A concise synthesis of indole-fused azepino- and azocino-indoles via acid-catalyzed 1,2-migration

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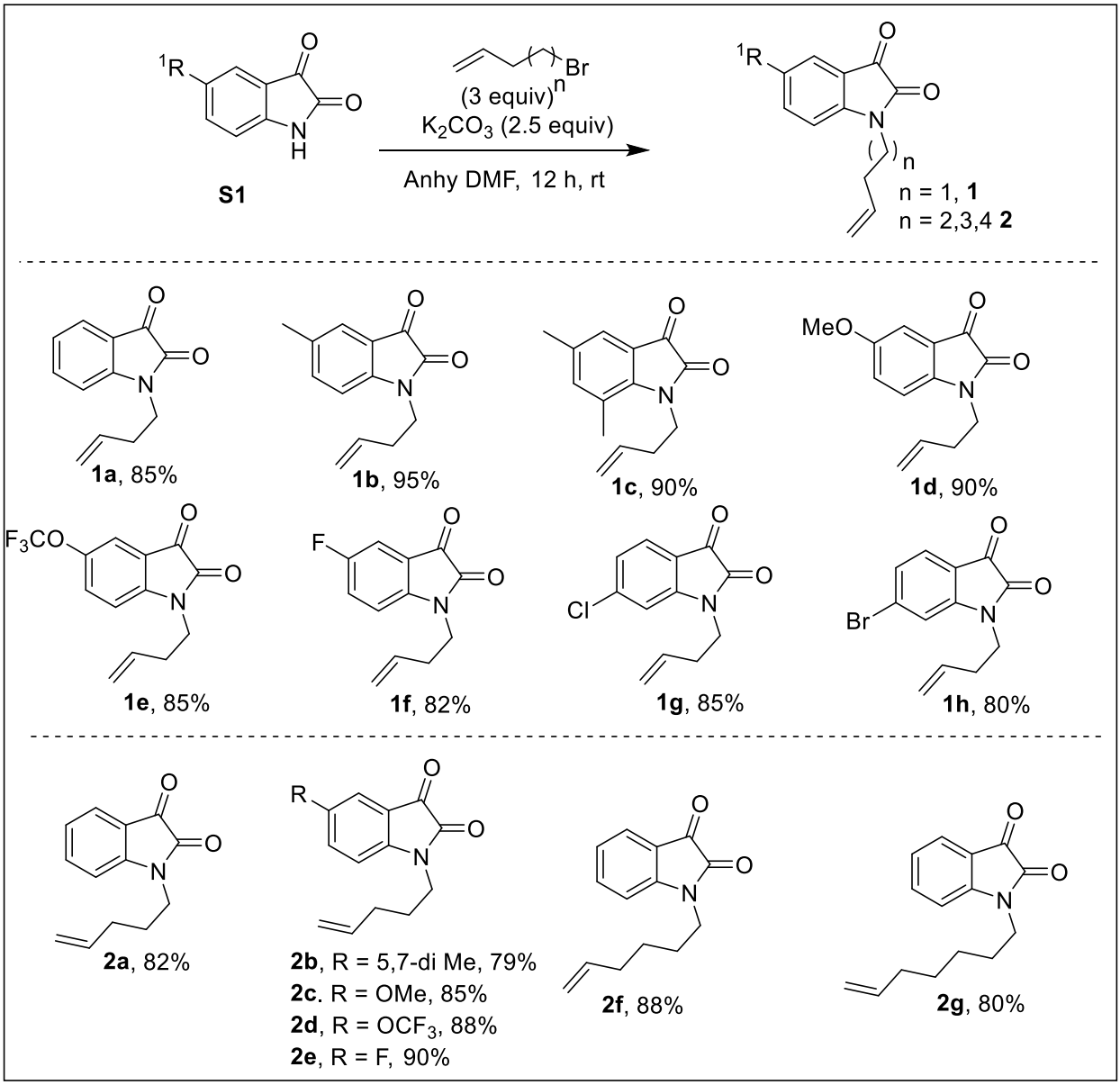
Contents

1.0 General information

All solvents and reagents were purified by standard techniques or used as supplied from commercial sources. All experiments were carried out under an inert atmosphere of argon in flame-dried flasks. TLC was performed on Kieselgel 60 F254 plates, and spots were visualized under UV light. Products were purified by column chromatography on silica gel (100-200 mesh). Unless otherwise stated, yields refer to analytical pure samples. NMR spectra were recorded in chloroform ($CDCl_3$) at 298K. ^1H spectra were recorded using 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, integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on 600 MHz (150 MHz), 400 MHz (100 MHz) instruments at 298K with complete proton decoupling. 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 instruments by +ve mode electrospray ionization. Single Crystal XRD was recorded on Micro-focus diffractometer equipped with PHOTON II Detector.

2.0 Synthesis of *N*-protected isatins

N-alkylated isatin derivatives **1a-h** and **2a-g** were prepared using reported procedures[1] from commercially available isatins **S1** by reaction with the corresponding alkyl bromides in the presence of K_2CO_3 in DMF at room temperature for 12 h (Scheme S1).

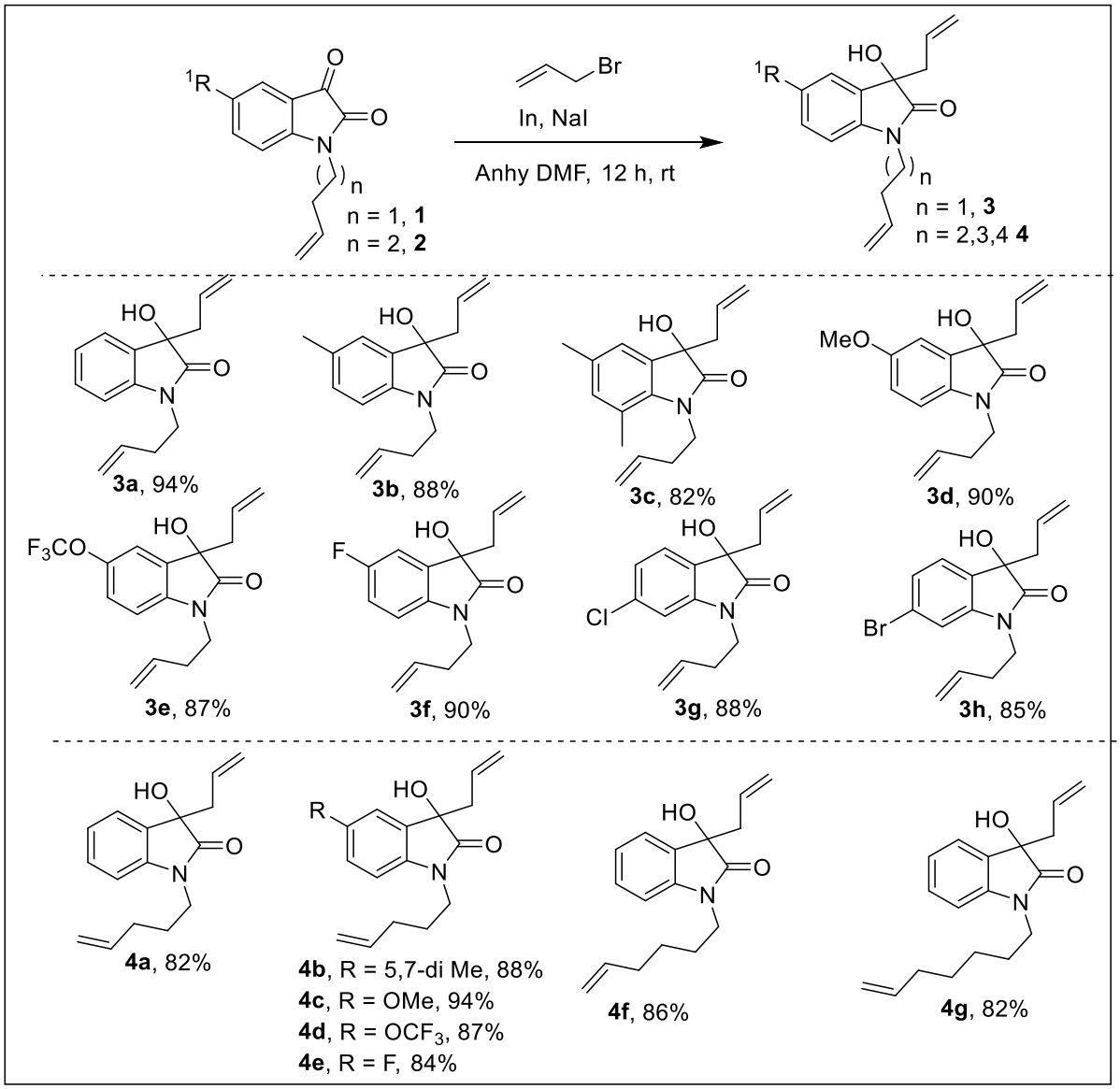


Scheme S1. Synthesis of *N*-protected isatins **1a-h** and **2a-g**.

3.0 General procedure for the preparation of 3-allyl-3-hydroxy 2-oxindole derivatives

Using reported procedures,[2] a mixture of indium metal (1.0 mmol, cut into small pieces), alkene-containing alkyl bromide (1.6 mmol), *N*-protected isatin **1** or **2** (0.8 mmol) and NaI (1.6

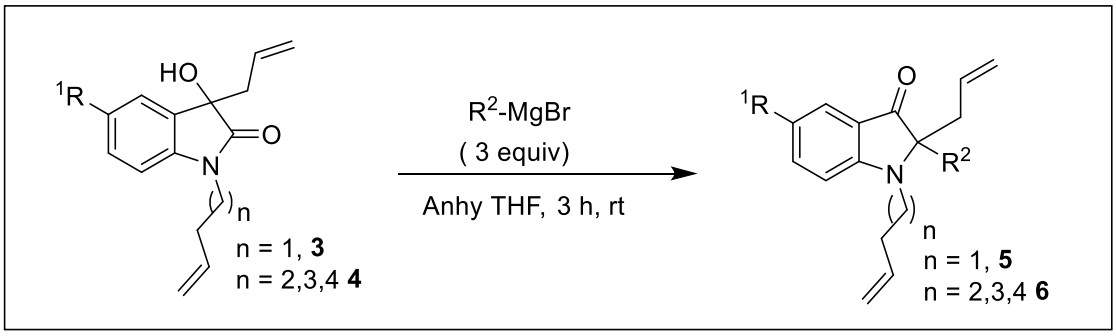
mmol) was stirred in DMF (6 mL) at rt until complete consumption of the isatin, as monitored by TLC. The reaction mixture was then quenched with a few drops of 1 N HCl and extracted with EtOAc (3 × 15 mL). The combined organic extracts were washed with aq. sat. $NaHCO_3$ solution (15 mL), brine (15 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography (30% EtOAc-hexane) to obtain the desired 3-allyl-3-hydroxy-2-oxindole derivatives **3a-h** or **4a-g** (Scheme S2).



Scheme S2. Synthesis of 3-allyl-3-hydroxy 2-oxindole derivatives **3a-h** and **4a-g**.

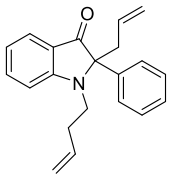
4. General procedure for the Grignard reaction of 3-allyl-3-hydroxy-2-oxindole derivatives (GP-1)

To a solution of 3-allyl-3-hydroxy 2-oxindole derivative **3** or **4** in anhydrous THF, alkyl/aryl magnesium bromide solution (3 equiv) was added dropwise at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 3 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was then purified by column chromatography on silica gel with EtOAc–hexane (5/95 to 10/90) as the eluent to afford compounds **5a-n** or **6a-a′′** (Scheme S3).



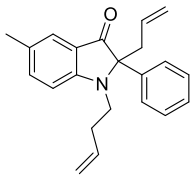
Scheme S3. Synthesis of 2-allyl-2-aryl/alkyl-3-oxindole **5a-n** and **6a-a′′.**

2-Allyl-1-benzyl-7-bromo-2-(but-3-en-1-yl)indolin-3-one **(5a):** Using the general procedure



GP-1, compound **3a** (400 mg, 1.64 mmol) and phenylmagnesium bromide (5.0 mL, 4.93 mmol) provided compound **5a** (409 mg, 90%) as a green fluorescent oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.32 – 7.24 (m, 5H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.76 – 6.72 (m, 1H), 5.81 – 5.70 (m, 1H), 5.63 – 5.53 (m, 1H), 5.24 (d, *J* = 17.0 Hz, 1H), 5.11 – 5.01 (m, 3H), 3.47 – 3.39 (m, 1H), 3.35 – 3.25 (m, 2H), 3.03 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.39 – 2.29 (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 201.1, 161.2, 137.9, 135.1, 131.9, 129.0, 128.1, 126.5, 125.4, 119.4, 119.3, 117.3, 117.1, 108.2, 75.9, 43.7, 38.0, 33.3; HRMS (ESI) calcd for $C_{21}H_{22}NO$ $[M+H]^+$: 304.1701; Found: 304.1702.

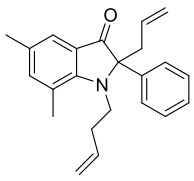
2-Allyl-1-(but-3-en-1-yl)-5-methyl-2-phenylindolin-3-one **(5b):** Using the general procedure



GP-1, compound **3b** (400 mg, 1.56 mmol) and phenylmagnesium bromide (4.7 mL, 4.67 mmol) provided compound **5b** (410 mg, 83%) as a green fluorescent oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.21 (d, *J* = 6.5 Hz, 2H), 6.79 (d, *J* = 8.4 Hz,

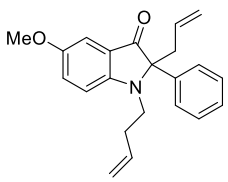
1H), 5.79 – 5.70 (m, 1H), 5.57 – 5.49 (m, 1H), 5.21 (d, *J* = 17.0 Hz, 1H), 5.09 – 5.01 (m, 3H), 3.41 – 3.35 (m, 1H), 3.30 – 3.21 (m, 2H), 2.98 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.35 – 2.26 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 159.8, 139.2, 138.0, 135.1, 131.9, 128.9, 128.0, 126.5, 126.4, 124.8, 119.3, 119.2, 116.9, 107.9, 76.1, 43.7, 37.9, 33.3, 20.4; HRMS (ESI) calcd for $C_{22}H_{24}NO$ $[M+H]^+$: 318.1858; Found: 318.1859.

2-Allyl-(but-3-en-1-yl)-5,7-dimethyl-2-phenylindolin-3-one **(5c):** Using the general procedure



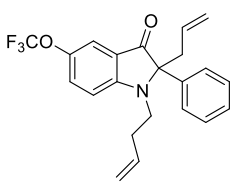
GP-1, compound **3c** (250 mg, 0.92 mmol) and phenylmagnesium bromide (2.8 mL, 2.75 mmol) provided compound **5c** (255 mg, 84%) as a green fluorescent oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 6H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.69 – 5.62 (m, 1H), 5.57 – 5.50 (m, 1H), 5.24 – 5.20 (m, 1H), 5.04 – 4.97 (m, 3H), 3.63 – 3.57 (m, 1H), 3.47 – 3.41 (m, 1H), 3.27 (dd, *J* = 14.2, 6.9 Hz, 1H), 3.01 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.58 (s, 3H), 2.40 – 2.31 (m, 1H), 2.26 (s, 3H), 2.14 – 2.05 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.8, 159.1, 143.3, 139.1, 135.1, 132.4, 130.2, 129.5, 128.7, 127.5, 127.3, 123.3, 121.0, 119.8, 119.5, 117.4, 116.0, 76.6, 44.7, 38.4, 36.9, 20.7, 20.4; HRMS (ESI) calcd for $C_{23}H_{26}NO$ $[M+H]^+$: 332.2014; Found: 332.2015.

2-Allyl-(but-3-en-1-yl)-5-methoxy-2-phenylindolin-3-one **(5d):** Using the general procedure



GP-1, compound **3d** (400 mg, 1.45 mmol) and phenylmagnesium bromide (4.4 mL, 4.37 mmol) provided compound **5d** (410 mg, 84%) as a green fluorescent oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ δ 7.35 – 7.28 (m, 3H), 7.25 – 7.21 (m, 3H), 7.07 (d, *J* = 2.8 Hz, 1H), 6.83 (dd, *J* = 8.7, 6.4 Hz, 1H), 5.78 – 5.70 (m, 1H), 5.58 – 5.49 (m, 1H), 5.22 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.09 – 5.02 (m, 3H), 3.78 (s, 3H), 3.41 – 3.34 (m, 1H), 3.31 – 3.21 (m, 2H), 2.99 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.38 – 2.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 157.6, 152.1, 137.8, 135.1, 131.8, 129.5, 128.9, 128.6, 128.0, 126.4, 119.3, 116.9, 109.3, 105.4, 76.5, 55.8, 43.8, 38.0, 33.6.; HRMS (ESI) calcd for $C_{22}H_{24}NO_2$ $[M+H]^+$: 334.1807; Found: 334.1808.

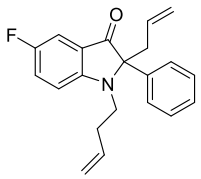
2-Allyl-(but-3-en-1-yl)-2-phenyl-5-(trifluoromethoxy)indolin-3-one **(5e):** Using the general



procedure **GP-1**, compound **3e** (400 mg, 1.22 mmol) and phenylmagnesium bromide (3.7 mL, 3.67 mmol) provided compound **5e** (350 mg, 74%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 2.4, 1.1 Hz, 1H), 7.39 – 7.29 (m, 4H), 7.19 (dd, *J* = 7.7, 2.0 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 1H), 5.78 – 5.64 (m, 1H), 5.58 – 5.44 (m, 1H), 5.24 – 5.17 (m, 1H), 5.09 – 5.02 (m, 3H), 3.43 – 3.20 (m, 3H), 2.98 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.39

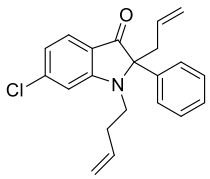
– 2.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 160.1, 141.0, 137.7, 135.3, 132.1, 131.9, 129.7, 129.0, 127.0, 123.0, 120.4, 119.9, 118.4, 117.9, 109.3, 77.5, 44.3, 38.6, 33.7; HRMS (ESI) calcd for $C_{22}H_{21}F_3NO_2$ $[M+H]^+$: 388.1524; Found: 388.1525.

2-Allyl-1-(but-3-en-1-yl)-5-fluoro-2-phenylindolin-3-one **(5f):** Using the general procedure



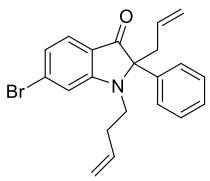
GP-1, compound **3f** (500 mg, 1.91 mmol) and phenylmagnesium bromide (5.8 mL, 5.74 mmol) provided compound **5f** (450 mg, 73%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 7.22 – 7.19 (m, 2H), 6.80 (dd, J = 8.8, 3.6 Hz, 1H), 5.80 – 5.66 (m, 1H), 5.59 – 5.45 (m, 1H), 5.25 – 5.17 (m, 1H), 5.11 – 5.01 (m, 3H), 3.43 – 3.19 (m, 3H), 3.02 – 2.94 (m, 1H), 2.36 – 2.24 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 156.1 (d, $J_{C\text{-}F}$ = 237.9 Hz), 154.6, 138.1, 135.5, 132.1, 129.6, 128.9, 127.0, 126.5, 126.1, 120.2, 119.9 (d, $J_{C\text{-}F}$ = 6.9 Hz), 117.8, 111.0, 110.7, 109.38 (d, $J_{C\text{-}F}$ = 7.3 Hz), 77.4, 44.4, 38.7, 33.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -127.67; HRMS (ESI) calcd for $C_{21}H_{21}FNO$ $[M+H]^+$: 322.1607; Found: 322.1608.

2-Allyl-1-(but-3-en-1-yl)-6-chloro-2-phenylindolin-3-one **(5g):** Using the general procedure



GP-1, compound **3g** (400 mg, 1.44 mmol) and phenylmagnesium bromide (4.4 mL, 4.33 mmol) provided compound **5g** (414 mg, 85%) as a green fluorescent oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 1H), 7.35 – 7.31 (m, 3H), 7.22 (d, J = 7.5 Hz, 2H), 6.86 (s, 1H), 6.74 (d, J = 8.1 Hz, 1H), 5.78 – 5.69 (m, 1H), 5.58 – 5.49 (m, 1H), 5.23 (d, J = 17.0 Hz, 1H), 5.10 – 5.04 (m, 3H), 3.41 – 3.34 (m, 1H), 3.31 – 3.23 (m, 2H), 3.00 (dd, J = 14.3, 6.9 Hz, 1H), 2.38 – 2.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 161.3, 144.4, 137.3, 134.7, 131.4, 129.0, 128.3, 126.4, 126.3, 119.7, 118.0, 118.0, 117.3, 108.1, 76.5, 43.6, 37.8, 33.0; HRMS (ESI) calcd for $C_{21}H_{21}ClNO$ $[M+H]^+$: 338.1312; Found: 338.1313.

2-Allyl-1-(but-3-en-1-yl)-6-chloro-2-phenylindolin-3-one **(5h):** Using the general procedure



GP-1, compound **3h** (600 mg, 1.57 mmol) and phenylmagnesium bromide (4.72 mL, 4.72 mmol) provided compound **5h** (580 mg, 82%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.19 (dd, J = 7.8, 2.0 Hz, 2H), 7.02 (d, J = 1.5 Hz, 1H), 6.87 (dd, J = 8.2, 1.5 Hz, 1H), 5.78 – 5.64 (m, 1H), 5.58 – 5.44 (m, 1H), 5.24 – 5.17 (m, 1H), 5.10 – 5.00 (m, 3H), 3.40 – 3.18 (m, 3H), 2.97 (dd, J = 14.3, 6.8 Hz, 1H), 2.36 – 2.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.04 161.3, 137.2, 134.6, 133.4, 131.3, 129.0, 128.3,

126.4, 126.3, 120.8, 119.8, 118.3, 117.3, 111.1, 76.4, 43.6, 37.8, 32.9; HRMS (ESI) calcd for $C_{21}H_{21}BrNO$ $[M+H]^+$: 382.0807; Found: 382.0808.

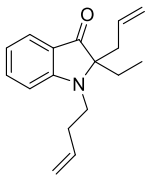
2-Allyl-1-(but-3-en-1-yl)-2-(4-methoxyphenyl)indolin-3-one **(5i):** Using the general procedure **GP-1**, compound **3a** (300 mg, 1.23 mmol) and 4-methoxyphenylmagnesium bromide (3.7 mL, 3.70 mmol) provided compound **5i** (324 mg, 79%) as a green fluorescent oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.15 (dd, *J* = 12.5, 8.7 Hz, 2H), 6.85 (dd, *J* = 9.3, 7.2 Hz, 3H), 6.75 (t, *J* = 7.4 Hz, 1H), 5.79 – 5.72 (m, 1H), 5.56 – 5.50 (m, 1H), 5.22 – 5.19 (m, 1H), 5.10 – 5.01 (m, 3H), 3.79 (s, 3H), 3.40 – 3.35 (m, 1H), 3.30 – 3.23 (m, 2H), 2.96 (dd, *J* = 14.1, 6.8 Hz, 1H), 2.38 – 2.25 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.6, 161.1, 159.4, 137.7, 135.1, 131.8, 129.7, 127.7, 125.4, 119.3, 117.1, 117.0, 114.3, 108.7, 108.0, 75.5, 55.3, 43.5, 38.0, 33.2; HRMS (ESI) calcd for $C_{22}H_{24}NO_2$ $[M+H]^+$: 334.1807; Found: 334.1808.

2-Allyl-2-(benzo[d][1,3]dioxol-5-yl)-1-(but-3-en-1-yl)indolin-3-one **(5j):** Using the general procedure **GP-1**, compound **3a** (300 mg, 1.23 mmol) and benzo[d][1,3]dioxol-5-ylmagnesium bromide (3.7 mL, 3.70 mmol) provided compound **5j** (385 mg, 90%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 6.85 (t, *J* = 9.7 Hz, 1H), 6.77 – 6.63 (m, 4H), 5.92 (d, *J* = 5.1 Hz, 2H), 5.82 – 5.69 (m, 1H), 5.57 – 5.43 (m, 1H), 5.21 – 4.98 (m, 4H), 3.42 – 3.15 (m, 3H), 2.93 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.40 – 2.26 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 161.1, 148.2, 147.5, 137.8, 135.0, 131.6, 131.5, 125.4, 119.9, 119.4, 119.2, 117.2, 117.0, 108.5, 108.0, 106.9, 101.2, 75.5, 43.5, 38.1, 33.2; HRMS (ESI) calcd for $C_{22}H_{22}NO_3$ $[M+H]^+$: 348.1600; Found: 348.1601

2-Allyl-1-(but-3-en-1-yl)-2-(thiophen-2-yl)indolin-3-one **(5k):** Using the general procedure **GP-1**, compound **3a** (300 mg, 1.23 mmol) and thiophen-2-ylmagnesium bromide (3.7 mL, 3.70 mmol) provided compound **5k** (260 mg, 68%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.1 Hz, 1H), 7.22 (dd, *J* = 4.4, 1.9 Hz, 1H), 6.99 – 6.96 (m, 2H), 6.89 – 6.74 (m, 2H), 5.90 – 5.71 (m, 1H), 5.58 – 5.44 (m, 1H), 5.25 – 5.00 (m, 4H), 3.44 – 3.36 (m, 2H), 3.23 (dd, *J* = 14.3, 6.8 Hz, 1H), 3.01 (dd, *J* = 14.4, 6.9 Hz, 1H), 2.41 – 2.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 160.4, 141.8, 137.9, 135.0, 131.2, 127.2, 125.6, 125.3,

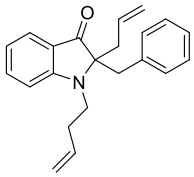
125.2, 119.7, 118.7, 117.6, 117.0, 108.4, 73.8, 43.5, 39.6, 33.2; HRMS (ESI) calcd for $C_{19}H_{20}NOS$ $[M+H]^+$: 310.2264; Found: 310.2265.

2-Allyl-1-(but-3-en-1-yl)-2-ethylindolin-3-one **(5l):** Using the general procedure **GP-1**,



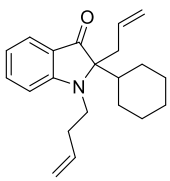
compound **3a** (250 mg, 1.02 mmol) and ethylmagnesium bromide (3.1 mL, 3.1 mmol) provided compound **5l** (199 mg, 76%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 8.3 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 5.95 – 5.81 (m, 1H), 5.44 – 5.01 (m, 4H), 4.89 (d, *J* = 9.3 Hz, 1H), 3.38 (t, *J* = 7.9 Hz, 2H), 2.63 – 2.39 (m, 4H), 1.91 (dt, *J* = 14.7, 7.3 Hz, 1H), 1.76 – 1.66 (m, 2H), 0.60 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.4, 160.9, 137.5, 135.0, 131.8, 124.3, 120.6, 118.5, 117.1, 116.5, 108.0, 74.5, 42.2, 40.9, 33.6, 29.0, 7.7; HRMS (ESI) calcd for $C_{17}H_{22}NO$ $[M+H]^+$: 256.1701; Found: 256.1702.

2-Allyl-2-benzyl-1-(but-3-en-1-yl)indolin-3-one **(5m):** Using the general procedure **GP-1**,



compound **3a** (300 mg, 1.23 mmol) and phenylmagnesium bromide (3.70 mL, 3.70 mmol) provided compound **5m** (266 mg, 68%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.08 – 6.98 (m, 5H), 6.58 – 6.52 (m, 2H), 5.92 – 5.78 (m, 1H), 5.56 – 5.42 (m, 1H), 5.21 – 5.08 (m, 3H), 4.99 – 4.95 (m, 1H), 3.54 – 3.34 (m, 2H), 3.23 (d, *J* = 14.0 Hz, 1H), 2.96 (d, *J* = 14.0 Hz, 1H), 2.73 (dd, *J* = 15.0, 7.6 Hz, 1H), 2.60 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.51 – 2.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 160.3, 137.3, 135.1, 134.9, 131.7, 129.6, 127.8, 126.6, 124.2, 120.6, 119.0, 117.2, 116.5, 108.0, 74.7, 42.8, 41.8, 40.8, 33.3; HRMS (ESI) calcd for $C_{22}H_{24}NO$ $[M+H]^+$: 318.1858; Found: 318.1859.

2-Allyl-1-(but-3-en-1-yl)-2-cyclohexylindolin-3-one **(5n):** Using the general procedure **GP-1**,



compound **3a** (300 mg, 1.23 mmol) and cyclohexylmagnesium bromide (3.70 mL, 3.70 mmol) provided compound **5n** (301 mg, 76%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 6.77 – 6.64 (m, 2H), 5.95 – 5.81 (m, 1H), 5.32 – 5.00 (m, 4H), 4.88 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.39 – 3.34 (m, 1H), 2.75 (dd, *J* = 14.3, 6.4 Hz, 1H), 2.58 – 2.36 (m, 3H), 1.81 – 1.56 (m, 9H), 1.24 – 1.08 (m, 3H), 0.94 – 0.80 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 203.5, 160.8, 137.3, 135.0, 132.3, 124.1, 120.9, 118.4, 117.1, 116.4, 107.8, 76.3, 44.5, 42.7, 38.2, 33.2, 27.1, 26.6, 26.6, 26.2, 25.5; HRMS (ESI) calcd for $C_{21}H_{28}NO$ $[M+H]^+$: 310.2171; Found: 310.2172.

2-Allyl-1-(pent-4-en-1-yl)-2-phenylindolin-3-one **(6a):** Using the general procedure **GP-1**, compound **4a** (400 mg, 1.56 mmol) and phenylmagnesium bromide (4.7 mL, 4.6 mmol) provided compound **6a** (299 mg, 88%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.25 – 7.17 (m, 3H), 7.12 (dd, *J* = 7.8, 1.9 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.64 (t, *J* = 7.1 Hz, 1H), 5.74 – 5.60 (m, 1H), 5.50 – 5.37 (m, 1H), 5.14 – 5.07 (m, 1H), 4.95 – 4.88 (m, 3H), 3.29 – 3.04 (m, 3H), 2.88 (dd, *J* = 14.2, 6.7 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.68 – 1.52 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.4, 161.5, 138.0, 137.9, 137.5, 131.9, 129.0, 128.2, 126.6, 125.6, 119.4, 119.4, 117.2, 115.6, 108.1, 76.1, 43.6, 38.1, 31.4, 27.9; HRMS (ESI) calcd for $C_{22}H_{24}NO$ $[M+H]^+$: 318.1858; Found: 318.1859.

2-Allyl-5,7-dimethyl-1-(pent-4-en-1-yl)-2-phenylindolin-3-one **(6b):** Using the general procedure **GP-1**, compound **4b** (300 mg, 1.10 mmol) and phenylmagnesium bromide (3.3 mL, 3.30 mmol) provided compound **6b** (276 mg, 76%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 6H), 7.10 (s, 1H), 5.75 – 5.47 (m, 2H), 5.23 – 5.17 (m, 1H), 5.03 – 4.91 (m, 3H), 3.58 – 3.48 (m, 1H), 3.37 – 3.21 (m, 2H), 2.98 (dd, *J* = 14.2, 6.5 Hz, 1H), 2.54 (s, 3H), 2.23 (s, 3H), 1.97 – 1.89 (m, 2H), 1.80 – 1.64 (m, 1H), 1.55 – 1.40 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.1, 158.8, 142.6, 138.7, 137.4, 131.9, 128.9, 128.1, 126.7, 126.7, 122.7, 120.7, 119.2, 118.9, 115.4, 76.1, 44.5, 37.9, 31.2, 31.1, 20.1, 20.0; HRMS (ESI) calcd for $C_{24}H_{28}NO$ $[M+H]^+$: 346.2171; Found: 346.2172.

2-Allyl-5-methoxy-1-(pent-4-en-1-yl)-2-phenylindolin-3-one **(6c):** Using the general procedure **GP-1**, compound **4c** (300 mg, 1.04 mmol) and phenylmagnesium bromide (3.13 mL, 3.13 mmol) provided compound **6c** (290 mg, 80%) as a green fluorescent oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 3H), 7.23 – 7.20 (m, 3H), 7.05 (d, *J* = 2.7 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 1H), 5.80 – 5.72 (m, 1H), 5.56 – 5.48 (m, 1H), 5.21 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.03 – 4.99 (m, 3H), 3.78 (s, 3H), 3.34 – 3.25 (m, 2H), 3.19 – 3.13 (m, 1H), 2.96 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.03 (q, *J* = 7.2 Hz, 2H), 1.71 – 1.63 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 157.7, 152.0, 138.0, 137.5, 131.9, 128.9, 128.5, 128.0, 126.4, 119.2, 118.8, 115.4, 109.2, 105.4, 76.5, 55.9, 43.6, 38.0, 31.2, 28.1; HRMS (ESI) calcd for $C_{23}H_{26}NO_2$ $[M+H]^+$: 348.1964; Found: 348.1965.

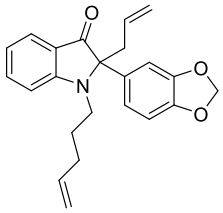
2-Allyl-1-(pent-4-en-1-yl)-2-phenyl-5-(trifluoromethoxy)indolin-3-one **(6d):** Using the general procedure **GP-1**, compound **4d** (300 mg, 0.88 mmol) and phenylmagnesium bromide (2.64 mL, 2.64 mmol) provided compound **6d** (254 mg, 72%) as a green fluorescent oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.5 Hz, 1H), 7.39 – 7.31 (m, 4H), 7.22 (d, *J* = 6.9 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 1H), 5.80 – 5.73 (m, 1H), 5.56 – 5.49 (m, 1H), 5.23 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.06 – 5.01 (m, 3H), 3.37 – 3.31 (m, 1H), 3.28 (dd, *J* = 14.2, 6.9 Hz, 1H), 3.23 – 3.18 (m, 1H), 2.99 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.06 – 2.02 (m, 2H), 1.75 – 1.60 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.6, 159.6, 140.2, 137.2, 137.1, 131.5, 131.3, 129.0, 128.3, 126.3, 120.6 (q, J_{C-F} = 256.7 Hz), 119.7, 119.2, 117.8, 115.7, 108.6, 76.9, 43.5, 38.0, 31.1, 27.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -58.67; HRMS (ESI) calcd for $C_{23}H_{23}F_3NO_2$ $[M+H]^+$: 402.1681; Found: 402.1682.

2-Allyl-5-fluoro-1-(pent-4-en-1-yl)-2-phenylindolin-3-one **(6e):** Using the general procedure **GP-1**, compound **4e** (400 mg, 1.45 mmol) and phenylmagnesium bromide (4.36 mL, 4.36 mmol) provided compound **6e** (365 mg, 75%) as a green fluorescent oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 7.23 – 7.21 (m, 2H), 6.80 – 6.78 (m, 1H), 5.80 – 5.74 (m, 1H), 5.56 – 5.49 (m, 1H), 5.22 (d, *J* = 17.1 Hz, 1H), 5.05 – 5.01 (m, 3H), 3.35 – 3.26 (m, 2H), 3.21 – 3.16 (m, 1H), 2.98 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.04 (q, *J* = 7.1 Hz, 2H), 1.73 – 1.61 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.0, 158.3, 155.4 (d, J_{C-F} = 237.7 Hz), 137.55 (d, J_{C-F} = 5.1 Hz), 137.3, 131.5, 129.0, 128.2, 126.4, 125.71 (d, J_{C-F} = 25.1 Hz), 119.6, 119.1, 115.6, 110.14 (d, J_{C-F} = 22.8 Hz), 108.7 (d, J_{C-F} = 7.5 Hz), 76.7, 43.6, 38.0, 31.2, 27.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -127.84; HRMS (ESI) calcd for $C_{22}H_{23}FNO$ $[M+H]^+$: 336.1764; Found: 336.1765.

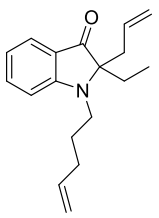
2-Allyl-2-(4-methoxyphenyl)-1-(pent-4-en-1-yl)indolin-3-one **(6f):** Using the general procedure **GP-1**, compound **4a** (300 mg, 1.16 mmol) and phenylmagnesium bromide (3.50 mL, 3.50 mmol) provided compound **6f** (303 mg, 75%) as a green fluorescent oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.84 (dd, *J* = 14.4, 8.7 Hz, 3H), 6.73 (t, *J* = 7.4 Hz, 1H), 5.84 – 5.73 (m, 1H), 5.58 – 5.48 (m, 1H), 5.23 – 5.17 (m, 1H), 5.05 – 4.99 (m, 3H), 3.78 (s, 3H), 3.36 – 3.16 (m, 3H), 2.95 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.05 (q, *J* = 7.3 Hz, 2H), 1.74 – 1.63 (m,

2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.6, 161.3, 159.3, 137.7, 137.4, 131.8, 129.8, 127.7, 125.4, 119.2, 116.9, 115.5, 114.3, 107.9, 75.5, 55.3, 43.3, 38.0, 31.3, 27.8; HRMS (ESI) calcd for $C_{23}H_{26}NO_2$ $[M+H]^+$: 348.1964; Found: 348.1965.

2-Allyl-2-(benzo[d][1,3]dioxol-5-yl)-1-(pent-4-en-1-yl)indolin-3-one **(6g):** Using the general procedure **GP-1**, compound **4a** (150 mg, 0.58 mmol) and benzo[d][1,3]dioxol-5-ylmagnesium bromide (1.74 mL, 1.74 mmol) provided compound **6g** (179 mg, 85%) as a green fluorescent oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.1 Hz, 1H), 6.81 – 6.70 (m, 4H), 6.63 (d, *J* = 1.6 Hz, 1H), 5.92 (d, *J* = 4.0 Hz, 2H), 5.85 – 5.72 (m, 1H), 5.56 – 5.42 (m, 1H), 5.21 – 5.14 (m, 1H), 5.06 – 4.97 (m, 3H), 3.36 – 3.13 (m, 3H), 2.90 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.05 (q, *J* = 7.2 Hz, 2H), 1.74 – 1.63 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.3, 161.2, 148.1, 147.4, 137.8, 137.4, 131.6, 131.5, 125.4, 119.9, 119.3, 119.1, 117.1, 115.5, 108.5, 107.9, 106.9, 101.2, 75.5, 43.3, 38.1, 31.3, 27.8; HRMS (ESI) calcd for $C_{23}H_{24}NO_3$ $[M+H]^+$: 362.1756; Found: 362.1757.



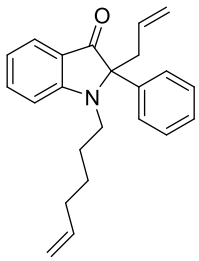
2-Allyl-2-ethyl-1-(pent-4-en-1-yl)indolin-3-one **(6h):** Using the general procedure **GP-1**, compound **4a** (300 mg, 1.16 mmol) and ethylmagnesium bromide (3.50 mL, 3.50 mmol) provided compound **6h** (226 mg, 72%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.62 (t, *J* = 7.4 Hz, 1H), 5.91 – 5.77 (m, 1H), 5.40 – 5.26 (m, 1H), 5.11 – 4.95 (m, 3H), 4.84 (dd, *J* = 10.0, 1.2 Hz, 1H), 3.28 (t, *J* = 8.0 Hz, 2H), 2.54 (dd, *J* = 14.3, 6.9 Hz, 1H), 2.40 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.15 (q, *J* = 7.2 Hz, 2H), 1.91 – 1.62 (m, 4H), 0.55 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.4, 161.0, 137.4, 137.4, 131.9, 124.2, 120.5, 118.4, 116.3, 115.6, 107.9, 74.5, 41.9, 40.9, 31.4, 29.0, 28.1, 7.7; HRMS (ESI) calcd for $C_{18}H_{24}NO$ $[M+H]^+$: 270.1858; Found: 270.1859.



2-Allyl-2-benzyl-1-(pent-4-en-1-yl)indolin-3-one **(6i):** Using the general procedure **GP-1**, compound **4a** (350 mg, 1.36 mmol) and phenylmagnesium bromide (4.1 mL, 4.08 mmol) provided compound **6i** (293 mg, 65%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.06 – 6.97 (m, 5H), 6.53 (t, *J* = 7.8 Hz, 2H), 5.92 – 5.78 (m, 1H), 5.53 – 5.40 (m, 1H), 5.13 – 5.04 (m, 3H), 4.98 – 4.93 (m, 1H), 3.46 – 3.18 (m, 2H), 3.20 (d, *J* = 14.0 Hz, 1H), 2.94 (d, *J* = 14.1 Hz, 1H), 2.71 (dd, *J*

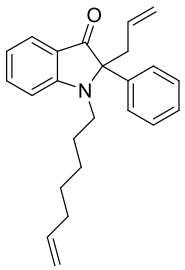
= 14.4, 7.1 Hz, 1H), 2.57 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.14 (q, *J* = 7.3 Hz, 2H), 1.85 – 1.68 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.3, 161.1, 138.0, 137.9, 135.8, 132.3, 130.2, 128.4, 127.2, 124.9, 121.1, 119.5, 117.0, 116.3, 108.5, 75.3, 43.3, 42.4, 41.4, 32.0, 28.5; HRMS (ESI) calcd for $C_{23}H_{26}NO$ $[M+H]^+$: 332.2014; Found: 332.2015.

2-Allyl-1-(hex-5-en-1-yl)-2-phenylindolin-3-one **(6a′):** Using the general procedure **GP-1**,



compound **4f** (300 mg, 1.11 mmol) and phenylmagnesium bromide (3.50 mL, 3.32 mmol) provided compound **6a′** (285 mg, 78%) as a green fluorescent oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.25 – 7.23 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 5.82 – 5.74 (m, 1H), 5.60 – 5.52 (m, 1H), 5.23 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.05 – 4.98 (m, 3H), 3.37 – 3.28 (m, 2H), 3.23 – 3.17 (m, 1H), 3.00 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.08 – 2.04 (m, 2H), 1.66 – 1.60 (m, 2H), 1.43 – 1.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.3, 161.4, 138.2, 137.9, 137.8, 131.8, 128.9, 128.0, 126.4, 125.4, 119.3, 119.2, 117.0, 115.0, 108.0, 76.0, 43.9, 38.0, 33.3, 28.2, 26.5; HRMS (ESI) calcd for $C_{23}H_{26}NO$ $[M+H]^+$: 332.2014; Found: 332.2015.

2-Allyl-1-(hept-6-en-1-yl)-2-phenylindolin-3-one **(6a″):** Using the general procedure **GP-1**,

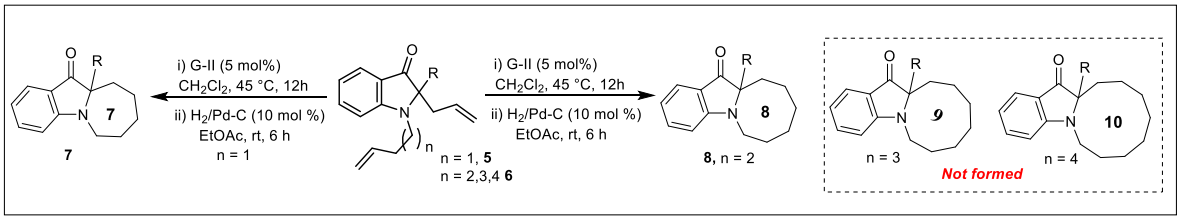


compound **4g** (300 mg, 1.05 mmol) and phenylmagnesium bromide (3.2 mL, 3.16 mmol) provided compound **6a″** (225 mg, 84%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.24 – 7.19 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 5.86 – 5.73 (m, 1H), 5.61 – 5.47 (m, 1H), 5.22 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.04 – 4.95 (m, 3H), 3.37 – 3.12 (m, 3H), 2.98 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.07 – 1.99 (m, 2H), 1.66 – 1.54 (m, 2H), 1.42 – 1.25 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 161.5, 138.6, 137.8, 137.8, 131.8, 129.4, 128.9, 128.0, 126.4, 125.5, 119.3, 119.1, 117.0, 115.4, 114.6, 108.0, 76.0, 44.1, 37.9, 33.6, 28.6, 28.5, 26.7; HRMS (ESI) calcd for $C_{24}H_{28}NO$ $[M+H]^+$: 346.2171; Found: 346.2172.

5.0 General procedure for the synthesis of azepino[1,2-a]indolones 7a-n and azocino[1,2-a]indolones 8a-i (GP-2)

To a solution of compound **5** or **6** (1.0 equiv) in anhydrous CH_2Cl_2 (10 mL) was added Grubbs second-generation catalyst (G-II)[3] (5 mol%), and the reaction mixture was stirred at 45 °C for 12 h. After completion, the reaction mixture was concentrated *in vacuo*.

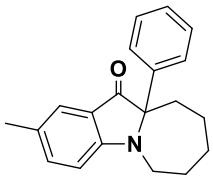
The crude residue was then dissolved in EtOAc (10 mL), and Pd/C (10 mol%) was added. The resulting suspension was stirred at room temperature under an atmosphere of hydrogen for 6 h. After completion of the reaction (monitored by TLC), the mixture was filtered through a Celite pad and washed with ethyl acetate. The filtrate was concentrated *in vacuo*, and the crude product was purified by silica gel column chromatography using EtOAc/hexane (5:95 to 10:90) as the eluent to afford the corresponding azepino[1,2-a]indolones **7a-n** or azocino[1,2-a]indolones **8a-i** (Scheme S4).



Scheme S4. Synthesis of azepino[1,2-a]indolones **7a-n** and azocino[1,2-a]indolones **8a-i**.

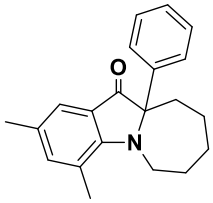
10a-Phenyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one **(7a):** Using the general procedure **GP-2,** compound **5a** (200 mg, 0.67 mmol) and **G-II** (28 mg, 0.03 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 20 mg) provided compound **7a** (137 mg, 75%) as a green fluorescent oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.43 – 7.40 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.1 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 4.06 (d, *J* = 14.9 Hz, 1H), 3.31 – 3.24 (m, 1H), 3.06 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.05 (dd, *J* = 14.2, 11.1 Hz, 1H), 1.90 – 1.80 (m, 2H), 1.75 – 1.66 (m, 2H), 1.39 – 1.27 (m, 1H), 1.03 – 0.89 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 160.7, 140.0, 137.5, 128.8, 127.5, 125.6, 119.1, 117.0, 108.8, 76.1, 43.1, 39.0, 30.3, 26.1, 23.6; HRMS (ESI) calcd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1545; Found: 278.1546.

2-Methyl-10a-phenyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one **(7b):**



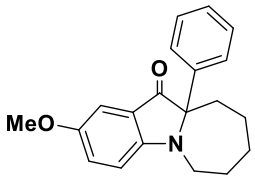
Using the general procedure **GP-2,** compound **5b** (150 mg, 0.47 mmol) and **G-II** (20 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 15 mg) provided compound **7b** (125 mg, 76%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 7H), 6.84 (d, *J* = 8.9 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.26 – 3.17 (m, 1H), 3.03 (dd, *J* = 14.5, 8.2 Hz, 1H), 2.26 (s, 3H), 2.05 – 1.95 (m, 1H), 1.83 – 1.61 (m, 4H), 1.31 – 1.25 (m, 1H), 0.96 – 0.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 159.4, 140.4, 139.1, 128.8, 127.5, 126.4, 125.7, 125.0, 119.3, 108.8, 76.4, 43.2, 39.2, 30.4, 26.2, 23.7, 20.5; HRMS (ESI) calcd for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1701; Found:292.1702.

2,4-Dimethyl-10a-phenyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one **(7c):**

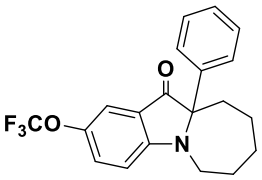


Using the general procedure **GP-2,** compound **5c** (150 mg, 0.45 mmol) and **G-II** (19 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 15 mg) provided compound **7c** (103 mg, 75%) as a green fluorescent oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.34 – 7.23 (m, 4H), 7.12 (s, 1H), 4.39 – 4.31 (m, 1H), 3.23 – 3.10 (m, 2H), 2.55 (s, 3H), 2.24 (s, 3H), 1.94 (dd, *J* = 14.4, 11.3 Hz, 1H), 1.81 – 1.57 (m, 5H), 1.31 – 1.19 (m, 1H), 0.93 – 0.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.4, 159.1, 142.4, 141.2, 129.3, 128.0, 127.9, 126.3, 123.3, 121.7, 121.1, 77.5, 45.4, 39.9, 30.2, 29.7, 24.1, 21.2, 20.8; HRMS (ESI) calcd for $C_{21}H_{24}NO$ $[M+H]^+$: 306.1858; Found: 306.1859.

2-Methoxy-10a-phenyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one **(7d):**

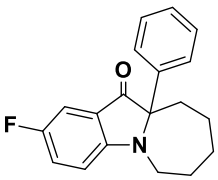


Using the general procedure **GP-2,** compound **5d** (210 mg, 0.63 mmol) and **G-II** (27 mg, 0.03 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 21 mg) provided compound **7d** (156 mg, 81%) as a green fluorescent oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.01 (d, *J* = 2.8 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 4.02 (d, *J* = 15.0 Hz, 1H), 3.75 (s, 3H), 3.28 – 3.23 (m, 1H), 3.03 (dd, *J* = 14.3, 8.2 Hz, 1H), 2.02 (dd, *J* = 14.0, 11.3 Hz, 1H), 1.81 (d, *J* = 12.0 Hz, 2H), 1.72 – 1.64 (m, 2H), 0.94 – 0.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 157.7, 152.6, 140.9, 129.4, 129.0, 128.0, 126.2, 119.4, 110.8, 106.1, 77.3, 56.5, 43.9, 39.8, 30.9, 26.9, 24.2; HRMS (ESI) calcd for $C_{20}H_{22}NO_2$ $[M+H]^+$: 308.1651; Found: 308.1652.

***10a-Phenyl-2-(trifluoromethoxy)-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one* (7e):** 

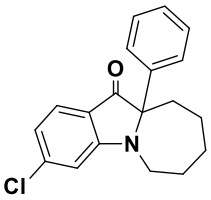
Using the general procedure **GP-2,** compound **5e** (150 mg, 0.46 mmol) and **G-II** (20 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 15 mg) provided compound **7e** (105 mg, 75%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 7H), 6.91 (d, *J* = 9.1 Hz, 1H), 4.04 (d, *J* = 15.0 Hz, 1H), 3.34 – 3.25 (m, 1H), 3.04 (dd, *J* = 14.5, 8.1 Hz, 1H), 2.05 (dd, *J* = 14.4, 10.7 Hz, 1H), 1.90 – 1.79 (m, 2H), 1.78 – 1.67 (m, 2H), 1.41 – 1.26 (m, 1H), 1.00 – 0.91 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.7, 159.6, 140.9, 140.0, 131.9, 129.5, 128.4, 126.1, 123.1, 121.4 (q, *J* = 255.2 Hz), 119.8, 118.7, 109.9, 44.0, 39.7, 30.8, 26.7, 24.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.03; HRMS (ESI) calcd for $C_{20}H_{19}F_3NO_2$ $[M+H]^+$: 362.1368; Found: 362.1369.

***2-Fluoro-10a-phenyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one* (7f):**



Using the general procedure **GP-2,** compound **5f** (200 mg, 0.62 mmol) and **G-II** (27 mg, 0.03 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 20 mg) provided compound **7f** (134 mg, 73%) as a green fluorescent oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.26 (m, 4H), 7.21 (dd, *J* = 7.4, 2.6 Hz, 1H), 6.87 (dd, *J* = 9.0, 3.6 Hz, 1H), 4.02 (d, *J* = 15.1 Hz, 1H), 3.28 (dd, *J* = 14.7, 12.1 Hz, 1H), 3.03 (dd, *J* = 14.5, 8.1 Hz, 1H), 2.03 (dd, *J* = 14.4, 11.2 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.74 – 1.66 (m, 2H), 1.36 – 1.27 (m, 1H), 0.95 – 0.87 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.2, 158.2, 156.10 (d, $J_{C\text{-}F}$ = 237.7 Hz), 140.4, 129.5, 128.2, 126.2 (d, $J_{C\text{-}F}$ = 25.5 Hz), 126.1, 119.8 (d, $J_{C\text{-}F}$ = 7.1 Hz), 111.0, 110.7, 110.2 (d, $J_{C\text{-}F}$ = 7.3 Hz), 77.5, 43.9, 39.8, 30.8, 26.6, 24.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -128.01; HRMS (ESI) calcd for $C_{19}H_{19}FNO$ $[M+H]^+$: 296.1451; Found: 296.1452.

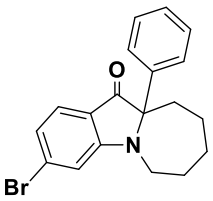
***3-Chloro-10a-phenyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one* (7g):**



Using the general procedure **GP-2,** compound **5g** (190 mg, 0.56 mmol) and **G-II** (24 mg, 0.03 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 19 mg) provided compound **7g** (127 mg, 73%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.21 (m, 5H), 6.90 (d, *J* = 1.7 Hz, 1H), 6.66 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.99 – 3.91 (m, 1H), 3.28 – 3.18 (m, 1H), 3.00 (dd, *J* = 14.5, 8.1 Hz, 1H), 2.04 – 1.95 (m, 1H), 1.87 – 1.76 (m, 2H), 1.74 – 1.64 (m, 2H), 1.34 – 1.23 (m, 1H), 0.96 – 0.83 (m, 1H); ^{13}C NMR (75

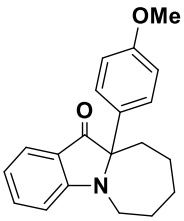
MHz, $CDCl_3$) δ 201.0, 161.4, 144.8, 140.1, 129.5, 128.3, 127.2, 126.1, 118.5, 118.3, 109.2, 77.3, 43.9, 39.5, 30.8, 26.7, 24.2; HRMS (ESI) calcd for $C_{19}H_{19}ClNO$ $[M+H]^+$: 312.1155; Found: 312.1156.

3-Bromo-10a-phenyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one **(7h):**



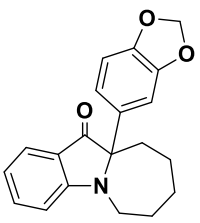
Using the general procedure **GP-2,** compound **5h** (550 mg, 1.44 mmol) and **G-II** (61 mg, 0.07 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 55 mg) provided compound **7h** (394 mg, 77%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 6H), 7.12 (d, *J* = 1.5 Hz, 1H), 6.85 (dd, *J* = 8.2, 1.5 Hz, 1H), 3.97 (d, *J* = 15.0 Hz, 1H), 3.30 – 3.20 (m, 1H), 3.03 (dd, *J* = 14.5, 8.1 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.90 – 1.80 (m, 2H), 1.79 – 1.64 (m, 2H), 1.39 – 1.24 (m, 1H), 0.99 – 0.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 160.8, 139.4, 133.2, 128.9, 127.7, 126.6, 125.4, 120.6, 118.0, 111.7, 76.6, 43.2, 38.9, 30.2, 26.0, 23.6; HRMS (ESI) calcd for $C_{19}H_{19}BrNO$ $[M+H]^+$: 356.0650; Found: 356.0651.

10a-(4-Methoxyphenyl)-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one **(7i):**



Using the general procedure **GP-2,** compound **5i** (100 mg, 0.30 mmol) and **G-II** (13 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 10 mg) provided compound **7i** (63 mg, 69%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 7.19 (d, *J* = 8.9 Hz, 2H), 6.78 (dd, *J* = 14.7, 8.6 Hz, 3H), 6.63 – 6.57 (m, 1H), 3.95 – 3.87 (m, 1H), 3.66 (s, 3H), 3.18 – 3.09 (m, 1H), 2.90 (dd, *J* = 14.4, 8.1 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.75 – 1.52 (m, 4H), 1.23 – 1.17 (m, 1H), 0.86 – 0.73 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.3, 160.7, 159.2, 137.6, 132.1, 126.9, 125.7, 119.2, 117.1, 114.3, 108.8, 75.7, 55.4, 43.1, 39.0, 30.4, 26.2, 23.7; HRMS (ESI) calcd for $C_{20}H_{22}NO_2$ $[M+H]^+$: 308.1651; Found: 308.1652.

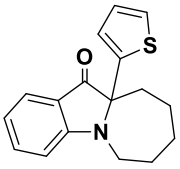
10a-(Benzo[d][1,3]dioxol-5-yl)-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one



(7j): Using the general procedure **GP-2,** compound **5j** (210 mg, 0.60 mmol) and **G-II** (30 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 21 mg) provided compound **7j** (159 mg, 82%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 6.90 – 6.82 (m, 3H), 6.72 (dd, *J* = 13.7, 7.7 Hz, 2H), 5.91 (s, 2H), 4.03 – 3.97 (m, 1H), 3.23 (t, *J* = 13.5 Hz, 1H), 2.94 (dd, *J* = 14.3, 8.1 Hz, 1H), 1.97 (dd, *J* = 14.3,

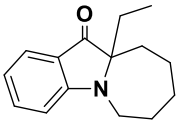
11.2 Hz, 1H), 1.84 – 1.62 (m, 4H), 1.37 – 1.24 (m, 1H), 0.94 – 0.81 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.9, 160.5, 148.0, 147.0, 137.5, 133.8, 125.6, 119.0, 118.7, 117.1, 108.7, 108.4, 106.4, 101.1, 75.7, 43.0, 38.9, 30.2, 26.0, 23.6; HRMS (ESI) calcd for $C_{20}H_{20}NO_3$ $[M+H]^+$: 322.1443; Found: 322.1444.

10a-(Benzo[d][1,3]dioxol-5-yl)-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one

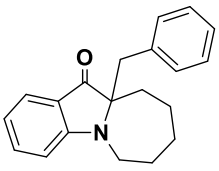


(7k): Using the general procedure **GP-2,** compound **5k** (100 mg, 0.30 mmol) and **G-II** (13 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 10 mg) provided compound **7k** (59 mg, 65%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.12 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.01 (dd, *J* = 3.6, 1.3 Hz, 1H), 6.95 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 3.99 (d, *J* = 15.1 Hz, 1H), 3.42 – 3.33 (m, 1H), 2.95 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.07 (dd, *J* = 13.8, 11.3 Hz, 1H), 1.83 – 1.63 (m, 4H), 1.38 – 1.23 (m, 1H), 0.90 – 0.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7, 160.5, 144.8, 137.6, 127.7, 125.7, 124.2, 123.4, 119.0, 117.6, 109.3, 74.4, 43.2, 39.6, 30.2, 26.0, 23.6; HRMS (ESI) calcd for $C_{17}H_{18}NOS$ $[M+H]^+$: 284.1109; Found: 284.1110.

10a-Ethyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one **(7l):** Using the general procedure **GP-2,** compound **5l** (100 mg, 0.30 mmol) and **G-II** (13 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 10 mg) provided compound **7l** (64 mg, 72%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 3.88 (d, *J* = 16.1 Hz, 1H), 3.18 – 3.10 (m, 1H), 2.37 (dd, *J* = 14.6, 7.8 Hz, 1H), 1.80 – 1.45 (m, 8H), 1.26 – 1.11 (m, 1H), 0.58 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.4, 161.2, 137.1, 124.3, 121.1, 116.3, 109.1, 74.5, 41.9, 38.7, 30.4, 30.3, 26.0, 23.5, 7.6; HRMS (ESI) calcd for $C_{15}H_{20}NO$ $[M+H]^+$: 230.1545; Found: 230.1546.

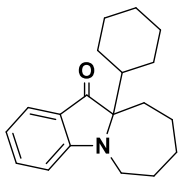


10a-Benzyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one **(7m):** Using the general procedure **GP-2,** compound **5m** (150 mg, 0.47 mmol) and **G-II** (20 mg, 0.03 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 15 mg) provided compound **7m** (89 mg, 65%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.11 – 7.02 (m, 5H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.55 – 6.50 (m, 1H), 3.87 –

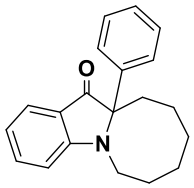


3.81 (m, 1H), 3.06 – 2.96 (m, 1H), 2.92 (d, *J* = 13.2 Hz, 1H), 2.79 (d, *J* = 13.2 Hz, 1H), 2.52 (dd, *J* = 14.6, 7.8 Hz, 1H), 1.75 – 1.47 (m, 5H), 1.22 – 1.07 (m, 1H), 0.66 – 0.54 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 160.7, 137.1, 135.7, 130.1, 127.6, 126.5, 124.3, 120.8, 116.5, 109.3, 74.6, 43.0, 42.7, 37.3, 30.2, 26.2, 23.5; HRMS (ESI) calcd for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1701; Found: 292.1702.

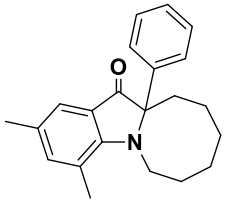
10a-cyclohexyl-6,7,8,9,10,10a-hexahydro-11H-azepino[1,2-a]indol-11-one **(7n):** Using the general procedure **GP-2,** compound **5n** (150 mg, 0.48 mmol) and **G-II** (20 mg, 0.03 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 15 mg) provided compound **7n** (98 mg, 72%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 3.90 (d, *J* = 15.1 Hz, 1H), 3.24 – 3.14 (m, 1H), 2.42 (dd, *J* = 14.4, 7.9 Hz, 1H), 1.73 – 1.53 (m, 11H), 1.26 – 1.01 (m, 5H), 0.90 – 0.81 (m, 1H), 0.64 – 0.51 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.9, 161.2, 136.9, 124.1, 121.7, 116.3, 109.2, 76.2, 46.1, 42.8, 35.7, 30.4, 27.3, 26.8, 26.6, 26.3, 26.2, 25.5, 23.4; HRMS (ESI) calcd for $C_{19}H_{26}NO$ $[M+H]^+$: 284.2014; Found: 284.2015.



11a-Phenyl-7,8,9,10,11,11a-hexahydroazocino[1,2-a]indol-12(6H)-one **(8a):** Using the general procedure **GP-2,** compound **6a** (200 mg, 0.63 mmol) and **G-II** (26 mg, 0.03 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 20 mg) provided compound **8a** (150 mg, 82%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H), 7.32 – 7.21 (m, 5H), 6.88 – 6.84 (m, 1H), 6.71 – 6.66 (m, 1H), 3.89 – 3.81 (m, 1H), 3.26 – 3.16 (m, 1H), 2.71 – 2.63 (m, 1H), 2.29 – 2.17 (m, 1H), 2.05 – 1.91 (m, 1H), 1.67 – 1.30 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 160.7, 138.6, 137.7, 129.0, 127.7, 126.2, 125.8, 118.9, 116.7, 108.1, 76.1, 43.2, 30.9, 26.7, 26.5, 24.2, 22.6; HRMS (ESI) calcd for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1701; Found: 292.1702.

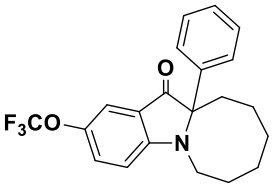


2,4-Dimethyl-11a-phenyl-7,8,9,10,11,11a-hexahydroazocino[1,2-a]indol-12(6H)-one **(8b):** Using the general procedure **GP-2,** compound **6b** (150 mg, 0.43 mmol) and **G-II** (18 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 15 mg) provided compound **8b** (104 mg, 75%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.21 (m, 4H), 7.10 (s, 1H), 4.34 – 4.26 (m, 1H), 3.20 – 3.10 (m, 1H), 2.74 –

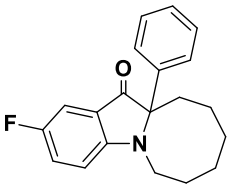


2.65 (m, 1H), 2.60 (s, 3H), 2.22 (s, 3H), 2.18 – 2.12 (m, 1H), 1.84 – 1.68 (m, 3H), 1.58 – 1.27 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 157.9, 142.3, 139.5, 128.8, 127.5, 126.4, 126.1, 122.8, 120.3, 119.0, 76.9, 44.7, 30.7, 30.7, 26.3, 24.4, 22.4, 20.1, 20.0; HRMS (ESI) calcd for $C_{22}H_{26}NO$ $[M+H]^+$: 320.2014; Found: 320.2015.

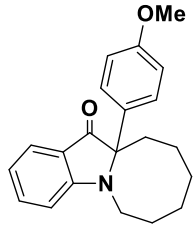
11a-Phenyl-2-(trifluoromethoxy)-7,8,9,10,11,11a-hexahydroazocino[1,2-a]indol-12(6H)-one **(8d):** Using the general procedure **GP-2,** compound **6d** (200 mg, 0.50 mmol) and **G-II** (22 mg, 0.03 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 20 mg) provided compound **8d** (134 mg, 72%) as a green fluorescent oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 7H), 6.85 (d, *J* = 8.9 Hz, 1H), 3.89 – 3.81 (m, 1H), 3.28 – 3.18 (m, 1H), 2.72 – 2.64 (m, 1H), 2.29 – 2.20 (m, 1H), 2.01 – 1.90 (m, 1H), 1.67 – 1.31 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4, 158.9, 140.0, 138.0, 131.5, 129.1, 128.0, 126.1, 121.0 (q, $J_{C\text{-}F}$ = 256.7 Hz), 118.8, 118.1, 108.8, 77.1, 43.4, 31.0, 26.5, 26.3, 24.1, 22.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.65; HRMS (ESI) calcd for $C_{21}H_{21}F_3NO_2$ $[M+H]^+$: 376.1524; Found: 376.1525.



2-Fluoro-11a-phenyl-7,8,9,10,11,11a-hexahydroazocino[1,2-a]indol-12(6H)-one **(8e):** Using the general procedure **GP-2,** compound **6e** (200 mg, 0.72 mmol) and **G-II** (31 mg, 0.04 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 20 mg) provided compound **8e** (154 mg, 70%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 7H), 6.80 (dd, *J* = 8.9, 3.6 Hz, 1H), 3.87 – 3.79 (m, 1H), 3.27 – 3.17 (m, 1H), 2.70 – 2.62 (m, 1H), 2.27 – 2.17 (m, 1H), 2.02 – 1.88 (m, 1H), 1.67 – 1.29 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.4 (d, $J_{C\text{-}F}$ = 3.4 Hz), 158.0, 155.8 (d, $J_{C\text{-}F}$ = 237.2 Hz), 138.9, 129.6, 128.4, 126.7, 126.2 (d, $J_{C\text{-}F}$ = 25.4 Hz), 119.2 (d, $J_{C\text{-}F}$ = 7.0 Hz), 111.1 (d, $J_{C\text{-}F}$ = 22.3 Hz), 109.3 (d, $J_{C\text{-}F}$ = 7.3 Hz), 77.4, 43.9, 31.6, 27.2, 26.9, 24.7, 23.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -128.50; HRMS (ESI) calcd for $C_{21}H_{21}FNO$ $[M+H]^+$: 310.1607; Found: 310.1608.

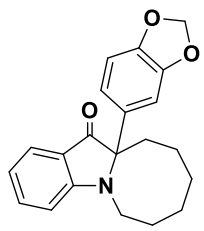


11a-(4-Methoxyphenyl)-7,8,9,10,11,11a-hexahydroazocino[1,2-a]indol-12(6H)-one **(8f):**



Using the general procedure **GP-2,** compound **6f** (100 mg, 0.32 mmol) and **G-II** (13 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 10 mg) provided compound **8f** (66 mg, 72%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.15 – 7.12 (m, 2H), 6.85 – 6.80 (m, 3H), 6.67 (t, *J* = 7.4 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.75 (s, 3H), 3.24 – 3.14 (m, 1H), 2.65 – 2.58 (m, 1H), 2.23 – 2.13 (m, 1H), 2.06 – 1.89 (m, 1H), 1.63 – 1.44 (m, 5H), 1.41 – 1.29 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.4, 160.4, 159.1, 137.5, 130.4, 127.3, 125.7, 118.7, 116.5, 114.3, 107.9, 75.5, 55.3, 42.9, 30.8, 26.6, 26.4, 24.0, 22.4; HRMS (ESI) calcd for $C_{21}H_{24}NO_2$ $[M+H]^+$: 322.1807; Found: 322.1808.

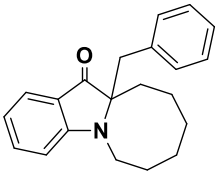
11a-(Benzo[d][1,3]dioxol-5-yl)-7,8,9,10,11,11a-hexahydroazocino[1,2-a]indol-12(6H)-one



(8g): Using the general procedure **GP-2,** compound **6g** (150 mg, 0.42 mmol) and **G-II** (13 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 15 mg) provided compound **8g** (111 mg, 80%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.74 – 6.62 (m, 4H), 5.88 (d, *J* = 2.0 Hz, 2H), 3.80 (d, *J* = 15.3 Hz, 1H), 3.23 – 3.13 (m, 1H), 2.60 – 2.52 (m, 1H), 2.20 – 2.11 (m, 1H), 2.00 – 1.84 (m, 1H), 1.62 – 1.42 (m, 5H), 1.36 – 1.26 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 160.4, 148.1, 147.1, 137.7, 132.3, 125.7, 119.5, 118.7, 116.6, 108.5, 108.0, 106.7, 101.1, 75.6, 43.0, 30.8, 26.5, 26.4, 24.1, 22.4; HRMS (ESI) calcd for $C_{21}H_{22}NO_3$ $[M+H]^+$: 336.1600; Found: 336.1601.

11a-Ethyl-7,8,9,10,11,11a-hexahydroazocino[1,2-a]indol-12(6H)-one **(8h):** Using the general procedure **GP-2,** compound **6h** (100 mg, 0.37 mmol) and **G-II** (13 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 10 mg) provided compound **8h** (68 mg, 75%) as a green fluorescent oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.60 (t, *J* = 7.4 Hz, 1H), 3.77 – 3.69 (m, 1H), 3.30 – 3.20 (m, 1H), 2.07 – 1.89 (m, 2H), 1.81 – 1.71 (m, 2H), 1.67 – 1.53 (m, 3H), 1.46 – 1.31 (m, 3H), 1.24 – 1.06 (m, 2H), 0.49 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.4, 160.6, 137.4, 124.3, 120.4, 115.7, 108.2, 73.5, 41.3, 32.6, 30.2, 26.6, 26.5, 24.2, 22.6, 7.6; HRMS (ESI) calcd for $C_{16}H_{22}NO$ $[M+H]^+$: 244.1701; Found: 244.1702.

11a-Benzyl-7,8,9,10,11,11a-hexahydroazocino[1,2-a]indol-12(6H)-one **(8i):** Using the general procedure **GP-2,** compound **6i** (150 mg, 0.45 mmol) and **G-II** (19 mg, 0.02 mmol) provided the intermediate, which was then treated with Pd-C (10 mol %, 15 mg) provided compound **8i** (93 mg, 68%) as a green fluorescent oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.1 Hz, 1H), 7.09 – 7.04 (m, 3H), 6.98 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.50 (t, *J* = 7.4 Hz, 1H), 3.81 – 3.76 (m, 1H), 3.41 – 3.35 (m, 1H), 3.00 (d, *J* = 13.4 Hz, 1H), 2.88 (d, *J* = 13.4 Hz, 1H), 2.20 – 2.15 (m, 1H), 2.02 – 1.90 (m, 2H), 1.67 – 1.56 (m, 2H), 1.50 – 1.36 (m, 3H), 1.31 (dd, *J* = 8.2, 3.4 Hz, 1H), 1.10 – 1.02 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.1, 160.4, 137.6, 135.8, 130.4, 128.2, 127.1, 124.9, 121.0, 116.4, 109.0, 74.7, 44.6, 43.0, 31.6, 27.0, 25.9, 24.7, 23.8; HRMS (ESI) calcd for $C_{21}H_{24}NO$ $[M+H]^+$: 306.1858; Found: 306.1859.

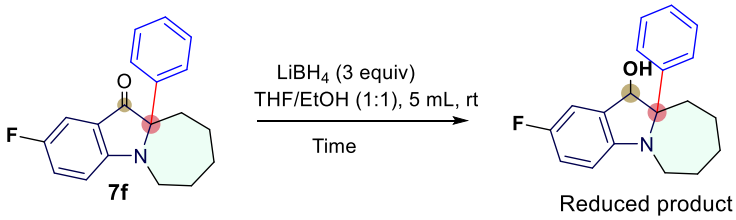


6.0 Use of LiCl and $NaBH_4$

LiCl was not used as an independent reducing agent. Its role is to generate $LiBH_4$ in situ from $NaBH_4$, as reported in the literature.[4] This approach was adopted because commercially available $LiBH_4$ is significantly more expensive, and in situ generation using LiCl provides a cost-effective alternative.

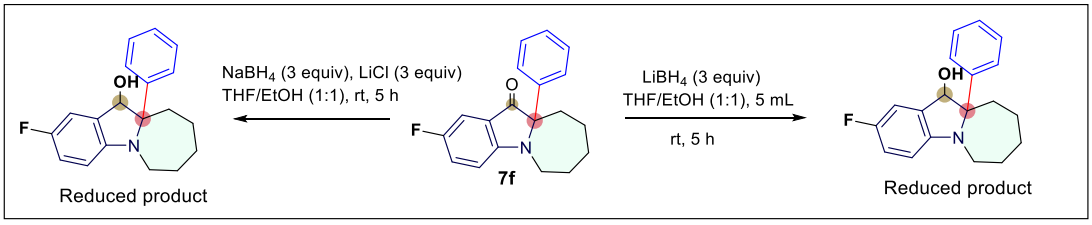
Optimization studies were initially performed using commercial $LiBH_4$ (Sigma-Aldrich), which showed that 3 equivalents are required for complete reduction of the ketone; lower equivalents led to incomplete conversion (Table S1). Based on these results, 3 equivalents each of $NaBH_4$ and LiCl were employed to ensure efficient in situ formation of $LiBH_4$ (Scheme S5).

Table S1. **Optimization studies for the reduction of ketone 7f to the corresponding alcohol**[a]



Entry	$LiBH_4$ (equiv.)	Time	Conversion (%)
1.	1 equiv	5 h	Trace
2.	2 equiv	5 h	60%
3.	2 equiv	12 h	60%
4.	3 equiv	5 h	100%

[a]Reactions were carried out with **7f** (0.14 mmol, 1 equiv) and $LiBH_4$ under an argon atmosphere. Conversions refer to isolated yields of the reduced product.

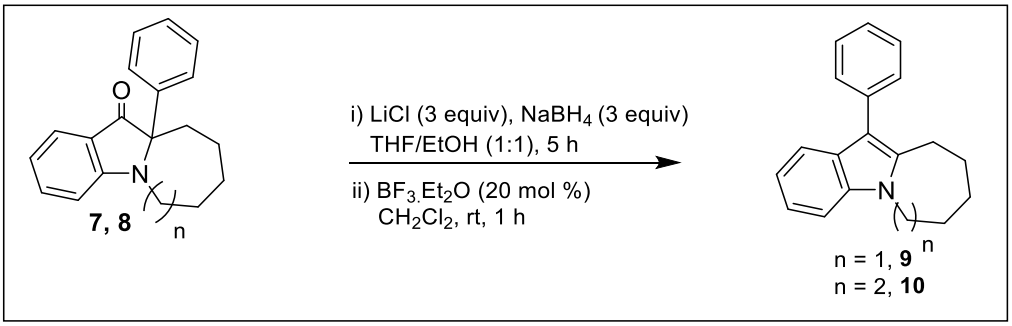


Scheme S5. Reduction of ketone to the corresponding alcohol using $LiBH_4$ and a mixture of $NaBH_4$/LiCl.

7.0 General procedure for the synthesis of azepino[1,2-a]indoles 9a-n and azocino[1,2-a]indoles 10a-i derivatives (GP-3)

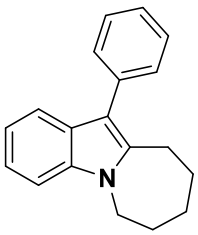
A mixture of anhydrous LiCl (3 equiv) and $NaBH_4$ (3 equiv) was added to anhydrous THF/EtOH (1:1, 15 mL) at 0 °C and stirred for 30 min. The corresponding indolone compound **7** or **8** (1.0 equiv) was then added, resulting in an immediate colour change of the solution to green. The reaction mixture was stirred at room temperature for 5 h until the solution colour changed to white. The solvent was removed under reduced pressure, and the residue was quenched with aqueous NH_4Cl solution and extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to afford the crude indolol intermediate.

The crude product was dissolved in anhydrous CH_2Cl_2 (10 mL), and $BF_3 \cdot Et_2O$ (50% solution in CH_2Cl_2, 20 mol%) was added dropwise at 0 °C. The reaction mixture was then stirred at room temperature for 1 h. Upon completion of the reaction, the mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 (2 × 5 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography using hexane as the eluent to afford azepino[1,2-a]indoles **9a-n** or azocino[1,2-a]indoles **10a-i** (Scheme S6).



Scheme S6. Synthesis of azepino[1,2-a]indolones **9a-n** and azocino[1,2-a]indoles derivatives **10a-i**.

11-Phenyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9a):** Using the general procedure



GP-3, anhydrous LiCl (55 mg, 1.29 mmol) $NaBH_4$ (49 mg, 1.29 mmol) and compound **7a** (120 mg, 0.43 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (172 µL, 0.10 mmol) to furnish compound **9a** (95 mg, 88%) as a white solid with a melting point of 135-137 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.9 Hz, 1H), 7.61 – 7.53 (m, 4H), 7.42 (t, J = 6.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 4.37 – 4.28 (m, 2H), 3.13 – 3.05 (m, 2H), 2.01 – 1.89 (m, 4H), 1.87 – 1.81 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7, 135.9, 130.1, 128.4, 127.0, 125.7, 121.0, 119.3, 118.9, 113.6, 108.6, 44.7, 31.1, 29.4, 27.9, 25.8; HRMS (ESI) calcd for $C_{19}H_{20}N$ $[M+H]^+$: 262.1596; Found: 262.1597.

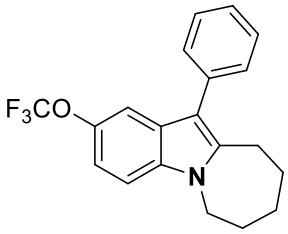
2-Methyl-11-phenyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9b):** Using the general procedure **GP-3,** anhydrous LiCl (43 mg, 1.03 mmol) $NaBH_4$ (39 mg, 1.03 mmol) and compound **7b** (100 mg, 0.34 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (136 µL, 0.10 mmol) to furnish compound **9b** (95 mg, 88%) as a white solid with a melting point of 144-146 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 5H), 7.44 – 7.41 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 8.4, 1.7 Hz, 1H), 4.31 – 4.29 (m, 2H), 3.10 – 3.08 (m, 2H), 2.56 (s, 3H), 2.01 – 1.96 (m, 2H), 1.92 (t, *J* = 5.2 Hz, 2H), 1.85 (h, *J* = 5.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 136.1, 134.4, 130.2, 128.7, 128.5, 127.2, 125.7, 122.6, 118.7, 113.2, 108.4, 44.8, 31.2, 29.5, 28.0, 25.9, 21.6; HRMS (ESI) calcd for $C_{20}H_{22}N$ $[M+H]^+$: 276.1752; Found: 276.1750.

2,4-Dimethyl-11-phenyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9c):** Using the general procedure **GP-3,** anhydrous LiCl (42 mg, 0.98 mmol) $NaBH_4$ (37 mg, 0.98 mmol) and compound **7c** (100 mg, 0.33 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (132 µL, 0.10 mmol) to furnish compound **9c** (95 mg, 83%) as a yellowish solid with a melting point of 142-144 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 4H), 7.39 – 7.35 (m, 1H), 7.32 (s, 1H), 6.82 (s, 1H), 4.59 – 4.58 (m, 2H), 3.02 – 2.99 (m, 2H), 2.78 (s, 3H), 2.43 (s, 3H), 1.92 – 1.91 (m, 4H), 1.79 (p, *J* = 5.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 136.2, 132.8, 130.3, 128.6, 128.4, 128.0, 126.5, 125.7, 119.6, 116.8, 113.6, 46.1, 30.6, 29.7, 28.0, 25.5, 21.1; HRMS (ESI) calcd for $C_{21}H_{24}N$ $[M+H]^+$: 290.1909; Found: 290.1908.

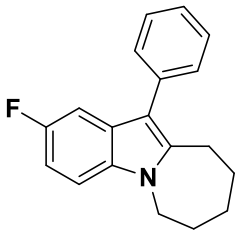
2-Methoxy-11-phenyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9d):** Using the general procedure **GP-3,** anhydrous LiCl (42 mg, 0.98 mmol) $NaBH_4$ (39 mg, 0.98 mmol) and compound **7d** (100 mg, 0.33 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (132 µL, 0.10 mmol) to furnish compound **9d** (95 mg, 90%) as a white solid with a melting point of 75-77 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 5.3 Hz, 4H), 7.37 – 7.34 (m, 1H), 7.26 (d, *J* = 8.9 Hz, 1H), 7.17 (d, *J* = 2.6 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.25 – 4.23 (m, 2H), 3.86 (s, 3H), 3.02 – 3.00 (m, 2H), 1.93 (p, *J* = 5.6 Hz, 2H), 1.87 (q, *J* = 5.0 Hz, 2H), 1.79 (p, *J* = 5.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 140.4, 136.0, 131.2, 130.0, 128.5, 127.1, 125.7, 113.3, 111.1, 109.3,

101.0, 56.1, 44.9, 31.1, 29.4, 27.9, 25.9; HRMS (ESI) calcd for $C_{20}H_{22}N$ $[M+H]^+$: 292.1701; Found: 292.1700.

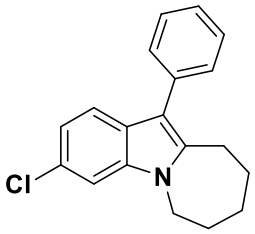
11-Phenyl-2-(trifluoromethoxy)-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9e):** Using the general procedure **GP-3,** anhydrous LiCl (53 mg, 1.24 mmol) $NaBH_4$ (47 mg, 1.24 mmol) and compound **7e** (150 mg, 0.41 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (164 µL, 0.10 mmol) to furnish compound **9e** (117 mg, 82%) as a white solid with a melting point of 100-102 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 3H), 7.47 – 7.45 (m, 2H), 7.38 – 7.35 (m, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.10 (dd, *J* = 8.9, 2.3 Hz, 1H), 4.27 – 4.25 (m, 2H), 3.03 – 3.01 (m, 2H), 1.96 – 1.86 (m, 4H), 1.81 – 1.77 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 141.6, 135.0, 134.2, 129.9, 128.6, 127.0, 126.1, 120.87 (q, *J* = 255.2 Hz) , 114.9, 114.0, 111.5, 109.1, 45.1, 31.0, 29.2, 27.7, 25.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.03; HRMS (ESI) calcd for $C_{20}H_{19}F_3NO$ $[M+H]^+$: 346.1419; Found: 346.1418.



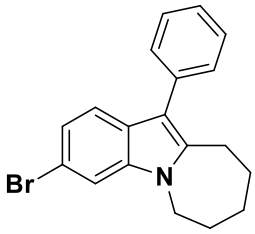
2-Fluoro-11-phenyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9f):** Using the general procedure **GP-3,** anhydrous LiCl (52 mg, 1.22 mmol) $NaBH_4$ (46 mg, 1.22 mmol) and compound **7f** (120 mg, 0.41 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (164 µL, 0.10 mmol) to furnish compound **9f** (89 mg, 79%) as a brown solid with a melting point of 144-146 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 4H), 7.38 – 7.33 (m, 2H), 7.28 – 7.25 (m, 1H), 7.00 – 6.96 (m, 1H), 4.26 – 4.24 (m, 2H), 3.04 – 3.02 (m, 2H), 1.93 (p, *J* = 5.8 Hz, 2H), 1.89 – 1.86 (m, 2H), 1.80 (h, *J* = 5.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (d, $J_{C\text{-}F}$ = 233.5 Hz), 141.4, 135.4, 132.5, 129.9, 128.6, 127.18 (d, $J_{C\text{-}F}$ = 9.6 Hz), 126.0, 113.65 (d, $J_{C\text{-}F}$ = 4.7 Hz), 109.2, 109.0 (d, $J_{C\text{-}F}$ = 13.6 Hz), 103.79 (d, $J_{C\text{-}F}$ = 23.6 Hz), 45.0, 31.0, 29.3, 27.7, 25.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -125.50; HRMS (ESI) calcd for $C_{19}H_{19}FN$ $[M+H]^+$: 280.1502; Found: 280.1500.



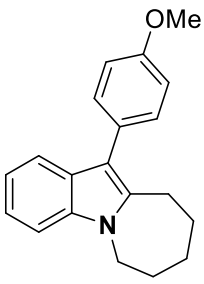
3-Chloro-11-phenyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9g):** Using the general procedure **GP-3,** anhydrous LiCl (49 mg, 1.15 mmol) $NaBH_4$ (44 mg, 1.15 mmol) and compound **7g** (120 mg, 0.39 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (156 µL, 0.10 mmol) to furnish compound **9g** (97 mg, 85%) as a white solid with a melting point of 169-171 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.46 (m, 4H), 7.38 – 7.35 (m, 2H), 7.10 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.22 – 4.20 (m, 2H), 3.02 – 3.00 (m, 2H), 1.93 (q, *J* = 5.8 Hz, 2H), 1.86 (p, *J* = 5.4 Hz, 2H), 1.79 (p, *J* = 5.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 136.3, 135.3, 130.0, 128.6, 127.0, 126.1, 125.6, 119.9, 119.8, 113.8, 108.8, 44.9, 31.0, 29.3, 27.8, 25.8; HRMS (ESI) calcd for $C_{19}H_{19}ClN$ $[M+H]^+$: 296.1206; Found: 296.1205.



3-Bromo-11-phenyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9h):** Using the general procedure **GP-3,** anhydrous LiCl (28 mg, 0.67 mmol) $NaBH_4$ (26 mg, 0.67 mmol) and compound **7h** (80 mg, 0.23 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (92 µL, 0.05 mmol) to furnish compound **9h** (66 mg, 87%) as a yellowish solid with a melting point of 171-173 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 4H), 7.45 – 7.43 (m, 2H), 7.36 – 7.32 (m, 1H), 7.19 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.22 – 4.20 (m, 2H), 3.00 – 2.98 (m, 2H), 1.91 (q, *J* = 5.6 Hz, 2H), 1.85 (p, *J* = 5.1 Hz, 2H), 1.77 (p, *J* = 5.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 136.7, 135.2, 130.0, 128.5, 126.0, 125.9, 122.4, 120.2, 114.6, 113.8, 111.7, 44.9, 30.9, 29.3, 27.8, 25.8; HRMS (ESI) calcd for $C_{19}H_{19}BrN$ $[M+H]^+$: 340.0701; Found: 340.0702.

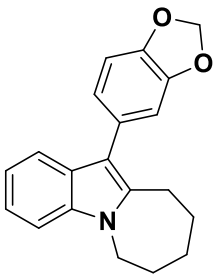


11-(4-Methoxyphenyl)-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9i):** Using the general procedure **GP-3,** anhydrous LiCl (41 mg, 0.98 mmol) $NaBH_4$ (37 mg, 0.98 mmol) and compound **7i** (100 mg, 0.33 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (132 µL, 0.06 mmol) to furnish compound **9i** (81 mg, 86%) as a white solid with a melting point of 159-161 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.19 – 7.15 (m, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 4.31 – 4.28 (m, 2H), 3.94 (s, 3H), 3.06 – 3.03 (m, 2H), 1.98 – 1.88 (m, 4H), 1.82 (q, *J* = 5.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9,

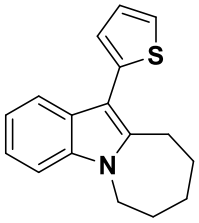


139.5, 135.8, 131.1, 128.2, 127.2, 121.0, 119.2, 119.0, 114.0, 113.2, 108.6, 55.4, 44.7, 31.2, 29.5, 28.0, 25.9; HRMS (ESI) calcd for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1701; Found: 292.1700.

11-(Benzo[d][1,3]dioxol-5-yl)-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9j):** Using the general procedure **GP-3,** anhydrous LiCl (47 mg, 1.12 mmol) $NaBH_4$ (42 mg, 1.12 mmol) and compound **7j** (120 mg, 0.37 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (148 µL, 0.07 mmol) to furnish compound **9j** (92 mg, 84%) as a colorless liquid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.98 (m, 3H), 6.06 (s, 2H), 4.29 – 4.26 (m, 2H), 3.05 – 3.02 (m, 2H), 1.96 – 1.76 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 145.8, 139.6, 135.7, 129.7, 127.1, 123.3, 121.1, 119.3, 118.9, 113.3, 110.6, 108.6, 108.5, 100.9, 44.7, 31.1, 29.4, 28.0, 25.9; HRMS (ESI) calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1494; Found: 306.1495.



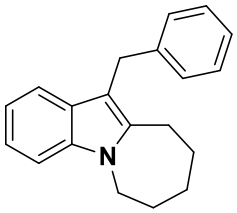
11-(Thiophen-2-yl)-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9k):** Using the general procedure **GP-3,** anhydrous LiCl (42 mg, 1.1 mmol) $NaBH_4$ (38 mg, 1.1 mmol) and compound **7k** (100 mg, 0.35 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (140 µL, 0.07 mmol) to furnish compound **9k** (74 mg, 78%) as a colorless liquid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.26 – 7.19 (m, 1H), 7.18 – 7.10 (m, 2H), 7.07 (dd, *J* = 3.5, 1.2 Hz, 1H), 4.25 – 4.22 (m, 2H), 3.12 – 3.09 (m, 2H), 1.94 – 1.73 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 137.4, 135.8, 127.3, 127.2, 125.4, 123.9, 121.3, 119.6, 119.1, 108.6, 106.4, 44.8, 31.0, 29.2, 27.6, 26.0; HRMS (ESI) calcd for $C_{17}H_{18}NS$ $[M+H]^+$: 268.1160; Found: 268.1161.



11-Ethyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9l):** Using the general procedure **GP-3,** anhydrous LiCl (55 mg, 1.31 mmol) $NaBH_4$ (50 mg, 1.31 mmol) and compound **7i** (100 mg, 0.43 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (172 µL, 0.08 mmol) to furnish compound **9l** (76 mg, 82%) as a colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 4.24 – 4.15 (m, 2H), 2.96 – 2.90 (m, 2H), 2.81 (q, *J* = 7.5 Hz, 2H), 1.96 – 1.88 (m, 2H), 1.85 – 1.74 (m, 4H), 1.28 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

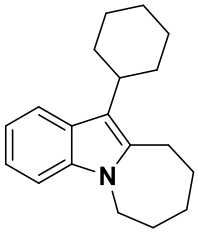
138.6, 135.8, 127.3, 120.3, 118.3, 118.2, 112.6, 108.4, 44.5, 31.2, 29.7, 28.2, 25.4, 17.6, 16.4; HRMS (ESI) calcd for $C_{15}H_{20}N$ $[M+H]^+$: 214.1596; Found: 214.1597.

11-Benzyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9m):** Using the general procedure



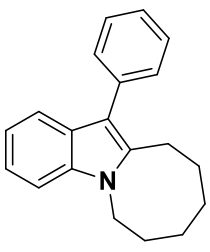
GP-3, anhydrous LiCl (65 mg, 1.54 mmol) $NaBH_4$ (59 mg, 1.54 mmol) and compound **7m** (150 mg, 0.51 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (204 µL, 0.11 mmol) to furnish compound **9m** (106 mg, 75%) as a yellowish solid with a melting point of 75-77 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.30 (m, 5H), 7.24 – 7.21 (m, 2H), 7.10 (t, *J* = 7.1 Hz, 1H), 4.26 – 4.24 (m, 2H), 4.20 (s, 2H), 2.99 – 2.97 (m, 2H), 1.93 (q, *J* = 5.7 Hz, 2H), 1.86 (q, *J* = 5.2 Hz, 2H), 1.78 (q, *J* = 5.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.3, 140.0, 136.0, 128.3, 127.9, 125.6, 120.6, 118.7, 118.6, 109.0, 108.4, 44.7, 31.2, 30.3, 29.7, 28.0, 25.7; HRMS (ESI) calcd for $C_{20}H_{22}N$ $[M+H]^+$: 276.1752; Found: 276.1750.

11-cyclohexyl-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indole **(9n):** Using the general procedure



GP-3, anhydrous LiCl (40 mg, 0.95 mmol) $NaBH_4$ (36 mg, 1.54 mmol) and compound **7n** (0.32 mg, 0.51 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (204 µL, 0.10 mmol) to furnish compound **9n** (66 mg, 78%) as a white solid with a melting point of 70-72 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.17 (t, *J* = 7.1 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 4.20 – 4.17 (m, 2H), 2.97 – 2.93 (m, 2H), 2.89 – 2.79 (m, 1H), 2.01 – 1.71 (m, 13H), 1.51 – 1.34 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.2, 135.9, 126.5, 120.0, 119.8, 117.9, 115.9, 108.5, 44.3, 36.9, 33.7, 31.1, 29.5, 28.3, 27.5, 26.5, 25.6; HRMS (ESI) calcd for $C_{19}H_{26}N$ $[M+H]^+$: 268.2065; Found: 268.2066.

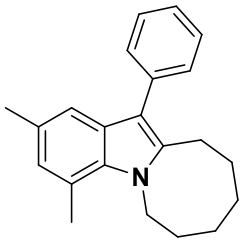
12-Phenyl-6,7,8,9,10,11-hexahydroazocino[1,2-a]indole **(10a):** Using the general procedure



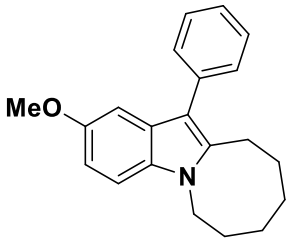
GP-3, anhydrous LiCl (41mg, 0.98 mmol) $NaBH_4$ (37 mg, 0.98 mmol) and compound **8a** (100 mg, 0.34 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (136 µL, 0.07 mmol) to furnish compound **10a** (79 mg, 84%) as a white solid with a melting point of 146-148 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.58 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.27 (t, *J* = 7.5 Hz,

1H), 7.18 (t, *J* = 7.9 Hz, 1H), 4.37 – 4.35 (m, 2H), 3.01 – 2.98 (m, 2H), 1.96 – 1.89 (m, 4H), 1.67 – 1.63 (m, 2H), 1.42 – 1.38 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 136.1, 135.3, 129.8, 128.5, 127.5, 125.7, 121.0, 119.5, 119.0, 113.3, 109.0, 40.8, 33.1, 29.8, 25.9, 24.3, 24.0; HRMS (ESI) calcd for $C_{20}H_{22}N$ $[M+H]^+$: 276.1752; Found: 276.1750.

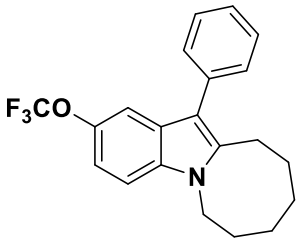
2-Methyl-12-phenyl-6,7,8,9,10,11-hexahydroazocino[1,2-a]indole **(10b):** Using the general procedure **GP-3,** anhydrous LiCl (42 mg, 0.98 mmol) $NaBH_4$ (37 mg, 0.98 mmol) and compound **8b** (100 mg, 0.33 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (132 µL, 0.07 mmol) to furnish compound **10b** (76 mg, 80%) as a yellowish solid with a melting point of 152-154 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 4H), 7.42 – 7.39 (m, 1H), 7.34 (s, 1H), 6.87 (s, 1H), 4.53 (t, *J* = 5.7 Hz, 2H), 2.97 (t, *J* = 6.0 Hz, 2H), 2.84 (s, 3H), 2.47 (s, 3H), 1.98 – 1.86 (m, 4H), 1.67 (p, *J* = 5.8 Hz, 2H), 1.41 (p, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 136.4, 132.4, 130.2, 128.9, 128.8, 128.4, 126.2, 125.8, 120.0, 116.7, 113.5, 42.1, 33.0, 32.8, 26.3, 24.1, 24.1, 21.2, 20.2; HRMS (ESI) calcd for $C_{22}H_{26}N$ $[M+H]^+$: 304.2065; Found: 304.2066.



2-Methoxy-12-phenyl-6,7,8,9,10,11-hexahydroazocino[1,2-a]indole **(10c):** Using the general procedure **GP-3,** anhydrous LiCl (59 mg, 1.40 mmol) $NaBH_4$ (53 mg, 1.40 mmol) and compound **8c** (150 mg, 0.47 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (188 µL, 0.10 mmol) to furnish compound **10c** (115 mg, 81%) as a brown solid with a melting point of 80-82 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.32 – 4.28 (m, 2H), 3.86 (s, 3H), 2.98 – 2.90 (m, 2H), 1.93 – 1.83 (m, 4H), 1.64 – 1.59 (m, 2H), 1.39 – 1.34 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 139.4, 136.2, 130.6, 129.7, 128.5, 127.7, 125.7, 112.9, 111.0, 109.7, 101.0, 56.0, 40.9, 33.1, 29.9, 25.9, 24.3, 24.0; HRMS (ESI) calcd for $C_{21}H_{24}NO$ $[M+H]^+$: 306.1858; Found: 306.1857.

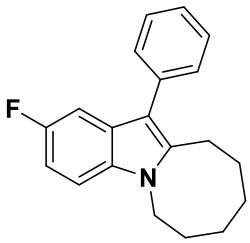


12-Phenyl-2-(trifluoromethoxy)-6,7,8,9,10,11-hexahydroazocino[1,2-a]indole **(10d):** Using



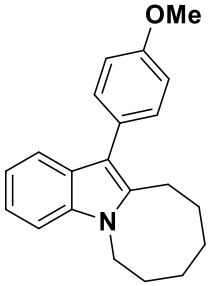
the general procedure **GP-3,** anhydrous LiCl (51 mg, 1.20 mmol) $NaBH_4$ (45 mg, 1.20 mmol) and compound **8d** (150 mg, 0.40 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (160 µL, 0.10 mmol) to furnish compound **10d** (110 mg, 76%) as a yellowish solid with a melting point of 94-96 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.54 (d, *J* = 4.4 Hz, 4H), 7.40 (p, *J* = 4.3 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 4.35 – 4.32 (m, 2H), 2.99 – 2.96 (m, 2H), 1.95 – 1.88 (m, 4H), 1.67 – 1.62 (m, 2H), 1.42 – 1.36 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 140.7, 135.4, 133.8, 129.7, 128.7, 127.7, 126.2, 212.0 (q, J_{C-F} = 256.7 Hz), 114.9, 113.8, 111.6, 109.5, 41.2, 33.1, 29.9, 25.9, 24.3, 24.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.90; HRMS (ESI) calcd for $C_{21}H_{21}F_3NO$ $[M+H]^+$: 360.1575; Found: 360.1576.

2-Fluoro-12-phenyl-6,7,8,9,10,11-hexahydroazocino[1,2-a]indole **(10e):** Using the general



procedure **GP-3,** anhydrous LiCl (41 mg, 0.97 mmol) $NaBH_4$ (37 mg, 0.97 mmol) and compound **8e** (100 mg, 0.32 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (128 µL, 0.06 mmol) to furnish compound **10e** (77 mg, 82%) as a brown solid with a melting point of 135-137 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 4H), 7.36 – 7.33 (m, 2H), 7.28 – 7.26 (m, 1H), 7.00 – 6.95 (m, 1H), 4.32 – 4.30 (m, 2H), 2.95 (dd, *J* = 7.2, 4.9 Hz, 2H), 1.89 (h, *J* = 6.5 Hz, 4H), 1.62 (p, *J* = 6.9, 6.4 Hz, 2H), 1.38 – 1.34 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.26 (d, J_{C-F} = 233.3 Hz), 140.4, 135.6, 131.9, 129.6, 128.6, 127.72 (d, J_{C-F} = 9.8 Hz), 125.9, 113.32 (d, J_{C-F} = 4.4 Hz), 109.45 (d, J_{C-F} = 9.8 Hz), 109.07 (d, J_{C-F} = 26.0 Hz), 103.91 (d, J_{C-F} = 24.0 Hz), 41.0, 33.0, 29.8, 25.9, 24.3, 24.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ -125.18; HRMS (ESI) calcd for $C_{20}H_{21}FN$ $[M+H]^+$: 294.1658; Found: 294.1659.

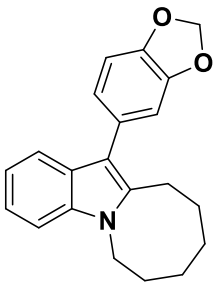
12-(4-Methoxyphenyl)-6,7,8,9,10,11-hexahydroazocino[1,2-a]indole **(10f):** Using the



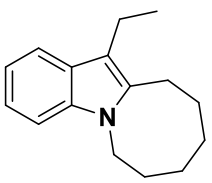
general procedure **GP-3,** anhydrous LiCl (39 mg, 0.93 mmol) $NaBH_4$ (35 mg, 0.93 mmol) and compound **8f** (100 mg, 0.31 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (124 µL, 0.06 mmol) to furnish compound **10f** (79 mg, 83%) as a white solid with a melting point of 169-171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.28

– 7.20 (m, 1H), 7.16 – 7.10 (m, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 4.35 – 4.31 (m, 2H), 3.90 (s, 3H), 2.96 – 2.92 (m, 2H), 1.94 – 1.82 (m, 4H), 1.62 (dd, *J* = 10.8, 5.8 Hz, 2H), 1.40 – 1.32 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.8, 138.4, 135.2, 130.8, 128.4, 127.7, 120.8, 119.4, 118.9, 113.9, 112.8, 108.9, 55.3, 40.8, 33.1, 29.8, 25.9, 24.3, 23.9; HRMS (ESI) calcd for $C_{21}H_{24}NO$ $[M+H]^+$: 306.1858; Found: 306.1857.

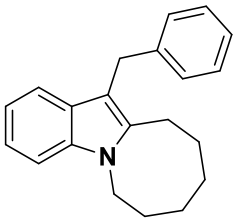
12-(Benzo[d][1,3]dioxol-5-yl)-6,7,8,9,10,11-hexahydroazocino[1,2-a]indole **(10g):** Using the general procedure **GP-3,** anhydrous LiCl (38 mg, 0.90 mmol) $NaBH_4$ (34 mg, 0.90 mmol) and compound **8g** (100 mg, 0.30 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (120 µL, 0.06 mmol) to furnish compound **10g** (84 mg, 88%) as a colorless liquid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.19 – 7.13 (m, 1H), 7.04 (d, *J* = 1.5 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.04 (s, 2H), 4.34 – 4.30 (m, 2H), 2.97 – 2.93 (m, 2H), 1.94 – 1.82 (m, 4H), 1.65 – 1.57 (m, 2H), 1.40 – 1.33 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 145.8, 138.5, 135.2, 129.9, 127.6, 123.0, 121.0, 119.5, 118.9, 112.9, 110.4, 109.0, 108.5, 100.9, 40.8, 33.1, 29.8, 25.9, 24.3, 23.9; HRMS (ESI) calcd for $C_{21}H_{22}NO_2$ $[M+H]^+$: 320.1651; Found: 320.1652.



12-Ethyl-6,7,8,9,10,11-hexahydroazocino[1,2-a]indole **(10h):** Using the general procedure **GP-3,** anhydrous LiCl (52 mg, 1.23 mmol) $NaBH_4$ (47 mg, 1.23 mmol) and compound **8h** (100 mg, 0.41 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (164 µL, 0.08 mmol) to furnish compound **10h** (73 mg, 78%) as a colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.15 (m, 2H), 4.31 – 4.28 (m, 2H), 2.97 – 2.93 (m, 2H), 2.86 (q, *J* = 7.5 Hz, 2H), 1.92 – 1.81 (m, 4H), 1.61 – 1.54 (m, 2H), 1.38 – 1.29 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 135.3, 127.9, 120.2, 118.5, 118.3, 112.2, 108.8, 40.8, 32.5, 30.3, 25.9, 24.4, 23.3, 17.7, 16.4; HRMS (ESI) calcd for $C_{16}H_{22}N$ $[M+H]^+$: 228.1752; Found: 228.1753.



12-Benzyl-6,7,8,9,10,11-hexahydroazocino[1,2-a]indole **(10i):** Using the general procedure



GP-3, anhydrous LiCl (49 mg, 1.18 mmol) $NaBH_4$ (45 mg, 1.18 mmol) and compound **8i** (120 mg, 0.39 mmol) provided the intermediate, which was then treated with $BF_3.Et_2O$ (50% in CH_2Cl_2) (156 µL, 0.08 mmol) to furnish compound **10i** (83 mg, 73%) as a yellowish solid with a melting point of 74-76 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.23 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 4.31 – 4.26 (m, 2H), 4.15 (s, 2H), 2.90 – 2.88 (m, 2H), 1.84 (p, *J* = 6.2 Hz, 2H), 1.65 (p, *J* = 6.2 Hz, 2H), 1.49 (p, *J* = 5.8 Hz, 2H), 1.26 (p, *J* = 6.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 139.0, 135.2, 128.4, 128.3, 128.2, 125.6, 120.4, 118.8, 118.6, 108.8, 108.5, 40.8, 31.8, 30.2, 30.1, 25.8, 24.3, 23.5; HRMS (ESI) calcd for $C_{21}H_{24}N$ $[M+H]^+$: 290.1909; Found: 290.1908.

8.0 X-Ray Crystallography of compounds 9f and 10a: Intensity data were collected on a Bruker's Kappa Apex II CCD Duo diffractometer with graphite monochromated MoKα radiation (0.71073 Å) at the temperature of 296 K. Scaling and multi-scan absorption correction were employed using SADABS. The structure was solved by direct methods and all the non-hydrogen atoms were refined anisotropically while the hydrogen atoms fixed in the predetermined positions by Shelxs-97 and Shelxl-97 packages respectively.

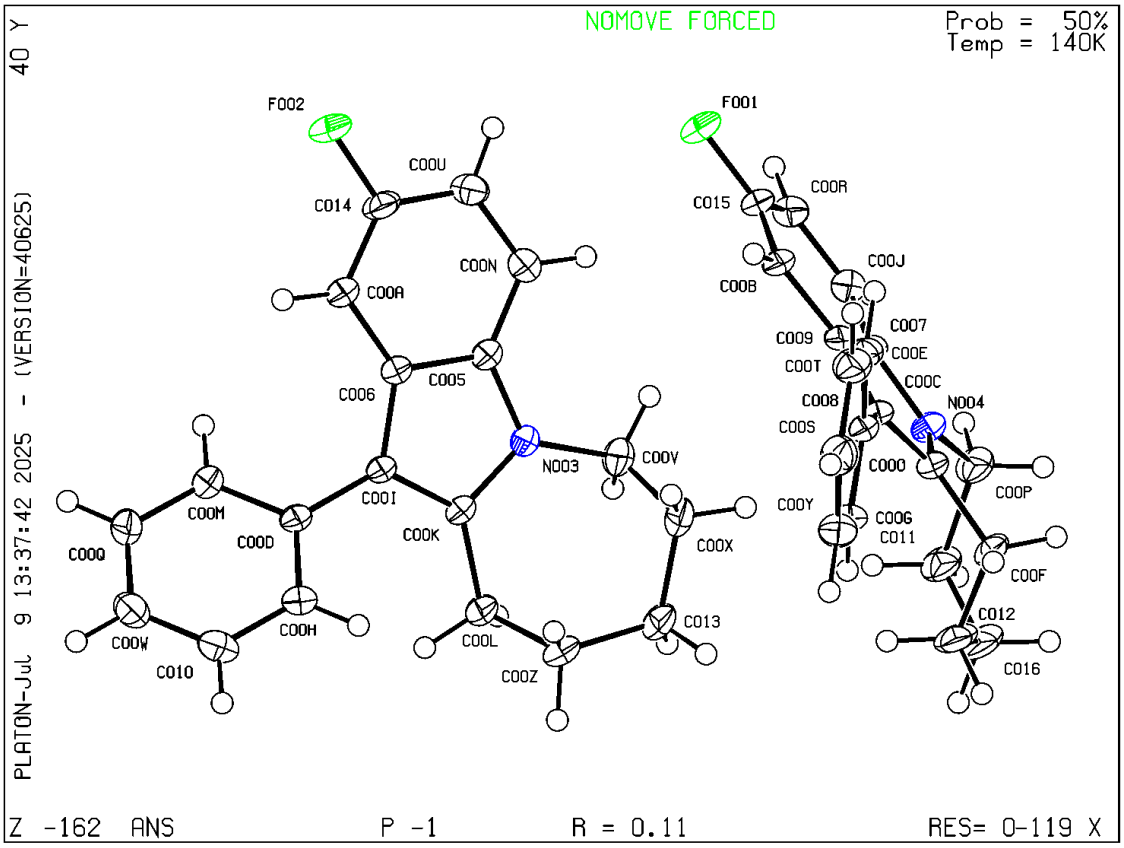


Figure S1. The ORTEP diagram of **9f** showing 50% probability thermal ellipsoid.

Table S2: Crystal data and structure refinement for 9f.	
Identification code	ANS
Empirical formula	$C_{38}H_{36}F_2N_2$
Formula weight	558.720
Temperature/K	139.99
Crystal system	triclinic
Space group	P-1
a/Å	8.1550(13)
b/Å	12.2573(19)
c/Å	14.773(2)
α/°	102.430(6)
β/°	95.802(6)
γ/°	90.091(6)
Volume/Å^3	1434.3(4)
Z	2
ρ_{calc}g/cm^3	1.294
μ/mm^{-1}	0.084
F(000)	592.4
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.88 to 69.28

Index ranges	$-11 \leq h \leq 12, -15 \leq k \leq 18, -23 \leq l \leq 21$
Reflections collected	19064
Independent reflections	9745 [$R_{int} = 0.0805$, $R_{sigma} = 0.1255$]
Data/restraints/parameters	9745/0/523
Goodness-of-fit on F^2	1.147
Final R indexes [I>=2σ (I)]	$R_1 = 0.1217$, $wR_2 = 0.2924$
Final R indexes [all data]	$R_1 = 0.1719$, $wR_2 = 0.3648$
Largest diff. peak/hole / e $Å^{-3}$	0.95/-1.05

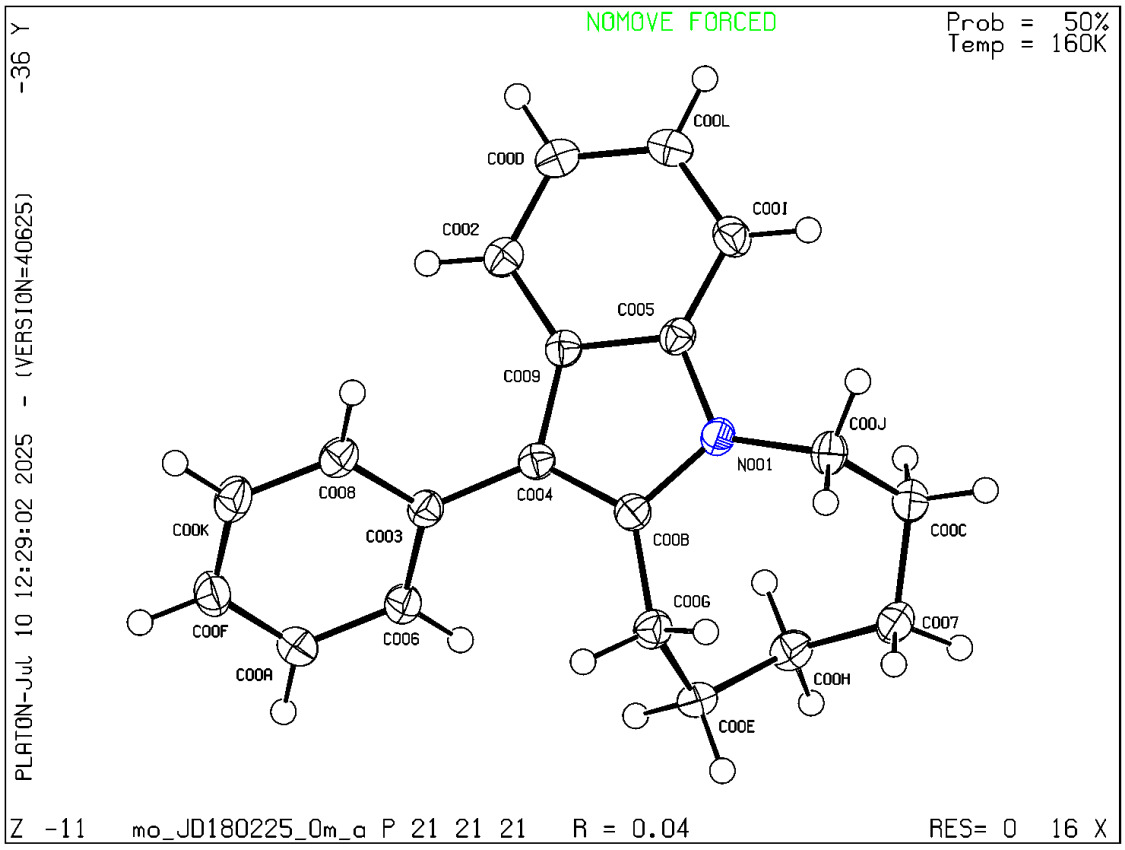


Figure S2. The ORTEP diagram of **10a** showing 50% probability thermal ellipsoid.

Table S3: Crystal data and structure refinement for 10a.	
Identification code	mo_JD180225_0m_a
Empirical formula	$C_{20}H_{21}N$
Formula weight	275.396
Temperature/K	160.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.9325(2)
b/Å	11.0390(4)
c/Å	19.2749(8)
α/°	90

β/°	90
γ/°	90
Volume/Å^3	1475.07(9)
Z	4
ρ_{calc}g/cm^3	1.240
μ/mm^{-1}	0.071
F(000)	592.3
Crystal size/mm^3	0.2 × 0.15 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.22 to 56.02
Index ranges	-9 ≤ h ≤ 8, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25
Reflections collected	34507
Independent reflections	3546 [R_{int} = 0.0587, R_{sigma} = 0.0297]
Data/restraints/parameters	3546/0/190
Goodness-of-fit on F^2	0.950
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.1117
Final R indexes [all data]	R_1 = 0.0399, wR_2 = 0.1127
Largest diff. peak/hole / e Å^{-3}	0.23/-0.21
Flack parameter	-0.7(11)

9.0 References.

[1] K. Dhara, T. Mandal, J. Das, J. Dash, *Angew. Chem. Int. Ed.* **2015**, *54*, 15831 –15835.

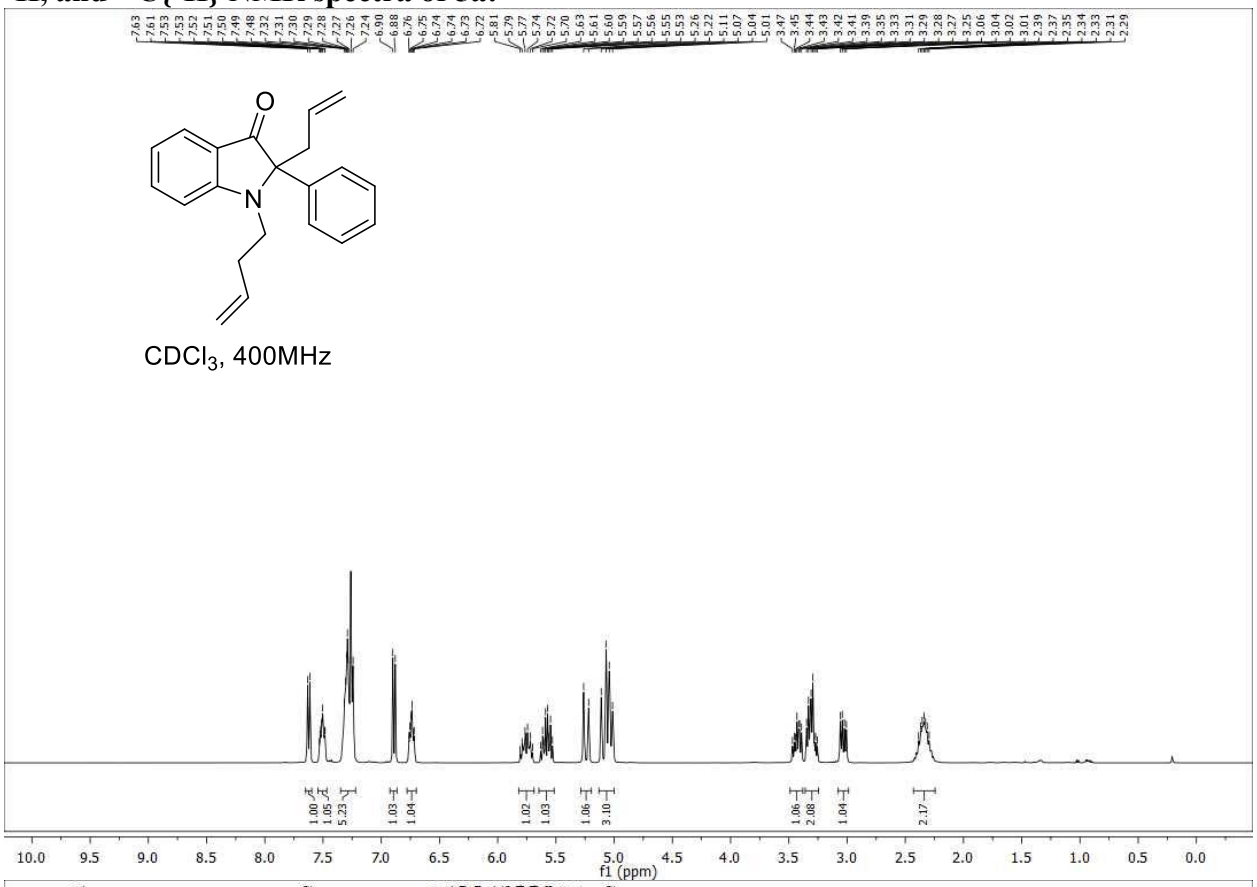
[2] T. Mandal, G. Chakraborti, S. Karmakar, J. Dash, *Org. Lett*. **2018**, *20*, 4759−4763.

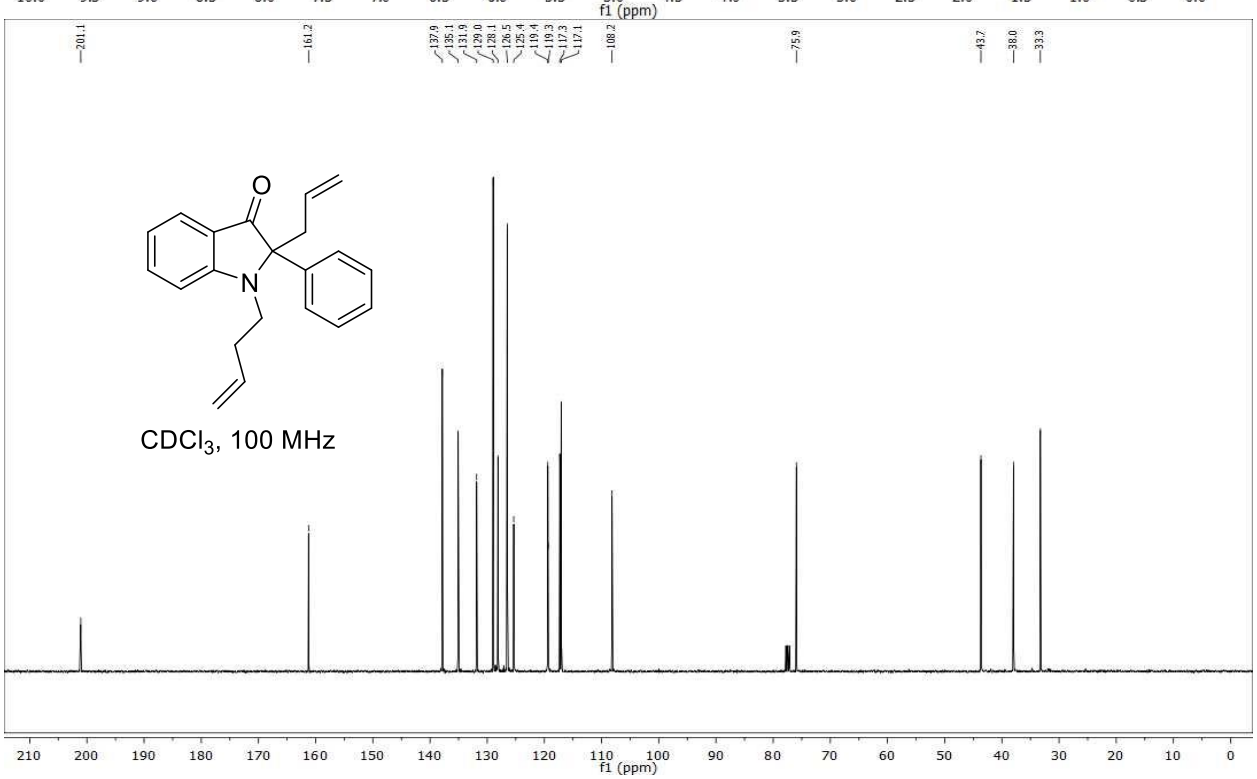
[3] N. Parui, T. Mandal, S. Maiti, J. Dash *Chem. Eur. J.* **2024***, 30,* e202401059.

[4] H. C. Brown, Y. M. Choi, S. Narasimhan, *Inorg. Chem*., **1982**, *21*, 3657-3661.

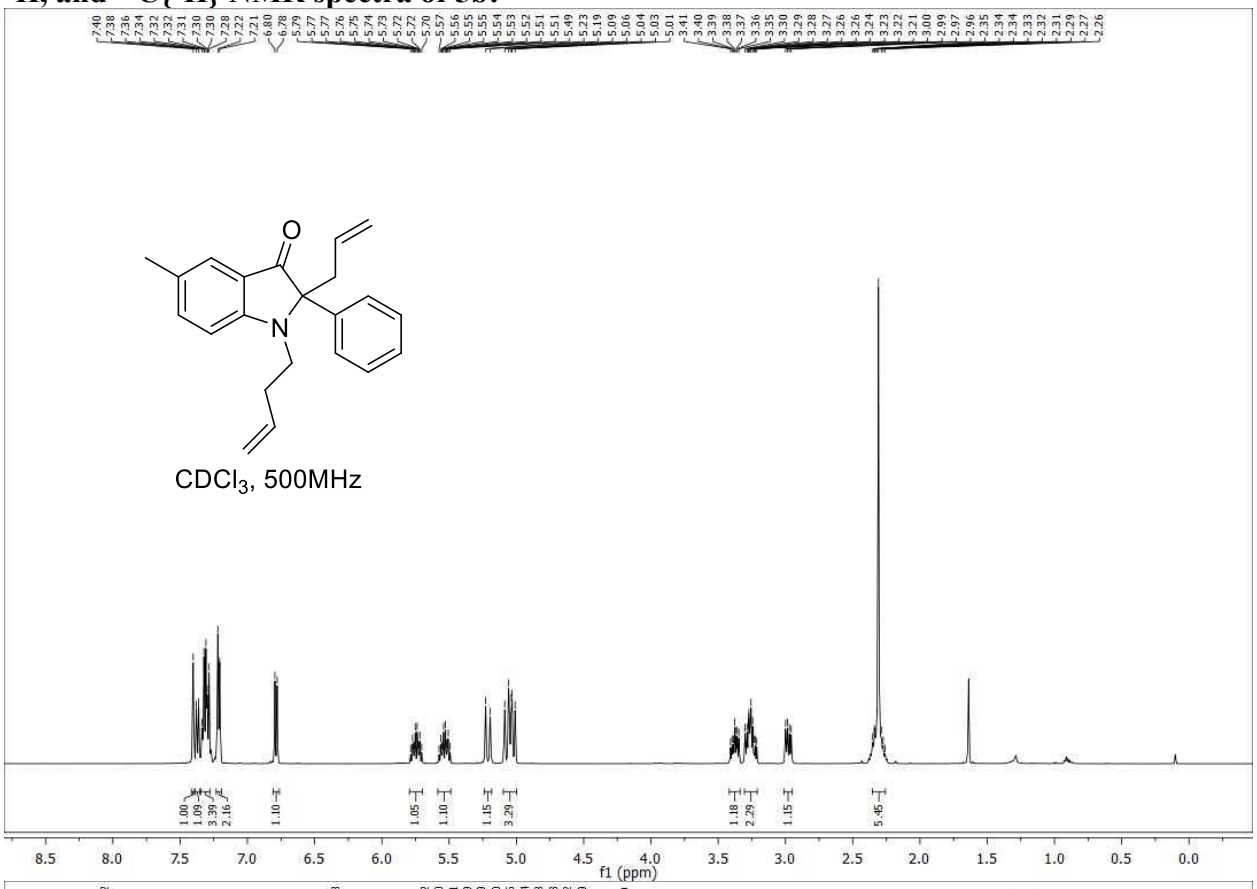
10.0 NMR spectra of all compounds

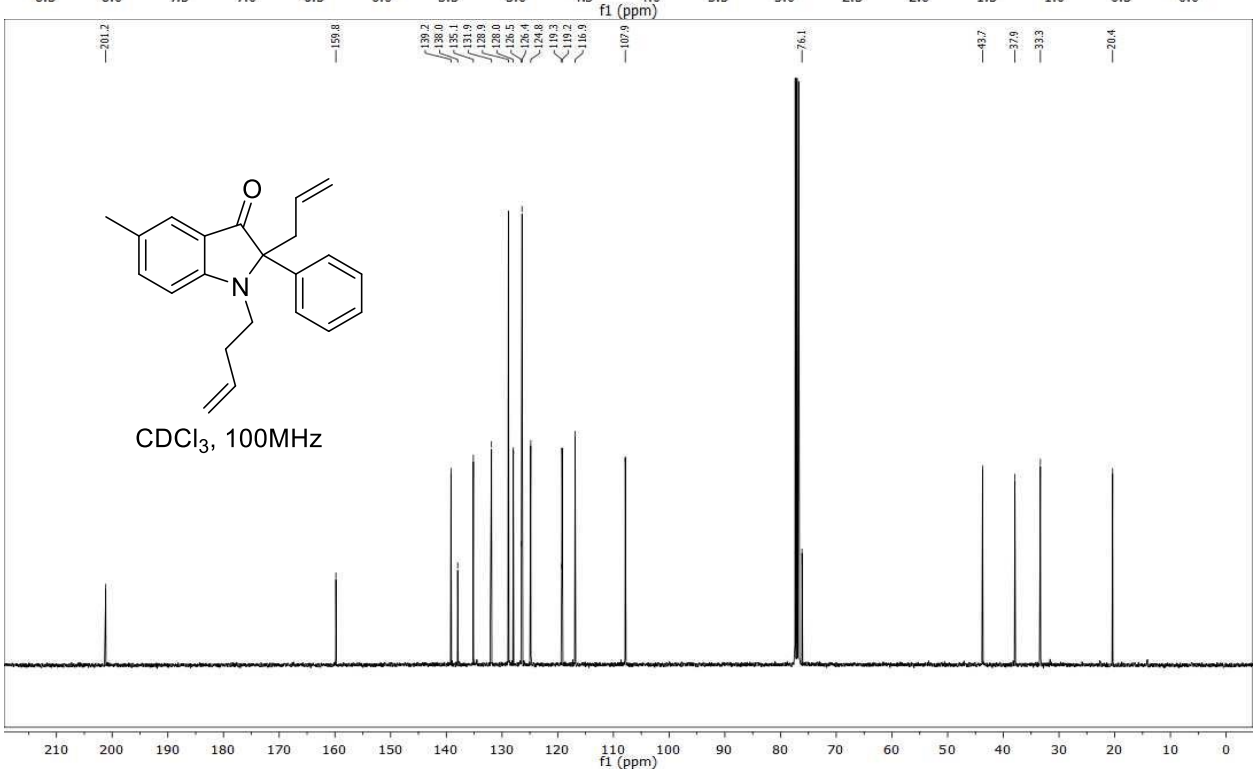
^{1}H, and $^{13}C\{^{1}H\}$ NMR spectra of 5a:



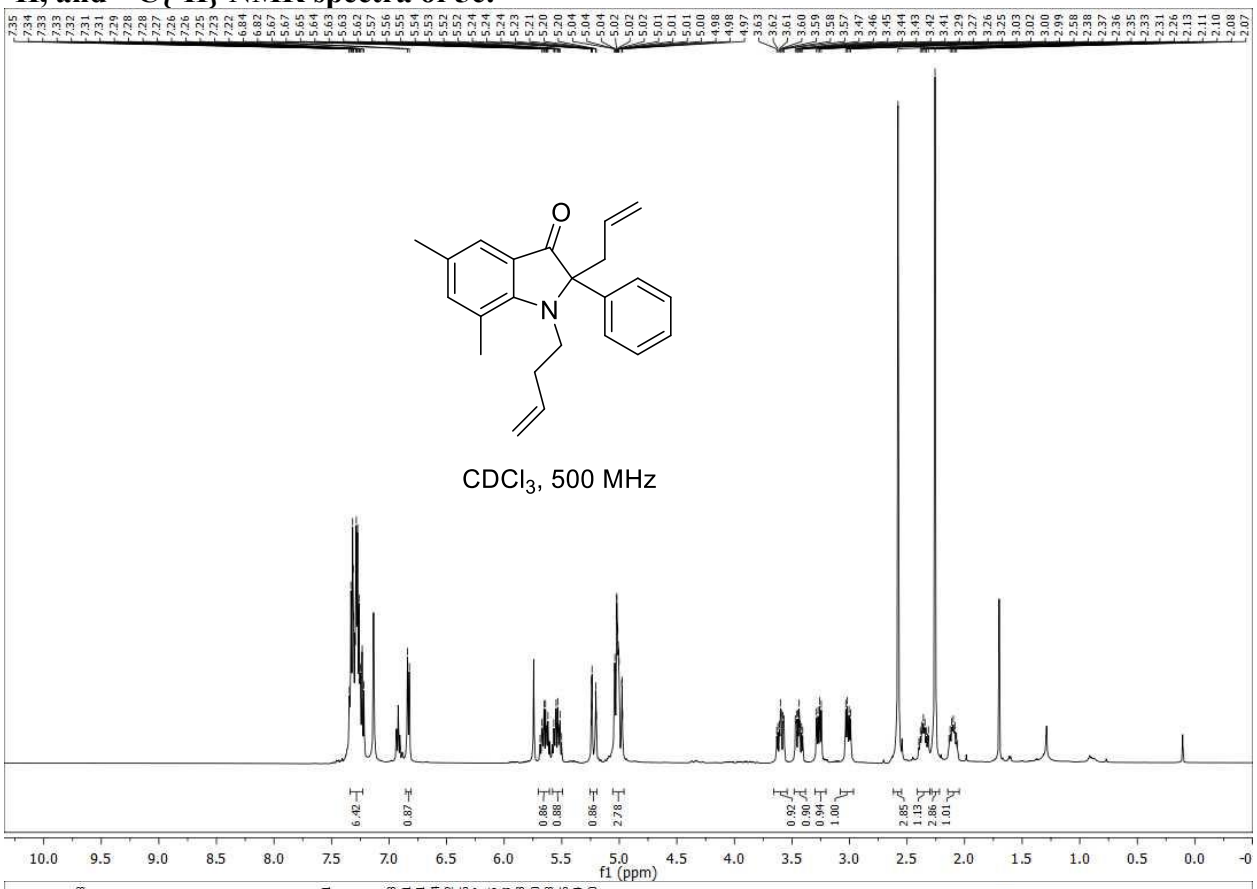


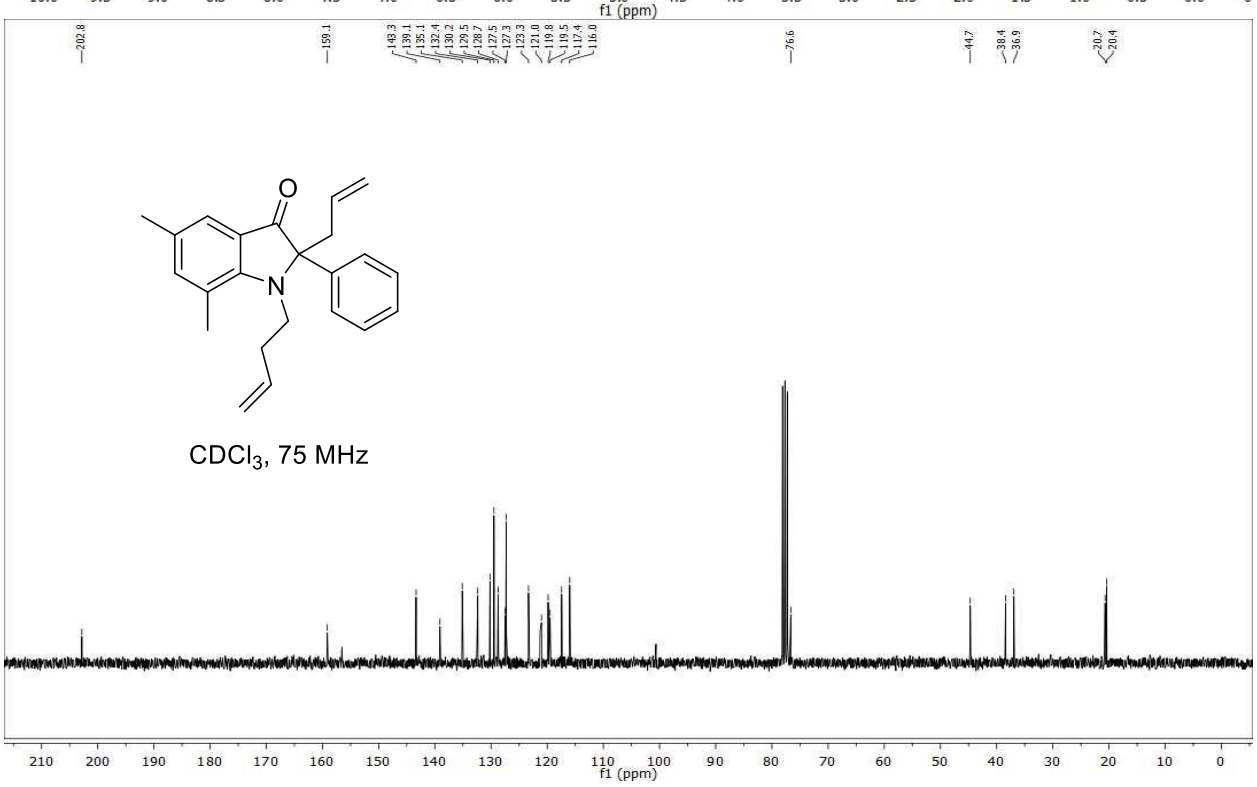
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5b:



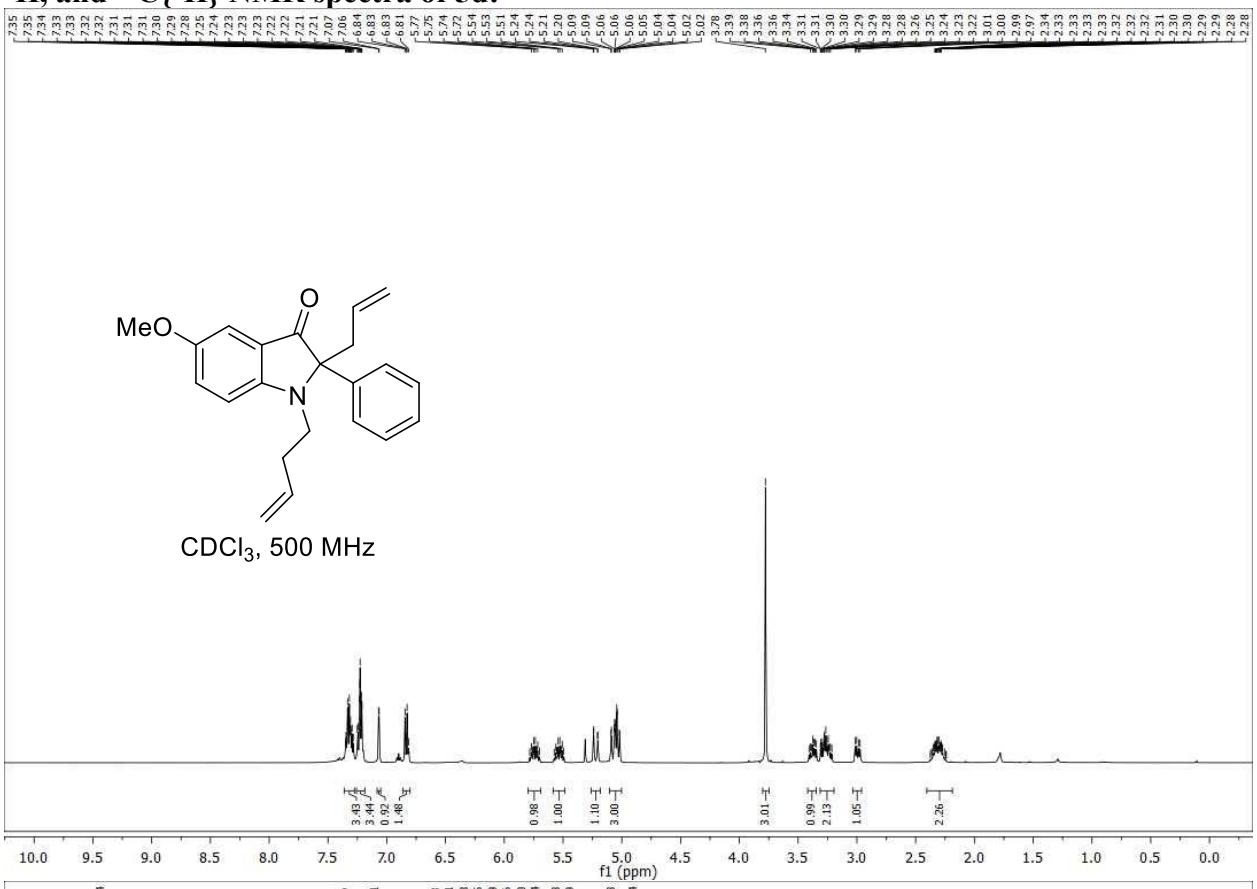


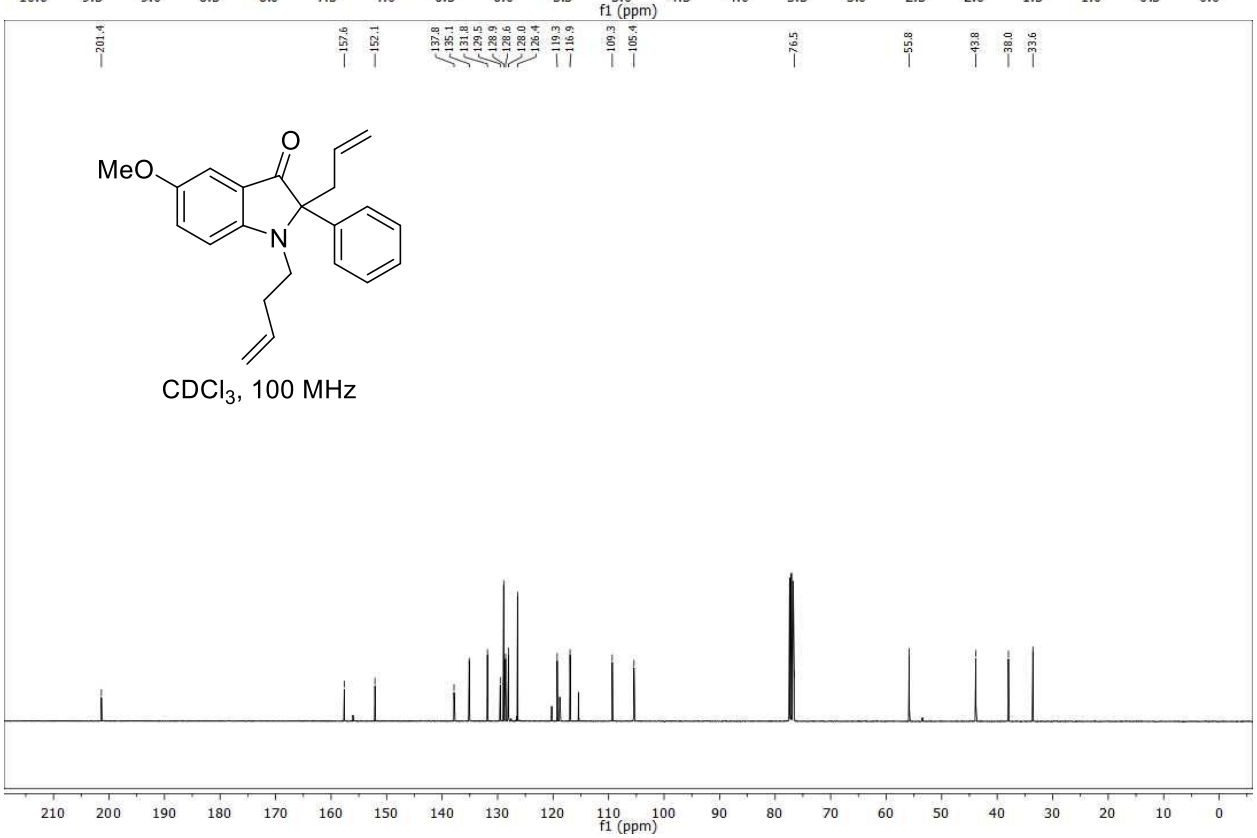
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5c:



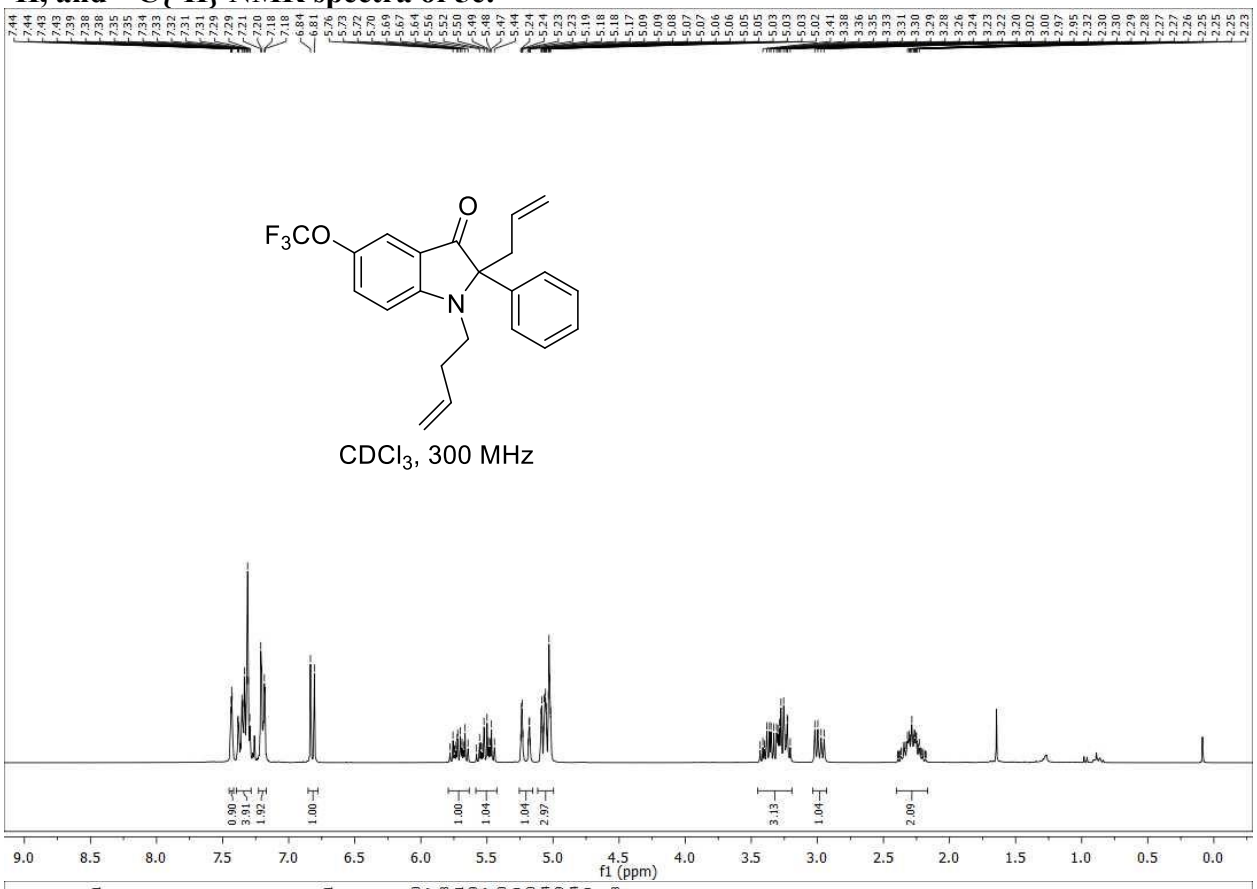


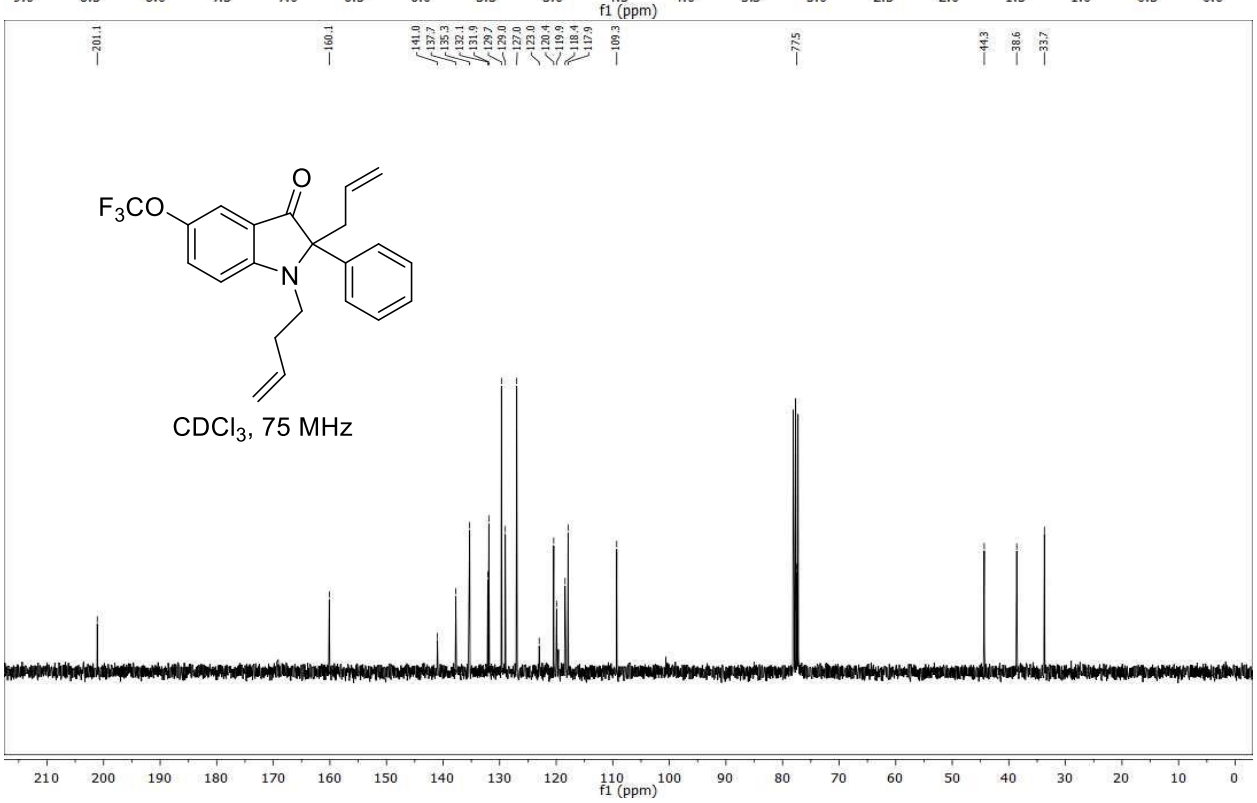
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5d:



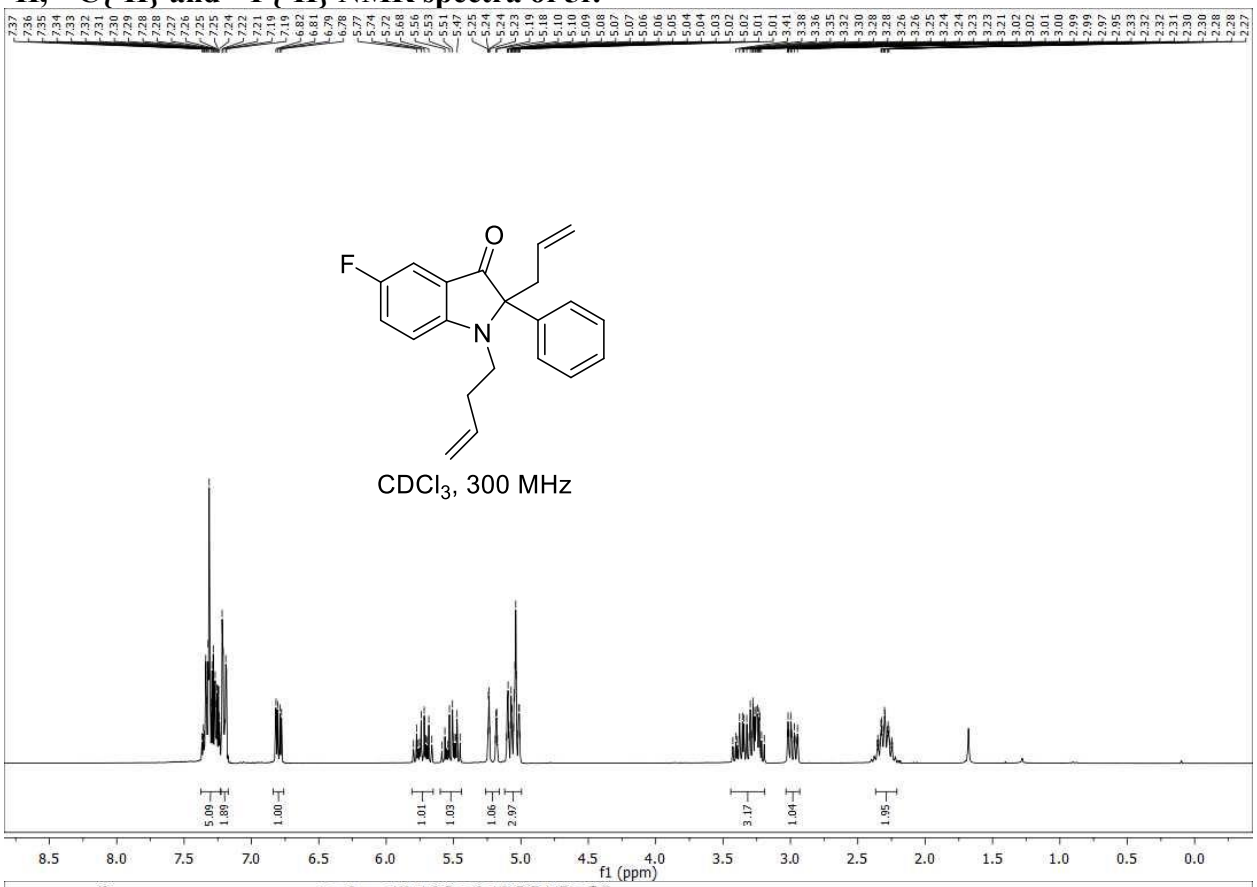


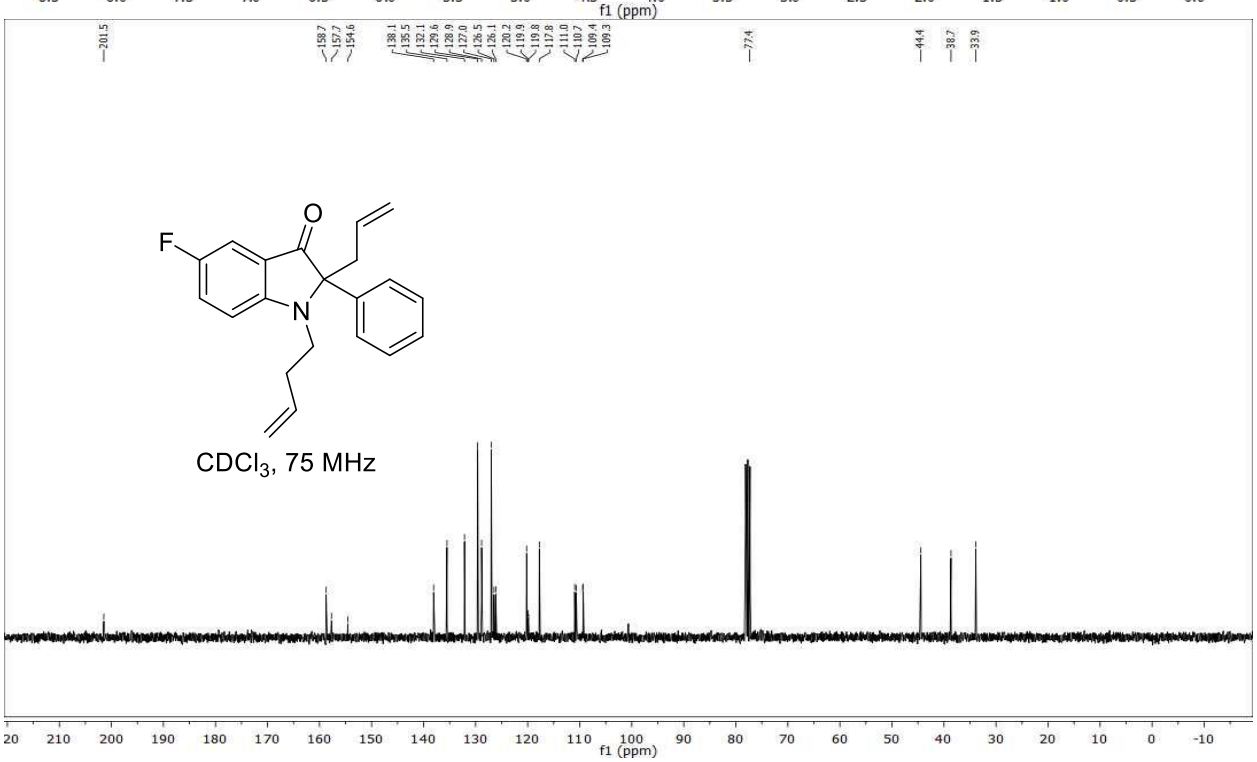
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5e:

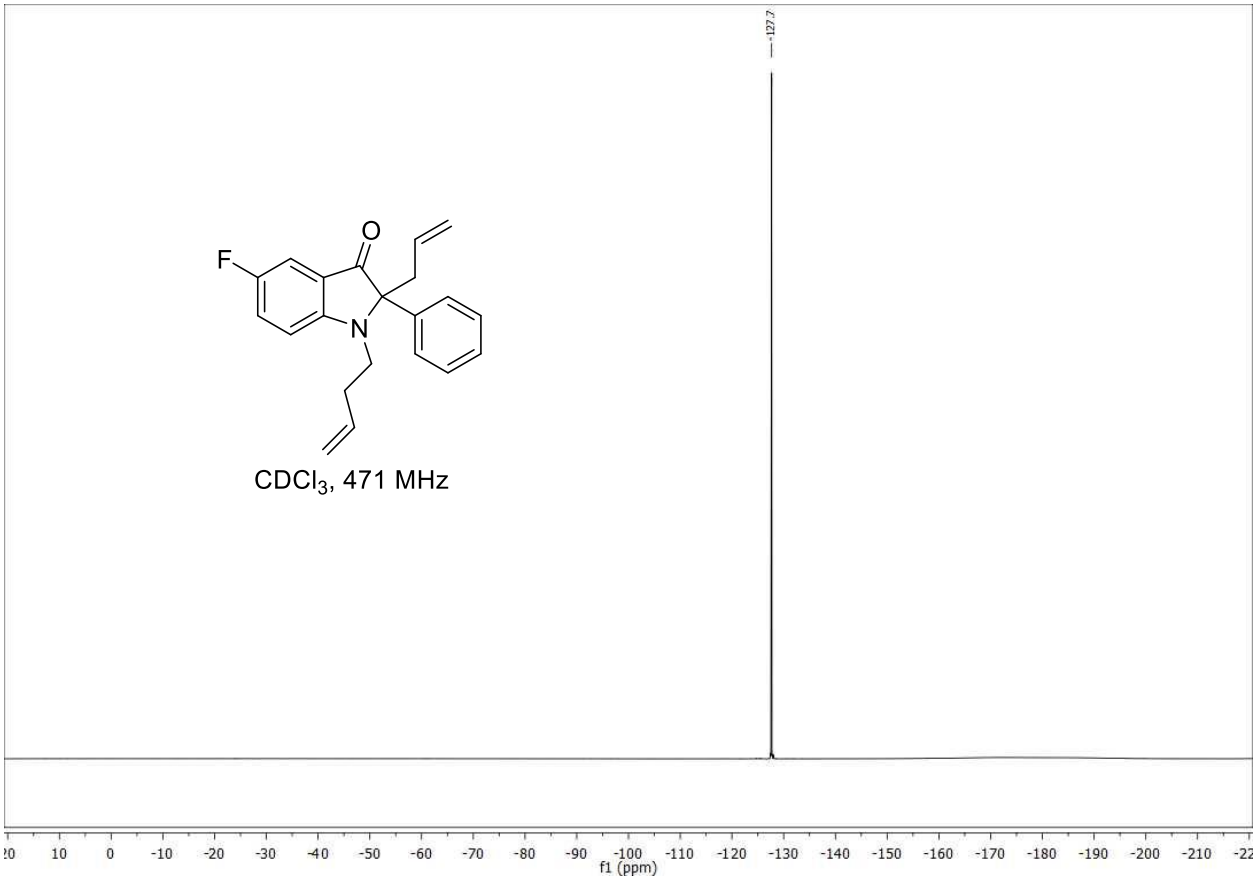




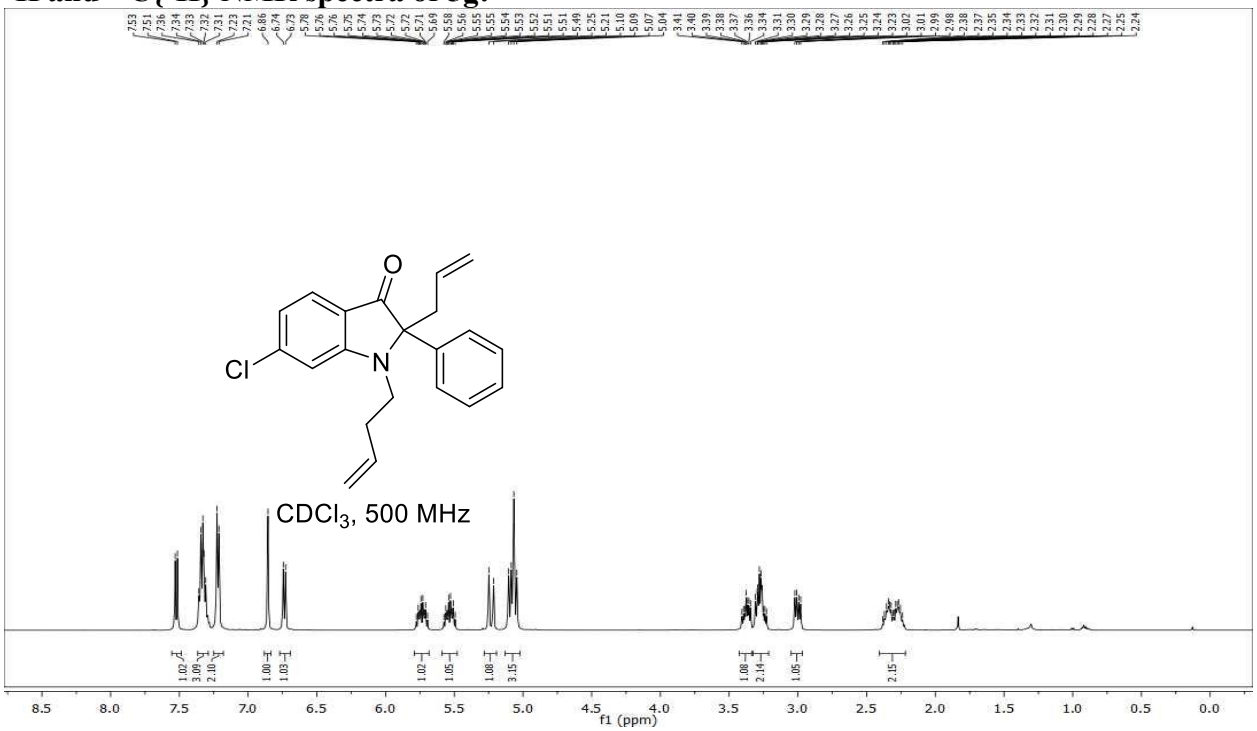
^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectra of 5f:

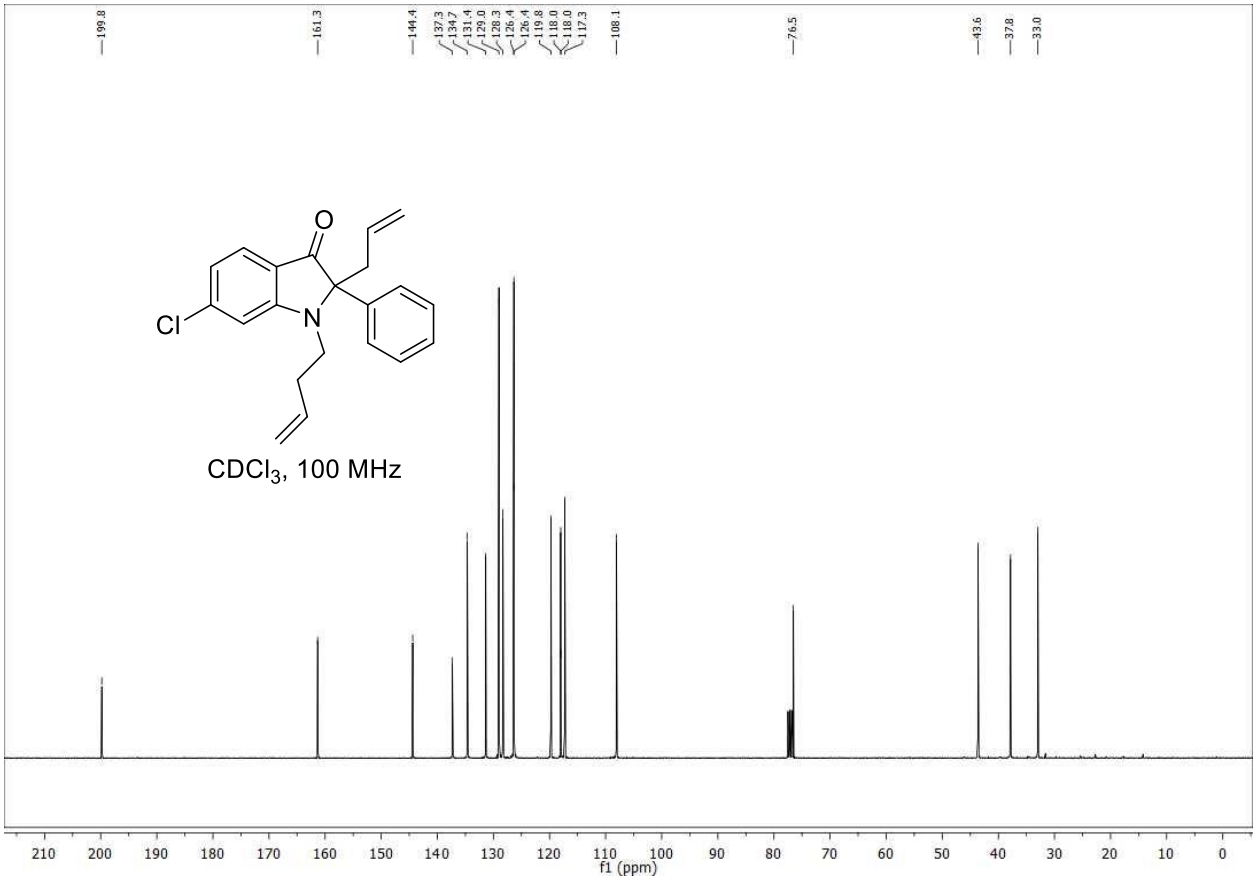




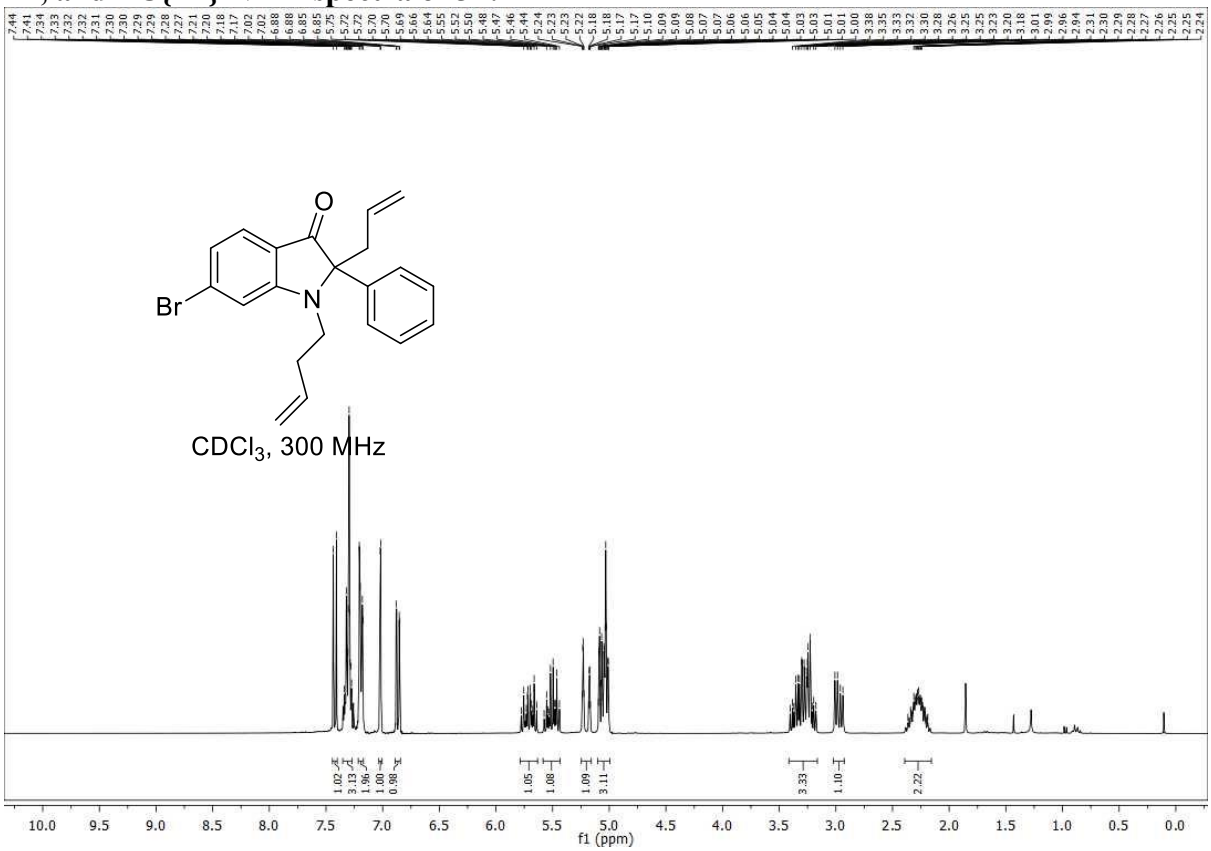


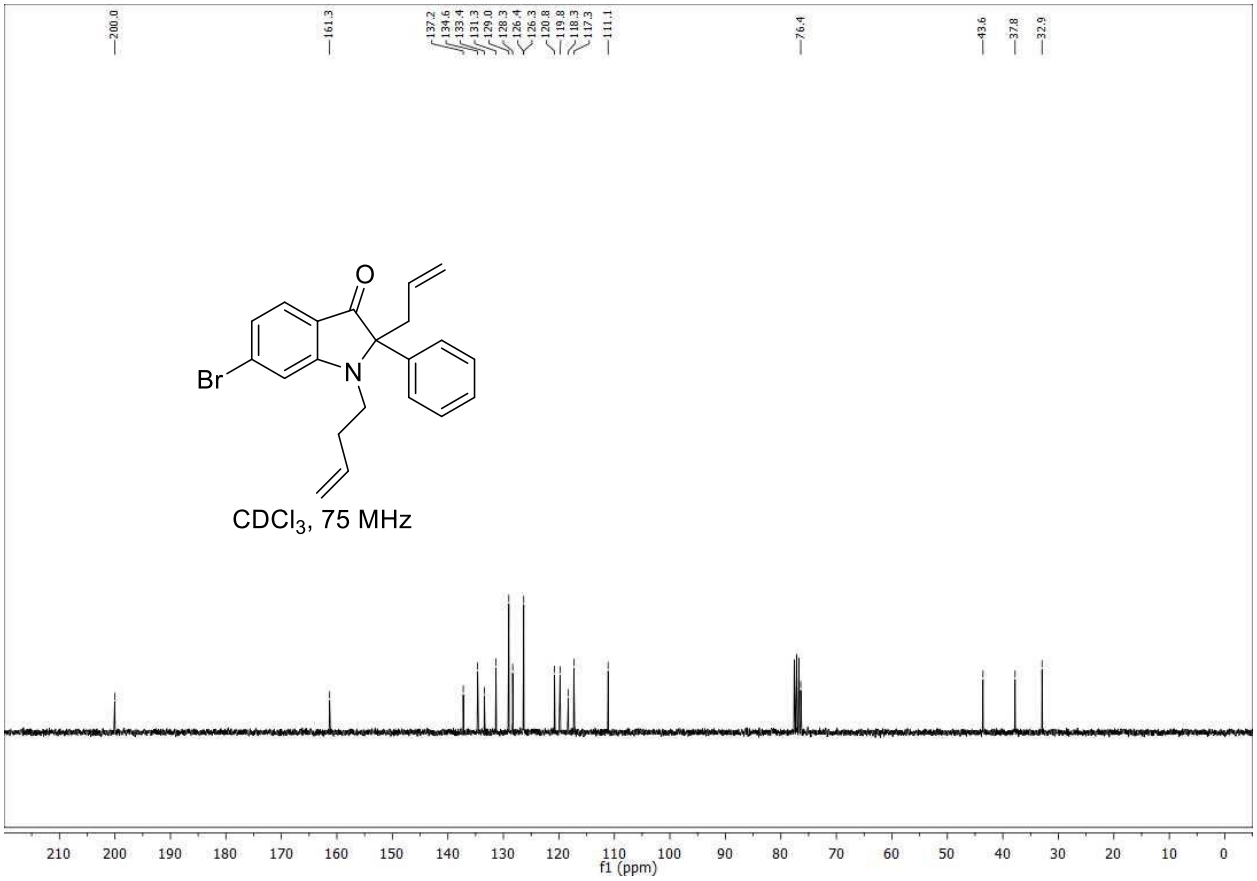
^{1}H and ^{13}C{^{1}H} NMR spectra of 5g:



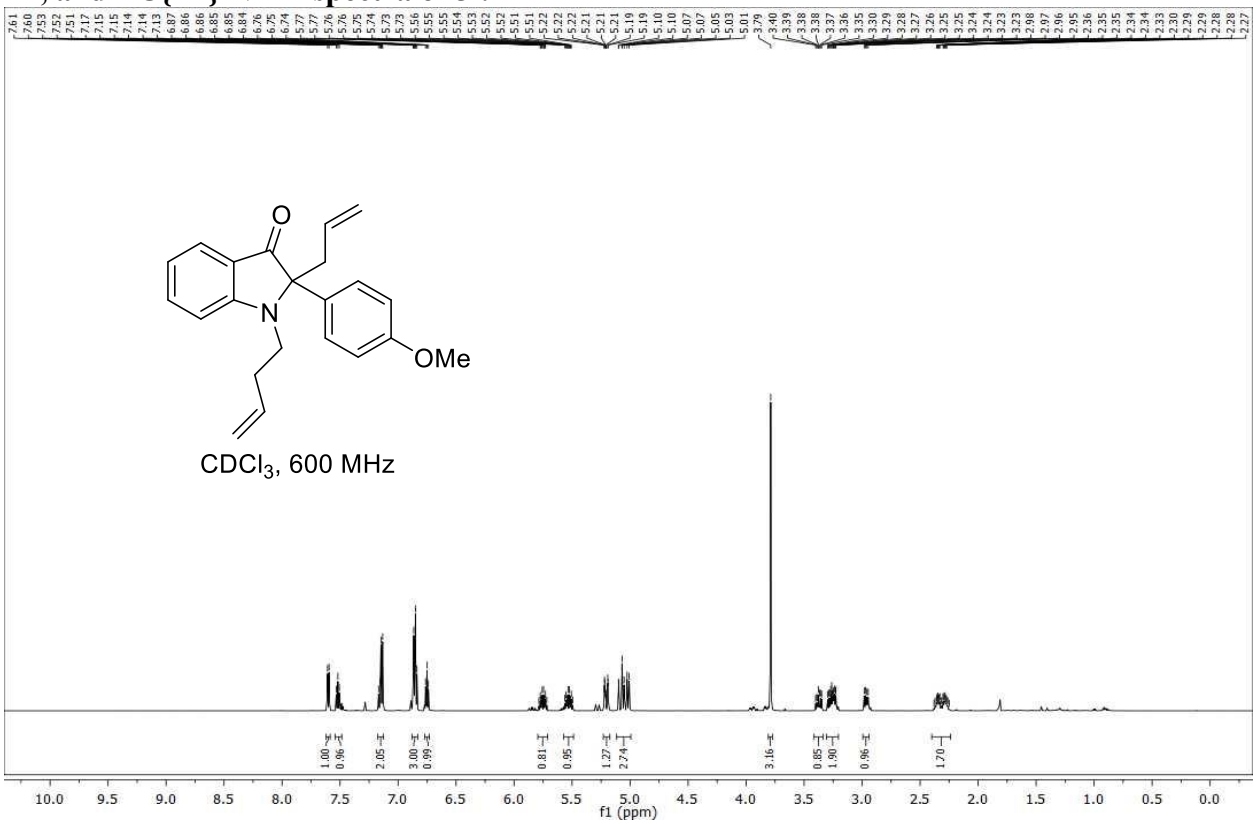


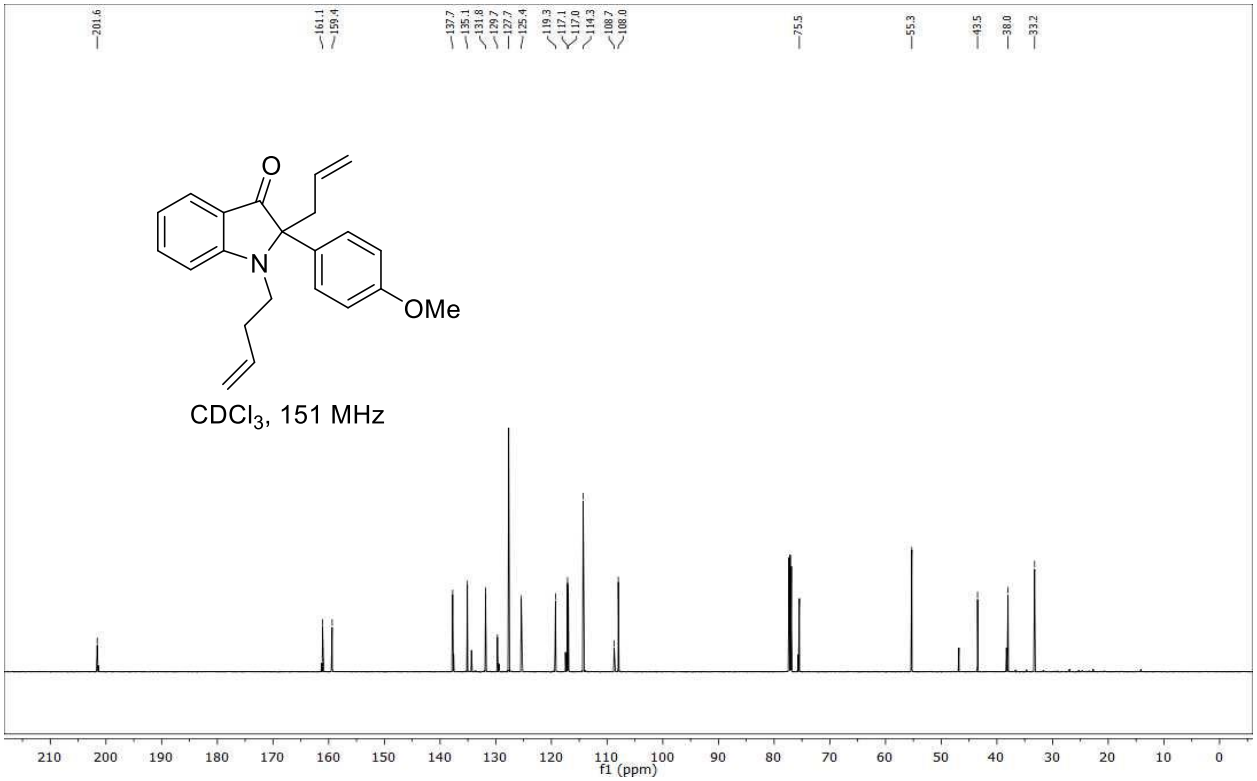
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5h:



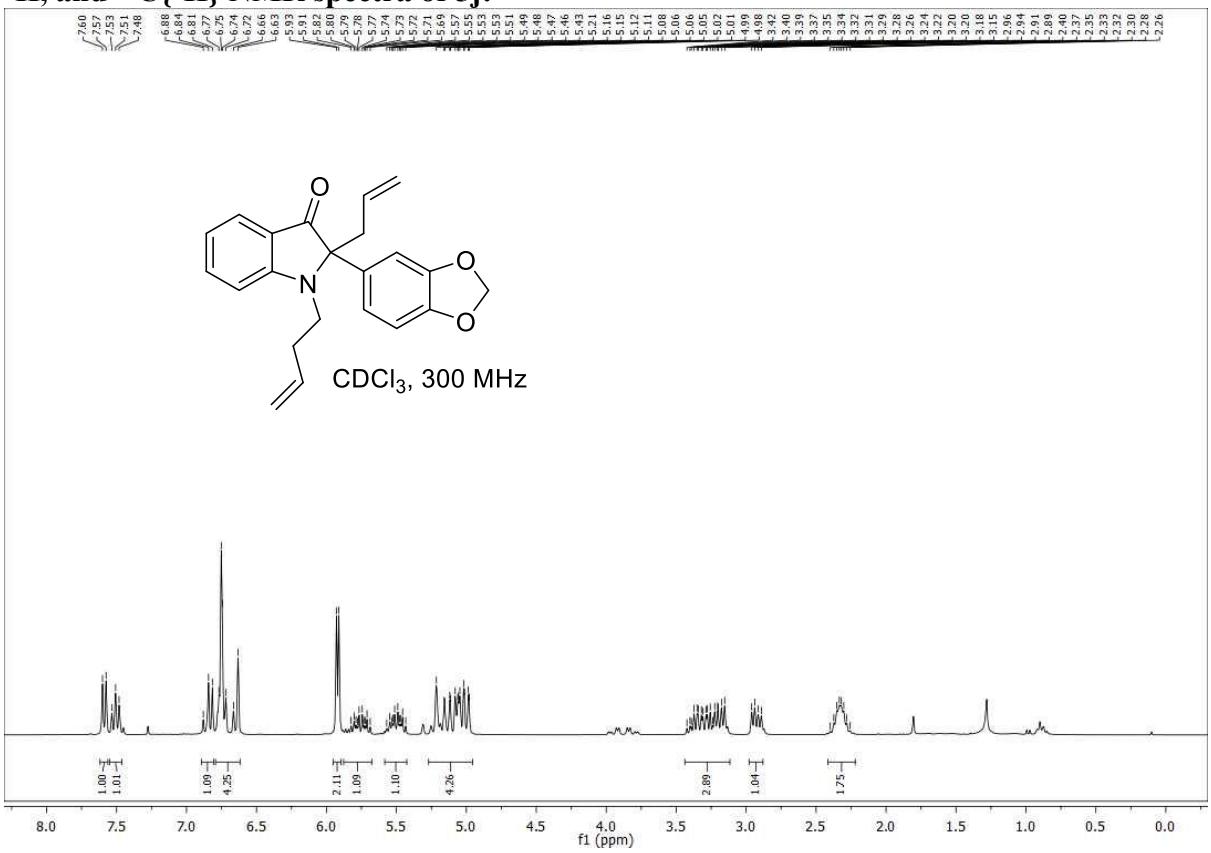


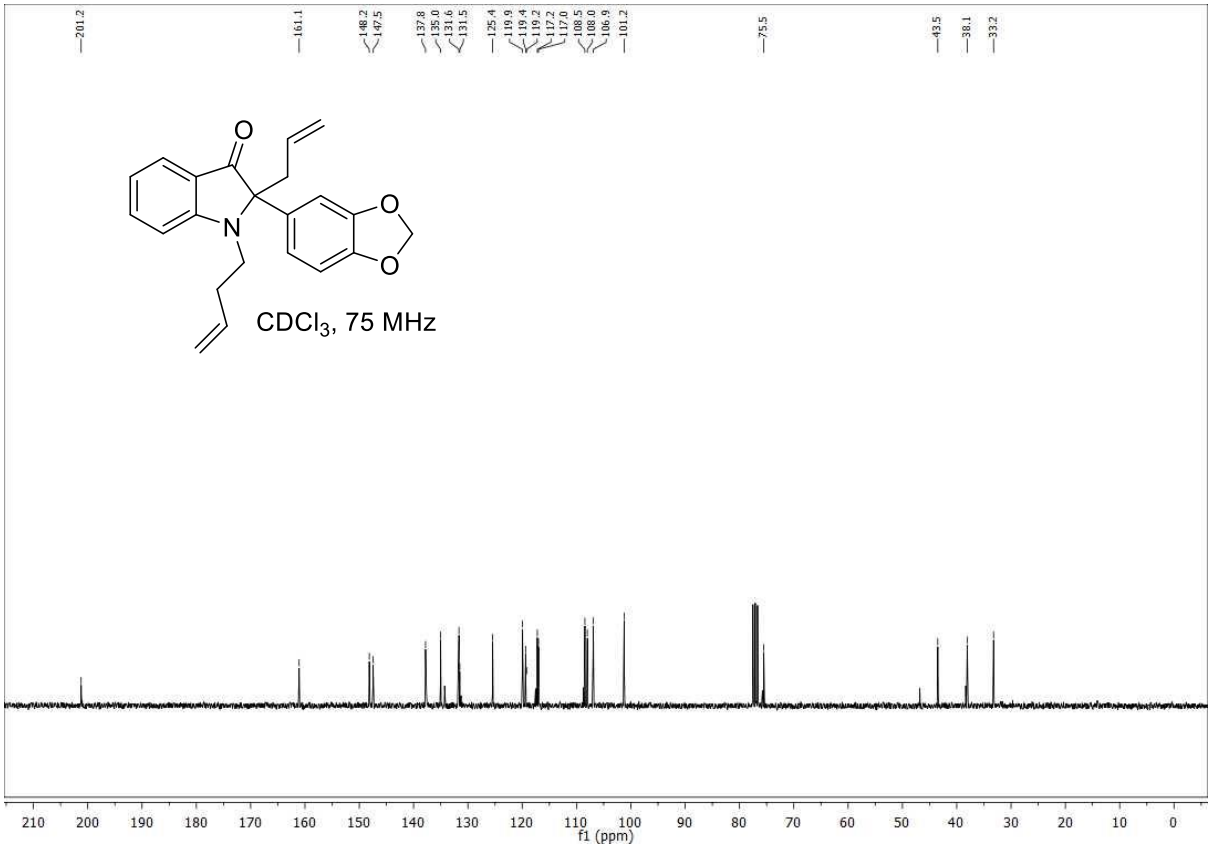
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5i:



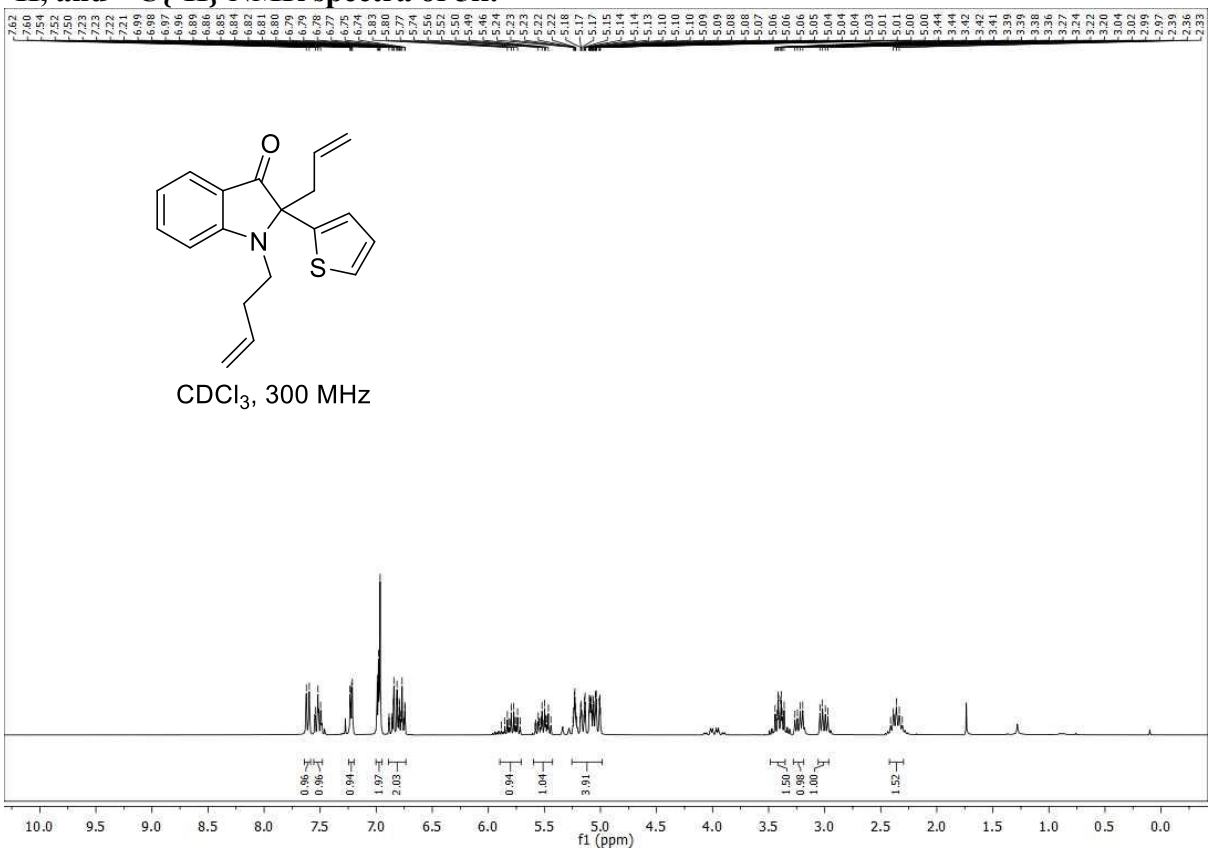


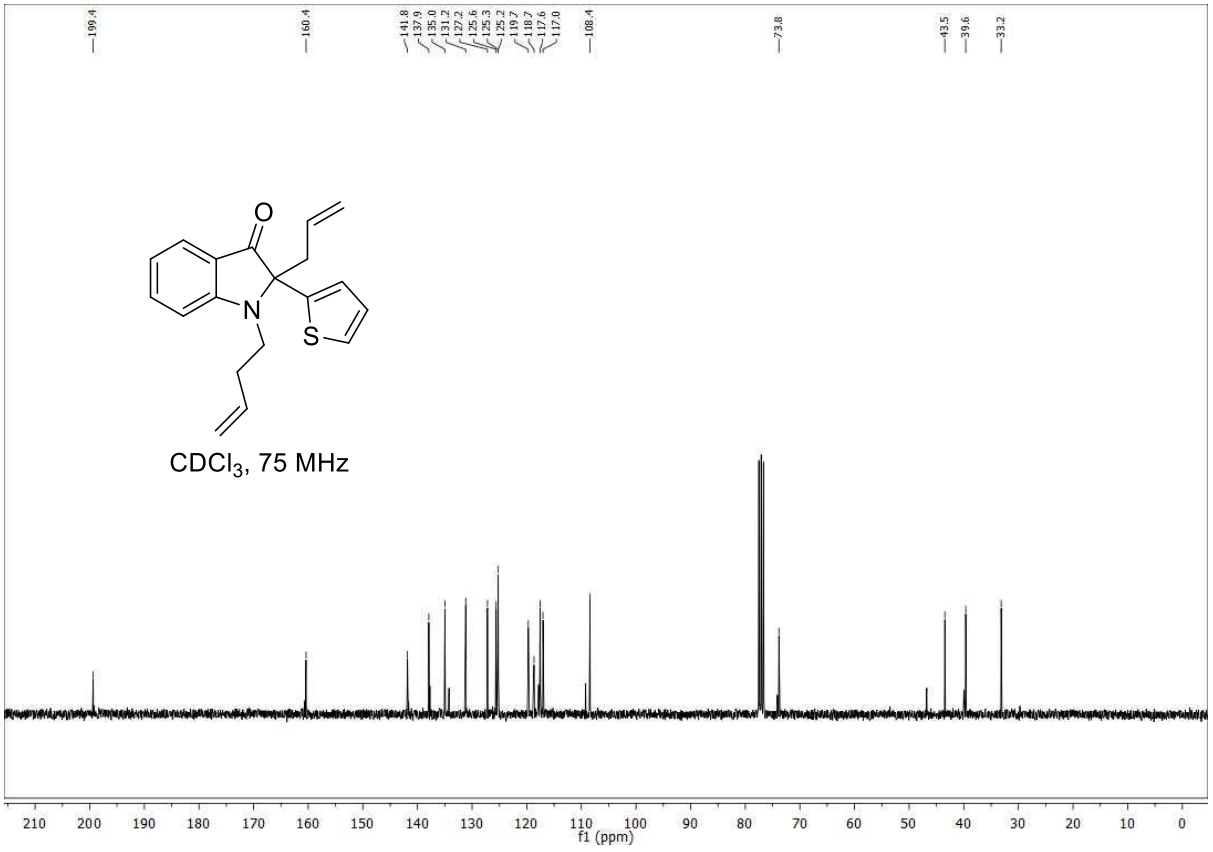
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5j:



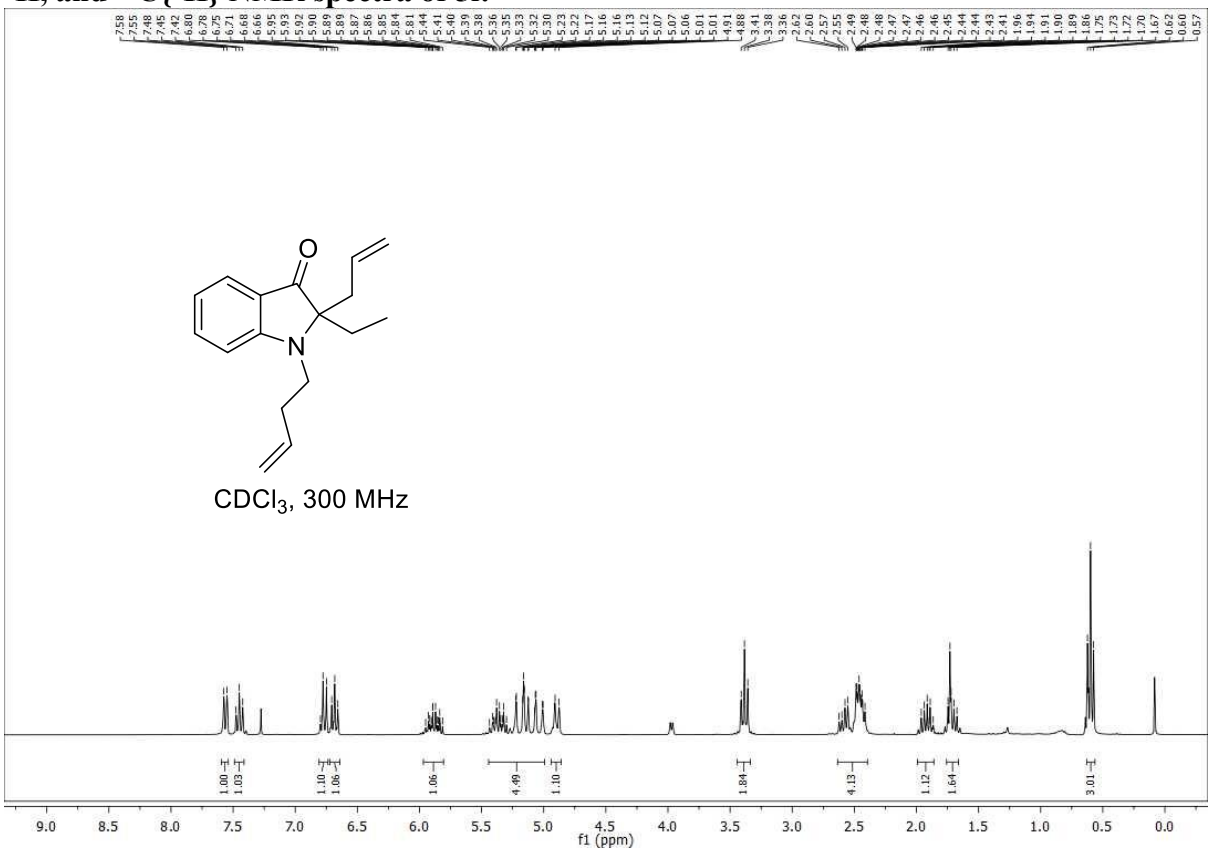


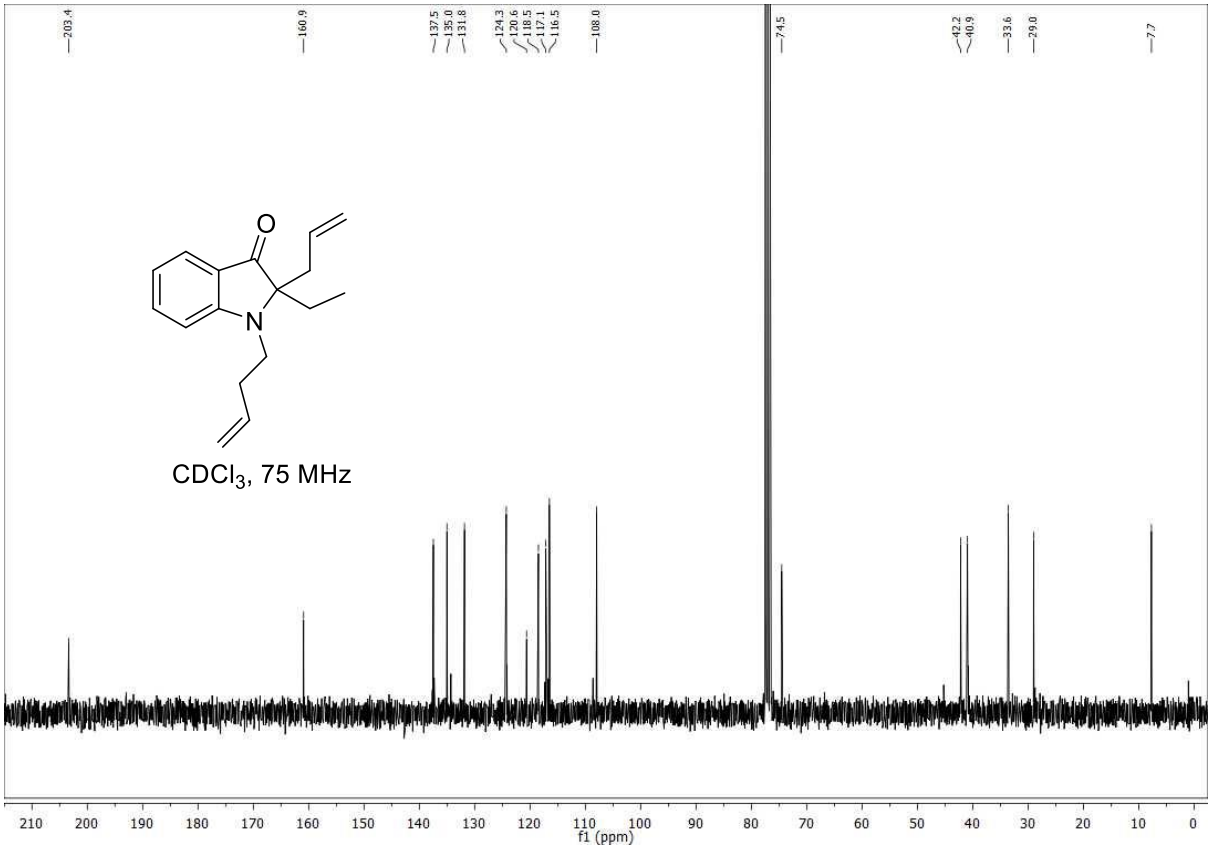
^{1}H, and $^{13}C\{^{1}H\}$ NMR spectra of 5k:



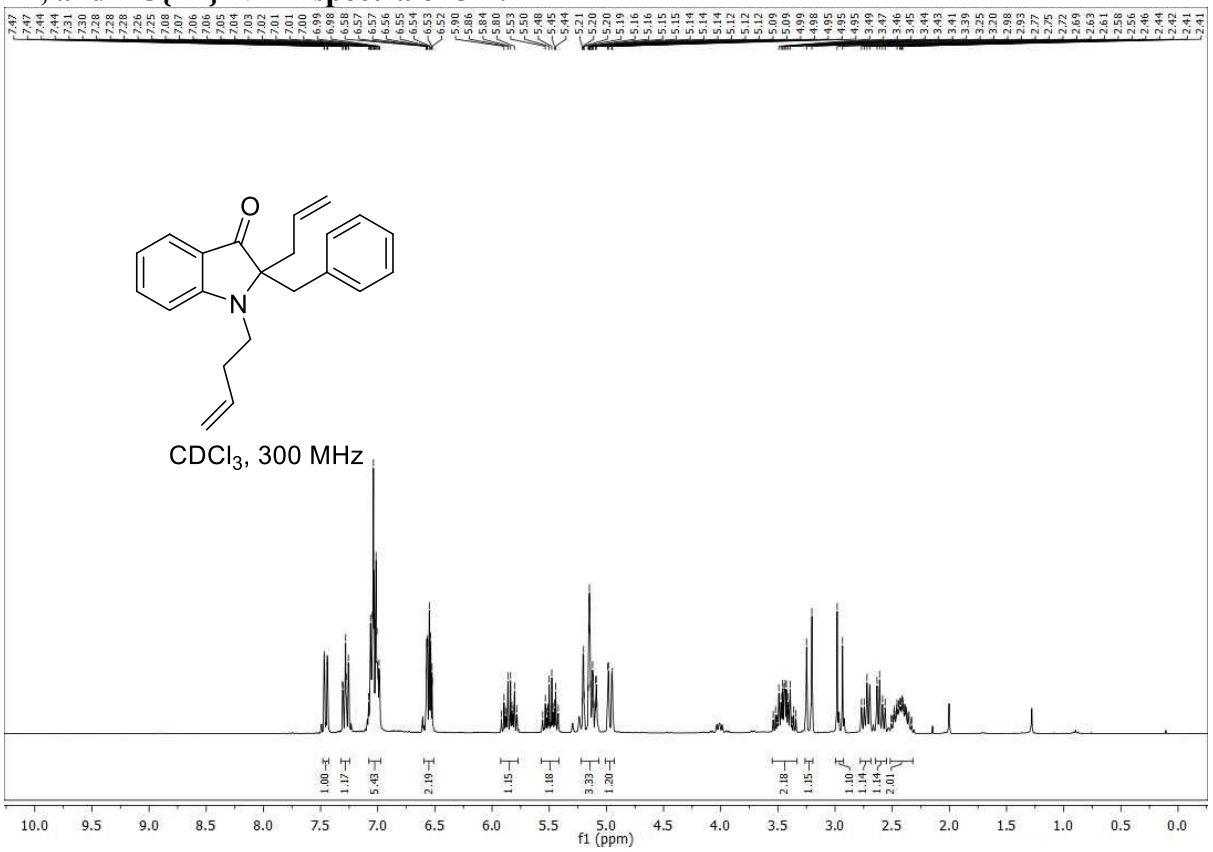


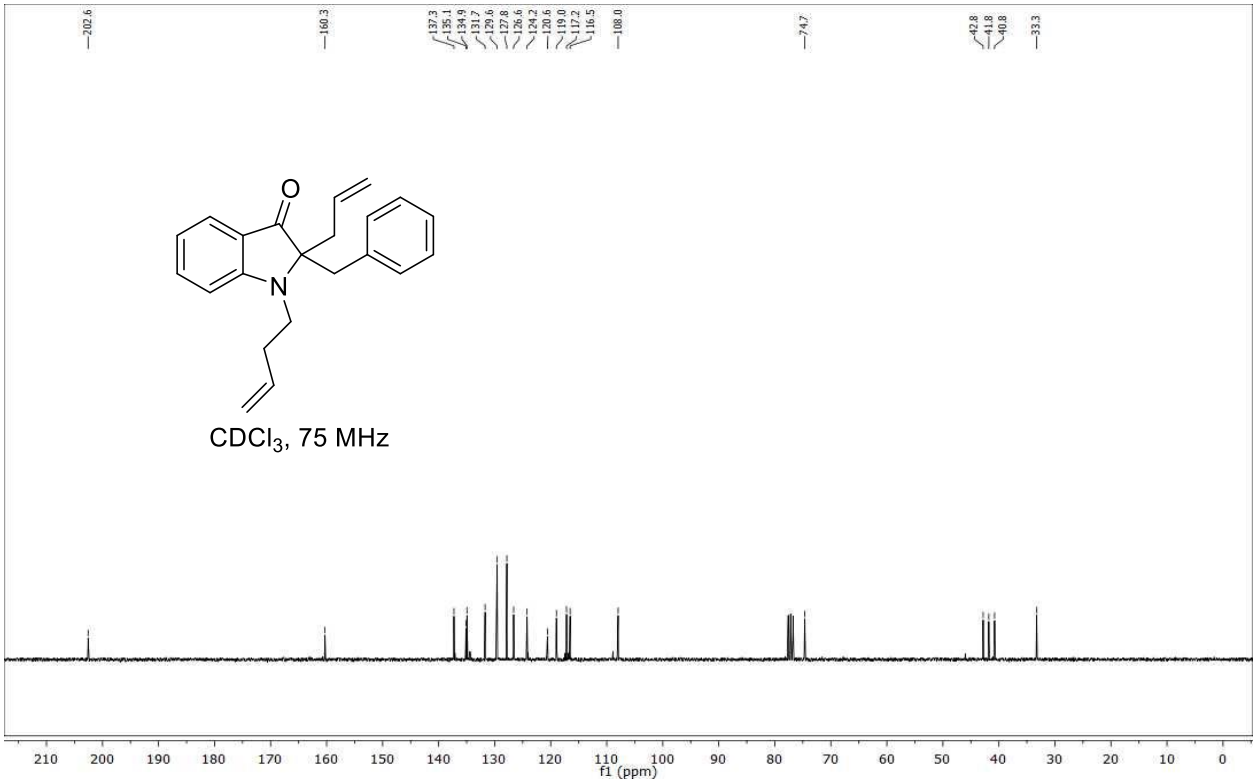
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5l:



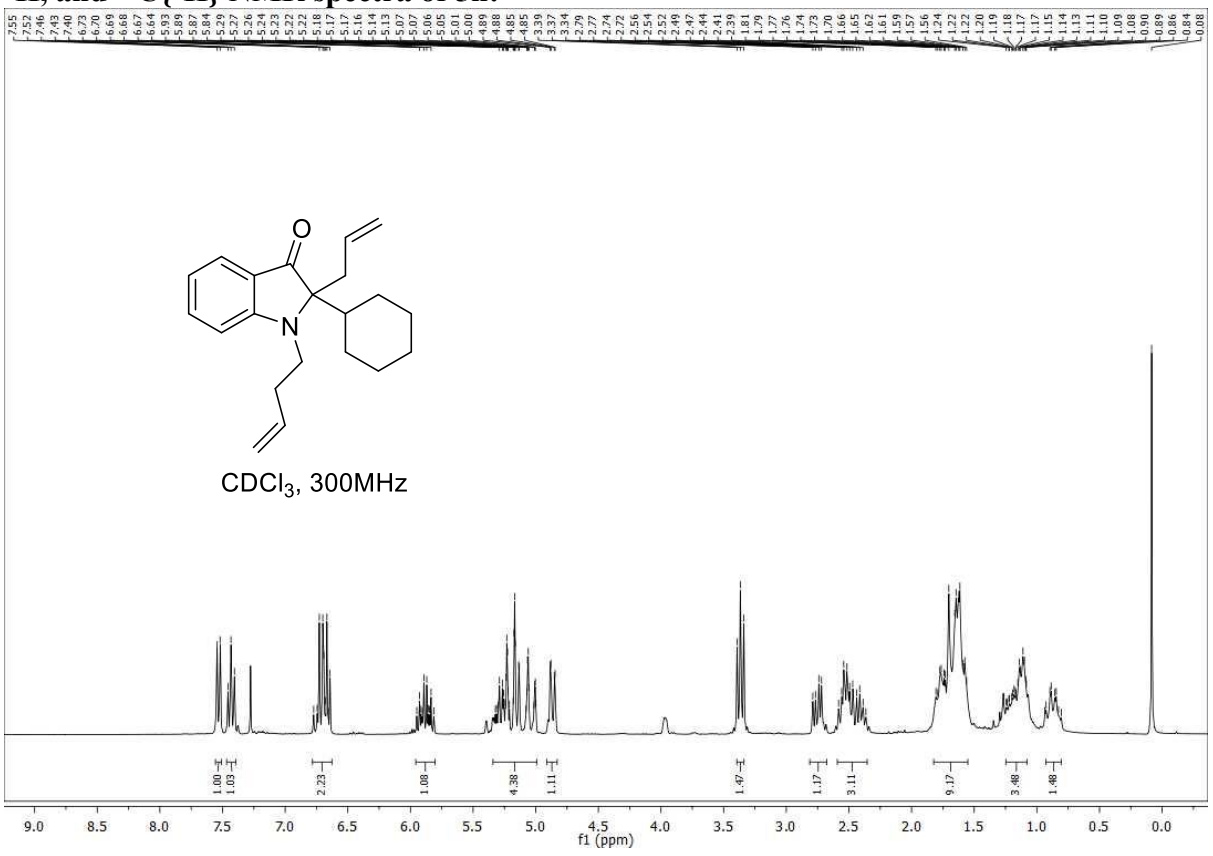


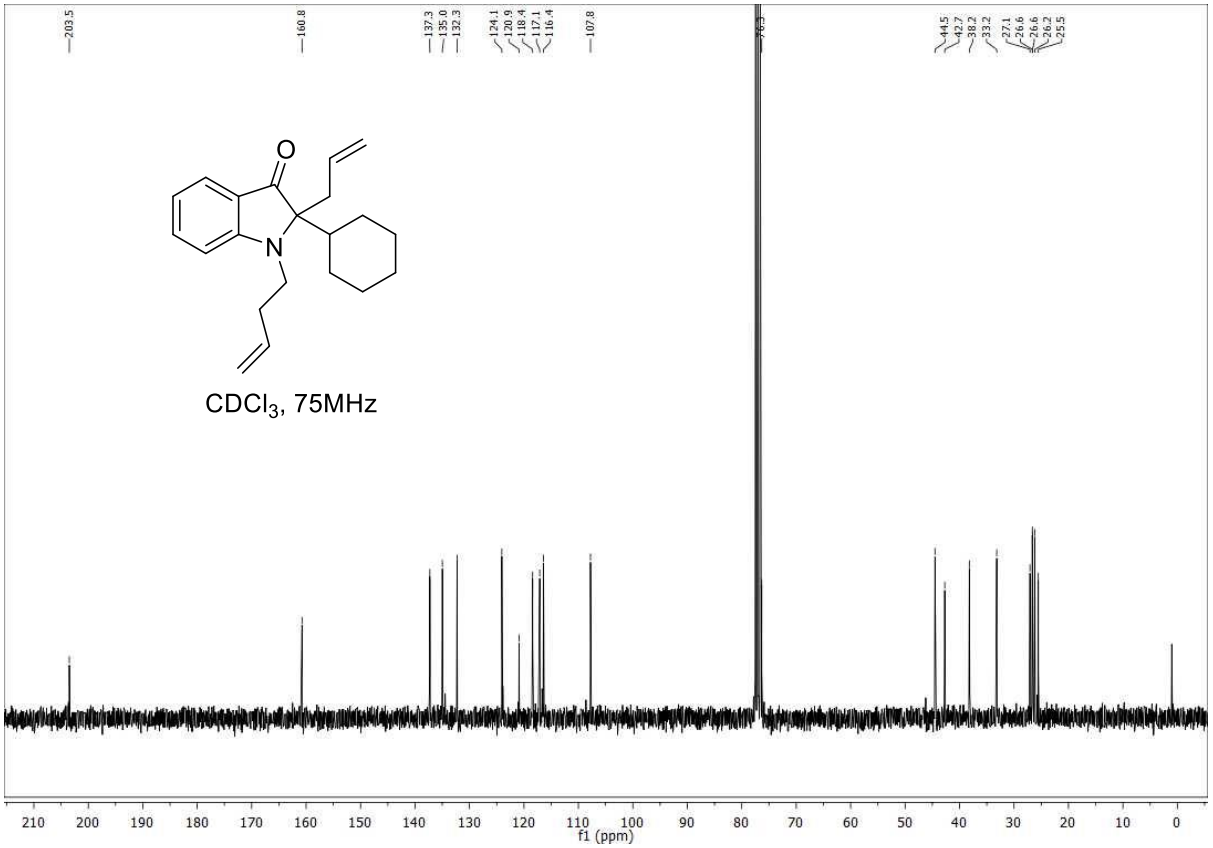
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5m:



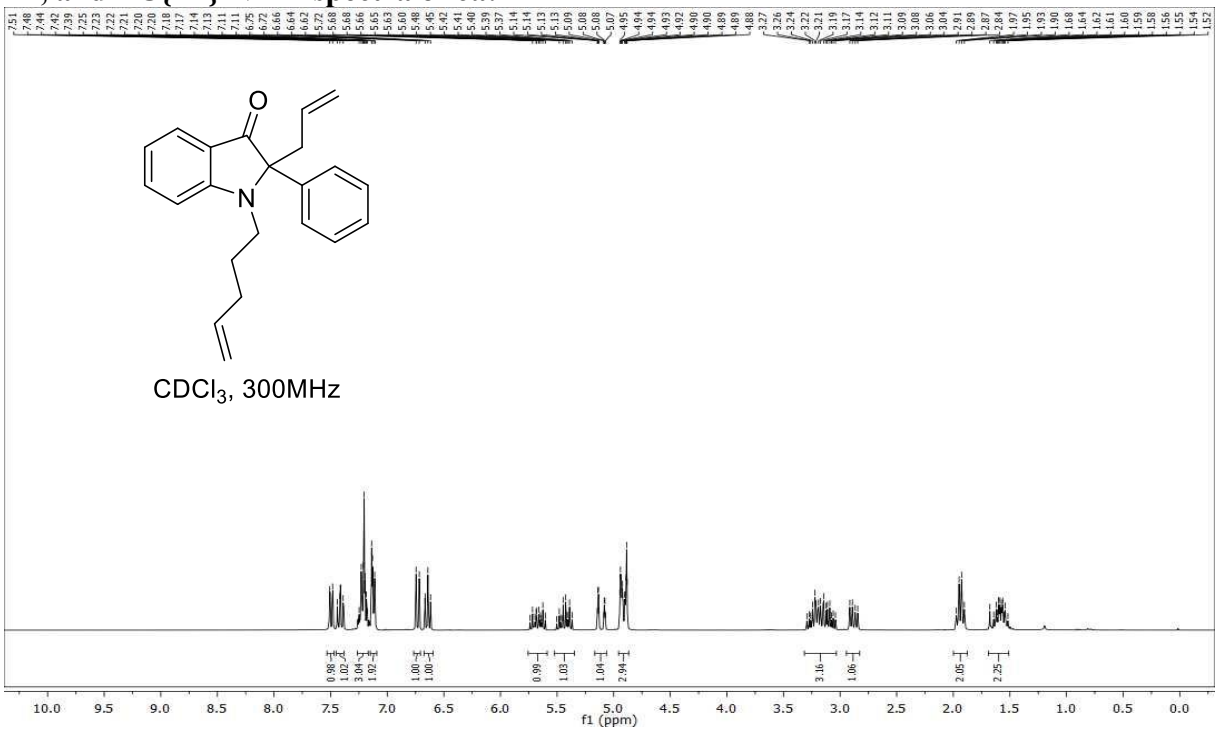


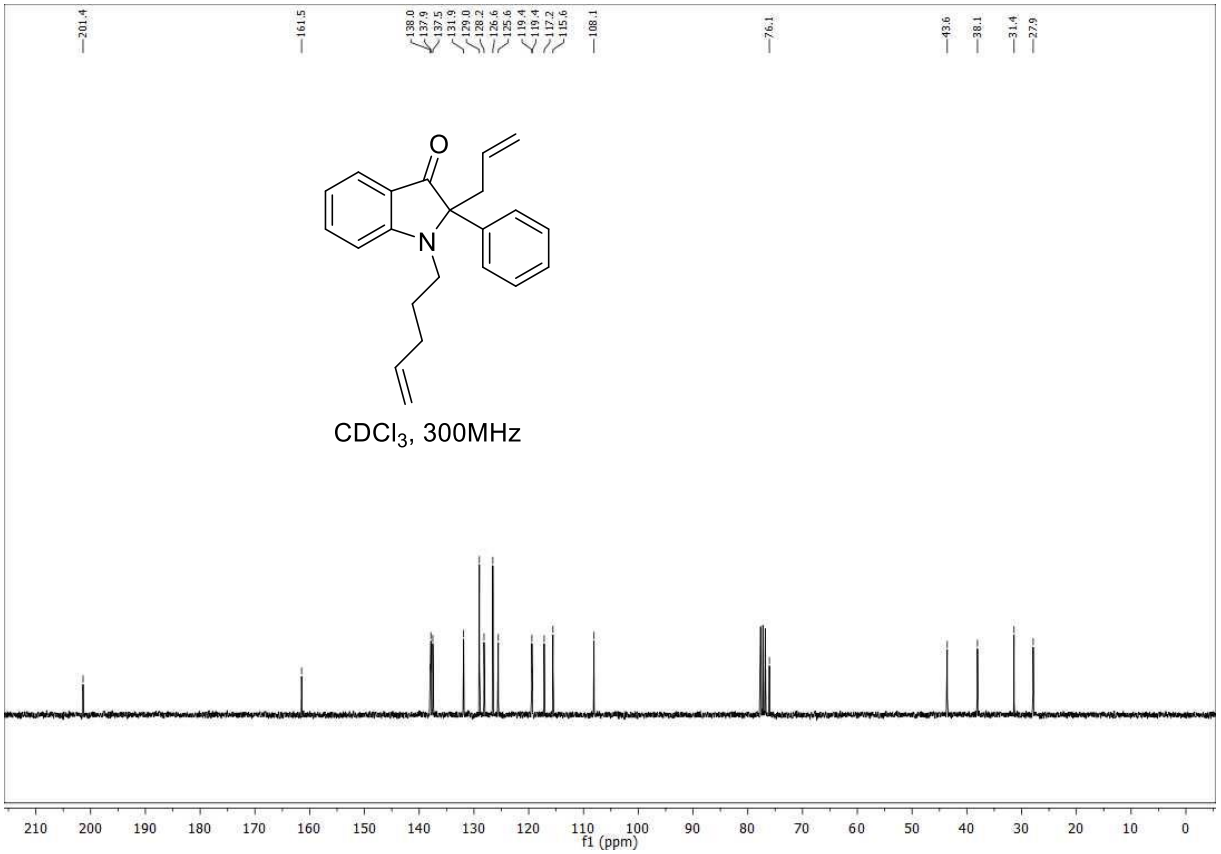
^{1}H, and ^{13}C{^{1}H} NMR spectra of 5n:



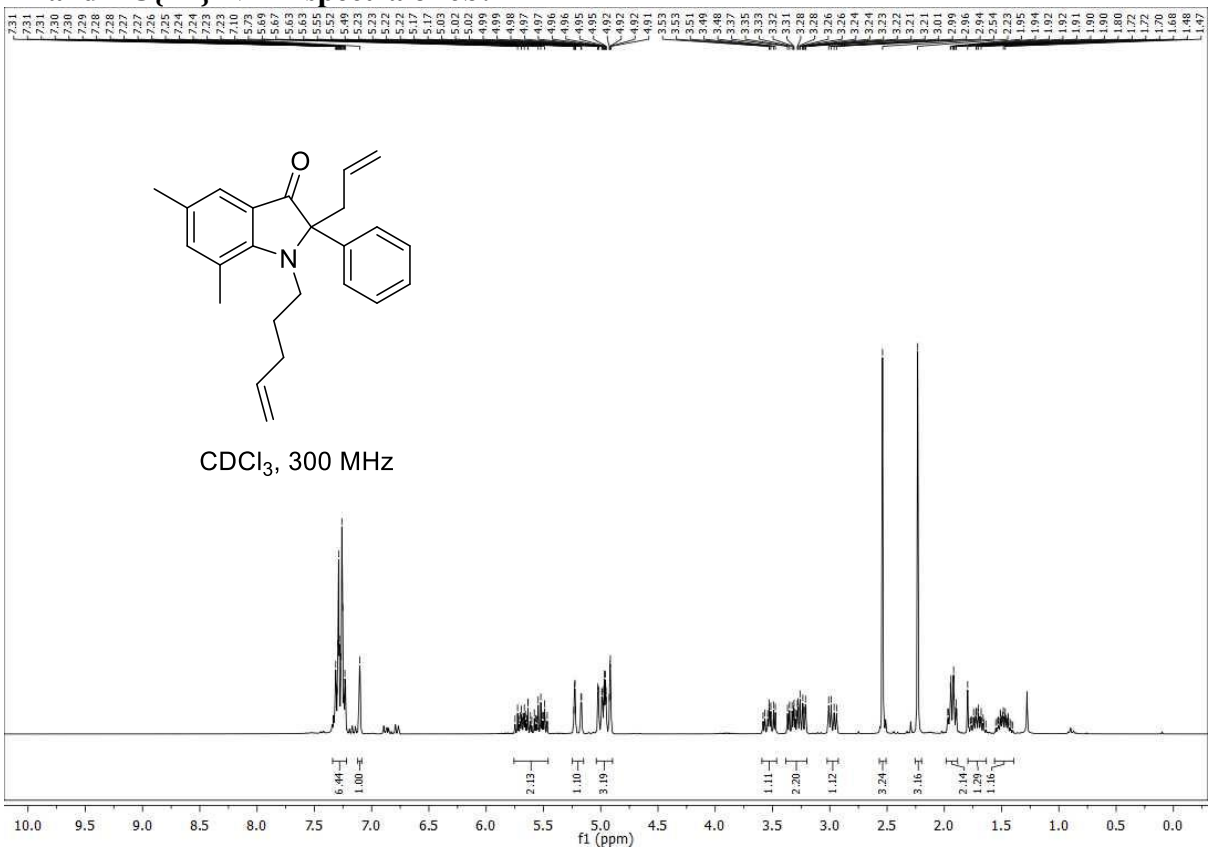


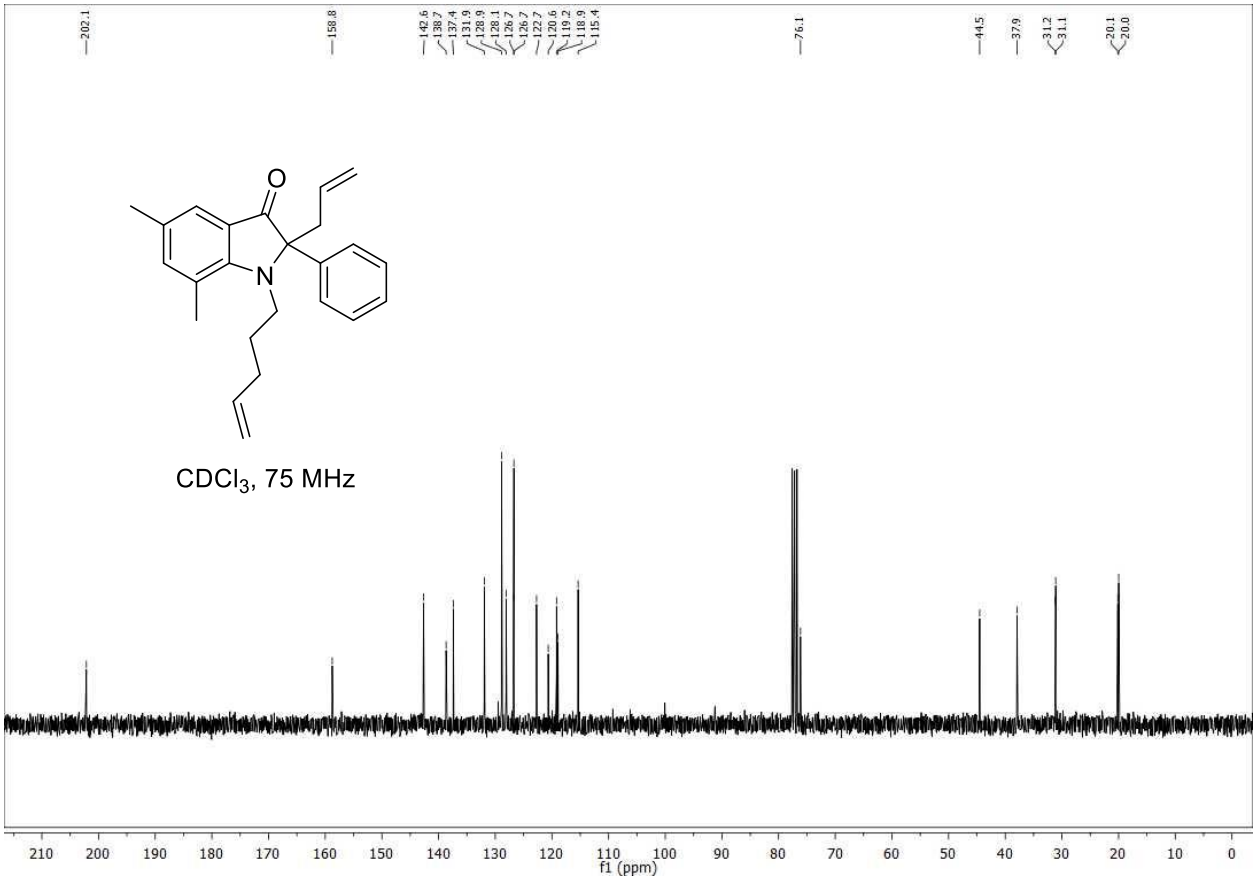
^{1}H, and ^{13}C{^{1}H} NMR spectra of 6a:



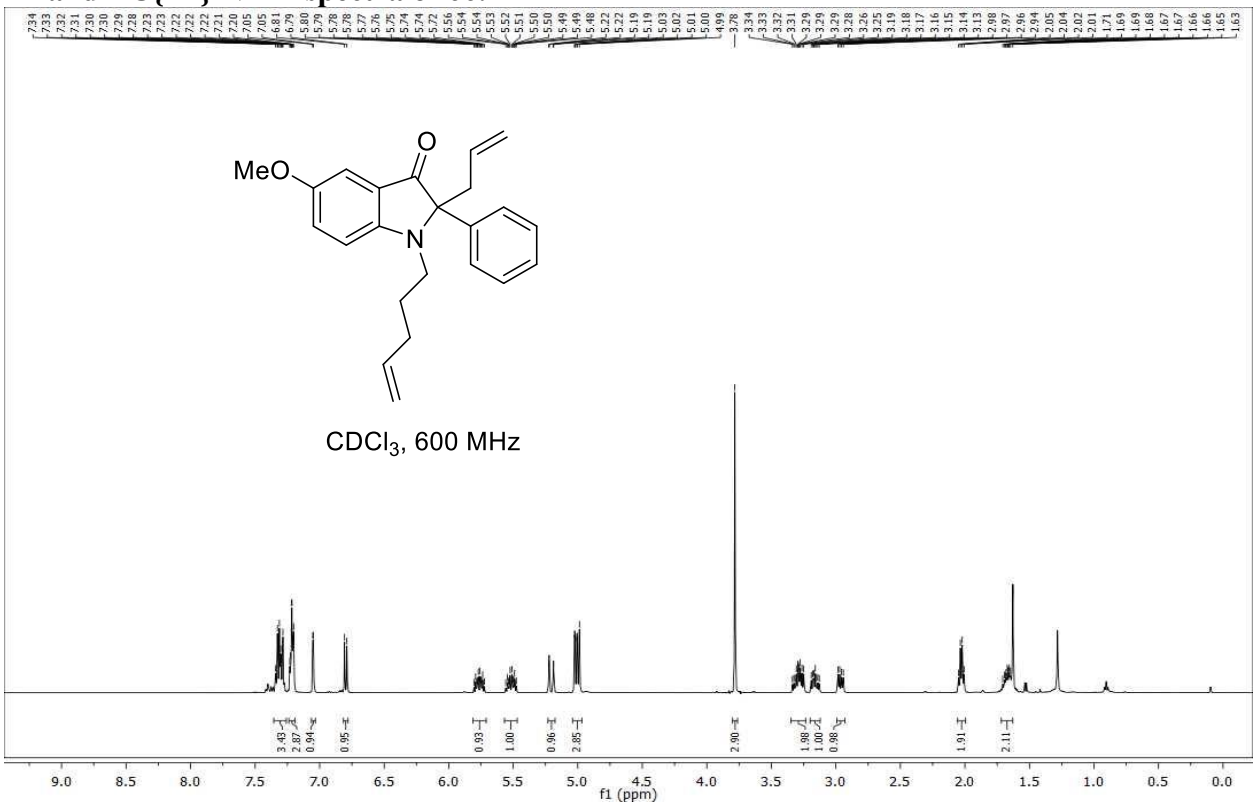


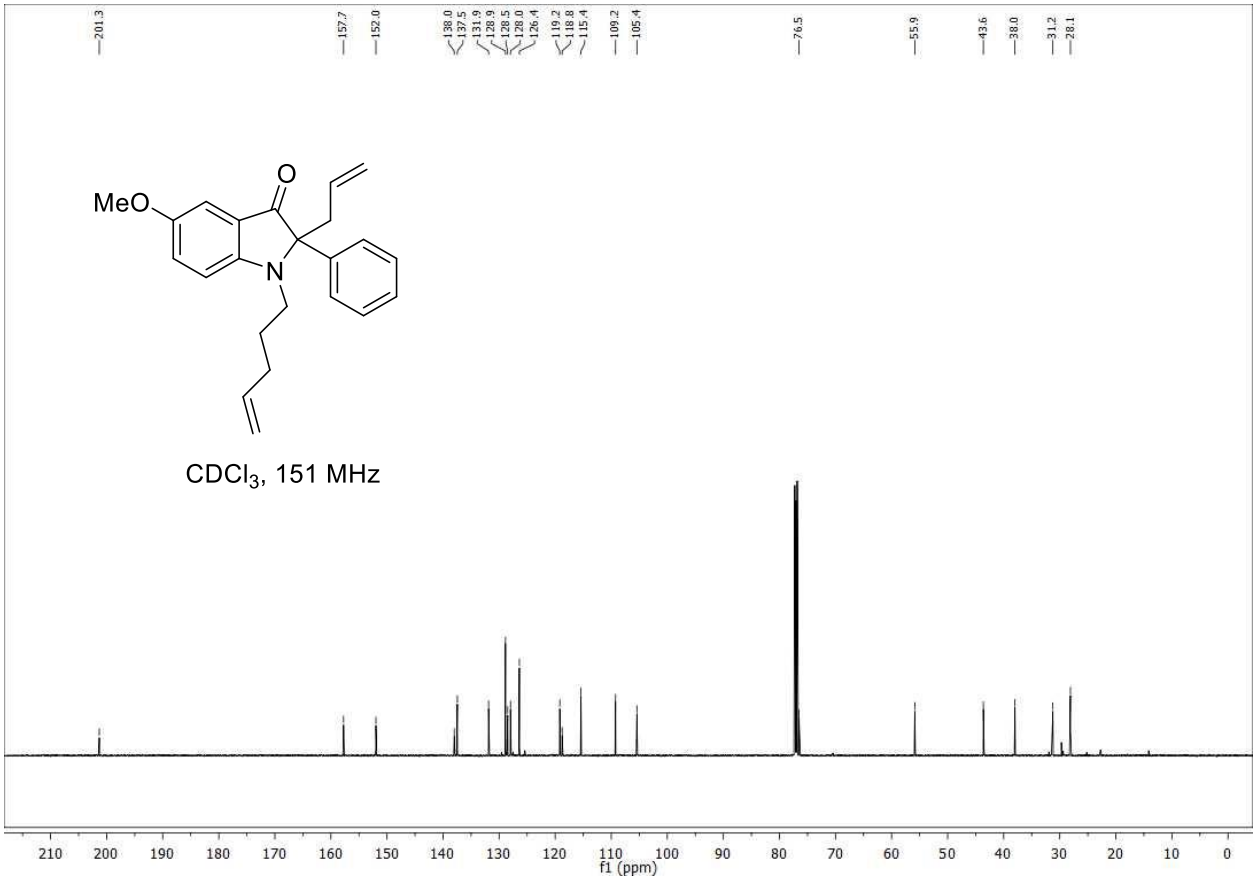
^{1}H and ^{13}C{^{1}H} NMR spectra of 6b:



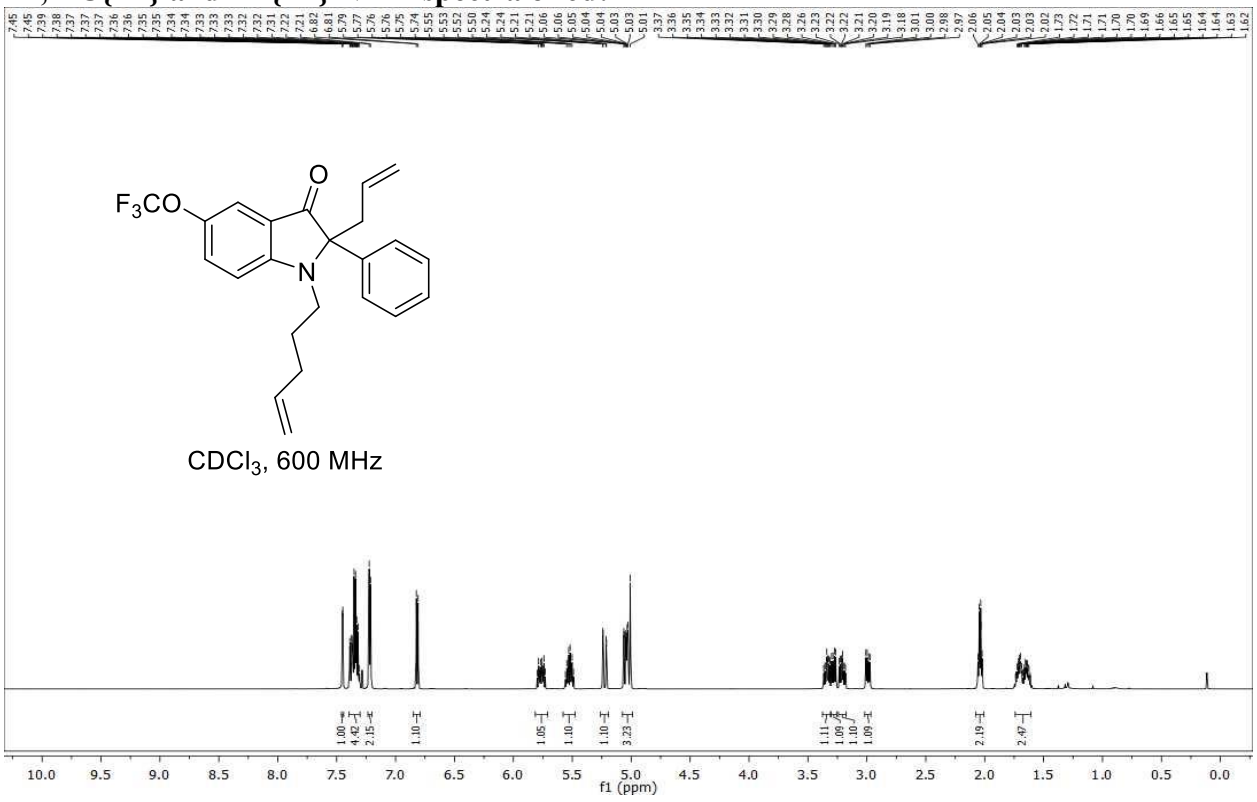


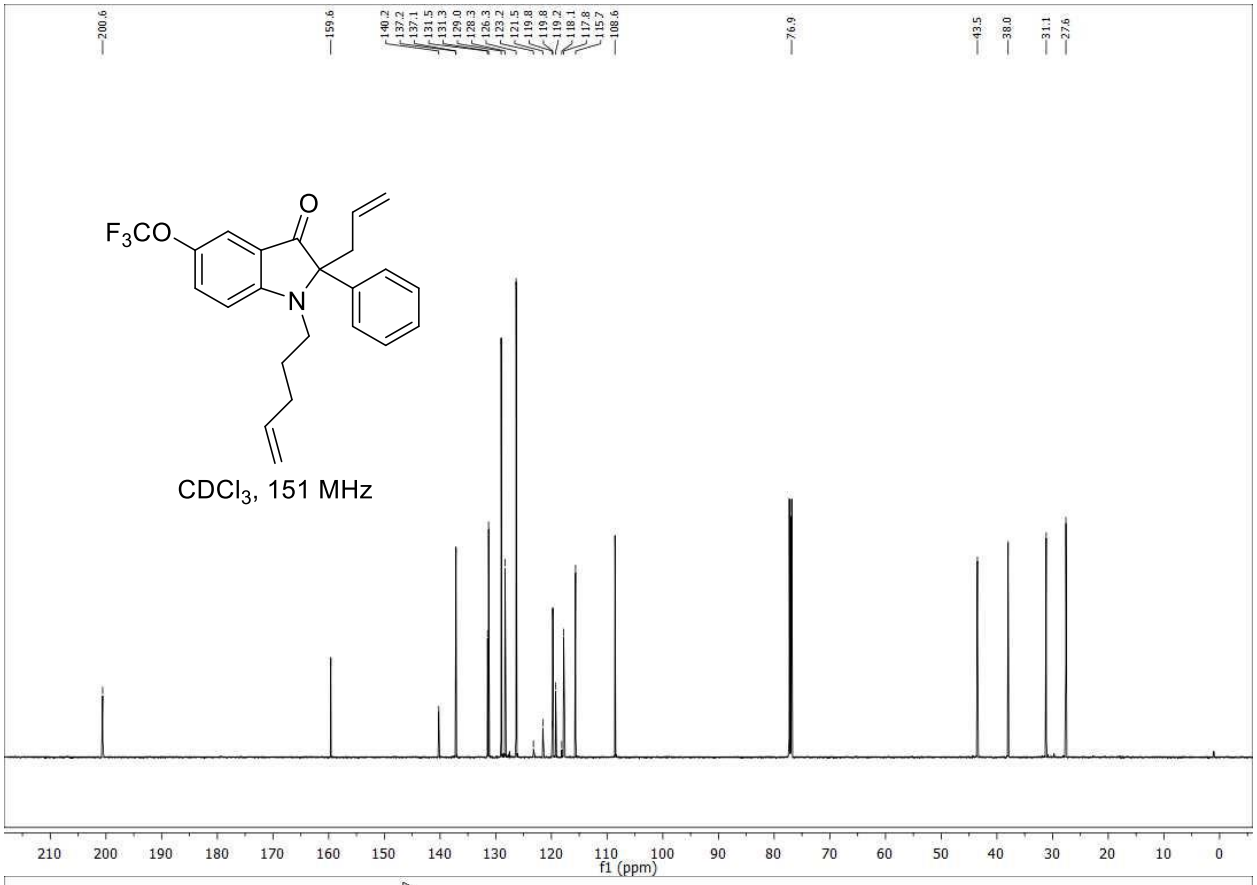
^{1}H and ^{13}C{^{1}H} NMR spectra of 6c:





^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectra of 6d:

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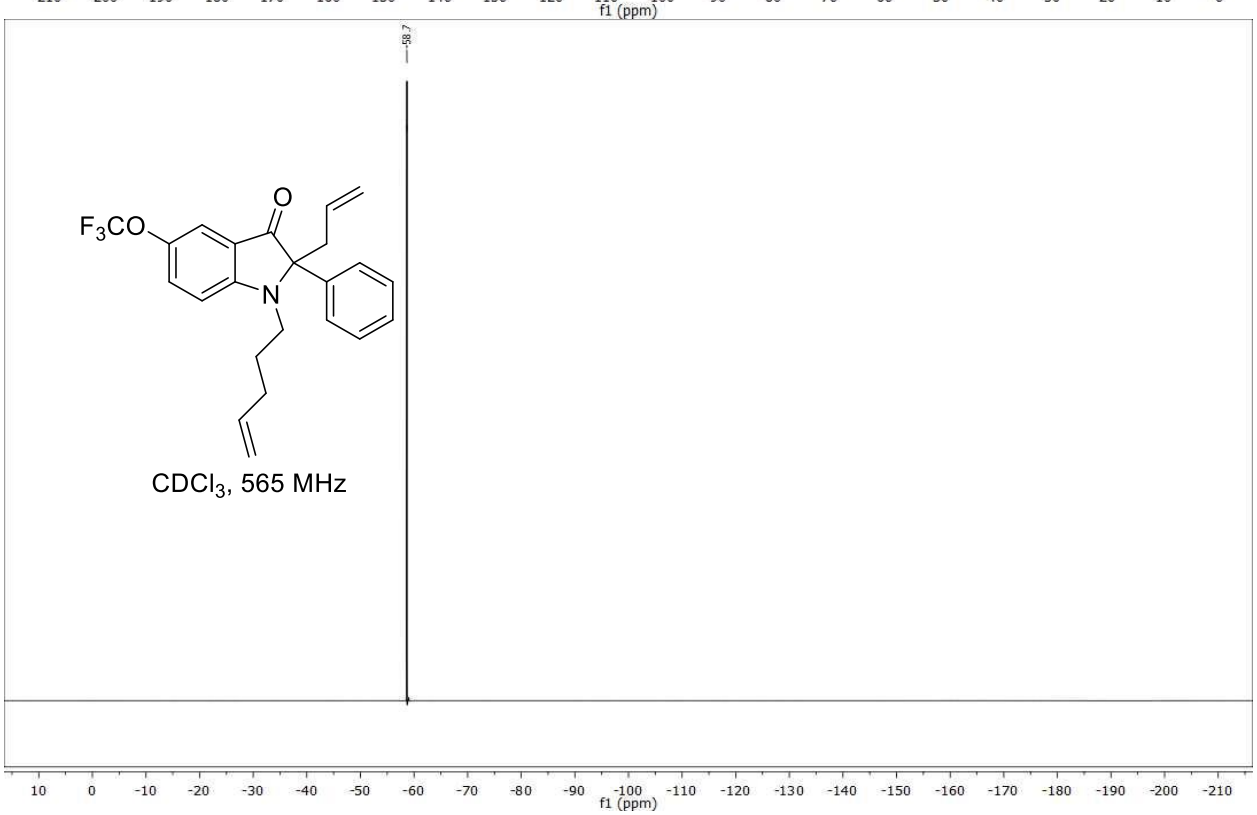
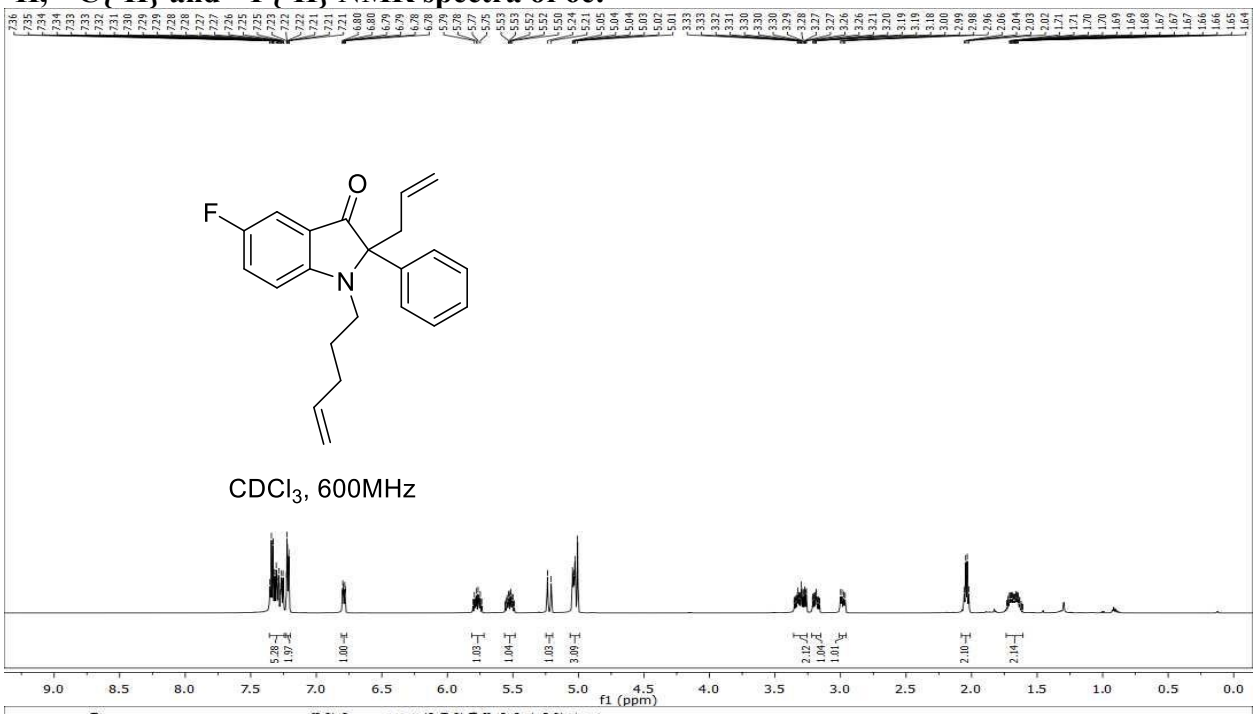
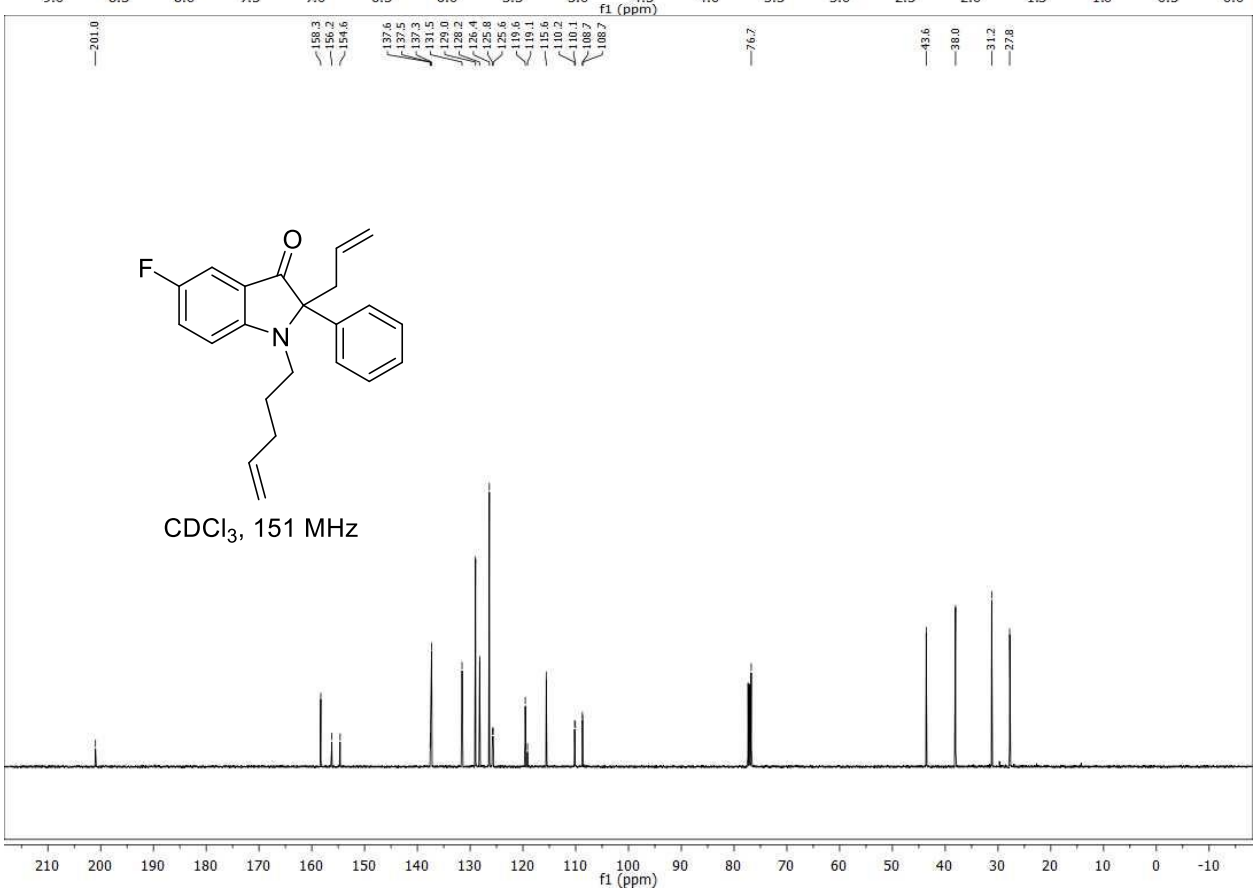
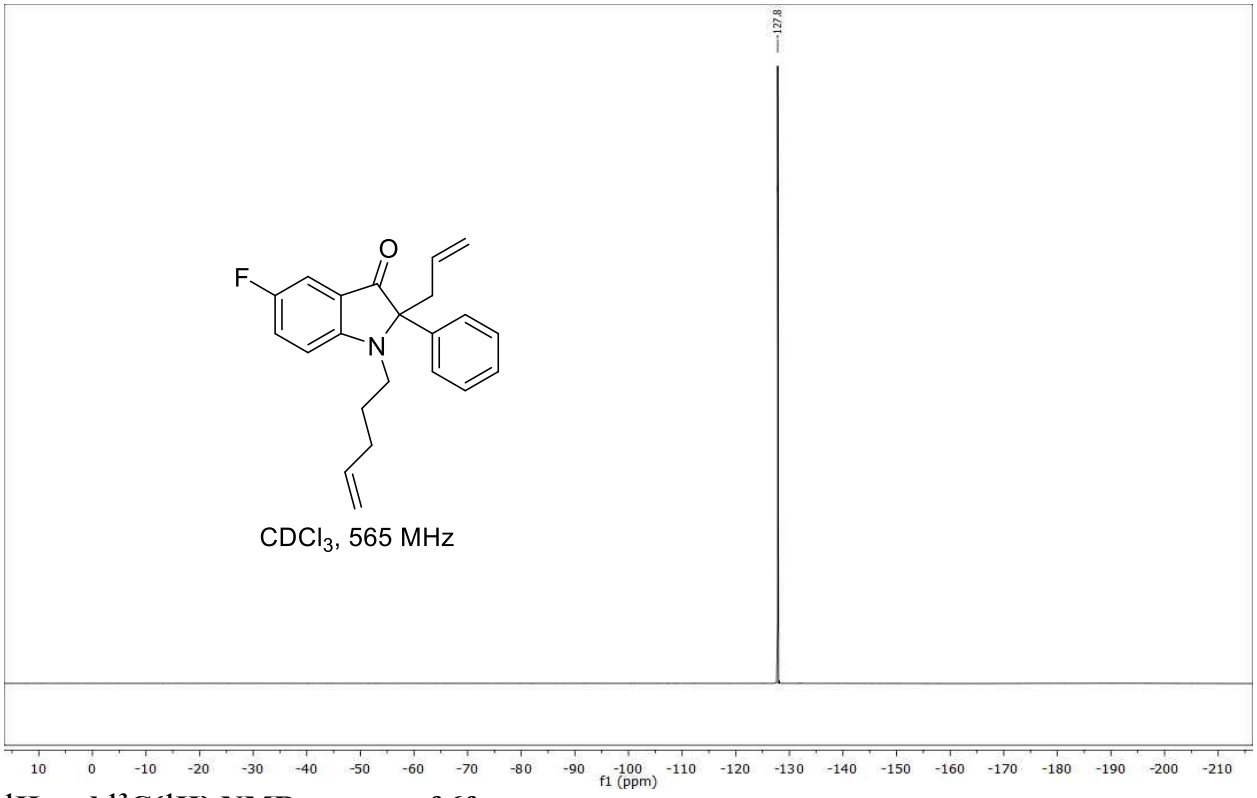
159.6
140.2
137.2
137.1
131.5
131.3
129.0
128.3
126.3
123.2
121.5
119.8
119.8
119.2
118.1
117.8
115.7
108.6
76.9
43.5
38.0
31.1
27.6
O
F3CO
N
CDCl3, 151 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


58.7
O
F3CO
N
CDCl3, 565 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

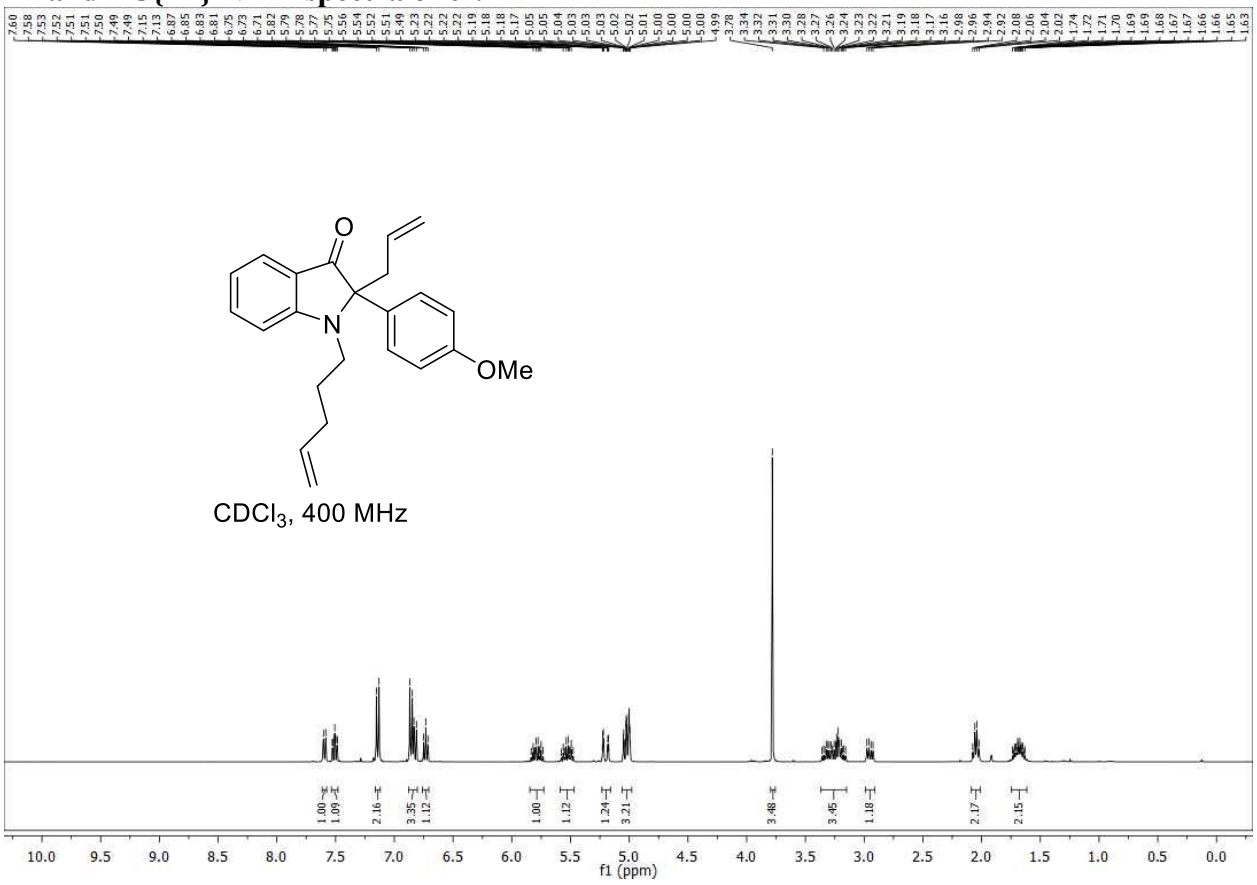
^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectra of 6e:

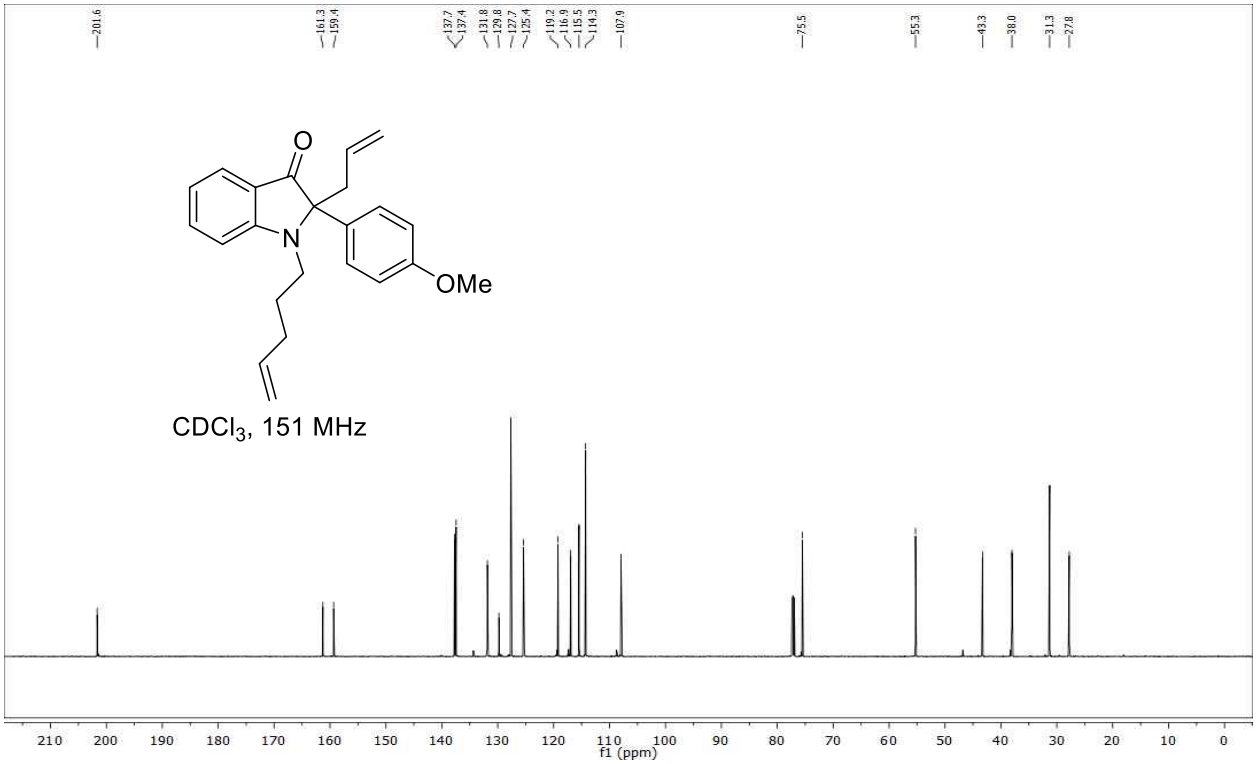




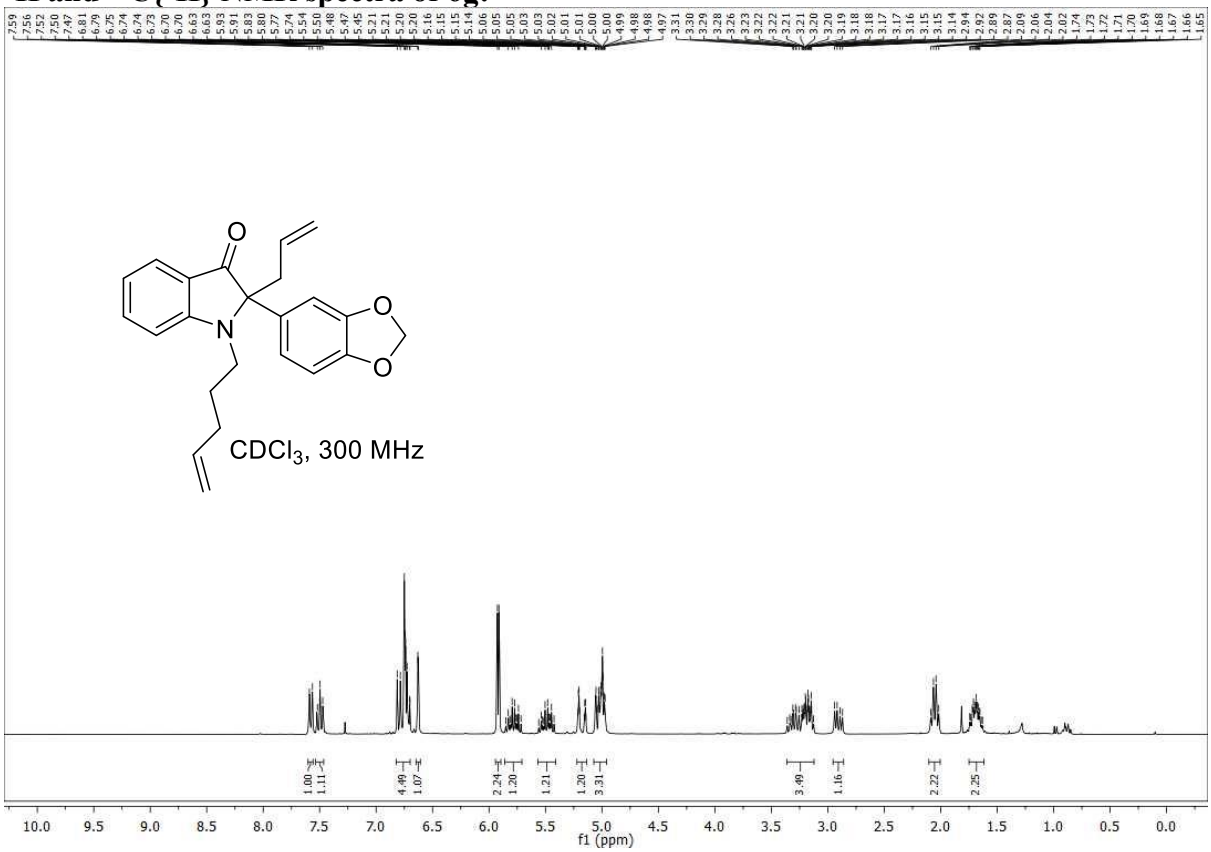


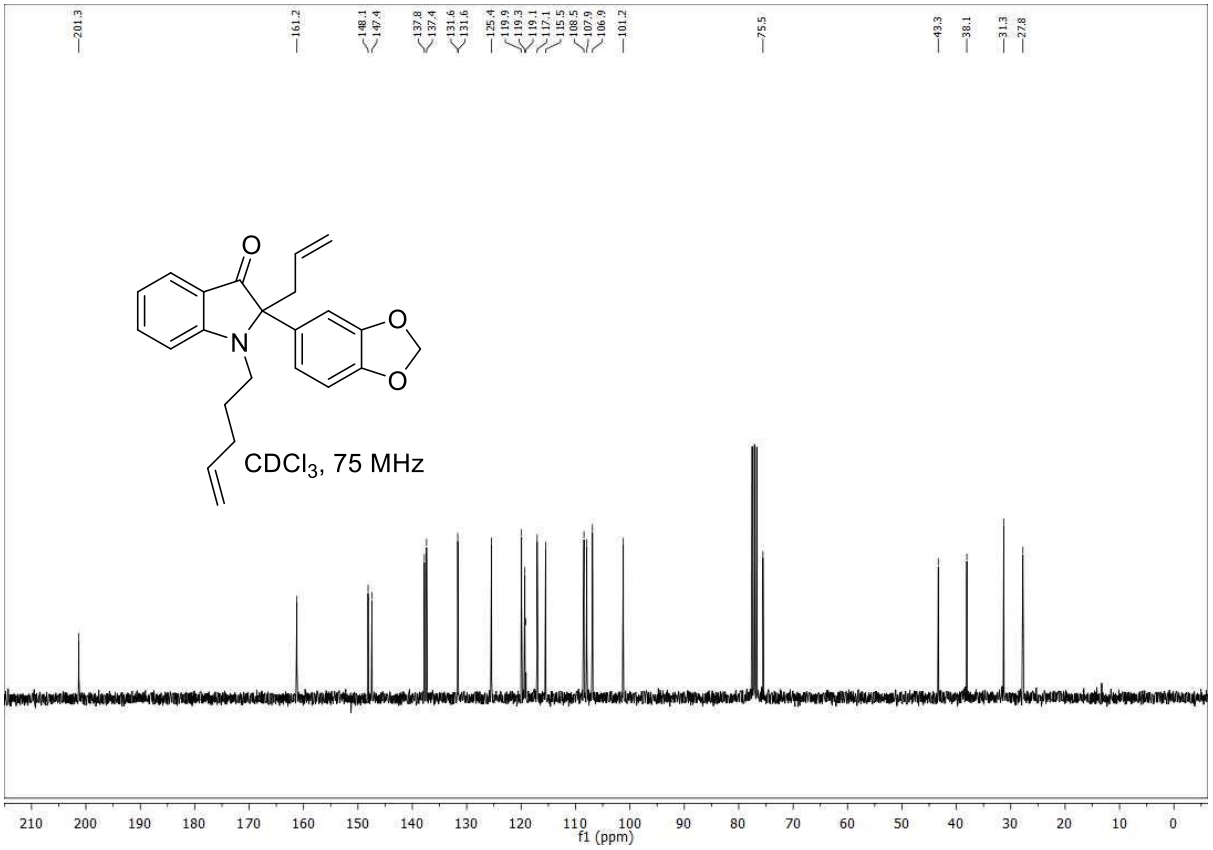
^{1}H and ^{13}C{^{1}H} NMR spectra of 6f:



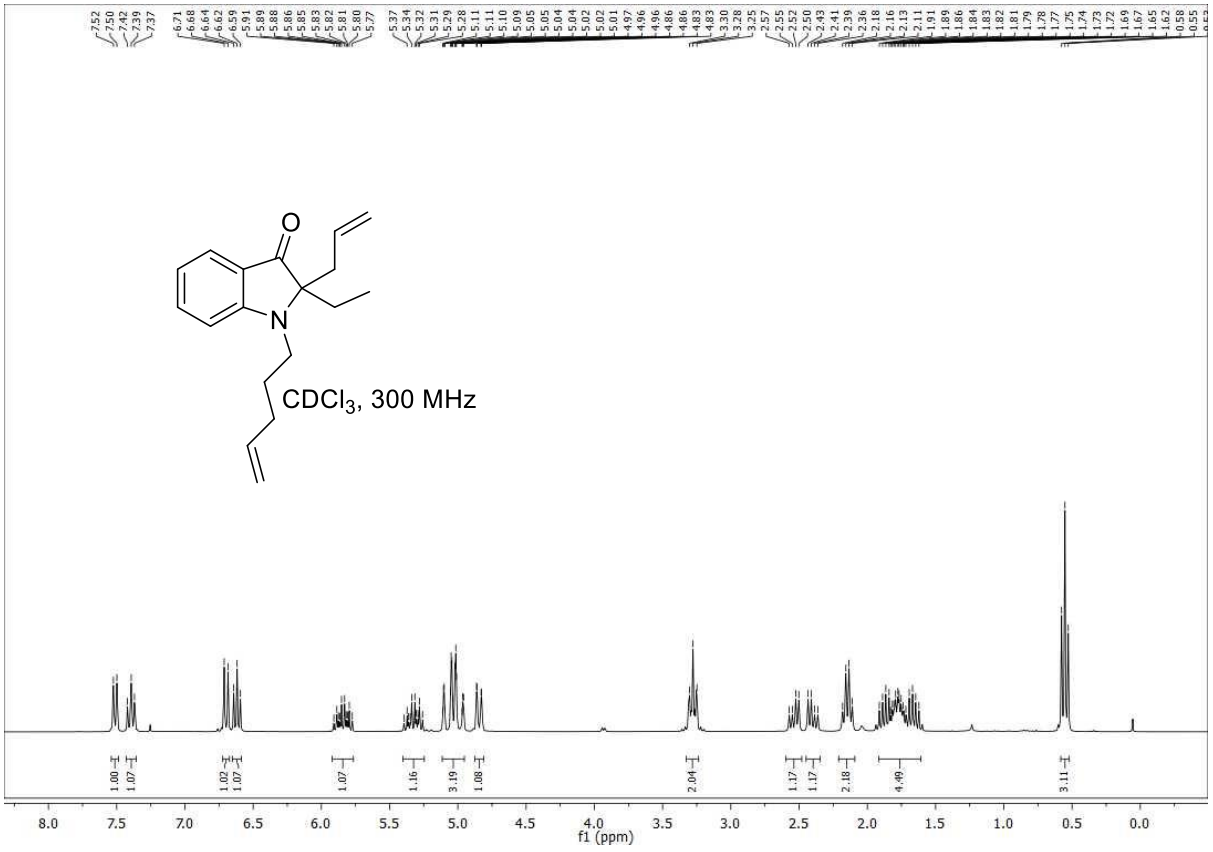


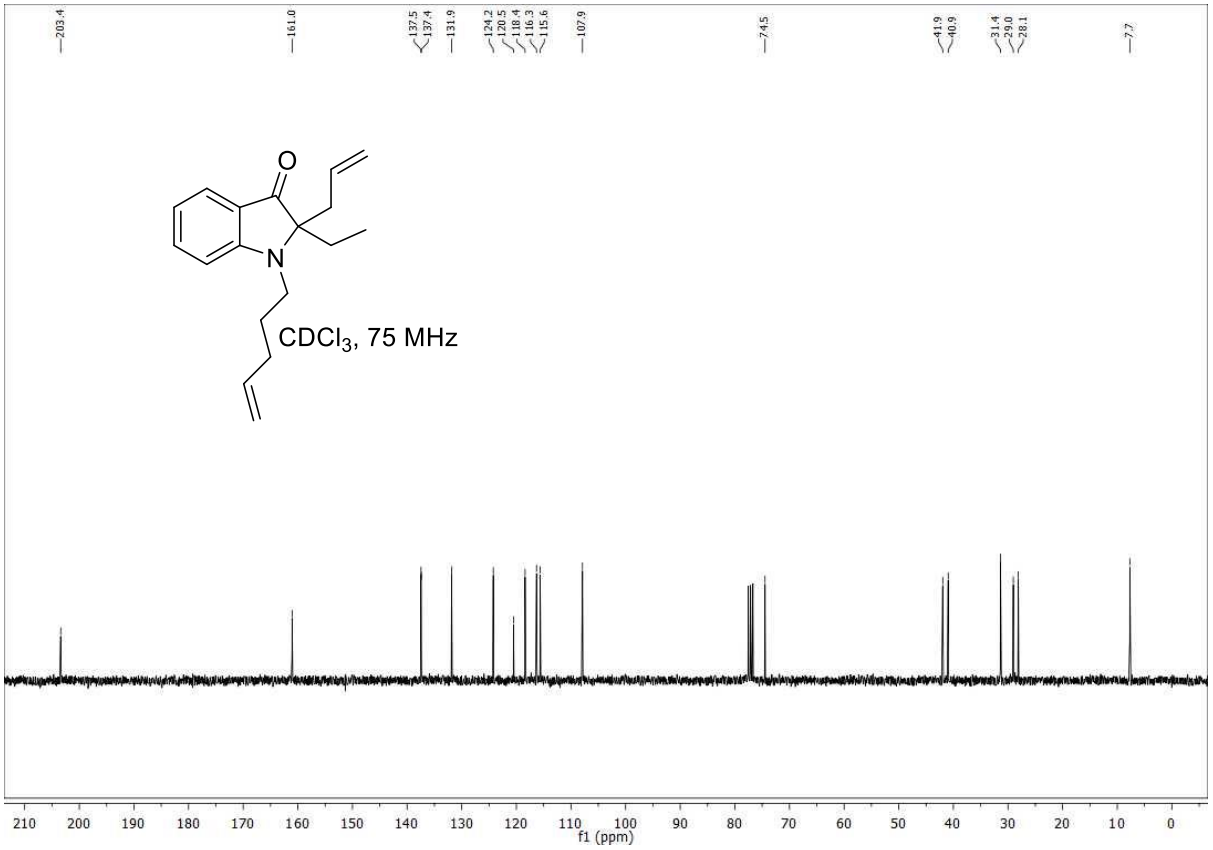
^{1}H and ^{13}C{^{1}H} NMR spectra of 6g:



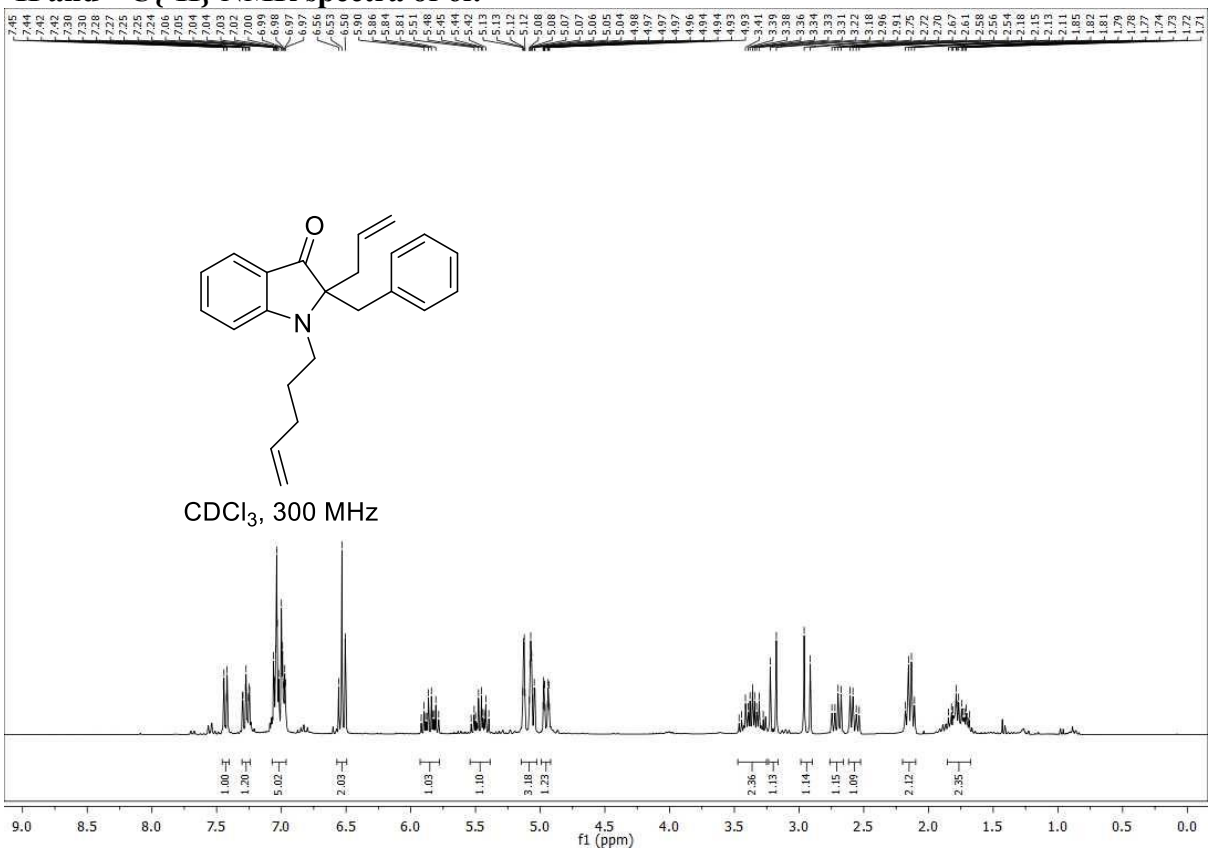


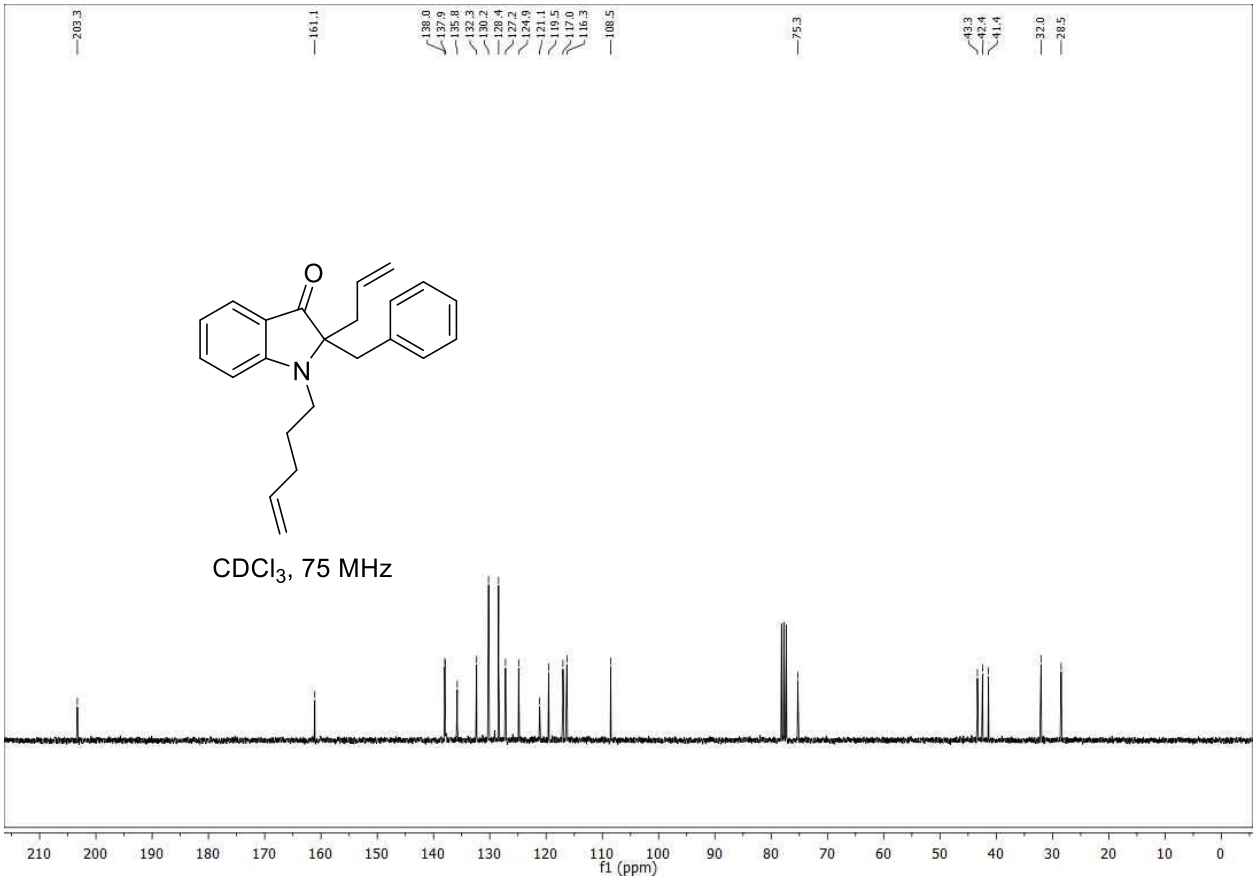
^{1}H and ^{13}C{^{1}H} NMR spectra of 6h:



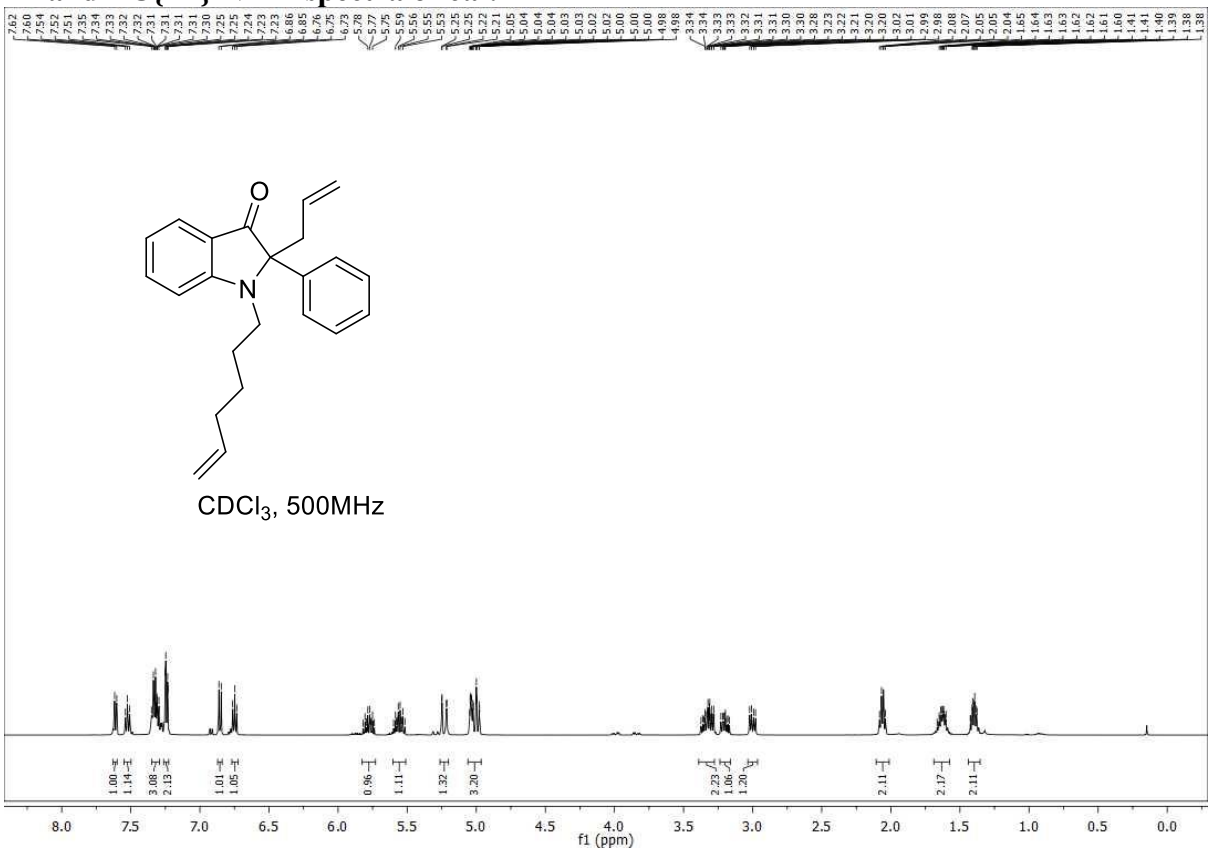


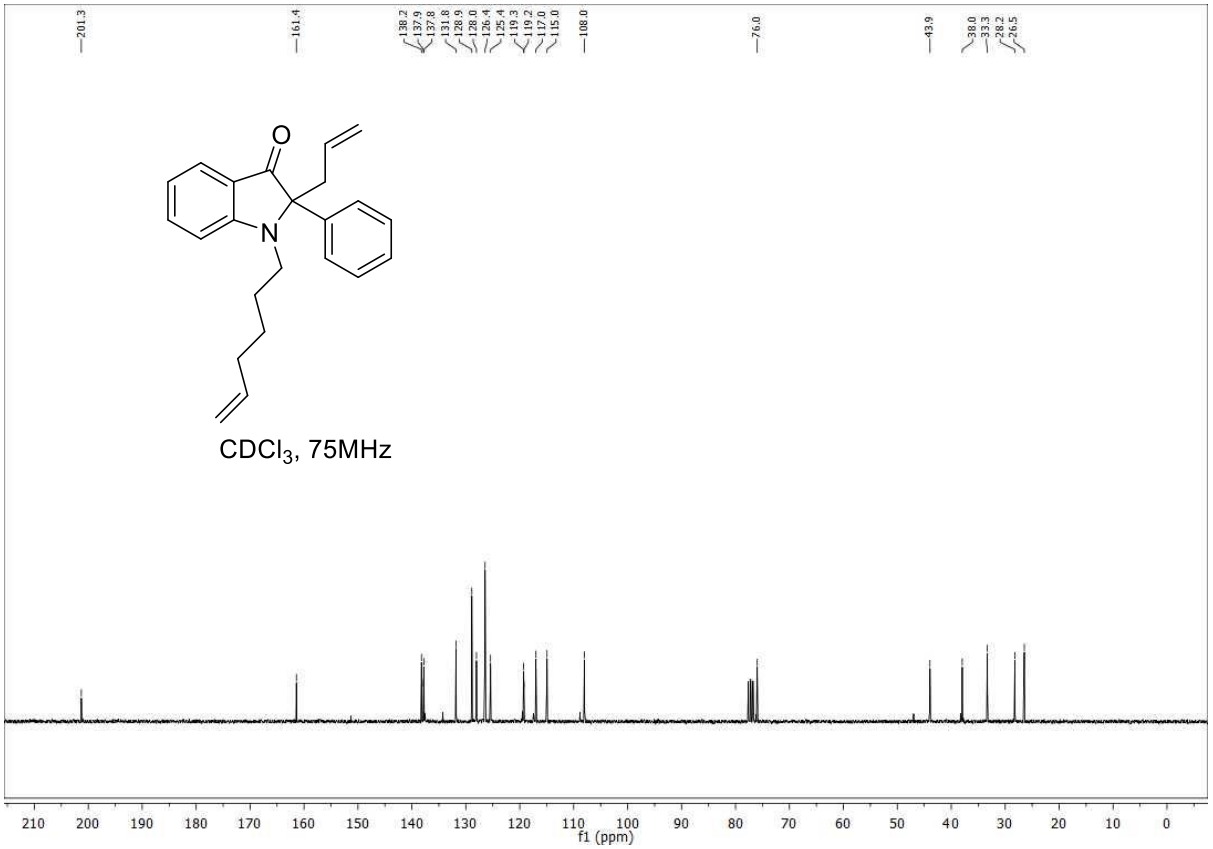
^{1}H and ^{13}C{^{1}H} NMR spectra of 6i:



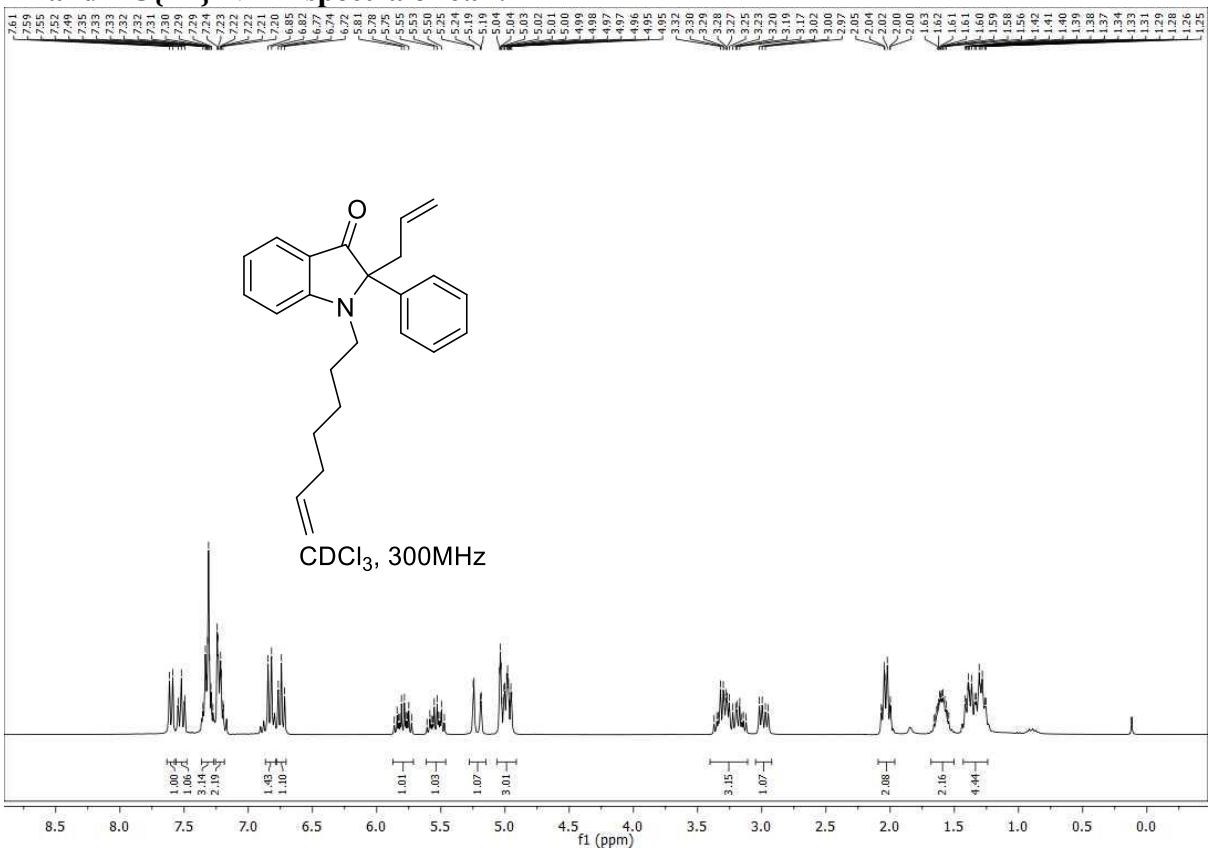


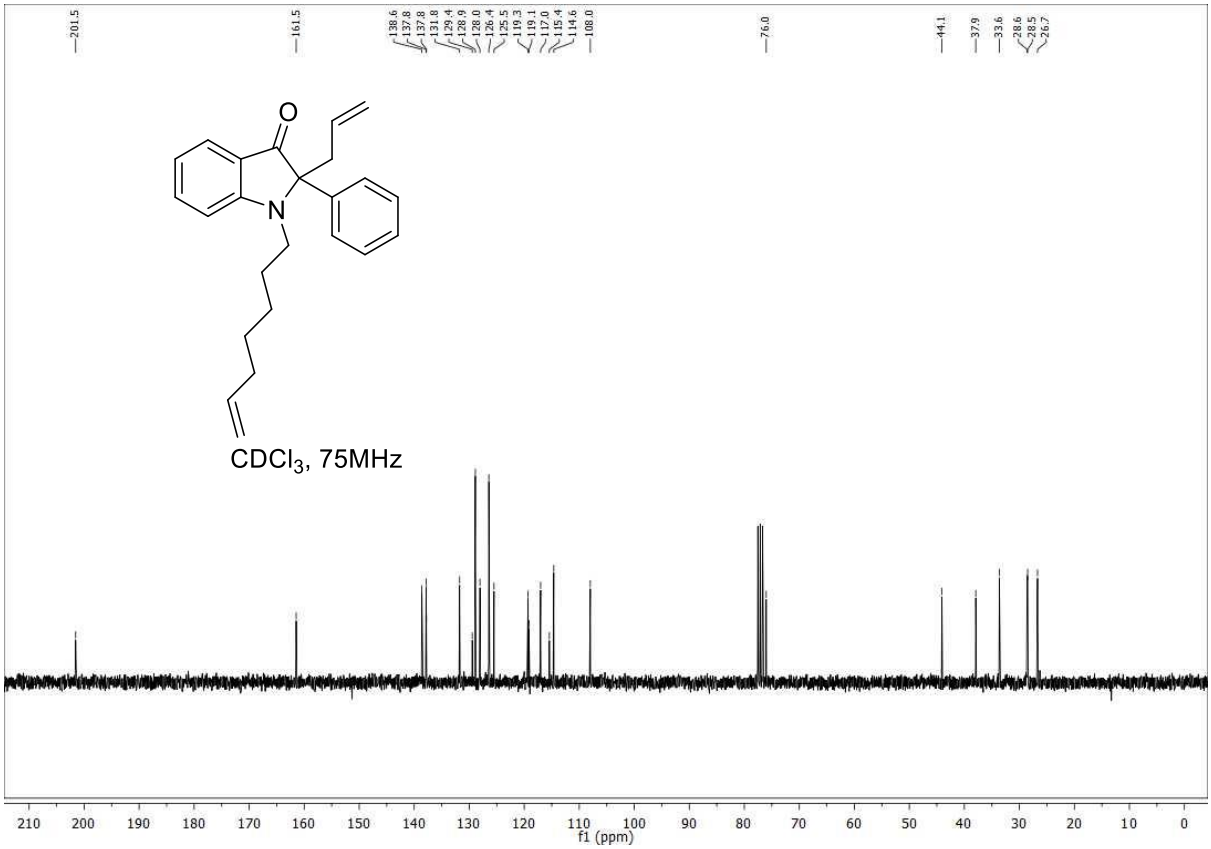
^{1}H and ^{13}C{^{1}H} NMR spectra of 6a′:



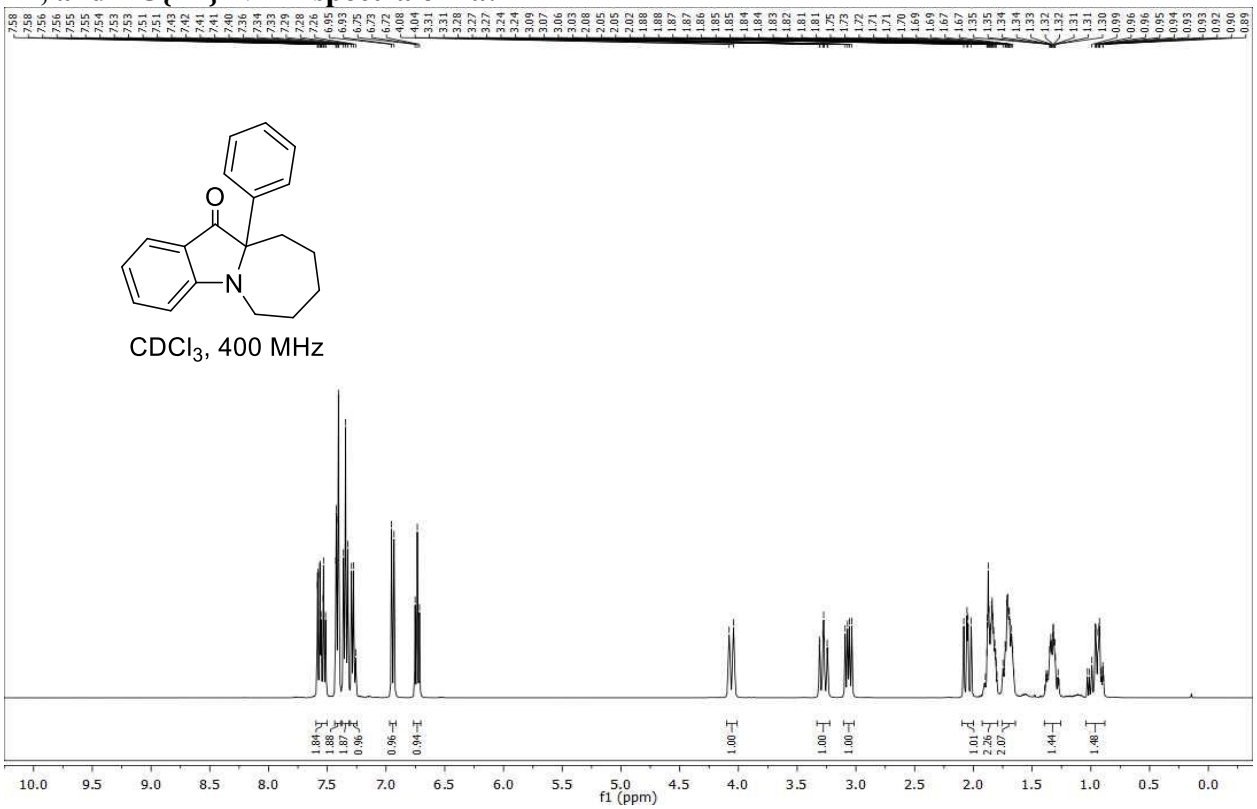


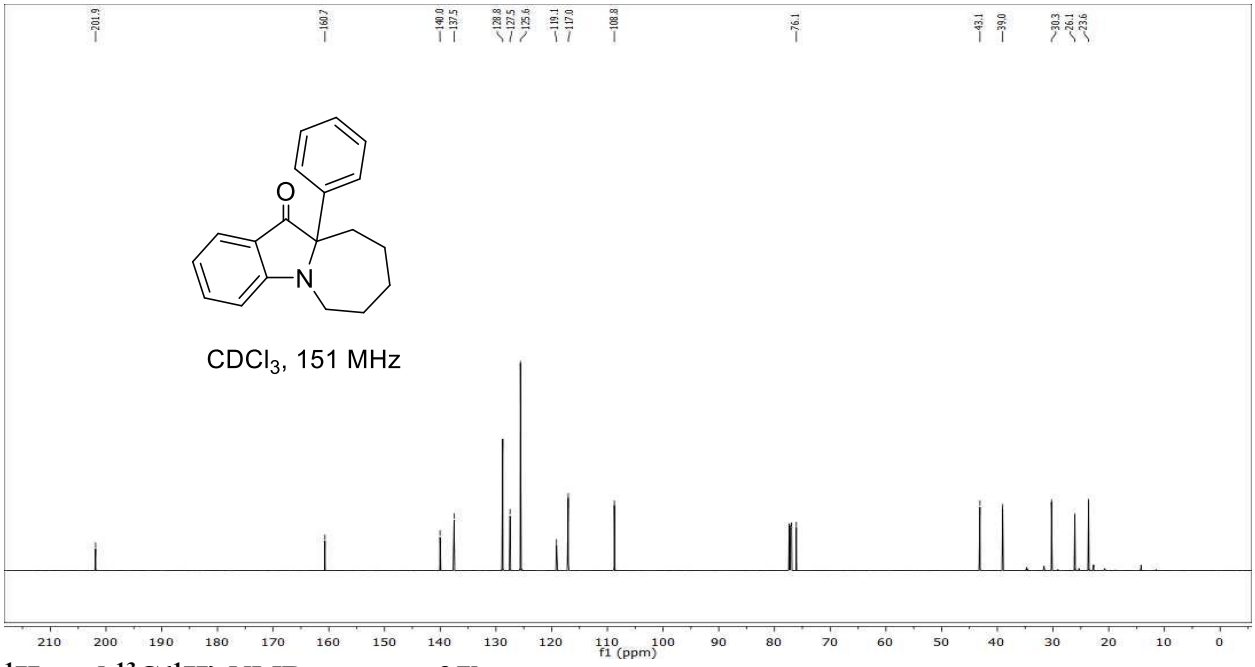
^{1}H and ^{13}C{^{1}H} NMR spectra of 6a′′:



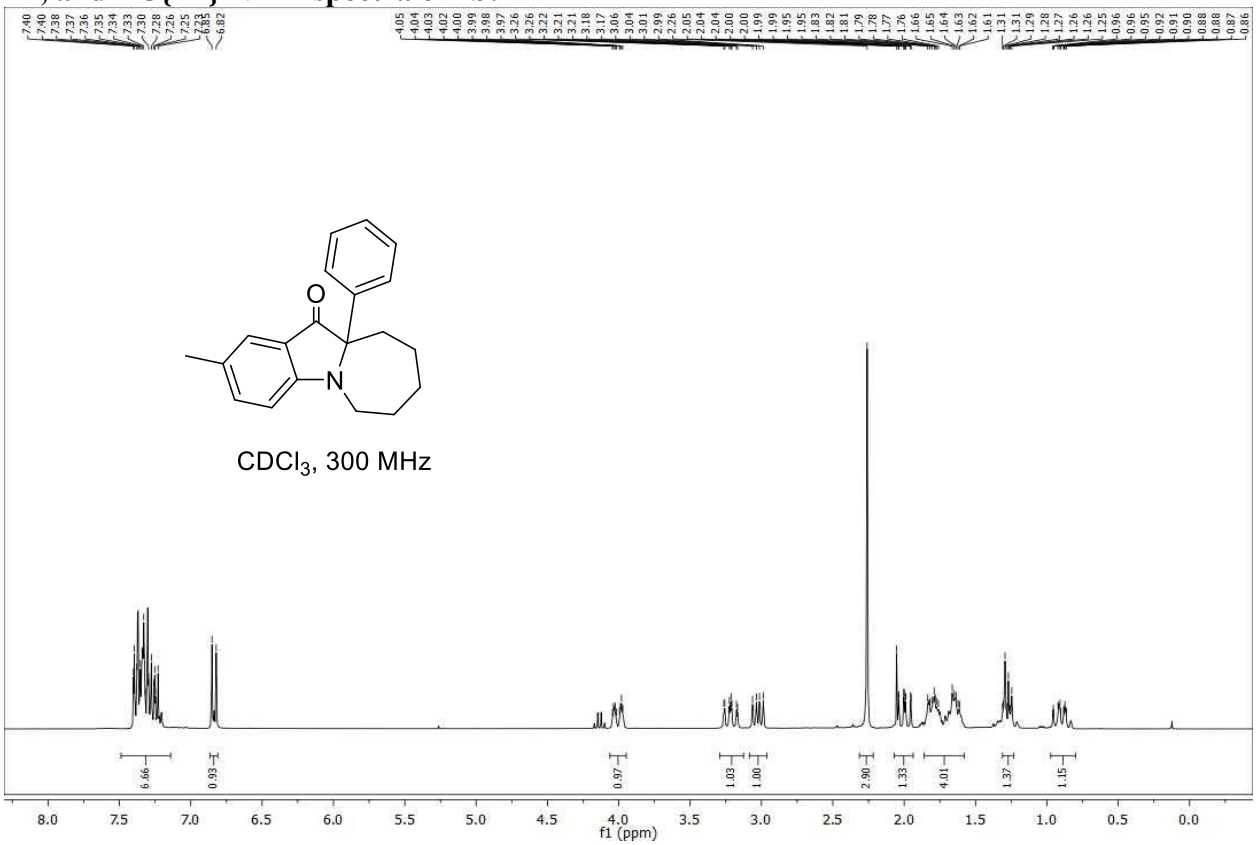


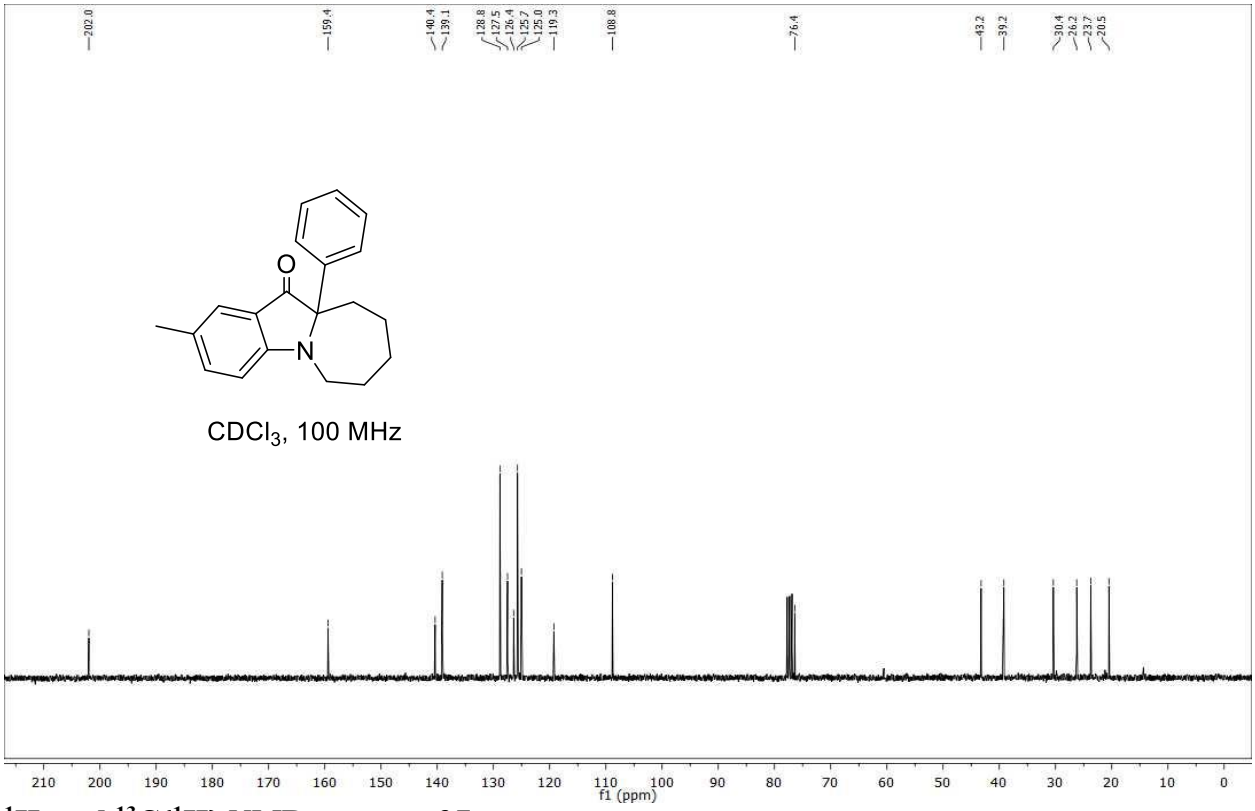
^{1}H, and ^{13}C{^{1}H} NMR spectra of 7a:



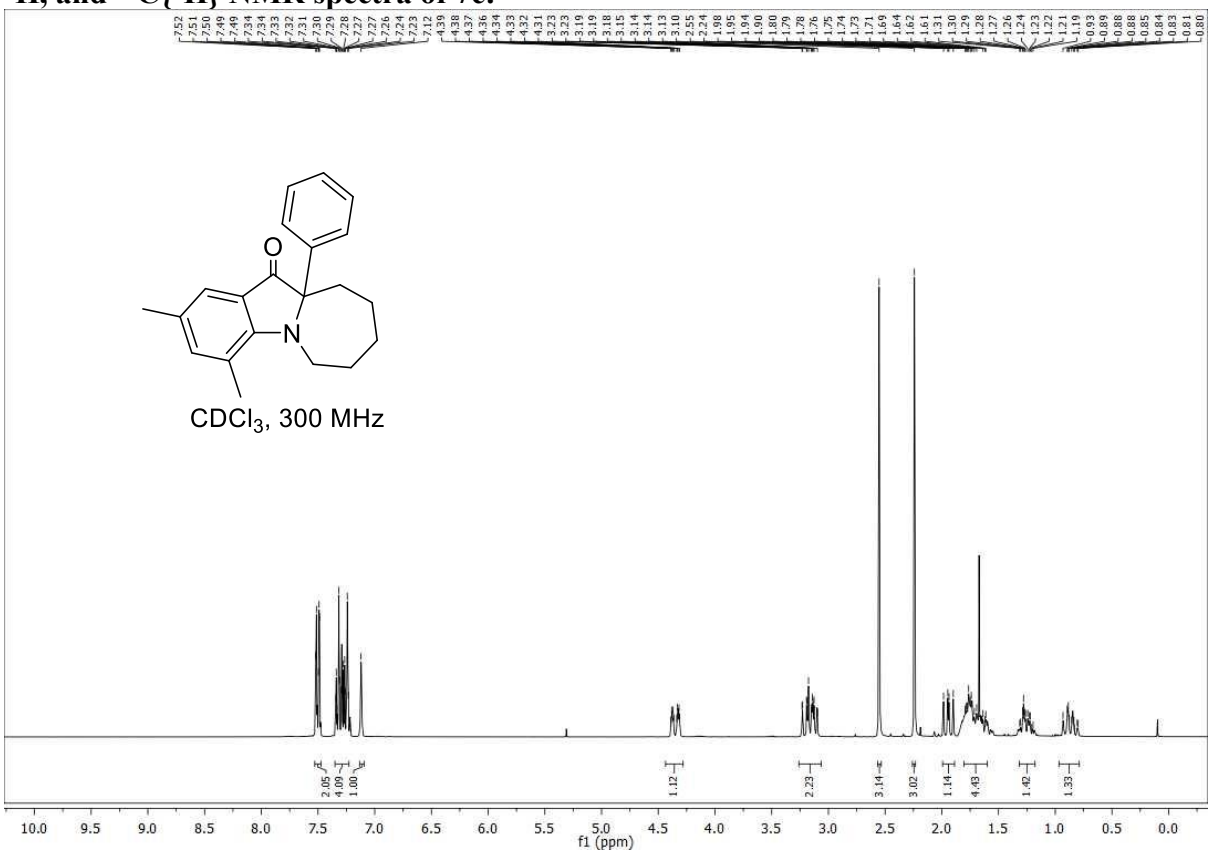


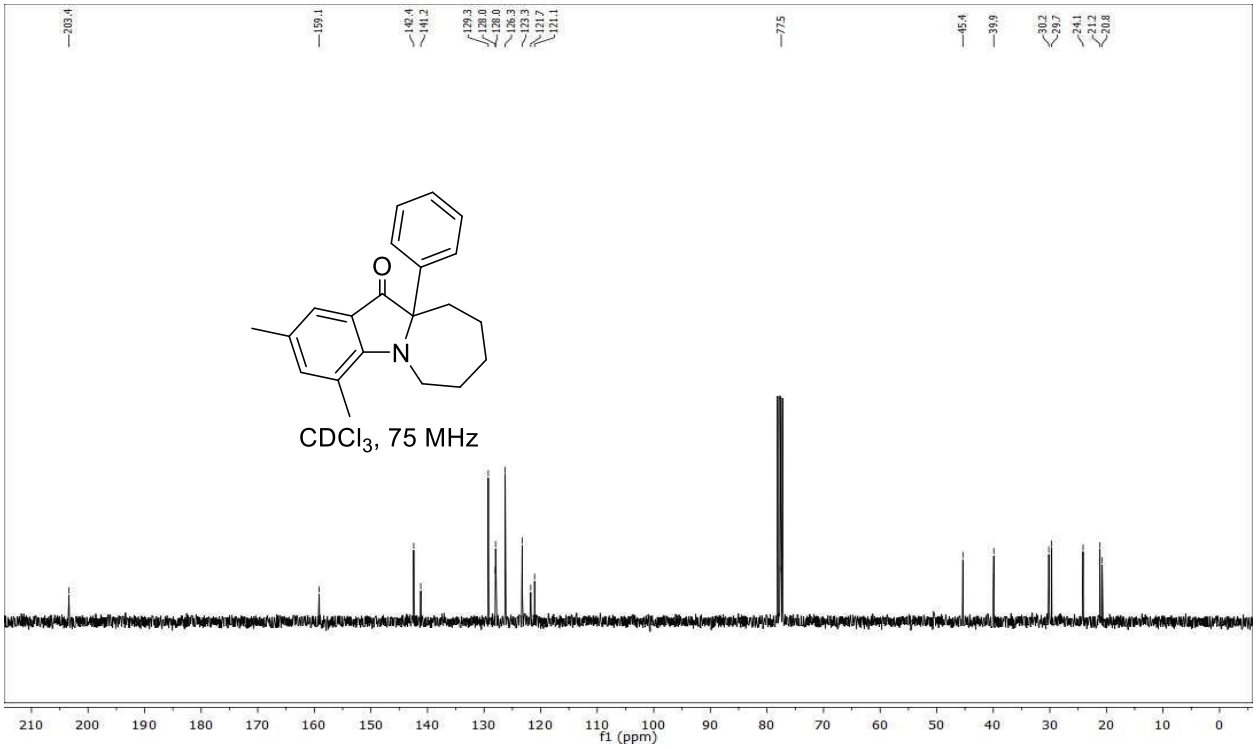
^{1}H, and ^{13}C{^{1}H} NMR spectra of 7b:



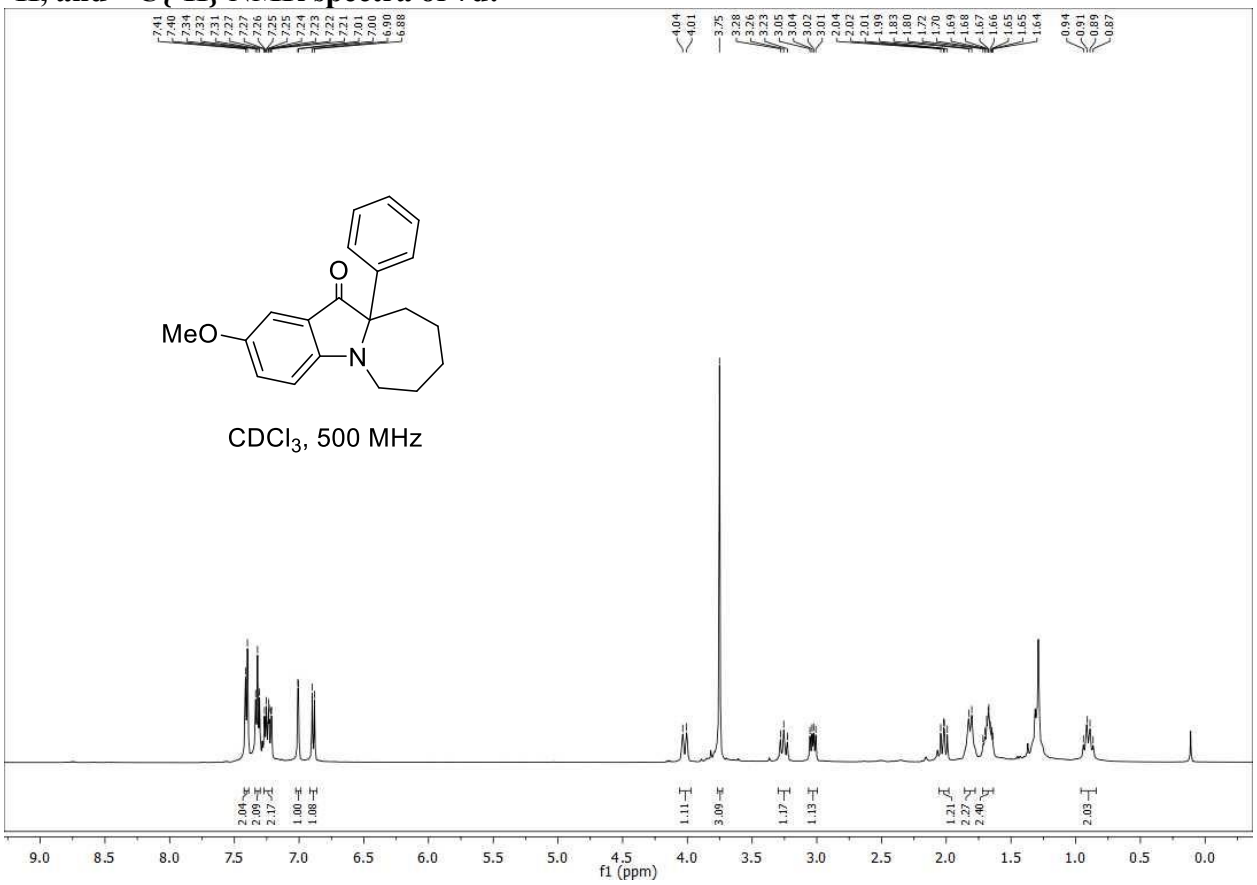


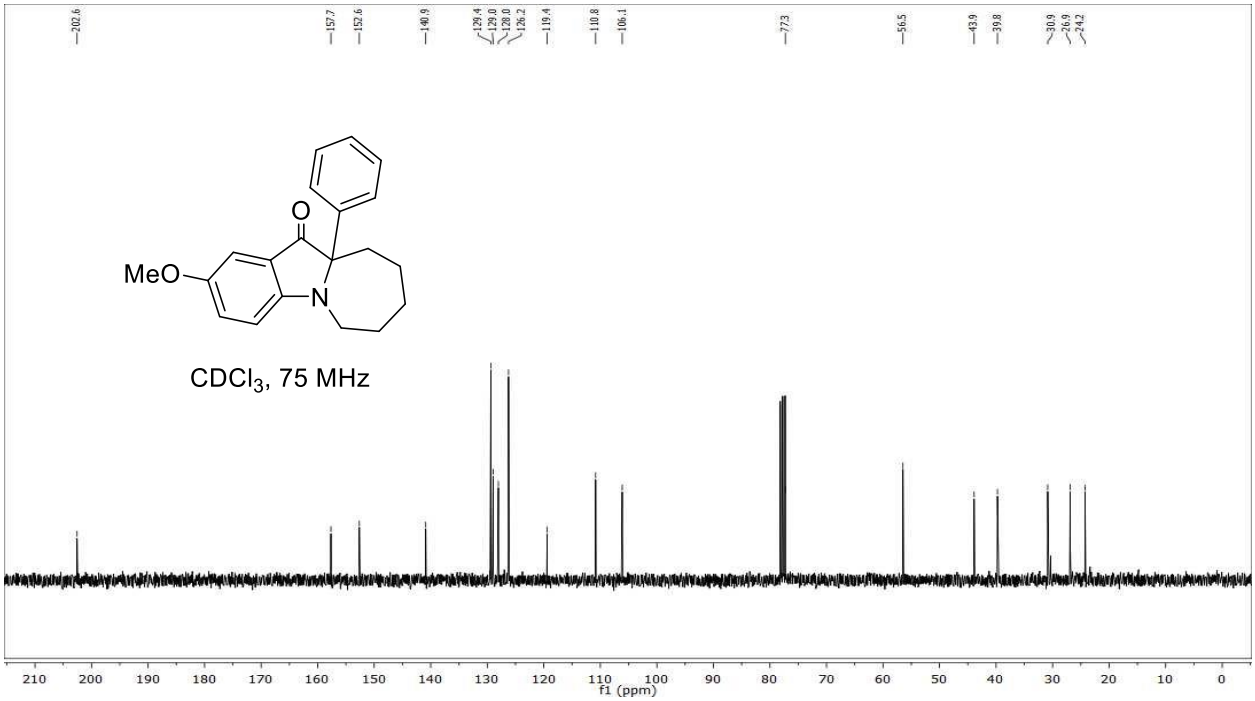
^{1}H, and ^{13}C{^{1}H} NMR spectra of 7c:



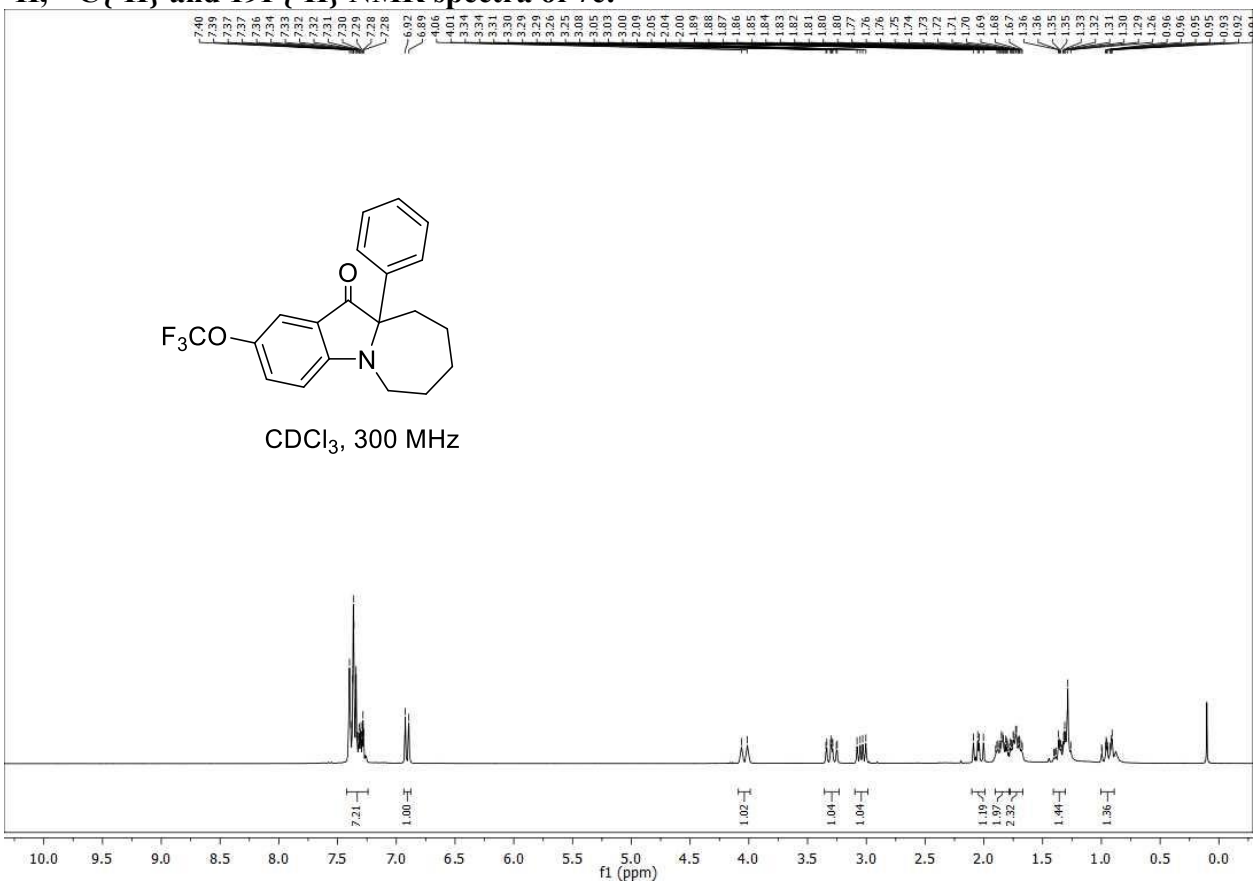


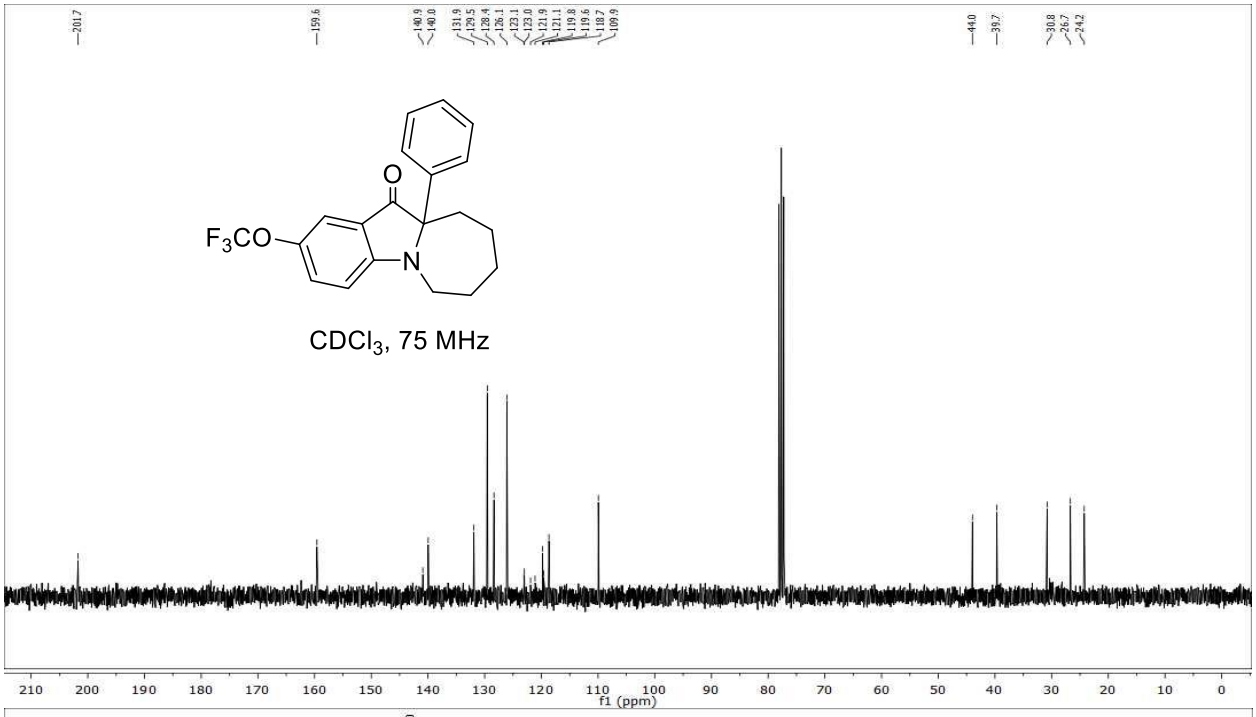
^{1}H, and ^{13}C{^{1}H} NMR spectra of 7d:

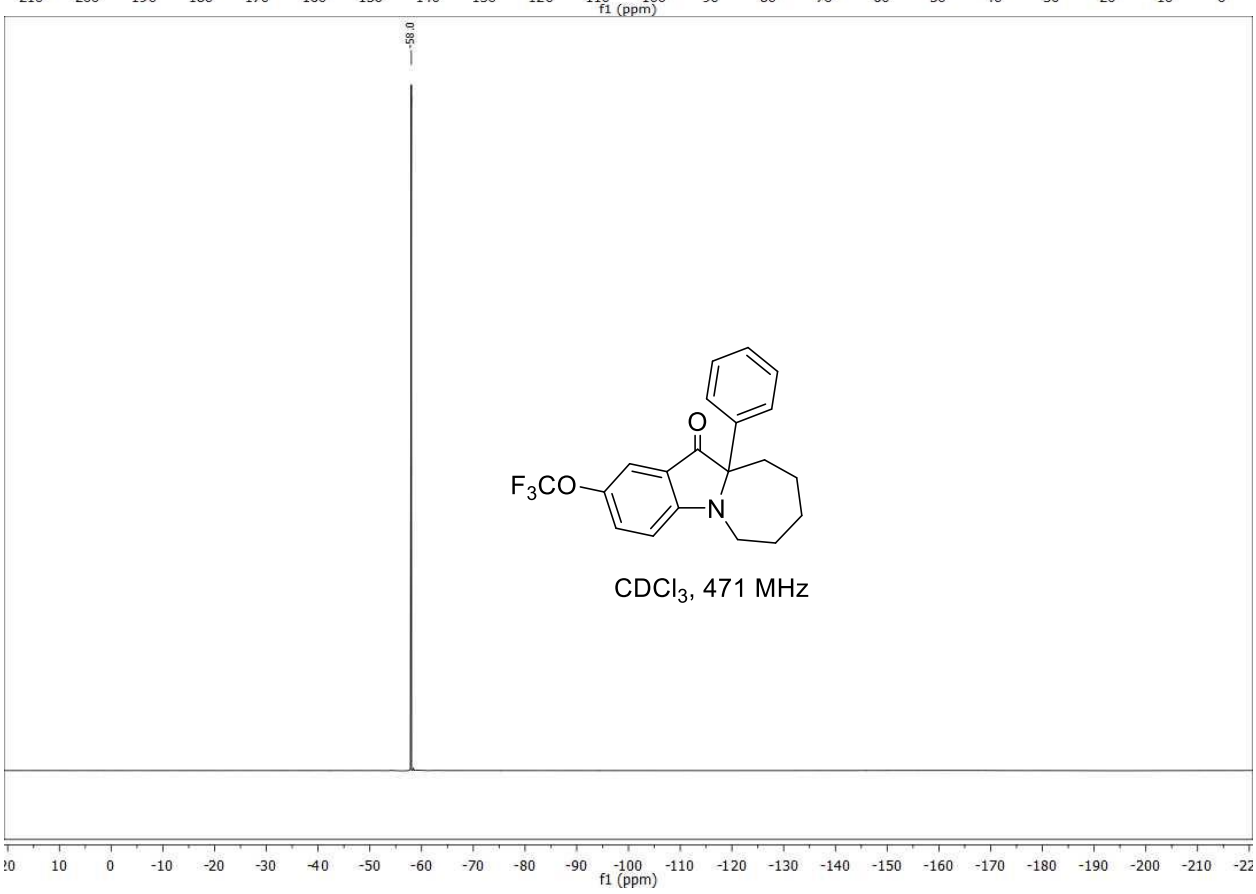




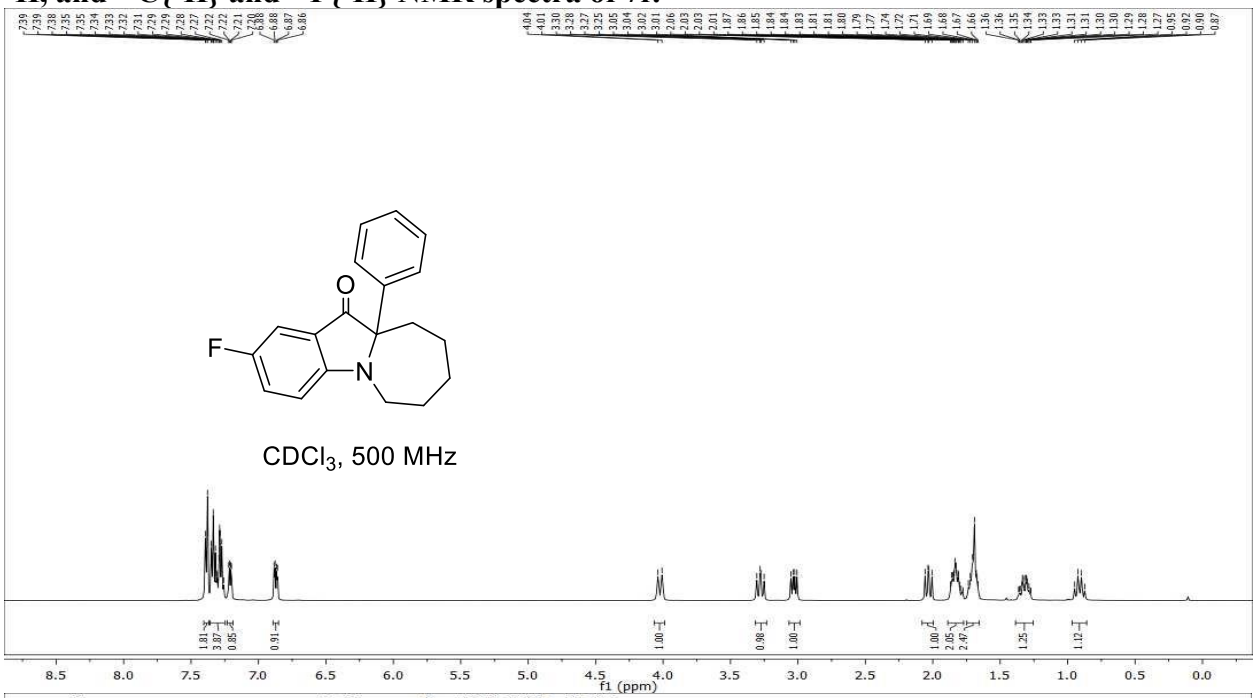
^{1}H, ^{13}C{^{1}H} and 19F{^{1}H} NMR spectra of 7e:

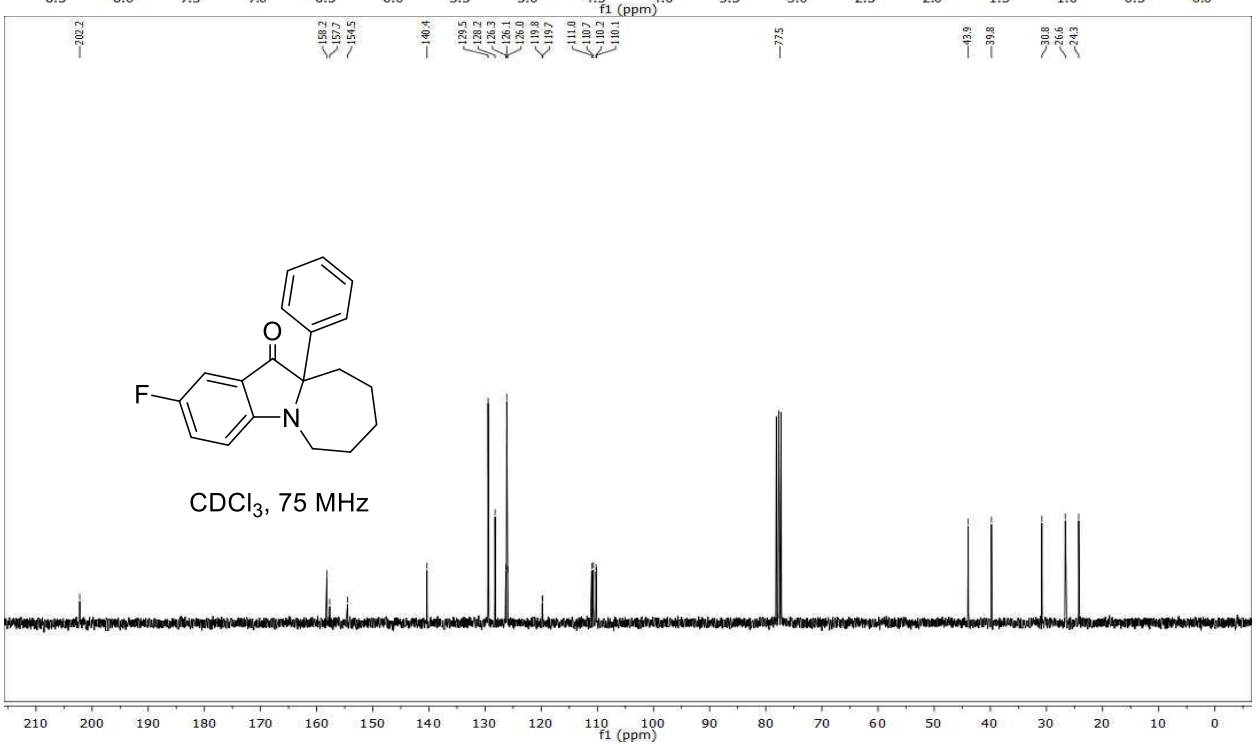


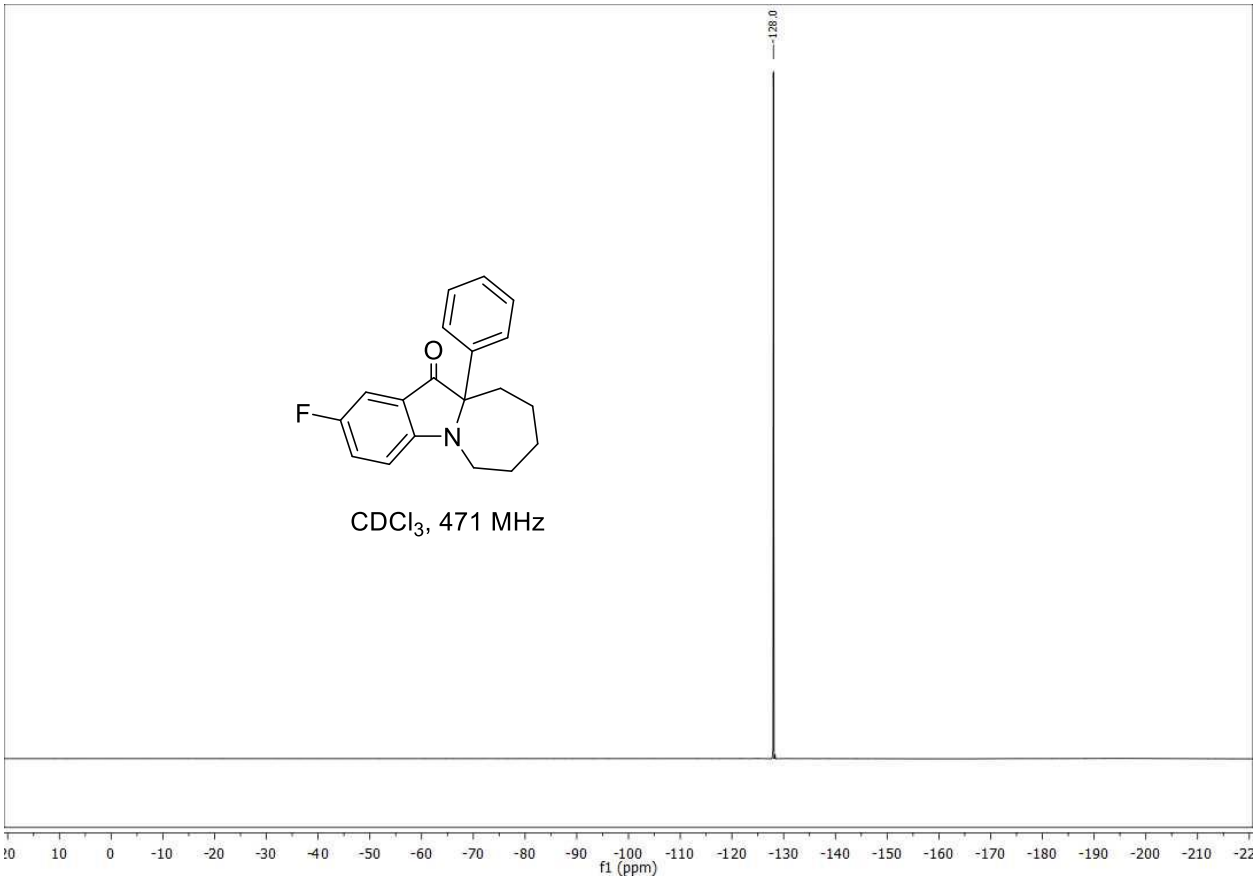

201.7
159.6
140.9
140.0
131.9
129.5
128.4
126.1
123.1
123.0
121.9
121.1
119.8
119.6
118.7
109.9
44.0
39.7
30.8
26.7
24.2
O
F3CO
N
CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-58.0
O
F3CO
N
CDCl3, 471 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

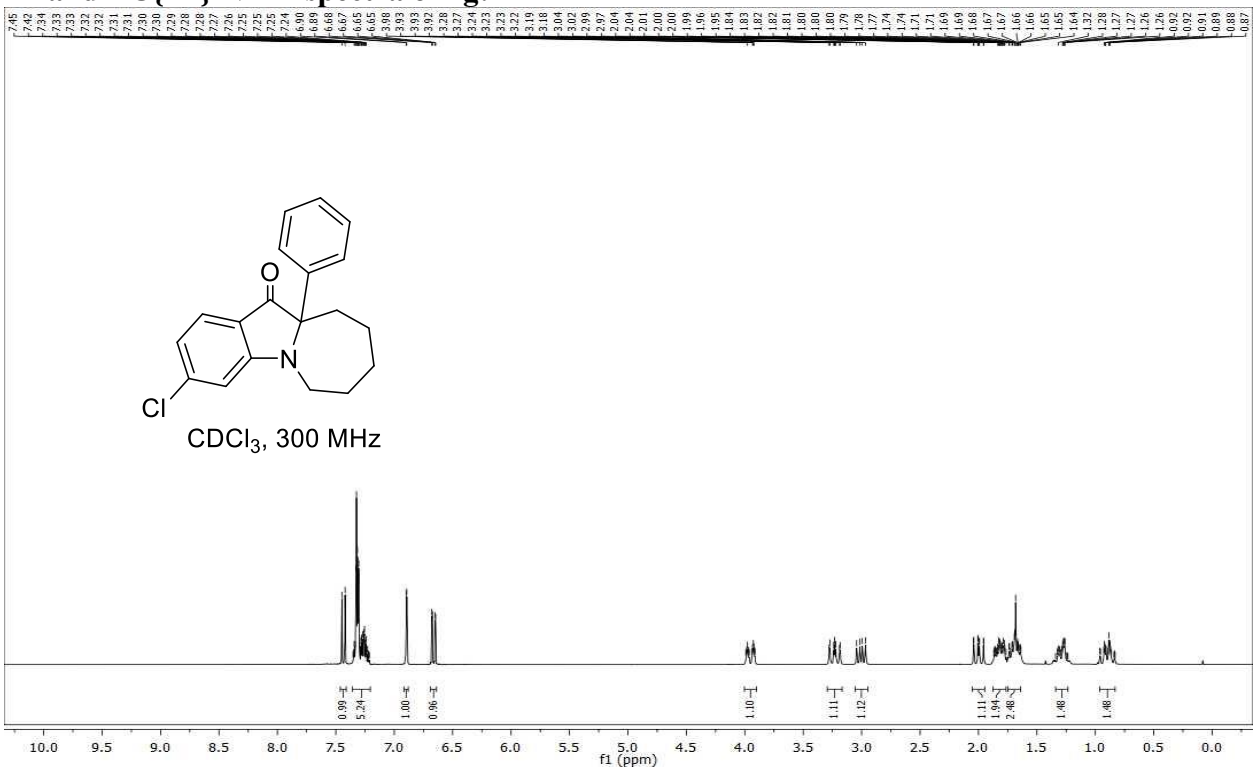
^{1}H, and ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectra of 7f:

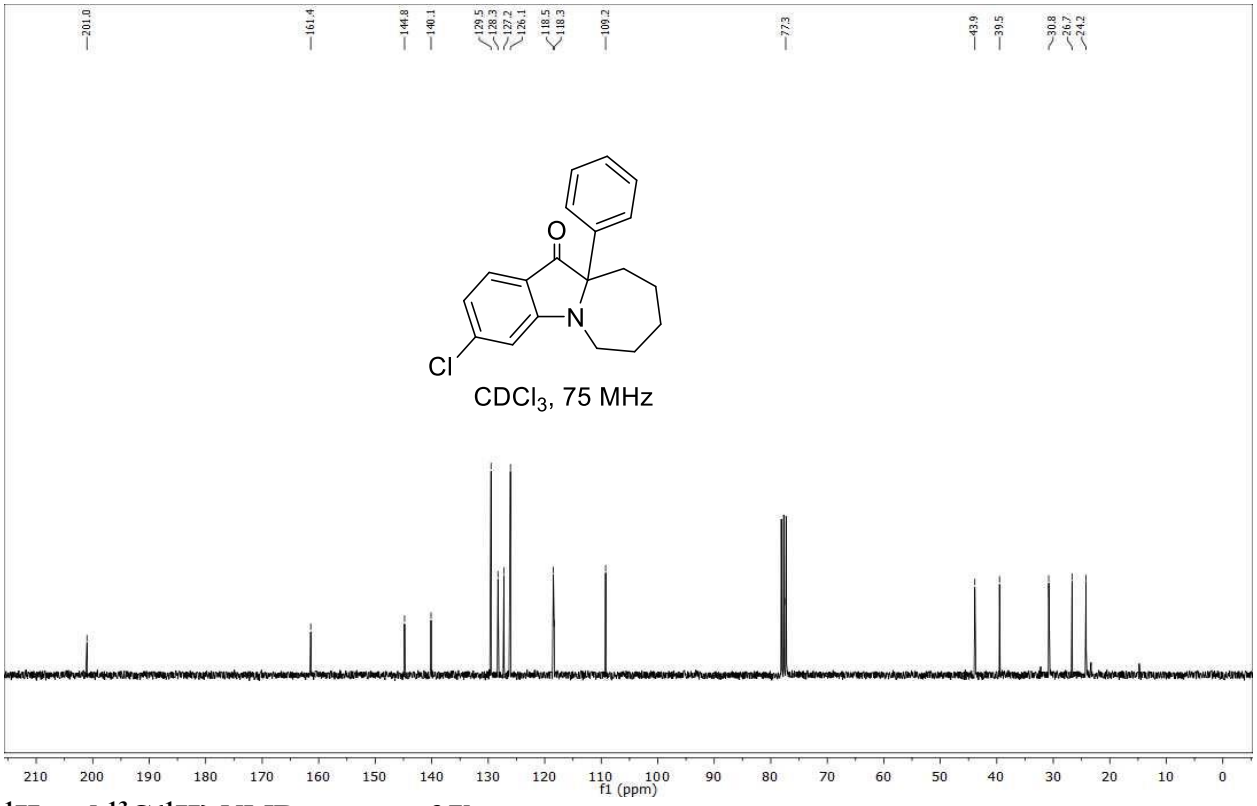




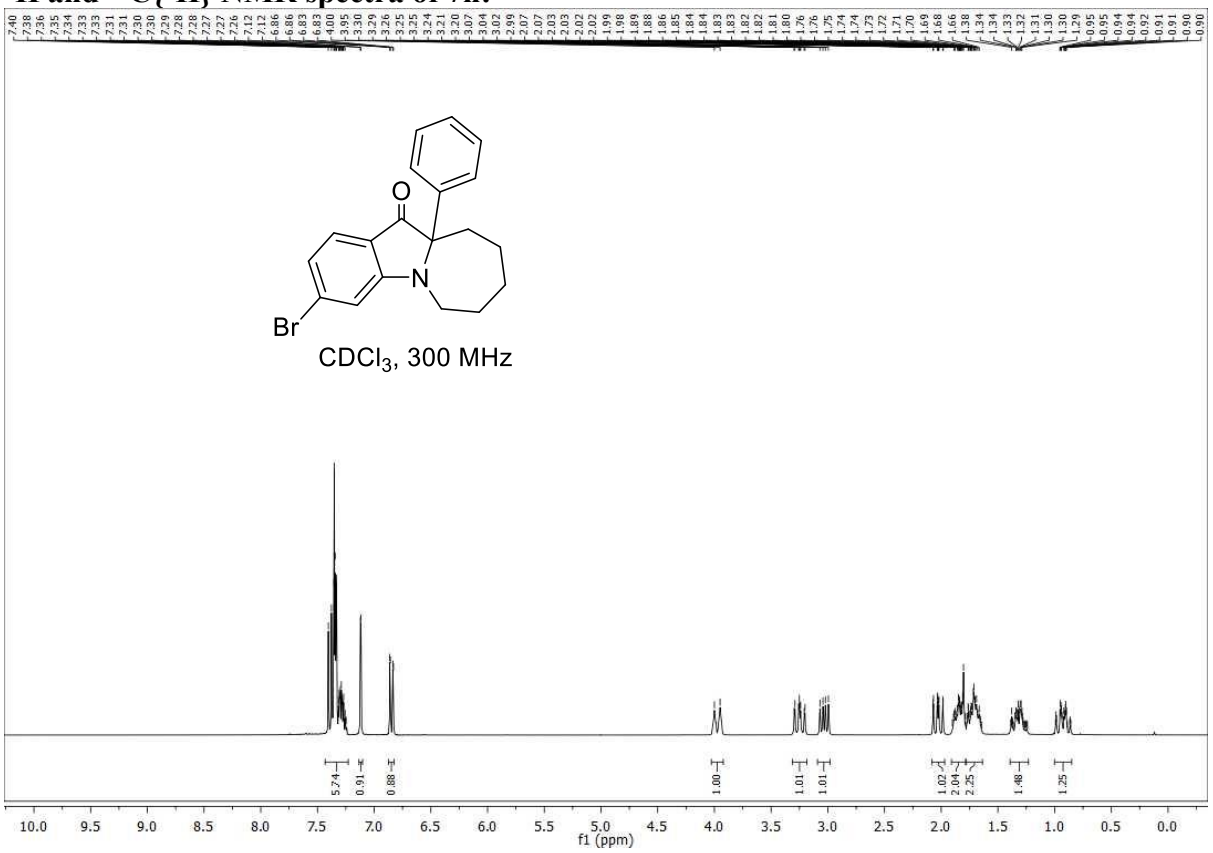


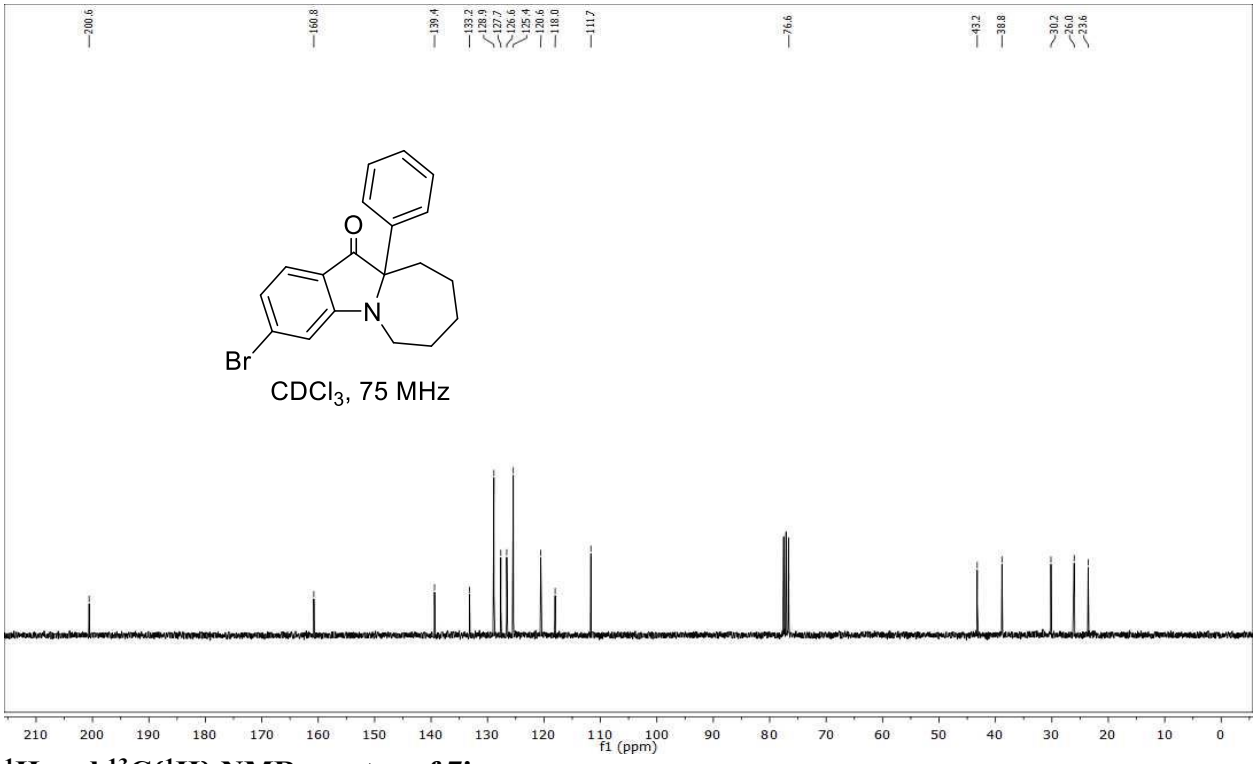
^{1}H and ^{13}C{^{1}H} NMR spectra of 7g:



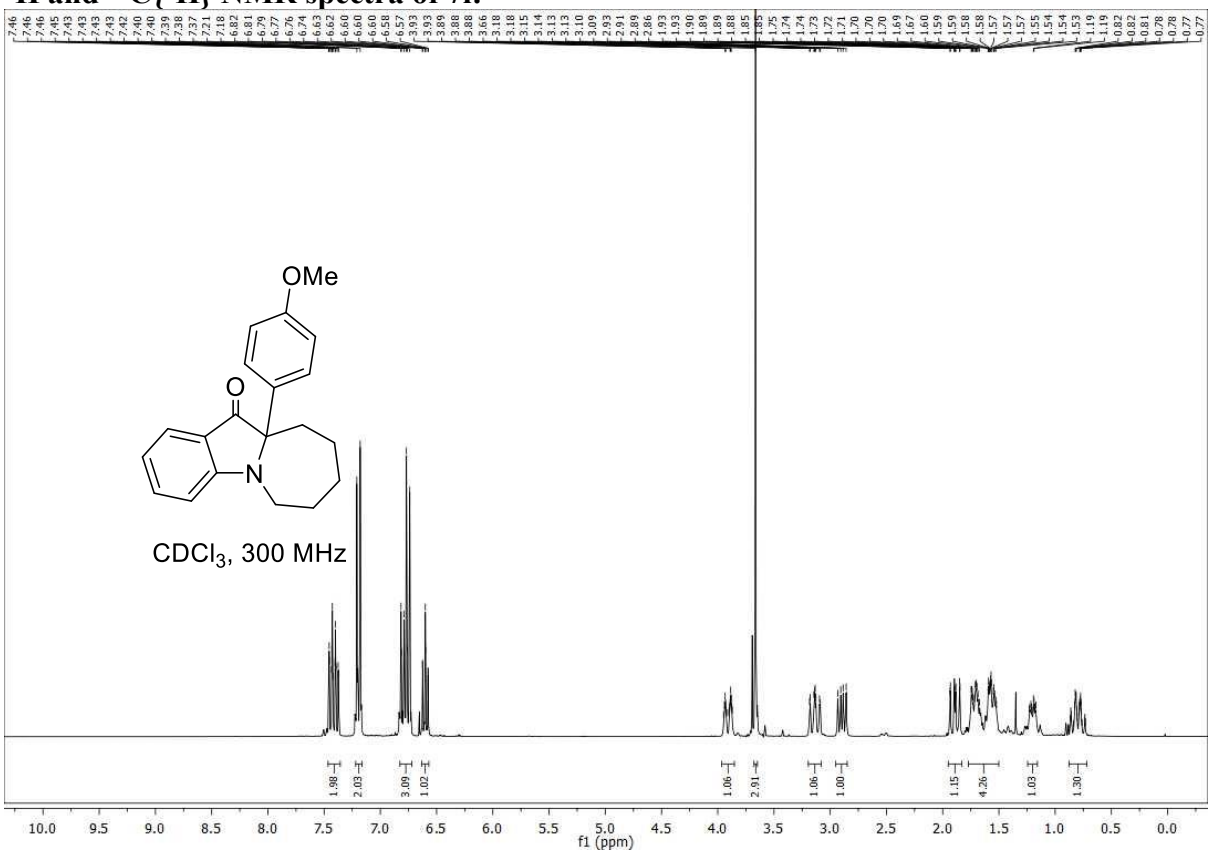


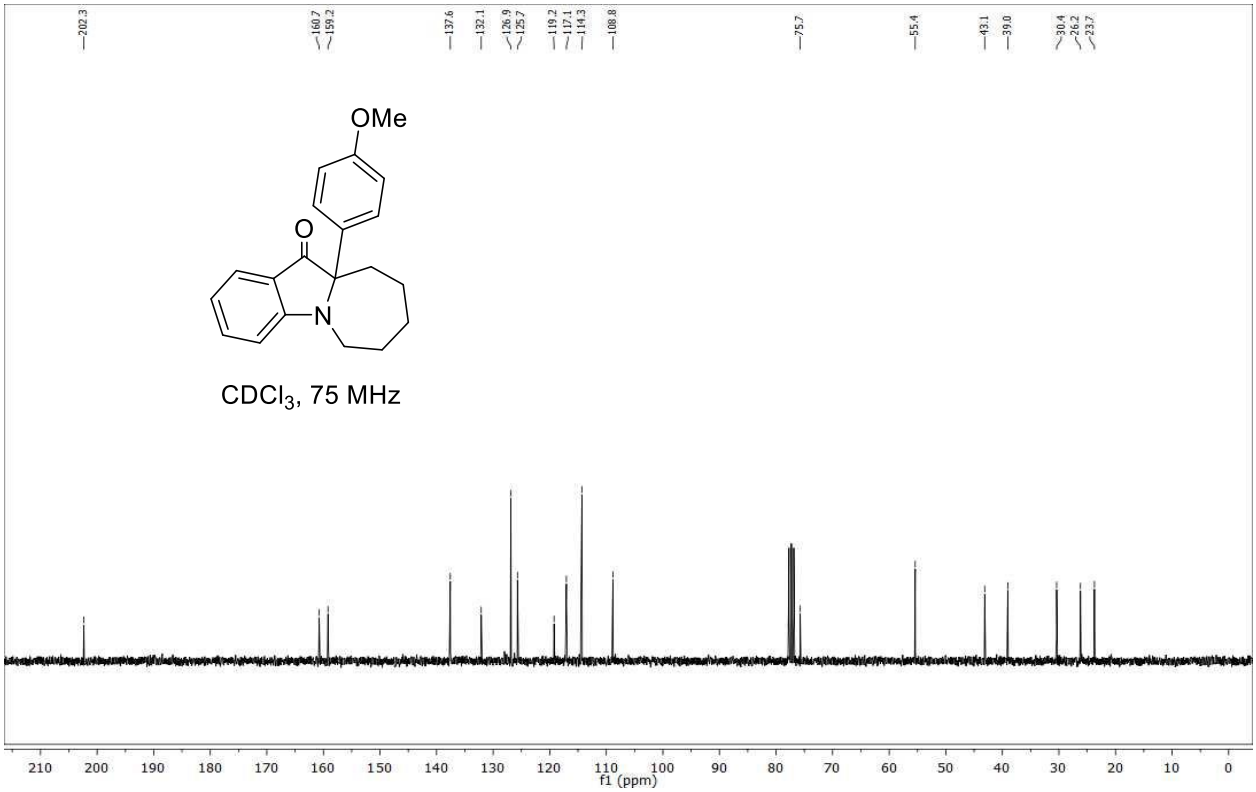
^{1}H and ^{13}C{^{1}H} NMR spectra of 7h:



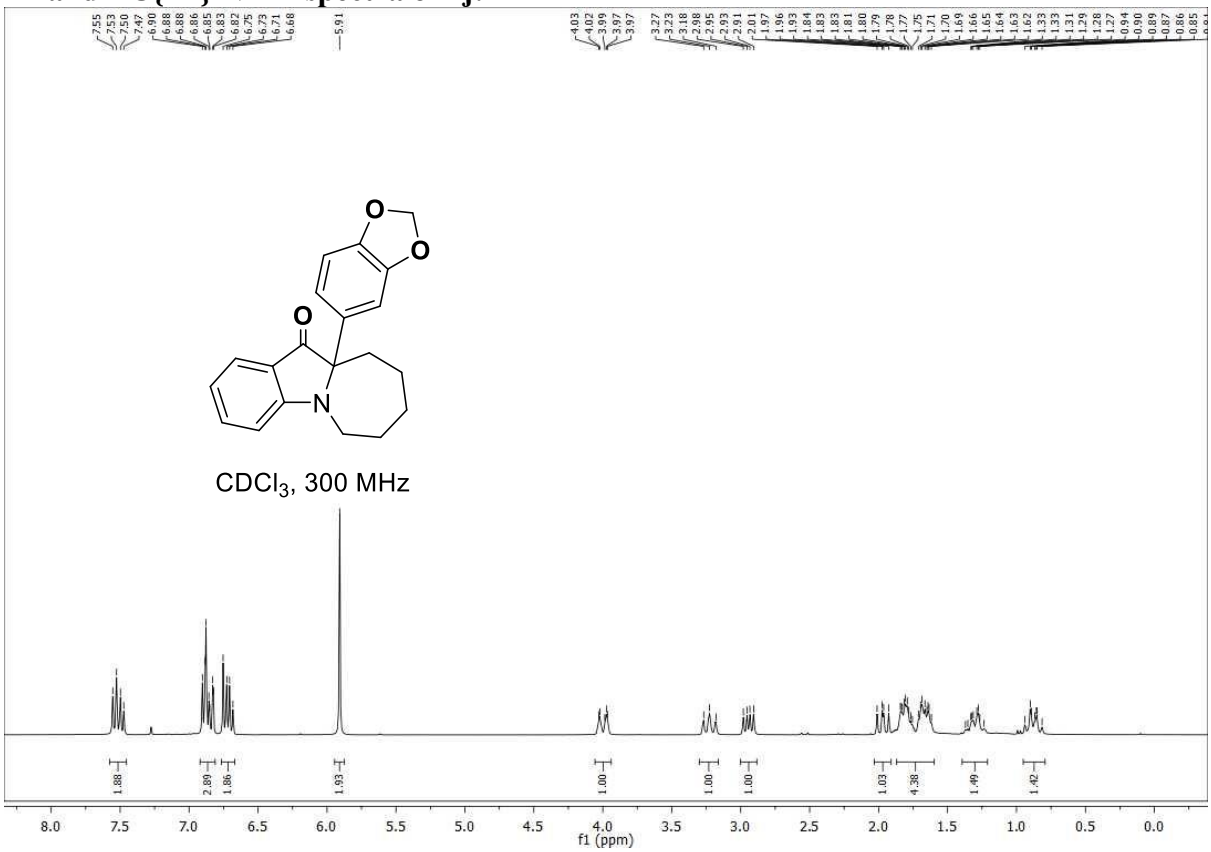


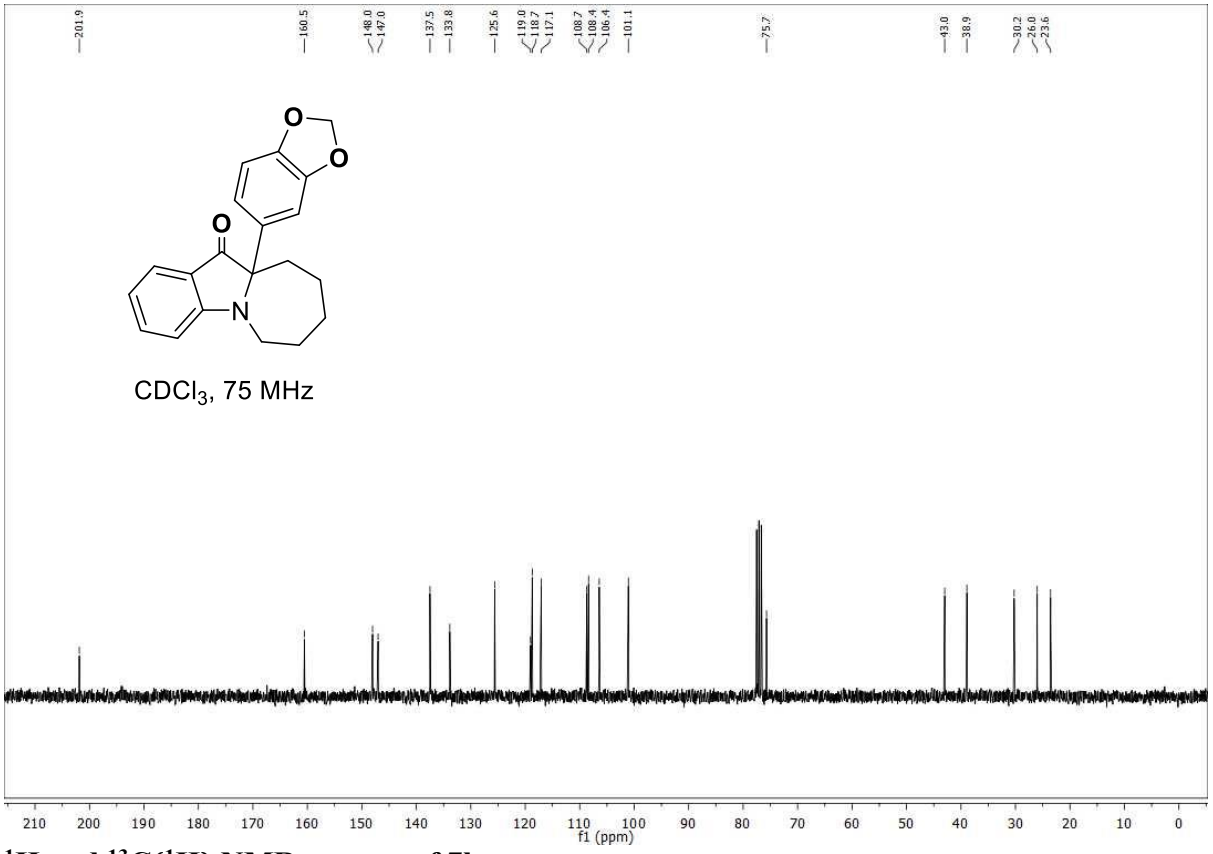
^{1}H and ^{13}C{^{1}H} NMR spectra of 7i:



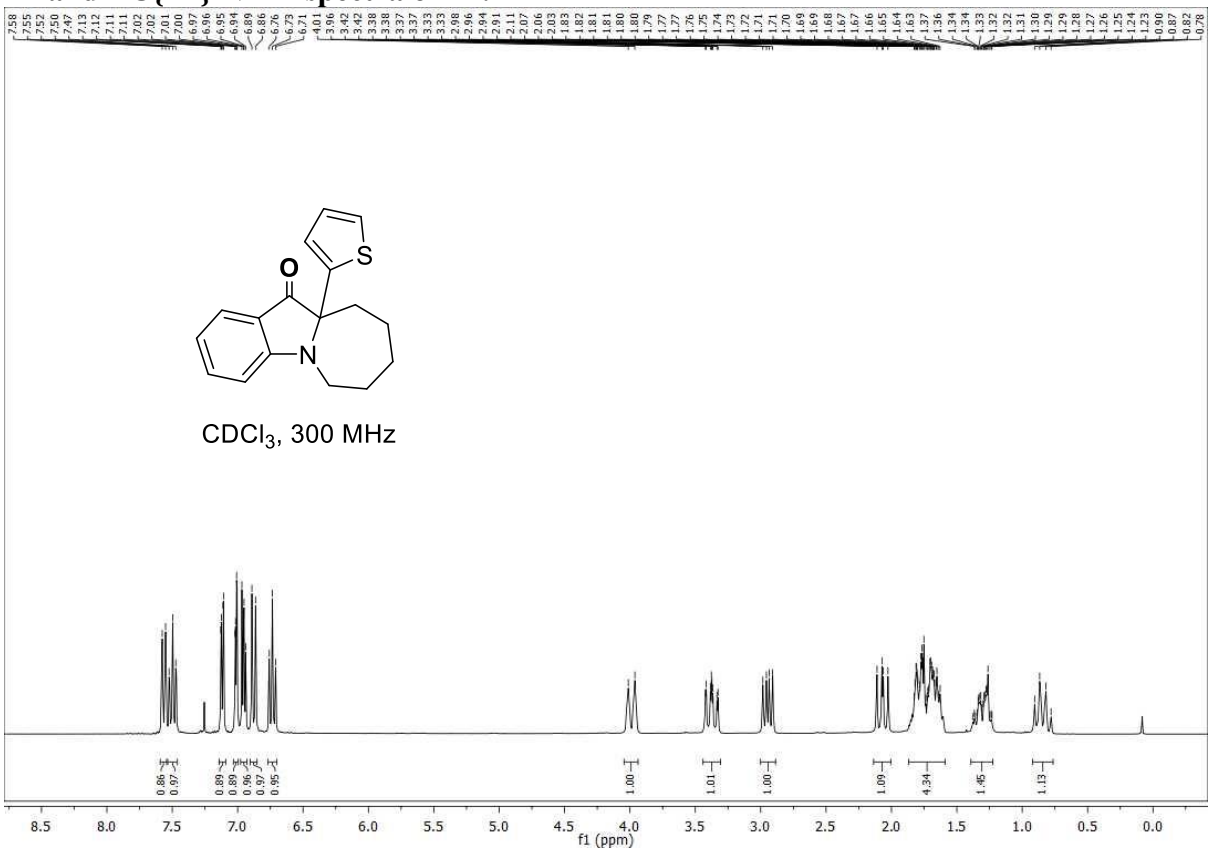


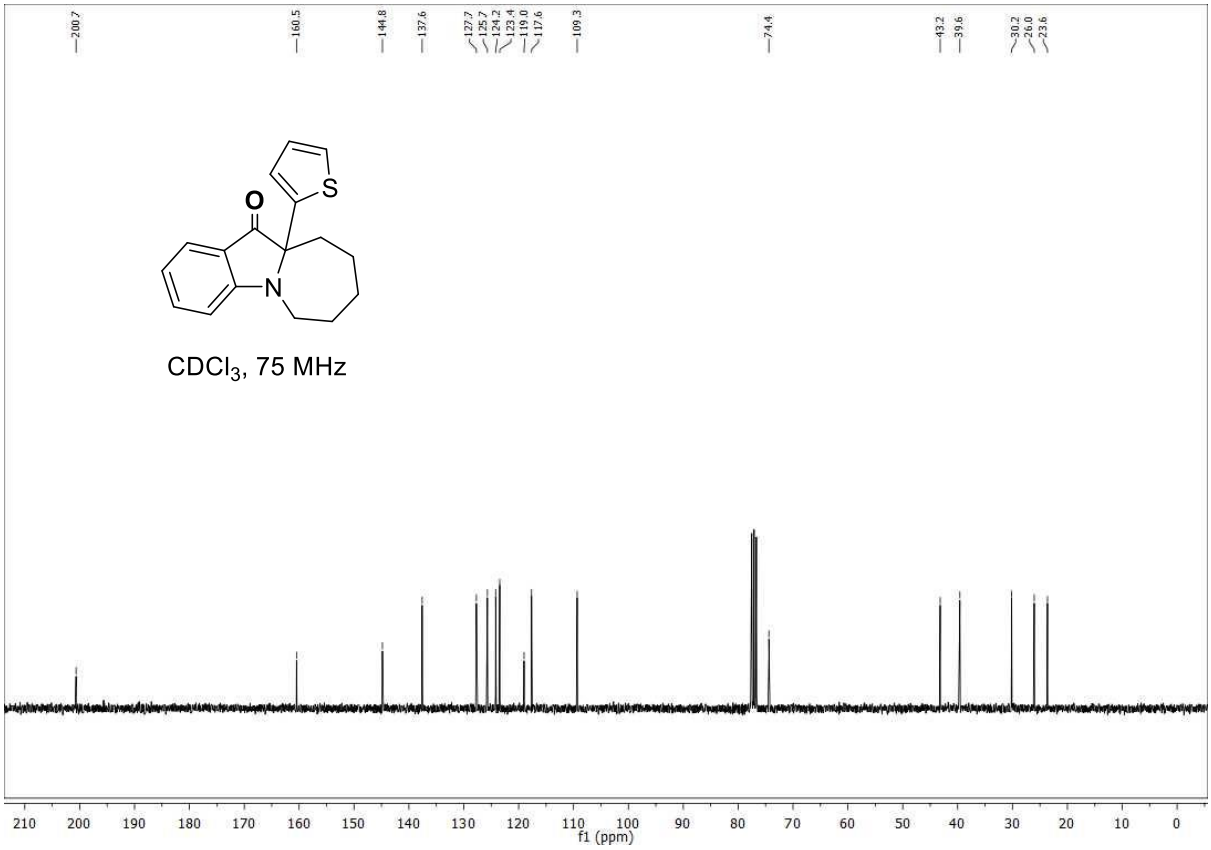
^{1}H and ^{13}C{^{1}H} NMR spectra of 7j:



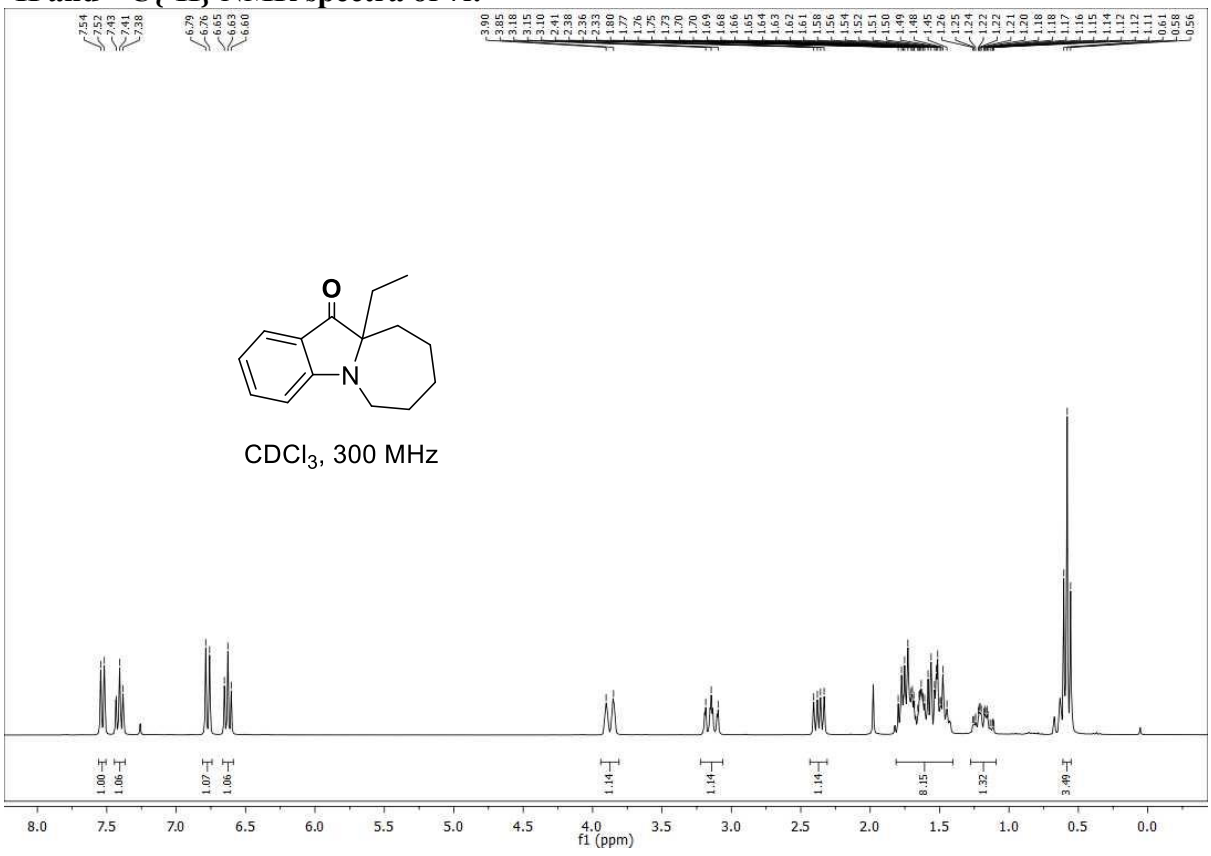


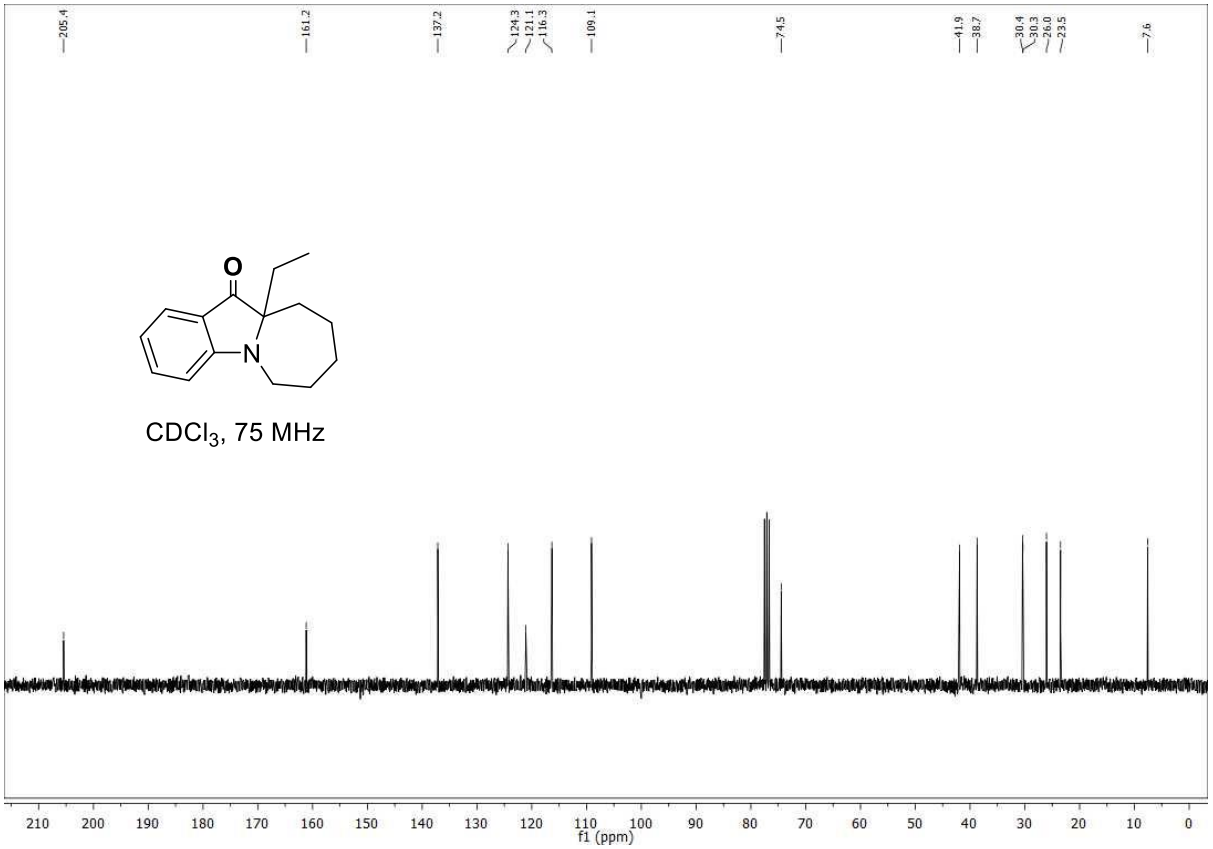
^{1}H and ^{13}C{^{1}H} NMR spectra of 7k:



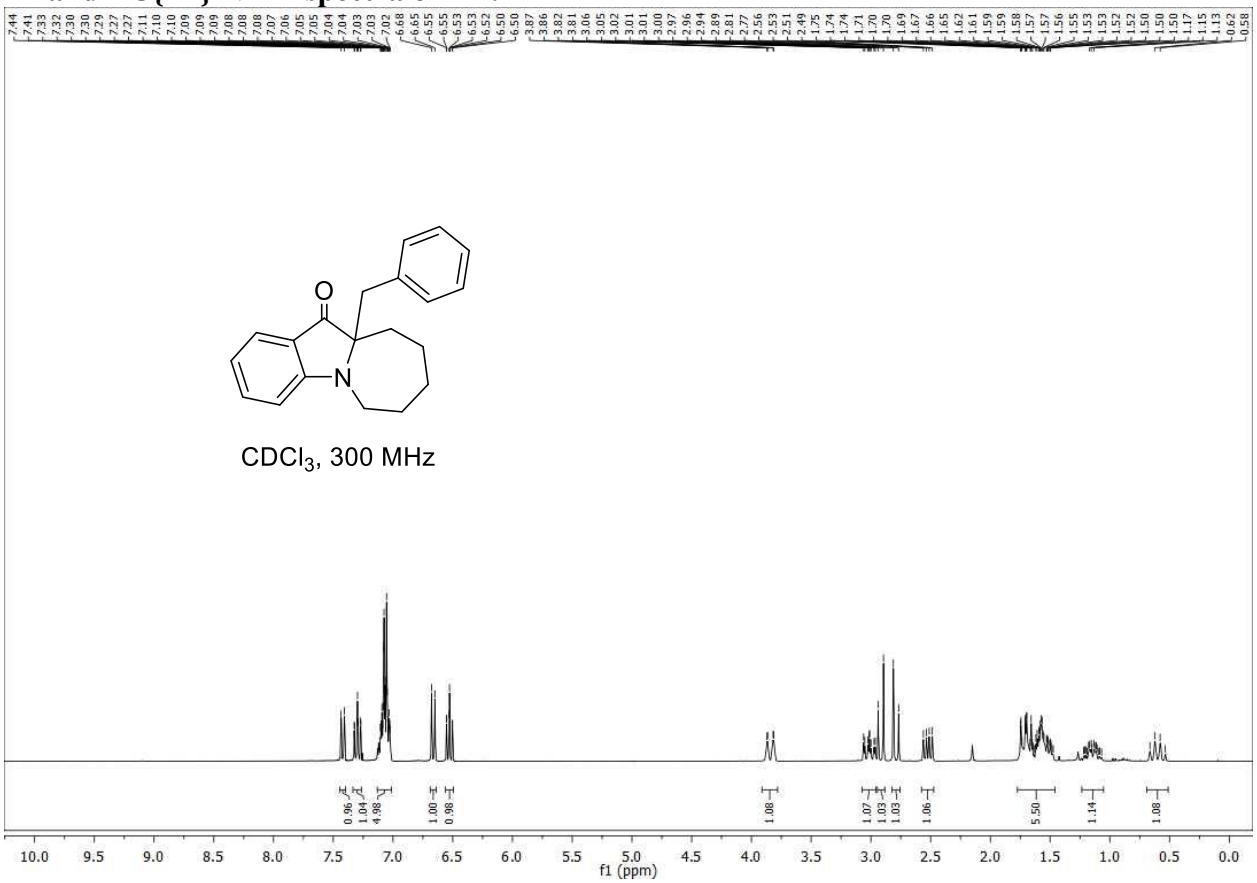


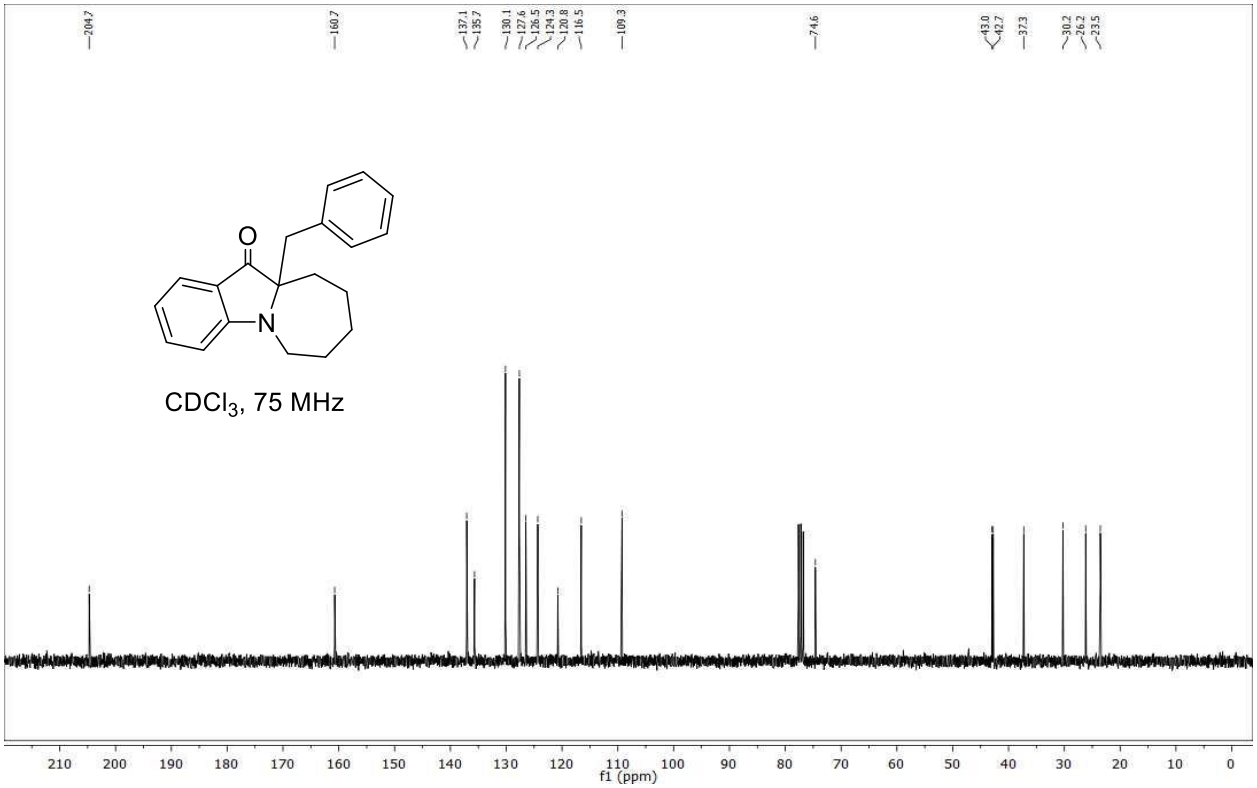
^{1}H and ^{13}C{^{1}H} NMR spectra of 7l:



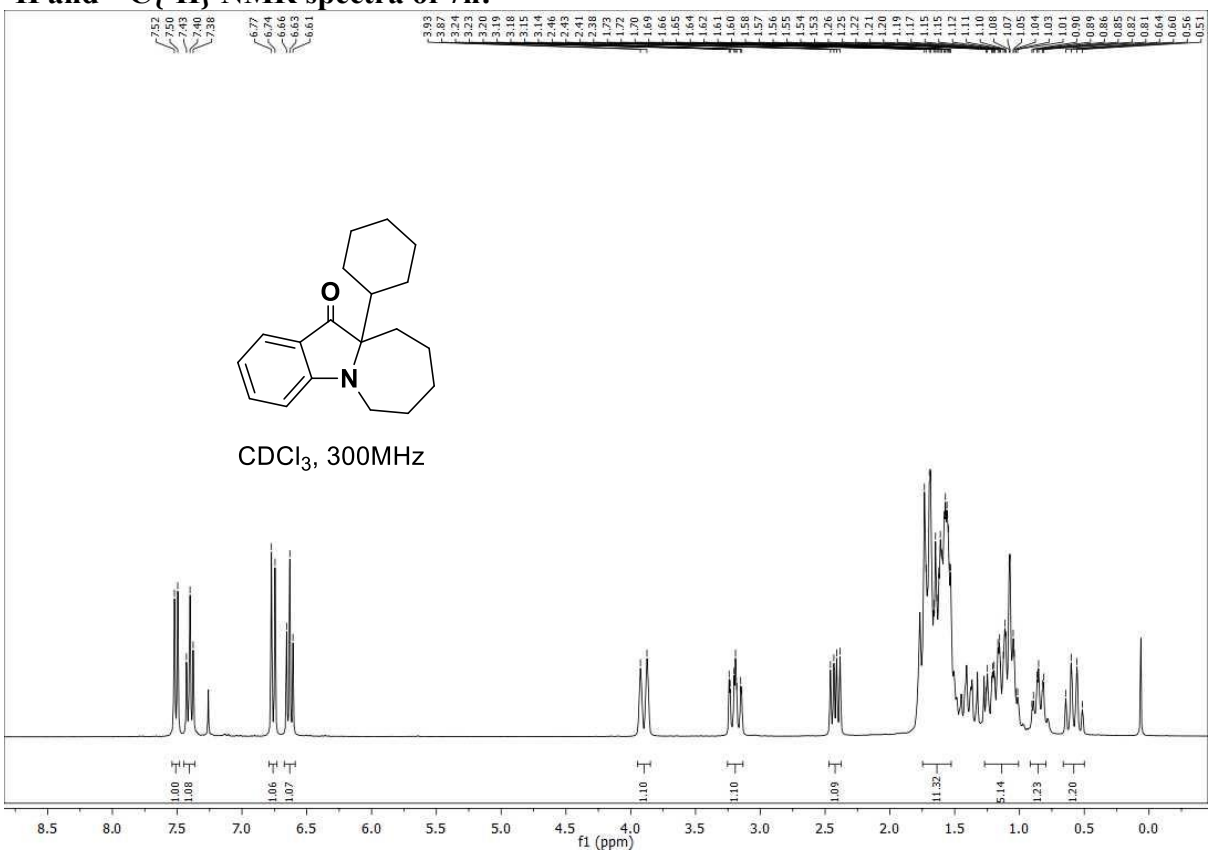


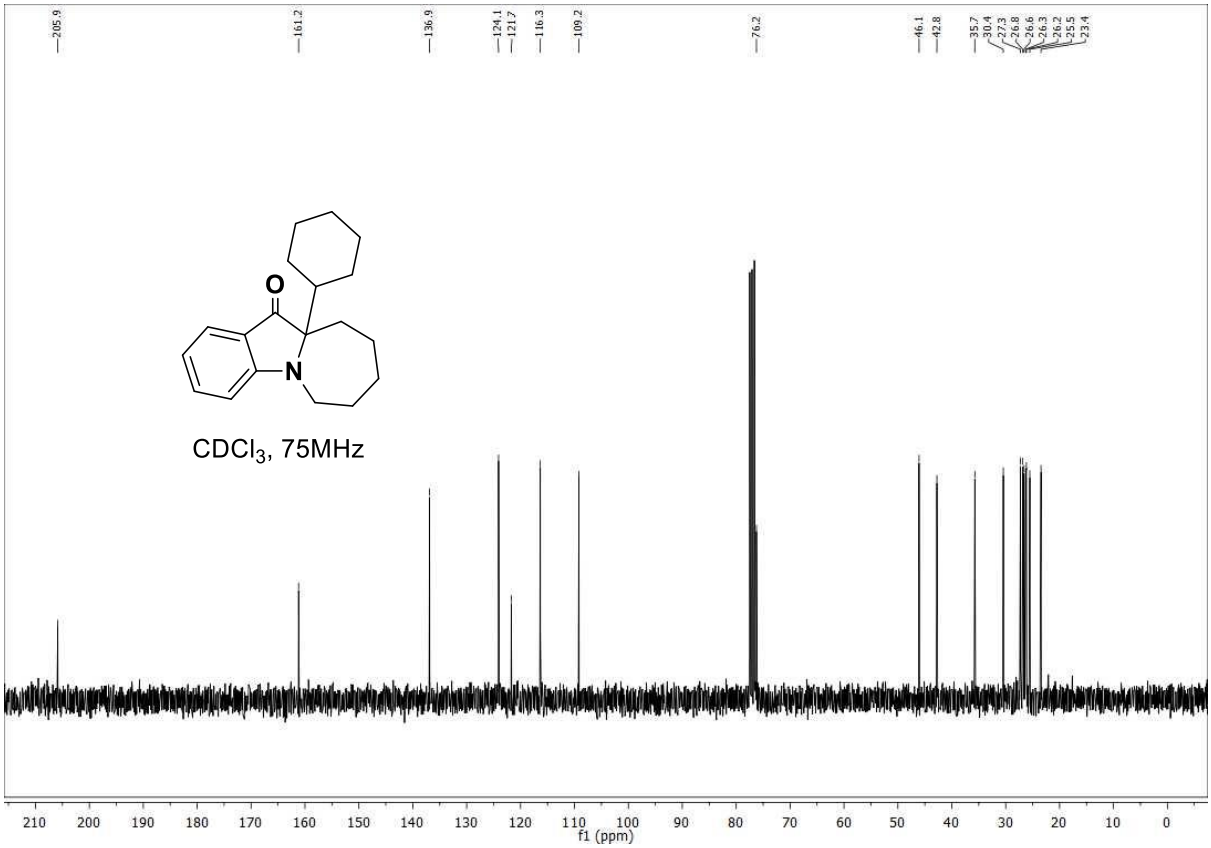
^{1}H and ^{13}C{^{1}H} NMR spectra of 7m:



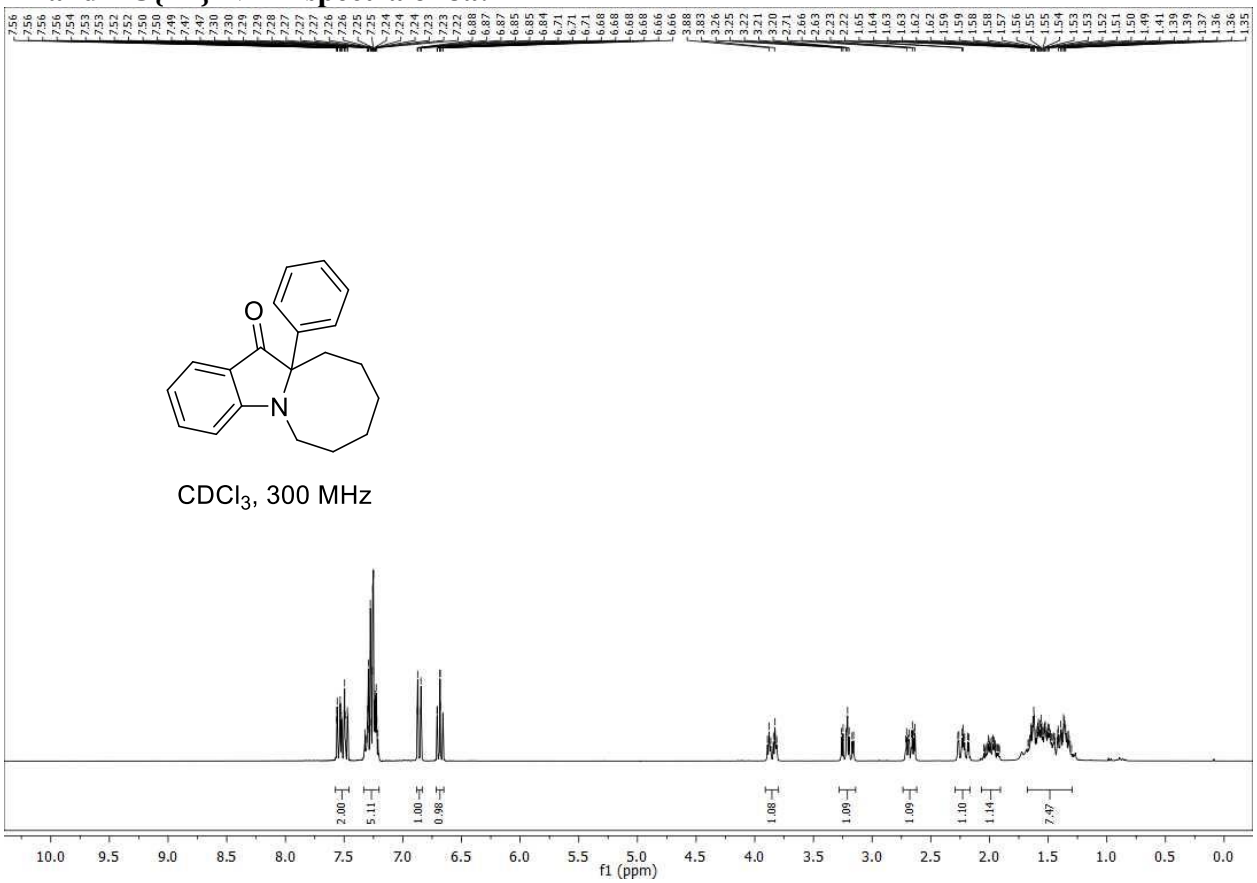


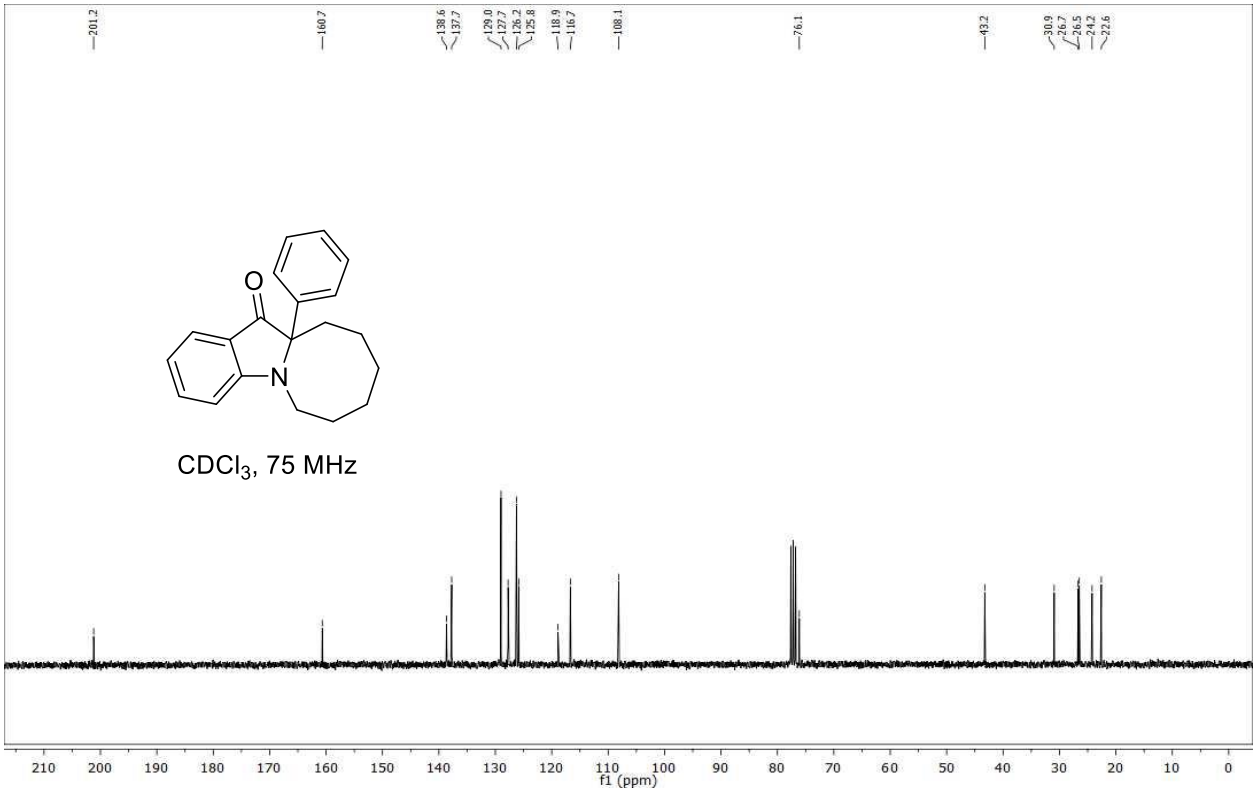
^{1}H and ^{13}C{^{1}H} NMR spectra of 7n:



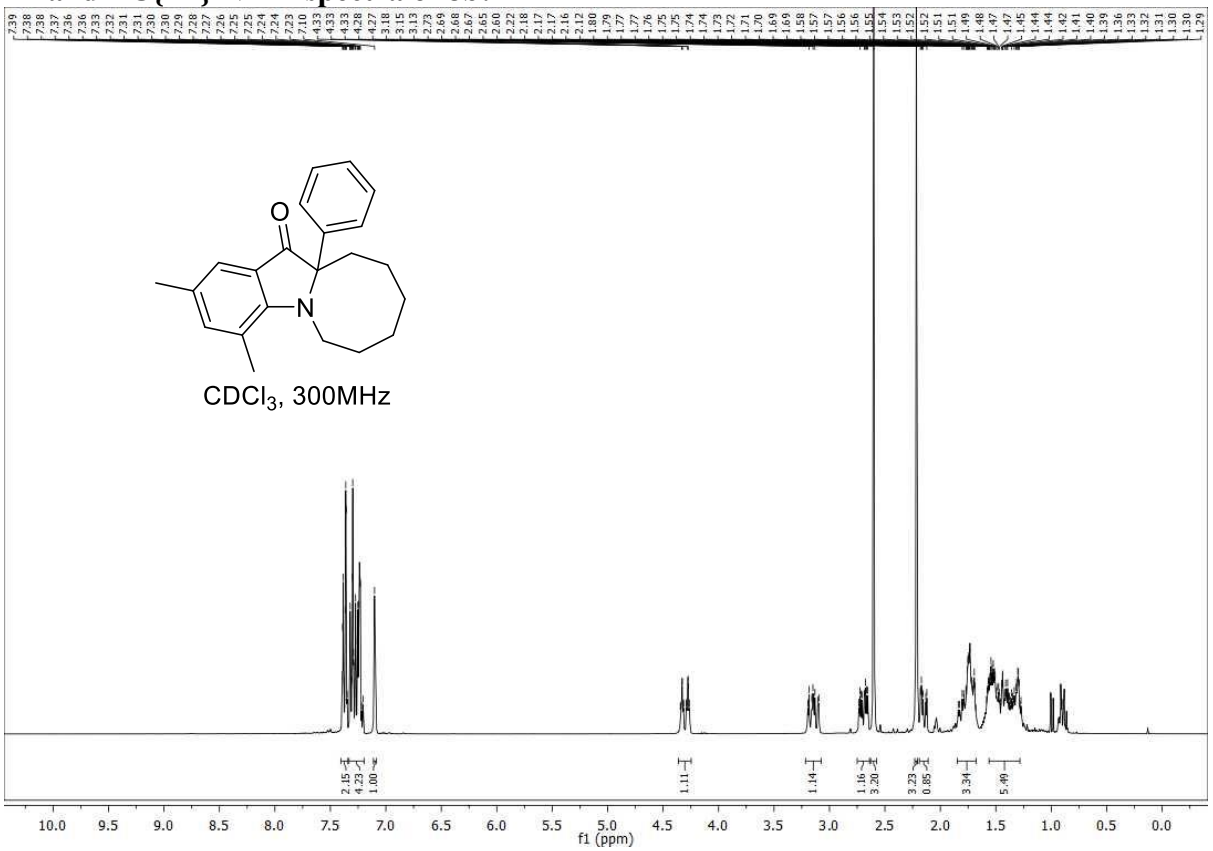


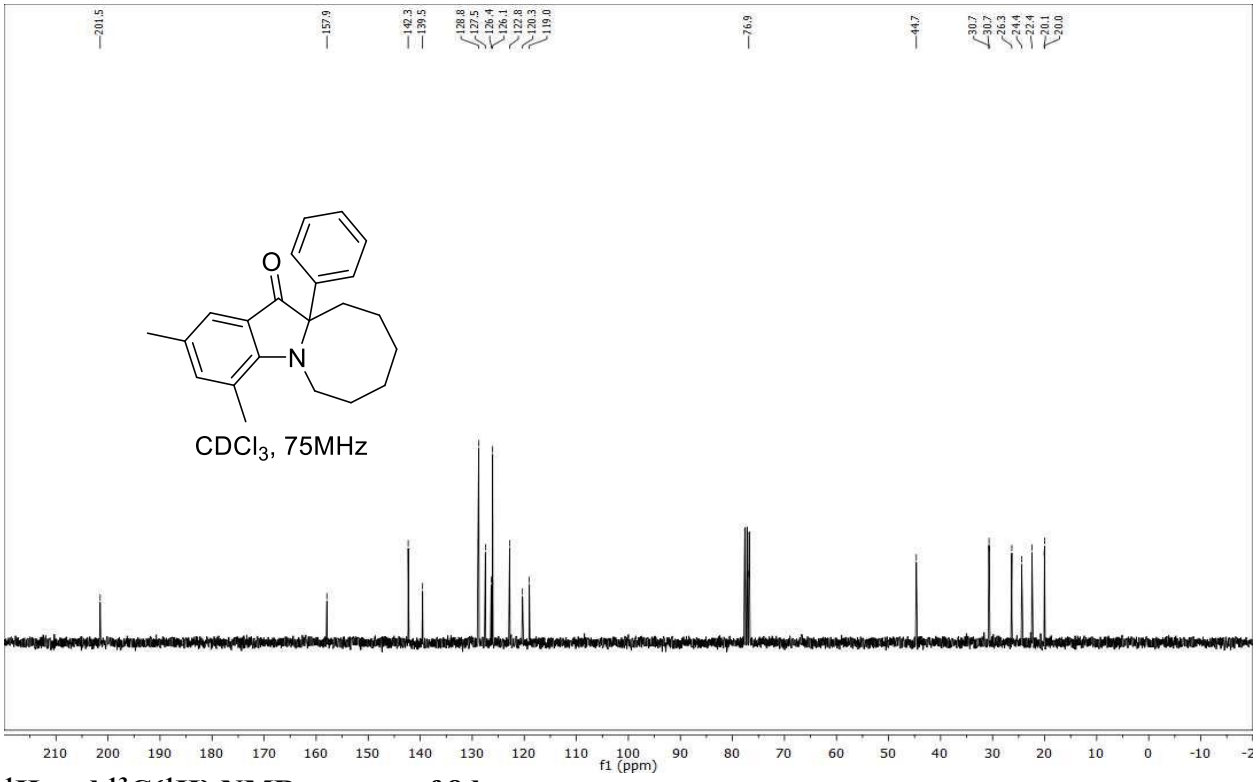
^{1}H and ^{13}C{^{1}H} NMR spectra of 8a:



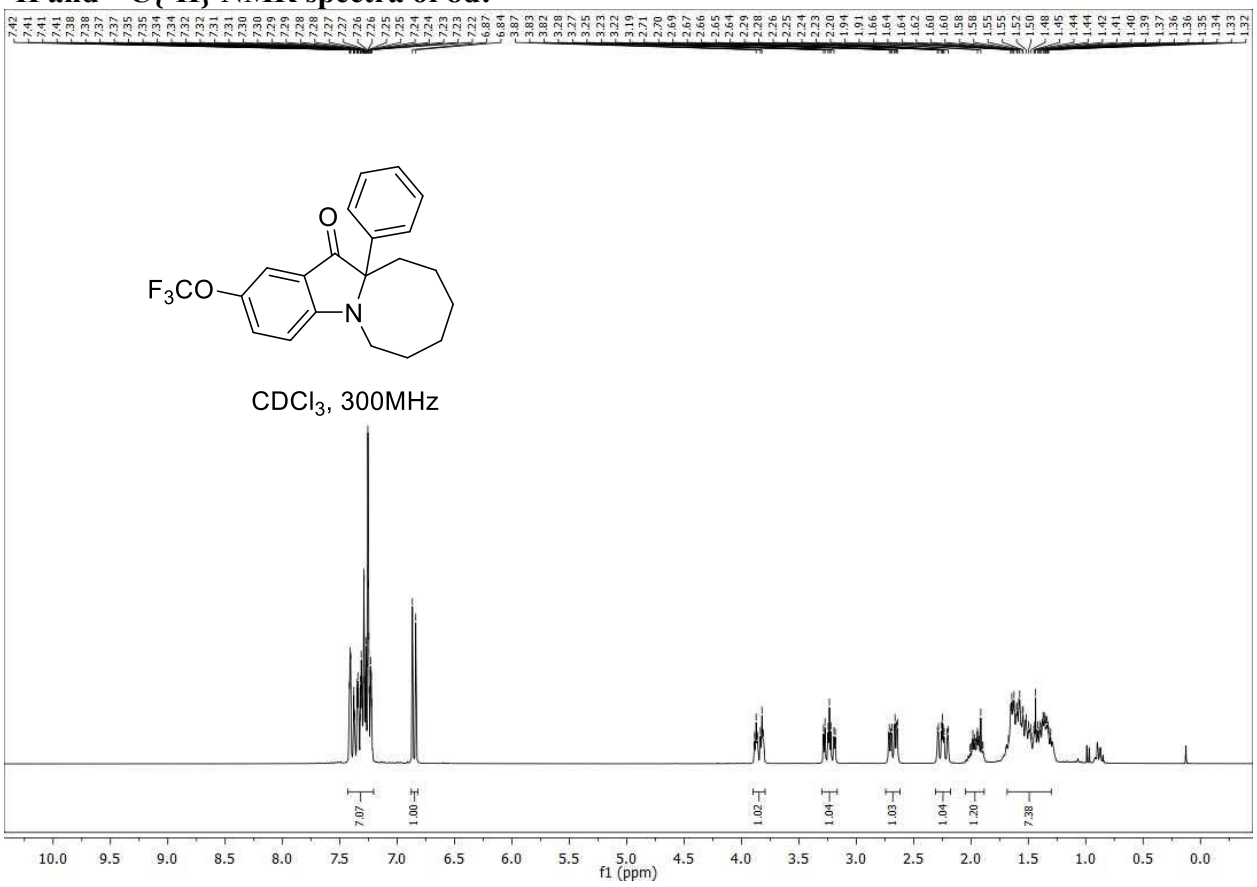


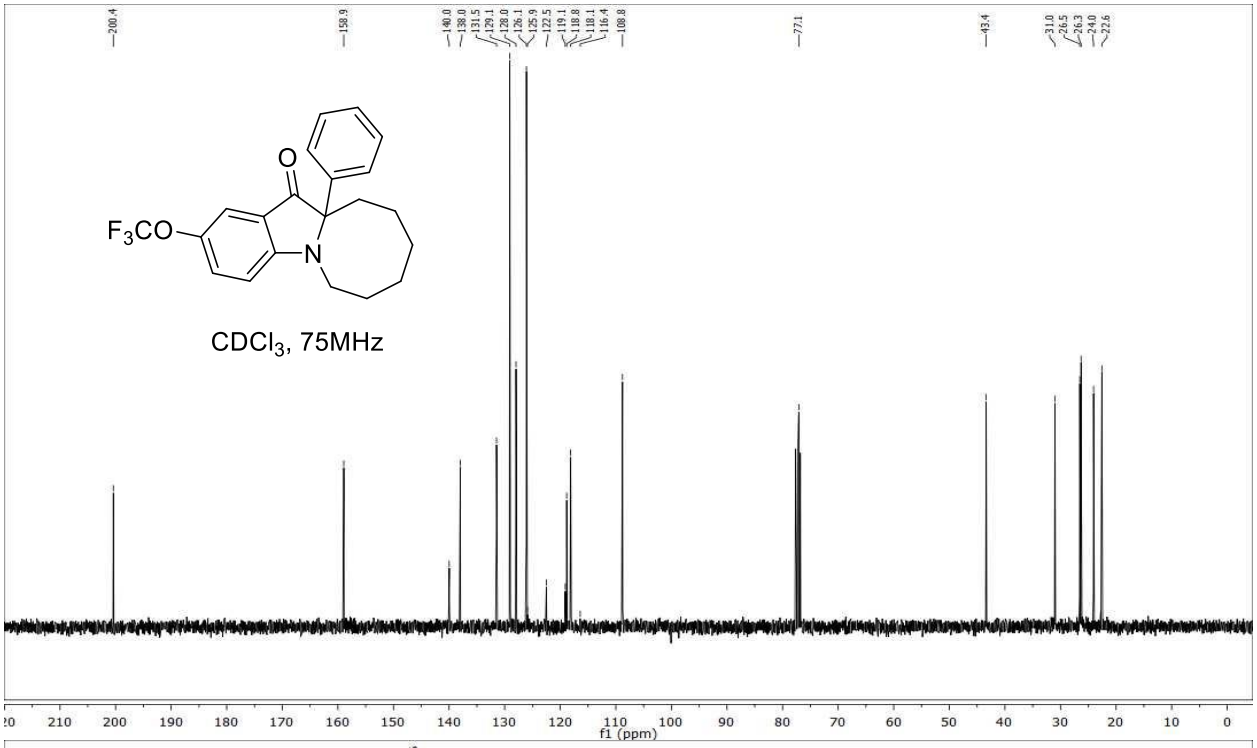
^{1}H and ^{13}C{^{1}H} NMR spectra of 8b:





^{1}H and ^{13}C{^{1}H} NMR spectra of 8d:




200.4
159.9
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138.0
131.5
129.1
128.0
126.1
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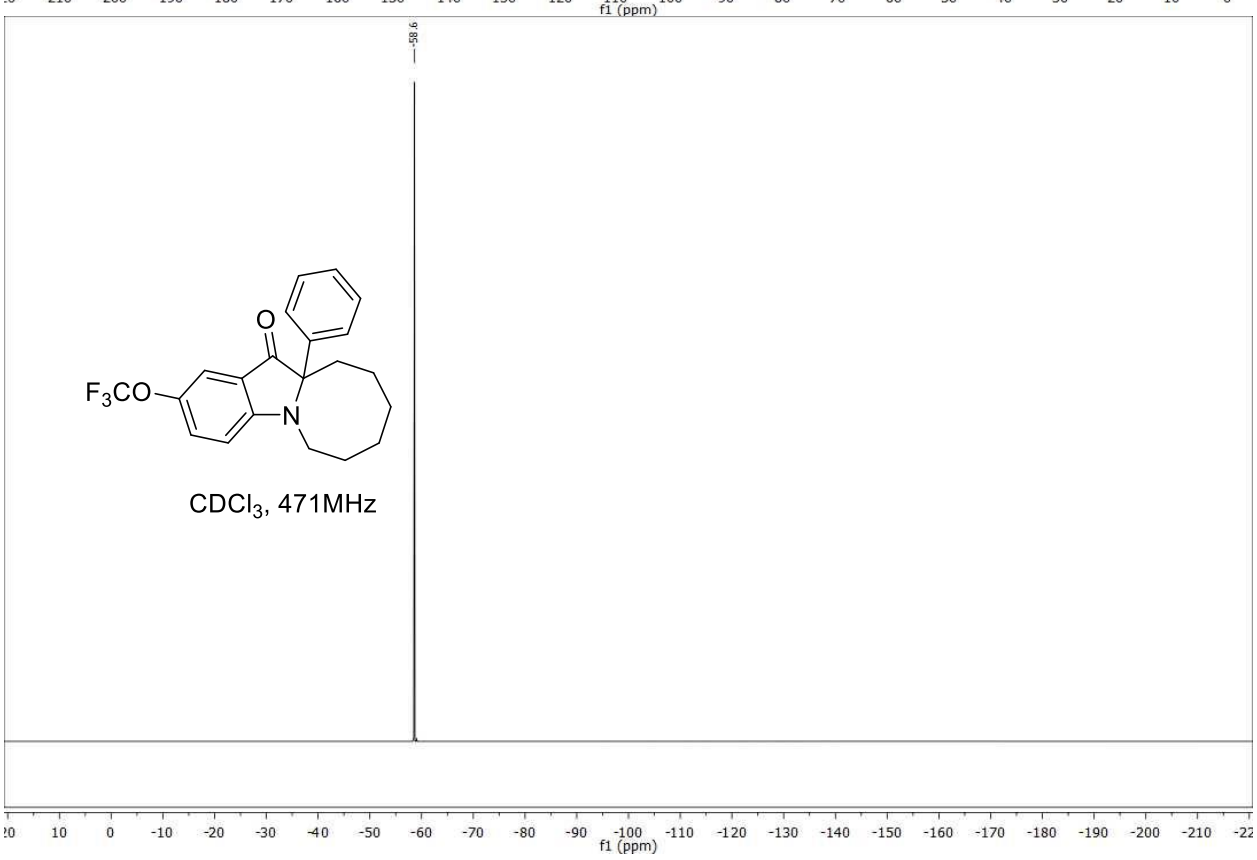
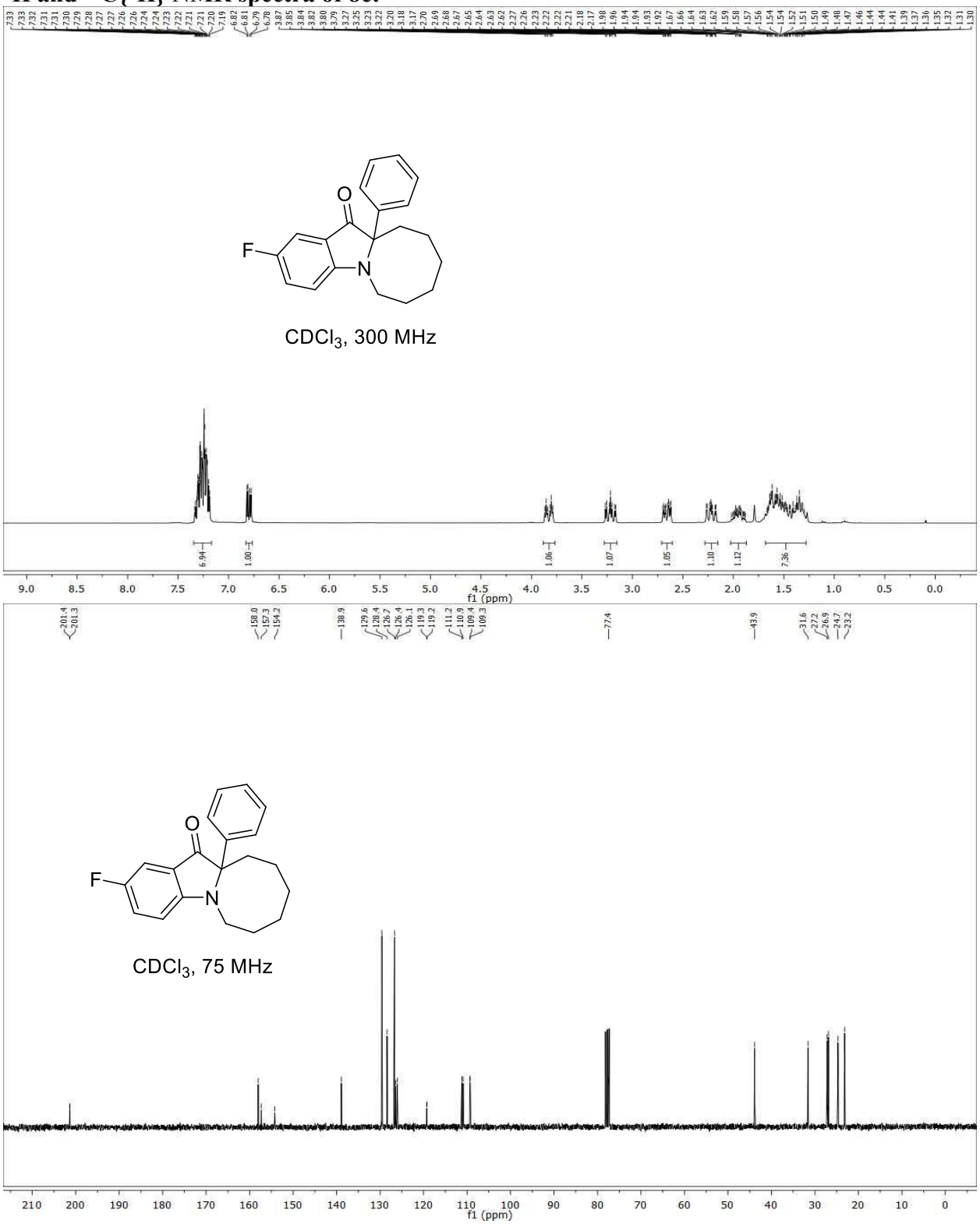
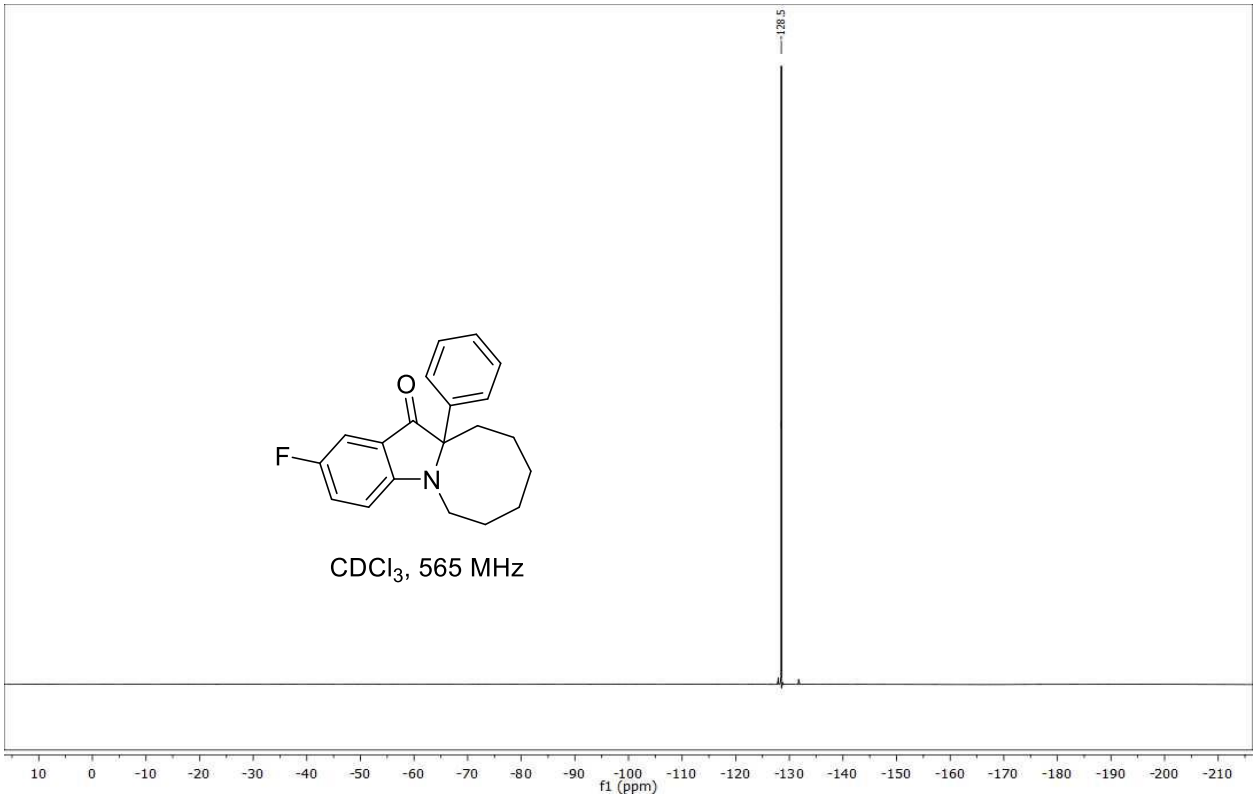
122.5
119.1
118.8
118.1
116.4
108.8
77.1
43.4
31.0
26.5
26.3
24.0
22.6
O
F3CO
N
CDCl3, 75MHz
f1 (ppm)

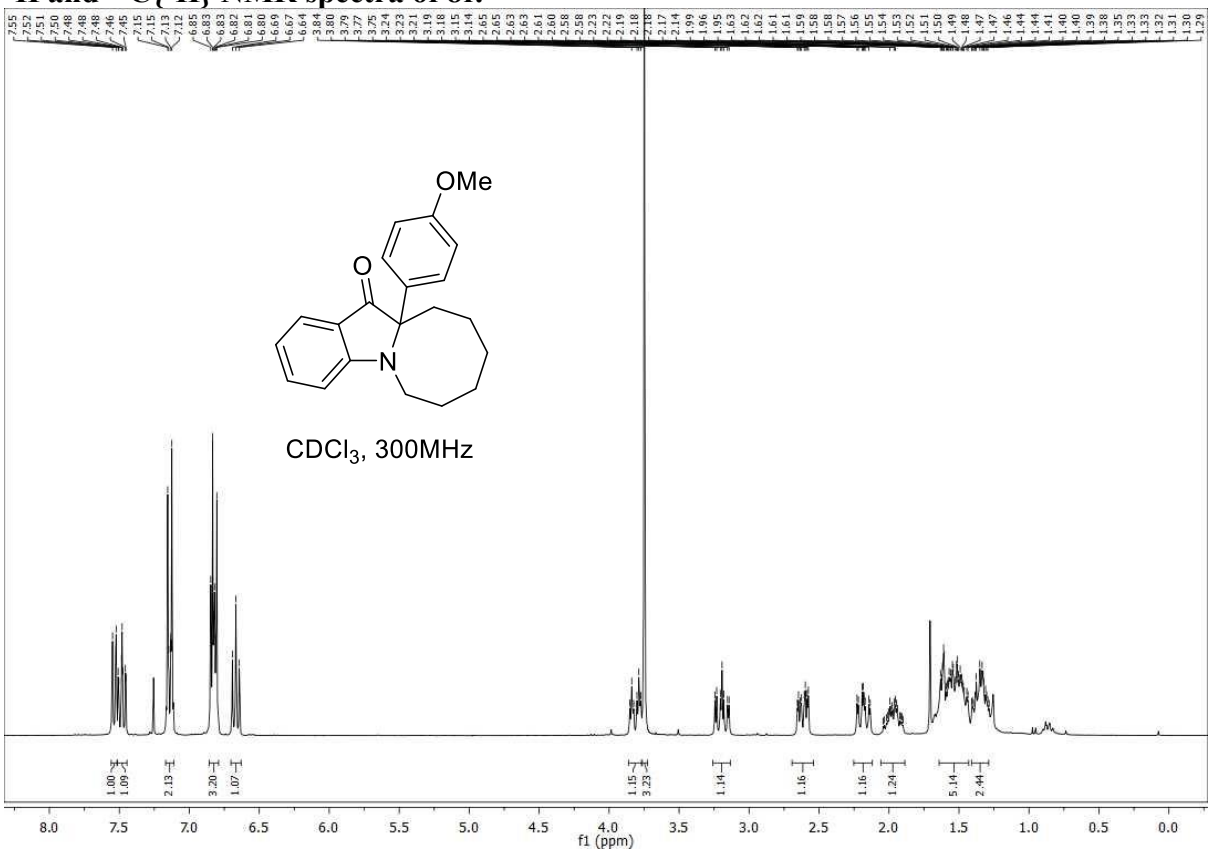

58.6
O
F3CO
N
CDCl3, 471MHz
f1 (ppm)

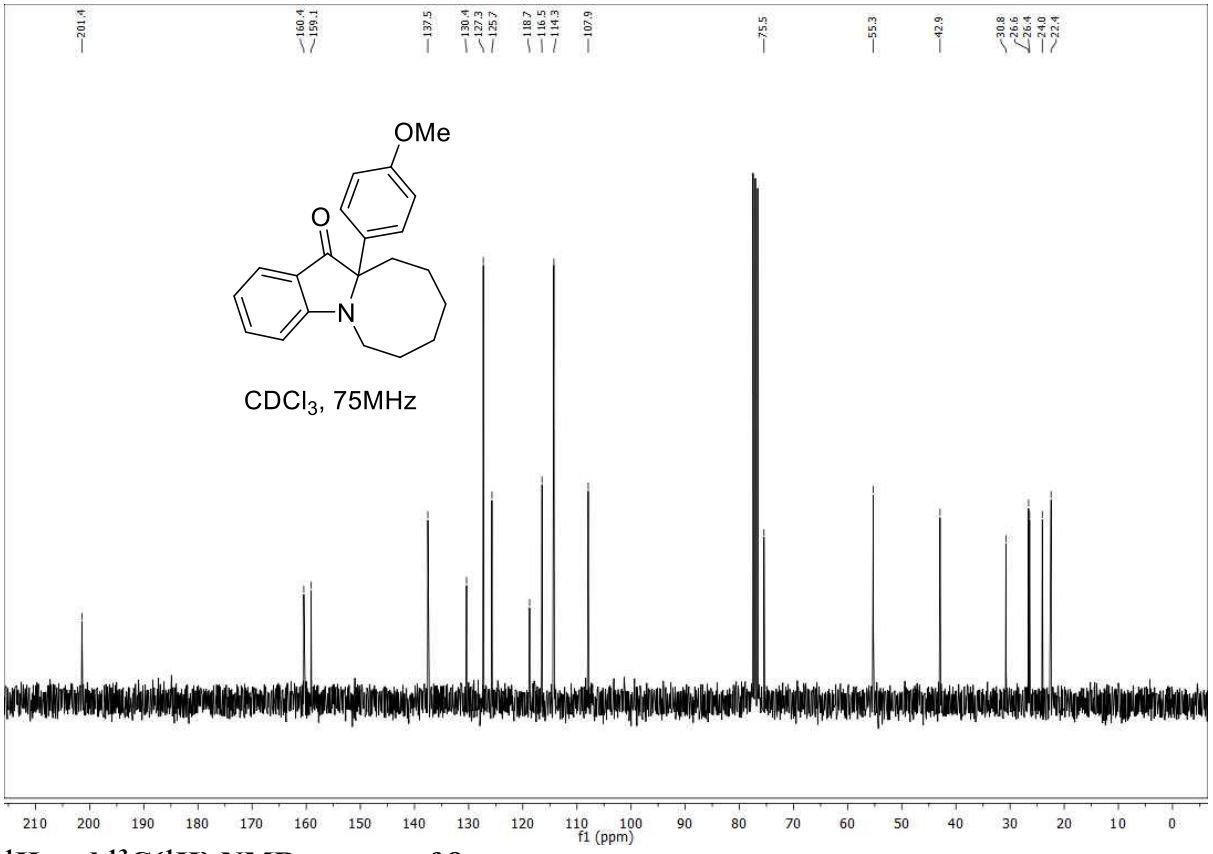
^{1}H and ^{13}C{^{1}H} NMR spectra of 8e:



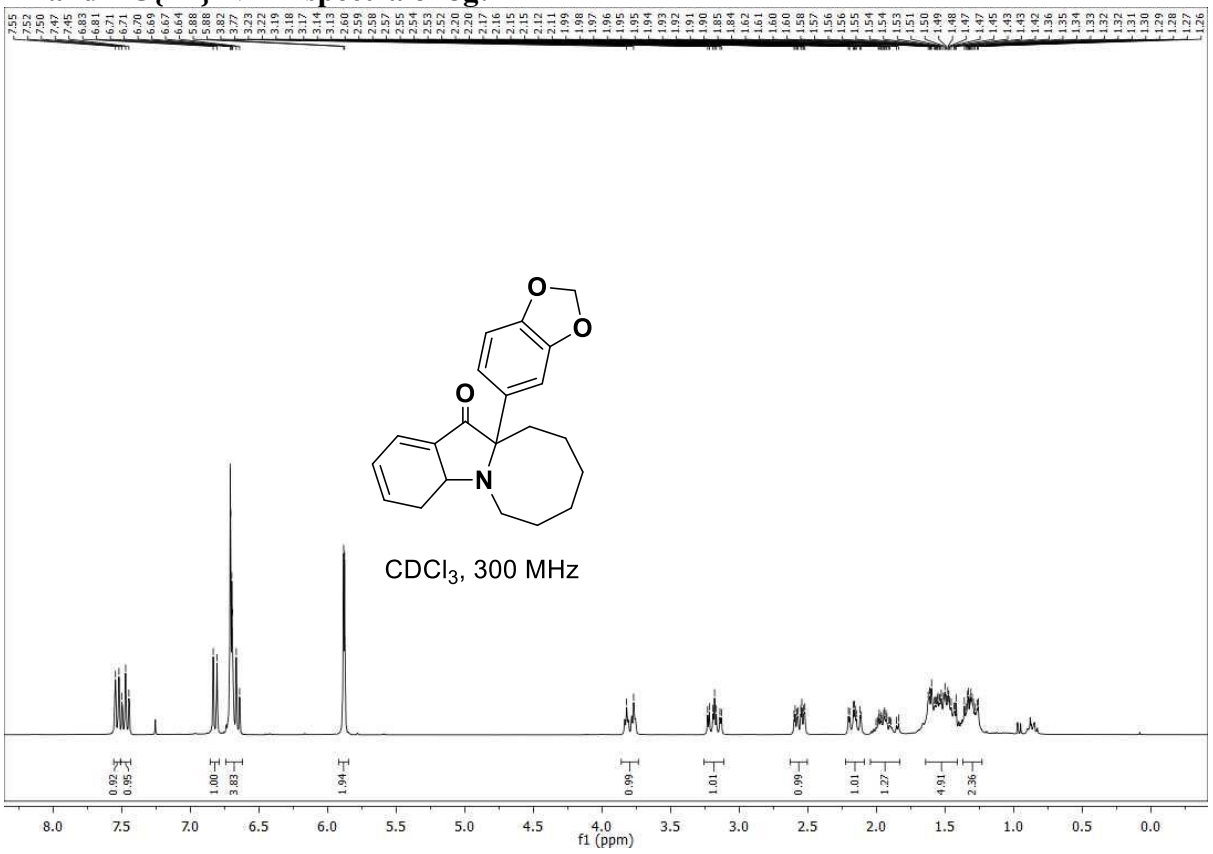


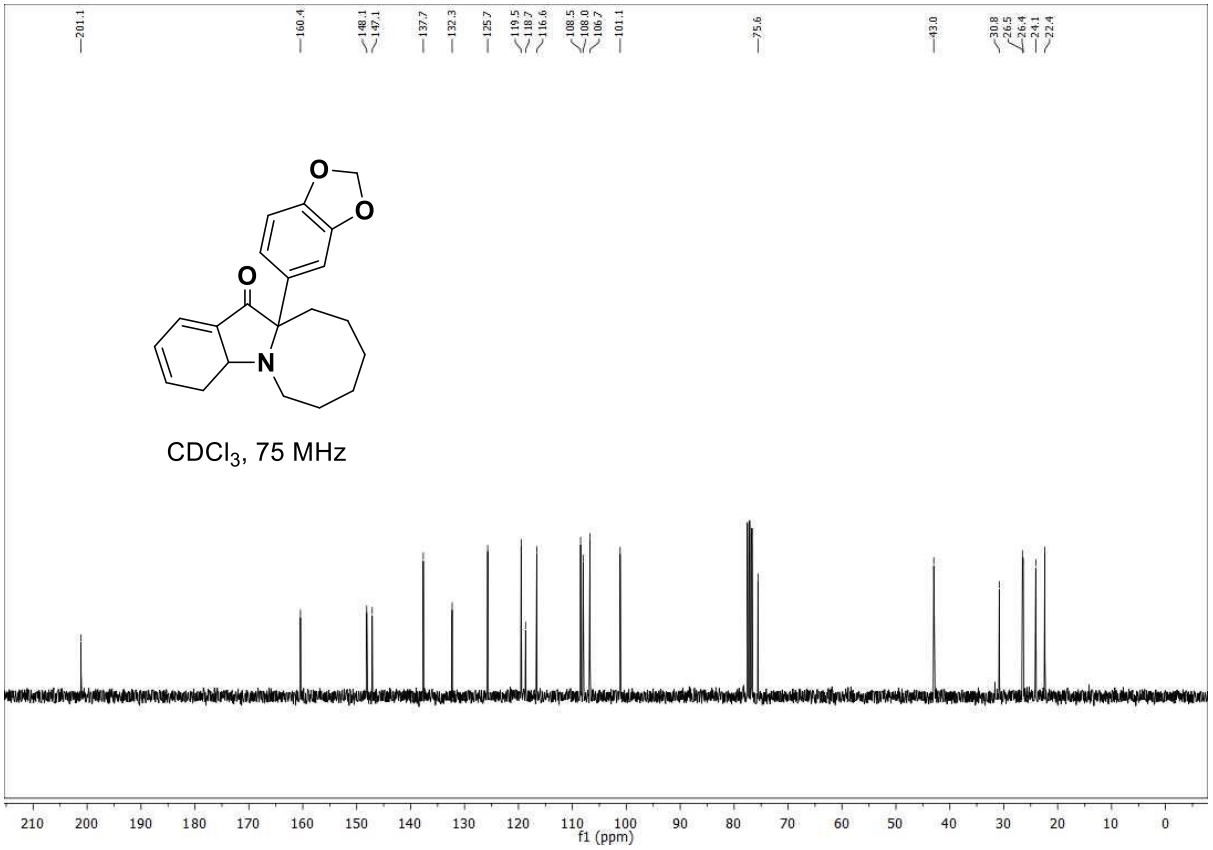
^{1}H and ^{13}C{^{1}H} NMR spectra of 8f:



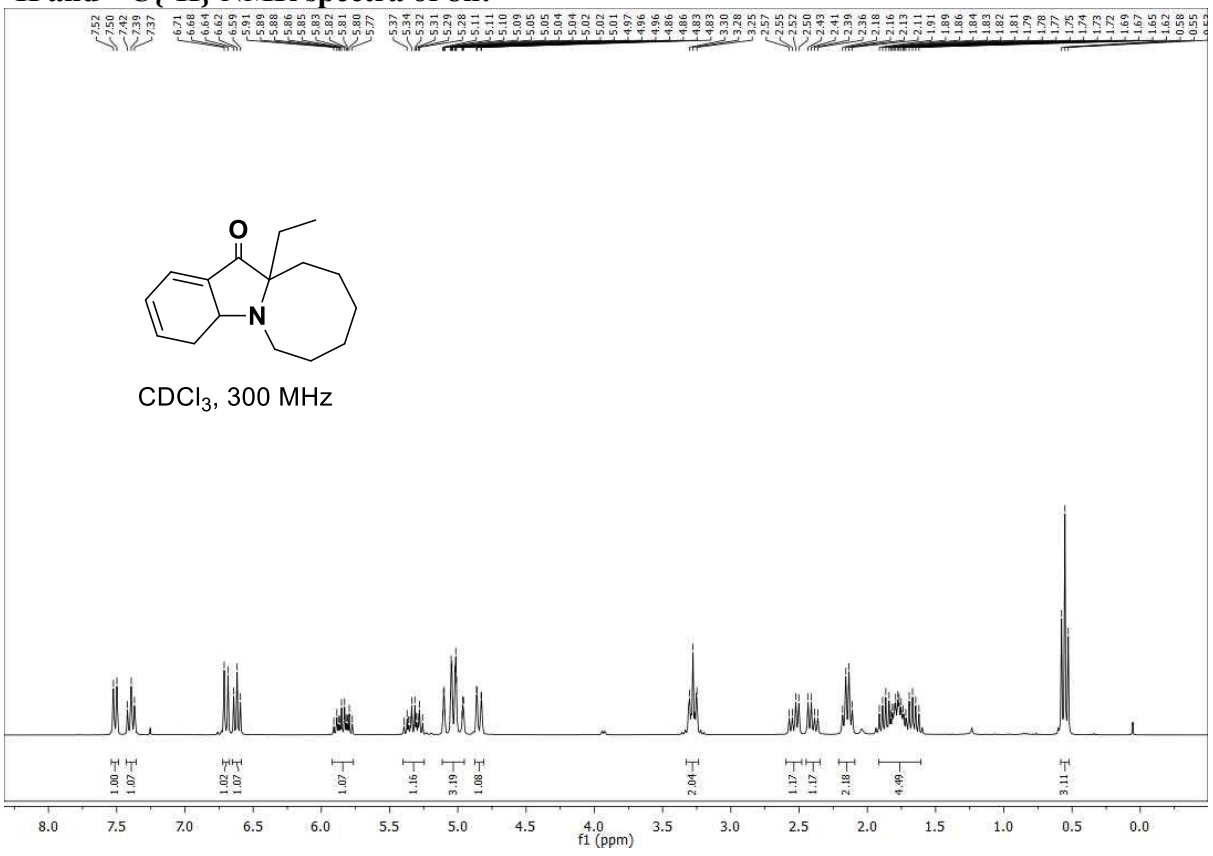


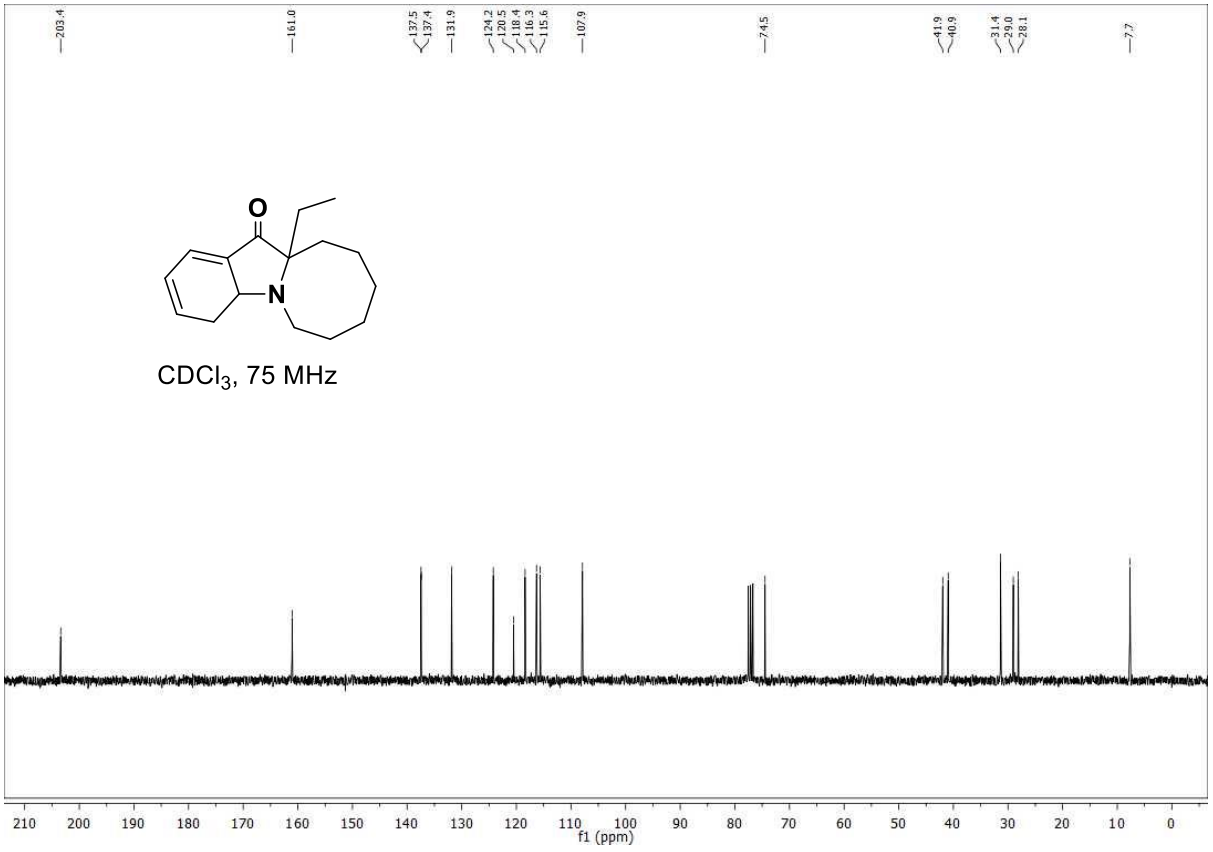
^{1}H and ^{13}C{^{1}H} NMR spectra of 8g:



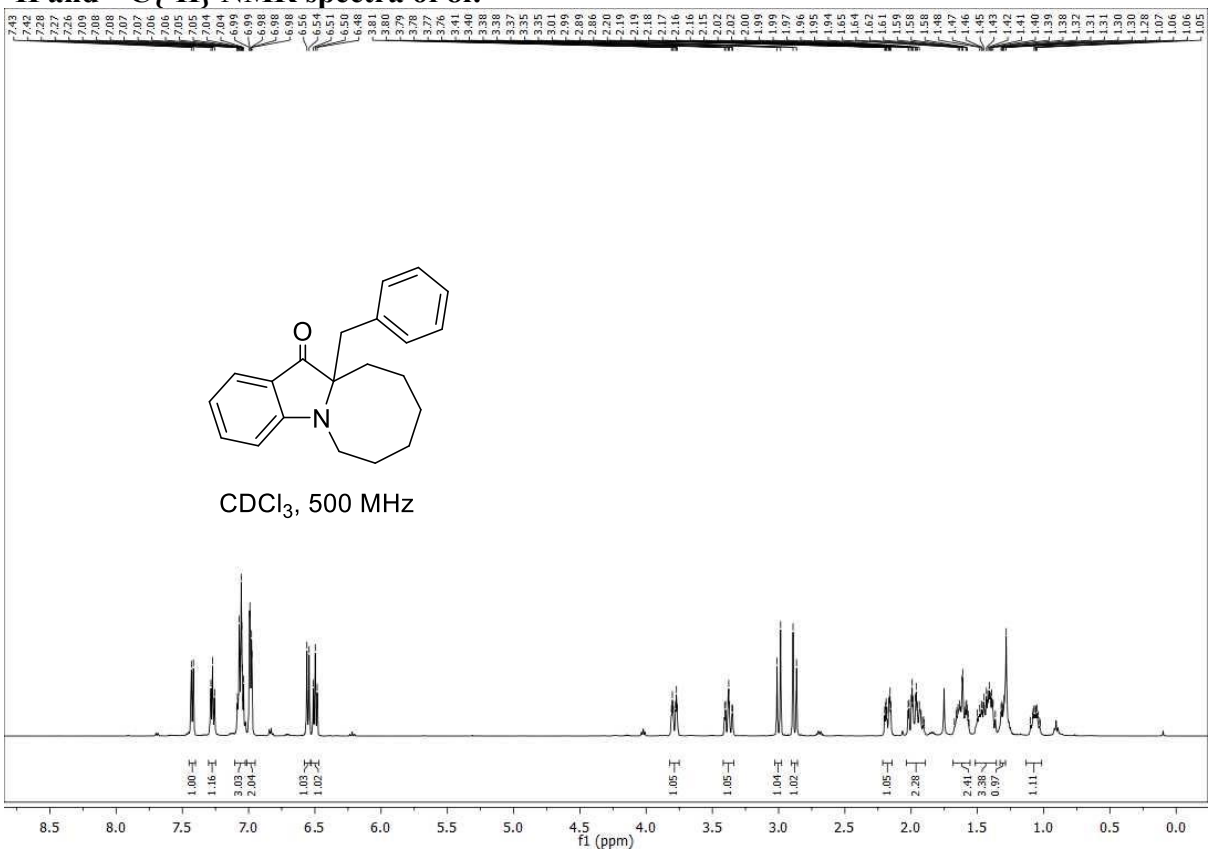


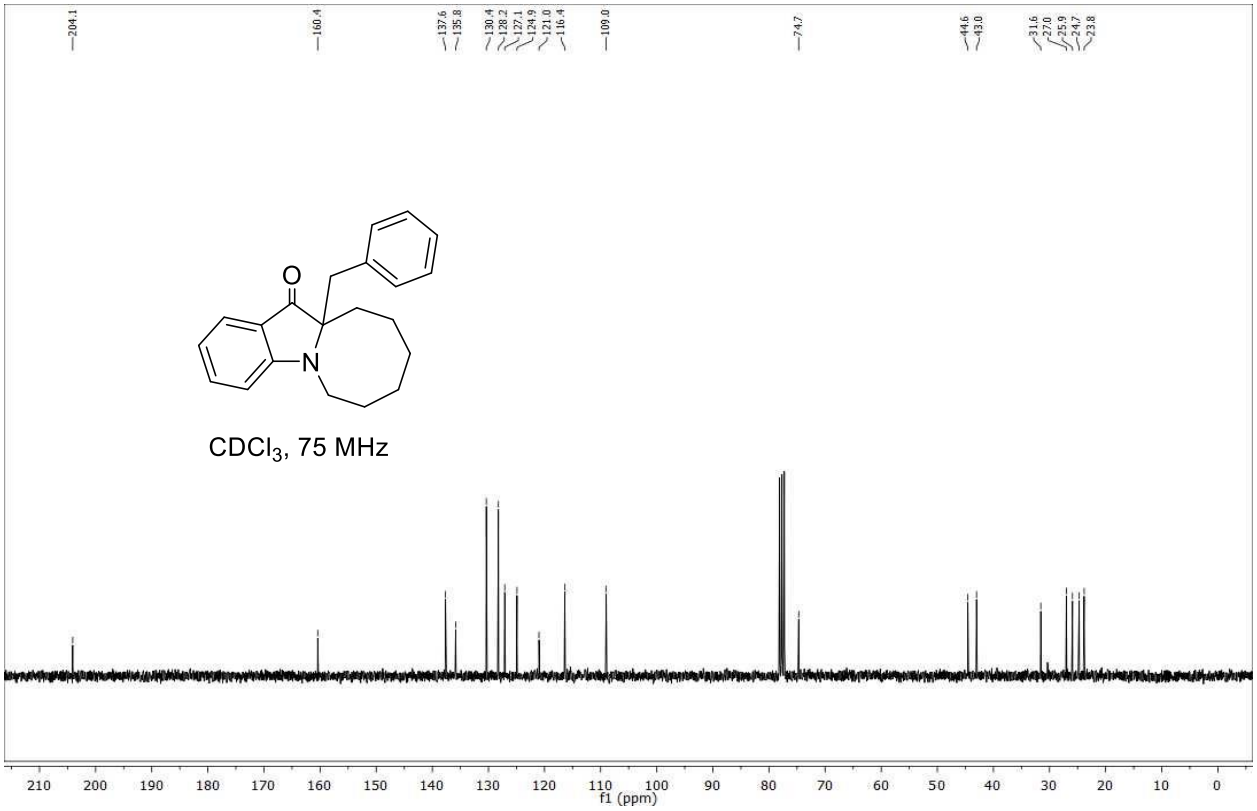
^{1}H and ^{13}C{^{1}H} NMR spectra of 8h:



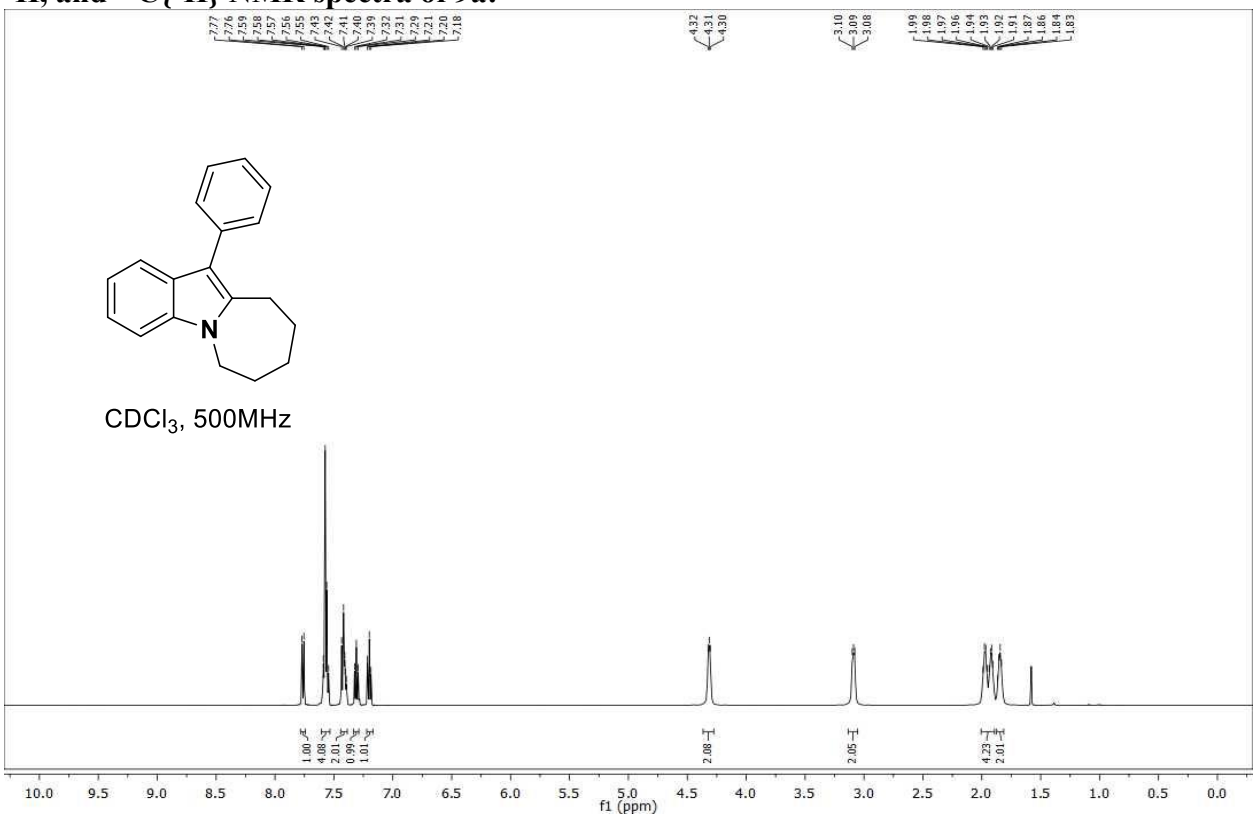


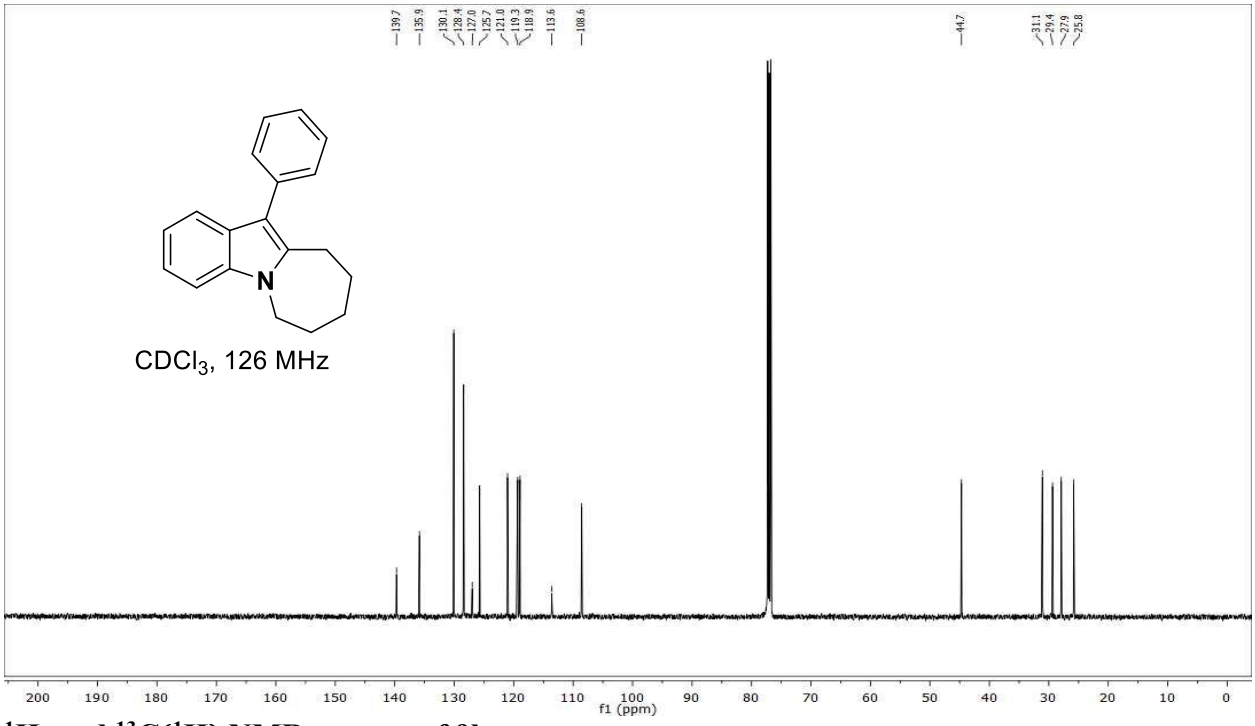
^{1}H and ^{13}C{^{1}H} NMR spectra of 8i:



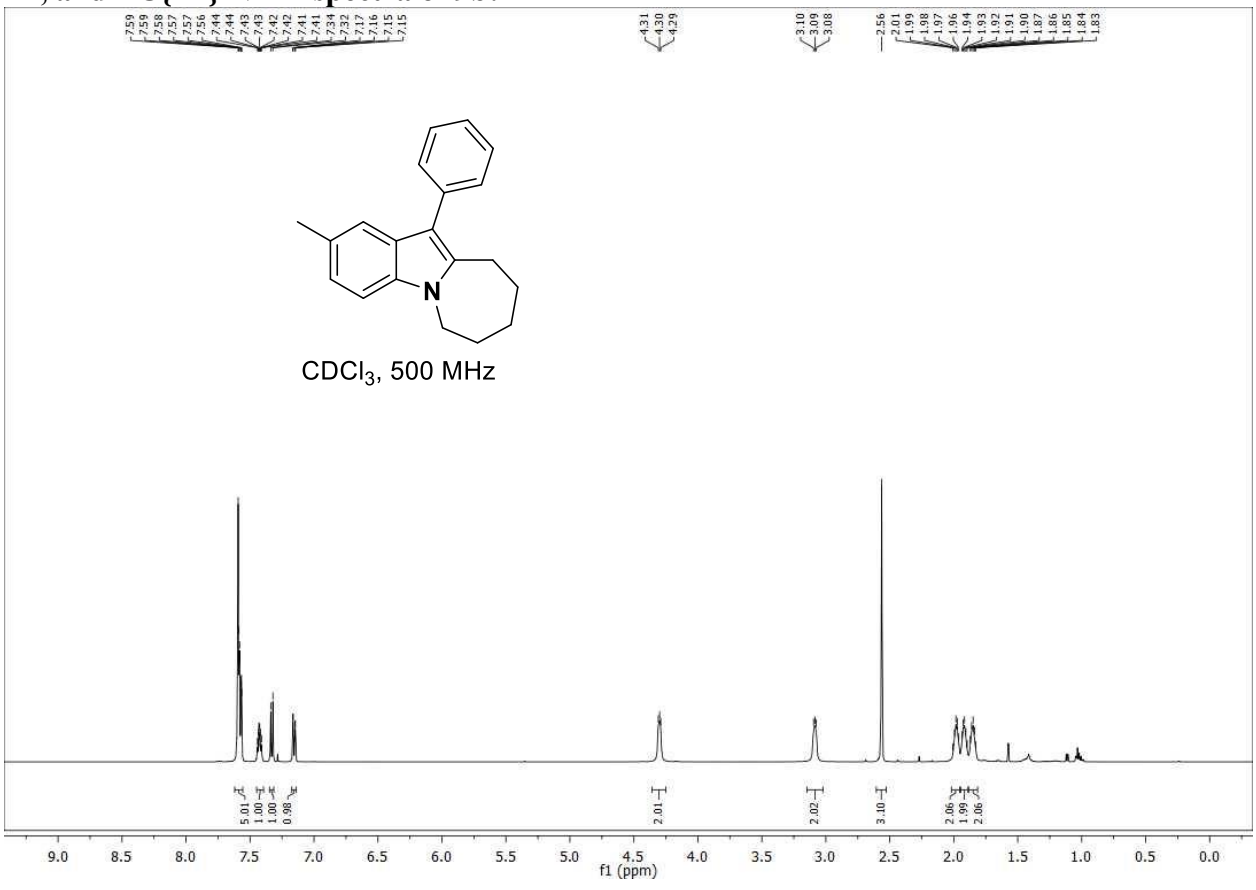


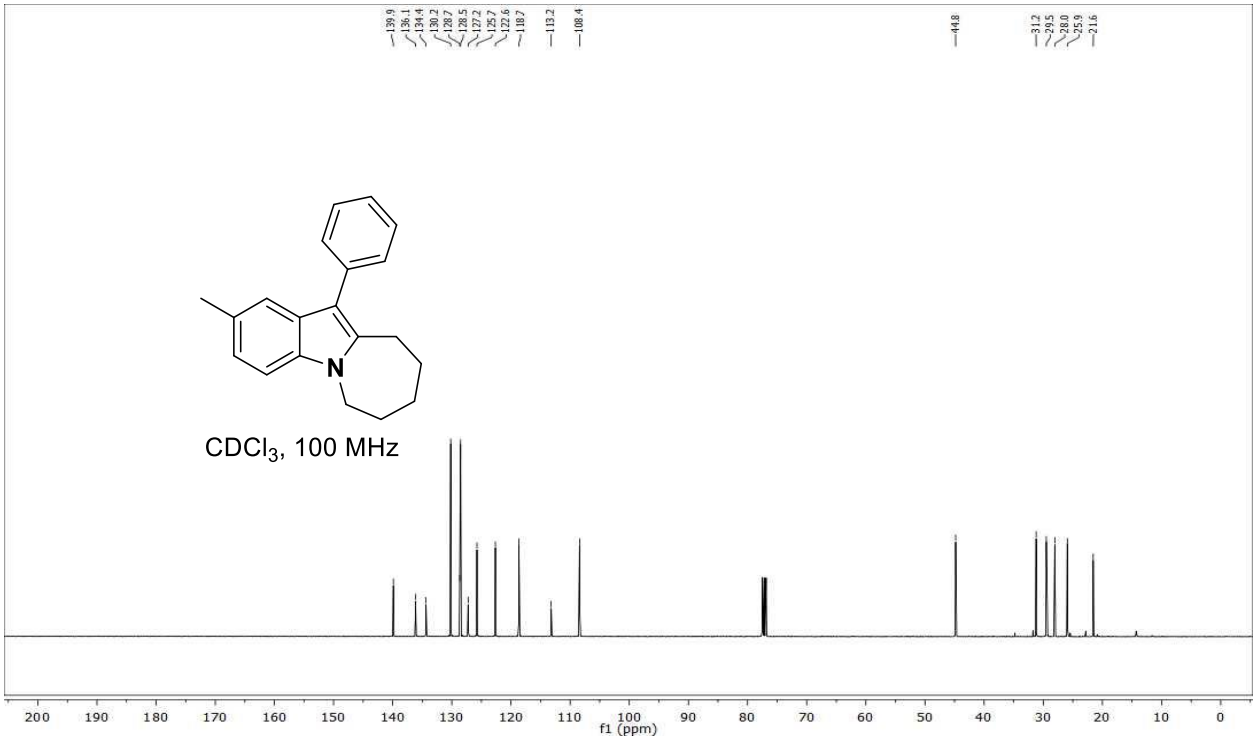
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9a:



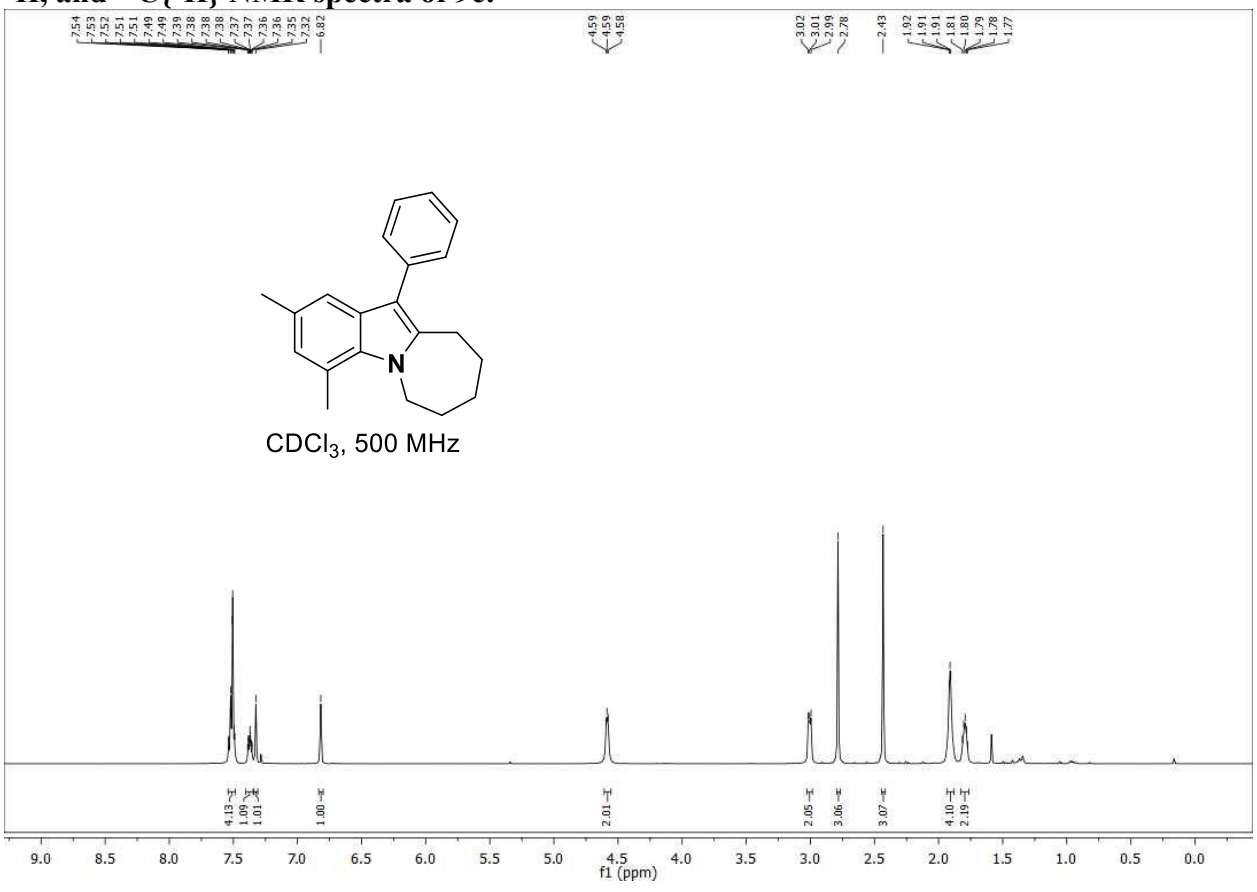


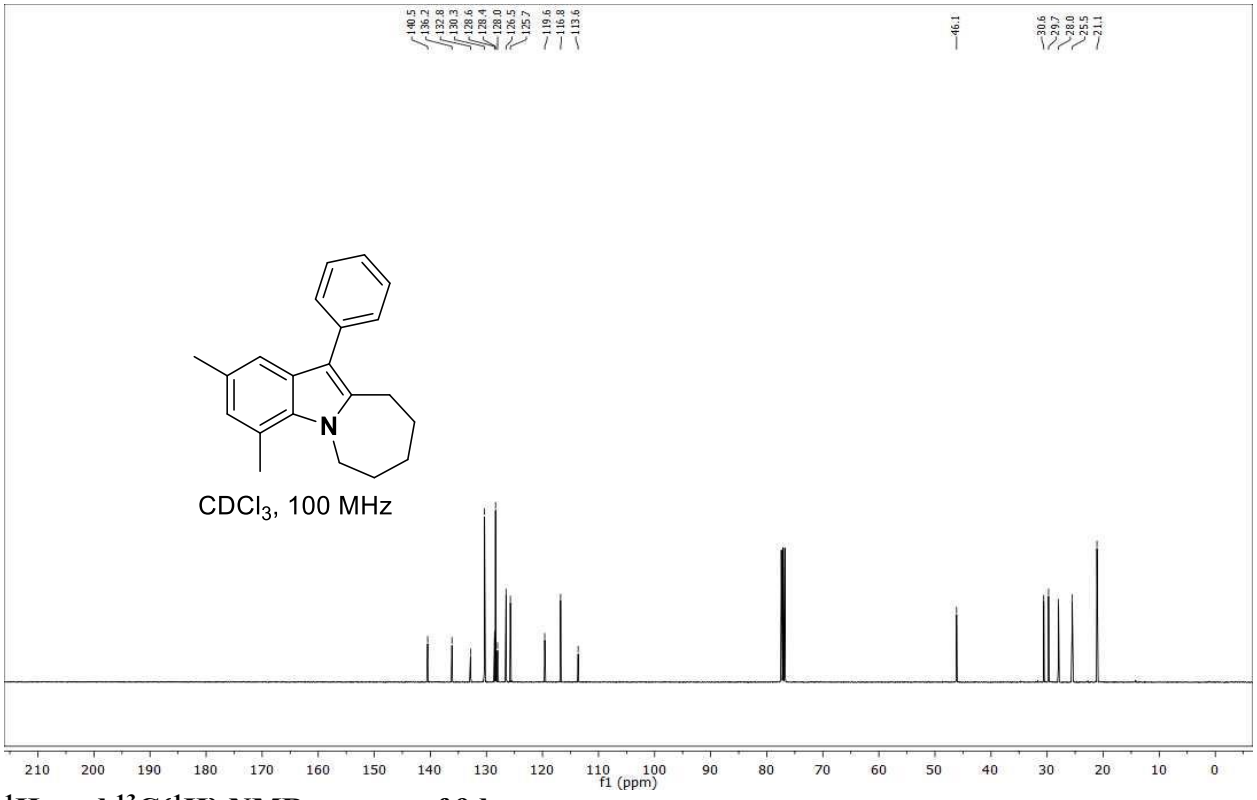
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9b:



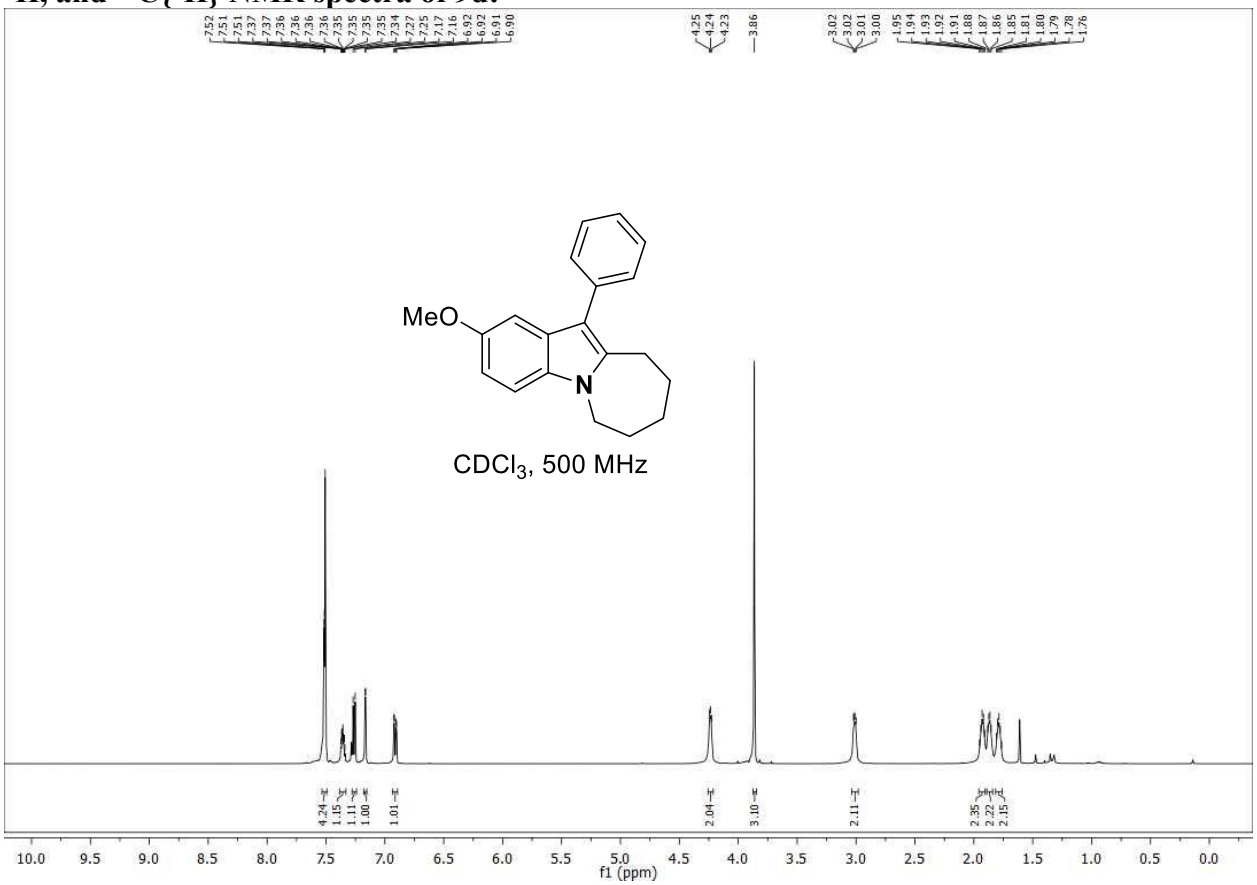


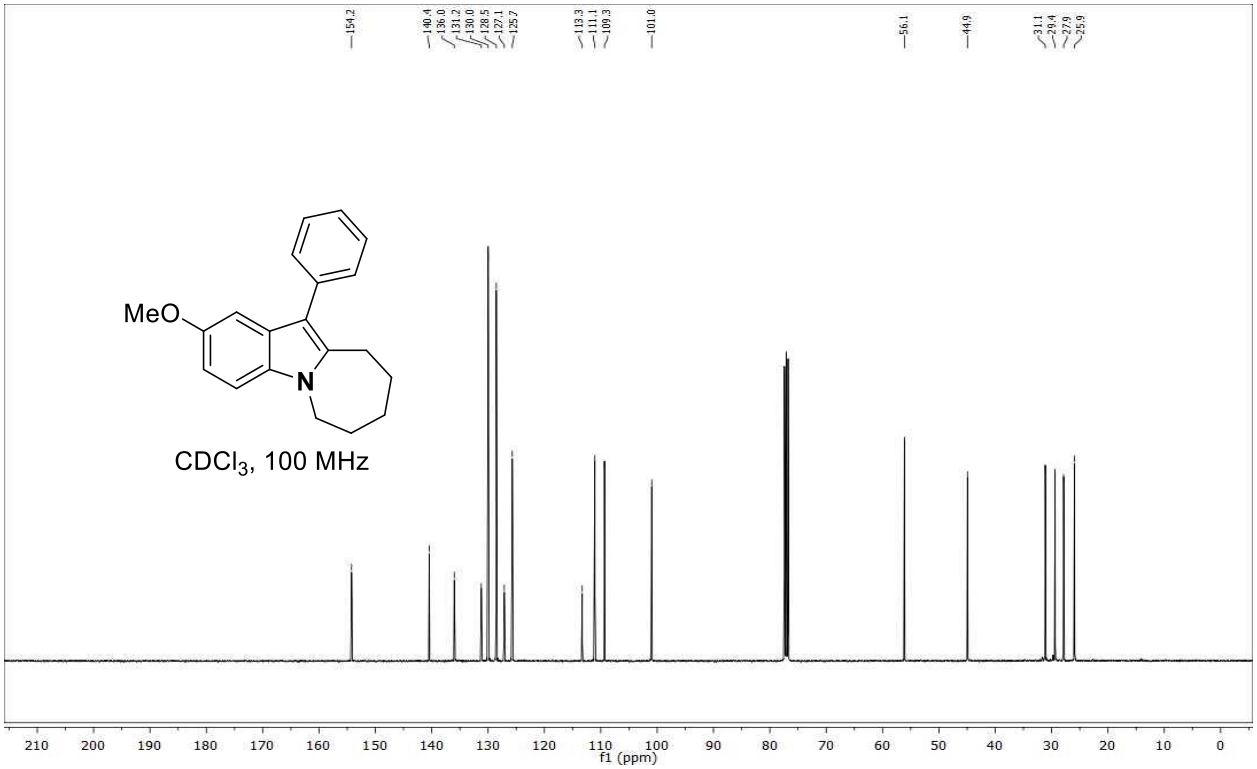
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9c:



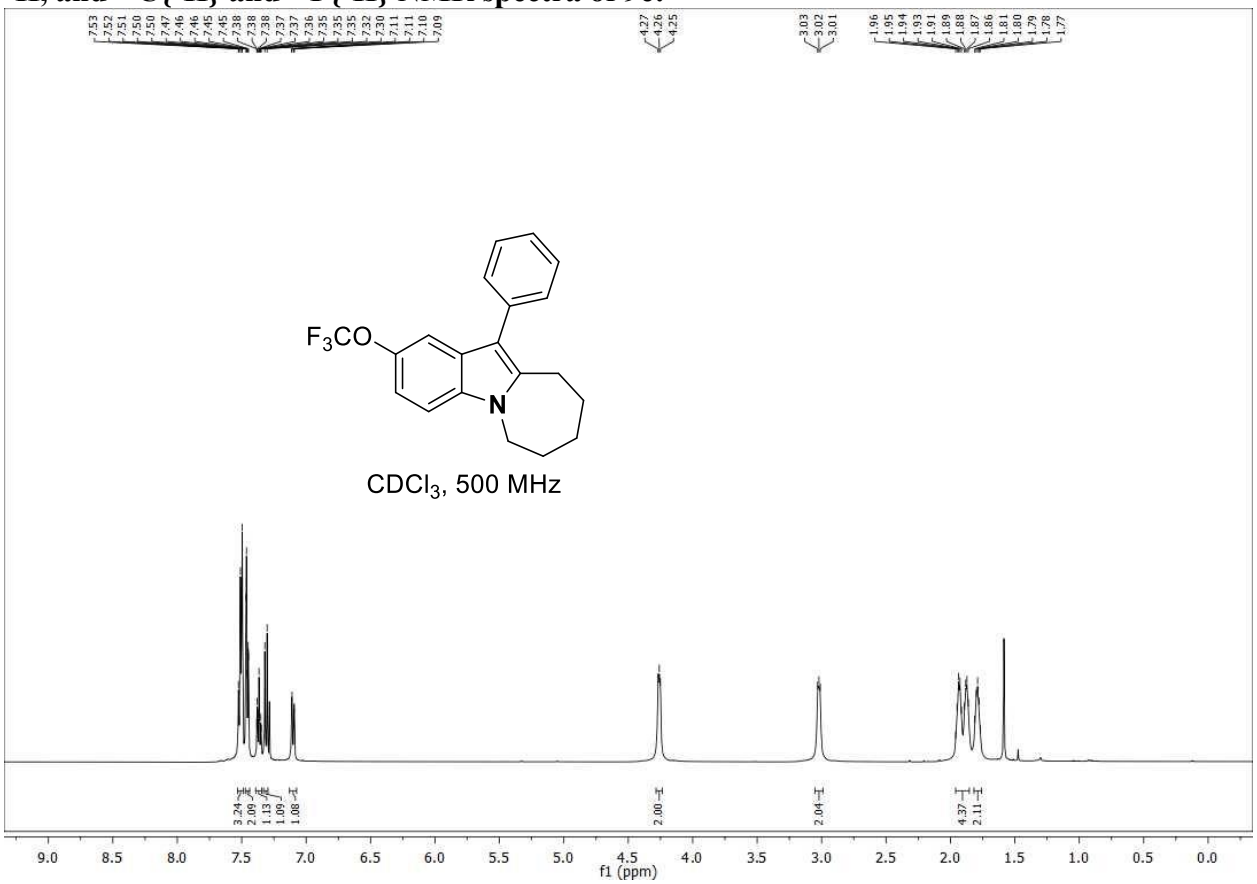


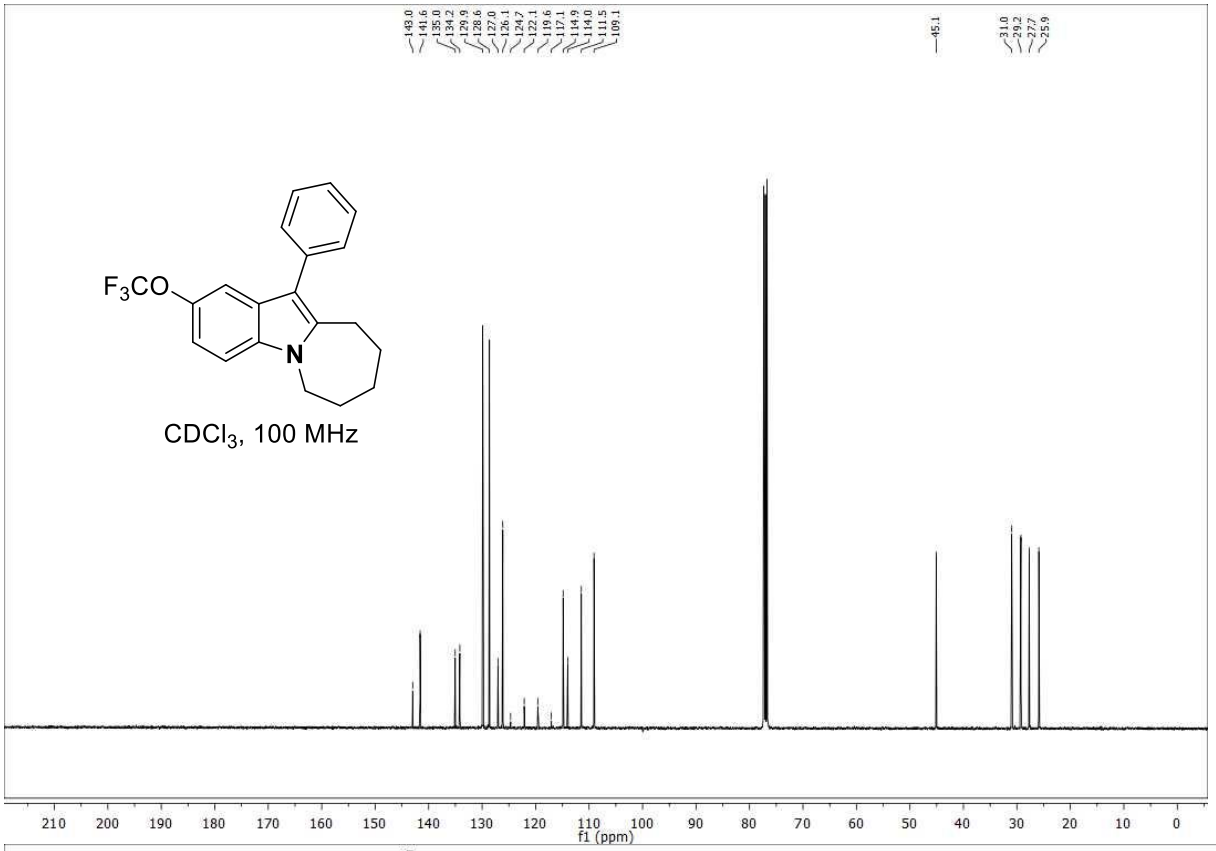
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9d:





^{1}H, and ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectra of 9e:




143.0
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126.1
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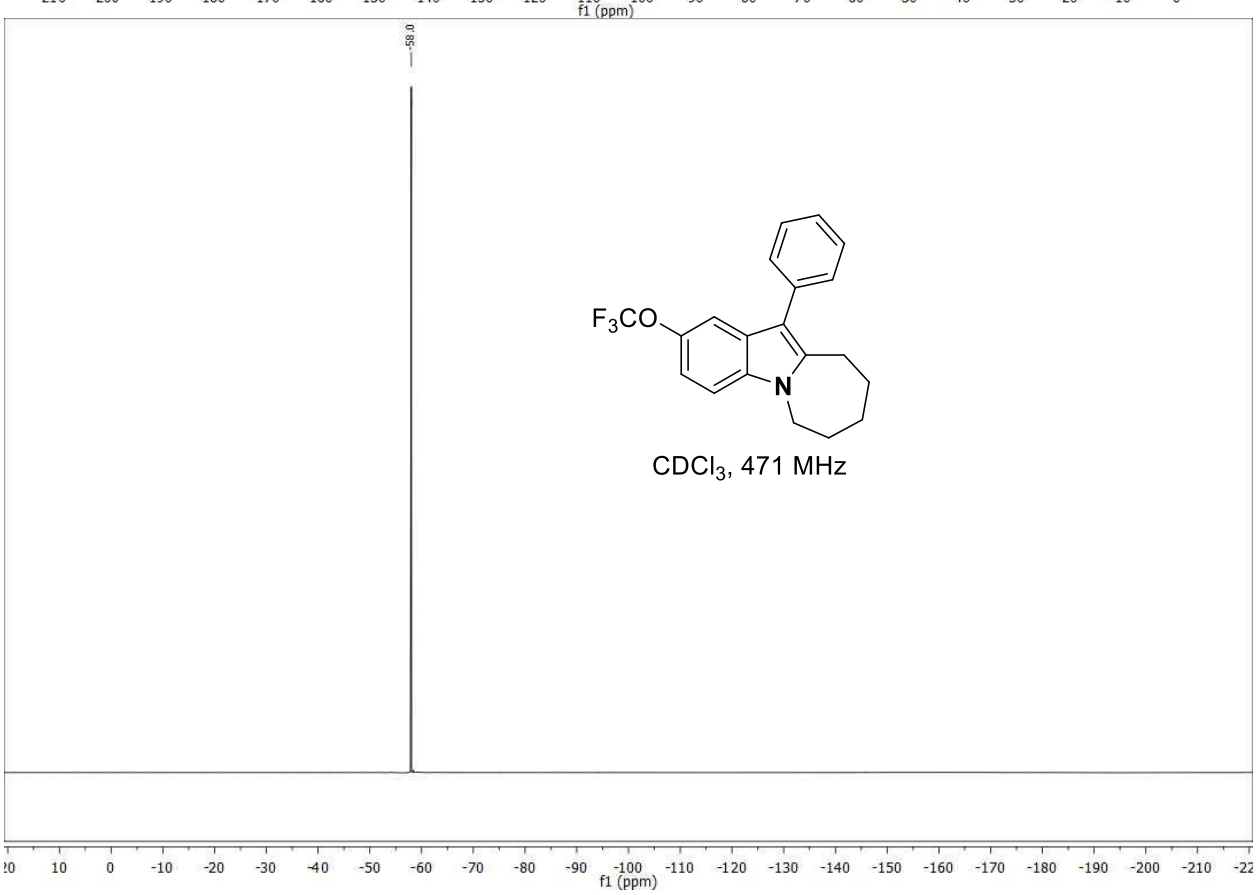
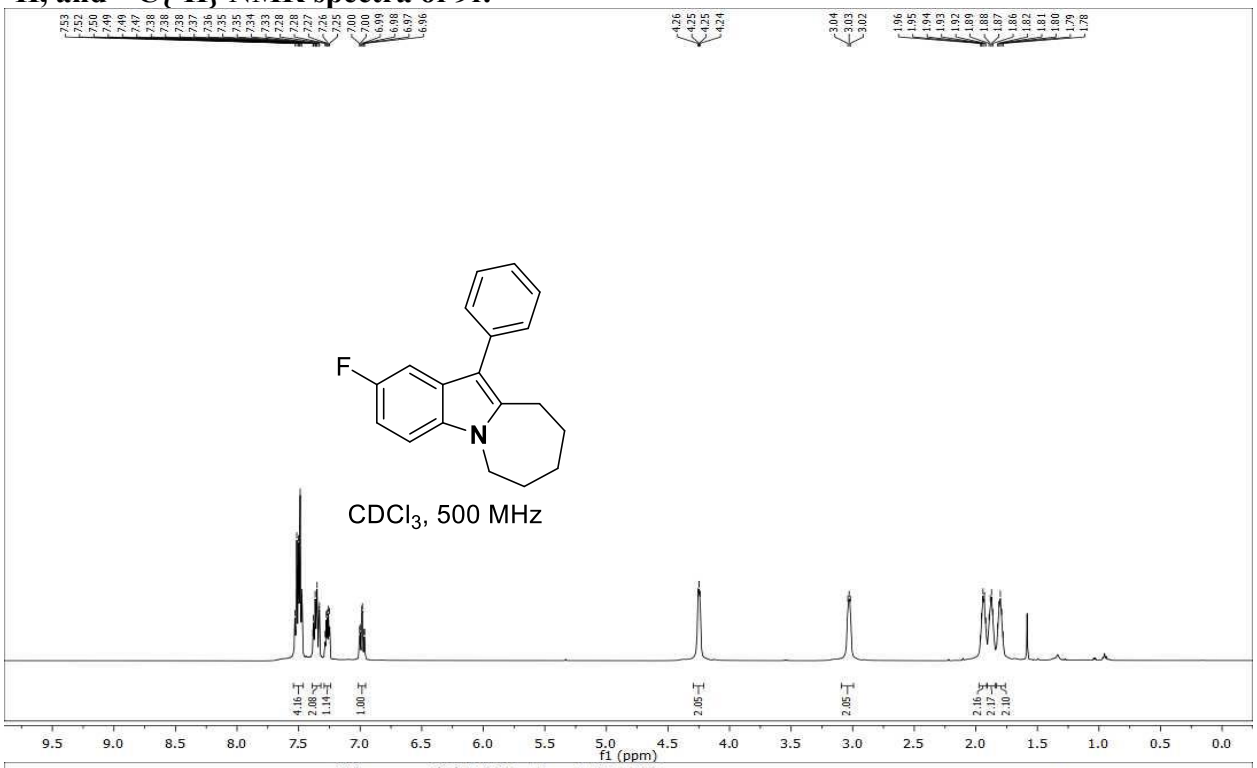
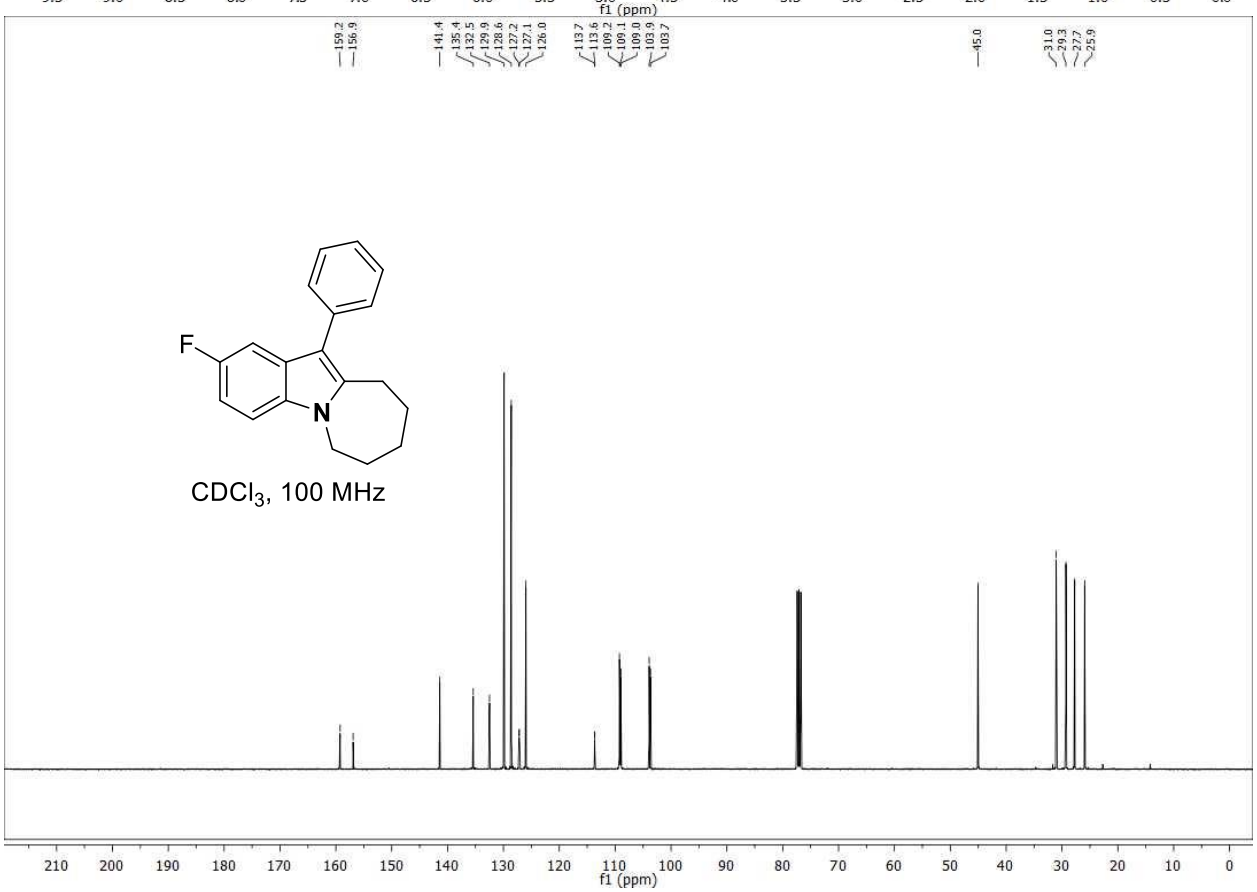
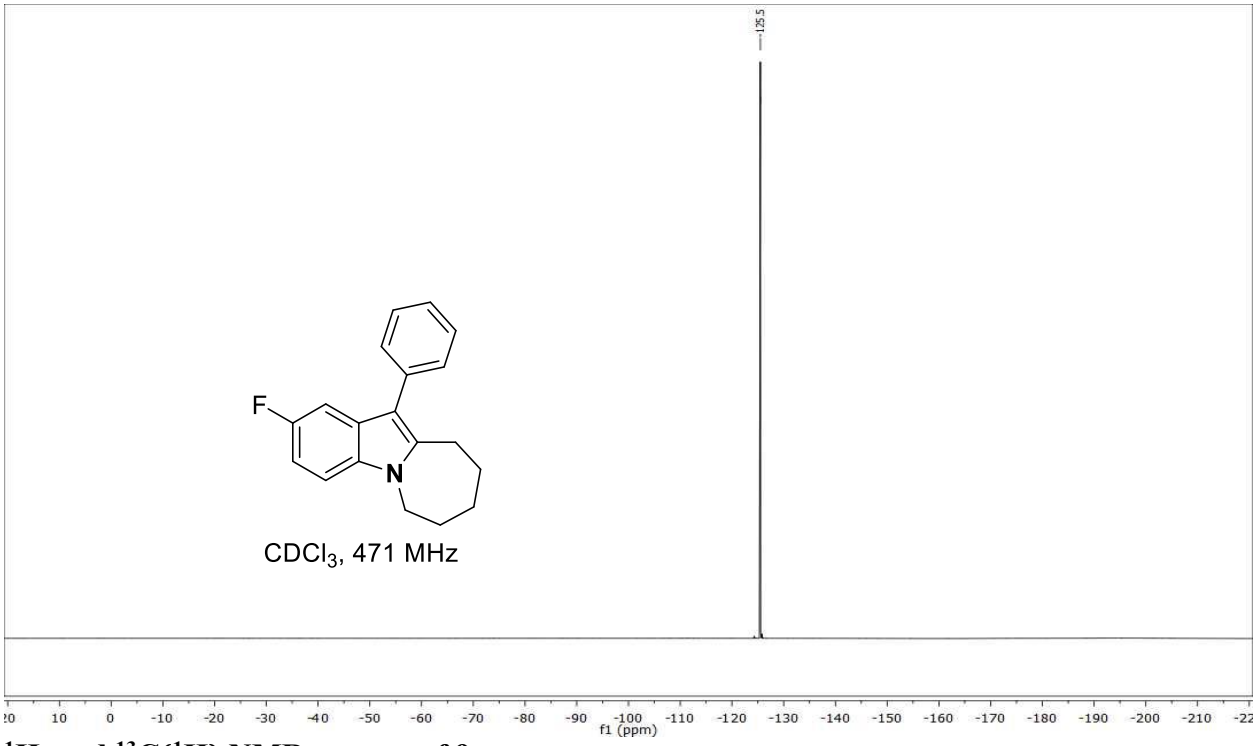
117.1
114.9
114.0
111.5
109.1
45.1
31.0
29.2
27.7
25.9
F3CO
N
CDCl3, 100 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-58.0
F3CO
N
CDCl3, 471 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

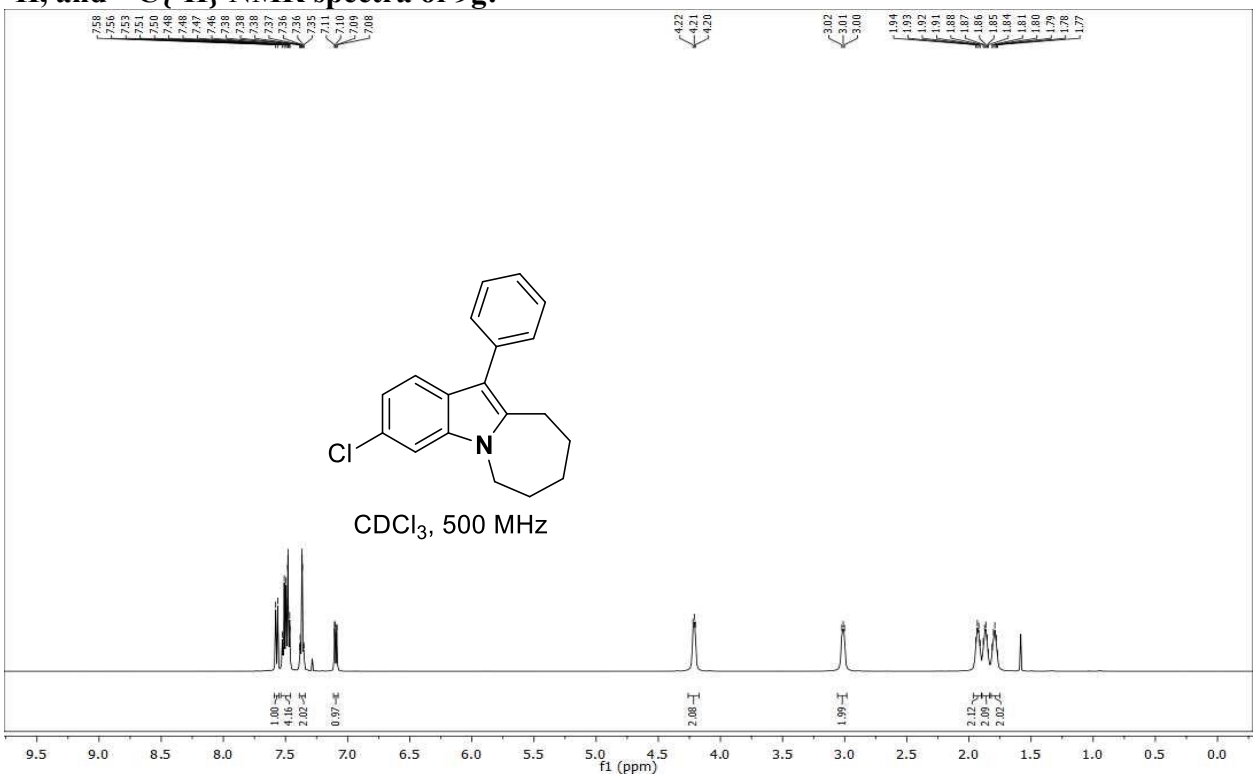
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9f:

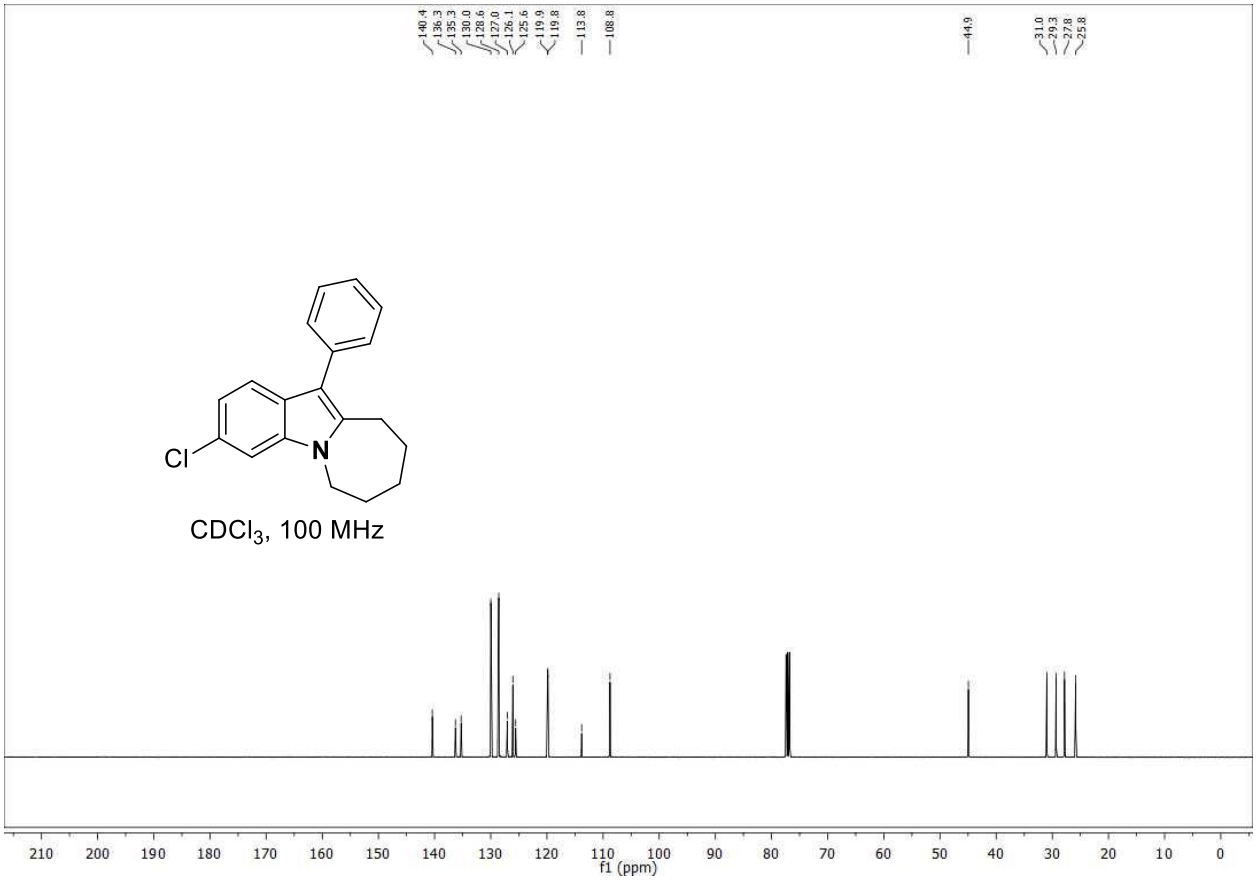




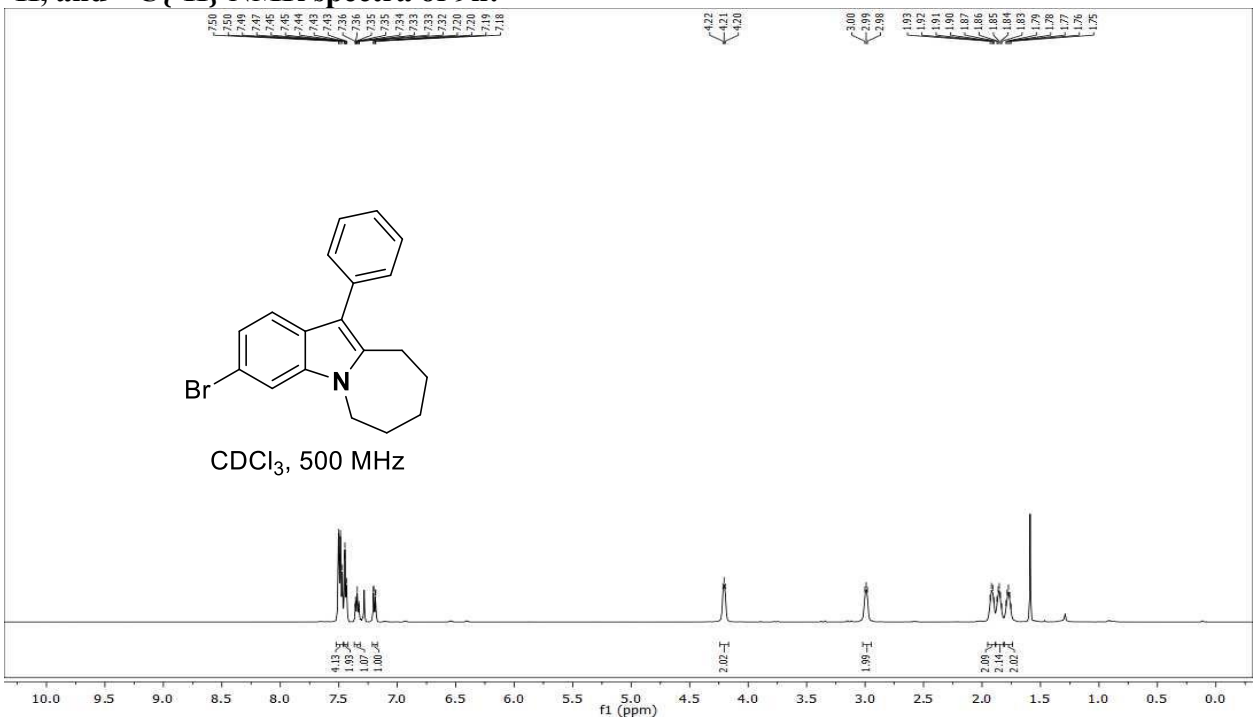


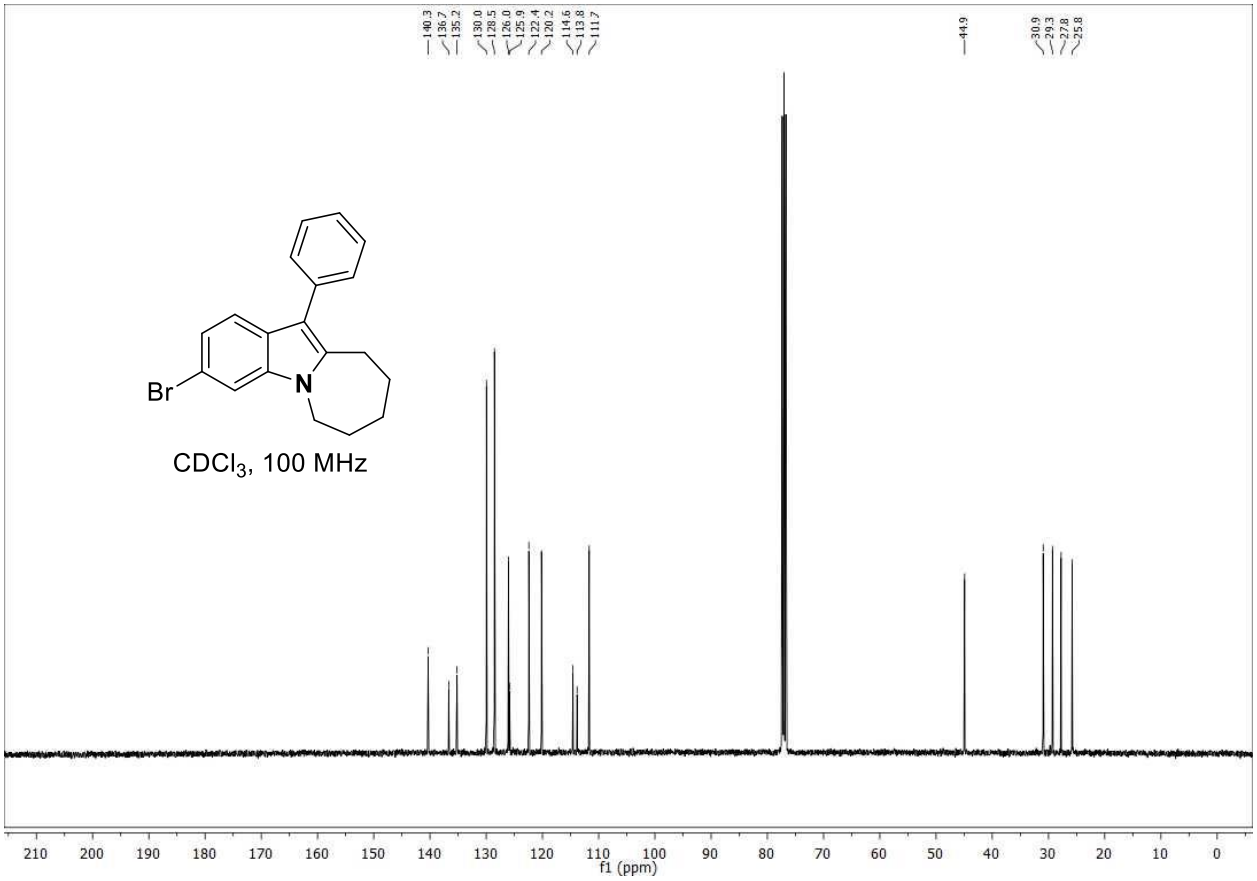
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9g:



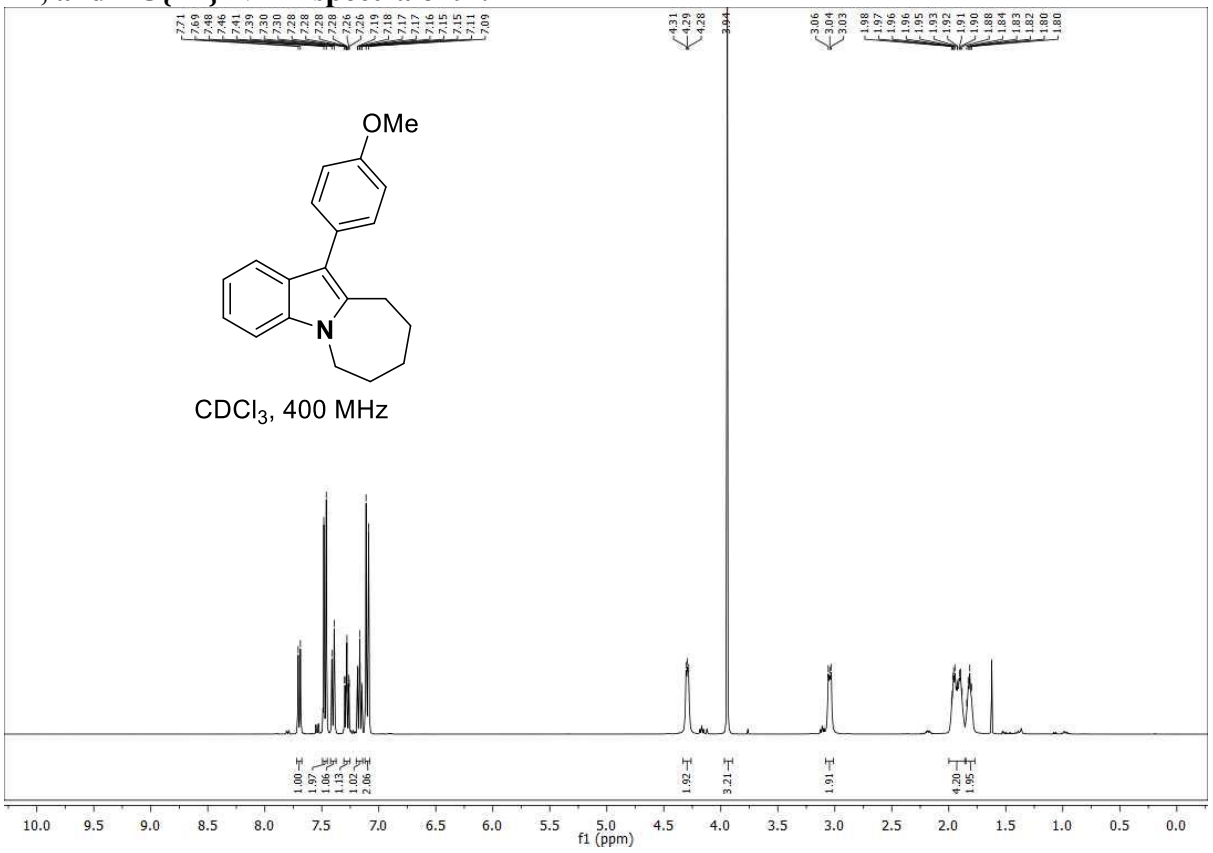


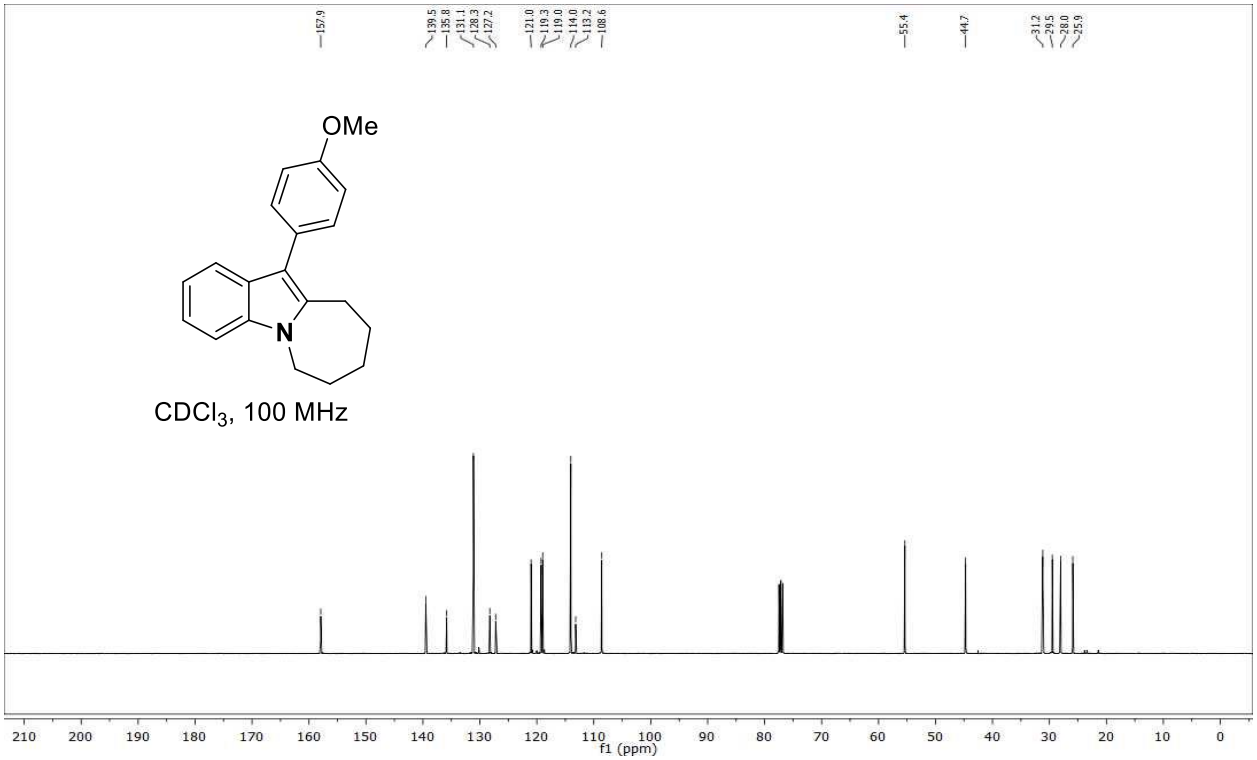
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9h:



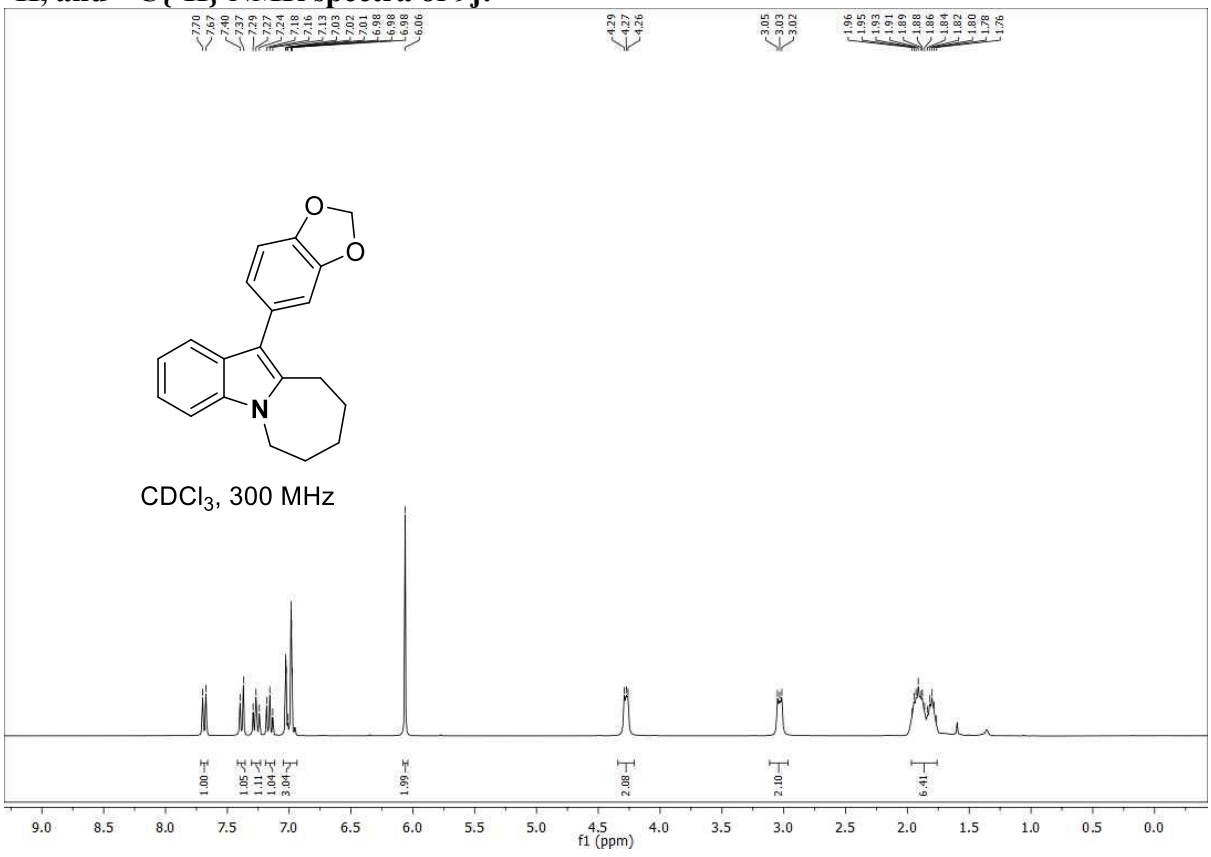


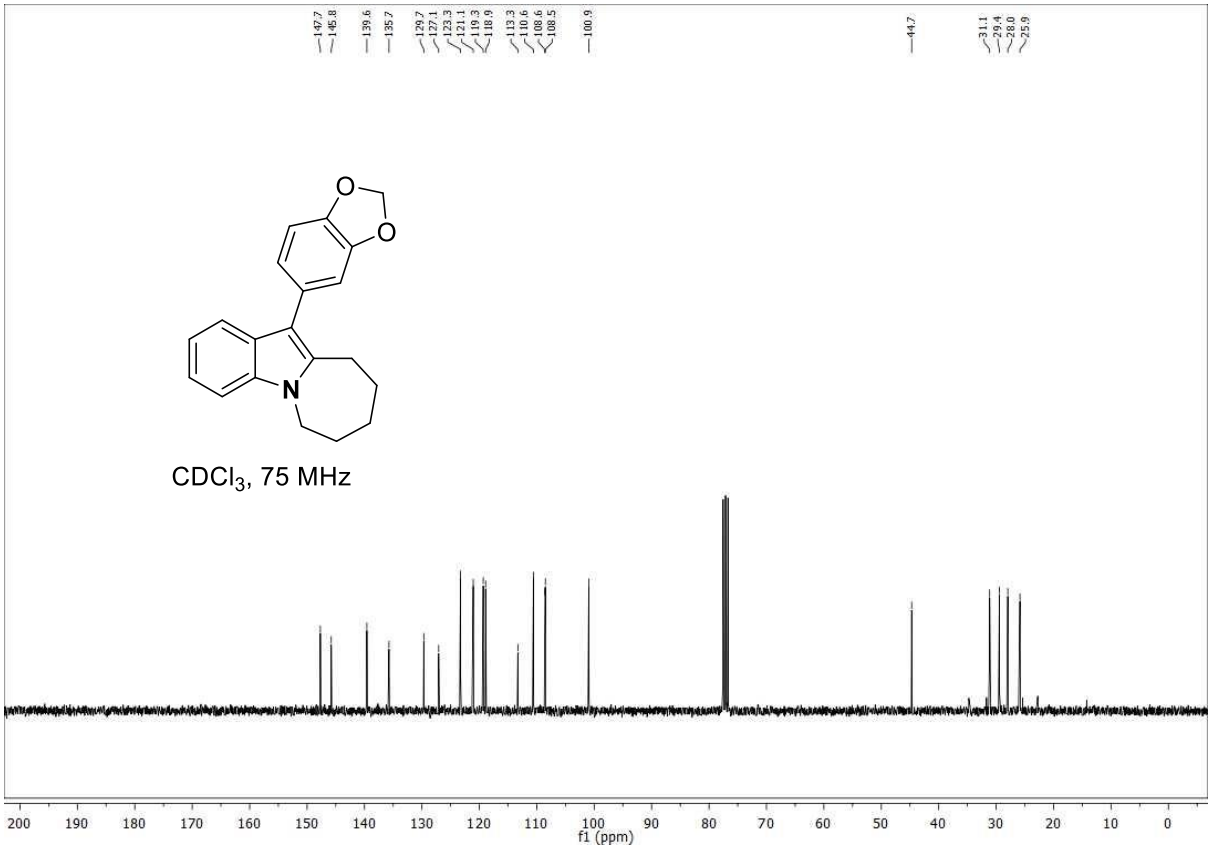
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9i:



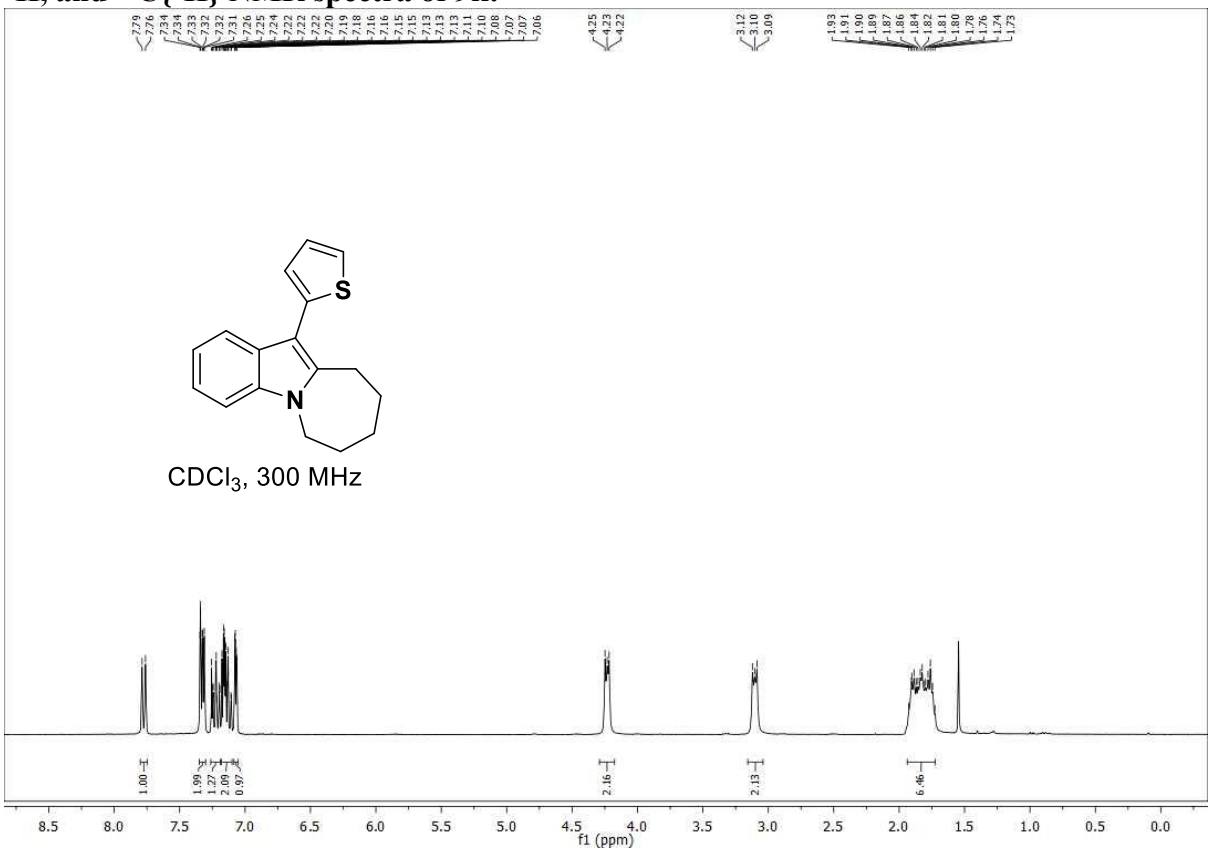


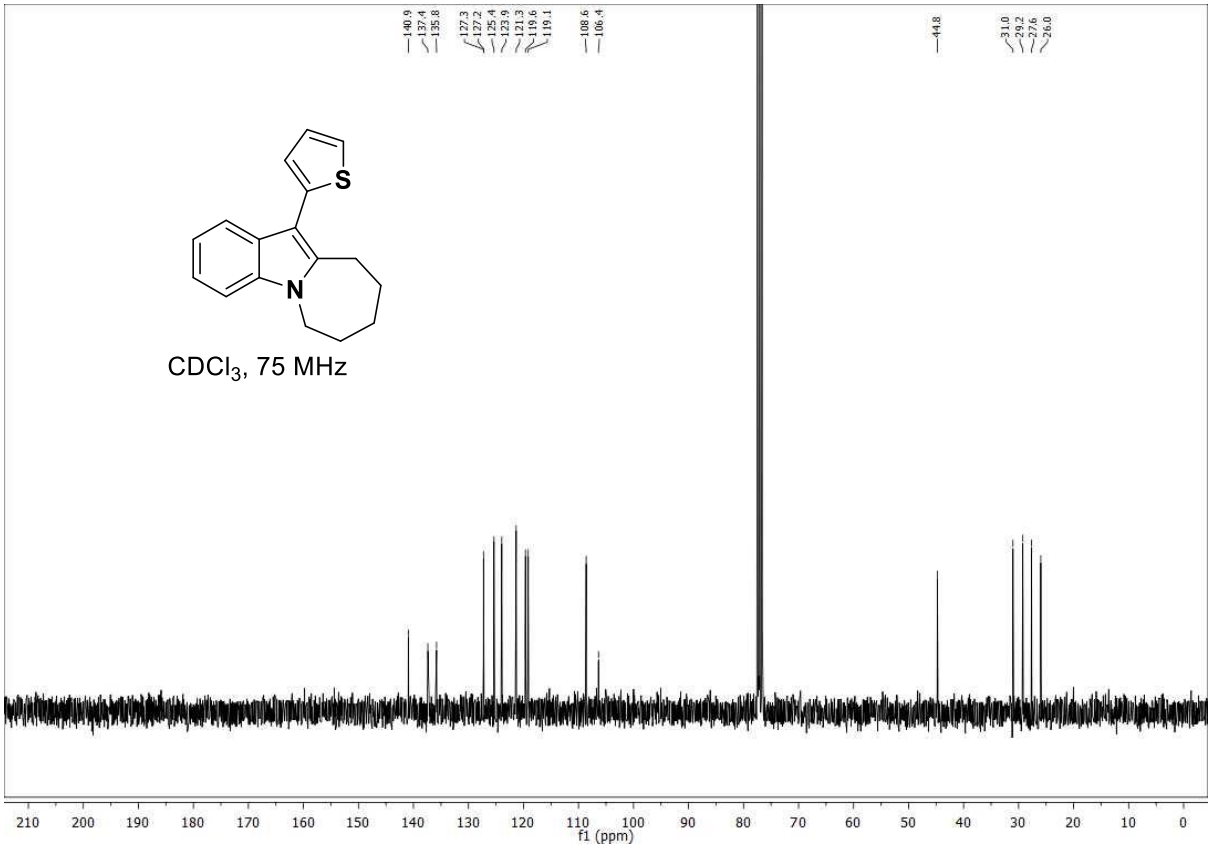
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9j:



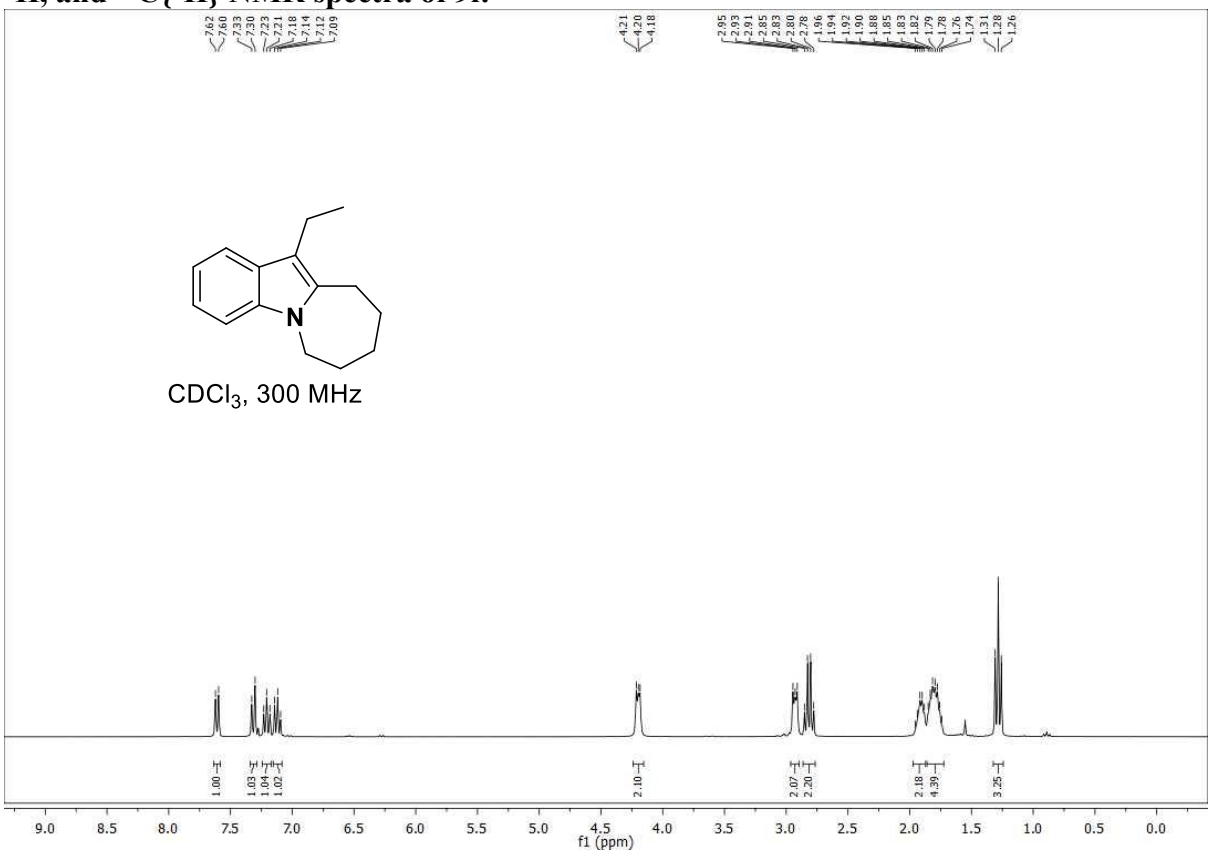


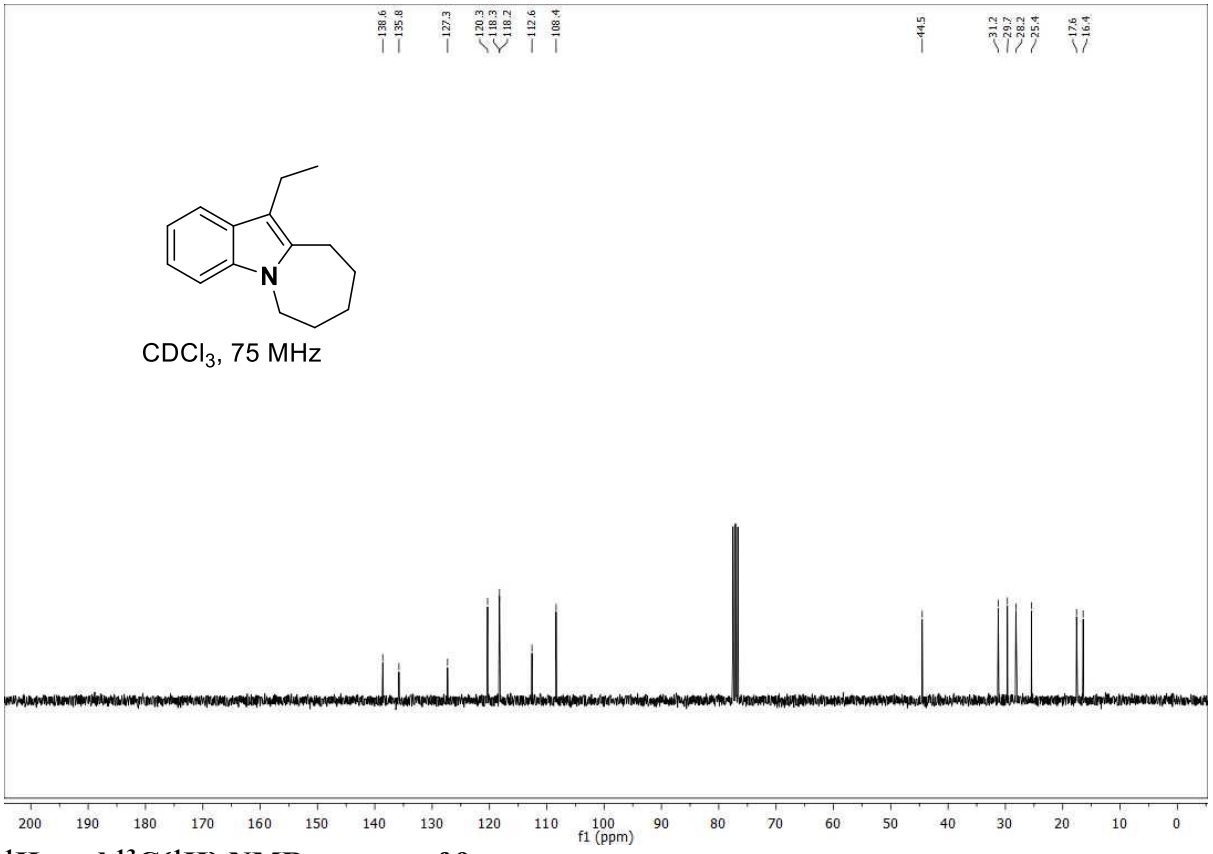
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9k:



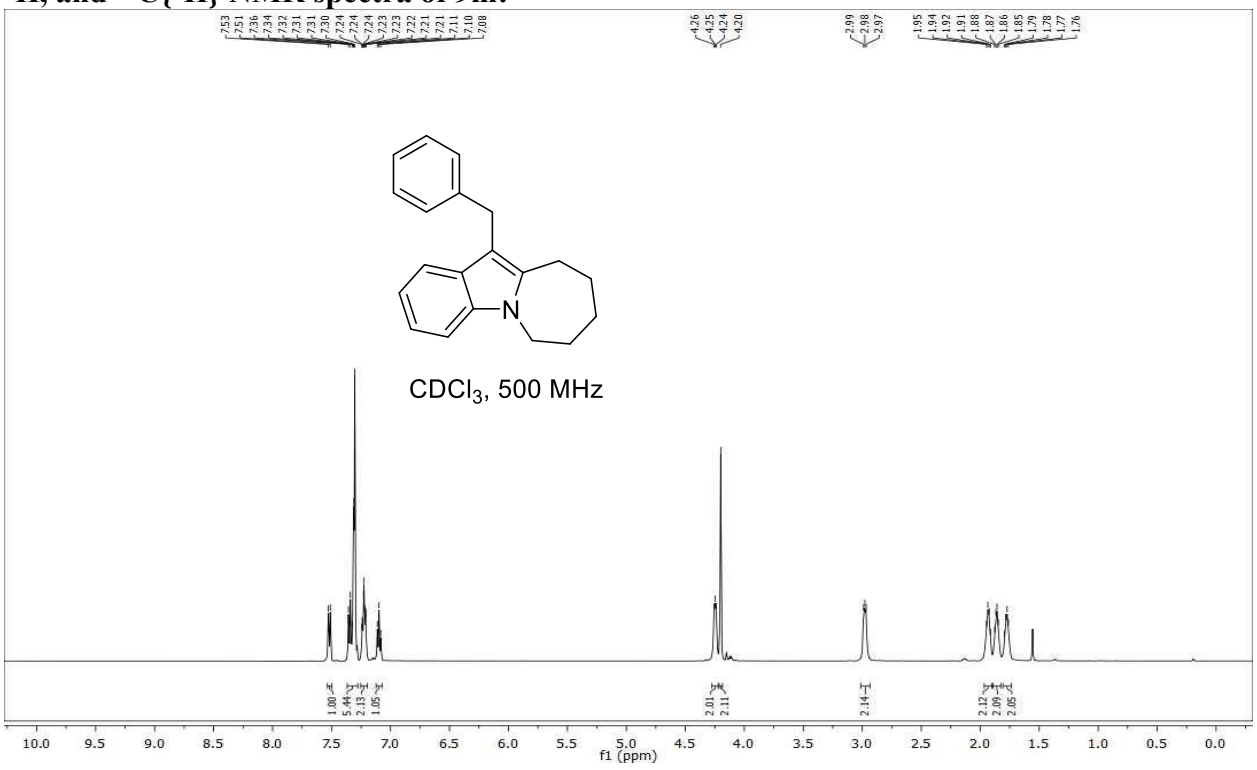


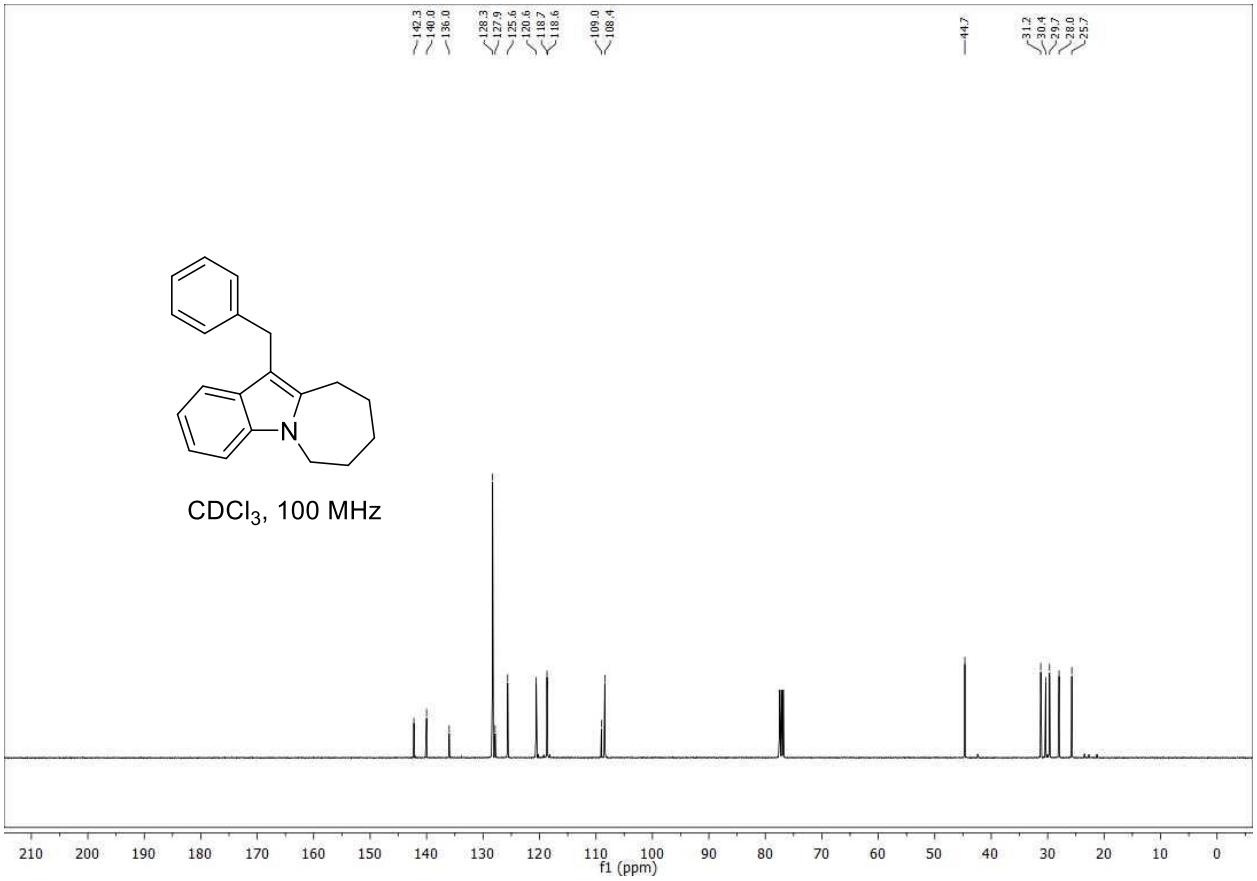
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9l:



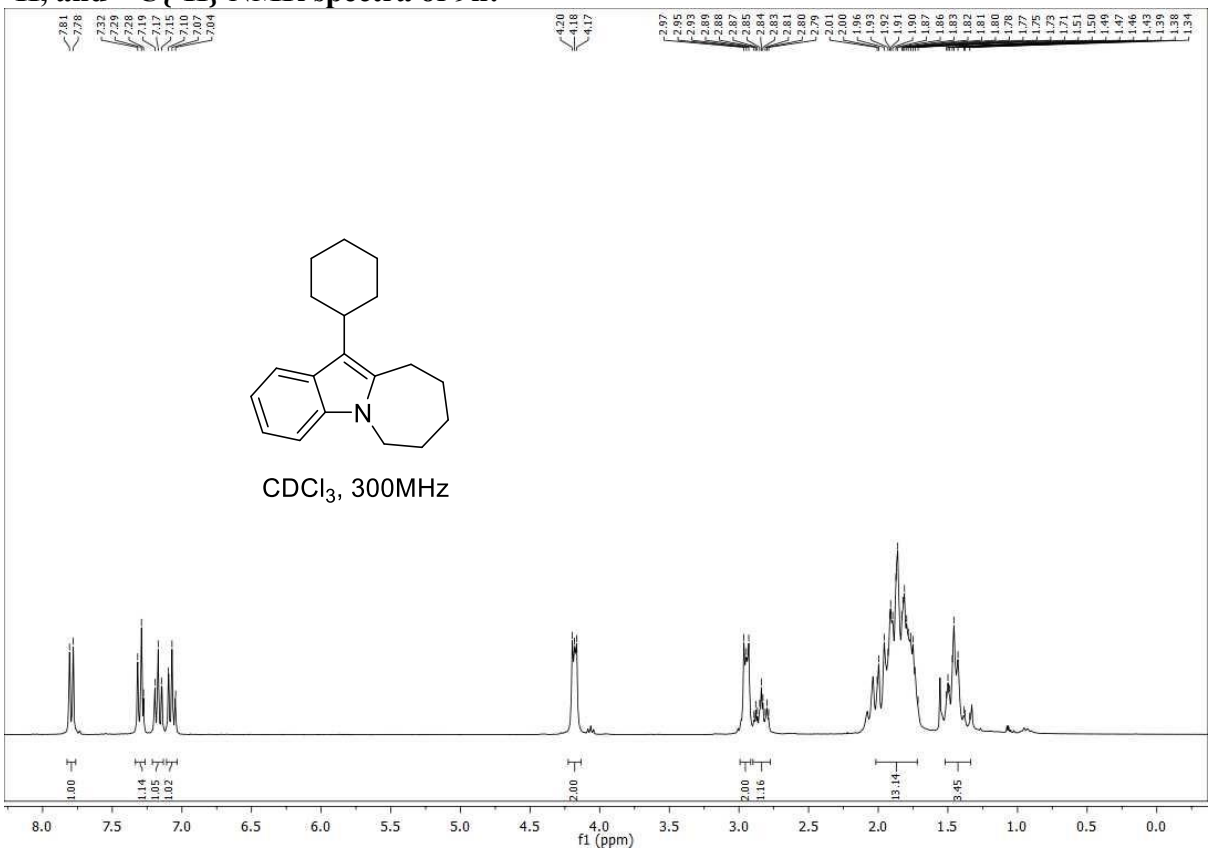


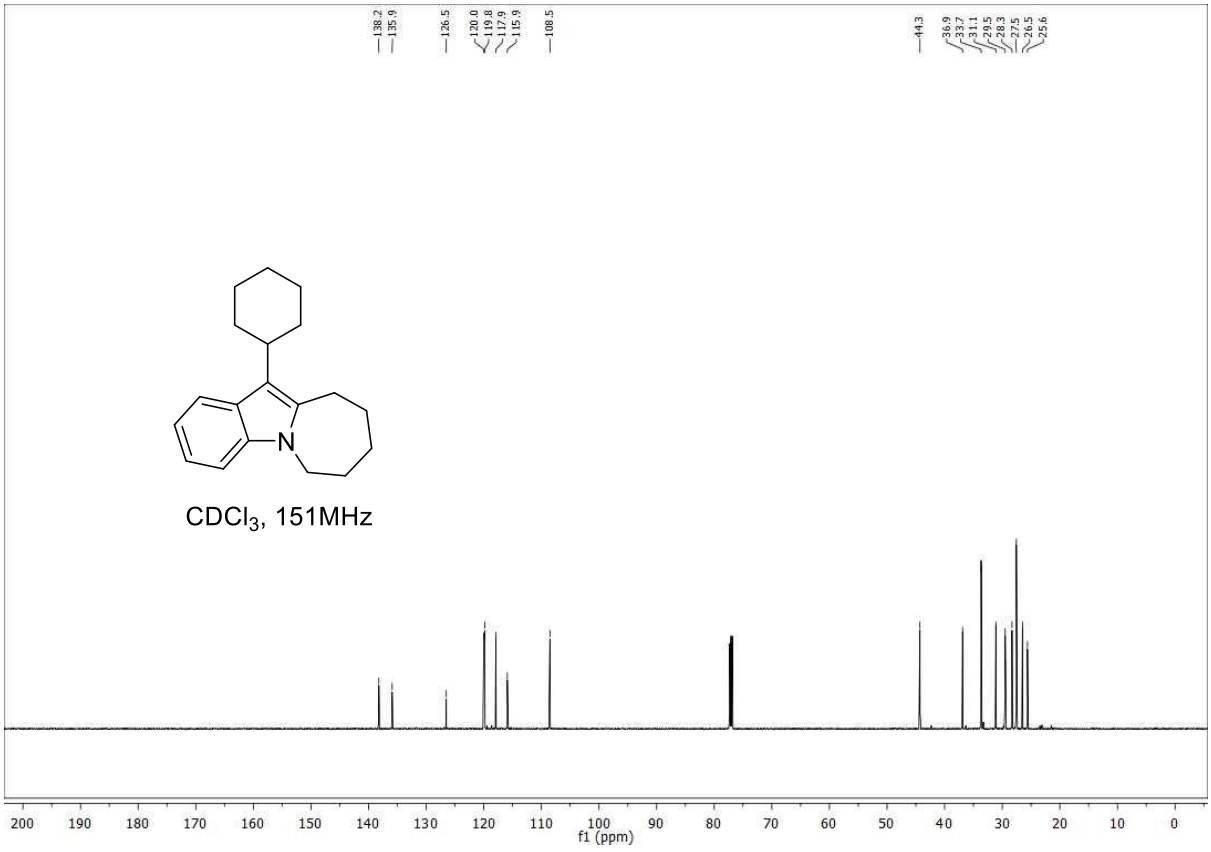
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9m:



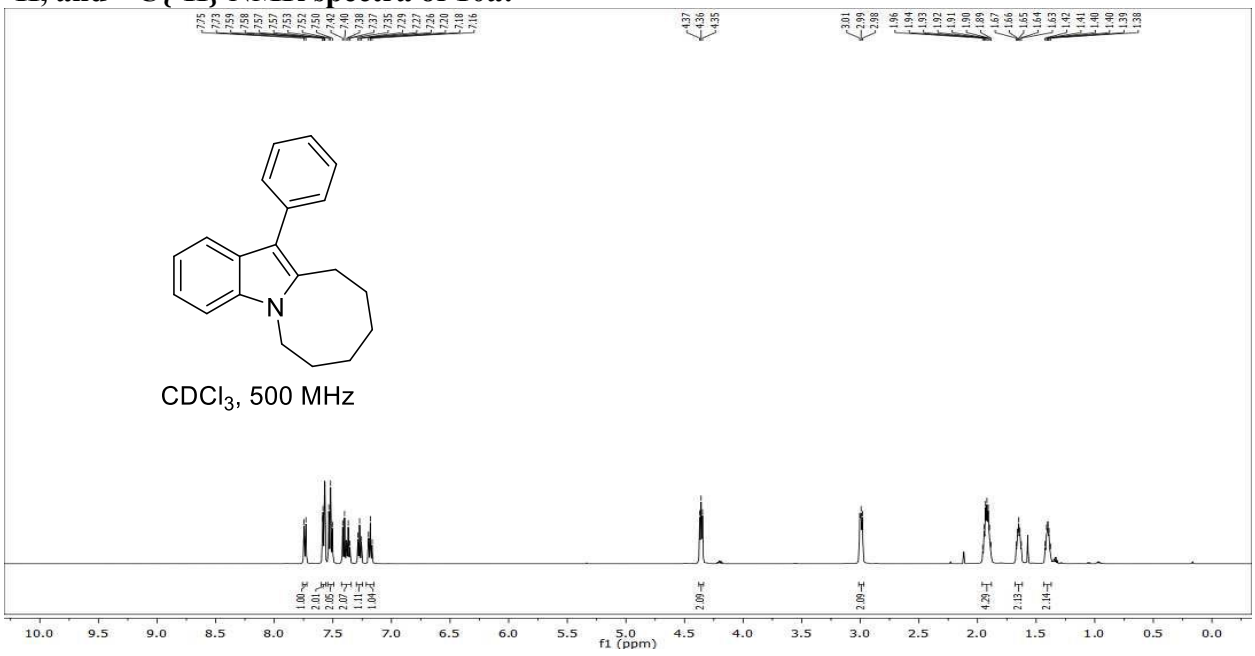


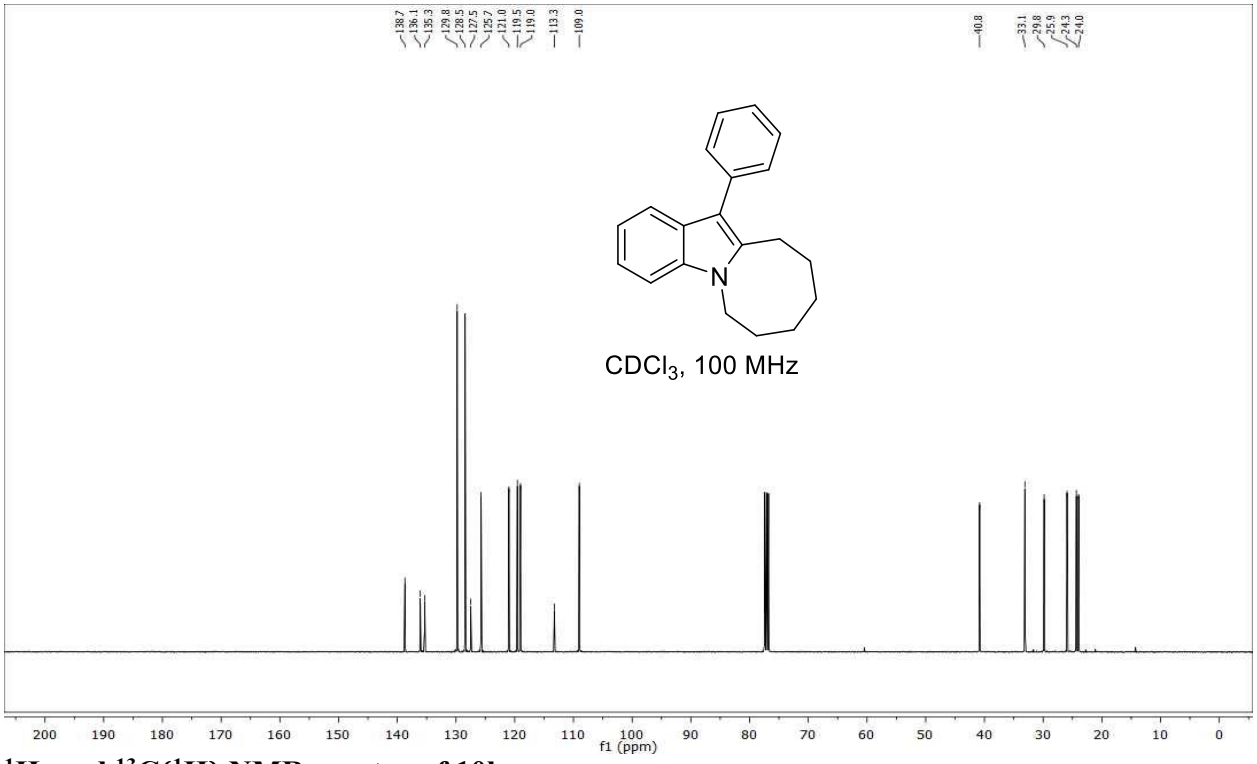
^{1}H, and ^{13}C{^{1}H} NMR spectra of 9n:



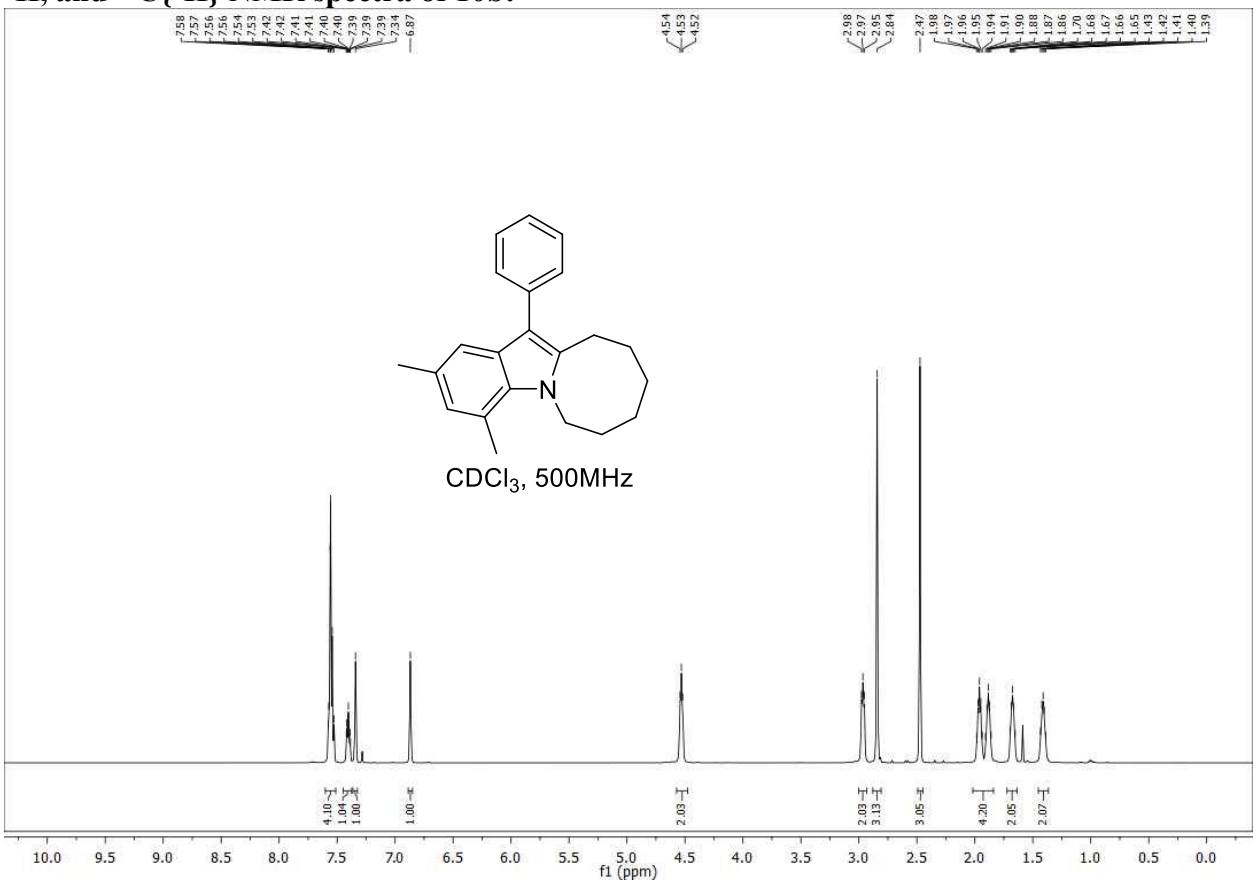


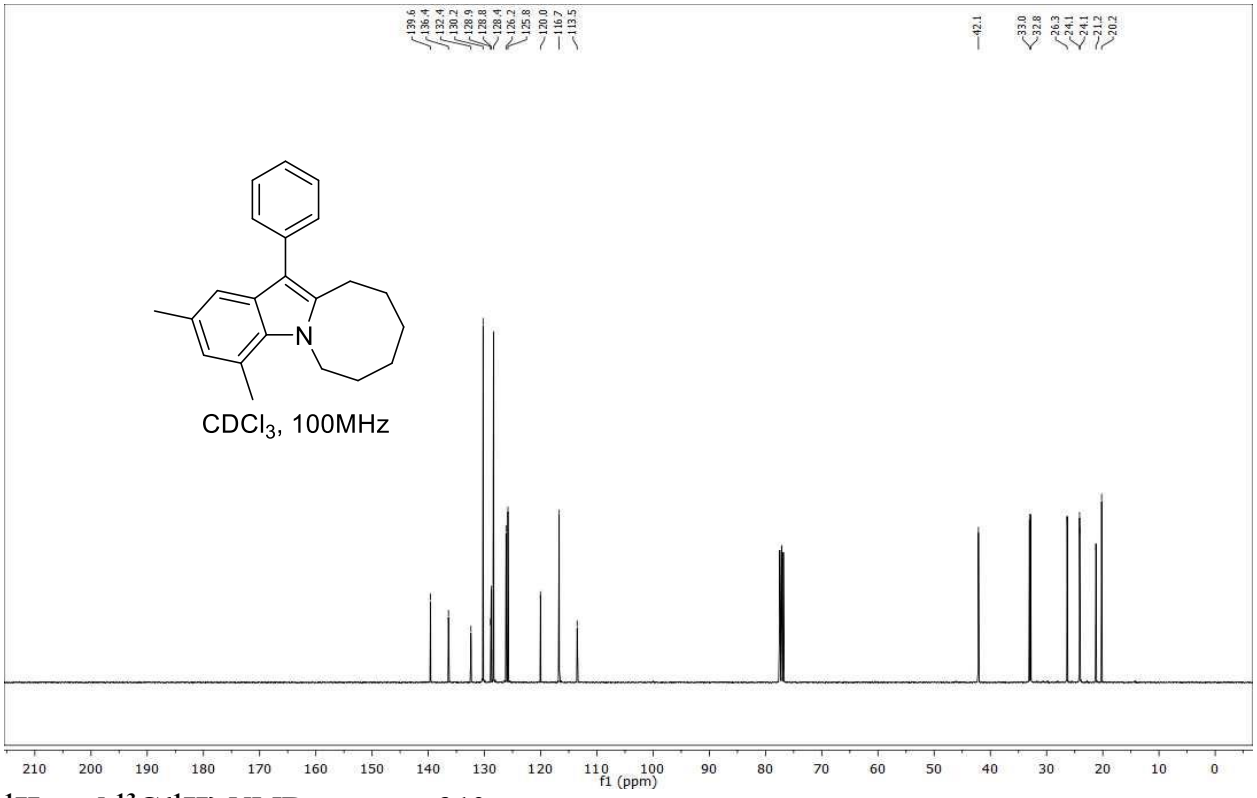
^{1}H, and ^{13}C{^{1}H} NMR spectra of 10a:



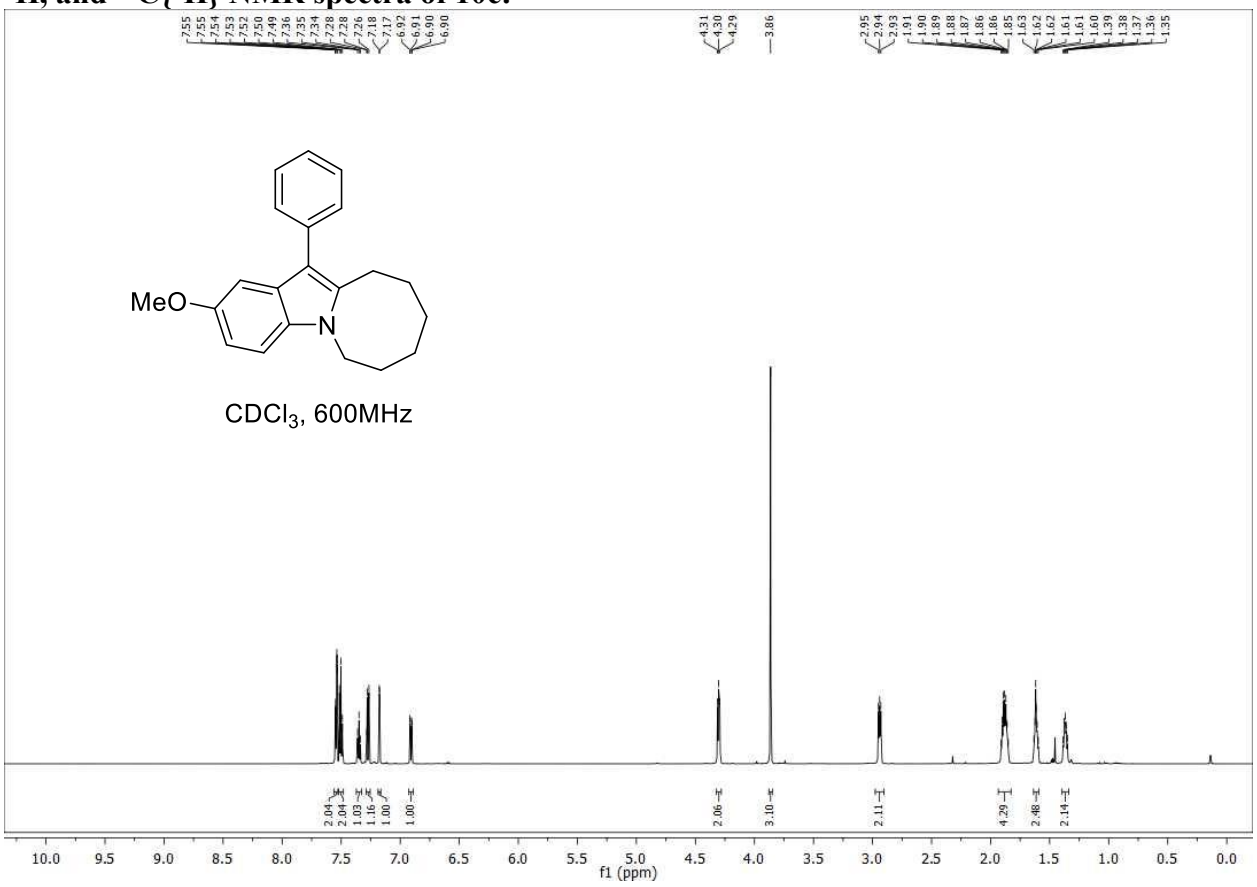


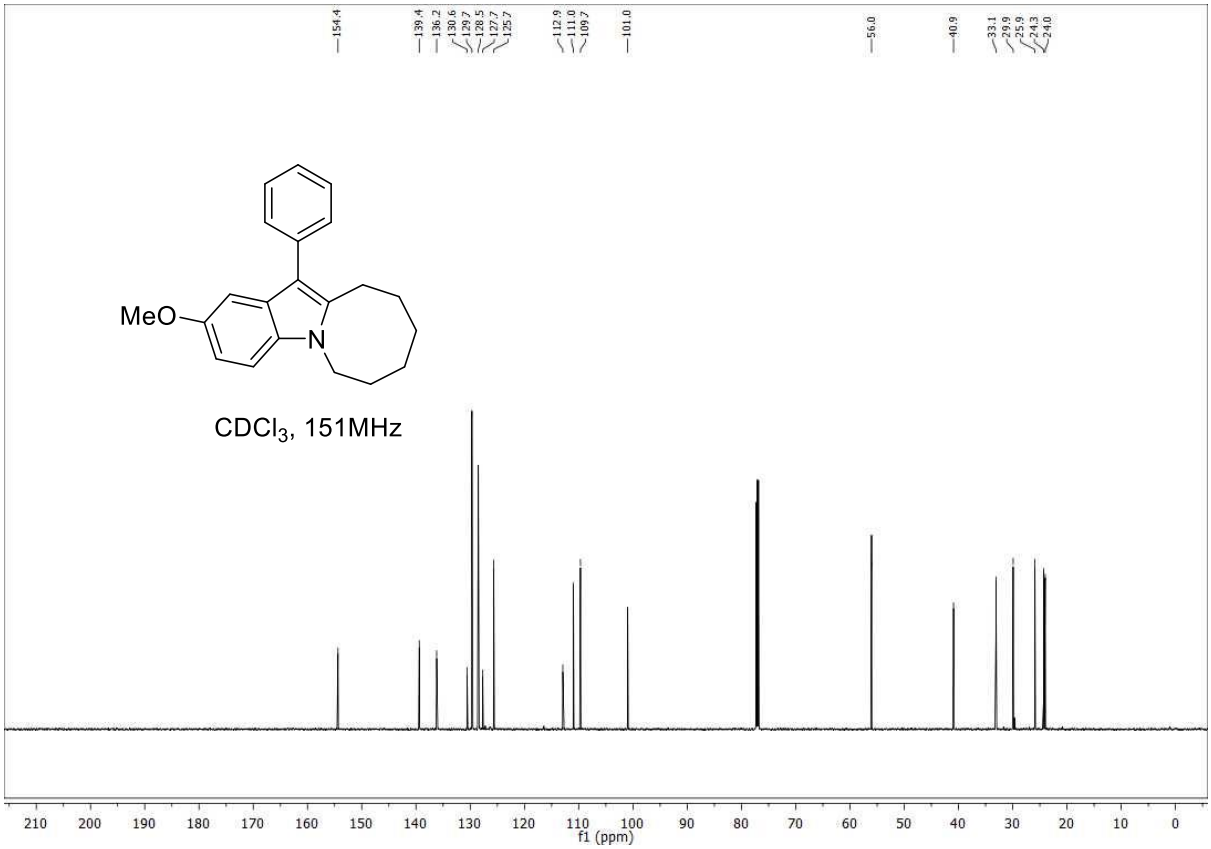
^{1}H, and ^{13}C{^{1}H} NMR spectra of 10b:



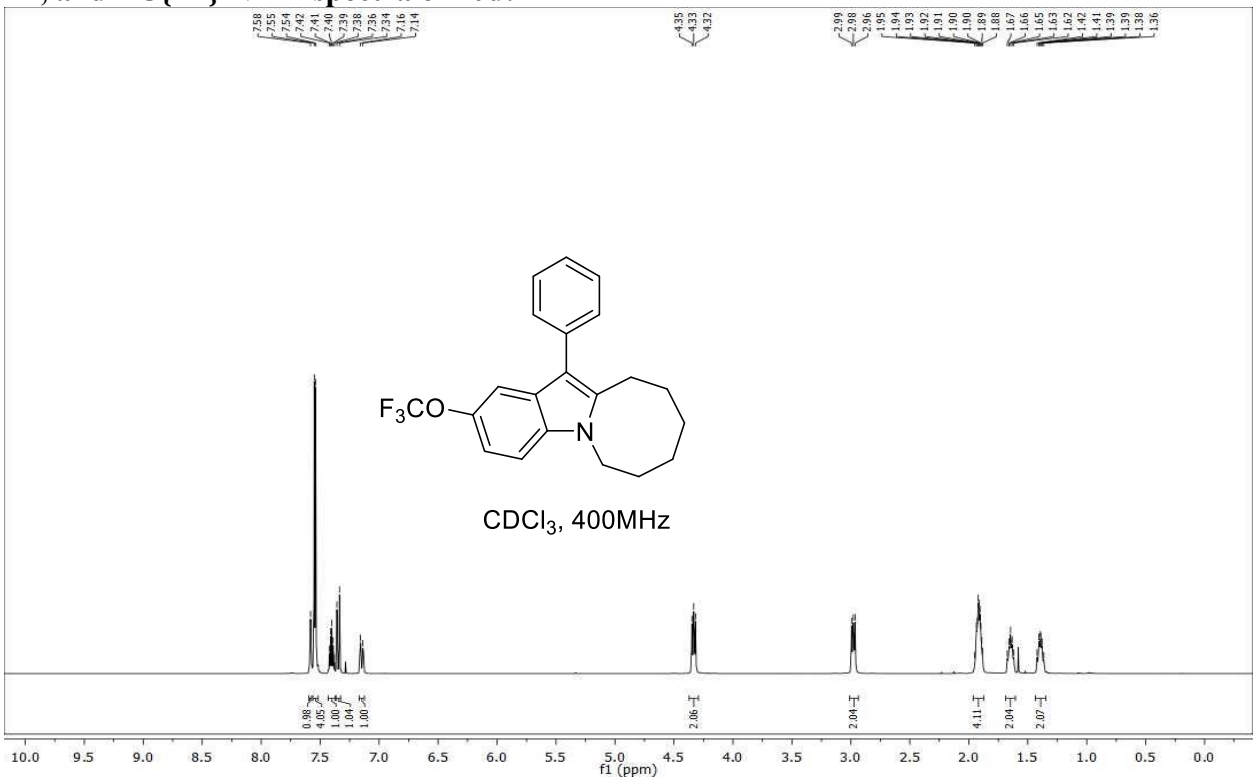


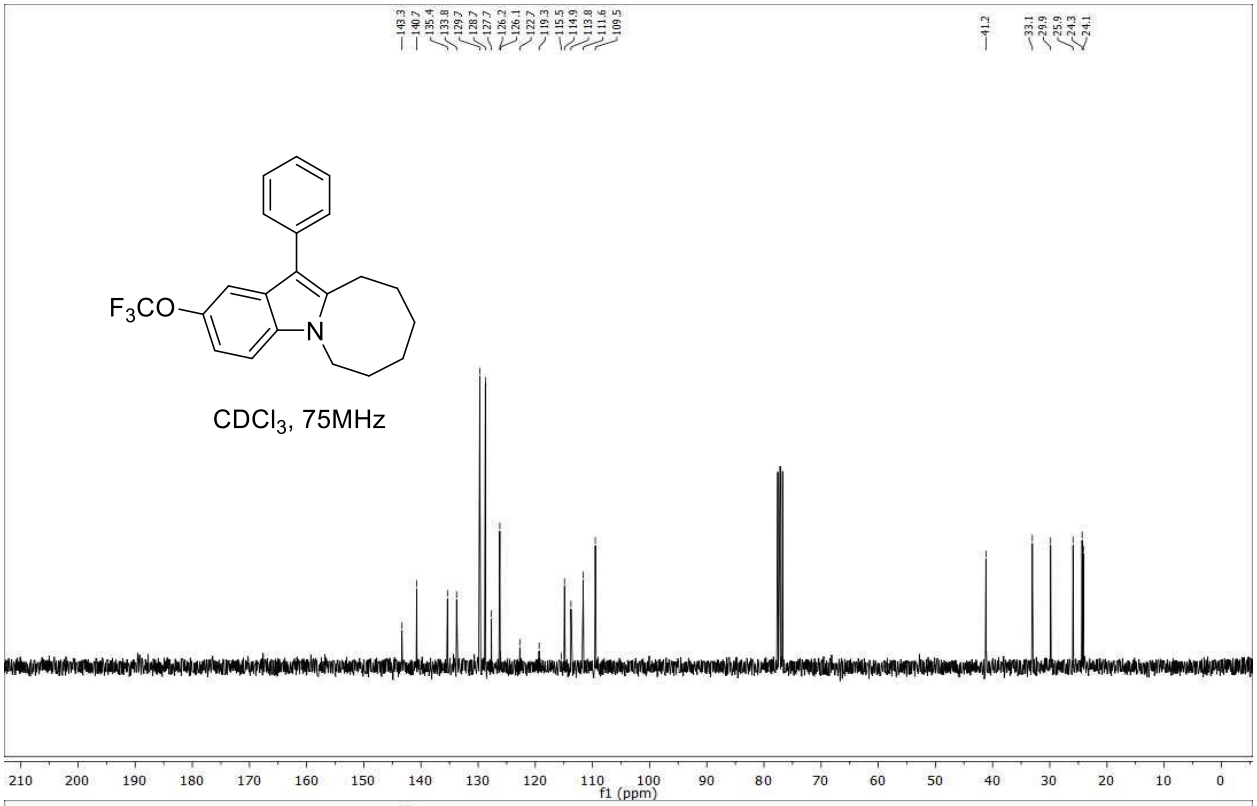
^{1}H, and ^{13}C{^{1}H} NMR spectra of 10c:

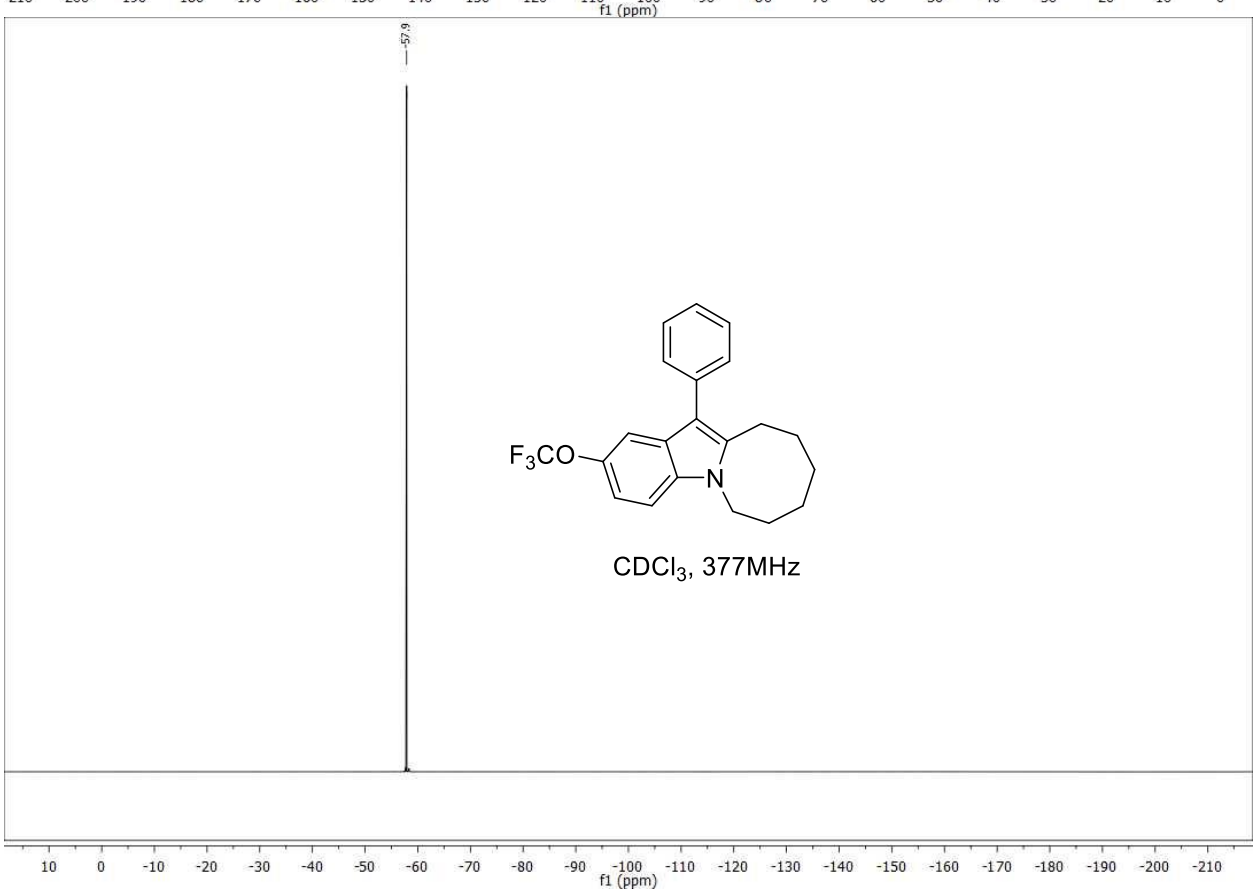




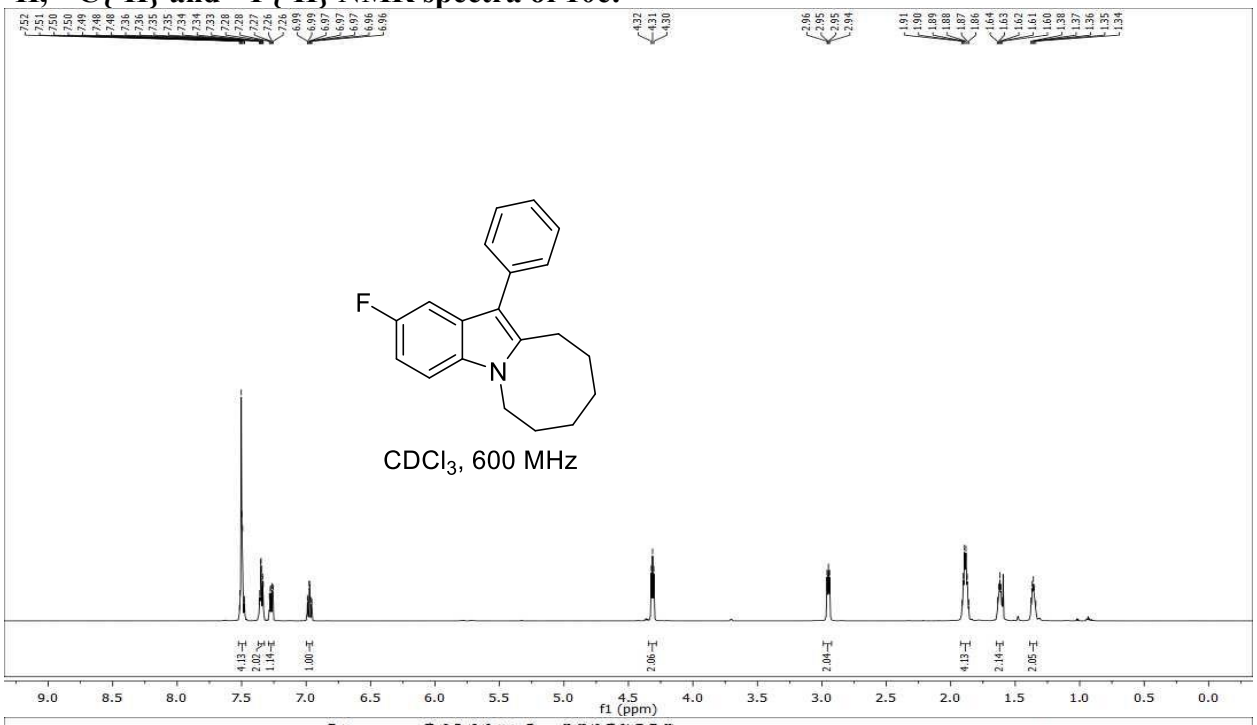
^{1}H, and ^{13}C{^{1}H} NMR spectra of 10d:

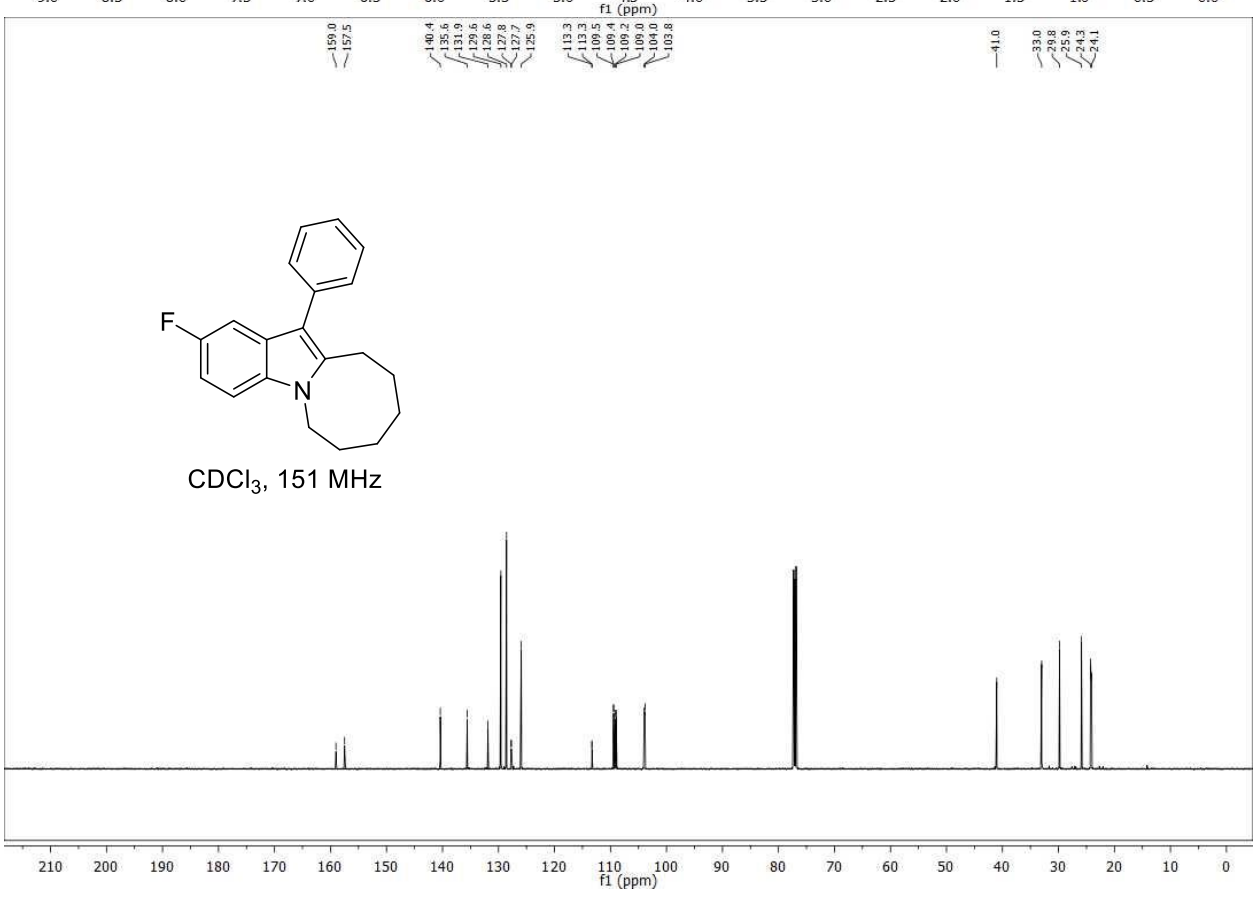


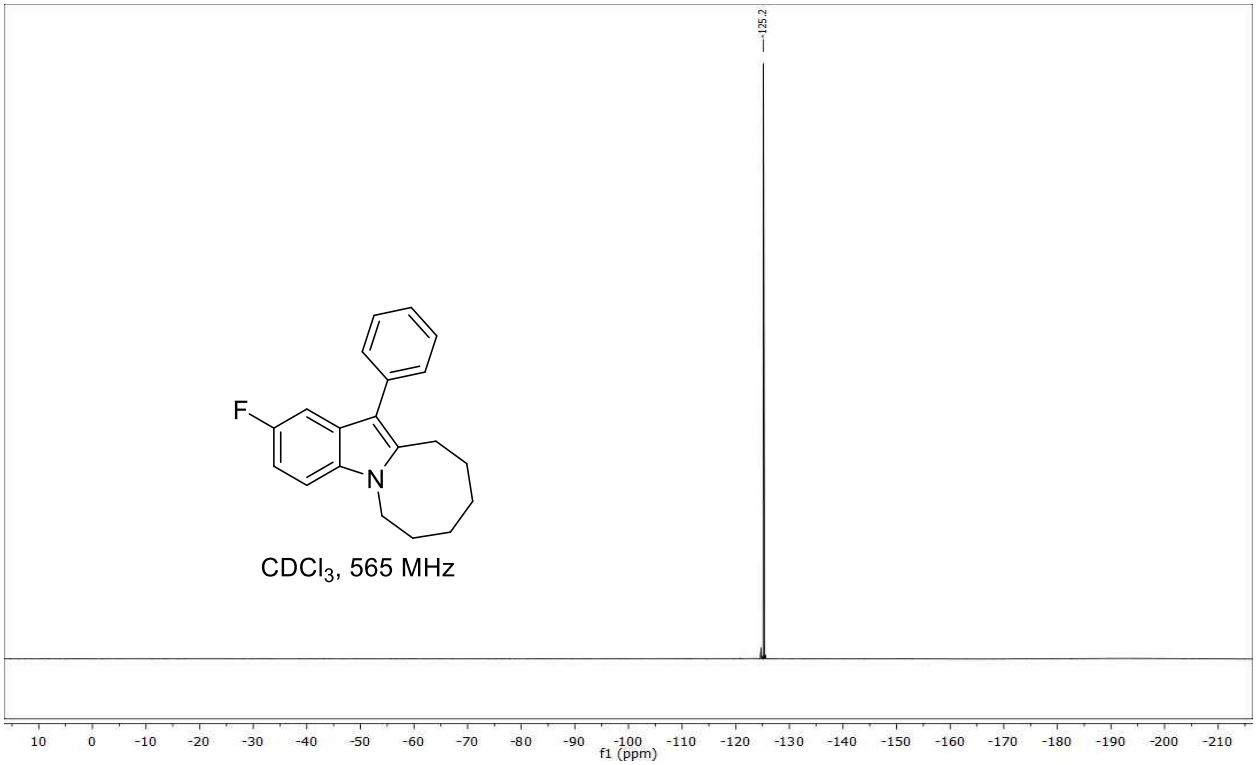

143.3
140.7
135.4
133.8
129.7
128.7
127.7
126.2
126.1
122.7
119.3
115.5
114.9
113.8
111.6
109.5
41.2
33.1
29.9
25.9
24.3
24.1
F3CO
N
CDCl3, 75MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-57.9
F3CO
N
CDCl3, 377MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

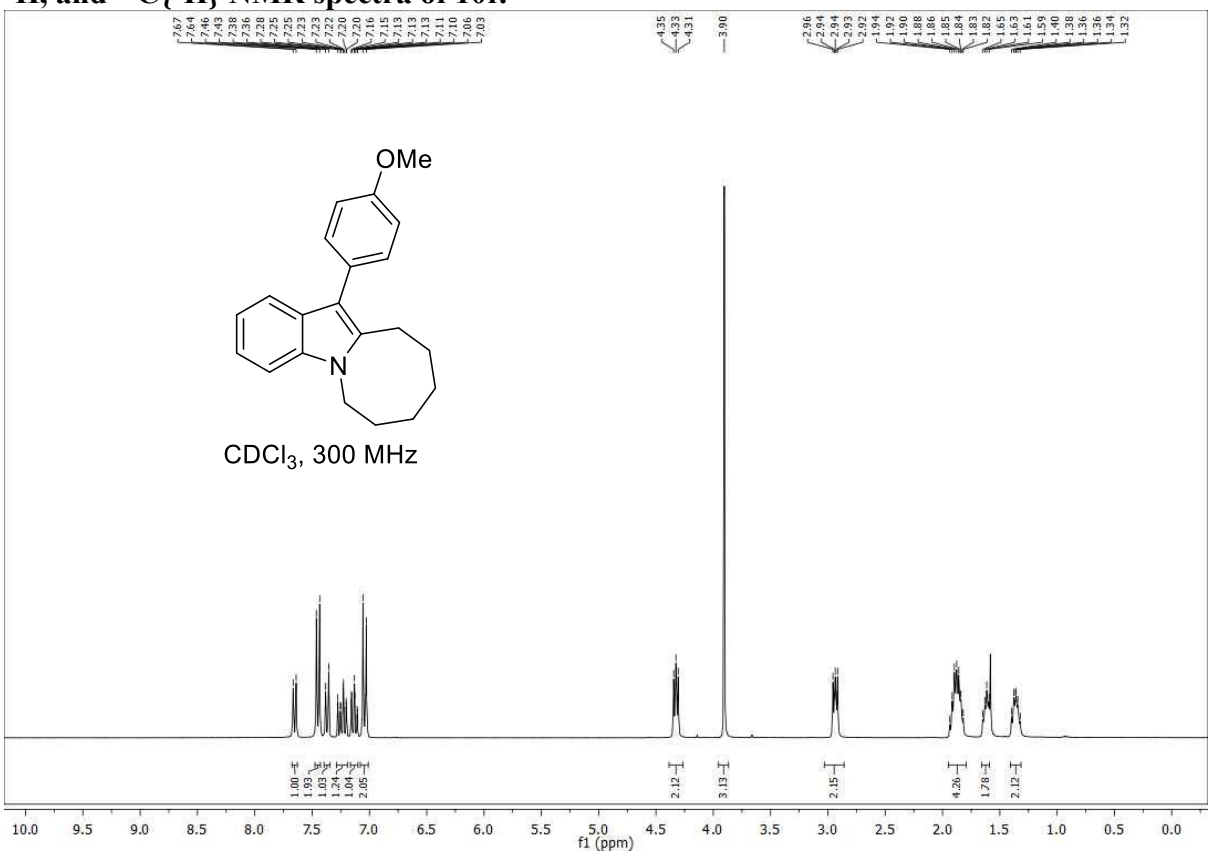
^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra of 10e:

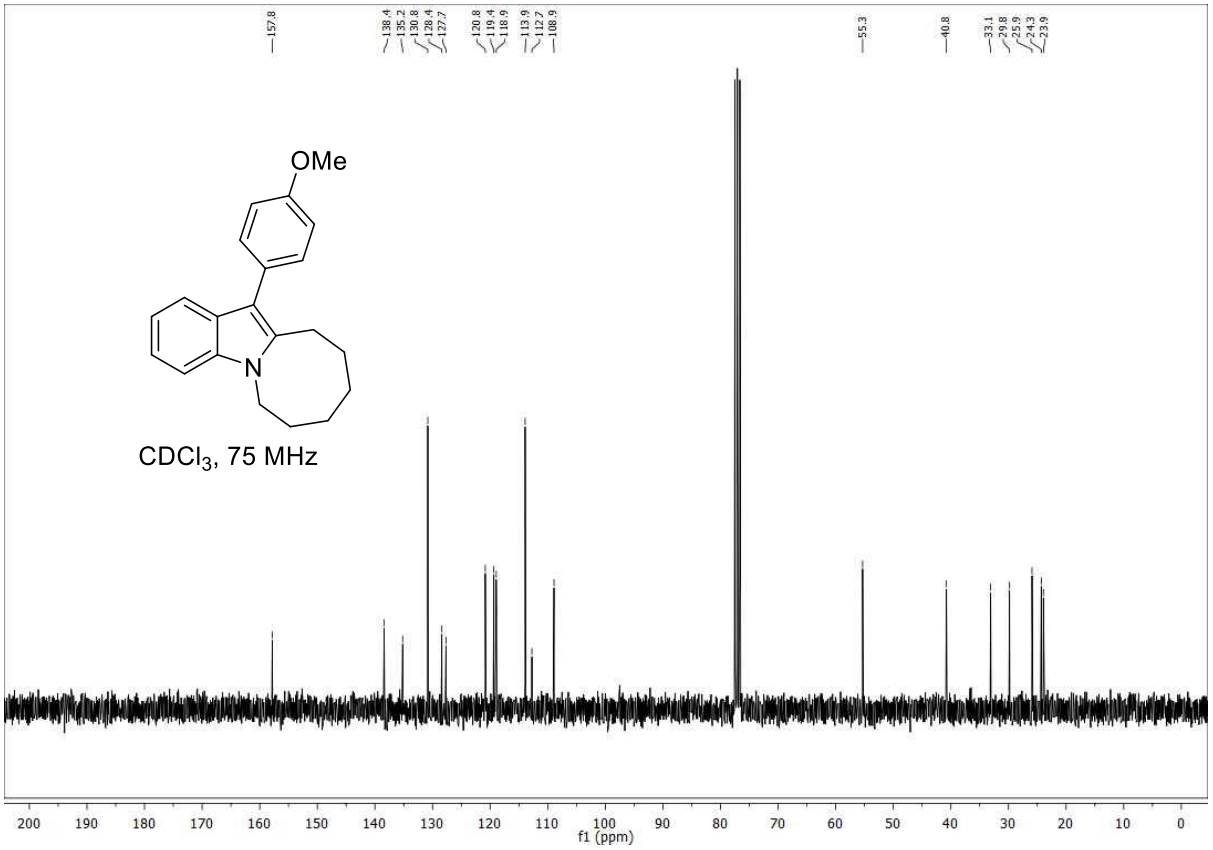




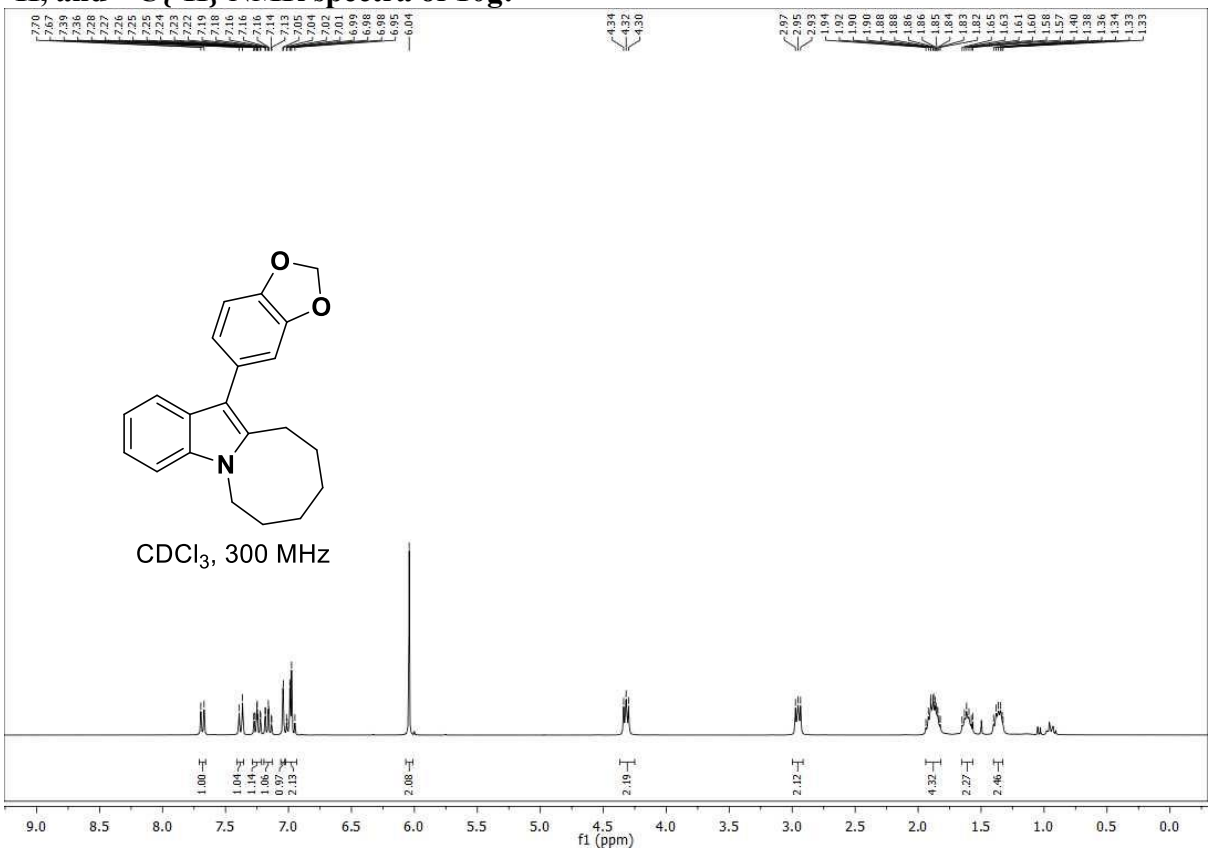


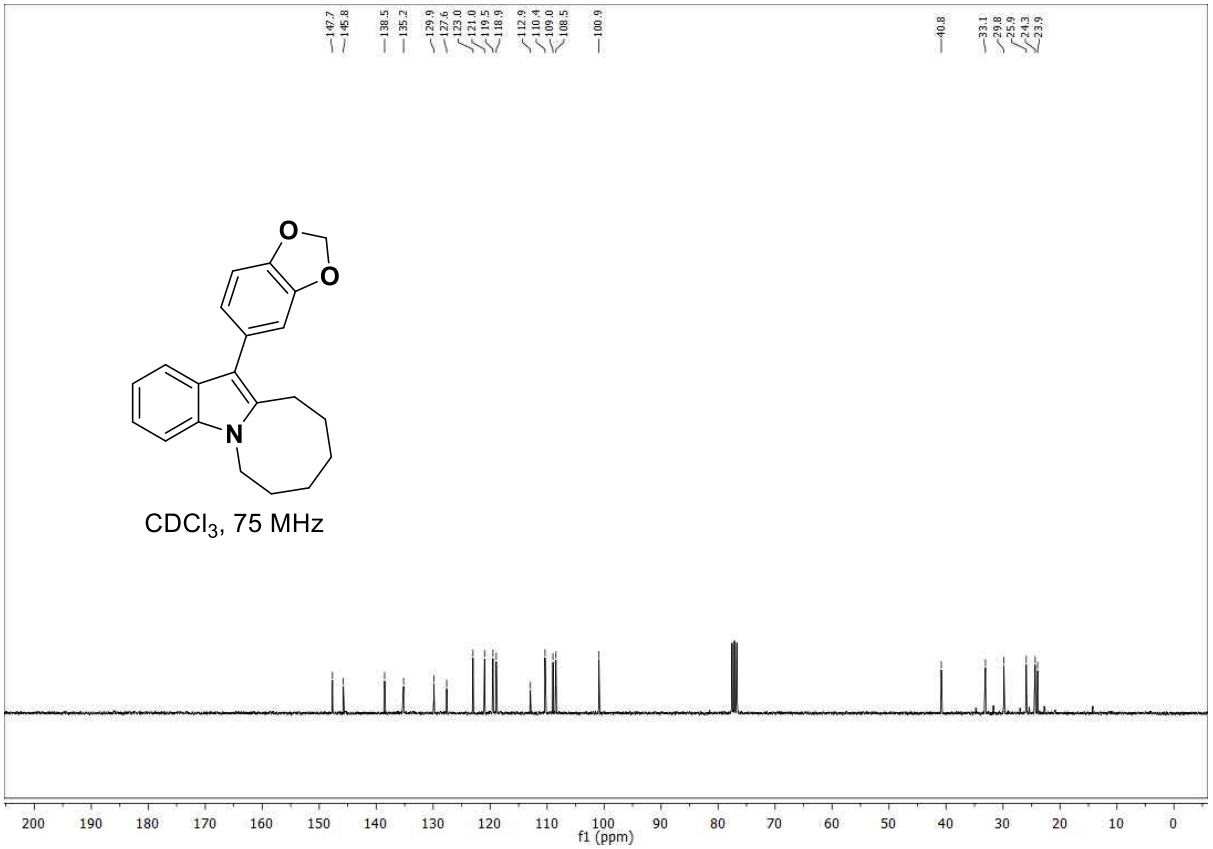
^{1}H, and ^{13}C{^{1}H} NMR spectra of 10f:



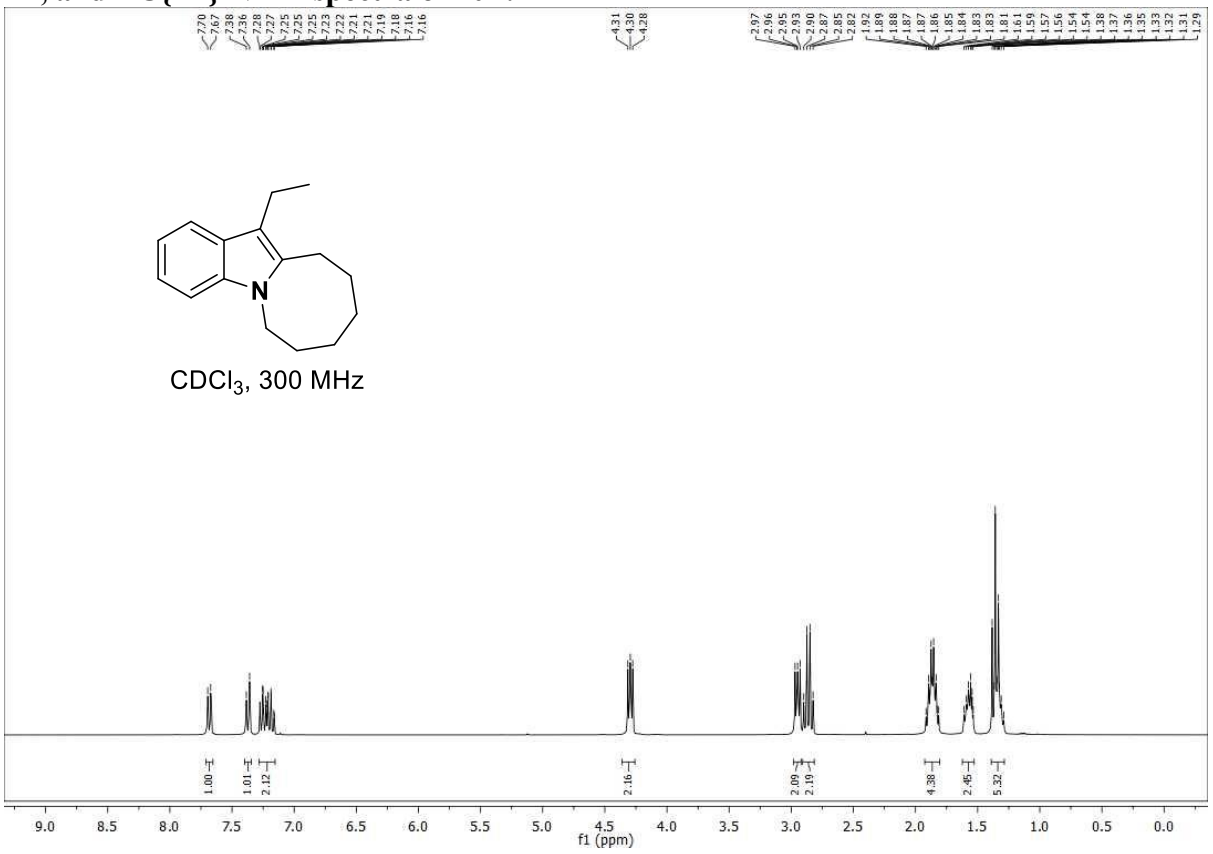


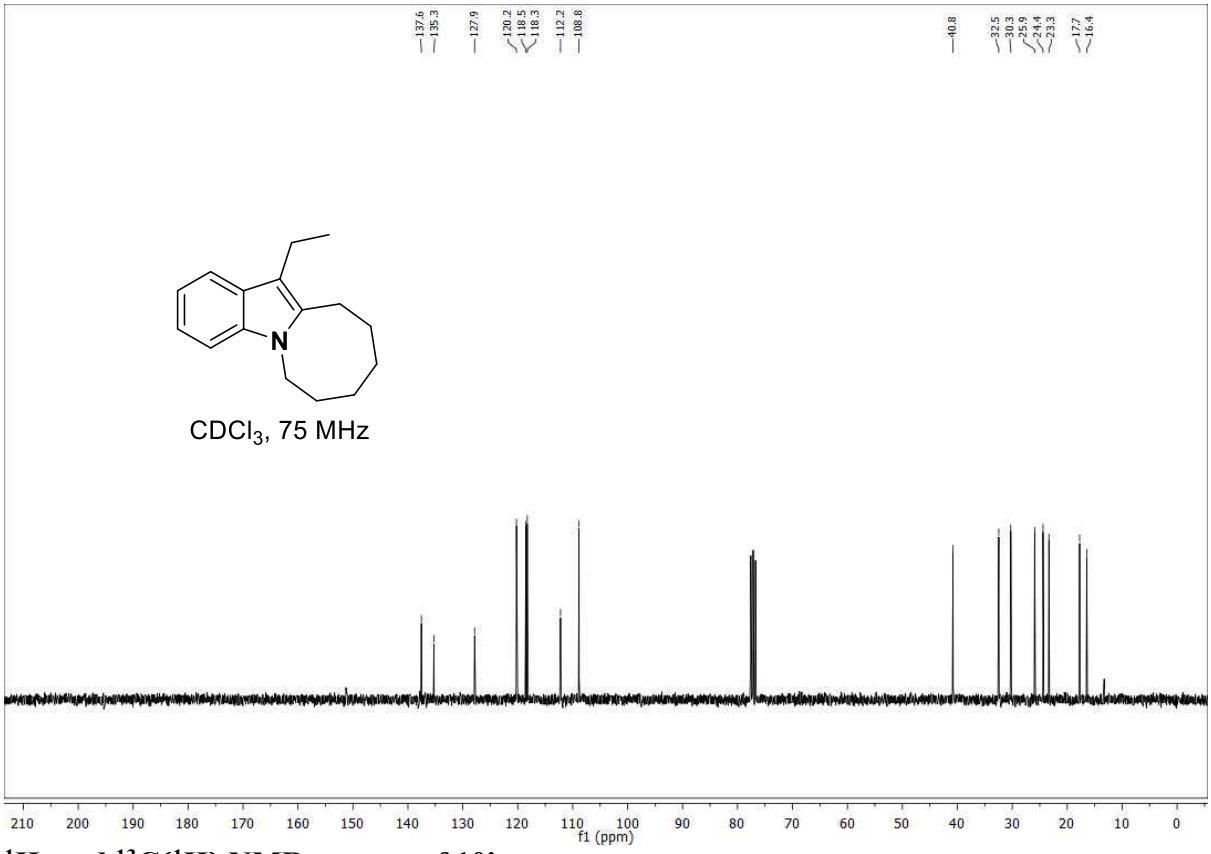
^{1}H, and ^{13}C{^{1}H} NMR spectra of 10g:



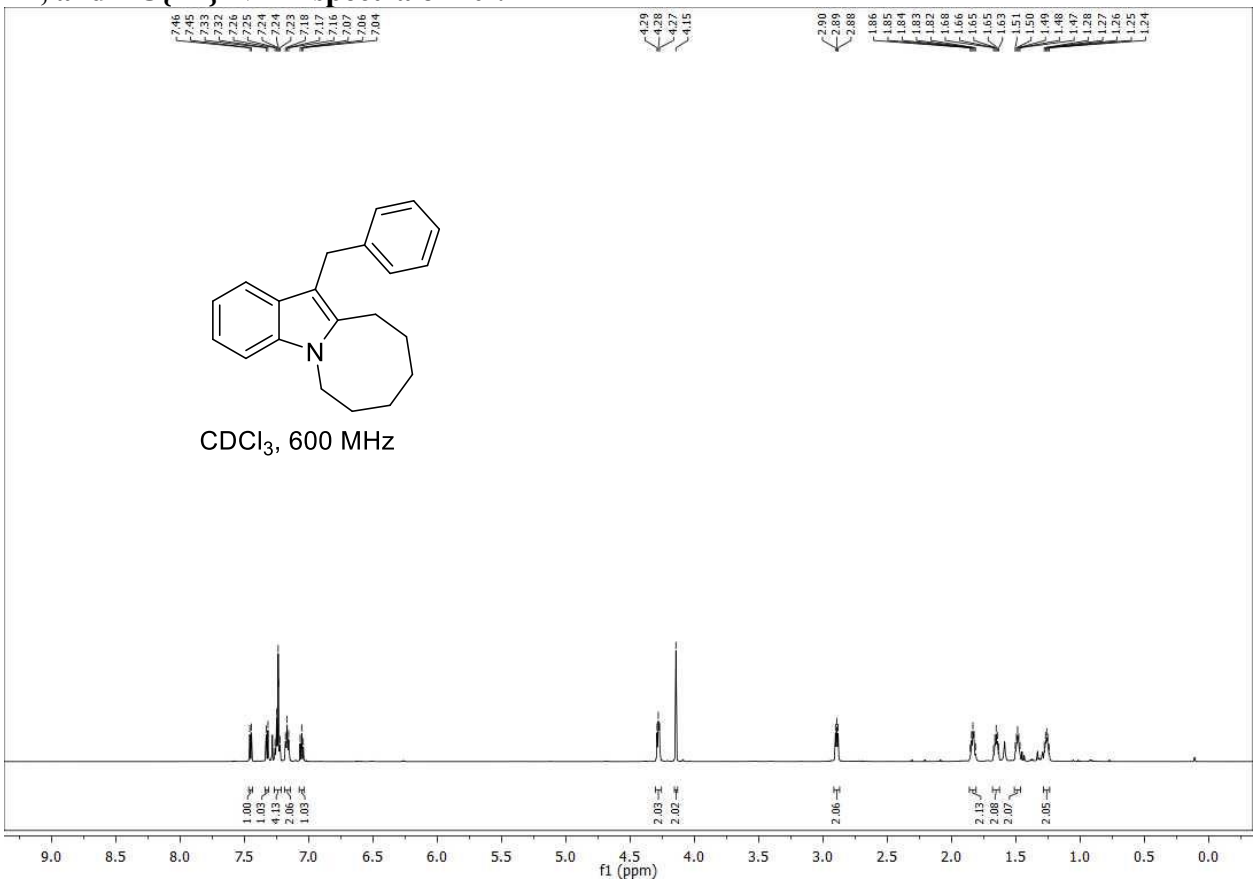


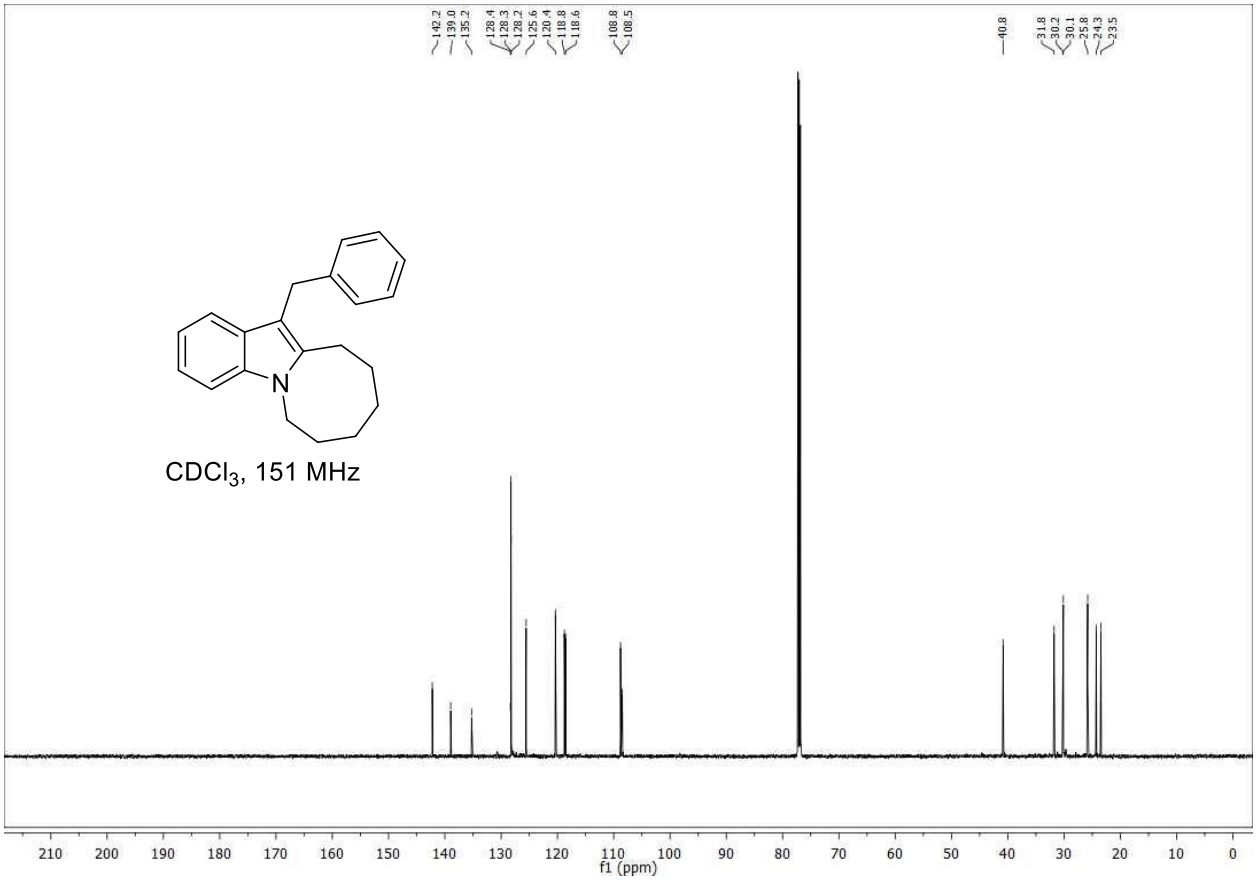
^{1}H, and ^{13}C{^{1}H} NMR spectra of 10h:





^{1}H, and ^{13}C{^{1}H} NMR spectra of 10i:




142.2
139.0
135.2
128.4
128.3
128.2
125.6
120.4
118.8
118.6
108.8
108.5
40.8
31.8
30.2
30.1
25.8
24.3
23.5
N
CDCl3, 151 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)