Supporting information for

Electrochemical cross-dehydrogenative coupling of isochroman with sulfonamide and indole

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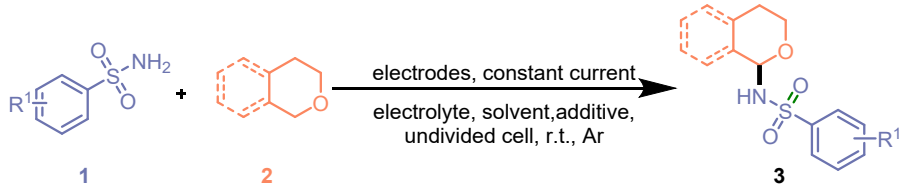
1. General Information

All reagents were used in analytical grades and were obtained from commercial sources without further purification unless otherwise noted. Solvents used in all experiments were dried and degassed by standard methods.[1] Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum plates with F-254 indicator, visualized by irradiation with UV light. Flash chromatography columns were packed with 200-300 mesh silica gel which was purchased from Qing Dao Hai Yang Chemical Industry. Digital Single Channel Adjustable Automatic Electronic Pipette Micropipette dPettee+ were purchased from Dragon Laboratory Instruments Limited. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz relative to tetramethylsilane as internal standard (δ = 0 ppm). For the ^{19}F spectra, α-trifluorotoluene served as external standard (δ = -63.9 ppm). High resolution mass spectra (HRMS) were obtained on a waters UPLC G2-XS Qtof spectrometer (Waters World Science & Technology Co., Ltd., Wilmslow, UK) using electrospray ionization (ESI). Low resolution mass spectrometry (LRMS) was obtained on Agilent 1260-6120 single quadrupole LC-MS using electrospray ionization (ESI). The Cyclic voltammetry (CV) was recorded in CH_3CN by CHI1040C. Electrolysis was conducted using a DC power supply (MWSTEK DP3005B) in constant current mode. The anode electrode is graphite rod (Φ = 6 mm) and cathode electrode is tungsten electrode (10 mm × 10 mm × 0.2 mm). The X-ray single-crystal structure was determined by a GeminiE X-ray single-crystal diffractometer (Oxford Diffraction Limited, Oxford, UK).

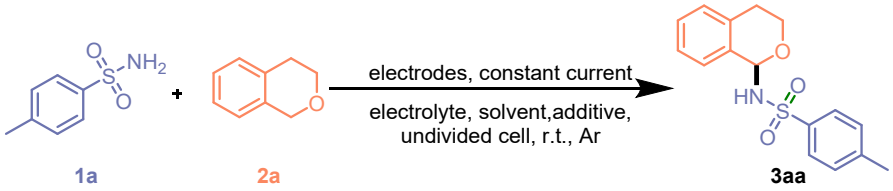
2. Experimental Procedures

2.1 General procedure for synthesis of *N*-(isochroman-1-yl)methylbenzenesulfonamide



Compounds **1**, compounds **2**, acid, electrolyte and solvent were added to the over-dried 10 mL three-neck flask with an anode and a cathode. The doses of all reagents, additives and solvents are given in the manuscript. The reaction mixture was electrolyzed under the indicated constant current. After the reaction, the electrodes were rinsed with ethyl acetate (15 mL), which was combined with the reaction mixture. The reaction mixture was washed with 20 mL saturated saline water, then extracted with ethyl acetate (3×15 mL). The organic layer was dried by Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1:10 to 1:20, v/v) to give the desired products **3**.

Table S1: Optimization of the reaction conditions[a].

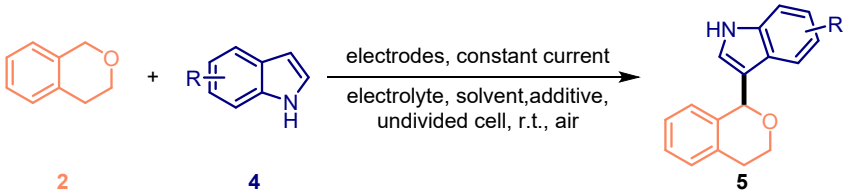


entry	electrode	electrolyte	additive	yield (%)
1[b]	C/W	*n*-Bu_4NBF_4	TFA	57
2[c]	C/W	*n*-Bu_4NBF_4	TFA	54
3[d]	C/W	*n*-Bu_4NBF_4	TFA	43
4[e]	C/W	*n*-Bu_4NBF_4	TFA	50
5	C/W	*n*-Bu_4NPF_6	TFA	58
6[f]	C/W	*n*-Bu_4NBF_4	AcOH	46
7[g]	C/W	*n*-Bu_4NBF_4	AcOH	35
8[h]	C/W	*n*-Bu_4NBF_4	AcOH	49

9[i]	C/W	*n*-Bu_4NBF_4	AcOH	36
10[j]	C/W	*n*-Bu_4NBF_4	AcOH	12
11[k]	C/W	*n*-Bu_4NBF_4	AcOH	trace
12[l]	C/W	*n*-Bu_4NBF_4	AcOH	52
13[m]	C/W	*n*-Bu_4NBF_4	AcOH	47

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (1.2 mmol, 4.0 equiv.), I = 15 mA, electrolyte (0.1 M), additive (0.3 mmol, 1.0 equiv.), MeCN (5 mL), at room temperature under Ar for 7 hours. Yields of isolated products are shown. [b]I = 12 mA, [c]I = 18 mA, 5 hours, [d]**2a** (0.9 mmol, 3.0 equiv.), [e]**2a** (1.5 mol, 5.0 equiv.), [f]additive (0.45 mmol, 1.5 equiv.), [g]additive (0.15 mmol, 0.5 equiv.), [h]CH_3COCH_3 instead of MeCN, [i]DCM instead of MeCN, [j]DMSO instead of MeCN, [k]EtOH instead of MeCN, [l]6 hours, [m]8 hours, [n]air instead of Ar.

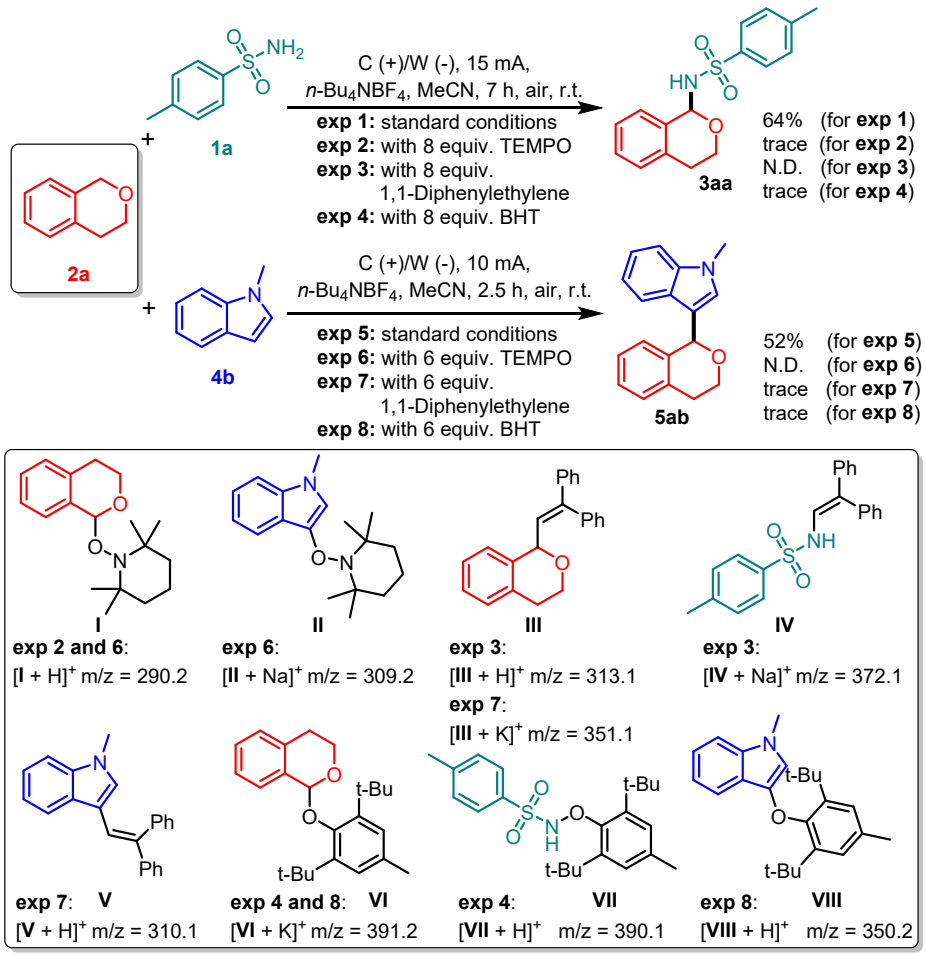
2.2 General procedure for synthesis of 3-(isochroman-1-yl)-1*H*-indole



2 4 5

Compounds **2**, compounds **4**, acid, electrolyte and solvent were added to the over-dried 10 mL three-neck flask with an anode and a cathode. The doses of all reagents, additives and solvents are given in the manuscript. The reaction mixture was electrolyzed under the indicated constant current. After the reaction, the electrodes were rinsed with ethyl acetate (15 mL), which was combined with the reaction mixture. The reaction mixture was washed with 20 mL saturated saline water, then extracted with ethyl acetate (3×15 mL). The organic layer was dried by Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1:12 to 1:10, v/v) to give the desired products **5**.

3. Control experiments



Scheme S1. Control experiments

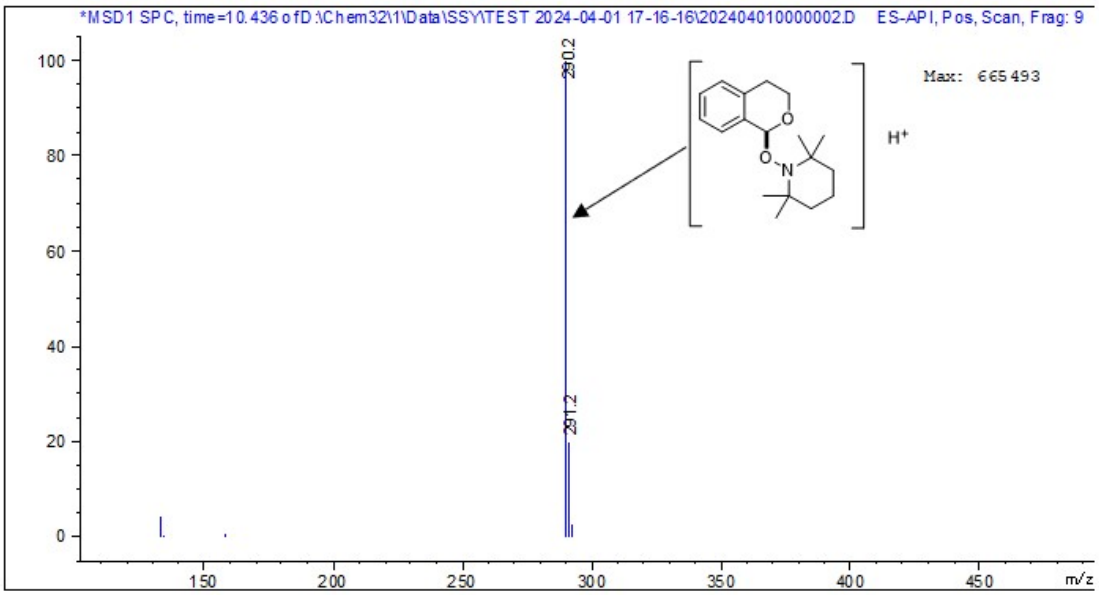


Figure S1. LC-MS spectrum of [**I** + H]$^+$ for **exp 2** and **exp 6**

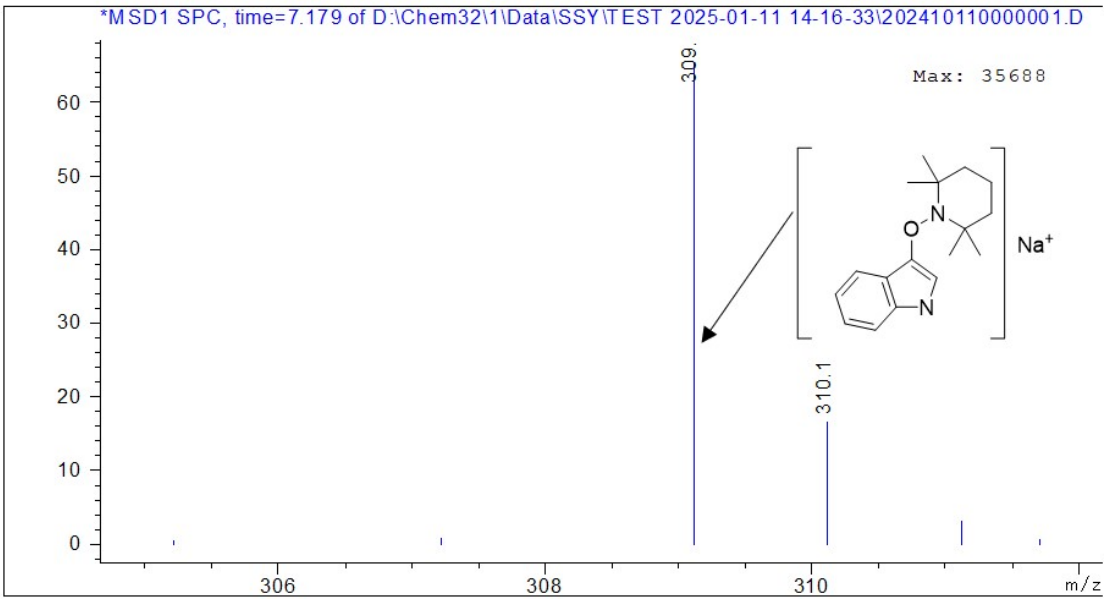


Figure S2. LC-MS spectrum of [**II** + Na]$^+$ for **exp 6**

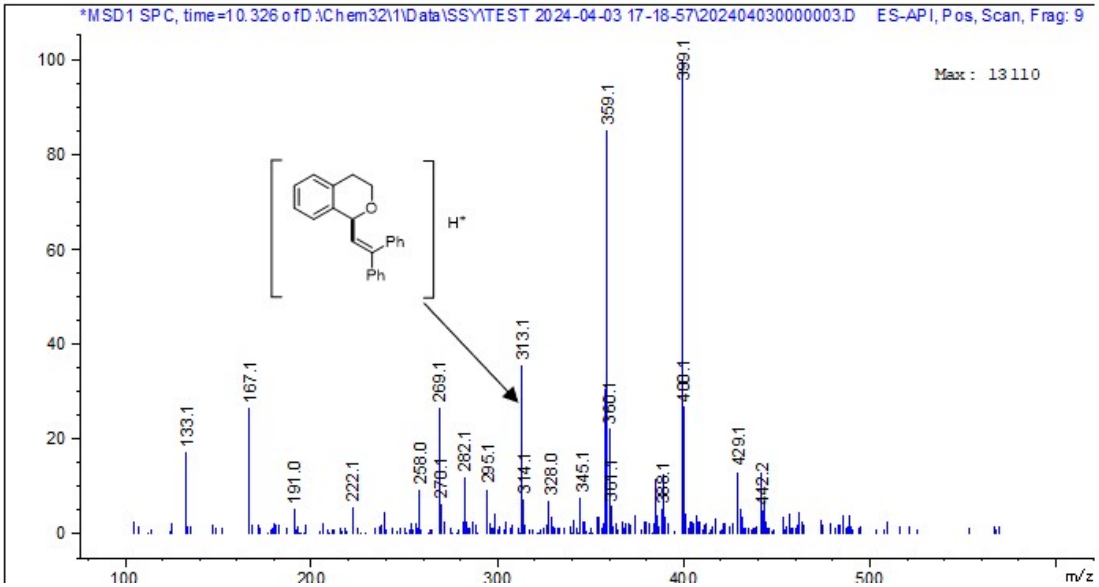


Figure S3. LC-MS spectrum of [**III** + H]$^+$ for **exp 3**

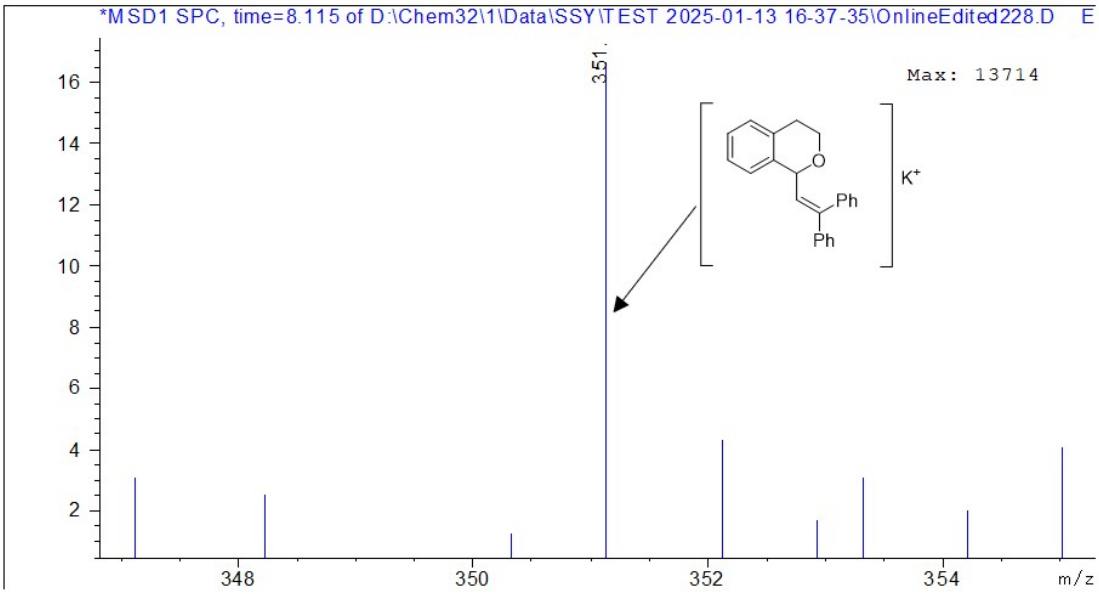


Figure S4. LC-MS spectrum of [**III** + K]$^+$ for **exp 3**

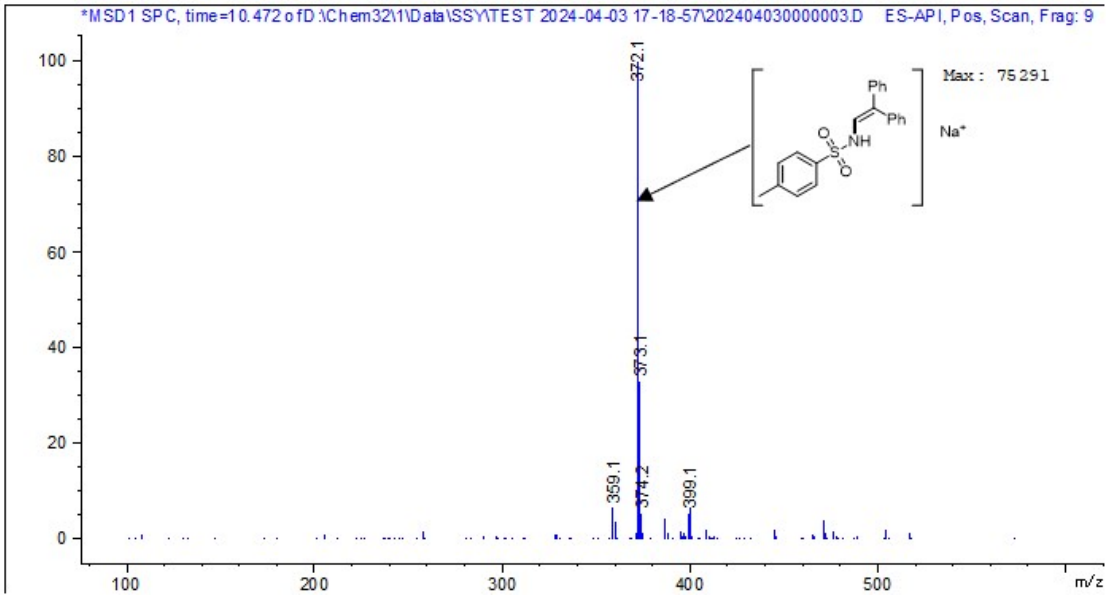


Figure S5. LC-MS spectrum of [**IV** + Na]$^+$ for **exp 3**

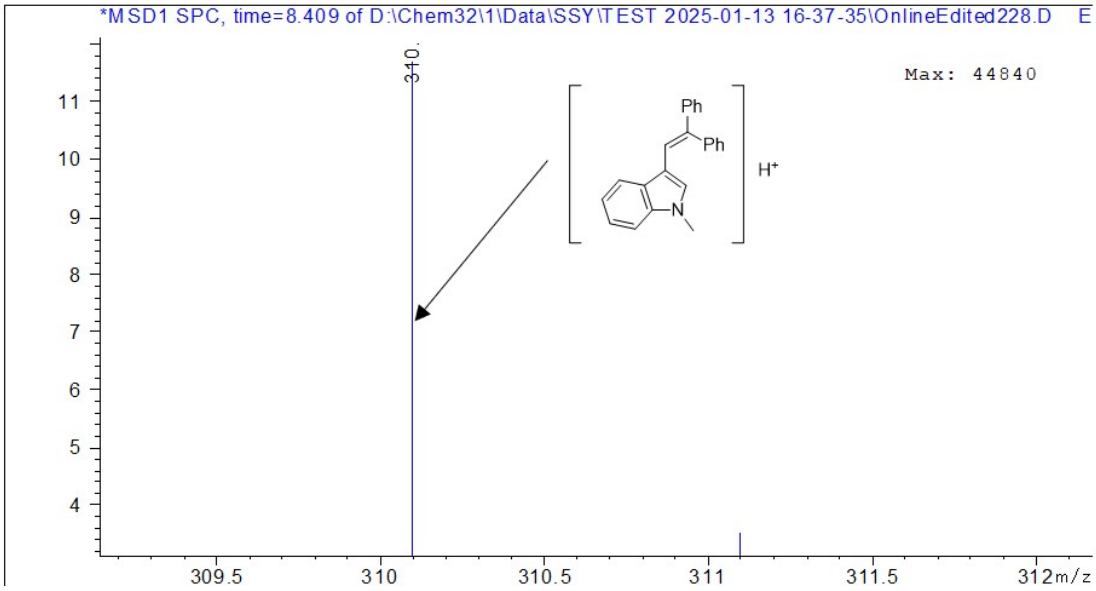


Figure S6. LC-MS spectrum of [**V** + H]$^+$ for **exp 7**

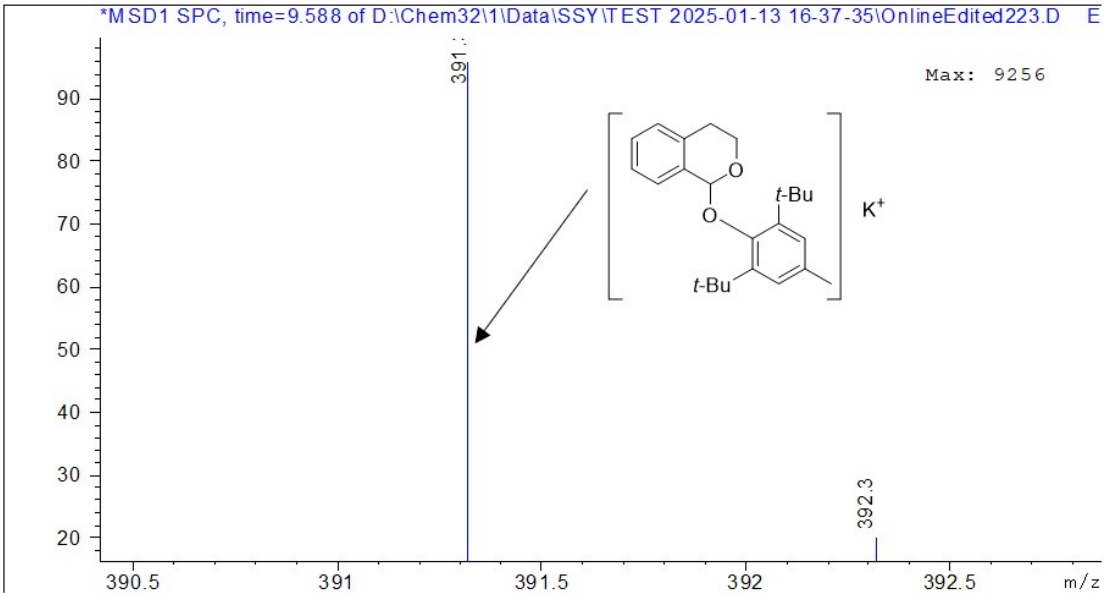


Figure S7. LC-MS spectrum of [**VI** + K]$^+$ for **exp 4** and **exp 8**

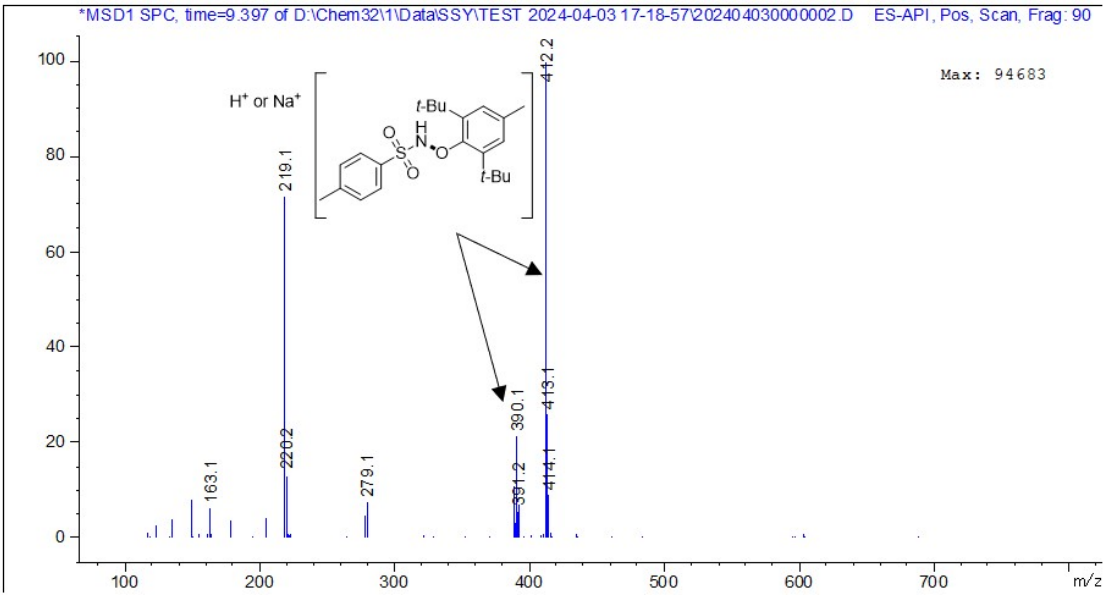


Figure S8. LC-MS spectrum of [**VII** + H]$^+$ and [**VII** + Na]$^+$ for **exp 4**

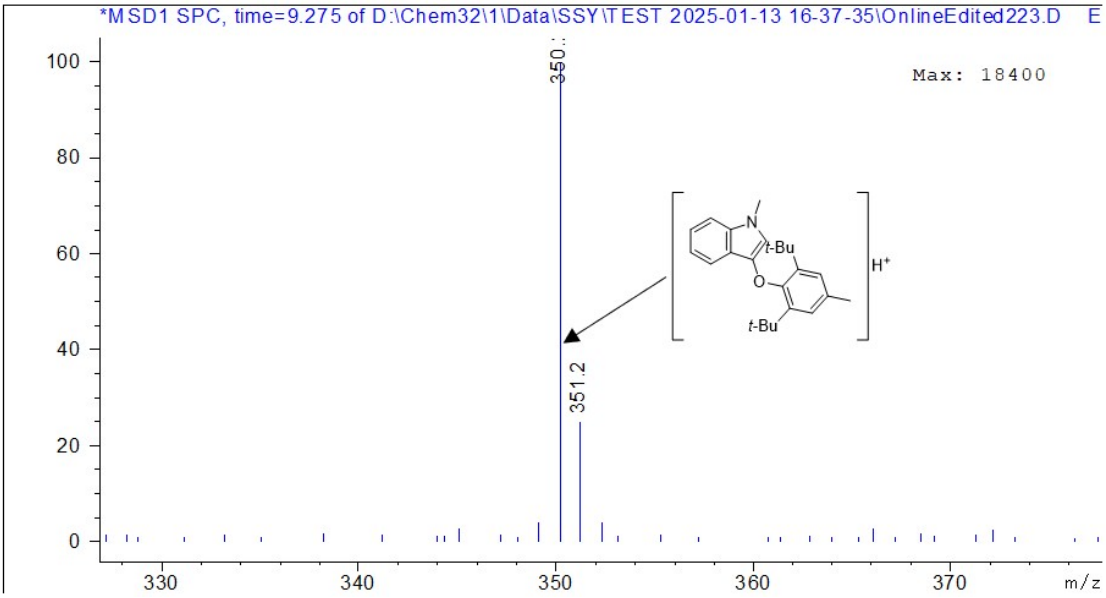


Figure S9. LC-MS spectrum of [**VIII** + H]$^+$ for **exp 8**

4. Cyclic Voltammetry Experiments

1) UV/VIS Absorption spectra

Cyclic voltammetry (CV) was measured in a glass cell with CHI1040C electrochemical workstation under Ar atmosphere with a conventional three-electrode system. The working electrode was a steady glassy carbon disk electrode, and the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in the saturated aqueous KCl solution. 6 mL of CH_3CN containing 0.05 M *n*-Bu_4NBF_4 were poured into the electrochemical cell in all experiments. The CV of substrates (**1a, 2a** and **4b**) were measured at the concentration of 10 mM. The scan rate was 0.1 V/s, ranging from 0 V to 3 V.

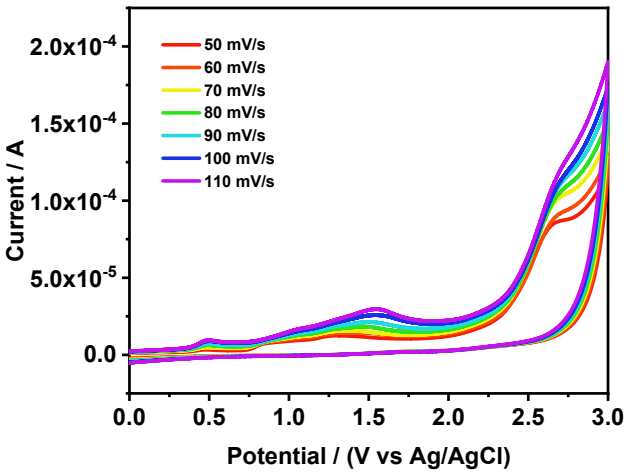


Figure S10. Cyclic voltammograms of 4-methylbenzenesulfonamide (**1a**) at different scan rates. Curves were obtained at 50, 60, 70, 80, 90, 100, 110 mV/s, respectively.

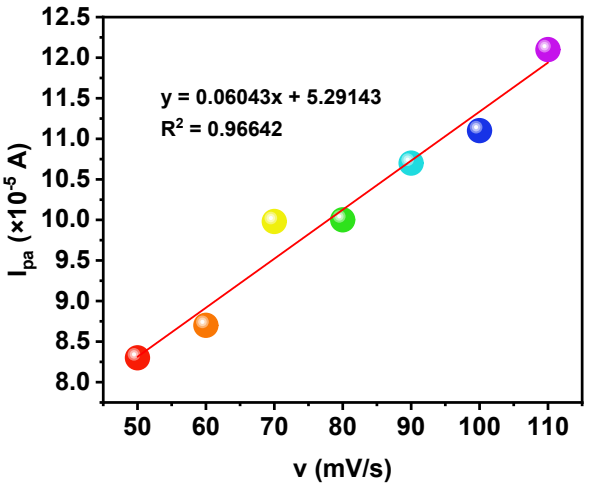


Figure S11. The plot of peak current *vs* scan rate for 4-methylbenzenesulfonamide (**1a**).

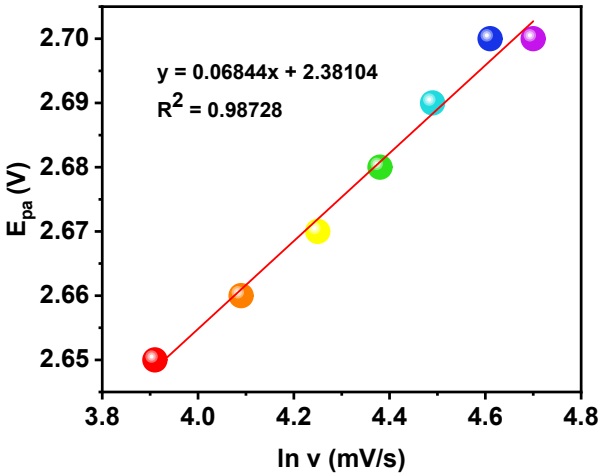


Figure S12. The relationship between E_{pa} and lnν for 4-methylbenzenesulfonamide (**1a**).

The peak current increased linearly with the scan rate in the range of 50-110 mV/s and the equation could be expressed as follows: y = 0.06043 x + 5.29143, R^2 = 0.96642. It could be seen that the oxidation of compound **1a** was an absorption-controlled process. For an adsorption-controlled and irreversible electrode process, according to Laviron method,[1] E_{pa} is defined by the following equation: $E_{pa} = E^0 + (RT/\alpha nF) \ln (RTk^0/\alpha nF) + (RT/\alpha nF) \ln \nu$.

Where α is transfer coefficient, k^0 is standard rate constant of the reaction, n is electron transfer number involved in the rate-determining step, ν is scan rate, and E^0 is formal potential. Other symbols have their usual meanings. Thus, the value of α can be easily calculated from the slope of E_{pa}-lnν. In this system, the slope is 0.06844. Generally, transfer coefficient α was assumed as 0.5, so the value of the number of electron (n) was calculated to be 1.

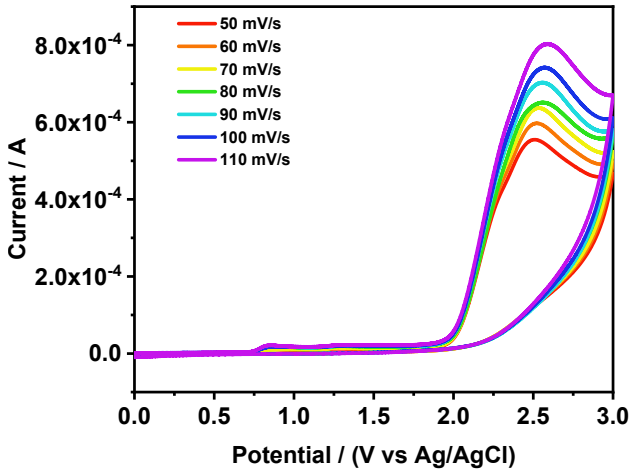


Figure S13. Cyclic voltammograms of isochroman (**2a**) at different scan rates. Curves were obtained at 50, 60, 70, 80, 90, 100, 110 mV/s, respectively.

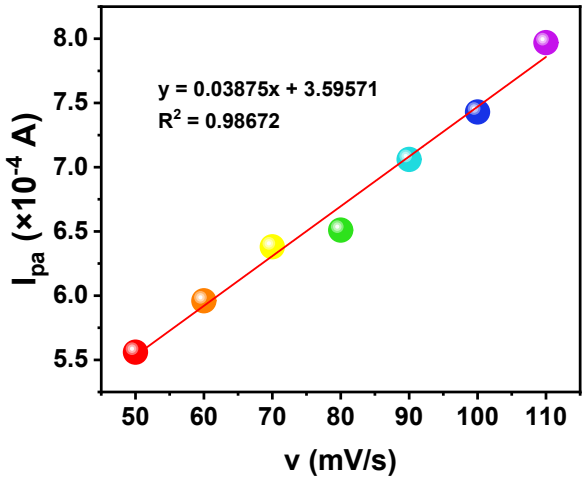


Figure S14. The plot of peak current *vs* scan rate for isochroman (**2a**).

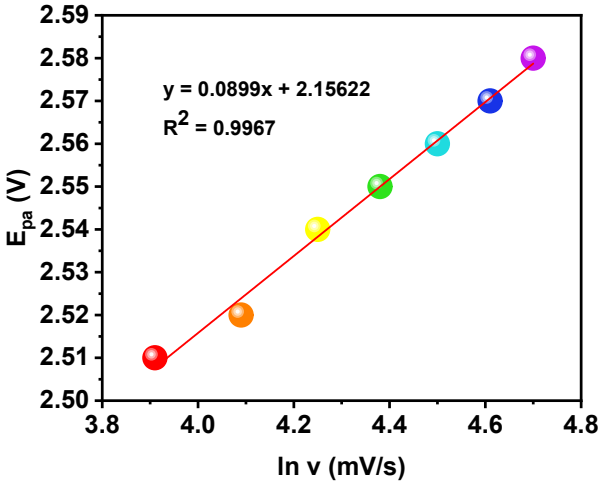


Figure S15. The relationship between E_{pa} and lnν for isochroman (**2a**).

The peak current increased linearly with the scan rate in the range of 50-110 mV/s and the equation could be expressed as follows: y = 0.03857 x + 3.59571, R^2 = 0.98672. It could be seen that the oxidation of compound **2a** was an absorption-controlled process. For an adsorption-controlled and irreversible electrode process, according to Laviron method,[1] E_{pa} is defined by the following equation: $E_{pa} = E^0 + (RT/\alpha nF) \ln (RTk^0/\alpha nF) + (RT/\alpha nF) \ln \nu$.

Where α is transfer coefficient, k^0 is standard rate constant of the reaction, n is electron transfer number involved in the rate-determining step, ν is scan rate, and E^0 is formal potential. Other symbols have their usual meanings. Thus, the value of α can be easily calculated from the slope of E_{pa}-lnν. In this system, the slope is 0.0899. Generally, transfer coefficient α was assumed as 0.5, so the value of the number of electron (n) was calculated to be 1.

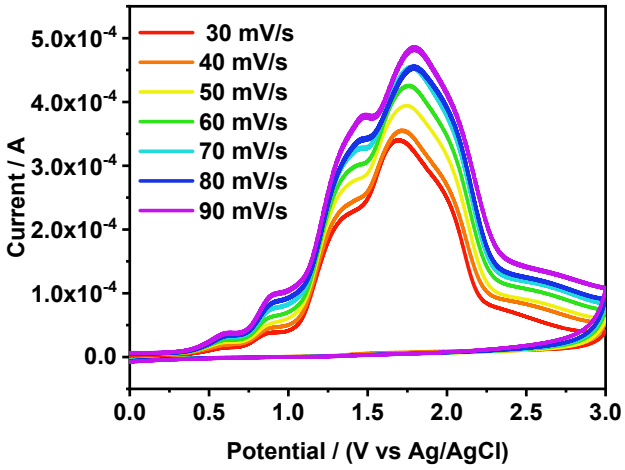


Figure S16. Cyclic voltammograms of *N*-methylindole (**4b**) at different scan rates. Curves were obtained at 30, 40, 50, 60, 70, 80, 90 mV/s, respectively.

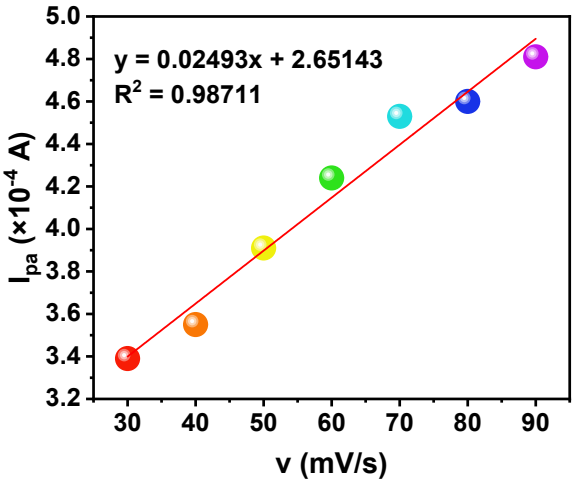


Figure S17. The plot of peak current *vs* scan rate for *N*-methylindole (**4b**).

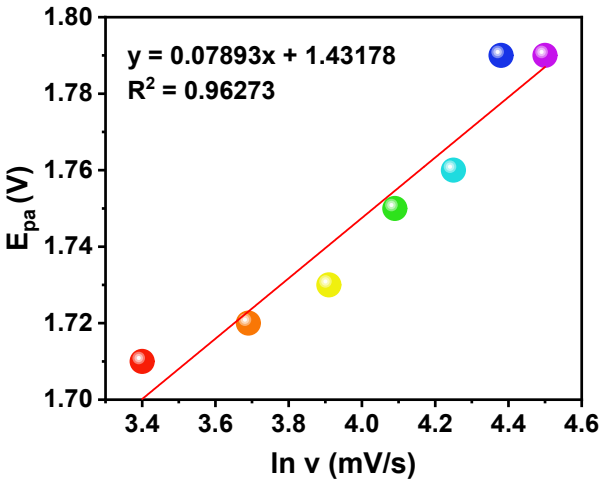
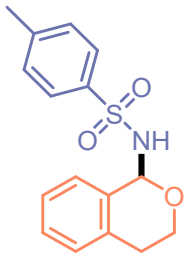


Figure S18. The relationship between E_{pa} and lnν for *N*-methylindole (**4b**).

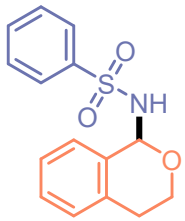
The peak current increased linearly with the scan rate in the range of 30-90 mV/s and the equation could be expressed as follows: y = 0.02493 x + 2.65143, R^2 = 0.98711. It could be seen that the oxidation of compound **4b** was an absorption-controlled process. For an adsorption-controlled and irreversible electrode process, according to Laviron method,[1] E_{pa} is defined by the following equation: $E_{pa} = E^0 + (RT/\alpha nF) \ln (RTk^0/\alpha nF) + (RT/\alpha nF) \ln \nu$.

Where α is transfer coefficient, k^0 is standard rate constant of the reaction, n is electron transfer number involved in the rate-determining step, ν is scan rate, and E^0 is formal potential. Other symbols have their usual meanings. Thus, the value of α can be easily calculated from the slope of E_{pa}-lnν. In this system, the slope is 0.07893. Generally, transfer coefficient α was assumed as 0.5, so the value of the number of electron (n) was calculated to be 1

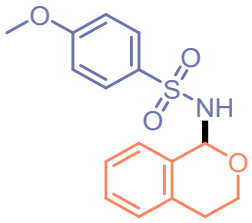
5. Characterization Data



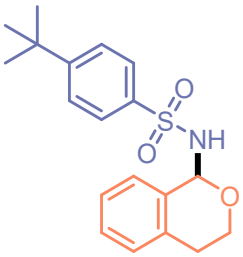
***N*-(isochroman-1-yl)-4-methylbenzenesulfonamide (3aa)**[2, 3] White solid (60.8 mg, 67%). mp. 187.4-187.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.19 Hz, 2H), 7.31 (d, J = 8.07 Hz, 2H), 7.25-7.17 (m, 3H), 7.08 (d, J = 6.72 Hz, 1H), 6.10 (d, J = 8.56 Hz, 1H), 5.43 (d, J = 8.31 Hz, 1H), 3.73-3.58 (m, 2H), 2.91-2.78 (m, 1H), 2.65-2.55 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 138.8, 134.5, 132.8, 129.5, 128.8, 128.4, 127.2, 126.8, 126.7, 79.9, 58.7, 27.6, 21.6. HRMS (ESI), calcd. for $C_{16}H_{17}NNaO_3S$ $(M+Na)^+$: 326.0821, found: 326.0819.



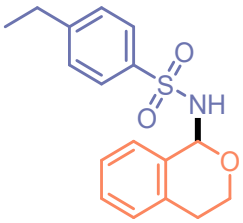
***N*-(isochroman-1-yl)benzenesulfonamide (3ba)**[3] White solid (59.6 mg, 70%). mp. 184.3-184.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.46 Hz, 2H), 7.65-7.43 (m, 3H), 7.24-7.12 (m, 3H), 7.06 (d, J = 6.97 Hz, 1H), 6.08 (d, J = 8.56 Hz, 1H), 5.64 (d, J = 8.56 Hz, 1H), 3.70-3.52 (m, 2H), 2.90-2.75 (m, 1H), 2.63-2.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 134.5, 132.7, 132.6, 128.9, 128.8, 128.5, 127.2, 126.8, 126.7, 79.9, 58.7, 27.5. HRMS (ESI), calcd. for $C_{15}H_{15}NO_3NaS$ $(M+Na)^+$: 312.0665, found: 312.0668.



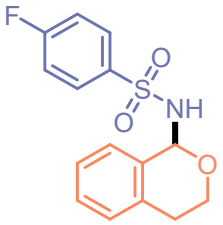
***N*-(isochroman-1-yl)-4-methoxybenzenesulfonamide (3ca)**[3] White solid (61.4 mg, 65%). mp. 180.0-181.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.80 Hz, 2H), 7.25-7.17 (m, 3H), 7.07 (d, J = 6.72 Hz, 1H), 6.98 (d, J = 8.80 Hz, 2H), 6.08 (d, J = 8.56 Hz, 1H), 5.44 (d, J = 8.44 Hz, 1H), 3.88 (s, 3H), 3.72-3.58 (m, 2H), 2.90-2.78 (m, 1H), 2.61 (dt, J = 16.51, 3.42 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 134.5, 133.4, 132.9, 129.4, 128.8, 128.4, 126.8, 126.7, 114.0, 79.9, 58.7, 55.6, 27.6. HRMS (ESI), calcd. for $C_{16}H_{18}NO_4S$ $(M+H)^+$: 320.0951, found: 320.0950.



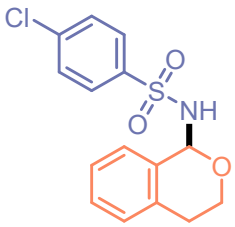
4-(tert-butyl)-*N*-(isochroman-1-yl)benzenesulfonamide (3da) White solid (66.3 mg, 74%). mp. 134.1-134.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.44 Hz, 2H), 7.52 (d, J = 8.44 Hz, 2H), 7.25-7.15 (m, 3H), 7.08 (d, J = 6.97 Hz, 1H), 6.10 (d, J = 8.56 Hz, 1H), 5.50 (t, J = 8.56 Hz, 1H), 3.74-3.58 (m, 2H), 2.90-2.79 (m, 1H), 2.65-2.56 (m, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 138.7, 134.5, 132.9, 128.8, 128.4, 127.0, 126.8, 126.7, 125.8, 79.9, 58.8, 35.2, 31.1, 27.6. HRMS (ESI), calcd. for $C_{19}H_{23}NO_3NaS$ $(M+Na)^+$: 368.1291, found: 368.1293.



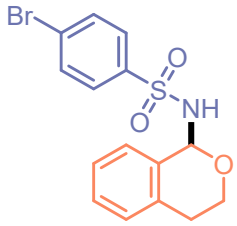
4-ethyl-*N*-(isochroman-1-yl)benzenesulfonamide (3ea) White solid (57.6 mg, 60%). mp. 190.6-191.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.19 Hz, 2H), 7.33 (d, J = 8.19 Hz, 2H), 7.25-7.15 (m, 3H), 7.07 (d, J = 6.97 Hz, 1H), 6.09 (d, J = 8.56 Hz, 1H), 5.48 (d, J = 8.56 Hz, 1H), 3.73-3.57 (m, 2H), 2.90-2.79 (m, 1H), 2.74 (q, J = 7.58 Hz, 2H), 2.61 (m, 1H), 1.27 (t, J = 7.58 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 138.9, 134.5, 132.8, 128.9, 128.4, 128.3, 127.3, 126.8, 126.7, 79.9, 58.7, 28.9, 27.6, 15.2. HRMS (ESI), calcd. for $C_{17}H_{20}NO_3S$ $(M+H)^+$: 318.1158, found: 318.1161.



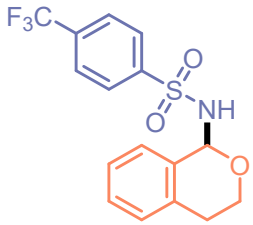
4-fluoro-*N*-(isochroman-1-yl)benzenesulfonamide (3fa) White solid (65. mg, 71%). mp. 162.5-163.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.91 (m, 2H), 7.25-7.14 (m, 5H), 7.07 (d, J = 7.34 Hz, 1H), 6.10 (d, J = 8.56 Hz, 1H), 5.61 (d, J = 8.56 Hz, 1H), 3.68-3.55 (m, 2H), 2.89-2.77 (m, 1H), 2.64-2.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0 (d, ^1J = 254.6 Hz), 137.9 (d, ^4J = 2.9 Hz), 134.5, 132.5, 130.0 (d, ^3J = 9.5 Hz), 128.9, 128.6, 126.8, 126.7, 116.0 (d , ^2J = 22.7 Hz), 80.0, 58.7, 27.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -105.5. HRMS (ESI), calcd. for $C_{15}H_{14}FNO_3NaS$ $(M+Na)^+$: 330.0571, found: 330.0577. The structure was confirmed by X-ray analysis, CCDC: 2427060.



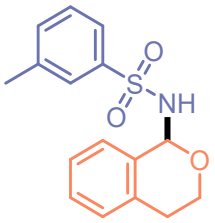
4-chloro-*N*-(isochroman-1-yl)benzenesulfonamide (3ga)[3] White solid (57.4 mg, 59%). mp. 149.6-151.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.68 Hz, 2H), 7.48 (d, J = 8.68 Hz, 2H), 7.29-7.17 (m, 3H), 7.08 (d, J = 7.21 Hz, 1H), 6.11 (d, J = 8.56 Hz, 1H), 5.57 (d, J = 8.56 Hz, 1H), 3.67-3.56 (m, 2H), 2.90-2.77 (m, 1H), 2.66-2.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 134.5, 132.4, 132.1, 128.9, 128.8, 128.6, 127.6, 126.8, 126.8, 80.0, 58.8, 27.5. HRMS (ESI), calcd. for $C_{15}H_{14}ClNO_3NaS$ $(M+Na)^+$: 346.0275, found: 346.0277.



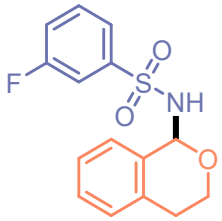
4-bromo-*N*-(isochroman-1-yl)benzenesulfonamide (3ha) White solid (50.6 mg, 46%). mp. 171.9-173.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.56 Hz, 2H), 7.64 (d, J = 8.56 Hz, 2H), 7.25-7.16 (m, 3H), 7.07 (d, J = 7.09 Hz, 1H), 6.10 (d, J = 8.56 Hz, 1H), 5.61 (d, J = 8.56 Hz, 1H), 3.67-3.54 (m, 2H), 2.90-2.76 (m, 1H), 2.65-2.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$ & MeOD (v:v = 30:1)): δ 141.1, 134.4, 132.5, 132.0, 128.8, 128.7, 128.4, 127.4, 126.9, 126.7, 79.8, 58.6, 27.5. HRMS (ESI), calcd. for $C_{15}H_{15}BrNO_3S$ $(M+H)^+$: 367.9951, found: 367.9951.



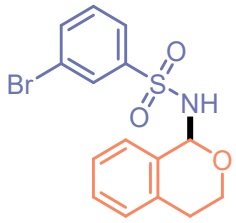
***N*-(isochroman-1-yl)-4-(trifluoromethyl)benzenesulfonamide (3ia)** White solid (64.3 mg, 60%). mp. 182.9-183.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.31 Hz, 2H), 7.77 (d, J = 8.31 Hz, 2H), 7.34-7.15 (m, 3H), 7.08 (d, J = 6.48 Hz, 1H), 6.14 (d, J = 8.56 Hz, 1H), 5.68 (d, J = 8.56 Hz, 1H), 3.65-3.50 (m, 2H), 2.90-2.76 (m, 1H), 2.56 (d, J = 16.63 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 134.5, 134.3 (q, ^2J = 33.0 Hz), 132.2, 128.9, 128.7, 127.8, 126.9, 126.8, 126.0 (q, ^3J = 3.7 Hz), 123.3 (q, ^1J = 272.9 Hz), 80.1, 58.8, 27.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.1. HRMS (ESI), calcd. for $C_{16}H_{14}F_3NO_3NaS$ $(M+Na)^+$: 380.0539, found: 380.0543.



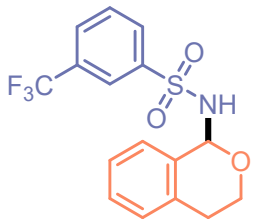
***N*-(isochroman-1-yl)-3-methylbenzenesulfonamide (3ja)**[3] White solid (35.2 mg, 39%). mp. 129.7-130.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.76 (d, J =6.11 Hz, 1H), 7.43-7.75 (m, 2H), 7.24-7.14 (m, 3H), 7.07 (d, J = 7.09 Hz, 1H), 6.08 (d, J = 8.56 Hz, 1H), 5.52 (d, J = 8.44 Hz, 1H), 3.74-3.55 (m, 2H), 2.92-2.76 (m, 1H), 2.69-2.53 (m, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 139.0, 134.5, 133.4, 132.8, 128.9, 128.8, 128.4, 127.5, 126.8, 126.7, 124.3, 79.6, 58.7, 27.5, 21.4. HRMS (ESI), calcd. for $C_{16}H_{17}NO_3NaS$ $(M+Na)^+$: 326.0821, found: 326.0820.



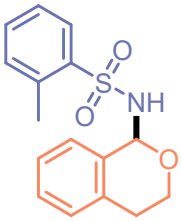
3-fluoro-*N*-(isochroman-1-yl)benzenesulfonamide (3ka) White solid (48.9 mg, 53%). mp. 158.5-158.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 7.95 Hz, 1H), 7.71-7.63 (m, 1H), 7.56-7.45 (m, 1H), 7.34-7.16 (m, 4H), 7.08 (d, J = 6.48 Hz, 1H), 6.11 (d, J = 8.56 Hz, 1H), 5.64 (d, J = 8.44 Hz, 1H), 3.70-3.56 (m, 2H), 2.92-2.77 (m, 1H), 2.60 (dt, J = 16.63, 3.55 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 (d, ^{1}J = 250.9 Hz), 143.8 (d, ^{3}J = 7.3 Hz), 134.5, 132.4, 130.6 (d, ^{3}J = 7.3 Hz), 128.9, 128.6, 126.9, 126.8, 123.0 (d, ^{4}J = 2.9 Hz), 119.8 (d, ^{2}J = 21.3 Hz), 114.7 (d, ^{2}J = 24.2 Hz), 80.0, 58.8, 27.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.0. HRMS (ESI), calcd. for $C_{15}H_{14}FNO_3NaS$ $(M+Na)^+$: 330.0571, found: 330.0574.



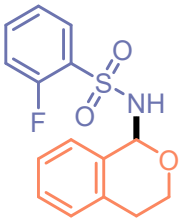
3-bromo-*N*-(isochroman-1-yl)benzenesulfonamide (3la) White solid (42.9 mg, 39%). mp. 153.8-154.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.90 (d, J = 6.85 Hz, 1H), 7.71 (d, J = 7.95 Hz, 1H), 7.40 (t, J = 7.95 Hz, 1H), 7.29-7.16 (m, 3H), 7.09 (d, J = 7.70 Hz, 1H), 6.12 (d, J = 8.44 Hz, 1H), 5.54 (d, J = 8.31 Hz, 1H), 3.69-3.56 (m, 2H), 2.92-2.78 (m, 1H), 2.61 (d, J = 16.51 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 135.6, 134.5, 132.3, 130.4, 130.2, 128.9, 128.6, 126.8, 126.8, 125.8, 122.7, 80.0, 58.8, 27.5. HRMS (ESI), calcd. for $C_{15}H_{15}BrNO_3S$ $(M+H)^+$: 367.9951, found: 367.9950.



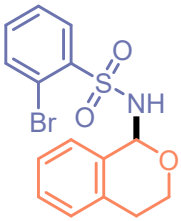
***N*-(isochroman-1-yl)-3-(trifluoromethyl)benzenesulfonamide (3ma)** White solid (58.1 mg, 54%). mp. 167.6-168.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.16 (d, J = 7.58 Hz, 1H), 7.84 (d, J = 7.58 Hz, 1H), 7.66 (t, J = 7.70 Hz, 1H), 7.34-7.15 (m, 3H), 7.08 (d, J = 6.24 Hz, 1H), 6.15 (d, J =8.31 Hz, 1H), 5.64 (d, J = 8.19 Hz, 1H), 3.66-3.53 (m, 2H), 2.92-2.76 (m, 1H), 2.60 (d, J = 16.63 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 134.5, 132.2, 131.5 (d, ^{2}J = 33.0 Hz), 130.5, 129.6, 129.2 (q, ^{3}J = 3.7 Hz), 128.9, 128.7, 126.8, 126.8, 124.5 (q, ^{3}J = 3.7 Hz), 123.3 (q, ^{1}J = 272.9 Hz), 80.0, 58.7, 27.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.8. HRMS (ESI), calcd. for $C_{16}H_{15}F_3NO_3S$ $(M+H)^+$: 358.0719, found: 358.0726.



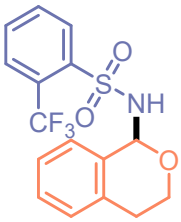
***N*-(isochroman-1-yl)-2-methylbenzenesulfonamide (3na)**[3] White solid (57.7 mg, 64%). mp. 159.5-160.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.95 Hz, 1H), 7.53-7.44 (m, 1H), 7.39-7.30 (m, 2H), 7.28-7.16 (m, 3H), 7.08 (d, J = 6.85 Hz, 1H), 6.00 (d, J = 8.44 Hz, 1H), 5.55 (d, J = 8.44 Hz, 1H), 3.78-3.68 (m, 1H), 3.68-3.58 (m, 1H), 2.88-2.77 (m, 1H), 2.67 (s, 3H), 2.65-2.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 136.9, 134.6, 132.9, 132.8, 132.3, 129.3, 128.9, 128.5, 126.8, 126.7, 126.3, 80.0, 59.1, 27.6, 20.5. HRMS (ESI), calcd. for $C_{16}H_{17}NO_3NaS$ $(M+Na)^+$: 326.0821, found: 326.0820.



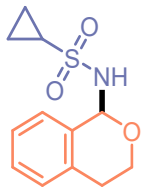
2-fluoro-*N*-(isochroman-1-yl)benzenesulfonamide (3oa) White solid (57.0 mg, 62%). mp. 182.6-183.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (t, J = 7.21 Hz,1H), 7.60 (d, J = 5.62 Hz, 1H), 7.39-7.16 (m, 5H), 7.10 (d, J = 5.99 Hz, 1H), 6.06 (d, J = 9.17 Hz, 1H), 5.85 (d, J =8.80 Hz, 1H), 3.82-3.51 (m, 2H), 2.93-2.74 (m, 1H), 2.62 (d, J = 16.51 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9 (d, ^1J = 253.8 Hz), 134.9 (d, ^3J = 8.8 Hz), 134.6, 132.3, 130.0, 129.8 (d, ^3J = 8.1 Hz), 128.9, 128.6, 127.0, 126.8, 124.5 (d, ^4J = 3.7 Hz), 116.6 (d, ^2J = 20.5 Hz), 80.0, 59.0, 27.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.9. HRMS (ESI), calcd. for $C_{15}H_{14}FNO_3NaS$ $(M+Na)^+$: 330.0571, found: 330.0569.



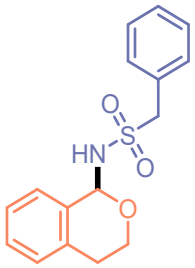
2-bromo-*N*-(isochroman-1-yl)benzenesulfonamide (3pa) White solid (52.7 mg, 48%). mp. 160.8-161.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 7.83 Hz, 1H), 7.75 (d, J = 7.70 Hz, 1H), 7.59-7.47 (m, 1H), 7.47-7.39 (m, 1H), 7.35-7.19 (m, 3H), 7.11 (d, J = 6.60 Hz, 1H), 6.18 (d, J = 9.05 Hz, 1H), 6.06 (d, J = 9.17 Hz, 1H), 3.80-3.66 (m, 1H), 3.60-3.46 (m, 1H), 2.92-2.76 (m, 1H), 2.59 (d, J = 16.51 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 141.0, 134.7, 133.6, 132.1, 131.0, 128.9, 128.6, 128.0, 127.2, 126.8, 119.6, 80.1, 59.0, 27.6. HRMS (ESI), calcd. for $C_{15}H_{14}BrNO_3NaS$ $(M+Na)^+$: 389.9770, found: 389.9769.



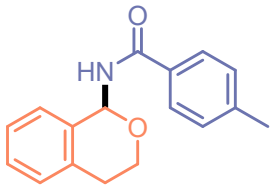
***N*-(isochroman-1-yl)-2-(trifluoromethyl)benzenesulfonamide (3qa)** White solid (47.9 mg, 45%). mp. 147.3-148.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43-8.33 (m, 1H), 7.93-7.84 (m, 1H), 7.79-7.68 (m, 2H), 7.31-7.18 (m, 3H), 7.10 (d, J = 6.97 Hz, 1H), 6.11 (d, J = 9.05 Hz, 1H), 5.75 (d, J = 9.05 Hz, 1H), 3.62-3.43 (m, 2H), 2.87-2.84 (m, 1H), 2.59 (dt, J = 16.63, 3.55 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 134.5, 132.7, 132.5, 132.1, 131.8, 128.9, 128.6, 128.1 (q, ^3J = 6.6 Hz), 127.3 (q, ^2J = 33.0 Hz),127.0, 126.8, 123.1 (q, ^1J = 273.6 Hz), 80.2, 58.7, 27.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.8. HRMS (ESI), calcd. for $C_{16}H_{14}F_3NO_3NaS$ $(M+Na)^+$: 380.0539, found: 380.0538.



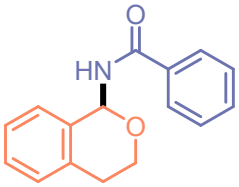
***N*-(isochroman-1-yl)cyclopropanesulfonamide (3ra)** White solid (29.2 mg, 38%). mp. 114.7-114.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 1H), 7.29-7.18 (m, 2H), 7.15-7.07 (m, 1H), 6.03 (d, J = 9.29 Hz, 1H), 5.41 (d, J = 9.17 Hz, 1H), 4.12-4.01 (m, 1H), 4.01-3.91 (m, 1H), 2.97-2.85 (m, 1H), 2.83-2.62 (m, 2H), 1.33-1.24 (m, 1H), 1.18-0.94 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 132.8, 128.8, 128.4, 127.0, 126.7, 80.2, 59.5, 32.5, 27.8, 6.2, 5.8. HRMS (ESI), calcd. for $C_{12}H_{16}NO_3S$ $(M+H)^+$: 254.0845, found: 254.0848.



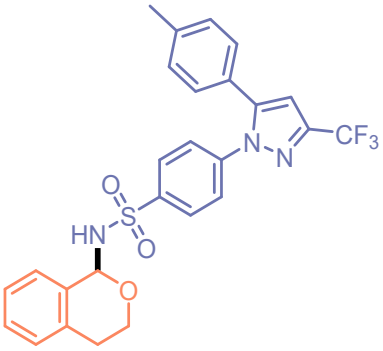
***N*-(isochroman-1-yl)-1-phenylmethanesulfonamide (3sa)** White solid (48.4 mg, 53%). mp. 157.5-159.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.42 (m, 2H), 7.39-7.32 (m, 3H), 7.29 (d, J = 7.09 Hz, 1H), 7.23-7.15 (m, 2H), 7.09 (d, J = 7.21 Hz, 1H), 6.07 (d, J = 9.54 Hz, 1H), 5.30 (d, J = 9.66 Hz, 1H), 4.52-4.36 (m, 2H), 4.02-3.94 (m, 2H), 2.93-2.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 132.7, 131.0, 129.2, 128.8, 128.7, 128.4, 126.9, 126.8, 80.5, 61.0, 60.6, 27.9. HRMS (ESI), calcd. for $C_{16}H_{17}NO_3NaS$ $(M+Na)^+$: 326.0821, found: 326.0826.



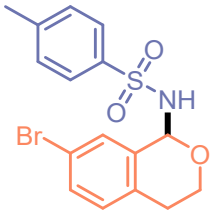
***N*-(isochroman-1-yl)-4-methylbenzamide (3ta)** White solid (13.6 mg, 17%). mp. 183.4-185.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.07 Hz, 2H), 7.31-7.24 (m, 5H), 7.18 (d, J = 7.09 Hz, 1H), 6.84 (d, J = 8.56 Hz, 1H), 6.68 (d, J = 8.68 Hz, 1H), 4.15-4.00 (m, 2H), 2.94-2.86 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 142.6, 135.1, 134.5, 131.0, 129.3, 129.0, 128.1, 127.2, 126.7, 126.4, 76.0, 61.1, 28.2, 21.5. HRMS (ESI), calcd. for $C_{17}H_{17}NO_2Na$ $(M+Na)^+$: 290.1151, found: 290.1153.



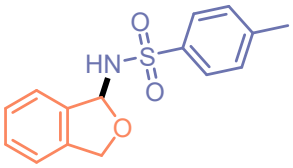
***N*-(isochroman-1-yl)benzamide (3ua)**[4] White solid (12.2 mg, 16%). mp. 176.5-177.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.34 Hz, 2H), 7.57-7.49 (m, 1H), 7.48-7.71 (m, 2H), 7.30-7.23 (m, 3H), 7.18 (d, J = 7.09 Hz, 1H), 6.88 (d, J = 7.83 Hz, 1H), 6.69 (d, J = 8.80 Hz, 1H), 4.15-4.00 (m, 2H), 2.98-2.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 135.1, 134.4, 133.9, 132.0, 129.0, 128.7, 128.2, 127.2, 126.8, 126.3, 76.1, 61.1, 28.1. HRMS (ESI), calcd. for $C_{16}H_{15}NO_2Na$ $(M+Na)^+$: 276.0995, found: 276.0993.



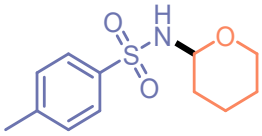
***N*-(isochroman-1-yl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (3va)** White solid (101.8 mg, 66%). mp. 175.9-176.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.68 Hz, 2H), 7.45 (d, J = 8.56 Hz, 2H), 7.28-7.15 (m, 5H), 7.14-7.03 (m, 3H), 6.75 (s, 1H), 6.09 (d, J = 8.44 Hz, 1H), 5.64 (d, J = 8.56 Hz, 1H), 3.63-3.53 (m, 2H), 2.90-2.78 (m, 1H), 2.64-2.54 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 144.1, 144.0 (q, ^2J = 38.2 Hz), 142.3, 141.2, 139.8, 134.5, 132.3, 129.7, 128.9, 128.8, 128.6, 128.3, 126.8, 125.8, 125.3, 121.1 (q, ^1J = 269.2 Hz), 106.3, 80.0, 58.7, 27.5, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.4. HRMS (ESI), calcd. for $C_{26}H_{22}F_3N_3O_3S$ $(M+H)^+$: 514.1407, found: 514.1406.



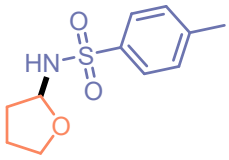
***N*-(7-bromoisochroman-1-yl)-4-methylbenzenesulfonamide (3ab)** White solid (76 mg, 66%). mp. 169.8-171.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.19 Hz, 2H), 7.34-7.27 (m, 4H), 6.93 (d, J = 7.95 Hz, 1H), 5.99 (d, J = 9.05 Hz, 1H), 5.76 (d, J = 8.93 Hz, 1H), 3.70-3.56 (m, 2H), 2.80-2.69 (m, 1H), 2.61-2.50 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 138.5, 134.8, 133.5, 131.5, 130.5, 129.7, 129.6, 127.1, 120.0, 79.3, 58.7, 27.1, 21.6. HRMS (ESI), calcd. for $C_{16}H_{16}BrNO_3NaS$ $(M+Na)^+$: 403.9926, found: 403.9925.



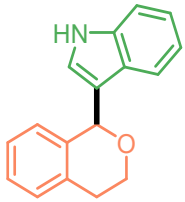
***N*-(1,3-dihydroisobenzofuran-1-yl)-4-methylbenzenesulfonamide (3ac)**[2] White solid (31.2 mg, 36%). mp. 175.9-176.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.31 Hz, 2H), 7.39-7.29 (m, 5H), 7.21 (d, J = 6.97 Hz, 1H), 6.59-6.50 (m, 1H), 5.22 (d, J = 10.15 Hz, 1H), 5.03-4.88 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 139.3, 138.6, 136.6, 129.6, 129.5, 128.1, 127.2, 123.0, 121.2, 88.9, 72.0, 21.6. HRMS (ESI), calcd. for $C_{15}H_{15}NO_3S$ $(M+Na)^+$: 312.0665, found: 312.0665.



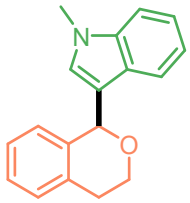
4-methyl-*N*-(tetrahydro-2*H*-pyran-2-yl)benzenesulfonamide (3ad)[2] Colorless oil (23 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.19 Hz, 2H), 7.27 (d, J = 7.34 Hz, 2H), 5.21 (d, J = 9.54 Hz, 1H), 4.80-4.72 (m, 1H), 3.77-3.67 (m, 1H), 3.44-3.33 (m, 1H), 2.41 (s, 3H), 1.88-1.76 (m, 2H), 1.66-1.50 (m, 2H), 1.47-1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 138.8, 129.4, 127.2, 82.1, 66.3, 31.9, 24.7, 22.5, 21.6. HRMS (ESI), calcd. for $C_{12}H_{17}NO_3S$ $(M+Na)^+$: 278.0821, found: 278.0820.



4-methyl-*N*-(tetrahydrofuran-2-yl)benzenesulfonamide (3ae)[2] Colorless oil (20.9 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.19 Hz, 2H), 7.28 (d, J = 7.83 Hz, 2H), 5.77 (d, J = 8.80 Hz, 1H), 5.36-5.31 (m, 1H), 3.72-3.65 (m, 2H), 2.42 (s, 3H), 2.17-2.10 (m, 1H), 1.91-1.79 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 138.5, 129.5, 127.1, 85.0, 67.2, 32.6, 24.0, 21.6. HRMS (ESI), calcd. for $C_{11}H_{15}NO_3S$ $(M+Na)^+$: 264.0665, found: 264.0663.

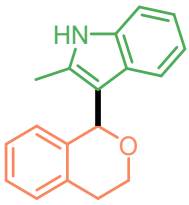


3-(isochroman-1-yl)-1*H*-indole (5aa)[5] Green oil (12.5 mg, 17%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.45 (d, J = 7.82 Hz, 1H), 7.25-7.16 (m, 3H), 7.16-7.09 (m, 1H), 7.08-6.98 (m, 2H), 6.93 (d, J = 7.70 Hz, 1H), 6.78 (d, J = 2.32 Hz, 1H), 6.11 (s, 1H), 4.20-4.08 (m, 1H), 3.99-3.87 (m, 1H), 3.11-2.99 (m, 1H), 2.89 (dt, J = 16.38, 5.01 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 136.7, 134.0, 128.8, 126.8, 126.6, 126.4, 125.9, 125.0, 122.3, 120.0, 119.9, 117.2, 111.3, 72.6, 62.7, 29.0. HRMS (ESI), calcd. for $C_{17}H_{16}NO$ $(M+H)^+$: 250.1226, found: 250.1226.

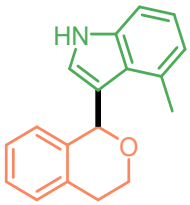


3-(isochroman-1-yl)-1-methyl-1*H*-indole (5ab)[5] Yellow oil (41.2 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 7.95 Hz, 1H), 7.30-7.24 (m, 1H), 7.23-7.14 (m, 3H), 7.11-7.02 (m, 2H), 6.99 (d, J = 7.58 Hz, 1H), 6.83 (s, 1H), 6.13 (s, 1H), 4.17-4.08 (m, 1H), 3.97-3.87 (m, 1H), 3.70 (s, 3H), 3.08-2.97 (m, 1H), 2.95-2.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 134.0, 129.4, 128.8, 127.1,

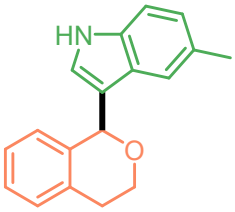
126.8, 126.5, 125.8, 121.9, 120.1, 119.5, 116.1, 109.3, 72.3, 62.4, 32.8, 28.9. HRMS (ESI), calcd. for $C_{18}H_{18}NO$ $(M+H)^+$: 264.1383, found: 264.1384.



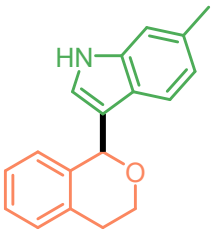
3-(isochroman-1-yl)-2-methyl-1*H*-indole (5ac)[5] Yellow oil (47 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.22-7.12 (m, 3H), 7.11-6.96 (m, 3H), 6.95-6.86 (m, 1H), 6.79 (d, J = 7.58 Hz, 1H), 6.05 (s, 1H), 4.36-4.25 (m, 1H), 4.07-3.96 (m, 1H), 3.35-3.21 (m, 1H), 2.84 (d, J = 12.26 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 135.4, 134.4, 133.8, 128.6, 127.5, 126.5, 126.4, 126.3, 121.1, 119.5, 119.1, 112.2, 110.3, 72.5, 64.9, 29.2, 11.8. HRMS (ESI), calcd. for $C_{18}H_{18}NO$ $(M+H)^+$: 264.1383, found: 264.1384.



3-(isochroman-1-yl)-4-methyl-1*H*-indole (5ad)[5] Light brown oil (42.2 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.21-7.15 (m, 2H), 7.13 (d, J = 8.19 Hz, 1H), 7.10-7.03 (m, 2H), 6.98 (d, J = 7.21 Hz, 1H), 6.88 (d, J = 6.97 Hz, 1H), 6.65 (s, 1H), 6.30 (s, 1H), 4.18-4.04 (m, 1H), 3.96-3.83 (m, 1H), 2.94 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 137.1, 134.2, 131.5, 128.8, 127.0, 126.6, 126.0, 125.6, 125.5, 122.4, 121.7, 118.0, 109.0, 72.5, 61.3, 28.8, 20.4. HRMS (ESI), calcd. for $C_{18}H_{18}NO$ $(M+H)^+$: 264.1383, found: 264.1385.

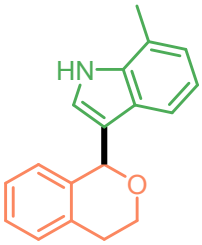


3-(isochroman-1-yl)-5-methyl-1*H*-indole (5ae)[5] Light purple oil (23.3 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.33 (s, 1H), 7.27-7.14 (m, 3H), 7.12-7.04 (m, 1H), 7.03-6.94 (m, 2H), 6.84 (s, 1H), 6.13 (s, 1H), 4.18-4.07 (m, 1H), 4.00-3.87 (m, 1H), 3.09-2.98 (m, 1H), 2.98-2.87 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 135.0, 134.0, 129.2, 128.8, 126.7, 126.5, 125.8, 124.9, 124.0, 119.5, 117.1, 110.8, 72.4, 62.3, 28.9, 21.6. HRMS (ESI), calcd. for $C_{18}H_{18}NO$ $(M+H)^+$: 264.1383, found: 264.1383.

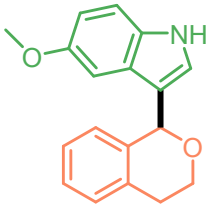


3-(isochroman-1-yl)-6-methyl-1*H*-indole (5af) Light yellow oil (24.5 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.35 (d, J = 8.19 Hz, 1H), 7.22-7.14 (m, 2H), 7.12 (s, 1H), 7.10-7.02 (m, 1H),

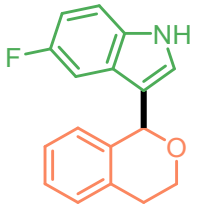
6.97 (d, J = 7.83 Hz, 1H), 6.93-6.85 (m, 2H), 6.11 (s, 1H), 4.19-4.09 (m, 1H), 3.99-3.89 (m, 1H), 3.10-2.99 (m, 1H), 2.97-2.87 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 137.1, 133.9, 132.2, 128.7, 126.7, 126.5, 125.8, 124.3, 124.1, 121.7, 119.7, 117.5, 111.1, 72.5, 62.5, 28.9, 21.7. HRMS (ESI), calcd. for $C_{18}H_{18}NO$ $(M+H)^+$: 264.1383, found: 264.1384.



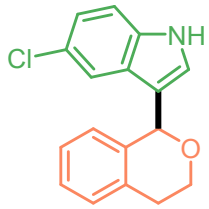
3-(isochroman-1-yl)-7-methyl-1*H*-indole (5ag)[5] Purple oil (27.8 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.37-7.32 (m, 1H), 7.19 (d, J = 4.03 Hz, 2H), 7.09-7.04 (m, 1H), 7.01-6.94 (m, 4H), 6.13 (s, 1H), 4.19-4.07 (m, 1H), 4.00-3.88 (m, 1H), 3.10-2.99 (m, 1H), 2.99-2.86 (m, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 136.2, 134.0, 128.7, 126.7, 126.5, 126.0, 125.8, 124.4, 122.9, 120.3, 120.2, 118.2, 117.8, 72.5, 62.5, 28.9, 16.6. HRMS (ESI), calcd. for $C_{18}H_{18}NO$ $(M+H)^+$: 264.1383, found: 264.1384.



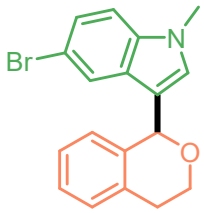
3-(isochroman-1-yl)-5-methoxy-1*H*-indole (5ah)[5] Light yellow oil (26.6 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.21-7.15 (m, 3H), 7.12-7.04 (m, 1H), 6.98 (d, J = 7.70 Hz, 1H), 6.93 (d, J = 2.32 Hz, 1H), 6.87 (d, J = 2.45 Hz, 1H), 6.82 (dd, J = 8.80, 2.45 Hz, 1H), 6.12 (s, 1H), 4.17-4.08 (m, 1H), 3.98-3.89 (m, 1H), 3.74 (s, 3H), 3.07-2.97 (m, 1H), 2.97-2.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 137.2, 134.0, 131.7, 128.7, 126.9, 126.8, 126.6, 125.9, 125.6, 117.3, 112.6, 111.9, 101.6, 72.3, 62.3, 55.8, 28.9. HRMS (ESI), calcd. for $C_{18}H_{18}NO_2$ $(M+H)^+$: 280.1332, found: 280.1337.



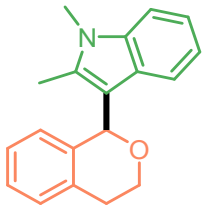
5-fluoro-3-(isochroman-1-yl)-1*H*-indole (5ai)[5] Yellow oil (17.7 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.34-7.14 (m, 3H), 7.14-7.01 (m, 3H), 7.00-6.84 (m, 2H), 6.06 (s, 1H), 4.24-4.06 (m, 1H), 4.04-3.87 (m, 1H), 3.19-3.01 (m, 1H), 2.90 (dt, J = 16.38, 4.52 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3 (d, ^1J = 234.8 Hz), 136.9, 133.9, 133.2, 128.9, 126.8, 126.7, 126.5, 126.4, 125.9, 117.8 (d, ^4J = 4.4 Hz), 111.8 (d, ^3J = 9.5 Hz), 110.8 (d, ^2J = 26.4 Hz), 105.2 (d, ^2J = 23.5 Hz), 72.5, 63.0, 28.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.0. HRMS (ESI), calcd. for $C_{17}H_{15}FNO$ $(M+H)^+$: 268.1132, found: 268.1131.



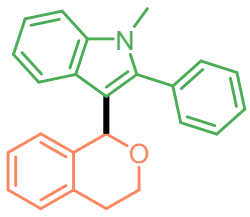
5-chloro-3-(isochroman-1-yl)-1*H*-indole (5aj)[5] Yellow oil (13.2 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.46 (d, J = 1.83 Hz, 1H), 7.24-7.17 (m, 3H), 7.14-7.05 (m, 2H), 6.98 (d, J = 2.45 Hz, 1H), 6.93 (d, J = 7.70 Hz, 1H), 6.07 (s, 1H), 4.19-4.09 (m, 1H), 4.00-3.90 (m, 1H), 3.14-3.02 (m, 1H), 2.91 (dt, J = 16.51, 4.89 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 135.0, 133.9, 128.9, 127.4, 126.8, 126.5, 126.0, 125.9, 125.6, 122.8, 119.6, 117.4, 112.2, 72.4, 62.9, 28.8. HRMS (ESI), calcd. for $C_{17}H_{15}ClNO$ $(M+H)^+$: 284.0837, found: 284.0839.



5-bromo-3-(isochroman-1-yl)-1-methyl-1*H*-indole (5ak) Brown oil (31.9 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 1.71 Hz, 1H), 7.31-7.26 (m, 1H), 7.21-7.17 (m, 2H), 7.15 (d, J = 8.68 Hz, 1H) 7.12-7.06 (m, 1H), 6.96 (d, J = 7.70 Hz, 1H), 6.83 (s, 1H), 6.07 (s, 1H), 4.15-4.06 (m, 1H), 3.97-3.88 (m, 1H), 3.70 (s, 3H), 3.10-2.99 (m, 1H), 2.96-2.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 136.1, 134.0, 130.3, 128.9, 128.6, 126.7, 126.6, 125.8, 124.8, 122.7, 115.8, 113.0, 110.8, 72.0, 62.6, 33.0, 28.8. HRMS (ESI), calcd. for $C_{18}H_{17}BrNO$ $(M+H)^+$: 342.0488, found: 342.0491

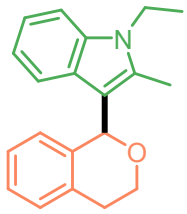


3-(isochroman-1-yl)-1,2-dimethyl-1*H*-indole (5al)[5] Yellow oil (52.1 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.12 (m, 3H), 7.12-7.03 (m, 2H), 6.99 (t, J = 7.21 Hz, 1H), 6.90 (t, J = 7.21 Hz, 1H), 6..80 (d, J =7.58 Hz, 1H), 6.07 (s, 1H), 4.36-4.19 (m, 1H), 4.07-3.92 (m, 1H), 3.65 (s, 3H), 3.35-3.17 (m, 1H), 2.82 (d, J = 16.38 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.9, 135.9, 133.9, 128.5, 126.8, 126.5, 126.4, 126.2, 120.7, 119.3, 119.2, 111.9, 108.6, 72.8, 65.0, 29.5, 29.2, 10.8. HRMS (ESI), calcd. for $C_{19}H_{20}NO$ $(M+H)^+$: 278.1539, found: 278.1537.



3-(isochroman-1-yl)-1-methyl-2-phenyl-1*H*-indole (5am) Light red oil (53.9 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.09 Hz, 2H), 7.52-7.40 (m, 3H), 7.30 (d, J = 8.19 Hz, 1H), 7.20-7.08 (m,

3H), 7.02 (d, J = 7.95 Hz, 1H), 6.99-6.88 (m, 2H), 6.84 (d, J = 7.70 Hz, 1H), 5.79 (s, 1H), 4.33-4.25 (m, 1H), 3.95-3.86 (m, 1H), 3.62 (s, 3H), 3.32-3.21 (m, 1H), 2.77 (d, J = 16.26 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 138.4, 137.7, 133.9, 131.3, 130.9, 128.5, 126.6, 126.3, 126.2, 126.1, 121.9, 120.7, 119.9, 113.6, 109.4, 73.2, 65.0, 31.0, 29.2. HRMS (ESI), calcd. for $C_{24}H_{22}NO$ $(M+H)^+$: 340.1696, found: 340.1696.



1-ethyl-3-(isochroman-1-yl)-2-methyl-1*H*-indole (5an) Light green oil (58.2 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J = 8.19 Hz, 1H), 7.20-7.11 (m, 2H), 7.10-7.04 (m, 2H), 7.02-6.96 (m, 1H), 6.93-6.87 (m, 1H), 6.79 (d, J = 7.82 Hz, 1H), 6.07 (s, 1H), 4.34-4.23 (m, 1H), 4.12 (q, J = 7.21 Hz, 2H), 4.00 (td, J = 10.76, 3.55 Hz, 1H), 3.35-3.21 (m, 1H), 2.82 (d, J = 16.26 Hz, 1H), 2.39 (s, 3H), 1.33 (t, J = 7.21 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 135.8, 135.0, 133.8, 128.5, 127.0, 126.5, 126.4, 126.2, 120.7, 119.3, 119.2, 111.9, 108.7, 72.8, 65.0, 37.8, 29.2, 15.3, 10.5. HRMS (ESI), calcd. for $C_{20}H_{22}NO$ $(M+H)^+$: 292.1696, found: 292.1697.

6. NMR Spectra: ^{1}H, ^{13}C and ^{19}F NMR Spectra

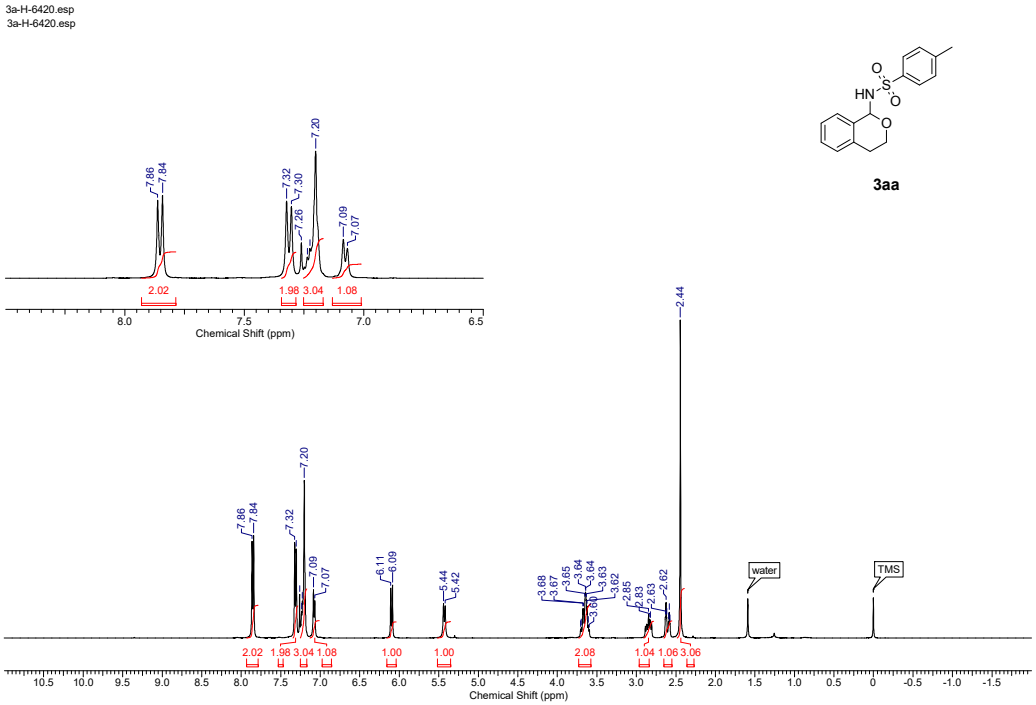


Figure S19. ^{1}H NMR spectra of compound **3aa**

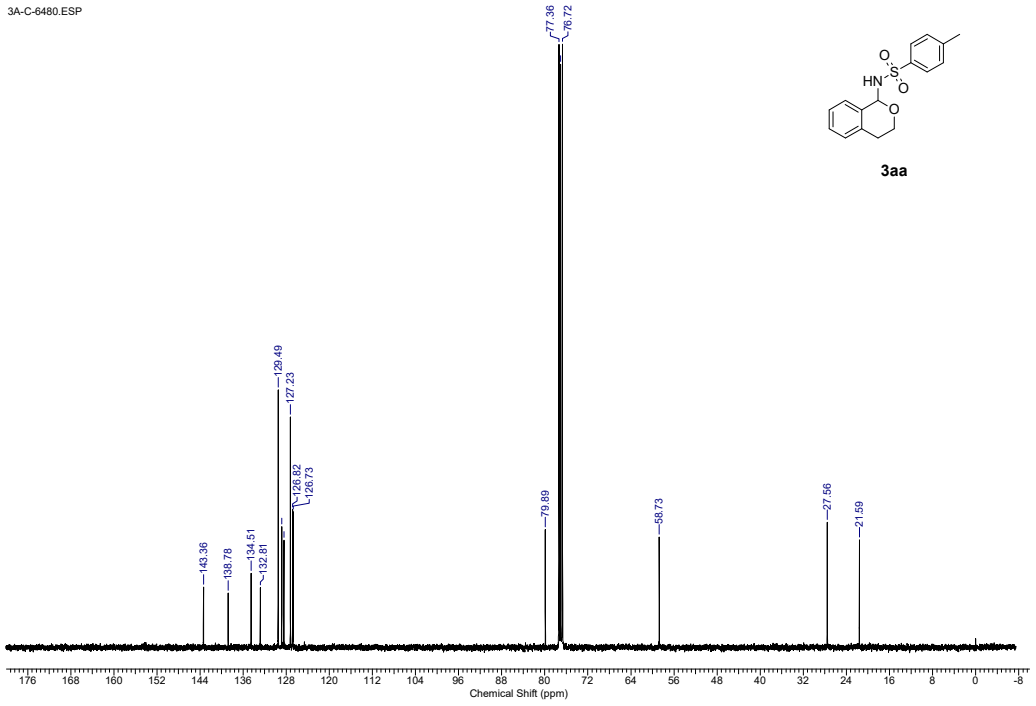


Figure S20. ^{13}C NMR spectra of compound **3aa**

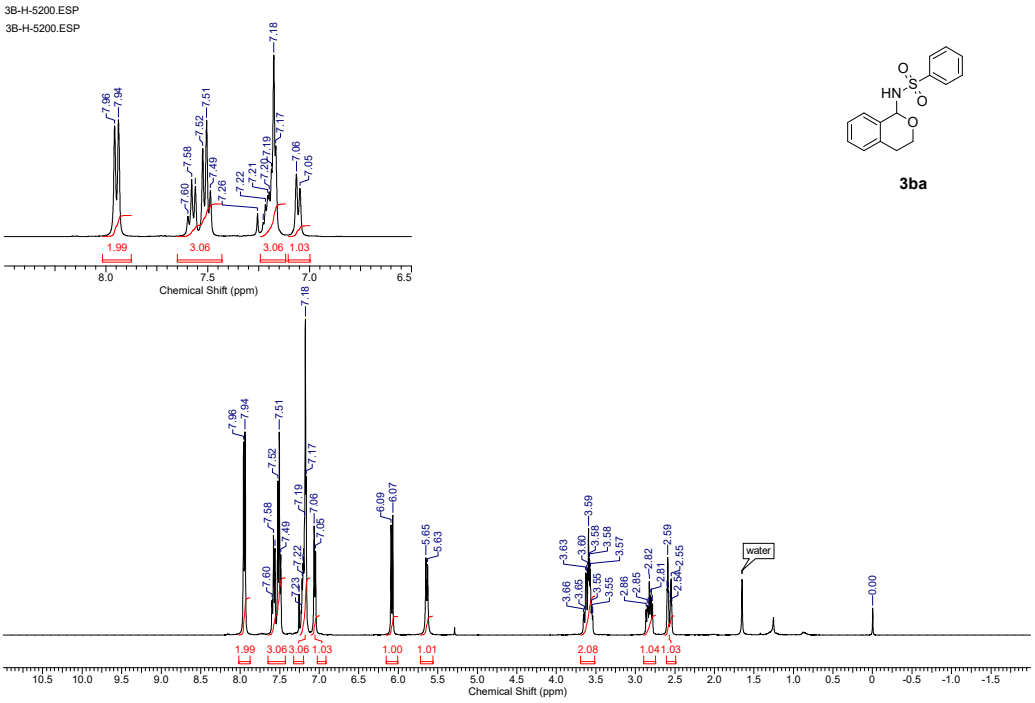


Figure S21. ^{1}H NMR spectra of compound **3ba**

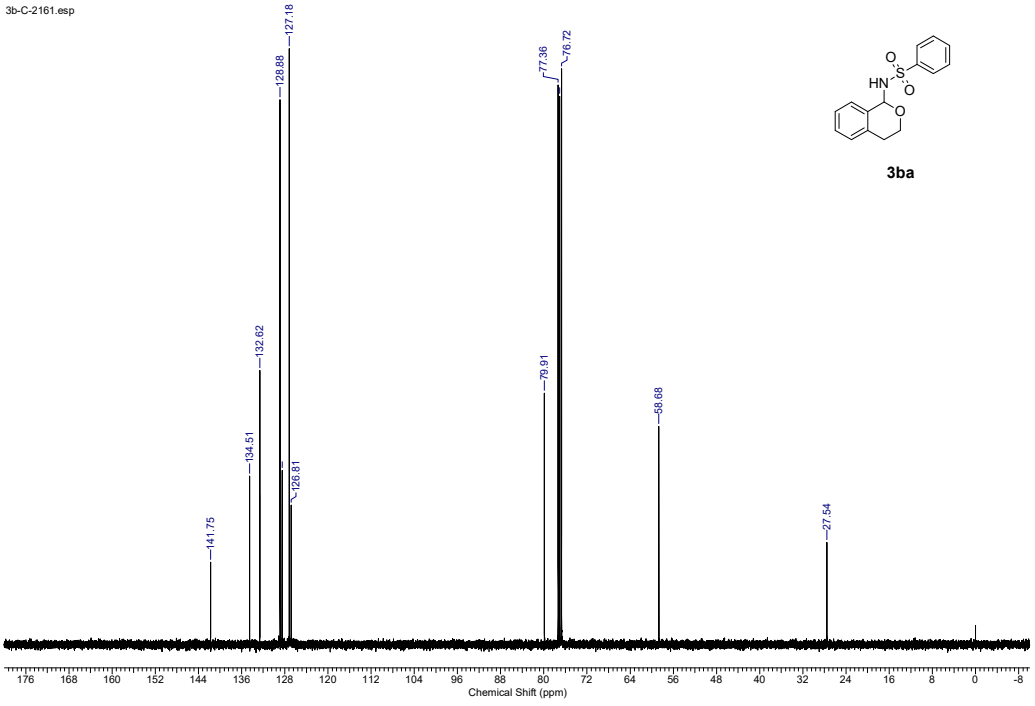


Figure S22. ^{13}C NMR spectra of compound **3ba**

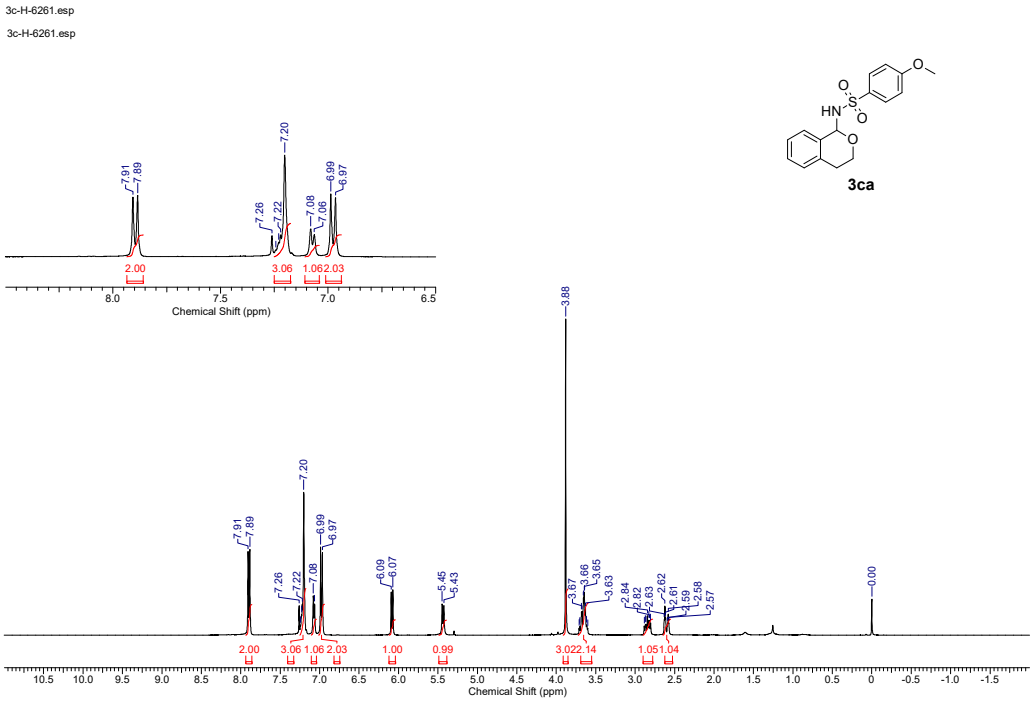


Figure S23. ^{1}H NMR spectra of compound **3ca**

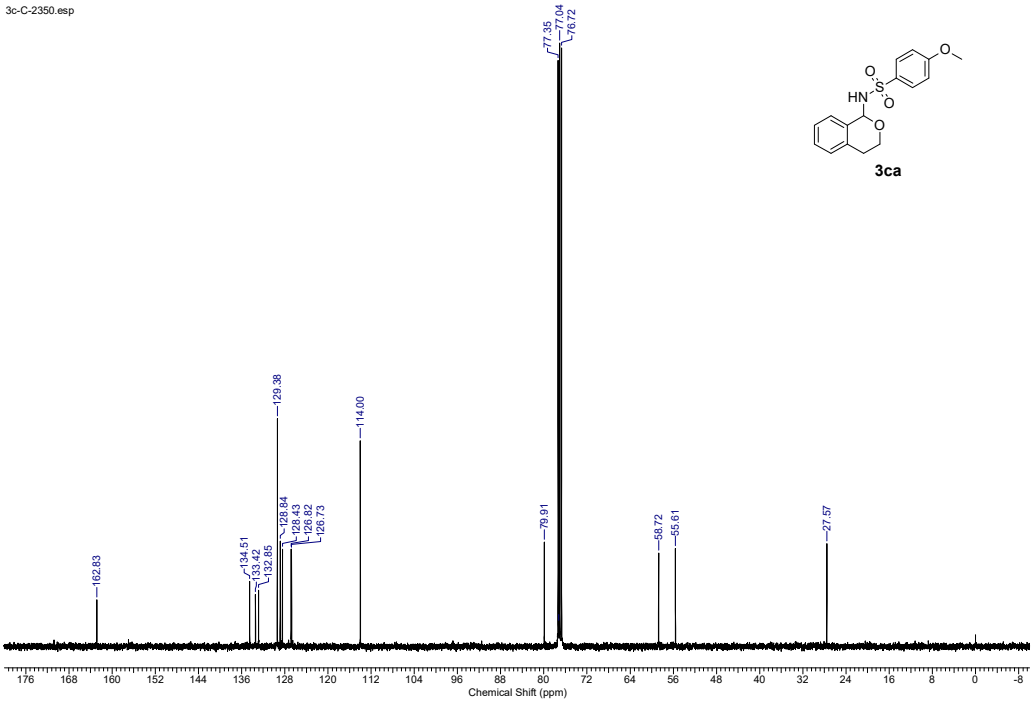


Figure S24. ^{13}C NMR spectra of compound **3ca**

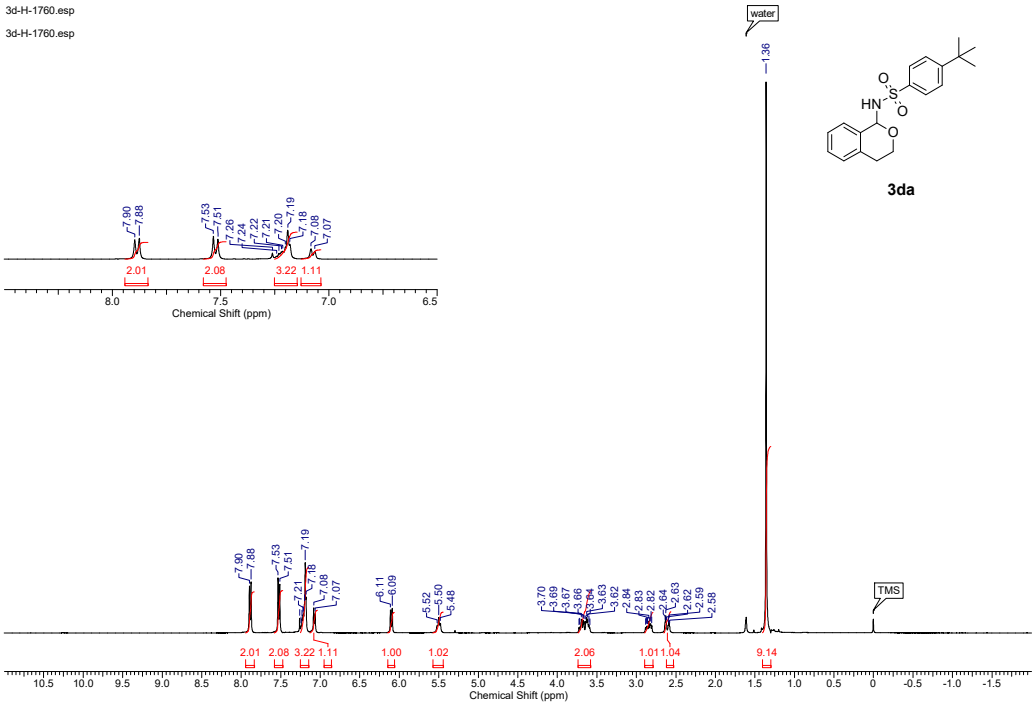


Figure S25. ^{1}H NMR spectra of compound **3da**

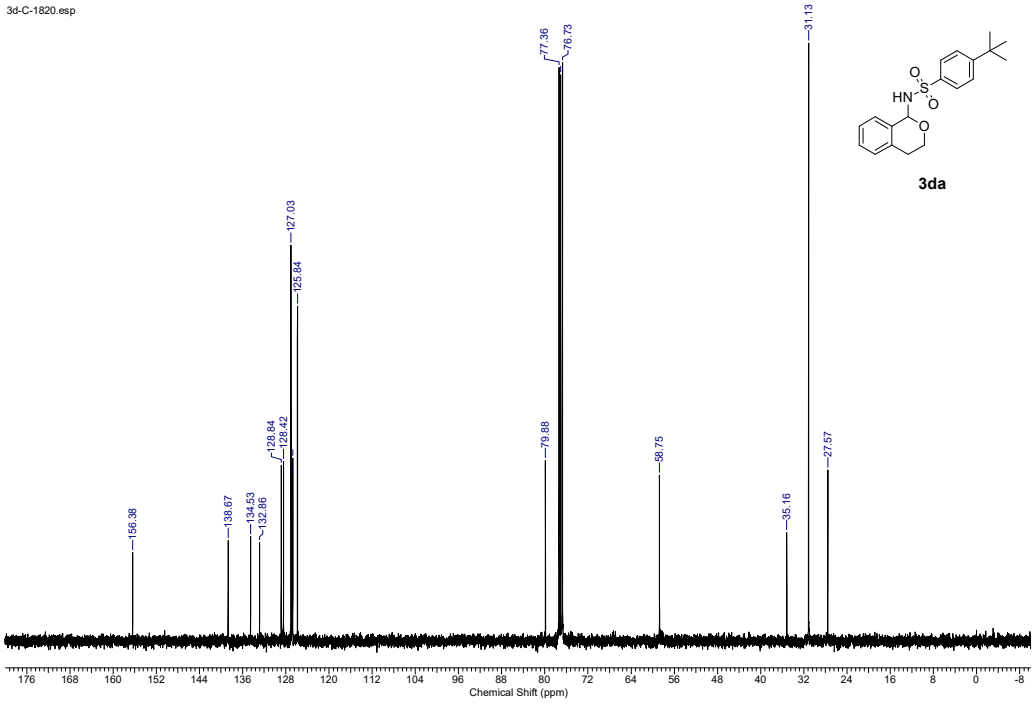


Figure S26. ^{13}C NMR spectra of compound **3da**

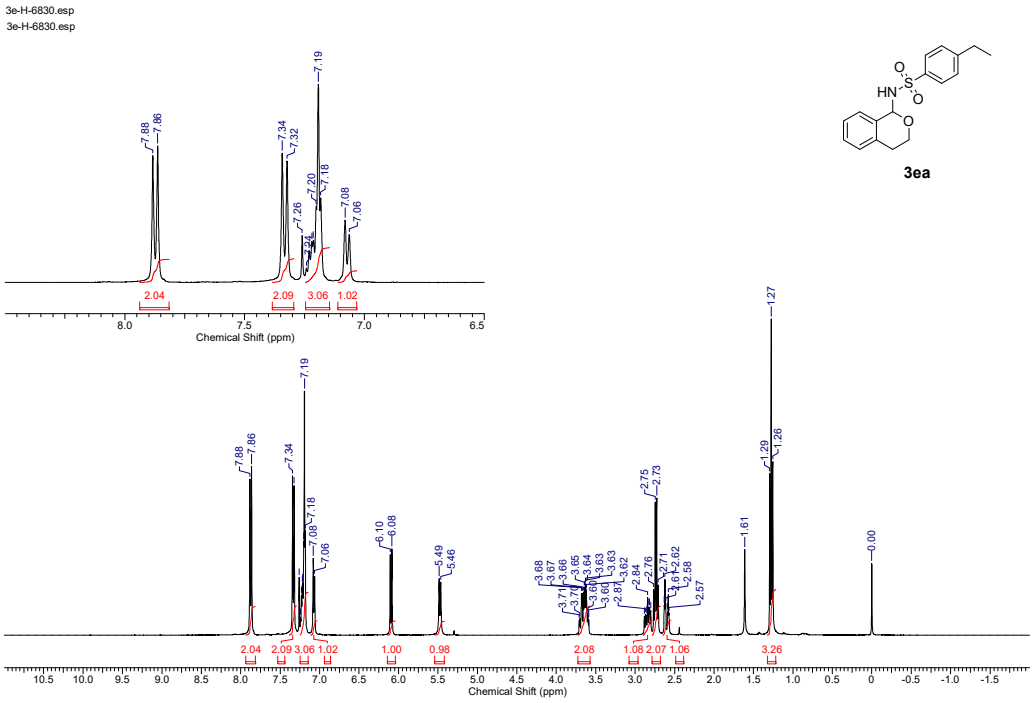


Figure S27. ^{1}H NMR spectra of compound **3ea**

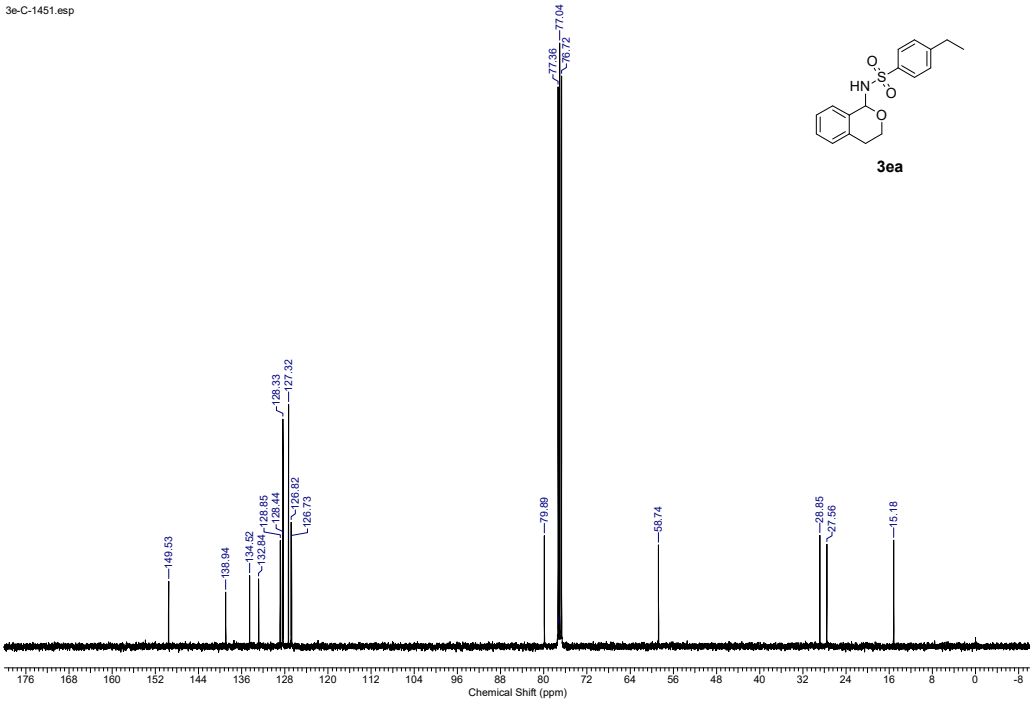


Figure S28. ^{13}C NMR spectra of compound **3ea**

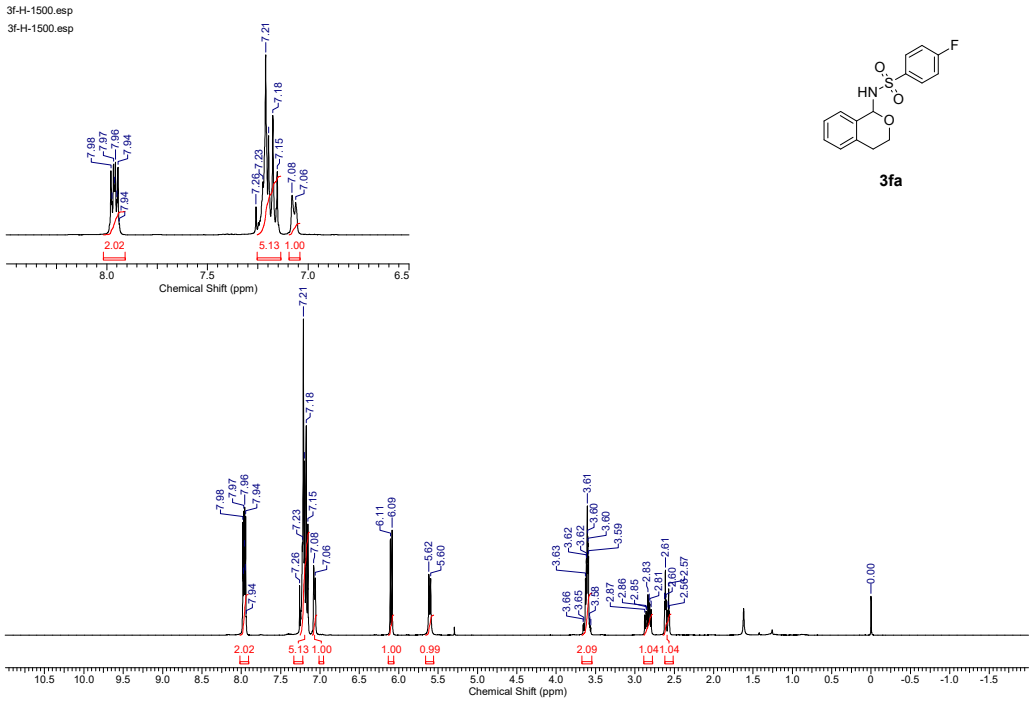


Figure S29. ^{1}H NMR spectra of compound **3fa**

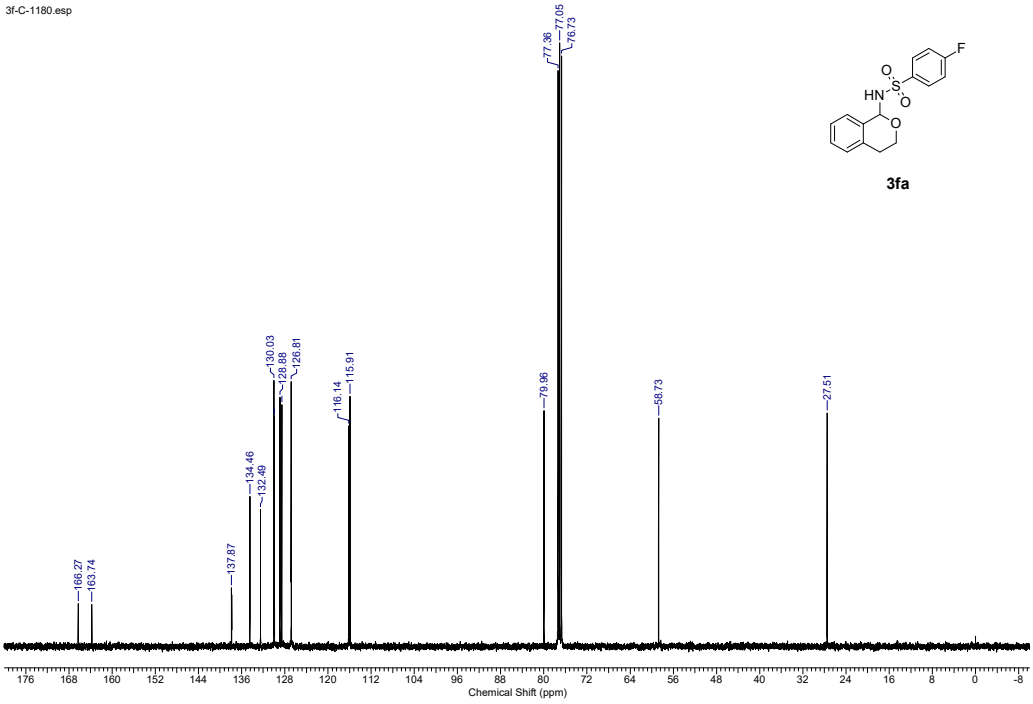


Figure S30. ^{13}C NMR spectra of compound **3fa**

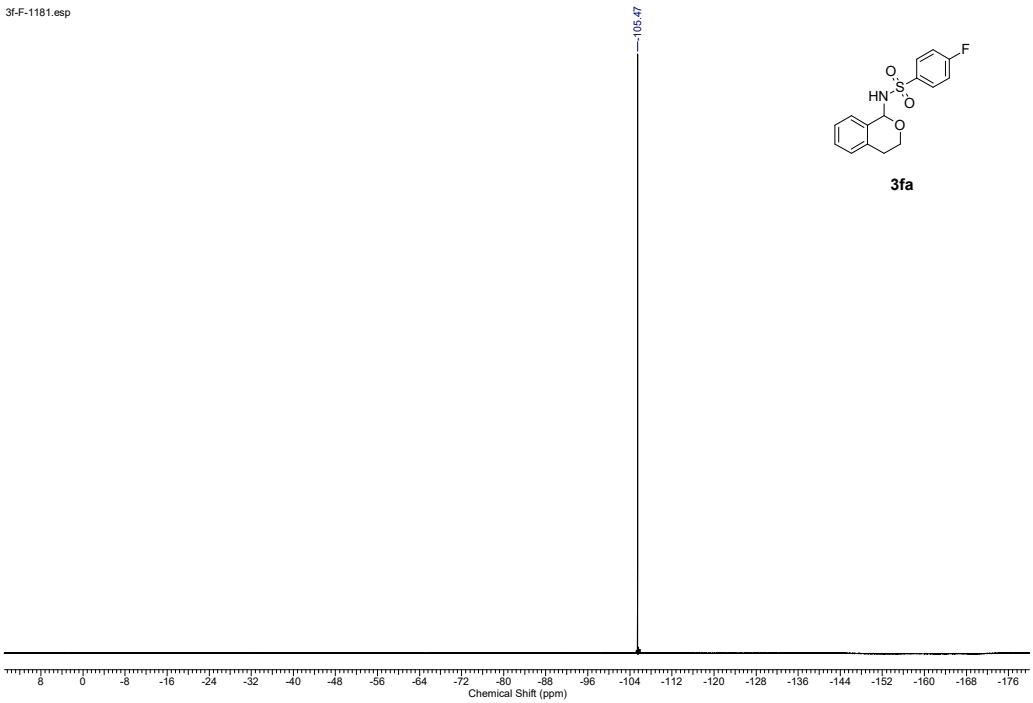


Figure S31. ^{19}F NMR spectra of compound **3fa**

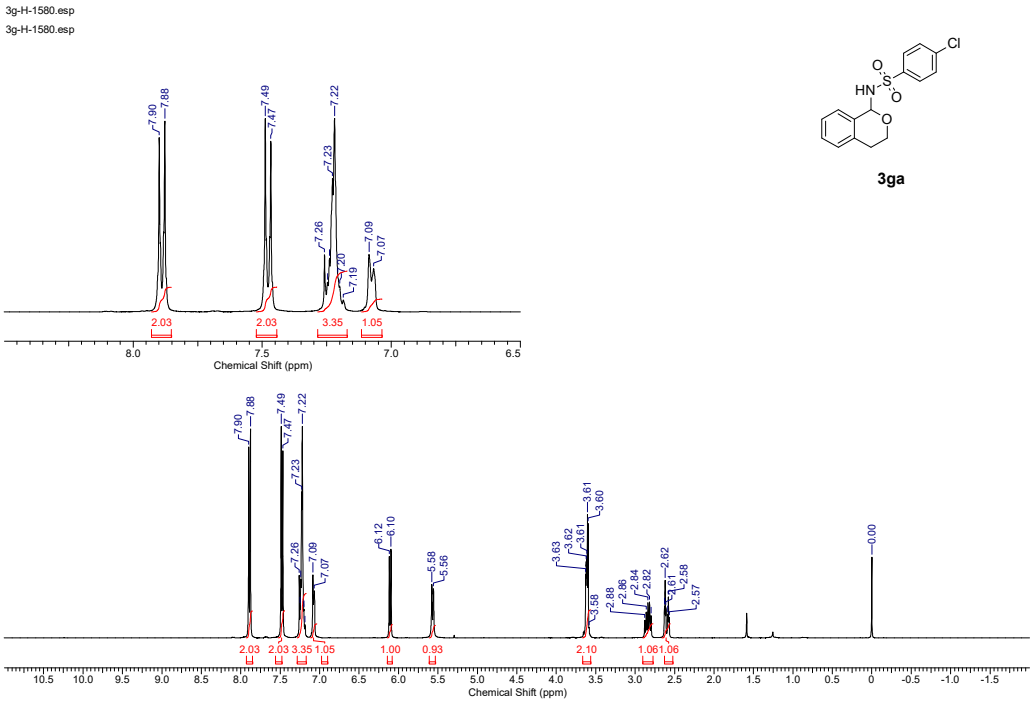


Figure S32. ^{1}H NMR spectra of compound **3ga**

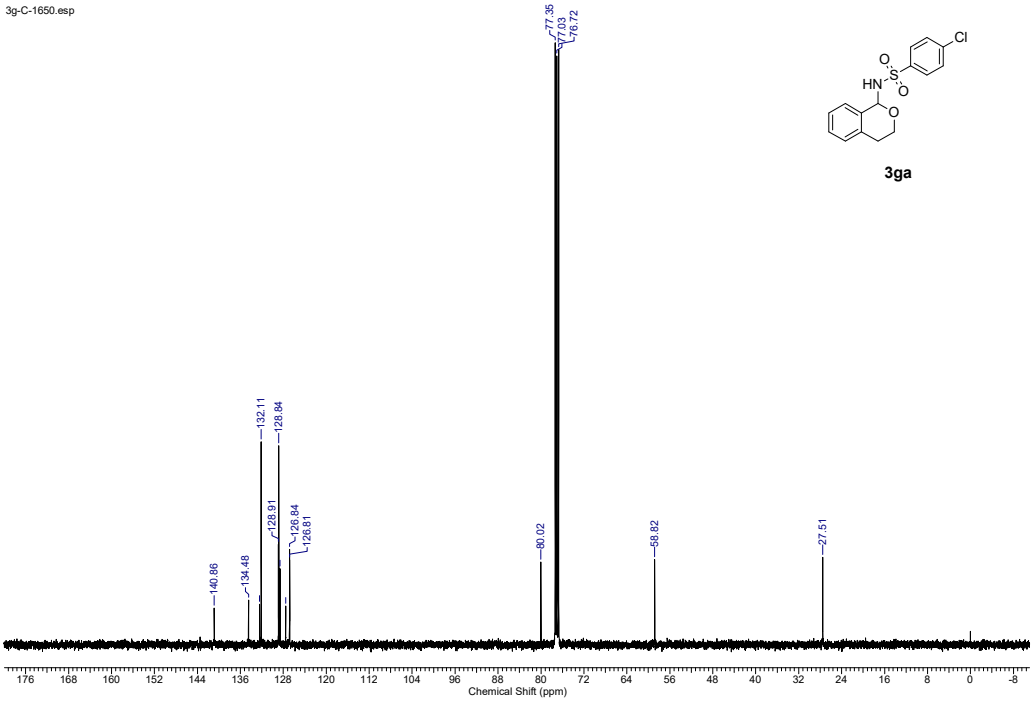


Figure S33. ^{13}C NMR spectra of compound **3ga**

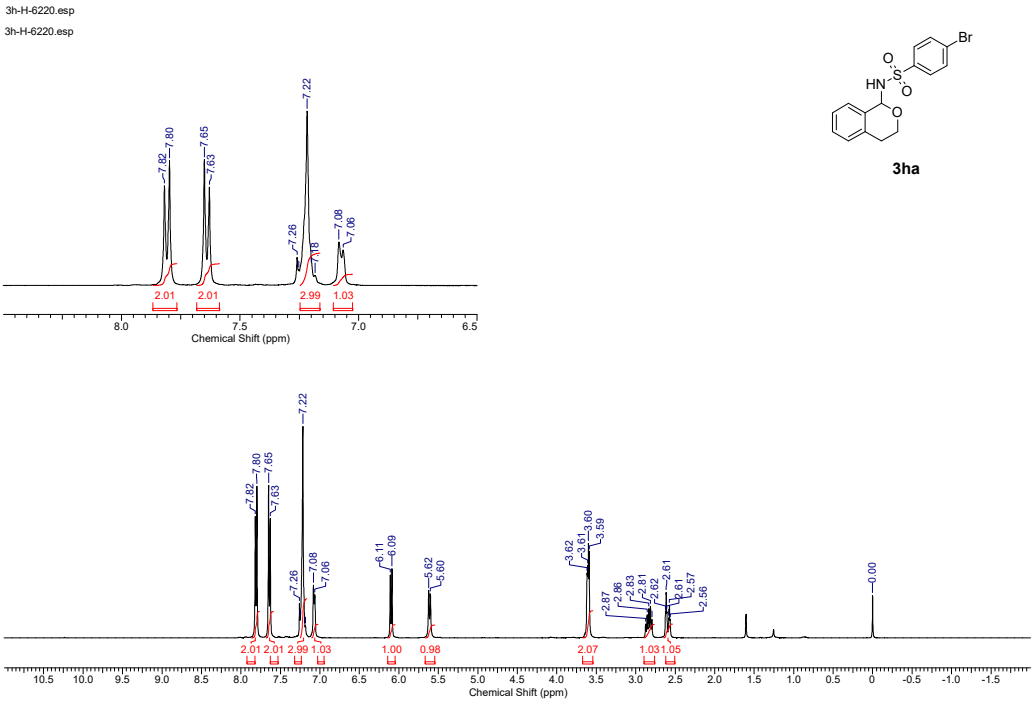


Figure S34. ^{1}H NMR spectra of compound **3ha**

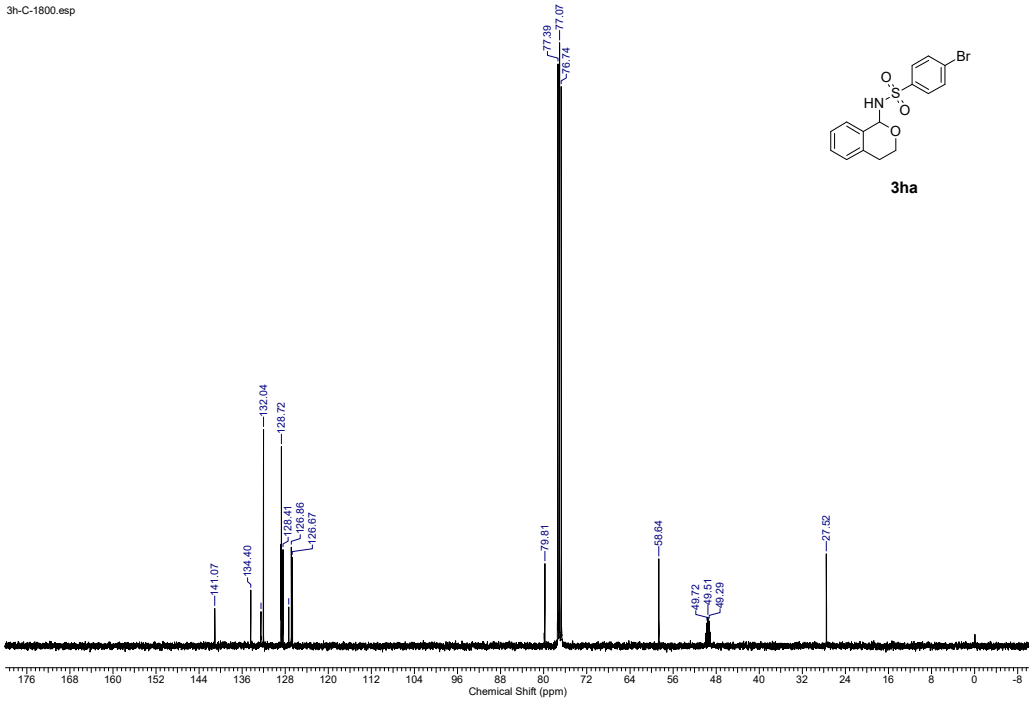


Figure S35. ^{13}C NMR spectra of compound **3ha**

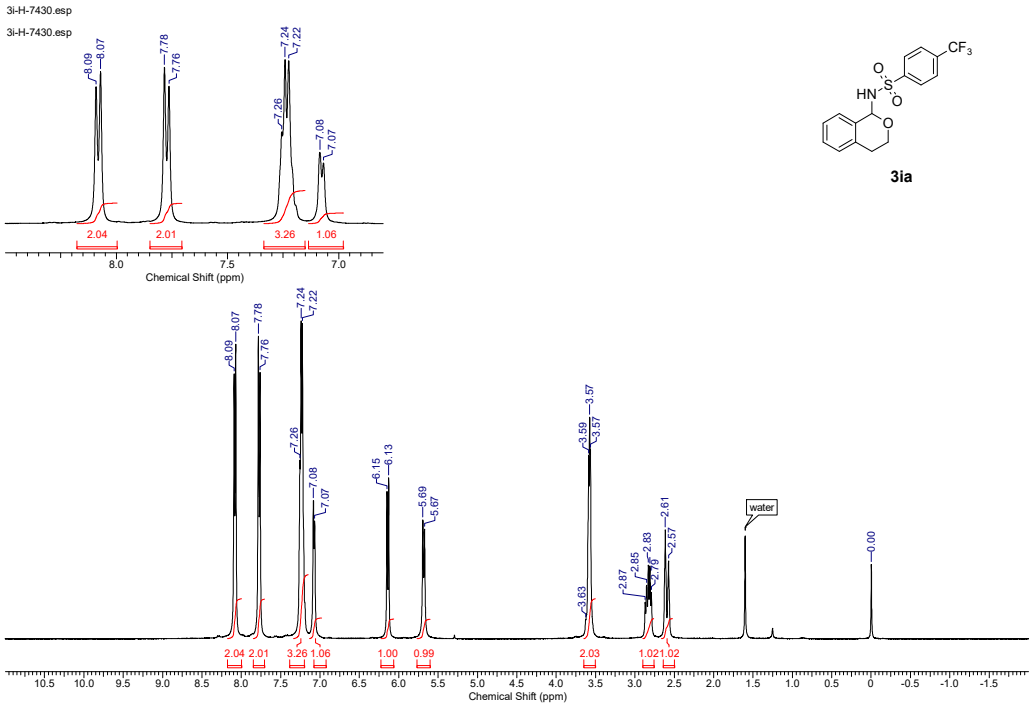


Figure S36. ^{1}H NMR spectra of compound **3ia**

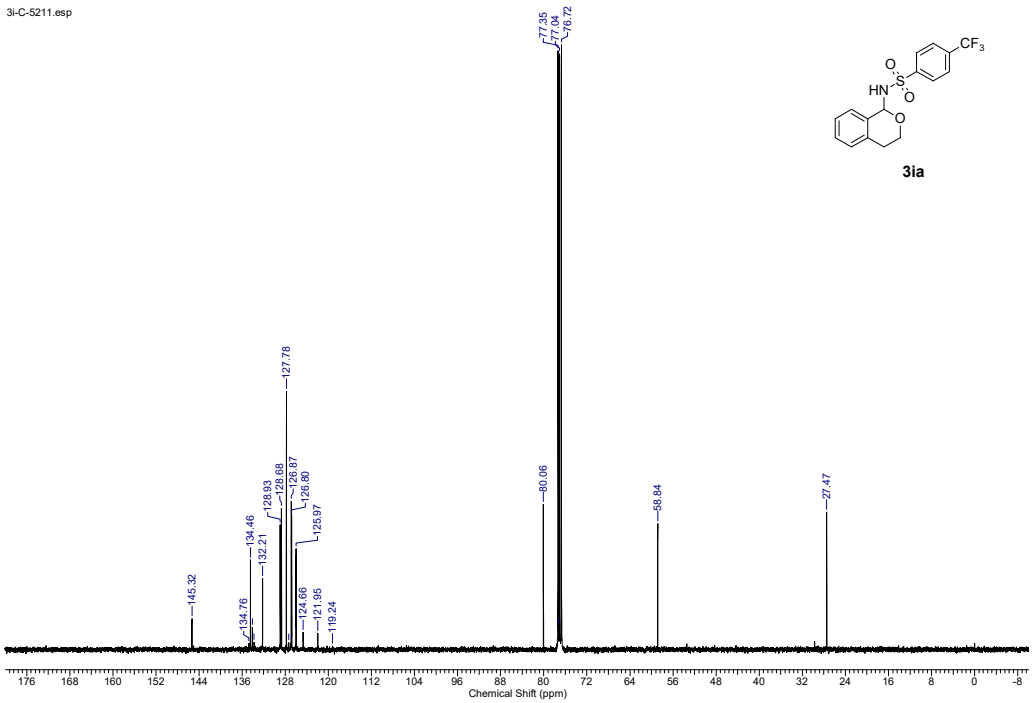


Figure S37. ^{13}C NMR spectra of compound **3ia**

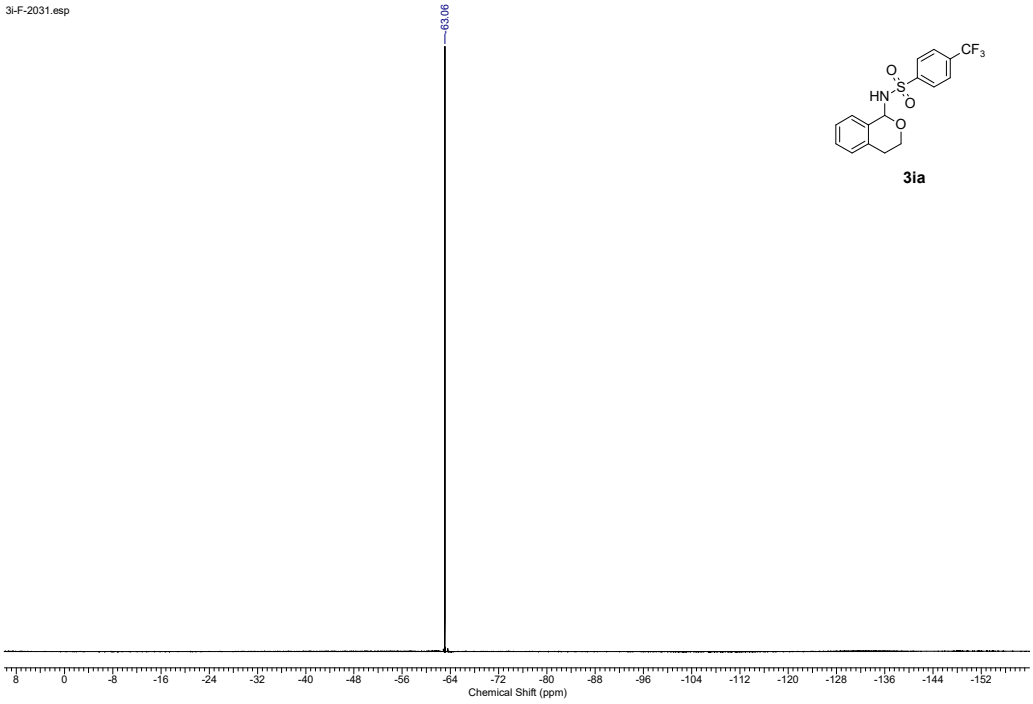


Figure S38. ^{19}F NMR spectra of compound **3ia**

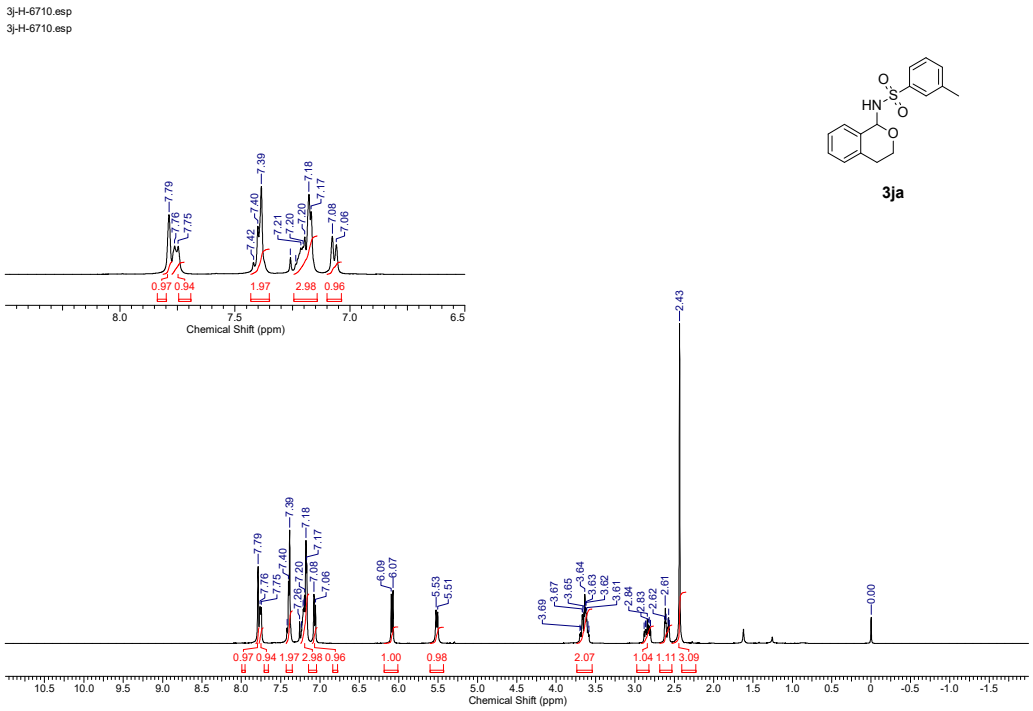


Figure S39. ^{1}H NMR spectra of compound **3ja**

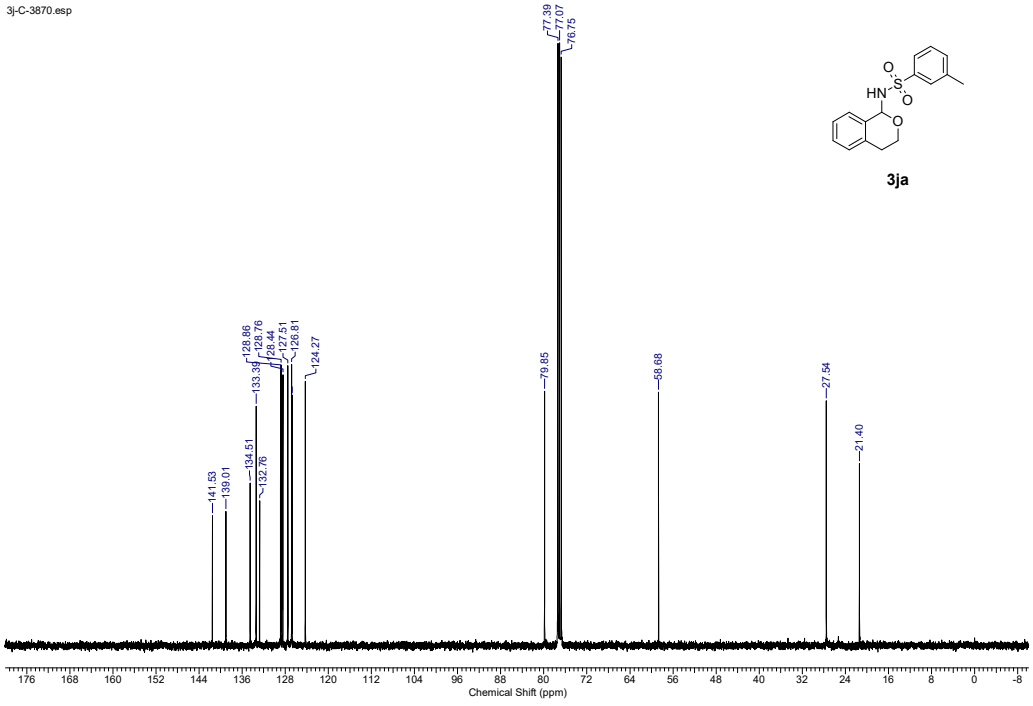


Figure S40. ^{13}C NMR spectra of compound **3ja**

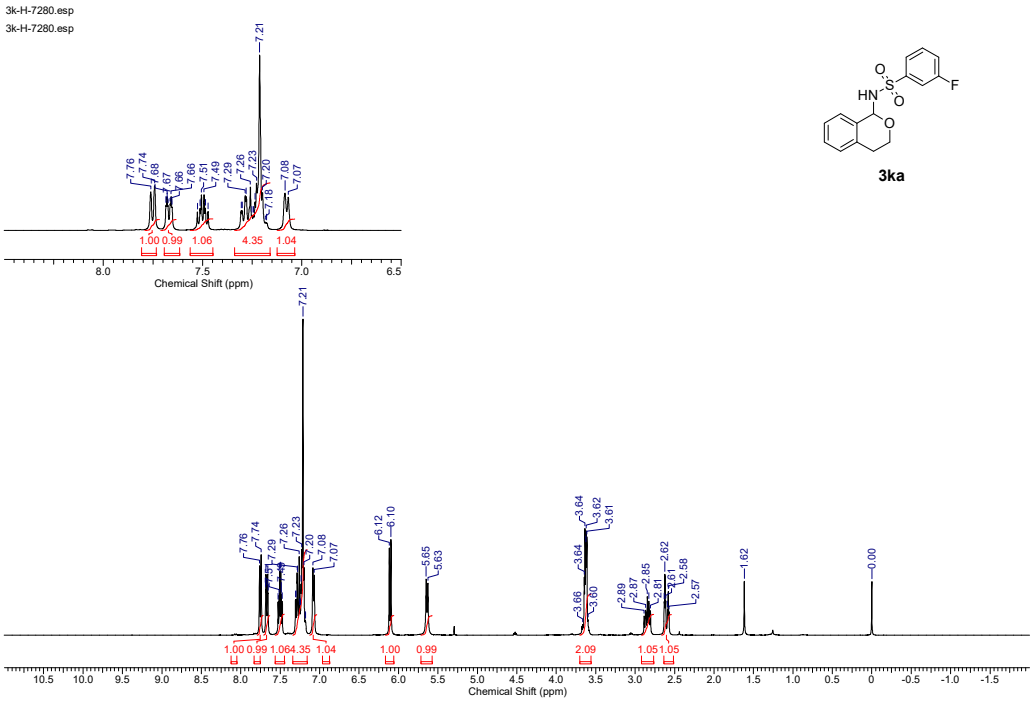


Figure S41. ^{1}H NMR spectra of compound **3ka**

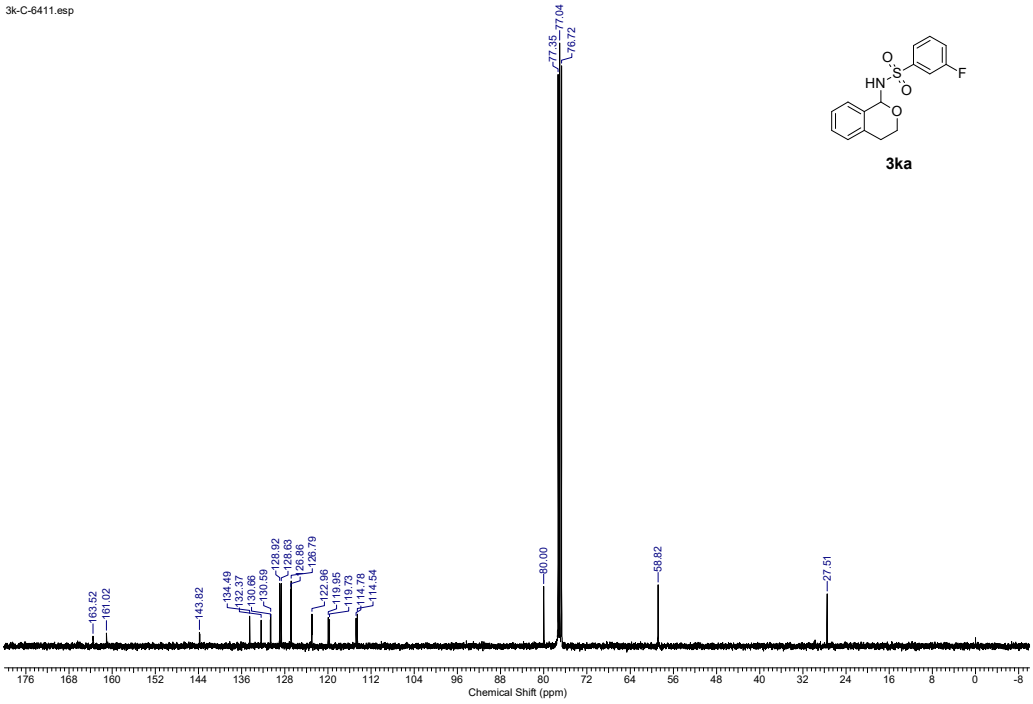


Figure S42. ^{13}C NMR spectra of compound **3ka**

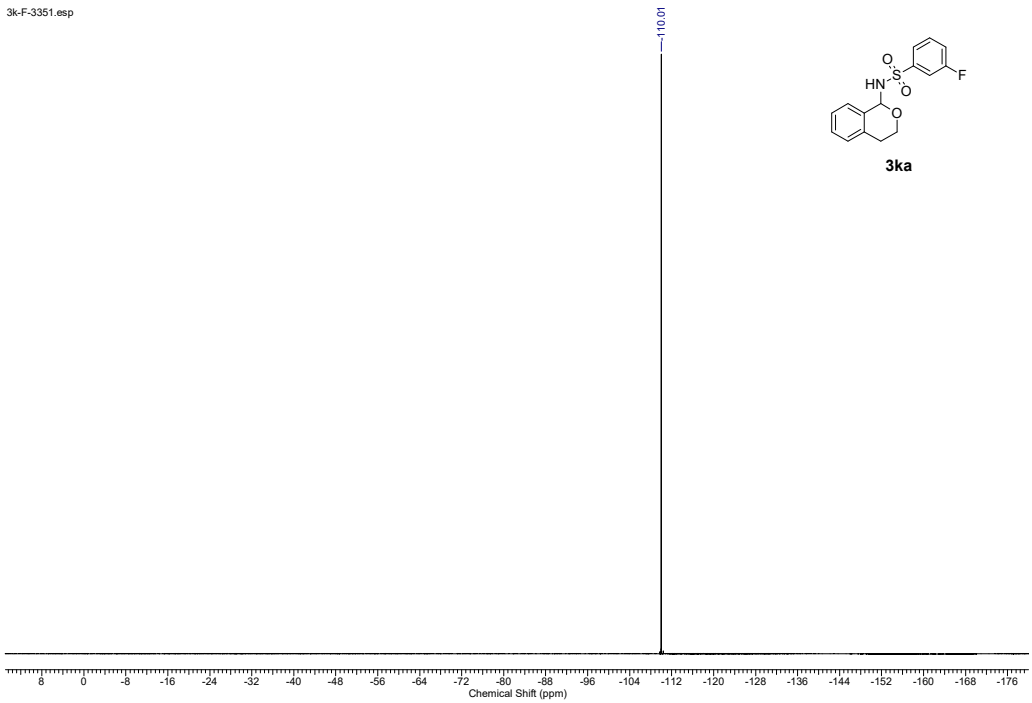


Figure S43. ^{19}F NMR spectra of compound **3ka**

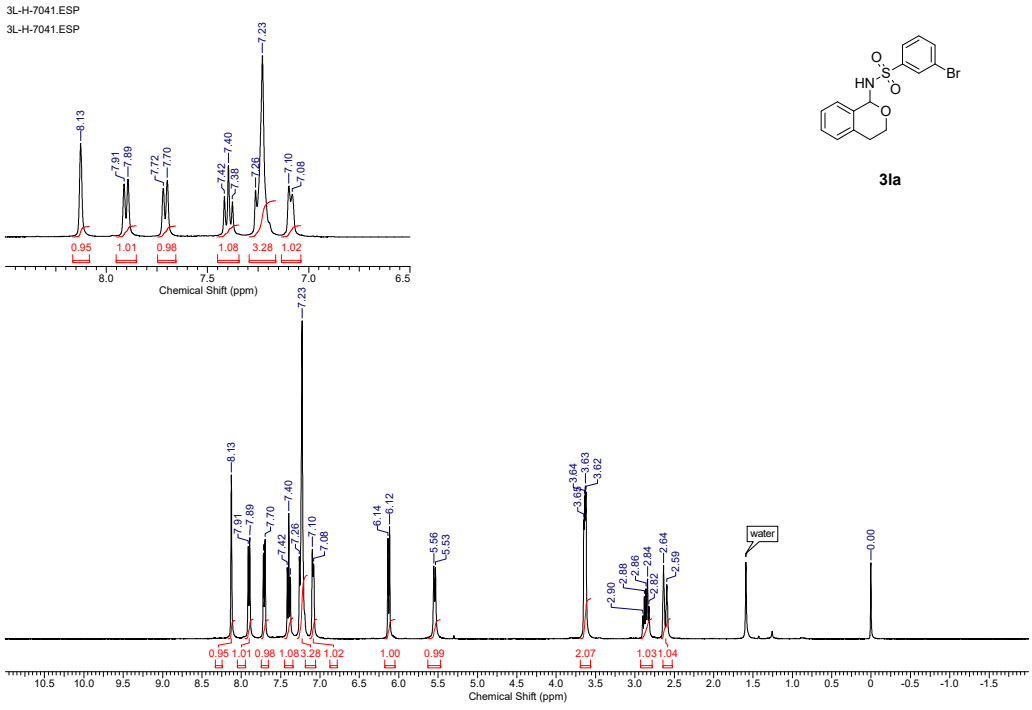


Figure S44. ^{1}H NMR spectra of compound **3la**

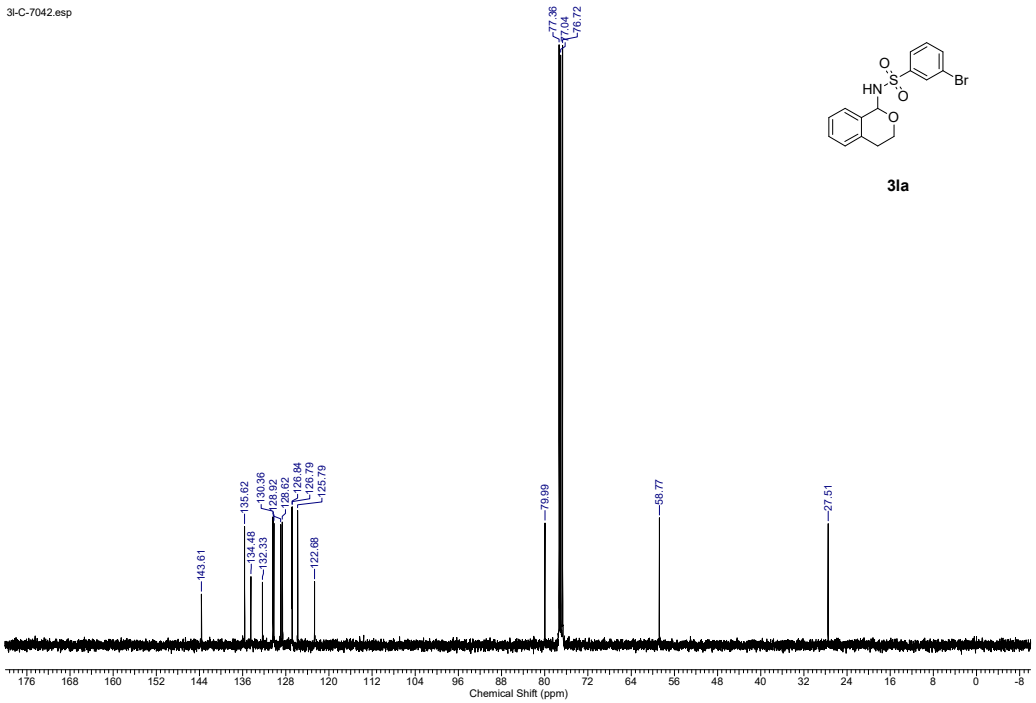


Figure S45. ^{13}C NMR spectra of compound **3la**

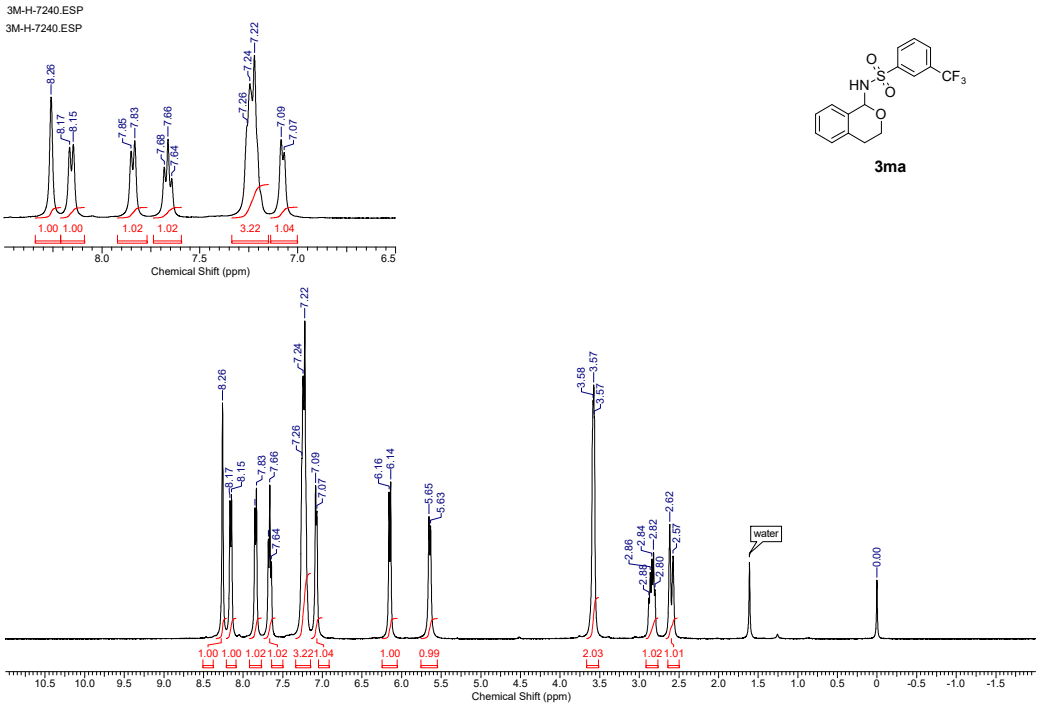


Figure S46. ^{1}H NMR spectra of compound **3ma**

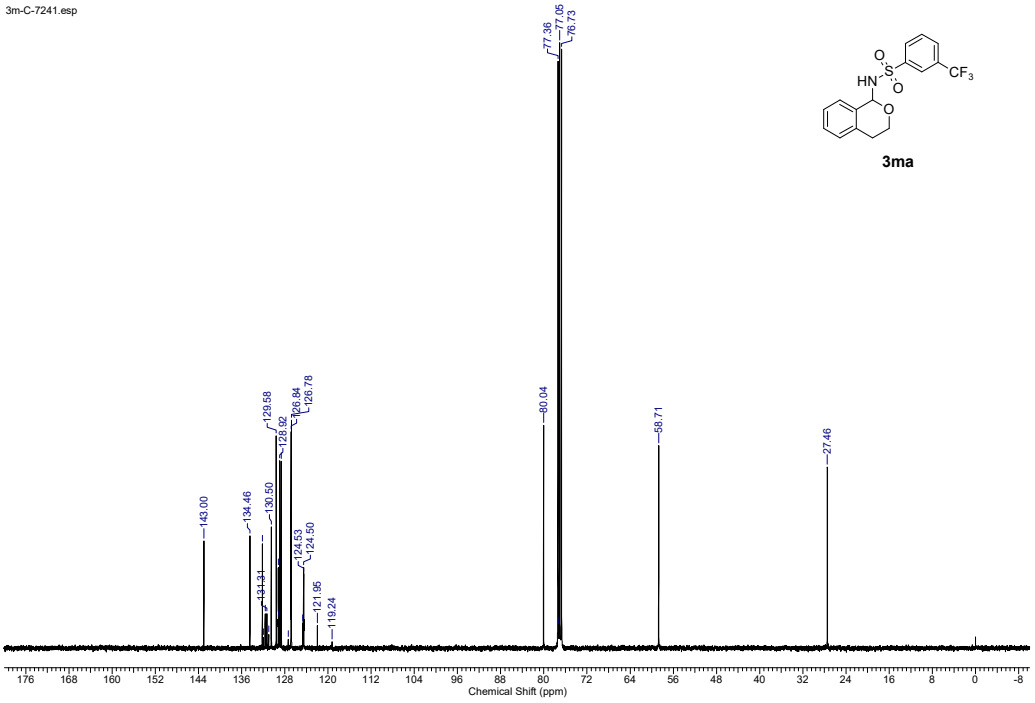


Figure S47. ^{13}C NMR spectra of compound **3ma**

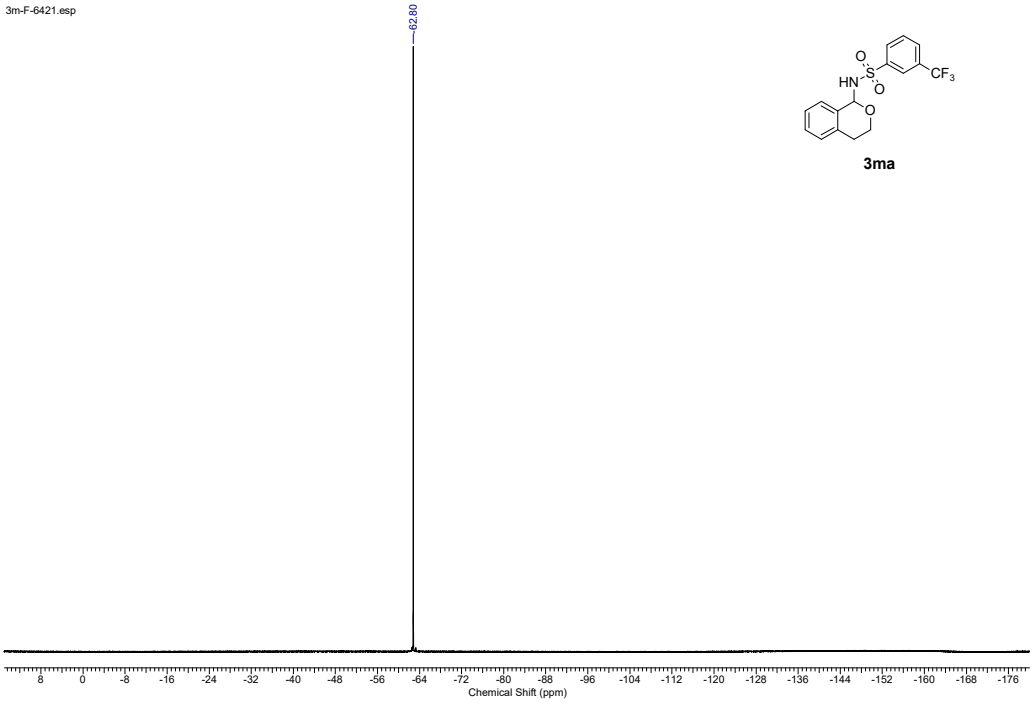


Figure S48. ^{19}F NMR spectra of compound **3ma**

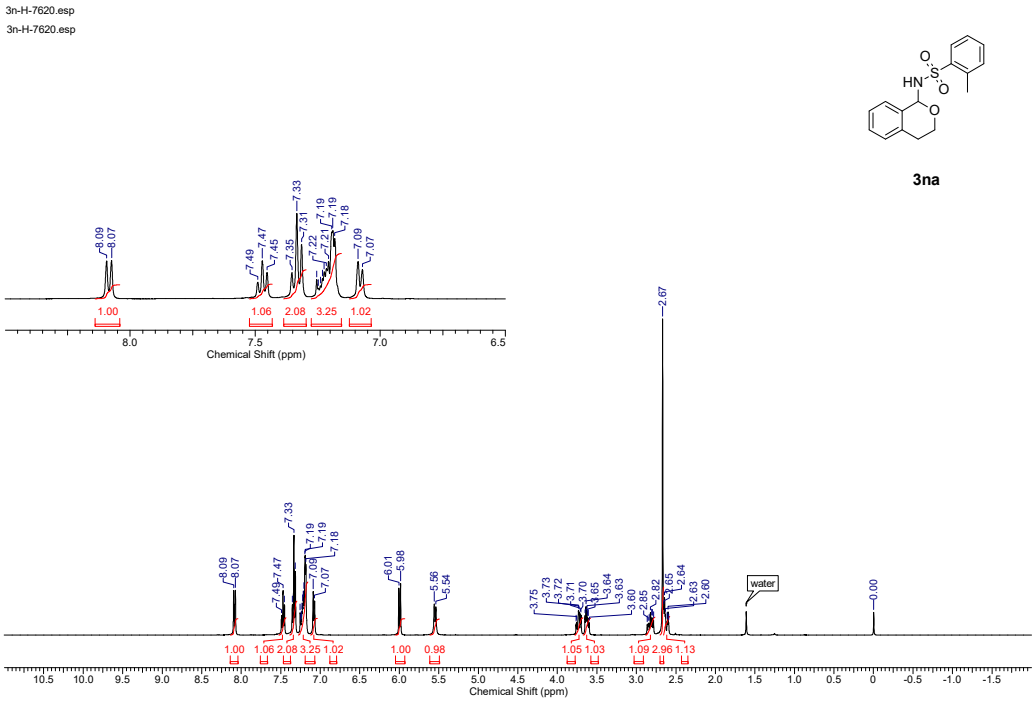


Figure S49. ^{1}H NMR spectra of compound **3na**

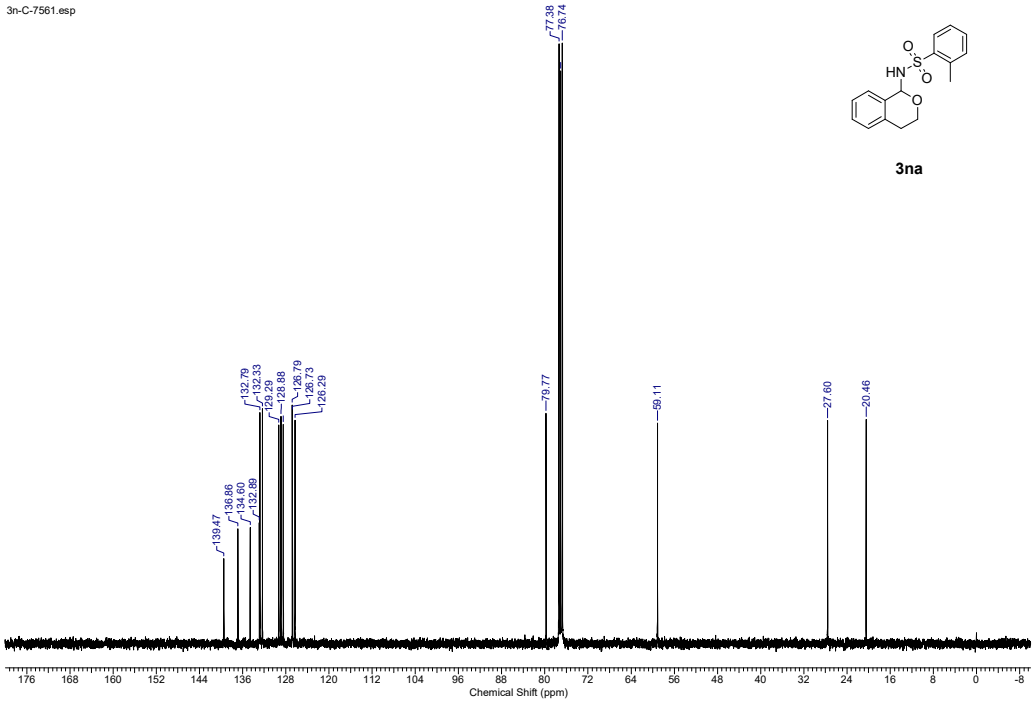


Figure S50. ^{13}C NMR spectra of compound **3na**

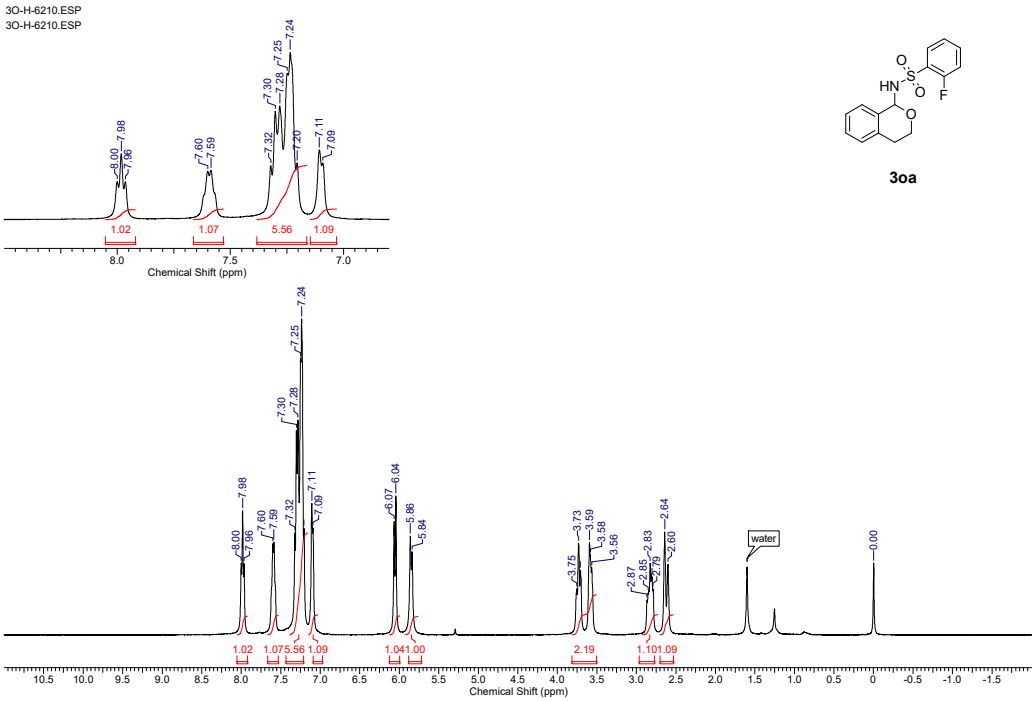


Figure S51. ^{1}H NMR spectra of compound **3oa**

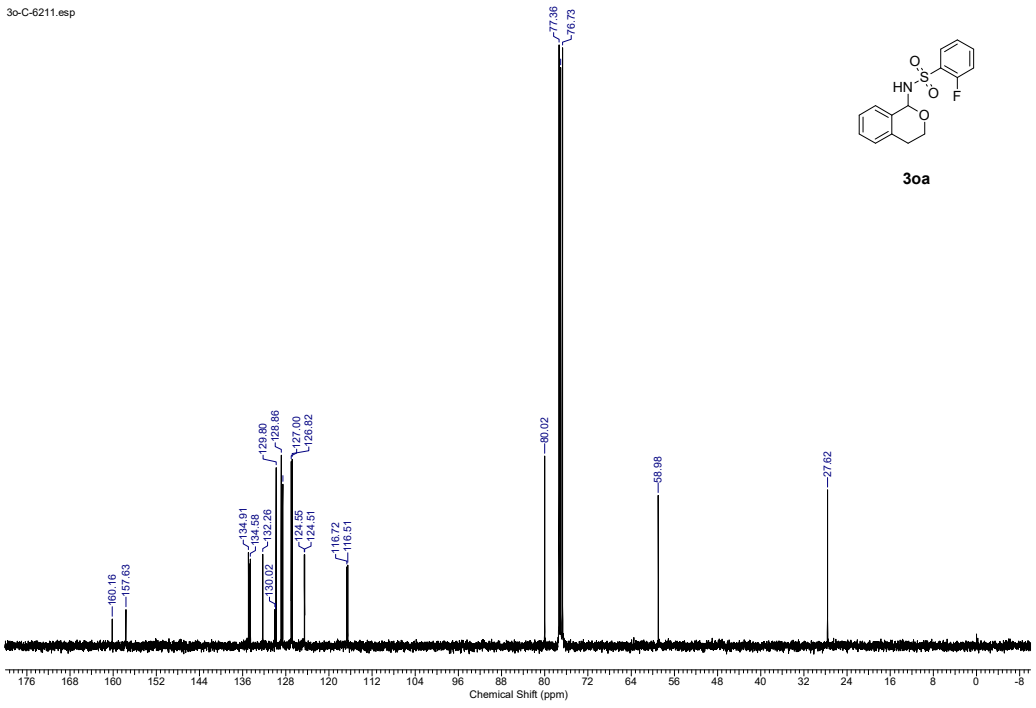


Figure S52. ^{13}C NMR spectra of compound **3oa**

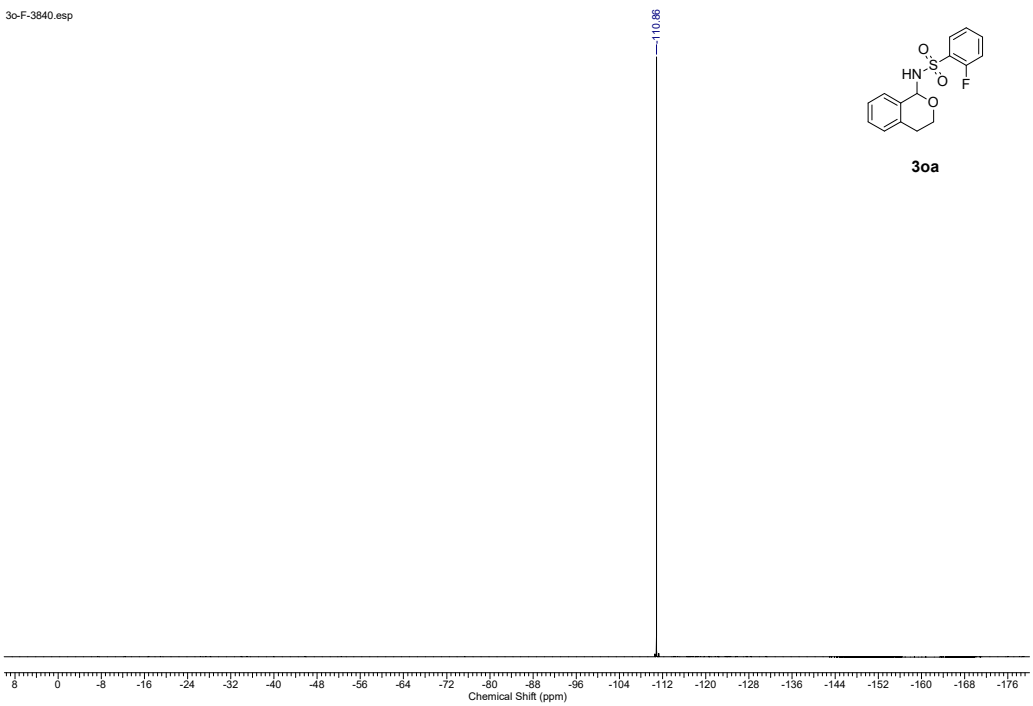


Figure S53. ^{13}C NMR spectra of compound **3oa**

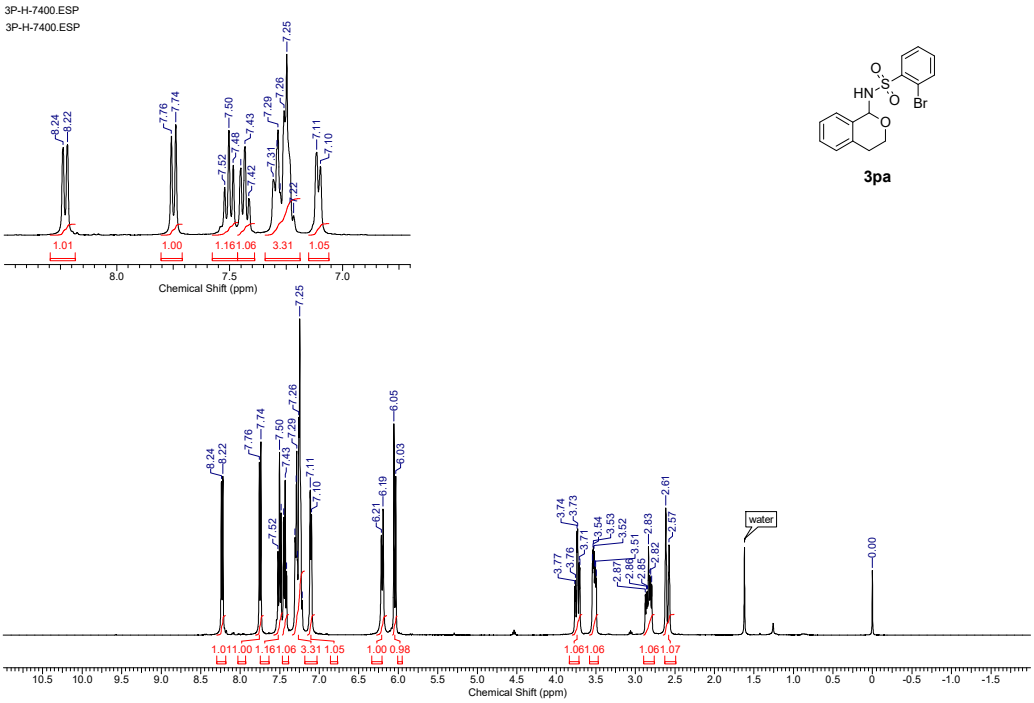


Figure S54. ^{1}H NMR spectra of compound **3pa**

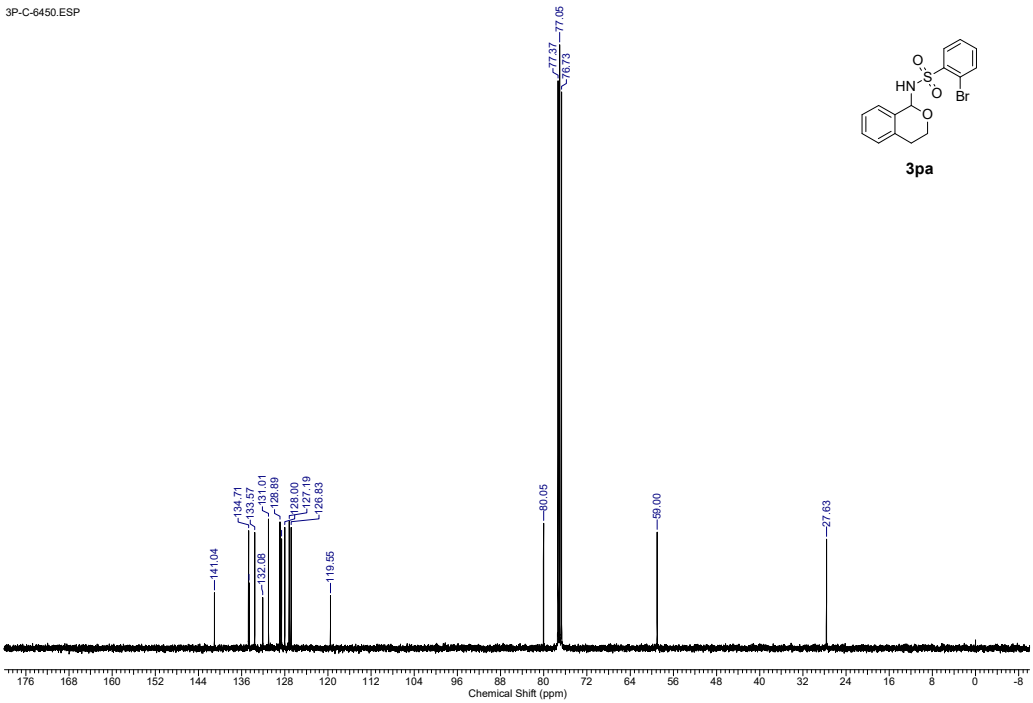


Figure S55. ^{13}C NMR spectra of compound **3pa**

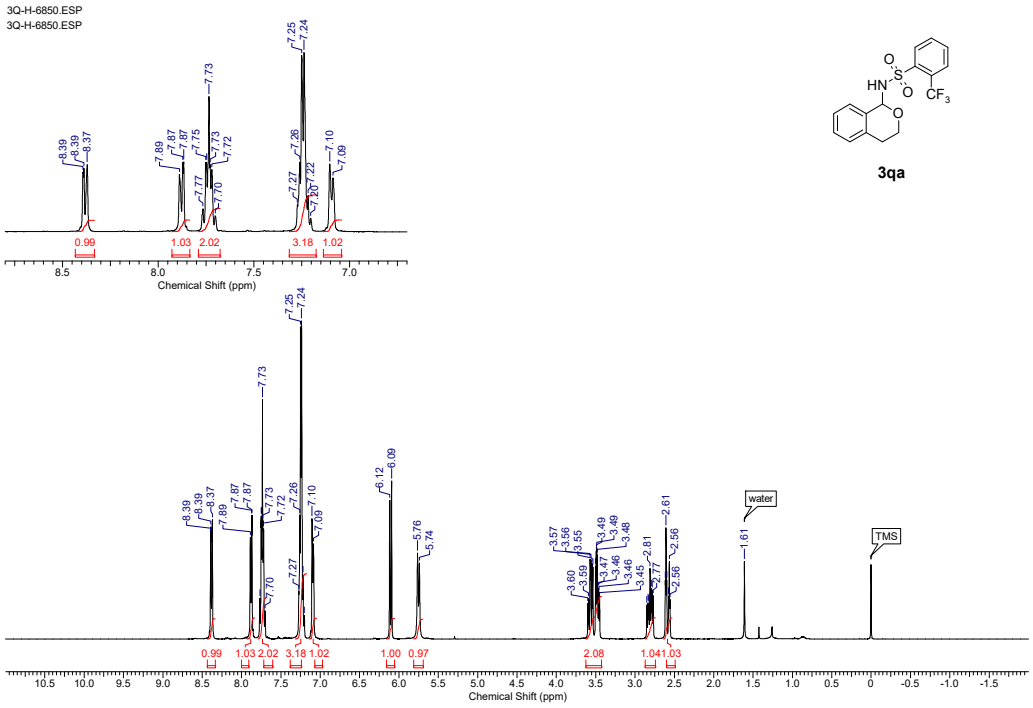


Figure S56. ^{1}H NMR spectra of compound **3qa**

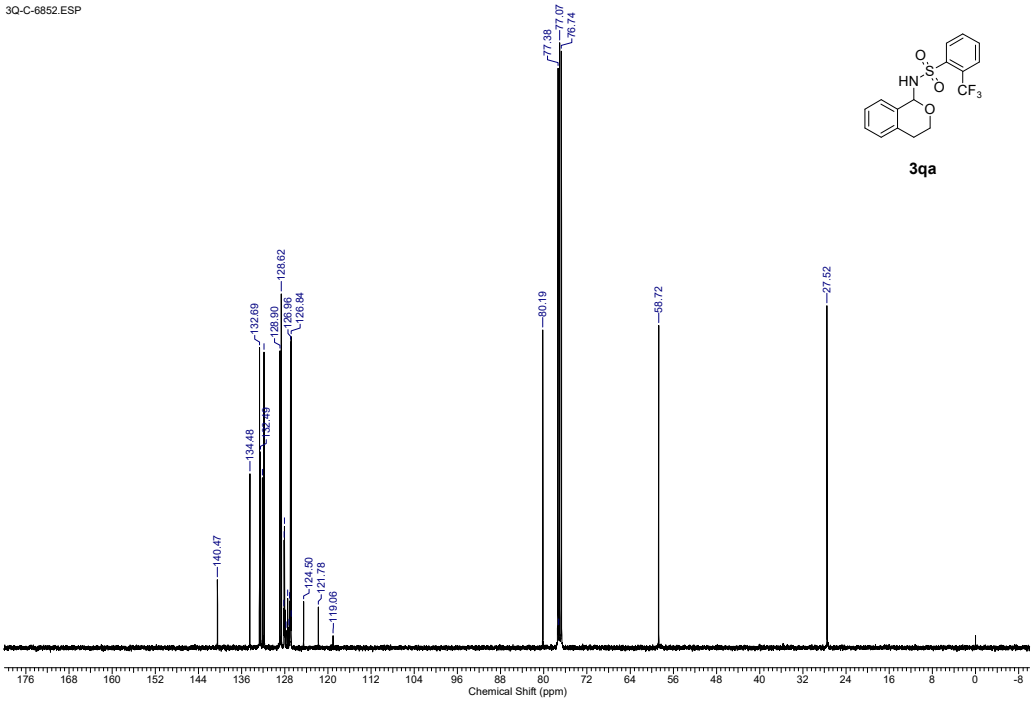


Figure S57. ^{13}C NMR spectra of compound **3qa**

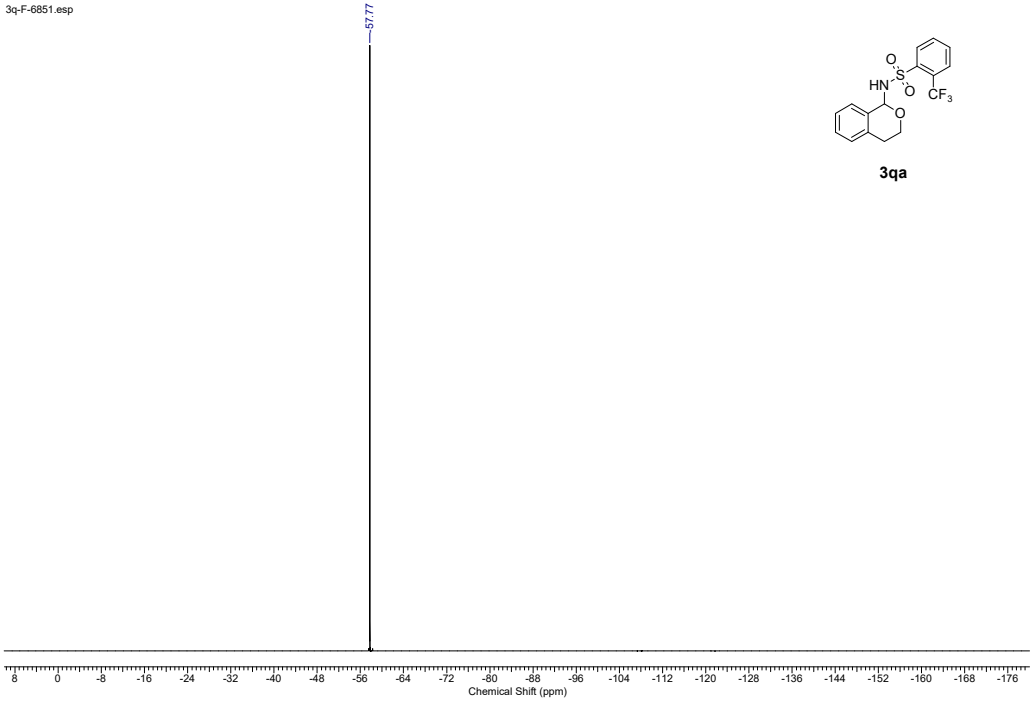


Figure S58. ^{19}F NMR spectra of compound **3qa**

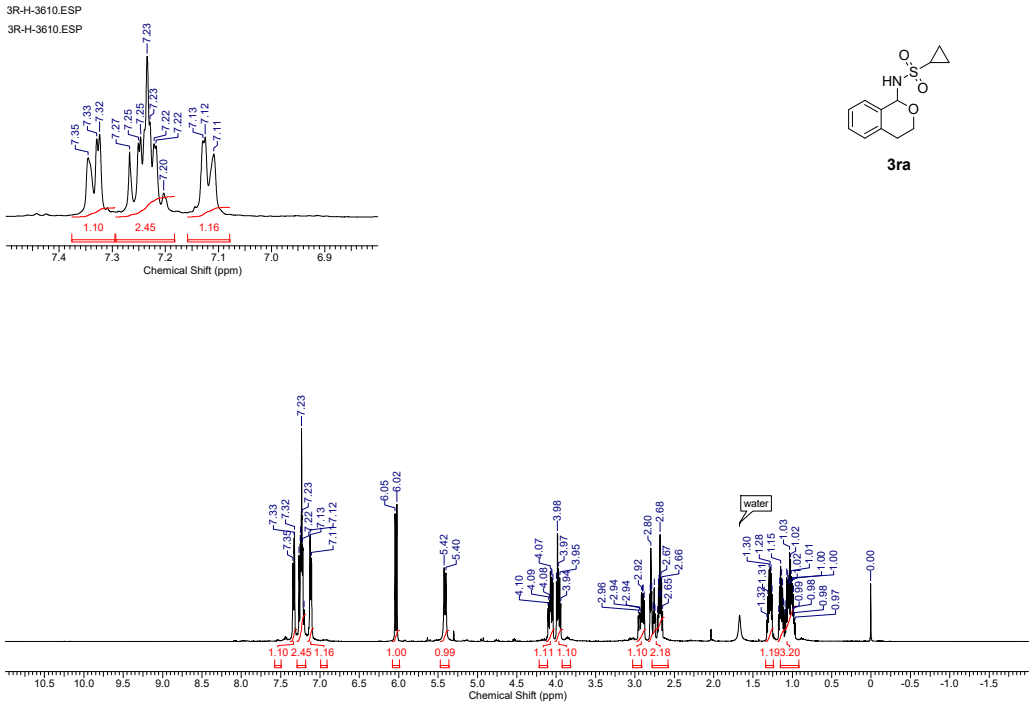


Figure S59. ^{1}H NMR spectra of compound **3ra**

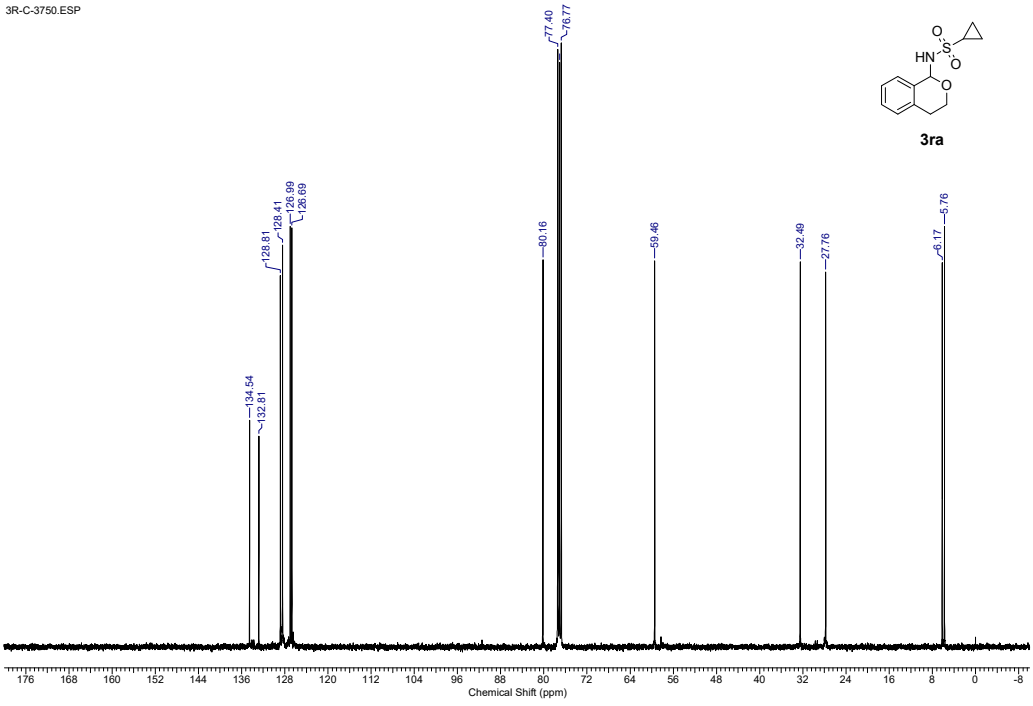


Figure S60. ^{13}C NMR spectra of compound **3ra**

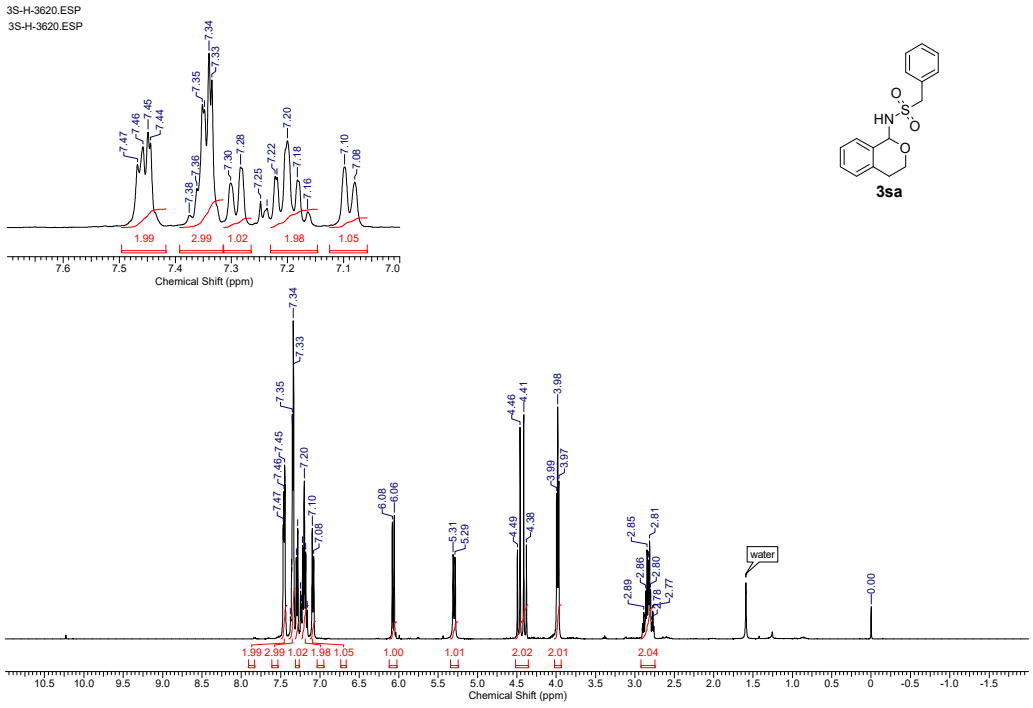


Figure S61. ^{1}H NMR spectra of compound **3sa**

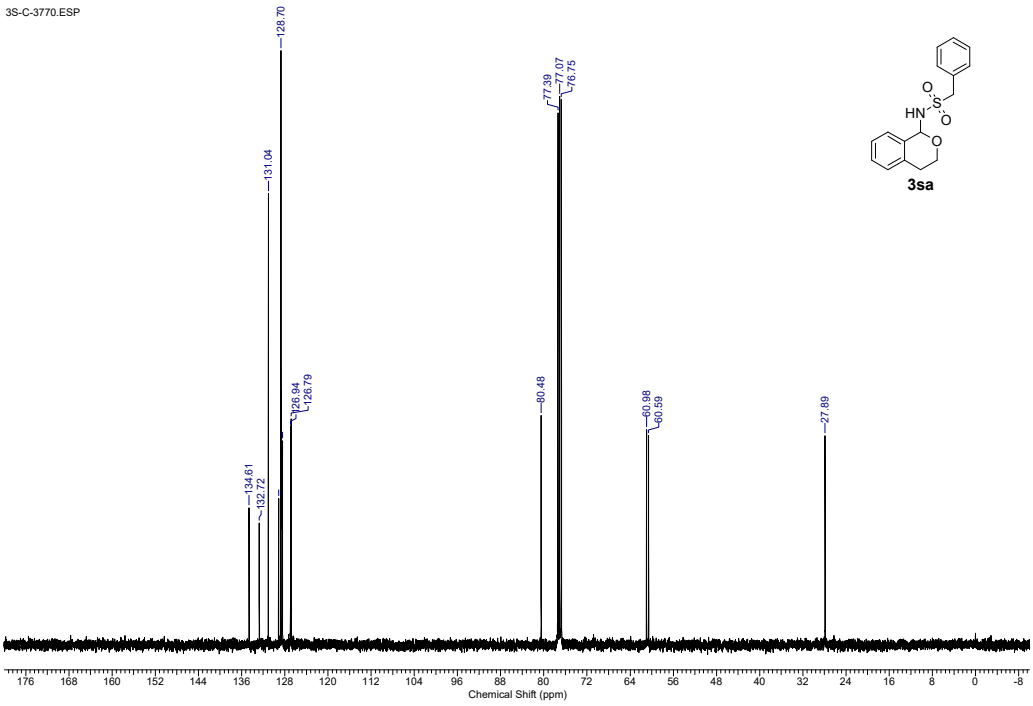


Figure S62. ^{13}C NMR spectra of compound **3sa**

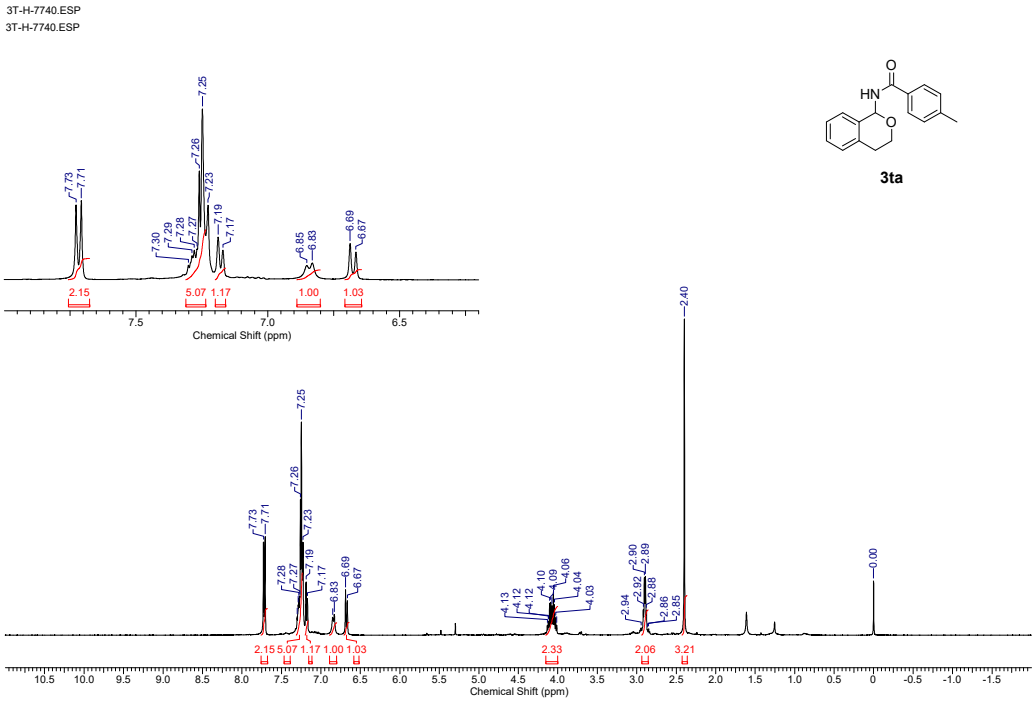


Figure S63. ^{1}H NMR spectra of compound **3ta**

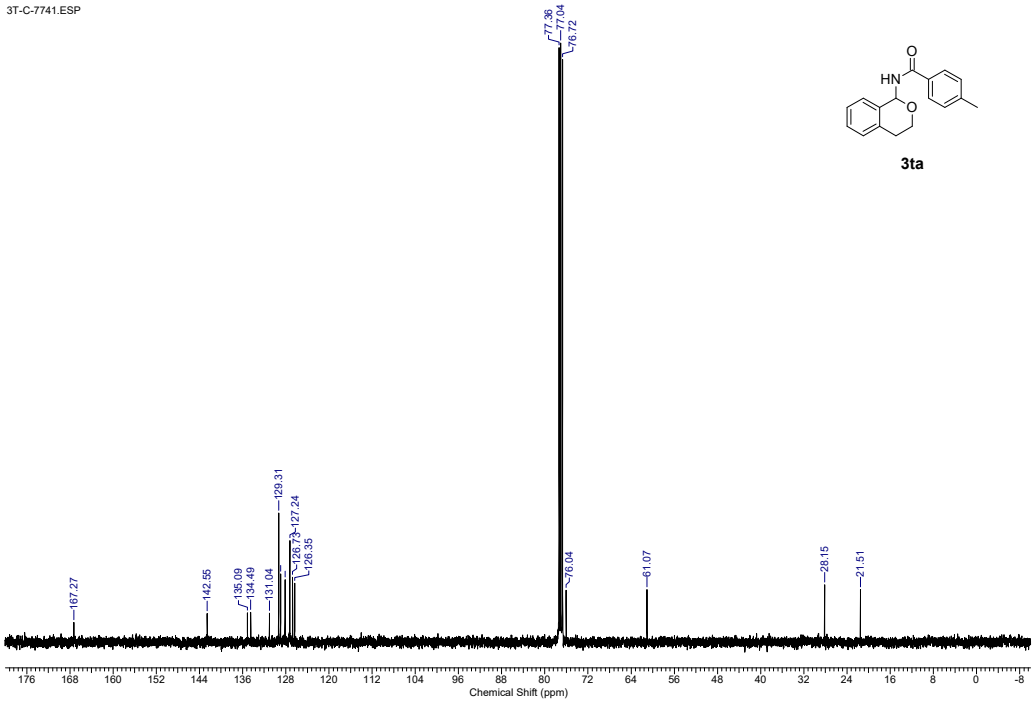


Figure S64. ^{13}C NMR spectra of compound **3ta**

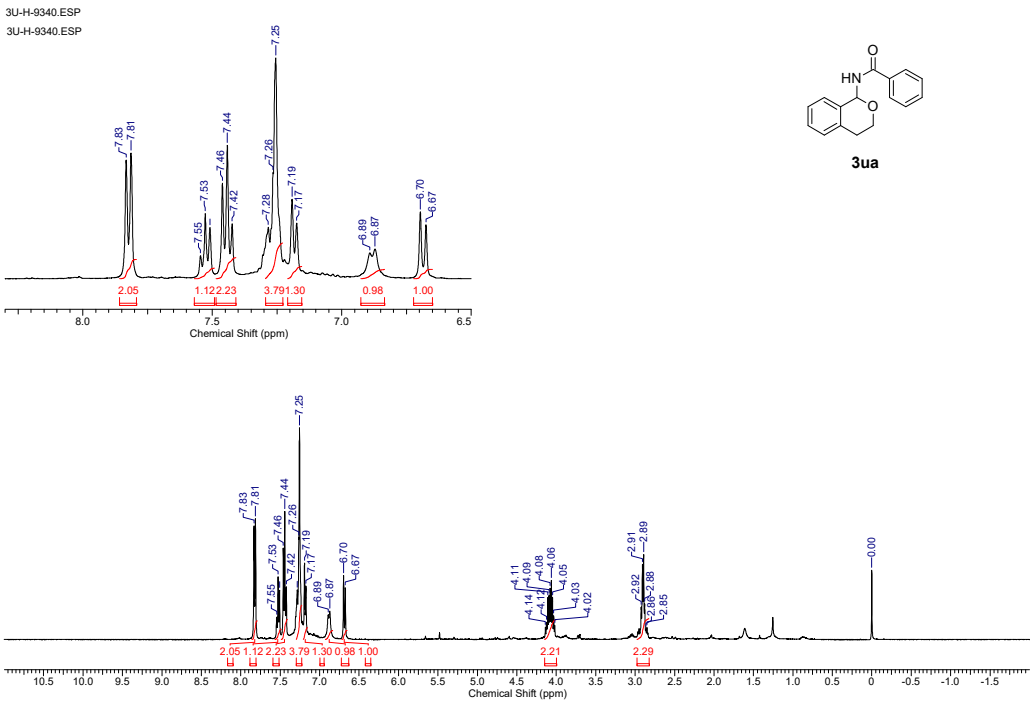


Figure S65. ^{1}H NMR spectra of compound **3ua**

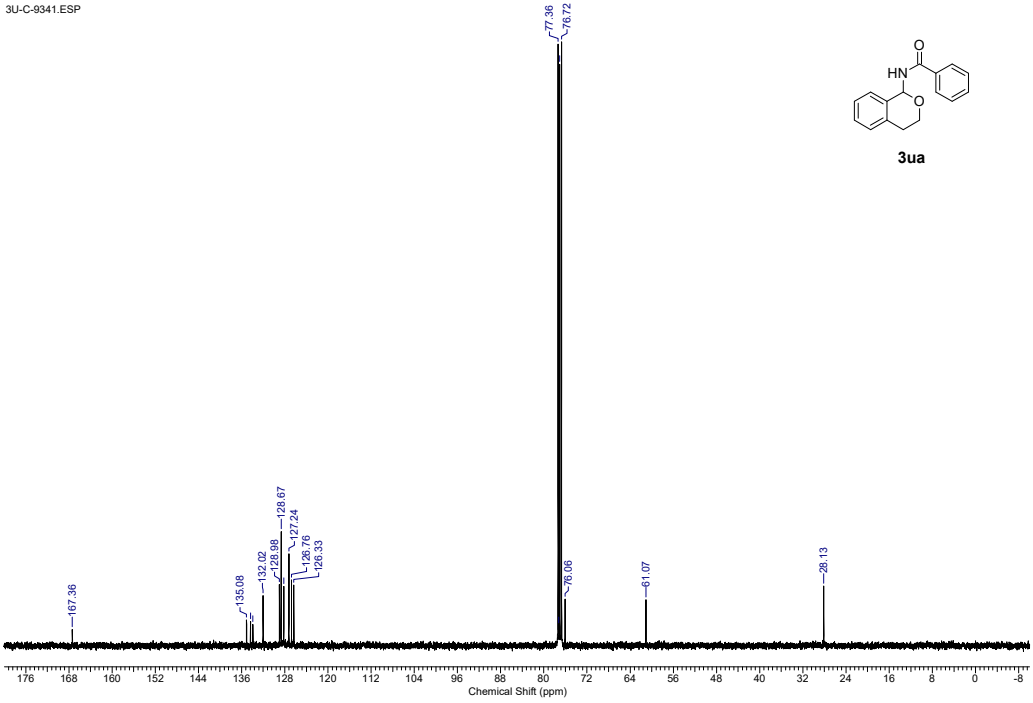


Figure S66. ^{13}C NMR spectra of compound **3ua**

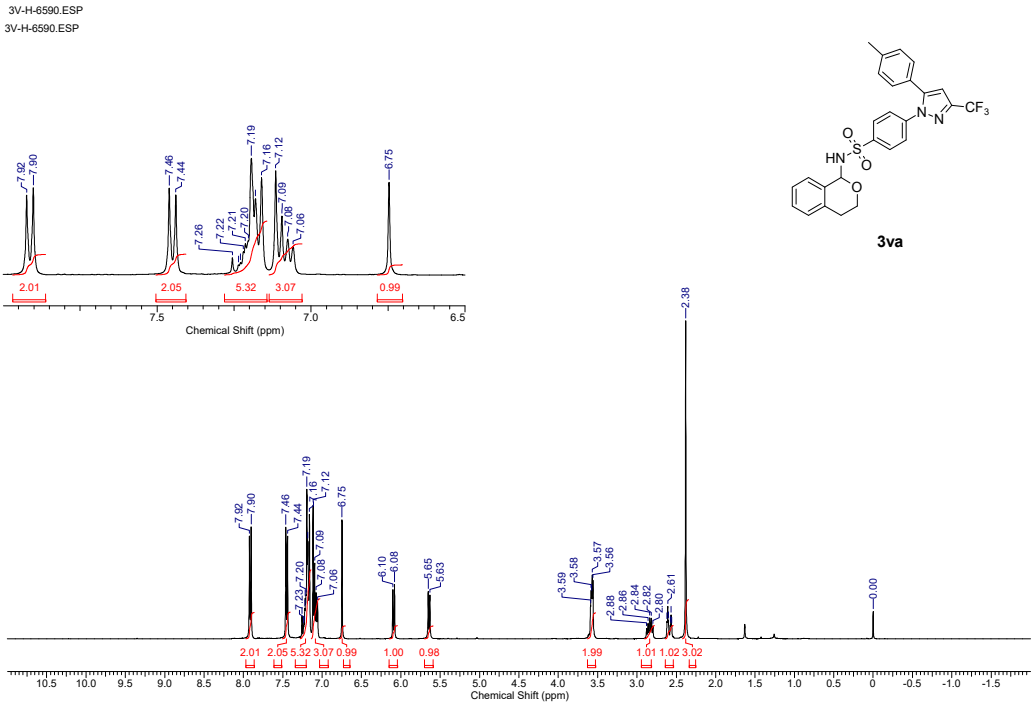


Figure S67. ^{1}H NMR spectra of compound **3va**

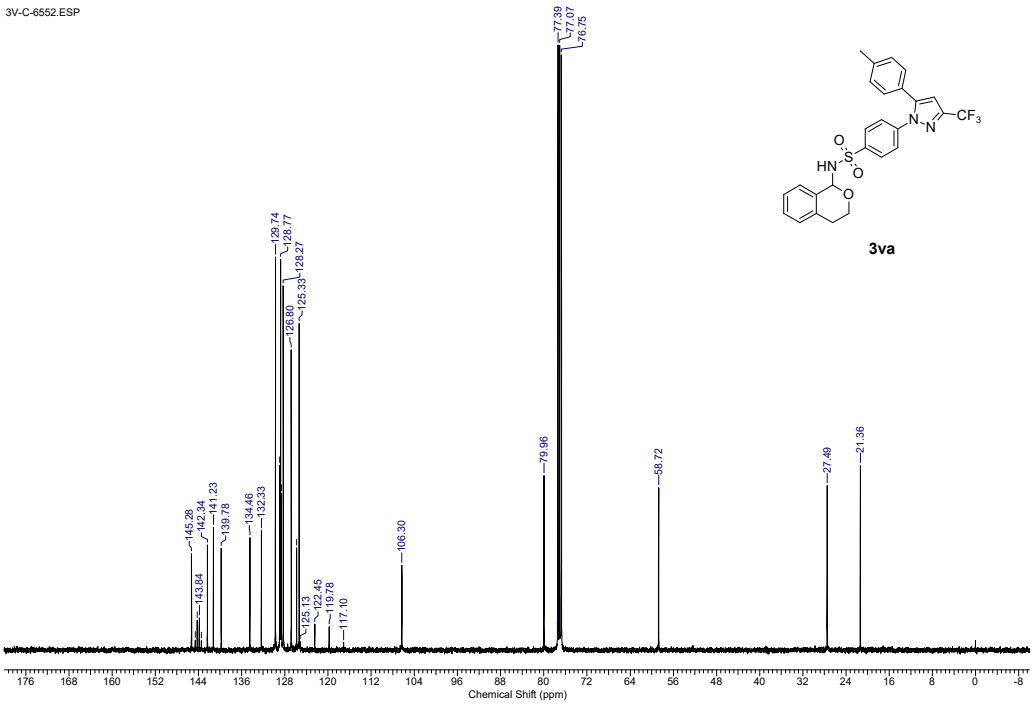


Figure S68. ^{13}C NMR spectra of compound **3va**

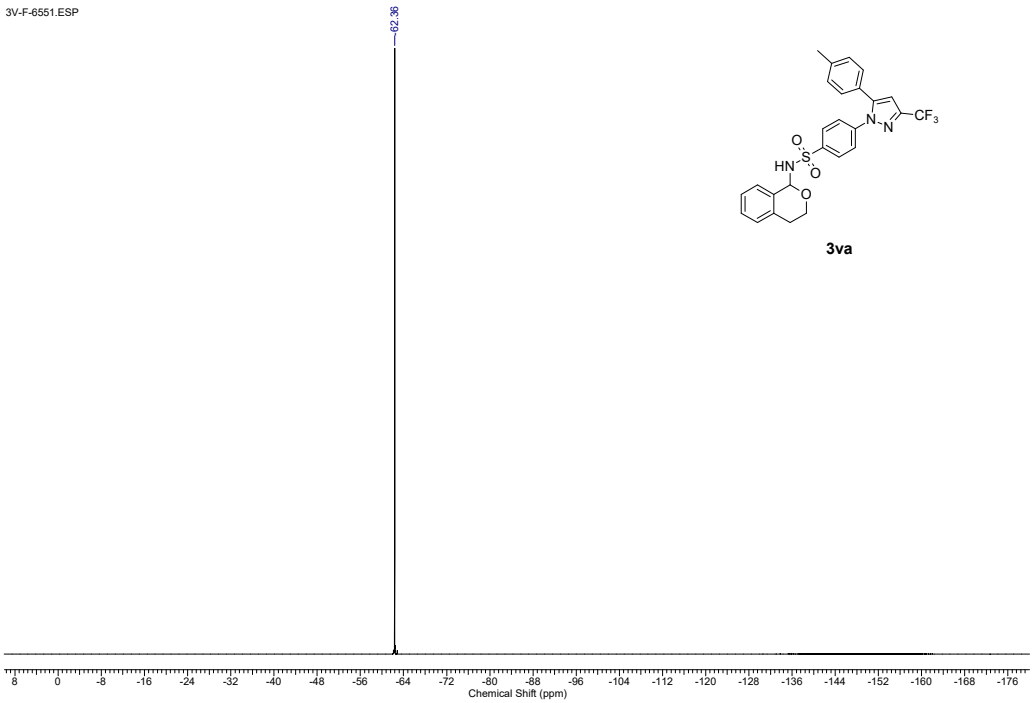


Figure S69. ^{19}F NMR spectra of compound **3va**

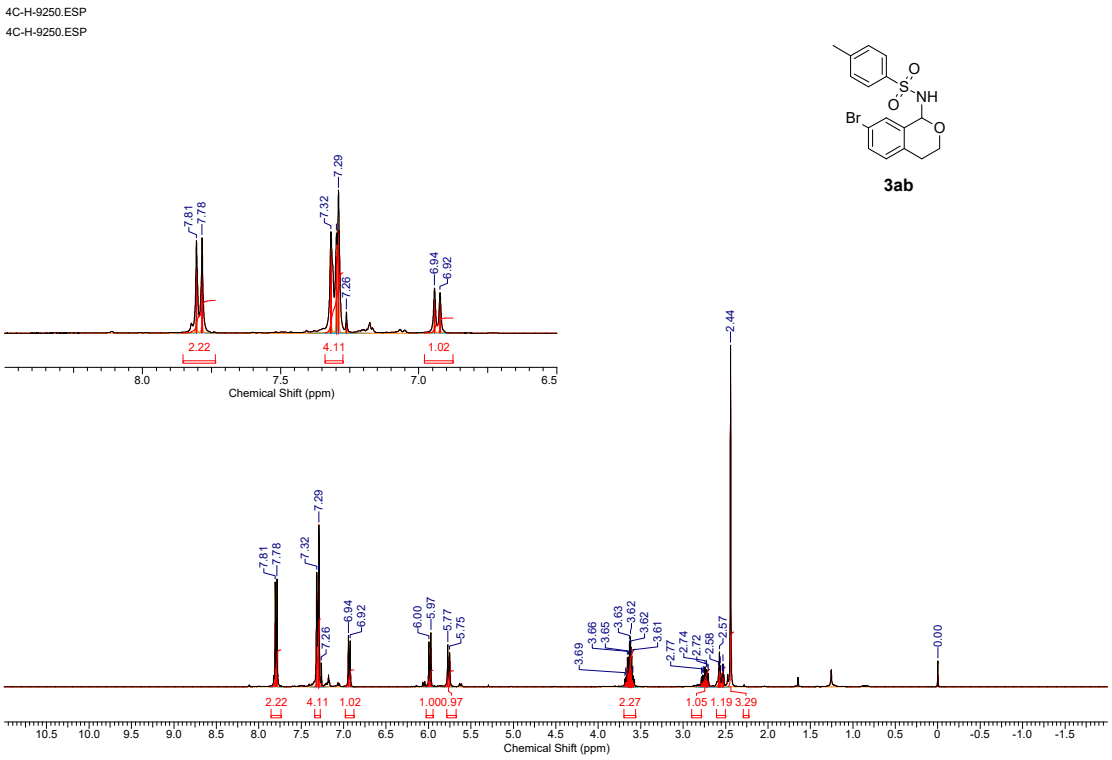


Figure S70. ^{1}H NMR spectra of compound **3ab**

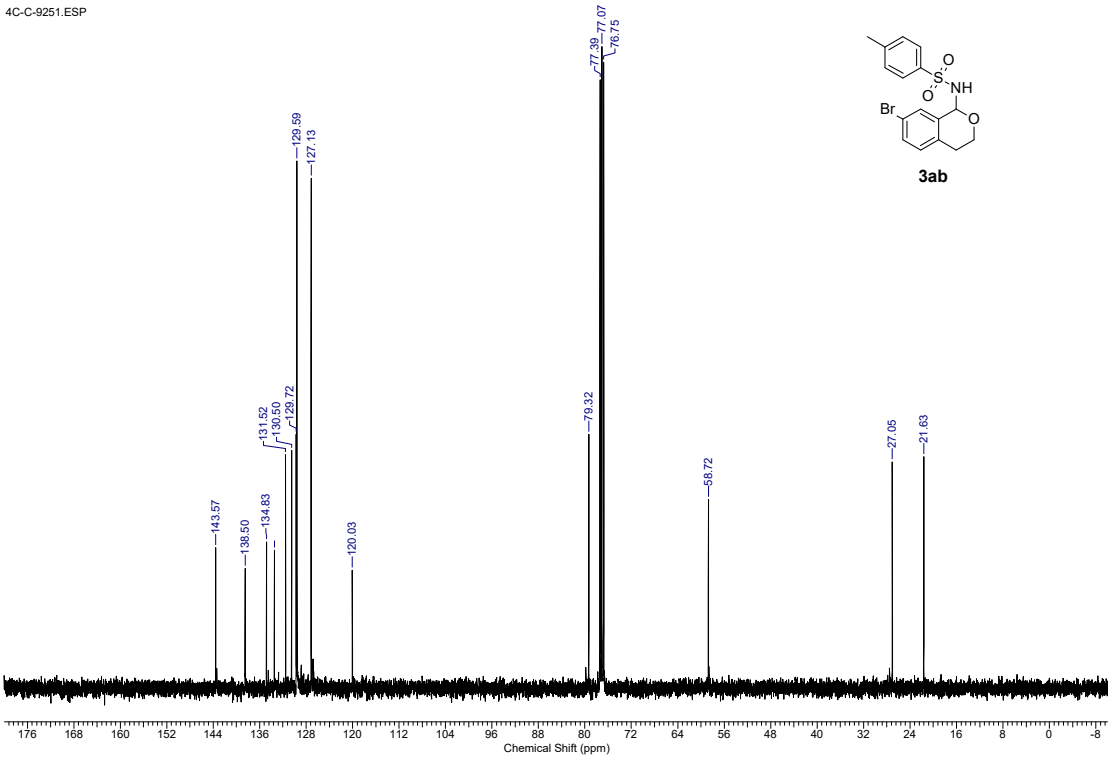


Figure S71. ^{13}C NMR spectra of compound **3ab**

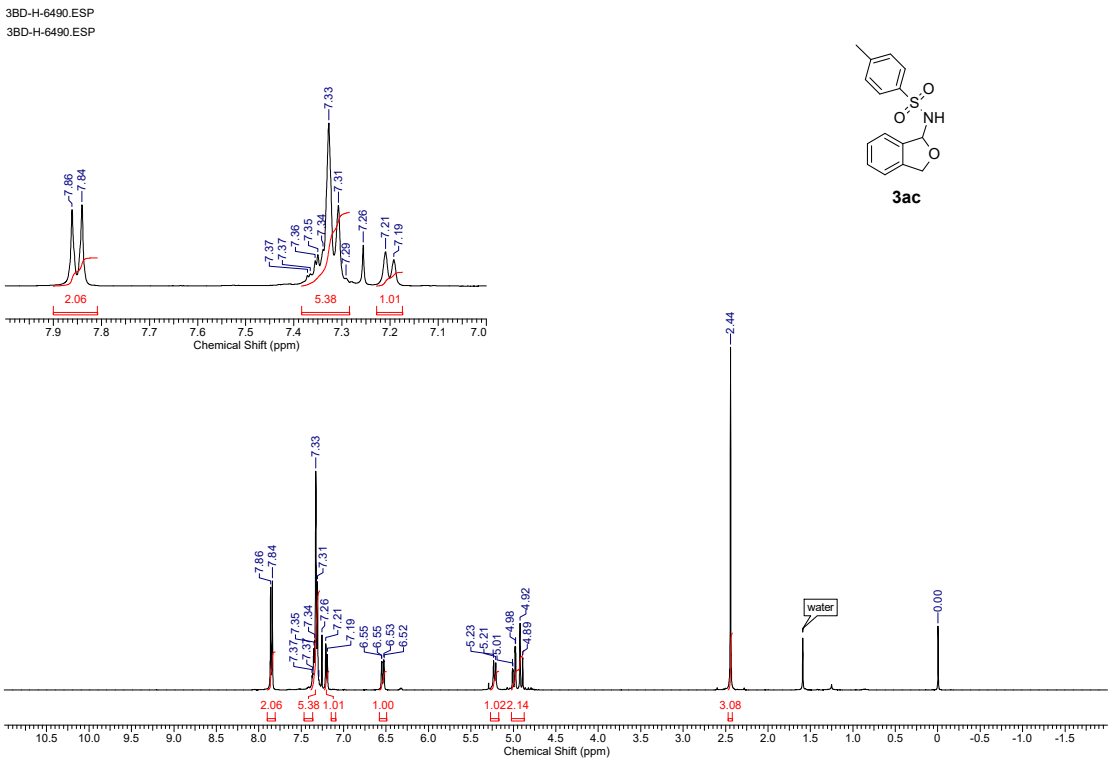


Figure S72. ^{1}H NMR spectra of compound **3ac**

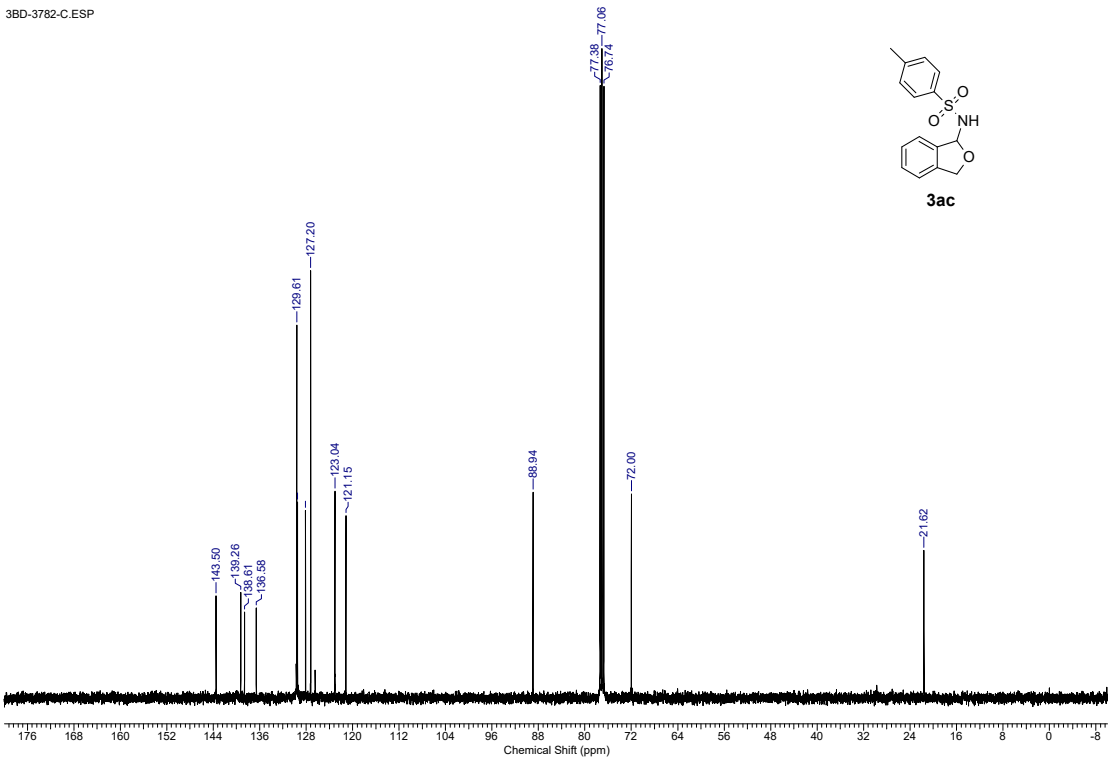


Figure S73. ^{13}C NMR spectra of compound **3ac**

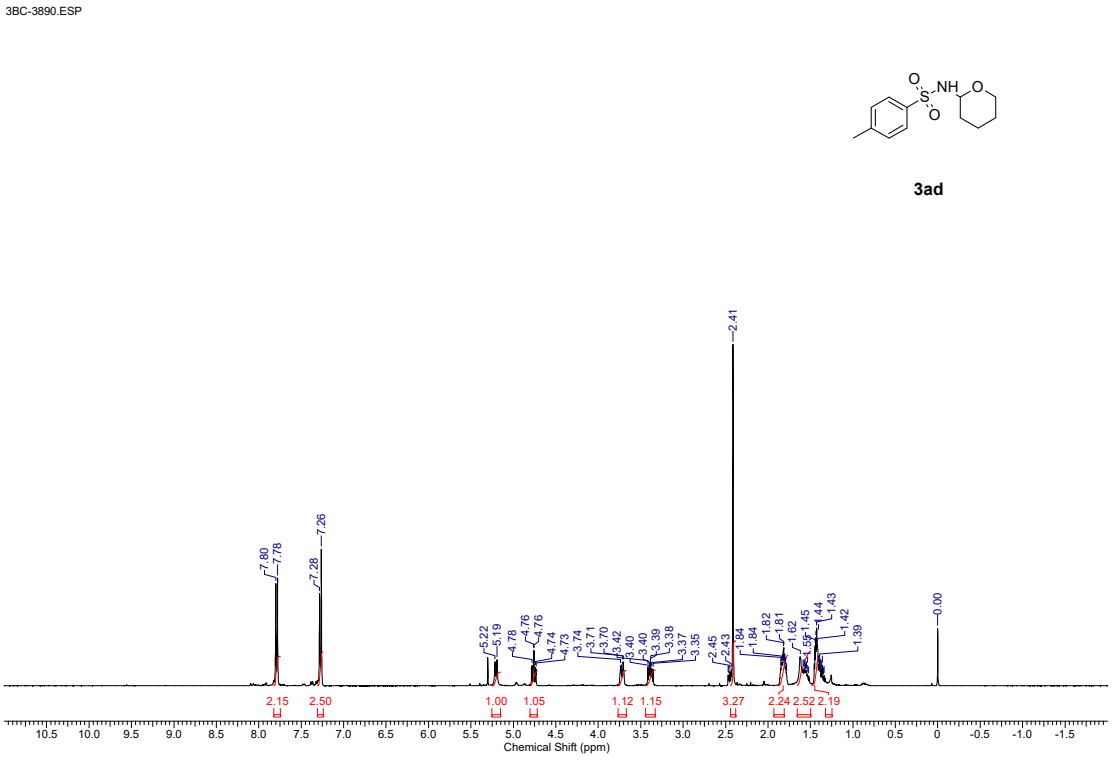


Figure S74. ^{1}H NMR spectra of compound **3ad**

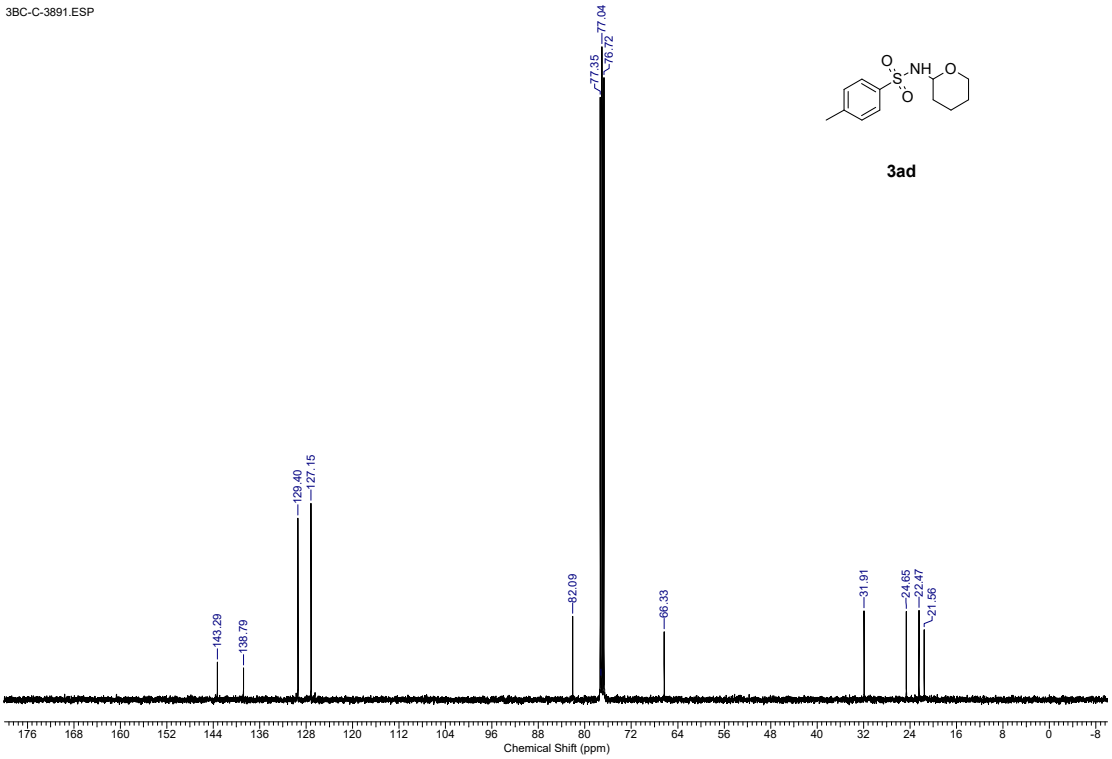


Figure S75. ^{13}C NMR spectra of compound **3ad**

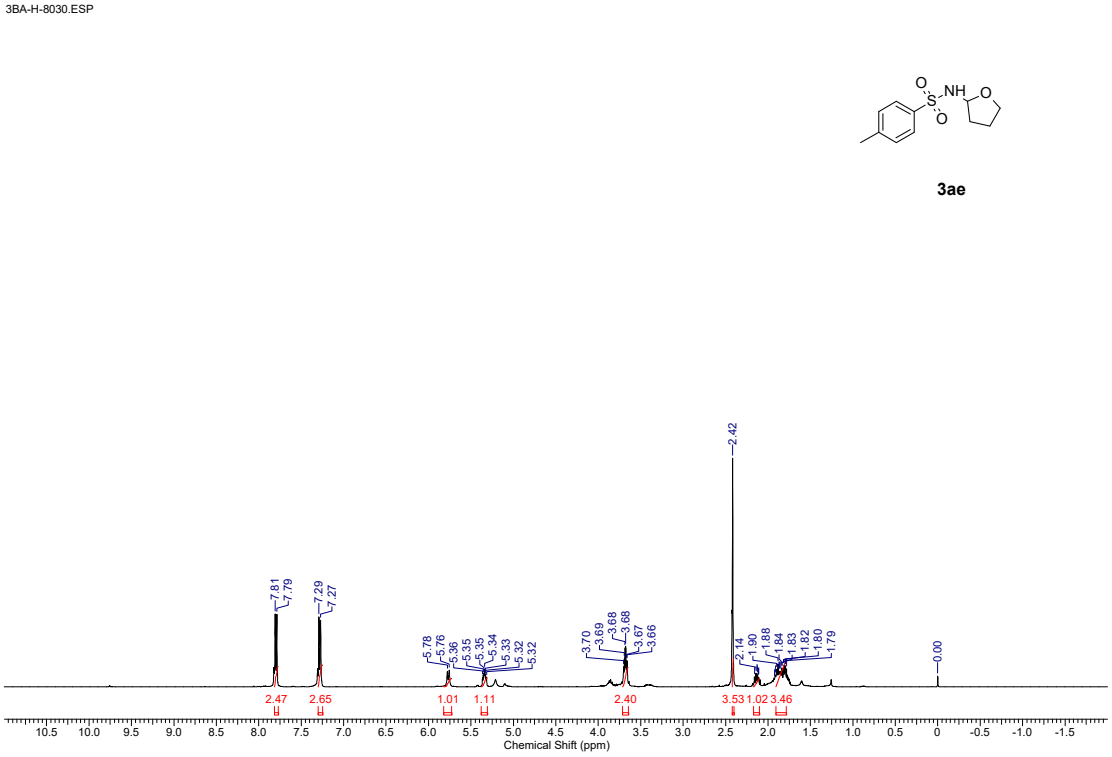


Figure S76. ^{1}H NMR spectra of compound **3ae**

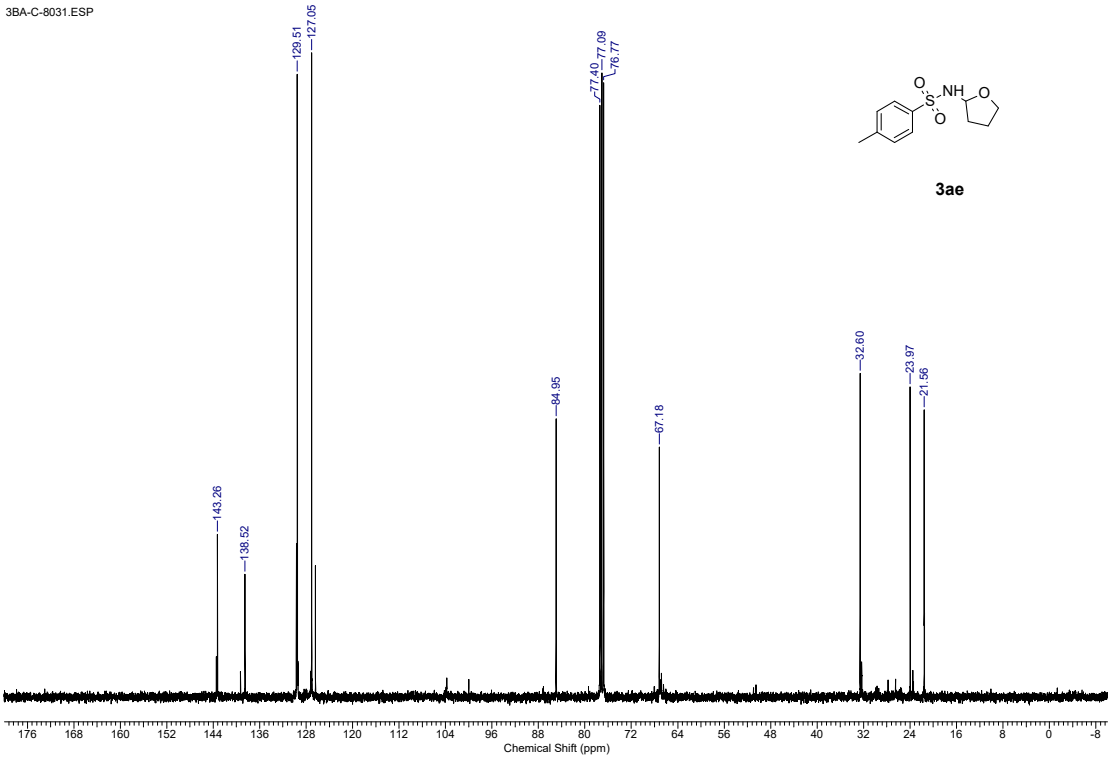


Figure S77. ^{13}C NMR spectra of compound **3ae**

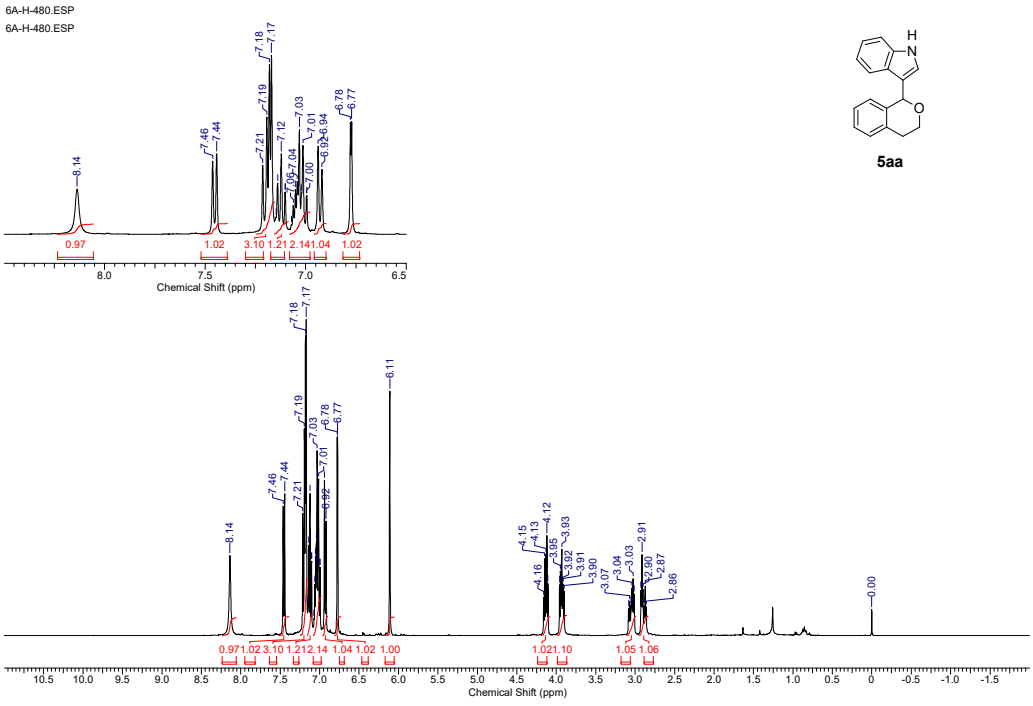


Figure S78. ^{1}H NMR spectra of compound **5aa**

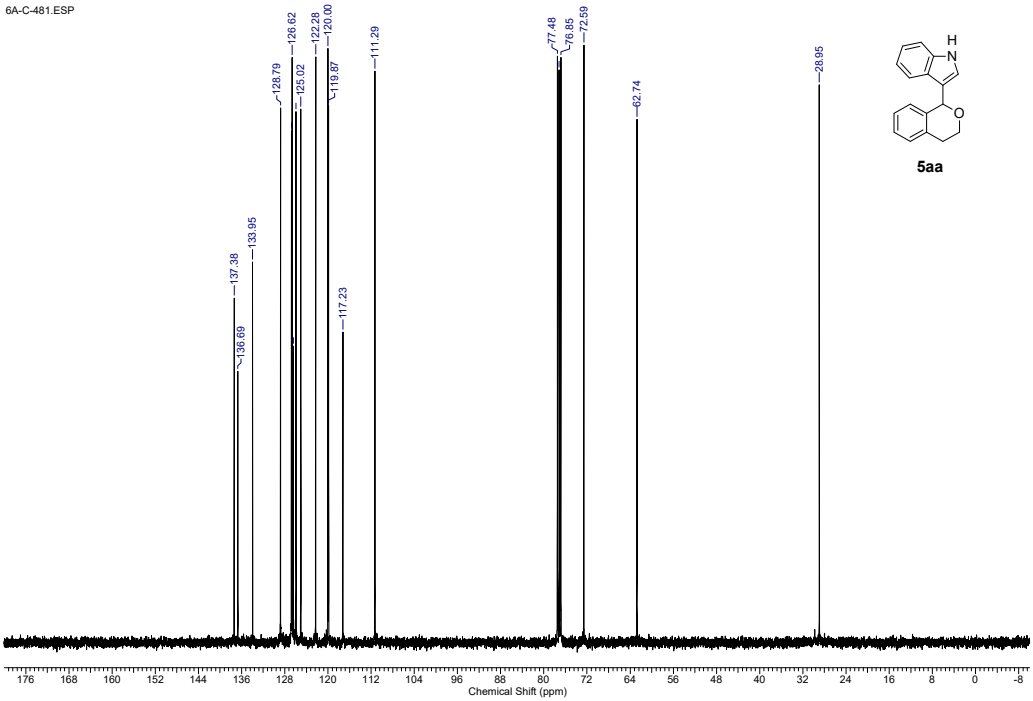


Figure S79. ^{13}C NMR spectra of compound **5aa**

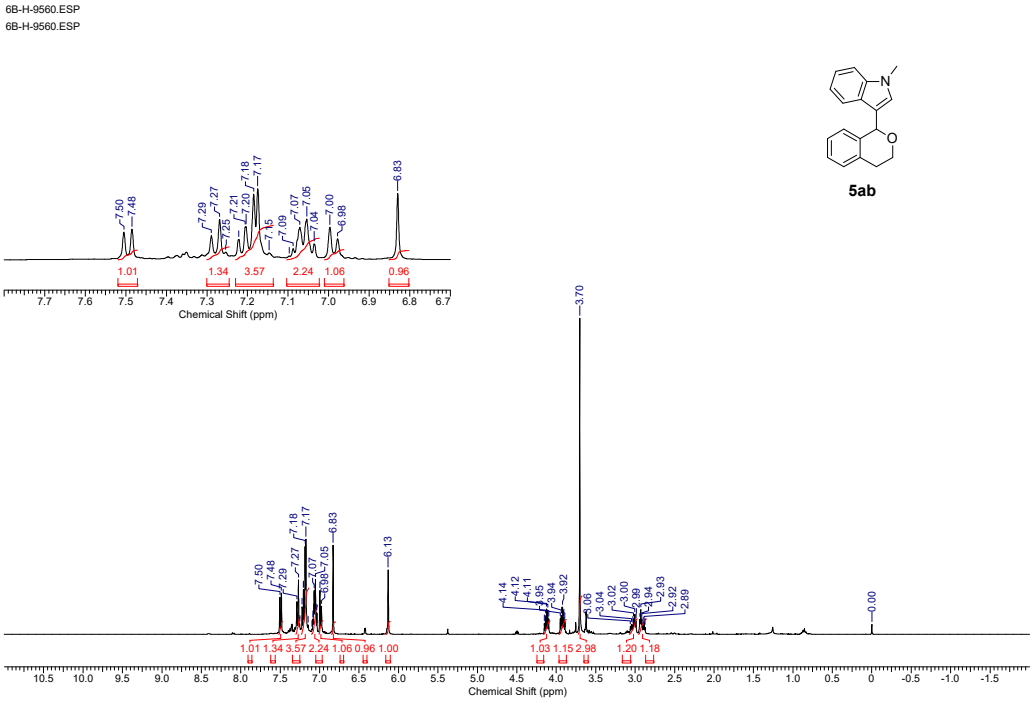


Figure S80. ^{1}H NMR spectra of compound **5ab**

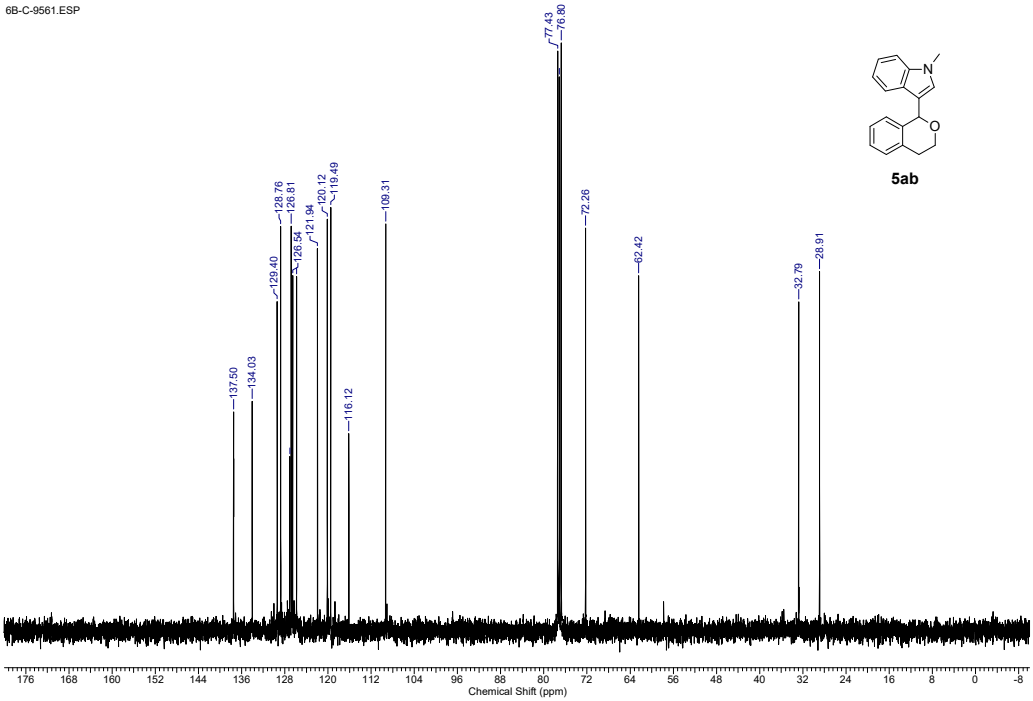


Figure S81. ^{13}C NMR spectra of compound **5ab**

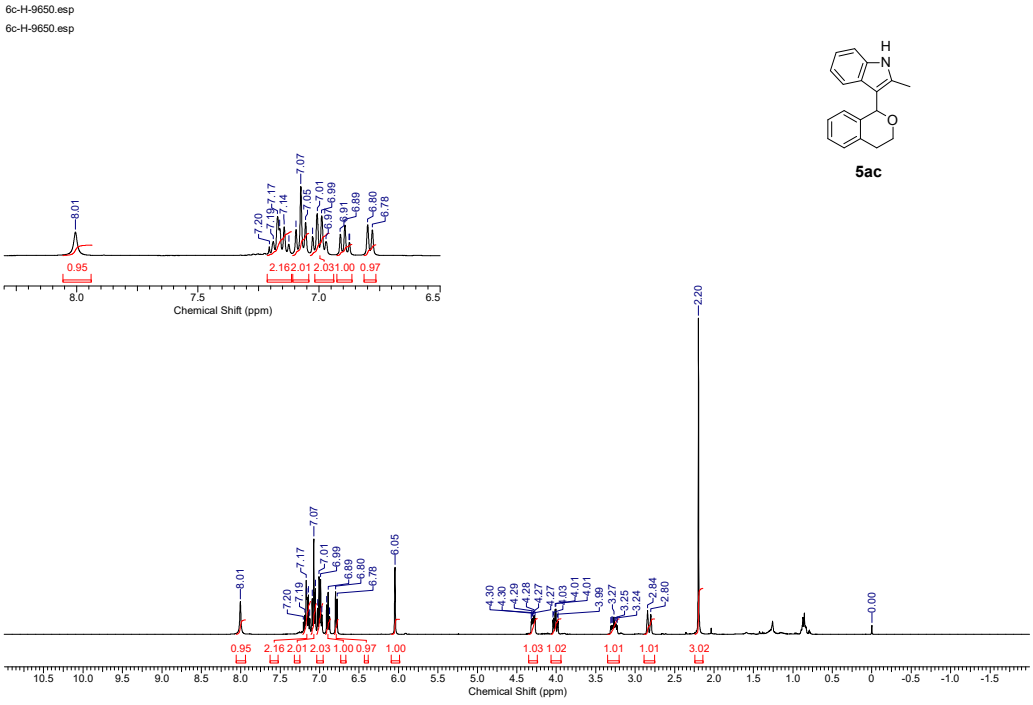


Figure S82. ^{1}H NMR spectra of compound **5ac**

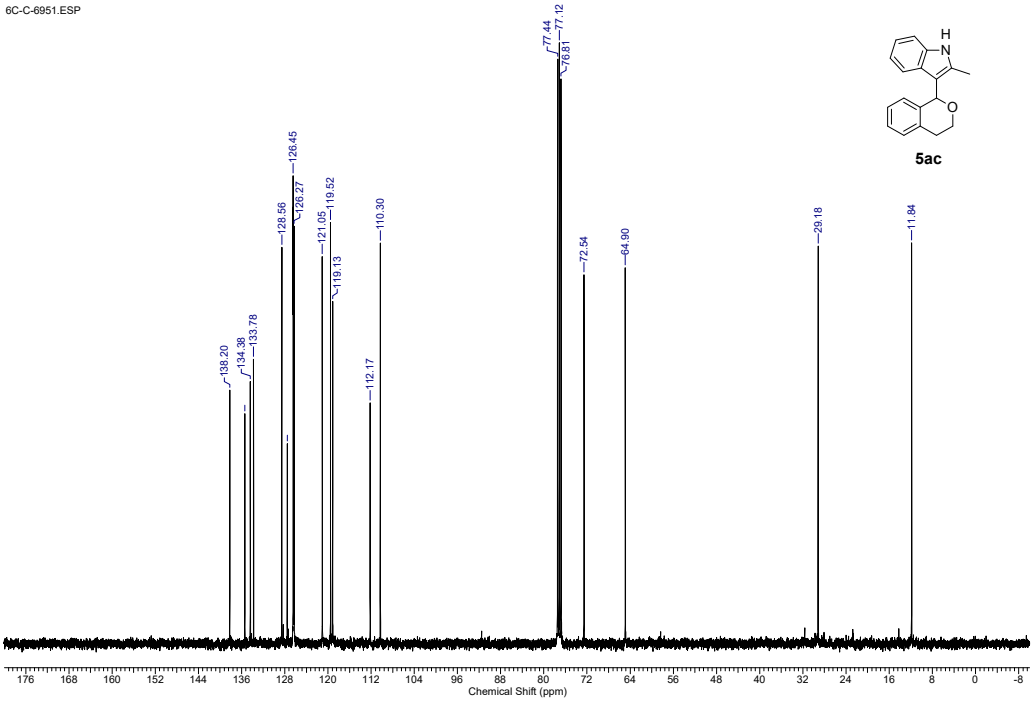


Figure S83. ^{13}C NMR spectra of compound **5ac**

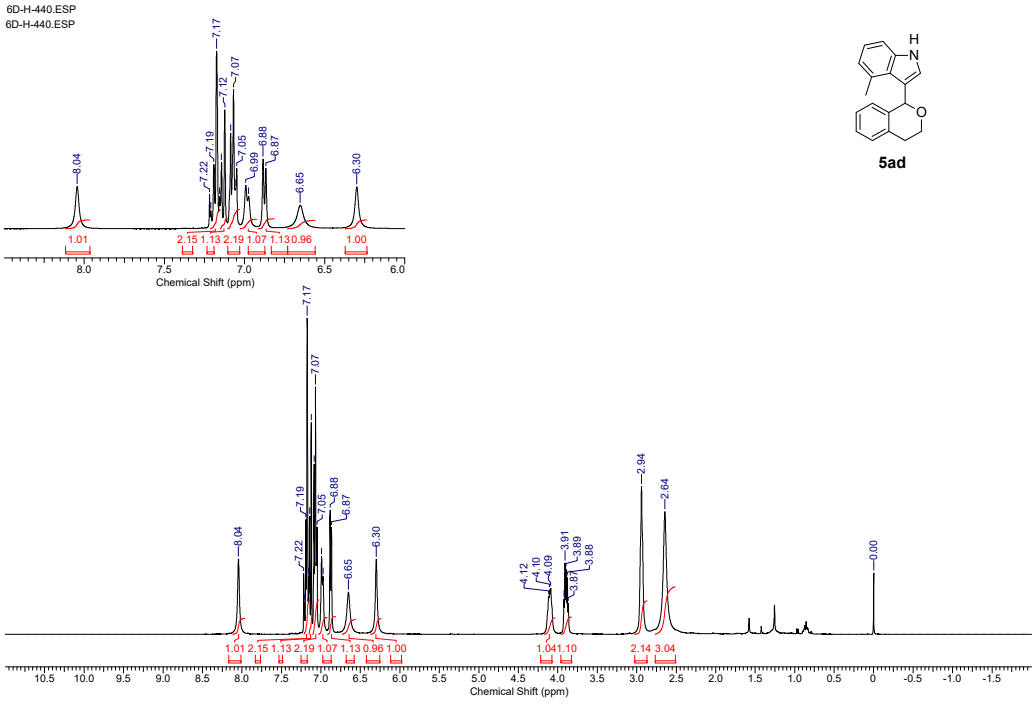


Figure S84. ^{1}H NMR spectra of compound **5ad**

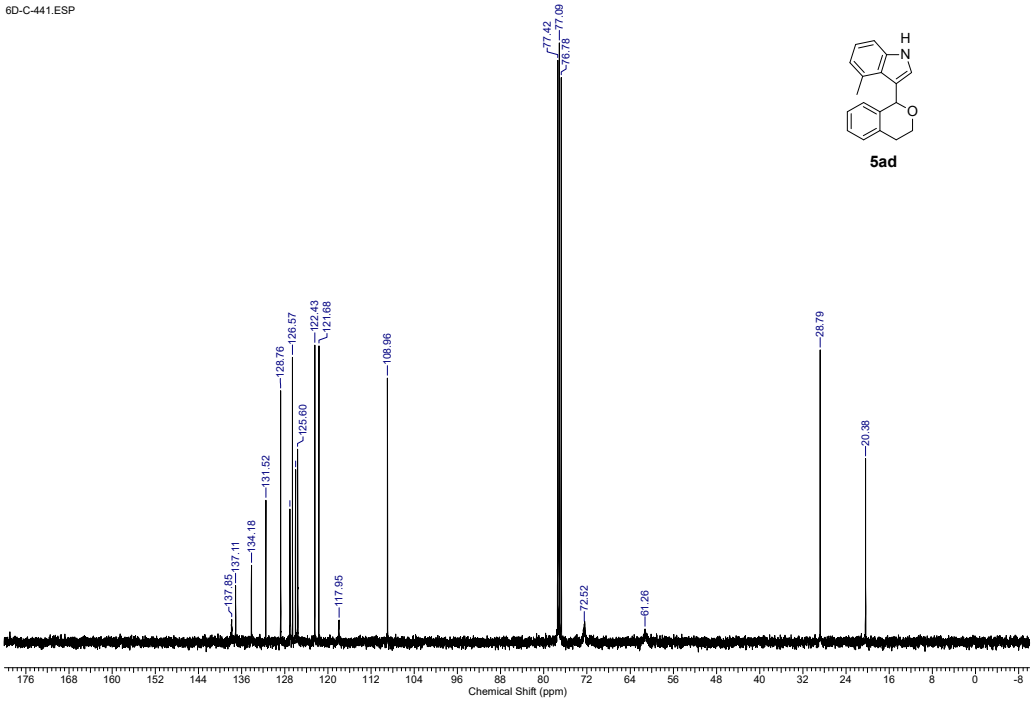


Figure S85. ^{13}C NMR spectra of compound **5ad**

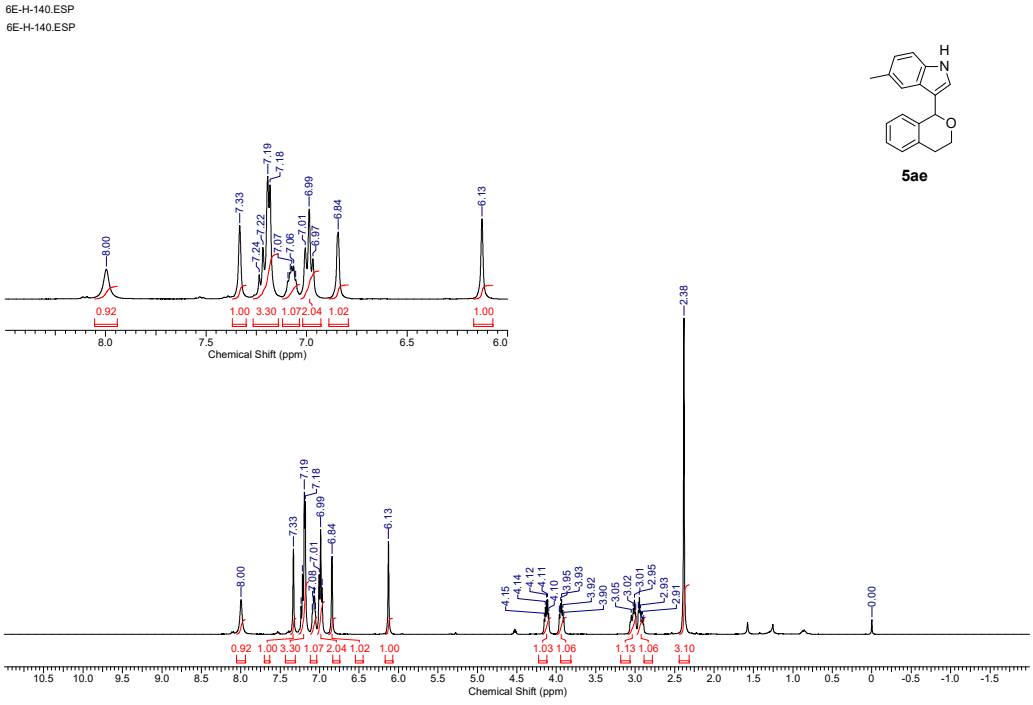


Figure S86. ^{1}H NMR spectra of compound **5ae**

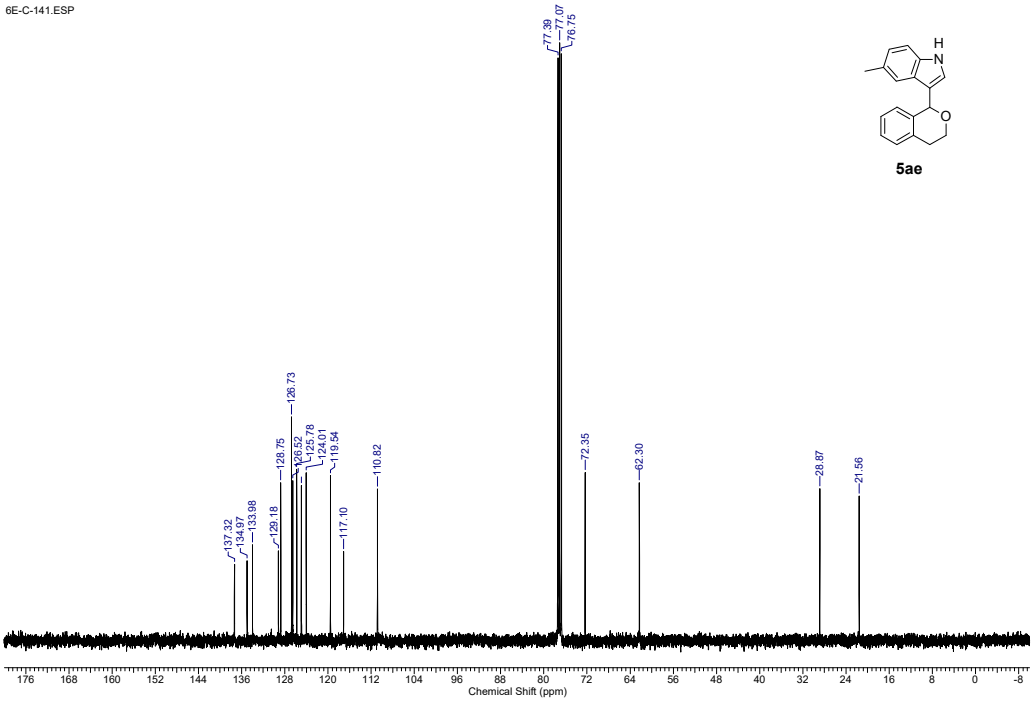


Figure S87. ^{13}C NMR spectra of compound **5ae**

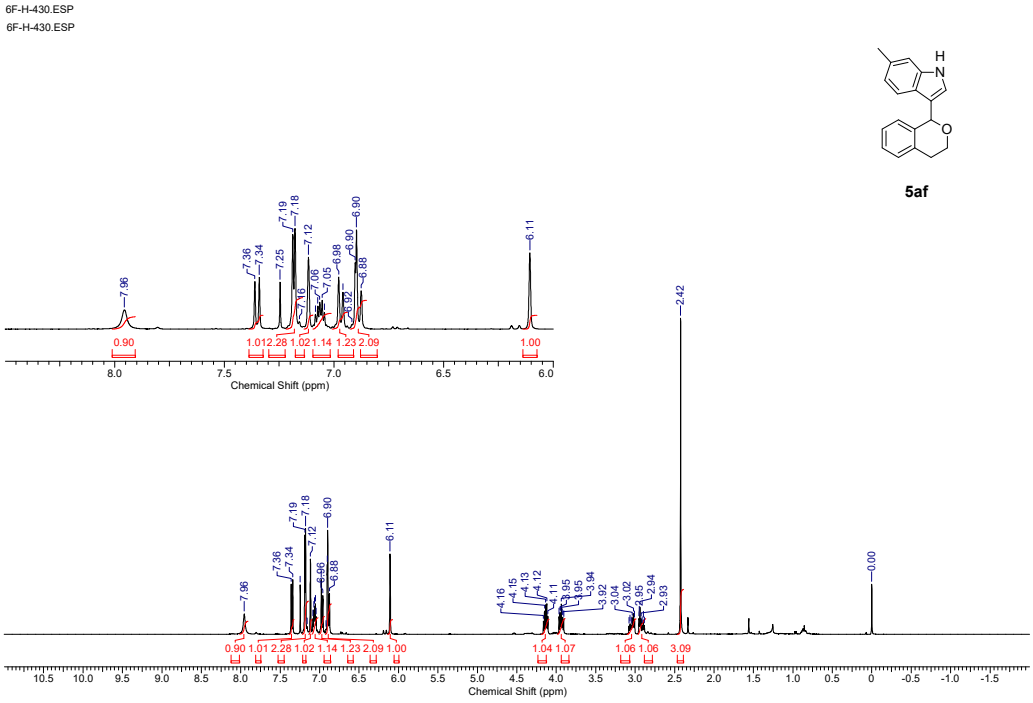


Figure S88. ^{1}H NMR spectra of compound **5af**

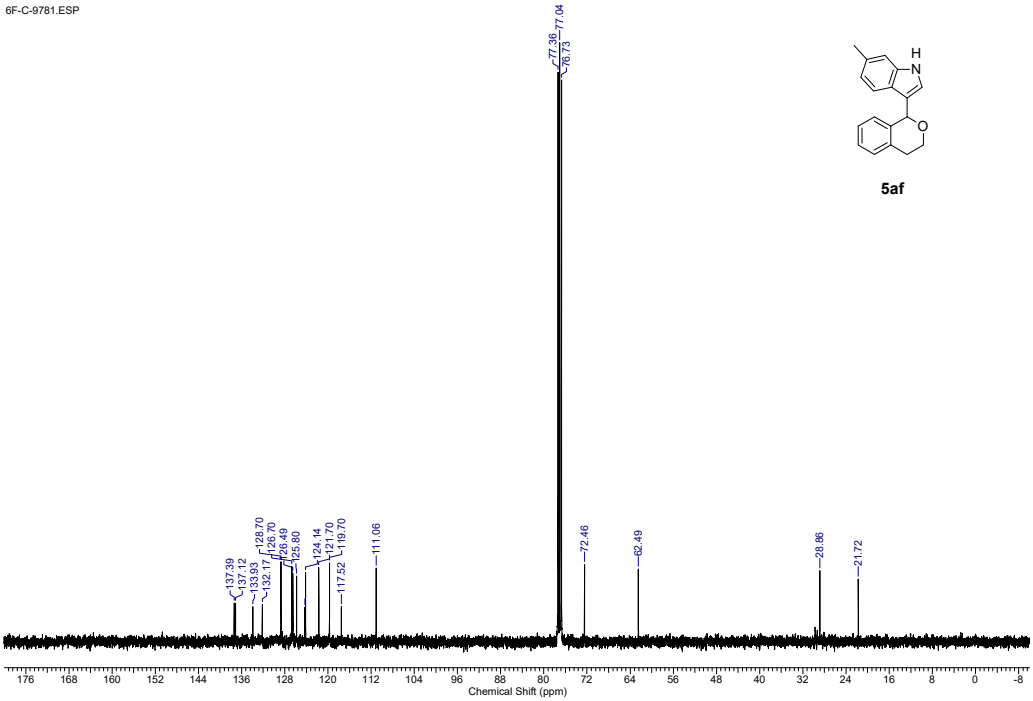


Figure S89. ^{13}C NMR spectra of compound **5af**

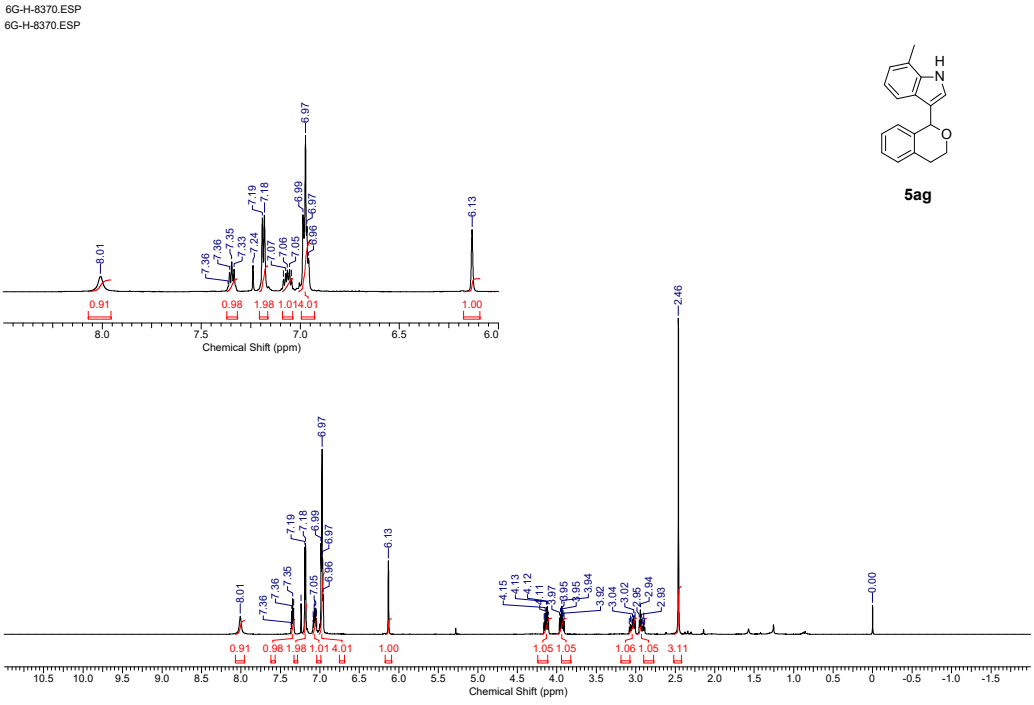


Figure S90. ^{1}H NMR spectra of compound **5ag**

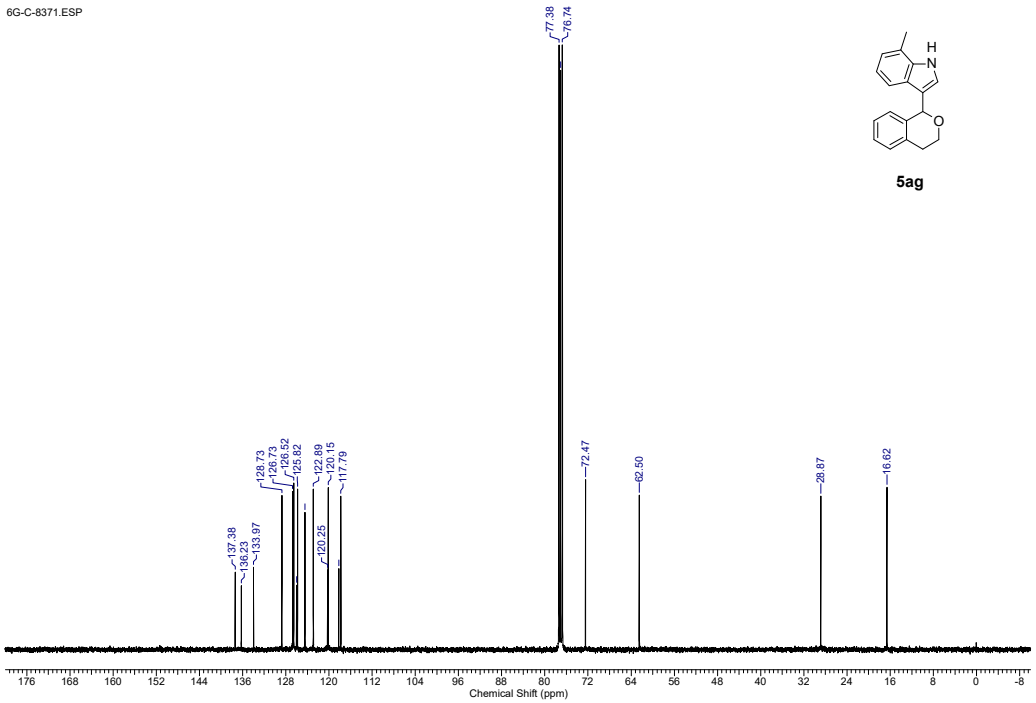


Figure S91. ^{13}C NMR spectra of compound **5ag**

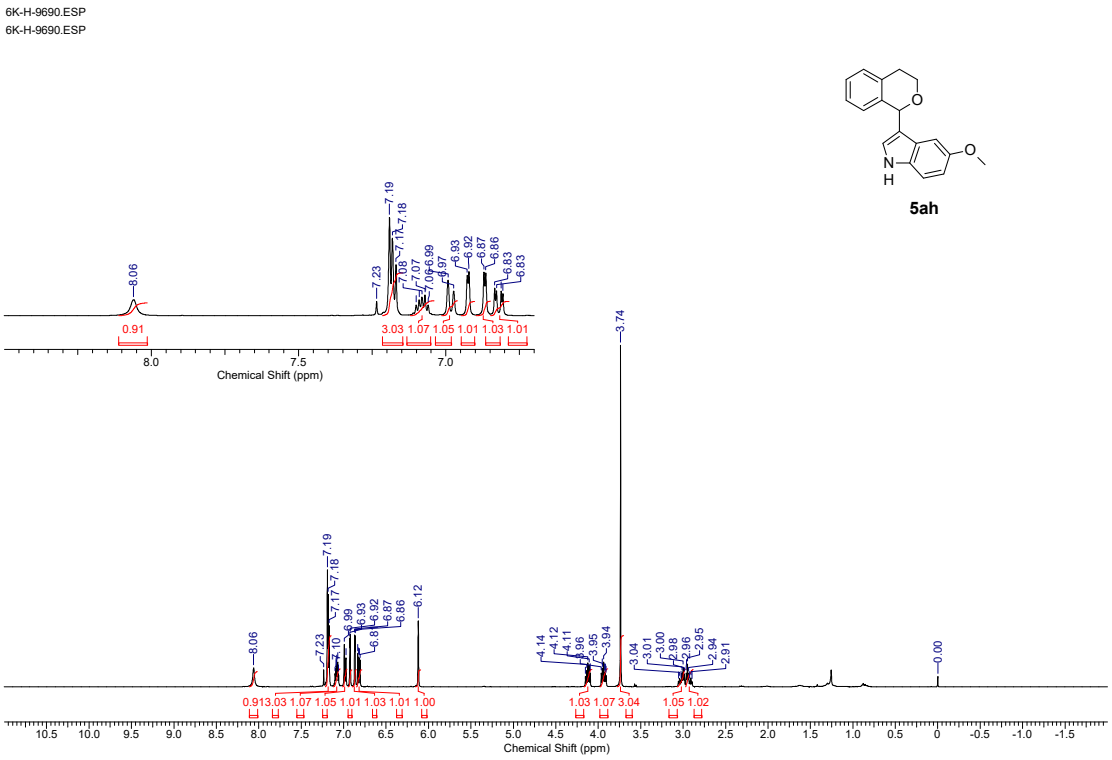


Figure S92. ^{1}H NMR spectra of compound **5ah**

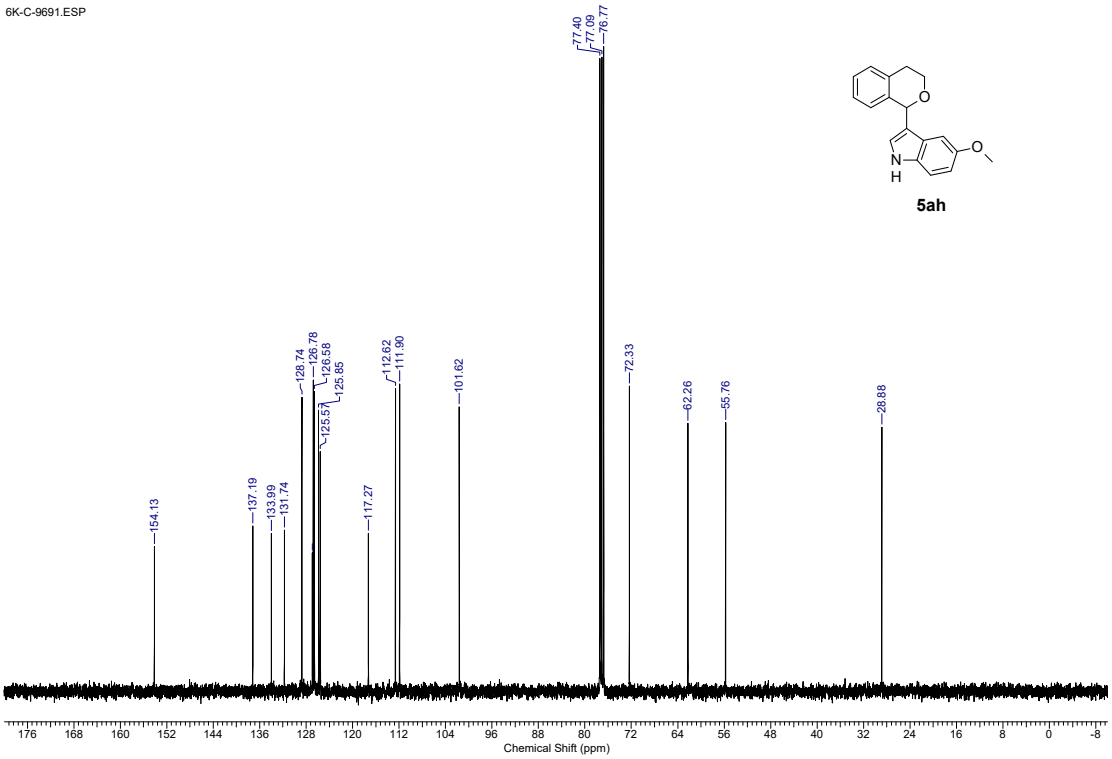


Figure S93. ^{13}C NMR spectra of compound **5ah**

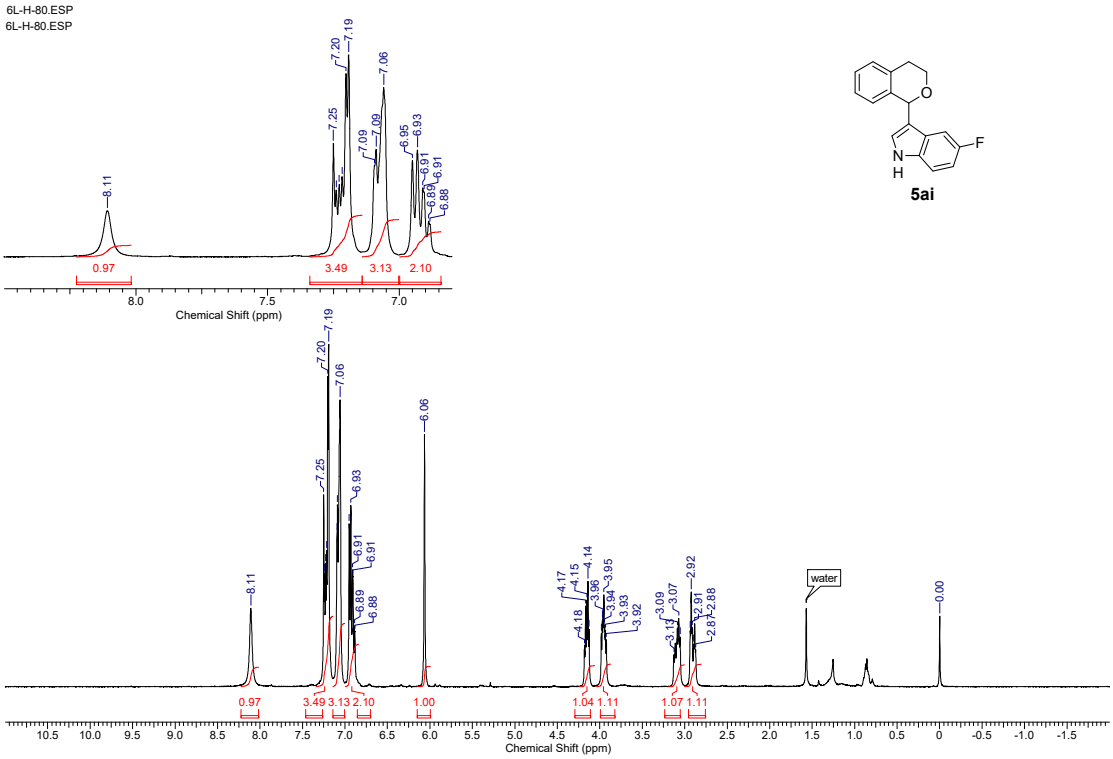


Figure S94. ^{1}H NMR spectra of compound **5ai**

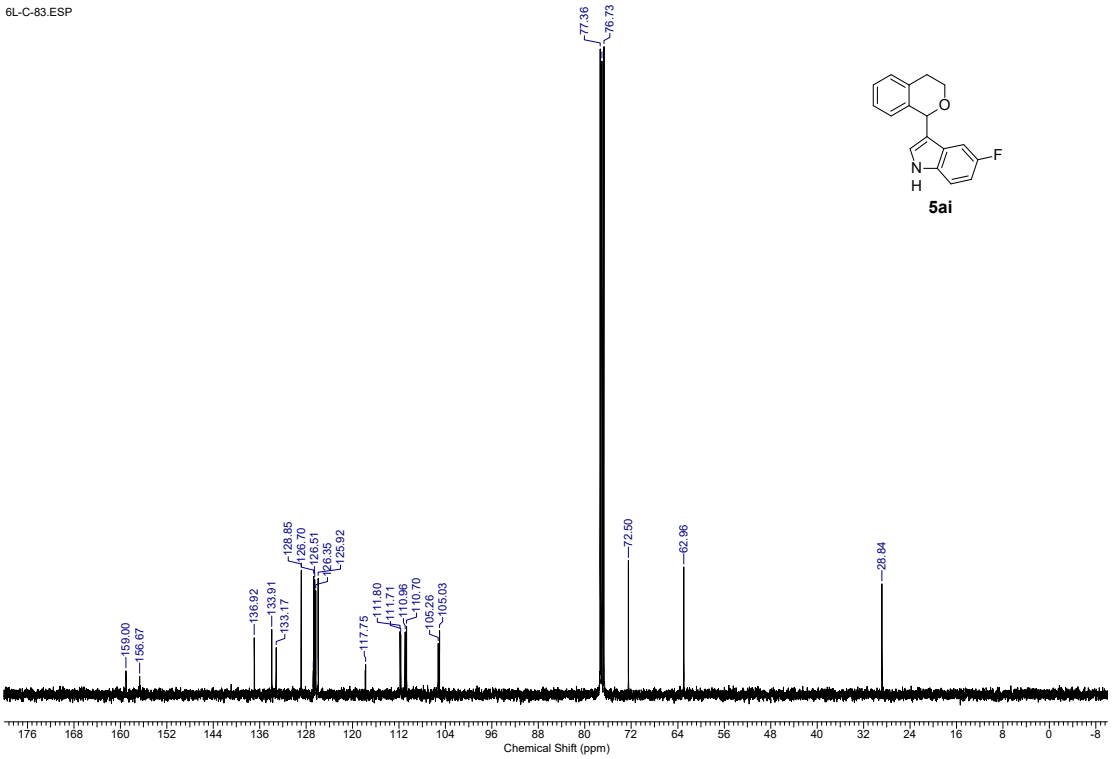


Figure S95. ^{13}C NMR spectra of compound **5ai**

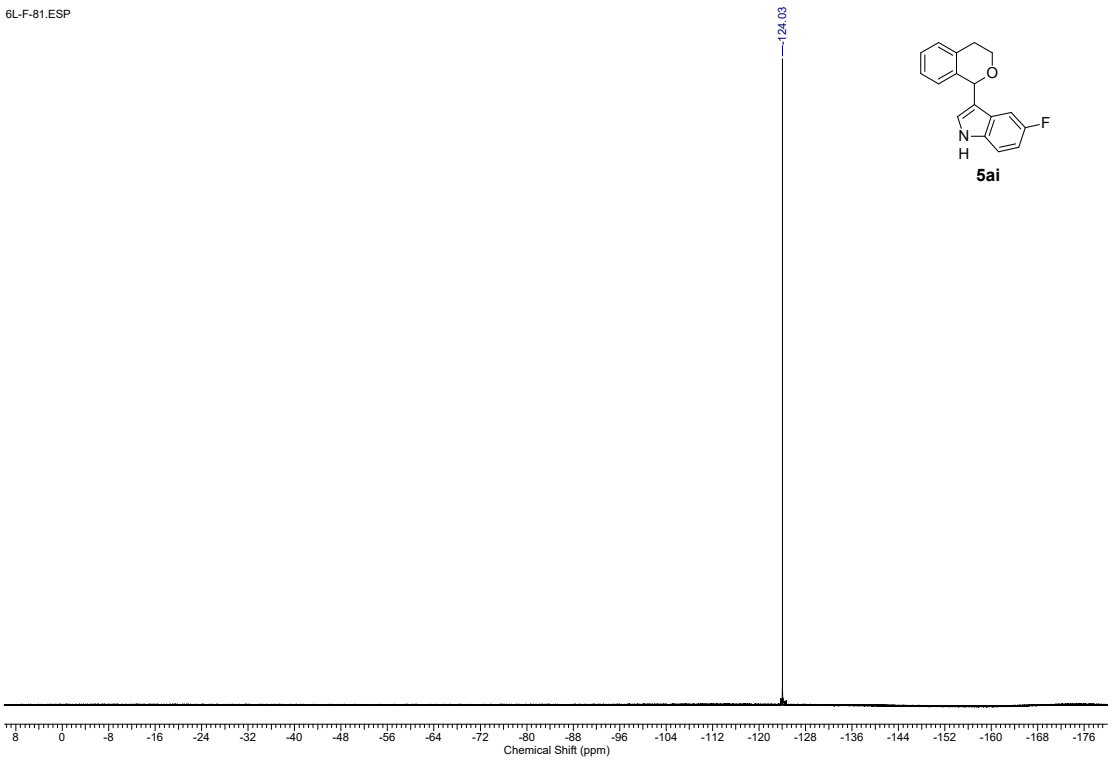


Figure S96. ^{19}F NMR spectra of compound **5ai**

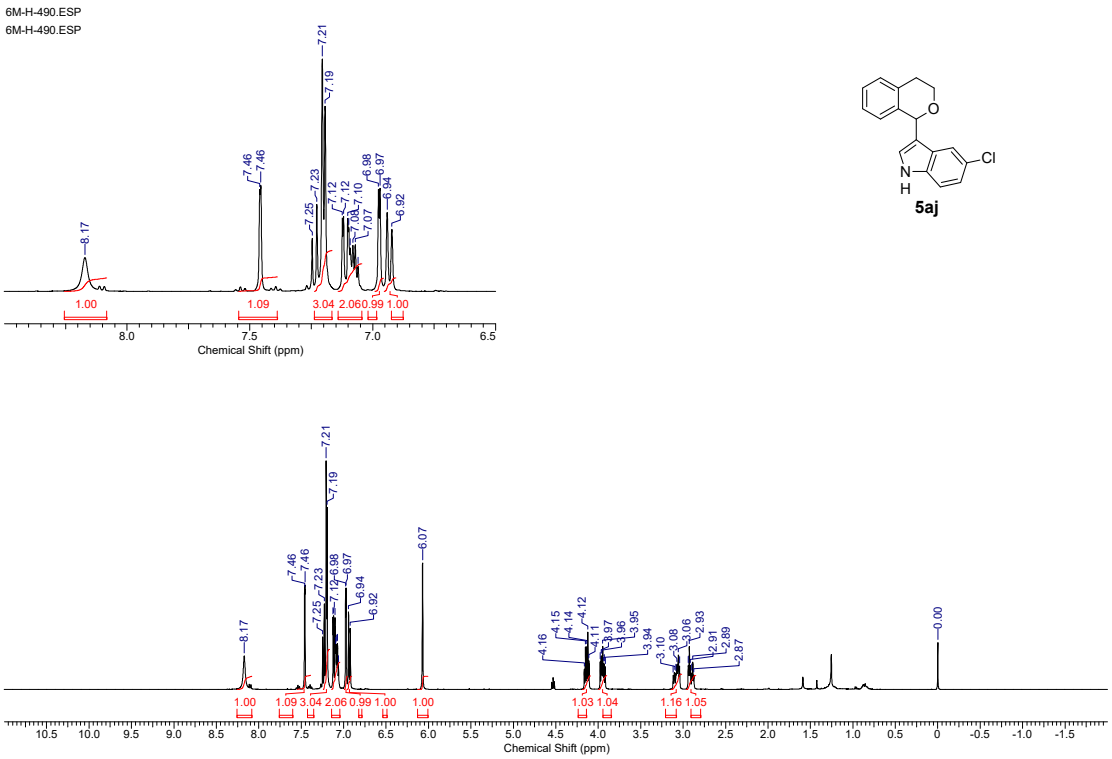


Figure S97. ^{1}H NMR spectra of compound **5aj**

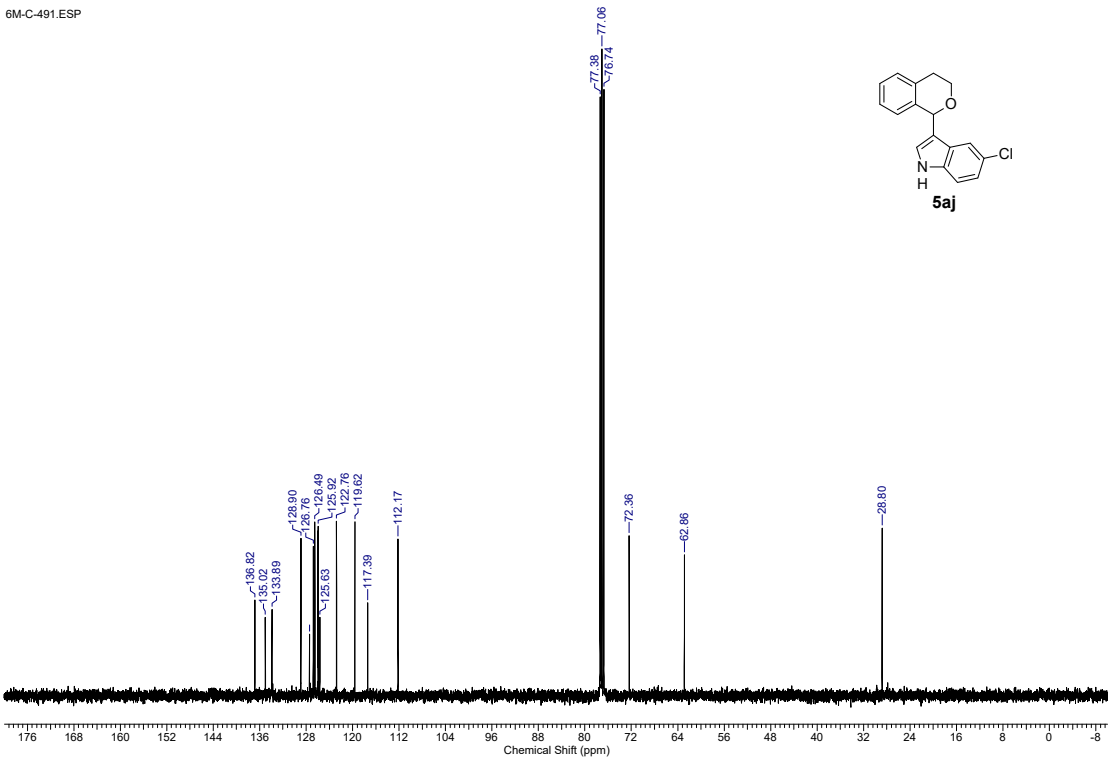


Figure S98. ^{13}C NMR spectra of compound **5aj**

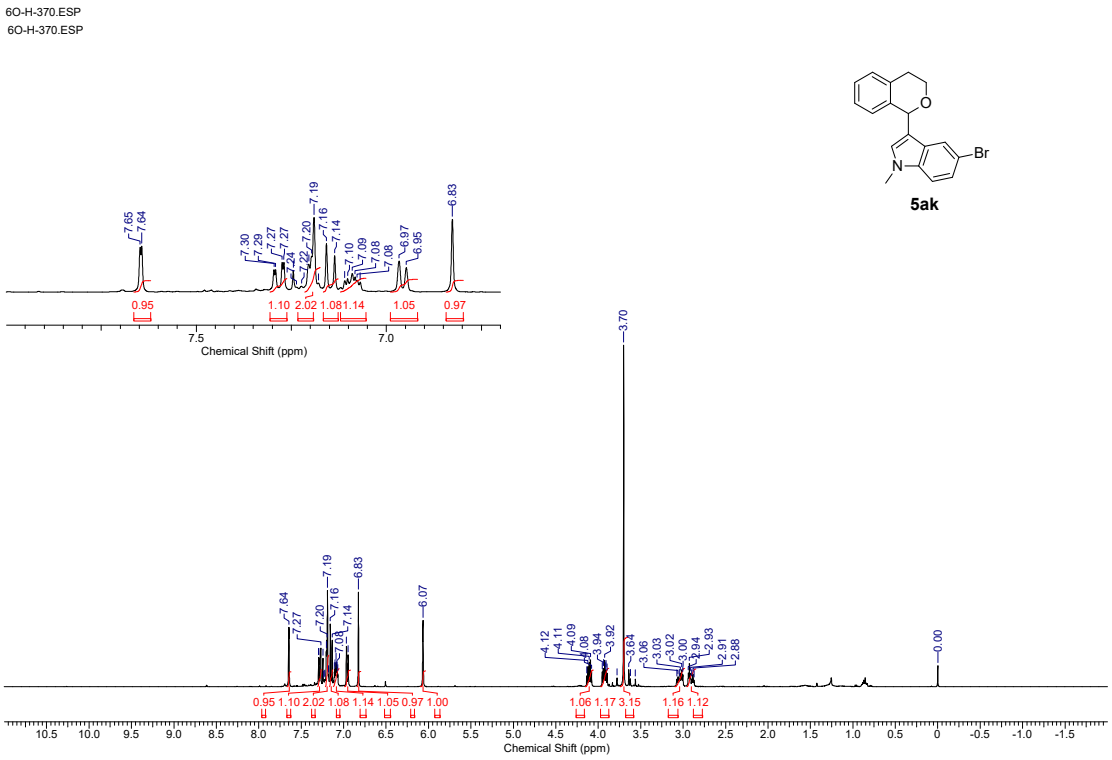


Figure S99. ^{1}H NMR spectra of compound **5ak**

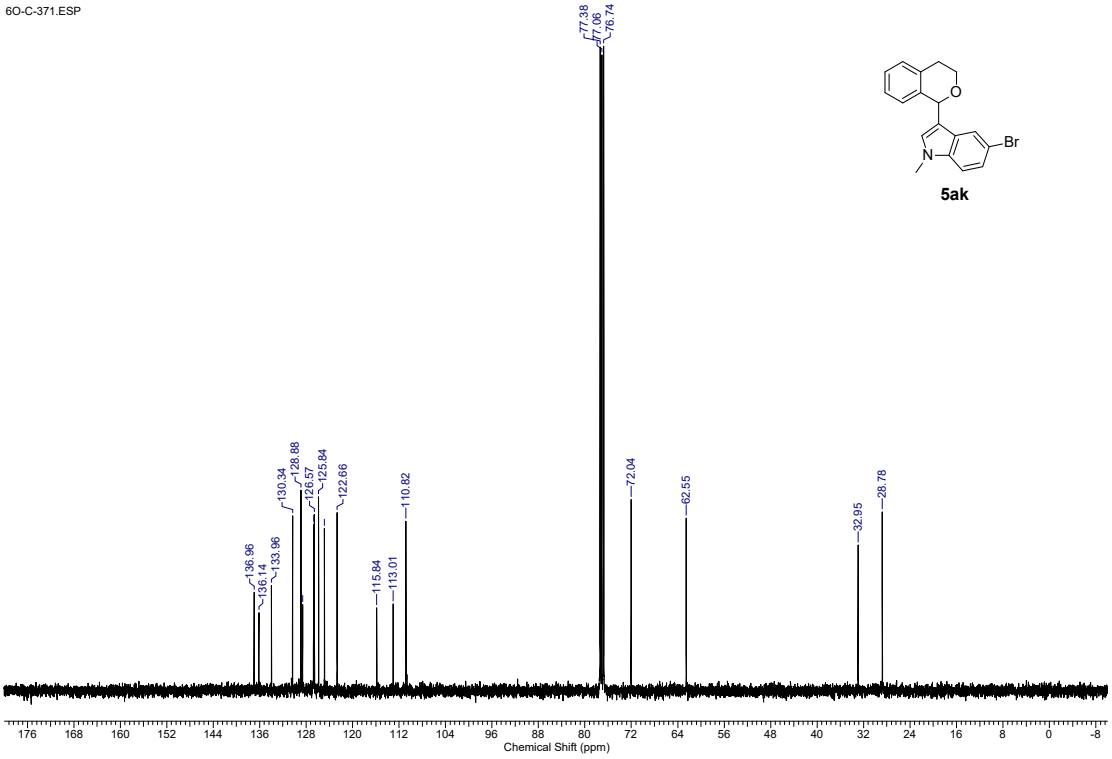


Figure S100. ^{13}C NMR spectra of compound **5ak**

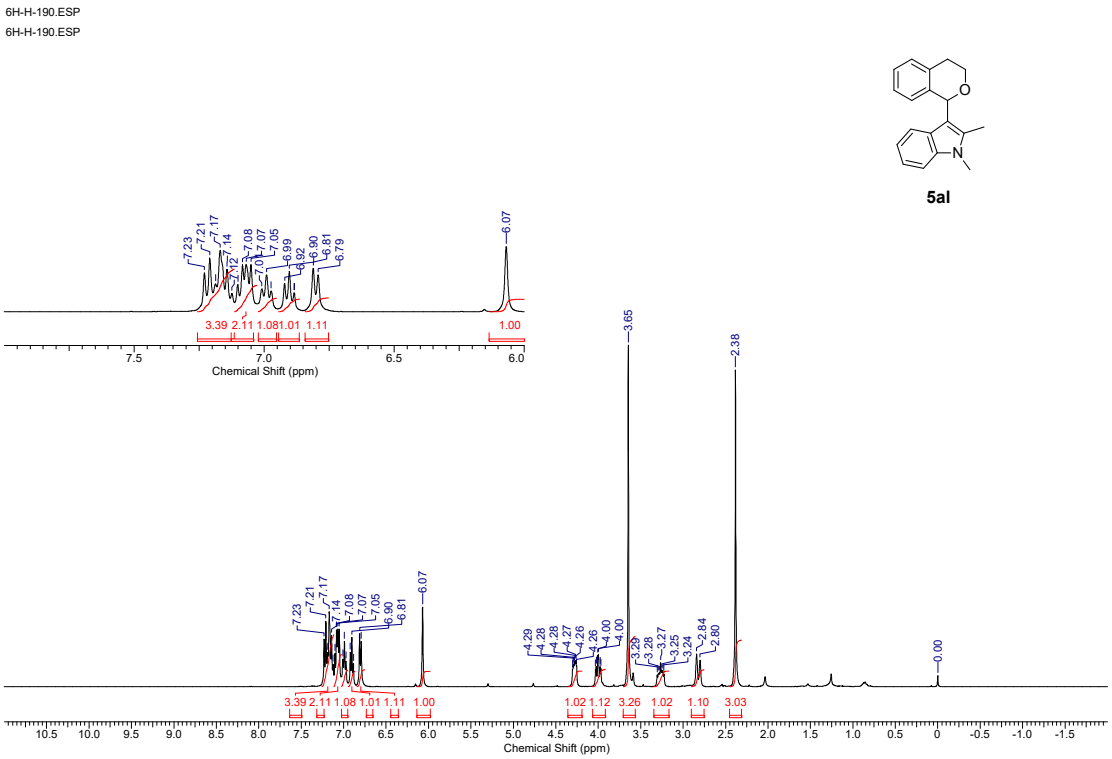


Figure S101. ^{1}H NMR spectra of compound **5al**

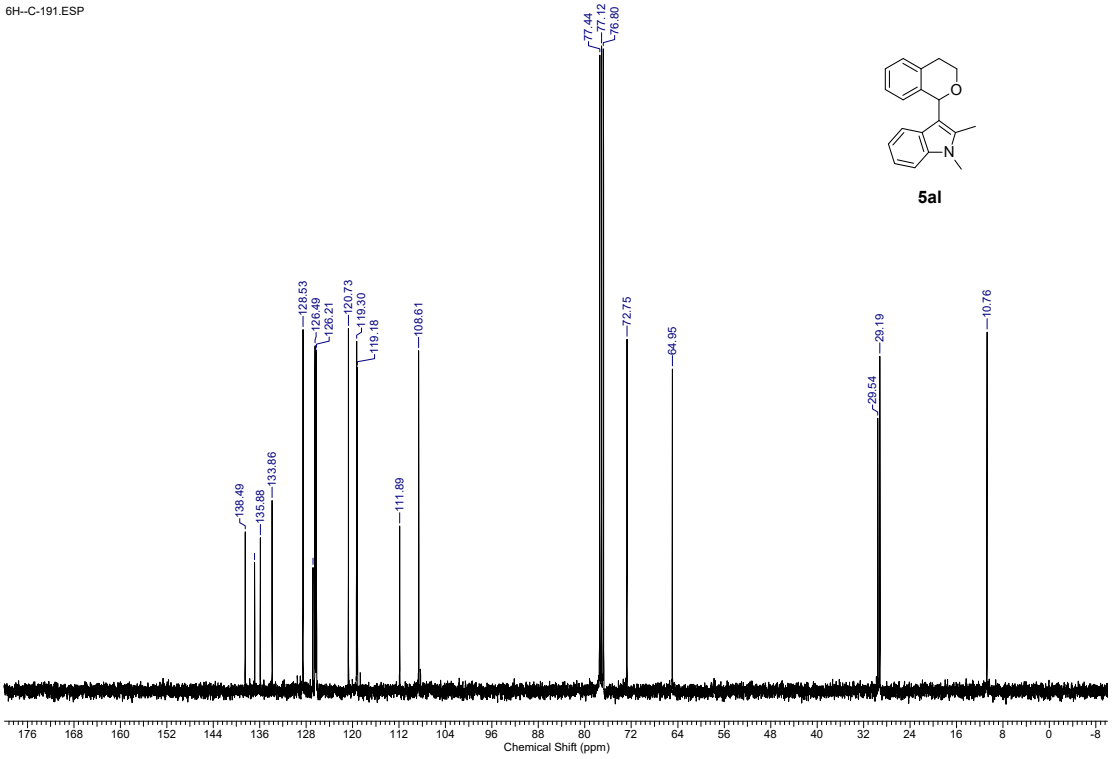


Figure S102. ^{13}C NMR spectra of compound **5al**

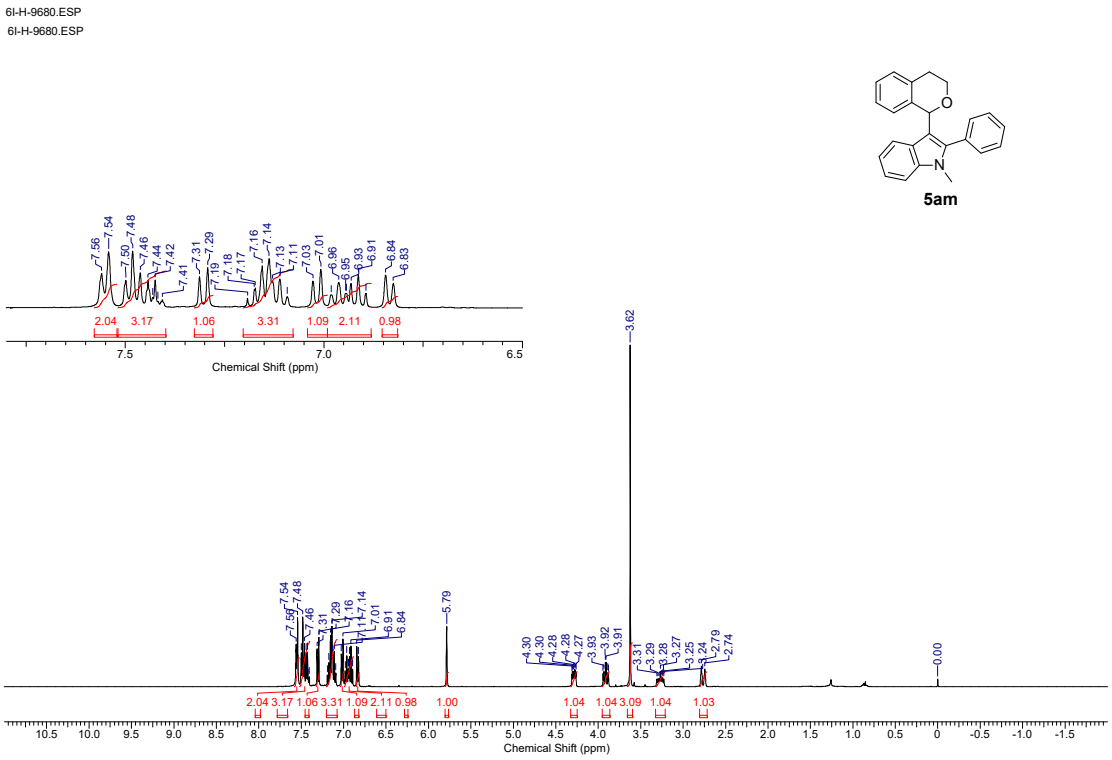


Figure S103. ^{1}H NMR spectra of compound **5am**

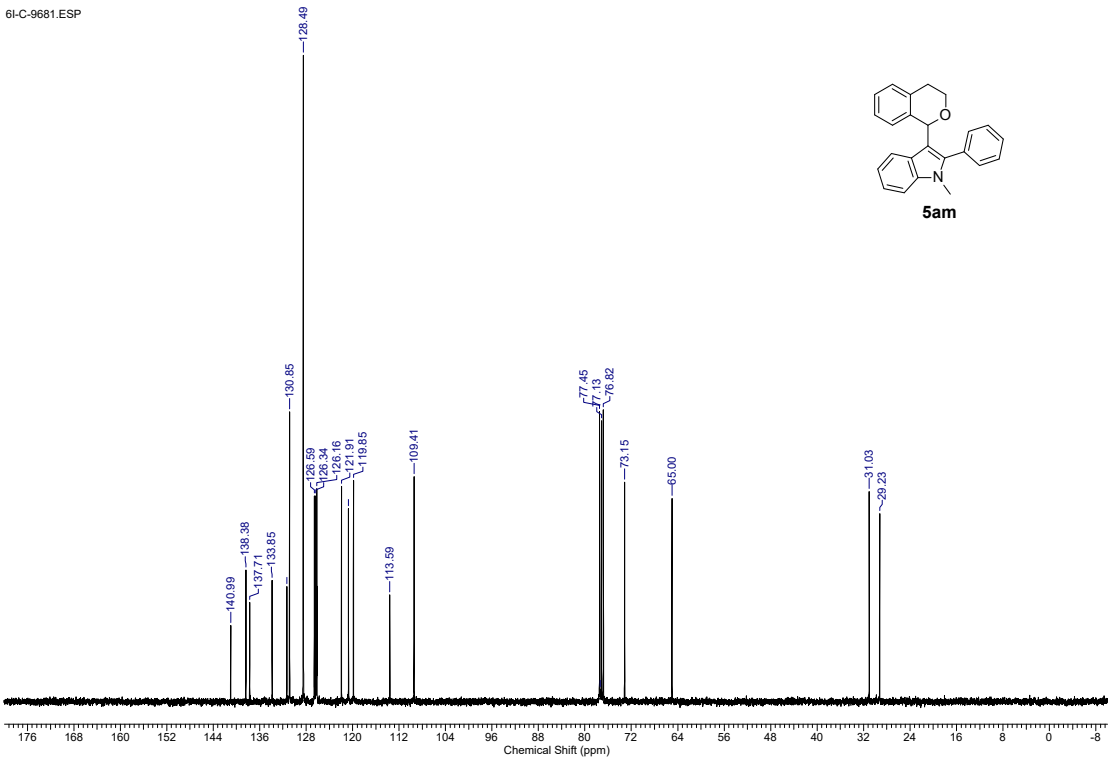


Figure S104. ^{13}C NMR spectra of compound **5am**

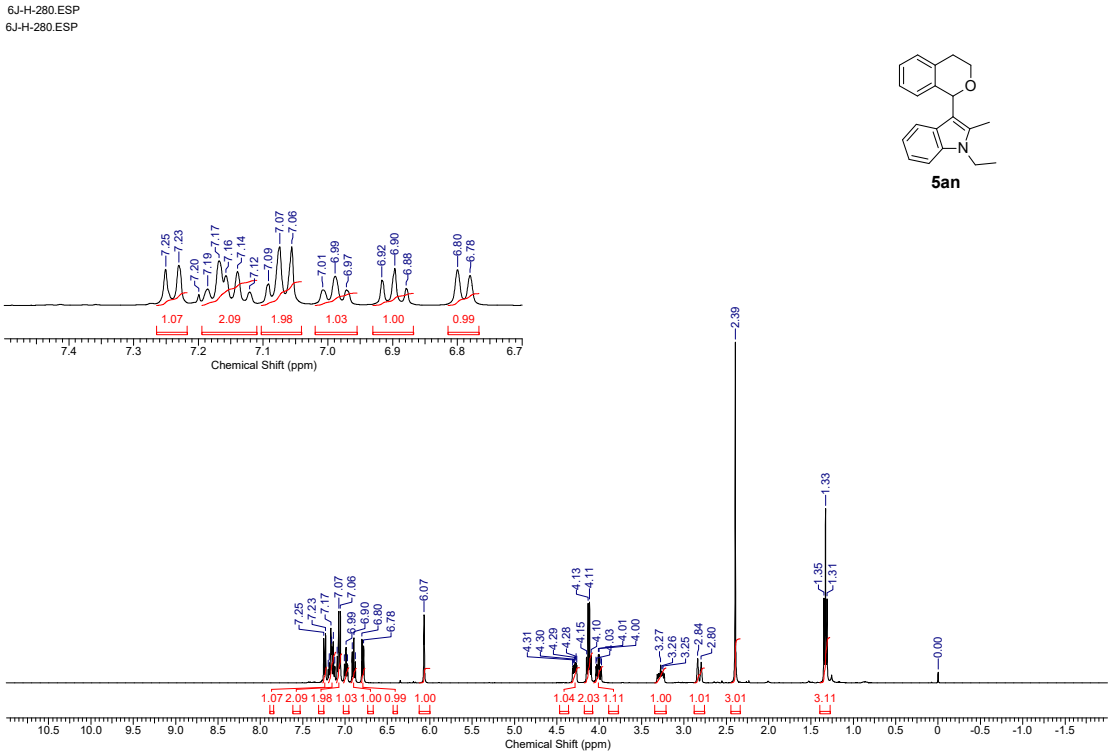


Figure S105. ^{1}H NMR spectra of compound **5an**

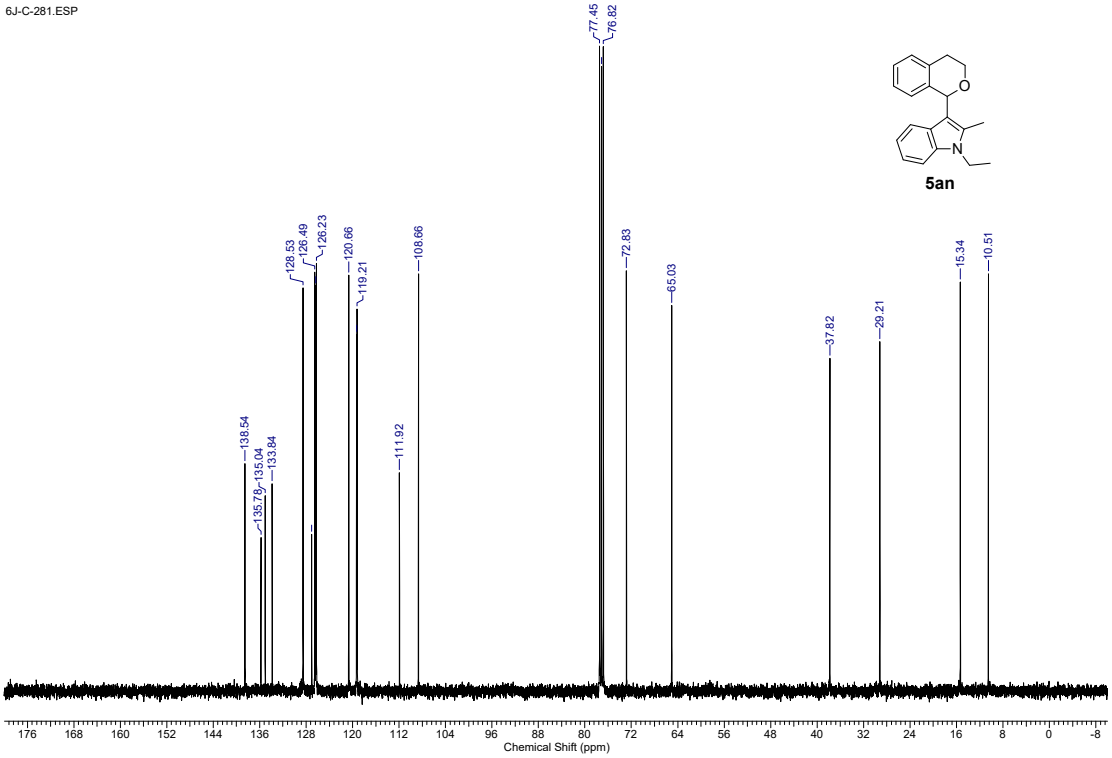


Figure S106. ^{13}C NMR spectra of compound **5an**

7. References

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[2] L. Wang, D.-W. Agnew, X. Yu, J.-S. Figueroa and S.-M. Cohen, *Angew. Chem. Int. Ed.*, 2018, **57**, 511-515.

[3] K. Yano, A. Ohshimo, E.-E. Elboray, Y. Kobayashi, T. Furuta and S. Hamada, *SynOpen*, 2024, **8**, 125-129.

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[5] L. Jin, J. Feng, G. Lu and C. Cai, *Adv. Synth. Catal.*, 2015, **357**, 2105-2110.