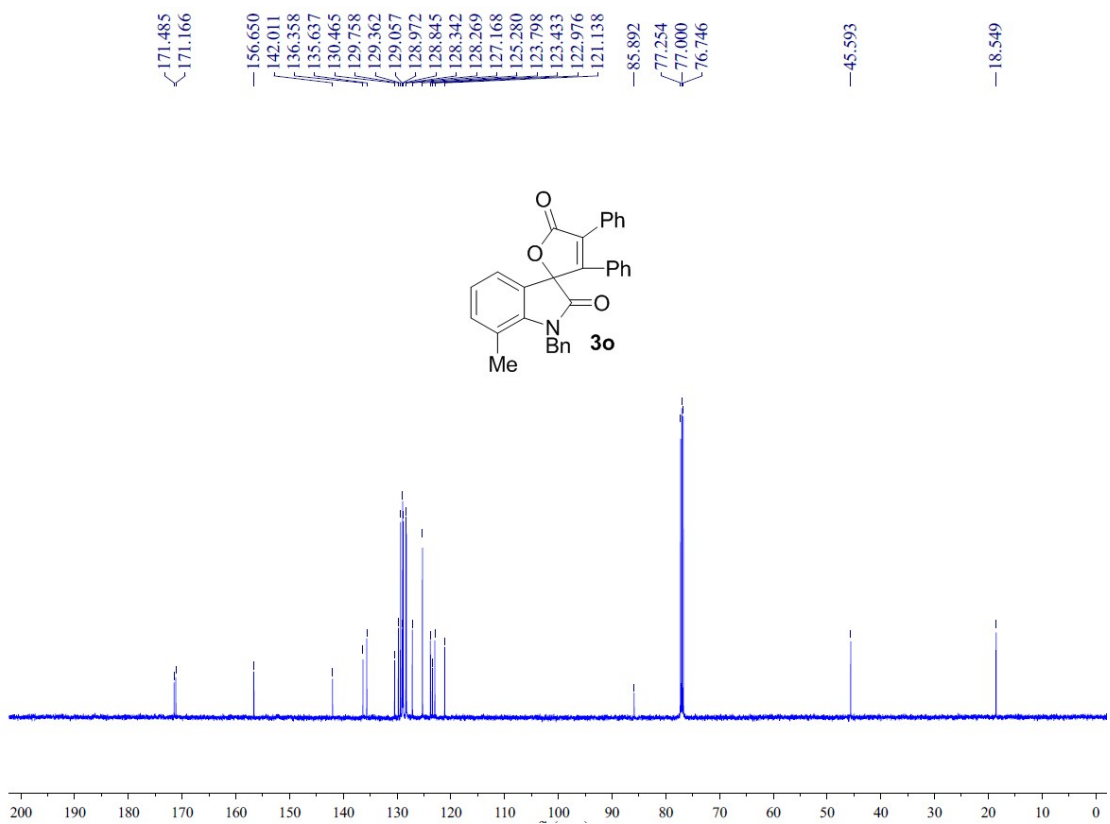
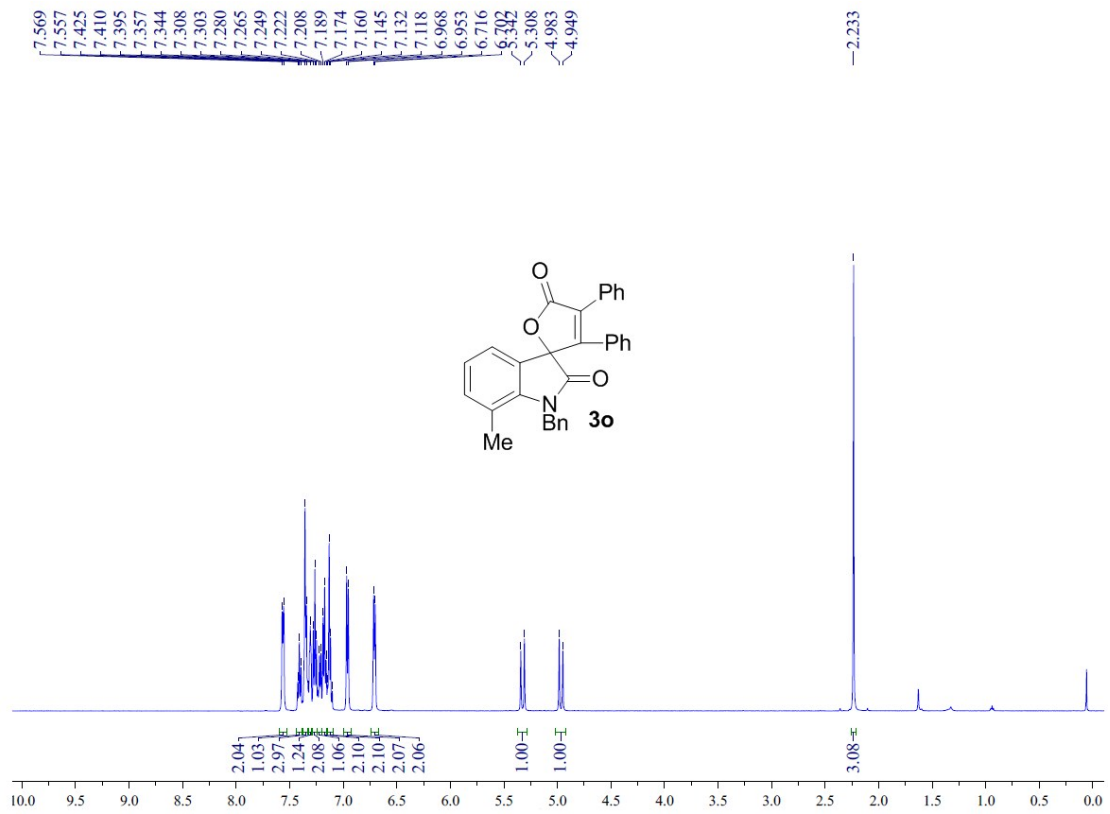
44.453

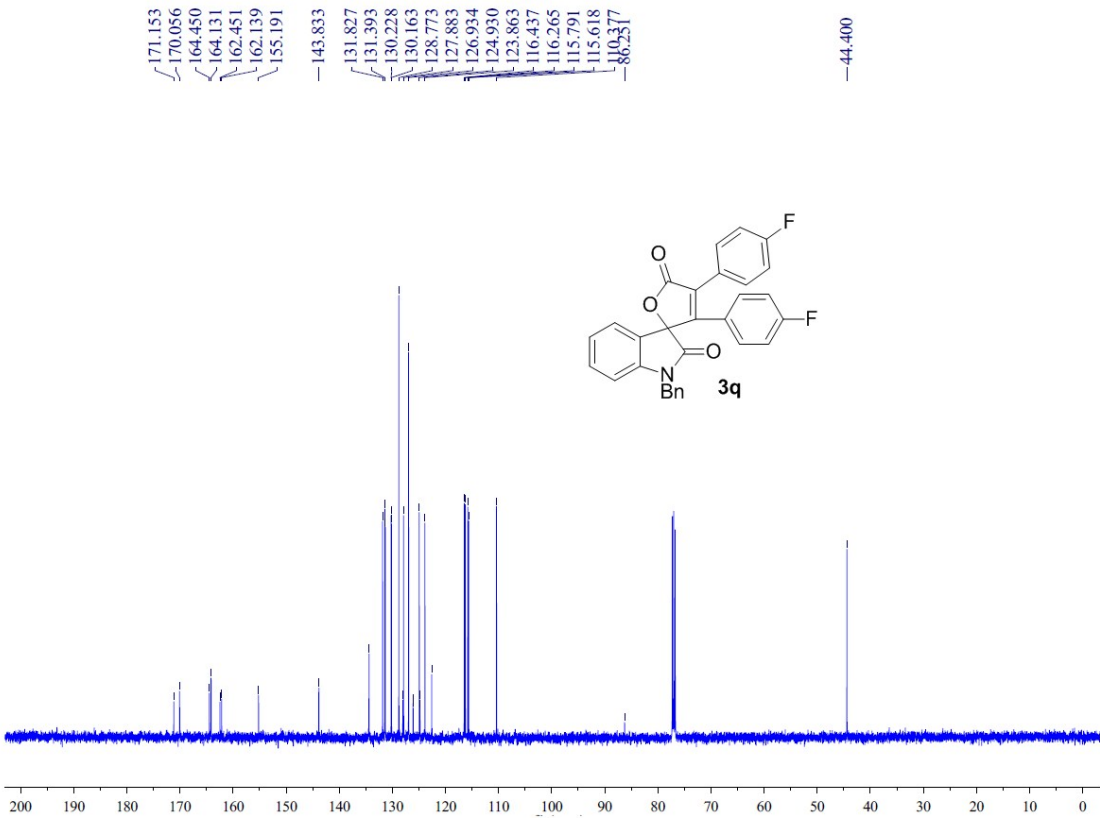
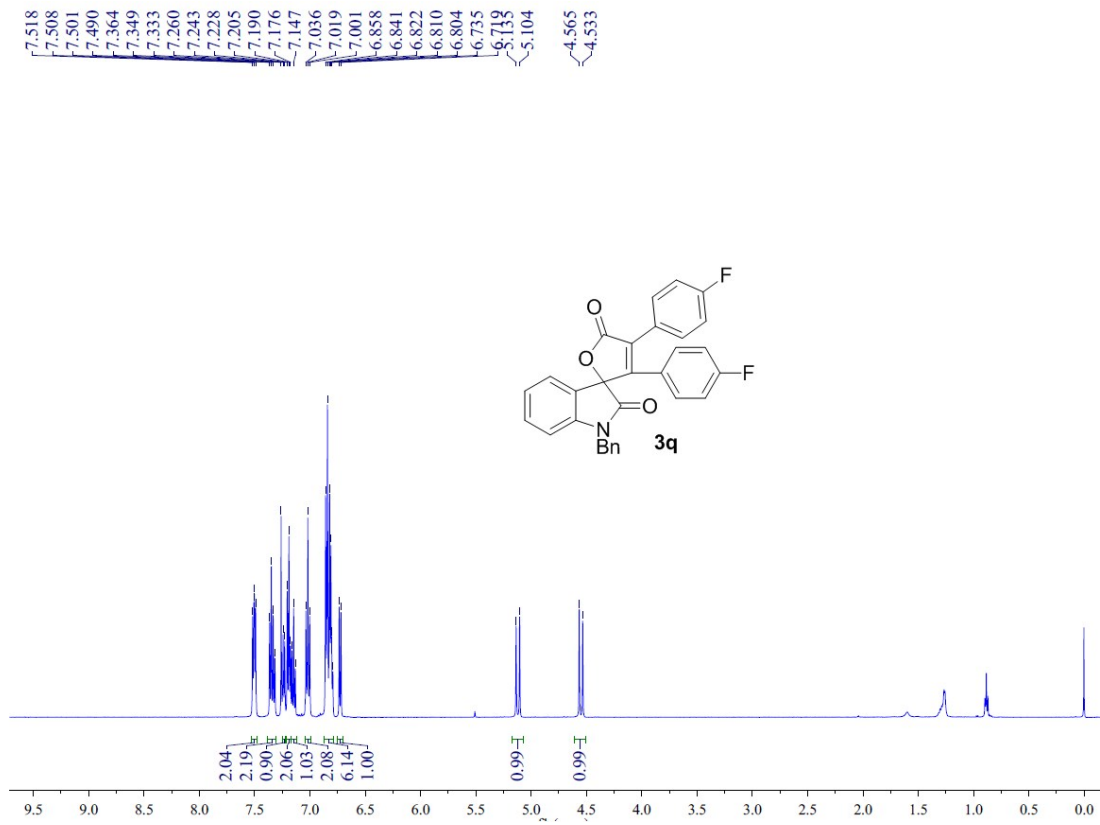


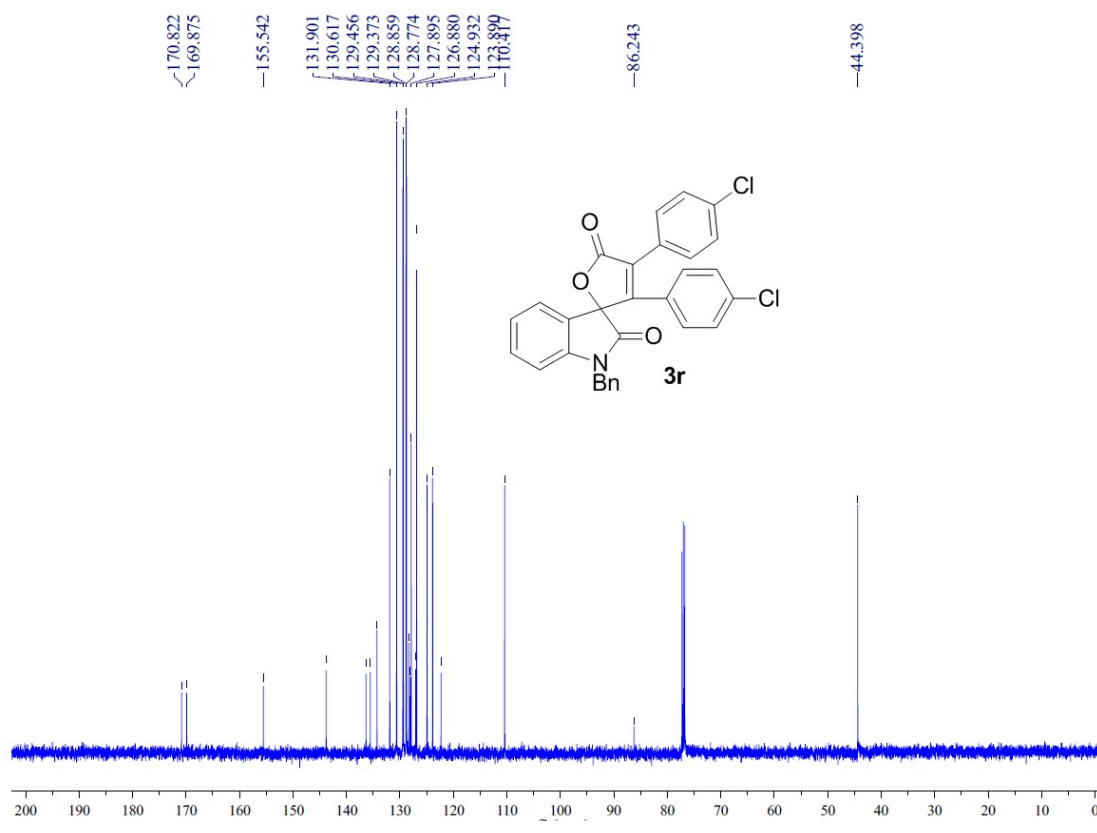
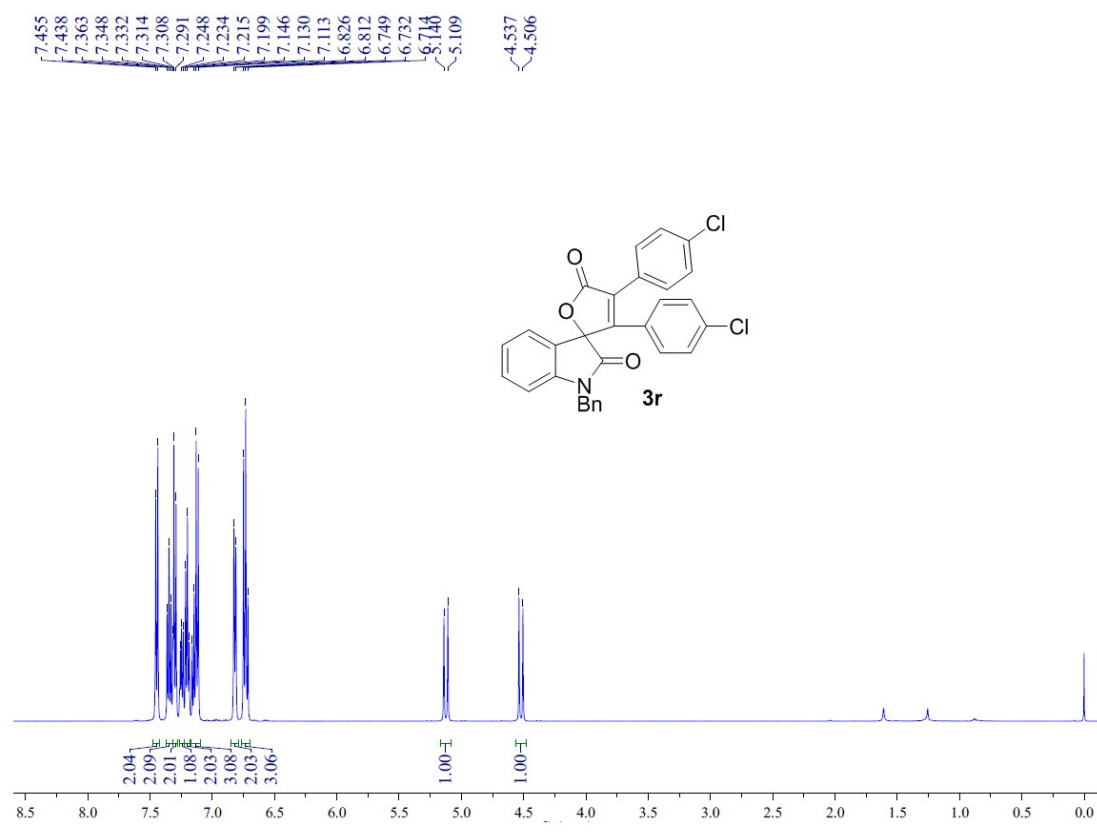


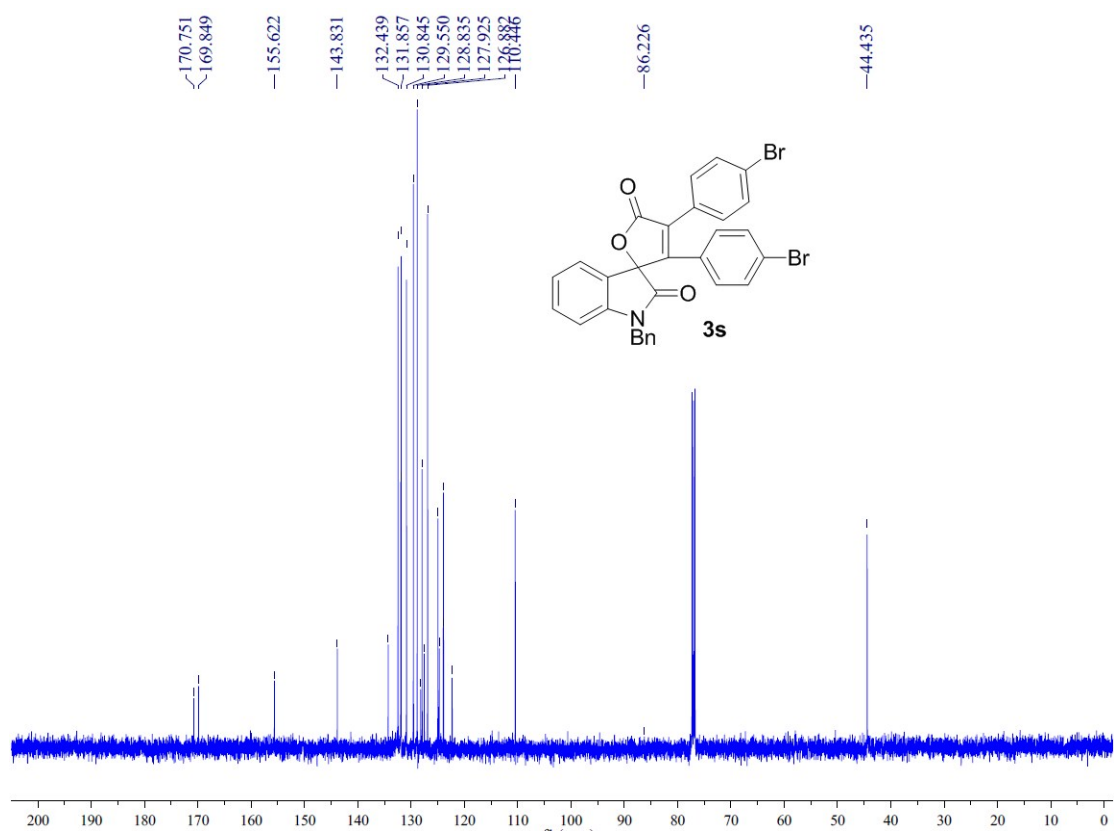
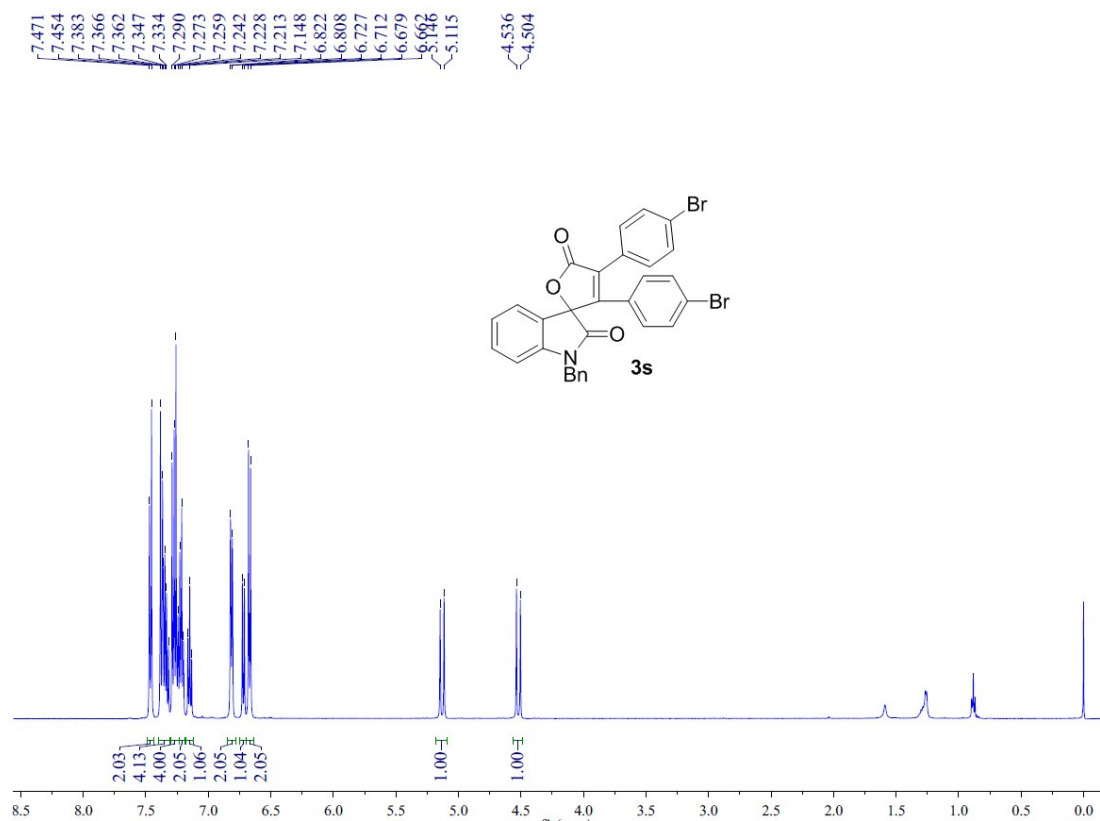


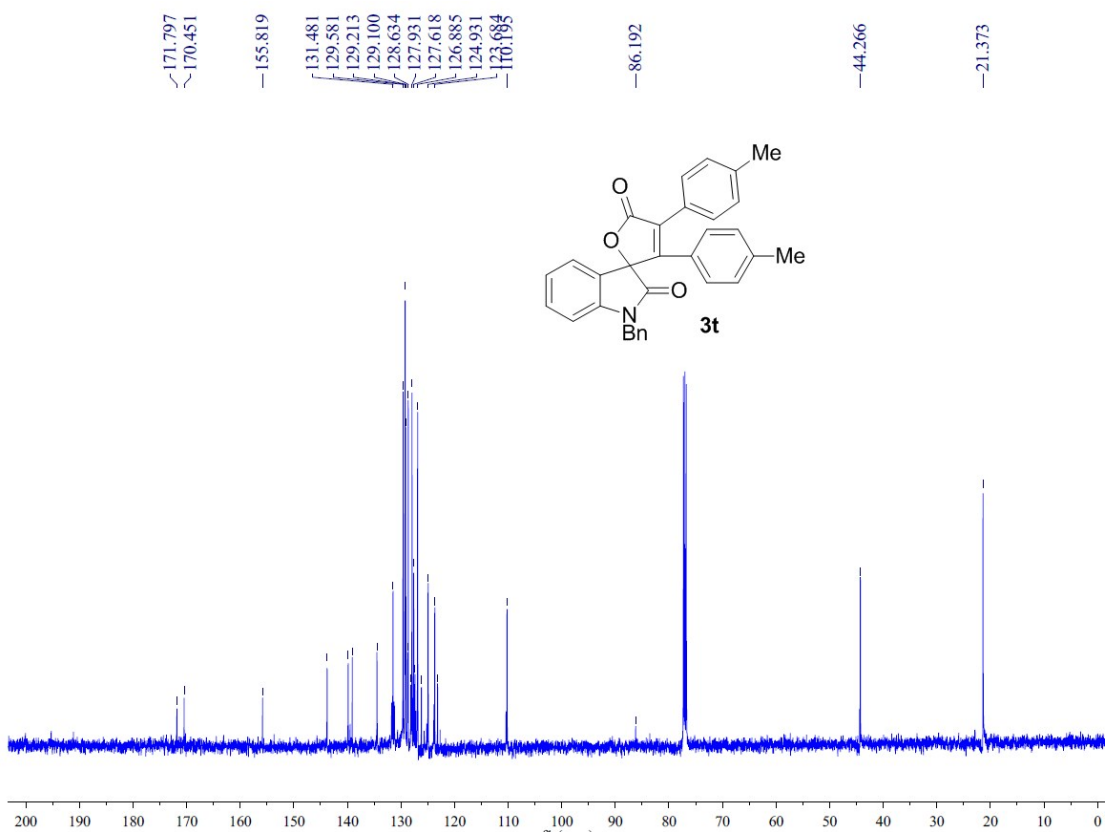
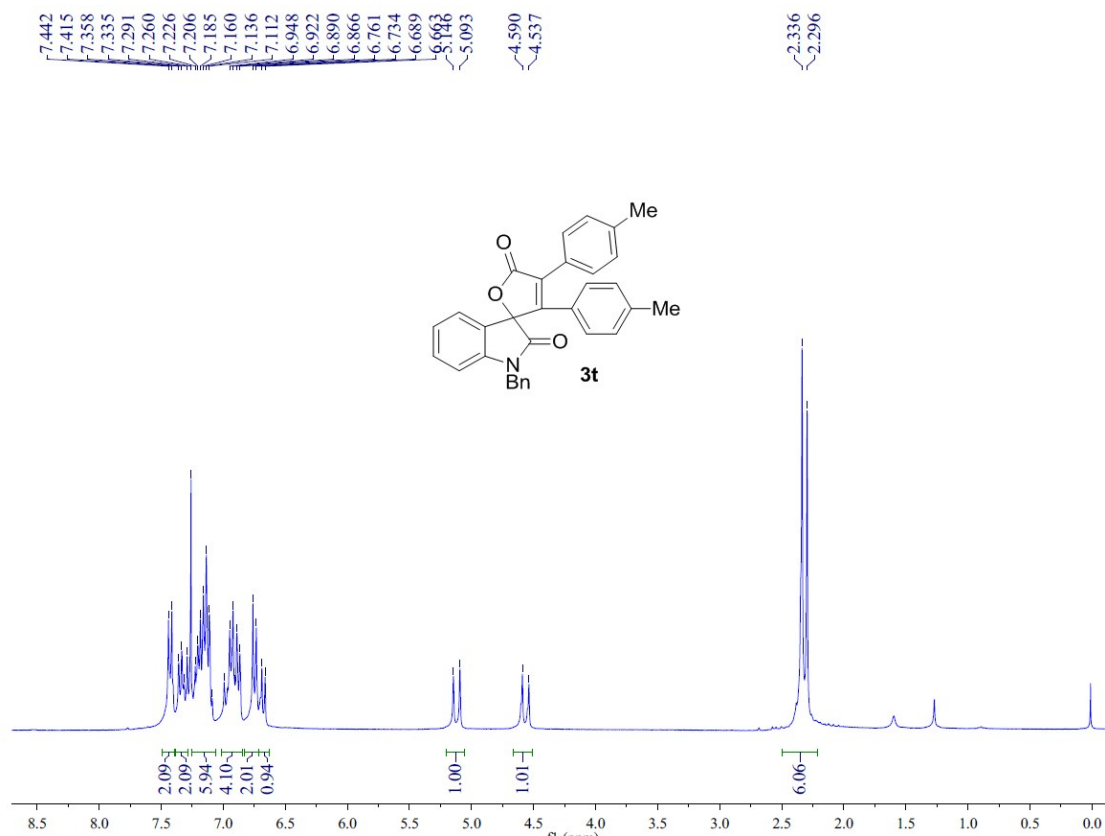


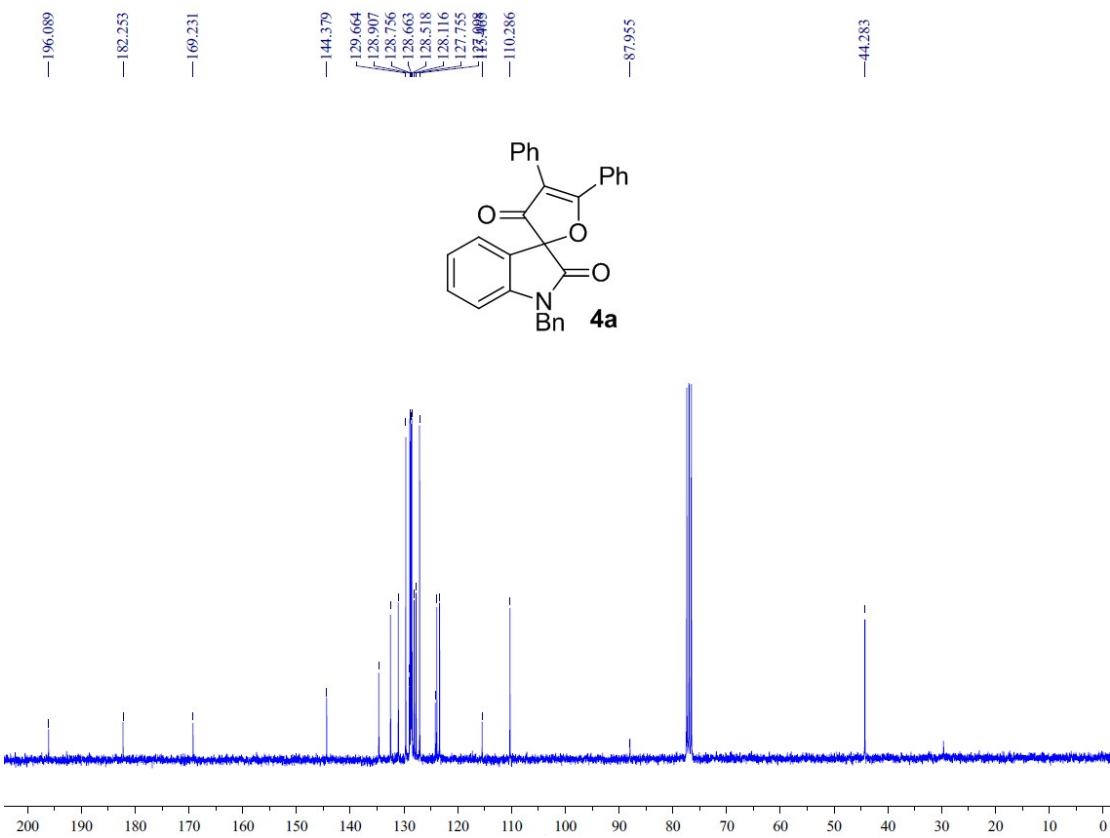
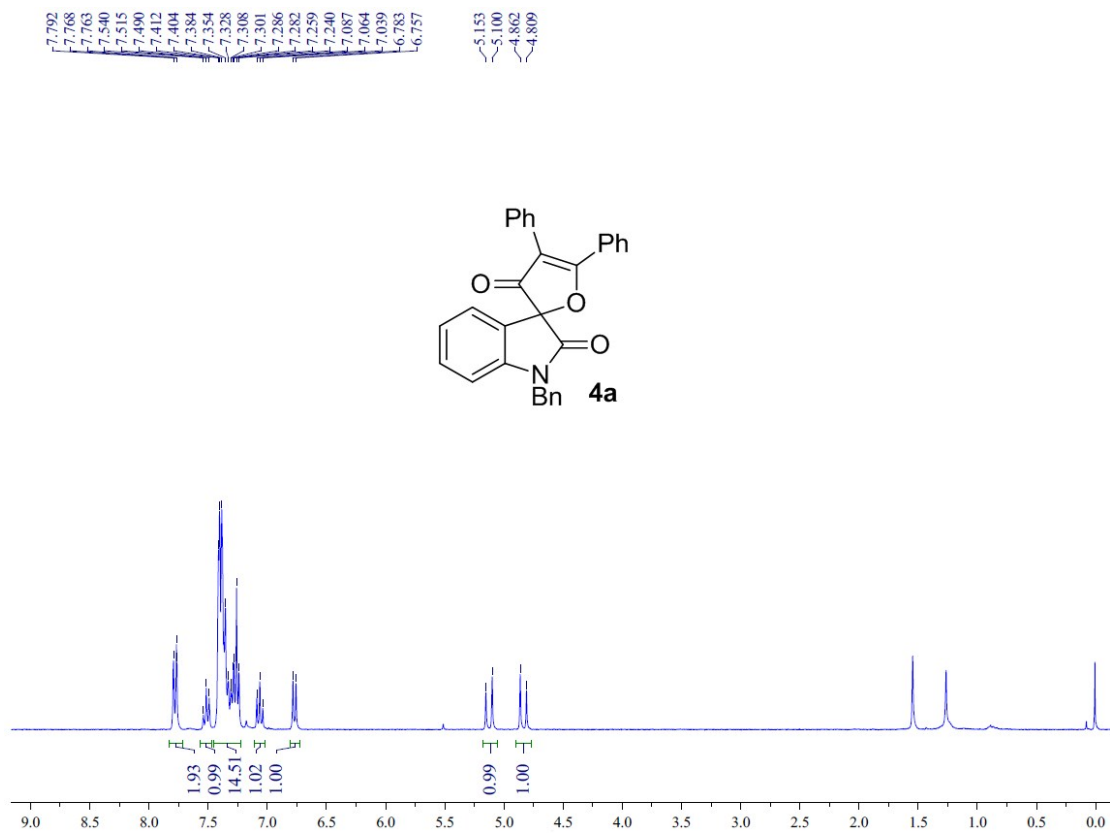




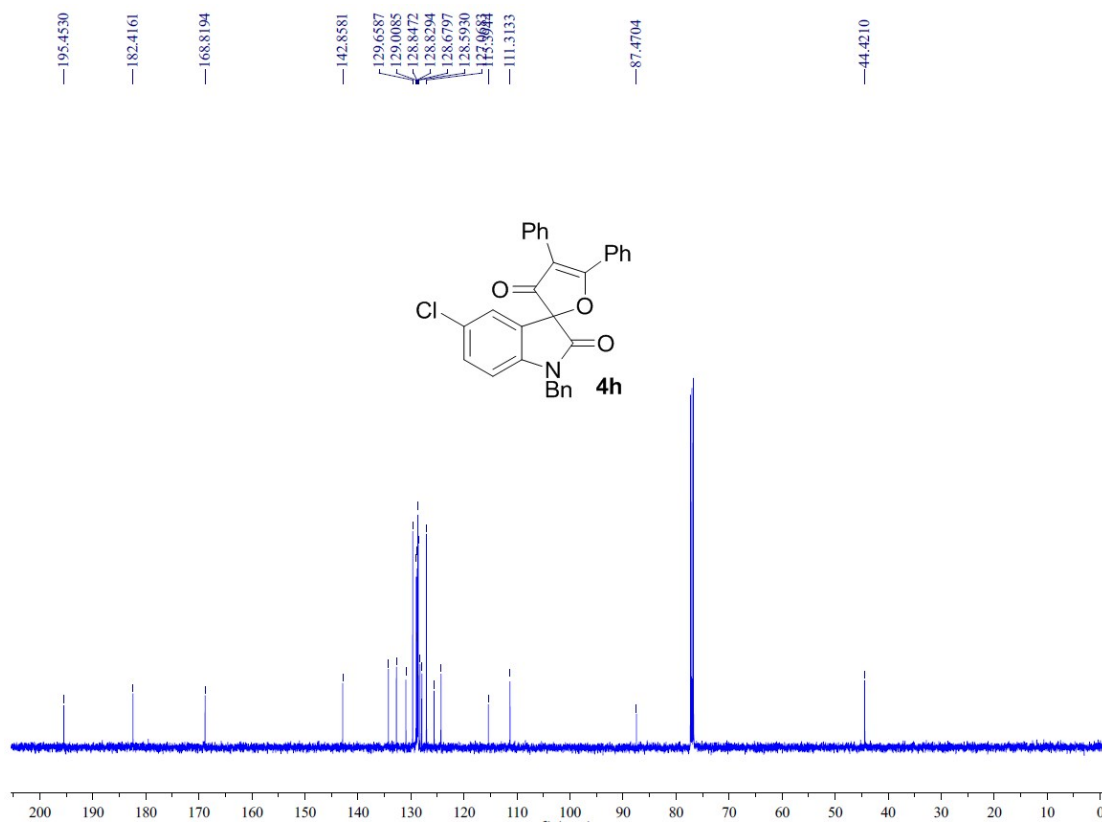
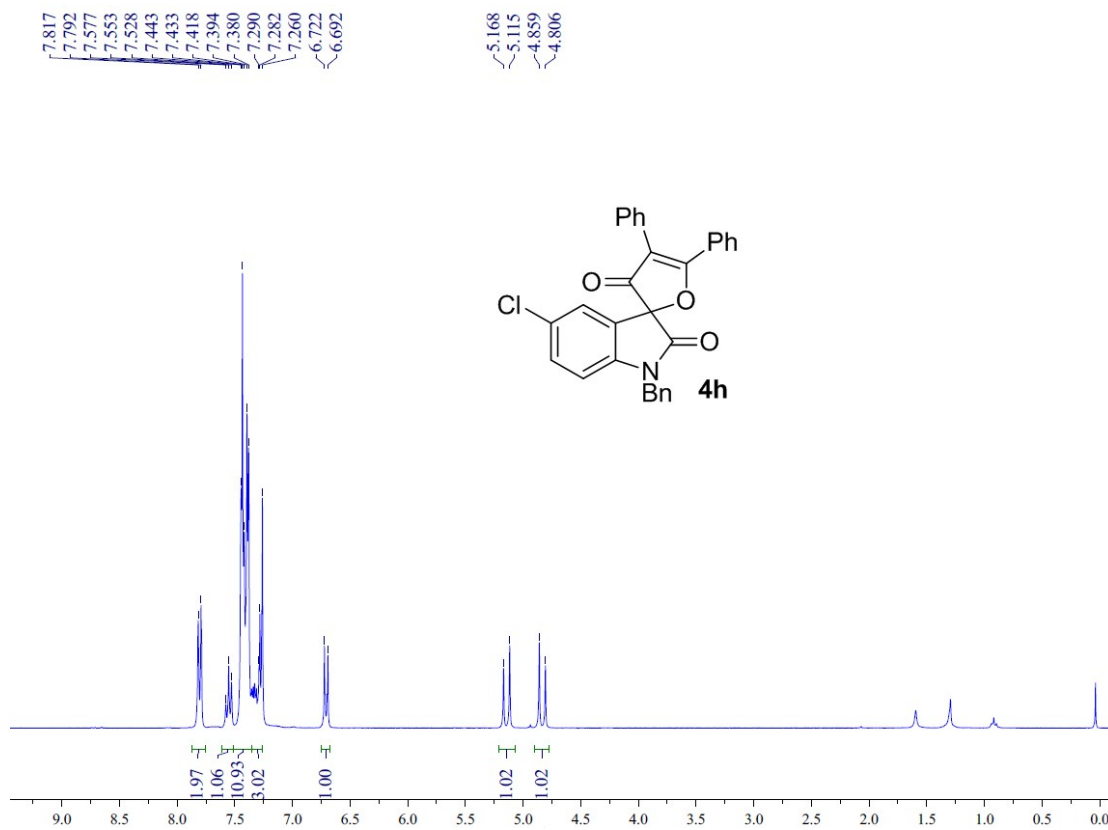


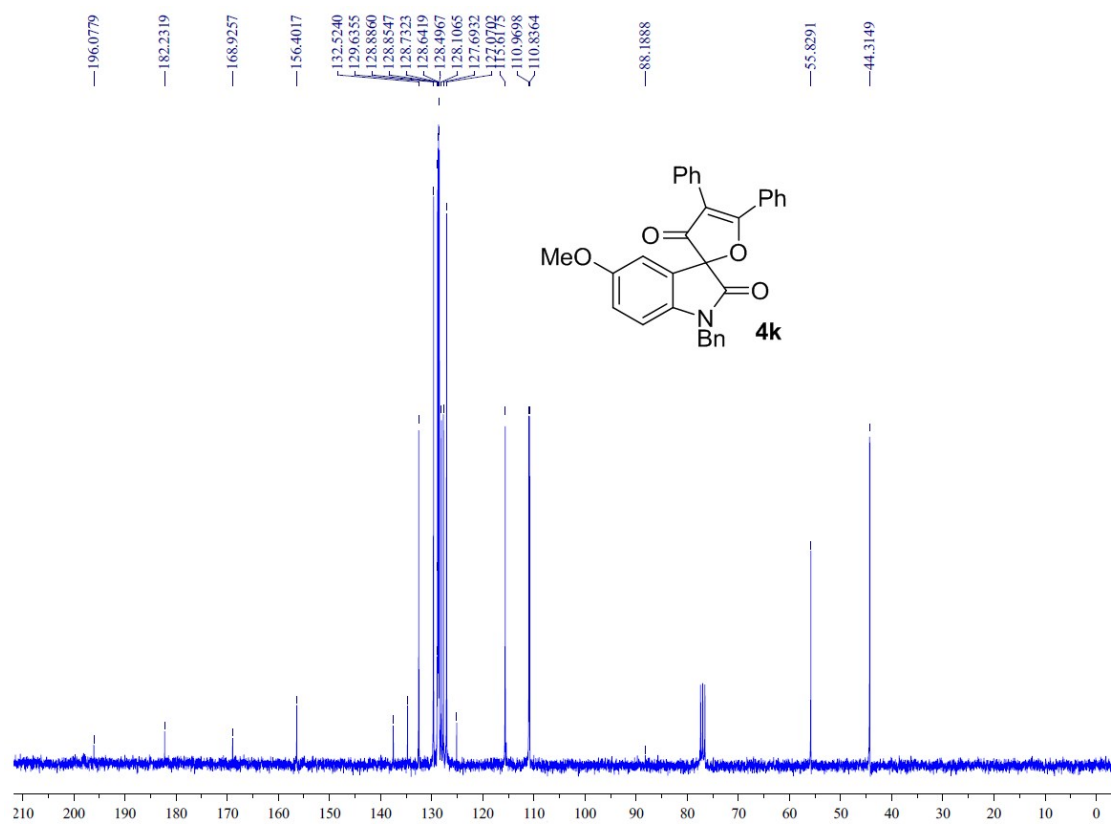
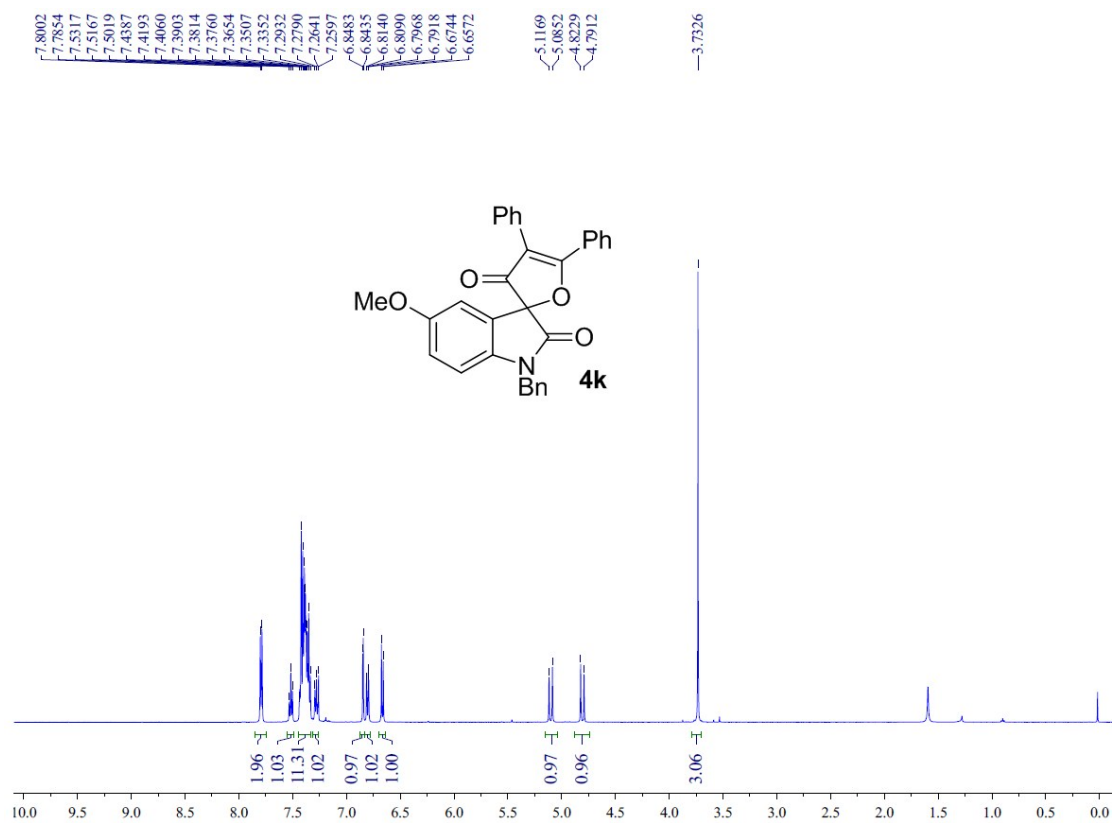


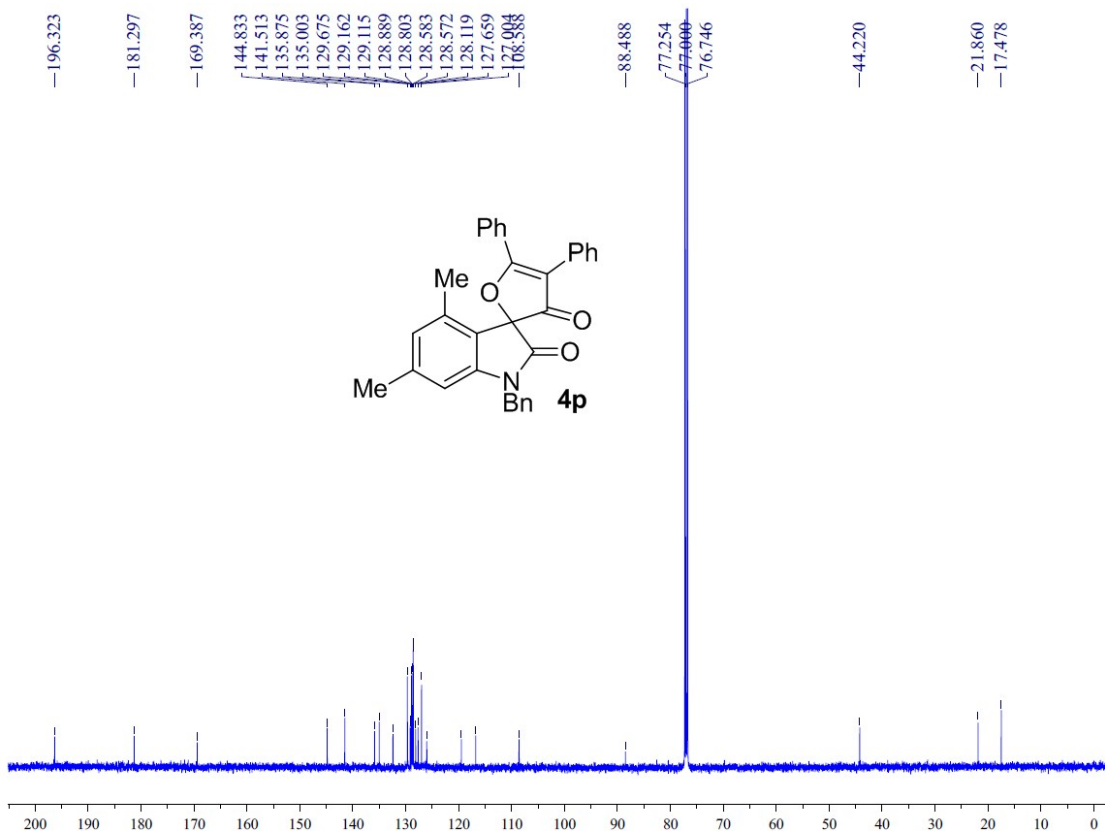
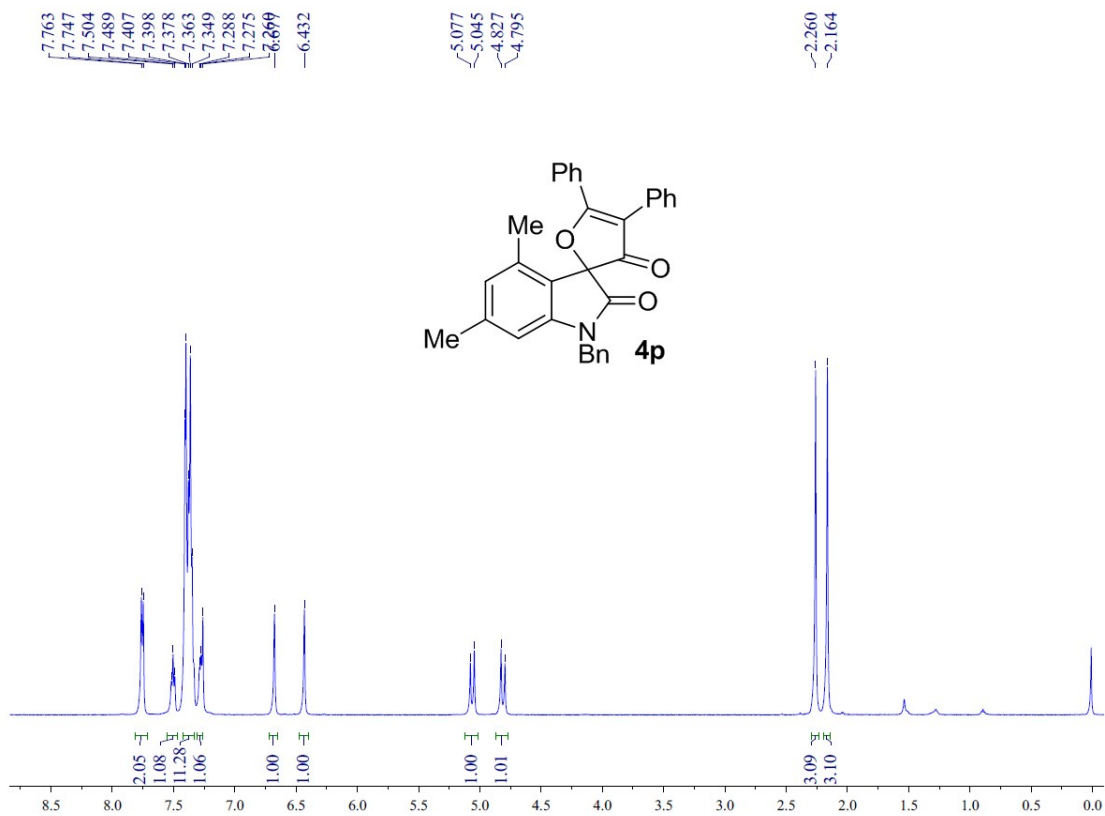


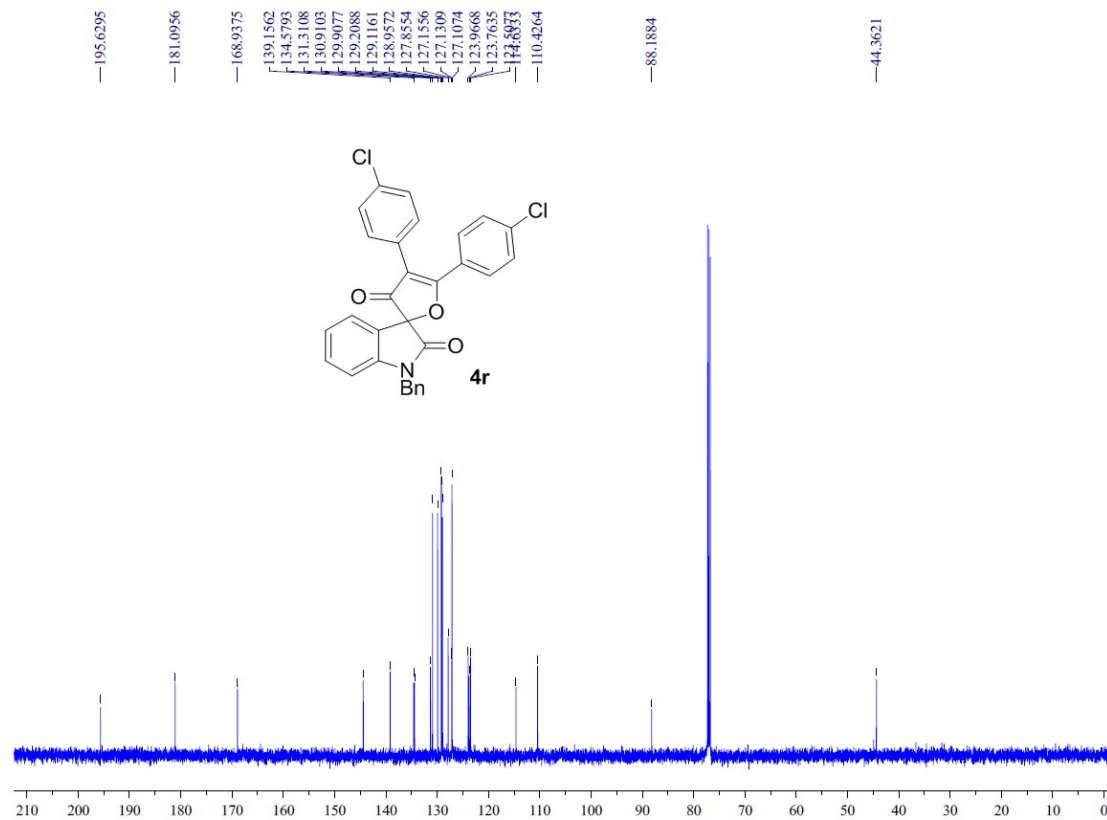
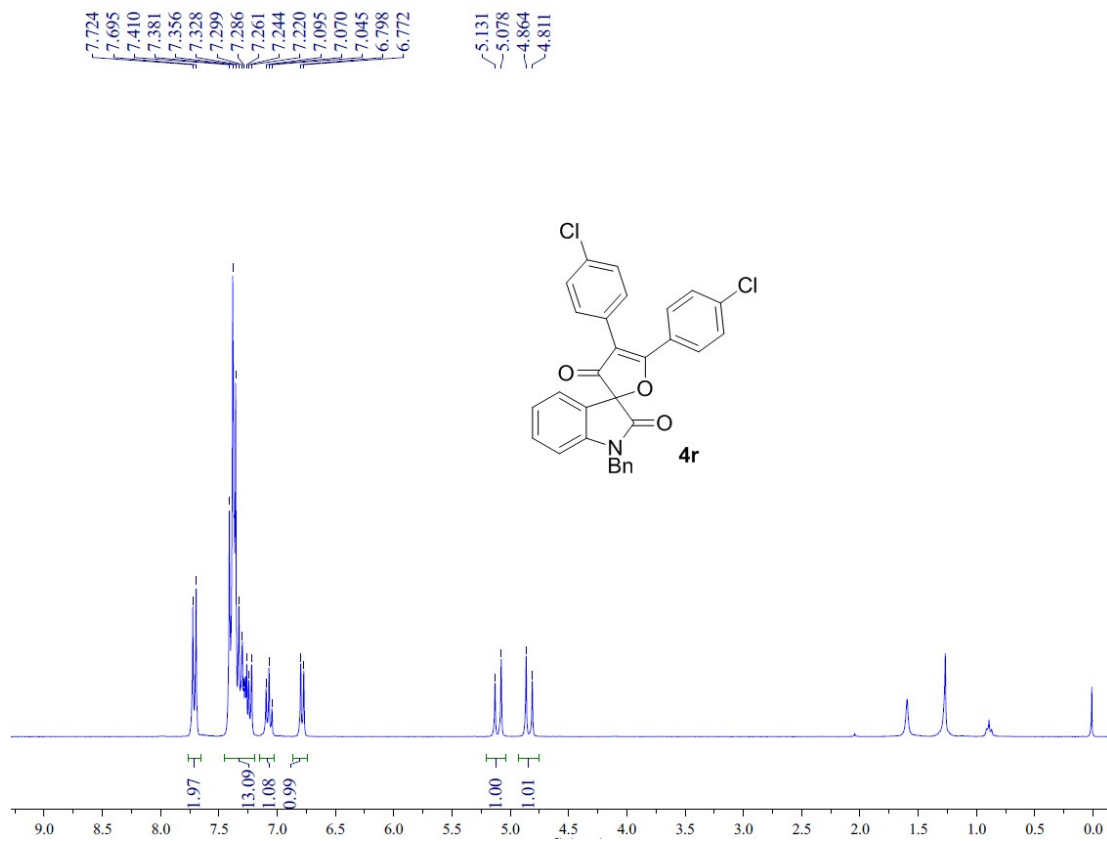


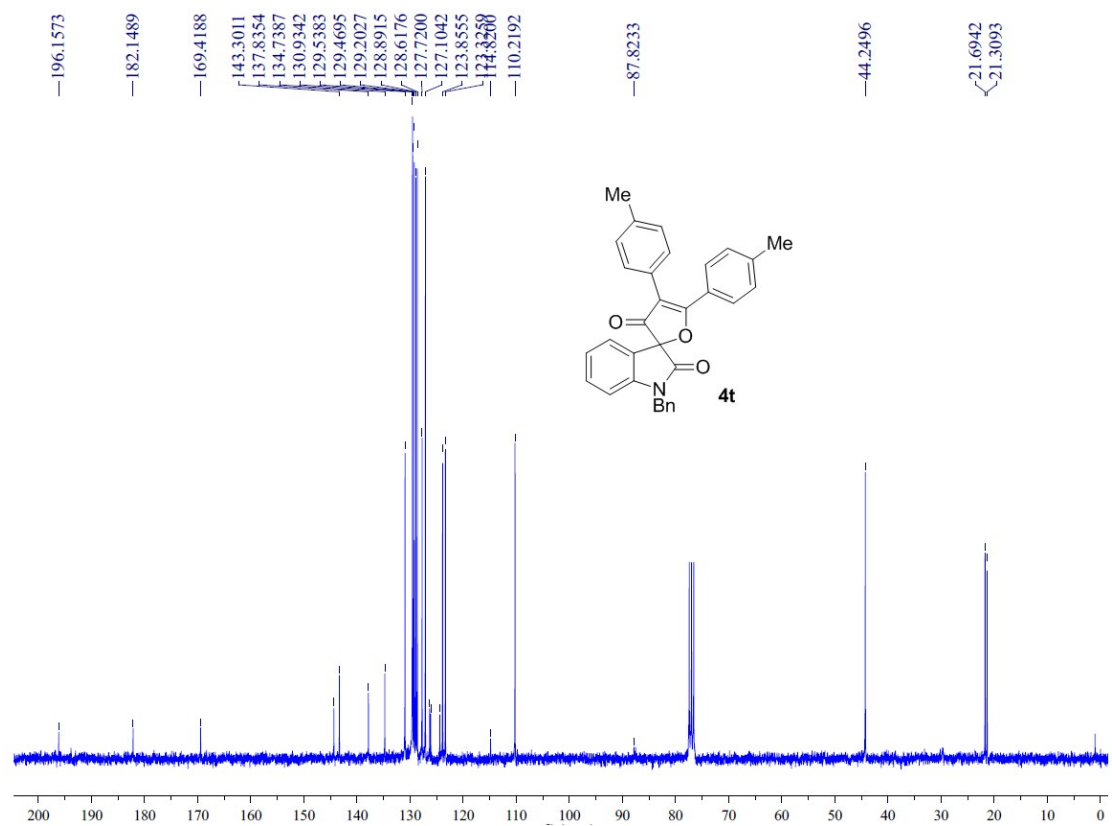
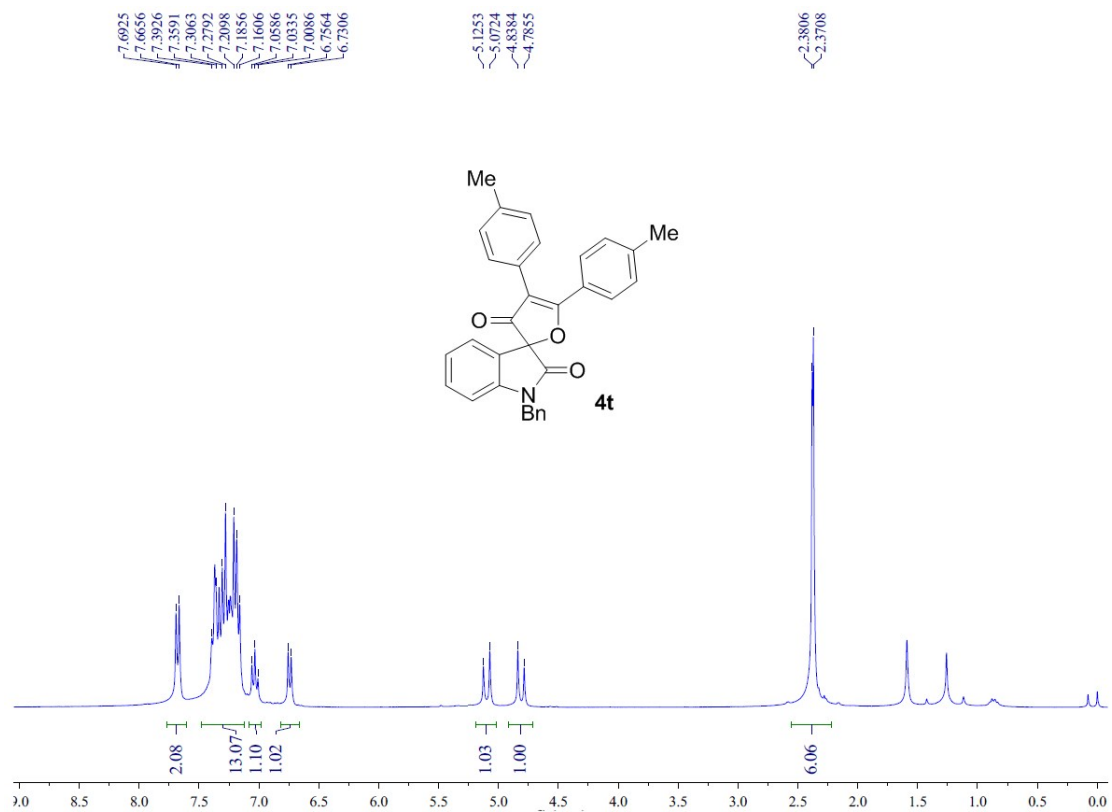






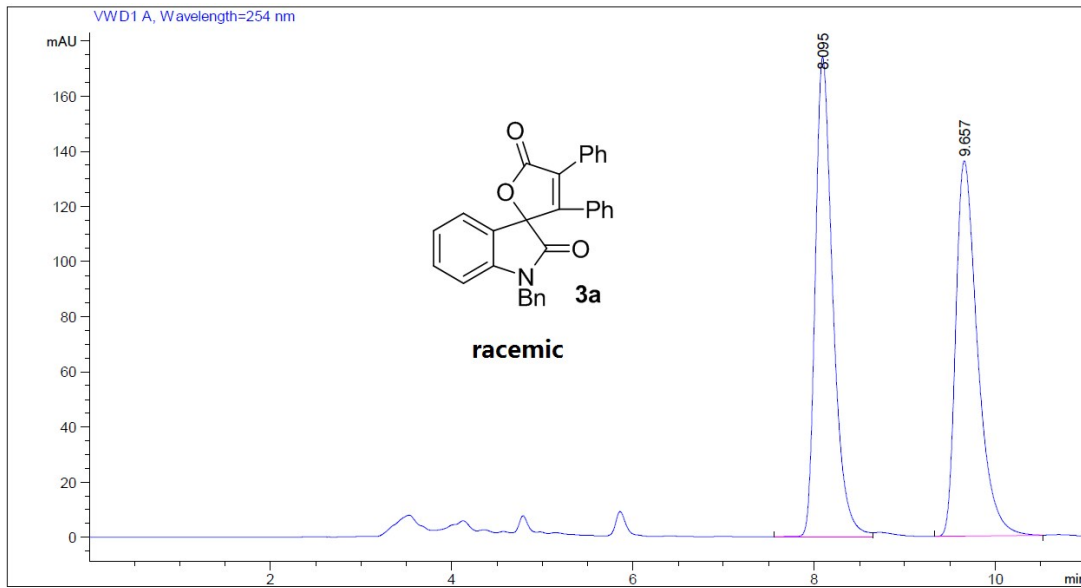




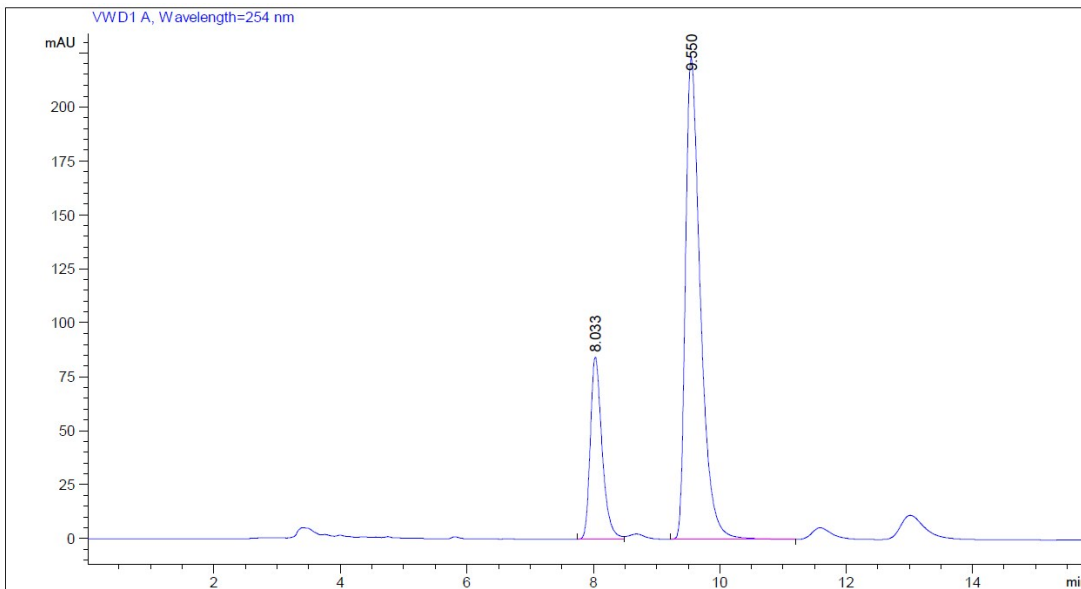


Product 3a

Conditions: *n*-hexane/*iso*-propanol : 70/30, 1.0 mL/min, wavelength = 254 nm



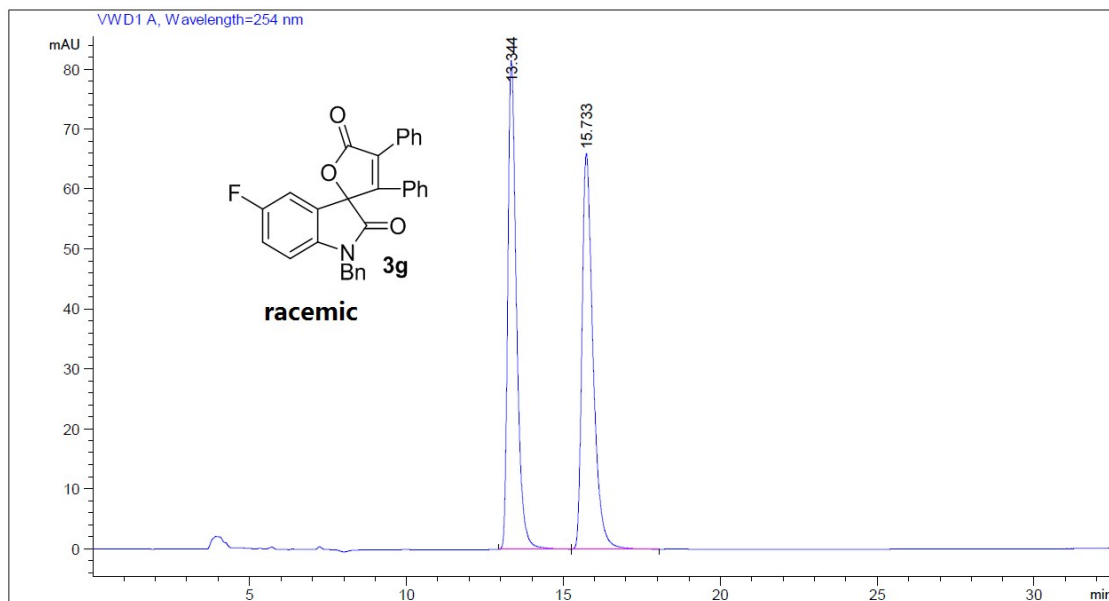
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	8.095	BV	0.2035	2334.52637	174.08165	50.6523
2	9.657	BB	0.2527	2274.39380	136.25620	49.3477



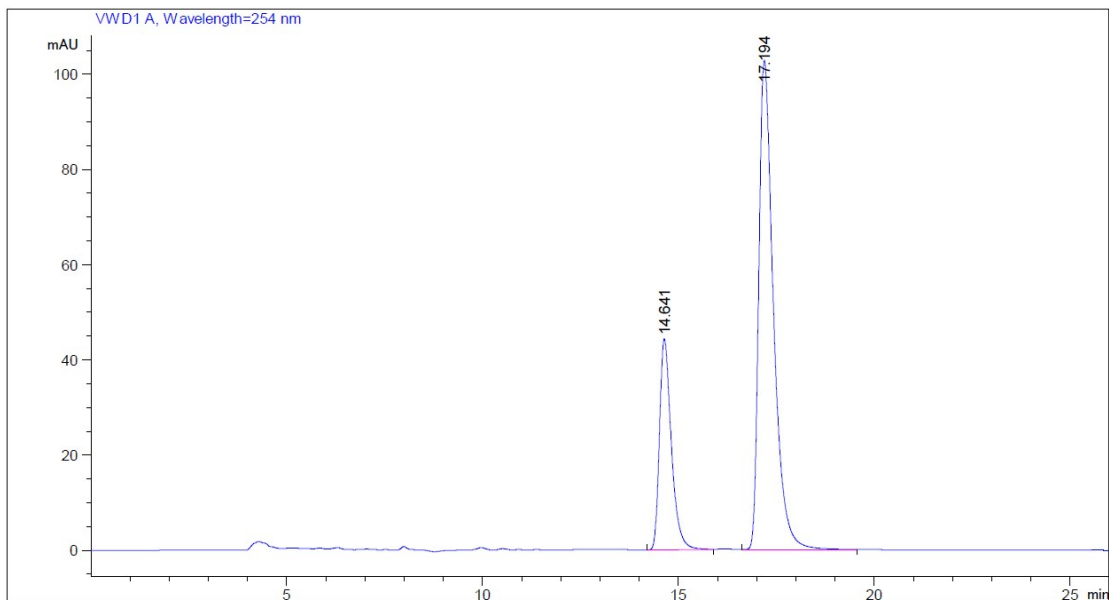
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	8.033	BV	0.1955	1089.04285	84.39812	22.9091
2	9.550	BB	0.2487	3664.71484	223.00858	77.0909

### Product 3g

Conditions: *n*-hexane/*iso*-propanol : 85/15, 1.0 mL/min, wavelength = 254 nm



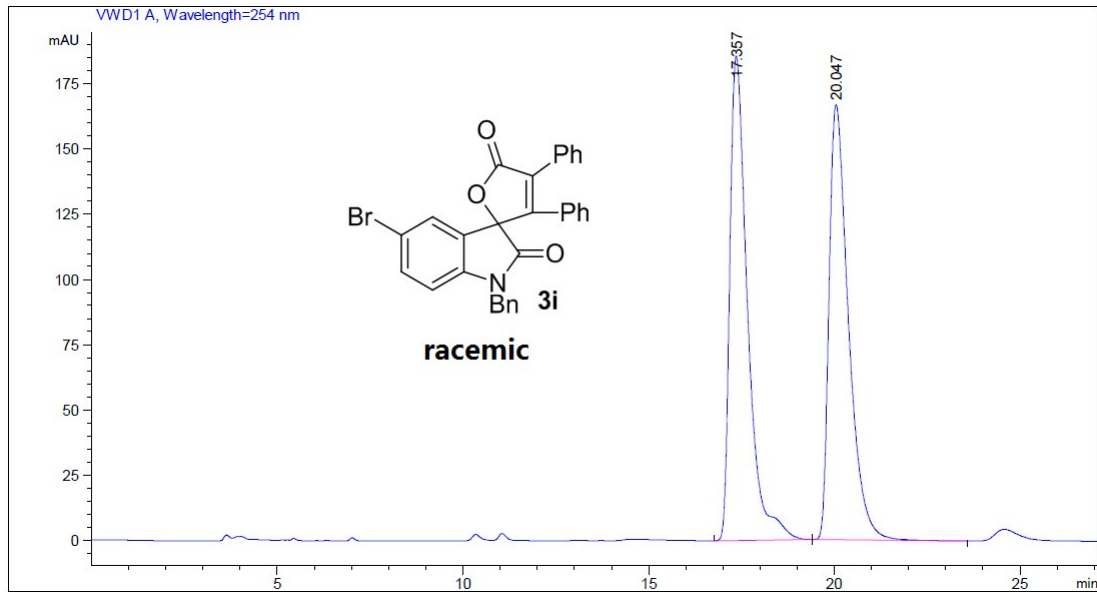
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	13.344	BB	0.2914	1568.17139	81.52502	49.3591
2	15.733	BB	0.3683	1608.89307	66.02481	50.6409



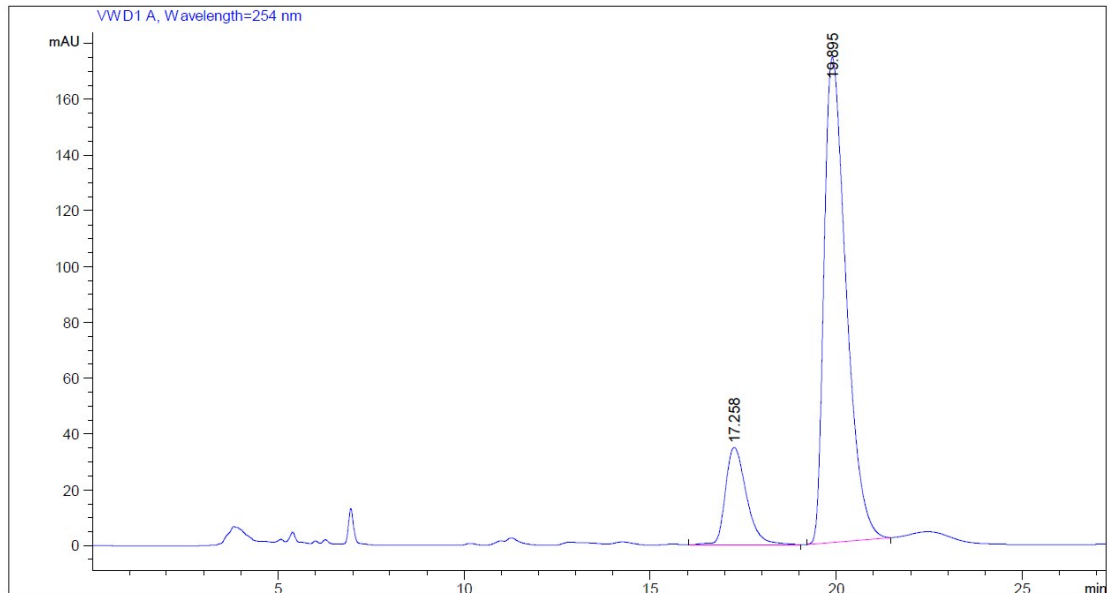
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	14.641	BB	0.3194	932.86615	44.35792	25.9195
2	17.194	BB	0.3907	2666.22974	102.76986	74.0805

Product **3i**

Conditions: *n*-hexane/*iso*-propanol : 90/10, 1.0 mL/min, wavelength = 254 nm



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	17.357	BB	0.4991	6154.05859	185.49564	50.4692
2	20.047	BB	0.5478	6039.62646	166.66092	49.5308

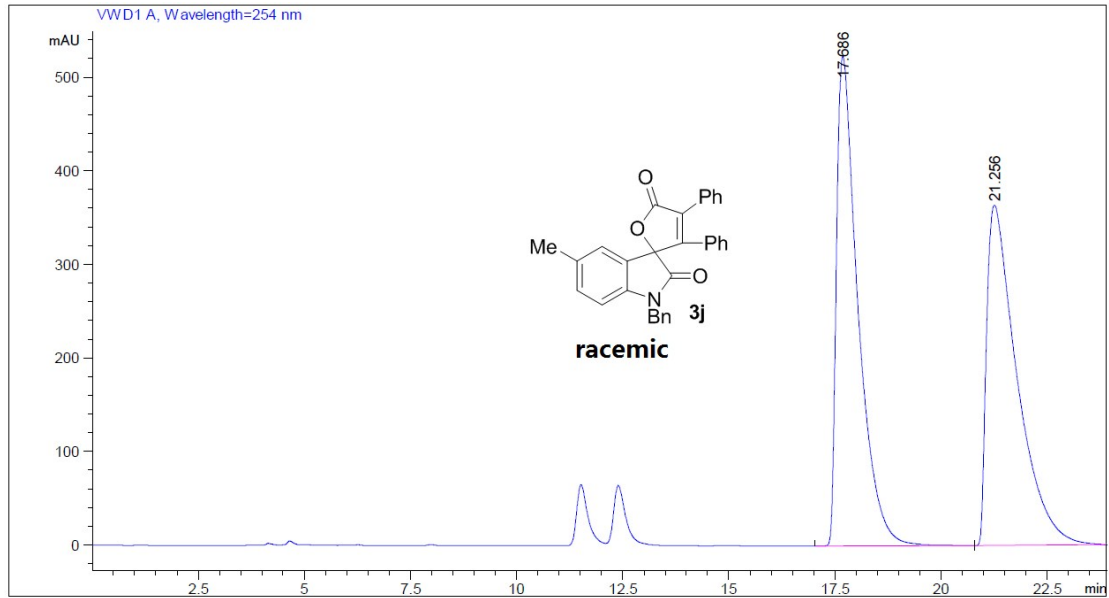


Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	17.258	BB	0.6041	1363.93225	34.89117	16.0114
2	19.895	BB	0.6320	7154.57813	173.88145	83.9886

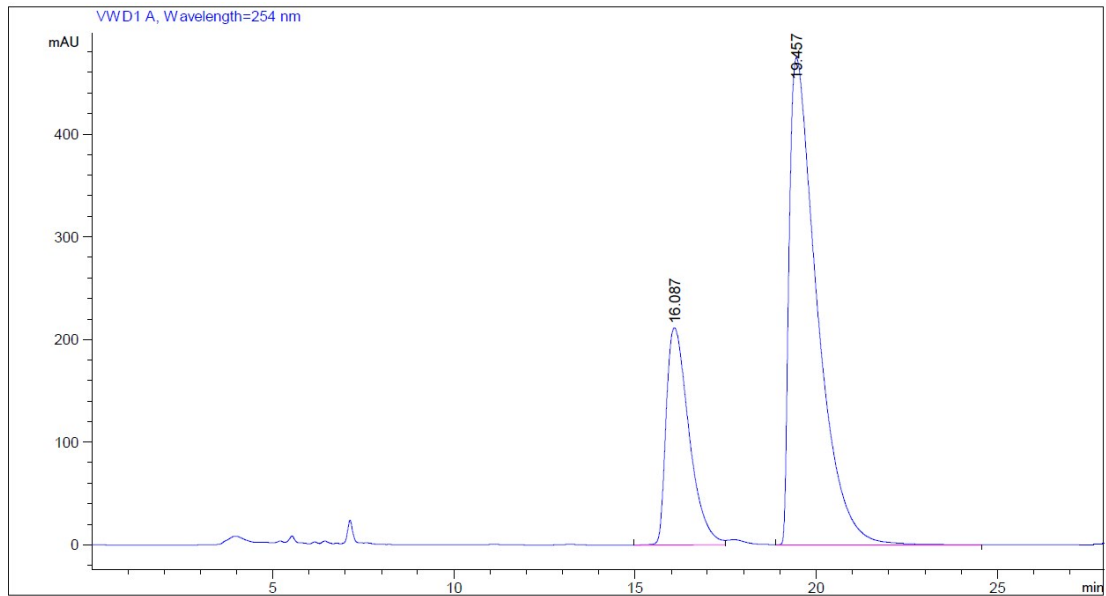


Product **3j**

Conditions: *n*-hexane/*iso*-propanol : 90/10, 1.0 mL/min, wavelength = 254 nm



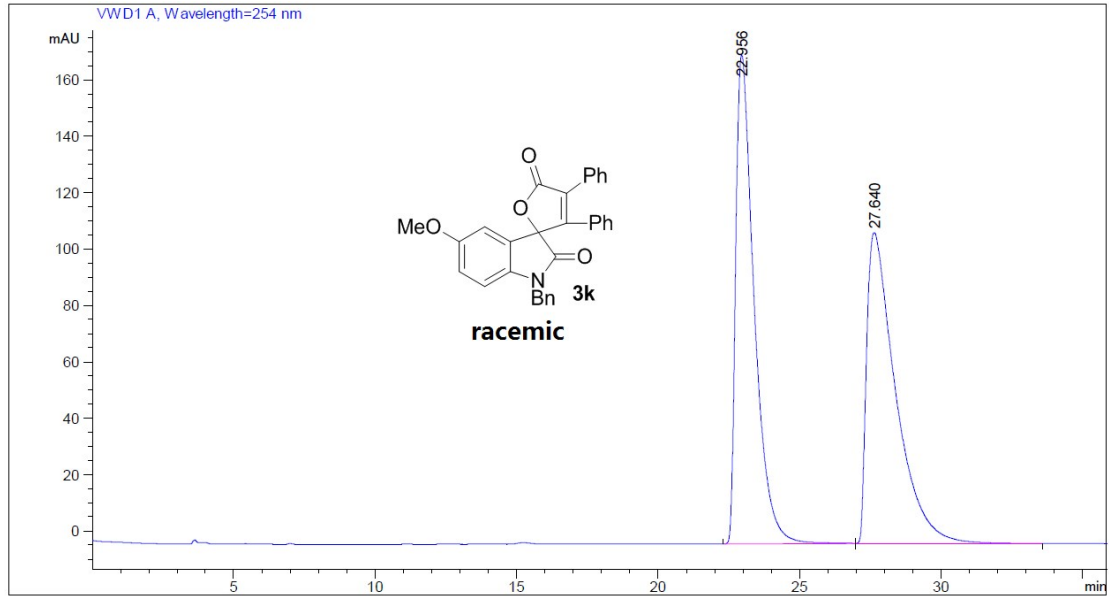
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	17.686	BB	0.5192	1.84022e4	523.33984	50.4575
2	21.256	BBA	0.7336	1.80685e4	363.72095	49.5425



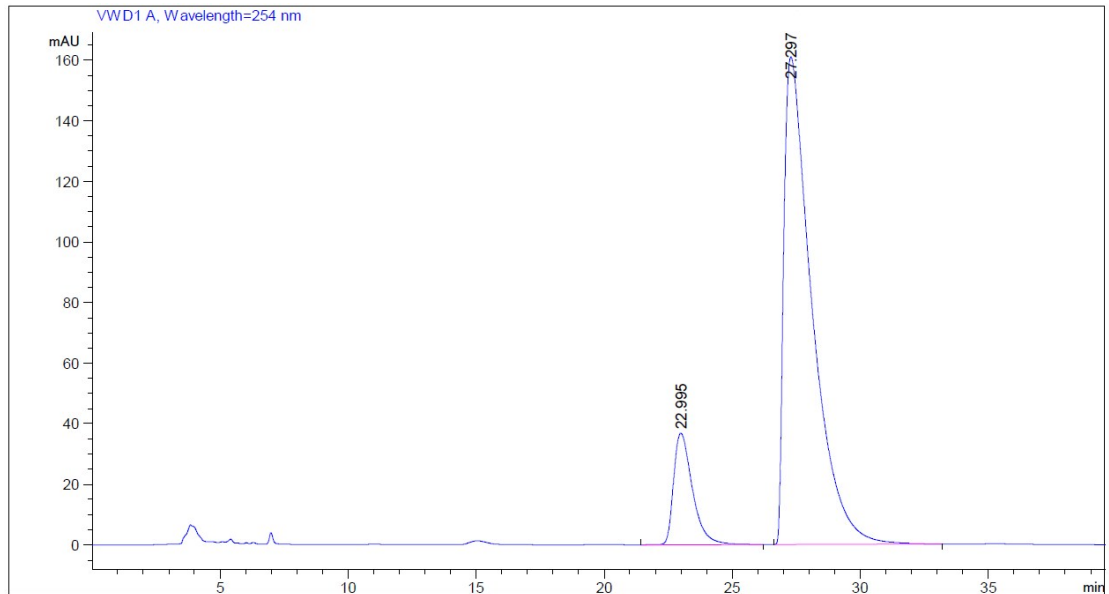
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	16.087	BV	0.6777	9260.46777	211.54900	26.8537
2	19.457	BB	0.7906	2.52244e4	474.18307	73.1463

Product **3k**

Conditions: *n*-hexane/*iso*-propanol : 90/10, 1.0 mL/min, wavelength = 254 nm



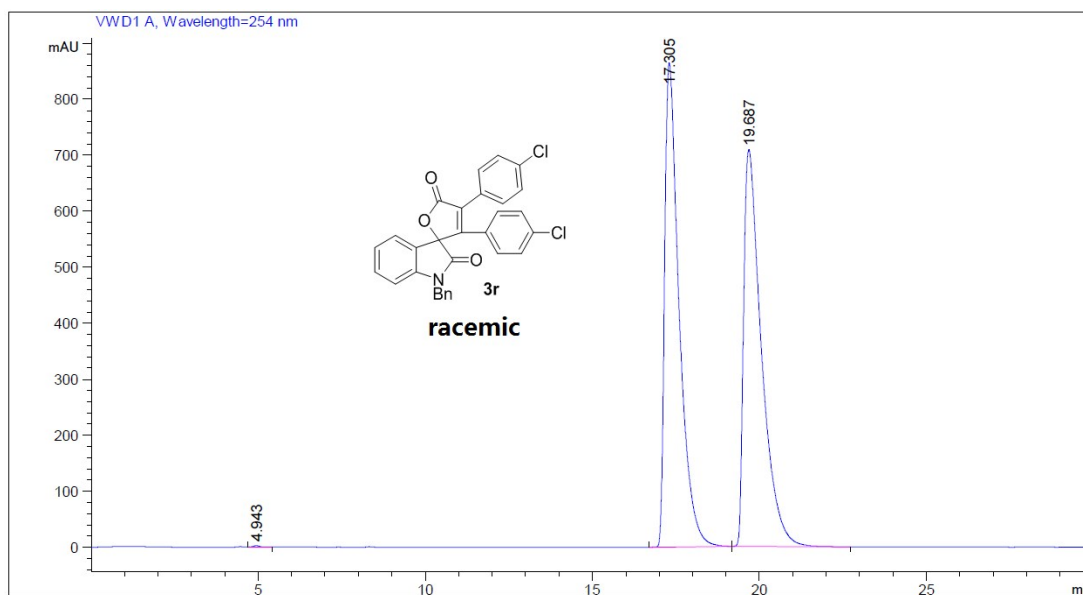
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	22.956	BB	0.6810	7852.05127	173.50180	50.0637
2	27.640	BB	1.0423	7832.08057	110.31128	49.9363



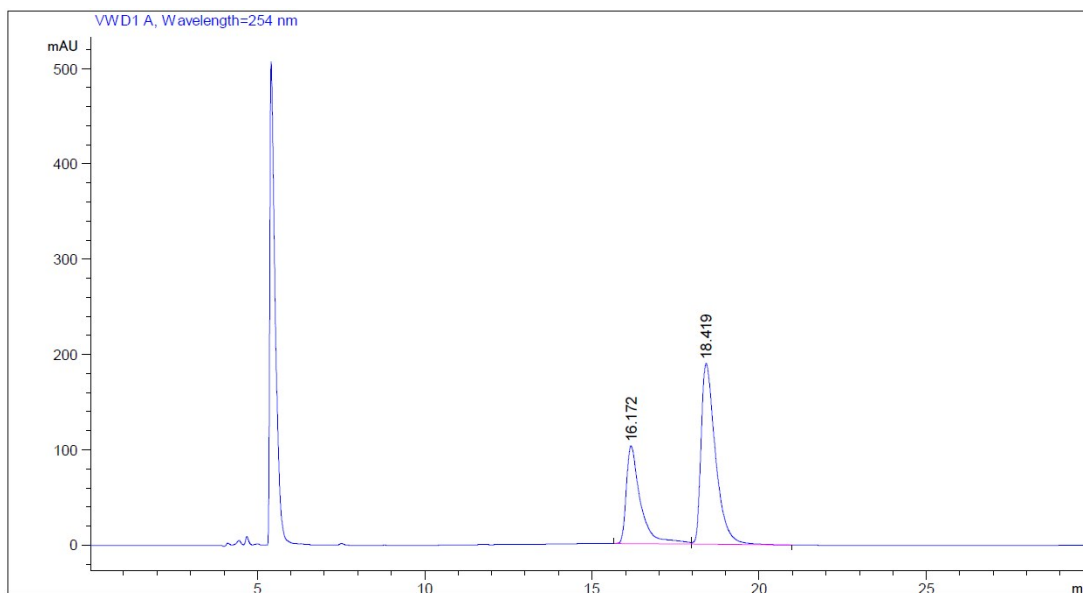
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	22.995	BB	0.7765	1878.58850	36.86554	13.2984
2	27.297	BB	1.1190	1.22478e4	160.91866	86.7016

### Product 3r

Conditions: *n*-hexane/*iso*-propanol : 85/15, 1.0 mL/min, wavelength = 254 nm



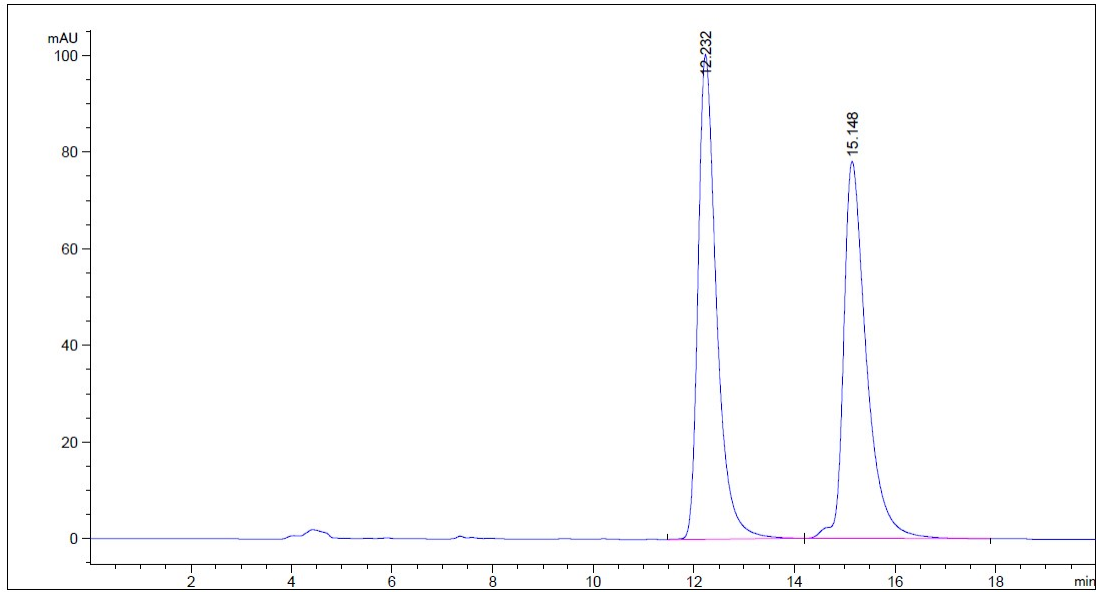
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	4.943	BB	0.1835	31.53531	2.61837	0.0604
2	17.305	BB	0.4424	2.59696e4	864.68646	49.7228
3	19.687	BB	0.5428	2.62276e4	708.61987	50.2168



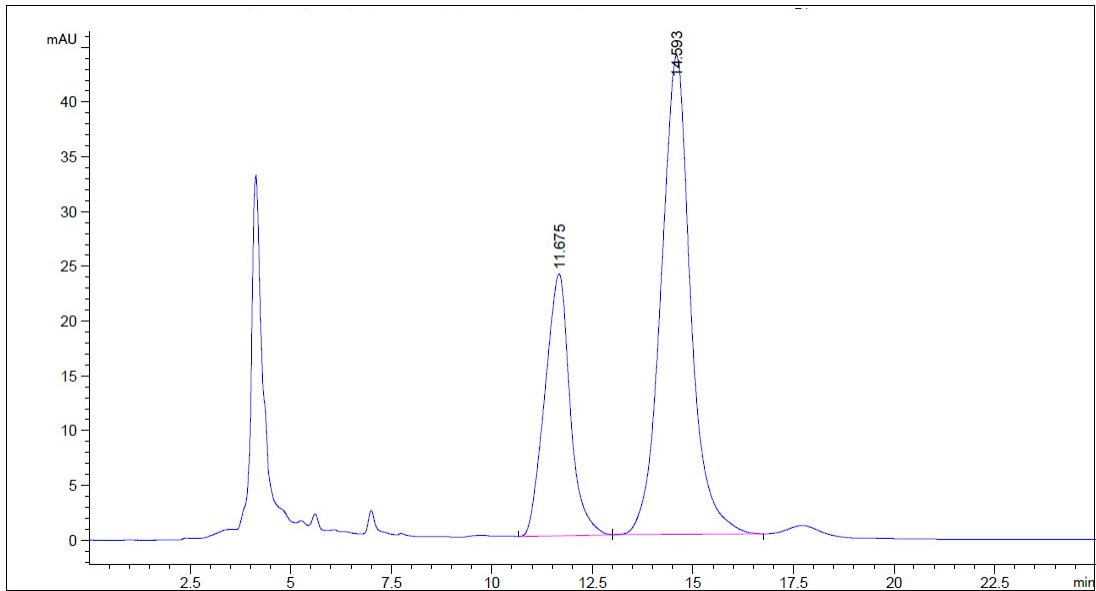
Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	16.172	BV	0.4324	3044.38208	102.53335	34.8232
2	18.419	VB	0.4512	5698.02002	189.81140	65.1768

Product 3t

Conditions: *n*-hexane/*iso*-propanol : 80/20, 1.0 mL/min, wavelength = 254 nm



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	12.232	BB	0.3834	2548.09961	100.28635	51.1046
2	15.148	BB	0.4676	2437.94702	78.00513	48.8954



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAu*S]	Height [mAu]	Area %
1	11.675	BB	0.6625	1035.57715	23.89983	31.7359
2	14.593	BB	0.7684	2227.53711	43.72440	68.2641