Supporting Information

Metal-free Sulfonyl Radical-initiated Cascade Cyclization to Access Sulfonated Indolo[1,2-*a*]quinolines

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1. General information

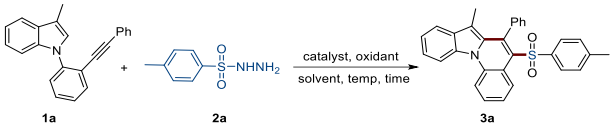
1.1 Materials and instruments

Tert-butyl hydroperoxide (TBHP), tetrabutylammonium iodide (TBAI) were purchased from Energy Chemical Co., Shanghai, China. Other reagents were purchased from Zhengzhou Alfa chem Co., Ltd. Unless otherwise stated, all commercially available reagents were directly used without further purification. All solvents were purified by standard methods prior to use. Twice-distilled water was used throughout all experiments. All reactions were monitored by thin layer chromatography (TLC), and column chromatography was carried out on 100-200 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz in $CDCl_3$ at room temperature (20 ± 3 °C), using tetramethylsilane as internal standard. High resolution mass spectra (HRMS) were conducted on a 3000-mass spectrometer, using Waters Q-Tof MS/MS system with the ESI technique. UV−Vis spectra were measured on an Agilent 8453 and one-photon fluorescence spectra were obtained with Hitachi F-4600 spectrophotometer, respectively. MTT assay was performed using a TRITURUS microplate reader. X-ray single-crystal diffraction data were collected on a Bruker SMART1000 CCD diffractometer at variable temperatures. The bioimaging of HepG-2 cells performed on the Leica TCS SP8 confocal microscopy system.

2. Experimental procedures

We initiated the study by establishing optimal experimental conditions using the model reaction of 3-methyl-1-(2-(phenylethynyl)phenyl)indole (**1a**) with $TsNHNH_2$ (**2a**) under open-air condition, as summarized in Table S1. Gratifyingly, the desired product **3a** was isolated in 54% yield when using 10 mol% of KI and 4 equiv. of TBHP in CH_3CN at 65 °C for 8 h (entry 1). The screening on four other iodine-containing reagents, including NaI, NH_4I, I_2 and TBAI, indicated that TBAI was the best choice, giving **3a** in 62% yield (entries 2-5). The ideal amount of TBAI was also explored (entries 5-7). As it can be seen, the yield increased from 45% to 62% with the increase of the amount of TBAI from 5 mol% to 10 mol% (entries 5-6), and then a slight decrease was observed as the amount of TBAI continuously increased up to 15 mol% (entry 7). Following that, three other commonly used oxidants including DTBP, BPO and $K_2S_2O_8$ were tested (entries 8-10), however, no better results were observed. The ideal amount of TBHP was explored either (entries 5, 11-12). As can be seen, the yield of **3a** was increased gradually from 48% to 64% with the increase of the amount of TBHP from 2 to 3 equiv. (entries 11-12). More solvents were then examined as shown in entries 13-17. Much to our delight, the yield of **3a** was dramatically increased to 85% (entry 15) when the reaction was performed in MeOH. Both reaction temperature and time were examined. The results showed that 65 °C and 8 h were still the best choices (entries 18-22). Besides, the results from entries 23-24 reminded that the reaction could not occur in the absence of TBAI or TBHP. After intensive experimentation, the optimized reaction conditions were established as follows: **1a** (0.5 mmol), **2a** (1 mmol), TBAI (10 mol%) and TBHP (3 equiv.) were mixed in MeOH at 65 °C for 8 h.

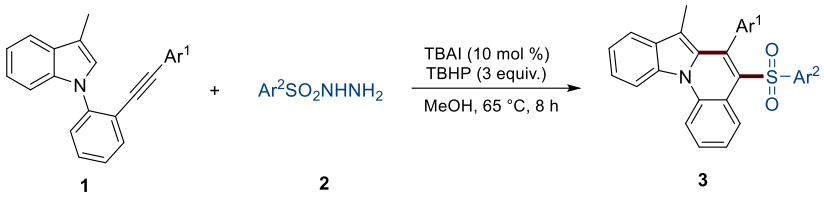
Table S1. Optimization of reaction conditions[a]



entry	catalyst (mol%)	oxidant (equiv.)	solvent	yield[b] %
1	KI (10)	TBHP (4)	CH_3CN	54
2	NaI (10)	TBHP (4)	CH_3CN	56
3	NH_4I (10)	TBHP (4)	CH_3CN	47
4	I_2 (10)	TBHP (4)	CH_3CN	28
5	TBAI (10)	TBHP (4)	CH_3CN	62
6	TBAI (5)	TBHP (4)	CH_3CN	45
7	TBAI (15)	TBHP (4)	CH_3CN	58
8	TBAI (10)	DTBP (4)	CH_3CN	trace
9	TBAI (10)	BPO (4)	CH_3CN	16
10	TBAI (10)	$K_2S_2O_8$ (4)	CH_3CN	45
11	TBAI (10)	TBHP (2)	CH_3CN	48
12	TBAI (10)	TBHP (3)	CH_3CN	64
13	TBAI (10)	TBHP (3)	DMSO	trace
14	TBAI (10)	TBHP (3)	DMF	trace
15	TBAI (10)	TBHP (3)	MeOH	85
16	TBAI (10)	TBHP (3)	EtOH	76
17	TBAI (10)	TBHP (3)	DCE	43
18[c]	TBAI (10)	TBHP (3)	MeOH	52
19[d]	TBAI (10)	TBHP (3)	MeOH	82
20[e]	TBAI (10)	TBHP (3)	MeOH	N.D.
21[f]	TBAI (10)	TBHP (3)	MeOH	42
22[g]	TBAI (10)	TBHP (3)	MeOH	76
23	---	TBHP (3)	MeOH	N.D.
24	TBAI (10)	---	MeOH	N.D.

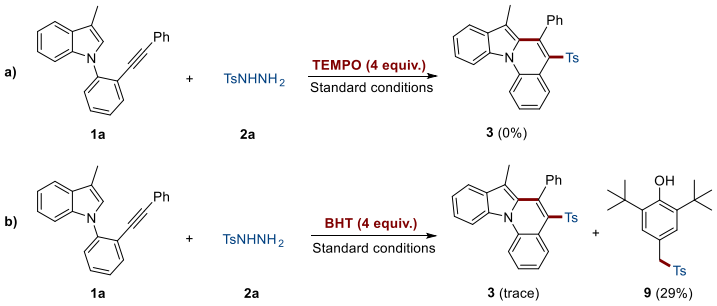
[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol), catalyst (5-15 mol%), oxidant (2-4 equiv.), solvent (10 mL) at 65 °C for 8 h. TBHP = *tert*-butyl hydroperoxide (70% aqueous solution), TBAI = tetrabutylammonium iodide, DTBP = di-*tert*-butyl peroxide, BPO = benzoyl peroxide, DCE = 1,2-Dichloroethane, N.D. = Not detected. [b]Isolated yields. [c]For 6 h. [d] For 12 h. [e] At room temperature. [f]At 45 °C. [g]At 85 °C.

2.1 General experimental procedures for sulfonyl substituted indolo[1,2-*a*]quinolines (3)



In a 25 mL flask, 1-(2-(arylethynyl)phenyl)indoles **1** (0.5 mmol) was dissolved in CH_3CN (5 mL), and sulfonyl hydrazides **2** (2.0 equiv.), TBAI (10 mol%), TBHP (3 equiv.) were added. The mixture was allowed to stir at 65 °C for 8 h. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the dichloromethane (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1) to afford the desired product.

2.2 Control experiments



Scheme S1. Control experiments

In a 25 mL flask, 1-(2-(arylethynyl)phenyl)indoles **1** (0.5 mmol) was dissolved in CH_3CN (5 mL), and sulfonyl hydrazides **2** (2.0 equiv.), TBAI (10 mol %), TBHP (3 equiv.) were added. Afterward, ((2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl) (TEMPO, 4 equiv.) was added in the mixture. The mixture was allowed to stir at 65 °C for 8 h. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the dichloromethane (15 mL) was added three times for extraction. The reaction mixture was tested using HRMS and no desired product was detected.

In a 25 mL flask, 1-(2-(arylethynyl)phenyl)indoles **1** (0.5 mmol) was dissolved in CH_3CN (5 mL), and sulfonyl hydrazides **2** (2.0 equiv.), TBAI (10 mol%), TBHP (3 equiv.) were added. Afterward, (2,6-ditert-butyl-4-methyl-phenol) (BHT, 4 equiv.) was added in the mixture. The mixture was allowed to stir at 65 °C for 8 h. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the dichloromethane (15 mL) was added three times for extraction. The reaction mixture was tested using HRMS and product **9** was successfully detected. Furthermore, product **9** was isolated in 29% yield.

3. Cell viability measured by MTT assay

HepG-2 cells were cultured in in DMEM supplemented with 10% FBS and 1% penicillin-streptomycin and incubated in a humidified 5% CO_2 incubator at 37 °C with the medium changed every other day. A standard MTT assay was used to evaluate the cytotoxicity of TPAP-BB. Cells were seeded in 96-well plates at a density of 50000 cells per well. After an overnight incubation, the medium was replaced with 100 μL of fresh medium supplemented with different concentrations of **3z** for 24 h. 10 μL of MTT (5 mg/mL in PBS) was added. After 4 h incubation, 100 μL of dimethyl sulfoxide (DMSO) was then added. After 15 min, the absorbance at 570 nm was then monitored by the microplate Reader. Each experiment (i.e., each **3z** concentration) was conducted in quintuplicate.

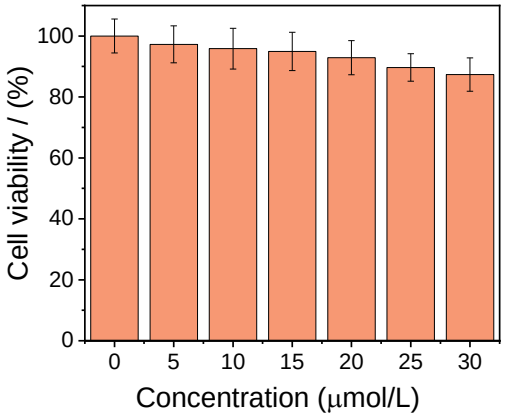
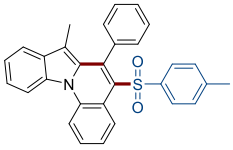


Figure S1 Cell viability of **3z** to HepG-2 cells measured by MTT assay

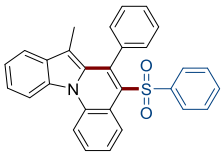
4. Characterization of compounds

*7-methyl-6-phenyl-5-tosylindolo[1,2-a]quinoline (**3a**)*



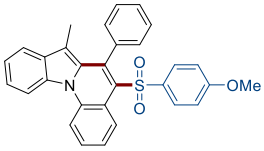
196 mg, 85%; Yellow solid, m.p. 159-161°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.46 (d, *J* = 8.0, 1H), 8.37 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.0, 1H), 7.57-7.55 (m, 2H), 7.54-7.34 (m, 6H), 7.31-7.20 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 140.4, 140.1, 136.1, 135.8, 132.4, 131.6, 130.3, 130.1, 129.4, 129.0, 128.4, 128.1, 127.8, 127.7, 126.7, 124.6, 122.8, 122.0, 120.1, 119.2, 115.4, 114.6, 114.4, 21.6, 10.1. HRMS Calcd for $C_{30}H_{24}NO_2S$ $[M + H]^+$: m/z 462.1522, Found: 462.1524

*7-methyl-6-phenyl-5-(phenylsulfonyl)indolo[1,2-a]quinoline (**3b**)*



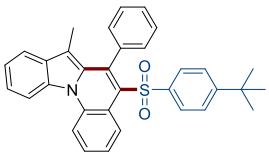
188 mg, 84%; Yellow solid, m.p. 204-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.67-7.65 (m, 2H), 7.56-7.50 (m, 2H), 7.45-7.34 (m, 5H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.29-7.24 (m, 3H), 1.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ143.4, 140.4, 136.1, 135.6, 132.5, 132.4, 131.6, 130.3, 130.2, 129.1, 128.8, 128.4, 127.9, 127.7, 126.6, 124.7, 122.8, 122.0, 120.1, 119.2, 115.4, 114.6, 114.5, 10.1. HRMS Calcd for $C_{29}H_{22}NO_2S$ $[M + H]^+$: m/z 448.1366, Found: 448.1367

*5-((4-methoxyphenyl)sulfonyl)-7-methyl-6-phenylindolo[1,2-a]quinoline (**3c**)*



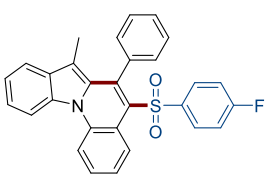
176 mg, 74%; Yellow solid, m.p.125-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.47-7.36 (m, 4H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.28-7.23 (m, 3H), 6.75 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 139.8, 136.1, 135.9, 135.0, 132.4, 131.6, 130.4, 130.2, 129.1, 129.0, 128.7, 128.4, 127.9, 127.8, 124.6, 122.8, 122.0, 120.1, 119.3, 115.5, 114.6, 114.3, 114.1, 55.6, 10.1. HRMS Calcd for $C_{30}H_{24}NO_3S$ $[M + H]^+$: m/z 478.1471, Found:478.1469

*5-((4-(tert-butyl)phenyl)sulfonyl)-7-methyl-6-phenylindolo[1,2-a]quinoline (**3d**)*



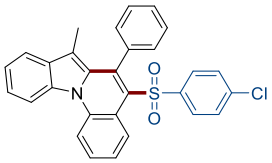
161 mg, 64%; Yellow solid, m.p. 192-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 7.6, 1H), 8.48 (d, *J* = 8.4, 1H), 8.38 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.57-7.54 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.43-7.40 (m, 1H), 7.38-7.28 (m, 6H), 7.25 (d, *J* = 8.0, 2H), 1.55 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 140.3, 139.9, 136.1, 135.6, 132.4, 131.6, 130.4, 130.3, 129.0, 128.5, 128.3, 127.9, 127.8, 126.5, 125.8, 124.5, 122.8, 122.0, 120.0, 119.3, 115.4, 114.6, 114.2, 35.1, 31.1, 10.1. HRMS Calcd for $C_{33}H_{30}NO_2S$ $[M + H]^+$: m/z 504.1992, Found: 504.1992

*5-((4-fluorophenyl)sulfonyl)-7-methyl-6-phenylindolo[1,2-a]quinoline (**3e**)*



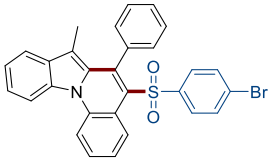
165 mg, 71%; Yellow solid, m.p. 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.48 (d, *J* = 8.4, 1H), 8.38 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.0, 1H), 7.65-7.61 (m, 2H), 7.58-7.54 (m, 1H), 7.52-7.48 (m, 1H), 7.46-7.42 (m, 1H), 7.40-7.35 (m, 3H), 7.31-7.27 (m, 1H), 7.25-7.23 (m, 2H), 7.00-6.95 (m, 2H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8 (d, *J* = 256.1 Hz), 140.2, 139.4 (d, *J* = 3.3 Hz) 136.1, 135.4, 132.5, 131.6, 130.3, 130.2, 129.5 (d, *J* = 9.5 Hz), 129.2, 128.6, 128.1, 127.9, 127.6, 124.8, 122.9, 122.1, 120.1, 119.1, 116.0 (d, *J* = 22.9 Hz), 115.5, 114.6, 114.6, 10.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.1. HRMS Calcd for $C_{29}H_{21}FNO_2S$ [M + H]$^{+}$: m/z 466.1272, Found: 466.1263

*5-((4-chlorophenyl)sulfonyl)-7-methyl-6-phenylindolo[1,2-a]quinoline (**3f**)*



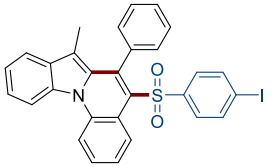
170 mg, 71%; Yellow solid, m.p.217-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.0, 1H), 7.60-7.51 (m, 4H), 7.47-7.43 (m, 1H), 7.40-7.36 (m, 3H), 7.32-7.28 (m, 2H), 7.27-7.24 (m, 3H), 1.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 140.4, 139.0, 136.0, 135.4, 132.5, 131.6, 130.3, 130.2, 129.2, 129.0, 128.6, 128.1, 127.9, 127.8, 127.6, 124.8, 122.9, 122.1, 120.1, 119.1, 115.5, 114.7, 114.6, 100.0, 10.2. HRMS Calcd for $C_{29}H_{21}ClNO_2S$ [M + H]$^{+}$: m/z 482.0976, Found: 482.0989

*5-((4-bromophenyl)sulfonyl)-7-methyl-6-phenylindolo[1,2-a]quinoline (**3g**)*



200 mg, 76%; Yellow solid, m.p. 233-235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4, 1H), 7.59-7.55 (m, 1H), 7.54-7.50 (m, 1H), 7.49-7.42 (m, 5H), 7.40-7.36 (m, 3H), 7.32-7.28 (m, 1H), 7.25-7.23 (m, 2H), 1.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 140.4, 136.0, 135.3, 132.5, 132.0, 131.6, 130.3, 130.2, 129.2, 128.6, 128.2, 127.9, 127.8, 127.6, 124.8, 122.9, 122.1, 120.1, 119.1, 115.5, 114.7, 114.6, 10.2. HRMS Calcd for $C_{29}H_{21}BrNO_2S$ [M + H]$^{+}$: m/z 526.0471, Found: 526.0481

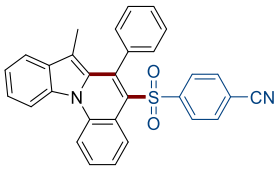
*5-((4-iodophenyl)sulfonyl)-7-methyl-6-phenylindolo[1,2-a]quinoline (**3h**)*



167 mg, 58%; m.p. 246-248 °C; Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.0, 1H), 8.49 (d, *J* = 8.4, 1H), 8.39 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.59-7.50 (m, 2H), 7.47-7.44 (m, 1H), 7.40-7.36 (m, 3H), 7.33-7.30 (m, 3H), 7.25-7.23 (m, 2H), 1.56 (s, 3H). ^{13}C

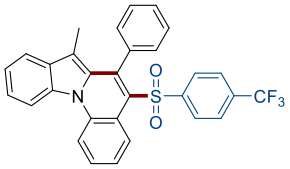
NMR (101 MHz, $CDCl_3$) δ 143.1, 140.4, 138.0, 136.0, 135.3, 132.5, 131.6, 130.3, 130.2, 129.2, 128.6, 128.1, 127.9, 127.8, 127.6, 124.8, 122.9, 122.1, 120.1, 119.0, 115.5, 114.7, 114.6, 100.0, 10.2. HRMS Calcd for $C_{29}H_{21}INO_2S$ $[M + H]^+$: m/z 574.0332, Found: 574.0339

*4-((7-methyl-6-phenylindolo[1,2-a]quinolin-5-yl)sulfonyl)benzonitrile (**3i**)*



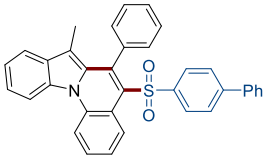
163 mg, 69%; Yellow solid, m.p. 253-256 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.4, 1H), 8.54 (d, *J* = 8.4, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.4, 2H), 7.65-7.56 (m, 4H), 7.51-7.47 (m, 1H), 7.45-7.38 (m, 3H), 7.36-7.33 (m, 1H), 7.26-7.24 (m, 2H), 1.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 140.9, 136.0, 134.9, 132.5, 131.6, 130.5, 130.0, 129.5, 128.8, 128.0, 127.4, 127.2, 125.1, 123.0, 122.3, 120.3, 118.9, 117.3, 116.0, 115.6, 115.2, 114.7, 10.3. HRMS Calcd for $C_{30}H_{21}N_2O_2S$ $[M + H]^+$: m/z 473.1318, Found: 473.1322

*7-methyl-6-phenyl-5-((4-(trifluoromethyl)phenyl)sulfonyl)indolo[1,2-a]quinoline (**3j**)*



136 mg, 53%; Yellow solid, m.p. 235-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.49 (d, *J* = 8.4, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.60-7.50 (m, 4H), 7.45-7.38 (m, 2H), 7.36-7.29 (m, 3H), 7.24-7.19 (m, 2H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 140.6, 136.0, 135.1, 134.0 (q, *J* = 32.8 Hz), 132.6, 131.6, 130.5, 130.1, 129.4, 128.7, 127.9, 127.5, 127.1, 125.9 (q, *J* = 3.6 Hz), 124.9, 123.6 (q, *J* = 226.6 Hz), 123.0, 122.2, 120.2, 119.0, 115.5, 114.9, 114.7, 10.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2. HRMS Calcd for $C_{30}H_{21}F_3NO_2S$ $[M + H]^+$: m/z 516.1240, Found: 516.1242

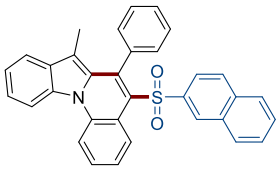
*5-([1,1'-biphenyl]-4-ylsulfonyl)-7-methyl-6-phenylindolo[1,2-a]quinoline (**3k**)*



167 mg, 64%; Yellow solid, m.p. 194-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.63-7.53 (m, 6H), 7.51-7.46 (m, 3H), 7.43-7.40 (m, 4H), 7.37-7.32 (m, 3H), 1.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 141.9, 140.1, 139.3, 136.1, 135.6, 132.5, 131.6, 130.3, 129.1, 129.0, 128.5, 128.4,

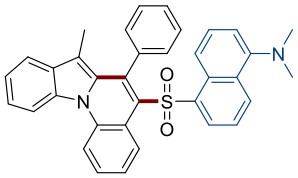
128.3, 127.9, 127.8, 127.4, 127.3, 127.2, 124.6, 122.9, 122.0, 120.1, 119.3, 115.5, 114.6, 114.4, 10.1. HRMS Calcd for $C_{35}H_{26}NO_2S$ [M + H]$^+$: m/z 524.1679, Found: 524.1675

*7-methyl-5-(naphthalen-2-ylsulfonyl)-6-phenylindolo[1,2-a]quinoline (**3l**)*



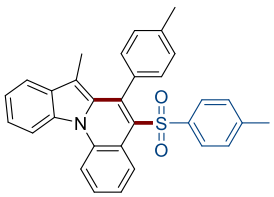
184 mg, 74%; Yellow solid, m.p. 212-216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 1.7 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.77-7.74 (m, 2H), 7.63 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.60-7.48 (m, 4H), 7.39-7.32 (m, 2H), 7.30-7.25 (m, 5H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 140.0, 136.1, 135.4, 134.7, 132.5, 132.0, 131.6, 130.35, 130.31, 129.4, 129.1, 129.0, 128.8, 128.6, 128.2, 127.82, 127.80, 127.7, 127.3, 124.6, 122.9, 122.0, 121.9, 120.1, 119.3, 115.4, 114.6, 114.4, 10.2. HRMS Calcd for $C_{33}H_{24}NO_2S$ [M + H]$^+$: m/z 498.1522, Found: 498.1521

*N,N-dimethyl-5-((7-methyl-6-phenylindolo[1,2-a]quinolin-5-yl)sulfonyl)naphthalen-1-amine (**3m**)*



116 mg, 43%; Yellow solid, m.p. 237-239 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (dd, *J* = 8.4, 1H), 8.49 (d, *J* = 8.4, 1H), 8.36 (d, *J* = 8.8 Hz, 1H), 8.27 (d, *J* = 8.4, 1H), 7.77 (d, *J* = 8.4, 1H), 7.63 (d, *J* = 8.0, 1H), 7.60-7.56 (m, 1H), 7.54-7.52 (m, 1H), 7.48-7.44 (m, 1H), 7.38-7.34 (m, 1H), 7.32-7.28 (m, 1H), 7.22-7.18 (m, 2H), 7.12-7.08 (m, 1H), 7.02 (t, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 7.6, 1H), 6.76-6.74 (m, 2H), 2.78 (s, 6H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 138.5, 138.2, 136.3, 134.3, 132.4, 131.7, 130.7, 130.5, 129.7, 129.6, 129.33, 129.31, 128.7, 128.6, 128.1, 127.9, 127.6, 124.4, 123.6, 122.8, 122.0, 119.8, 119.3, 118.8, 115.3, 114.9, 114.7, 113.7, 77.4, 45.4, 10.4. HRMS Calcd for $C_{35}H_{29}N_2O_2S$ [M + H]$^+$: m/z 541.1944, Found: 541.1942

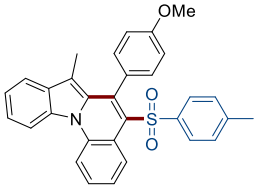
*7-methyl-6-(p-tolyl)-5-tosylindolo[1,2-a]quinoline (**3n**)*



187 mg, 79%; Yellow solid, m.p. 173-176 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.43 (d, *J* = 8.4, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H),

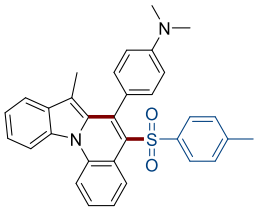
7.52-7.44 (m, 2H), 7.34 (t, *J* = 8.0, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.20-7.15 (m, 4H), 7.10 (d, *J* = 8.4 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 140.5, 140.3, 138.2, 136.1, 132.7, 132.4, 131.6, 130.5, 130.0, 129.3, 129.0, 128.5, 128.3, 127.7, 126.8, 124.5, 122.7, 122.0, 120.1, 119.3, 115.4, 114.6, 114.4, 21.6, 21.6, 10.3. HRMS Calcd for $C_{31}H_{26}NO_2S$ [M + H]$^+$: m/z 476.1679, Found: 476.1668

*6-(4-methoxyphenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3o**)*



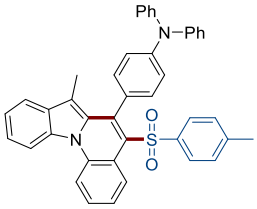
182 mg, 74%; Yellow solid, m.p. 207-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.49 (d, *J* = 8.4, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0, 1H), 7.59-7.51 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.34-7.29 (m, 1H), 7.22-7.18 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.96-6.93 (m, 2H), 3.94 (s, 3H), 2.37 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 143.2, 140.6, 139.9, 136.0, 132.5, 131.6, 131.5, 130.8, 129.3, 129.0, 128.8, 127.8, 127.7, 126.7, 124.5, 122.7, 122.0, 120.0, 119.4, 115.4, 114.6, 114.2, 113.3, 55.4, 21.6, 10.5. HRMS Calcd for $C_{31}H_{26}NO_3S$ [M + H]$^+$: m/z 492.1628, Found:492.1625

*N, N-dimethyl-4-(7-methyl-5-tosylindolo[1,2-a]quinolin-6-yl)aniline (**3p**)*



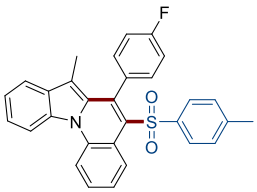
131 mg, 53%; Yellow solid, m.p. 204-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.49 (d, *J* = 8.4, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0, 1H), 7.59-7.50 (m, 4H), 7.42-7.29 (m, 2H), 7.10-7.05 (m, 4H), 6.68 (d, *J* = 8.8 Hz, 2H), 3.08 (s, 6H), 2.36 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 142.7, 140.8, 140.4, 135.9, 132.5, 131.7, 131.5, 131.3, 129.2, 128.8, 127.9, 126.7, 124.3, 122.8, 122.6, 121.8, 120.0, 119.7, 115.2, 114.7, 114.1, 111.4, 40.5, 21.5, 10.8. HRMS Calcd for $C_{32}H_{29}N_2O_2S$ [M + H]$^+$: m/z 505.1944, Found: 505.1956

*4-(7-methyl-5-tosylindolo[1,2-a]quinolin-6-yl)-N,N-diphenylaniline (**3q**)*



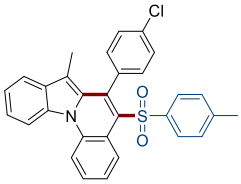
160 mg, 51%; Yellow solid, m.p. 238-240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.50 (d, J = 8.6 Hz, 1H), 8.42 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.63-7.52 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36-7.28 (m, 5H), 7.23-7.17 (m, 6H), 7.14-7.07 (m, 6H), 2.36 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.5, 143.3, 140.7, 140.1, 136.0, 132.5, 131.7, 131.2, 130.8, 129.4, 129.4, 129.0, 129.0, 128.5, 127.8, 126.7, 124.8, 124.5, 123.3, 122.8, 122.2, 122.0, 120.0, 119.4, 115.3, 114.7, 114.1, 21.6, 10.4. HRMS Calcd for $C_{42}H_{33}N_2O_2S$ $[M + H]^+$: m/z 629.2257, Found: 629.2260

*6-(4-fluorophenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3r**)*



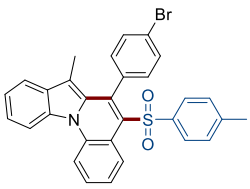
143 mg, 60 %; Yellow solid, m.p. 224-227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.3 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.63-7.40 (m, 4H), 7.40-7.17 (m, 4H), 7.16-6.95 (m, 4H), 2.31 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 252.5 Hz), 143.6, 140.4, 139.0, 136.1, 132.5, 132.0 (d, *J* = 8.9 Hz), 131.7 (d, *J* = 3.4 Hz), 131.6, 130.3, 129.5, 129.2, 128.7, 127.8, 126.7, 124.8, 122.9, 122.1, 120.1, 119.2, 115.5, 115.0 (d, *J* = 21.8 Hz), 114.6, 114.2, 21.6, 10.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8. HRMS Calcd for $C_{30}H_{23}FNO_2S$ $[M + H]^+$: m/z 480.1428, Found:480.1421

*6-(4-chlorophenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3s**)*



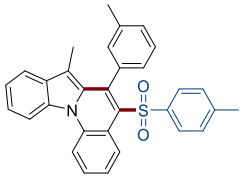
188 mg, 76%; Yellow solid, m.p. 204-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.56-7.49 (m, 4H), 7.40-7.36 (m, 3H), 7.29-7.22 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 140.3, 138.7, 136.1, 134.6, 134.3, 132.5, 131.6, 131.5, 130.0, 129.5, 129.2, 128.6, 128.1, 127.8, 126.7, 124.8, 122.9, 122.1, 120.1, 119.1, 115.4, 114.6, 114.1, 21.6, 10.5. HRMS Calcd for $C_{30}H_{23}ClNO_2S$ $[M + H]^+$: m/z 496.1133, Found:496.1135

*6-(4-bromophenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3t**)*



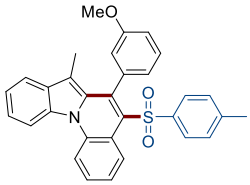
209 mg, 78%; Yellow solid, m.p. 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.53 (q, *J* = 6.9, 5.0 Hz, 6H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30-7.23 (m, 1H), 7.21-7.11 (m, 4H), 2.35 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 140.2, 138.6, 136.1, 134.8, 132.5, 131.8, 131.6, 131.1, 129.8, 129.5, 129.3, 128.5, 127.8, 126.7, 124.8, 122.9, 122.8, 122.1, 120.1, 119.0, 115.5, 114.6, 114.1, 21.6, 10.5. HRMS Calcd for $C_{30}H_{23}BrNO_2S$ $[M + H]^+$: m/z 540.0627, Found: 540.0628

*7-methyl-6-(m-tolyl)-5-tosylindolo[1,2-a]quinoline (**3u**)*



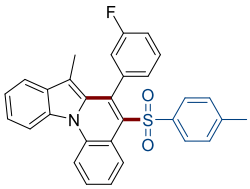
203 mg, 85%; Yellow solid, m.p. 161-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.4, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.53-7.43 (m, 4H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.30-7.25 (m, 2H), 7.22-7.13 (m, 2H), 7.07 (d, *J* = 8.0z Hz, 2H), 6.91 (s, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.6, 140.1, 137.3, 136.0, 135.4, 132.4, 131.6, 130.9, 130.4, 129.3, 129.1, 129.0, 128.6, 127.8, 127.7, 127.6, 126.9, 124.5, 122.8, 122.0, 120.0, 119.4, 115.4, 114.6, 114.2, 21.6, 21.5, 10.2. HRMS Calcd for $C_{31}H_{26}NO_2S$ $[M + H]^+$: m/z 476.1679, Found:476.1681

*6-(3-methoxyphenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3v**)*



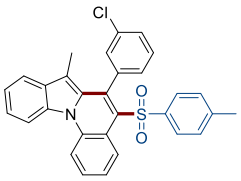
210 mg, 86%; Yellow solid, m.p. 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.3 Hz, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.36 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.61-7.43 (m, 4H), 7.41-7.20 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.96 (dt, *J* = 8.6, 4.6 Hz, 2H), 6.68 (t, *J* = 2.0 Hz, 1H), 3.73 (s, 3H), 2.32 (s, 3H), 1.63 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 143.3, 140.4, 139.4, 136.7, 136.1, 132.4, 131.6, 130.2, 129.4, 129.1, 128.9, 128.7, 127.9, 126.9, 124.6, 123.1, 122.8, 122.0, 120.1, 119.3, 115.6, 115.4, 114.6, 114.5, 114.2, 55.2, 31.6, 21.5, 10.2. HRMS Calcd for $C_{31}H_{26}NO_3S$ $[M + H]^+$: m/z 492.1628, Found:492.1629

*6-(3-fluorophenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3w**)*



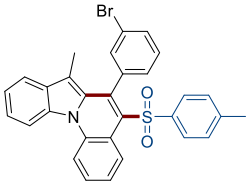
189 mg, 79%; Yellow solid, m.p. 187-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.41-7.32 (m, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.14-7.08 (m, 4H), 6.92 (d, *J* = 9.2 Hz, 1H), 2.27 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 (d, *J* = 247.7 Hz), 143.8, 140.2, 138.3 (d, *J* = 1.5 Hz), 137.9 (d, *J* = 8.2 Hz), 136.1, 132.4, 131.6, 129.7, 129.6, 129.5 (d, *J* = 8.8 Hz), 129.4, 128.5, 127.8, 126.8, 126.3 (d, *J* = 2.7 Hz), 124.8, 122.9, 122.2, 120.1, 119.0, 117.4 (d, *J* = 22.5 Hz) , 115.5, 115.4 (d, *J* = 20.6 Hz), 114.6, 114.2, 21.6, 10.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.3. HRMS Calcd for $C_{30}H_{23}FNO_2S$ $[M + H]^+$: m/z 480.1428, Found:480.1424

*6-(3-chlorophenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3x**)*



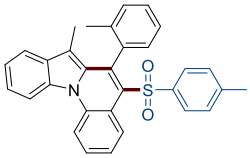
187mg, 76%; Yellow solid, m.p. 198-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.4, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.59-7.48 (m, 4H), 7.45-7.30 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 1H), 2.37 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 140.2, 138.0, 137.4, 136.1, 133.9, 132.4, 131.6, 130.2, 129.8, 129.6, 129.4, 129.1, 129.0, 128.9, 128.6, 127.9, 126.8, 124.8, 122.9, 122.2, 120.1, 119.1, 115.5, 114.6, 114.0, 21.6, 10.4. HRMS Calcd for $C_{30}H_{23}ClNO_2S$ $[M + H]^+$: m/z 496.1133, Found:496.1134

*6-(3-bromophenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3y**)*



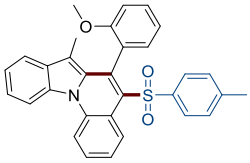
214 mg, 79%; Yellow solid, m.p. 205-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 8.3, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.57-7.46 (m, 5H), 7.38-7.28 (m, 4H), 7.15-7.11 (m, 3H), 2.35 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 140.2, 137.9, 137.5, 136.1, 133.0, 132.4, 131.6, 131.5, 129.8, 129.6, 129.4, 129.4, 129.4, 129.1, 127.9, 126.8, 124.8, 122.9, 122.2, 121.9, 120.1, 119.1, 115.5, 114.6, 114.0, 21.7, 10.4. HRMS Calcd for $C_{30}H_{23}BrNO_2S$ $[M + H]^+$: m/z 540.0627, Found: 540.0638

*7-methyl-6-(o-tolyl)-5-tosylindolo[1,2-a]quinoline (**3z**)*



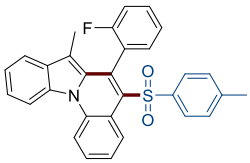
178 mg, 75%; Yellow solid, m.p. 215-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.4, 1H), 8.49 (d, *J* = 8.0, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55-7.46 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.27-7.21 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 3H), 2.33 (s, 3H), 2.15 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 143.6, 140.4, 140.4, 139.9, 137.7, 136.2, 136.2, 135.7, 132.6, 131.6, 129.8, 129.8, 129.6, 129.5, 129.4, 129.1, 129.1, 128.8, 128.8, 127.9, 127.6, 126.9, 126.9, 125.5, 125.5, 124.7, 124.7, 122.9, 122.9, 122.1, 122.0, 120.2, 119.2, 115.6, 115.6, 114.7, 114.2, 21.6, 20.1, 20.1, 9.3, 9.3. HRMS Calcd for $C_{31}H_{26}NO_2S$ $[M + H]^+$: m/z 476.1679, Found:476.1680

*6-(2-methoxyphenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3aa**)*



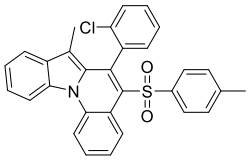
172 mg, 70%; Yellow solid, m.p. 180-182 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 7.72-7.68 (m, 3H), 7.45-7.36 (m, 3H), 7.30-7.24 (m, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.09-7.02 (m, 3H), 6.83 (d, *J* = 8.4 Hz, 1H), 3.62 (s, 3H), 2.24 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 143.3, 140.5, 137.4, 136.3, 132.4, 131.5, 131.3, 130.3, 129.7, 129.4, 128.9, 128.1, 127.5, 126.8, 125.1, 124.4, 122.7, 121.9, 120.5, 120.1, 119.2, 115.6, 114.6, 113.6, 110.4, 77.3, 55.4, 21.6, 9.5. HRMS Calcd for $C_{31}H_{26}NO_3S$ $[M + H]^+$: m/z 492.1628, Found:492.1627

*6-(2-fluorophenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3ab**)*



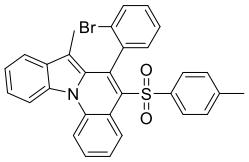
163 mg, 68%; Yellow solid, m.p. 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 7.76-7.71 (m, 3H), 7.52-7.44 (m, 3H), 7.41-7.33 (m, 2H), 7.27 (td, *J* = 7.6, 1.1 Hz, 1H), 7.22-7.18 (m, 1H), 7.16-7.11 (m, 3H), 2.30 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3 (d, *J* = 245.0 Hz), 143.7, 140.0, 136.3, 134.1, 132.5, 132.0 (d, *J* = 2.9 Hz), 131.5, 130.7 (d, *J* = 7.9 Hz), 129.6, 129.3, 128.9 (d, *J* = 79.3 Hz), 127.6, 126.8 (d, *J* = 1.7 Hz), 124.7, 124.1 (d, *J* = 17.1 Hz), 123.9 (d, *J* = 3.3 Hz), 122.5 (d, *J* = 76.4 Hz), 120.2, 118.8, 115.6, 115.3 (d, *J* = 21.4 Hz), 114.5, 113.8, 21.6, 9.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.3. HRMS Calcd for $C_{30}H_{23}FNO_2S$ $[M + H]^+$: m/z 480.1428, Found:480.1427

*6-(2-chlorophenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3ac**)*



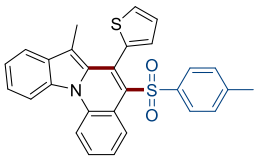
149 mg, 60%; Yellow solid, m.p. 243-245 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.4, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 8.4 Hz, 3H), 7.53-7.35 (m, 7H), 7.22-7.17 (m, 3H), 2.32 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 140.1, 137.3, 136.3, 135.4, 134.1, 132.6, 131.6, 131.5, 130.0, 129.6, 129.3, 129.3, 128.9, 127.7, 127.5, 126.9, 126.6, 124.7, 122.8, 122.1, 120.2, 118.6, 115.5, 114.6, 113.9, 21.6, 9.2. HRMS Calcd for $C_{30}H_{23}ClNO_2S$ $[M + H]^+$: m/z 496.1133, Found:496.1133

*6-(2-bromophenyl)-7-methyl-5-tosylindolo[1,2-a]quinoline (**3ad**)*



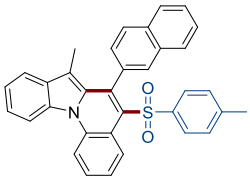
175 mg, 65%; Yellow solid, m.p. 247-249 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.50-7.42 (m, 4H), 7.37-7.32 (m, 2H), 7.21-7.16 (m, 3H), 2.30 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 140.1, 138.8, 137.3, 136.4, 132.6, 132.4, 131.6, 131.5, 130.1, 129.6, 129.3, 128.9, 127.6, 127.5, 127.1, 127.0, 124.7, 124.4, 122.8, 122.1, 120.2, 118.6, 115.6, 114.6, 114.0, 21.6, 9.4. HRMS Calcd for $C_{30}H_{23}BrNO_2S$ $[M + H]^+$: m/z 540.0627, Found: 540.0635

*7-methyl-6-(thiophen-2-yl)-5-tosylindolo[1,2-a]quinoline (**3ae**)*



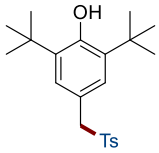
167 mg, 66%; Yellow solid, m.p. 205-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.43 (d, *J* = 8.4, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.0, 1H), 7.61 (d, *J* = 8.0, 2H), 7.54-7.47 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.27-7.22 (m, 1H), 7.14 (d, *J* = 8.4, 2H), 7.09-7.07 (m, 1H), 7.05-7.04 (m, 1H), 2.33 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 140.3, 136.3, 135.3, 132.6, 132.4, 131.6, 130.8, 130.6, 130.4, 129.5, 129.4, 128.0, 127.7, 126.7, 126.6, 124.6, 122.7, 122.1, 120.1, 119.1, 115.3, 114.6, 114.4, 21.5, 9.5. HRMS Calcd for $C_{28}H_{22}NO_2S_2$ $[M + H]^+$: m/z 468.1086, Found:468.1089

*7-methyl-6-(naphthalen-2-yl)-5-tosylindolo[1,2-a]quinoline (**3af**)*



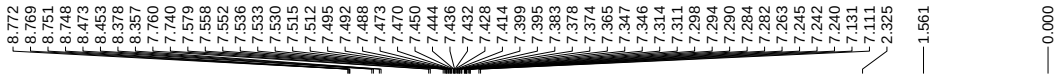
174 mg, 68%; Yellow solid, m.p. 235-237 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 7.8, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.82-7.75 (m, 2H), 7.67 (s, 1H), 7.64-7.53 (m, 4H), 7.48-7.44 (m, 3H), 7.42-7.34 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 140.4, 139.6, 136.1, 133.0, 133.0, 132.7, 132.4, 131.6, 130.5, 129.3, 129.3, 129.2, 129.1, 128.4, 128.2, 127.9, 127.9, 127.2, 126.8, 126.6, 126.3, 124.6, 122.8, 122.0, 120.0, 119.4, 115.4, 114.6, 114.2, 21.5, 10.4. HRMS Calcd for $C_{34}H_{26}NO_2S$ [M + H]$^+$: m/z 512.1679, Found: 512.1679

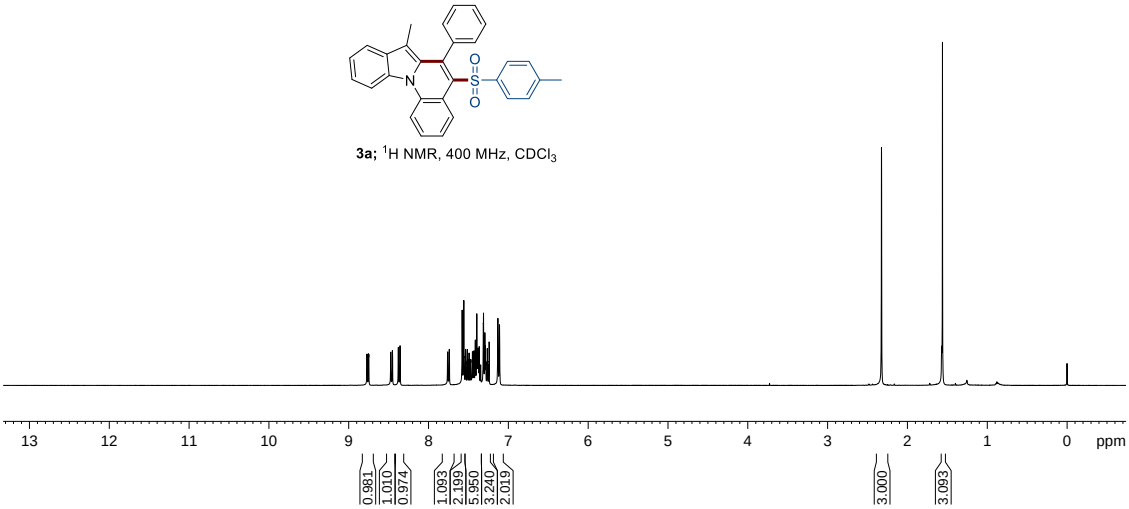
*2,6-di-tert-butyl-4-(tosylmethyl)phenol (**9**)*

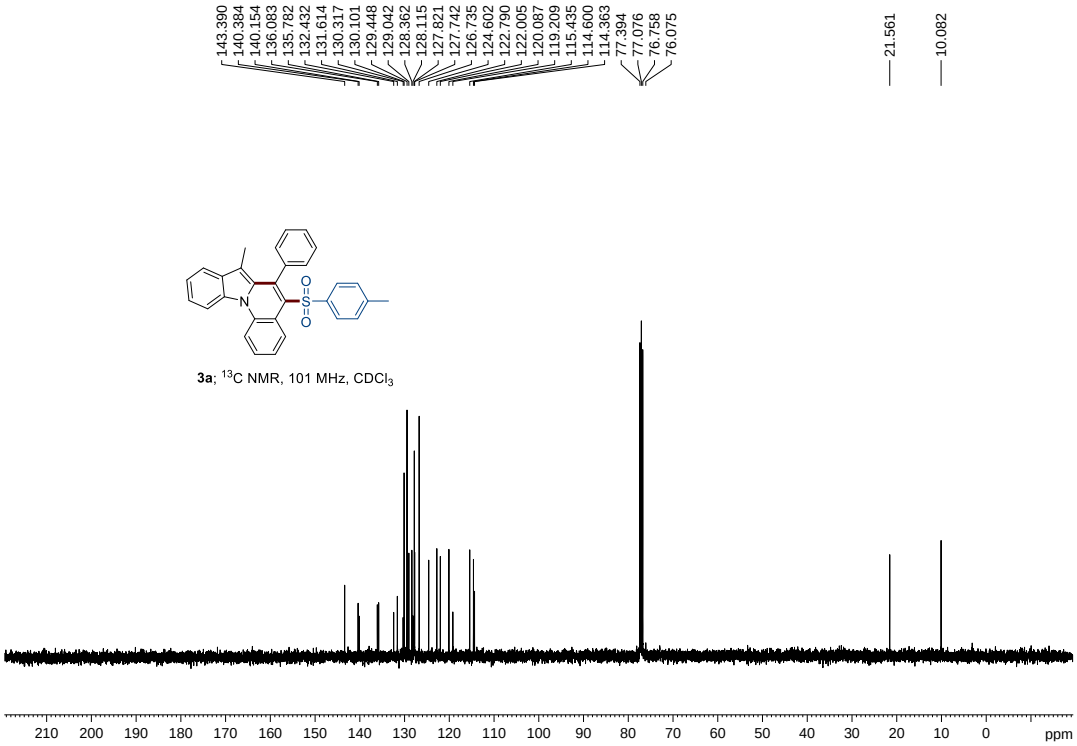


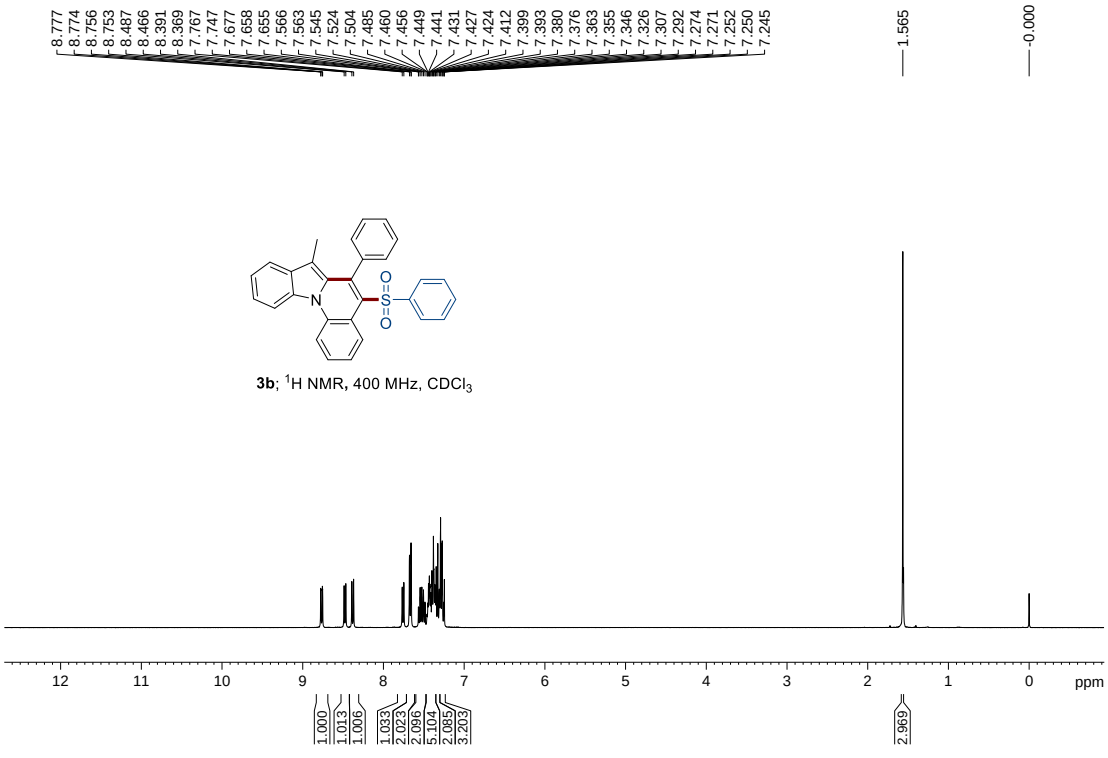
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 2H), 5.26 (s, 1H), 4.21 (s, 2H), 2.43 (s, 3H), 1.34 (s, 19H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 144.3, 136.0, 134.9, 129.3, 128.9, 127.7, 118.9, 63.3, 34.1, 30.0, 21.5. HRMS Calcd for $C_{22}H_{31}O_3S$ [M + H]$^+$: m/z 375.1988, Found: 375.1984

5. NMR copies of products






143.390
140.384
140.154
136.083
135.782
132.432
131.614
130.317
130.101
129.448
129.042
128.362
128.115
127.821
127.742
126.735
124.602
122.790
122.005
120.087
119.209
115.435
114.600
114.363
77.394
77.076
76.758
76.075
21.561
10.082
O
S
O
N
3a; 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.777
8.774
8.756
8.753
8.487
8.466
8.391
8.369
7.767
7.747
7.677
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7.566
7.563
7.545
7.524
7.504
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7.456
7.449
7.441
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7.427
7.424
7.412
7.399
7.393
7.380
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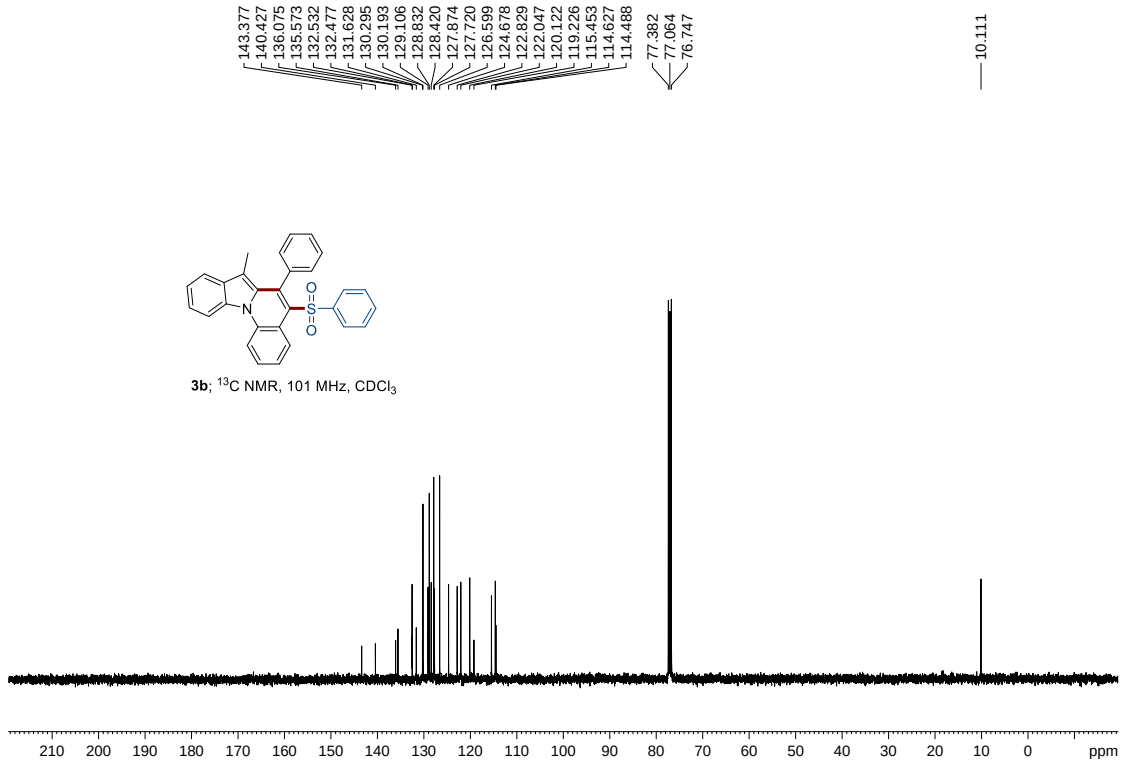
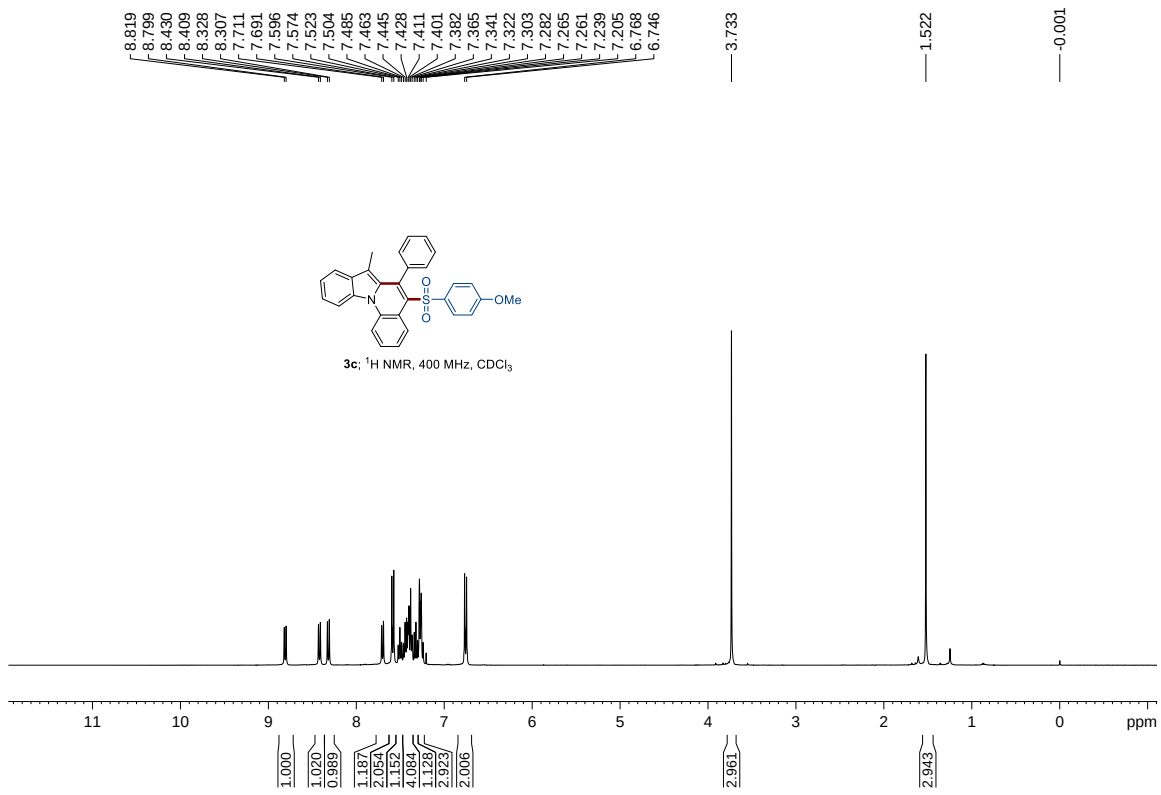
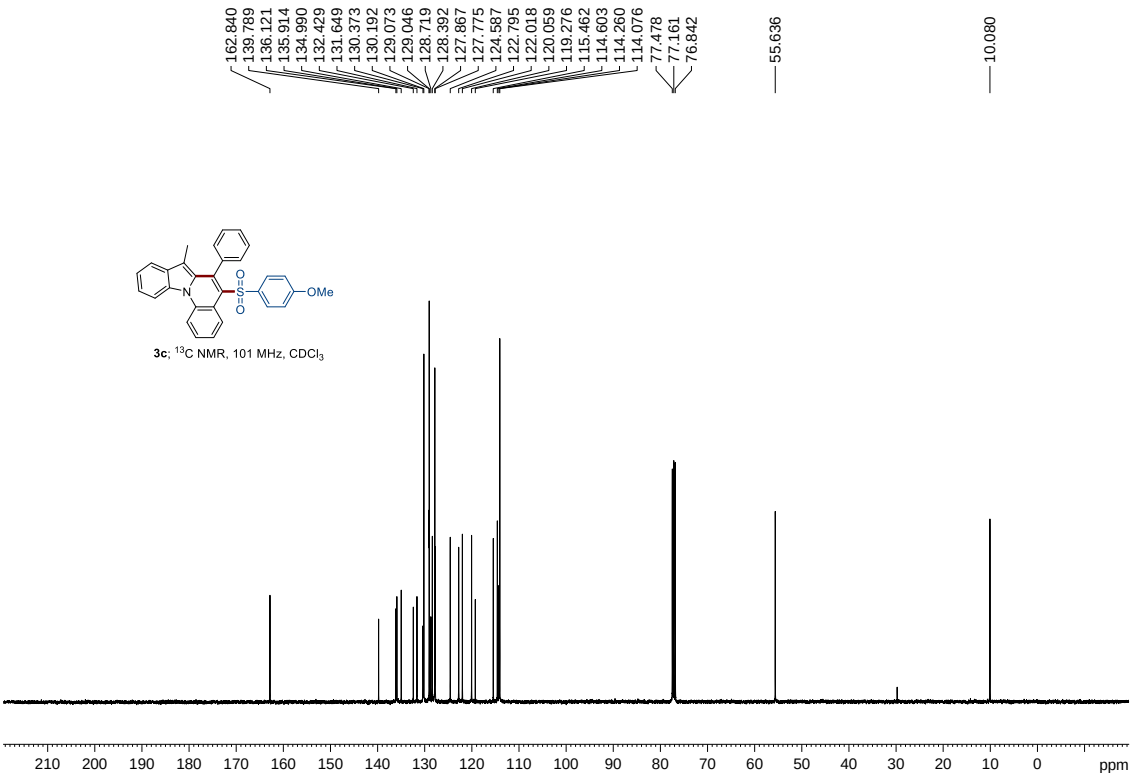
7.363
7.355
7.346
7.326
7.307
7.292
7.274
7.271
7.252
7.250
7.245
1.565
-0.000
O
S
O
N
3b; 1H NMR, 400 MHz, CDCl3
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.013
1.006
1.033
2.023
2.096
5.104
2.085
3.203
2.969



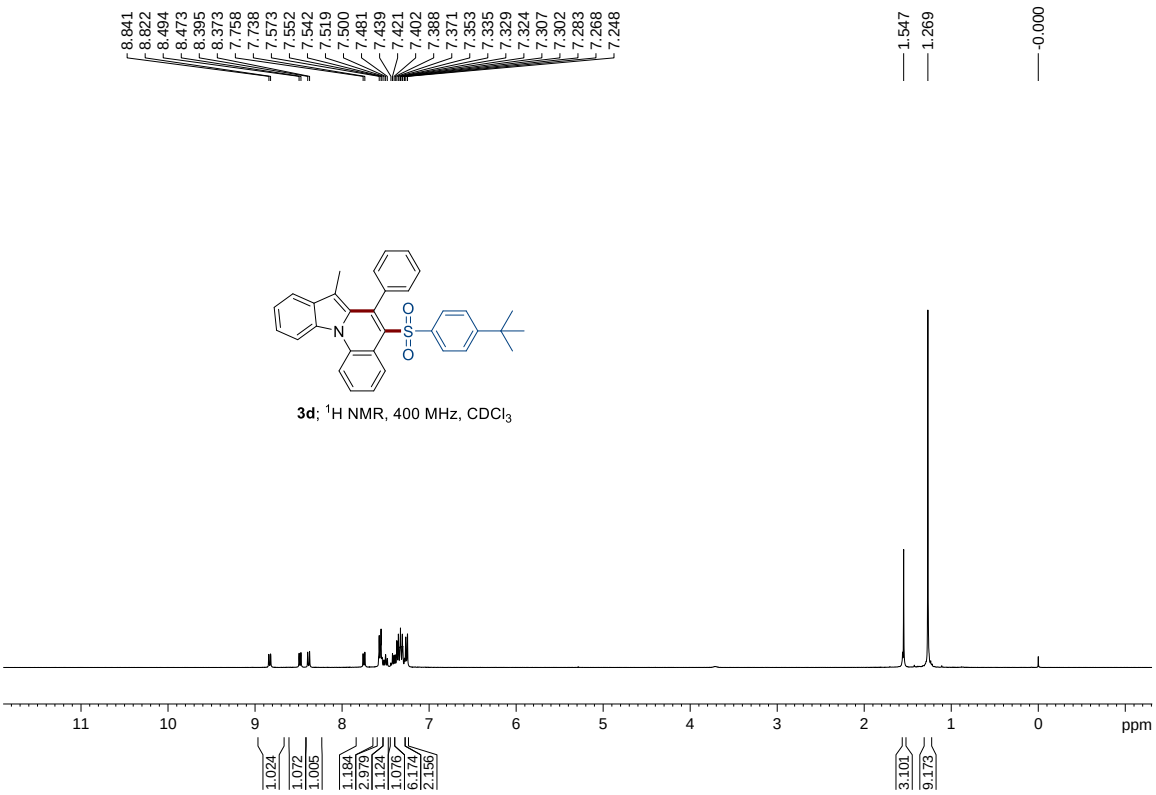
3b; ^{13}C NMR, 101 MHz, $CDCl_3$



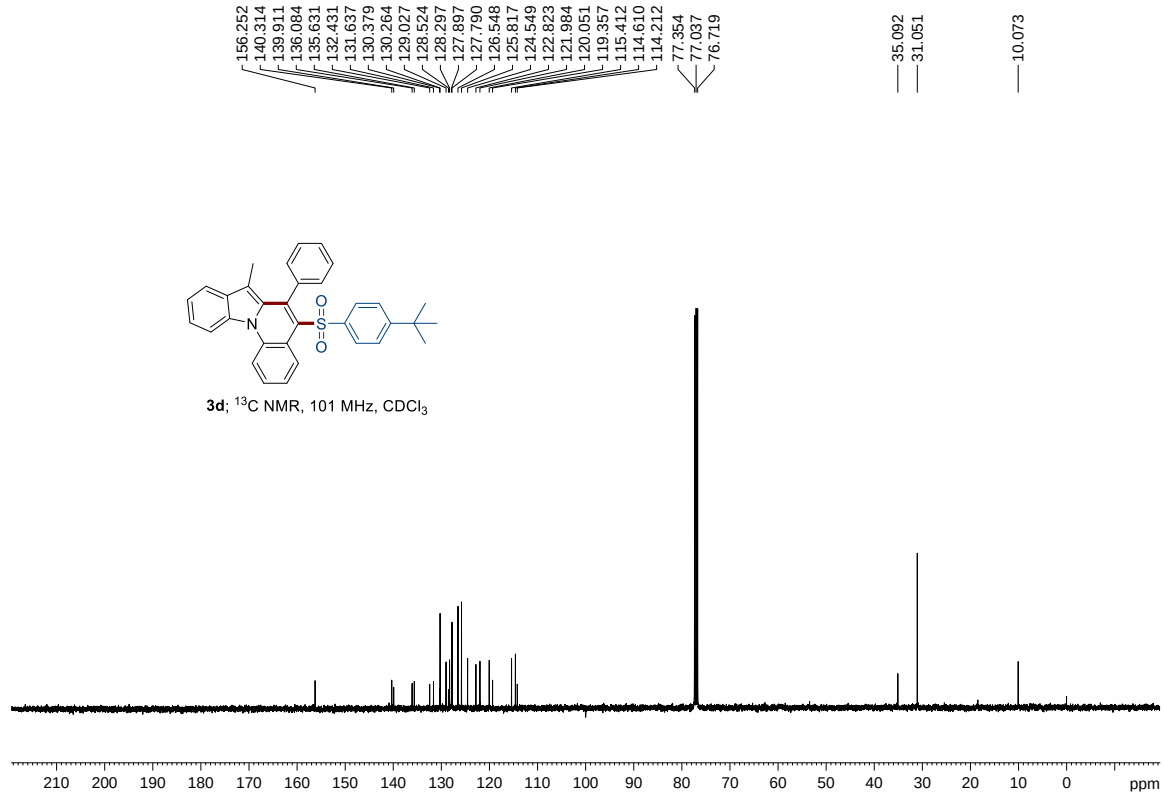
3c; ^{1}H NMR, 400 MHz, $CDCl_3$



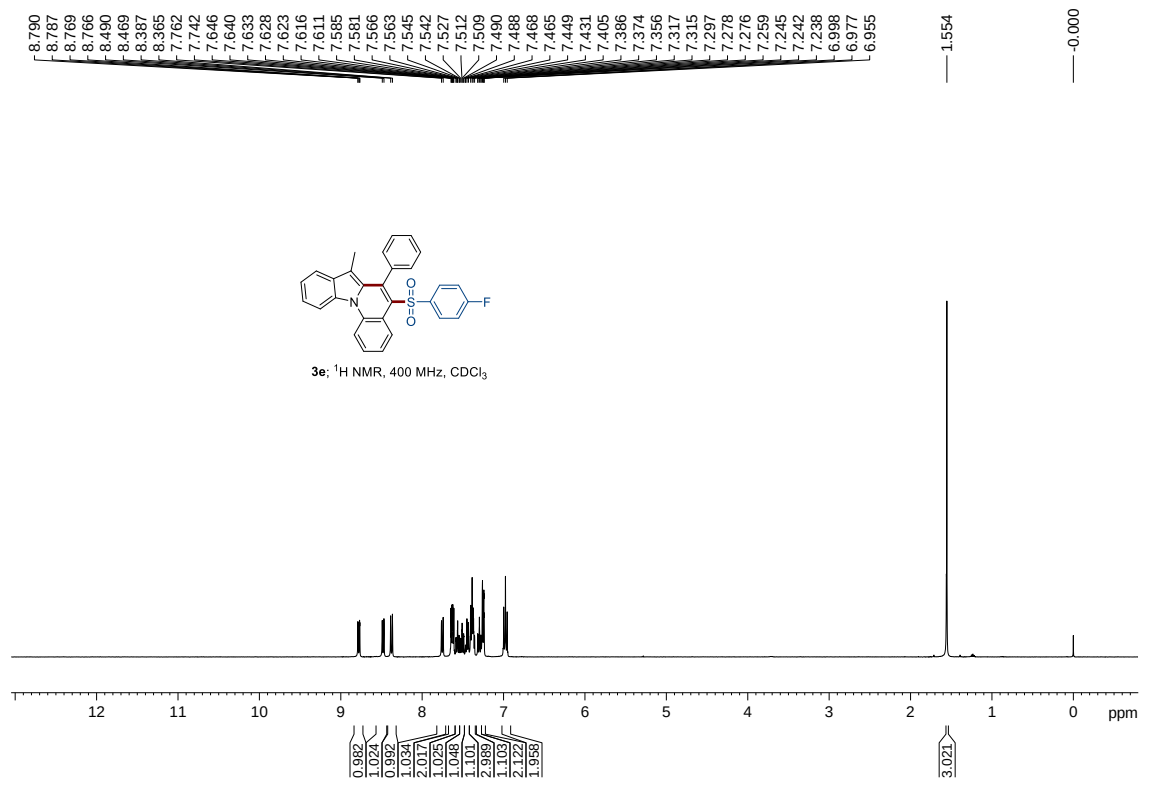
3c; ^{13}C NMR, 101 MHz, $CDCl_3$



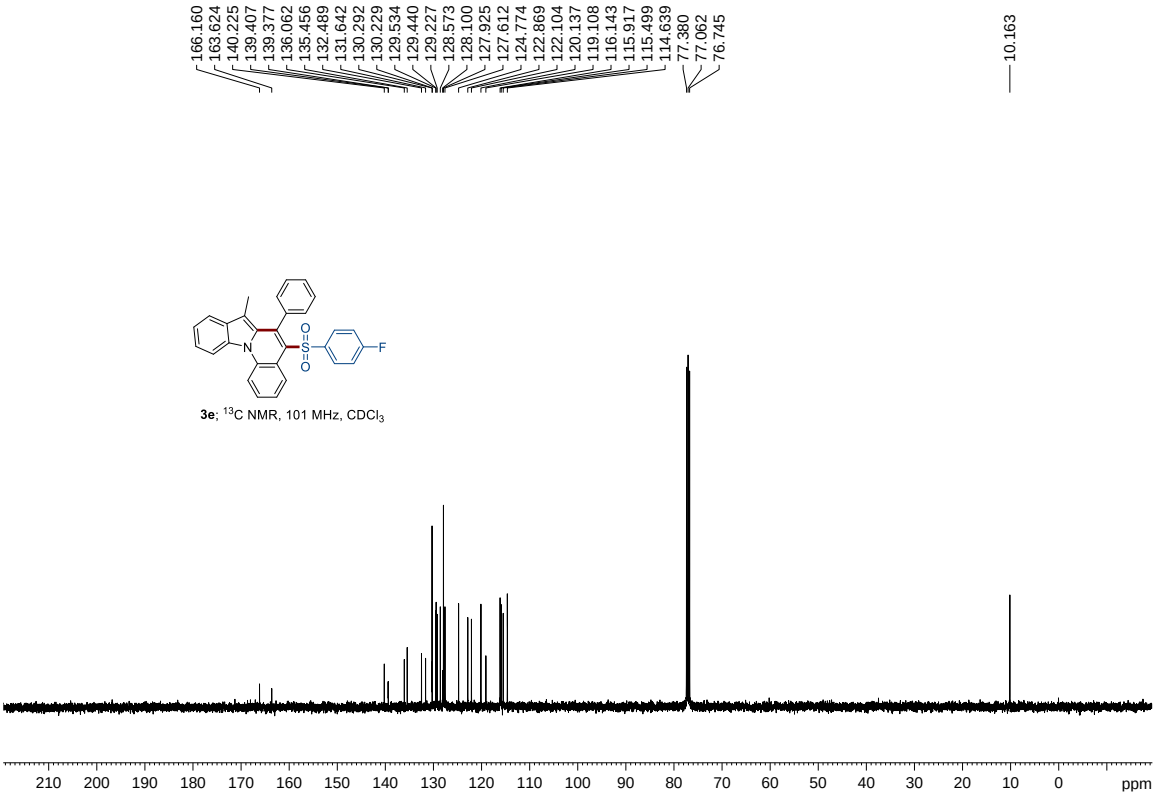
3d; ^{1}H NMR, 400 MHz, $CDCl_3$

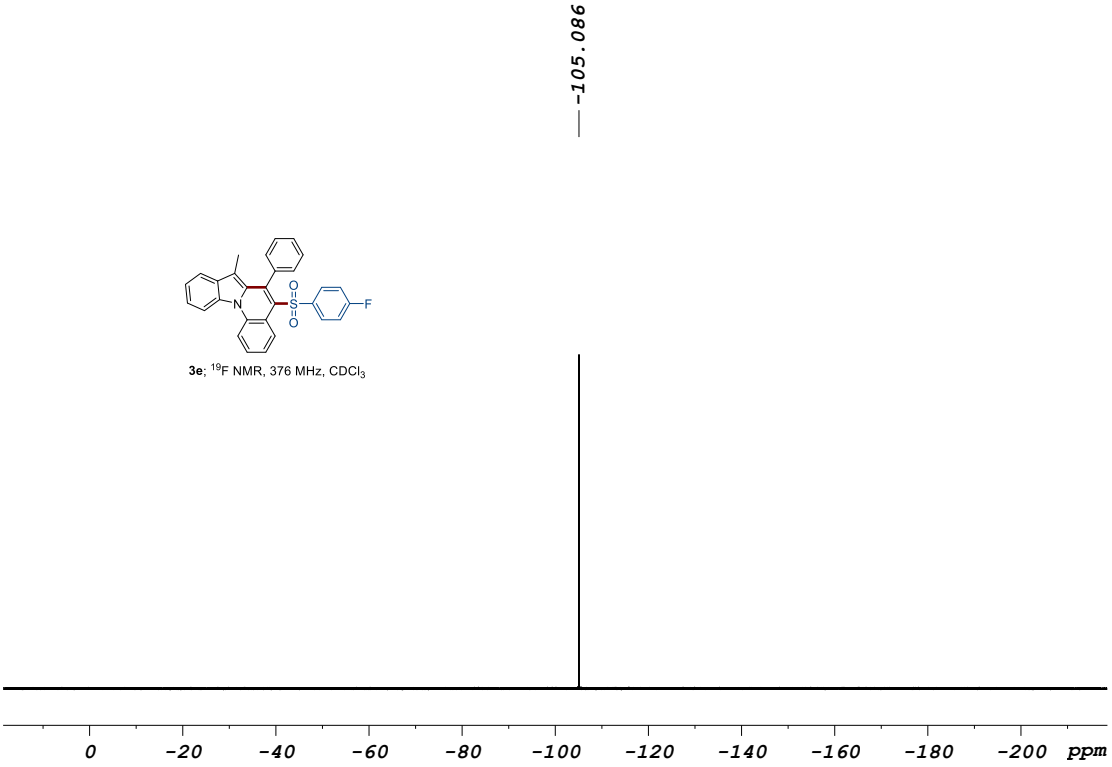


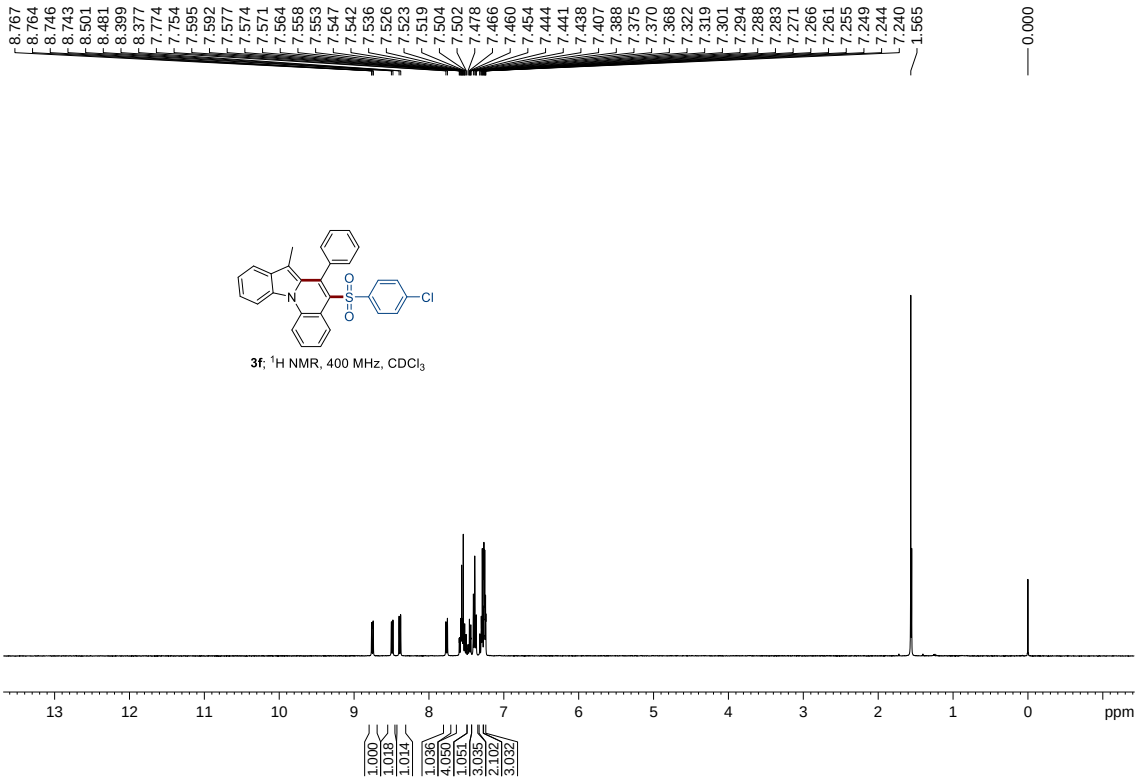
3d; ^{13}C NMR, 101 MHz, $CDCl_3$



3e; ^{1}H NMR, 400 MHz, $CDCl_3$


166.160
163.624
140.225
139.407
139.377
136.062
135.456
132.489
131.642
130.292
130.229
129.534
129.440
129.227
128.573
128.100
127.925
127.612
124.774
122.869
122.104
120.137
119.108
116.143
115.917
115.499
114.639
77.380
77.062
76.745
10.163
O
S
O
F
3e; 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-105.086
O
S
O
F
3e; 19F NMR, 376 MHz, CDCl3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm


8.767
8.764
8.746
8.743
8.501
8.481
8.399
8.377
7.774
7.754
7.595
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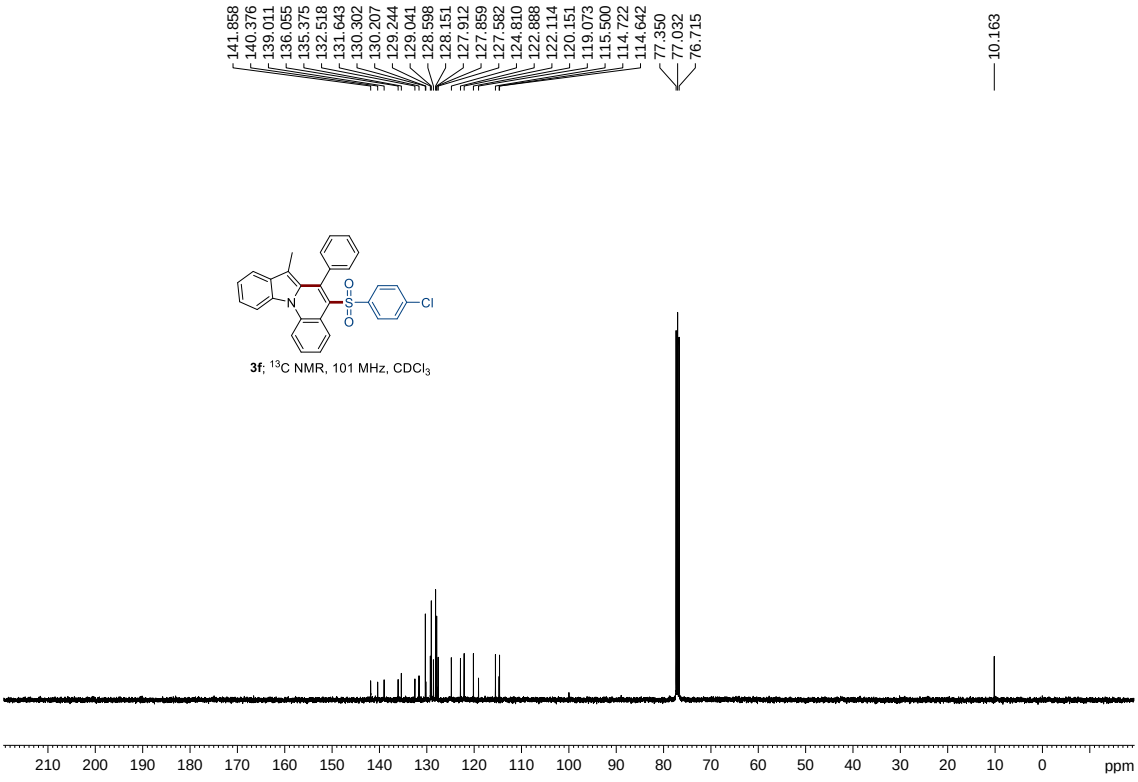
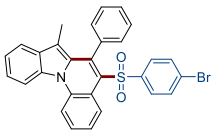
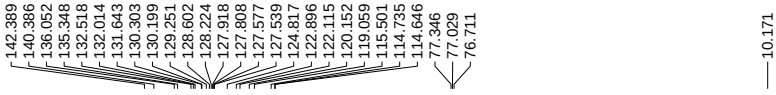
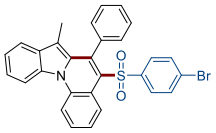
7.577
7.574
7.571
7.564
7.558
7.553
7.547
7.542
7.536
7.526
7.523
7.519
7.504
7.502
7.478
7.466
7.460
7.454
7.444
7.441
7.438
7.407
7.388
7.375
7.370
7.368
7.322
7.319
7.301
7.294
7.288
7.283
7.271
7.266
7.261
7.255
7.249
7.244
7.240
1.565
0.000
Cl
3f; 1H NMR, 400 MHz, CDCl3
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.018
1.014
1.036
4.050
1.051
3.035
2.102
3.032


141.858
140.376
139.011
136.055
135.375
132.518
131.643
130.302
130.207
129.244
129.041
128.598
128.151
127.912
127.859
127.582
124.810
122.888
122.114
120.151
119.073
115.500
114.722
114.642
77.350
77.032
76.715
10.163
Cl
3f; 13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

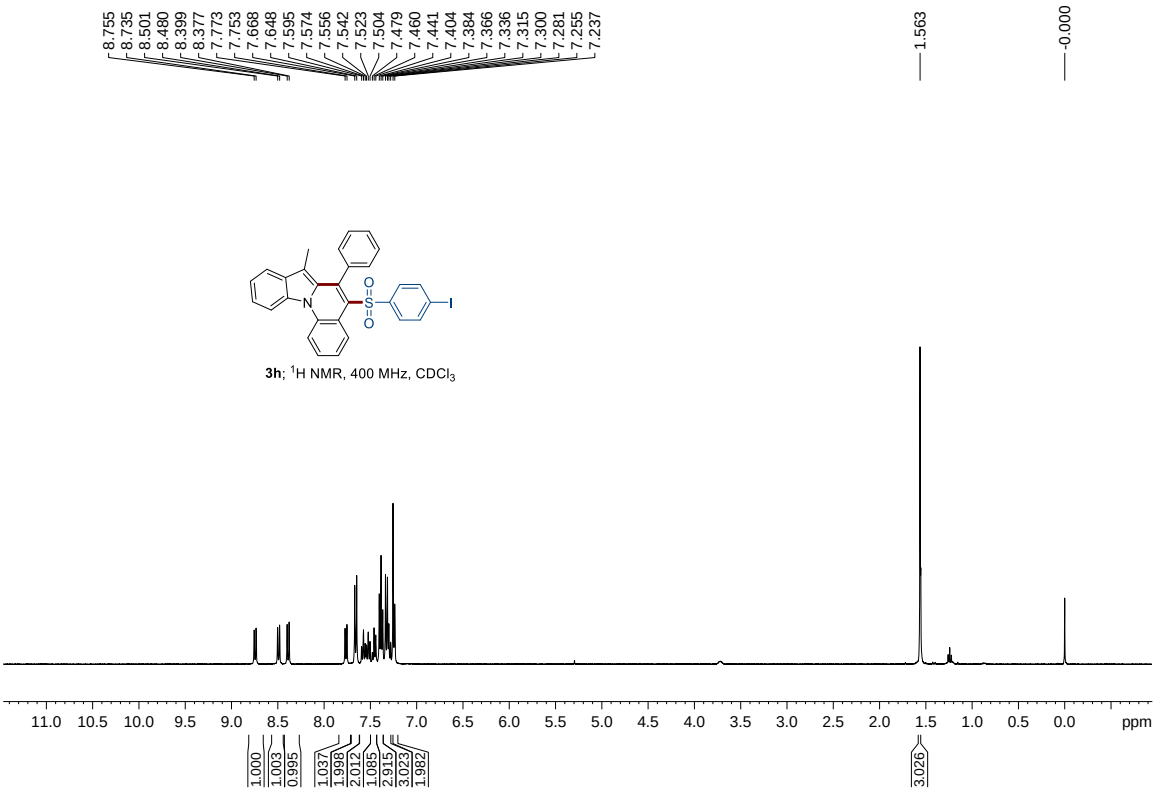


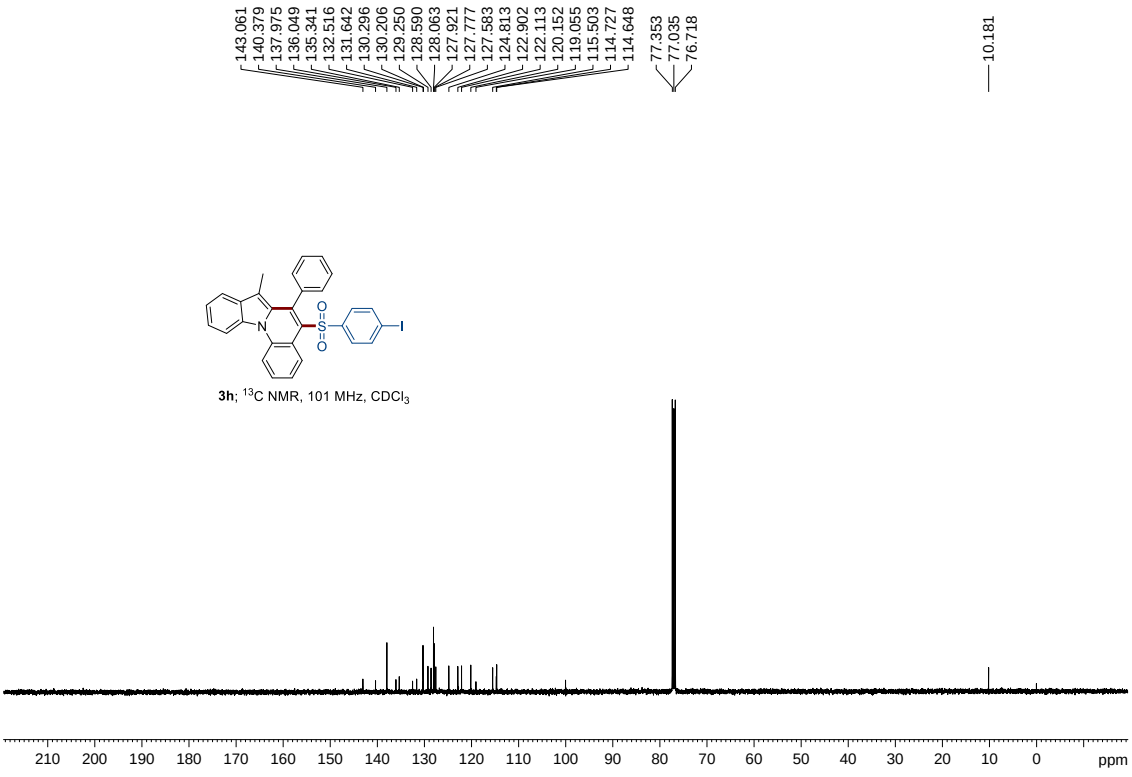
3g; ^{1}H NMR, 400 MHz, $CDCl_3$

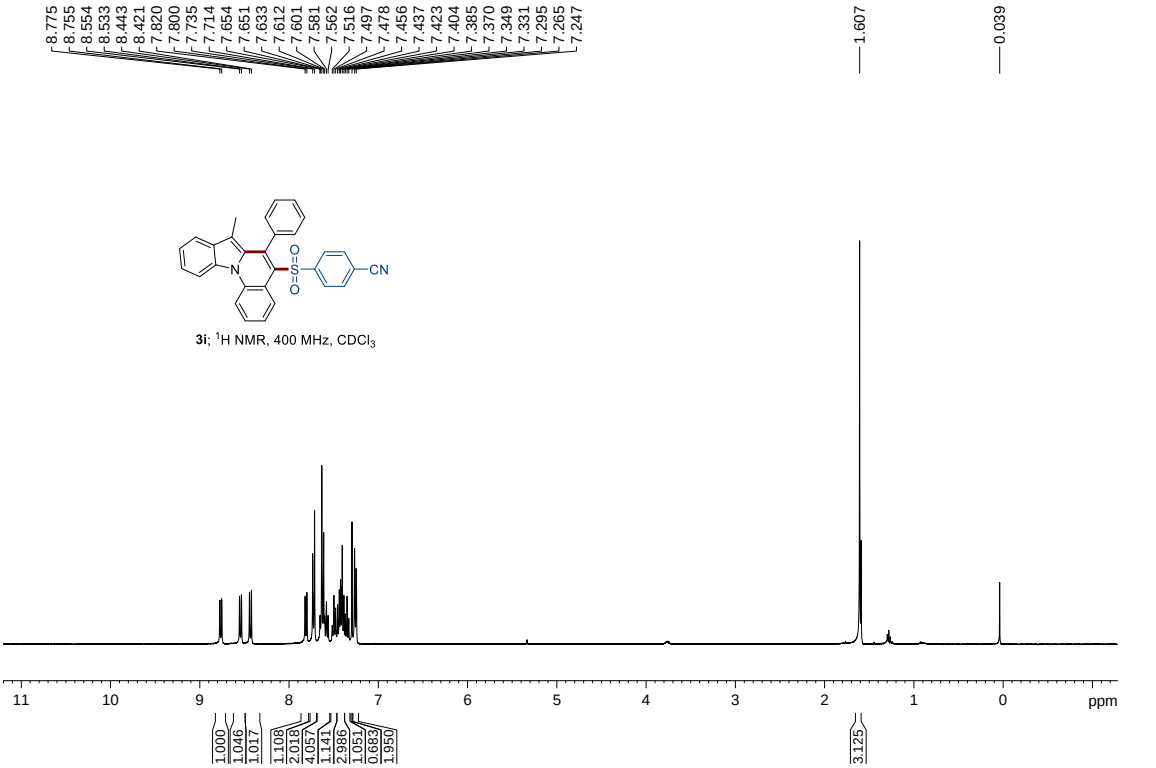




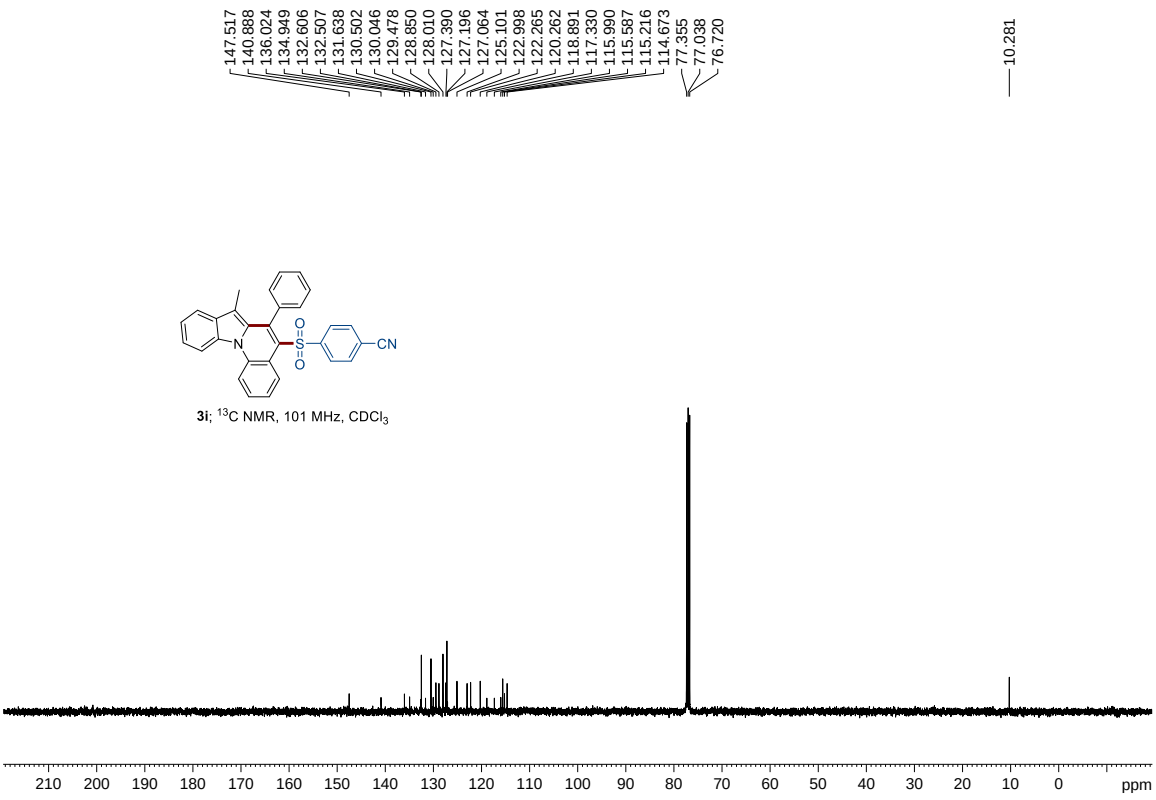
3g; ^{13}C NMR, 101 MHz, $CDCl_3$


8.755
8.735
8.501
8.480
8.399
8.377
7.773
7.753
7.668
7.648
7.595
7.574
7.556
7.542
7.523
7.504
7.479
7.460
7.441
7.404
7.384
7.366
7.336
7.315
7.300
7.281
7.255
7.237
1.563
-0.000
I
3h; 1H NMR, 400 MHz, CDCl3
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.000
1.003
0.995
1.037
1.998
2.012
1.085
2.915
3.023
1.982
3.026

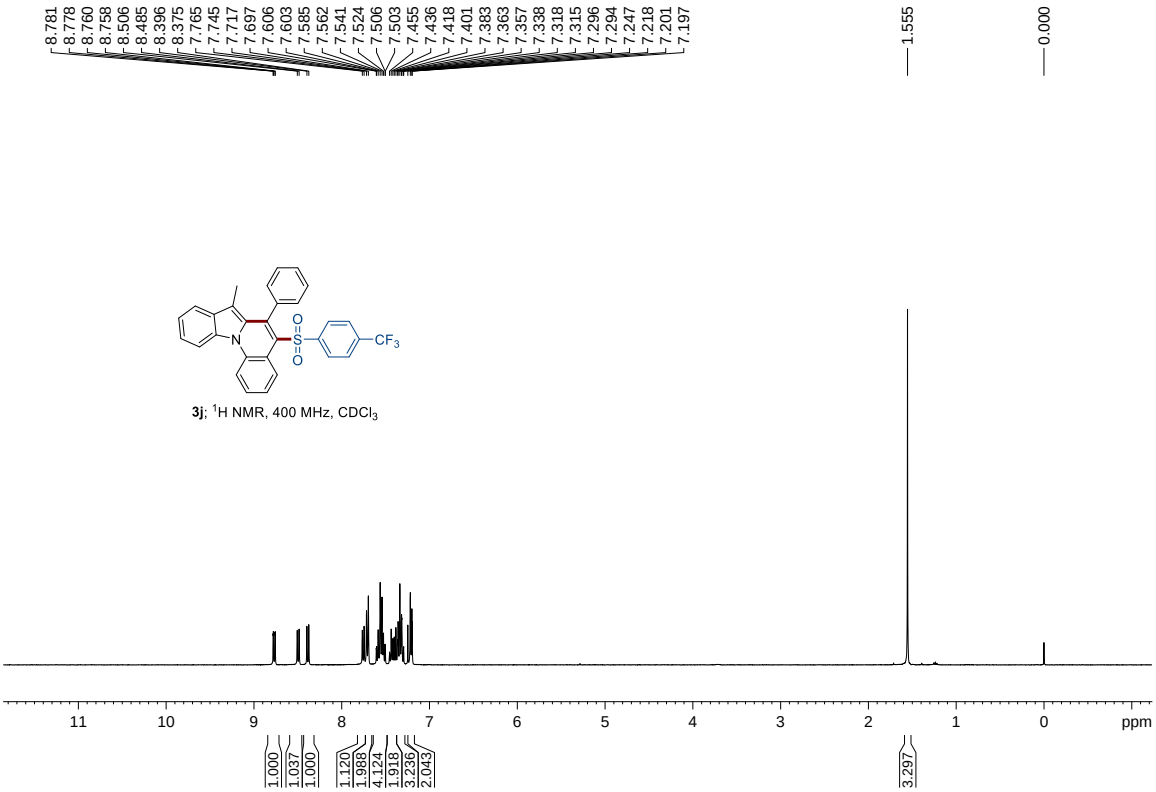

143.061
140.379
137.975
136.049
135.341
132.516
131.642
130.296
130.206
129.250
128.590
128.063
127.921
127.777
127.583
124.813
122.902
122.113
120.152
119.055
115.503
114.727
114.648
77.353
77.035
76.718
10.181
I
3h; 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



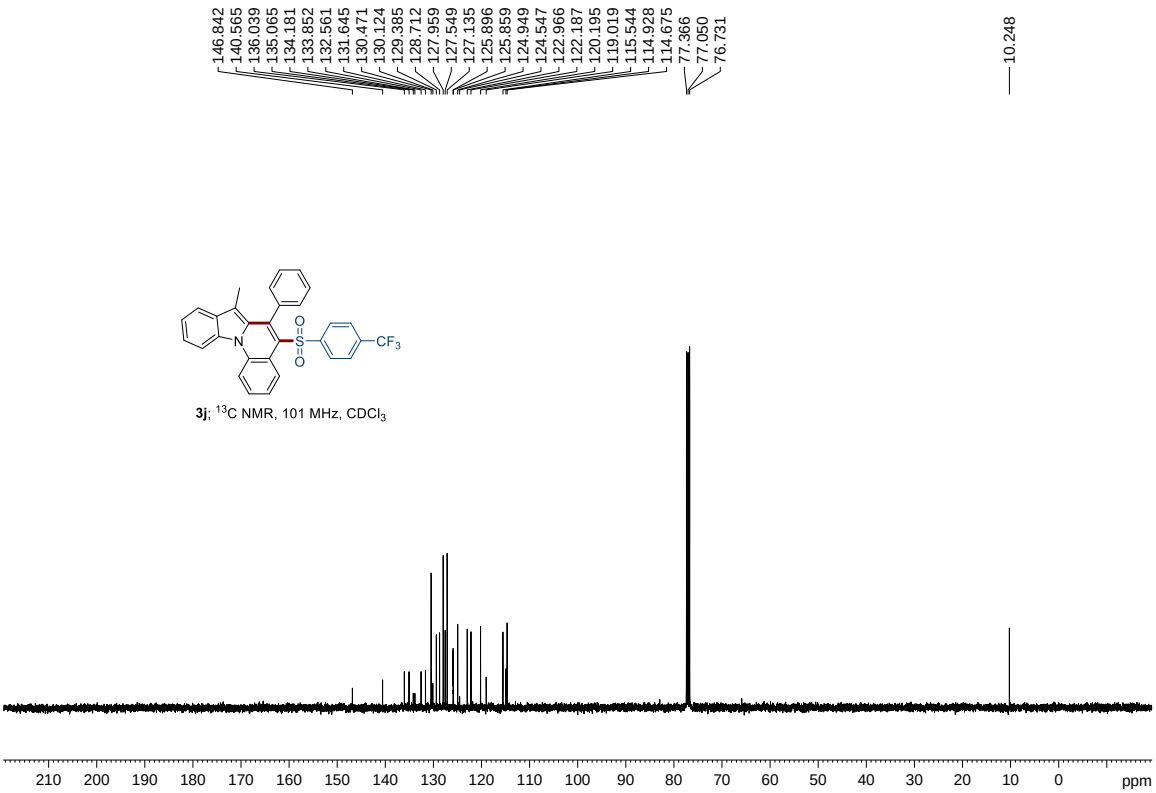
3i; ^{1}H NMR, 400 MHz, $CDCl_3$



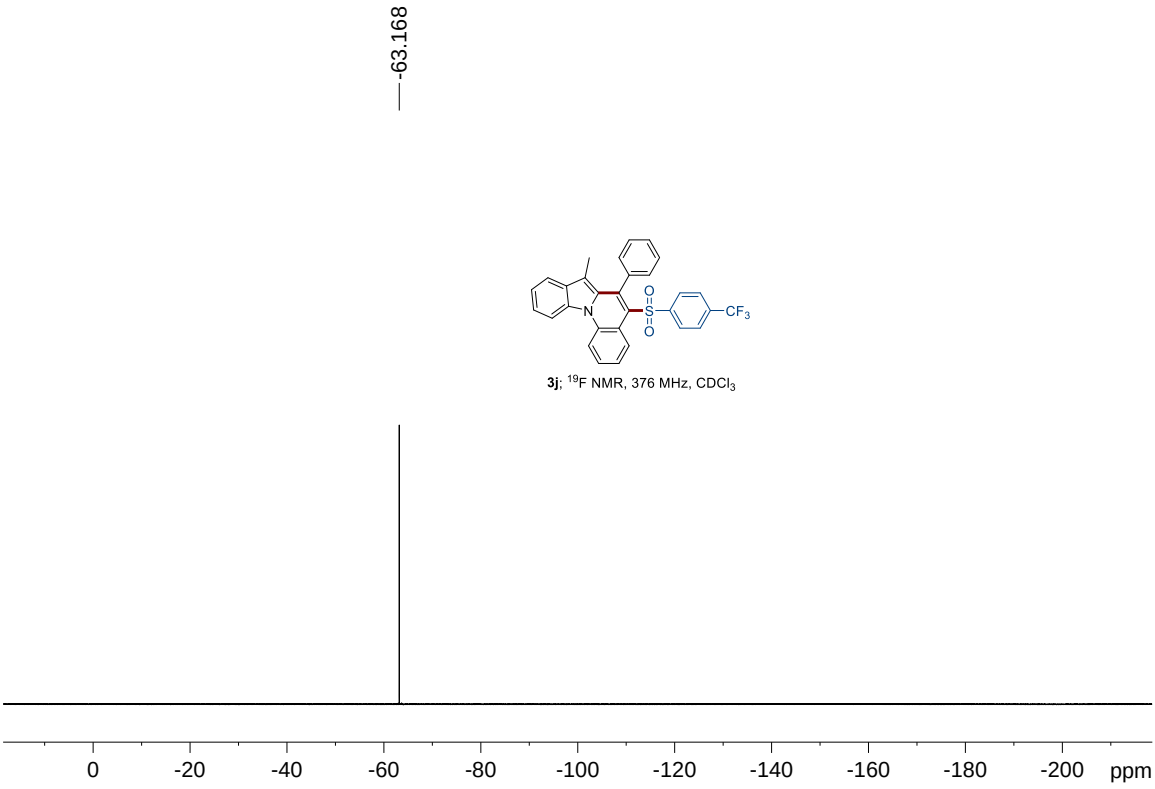
3i; ^{13}C NMR, 101 MHz, $CDCl_3$



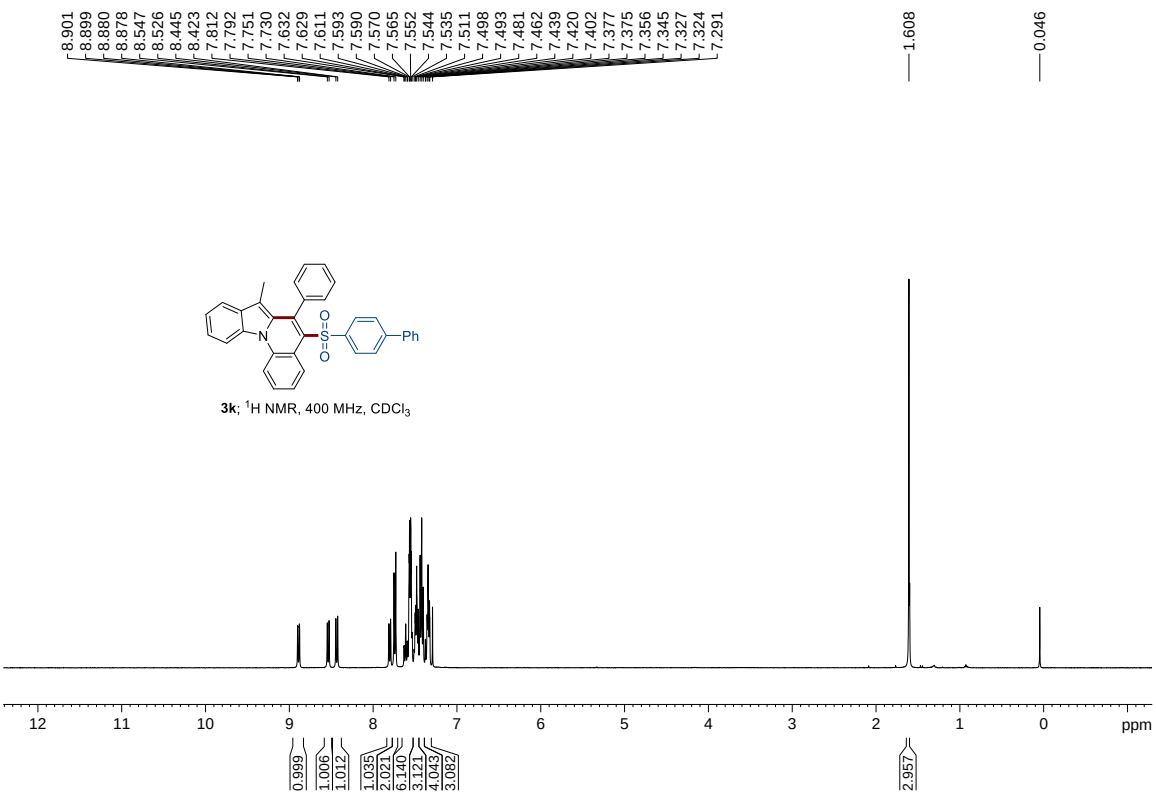
3j; ^{1}H NMR, 400 MHz, $CDCl_3$



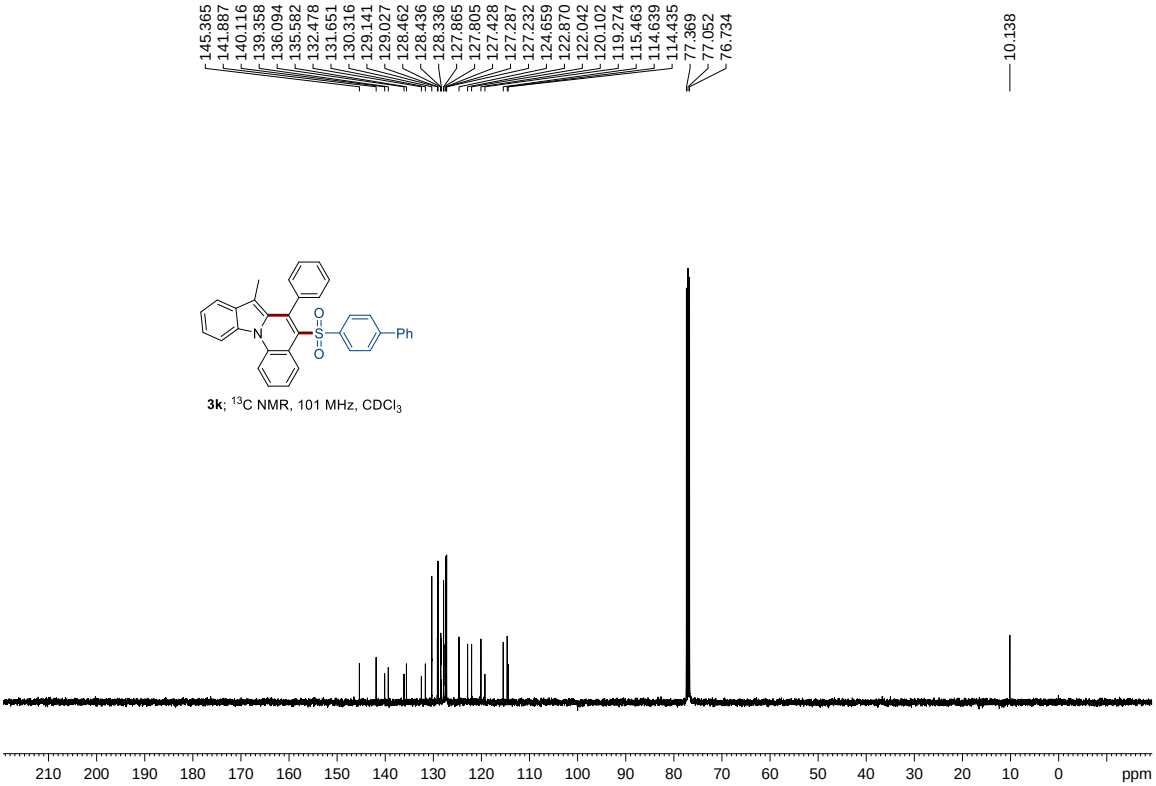
3j; ^{13}C NMR, 101 MHz, $CDCl_3$



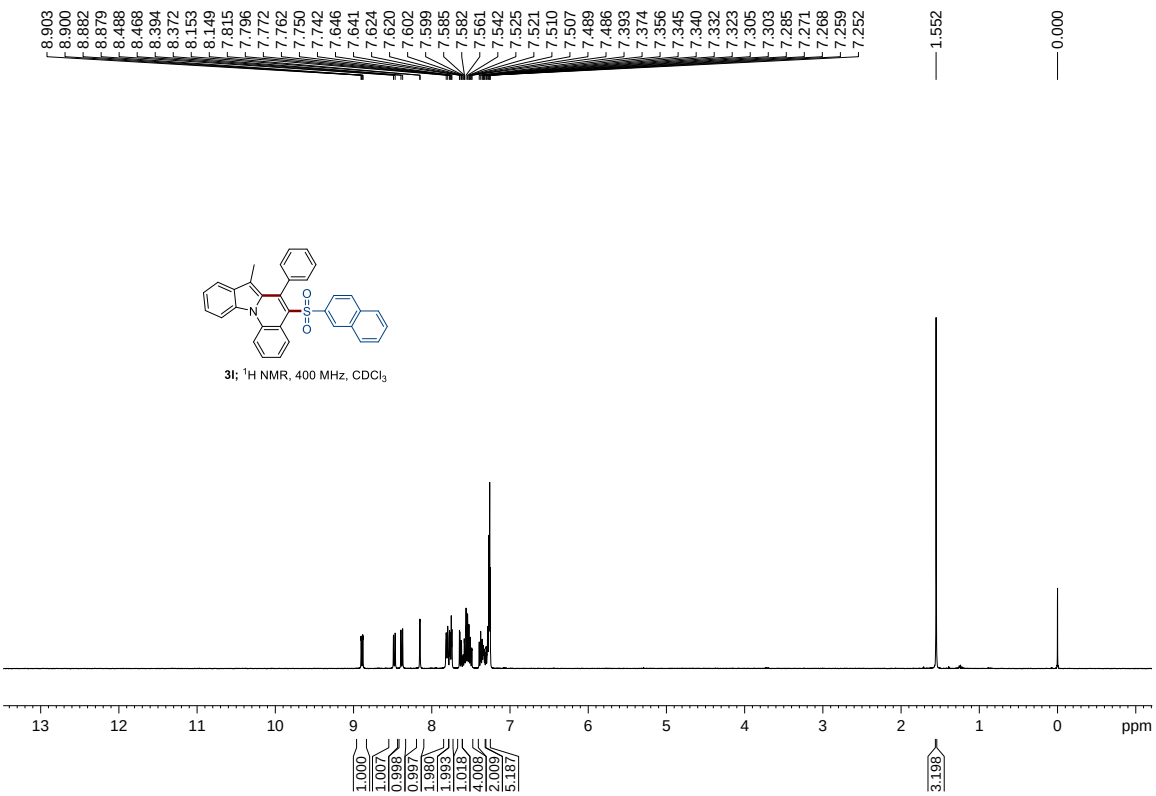
3j; ^{19}F NMR, 376 MHz, $CDCl_3$



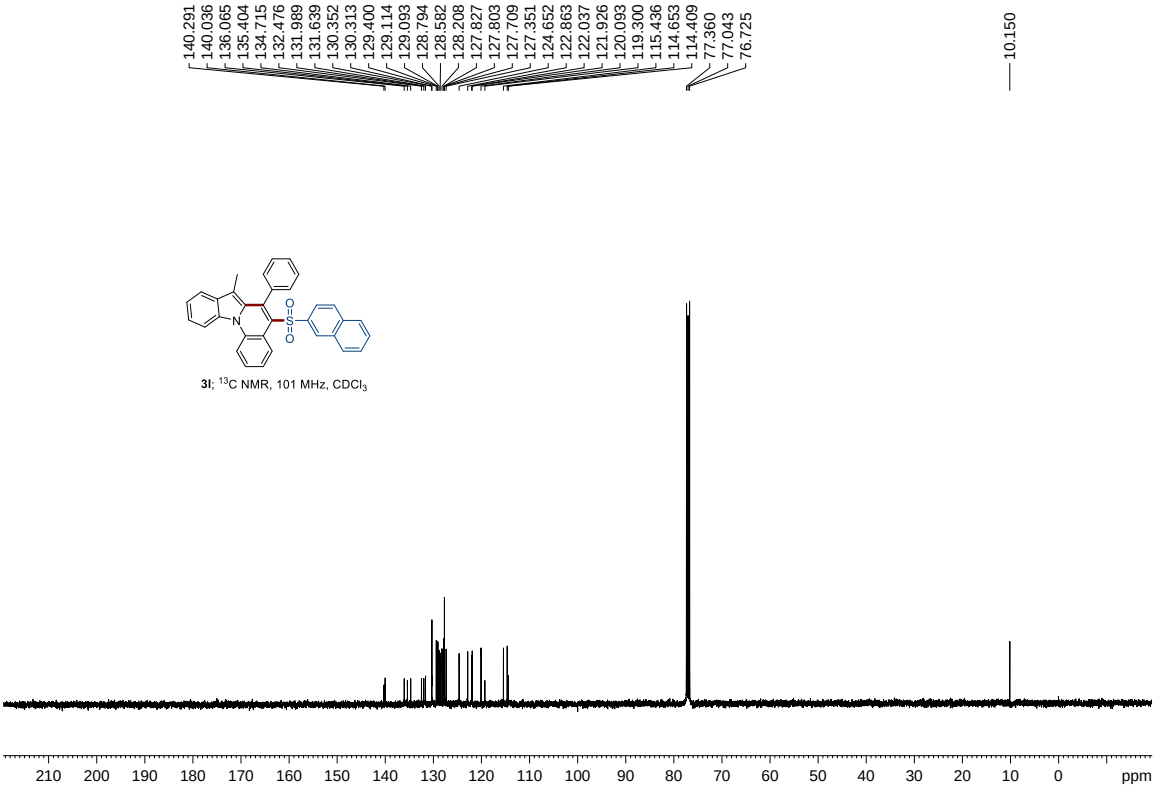
3k; ^{1}H NMR, 400 MHz, $CDCl_3$

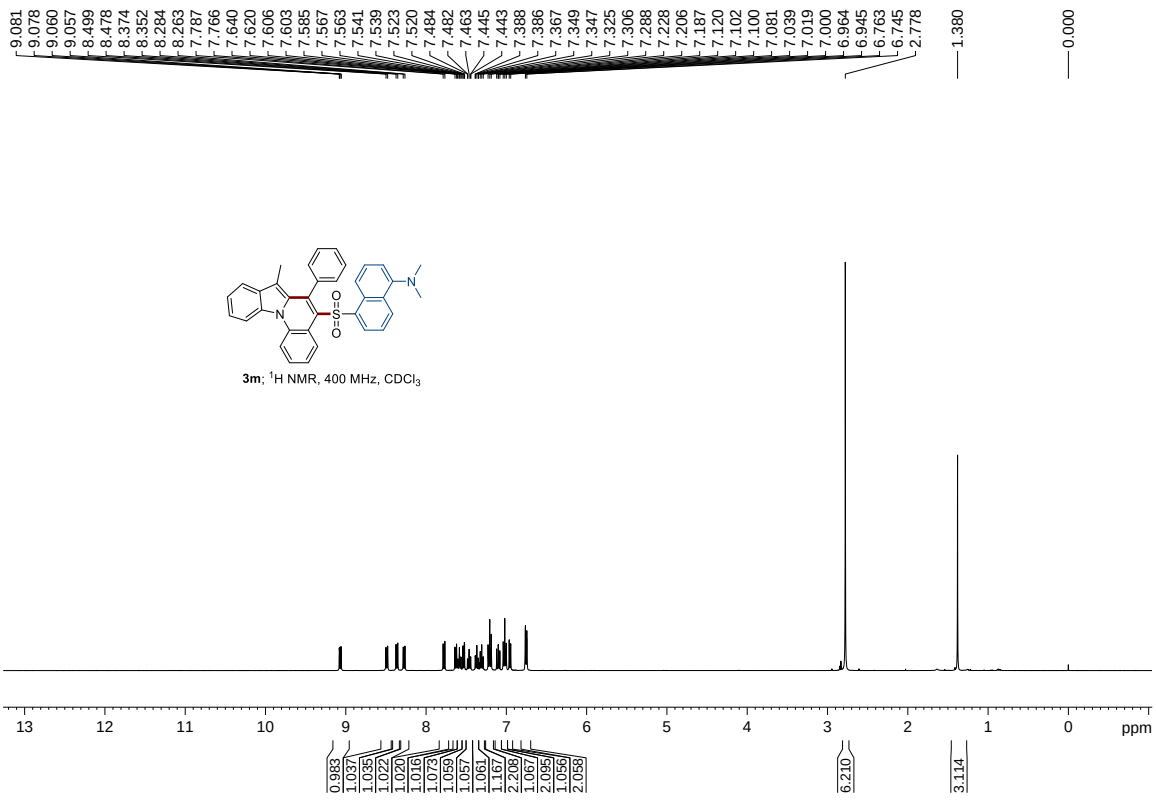


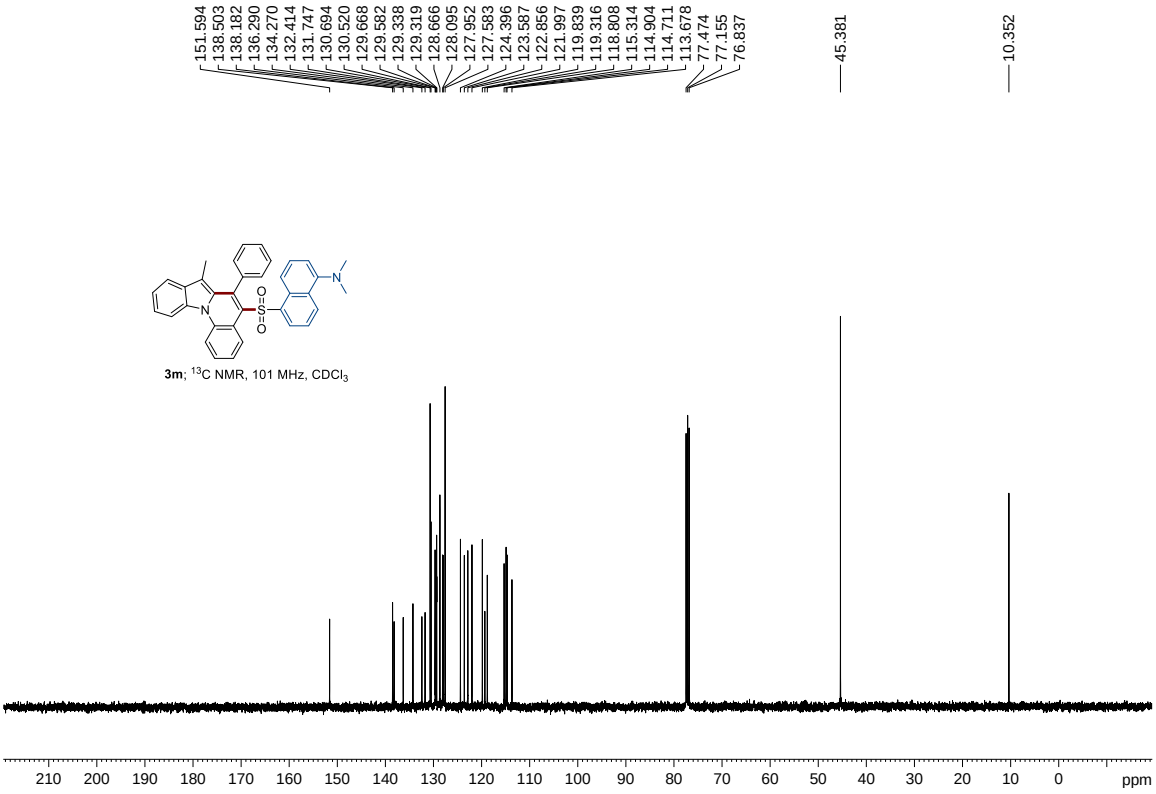
3k; ^{13}C NMR, 101 MHz, $CDCl_3$

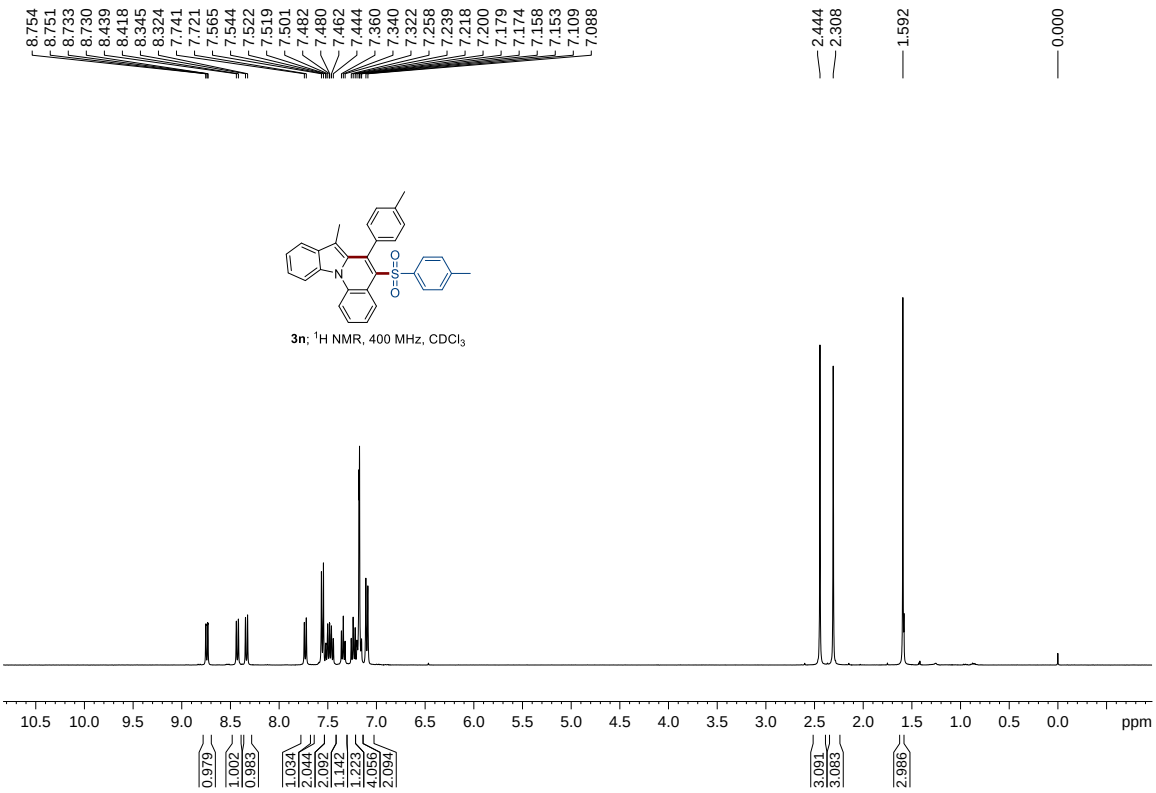


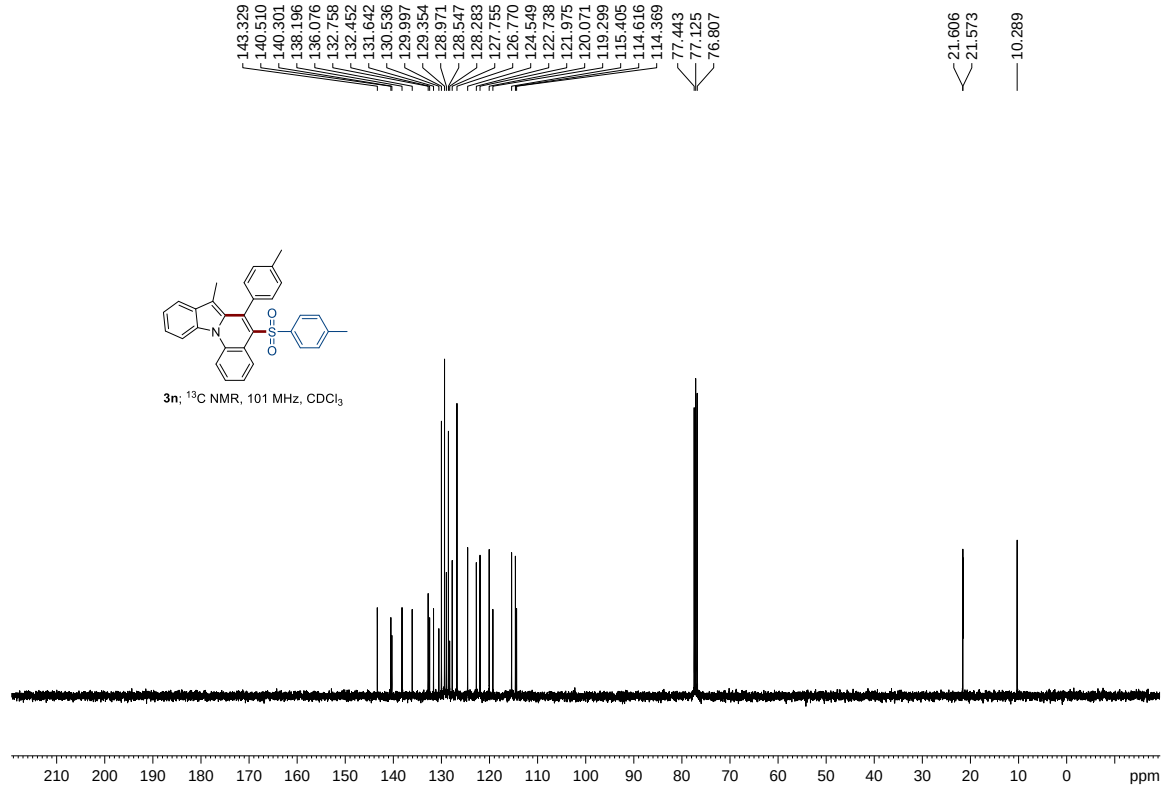
3l; ^{1}H NMR, 400 MHz, $CDCl_3$

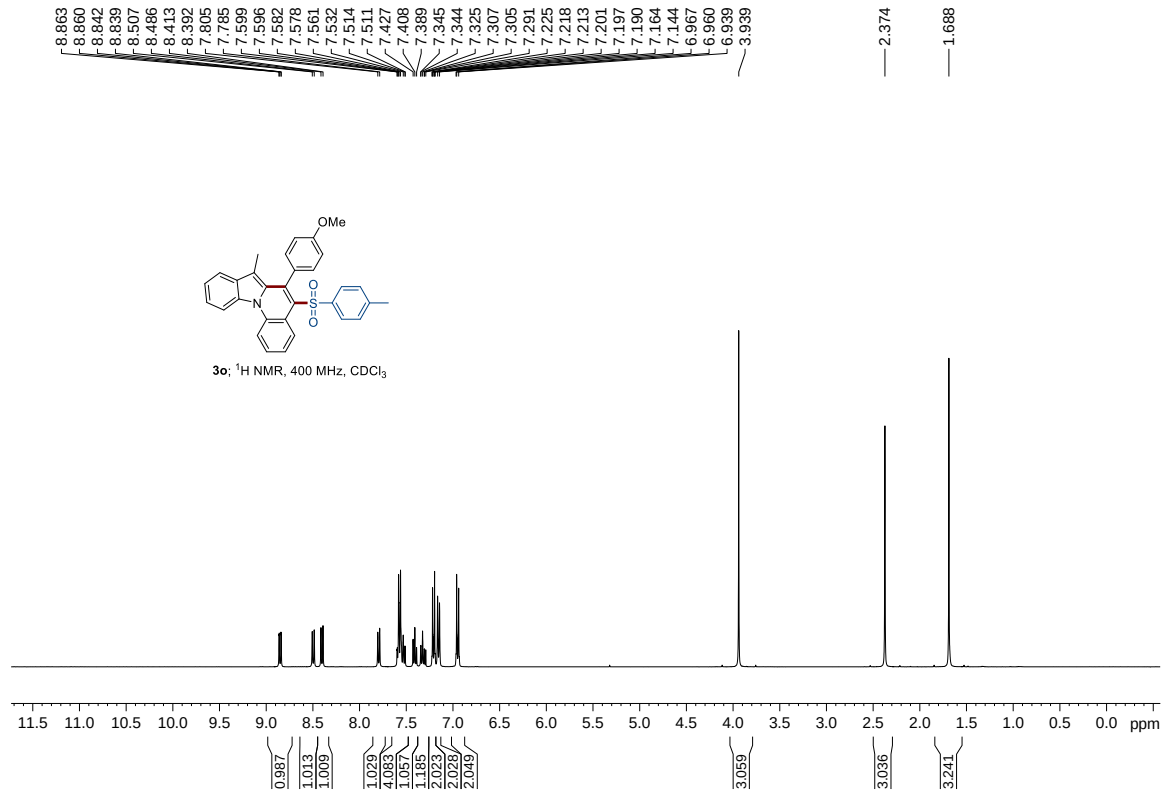

140.291
140.036
136.065
135.404
134.715
132.476
131.989
131.639
130.352
130.313
129.400
129.114
129.093
128.794
128.582
128.208
127.827
127.803
127.709
127.351
124.652
122.863
122.037
121.926
120.093
119.300
115.436
114.653
114.409
77.360
77.043
76.725
10.150
3l; 13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

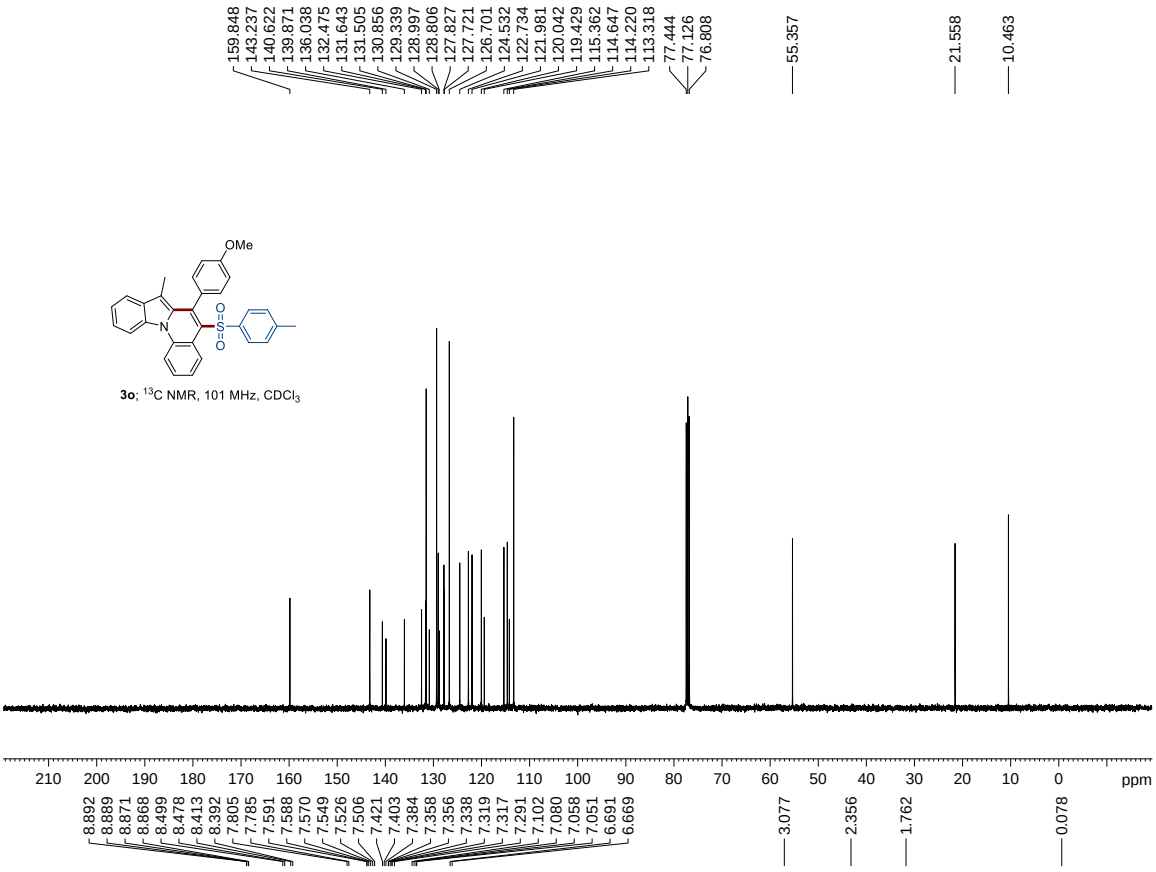

9.081
9.078
9.060
9.057
8.499
8.478
8.374
8.352
8.284
8.263
7.787
7.766
7.640
7.620
7.606
7.603
7.585
7.567
7.563
7.541
7.539
7.523
7.520
7.484
7.482
7.463
7.445
7.443
7.388
7.386
7.367
7.349
7.347
7.325
7.306
7.288
7.228
7.206
7.187
7.120
7.102
7.100
7.081
7.039
7.019
7.000
6.964
6.945
6.763
6.745
2.778
1.380
0.000
3m; 1H NMR, 400 MHz, CDCl3
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.983
1.037
1.035
1.022
1.020
1.016
1.073
1.059
1.057
1.061
1.167
2.208
1.067
2.095
1.056
2.058
6.210
3.114

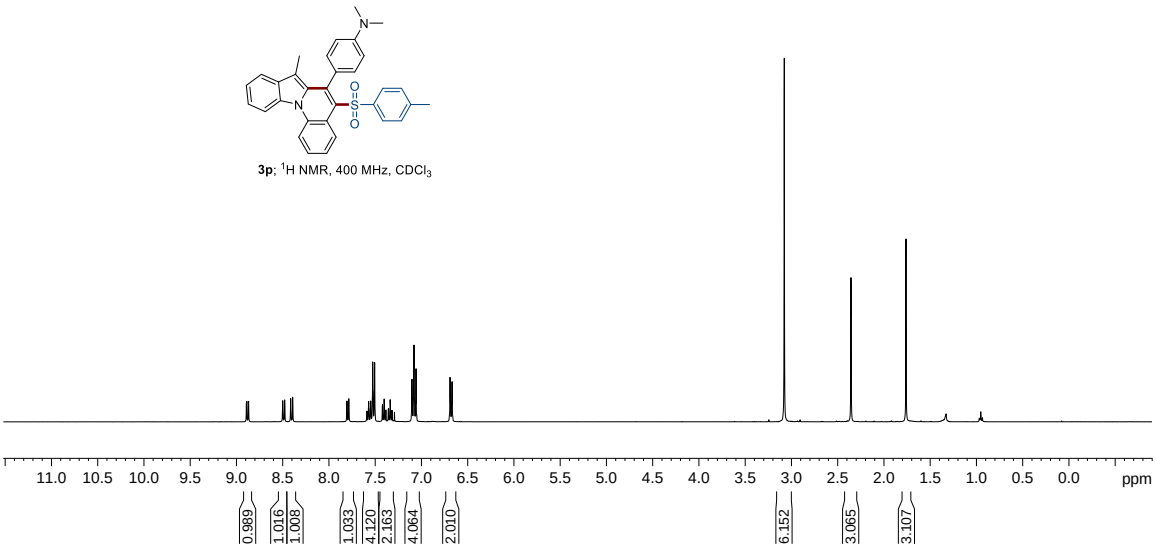

151.594
138.503
138.182
136.290
134.270
132.414
131.747
130.694
130.520
129.668
129.582
129.338
129.319
128.666
128.095
127.952
127.583
124.396
123.587
122.856
121.997
119.839
119.316
118.808
115.314
114.904
114.711
113.678
77.474
77.155
76.837
45.381
10.352
3m; 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

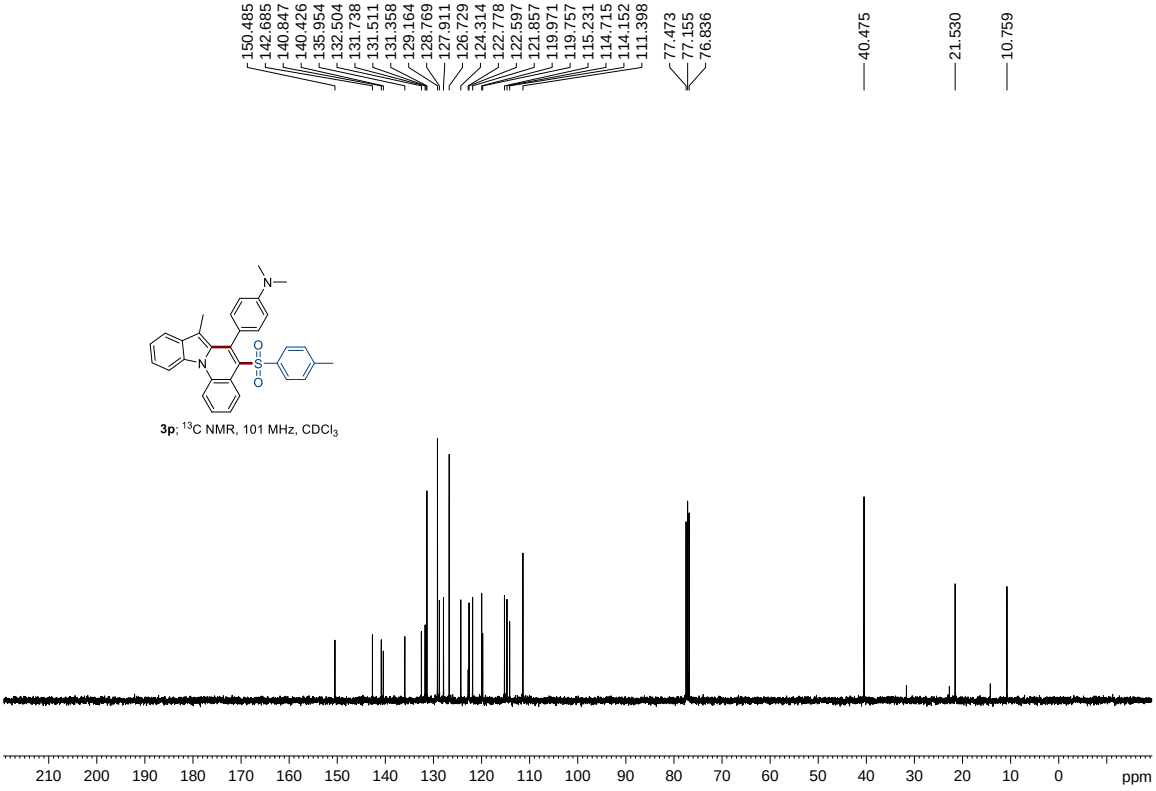

8.754
8.751
8.733
8.730
8.439
8.418
8.345
8.324
7.741
7.721
7.565
7.544
7.522
7.519
7.501
7.482
7.480
7.462
7.444
7.360
7.340
7.322
7.258
7.239
7.218
7.200
7.179
7.174
7.158
7.153
7.109
7.088
2.444
2.308
1.592
0.000
3n; 1H NMR, 400 MHz, CDCl3
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.979
1.002
0.983
1.034
2.044
2.092
1.142
1.223
4.056
2.094
3.091
3.083
2.986

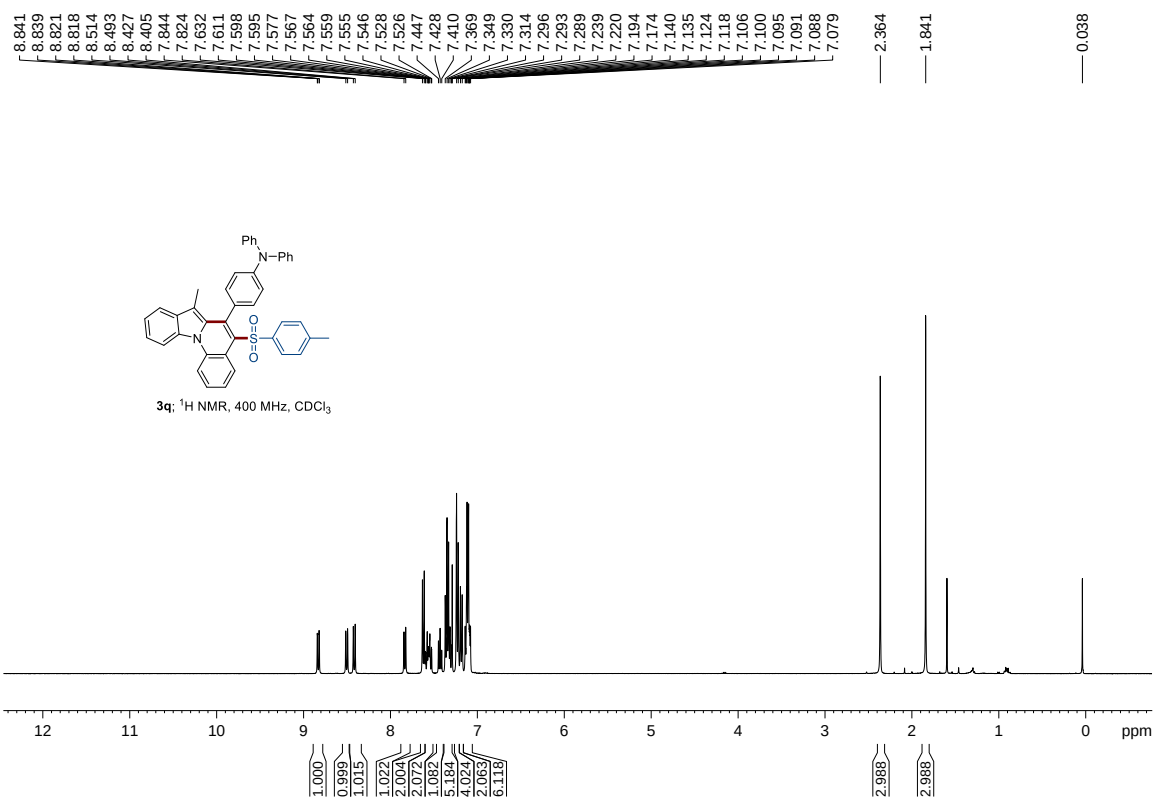

143.329
140.510
140.301
138.196
136.076
132.758
132.452
131.642
130.536
129.997
129.354
128.971
128.547
128.283
127.755
126.770
124.549
122.738
121.975
120.071
119.299
115.405
114.616
114.369
77.443
77.125
76.807
21.606
21.573
10.289
3n; 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

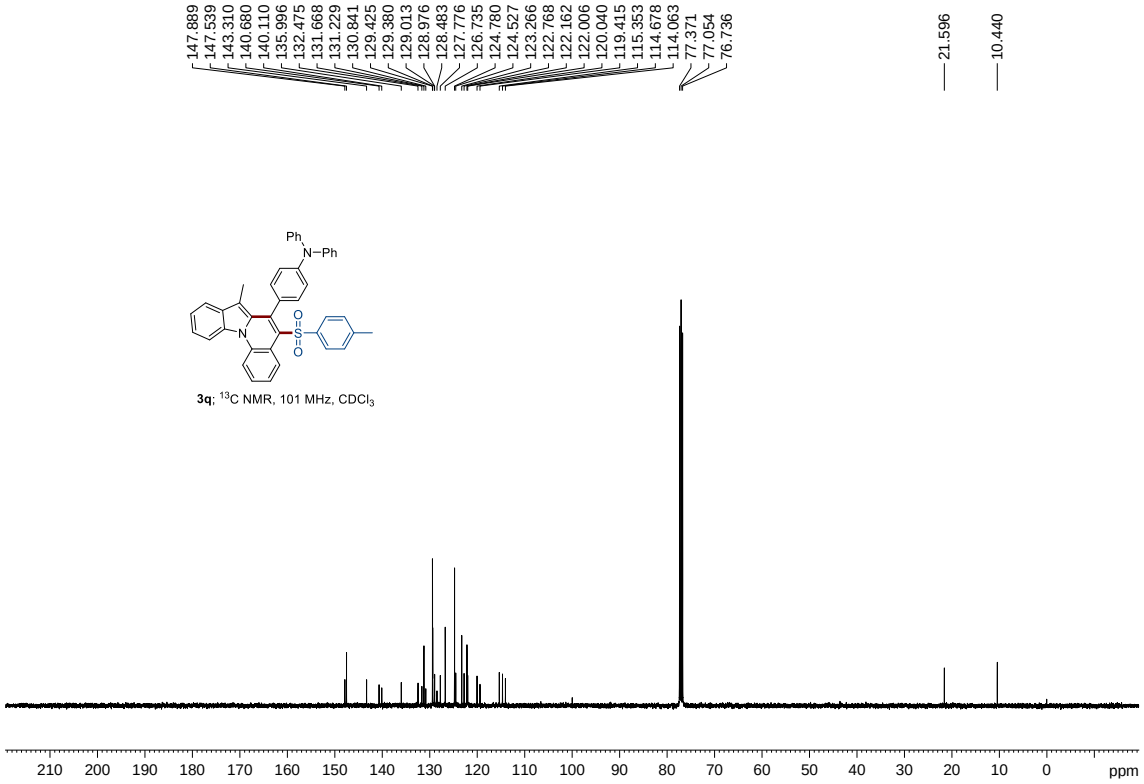

8.863
8.860
8.842
8.839
8.507
8.486
8.413
8.392
7.805
7.785
7.599
7.596
7.582
7.578
7.561
7.532
7.514
7.511
7.427
7.408
7.389
7.345
7.344
7.325
7.307
7.305
7.291
7.225
7.218
7.213
7.201
7.197
7.190
7.164
7.144
6.967
6.960
6.939
3.939
2.374
1.688
OMe
3o; 1H NMR, 400 MHz, CDCl3
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.987
1.013
1.009
1.029
4.083
1.057
1.185
2.023
2.028
2.049
3.059
3.036
3.241


159.848
143.237
140.622
139.871
136.038
132.475
131.643
131.505
130.856
129.339
128.997
128.806
127.827
127.721
126.701
124.532
122.734
121.981
120.042
119.429
115.362
114.647
114.220
113.318
77.444
77.126
76.808
55.357
21.558
10.463
OMe
3o; 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
8.892
8.889
8.871
8.868
8.499
8.478
8.413
8.392
7.805
7.785
7.591
7.588
7.570
7.549
7.526
7.506
7.421
7.403
7.384
7.358
7.356
7.338
7.319
7.317
7.291
7.102
7.080
7.058
7.051
6.691
6.669
3.077
2.356
1.762
0.078

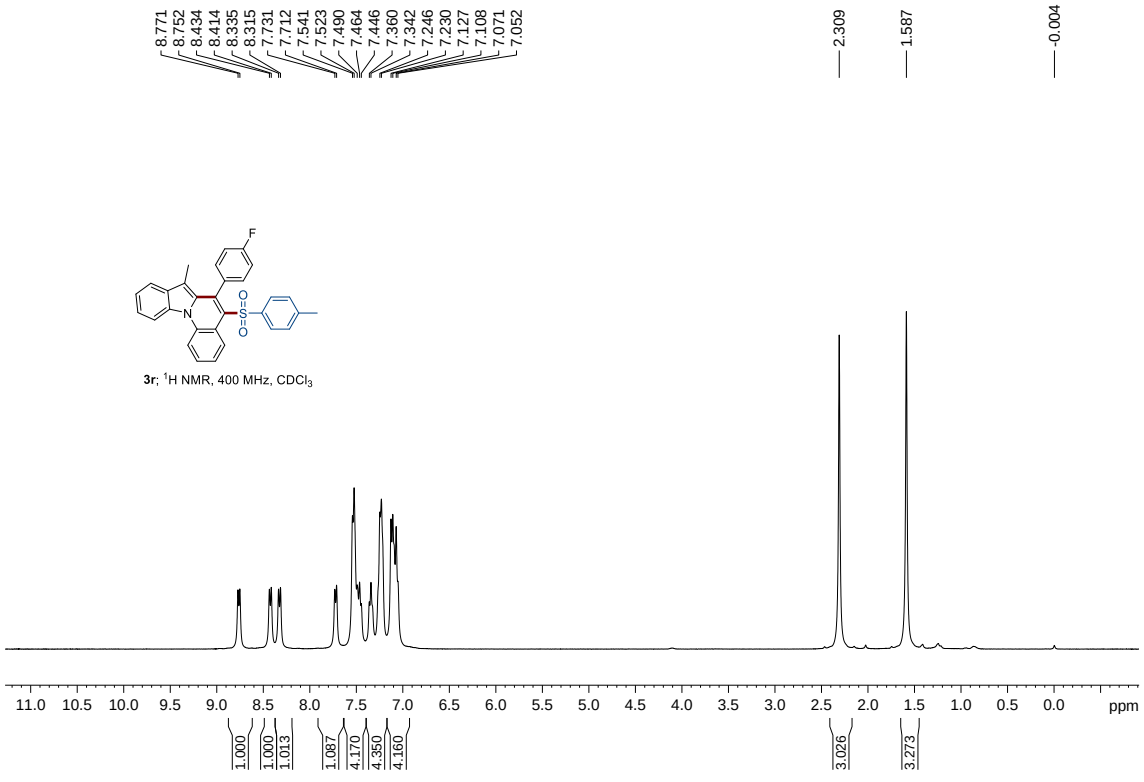

3p; 1H NMR, 400 MHz, CDCl3
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.989
1.016
1.008
1.033
4.120
2.163
4.064
2.010
6.152
3.065
3.107


150.485
142.685
140.847
140.426
135.954
132.504
131.738
131.511
131.358
129.164
128.769
127.911
126.729
124.314
122.778
122.597
121.857
119.971
119.757
115.231
114.715
114.152
111.398
77.473
77.155
76.836
40.475
21.530
10.759
N
O
S
O
3p; 13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

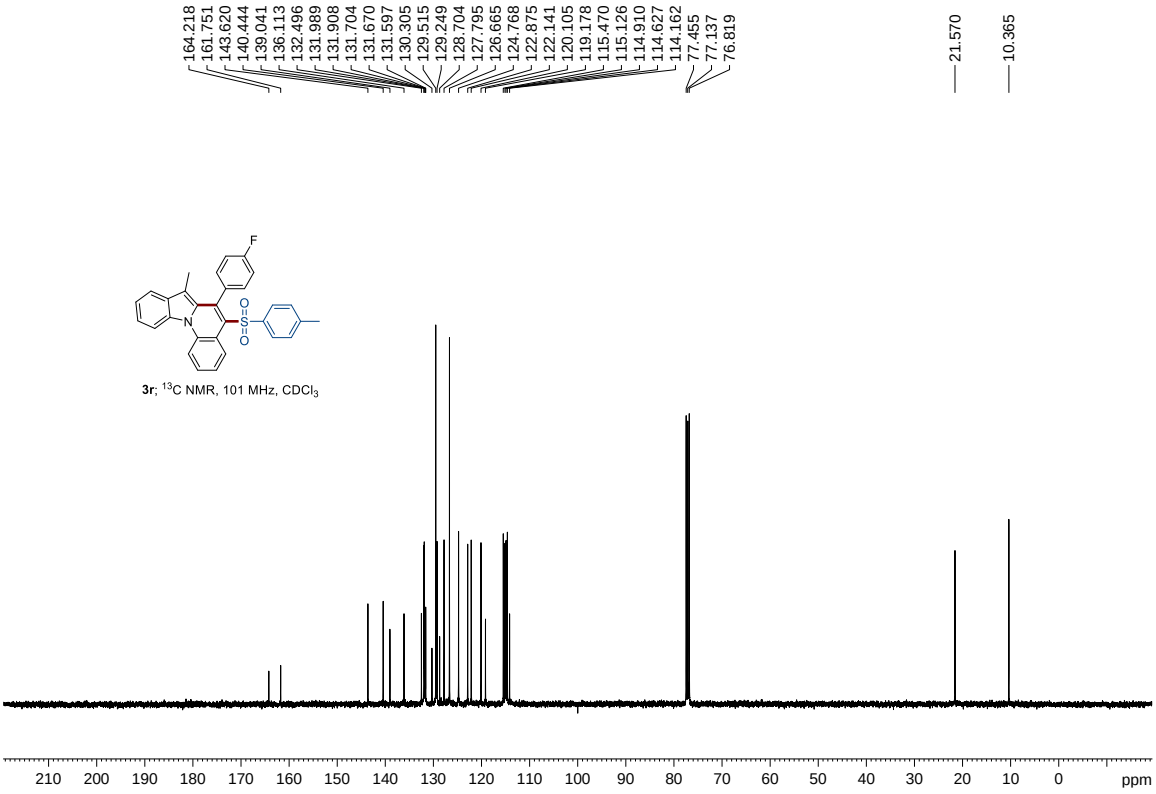

8.841
8.839
8.821
8.818
8.514
8.493
8.427
8.405
7.844
7.824
7.632
7.611
7.598
7.595
7.577
7.567
7.564
7.559
7.555
7.546
7.528
7.526
7.447
7.428
7.410
7.369
7.349
7.330
7.314
7.296
7.293
7.289
7.239
7.220
7.194
7.174
7.140
7.135
7.124
7.118
7.106
7.100
7.095
7.091
7.088
7.079
2.364
1.841
0.038
Ph
N–Ph
O
S
O
3q; 1H NMR, 400 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.999
1.015
1.022
2.004
2.072
1.082
5.184
4.024
2.063
6.118
2.988
2.988

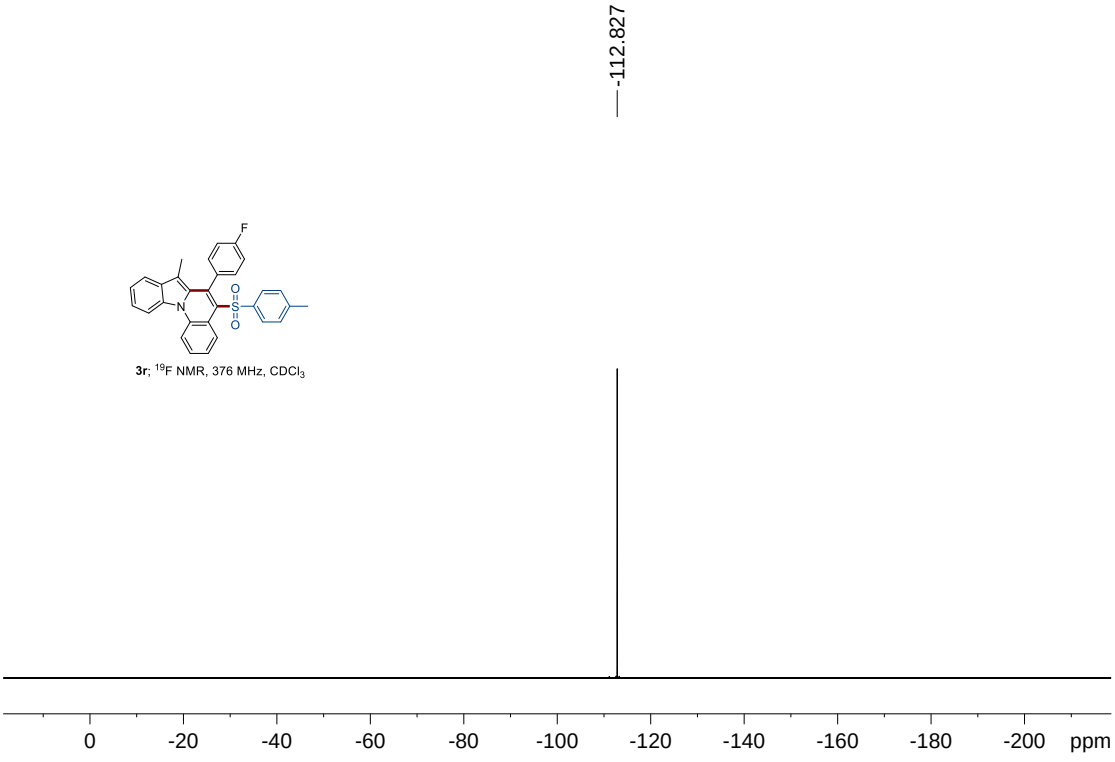


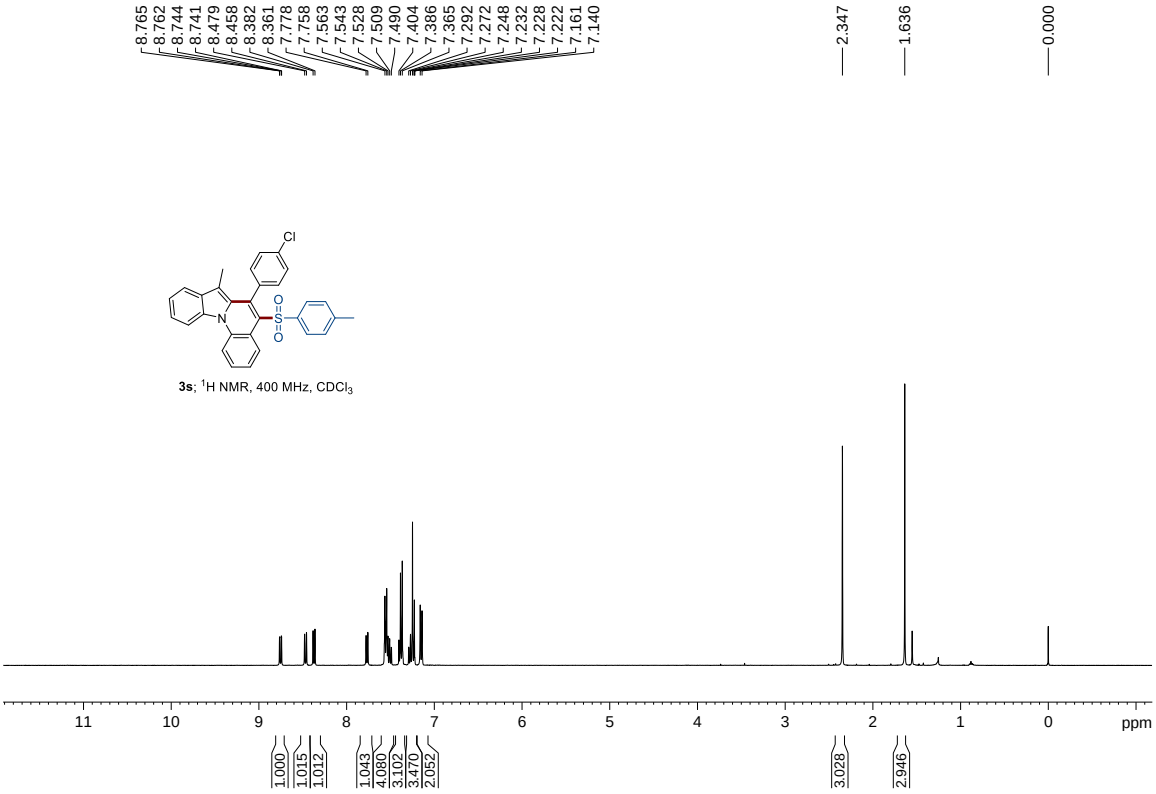
3q; ^{13}C NMR, 101 MHz, $CDCl_3$



3r; ^{1}H NMR, 400 MHz, $CDCl_3$


164.218
161.751
143.620
140.444
139.041
136.113
132.496
131.989
131.908
131.704
131.670
131.597
130.305
129.515
129.249
128.704
127.795
126.665
124.768
122.875
122.141
120.105
119.178
115.470
115.126
114.910
114.627
114.162
77.455
77.137
76.819
21.570
10.365
F
O
S
O
N
3r; 13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-112.827
F
O
S
O
N
3r; 19F NMR, 376 MHz, CDCl3
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


8.765
8.762
8.744
8.741
8.479
8.458
8.382
8.361
7.778
7.758
7.563
7.543
7.528
7.509
7.490
7.404
7.386
7.365
7.292
7.272
7.248
7.232
7.228
7.222
7.161
7.140
2.347
1.636
0.000
Cl
O
S
O
3s; 1H NMR, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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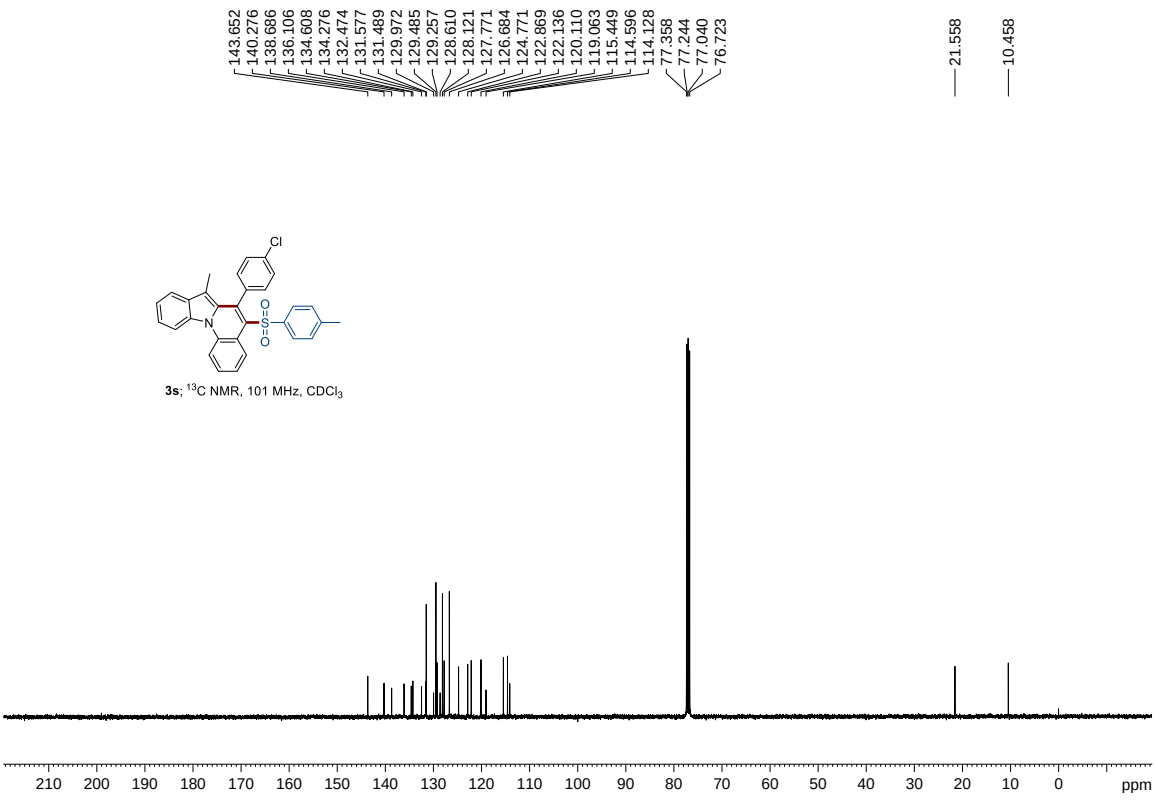
1.015
1.012
1.043
4.080
3.102
3.470
2.052
3.028
2.946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140.276
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131.577
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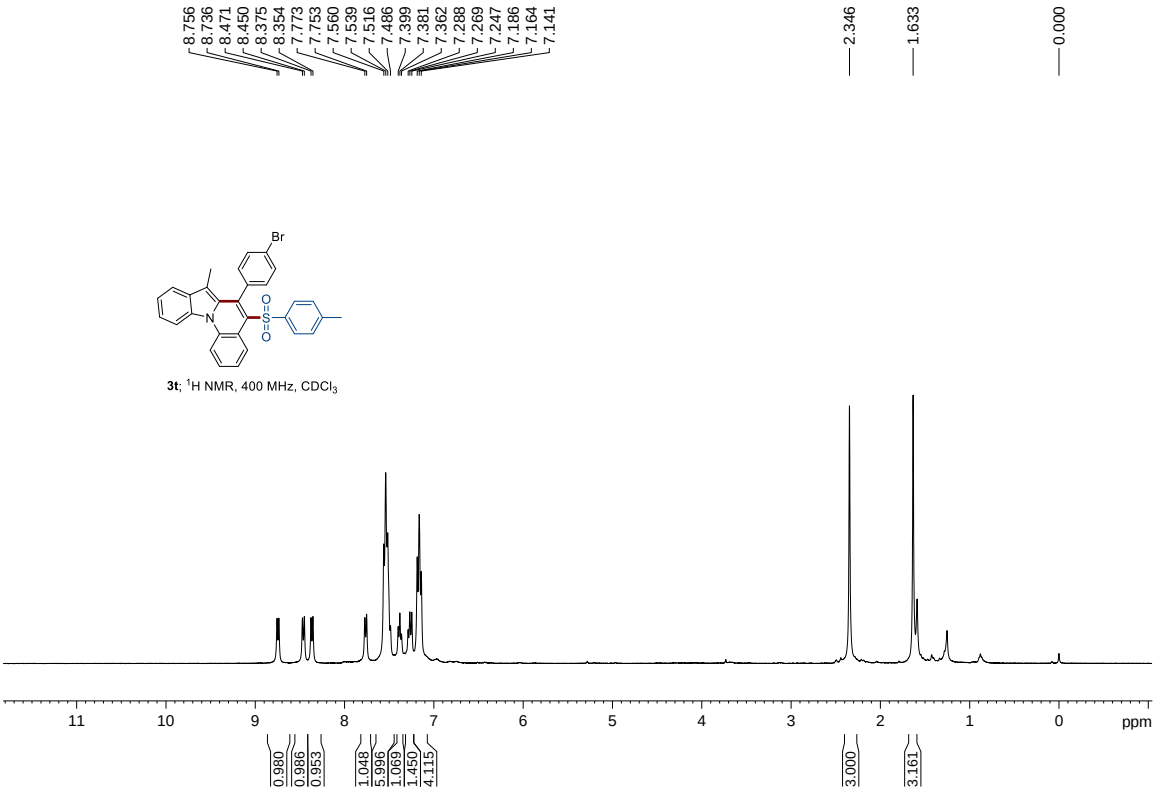
129.485
129.257
128.610
128.121
127.771
126.684
124.771
122.869
122.136
120.110
119.063
115.449
114.596
114.128
77.358
77.244
77.040
76.723
21.558
10.458
Cl
O
S
O
3s; 13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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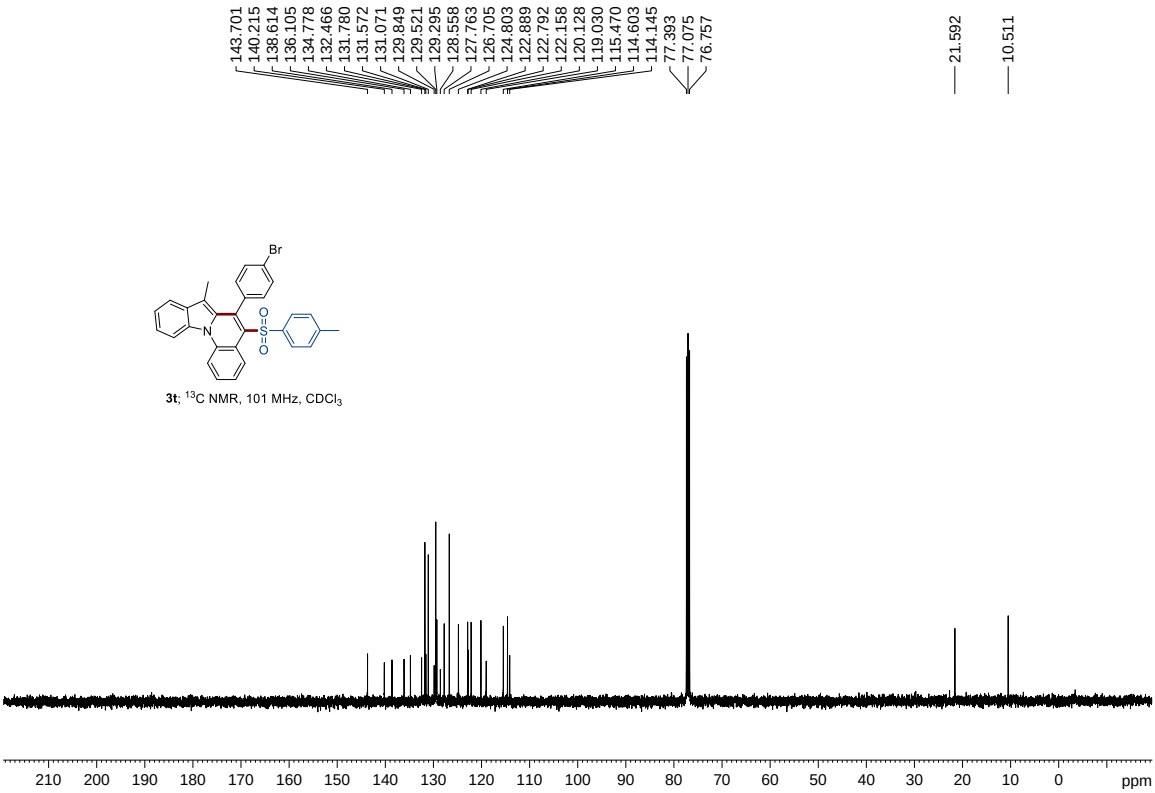
8.736
8.471
8.450
8.375
8.354
7.773
7.753
7.560
7.539
7.516
7.486
7.399
7.381
7.362
7.288
7.269
7.247
7.186
7.164
7.141
2.346
1.633
0.000
Br
O
S
O
3t; 1H NMR, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.980
0.986
0.953
1.048
5.996
1.069
1.450
4.115
3.000
3.161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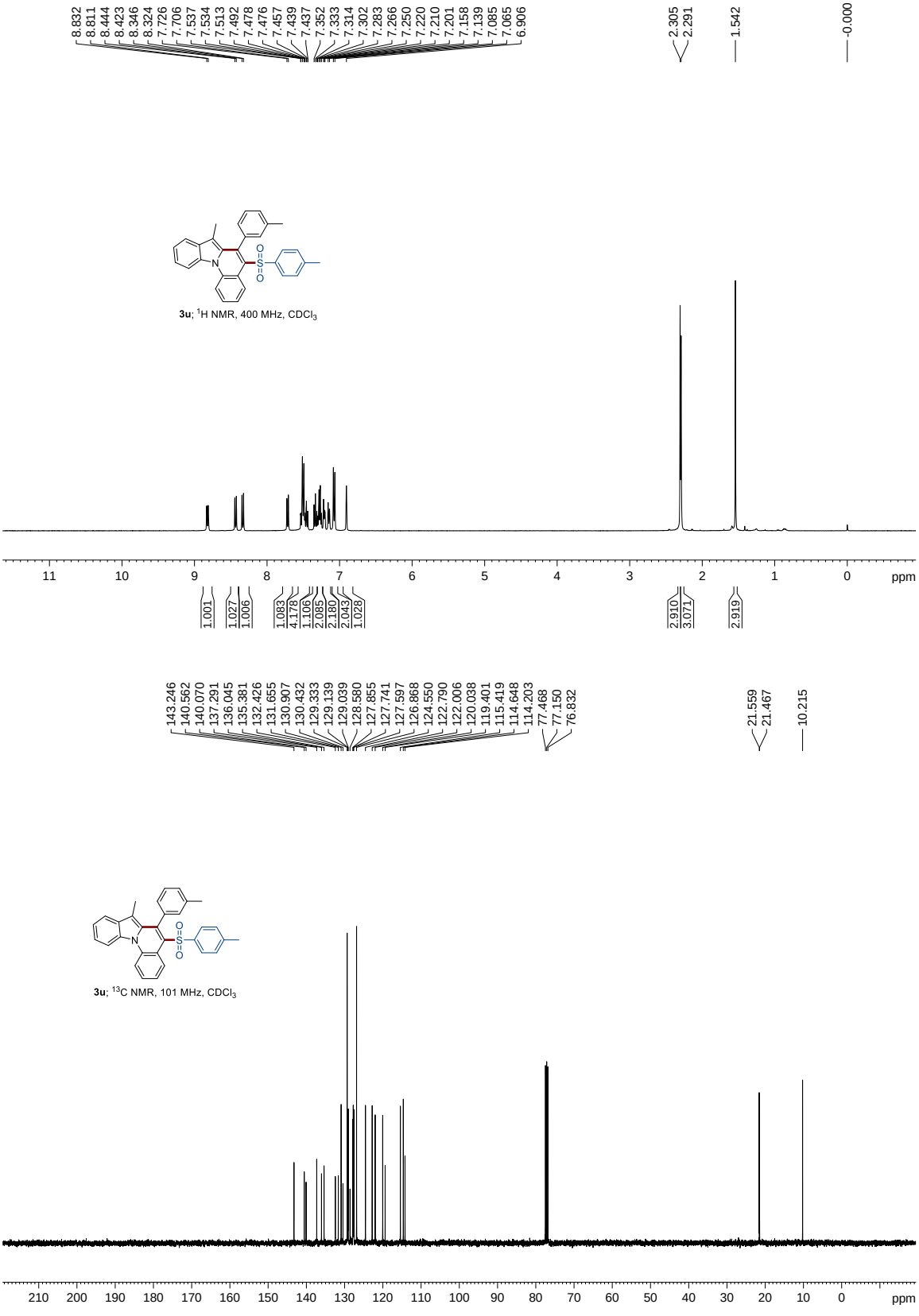
140.215
138.614
136.105
134.778
132.466
131.780
131.572
131.071
129.849
129.521
129.295
128.558
127.763
126.705
124.803
122.889
122.792
122.158
120.128
119.030
115.470
114.603
114.145
77.393
77.075
76.757
21.592
10.511
Br
O
S
O
3t; 13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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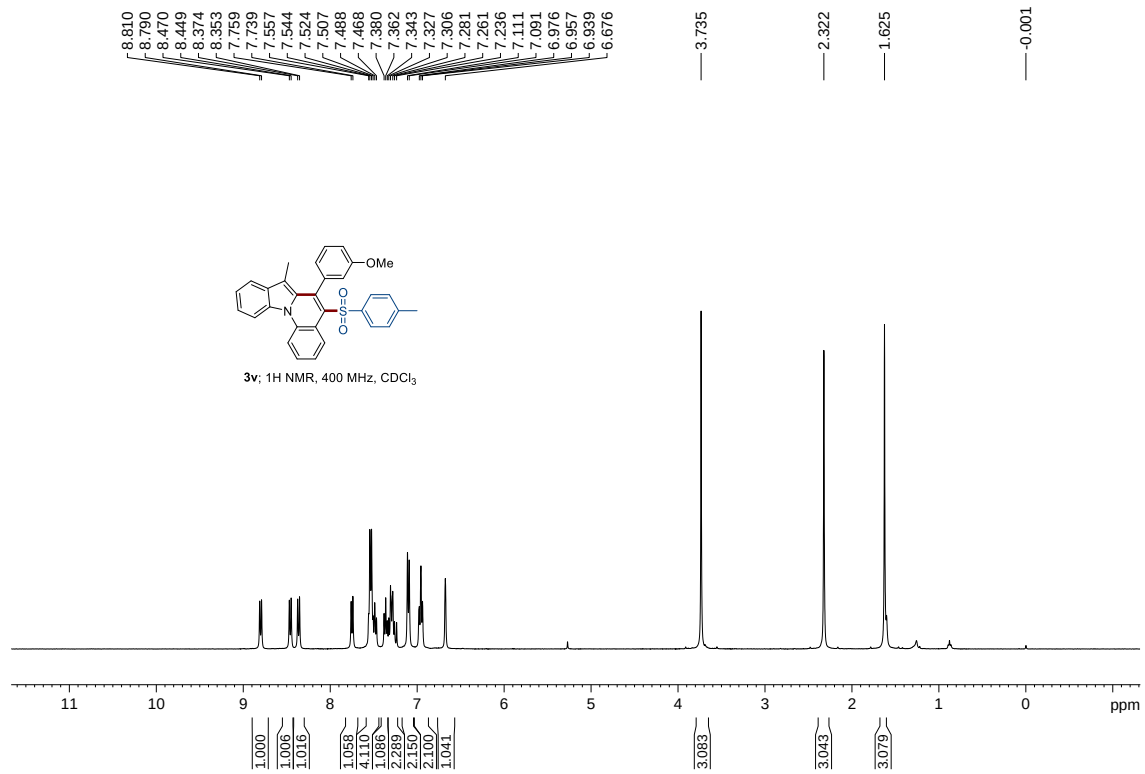
8.811
8.444
8.423
8.346
8.324
7.726
7.706
7.537
7.534
7.513
7.492
7.478
7.476
7.457
7.439
7.437
7.352
7.333
7.314
7.302
7.283
7.266
7.250
7.220
7.210
7.201
7.158
7.139
7.085
7.065
6.906
2.305
2.291
1.542
-0.000
3u; 1H NMR, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.001
1.027
1.006
1.083
4.178
1.106
2.085
2.180
2.043
1.028
2.910
3.071
2.919
143.246
140.562
140.070
137.291
136.045
135.381
132.426
131.655
130.907
130.432
129.333
129.139
129.039
128.580
127.855
127.741
127.597
126.868
124.550
122.790
122.006
120.038
119.401
115.419
114.648
114.203
77.468
77.150
76.832
21.559
21.467
10.215
3u; 13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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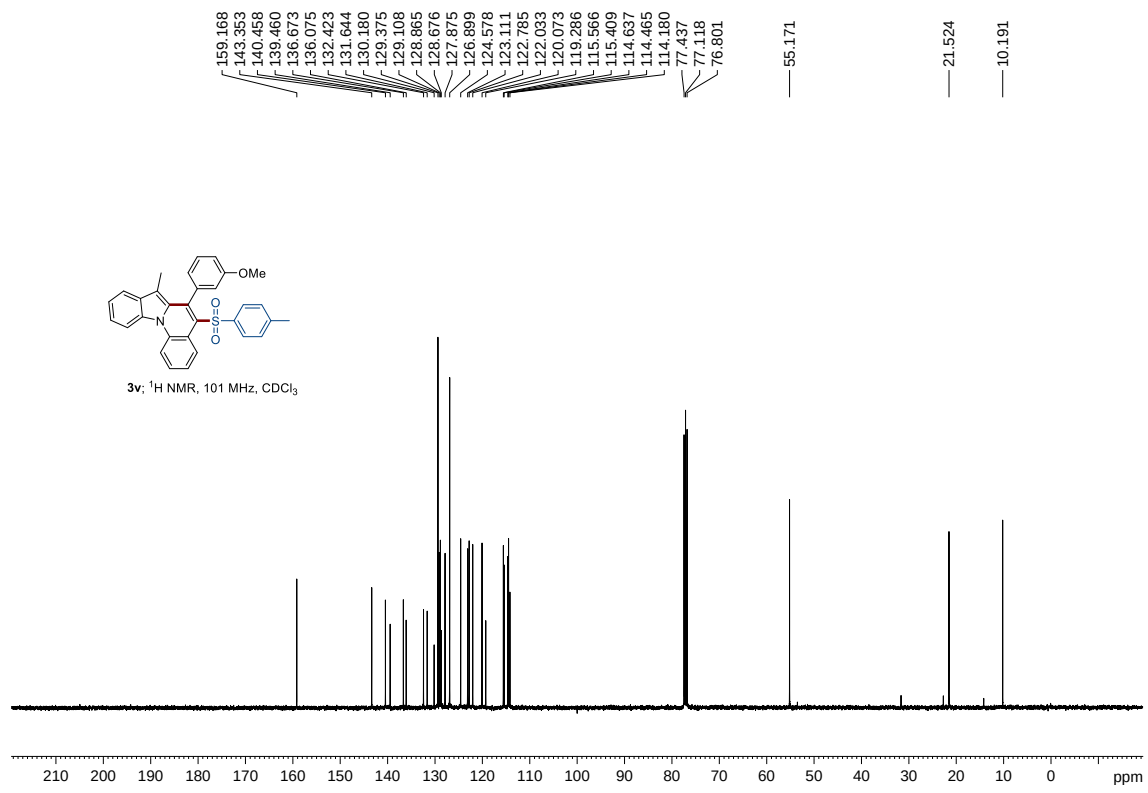
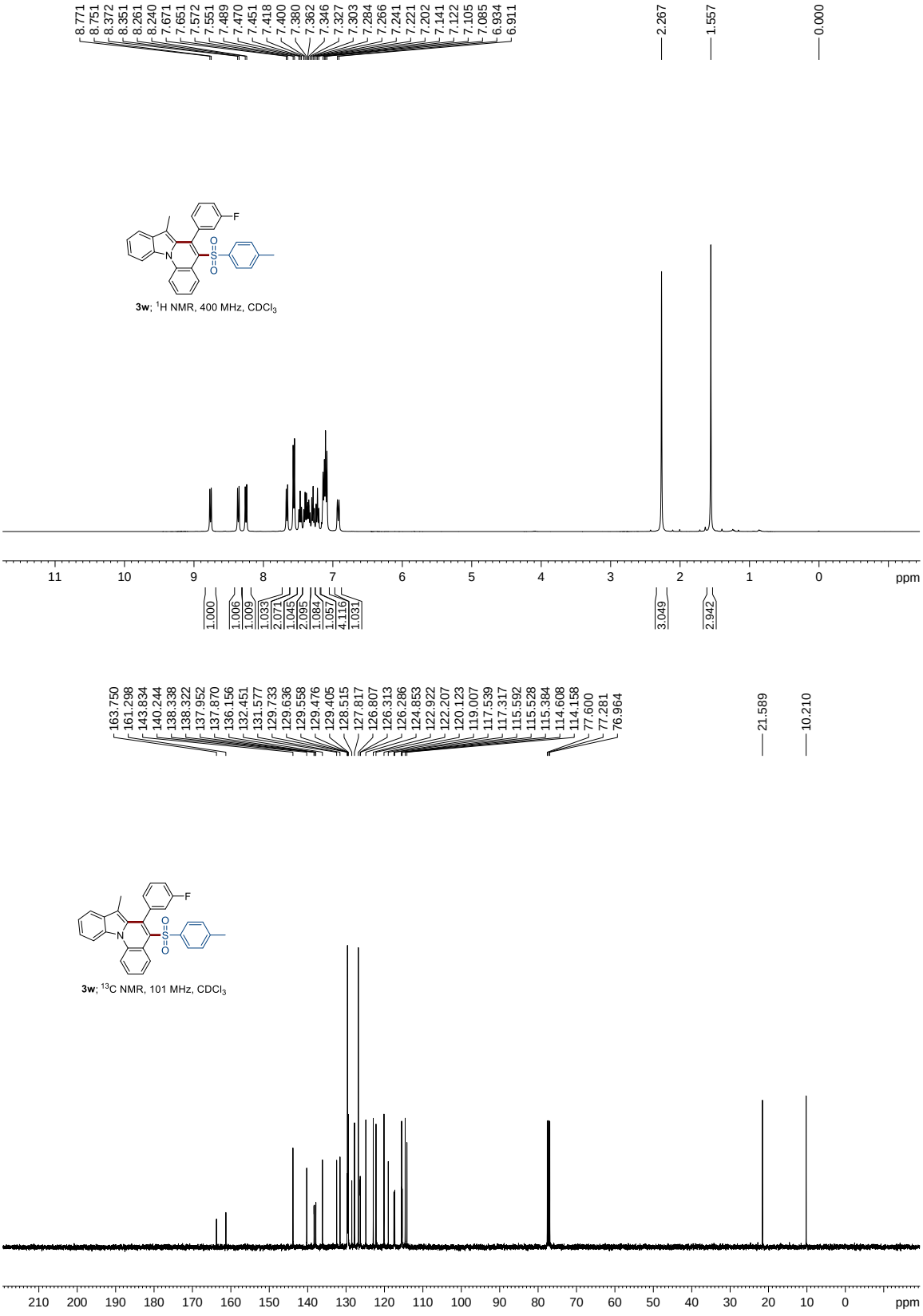
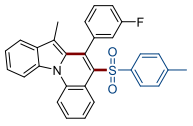
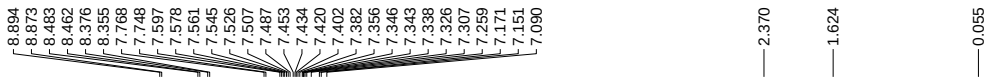
8.790
8.470
8.449
8.374
8.353
7.759
7.739
7.557
7.544
7.524
7.507
7.488
7.468
7.380
7.362
7.343
7.327
7.306
7.281
7.261
7.236
7.111
7.091
6.976
6.957
6.939
6.676
3.735
2.322
1.625
-0.001
OMe
O
S
O
3v; 1H NMR, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.006
1.016
1.058
4.110
1.086
2.289
2.150
2.100
1.041
3.083
3.043
3.079

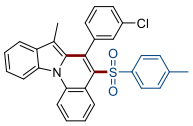

159.168
143.353
140.458
139.460
136.673
136.075
132.423
131.644
130.180
129.375
129.108
128.865
128.676
127.875
126.899
124.578
123.111
122.785
122.033
120.073
119.286
115.566
115.409
114.637
114.465
114.180
77.437
77.118
76.801
55.171
21.524
10.191
OMe
O
S
O
3v; 1H NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.771
8.751
8.372
8.351
8.261
8.240
7.671
7.651
7.572
7.551
7.489
7.470
7.451
7.418
7.400
7.380
7.362
7.346
7.327
7.303
7.284
7.266
7.241
7.221
7.202
7.141
7.122
7.105
7.085
6.934
6.911
2.267
1.557
0.000
F
O
S
O
N
3w; 1H NMR, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.006
1.009
1.033
2.071
1.045
2.095
1.084
1.057
4.116
1.031
3.049
2.942
163.750
161.298
143.834
140.244
138.338
138.322
137.952
137.870
136.156
132.451
131.577
129.733
129.636
129.558
129.476
129.405
128.515
127.817
126.807
126.313
126.286
124.853
122.922
122.207
120.123
119.007
117.539
117.317
115.592
115.528
115.384
114.608
114.158
77.600
77.281
76.964
21.589
10.210
F
O
S
O
N
3w; 13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

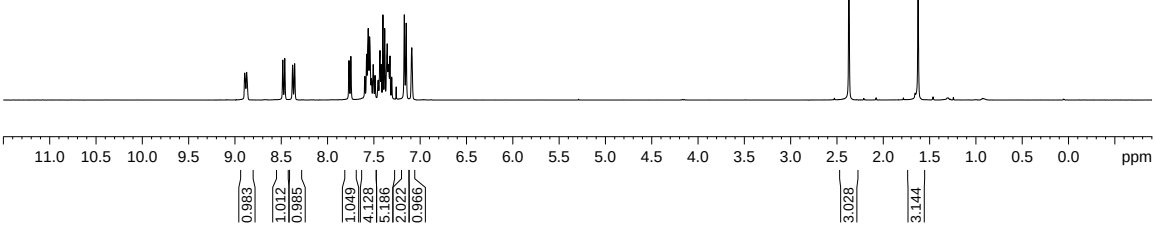


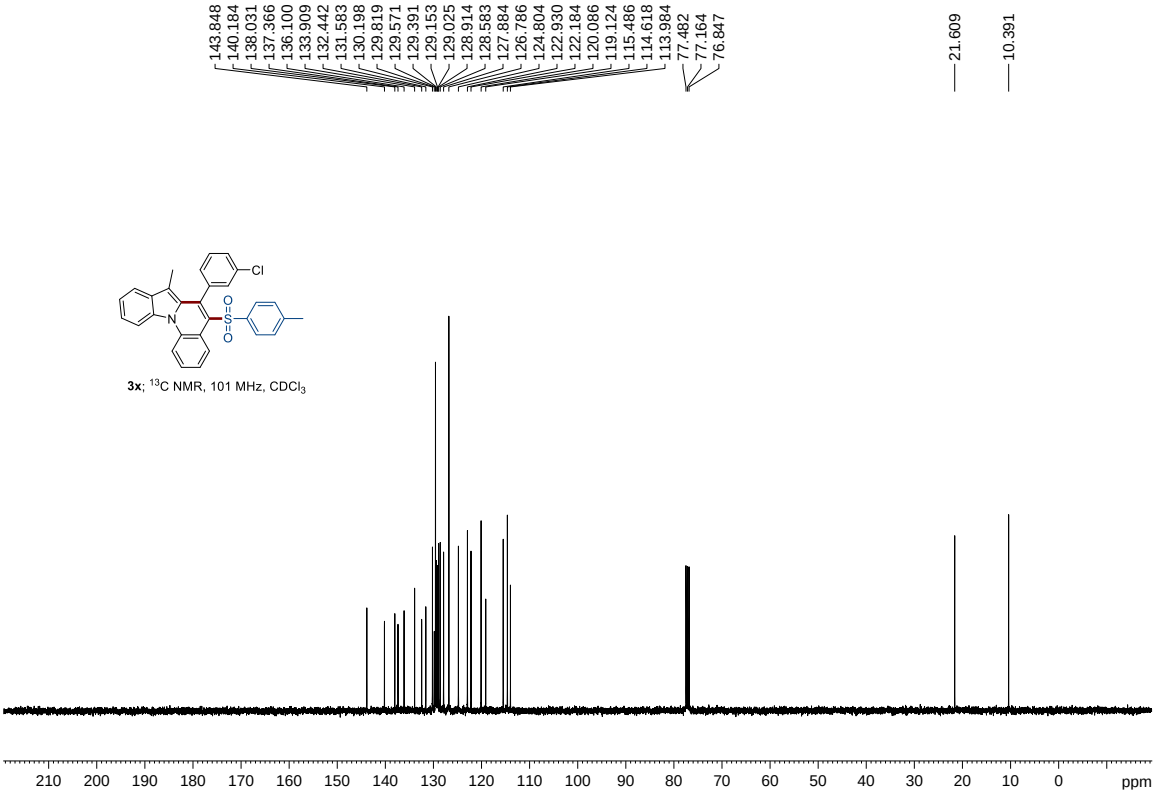
3w; ^{19}F NMR, 376 MHz, $CDCl_3$





3x; ^{1}H NMR, 400 MHz, $CDCl_3$

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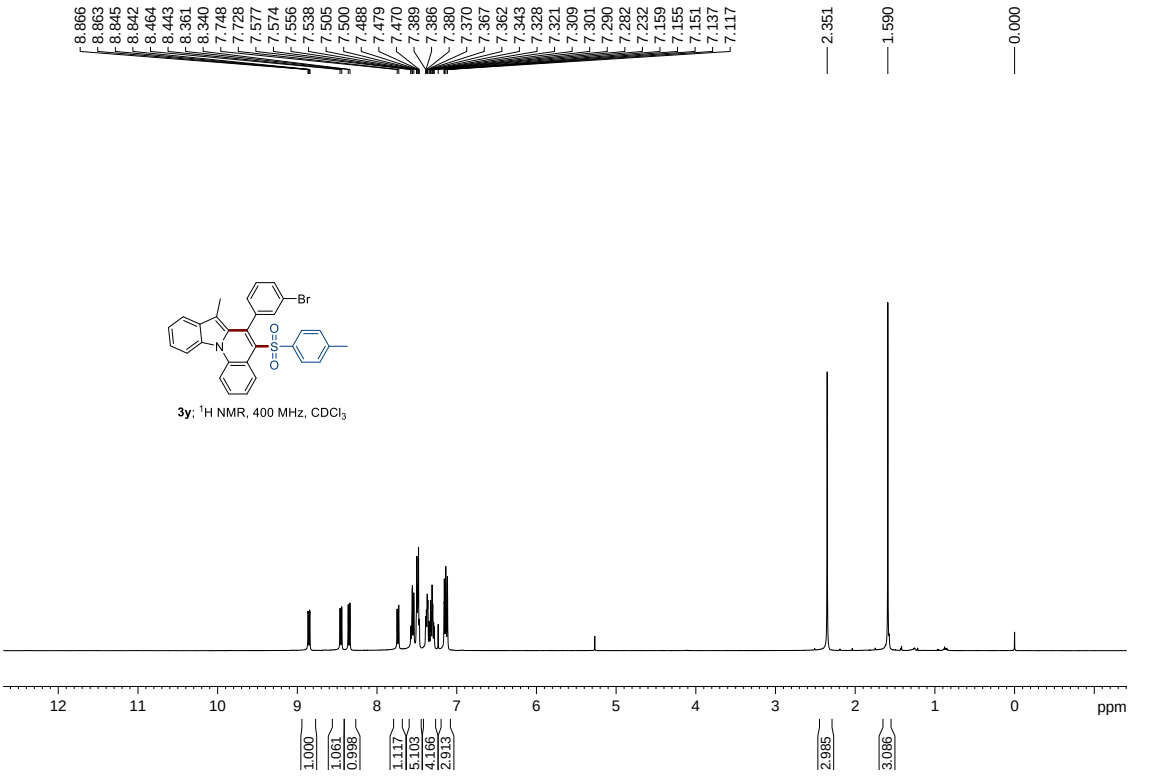
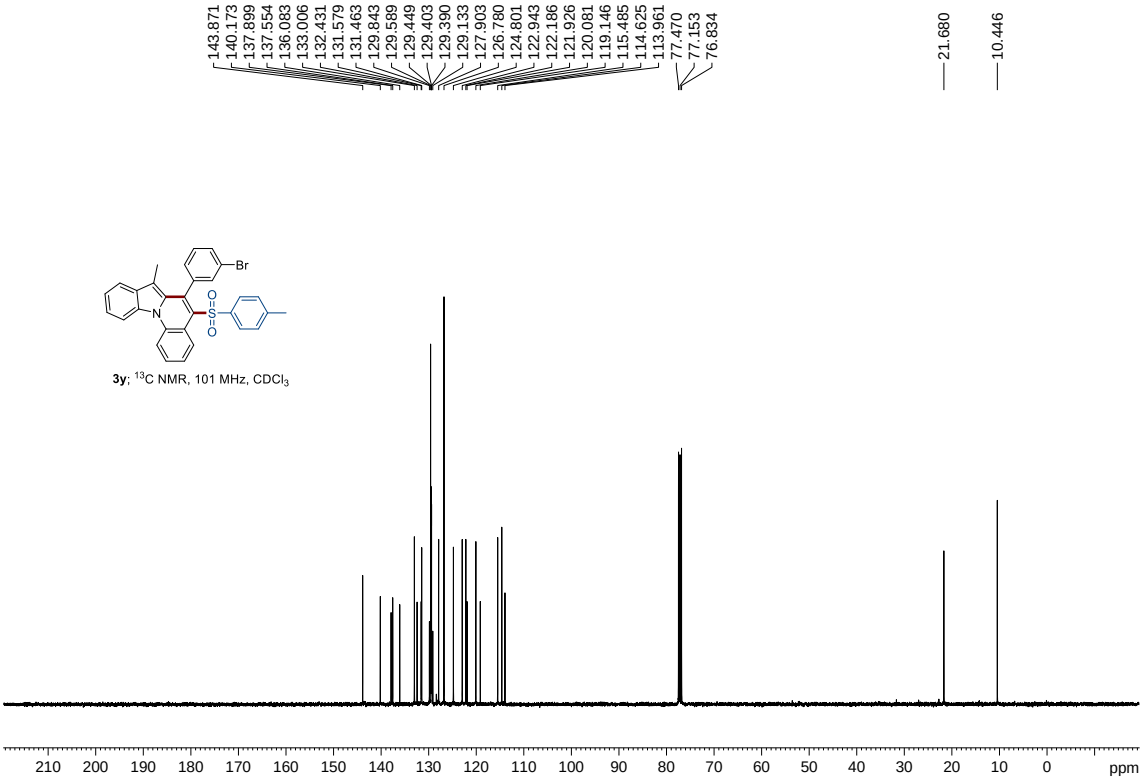
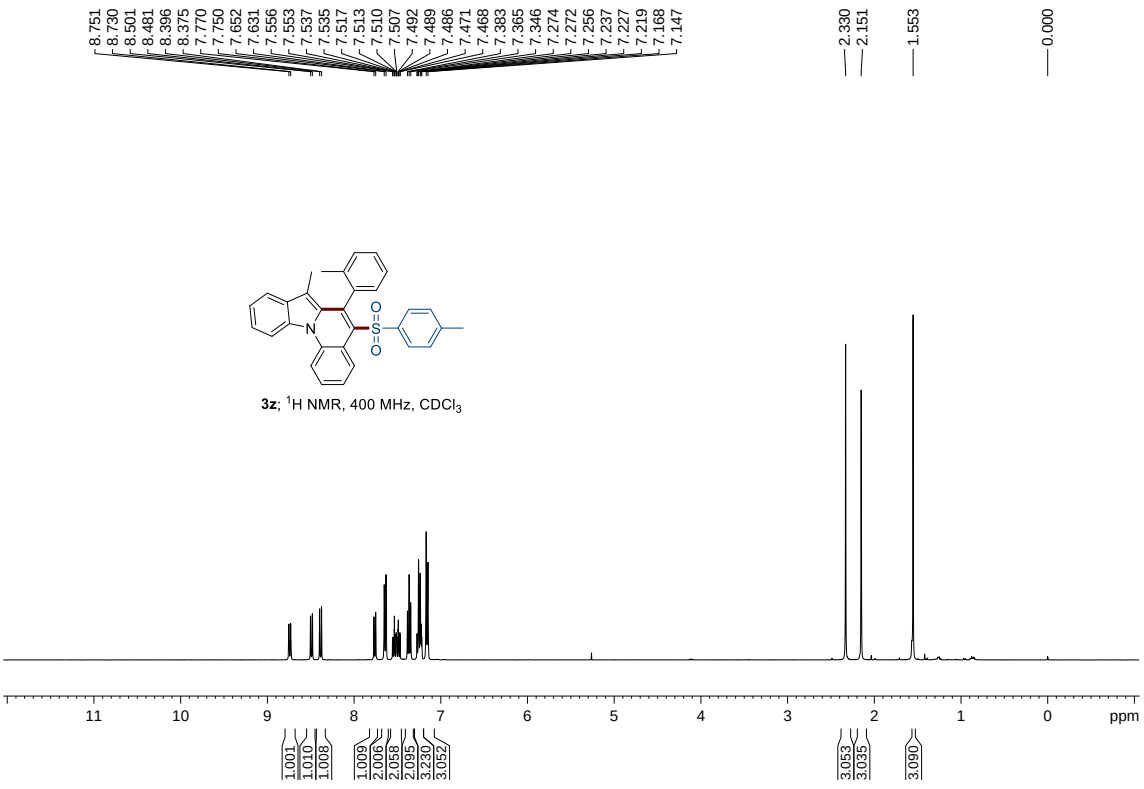
140.184
138.031
137.366
136.100
133.909
132.442
131.583
130.198
129.819
129.571
129.391
129.153
129.025
128.914
128.583
127.884
126.786
124.804
122.930
122.184
120.086
119.124
115.486
114.618
113.984
77.482
77.164
76.847
21.609
10.391
Cl
O
S
O
N
3x; 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

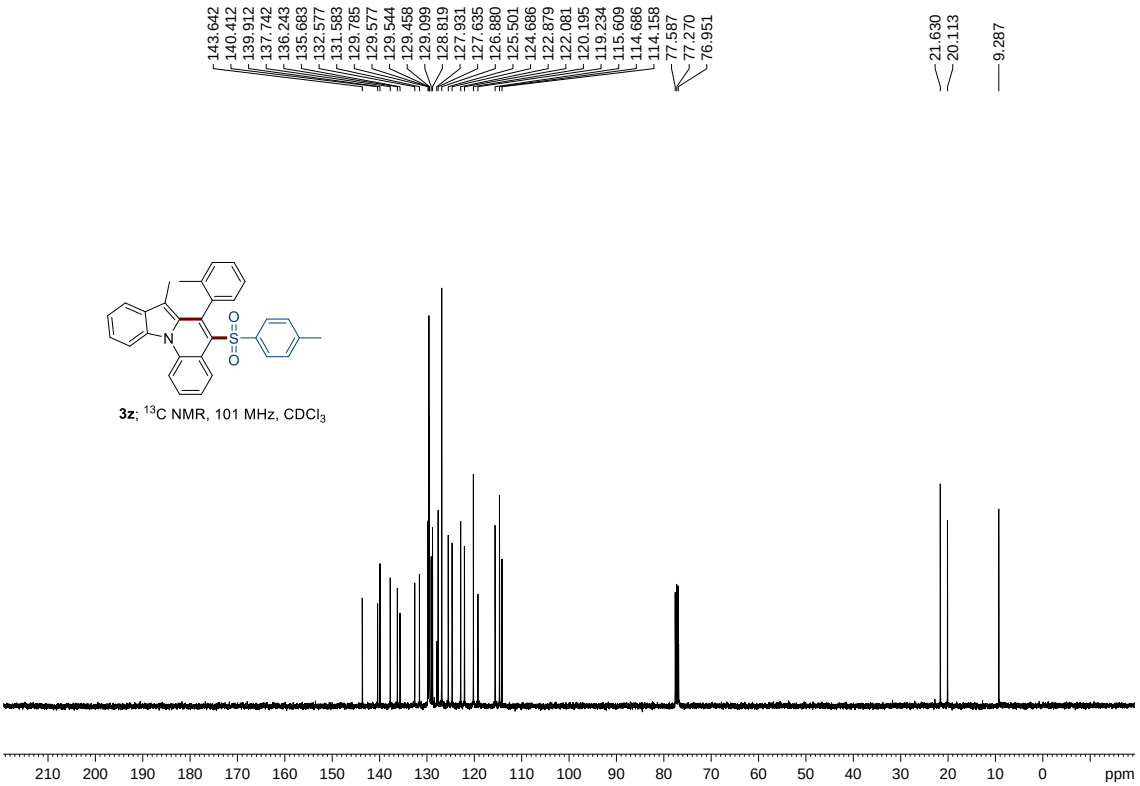

8.866
8.863
8.845
8.842
8.464
8.443
8.361
8.340
7.748
7.728
7.577
7.574
7.556
7.538
7.505
7.500
7.488
7.479
7.470
7.389
7.386
7.380
7.370
7.367
7.362
7.343
7.328
7.321
7.309
7.301
7.290
7.282
7.232
7.159
7.155
7.151
7.137
7.117
2.351
1.590
0.000
Br
O
S
O
N
3y; 1H NMR, 400 MHz, CDCl3
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.061
0.998
1.117
5.103
4.166
2.913
2.985
3.086



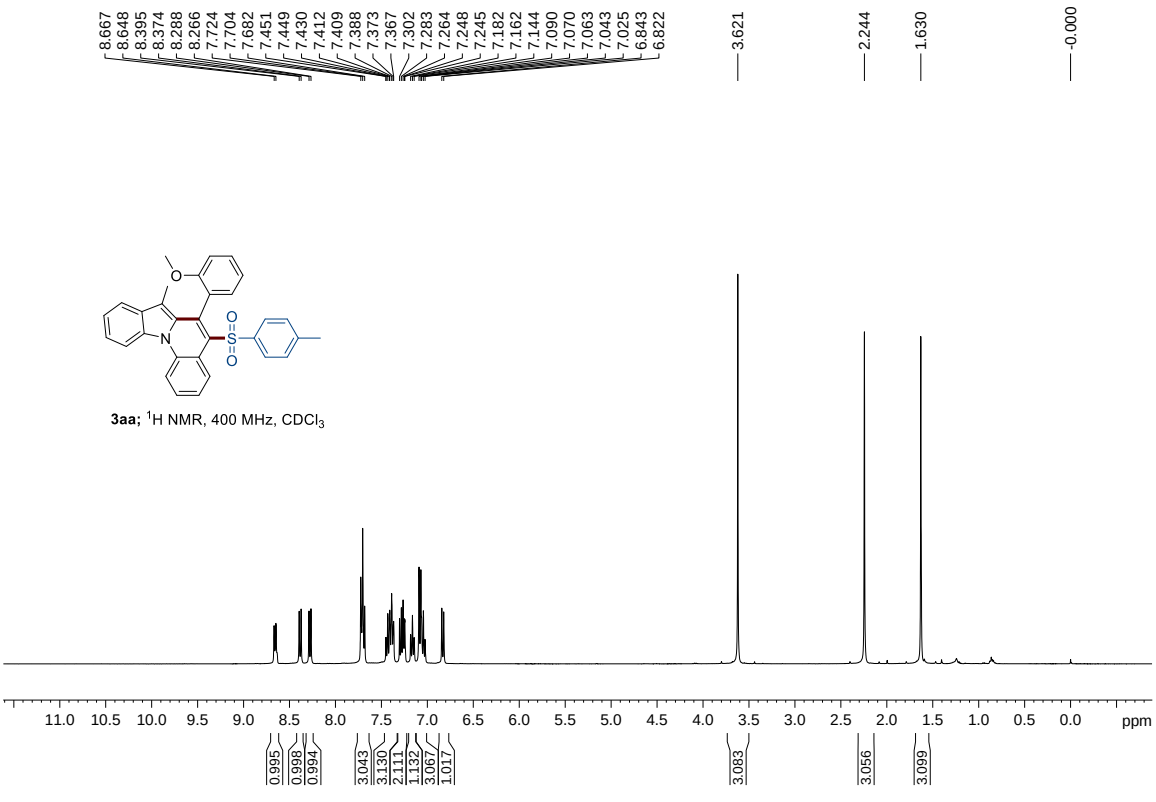
3y; ^{13}C NMR, 101 MHz, $CDCl_3$



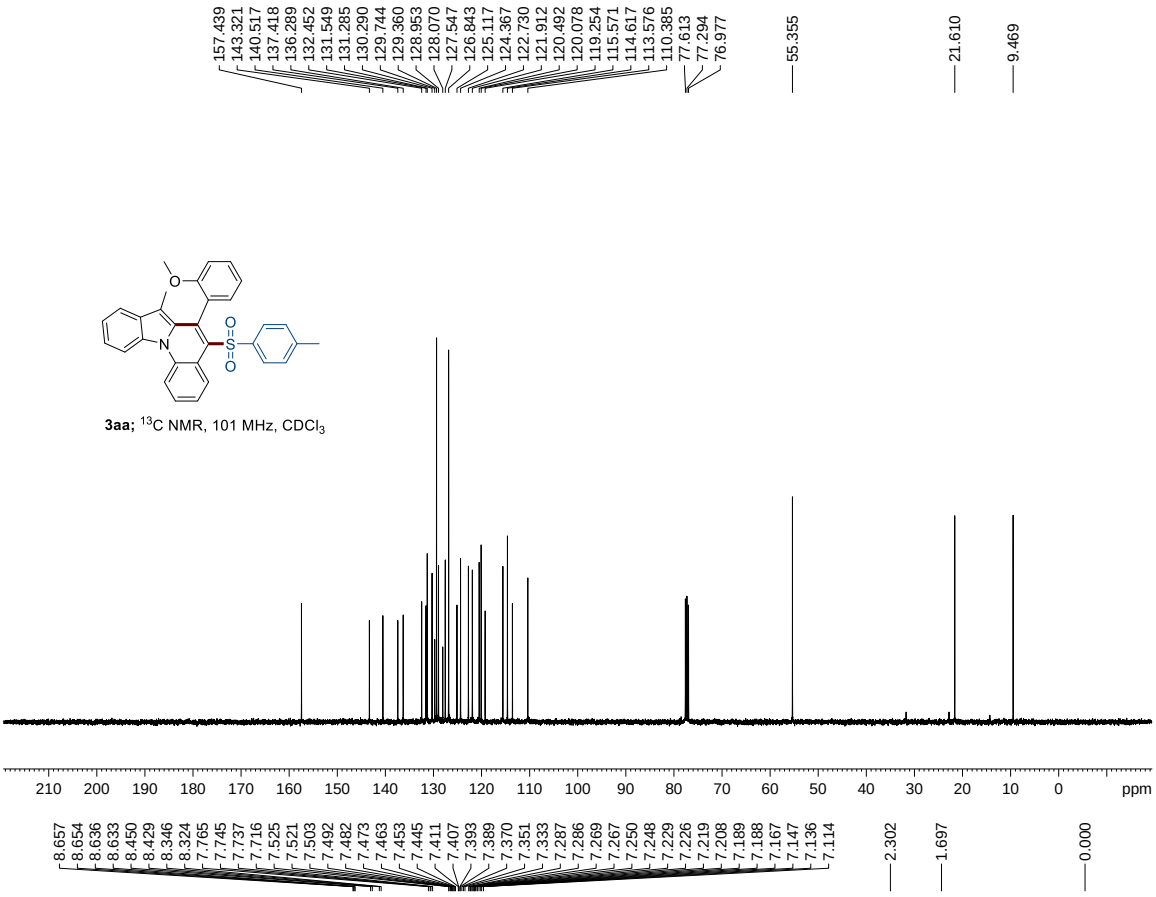
3z; ^{1}H NMR, 400 MHz, $CDCl_3$

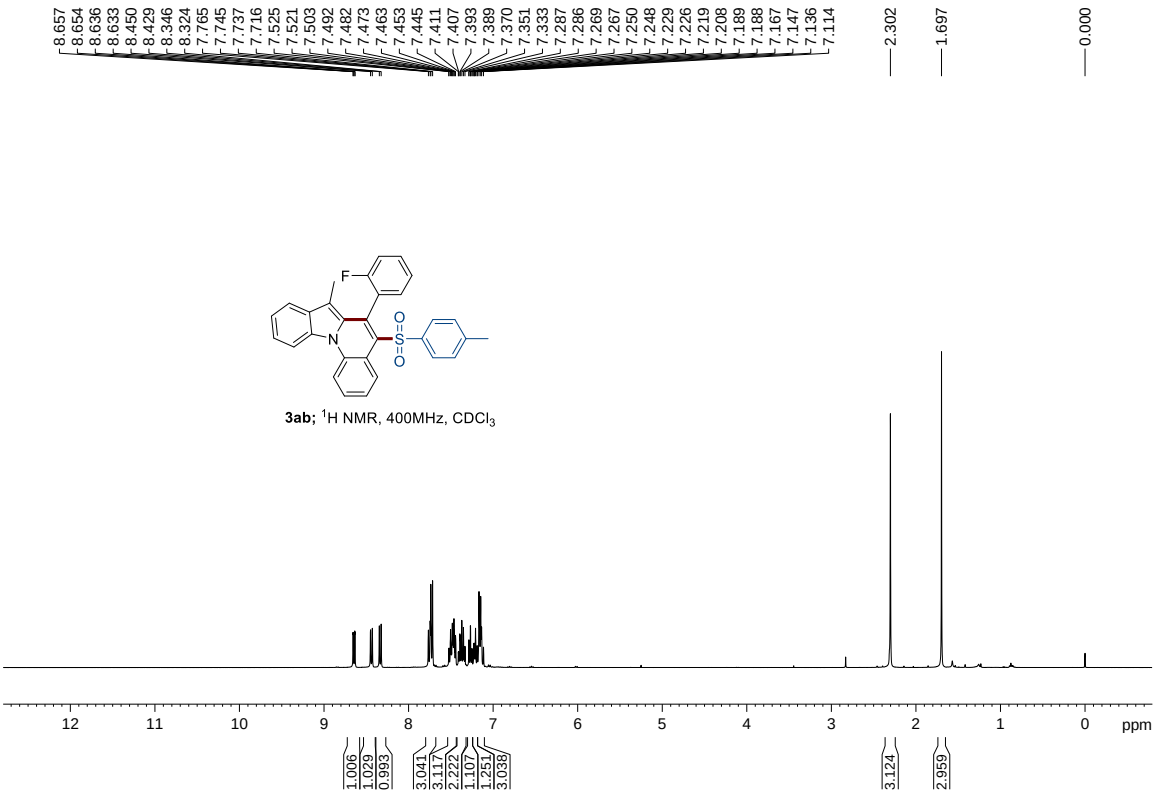


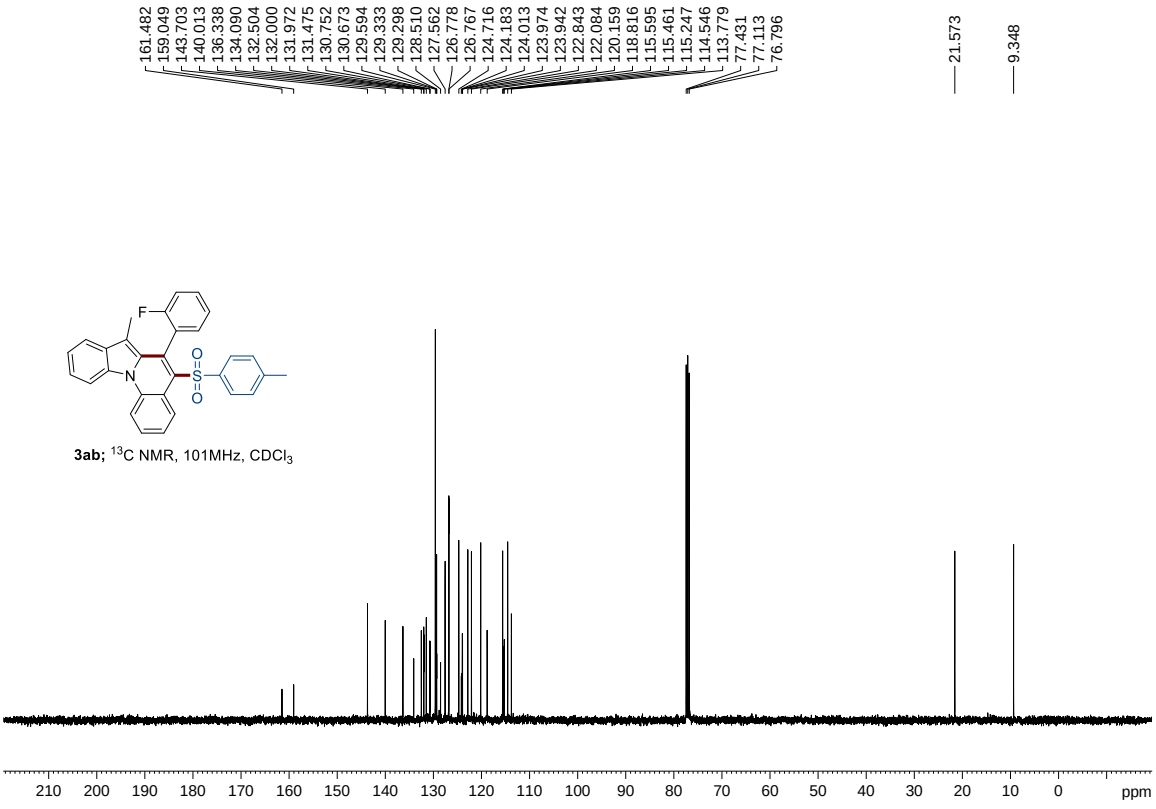
3z; ^{13}C NMR, 101 MHz, $CDCl_3$



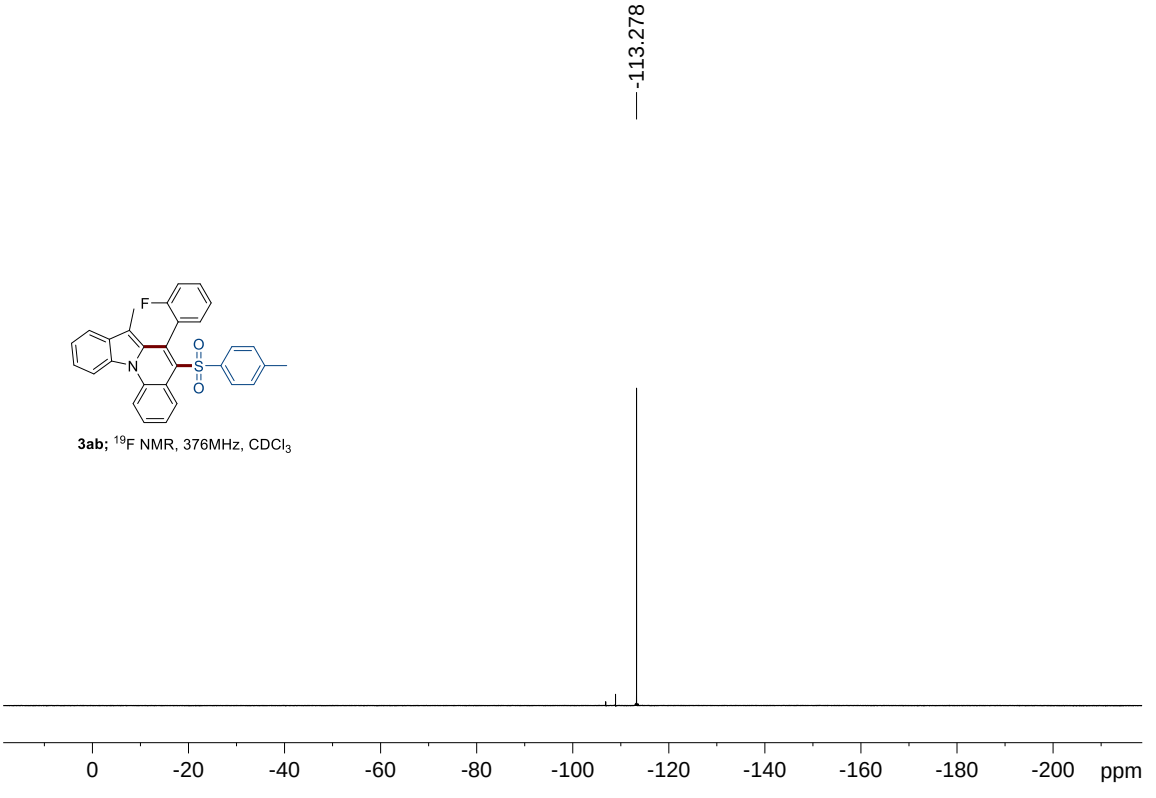
3aa; ^{1}H NMR, 400 MHz, $CDCl_3$


157.439
143.321
140.517
137.418
136.289
132.452
131.549
131.285
130.290
129.744
129.360
128.953
128.070
127.547
126.843
125.117
124.367
122.730
121.912
120.492
120.078
119.254
115.571
114.617
113.576
110.385
77.613
77.294
76.977
55.355
21.610
9.469
O
N
O
S
O
3aa; 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

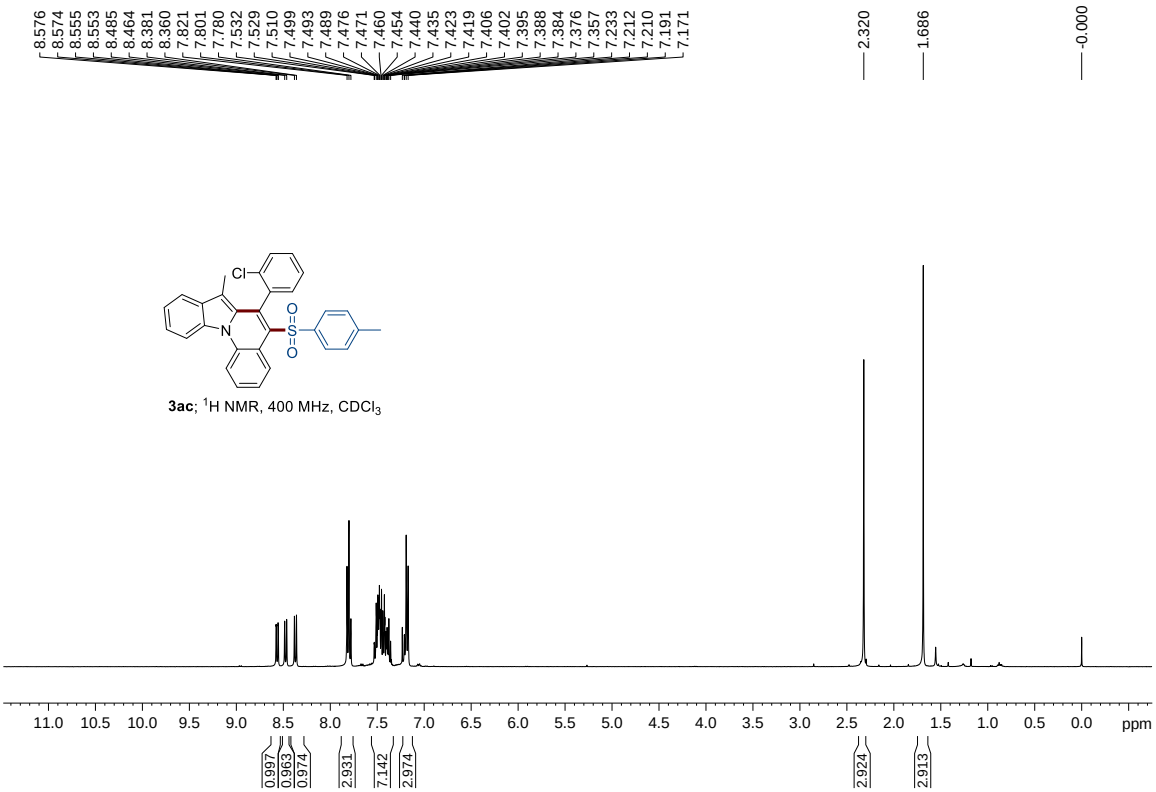

8.657
8.654
8.636
8.633
8.450
8.429
8.346
8.324
7.765
7.745
7.737
7.716
7.525
7.521
7.503
7.492
7.482
7.473
7.463
7.453
7.445
7.411
7.407
7.393
7.389
7.370
7.351
7.333
7.287
7.286
7.269
7.267
7.250
7.248
7.229
7.226
7.219
7.208
7.189
7.188
7.167
7.147
7.136
7.114
2.302
1.697
0.000
F
N
O
S
O
3ab; 1H NMR, 400MHz, CDCl3
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.006
1.029
0.993
3.041
3.117
2.222
1.107
1.251
3.038
3.124
2.959

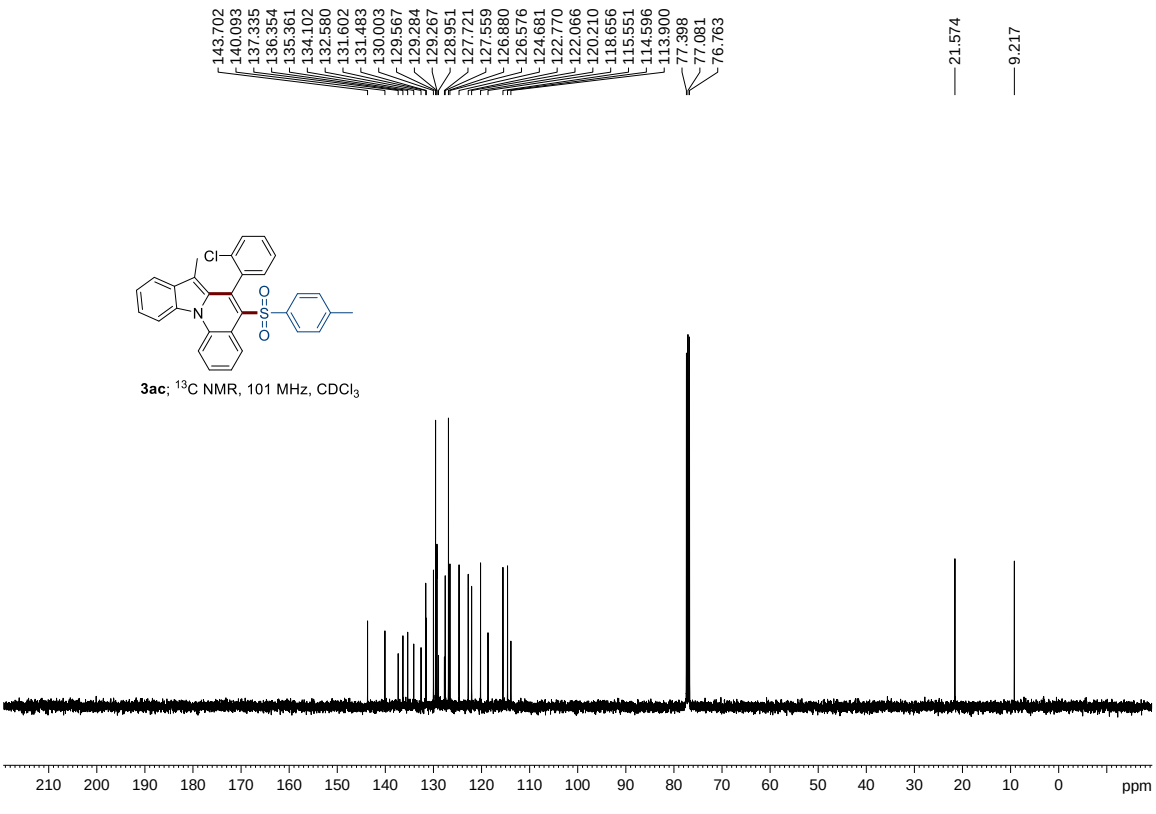


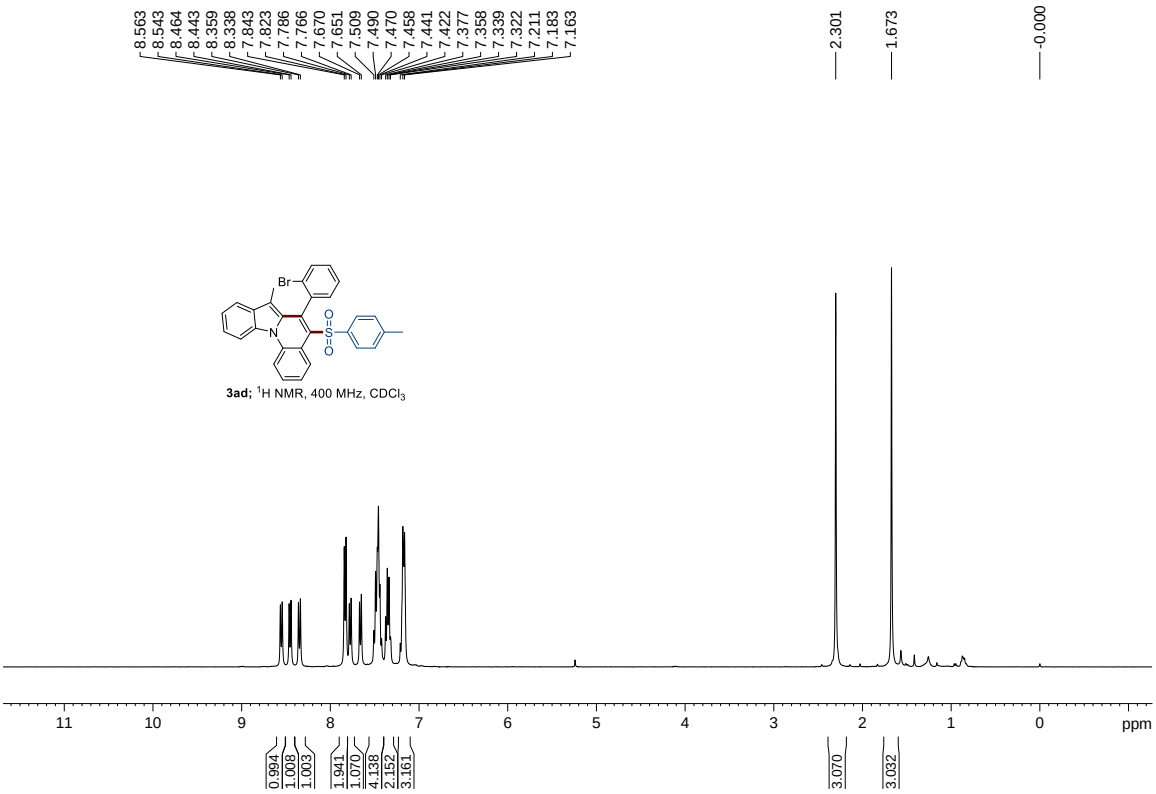
3ab; ^{13}C NMR, 101MHz, $CDCl_3$

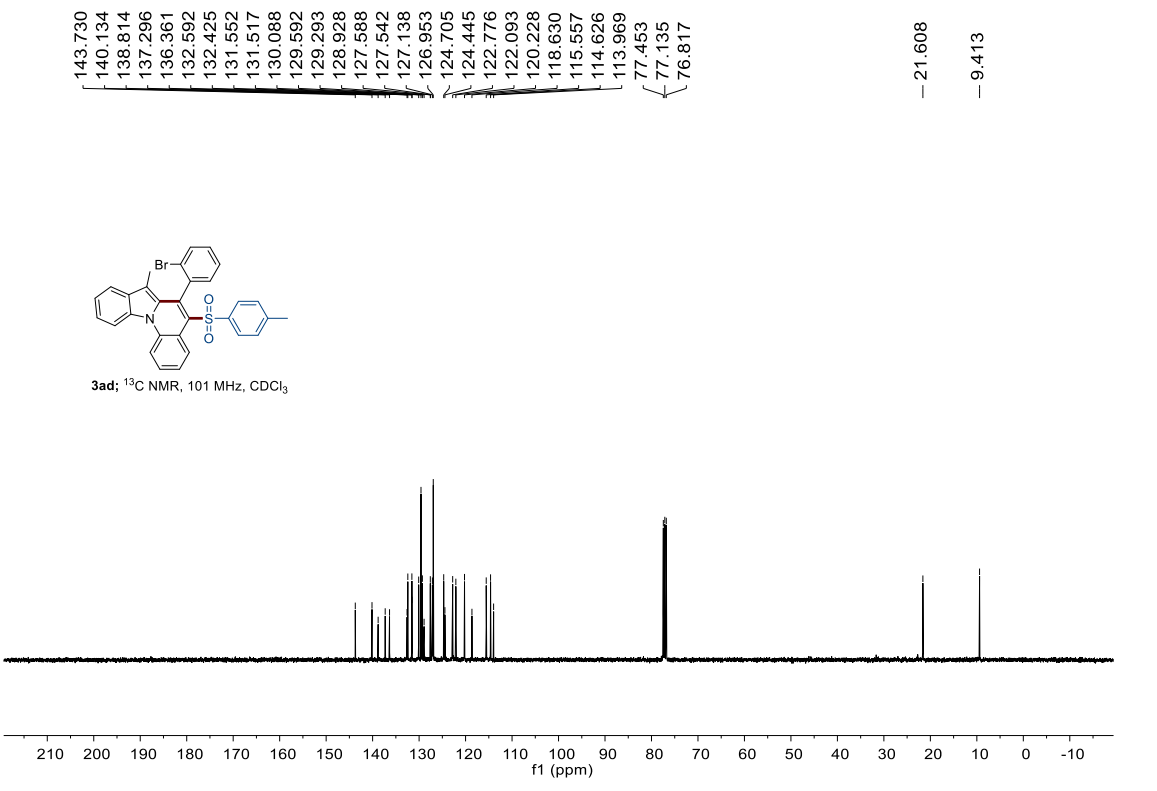


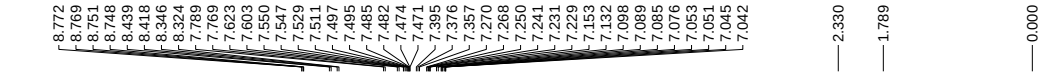
3ab; ^{19}F NMR, 376MHz, $CDCl_3$

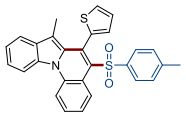

8.576
8.574
8.555
8.553
8.485
8.464
8.381
8.360
7.821
7.801
7.780
7.532
7.529
7.510
7.499
7.493
7.489
7.476
7.471
7.460
7.454
7.440
7.435
7.423
7.419
7.406
7.402
7.395
7.388
7.384
7.376
7.357
7.233
7.212
7.210
7.191
7.171
2.320
1.686
-0.000
Cl
N
O
S
O
3ac; 1H NMR, 400 MHz, CDCl3
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.997
0.963
0.974
2.931
7.142
2.974
2.924
2.913


143.702
140.093
137.335
136.354
135.361
134.102
132.580
131.602
131.483
130.003
129.567
129.284
129.267
128.951
127.721
127.559
126.880
126.576
124.681
122.770
122.066
120.210
118.656
115.551
114.596
113.900
77.398
77.081
76.763
21.574
9.217
Cl
N
O
S
O
3ac; 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

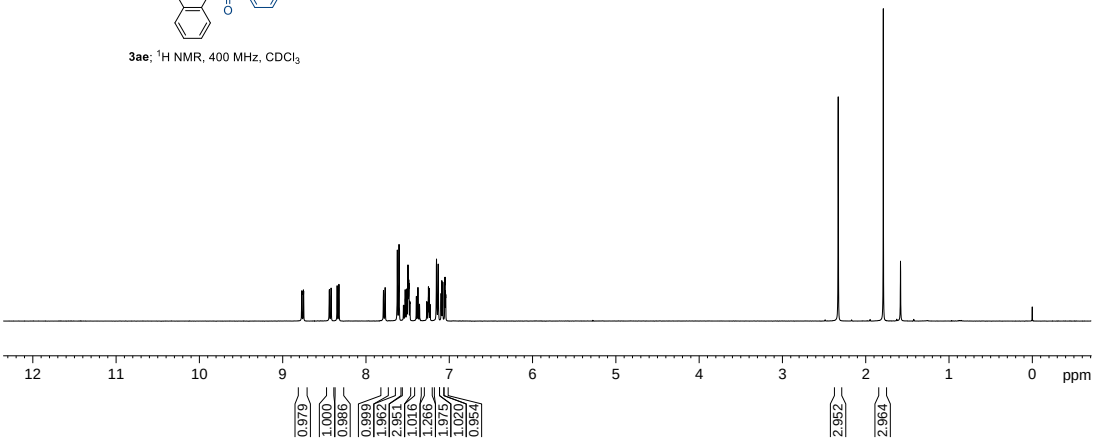

8.563
8.543
8.464
8.443
8.359
8.338
7.843
7.823
7.786
7.766
7.670
7.651
7.509
7.490
7.470
7.458
7.441
7.422
7.377
7.358
7.339
7.322
7.211
7.183
7.163
2.301
1.673
-0.000
Br
O
S
O
N
3ad; 1H NMR, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.994
1.008
1.003
1.941
1.070
4.138
2.152
3.161
3.070
3.032

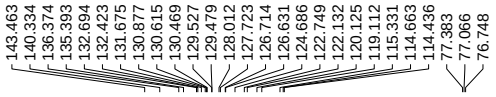

143.730
140.134
138.814
137.296
136.361
132.592
132.425
131.552
131.517
130.088
129.592
129.293
128.928
127.588
127.542
127.138
126.953
124.705
124.445
122.776
122.093
120.228
118.630
115.557
114.626
113.969
77.453
77.135
76.817
21.608
9.413
Br
O
S
O
N
3ad; 13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

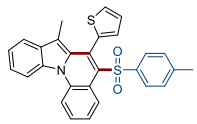




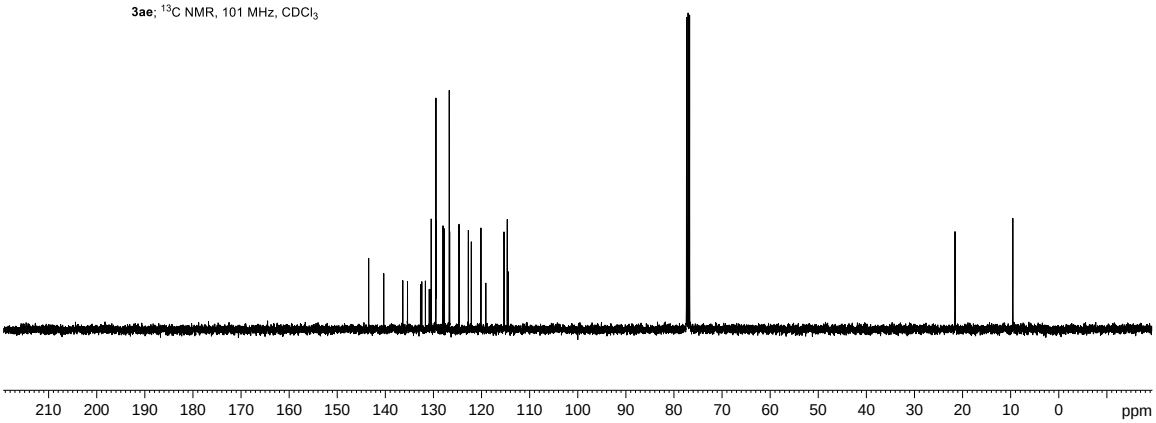
3ae; ^{1}H NMR, 400 MHz, $CDCl_3$

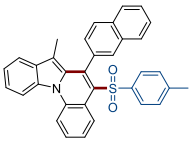




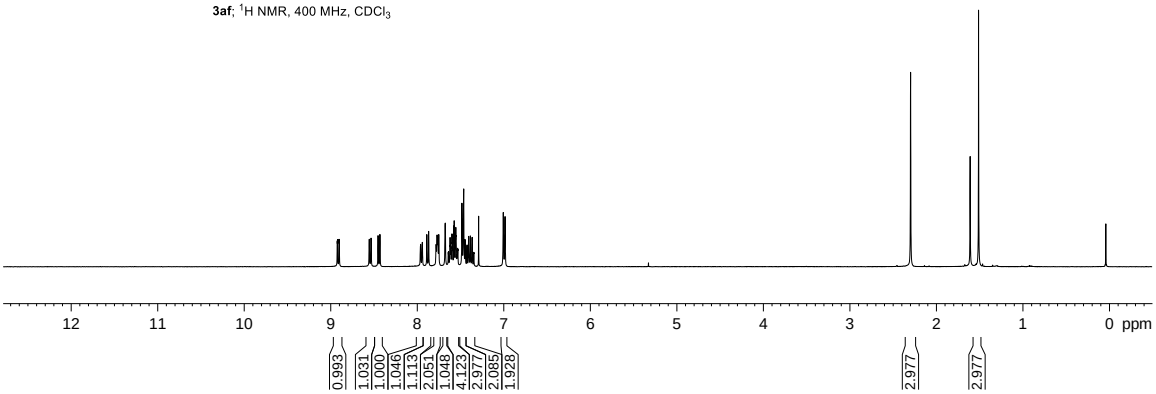


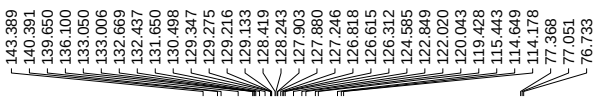
3ae; ^{13}C NMR, 101 MHz, $CDCl_3$

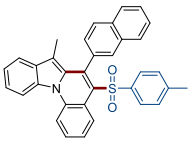




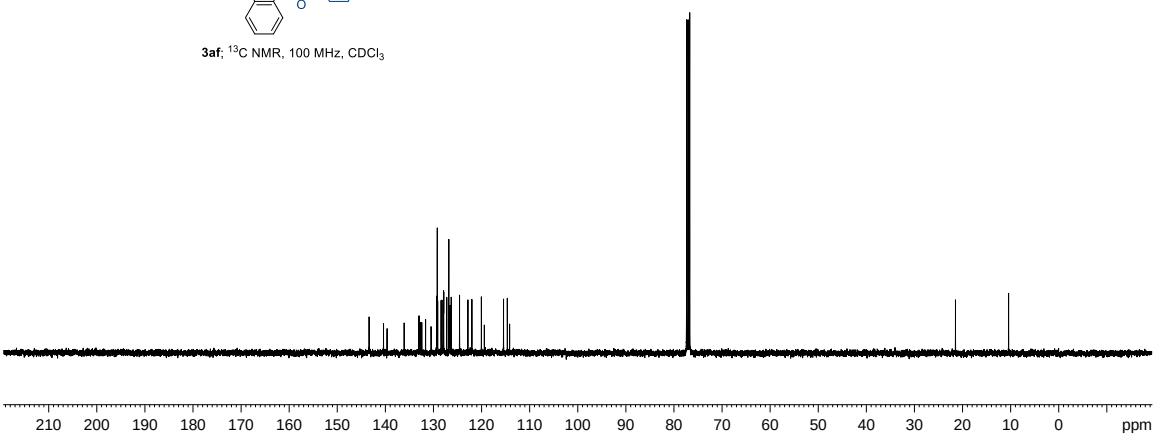
3af; ^{1}H NMR, 400 MHz, $CDCl_3$

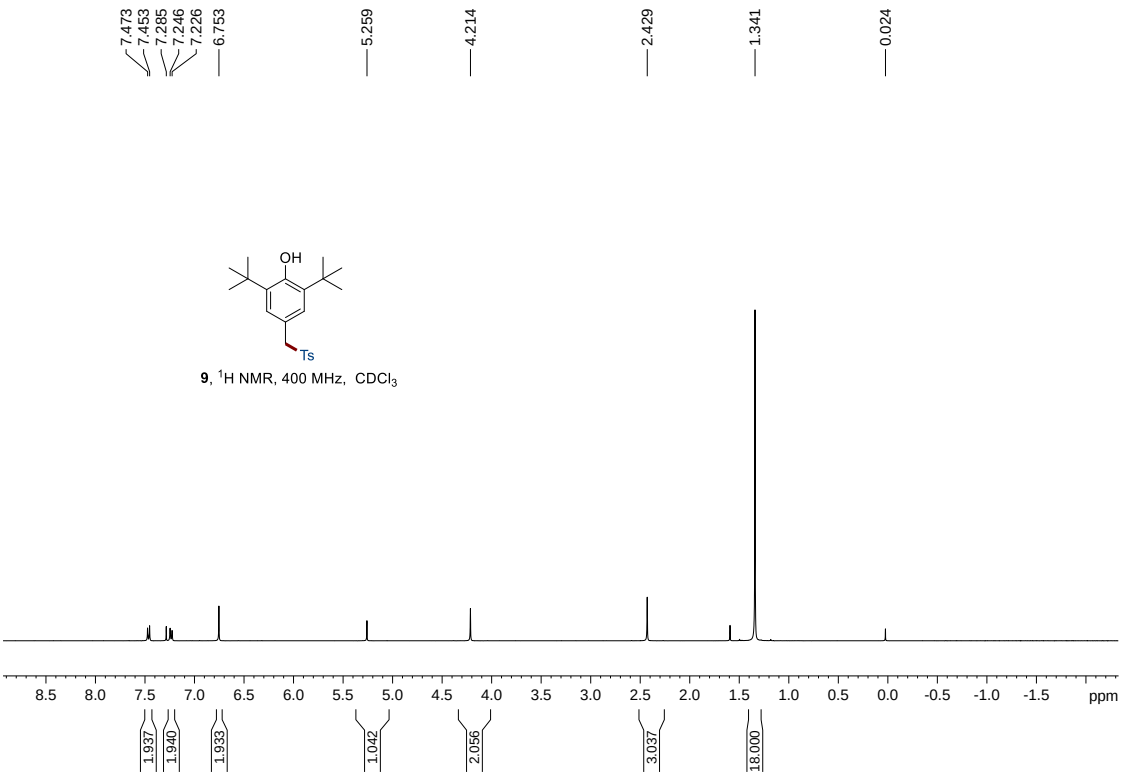




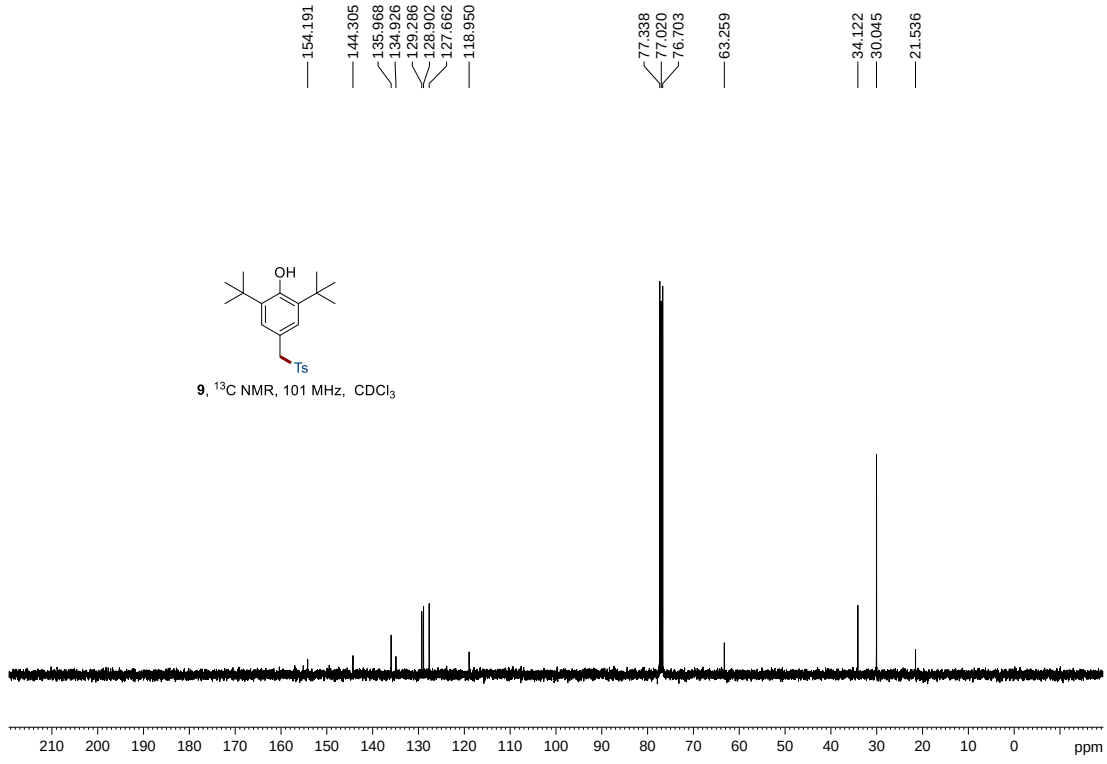


3af; ^{13}C NMR, 100 MHz, $CDCl_3$





9, ^{1}H NMR, 400 MHz, $CDCl_3$



9, ^{13}C NMR, 101 MHz, $CDCl_3$

Table S2 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{30}H_{23}NO_2S$
Formula weight	461.55
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.3349(6)
b/Å	13.9186(7)
c/Å	16.1835(8)
α/°	67.849(5)
β/°	83.386(4)
γ/°	89.464(4)
Volume/Å^3	2347.4(2)
Z	4
ρ_{calc}g/cm^3	1.306
μ/mm^{-1}	1.442
F(000)	968.0
Crystal size/mm^3	0.2 × 0.15 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.862 to 134.156
Index ranges	$-8 \le h \le 13$, $-16 \le k \le 16$, $-19 \le l \le 17$
Reflections collected	17329
Independent reflections	8385 [R_{int} = 0.0331, R_{sigma} = 0.0485]
Data/restraints/parameters	8385/52/624
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1373
Final R indexes [all data]	R_1 = 0.0736, wR_2 = 0.1566
Largest diff. peak/hole / e Å^{-3}	0.27/-0.31

Table S3 Crystal data and structure refinement for 3z.

Identification code	**3z**
Empirical formula	$C_{31}H_{25}NO_2S$
Formula weight	475.58
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.3570(6)
b/Å	8.1337(4)
c/Å	14.8816(8)
α/°	90
β/°	108.017(2)
γ/°	90
Volume/Å^3	1192.16(11)
Z	2
ρ_{calc}g/cm^3	1.325
μ/mm^{-1}	0.166
F(000)	500.0
Crystal size/mm^3	0.2 × 0.2 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.136 to 55.156
Index ranges	$-13 \leq h \leq 13$, $-10 \leq k \leq 10$, $-19 \leq l \leq 19$
Reflections collected	23659
Independent reflections	5521 [R_{int} = 0.0487, R_{sigma} = 0.0477]
Data/restraints/parameters	5521/31/307
Goodness-of-fit on F^2	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.1072, wR_2 = 0.2598
Final R indexes [all data]	R_1 = 0.1416, wR_2 = 0.2842
Largest diff. peak/hole / e Å^{-3}	1.04/-0.65
Flack parameter	0.19(3)