Supporting Information for

Transition-Metal-Free Synthesis of Indole Fused Dibenzo[b,f][1,4]oxazepines *via* Smiles Rearrangement

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CONTENTS

1. General information

The reactions were performed under a nitrogen atmosphere in a Schlenk tube. 2-(1H-indol-2-yl)phenols and 2-(1H-benzo[d]imidazol-2-yl)phenols were prepared according to the literature procedures.[1, 2] Other reagents were obtained from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz) or 300 (300 MHz) spectrometer, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Melting points (m.p.) were measured with a Tektronix XT-4 instrument. HRMS spectra were determined on a VG ZAB-HS mass spectrometer (Brucker Apex IV FTMS spectrometer) or a Q-TOF6510 spectrograph (Agilent).

2. General experimental procedure for synthesis of indole fused dibenzo[b,f][1,4]oxazepines

2-(1H-indol-2-yl)phenols (0.30 mmol), 1,2-dihalobenzenes or 2-halonitroarenes (0.30mmol) and potassium phosphate (0.90 mmol) were successively added to a 10 mL Schlenk tube. The reaction mixture was degassed two times, and then DMF (2 mL) was introduced using a syringe. The resulting solution was stirred at 100 ^{o}C for 3 hours. After the reaction cooled to room temperature, the mixture was extracted with ethyl acetate (10 mL) three times. Next, the combined organic phase was washed with brine, dried over anhydrous sodium sulfate (Na_2SO_4) and filtered. The solvent was then removed *in vacuo* to obtain a crude mixture, which was purified by silica gel column chromatography to afford the desired product.

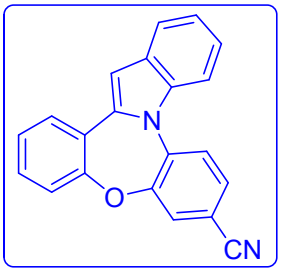
3. Details of Crystal Structure Determination for 3a

Single crystal X-ray diffraction data were collected on a Bruker SMART CCD X-ray diffractometer (APEX II) with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods (SHELEX-97) and refined by the full-matrix least-squares methods on F^2 (SHELXL-97).

Compound	**3a**
Deposition No. of CCDC	1495439
Chemical formula	$C_{21}H_{12}N_2O$
Formula Mass	308.0950
Crystal system	monoclinic
a/Å	10.672
b/Å	7.6389
c/Å	36.525
α/°	90.00
β/°	92.495
γ/°	90.00
Unit cell volume/Å^3	2974.8
Temperature/K	298
Space group	P2(1)/c
No. of formula units per unit cell, *Z*	4
No. of reflections measured	14903
No. of independent reflections	5149
R_{int}	0.0429
Final R_1 values ($I > 2\sigma(I)$)	0.0659
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0937
Final R_1 values (all data)	0.1038
Final $wR(F^2)$ values (all data)	0.1034

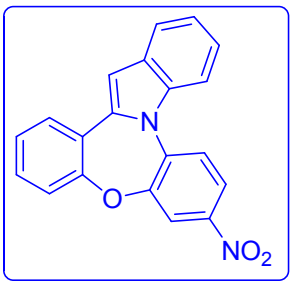
4. Characterization data for the products

dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (3a)[3]



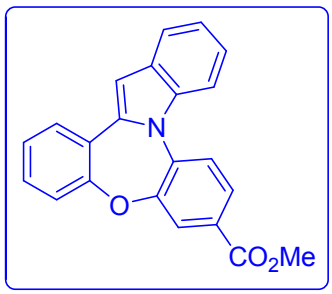
Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). Light yellow solid (91.5 mg, yield 99%). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.73-7.67 (m, 4H), 7.56 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.40-7.23 (m, 5H), 6.92 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.09, 153.21, 136.65, 136.55, 136.50, 130.25, 129.53, 129.50, 129.32, 126.64, 126.25, 125.08, 124.20, 123.51, 122.31, 121.45, 120.84, 117.69, 111.30, 109.78, 104.73.

8-nitrodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3b)



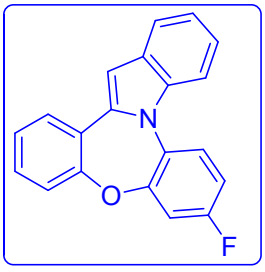
Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 1,2-difluoro-4-nitrobenzene (47.7 mg, 0.30 mmol). Yellow solid (92 mg, yield 93%). mp: 212.5-213.5 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 2.6 Hz, 1H), 8.17 (dd, *J* = 8.8 Hz, 2.6 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.73-7.69 (m, 3H), 7.39-7.36 (m, 2H), 7.32-7.25 (m, 3H), 6.94 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.01, 152.92, 145.18, 138.08, 136.69, 130.35, 129.61, 129.33, 126.34, 124.28, 124.10, 123.67, 122.50, 121.51, 121.03, 120.94, 118.71, 111.38, 105.03. HRMS (ESI, m/z): calcd for $C_{20}H_{13}N_2O_3$ $[M+H]^+$ 329.0921, found 329.0921.

methyl dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carboxylate (3c)



Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and methyl 4-fluoro-3-nitrobenzoate (59.7 mg, 0.30 mmol). Yellow solid (67.1 mg, yield 66%). mp: 146.5-148.5 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 1.9 Hz, 1H), 7.96 (dd, *J* = 8.4 Hz, 1.9 Hz, 1H), 7.84-7.81 (m, 1H), 7.75-7.70 (m, 3H), 7.38-7.34 (m, 2H), 7.32-7.22 (m, 3H), 6.91 (s, 1H), 3.94 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.82, 157.64, 153.15, 137.01, 136.76, 136.15, 130.04, 129.45, 129.25, 128.53, 126.94, 125.91, 124.60, 124.16, 124.10, 123.21, 121.95, 121.28, 121.02, 111.59, 104.15, 52.35. HRMS (ESI, m/z): calcd for $C_{22}H_{16}NO_3$ $[M+H]^+$ 342.1125, found 342.1118.

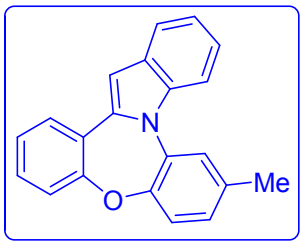
8-fluorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3d)



Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 1,4-difluoro-2-nitrobenzene (47.7 mg, 0.30 mmol). Light yellow solid (41.1 mg, yield 46%). mp: 132-134 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.72-7.66 (m, 4H), 7.36-7.15 (m, 6H),

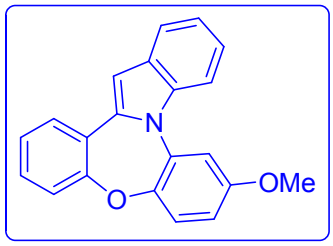
7.02-6.96 (m, 1H), 6.86 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 162.13, 158.84, 157.69, 154.37 (d, J_{CF} = 10.5 Hz), 136.76 (d, J_{CF} = 3.0 Hz), 129.82, 129.24, 129.07, 128.32 (d, J_{CF} = 3.8 Hz), 125.09, 124.96, 124.79, 124.44 (d, J_{CF} = 228.0 Hz), 121.46, 121.19, 120.90, 112.48 (d, J_{CF} = 21.8 Hz), 111.21, 110.36 (d, J_{CF} = 23.2 Hz), 103.29. HRMS (ESI, m/z): calcd for $C_{20}H_{13}FNO$ $[M+H]^+$ 302.0976, found 302.0969.

7-methyldibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3e)



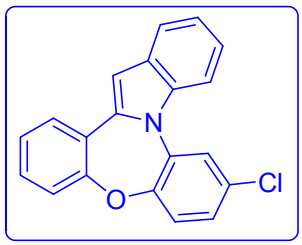
Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 2-fluoro-4-methyl-1-nitrobenzene (46.5 mg, 0.30 mmol). Light yellow solid (58.5 mg, yield 66%). mp: 147-148 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.77 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 7.0 Hz, 2H), 7.57 (d, J = 1.7 Hz, 1H), 7.33-7.27 (m, 3H), 7.25-7.19 (m, 3H), 7.05 (dd, J = 8.2 Hz, 1.6 Hz, 1H), 6.86 (s, 1H). 2.38 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.25, 151.62, 137.21, 136.66, 135.36, 131.40, 129.68, 129.18, 129.13, 127.46, 125.50, 125.00, 124.82, 122.62, 122.16, 121.27, 121.03, 120.83, 111.60, 103.08, 20.96. HRMS (ESI, m/z): calcd for $C_{21}H_{16}NO$ $[M+H]^+$ 298.1226, found 298.1225.

7-methoxydibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3f)



Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 2-fluoro-4-methoxy-1-nitrobenzene (51.3 mg, 0.30 mmol). Light yellow solid (45.2 mg, yield 48%). mp: 103-104 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.80 (d, J = 8.0 Hz, 1H) 7.70 (d, J = 7.1 Hz, 2H), 7.34-7.17 (m, 7H), 6.86 (s, 1H), 6.75 (dd, J = 8.9 Hz, 3.0 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.40, 156.87, 147.57, 137.27, 136.64, 132.27, 129.74, 129.21, 125.48, 124.93, 122.88, 122.77, 121.39, 121.09, 120.71, 111.84, 111.59, 110.00, 103.31, 55.79. HRMS (ESI, m/z): calcd for $C_{21}H_{16}NO_2$ $[M+H]^+$ 314.1176, found 314.1170.

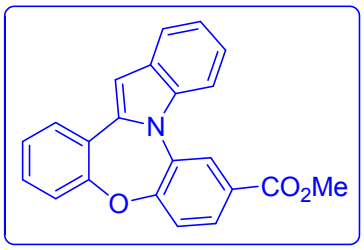
7-chlorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3g)



Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 4-chloro-2-fluoro-1-nitrobenzene (52.7 mg, 0.30 mmol). Light yellow solid (51.7 mg, yield 54%). mp: 171-173 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74-7.70 (m, 4H), 7.37-7.20 (m, 7H), 6.88 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.71, 152.20, 136.85, 136.57, 132.87, 130.57, 129.91, 129.26, 126.70, 125.87, 124.64, 124.35, 123.65, 123.17, 121.78, 121.22, 120.82, 111.30, 103.81. HRMS (ESI, m/z): calcd for $C_{20}H_{13}ClNO$ $[M+H]^+$ 318.0680, found 318.0672.

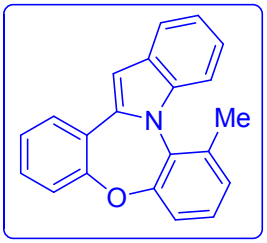
methyl dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-7-carboxylate (3h)

Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and methyl 3-fluoro-4-



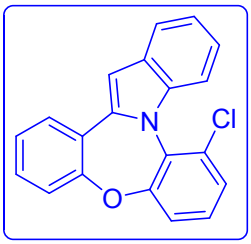
nitrobenzoate (59.7 mg, 0.30 mmol). Brown solid (63.4 mg, yield 62%). mp: 183-185 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.47 (d, *J* = 2.0 Hz, 1H), 7.95 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.77-7.71 (m, 3H), 7.50-7.47 (m, 1H), 7.35-7.22 (m, 5H), 6.90 (s, 1H), 3.91 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.87, 157.37, 157.15, 136.78, 136.72, 132.04, 129.91, 129.28, 129.26, 128.39, 127.75, 126.04, 126.01, 124.73, 123.23, 122.79, 121.72, 121.20, 120.99, 111.36, 103.76, 52.39. HRMS (ESI, m/z): calcd for $C_{22}H_{16}NO_3$ $[M+H]^+$ 342.1125, found 342.1117.

6-methyldibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3i)



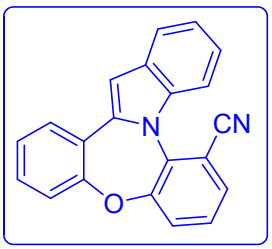
Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 2-fluoro-1-methyl-3-nitrobenzene (46.5 mg, 0.30 mmol). Yellow solid (84 mg, yield 94%). mp: 178-179 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.71-7.68 (m, 2H), 7.28-7.15 (m, 7H), 7.11-7.07 (m, 2H), 6.81 (d, *J* = 0.7 Hz, 1H), 2.03 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.24, 156.94, 137.21, 136.81, 134.93, 129.97, 129.55, 128.46, 128.41, 128.19, 127.11, 125.61, 125.46, 122.11, 120.90, 120.71, 119.09, 112.52, 103.22, 20.10. HRMS (ESI, m/z): calcd for $C_{21}H_{16}NO$ $[M+H]^+$ 298.1226, found 298.1222.

6-chlorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3j)[3]



Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 1,2-dichloro-3-nitrobenzene (57.6 mg, 0.30 mmol). Light yellow solid (65.8 mg, yield 69%). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.74-7.69 (m, 2H), 7.38-7.20 (m, 9H), 6.85 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.85, 157.73, 136.55, 136.22, 130.00, 129.70, 129.51, 128.79, 128.27, 127.96, 127.59, 126.03, 125.20, 122.11, 121.12, 120.83, 120.78, 120.48, 113.76, 104.31.

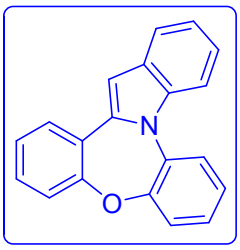
dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-6-carbonitrile (3k)



Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 2,3-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (88.4 mg, yield 96%). mp: 213-215 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.76-7.66 (m, 3H), 7.63-7.60 (m, 1H), 7.48-7.45 (m, 1H), 7.39-7.25 (m, 6H), 6.91 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.15, 155.97, 136.37, 136.29, 133.83, 131.26, 130.02, 129.16, 128.85, 127.45, 127.17, 126.34, 124.65, 122.81, 122.28, 121.21, 120.73, 116.18, 112.35, 109.58, 105.41. HRMS (ESI, m/z): calcd for $C_{21}H_{13}N_2O$ $[M+H]^+$ 309.1022, found 309.1022.

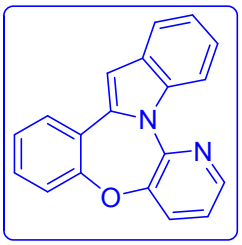
dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3l)[3]

Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 1-fluoro-2-nitrobenzene (42.3 mg, 0.30 mmol). Yellow solid (69.3 mg, yield 82%). **^{1}H NMR (300**



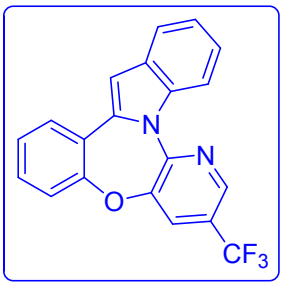
MHz, $CDCl_3$) δ 7.74-7.67 (m, 4H), 7.42-7.39 (m, 1H), 7.29-7.15 (m, 7H), 6.85 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.05, 153.74, 137.07, 136.72, 131.88, 129.69, 129.14, 126.90, 125.59, 125.46, 124.95, 124.47, 122.72, 122.58, 121.35, 121.05, 120.89, 111.51, 103.21.

benzo[6,7]pyrido[3',2':2,3][1,4]oxazepino[4,5-a]indole (3m)



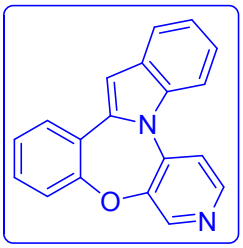
Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 2-chloro-3-nitropyridine (47.6 mg, 0.30 mmol). Light yellow solid (64.4 mg, yield 76%). mp: 103-104.5 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.36 (dd, J = 4.7 Hz, 1.5 Hz, 1H), 8.29 (d, J = 8.2 Hz, 1H), 7.71-7.65 (m, 3H), 7.34-7.13 (m, 6H), 6.90 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 156.72, 147.98, 146.16, 144.50, 137.09, 135.56, 130.40, 129.79, 129.69, 129.17, 125.92, 124.74, 123.49, 122.04, 121.66, 120.56, 120.52, 114.26, 104.93. HRMS (ESI, m/z): calcd for $C_{19}H_{13}N_2O$ $[M+H]^+$ 285.1022, found 285.1017.

8-(trifluoromethyl)benzo[6,7]pyrido[3',2':2,3][1,4]oxazepino[4,5-a]indole (3n)



Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 2,3-dichloro-5-(trifluoromethyl)pyridine (64.8 mg, 0.30 mmol). White solid (99 mg, yield 94%). mp: 102-103 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.66-8.65 (m, 1H), 8.29 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 2.0 Hz, 1H), 7.73-7.67 (m, 2H), 7.41-7.24 (m, 5H), 6.96 (d, J = 0.5 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 156.05, 149.00, 147.07, 141.50 (q, J_{CF} = 4.5 Hz), 137.16, 135.35, 130.25, 129.90, 129.42, 127.78 (q, J_{CF} = 3.8 Hz), 126.42, 124.36 (q, J_{CF} = 33.0 Hz), 124.28, 124.07, 122.91 (q, J_{CF} = 270.0 Hz), 122.80, 120.82, 120.59, 114.51, 106.30. HRMS (ESI, m/z): calcd for $C_{20}H_{12}F_3N_2O$ $[M+H]^+$ 353.0896, found 353.0893.

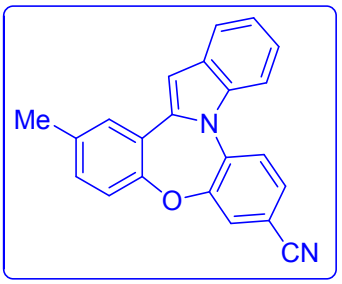
benzo[6,7]pyrido[3',4':2,3][1,4]oxazepino[4,5-a]indole (3o)



Prepared from 2-(1H-indol-2-yl)phenol (62.7 mg, 0.30 mmol) and 4-chloro-3-nitropyridine (47.6 mg, 0.30 mmol). Gray solid (62.1 mg, yield 73%). mp: 107.5-109 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.71 (s, 1H), 8.47 (d, J = 5.3 Hz, 1H), 7.76-7.68 (m, 4H), 7.357.20 (m, 5H), 6.91 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.43, 149.25, 146.96, 144.81, 138.82, 136.74, 136.25, 130.23, 129.59, 129.44, 125.96, 124.00, 123.52, 122.33, 121.38, 120.92, 117.76, 111.42, 105.09. HRMS (ESI, m/z): calcd for $C_{19}H_{13}N_2O$ $[M+H]^+$ 285.1022, found 285.1015.

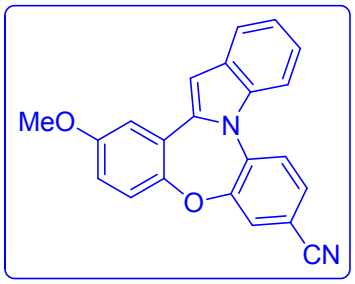
13-methyldibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4a)

Prepared from 2-(1H-indol-2-yl)-4-methylphenol (67.0 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (84.7 mg, yield 88%). mp: 245-



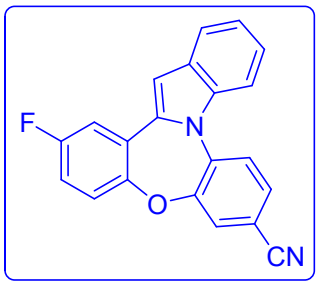
246.5 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.86-7.83 (m, 1H), 7.72-7.66 (m, 3H), 7.56-7.51 (m, 2H), 7.32-7.14 (m, 4H), 6.91 (s, 1H), 2.38 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.13, 153.45, 136.88, 136.57, 135.95, 130.86, 129.59, 129.55, 129.41, 126.56, 125.11, 123.73, 123.42, 122.26, 121.40, 120.51, 117.72, 111.30, 109.77, 104.47, 20.82. HRMS (ESI, m/z): calcd for $C_{22}H_{15}N_2O$ $[M+H]^+$ 323.1179, found 323.1179.

13-methoxydibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4b)



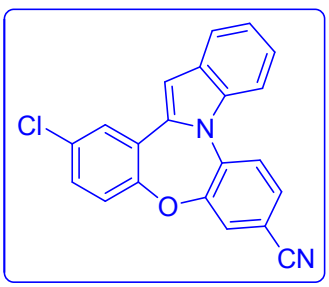
Prepared from 2-(1H-indol-2-yl)-4-methoxyphenol (71.7 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (84.8 mg, yield 84%). mp: 207-208 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87-7.85 (m, 1H), 7.72-7.67 (m, 3H), 7.56 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.32-7.24 (m, 3H), 7.20 (d, J = 3.0 Hz, 1H), 6.93 (s, 1H), 6.88 (dd, J = 8.8 Hz, 3.0 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.41, 153.73, 151.11, 136.68, 136.51, 129.47, 129.40, 126.46, 125.18, 124.82, 123.59, 122.33, 121.61, 121.48, 117.71, 115.50, 113.73, 111.33, 109.89, 104.71, 55.80. HRMS (ESI, m/z): calcd for $C_{22}H_{15}N_2O_2$ $[M+H]^+$ 339.1128, found 339.1137.

13-fluorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4c)



Prepared from 4-fluoro-2-(1H-indol-2-yl)phenol (68.1 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). Light yellow solid (73.8 mg, yield 75%). mp: 204-205.5 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.89-7.86 (m, 1H), 7.75-7.68 (m, 3H), 7.61-7.58 (m, 1H), 7.40 (dd, J = 9.0 Hz, 3.0 Hz, 1H), 7.36-7.26 (m, 3H), 7.09-7.02 (m, 1H), 6.94 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 161.80, 158.55, 153.22, 153.04 (d, J_{CF} = 2.3 Hz), 136.76, 136.33, 135.56 (d, J_{CF} = 2.3 Hz), 129.37, 128.11 (d, J_{CF} = 237.0 Hz), 125.71 (d, J_{CF} = 9.0 Hz), 125.18, 123.99, 122.53, 122.31 (d, J_{CF} = 9.0 Hz), 121.71, 117.56, 116.64 (d, J_{CF} = 23.2 Hz), 115.34 (d, J_{CF} = 24.8 Hz), 111.40, 110.10, 105.51. HRMS (ESI, m/z): calcd for $C_{21}H_{12}FN_2O$ $[M+H]^+$ 327.0928, found 327.0926.

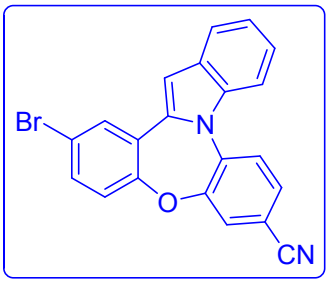
13-chlorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4d)



Prepared from 4-chloro-2-(1H-indol-2-yl)phenol (73.0 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (69.7 mg, yield 68%). mp: 252-254 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88-7.86 (m, 1H), 7.73-7.67 (m, 4H), 7.59 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 7.34-7.25 (m, 4H), 6.94 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.46, 152.91, 136.72, 136.27, 135.25, 131.51, 129.85,

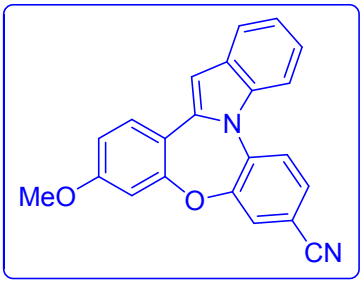
129.78, 129.34, 128.77, 126.58, 125.73, 125.18, 123.99, 122.53, 122.24, 121.71, 117.54, 111.37, 110.05, 105.56. HRMS (ESI, m/z): calcd for $C_{21}H_{12}ClN_2O$ $[M+H]^+$ 343.0633, found 343.0637.

13-bromodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4e)



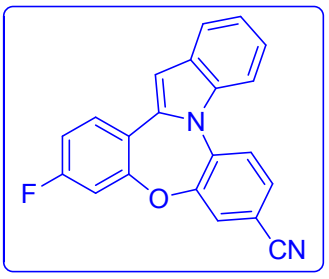
Prepared from 4-bromo-2-(1H-indol-2-yl)phenol (86.4 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). Light yellow solid (103 mg, yield 89%). mp: 258-260 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.87-7.83 (m, 2H), 7.73-7.66 (m, 3H), 7.58 (dd, J = 8.4 Hz, 1.9 Hz, 1H), 7.45 (dd, J = 8.6 Hz, 2.4 Hz, 1H), 7.35-7.27 (m, 2H), 7.22-7.19 (m, 1H), 6.94 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.97, 152.82, 136.71, 136.25, 135.08, 132.81, 131.71, 129.78, 129.33, 126.57, 126.16, 125.16, 124.00, 122.58, 122.53, 121.72, 119.02, 117.52, 111.35, 110.04, 105.61. HRMS (ESI, m/z): calcd for $C_{21}H_{12}BrN_2O$ $[M+H]^+$ 387.0128, found 387.0132.

12-methoxydibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4f)



Prepared from 2-(1H-indol-2-yl)-5-methoxyphenol (71.7 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). Light yellow solid (78.2 mg, yield 77%). mp: 233-234 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.87 (d, J = 8.4 Hz, 1H), 7.72-7.55 (m, 5H), 7.29-7.22 (m, 2H), 6.88-6.81 (m, 3H), 3.86 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 161.45, 158.02, 152.95, 136.84, 136.62, 136.29, 129.99, 129.72, 129.57, 126.62, 125.11, 123.08, 122.25, 121.16, 117.72, 116.50, 112.63, 111.25, 109.61, 106.06, 103.44, 55.69. HRMS (ESI, m/z): calcd for $C_{22}H_{15}N_2O_2$ $[M+H]^+$ 339.1128, found 339.1127.

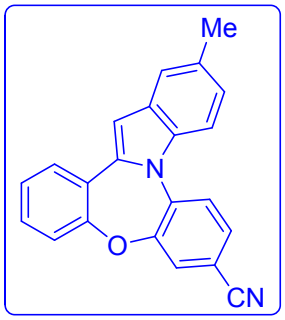
12-fluorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4g)



Prepared from 5-fluoro-2-(1H-indol-2-yl)phenol (68.1 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (70.4 mg, yield 72%). mp: 235-236 °C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.88 (d, J = 8.4 Hz, 1H), 7.72-7.66 (m, 4H), 7.59 (dd, J = 8.4 Hz, 1.9 Hz, 1H), 7.33-7.24 (m, 2H), 7.10-6.99 (m, 2H), 6.86 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 164.97, 161.63, 157.72 (d, J_{CF} = 11.2 Hz), 152.74, 136.41 (d, J_{CF} = 12.0 Hz), 135.84, 130.36, 130.24, 129.85, 129.51, 125.19, 125.12 (d, J_{CF} = 223.5 Hz), 122.47, 121.47, 120.58 (d, J_{CF} = 3.8 Hz), 117.53, 113.72 (d, J_{CF} = 21.8 Hz), 111.32, 109.97, 108.84 (d, J_{CF} = 24.0 Hz), 104.68. HRMS (ESI, m/z): calcd for $C_{21}H_{12}FN_2O$ $[M+H]^+$ 327.0928, found 327.0933.

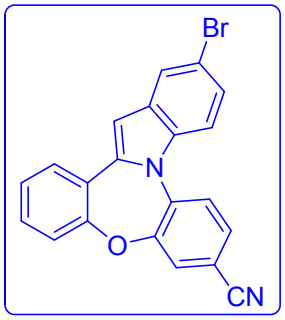
2-methyldibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4h)

Prepared from 2-(5-methyl-1H-indol-2-yl)phenol (67.0 mg, 0.30 mmol) and 3,4-



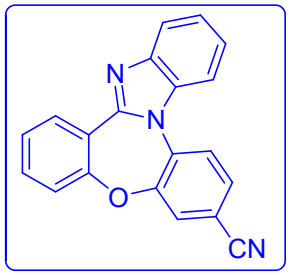
difluorobenzonitrile (41.7 mg, 0.30 mmol). Light yellow solid (90.7 mg, yield 94%). mp: 195-197 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.71-7.70 (m, 2H), 7.57-7.54 (m, 2H), 7.49 (s, 1H), 7.38-7.25 (m, 3H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.84 (s, 1H), 2.48 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.99, 153.05, 136.72, 136.69, 134.94, 131.83, 130.14, 129.83, 129.53, 129.28, 126.59, 126.21, 125.07, 124.94, 124.32, 121.14, 120.83, 117.74, 111.03, 109.55, 104.39, 21.36. HRMS (ESI, m/z): calcd for $C_{22}H_{15}N_2O$ $[M+H]^+$ 323.1179, found 323.1174.

2-bromodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4i)



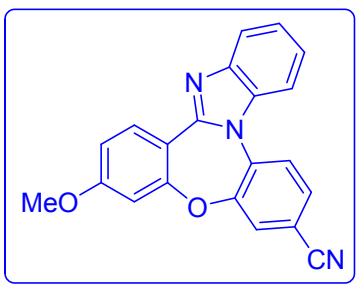
Prepared from 2-(5-bromo-1H-indol-2-yl)phenol (86.4 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (108.2 mg, yield 93%). mp: 233-235 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83-7.69 (m, 4H), 7.59-7.53 (m, 2H), 7.42-7.26 (m, 4H), 6.85 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.16, 153.33, 137.85, 136.08, 135.23, 131.18, 130.70, 129.65, 129.41, 126.75, 126.38, 126.28, 125.01, 123.91, 123.75, 120.94, 117.50, 115.39, 112.71, 110.33, 103.86. HRMS (ESI, m/z): calcd for $C_{21}H_{11}BrN_2ONa$ $[M+Na]^+$ 408.9947, found 408.9933.

dibenzo[b,f]benzo[4,5]imidazo[1,2-d][1,4]oxazepine-8-carbonitrile (4j)



Prepared from 2-(1H-benzo[d]imidazol-2-yl)phenol (63.0 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (62.4 mg, yield 67%). mp: 265-268 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24-8.21 (m, 1H), 7.95-7.88 (m, 2H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.70-7.63 (m, 2H), 7.56-7.52 (m ,1H), 7.45-7.36 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.41, 152.78, 149.41, 143.94, 134.42, 133.79, 132.79, 130.85, 129.95, 126.89, 126.54, 124.42, 124.38, 123.90, 122.32, 120.90, 120.85, 117.22, 111.48, 111.17. HRMS (ESI, m/z): calcd for $C_{20}H_{12}N_3O$ $[M+H]^+$ 310.0975, found 310.0974.

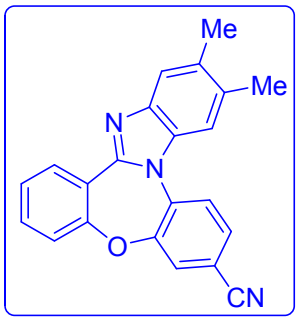
12-methoxydibenzo[b,f]benzo[4,5]imidazo[1,2-d][1,4]oxazepine-8-carbonitrile (4k)



Prepared from 2-(1H-benzo[d]imidazol-2-yl)-5-methoxyphenol (72.0 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (85.1 mg, yield 84%). mp: 278-280 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 1.7 Hz, 1H), 7.68-7.63 (m, 2H), 7.43-7.36 (m, 2H), 6.94-6.89 (m, 2H), 3.90 (s, 3H). **^{13}C**

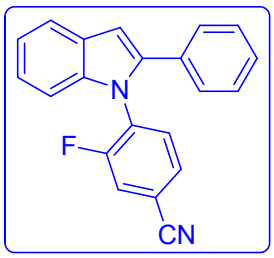
NMR (100 MHz, $CDCl_3$) δ 163.48, 159.54, 152.43, 149.70, 144.05, 134.62, 133.66, 131.69, 129.98, 126.89, 124.30, 123.96, 123.85, 120.59, 117.28, 114.51, 112.83, 111.28, 111.12, 106.09, 55.81. HRMS (ESI, m/z): calcd for $C_{21}H_{14}N_3O_2$ $[M+H]^+$ 340.1081, found 340.1080.

2,3-dimethyldibenzo[b,f]benzo[4,5]imidazo[1,2-d][1,4]oxazepine-8-carbonitrile (4l)



Prepared from 2-(5,6-dimethyl-1H-benzo[d]imidazol-2-yl)phenol (71.4 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (79.0 mg, yield 78%). mp: 255.5-256.5 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (d, J = 7.4 Hz, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.77 (s, 1H), 7.68-7.64 (m, 2H), 7.53-7.45 (m, 2H), 7.38-7.34 (m, 2H), 2.43 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.19, 152.57, 148.56, 142.51, 134.70, 133.81, 133.53, 132.46, 132.27, 130.73, 129.95, 126.79, 126.46, 123.81, 122.51, 120.83, 120.78, 117.34, 111.36, 111.11, 20.75, 20.31. HRMS (ESI, m/z): calcd for $C_{22}H_{16}N_3O$ $[M+H]^+$ 338.1288, found 338.1284.

3-fluoro-4-(2-phenyl-1H-indol-1-yl)benzonitrile (6a)



Prepared from 2-phenyl-1H-indole (58 mg, 0.30 mmol) and 3,4-difluorobenzonitrile (41.7 mg, 0.30 mmol). White solid (25.6 mg, yield 27%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71-7.67 (m, 1H), 7.51-7.48 (m, 2H), 7.39-7.35 (m, 1H), 7.30-7.22 (m, 7H), 7.12-7.10 (m, 1H), 6.85 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.55, 156.00, 139.67 (d, J_{CF} = 255.7 Hz), 131.70, 131.52, 131.39, 131.32, 128.84, 128.72 (d, J_{CF} = 4.1 Hz), 128.43 (d, J_{CF} = 19.4 Hz), 128.01, 123.14, 121.62, 120.97, 120.87 (d, J_{CF} = 23.3 Hz), 117.00 (d, J_{CF} = 2.3 Hz), 112.57 (d, J_{CF} = 8.6 Hz), 110.23, 105.36. HRMS (ESI, m/z): calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$ 313.1136, found 313.1134.

5. References

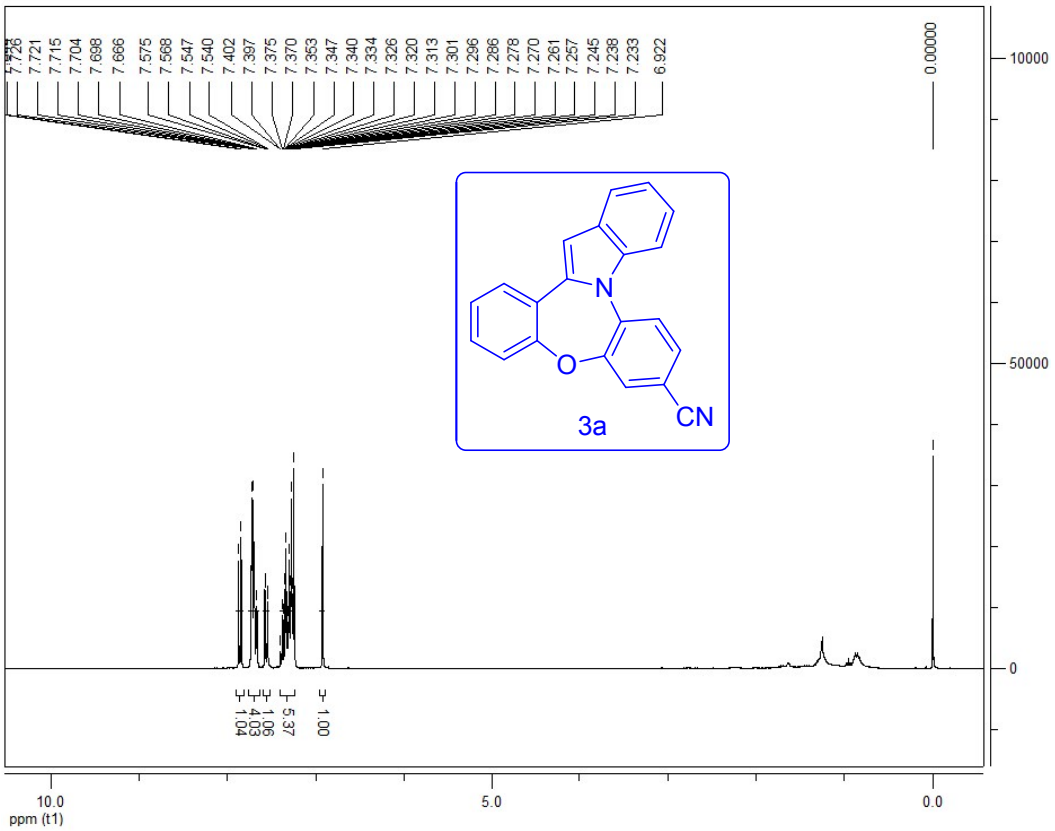
[1] X.-H. Xu, M. Taniguchi, A. Azuma, G. K. Liu, E. Tokunaga and N. Shibata, *Org. Lett.*, 2013, **15**, 686-689.

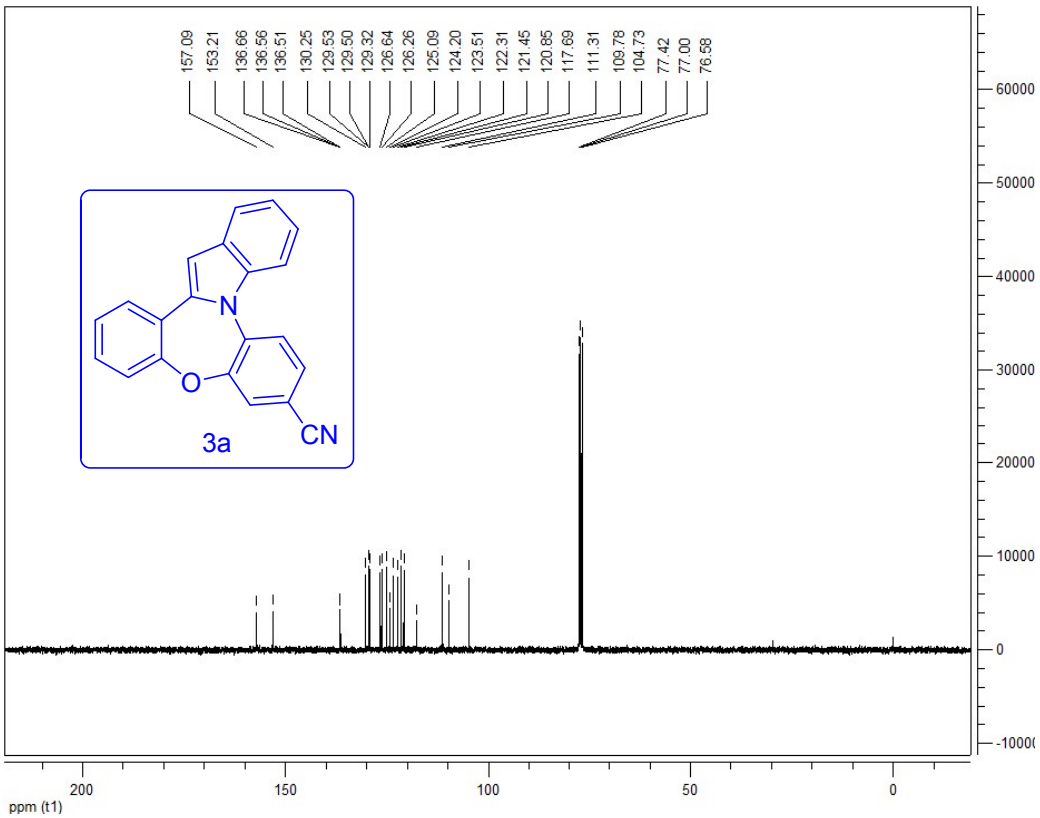
[2] Y. Yin, Y.-Q. Zhang, B. Jin, S. Sha, X. Wu, C. B. Sangani, S.-F. Wang, F. Qiao, A.-M. Lu, P.-C. Lv and H.-L. Zhu, *Bioorg. Med. Chem.*, 2015, **23**, 1231-1240.

[3] P. Sang, M. Yu, H. Tu, J. Zou and Y. Zhang, *Chem. Commun.*, 2013, **49**, 701-703.

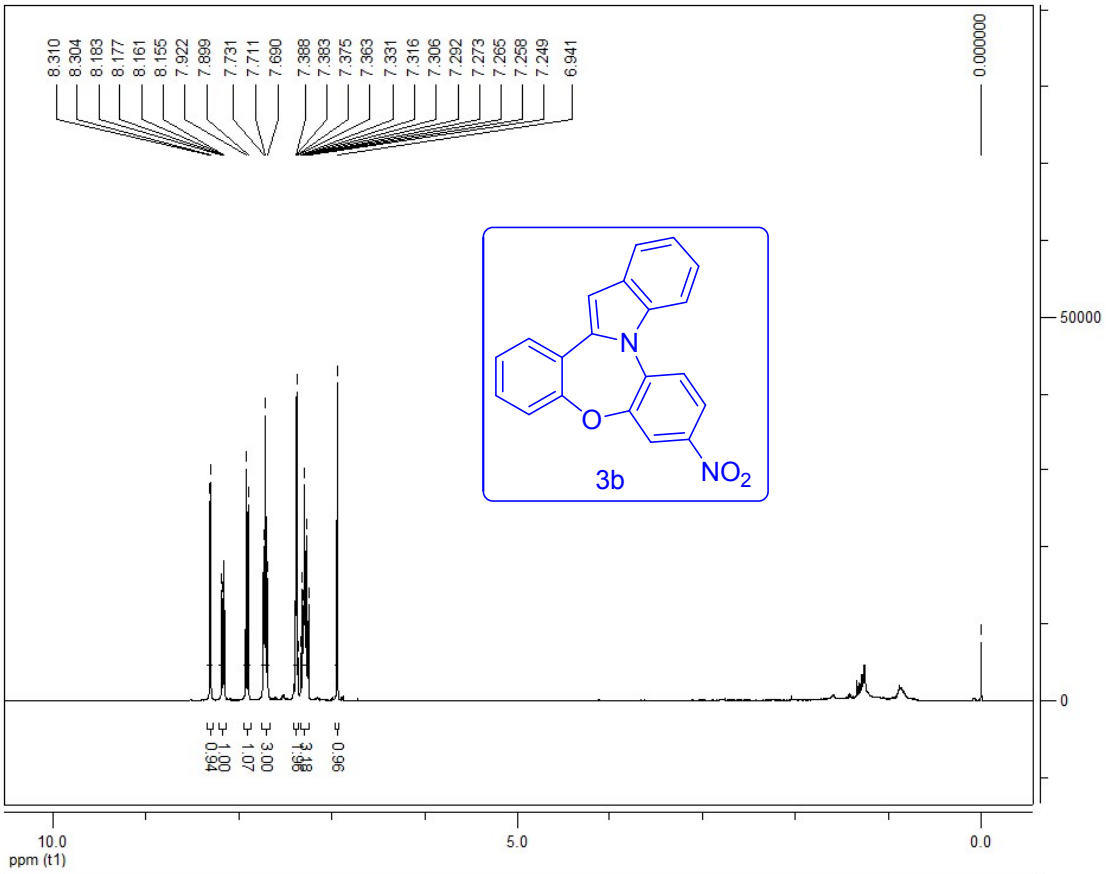
6. ^{1}H and ^{13}C NMR spectra of products

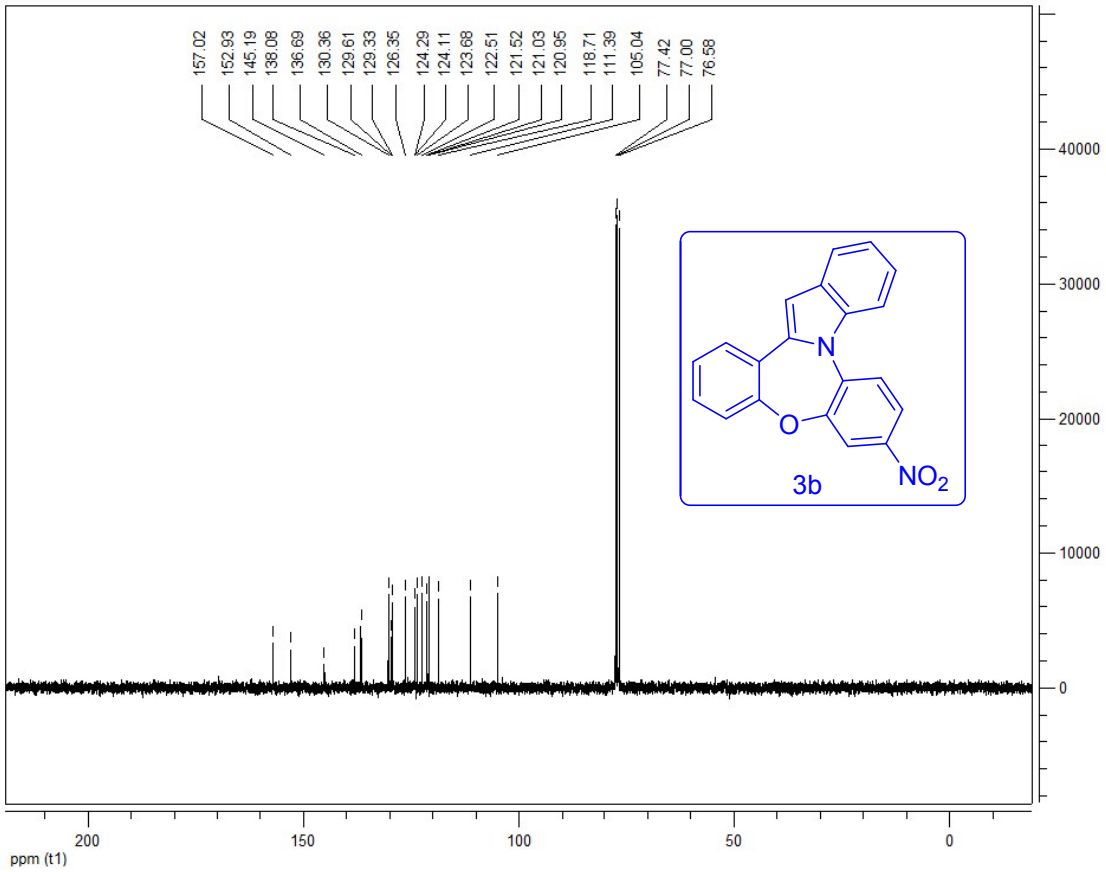
dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (3a)



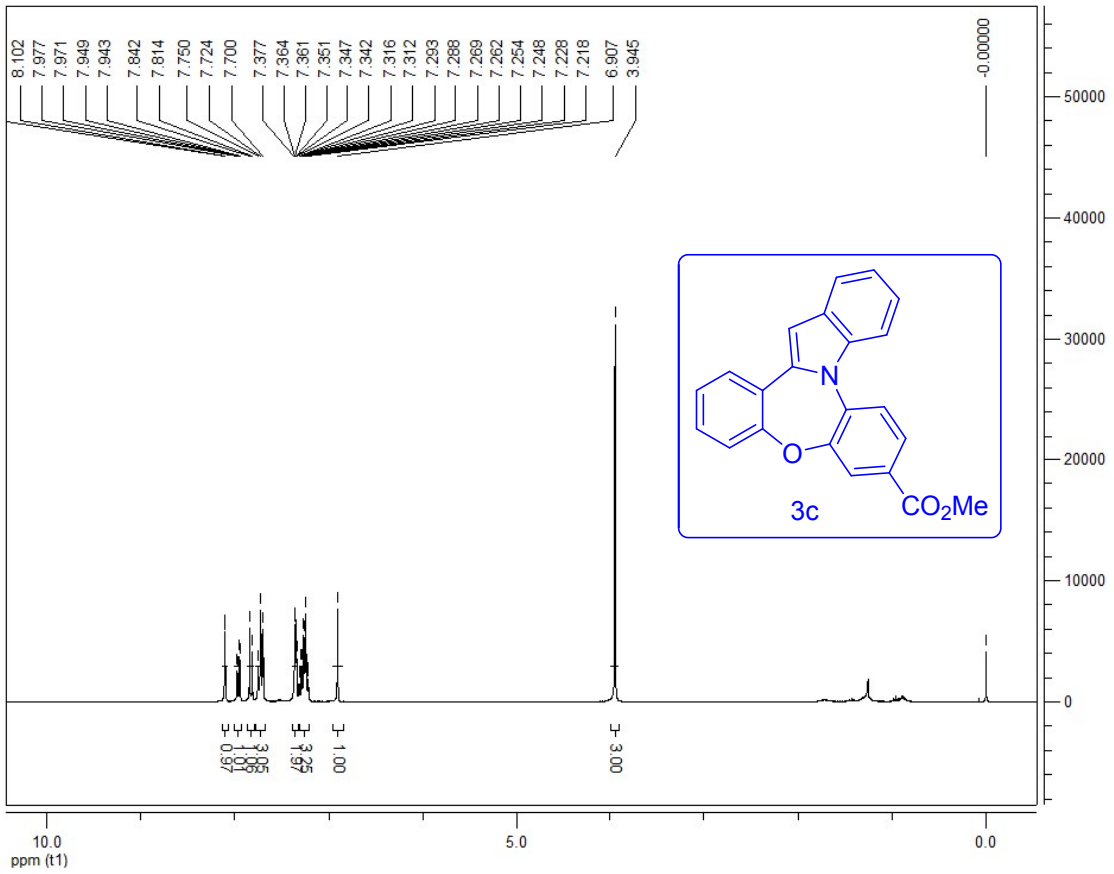


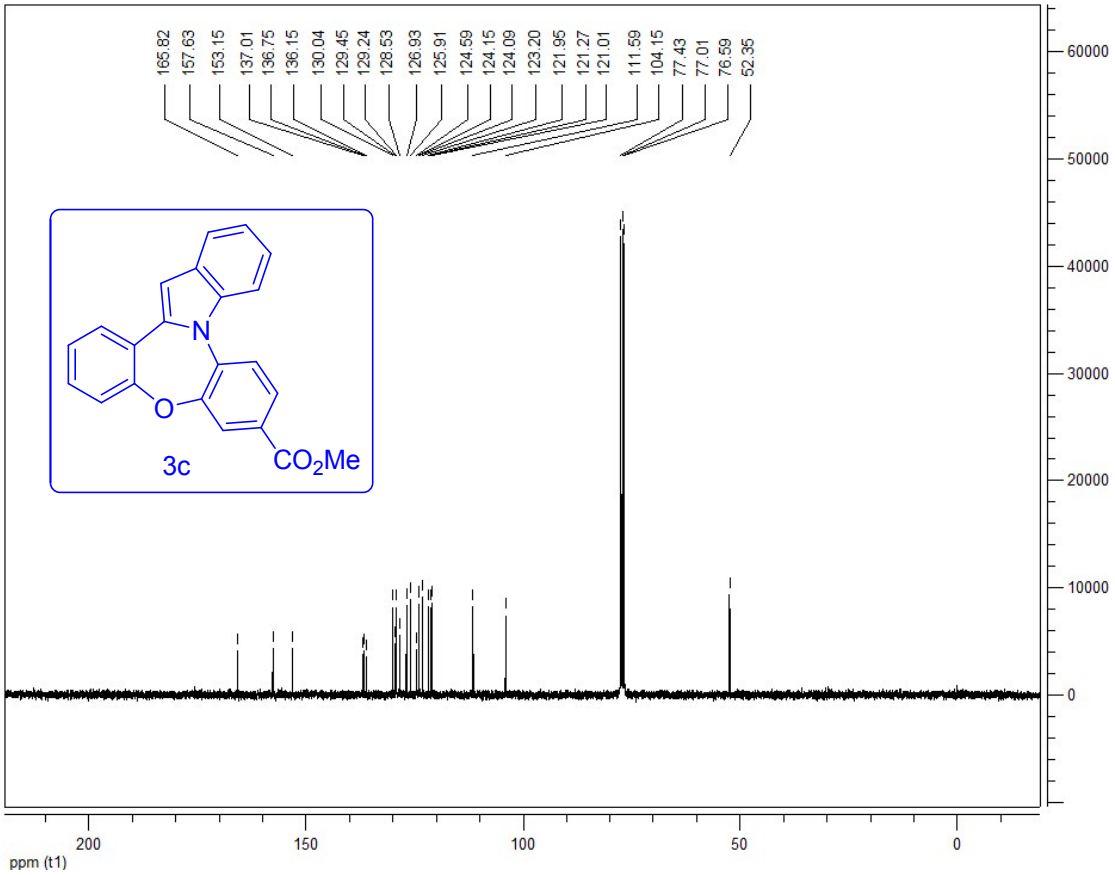
8-nitrodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3b)



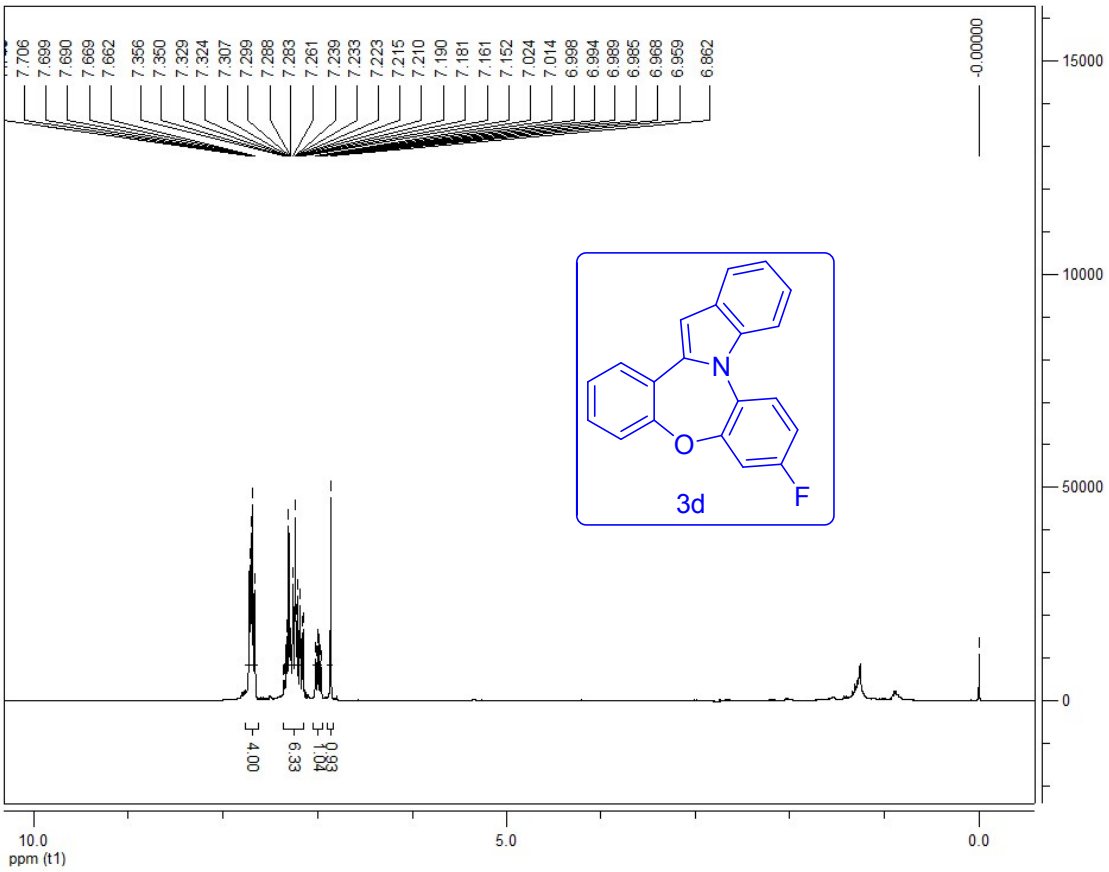


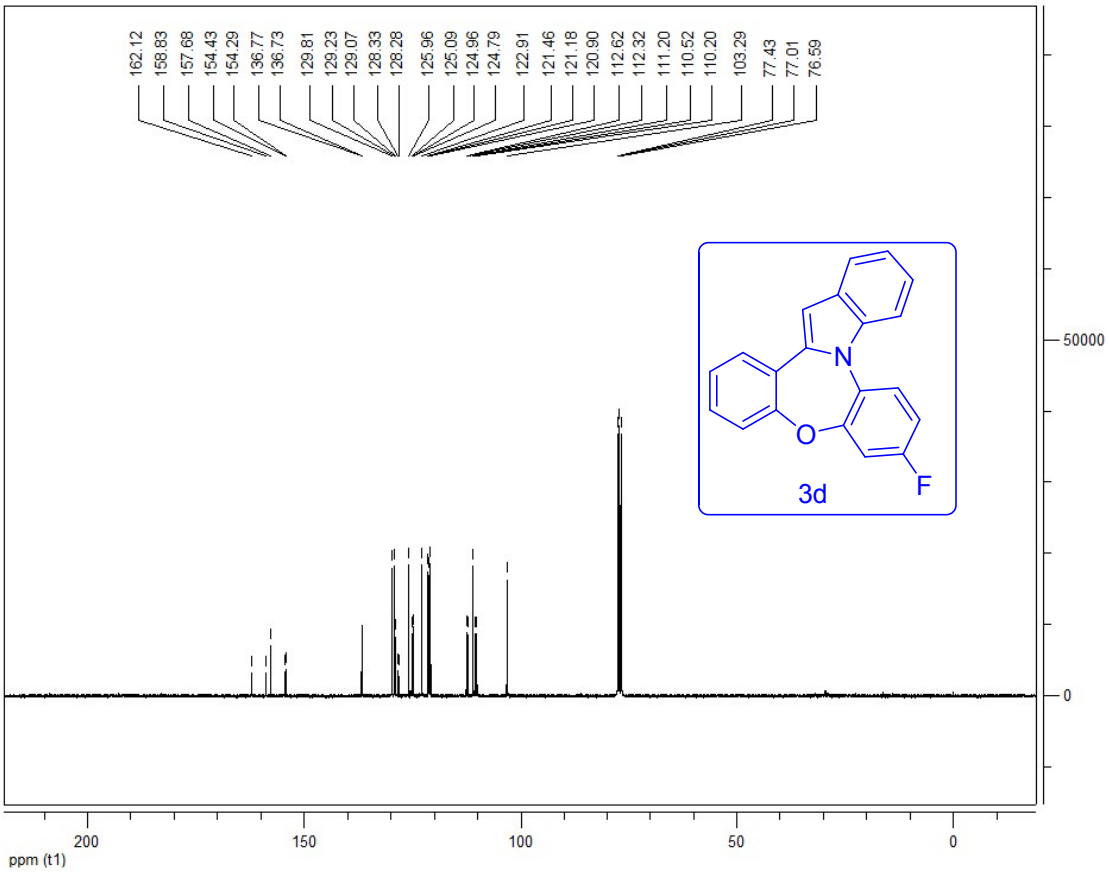
methyl dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carboxylate (3c)



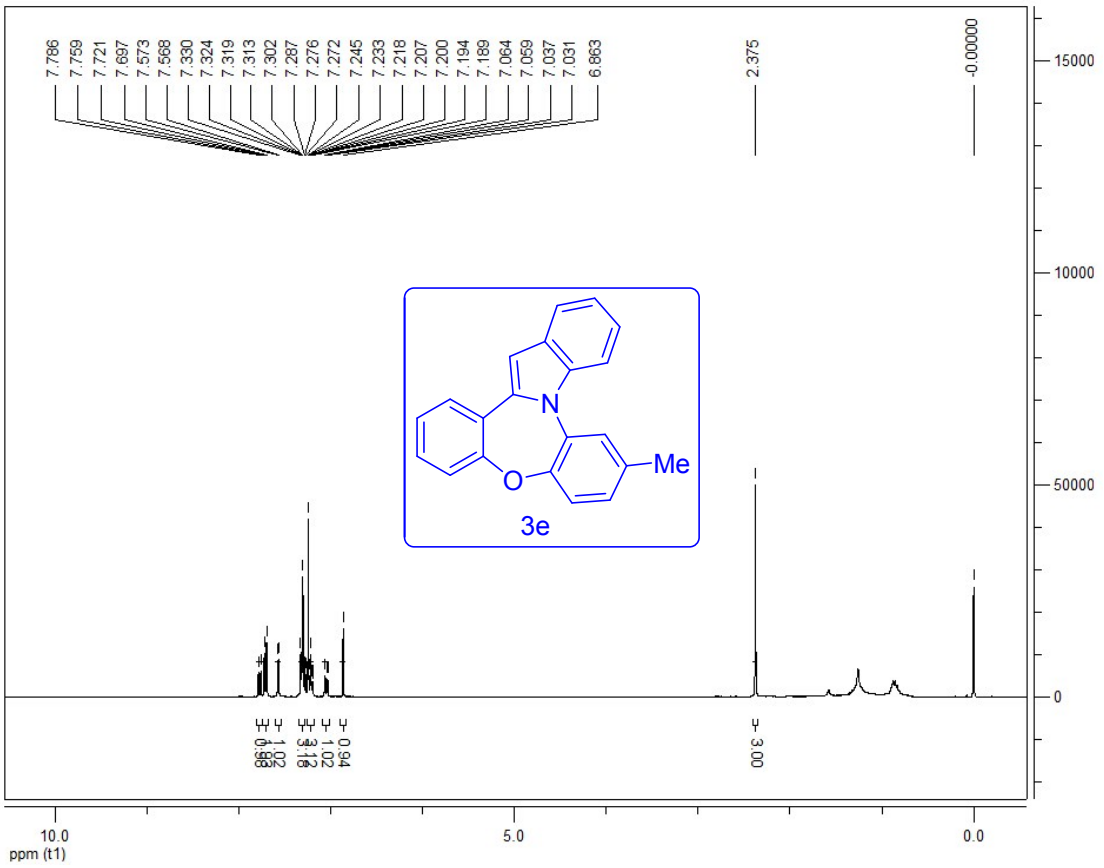


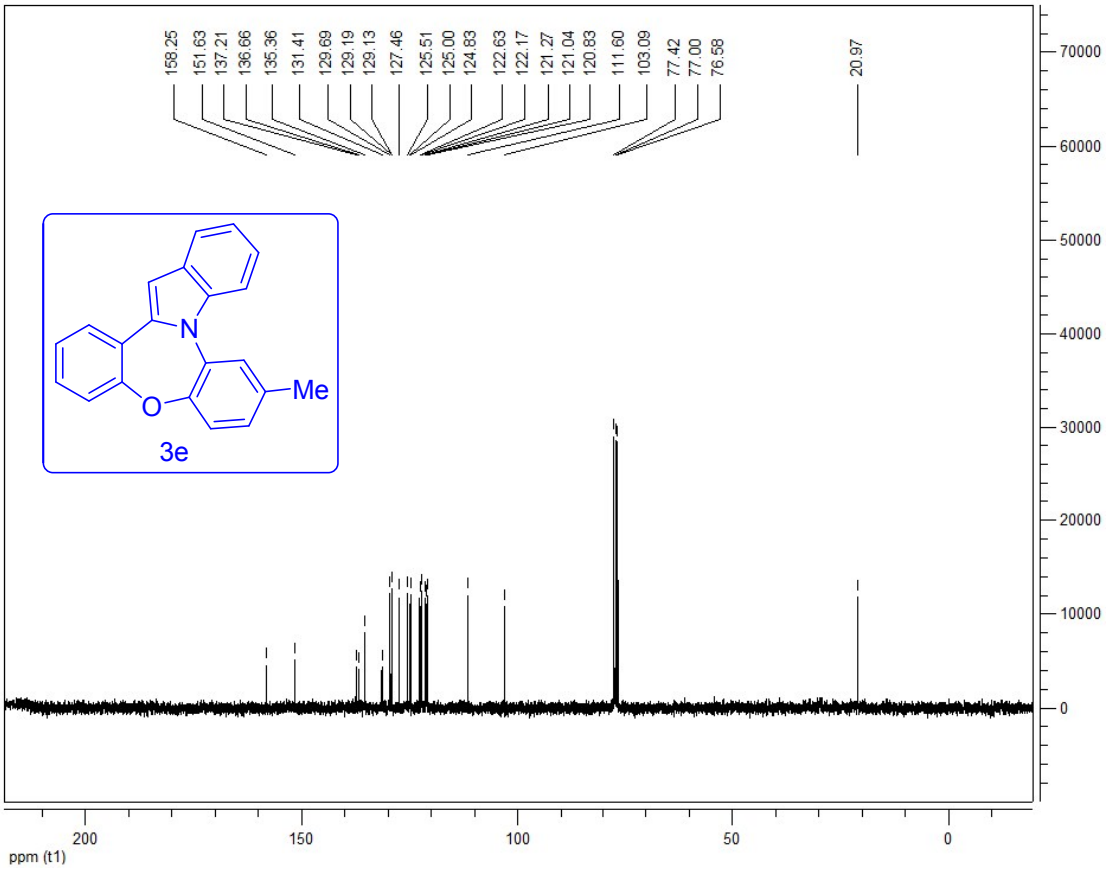
8-fluorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3d)



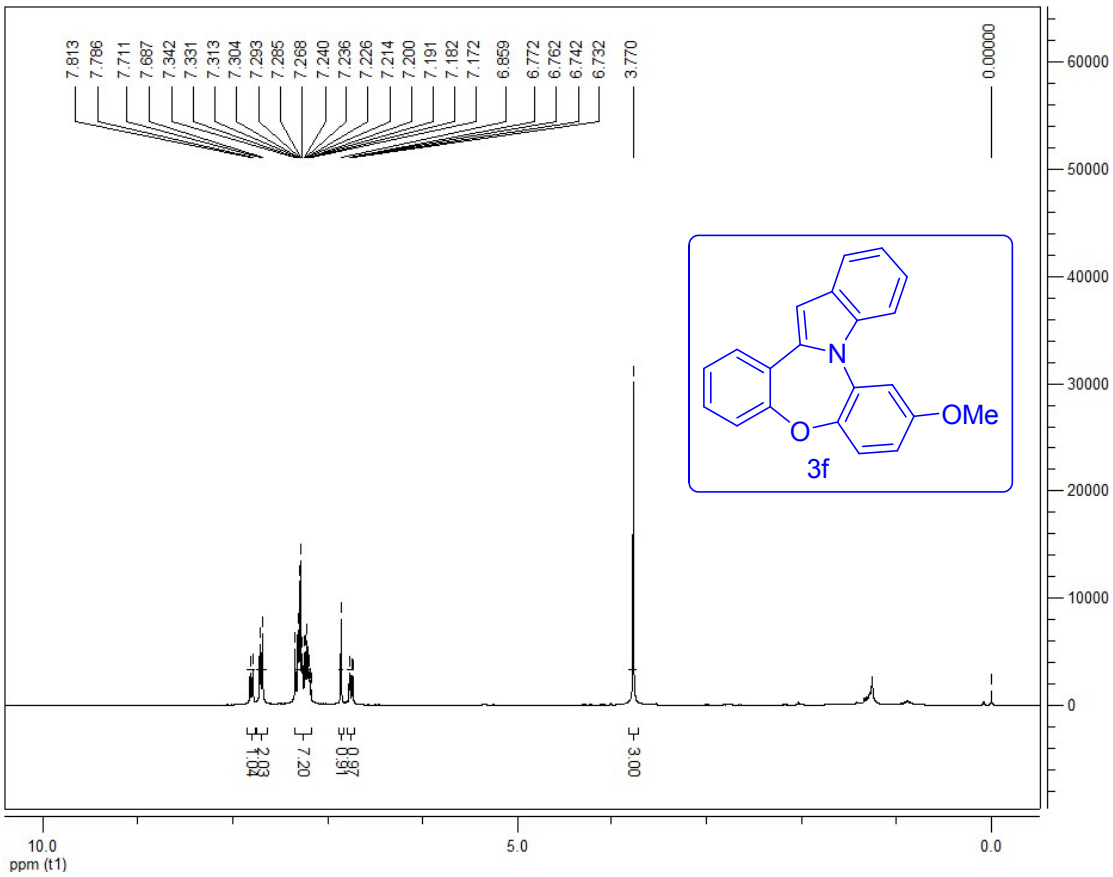


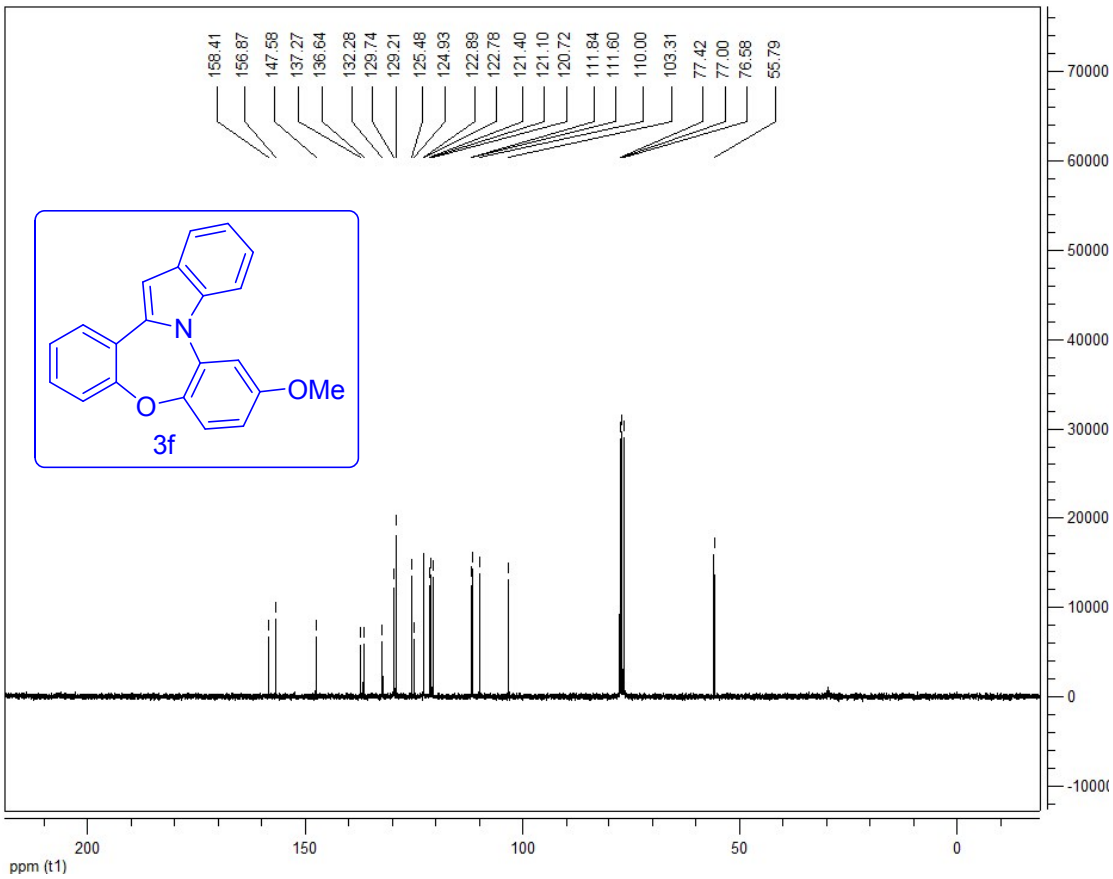
7-methyldibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3e)



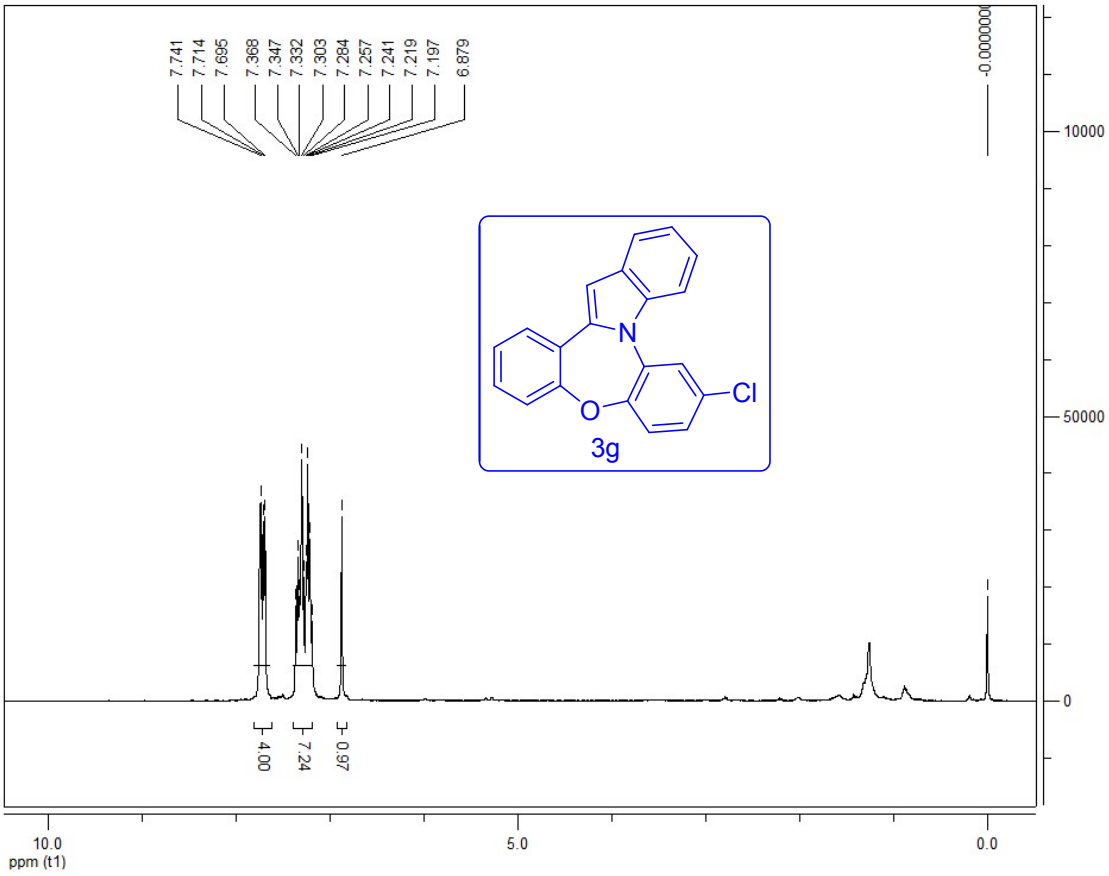


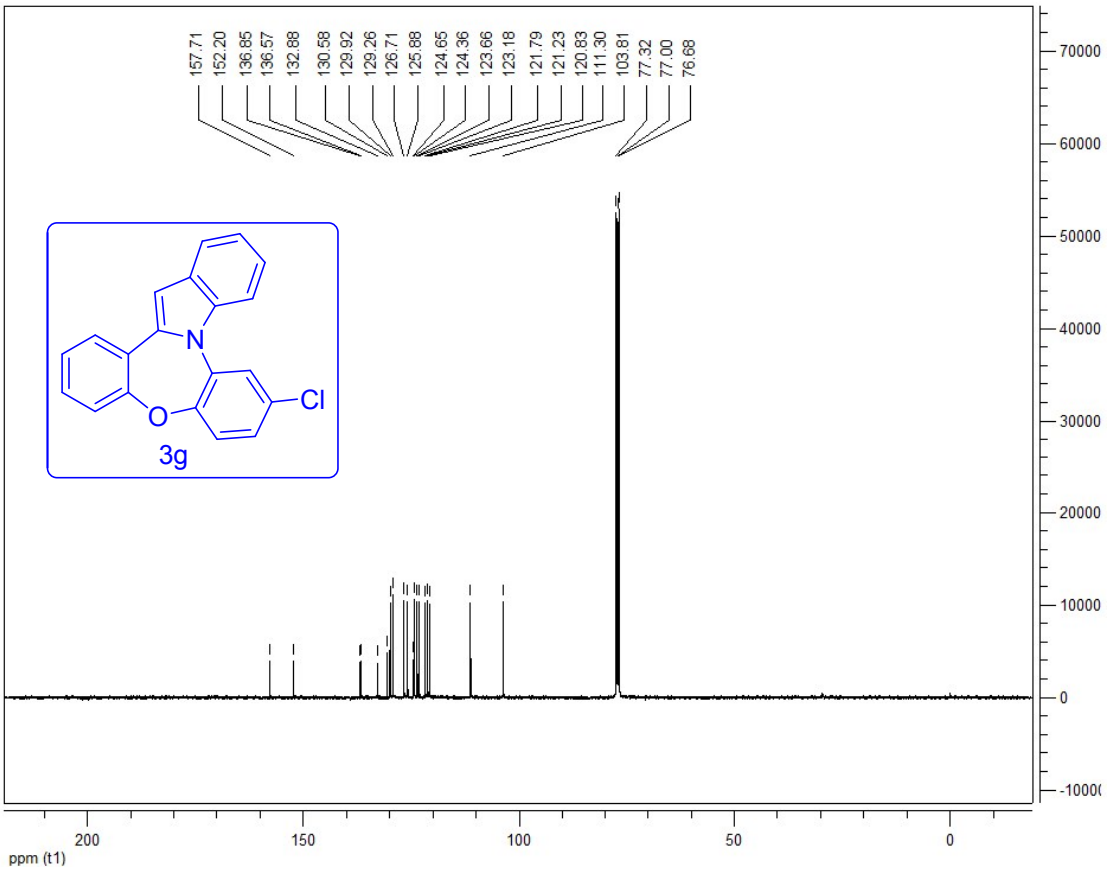
7-methoxydibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3f)



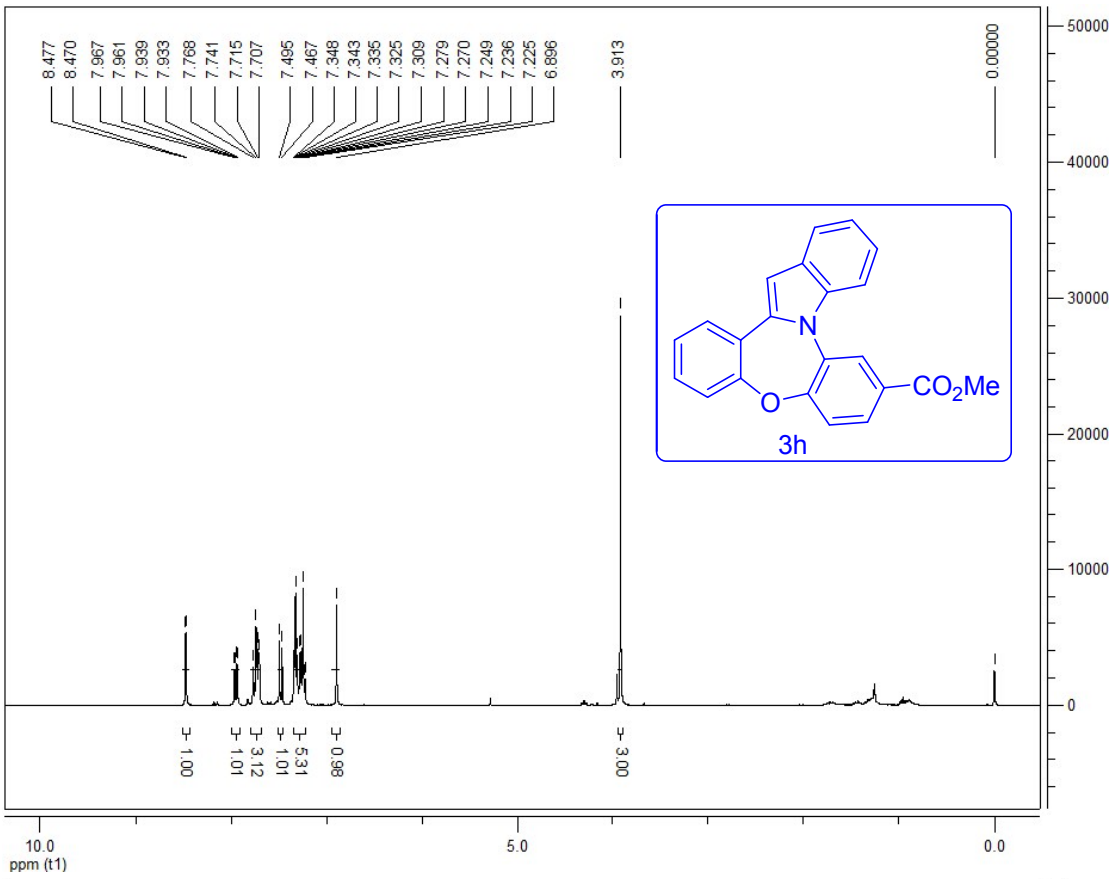


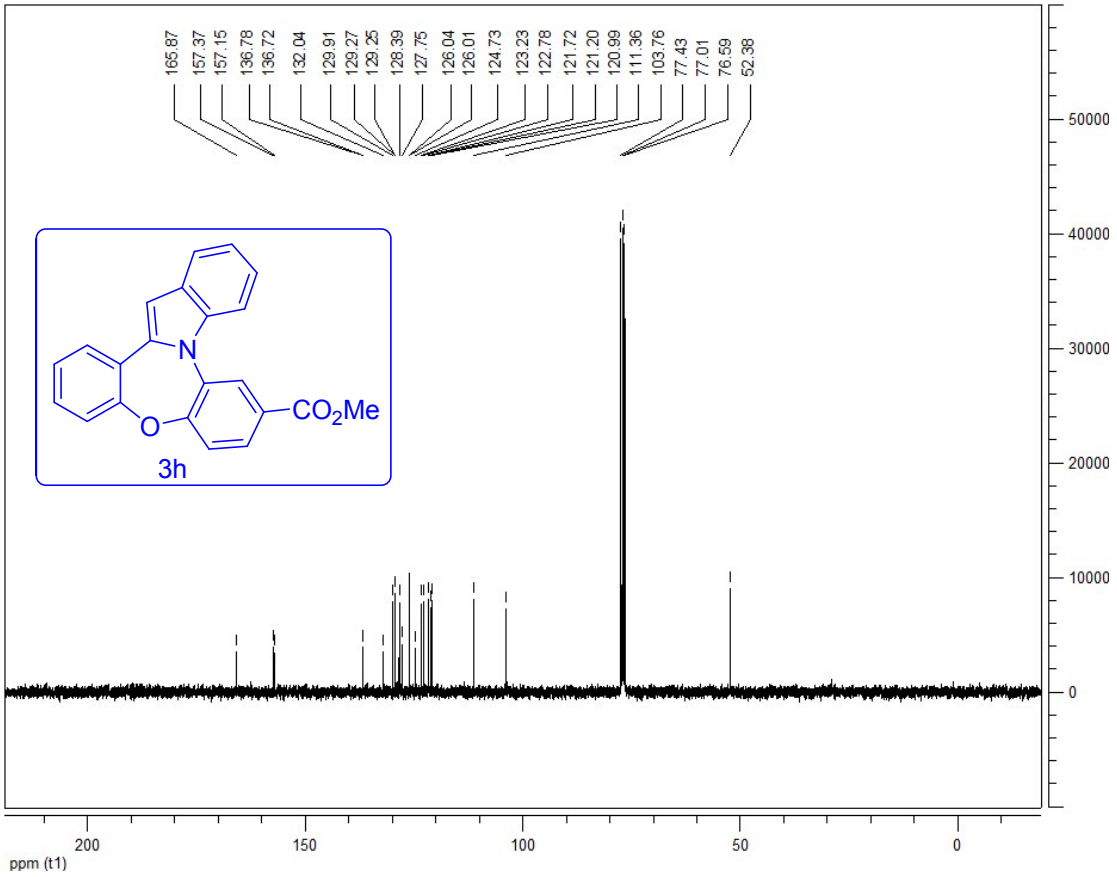
7-chlorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3g)



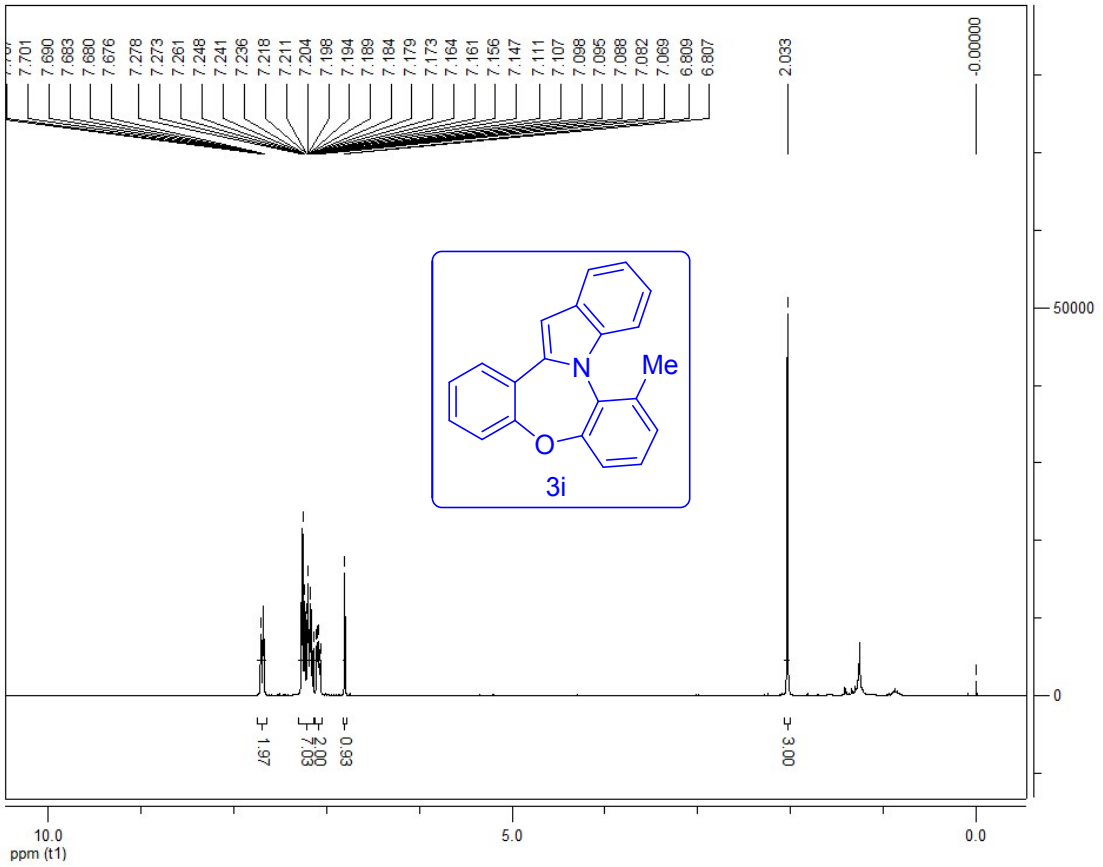


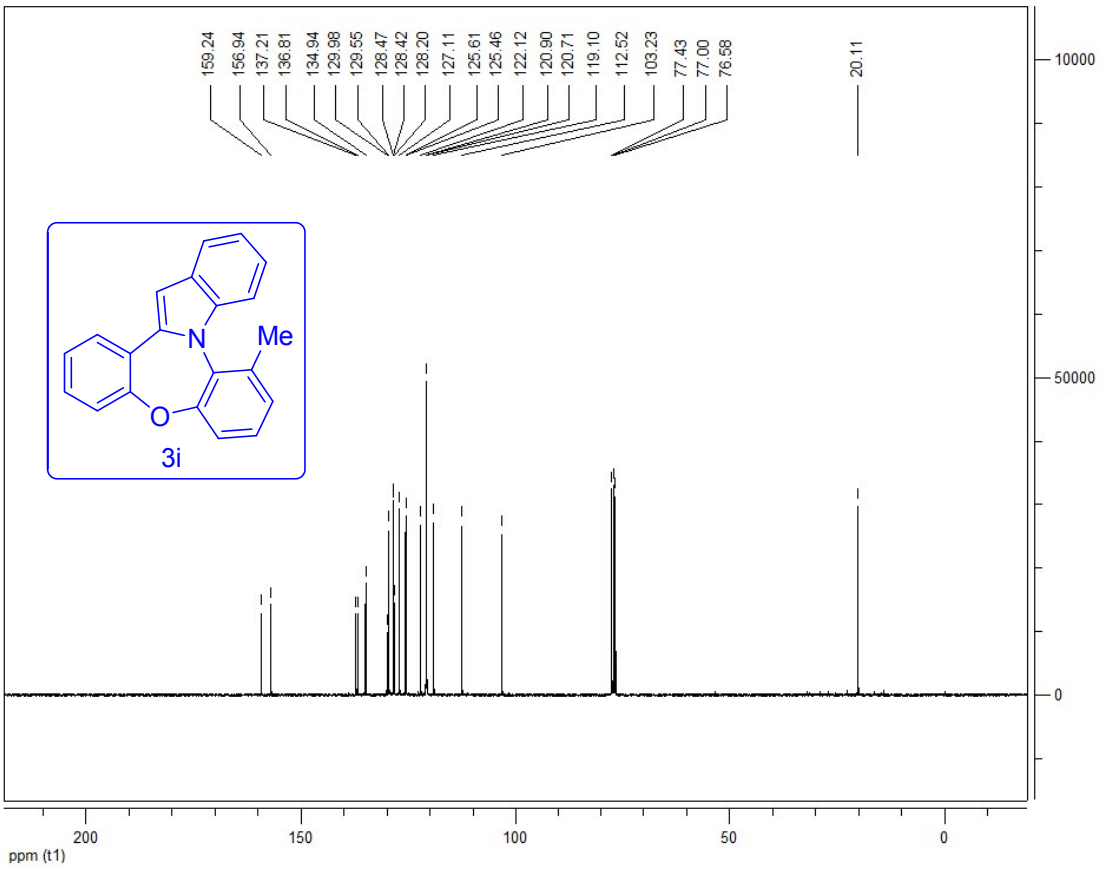
methyl dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-7-carboxylate (3h)



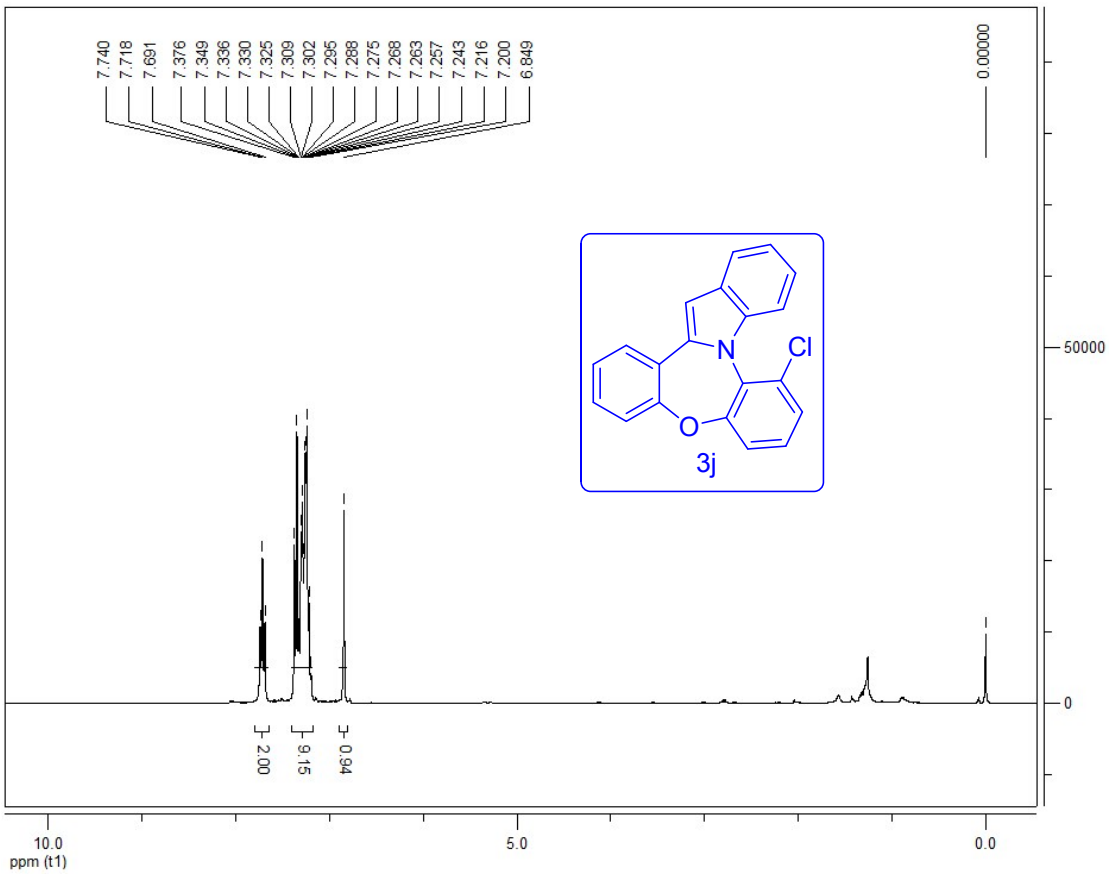


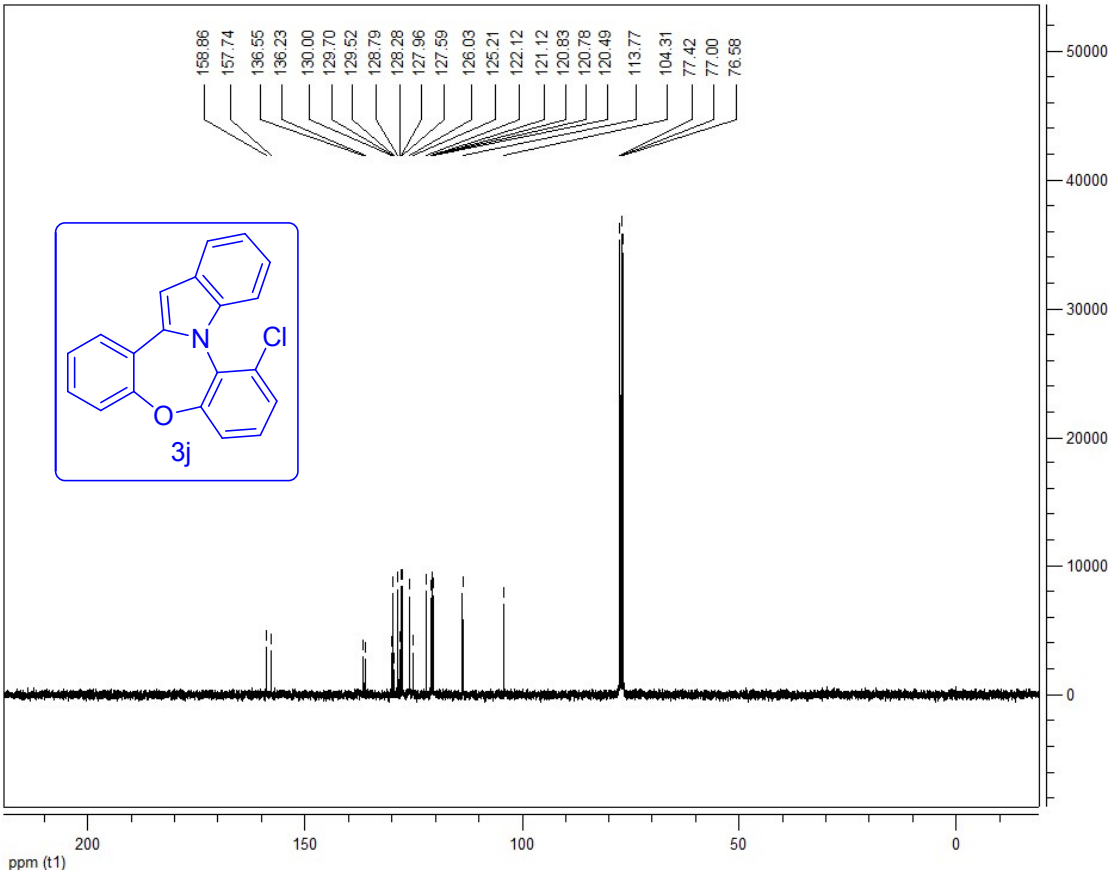
6-methyldibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3i)



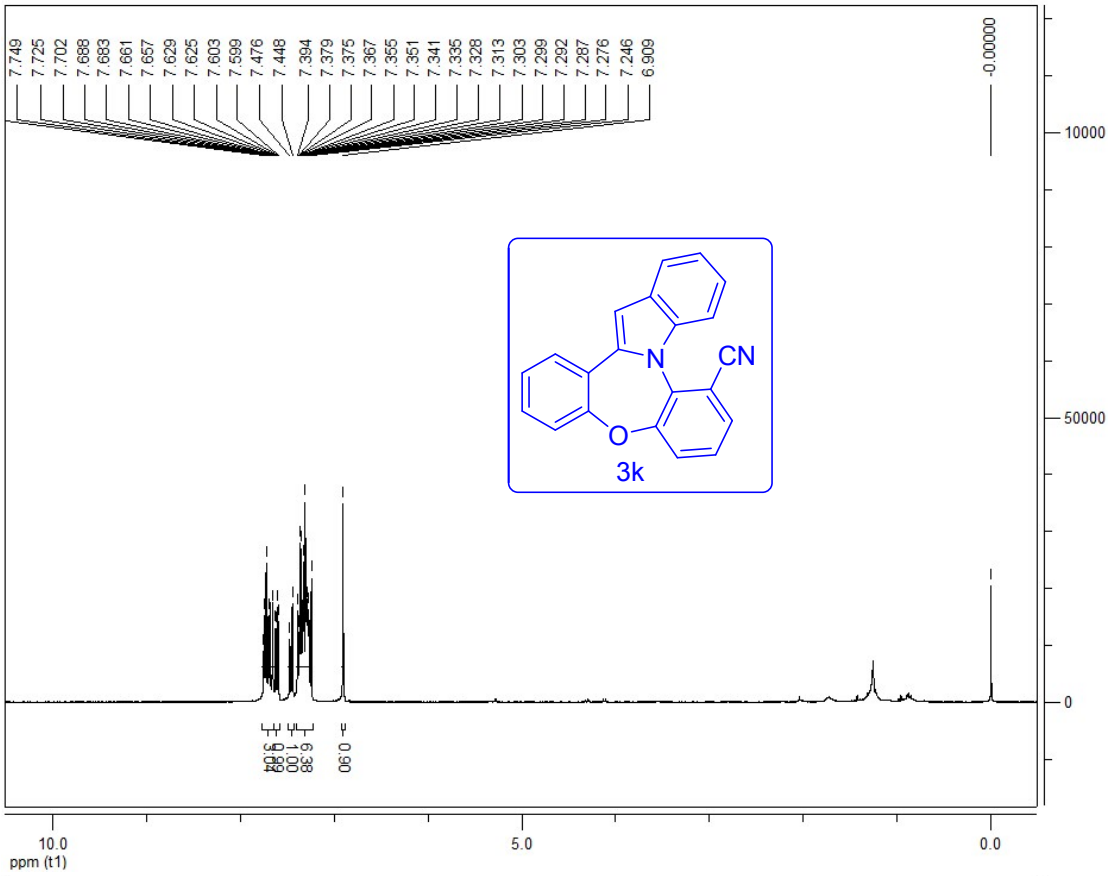


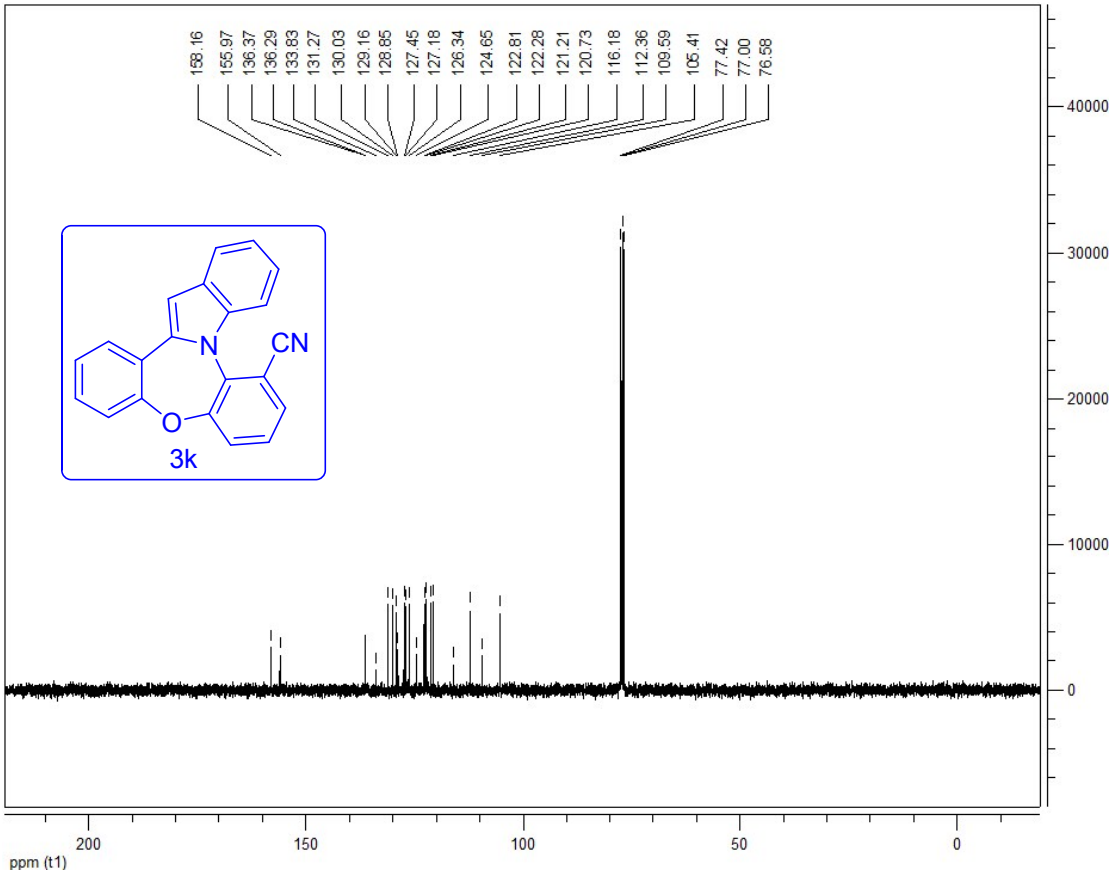
6-chlorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3j)



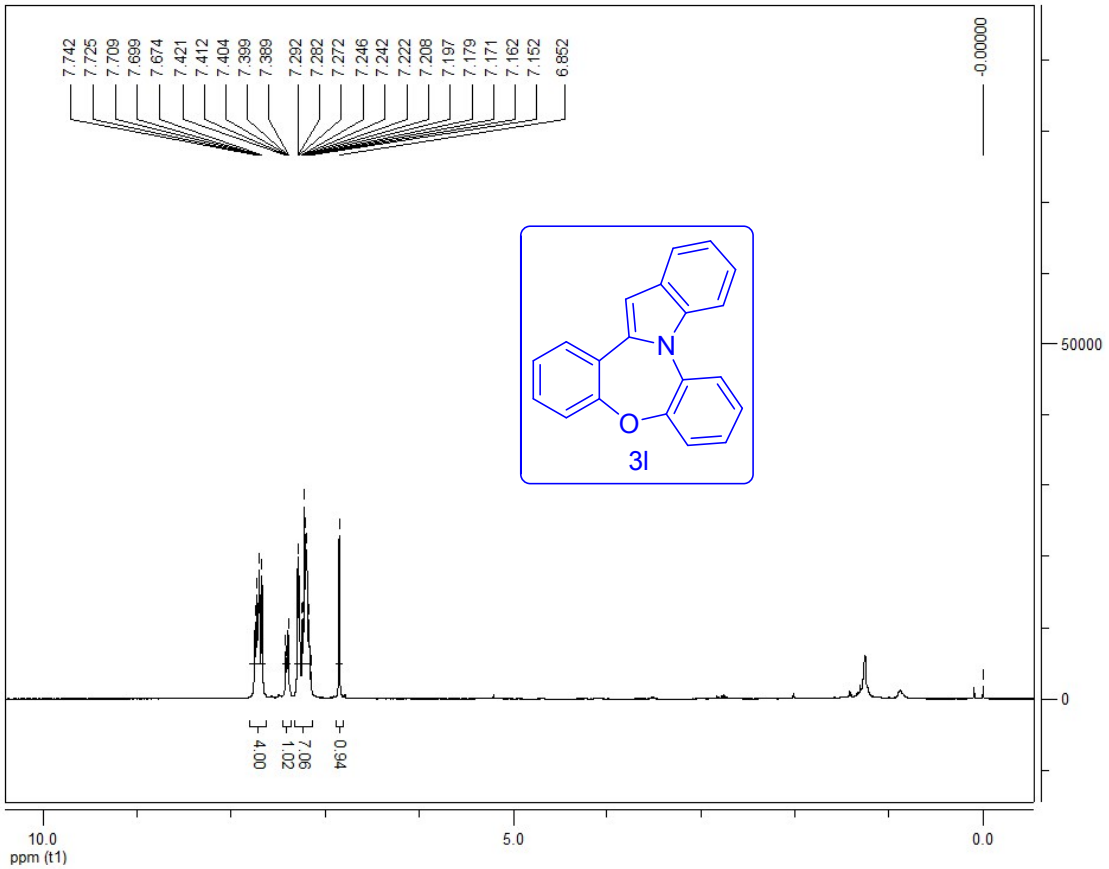


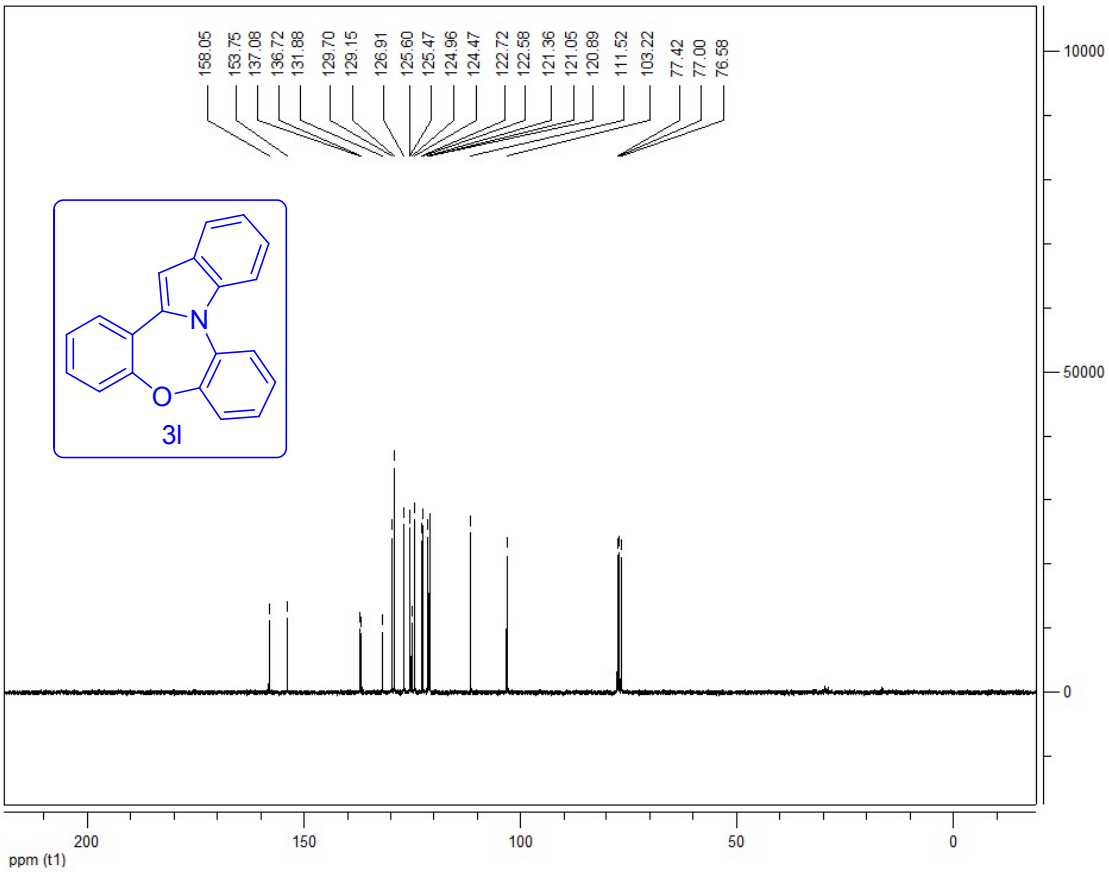
dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-6-carbonitrile (3k)



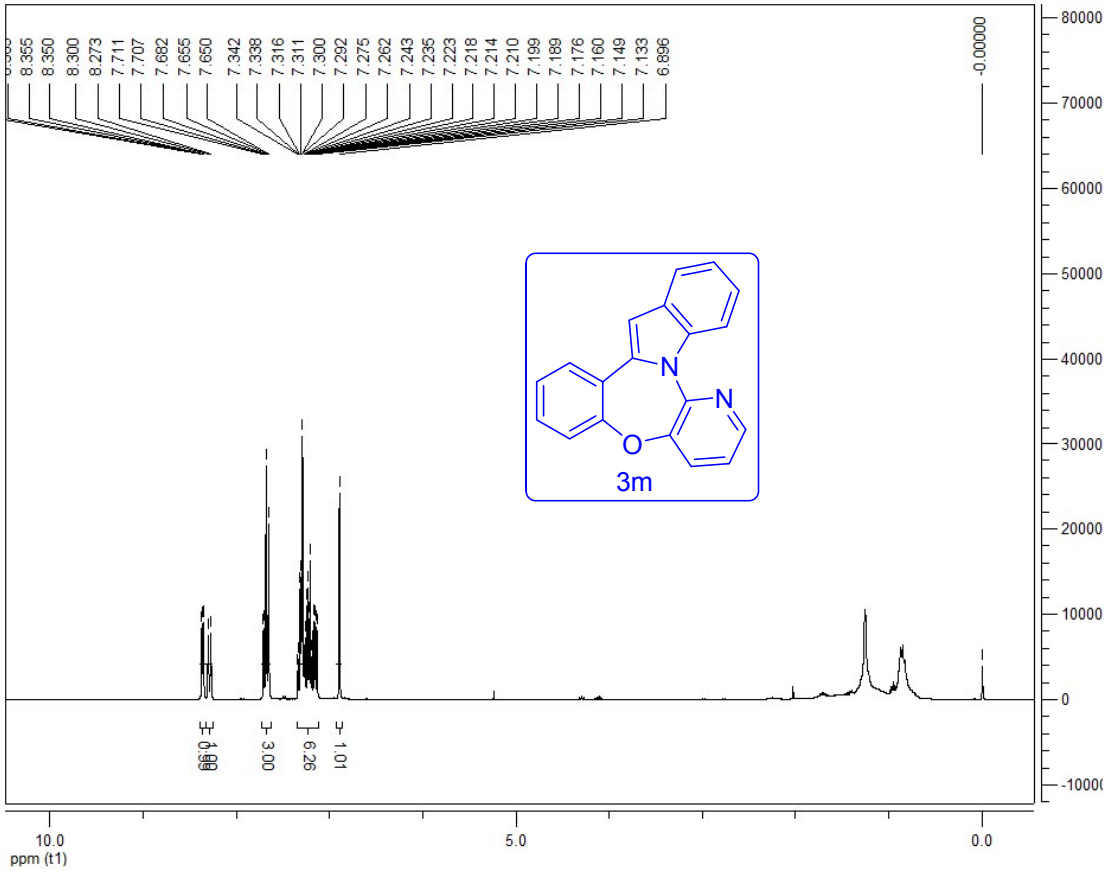


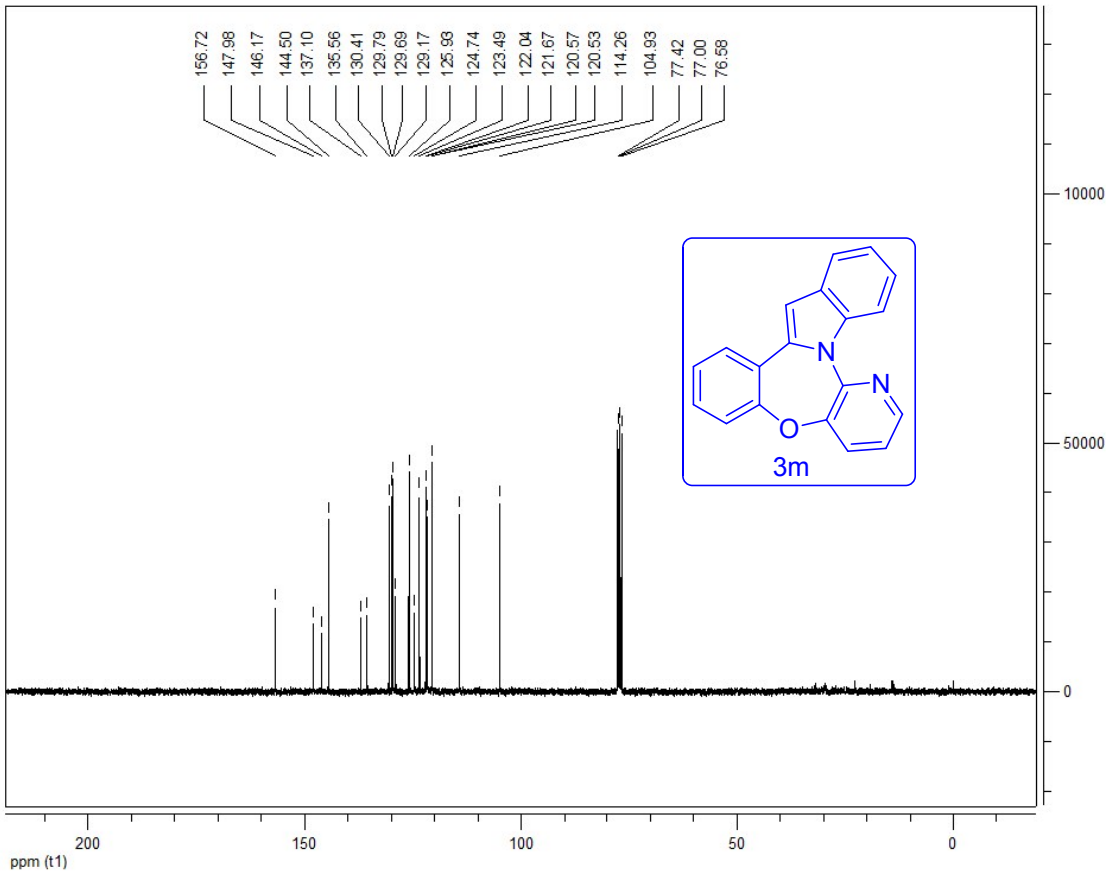
dibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole (3l)



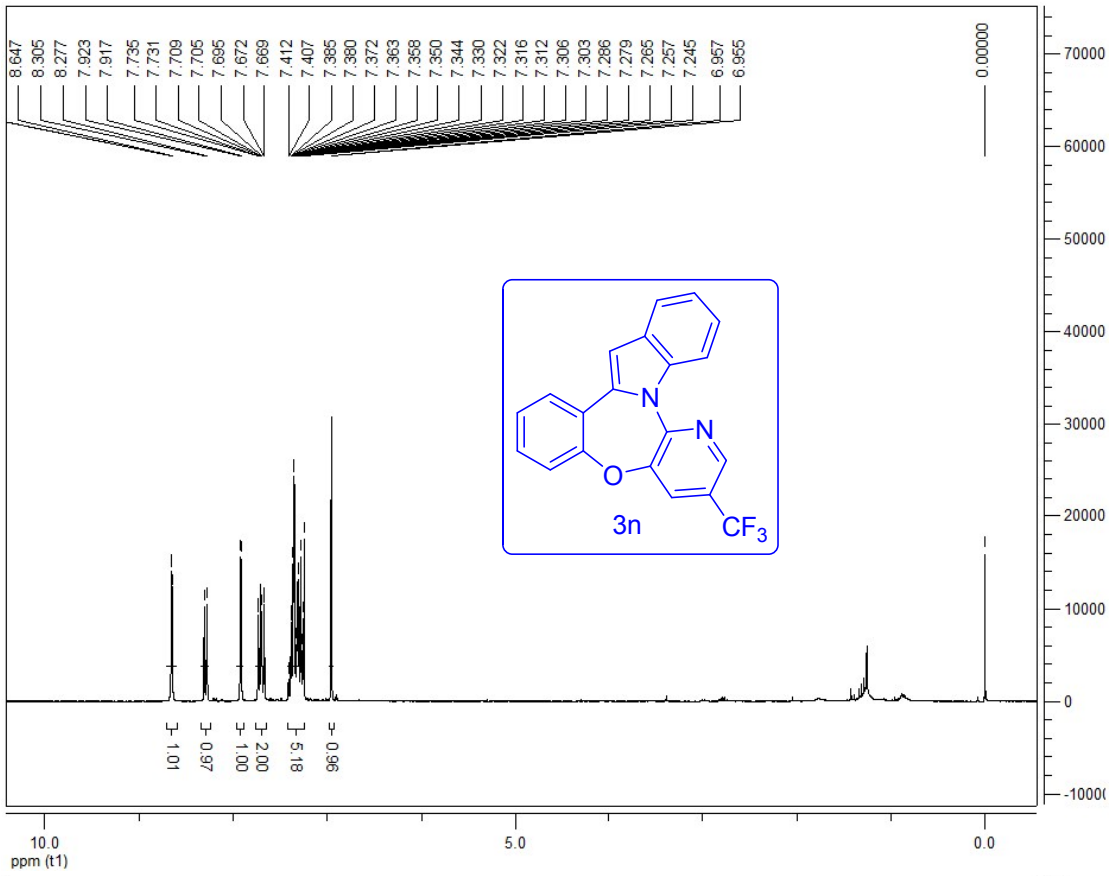


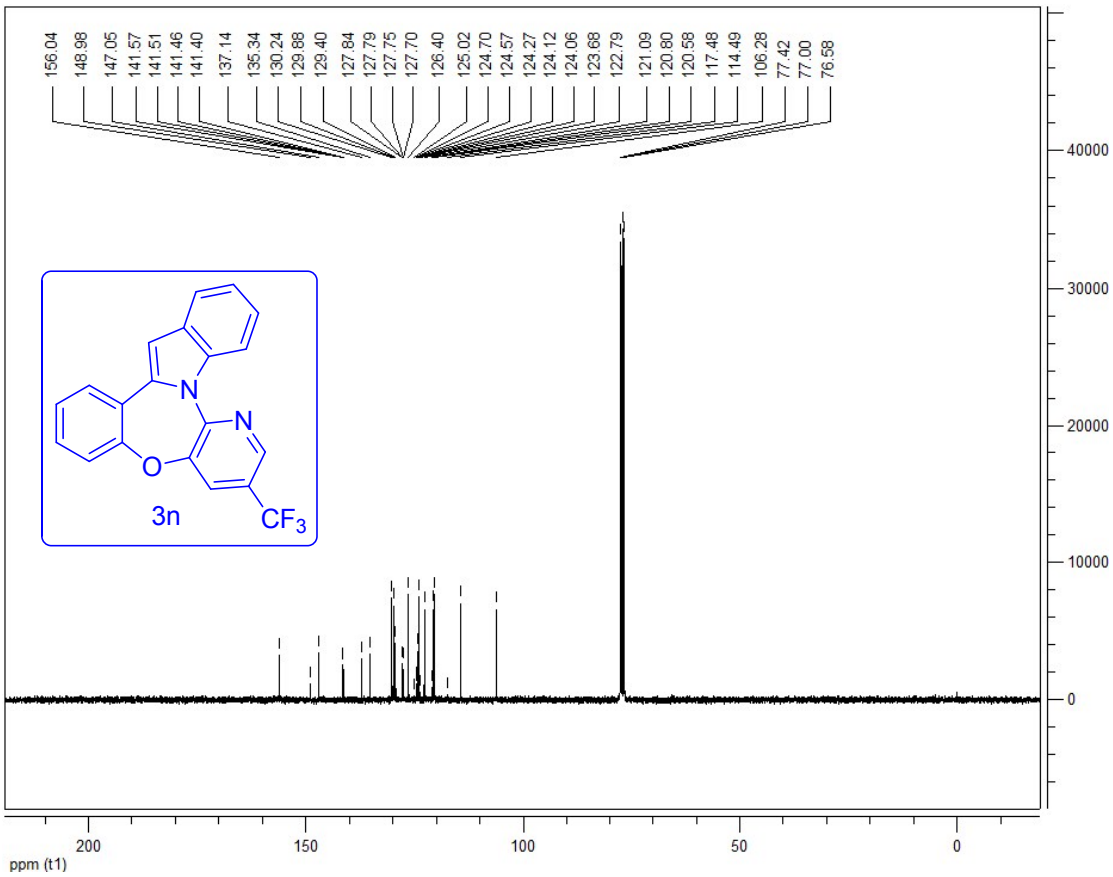
benzo[6,7]pyrido[3',2':2,3][1,4]oxazepino[4,5-a]indole (3m)



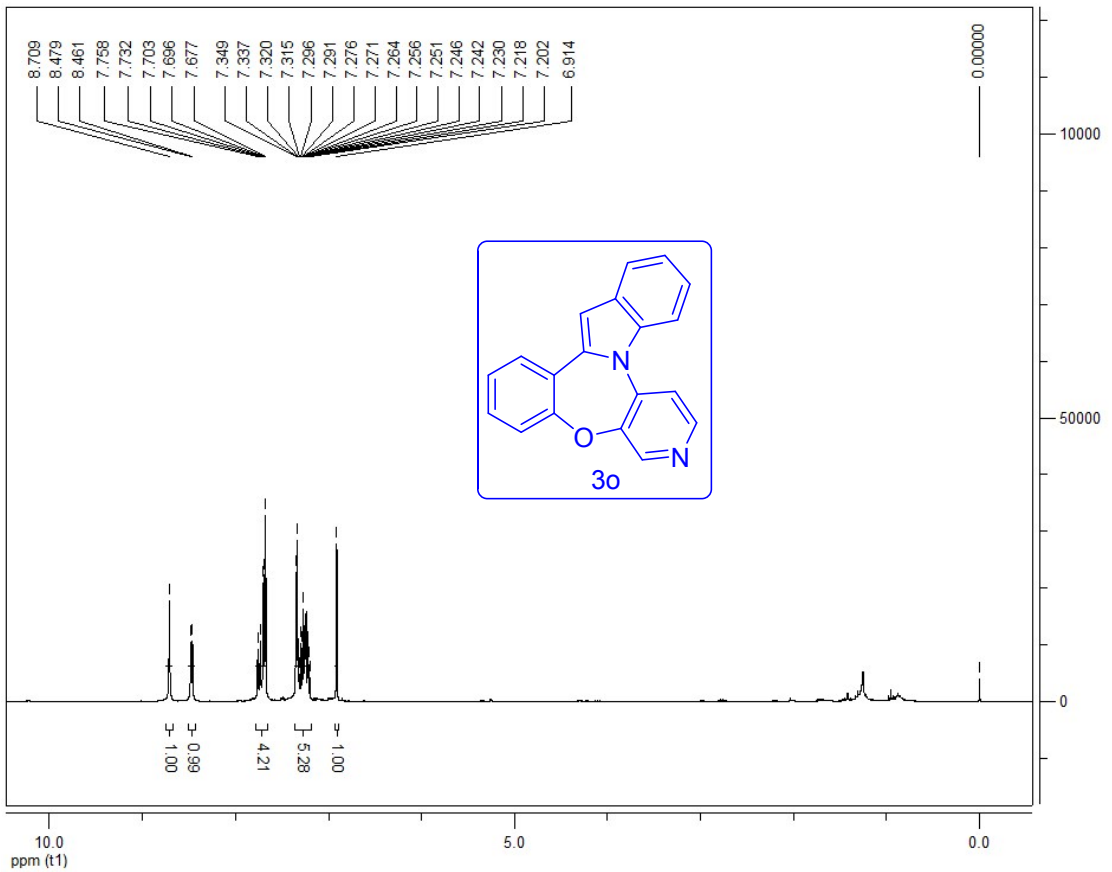


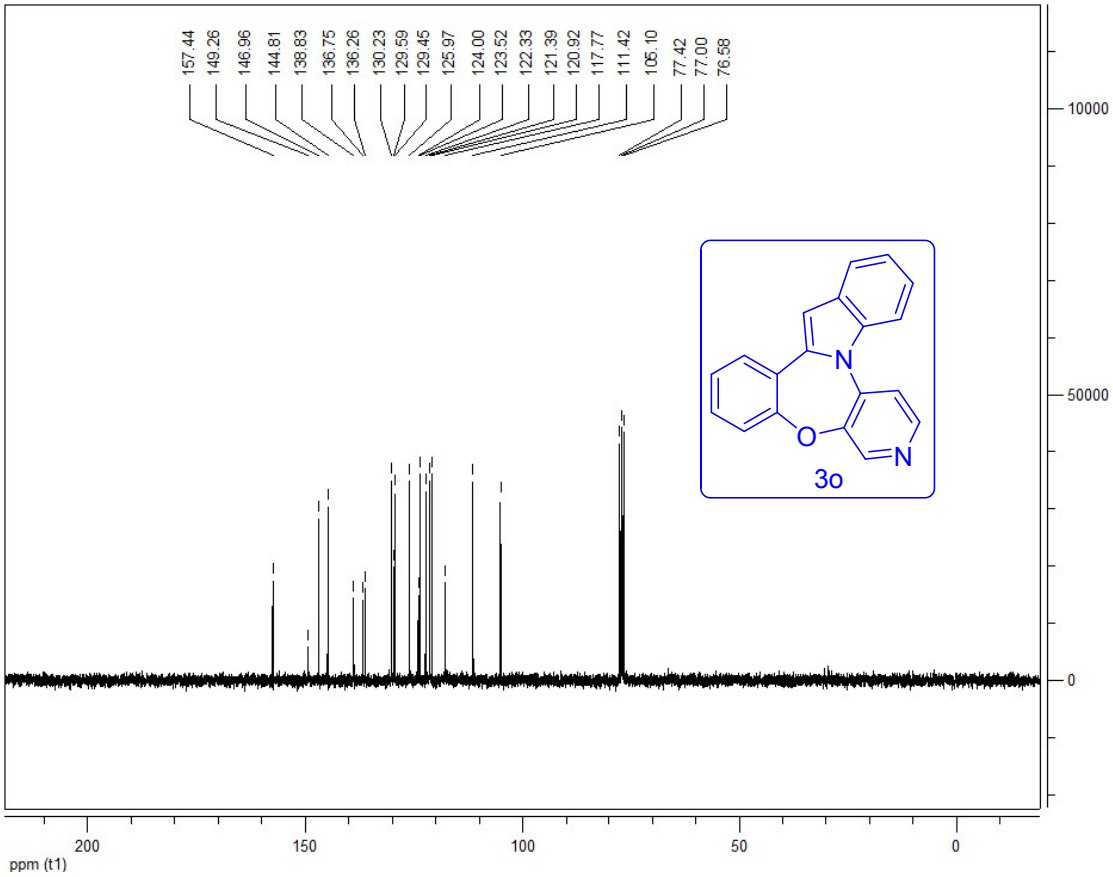
8-(trifluoromethyl)benzo[6,7]pyrido[3',2':2,3][1,4]oxazepino[4,5-a]indole (3n)



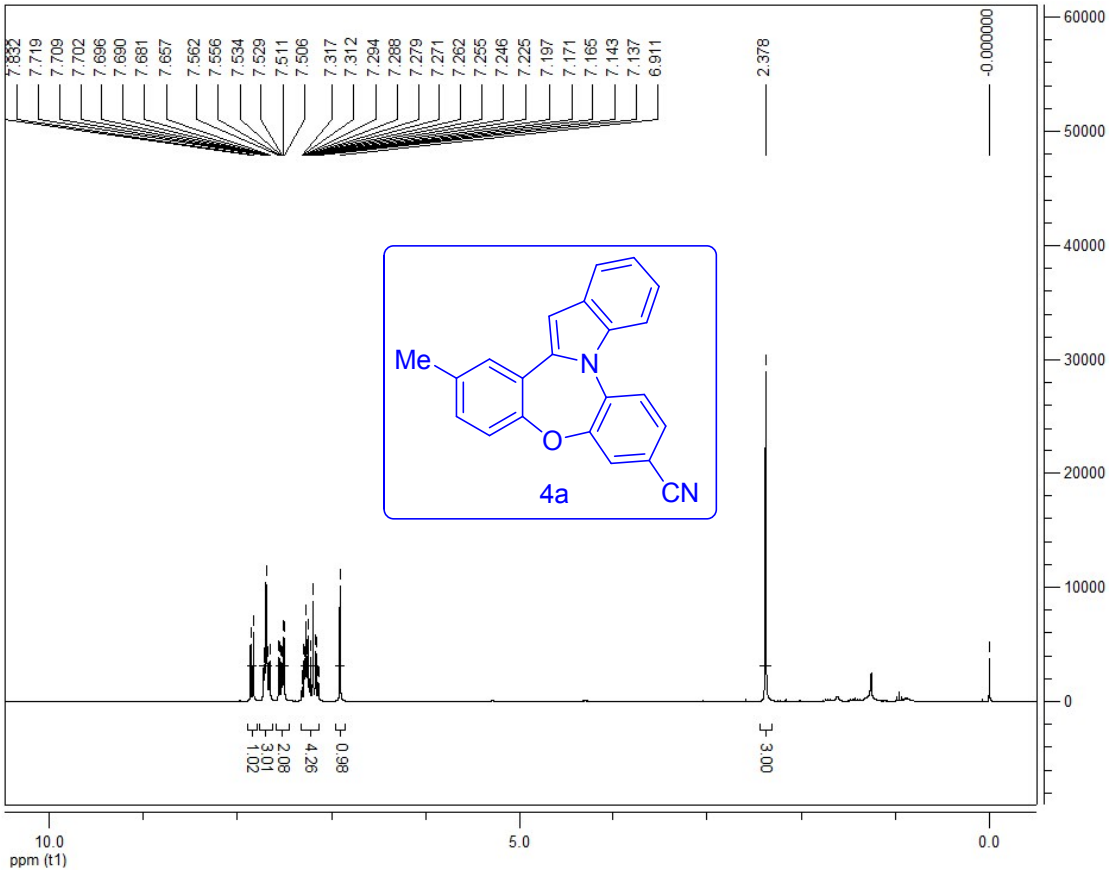


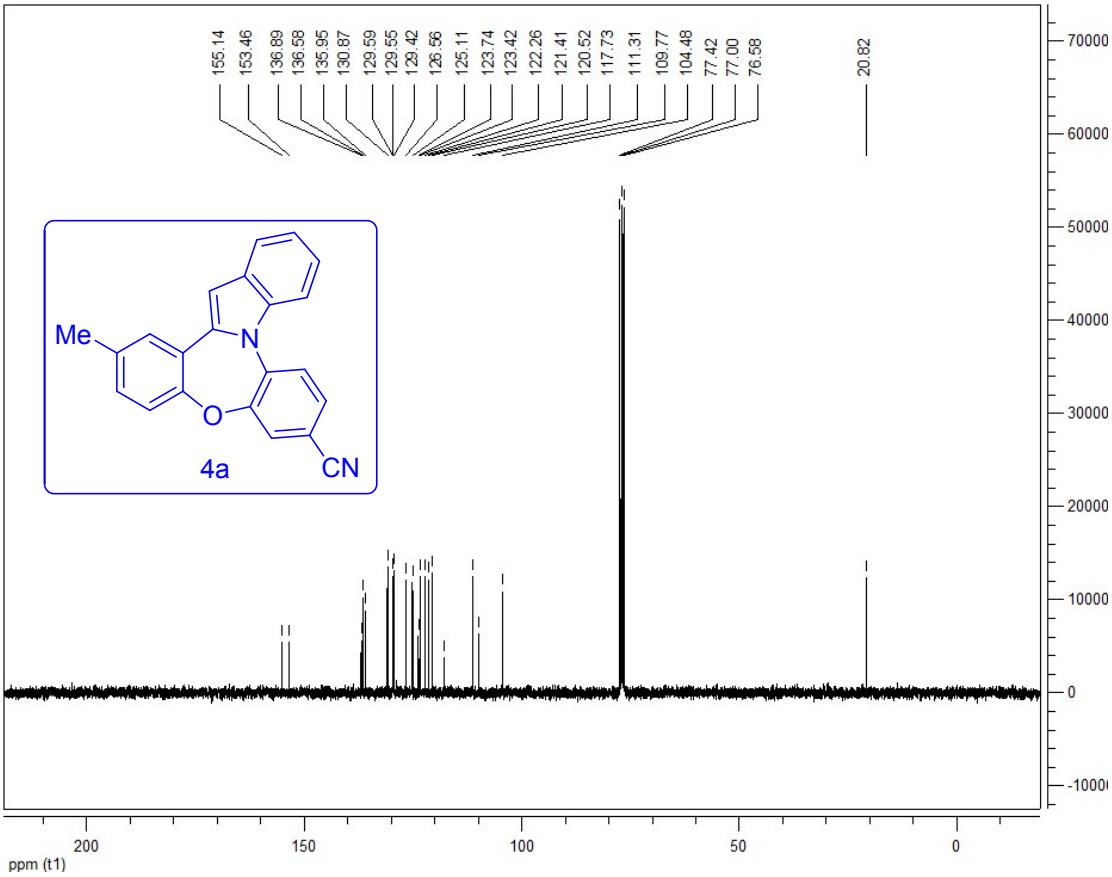
benzo[6,7]pyrido[3',4':2,3][1,4]oxazepino[4,5-a]indole (3o)



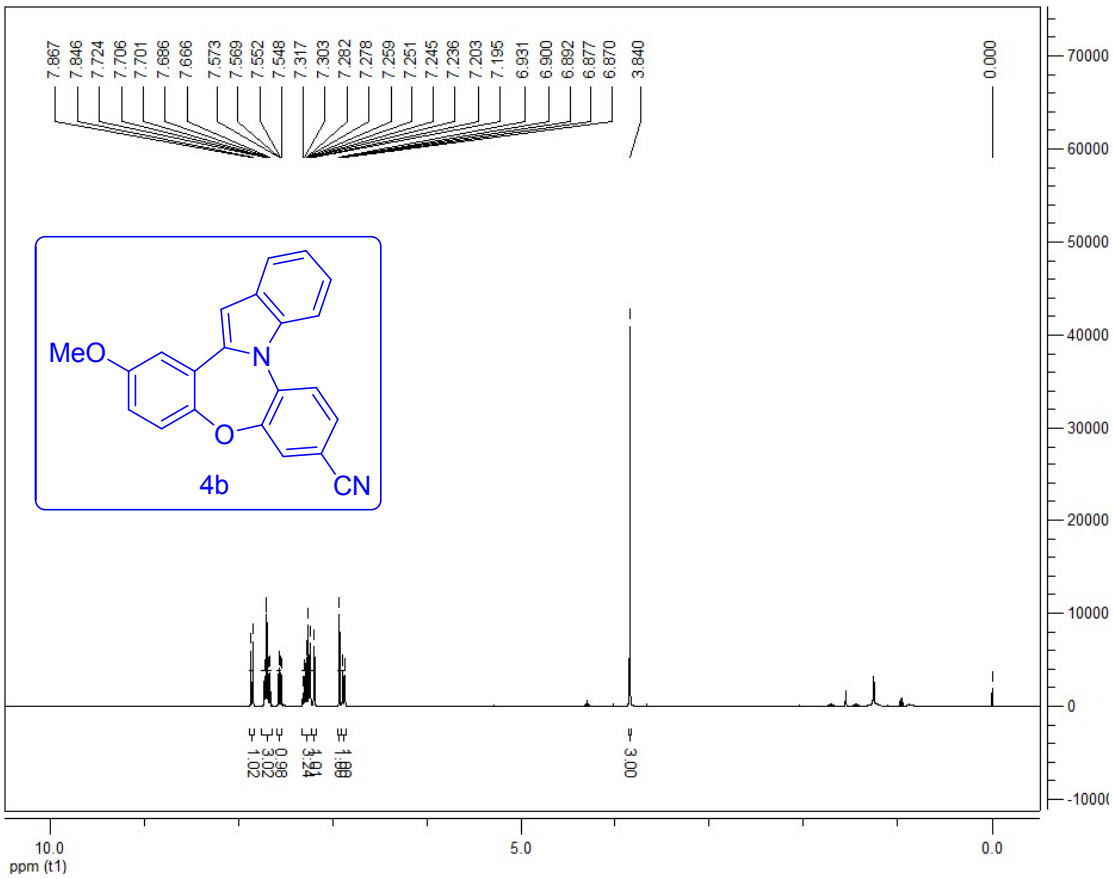


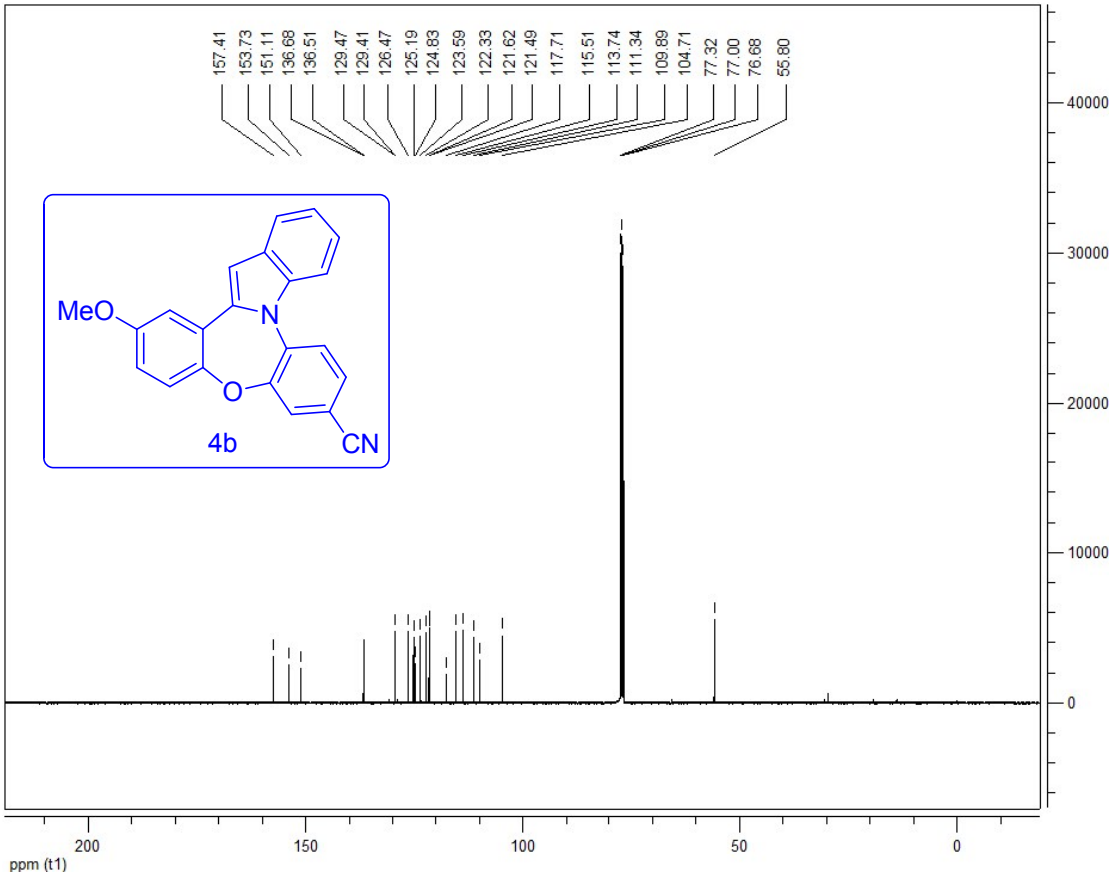
13-methyldibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4a)



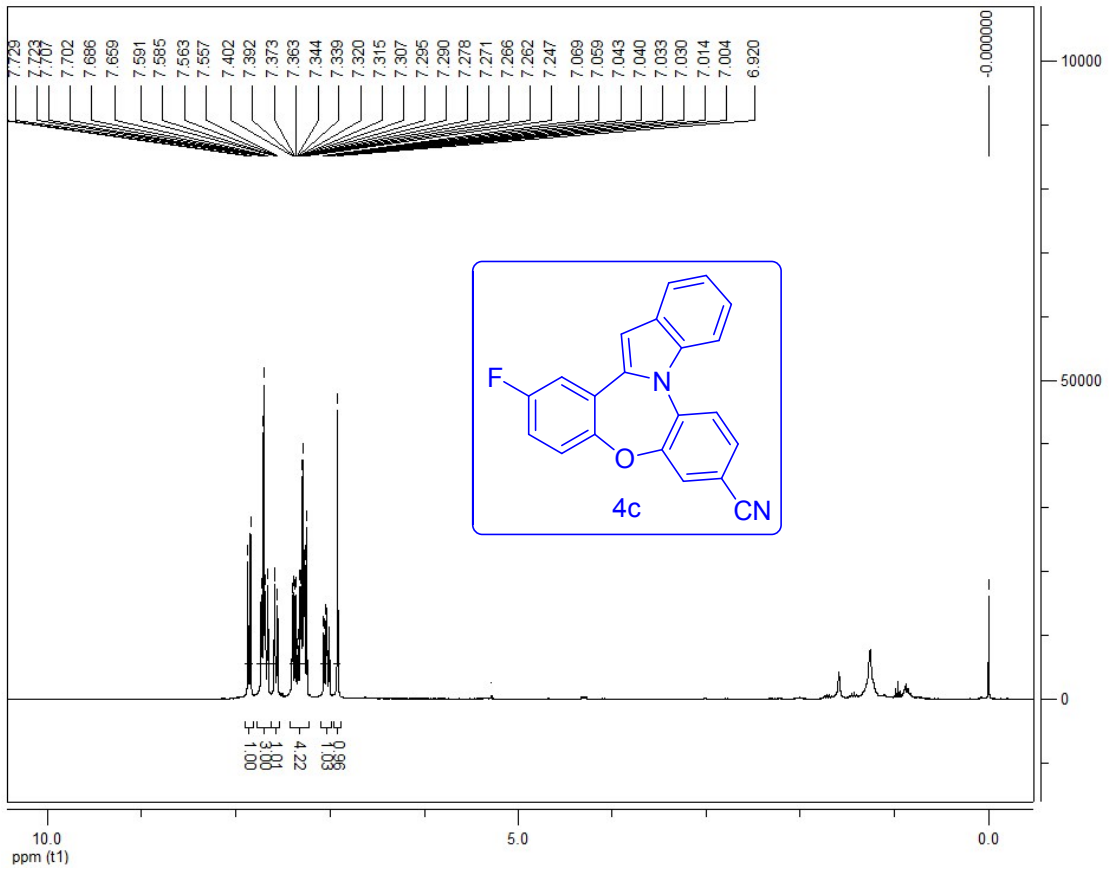


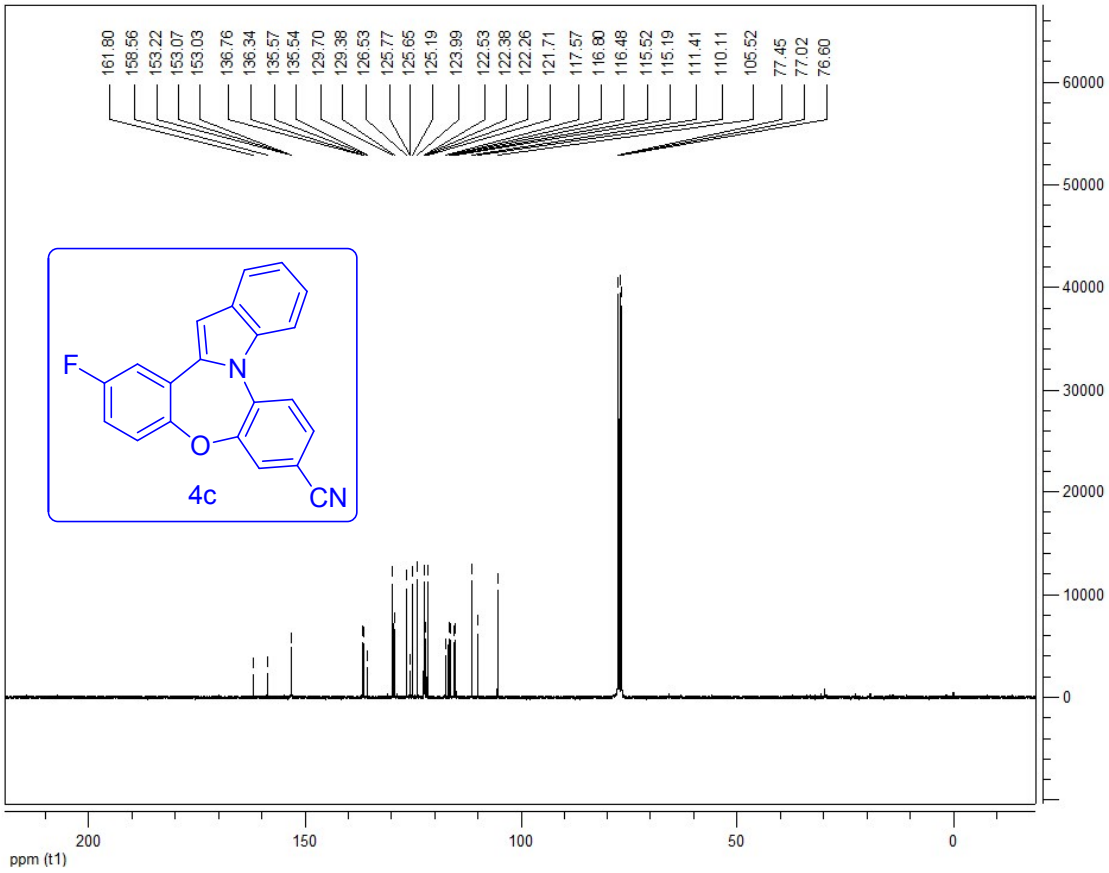
13-methoxydibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4b)



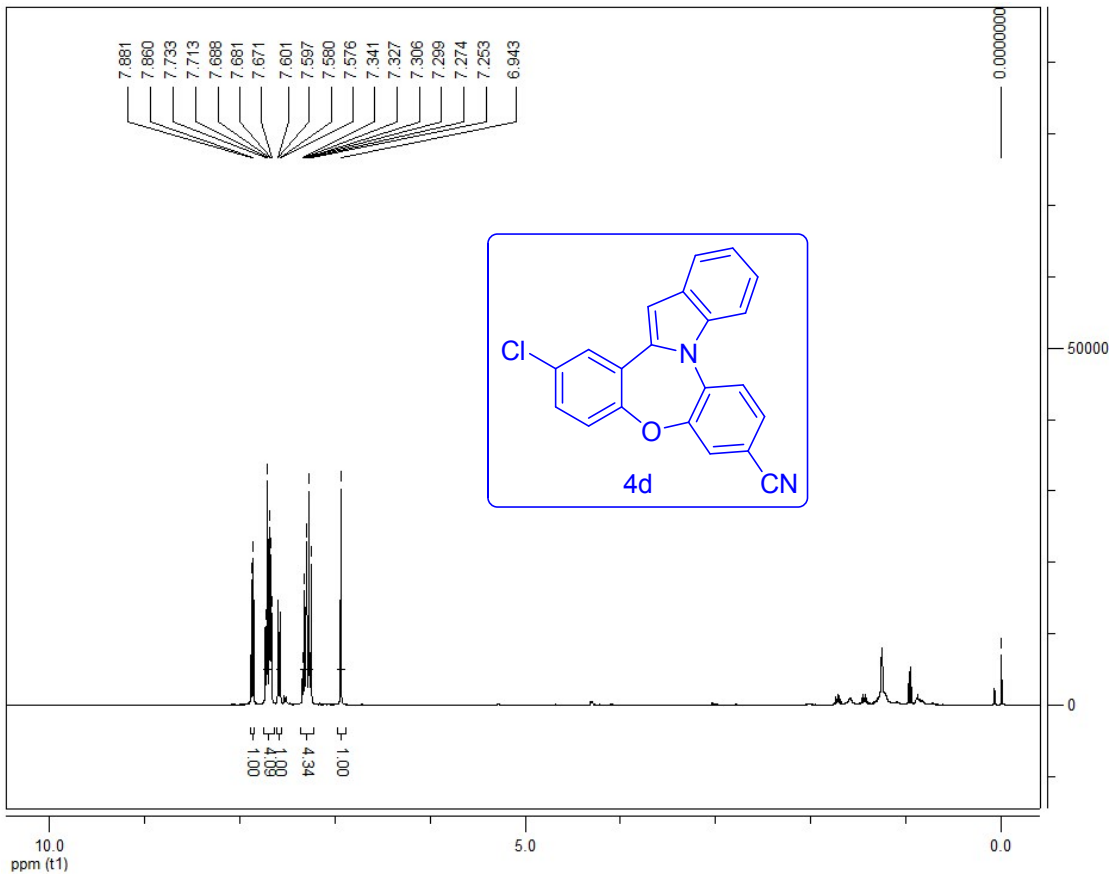


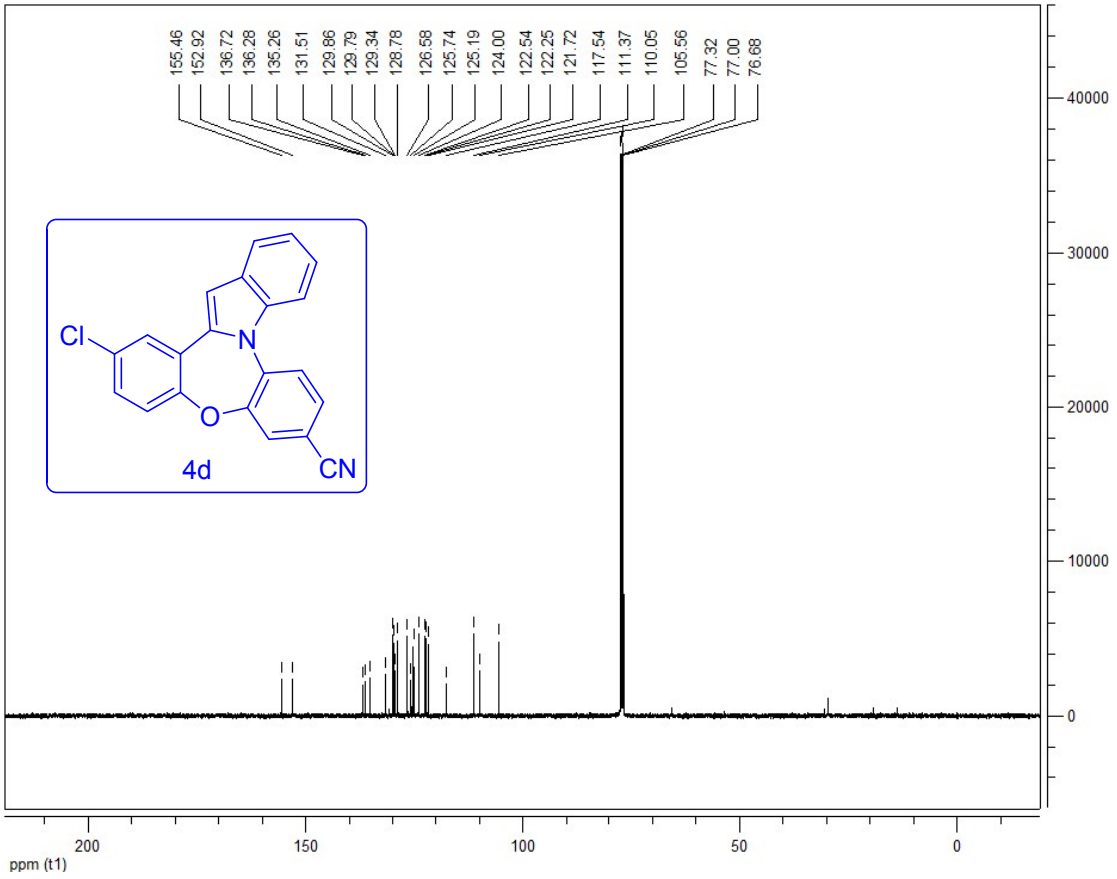
13-fluorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4c)



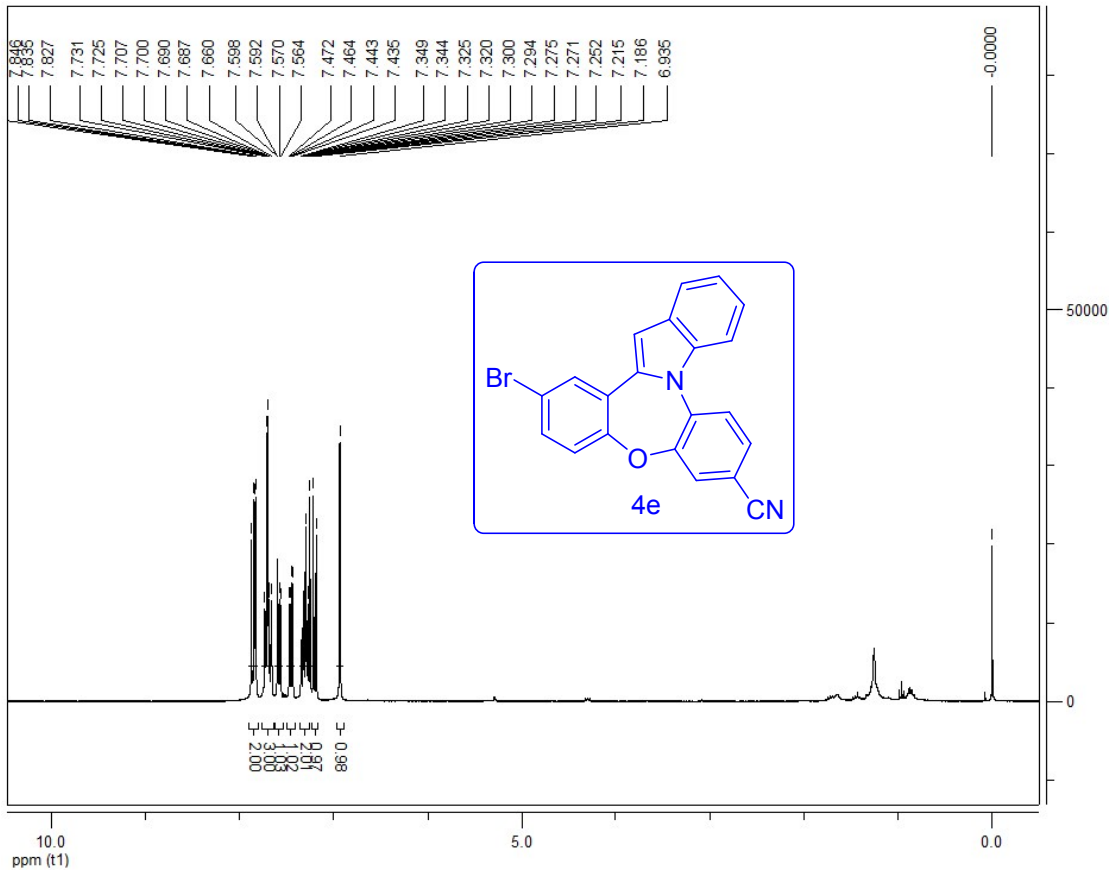


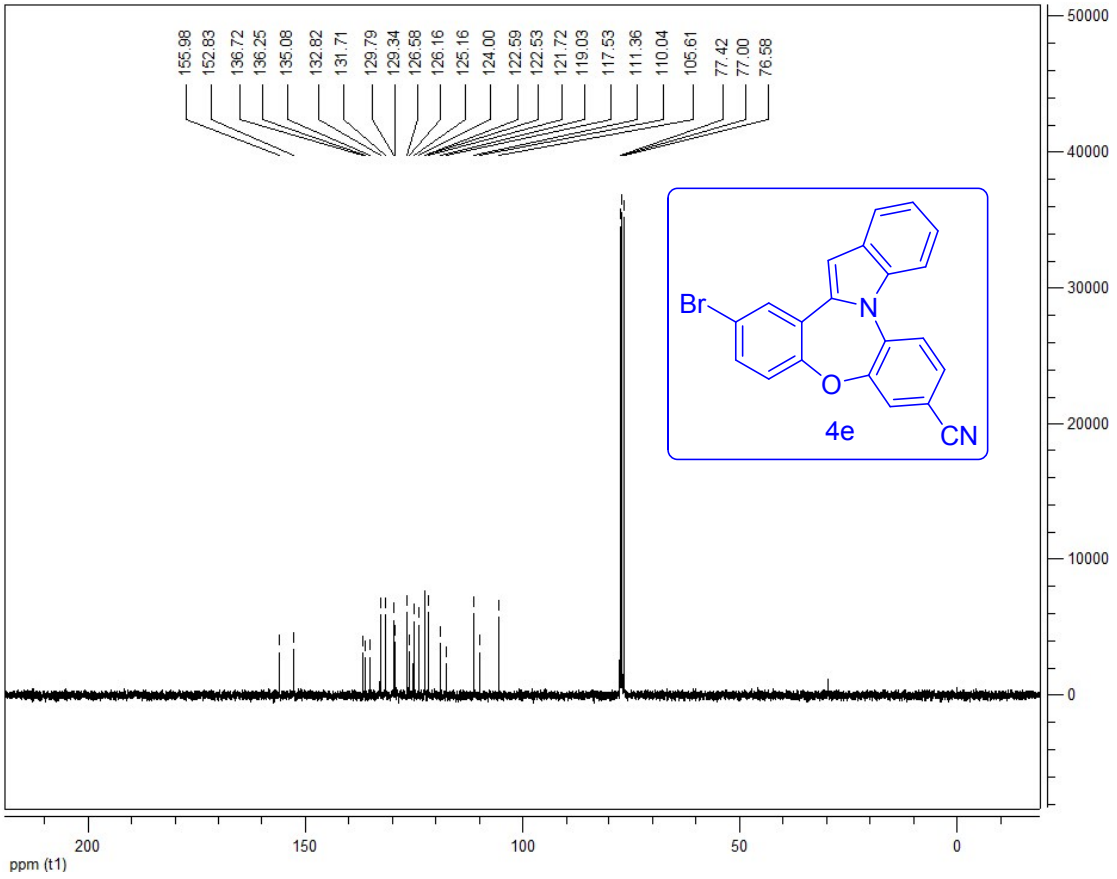
13-chlorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4d)



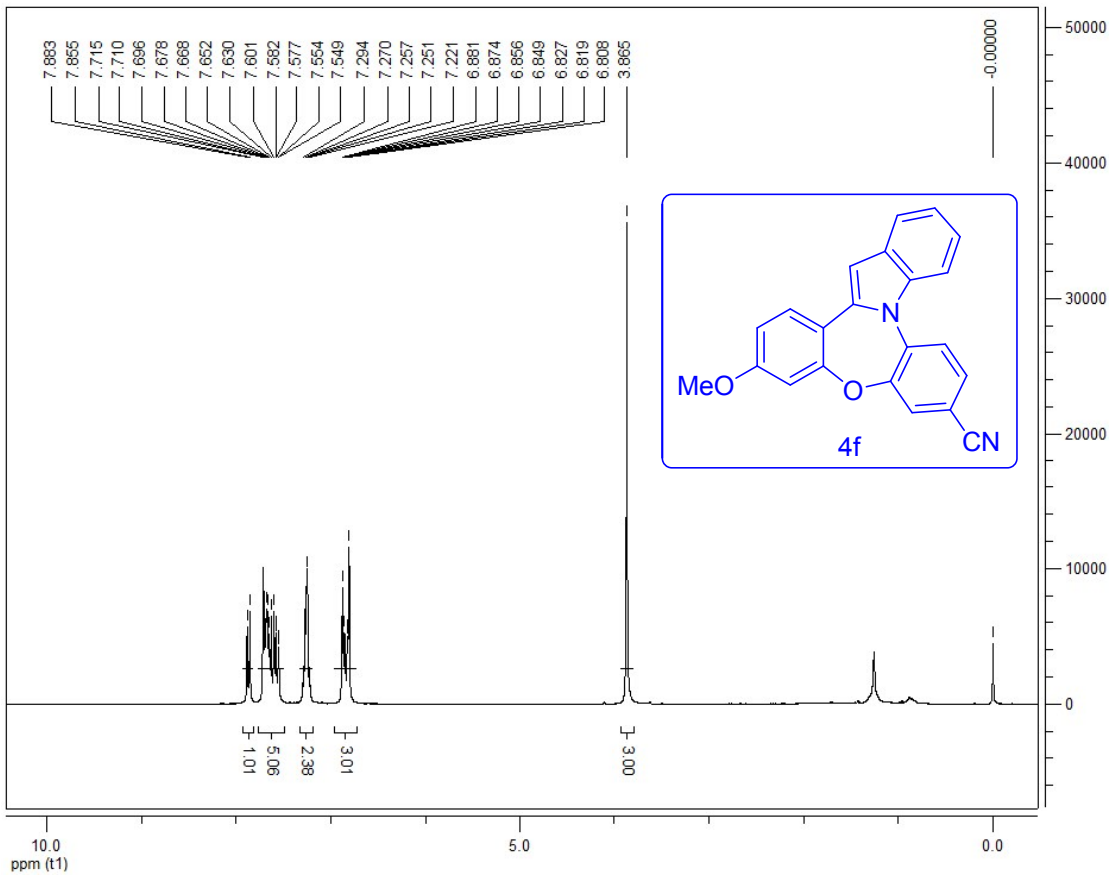


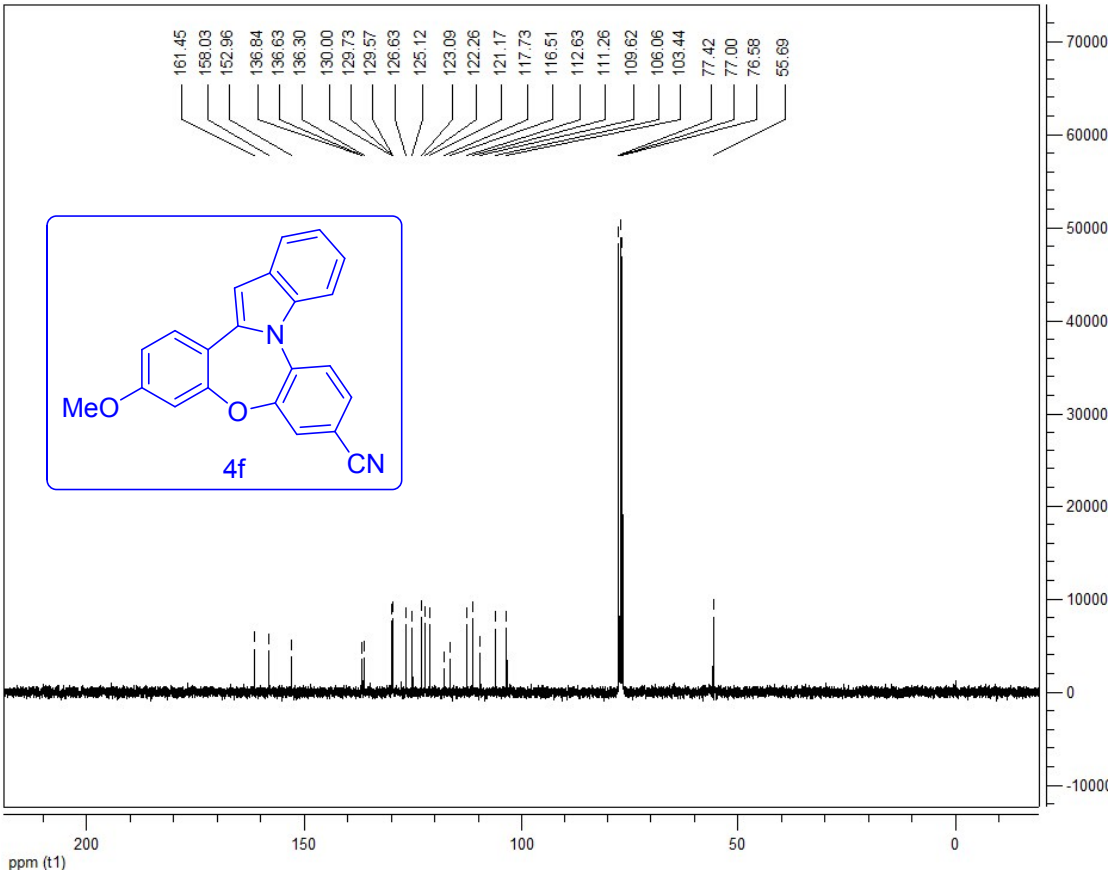
13-bromodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4e)



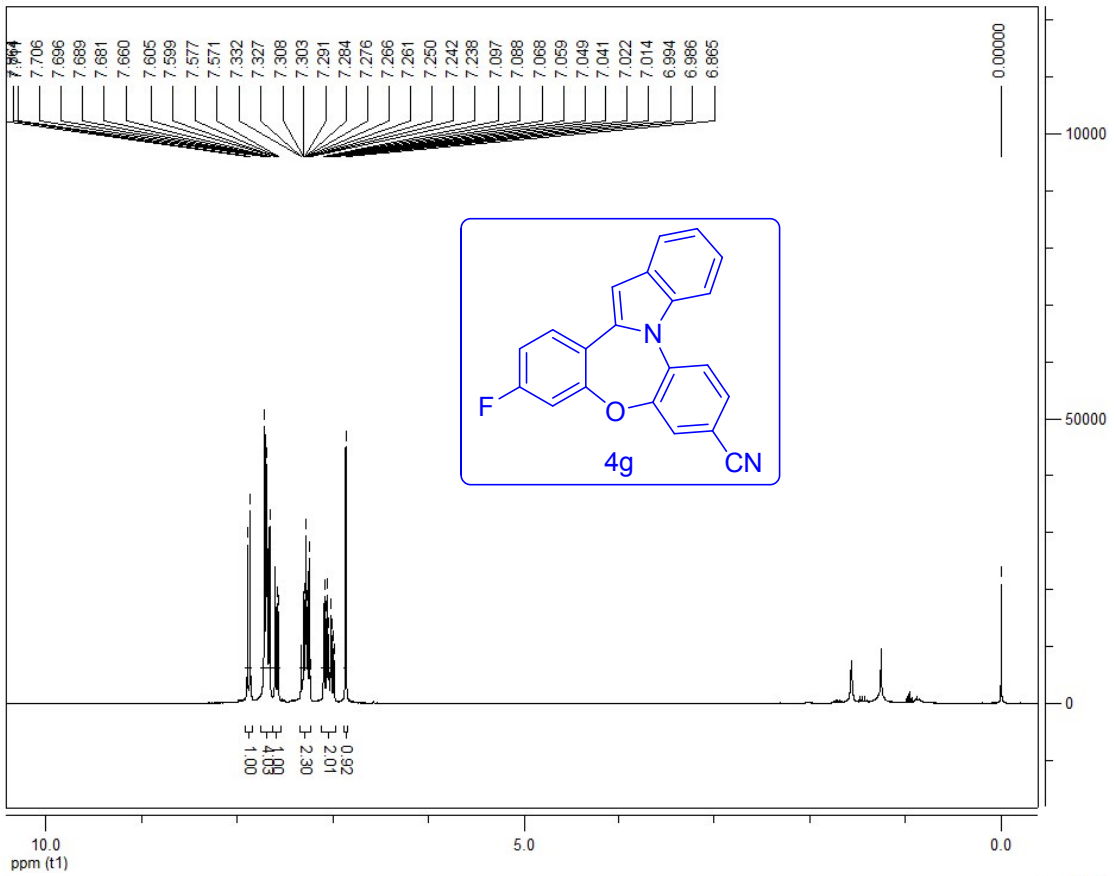


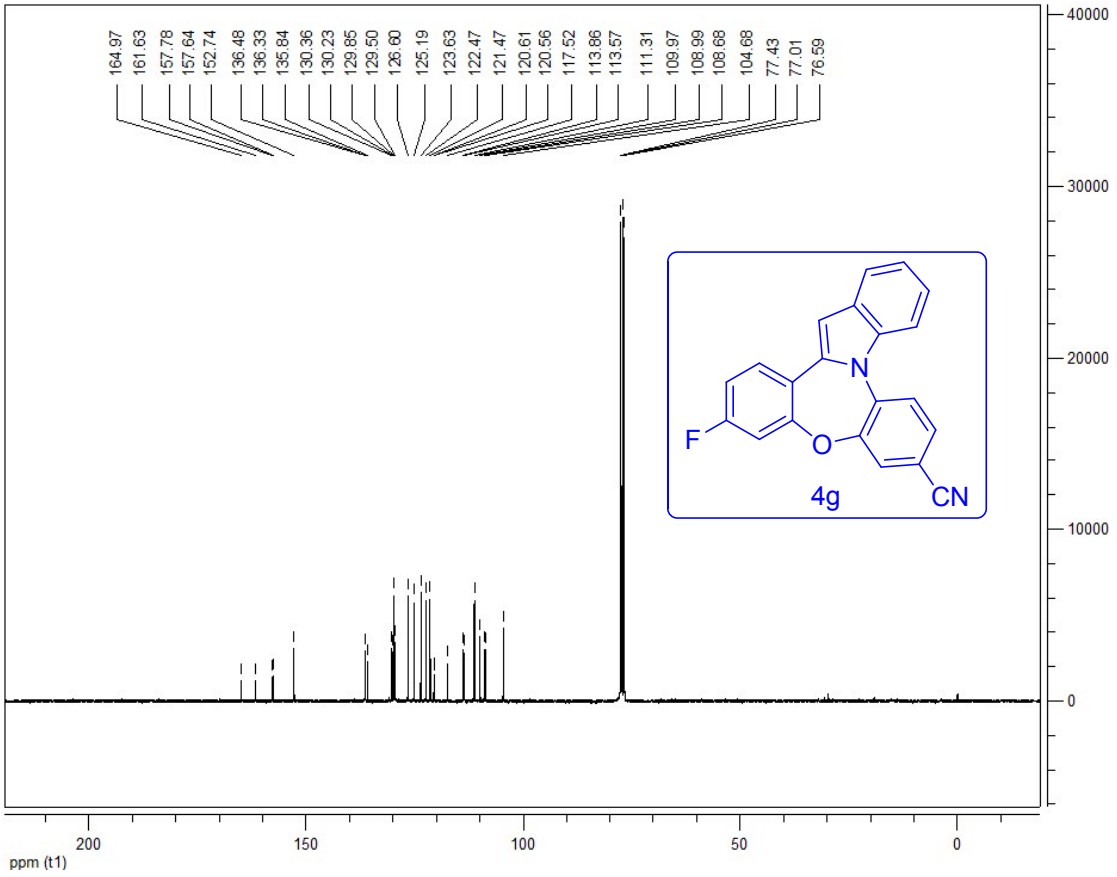
12-methoxydibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4f)



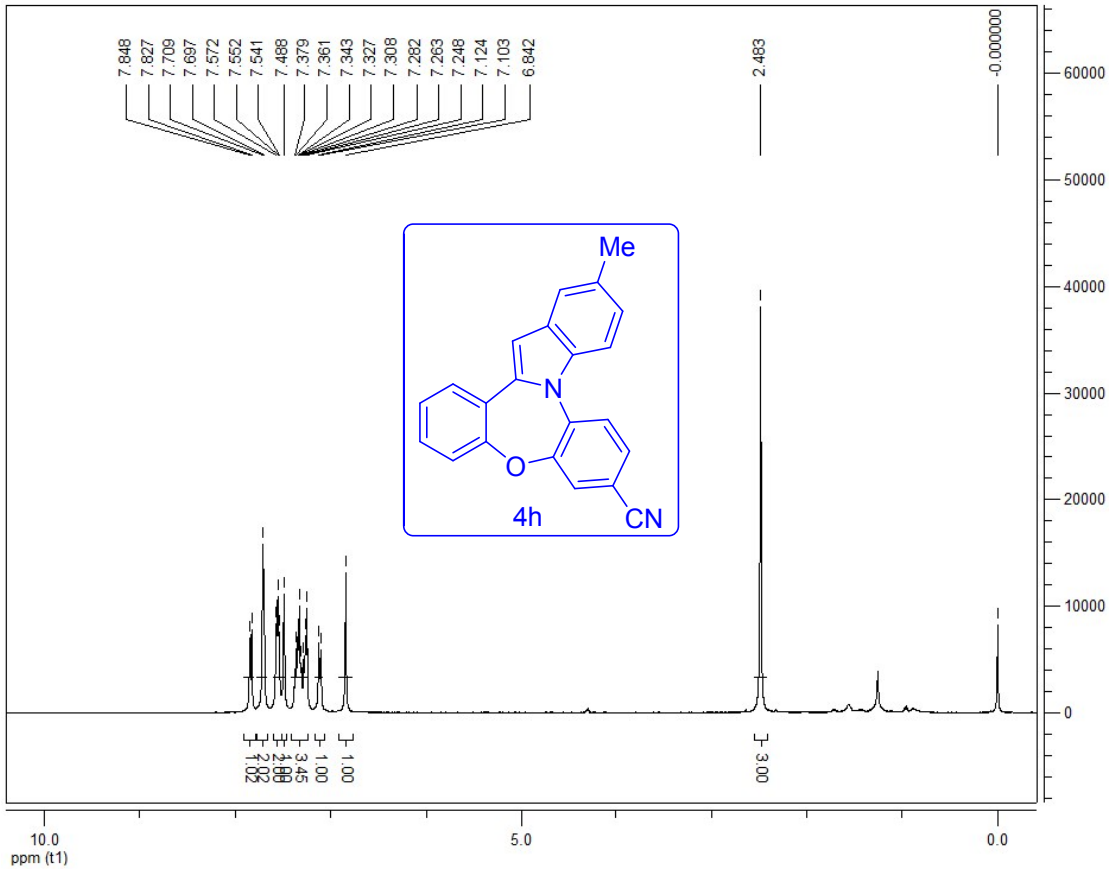


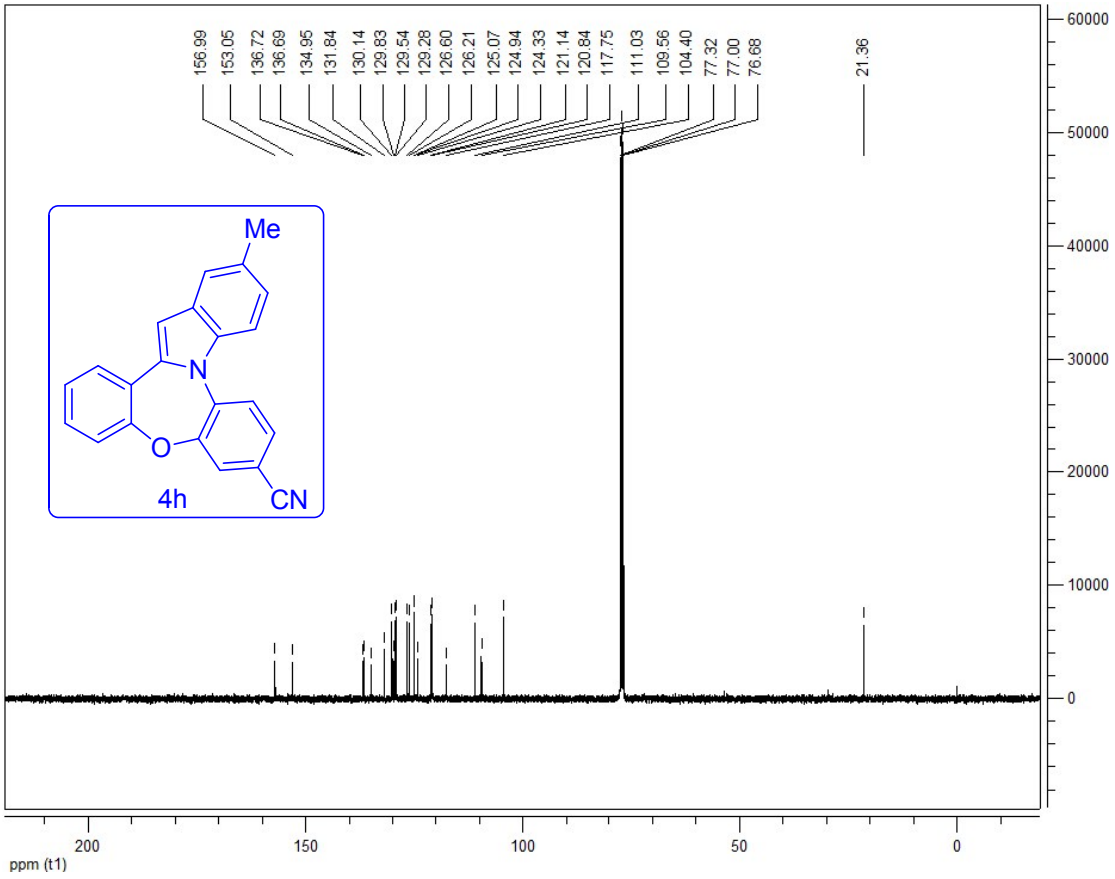
12-fluorodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4g)



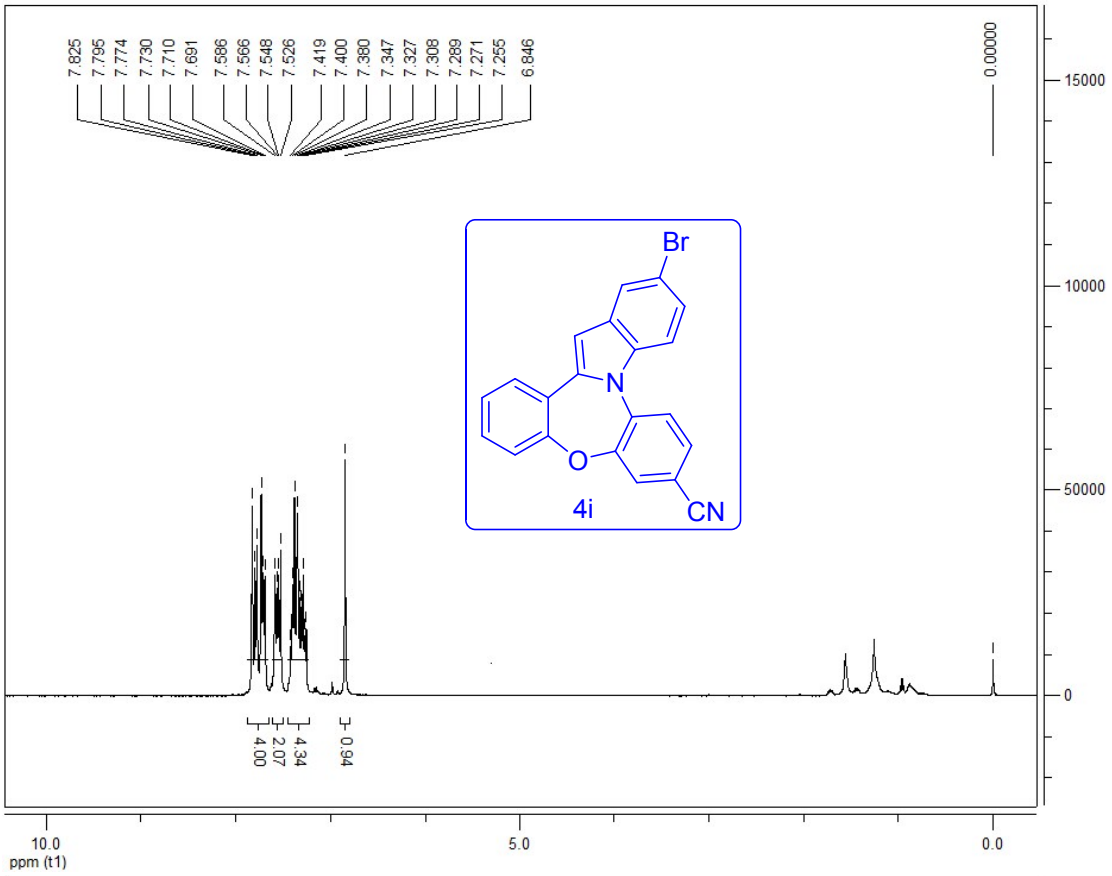


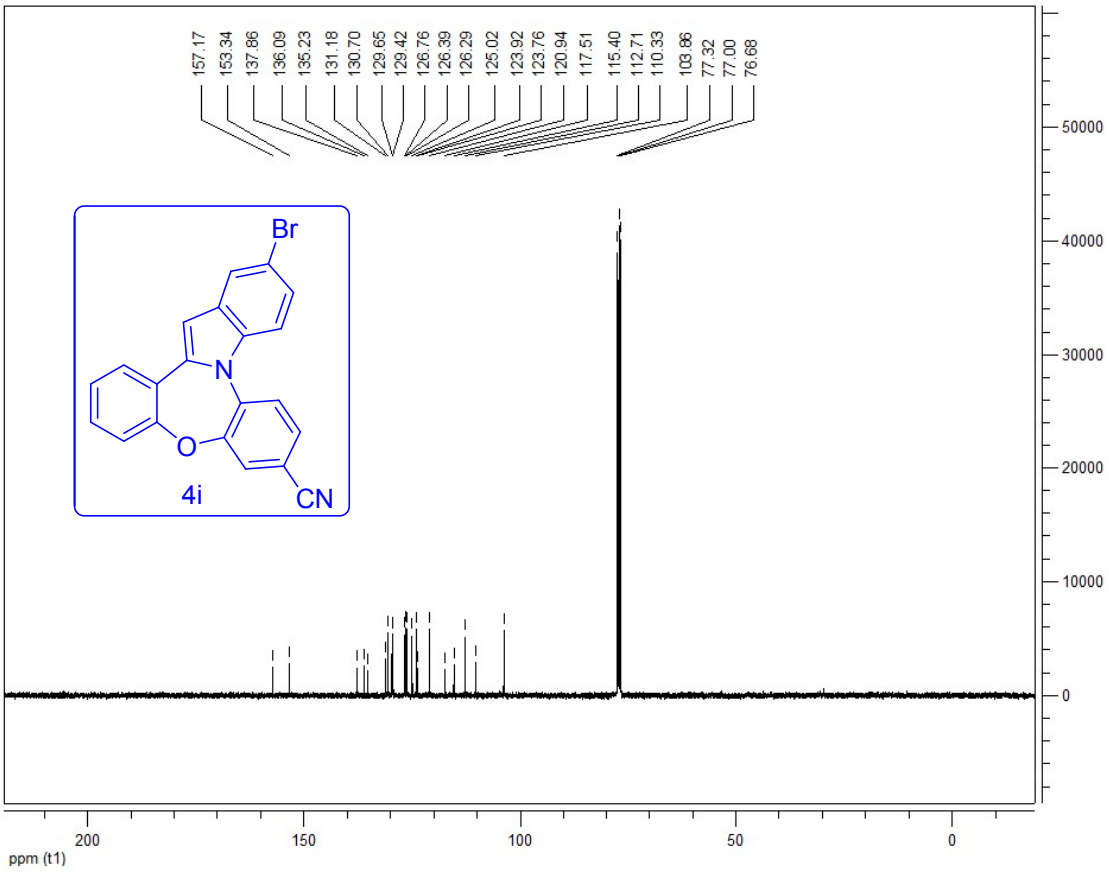
2-methyldibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4h)



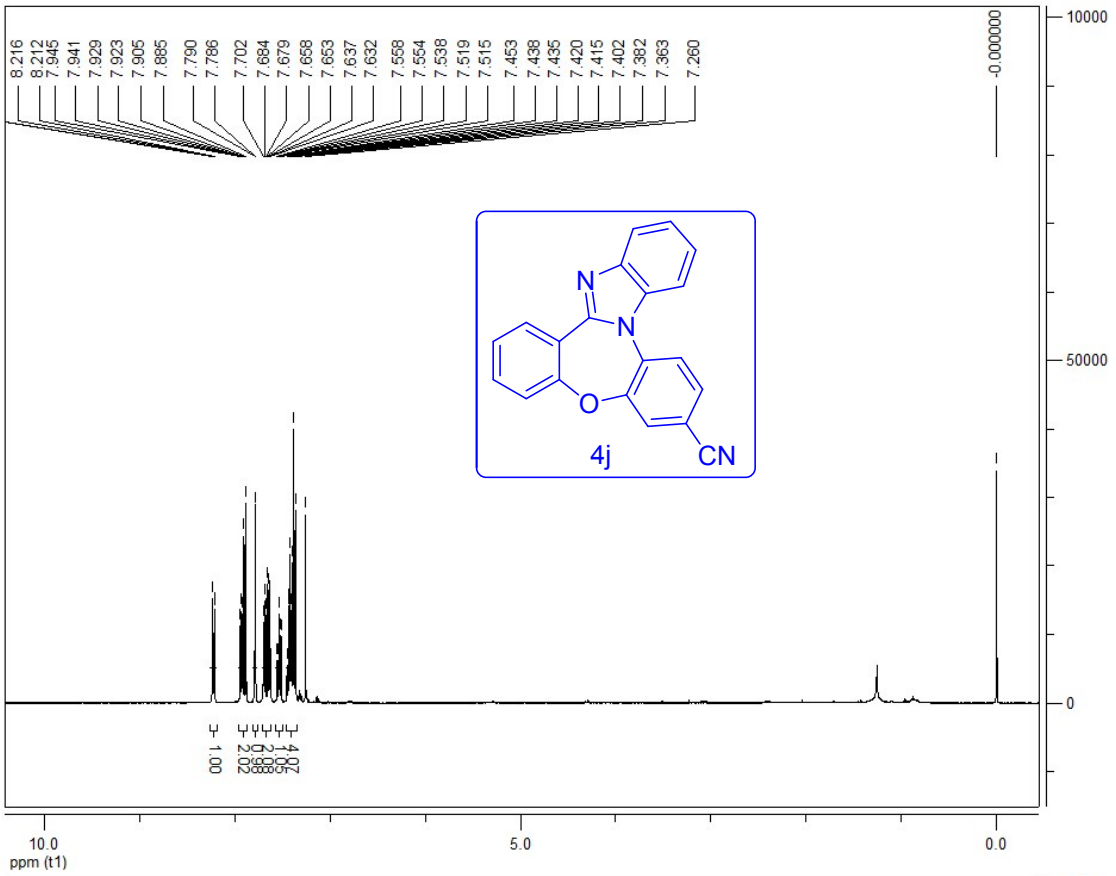


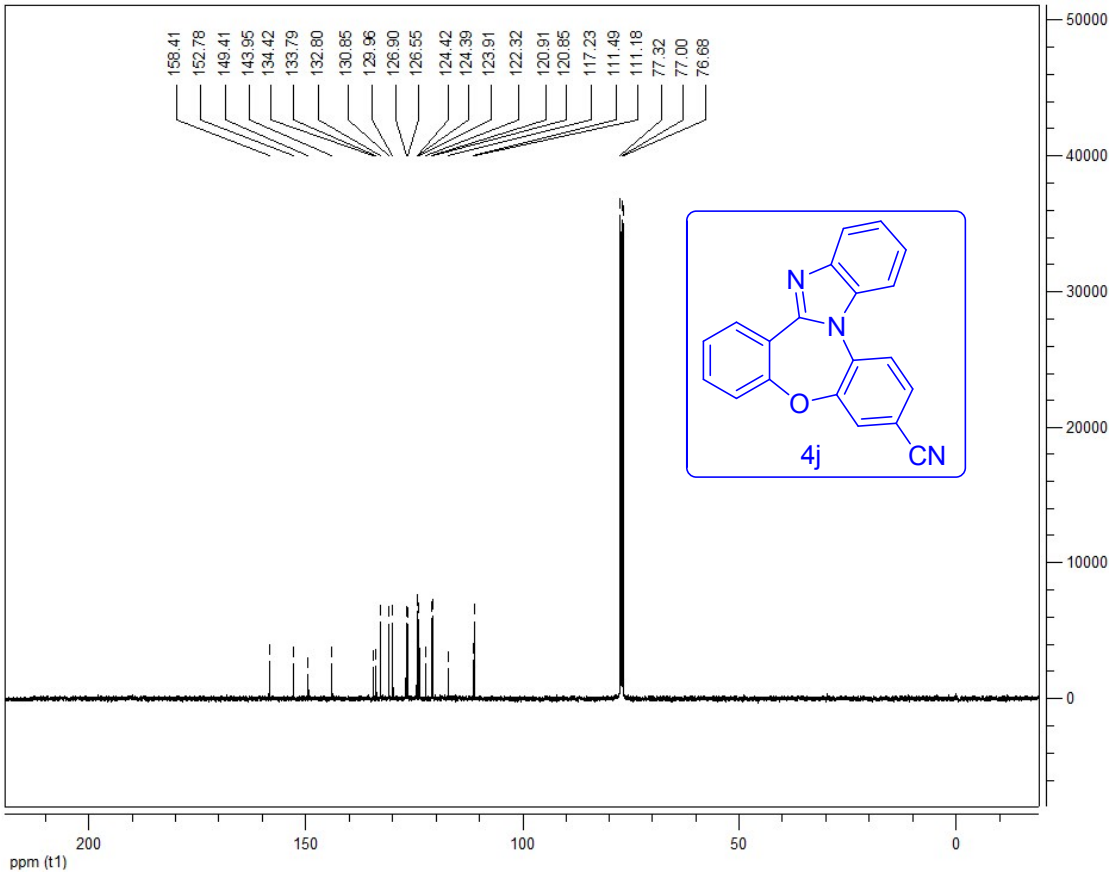
2-bromodibenzo[2,3:6,7][1,4]oxazepino[4,5-a]indole-8-carbonitrile (4i)





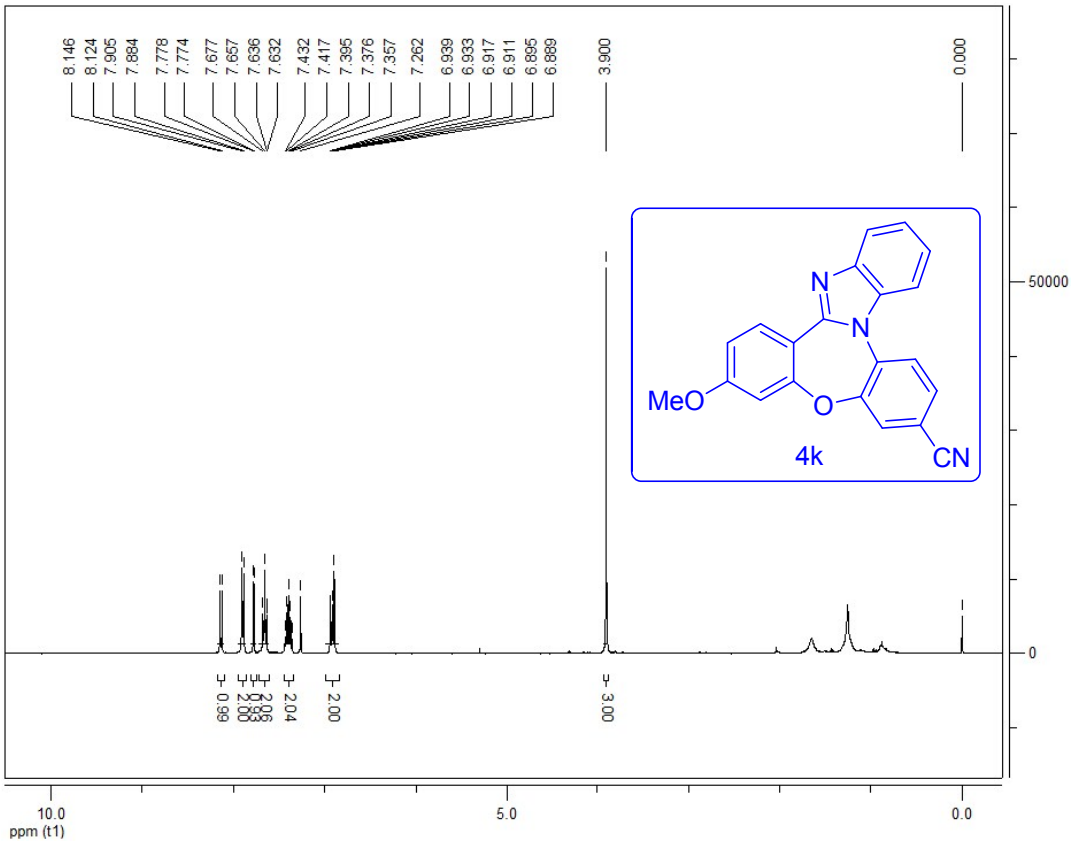
dibenzo[b,f]benzo[4,5]imidazo[1,2-d][1,4]oxazepine-8-carbonitrile (4j)

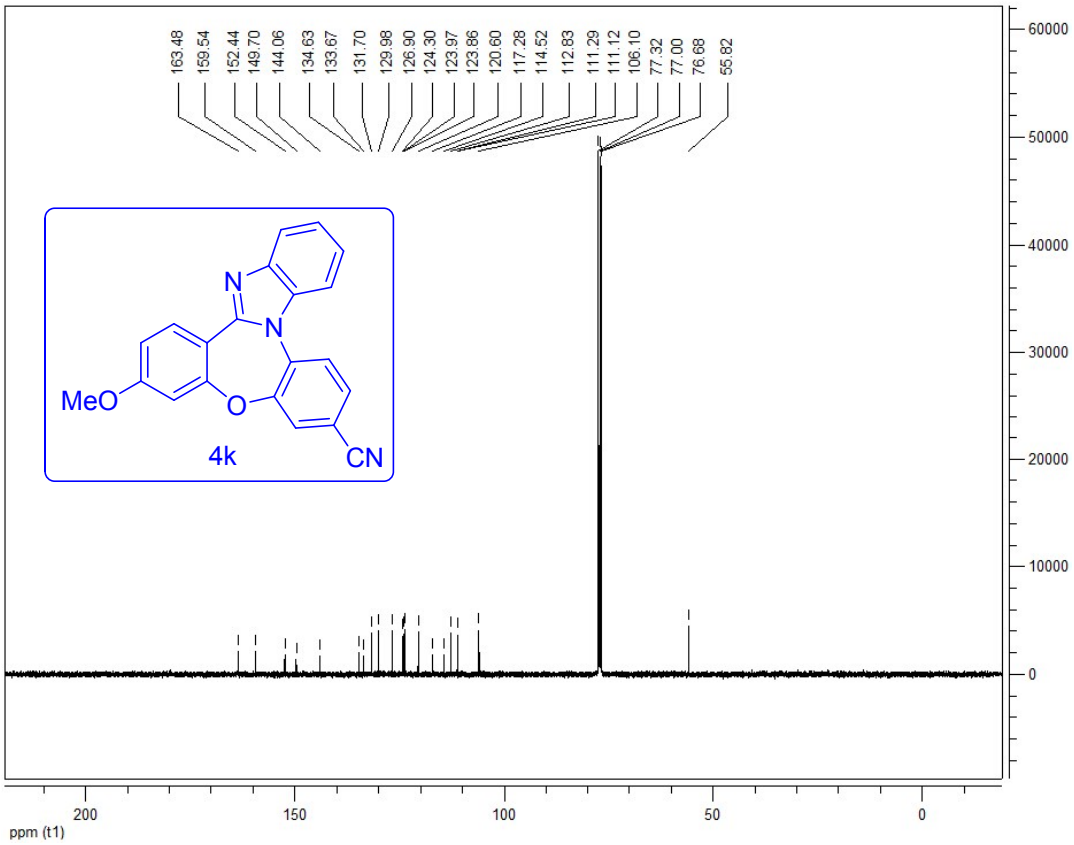




12-methoxydibenzo[b,f]benzo[4,5]imidazo[1,2-d][1,4]oxazepine-8-carbonitrile

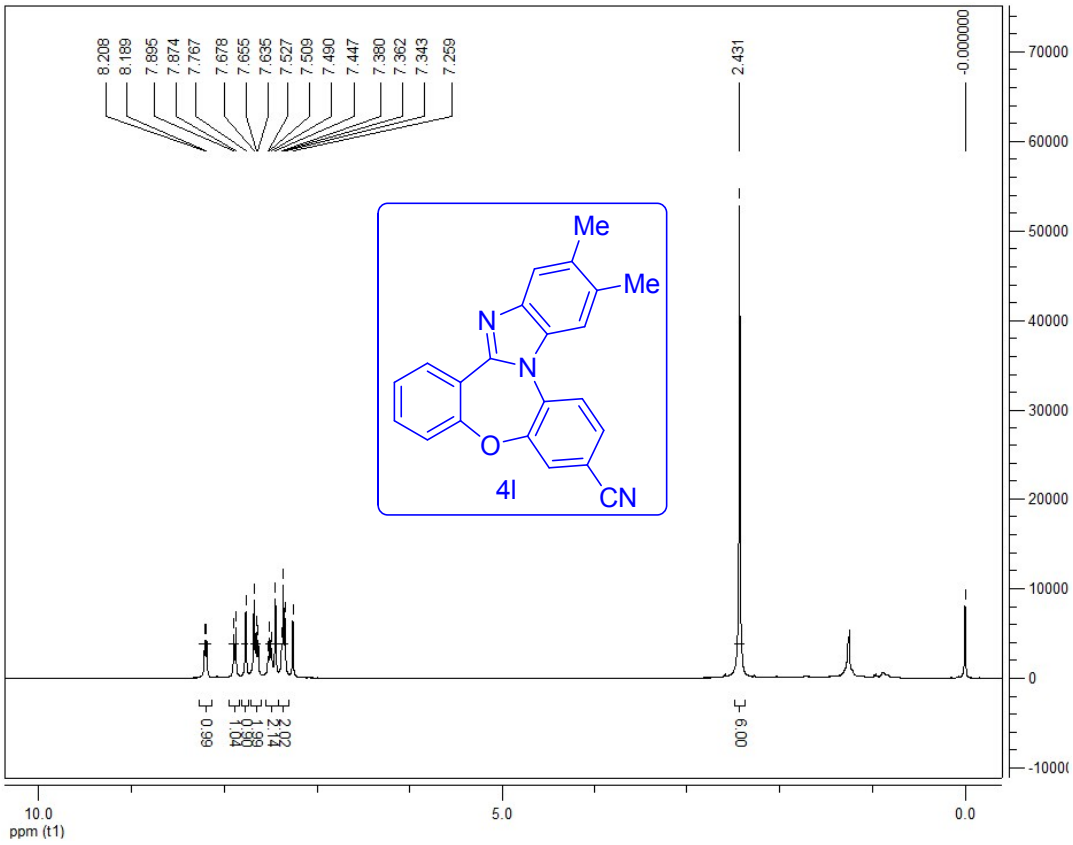
(4k)

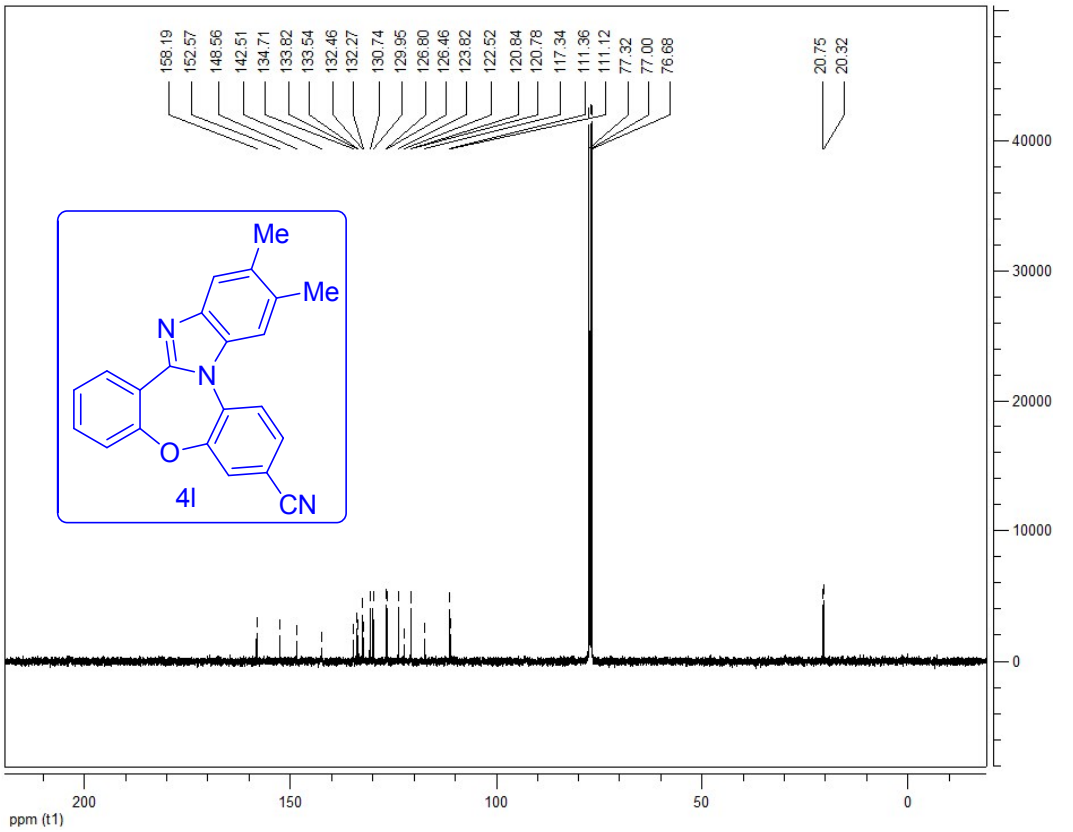




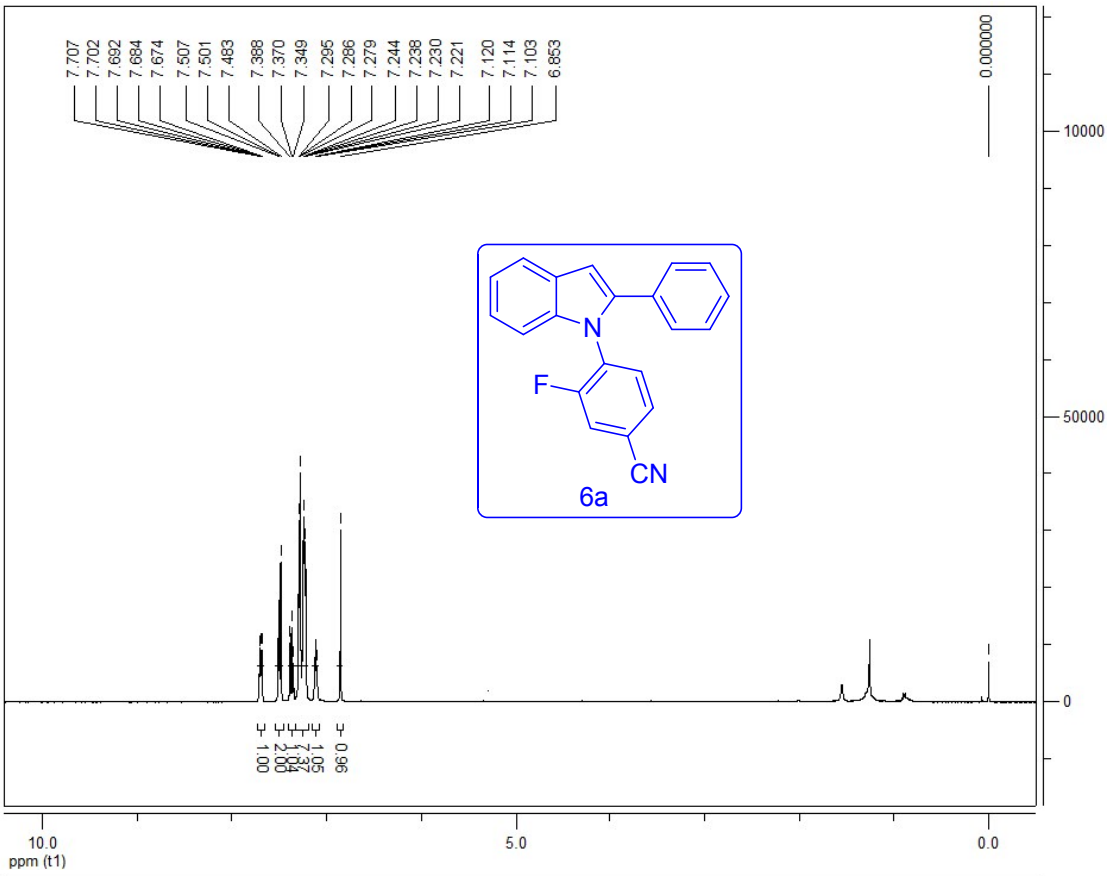
2,3-dimethyldibenzo[b,f]benzo[4,5]imidazo[1,2-d][1,4]oxazepine-8-carbonitrile

(4l)





3-fluoro-4-(2-phenyl-1H-indol-1-yl)benzonitrile (6a)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7.103
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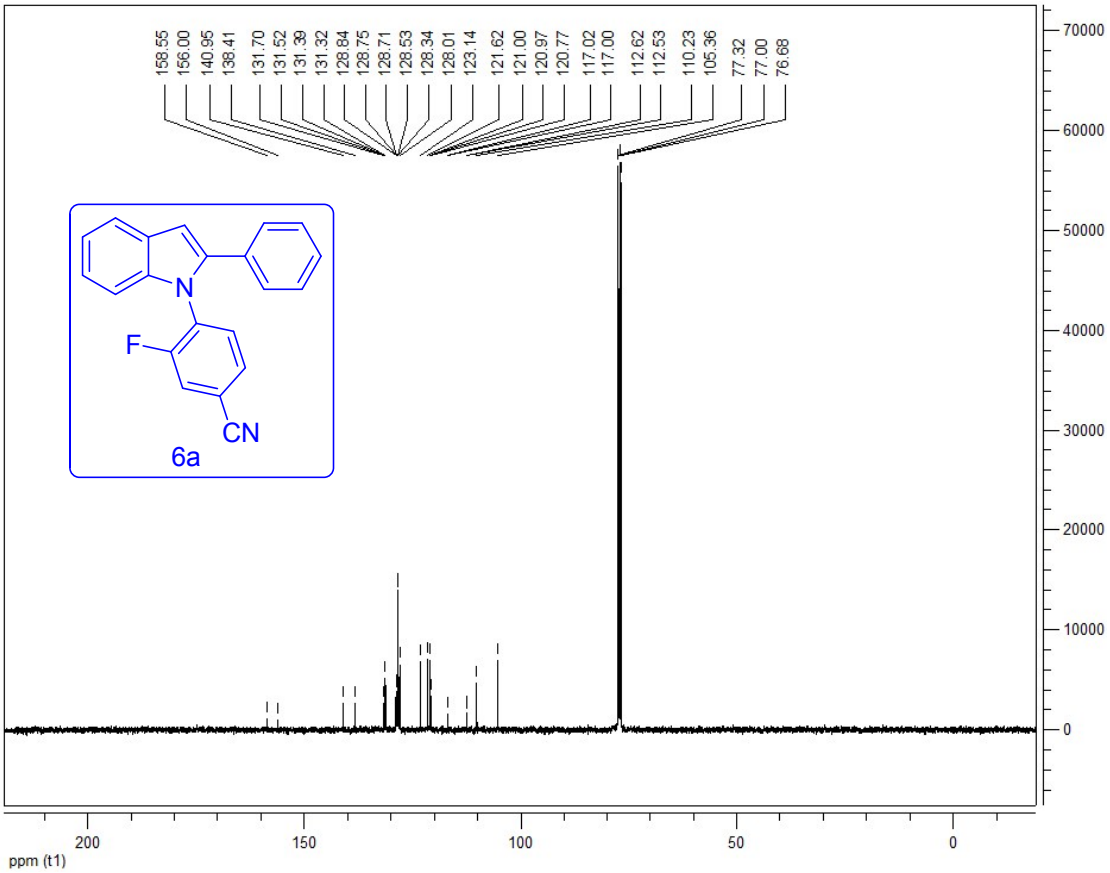
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128.34
128.01
123.14
121.62
121.00
120.97
120.77
117.02
117.00
112.62
112.53
110.23
105.36
77.32
77.00
76.68
70000
60000
50000
40000
30000
20000
10000
0
N
F
CN
6a
200
150
100
50
0
ppm (t1)