Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Benzo[c]carbazole derivatives produced by an effective Diels-Alder reaction: Synthesis and structure-activity-relationship for surface coating

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S1. Additional figures

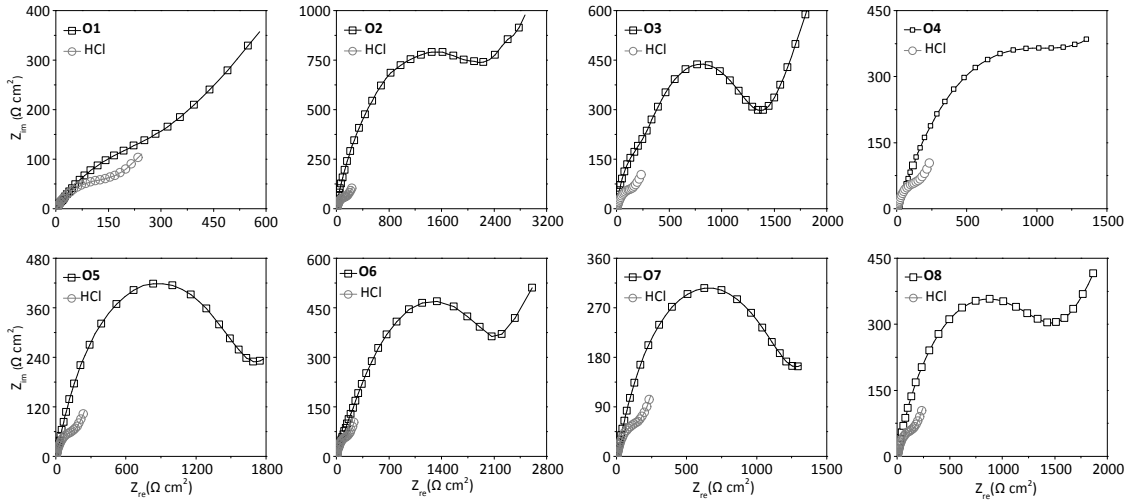


Figure S1. Nyquist plots for copper in 1 M HCl in the absence or presence of corrosion inhibitors **O1**-**O8** (10^{-4} M).

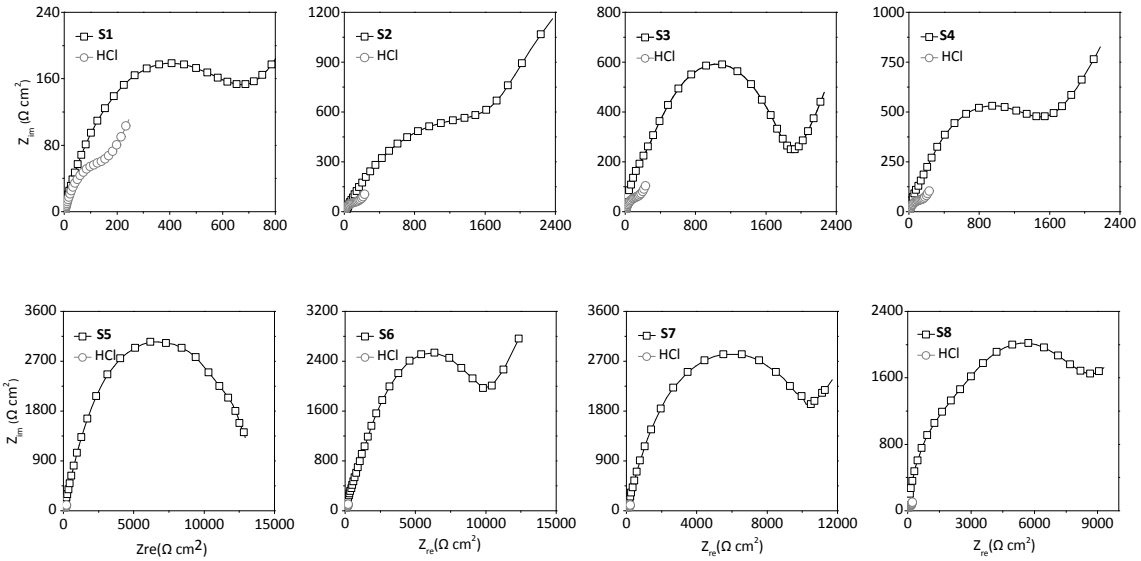


Figure S2. Nyquist plots for copper in 1 M HCl in the absence or presence of corrosion inhibitors **S1**-**S8** (10^{-4} M).

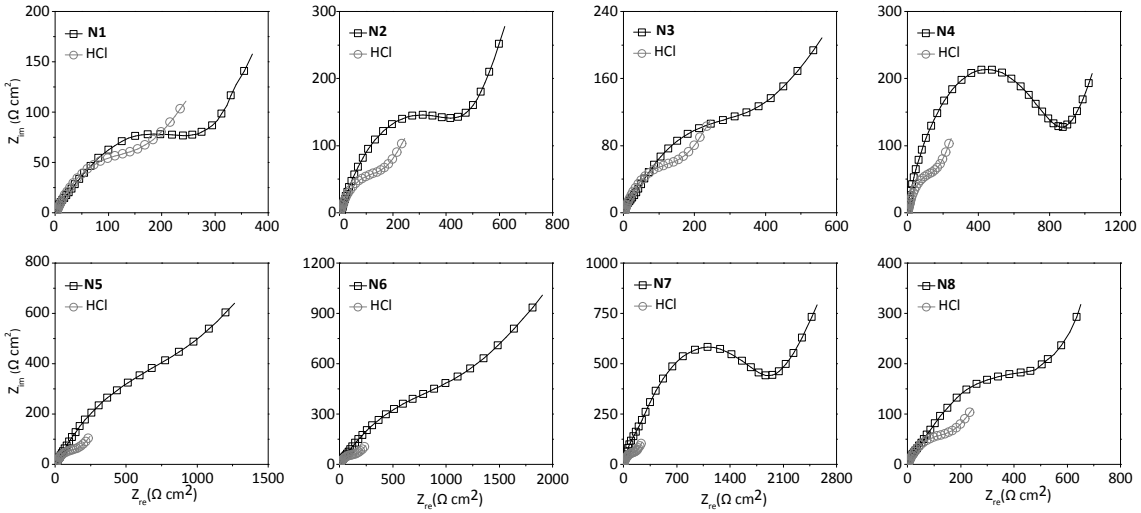


Figure S3. Nyquist plots for copper in 1 M HCl in the absence or presence of corrosion inhibitors **N1**-**N8** (10^{-4} M).

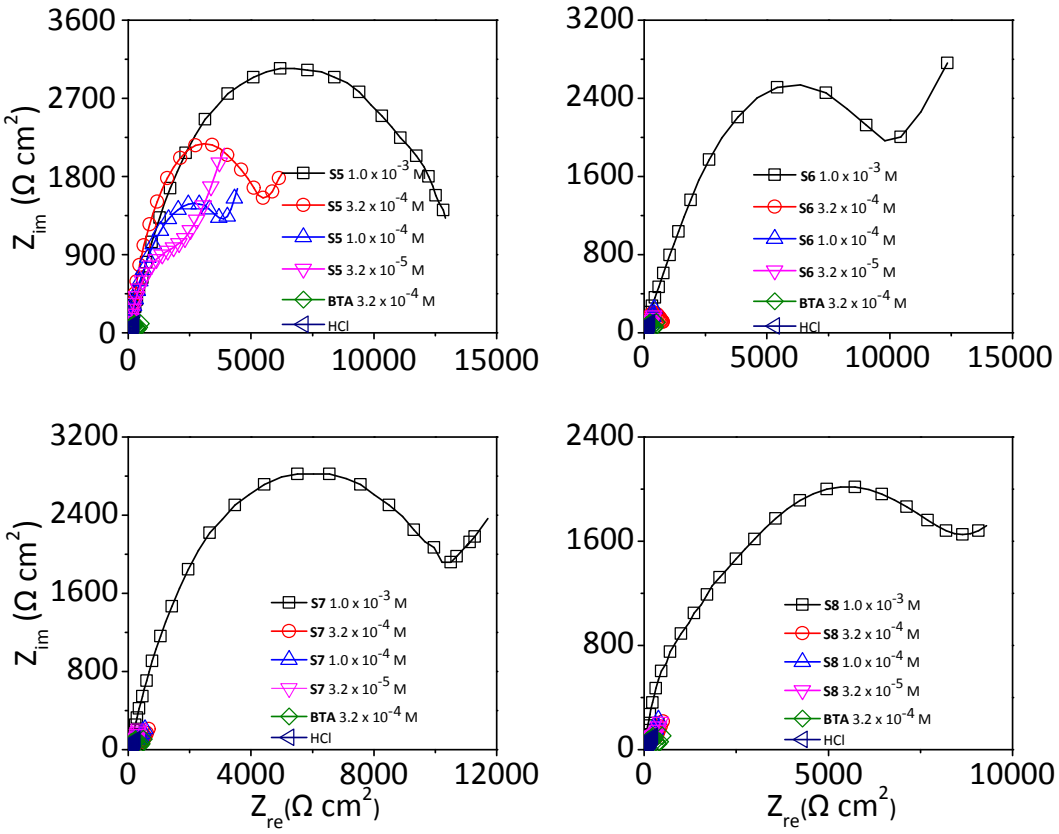


Figure S4. Nyquist plots for copper in 1 M HCl in the absence or presence of **S5**, **S6**, **S7** and **S8** of different concentrations with **BTA** as control.

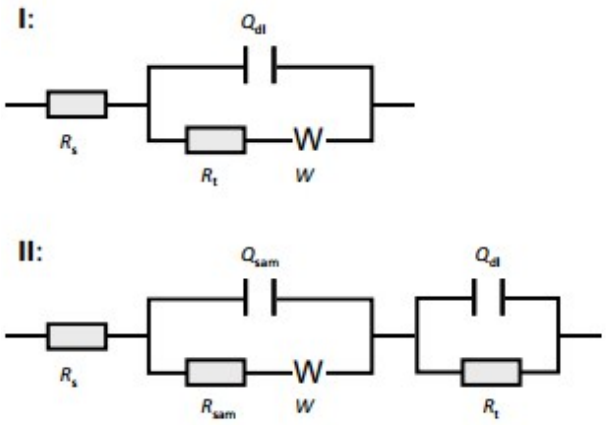


Figure S5. Equivalent circuit models used to fit the obtained electrochemical impedance spectroscopy (EIS) data, where R_s is the solution resistance, R_t the charge transfer resistance corresponding to the corrosion reaction at the copper/solution interface, R_{sam} the polarization resistance of transfer resistance of electrons through the protective molecular layer (if any) on copper surface, W the Warburg impedance, L the inductance, Q_{dl} the constant phase elements as a surrogate for the double-layer capacitance, and Q_{sam} the capacitance of the molecular film formed on copper.

Table S1. EIS parameters fitted for copper in 1 M HCl in the absence (blank) and presence of different inhibitors (10^{-4} M) at 25 °C

Compd.	R_s (Ω cm^2)	Q_{sam} (μF cm^{-2})	n_1	R_{sam} (Ω cm^2)	W (mΩ^{-1} cm^{-2} s$^{1/2}$)	Q_{dl} (μF cm^{-2})	n_2	R_t (Ω cm^2)	η (%)
Blank	1.7	n.a.[a]	0.7	n.a.	52.7	2522	n.a.	174.8	n.a.
S1	2.9	405.5	0.8	10.9	20.6	43.8	0.8	401.1	56.5
S2	3.0	265.7	0.8	439.7	18.7	54.6	0.8	2497.1	93.0
S3	4.5	387.8	0.8	389.1	19.9	78.67	0.7	1248.6	86.2
S4	2.1	454.6	0.7	354.6	20.9	67.9	0.7.	1165.3	85.0
S5	2.1	556.8	0.8	789.4	58.7	43.2	0.8	17480	99.0
S6	1.8	456.3	0.8	667.6	45.6	44.6	0.9	10282	98.3
S7	6.0	461.0	0.8	224.3	10.2	25.7	0.8	12485.6	98.6
S8	1.9	501.9	0.8	339.2	22.3	34.3	0.8	8740	98.0
O1	1.1	665.4	0.9	15.9	35.3	45.7	0.8	236.2	26.2
O2	0.9	197.4	0.8	456.8	19.8	74.3	0.8	2913.3	94.0
O3	3.7	475.7	0.8	239.7	28.7	78.1	0.9	1085.7	83.0
O4	0.5	347.4	0.7	334.5	29.9	50.3	0.7	582.6	70.1
O5	3.6	345.7	0.8	563.2	34.5	37.8	0.8	1748	90.0
O6	4.8	199.8	0.7	439.3	20.7	64.9	0.7	2913	94.0
O7	2.7	300.1	0.8	439.2	18.7	34.1	0.8	1456	88.0
O8	0.8	265.3	0.8	371.1	11.1	23.6	0.7	1589	89.0
N1	1.4	701.3	0.9	19.5	56.7	43.7	0.8	249	30.3
N2	3.9	362.4	0.8	437.6	28.1	51.1	0.8	437	60.1
N3	0.6	162.9	0.8	31.5	15.9	23.7	0.9	349.6	50.2
N4	1.5	331.9	0.7	45.7	54.2	41.4	0.7	448	61.2
N5	5.1	229.1	0.8	321.7	15.8	27.8	0.8	971	82.1
N6	1.6	95.6	0.8	139.3	10.7	38.6	0.8	832	79.1
N7	3.3	656.3	0.9	389.1	28.4	34.7	0.8	1589	89.0
N8	0.5	519.7	0.8	234.1	18.2	24.6	0.7	971	82.1

[a]n.a. means not available.

Table S2. EIS parameters fitted for copper in 1M HCl in various corrosive media in the absence (blank) and presence of inhibitor with different concentrations at 25 °C([a] n.a. means not available.)

Compd.	Conc. (M)	R_s (Ω cm^2)	Q_{sam} (μF cm^{-2})	n_1	R_{sam} (Ω cm^2)	W (mΩ^{-1} cm^{-2} s$^{1/2}$)	Q_{dl} (μF cm^{-2})	n_2	R_t (Ω cm^2)	η (%)
Blank	0	1.7	n.a.[a]	0.7	n.a.	52.7	2522	n.a.	174.8	n.a.
S5	1.0×10^{-3}	2.1	556.8	0.8	789.4	58.7	43.2	0.8	17480	99
	3.2×10^{-4}	4.8	576.7	0.8	677.9	49.6	43.8	0.8	6509	96.9
	1.0×10^{-4}	2.7	365.4	0.9	698.3	19.7	56.4	0.7	5730	96.7
	3.2×10^{-5}	2.2	432.5	0.7	358.6	27.9	37.9	0.7	3722	95
S6	1.0×10^{-3}	1.8	456.3	0.8	667.6	45.6	44.6	0.9	10282	98.3
	3.2×10^{-4}	1.6	196.5	0.8	112.6	34.5	37.5	0.9	725.8	76
	1.0×10^{-4}	1.1	447	0.7	346.2	18.9	76.8	0.8	451.3	58
	3.2×10^{-5}	0.7	262.7	0.8	275.1	19.5	87.9	0.9	378.5	53.6
S7	1.0×10^{-3}	6.0	461.0	0.8	224.3	10.2	25.7	0.8	12485.6	98.6
	3.2×10^{-4}	3.3	351.2	0.9	483.4	45.1	56.6	0.8	683.9	74.4
	1.0×10^{-4}	2.6	254.6	0.9	582.5	53.4	36.8	0.8	561.5	68
	3.2×10^{-5}	3.2	536.2	0.8	345.2	35.7	54.2	0.9	401.6	56
S8	1.0×10^{-3}	1.9	501.9	0.8	339.2	22.3	34.3	0.8	8740	98
	3.2×10^{-4}	3.6	256.3	0.7	433.6	10.9	35.6	0.8	598.7	70.9
	1.0×10^{-4}	3.6	211.5	0.8	198.5	18.7	36.2	0.8	386	54.9
	3.2×10^{-5}	2.3	278.3	0.7	119.5	34.7	22.5	0.7	226.4	23
BTA	1.0×10^{-3}	2.3	778.1	0.7	29.80	18.7	1428	0.7	304.0	42.5
	3.0×10^{-4}	1.9	679.8	0.8	2145	0.70	1567	0.8	277.9	36.4
	1.0×10^{-4}	2.0	657.7	0.9	1120	1.30	1879	0.9	263	33.5
	3.0×10^{-5}	1.8	698.4	0.7	908.5	1.80	2012	0.7	247	29.3

[a]n.a. means not available.

Table S3. Parameters obtained from polarization and isothermal analyses for copper in various corrosive media in the absence (blank) or presence of **S5** with different concentrations at 25 °C

S5 (M)	E_{corr} (mV *vs.* SCE)	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	i_{corr} (μA cm^{-2})	η (%)
Blank	-215.8	315.9	57.4	33.6	n.a.[a]
3.2×10^{-5}	-223.5	254.3	73.4	1.3	96.1
1.0×10^{-4}	-251.4	246.9	56.5	1.1	96.8
3.2×10^{-4}	-242.1	252.2	70.5	1.2	96.3
1.0×10^{-3}	-241.7	252.5	85.4	1.0	97.0

[a]n.a. means not available.

S2. Experimental section

General. All purchased chemicals and reagents are of high commercially available grade. Anhydrous solvents were distilled prior to use. THF, Et_2O, and toluene were distilled from sodium-benzophenone, MeCN was distilled from P_2O_5 and CH_2Cl_2 was distilled from CaH_2. Petroleum ether refers to the fraction with boiling point in the range of 60-90 °C. Solvents were purified by standard procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer in $CDCl_3$, D_2O, or d_6-DMSO. Optical rotations were measured using a Perkin-Elmer 241 polarimeter at room temperature (rt) and a 10 cm/1 mL cell. Chemical shifts are expressed in ppm and *J* values are given in Hz. Melting points are uncorrected. The copper strips (99.9 wt.%) used were mechanically cut into 1.2 cm × 1.0 cm × 0.2 cm dimensions for electrochemical experiments. Prior to use, the specimens were abraded successively with grade-emery papers up to 1200 grit, which were then washed in deionized water, degreased ultrasonically in ethanol and acetone, and then dried at rt.

Electrochemistry. The electrochemical experiments were carried out using a conventional three-electrode cell assembly at rt in HCl with or without the inhibitors. Copper strips with a 1.4 cm^2 exposed surface (partially wrapped) were used as the working electrode, platinum foil used as the counter electrode, and a saturated calomel electrode (SCE) used as the reference electrode. The potentiodynamic polarization curves were recorded from -250 mV SCE to +250 mV SCE (versus open circuit potential [OCP]) with a sweep rate of 0.5 mV/s with a CHI660C apparatus. Electrochemical impedance spectroscopy was carried out within a 100 kHz to10 mHz frequency range at the steady OCP disturbed with an amplitude of 10 mV. The raw electrochemical data were fitted by ZSimpWin. The inhibition efficiency (η, %) was calculated by the following equations:

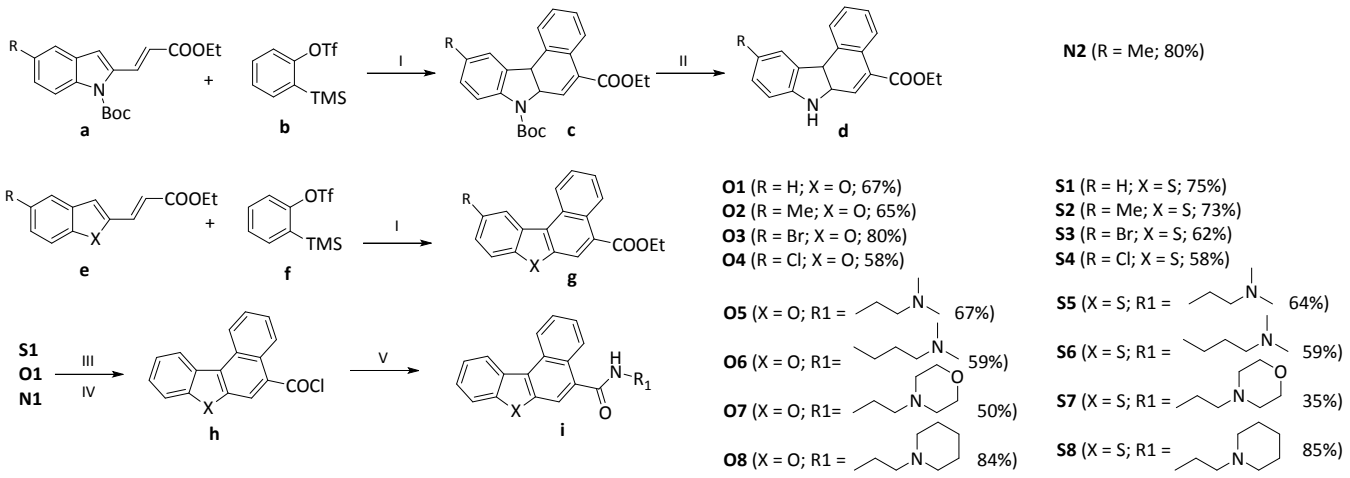
$$\eta\ (\%) = [R_{ct} - R_{ct(0)}]/R_{ct} \times 100 \quad (1)$$

$$\eta\ (\%) = [R_{p} - R_{p(0)}]/R_{p} \times 100 \quad (2)$$

where R_{ct} and $R_{ct(0)}$ are the charge-transfer resistances in the presence and absence of the inhibitors, respectively, and R_p and $R_{p(0)}$ are the polarization resistances in the presence and absence of the inhibitors, respectively.

Scanning Electron microscope (SEM). The surface morphology of specimens (1.2 cm × 1.0 cm × 0.2 cm) after immersion in 1 M HCl in the absence and presence of 3.2×10^{-3} M of inhibitor was recorded with a JSM-6360LV scanning electron microscope with an accelerating voltage of 15 kV.

Synthesis of the heteroatom-fused Benzo[*c*]carbazole derivatives by Diels-Alder reaction. Synthesis and characterization of compounds **N1** and **N3-N8** have been described in our previous reports.[1,2] Methods for the synthesis of other new compounds is shown below.



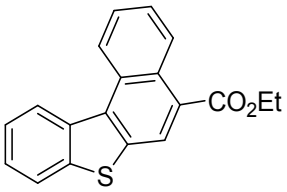
Scheme S1. (I) CsF, $CsCO_3$ in MeOH and toluene in O_2 atmosphere at 373 K; (II) CF_3COOH in CH_2Cl_2 at rt; (III) NaOH, EtOH at reflux; (IV) $(COCl)_2$ in DMF and THF; (V) R_1-NH_2 in THF.

Synthesis of intermediates (c and g). Under an oxygen atmosphere, compound **a** or **e** (0.3 mmol) and Cs_2CO_3 (107.5 mg, 0.33 mmol) were placed in a 25 mL Schlenk tube equipped with a stir bar. Then 0.6 mL of MeCN and 2.4 mL of toluene and **b** or **f** (0.45 mmol) were added. The reaction mixture was stirred at 100°C. The reaction mixture was then filtered through a short column of silica gel and eluted with CH_2Cl_2. The filtrate was concentrated under reduced pressure to afford a residue, which was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1) to afford **c** and **g** as a yellow solid (98% yield; mp 92−93 °C).

Synthesis of products (d, which involves N2, O1-O4 and S1-S4). To a solution of compound **c** was added CF_3COOH (1.0 mmol) dropwise at 0°C. Then, the reaction mixture was stirred at rt. The mixture was then diluted with dichloromethane (10 mL) and quenched carefully with saturated $NaHCO_3$ (aq). After removing the organic layer, the resulting aqueous layer was extracted with dichloromethane (2 × 10 mL). The organic layers were combined and dried over Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1) to afford **d**.

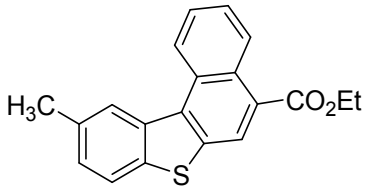
Synthesis of branched products (i, which involves O5-O8 and S5-S8). S1, **O1** or **N1** (0.6 mmol) was dissolved in 2 mL of ethanol, and 3 M NaOH (1 mL) was added slowly to the mixture followed by heating to reflux for 2 h. Dilute hydrochloric acid was added dropwise until pH < 7. The water layer was then extracted with CH_2Cl_2 (5 mL × 3). The organic layers were combined and dried over Na_2SO_4. The solvent was removed under reduced pressure to give the crude product, which (0.3 mmol) was dissolved in 5 mL of anhydrous tetrahydrofuran (THF), and then one drop of anhydrous N,N-dimethyl methanamide (DMF) was added. The mixture was cooled to 0 °C followed by addition of 15 drops of oxalyl chloride; then the mixture was warmed to rt and stirred for 30 min. The solvent was removed under reduced pressure to give the acyl chloride **h** as light yellow solid, which was used directly without any purification. The freshly prepared acyl chloride was dissolved in 5 mL of anhydrous THF. Then, N,N-dimethylethylenediamine (66.1 mg, 0.75 mmol) was added dropwise, and the resulting mixture was stirred for 2 h at rt. After removing the solvent under

reduced pressure, the resulting residue was poured onto ice water to generate a solid, which was precipitated, filtered, and dried under vacuum. Then the residue was purified by silica gel chromatography (petroleum ether/dichloromethane/ammonium hydroxide = 100/10/1) to give **i** as a white solid.



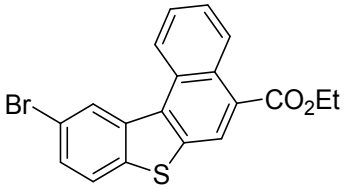
Ethyl benzo[*b*]naphtho[*1,2-d*]thiophene-5-carboxylate

Yellow solid, 82 mg, 90%, mp 97.9-99.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (d, *J* = 8.0 Hz, 1H), 8.98 (d, *J* = 8.4 Hz, 1H), 8.80 (d, *J* = 8.0 Hz, 1H), 8.54 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 4.51 (q, *J* = 7.6 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 141.1, 136.7, 136.0, 132.4, 130.9, 129.5, 127.1, 127.1, 126.5, 126.1, 126.1, 125.4, 125.3, 125.0, 123.4, 123.3, 61.3, 14.4; IR (neat): 2975, 2921, 1715, 1511, 1179, 1146, 1030, 744 cm^{-1}; HRMS calcd for $C_{19}H_{14}O_2S$ [M+]$^+$:306.0715 , found: 306.0717.



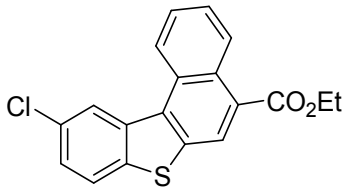
Ethyl 10-methylbenzo[*b*]naphtho[*1,2-d*]thiophene-5-carboxylate

Yellow solid, 70 mg, 73%, mp 103.7-105.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (d, *J* = 8.4 Hz, 1H), 8.97 (d, *J* = 8.0 Hz, 1H), 8.57 (s, 1H), 8.52 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 6.8 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 4.51 (q, *J* = 6.8 Hz, 2H), 2.59 (s, 3H), 1.49 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 138.2, 137.0, 136.2, 134.7, 132.2, 131.0, 129.4, 127.7, 127.0, 127.0, 126.3, 125.9, 125.5, 125.5, 123.4, 122.8, 61.2, 21.9, 14.4; IR (neat): 2975, 2917, 1710, 1507, 1246, 1183, 1146, 1030, 730 cm^{-1}; HRMS calcd for $C_{20}H_{16}O_2S$ [M+H]$^+$: 321.0949 , found: 321.0945.



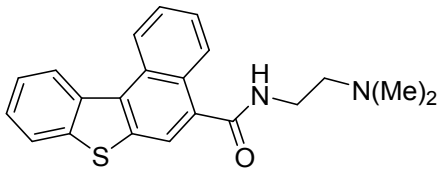
Ethyl 10-bromobenzo[*b*]naphtho[*1,2-d*]thiophene-5-carboxylate

Yellow solid, 72 mg, 62%, mp 170.5-172.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (d, *J* = 8.4 Hz, 1H), 8.86 (d, *J* = 8.0 Hz, 1H), 8.76 (d, *J* = 2.0 Hz, 1H), 8.51 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.48 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, 1H), 4.53 (q, *J* = 7.6 Hz, 2H), 1.51 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 139.1, 137.7, 137.1, 137.1, 131.4, 131.3, 130.7, 129.4, 127.5, 127.4, 127.2, 126.4, 126.4, 125.1, 124.1, 123.1, 61.5, 14.4; IR (neat): 2967, 2913, 2351, 1718, 1511, 1262, 1188, 1154, 802,764 cm^{-1}; HRMS calcd for $C_{19}H_{13}BrO_2S$ [M+]$^+$:383.9820 , found: 383.9819.



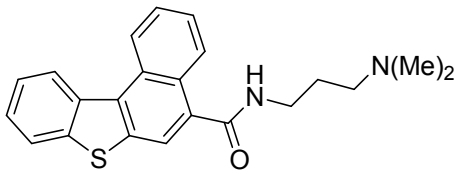
Ethyl 10-chlorobenzo[*b*]naphtho[*1,2-d*]thiophene-5-carboxylate

Yellow solid, 59 mg, 58%, mp 98.8-100.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (d, *J* = 8.8 Hz, 1H), 8.85 (d, *J* = 8.4 Hz, 1H), 8.75 (d, *J* = 2.0 Hz, 1H), 8.50 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.48 (dd, *J* = 1.6 Hz, *J* = 2.0 Hz, 1H), 4.53 (q, *J* = 6.8 Hz, 2H), 1.51 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 139.1, 137.7, 137.0, 131.4, 131.3, 130.7, 129.4, 127.5, 127.3, 127.2, 127.1, 126.4, 126.3, 125.0, 124.0, 123.0, 61.5, 14.4; IR (neat): 2967, 2913, 2351, 1718, 1511, 1262, 1188, 1154, 802,764 cm^{-1}; HRMS calcd for $C_{19}H_{13}ClO_2S$ $[M+H]^+$:341.0403 , found: 341.0398.



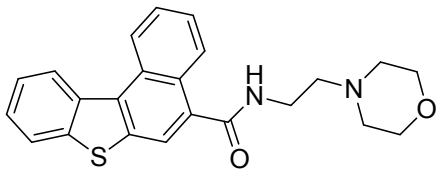
***N*-(2-(dimethylamino)ethyl)benzo[*b*]naphtho[*1,2-d*]thiophene-5-carboxamide**

White solid, 60 mg, 64%, mp 138.8-139.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (d, *J* = 8.4 Hz, 1H), 8.82 (d, *J* = 8.4 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 10.0 Hz, 2H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 6.8 Hz, 1H), 6.79 (s, 1H), 3.64 (q, *J* = 5.6 Hz, 2H), 2.56 (t, *J* = 6.0 Hz, 2H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 140.3, 137.0, 136.1, 134.1, 130.8, 130.5, 128.6, 127.4, 126.9, 125.7, 125.6, 125.0, 125.0, 123.3, 123.2, 120.3, 57.7, 45.1, 37.4; IR (neat): 3270, 2921, 2764, 1635, 1536, 1287, 789 cm^{-1}; HRMS calcd for $C_{21}H_{20}N_2OS$ $[M+]^+$:348.1296 , found: 348.1299.



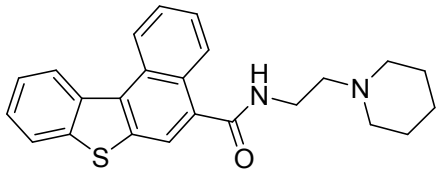
***N*-(3-(dimethylamino)propyl)benzo[*b*]naphtho[*1,2-d*]thiophene-5-carboxamide**

White solid, 95 mg, 59%, mp 154.4-155.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (t, *J* = 8.0 Hz, 1H), 8.81-8.78 (m, 1H), 8.47-8.44 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.88 (s, 1H), 7.70-7.69 (m, 1H), 7.58 (t, *J* = 4.8 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 3.62 (t, *J* = 5.6 Hz, 2H), 2.46-2.42 (m, 2H), 2.17 (s, 6H), 1.81-1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 140.2, 137.0, 136.1, 134.4, 130.8, 130.3, 128.6, 127.3, 126.9, 125.6, 125.5, 125.0, 124.9, 123.2, 123.2, 120.1, 58.7, 45.4, 40.0, 26.0; IR (neat): 3270, 3058, 2929, 2764, 1635, 1536, 1457, 1275, 760 cm^{-1}; HRMS calcd for $C_{22}H_{22}N_2OS$ $[M+]^+$:362.1451 , found: 362.1454.



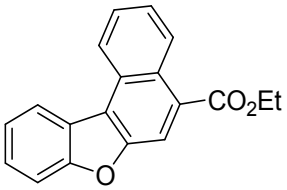
***N*-(2-morpholinoethyl)benzo[*b*]naphtho[*1,2-d*]thiophene-5-carboxamide**

White solid, 60 mg, 35%, mp 201.9-202.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (d, *J* = 8.4 Hz, 1H), 8.83 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.75 (t, *J* = 6.8 Hz, 1H), 7.63-7.55 (m, 2H), 7.53 (t, *J* = 6.8 Hz, 1H), 6.69 (s, 1H), 3.70-3.64 (m, 6H), 2.63 (t, *J* = 6.0 Hz, 2H), 2.51 (t, *J* = 4.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 140.3, 137.1, 136.1, 134.1, 130.8, 130.5, 128.6, 127.5, 126.8, 125.8, 125.6, 125.1, 125.0, 123.4, 123.3, 120.4, 66.9, 57.1, 53.3, 36.3; IR (neat): 3274, 3058, 2950, 2921, 2851, 2801, 1631, 1532, 1113, 770 cm^{-1}; HRMS calcd for $C_{23}H_{22}N_2O_2S$ [M+]$^+$:390.1402 , found: 390.1400.



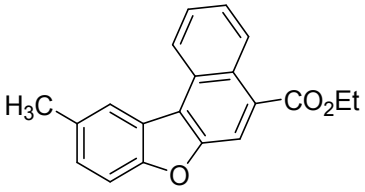
***N*-(2-(piperidin-1-yl)ethyl)benzo[*b*]naphtho[*1,2-d*]thiophene-5-carboxamide**

White solid, 120 mg, 85%, mp 142.0-143.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (d, *J* = 8.4 Hz, 1H), 8.86 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.05 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.77-7.73 (m, 1H), 7.64-7.60 (m, 2H), 7.55-7.51 (m, 1H), 6.80 (s, 1H), 3.67 (q, *J* = 6.0 Hz, 2H), 2.60 (t, *J* = 6.0 Hz, 2H), 2.45 (s, 4H), 1.59-1.53 (m, 4H), 1.44 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 140.4, 137.2, 136.2, 134.3, 130.9, 130.5, 128.7, 127.5, 126.9, 125.8, 125.7, 125.1, 125.0, 123.4, 123.3, 120.4, 57.2, 54.3, 36.8, 25.9, 24.3; IR (neat): 3277, 2929, 2849, 1634, 1534, 1424, 780, 764 cm^{-1}; HRMS calcd for $C_{24}H_{24}N_2OS$ [M+H]$^+$:389.1688 , found: 389.1685.



Ethyl naphtho[*2,1-b*]benzofuran-5-carboxylate

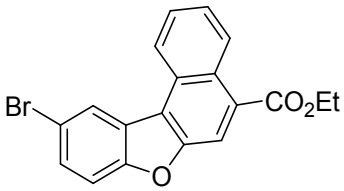
Yellow solid, 58 mg, 67%. mp 97.3-98.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H), 8.45 (s, 1H), 8.41 (d, *J* = 7.6 Hz, 1H), 7.74-7.70 (m, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H),7.48 (t, *J* = 7.2 Hz, 1H), 4.53 (q, *J* = 7.2 Hz, 2H), 1.50 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 156.9, 152.4, 129.5, 128.5, 127.3, 127.2, 127.2, 125.9, 125.9, 124.2, 123.7, 123.5, 122.6, 121.4, 116.7, 112.2, 61.4, 14.4; IR (neat): 2958, 2917, 1715, 1453, 1275, 1221, 1188, 744 cm^{-1}; HRMS calcd for $C_{19}H_{14}O_3$ [M+H]$^+$:291.1021 , found: 291.1026.



Ethyl 10-methylnaphtho[*2,1-b*]benzofuran-5-carboxylate

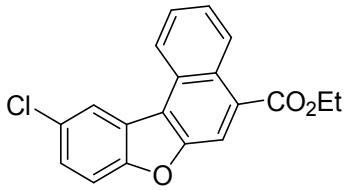
Yellow solid, 50 mg, 55%. mp 99.3-100.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.4 Hz, 1H), 8.39 (s, 1H), 8.12 (s, 1H), 7.70 (t, *J* = 6.0 Hz, 1H), 7.62 (t, *J* = 6.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 4.51 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 1.49 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 155.2, 152.5, 133.0, 129.4, 128.4, 128.3, 127.1, 127.1, 126.9, 125.7, 124.1, 123.7, 122.5,

121.2, 116.7, 111.5, 61.3, 21.6, 14.4; IR (neat): 2979, 2921, 1706, 1329, 1229, 1192, 1146, 1030, 802, 735 cm^{-1}; HRMS calcd for $C_{20}H_{16}O_3$ $[M+]^+$:304.1099 , found: 304.1102.



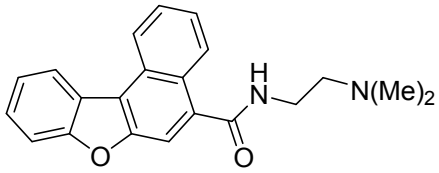
Ethyl 10-bromonaphtho[*2,1-b*]benzofuran-5-carboxylate

Yellow solid, 75 mg, 68%. mp 151.1-153.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (d, *J* = 8.0 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.29 (s, 1H), 8.21 (d, *J* = 2.0 Hz, 1H), 7.70-7.66 (m, 1H), 7.63-7.59 (m, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.43 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, 1H), 4.52 (q, *J* = 7.2 Hz, 2H), 1.51(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 155.0, 153.1, 129.1, 128.9, 128.3, 128.0, 127.5, 127.2, 127.1, 126.0, 125.3, 123.3, 122.1, 120.3, 116.4, 113.0, 61.4, 14.4; IR (neat): 2968, 2914, 1710, 1634, 1443, 1217, 726 cm^{-1}; HRMS calcd for $C_{19}H_{13}BrO_3$ $[M+]^+$:368.0048 , found: 368.0049.



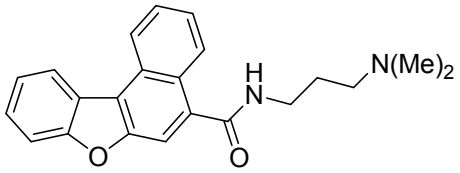
Ethyl 10-chloronaphtho[*2,1-b*]benzofuran-5-carboxylate

Yellow solid, 57 mg, 58%. mp 106.9-108.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, *J* = 8.4 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.35 (s, 1H), 8.28 (d, *J* = 1.6 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.47 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, 1H), 4.53 (q, *J* = 6.8 Hz, 2H), 1.51(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 155.0, 153.1, 129.1, 129.0, 128.4, 128.1, 127.6, 127.2, 127.1, 126.1, 125.3, 123.4, 122.2, 120.3, 116.4, 113.0, 61.5, 14.4; IR (neat): 2968, 2914, 1710, 1634, 1443, 1217, 726 cm^{-1}; HRMS calcd for $C_{19}H_{13}ClO_3$ $[M+]^+$:324.0553 , found: 324.0548.



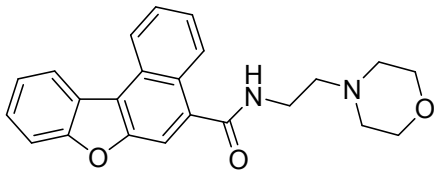
***N*-(2-(dimethylamino)ethyl)naphtho[*2,1-b*]benzofuran-5-carboxamide**

White solid, 40 mg, 35%, mp 127.7-129.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.74-7.69 (m, 2H), 7.60-7.46 (m, 3H), 6.80 (s, 1H), 3.66 (q, *J* = 5.6 Hz, 2H), 2.59 (t, *J* = 6.0 Hz, 2H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 159.8, 156.4, 152.7, 135.0, 129.5, 127.6, 127.4, 126.9, 126.6, 125.3, 124.4, 123.7, 123.4, 122.3, 119.1, 112.0, 57.5, 45.2, 37.1; IR (neat): 3274, 2917, 1631, 1540, 1457, 1345, 1275, 744 cm^{-1}; HRMS calcd for $C_{21}H_{20}N_2O_2$ $[M+]^+$:332.1525 , found: 332.1530.



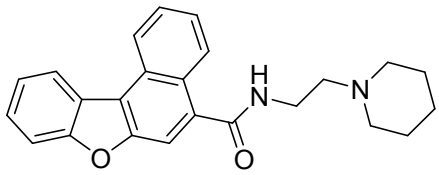
***N*-(3-(dimethylamino)propyl)naphtho[*2,1-b*]benzofuran-5-carboxamide**

White solid, 70 mg, 59%, mp 146.9-149.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 8.4 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 7.2 Hz, 1H), 7.96 (s, 1H), 7.87 (s, 1H), 7.73-7.68 (m, 2H), 7.59-7.46 (m, 3H), 3.67 (q, *J* = 6.0 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 159.9, 156.3, 152.7, 135.3, 129.4, 127.5, 127.4, 127.0, 126.5, 125.1, 124.4, 123.6, 123.4, 122.2, 118.9, 112.0, 58.0, 45.4, 39.0, 25.8; IR (neat): 3270, 3054, 2921, 1635, 1536, 1449, 1345, 1241, 744 cm^{-1}; HRMS calcd for $C_{22}H_{22}N_2O_2$ $[M+]^+$:346.1681 , found: 346.1678.



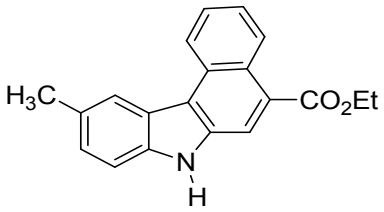
***N*-(2-morpholinoethyl)naphtho[*2,1-b*]benzofuran-5-carboxamide**

White solid, 65 mg, 50%, mp 189.3-189.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 7.6 Hz, 1H), 7.91 (s, 1H), 7.77-7.70 (m, 2H), 7.62-7.49 (m, 3H), 6.67 (s, 1H), 3.71 (t, *J* = 4.8 Hz, 6H), 2.67 (t, *J* = 6.0 Hz, 2H), 2.54 (t, *J* = 3.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 156.4, 152.7, 134.9, 129.5, 127.6, 127.4, 126.8, 126.7, 125.3, 124.4, 123.8, 123.5, 122.3, 119.2, 112.1, 66.9, 57.0, 53.4, 36.3; IR (neat): 3277, 2980, 1635, 1541, 1534, 1346, 740 cm^{-1}; HRMS calcd for $C_{23}H_{22}N_2O_3$ $[M+]^+$:374.1630 , found: 374.1634.

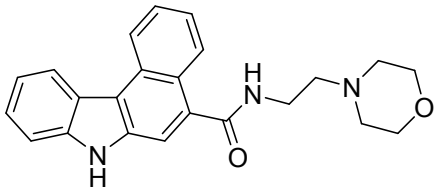


***N*-(2-(piperidin-1-yl)ethyl)naphtho[*2,1-b*]benzofuran-5-carboxamide**

White solid, 110 mg, 84%, mp 131.0-131.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59-8.56 (m, 1H), 8.47 (d, *J* = 7.2 Hz, 1H), 8.34 (d, *J* = 6.4 Hz, 1H), 7.86 (d, *J* = 2.8 Hz, 1H), 7.69-7.67 (m, 2H), 7.58-7.46 (m, 3H), 6.86 (s, 1H), 3.65 (q, *J* = 5.6 Hz, 2H), 2.59 (t, *J* = 5.6 Hz, 2H), 2.44 (s, 4H), 1.58-1.53 (m, 4H), 1.43 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 156.3, 152.7, 135.0, 129.4, 127.5, 127.3, 126.9, 126.5, 125.2, 124.3, 123.6, 123.4, 122.2, 119.0, 112.0, 112.0, 57.1, 54.3, 36.8, 25.9, 24.3; IR (neat): 3282, 2934, 1631, 1540, 1453, 1341, 764, 748 cm^{-1}; HRMS calcd for $C_{24}H_{24}N_2O_2$ $[M+H]^+$:373.1916 , found: 373.1912.



ethyl 10-methyl-7H-benzo[c]carbazole-5-carboxylate. Yellow solid, mp170-171°C, ^{1}H NMR($CDCl_3$, 400MHz): δ 9.06 (d, J = 8.8 Hz, 1H), 8.83 (d, J = 8.0 Hz, 1H), 8.49 (s, 1H), 8.37 (s, 1H), 8.32 (s, 1H), 7.73 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 4.52 (q, J = 6.8 Hz, 2H), 2.62 (s, 3H), 1.49 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.00, 137.9, 135.3, 130.3, 129.9, 127.2, 127.0, 126.9, 126.8, 125.7, 124.2, 123.6, 123.5, 122.5, 118.8, 117.2, 111.1, 61.1, 21.8, 14.4; IR (neat): 3319, 2980, 2922, 1683, 1620, 1468, 1369, 1223, 1030, 779, 696, 612 cm^{-1}; HRMS (EI) Calcd for $C_{19}H_{15}NO_2$289.1103, found 289.1104.



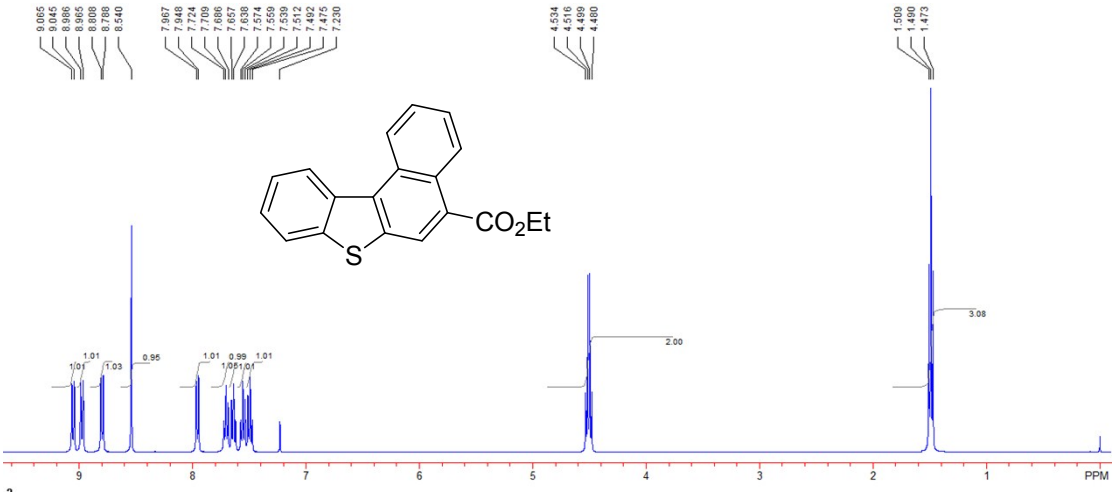
***N*-(2-morpholinoethyl)-7*H*-benzo[c]carbazole-5-carboxamide(9d).** White solid, 63.9 mg, 57%, m.p: 213.3-214.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.94 (s, 1H), 8.83 (d, J = 8.4 Hz, 1H), 8.63-8.56 (m, 2H), 8.42 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.76-7.68 (m, 2H), 7.53-7.44 (m, 2H), 7.36-7.31 (m, 1H), 3.64 (t, J = 8.0 Hz, 4H), 3.54-3.49 (m, 2H), 2.59-2.55 (m, 2H), 2.49 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.0, 139.2, 136.0, 134.1, 129.5, 127.1, 127.0, 125.4, 124.5, 123.2, 123.0, 122.6, 121.9, 119.8, 114.9, 112.6, 111.8, 66.3, 57.4, 53.3, 36.3; IR (neat): 3254, 2923, 2852, 1635, 1523, 1457, 1359, 1287, 1114, 748 cm^{-1}; HRMS calcd for $C_{23}H_{24}N_3O_2$ $[M+H]^+$: 374.1869, found 374.1866.

References：

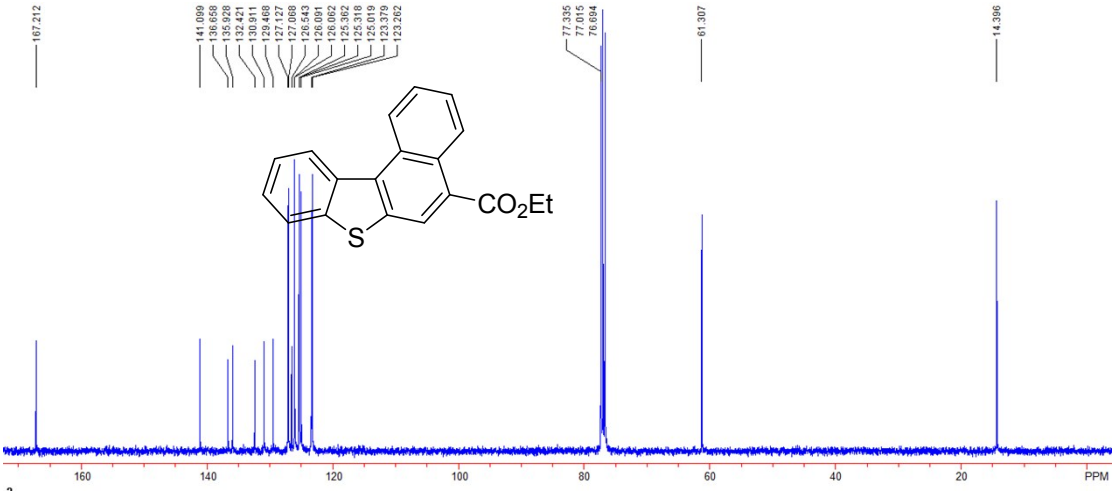
1 F. Sha, Y. Tao, C.-Y. Tang, F. Zhang and X.-Y. Wu, *J. Org. Chem.,* 2015, **80**, 8122.

2 Y. Tao, F. Zhang, C.-Y. Tang, X.-Y. Wu and F. Sha, *Asian J. Org. Chem.,* 2014, **3**, 1292.

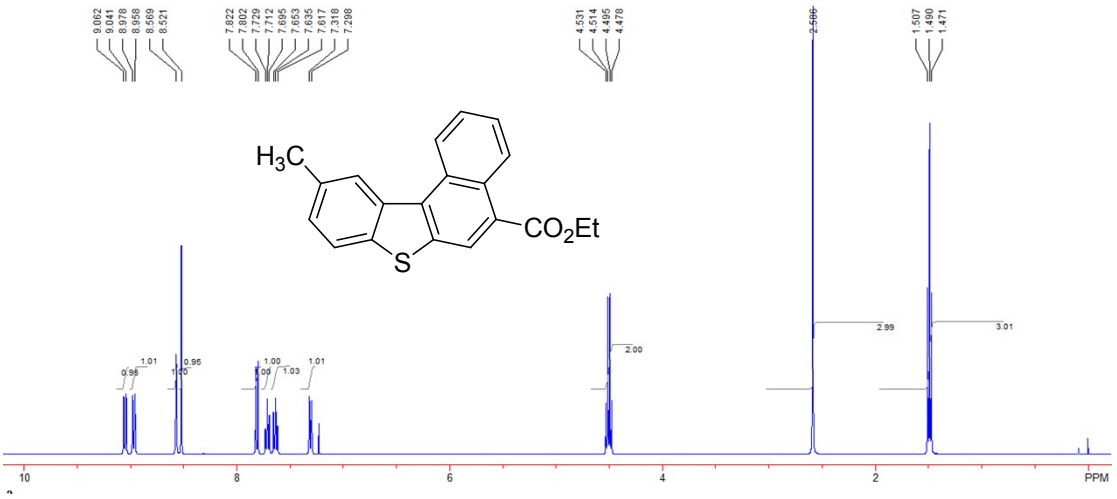
S3. Original spectral copies of new compounds



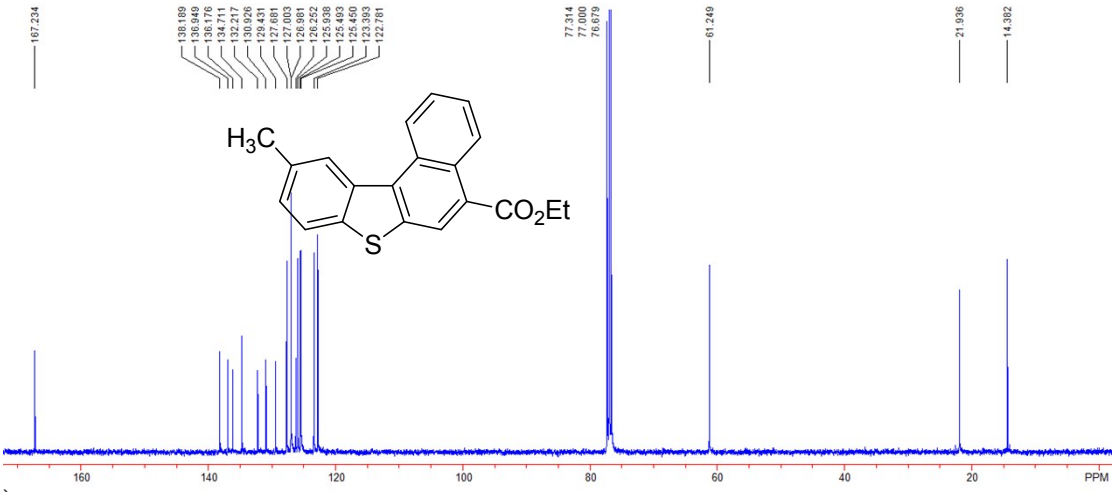
^{1}H NMR of **S1**



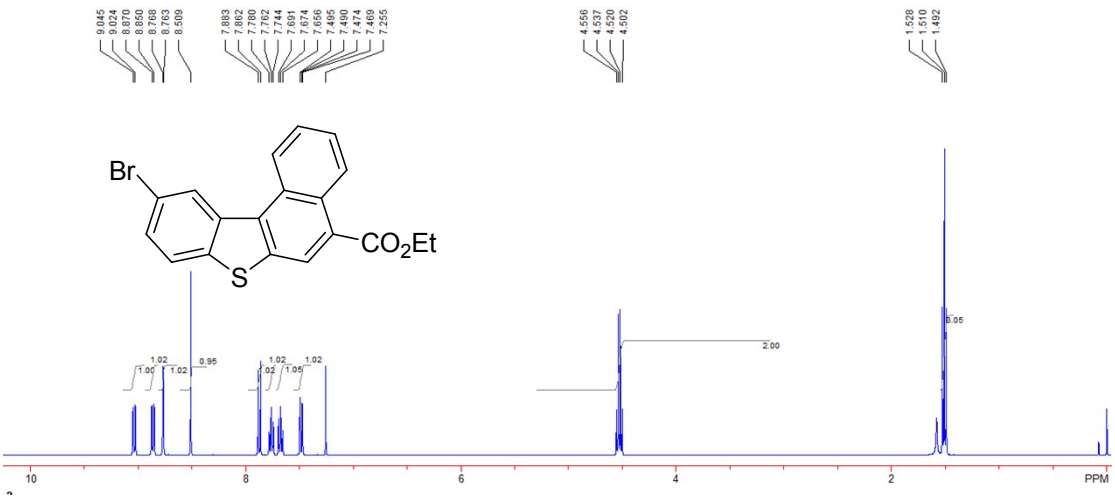
^{13}C NMR of **S1**



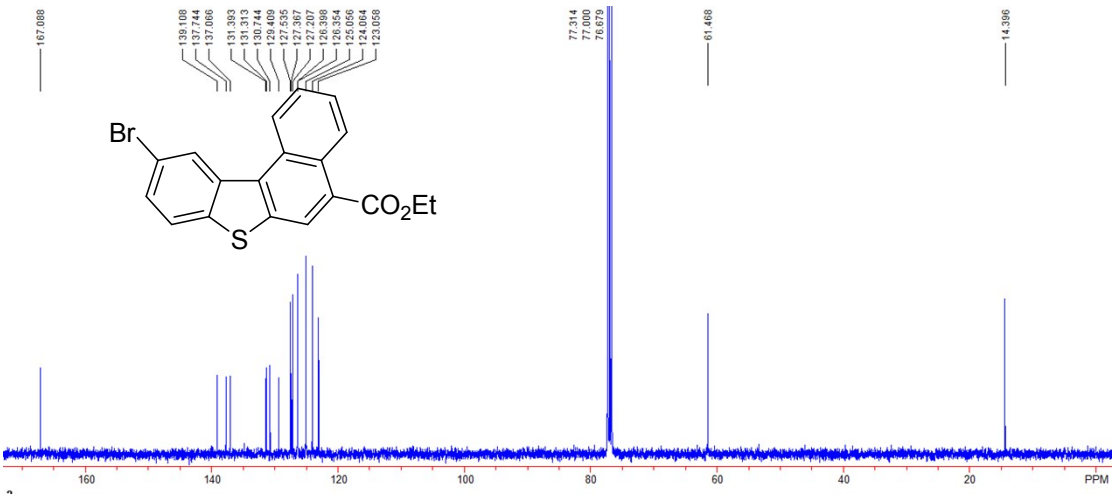
^{1}H NMR of **S2**



^{13}C NMR of **S2**



^{1}H NMR of **S3**



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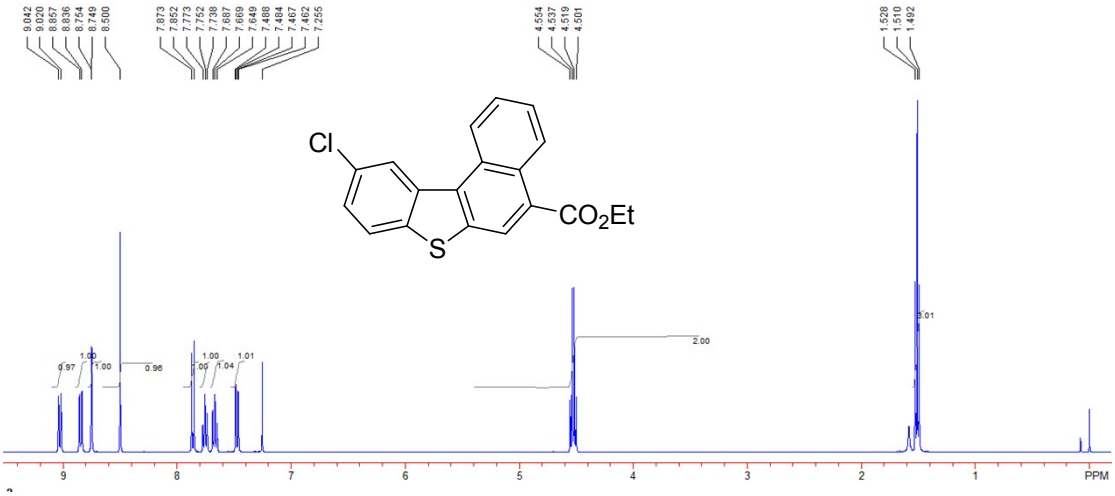

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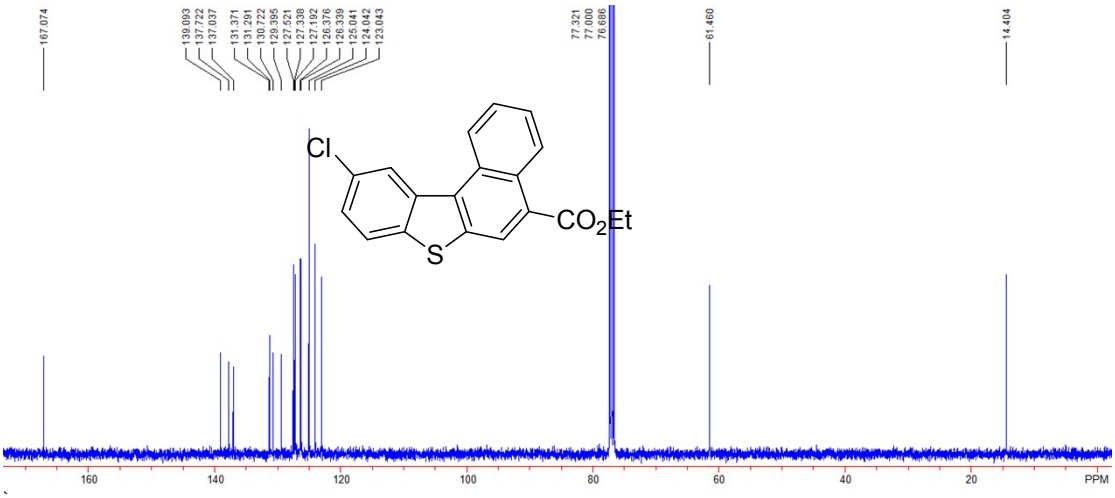
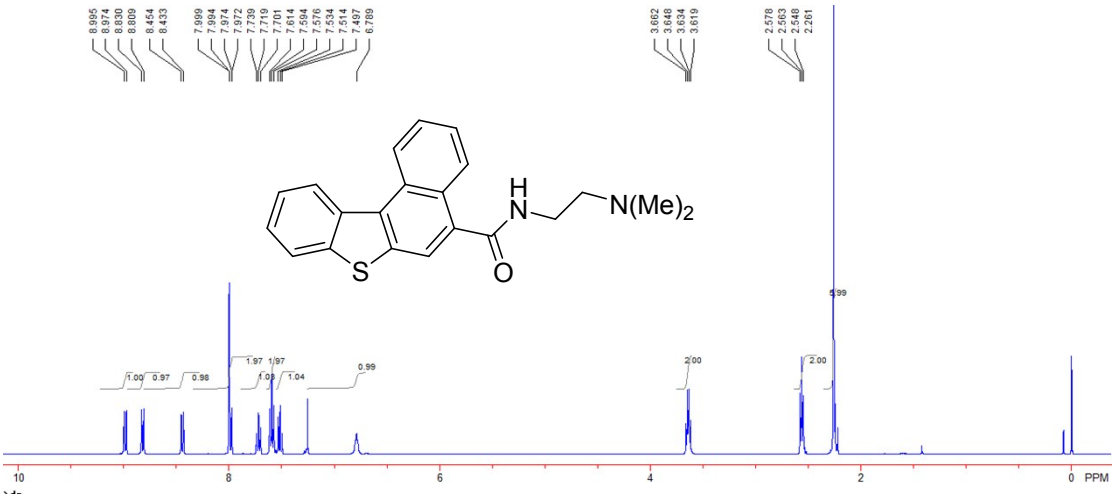
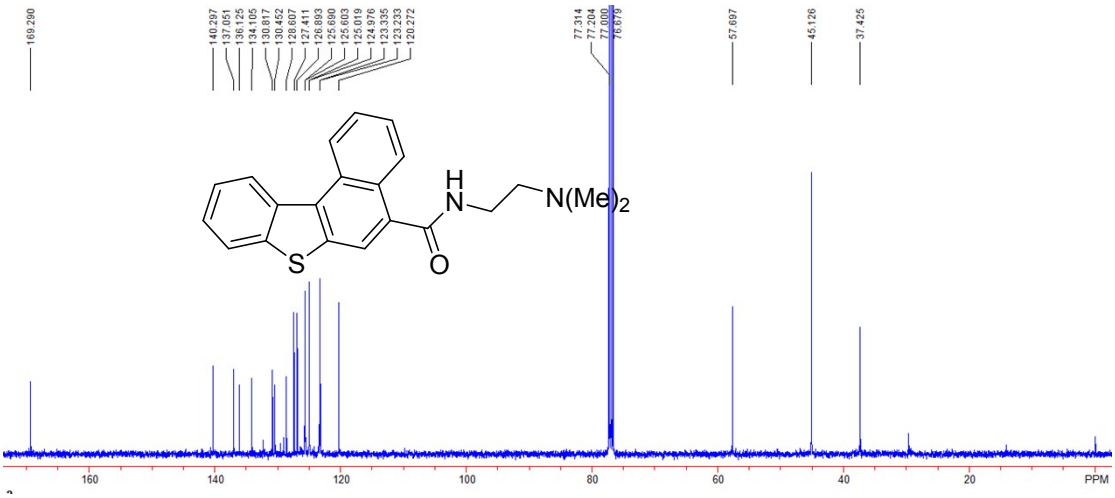


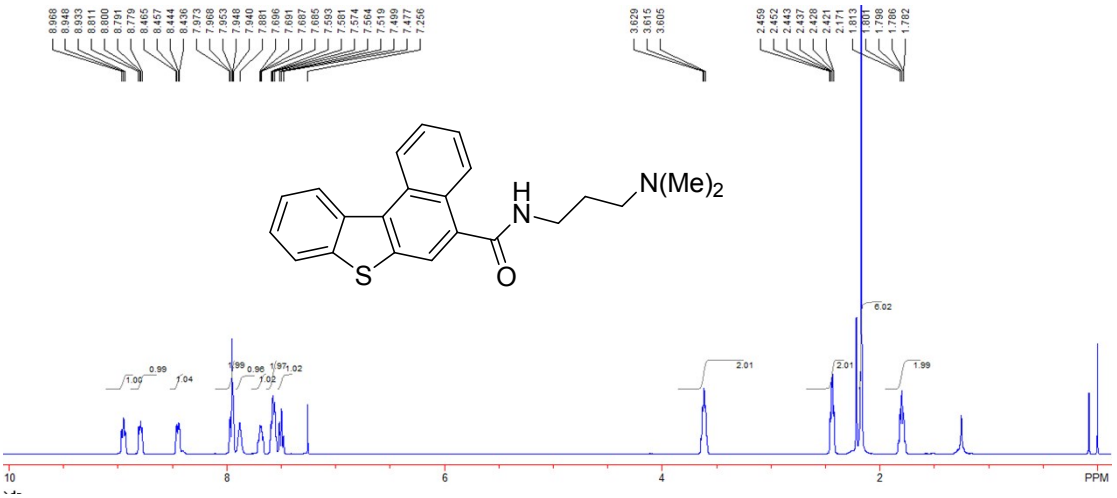
^{13}C NMR of **S4**



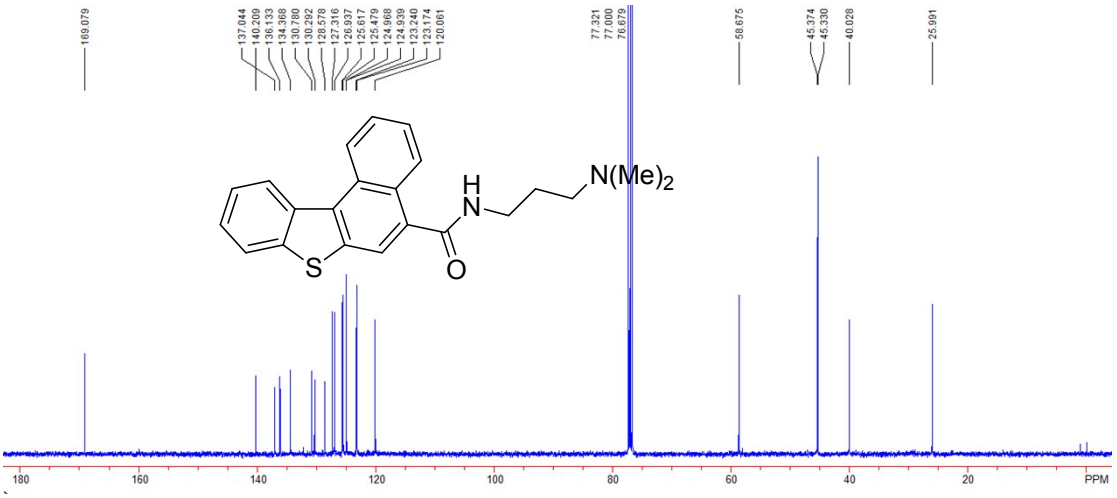
^{1}H NMR of **S5**



^{13}C NMR of **S5**



^{1}H NMR of **S6**



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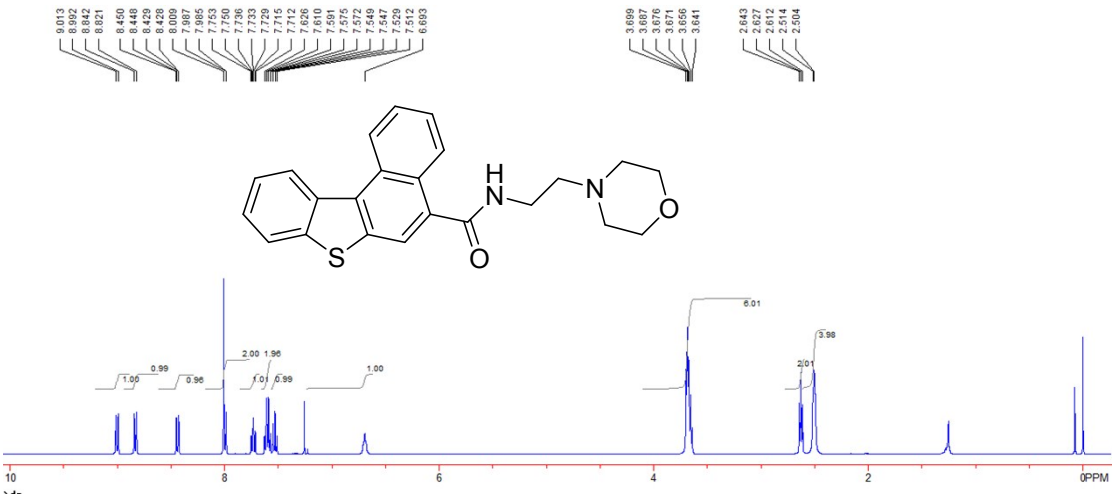
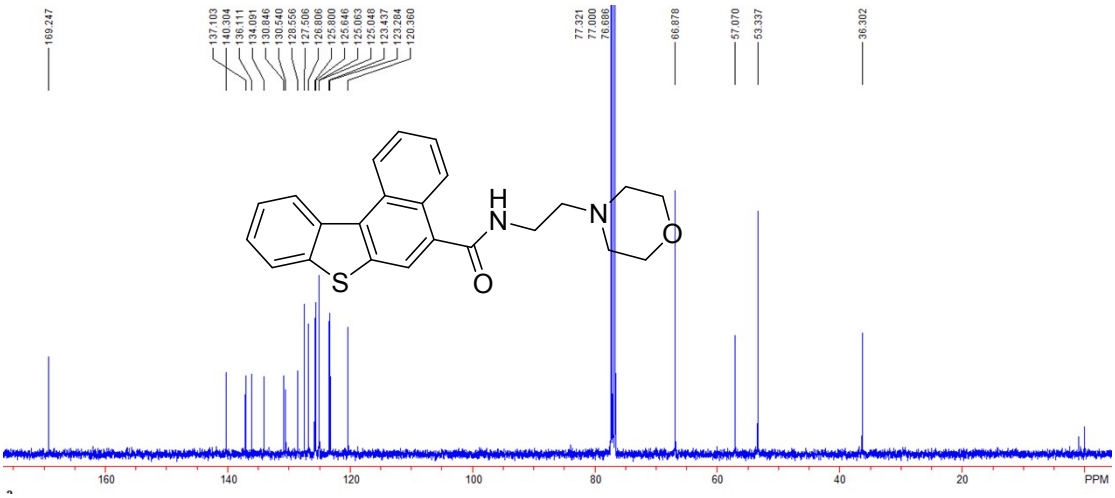
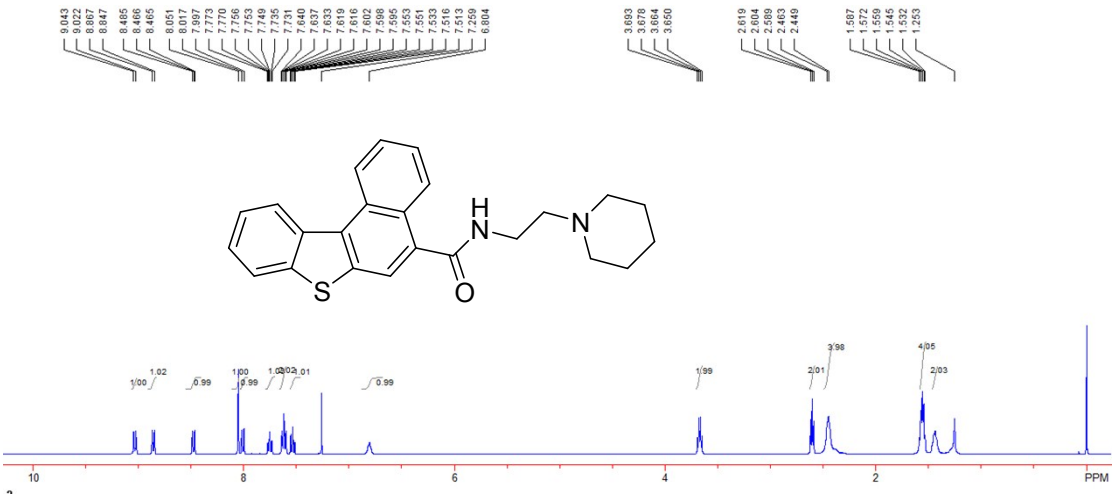


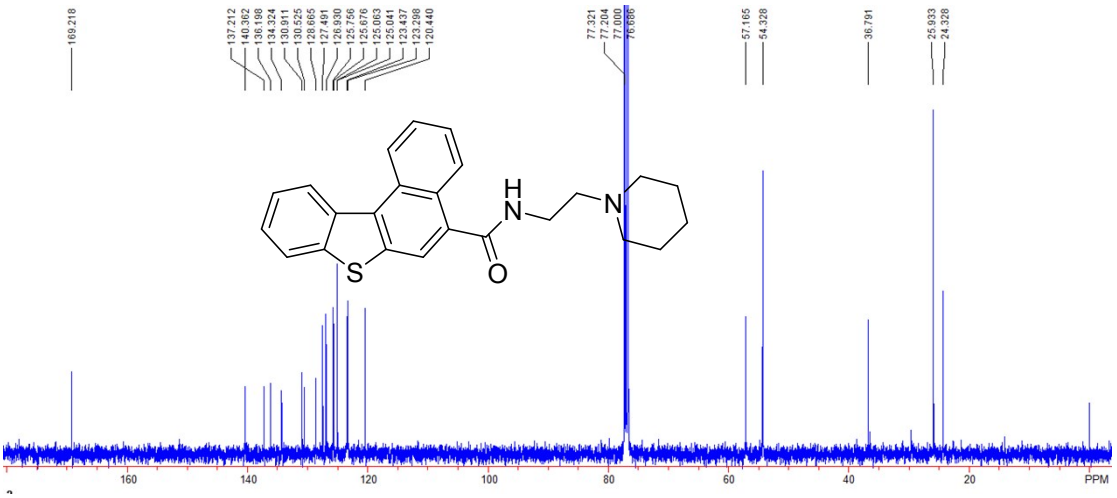
^{1}H NMR of **S7**



^{13}C NMR of **S7**



^{1}H NMR of **S8**



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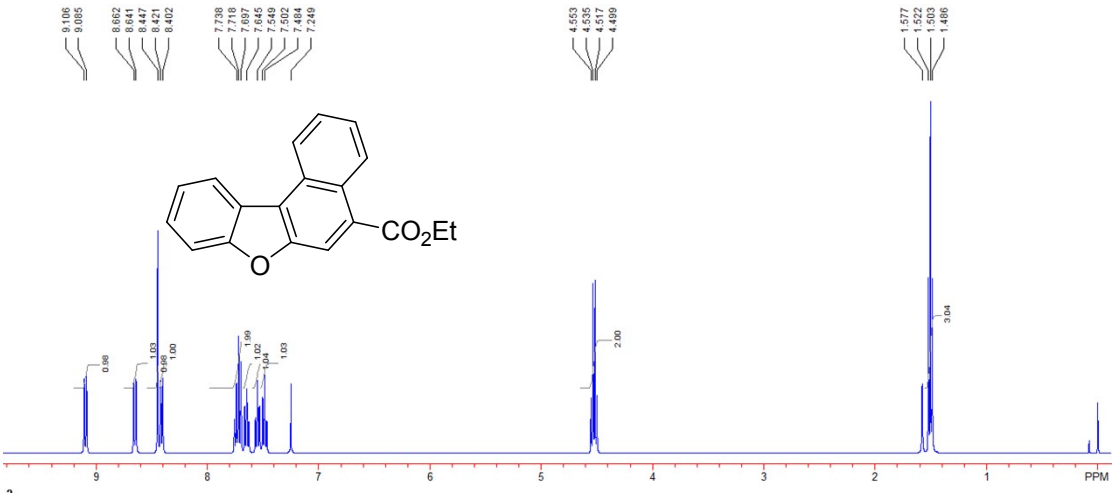
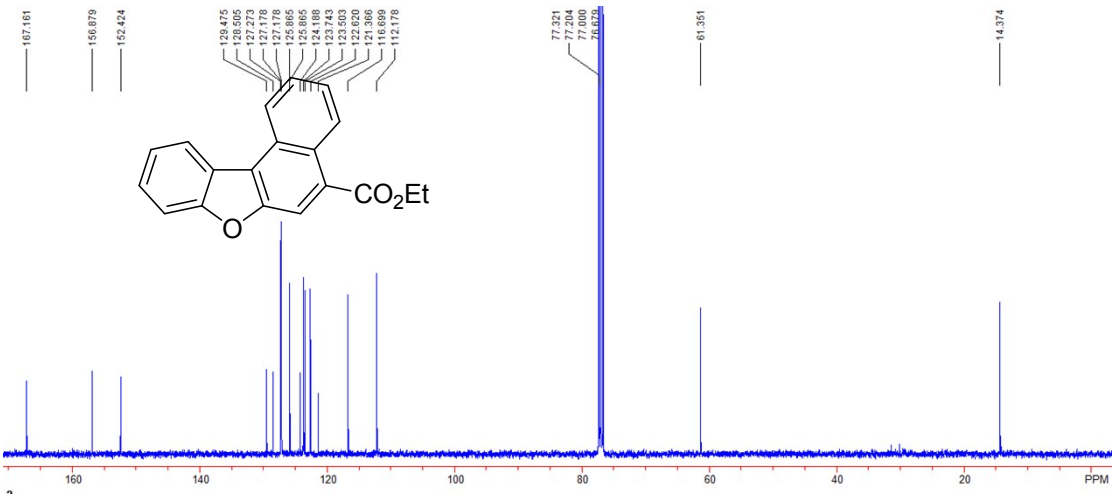
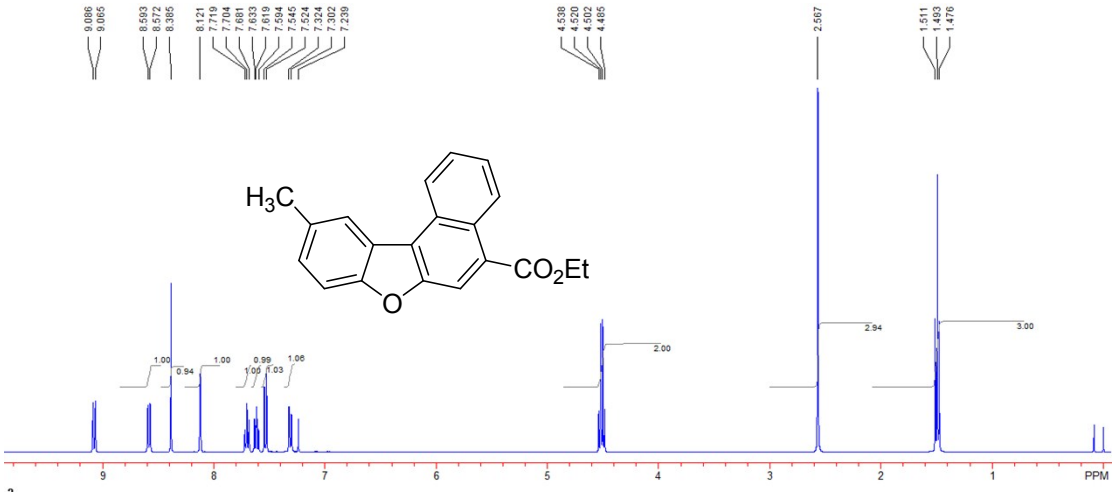


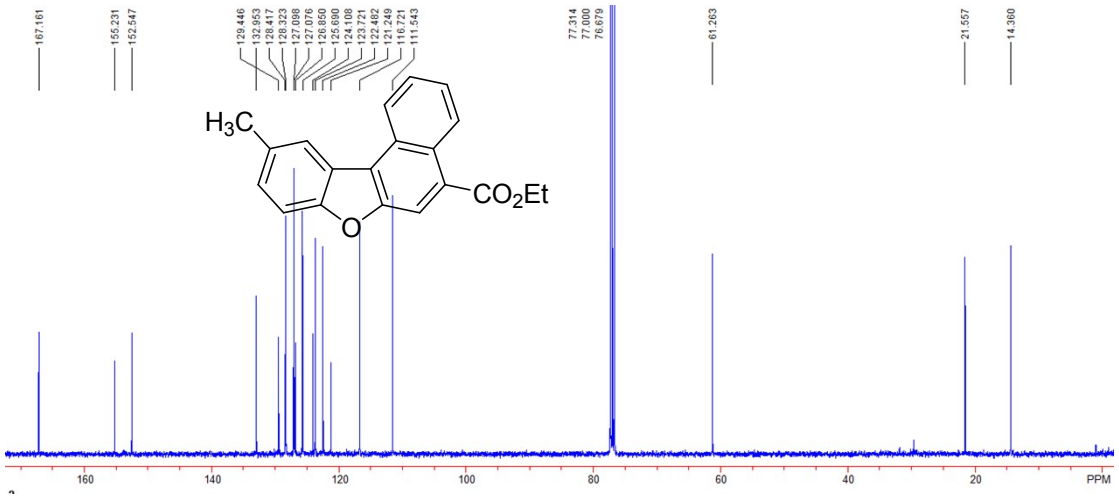
^{1}H NMR of **O1**



^{13}C NMR of **O1**



^{1}H NMR of **O2**



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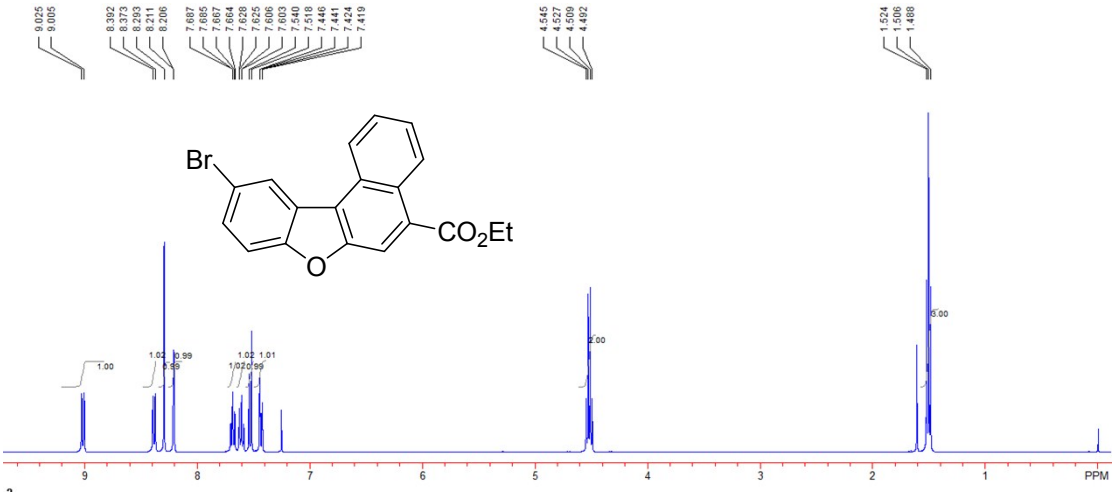
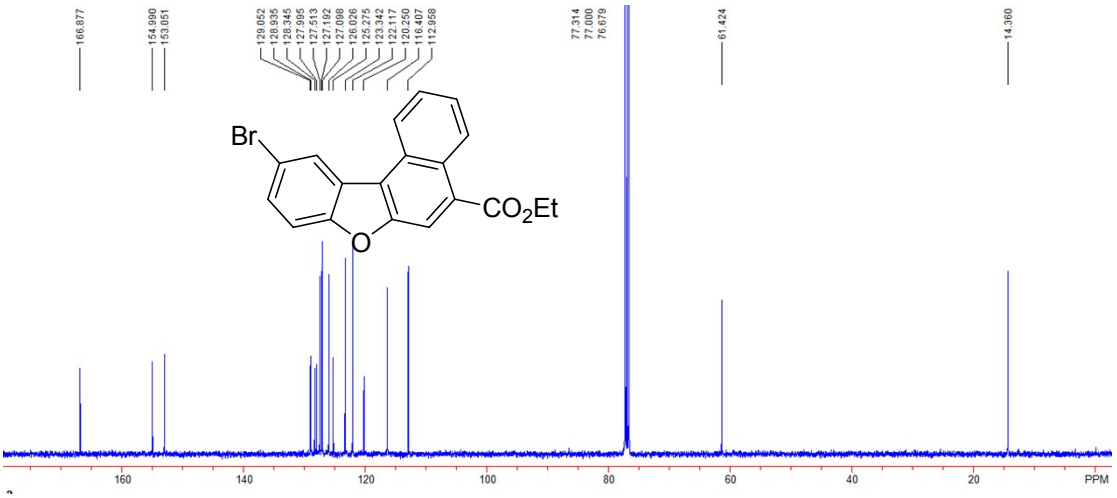
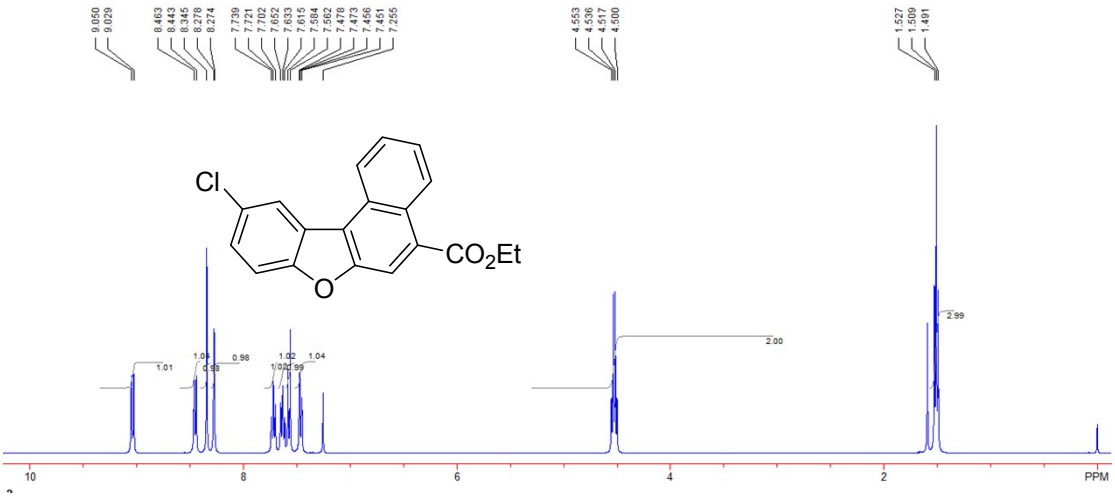


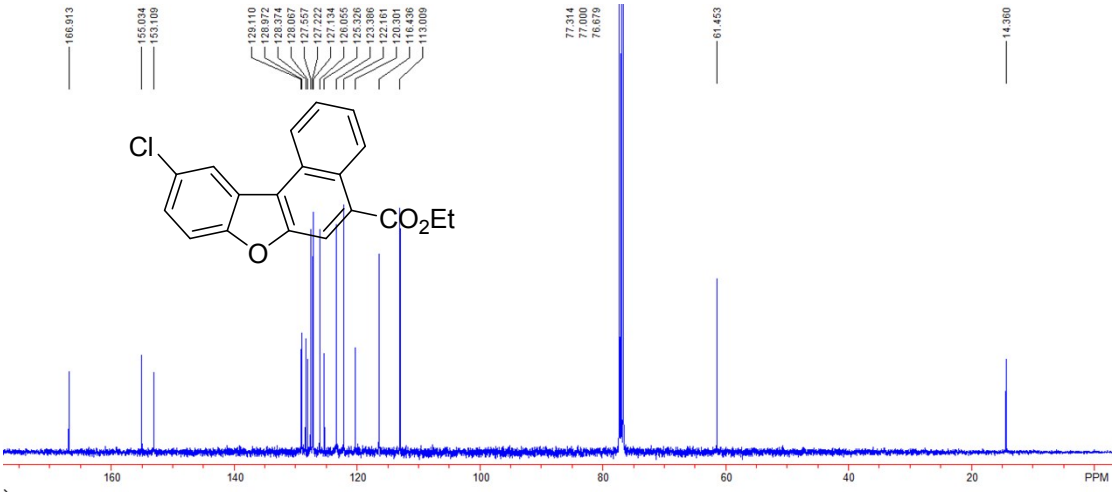
^{1}H NMR of **O3**



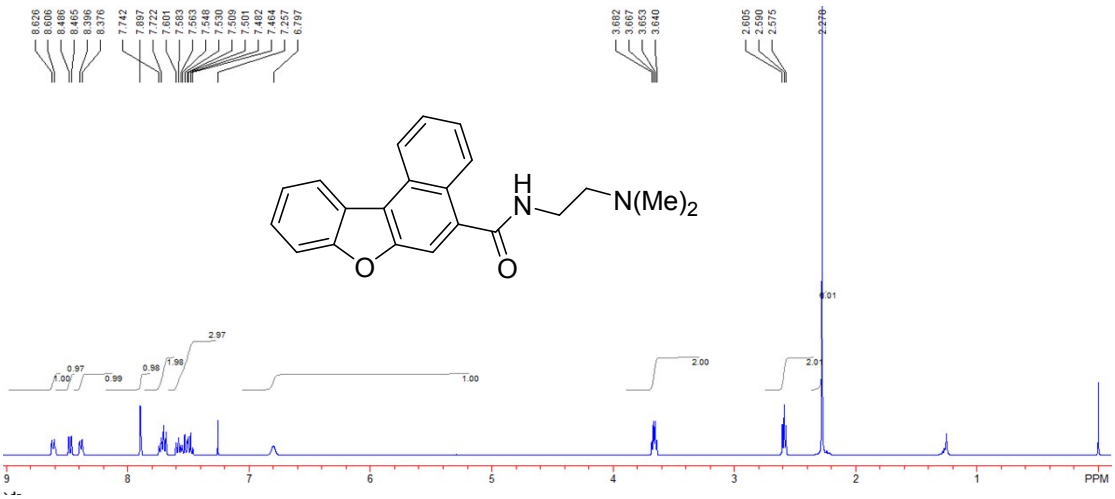
^{13}C NMR of **O3**



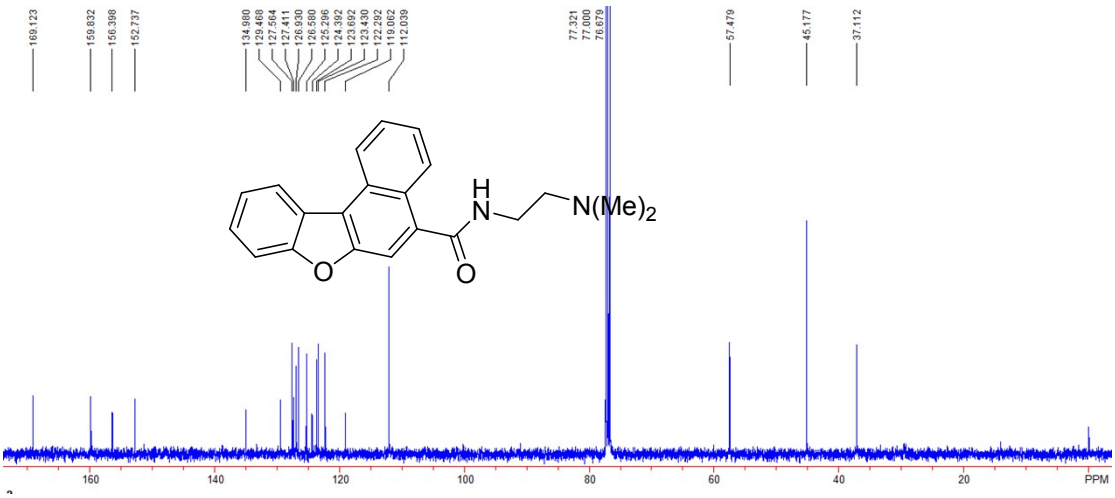
^{1}H NMR of **O4**



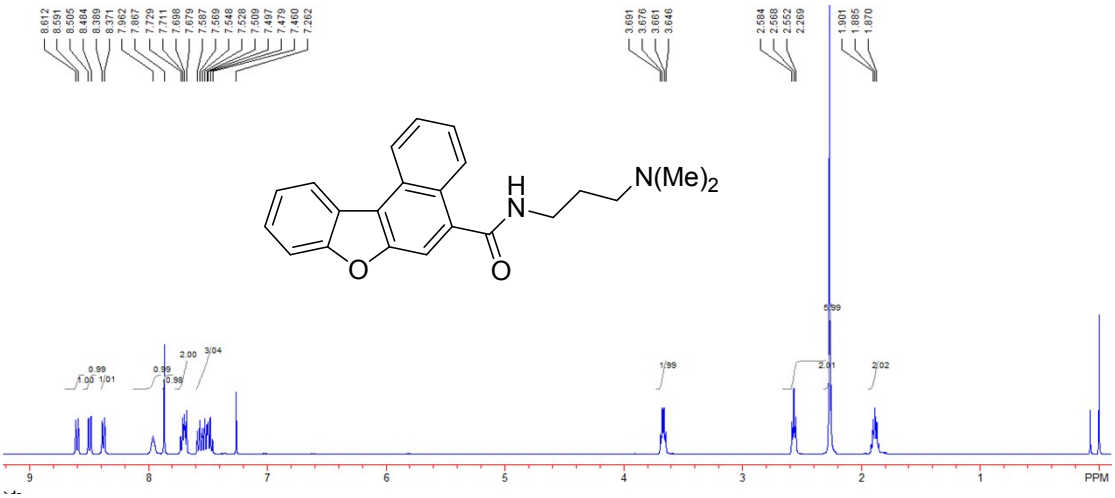
^{13}C NMR of **O4**



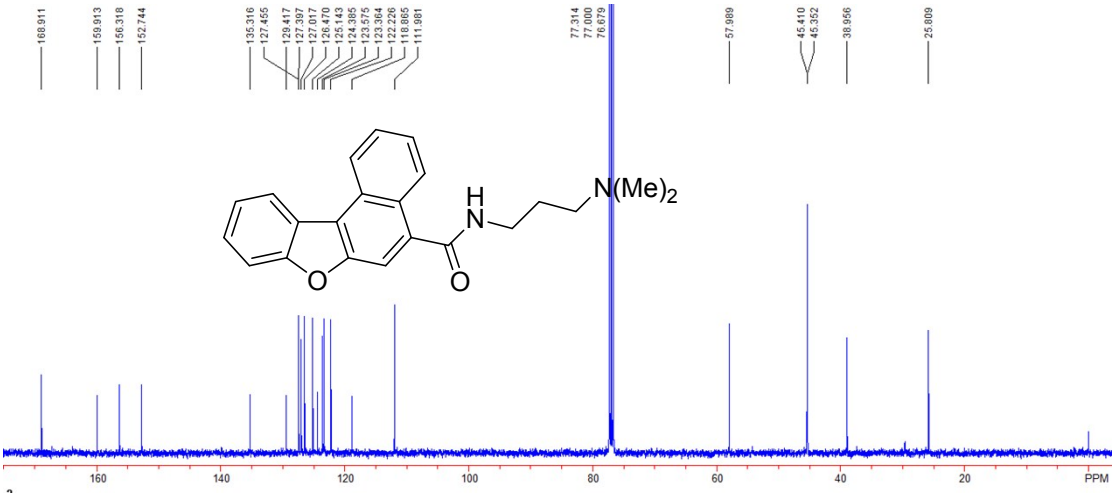
^{1}H NMR of **O5**



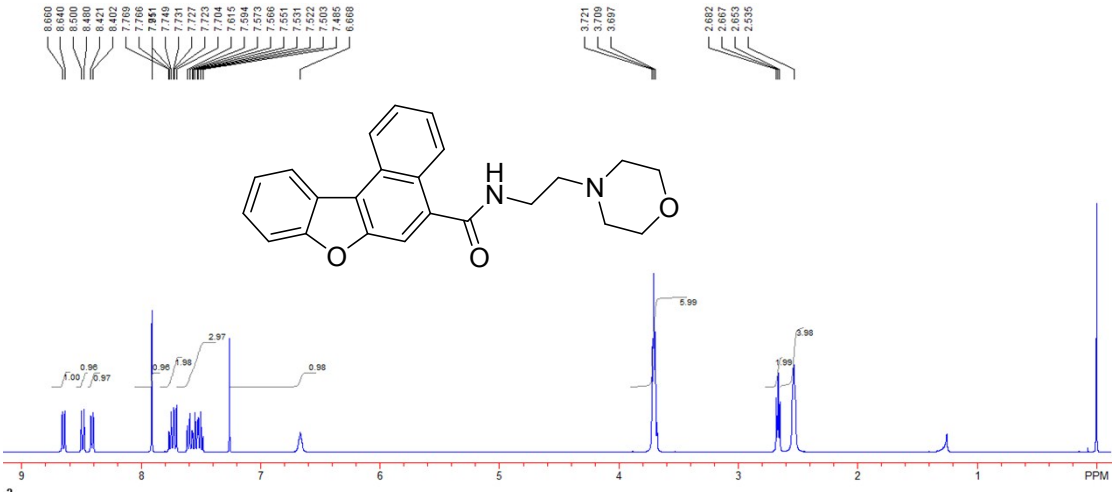
^{13}C NMR of **O5**



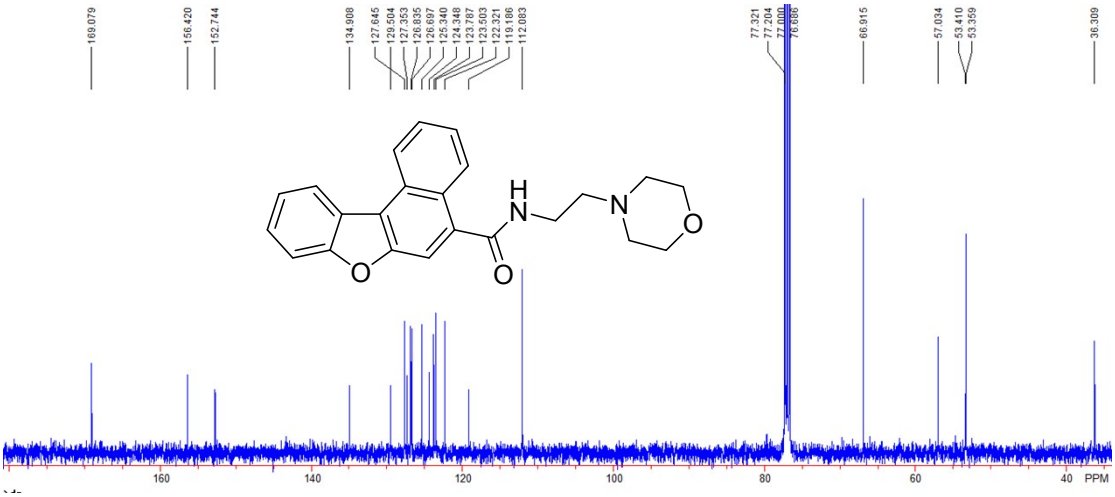
^{1}H NMR of **O6**



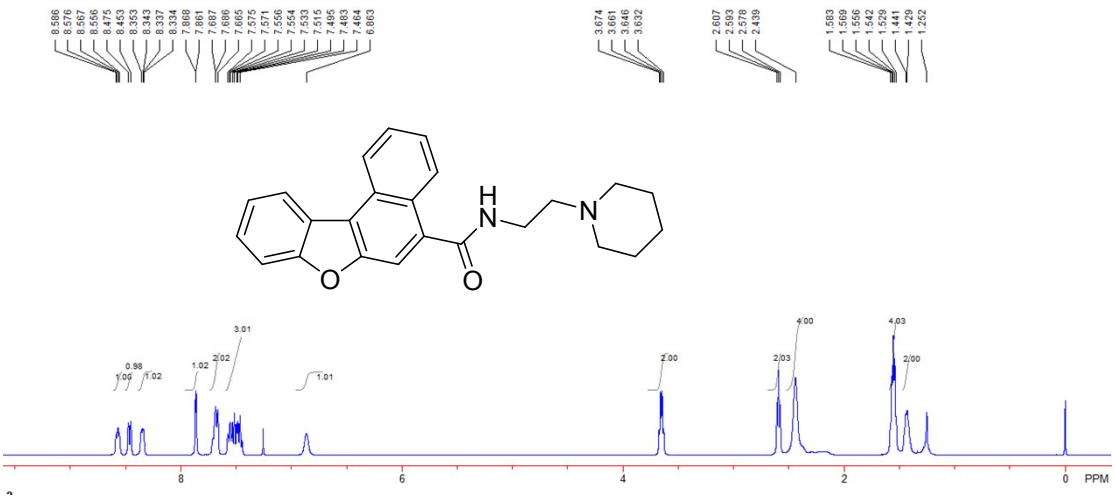
^{13}C NMR of **O6**



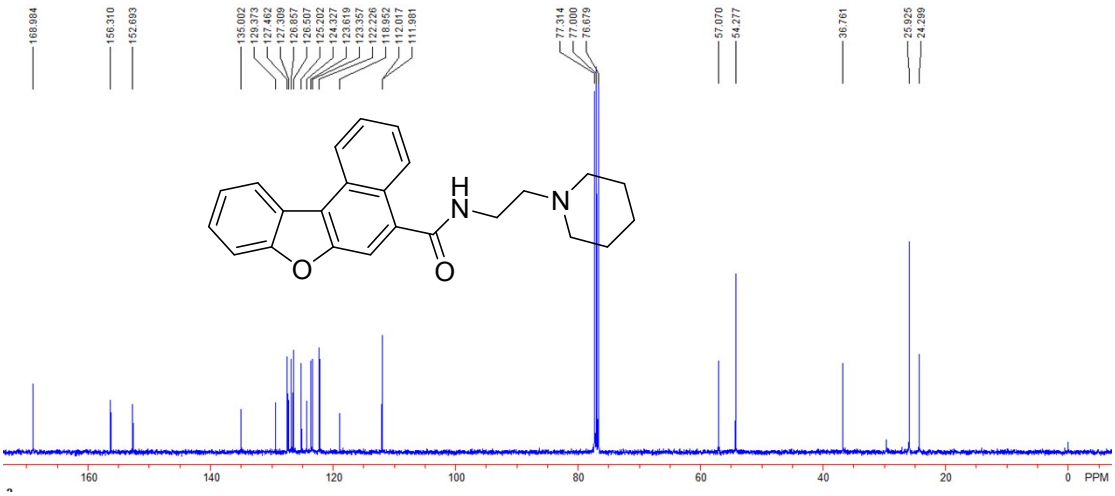
^{1}H NMR of **O7**



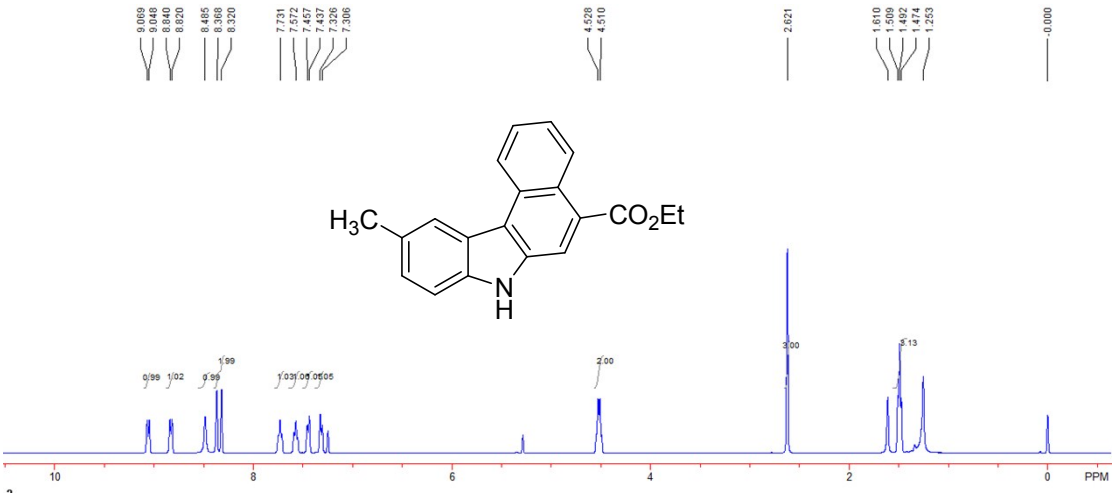
^{13}C NMR of **O7**



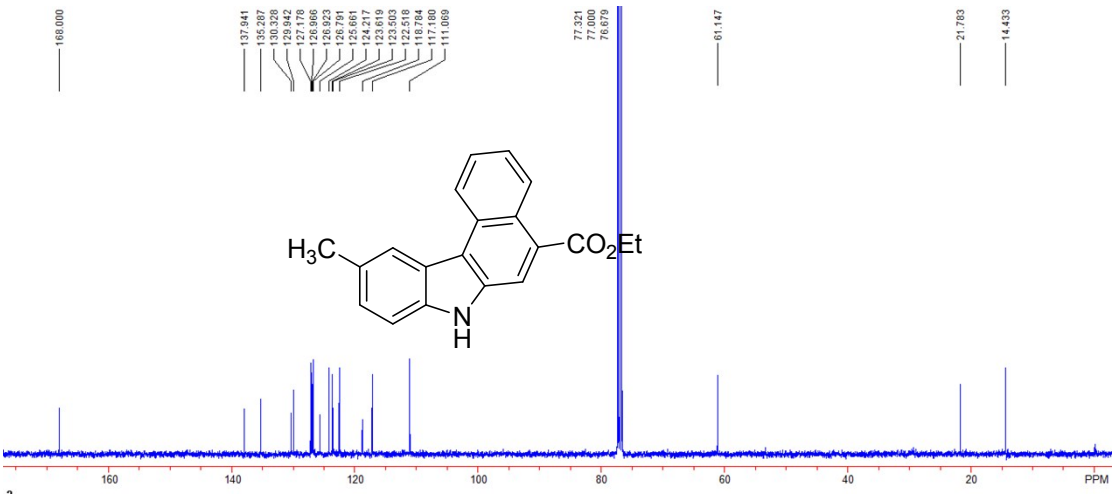
^{1}H NMR of **O8**



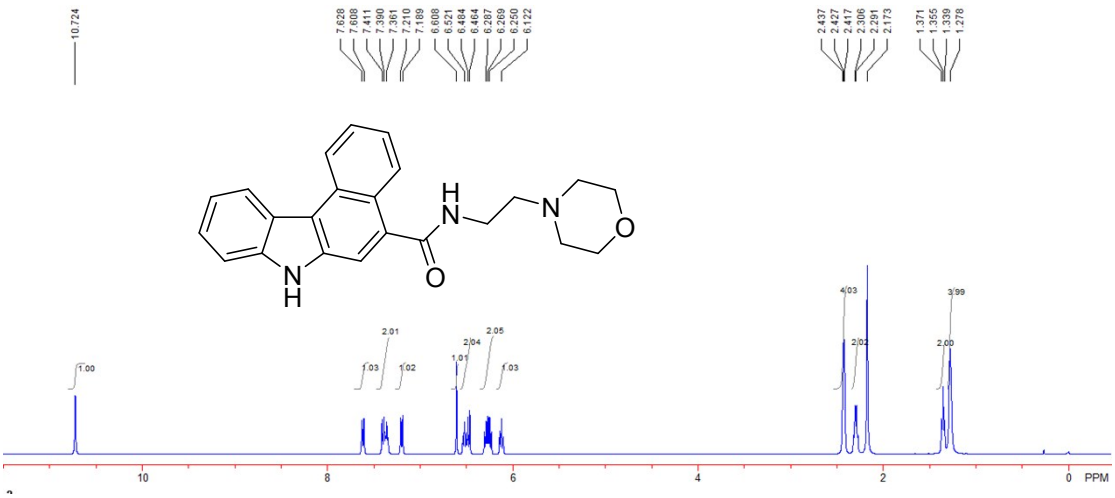
^{13}C NMR of **O8**



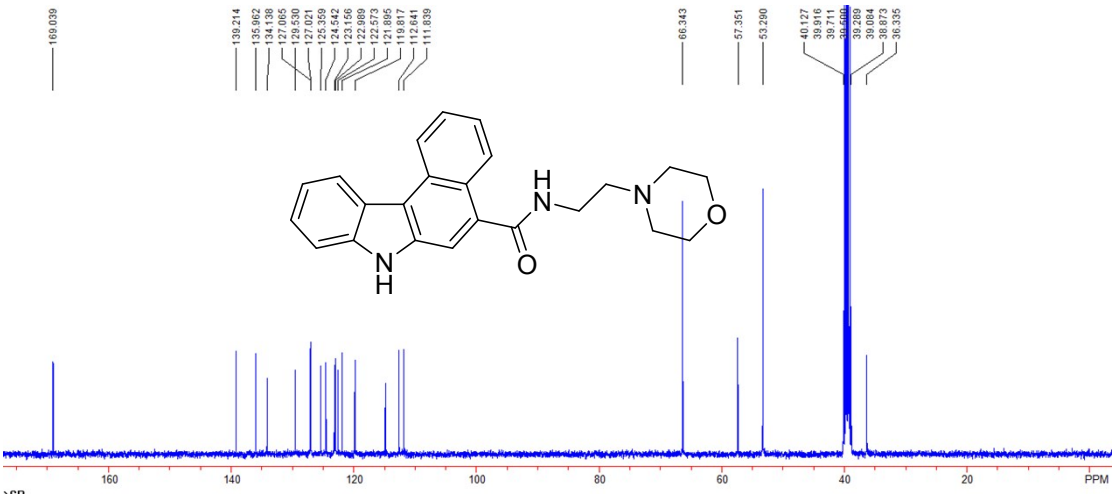
^{1}H NMR of **N2**



^{13}C NMR of **N2**



^{1}H NMR of **N7**



^{13}C NMR of **N7**