

Synthesis of Spiro[indane-1,3-dione-1-pyrrolines] via Copper-catalyzed Heteroannulation of Ketoxime Acetates with 2-Arylideneindane-1,3-diones

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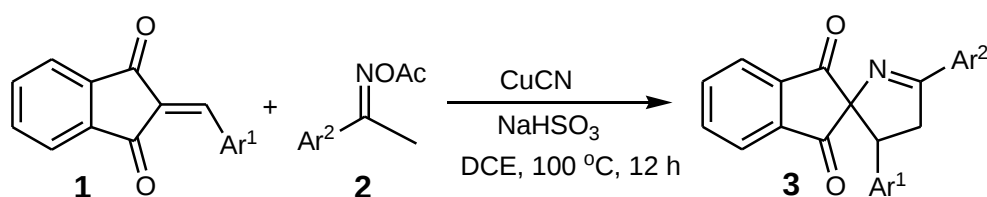
Experimental section

General

All reactions were carried out with dry, freshly distilled solvents in anhydrous conditions. Toluene and THF were distilled from sodium, while dichloromethane was distilled from CaH₂ immediately prior to use. All chemicals were used without further purification as commercially available unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300–400 mesh). NMR (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR) spectra were recorded in CDCl₃ or Acetone with TMS as the internal standard. Chemical shifts are reported in ppm and coupling constants are given in Hz. Data for ¹H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectral (HRMS) analyses were measured using ESI techniques. Melting points were determined in a hanon auto melting point system (MP 450).

A variety of 2-arylidene-1,3-indandiones¹ and ketoxime acetates² were prepared using general procedures reported in the literatures.

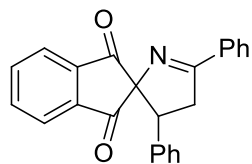
General Procedure for the Reaction



In a sealed tube, 2-arylideneindane-1,3-diones **1** (0.2 mmol), ketoxime acetates **2** (0.26 mmol), CuCN (10 mol %), and NaHSO₃ (0.4 mmol) were mixed in DCE (3.0 mL) and stirred at 100 °C for 12 h. After removal of the solvent, the crude residue was purified by column chromatography (petroleum ether/ethyl acetate 5/1 v/v) on silica gel to give the corresponding product **3**.

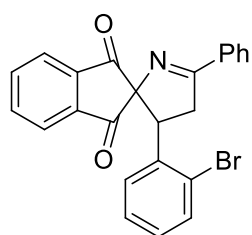
Compounds characterization

3',5'-Diphenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3a)



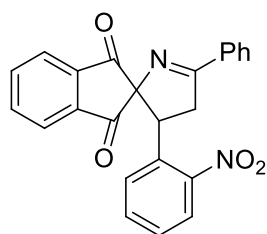
Prepared according to general procedure to afford **3a** (67 mg, 95 % yield) as a yellow solid; m.p. 155-158 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, J = 7.6 Hz, 1H), 7.94-7.92 (m, 2H), 7.81-7.77 (m, 1H), 7.74-7.69 (m, 2H), 7.49-7.42 (m, 3H), 7.13-7.08 (m, 5H), 4.27(dd, J = 11.2, 8.8 Hz, 1H), 3.85(dd, J = 16.4, 11.2 Hz, 1H), 3.61(dd, J = 16.4, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 200.2, 197.7, 179.8, 142.2, 141.9, 136.2, 135.9, 135.6, 133.4, 131.6, 128.6, 128.5, 128.2, 128.1, 127.4, 123.6, 88.0, 51.5, 41.1; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{17}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 374.1151, Found 374.1152.

3'-(2-Bromophenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3b)



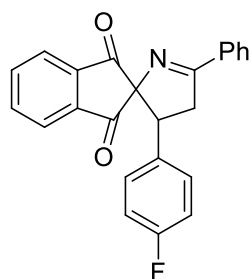
Prepared according to general procedure to afford **3b** (79 mg, 92 % yield) as a yellow solid; m.p. 196-198 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, J = 7.2 Hz, 1H), 7.97-7.95 (m, 2H), 7.83-7.79 (m, 1H), 7.76-7.69 (m, 2H), 7.53-7.38 (m, 4H), 7.31-7.23 (m, 2H), 7.00-6.97 (m, 1H), 4.74(t, J = 8.4 Hz, 1H), 3.80(dd, J = 17.2, 9.6 Hz, 1H), 3.66(dd, J = 17.2, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.1, 197.1, 179.2, 141.9, 141.8, 136.6, 136.1, 136.0, 133.1, 132.7, 131.7, 129.7, 128.8, 128.6, 128.4, 127.6, 125.4, 123.9, 123.4, 88.1, 49.2, 43.4; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{16}\text{BrNNaO}_2$ $[\text{M}+\text{Na}]^+$ 452.0257, Found 452.0259.

3'-(2-Nitrophenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3c)



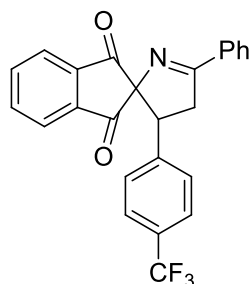
Prepared according to general procedure to afford **3c** (62 mg, 78 % yield) as a yellow solid; m.p. 185-187 °C; ^1H NMR (400 MHz, $\text{Acetone-}d_6$): δ 8.12 (d, J = 7.6 Hz, 1H), 8.07-7.97 (m, 4H), 7.85-7.83 (m, 1H), 7.76-7.67 (m, 2H), 7.64-7.58 (m, 2H), 7.54-7.47 (m, 3H), 4.51 (dd, J = 9.2, 4.8 Hz, 1H), 4.00 (dd, J = 18.0, 9.2 Hz, 1H), 3.85(dd, J = 18.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $\text{Acetone-}d_6$): δ 198.5, 196.2, 177.9, 149.6, 142.2, 141.2, 136.5, 136.4, 134.2, 133.1, 132.8, 131.6, 130.7, 128.7, 128.3, 128.2, 123.8, 123.7, 123.3, 87.9, 44.0, 43.9; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{16}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 419.1002, Found 419.1006.

3'-(4-Fluorophenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3d)



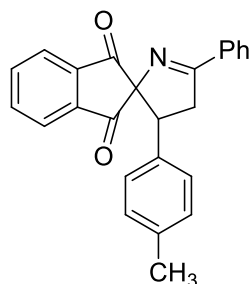
Prepared according to general procedure to afford **3d** (63 mg, 85 % yield) as a yellow solid; m.p. 160-163 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, J = 7.6 Hz, 1H), 7.93-7.91 (m, 2H), 7.84-7.79 (m, 1H), 7.77-7.72 (m, 2H), 7.52-7.42 (m, 3H), 7.13-7.09 (m, 2H), 6.83-6.79 (m, 2H), 4.25(dd, J = 10.8, 9.2 Hz, 1H), 3.79(dd, J = 16.4, 10.8 Hz, 1H), 3.62(dd, J = 16.4, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 200.1, 197.7, 179.6, 163.1($J_{\text{C-F}}$ = 245.1 Hz), 142.2, 141.8, 136.3, 136.1, 133.3, 131.6, 131.4($J_{\text{C-F}}$ = 3.1 Hz), 129.8($J_{\text{C-F}}$ = 8.0 Hz), 128.6, 128.2, 123.6, 115.5($J_{\text{C-F}}$ = 21.3 Hz), 87.9, 50.6, 41.5; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{16}\text{FNNaO}_2$ $[\text{M}+\text{Na}]^+$ 392.1057, Found 392.1061.

5'-Phenyl-3'-(4-(trifluoromethyl)phenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3e)



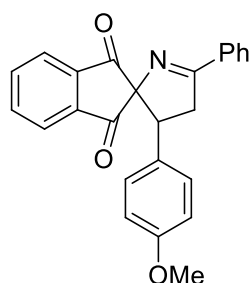
Prepared according to general procedure to afford **3e** (73 mg, 88 % yield) as a yellow solid; m.p. 148-150 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, J = 7.6 Hz, 1H), 7.93-7.91 (m, 2H), 7.85-7.81 (m, 1H), 7.78-7.72 (m, 2H), 7.52-7.48 (m, 1H), 7.45-7.38 (m, 4H), 7.28-7.26 (m, 2H), 4.33(dd, J = 10.8, 9.2 Hz, 1H), 3.87(dd, J = 16.4, 11.2 Hz, 1H), 3.66(dd, J = 16.8, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.6, 197.4, 179.3, 142.1, 141.7, 140.1, 136.5, 136.3, 133.2, 131.8, 129.6(q, J = 32.6 Hz), 128.7, 128.6, 128.2, 125.4(q, J = 3.6 Hz), 125.2, 123.8, 122.5, 87.7, 50.4, 41.3; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{16}\text{F}_3\text{NNaO}_2$ [$\text{M}+\text{Na}$] $^+$ 442.1025, Found 442.1027.

5'-Phenyl-3'-(p-tolyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3f)



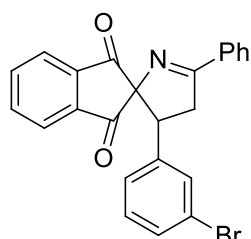
Prepared according to general procedure to afford **3f** (59 mg, 81 % yield) as a yellow solid; m.p. 175-177 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, J = 7.2 Hz, 1H), 7.93-7.92 (m, 2H), 7.79-7.72 (m, 3H), 7.49-7.43 (m, 3H), 7.02-7.00 (m, 2H), 6.93-6.91 (m, 2H), 4.25(t, J = 9.6 Hz, 1H), 3.83(dd, J = 16.4, 11.2 Hz, 1H), 3.59(dd, J = 16.4, 8.8 Hz, 1H), 2.18(s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 200.3, 197.8, 179.8, 142.3, 141.9, 137.0, 136.1, 135.9, 133.5, 132.5, 131.5, 129.1, 128.6, 128.2, 128.0, 123.6, 123.5, 87.9, 51.1, 41.3, 20.9; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{19}\text{NNaO}_2$ [$\text{M}+\text{Na}$] $^+$ 388.1308, Found 388.1310.

3'-(4-Methoxyphenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3g)

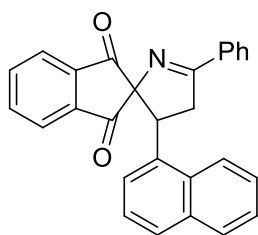


Prepared according to general procedure to afford **3g** (46 mg, 61 % yield) as a yellow solid; m.p. 175-178 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, J = 7.2 Hz, 1H), 7.94-7.92 (m, 2H), 7.82-7.79 (m, 1H), 7.76-7.73 (m, 2H), 7.52-7.42 (m, 3H), 7.06-7.04 (m, 2H), 6.66-6.64 (m, 2H), 4.23(t, J = 9.6 Hz, 1H), 3.79(dd, J = 16.4, 11.6 Hz, 1H), 3.69(s, 3H), 3.59(dd, J = 16.4, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 200.4, 197.9, 179.9, 158.7, 142.3, 141.9, 136.2, 135.9, 133.5, 131.6, 129.2, 128.6, 128.2, 127.4, 123.6, 123.5, 113.8, 87.9, 55.2, 50.9, 41.5; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{19}\text{NNaO}_3$ [$\text{M}+\text{Na}$] $^+$ 404.1257, Found 404.1261.

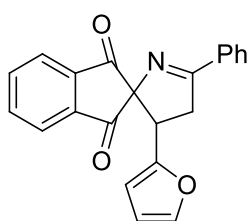
3'-(3-Bromophenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3h)



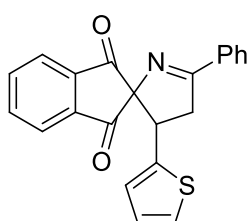
Prepared according to general procedure to afford **3h** (81 mg, 95 % yield) as a yellow solid; m.p. 180-183 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.07 (d, J = 7.6 Hz, 1H), 7.92-7.89 (m, 2H), 7.86-7.82 (m, 1H), 7.79-7.74 (m, 2H), 7.52-7.42 (m, 3H), 7.29-7.22 (m, 2H), 7.08-6.98 (m, 2H), 4.22(dd, J = 10.8, 9.2 Hz, 1H), 3.80(dd, J = 16.4, 11.2 Hz, 1H), 3.61(dd, J = 16.4, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.8, 197.3, 179.3, 142.1, 141.8, 138.2, 136.4, 136.2, 133.2, 131.7, 131.3, 130.6, 129.9, 128.6, 128.2, 126.8, 123.8, 123.7, 122.6, 87.7, 50.5, 41.2; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{16}\text{BrNNaO}_2$ [$\text{M}+\text{Na}$] $^+$ 452.0257, Found 452.0259.

3'-(Naphthalen-1-yl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3i)

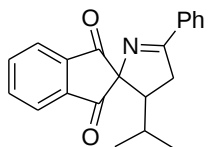
Prepared according to general procedure to afford **3i** (41 mg, 51 % yield) as a yellow solid; m.p. 178-180 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.87-7.81 (m, 2H), 7.67-7.45 (m, 9H), 7.41-7.37 (m, 1H), 7.35-7.25 (m, 2H), 5.15(t, *J* = 9.6 Hz, 1H), 4.00(dd, *J* = 16.8, 10.0 Hz, 1H), 3.75(dd, *J* = 16.8, 8.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 200.6, 197.5, 179.9, 142.0, 141.3, 135.9, 135.6, 133.6, 133.4, 131.9, 131.6, 131.5, 128.8, 128.6, 128.3, 127.9, 126.3, 126.2, 125.5, 125.1, 123.4, 123.2, 122.9, 88.2, 45.9, 42.8; HRMS (ESI): *m/z* calcd for C₂₈H₁₉NNaO₂ [M+Na]⁺ 424.1308, Found 424.1311.

3'-(Furan-2-yl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3j)

Prepared according to general procedure to afford **3j** (38 mg, 56 % yield) as a yellow solid; m.p. 138-141 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 7.2 Hz, 1H), 7.91-7.82 (m, 5H), 7.51-7.47 (m, 1H), 7.44-7.41 (m, 2H), 7.52-7.42 (m, 3H), 7.02 (d, *J* = 1.2 Hz, 1H), 6.17-6.16 (m, 1H), 6.09(d, *J* = 3.2 Hz, 1H), 4.27(t, *J* = 9.6 Hz, 1H), 3.74(dd, *J* = 16.4, 10.4 Hz, 1H), 3.65(dd, *J* = 16.4, 9.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 199.4, 196.7, 178.8, 150.9, 142.1, 141.9, 141.8, 136.2, 136.0, 133.2, 131.6, 128.6, 128.2, 123.9, 123.7, 110.4, 107.2, 86.4, 43.8, 40.4; HRMS (ESI): *m/z* calcd for C₂₂H₁₅NNaO₃ [M+Na]⁺ 364.0944, Found 364.0946.

5'-Phenyl-3'-(thiophen-2-yl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3k)

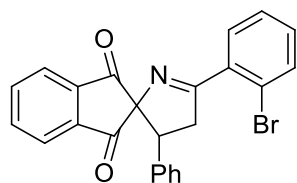
Prepared according to general procedure to afford **3k** (38 mg, 54 % yield) as a yellow solid; m.p. 195-198 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.92-7.89 (m, 2H), 7.87-7.83 (m, 1H), 7.82-7.79 (m, 2H), 7.52-7.42 (m, 3H), 7.01-6.99 (m, 1H), 6.78-6.76 (m, 2H), 4.50(dd, *J* = 11.2, 8.8 Hz, 1H), 3.80(dd, *J* = 16.4, 11.2 Hz, 1H), 3.71(dd, *J* = 16.4, 9.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 199.8, 197.2, 179.3, 142.5, 141.9, 138.7, 136.3, 136.0, 133.2, 131.7, 128.5, 128.2, 126.9, 126.0, 124.3, 123.8, 123.7, 87.3, 46.1, 43.1; HRMS (ESI): *m/z* calcd for C₂₂H₁₅NNaO₂S [M+Na]⁺ 380.0716, Found 380.0718.

3'-(2-methylpropyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3l)

Prepared according to general procedure to afford **3l** (27.5 mg, 22 % yield) as a yellow solid; ¹H NMR (500 Hz, CDCl₃): δ (ppm) 8.10-8.09 (m, 1H), 8.03-8.01 (m, 1H), 7.92-7.87 (m, 2H), 7.81-7.79 (m, 2H), 7.45-7.42 (m, 1H), 7.39-7.36 (m, 1H), 3.44-3.39 (m, 1H), 3.23-3.18 (m, 1H), 2.83-2.77 (m, 1H), 2.06-1.97 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.53 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (125 Hz, CDCl₃): δ (ppm) 200.4, 198.5, 178.8, 141.9, 136.3, 136.2, 133.8, 131.4, 128.5, 128.2, 124.4, 123.9, 85.8, 51.9, 42.5, 29.3, 22.8. HRMS: exact mass calculated for [M+H]⁺ (C₂₁H₂₀NO₂) requires *m/z* 318.1489, found *m/z* 318.1486.

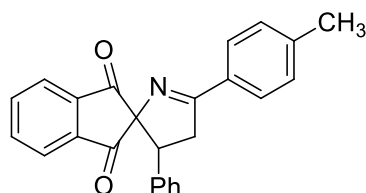
5'-(2-Bromophenyl)-3'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3m)

Prepared according to general procedure to afford **3m** (70 mg, 82 % yield) as a yellow solid; m.p.



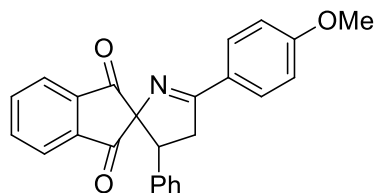
171-173 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, J = 7.6 Hz, 1H), 7.84-7.78 (m, 2H), 7.73-7.71 (m, 2H), 7.47-7.44 (m, 1H), 7.40-7.36 (m, 1H), 7.34-7.29 (m, 1H), 7.14-7.08 (m, 5H), 4.31(dd, J = 11.6, 8.8 Hz, 1H), 4.05(dd, J = 16.8, 11.6 Hz, 1H), 3.68(dd, J = 16.8, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.7, 197.0, 180.7, 142.3, 141.9, 136.2, 135.9, 135.3, 133.8, 133.0, 131.5, 131.1, 130.5, 128.5, 128.2, 127.5, 126.9, 123.6, 123.5, 87.1, 51.9, 44.3; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{16}\text{BrNNaO}_2$ $[\text{M}+\text{Na}]^+$ 452.0257, Found 452.0259.

3'-Phenyl-5'-(p-tolyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3n)



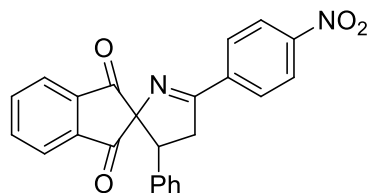
Prepared according to general procedure to afford **3n** (62 mg, 85 % yield) as a yellow solid; m.p. 170-172 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, J = 7.2 Hz, 1H), 7.83-7.77 (m, 3H), 7.74-7.68 (m, 2H), 7.26-7.23 (m, 2H), 7.12-7.07 (m, 5H), 4.25(dd, J = 11.2, 9.2 Hz, 1H), 3.83(dd, J = 16.4, 11.2 Hz, 1H), 3.59(dd, J = 16.4, 8.8 Hz, 1H), 2.41(s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 200.4, 197.8, 179.7, 142.2, 142.0, 141.9, 136.1, 135.9, 135.7, 130.8, 129.3, 128.4, 128.2, 128.1, 127.4, 123.6, 87.9, 51.5, 41.1, 21.6; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{19}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 388.1308, Found 388.1311.

5'-(4-Methoxyphenyl)-3'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3o)



Prepared according to general procedure to afford **3o** (65 mg, 86 % yield) as a yellow solid; m.p. 178-180 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, J = 7.6 Hz, 1H), 7.89-7.87 (m, 2H), 7.81-7.77 (m, 1H), 7.73-7.68 (m, 2H), 7.12-7.07 (m, 5H), 6.95-6.93 (m, 2H), 4.24 (dd, J = 11.2, 8.8 Hz, 1H), 3.86 (s, 3H), 4.05(dd, J = 16.4, 11.2 Hz, 1H), 3.58(dd, J = 16.4, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 200.5, 198.0, 178.9, 162.3, 142.2, 141.9, 136.1, 135.9, 135.8, 130.0, 128.4, 128.1, 127.4, 126.3, 123.5, 113.9, 87.9, 55.4, 51.6, 41.0; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{19}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 404.1257, Found 404.1259.

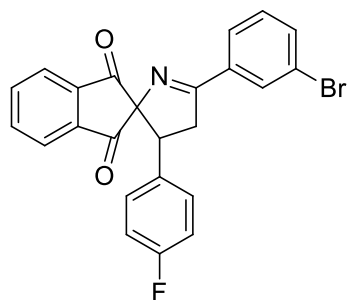
5'-(4-Nitrophenyl)-3'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3p)



Prepared according to general procedure to afford **3p** (68 mg, 86 % yield) as a yellow solid; m.p. 180-182 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.37-8.29 (m, 2H), 8.12-8.06 (m, 3H), 7.86-7.82 (m, 1H), 7.78-7.68 (m, 2H), 7.27-7.12 (m, 5H), 4.32 (t, J = 9.6 Hz, 1H), 3.88 (dd, J = 16.4, 11.2 Hz, 1H), 3.62 (dd, J = 16.4, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.4, 196.8, 177.9, 149.5, 142.2, 141.8, 138.9, 136.4, 136.2, 134.9, 129.2, 128.6, 128.1, 127.7, 123.8, 123.7, 88.3, 51.6, 41.1; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{16}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 419.1002, Found 419.1006.

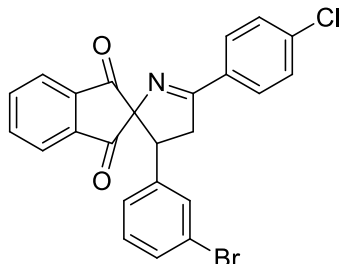
5'-(3-Bromophenyl)-3'-(4-fluorophenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3q)

Prepared according to general procedure to afford **3q** (83 mg, 93 % yield) as a yellow solid; m.p. 155-160 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.09-8.04 (m, 2H), 7.85-7.78 (m, 2H), 7.76-7.72 (m, 2H), 7.63-7.61 (m, 1H), 7.34-7.27 (m, 1H), 7.11-7.08 (m, 2H), 6.83-6.79 (m, 2H), 4.27-4.22(m,



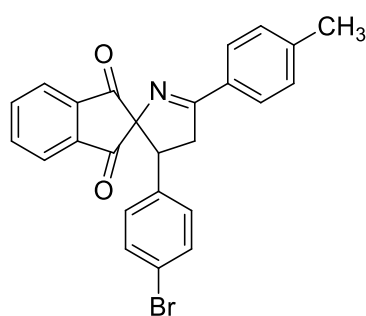
1H), 3.76(dd, $J = 16.4, 11.2$ Hz, 1H), 3.58(dd, $J = 16.4, 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.7, 197.3, 178.3, 163.2($J_{\text{C-F}} = 244.7$ Hz), 142.2, 141.8, 136.4, 136.2, 135.2, 134.5, 131.1($J_{\text{C-F}} = 3.0$ Hz), 130.1, 129.7($J_{\text{C-F}} = 8.0$ Hz), 126.8, 123.7, 122.9, 115.5($J_{\text{C-F}} = 21.3$ Hz), 87.8, 50.6, 41.4; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{15}\text{BrFNNaO}_2$ [$\text{M}+\text{Na}$] $^+$ 470.0162, Found 470.0166.

3'-(3-Bromophenyl)-5'-(4-chlorophenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3r)



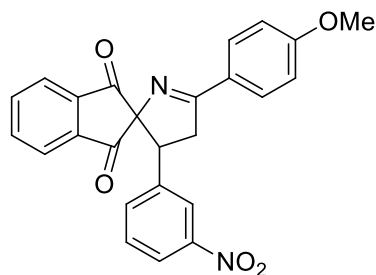
Prepared according to general procedure to afford **3r** (77 mg, 84 % yield) as a yellow solid; m.p. 193-195 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.07 (d, $J = 7.6$ Hz, 1H), 7.85-7.83 (m, 3H), 7.79-7.74 (m, 2H), 7.42-7.39 (m, 2H), 7.27-7.22 (m, 2H), 7.06-6.97 (m, 2H), 4.22(dd, $J = 10.8, 9.2$ Hz, 1H), 3.77(dd, $J = 16.8, 10.8$ Hz, 1H), 3.57(dd, $J = 16.8, 9.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.6, 197.1, 178.2, 142.1, 141.7, 137.9, 137.8, 136.5, 136.3, 131.7, 131.3, 130.7, 130.0, 129.5, 128.9, 126.8, 123.8, 123.7, 122.6, 87.8, 50.6, 41.1; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{15}\text{BrClNNaO}_2$ [$\text{M}+\text{Na}$] $^+$ 485.9867, Found 485.9869.

3'-(4-Bromophenyl)-5'-(p-tolyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3s)



Prepared according to general procedure to afford **3s** (77 mg, 87 % yield) as a yellow solid; m.p. 195-198 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.05-8.03 (m, 1H), 7.80-7.75 (m, 5H), 7.24-7.11 (m, 4H), 7.02-7.01 (m, 2H), 4.21-4.19 (m, 1H), 3.81-3.74 (m, 1H), 3.62-3.57(m, 1H), 2.40(s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 200.1, 197.7, 179.3, 142.2, 142.1, 141.8, 136.4, 136.2, 134.9, 131.6, 130.6, 129.9, 129.3, 128.2, 123.8, 123.7, 121.3, 87.6, 50.4, 41.3, 21.6; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{18}\text{BrNNaO}_2$ [$\text{M}+\text{Na}$] $^+$ 466.0413, Found 466.0416.

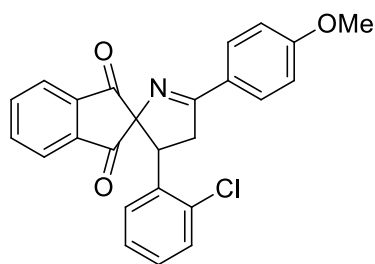
5'-(4-Methoxyphenyl)-3'-(3-nitrophenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3t)



Prepared according to general procedure to afford **3t** (71 mg, 84 % yield) as a yellow solid; m.p. 185-188 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.09 (d, $J = 8.0$ Hz, 1H), 8.02-7.97 (m, 2H), 7.88-7.84 (m, 3H), 7.80-7.73 (m, 2H), 7.49-7.47 (m, 1H), 7.35-7.31 (m, 1H), 6.95 (d, $J = 8.4$ Hz, 2H), 4.36 (t, $J = 9.6$ Hz, 1H), 3.89-3.83 (m, 1H), 3.88 (s, 3H), 3.69 (dd, $J = 16.4, 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.6, 197.5, 178.1, 162.5, 148.1, 142.0, 141.7, 138.6, 136.5, 136.4, 134.3, 130.1, 129.4, 125.8, 123.9, 123.8, 123.2, 122.5, 113.9, 87.4, 55.5, 49.9, 41.4; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{18}\text{N}_2\text{NaO}_5$ [$\text{M}+\text{Na}$] $^+$ 449.1108, Found 449.1111.

3'-(2-Chlorophenyl)-5'-(4-methoxyphenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3u)

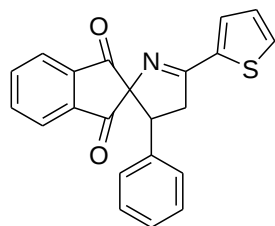
Prepared according to general procedure to afford **3u** (76 mg, 92 % yield) as a yellow solid; m.p. 169-171 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, $J = 7.2$ Hz, 1H), 7.92-7.90 (m, 2H), 7.83-7.79



(m, 1H), 7.75-7.68 (m, 2H), 7.44-7.42 (m, 1H), 7.23-7.19 (m, 1H), 7.09-7.04 (m, 2H), 6.97-6.95 (m, 2H), 4.73 (t, $J = 8.8$ Hz, 1H), 3.87 (s, 3H), 3.72-3.69 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.5, 197.6, 178.4, 162.4, 141.9, 141.6, 136.0, 135.9, 134.6, 134.5, 130.1, 129.4, 129.3, 128.5, 126.9, 125.9, 123.8, 123.3, 113.9, 87.8, 55.4, 46.7, 42.5; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{18}\text{ClNNaO}_3$ $[\text{M}+\text{Na}]^+$ 438.0867, Found

438.0872.

3'-phenyl-5'-(thiophen-2-yl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3v)



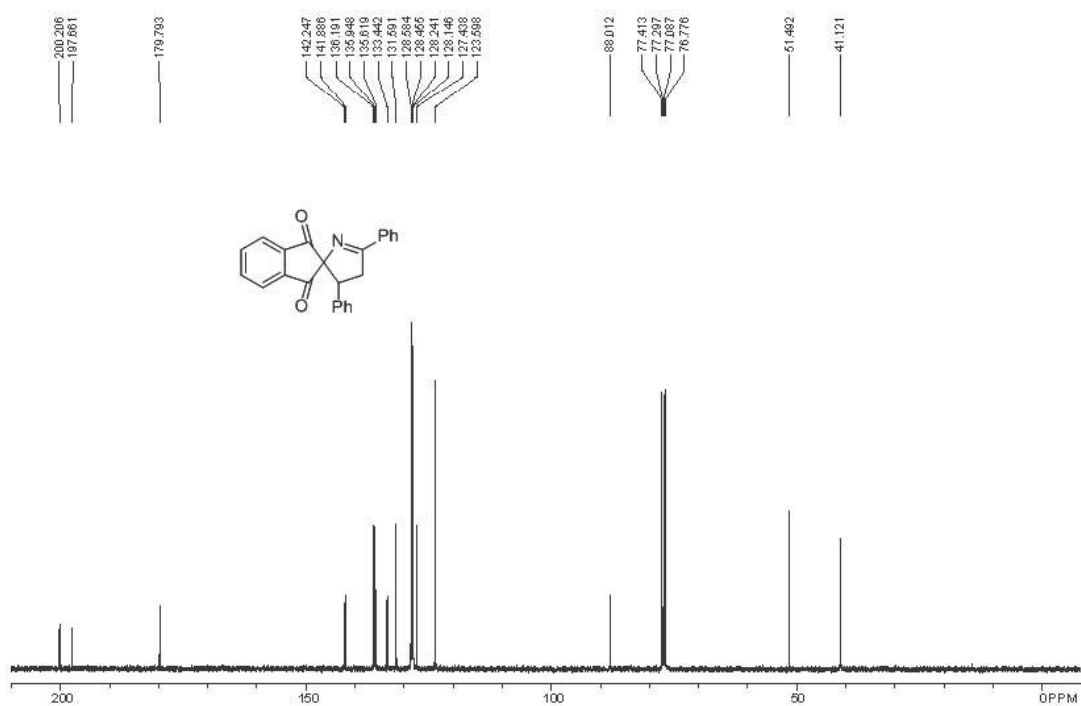
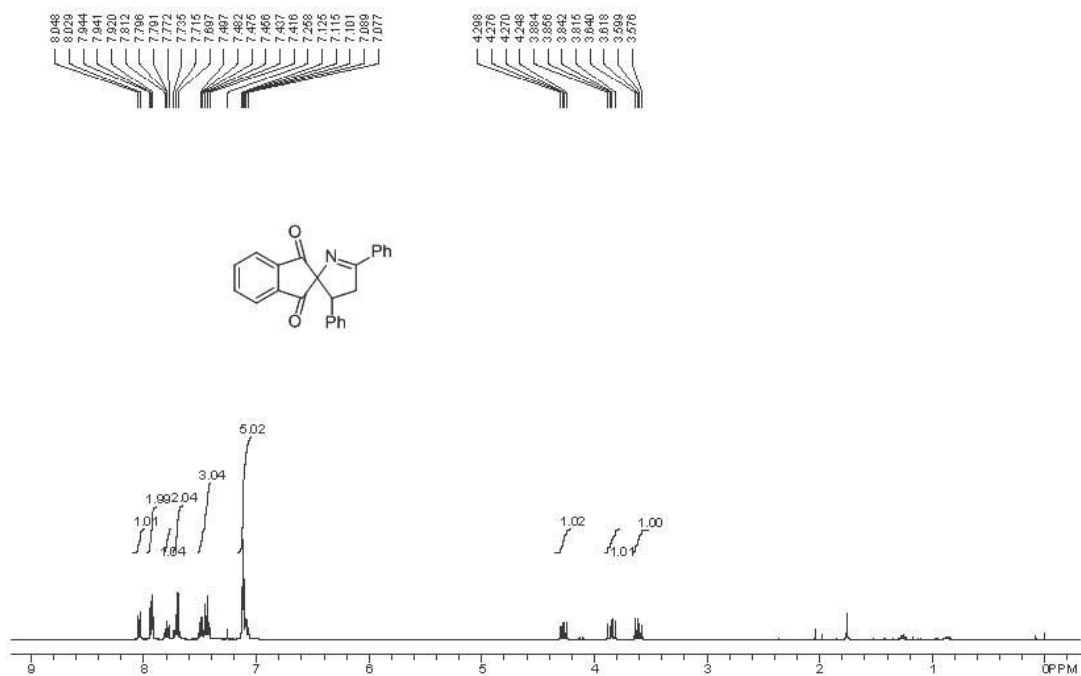
Prepared according to general procedure to afford **3v** (55.8 mg, 77 % yield); ^1H NMR (500 MHz, CDCl_3): δ 8.01 (d, $J = 7.5$ Hz, 1H), 7.78 (t, $J = 7.3$ Hz, 1H), 7.72-7.67 (m, 2H), 7.53-7.51 (m, 2H), 7.13-7.07 (m, 6H), 4.30-4.26 (m, 1H), 3.88-3.83 (m, 1H), 3.59-3.54 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3): δ 200.1, 197.8, 174.0, 142.4, 141.9, 138.1, 136.3, 136.1, 135.4, 131.2, 131.0, 128.6, 128.2, 127.8, 127.6, 123.7, 87.7, 51.9, 41.7; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{16}\text{NSO}_2$ $[\text{M}+\text{H}]^+$ 358.0896, Found 358.0889.

References

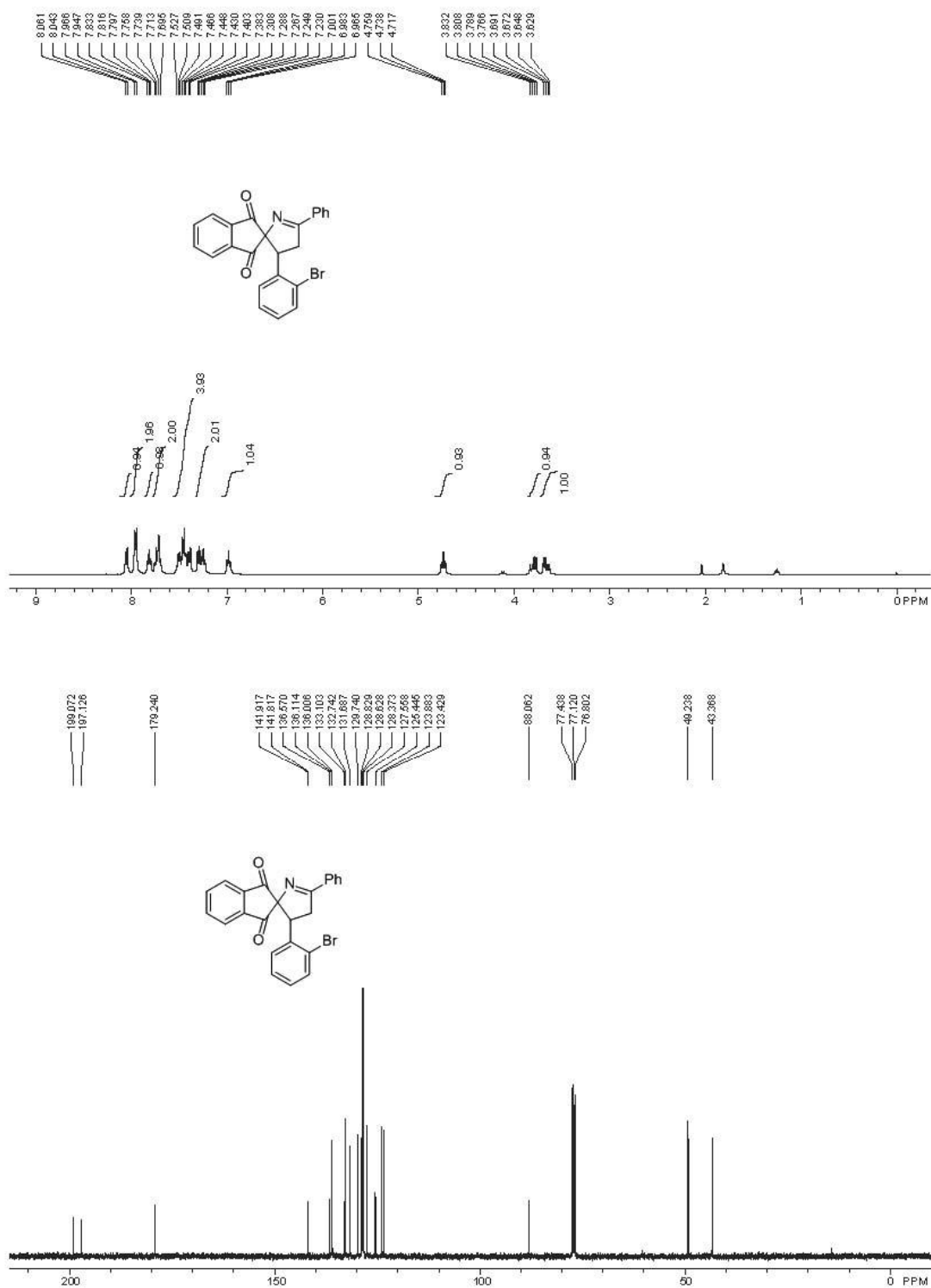
1. E. Li, Y. Huang, L. Liang, P. Xie, *Org. Lett.*, **2013**, *15*, 3138.
2. M. Zhao, R. Hui, Z. Ren, Y. Wang, Z. Guan, *Org. Lett.*, **2014**, *16*, 3082.

NMR Spectra of compounds 3a-t

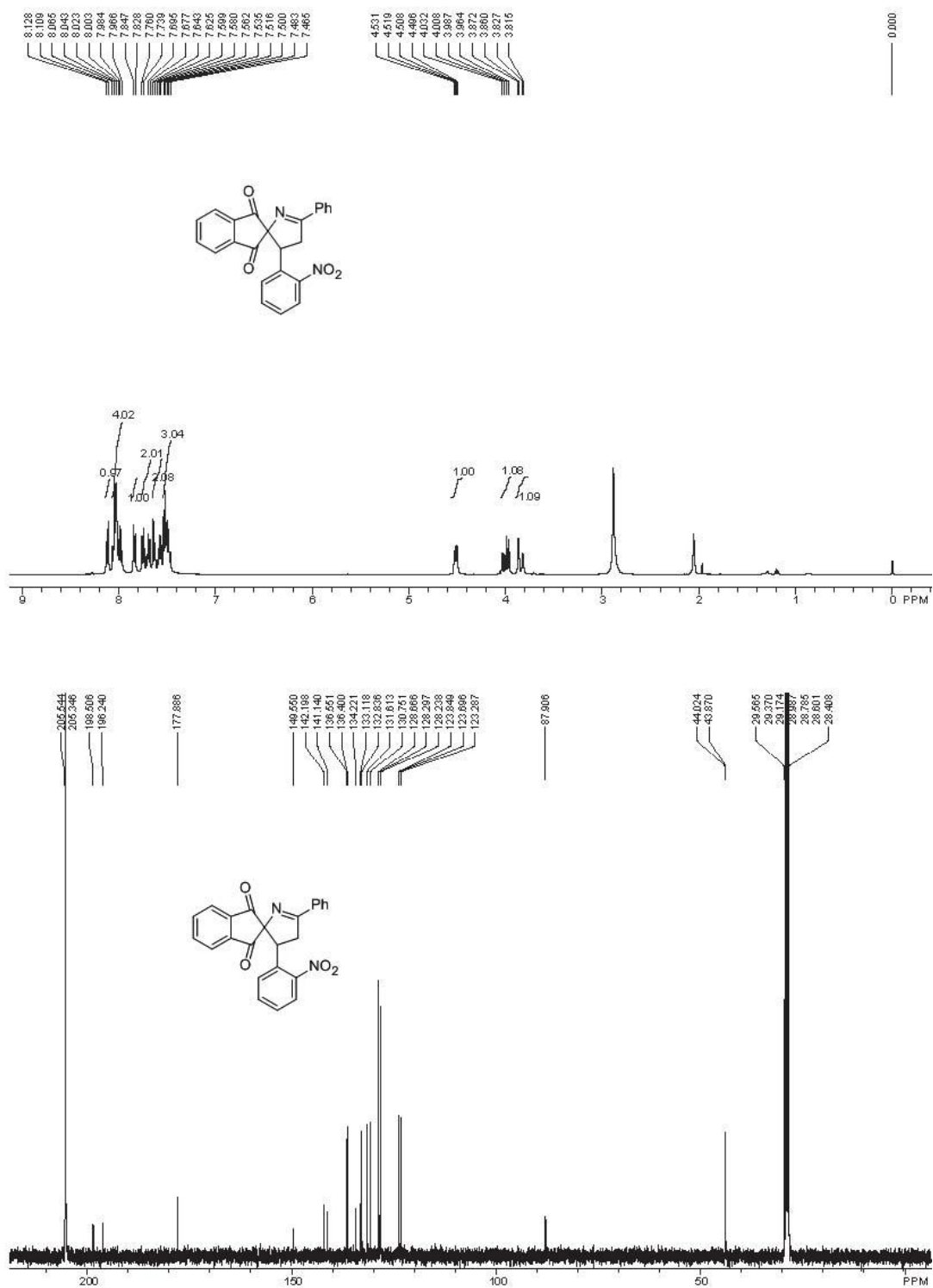
3',5'-Diphenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3a)



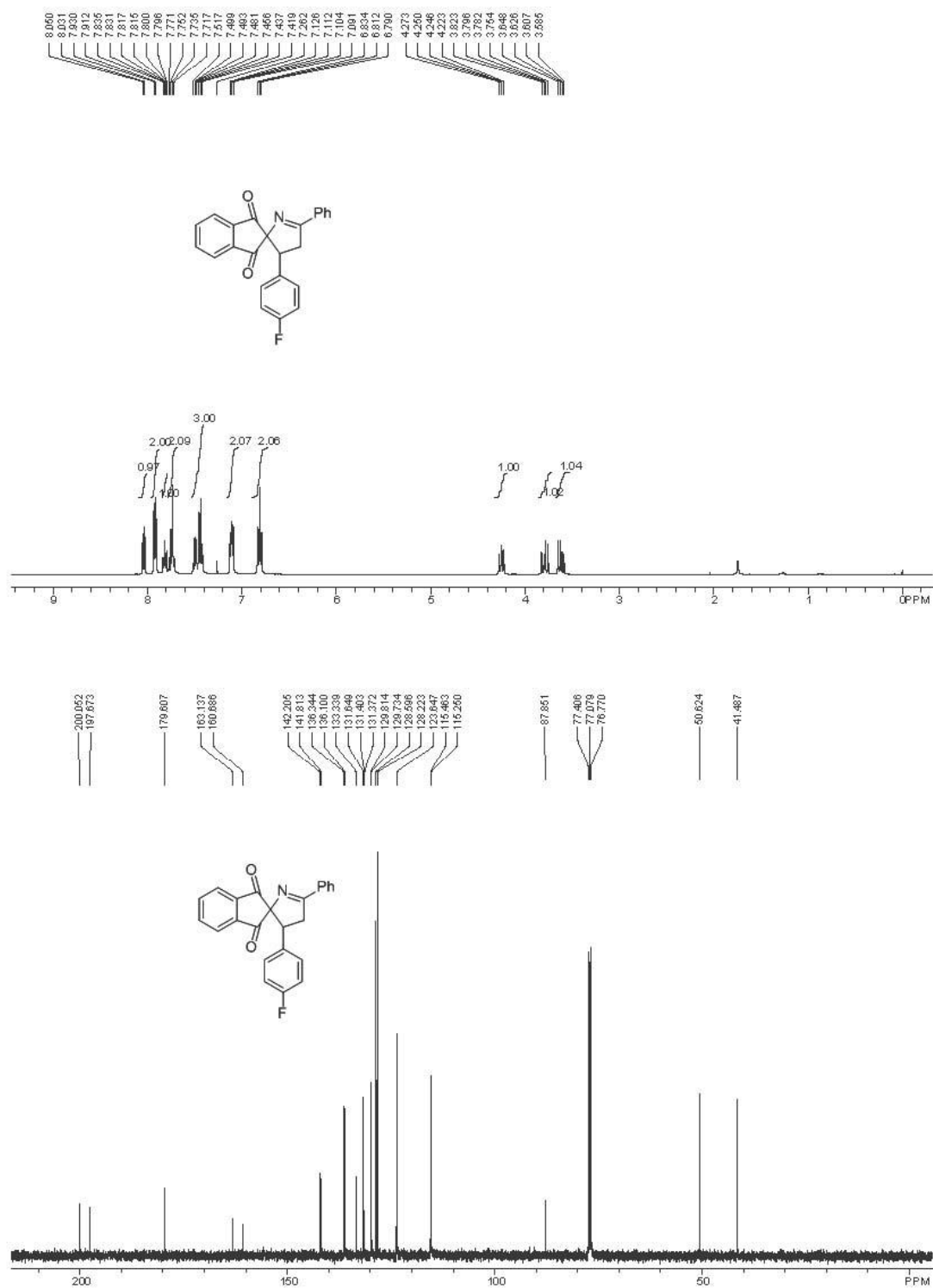
3'-(2-Bromophenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3b)



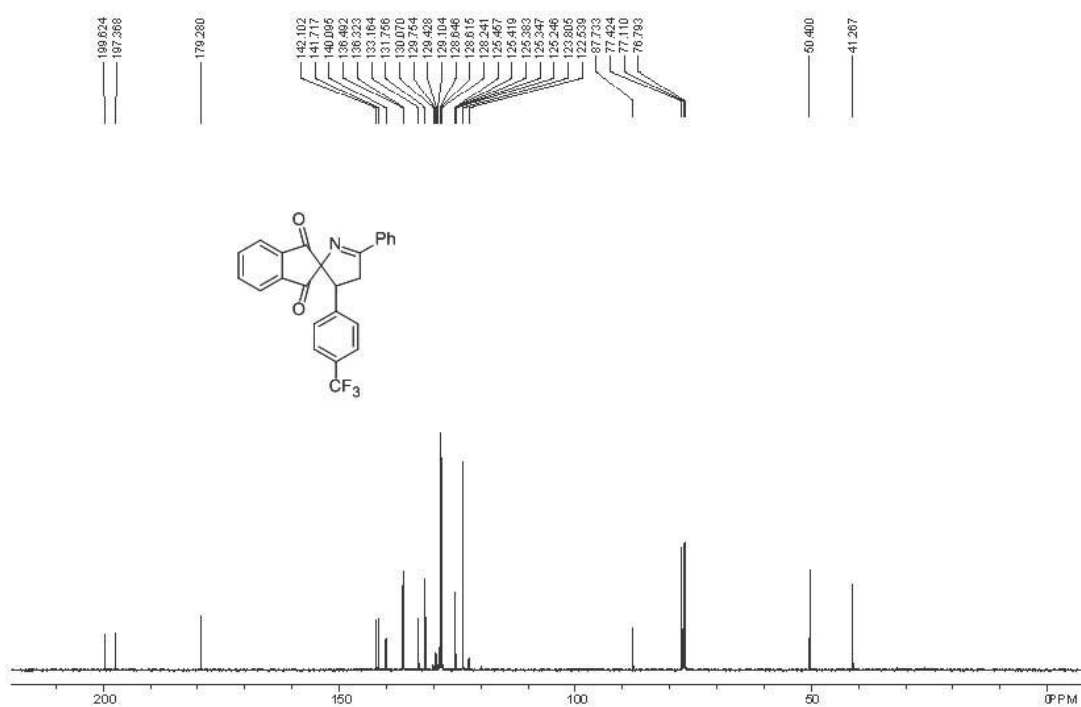
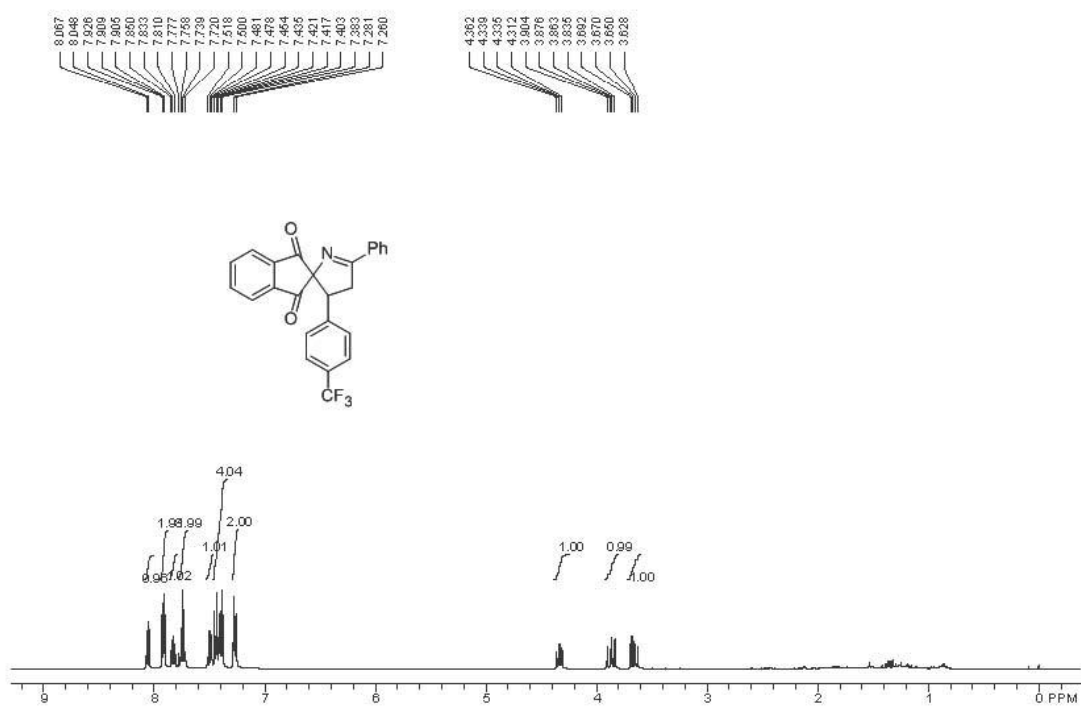
3'-(2-Nitrophenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3c)



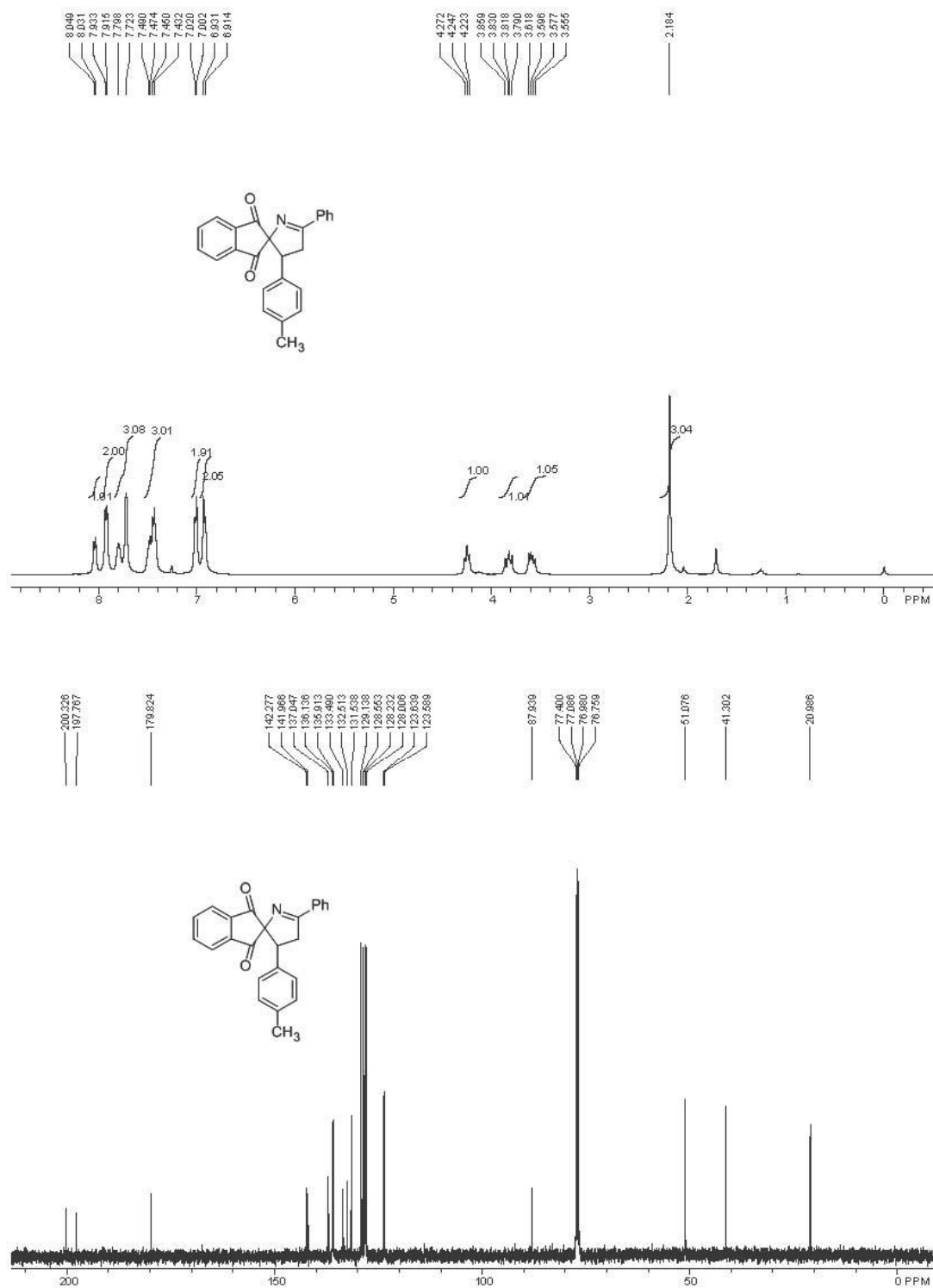
3'-(4-Fluorophenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3d)



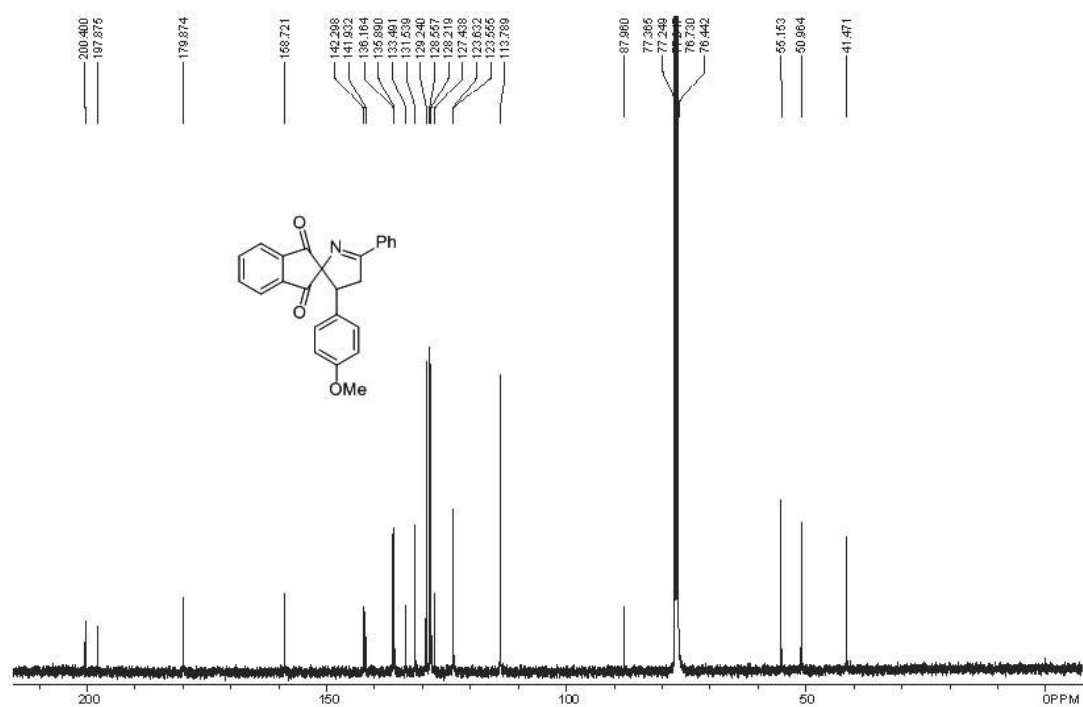
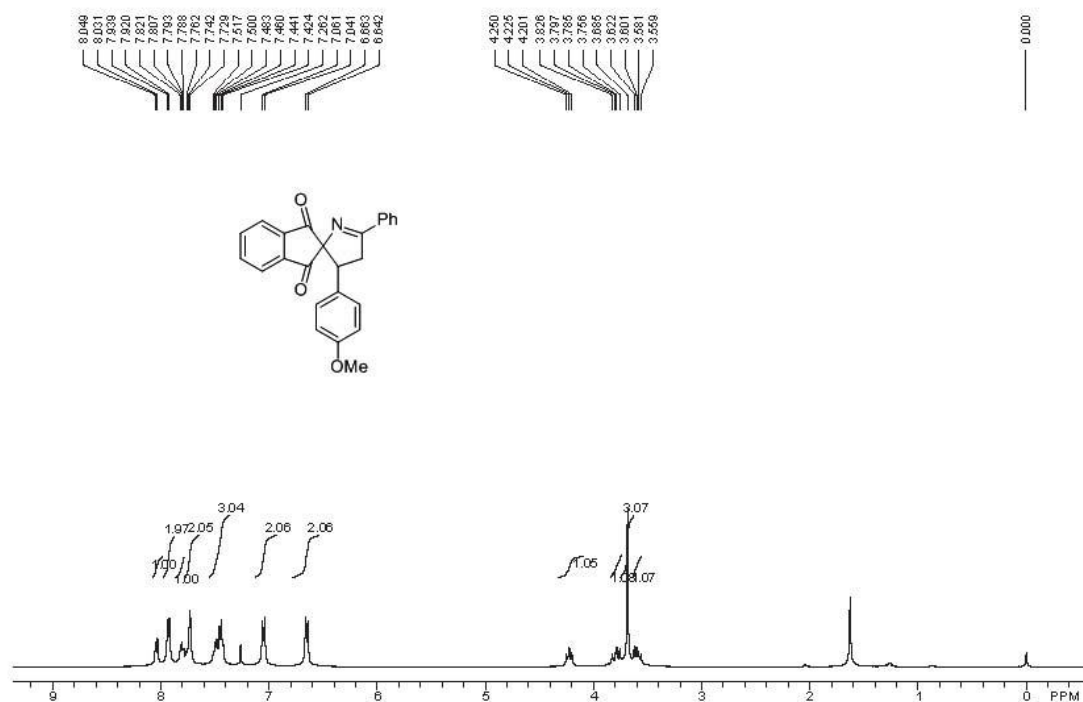
5'-Phenyl-3'-(4-(trifluoromethyl)phenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3e)



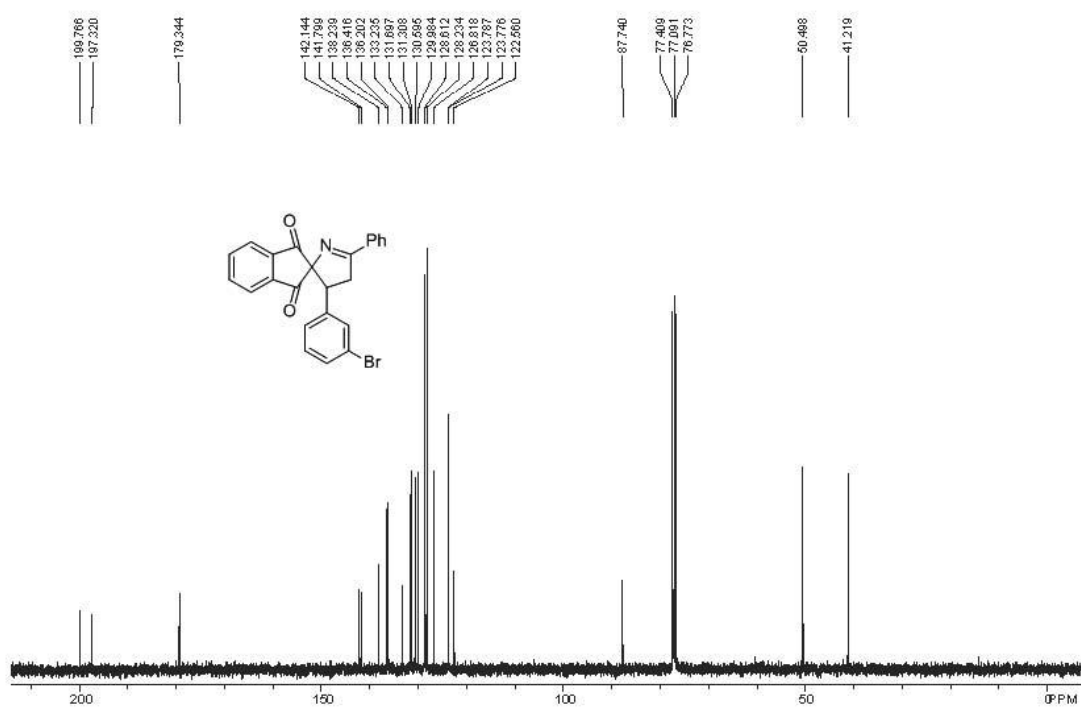
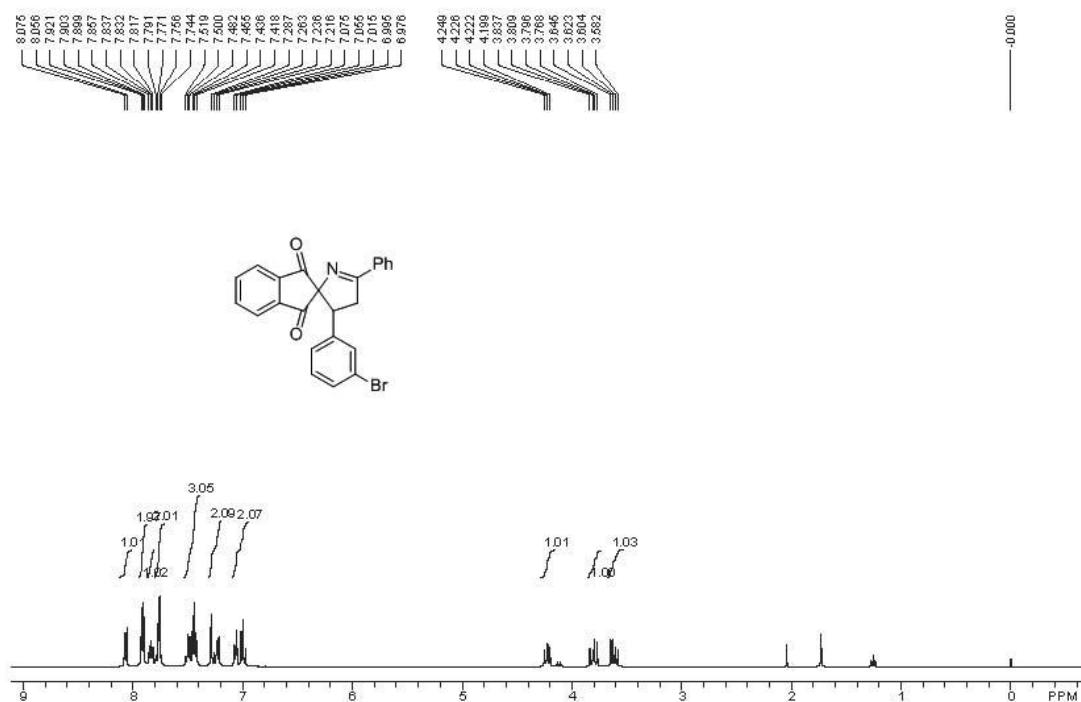
5'-Phenyl-3'-(p-tolyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3f)



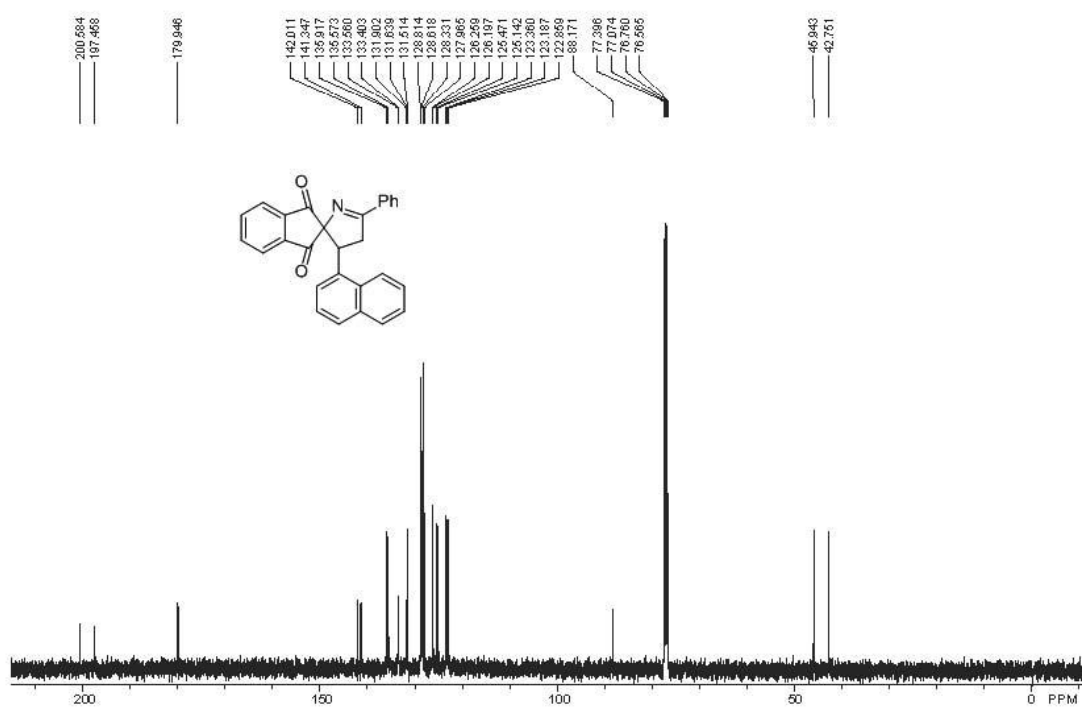
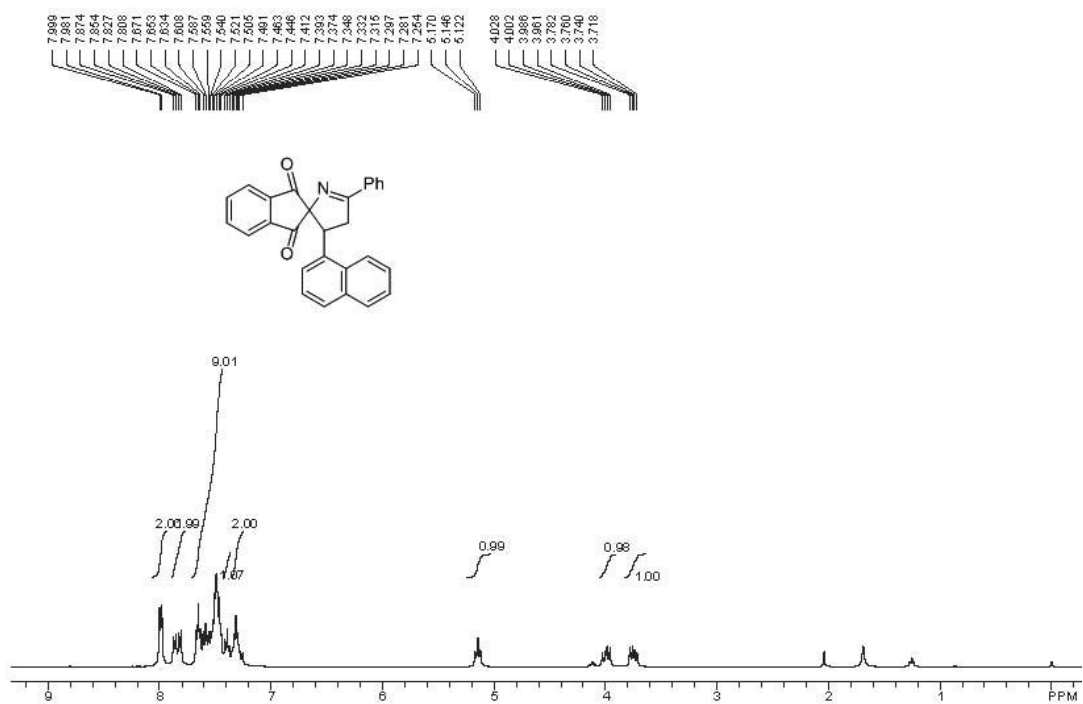
3'-(4-Methoxyphenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3g)



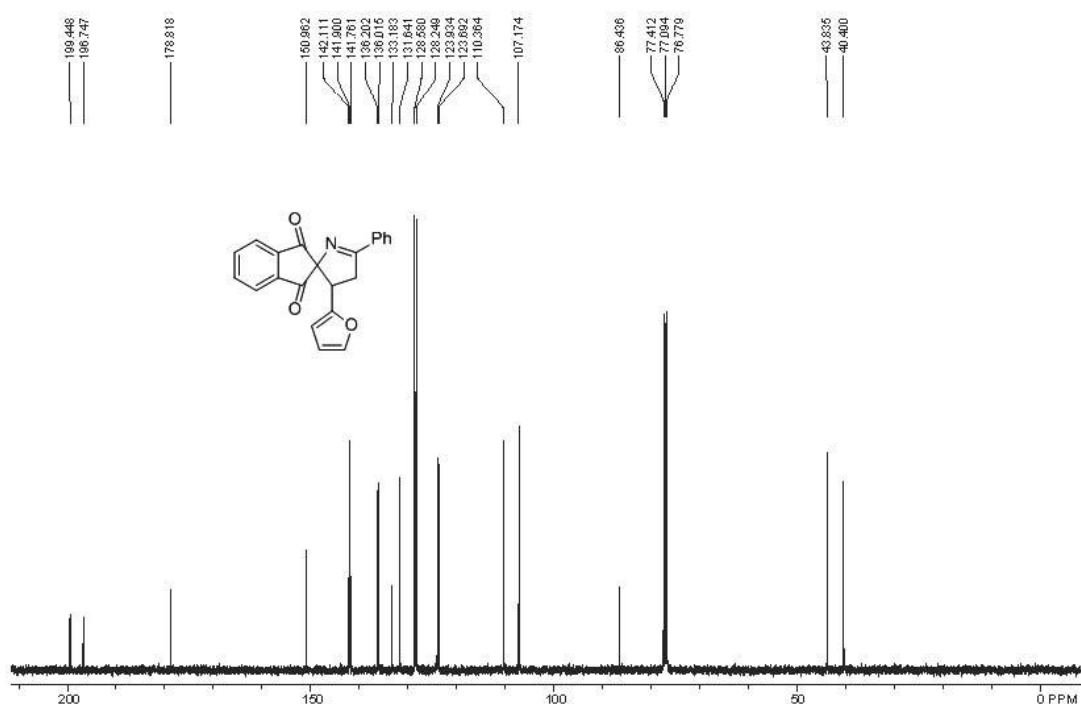
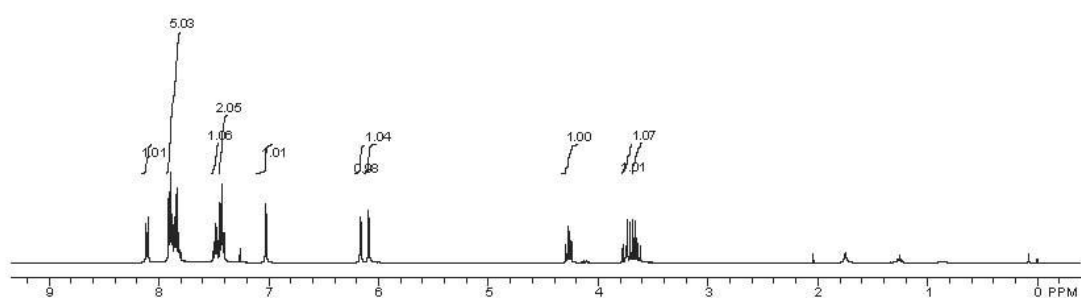
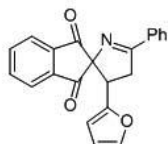
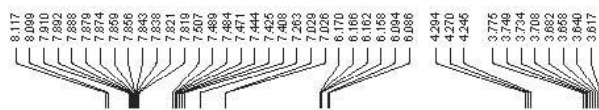
3'-(3-Bromophenyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3h)



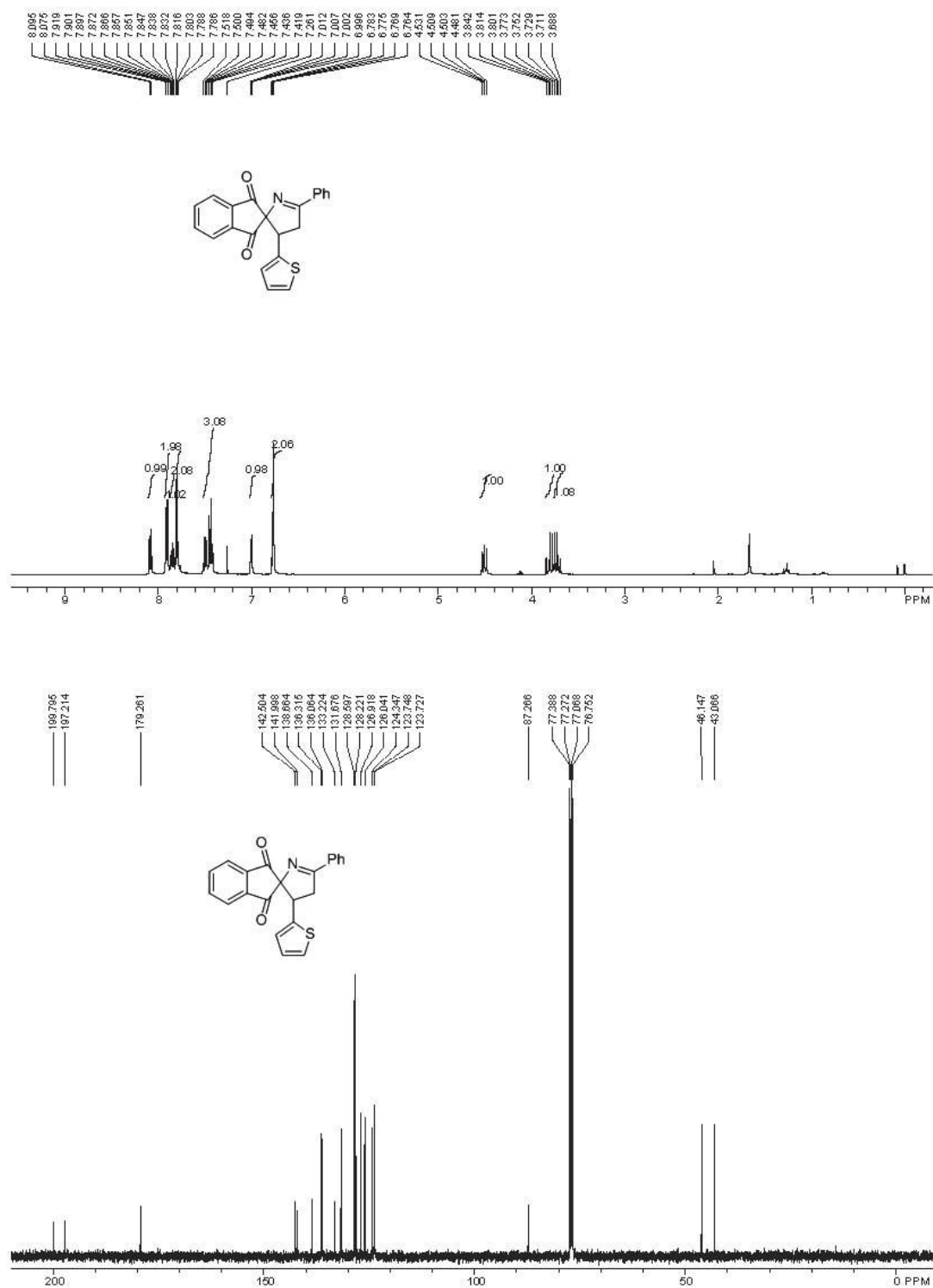
3'-(Naphthalen-1-yl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3i)



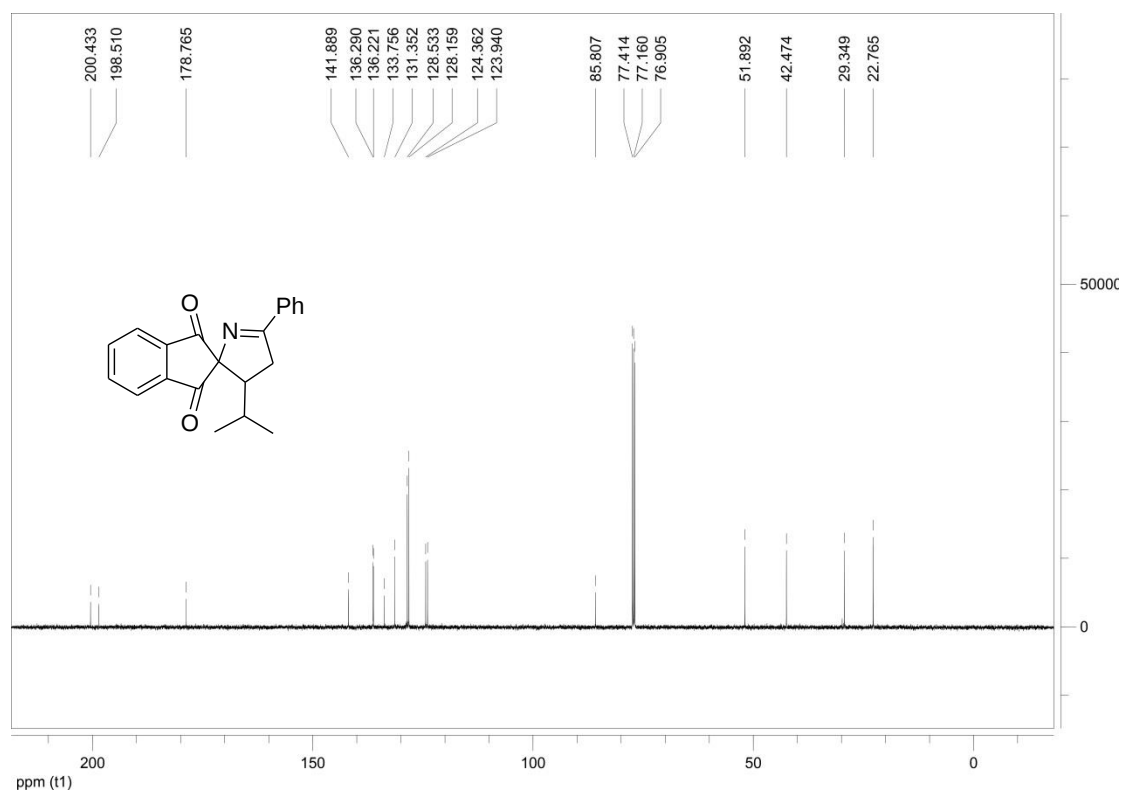
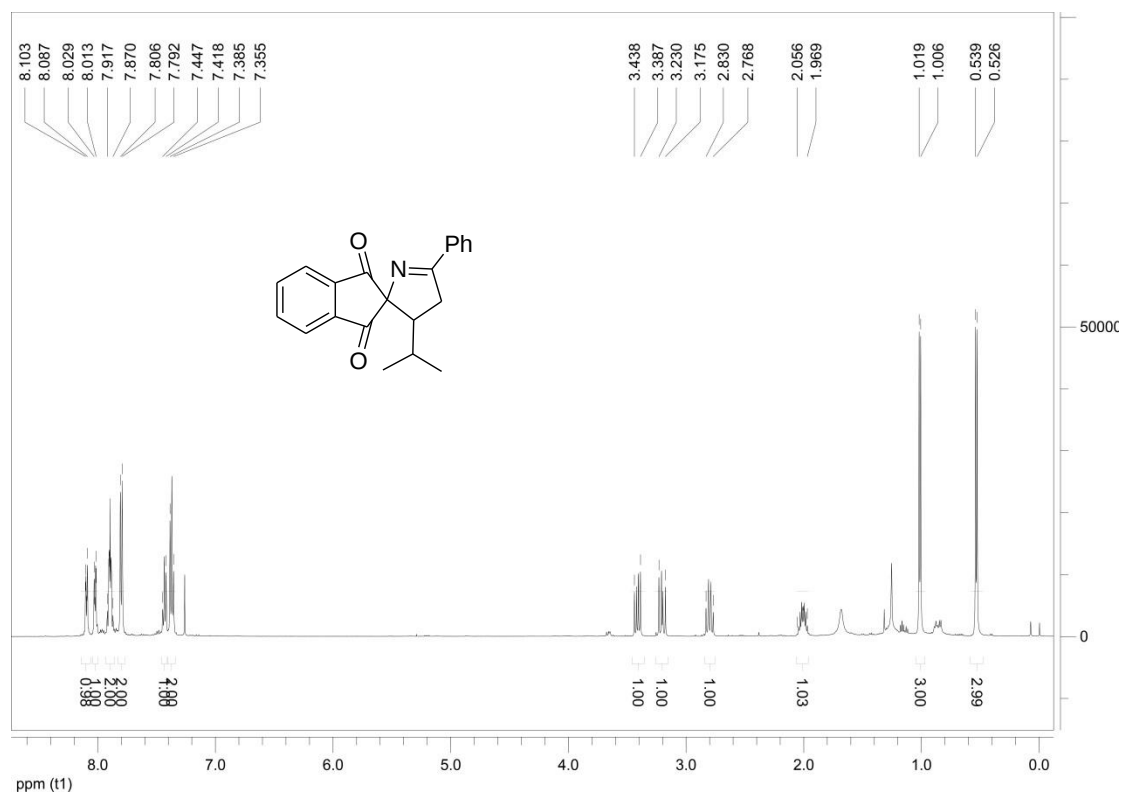
3'-(Furan-2-yl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3j)



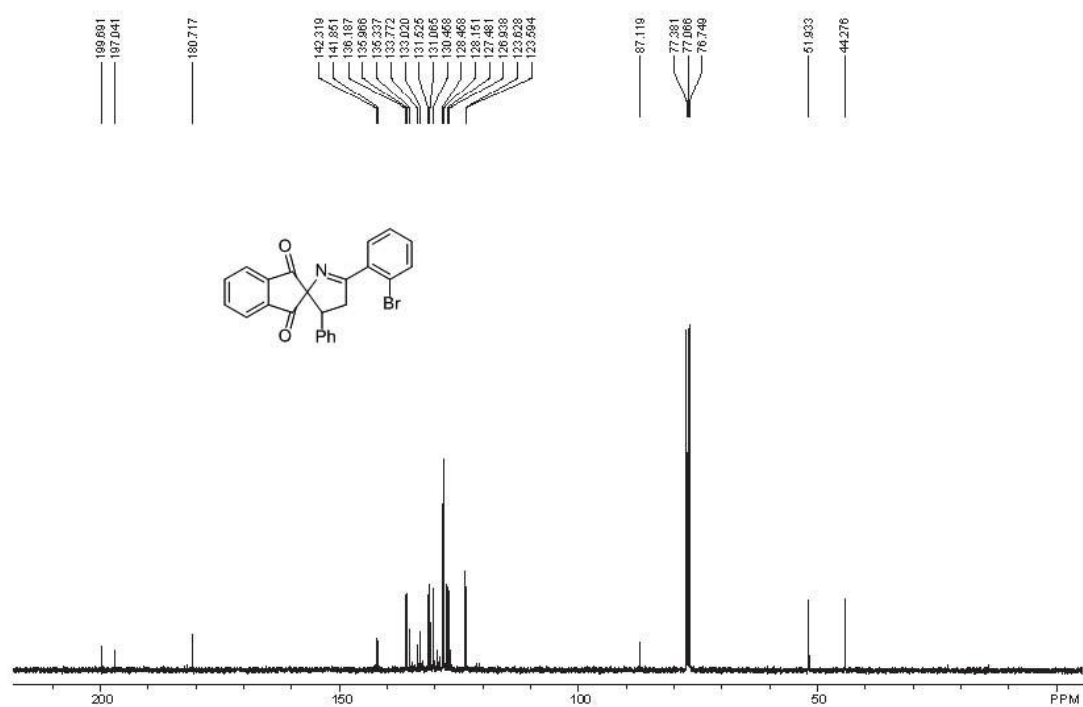
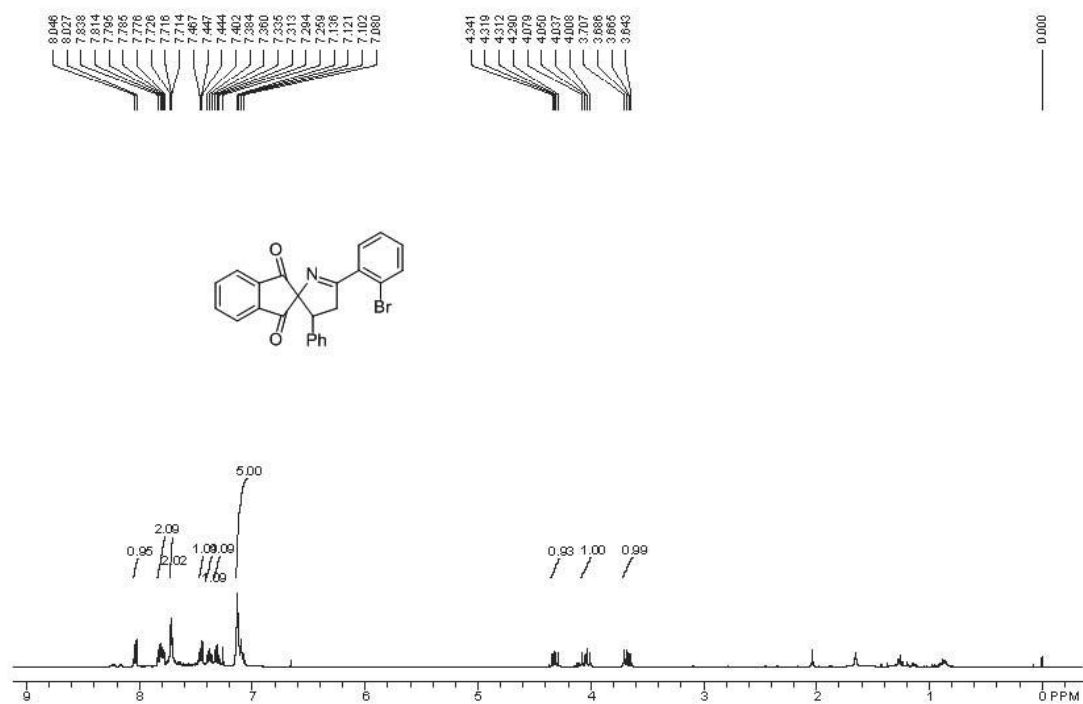
5'-Phenyl-3'-(thiophen-2-yl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3k)



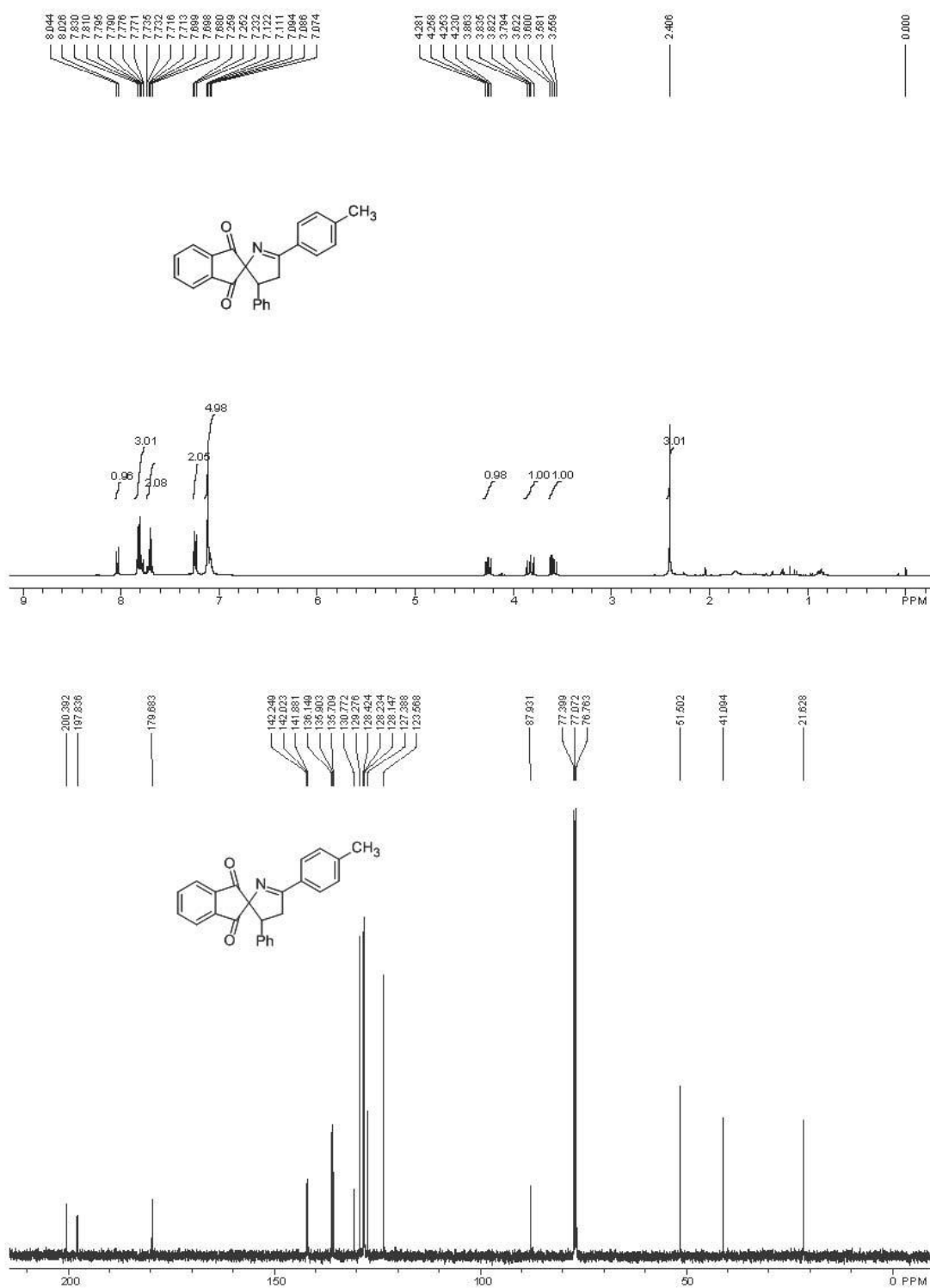
3'-(2-methylpropyl)-5'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3l)



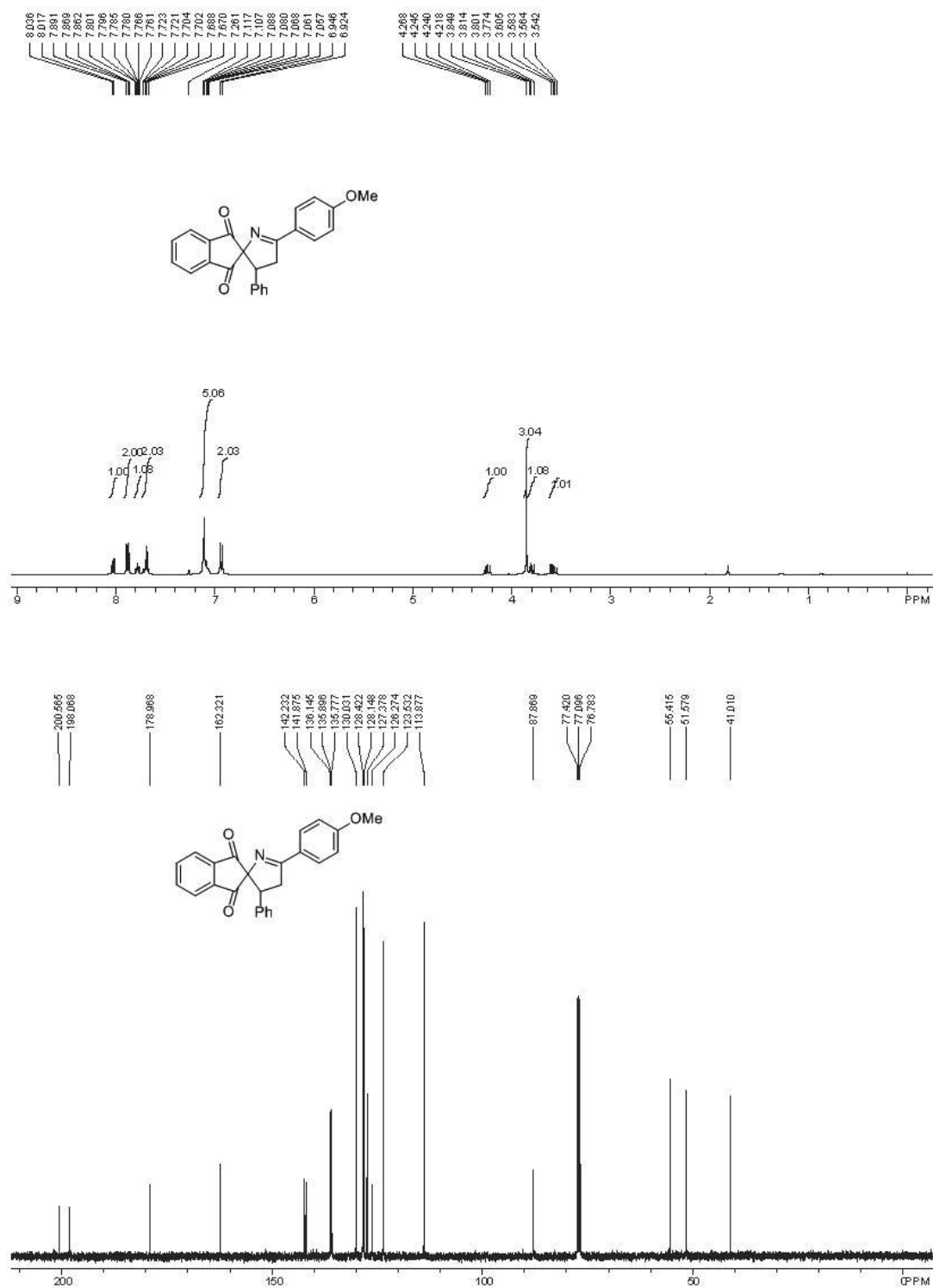
5'-(2-Bromophenyl)-3'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3m)



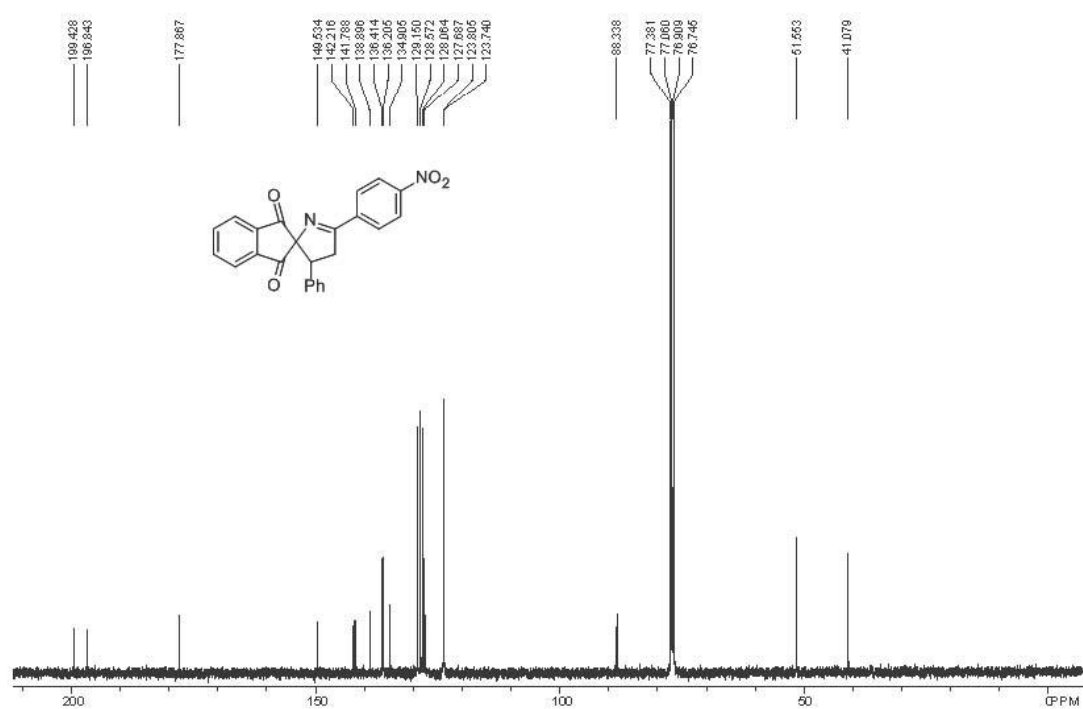
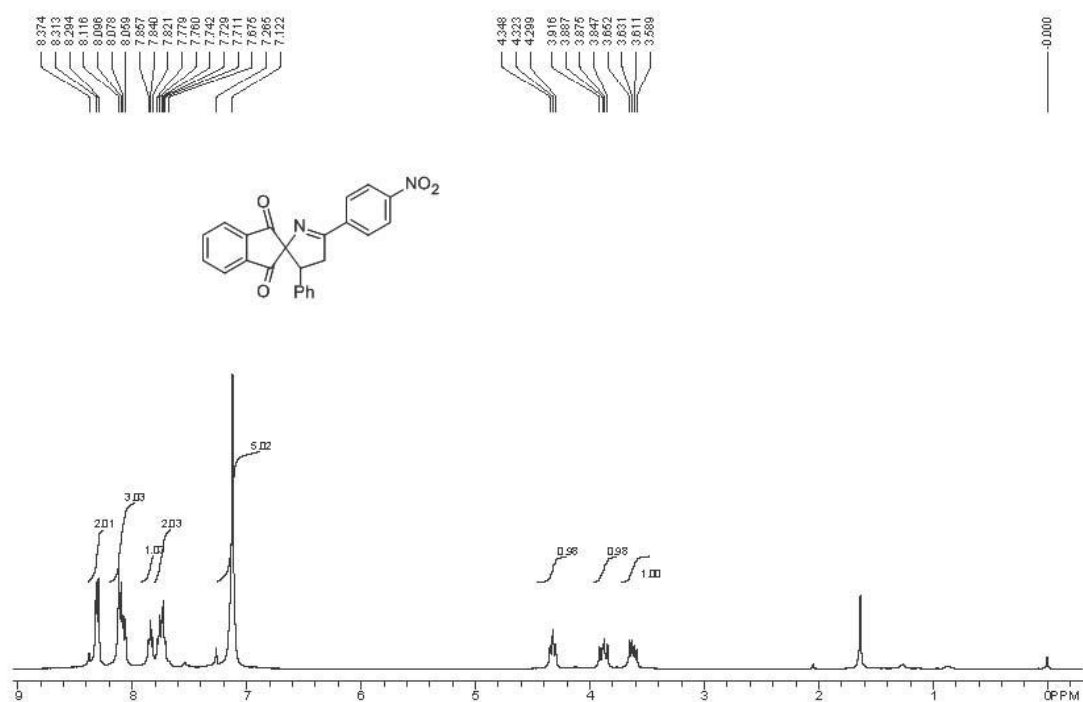
3'-Phenyl-5'-(p-tolyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3n)



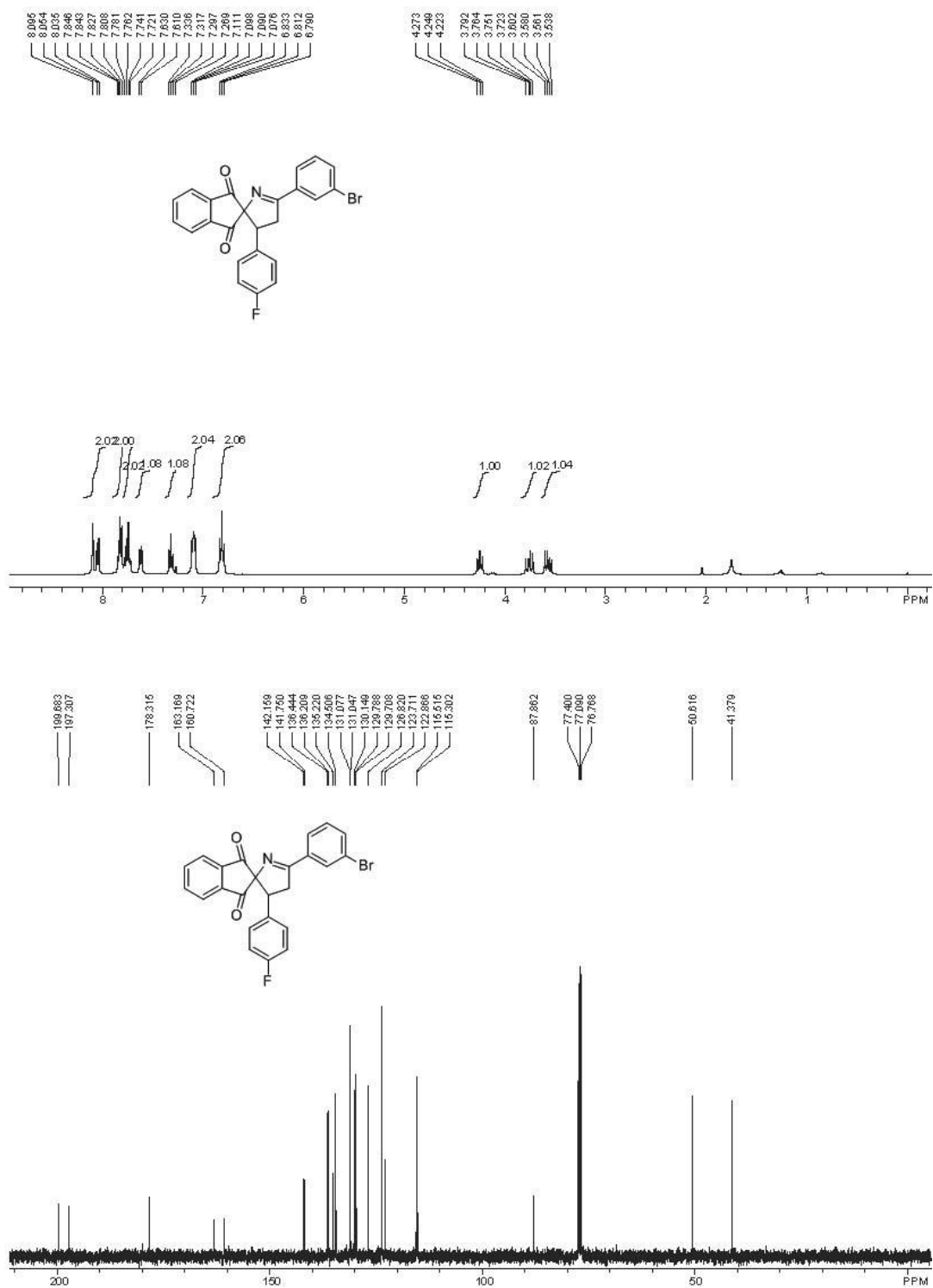
5'-(4-Methoxyphenyl)-3'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3o)



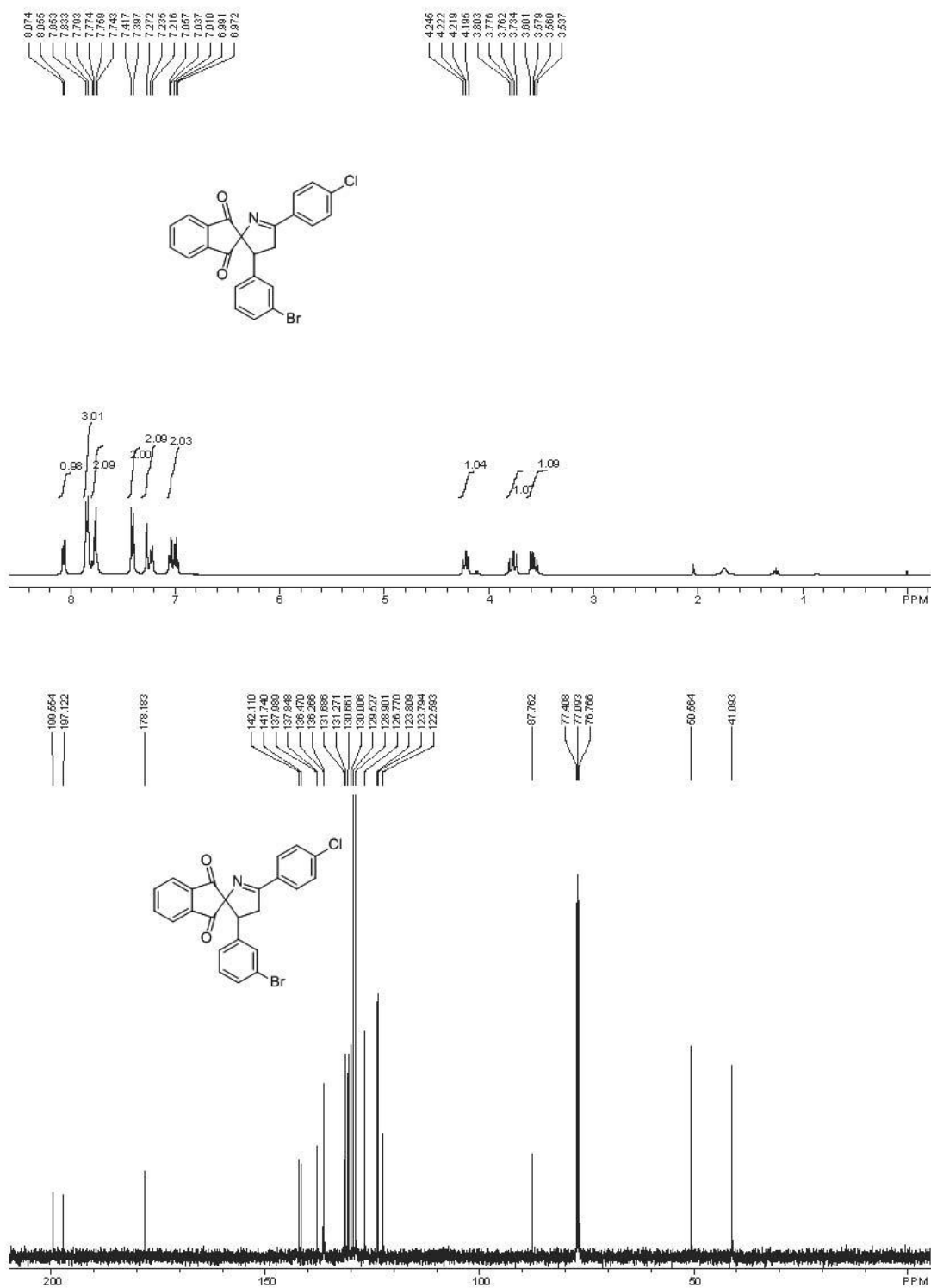
5'-(4-Nitrophenyl)-3'-phenyl-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3p)



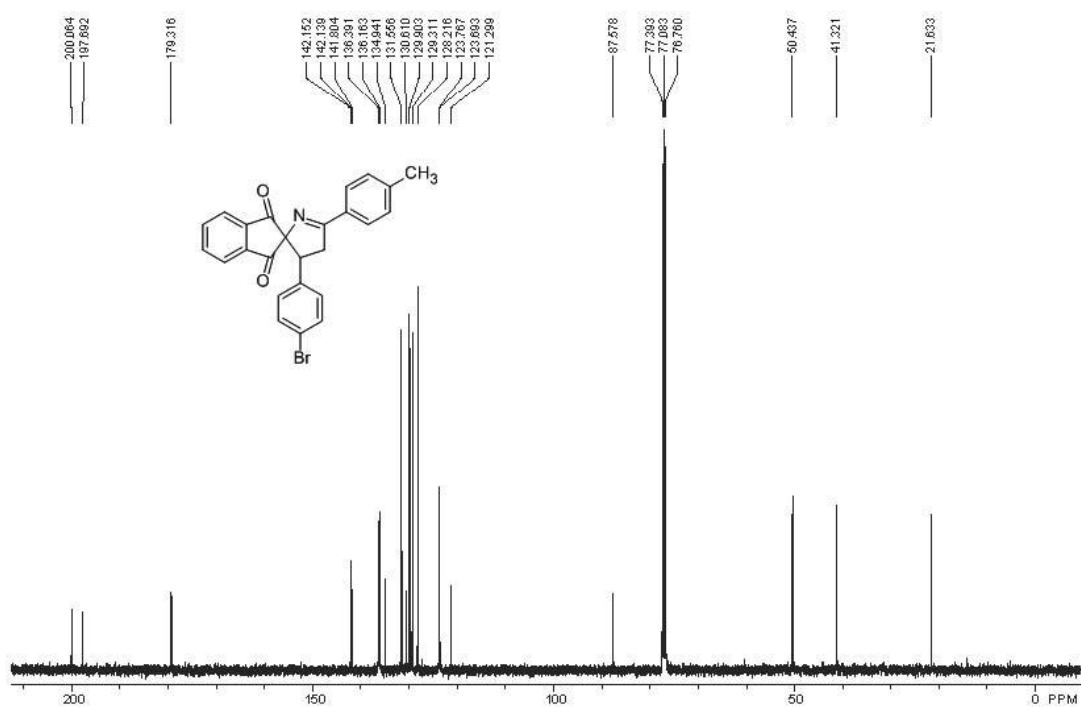
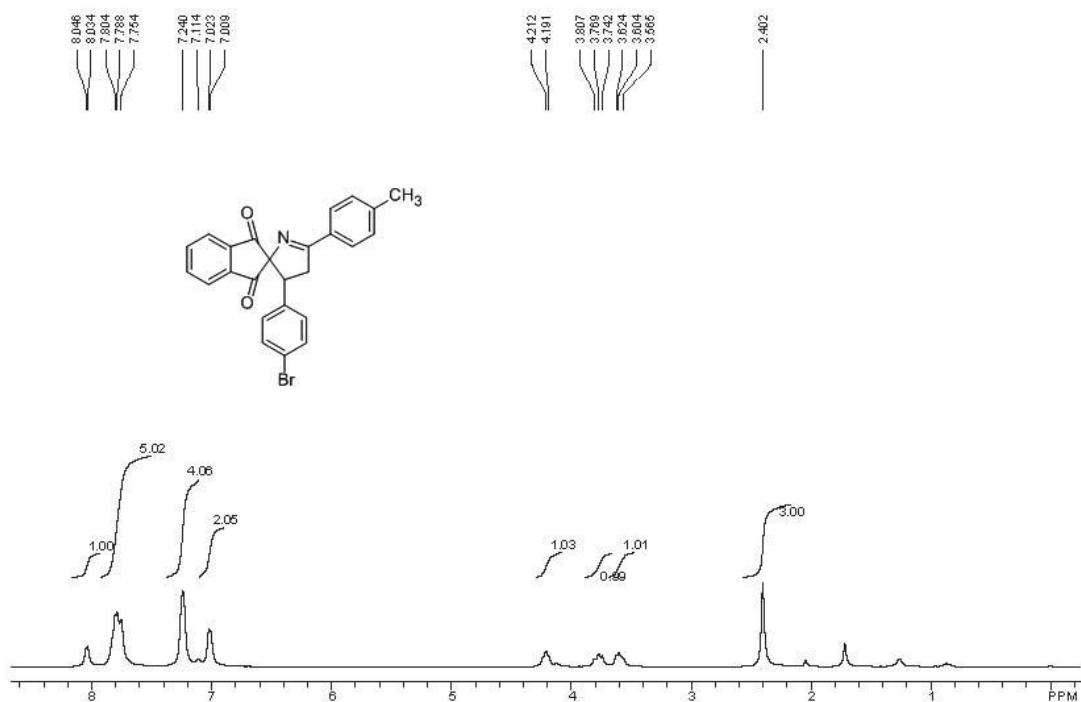
5'-(3-Bromophenyl)-3'-(4-fluorophenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3g)



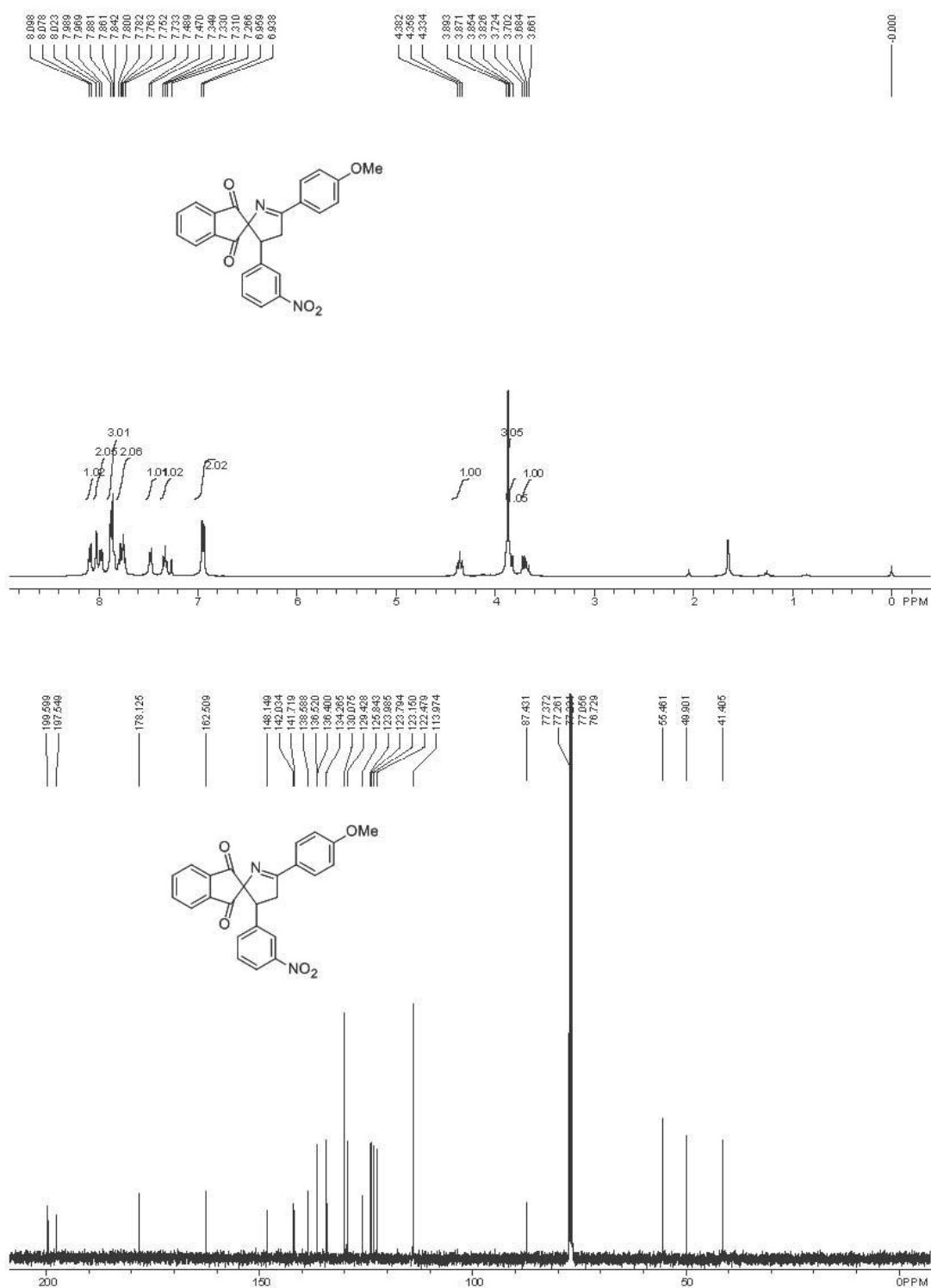
3'-(3-Bromophenyl)-5'-(4-chlorophenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3r)



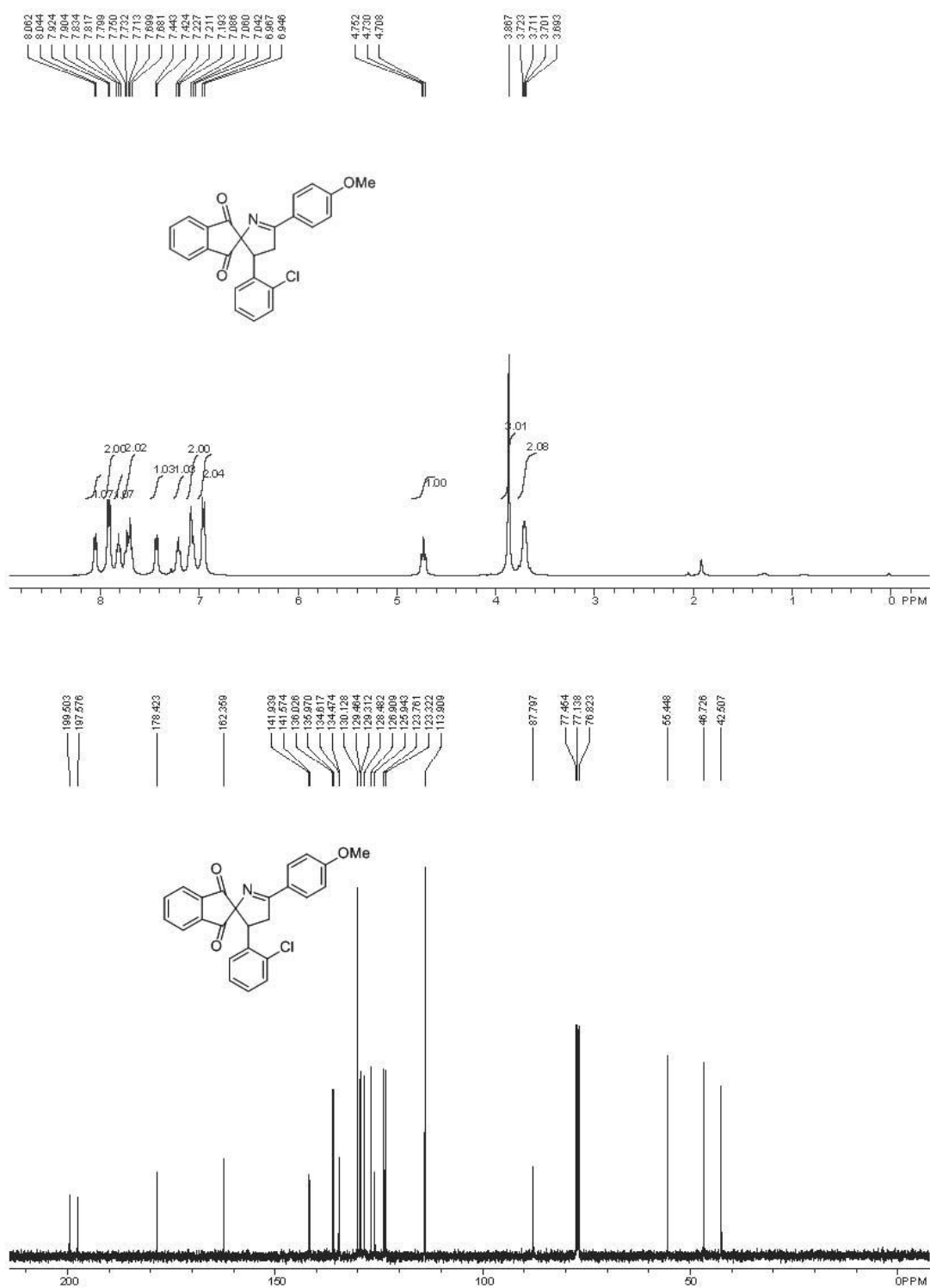
3'-(4-Bromophenyl)-5'-(p-tolyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3s)



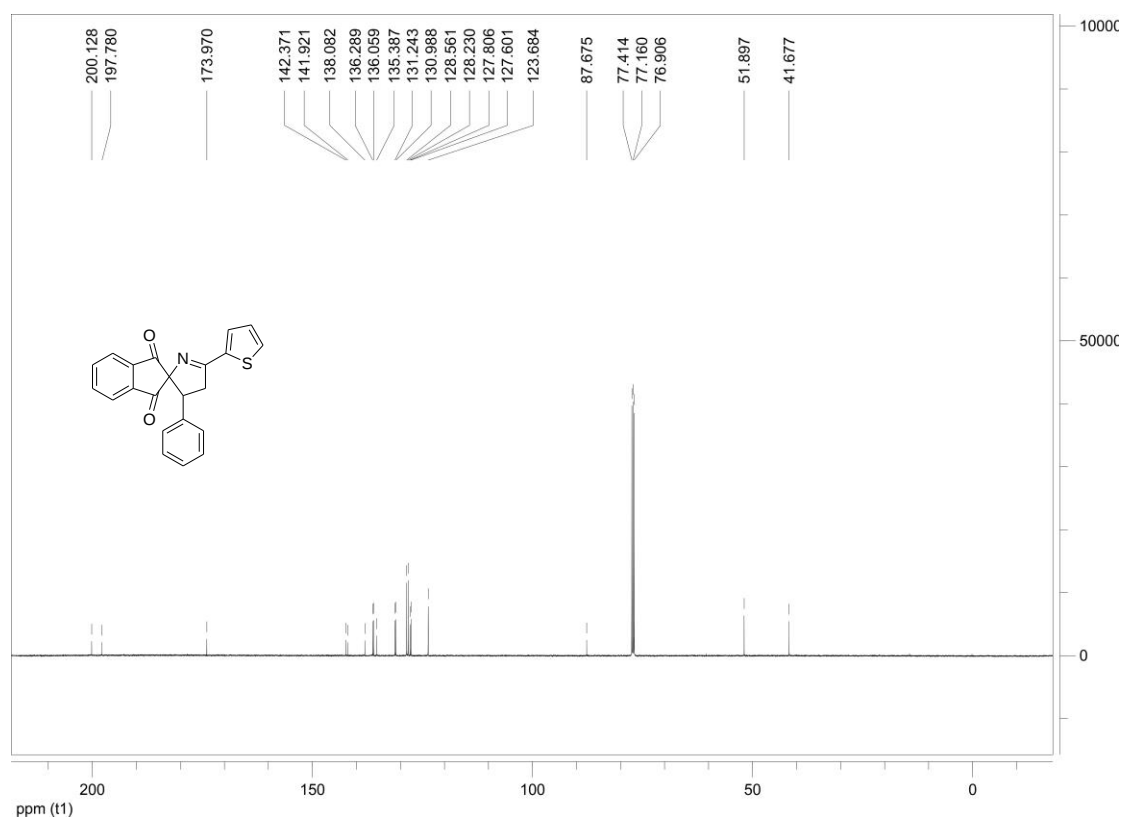
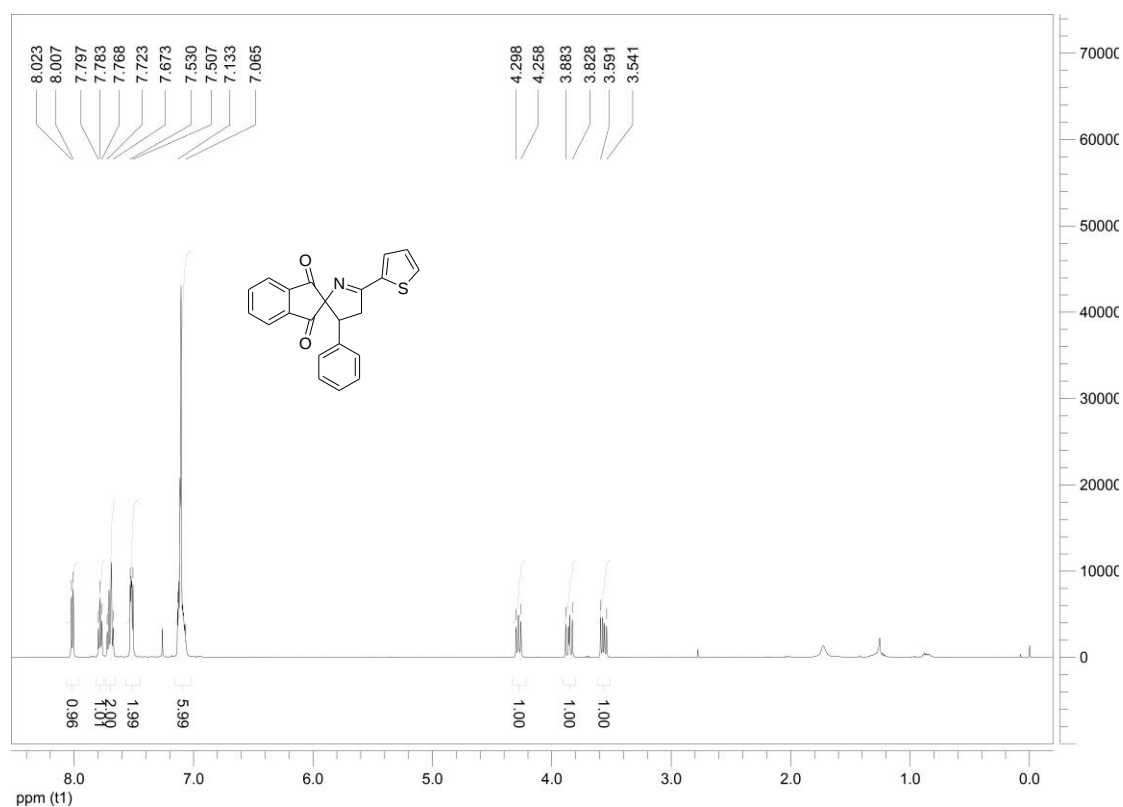
5'-(4-Methoxyphenyl)-3'-(3-nitrophenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3t)



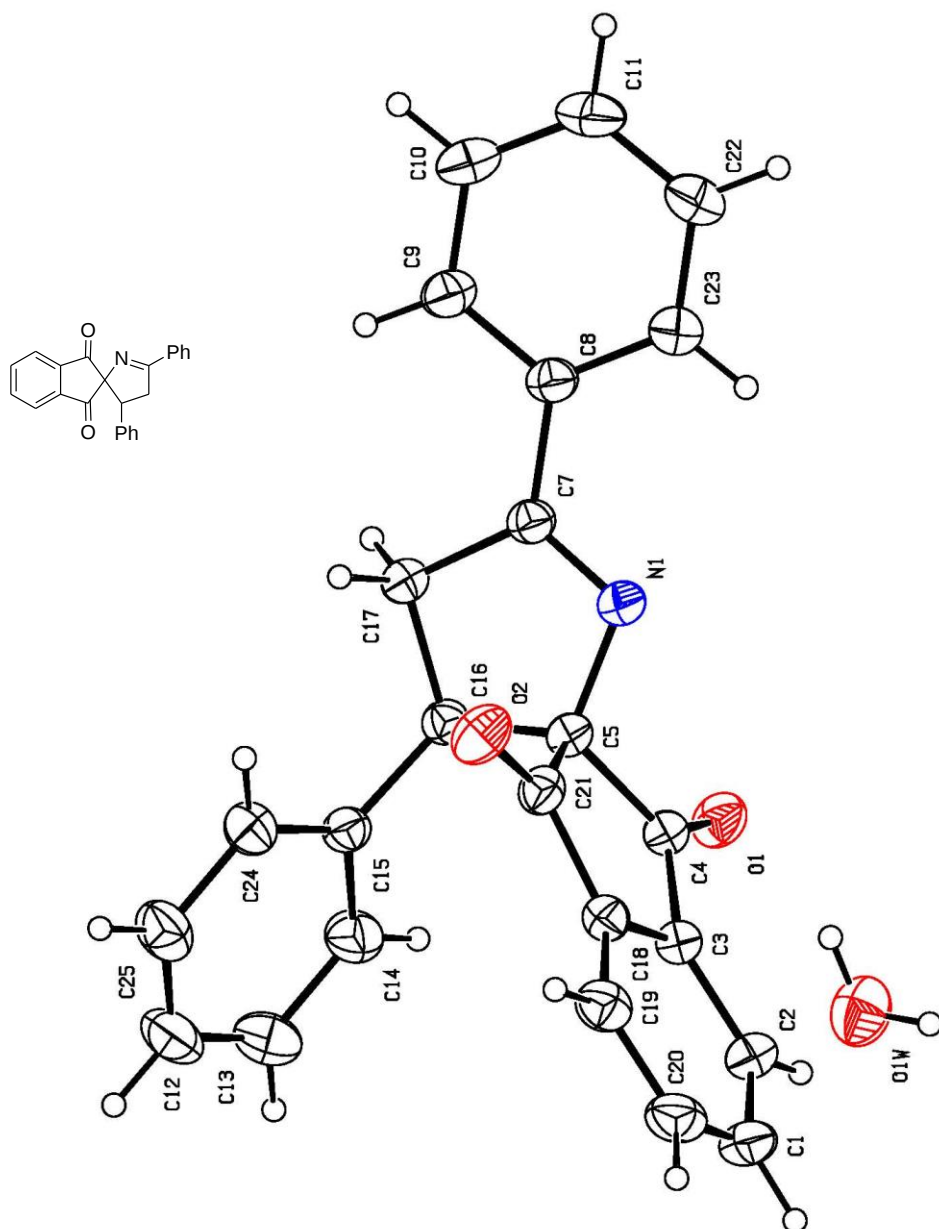
3'-(2-Chlorophenyl)-5'-(4-methoxyphenyl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3u)



3'-phenyl-5'-(thiophen-2-yl)-3',4'-dihydrospiro[indene-2,2'-pyrrole]-1,3-dione(3v)



Crystal Structure and data for compound 3a



Crystal data and structure refinement for compound **3a**

Identification code	shelx	
Empirical formula	C ₂₄ H ₁₉ N O ₃	
Formula weight	369.40	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.30340(10) Å	α = 101.875(7) °
	b = 9.6541(2) Å	β = 106.962(8) °
	c = 11.6687(8) Å	γ = 96.397(7) °
Volume	964.39(8) Å ³	
Z	2	
Density (calculated)	1.272 Mg/m ³	
Absorption coefficient	0.675 mm ⁻¹	
F(000)	388	
Crystal size	0.20 x 0.20 x 0.20 mm ³	
Theta range for data collection	7.023 to 68.334 °	
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -14 ≤ l ≤ 13	
Reflections collected	13309	
Independent reflections	3411 [R(int) = 0.0572]	
Completeness to theta = 67.687 °	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.881 and 0.493	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3411 / 0 / 253	
Goodness-of-fit on F ²	1.094	
Final R indices [I > 2σ(I)]	R1 = 0.0529, wR2 = 0.1351	
R indices (all data)	R1 = 0.0565, wR2 = 0.1403	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.234 and -0.346 e.Å ⁻³	