Electronic Supplementary Information

Oxidative trifunctionalization of indoles with 2-aminobenzyl alcohols: access to iodo-indoloquinoline scaffolds

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1. General Information

All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR, infrared spectra (IR), and mass spectra (MS), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, all the new compounds were further characterized by high resolution mass spectra (HRMS). Melting points (m.p.) were performed using a Büchi AG M-565. IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR, ^{13}C-NMR spectra were obtained on Bruker-400. Mass spectra were recorded on Trace ISQ GC/MS (Ion Source : EI). High-resolution mass spectra (HRMS) were performed with a thermo fisher Q Exactive Ultimate 3000 UPLC mass spectrometer with Orbitrap analyzer. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); Column chromatography was performed on silica gel (200-300 mesh). Reactions were monitored by using thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254). All the reagents were purchased from Bide Pharmatech Ltd. and Energy Chemical. All the solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification. All the reactions were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com).

All 2-aminobenzyl alcohols **1** were prepared according to the previous reports.[1] 2-aminobenzyl alcohol **1a** are commercially available reagent. All indoles **2** were prepared according to the previous reports.[2] 1-methyl-1*H*-indole **2a**, 1,6-dimethyl-1*H*-indole **2b** and 6-methoxy-1*H*-indole **2k** are commercially avail-able reagents. 2-aminobenzyl alcohols **1b**−**1k** and indoles **2c**−**2j** were unknow compounds.

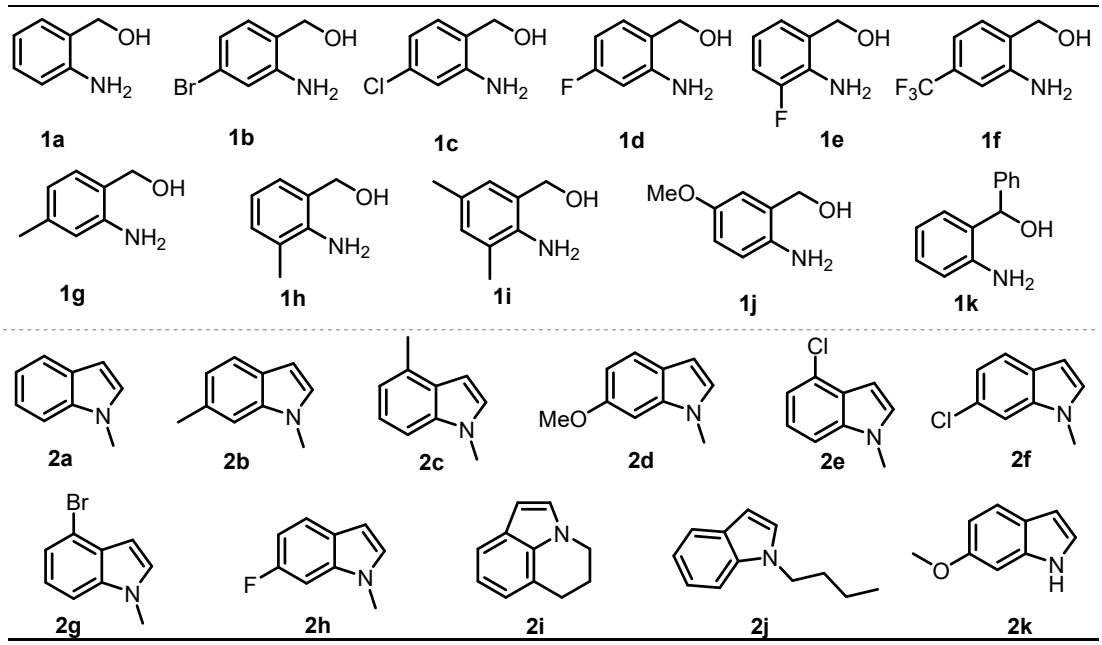
2. Experimental Procedure

2.1 General procedure for the preparation of 2-aminobenzyl alcohols (1b-1k)[1]

To a solution of substituted 2-amino-benzoic acid (10 mmol) in dry THF (20 mL) was added dropwise a solution of $LiAlH_4$ in THF (1 M, 20 mL) while the temperature was maintained at 0 °C. The resulting mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was then hydrolyzed by addition of water (2 mL) and 5% NaOH (3.5 mL). The resulting suspension was filtered, and the precipitate was washed with ethyl acetate. Then the combined organic collection was evaporated. The crude product was purified by flash chromatography on silica gel to provide desired corresponding alcohols.

2.2 General procedure for the preparation of indoles (2c-2j)[2]

To a suspended solution of NaH (0.55 g, 65% dispersion in mineral oil, 15.0 mmol) in DMF (5 mL), substituted indole (10.0 mmol) in DMF (5 mL) was added dropwise at 0 °C. The heterogeneous mixture was stirred at 0 °C for 15 min and 1 h at room temperature. The mixture was then cooled to 0 °C, treated with iodomethane (0.83 mL, 13.0 mmol), and allowed to warm to room temperature. After 30 min, the reaction mixture was cooled to 0 °C, quenched with saturated NH_4Cl (20 mL), and extracted with ether (3×20 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting oil was purified by column chromatography on silica gel.



Scheme S1. Substrates employed for the synthetic protocol.

2.3 Experimental Procedure for Synthesizing the Product 3

2-aminobenzyl alcohols **1** (0.25 mmol), indoles **2** (0.375 mmol), molecular iodine (0.30 mmol) and DMSO (1.5 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar under 1 atm of O_2 atmosphere (using O_2 balloon), the Schlenk tube was then closed and the resulting reaction mixture was heated at 130 °C for 18 h. After cooling to room temperature, the reaction mixture was filtrated, water (10 mL) and dichloromethane (30 mL) were added to obtained layered solution, then the aqueous layer was extracted with dichloromethane (2×10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was directly purified by preparative TLC on silica, eluting with petroleum ether (PE, 60-90 °C) : ethyl acetate (EA) to **3**.

2.4 Typical procedure for the synthesis of 6-methyl-9-phenyl-6*H*-indolo[2,3-*b*]quinoline (5)

Under N_2 atmosphere, 9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (0.1 mmol, 35.8 mg), phenylboronic acid (0.12 mmol, 14.6 mg), Tetrakis(triphenylphosphine)palladium (5 mol %, 5.7 mg), K_2CO_3 (0.2 mmol, 27.6 mg) and ethanol (1 mL) were introduced were introduced in a Schlenk tube (50 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 80 °C for 12 h. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with PE (60-90 °C) : EA (30 : 1, v/v) to give 6-methyl-9-phenyl-6*H*-indolo[2,3-*b*]quinoline **5** as light yellow solid (21.6 mg, 70%).

3. Single Crystal X-ray Diffraction of 3ea

Yellow block-like single crystals of **3ea** (CCDC NO. 2392817) were grown by layering a dichloromethane solution with n-hexane at ambient temperature. The bond formed between C12 and Cl1 is caused by solvent disorder. X-Ray diffraction data of one these crystals were collected on a Bruker APEX-II CCD. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 296 (2) K, using the phi and omega scans to a maximum θ value of 24.997°. The data were refined by full-matrix least-squares techniques on F2 with SHELXL-2014. And the structures were solved by direct methods SHELXL-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. An ORTEP representation of the structure is shown below.

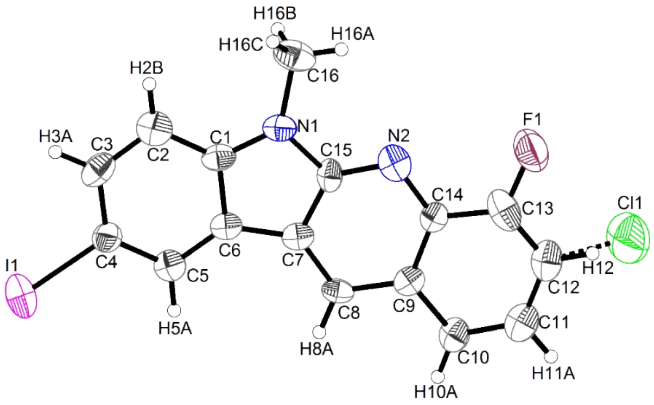


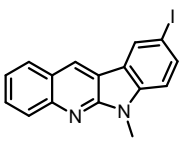
Figure S1. ORTEP drawing of **3ea** with the numbering scheme

Table S1. Crystal data and structure refinement for **3ea**.

Identification code	**3ea**	
Empirical formula	$C_{32}H_{19}ClF_2I_2N_4$	
Formula weight	786.76	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 4.770(5) Å	$\alpha = 90°$
	b = 21.58(2) Å	$\beta = 97.751(18)°$
	c = 13.886(14) Å	$\gamma = 90°$
Volume	1416(2) $Å^3$	
Z	2	
Density (calculated)	1.845 mg/m^3	
Absorption coefficient	2.358 mm^{-1}	
F(000)	760	
Crystal size	0.220 x 0.200 x 0.180 mm^3	
Theta range for data collection	1.755 to 24.997°	
Index ranges	-5<=h<=5, -25<=k<=25, -16<=l<=15	
Reflections collected	5264	

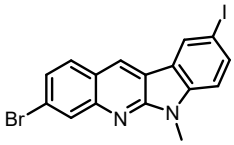
4. Analytical Data of the Obtained Compounds

(1) 9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3aa)



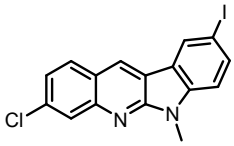
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (63.5 mg, 71% yield), m.p.: 143-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 8.22 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.42 (t, J = 16.0 Hz, 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.1, 146.9, 141.8, 136.1, 129.9, 129.2, 128.6, 127.7, 127.5, 124.0, 123.1, 122.6, 116.5, 110.5, 82.0, 27.6; IR (KBr): v = 3121, 2985, 2830, 1615, 1569, 1439, 1366, 1273, 1006, 897, 798 cm^{-1}; HRMS (ESI) Calcd. for $C_{16}H_{12}IN_2$ [M+H]$^+$: 359.0040; Found: m/z 359.0036.

(2) 3-bromo-9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3ba)



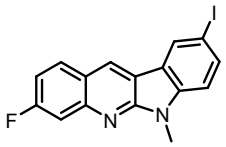
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (66.5 mg, 61% yield), m.p.: 198-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.22 (d, J = 12.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 12.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.2, 147.4, 141.8, 136.5, 130.0, 129.8, 129.6, 127.4, 126.6, 123.4, 122.5, 122.3, 116.7, 110.7, 27.6; IR (KBr): v = 2920, 1601, 1494, 1370, 1170, 1010, 884, 799 cm^{-1}; HRMS (ESI) Calcd. for $C_{16}H_{11}BrIN_2$ [M+H]$^+$: 436.9145; Found: m/z 436.9141.

(3) 3-chloro-9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3ca)



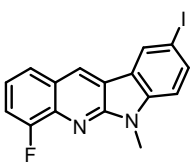
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (64.5 mg, 66% yield), m.p.: 136-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.21 (s, 1H), 8.00 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 12.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.3, 147.2, 141.7, 136.4, 135.0, 129.9, 129.5, 127.2, 126.5, 124.0, 122.3, 122.2, 116.6, 110.7, 82.4, 27.6; IR (KBr): v = 2959, 2888, 1766, 1634, 1488, 1368, 1239, 1066, 854, 796 cm^{-1}; HRMS (ESI) Calcd. for $C_{16}H_{11}ClIN_2$ [M+H]$^+$: 392.9650; Found: m/z 392.9645.

(4) 3-fluoro-9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3da)



This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (70.3 mg, 75% yield), m.p.: 87-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 8.07 (s, 1H), 7.74 – 7.68 (m, 1H), 7.67 – 7.57 (m, 2H), 7.17 – 7.10 (m, 1H), 6.89 (d, J = 8.0 Hz, 1H), 3.66 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 163.2 (d, J = 250.1 Hz), 152.3, 147.7 (d, J = 13.1 Hz), 141.3, 136.0, 130.3 (d, J = 10.5 Hz), 129.6, 127.3, 122.3, 120.8, 115.7 (d, J = 2.6 Hz), 113.4 (d, J = 25.8 Hz), 111.1 (d, J = 21.1 Hz), 110.5, 82.3, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.70; IR (KBr): v = 2984, 2890, 1769, 1623, 1492, 1369, 1173, 1067, 928, 796 cm^{-1}; HRMS (ESI) Calcd. for $C_{16}H_{11}FIN_2$ [M+H]$^+$: 376.9946; Found: m/z 376.9943.

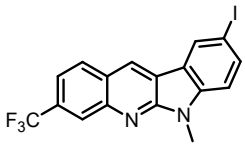
(5) 4-fluoro-9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3ea)



This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (65.6 mg, 70% yield), m.p.: 176-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.24 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0

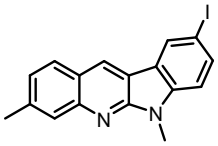
Hz, 1H), 7.42 – 7.35 (m, 1H), 7.34 – 7.27 (m, 1H), 7.05 (d, J = 8.0 Hz, 1H), 3.85 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 157.2 (d, J = 253.6 Hz), 151.9, 142.0, 136.6, 130.1, 127.4, 125.7, 124.1 (d, J = 4.3 Hz), 122.3, 122.3,122.2, 117.3, 113.1 (d, J = 19.3 Hz), 110.8, 82.3, 27.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -127.19; IR (KBr): ν = 3032, 2920, 1637, 1515, 1367, 1274, 1137, 1083, 959, 800, 707 cm^{-1}; HRMS (ESI) Calcd. for $C_{16}H_{11}FIN_2$ $[M+H]^+$: 376.9946; Found: m/z 376.9941.

(6) 9-iodo-6-methyl-3-(trifluoromethyl)-6*H*-indolo[2,3-*b*]quinoline (3fa)



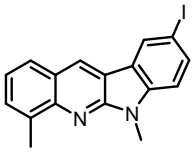
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (58.4 mg, 55% yield), m.p.: 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 8.14 (s, 1H), 8.10 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 12.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 3.65 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 152.5, 145.7, 142.0, 137.0, 130.7, 130.3 (d, J = 3.1 Hz), 129.5, 127.0 (d, J = 3.6 Hz), 125.7, 125.4 - 125.0 (m), 123.0, 122.0 (d, J = 3.1 Hz), 118.7 - 118.5 (m), 118.0 (d, J = 4.0 Hz), 110.8, 82.5, 27.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.25; IR (KBr): ν = 2960, 2889, 1766, 1600, 1496, 1443, 1327, 1278, 1122, 1062, 954, 801 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{11}F_3IN_2$ $[M+H]^+$: 426.9914; Found: m/z 426.9907.

(7) 9-iodo-3,6-dimethyl-6*H*-indolo[2,3-*b*]quinoline (3ga)



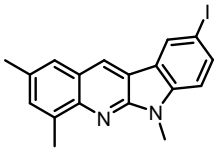
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (41.9 mg, 45% yield), m.p.: 142-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.2 (s, 1H), 7.84 (s, 1H), 7.76 – 7.67 (m, 2H), 7.23 (d, J = 9.6 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 3.77 (s, 3H), 2.57 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 152.1, 147.1, 141.6, 139.7, 135.8, 129.7, 128.2, 127.5, 126.5, 125.4, 122.8, 122.1, 115.8, 110.5, 82.0, 27.6, 22.1. IR (KBr): ν =2956, 1625, 1501,1397, 1276, 1140, 901, 794, 681 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{14}IN_2$ $[M+H]^+$: 373.0196; Found: m/z 373.0197.

(8) 9-iodo-4,6-dimethyl-6*H*-indolo[2,3-*b*]quinoline (3ha)



This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (55.8 mg, 60% yield), m.p.: 163-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.34 (s, 1H), 7.82 – 7.76 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H), 2.87 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 151.4, 146.0, 141.9, 136.0, 135.4, 130.1, 129.3, 128.0, 126.6, 123.9, 122.8, 116.1, 110.6, 81.9, 27.5, 18.2; IR (KBr): ν = 2984, 2831, 1611, 1492, 1467, 1172, 1007, 899, 796, 706 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{14}IN_2$ $[M+H]^+$: 373.0196; Found: m/z 373.0195.

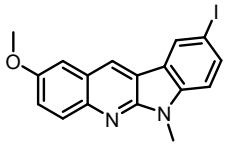
(9) 9-iodo-2,4,6-trimethyl-6*H*-indolo[2,3-*b*]quinoline (3ia)



This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (67.6 mg, 70% yield), m.p.: 163-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.27 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.48 (s, 1H), 7.39 (s, 1H), 7.03 (d, J = 8.8 Hz, 1H), 3.81 (s, 3H), 2.81 (s, 3H), 2.51 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 150.9, 144.5, 141.7, 135.7, 134.9, 132.0, 131.5, 129.8, 127.0, 125.3, 123.9,

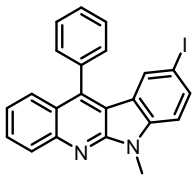
122.7, 115.8, 110.4, 81.6, 27.3, 21.5, 18.1; IR (KBr): ν = 2960, 2892, 1765, 1626, 1368, 1173, 1066, 990, 926, 799 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{16}IN_2$ $[M+H]^+$: 387.0353; Found: m/z 387.0347.

(10) 9-iodo-2-methoxy-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3ja)



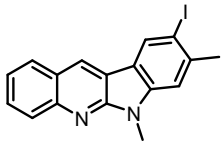
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (35.9 mg, 37% yield), m.p.: 184-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.33 (s, 1H), 8.01 (d, J = 9.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.20 (s, 1H), 7.10 (d, J = 8.0 Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.4, 151.2, 143.0, 141.8, 136.1, 130.0, 128.8, 126.5, 124.7, 122.5, 122.0, 116.7, 110.6, 106.2, 81.7, 55.6, 27.7; IR (KBr): ν = 3036, 2925, 1599, 1480, 1368, 1274, 1115, 900, 827, 795 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{14}IN_2O$ $[M+H]^+$: 389.0145; Found: m/z 389.0146.

(10) 9-iodo-6-methyl-11-phenyl-6*H*-indolo[2,3-*b*]quinoline (3ka)



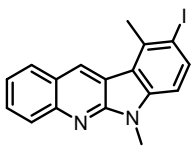
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (44.5 mg, 41% yield), m.p.: 181-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.0 Hz, 1H), 7.78 – 7.62 (m, 6H), 7.49 (s, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.30 (s, 1H), 7.11 (d, J = 8.0 Hz, 1H), 3.96 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.9, 147.1, 143.0, 142.1, 136.0, 131.7, 129.2, 129.1, 129.1, 128.9, 127.7, 126.5, 123.8, 123.1, 123.0, 114.7, 110.4, 82.1, 27.7; IR (KBr): ν = 3055, 2923, 1622, 1490, 1368, 1258, 1051, 935, 883, 759 cm^{-1}; HRMS (ESI) Calcd. for $C_{22}H_{16}IN_2$ $[M+H]^+$: 435.0353; Found: m/z 435.0354.

(11) 9-iodo-6,8-dimethyl-6*H*-indolo[2,3-*b*]quinoline (3ab)



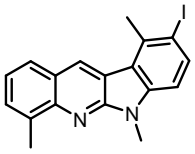
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (75.3 mg, 81% yield), m.p.: 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.40 (s, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.17 (s, 1H), 3.83 (d, J = 1.3 Hz, 3H), 2.59 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.5, 146.6, 143.0, 140.6, 131.2, 129.0, 128.5, 127.4, 127.2, 124.1, 123.1, 120.4, 116.7, 109.7, 89.4, 29.3, 27.7; IR (KBr): ν = 3045, 2920, 1606, 1509, 1372, 1259, 1140, 952, 907, 749 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{14}IN_2$ $[M+H]^+$: 373.0198; Found: m/z 373.0196.

(12) 9-iodo-6,10-dimethyl-6*H*-indolo[2,3-*b*]quinoline (3ac)



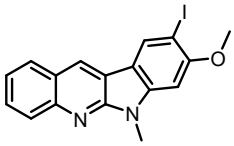
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (70.7 mg, 76% yield), m.p.: 208-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.96 (t, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.46 (t, J= 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 2.97 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.8, 146.2, 142.4, 137.7, 137.1, 129.8, 129.1, 128.7, 127.3, 124.0, 123.0, 119.3, 117.9, 108.1, 90.9, 27.6, 25.6; IR (KBr): ν = 2921, 2830, 1616, 1494, 1367, 1332, 1172, 1009, 799 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{14}IN_2$ $[M+H]^+$: 373.0196; Found: m/z 373.0199.

(13) 9-iodo-4,6,10-trimethyl-6*H*-indolo[2,3-*b*]quinoline (3hc)



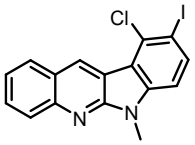
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (59.8 mg, 62% yield), m.p.: 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 3.68 (s, 3H), 2.83 (s, 3H), 2.76 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 150.9, 145.1, 142.3, 137.4, 137.0, 135.0, 129.7, 129.0, 126.6, 123.7, 122.5, 119.3, 117.1, 107.9, 90.6, 27.2, 25.5, 18.1; IR (KBr): *v* = 2948, 1768, 1613, 1493, 1368, 1332, 1172, 1088, 799, 722 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{16}IN_2$ [M+H]$^+$: 387.0353; Found: m/z 387.0346.

(14) 9-iodo-8-methoxy-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3ad)



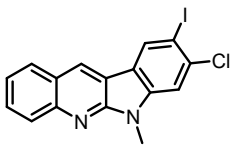
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (52.4 mg, 54% yield), m.p.: 204-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 2H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 6.57 (s, 1H), 3.93 (s, 3H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.0, 152.4, 145.8, 144.2, 131.5, 128.6, 128.4, 127.3, 126.0, 124.3, 123.1, 116.8, 115.5, 91.7, 56.5, 27.6; IR (KBr): *v* = 2983, 2859, 1604, 1493, 1391, 1273, 1063, 895, 749 cm^{-1}; HRMS (ESI) Calcd. for $C_{17}H_{14}IN_2O$ [M+H]$^+$: 389.0145; Found: m/z 389.0146.

(15) 10-chloro-9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3ae)



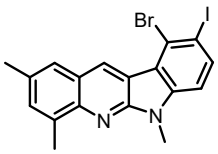
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (28.3 mg, 29% yield), m.p.: 199-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.5, 146.7, 143.2, 137.9, 133.3, 130.8, 129.6, 129.0, 127.3, 124.1, 123.3, 118.8, 116.4, 108.7, 87.2, 27.9; IR (KBr): *v* = 2920, 1562, 1495, 1430, 1273, 1076, 993, 799 cm^{-1}; HRMS (ESI) Calcd. for $C_{16}H_{11}ClIN_2$ [M+H]$^+$: 392.9650; Found: m/z 392.9650.

(16) 8-chloro-9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3af)



This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (55.7 mg, 57% yield), m.p.: 134-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 12.0 Hz, 2H), 8.06 (d, *J* = 12.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.33 (s, 1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.4, 146.9, 143.1, 137.1, 131.9, 129.4, 128.6, 127.7, 127.6, 124.2, 123.5, 121.0, 115.9, 109.5, 85.8, 27.7; IR (KBr): *v* = 2983, 2831, 1768, 1627, 1492, 1404, 1172, 1086, 954, 799 cm^{-1}; HRMS (ESI) Calcd. for $C_{16}H_{11}ClIN_2$ [M+H]$^+$: 392.9650; Found: m/z 392.9645.

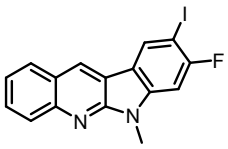
(17) 10-bromo-9-iodo-2,4,6-trimethyl-6*H*-indolo[2,3-*b*]quinoline (3ig)



This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (35.9 mg, 31% yield), m.p.: 208-209 °C; ^{1}H NMR (400

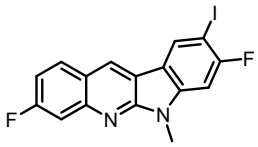
MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 1H), 7.36 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 2.79 (s, 3H), 2.53 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 150.3, 144.3, 142.8, 137.3, 134.6, 132.1, 131.9, 129.9, 125.8, 124.3, 123.7, 121.0, 116.5, 108.9, 90.4, 27.5, 21.5, 18.0; IR (KBr): *v* = 3028, 2917, 1612, 1518, 1370, 1190, 987, 875, 634 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{15}BrIN_2$ $[M+H]^+$: 464.9458; Found: m/z 464.9453.

(18) 8-fluoro-9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3ah)



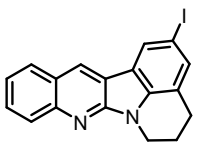
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (43.1 mg, 46% yield), m.p.: 195-196 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.31 (d, *J* = 4.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.48 – 7.42 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.2 (d, *J* = 245.1 Hz), 152.7, 146.5, 143.9 (d, *J* = 11.7 Hz), 131.2 (d, *J* =3.3 Hz), 129.3, 128.5, 127.6, 127.3, 124.3, 123.5, 118.8 (d, *J* = 1.7 Hz), 116.2, 96.6 (d, *J* = 30.3 Hz), 27.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -91.58; IR (KBr): *v* = 3033, 2919, 1606, 1510, 1367, 1260, 1141, 971, 752 cm^{-1}; HRMS (ESI) Calcd. for $C_{16}H_{11}FIN_2$ $[M+H]^+$: 376.9946; Found: m/z 376.9943.

(19) 3,8-difluoro-9-iodo-6-methyl-6*H*-indolo[2,3-*b*]quinoline (3dh)



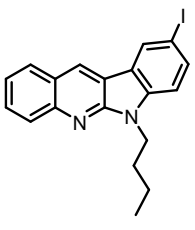
This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. White solid (45.2 mg, 46% yield), m.p.: 208-209 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* =8.0 Hz, 1H), 7.68 (d, *J* = 8.0, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 163.4 (d, *J* = 213.1Hz), 160.9 (d, *J* = 208.1 Hz), 153.2, 147.5 (d, *J* = 13.2 Hz), 143.5 (d, *J* = 11.4 Hz), 131.0 (d, *J* = 3.2 Hz), 130.2 (d, *J* = 10.4 Hz), 127.1, 121.1, 118.7, 115.6, 113.8 (d, *J* = 25.4 Hz), 111.4 (d, *J* = 21.1 Hz), 96.6 (d, *J* = 29.8 Hz), 70.0 (d, *J* = 28.3), 27.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -91.42, -109.81; IR (KBr): *v* = 2919, 1602, 1492, 1367, 1219, 1009, 886, 774 cm^{-1}; HRMS (ESI) Calcd. for $C_{16}H_{10}F_2IN_2$ $[M+H]^+$: 394.9851; Found: m/z 394.9847.

(20) 2-iodo-5,6-dihydro-4*H*-pyrrolo[2,3-*b*:4,5,1-*i'j'*]diquinoline (3ai)



This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (55.7 mg, 58% yield), m.p.: 150-151 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.19 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.71(d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 4.36 (t, *J* = 8.0 Hz, 2H), 2.98 (t, *J* = 8.0 Hz, 2H), 2.29 – 2.20 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 151.2, 146.7, 138.3, 134.0, 129.1, 128.7, 128.3, 127.7, 127.3, 123.9, 123.2, 123.0, 120.4, 117.1, 82.0, 39.8, 24.6, 21.7; IR (KBr): *v* = 3053, 2865, 1632, 1567, 1480, 1366,1247, 851, 752 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{14}IN_2$ $[M+H]^+$: 385.0196; Found: m/z 385.0199.

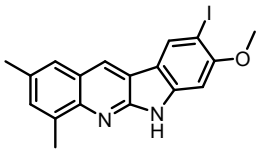
(21) 6-butyl-9-iodo-6*H*-indolo[2,3-*b*]quinoline (3aj)



This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as

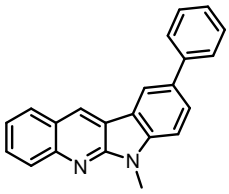
eluant. Light yellow solid (45.0 mg, 45% yield), m.p.: 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 8.40 (d, *J* = 2.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.76 – 7.69 (m, 1H), 7.48 – 7.42 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.45 (t, *J* = 8.0 Hz, 2H), 1.95 – 1.84 (m, 2H), 1.48 – 1.36 (m, 2H), 0.97 (t, *J* = 8.0 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.1, 147.1, 141.4, 136.1, 130.2, 129.1, 128.6, 127.8, 127.7, 124.2, 123.1, 122.9, 116.7, 111.0, 81.8, 41.3, 30.6, 20.3, 13.9; IR (KBr): *v* = 3047, 2863, 1634, 1511, 1370, 1211, 953, 874, 751 cm^{-1}; HRMS (ESI) Calcd. for $C_{19}H_{18}IN_2$ $[M+H]^+$: 401.0509; Found: m/z 401.0511.

(22) 9-iodo-8-methoxy-2,4-dimethyl-6H-indolo[2,3-*b*]quinoline (3ik)



This product was purified by preparative TLC on silica using PE : EA (20 : 1, v/v) as eluant. Light yellow solid (38.2 mg, 38% yield), m.p.: 228-229 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.26 (s, 1H), 7.51 (s, 1H), 7.34 (s, 1H), 6.80 (s, 1H), 3.85 (s, 3H), 2.73 (s, 3H), 2.51 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.1, 150.7, 142.1, 140.4, 133.3, 132.5, 132.5, 131.6, 127.6, 125.5, 124.0, 117.4, 115.8, 94.1, 56.5, 21.4, 18.4; IR (KBr): *v* = 3035, 2878, 1517, 1429, 1258, 1157, 957, 754; HRMS (ESI) Calcd. for $C_{18}H_{16}IN_2O$ $[M+H]^+$: 403.0302; Found: m/z 403.0301.

(23) 6-methyl-9-phenyl-6*H*-indolo[2,3-*b*]quinoline (5)



This product was purified by preparative TLC on silica using PE : EA (30 : 1, v/v) as eluant. Light yellow solid (53.9 mg, 70% yield), m.p.: 139-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 8.32 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.70 (m, 3H), 7.54 – 7.49 (m, 2H), 7.48 – 7.44 (m, 1H), 7.42 – 7.36 (m, 2H), 3.96 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.0, 146.9, 142.2, 141.6, 133.5, 129.0, 128.9, 128.6, 127.5, 127.5, 127.4, 127.2, 126.8, 124.1, 123.0, 120.9, 119.9, 118.3, 108.9, 27.8; IR (KBr):3031, 2924, 1609,1478, 1388, 1261, 1170, 1011, 905, 855, 801, 749; HRMS (ESI) Calcd. for $C_{22}H_{17}N_2$ $[M+H]^+$: 309.1386; Found: m/z 309.1380.

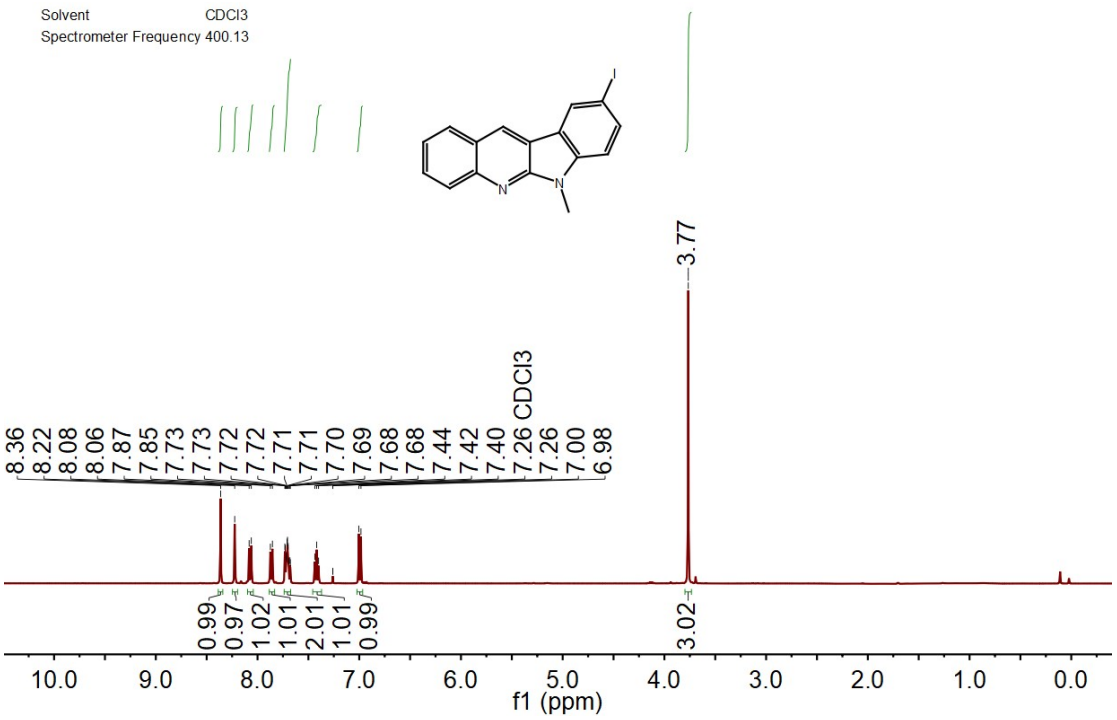
5. Reference

1 H. Jia, H. Liu, Z. Guo, J. Huang and H. Guo, Tandem [3 + 2] Cycloaddition/1,4-Addition Reaction of Azomethine Ylides and Aza-o-quinone Methides for Asymmetric Synthesis of Imidazolidines, *Org. Lett.,* 2017, **19**, 5236-5239.

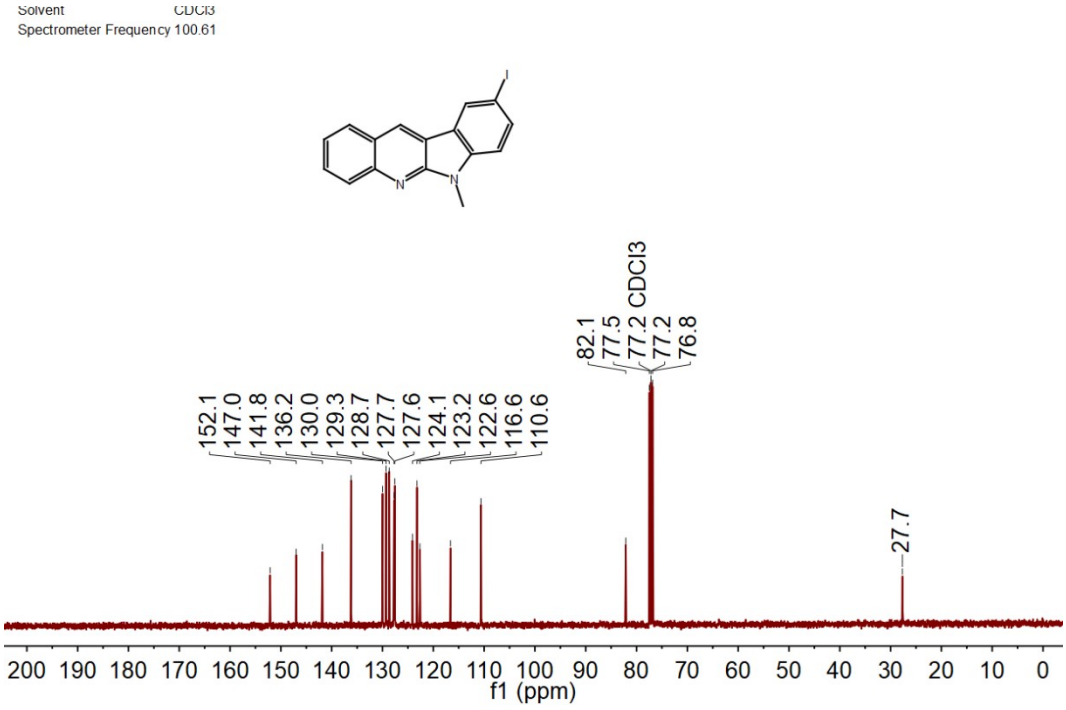
2 X. Hong, Q. Tan, B. Liu and B. Xu, Isocyanide-Induced Activation of Copper Sulfate: Direct Access to Functionalized Heteroarene Sulfonic Esters. *Angew. Chem. Int. Ed.,* 2017, **56**, 3961-3965.

6. NMR Spectra of the Obtained Compounds

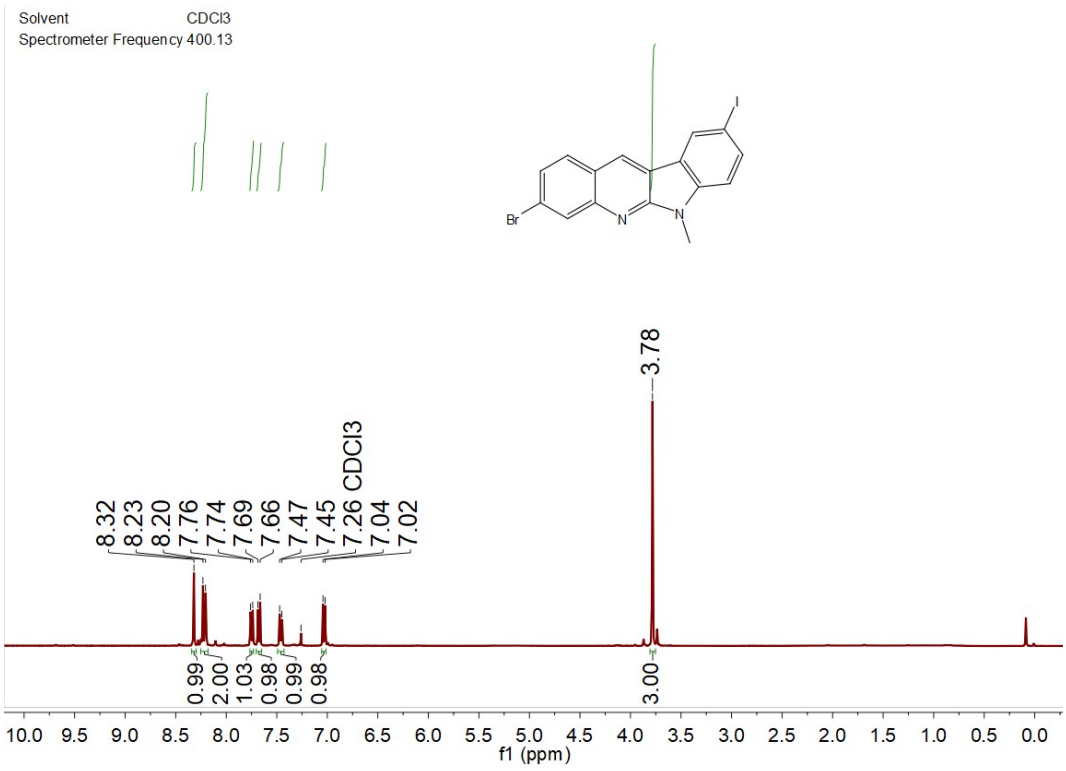
^{1}H NMR spectrum of 3aa



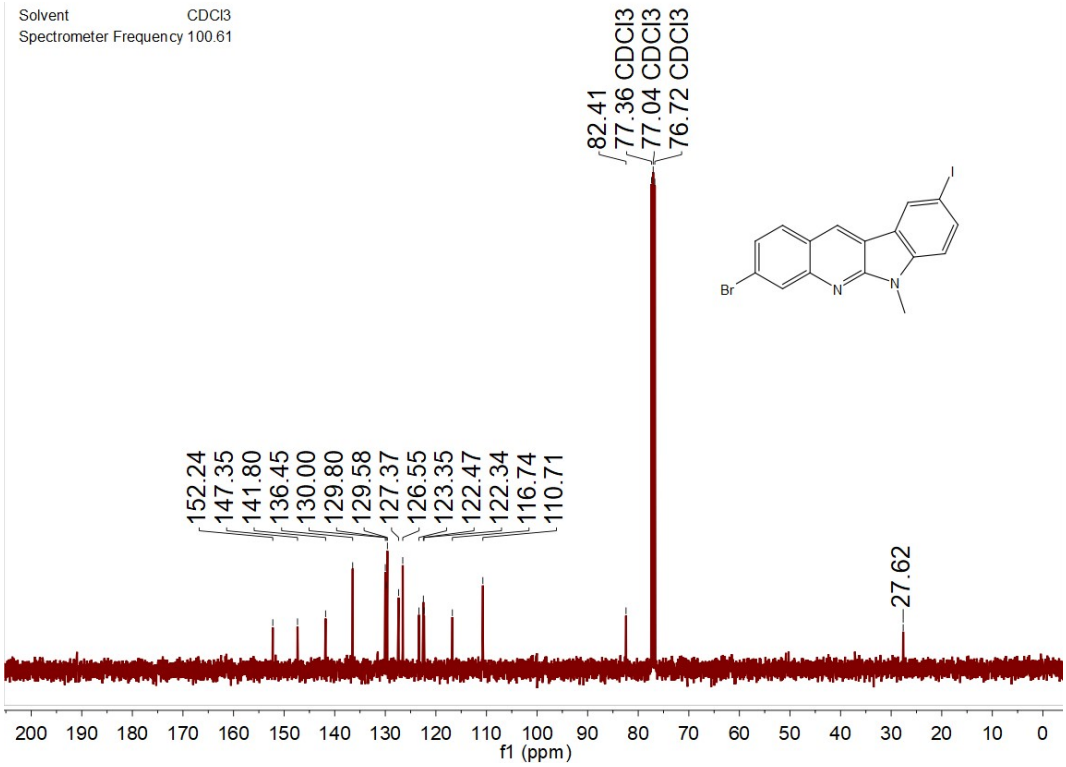
^{13}C{^{1}H} NMR spectrum of 3aa



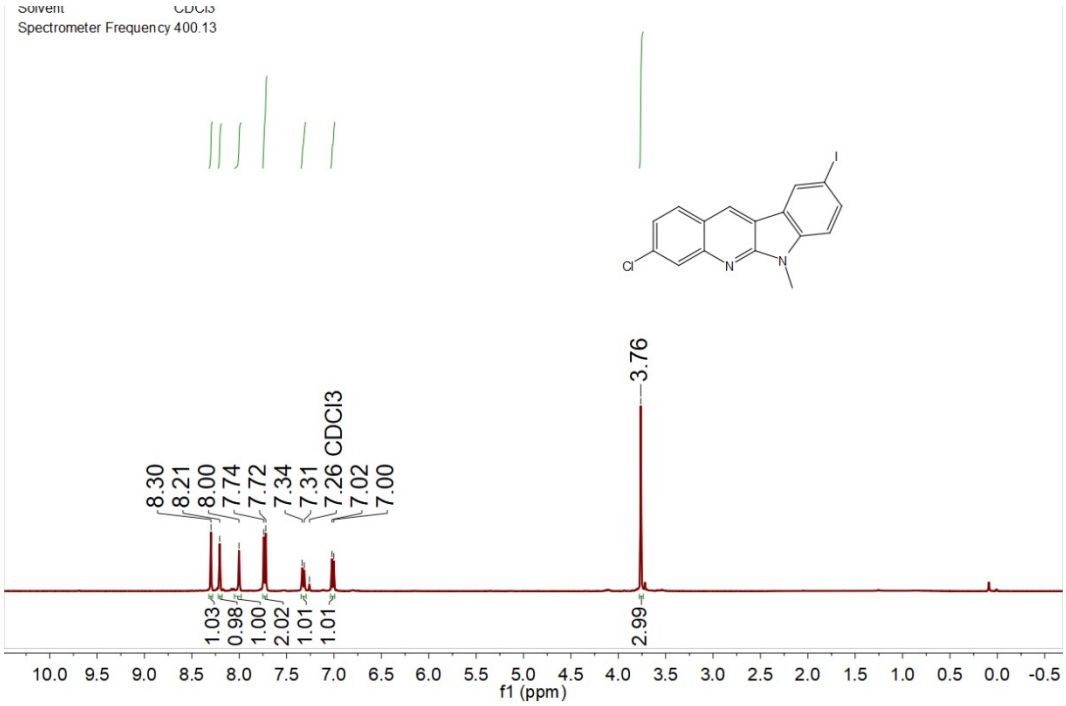
^{1}H NMR spectrum of 3ba



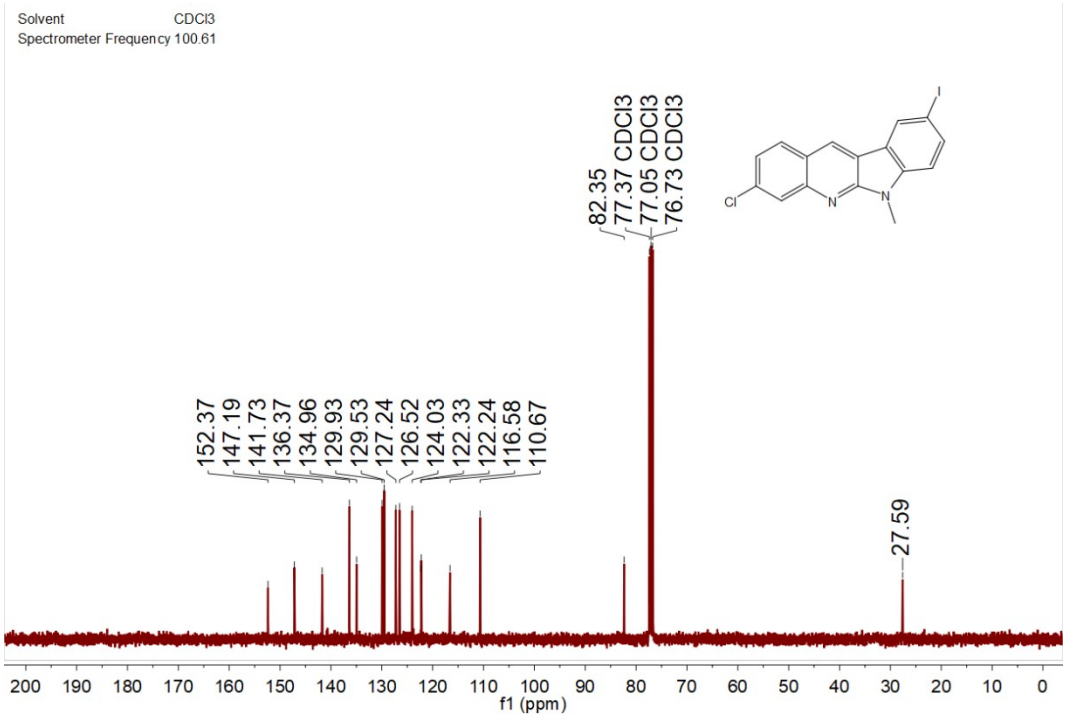
$^{13}C\{^{1}H\}$ NMR spectrum of 3ba



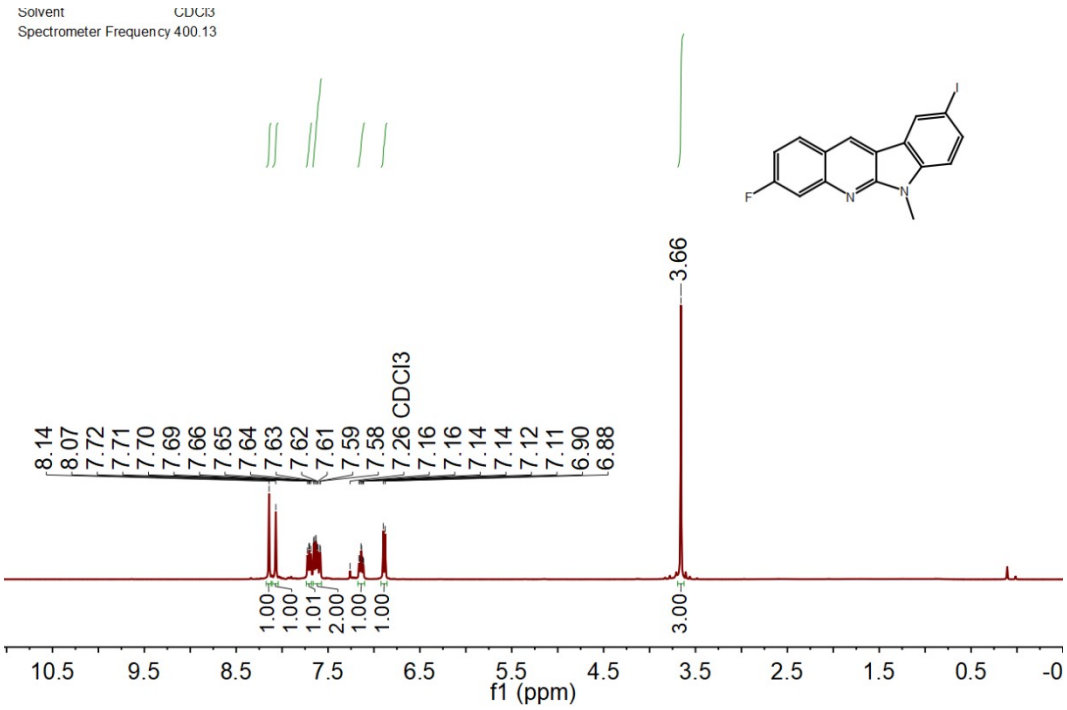
^{1}H NMR spectrum of 3ca



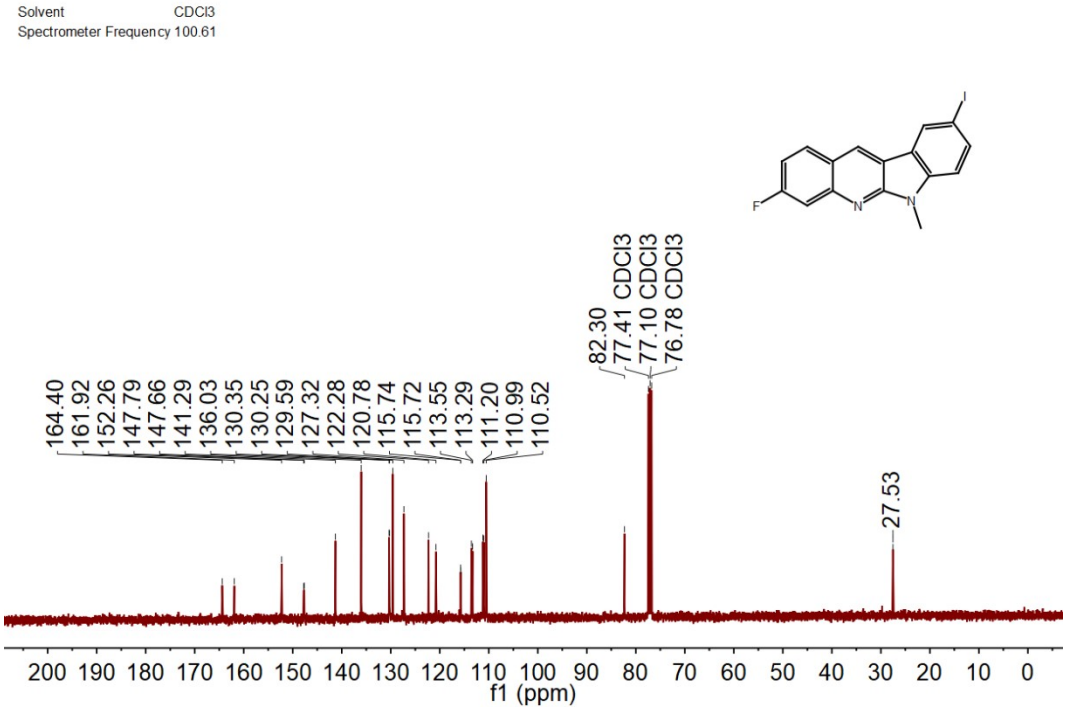
$^{13}C\{^{1}H\}$ NMR spectrum of 3ca



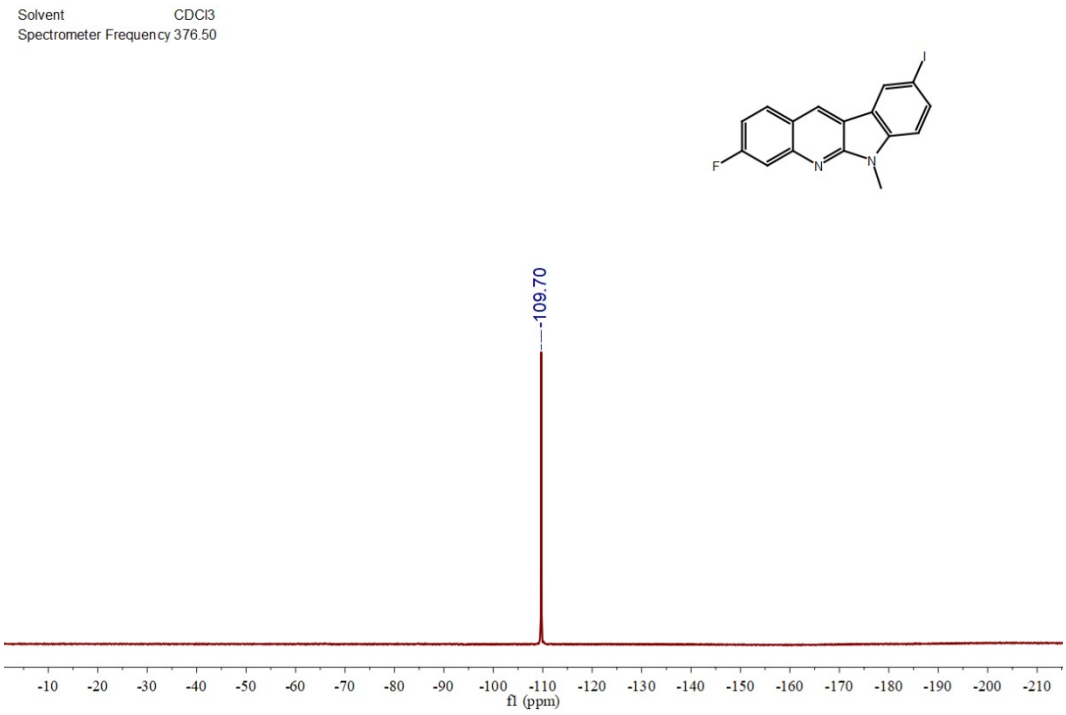
^{1}H NMR spectrum of 3da



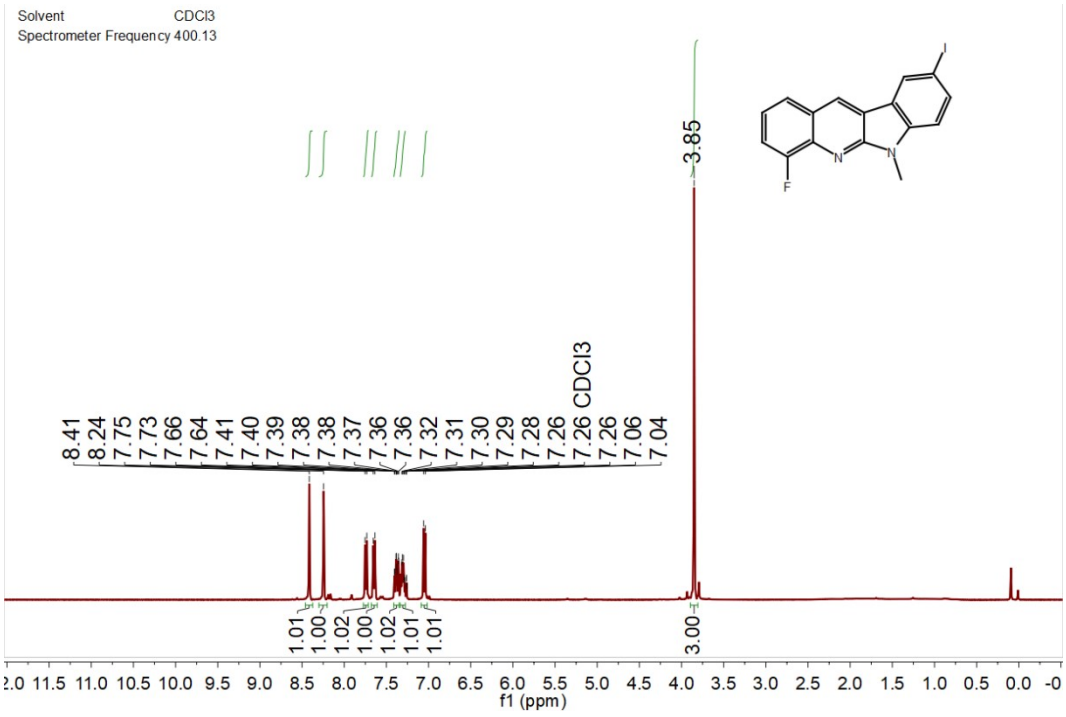
$^{13}C\{^{1}H\}$ NMR spectrum of 3da



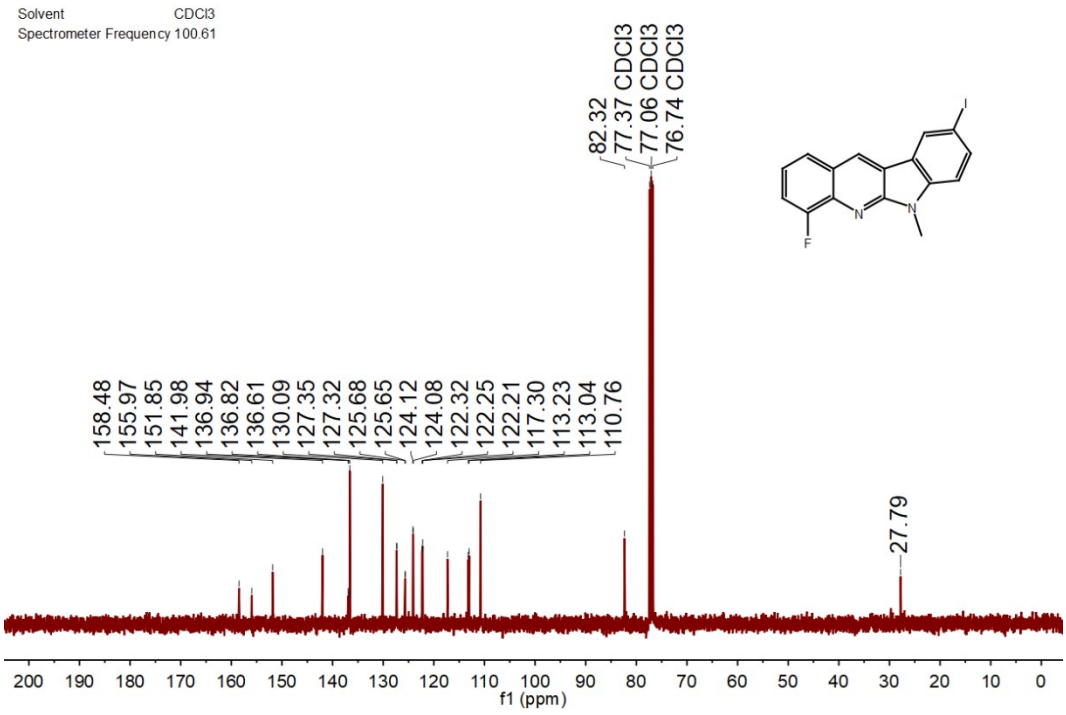
^{19}F NMR spectrum of 3da



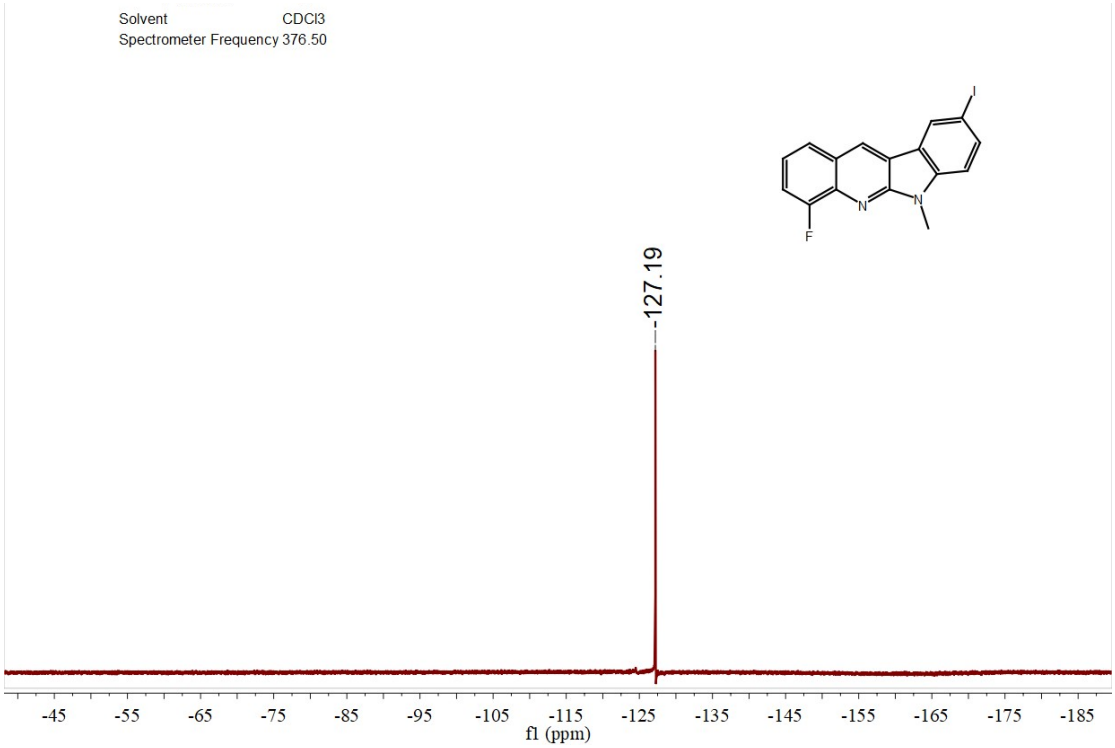
^{1}H NMR spectrum of 3ea



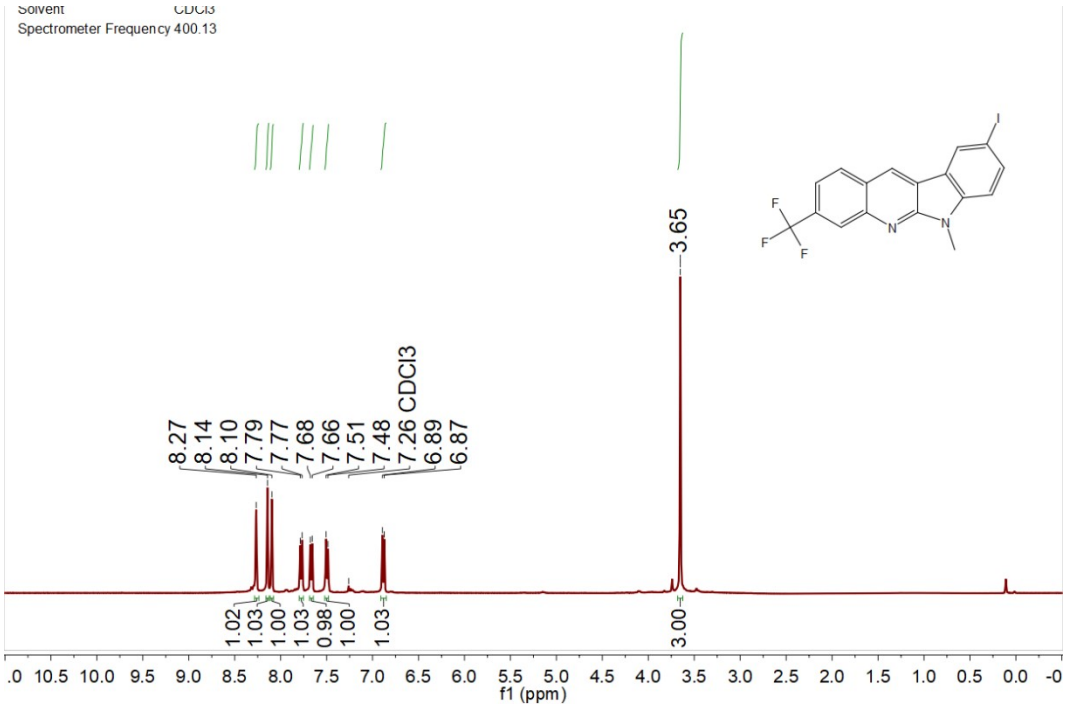
^{13}C{^{1}H} NMR spectrum of 3ea



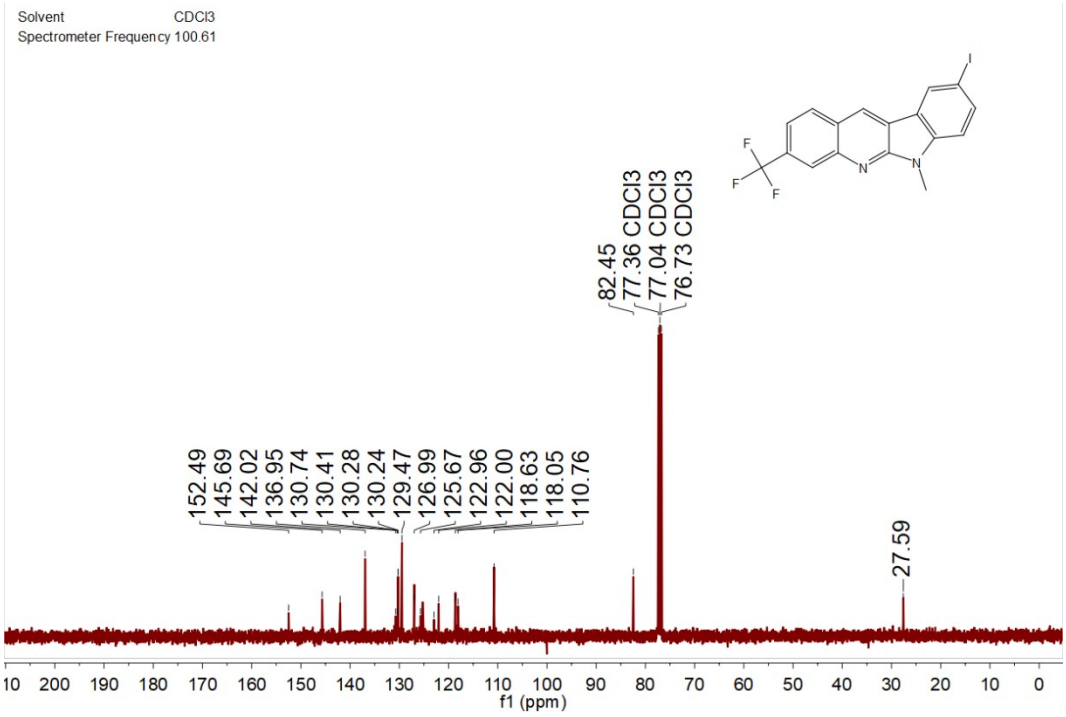
^{19}F NMR spectrum of 3ea



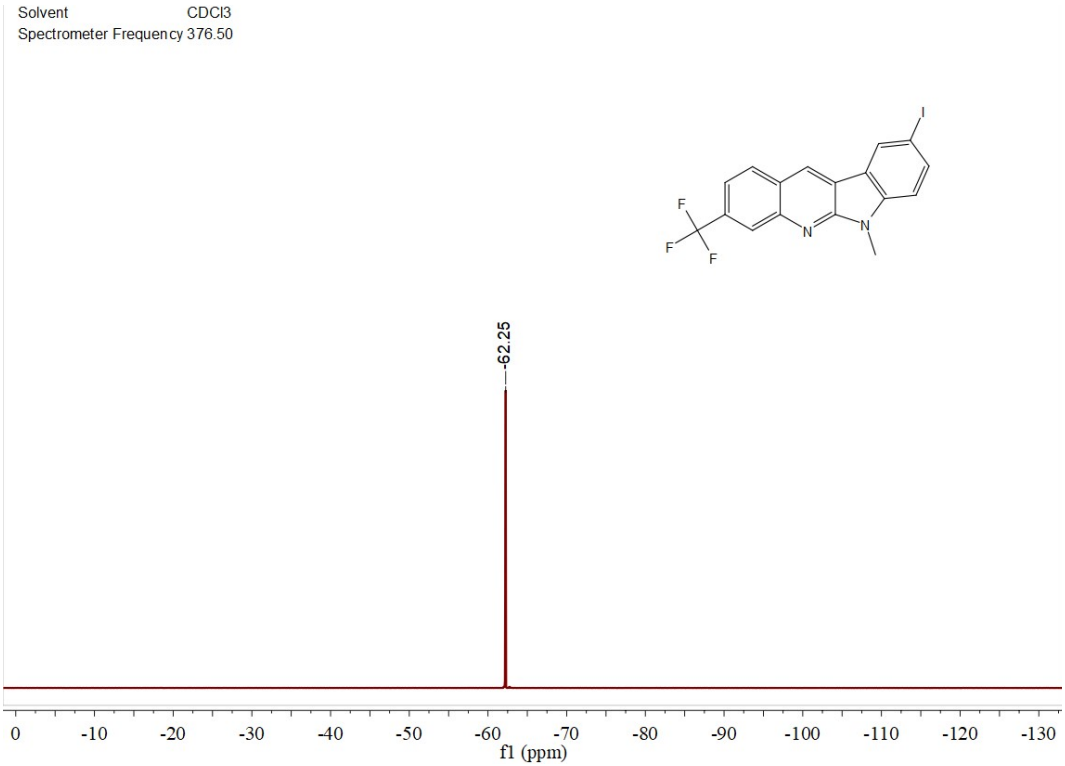
^{1}H NMR spectrum of 3fa



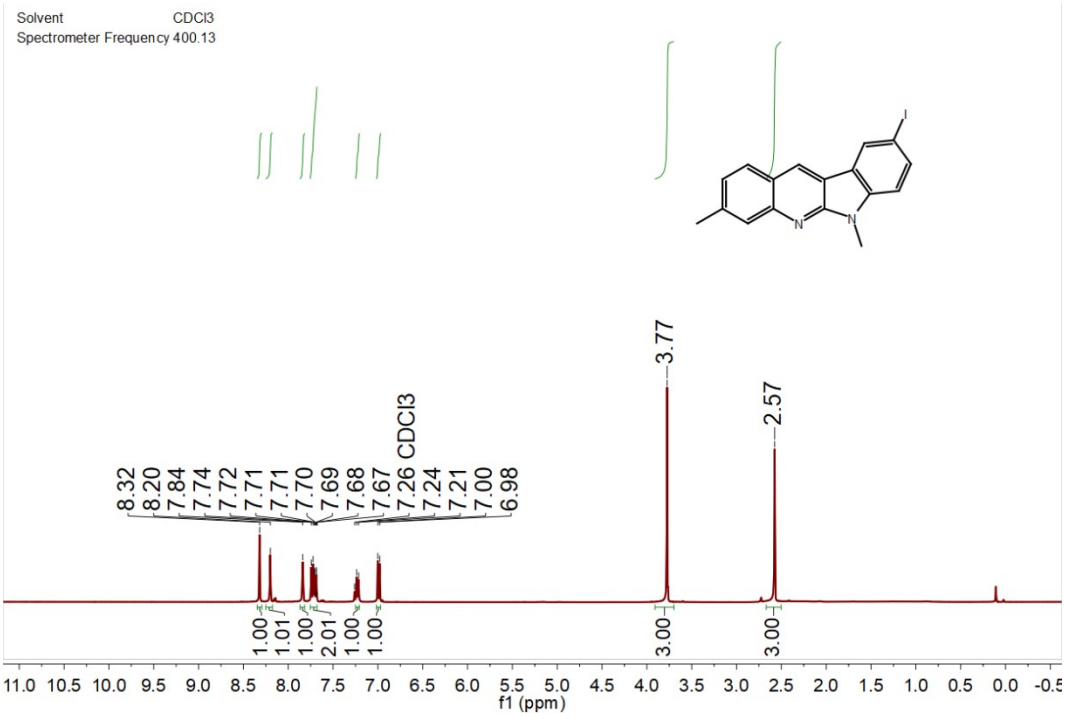
$^{13}C\{^{1}H\}$ NMR spectrum of 3fa



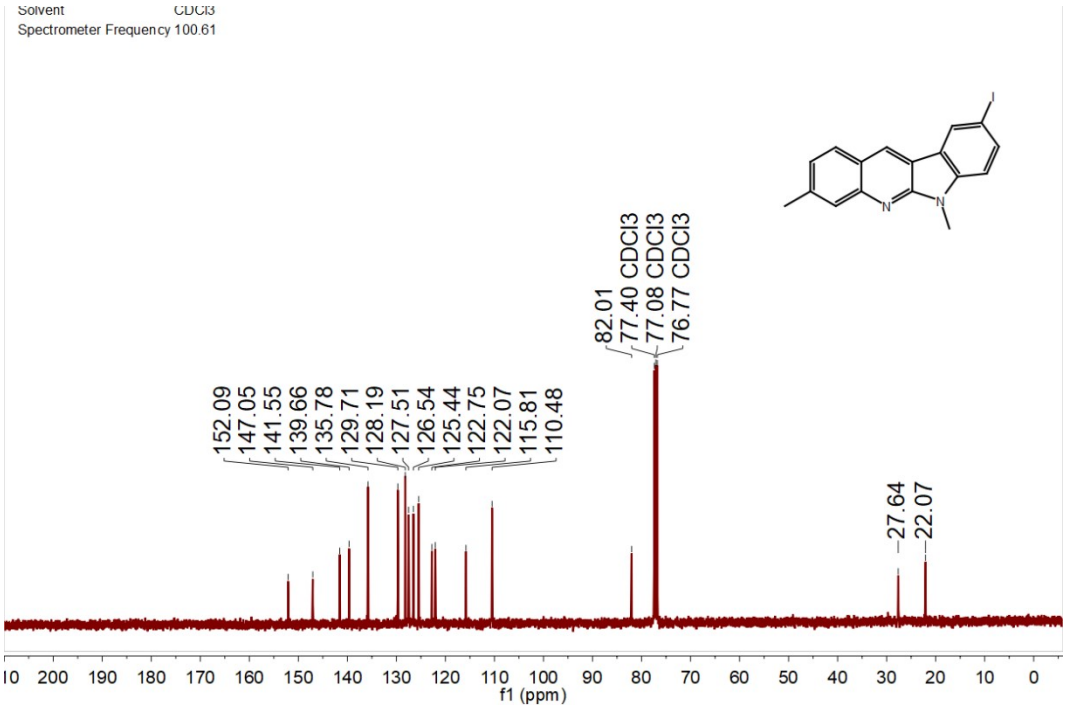
^{19}F NMR spectrum of 3fa



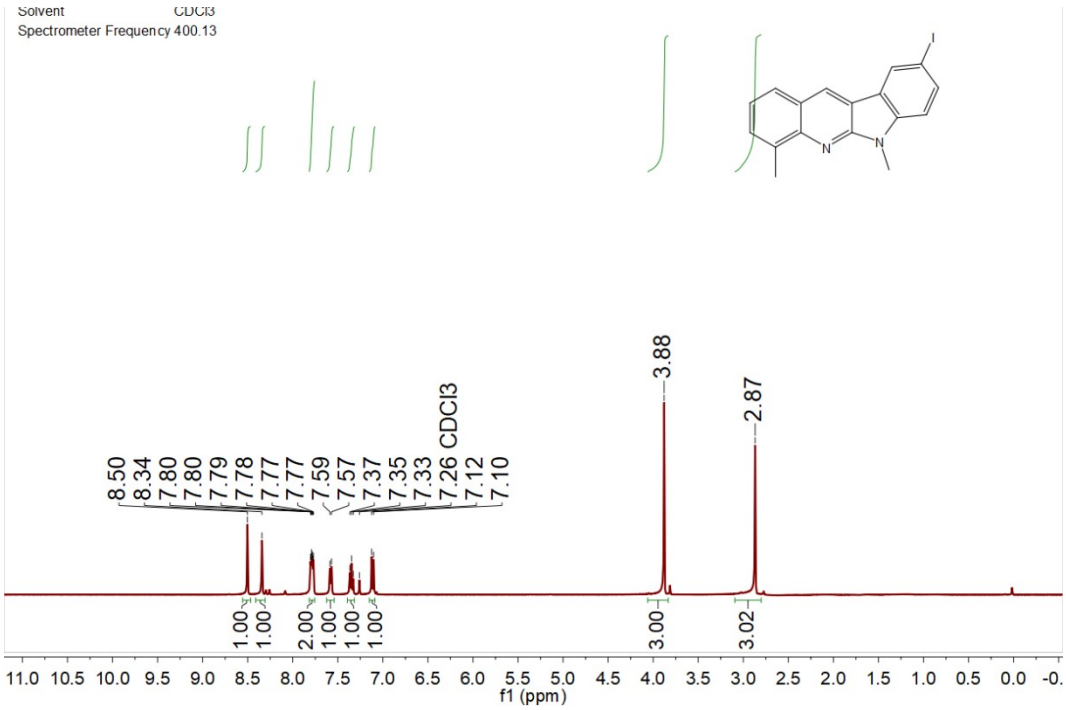
^{1}H NMR spectrum of 3ga



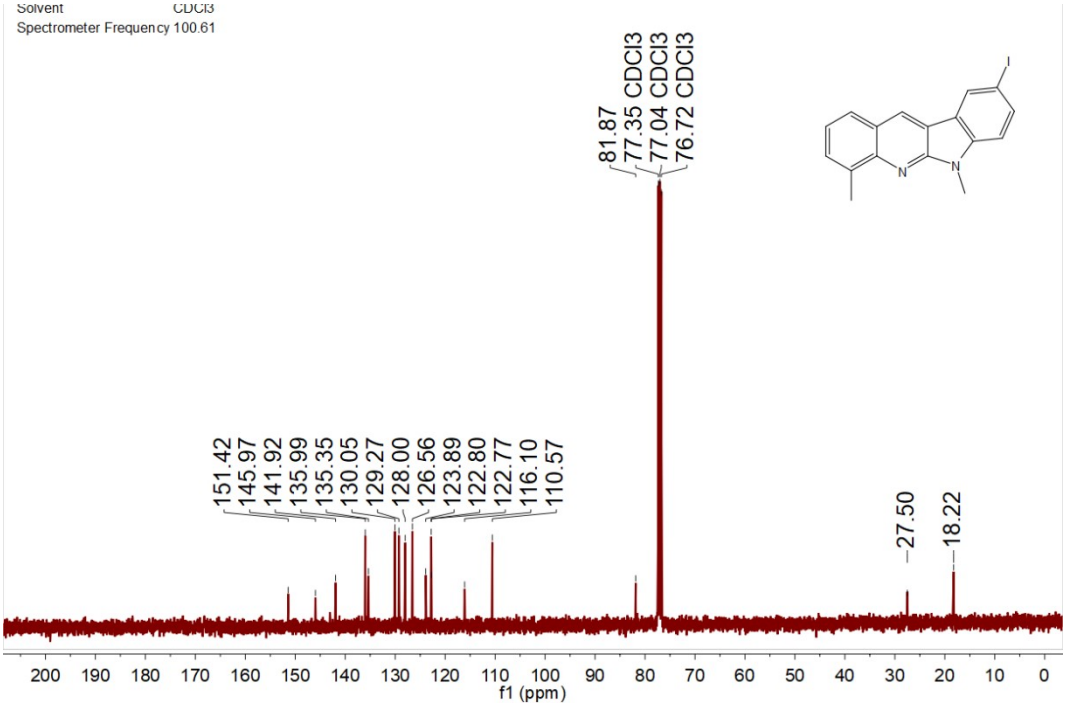
^{13}C{^{1}H} NMR spectrum of 3ga



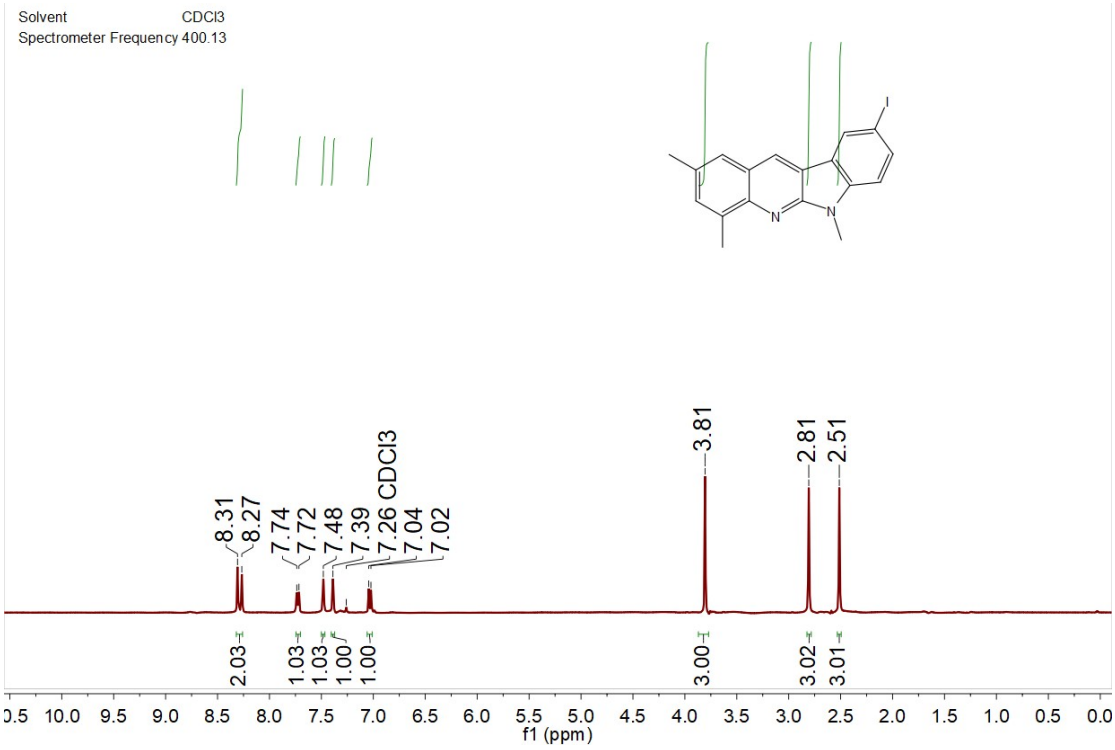
^{1}H NMR spectrum of 3ha



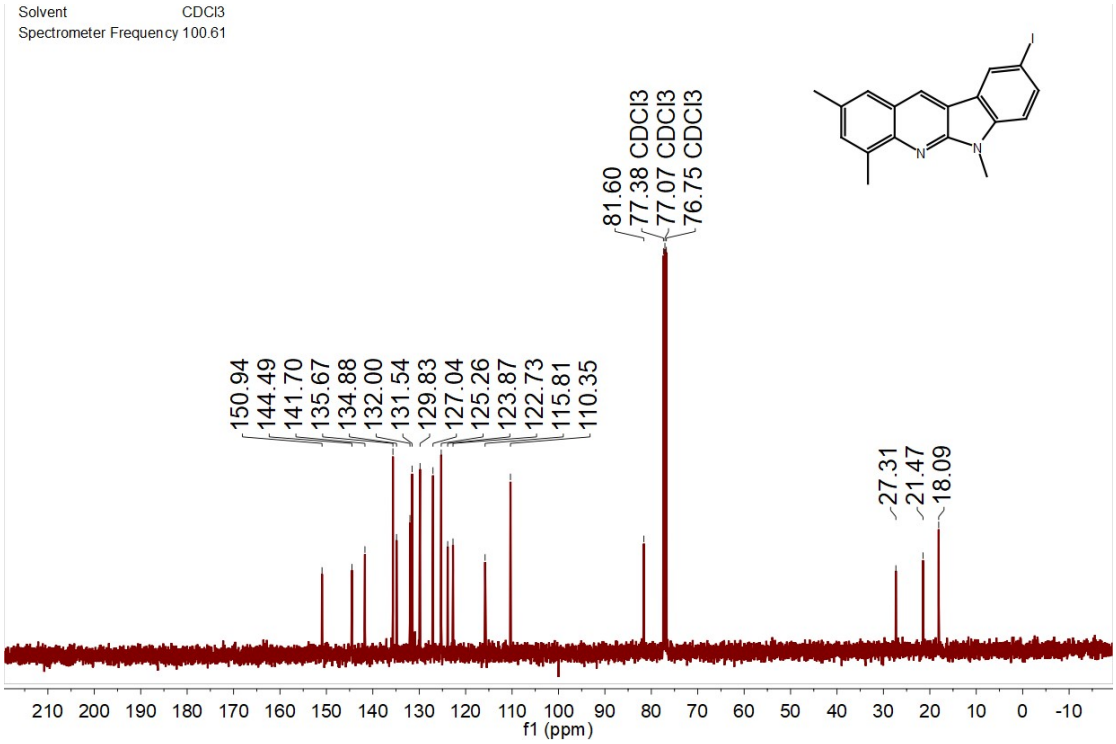
^{13}C{^{1}H} NMR spectrum of 3ha



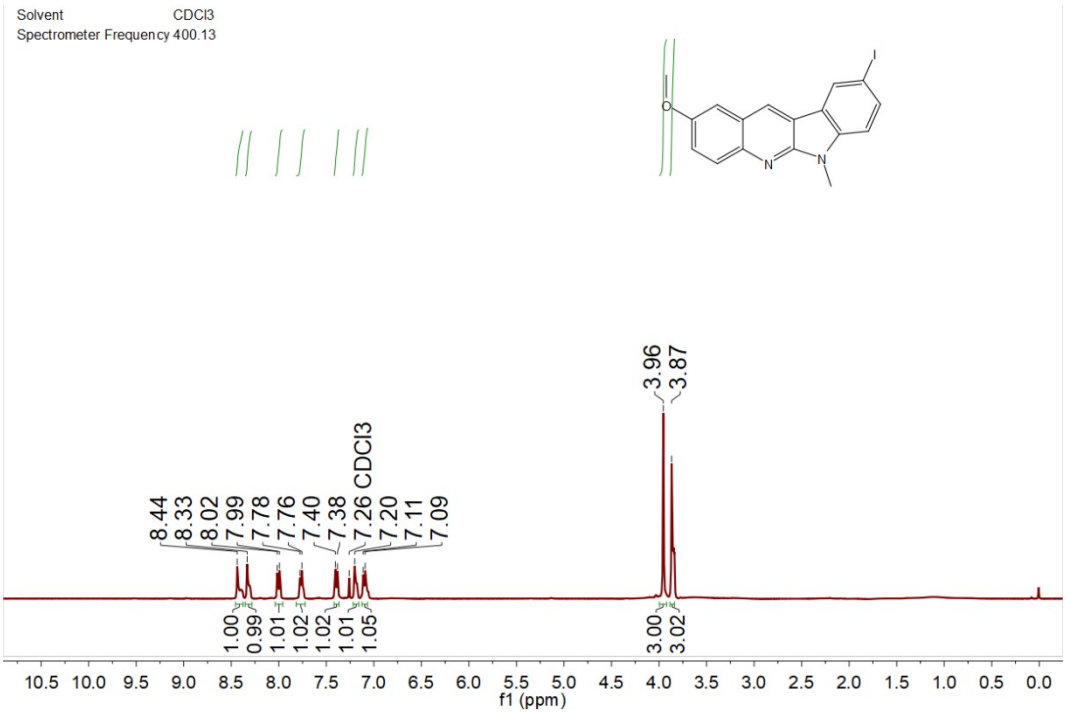
^{1}H NMR spectrum of 3ia



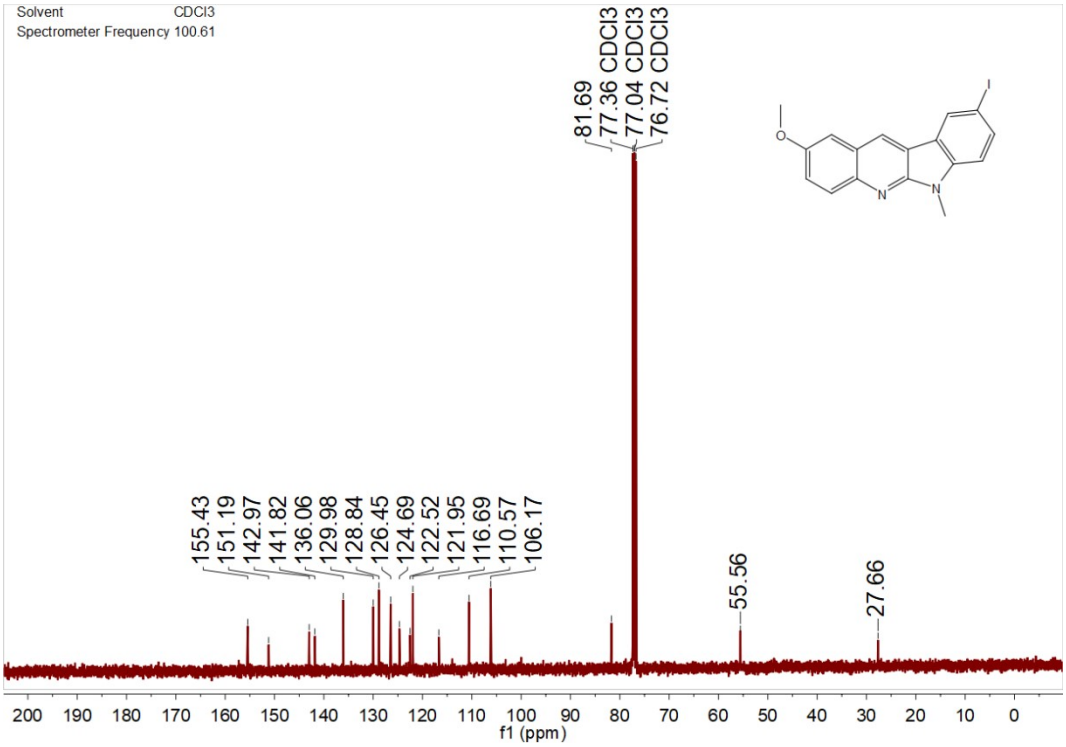
^{13}C{^{1}H} NMR spectrum of 3ia



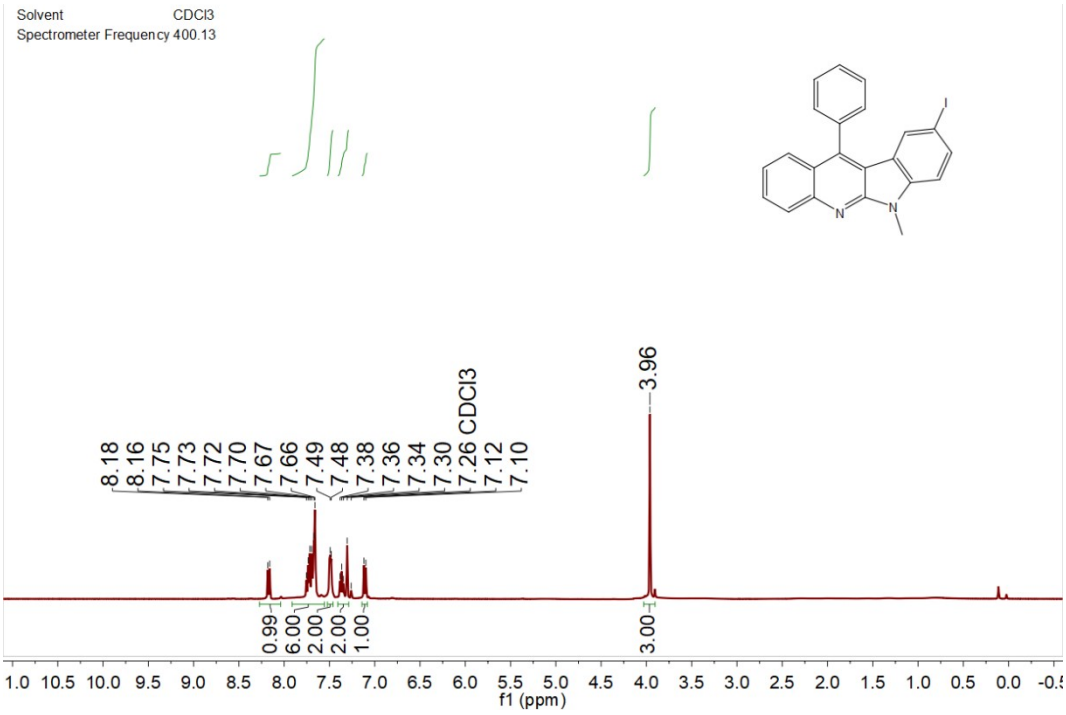
^{1}H NMR spectrum of 3ja



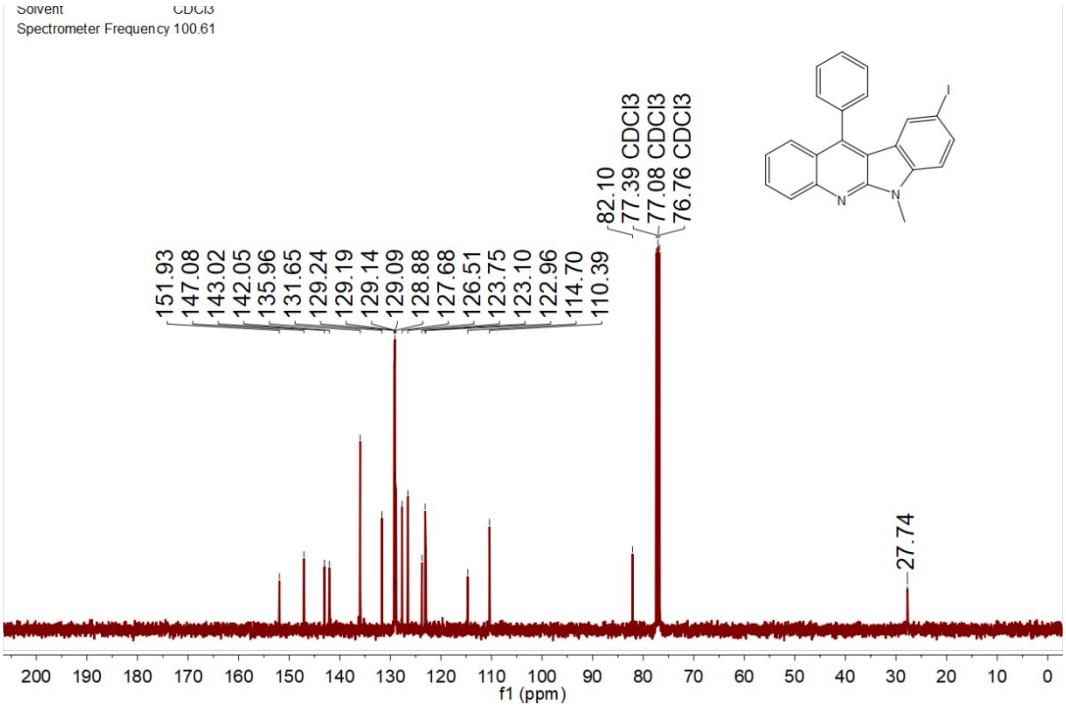
$^{13}C\{^{1}H\}$ NMR spectrum of 3ja



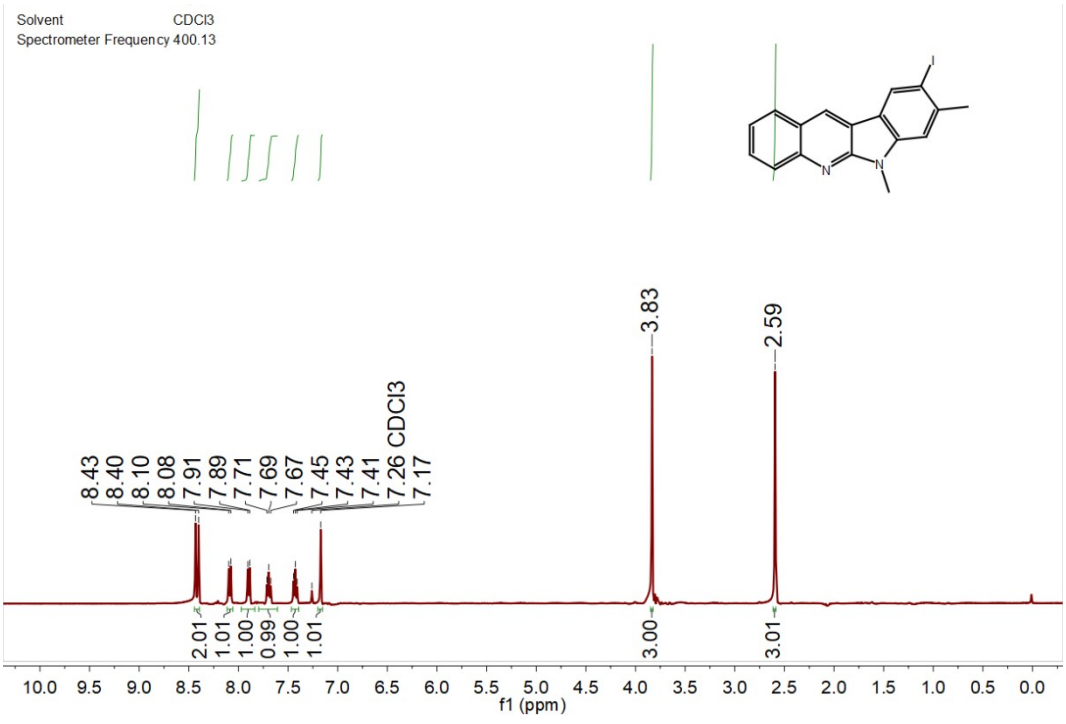
^{1}H NMR spectrum of 3ka



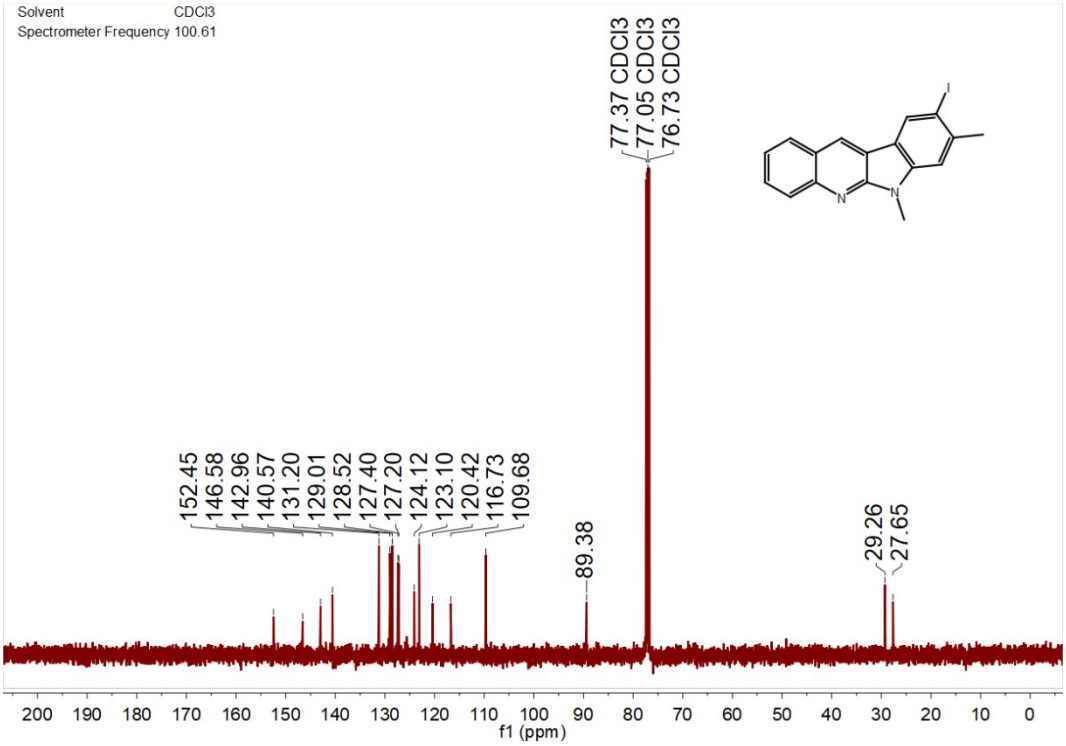
$^{13}C\{^{1}H\}$ NMR spectrum of 3ka



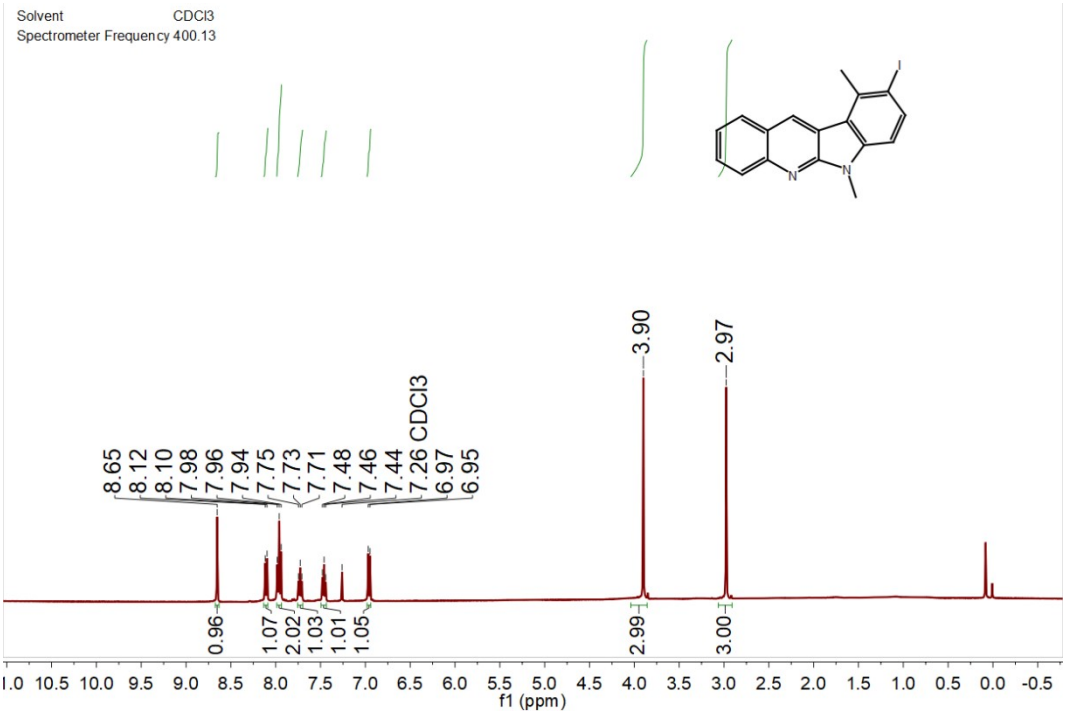
^{1}H NMR spectrum of 3ab



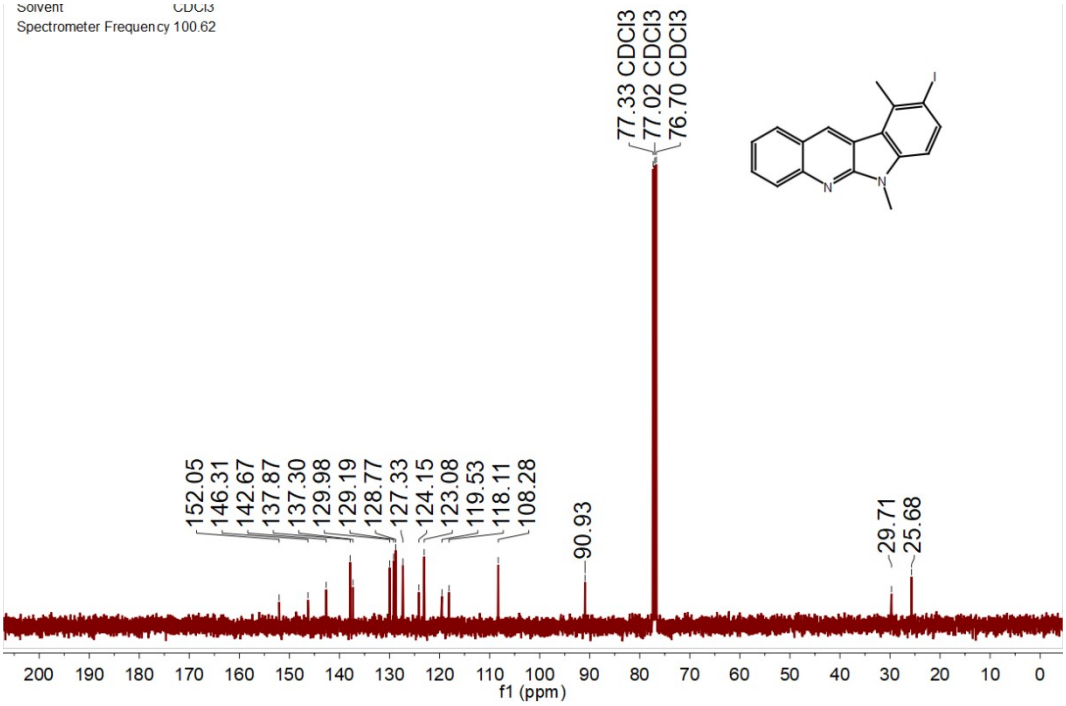
^{13}C{^{1}H} NMR spectrum of 3ab



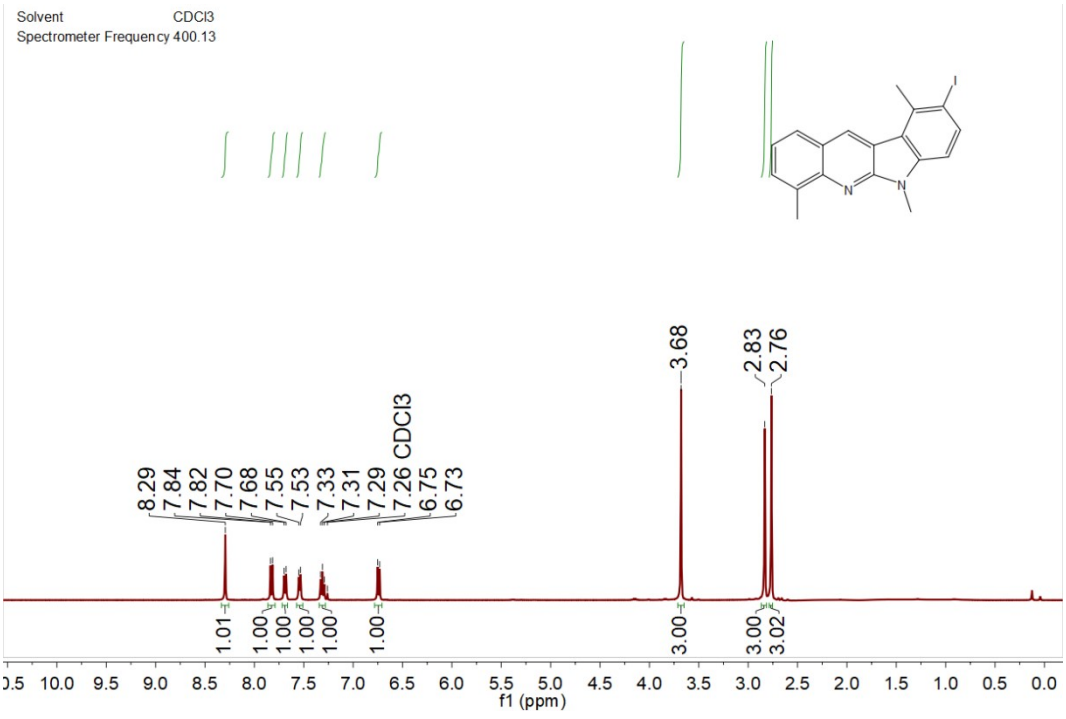
^{1}H NMR spectrum of 3ac



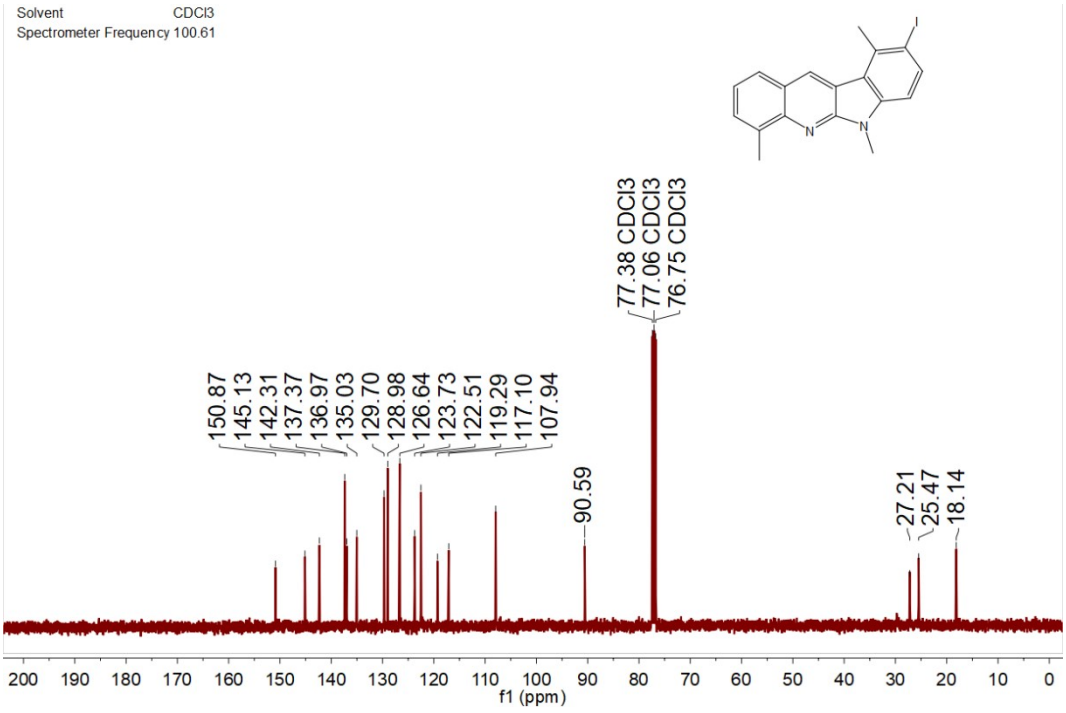
^{13}C{^{1}H} NMR spectrum of 3ac



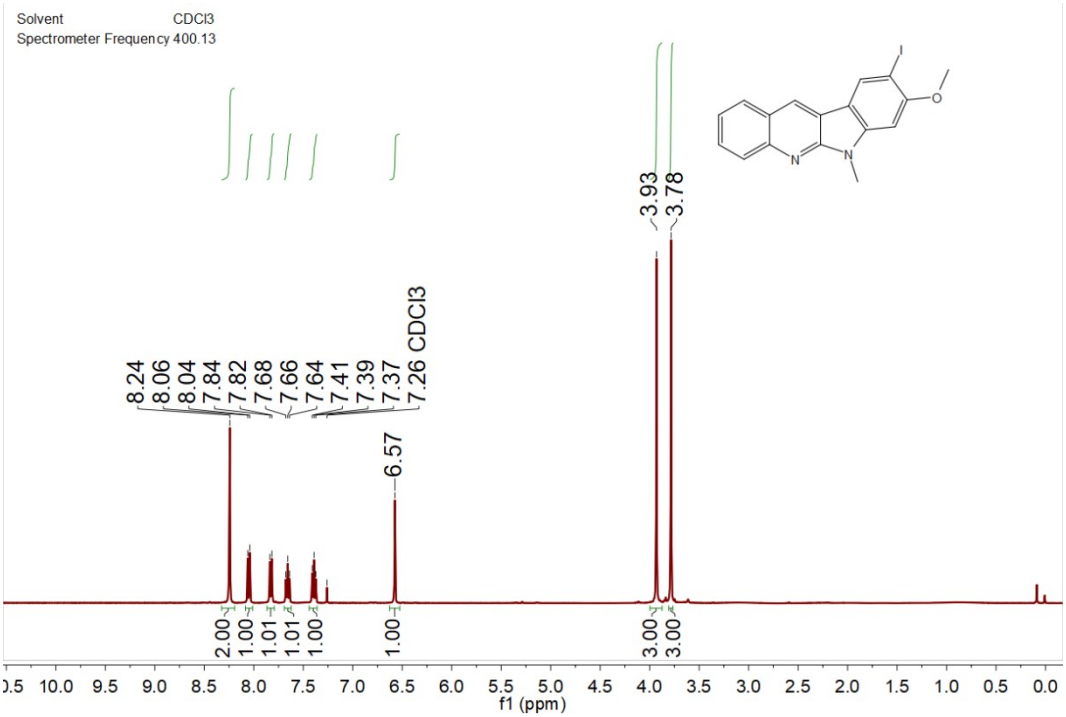
^{1}H NMR spectrum of 3hc



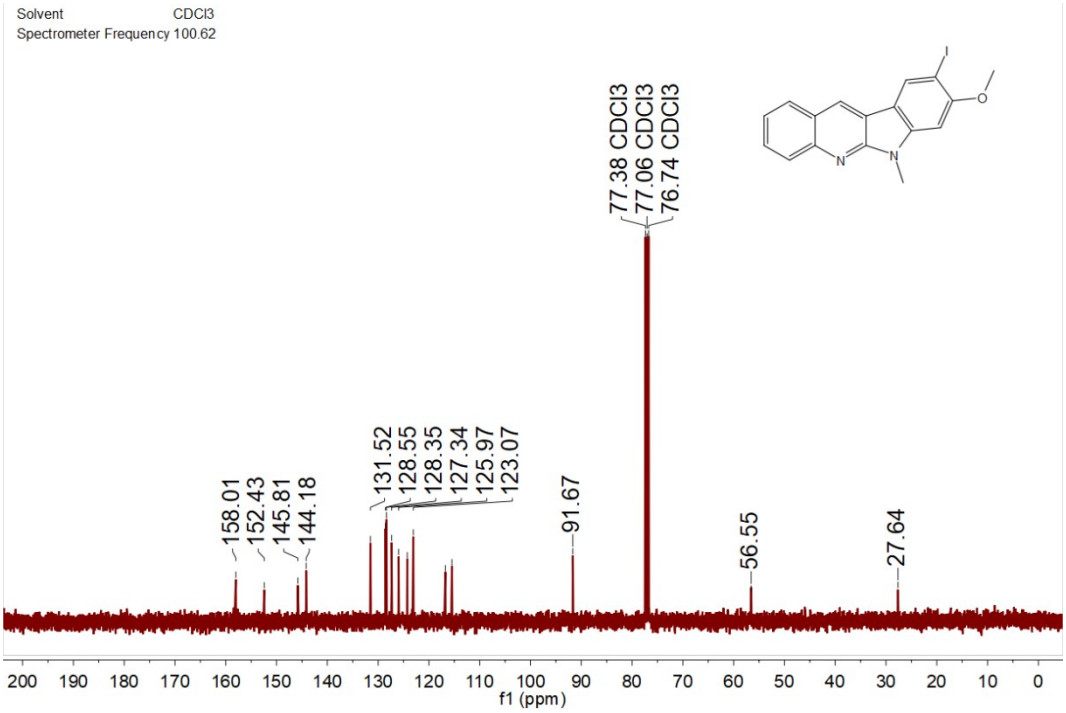
^{13}C{^{1}H} NMR spectrum of 3hc



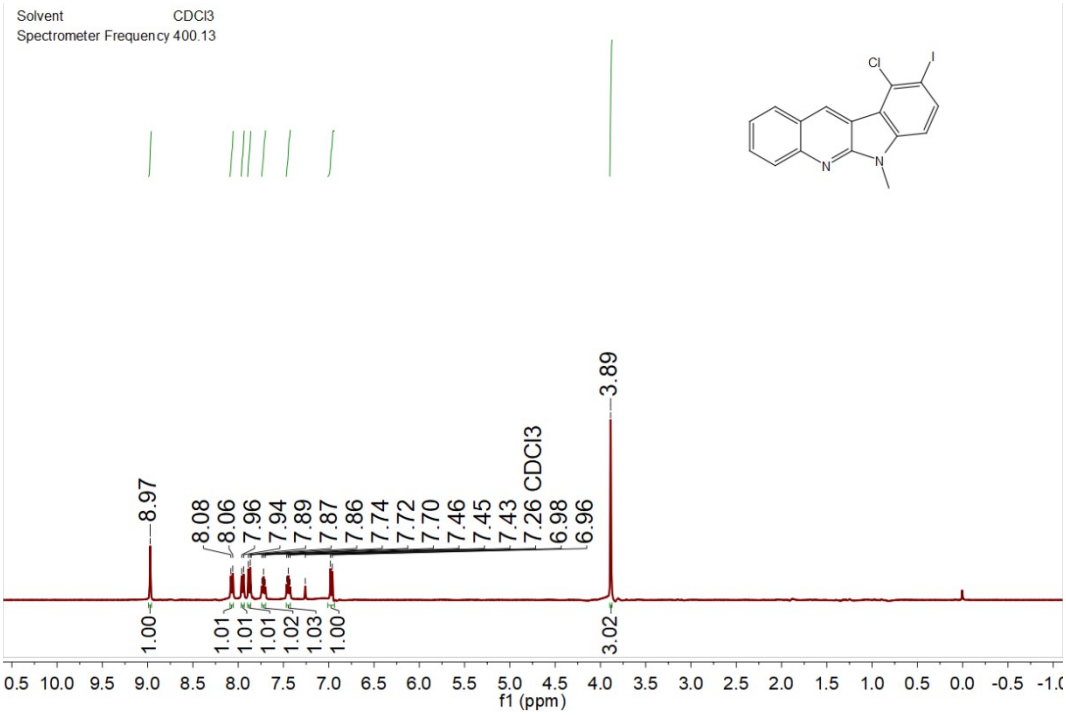
^{1}H NMR spectrum of 3ad



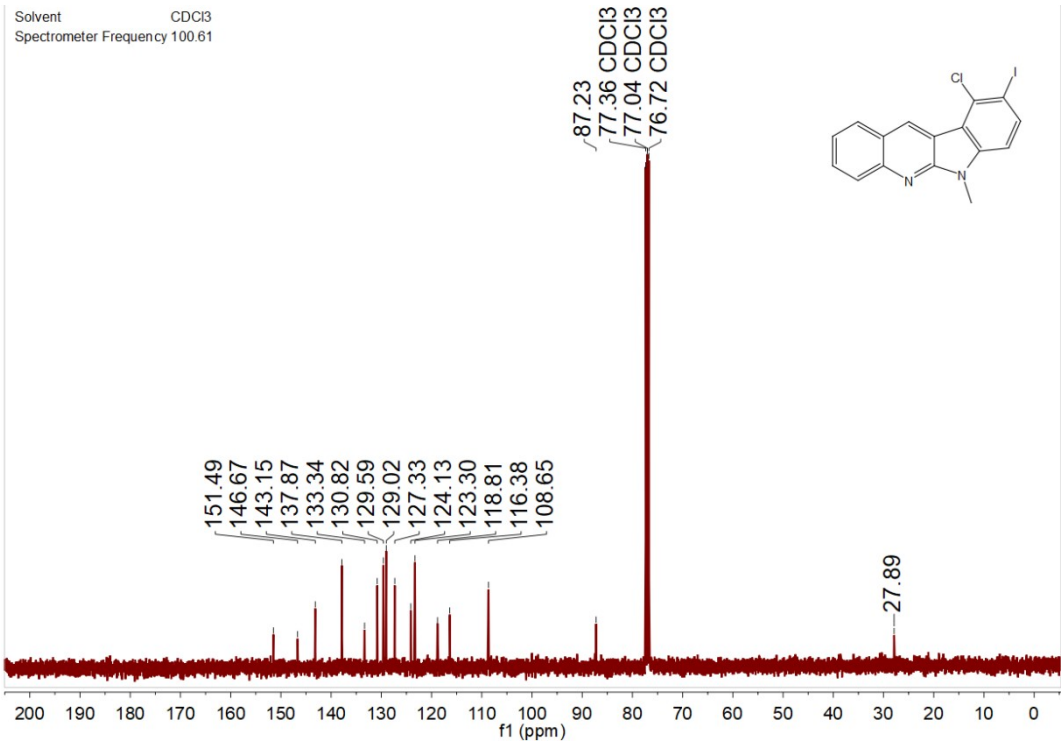
^{13}C{^{1}H} NMR spectrum of 3ad



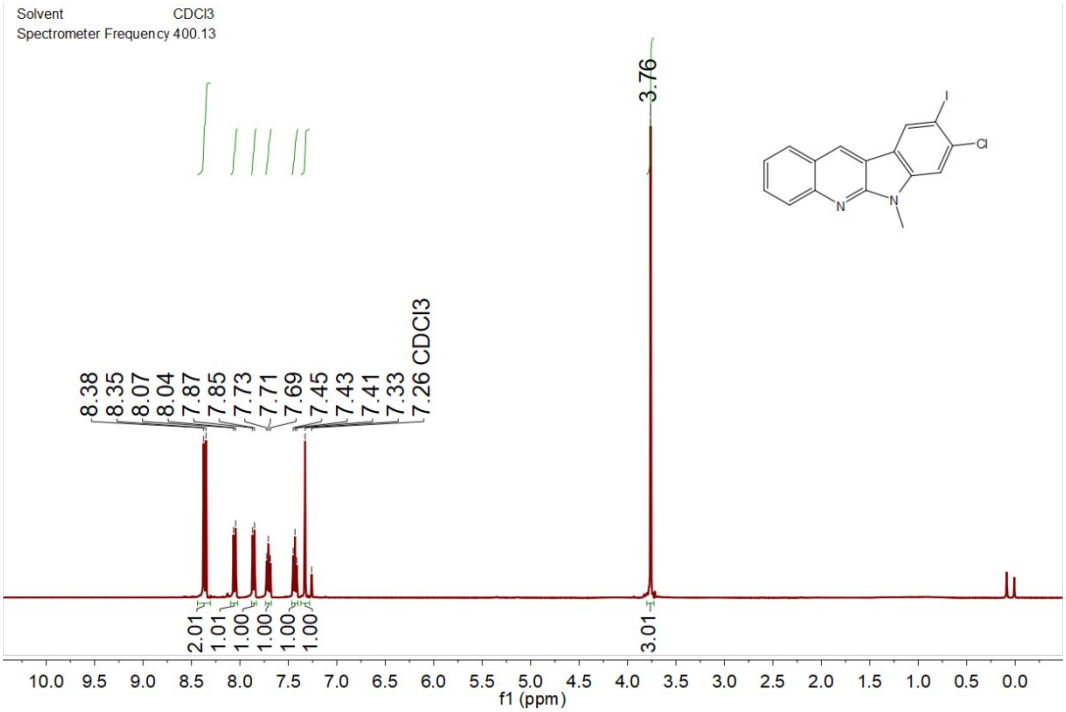
^{1}H NMR spectrum of 3ae



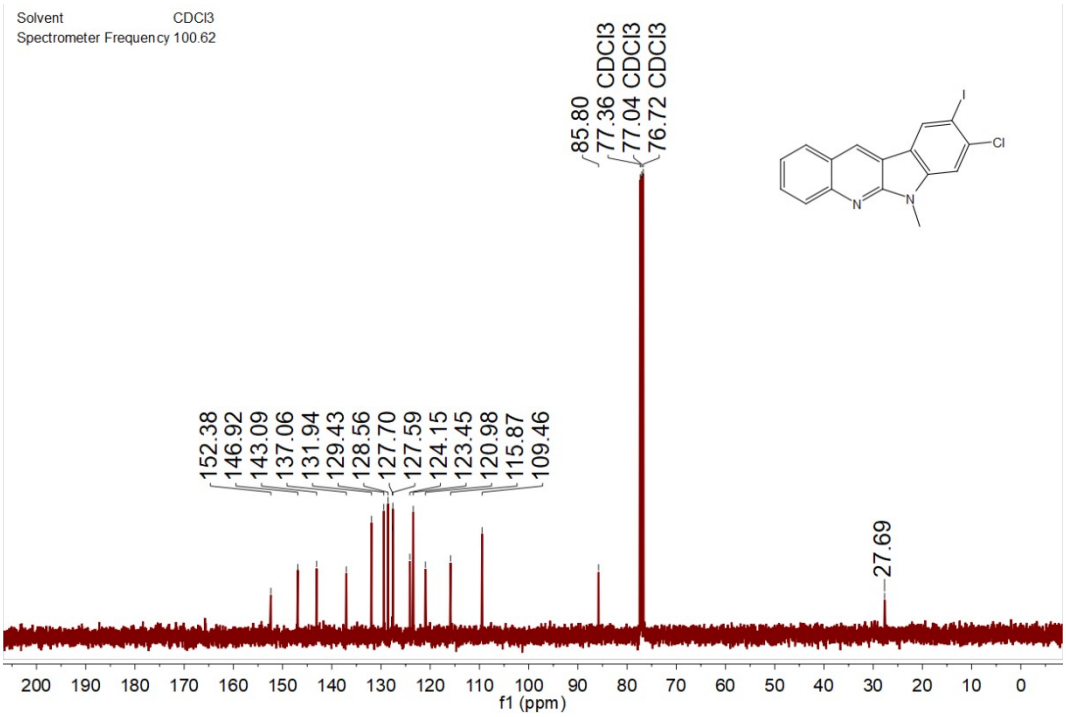
^{13}C{^{1}H} NMR spectrum of 3ae



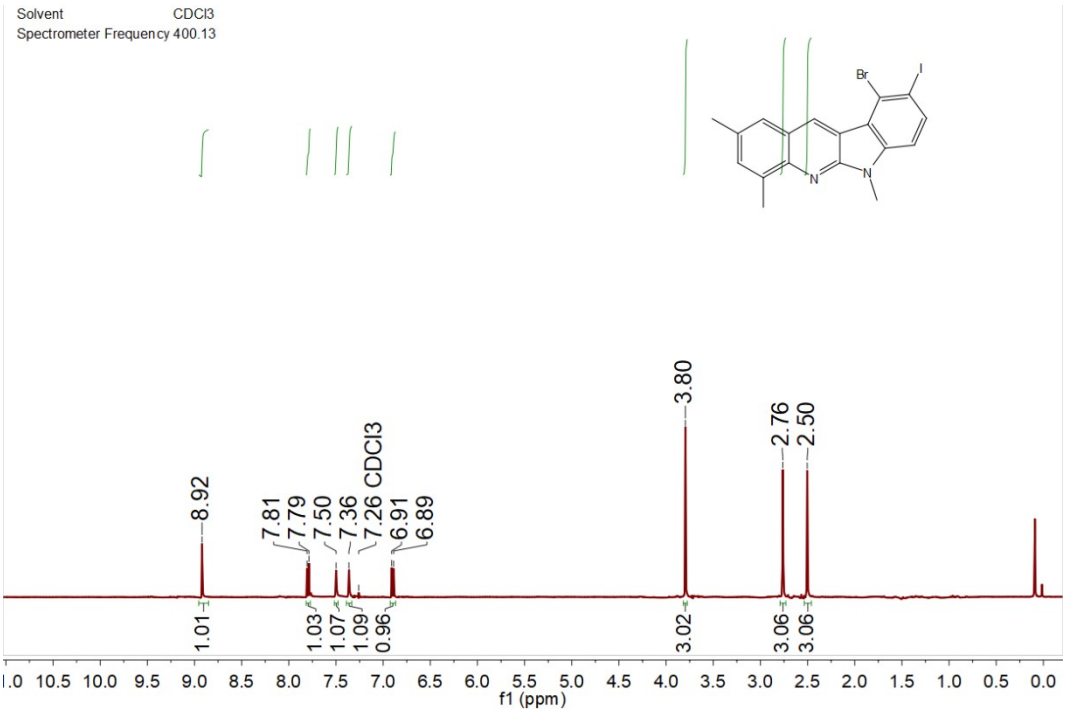
^{1}H NMR spectrum of 3af



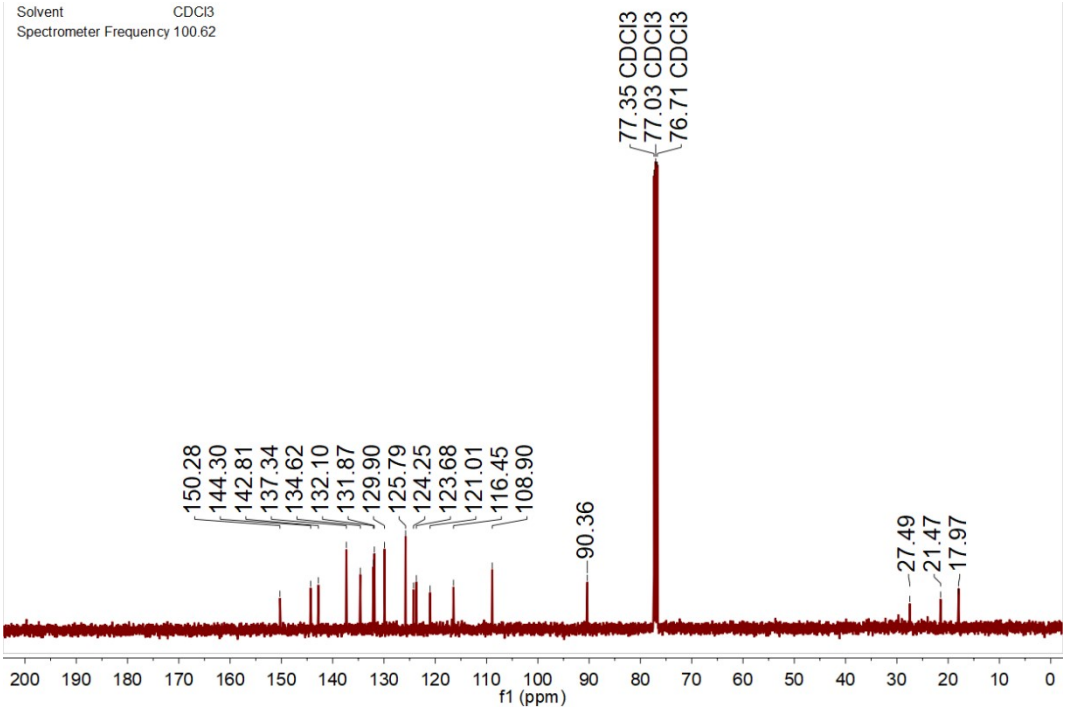
$^{13}C\{^{1}H\}$ NMR spectrum of 3af



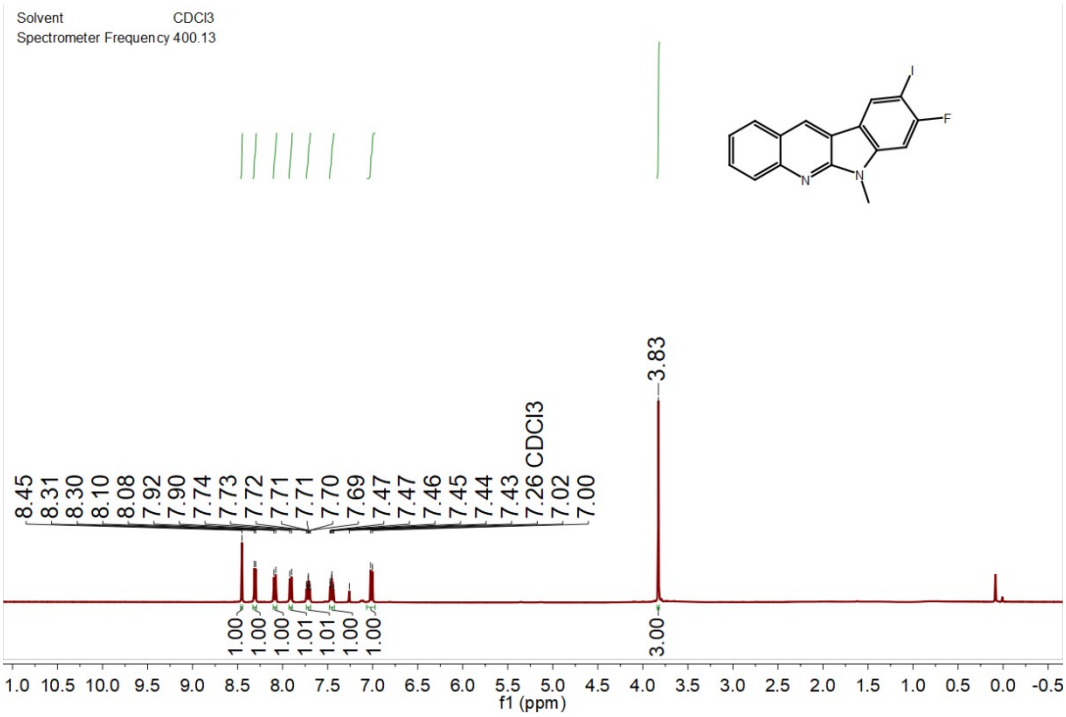
^{1}H NMR spectrum of 3ig



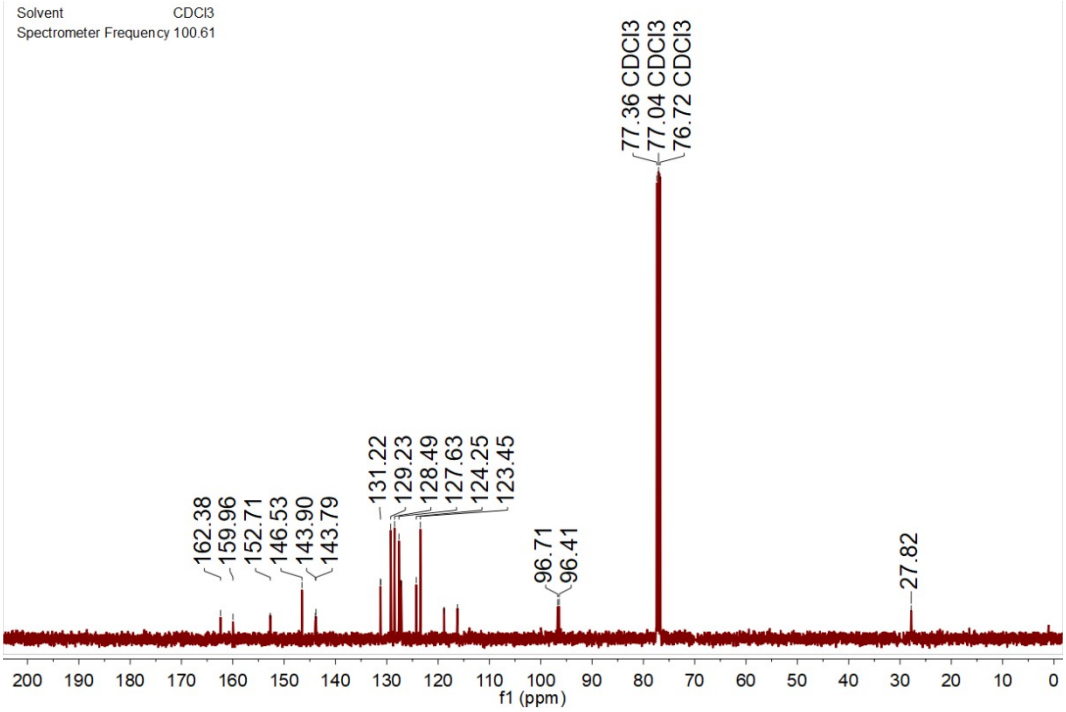
$^{13}C\{^{1}H\}$ NMR spectrum of 3ig



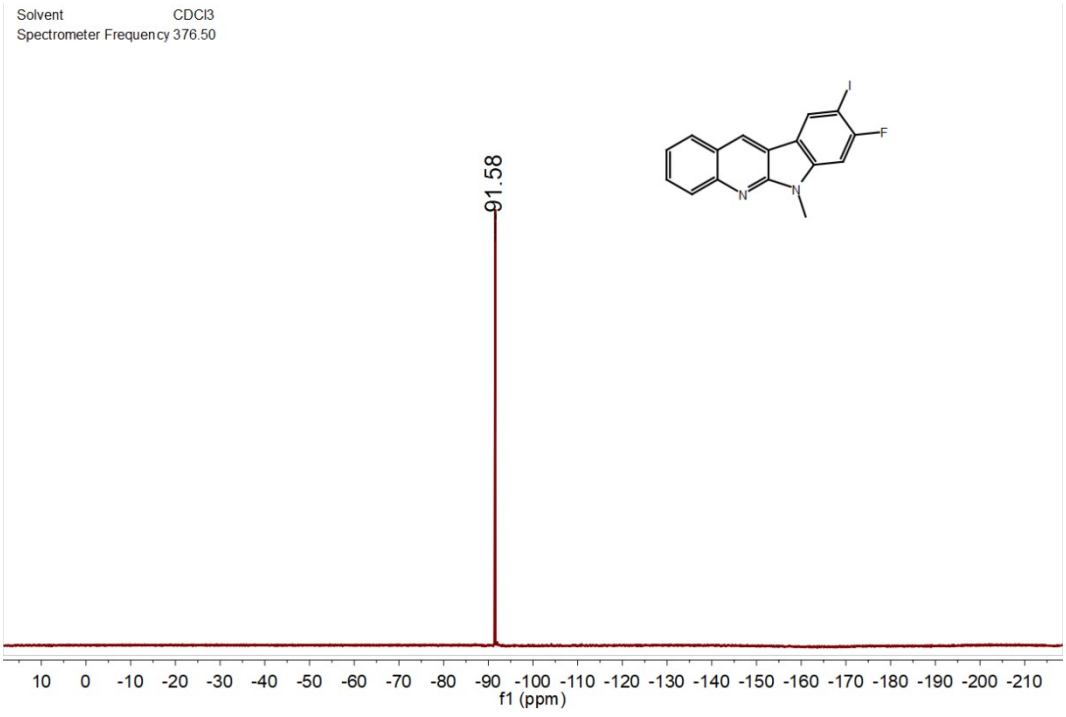
^{1}H NMR spectrum of 3ah



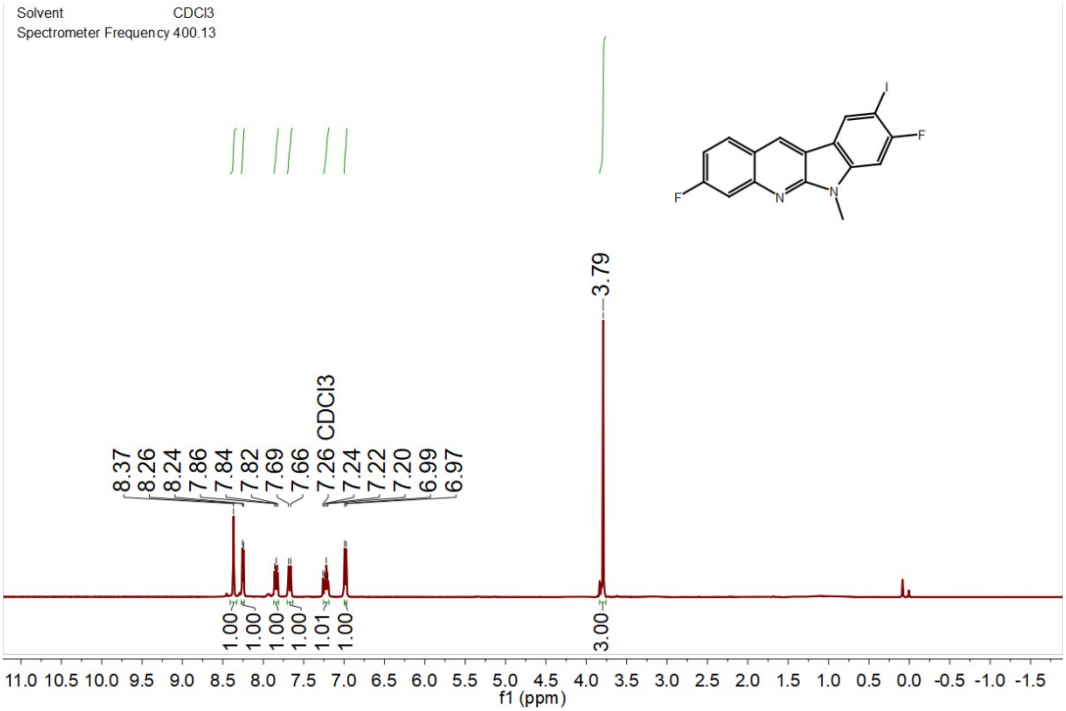
$^{13}C\{^{1}H\}$ NMR spectrum of 3ah



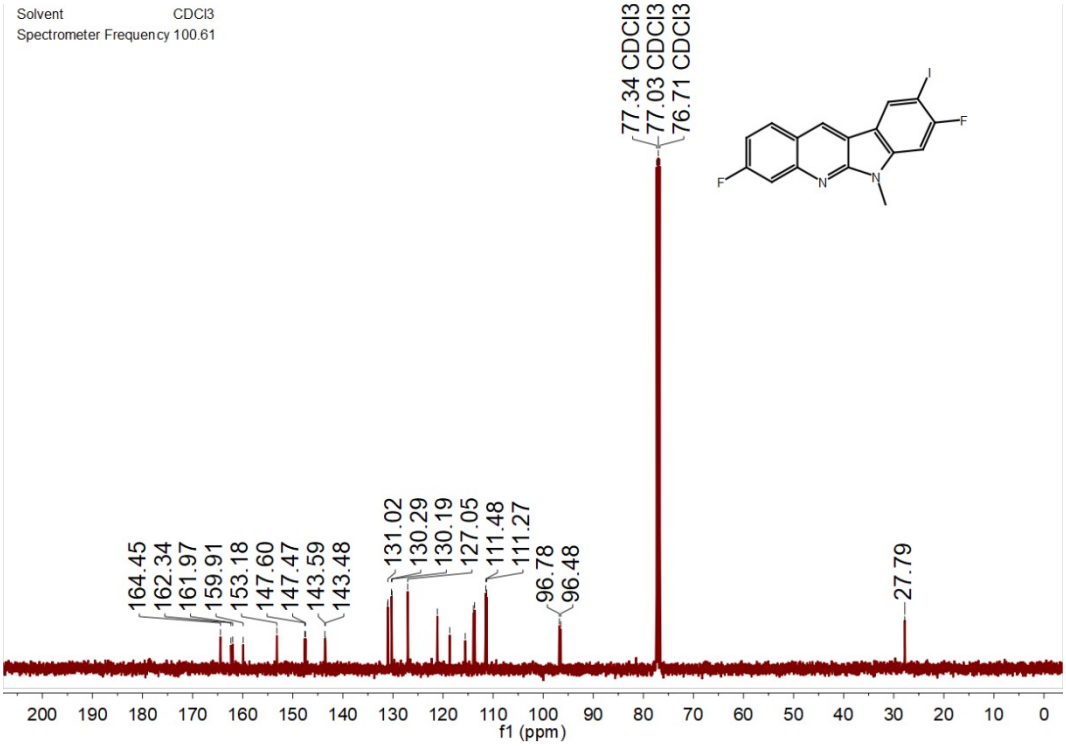
^{19}F NMR spectrum of 3ah



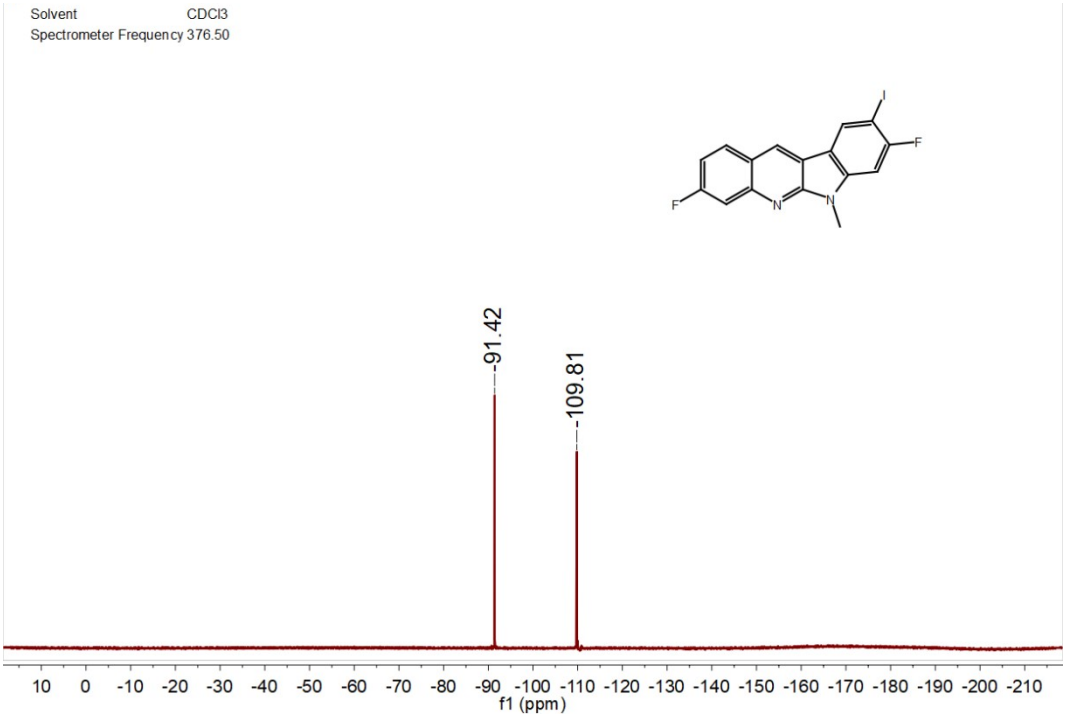
^{1}H NMR spectrum of 3dh



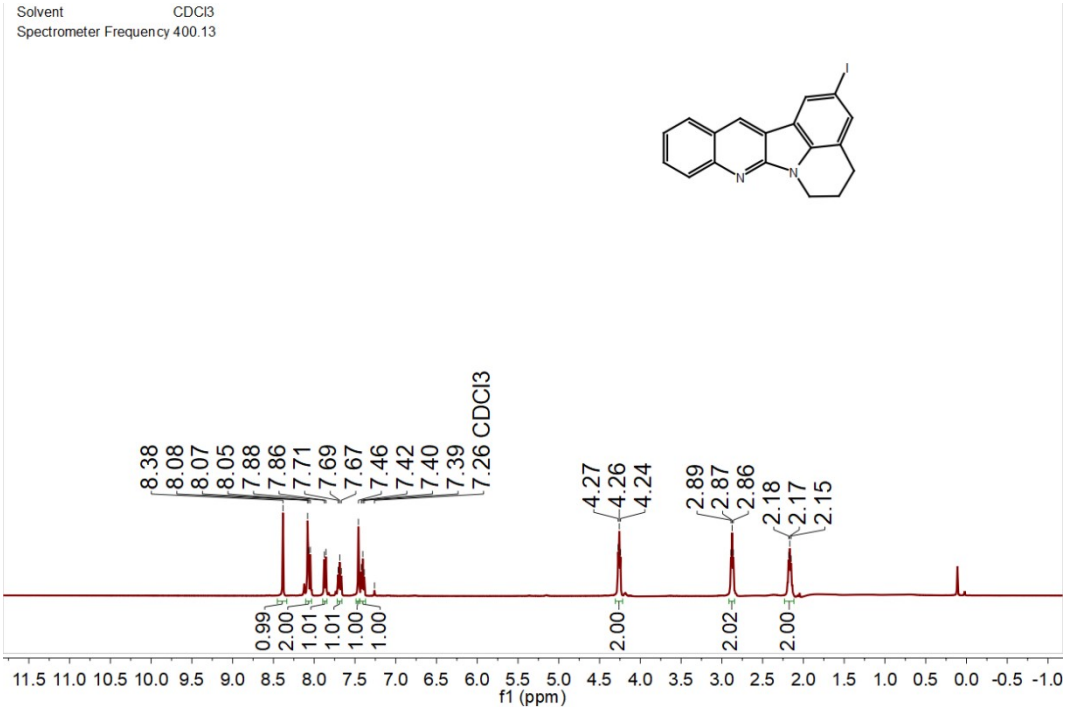
^{13}C{^{1}H} NMR spectrum of 3dh



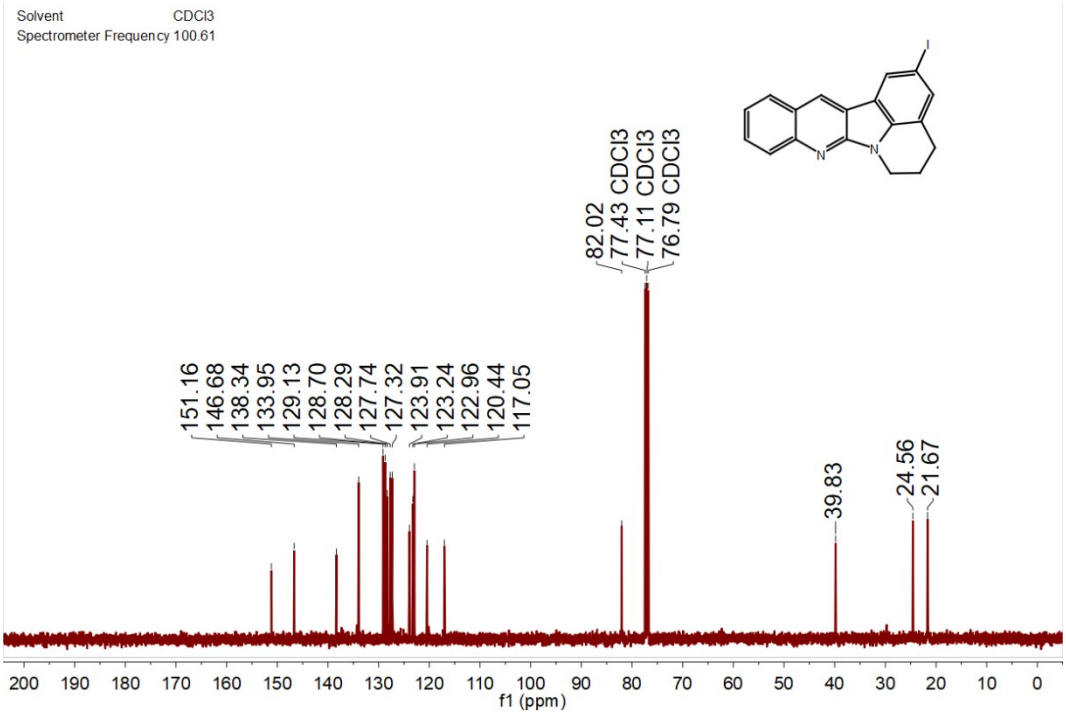
^{19}F NMR spectrum of 3dh



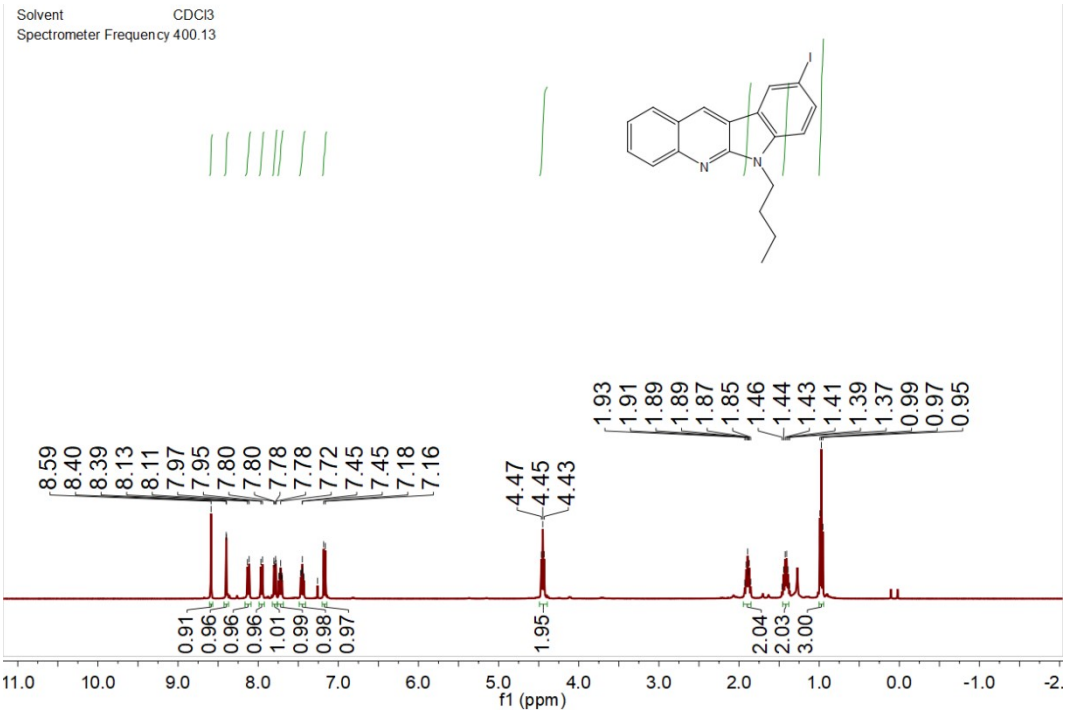
^{1}H NMR spectrum of 3ai



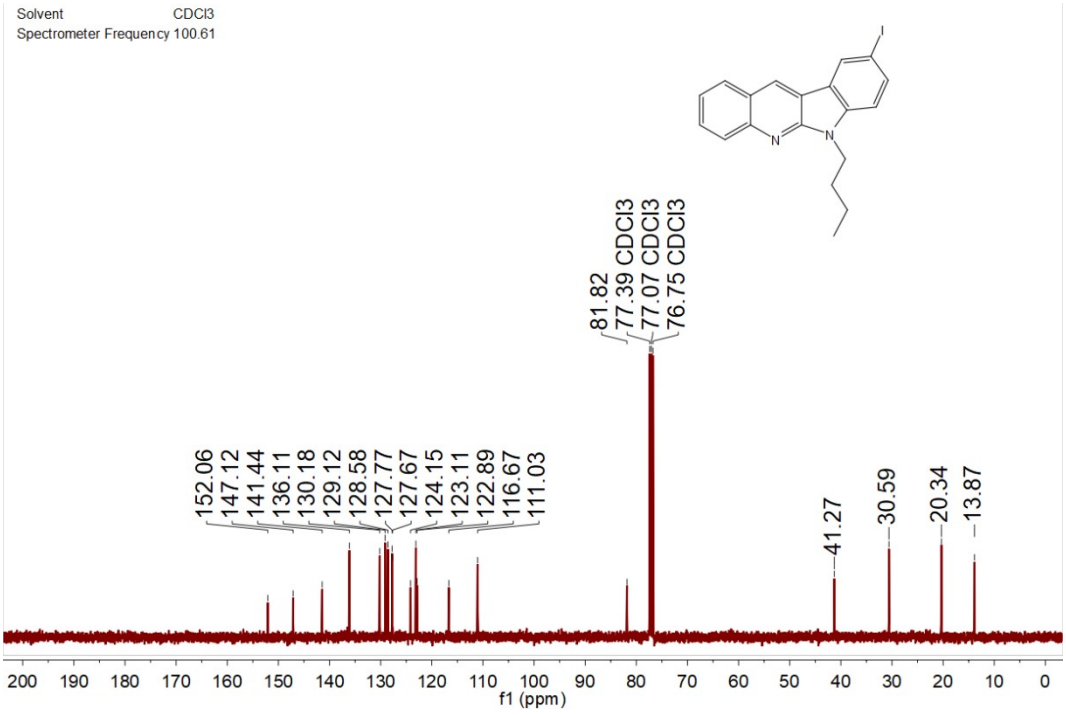
$^{13}C\{^{1}H\}$ NMR spectrum of 3ai



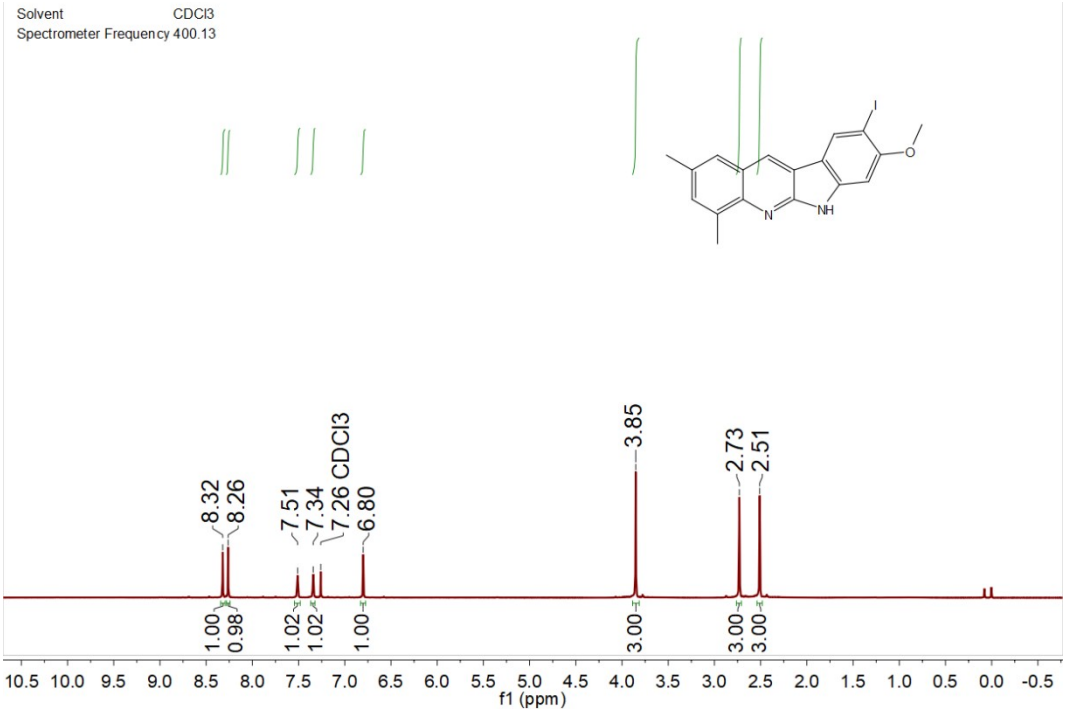
^{1}H NMR spectrum of 3aj



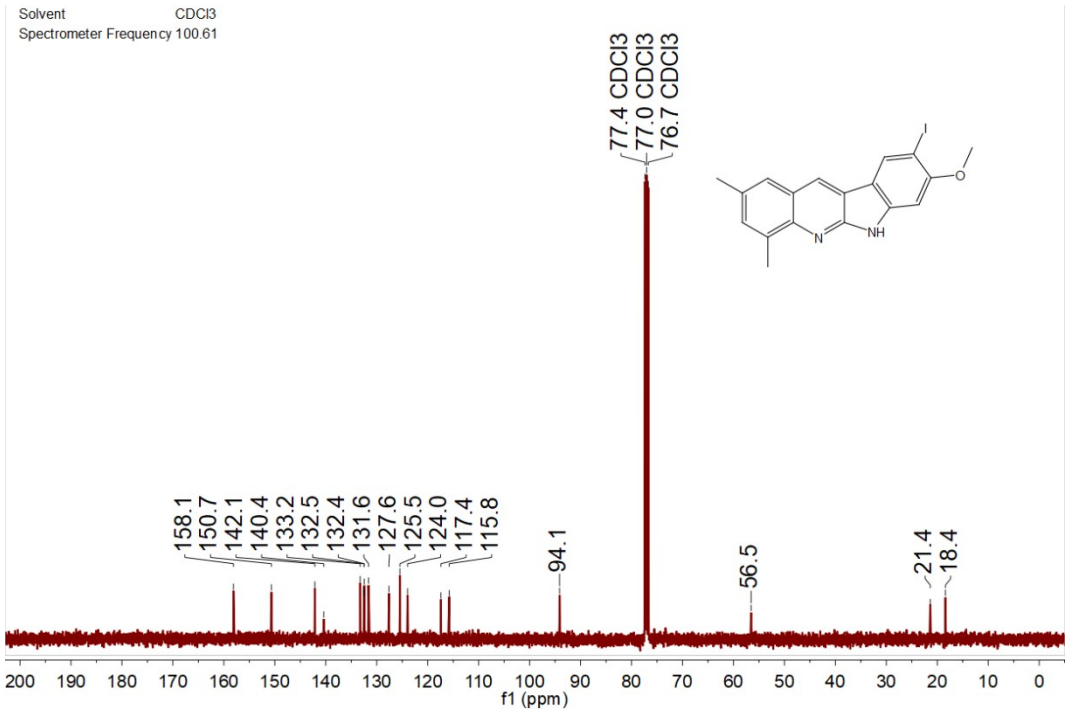
$^{13}C\{^{1}H\}$ NMR spectrum of 3aj



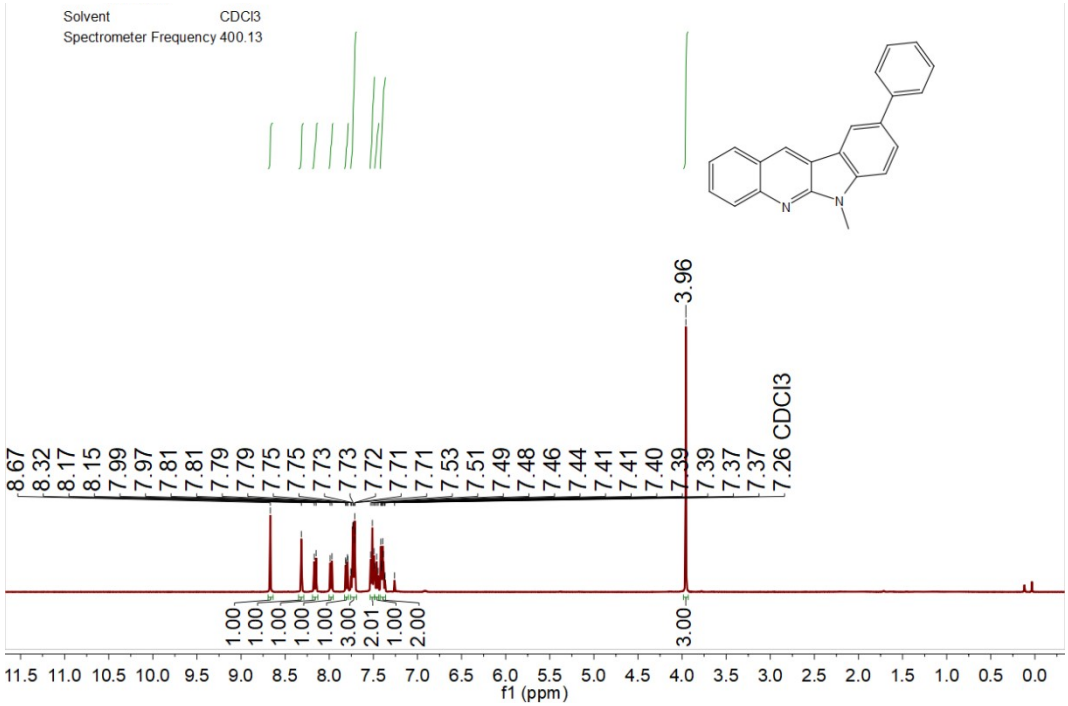
^{1}H NMR spectrum of 3ik



$^{13}C\{^{1}H\}$ NMR spectrum of 3ik



^{1}H NMR spectrum of 5



$^{13}C\{^{1}H\}$ NMR spectrum of 5