Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Copper-Catalyzed Radical 1,2-Cyclization of Indoles with Arylsulfonyl Hydrazides: Access to 2-Thiolated *3H*-pyrrolo[1,2-*a*]indoles

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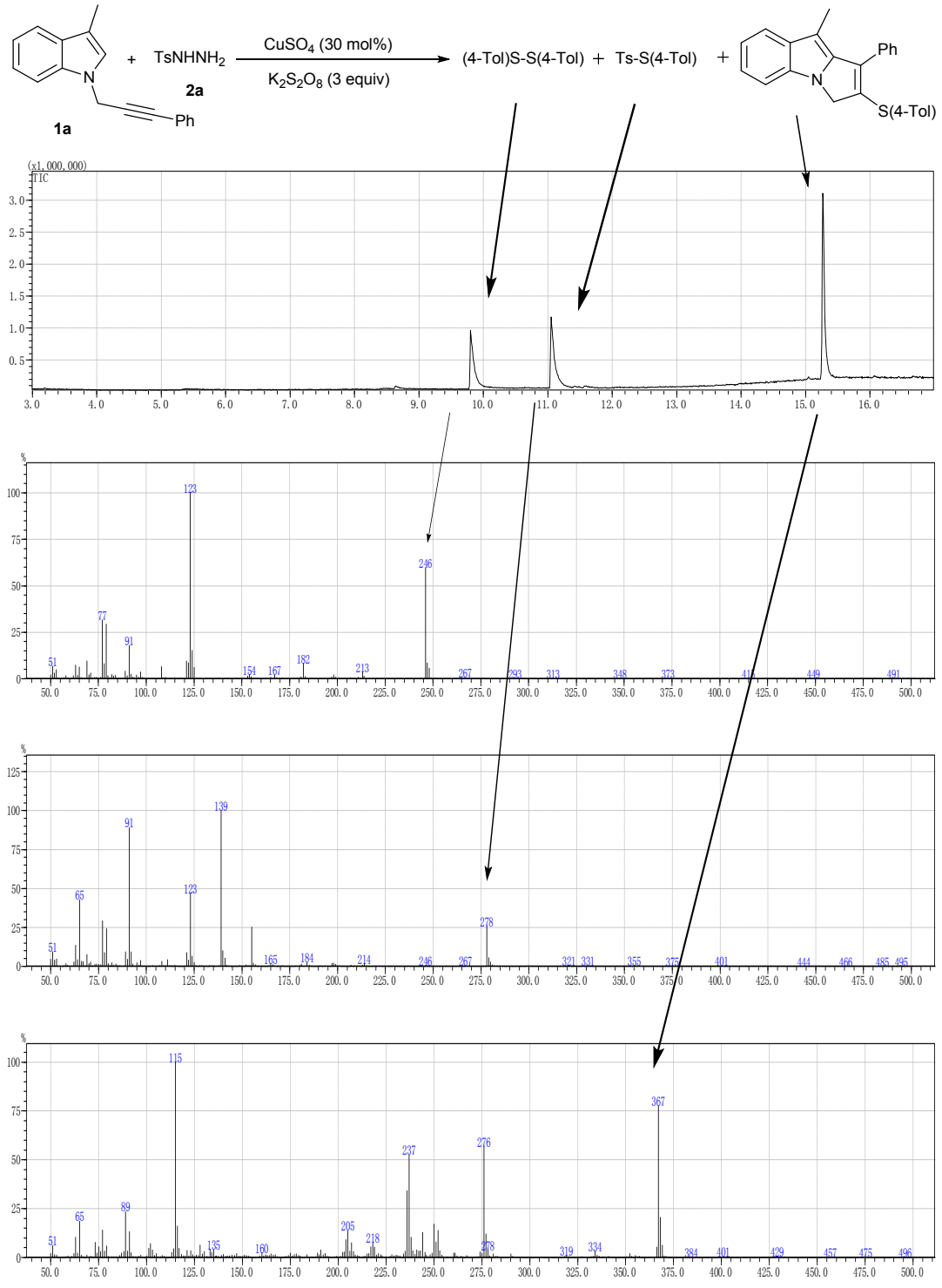
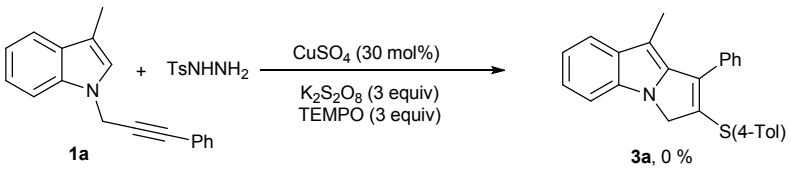
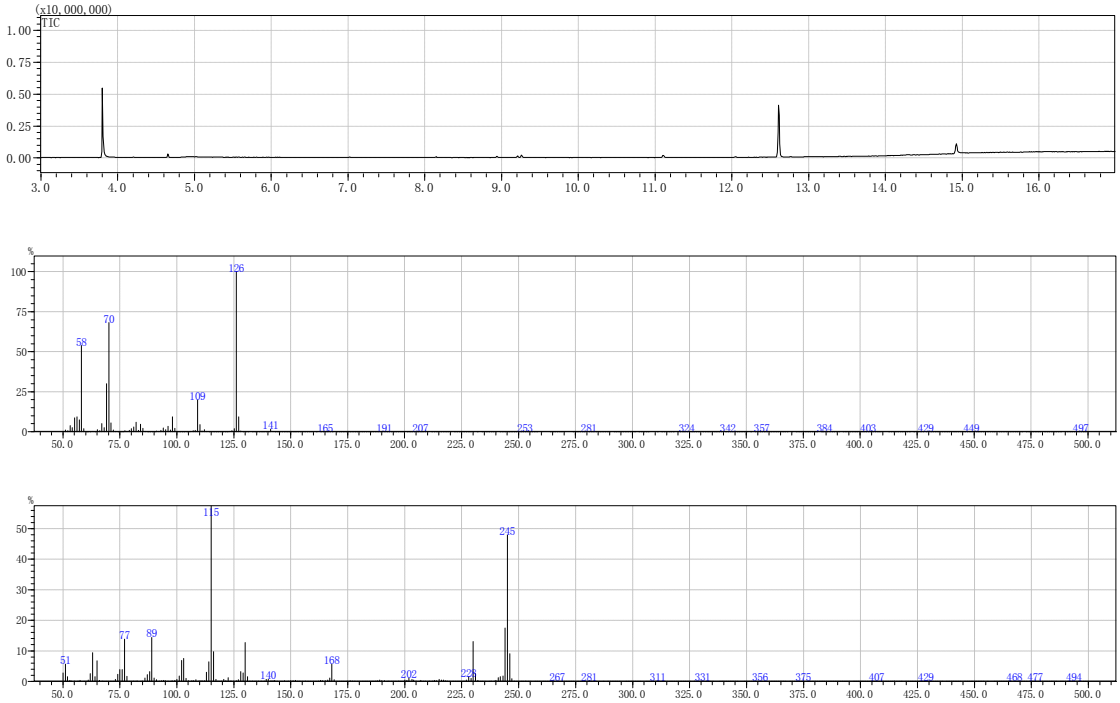
1.1. GC-MS study of the reaction mixture of 1a with 2a.

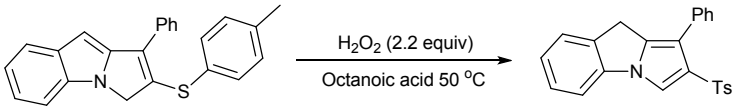


1.2. GC-MS study of the reaction mixture of 1a, 2a and TEMPO





1.3. **The preparation of 4s**[1]



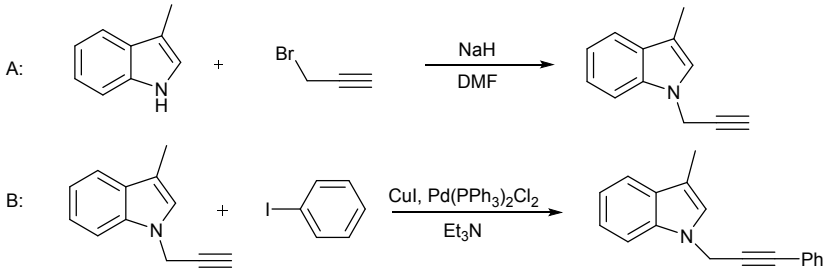
3s **4s**

2. General Considerations

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, etc) and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

3. Preparation of starting materials

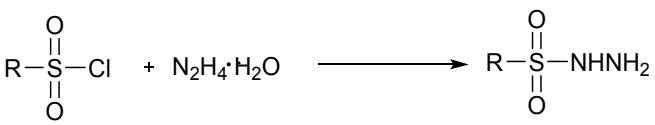
3.1 Synthesis of 3-methyl-1-(3-phenylprop-2-yn-1-yl)-1*H*-indole.



A.[2] To a solution of the indole derivative (100 mmol) in DMF (250 mL) was added NaH (60%, 2.0 equiv) slowly at 0 °C. The resulting solution was stirred for 1 h at 0 °C. Then, the propargylic bromide (2.0 equiv) was added dropwise through a syringe. The reaction mixture was stirred at room temperature for another 2 h. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched with water (200 mL) and extracted with ethyl acetate (3 × 150 mL). The combined organic layers were dried over anhydrous Na_2SO_4, Na_2SO_4 was removed by decantation, and the organic phase was concentrated under reduced pressure and purified by silica gel flash column chromatography (petroleum ether/EtOAc 30/1) in 70−90% yields.

B.[3] An oven-dried round bottom flask (250 mL) with a magnetic stir bar was charged with previous product (2.53 g, 15 mmol, 1.0 equiv), triethylamine (94 mL), iodobenzene (3.37 g, 16.5 mmol, 1.1 equiv), bis(triphenylphosphine)palladium dichloride (210.6 mg, 0.3 mmol, 0.02 equiv), and copper iodide (29 mg, 0.015 mmol, 0.01 equiv). The reaction mixture is stirred at 40 °C for 6 h. The reaction mixture was filtered, and then diluted with 250 mL of AcOEt. The mixture was washed with brine three times. The combined organic phases are dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum and the crude product was purified by silica gel chromatography using a petroleum ether/AcOEt mixture [20:1 (v/v)] as the eluent to give the *N*-(3-phenyl-2-propynyl)aniline (**1a**, 3.38 g, 92%) as a yellowish oil.

3.2 The general procedure for the preparation of Arylsulfonyl Hydrazides[4]:



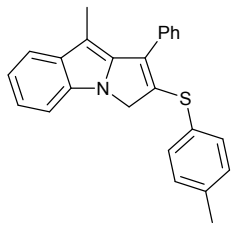
Preparation of Arylsulfonyl Hydrazides. Arylsulfonyl hydrazides were prepared according to a literature procedure. Hydrazine monohydrate (80% aqueous) (275 mg, 4.4 mmol) was added water (260 mg) and was cooled to 0 °C. To this solution was added dropwise a solution of arylsulfonyl chloride (2.0 mmol) in THF (10 mL) at 0 °C. The mixture was further stirred at 0 °C for 30 min., flowed by addition of diethyl ether (10 mL). The mixture was extracted with saturated brine (3 × 10 mL). The organic layer was dried over sodium sulfate, filtered through Celite. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product (yield: 75-91 %)

4. Experimental Procedures

Under nitrogen, a 20 mL Schlenk tube equipped with a stir bar was charged with **1a** (0.2 mmol), **2** (0.4 mmol), $K_2S_2O_8$ (0.6 mmol), $CuSO_4$ (0.06 mmol), DCE (2 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 120 °C for 10 h in oil bath. After the completion of the reaction, the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product.

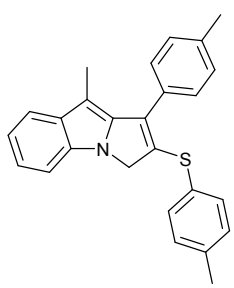
5. Characterization Data for the Products

9-methyl-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 80) give **3a** (62.3 mg, 85% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, J = 7.9 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.37-7.33 (m, 1H), 7.24-7.18 (m, 6H), 6.98 (s, 4H), 5.21 (s, 2H), 2.47 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 135.5, 133.2, 131.7, 129.8, 128.2, 128.0, 127.9, 126.6, 124.2, 123.5, 122.5, 120.5, 119.6, 119.6, 110.3, 84.0, 83.6, 33.8, 20.8, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{25}H_{21}NS$ $(M+Na)^+$ 390.1287, found.390.1287. MS (m/z): 367.1 $[M]^+$

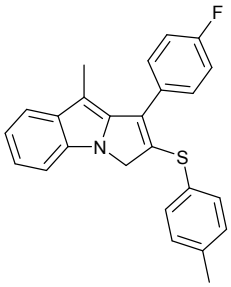
9-methyl-1-(*p*-tolyl)-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 80) give **3c** (55.6 mg, 73% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, J = 7.9 Hz, 1H) 7.55

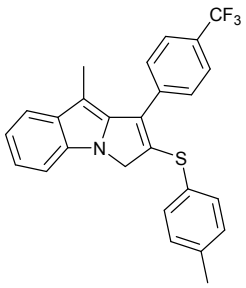
(d, J = 8.3 Hz, 1H), 7.21-7.18 (m, 1H), 7.10-6.95 (m, 8H), 5.20 (s, 2H), 2.46 (s, 3H), 2.30 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 137.3, 135.4, 133.2, 131.6, 129.8, 128.8, 127.9, 126.6, 124.1, 123.5, 120.4, 119.6, 119.5, 119.4, 110.3, 83.8, 83.3, 33.8, 21.4, 20.8, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{26}H_{23}NS$ $(M+Na)^+$ 404.1443, found.404.1443. MS (m/z): 381.1 $[M]^+$

1-(4-fluorophenyl)-9-methyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3c)



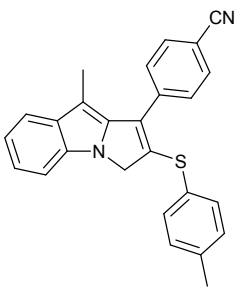
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 80) give **3d** (52.3 mg, 68% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68-7.66 (m, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.39-7.33 (m, 1H), 7.24-7.14 (m, 3H), 6.98 (s, 4H), 6.94-6.89 (m, 2H), 5.20 (s, 2H), 2.48 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, (d, $J_{C\text{-}F}$ = 247.5 Hz), 137.2, 135.4, 133.6 (d, $J_{C\text{-}F}$ = 8.3 Hz), 133.2, 129.7, 127.9, 126.6, 124.1, 123.5, 120.6, 119.6 (d, $J_{C\text{-}F}$ = 4.5 Hz), 118.6 (d, $J_{C\text{-}F}$ = 3.8 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.8 Hz), 110.1, 83.8, 83.8, 82.6, 33.7, 20.8, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{25}H_{20}FNS$ $(M+Na)^+$ 408.1193, found.408.1193. MS (m/z): 385.1 $[M]^+$

9-methyl-2-(*p*-tolylthio)-1-(4-(trifluoromethyl)phenyl)-3*H*-pyrrolo[1,2-*a*]indole (3d)



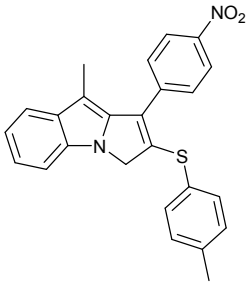
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **3d** (60.9 mg, 70% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68-7.65 (m, 1H), 7.51-7.44 (m, 3H), 7.37-7.32 (m, 1H), 7.23-7.18 (m, 3H), 6.96 (s, 4H), 5.21 (s, 2H), 2.47 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 135.5, 133.1, 131.9, 129.6 (q, $J_{C\text{-}F}$ = 36.0 Hz), 127.9, 126.6, 125.6, 124.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.1, 123.8 (q, $J_{C\text{-}F}$ = 270.7 Hz), 120.78, 119.8, 119.7, 110.0, 86.6, 82.3, 33.6, 20.8, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{26}H_{20}F_3NS$ $(M+Na)^+$ 458.1161, found.458.1160. MS (m/z): 435.1 $[M]^+$

4-(9-methyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indol-1-yl)benzonitrile (3e)



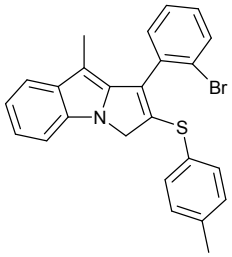
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3e** (52.5 mg, 67% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.67 (d, J = 7.9 Hz, 1H), 7.51-7.46 (m, 3H), 7.38-7.32 (m, 1H), 7.24-7.18 (m, 3H), 6.96 (s, 3H), 5.22 (s, 2H), 2.47 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 135.5, 133.0, 132.2, 131.7, 129.8, 127.9, 127.4, 126.6, 124.1, 123.7, 120.9, 119.8, 119.7, 118.4, 111.6, 109.9, 88.7, 82.0, 33.6, 20.8, 19.2, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{26}H_{20}N_2S$ $(M+Na)^+$ 415.1239, found.415.1237. MS (m/z): 392.1 $[M]^+$

9-methyl-1-(4-nitrophenyl)-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3f)



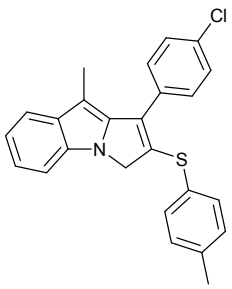
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **3f** (42.0 mg, 51% yield) as yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.06-8.03 (m, 2H), 7.65-7.62 (m, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.35-7.29 (m, 1H), 7.25-7.15 (m, 3H), 6.93 (s, 4H), 5.21 (s, 2H), 2.44 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 137.2, 135.6, 133.0, 132.4, 129.8, 129.4, 128.0, 126.6, 124.1, 123.7, 123.3, 121.0, 119.9, 119.8, 109.9, 89.6, 81.8, 33.6, 20.8, 10.1. HRMS (ESI) m/z calcd for Chemical Formula: $C_{25}H_{20}N_2O_2S$ $(M+Na)^+$ 435.1138, found.435.1137. MS (m/z): 412.1 $[M]^+$

1-(2-bromophenyl)-9-methyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3g)



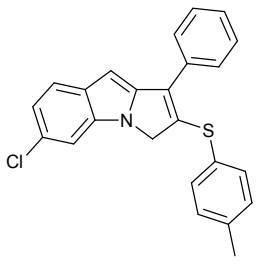
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **3f** (55.2 mg, 62% yield) as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 7.9 Hz, 1H), 7.57-7.55 (m, 1H), 7.44-7.36 (m, 3H), 7.30-7.26 (m, 1H), 7.17-7.10 (m, 2H), 7.06 (s, 4H), 5.26 (s, 2H), 2.56 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.5, 134.4, 133.0, 131.3, 130.2, 129.7, 129.4, 127.9, 126.6, 124.4, 124.1, 123.6, 121.8, 120.6, 119.7, 119.6, 110.0, 85.5, 82.0, 33.6, 20.9, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{25}H_{20}BrNS$ $(M+Na)^+$ 468.0396, found.468.0395. MS (m/z): 445.1 $[M]^+$

1-(4-chlorophenyl)-9-methyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **3h** (56.4 mg, 80% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 7.9 Hz, 1H), 7.58-7.56 (m, 1H), 7.43-7.39 (m, 1H), 7.29-7.27 (m, 1H), 7.25-7.23 (m, 2H), 7.17-7.13 (m, 2H), 7.04 (s, 4H), 5.25 (s, 2H), 2.54 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 135.4, 134.2, 133.1, 132.9, 129.7, 128.3, 127.9, 126.5, 124.1, 123.6, 120.9, 120.6, 119.7, 119.6, 110.1, 85.1, 82.5, 33.6, 20.8, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{25}H_{20}ClNS$ $(M+Na)^+$ 424.0897, found.424.0897. MS (m/z): 401.1 $[M]^+$

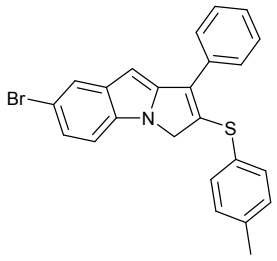
6-chloro-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3i)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **3i** (56.5 mg, 73% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (s, 1H), 7.53-7.50 (m, 2H), 7.48-7.45 (m, 2H), 7.37-7.31 (m, 3H), 7.16-7.13 (m, 1H), 7.06-6.98 (m, 4H), 5.09 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 135.0, 134.9, 133.7, 131.8,

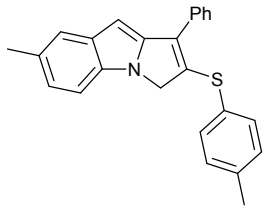
129.5, 128.9, 128.6, 128.4, 126.4, 121.8, 121.6, 120.9, 110.1, 103.0, 86.3, 81.7, 37.1, 20.9. HRMS (ESI) m/z calcd for Chemical Formula: $C_{24}H_{18}ClNS$ $(M+Na)^+$ 410.0741, found.410.0740. MS (m/z): 387.1 $[M]^+$

7-bromo-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3j)



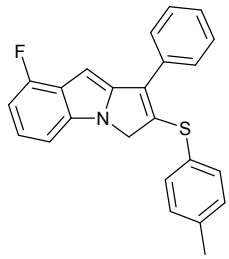
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **3j** (46.5 mg, 54% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78-7.77 (m, 3H), 7.57 (s, 1H), 7.46-7.32 (m, 7H), 7.06-6.99 (m, 4H), 5.10 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.3, 135.0, 134.9, 134.4, 131.9, 131.8, 129.6, 128.9, 128.4, 126.3, 125.8, 122.5, 121.8, 114.5, 111.5, 102.2, 86.3, 81.7, 37.2, 20.9. HRMS (ESI) m/z calcd for Chemical Formula: $C_{24}H_{18}BrNS$ $(M+Na)^+$ 454.0236, found.454.0236. MS (m/z): 431.0 $[M]^+$

7-methyl-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3k)



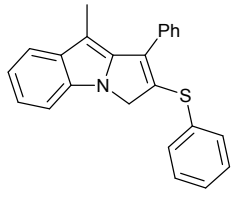
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **3k** (32.8 mg, 62% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.52 (m, 2H), 7.48-7.46 (m, 2H), 7.37-7.32 (m, 3H), 7.12-7.01 (m, 6H), 5.35 (s, 2H), 2.93 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 134.9, 134.5, 131.7, 131.1, 129.4, 128.7, 128.3, 126.1, 125.7, 122.0, 121.5, 121.0, 118.0, 102.2, 86.2, 83.9, 39.6, 20.8, 19.4. HRMS (ESI) m/z calcd for Chemical Formula: $C_{25}H_{21}NS$ $(M+Na)^+$ 390.1287, found.390.1287. MS (m/z): 367.1 $[M]^+$

8-fluoro-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3l)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 60) give **3l** (32.3 mg, 42% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52-7.46 (m, 3H), 7.36-7.13 (m, 7H), 7.04-7.03 (m, 2H), 6.86-6.82 (m, 1H), 5.11-5.10 (m, 2H), 2.28-2.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (d, $J_{C\text{-}F}$ = 247.3 Hz), 139.4 (d, $J_{C\text{-}F}$ = 10.0 Hz), 135.9, 135.0, 133.6, 131.8, 129.5, 128.9, 128.4, 126.9, 123.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 121.8, 118.6 (d, $J_{C\text{-}F}$ = 17.7 Hz), 106.5 (d, $J_{C\text{-}F}$ = 19.0 Hz), 106.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 101.1, 86.3, 81.7, 37.3, 20.9. HRMS (ESI) m/z calcd for Chemical Formula: $C_{24}H_{18}FNS$ $(M+Na)^+$ 394.1036, found. 394.1034. MS (m/z): 371.1 $[M]^+$

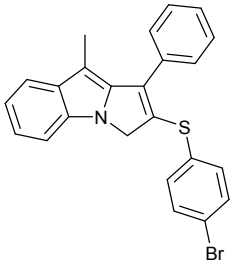
9-methyl-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3m)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 80) give **3m** (56.5 mg, 80% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, J = 7.9 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.38-7.34 (m, 1H), 7.25-7.17 (m, 8H), 7.11-

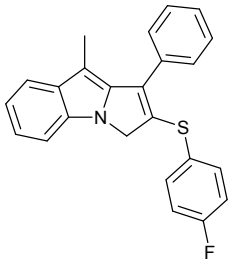
7.05 (m, 3H), 5.22 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.9, 131.7, 129.0, 128.2, 128.0, 127.9, 126.1, 125.5, 123.6, 123.5, 122.5, 120.8, 119.7, 119.6, 110.3, 84.0, 83.8, 33.8, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{24}H_{19}NS$ $(M+Na)^+$ 376.1130, found. 376.1130. MS (m/z): 353.1 $[M]^+$

2-((4-bromophenyl)thio)-9-methyl-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3n)



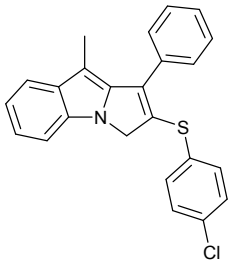
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 60 give **3n** (60.3 mg, 70% yield) as a yellow solid. m.p. 85 - 86 ^{o} C ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.45-7.42 (m, 1H), 7.35-7.28 (m, 6H), 7.23-7.21 (m, 2H), 6.99-6.92 (m, 2H), 5.25 (s, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.2, 131.9, 131.7, 128.3, 128.1, 127.8, 127.7, 123.9, 122.8, 122.2, 121.1, 119.8, 119.7, 119.3, 110.3, 83.9, 83.8, 33.7, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{24}H_{18}BrNS$ $(M+Na)^+$ 454.0236, found. 454.0235. MS (m/z): 431.0 $[M]^+$

2-((4-fluorophenyl)thio)-9-methyl-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3o)



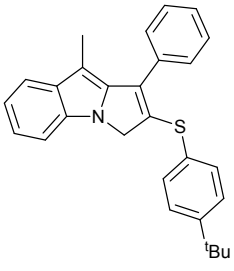
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 60 give **3n** (49.7 mg, 67% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75-7.73 (m, 1H), 7.63-7.61 (m, 1H), 7.46-7.42 (m, 1H), 7.33-7.26 (m, 6H), 7.15-7.12 (m, 2H), 6.98-6.93 (m, 2H), 5.28 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, $J_{C\text{-}F}$ = 243.7 Hz), 137.3, 131.7 (d, $J_{C\text{-}F}$ = 3.1 Hz), 131.6, 128.3, 128.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.1, 127.8, 123.8, 123.7, 122.3, 120.7, 119.8, 119.6, 116.0 (d, $J_{C\text{-}F}$ = 22.0 Hz), 110.3, 83.9, 83.8, 33.7, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{24}H_{18}FNS$ $(M+Na)^+$ 394.1036, found. 394.1036. MS (m/z): 371.1 $[M]^+$

2-((4-chlorophenyl)thio)-9-methyl-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3p)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 60 give **3p** (55.7 mg, 72% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.72 (m, 1H), 7.61-7.59 (m, 1H), 7.45-7.41 (m, 1H), 7.31-7.27 (m, 4H), 7.24-7.18 (m, 4H), 7.05-7.03 (m, 2H), 5.24 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 135.4, 131.6, 131.4, 129.0, 128.3, 128.1, 127.7, 127.5, 123.8, 122.9, 122.2, 121.0, 119.8, 119.7, 110.3, 83.9, 83.8, 33.7, 10.0. HRMS (ESI) m/z calcd for Chemical Formula: $C_{24}H_{18}ClNS$ $(M+Na)^+$ 410.0741, found. 410.0741. MS (m/z): 387.1 $[M]^+$

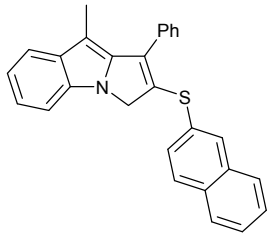
2-((4-(tert-butyl)phenyl)thio)-9-methyl-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3q)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 60 give **3q** (53.2mg, 65% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75-7.73 (m, 1H), 7.64-7.62

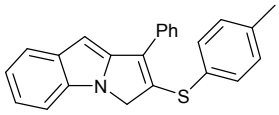
(m, 1H), 7.45-7.41 (m, 1H), 7.32-7.26 (m, 8H), 7.10-7.08 (m, 2H), 5.30 (s, 2H), 2.56 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 137.3, 133.3, 131.7, 128.2, 128.0, 127.9, 126.1, 126.0, 123.9, 123.5, 122.5, 120.6, 119.6, 119.6, 110.3, 84.1, 83.6, 34.3, 33.7, 31.2, 10.1. HRMS (ESI) m/z calcd for Chemical Formula: $C_{28}H_{27}NS$ $(M+Na)^+$ 432.1756, found. 432.1756. MS (m/z): 409.2 $[M]^+$

9-methyl-2-(naphthalen-2-ylthio)-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3r)



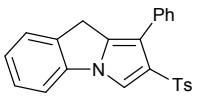
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 40) give **3r** (36.5 mg, 43% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.73-7.65 (m, 3H), 7.60-7.57 (m, 2H), 7.48-7.47 (m, 1H), 7.25-7.16 (m, 3H), 7.11-7.07 (m, 2H), 6.99-6.97 (m, 2H), 5.24 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 134.3, 133.8, 131.6, 128.7, 128.1, 128.0, 127.9, 127.7, 127.1, 126.5, 125.4, 124.6, 124.3, 123.7, 123.5, 122.2, 120.9, 119.7, 119.7, 110.4, 83.9, 83.8, 33.8, 10.1. HRMS (ESI) m/z calcd for Chemical Formula: $C_{28}H_{21}NS$ $(M+Na)^+$ 426.1287, found. 426.1287. MS (m/z): 403.1 $[M]^+$

1-phenyl-2-(p-tolylthio)-3H-pyrrolo[1,2-a]indole (3s)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 40) give **3s** (49.4 mg, 70% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.68-7.65 (m, 1H), 7.60 (s, 1H), 7.56-7.54 (m, 1H), 7.48-7.46 (m, 2H), 7.36-7.31 (m, 4H), 7.24-7.20 (m, 1H), 7.10-7.07 (m, 2H), 7.01-6.99 (m, 2H),5.14 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 135.5, 134.6, 133.3, 131.8, 130.1, 129.4, 128.8, 128.3, 126.2, 122.8, 122.0, 120.8, 120.0, 109.9, 102.3, 85.9, 82.2, 37.0, 20.8. HRMS (ESI) m/z calcd for Chemical Formula: $C_{24}H_{19}NS$ $(M+Na)^+$ 376.1130, found. 376.1130. MS (m/z): 353.1 $[M]^+$

1-phenyl-2-tosyl-9H-pyrrolo[1,2-a]indole (4S) [1]



Exact Mass: 385.1136

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 40) give **4s** as a white solid; m.p. 206.1-207.1 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.92 (s, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.44-7.30 (m, 8H), 7.20-7.16 (m, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 3.78 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 139.6, 139.3, 135.2, 133.8, 132.3, 129.5, 129.0, 127.9, 127.8, 127.0, 126.8, 126.0, 125.0, 117.2, 115.4, 110.7, 28.9, 21.3. MS (m/z): 385.1 $[M]^+$

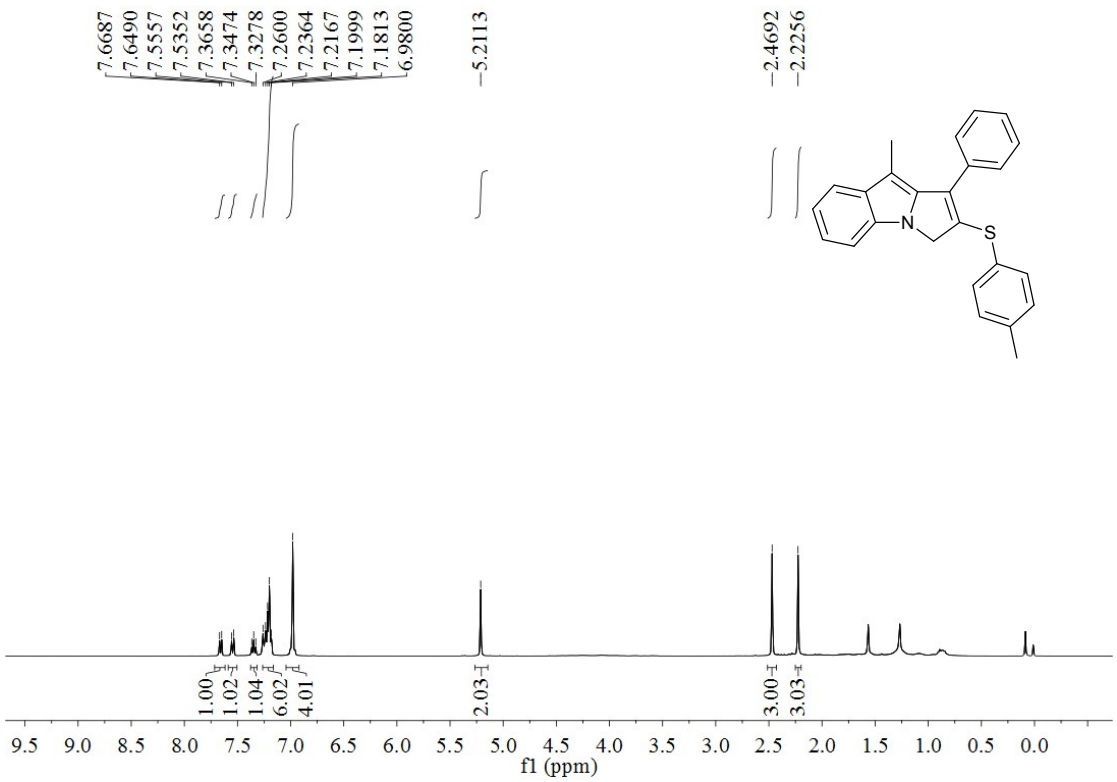
6. References

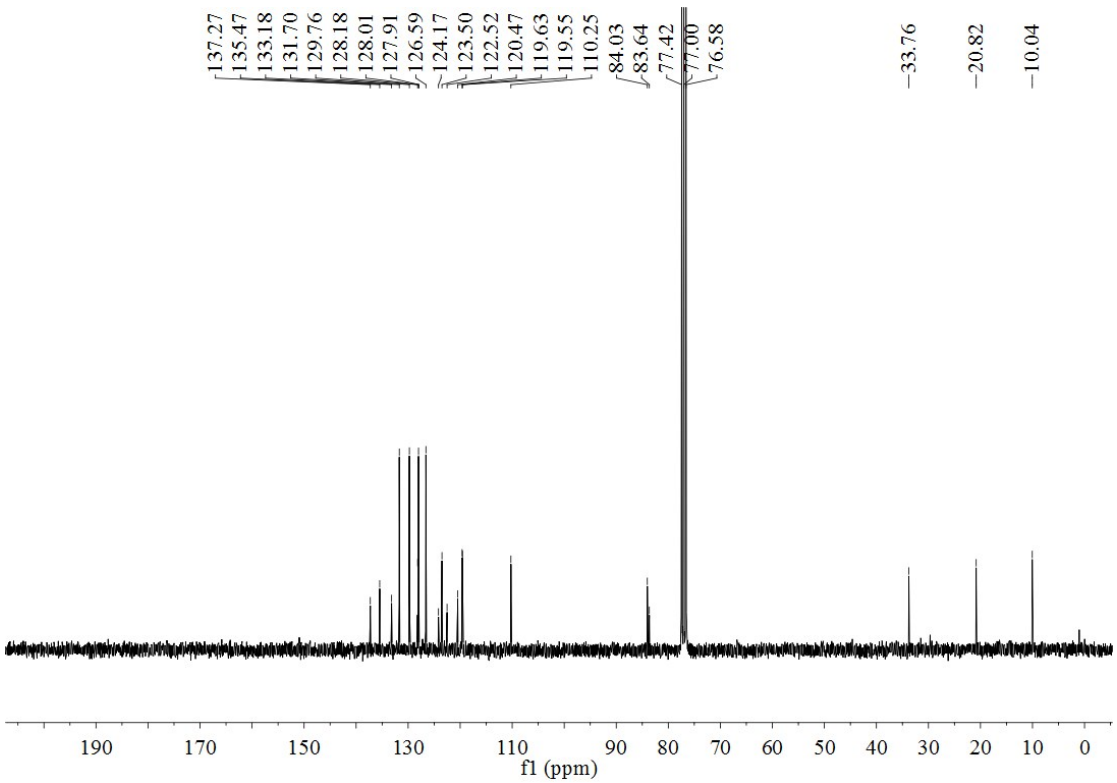
1. G. Tang, P. Zhang, Y. Gao, S. Chen and Y. Zhao, *Org. Chem. Front.,* 2017, DOI: 10.1039/C7QO00167C.

2. J. Wang, H.-T. Zhu, S. Chen, Y. Xia, D.-P. Jin, Y.-F. Qiu, Y.-X. Li and Y.-M. Liang. *J. Org. Chem.*, 2016, **81**, 10975.
3. L.-L. Zhang, S. Chen, Y.-Z. Gao, P.-B. Zhang, Y.-L. Wu, G. Tang and Y..-F. Zhao. *Org. Lett.,* 2016, **18**, 1286.
4. C.-R. Liu, L.-H. Ding, G. Guo, W.-W. Liu and F.-L. Yang. *Org. Biomol. Chem*., 2016, **14**, 2824.

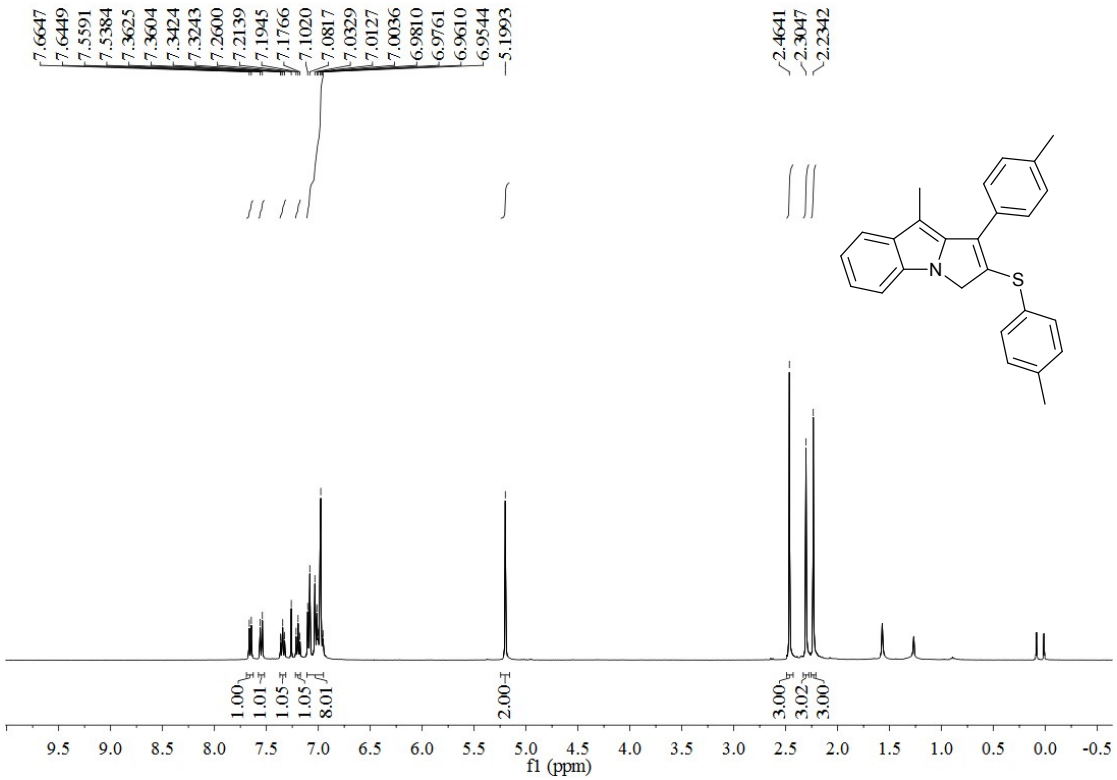
7. Copies of the ^{1}H NMR and ^{13}C NMR Spectra

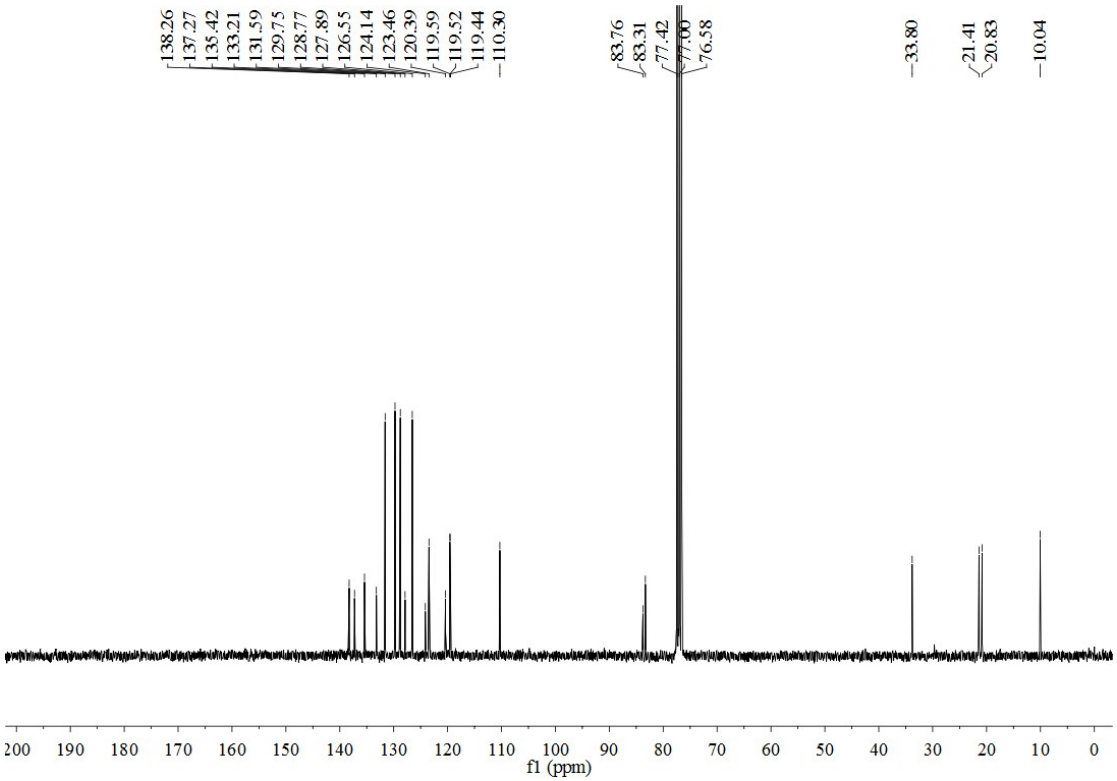
9-methyl-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3a)



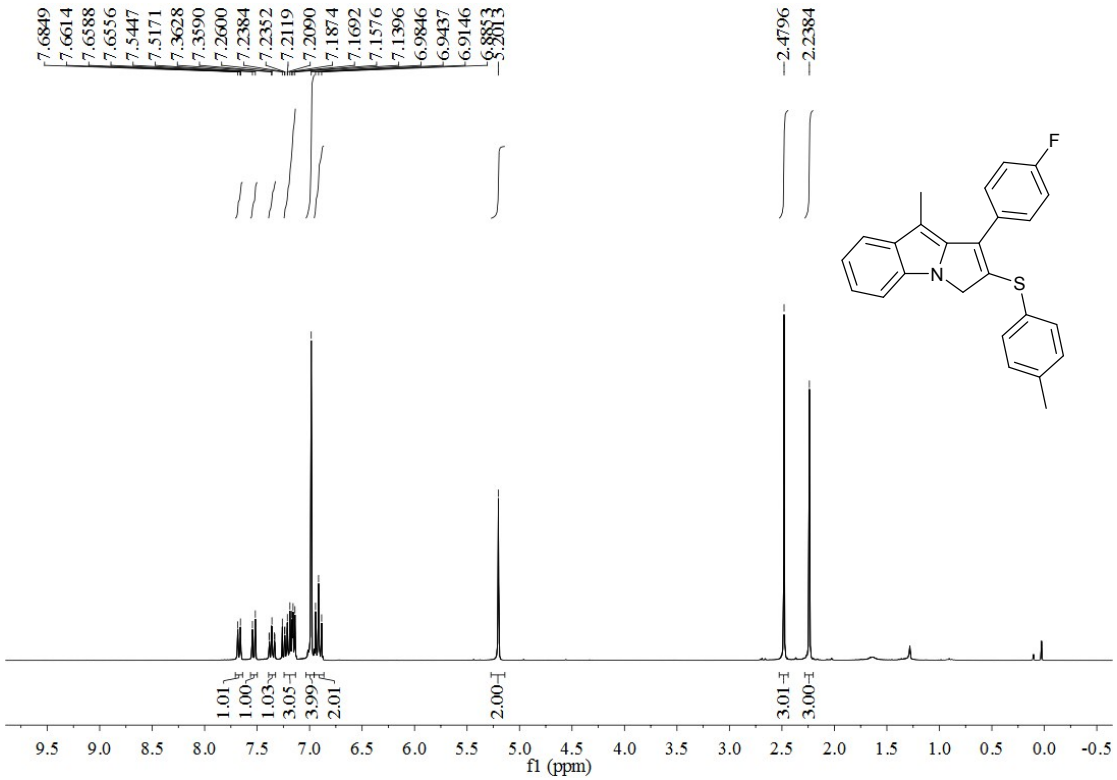


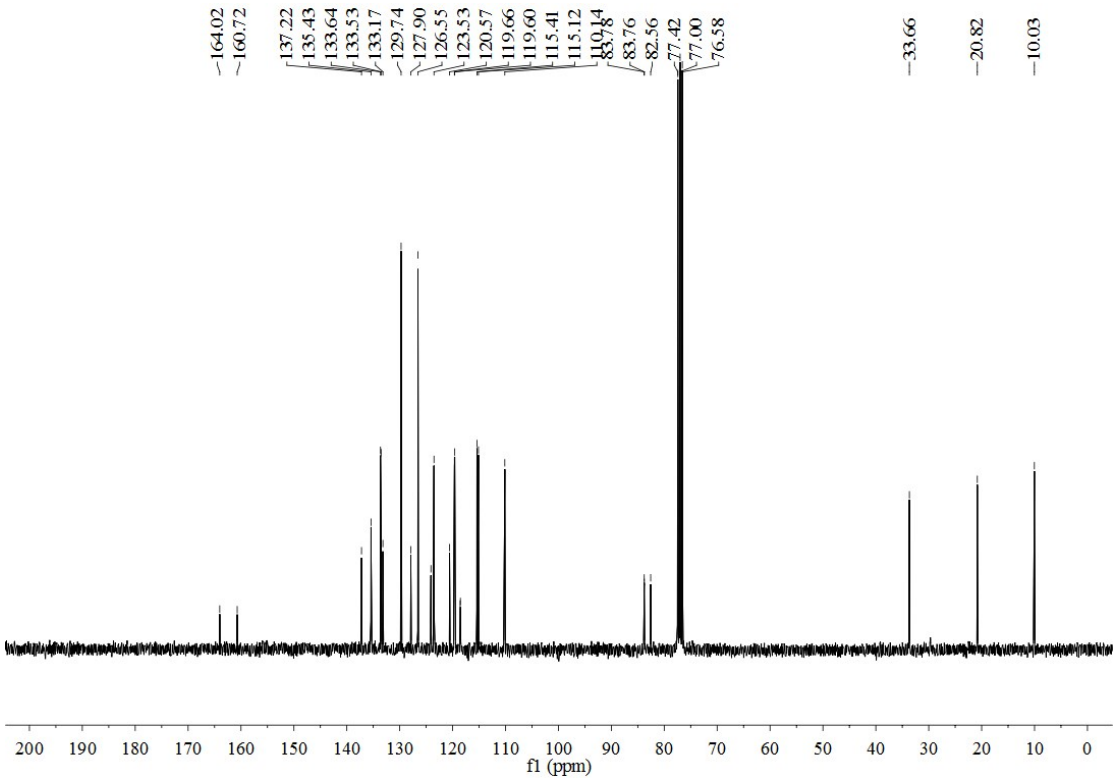
9-methyl-1-(*p*-tolyl)-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3b)



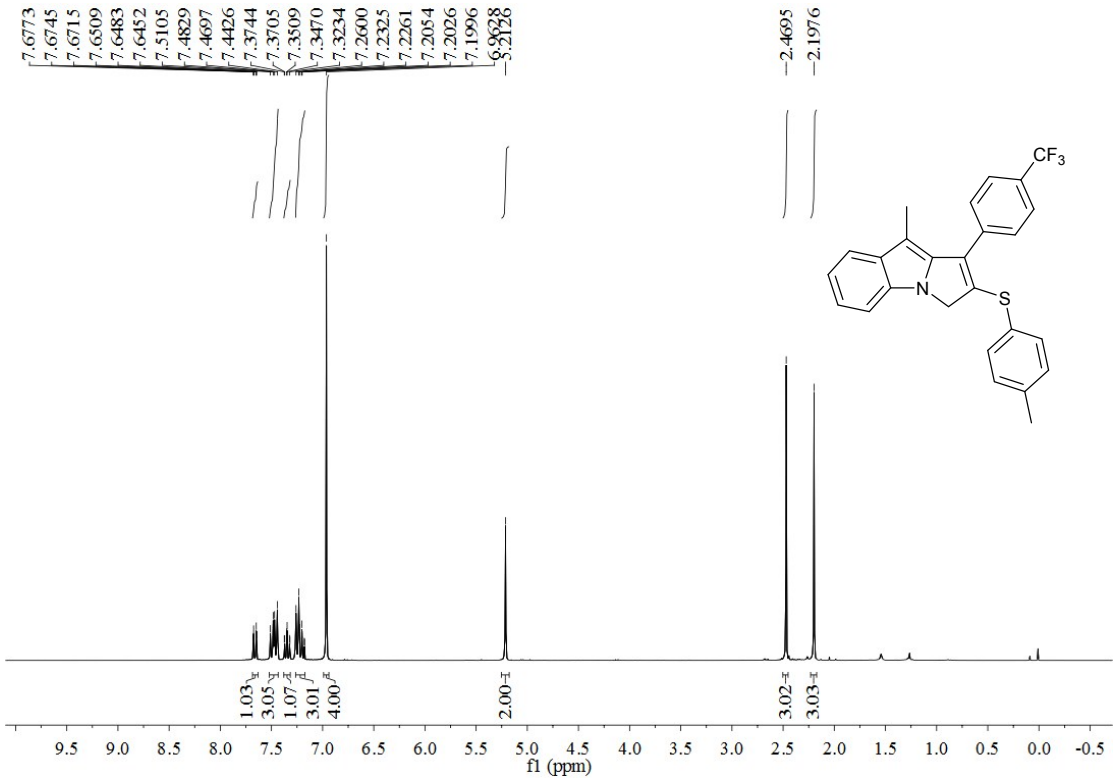


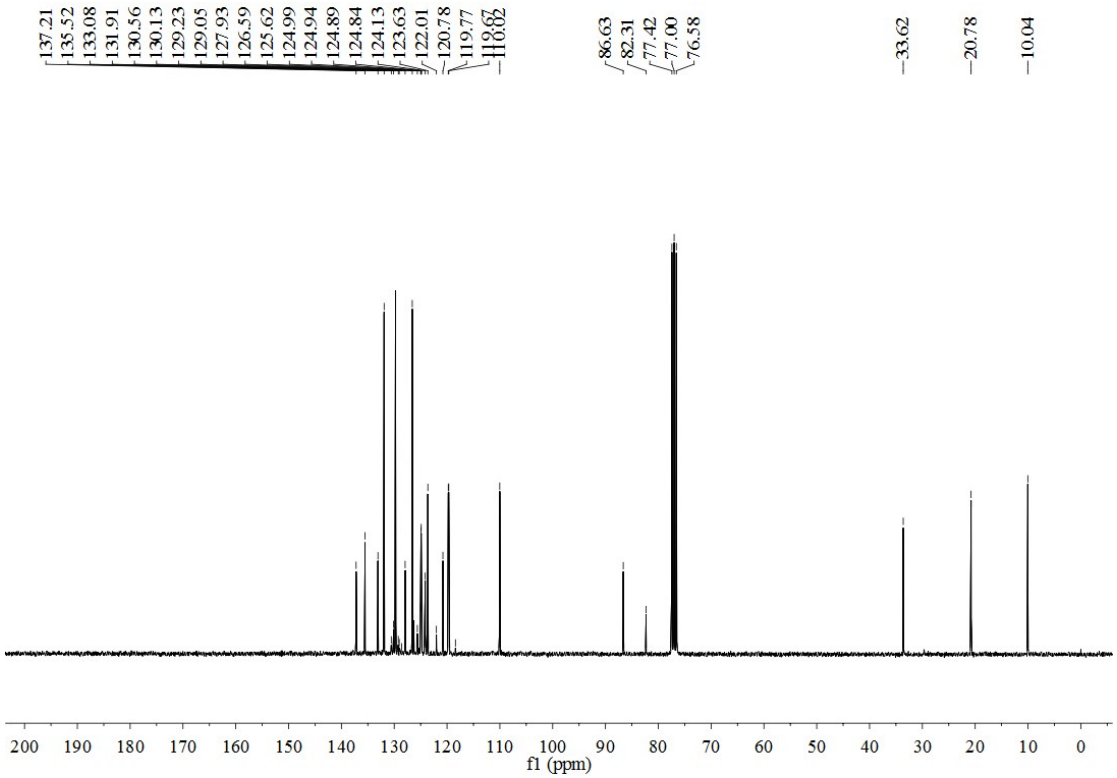
1-(4-fluorophenyl)-9-methyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3c)



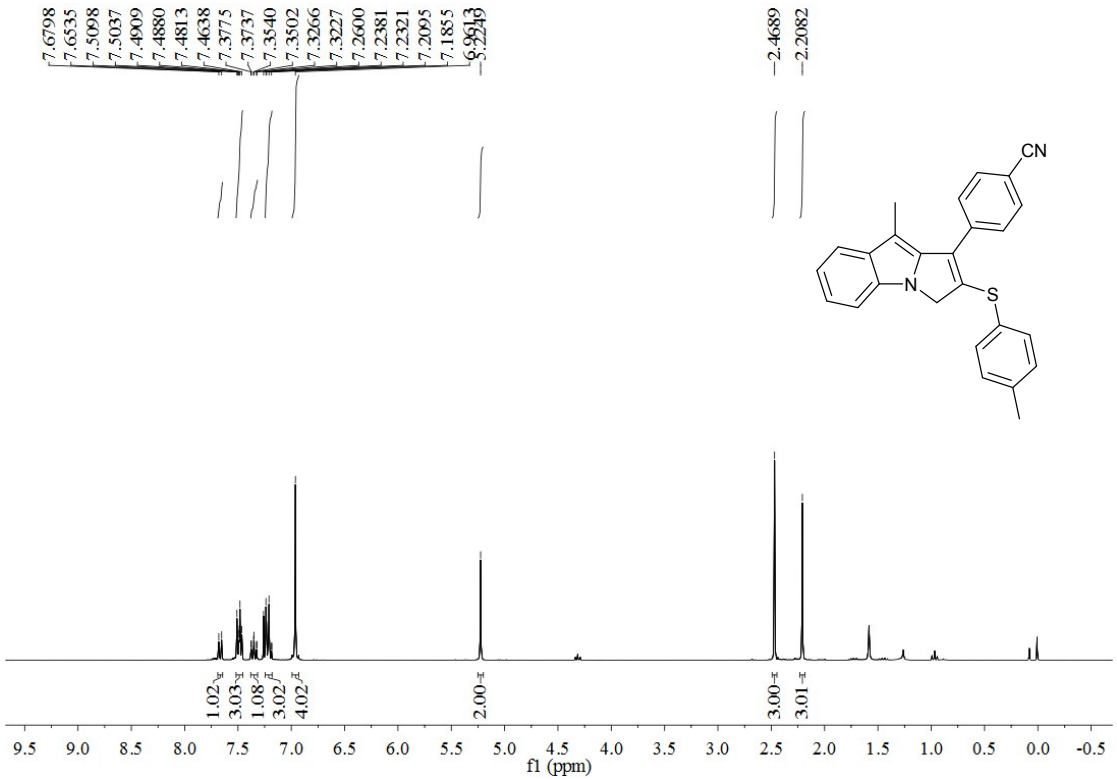


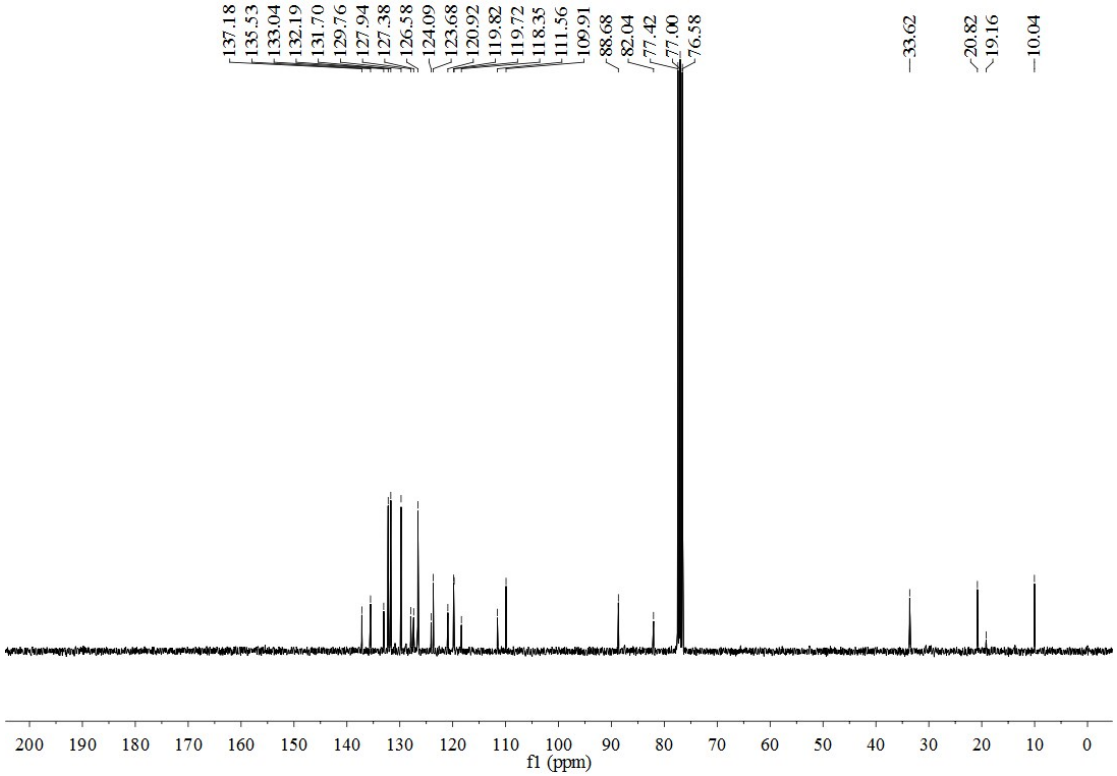
9-methyl-2-(*p*-tolylthio)-1-(4-(trifluoromethyl)phenyl)-3*H*-pyrrolo[1,2-*a*]indole (3d)



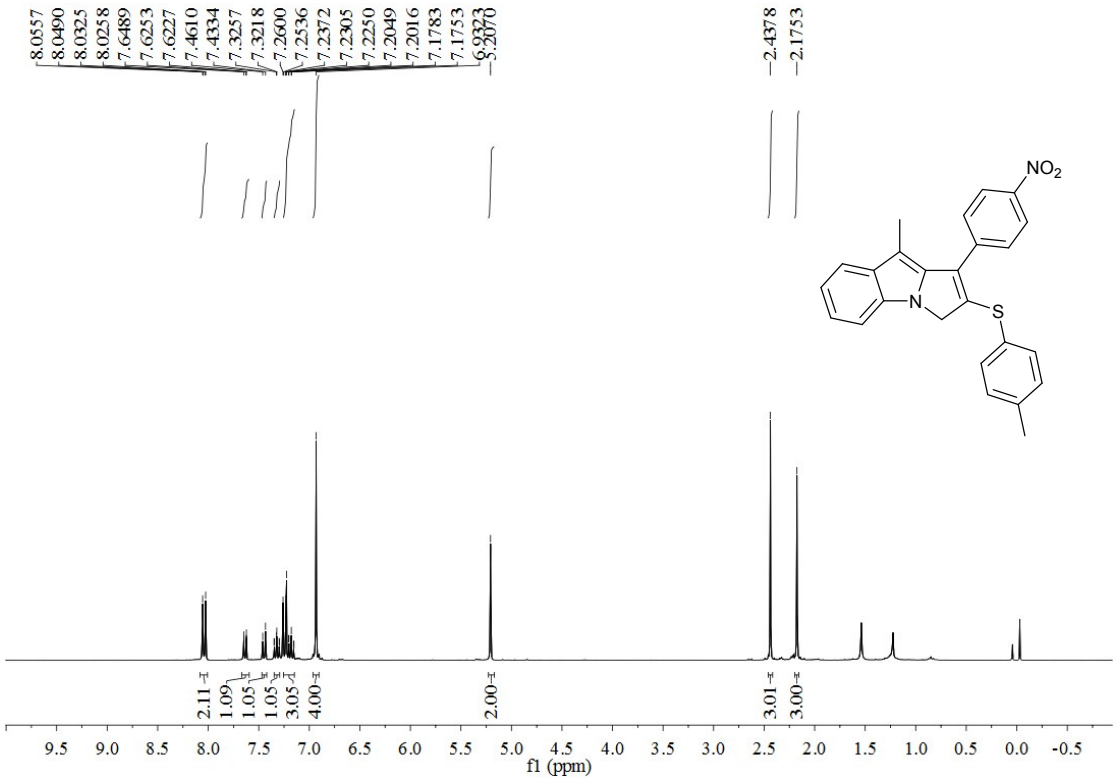


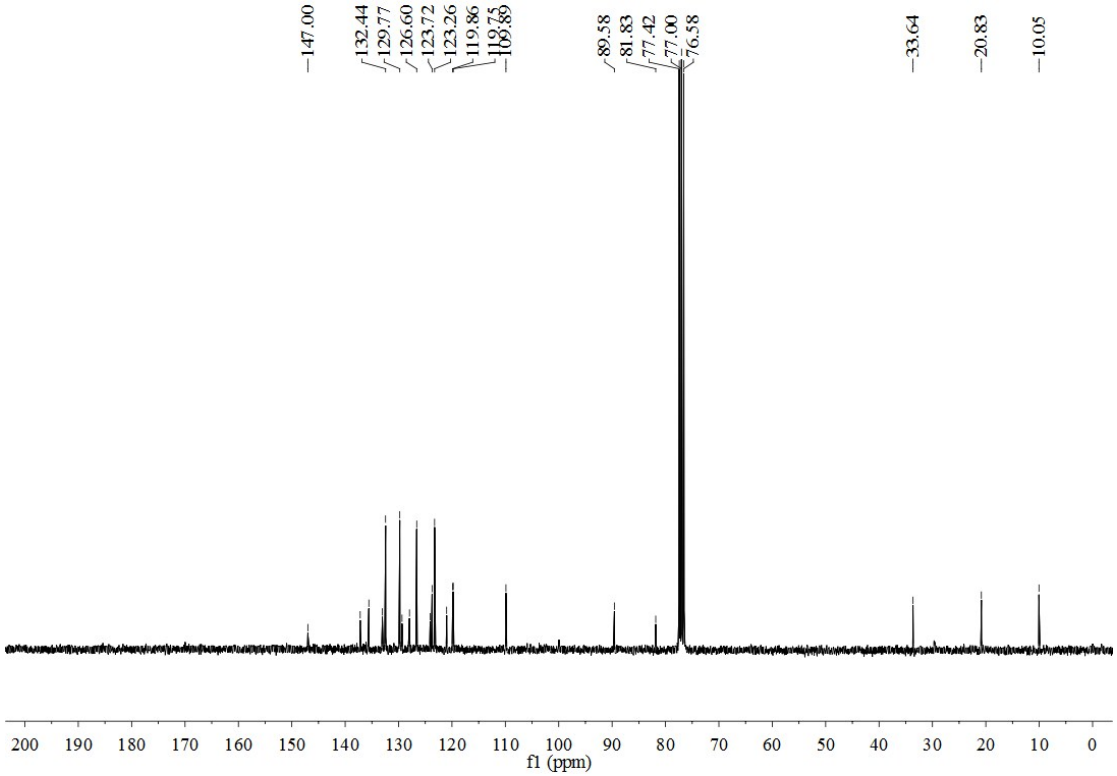
4-(9-methyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indol-1-yl)benzonitrile (3e)



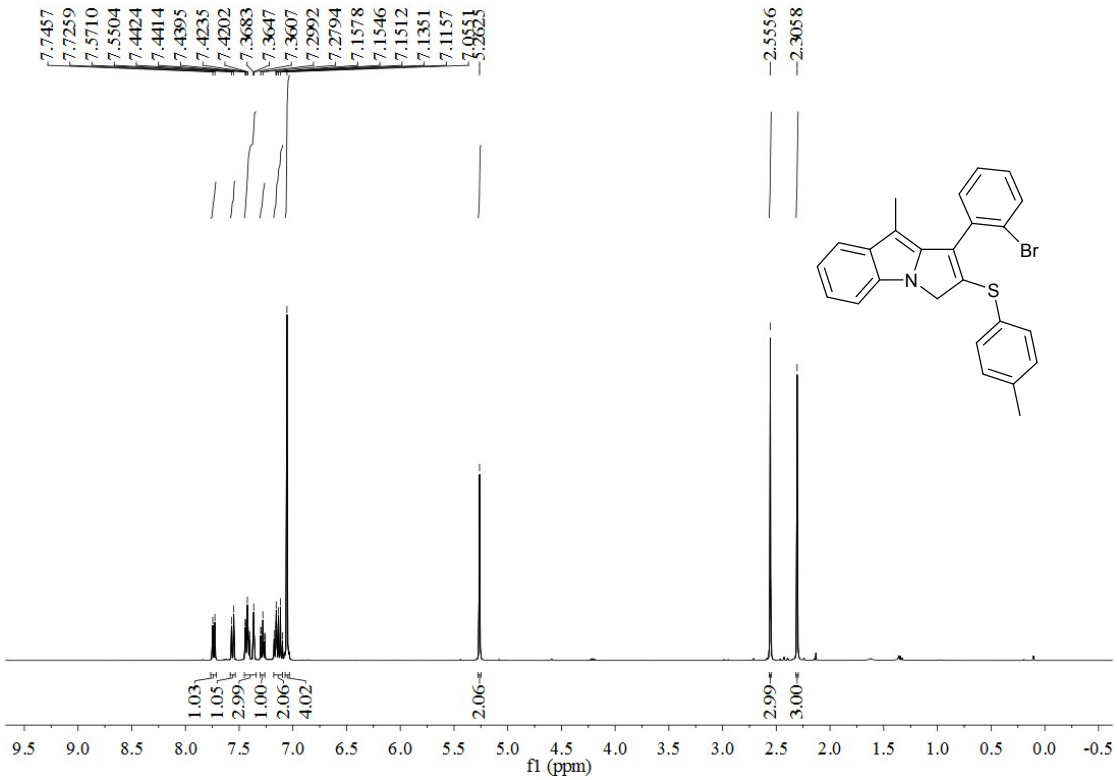


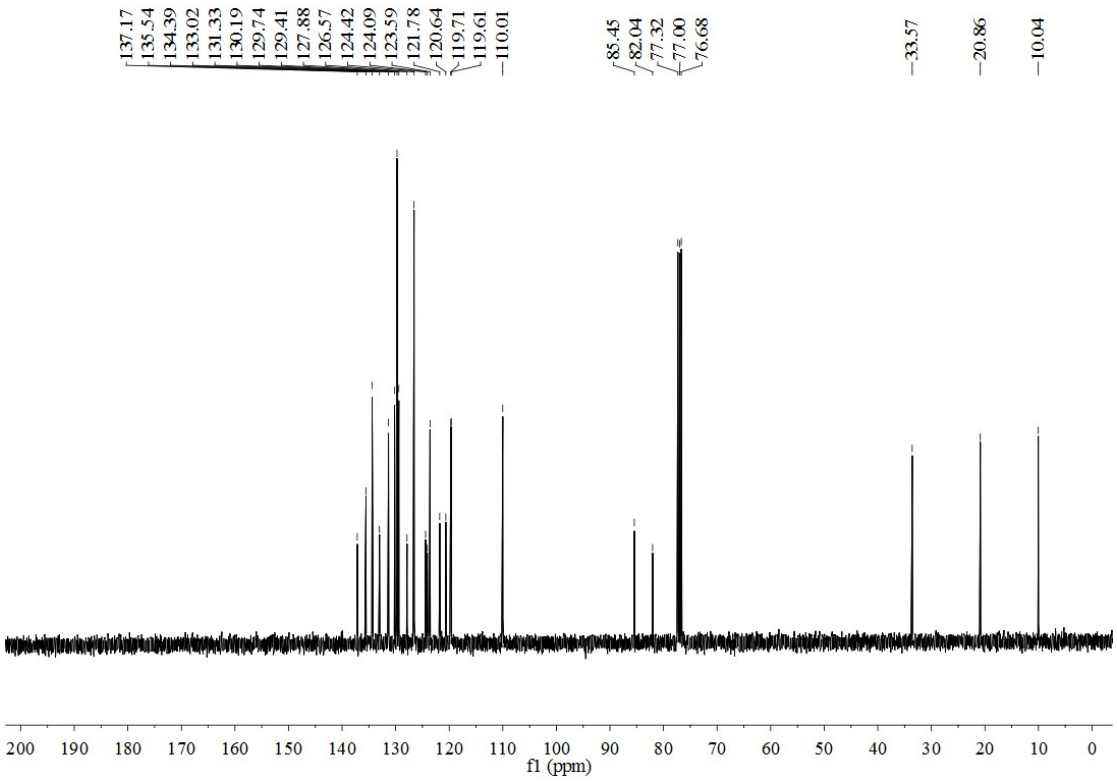
9-methyl-1-(4-nitrophenyl)-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3f)



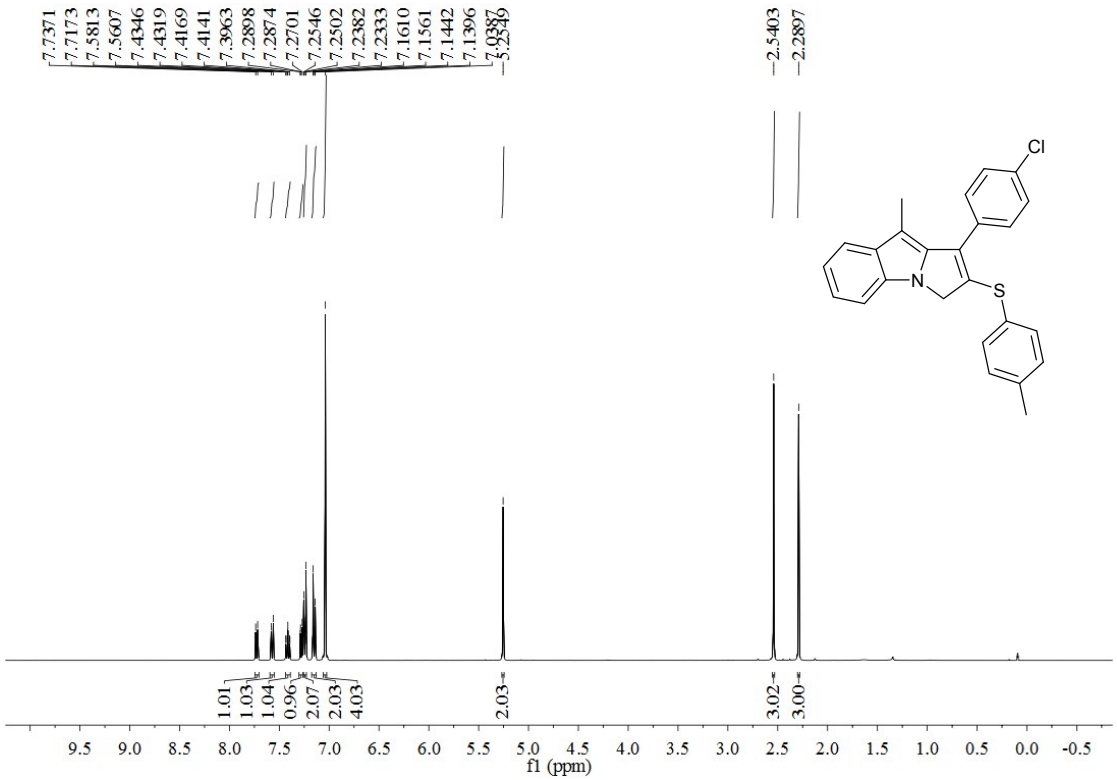


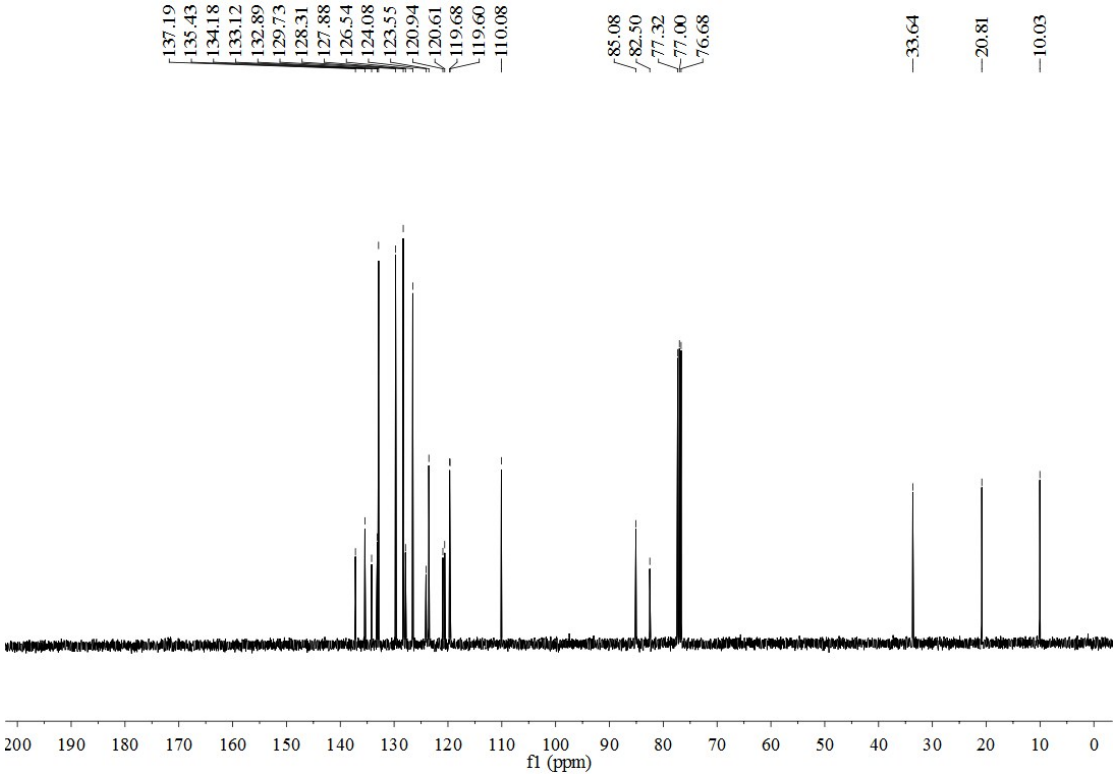
1-(2-bromophenyl)-9-methyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3g)



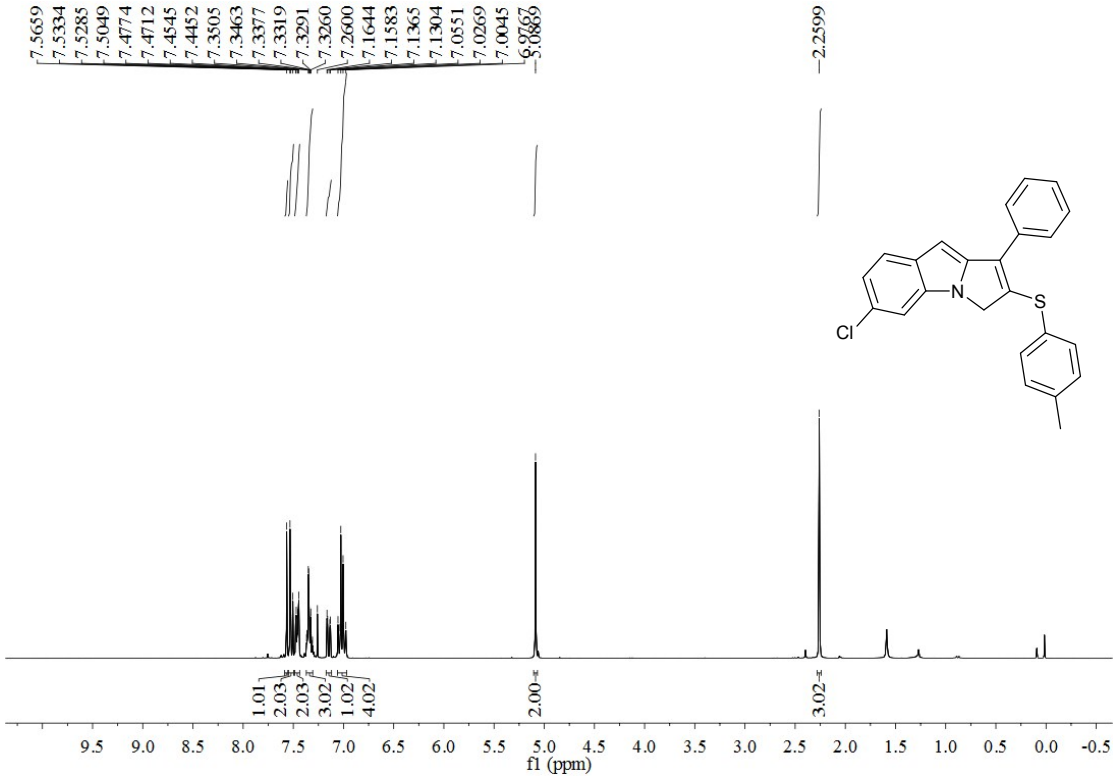


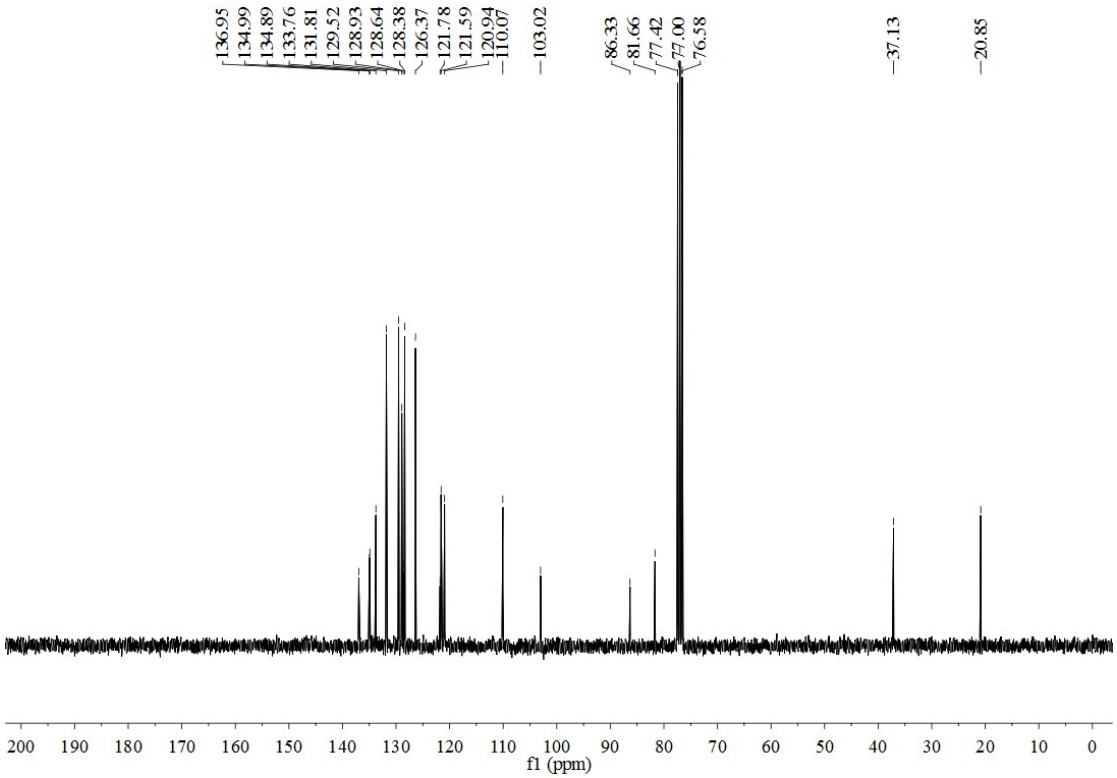
1-(4-chlorophenyl)-9-methyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3h)



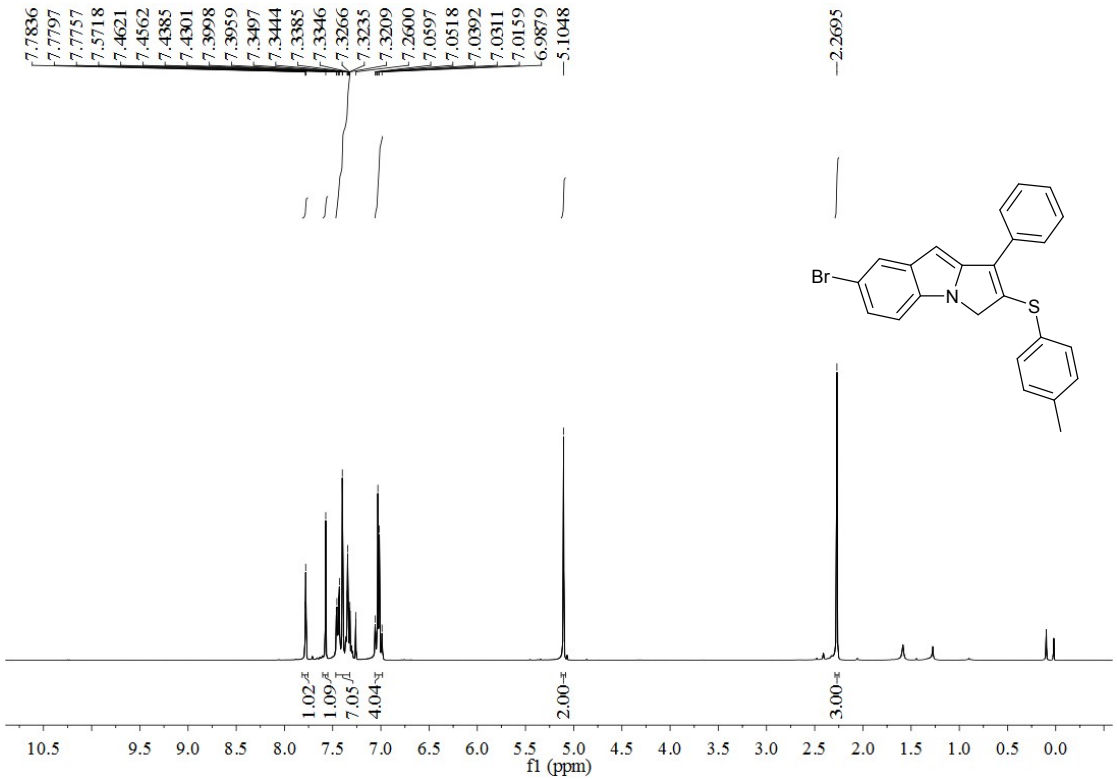


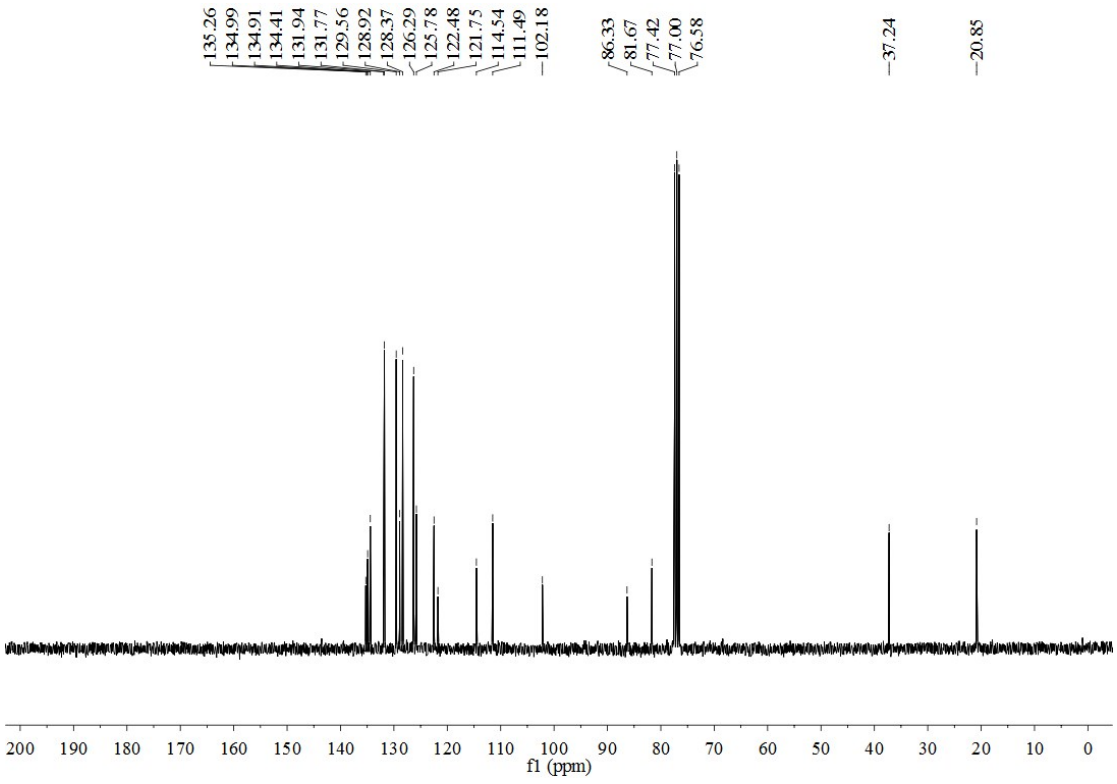
6-chloro-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3i)



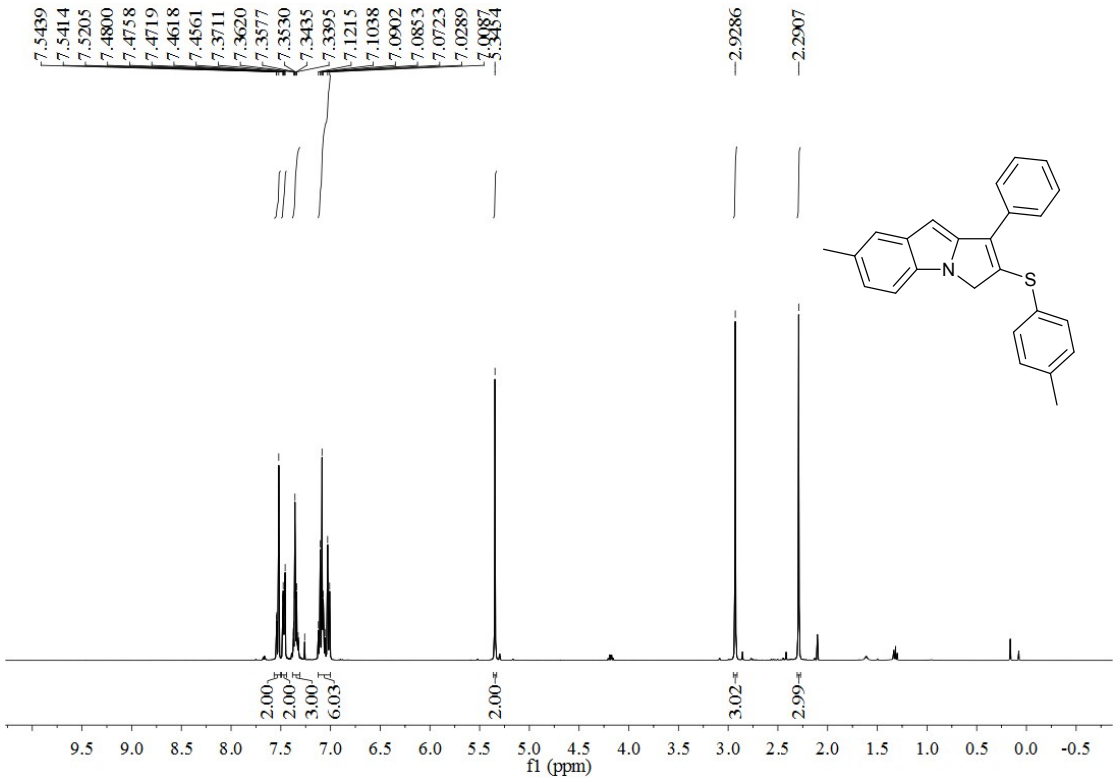


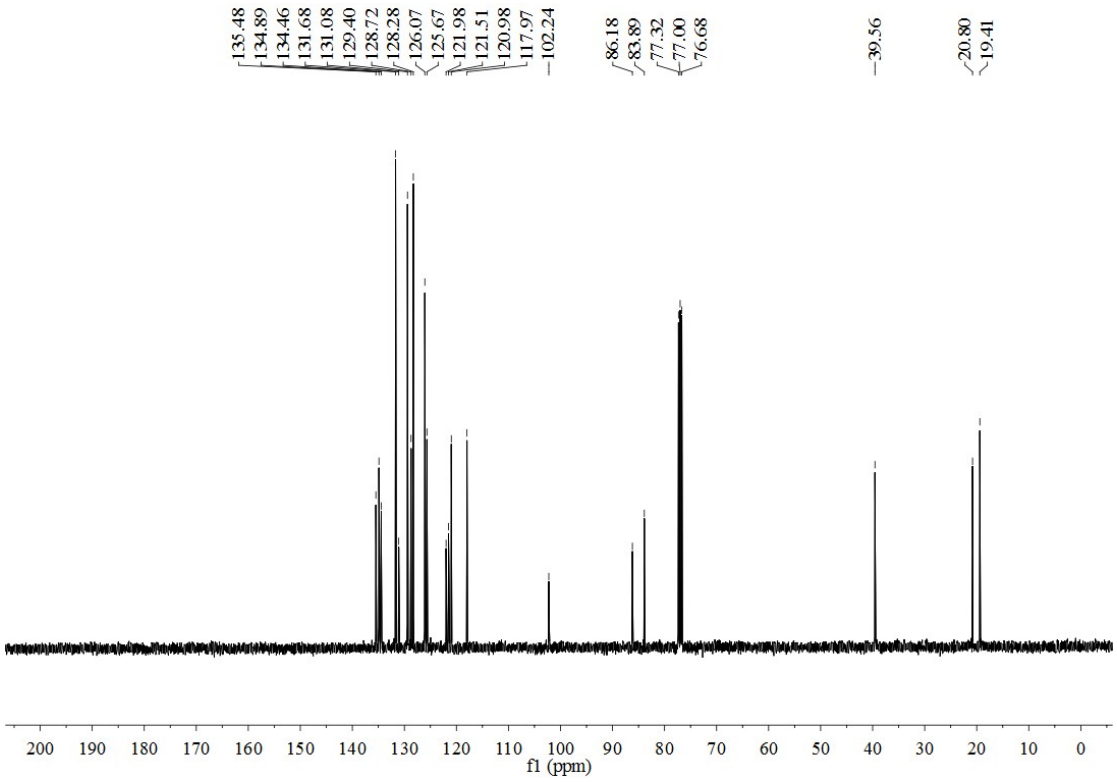
7-bromo-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3j)



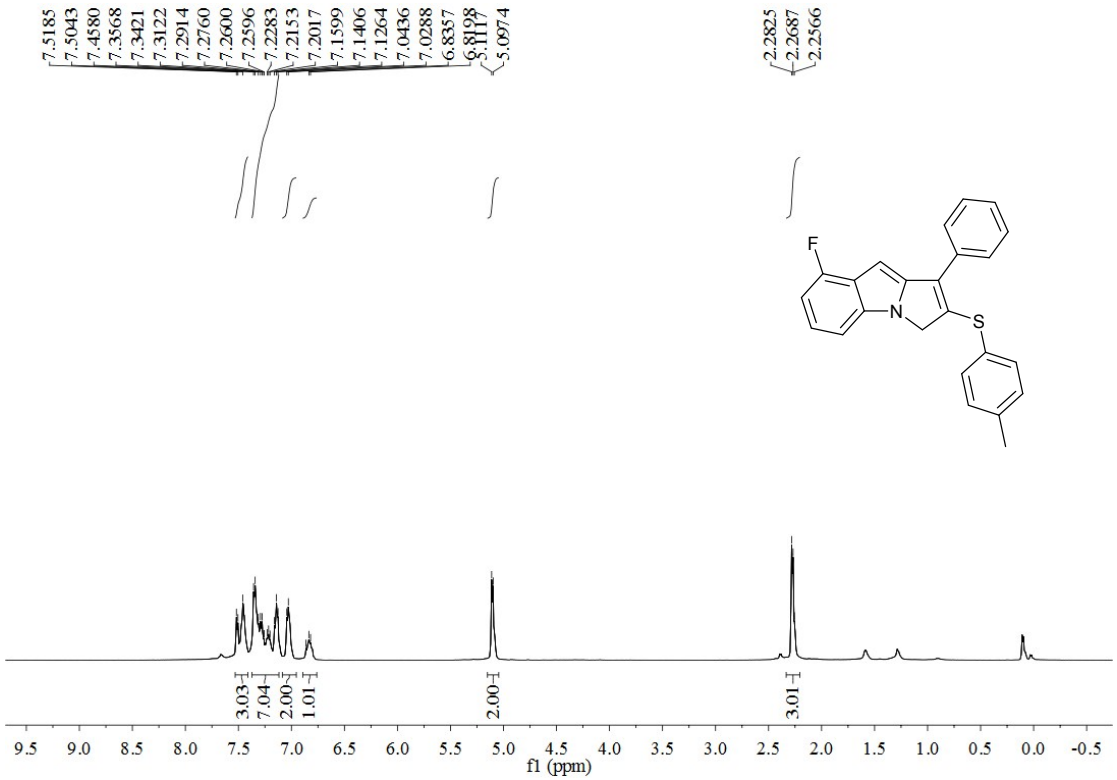


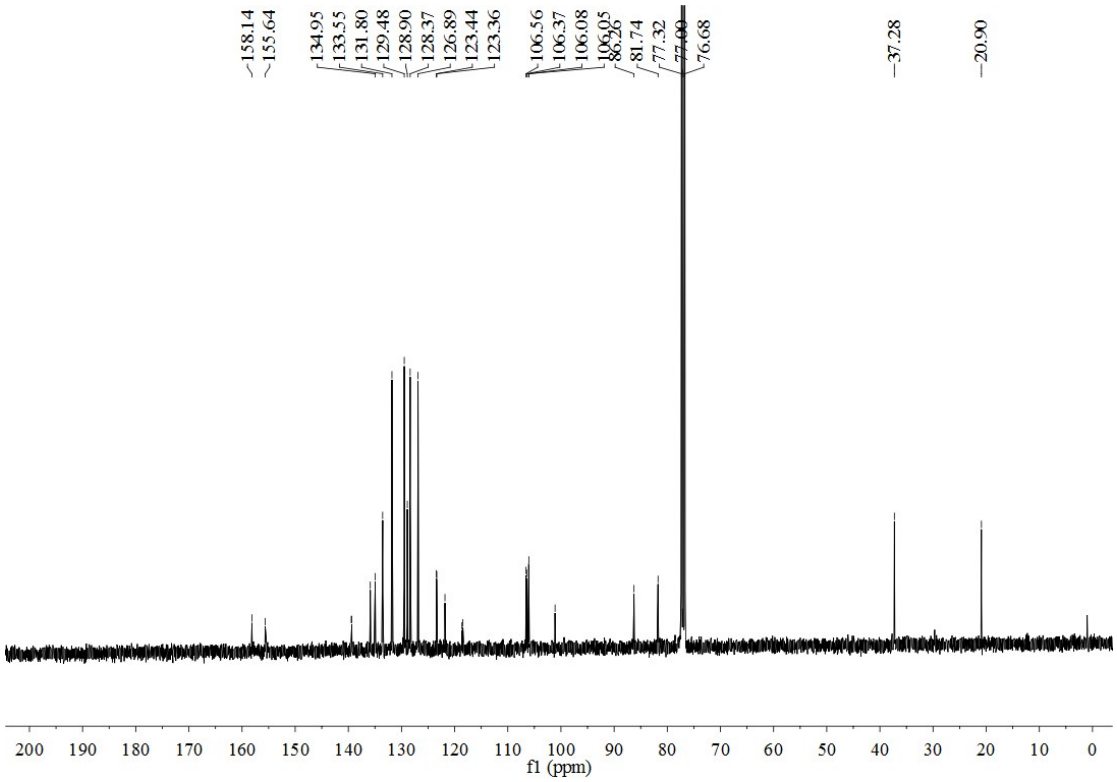
7-methyl-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3k)



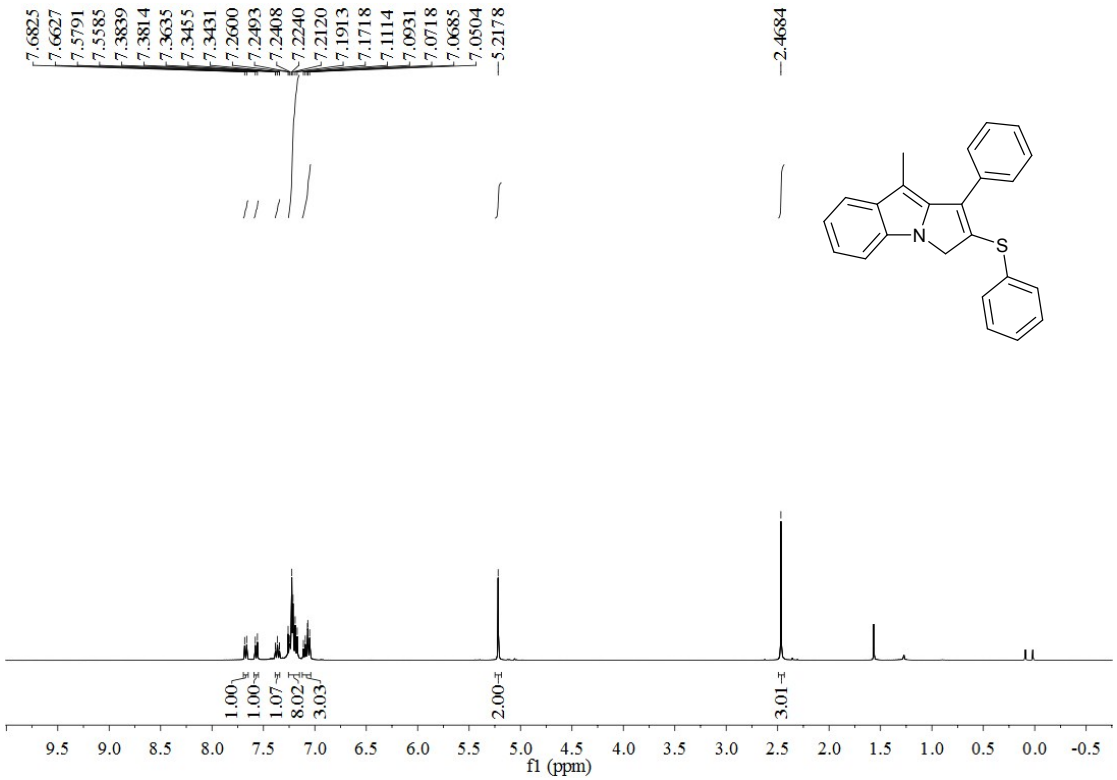


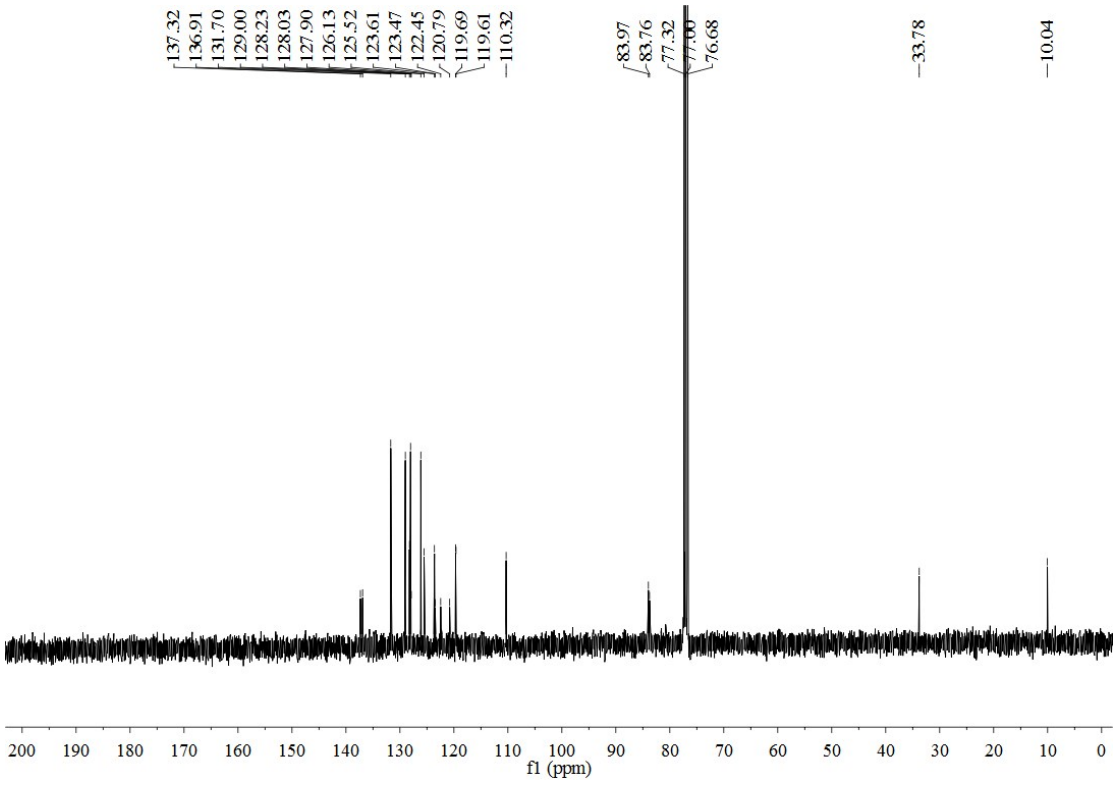
8-fluoro-1-phenyl-2-(*p*-tolylthio)-3*H*-pyrrolo[1,2-*a*]indole (3l)



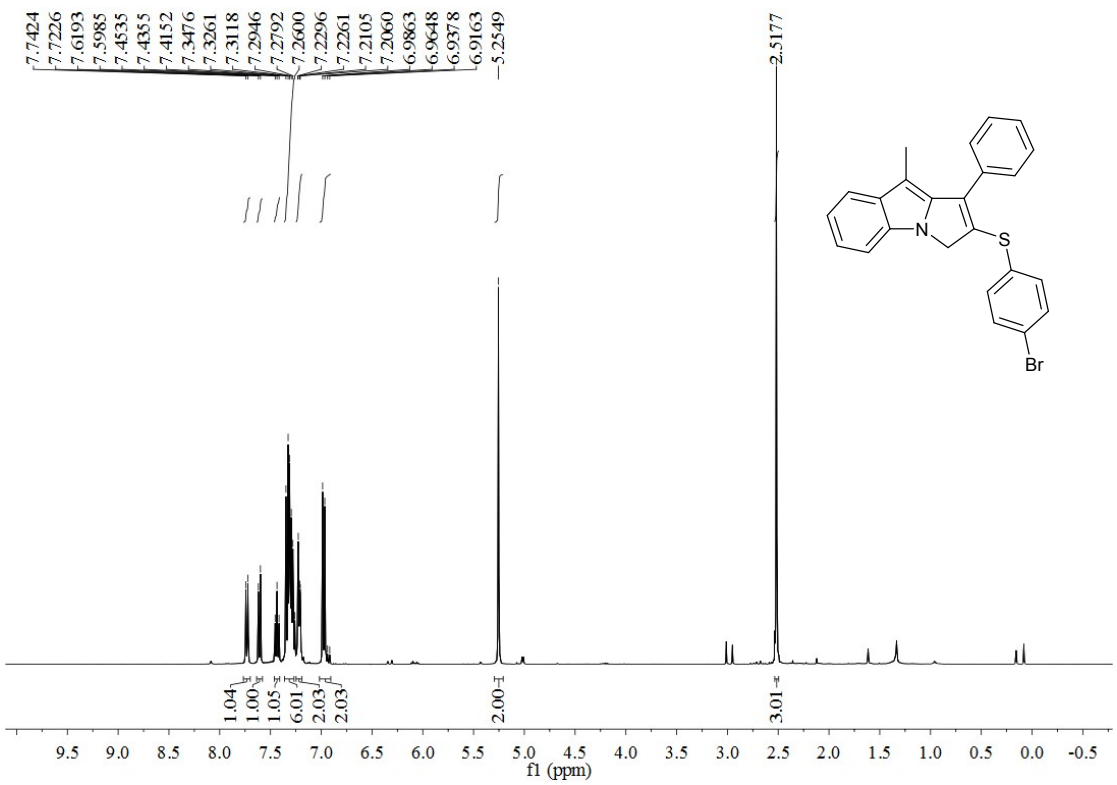


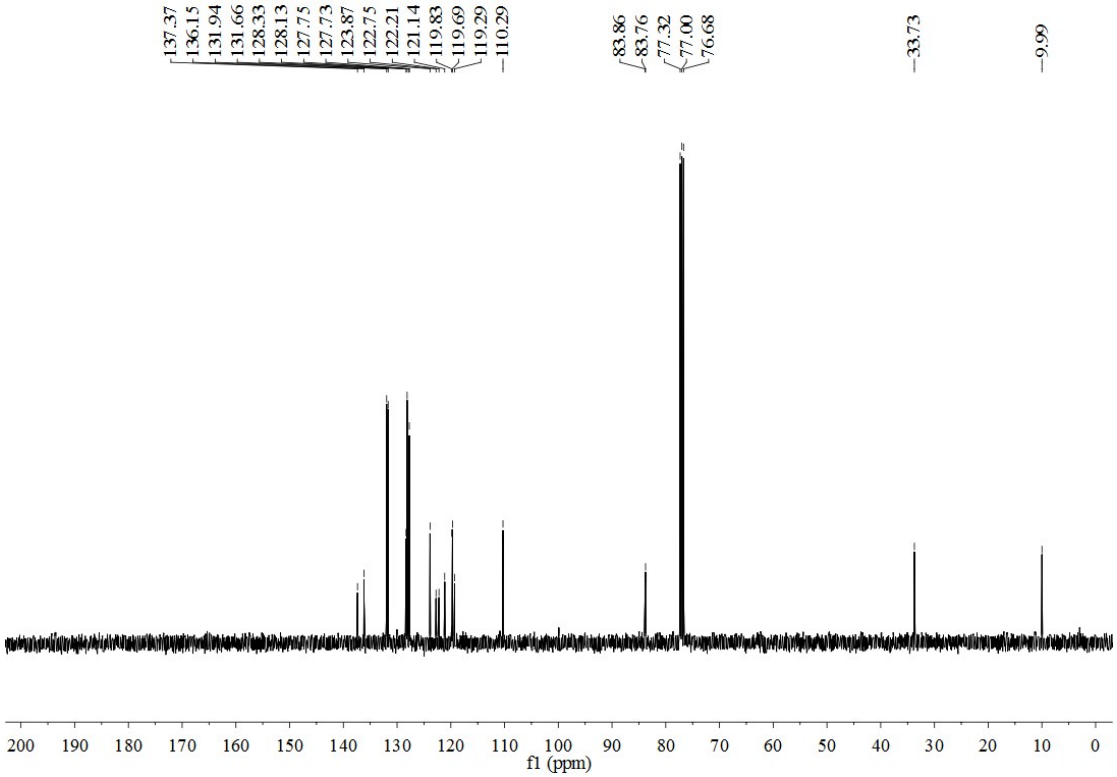
9-methyl-1-phenyl-2-(phenylthio)-3*H*-pyrrolo[1,2-*a*]indole (3m)



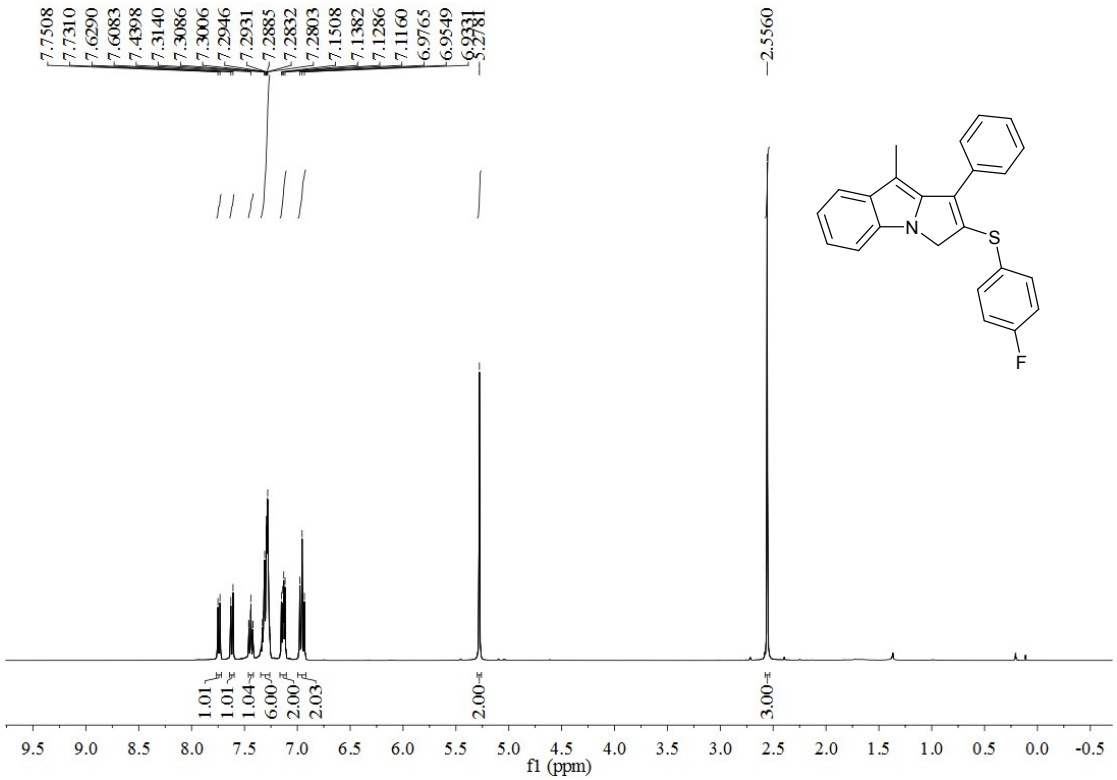


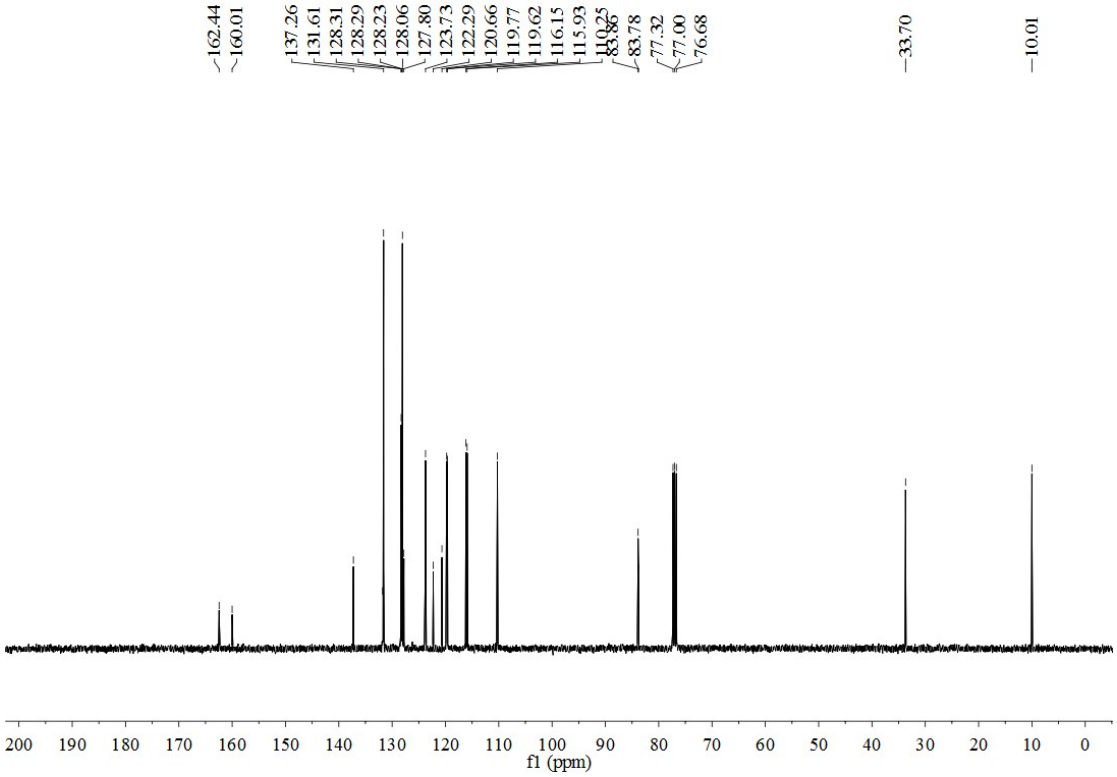
2-((4-bromophenyl)thio)-9-methyl-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3n)



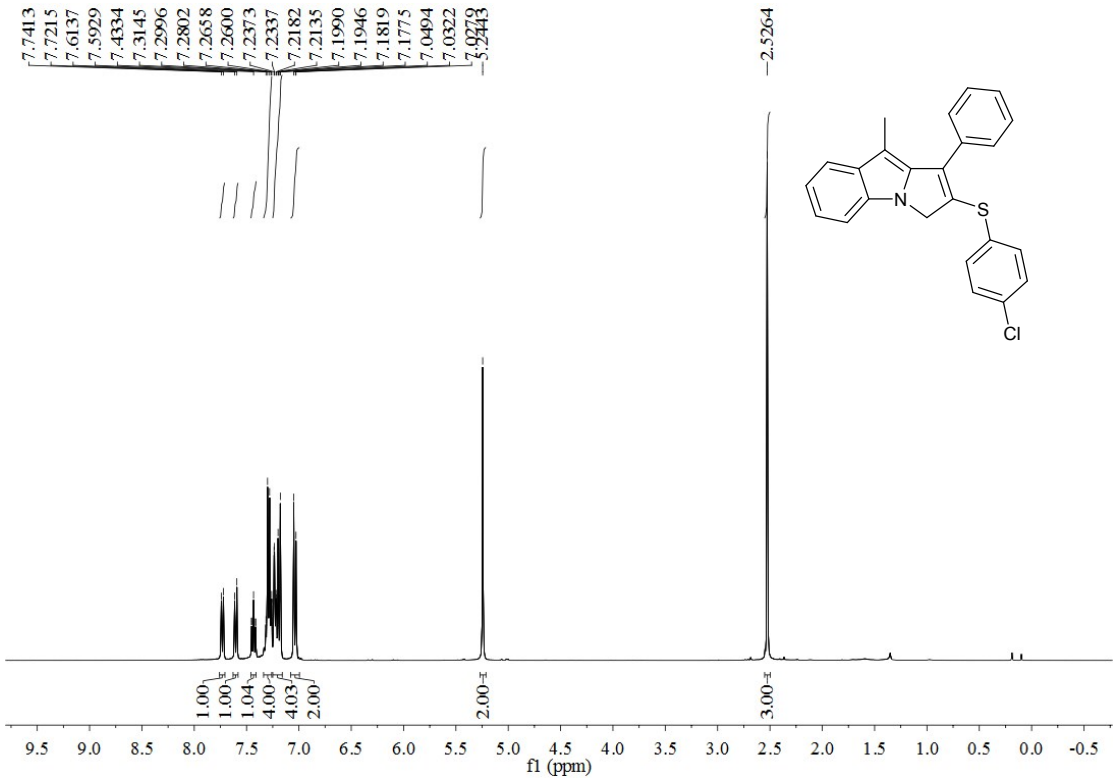


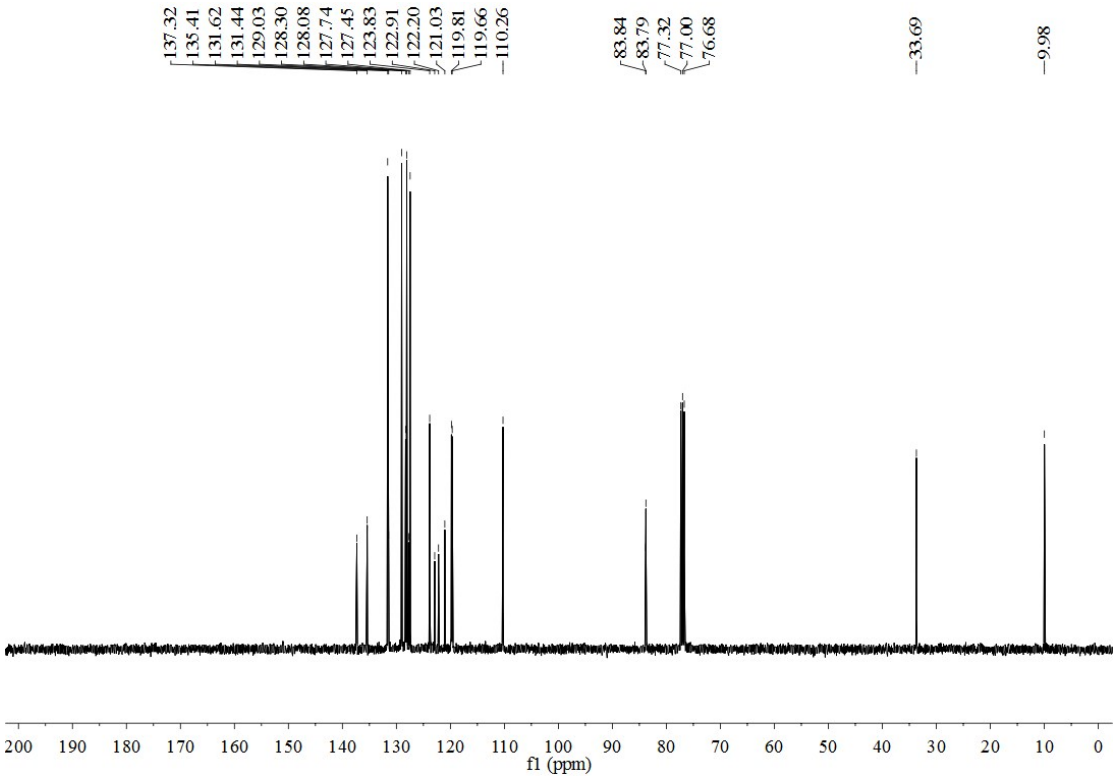
2-((4-fluorophenyl)thio)-9-methyl-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3o)



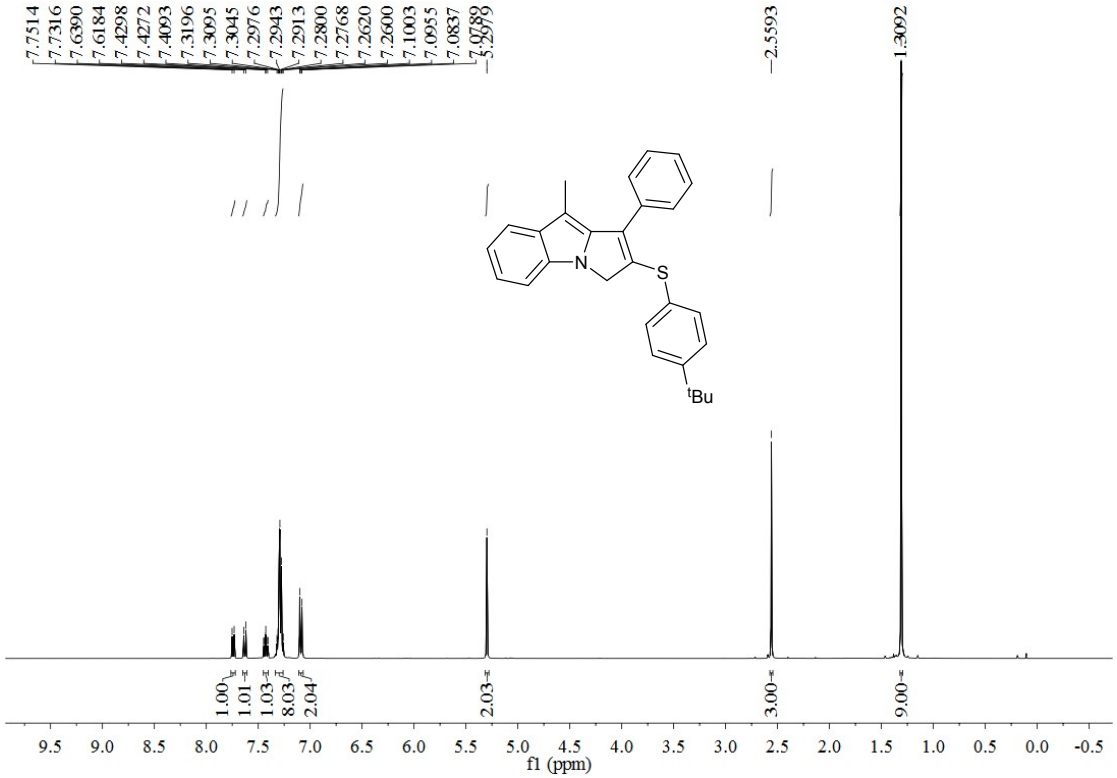


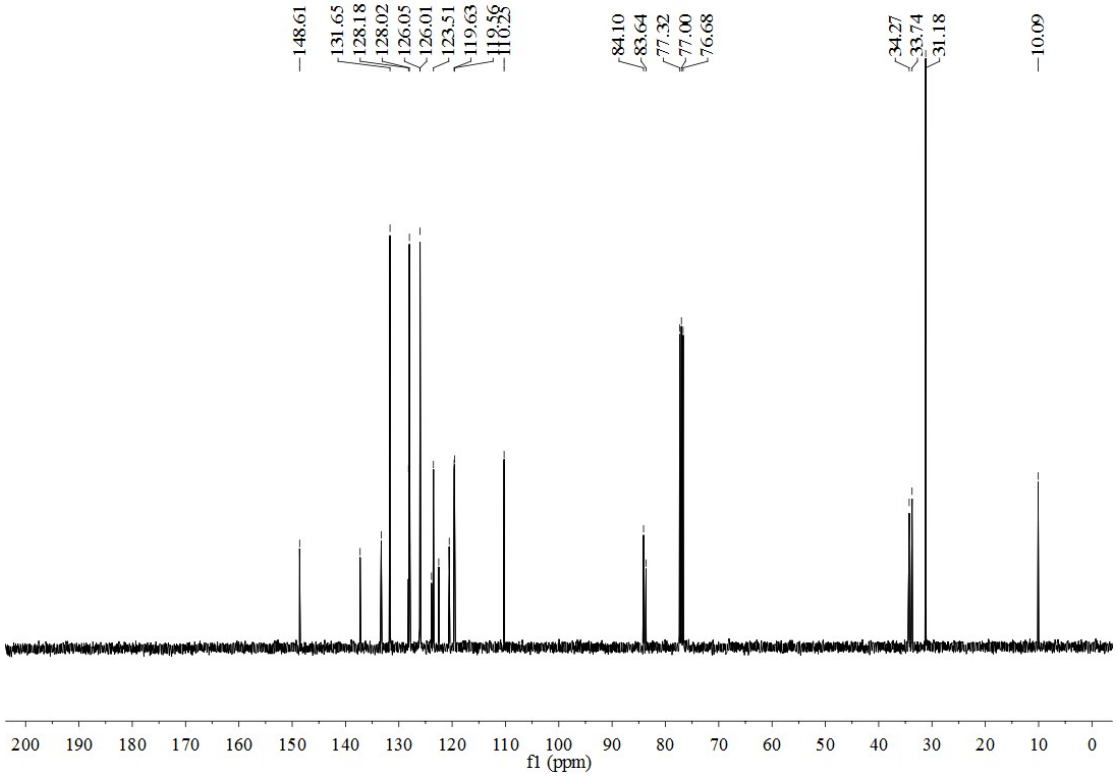
2-((4-chlorophenyl)thio)-9-methyl-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3p)



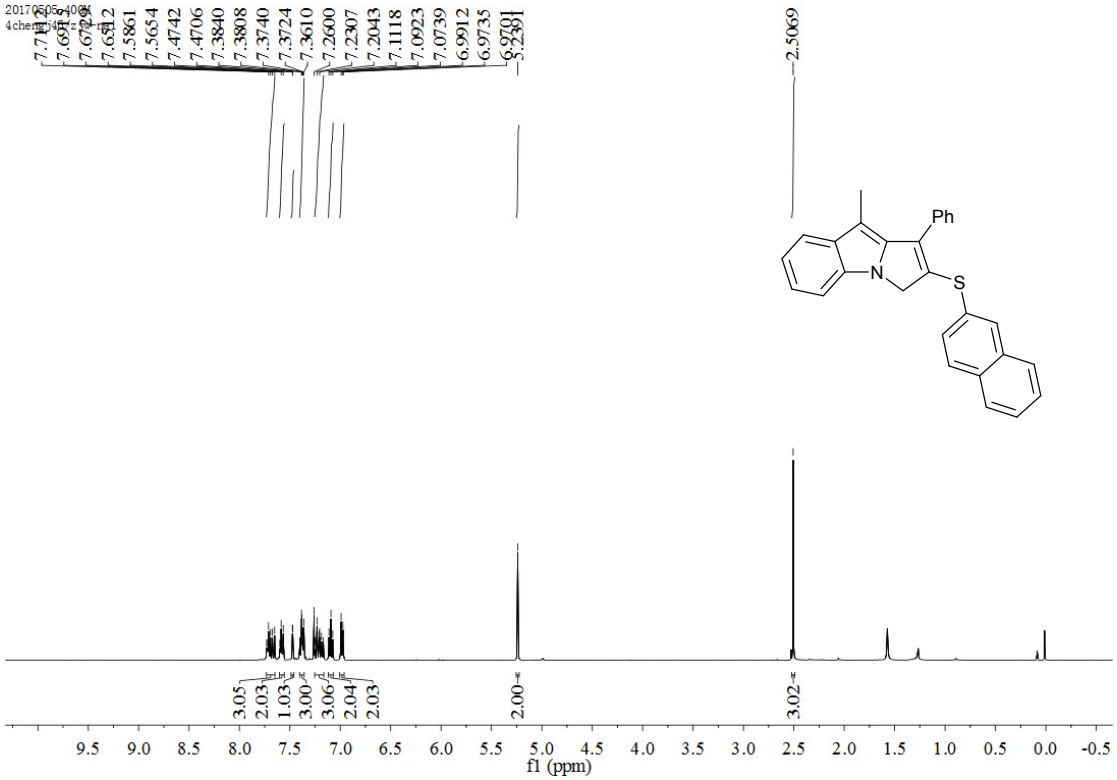


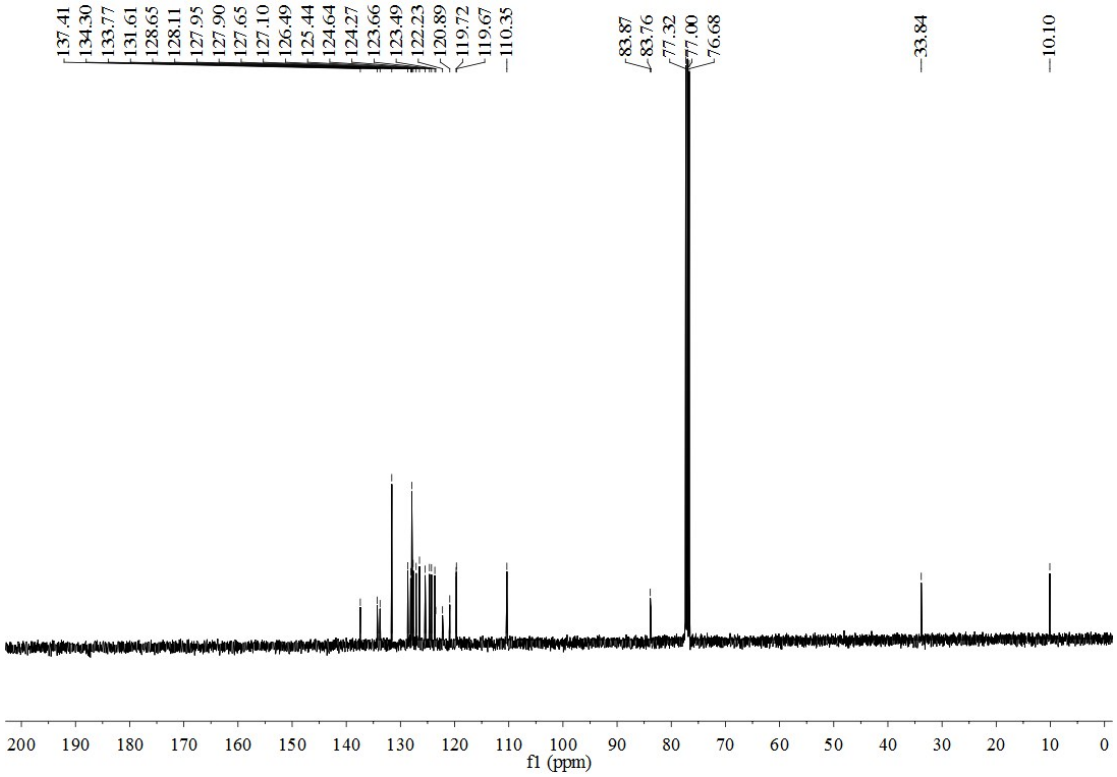
2-((4-(tert-butyl)phenyl)thio)-9-methyl-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3q)



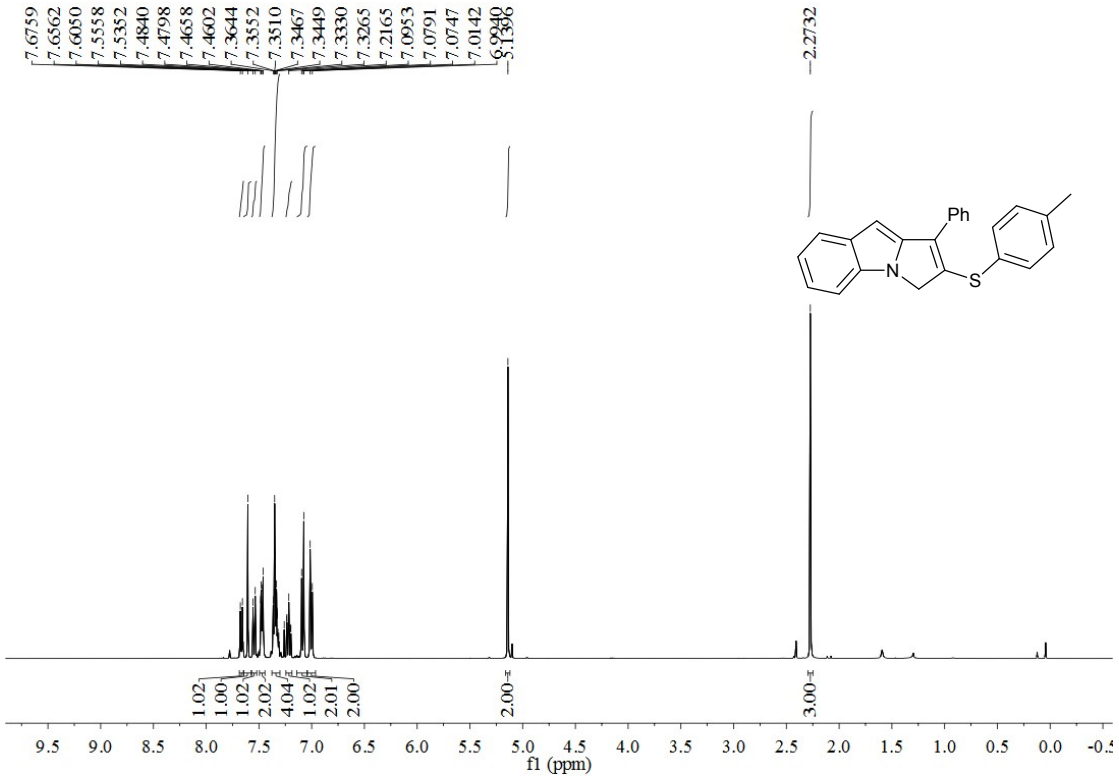


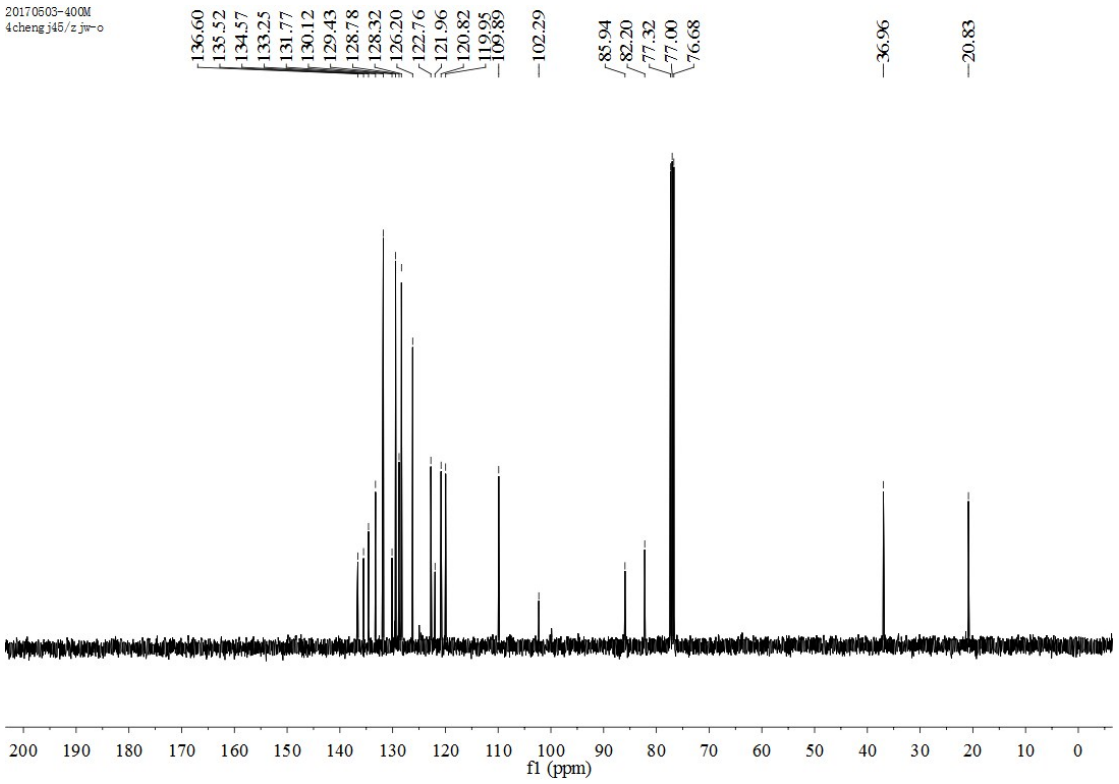
9-methyl-2-(naphthalen-2-ylthio)-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (3r)





1-phenyl-2-(p-tolylthio)-*3H*-pyrrolo[1,2-a]indole (3s)





1-phenyl-2-tosyl-*9H*-pyrrolo[1,2-a]indole (4s)