Synthesis of thieno[2,3-b]indoles via Cloke–Wilson rearrangement of spiro donor–acceptor cyclopropanes

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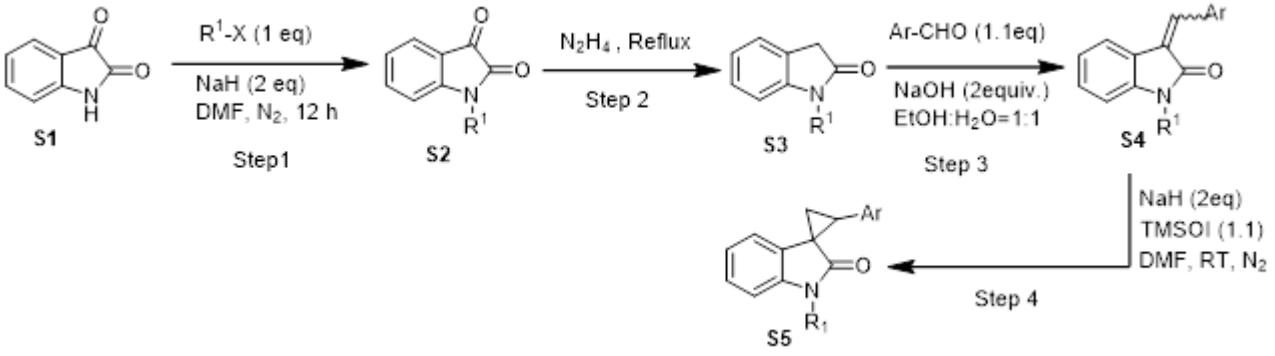
1. General information:

All solvents and reagents were either purified by standard techniques; or used as supplied from commercial sources (Sigma-Aldrich Corporation® unless stated otherwise). All experiments were carried out under an inert atmosphere of argon in flame-dried flasks. TLC was performed on Merck Kieselgel 60 F254 plates, and spots were visualized under UV light. Products were purified by column chromatography on silica gel (100-200 mesh, Merck). Unless otherwise stated, yields refer to analytical pure samples. NMR spectra were recorded in chloroform ($CDCl_3$) at 298K. ^1H spectra were recorded using Brüker AVANCE 600 MHz, 400 MHz or 300 MHz instruments at 298K. Signals are quoted as δ values in ppm using the residual protonated solvent signal as internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants *J* (Hz) and integration. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.16 ppm). Coupling constants are quoted in Hertz and are denoted as *J*. High-resolution mass spectrometry (HRMS) analyses were performed with Q-TOF YA263 high-resolution (Water Corporation) instruments by +ve mode electrospray ionization. Single Crystal XRD was recorded on Bruker D8VENTURE Microfocus diffractometer equipped with a PHOTON II Detector.

2. Synthesis of spirocyclopropyl oxindoles:

Reported starting materials are synthesized following literature procedures.[1,2]



Scheme S1. Synthesis of spirocyclopropyl oxindoles.

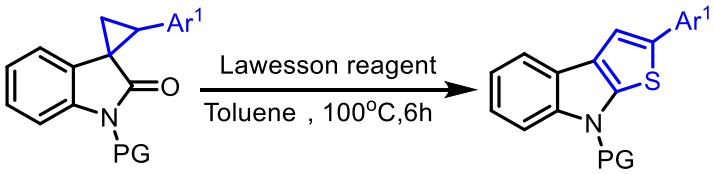
Synthesis of *N*-alkyl isatin (S2): Isatin **S1** (5 mmol, 1 equiv) was added to a suspension of NaH (10 mmol, 2 equiv, 60 % dispersion in mineral oil) in DMF (15 mL) at 0 °C under a nitrogen atmosphere.[2a] The resulting mixture was stirred at room temperature for 30 mins and then alkyl halide (10 mmol, 2 equiv) was added dropwise. The mixture was further stirred at room temperature for 12 h. After completion, the reaction mixture was diluted with ethyl acetate and washed successively with ice-water (2 × 30 mL) and brine (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using ethyl acetate/hexane as the eluent to afford the desired *N*-alkylated isatin **S2**.

Synthesis of *N*-alkyl-2-oxindole (S3): A mixture of the *N*-alkylated isatin **S2** (4 mmol, 1 equiv) and hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 10 mmol, 2.5 equiv) was stirred at 120 °C for 5 h under air.[2a] After completion, the reaction mixture was diluted with ethyl acetate and washed with water (2 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography using ethyl acetate/hexane as the eluent to afford the corresponding products **S3**.

Synthesis of 3-arylidene *N*-alkyl-2-oxindole (S4): A mixture of N-alkylated oxindole **S3** (3 mmol, 1 equiv), aldehyde (3.3 mmol, 1.1 equiv) and NaOH (6 mmol, 2 equiv) in EtOH (8 mL) and water (8 mL) was stirred at room temperature for 3 h. The reaction mixture was then poured into water (2 x 20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product **S4** was purified by silica gel column chromatography using ethyl acetate/hexane as the eluent.

Synthesis of spirocyclopropyl oxindoles (1, 5, 6): Trimethylsulfoxonium iodide (3.3 mmol, 1.5 equiv) was added to a suspension of NaH (3.3 mmol, 1.1 equiv, 60 % dispersion in mineral oil) in DMF (3 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 30 mins and then a solution of alkene **S4** (3 mmol, 1 equiv) in DMF (20 mL) was added dropwise. The resulting mixture was stirred at room temperature for 3 h. After completion, as monitored by TLC, the reaction mixture was diluted with ethyl acetate, washed with ice-water (2 × 20 mL) and brine (2 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the crude product was purified as diastereomeric mixture by silica gel column chromatography using ethyl acetate/hexane as the eluent.

3. Annulation of spirocyclopropyl oxindoles (GP1):



To a 10 mL reaction tube, spirocyclopropyl oxindole (0.35 mmol) and Lawesson's reagent (0.70 mmol) were added, followed by the addition of anhydrous toluene (4 mL). The reaction tube was sealed and heated in an oil bath maintained at 100 °C for 6 h. The progress of the reaction was monitored by Thin Layer Chromatography (TLC) using a mixture of ethyl acetate and hexanes as the eluent, until complete consumption of the starting material was observed. Upon completion, the reaction mixture was cooled to room temperature and quenched with saturated aqueous $NaHCO_3$ solution. The resulting biphasic mixture was stirred vigorously for 15 minutes. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of ethyl acetate/hexanes to afford the desired thieno[2,3-b] indole derivative (**2** or **3** or **4**) as a pure compound.

Unsuccessful substrate scope: Spirocyclopropyl oxindoles (**1f-1k**) were subjected to the standard reaction conditions but in all cases, no formation of the desired thieno[2,3-b]indole product was observed.

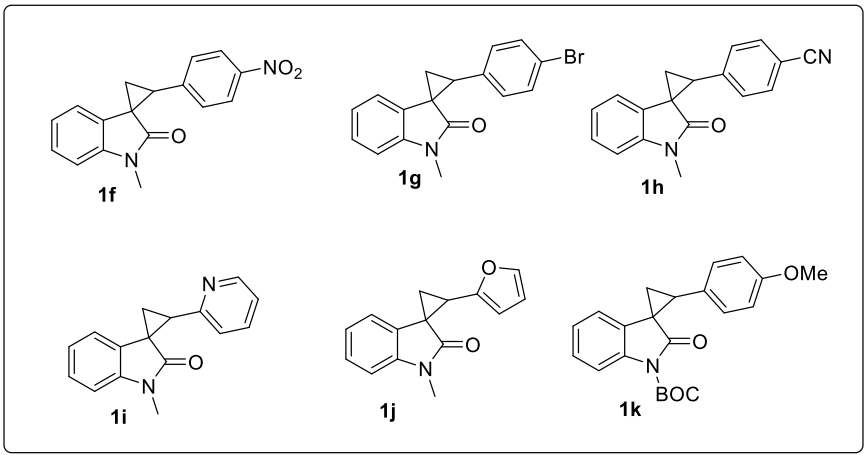


Figure S1. Unsuccessful substrates examined under the optimized reaction conditions.

4. Crystal structure of thieno[2,3-b] indole 2a:

Compound **2a** was dissolved in dichloromethane (DCM) and and allowed to undergo slow evaporation over three days. Needle-shaped colorless crystals were formed, which were subsequently analyzed by X-ray diffraction.

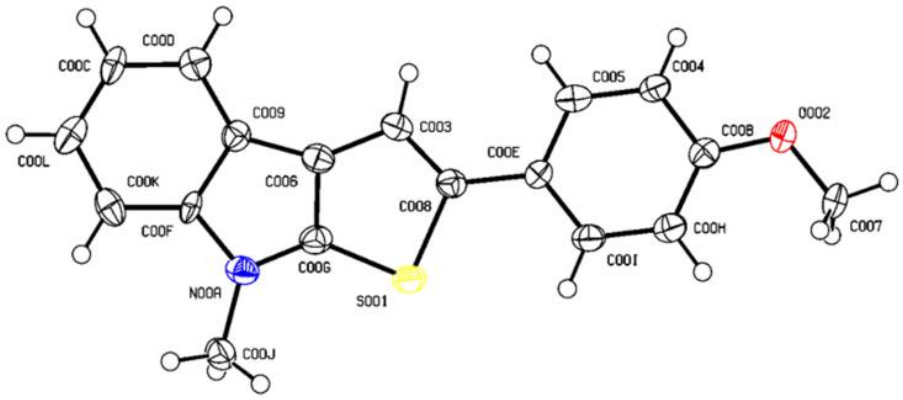


Table S1. Crystal data and structure refinement for mo_JRG251125A_0m_a.	
Identification code	mo_JRG251125A_0m_a
Empirical formula	$C_{18}H_{15}NOS$
Formula weight	293.392
Temperature/K	159.91
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.5223(1)
b/Å	8.7061(3)
c/Å	29.2709(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1407.28(7)
Z	4
ρ_{calc}g/cm^3	1.385
μ/mm^{-1}	0.228
F(000)	616.8
Crystal size/mm^3	0.15 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.44 to 69.5
Index ranges	$-8 \leq h \leq 8$, $-10 \leq k \leq 13$, $-46 \leq l \leq 43$
Reflections collected	19556
Independent reflections	5238 [R_{int} = 0.0628, R_{sigma} = 0.0558]
Data/restraints/parameters	5238/0/192
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0420, wR_2 = 0.1009
Final R indexes [all data]	R_1 = 0.0520, wR_2 = 0.1103
Largest diff. peak/hole / e Å^{-3}	0.42/-0.39
Flack parameter	0.06(4)

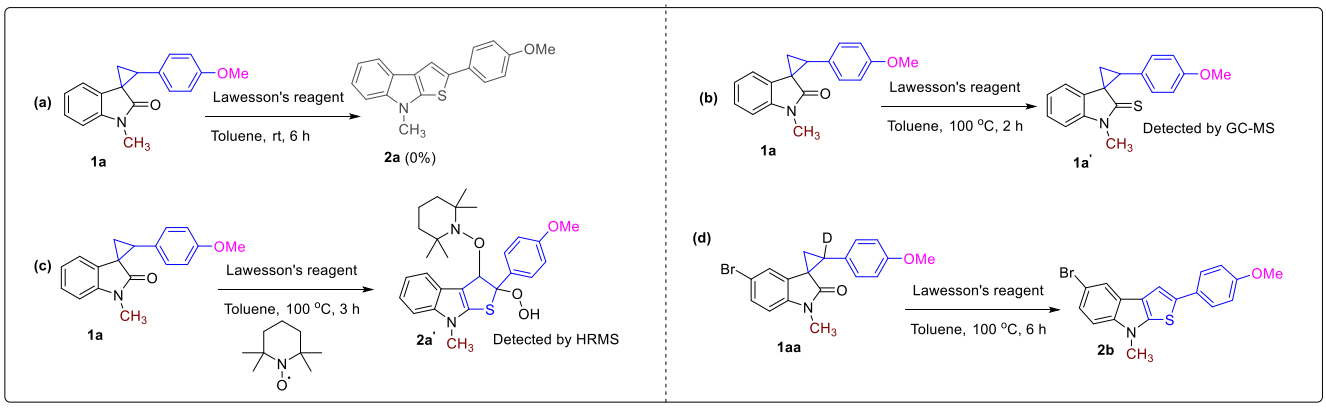
5. Control experiments: Control experiments were performed following the standard reaction conditions unless otherwise noted.

Temperature dependence: When the reaction was conducted at room temperature, the desired thieno[2,3-b]indole **2a** was not formed, indicating that thermal activation is essential for thionation and the subsequent rearrangement (Scheme S2).

Reaction progress study: Quenching the reaction at 2h instead of the standard reaction time resulted in the detection of a thioamide intermediate (m/z 295) by GC–MS, supporting an initial O→S exchange prior to cyclopropane ring opening (Figure S2).

Radical trapping experiment: The addition of radical like TEMPO (1.0 equiv) significantly suppressed the formation of the desired product **2a**, and a TEMPO adduct **2a'** was detected by HRMS, suggesting the involvement of a transient radical or radical-like species under the reaction conditions. HRMS (ESI): m/z [M + H] calcd for $C_{27}H_{34}N_2O_4S$, 483.2218; found, 483.2224 (Figure S3).

4.1.4 Deuterium-labelling experiment: A benzylic-deuterated spirocyclopropyl oxindole substrate **1aa** was synthesized and subjected to the standard reaction conditions. The resulting product showed complete loss of the benzylic deuterium, supporting an aromatization step involving H/D loss during the oxidative process



Scheme S2. Control experiments probing the reaction mechanism.

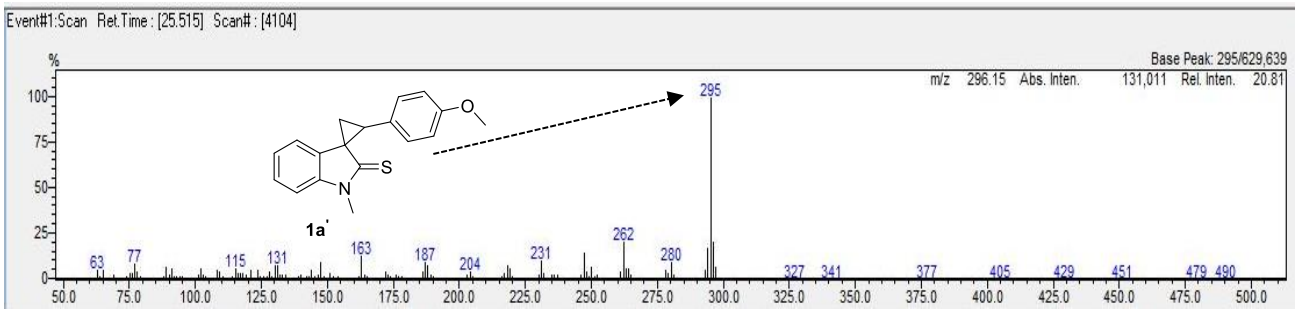


Figure S2. GC–MS spectrum of the thioamide intermediate detected after 2 h.

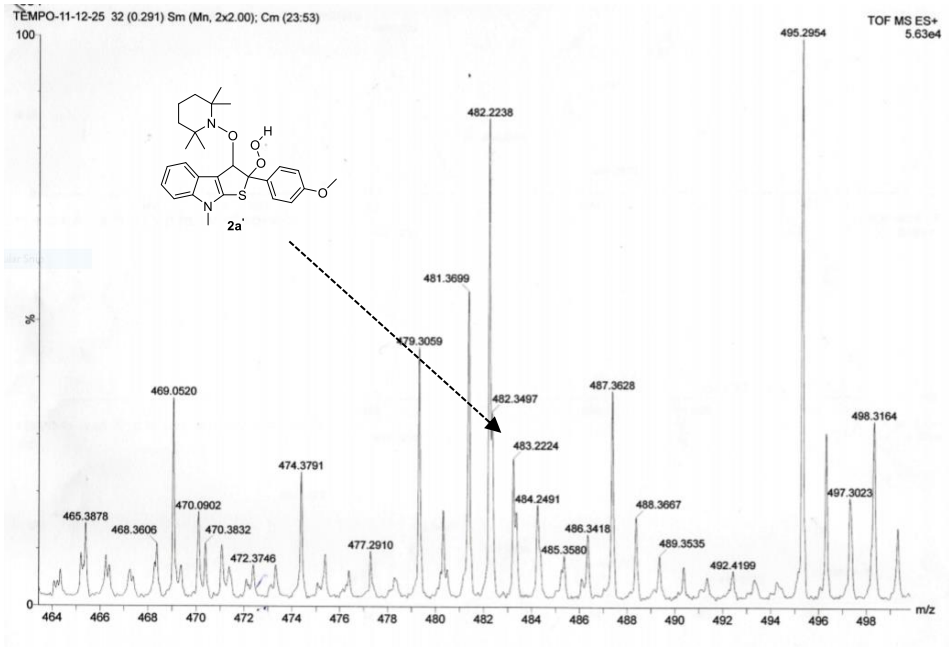


Figure S3. HRMS spectrum of the TEMPO adduct (2aa).

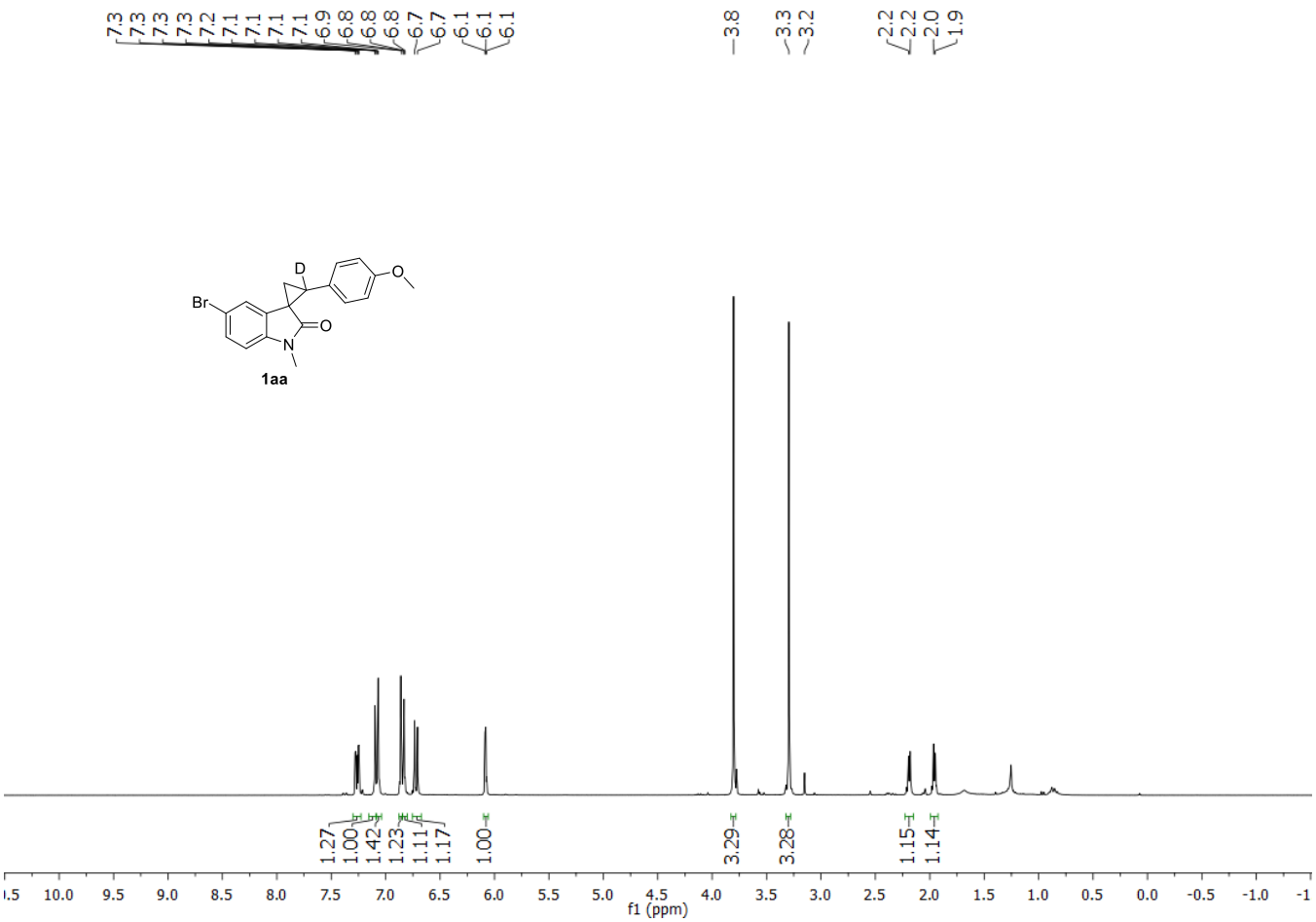
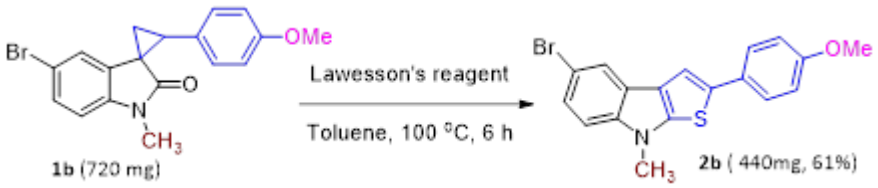


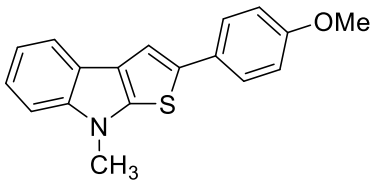
Figure S4. ^{1}H NMR spectrum of the deuterium-labelled starting material 1aa.

Scale-up experiment: The reaction of spirocyclopropyl oxindole **1b** (700 mg, 2.0 mmol) was conducted under the standard reaction conditions. The desired thieno[2,3-b]indole product **2b** was obtained in 61% isolated yield, comparable to that observed on smaller scale.



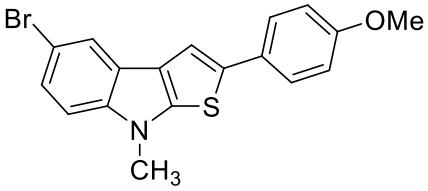
6. Characterization data:

2-(4-Methoxyphenyl)-8-methyl-8H-thieno[2,3-b] indole (2a): Using general procedure (**GP-1**), compound **2a** (88 mg, 86%) was obtained as a white solid; mp = 184 °C-186 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.50 (s, 1H), 7.38 – 7.24 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.8 (s, 6H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.6, 143.4, 141.8, 135.7, 128.6, 126.5, 123.4, 122.2, 121.8, 119.4, 119.2, 114.0, 113.1, 109.0, 55.4, 32.3; IR (ATR, ν_{max}/cm^{-1}): 3050, 2932, 2851, 1880, 1771, 1609, 1510, 1463, 1243, 1032, 821, 737, HRMS (ESI): [M+H] calcd for $C_{18}H_{15}NOS$: 294.0953; found: 294.0955.



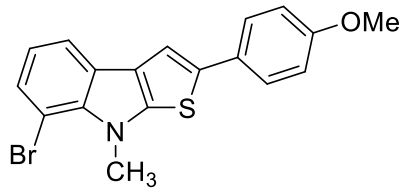
5-Bromo-2-(4-methoxyphenyl)-8-methyl-8H-thieno[2,3-b] indole (2b):

Using general procedure (**GP-1**), compound **2b** (80 mg, 62%) was obtained as a white solid; mp = 166 °C-168 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) 7.92 (s, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.43 (s, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.9, 144.3, 140.5, 136.5, 128.3, 126.6, 124.5, 123.6, 122.6, 121.9 (2C), 114.4, 112.8, 112.6, 110.4, 55.4; IR (ATR, ν_{max}/cm^{-1}): 2940, 2923, 2802, 1832, 1765, 1605, 1460, 842, 734; HRMS (ESI): [M+H] calcd for $C_{18}H_{14}BrNOS$: 372.0058; found: 372.0055.



7-Bromo-2-(4-methoxyphenyl)-8-methyl-8H-thieno[2,3-b] indole (2c):

Using general procedure (**GP-1**), compound **2c** (74 mg, 57%) was obtained as a white solid; mp =160 °C-163 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.43 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.22 (s, 3H), 3.87 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 159.2, 145.7, 137.8, 136.5, 128.2, 126.9, 126.6, 125.2, 122.8, 120.6, 118.5, 114.4, 112.7, 103.6, 55.4, 36.5. IR (ATR, ν_{max}/cm^{-1}): 2940, 2655, 1825, 1780, 1420, 1461, 1075, 1032, 122, 802, 755; HRMS (ESI): [M+H] calcd for $C_{18}H_{14}BrNOS$: 372.0058; found: 372.0054.



5-Fluoro-2-(4-methoxyphenyl)-8-methyl-8H-thieno[2,3-b] indole (2d):

Using general procedure (**GP-1**), compound **2d** (43 mg, 40%) was obtained as a white solid; mp =167 °C-170 °C Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.55 (t, *J* = 4.1 Hz, 2H), 7.46 (s, 1H), 7.08 (td, *J* = 7.9, 4.6 Hz, 1H), 6.99 (d, *J* = 5.4 Hz, 1H), 6.98 – 6.92 (m, 2H), 4.09 (d, *J* = 1.4 Hz, 3H), 3.87 (s, 3H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.9, 149.8 (d, J_{C-F} = 242.6 Hz) ,144.5, 136.7, 129.2, 128.3, 126.7, 125.7, 123.9, 119.7, 115.1, 114.4, 112.9, 107.9, 55.4, 35.2. ^{19}F{^{1}H} NMR 137.14. IR(ATR, ν_{max}/cm^{-1}): 3020, 2943, 1712, 1513, 1370, 1218, 1131, 930, 739; HRMS (ESI): [M+H] calcd for $C_{18}H_{14}FNOS$: 312.0858; found: 312.0851.

2-(4-Methoxyphenyl)-7,8-dimethyl-8H-thieno[2,3-b] indole (2e):

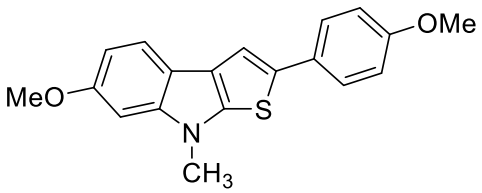
Using general procedure (**GP-1**), compound **2e** (75mg, 70%) was obtained as a white solid; mp = 184 °C-186 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (300 MHz, $CDCl_3$) δ δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.45 (s, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.96 – 6.85 (m, 2H), 4.07 (s, 3H), 3.85 (s, 3H), 2.79 (s, 3H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.7, 144.8, 140.5, 135.6, 128.7, 126.5, 124.9, 123.2, 121.1 (2C), 119.7, 117.4, 114.3,113.1, 55.4, 36.4, 19.6; IR(ATR, ν_{max}/cm^{-1}): 2810, 2803, 1711, 1503, 1371, 1352, 1245, 1011, 945, 740, 720; HRMS (ESI): [M+H] calcd for $C_{19}H_{17}NOS$: 308.1109; found: 308.1107.

2-(4-Methoxyphenyl)-7,8-dimethyl-8H-thieno[2,3-b]indole (2f):

Using general procedure (**GP-1**), compound **2f** (73 mg, 65%) was obtained as a white solid; mp = 158 °C-160 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v) .^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.8 Hz, 2H), 7.45 (s, 1H), 7.44 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 1H), 4.09 (s, 3H), 3.87 (s, 3H), 2.78 (s, 3H), 2.46 (s, 3H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.0, 145.0, 139.0, 135.3, 129.0, 128.7, 126.4, 126.4, 123.4, 123.0, 120.8, 117.3, 114.4, 113.2, 55.4, 36.3, 21.1, 19.5; IR (ATR, ν_{max}/cm^{-1}): 2921, 2855, 1715, 1608, 1533, 1481, 1461, 1243, 1032, 792, 748; HRMS (ESI): [M+H] calcd for $C_{20}H_{16}NOS$: 322.1166; found: 322.1168.

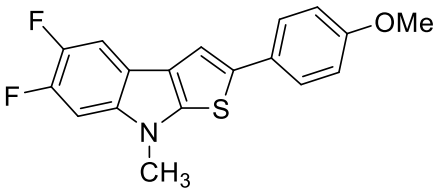
6-Methoxy-2-(4-methoxyphenyl)-8-methyl-8H-thieno[2,3-b]indole (2g):

Using general procedure (**GP-1**), compound **2g** (67 mg, 60%) was obtained as a white solid; mp = 180 °C-184 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.2 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.46 (s, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.86 (m, 2H), 3.94 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.6, 156.4, 142.8, 142.2, 135.5, 128.7, 126.5, 123.4, 119.8, 116.6, 114.4, 113.0, 108.0, 93.9, 55.8, 55.4, 32.3; IR(ATR, ν_{max}/cm^{-1}): 3032, 2920, 2726, 1930, 1745, 1635, 1461, 1227, 1105, 840, 707; HRMS (ESI): [M+H] calcd for $C_{19}H_{17}NO_2S$: 324.1058; found: 324.1056.



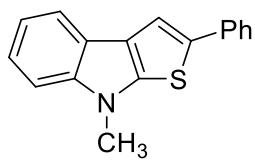
5,6-Difluoro-2-(4-methoxyphenyl)-8-methyl-8H-thieno[2,3-b] indole (2h):

Using general procedure (**GP-1**), compound **2h** (26 mg, 23%) was obtained as a white solid; mp = 180 °C-185 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.45 (s, 1H), 7.29 – 7.25 (m, 1H), 7.09 (m,1H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.85 (d, *J* = 15.6 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 158.9, 157.0, 145.0, 138.4, 136.0, 128.3, 126.6, 122.7, 114.4, 112.8 (d, $J_{C\text{-}F}$ = 37.4 Hz), 109.7, 109.5, 106.3, 104.8 (d, $J_{C\text{-}F}$ = 24.0 Hz), 97.6, 55.4, 32.6. ^{19}F{^{1}H} NMR 117.01,141.32; IR (ATR, ν_{max}/cm^{-1}): 3023, 2953, 1711, 1503, 1370, 1228, 1131, 938, 935, 739; HRMS (ESI): [M+H] calcd for $C_{19}H_{13}F_2NOS$: 330.0764; found: 330.0763.



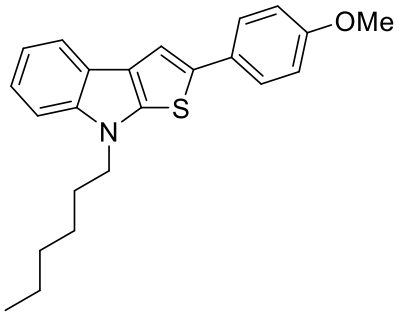
8-Methyl-2-phenyl-8H-thieno[2,3-b] indole (3a):

Using general procedure (**GP-1**), compound **3a** (46mg, 50%) was obtained as a white solid; mp = 136 °C-138 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.70 (s, 1H), 7.68 (s, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.38 (dd, *J* = 16.2, 7.6 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.28 – 7.23 (m, 1H), 3.89 (s, 3H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.0, 142.0, 135.8, 135.7, 129.0, 126.6, 125.2, 123.5, 122.2, 122.0, 119.6, 119.3, 114.3, 109.1, 32.3; IR (ATR, ν_{max}/cm^{-1}): 2945, 2729, 1415, 1411, 1120, 1050, 1002, 932, 930, 738; HRMS (ESI): [M+H] calcd for $C_{17}H_{13}NS$: 264.0847; found: 264.0845



8-Hexyl-2-(4-methoxyphenyl)-8H-thieno[2,3-b] indole (3b):

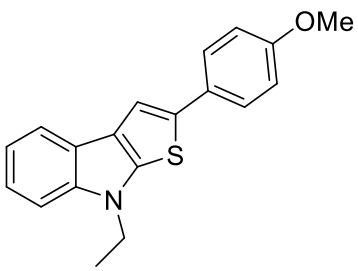
Compound Using general procedure (**GP-1**), compound **3b** (96mg, 75%) was obtained as a white solid; mp = 135 °C-137 °C; Eluent: petroleum ether/ethyl acetate (99/1, v/v).[1]H



NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.54 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 4.25 (t, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 2.04 – 1.93 (m, 2H), 1.46 – 1.32 (m, 6H), 0.92 (t, *J* = 6.9 Hz, 3H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.7, 142.5, 141.4, 135.7, 128.6, 126.5, 123.6, 122.2, 121.7, 119.3, 119.3, 114.4, 113.0, 109.3, 55.4, 46.3, 31.5, 28.9, 26.8, 22.5, 14.0; IR (ATR, ν_{max}/cm^{-1}): 2920, 2853, 1711, 1505, 1471, 1352, 1245, 1011, 1001, 945, 740; HRMS (ESI): [M+H] calcd for $C_{23}H_{25}NOS$: 364.1735; found: 364.1725

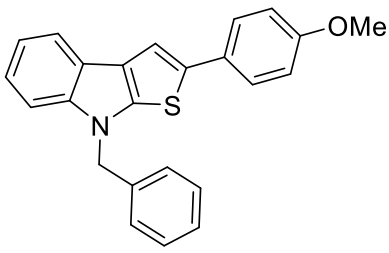
8-Ethyl-2-(4-methoxyphenyl)-8H-thieno[2,3-b] indole (3c):

Compound Using general procedure (**GP-1**), compound **3c** (76 mg, 72%) was obtained as



a white solid; mp = 160 °C-163 °C; Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^1H NMR (300 MHz, CDC_{l3}) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.52 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.28 (q, *J* = 7.3 Hz, 2H), 3.86 (s, 3H), 1.53 (t, *J* = 7.3 Hz, 3H).$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.3, 142.6, 141.6, 136.4, 129.3, 127.2, 124.5, 123.0, 122.4, 120.0, 115.4, 115.0, 113.7, 109.8, 56.0, 41.5, 14.5; IR (ATR, ν_{max}/cm^{-1}): 3045, 2829, 1715, 1425, 1520, 1450, 1222, 1032, 933, 738; HRMS (ESI): [M+H] calcd for $C_{19}H_{17}NOS$: 308.1109; found: 308.1107

8-Benzyl-2-(4-methoxyphenyl)-8H-thieno[2,3-b] indole (3d):

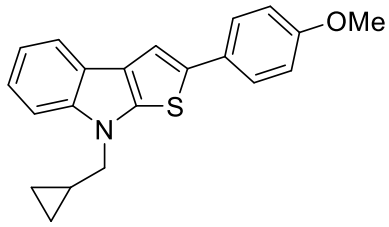


Using general procedure (**GP-1**), compound **3d** (90 mg, 70%) was obtained as a white solid; mp =163 °C-166 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.52 (d, *J* = 3.6 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.35 – 7.31 (m, 2H), 7.31 – 7.29 (m, 2H), 7.28 (d, *J*

= 5.3 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.42 (s, 2H), 3.86 (s, 3H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.7, 142.6, 141.6, 136.3, 135.8, 128.9, 128.5, 128.0, 127.5, 126.6, 124.1, 122.4, 122.0, 119.7, 119.4, 114.3, 113.0, 109.5, 55.4, 49.9; IR(ATR, ν_{max}/cm^{-1}): 3019, 2819, 1852, 1532, 1479, 1327, 1031, 1013, 806, 691; HRMS (ESI): [M+H] calcd for $C_{24}H_{19}NOS$: 370.1266; found: 370.1268

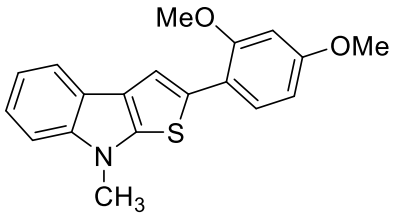
8-(Cyclopropylmethyl)-2-(4-methoxyphenyl)-8H-thieno[2,3-b] indole (3e):

Using general procedure (**GP-1**), compound **3e** (93 mg, 80%) was obtained as a white solid; mp = 140 °C-142 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.54 (s, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 4.14 (d, *J* = 6.7 Hz, 2H), 3.89 (s, 3H), 1.47 – 1.36 (m, 1H), 0.72 (d, *J* = 7.7 Hz, 2H), 0.54 (d, *J* = 5.2 Hz, 2H).$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.7, 142.4, 141.5, 135.8, 128.7, 126.6, 124.0, 122.2, 121.8, 119.4, 119.3, 114.4, 112.9, 109.3, 55.4, 50.7, 10.4, 4.4; IR(ATR, ν_{max}/cm^{-1}): 2945, 2855, 1725, 1680, 1535, 1485, 1420, 1461, 1175, 1032, 1223, 802, 750; HRMS (ESI): [M+H] calcd for $C_{21}H_{19}NOS$: 334.1266; found: 334.1265

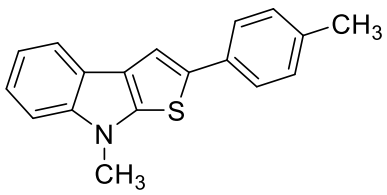


2-(2,4-Dimethoxyphenyl)-8-methyl-8H-thieno[2,3-b] indole (4a):

Using general procedure (**GP-1**), compound **4a** (101 mg, 80%) was obtained as a white solid; mp =166 °C-170 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.79 (m, 2H), 7.35 (t, *J* = 6.6 Hz, 1H), 7.29 (ddd, *J* = 9.4, 5.6, 3.8 Hz, 2H), 7.25 – 7.18 (m, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 6.78 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 3.86 (s, 3H).$^{13}C\{^1H\}$ NMR (101 MHz, CDCl3) δ 154.0, 149.9, 145.8, 142.2, 130.8, 125.6, 122.7, 122.3, 121.9, 119.4, 119.4, 116.8, 113.5, 113.3, 112.3, 109.0, 56.6, 55.9, 32.3; IR (ATR, ν_{max}/cm^{-1}): 3033, 2923, 2826, 1900, 1745, 1600, 1464, 1327,1155, 842,737,721; HRMS (ESI): [M+H] calcd for $C_{19}H_{17}NO_2S$: 324.1058; found: 324.1056



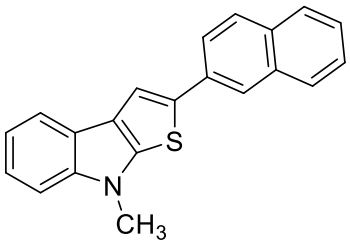
8-Methyl-2-(*p*-tolyl)-8H-thieno[2,3-b] indole (4b):



Using general procedure (**GP-1**), compound **4b** (67 mg, 70%) was obtained as a white solid; mp =110 °C-112 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.61 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 6.6 Hz, 2H), 7.22 (d, *J* = 4.9 Hz, 1H), 3.89 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.7, 141.9, 136.4, 136.0, 133.0, 129.6, 125.1, 123.4, 122.2, 121.9, 119.5, 119.3, 113.7, 109.1, 32.3, 21.1; IR (ATR, ν_{max}/cm^{-1}): 3019, 2919, 1894, 1611, 1572, 1532, 1479, 1465, 1327, 1120, 806, 734; HRMS (ESI): [M+H] calcd for $C_{18}H_{15}NS$: 278.1003; found: 278.1004

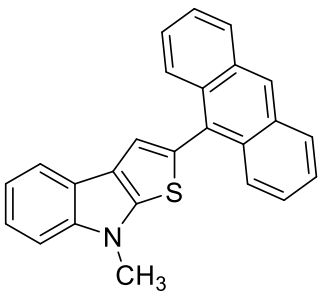
8-Methyl-2-(naphthalen-2-yl)-8H-thieno[2,3-b]indole (4c):

Using general procedure (**GP-1**), compound **4c** (69 mg, 63%) was obtained as a white solid; mp = 135 °C-136 °C; Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.96 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.1 Hz, 1H), 7.59 (d, *J* = 1.3 Hz, 2H), 7.55 (d, *J* = 7.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 6.1 Hz, 1H), 3.94 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.7, 141.9, 134.0, 133.4, 132.7, 132.3, 128.5, 128.4, 128.1, 126.5, 126.1, 126.0, 125.3, 123.2, 122.2, 122.0, 119.5, 119.3, 118.7, 109.1, 32.4; IR(ATR, ν_{max}/cm^{-1}): 2973, 1610, 1536, 1467, 1453, 1332, 1254, 1126, 1081, 835, 751, 736; HRMS (ESI): [M+H] calcd for $C_{21}H_{15}NS$: 314.1003; found: 314.1005



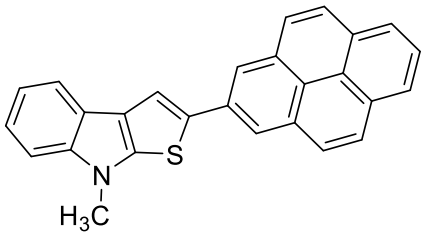
2-(Anthracen-9-yl)-8-methyl-8H-thieno[2,3-b] indole (4d):

Using general procedure (**GP-1**), compound **4d** (67 mg, 53%) was obtained as a white solid; mp = 180 °C-182 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (s, 2H), 8.16 – 8.12 (m, 2H), 8.10 (dd, *J* = 1.8, 1.0 Hz, 4H), 8.07 (s, 2H), 7.95 – 7.82 (m, 2H), 7.55 – 7.50 (m, 5H), 7.47 (ddd, *J* = 6.4, 3.5, 1.6 Hz, 7H), 7.44 – 7.35 (m, 3H), 7.31 – 7.25 (m, 5H), 3.97 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.4, 141.9, 132.6, 131.3, 129.6, 129.3, 128.3, 128.2, 126.9, 126.0, 125.3, 122.8, 122.2, 122.0, 120.7, 119.5, 119.3, 109.2, 32.5.



IR (ATR, ν_{max}/cm^{-1}): 3050, 2923, 1917, 1673, 1622, 1484, 1464, 1331, 1241, 1013, 731, 666; HRMS (ESI): [M+H] calcd for $C_{25}H_{17}NS$: 364.1160; found: 364.1162

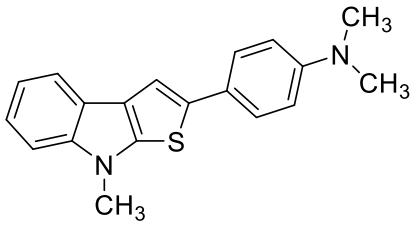
8-Methyl-2-(pyren-2-yl)-8H-thieno[2,3-b] indole (4e):



Using general procedure (**GP-1**), compound **4e** (88 mg, 65%) was obtained as a white solid; mp = 176 °C-178 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^1H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 9.3 Hz, 1H), 8.25 – 8.22 (m, 2H), 8.21 (t, *J* = 6.2 Hz, 2H), 8.16 – 8.12 (m, 2H), 8.11 (d, *J* = 9.0 Hz, 1H), 8.05 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.69 (s, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.30 (s, 1H), 3.96 (s, 3H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.2, 141.9, 133.4, 131.5, 131.0, 130.8, 130.7, 129.9, 129.4, 128.7, 127.9, 127.7, 127.4, 126.2, 125.3, 125.2, 125.0, 124.9, 124.6, 123.4, 122.3, 122.1, 119.6, 119.4, 119.3, 109.1, 32.5; IR (ATR, ν_{max}/cm^{-1}): 3041, 2923, 2852, 1916, 1716, 1600, 1464, 842, 734; HRMS (ESI): [M+H] calcd for $C_{27}H_{17}NS$: 388.1160; found: 388.1163.

N, N-Dimethyl-4-(8-methyl-8H-thieno[2,3-b]indol-2-yl) aniline (4f):

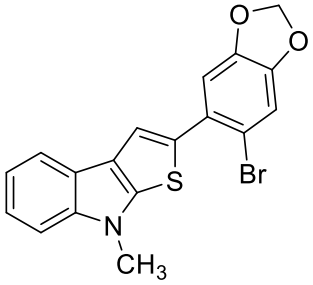
Compound Using general procedure (**GP-1**), compound **4f** (90 mg, 90%) was obtained as a white solid; mp = 176 °C-177 °C. Eluent**:** petroleum ether/ethyl acetate (99/1, v/v). ^1H



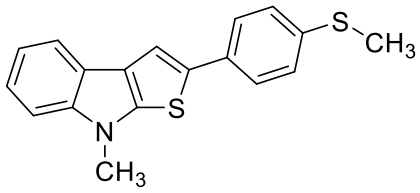
NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.46 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 3.02 (s, 6H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$). δ 149.6, 142.9, 141.8, 136.9, 126.3, 124.4, 123.4, 122.2, 121.6(2C), 112.9, 111.9, 109.0, 40.6, 32.3. IR (ATR, ν_{max}/cm^{-1}): 3050, 2962, 2798, 1876, 1608, 1532, 1464, 1480, 1328, 1050, 955, 845, 736; HRMS (ESI): [M+H] calcd for $C_{19}H_{18}N_2S$: 307.1269; found: 307.1266

2-(6-Bromobenzo[d][1,3] dioxol-5-yl)-8-methyl-8H-thieno[2,3-b] indole (4g):

Using general procedure (**GP-1**), compound **4g** (47mg, 40%) was obtained as a yellow solid; mp =185 °C-187 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.4 Hz, 1H), 7.47 (s, 1H), 7.41 – 7.29 (m, 2H), 7.25 – 7.19 (m, 1H), 7.17 (d, *J* = 9.7 Hz, 1H), 7.04 (s, 1H), 6.05 (s, 2H), 3.88 (s, 3H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.8, 147.3, 144.8, 141.9, 132.8, 129.4, 122.4, 122.2, 122.0, 119.5, 119.3, 119.0, 114.5, 113.3, 111.9, 109.0, 102.0, 32.4. IR (ATR, ν_{max}/cm^{-1}): 3050, 2929, 2898, 1715, 1607,1526,1467, 1413, 1327, 1230, 1036, 738; HRMS (ESI): [M+H] calcd for $C_{18}H_{12}NO_2SBr$: 385.9850; found: 385.9852



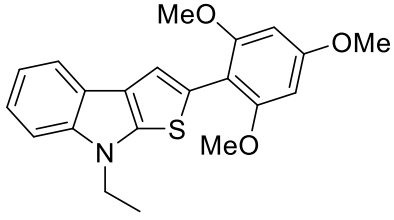
8-Ethyl-2-(2,4,6-trimethoxyphenyl)-8H-thieno[2,3-b] indole (4h):



Using general procedure (**GP-1**), compound **4h** (67mg, 62%) was obtained as a brown solid; mp = 162 °C-163 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.61 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.30 (s, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 3.88 (s, 3H), 2.55 (s, 3H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.9, 142.0, 136.5, 135.2, 132.9, 127.3, 125.5, 123.5, 122.2, 122.0, 119.6, 119.3, 114.0, 109.1, 32.3, 16.2; IR (ATR, ν_{max}/cm^{-1}): 2923, 2853, 1711, 1505, 1471, 1328, 1231, 1038, 935, 739; HRMS (ESI): [M+H] calcd for $C_{18}H_{15}NS_2$: 310.0724; found: 310.0725.

8-Ethyl-2-(2,4,6-trimethoxyphenyl)-8H-thieno[2,3-b] indole (4i):

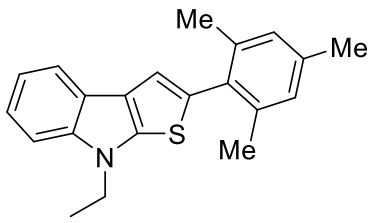
Using general procedure (**GP-1**), compound **4i** (118mg, 92%) was obtained as a brown solid; mp = 182 °C-183 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.4 Hz, 1H), 7.56 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.27 (s, 2H), 4.29 (t, *J* = 7.3 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 6H), 1.58 (t, 3H). 13C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 160.5, 159.0, 143.8, 141.0, 125.5, 122.5, 121.2, 119.3,



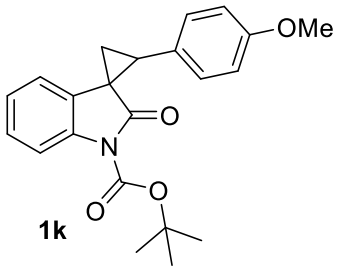
119.3, 118.9, 108.8, 106.4, 56.1, 55.4, 40.8, 14.0; IR (ATR, ν_{max}/cm^{-1}): 2925, 2833, 1607, 1554, 1530, 1458, 1248, 1296, 1177, 1034, 821, 770, 727; HRMS (ESI): [M+H] calcd for $C_{21}H_{21}NO_3S$: 368.1320; found: 368.1321

8-Ethyl-2-(2,4,6-trimethoxyphenyl)-8H-thieno[2,3-b]indole (4j):

Using general procedure (**GP-1**), compound **4i** (87 mg, 82%) was obtained as a brown solid; mp = 156 °C-158 °C. Eluent: petroleum ether/ethyl acetate (99/1, v/v).[1]H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.39 (t, *J* = 6.8 Hz, 1H), 7.18 (s, 2H), 4.43 (q, *J* = 7.3 Hz, 2H), 2.55 (s, 3H), 2.47 (s, 6H), 1.71 (t, *J* = 7.3 Hz, 3H).[13]C NMR (75 MHz, $CDCl_3$) δ 143.3, 140.8, 139.4, 138.2, 132.7, 131.9, 128.3, 123.2, 122.5, 121.8, 119.4, 117.7, 109.3, 41.1, 21.4, 21.1, 14.2; IR (ATR, ν_{max}/cm^{-1}): 3008, 2928, 2838, 1725, 1593, 1511, 1464, 1215, 1137, 1021, 745, 655; HRMS (ESI): [M+H] calcd for $C_{20}H_{19}NS$: 320.1473; found: 320.1475



***Tert*-butyl 2-(4-methoxyphenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1'-carboxylate (1k):** Using reported procedure,[1] compound **1k** (200 mg, 82%) was obtained as a viscous oil; Eluent: petroleum ether/ethyl acetate (99/1, v/v).[1]H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.85 (s, 1H), 6.83 (s, 1H), 6.83 – 6.78 (m, 1H), 5.98 (d, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.36 (t, *J* = 8.7 Hz, 1H), 2.28 (dd, *J* = 9.2, 4.5 Hz, 1H), 1.98 (dd, *J* = 8.1, 4.5 Hz, 1H), 1.70 (s, 9H).[13]C NMR (75 MHz, $CDCl_3$) δ 175.20, 159.01, 149.41, 139.68, 131.14, 126.74, 126.58, 126.36, 123.52, 120.50, 114.67, 113.87, 84.22, 55.24, 37.79, 33.75, 28.17, 24.55. HRMS (ESI): [M+H] calcd for $C_{22}H_{23}NO_4$: 365.1627; found: 365.1622

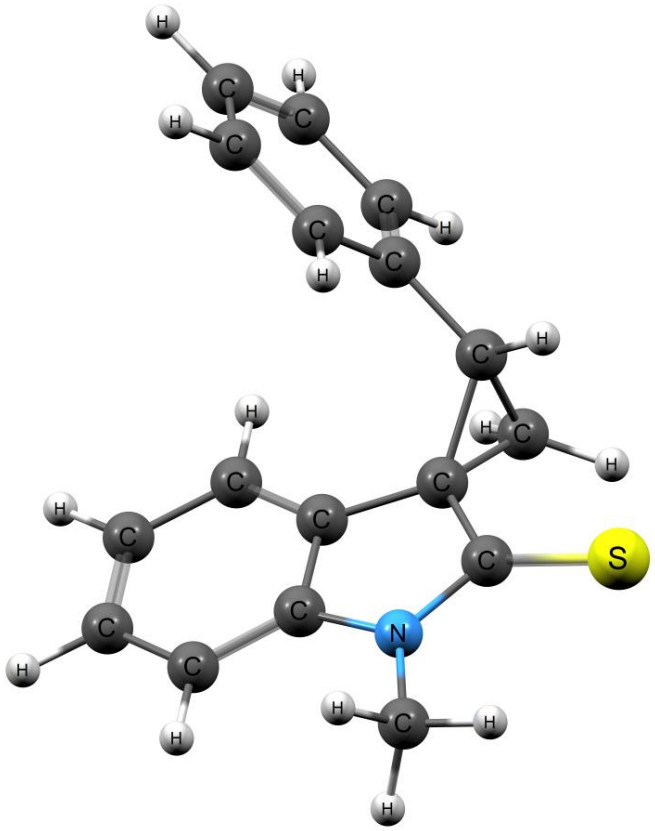


7. DFT studies:

All density functional theory (DFT) calculations were carried out using ORCA version 5.0.4. The B3LYP functional, as implemented in ORCA with 20% Hartree-Fock exchange, along with the def2-SVP basis set, was employed for all computations. The RIJCOSX approximation was applied using the def2/J auxiliary basis set. Dispersion effects were

accounted for by Grimme's D4 correction. Solvation was modeled using the CPCM approach with toluene as the solvent. The temperature was set to 373 K to align with experimental conditions.

A



Total Enthalpy: -1108.43438914 Eh

Final Gibbs free energy: -1108.51626174 Eh

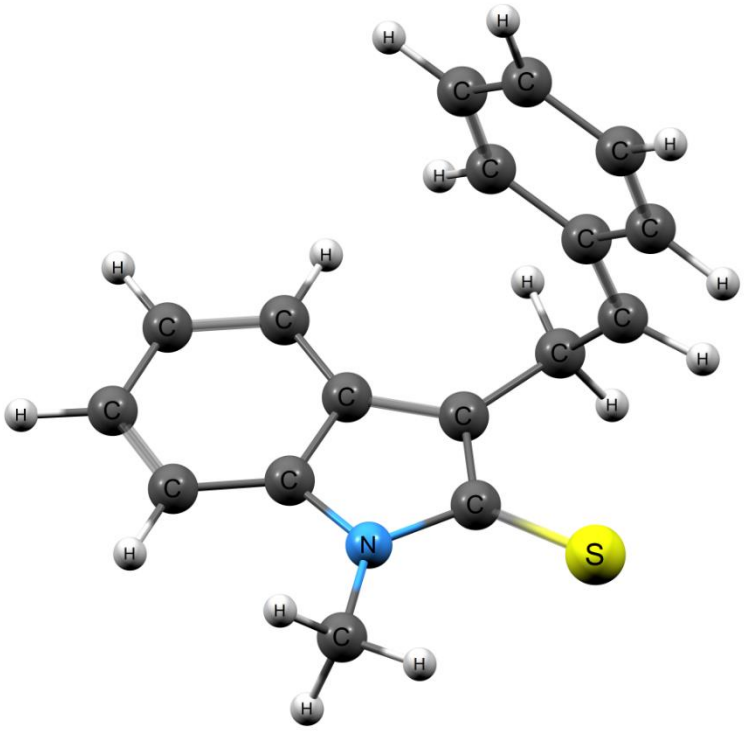
Cartesian coordinates:

C -1.34628203448210 -1.25197563287346 0.17188064736250

C	-1.43469414338516	-2.53422847390275	-0.38213365893110
C	-2.68252817574593	-3.10406643326665	-0.67947583951092
C	-3.83364010141811	-2.36959695021591	-0.41237576055253
C	-2.49843373128845	-0.50038558116706	0.44428788101734
C	-3.72786066717621	-1.08216970255719	0.14398311056708
C	-5.27873494196426	-2.64236826535761	-0.57491042653385
C	-5.98164453529919	-1.41042048015490	-0.09535986300112
H	-0.36522346002701	-0.82542022859609	0.39597209535993
H	-0.52224347565846	-3.09985738370091	-0.58560371085197
H	-2.74388135583602	-4.10525157581165	-1.10881970112575
H	-2.42807227269607	0.50017470895641	0.87389683733080
N	-5.01320066343877	-0.54238155260251	0.31861214256695
C	-5.87982475838751	-3.49721090848581	-1.68055628307078
C	-5.92772462265708	-4.01836486311516	-0.29447174283261
H	-5.16065861224880	-3.92732836099325	-2.38292956241150
H	-6.80658648066569	-3.10947328982276	-2.11216841896786
S	-7.62453983953510	-1.15747461456971	-0.06419677862717
C	-5.24507759907527	0.77563491795551	0.86927947643550
H	-4.76889221539311	1.54366122194323	0.23870412208671
H	-4.82795874714202	0.84369324834239	1.88687206754870
H	-6.32830103190034	0.94627043087147	0.90258940712084
H	-3.51841959973872	-6.19384796101723	3.04874935174313
C	-3.84469529449244	-6.19607490862702	2.00529659669066

C	-4.65188735243108	-5.16280385692576	1.52784153163661
H	-4.95165590582669	-4.34927876706577	2.19418435607308
C	-5.07541735395837	-5.14389150653330	0.18888338135694
C	-4.67853673793373	-6.18671997294270	-0.65935725177274
H	-5.00684720157960	-6.18939810945951	-1.70162447610427
C	-3.87072707022443	-7.22466136793118	-0.18304895029852
H	-3.57119169385321	-8.03205574234815	-0.85662247295662
C	-3.44928348066310	-7.23088462475076	1.14933203598842
H	-2.81544298741104	-8.03994665093897	1.52171934742080
H	-6.88984185646684	-3.89537676233523	0.21767050924333

TS_AB



Total Enthalpy ... -1108.38879157 Eh

Final Gibbs free energy ... -1108.47025869 Eh

Cartesian coordinates:

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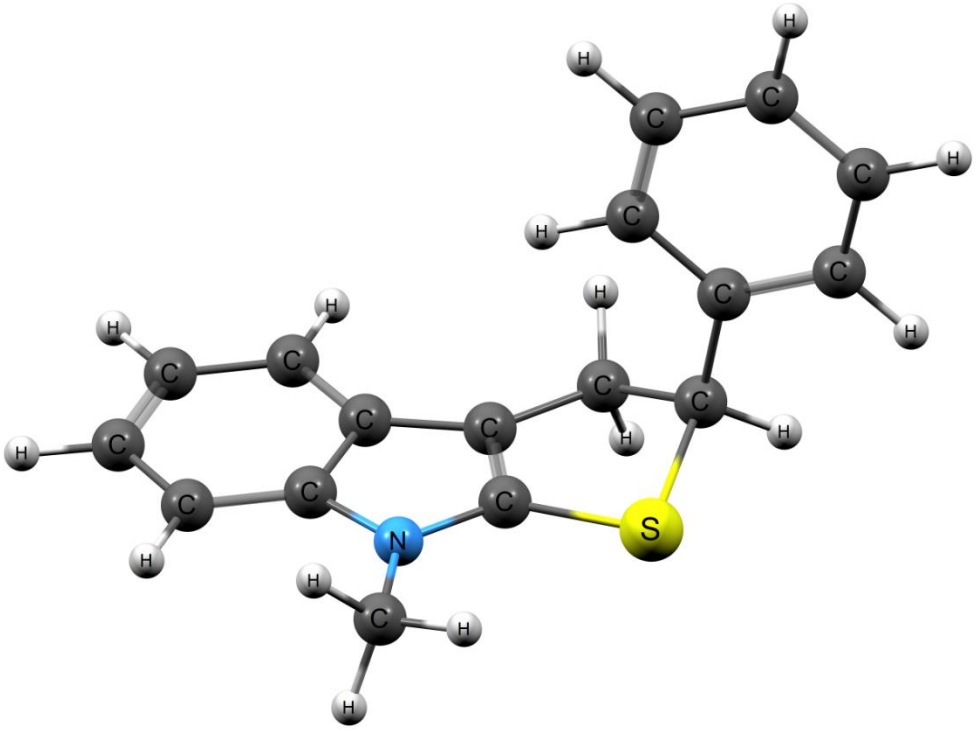
C	2.14541484761621	0.98735327097947	-1.23429235649440
C	0.81798493381201	1.21842406781100	-0.83245307352523
C	1.57397416699737	2.95918156033033	0.74243655400083
C	0.55544956290616	2.20314232999602	0.16617325613721
C	-0.44918079357118	0.68551530594140	-1.21380931778775
C	-1.44437948484452	1.27586283550063	-0.38227233982746
H	3.70762691451974	3.28668102192725	0.76174507979746
H	4.20649007362084	1.56312791730754	-0.95430509823506
H	2.37433846949963	0.23161629656381	-1.99100449313092
H	1.36048254832467	3.72136188730159	1.49456308199041
N	-0.81107689156014	2.23103586643026	0.40124986577861
C	-0.73170449245883	-0.36169607657879	-2.25168799134215
C	-1.48276994271776	-1.36418463984149	-1.47089314353120
H	0.22117921312289	-0.75359719922259	-2.64171406191407
H	-1.32593091454080	0.01661417904575	-3.09654137954836
S	-3.10623100048718	0.90889339123598	-0.29446848385003
C	-1.45175072603873	3.09585362748628	1.36524241098360

H	-1.40590470825352	4.15042058312236	1.04500115949976
H	-0.96462046041261	3.00583111133899	2.34975778191228
H	-2.50465735915331	2.79521202789875	1.44801711083735
H	1.92823009920415	-3.21415881646639	1.09448009853047
C	0.86014211087841	-3.13197740820364	0.87920322363963
C	0.42427317546925	-2.28718695415718	-0.12954876659767
H	1.15167450617203	-1.70341292388586	-0.69442917092084
C	-0.96326771796002	-2.17877668436188	-0.42629987541465
C	-1.88113998520498	-2.93834662253056	0.34609953182896
H	-2.94924535492468	-2.84092173997709	0.13801896339691
C	-1.43461603649788	-3.77655314499468	1.36315174000217
H	-2.15283206113213	-4.35163109599776	1.95242458750888
C	-0.06487592392754	-3.87845258049264	1.63110463292683
H	0.28854813753862	-4.53778341005122	2.42796841208084
H	-2.55119647486575	-1.46413528181842	-1.66491162352764

B



Total Enthalpy ... -1108.43774374 Eh

Final Gibbs free energy ... -1108.51960561 Eh

Cartesian coordinates:

C	-1.21487402525751	0.28299154832663	-0.18351717424485
C	-0.87272375215946	-0.70003392815319	-1.13510288944063
C	-1.76637925597063	-1.71182870446375	-1.48254068761954
C	-3.03269808251612	-1.74749897379128	-0.86937649811654
C	-2.46273742432344	0.27642857896353	0.44334105996057
C	-3.35949962775247	-0.73836918379142	0.09678850846743
C	-4.17975507782572	-2.59919505211714	-0.95866010853175
C	-5.11090663914574	-2.09095975354681	-0.08468784081447
H	-0.49303291023999	1.06462045961423	0.06701953414987

H	0.11220240637606	-0.66475615016662	-1.60844376175580
H	-1.49006129118628	-2.46753996919964	-2.22255054668033
H	-2.72656175483859	1.04132989148722	1.17718869650542
N	-4.64456261865046	-0.97692828161196	0.56830730815376
C	-4.65132144596788	-3.79339183169969	-1.73133656715330
C	-5.85142048277069	-4.38246856600481	-0.93963132710663
H	-3.88040170489929	-4.57117275894694	-1.85483915420788
H	-4.98175289709052	-3.50609072890500	-2.74641699117203
S	-6.64564339697009	-2.93533226748003	0.00871862927467
C	-5.34324824282486	-0.18990051973020	1.55996420172728
H	-5.63435172555817	0.79694023404695	1.16195912981362
H	-4.70811783422424	-0.03693329048563	2.44677729113245
H	-6.24981353158395	-0.72606498335180	1.87177608111231
H	-3.07749513690182	-6.46544764980828	2.23598847919699
C	-4.02110485081061	-6.48279897581379	1.68403003293666
C	-4.29858644128848	-5.47240037472321	0.76087203637681
H	-3.57396295591862	-4.67064295827756	0.60495694069379
C	-5.50579663082240	-5.47545871902479	0.04122116051900
C	-6.41886221818585	-6.51706080270290	0.26488608388869
H	-7.36055223230403	-6.53311566762963	-0.29179550268393
C	-6.14164460467293	-7.52945054432346	1.18726172532885
H	-6.86476950632225	-8.33418381414097	1.34474241300758
C	-4.94054041151820	-7.51458668620356	1.90211131523463

H	-4.71911905076350	-8.30564510699045	2.62334351313266
H	-6.63987464511113	-4.73653446935394	-1.61626509108540

O_2

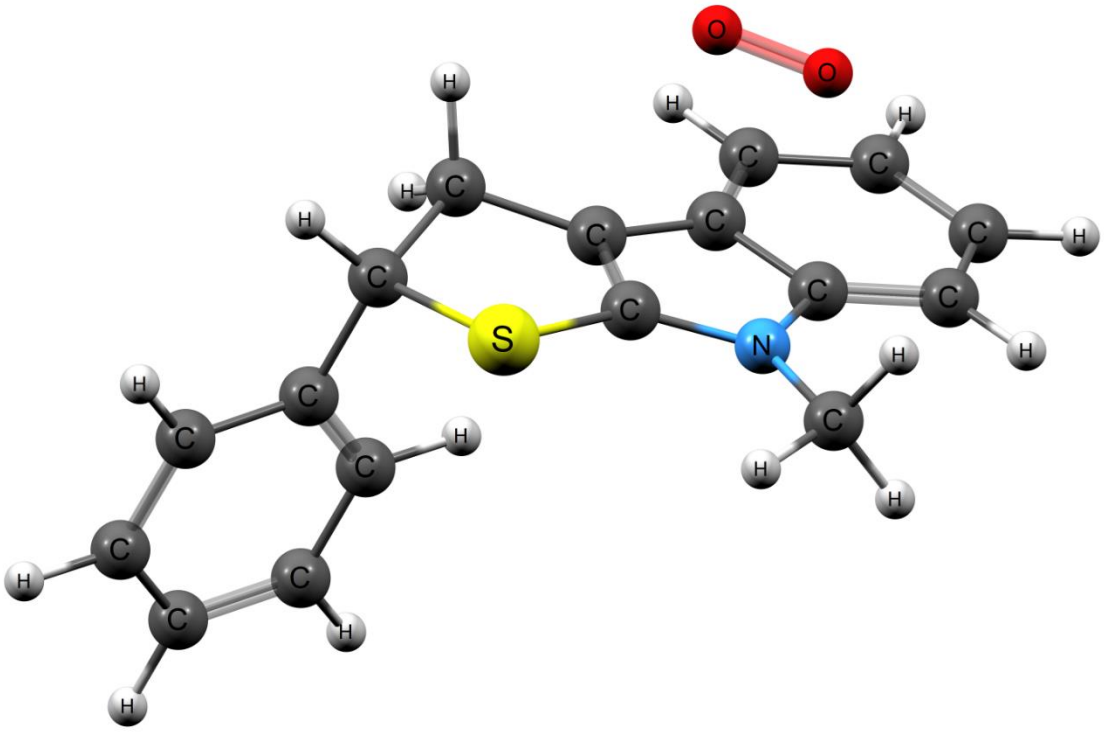
Total Enthalpy ... -150.13753713 Eh

Final Gibbs free energy ... -150.16757632 Eh

Cartesian coordinates:

O	-6.92325820736487	3.03341490047381	-0.00177828323100
O	-5.72343179263512	3.04378509952619	0.00177828323100

B_O_2



Total Enthalpy ... -1258.57970699 Eh

Final Gibbs free energy ... -1258.67486632 Eh

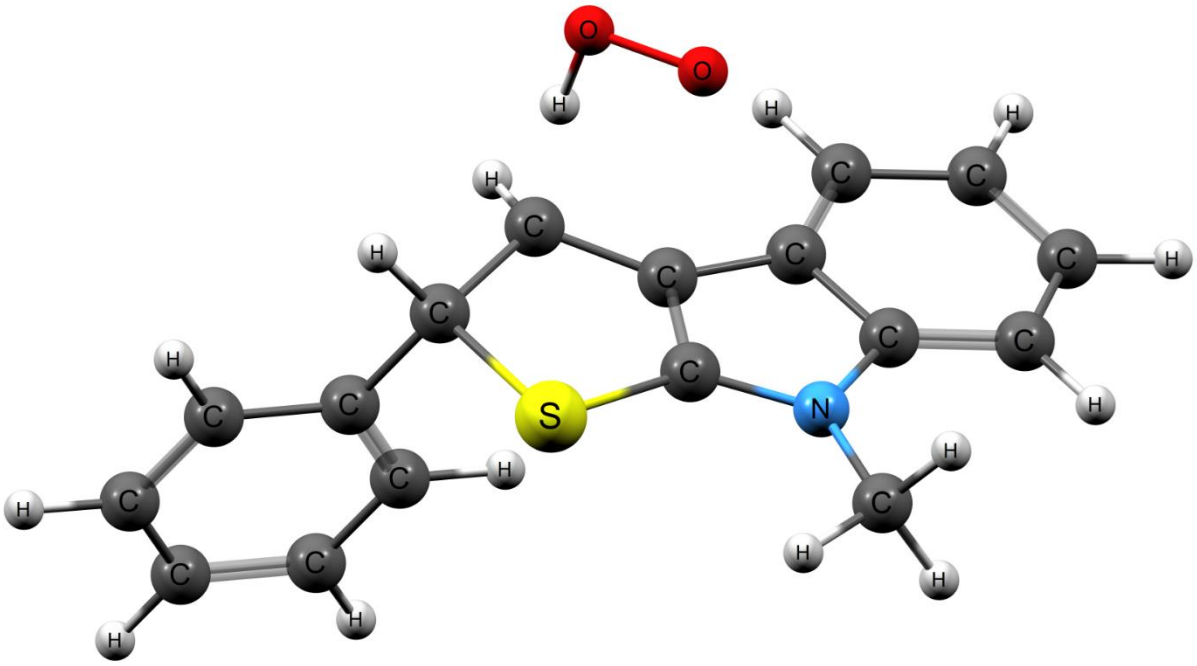
Cartesian coordinates:

C	1.57601090844277	0.92303363454585	-0.73689501548234
C	1.74745530166408	-0.43236959291490	-1.08767908696676
C	0.67326865046692	-1.32024475004091	-1.08585948930601
C	-0.60327436050277	-0.84910300689807	-0.72680977932394
C	0.32274272648370	1.42204467705135	-0.37677703855654
C	-0.75474922608328	0.53219602786124	-0.37409463860416
C	-1.90444169683054	-1.43309836685230	-0.61673292782681

C	-2.75216624272048	-0.42442831095634	-0.22075814181287
H	2.43734226130751	1.59585573694941	-0.74989752883608
H	2.74214762116437	-0.78981599844636	-1.36724232105049
H	0.81736246924464	-2.36829986729640	-1.36112615530075
H	0.19151346449520	2.47370637358301	-0.11269868979769
N	-2.08955293621907	0.76404785632520	-0.05871948835719
C	-2.66545707666628	2.03929086104156	0.30569110257796
H	-2.72630830969146	2.71578547961947	-0.56325424816788
H	-2.06118132888025	2.52277189556147	1.08883111577977
H	-3.67779549387287	1.87765949968464	0.70053711871280
S	-4.44669600579661	-0.83889042799891	-0.05840886278030
C	-2.58816955470421	-2.73720979098991	-0.88719912421225
C	-3.95925031054616	-2.67669561513112	-0.15834979782863
H	-2.74951623160590	-2.87764142116783	-1.97165664704825
H	-2.02560324465129	-3.61513548992437	-0.53056092066754
H	-5.98040877685918	-4.04818586982270	1.00911930490096
C	-5.12332302067428	-3.93989593873524	1.68040355731842
C	-5.18179532344641	-4.47365327665624	2.97068724659634
C	-4.09036344603595	-4.33895575147594	3.83336887422490
C	-2.94245472972966	-3.67014655107731	3.39406409295037
H	-2.08281852872936	-3.56331201171556	4.06114831822777
C	-2.88471371295613	-3.13868364347083	2.10418544059758
H	-1.98438890557324	-2.61492774498960	1.77628525816624

C	-3.97881549759303	-3.26426369298617	1.23096307832609
H	-4.75084333490337	-3.14045017460029	-0.76076590551807
O	-2.24854403094924	1.15526010167067	-3.03190091160117
O	-2.61323462764160	0.02827736354602	-3.24194541446144
H	-6.08160903668380	-4.99954847152814	3.30114873356293
H	-4.13163841272267	-4.75644374176442	4.84287889156503

TS_BC1



Total Enthalpy ... -1258.54016094 Eh

Final Gibbs free energy ... -1258.63233380 Eh

Cartesian coordinates:

C	3.85320154229079	2.40525585998236	-1.23387542568735
C	3.98515158710783	1.04159847038936	-1.55762157842681

C	2.90061923988936	0.16906292884223	-1.45259466222617
C	1.66643039935508	0.67188708546476	-1.01776679804189
C	2.63364584207289	2.93344776654205	-0.79845378346445
C	1.55290612357910	2.05787614841348	-0.69644124853512
C	0.36264601113331	0.09718310164474	-0.79567390354272
C	-0.45125557414392	1.15617237152065	-0.35995088155252
H	4.71856909760933	3.06639193515875	-1.32639060551315
H	4.95222518455962	0.66298268755599	-1.89788824095057
H	3.00828146771440	-0.88785033221995	-1.70818959715384
H	2.53538635887388	3.99290327160045	-0.55344792313519
N	0.24083733200939	2.32491335388157	-0.29215069250205
C	-0.26914374299134	3.62282725170983	0.09451237883641
H	-0.28208001826294	4.31330344364442	-0.76477609253163
H	0.35488624822483	4.05924355005246	0.89016369357980
H	-1.29323334190215	3.51051402048549	0.47412264777403
S	-2.11207364793468	0.75562911442659	-0.05001669967032
C	-0.33837535399400	-1.12146336080594	-0.99349650318076
C	-1.71882757118317	-1.08363778582589	-0.34253612818689
H	-0.66366735513409	-0.89743877325219	-2.49185957697377
H	0.17152821595418	-2.09084280578312	-1.01201917790318
H	-3.73286032843202	-2.73590948159376	0.43390161934995
C	-2.95067046368729	-2.66106932460421	1.19498609355325
C	-3.07336637535607	-3.37198713415258	2.39341694138374

C	-2.07572549736210	-3.27813028764017	3.36675457092465
C	-0.95419081224760	-2.47195504534155	3.13455091549162
H	-0.16880034185936	-2.39676531507284	3.89135245319486
C	-0.83174990197514	-1.76597312410699	1.93764462048051
H	0.04624213055824	-1.14023655275179	1.76044862098170
C	-1.83248110657018	-1.85140153385019	0.95588794365492
H	-2.51032685742801	-1.42404781266379	-1.02758517271821
O	-0.67214729690885	0.72017350497769	-3.52047368578393
O	-0.93293220763829	-0.54786164208356	-3.50299444324557
H	-3.95054062411802	-4.00162482268080	2.56450524371992
H	-2.16810836180302	-3.83317073186358	4.30395507800075

HOO•

Total Enthalpy ... -150.70876467 Eh

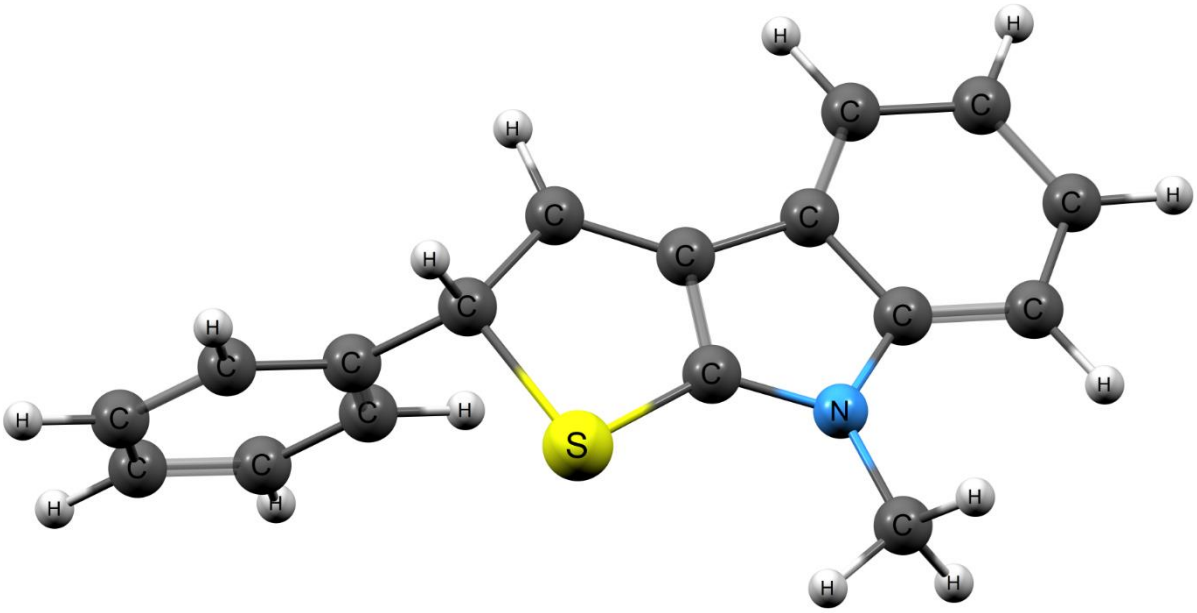
Final Gibbs free energy ... -150.74236599 Eh

Cartesian coordinates

O	-7.02494688128490	3.43925713212636	-0.00080494659987

O	-5.70998647504142	3.46021545258229	0.03268859483127
H	-7.27188664367367	2.93469741529135	-0.80713364823140

C1



Total Enthalpy ... -1107.81345487 Eh

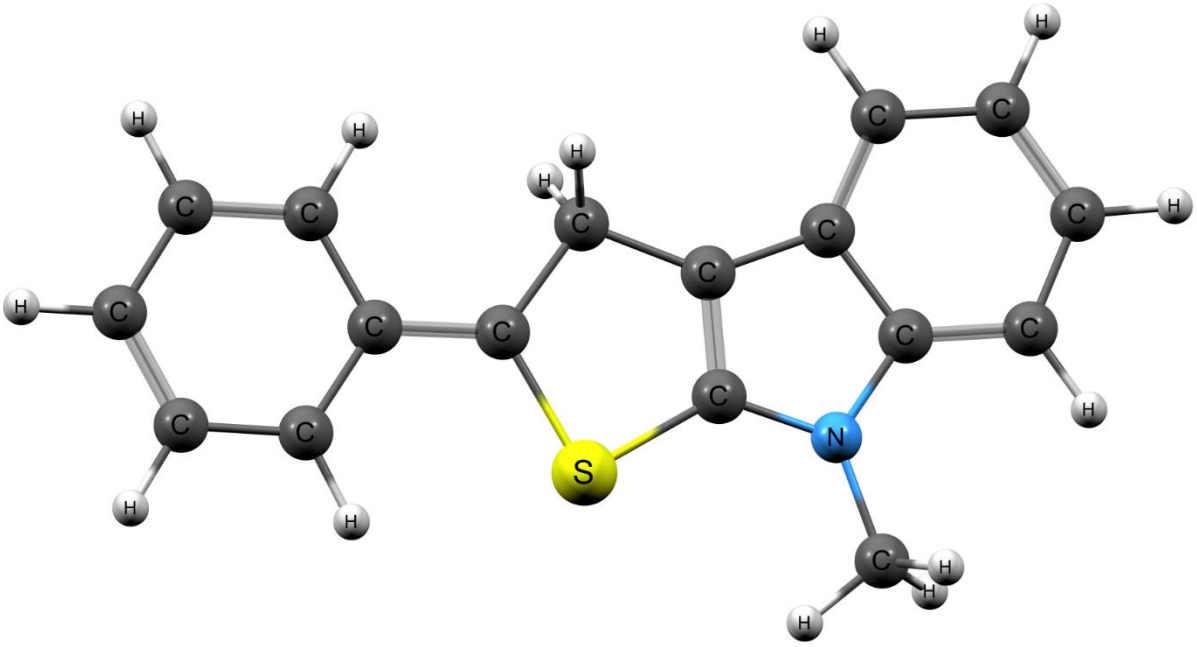
Final Gibbs free energy ... -1107.89705964 Eh

Cartesian coordinates:

C	1.66595665801713	1.16629163970236	-1.19063069575610
C	1.82934647476097	-0.21343369811189	-1.42248491818646
C	0.78648532750574	-1.11011611377317	-1.18291044142553
C	-0.43703997357734	-0.62079818422039	-0.70478496362460
C	0.45820281932636	1.68287951919776	-0.71343155167101
C	-0.58176812418213	0.78208370848177	-0.47220907418787
C	-1.70441309088725	-1.22834126180076	-0.35346868784947
C	-2.52539955652852	-0.16389056931072	0.05883242274820
H	2.49769214666986	1.84758040870293	-1.38796485120477
H	2.78686103353556	-0.58484035060253	-1.79645533946091

H	0.91928634728811	-2.17938657276755	-1.36635780649322
H	0.33580386663370	2.75367681993124	-0.53738492926851
N	-1.86814807843415	1.03597468794900	0.00071760569494
C	-2.39929391747661	2.33921847014858	0.33126959245786
H	-2.48945107123842	2.97415010181155	-0.56639272404086
H	-1.74761863514190	2.85031103680927	1.05798968961958
H	-3.39478658974402	2.22124109652454	0.77952156100335
S	-4.13559276206967	-0.60482677287886	0.55982566921346
C	-2.32135715183702	-2.48251382867017	-0.28719799294038
C	-3.74327915181578	-2.44089005063077	0.22144523249966
H	-1.86365370261168	-3.43917499720641	-0.53920241240172
H	-5.84662282511772	-4.10989541602993	0.70136842860347
C	-5.15025683965040	-4.07539105239303	1.54453746846329
C	-5.40201590743657	-4.83777865114457	2.69049476345114
C	-4.51343141294749	-4.79437475770054	3.76756869627067
C	-3.37120995466238	-3.98659932288528	3.69285048217338
H	-2.67189497476686	-3.94999299612775	4.53254147258461
C	-3.12104254645752	-3.22969494206618	2.54830254276527
H	-2.22983033502656	-2.59981259967130	2.48789676310949
C	-4.00988231922831	-3.26639783696535	1.46212279543973
H	-4.47016806927224	-2.73757242943254	-0.55533853899302
H	-6.29430252535834	-5.46766173524021	2.73961897460471
H	-4.70727515826851	-5.38920334962909	4.66410076680164

C2



Total Enthalpy ... -1107.81906968 Eh

Final Gibbs free energy ... -1107.90206265 Eh

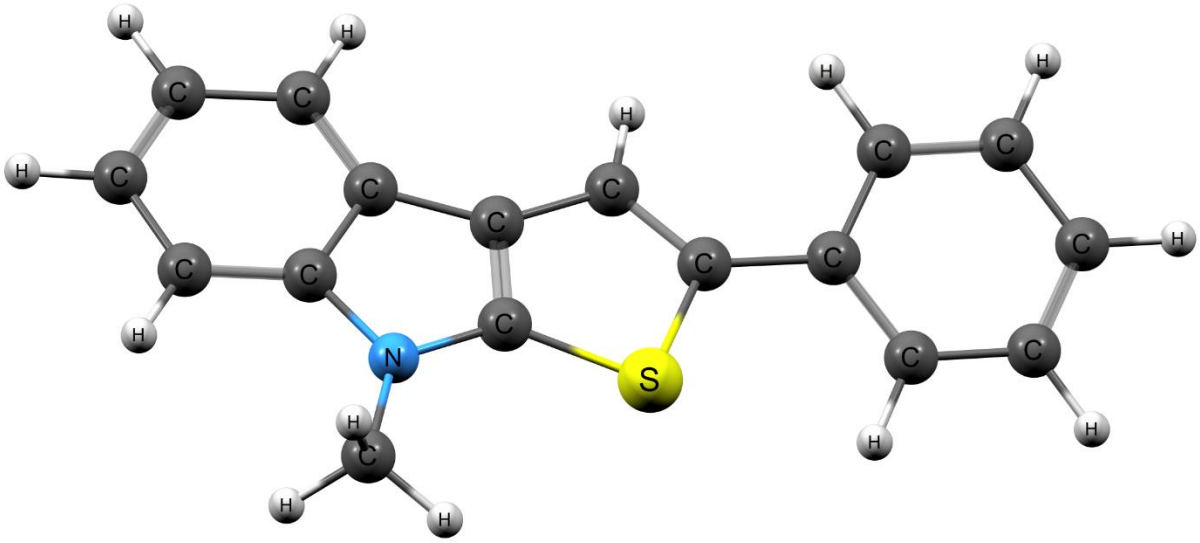
Cartesian coordinates:

C	-5.36312450531212	0.89143179882281	0.23711373595886
C	-4.64323863956632	2.03999191900620	-0.15392408618346

C	-3.25169425039631	2.07543287871756	-0.09295022528054
C	-2.55830851823773	0.94117267074707	0.36837344696595
C	-4.70646501274975	-0.24996120363710	0.69934681465959
C	-3.30968200653204	-0.21470141684489	0.76343346721239
C	-1.17966074676246	0.60599957425929	0.56499763200567
C	-1.16316475384274	-0.67885208811648	1.04825505802989
H	-6.45448525744134	0.89402965797217	0.17645975858522
H	-5.18995348609384	2.91653415021313	-0.51152167192394
H	-2.70397983385604	2.97040477664226	-0.39933993792884
H	-5.26658707823909	-1.13838734116567	0.99918374479769
N	-2.42521362001513	-1.20017917885825	1.18347070204806
C	-2.78650638213788	-2.52484319368793	1.63830091273317
H	-3.51357891100778	-2.46635202820961	2.46392544056781
H	-1.88875103001156	-3.04105218069713	2.00393134628688
H	-3.22809206879020	-3.12149801997271	0.82260911471906
S	0.42313883731725	-1.34834388321283	1.38113550253904
C	0.17303245053331	1.22277146175803	0.40733578053446
C	1.17334981511900	0.17320600894721	0.85505268099008
H	0.37839737275508	1.52838470941942	-0.63854098164856
H	0.28895922326112	2.14536982578328	1.01130848121413
H	2.53483002437170	2.37994146870141	0.10275604478887
C	3.17438854953273	1.56408324404884	0.44412378263798
C	4.55387323754330	1.74019339918445	0.45465401530232

H	4.97500582163082	2.69265664653132	0.12101777208227
C	5.40512222339194	0.71304662571505	0.88679168207023
C	4.84764004375693	-0.50258775498345	1.31160279011749
H	5.49917908762896	-1.31237997684713	1.65132013579440
C	3.47119580744126	-0.69138532669483	1.30611722194848
H	3.06339161700707	-1.64827982064579	1.64250709710134
C	2.58647899196075	0.33781082129396	0.87128800097364
H	6.48818299774114	0.85714177581034	0.89292474030038

3a



Total Enthalpy ... -1107.26573181 Eh

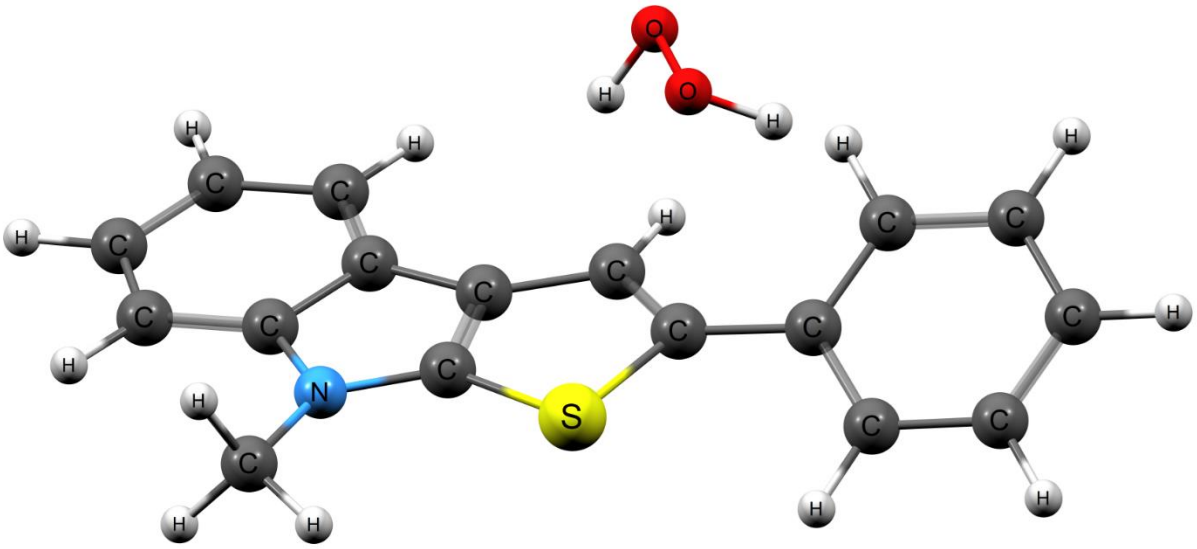
Final Gibbs free energy ... -1107.34653824 Eh

Cartesian coordinates:

C	-5.35866668399622	0.82386472612777	0.04455673081314
C	-4.62267699705768	1.92256887121618	-0.44163471184547
C	-3.23064618337356	1.94815637564854	-0.35824839712091
C	-2.56116028897651	0.85844071332426	0.21896625535173
C	-4.72163333302146	-0.27523201196827	0.62333280883864
C	-3.32543654337096	-0.25124780576176	0.70077759159845
C	-1.17958320145831	0.53422946321446	0.47909062775898
C	-1.19012813168723	-0.72221325463206	1.08701437317140
H	-6.44919097759370	0.83130781832518	-0.02985444690200
H	-5.15298063724343	2.76733378241575	-0.88860027201614
H	-2.66660178636445	2.80514402419975	-0.73502536898202

H	-5.29779999264403	-1.12155970512327	1.00307208264884
N	-2.46179515760442	-1.21461964891379	1.21909486747494
C	-2.85279236150559	-2.45767788610920	1.84525774668232
H	-3.24772092024748	-2.29483010819757	2.86290584880441
H	-1.98057799075255	-3.12303984061231	1.90736847836557
H	-3.62598550887868	-2.95899708832587	1.24346099615912
S	0.38457366630231	-1.30894721867360	1.48569678482602
C	0.14659896682742	1.03380518851617	0.32341776539013
C	1.11060354148323	0.17394717874373	0.80519610852232
H	2.49395347163901	2.49002197278107	0.53729827711296
C	3.14004895578048	1.61862428333292	0.66136707082168
C	4.52373358183795	1.78814083887691	0.66975235461886
H	4.94352415718899	2.78890094125176	0.53660195383914
C	5.37312532620855	0.69205529345716	0.86094949437468
C	4.81767858478494	-0.57848806425052	1.03933495489758
H	5.46709997092671	-1.44537750268256	1.18771580230761
C	3.43333918573945	-0.75304009209680	1.01991285826221
H	3.02134539075403	-1.75863147746347	1.13878485104866
C	2.56469440951872	0.34117256138816	0.83095706444444
H	6.45737711953040	0.82842063984303	0.87321273094554
H	0.39364036725409	1.98744703214826	-0.14401328221284

3a_H2O2_S



Total Enthalpy ... -1258.60739407 Eh

Final Gibbs free energy ... -1258.70153093 Eh

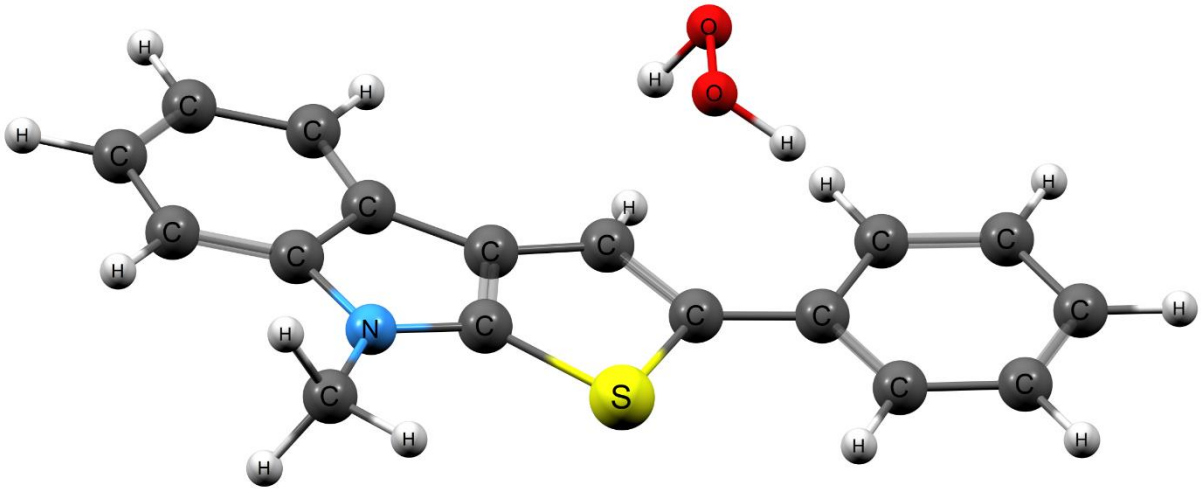
Cartesian coordinates:

C	-5.35470954867945	0.82082242634393	0.03489777381431
C	-4.61606276384543	1.89518285316540	-0.49935415775297
C	-3.22331612005363	1.91343522715047	-0.43134116004876
C	-2.55674593792340	0.84026432223659	0.17912871233121
C	-4.72023326997394	-0.26095066563898	0.64765582516984
C	-3.32312874032330	-0.24481298067543	0.70940420034577
C	-1.17533152094940	0.51621237554622	0.43952249333663
C	-1.18839578451971	-0.71742612645495	1.09532855377721
H	-6.44583709167410	0.83425096067687	-0.02832852827472
H	-5.14503095013705	2.72700026102684	-0.97131428536504
H	-2.65701407411258	2.75187233780881	-0.84451683950311

H	-5.29862417667006	-1.08779472477132	1.06484693260189
N	-2.46121812621429	-1.19515029628442	1.25518887458132
C	-2.85677775102096	-2.40862678021567	1.93560729246980
H	-3.24371108932920	-2.19901094887234	2.94747457629947
H	-1.98879951031060	-3.07681320350940	2.02052674382055
H	-3.63704179236160	-2.92838923094595	1.35940093213518
S	0.38646043564573	-1.30075701107281	1.49910275255627
C	0.15448338474371	0.99799318002578	0.25081270290991
C	1.11370368630930	0.14659083012660	0.76089130038277
H	0.21402439472929	2.11072726107478	2.27933250731949
H	2.45748525942962	2.49028345270263	0.79272508596640
C	3.12047987882218	1.62282354724211	0.79411735239774
C	4.50332084638229	1.80744981472086	0.83274545543592
H	4.91006175860117	2.82218907300722	0.83033225875953
C	5.36469653707833	0.70644212125666	0.89110614562196
C	4.82670373008788	-0.58456908520656	0.90949959495557
H	5.48874394908903	-1.45331142696926	0.95456786600288
C	3.44539783903068	-0.77509223560412	0.86191494066718
H	3.04221723165016	-1.79103939155340	0.85520404898484
C	2.56579139979741	0.32411327958182	0.80083119474738
O	0.76426881886069	2.65244601957766	2.87639489993111
O	1.48553569938631	1.63857301699683	3.59375210915603
H	2.32972943757472	1.61598120389753	3.10695083694012

H	6.44689030180565	0.85382121757068	0.92718710328835
H	0.41151265907454	1.92270232603830	-0.26745809576206

3a_H2O2_t



Total Enthalpy ... -1258.52509591 Eh

Final Gibbs free energy ... -1258.62160318 Eh

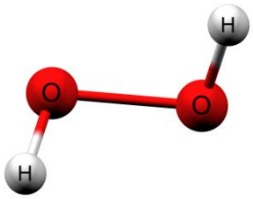
Cartesian coordinates:

C	-5.29266391442764	1.00641851987605	0.35646698653174
C	-4.56750346306782	2.11613713334055	-0.11184078020376
C	-3.16990853515103	2.10157719624286	-0.13913349777840
C	-2.49639247261726	0.95892085796180	0.30699359073743
C	-4.64340245259320	-0.14768207324372	0.81172861501926
C	-3.25070447136389	-0.15467815865773	0.78220733532484
C	-1.10000937973597	0.58987315669863	0.42708863555010
C	-1.10753951032343	-0.72420576268226	0.95651575642176
H	-6.38487442669753	1.04255903195847	0.36734363526044

H	-5.10552648075166	3.00168485268228	-0.45852780615991
H	-2.61077354191978	2.96731029537828	-0.50201221797595
H	-5.21214577413947	-1.00591944061785	1.17468541738816
N	-2.36986730471496	-1.17175726018838	1.17797557001744
C	-2.76607709910793	-2.46276525864815	1.69840109194551
H	-3.41473250329310	-2.33769742937656	2.57976547101715
H	-1.87080723454911	-3.02288324600772	1.99775853612525
H	-3.31193070728593	-3.04234542248362	0.93606093198773
S	0.46899337691524	-1.45329278862172	1.15869511948703
C	0.18233378054083	1.08836980261342	0.20162533777538
C	1.21441751010820	0.11256031165110	0.62497658129071
H	0.42606873966185	1.98994754151748	-0.35784105183581
H	0.31180582714501	2.16924710879569	1.99635364280946
H	2.51180454754713	2.42869853126739	0.13745267279146
C	3.16143592293595	1.61353900059920	0.45631644303956
C	4.51816680685739	1.83498112019412	0.59990537949023
H	4.92578797158350	2.82506207063700	0.37752816253664
C	5.38150674790098	0.80662065268191	1.03165554653369
C	4.84421757778581	-0.46500187567323	1.32917333834181
H	5.50619793691237	-1.26681431530251	1.66778070570309
C	3.49186490510449	-0.71166645318399	1.19634654220326
H	3.10076960170657	-1.70573782410764	1.42754030886821
C	2.58630178539877	0.32049318331953	0.74941605228344

O	0.74842716495152	2.41894591728081	2.84042830458267
O	0.83945398959388	1.14563592899858	3.49775408462346
H	1.72813981615166	0.84936580766021	3.23263334261711
H	6.45284376293857	0.99145628743974	1.13650871564978

H2O2



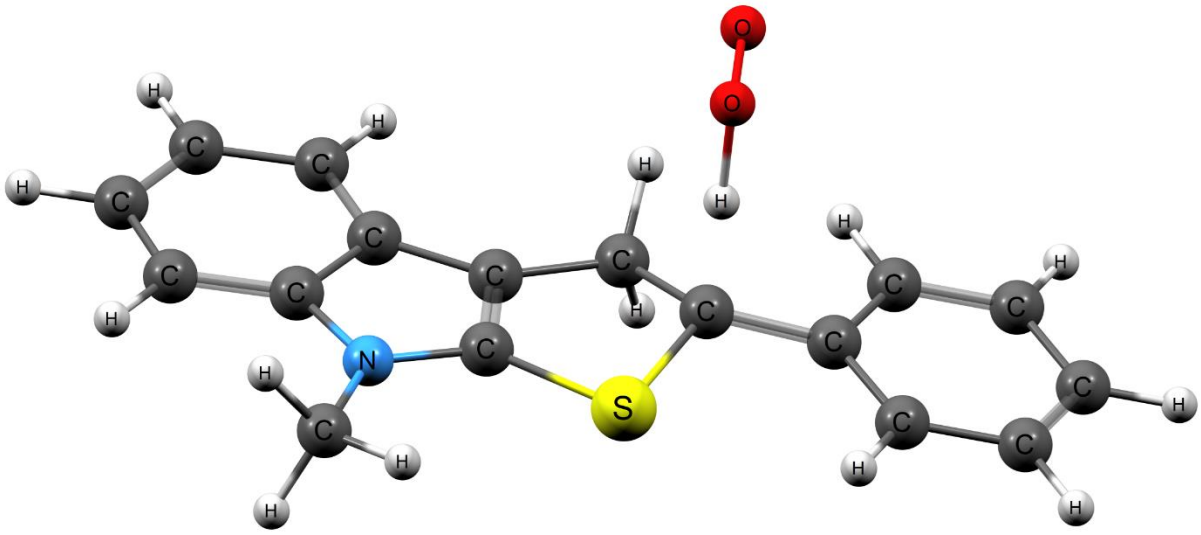
Total Enthalpy ... -151.33126495 Eh

Final Gibbs free energy ... -151.36503790 Eh

Cartesian coordinate:

O	-7.11229368848351	3.55223822583719	-0.06259105777906
O	-5.68793215915122	3.54200654695098	0.14592590371257
H	-7.21053220382629	2.84384735507675	-0.72134940107520
H	-5.63386194853897	3.20452787213508	1.05621455514169

TS_BC2



Total Enthalpy ... -1258.54686731 Eh

Final Gibbs free energy ... -1258.61306050 Eh

Cartesian coordinates:

C	-5.32018550735048	0.84949493950635	0.17152787253812
C	-4.61051292313493	2.01881519696358	-0.17582835728423
C	-3.22320588141872	2.07857007556021	-0.07021151571770
C	-2.52478038722919	0.94777421429253	0.39237498491427
C	-4.65830395431701	-0.28843773896213	0.63356911370800
C	-3.26505693195963	-0.22860496290125	0.74331002471166
C	-1.14743788905340	0.63503245009984	0.62494570250473
C	-1.12085251473261	-0.66019474155451	1.08914781656670
H	-6.40894027360487	0.83368063275202	0.07643905708563
H	-5.16264707555435	2.89151430156897	-0.53412037544542

H	-2.68197104188227	2.98843149000689	-0.34170553709354
H	-5.21121535777022	-1.19211470679435	0.89876893193054
N	-2.37634816602474	-1.20435492459758	1.17801898552889
C	-2.72796105029368	-2.53656493495740	1.61974162911461
H	-3.51172139547060	-2.49072966975300	2.39207867272016
H	-1.84251572703867	-3.01991577853461	2.05416196694128
H	-3.09351878952902	-3.15422615084919	0.78242242628327
S	0.46129330228789	-1.30299538307083	1.46717070264870
C	0.19520638944535	1.27491747767437	0.50778774457027
C	1.17346966110344	0.34424085215970	1.23807693133808
H	0.50847296117961	1.39780227588412	-0.54844811458907
H	0.23187921082697	2.28353906786164	0.95965494468847
H	2.53247524464725	2.51193783272893	0.36723734913736
C	3.18277301705351	1.66691445141799	0.59823561513244
C	4.56307281896754	1.81180474427974	0.46513247521661
H	4.97276943107206	2.76541229454616	0.12198860863319
C	5.42083934689162	0.74845582238074	0.76650593353534
C	4.88064382351267	-0.46604906742450	1.20618338419688
H	5.53980798932963	-1.30522579505991	1.44322389480247
C	3.50240383669545	-0.61574889912013	1.34307674272458
H	3.10352976618191	-1.57282743863548	1.68895243507099
C	2.62253818621649	0.44620309564545	1.03799895325693
O	0.89557620785224	2.77299512290684	3.21348033472006

O	0.91625847156588	1.53651373264883	3.53456019445609
H	1.04418246485954	0.90774581061138	2.56080327517472
H	6.50222994467534	0.86441252071860	0.66006367427889

Relaxed Surface Scan: The last step of the mechanism is barrierless as indicated by an exploration of the PES through a relaxed scan at the RIJCOSX-B3LYP-D4/def2-SVP level of theory starting format 1.6 Å to end point 1.1 Å in **C1** intermediate.

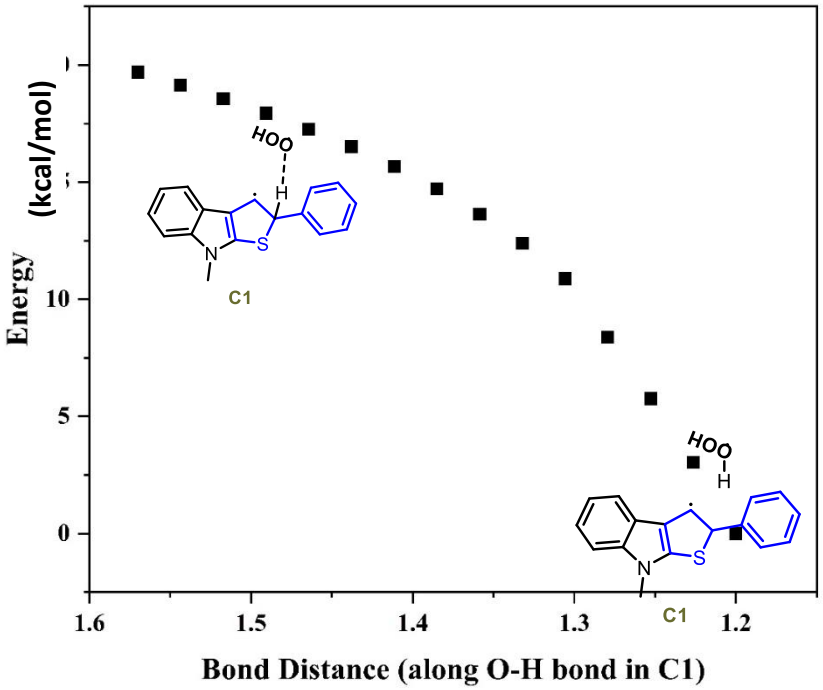


Figure S5. Relaxed PES scan from 1.6–1.1 Å in *C*$_1$ intermediate.

8. References:

1. Kar, S.; Sarkar, T.; Maharana, P. K.; K. Guhab, A.; and Punniyamurthy, T.; Bi-Catalysed 1,2-Reactivity of Spiro-Cyclopropyl Oxindoles with Dithianediol: Access to Spiro-Heterocycles. *Org. Lett.* **2022**, *24*, 4965−4970.

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(b) Andrey, A. A.; Mikhail. M.; Ekaterina M. B. Chameleon-Like Activating Nature of the Spirooxindole Group in Donor−Acceptor Cyclopropanes. *Org. Lett*. **2019***, 21*, 9795−9799.

3. Neese, F. Software update: The ORCA program system—Version 5.0. Wiley Interdisciplinary Reviews Computational Molecular Science 2022, 12 (5).

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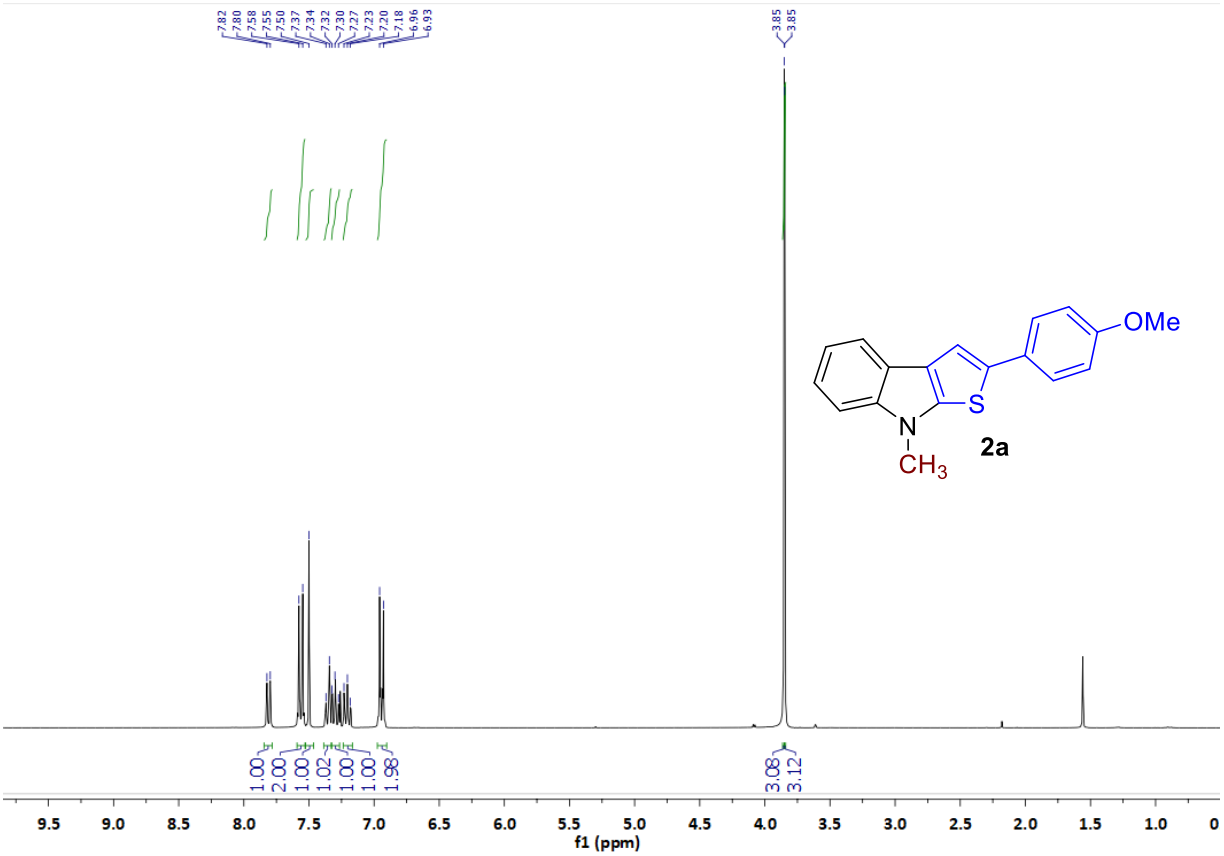
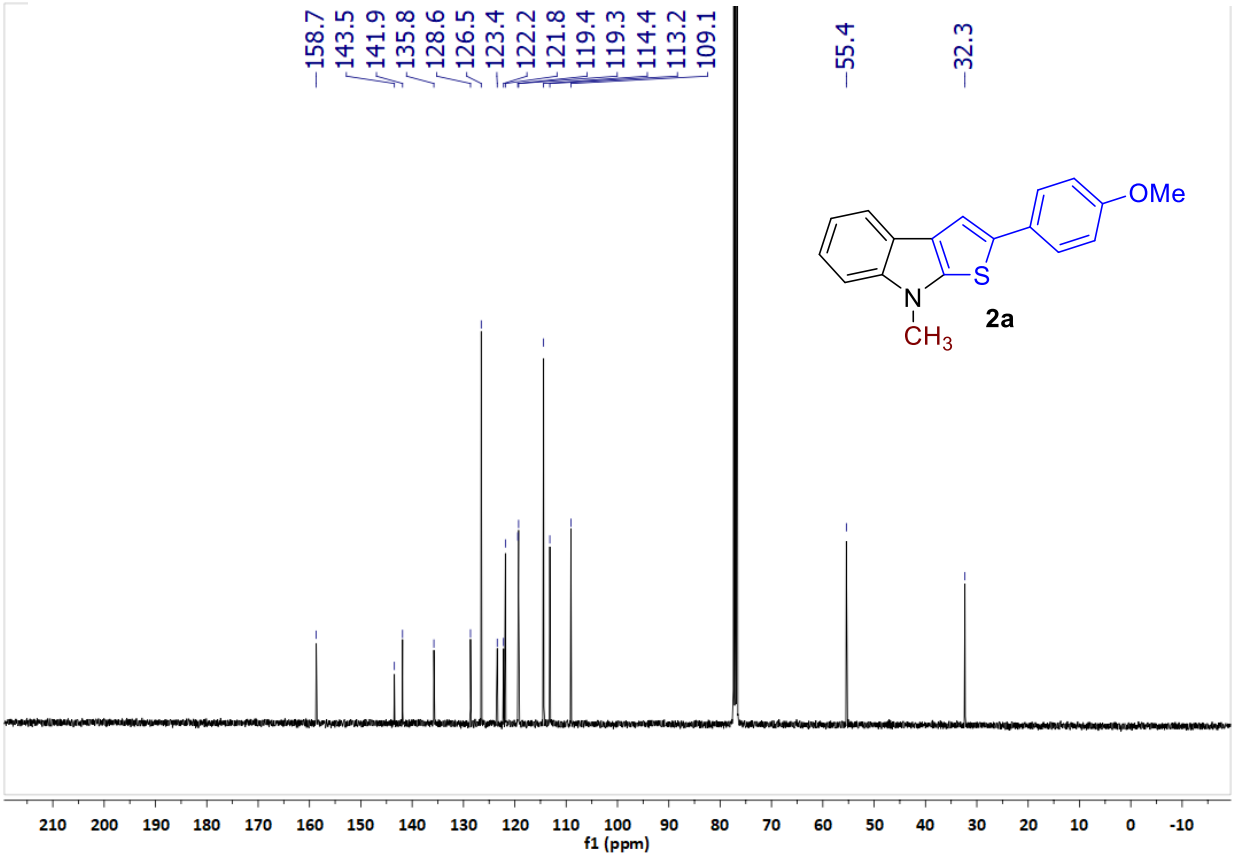
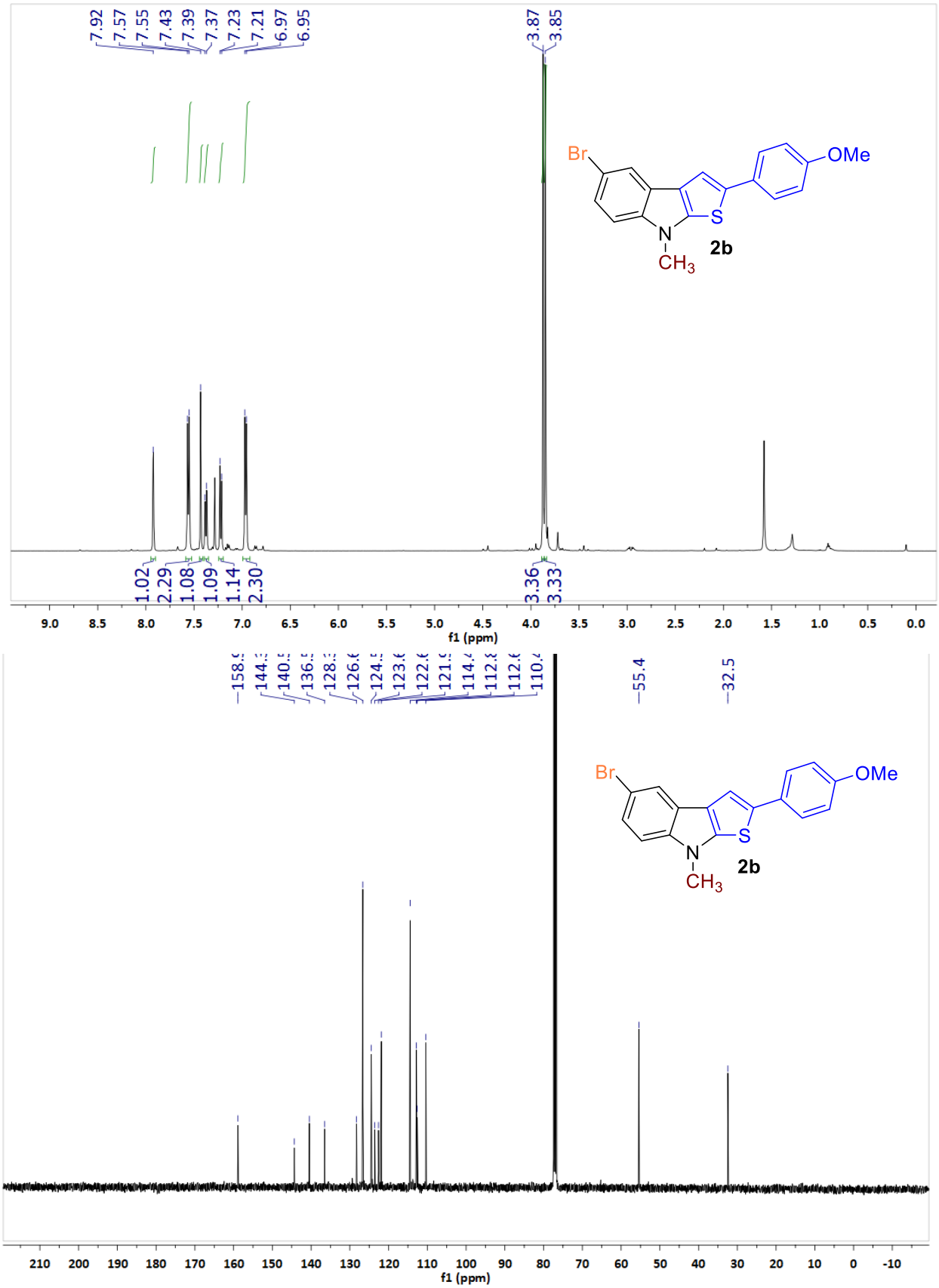
9.0 NMR spectra of compounds

^{1}H and ^{13}C{1H} NMR spectra of 2a:

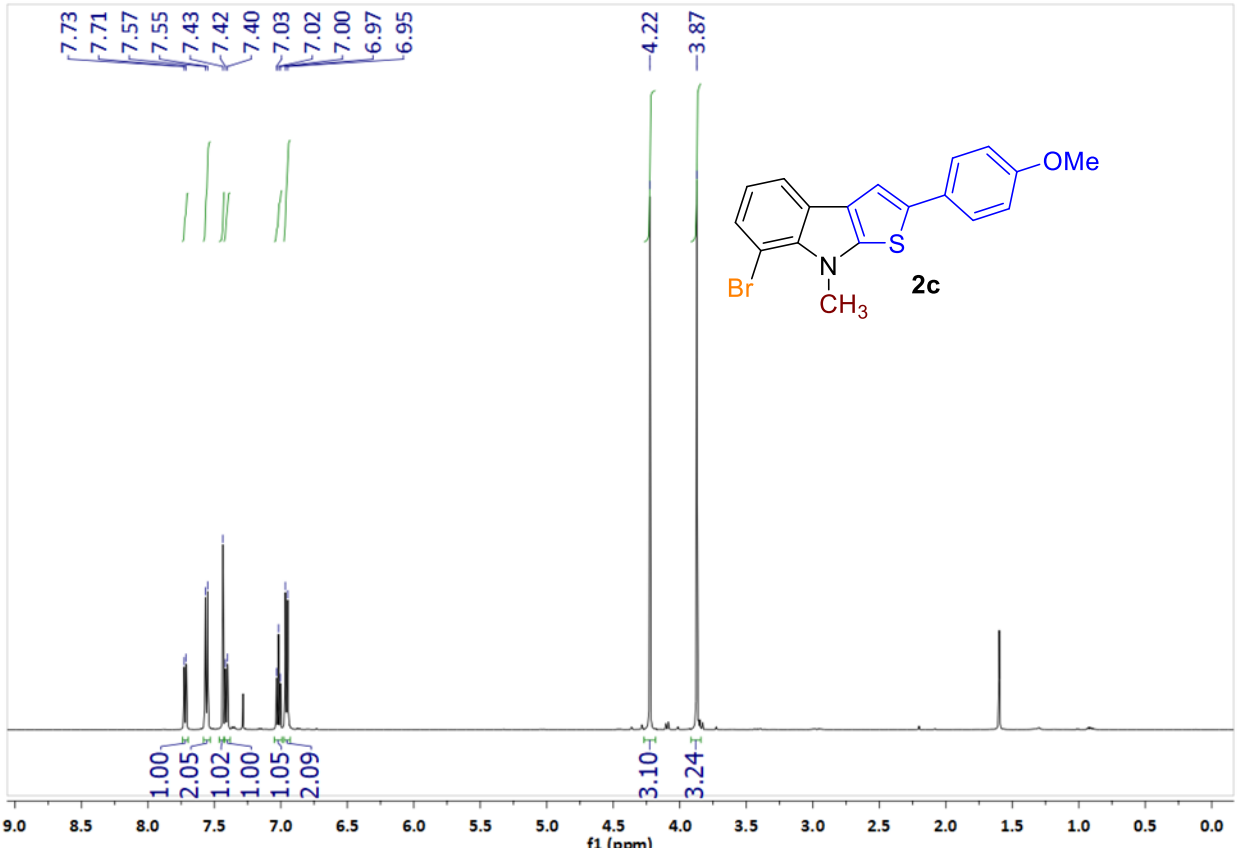


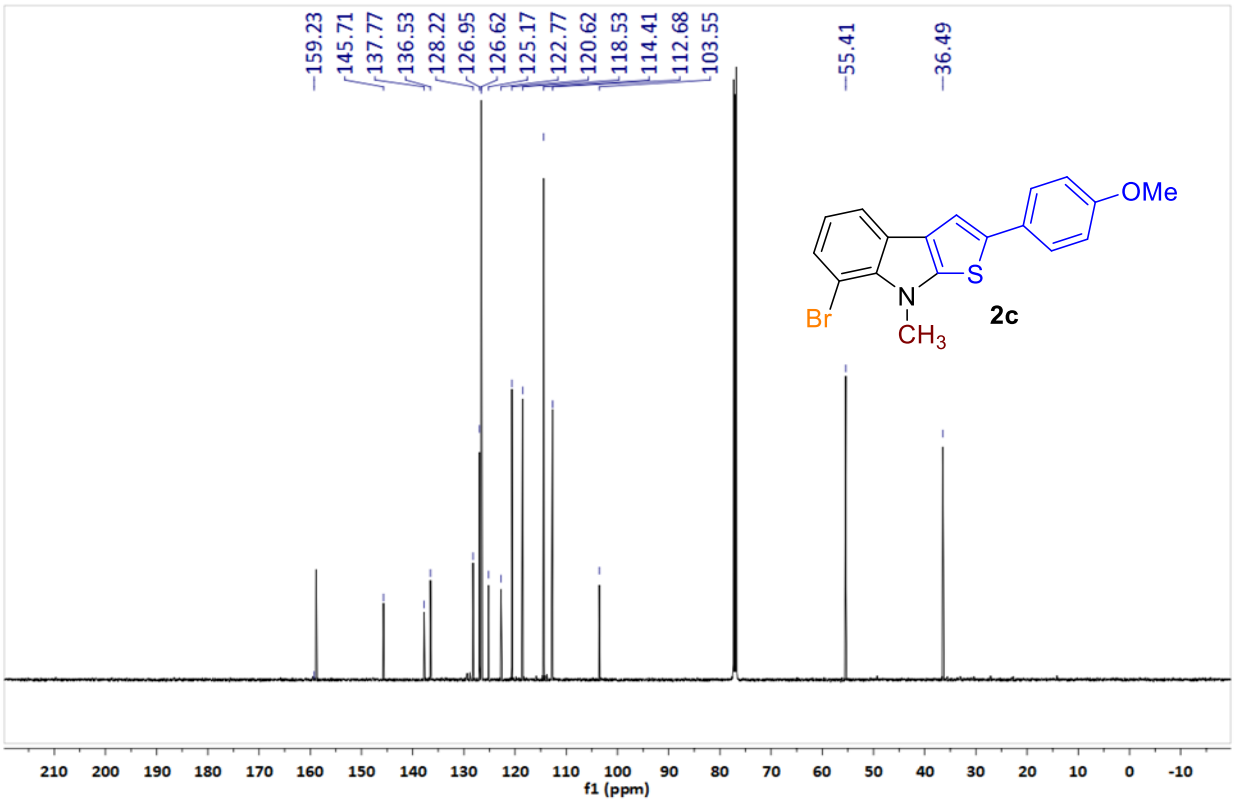


^{1}H and ^{13}C{1H} NMR spectra of

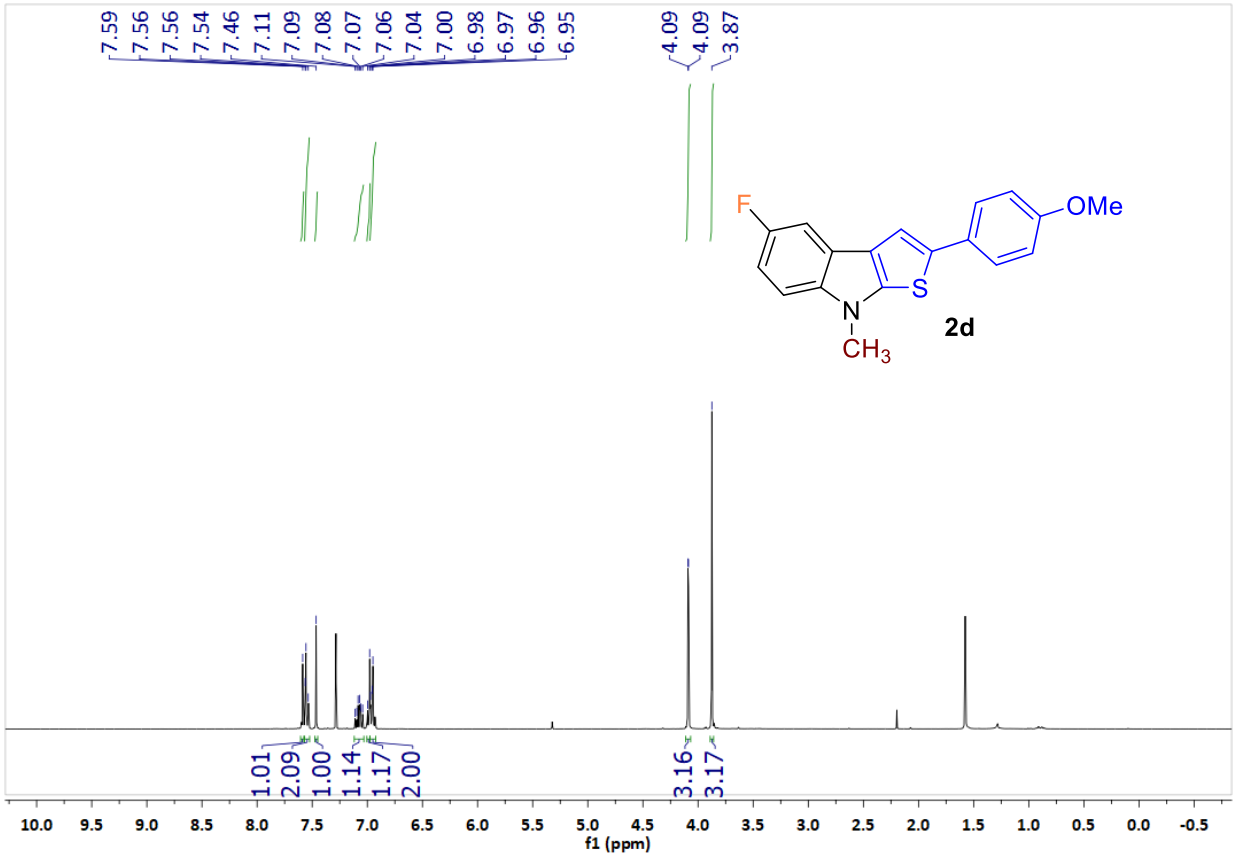


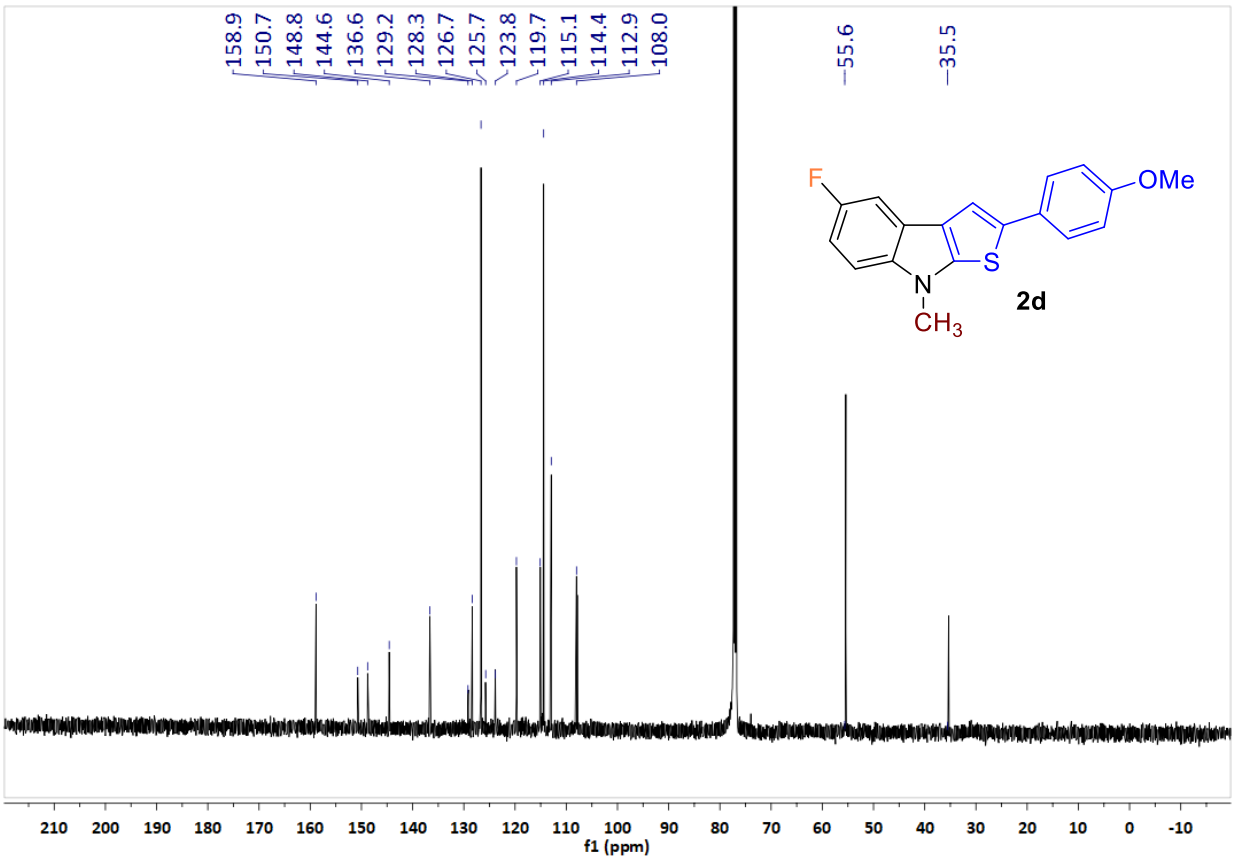
^{1}H and ^{13}C{1H} NMR spectra of 2c:



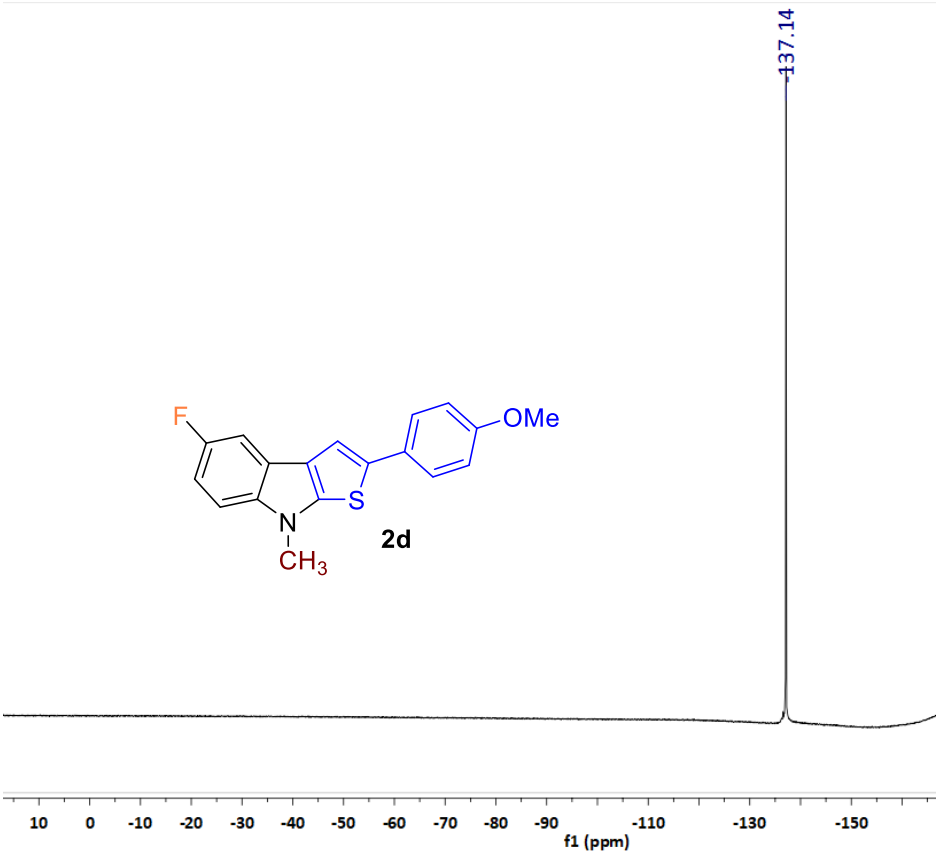


^{1}H and ^{13}C{1H} NMR spectra of 2d:

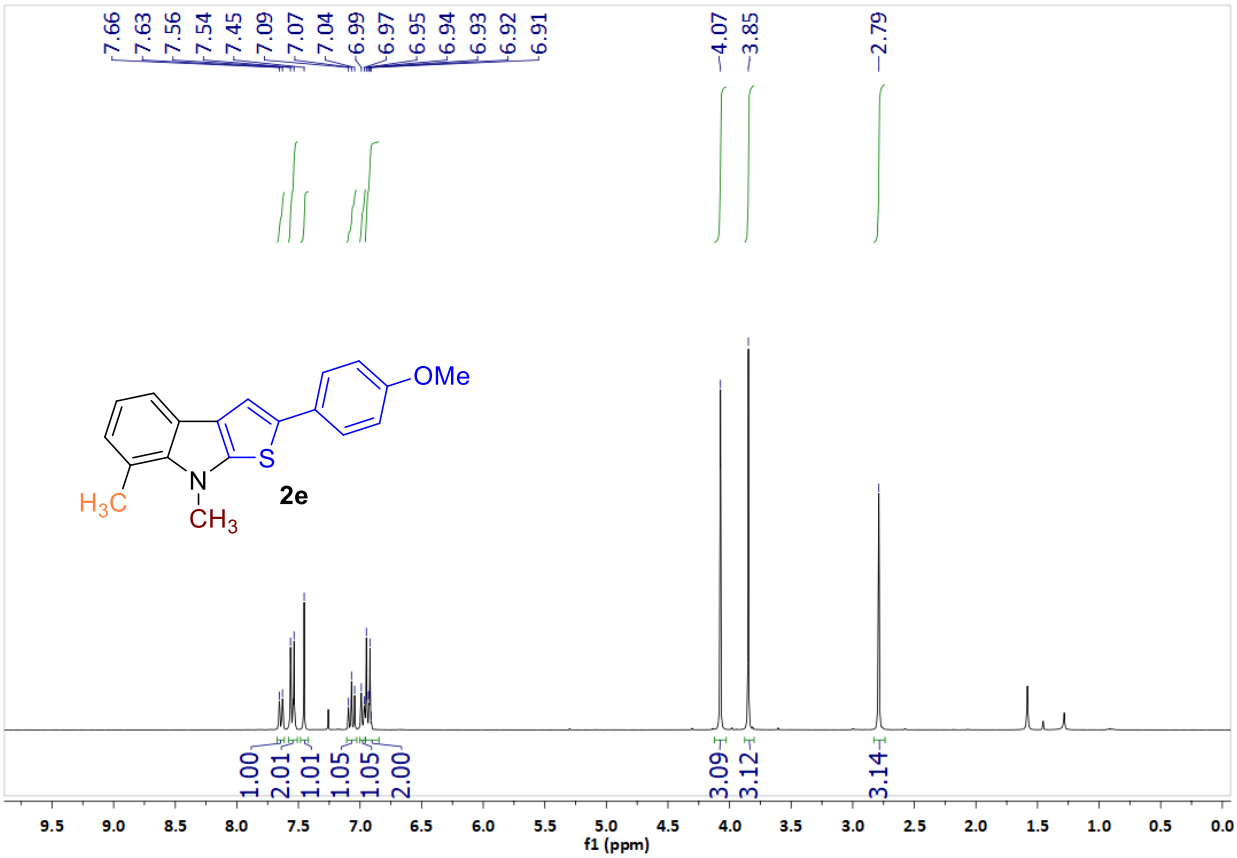


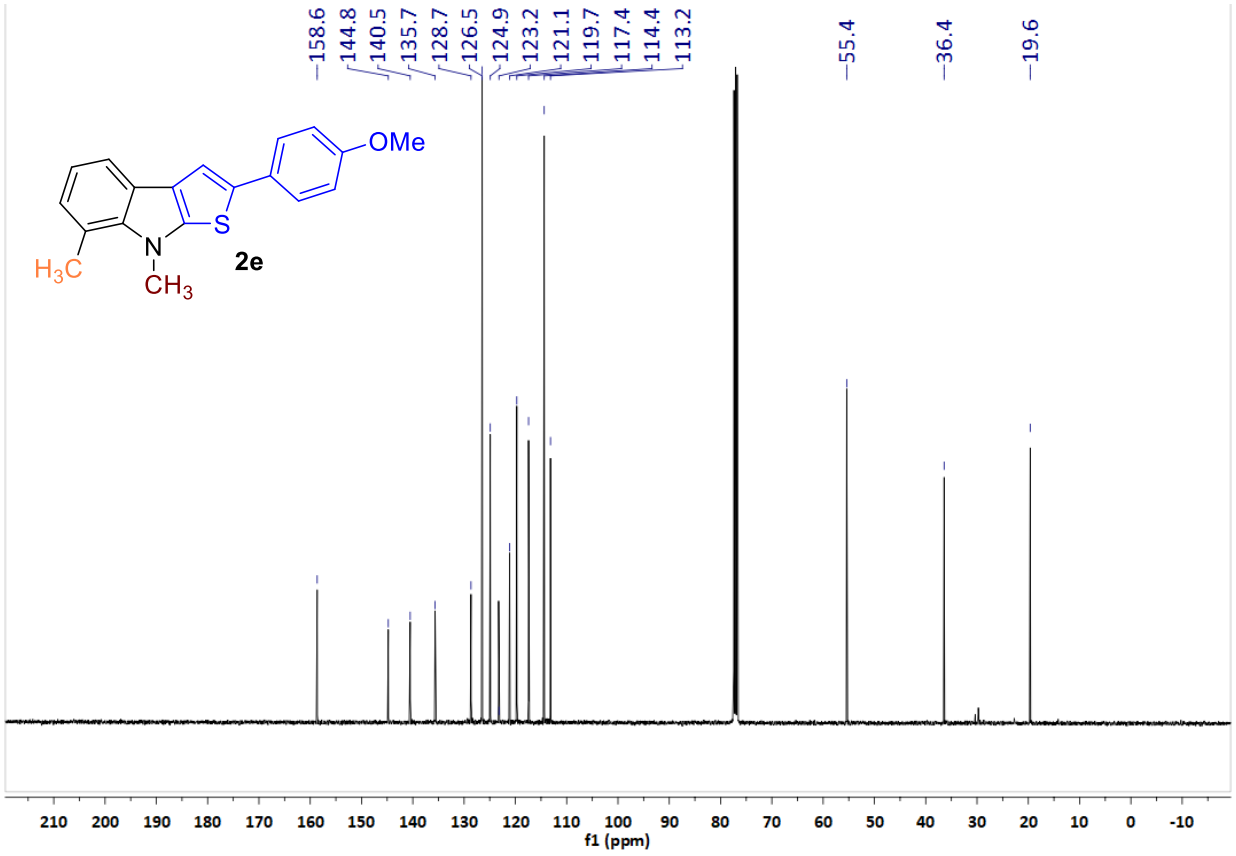


^{19}F NMR spectra of 2d:

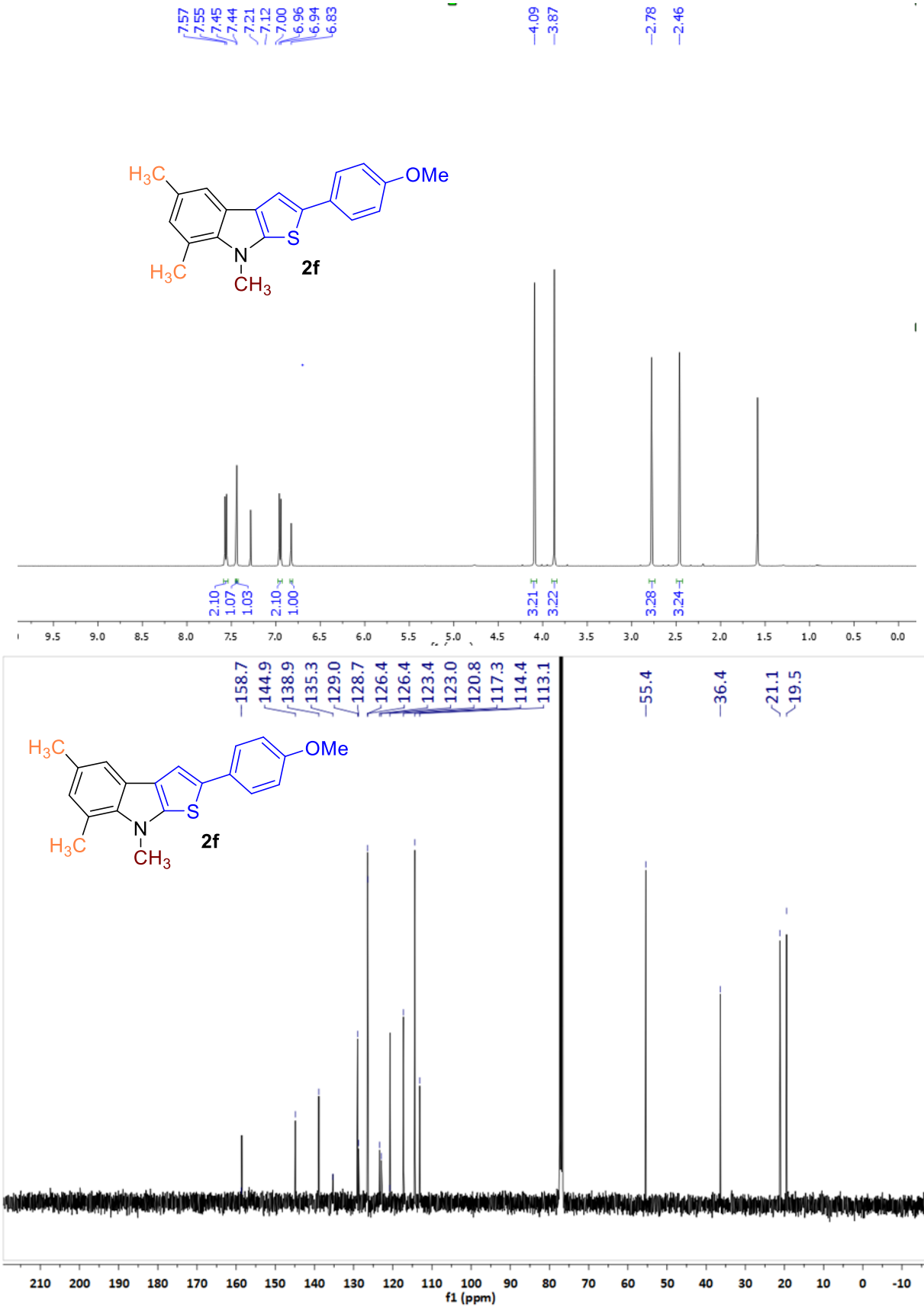


^{1}H and ^{13}C{1H} NMR spectra of 2e:

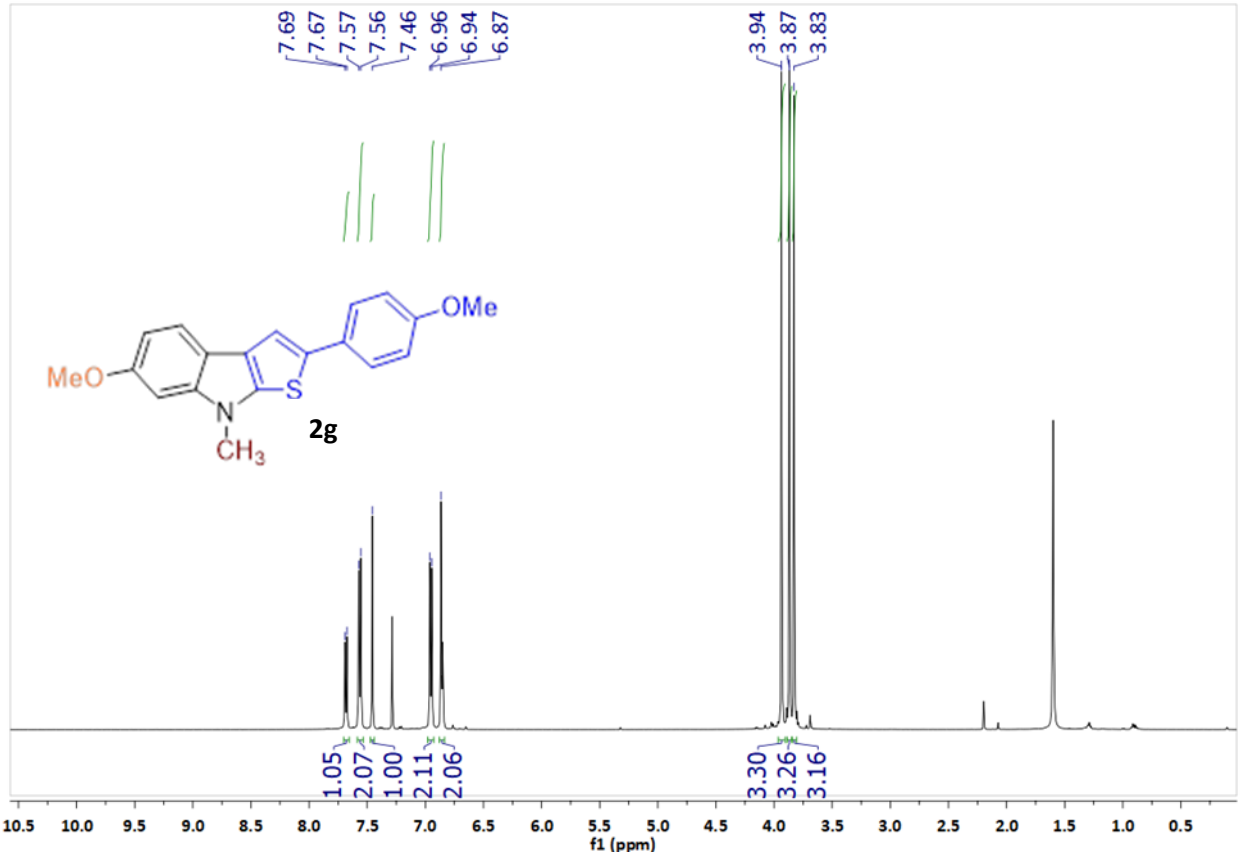


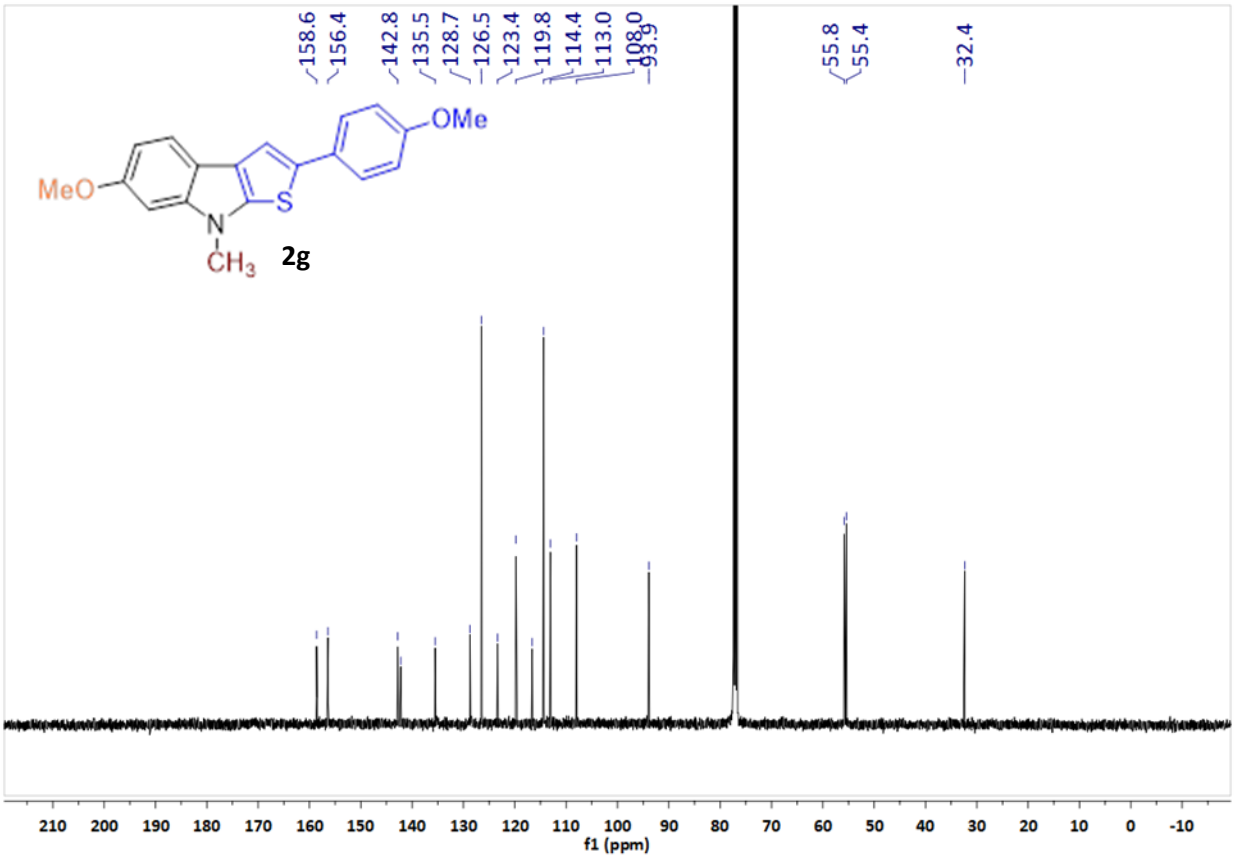


^{1}H and $^{13}C\{1H\}$ NMR spectra of 2f:

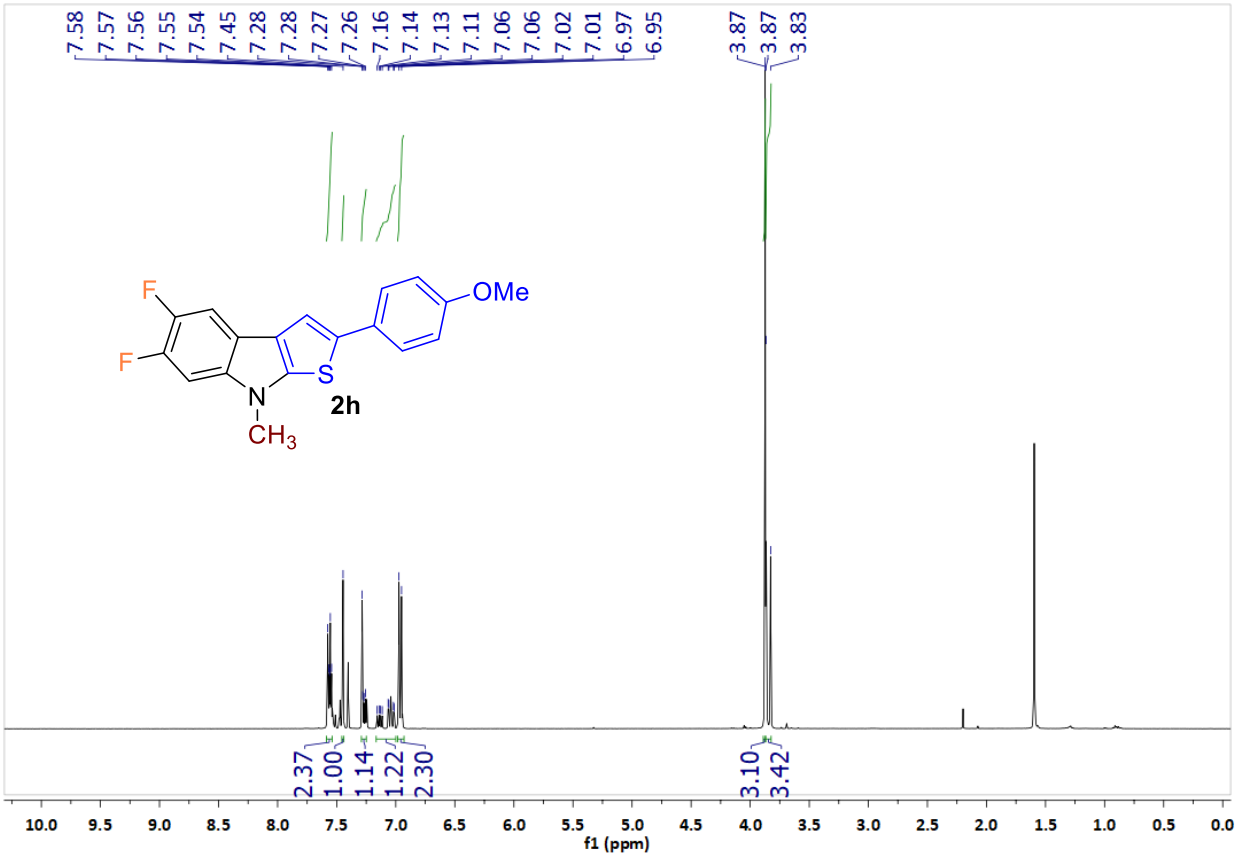


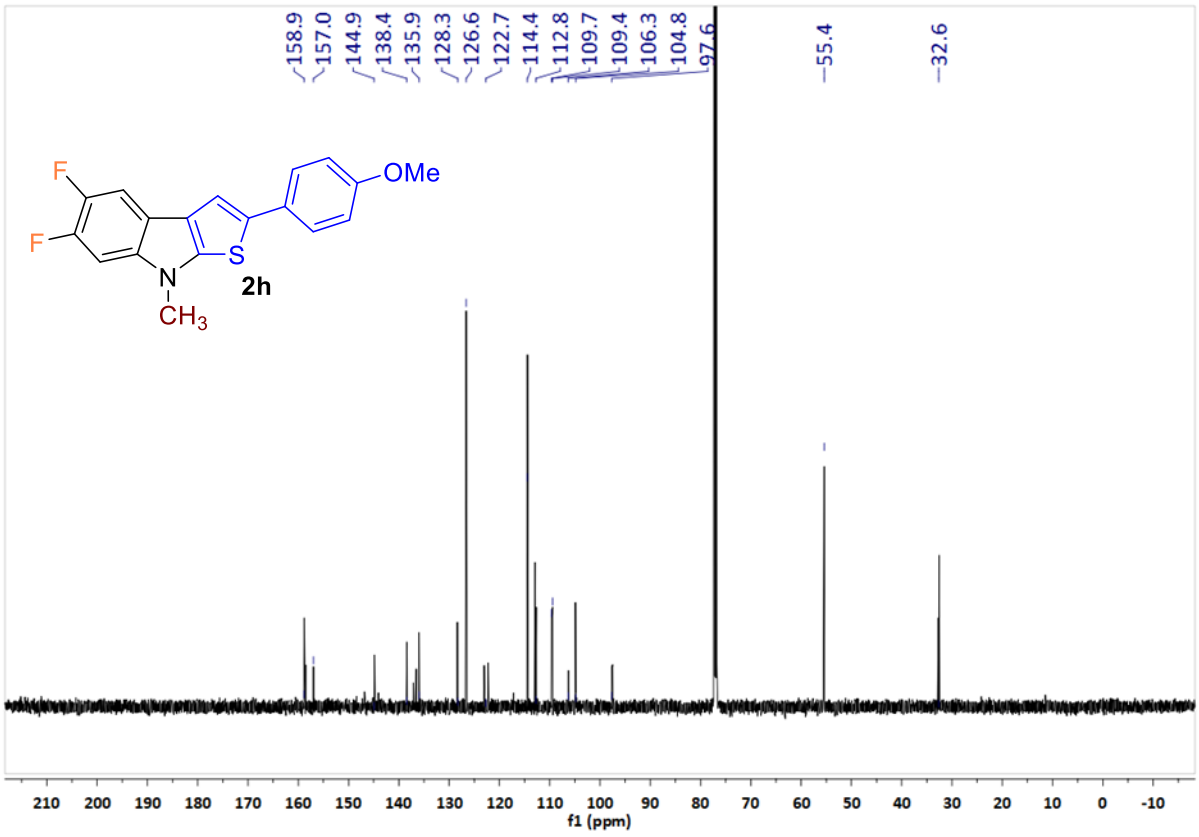
^{1}H and ^{13}C{1H} NMR spectra of 2g:



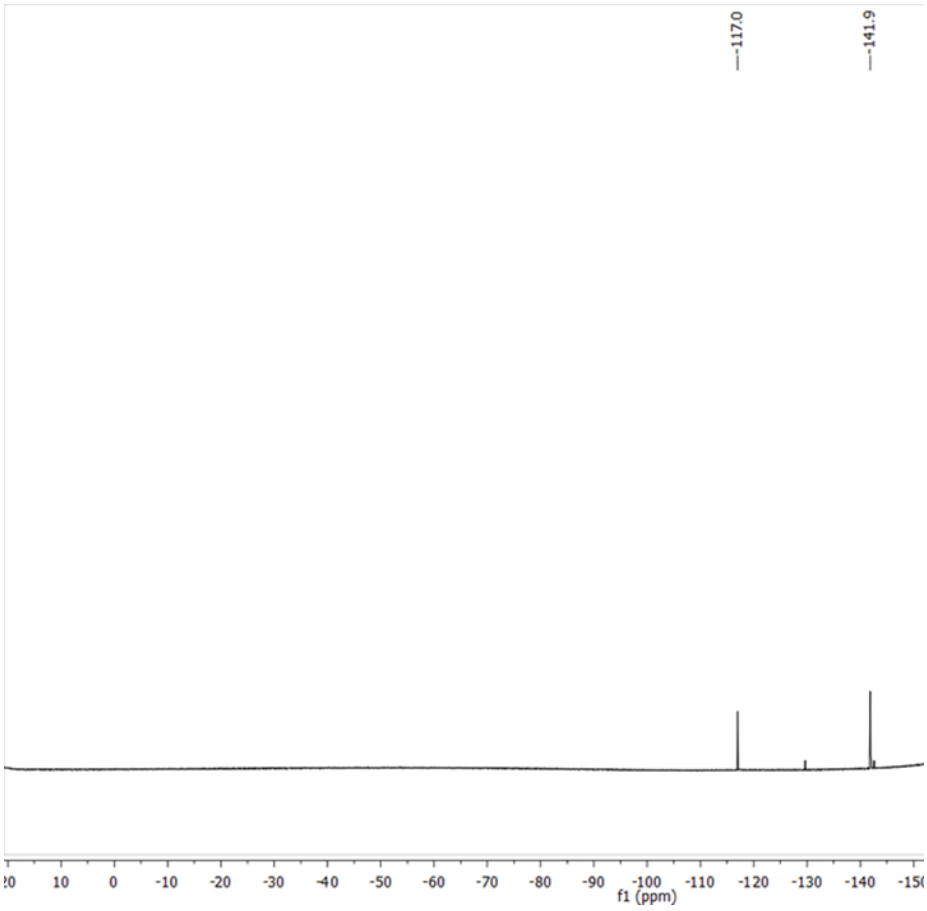


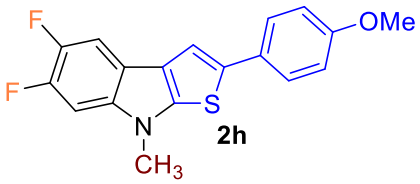
^{1}H and ^{13}C{1H} NMR spectra of 2h:





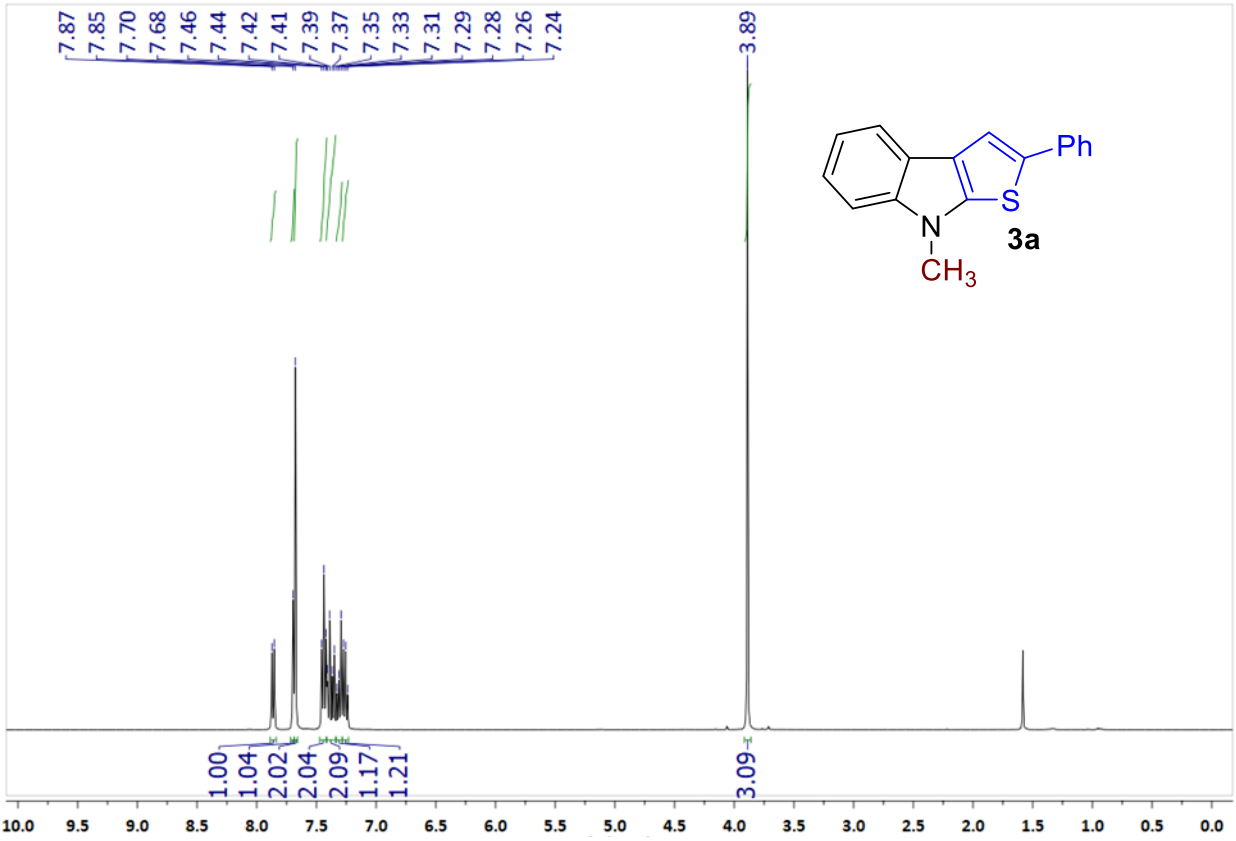
^{19}F NMR spectra of 2h:

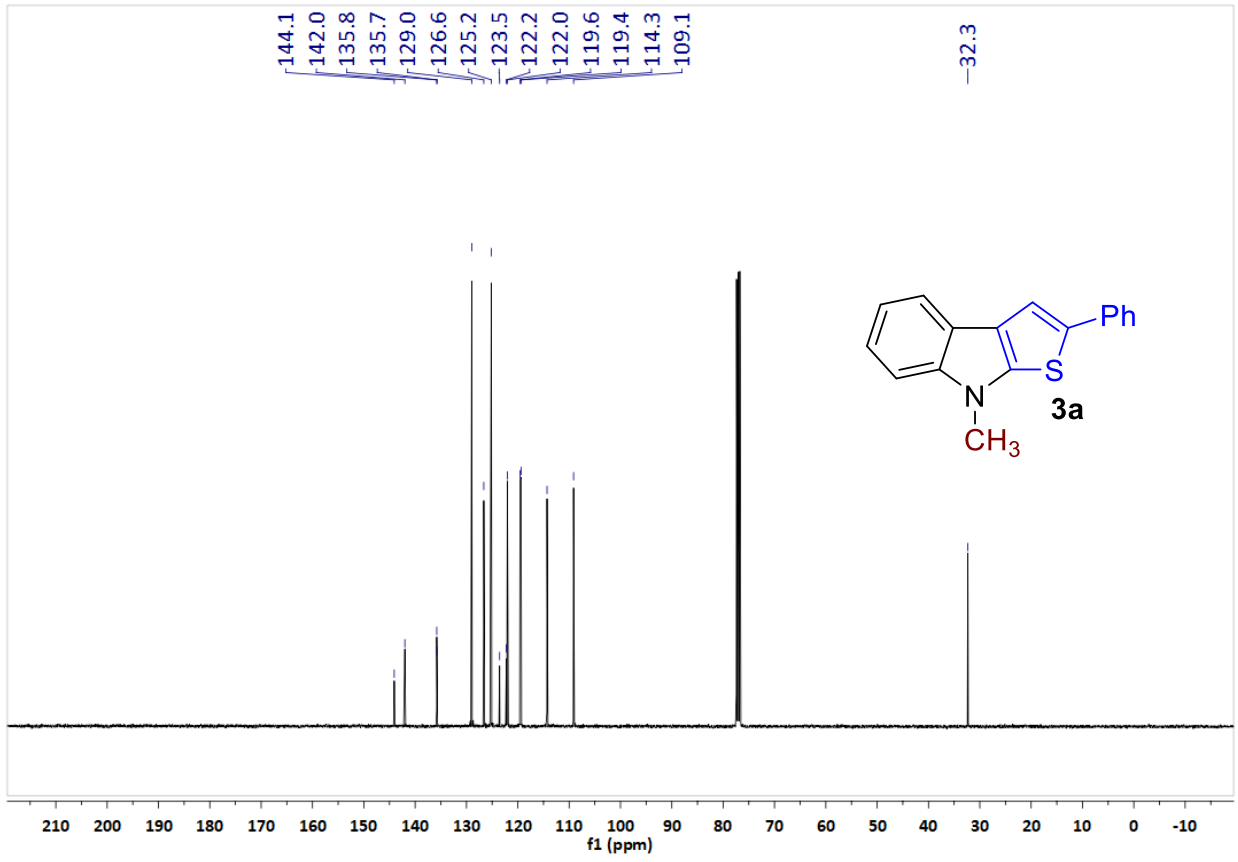




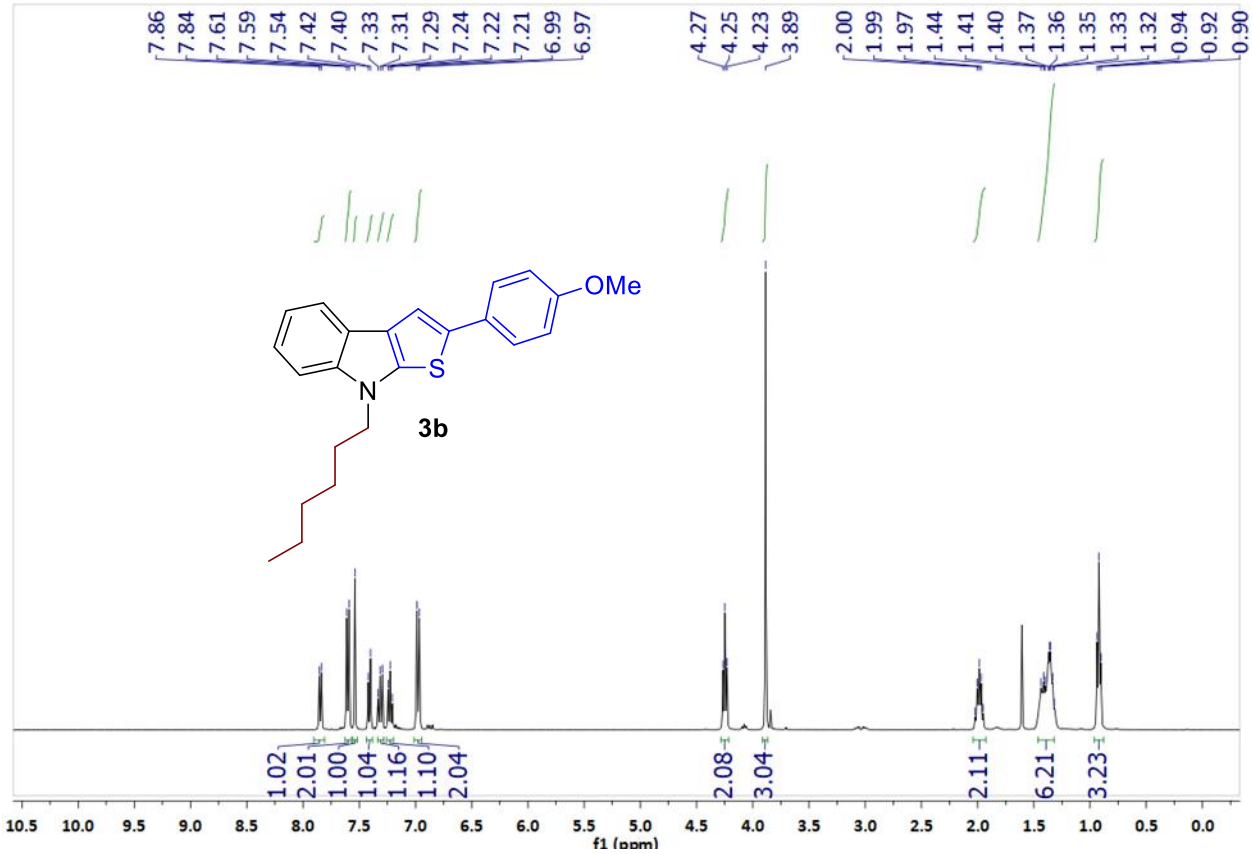
2h

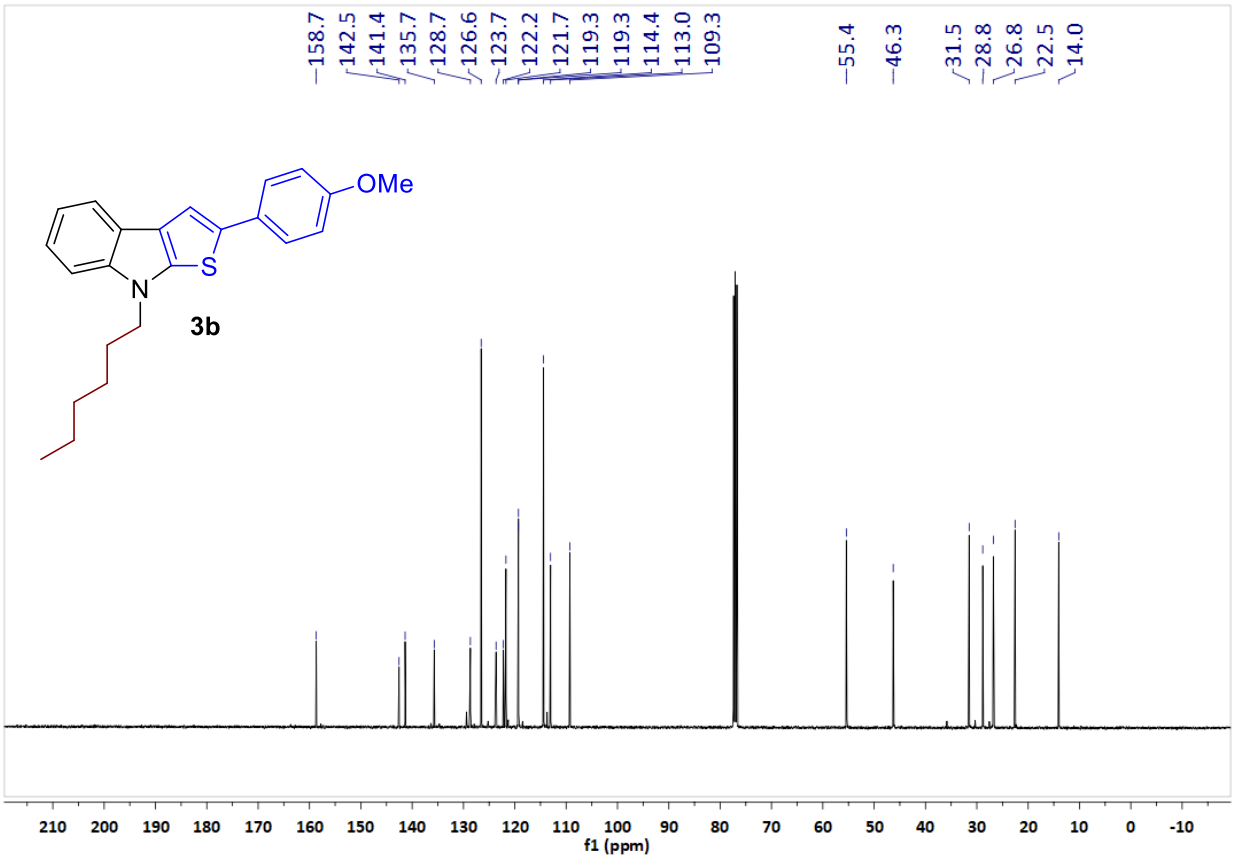
^{1}H and ^{13}C{1H} NMR spectra of 3a:



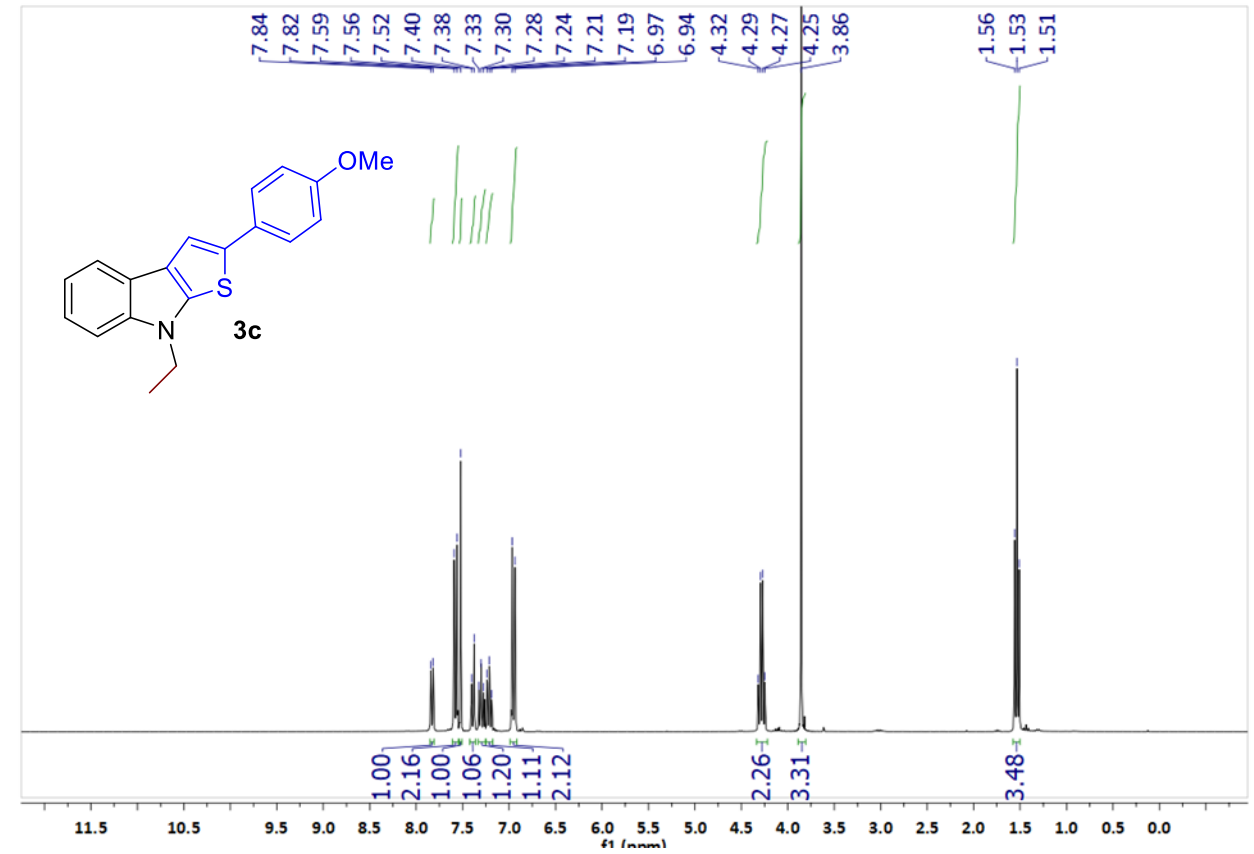


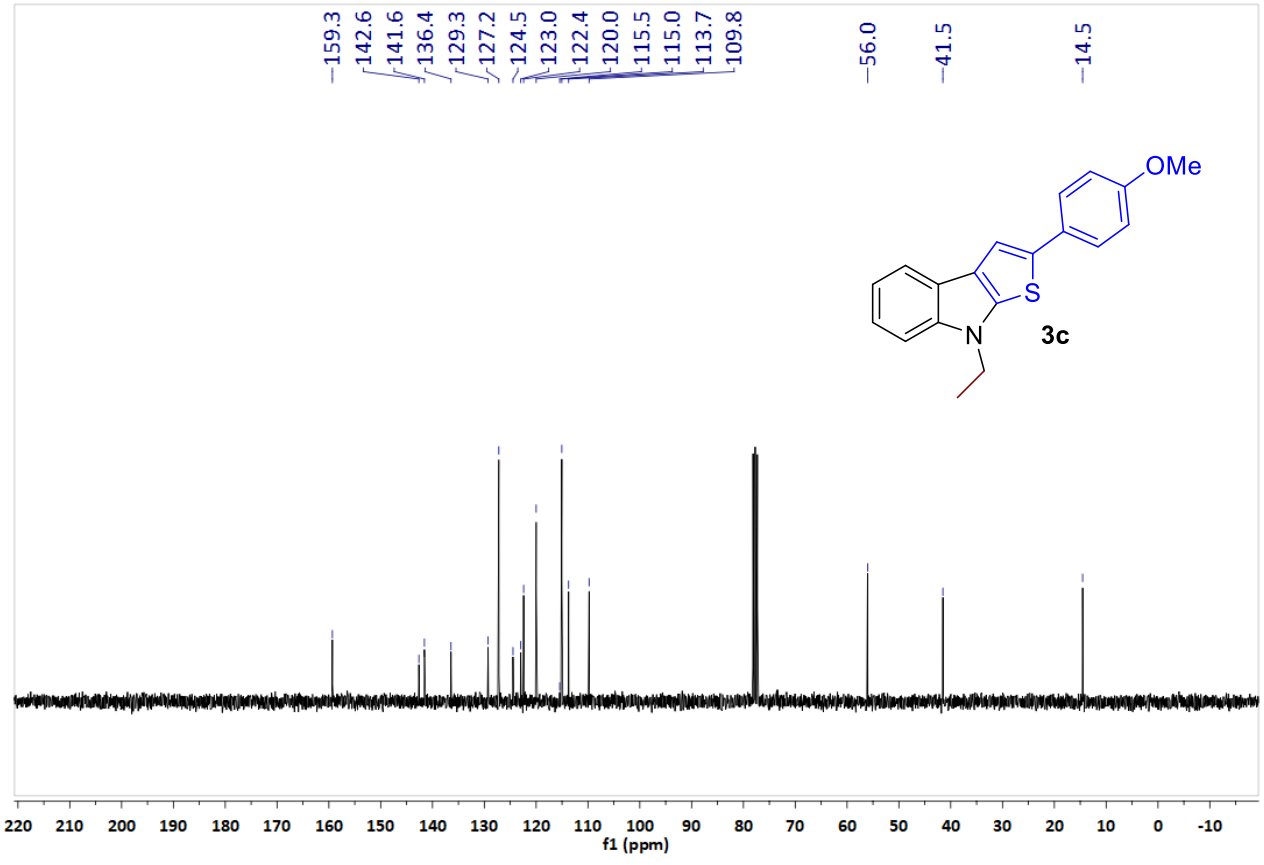
^{1}H and ^{13}C{1H} NMR spectra of 3b:



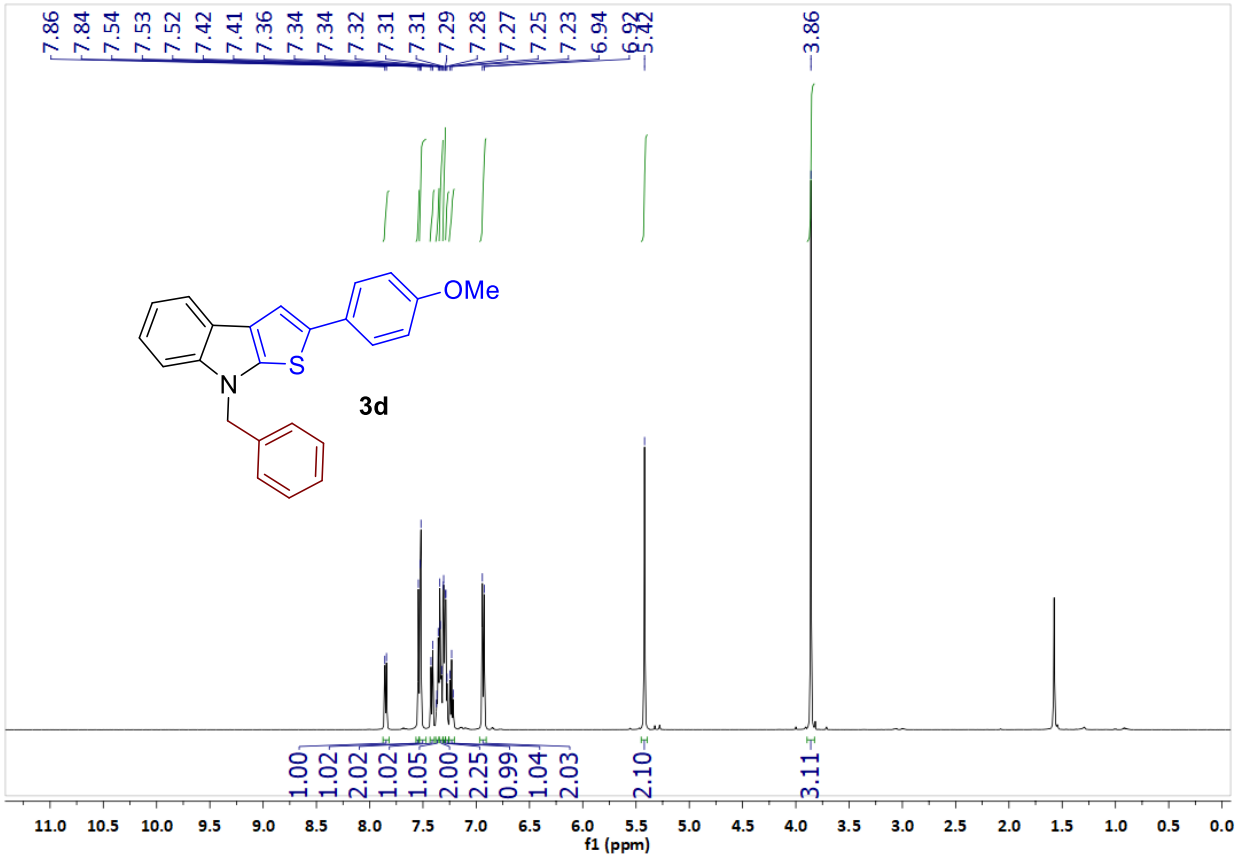


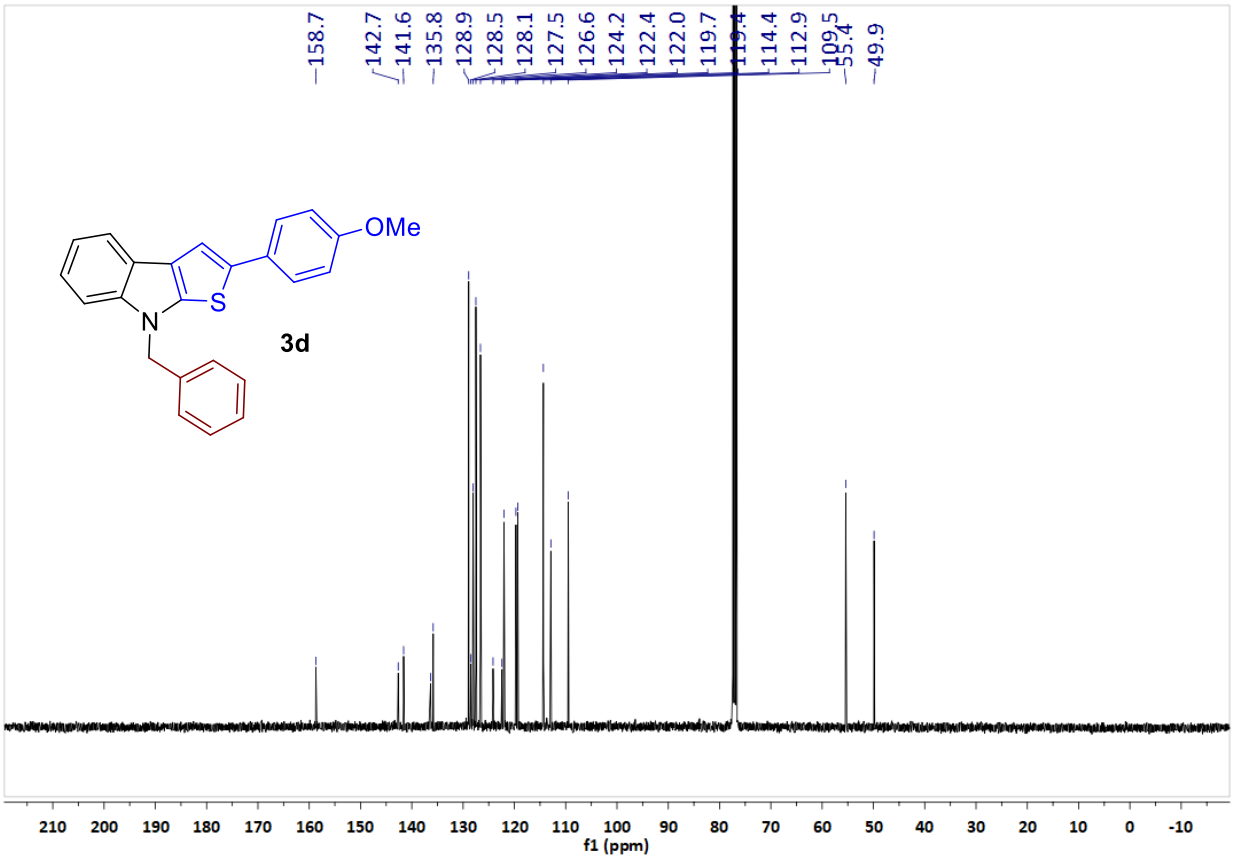
^{1}H and ^{13}C{1H} NMR spectra of 3c:



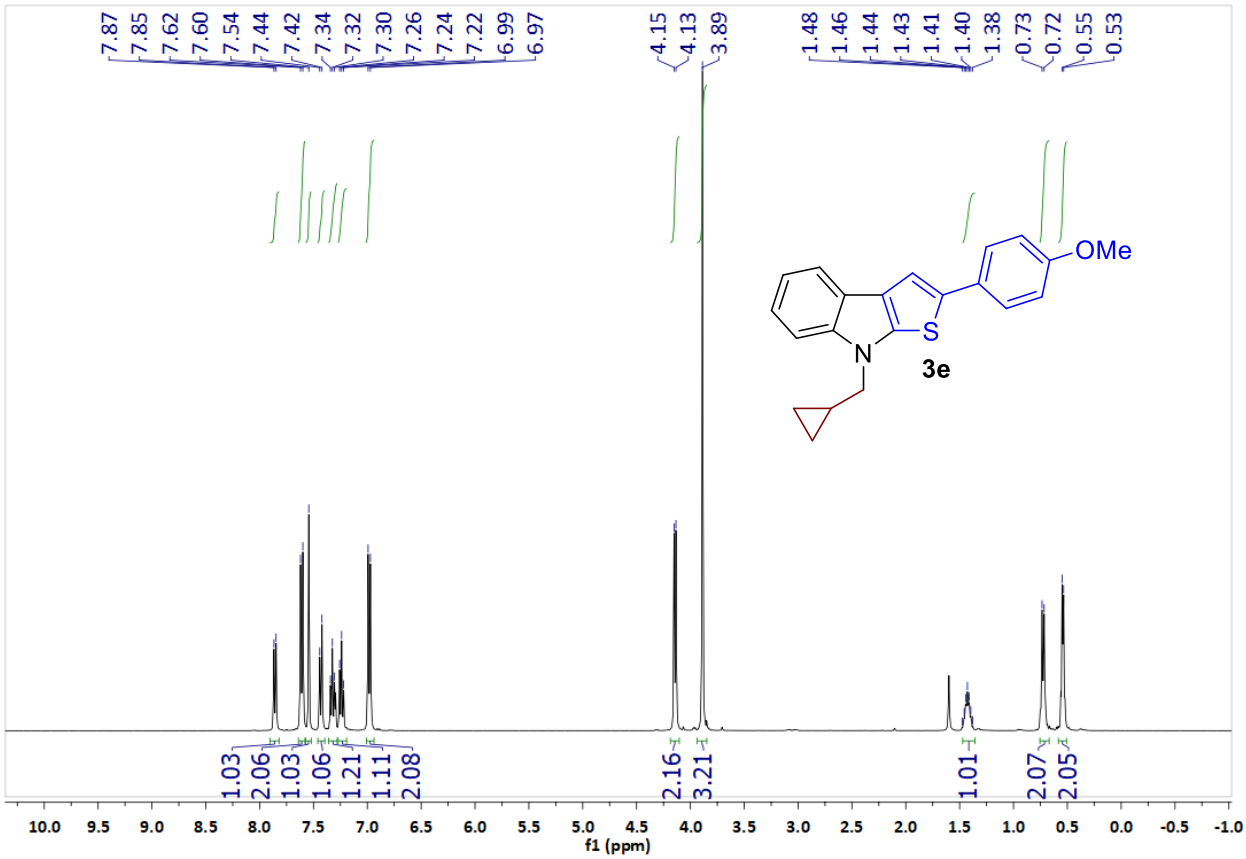


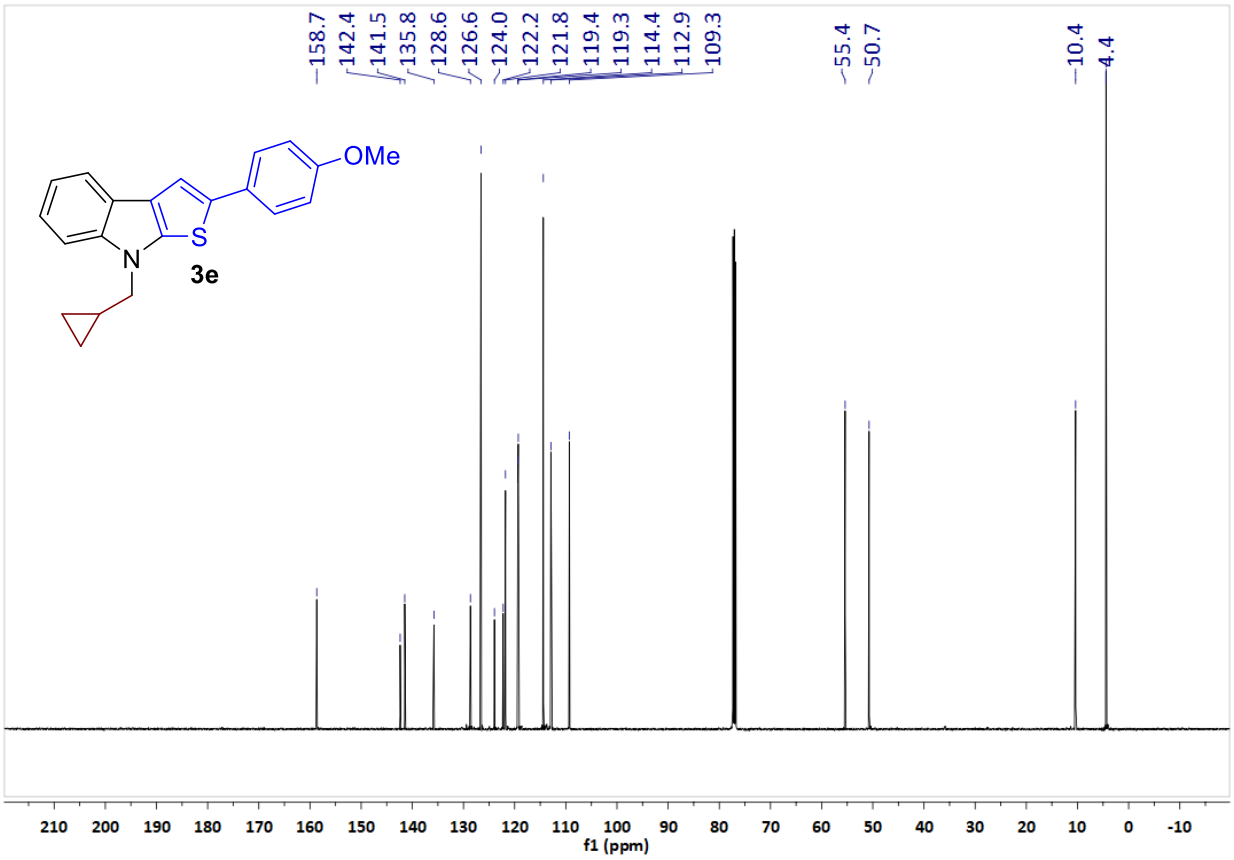
^{1}H and ^{13}C{1H} NMR spectra of 3d:



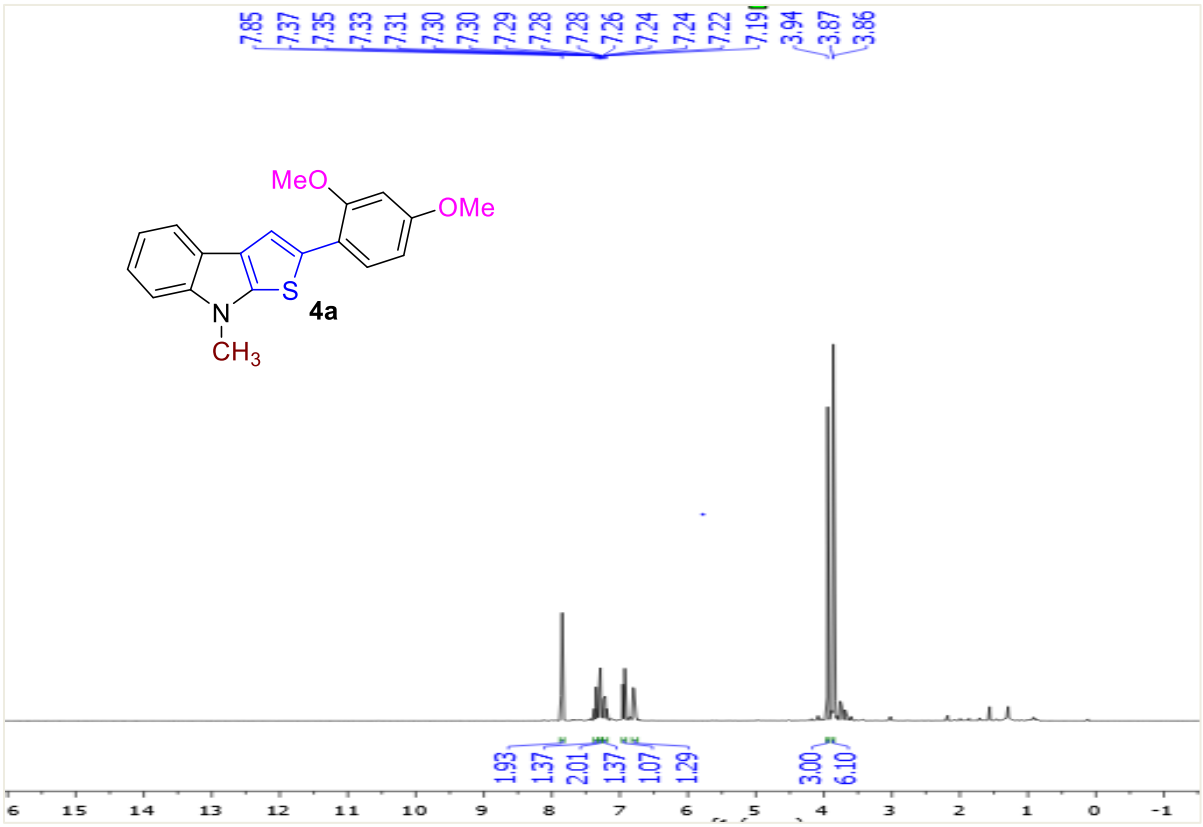


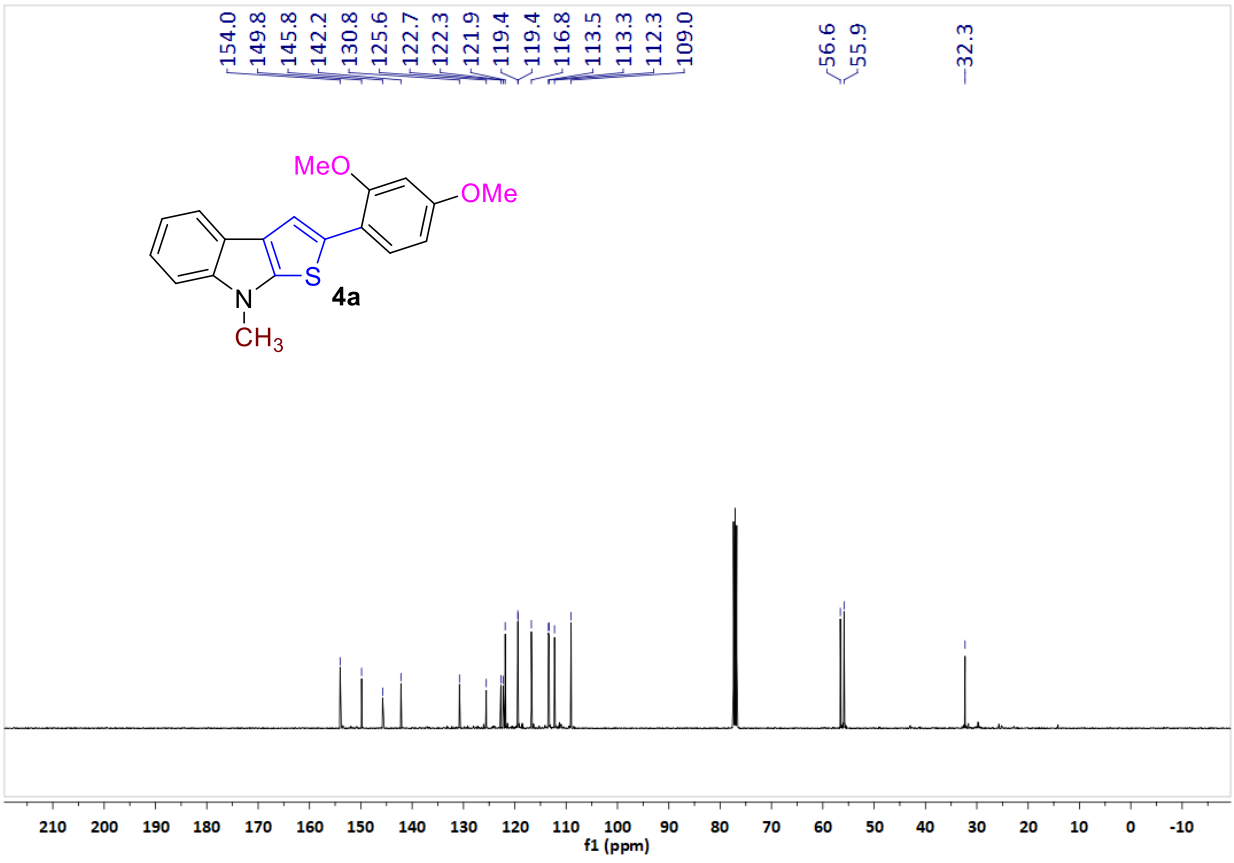
^{1}H and ^{13}C{1H} NMR spectra of 3e:



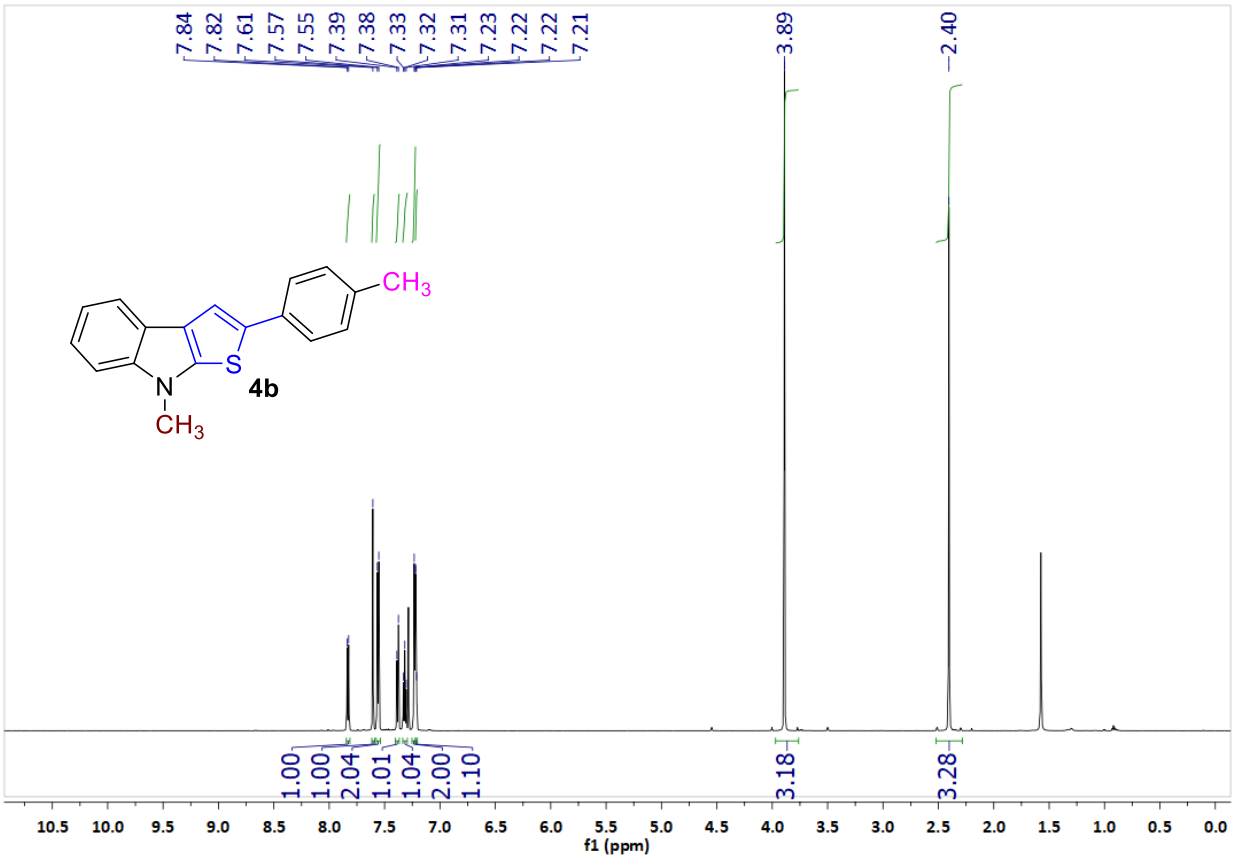


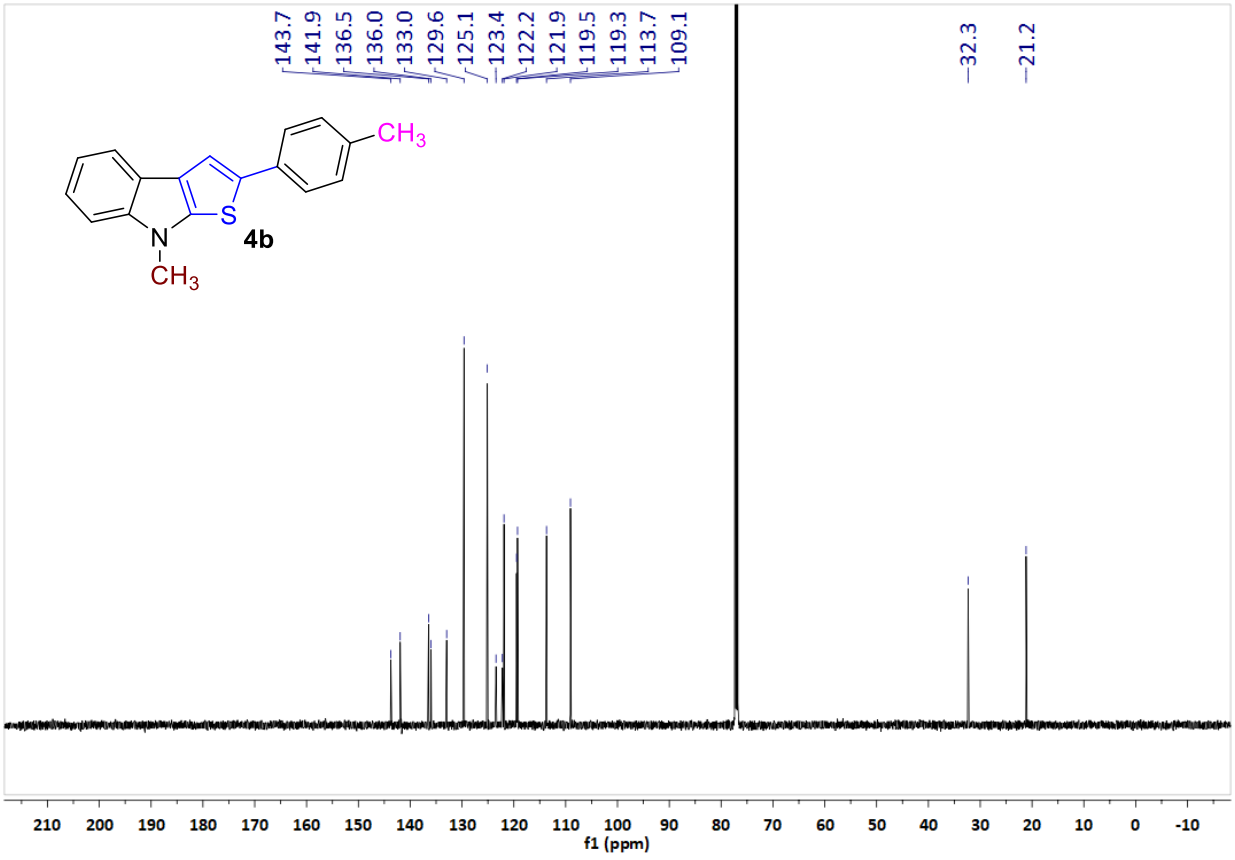
^{1}H and ^{13}C{1H} NMR spectra of 4a:



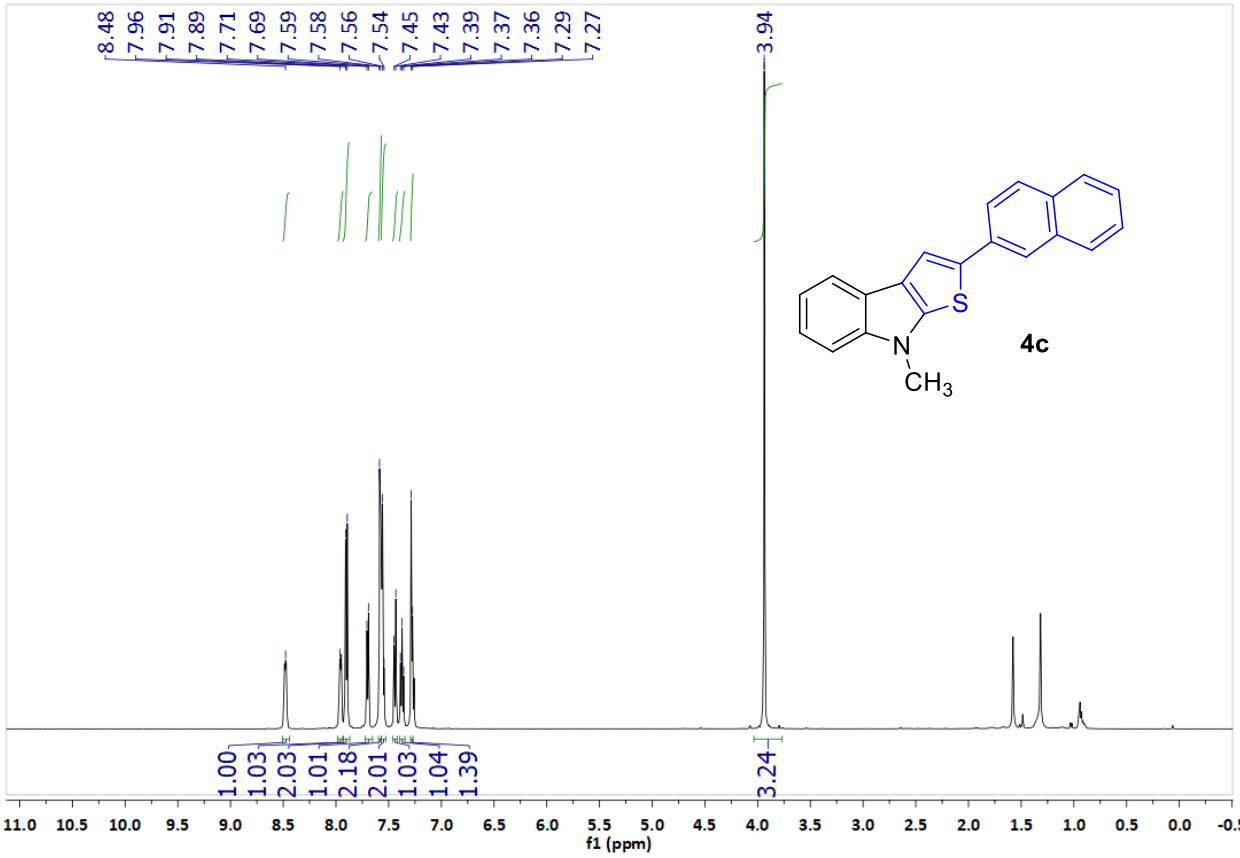


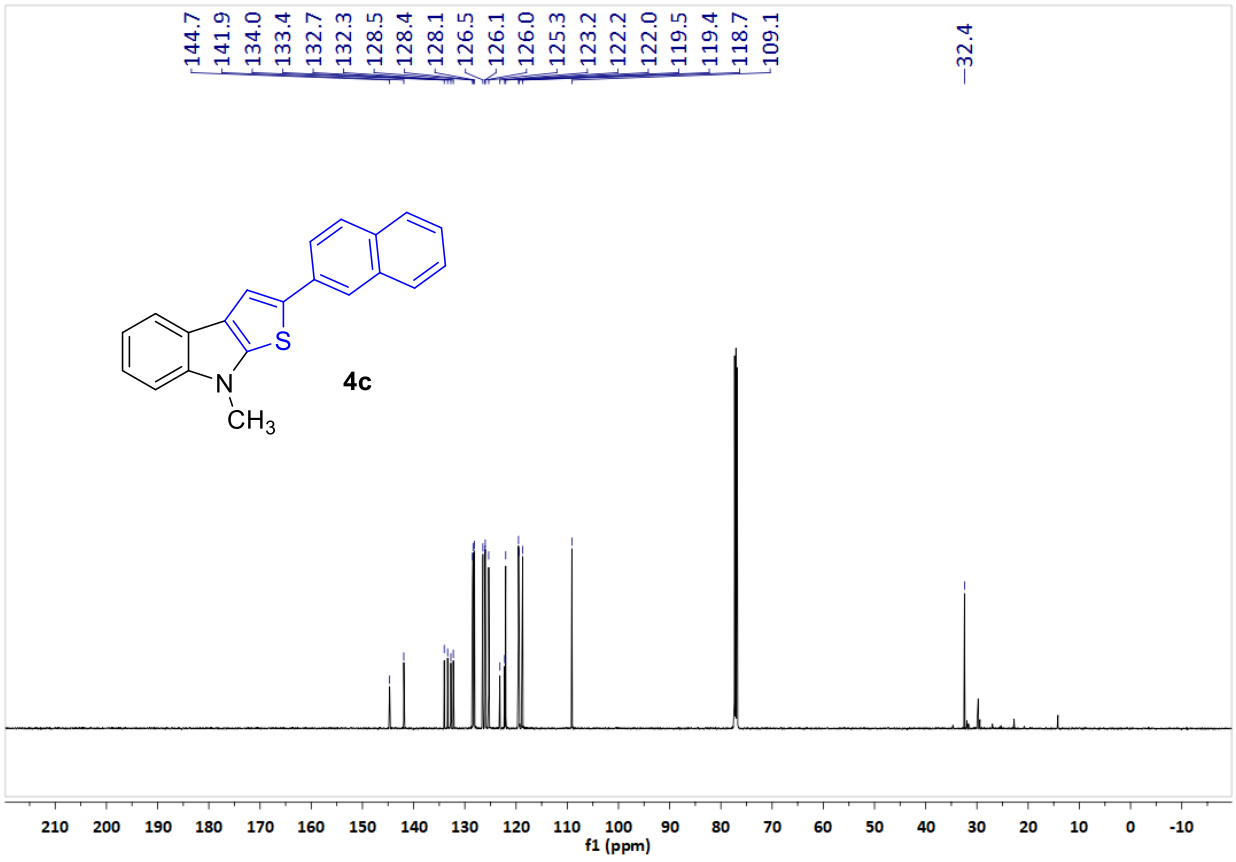
^{1}H and ^{13}C{1H} NMR spectra of 4b:



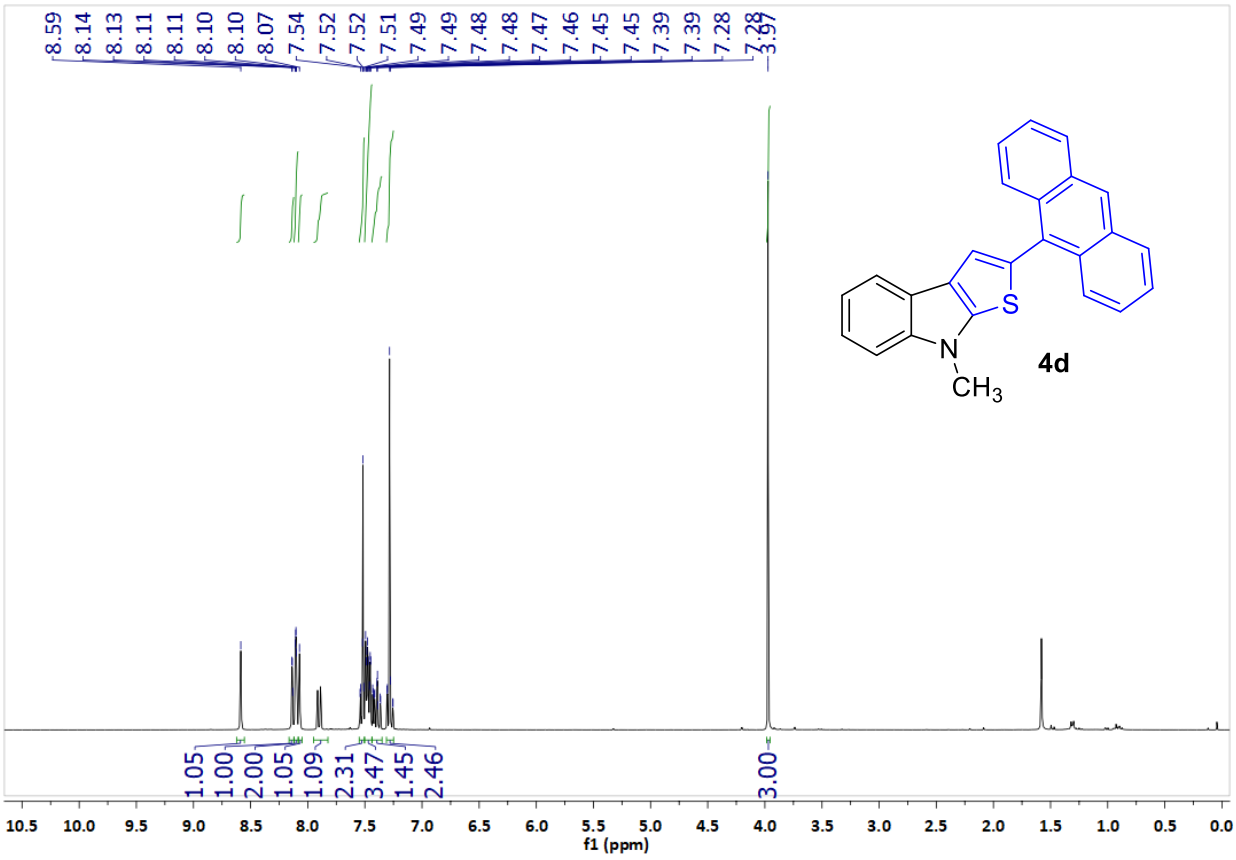


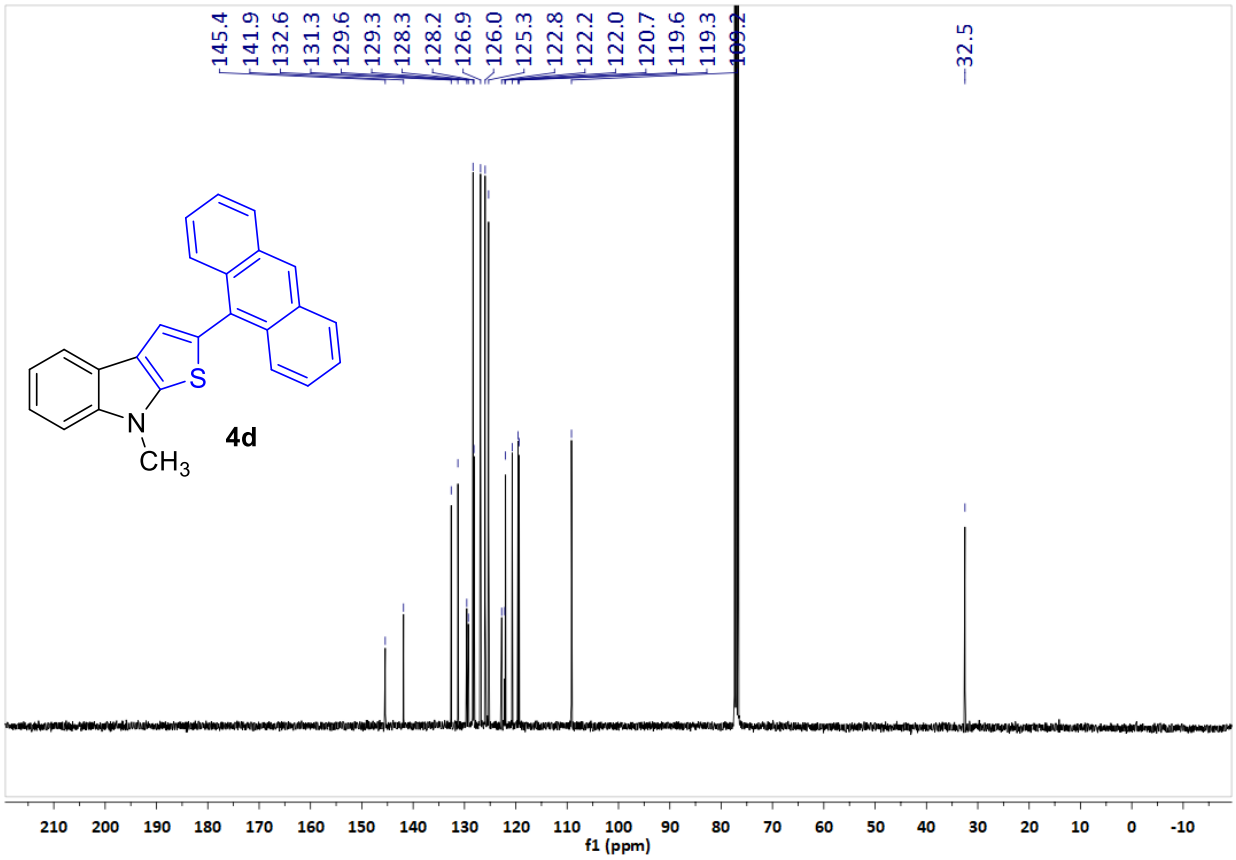
^{1}H and ^{13}C{1H} NMR spectra of 4c:



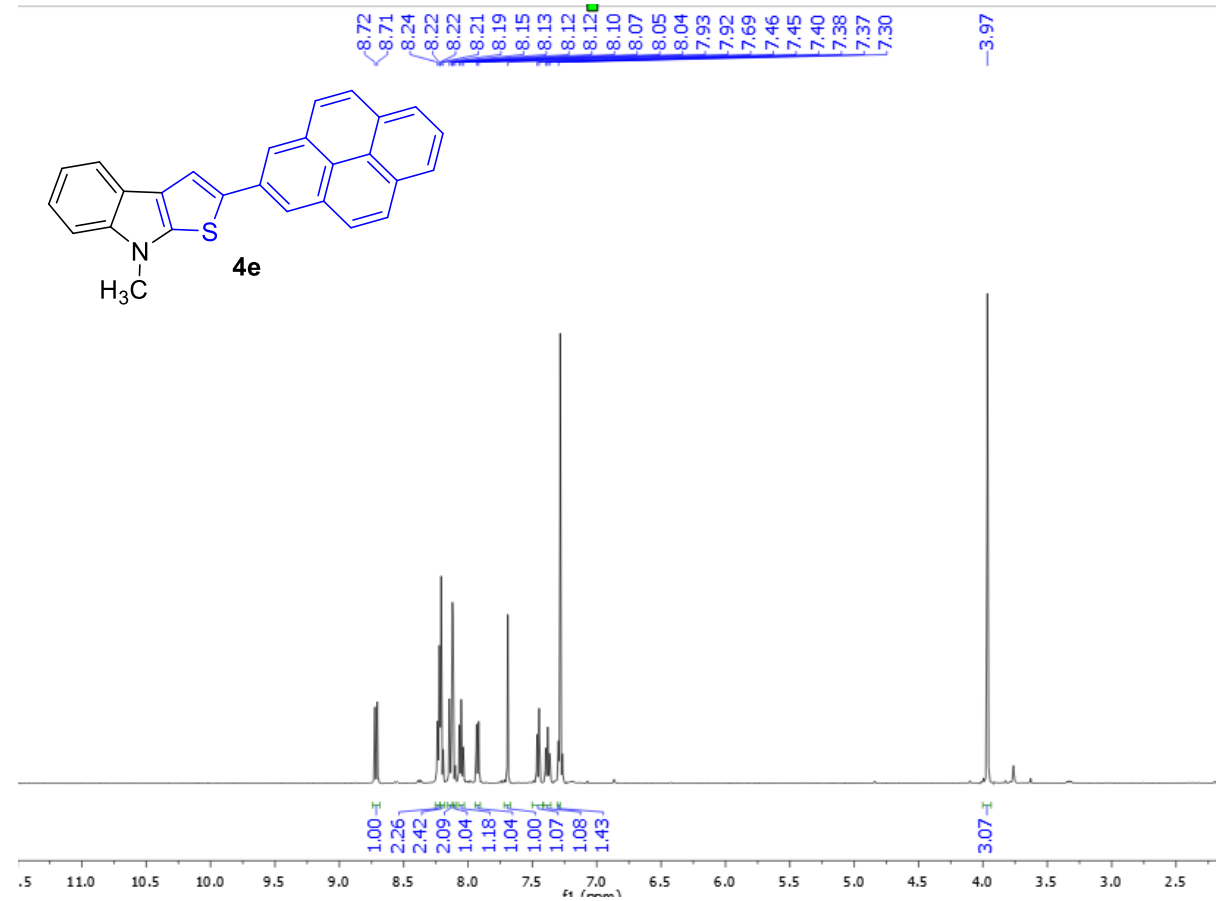


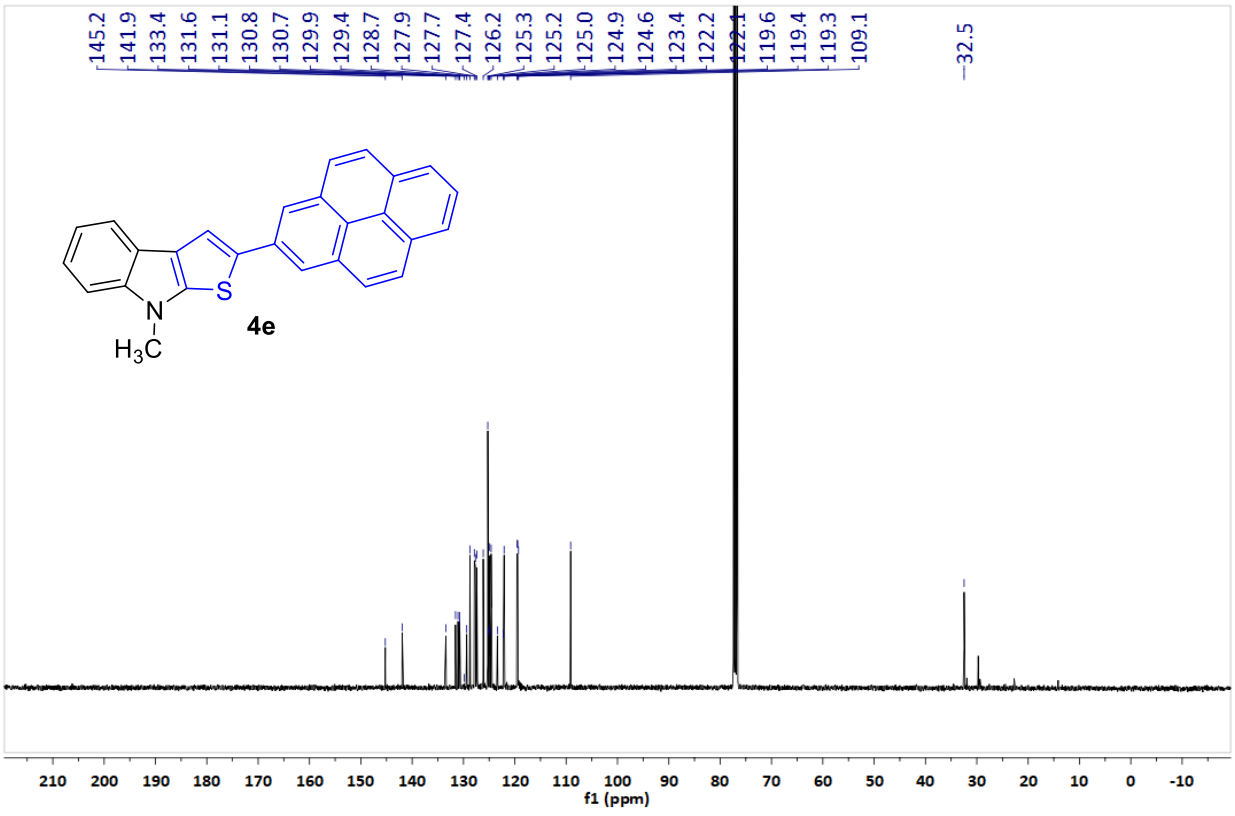
^{1}H and ^{13}C{1H} NMR spectra of 4d:



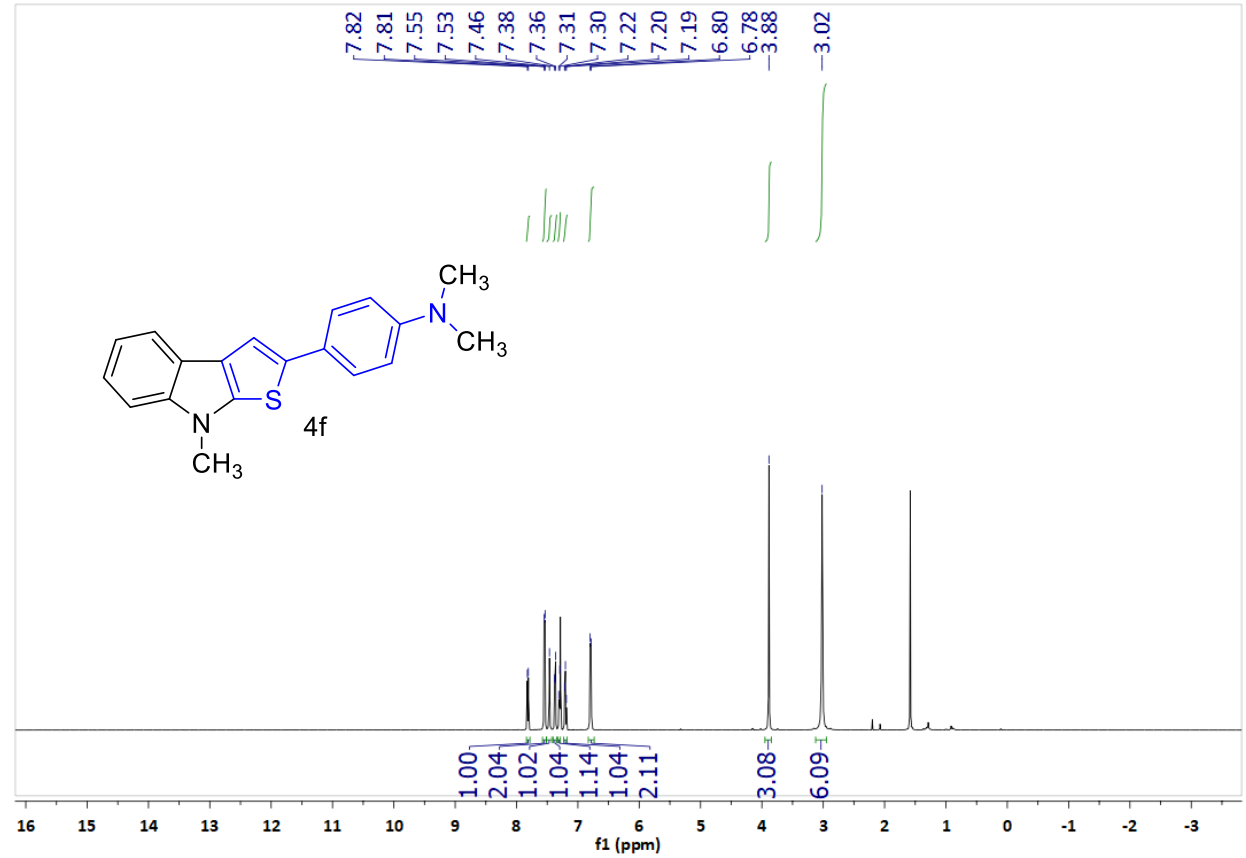


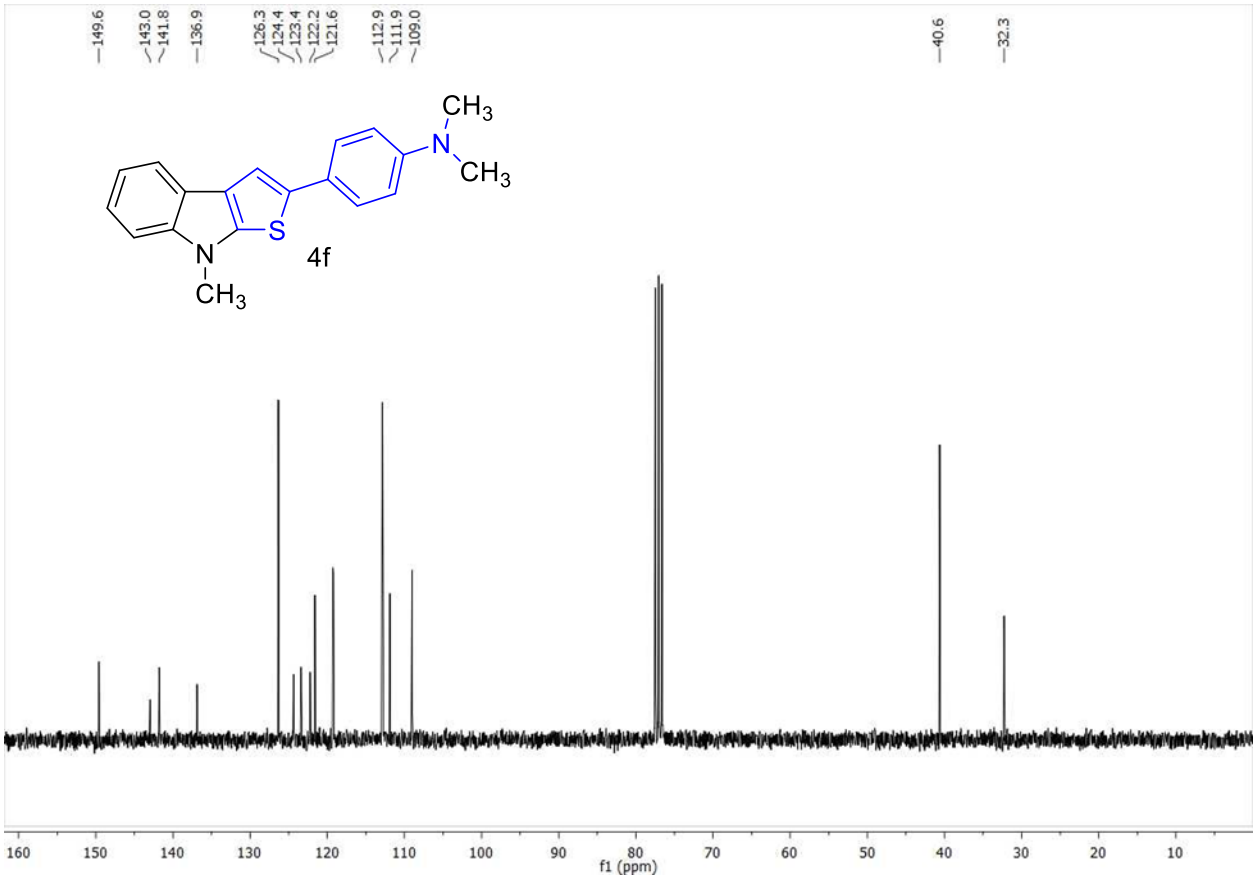
^{1}H and ^{13}C{1H} NMR spectra of 4e:



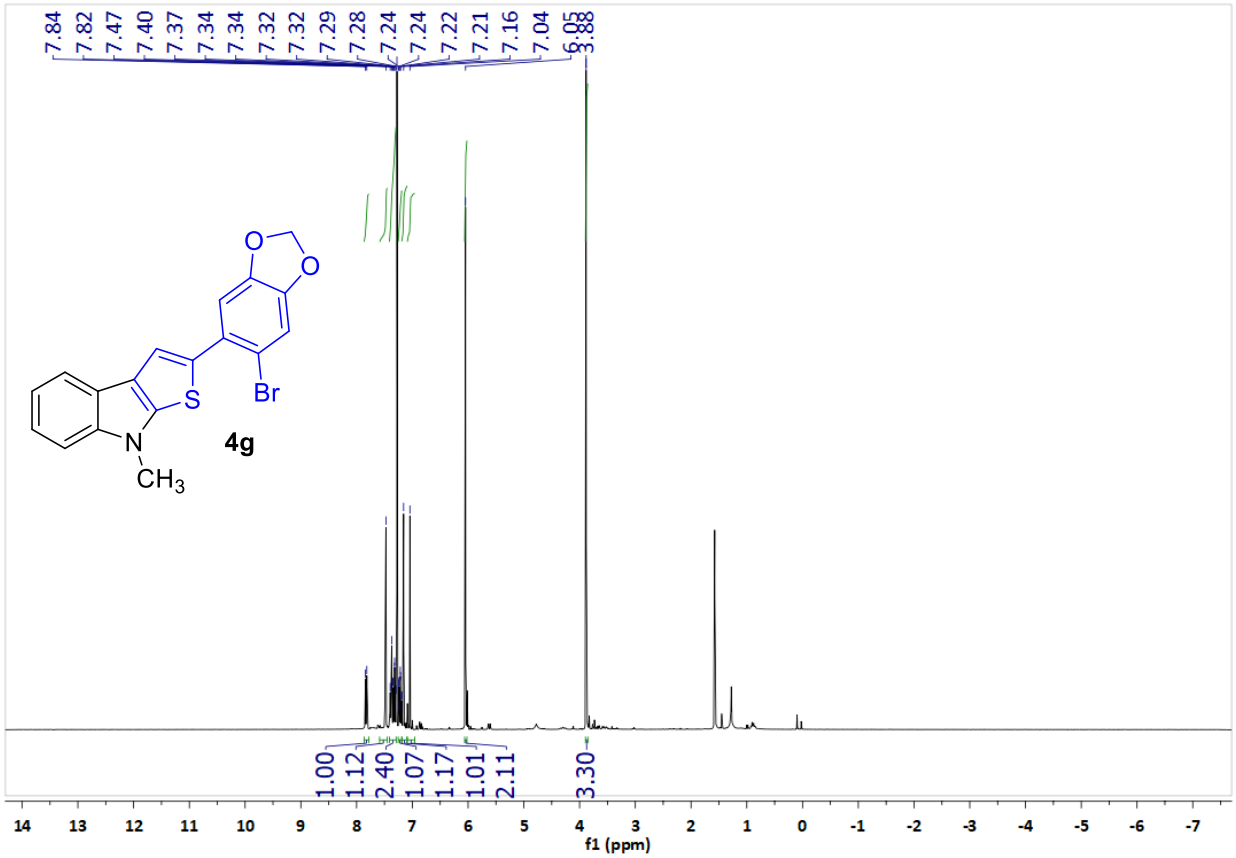


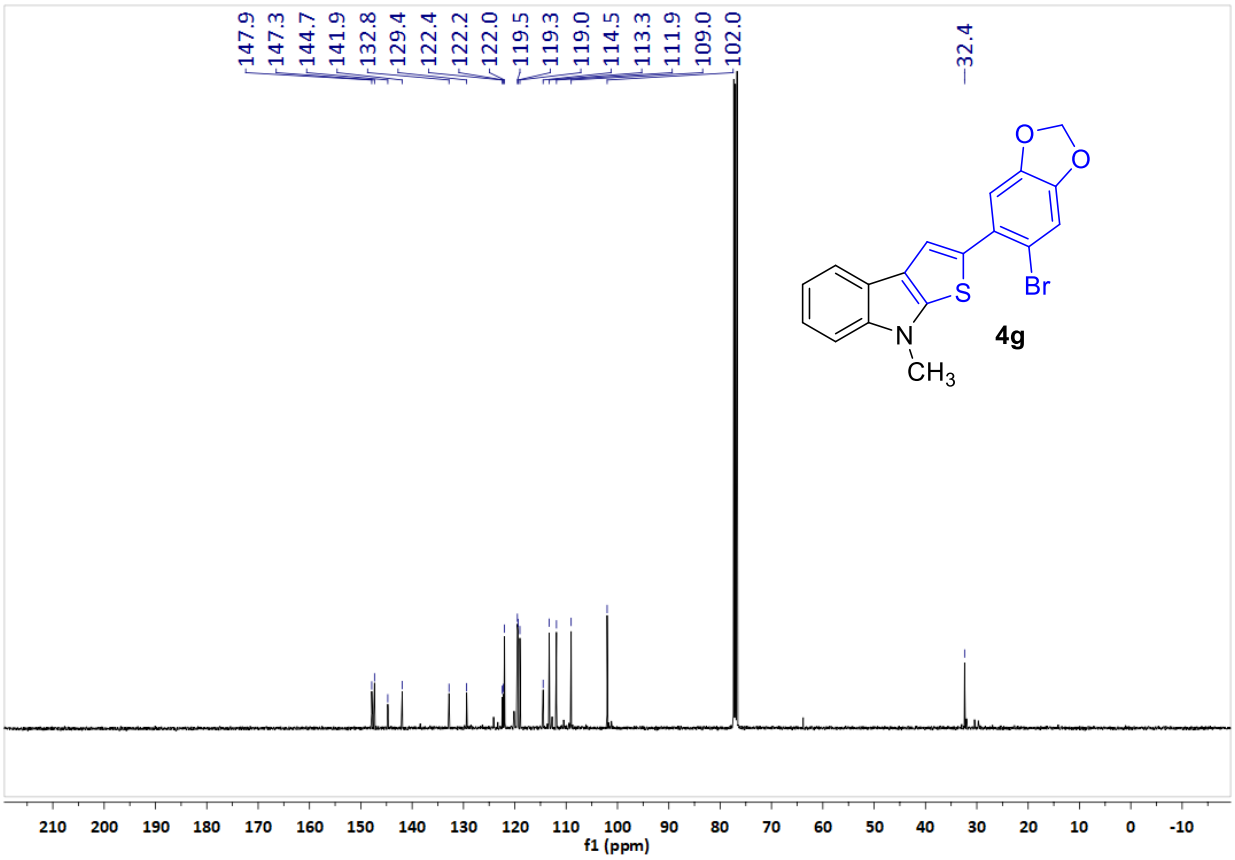
^{1}H and ^{13}C{1H} NMR spectra of 4f:



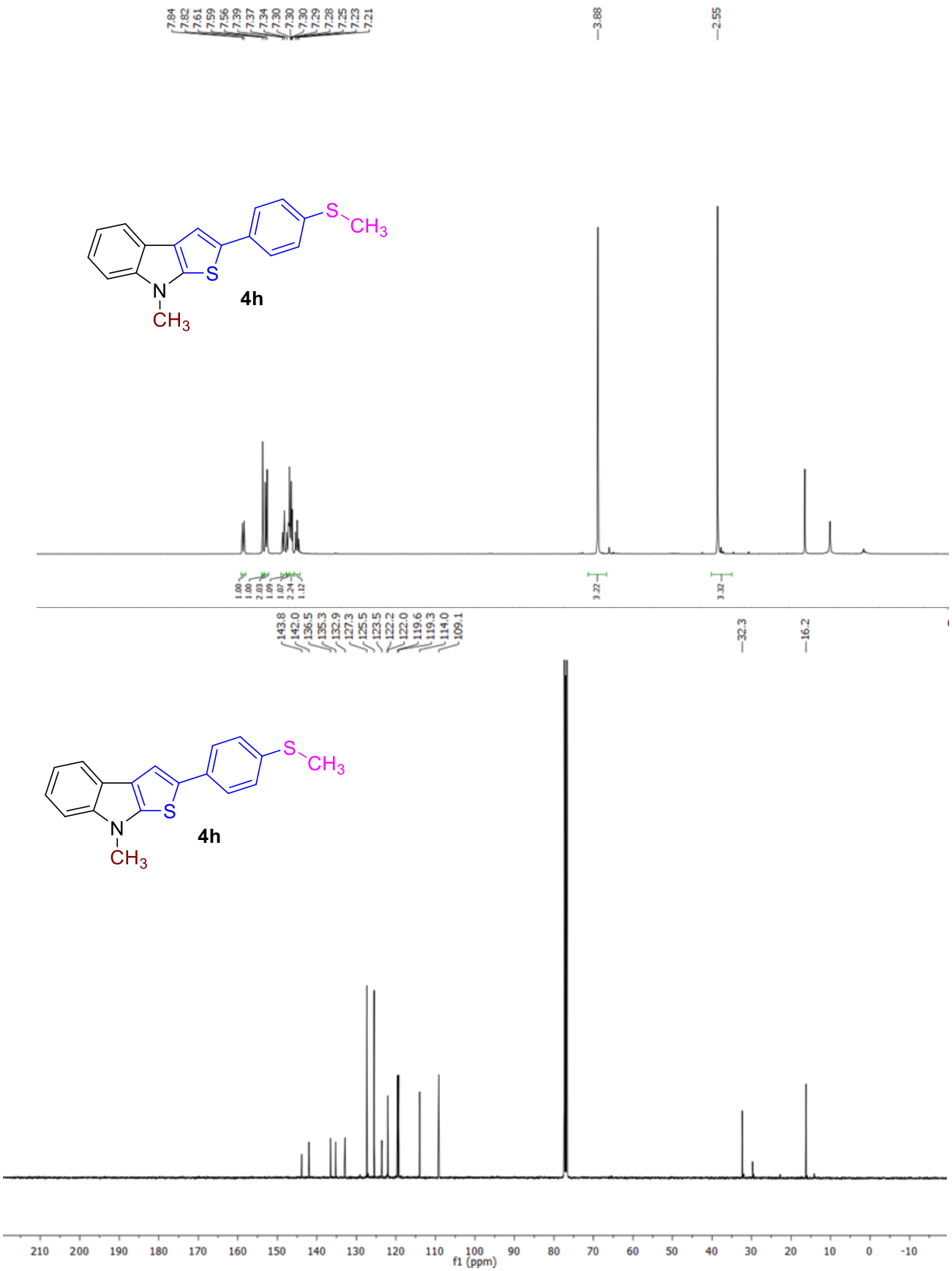


^{1}H and ^{13}C{1H} NMR spectra of 4g:

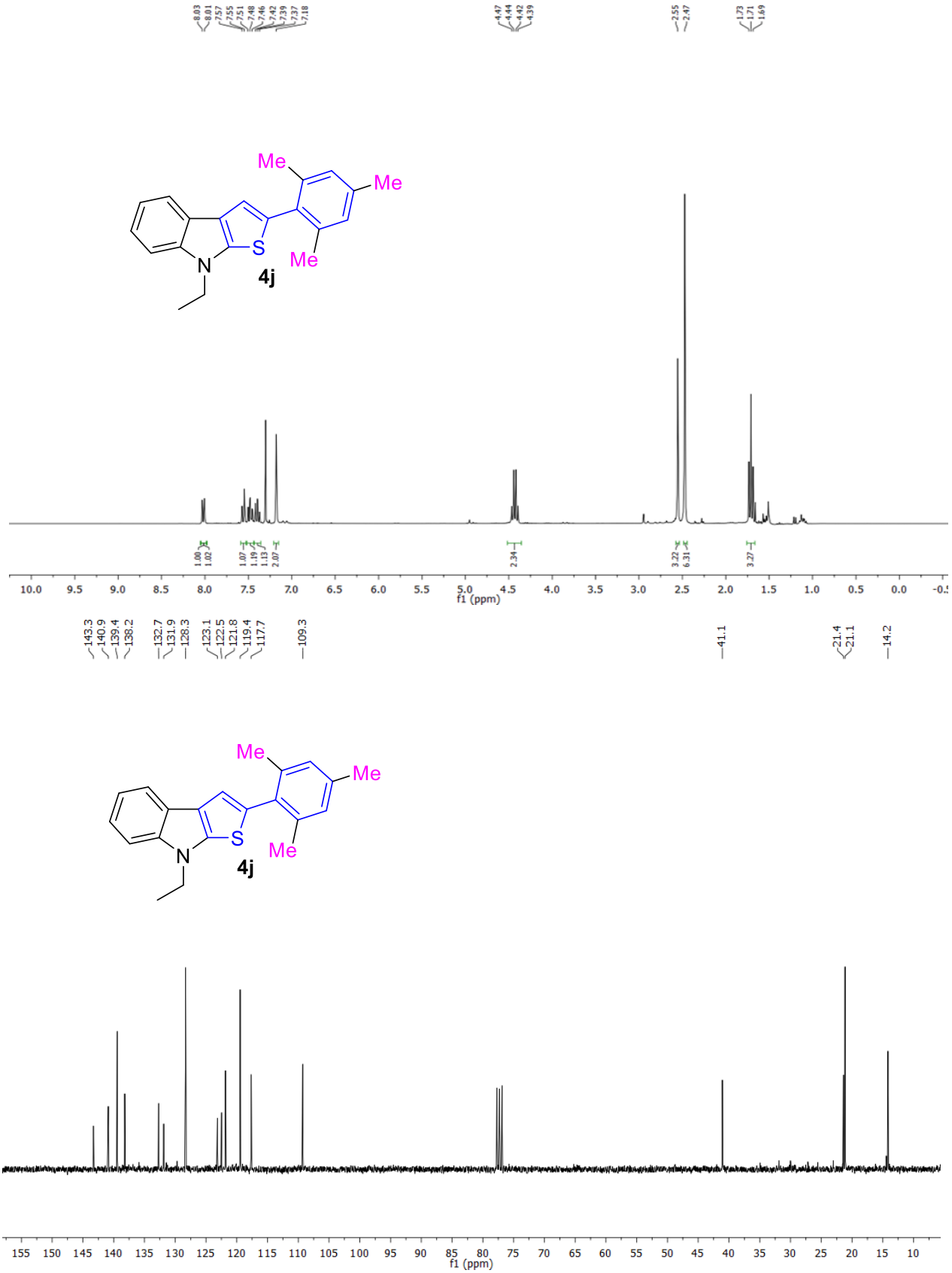




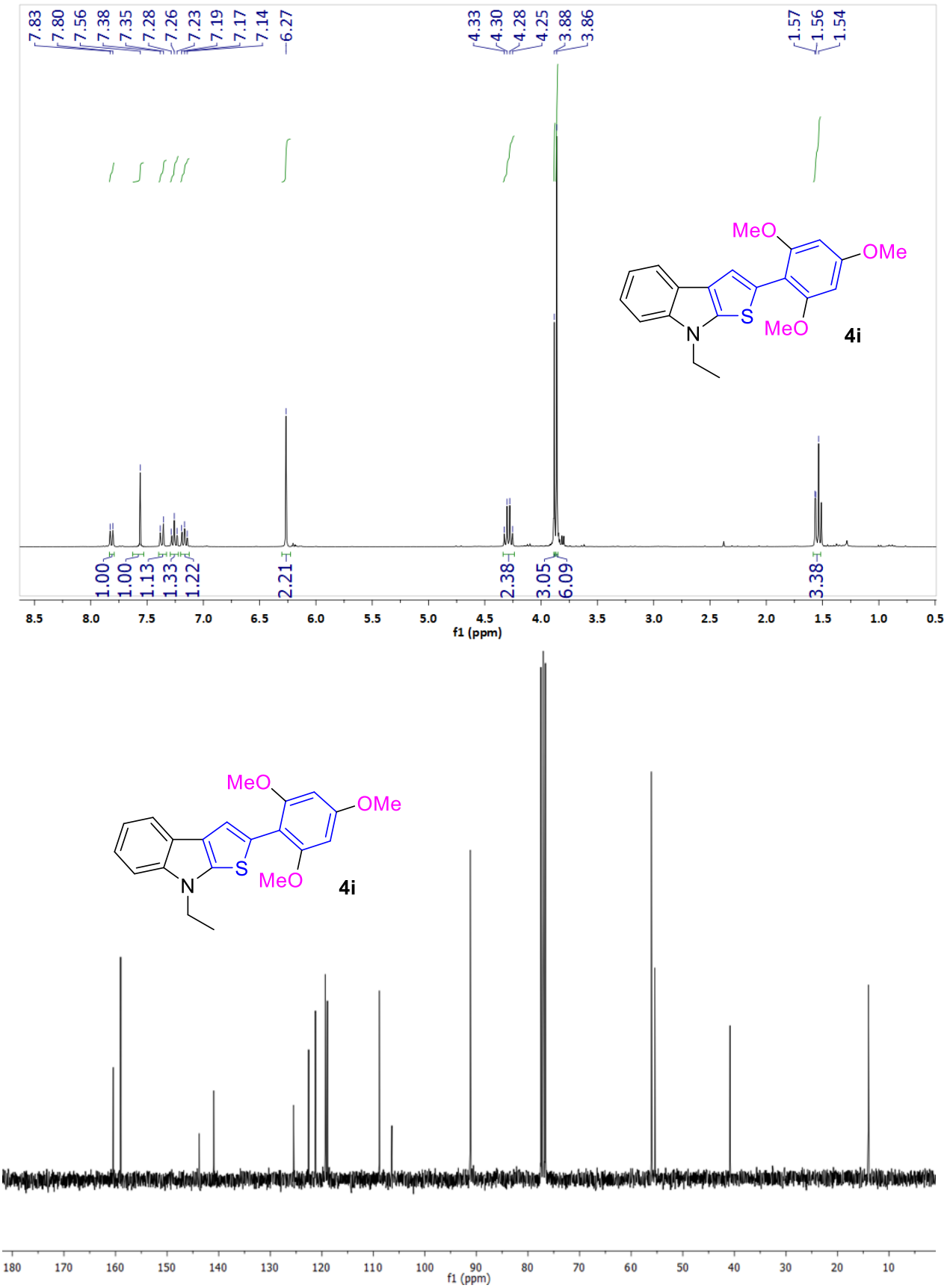
^{1}H and ^{13}C{1H} NMR spectra of 4h:



^{1}H and ^{13}C{1H} NMR spectra of 4j:



^{1}H and ^{13}C{1H} NMR spectra of 4i:



^{1}H and ^{13}C{1H} NMR spectra of 1k: