Supporting Information

One-pot multicomponent synthesis of thieno[2,3-*b*]indoles catalyzed by a magnetic nanoparticle-supported $[Urea]_4[ZnCl_2]$ deep eutectic solvent.

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Table of Contents

Section S1. Materials, equipment and analytical methods

Materials

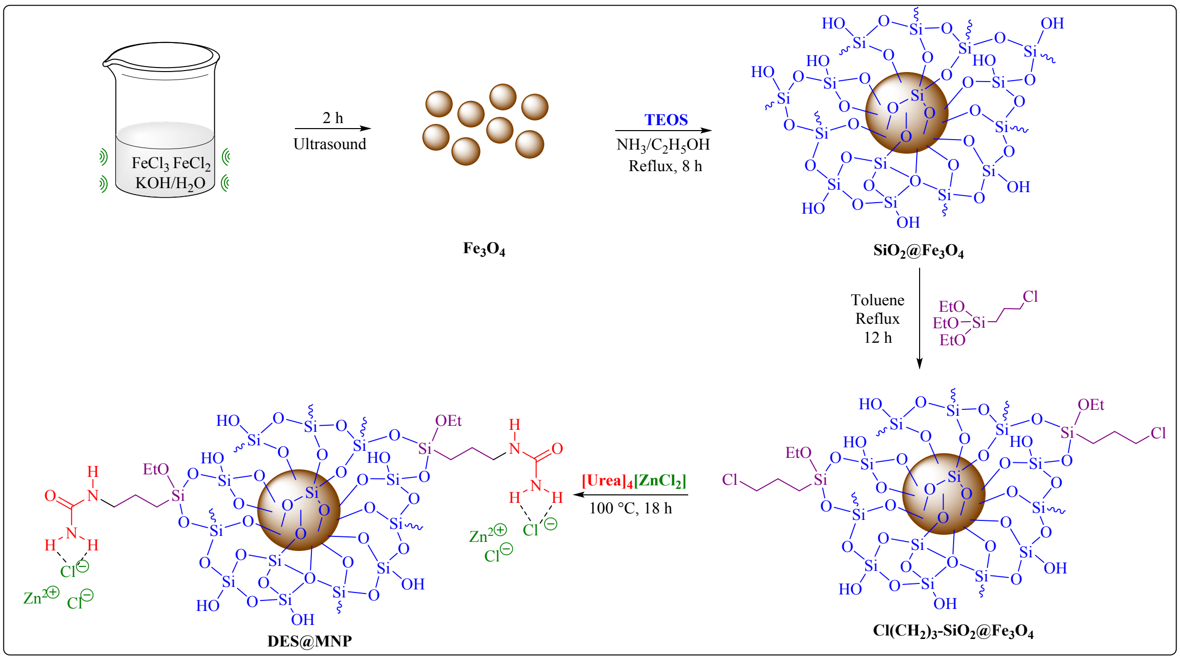
Sulfur (purity ≥ 99.5%), indole (purity ≥ 99%), 5-methylindole (purity ≥ 99%), 5-methoxyindole (purity ≥ 99%), 5-fluoroindole (purity ≥ 98%), 5-chloroindole (purity ≥ 98%), 5-bromoindole (purity ≥ 99%), 5-nitroindole (purity ≥ 99%), acetophenone (purity ≥ 98%), 4-methylacetophenone (purity ≥ 95%), 4-methoxyacetophenone (purity ≥ 98%), 4-fluoroacetophenone (purity ≥ 99%), 4-nitroacetophenone (purity ≥ 98%), 2-acetylthiophene (purity ≥ 98%), (3-chloropropyl)trimethoxysilane (purity ≥ 95%), choline chloride (purity ≥ 99%), urea (purity ≥ 98%), trifluoroacetic acid (purity ≥ 99%), aluminum chloride (anhydrous, purity ≥ 99%), zinc chloride (anhydrous, purity ≥ 97%), iron(III) chloride (anhydrous, purity ≥ 99%), tin(IV) chloride (anhydrous, purity ≥ 98%), copper(II) chloride (anhydrous, purity ≥ 98%), potassium hydroxide (purity > 85%), were purchased from Sigma-Aldrich. Tetraethyl orthosilicate (purity > 98%), acetic acid (purity > 98%), phosphoric acid (purity ≥ 85%), sulfuric acid (purity ≥ 97.5%), and silica gel 230–400 mesh for flash chromatography, TLC plates (silica gel 60 F254), 1,4-dioxane (anhydrous, purity ≥ 99.9%), ethanol (anhydrous, purity ≥ 99%), acetonitrile (anhydrous, purity ≥ 99.8%), toluene (anhydrous, purity ≥ 99%), dichloromethane (anhydrous, 99%), *n*-butanol (anhydrous, purity ≥ 99.8%), *tert*-butanol (anhydrous, purity ≥ 99.5%), tetrahydrofuran (anhydrous, purity ≥ 99.5%), ethyl acetate (anhydrous, purity ≥ 99%), *N*,*N*-dimethylformamide (anhydrous, purity > 99%), *p*-xylene (anhydrous, purity ≥ 99%) acetone and *n*-hexane (anhydrous, purity ≥ 99.5%) were obtained from Merck. Deuterated solvents, DMSO-d_6 and acetone-d_6, were purchased from Cambridge Isotope Laboratories (Andover, MA). All chemicals were used without further purification.

Equipment and analytical methods

The chemicals were measured on Ohaus 80251621 explorer precision balance. The reactions were conducted on an IKA C-MAG HS7 magnetic stirrer or Elma S30H Ultrasonic cleaning unit (ultrasonic frequency = 37 kHz). Analytical thin-layer chromatography (TLC) was performed on F-254 silica gel coated aluminum plates from Merck. Column chromatography was performed on silica gel 60, 0.04−0.06 mm (230–400 mesh). Melting points were recorded with a Buchi B-545 melting point Apparatus and are uncorrected.

Powder X-ray diffraction (PXRD) patterns were recorded using a D8 Advance diffractometer equipped with a LYNXEYE detector (Bragg-Brentano geometry, CuK_α radiation λ = 1.54056 Å). Thermal gravimetric analysis (TGA) was performed using a TA instruments Q-500 thermal gravimetric analyzer under airflow with temperature ramp of 5 °C.min^{-1}. Fourier transform infrared (FT-IR) spectra were measured on a Bruker E400 FT-IR spectrometer using potassium bromide pellets. Scanning electron microscope (SEM) images were taken on a Hitachi S-4800 scanning electron microscope operating at an accelerating voltage of 1 kV. Transmission electron microscope (TEM) images were taken on a Jem-Arm 300F grand atomic resolution electron microscope accelerating voltage of 300 kV. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed using an EMAX energy EX-400 EDX device. Vibrating sample magnetometer (VSM) analysis was recorded on Model 10 Mark II VSM. Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were acquired on a Bruker advance II 500 MHz NMR spectrometer. Chemical shifts were quoted in parts per million (ppm) and referenced to the appropriate solvent peak. High-resolution mass spectrometry (HRMS) was conducted in negative ionization mode on an Agilent 1200 series high-performance liquid chromatography coupled to a Bruker micrOTOF-QII EIS mass spectrometer detector. Gas chromatography-mass spectrometry (GC-MS) measurements were carried out on an Agilent GC System 7890 equipped with a mass selective detector (Agilent 5973N) and a capillary DB-5MS column (30 m × 250 µm × 0.25 µm). Inductively coupled plasma mass spectroscopy (ICP-MS) data were recorded on a PerkinElmer 350X. Raman spectra were recorded on a Horiba Xplora One using a 532 nm argon ion laser.

Section S2. Characterization of the catalyst



Scheme S1. The preparation of DES@MNP catalyst

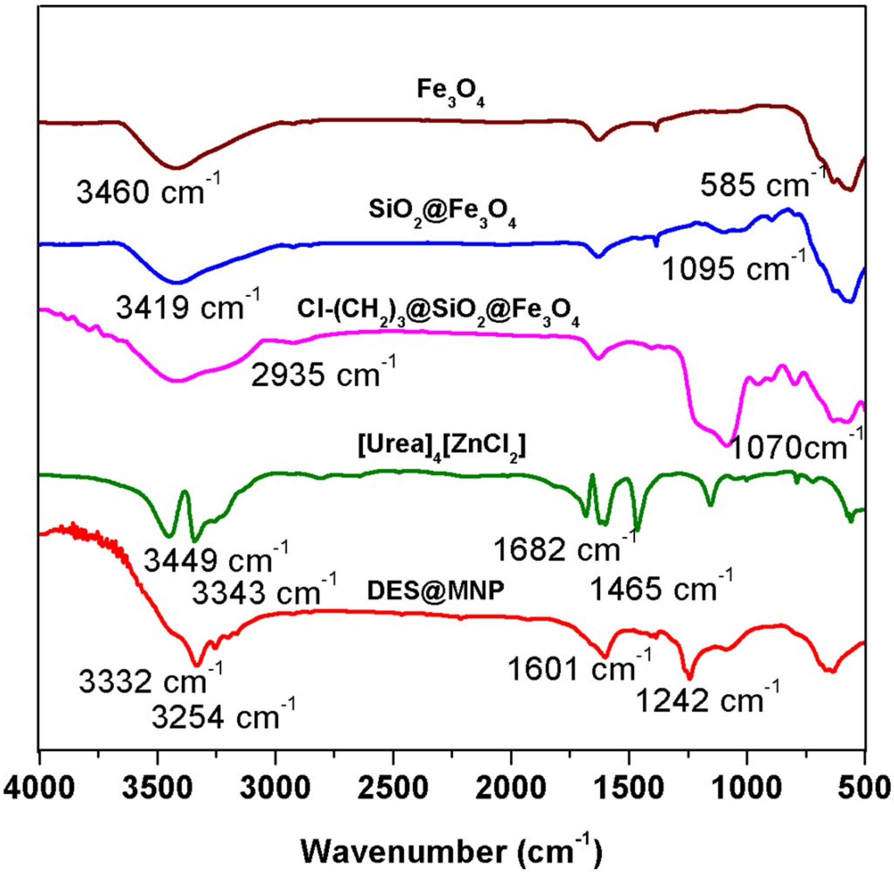


Figure S1. FT-IR spectrum of Fe_3O_4, $SiO_2@Fe_3O_4$, Cl-$(CH_2)_3@SiO_2@Fe_3O_4$, $[Urea]_4[ZnCl_2]$ and DES@MNP

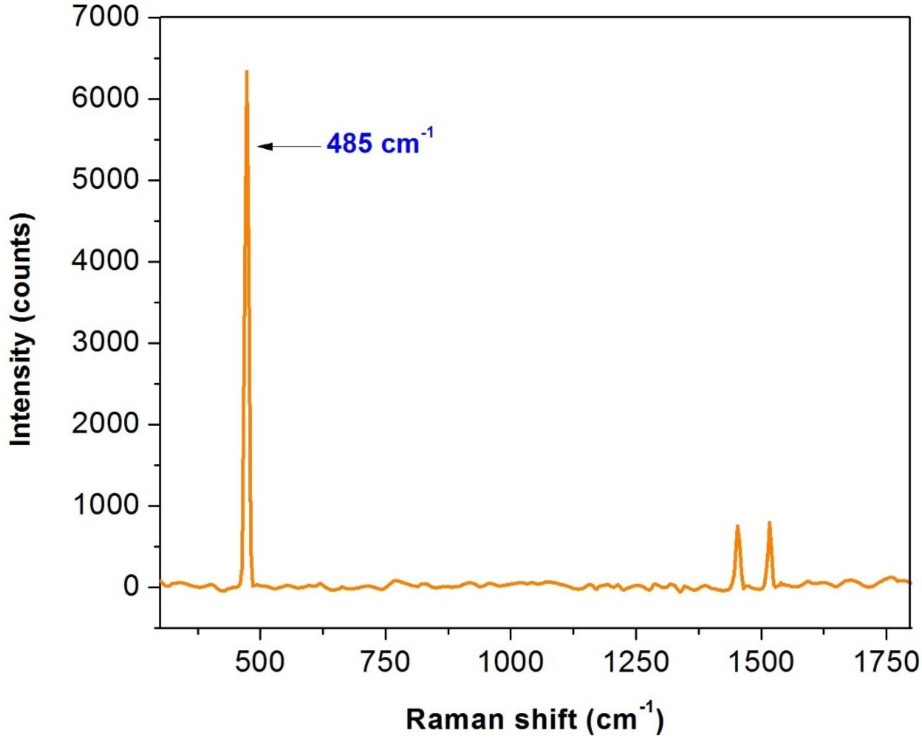


Figure S2. Raman spectra of DES@MNP

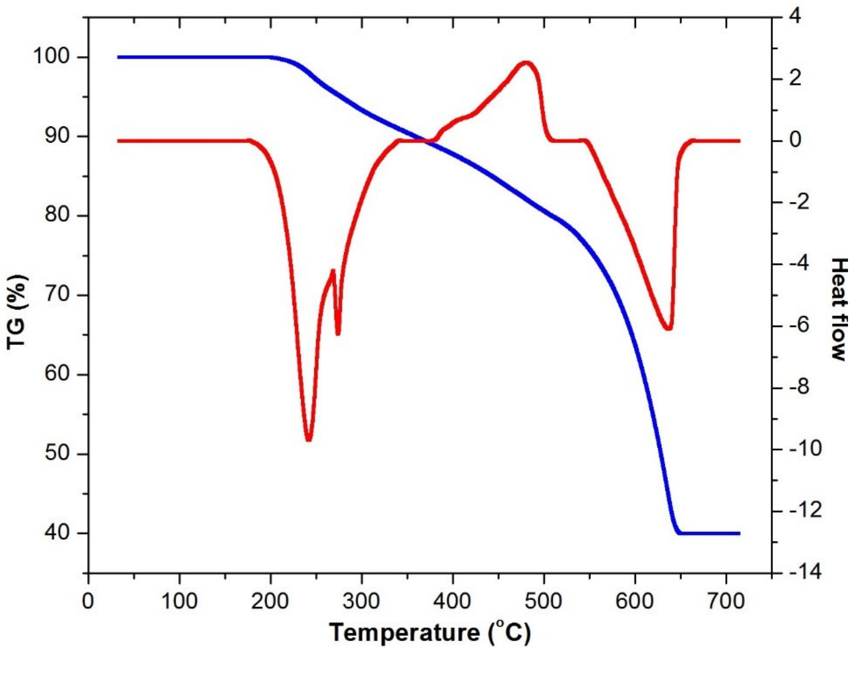


Figure S3. TG and DSC analysis of DES@MNP

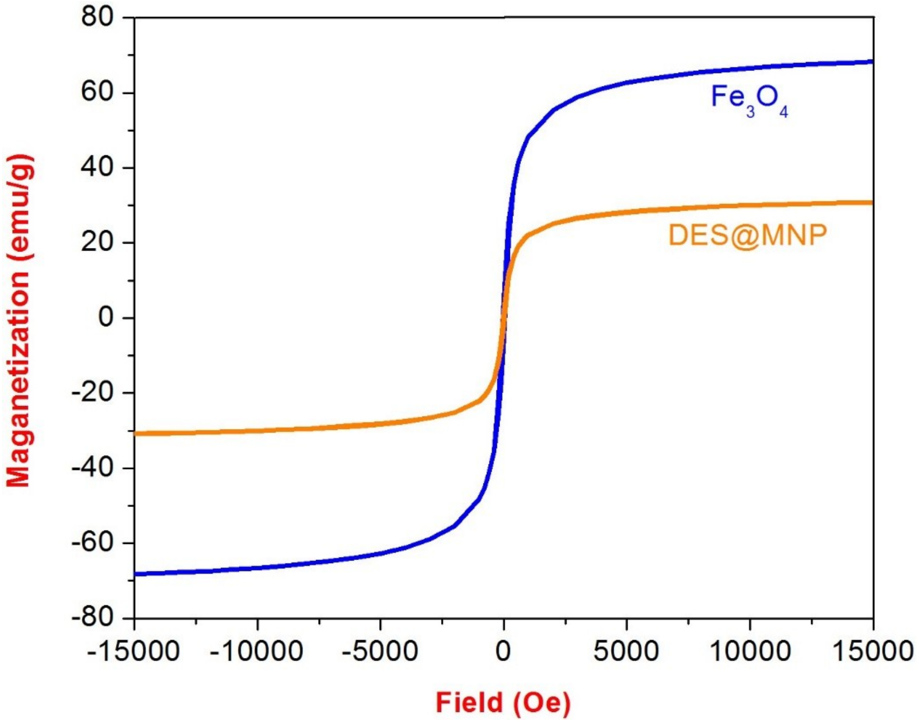


Figure S4. Magnetic curves of Fe_3O_4 and DES@MNP

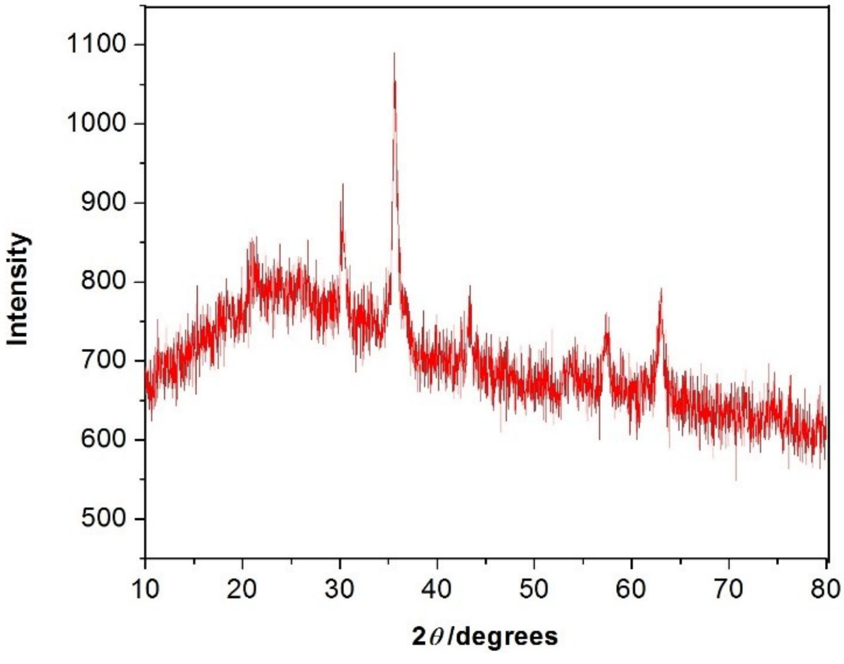
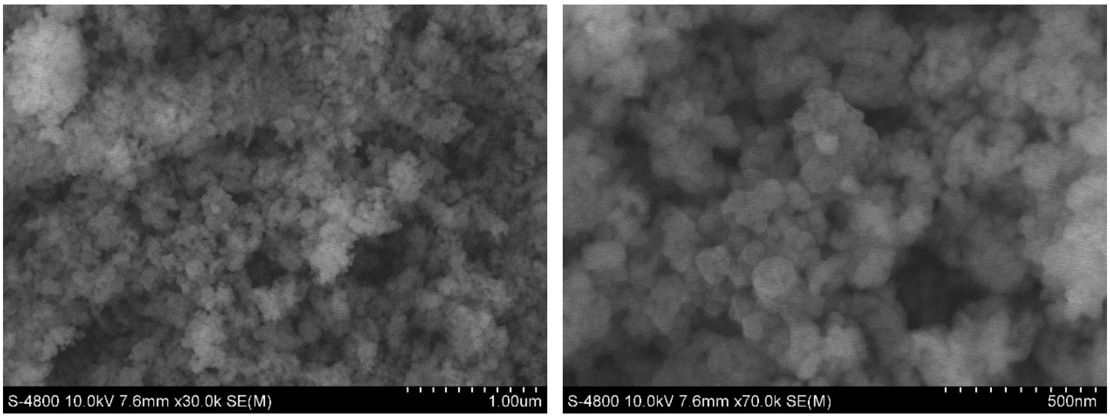
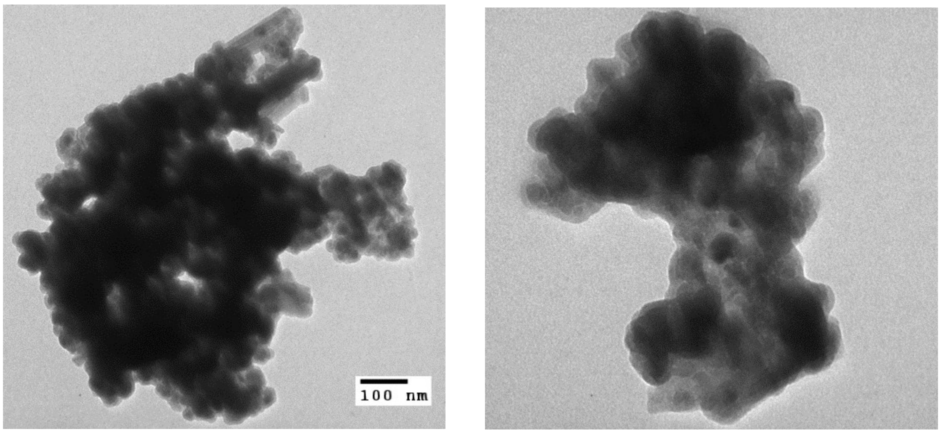


Figure S5. X-Ray diffraction pattern of DES@MNP



(a)



(b)

Figure S6. SEM (a) and TEM (b) images of DES@MNP

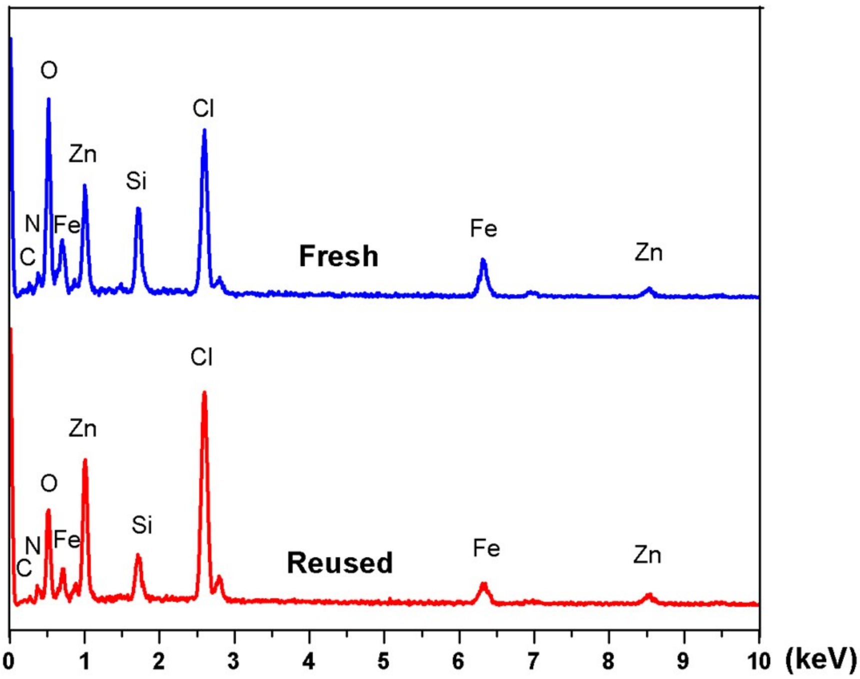


Figure S7. EDX spectrum of fresh catalyst and reused catalyst.

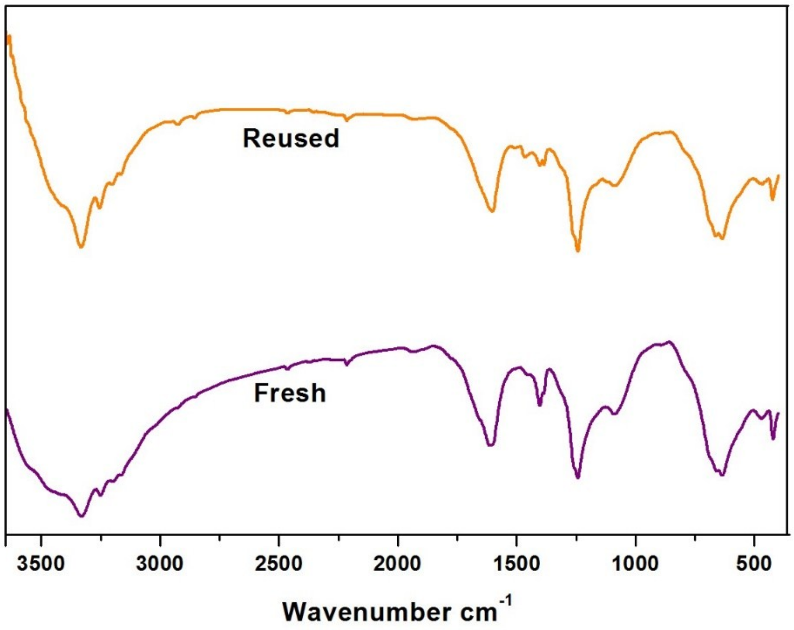


Figure S8. FT-IR spectra for the comparison of the fresh catalyst and the fifth-times reused catalyst.

Section S3. Optimization of the reaction conditions on the synthesis of 2-phenyl-8*H*-thieno[2,3-*b*]indole

Table S1. Effects of the additive on the synthesis of 2-phenyl-8*H*-thieno[2,3-*b*]indole

Entry[a]	Additives (1 equivment)	Yield[b] (%)
1	*N,N*-Dimethylformamide	87
2	Acetamide	43
3	Pyrrolidine	38
4	Piperidine	54
5	Triethylamine	44
6	Aniline	19
7	*N,N*-Dimethylaniline	26
8	1,4-Diazabicyclo[2.2.2]octane	75
9	4-Ethylmorpholine	81

[a]Reaction conditions: acetophenone (2.0 mmol, 240 mg), indole (1.0 mmol, 117 mg), sulfur (5.0 mmol, 160 mg), additive (1.0 mmol) and DES@MNP catalyst (10 mol%, 30 mg) were heated at 140 °C for 12 h.

[b]Yield of 2-phenyl-8*H*-thieno[2,3-*b*]indole was isolated yield by column chromatography (dichloromethane/petroleum ether 2:3).

Table S2. Effects of solvents on the synthesis of 2-phenyl-8*H*-thieno[2,3-*b*]indole

Entry[a]	Type of Solvent	Solvent	Yield[b] (%)
1	Polar protic	Ethanol	Trace
2		*tert*-Butanol	17
3		*n*-Butanol	21
4	Polar aprotic	Ethyl acetate	25
5		Acetonitrile	70
6		Tetrahydrofurane	32
7		*N,N*-Dimethylformamide	87
8	Non polar	1,4-Dioxane	78
9		Toluene	35
10		*p*-Xylene	23
11		*n*-Hexane	Trace

[a]Reaction conditions: acetophenone (2.0 mmol, 240 mg), indole (1.0 mmol, 117 mg), sulfur (5.0 mmol, 160 mg), DMF (0.3 mL) and DES@MNP catalyst (10 mol%, 30 mg) were heated in 1.5 mL solvent at 140 ˚C for 12 h.
[b]Yield of 2-phenyl-8*H*-thieno[2,3-*b*]indole was isolated yield by column chromatography (dichloromethane/ petroleum ether 2:3).

Table S3. Effects of temperature on the synthesis of 2-phenyl-8*H*-thieno[2,3-*b*]indole

Entry[a]	Temperature (°C)	Yield[b] (%)
1	80	Trace
2	100	17
3	120	45
4	130	68
5	140	87
6	150	87

[a]Reaction conditions: acetophenone (2.0 mmol, 240 mg), indole (1.0 mmol, 117 mg), sulfur (5.0 mmol, 160 mg), and DES@MNP catalyst (10 mol%, 30 mg) were heated in 1.5 mL DMF for 12 h.
[b]Yield of 2-phenyl-8*H*-thieno[2,3-*b*]indole was isolated yield by column chromatography (dichloromethane/ petroleum ether 2:3).

Table S4. Effects of time on the synthesis of 2-phenyl-8*H*-thieno[2,3-*b*]indole

Entry[a]	**Time (h)**	**Yield[b] (%)**
1	2	Trace
2	4	14
3	6	37
4	8	59
5	10	78
6	12	87
7	14	88

[a]Reaction conditions: acetophenone (2.0 mmol, 240 mg), indole (1.0 mmol, 117 mg), sulfur (5.0 mmol, 160 mg), and DES@MNP catalyst (10 mol%, 30 mg) were heated in 1.5 mL DMF at 140 ˚C.
[b]Yield of 2-phenyl-8*H*-thieno[2,3-*b*]indole was isolated by column chromatography (dichloromethane/ petroleum ether 2:3).

Table S5. Effects of reactant ratio on the synthesis of 2-phenyl-8*H*-thieno[2,3-*b*]indole

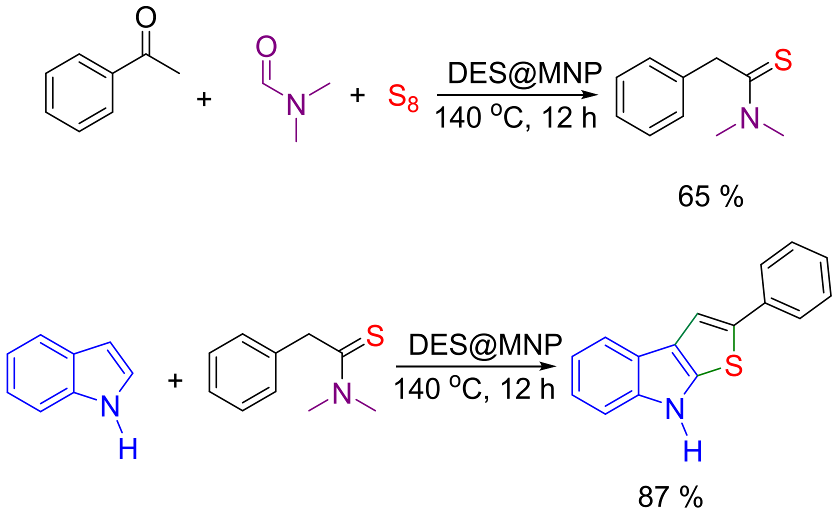
Entry[a]	**Molar ratio Indole:acetophenone:sulfur**	**Yield[b] (%)**
1	1.0:1.0:1.0	Trace
2	1.0:1.5:1.0	25
3	1.0:2.0:1.0	31
4	1.0:2.0:1.5	34
5	1.0:2.0:2.0	37
6	1.0:2.0:3.0	57
7	1.0:2.0:4.0	76

8	1.0:2.0:5.0	87

[a]Reaction conditions: acetophenone, indole, sulfur, and DES@MNP catalyst (10 mol%, 30 mg) were heated in 1.5 mL DMF at 140 °C for 12 h.

[b]Yield of 2-phenyl-8*H*-thieno[2,3-*b*]indole was isolated yield by column chromatography (dichloromethane/ petroleum ether 2:3).

Section S4. The experiment for proposed mechanism



Scheme S2. Control experiments for mechanism investigation.

Section S5. Spectral data

2-Phenyl-8*H*-thieno[2,3-*b*]indole (3a)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.40; yellowish solid, mp. 243−245 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3395, 3050, 1522, 1469, 1437, 1252, 830, 740, 687 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.69 (s, 1H), 7.87 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.66 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.43−7.39 (m, 2H), 7.26−7.23 (m, 1H), 7.20 (ddd, *J* = 8.5, 7.5, 1.0 Hz, 1H), 7.12 (dd, *J* = 7.5, 1.0 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 142.0, 141.1, 135.7, 135.2, 134.2, 129.6, 127.1, 125.0, 122.5, 122.1, 119.71, 119.3, 114.8, 112.2.

GC-MS (EI, 70 eV) *m/z* 249 $[M]^+$.

2-(*p*-Tolyl)-8*H*-thieno[2,3-*b*]indole (3b)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.35; white solid, mp. 223 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3431, 3028, 2955, 1647, 1026, 828, 768 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.66 (s, 1H), 7.80 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.19 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.13−7.08 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 141.5, 140.3, 135.9, 134.9, 132.5, 129.7, 124.5, 124.4, 121.9, 121.6, 119.2, 118.8, 113.6, 111.7, 20.7.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{17}H_{13}NS$ 263.0769, found 263.0724.

2-(4-Methoxyphenyl)-8*H*-thieno[2,3-*b*]indole (3c)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.45; white solid, mp. 220 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3391, 3051, 2957, 2918, 1529, 1480, 1431, 1290, 1255, 821, 742, 508 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 10.69 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.64 (s, 1H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.20 (td, *J* = 8.0, 1.0 Hz, 1H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6): δ = 159.8, 142.8, 141.2, 136.7, 129.4, 127.1, 126.2, 123.2, 122.8, 120.3, 119.7, 115.3, 113.5, 112.5, 55.7.

GC-MS (EI, 70 eV) *m/z* 279 $[M]^+$.

2-(4-Fluorophenyl)-8*H*-thieno[2,3-*b*]indole (3d)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.32; yellowish solid, mp. 251−252 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3383, 3051, 1527, 1476, 1427, 1236, 828, 811, 1126, 743, 674, 496 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.68 (s, 1H), 7.83 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71−7.68 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.28−7.23 (m, 2H), 7.20 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.11 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 161.5 (d, *J* = 242.2 Hz), 141.9 (s), 141.1 (s), 134.0 (s), 132.3 (d, *J* = 0.7 Hz), 126.9 (d, *J* = 7.9 Hz), 124.9 (s), 122.5 (s), 122.0 (s), 119.7 (s), 119.3 (s), 116.4 (d, *J* = 2.74 Hz), 114.9 (s), 112.2 (s).

HRMS (ESI) *m/z*: $[M−H]^+$ calcd for $C_{16}H_9NFS$ 266.0440, found 266.0445.

2-(4-Nitrophenyl)-8*H*-thieno[2,3-*b*]indole (3e)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.35; orange solid, mp. 257 °C.

FT-IR (KBr, 4000–400 cm^{-1}): 3433, 2256, 2129, 1646, 1026, 1000, 827, 765.

^{1}H NMR (500 MHz, DMSO-d_6) *δ* 11.88 (s, 1H), 8.24 (d, *J* = 9.0 Hz, 2H), 8.23 (s, 1H), 7.90 (d, *J* = 9.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.27–7.22 (m, 1H), 7.18–7.14 (m, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 142.2, 142.0, 141.7, 141.5, 138.4, 126.3, 125.1, 124.7, 124.7, 122.9, 119.9, 119.3, 118.5, 112.1.

GC-MS (EI, 70 eV) *m/z*: 294 ($[M]^+$).

2-(Thiophen-2-yl)-8*H*-thieno[2,3-*b*]indole (3f)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.30; organe solid, mp. 178 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3408, 1635, 1475, 1429, 1410, 1384, 812, 742, 684 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 11.68 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.23 (dd, *J* = 3.5, 1.0 Hz, 1H), 7.20 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.10 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.5 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 141.5, 140.1, 138.2, 128.1, 127.9, 124.0, 122.4, 122.4, 121.4, 119.3, 118.9, 117.9, 114.7, 111.8.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{14}H_9NS_2$ 255.0176, found 255.0171.

5-Methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (3g)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.35; white solid, mp. 220−221 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3378, 3027, 2920, 2852, 1524, 1478, 1443, 1254, 831, 753, 688, 588 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 11.55 (s, 1H), 7.82 (s, 1H), 7.66−7.64 (m, 2H), 7.58 (s, 1H), 7.42−7.39 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.26−7.22 (m, 1H), 7.02 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 140.7, 139.8, 135.3, 134.3, 129.1, 127.8, 126.5, 124.5, 124.2, 123.3, 121.7, 118.7, 114.2, 111.4, 21.1.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{17}H_{13}NS$ 263.0769, found 263.0722.

5-Methyl-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole (3h)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.40; white solid, mp. 245 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3370, 3017, 2916, 2853, 1530, 1480, 1425, 1256, 808, 752, 588, 487 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.53 (s, 1H), 7.75 (s, 1H), 7.56 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 140.3, 139.8, 135.8, 134.6, 132.5, 129.6, 127.7, 124.4, 124.1, 123.2, 121.7, 118.6, 113.5, 111.3, 21.2, 20.7.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{18}H_{15}NS$ 277.0925, found 277.0918.

2-(4-Methoxyphenyl)-5-methyl-8*H*-thieno[2,3-*b*]indole (3i)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.40; white solid, mp. 241 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3414, 3025, 2922, 1637, 1529, 1384, 1294, 1255, 821, 509 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.49 (s, 1H), 7.65 (s, 1H), 7.57 (m, 3H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.00 (m, 3H), 3.78 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 158.7, 140.5, 140.2, 135.0, 128.5, 128.2, 126.4, 124.6, 123.6, 122.2, 119.1, 115.0, 113.3, 111.8, 55.7, 21.7.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{18}H_{15}NOS$ 293.0874, found 293.0867.

2-(4-Fluorophenyl)-5-methyl-8*H*-thieno[2,3-*b*]indole (3j)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.50; white solid, mp. 231 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3372, 3029, 2922, 2853, 1639, 1529, 1478, 1233, 824, 810, 532 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.56 (s, 1H), 7.78 (s, 1H), 7.69−7.66 (m, 2H), 7.57 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 8.5 Hz, 2H), 7.02 (dd, *J* = 8.5, 1.0 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 161.0 (d, J = 242.4 Hz), 140.7 (s), 139.8 (s), 133.2 (s), 131.9 (d, J = 3.1 Hz), 127.8 (s), 126.4 (d, J = 7.9 Hz), 124.2 (s), 123.4 (s), 121.7 (s), 118.7 (s), 115.9 (d, J = 21.6 Hz), 114.4 (s), 111.4 (s), 21.1 (s).

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{17}H_{12}FNS$ 281.0674, found 281.0662.

5-Methoxy-2-phenyl-8*H*-thieno[2,3-*b*]indole (3k)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.37; white solid, mp. 210 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3410, 3057, 2990, 2831, 1525, 1480, 1428, 1266, 1215, 828, 753, 690, 475 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.52 (s, 1H), 7.84 (s, 1H), 7.64 (d, J = 7.0 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 9.0 Hz, 1H), 7.35 (d, J = 2.0 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 6.84 (dd, J = 9.0, 2.5 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 153.5, 141.2, 136.4, 135.3, 134.2, 129.1, 126.5, 124.4, 122.0, 114.3, 112.3, 111.2, 101.8, 55.4.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{17}H_{13}NOS$ 279.0718, found 279.0709.

5-Methoxy-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole (3l)

Analy-tical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.45; white solid, mp. 201 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3398, 3048, 2995, 2945, 1531, 1478, 1423, 1212, 833, 808, 751, 673 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.48 (s, 1H), 7.76 (s, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.5 Hz, 1H), 7.33 (d, J = 2.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 6.82 (dd, J = 8.5, 2.0 Hz, 1H), 3.81 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 153.4, 140.8, 136.4, 135.8, 134.4, 132.5, 129.6, 124.4, 124.4, 122.0, 113.6, 112.3, 111.0, 101.7, 55.4, 20.7.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{18}H_{15}NOS$ 293.0874, found 293.0864.

5-Methoxy-2-(4-methoxyphenyl)-8*H*-thieno[2,3-*b*]indole (3m)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.50; white solid, mp. 231 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3398, 3051, 2295, 2248, 1530, 1478, 1455, 1265, 1213, 1170, 1113, 1085, 833, 808, 751, 673 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 10.63 (s, 1H), 7.60 (s, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.84 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6): δ = 159.8, 155.2, 141.9, 137.9, 136.2, 129.5, 127.1, 126.1, 123.6, 115.4, 113.5, 113.1, 113.0, 112.2, 102.7, 56.1, 55.7.

GC-MS (EI, 70 eV) *m/z* 309 $[M]^+$.

5-Methoxy-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole (3n)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.47; white solid, mp. 200−201 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3433, 3021, 2923, 1626, 1530, 1479, 1423, 1218, 1168, 1025, 825 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.51 (s, 1H), 7.79 (s, 1H), 7.67 (dd, *J* = 9.0, 5.0 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.24 (m, 2H), 6.84 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 161.0 (d, *J* = 242.4 Hz), 153.5 (s), 141.1 (s), 136.4 (s), 132.98 (s), 131.9 (d, *J* = 3.1 Hz), 126.35 (d, *J* = 7.9 Hz), 124.4 (s), 121.9 (s), 116.0 (d, *J* = 21.6 Hz), 114.4 (s), 112.3 (s), 111.2 (s), 101.7 (s), 55.4 (s).

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{17}H_{12}FNOS$ 297.0624, found 297.0618.

5-Fluoro-2-phenyl-8*H*-thieno[2,3-*b*]indole (3o)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.54; yellowish solid, mp. 255 °C**.**

FT-IR (KBr, 4000−400 cm^{-1}): 3408, 3065, 1524, 1480, 1441, 1169, 1256, 1170, 1077, 830, 807, 739, 687 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.77 (s, 1H), 7.84 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.58 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.47 (dd, *J* = 9.0, 4.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.04 (td, *J* = 9.0, 2.5 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.8 (d, *J* = 231.0 Hz), 142.3 (s), 138.0 (s), 135.0 (d, *J* = 18.8 Hz), 129.1 (s), 126.7 (s), 124.6 (s), 124.3 (d, *J* = 4.0 Hz), 121.69 (d, *J* = 10.5 Hz), 114.19 (s), 112.5 (d, *J* = 9.6 Hz), 109.6 (d, *J* = 25.5 Hz), 104.2 (d, *J* = 24.0 Hz).

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{16}H_{10}FNS$ 267.0518, found 267.0514.

5-Fluoro-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole (3p)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.47; yellowish solid, mp. 264.5−265.5 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3391, 3047, 2919, 2852, 1530, 1482, 1427, 1257, 1170, 810, 756, 593 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.74 (s, 1H), 7.77 (s, 1H), 7.57 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.03 (td, *J* = 9.0, 2.5 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 156.8 (d, *J* = 231.0 Hz), 142.0 (s), 138.0 (s), 136.1 (s), 135.1 (s), 132.3 (s), 129.6 (s), 124.5 (s), 124.3 (d, *J* = 4.1 Hz), 121.7 (d, *J* = 10.4 Hz), 113.5 (s), 112.5 (d, *J* = 9.6 Hz), 109.5 (d, *J* = 25.5 Hz), 104.1 (d, *J* = 23.9 Hz), 20.65 (s).

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{17}H_{12}FNS$ 281.0674, found 281.0666.

5-Chloro-2-phenyl-8*H*-thieno[2,3-*b*]indole (3q)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.50; yellowish solid, mp. 216 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3387, 3075, 2922, 1519, 1477, 1433, 1244, 827, 792, 758, 689, 580 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.88 (s, 1H), 7.87 (s, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.20 (dd, *J* = 8.5, 2.0 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 142.0, 139.8, 135.3, 1345.0, 129.1, 126.8, 124.6, 123.9, 123.7, 122.5, 121.7, 118.3, 114.2, 113.1.

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{16}H_{10}ClNS$ 283.0222, found 283.0176.

5-Chloro-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole (3r)

Analyti-cal TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.45; yellowish solid, mp. 230 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3381, 3012, 2918, 2852, 1527, 1477, 1424, 1280, 1050, 811, 793, 698, 580, 488 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.85 (s, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.79 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 141.6, 139.8, 136.2, 135.6, 132.2, 129.7, 124.6, 123.8, 123.6, 122.5, 121.6, 118.2, 113.5, 113.1, 20.7.

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{17}H_{12}ClNS$ 297.0379, found 297.0364.

5-Chloro-2-(4-methoxyphenyl)-8*H*-thieno[2,3-*b*]indole (3s)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.45; yellowish solid, mp. 213−214 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3392, 3070, 2961, 2836, 1605, 1528, 1460, 1427, 1255, 1179, 1030, 917, 872, 820 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 11.55 (s, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.65 (s, 1H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6): δ = 159.7, 142.6, 141.0, 136.9, 129.0, 127.0, 125.1, 125.0, 123.8, 122.4, 119.0, 115.2, 113.6, 113.3, 55.6.

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{17}H_{12}ClNOS$ 313.0328, found 313.0320.

5-Chloro-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole (3t)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.55; yellowish solid, mp. 176 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3404, 3019, 2922, 2852, 1640, 1528, 1478, 1423, 1240, 1105, 1054, 816, 500 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.87 (s, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.81 (s, 1H), 7.70−7.64 (m, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.26 (m, 2H), 7.20 (dd, *J* = 8.5, 2.0 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 161.1 (d, *J* = 242.8 Hz), 142.0 (s), 139.8 (s), 134.2 (s), 131.6 (d, *J* = 3.2 Hz), 126.60 (d, *J* = 8.0 Hz), 123.78 (d, *J* = 15.6 Hz), 122.5 (s), 121.8 (s), 118.3 (s), 116.1 (s), 116.0 (s), 114.4 (s), 113.2 (s).

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{16}H_9ClFNS$ 301.0128, found 301.0087.

5-Bromo-2-phenyl-8*H*-thieno[2,3-*b*]indole (3u)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.50; yellowish solid, mp. 219−220 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3387, 3074, 1517, 1475, 1430, 1282, 1243, 827, 790, 757, 689, 588, 475 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.89 (s, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.87 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.42 (t, *J* = 7.5, 1H), 7.31 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 142.3, 140.6, 135.9, 135.5, 129.6, 127.3, 125.1, 124.8, 124.2, 123.7, 121.7, 114.7, 114.1, 112.1.

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{16}H_{10}BrNS$ 326.9717, found 326.9669.

5-Bromo-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole (3v)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone $R_f = 0.52$; golden solid, mp. 209 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3381, 3011, 2918, 2851, 1526, 1477, 1423, 1281, 811, 791, 688, 574, 446 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.86 (s, 1H), 7.99 (d, *J* = 1.5 Hz, 1H), 7.79 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.30 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 141.5, 140.0, 136.2, 135.6, 132.2, 129.7, 124.6, 124.2, 123.7, 123.2, 121.2, 113.6, 113.5, 111.5, 20.7.

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{17}H_{12}BrNS$ 340.9874, found 340.9827.

5-Bromo-2-(4-methoxyphenyl)-8*H*-thieno[2,3-*b*]indole (3w)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone $R_f = 0.47$; golden solid, mp. 219 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3411, 3051, 2956, 2838, 1605, 1526, 1470, 1421, 1296, 1254, 1179, 1031, 819, 804, 573, 511 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.84 (s, 1H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.70 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.30 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 158.4, 141.2, 140.0, 135.6, 127.6, 126.1, 124.1, 123.7, 123.1, 121.1, 114.6, 113.6, 112.8, 111.4, 55.2.

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{17}H_{12}BrNOS$ 358.9803, found 358.9804.

5-Bromo-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole (3x)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone $R_f = 0.47$; golden solid, mp. 178 °C.

FT-IR (KBr, 4000−400 cm^{-1}): 3417, 3078, 2922, 1602, 1562, 1529, 1482, 1452, 1236, 1159, 1098, 915, 816, 792, 687 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.88 (s, 1H), 7.99 (d, *J* = 1.5 Hz, 1H), 7.81 (s, 1H), 7.67 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.35−7.29 (m, 1H), 7.26 (m, 2H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 161.2 (d, J = 242.8 Hz), 141.8 (s), 140.1 (s), 134.2 (s), 131.6 (d, J = 3.1 Hz), 126.6 (d, J = 8.0 Hz), 124.3 (s), 123.7 (s), 123.1 (s), 121.2 (s), 116.0 (d, J = 21.6 Hz), 114.3 (s), 113.6 (s), 111.6 (s).

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{16}H_9BrFNS$ 344.9623, found 344.9577.

5-Nitro-2-phenyl-8*H*-thieno[2,3-*b*]indole (3y)

Analytical TLC on silica gel, 4:1 *n*-hexane/acetone R_f = 0.37; brown solid, mp. 250−251°C.

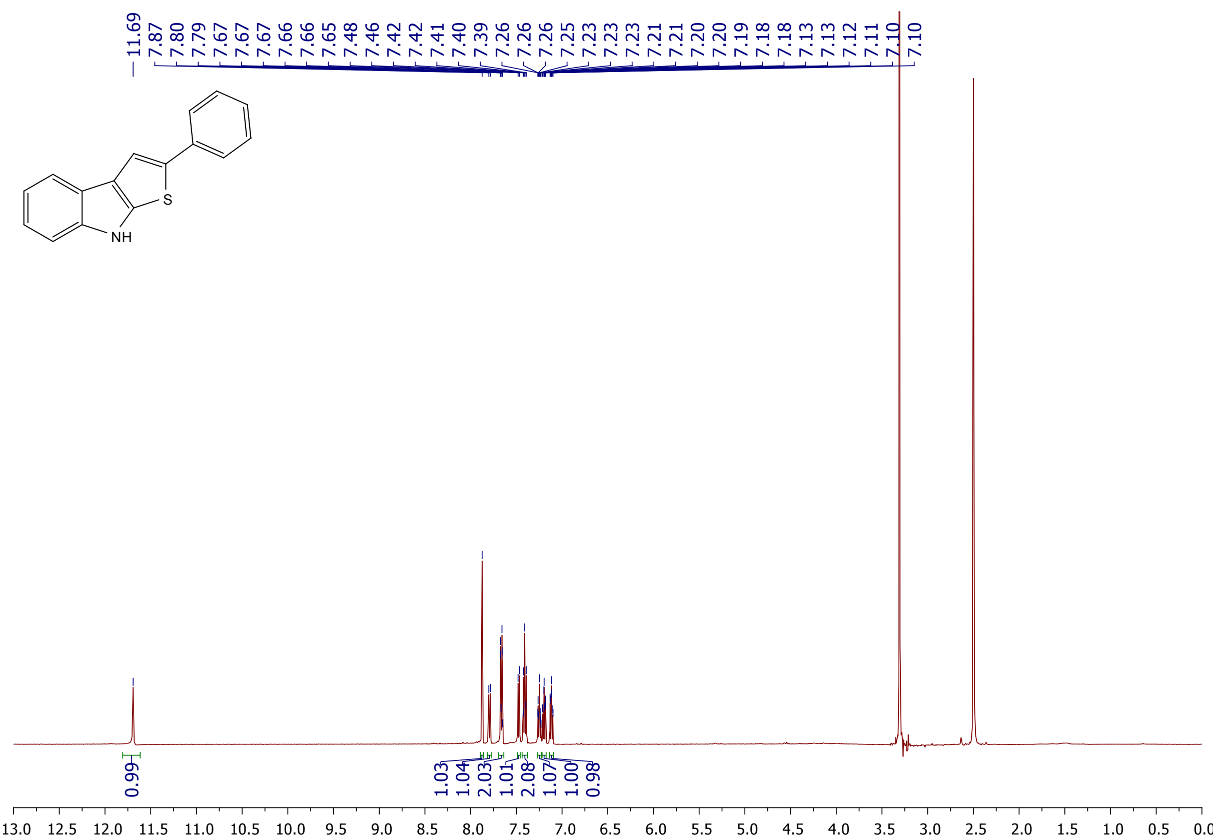
FT-IR (KBr, 4000−400 cm^{-1}): 3436, 3050, 2920, 1610, 1521, 1500, 1318, 1297, 1253, 1120, 1059, 925, 850, 819, 732, 677 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 11.46 (s, 1H), 8.82 (d, J = 2.0 Hz, 1H), 8.15 (dd, J = 9.0, 2.0 Hz, 1H), 7.98 (s, 1H), 7.71 (m, 3H), 7.44 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H).

^{13}C NMR (125 MHz, acetone-d_6): δ = 145.8, 144.5, 142.4, 139.0, 136.2, 130.1, 128.2, 127.1, 126.1, 122.4, 118.5, 116.6, 114.9, 112.8.

HRMS (ESI) *m/z* calcd for $[M]^+$ $C_{16}H_{10}N_2O_2S$ 294.0463, found 294.0418.

Section S6. Copies of ^{1}H , ^{13}C NMR and HRMS spectra of all products



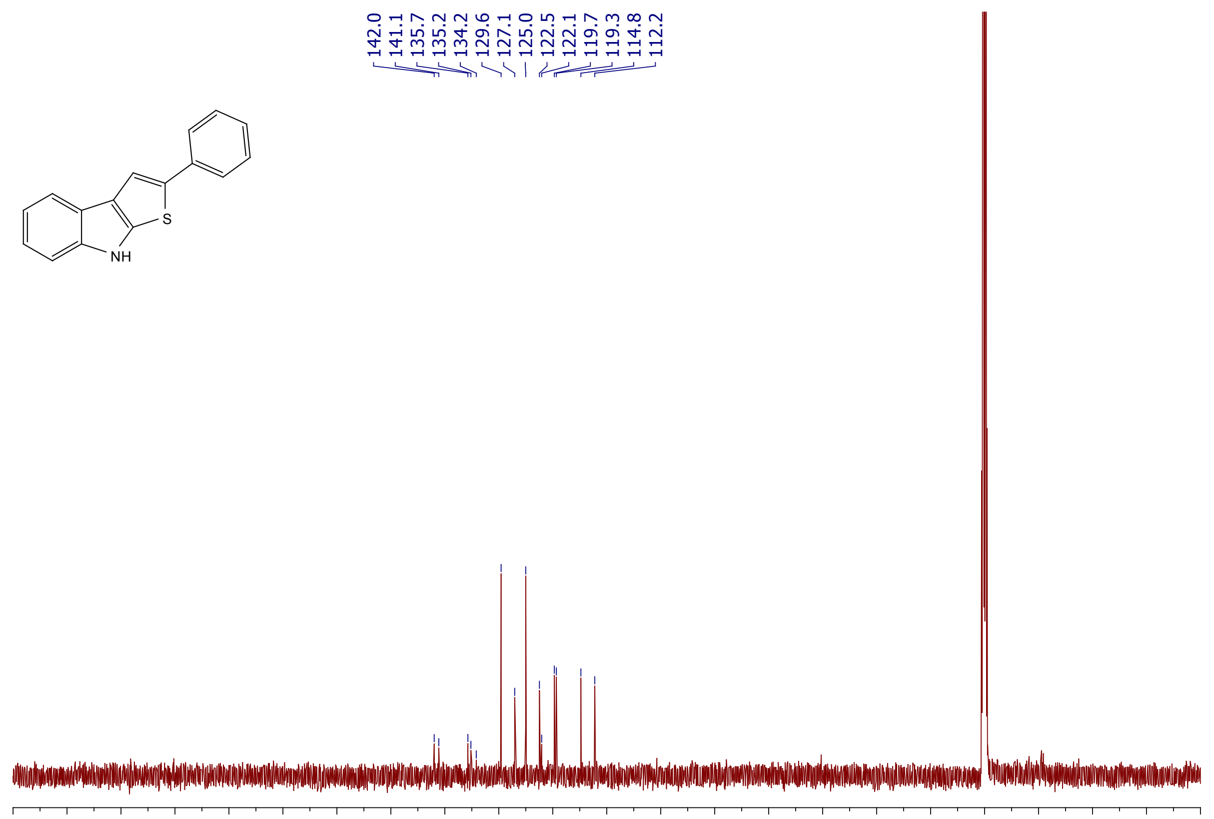
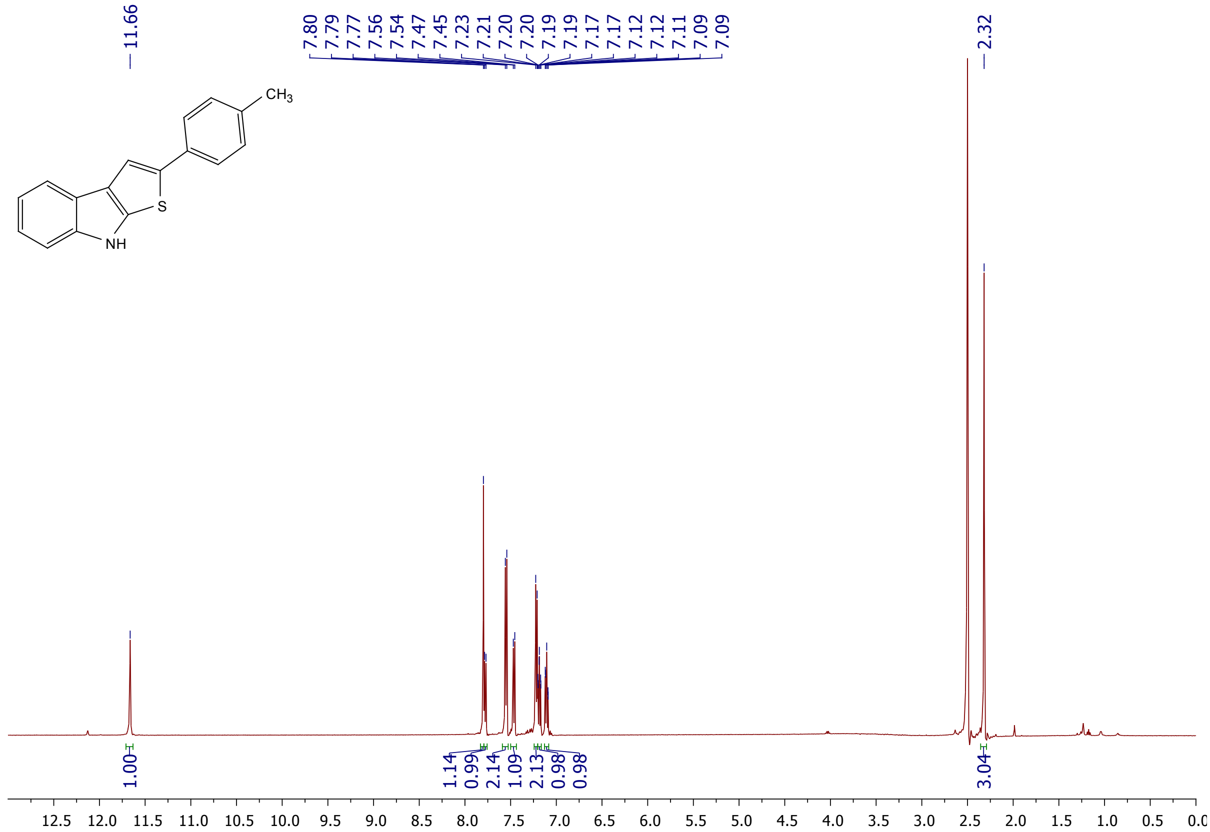


Figure S9. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-phenyl-8*H*-thieno[2,3-*b*]indole 3a



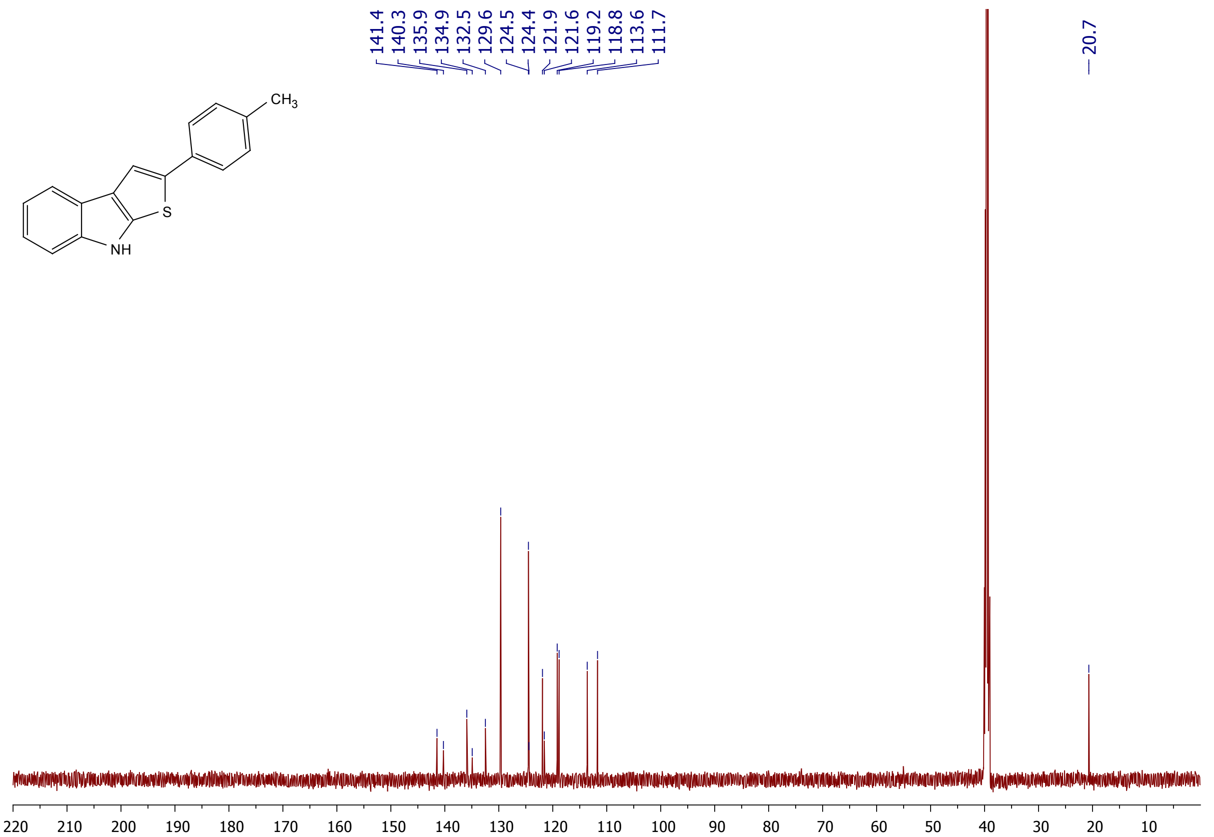
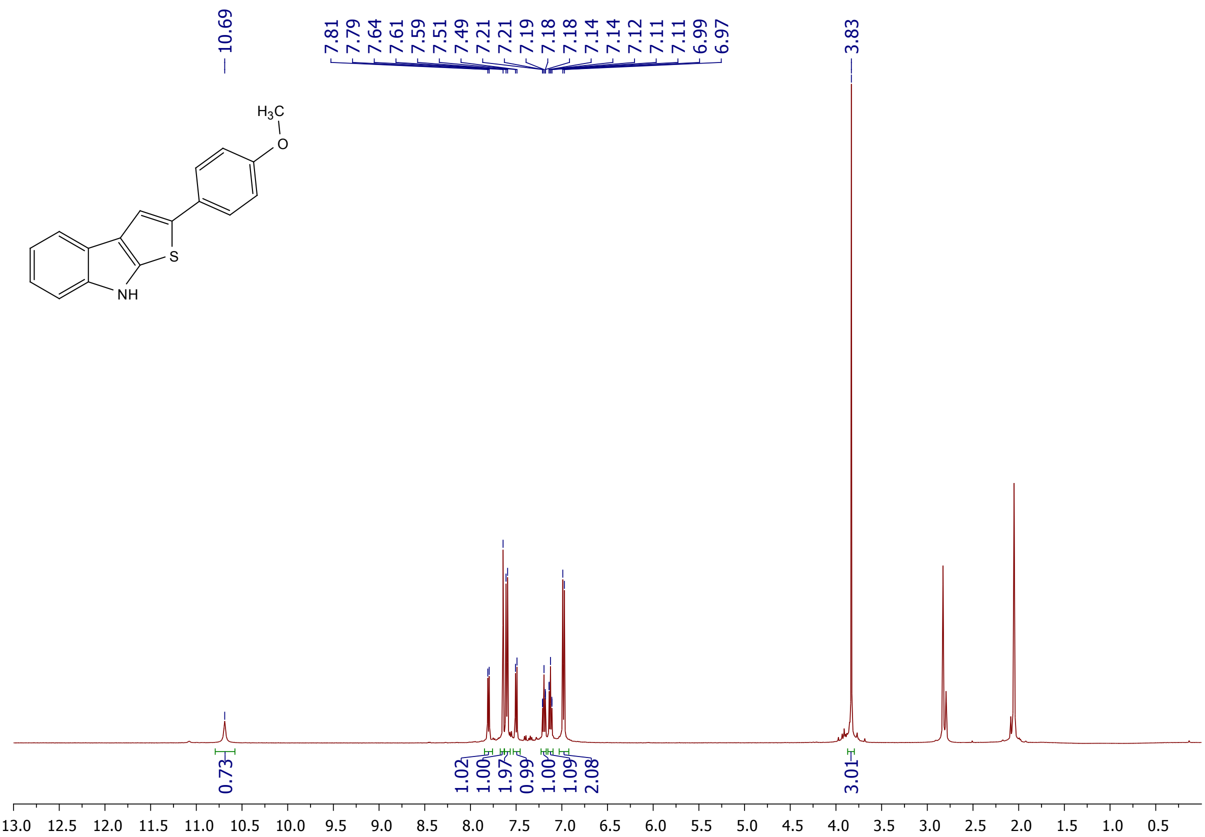


Figure S10. ¹H (top) and ¹³C (bottom) NMR spectra of 2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole 3b



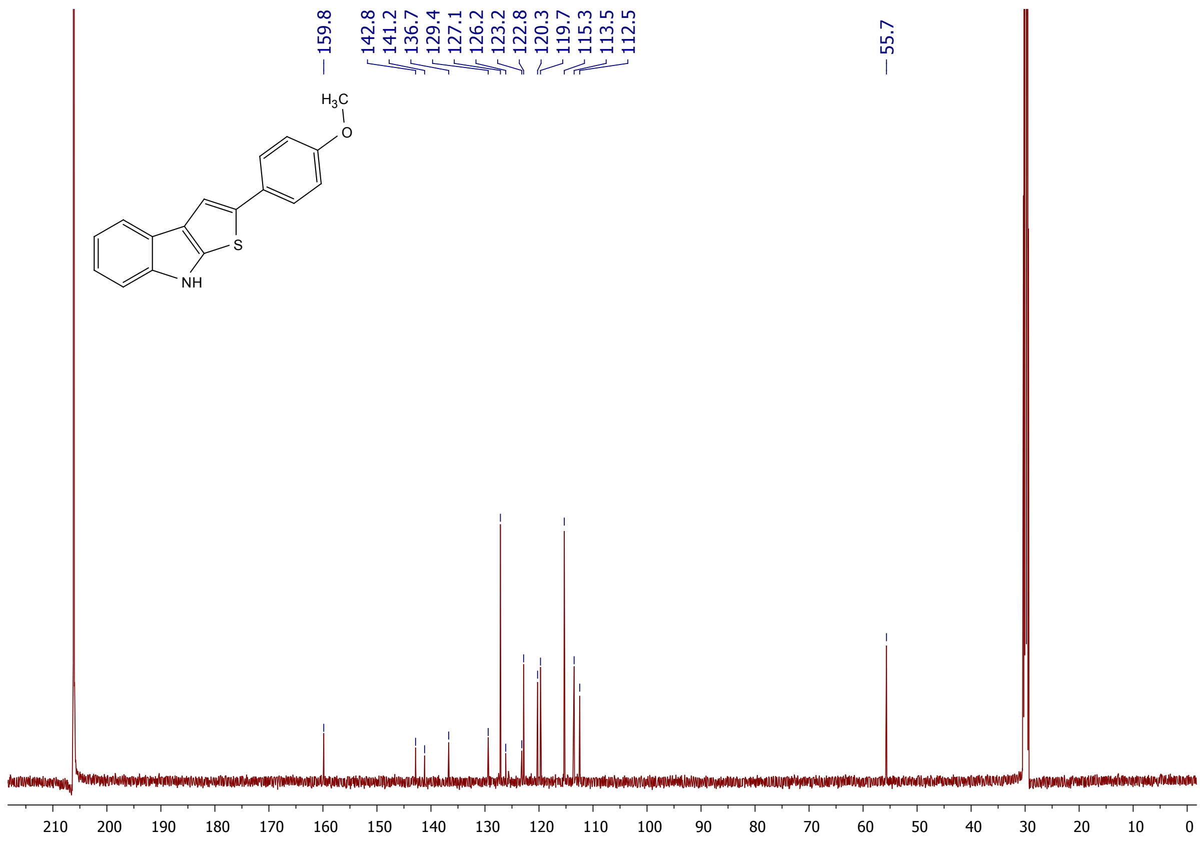
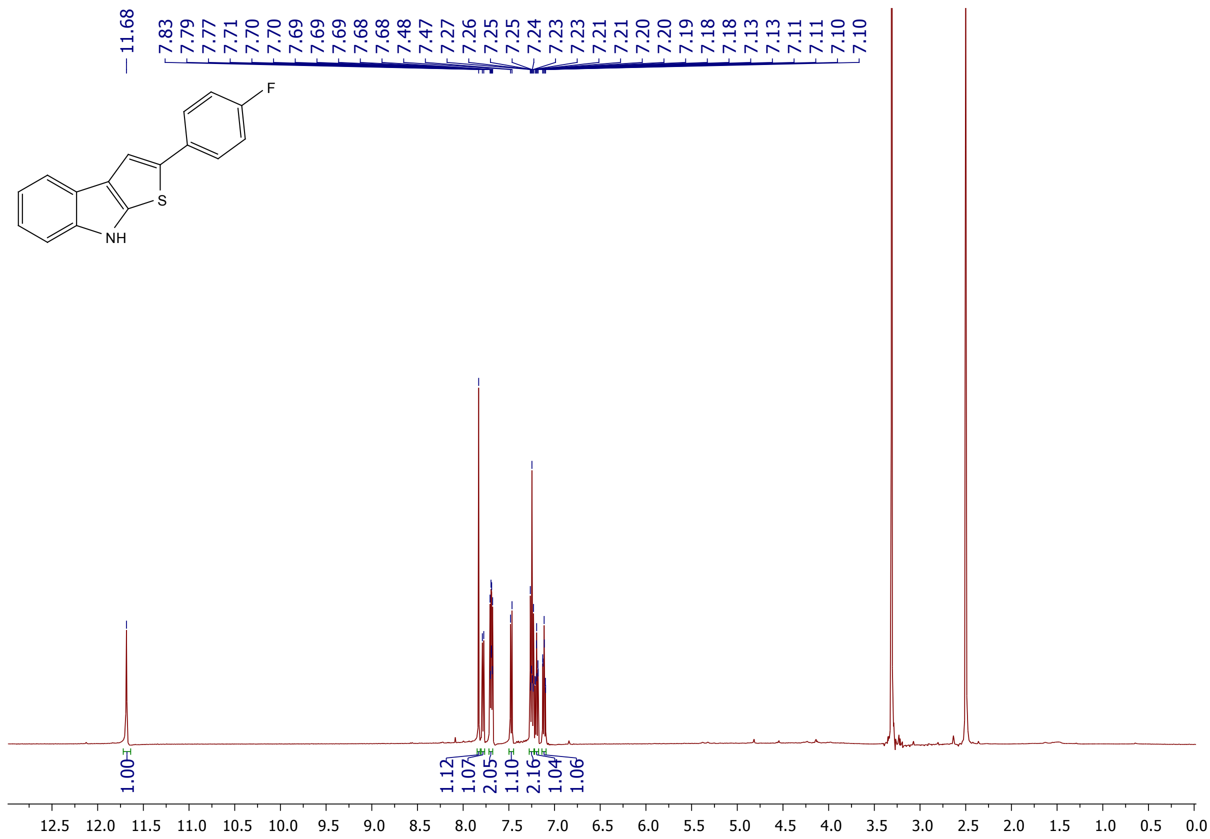


Figure S11. ^{1}H **(top) and** ^{13}C **(bottom) NMR spectra of 2-(4-methoxyphenyl)-8*H*-thieno[2,3-*b*]indole 3c**



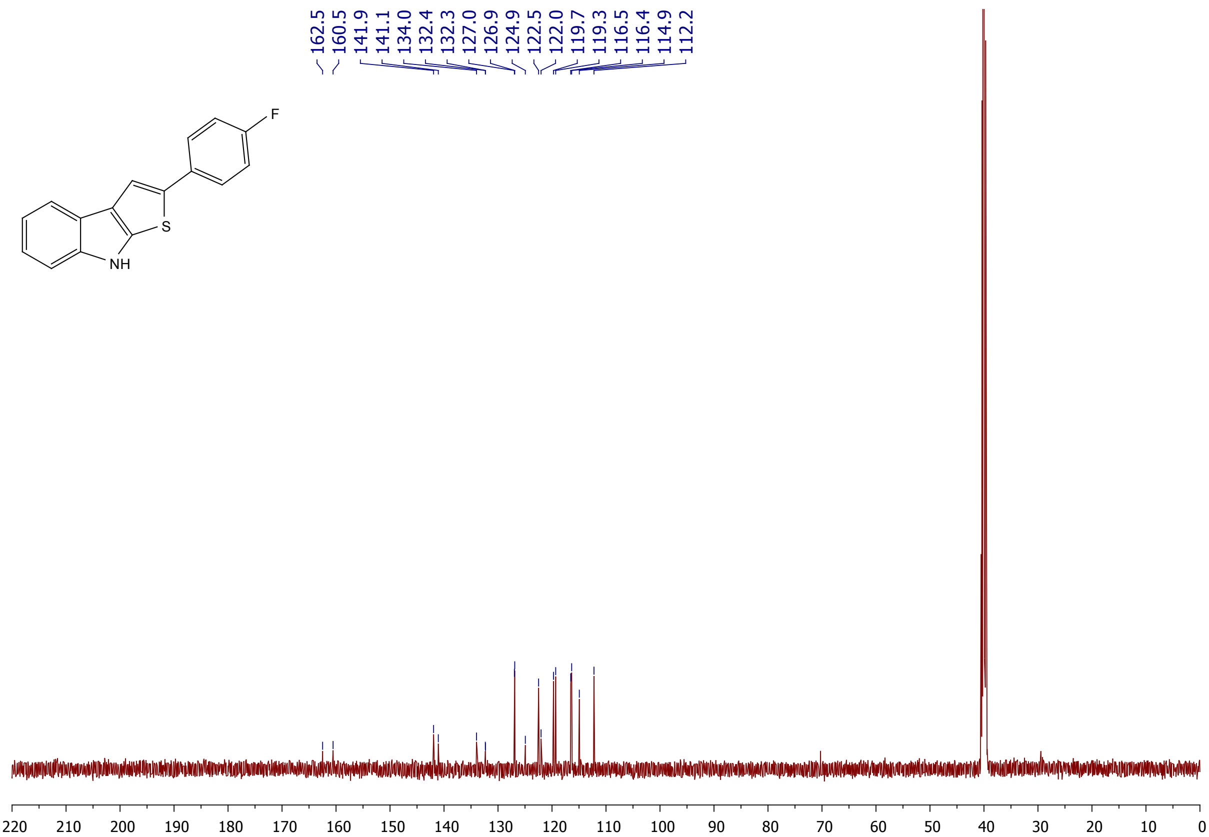
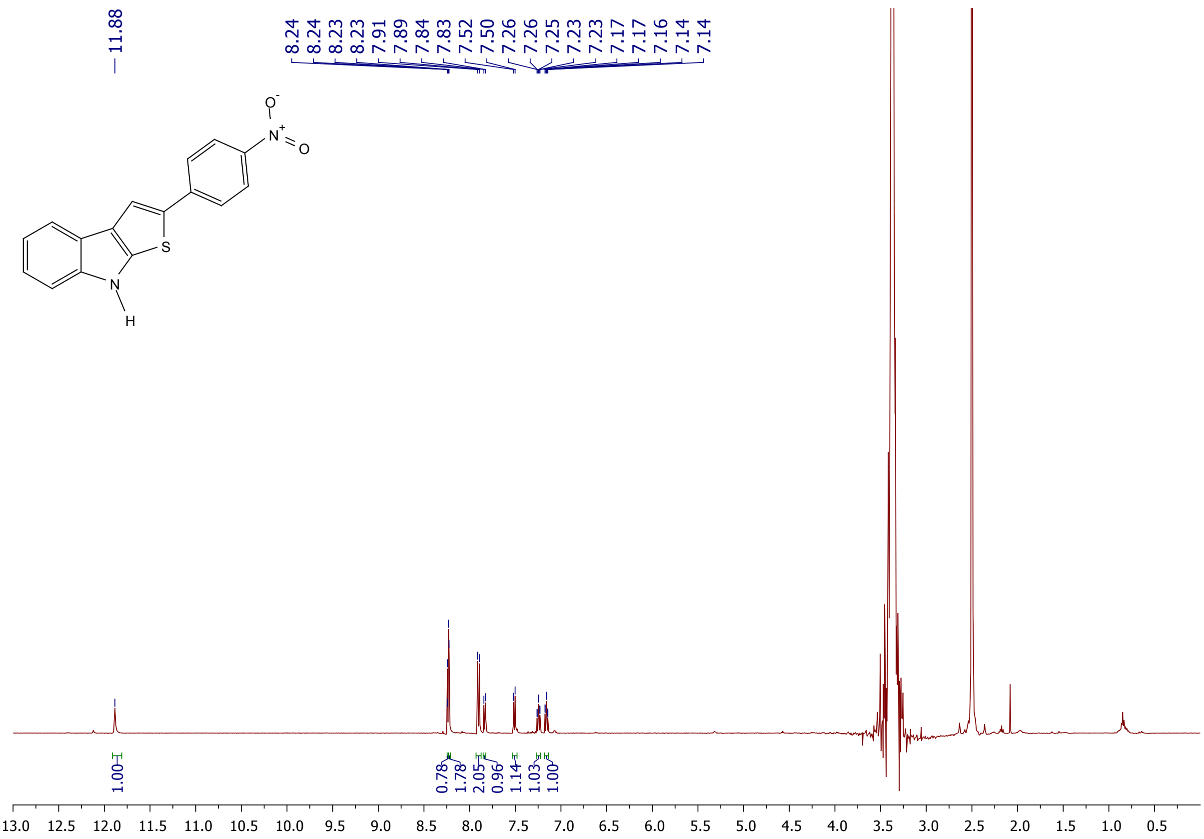
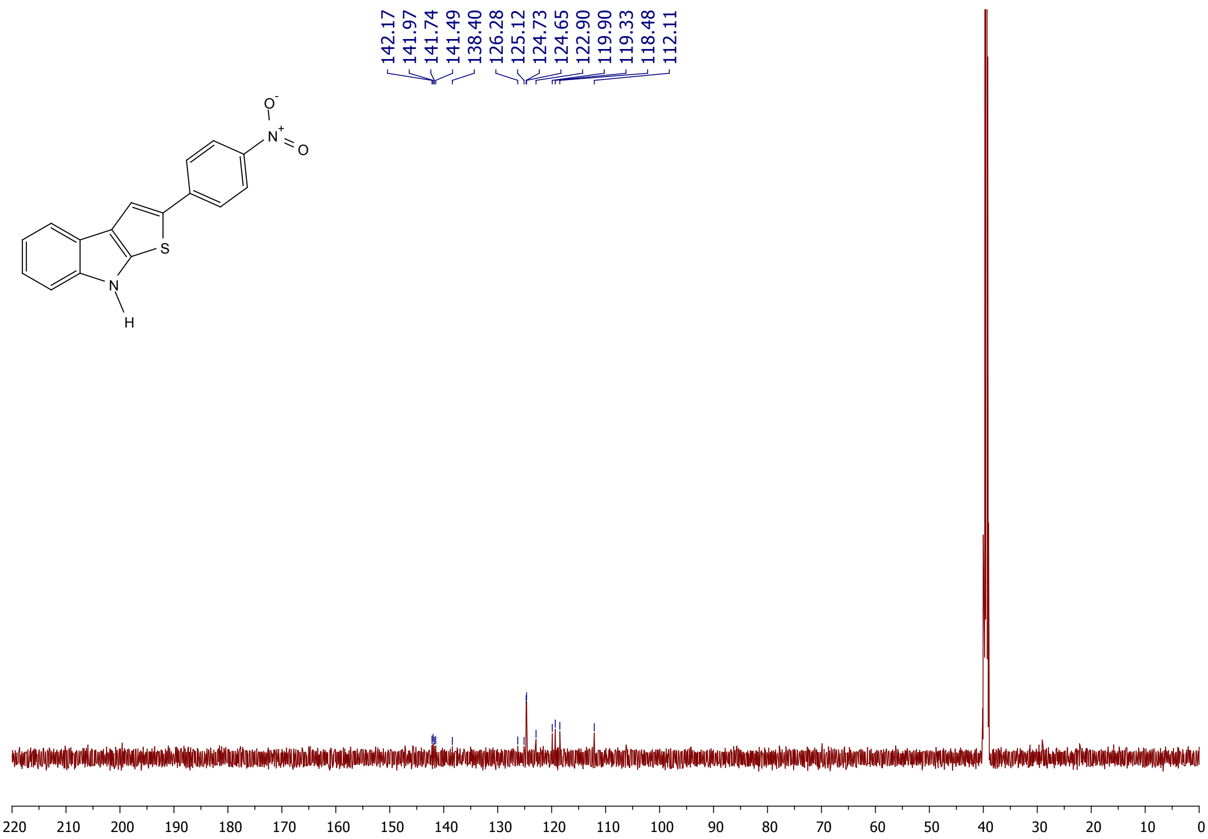
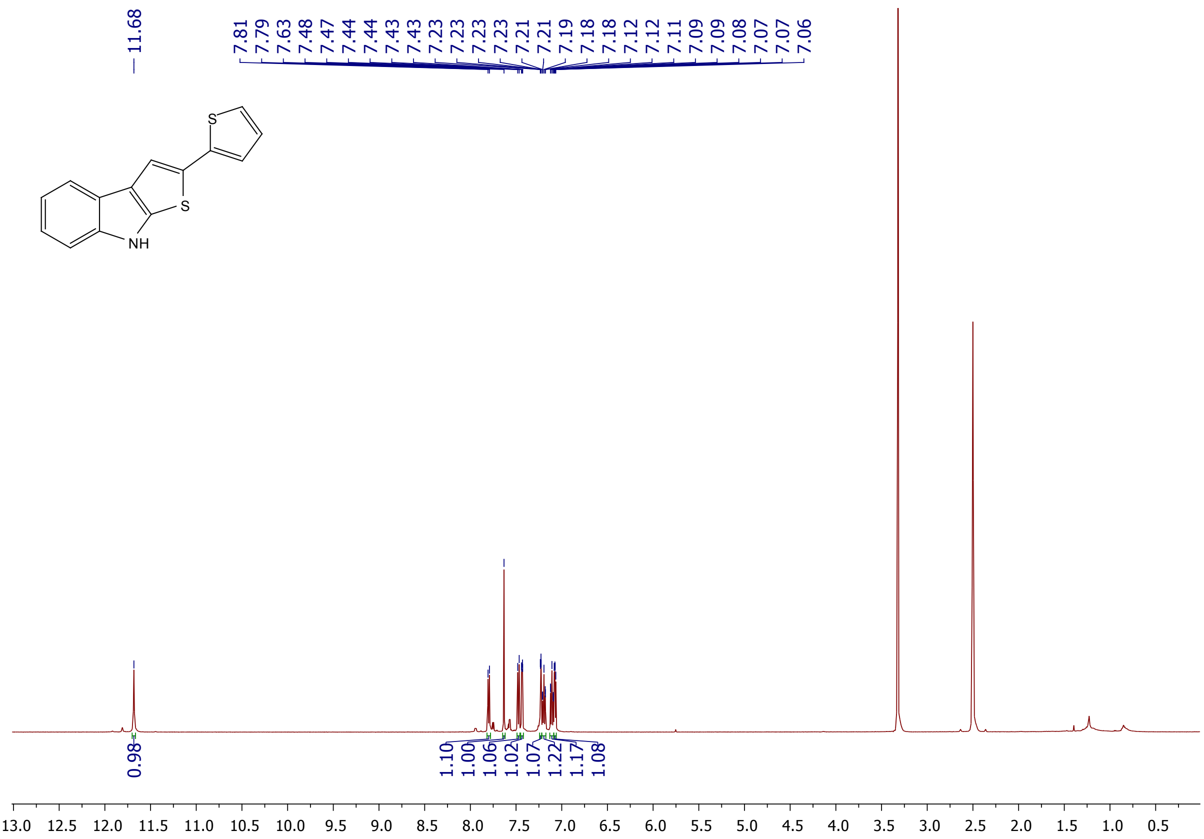


Figure S12. ¹H (top) and ¹³C (bottom) NMR spectra of 2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole 3d





^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-nitrophenyl)-8*H*-thieno[2,3-*b*]indole 3e



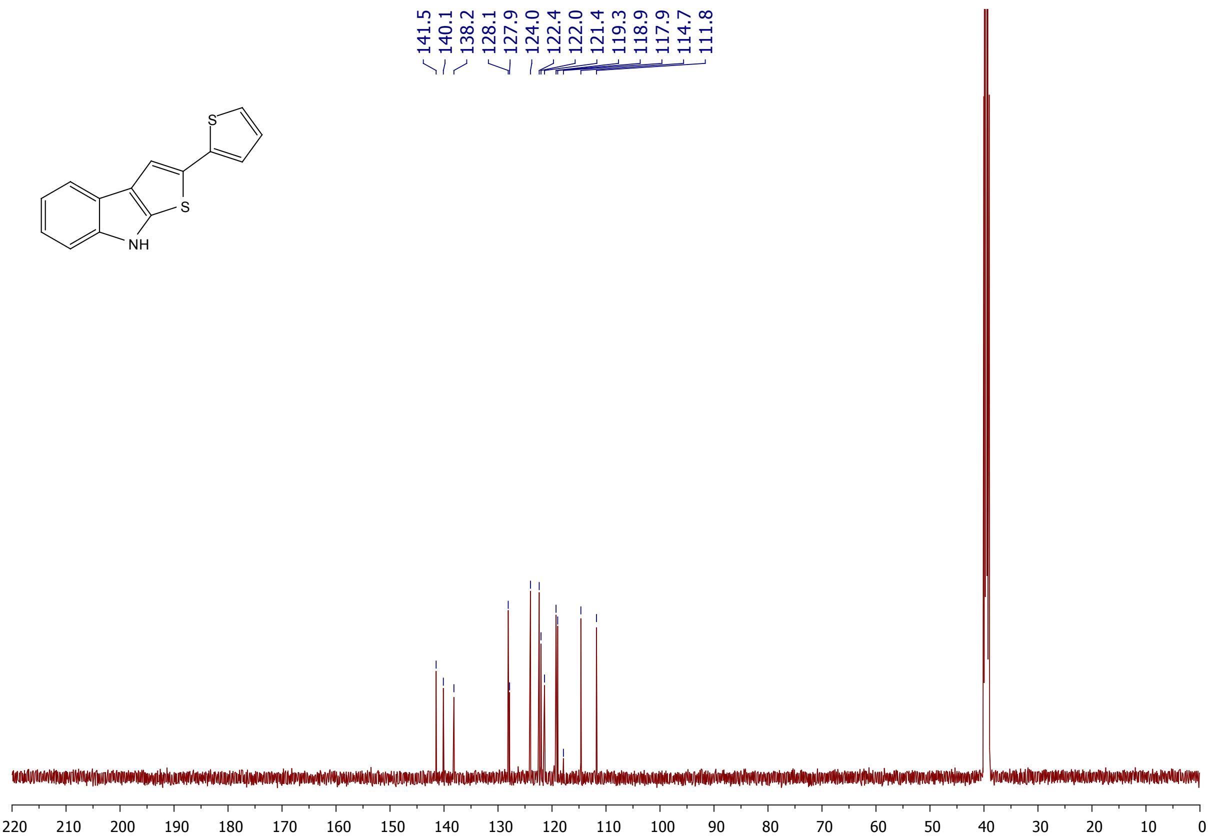
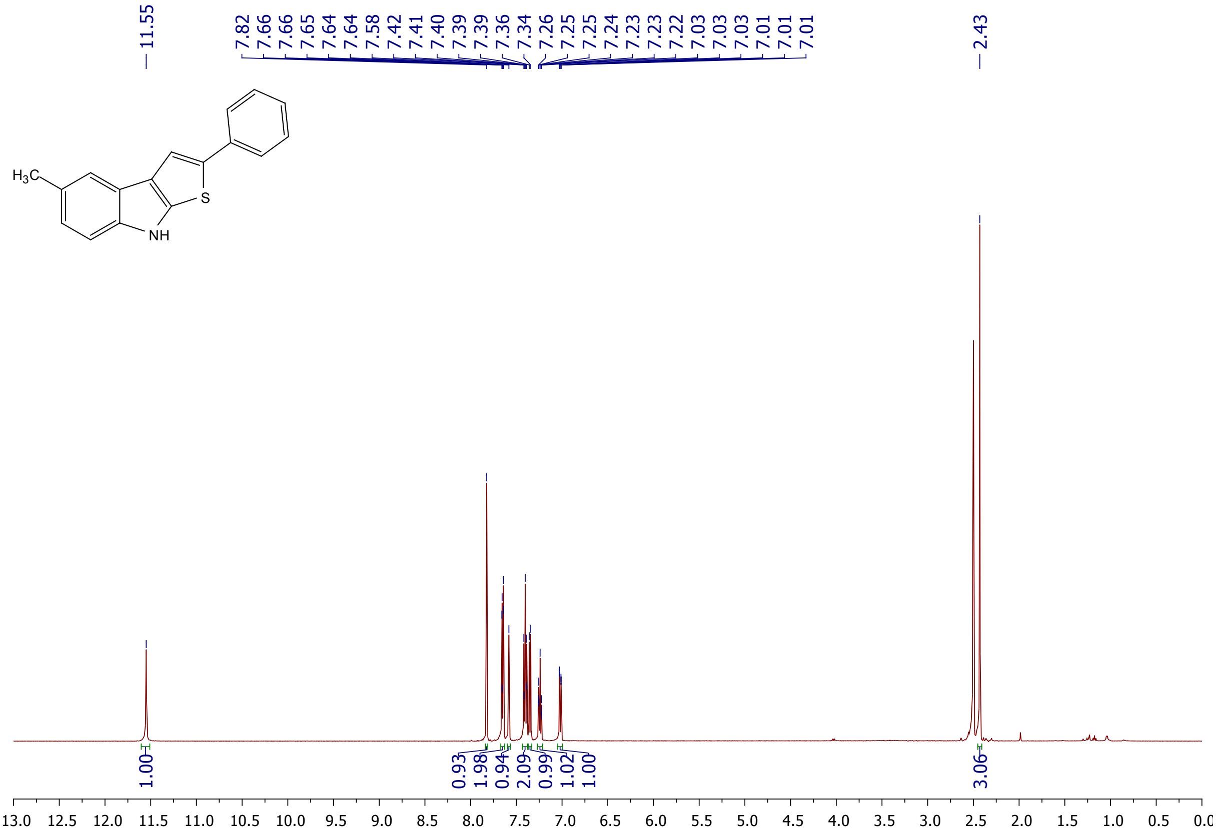


Figure S13. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(thiophen-2-yl)-8*H*-thieno[2,3-*b*]indole 3f



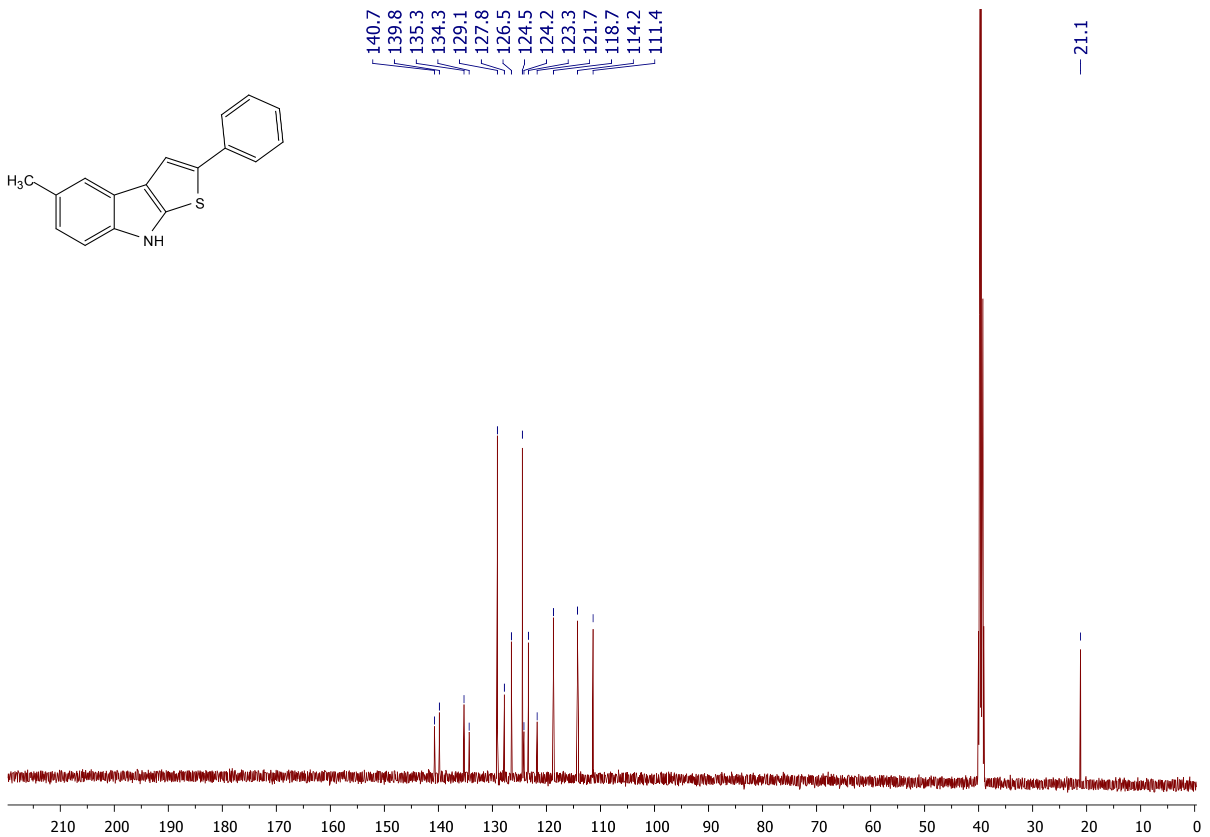
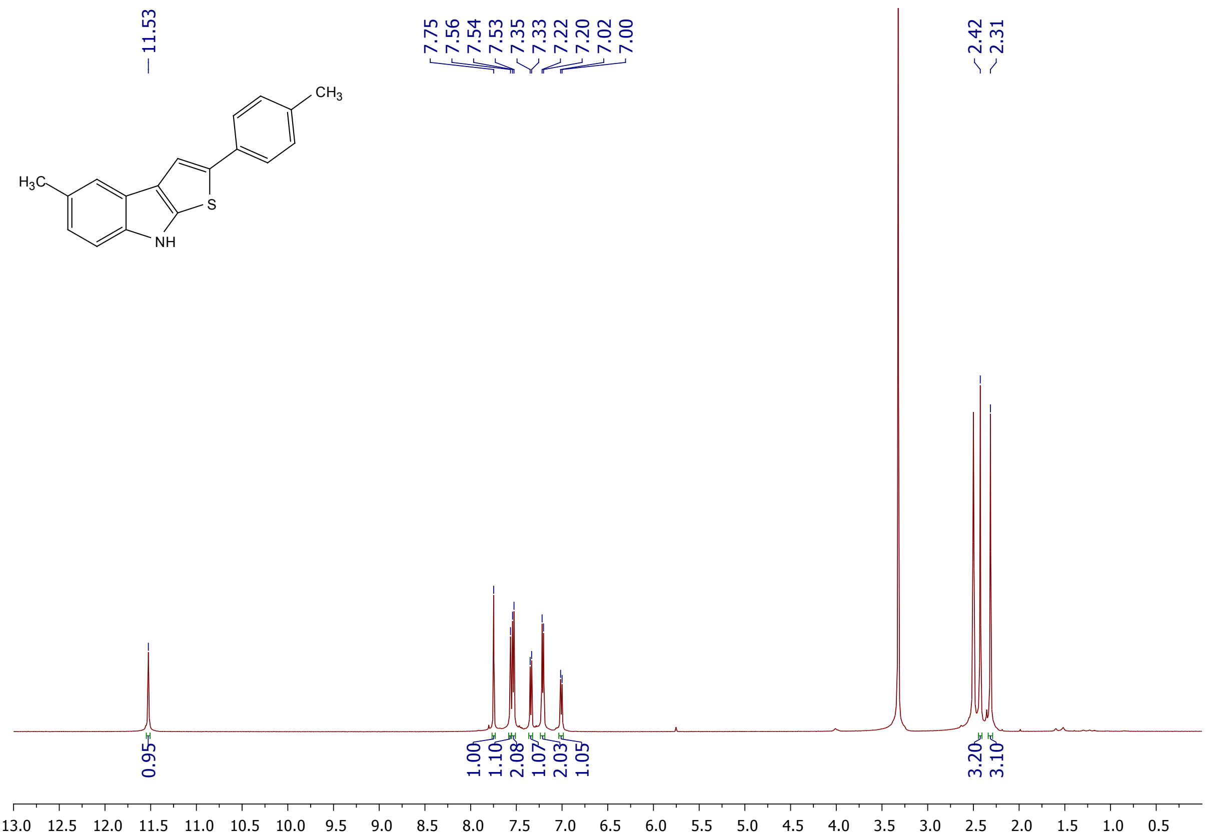


Figure S14. **^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole 3g**



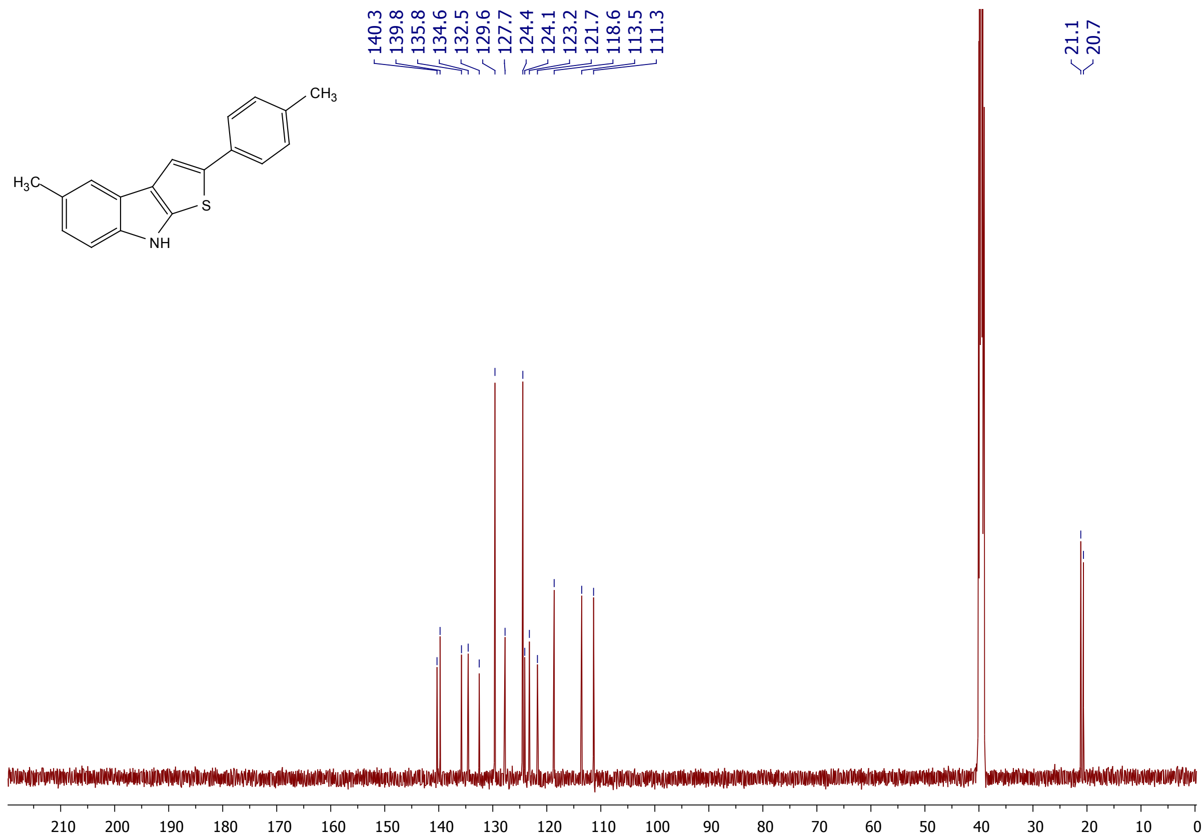
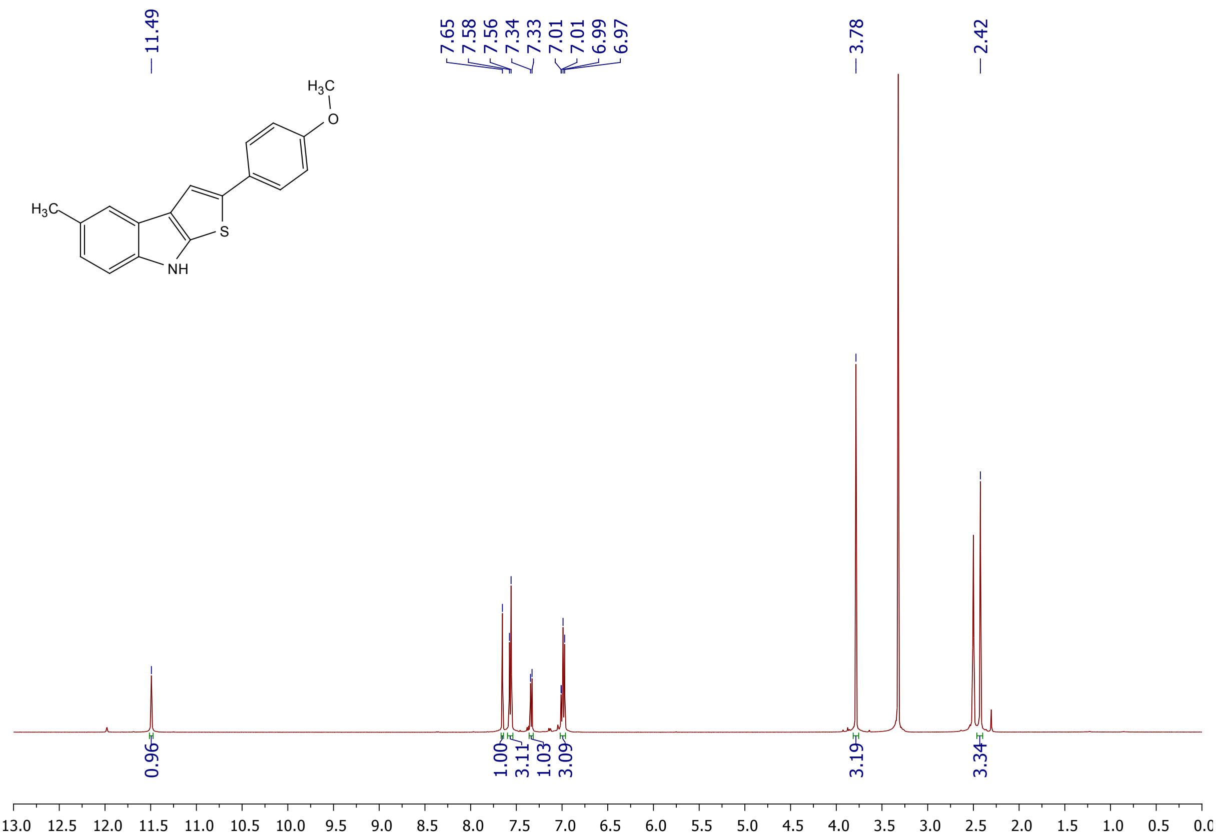


Figure S15. ^{1}H **(top) and** ^{13}C **(bottom) NMR spectra of 5-methyl-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole 3h**



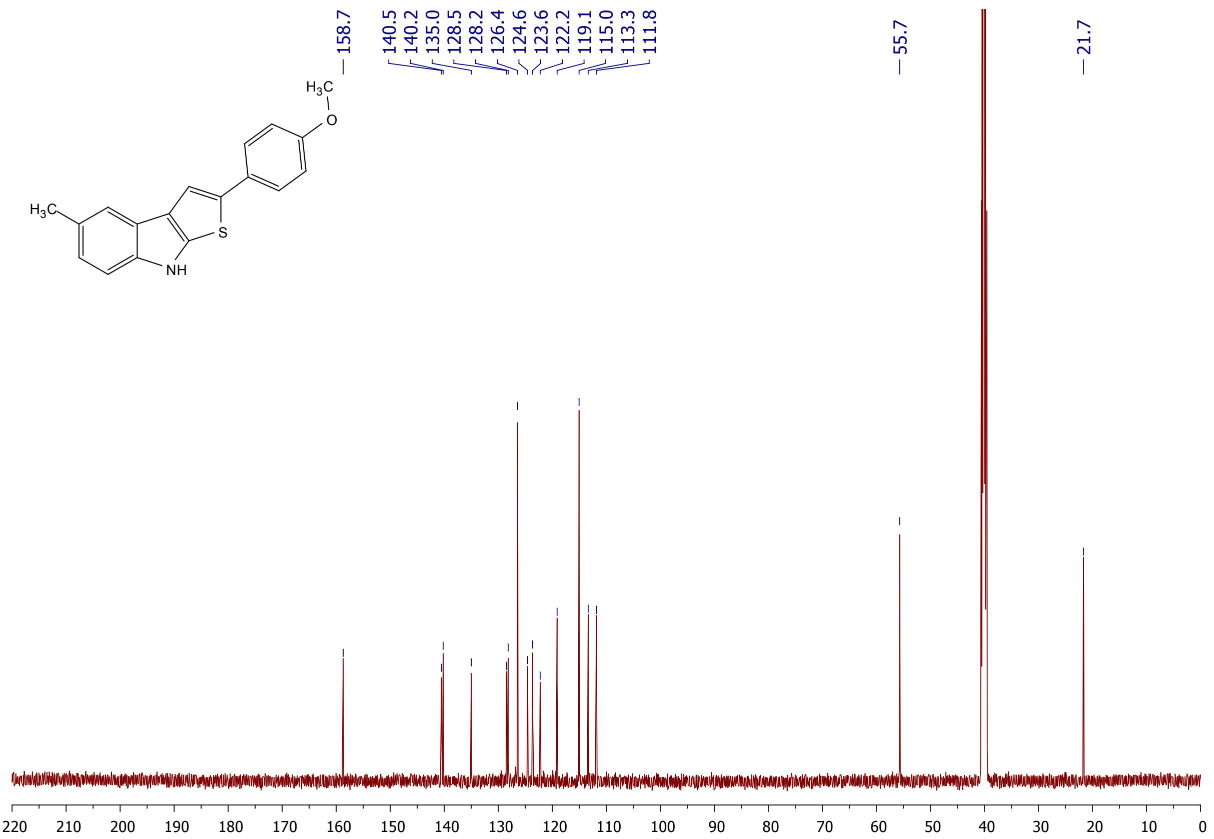
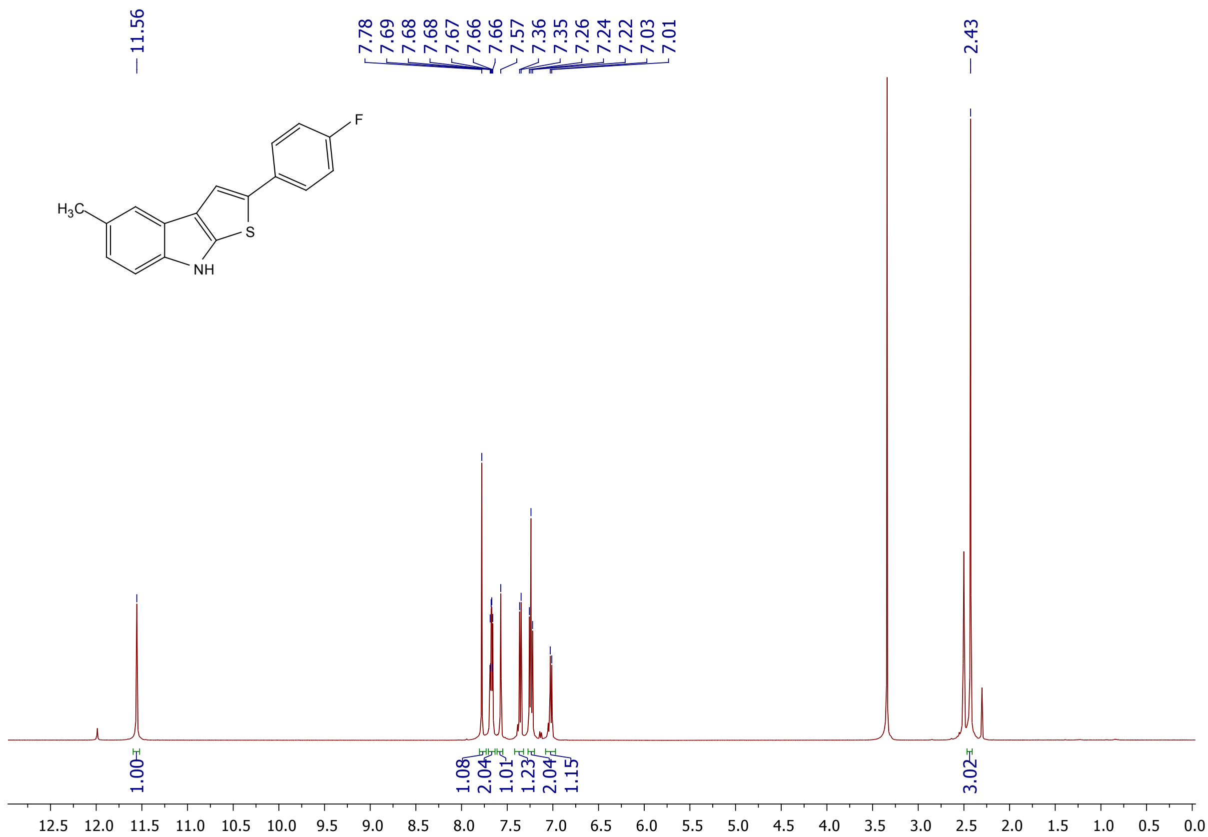


Figure S16. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-methoxyphenyl)-5-methyl-8*H*-thieno[2,3-*b*]indole 3i



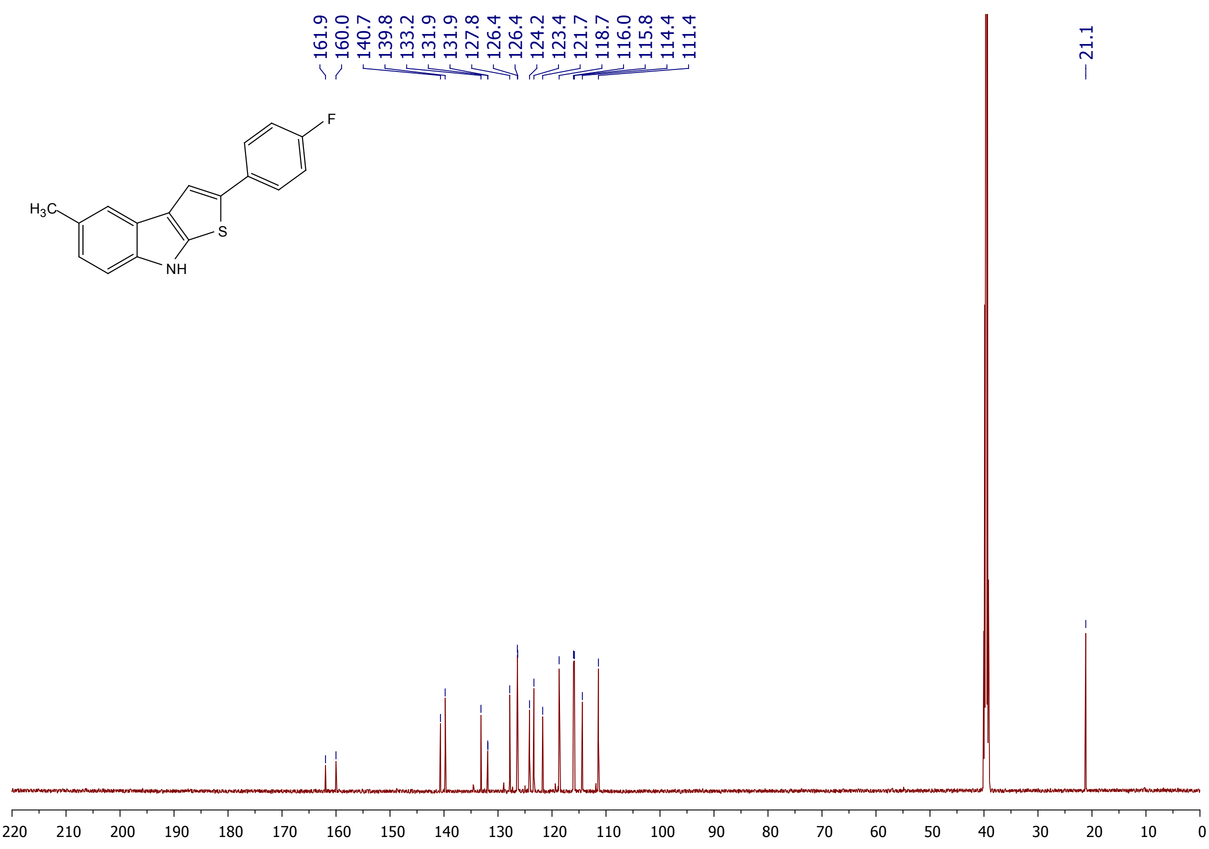
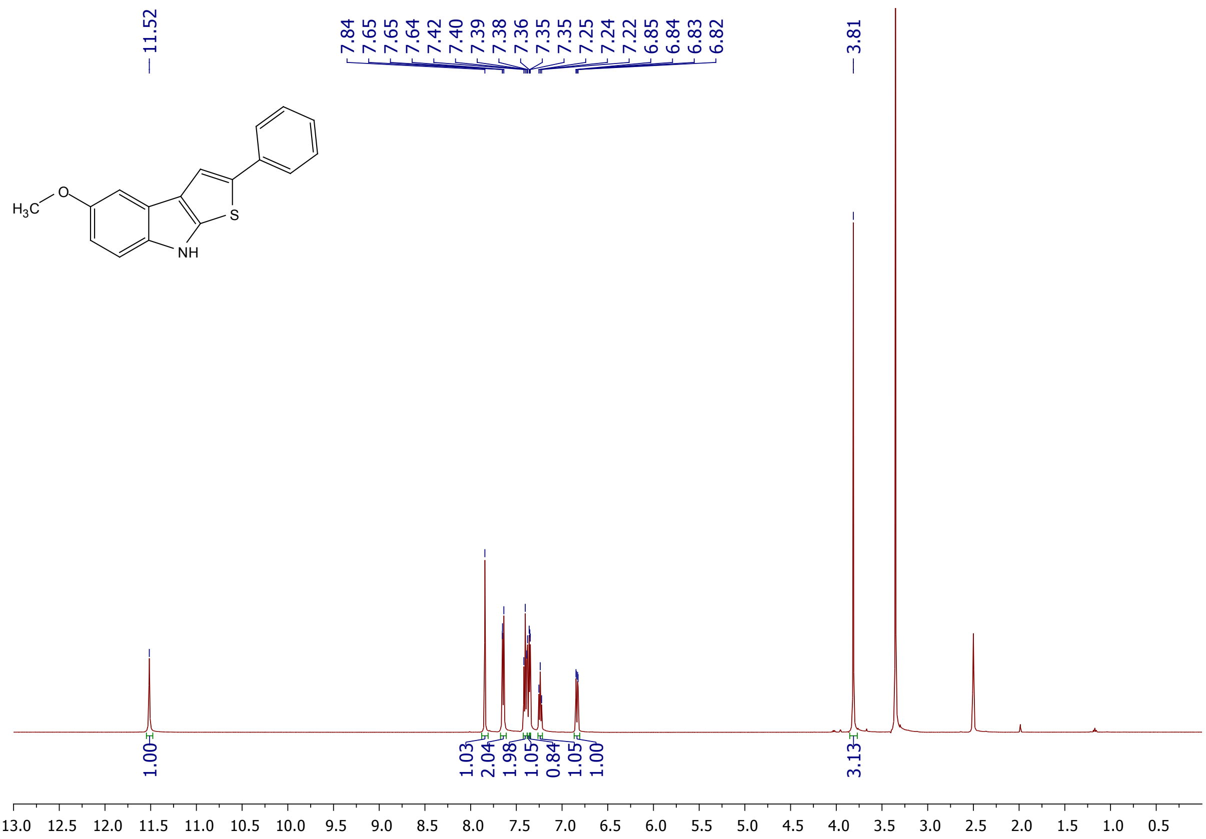


Figure S17. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-fluorophenyl)-5-methyl-8*H*-thieno[2,3-*b*]indole 3j



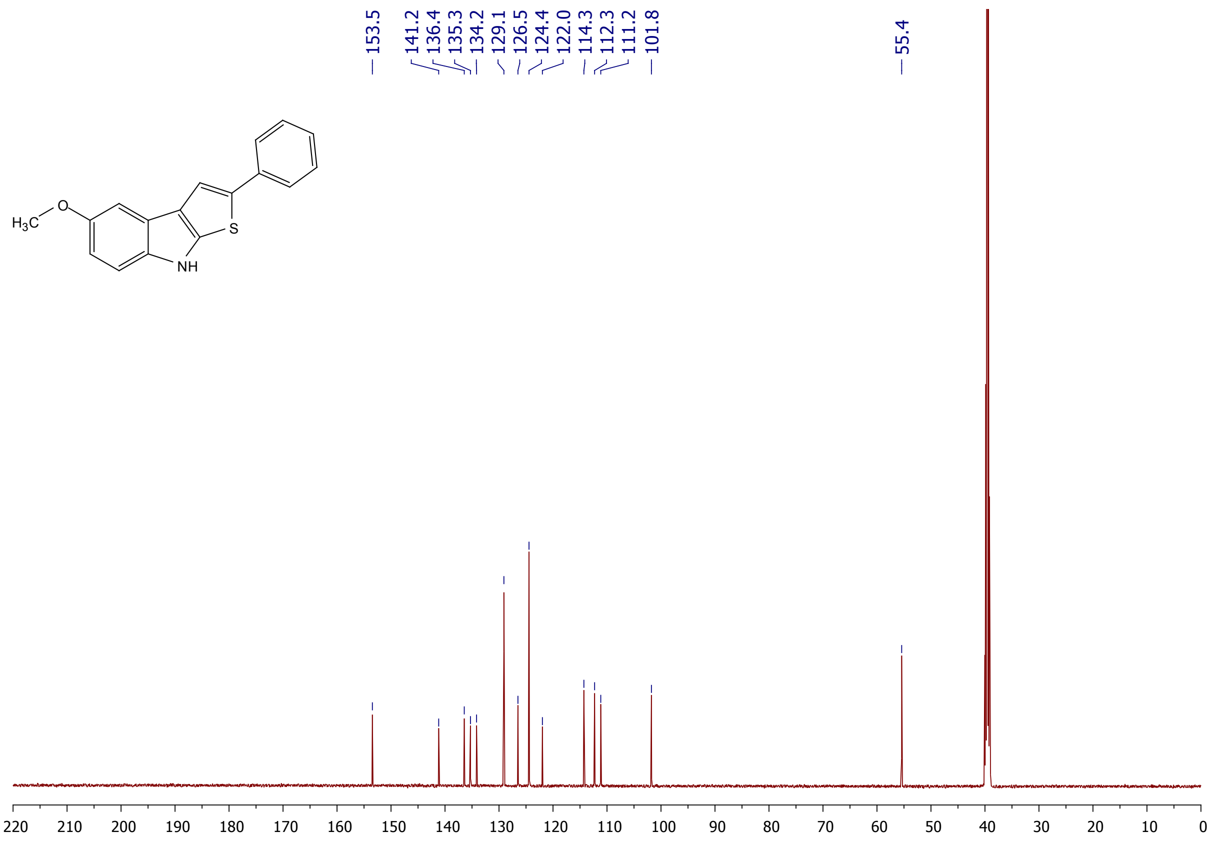
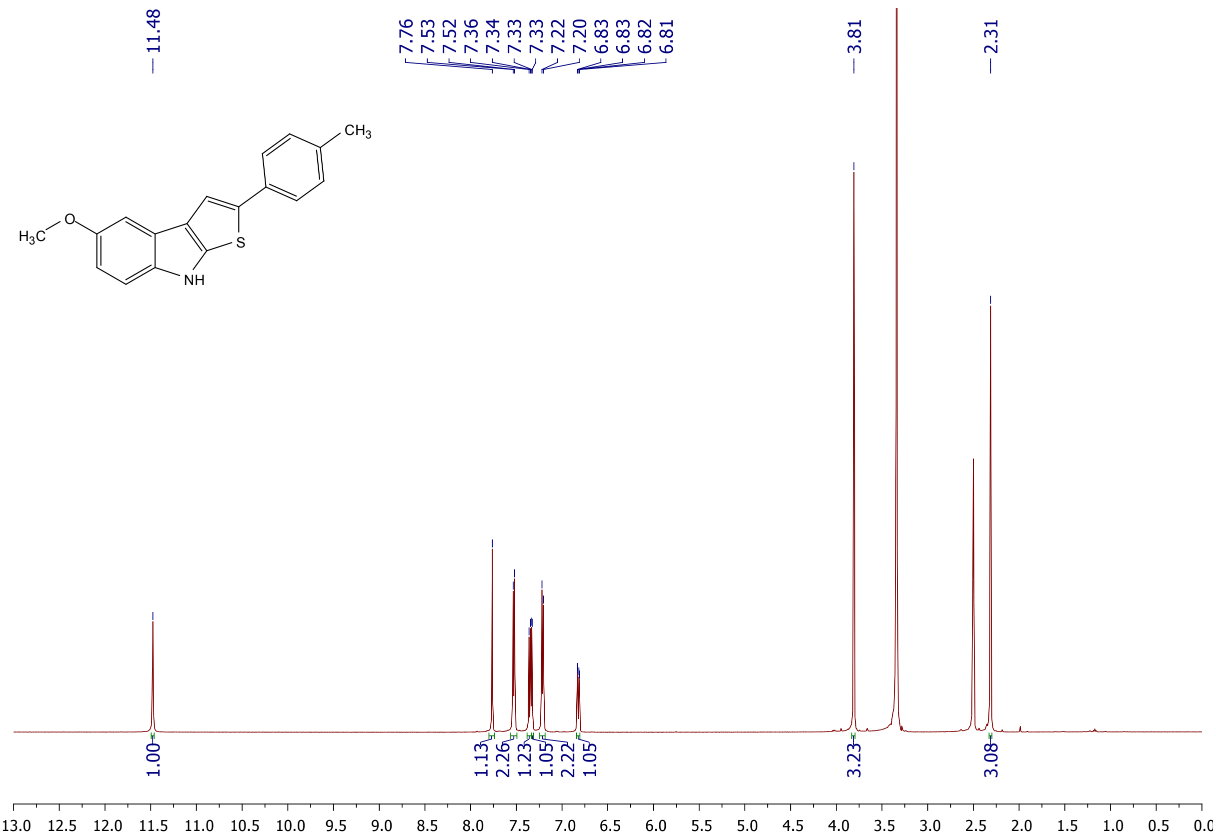


Figure S18. ^{1}**H (top) and** ^{13}**C (bottom) NMR spectra of 5-methoxy-2-phenyl-8*H*-thieno[2,3-*b*]indole 3k**



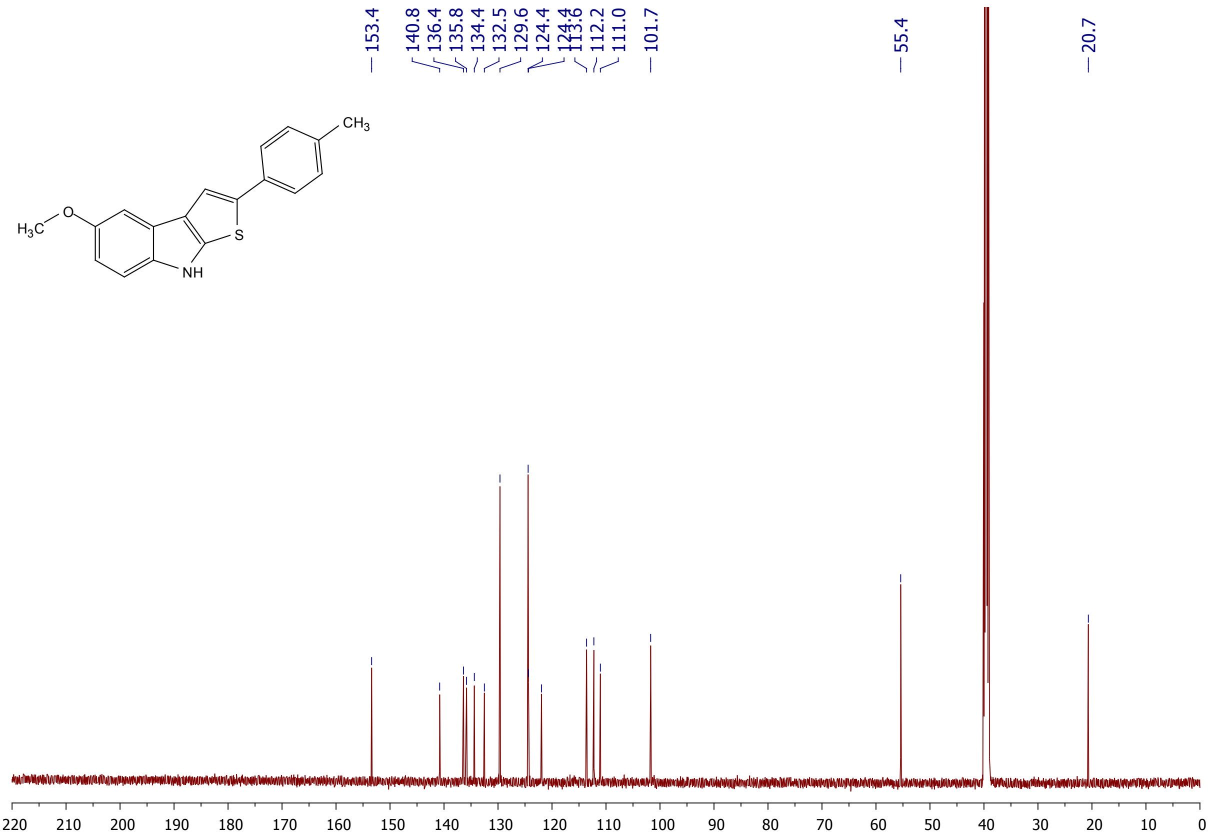


Figure S19. [1]H (top) and [13]C (bottom) NMR spectra of 5-methoxy-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole 3l

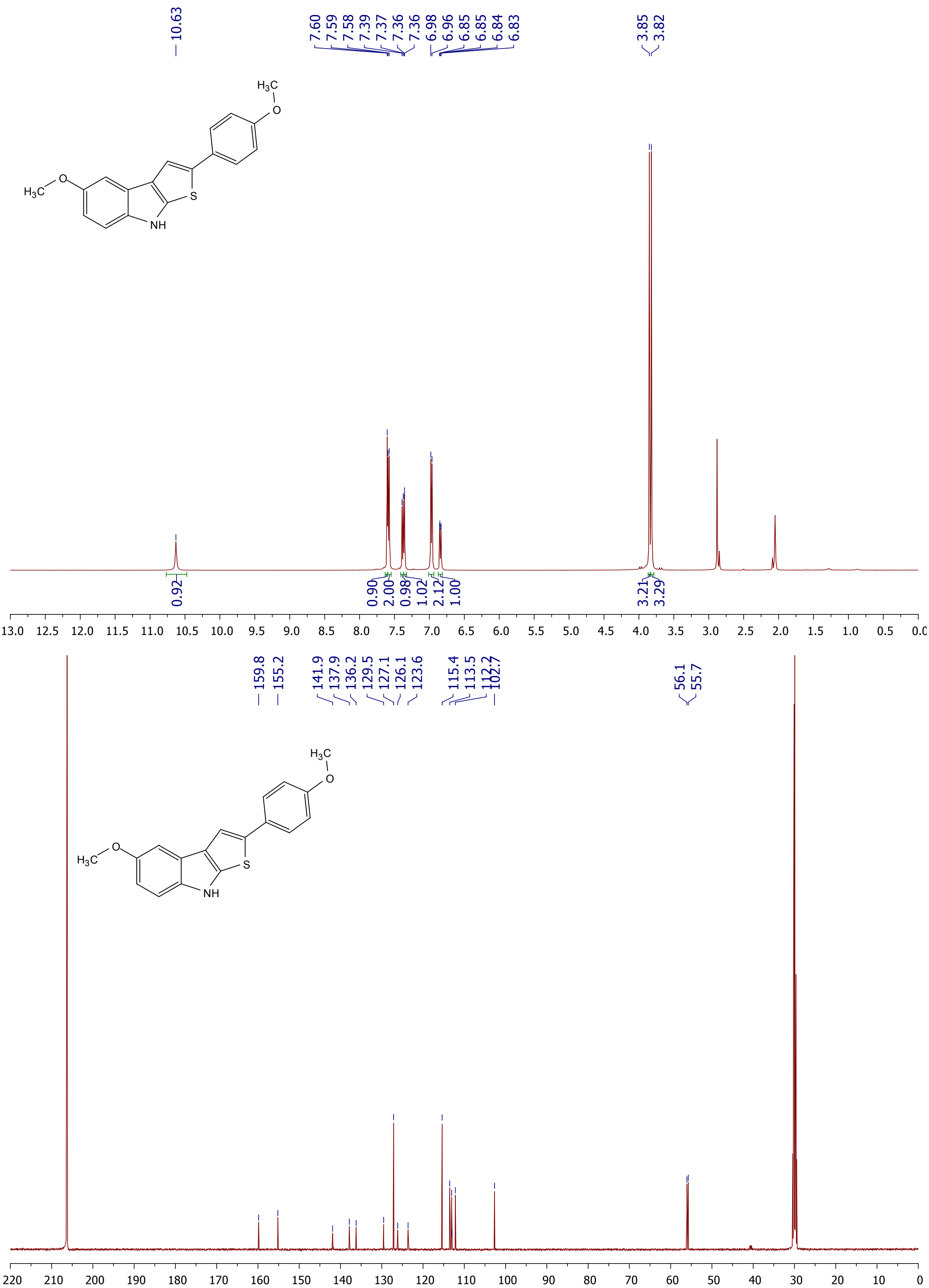
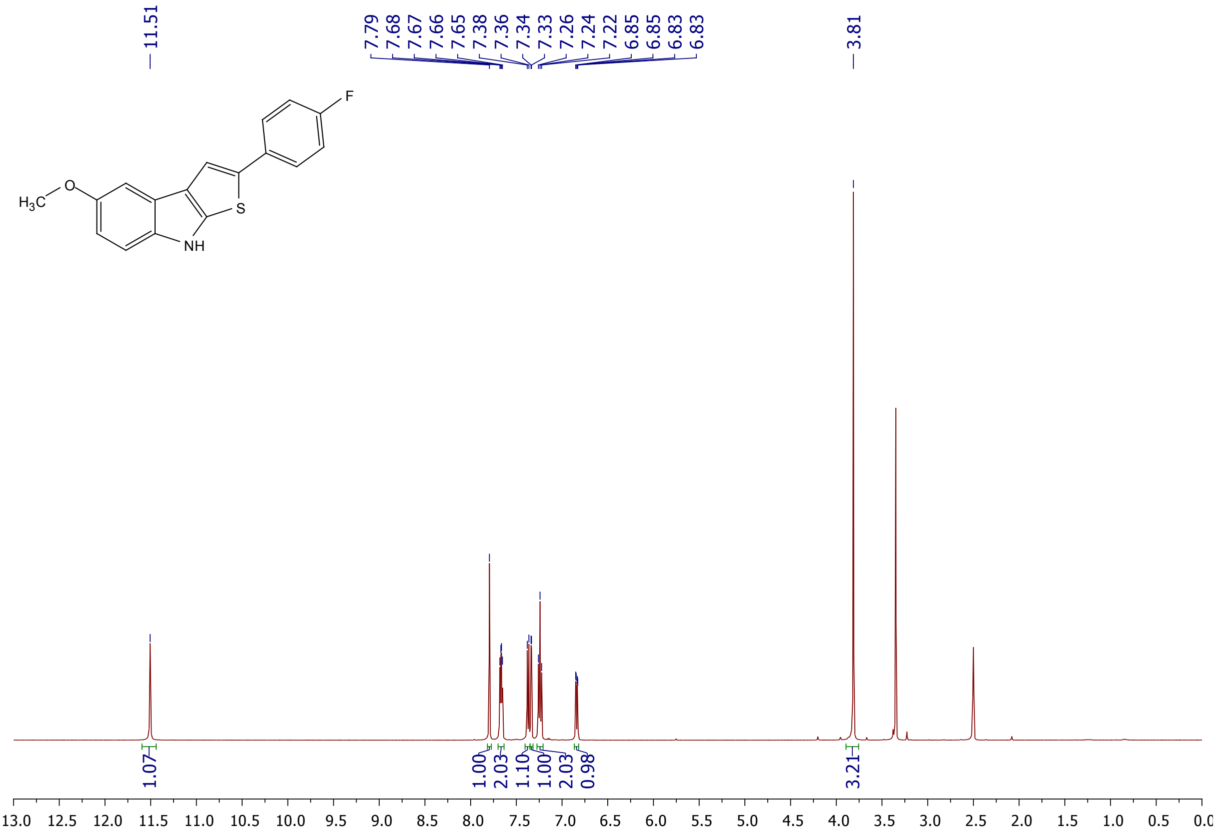


Figure S20. ^{1}H **(top) and** ^{13}C **(bottom) NMR spectra of 5-methoxy-2-(4-methoxyphenyl)-8*H*-thieno[2,3-*b*]indole 3m**



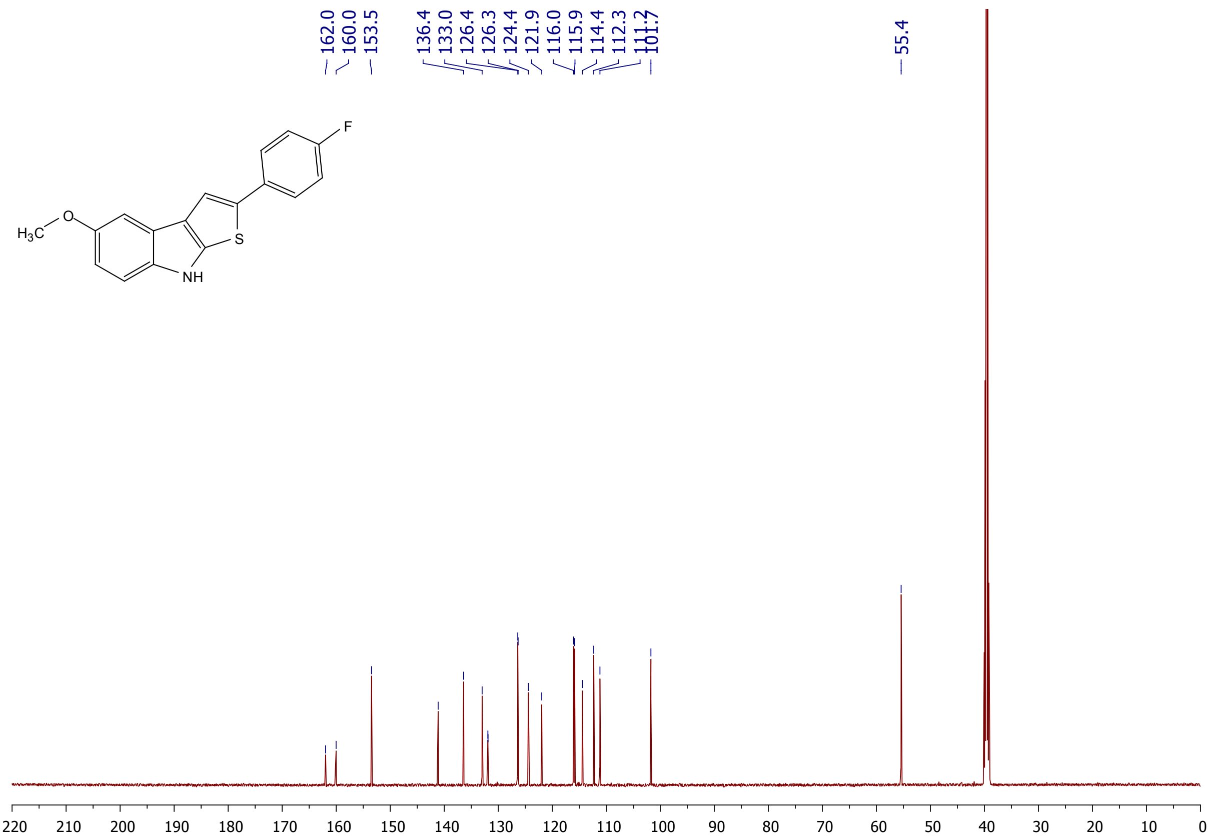
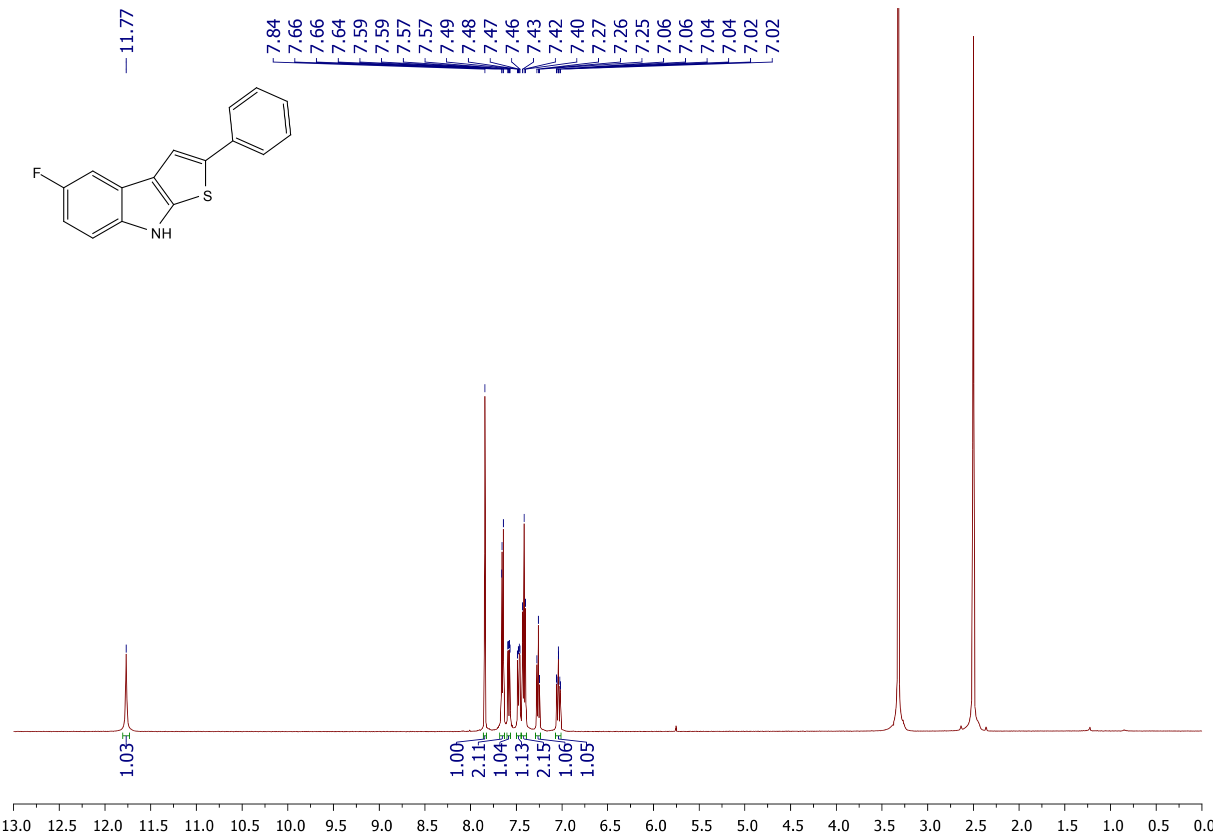


Figure S21. **^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-methoxy-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole 3n**



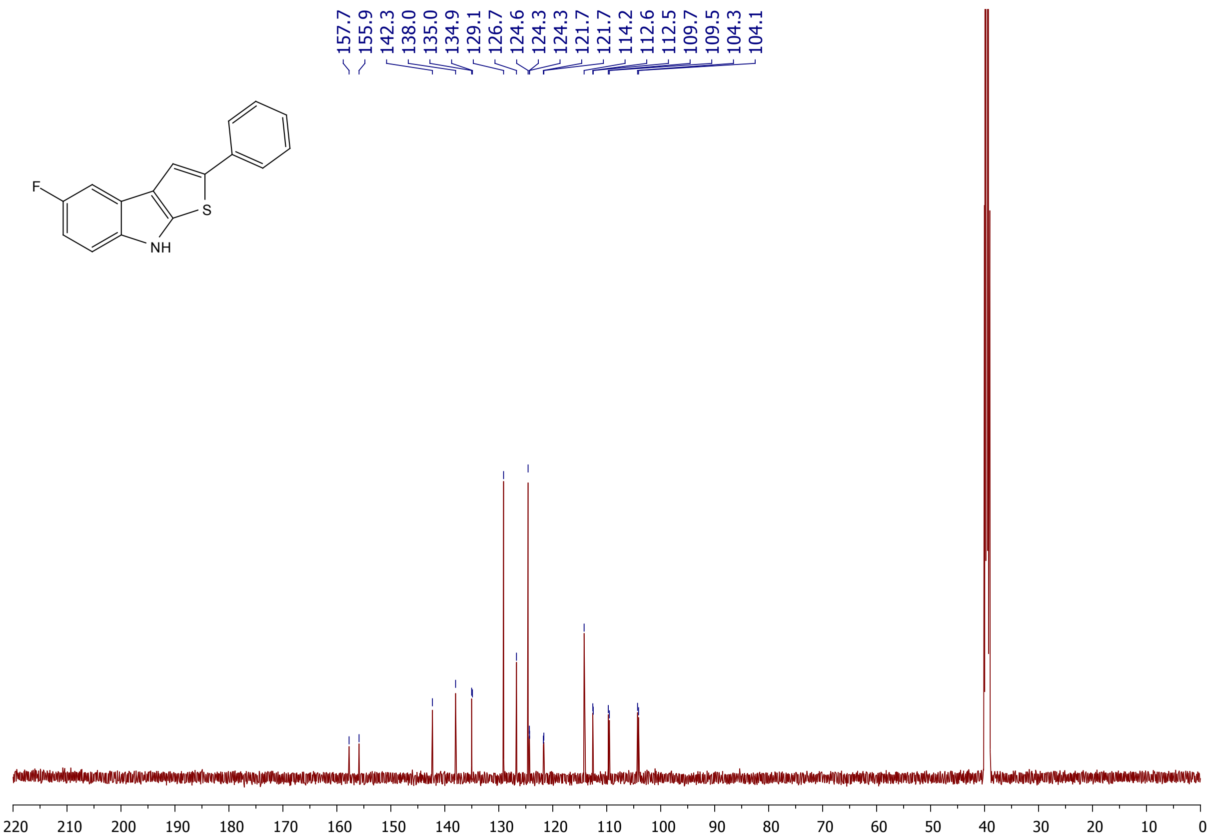
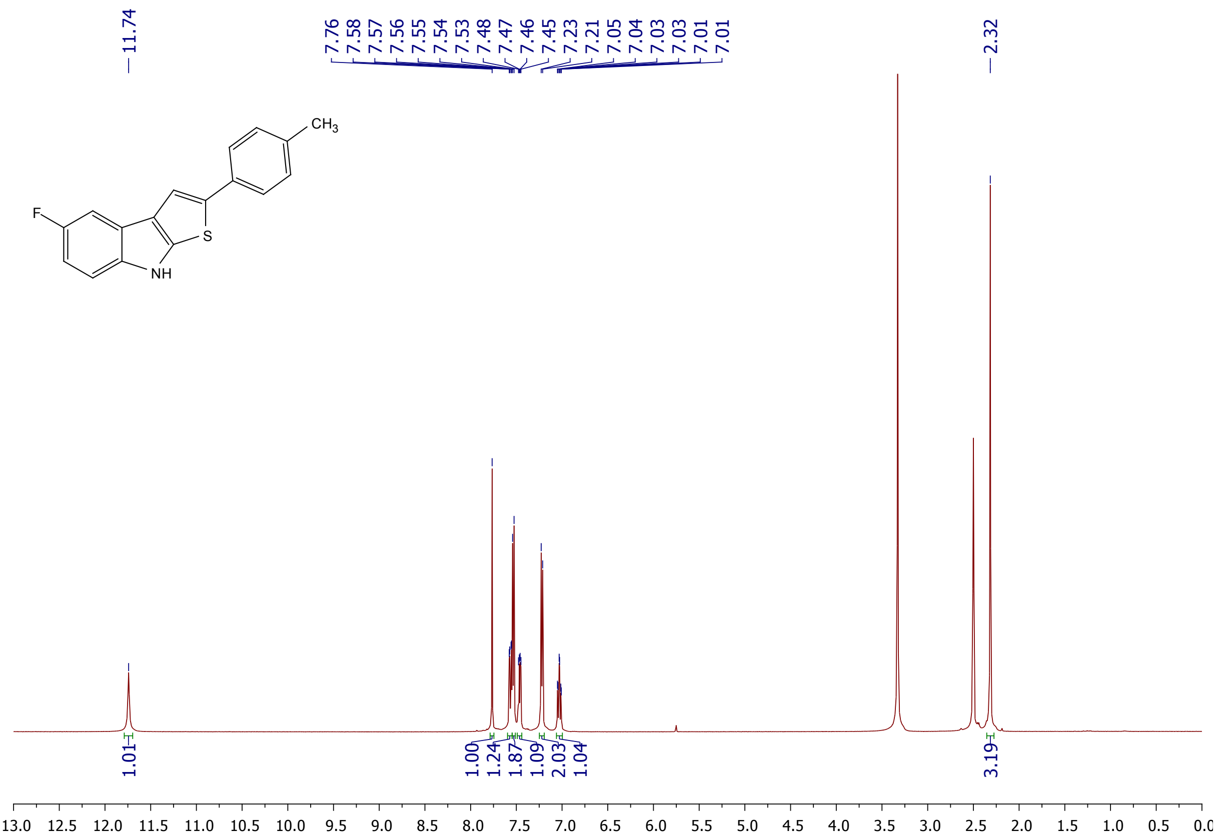


Figure S22. **^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-fluoro-2-phenyl-8*H*-thieno[2,3-*b*]indole 3o**



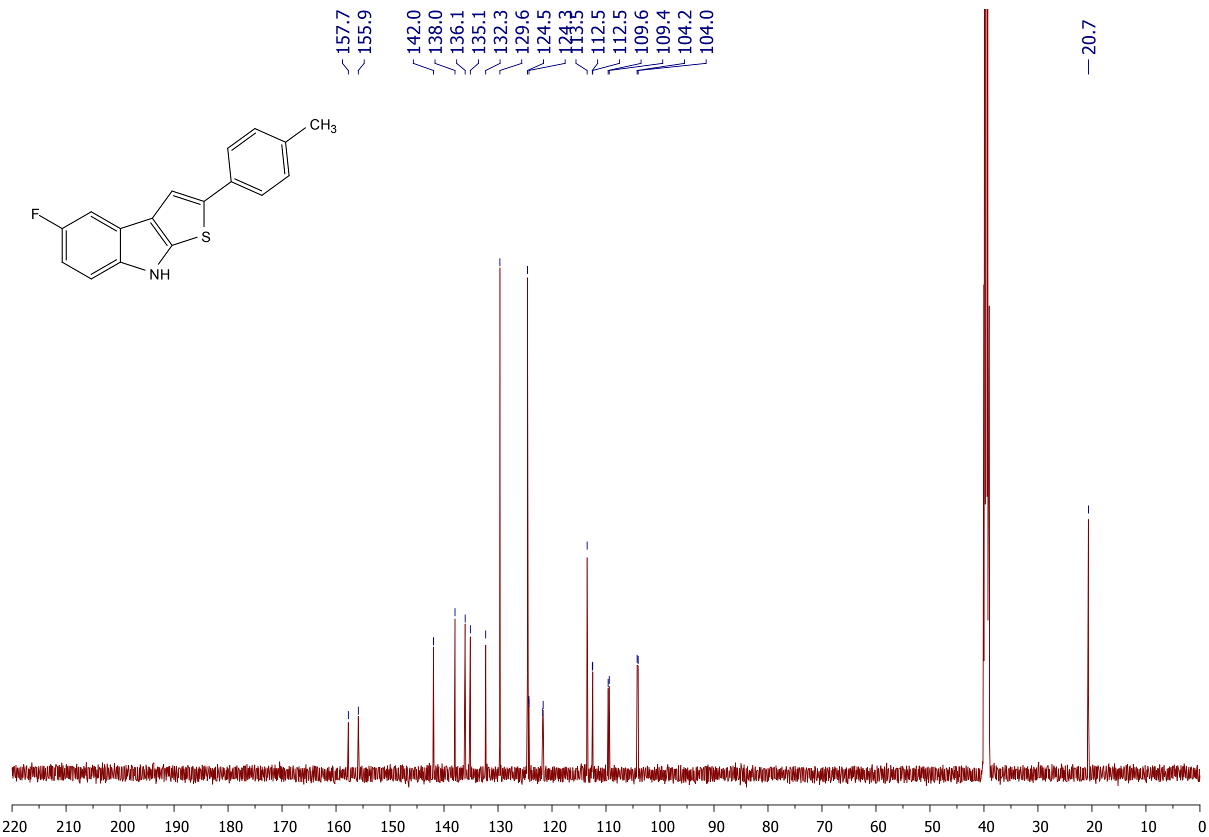


Figure S23. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-fluoro-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole 3p

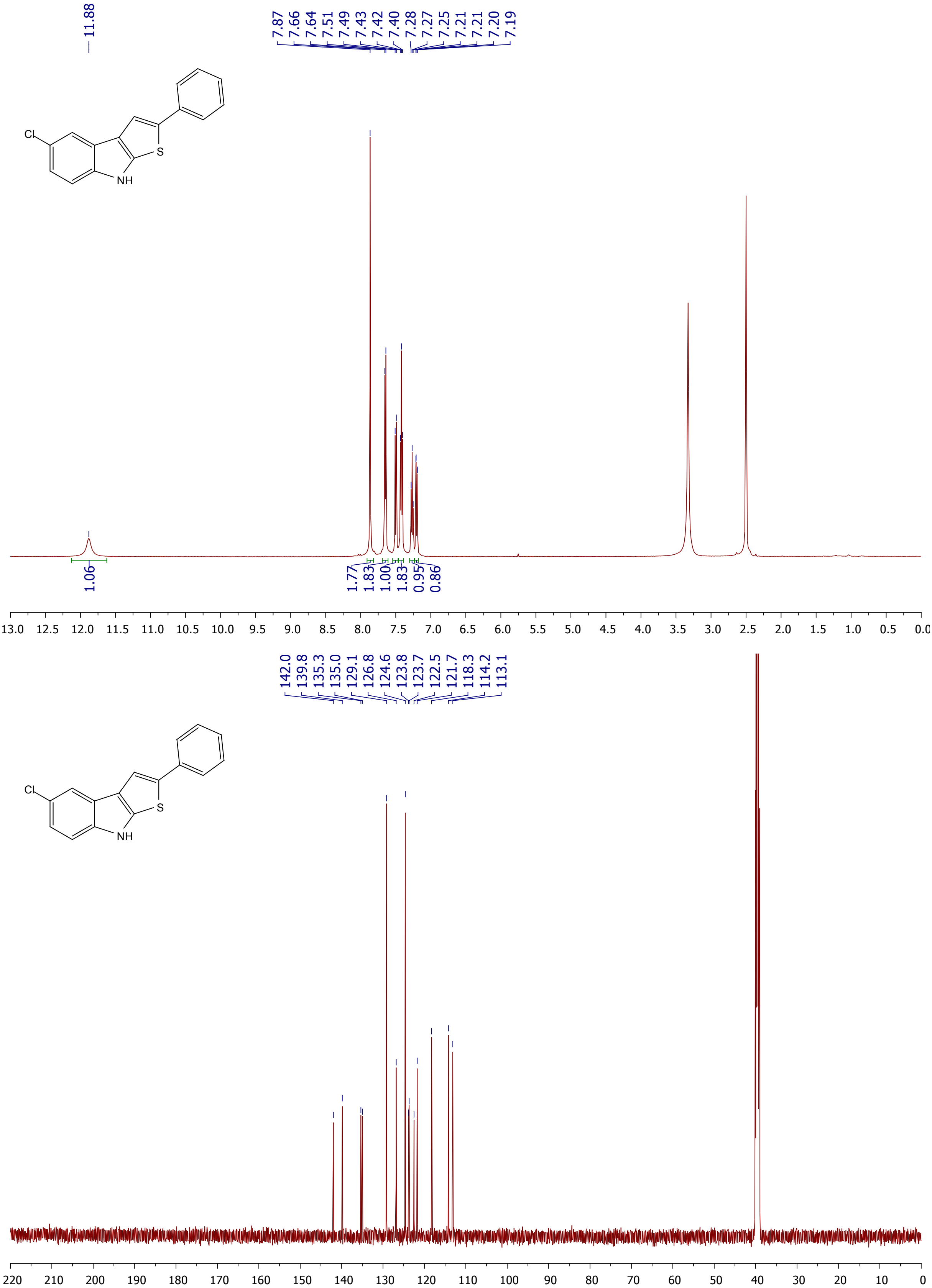
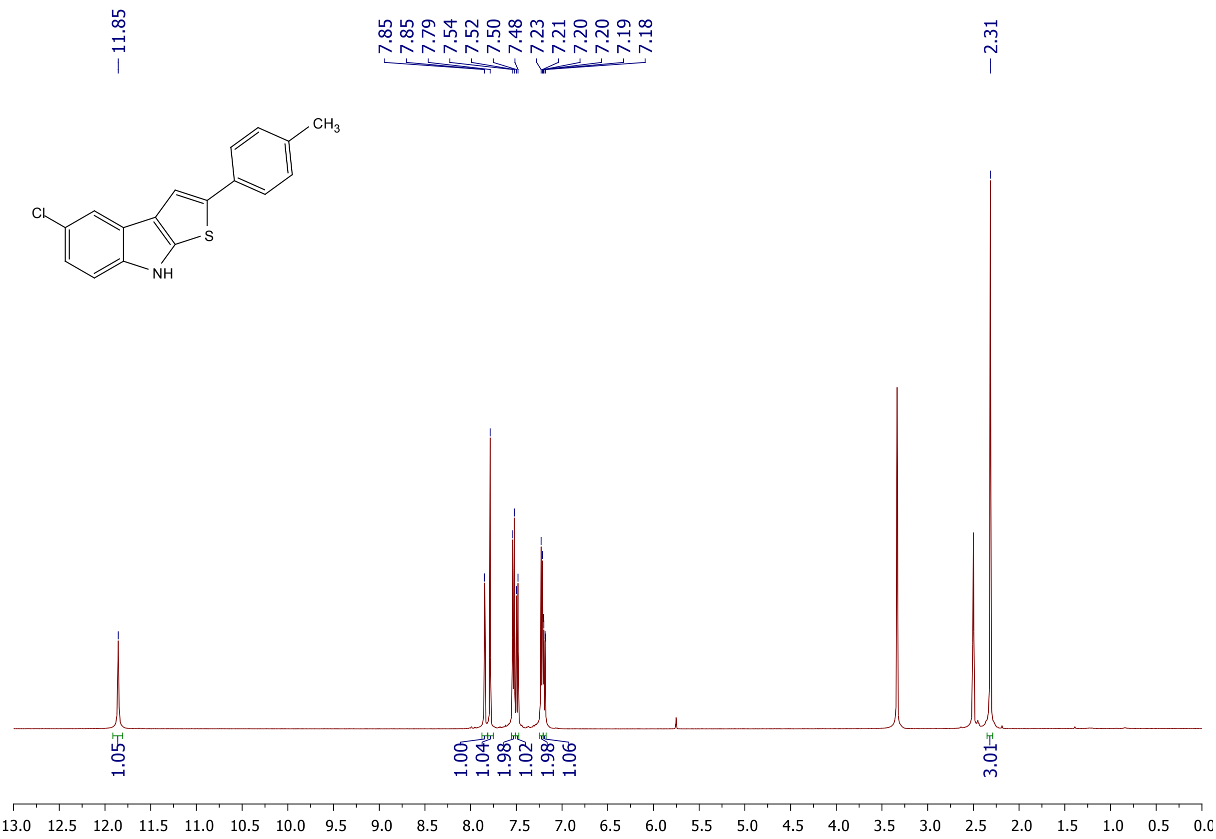


Figure S24. ^{1}H **(top) and** ^{13}C **(bottom) NMR spectra of 5-chloro-2-phenyl-8*H*-thieno[2,3-*b*]indole 3q**



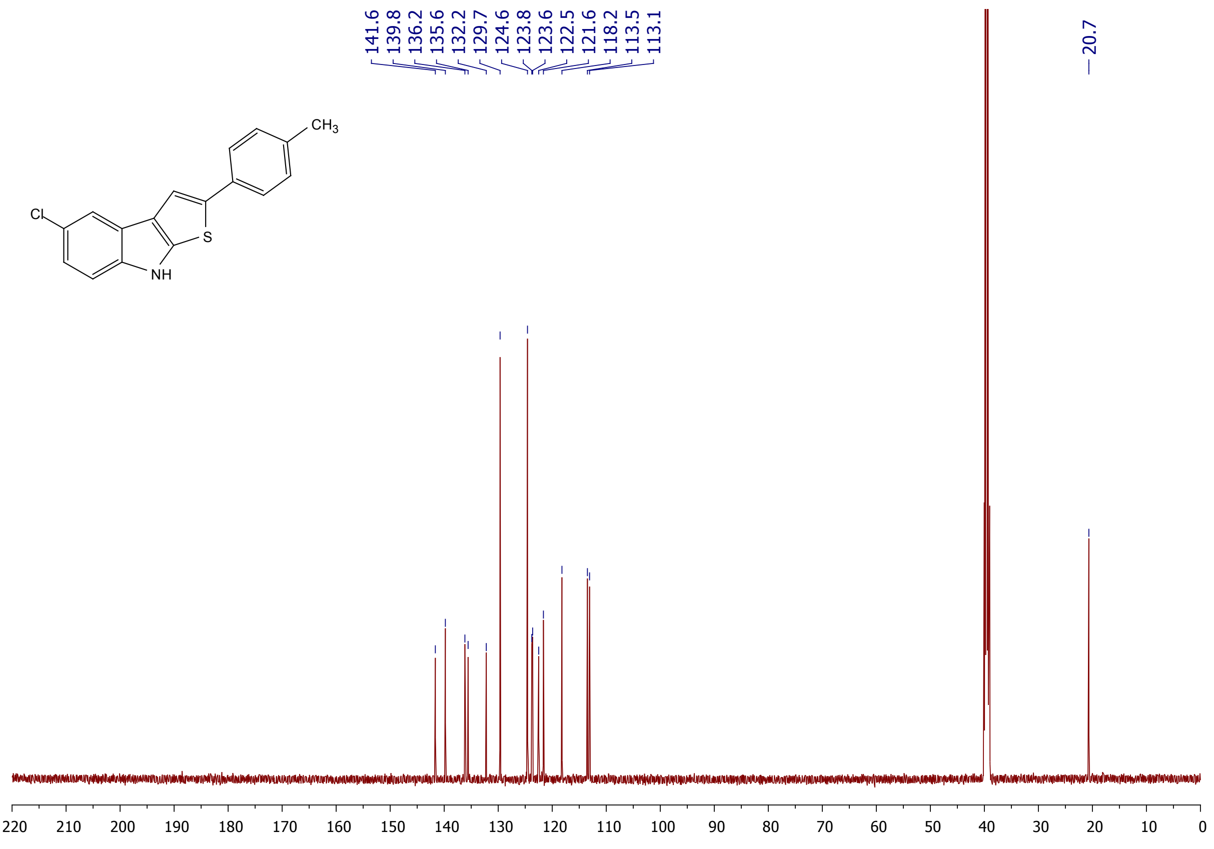


Figure S25. **^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-chloro-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole 3r**

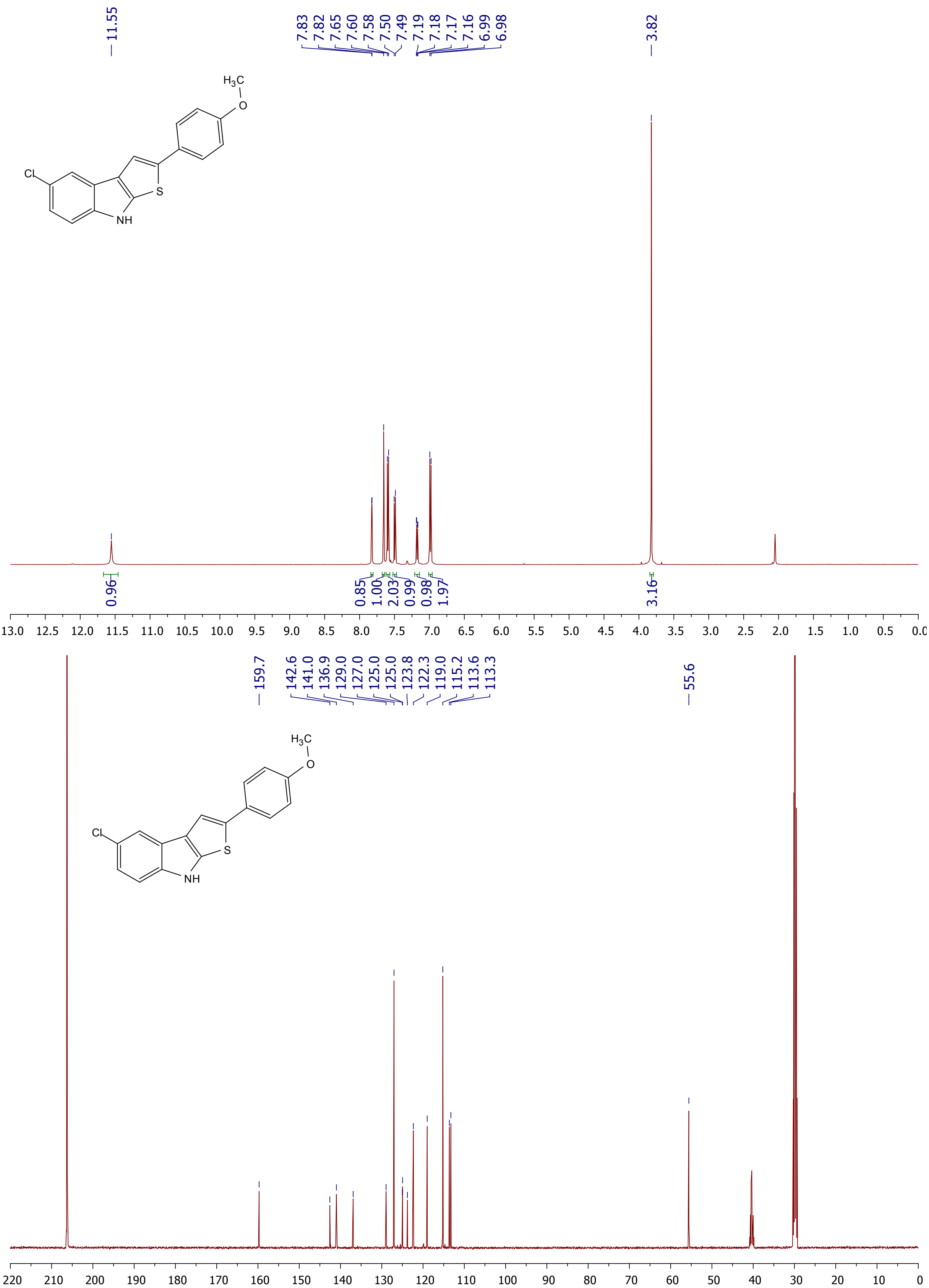


Figure S26. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-chloro-2-(4-methoxyphenyl)-8*H*-thieno[2,3-*b*]indole 3s

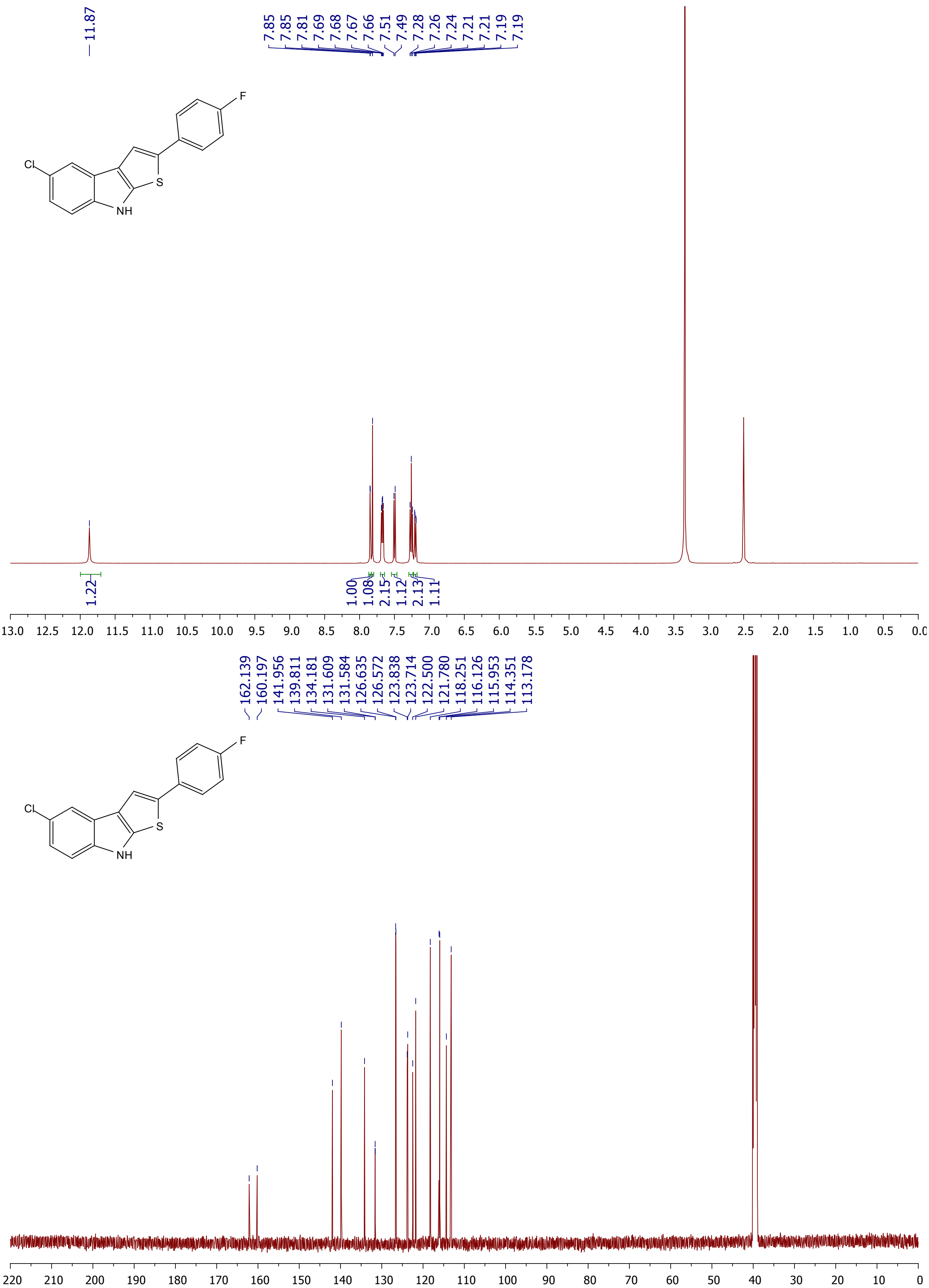


Figure S27. ^{1}H **(top) and** ^{13}C **(bottom) NMR spectra of 5-chloro-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole 3t**

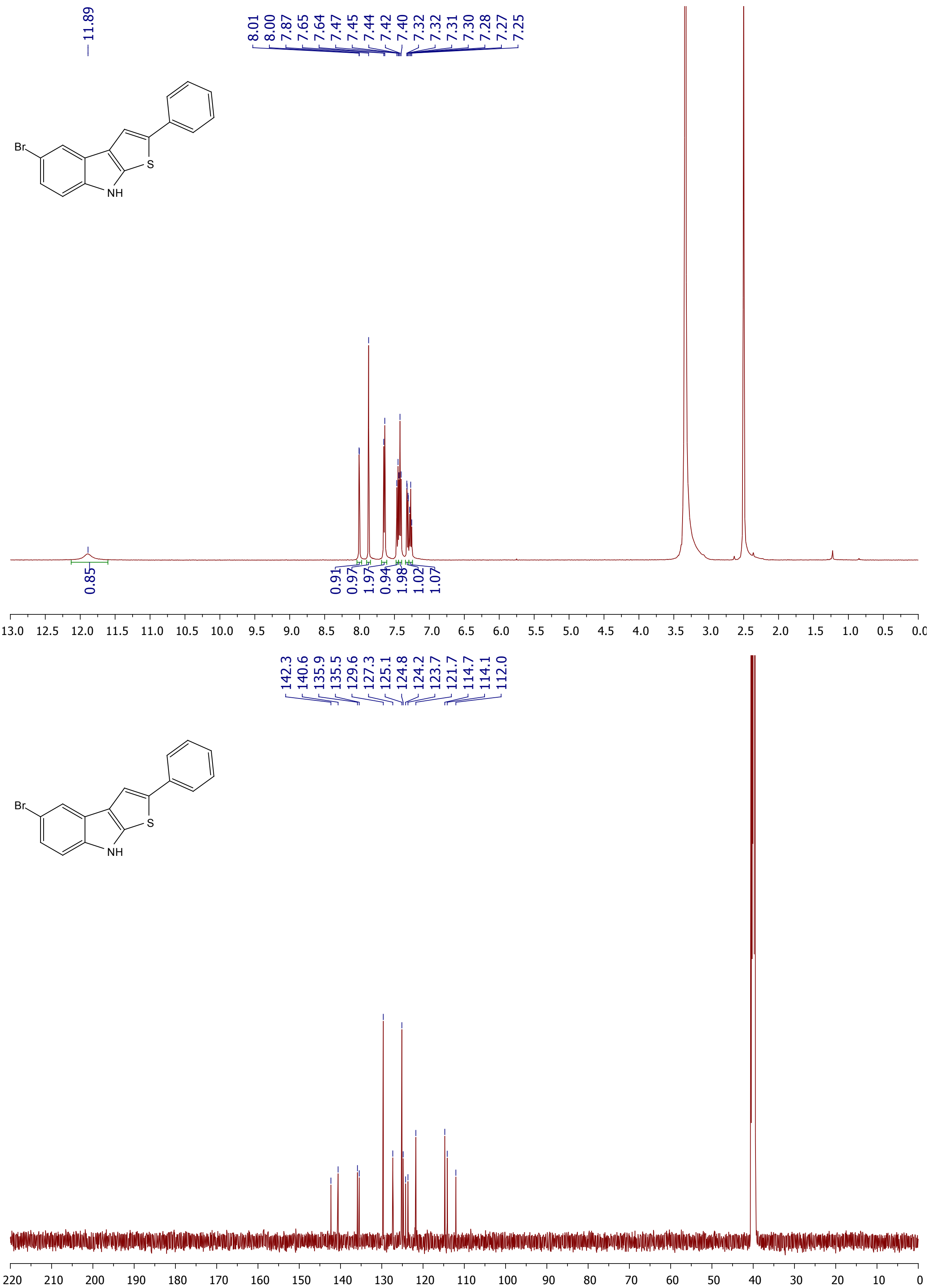
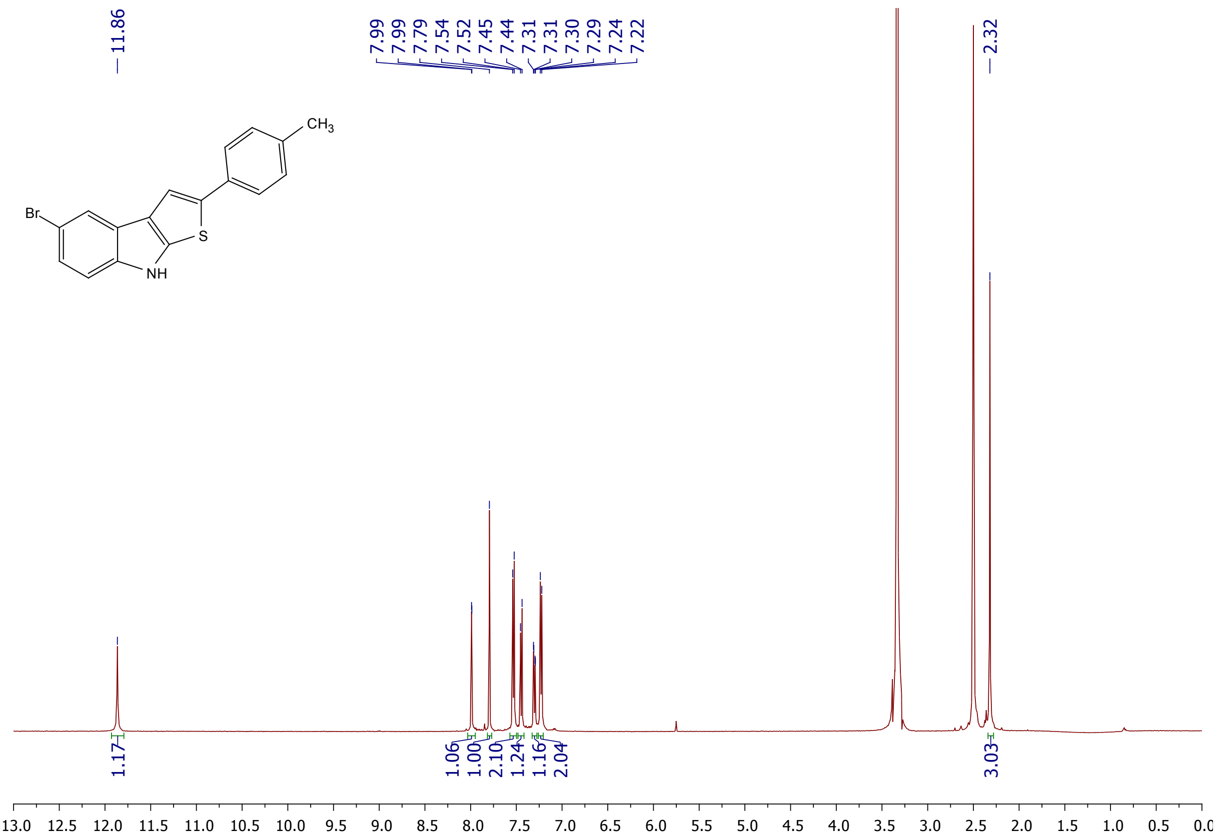


Figure S28. **^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-bromo-2-phenyl-8*H*-thieno[2,3-*b*]indole 3u**



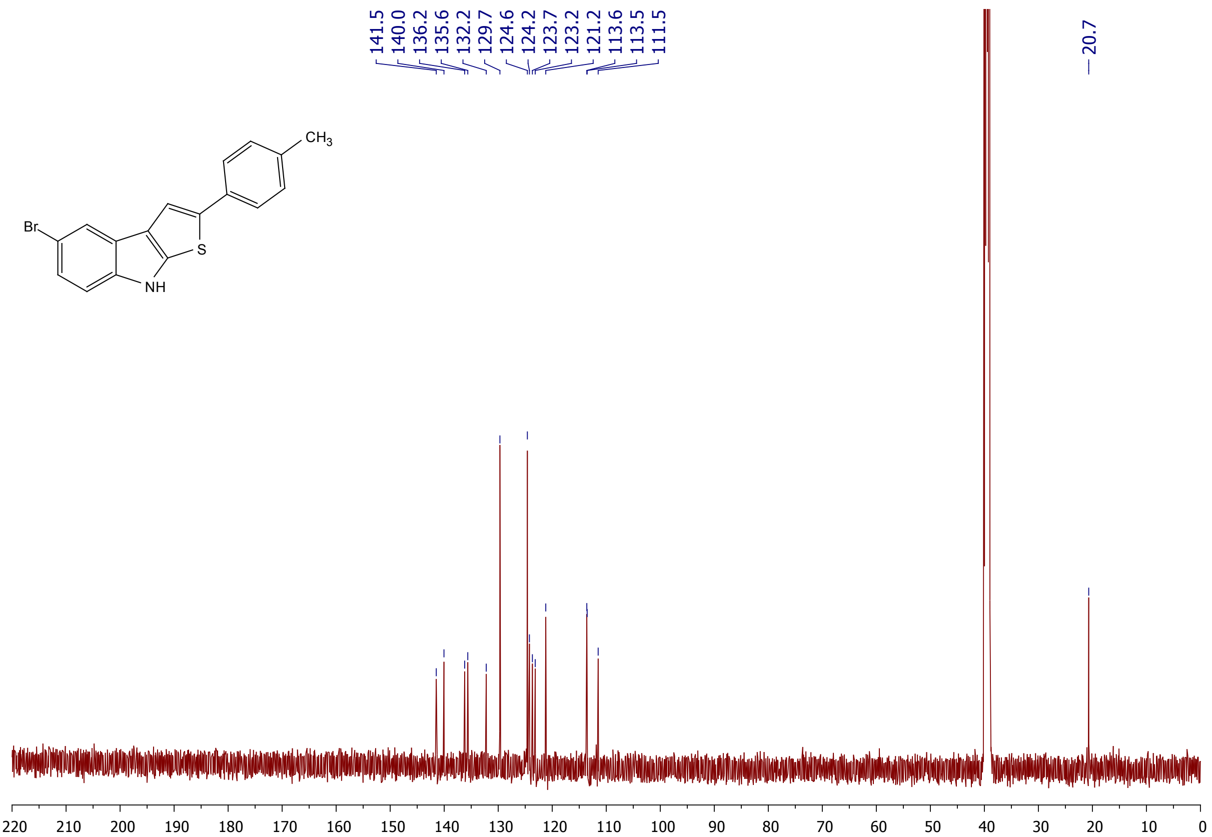
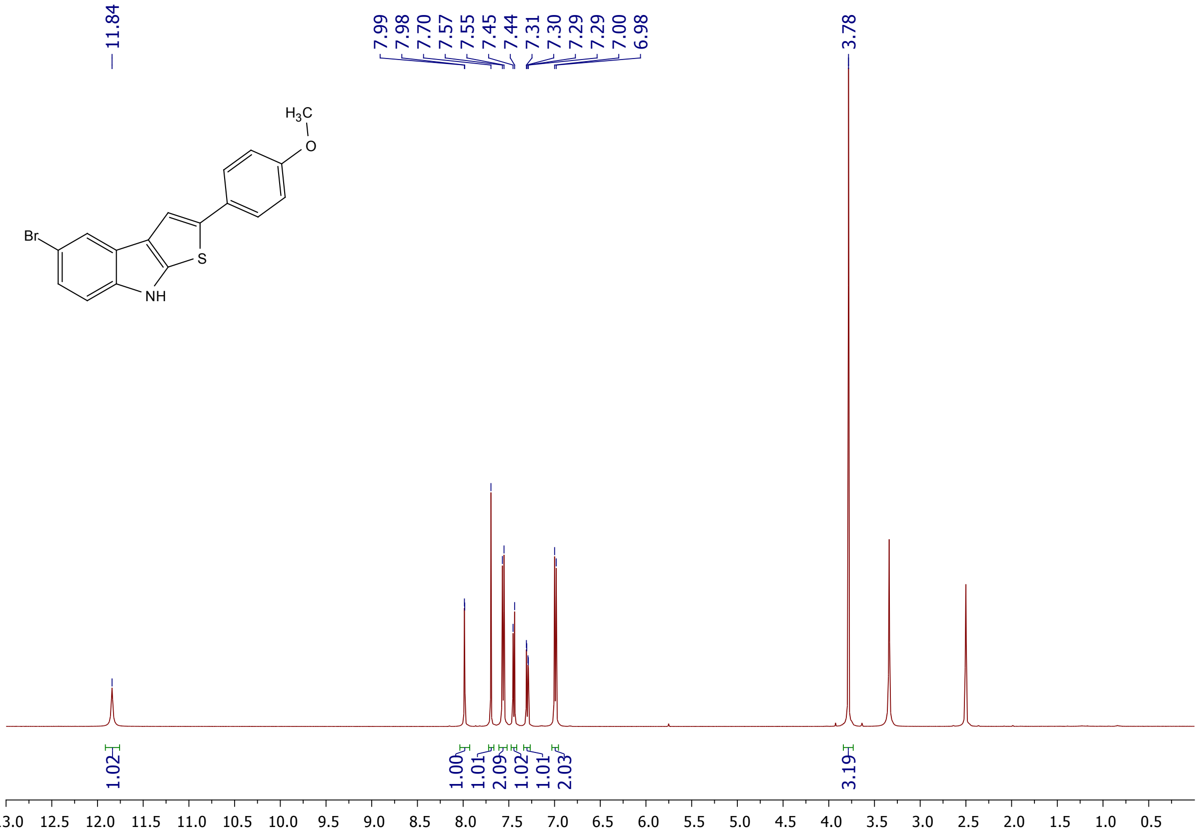


Figure S29. ^{1}H **(top) and** ^{13}C **(bottom) NMR spectra of 5-bromo-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole 3v**



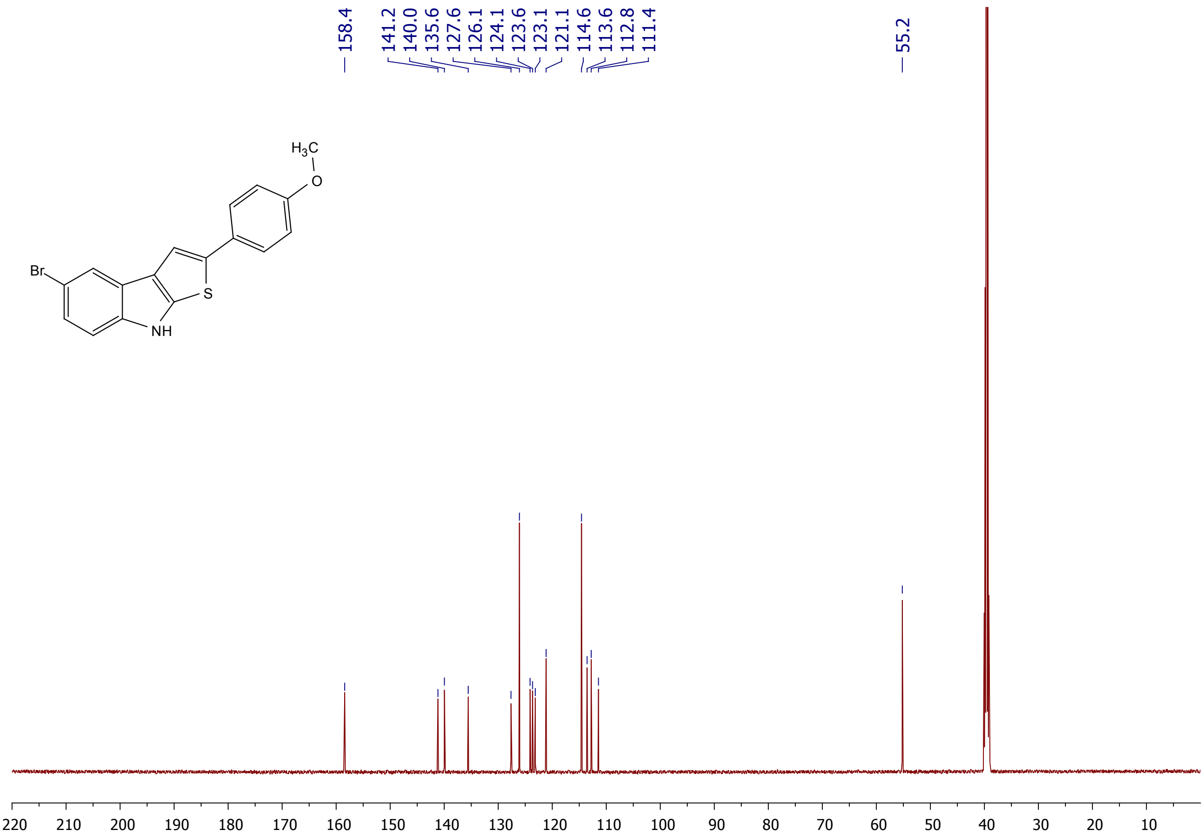


Figure S30. ^{1}**H (top) and** ^{13}**C (bottom) NMR spectra of 5-bromo-2-(4-methoxyphenyl)-8*H*-thieno[2,3-*b*]indole 3w**

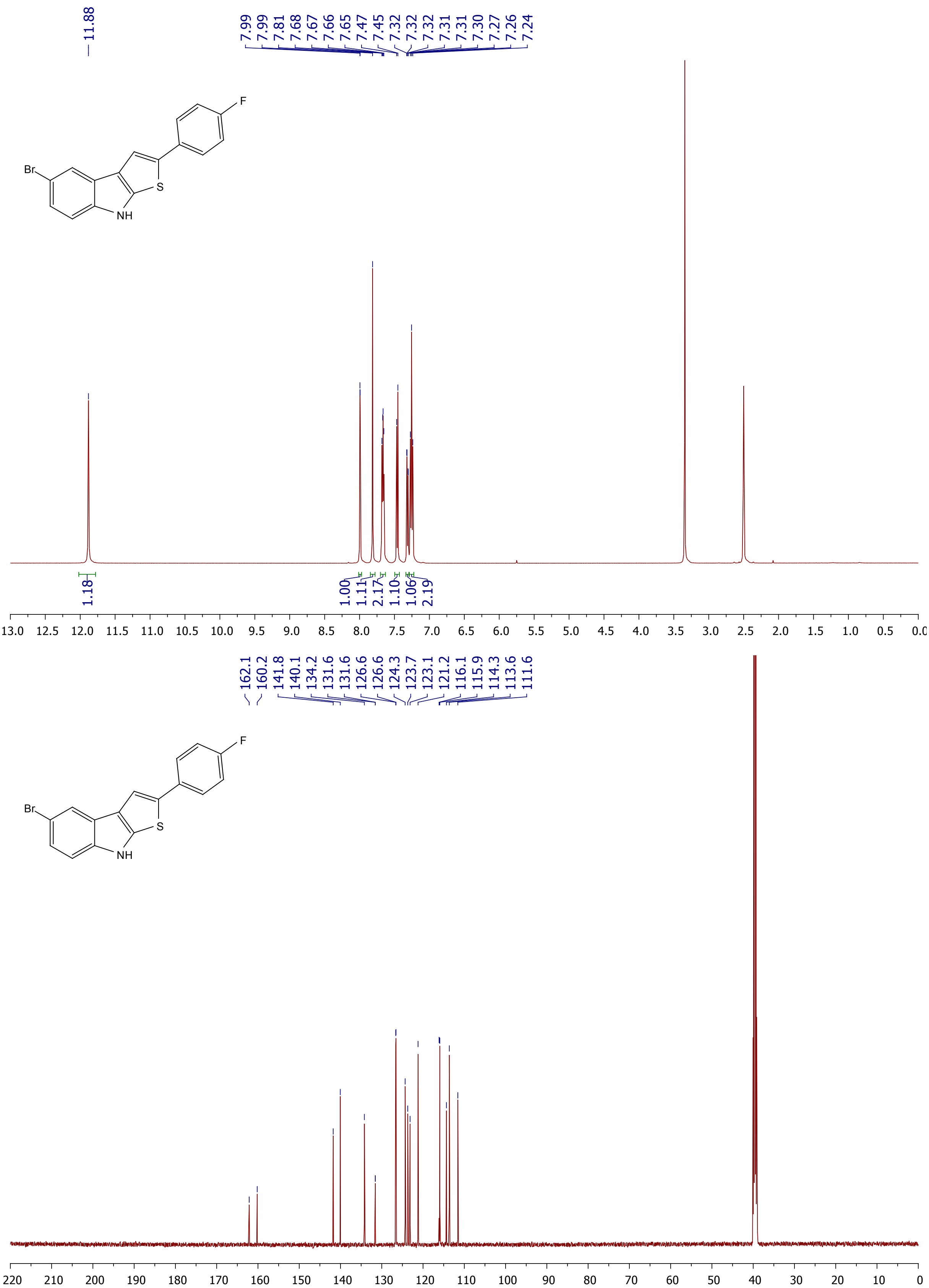
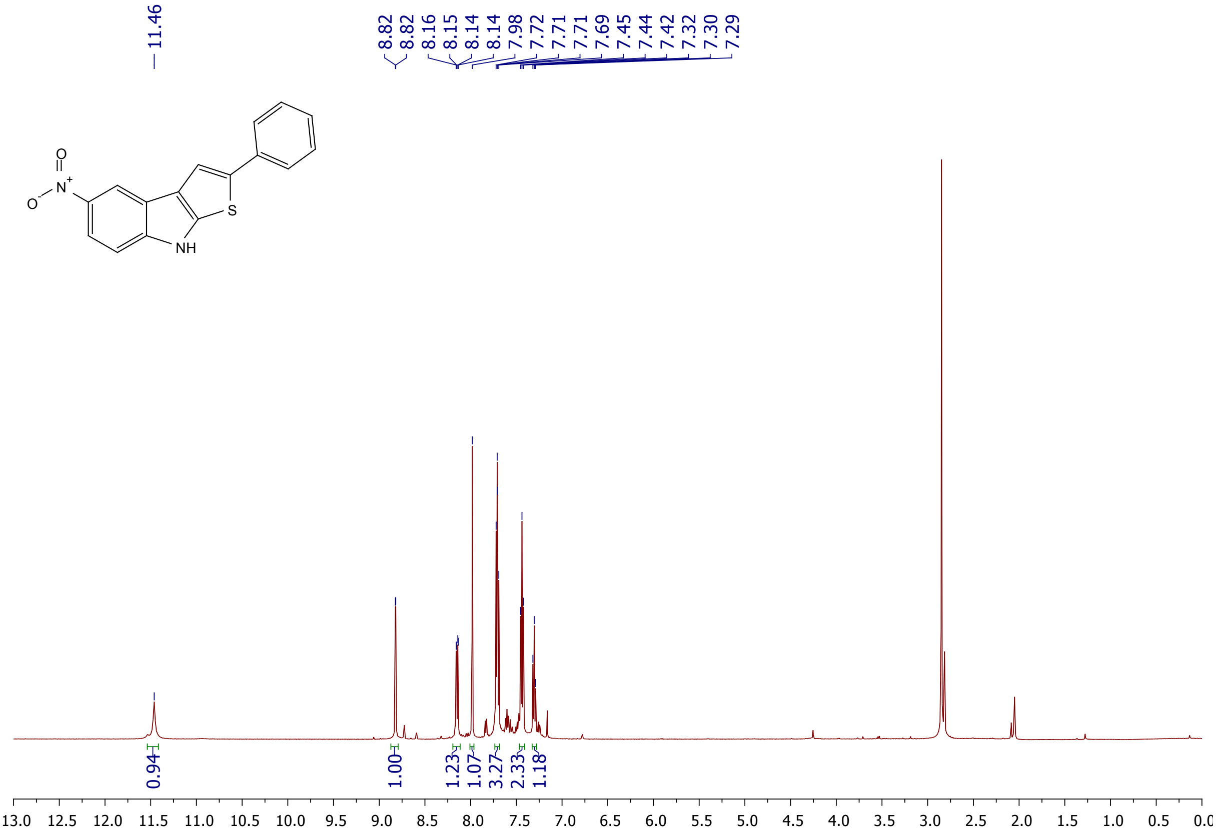


Figure S31. ^{1}**H (top) and** ^{13}**C (bottom) NMR spectra of 5-bromo-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole 3x**



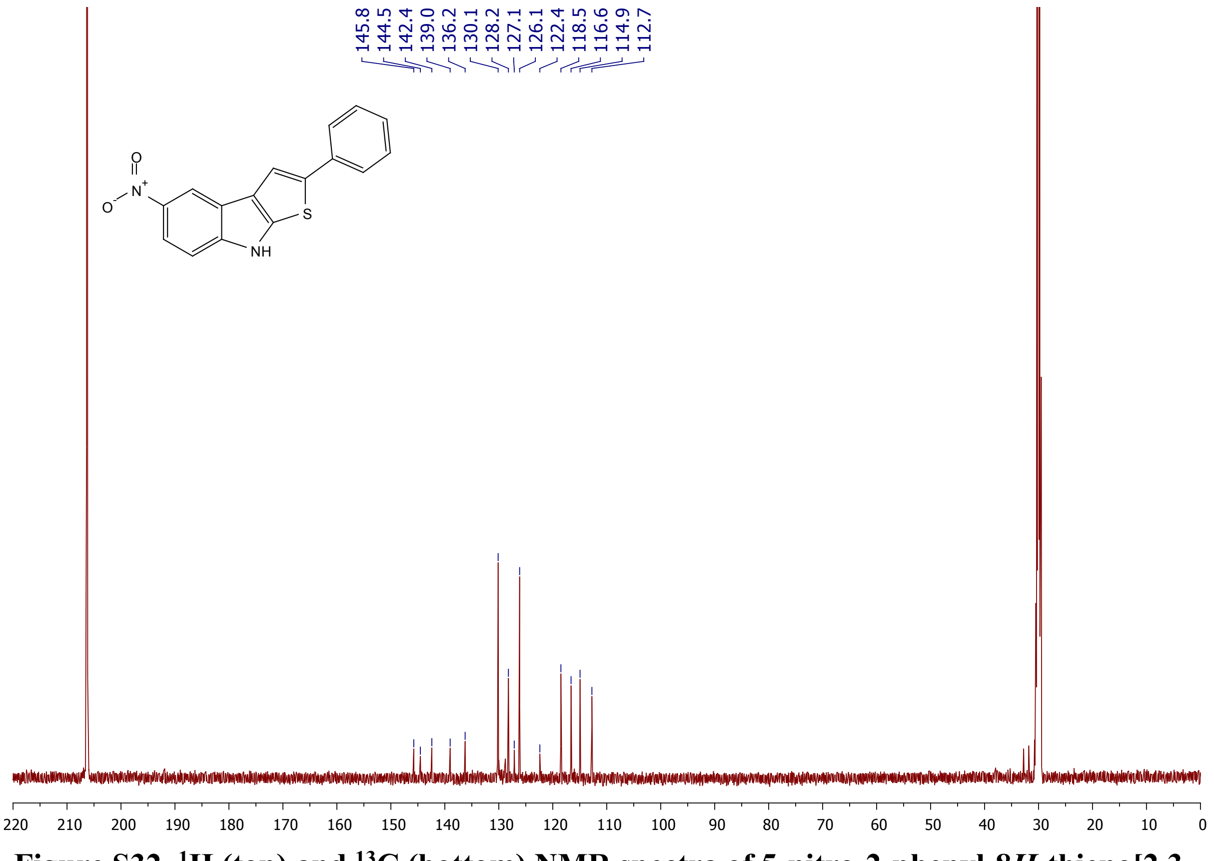


Figure S32. ^{1}**H (top) and** ^{13}**C (bottom) NMR spectra of 5-nitro-2-phenyl-8*H*-thieno[2,3-*b*]indole 3y**

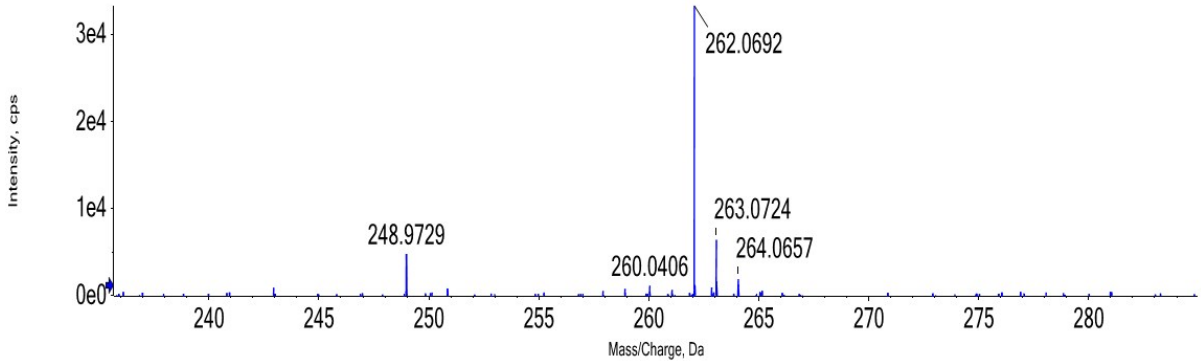


Figure S33. HMRS spectra of 2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole

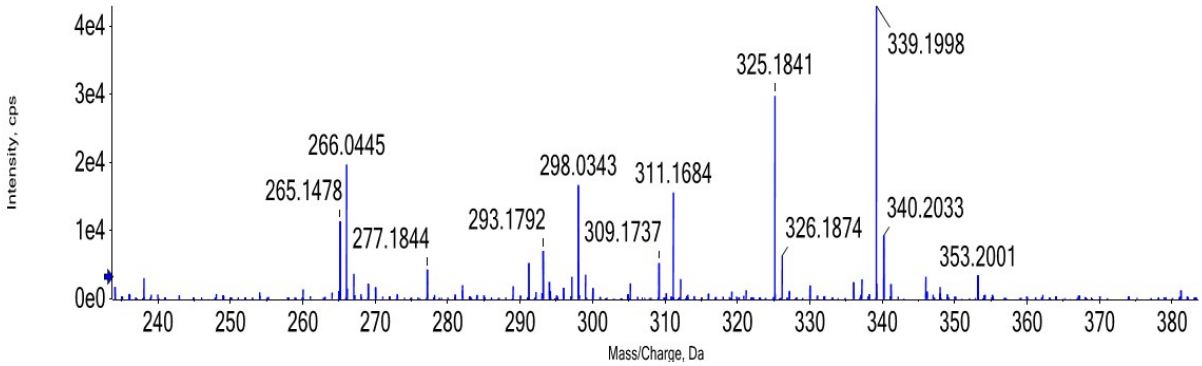


Figure S34. HRMS spectra of 2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole

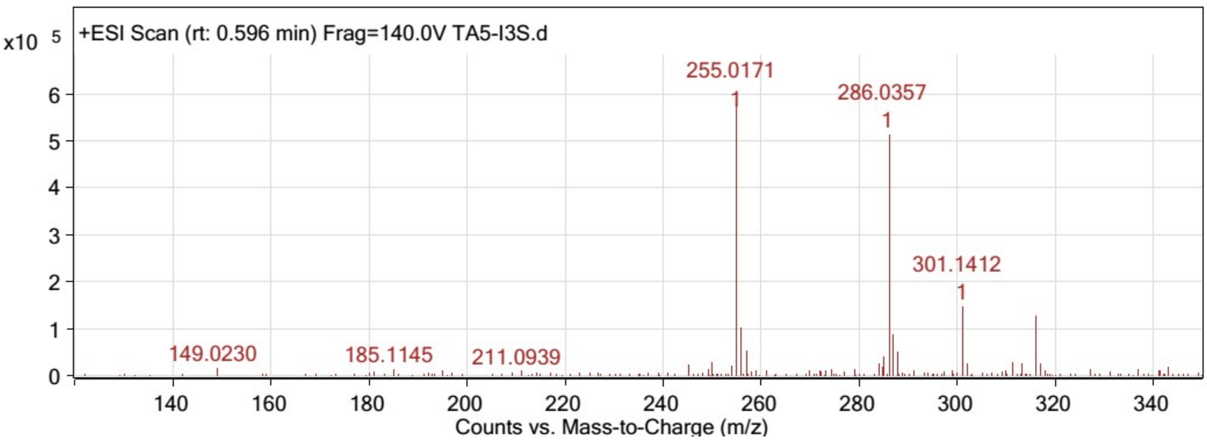


Figure S35. HRMS spectra of 2-(thiophen-2-yl)-8*H*-thieno[2,3-*b*]indole

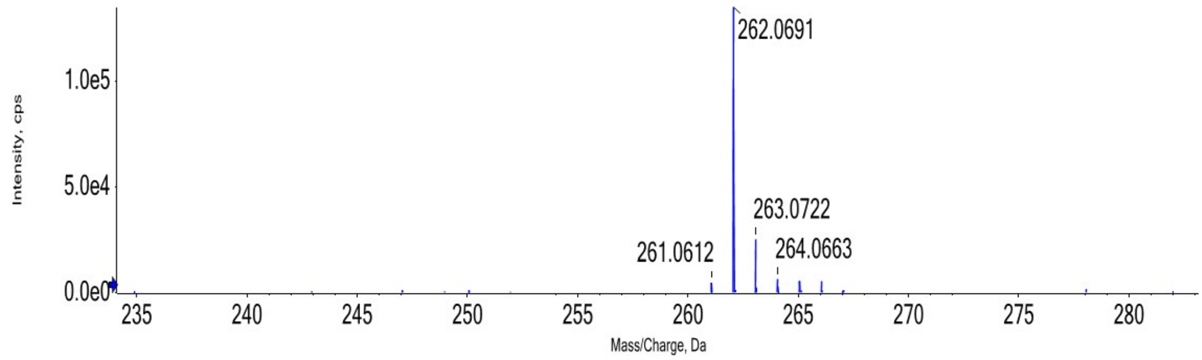


Figure S36. HRMS spectra of 5-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole

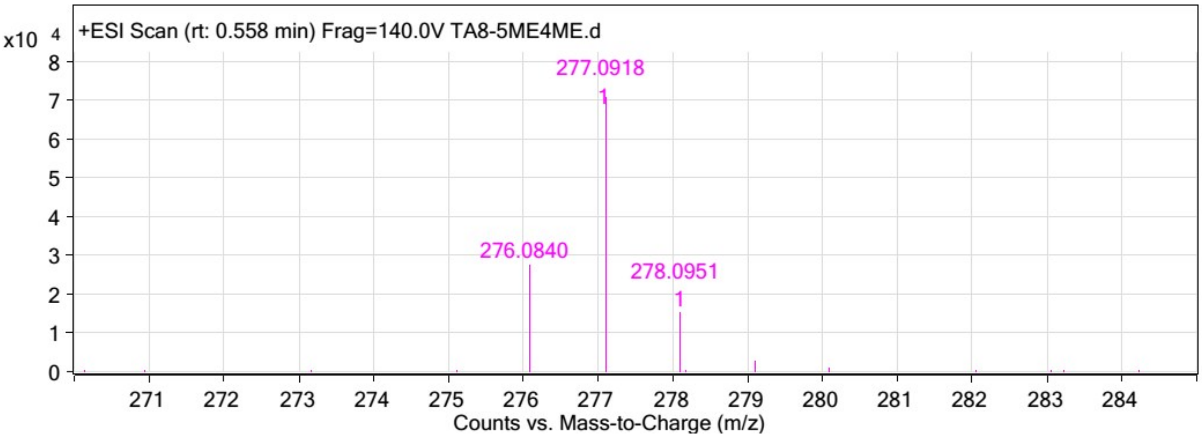


Figure S37. HRMS spectra of 5-methyl-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole

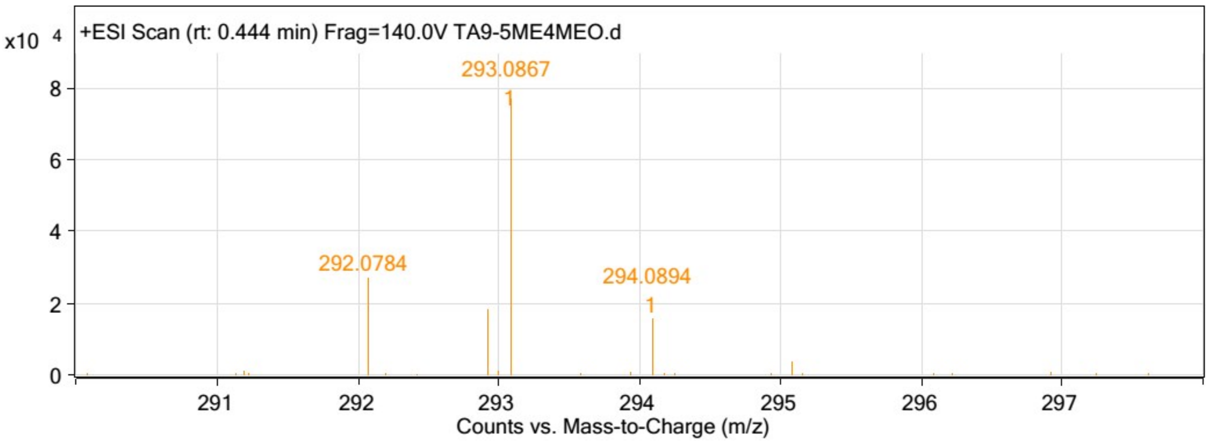


Figure S38. HRMS spectra of 2-(4-methoxyphenyl)-5-methyl-8*H*-thieno[2,3-*b*]indole

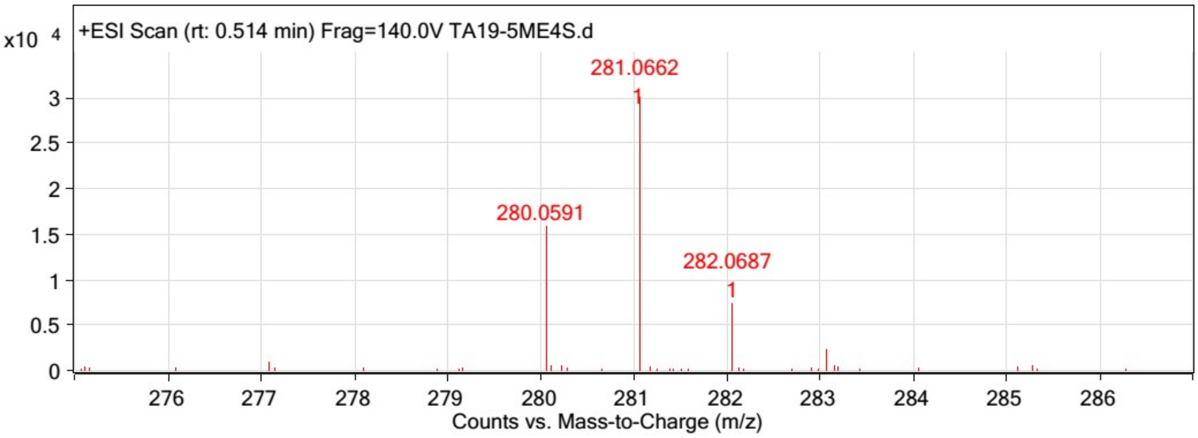


Figure S39. HRMS spectra of 2-(4-fluorophenyl)-5-methyl-8*H*-thieno[2,3-*b*]indole

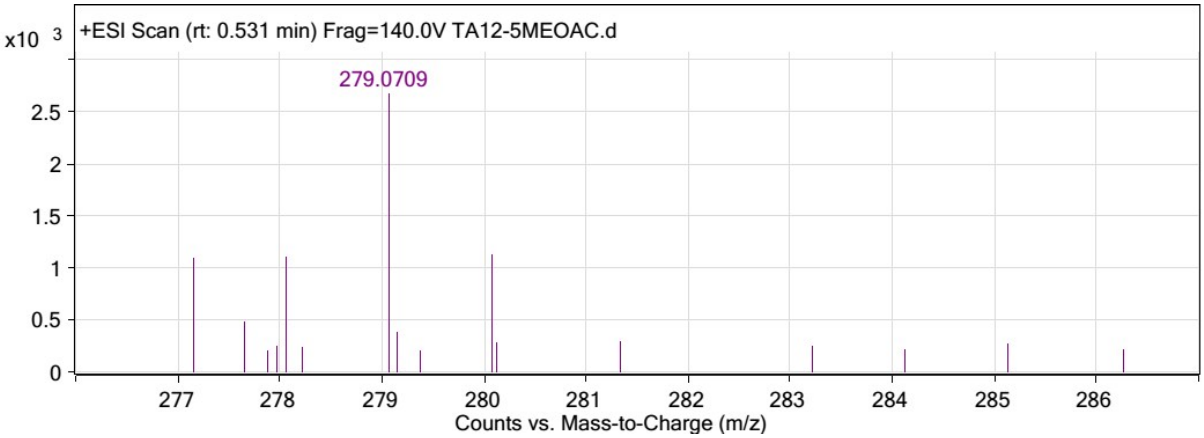


Figure S40. HRMS spectra of 5-methoxy-2-phenyl-8*H*-thieno[2,3-*b*]indole

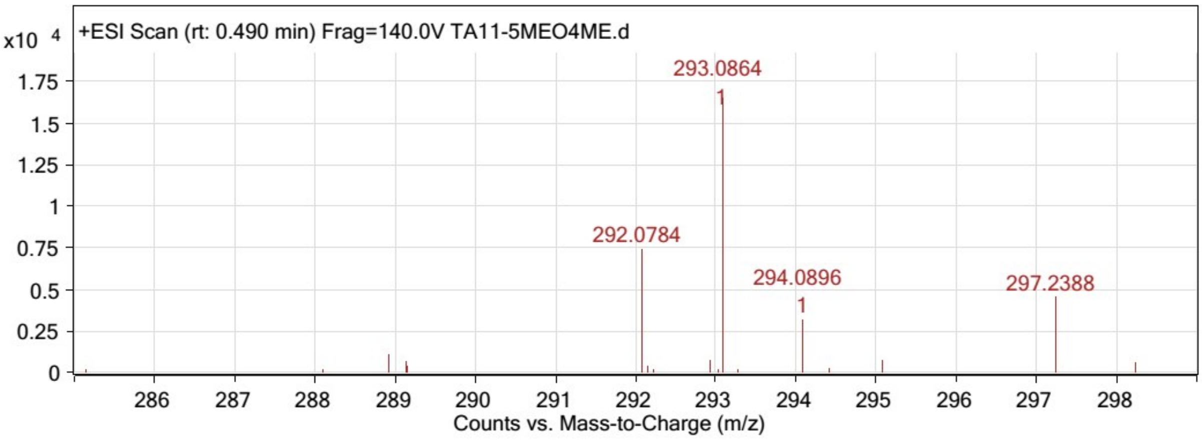


Figure S41. HRMS spectra of 5-methoxy-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole

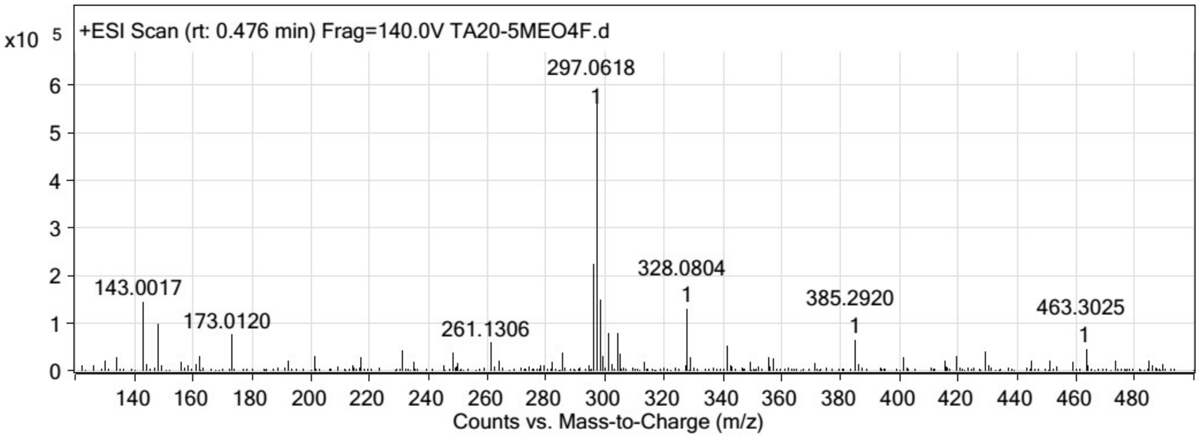


Figure S42. HRMS spectra of 5-methoxy-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole

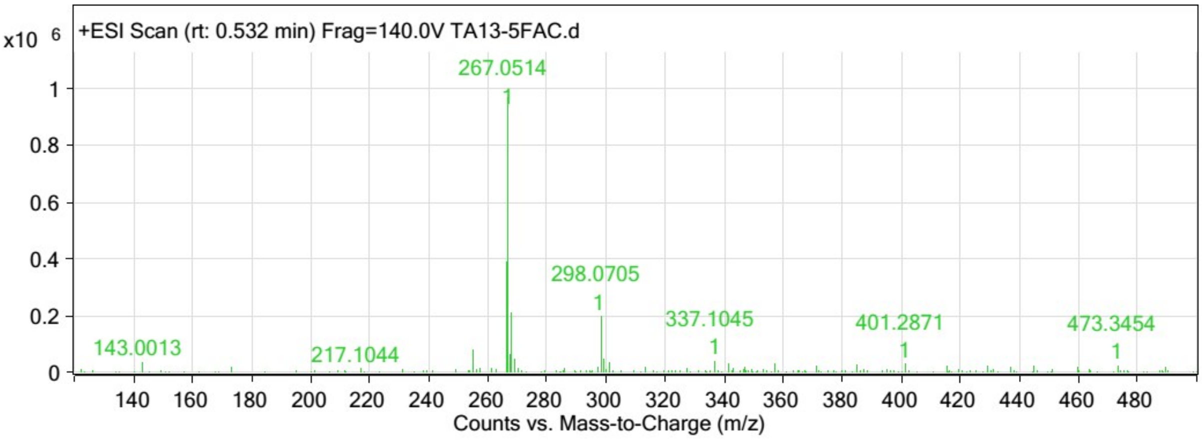


Figure S43. HRMS spectra of 5-fluoro-2-phenyl-8*H*-thieno[2,3-*b*]indole

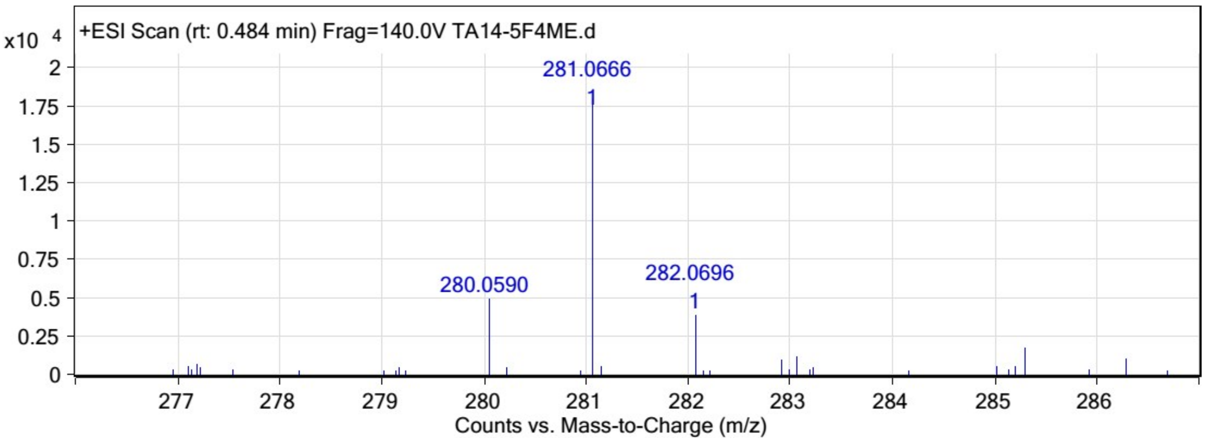


Figure S44. HRMS spectra of 5-fluoro-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole

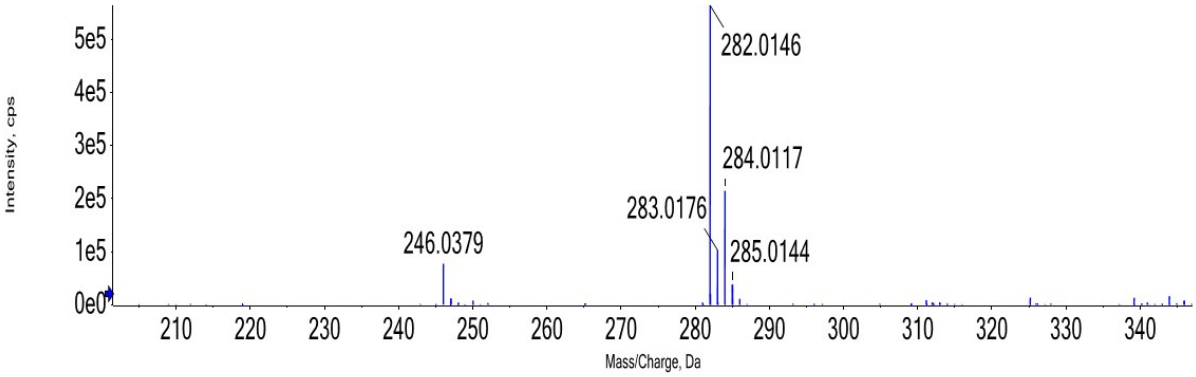


Figure S45. HRMS spectra of 5-chloro-2-phenyl-8*H*-thieno[2,3-*b*]indole

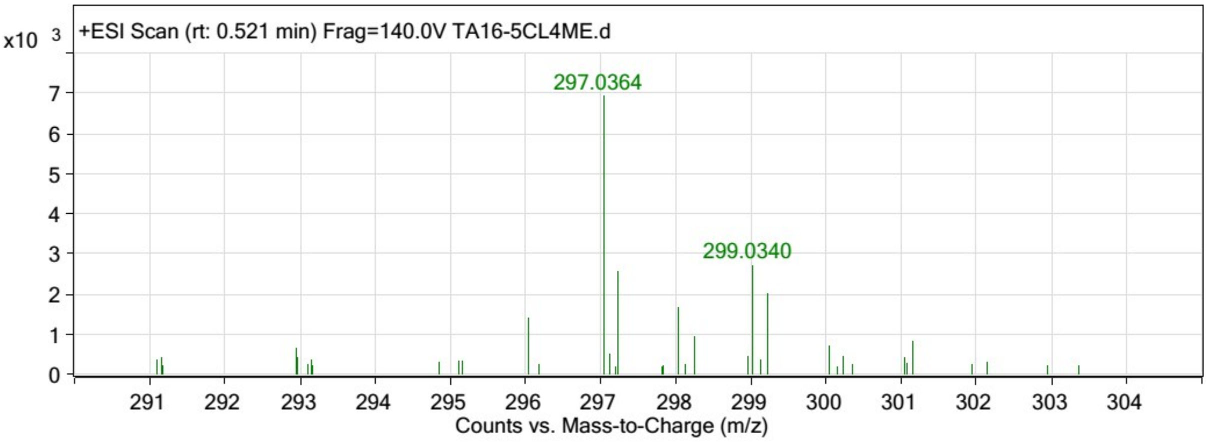


Figure S46. HRMS spectra of 5-chloro-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole

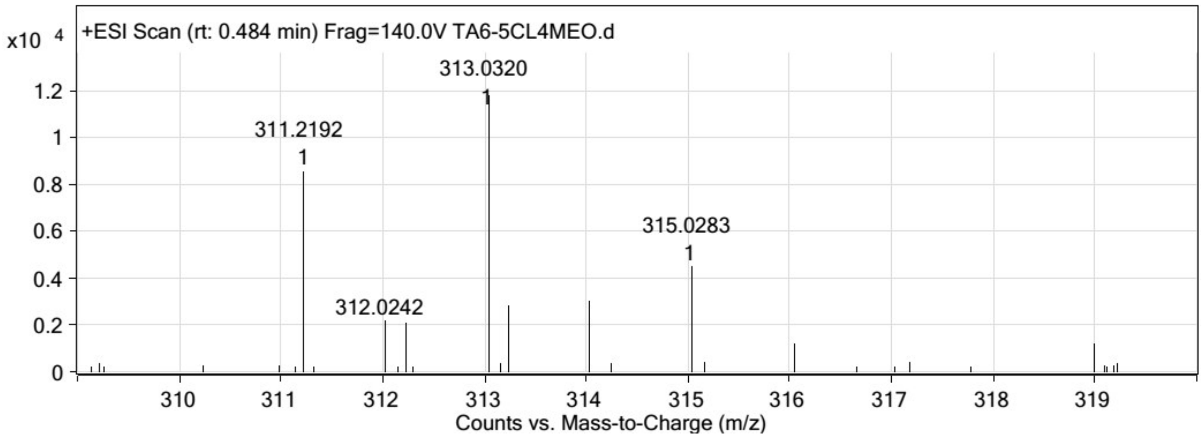


Figure S47. HRMS spectra of 5-chloro-2-(4-methoxyphenyl)-8*H*-thieno[2,3-*b*]indole

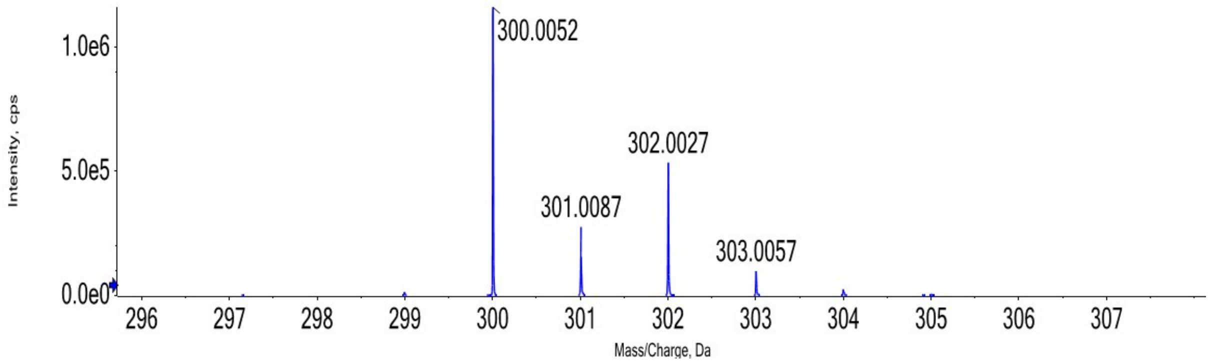


Figure S48. HRMS spectra of 5-chloro-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole

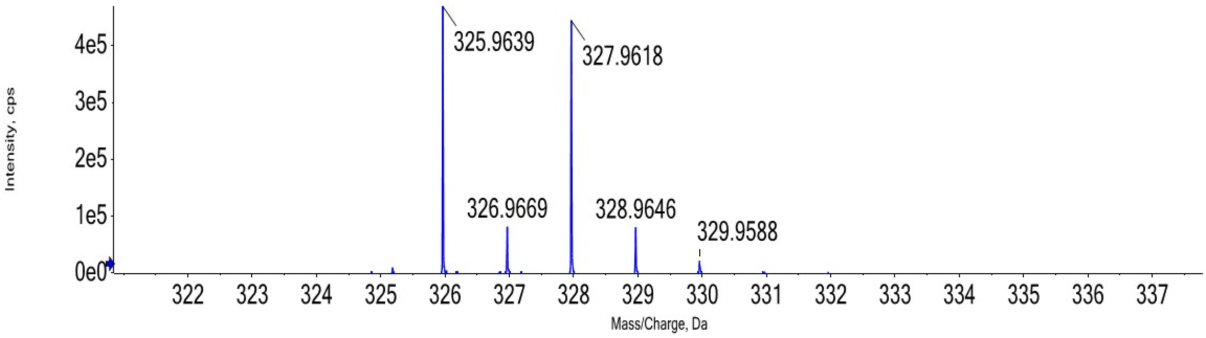


Figure S49. HRMS spectra of 5-bromo-2-phenyl-8*H*-thieno[2,3-*b*]indole

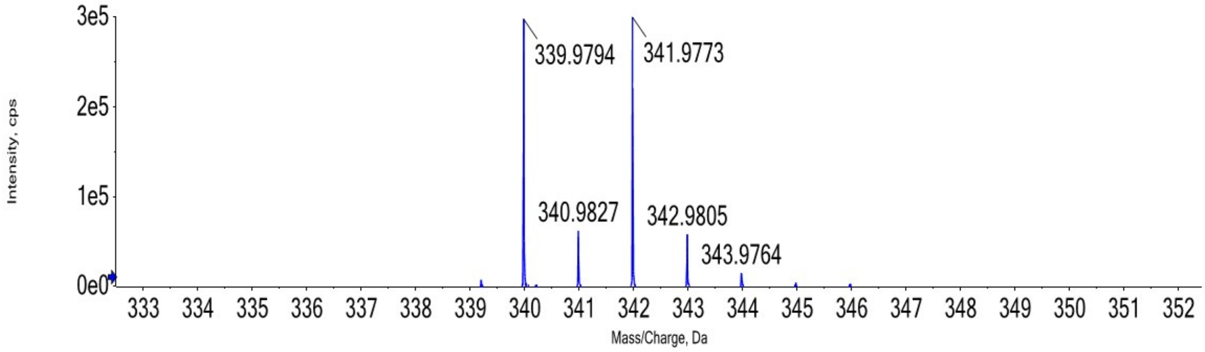


Figure S50. HRMS spectra of 5-bromo-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole

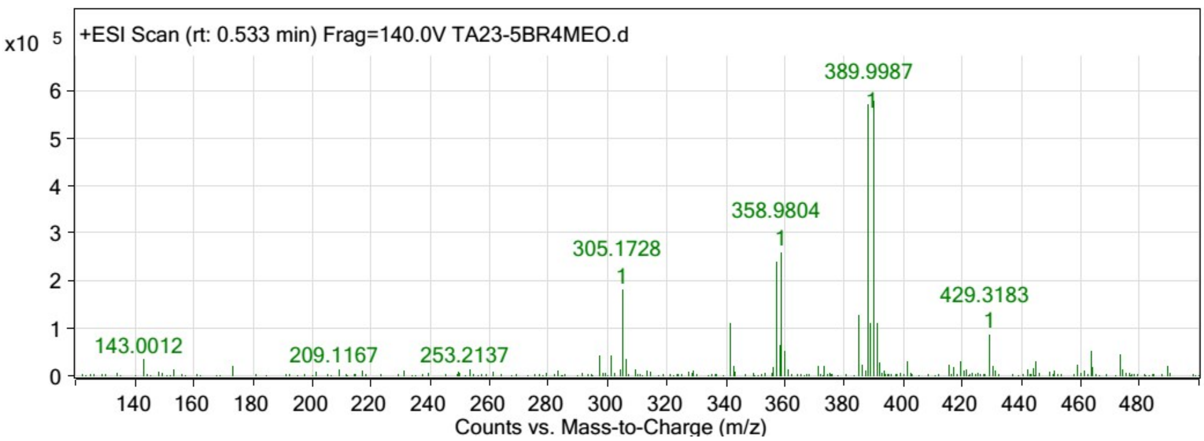


Figure S51. HRMS spectra of 5-bromo-2-(4-methoxyphenyl)-8*H*-thieno[2,3-*b*]indole

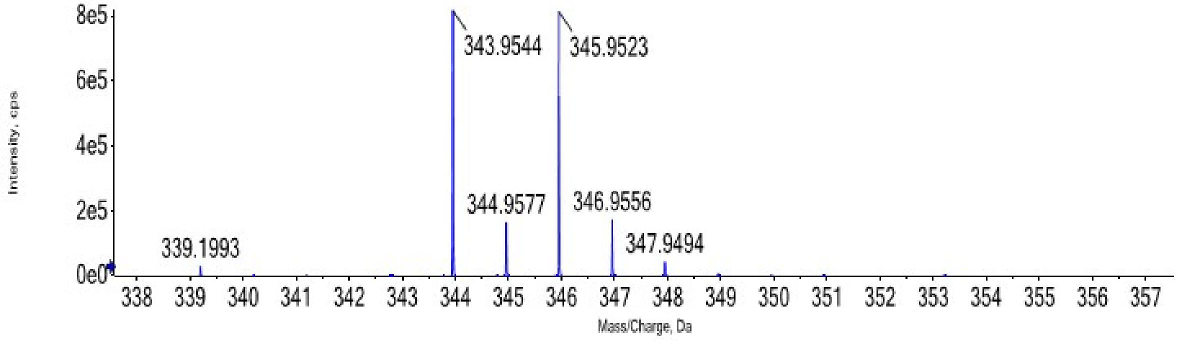


Figure S52. HRMS spectra of 5-bromo-2-(4-fluorophenyl)-8*H*-thieno[2,3-*b*]indole

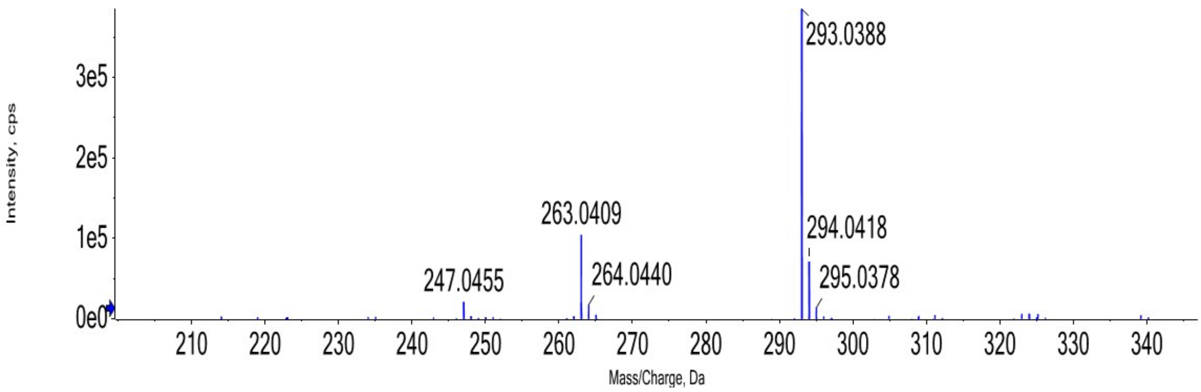


Figure S53. HRMS spectra of 5-nitro-2-phenyl-8*H*-thieno[2,3-*b*]indole