Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# *Supporting Information*

# Dearomatization of Indoles via Palladium-Catalyzed Carbonylation using $Co_2(CO)_8$ as Carbonyl Source Leading to Carbonyl-Containing Spiroindolenines

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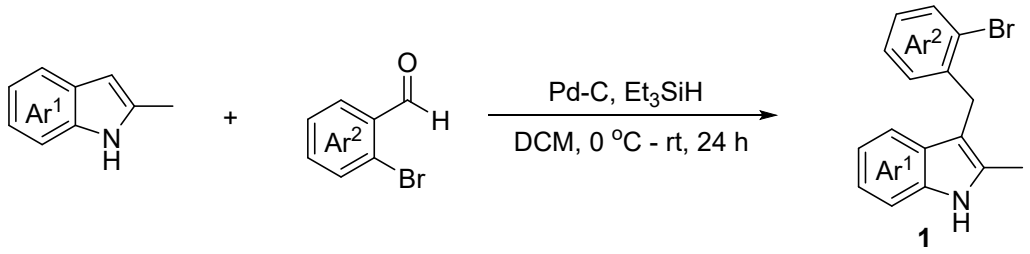
# I. General Information

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. $^{1}H$ NMR、$^{13}C$ NMR spectra were recorded at ambient temperature on a 500 MHz (125 MHz for $^{13}C$) NMR spectrometer. NMR experiments are reported in $\delta$ units, parts per million (ppm), and were referenced to $CDCl_3$ ($\delta$ 7.26 or 77.0 ppm) as the internal standard. The coupling constants $J$ are given in Hz. IR spectra were recorded on a spectrometer using KBr discs. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). High-resolution mass spectra (HRMS) were obtained using a Bruker micro TOF II focus spectrometer (ESI). All melting points were uncorrected.

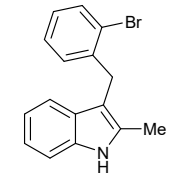
# II. Synthesis and Reaction

## Preparation of the substrates

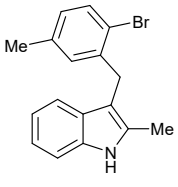
### General procedures for the synthesis of 1




Following a modified procedure,[1] in an oven dried 50 mL Schlenk tube, 10% Pd-C (75 mg, 10 mol%), TFA (1.15 mL, 15.0 mmol, 1.50 equiv.) and $Et_3SiH$ (2.2 equiv.) were added to DCM (50 mL) under argon at 0 °C and the mixture was stirred for 10 min. Then a solution of an indole derivative (10.0 mmol, 1.0 equiv.) and the corresponding 2-bromobenzaldehyde derivative (11.0 mmol, 1.10 equiv.) in DCM (50 mL) was added dropwise to the reaction mixture. After stirring for 4 hours at 0 °C, the reaction mixture was allowed to warm to room temperature and the stirring was continued for additional 20 hours. Then the reaction mixture was filtered through celite and concentrated in a rotary evaporator. The solvent was evaporated, and the crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc, 60:1-30:1) to obtain products **1** (**1a-1r**).




**1a,** 97%

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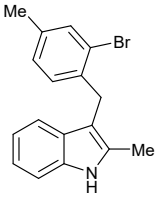


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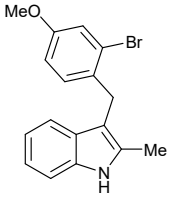
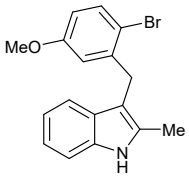



**1d,** 87%

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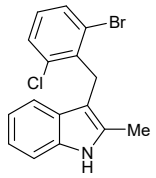


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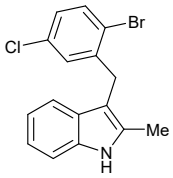


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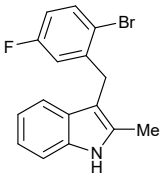
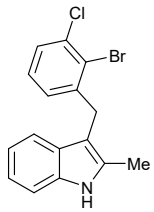
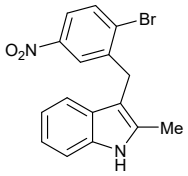



**1h,** 93%




**1i,** 43%

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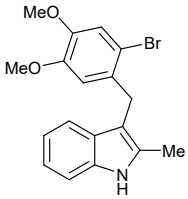


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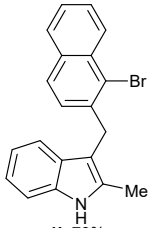


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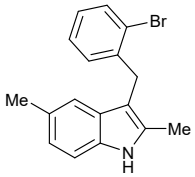


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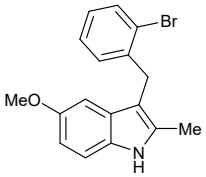


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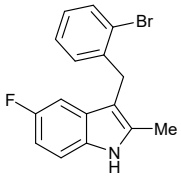


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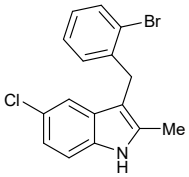
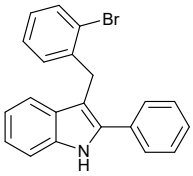
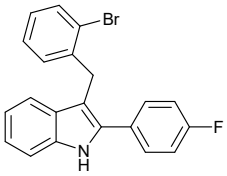



**1p,** 56%




**1q**, 67%

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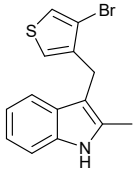
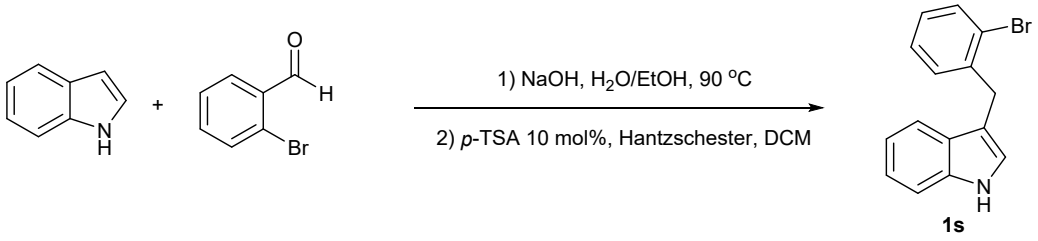



**1t**, 87%

## General procedures for the synthesis of 1s



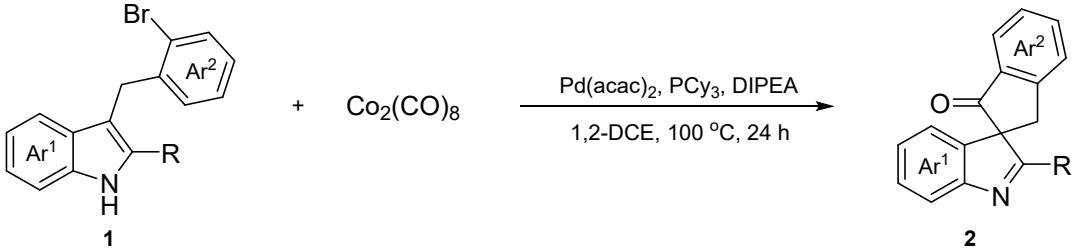

**1s**

According to the literature procedure,[2] in a 50 mL Schlenk tube, indole (1.0 mmol), 2-bromobenzaldehyde (1.2 mmol) and NaOH (1.0 mmol, 40 mg) were added to EtOH/$H_2O$ ($v_1$:$v_2$, 1:1, 2.0 mL), and the mixture was stirred at 90 °C for 1 hour. Then the reaction mixture was filtered through celite and concentrated in a rotary

evaporator. The solvent was evaporated, the crude product (2-bromophenyl)(1*H*-indol-3-yl)methanol was used for the next step without purification.

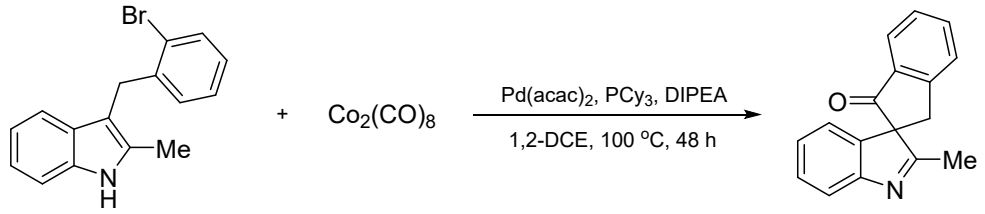
According to the literature procedure,[3] to a stirred solution of the crude product (2-bromophenyl) (1*H*-indol-3-yl) methanol (241.0 mg, 0.8 mmol) in DCM (3.0 mL), Hantzsch esters (253.3 mg, 1.0 mmol) was added. Then *p*-toluenesulfonic acid monohydrate (6.9 mg, 0.04 mmol) was added to the mixture and the resultant was stirred for 4 hours. After the reaction was completed by TLC, the solvent was removed in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 5:1) on silica gel to afford 3-(2- bromobenzyl)-1*H*-indole (**1s**) as a yellowish oil (212.8 mg, 93%).

**General procedure for the synthesis of 2**




Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with indole derivative **1** (0.10 mmol, 1.0 equiv.), $Co_2(CO)_8$ (0.1 mmol, 1.0 equiv.), $Pd(acac)_2$ (10 mol%), $PCy_3$ (20 mol%), DIPEA (2.0 equiv.) and toluene (1.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 100 °C for 24 h in oil bath. After the completion of the reaction, 5.0 mL of saturated brines was added to the mixture, and extracted with ethyl acetate (5 mL × 3). The combined organic extracts were dried over anhydrous $Na_2SO_4$. Subsequently, the solvent was filtered and evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (PE/EA, v/v, 3:1) as the eluent to give the desired product **2**.

**General Procedure for the 2.0 mmol scale preparation of 2a**

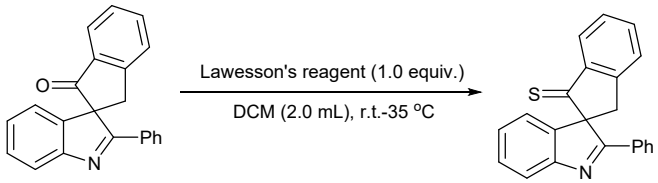



**1a**, 2.0 mmol

**2a**, 65%, 321 mg

Under air, a 100 mL of round-bottom flask equipped with a stir bar was charged with indole derivative **1a** (2.0 mmol, 1.0 equiv.), $Co_2(CO)_8$ (2.0 mmol), $Pd(acac)_2$ (10 mol%), $PCy_3$ (20 mol%), DIPEA (2.0 equiv.) and toluene (20 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 100 °C for 48 h in oil bath. After the completion of the reaction, 20 mL of saturated brines was added to the mixture, and extracted with ethyl acetate (15 mL × 3). The combined organic extracts were dried over anhydrous $Na_2SO_4$. Subsequently, the solvent was filtered and evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (PE/EA, v/v, 3:1) gave **2a** in 65% yield as a yellowish solid (321 mg).

**General procedure for preparation of thione 3**[4]

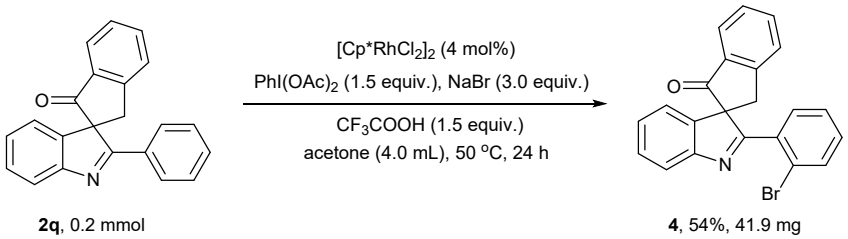



**2q**

**3**, 82%

To a solution of compound **2q** (0.2 mmol, 1.0 equiv.) in dry DCM (2.0 mL) was added Lawesson's reagent (80.9 mg, 0.2 mmol, 1.0 equiv.) under argon and the mixture was stirred at 35 °C until complete conversion was observed by TLC. Then the solvent was removed in vacuo, the residue was purified by flash column chromatography on silica gel (PE/EA = 6:1) to afford the desired product **3** as a yellowish oil (53.3 mg, 82%).

**General procedure for Rh-catalyzed C($sp^2$)-H bromination of 2q**

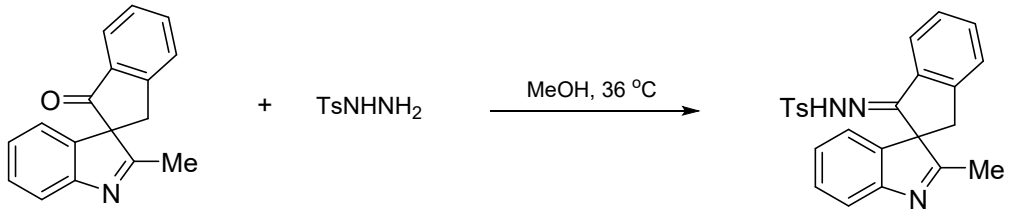



**2q**, 0.2 mmol

**4**, 54%, 41.9 mg

To a solution of compound **2t** (61.8 mg, 0.2 mmol, 1.0 equiv.) in acetone (4.0 mL) was added $[Cp^*RhCl_2]_2$ (4.0 mol%, 5.0 mg), $PhI(OAc)_2$ (96.6 mg, 0.3 mmol, 1.5 equiv.), NaBr (61.4 mg, 0.6 mmol, 3.0 equiv.) and $CF_3COOH$ (1.5 equiv.). The reaction mixture was then stirred at 50 °C for 24 h. Then, EtOAc (10mL) and $H_2O$ (10 mL) were added, the organic layer was dried over $Na_2SO_4$, and the solvent was removed in vacuo. The residue was purified by flash chromatography (PE/EA = 8:1) to afford the bromination product **4** as a white solid (41.9 mg, 54%).

**General procedure for the preparation of hydrazone 5**[5]

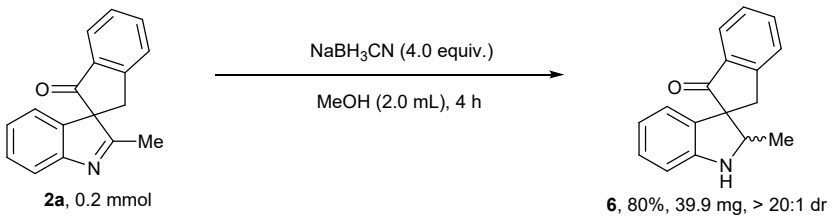



**2a**

**5**, 63%

To a solution of tosylhydrazide (1.0 equiv.) in MeOH (0.5 M) was added **2a** (49.4 mg, 0.2 mmol, 1.0 equiv.). The reaction mixture was stirred at 36 °C until complete conversion was observed by TLC. Then the solvent was removed in vacuo, the residue was purified by flash column chromatography on silica gel (PE/EA = 4:1) to afford the desired product **5** as a yellowish oil (52.3 mg, 63%).

**General procedure for reduction of 2a to spiroindoline 6**



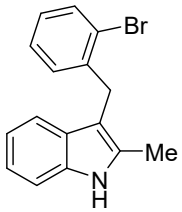

**2a**, 0.2 mmol

**6**, 80%, 39.9 mg, > 20:1 dr

Under argon, to a solution of **2a** (49.4 mg, 0.2 mmol, 1.0 equiv.) in MeOH (2.0 mL)

was added $NaBH_3CN$ (50.0 mg, 0.8 mmol, 4.0 equiv.). The reaction mixture was stirred at 40 °C until complete conversion was observed by TLC (4 h). 10 mL of saturated brines was added to the mixture, and extracted with ethyl acetate (5 mL × 3). The combined organic extracts were dried over anhydrous $Na_2SO_4$. Subsequently, the solvent was filtered and evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (PE/EA, v/v, 4:1) gave **6** in 80% yield as a yellowish oil (39.9 mg).

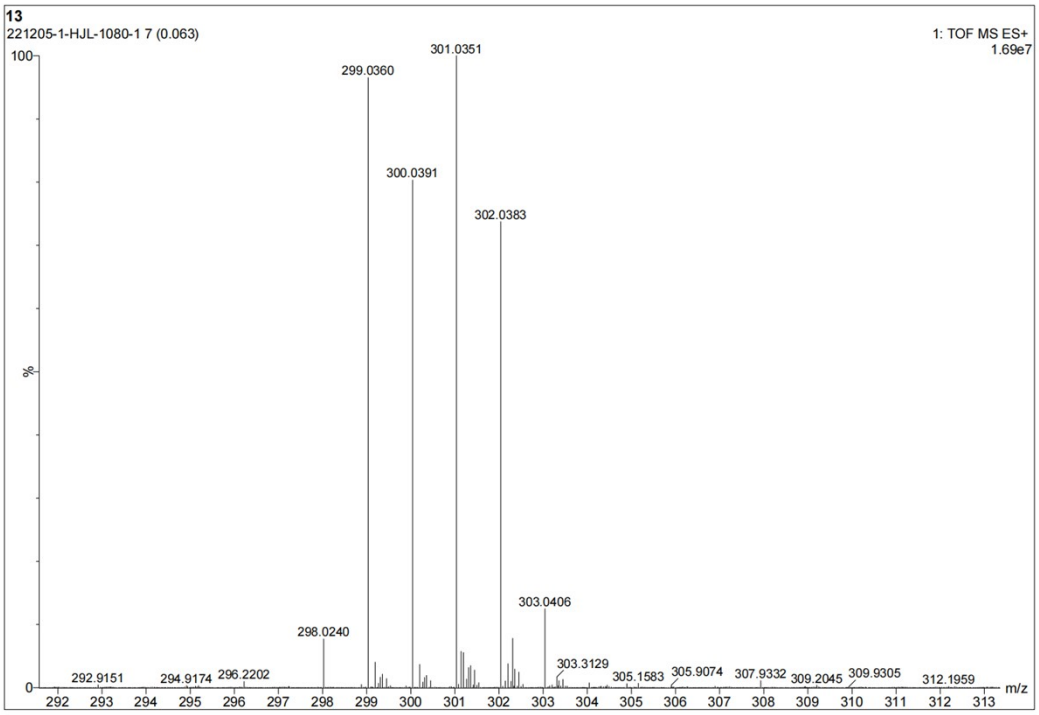
## III. Characterization Data

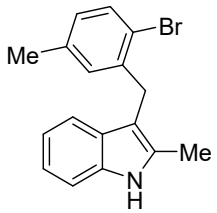



**1a**

**3-(2-bromobenzyl)-2-methyl-1*H*-indole (1a)**[1,3]

Flash column chromatography on a silica gel (PE/EA, v/v, 60:1) gives **1a** (880 mg, 97% yield) as a yellowish solid: m.p. 76-77 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.61 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.5 Hz, 1H), 7.37 (d, $J$ = 7.9 Hz, 1H), 7.31 (d, $J$ = 8.1 Hz, 1H), 7.18–7.14 (m, 1H), 7.13–7.09 (m, 1H), 7.07 (d, $J$ = 7.3 Hz, 1H), 7.06 – 7.03 (m, 1H), 6.98 (dd, $J_1$ = 7.5 Hz, $J_2$ = 1.9 Hz, 1H), 4.17 (s, 2H), 2.36 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 140.3, 135.4, 132.5, 132.4, 130.0, 129.0, 127.5, 127.3, 124.6, 121.2, 119.4, 118.5, 110.2, 109.0, 30.5, 11.9. IR ($cm^{-1}$): 3420(N-H), 3180(Ar-H), 1616(Ar C=C), 1402(C-H), 1087(Ar-Br), 933(C-C), 759(C-C), 741(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{15}BrN^+$ 300.0382, Found 300.0391.

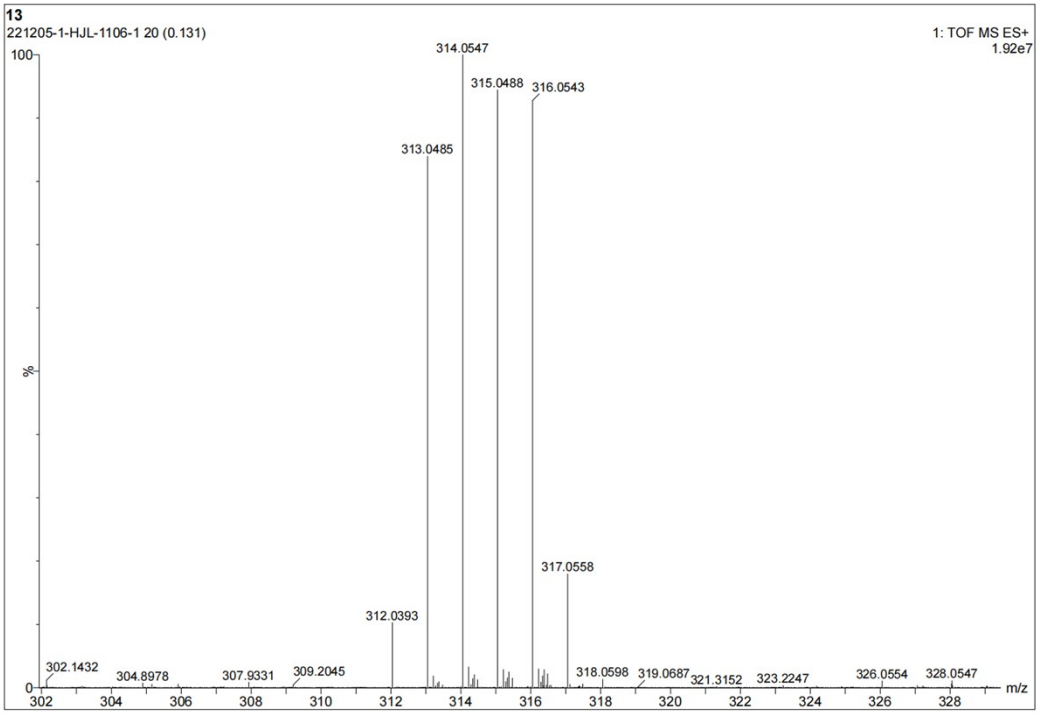


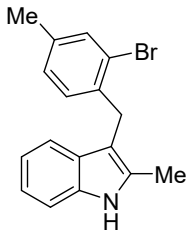



**1b**

**3-(2-bromo-5-methylbenzyl)-2-methyl-1*H*-indole (1b)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1b** (309 mg, 25% yield) as a yellow oil; $^{1}$H NMR (500 MHz,$CDCl_3$) δ 7.83 (s, 1H), 7.46 (d, $J$ = 8.1 Hz, 1H), 7.37 (d, $J_1$ = 7.9 Hz, 1H), 7.31 (d, $J_1$ = 8.0 Hz, 1H), 7.14 (td, $J_1$ = 8.1 Hz, $J_2$ = 7.6, $J_3$ = 1.2 Hz, 1H), 7.06–7.03 (m, 1H), 6.85 (d, $J_1$ = 8.1 Hz, 1H), 6.79 (s, 1H), 4.12 (s, 2H), 2.36 (s, 3H), 2.13 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 139.9, 137.2, 135.4, 132.3, 132.2, 130.7, 129.0, 128.3, 121.2, 121.1, 119.4, 118.5, 110.2, 109.2, 30.3, 21.0, 11.9. IR ($cm^{-1}$): 3403(N-H), 3180(Ar-H), 1621(Ar C=C), 1402(C-H), 1074(Ar-Br), 858(C-C), 740(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}BrN^+$ 314.0539, Found 314.0547.

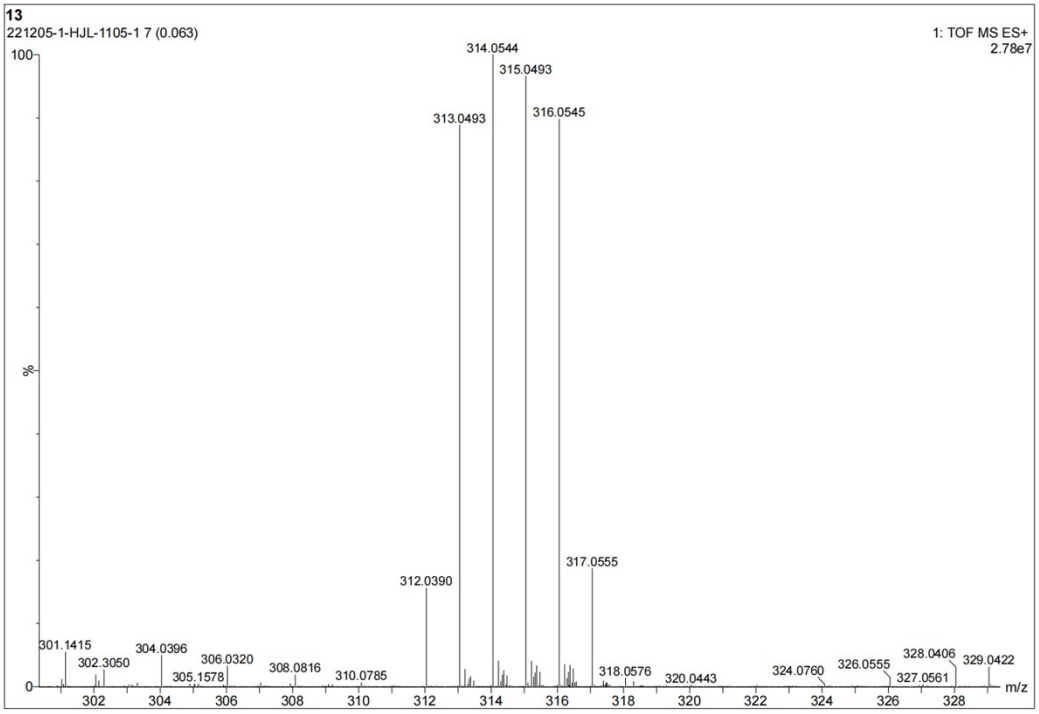


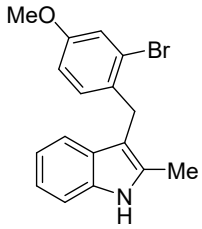



**1c**

**3-(2-bromo-4-methylbenzyl)-2-methyl-1*H*-indole (1c)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1c** (730 mg, 47% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.51–7.47 (m, 1H), 7.42 (dd, $J_1$ = 7.9 Hz, $J_2$ = 1.1 Hz, 1H), 7.31 (dt, $J_1$ = 8.1 Hz, $J_2$ = 0.9 Hz, 1H), 7.2 – 7.17 (m, 1H), 7.12–7.08 (m, 1H), 6.94 (dd, $J$ = 7.9 Hz, $J_2$ = 1.7 Hz, 1H), 6.89 (d, $J$ = 7.9 Hz, 1H), 4.17 (s, 2H), 2.36 (s, 3H), 2.32 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 137.4, 137.2, 135.4, 132.9, 132.3, 129.7, 129.0, 128.1, 124.3, 121.1, 119.4, 118.5, 110.2, 109.2, 30.0, 20.6, 11.8. IR ($cm^{-1}$): 3404(N-H), 3189(Ar-H), 1654(Ar C=C), 1402(C-H), 1083(Ar-Br), 930(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}BrN^+$ 314.0539, Found 314.0544.

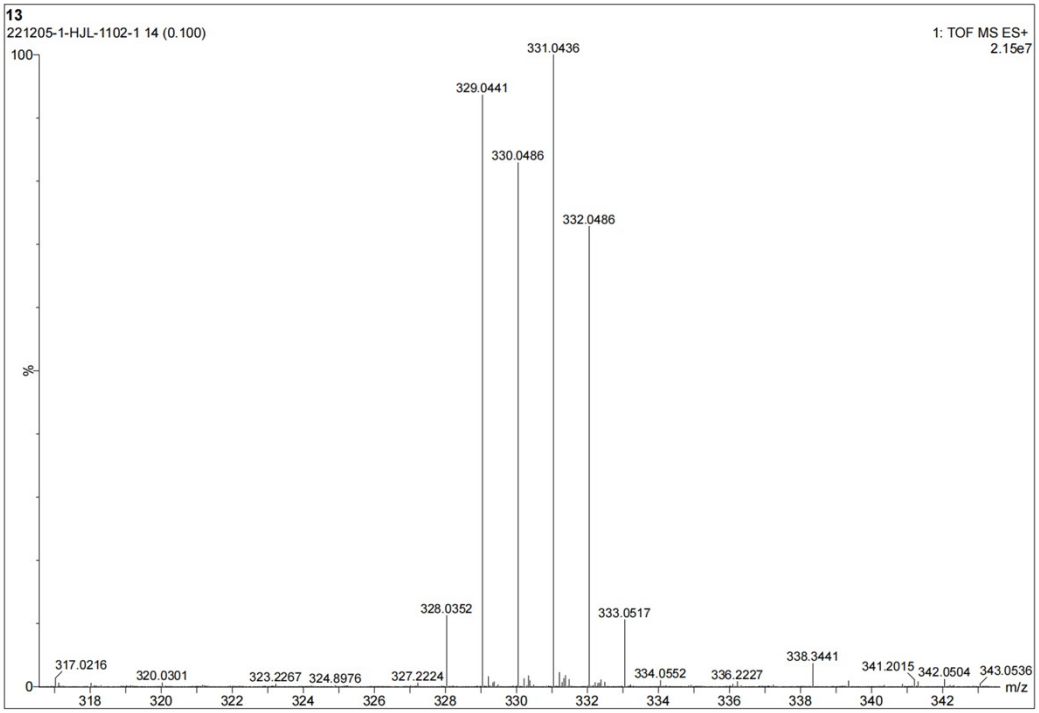


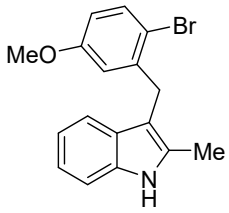



**1d**

**3-(2-bromo-4-methoxybenzyl)-2-methyl-1*H*-indole (1d)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1d** (1.15 g, 87% yield) as a reddish solid: m.p. 68-69 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.41 (d, $J$ = 8.0 Hz, 1H), 7.30 (d, $J$ = 8.1 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.12 – 7.08 (m, 1H), 6.91 (d, $J$ = 8.6 Hz, 1H), 6.70 (dd, $J_1$ = 8.6 Hz, $J_2$ = 2.7 Hz, 1H), 4.14 (s, 2H), 3.78 (s, 3H), 2.35 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 158.3, 135.4, 132.4, 132.3, 130.4, 129.0, 124.5, 121.2, 119.4, 118.5, 117.8, 113.5, 110.3, 109.4, 55.6, 29.6, 11.8. IR (cm$^{-1}$): 3394(N-H), 3181(Ar-H), 1647(Ar C=C), 1558(C-N), 1487(C-H), 1402(C-H), 1160(C-O-C), 1084(Ar-Br), 929(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}BrNO^+$ 330.0488, Found 330.0486.

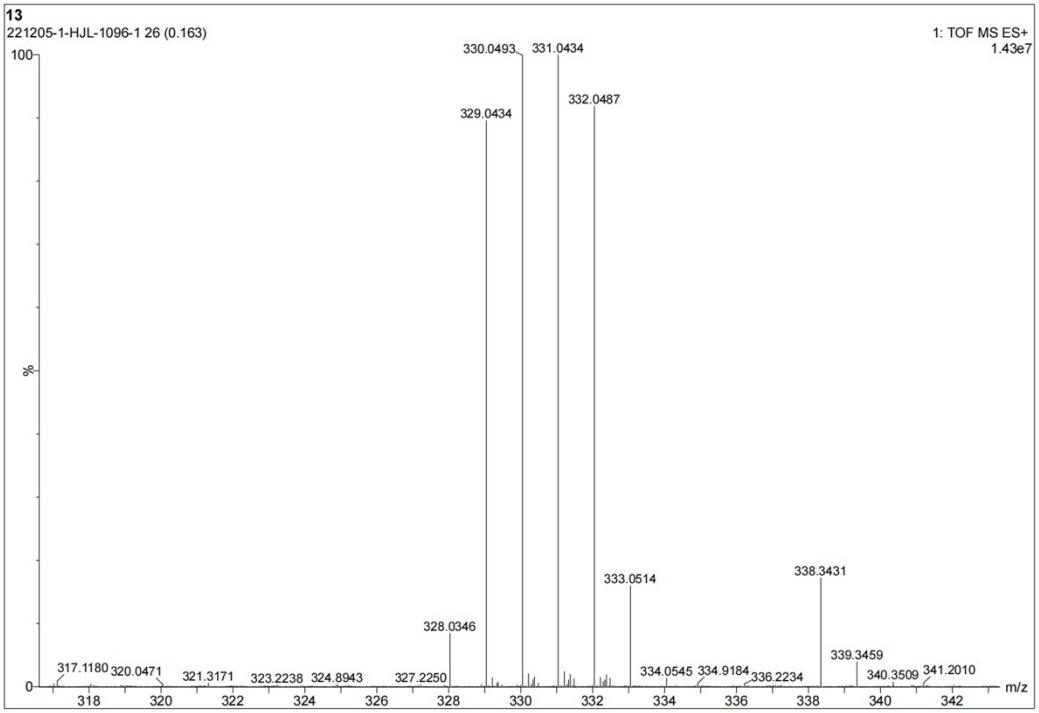


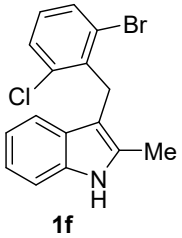



**1e**

**3-(2-bromo-5-methoxybenzyl)-2-methyl-1*H*-indole (1e)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1e** (1.44 g, 88% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.50 (dd, $J_1$ = 8.7 Hz, $J_2$ = 4.7 Hz, 1H), 7.39 (t, $J$ = 6.7 Hz, 1H), 7.28 (d, $J$ = 8.1 Hz, 1H), 7.17–7.12 (m, 1H), 7.10–7.02 (m, 1H), 6.65–6.61 (m, 1H), 6.59 – 6.55 (m, 1H), 4.13 (d, $J$ = 4.6 Hz, 2H), 3.61 (d, $J$ = 2.1 Hz, 3H), 2.34 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 159.0, 141.6, 135.4, 132.9, 132.4, 128.9, 121.2, 119.4, 118.4, 116.4, 115.1, 112.5, 110.2, 108.9, 55.3, 30.6, 11.8. IR ($cm^{-1}$): 3404(N-H), 3186(Ar-H), 1647(Ar C=C), 1558(C-N), 1462(C-H), 1402(C-H), 1157(C-O-C), 1084(Ar-Br), 930(C-C), 745(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}BrNO^+$ 330.0488, Found 330.0493.

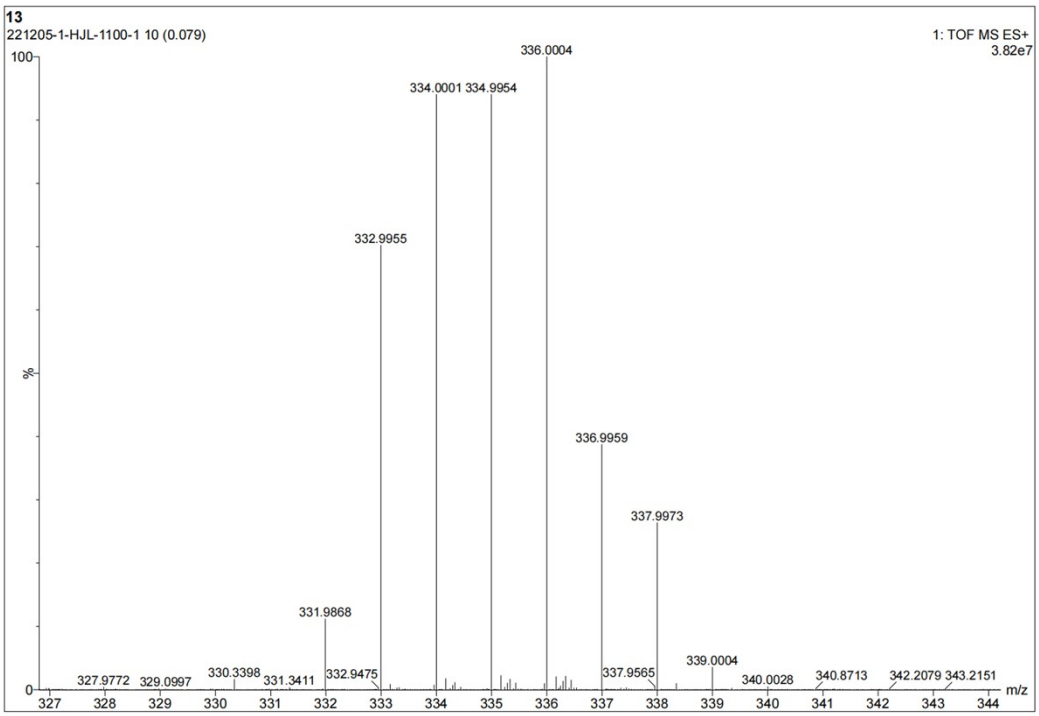


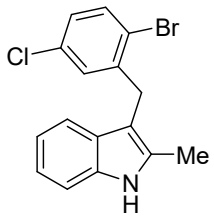



**1f**

**3-(2-bromo-5-fluorobenzyl)-2-methyl-1*H*-indole (1f)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1f** (1.35 g, 80% yield) as a light pink solid: m.p. 165-166 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.53 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.3 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.24 (d, $J$ = 8.0 Hz, 1H), 7.10 (td, $J_1$ = 8.0 Hz, $J_2$ = 7.6 Hz, $J_3$ = 1.2 Hz, 1H), 7.06 – 7.00 (m, 2H), 4.42 (s, 2H), 2.26 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 138.2, 136.2, 135.1, 131.8, 131.7, 129.1, 128.6, 128.3, 126.7, 120.8, 119.2, 118.6, 110.2, 107.4, 30.4, 12.2. IR (cm$^{-1}$): 3436(N-H), 2984(C-H), 1622(Ar C=C), 1454(C-H), 1067(Ar-Cl), 1003(Ar-Br), 910(C-C), 777(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{14}BrClN^+$ 333.9993, Found 334.0001.

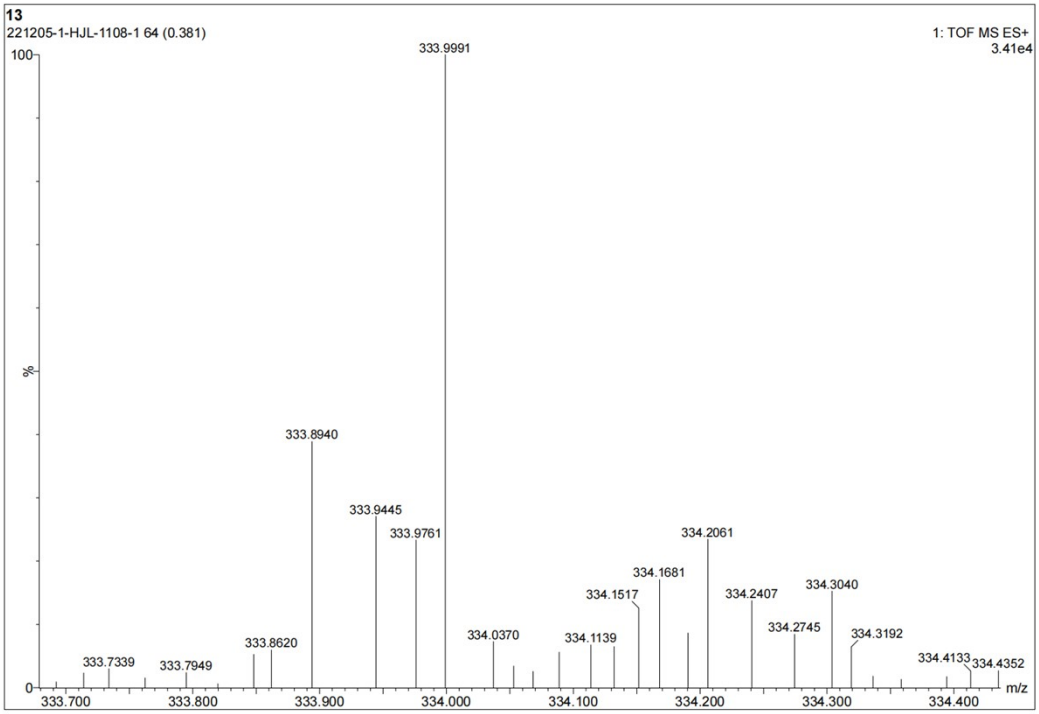


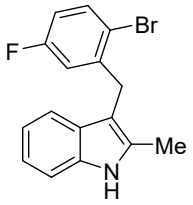



**1g**

**3-(2-bromo-5-chlorobenzyl)-2-methyl-1*H*-indole (1g)**

Flash column chromatography on a silica gel (PE/EA, v/v, 60:1) gives **1g** (1.03 g, 62% yield) as a yellowish solid: mp 68-69 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.58 (d, $J$ = 8.5 Hz, 1H), 7.48 (d, $J$ = 8.1 Hz, 1H), 7.36 – 7.34 (m, 1H), 7.30 – 7.26 (m, 1H), 7.21 – 7.18 (m, 1H), 7.10 (dd, $J_1$ = 8.5 Hz, $J_2$ = 2.6 Hz, 1H), 7.05 (d, $J$ = 2.6 Hz, 1H), 4.22 (s, 2H), 2.36 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 142.4, 135.4, 133.53, 133.49, 132.6, 129.9, 128.7, 127.7, 122.4, 121.4, 119.6, 118.2, 110.4, 108.2, 30.5, 11.9. IR (cm$^{-1}$): 3389(N-H), 3169(Ar-H), 1660(Ar C=C), 1458(C-H), 1402(C-H), 1093(Ar-Cl), 1030(Ar-Br), 935(C-C), 816(C-C), 737(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{14}BrClN^+$ 333.9993, Found 333.9991.

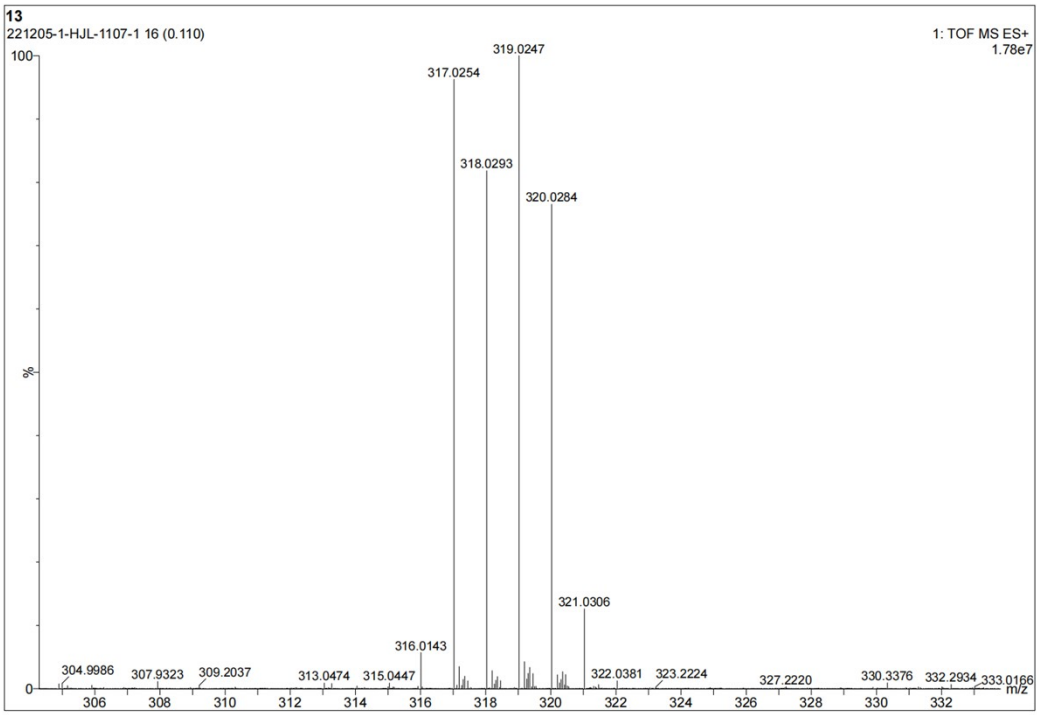


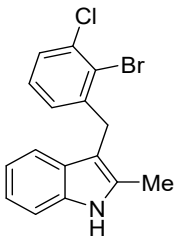



**1h**

**3-(2-bromo-5-fluorobenzyl)-2-methyl-1*H*-indole (1h)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1h** (1.47 g, 93% yield) as a yellowish soild: m.p. 121-122 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.58 (dd, $J_1$ = 8.7 Hz, $J_2$ = 5.4 Hz, 1H), 7.41 (d, $J$ = 7.9 Hz, 1H), 7.34 (d, $J$ = 8.1 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.15 – 7.11 (m, 1H), 6.82 (td, $J_1$ = 8.2 Hz, $J_2$ = 3.1 Hz, 1H), 6.72 (dd, $J_1$ = 9.9 Hz, $J_2$ = 3.1 Hz, 1H), 4.17 (s, 2H), 2.36 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 244.4 Hz), 142.9 (d, $J_{C\text{-}F}$ = 6.9 Hz), 135.5, 133.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 132.7, 128.8, 121.4, 119.7, 118.5 (d, $J_{C\text{-}F}$ = 2.9 Hz, 1H), 118.3, 117.0 (d, $J_{C\text{-}F}$ = 23.5 Hz), 114.7 (d, $J_{C\text{-}F}$ = 22.6 Hz), 110.5, 108.3, 30.6, 11.8. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -114.9. IR (cm$^{-1}$): 3388(N-H), 3050(Ar-H), 1610(Ar C=C), 1460(C-H), 1300(C-H), 1174(Ar-F), 1003(Ar-Br), 870(C-C), 815(C-C), 741(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{14}BrFN^+$ 318.0288, Found 318.0293.

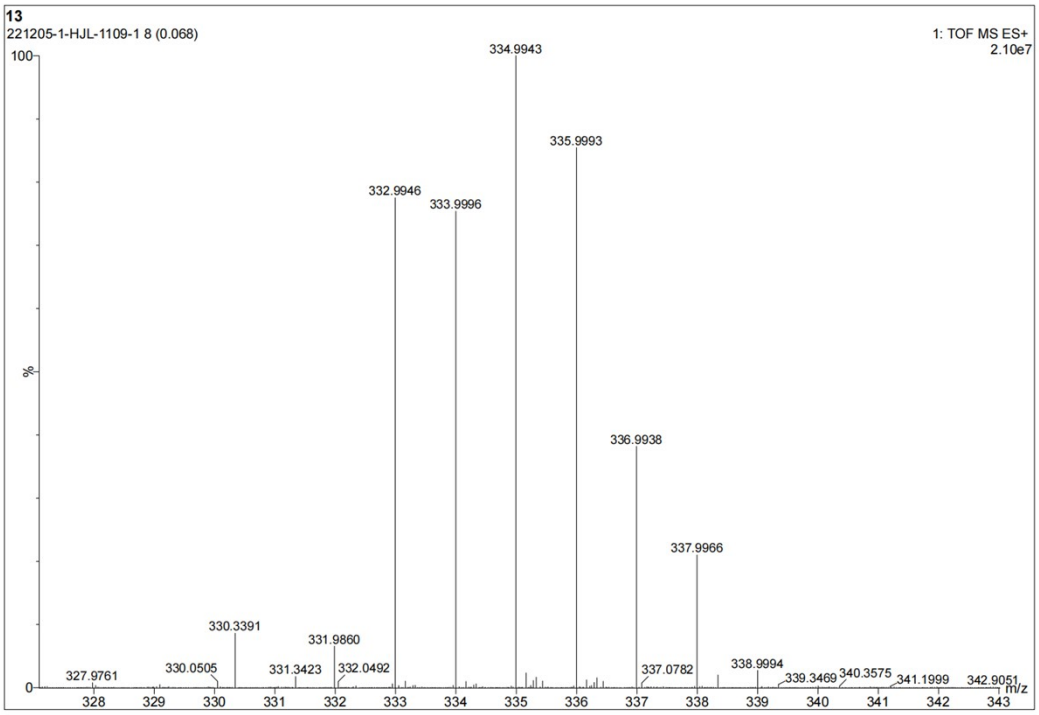


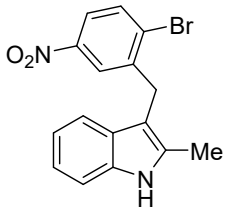



**1i**

**3-(2-bromo-3-chlorobenzyl)-2-methyl-1*H*-indole (1i)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1i** (580 mg, 43% yield) as a yellowish solid: m.p. 69-70 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.32 (d, *J* = 1.2 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.17 – 7.13 (m, 1H), 7.07 – 7.00 (m, 2H), 6.84 – 6.80 (m, 1H), 4.18 (s, 2H), 2.35 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 143.1, 135.4, 134.9, 132.6, 128.8, 127.9, 127.8, 127.7, 124.5, 121.3, 119.5, 118.3, 110.3, 108.7, 31.8, 11.8. IR ($cm^{-1}$): 3401(N-H), 3174(Ar-H), 1654(Ar C=C), 1402(C-H), 1085(Ar-Cl), 1000(Ar-Br), 930(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{14}BrClN^+$ 333.9993, Found 333.9996.

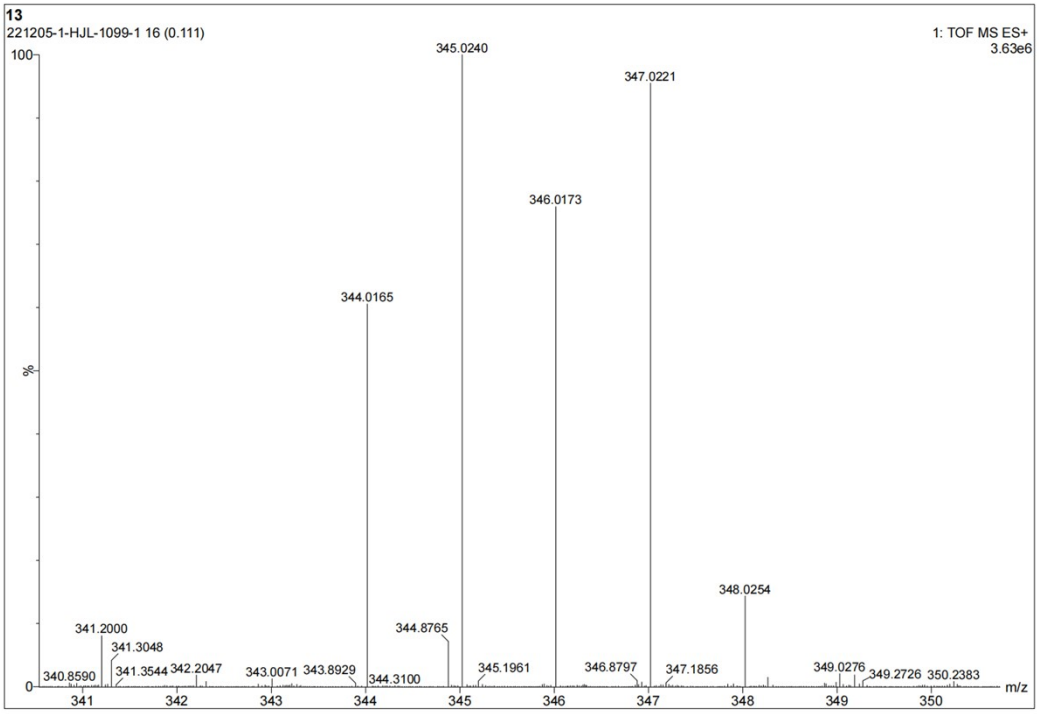


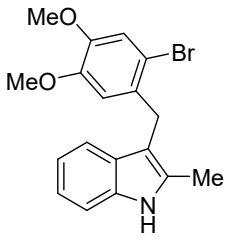



**1j**

**3-(2-bromo-5-nitrobenzyl)-2-methyl-1*H*-indole (1j)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1j** (1.26 g, 74% yield) as a yellow solid: m.p. 150-151 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.89 (dd, $J_1$ = 8.7 Hz, $J_2$ = 2.8 Hz, 1H), 7.85 – 7.70 (m, 2H), 7.32 (d, $J$ = 8.2 Hz, 1H), 7.29 (d, $J$ = 7.8 Hz, 1H), 7.16 (t, $J$ = 7.5 Hz, 1H), 7.06 (t, $J$ = 7.5 Hz, 1H), 4.20 (s, 2H), 2.39 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 147.5, 142.8, 135.5, 133.4, 132.7, 131.7, 128.4, 124.6, 122.2, 121.6, 119.7, 117.9, 110.5, 107.4, 30.7, 11.9. IR (cm$^{-1}$): 3389(N-H), 3169(Ar-H), 1654(Ar C=C), 1617($NO_2$), 1402(C-H), 1085(Ar-Br), 928(C-C), 746(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{14}BrN_2O_2^+$ 345.0233, Found 345.0240.

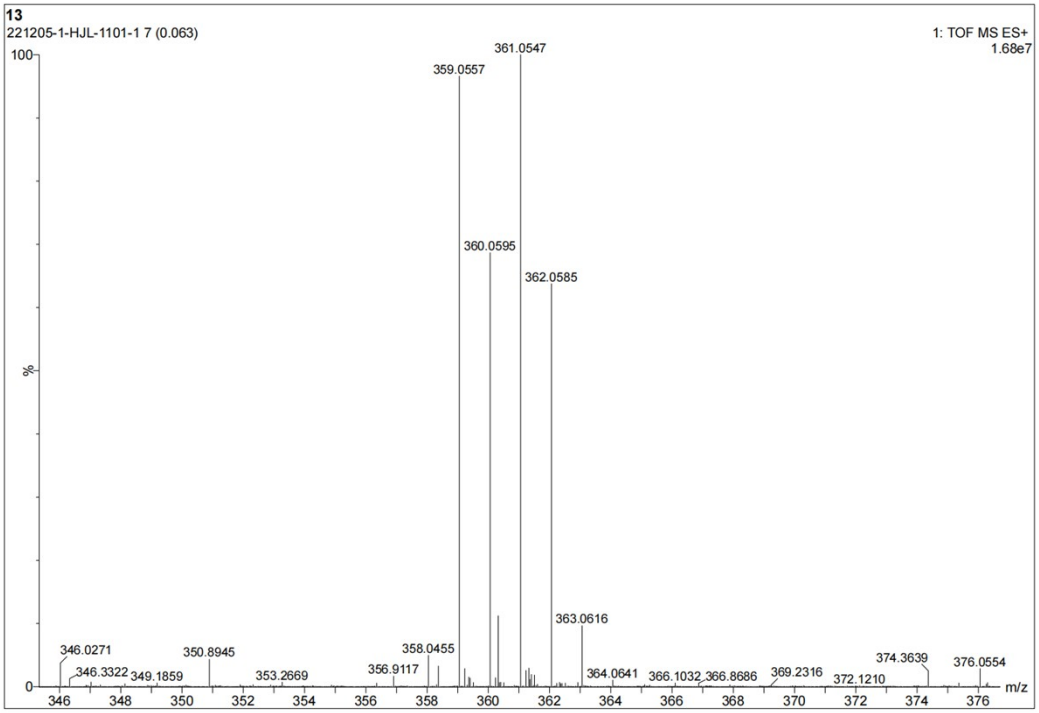


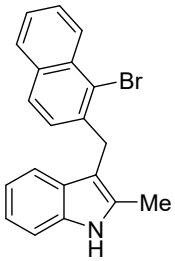



**1k**

**3-(2-bromo-4,5-dimethoxybenzyl)-2-methyl-1*H*-indole (1k)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1k** (470 mg, 26% yield) as a yellowish solid: m.p. 134-135 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.37 (dd, $J_1$ = 7.9 Hz, $J_2$ = 1.1 Hz, 1H), 7.28 (d, $J$ = 8.0 Hz, 1H), 7.13 – 7.10 (m, 1H), 7.08 – 7.00 (m, 2H), 6.57 (s, 1H), 4.08 (s, 2H), 3.85 (s, 3H), 3.56 (s, 3H), 2.36 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 148.4, 147.8, 135.4, 132.5, 132.1, 128.9, 121.1, 119.4, 118.5, 115.4, 114.1, 113.1, 110.2, 109.4, 56.2, 55.9, 30.0, 11.9. IR ($cm^{-1}$): 3359(N-H), 3187(Ar-H), 1654(Ar C=C), 1503(C-N), 1402(C-H), 1161(C-O-C), 1084(Ar-Br), 929(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}BrNO_2^+$ 360.0594, Found 360.0595.

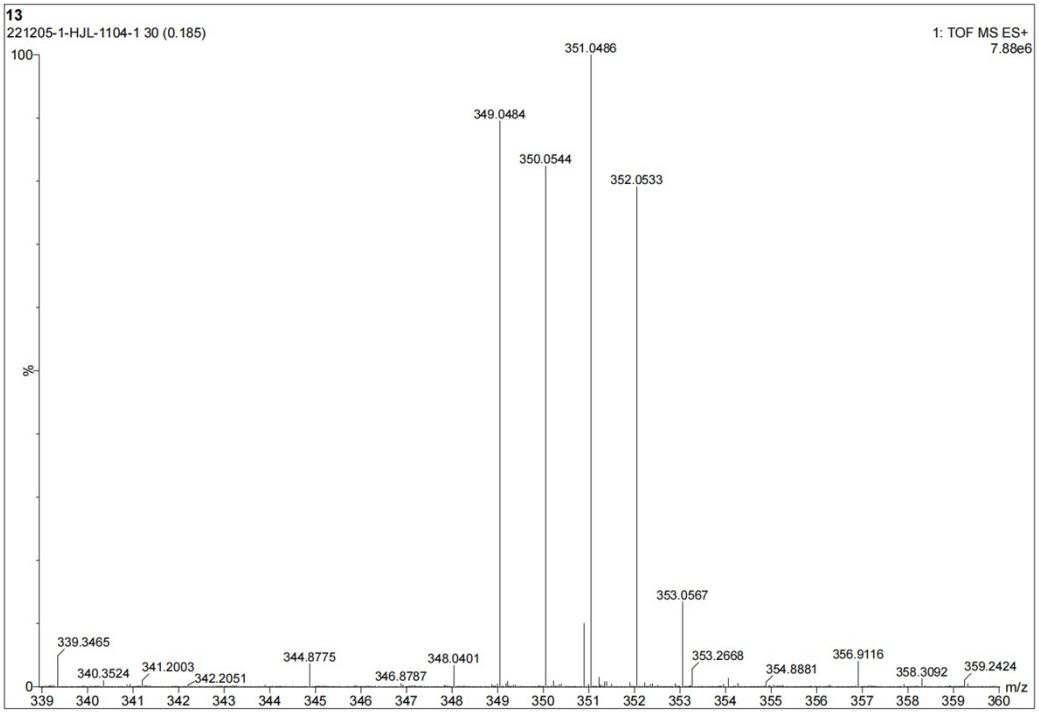


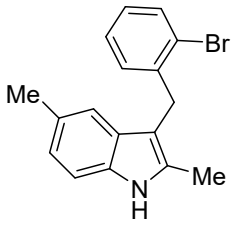



**1l**

**3-((1-bromonaphthalen-2-yl)methyl)-2-methyl-1*H*-indole (1l)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1l** (860 mg, 70% yield) as a yellow solid: m.p. 138-139 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, $J_1$ = 8.6 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.64 – 7.57 (m, 2H), 7.51 – 7.47 (m, 1H), 7.41 (d, $J$ = 7.9 Hz, 1H), 7.31 (d, $J$ = 8.0 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.06 (t, $J$ = 7.5 Hz, 1H), 4.44 (s, 2H), 2.37 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 138.7, 135.4, 133.4, 132.6, 132.4, 129.1, 128.1, 127.6, 127.4, 127.32, 127.28, 125.9, 123.7, 121.2, 119.5, 118.5, 110.3, 109.6, 31.5, 11.9. IR ($cm^{-1}$): 3375(N-H), 3165(Ar-H), 1616(Ar C=C), 1402(C-H), 1084(Ar-Br), 929(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{17}BrN^+$ 350.0539, Found 350.0544.

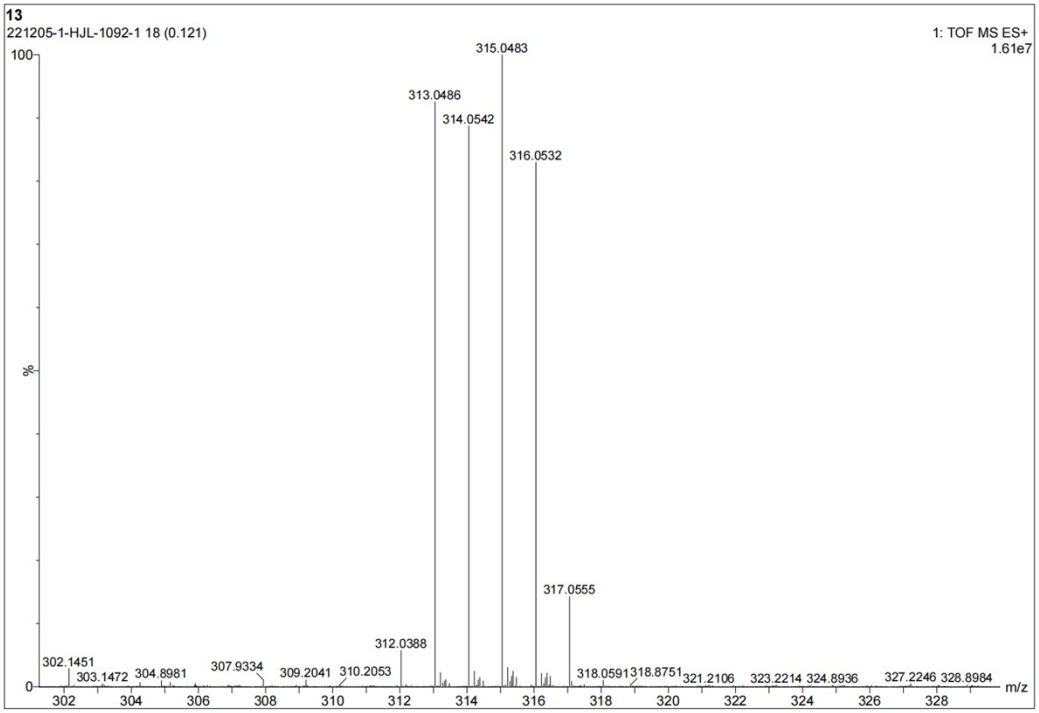


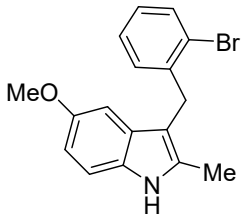



**1m**

**3-(2-bromobenzyl)-2,5-dimethyl-1*H*-indole (1m)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1m** (660 mg, 42% yield) as a white solid: m.p. 141-142 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.61 (dd, $J_1$ = 7.9 Hz, $J_2$ = 1.4 Hz, 1H), 7.21 (d, $J$ = 8.2 Hz, 1H), 7.16 (s, 1H), 7.13 – 7.10 (m, 1H), 7.08 – 7.04 (m, 1H), 6.99 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.6 Hz, 1H), 6.97 – 6.94 (m, 1H), 4.14 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 140.5, 133.7, 132.6, 132.4, 130.0, 129.3, 128.6, 127.42, 127.36, 124.7, 122.7, 118.2, 110.0, 108.5, 30.4, 21.6, 11.9. IR (cm$^{-1}$): 3390(N-H), 3178(Ar-H), 1647(Ar C=C), 1402(C-H), 1085(Ar-Br), 930(C-C), 750(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}BrN^+$ 314.0539, Found 314.0542.

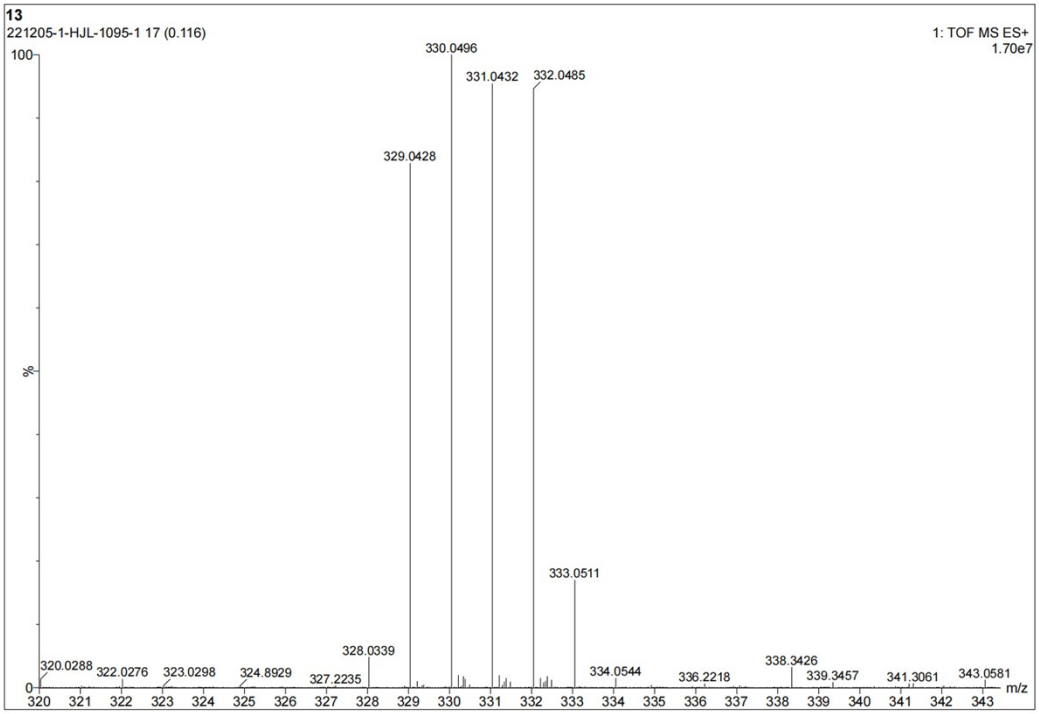


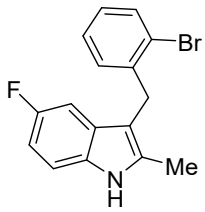



**1n**

**3-(2-bromobenzyl)-5-methoxy-2-methyl-1*H*-indole (1n)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1n** (270 mg, 16% yield) as a yellowish solid: m.p. 105-106 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.59 (dd, $J_1$ = 7.9 Hz, $J_2$ = 1.4 Hz, 1H), 7.18 (dd, $J_1$ = 8.6 Hz, $J_2$ = 0.6 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.06 – 7.02 (m, 1H), 6.97 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.9 Hz, 1H), 6.83–6.76 (m, 2H), 4.12 (s, 2H), 3.78 (s, 3H), 2.33 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 154.0, 140.3, 133.3, 132.5, 130.5, 130.0, 129.4, 127.5, 127.4, 124.6, 110.9, 110.8, 108.9, 100.9, 55.9, 30.5, 11.9. IR (cm$^{-1}$): 3403(N-H), 3180(Ar-H), 1654(Ar C=C), 1402(C-H), 1160(C-O-C), 1084(Ar-Br), 931(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}BrNO^+$ 330.0488, Found 330.0496.

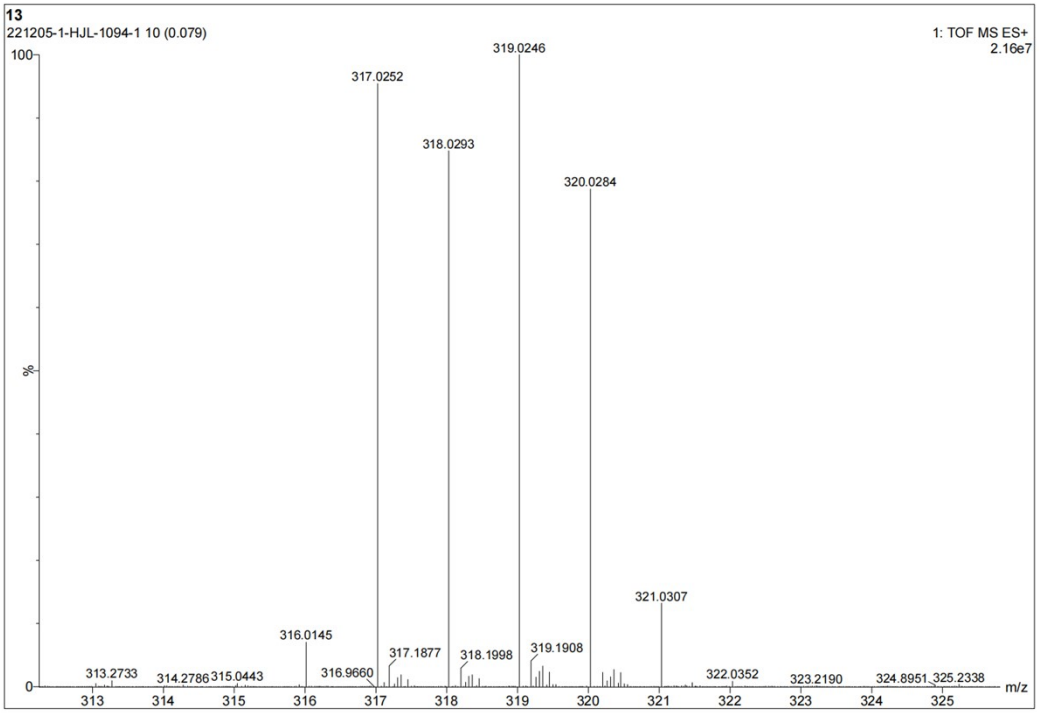


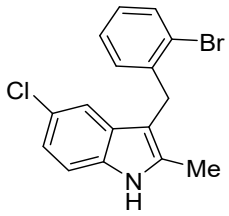



**1o**

**3-(2-bromobenzyl)-5-fluoro-2-methyl-1*H*-indole (1o)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1o** (320 mg, 20% yield) as a brown solid: m.p. 115-116 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.58 (dd, $J_1$ = 7.9 Hz, $J_2$ = 1.4 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.13 – 7.10 (m, 1H), 7.06 – 7.03 (m, 1H), 6.98 – 6.92 (m, 2H), 6.85 (td, $J_1$ = 9.0 Hz, $J_2$ = 2.5 Hz, 1H), 4.09 (s, 2H), 2.36 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 157.9 (d, $J_{C\text{-}F}$ = 232.8 Hz), 139.9, 134.3, 132.6, 131.8, 129.9, 129.4 (d, $J_{C\text{-}F}$ = 9.7 Hz), 127.5 (d, $J_{C\text{-}F}$ = 28.8 Hz), 124.6, 110.7 (d, $J_{C\text{-}F}$ = 9.7 Hz), 109.34 (d, $J_{C\text{-}F}$ = 4.2 Hz), 109.26, 109.1, 103.5 (d, $J_{C\text{-}F}$ = 23.5 Hz), 30.5, 12.0. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -124.8. IR ($cm^{-1}$): 3421(N-H), 3280(Ar-H), 1647(Ar C=C), 1402(C-H), 1092(Ar-F), 940(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{14}BrFN^+$ 318.0288, Found 318.0293.

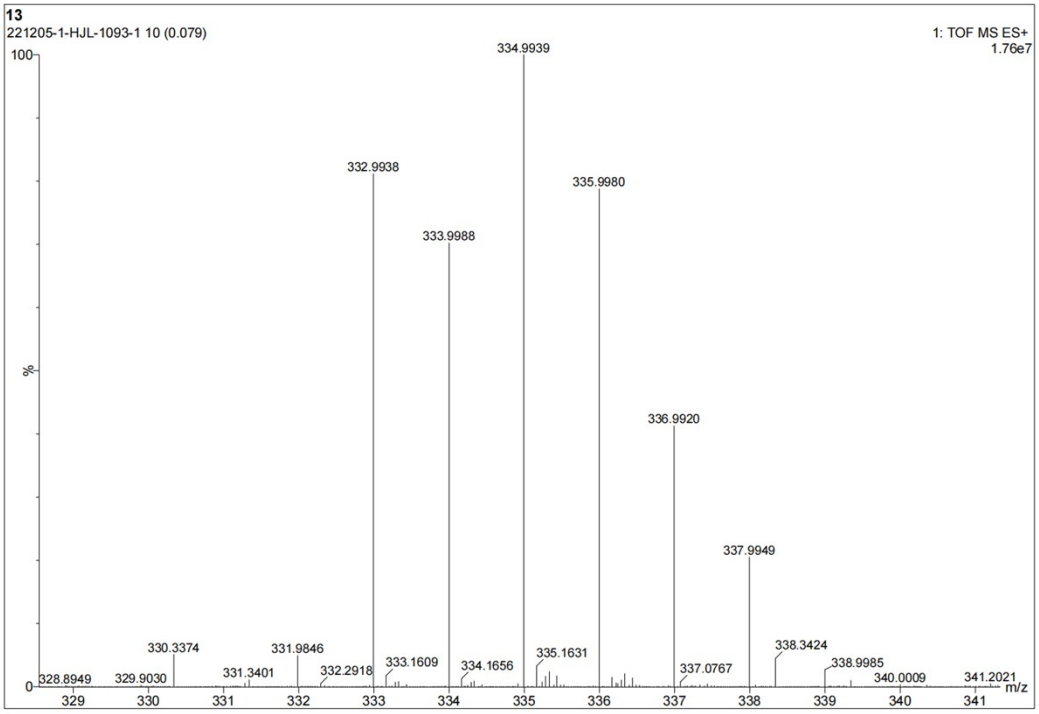


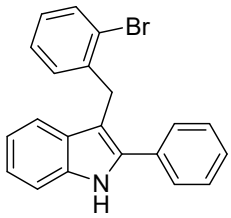



**1p**

**3-(2-bromobenzyl)-5-chloro-2-methyl-1*H*-indole (1p)**

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1p** (940 mg, 56% yield) as a yellowish solid: m.p. 137-138 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.59 (dd, $J_1$ = 7.9 Hz, $J_2$ = 1.4 Hz, 1H), 7.29 (d, $J$ = 2.0 Hz, 1H), 7.20 (d, $J$ = 8.4 Hz, 1H), 7.12 (t, $J$ = 7.4 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.91 (dd, $J_1$ = 7.7 Hz, $J_2$ = 1.8 Hz, 1H), 4.09 (s, 2H), 2.34 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 139.8, 134.0, 133.7, 132.6, 130.1, 129.8, 127.6, 127.4, 125.1, 124.6, 121.4, 117.9, 111.2, 108.9, 30.3, 11.9. IR (cm$^{-1}$): 3415(N-H), 3169(Ar-H), 1654(Ar C=C), 1467(C-H), 1402(C-H), 1085(Ar-Cl), 1000(Ar-Br), 930(C-C), 801(C-C), 754(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{14}BrClN^+$ 333.9993, Found 333.9988.

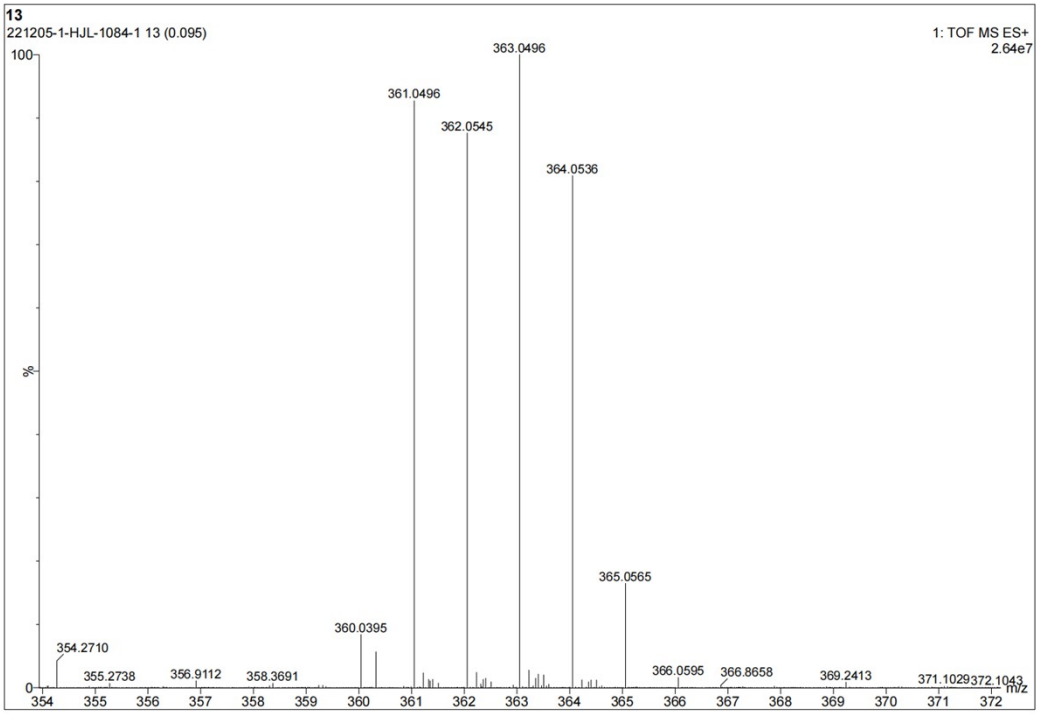


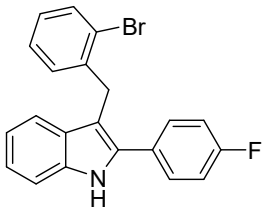



**1q**

**3-(2-bromobenzyl)-2-phenyl-1*H*-indole (1q)**[1]

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1q** (1.20 g, 67% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.64 (dd, $J_1$ = 7.7 Hz, $J_2$ = 1.7 Hz, 1H), 7.48 – 7.45 (m, 3H), 7.44 – 7.35 (m, 4H), 7.27 – 7.23 (m, 1H), 7.09 (m, 3H), 7.03 (dd, $J_1$ = 7.3 Hz, $J_2$ = 2.2 Hz, 1H), 4.34 (s, 2H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 140.3, 136.1, 135.9, 132.7, 132.5, 129.9, 129.5, 129.0, 127.9, 127.64, 127.57, 127.5, 124.7, 122.6, 120.0, 119.5, 110.88, 110.87, 109.9, 31.1. IR ($cm^{-1}$): 3426(N-H), 1614(Ar C=C), 1489(C-H), 1457(C-H), 1002(Ar-Br), 744(C-C), 692(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{17}BrN^+$ 362.0539, Found 362.0548.

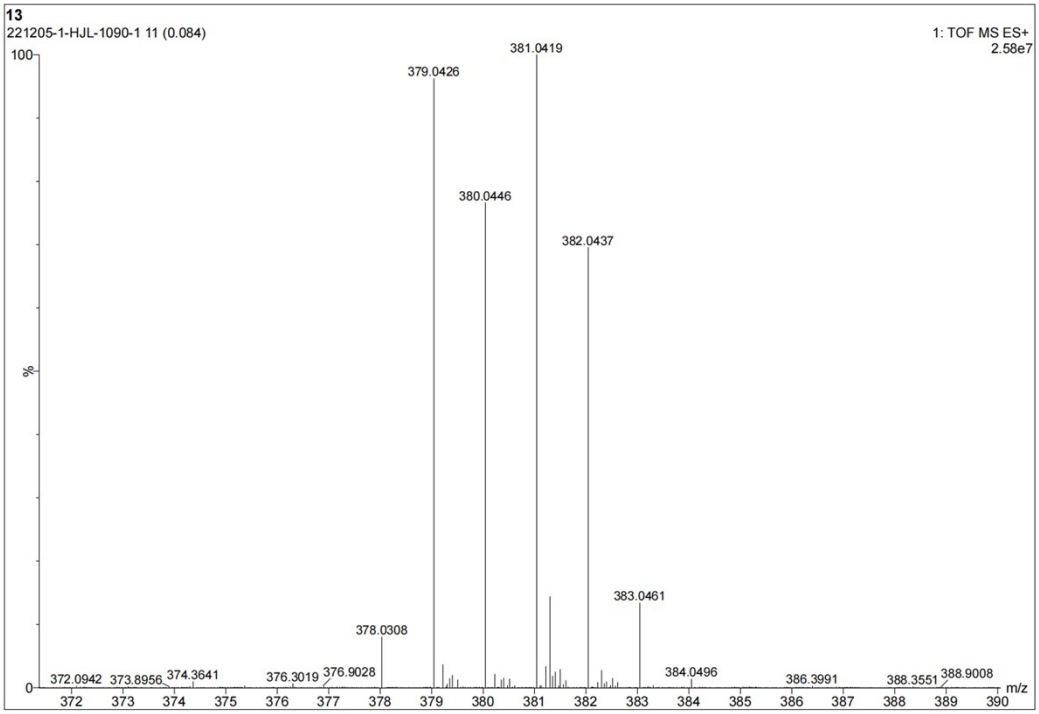


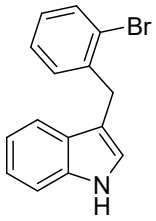



**1r**

**3-(2-bromobenzyl)-2-(4-fluorophenyl)-1*H*-indole (1r)**[1]

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1r** (865 mg, 46% yield) as a yellow solid: m.p. 116-117 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.62 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.41 (m, 4H), 7.24 (m, 1H), 7.14 – 7.05 (m, 5H), 6.99 (dd, $J_1$ = 7.3 Hz, $J_2$ = 2.1 Hz, 1H), 4.27 (s, 2H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 163.5, 161.5, 140.1, 136.0, 135.0, 132.6, 129.8, 129.43, 129.39, 129.36, 128.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 127.6, 127.5, 124.7, 122.7, 120.1, 119.5, 116.1 (d, $J_{C\text{-}F}$ = 21.6 Hz), 110.9, 110.0, 31.0. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -113.4. IR ($cm^{-1}$): 3464(N-H), 3063(Ar-H), 2985(C-H), 1613(Ar C=C), 1441(C-H), 1398(C-H), 1215(Ar-F), 1024(Ar-Br), 839(C-C), 745(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{16}BrFN^+$ 380.0445, Found 380.0446.

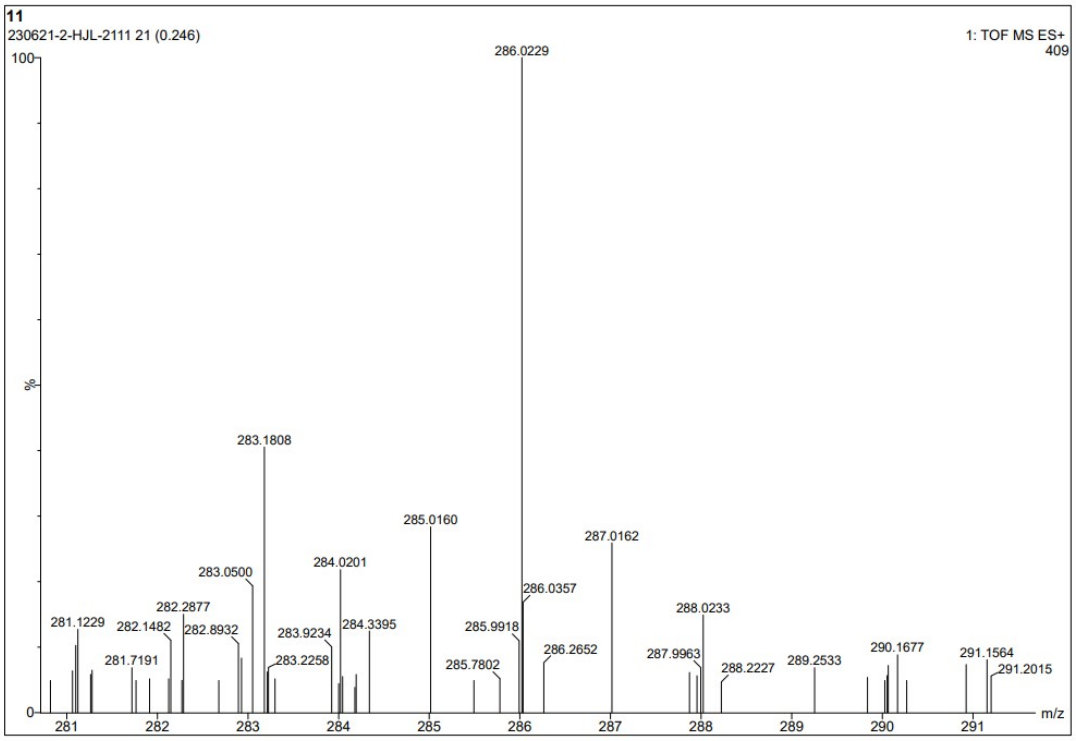


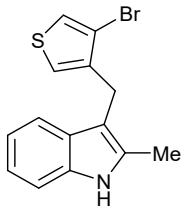



**1s**

**3-(2-bromobenzyl)-1*H*-indole (1s)**[3]

Flash column chromatography on a silica gel (PE/EA, v/v, 30:1) gives **1p** (266.3 mg, 93% yield) as a faint yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.57 (dd, $J_1$ = 15.4, $J_2$ = 7.8 Hz, 2H), 7.38 (d, $J$ = 8.2 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.13 – 7.05 (m, 2H), 6.98 – 6.92 (m, 1H), 4.23 (s, 2H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 140.4, 136.4, 132.7, 130.6, 127.6, 127.43, 127.39, 124.6, 122.8, 122.1, 119.5, 119.2, 114.1, 111.1, 31.9. IR ($cm^{-1}$): 3416(N-H), 3057(C=CH), 1592(C=C), 1441(C-H), 1107(C-N), 1044(Ar-Br), 740(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{13}BrN^+$ 286.0226; Found 286.0229.

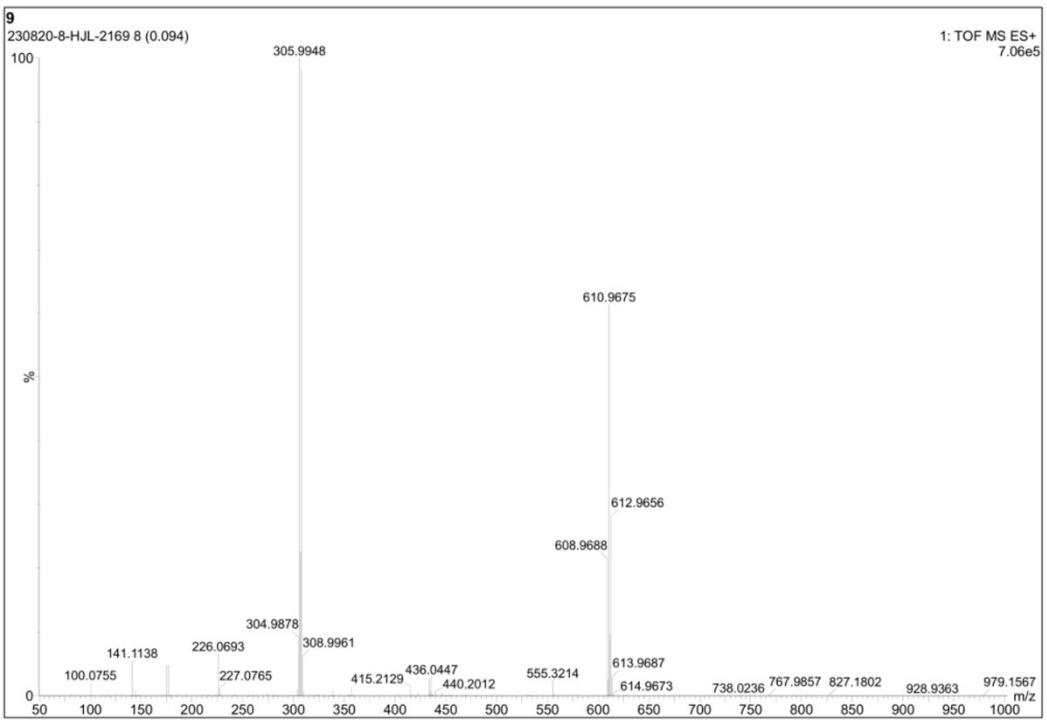


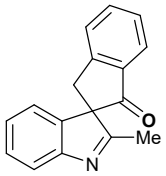



**1t**

**3-((4-bromothiophen-3-yl)methyl)-2-methyl-1*H*-indole (1t)**

Flash column chromatography on a silica gel (PE/EA, v/v, 60:1) gives **1t** (320.3 mg, 87% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.62 (d, *J* = 5.7 Hz, 1H), 4.00 – 3.94 (m, 2H), 2.39 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 141.1, 135.2, 131.6, 128.8, 128.6, 125.1, 121.2, 119.4, 118.3, 110.2, 109.7, 108.3, 24.4, 11.9. IR ($cm^{-1}$): 3389(N-H), 3169(C-H), 1654(Ar C=C), 1402(C-H), 1085(Ar-Br), 928(C-C), 746(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{13}BrNS^+$ 305.9947, Found 305.9948.

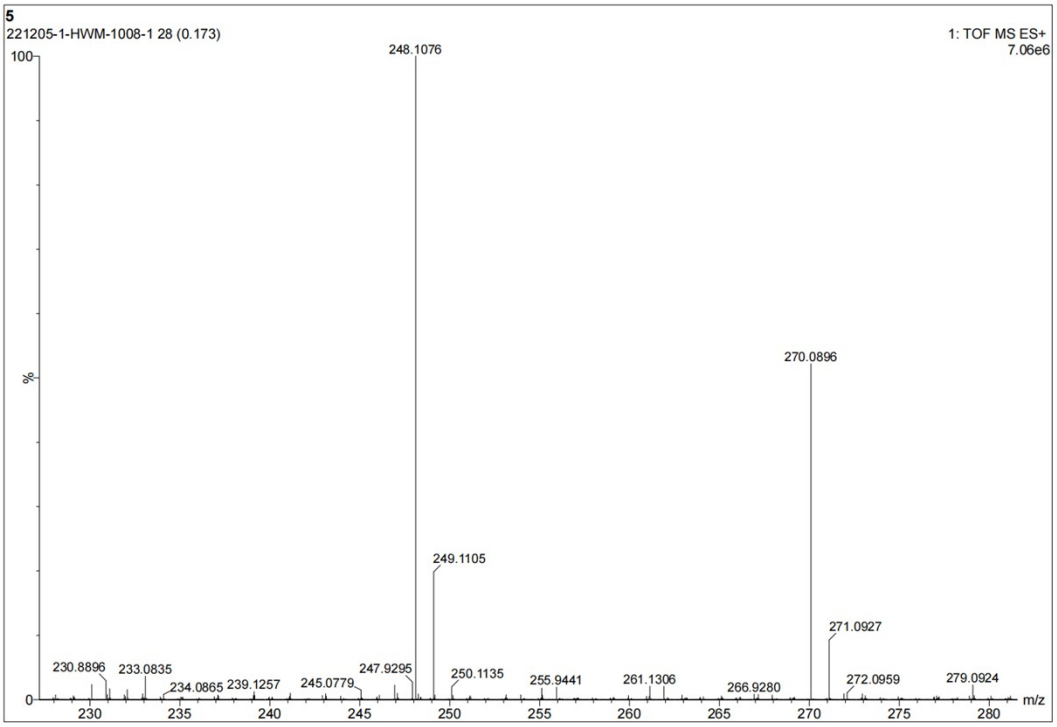


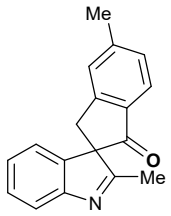



**2a**

**2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2a)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2a** (19.8 mg, 80% yield) as a yellow solid: m.p. 149-150 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, $J$ = 7.7 Hz, 1H), 7.74 (t, $J$ = 7.5, 1H), 7.66 – 7.59 (m, 2H), 7.52 – 7.44 (m, 1H), 7.35 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.13 (td, $J_1$ = 7.5 Hz, $J_2$ = 1.1 Hz, 1H), 7.00 (d, $J$ = 7.5 Hz, 1H), 3.62 (d, $J$ = 17.7 Hz, 1H), 3.49 (d, $J$ = 17.7 Hz, 1H), 2.16 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 200.3, 179.3, 156.4, 152.7, 140.6, 136.4, 135.8, 128.7, 128.2, 126.9, 125.8, 125.4, 121.1, 120.3, 72.4, 35.2, 16.4. IR (cm$^{-1}$): 2986(C-H), 1663(C=O), 1614(C=N), 1614(Ar C=C), 1441(C-H), 1174(C-N), 776(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{14}NO^+$ 248.1070, Found 248.1076.

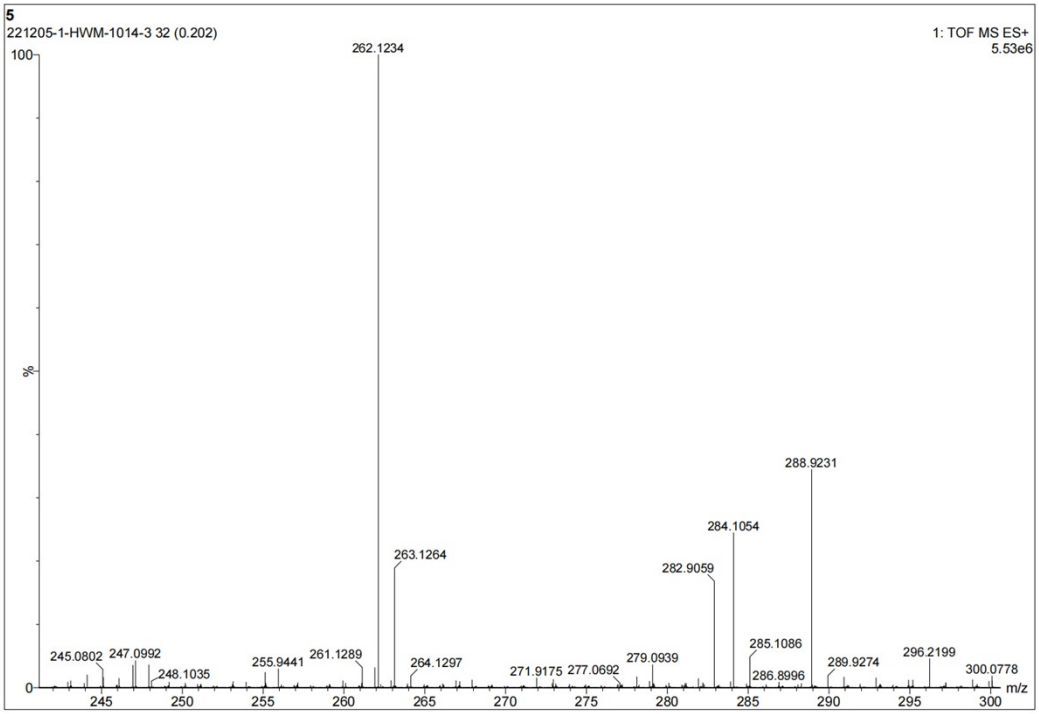


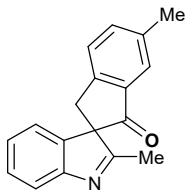



**2b**

**2',5-dimethylspiro[indene-2,3'-indol]-1(3*H*)-one (2b)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2b** (19.6 mg, 75% yield) as a yellow solid: m.p. 126-127 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.44 (s, 1H), 7.36 – 7.28 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 3.56 (d, *J* = 17.6 Hz, 1H), 3.43 (d, *J* = 17.6 Hz, 1H), 2.52 (s, 3H), 2.15 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 199.7, 179.6, 156.4, 153.3, 147.4, 140.8, 134.2, 129.6, 128.6, 127.3, 125.8, 125.3, 121.1, 120.3, 72.6, 35.1, 22.2, 16.4. IR ($cm^{-1}$): 2983(C-H), 1705(C=O), 1613(Ar C=C), 1613(C=N), 1440(C-H), 1174(C-N), 775(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{16}NO^+$ 262.1226, Found 262.1234.

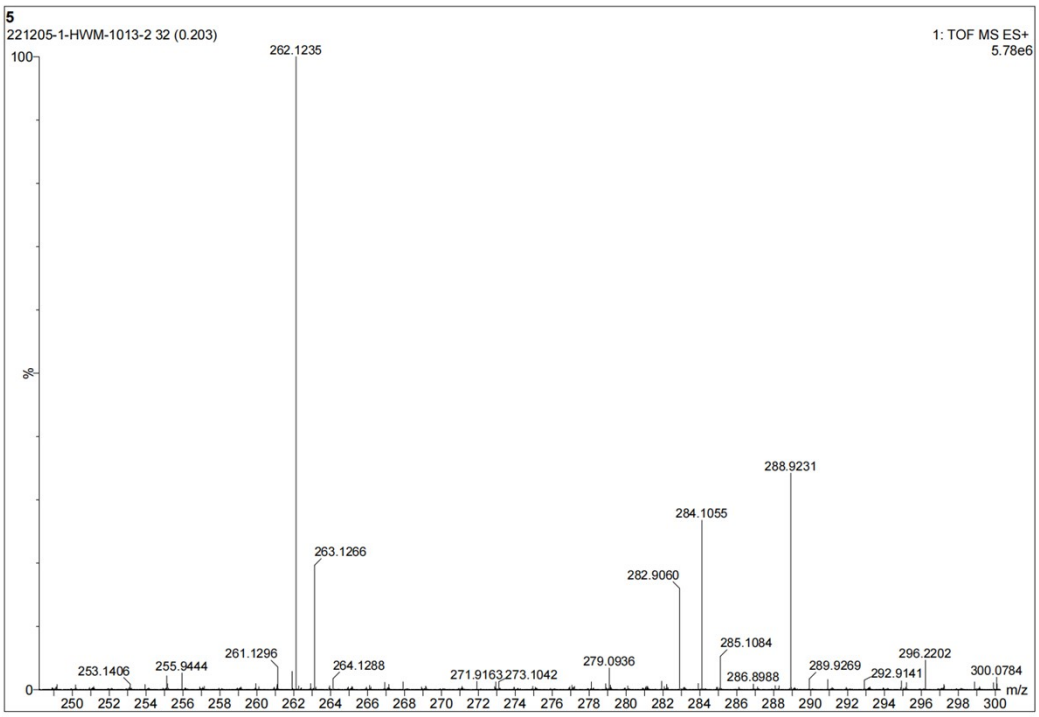


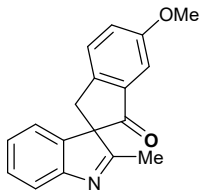



**2c**

**2',6-dimethylspiro[indene-2,3'-indol]-1(3*H*)-one (2c)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2c** (20.4 mg, 78% yield) as a yellow solid: m.p. 148-149 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.34 – 7.30 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 3.54 (d, *J* = 17.5 Hz, 1H), 3.42 (d, *J* = 17.5 Hz, 1H), 2.45 (s, 3H), 2.14 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 200.4, 179.5, 156.4, 150.2, 140.8, 138.4, 137.1, 136.6, 128.6, 126.6, 125.8, 125.3, 121.1, 120.2, 72.8, 34.9, 21.1, 16.4. IR (cm$^{-1}$): 2986(C-H), 1689(C=O), 1613(Ar C=C), 1558(C=N), 1441(C-H), 1174(C-N), 1007(C-C), 800(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{16}NO^+$ 262.1226, Found 262.1235.

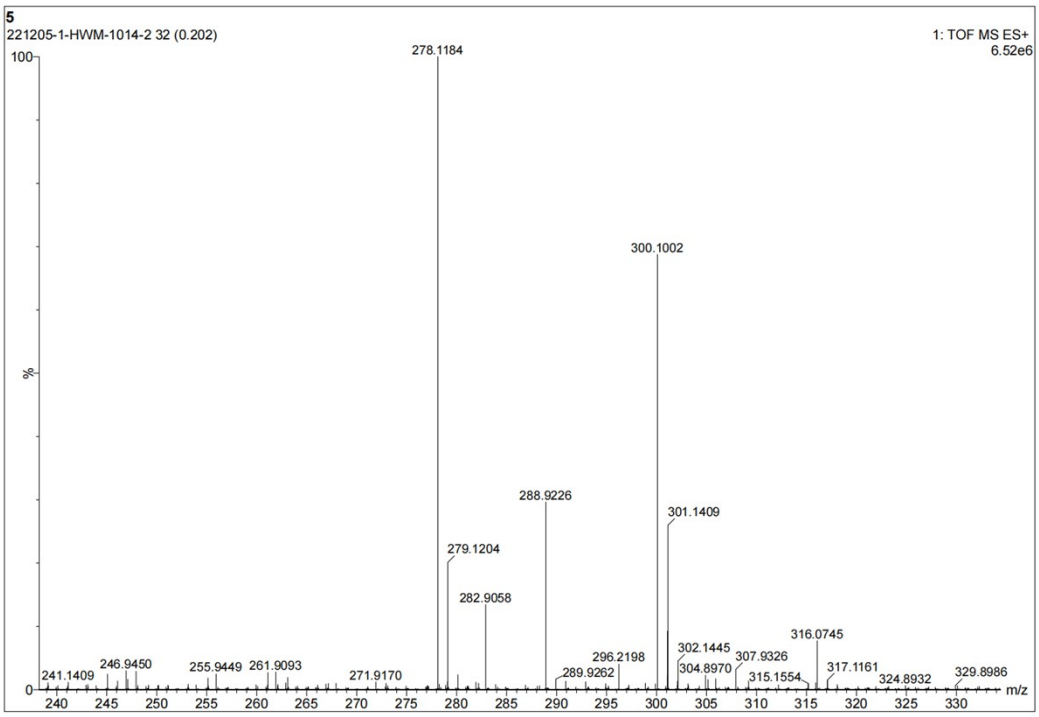


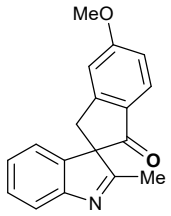



**2d**

**6-methoxy-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2d)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2d** (22.7 mg, 82% yield) as a yellow solid: m.p. 183-184 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.25 (d, *J* = 2.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 3.85 (s, 3H), 3.51 (d, *J* = 17.3 Hz, 1H), 3.39 (d, *J* = 17.3 Hz, 1H), 2.14 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 200.3, 179.4, 160.1, 156.4, 145.6, 140.7, 137.7, 128.7, 127.6, 125.8, 125.3, 121.1, 120.3, 106.4, 73.2, 55.7, 34.5, 16.4. IR ($cm^{-1}$): 2922(C-H), 1703(C=O), 1613(Ar C=C), 1580(C=N), 1434(C-H), 1172(C-N), 1024(C-O-C), 847(C-C), 779(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{16}NO_2^+$ 278.1176, Found 278.1184.

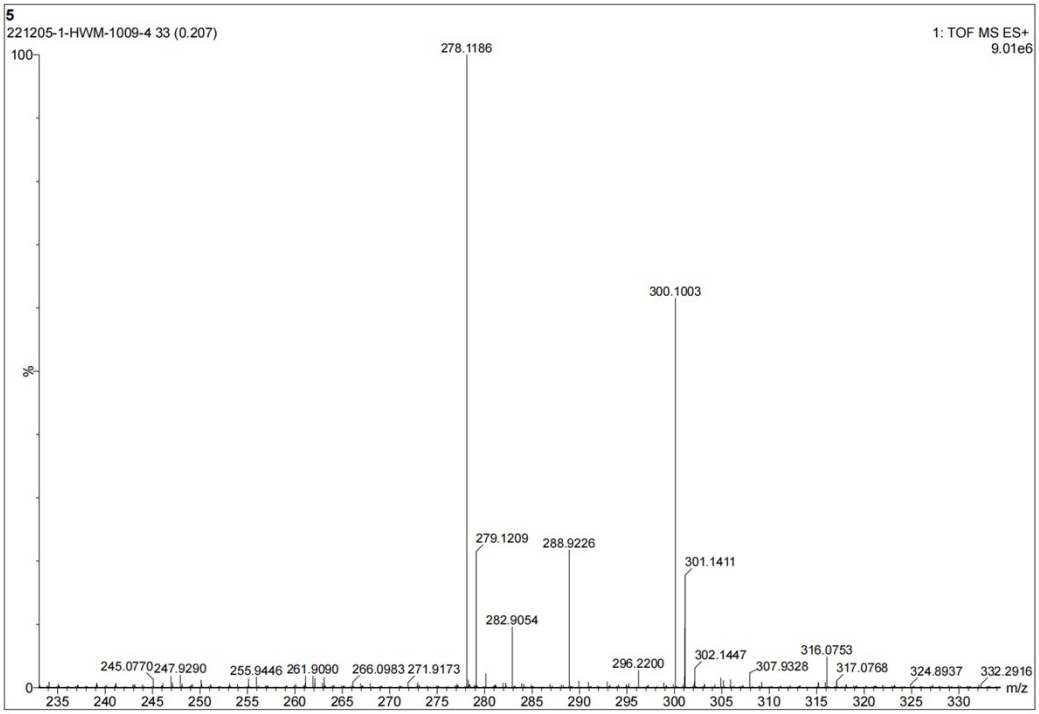


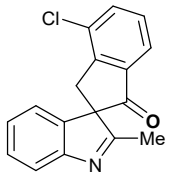



**2e**

**5-methoxy-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2e)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2e** (22.2 mg, 80% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, $J$ = 8.5 Hz, 1H), 7.59 (d, $J$ = 7.7 Hz, 1H), 7.34 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.13 (t, $J$ = 7.5 Hz, 1H), 7.05 (s, 1H), 7.03 – 6.99 (m, 2H), 3.95 (s, 3H), 3.55 (d, $J$ = 17.6 Hz, 1H), 3.43 (d, $J$ = 17.6 Hz, 1H), 2.16 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 198.3, 179.7, 166.2, 156.3, 155.9, 140.9, 129.6, 128.6, 127.1, 125.8, 121.1, 120.2, 116.3, 110.1, 72.7, 55.9, 35.2, 16.3. IR ($cm^{-1}$): 2987(C-H), 1705(C=O), 1613(Ar C=C), 1613(C=N), 1441(C-H), 1174(C-N), 1003(C-O-C), 780(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{16}NO_2^+$ 278.1176, Found 278.1186.

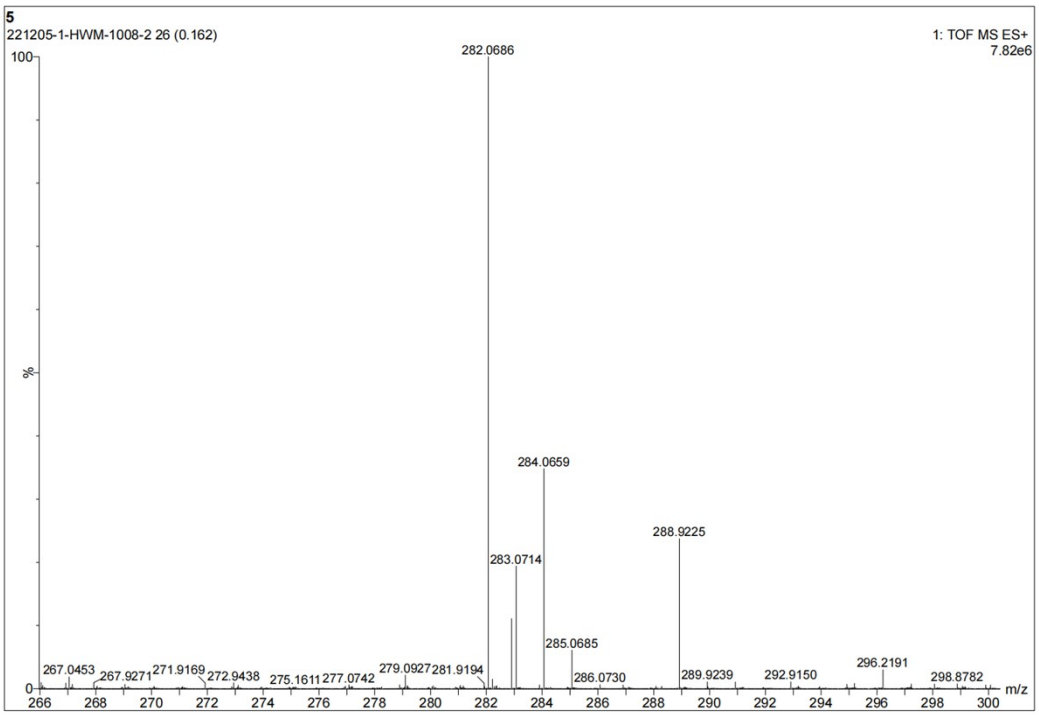


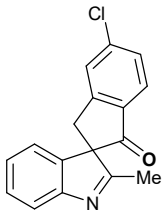



**2f**

**4-chloro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2f)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2f** (13.8 mg, 49% yield) as a yellowish solid: m.p. 101-102 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.61 (d, $J$ = 7.8 Hz, 1 H), 7.48 (t, $J$ = 7.7 Hz, 1H), 7.36 (dt, $J_1$ = 7.7 Hz, $J_2$ = 1.2 Hz, 1H), 7.15 (t, $J$ = 7.5 Hz, 1H), 7.0 (d, $J$ = 7.5 Hz, 1H), 3.59 (d, $J$ = 18.3 Hz, 1H), 3.48 (d, $J$ = 18.3 Hz, 1H), 2.17 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 199.4, 178.6, 156.3, 150.3, 140.2, 138.2, 135.4, 133.2, 129.9, 128.9, 126.0, 123.6, 121.1, 120.4, 72.1, 34.1, 16.4. IR (cm$^{-1}$): 2986(Ar-H), 1655(C=O), 1614(C=N), 1614(Ar C=C), 1441(C-H), 1051(C-Cl), 788(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{13}ClNO^+$ 282.0680, Found 282.0686.

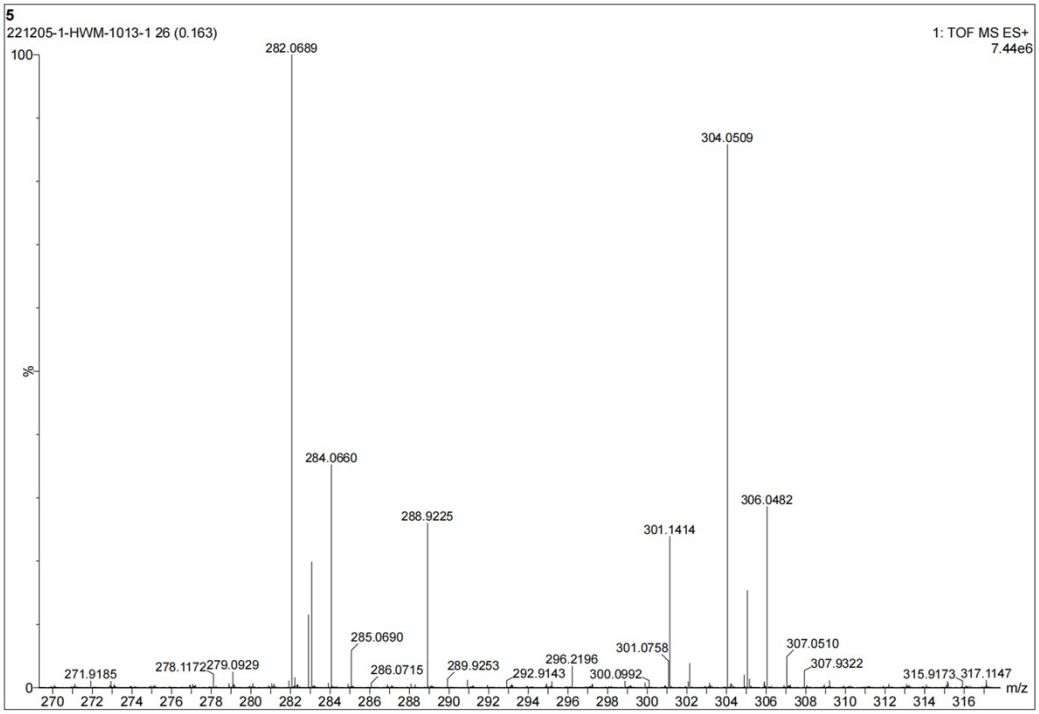


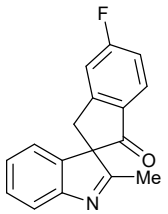



**2g**

**6-chloro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2g)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2g** (15.7 mg, 56% yield) as a yellowish solid: m.p. 142-143 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, $J$ = 8.2Hz, 1H), 7.64 (s, 1H), 7.59 (d, $J$ = Hz, 1H), 7.48-7.46 (m, 1H), 7.34 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.12 (dt, $J_1$ = 8.7 Hz, $J_2$ = 1.1 Hz, 1H), 6.98 (d, $J$ = 7.4 Hz, 1H), 3.57 (d, $J$ = 17.9 Hz, 1H), 3.45 (d, $J$ = 17.9 Hz, 1H), 2.15 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ198.8, 178.7, 156.3, 154.1, 142.5, 140.2, 134.8, 129.1, 128.8, 127.1, 126.3, 125.9, 121.0, 120.3, 72.3, 34.8, 16.3. IR (cm$^{-1}$): 2987(Ar-H), 1655(C=O), 1615(C=N), 1615(Ar C=C), 1439(C-H), 1067(C-Cl), 744(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{13}ClNO^+$ 282.0680, Found 282.0689.

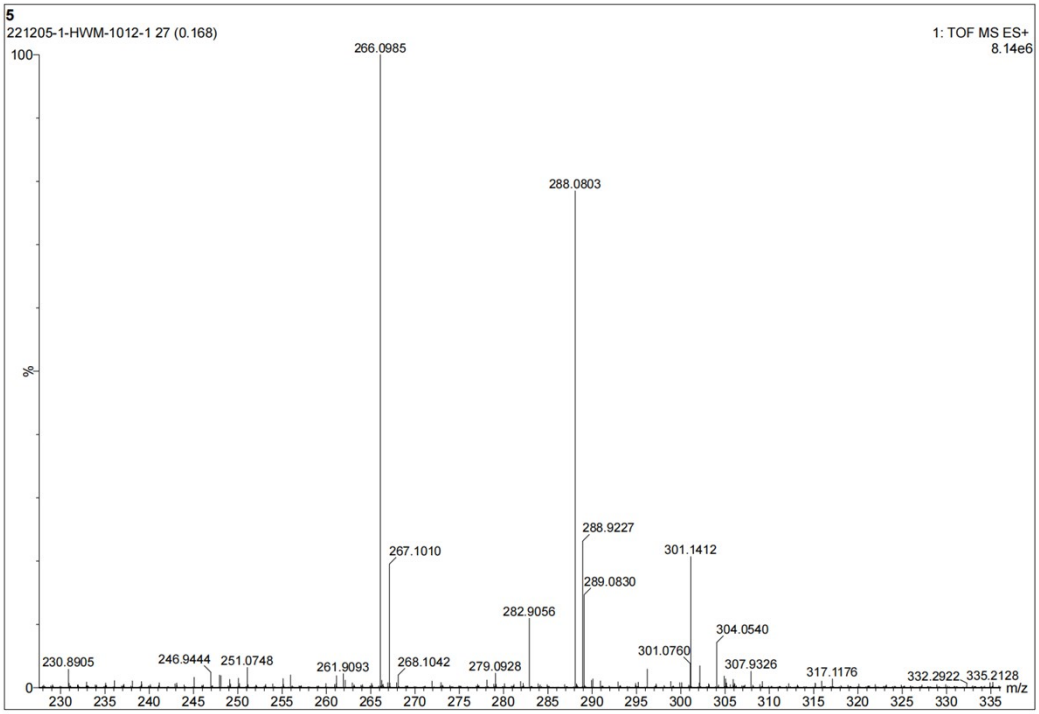


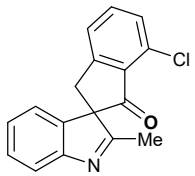



**2h**

**5-fluoro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2h)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2h** (11.9 mg, 45% yield) as a yellow solid: m.p. 138-139 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, $J_1$ = 8.5 Hz, $J_2$ = 5.2 Hz, 1H), 7.59 (d, $J$ = 7.8 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.19 (t, $J$ = 8.6 Hz, 1H), 7.13 (t, $J$ = 7.5 Hz, 1H), 6.99 (d, $J$ = 7.5 Hz, 1H), 3.58 (d, $J$ = 17.9 Hz, 1H), 3.45 (d, $J$ = 17.9 Hz, 1H), 2.15 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 198.4, 178.9, 167.7 (d, $J_{C\text{-}F}$ = 257.3 Hz), 156.3, 155.7 (d, $J_{C\text{-}F}$ = 10.2 Hz), 140.4, 132.8, 128.8, 127.7 (d, $J_{C\text{-}F}$ = 10.7 Hz), 125.9, 121.0, 120.4, 116.8 (d, $J_{C\text{-}F}$ = 23.7 Hz), 113.7 (d, $J_{C\text{-}F}$ = 22.6 Hz), 72.5, 35.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 16.4. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -100.3. IR ($cm^{-1}$): 2981(C-H), 1708(C=O), 1614(C=N), 1592(Ar C=C), 1454(C-H), 1250(C-F), 1174(C-N), 774(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{13}FNO^+$ 266.0976, Found 266.0985.

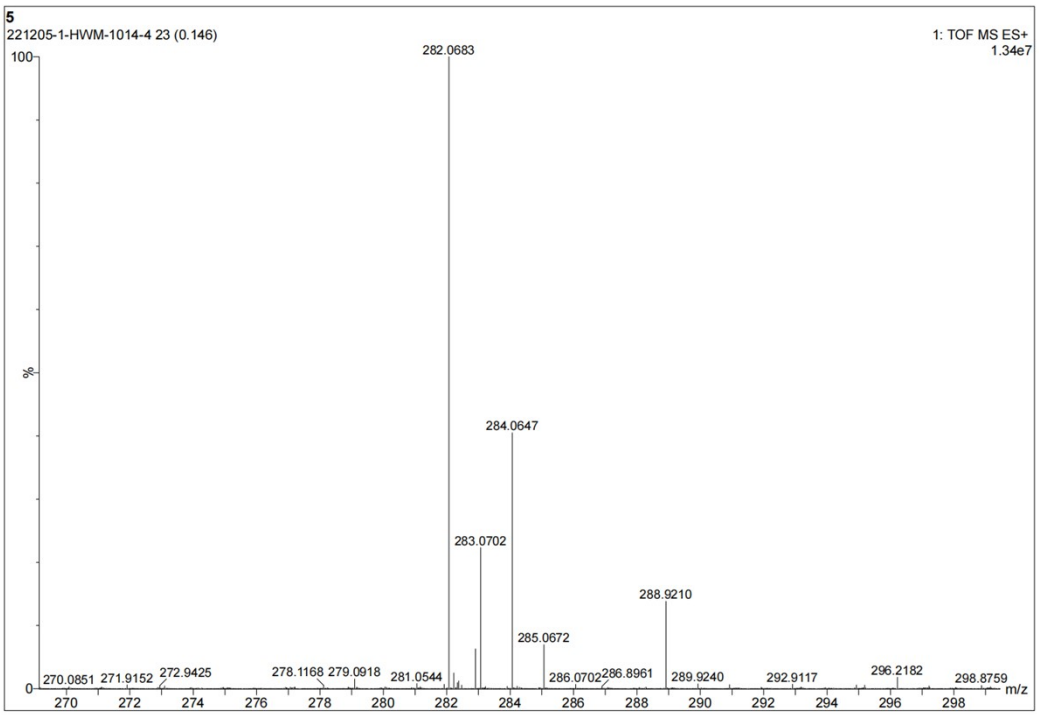


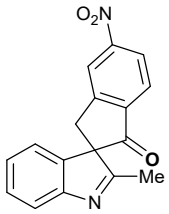



**2i**

**7-chloro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2i)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2i** (9.8 mg, 35% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.64-7.52 (m, 3H), 7.44 (d, $J$ = 7.6 Hz, 1H), 7.34 (dt, $J_1$ = 7.7 Hz, $J_2$ = 1.3 Hz, 1H), 7.12 (t, $J$ = 7.6 Hz, 1H), 6.98 (d, $J$ = 7.4 Hz, 1H), 3.58 (d, $J$ = 17.7 Hz, 1H), 3.42 (d, $J$ = 17.7 Hz, 1H), 2.18 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 196.8, 178.8, 156.2, 154.8, 140.4, 135.9, 133.4, 132.4, 129.9, 128.8, 125.8, 125.2, 121.0, 120.3, 72.7, 34.4, 16.5. IR ($cm^{-1}$): 2974(Ar-H), 1655(C=O), 1604(C=N), 1604(Ar C=C), 1452(C-H), 1050(C-Cl), 776(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{13}ClNO^+$ 282.0680, Found 282.0683.

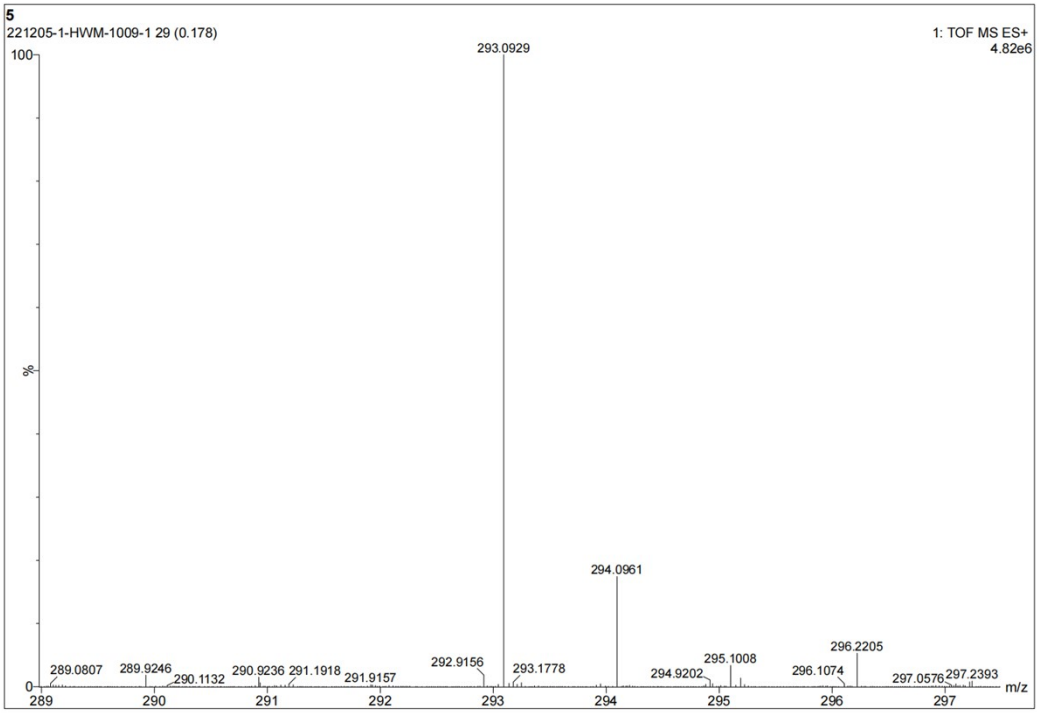


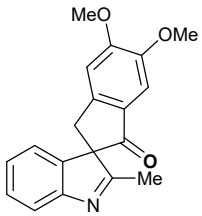



**2j**

**2'-methyl-5-nitrospiro[indene-2,3'-indol]-1(3*H*)-one (2j)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2j** (12.8 mg, 44% yield) as a yellowish solid: mp 182-183 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.36-8.33 (m, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.39-7.36 (m, 1H), 7.15 (t, *J* = 7.15 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 3.59 (d, *J* = 18.0 Hz, 1H), 3.72 (d, *J* = 18.0 Hz, 1H), 2.17 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 198.8, 177.9, 156.2, 153.4, 152.4, 140.3, 139.7, 129.2, 126.3, 126.1, 123.7, 122.3, 120.9, 120.6, 72.6, 35.0, 16.5. IR ($cm^{-1}$): 2986(Ar-H), 1655(C=O), 1614(C=N), 1614(Ar C=C), 1491(Ar C-$NO_2$), 1352(Ar C-$NO_2$), 1441(C-H), 1174(C-N), 788(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{13}N_2O_3^+$ 293.0921, Found 293.0929.

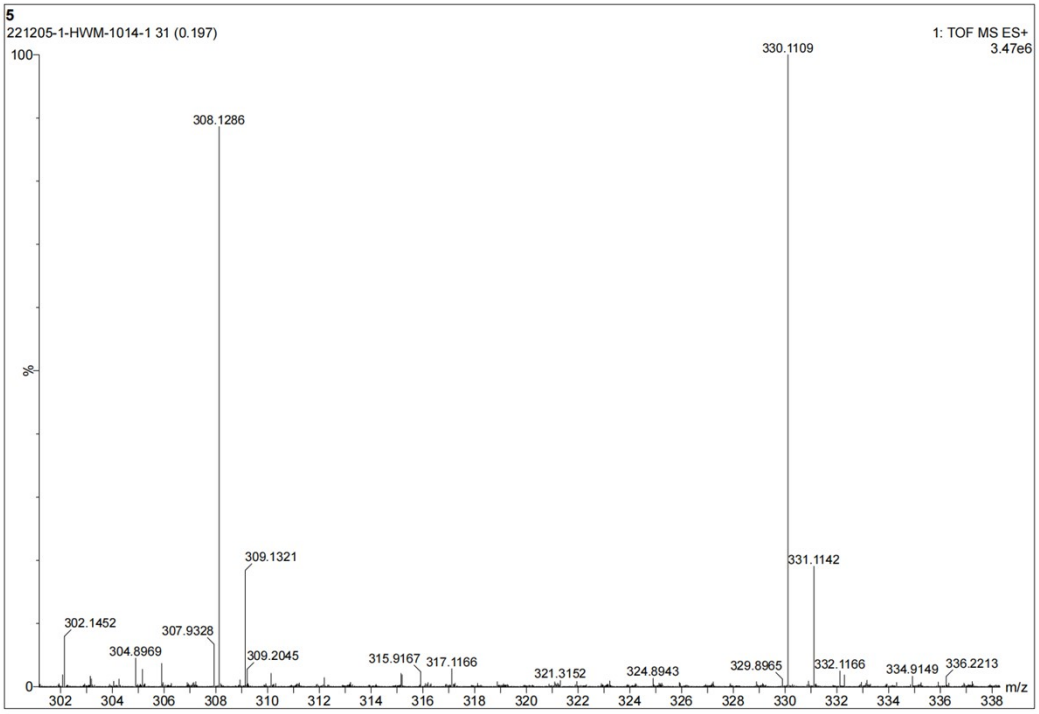


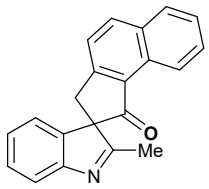



**2k**

**5,6-dimethoxy-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2k)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2k** (25.5 mg, 83% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, $J$ = 7.8 Hz, 1H), 7.34 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.3 Hz, 1H), 7.24 (s, 1H), 7.14 (t, $J$ = 7.5 Hz, 1H), 7.04-7.02 (m, 2H), 4.04 (s, 3H), 3.94 (s, 3H), 3.51 (d, $J$ = 17.5 Hz, 1H), 3.40 (d, $J$ = 17.5 Hz, 1H), 2.15 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 198.6, 179.7, 156.4, 156.3, 150.1, 148.2, 140.7, 129.3, 128.6, 125.8, 121.1, 120.2, 107.5, 105.5, 72.7, 56.4, 56.2, 34.9, 16.2. IR ($cm^{-1}$): 2988(C-H), 1675(C=O), 1613(Ar C=C), 1613(C=N), 1441(C-H), 1174(C-N), 1003(C-O-C), 787(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{18}NO_3^+$ 308.1281, Found 308.1286.

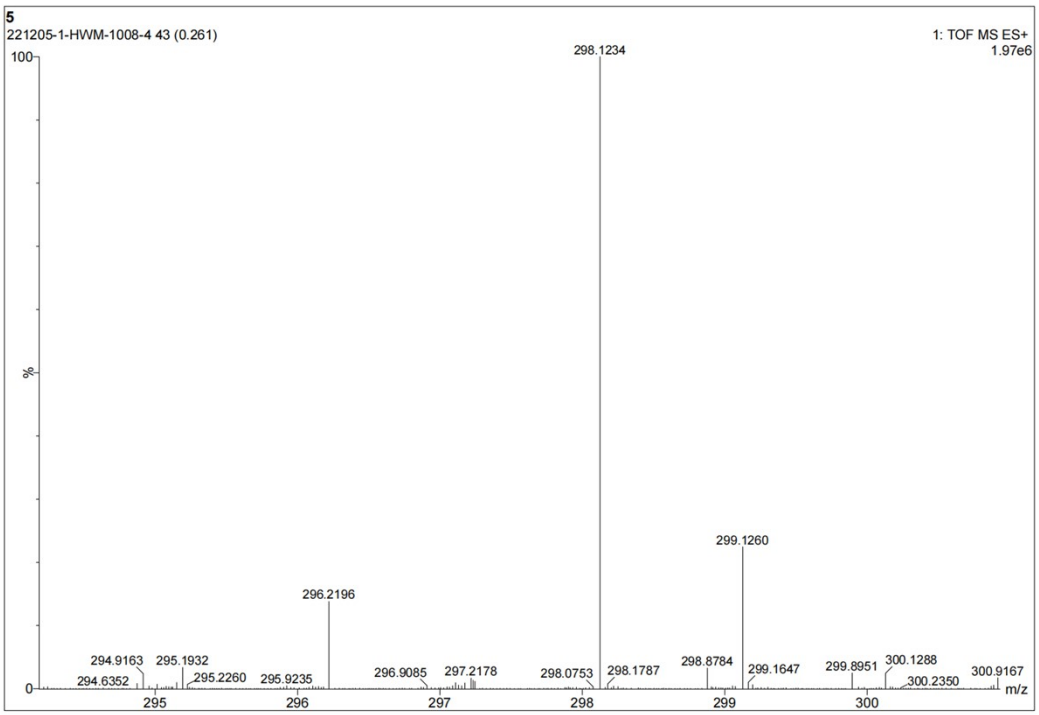


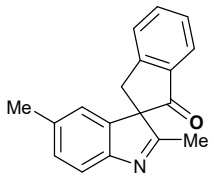



**2l**

**2'-methylspiro[cyclopenta[a]naphthalene-2,3'-indol]-1(3*H*)-one (2l)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2l** (23.4 mg, 79% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, $J$ = 8.3 Hz, 1H), 8.20 (d. $J$ = 8.4 Hz, 1H), 7.98 (d, $J$ = 8.2 Hz, 1H), 7.71-7.41 (m, 4H), 7.36 (dt, $J_1$ = 7.8 Hz, $J_2$ = 1.3 Hz, 1H), 7.13 (t, $J$ = 7.5 Hz, 1H), 7.03 (d, $J$ = 7.4 Hz, 1H), 3.71 (d, $J$ = 18.1 Hz, 1H), 3.59 (d, $J$ = 18.0 Hz, 1H), 2.19 (s, 3H) $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 200.2, 179.5, 156.5, 156.4, 140.6, 137.0, 133.0, 130.8, 129.8, 129.6, 128.6, 128.3, 127.3, 125.8, 124.0, 123.7, 121.0, 120.2, 72.8, 35.4, 16.3. IR (cm$^{-1}$): 2986(C-H), 1689(C=O), 1622(Ar C=C), 1613(C=N), 1454(C-H), 1174(C-N), 774(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{16}NO^+$ 298.1226, Found 298.1234.

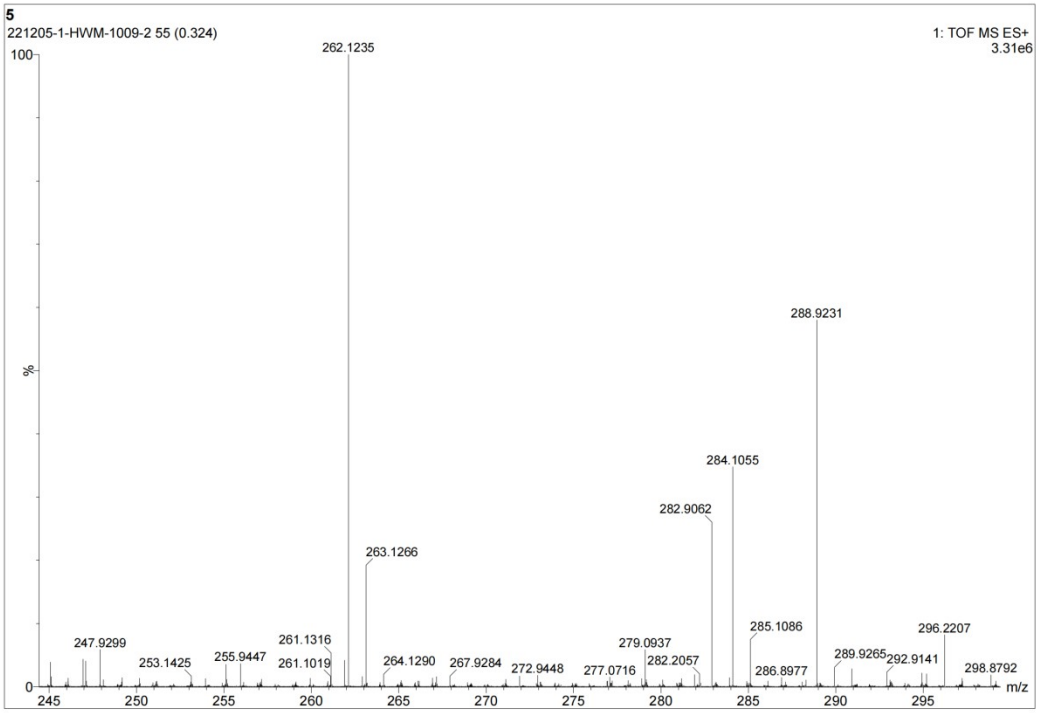


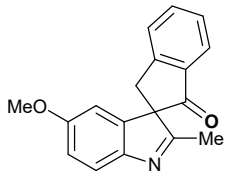



**2m**

**2',5'-dimethylspiro[indene-2,3'-indol]-1(3*H*)-one (2m)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2m** (21.1 mg, 81% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.80 (s, 1H), 3.60 (d, *J* = 17.6 Hz, 1H), 3.47 (d, *J* = 17.6 Hz, 1H), 2.28 (s, 3H), 2.13 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 200.7, 178.3, 154.2, 152.8, 140.8, 136.5, 135.78, 135.76, 129.3, 128.3, 126.9, 125.4, 121.9, 119.8, 72.3, 35.3, 21.3, 16.4. IR (cm$^{-1}$): 2988(C-H), 1662(C=O), 1613(C=N), 1613(Ar C=C), 1441(C-H), 1174(C-N), 788(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{16}NO^+$ 262.1226, Found 262.1235.

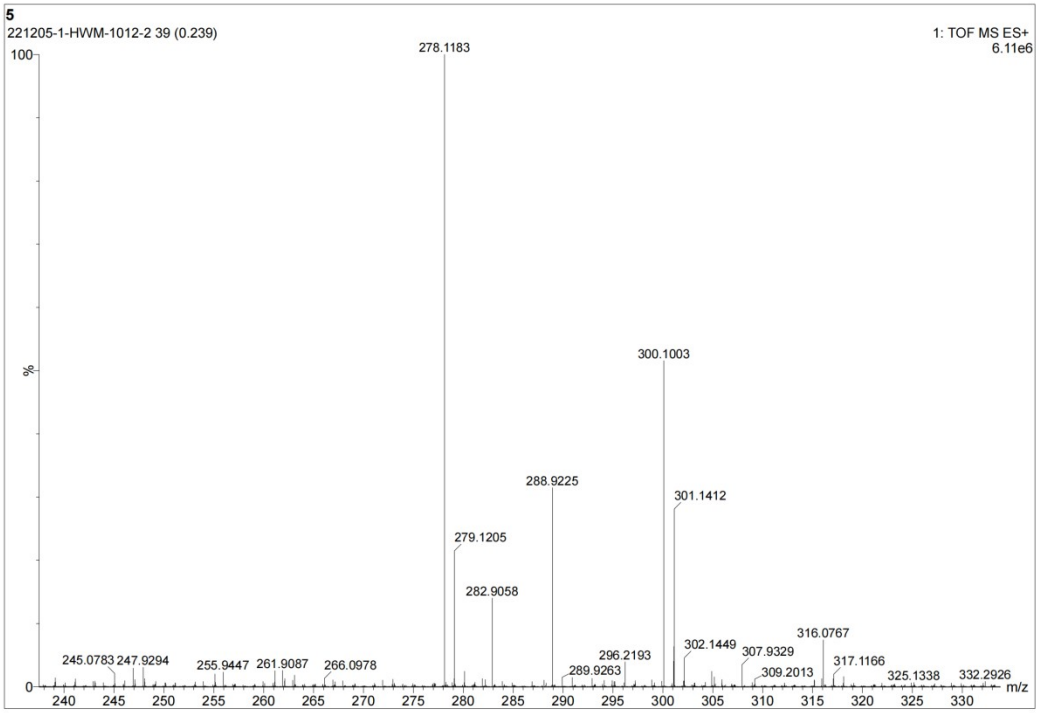


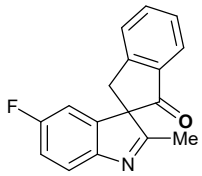



**2n**

**5'-methoxy-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2n)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2n** (22.2 mg, 80% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, $J$ = 7.8 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.63 (d, $J$ = 7.7 Hz, 1H), 7.50 – 7.45 (m, 2H), 6.84 (dd, $J_1$ = 8.5 Hz, $J_2$ = 2.6 Hz, 1H), 6.54 (d, $J$ = 2.4 Hz, 1H), 3.70 (s, 3H), 3.59 (d, $J$ = 17.6 Hz, 1H), 3.44 (d, $J$ = 17.6 Hz, 1H), 2.10 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 200.4, 177.1, 158.4, 152.8, 150.0, 142.1, 136.4, 135.8, 128.3, 127.0, 125.4, 120.5, 113.3, 108.0, 72.5, 55.7, 35.5, 16.3. IR (cm$^{-1}$): 2986(C-H), 1670(C=O), 1613(C=N), 1613(Ar C=C), 1441(C-H), 1174(C-N), 1067(C-O-C), 786(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{16}NO_2^+$ 278.1176, Found 278.1183.

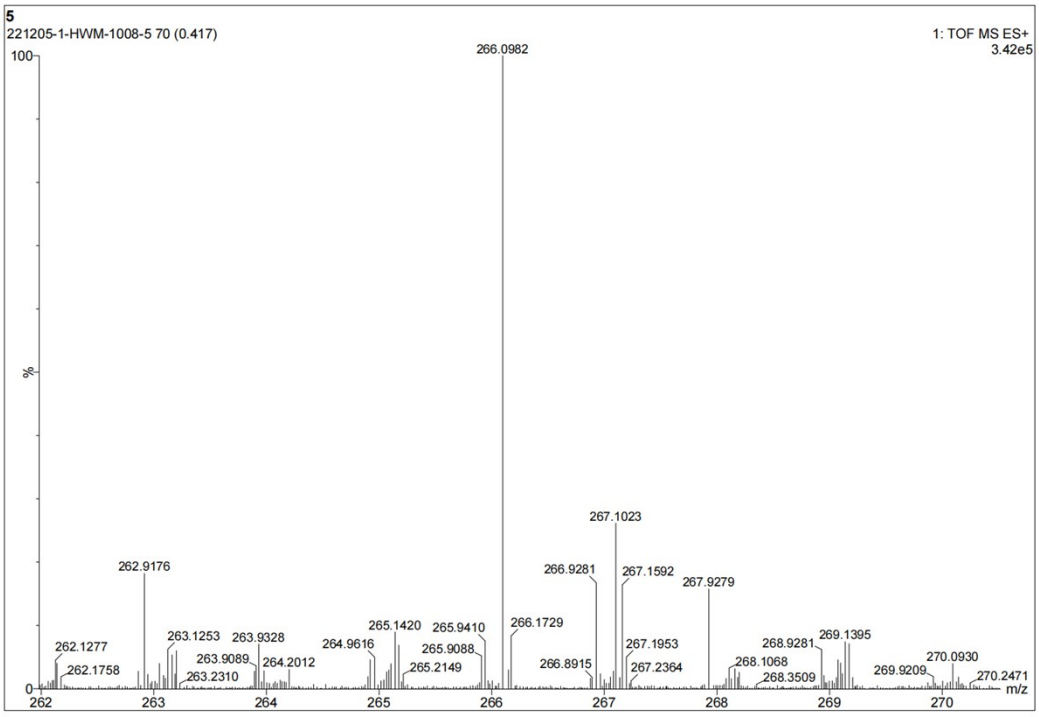


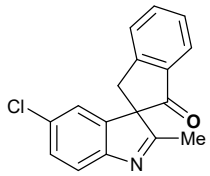



**2o**

**5'-fluoro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2o)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2o** (20.1 mg, 76% yield) as a yellow solid: m.p. 151-152 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, $J$ = 7.8 Hz, 1H), 7.77 (t, $J$ = 7.5 Hz, 1H), 7.67 (d, $J$ = 7.7 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.05 (td, $J_1$ = 8.9 Hz, $J_2$ = 2.5 Hz, 1H), 6.74 (dd, $J_1$ = 7.8 Hz, $J_2$ = 2.5 Hz, 1H), 3.65 (d, $J$ = 17.6 Hz, 1H), 3.50 (d, $J$ = 17.6 Hz, 1H), 2.16 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 199.6, 179.2, 161.3 (d, $J_{C\text{-}F}$ = 243.5 Hz), 152.5, 152.4, 142.2 (d, $J_{C\text{-}F}$ = 9.0 Hz), 136.2, 136.0, 128.5, 127.0, 125.6, 121.0 (d, $J_{C\text{-}F}$ = 8.8 Hz), 115.2 (d, $J_{C\text{-}F}$ = 23.4 Hz), 109.1 (d, $J_{C\text{-}F}$ = 24.8 Hz), 72.8 (d, $J_{C\text{-}F}$ = 2.4 Hz), 35.1, 16.4. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -116.2. IR (cm$^{-1}$): 2987(C-H), 1685(C=O), 1614(C=N), 1614(Ar C=C), 1440(C-H), 1174(C-F), 800(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{13}FNO^+$ 266.0976, Found 266.0982.

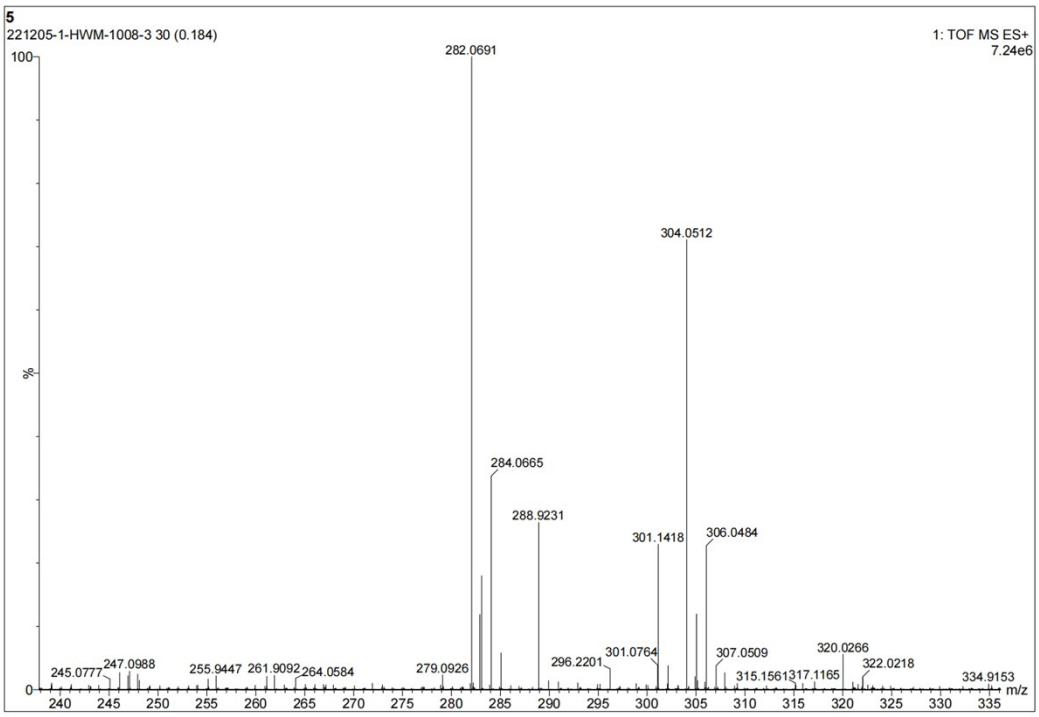


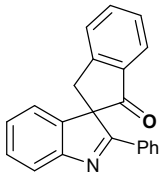



**2p**

**5'-chloro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2p)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2p** (21.9 mg, 78% yield) as a yellow solid: m.p. 97-98 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, $J$ = 7.7 Hz, 1H), 7.75 (t, $J$ = 7.5 Hz, 1H), 7.65 (d, $J$ = 7.6 Hz, 1H), 7.51 (dd, $J_1$ = 8.1 Hz, $J_2$ = 5.5 Hz, 2H), 7.31 (dd, $J_1$ = 8.3 Hz, $J_2$ = 2.1 Hz, 1H), 6.97 (d, $J$ = 2.1 Hz, 1H), 3.62 (d, $J$ = 17.7 Hz, 1H), 3.48 (d, $J$ = 17.6 Hz, 1H), 2.15 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 199.4, 179.9, 155.0, 152.5, 142.3, 136.13, 136.08, 131.5, 128.8, 128.5, 127.0, 125.6, 121.7, 121.1, 72.6, 35.1, 16.4. IR (cm$^{-1}$): 2976(C-H), 1714(C=O), 1608(Ar C=C), 1558(C=N), 1454(C-H), 1174(C-N), 1050(C-Cl), 786(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{16}ClNO^+$ 282.0680, Found 282.0691.

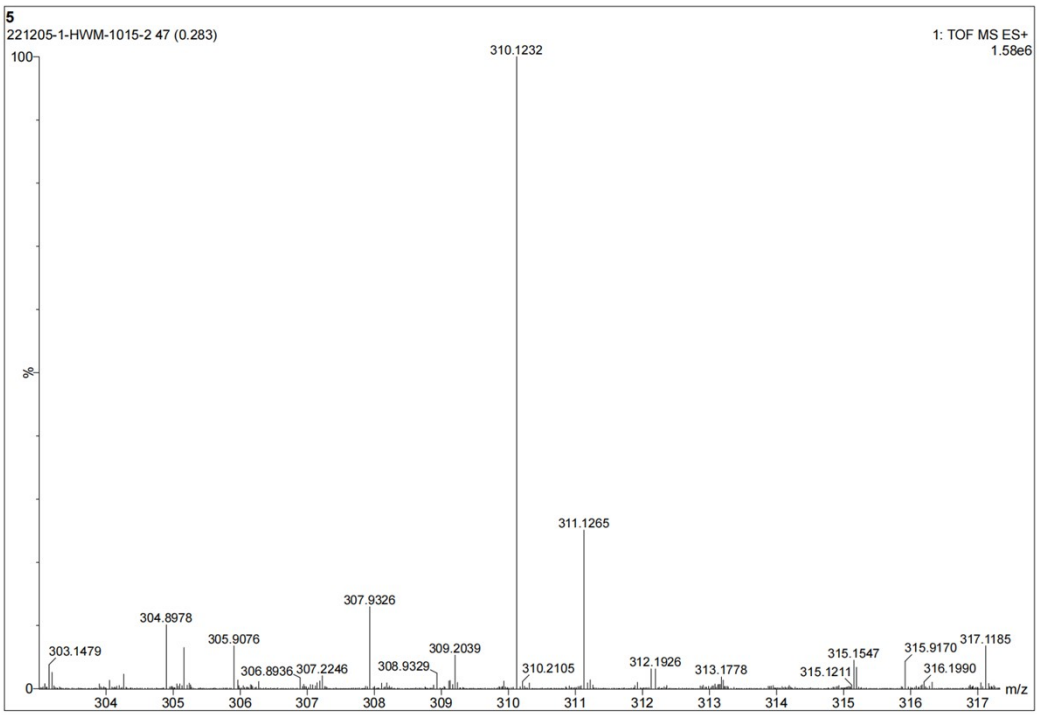


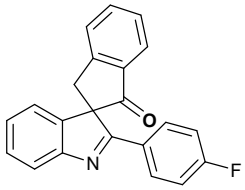



2q

**2'-phenylspiro[indene-2,3'-indol]-1(3*H*)-one (2q)**[1]

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2q** (18.5 mg, 60% yield) as a yellowish solid: m.p. 181-182 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.81-7.76 (m, 2H), 7.69-7.66 (m, 3H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.43-7.33 (m, 4H), 7.13 (dt, $J_1$ = 7.5 Hz, $J_2$ = 1.1 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 3.84 (d, *J* = 17.7 Hz, 1H), 3.51 (d, *J* = 17.7 Hz, 1H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 200.2, 177.2, 155.8, 152.5, 142.0, 136.4, 135.8 (2C), 131.7, 131.1, 128.9 (2C), 128.8, 128.4, 127.9, 127.3, 126.3, 125.9, 121.3, 120.1, 70.5, 37.6. IR ($cm^{-1}$): 2987(C-H), 1675(C=O), 1613(Ar C=C), 1613(C=N), 1441(C-H), 1174(C-N), 900(C-C), 799(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{16}NO^+$ 310.1226, Found 310.1232.

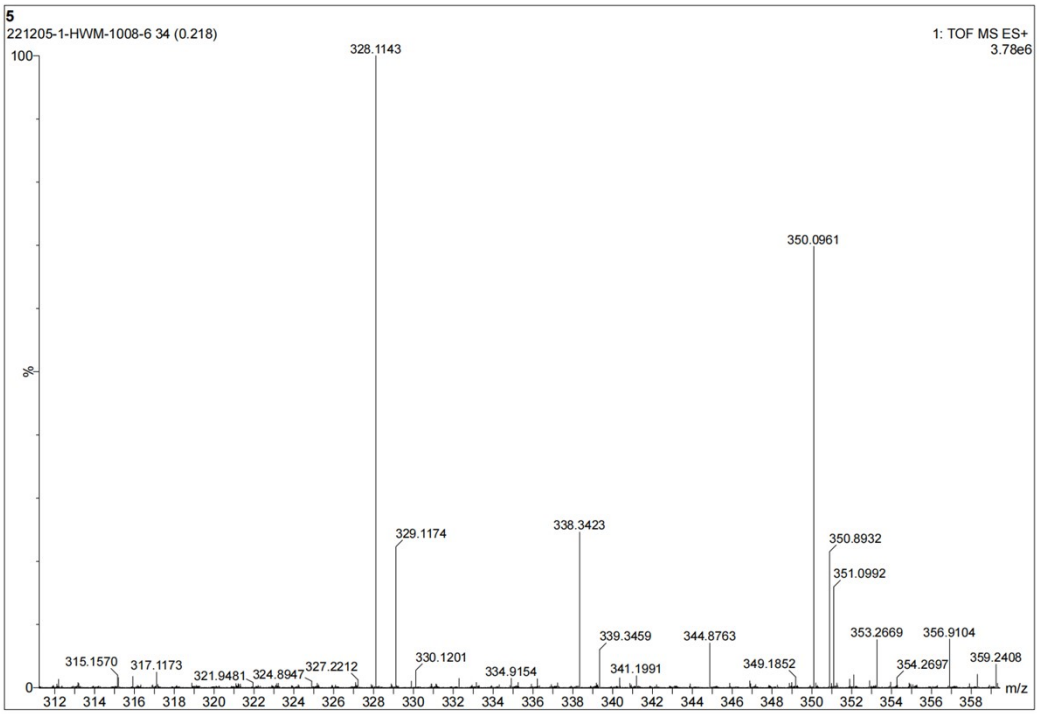


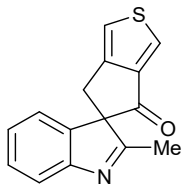



**2r**

**2'-(4-fluorophenyl)spiro[indene-2,3'-indol]-1(3*H*)-one (2r)**[1]

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **2r** (18.6 mg, 57% yield) as a yellow solid: m.p. 138-139 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, $J$ = 7.7 Hz, 1H), 7.81-7.56 (m, 5H), 7.57 (t, $J$ = 7.3 Hz, 1H), 7.39 (dt, $J_1$ = 7.8 Hz, $J_2$ = 1.2 Hz, 1H), 7.13 (dt, $J_1$ = 7.5 Hz, $J_2$ = 1.1 Hz, 1H), 7.05-7.02 (m, 2H), 6.91 (d, $J$ = 7.3 Hz, 1H), 3.79 (d, $J$ = 17.7 Hz, 1H), 3.52 (d, $J$ = 17.7 Hz, 1H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 200.0, 175.9, 164.5 (d, $J_{C-F}$ = 251.3 Hz), 155.7, 152.4, 141.9, 136.2, 136.0, 130.0 (d, $J_{C-F}$ = 8.8 Hz), 128.9, 128.5, 128.1 (d, $J_{C-F}$ = 2.5 Hz), 127.3, 126.3, 125.9, 121.2, 120.1, 116.1 (d, $J_{C-F}$ = 21.3 Hz), 70.4, 37.6. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -108.2. IR (cm$^{-1}$): 2988(C-H), 1714(C=O), 1668(C=N), 1613(Ar C=C), 1441(C-H), 1174(C-N), 910(C-C), 767(C-C). HRMS(ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{14}FNONa^+$ 350.0952, Found 350.0961.

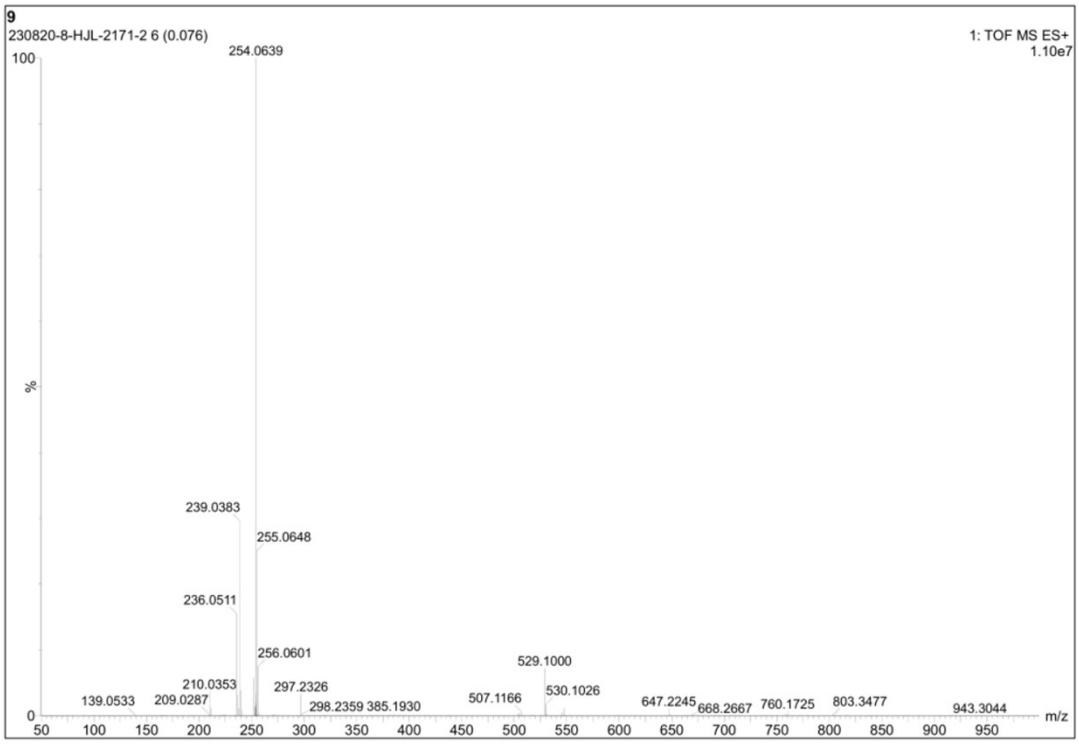


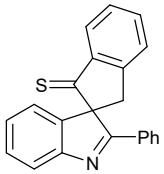



**2t**

**2'-methyl-4*H*,6*H*-spiro[cyclopenta[*c*]thiophene-5,3'-indol]-4-one (2t)**

Flash column chromatography on a silica gel (PE/EA, v/v, 20:1) gives **2t** (14.9 mg, 59% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.8 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 4.8 Hz, 1H), 7.16 (dt, *J* = 14.3, 7.0 Hz, 2H), 3.46 (d, *J* = 17.7 Hz, 1H), 3.36 (d, *J* = 17.7 Hz, 1H), 2.22 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 190.5, 178.9, 166.9, 156.0, 142.6, 141.0, 139.8, 128.9, 126.0, 124.1, 121.3, 120.3, 32.9, 16.2. IR ($cm^{-1}$): 2986(C-H), 1663(C=O), 1614(C=N), 1614(Ar C=C), 1441(C-H), 1174(C-N), 776(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{12}NOS^+$ 254.0634, Found 254.0639.

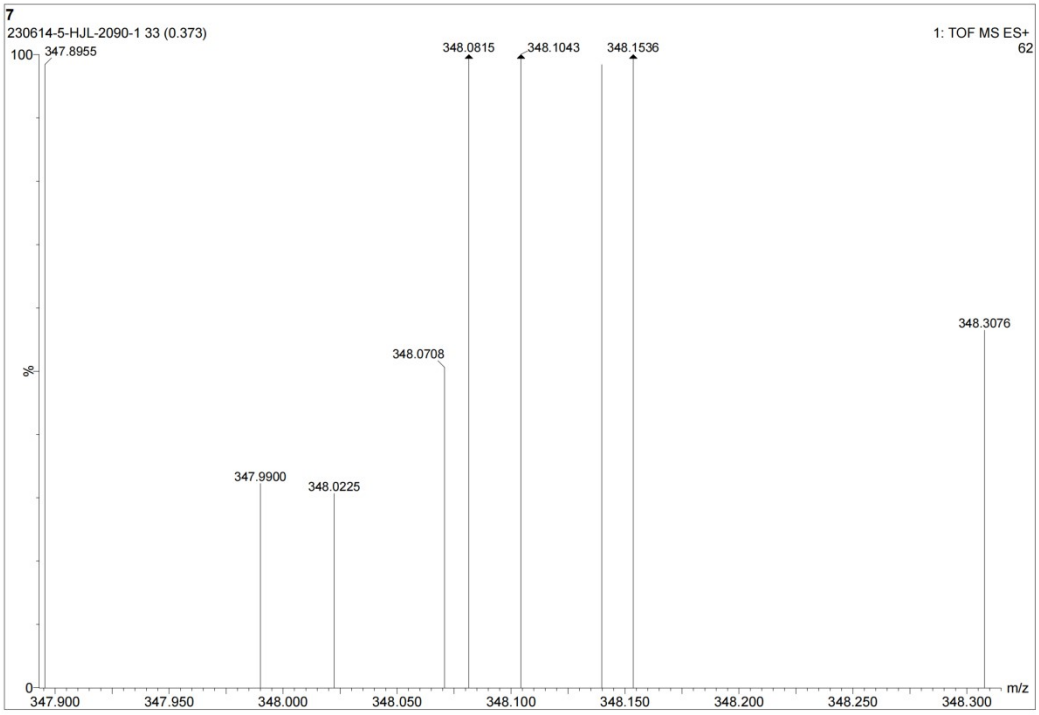


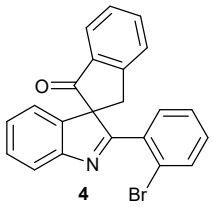



**3**

**2'-phenylspiro[indene-2,3'-indole]-1(3*H*)-thione (3)**

Flash column chromatography on a silica gel (PE/EA, v/v, 6:1) gives **3** (53.3 mg, 82% yield) as a yellowish oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.43 – 7.37 (m, 3H), 7.34 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 7.17 – 7.13 (m, 1H), 3.83 (d, *J* = 15.8 Hz, 1H), 3.46 (d, *J* = 15.7 Hz, 1H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 197.5, 162.4, 151.8, 137.7, 136.1, 135.8, 133.1, 129.7, 128.9, 128.6, 128.32 (2C), 128.29, 127.7, 125.5, 125.1 (2C), 125.0, 122.8, 117.9, 71.9, 35.8. IR (cm$^{-1}$): 2958(C-H), 1666(C=N), 1604(Ar C=C), 1463(C-H), 1182(C-N), 1076(C=S), 880(C-C), 758(C-C), 694(C-C). HRMS(ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{15}NSNa^+$ 348.0817, Found 348.0815.

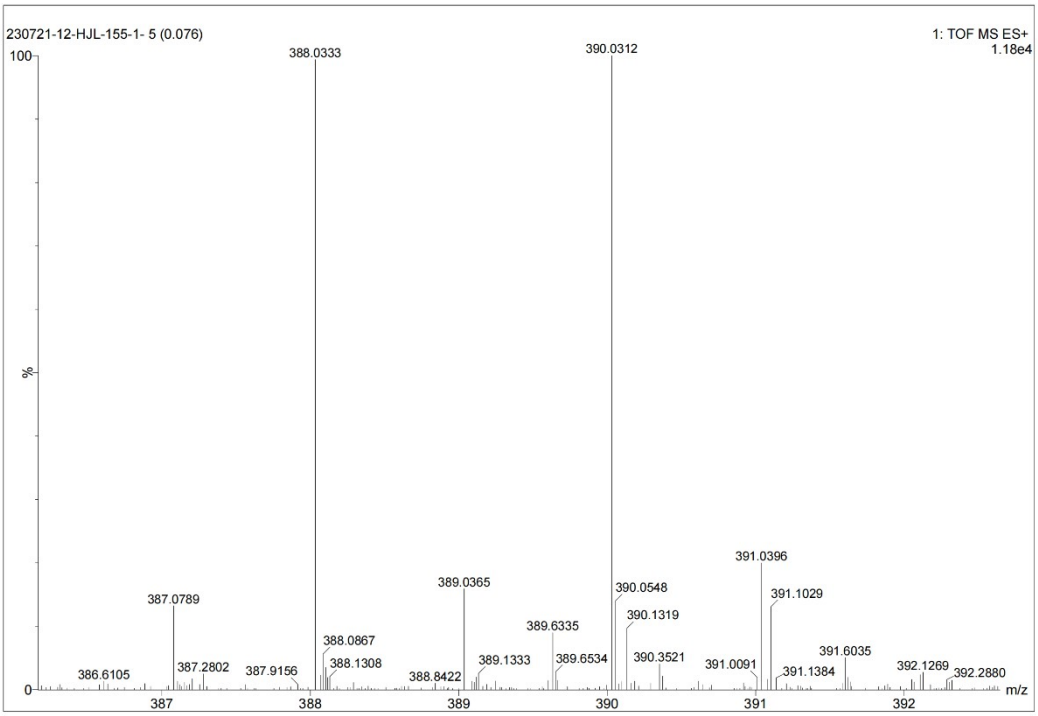


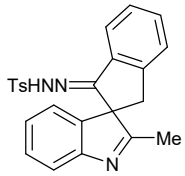



4

**2'-(2-bromophenyl)spiro[indene-2,3'-indol]-1(3*H*)-one (4)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **4** (41.9 mg, 54% yield) as a white solid: m.p. 143-144 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, $J$ = 8.3 Hz, 1H), 8.11 (d, $J$ = 7.5 Hz, 1H), 7.87 – 7.71 (m, 2H), 7.47 – 7.35 (m, 3H), 7.30 (dd, $J_1$ = 19.0 Hz, $J_2$ = 7.5 Hz, 2H), 7.22 – 7.19 (m, 2H), 7.17 (d, $J$ = 8.6 Hz, 1H), 3.83 (d, $J$ = 15.8 Hz, 1H), 3.46 (d, $J$ = 15.8 Hz, 1H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 197.5, 162.4, 151.7, 137.7, 136.1, 135.7 (2C), 133.1, 129.7, 128.9, 128.6, 128.33, 128.30, 127.7, 125.5 (2C), 125.1, 125.0, 122.8, 117.9, 71.9, 35.8. IR (cm$^{-1}$): 1719(C=O), 1665(Ar C=C), 1631(C=N), 1466(C-H), 1381(C-N), 1077(C-Br), 758(C-C), 697(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{15}BrNO^+$ 388.0332, Found 388.0333.

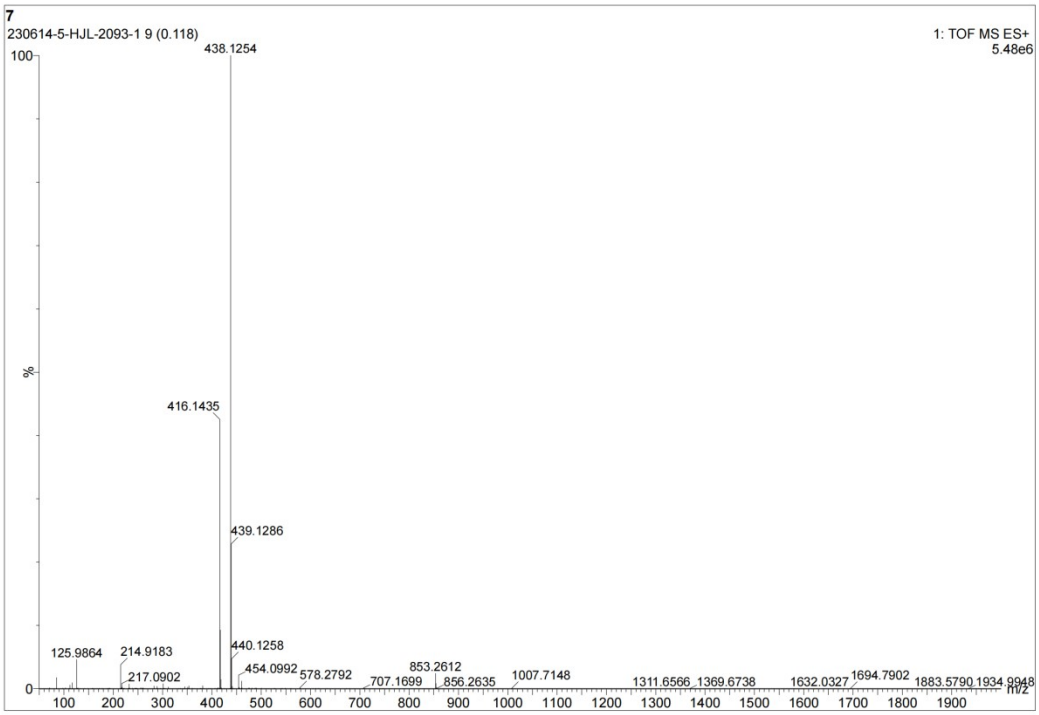


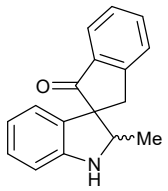



**5**

**4-methyl-N'-(2'-methylspiro[indene-2,3'-indol]-1(3*H*)-ylidene) benzenesulfonohydrazide (5)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **5** (52.3 mg, 63% yield) as a yellowish oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.36 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 7.1 Hz, 1H), 5.73 (s, 1H), 3.25 (d, *J* = 15.9 Hz, 1H), 2.89 (d, *J* = 16.0 Hz, 1H), 2.37 (s, 3H), 1.74 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 166.5, 149.8, 147.2, 143.7, 136.9, 131.5, 131.0, 129.43, 129.38, 129.1, 128.6, 128.1, 127.9, 127.8, 126.3, 123.7, 122.1, 120.6, 110.1, 98.4, 70.6, 37.8, 21.5, 18.9. IR ($cm^{-1}$): 2957(C-H), 1614(Ar C=C), 1605(C=N), 1468(C-H), 1166(C-N), 815(C-C), 739(C-C). HRMS(ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{21}N_3O_2SNa^+$ 438.1247, Found 438.1254.

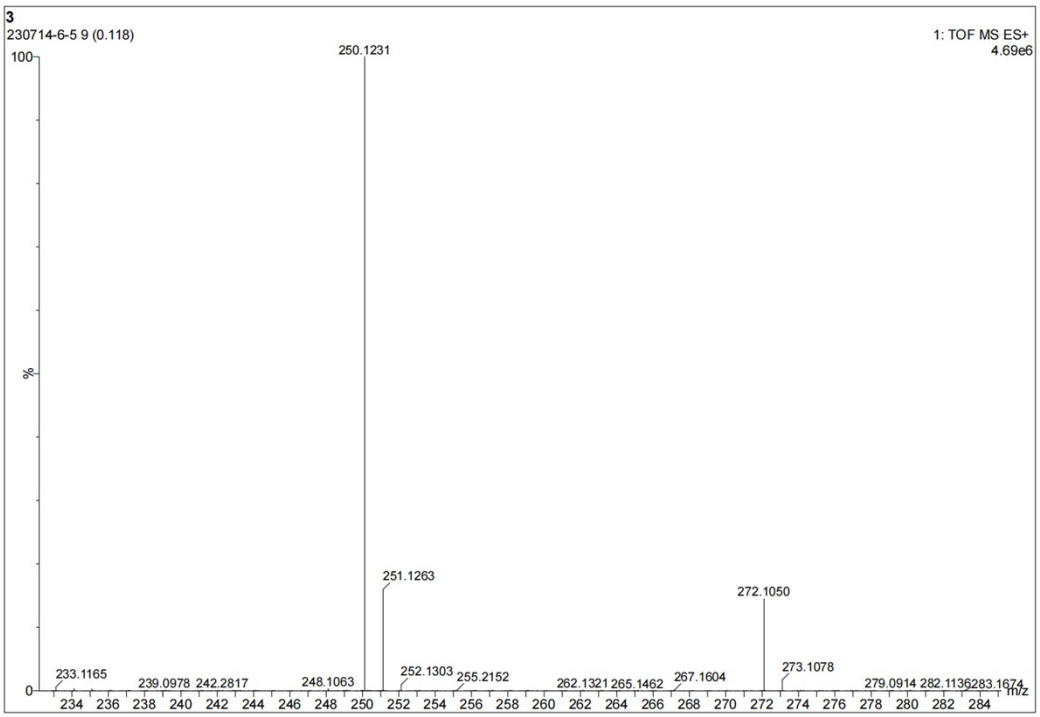





**6**

**2'-methylspiro[indene-2,3'-indolin]-1(3*H*)-one (6)**

Flash column chromatography on a silica gel (PE/EA, v/v, 4:1) gives **6** (39.9 mg, 80% yield) as a yellow oil; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.82 – 6.73 (m, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 4.12 (q, *J* = 6.6 Hz, 1H), 3.60 (d, *J* = 17.5 Hz, 1H), 3.24 (d, *J* = 17.5 Hz, 1H), 1.27 (d, *J* = 6.6 Hz, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 204.0, 152.7, 151.4, 136.1, 135.0, 133.0, 128.6, 128.0, 126.1, 124.7, 122.6, 119.6, 111.0, 65.4, 61.8, 40.9, 15.6. IR ($cm^{-1}$): 3418(N-H), 1714(C=O), 1602(Ar C=C), 1506(C=N), 1464(C-H), 1404(C-H), 879(C-C), 746(C-C). HRMS(ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{16}NO^+$ 250.1226, Found 250.1231.



## IV. References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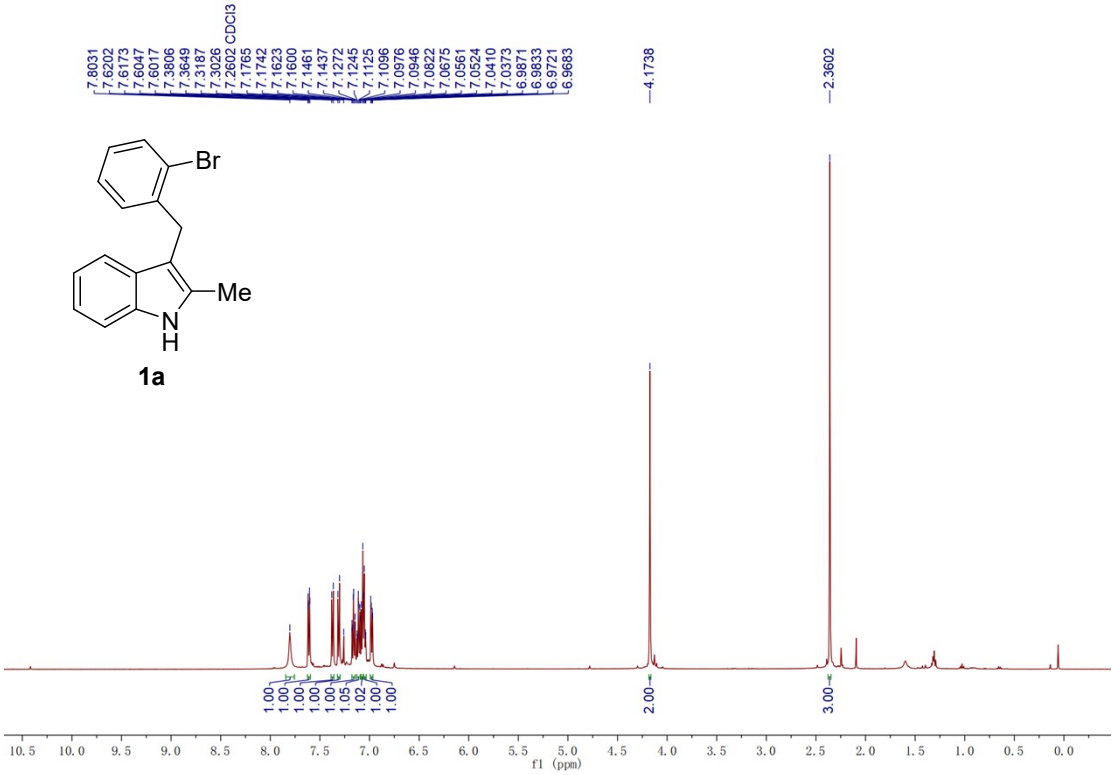
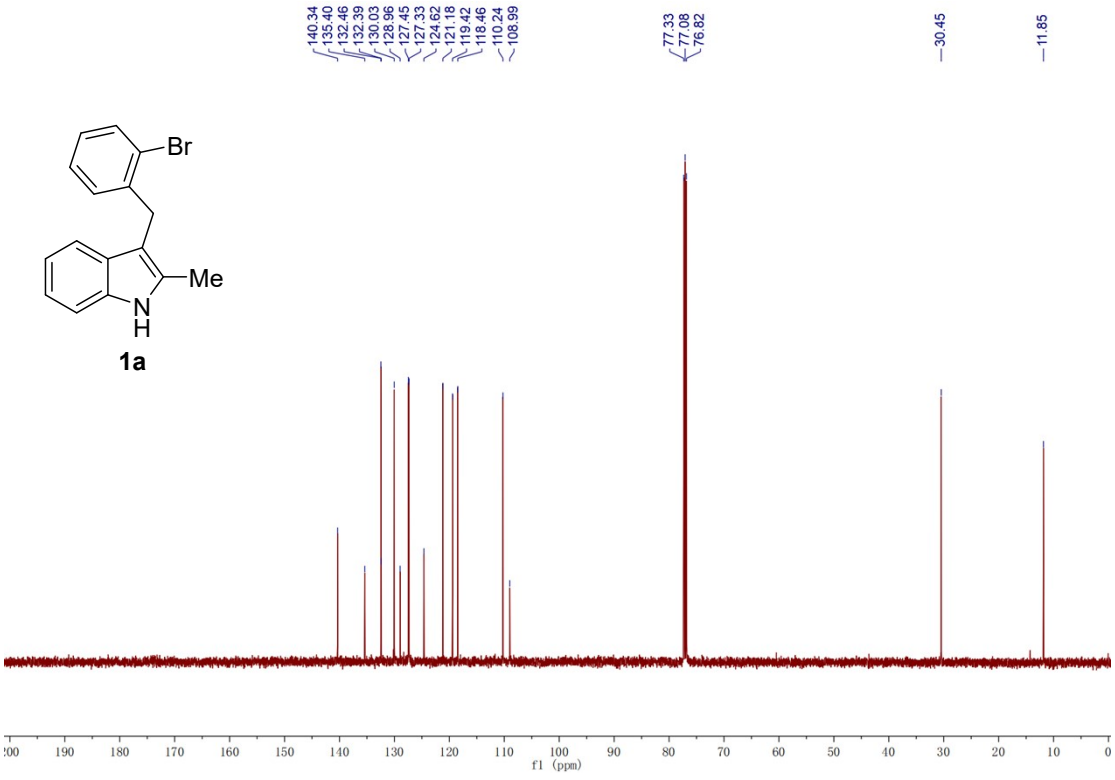
## V. Copies NMR Spectra

### 3-(2-bromobenzyl)-2-methyl-1*H*-indole (1a)

$^1$H NMR (500 MHz, $CDCl_3$)

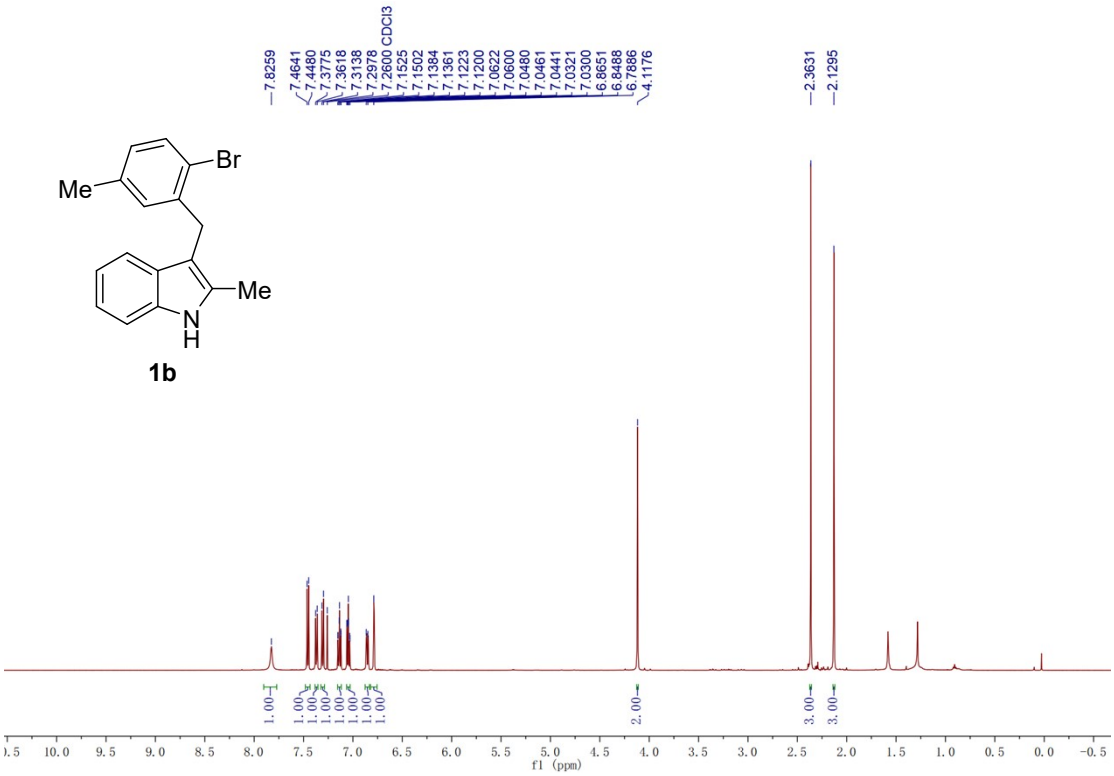



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

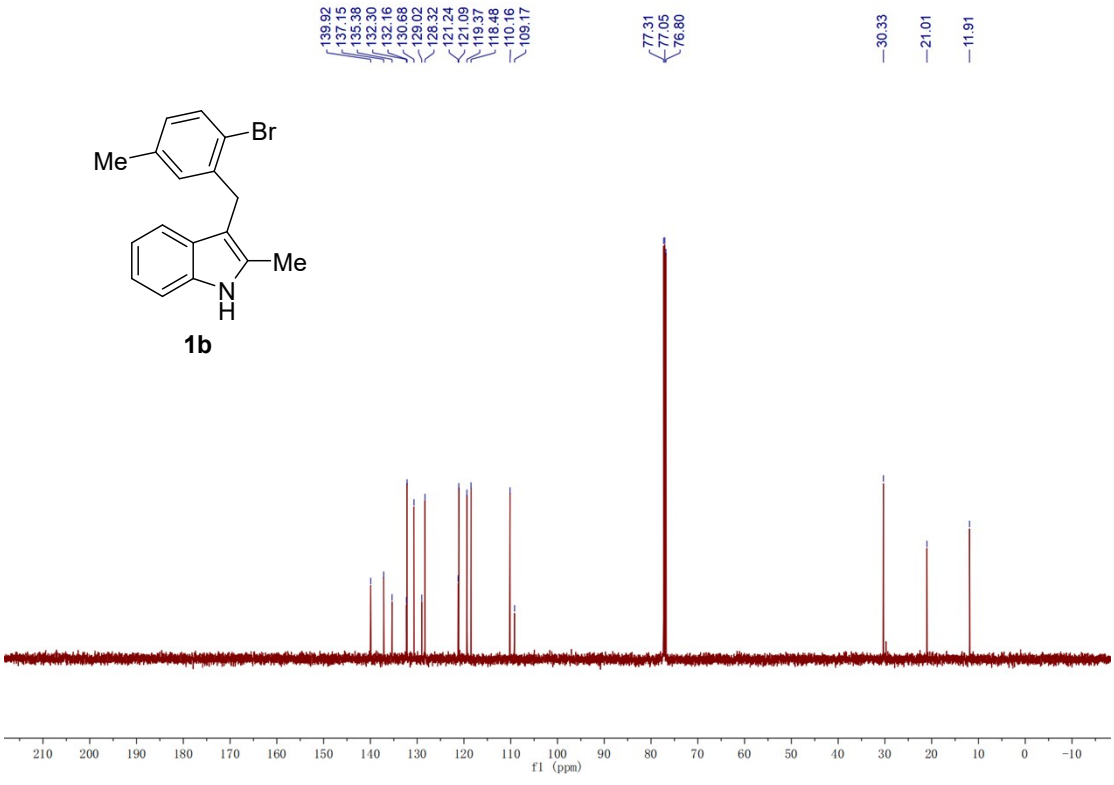


## 3-(2-bromo-5-methylbenzyl)-2-methyl-1*H*-indole (1b)

$^1$H NMR (500 MHz, $CDCl_3$)

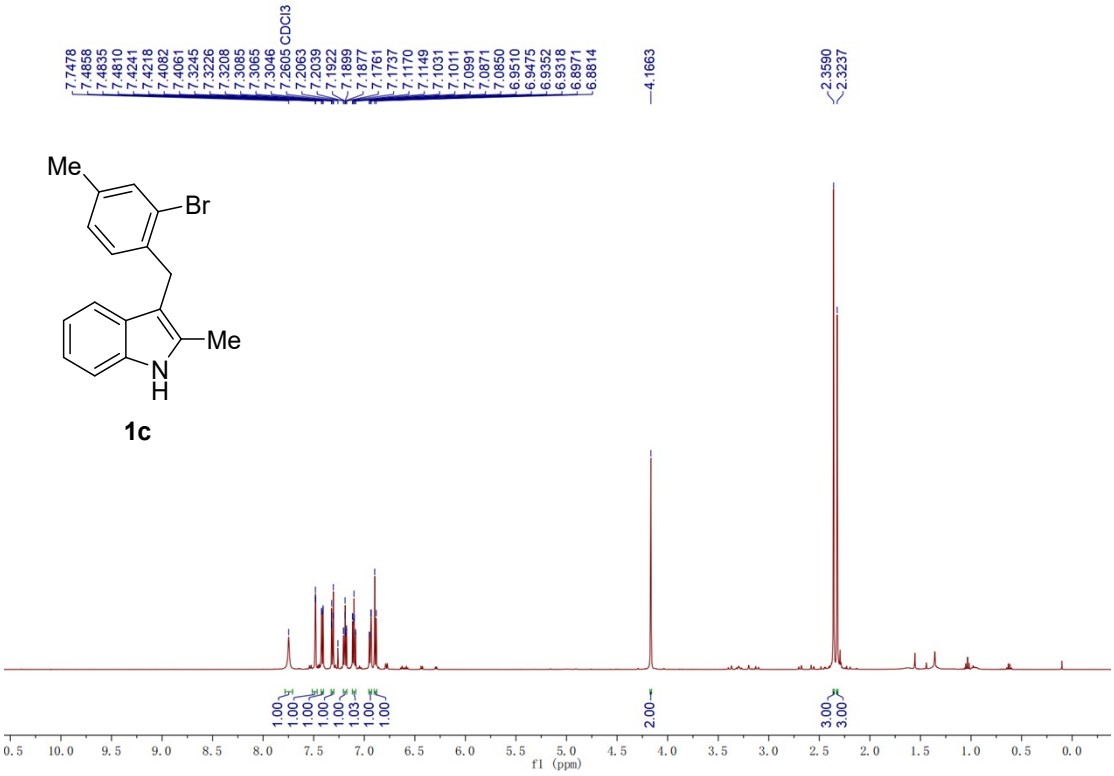



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

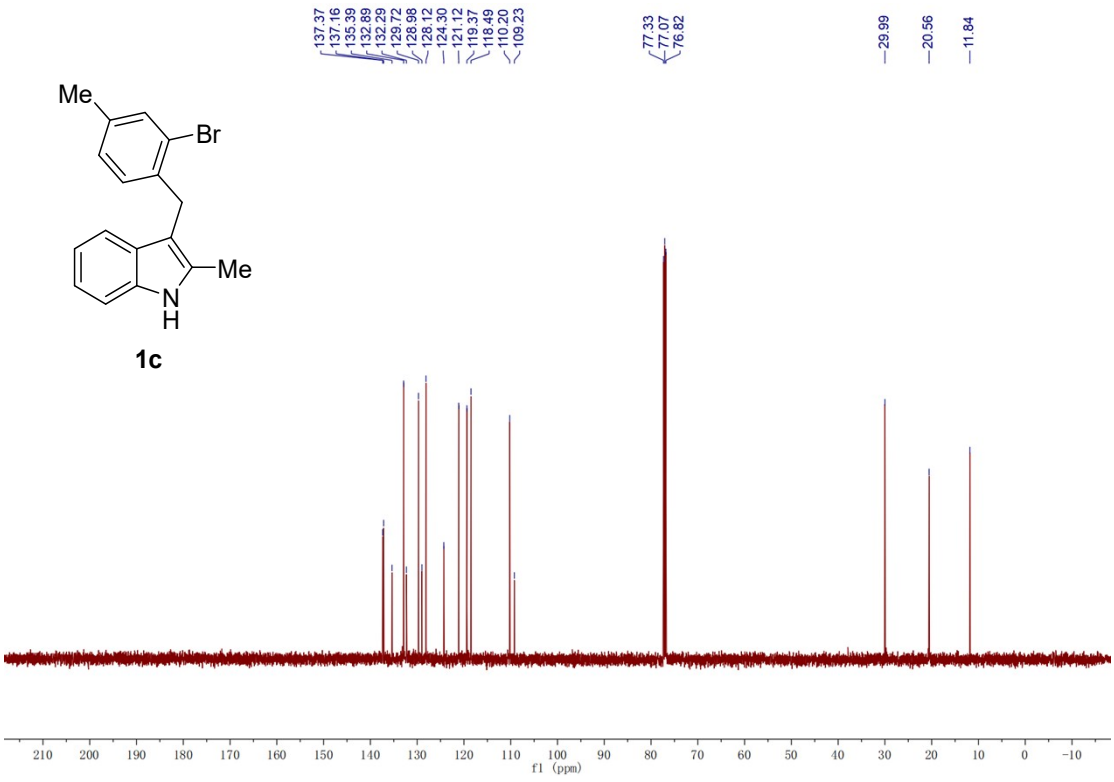


## 3-(2-bromo-4-methylbenzyl)-2-methyl-1*H*-indole (1c)

$^1$H NMR (500 MHz, $CDCl_3$)

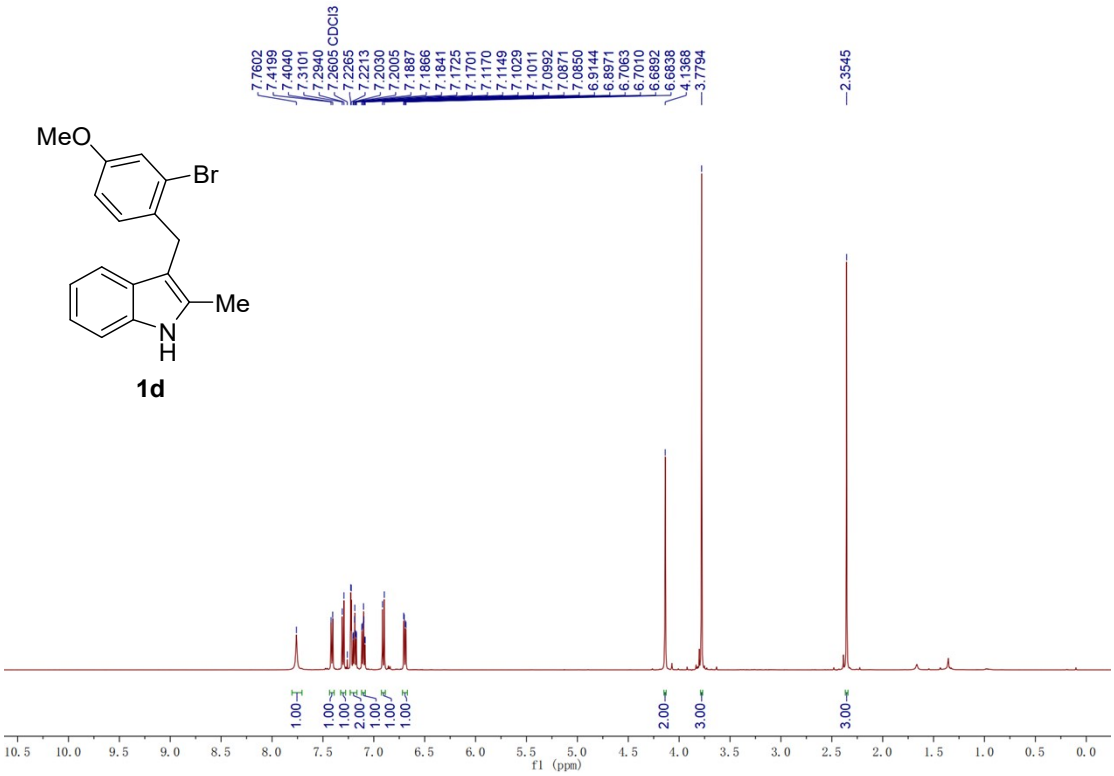



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

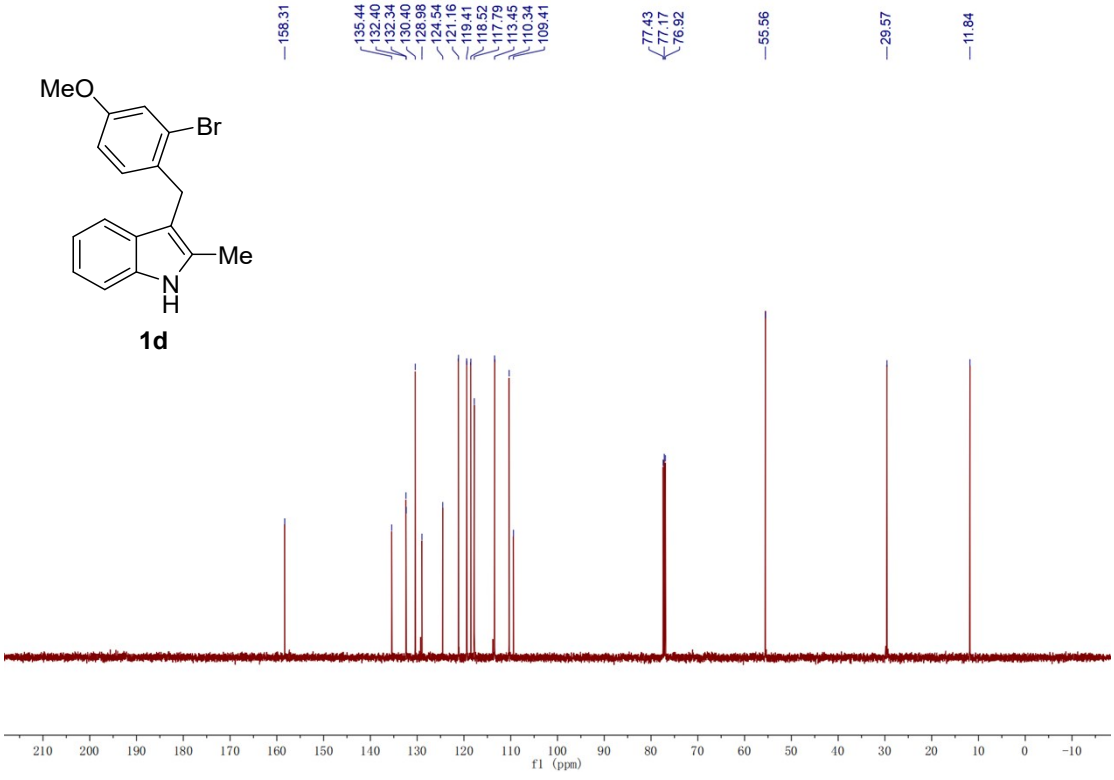


## 3-(2-bromo-4-methoxybenzyl)-2-methyl-1*H*-indole (1d)

$^1$H NMR (500 MHz, $CDCl_3$)

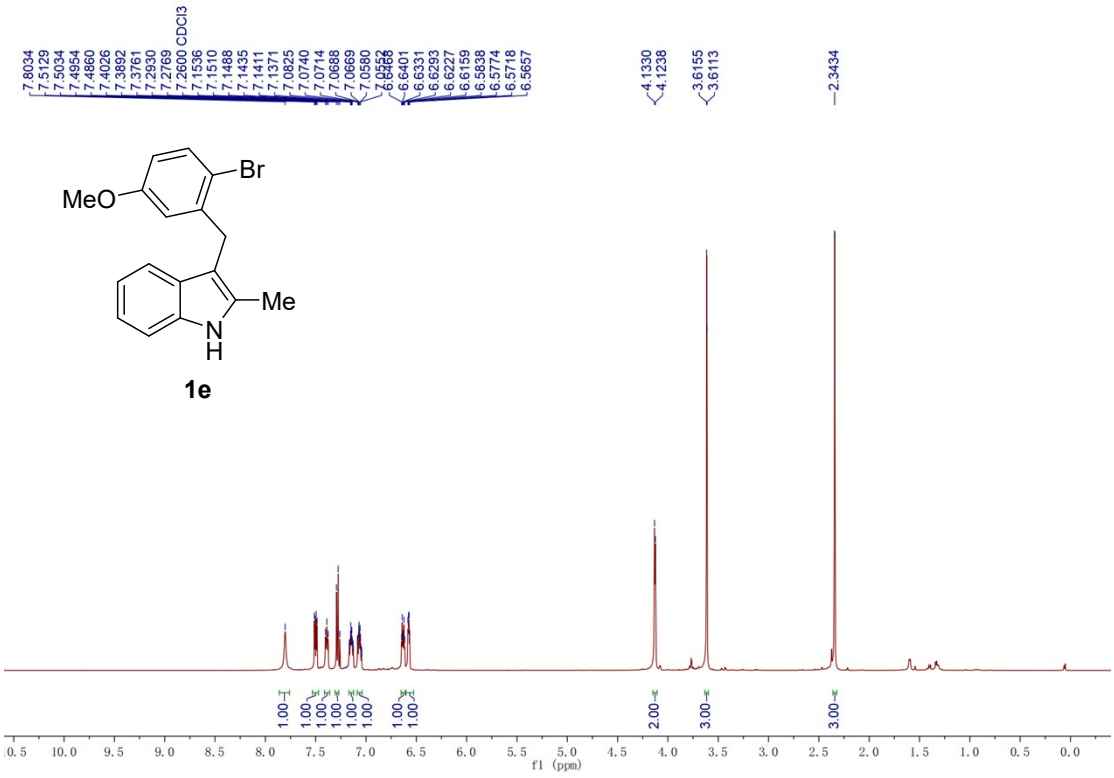



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

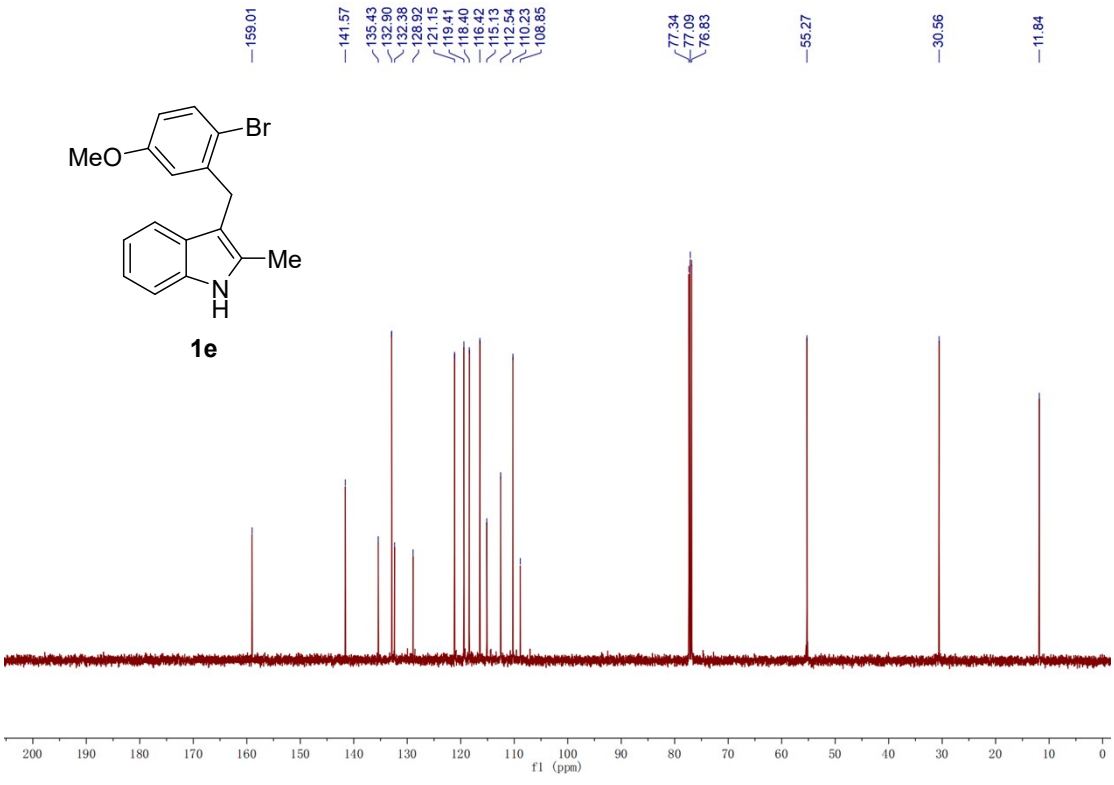


## 3-(2-bromo-5-methoxybenzyl)-2-methyl-1*H*-indole (1e)

$^1$H NMR (500 MHz, $CDCl_3$)

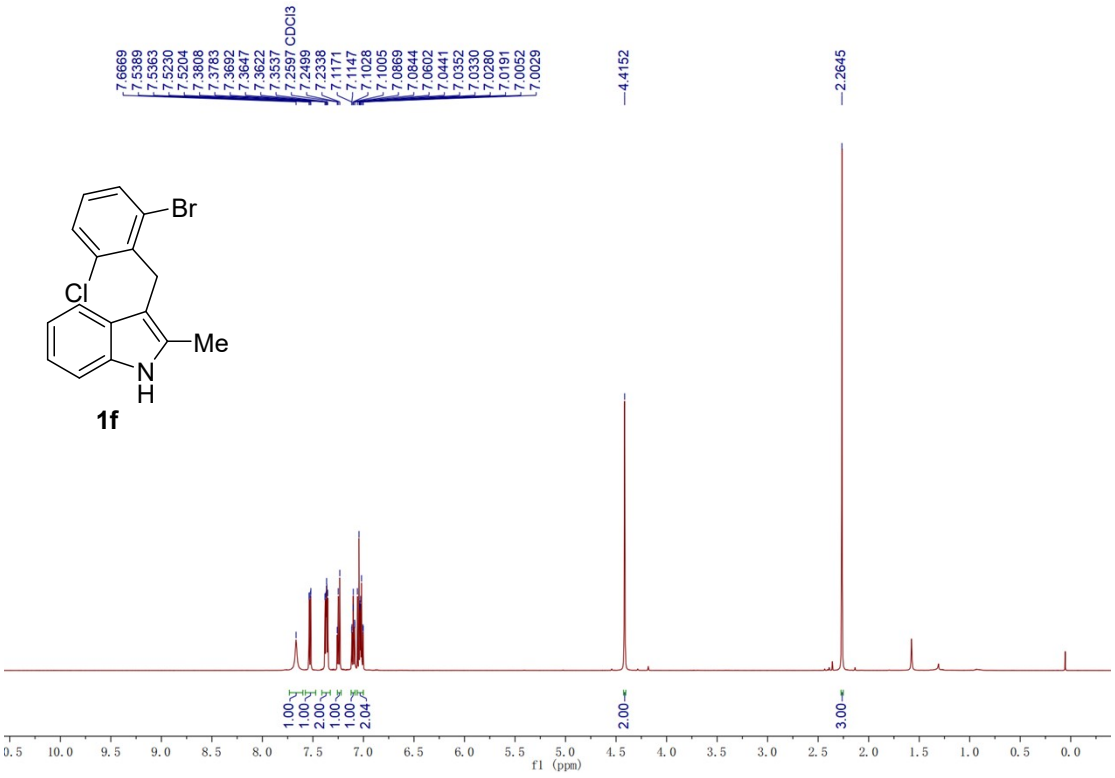



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

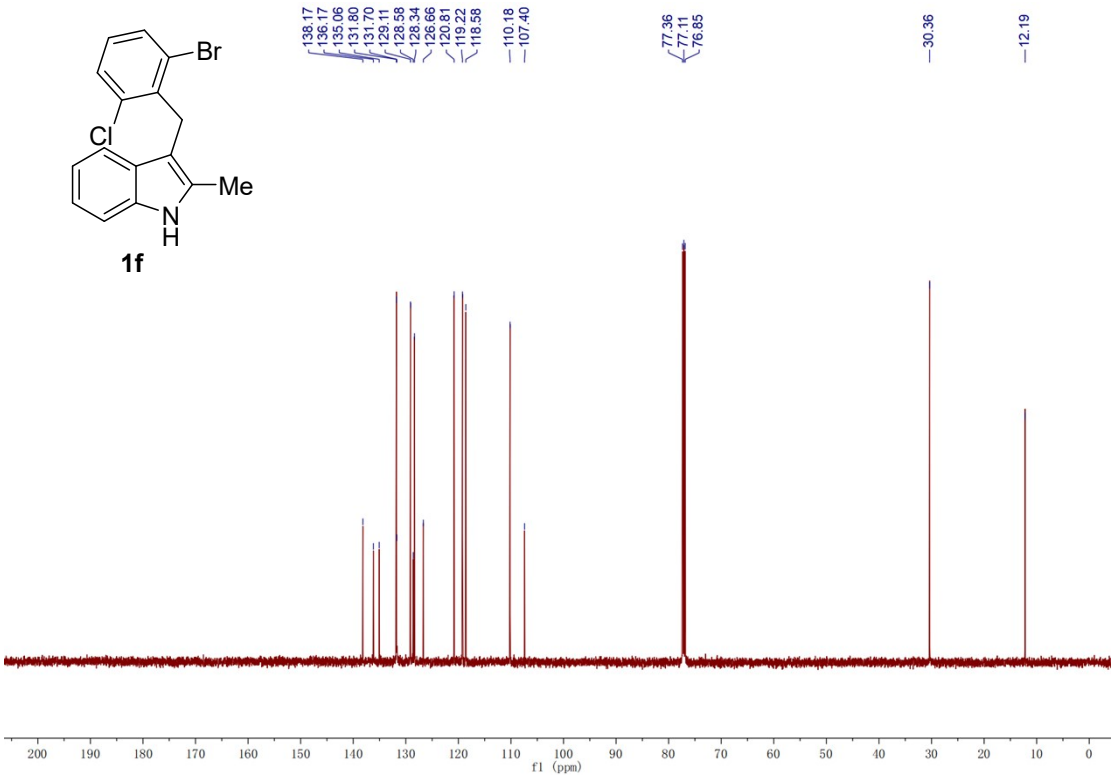


## 3-(2-bromo-5-fluorobenzyl)-2-methyl-1*H*-indole (1f)

$^1$H NMR (500 MHz, $CDCl_3$)

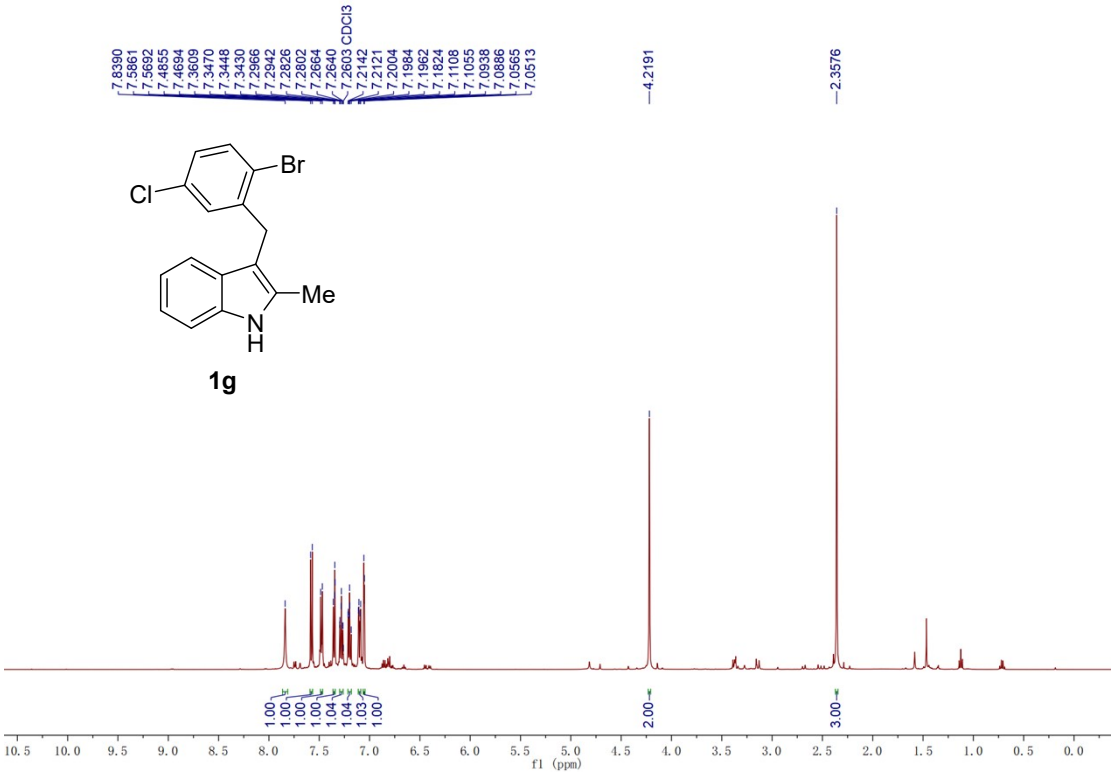



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

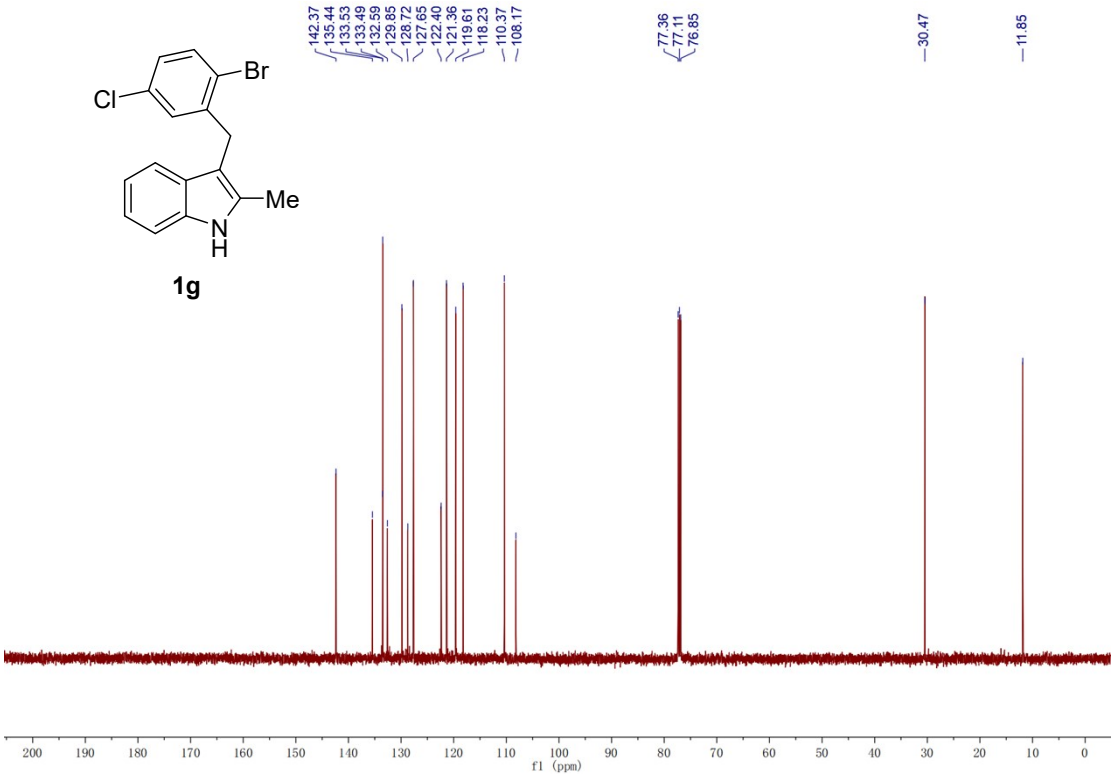


## 3-(2-bromo-5-chlorobenzyl)-2-methyl-1H-indole (1g)

$^1$H NMR (500 MHz, $CDCl_3$)

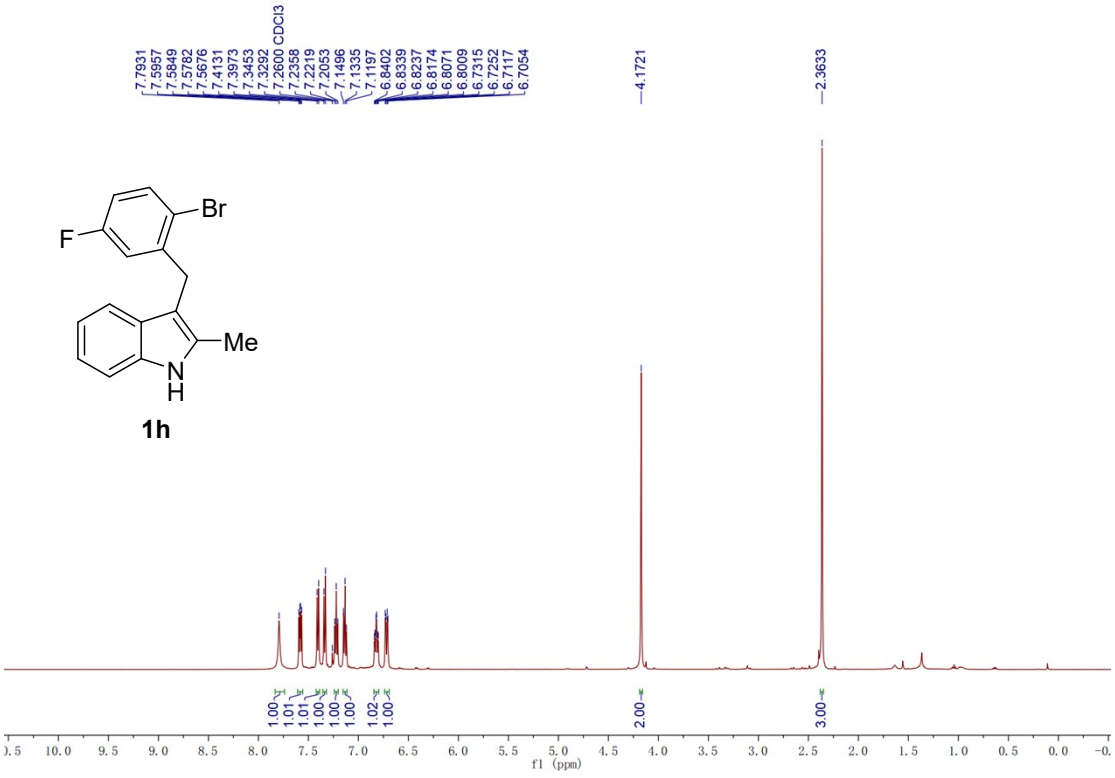



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

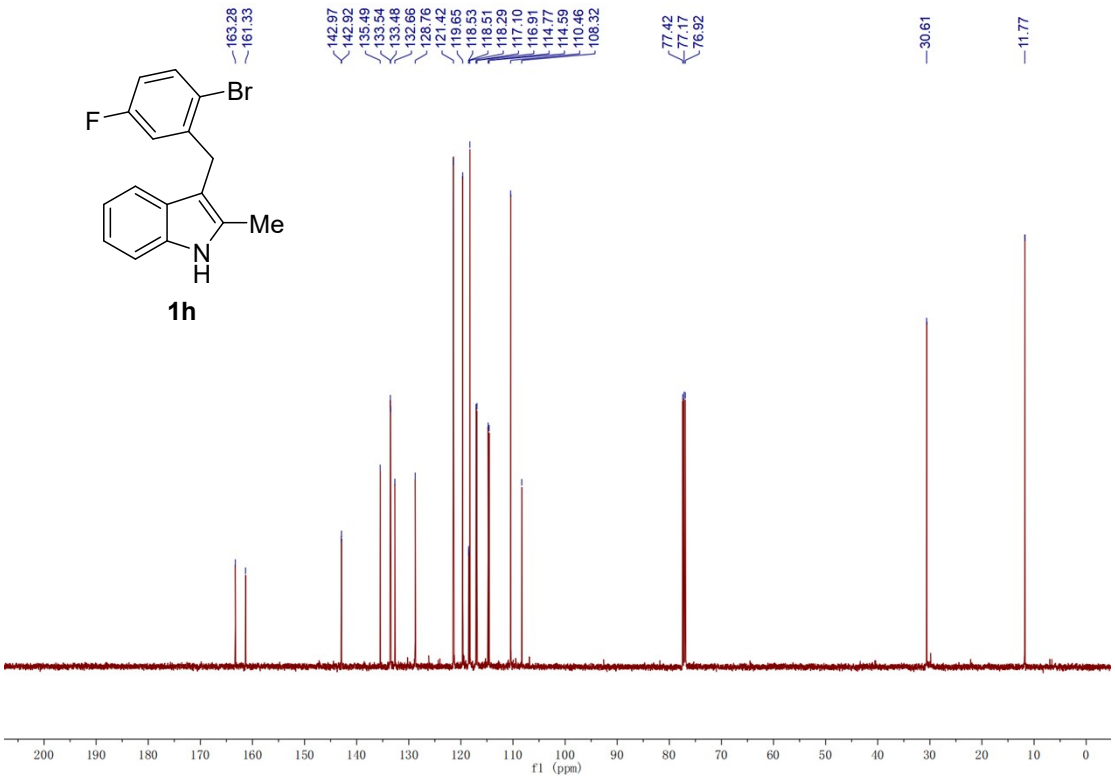


## 3-(2-bromo-5-fluorobenzyl)-2-methyl-1*H*-indole (1h)

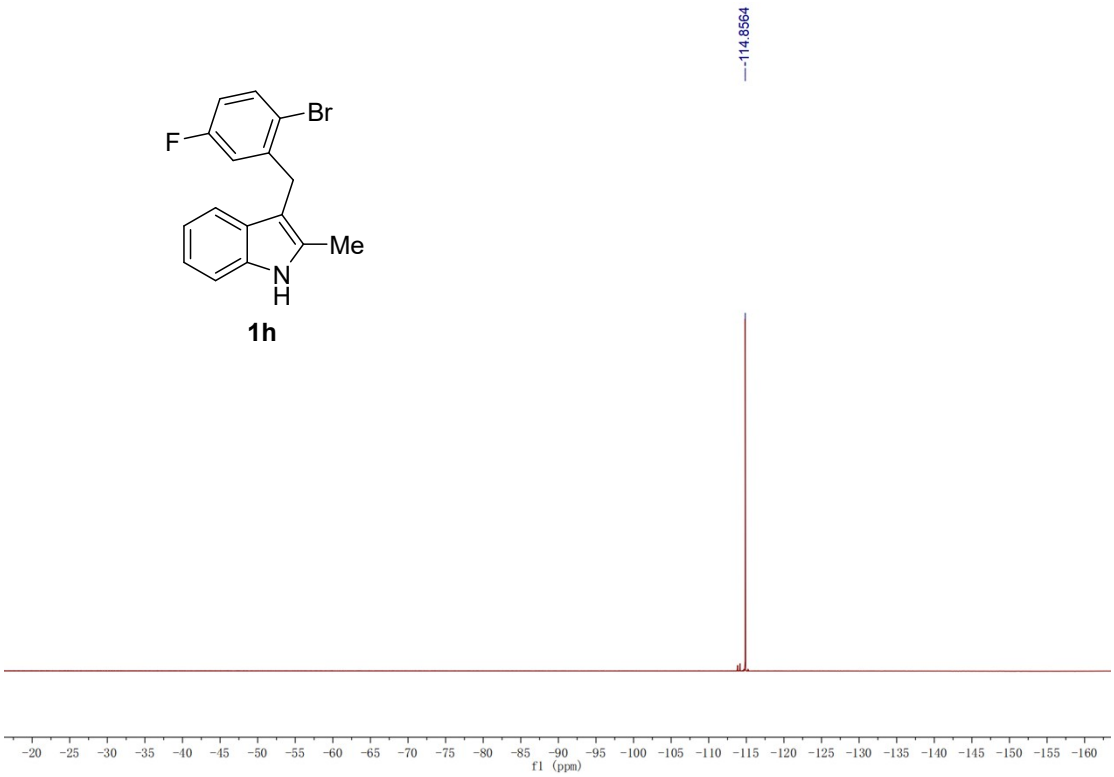
$^{1}$H NMR (500 MHz, $CDCl_3$)




$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)

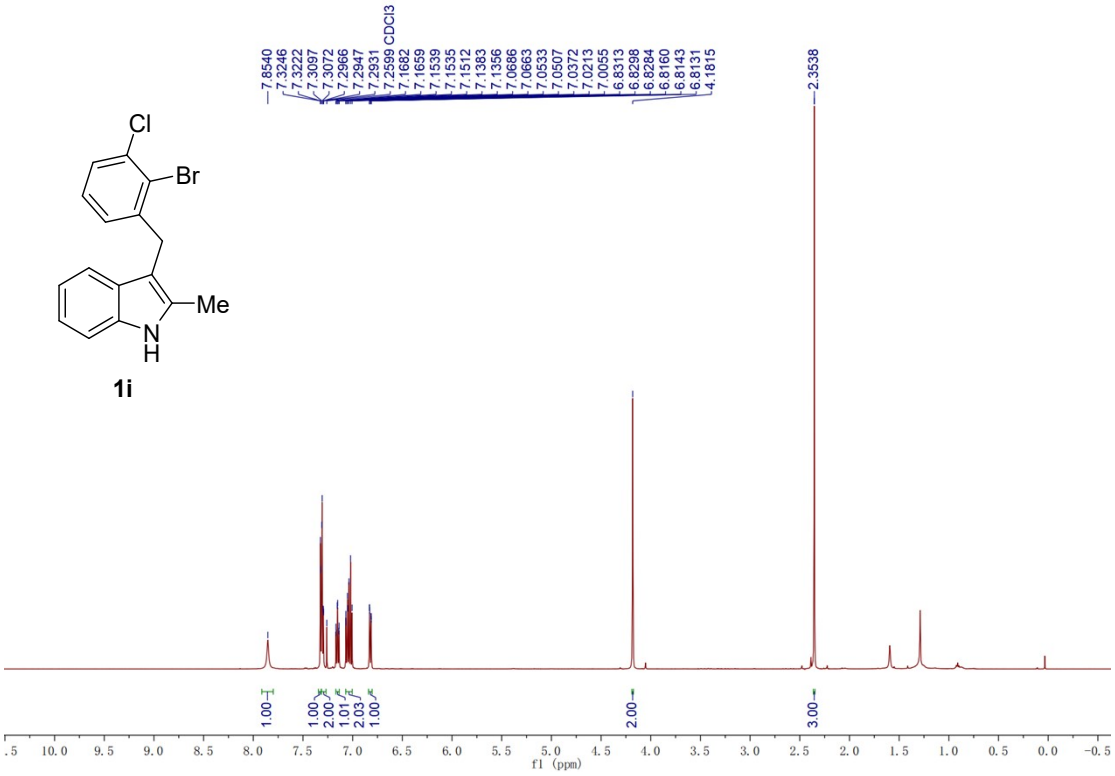


$^{19}$F NMR (471 MHz, $CDCl_3$)

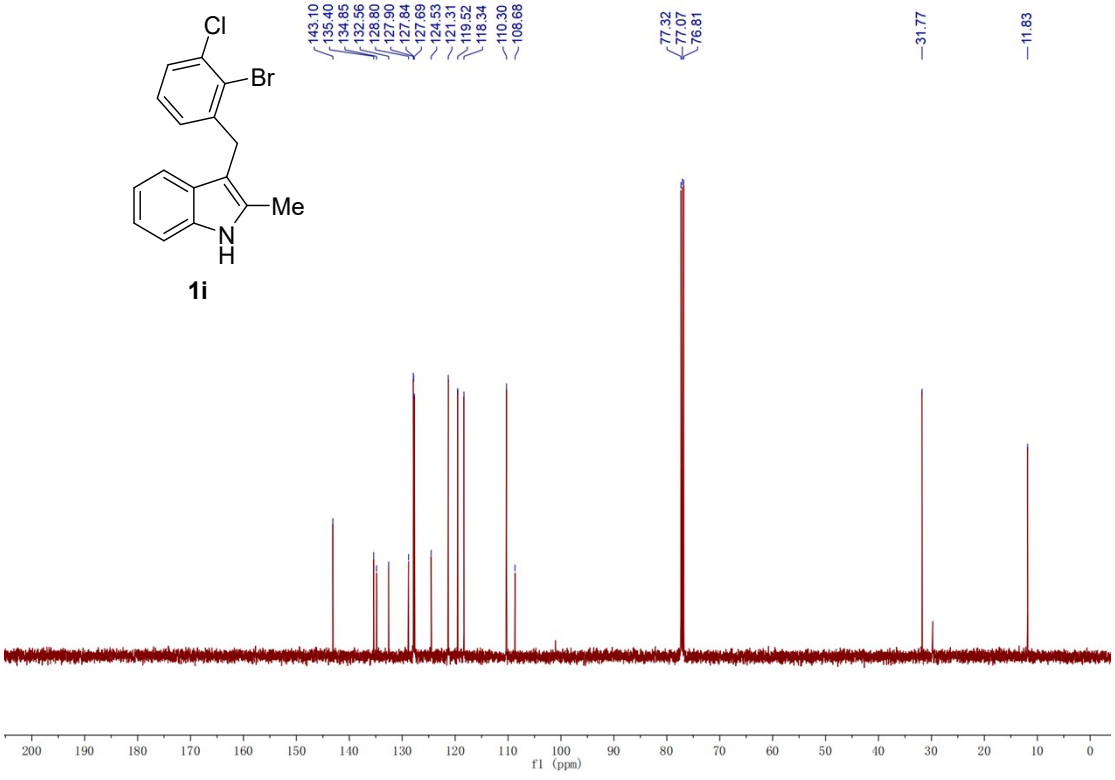


## 3-(2-bromo-3-chlorobenzyl)-2-methyl-1H-indole (1i)

$^1$H NMR (500 MHz, $CDCl_3$)

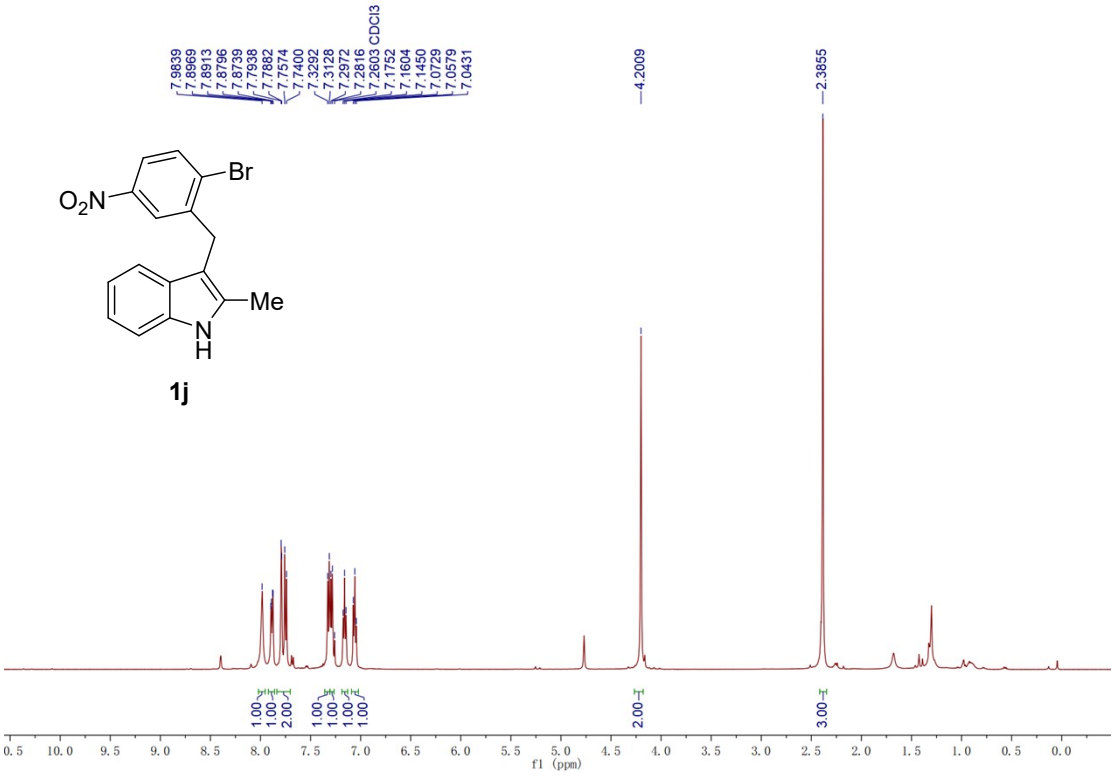



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

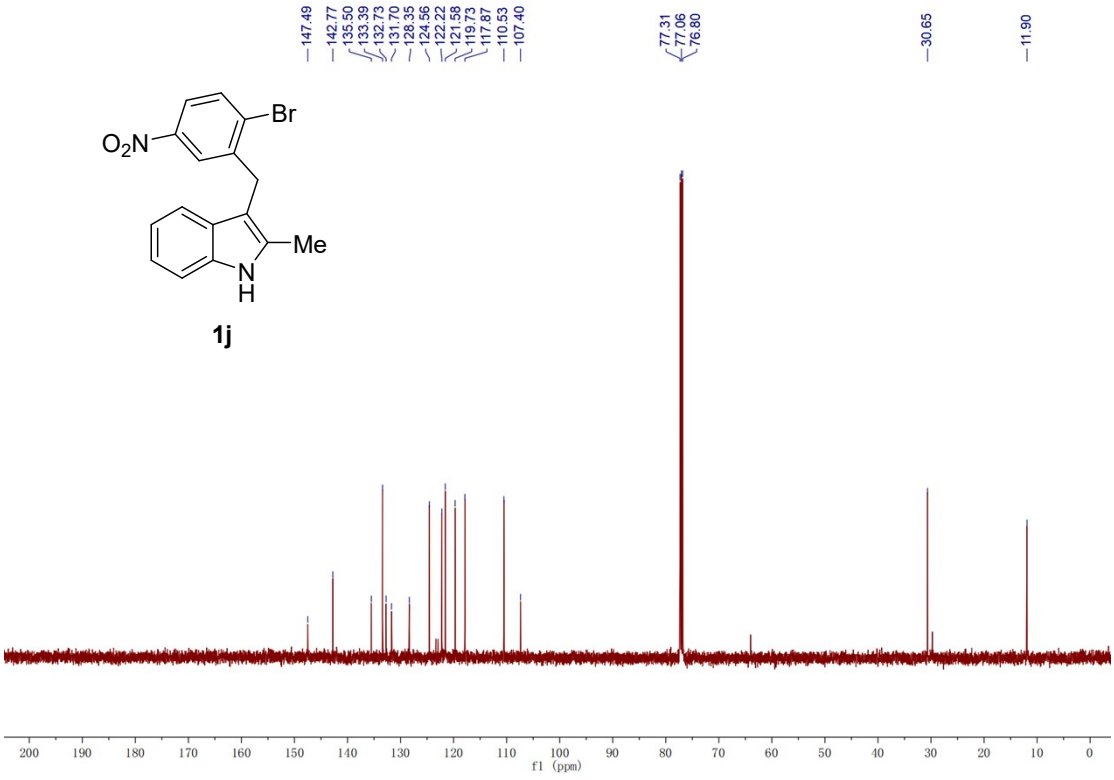


## 3-(2-bromo-5-nitrobenzyl)-2-methyl-1H-indole (1j)

$^1$H NMR (500 MHz, $CDCl_3$)

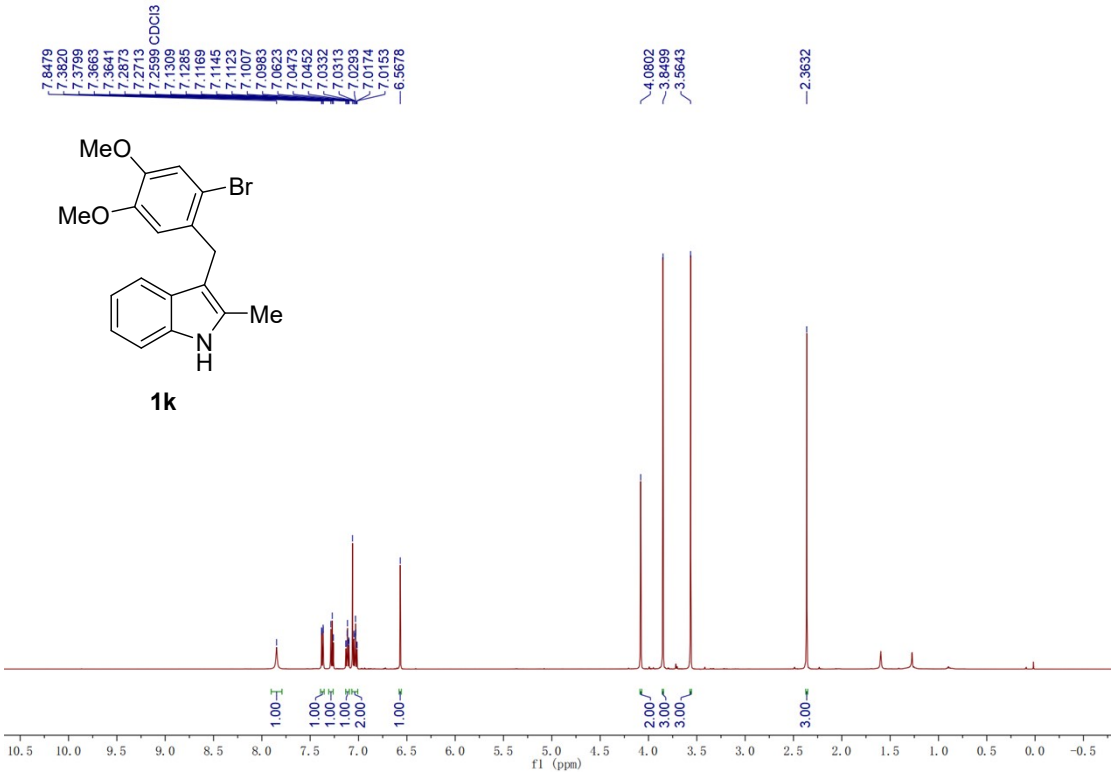



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

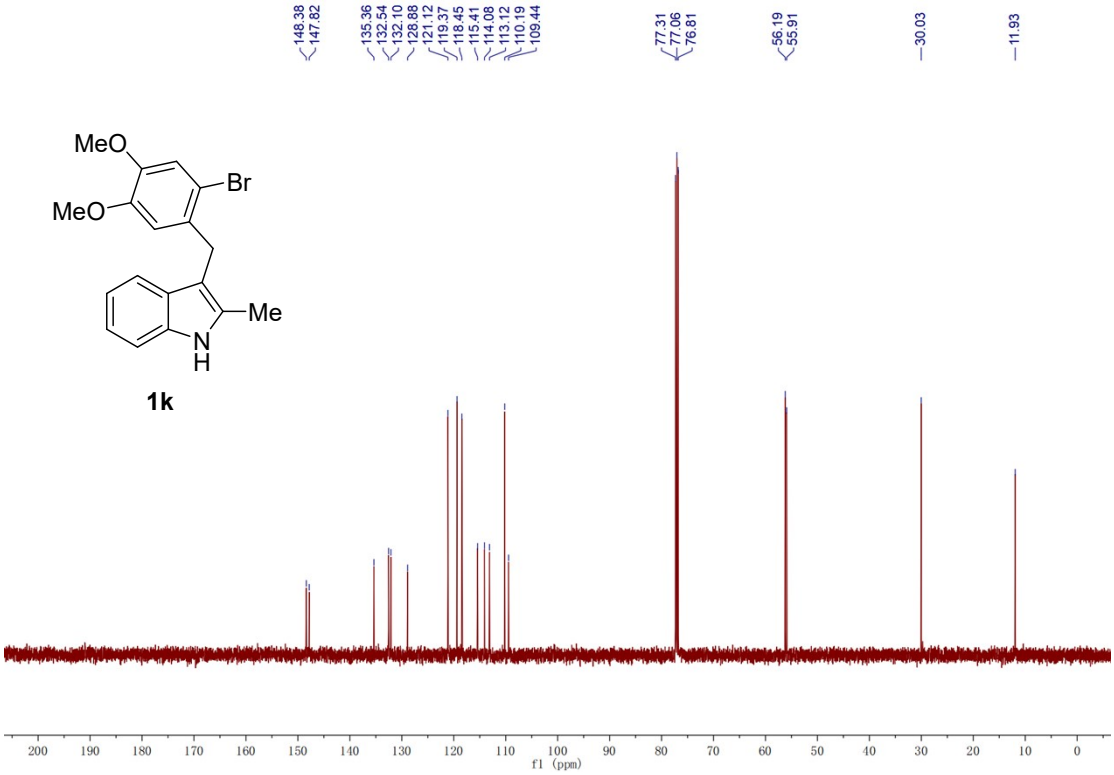


## 3-(2-bromo-4,5-dimethoxybenzyl)-2-methyl-1H-indole (1k)

$^{1}$H NMR (500 MHz, $CDCl_3$)

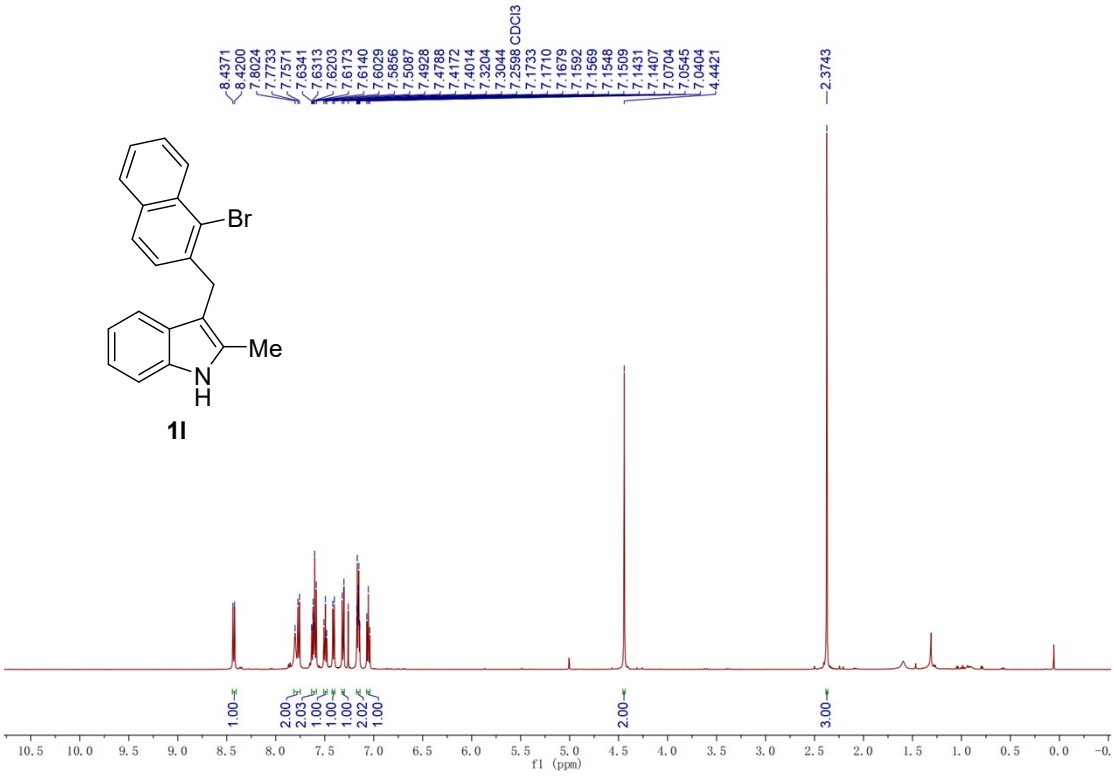



$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)

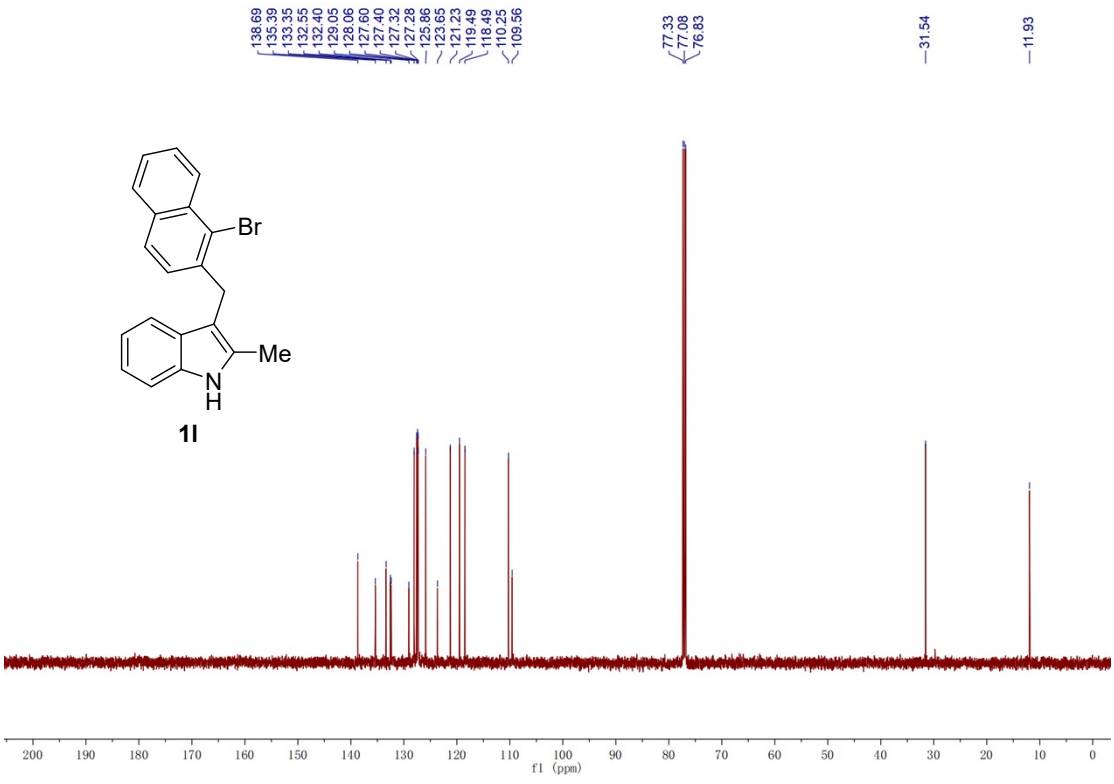


## 3-((1-bromonaphthalen-2-yl)methyl)-2-methyl-1H-indole (1l)

$^1$H NMR (500 MHz, $CDCl_3$)

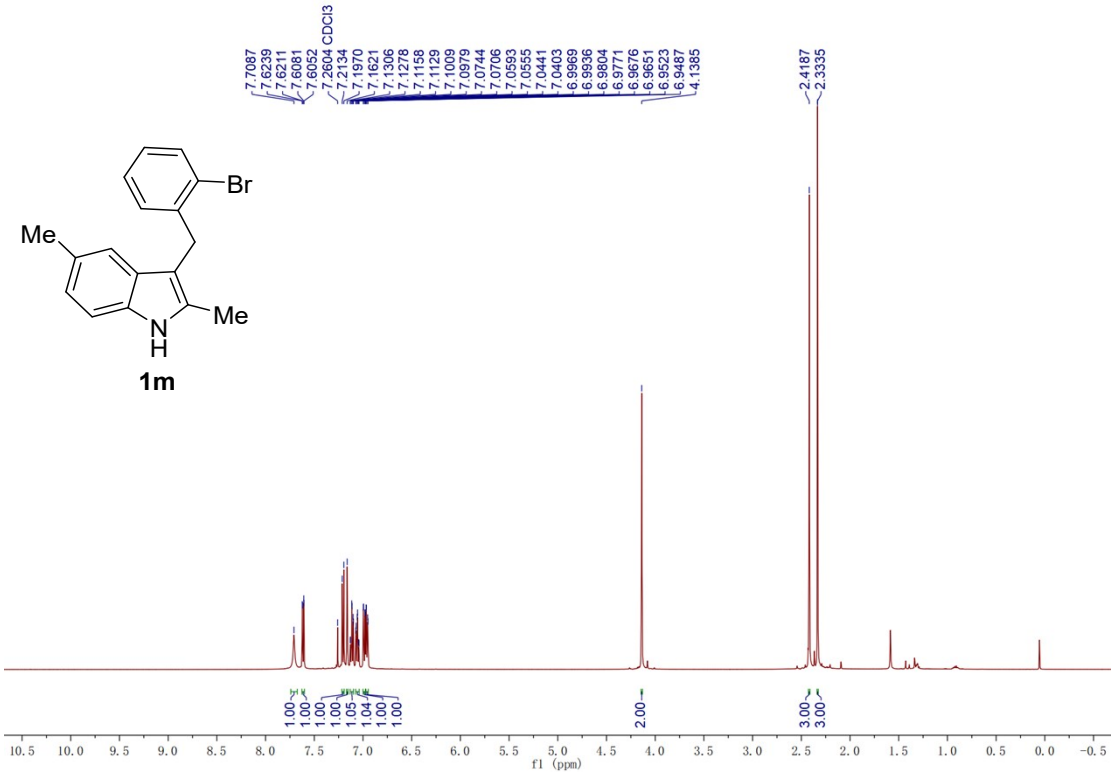



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

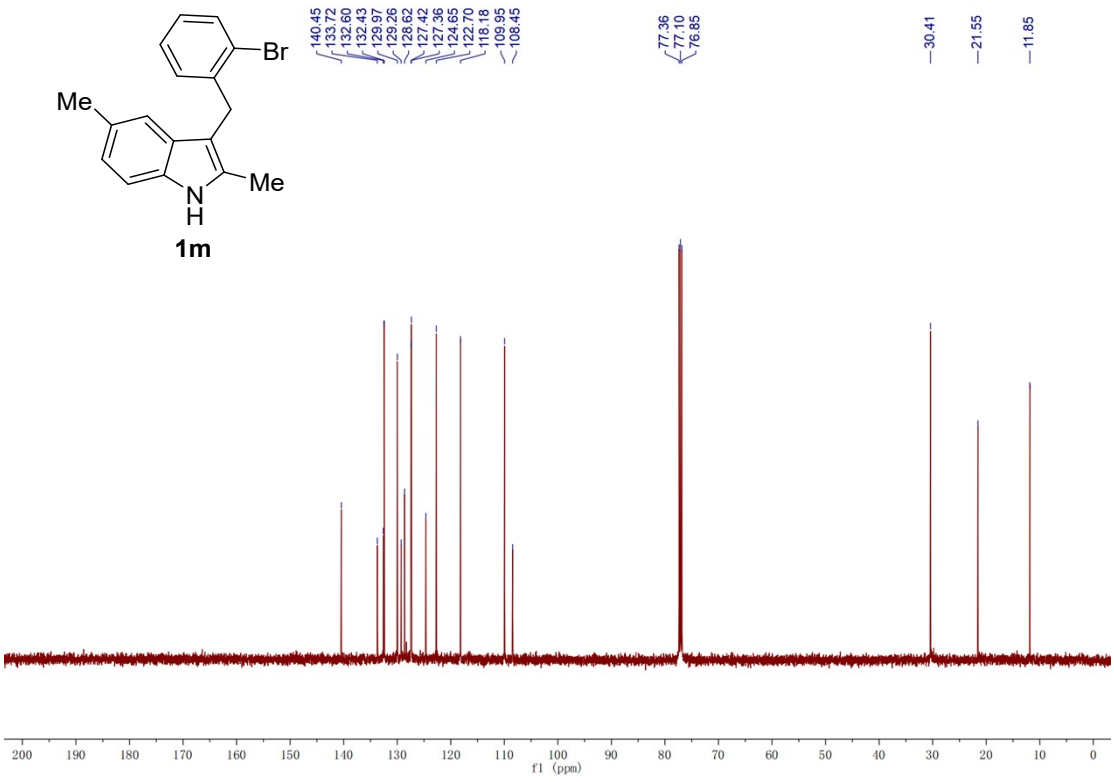


## 3-(2-bromobenzyl)-2,5-dimethyl-1*H*-indole (1m)

$^1$H NMR (500 MHz, $CDCl_3$)

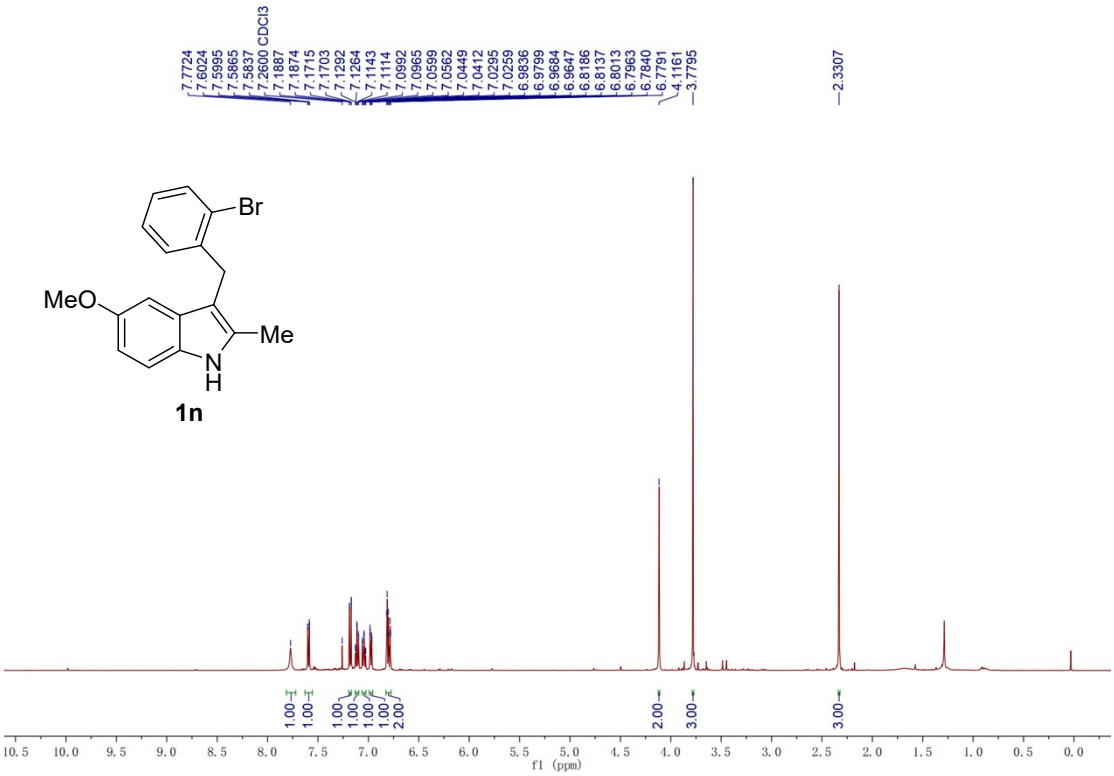



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

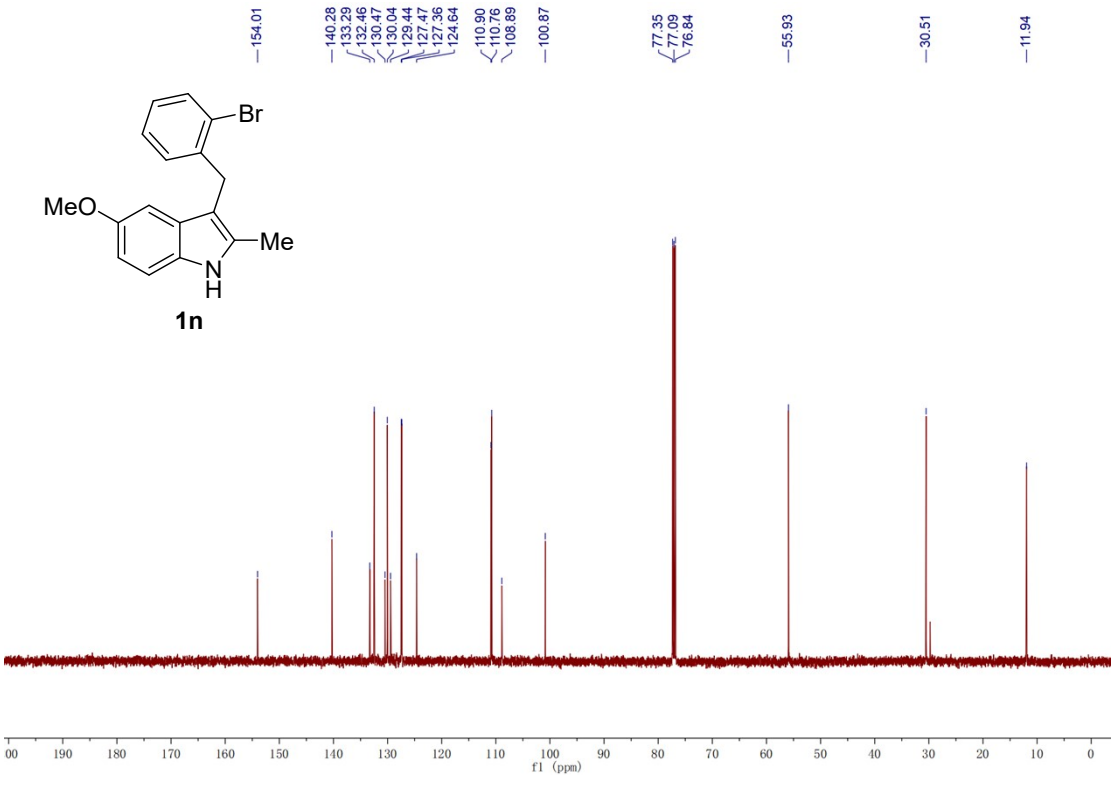


**3-(2-bromobenzyl)-5-methoxy-2-methyl-1*H*-indole (1n)**

$^{1}$H NMR (500 MHz, $CDCl_3$)

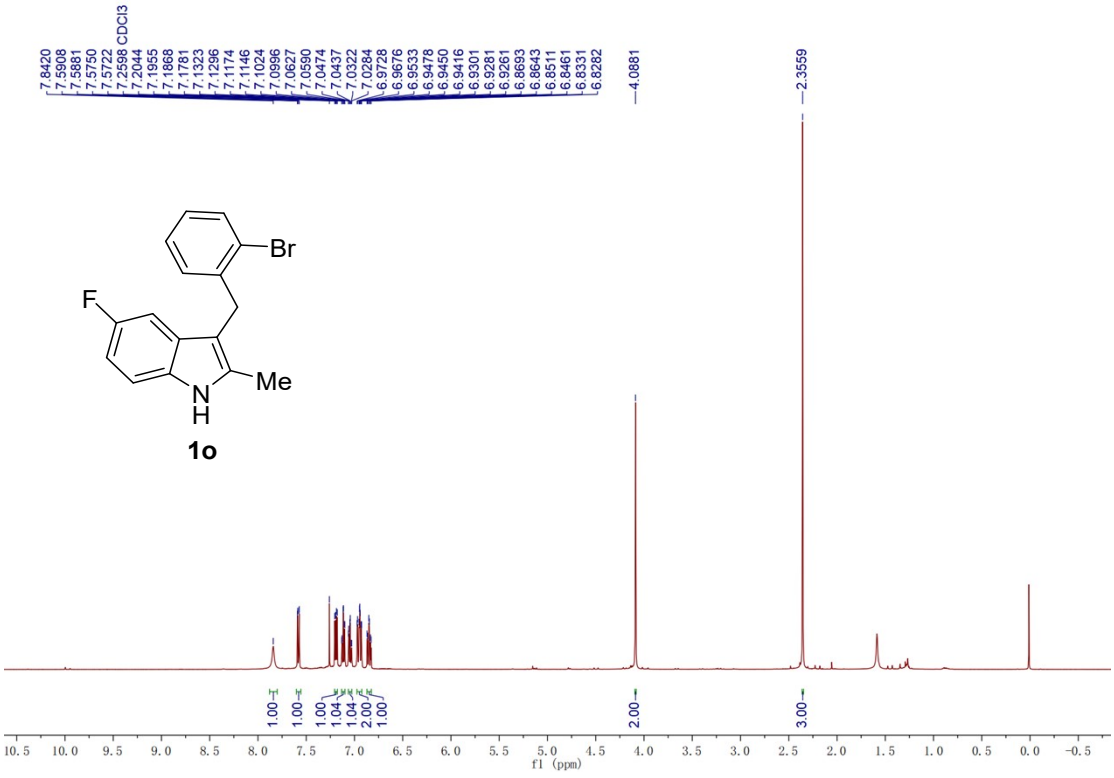



$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)

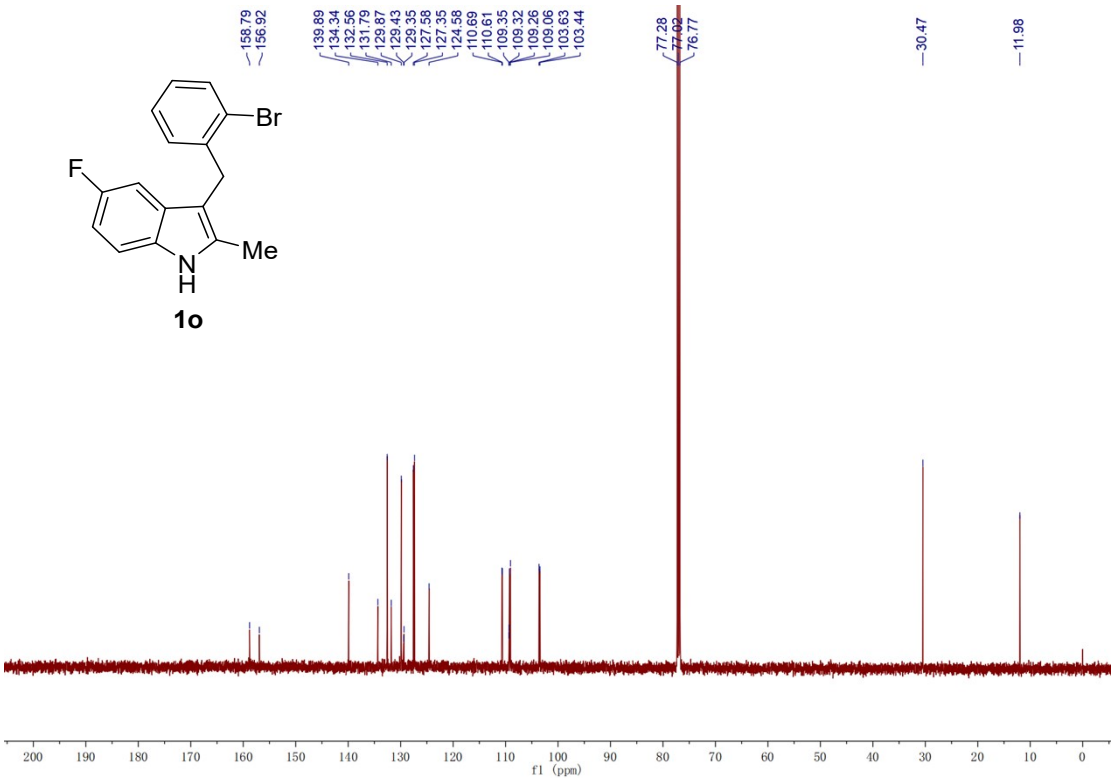


## 3-(2-bromobenzyl)-5-fluoro-2-methyl-1*H*-indole (1o)

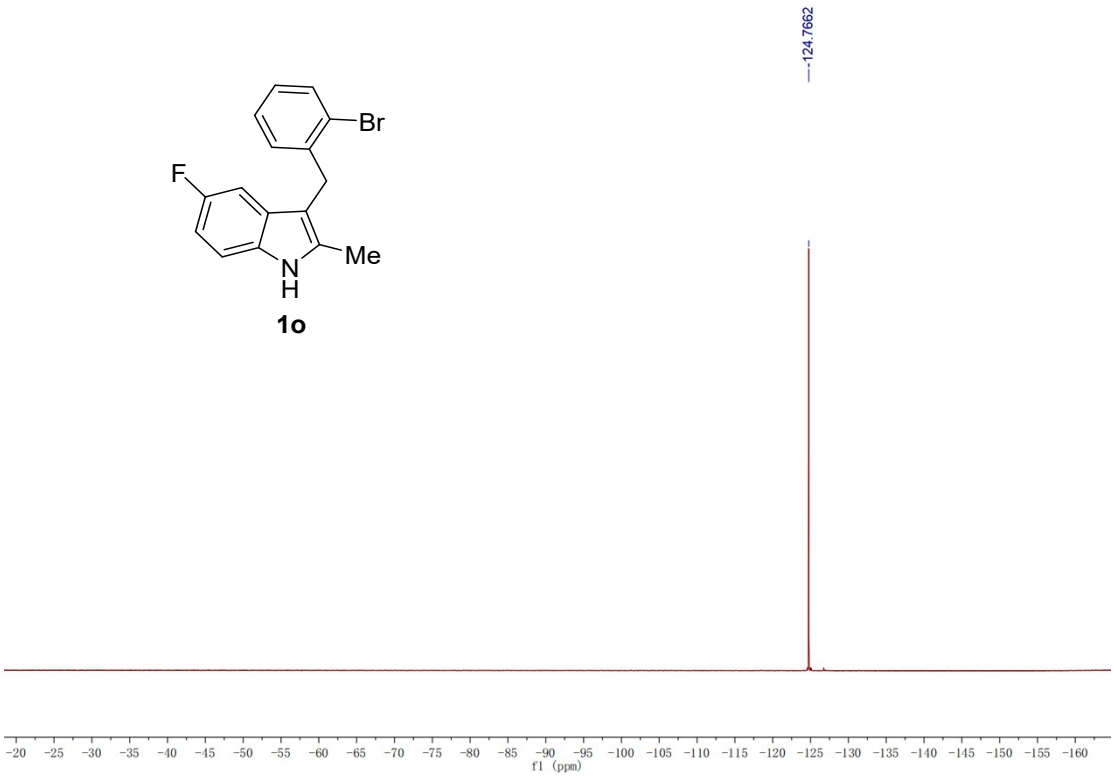
$^1$H NMR (500 MHz, $CDCl_3$)




$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

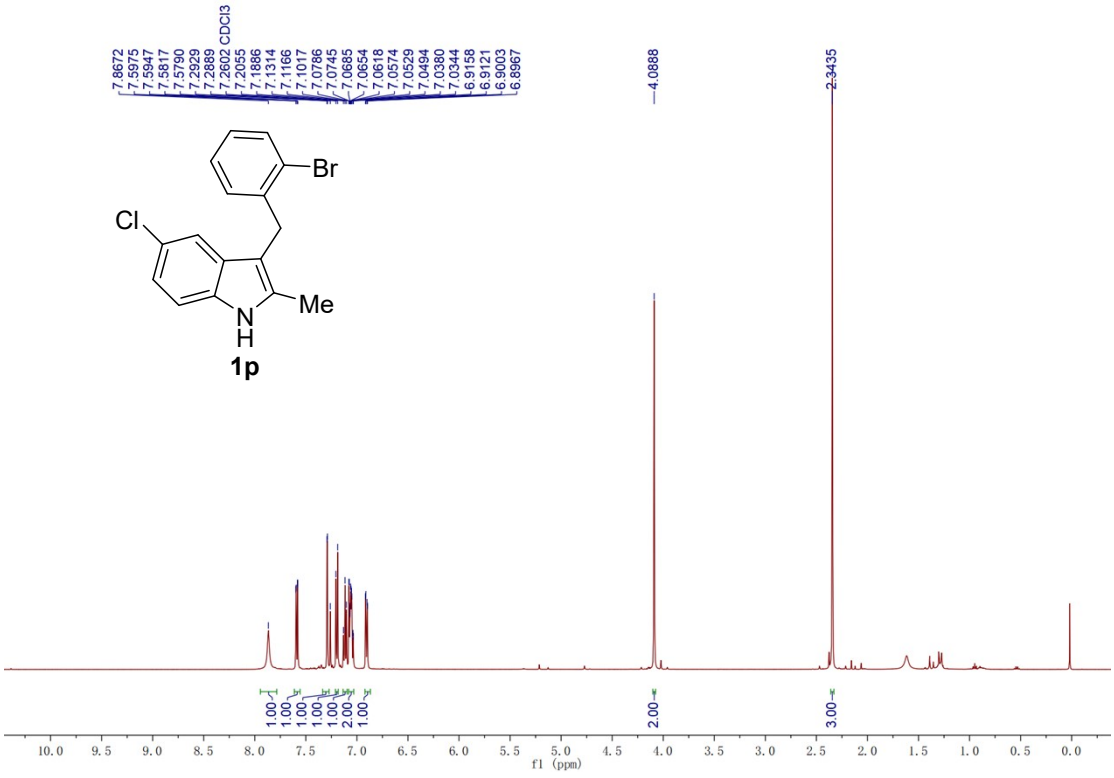


$^{19}F$ NMR (471 MHz, $CDCl_3$)

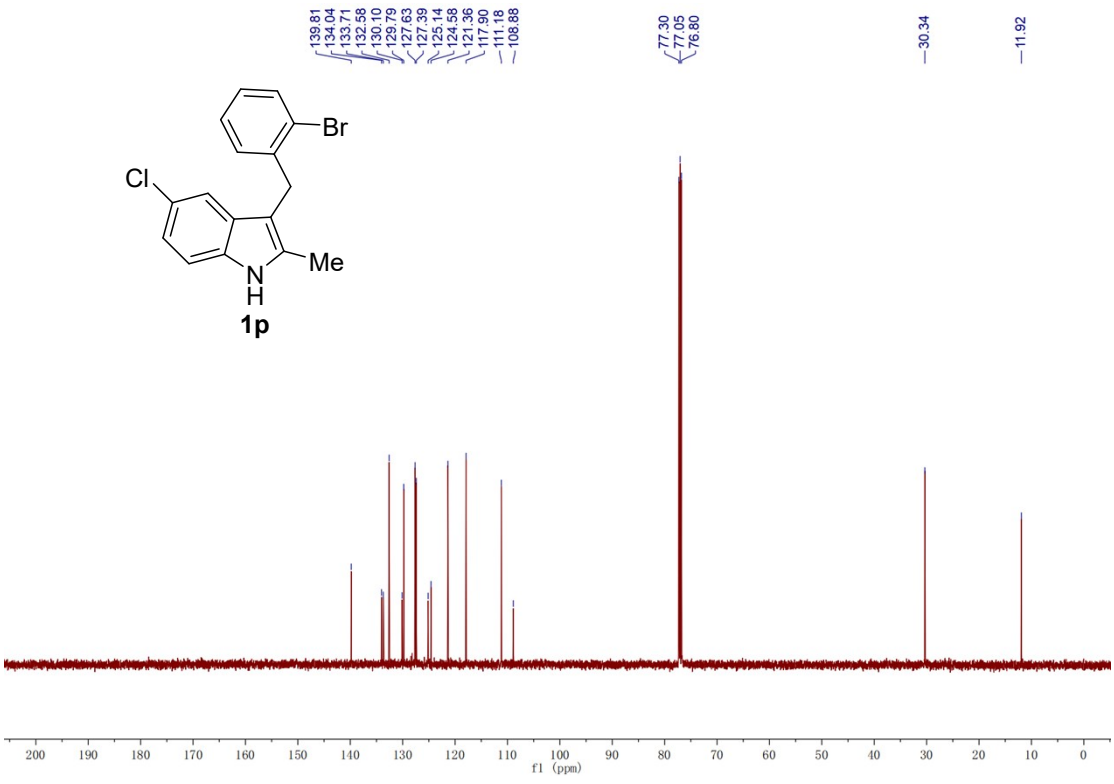


**3-(2-bromobenzyl)-5-chloro-2-methyl-1*H*-indole (1p)**

$^{1}$H NMR (500 MHz, $CDCl_3$)

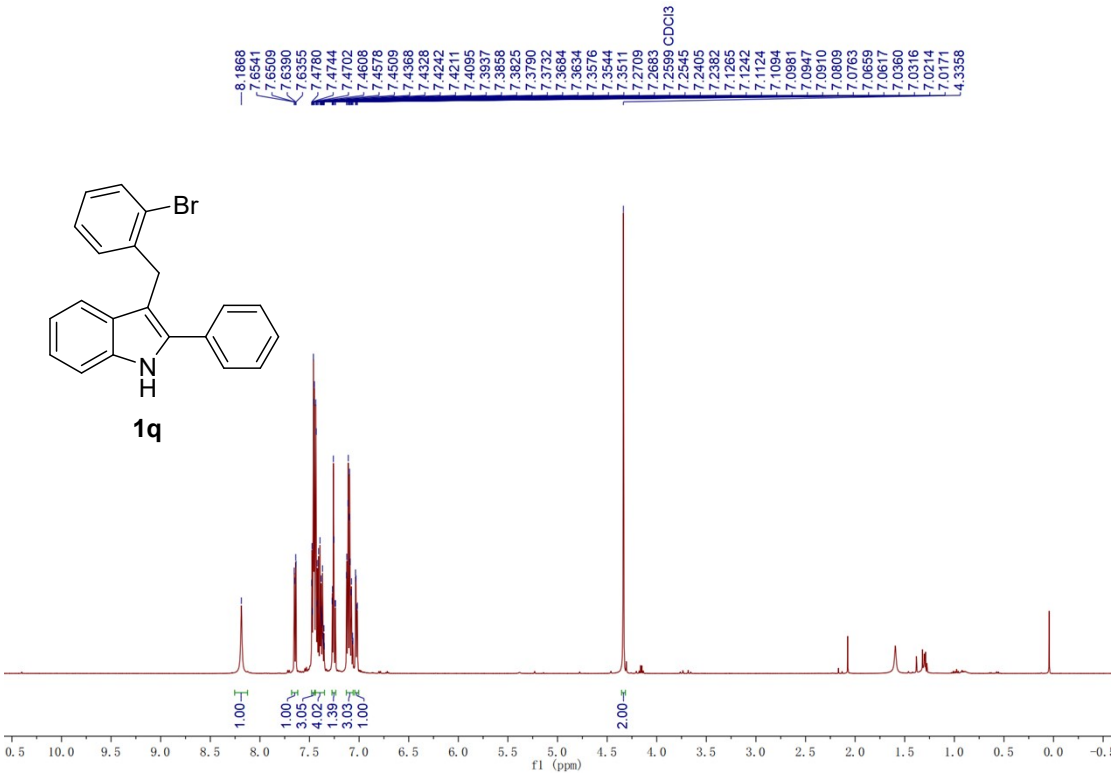



$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)

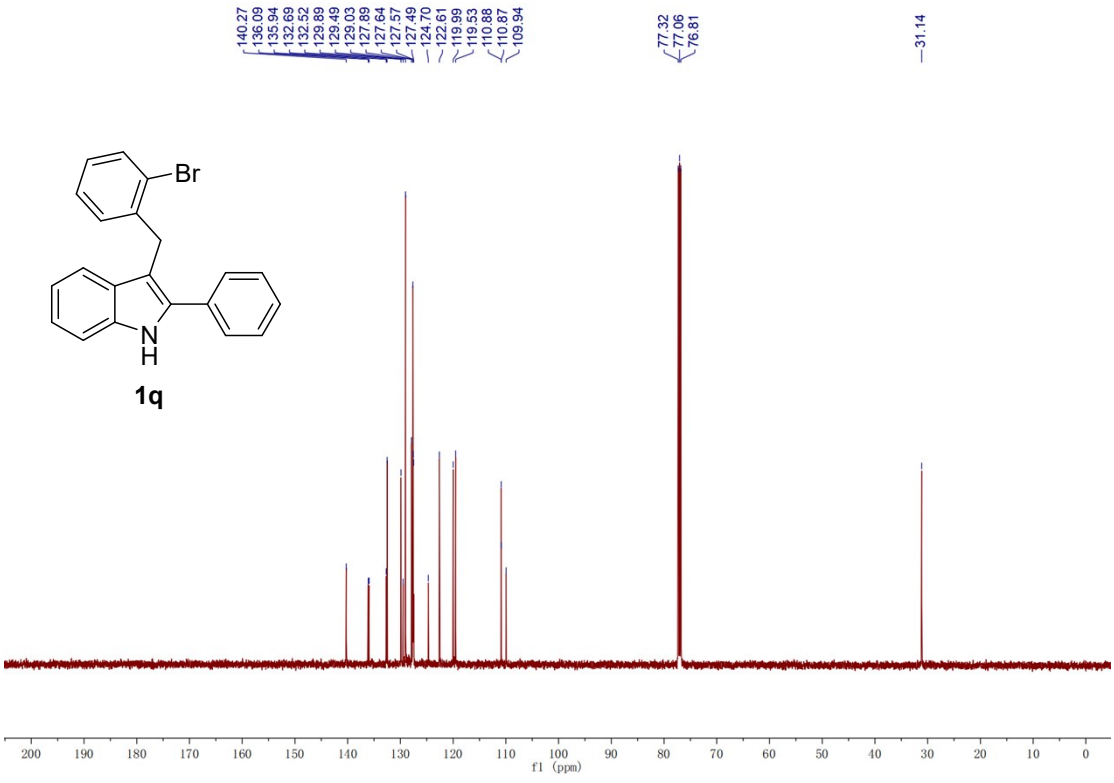


## 3-(2-bromobenzyl)-2-phenyl-1*H*-indole (1q)

$^1$H NMR (500 MHz, $CDCl_3$)

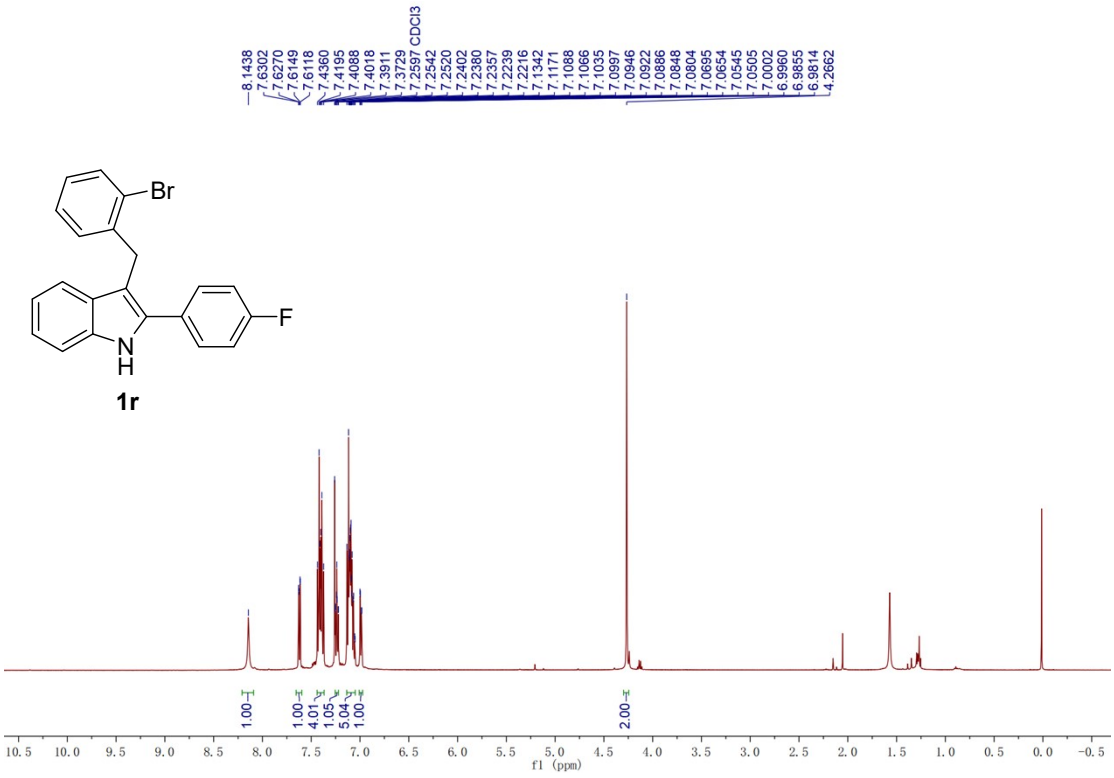



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

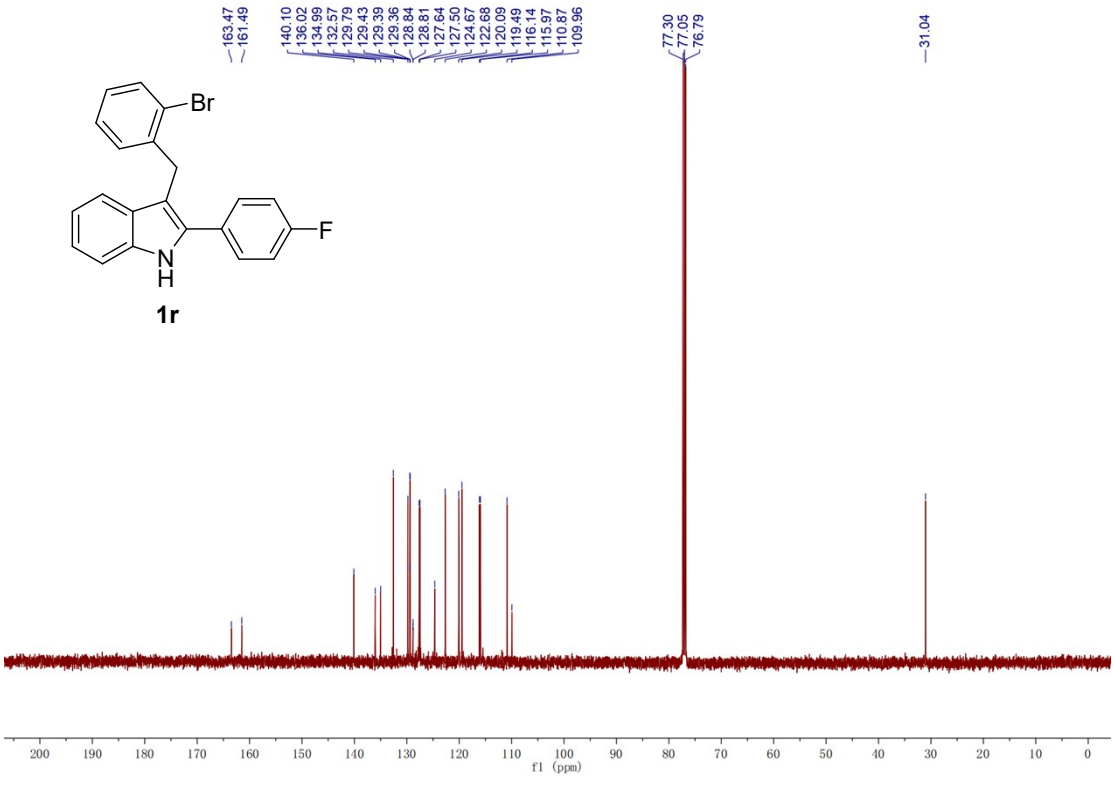


**3-(2-bromobenzyl)-2-(4-fluorophenyl)-1*H*-indole (1r)**

$^{1}$H NMR (500 MHz, $CDCl_3$)

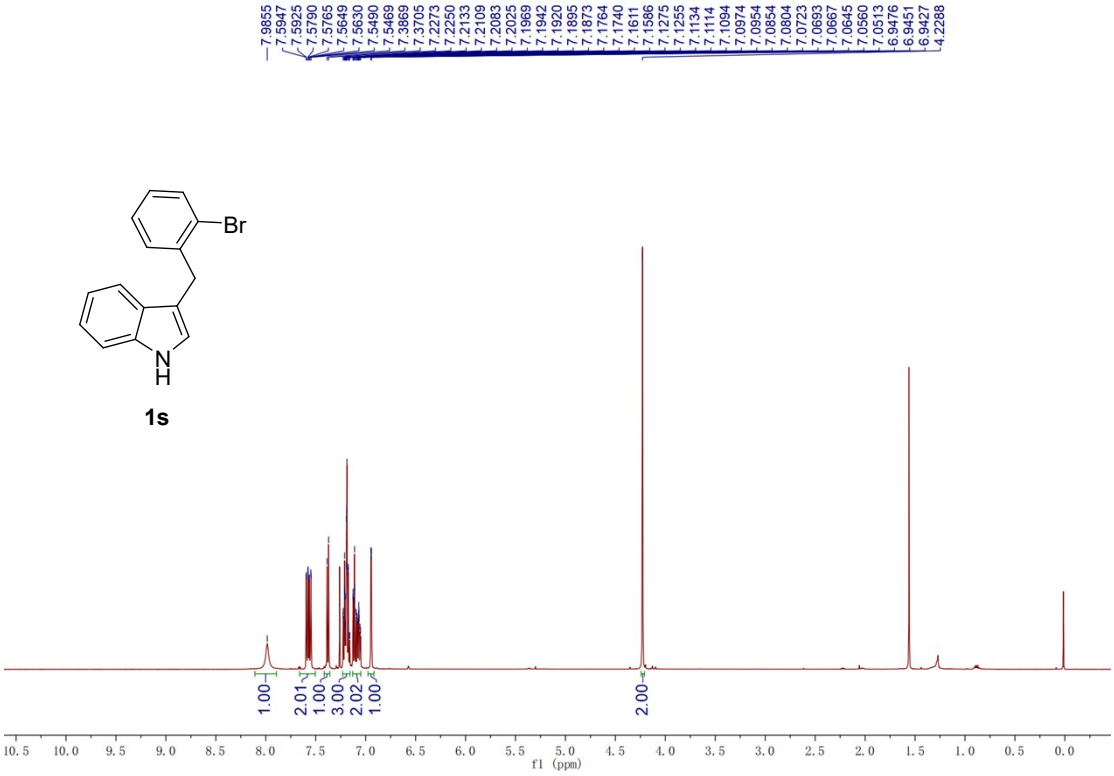


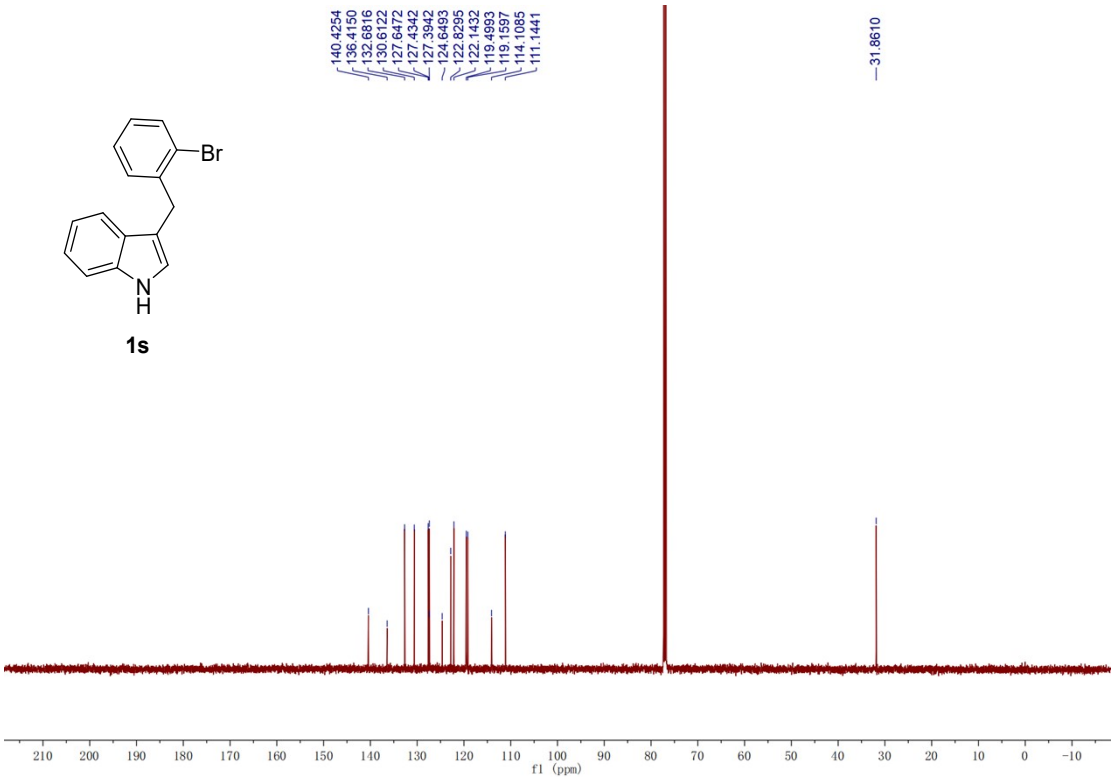

$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)



## 3-(2-bromobenzyl)-1*H*-indole (1s)

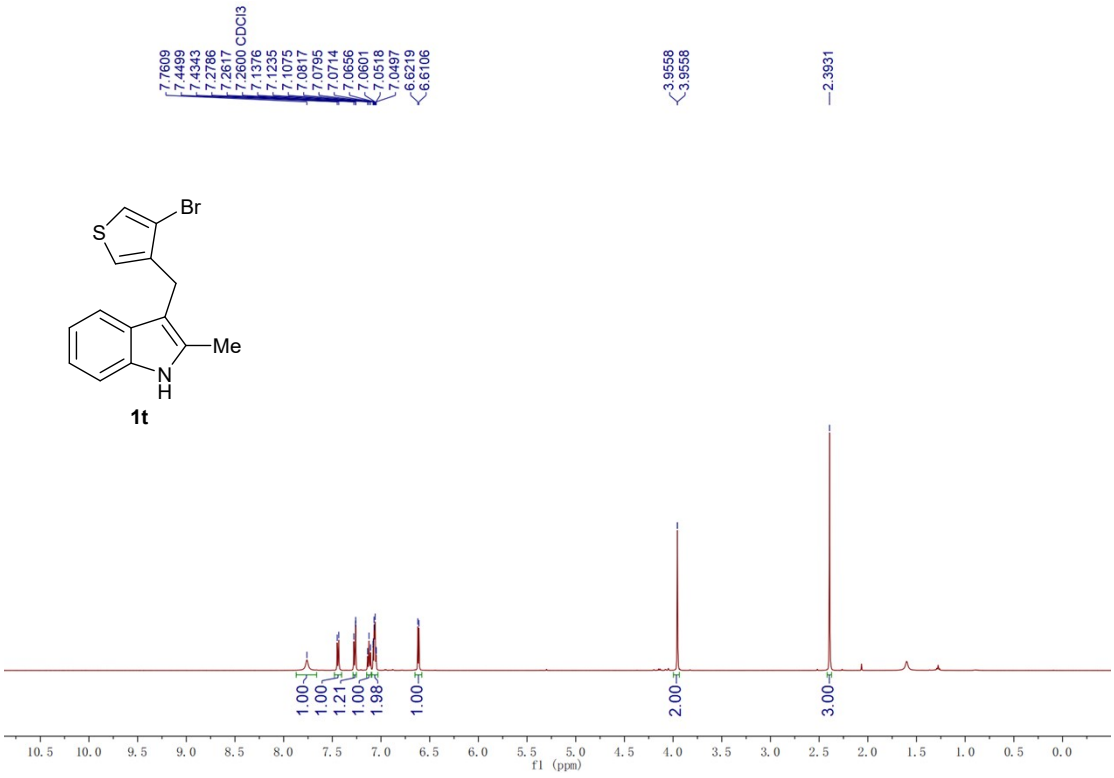
$^1$H NMR (500 MHz, $CDCl_3$)



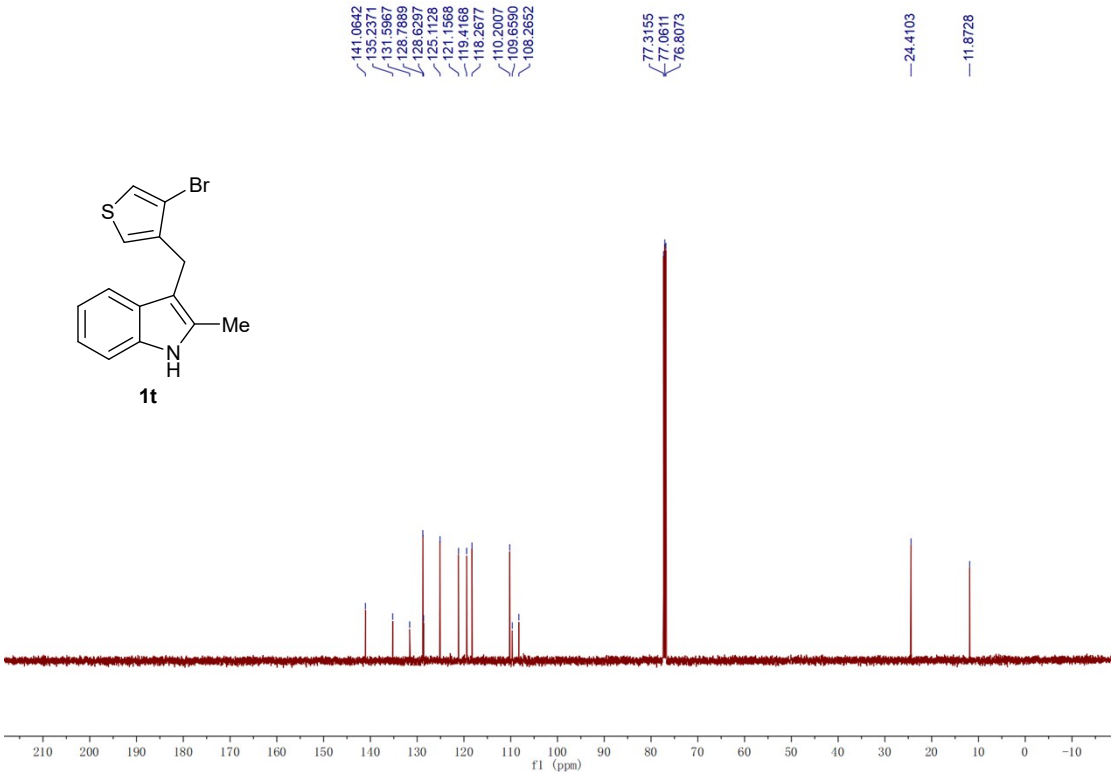



**3-((4-bromothiophen-3-yl)methyl)-2-methyl-1*H*-indole (1t)**

$^{1}$H NMR (500 MHz, $CDCl_3$)

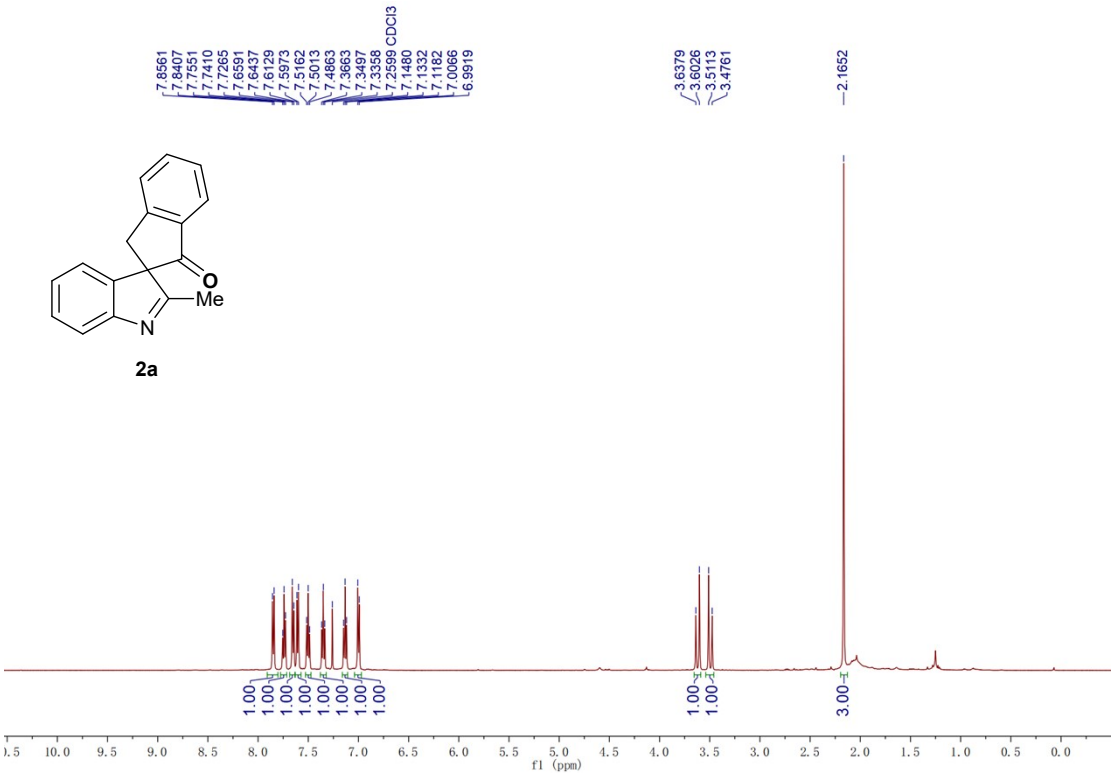



$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)



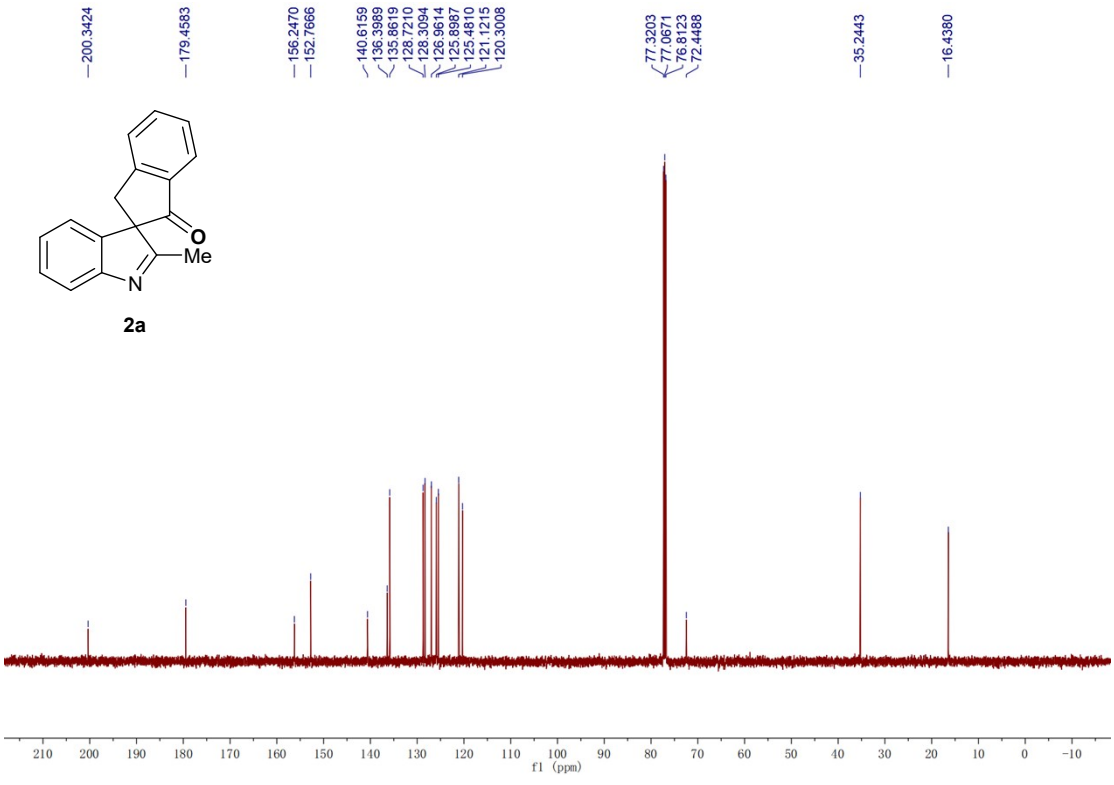
## 2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2a)

$^1$H NMR (500 MHz, $CDCl_3$)




2a

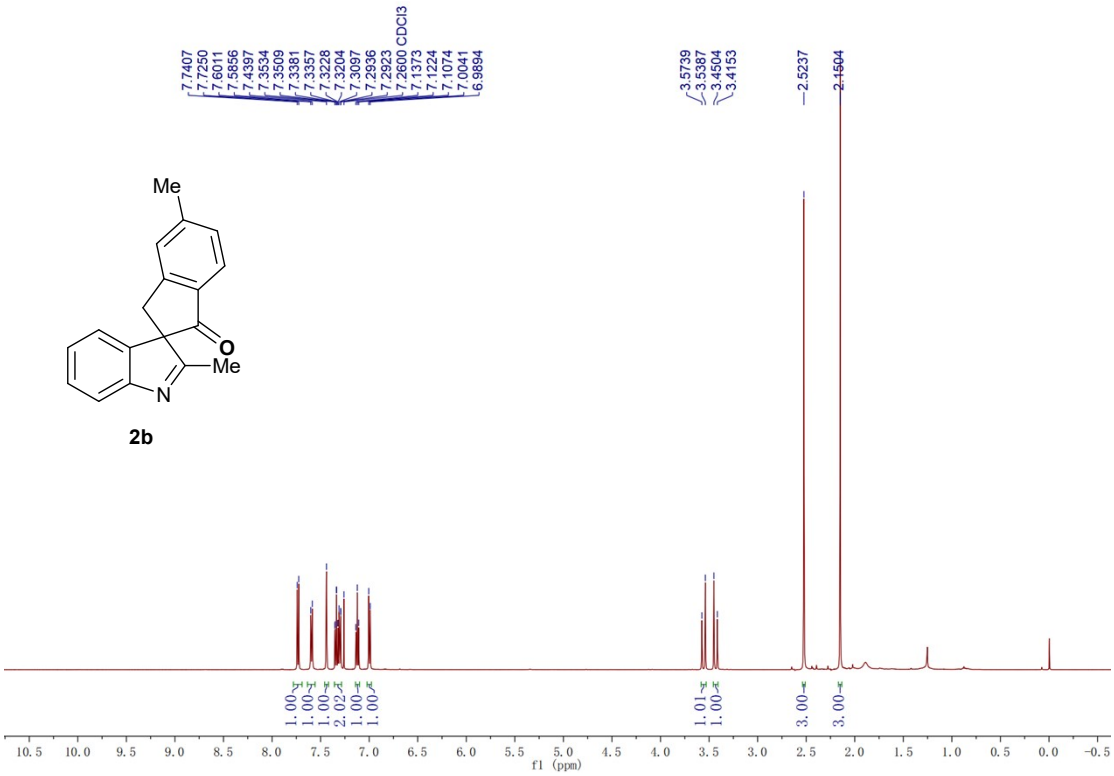
$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)




2a

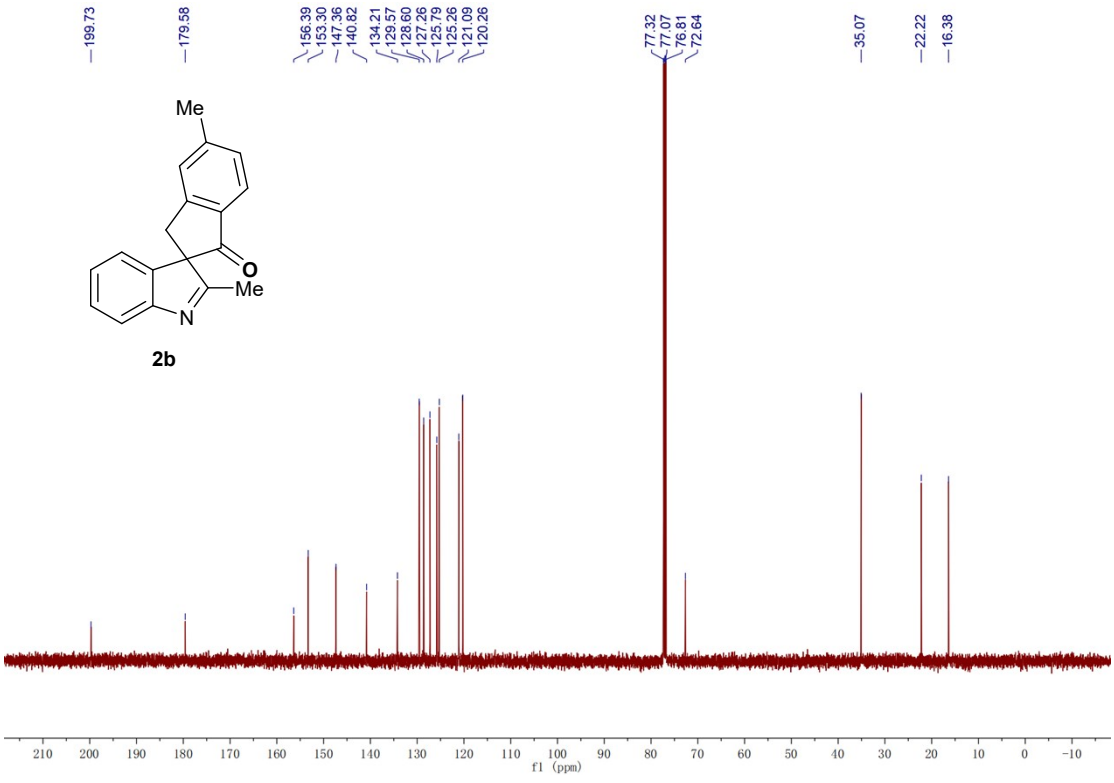
## 2',5-dimethylspiro[indene-2,3'-indol]-1(3*H*)-one (2b)

$^1$H NMR (500 MHz, $CDCl_3$)




**2b**

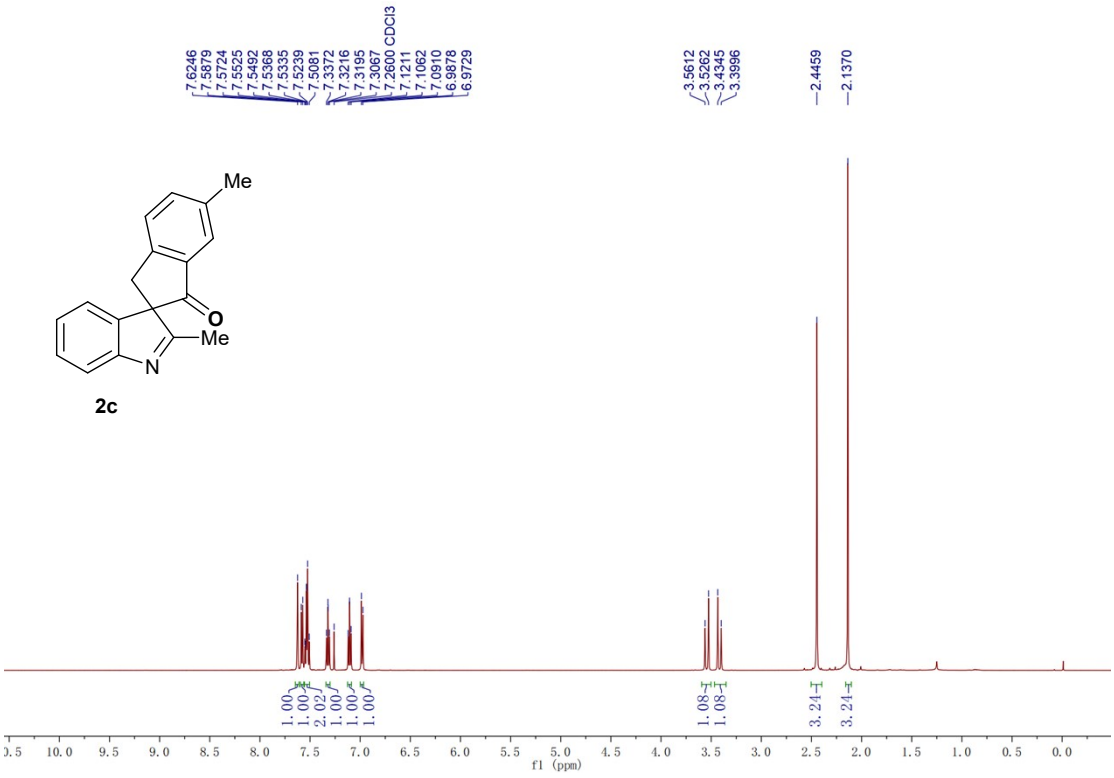
$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)



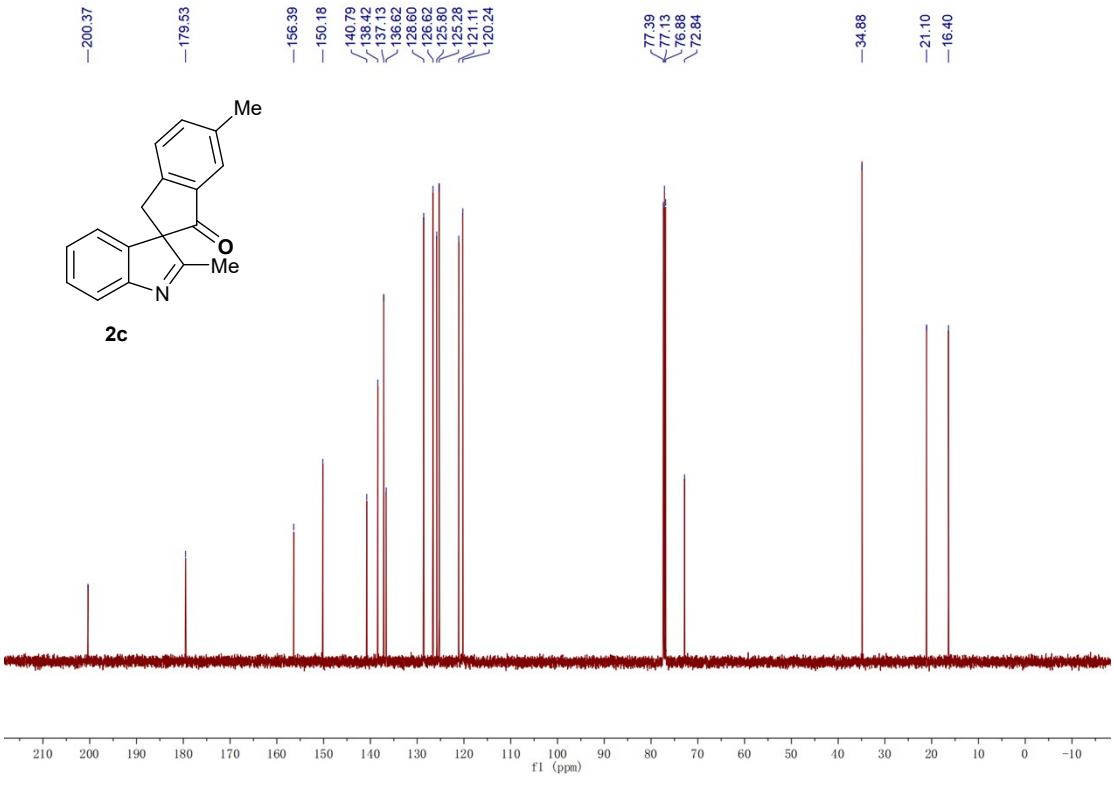

**2b**

## 2',6-dimethylspiro[indene-2,3'-indol]-1(3*H*)-one (2c)

$^1$H NMR (500 MHz, $CDCl_3$)

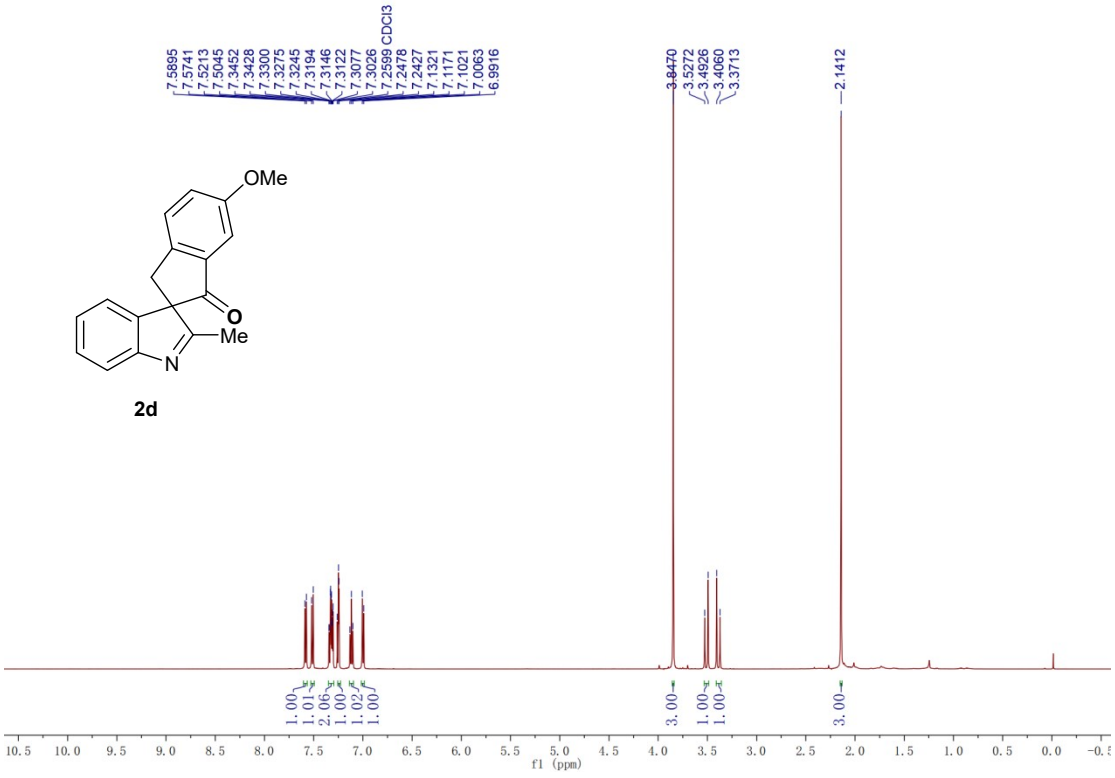



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

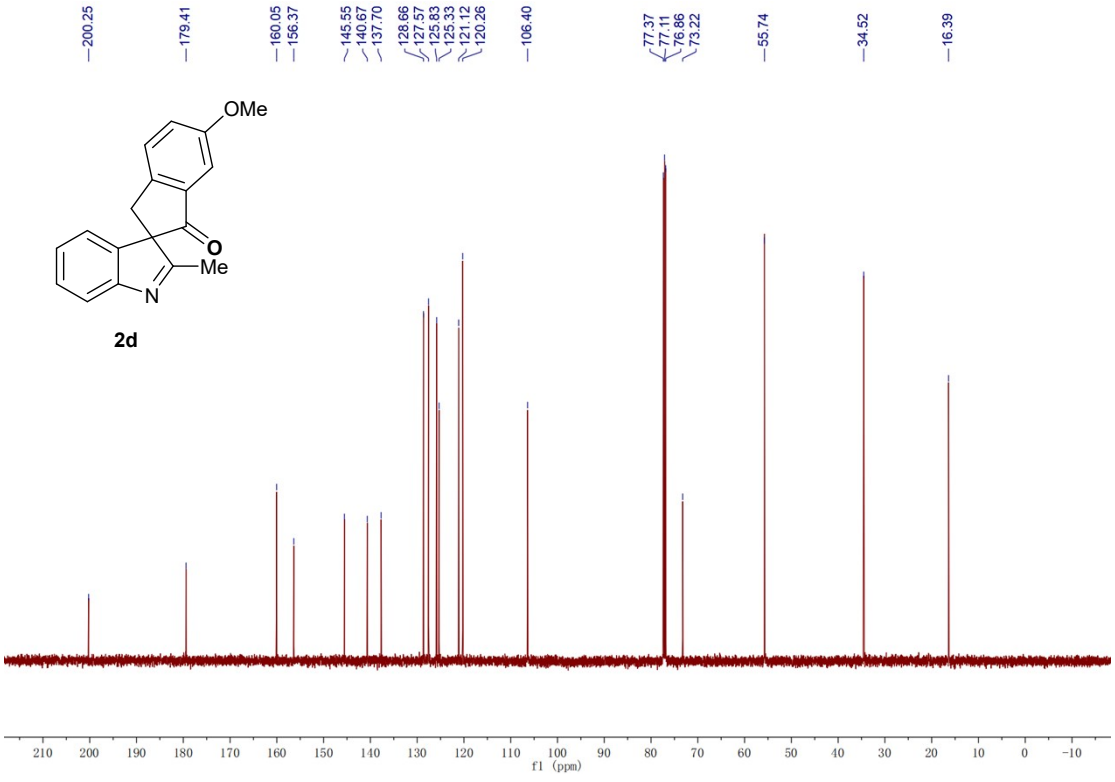


## 6-methoxy-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2d)

$^1$H NMR (500 MHz, $CDCl_3$)

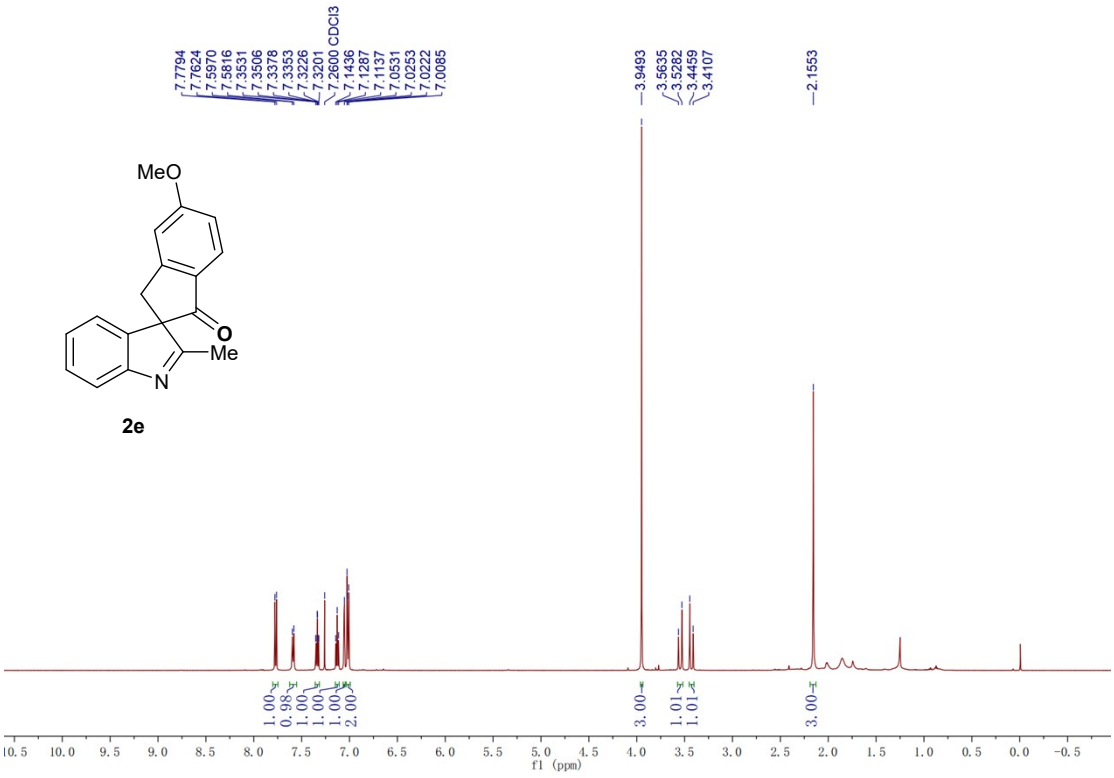



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

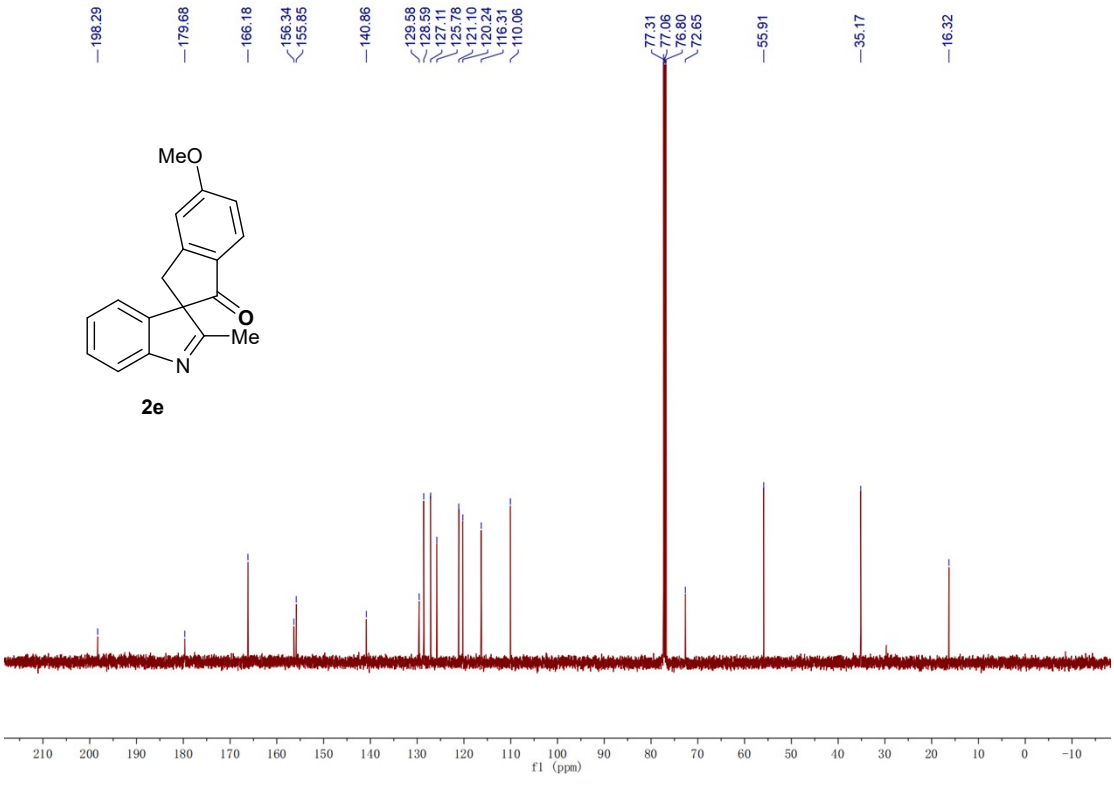


**5-methoxy-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2e)**

$^{1}$H NMR (500 MHz, $CDCl_3$)

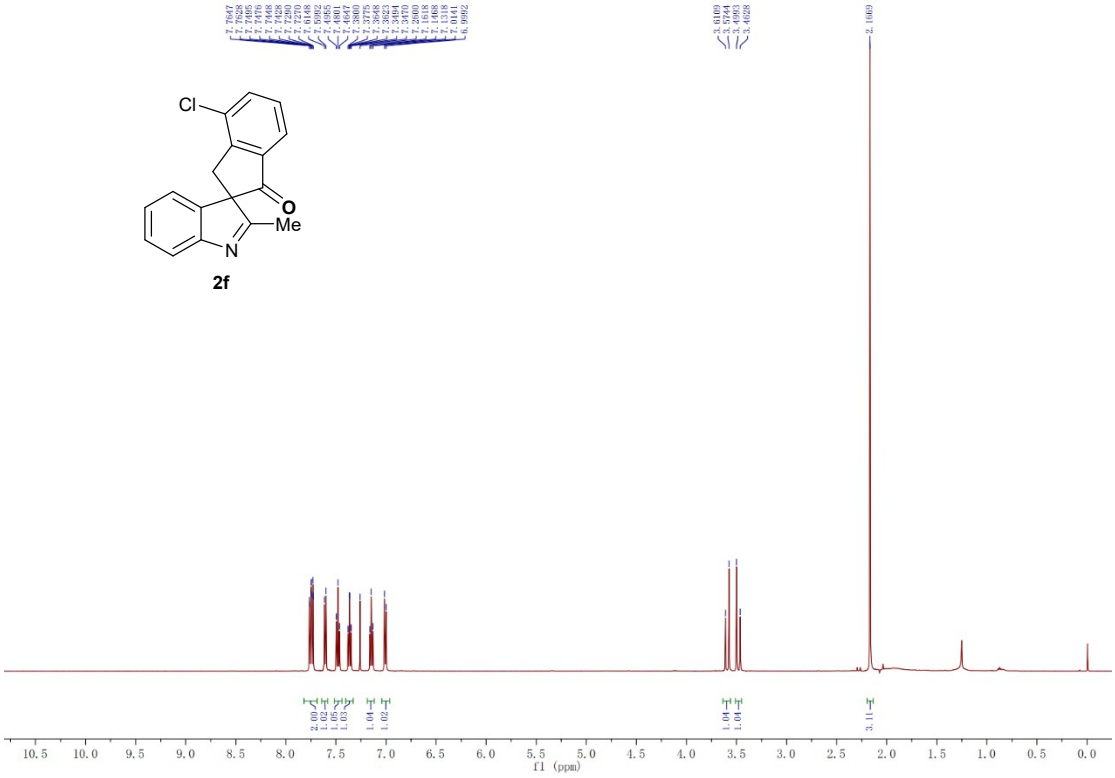



$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)

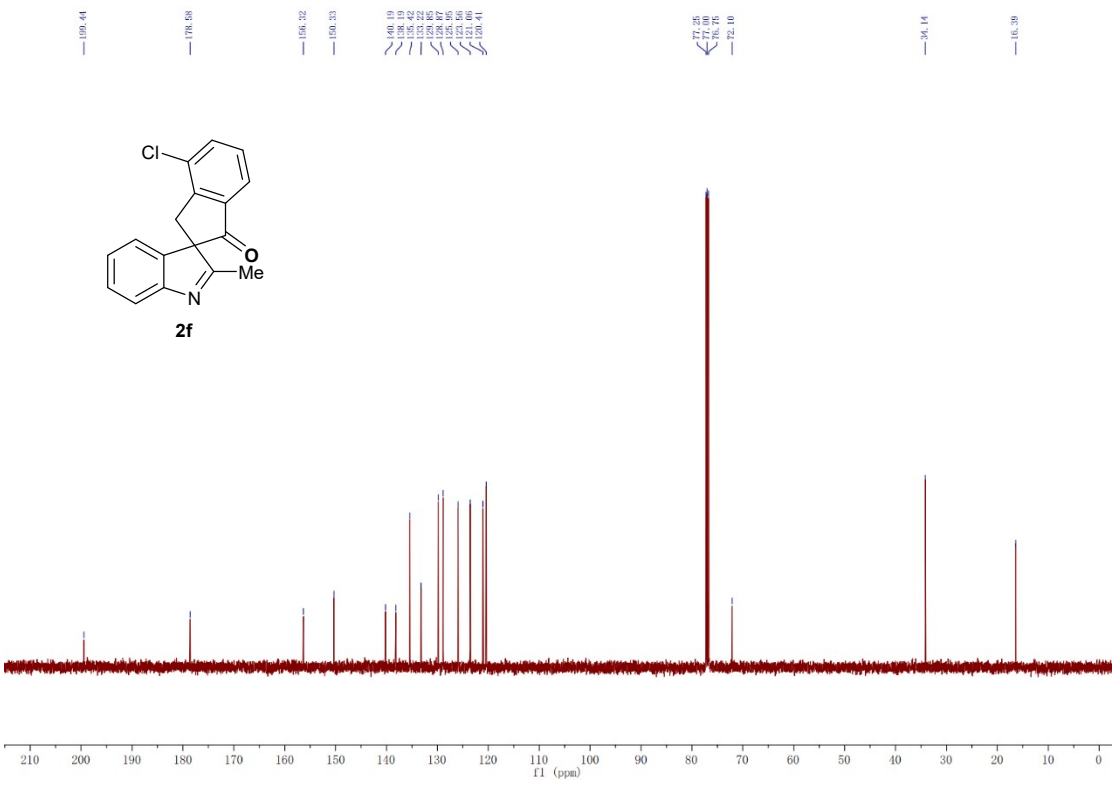


**4-chloro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2f)**

$^{1}$H NMR (500 MHz, $CDCl_3$)

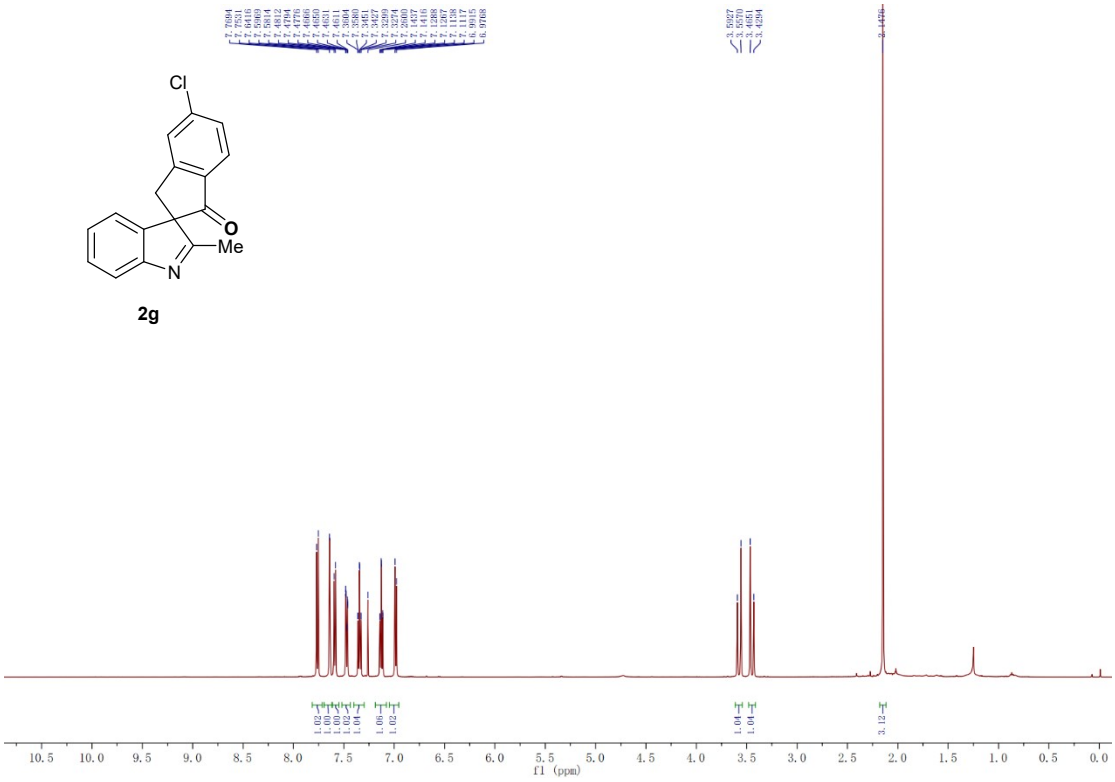



$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)

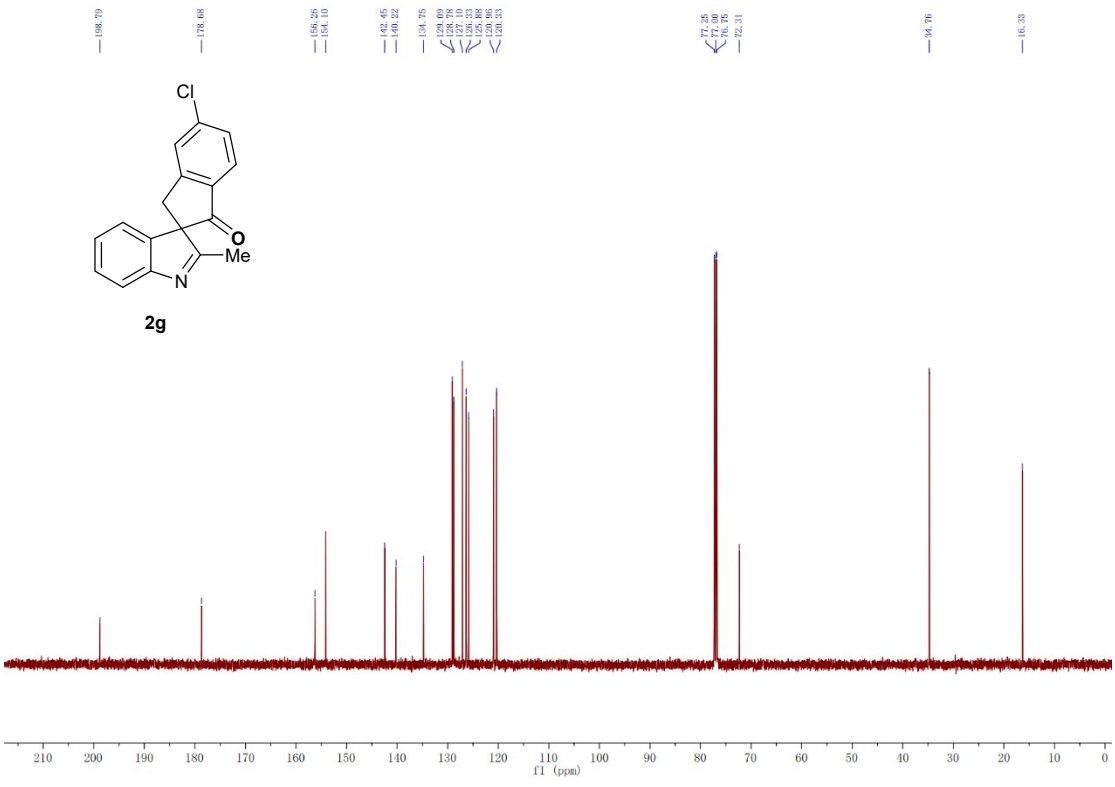


## 6-chloro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2g)

$^1$H NMR (500 MHz, $CDCl_3$)

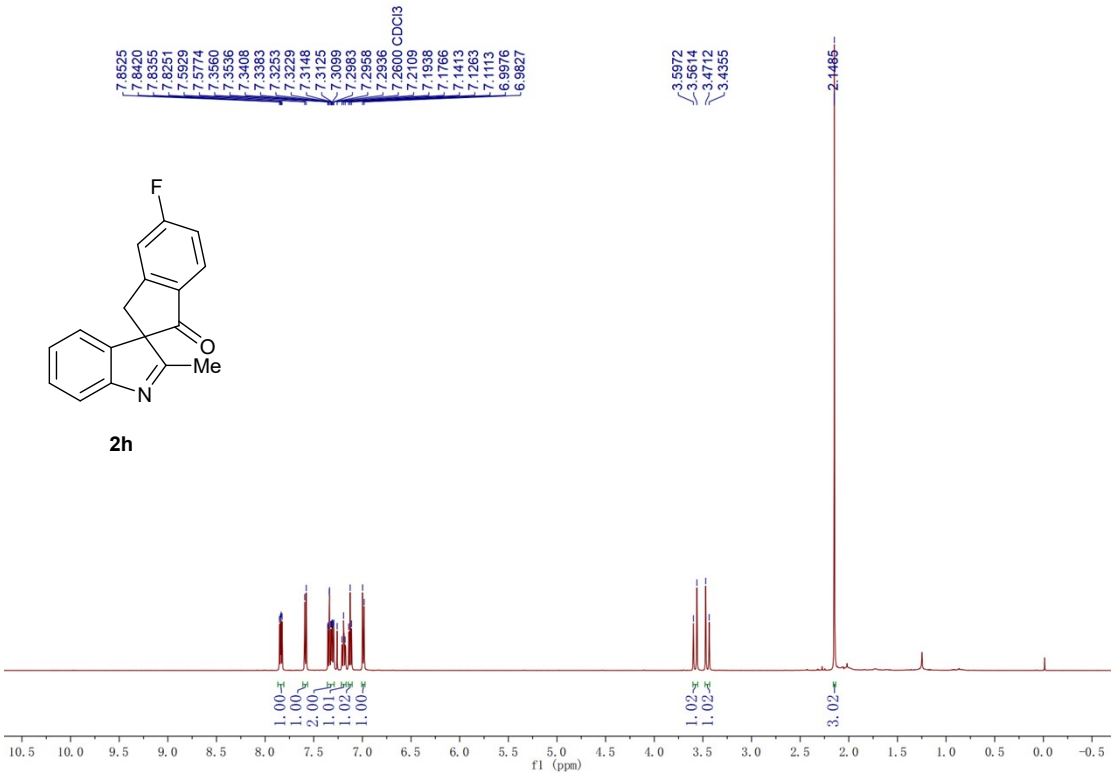



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

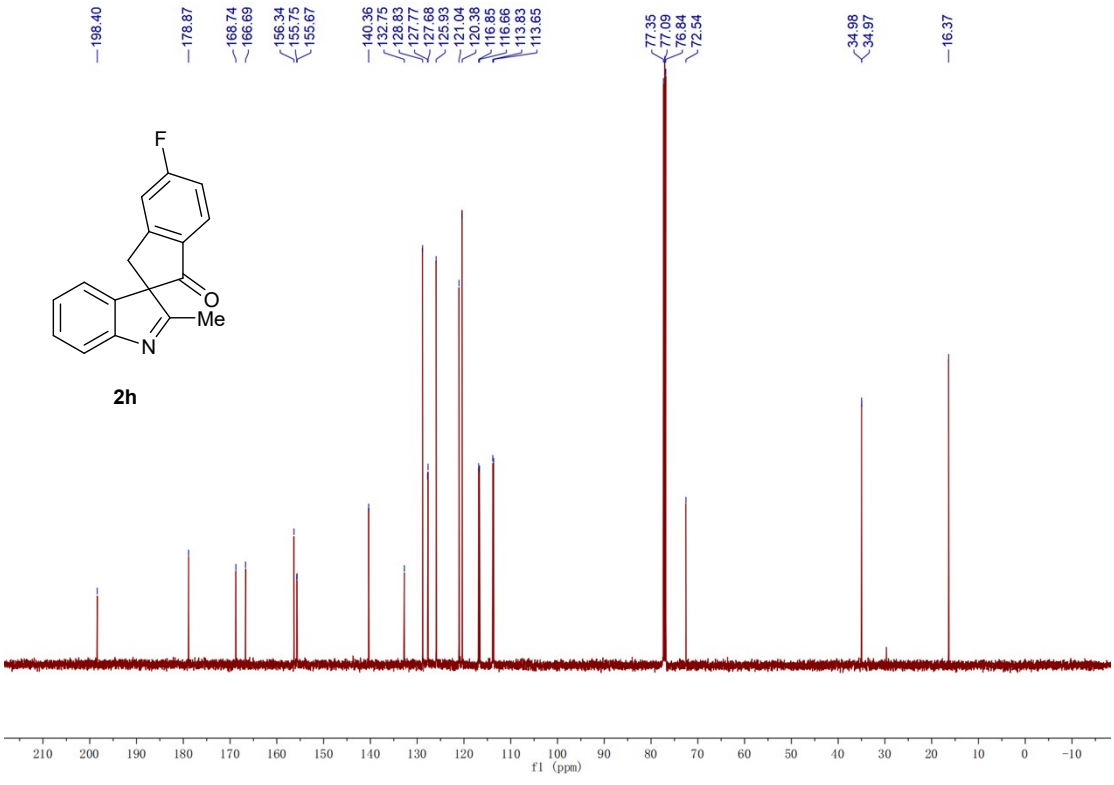


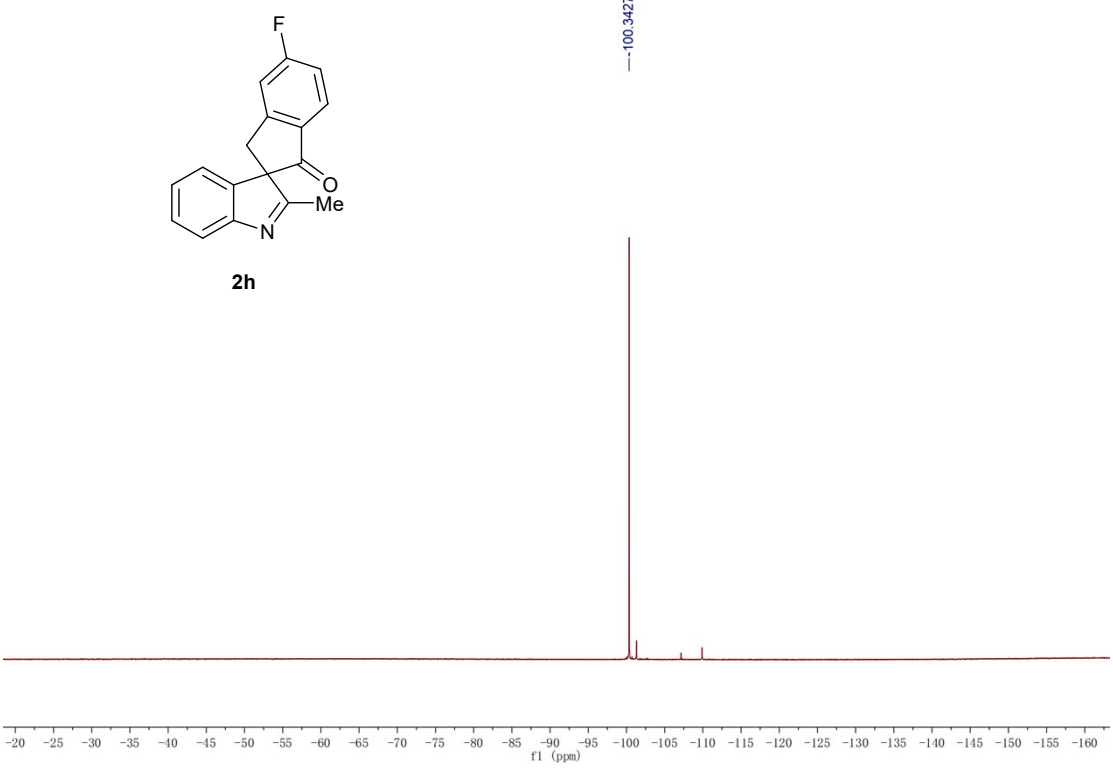
**5-fluoro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2h)**

$^1$H NMR (500 MHz, $CDCl_3$)




$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

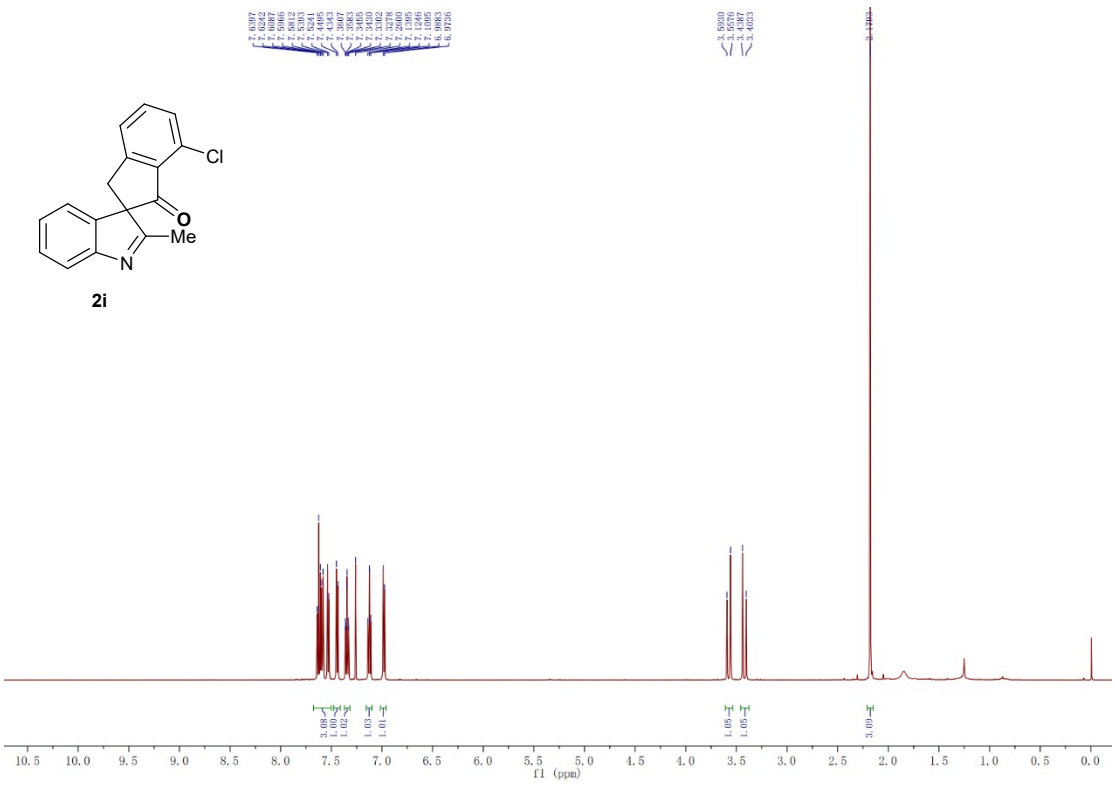



F
O
Me
N
-100.3427
−20 −25 −30 −35 −40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160
f1 (ppm)

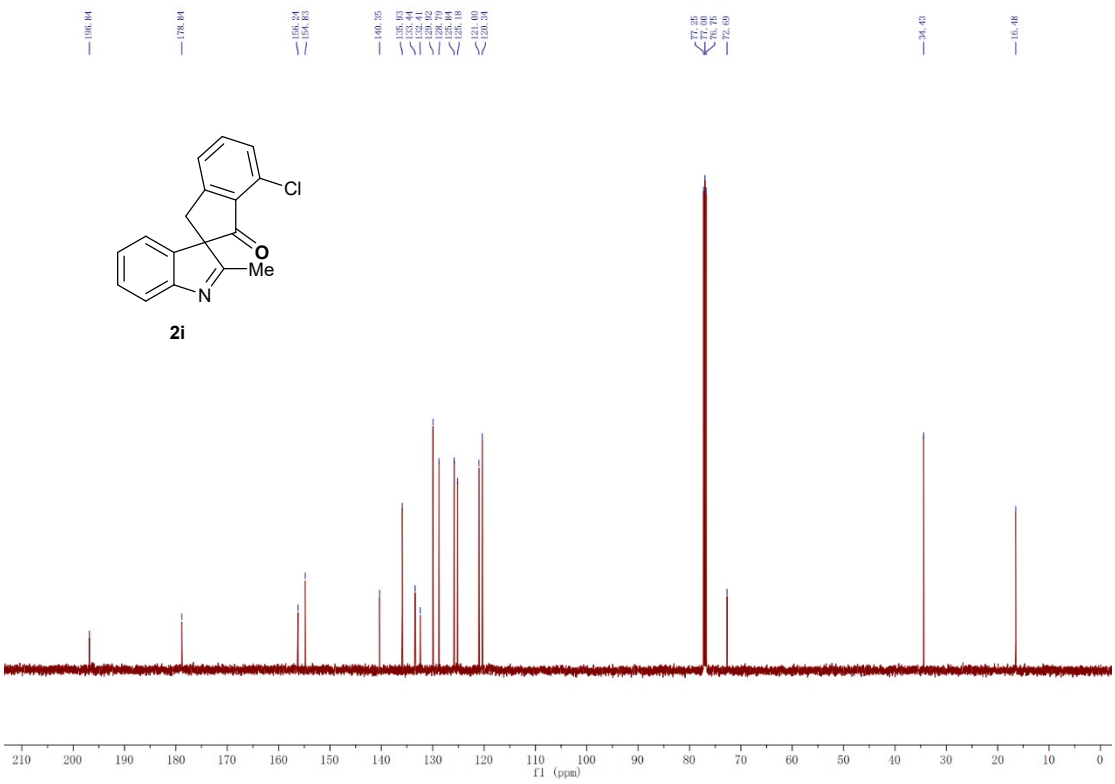
**2h**

## 7-chloro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2i)

$^{1}$H NMR (500 MHz, $CDCl_3$)

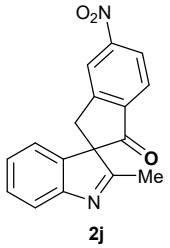



$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)

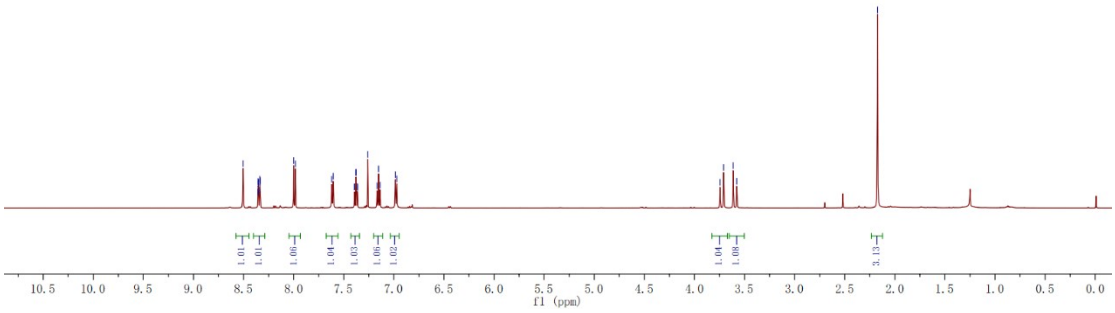


## 2'-methyl-5-nitrospiro[indene-2,3'-indol]-1(3*H*)-one (2j)

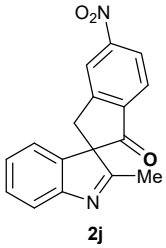
$^1$H NMR (500 MHz, $CDCl_3$)



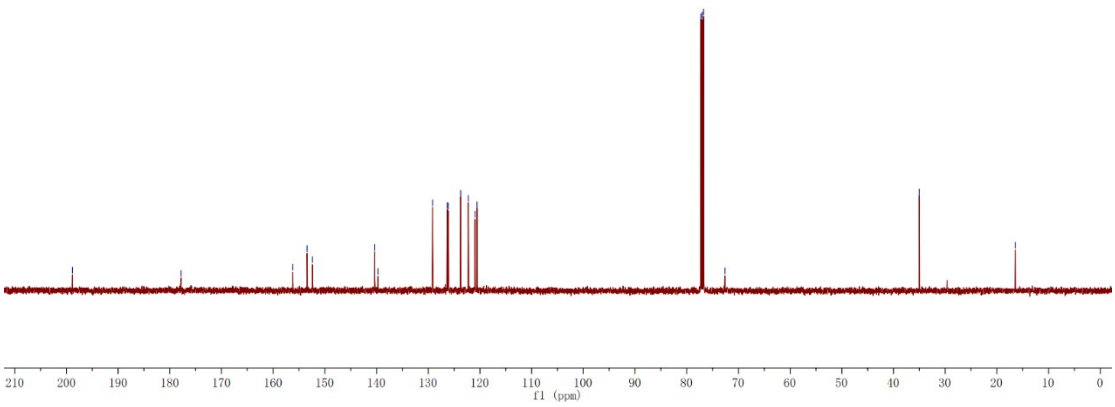

2j



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

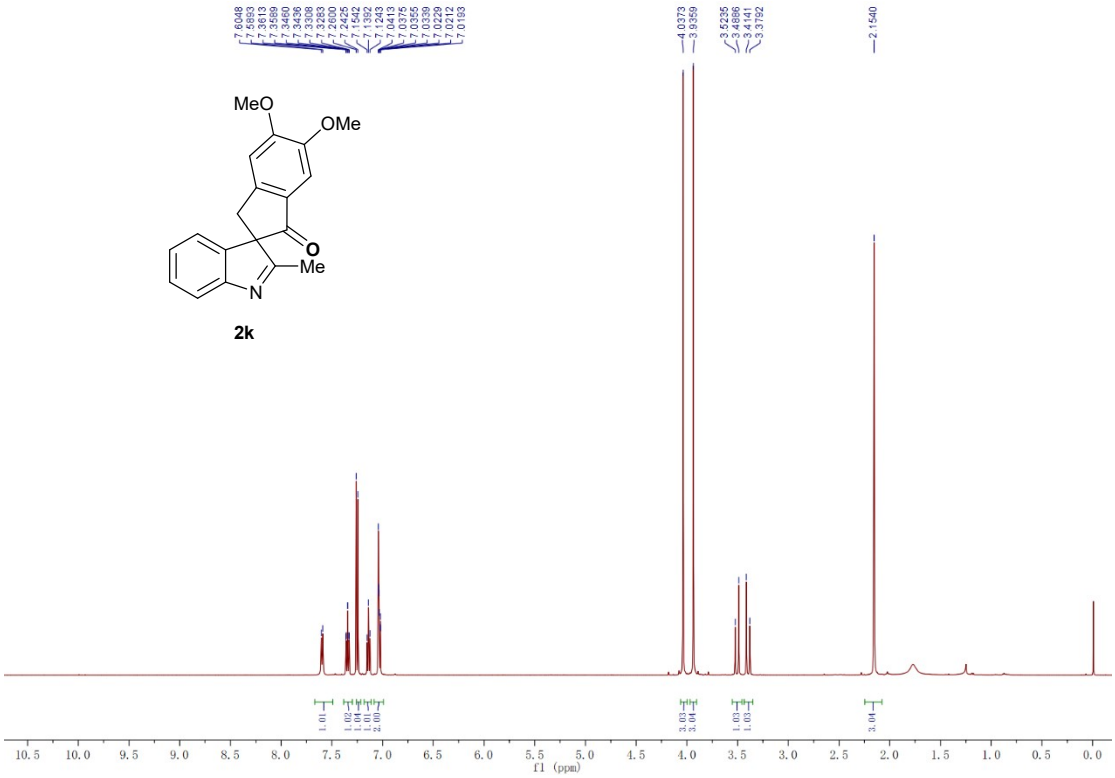



2j

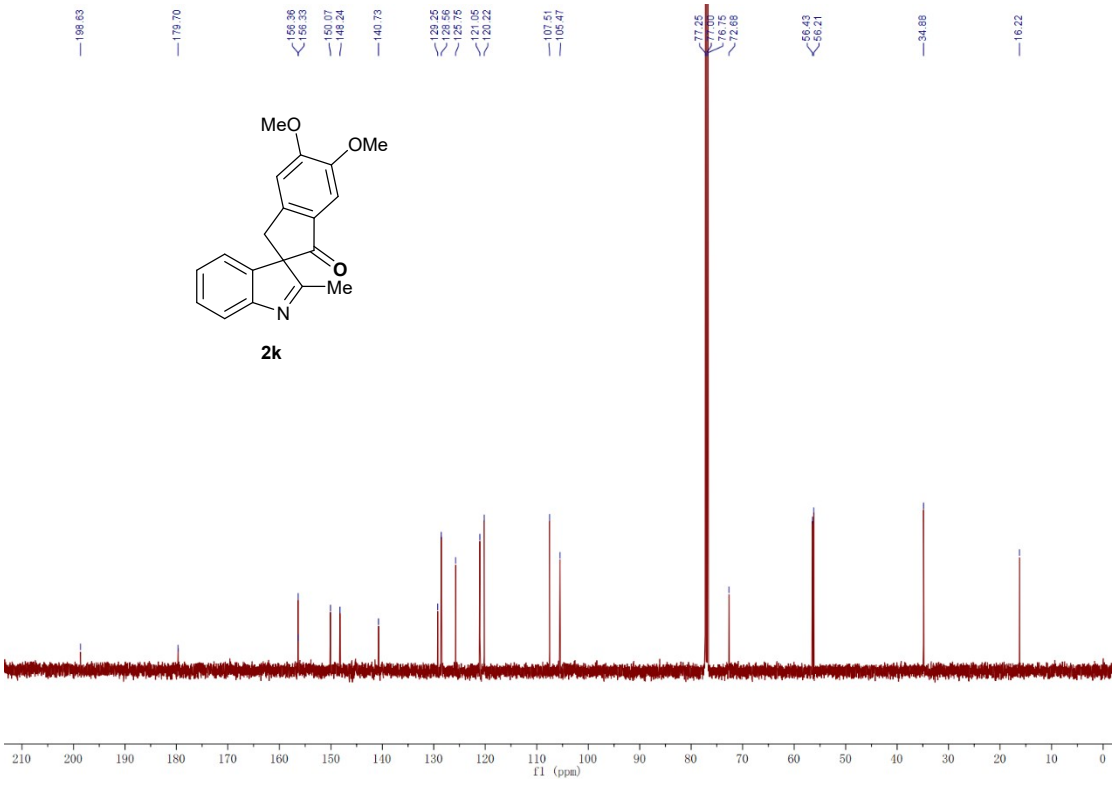


**5,6-dimethoxy-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2k)**

$^1$H NMR (500 MHz, $CDCl_3$)

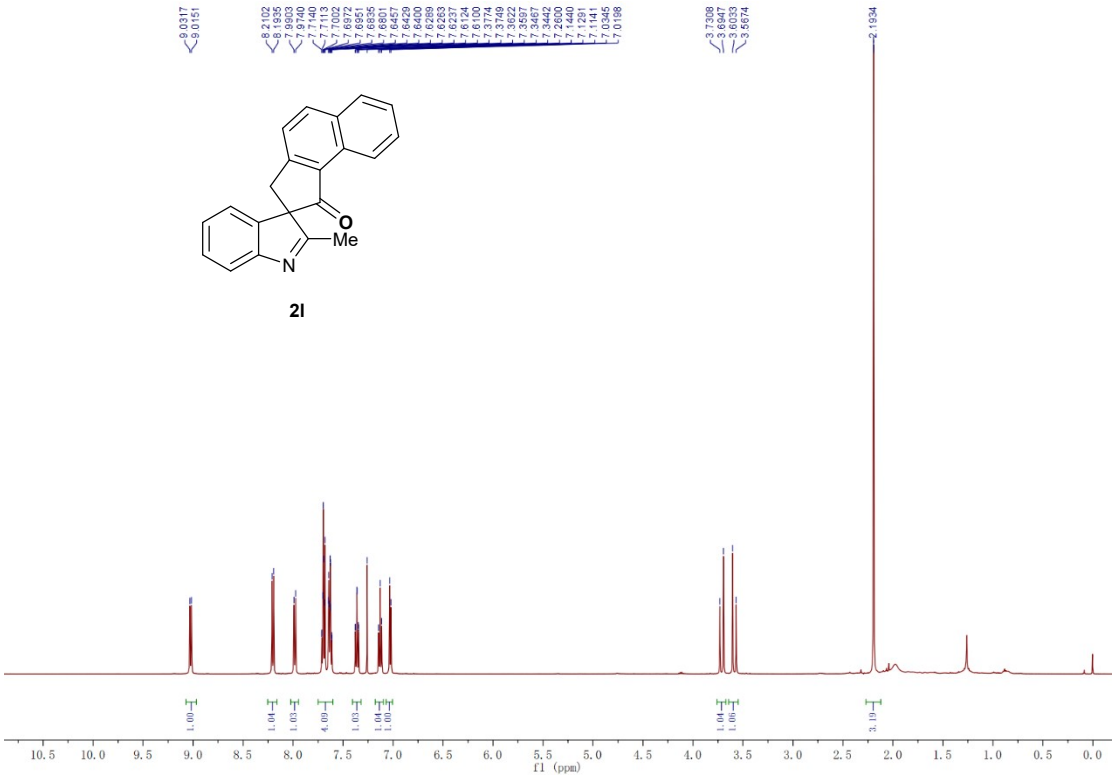



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

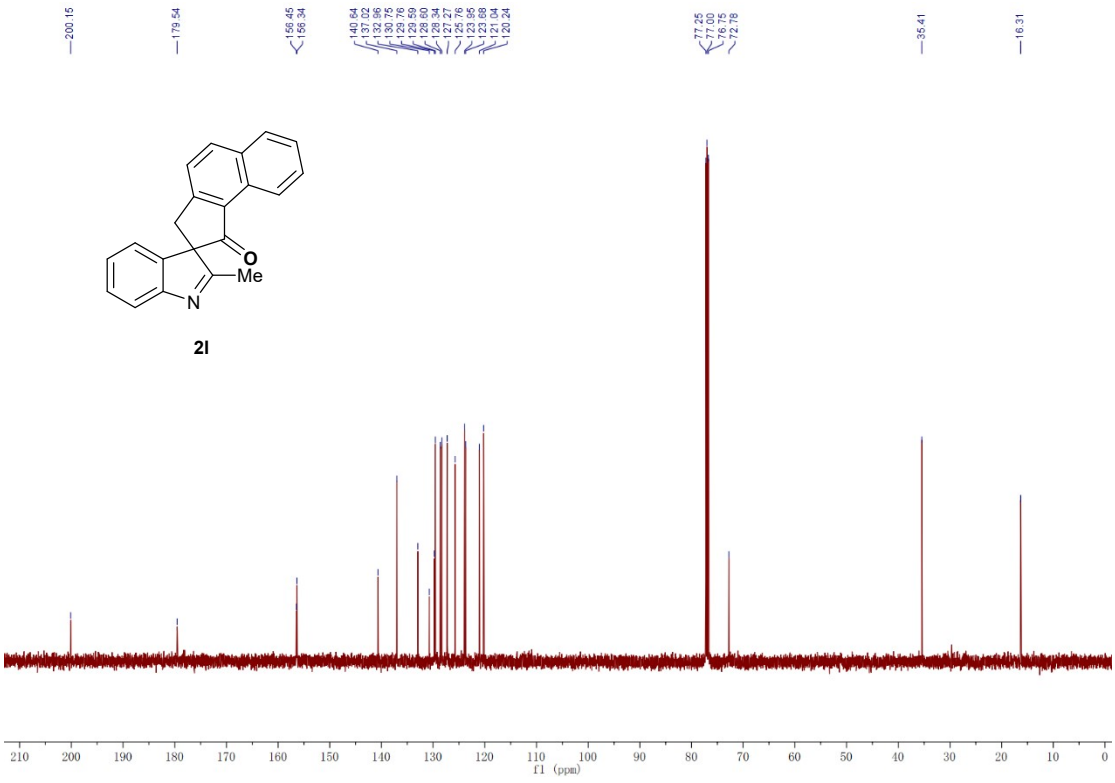


**2'-methylspiro[cyclopenta[a]naphthalene-2,3'-indol]-1(3*H*)-one (2l)**

$^1$H NMR (500 MHz, $CDCl_3$)

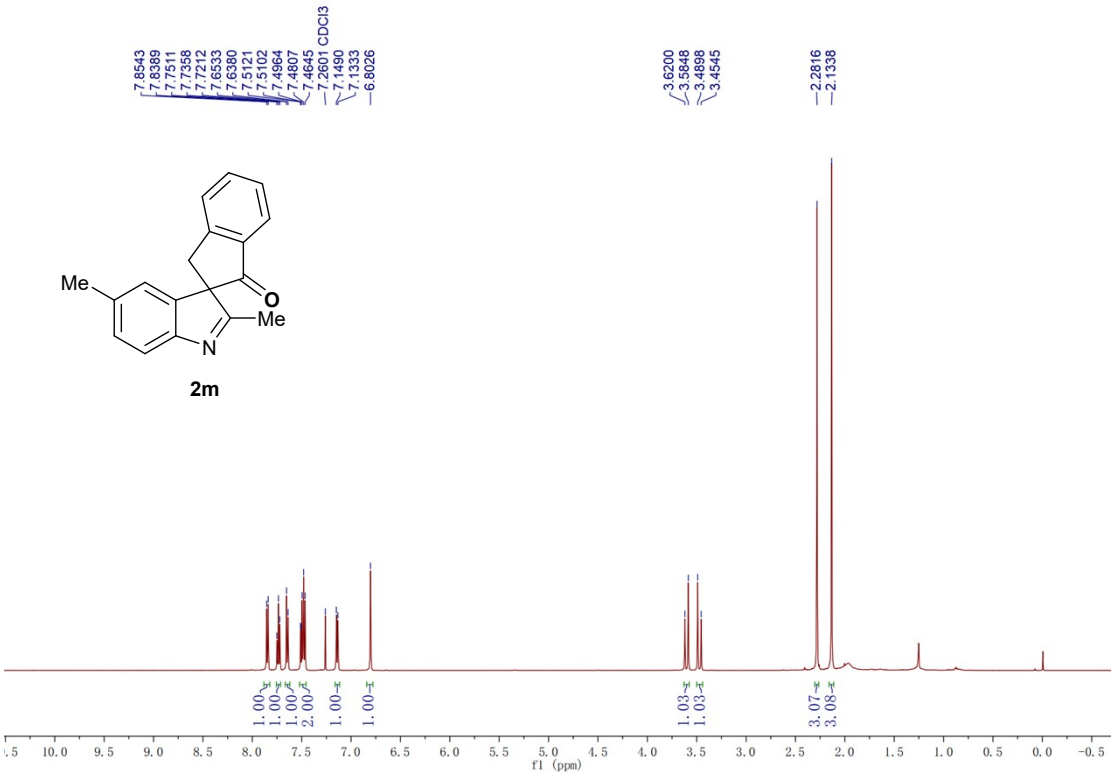



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

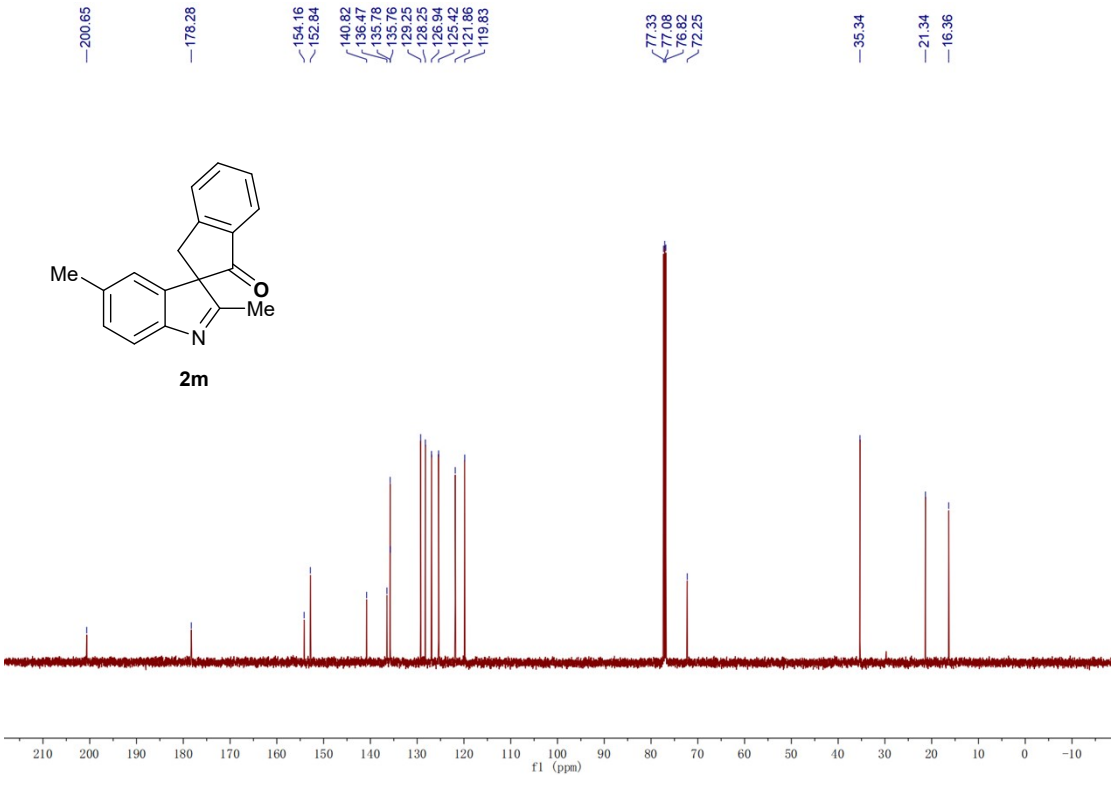


## 2',5'-dimethylspiro[indene-2,3'-indol]-1(3*H*)-one (2m)

$^1$H NMR (500 MHz, $CDCl_3$)

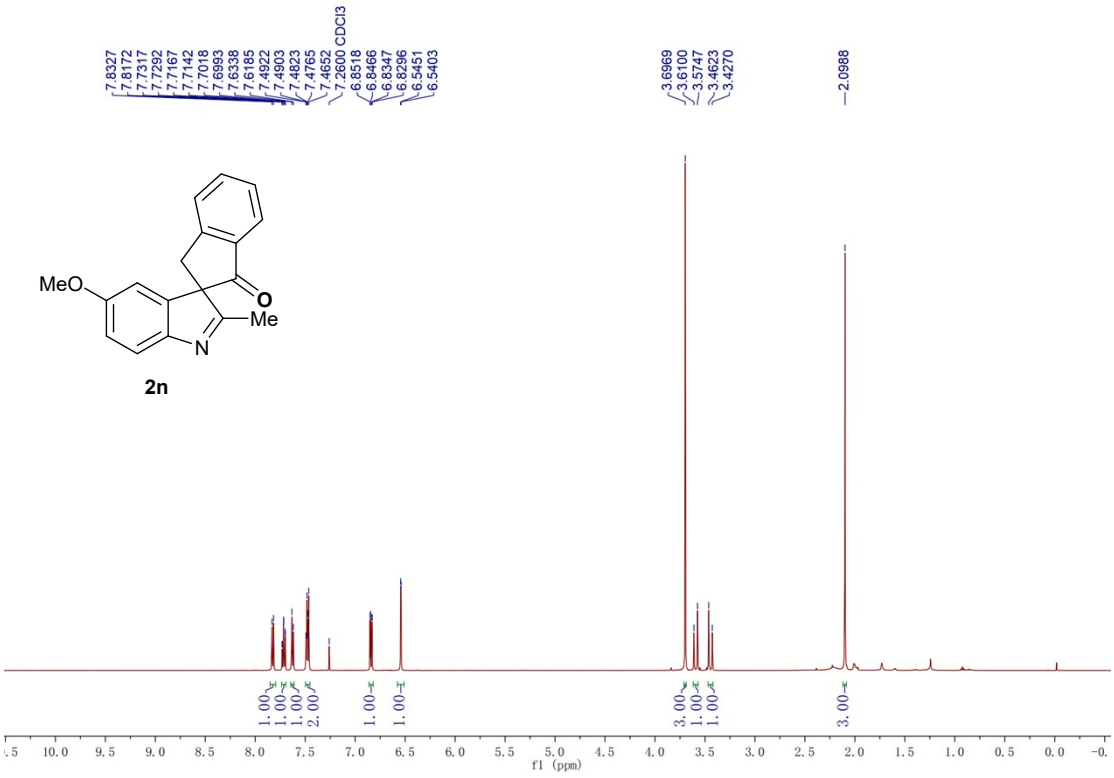



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

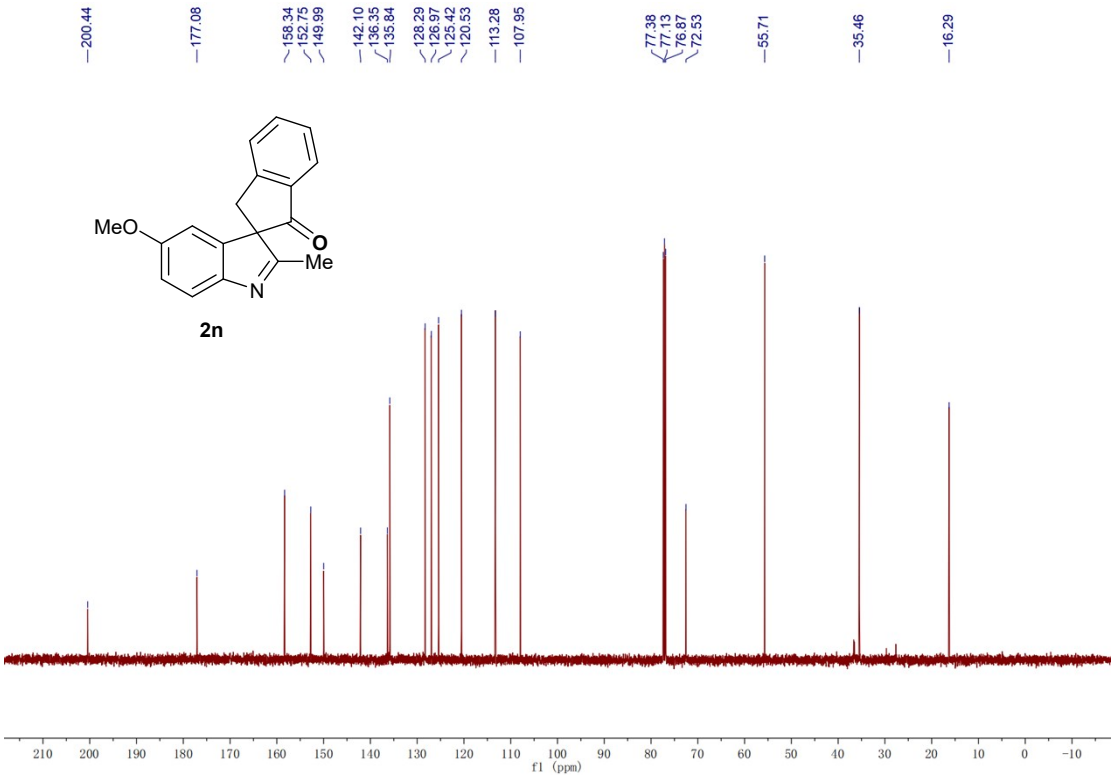


**5'-methoxy-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2n)**

$^1$H NMR (500 MHz, $CDCl_3$)

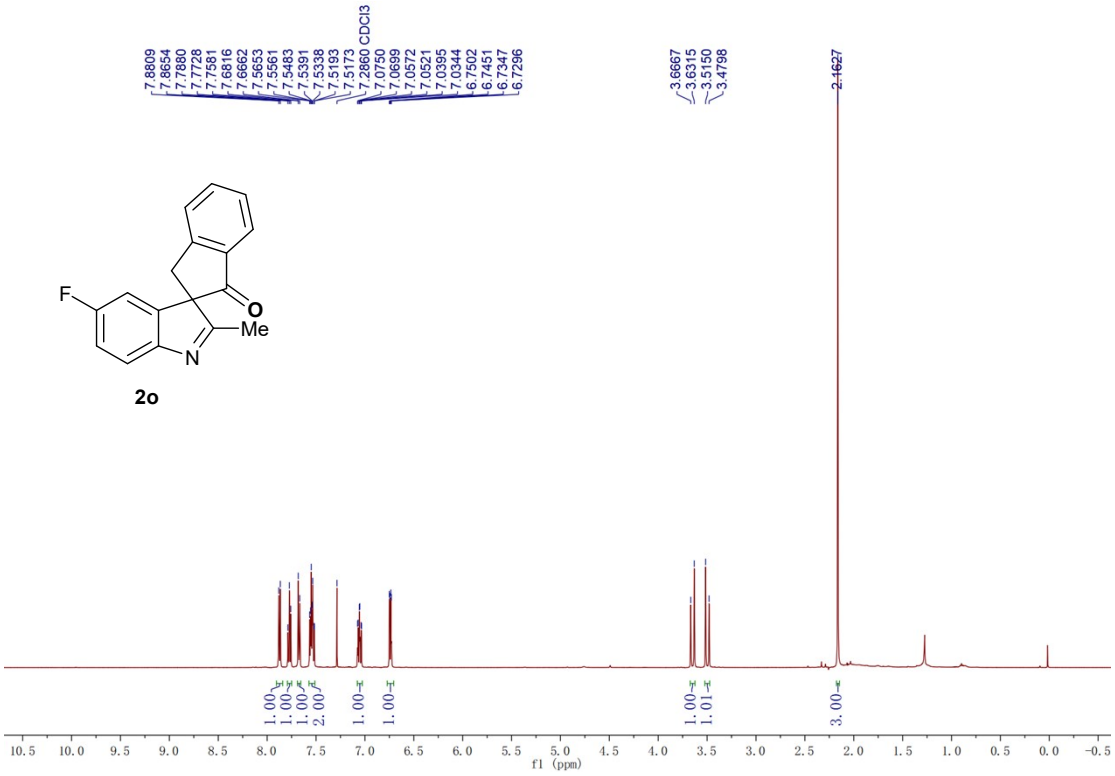



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

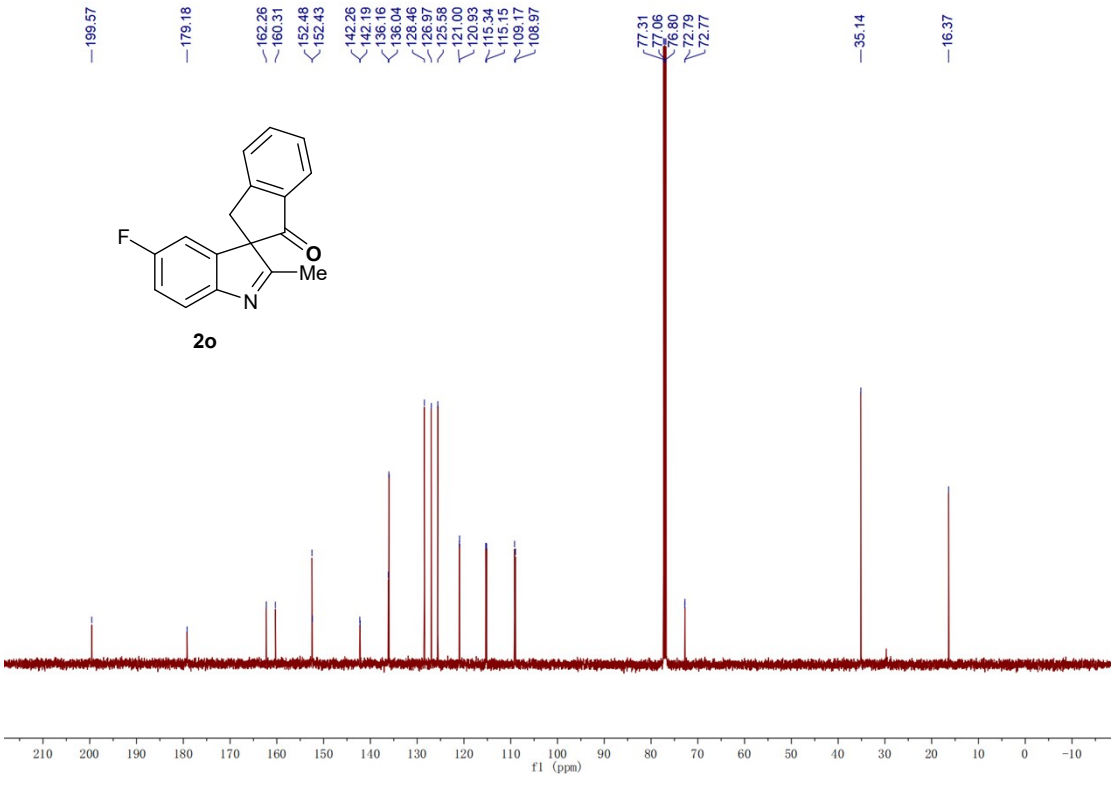


**5'-fluoro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2o)**

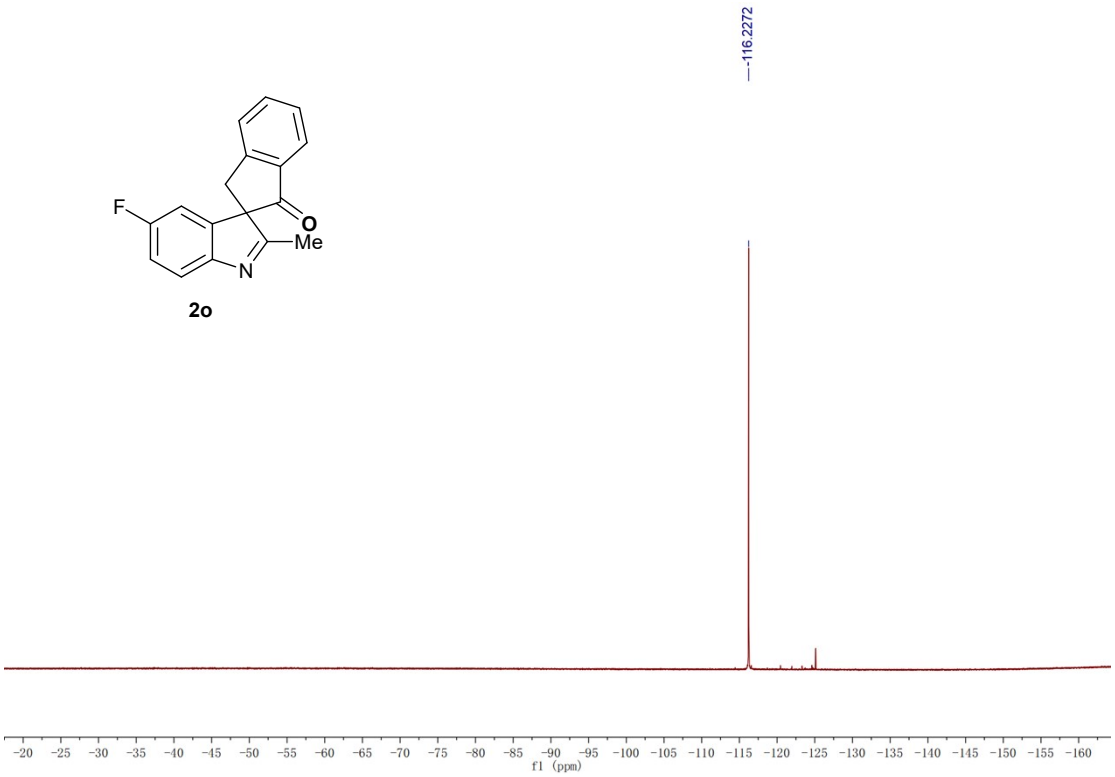
$^1$H NMR (500 MHz, $CDCl_3$)




$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

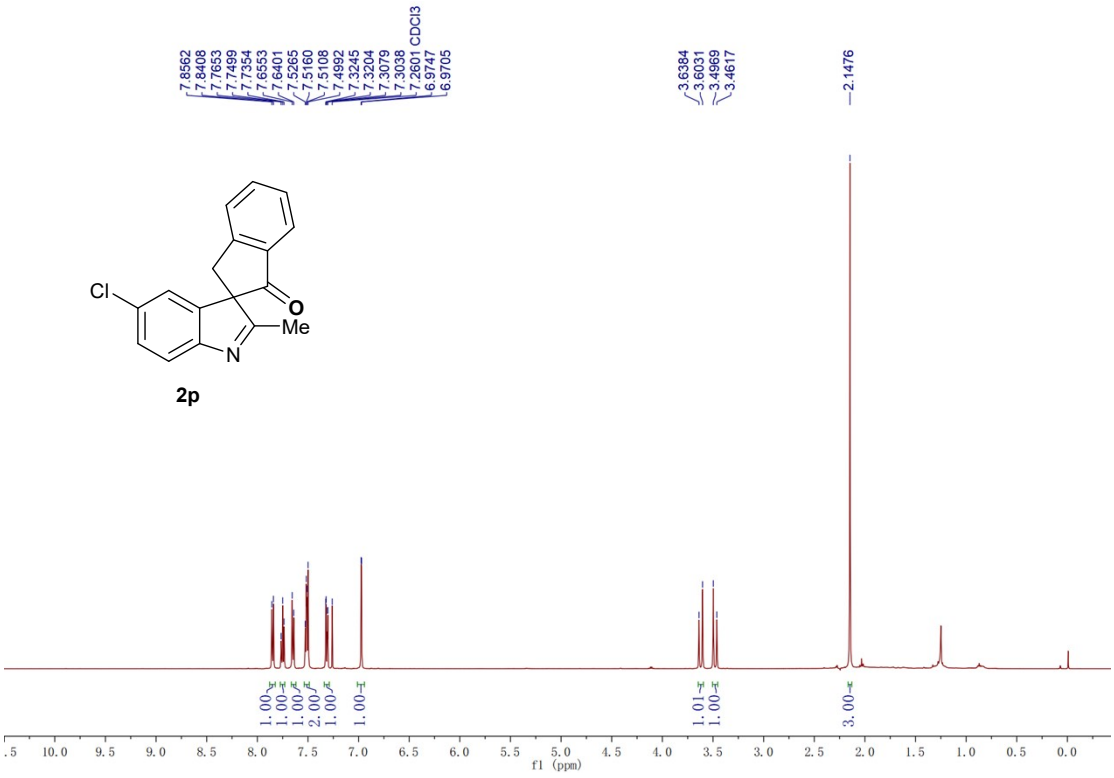


$^{19}$F NMR (471 MHz, $CDCl_3$)

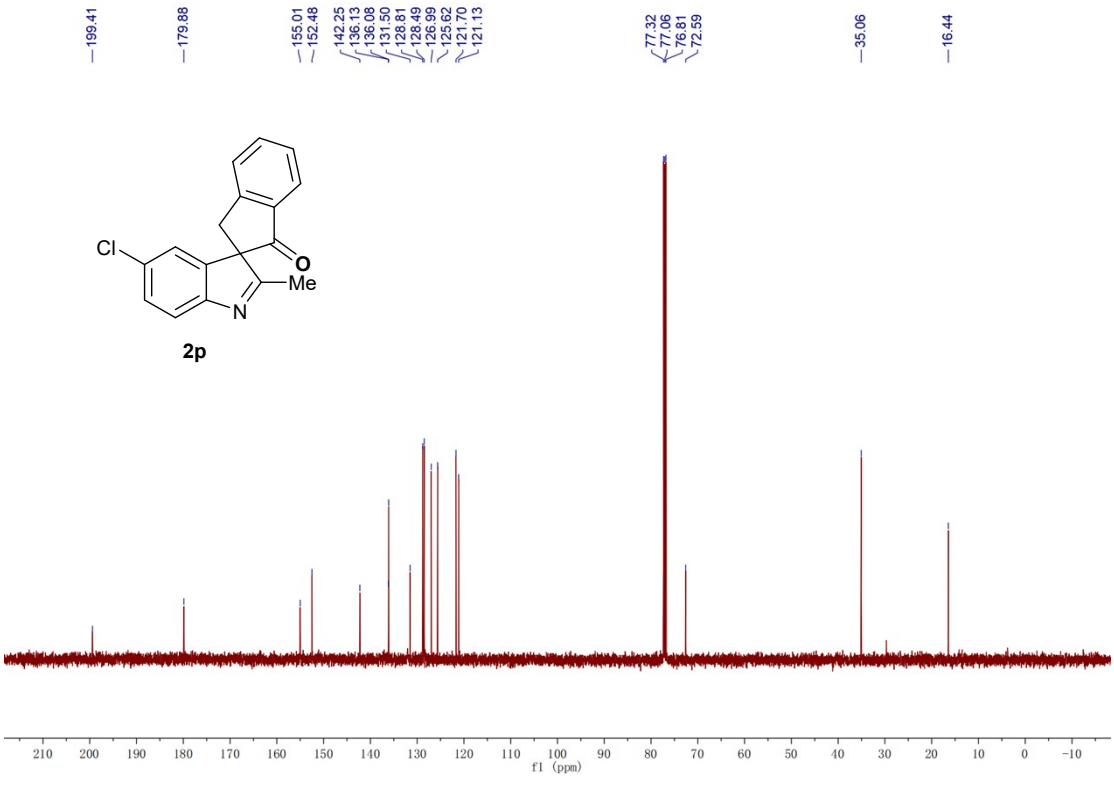


**5'-chloro-2'-methylspiro[indene-2,3'-indol]-1(3*H*)-one (2p)**

$^1$H NMR (500 MHz, $CDCl_3$)

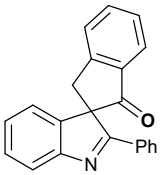



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

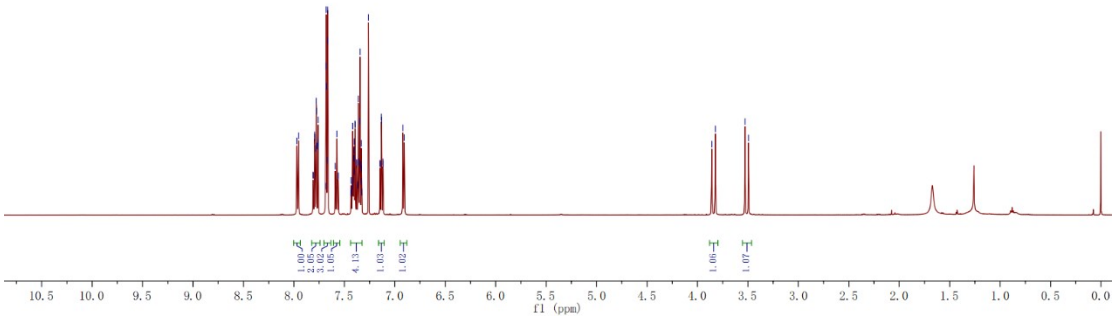


## 2'-phenylspiro[indene-2,3'-indol]-1(3*H*)-one (2q)

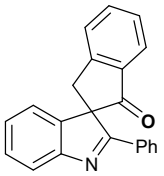
$^1$H NMR (500 MHz, $CDCl_3$)




**2q**



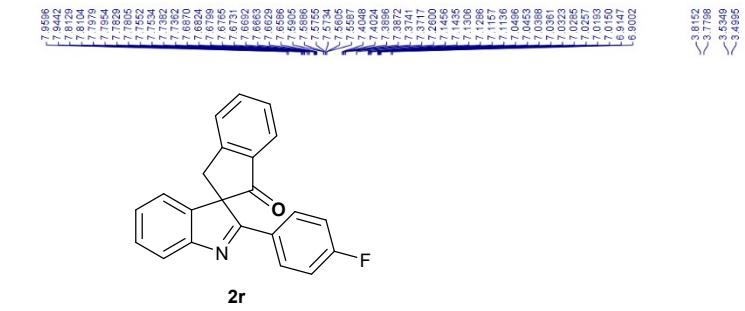

$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)




**2q**

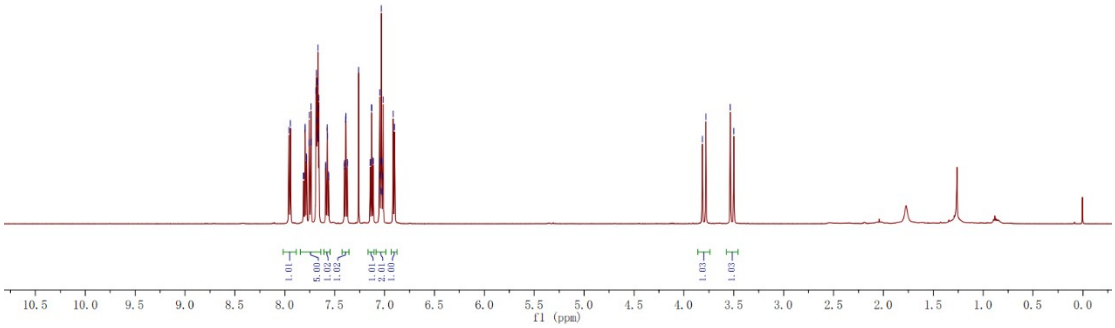
**2'-(4-fluorophenyl)spiro[indene-2,3'-indol]-1(3*H*)-one (2r)**

$^1$H NMR (500 MHz, $CDCl_3$)

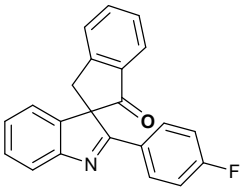





**2r**



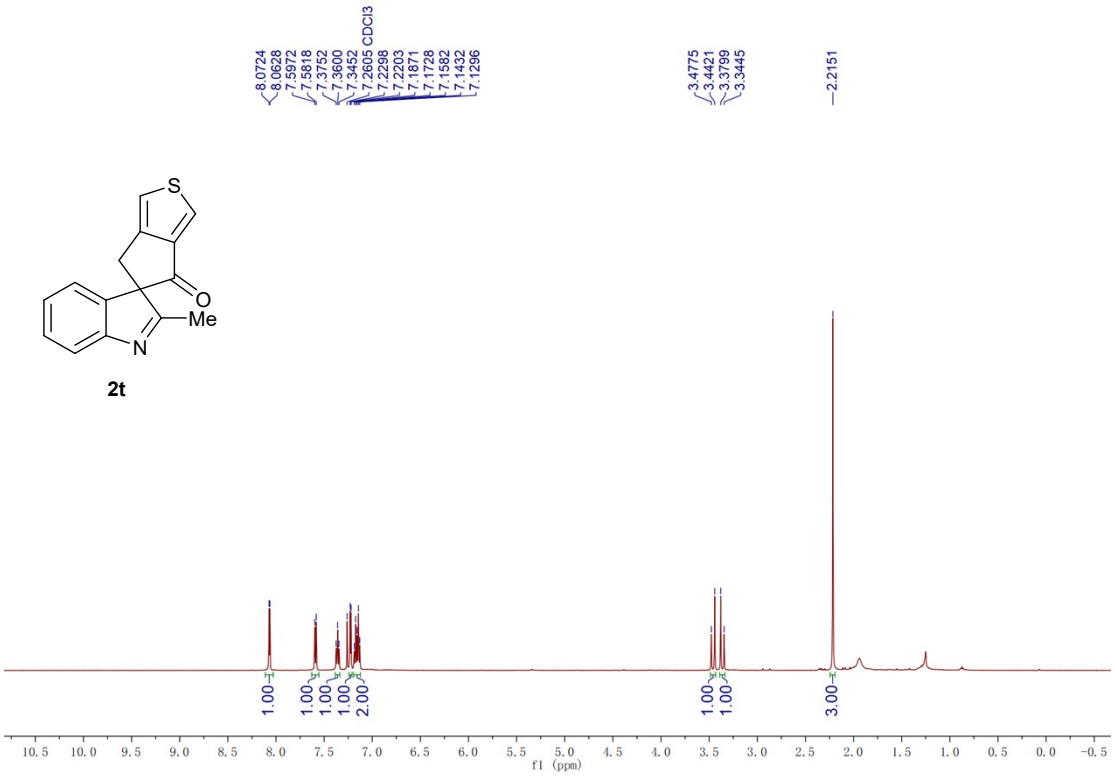
$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)




**2r**

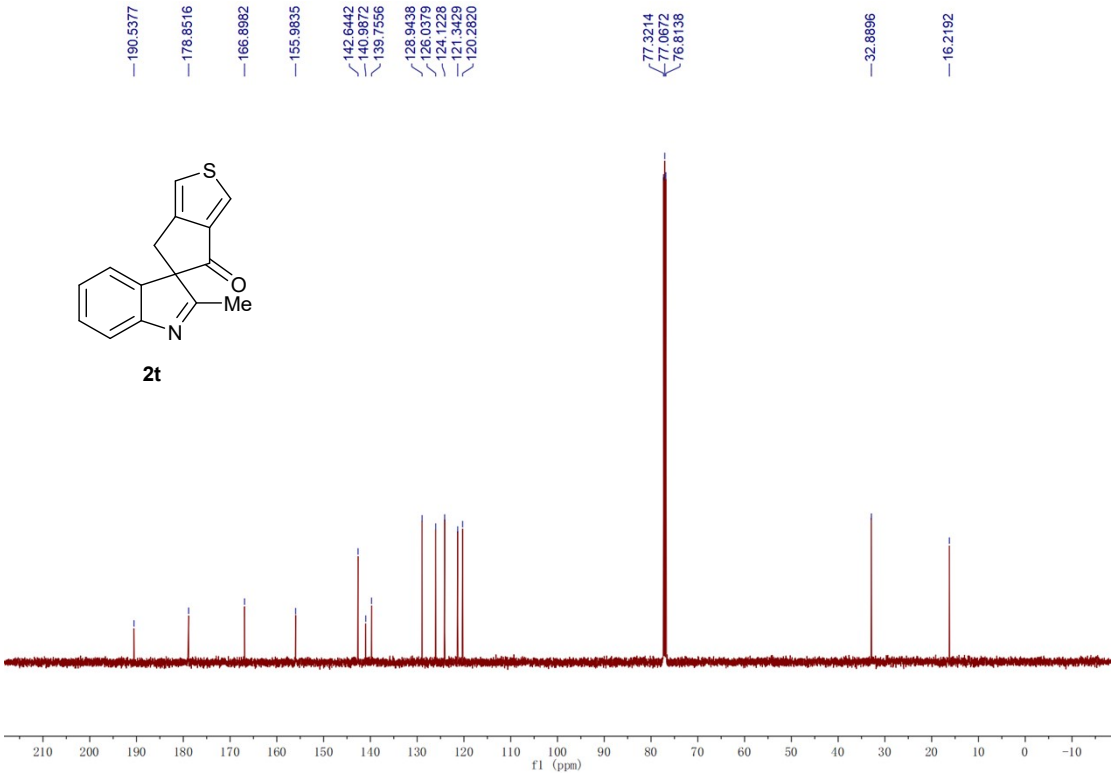
**2'-methyl-4*H*,6*H*-spiro[cyclopenta[*c*]thiophene-5,3'-indol]-4-one (2t)**

$^1$H NMR (500 MHz, $CDCl_3$)




**2t**

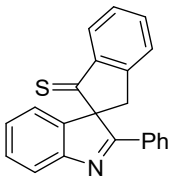
$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)



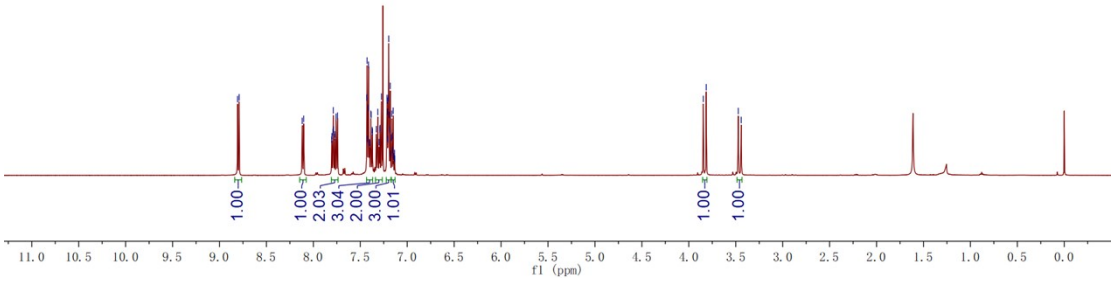

**2t**

## 2'-phenylspiro[indene-2,3'-indole]-1(*3H*)-thione (3)

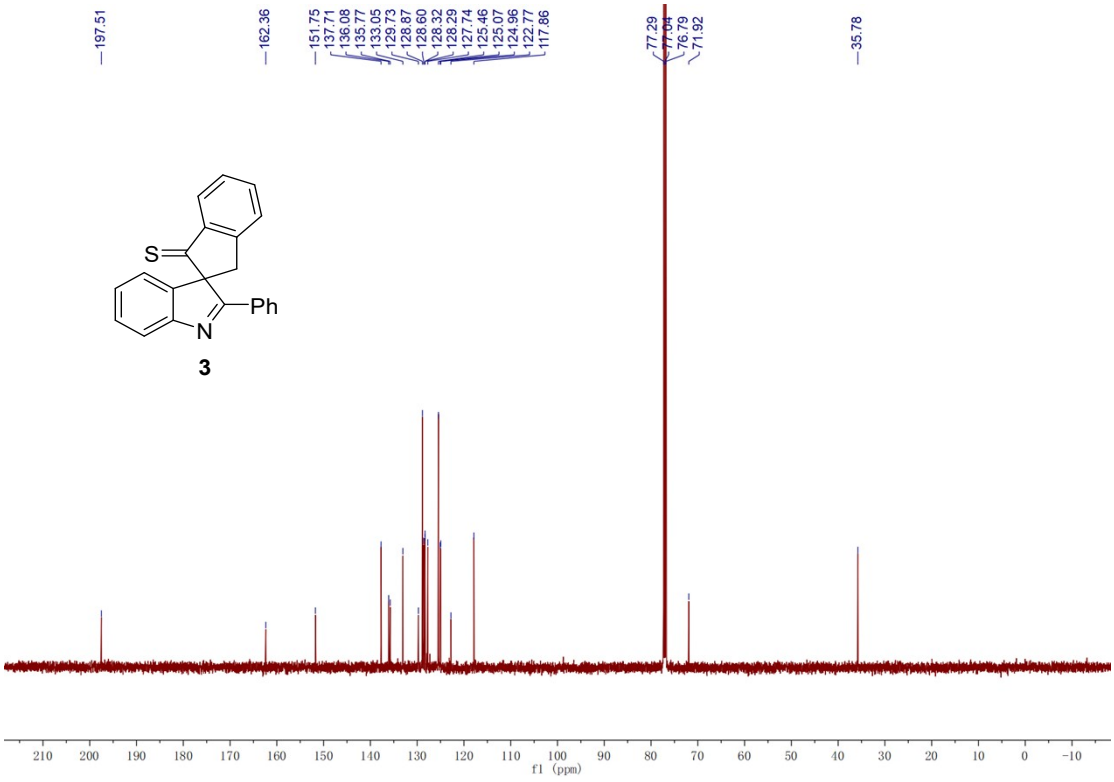
$^1$H NMR (500 MHz, $CDCl_3$)




**3**




$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)



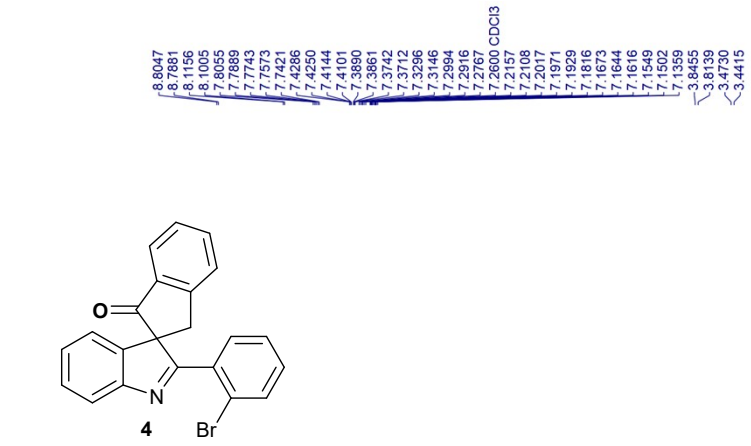




**3**

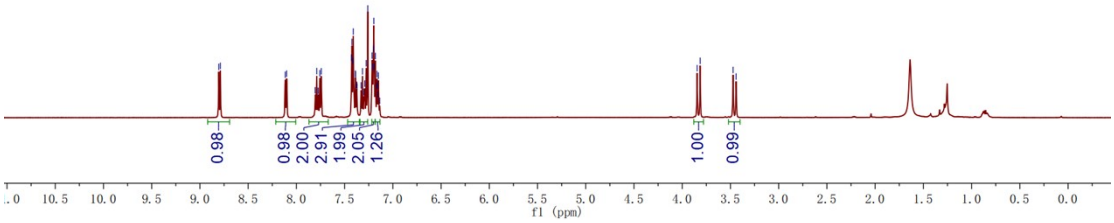
**2'-(2-bromophenyl)spiro[indene-2,3'-indol]-1(3*H*)-one (4)**

$^1$H NMR (500 MHz, $CDCl_3$)

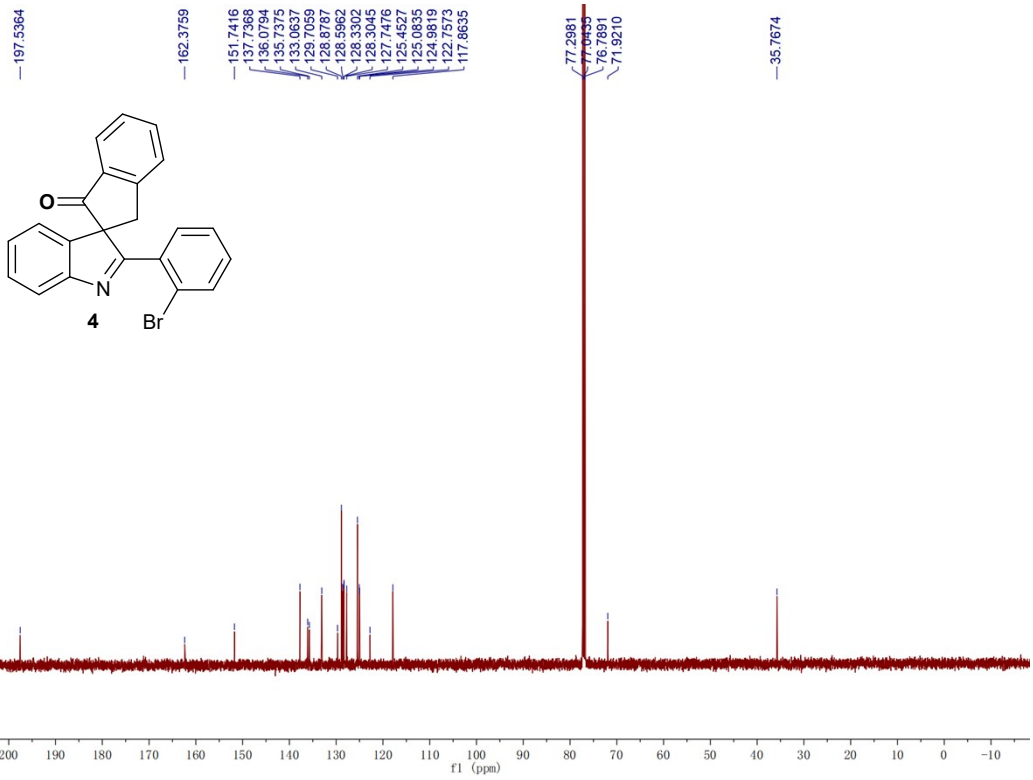






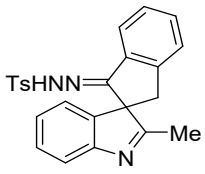



$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)

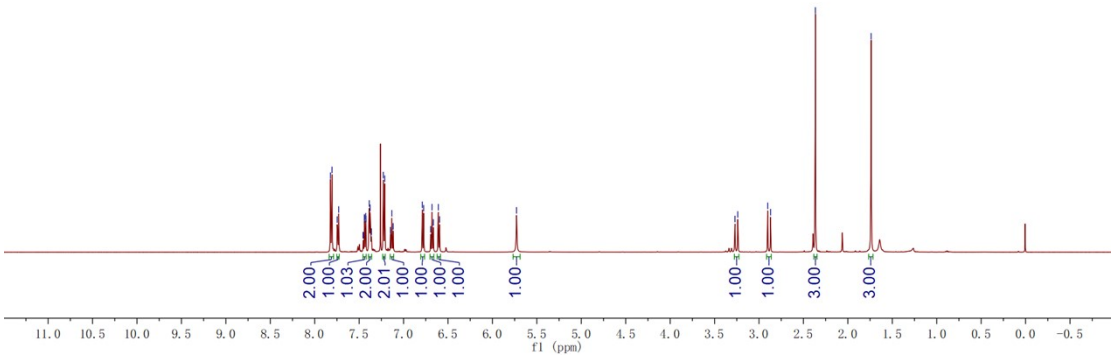


**4-methyl-N'-(2'-methylspiro[indene-2,3'-indol]-1(*3H*)-ylidene)benzenesulfonohydrazide (5)**

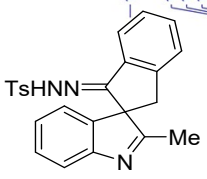
$^{1}$H NMR (500 MHz, $CDCl_3$)

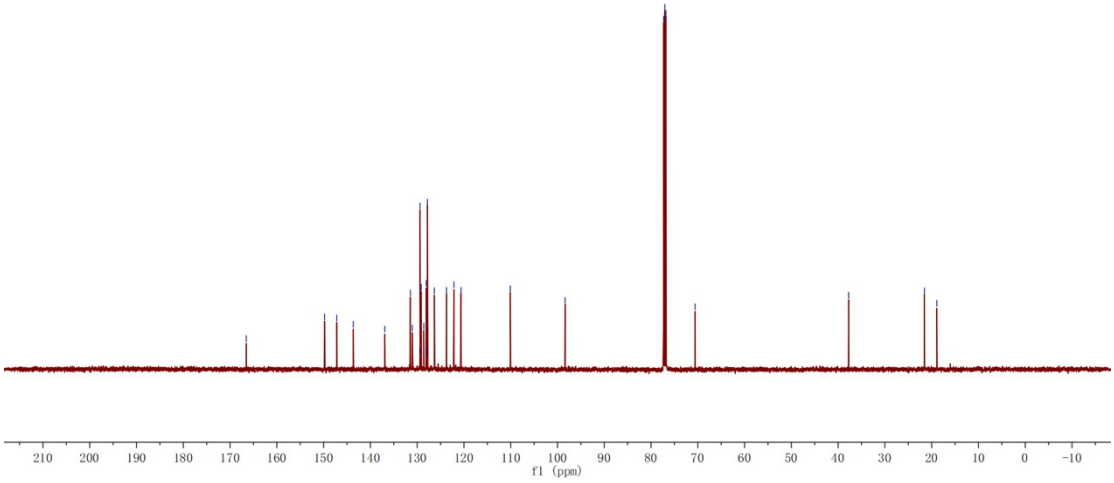

**5**




$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)

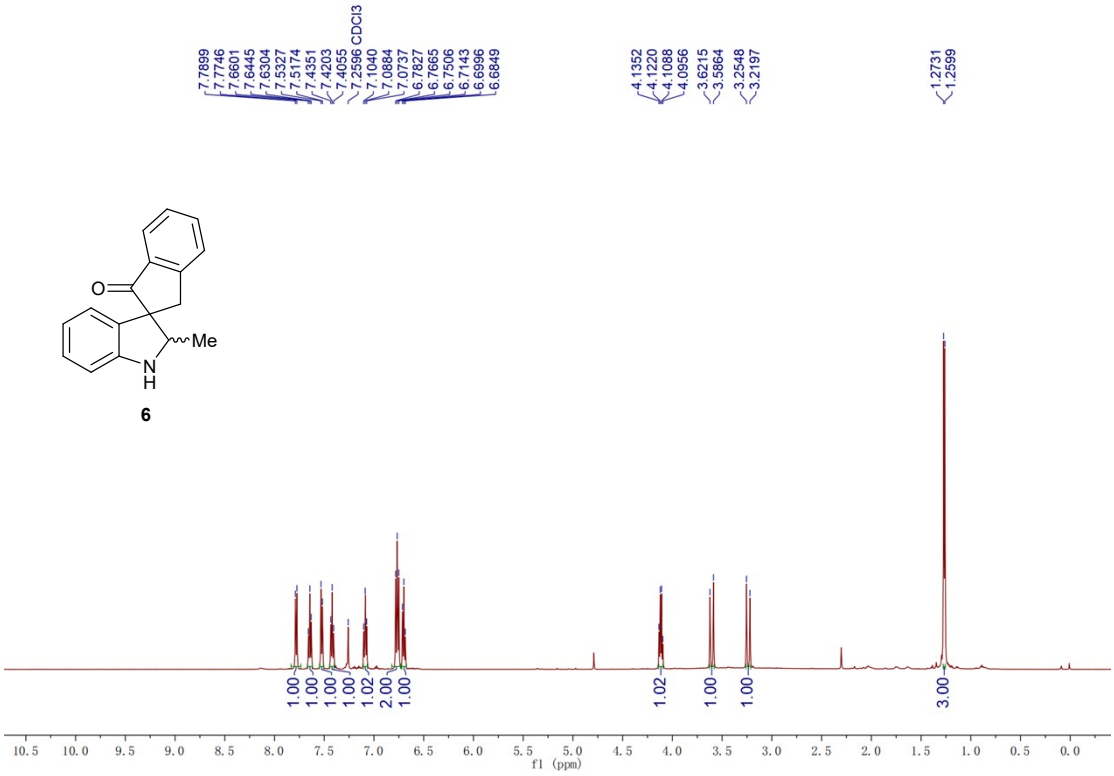




**5**



## 2'-methylspiro[indene-2,3'-indolin]-1(3*H*)-one (6)

$^1$H NMR (500 MHz, $CDCl_3$)




$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)