Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

An Electrolyte- and Catalyst-Free Electrooxidative Sulfonylation of Imidazo[1,2-a]pyridines

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1. General Information

Solvents were dried and degassed by standard methods before they were used. Commercial grade reagents were used without further purification except as indicated below. Imidazo[1,2-*a*]pyridines were synthesized according to the method in the literature.[1] Sodium sulfinates (**2a**-**2b**, **2e**, **2f**, **2k**) were purchased from commercial suppliers and (**2c-2d**, **2g**-**2j**) were prepared according to the method in the literature.[2] 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 Nickel plate electrode (10 mm × 10 mm × 0.2 mm). Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum plates with F-254 indicator, visualized by irradiation with UV light. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro$^+$ and Digital Single Channel Adjustable Automatic Electronic Pipette Micropipette dPettee$^+$ were purchased from Dragon Laboratory Instruments Limited. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. ^{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 NMR spectra, the chemical shifts δ are reported relative to $CFCl_3$ (δ= 0 ppm) as internal standard. High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionization (ESI). The Cyclic voltammetry (CV) was recorded in CH_3CN by CHI650A. The UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 35 Spectrometer and the fluorescence emission spectra were recorded using a F-4500 FL spectrophotometer. The X-ray single crystal structure is determined by the Oxford Diffraction Xcalibur CCD single crystal diffractometer.

2. Experimental Procedure

General procedure for the electrochemical synthesis of 2-phenyl-3-tosylimidazo[1,2-a]pyridine

Compounds **1** (0.3 mmol), **2** (0.9 mmol, 3.0 equiv.) and MeCN:H_2O (2:1, 7 mL) were added in a three-necked flask (10 mL). The reaction mixture was electrolyzed with a C|Ni electrode at a constant current of 5 mA in an undivided cell under air at room temperature for 9 hours. After electrolysis, the reaction mixture was extracted with ethyl acetate, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude products were purified through silica gel column chromatography using dichloromethane/ethyl acetate (30:1, v/v) as eluent to give the corresponding product.

Experimental setup

3. Cyclic Voltammetry Experiments

Cyclic voltammetry was measured under Ar balloon protection with conventional three-electrode system (Reference electrode: Ag/AgCl, working electrode: Glassy carbon, counter electrode: Pt wire, Supporting electrolyte: 0.1 M $TBAPF_6$ in CH_3CN)

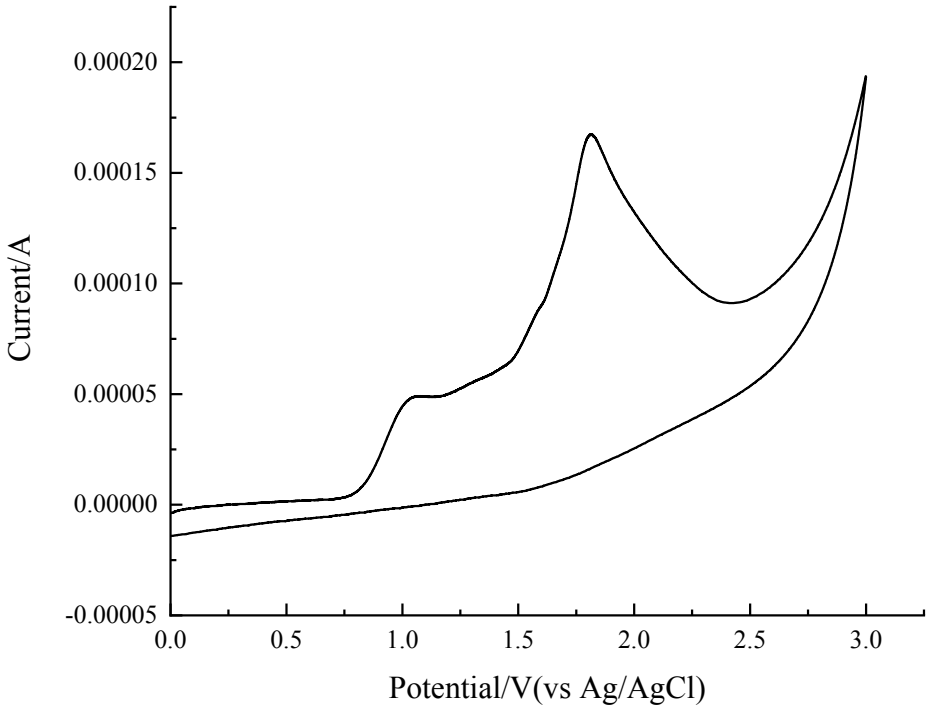
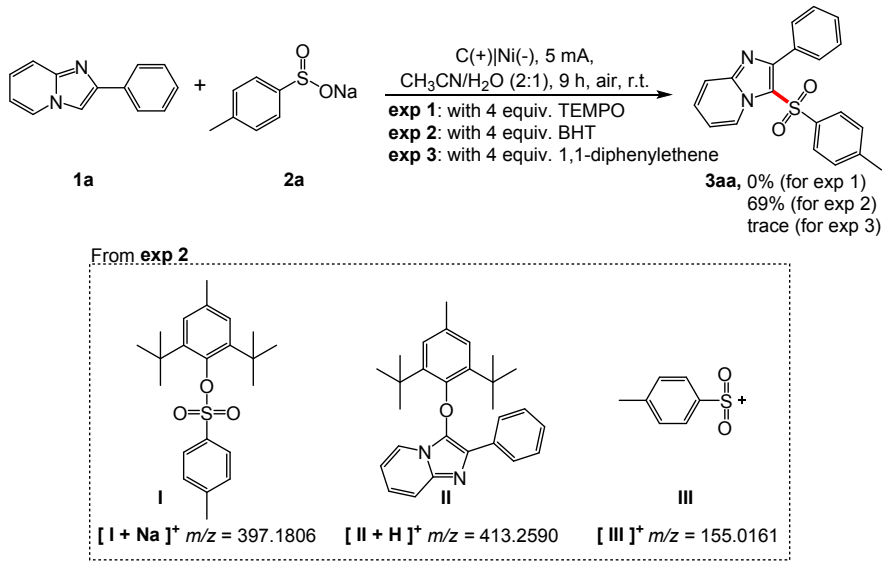


Figure S1. Cyclic voltammograms of sodium naphthalene-2-sulfinate (**2h**) in CH_3CN at 100 mV/s scan rates.

4. Control Experiments



Scheme S1. Control experiments.

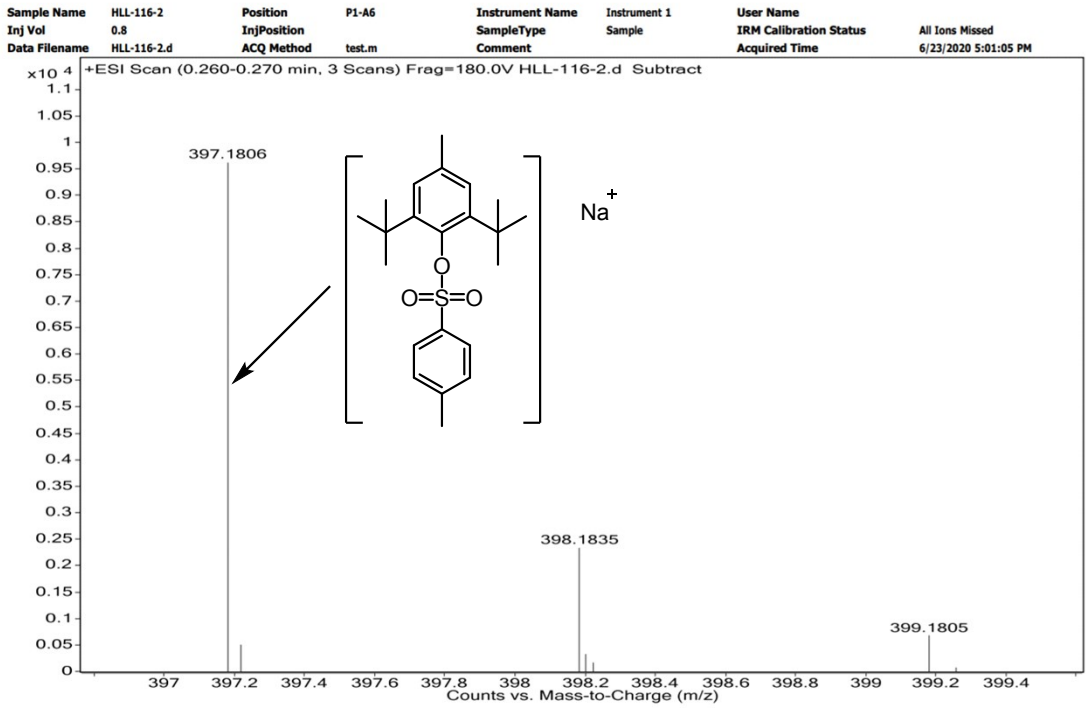


Figure S2. HRMS spectrum of compound **[I + Na]**+ for exp 2

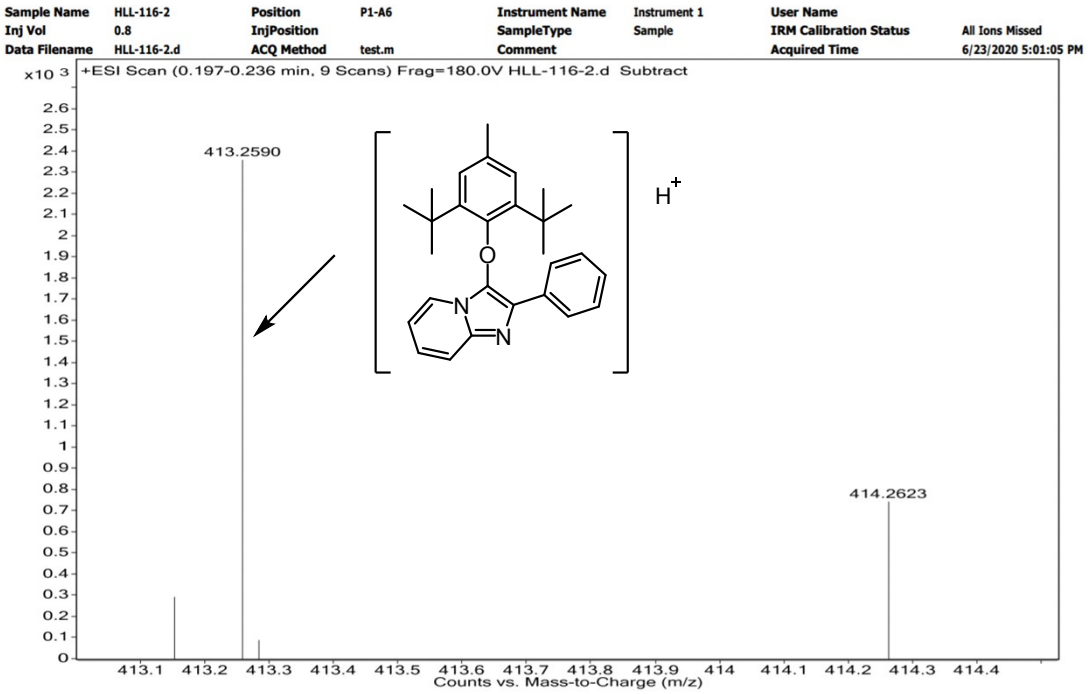


Figure S3. HRMS spectrum of compound **[II + H]**$^{+}$ for exp 2

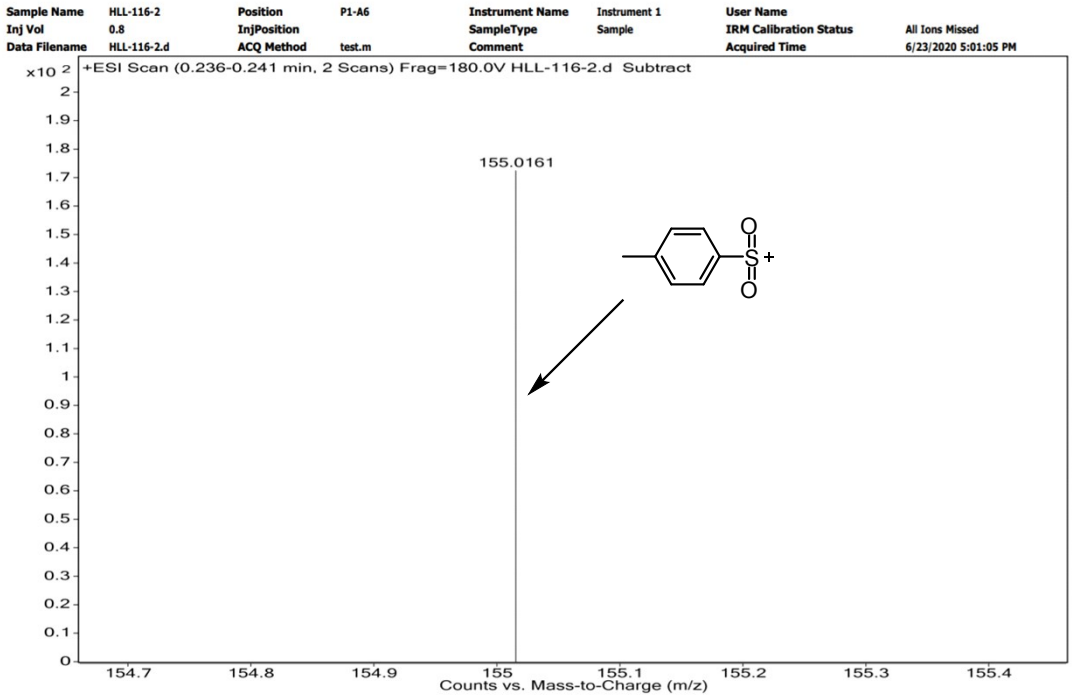


Figure S4. HRMS spectrum of compound **[III]**$^{+}$ for exp 2

5. Optical spectroscopy data

(1) The UV/Vis absorption spectra were recorded in CH_3CN of a $1x10^{-5}$ M solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

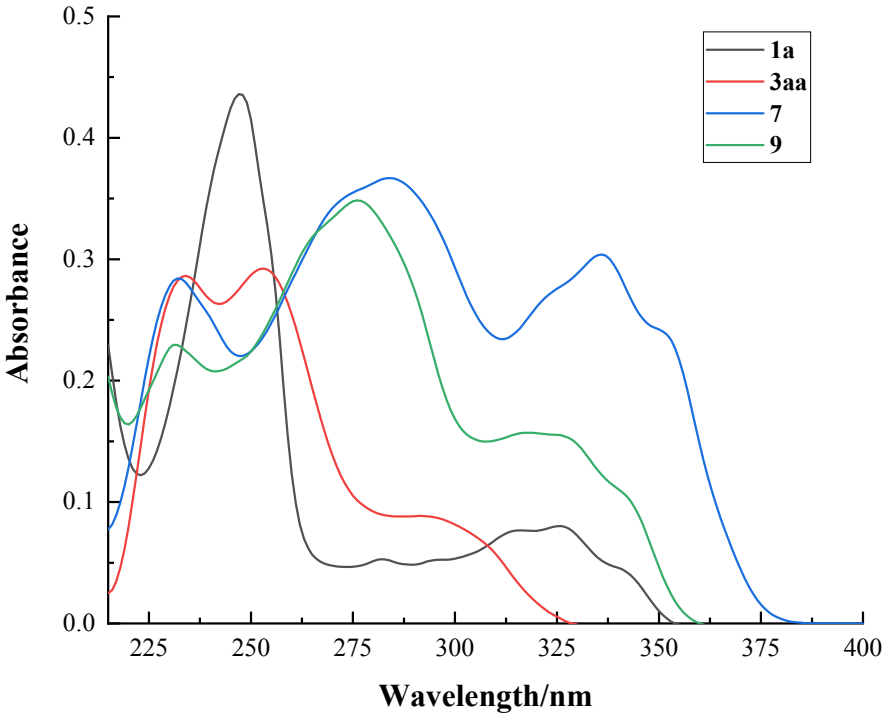


Figure S5. Absorption spectra of **1a**, **3aa**, **7** and **9** in CH_3CN

(2) Fluorescence emission spectra were recorded using a F-4500 FL spectrophotometer in CH_3CN.

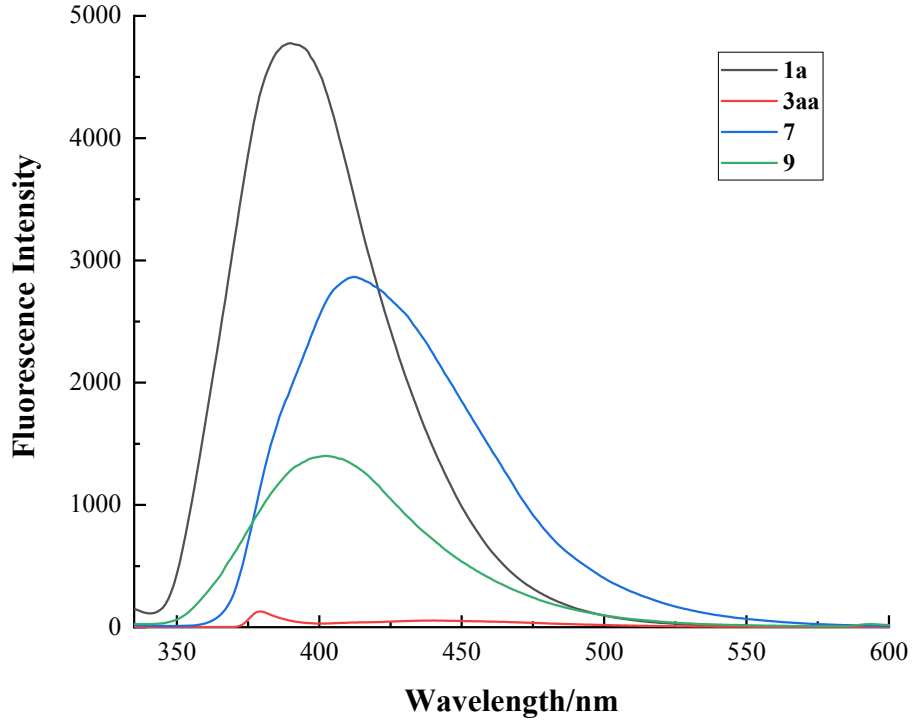


Figure S6. Fluorescence emission spectra of **1a**, **3aa**, **7** and **9** in CH_3CN

(3) The fluorescence quantum yields of the different samples were calculated using quinine sulfate (QY = 0.55) as the standard (in 0.1 M H_2SO_4).[3]

Table S1. Absorption, emission and fluorescence quantum yields (ΦF) of compounds **1a**, **3aa**, **7** and **9**

	λ_{abs} (nm)	λ_{em} (nm)	ΦF
1a	247, 326	389	0.43
3aa	234, 253, 291	440	0.006
7	232, 284, 336	411	0.16
9	231, 276, 317	402	0.08

6. Computational Details

All the calculations were performed using M06-2X method[4] and def2-TZVP(D) basis sets[5] with the Gaussian 16 program package.[6] The polarizable continuum model (PCM)[7] was employed to consider the solvent effect of CH_3CN/H_2O. The intrinsic reaction coordinate (IRC) analysis was carried out to confirm that all the saddle point connected the correct reactant and product on the potential energy surface. With the help of Multiwfn 3.7-dew[8] and VMD version 1.9.3 programs,[9] we drawn and analysed **TS** and the Electrostatic potential (ESP) map of **1a**.

1a

Sum of electronic and zero-point Energies= -610.691638
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Sum of electronic and thermal Free Energies= -610.729207

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C	-3.03382465	1.35265674	-0.05258306
N	-1.83582048	0.69024859	-0.02532515
C	-1.74914617	-0.69543301	0.02670916
C	-2.95047621	-1.44168992	0.05515284
C	-0.55158116	1.16895774	-0.04178485
C	0.25913043	0.05710660	0.00148961
N	-0.48635788	-1.08724595	0.04237687
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H	-5.12856632	1.16010159	-0.04769686
H	-2.98445191	2.43056378	-0.09393232
H	-2.88539199	-2.51961605	0.09694935
H	-0.34687084	2.22366282	-0.08762617
H	1.82124144	-2.11169959	-0.10861391
H	4.29360812	-2.19662757	-0.11396906
H	5.60517163	-0.09909505	-0.00558533
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2k

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C	-1.77302800	-0.00001200	0.82658100
H	-2.39244200	0.89386700	0.77100800
H	-2.39243200	-0.89389800	0.77101100
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A

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B

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C

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C	-0.43784100	0.34699000	-0.70333300
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C	4.73589600	-0.61925100	-0.24198600
C	4.05868500	-1.59355800	0.48790000
C	2.67732600	-1.60542900	0.53037700
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O	0.74526100	2.61316800	0.14107300
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H	2.15198000	-2.36531000	1.09264200
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H	-0.75421900	2.24754300	2.58296400
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C	1.88111900	-0.68632200	-0.19812700
C	2.56981500	0.20500200	-1.02484000
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3ak

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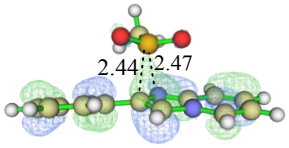
TS1



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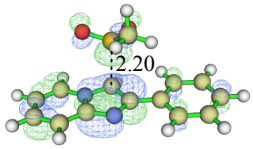
C	-1.73536900	-0.36988200	0.80956400
C	-2.92968000	-0.00932300	1.47094700
C	-0.54001300	-1.28953200	-0.82636100
C	0.29322100	-0.65616800	0.08326500
N	-0.47984900	-0.06784700	1.09614400
C	1.75185900	-0.71392400	0.16753100
C	2.50781100	-1.10035800	-0.94050700
C	3.88842700	-1.14350400	-0.85355500
C	4.52392400	-0.79981200	0.33505000
C	3.77464700	-0.41409400	1.43866800
C	2.39080300	-0.37049800	1.35911600
S	-0.07939900	1.64894000	-0.63217000
O	1.01513900	1.62258100	-1.53322000
O	-1.43543100	1.66612300	-1.04747600
H	-5.04294300	-0.17081600	1.43160300
H	-5.08555900	-1.52018700	-0.66512800
H	-2.94838300	-2.10028500	-1.80814500
H	-2.86184900	0.57643000	2.37602200
H	-0.33092500	-1.85604900	-1.71690600
H	2.01904600	-1.35257400	-1.87305100
H	4.47142700	-1.44132500	-1.71460000
H	5.60345600	-0.83397500	0.39938300
H	4.26720100	-0.15125900	2.36520900
H	1.79863400	-0.08564300	2.21894100
C	0.27713900	2.66726700	0.76737600
H	1.17770100	2.26052100	1.22142500
H	0.45335700	3.65656100	0.34173200
H	-0.58344700	2.62814800	1.42564000

TS2



Sum of electronic and zero-point Energies= -1199.143520
Sum of electronic and thermal Energies= -1199.127510
Sum of electronic and thermal Enthalpies= -1199.126566
Sum of electronic and thermal Free Energies= -1199.190167

C	-3.94758200	-1.74097100	0.19896800
C	-4.05545100	-0.63222300	-0.68211300
C	-2.93679000	0.01851100	-1.08836500
N	-1.72126600	-0.42465900	-0.65474500
C	-1.57200000	-1.50593200	0.20134600
C	-2.72860900	-2.17376700	0.63965000
C	-0.45349200	0.12114400	-0.86931600
C	0.42137300	-0.82717300	-0.22589100
N	-0.28581500	-1.74580200	0.45590300
C	1.87149500	-0.76906500	-0.22500900
C	2.54800900	0.27736600	-0.86343100
C	3.93310200	0.33168700	-0.84486900
C	4.66362500	-0.65289800	-0.19095500
C	3.99850500	-1.69506000	0.44822700
C	2.61591500	-1.75488900	0.43444600
H	-4.84660200	-2.24747300	0.52226000
H	-5.01948500	-0.29461100	-1.03044500
H	-2.93223000	0.87640900	-1.74379100
H	-2.61931300	-3.01468100	1.30881600
H	-0.25528700	0.61374700	-1.81400900
H	1.99273800	1.05918800	-1.36775500
H	4.44342300	1.14666600	-1.34129100
H	5.74466900	-0.60862900	-0.17743500
H	4.56334900	-2.46368500	0.95972700
H	2.09365700	-2.56215000	0.92997000
S	-0.44483600	1.99368900	0.29149900
O	0.37573100	2.98228500	-0.39497000
O	-1.83144700	2.34077100	0.57496200
C	0.34141400	1.60170000	1.84162700
H	0.28276500	2.50420400	2.44877400
H	-0.20686300	0.78337200	2.30368200
H	1.37476000	1.32682100	1.64356100

H_2O

Sum of electronic and zero-point Energies=			-76.412226
Sum of electronic and thermal Energies=			-76.409391
Sum of electronic and thermal Enthalpies=			-76.408447
Sum of electronic and thermal Free Energies=			-76.429870
O	0.00000000	0.00000000	0.11737400
H	0.00000000	-0.76221000	-0.46949600
H	0.00000000	0.76221000	-0.46949600

H-cation

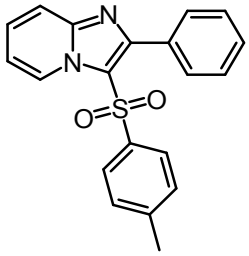
Sum of electronic and zero-point Energies=			-0.163351
Sum of electronic and thermal Energies=			-0.161935
Sum of electronic and thermal Enthalpies=			-0.160991
Sum of electronic and thermal Free Energies=			-0.173351
H	0.00000000	0.00000000	0.00000000

OH-anion

Sum of electronic and zero-point Energies=			-75.916164
Sum of electronic and thermal Energies=			-75.913804
Sum of electronic and thermal Enthalpies=			-75.912860
Sum of electronic and thermal Free Energies=			-75.932410
O	0.00000000	0.00000000	0.10682400
H	0.00000000	0.00000000	-0.85459600

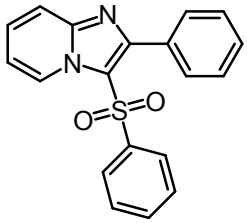
7. Characterization Data

2-phenyl-3-tosylimidazo[1,2-a]pyridine (3aa)[10,11,12]



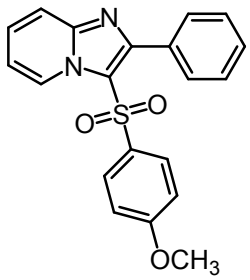
White solid (84.9 mg, 81%). mp. 137.2-138.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (dt, J_1 = 7.09 Hz, J_2 = 1.10 Hz, 1H), 7.77-7.69 (m, 3H), 7.55-7.50 (m, 2H), 7.49-7.41 (m, 4H), 7.14 (d, J = 8.07 Hz, 2H), 7.05 (td, J_1 = 6.97 Hz, J_2 = 1.22 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 146.6, 144.4, 139.0, 132.7, 130.5, 129.7, 129.3, 128.5, 127.8, 126.8, 126.4, 118.0, 117.8, 114.6, 21.5. HRMS (ESI) calcd. for $C_{20}H_{16}N_2O_2S$ $(M+H)^+$: 349.1005, found: 349.1006.

2-phenyl-3-(phenylsulfonyl)imidazo[1,2-a]pyridine (3ab)[10,12,13]



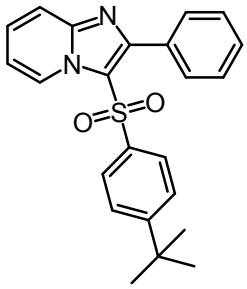
White solid (80.3 mg, 80%). mp. 123.9-124.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (d, J = 7.03 Hz, 1H), 7.73 (d, J = 8.03 Hz, 3H), 7.63 (d, J = 7.78 Hz, 2H), 7.47 (br. s., 5H), 7.38-7.31 (m, 2H), 7.07 (t, J = 6.78 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 146.7, 141.9, 133.4, 132.5, 130.5, 129.4, 129.1, 128.6, 127.8, 126.9, 126.3, 118.0, 117.4, 114.7. HRMS (ESI) calcd. for $C_{19}H_{14}N_2O_2S$ $(M+H)^+$: 335.0849, found: 335.0850.

3-((4-methoxyphenyl)sulfonyl)-2-phenylimidazo[1,2-a]pyridine (3ac)[10]



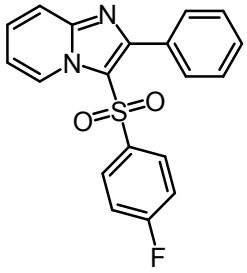
White solid (88.2mg, 81%). mp. 138.7-139.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (d, J = 7.03 Hz, 1H), 7.77-7.72 (m, 2H), 7.70 (d, J = 9.03 Hz, 1H), 7.60-7.55 (m, 2H), 7.48-7.40 (m, 4H), 7.03 (td, J_1 = 7.03 Hz, J_2 = 1.00 Hz, 1H), 6.81-6.76 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 152.3, 146.4, 133.4, 132.7, 130.5, 129.3, 128.7, 128.4, 127.8, 126.8, 118.2, 117.9, 114.6, 114.3, 55.6. HRMS (ESI) calcd. for $C_{20}H_{16}N_2O_3S$ $(M+H)^+$: 365.0954, found: 365.0955.

3-((4-(tert-butyl)phenyl)sulfonyl)-2-phenylimidazo[1,2-a]pyridine (3ad)[12]



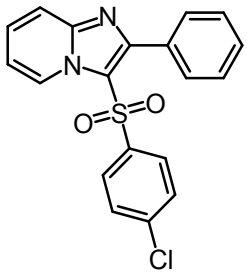
White solid (88.3 mg, 75%). mp. 149.9-150.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (d, J = 7.03 Hz, 1H), 7.76-7.70 (m, 3H), 7.57 (d, J = 8.53 Hz, 2H), 7.49-7.43 (m, 4H), 7.35 (d, J = 8.78 Hz, 2H), 7.06 (td, J_1 = 6.90 Hz, J_2 = 1.00 Hz, 1H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 152.7, 146.6, 138.9, 132.7, 130.5, 129.3, 128.5, 127.8, 126.9, 126.3, 126.1, 118.0, 117.9, 114.6, 35.2, 30.9. HRMS (ESI) calcd. for $C_{23}H_{22}N_2O_2S$ $(M+H)^+$: 391.1475, found: 391.1474.

3-((4-fluorophenyl)sulfonyl)-2-phenylimidazo[1,2-a]pyridine (3ae)[10,12]



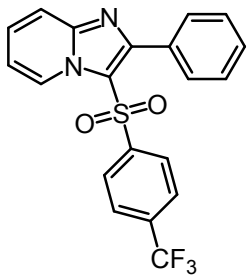
White solid (88.6mg, 84%). mp. 125.5-127.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (d, J = 7.03 Hz, 1H), 7.77-7.68 (m, 3H), 7.65-7.58 (m, 2H), 7.52-7.42 (m, 4H), 7.08 (t, J = 7.03 Hz, 1H), 7.03-6.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 164.2, 153.1, 146.7, 138.0, 132.4, 130.5, 129.5, 129.2, 128.7, 127.9, 126.8, 118.1, 117.4, 116.4, 116.2, 114.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.67. HRMS (ESI) calcd. for $C_{19}H_{13}FN_2O_2S$ $(M+H)^+$: 353.0755, found: 353.0756.

3-((4-chlorophenyl)sulfonyl)-2-phenylimidazo[1,2-a]pyridine (3af)[10,11]



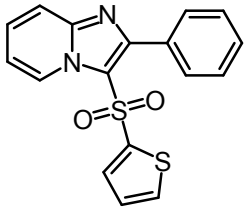
White solid (47.7 mg, 43%). mp. 120.2-121.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (d, J = 6.78 Hz, 1H), 7.79-7.66 (m, 3H), 7.57-7.41 (m, 6H), 7.29 (d, J = 8.28 Hz, 2H), 7.09 (t, J = 6.78 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 146.8, 140.4, 140.0, 132.3, 130.5, 129.6, 129.3, 128.8, 127.9, 127.8, 126.8, 118.1, 117.2, 114.9. HRMS (ESI) calcd. for $C_{19}H_{13}ClN_2O_2S$ $(M+H)^+$: 369.0459, found: 369.0460.

2-phenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)imidazo[1,2-a]pyridine (3ag)[10,12]



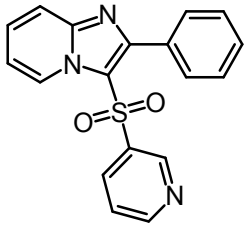
White solid (106 mg, 87%). mp. 137.6-138.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (d, J = 7.03 Hz, 1H), 7.77-7.67 (m, 5H), 7.58 (d, J = 8.28 Hz, 2H), 7.53-7.43 (m, 4H), 7.10 (t, J = 6.90 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 147.0, 145.4, 135.0, 134.7, 132.3, 130.5, 129.7, 129.1, 128.0, 126.8, 126.2, 124.4, 121.6, 118.2, 116.6, 115.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.28. HRMS (ESI) calcd. for $C_{20}H_{13}F_3N_2O_2S$ $(M+H)^+$: 403.0723.0738, found: 403.0722.

2-phenyl-3-(thiophen-2-ylsulfonyl)imidazo[1,2-a]pyridine (3ai)



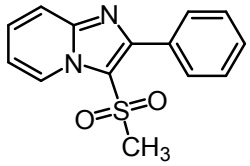
White solid (97.7 mg, 95%). mp. 186.8-187.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (d, J = 7.03 Hz, 1H), 7.81-7.72 (m, 3H), 7.53-7.43 (m, 6H), 7.09 (td, J_1 = 7.03 Hz, J_2 = 1.00 Hz, 1H), 6.95 (dd, J_1 = 4.89 Hz, J_2 = 3.89 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 146.7, 143.4, 133.2, 132.6, 132.3, 130.5, 129.4, 128.8, 127.8, 127.6, 126.9, 118.1, 117.8, 114.8. HRMS (ESI) calcd. for $C_{17}H_{12}N_2O_2S_2$ $(M+H)^+$: 341.0413, found: 341.0416.

2-phenyl-3-(pyridin-3-ylsulfonyl)imidazo[1,2-a]pyridine (3aj)



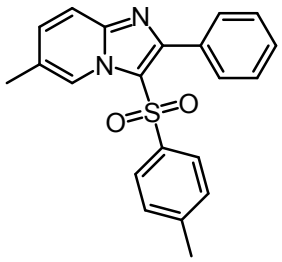
Yellow solid (88.9 mg, 88%). mp. 130.8-131.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22-9.14 (m, 1H), 8.84 (s, 1H), 8.71-8.63 (m, 1H), 7.81-7.67 (m, 4H), 7.54-7.42 (m, 4H), 7.27-7.22 (m, 1H), 7.15-7.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 147.3, 147.0, 138.5, 133.9, 132.2, 130.5, 129.7, 129.1, 128.0, 126.8, 123.6, 118.2, 116.8, 115.1. HRMS (ESI) calcd. for $C_{18}H_{13}N_3O_2S$ $(M+H)^+$: 336.0801, found: 336.0805.

3-(methylsulfonyl)-2-phenylimidazo[1,2-a]pyridine (3ak)



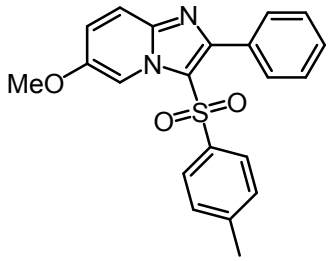
White solid (66.5 mg, 81%). mp. 186.9-187.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (d, J = 7.03 Hz, 1H), 7.91-7.85 (m, 2H), 7.78 (d, J = 9.03 Hz, 1H), 7.53-7.46 (m, 4H), 7.08 (t, J = 6.78 Hz, 1H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 146.5, 132.4, 130.2, 129.6, 128.6, 128.3, 127.1, 118.0, 117.0, 114.7, 45.0. HRMS (ESI) calcd. for $C_{14}H_{12}N_2O_2S$ $(M+H)^+$: 273.0692, found: 273.0689.

6-methyl-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3ba)



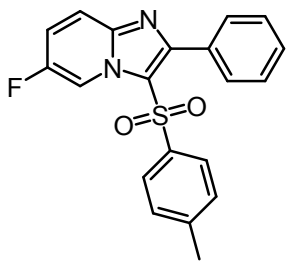
White solid (99.3 mg, 91%). mp. 148.7-149.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 7.74-7.68 (m, 2H), 7.61 (d, J = 9.29 Hz, 1H), 7.52 (d, J = 8.28 Hz, 2H), 7.47-7.42 (m, 3H), 7.29 (dd, J_1 = 9.16 Hz, J_2 = 1.38 Hz, 1H), 7.14 (d, J = 8.03 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 145.6, 144.3, 139.2, 132.8, 131.5, 130.5, 129.6, 129.2, 127.7, 126.4, 124.6, 117.3, 117.2, 21.5, 18.6. HRMS (ESI) calcd. for $C_{21}H_{18}N_2O_2S$ $(M+H)^+$: 363.1162, found: 363.1164.

6-methoxy-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3ca)



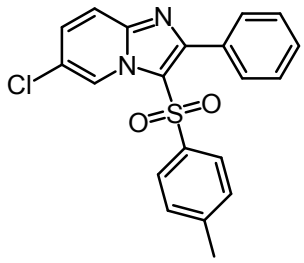
White solid (81.7 mg, 72%). mp. 174.8-175.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H) 7.72 (d, J = 4.02 Hz, 2H), 7.58 (d, J = 9.79 Hz, 1H), 7.51 (d, J = 8.03 Hz, 2H), 7.44 (d, J = 3.51 Hz, 3H), 7.21 (dd, J_1 = 9.54 Hz, J_2 = 1.76 Hz, 1H), 7.13 (d, J = 7.78 Hz, 2H), 3.91 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 150.4, 144.4, 143.4, 139.0, 132.8, 130.5, 129.6, 129.2, 127.7, 126.4, 123.2, 118.2, 117.9, 108.9, 56.4, 21.5. HRMS (ESI) calcd. for $C_{21}H_{18}N_2O_3S$ $(M+H)^+$: 379.1111, found: 379.1113.

6-fluoro-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3da)



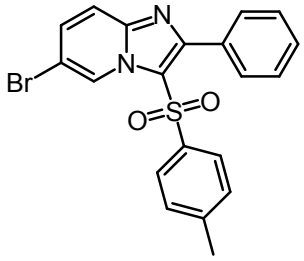
White solid (93.0 mg, 85%). mp. 144.1-145.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (dd, J_1 = 4.64 Hz, J_2 = 2.13 Hz, 1H), 7.74-7.65 (m, 3H), 7.51 (d, J = 8.53 Hz, 2H), 7.48-7.42 (m, 3H), 7.36 (ddd, J_1 = 9.85 Hz, J_2 = 7.47 Hz, J_3 = 2.51 Hz, 1H), 7.14 (d, J = 8.28 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 153.4, 152.8, 144.7, 144.1, 138.7, 132.4, 130.4, 129.8, 129.5, 127.9, 126.4, 120.4, 120.1, 119.2, 118.4, 114.5, 114.1, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -135.38. HRMS (ESI) calcd. for $C_{20}H_{15}FN_2O_2S$ $(M+H)^+$: 367.0911, found: 367.0912.

6-chloro-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3ea)



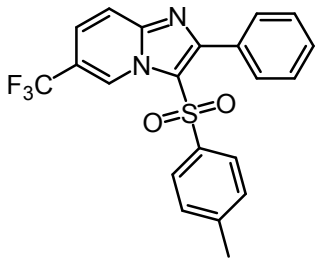
White solid (76.0 mg, 66%). mp. 173.7-174.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (d, J = 1.00 Hz, 1H), 7.71 (dd, J_1 = 7.65 Hz, J_2 = 1.63 Hz, 2H), 7.65 (d, J = 9.54 Hz, 1H), 7.52-7.40 (m, 6H), 7.15 (d, J = 8.03 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 144.8, 144.7, 138.7, 132.2, 130.5, 129.8, 129.5, 127.9, 126.5, 124.8, 122.9, 118.6, 118.2, 21.6. HRMS (ESI) calcd. for $C_{20}H_{15}ClN_2O_2S$ $(M+H)^+$: 383.0616, found: 383.0614.

6-bromo-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3fa)



White solid (56.3 mg, 44%). mp. 174.2-174.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.31 (s, 1H), 7.67-7.74 (m, 2H), 7.62-7.57 (m, 1H), 7.53-7.42 (m, 6H), 7.15 (d, J = 8.28 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 144.9, 144.7, 138.7, 132.2, 131.9, 130.5, 129.8, 129.5, 127.9, 126.9, 126.5, 118.5, 109.4, 21.6. HRMS (ESI) calcd. for $C_{20}H_{15}BrN_2O_2S$ $(M+H)^+$: 427.0110, found: 427.0110.

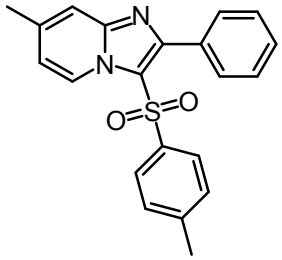
2-phenyl-3-tosyl-6-(trifluoromethyl)imidazo[1,2-a]pyridine (3ga)



White solid (52.4 mg, 42%). mp. 169.5-170.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.81 (d, J = 9.29 Hz, 1H), 7.76-7.70 (m, 2H), 7.60 (d, J = 9.54 Hz, 1H), 7.53-7.44 (m, 5H), 7.15 (d, J =

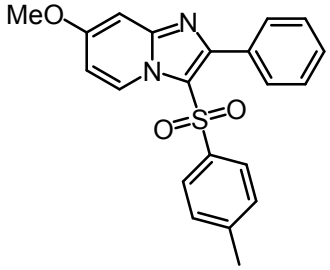
8.03 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 146.2, 145.0, 138.4, 131.9, 130.5, 129.8, 127.9, 126.6, 126.0, 124.5, 124.3, 121.8, 119.6, 119.0, 118.7, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.01. HRMS (ESI) calcd. for $C_{21}H_{15}F_3N_2O_2S$ $(M+H)^+$: 417.0879, found: 417.0881.

7-methyl-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3ha)



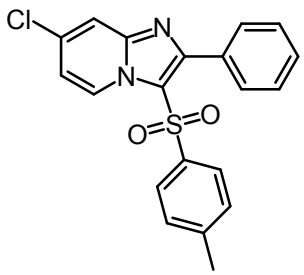
White solid (100.5 mg, 92%). mp. 157.6-158.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (d, J = 7.03 Hz, 1H), 7.77-7.71 (m, 2H), 7.51 (d, J = 8.28 Hz, 2H), 7.48-7.42 (m, 4H), 7.12 (d, J = 8.03 Hz, 2H), 6.87 (dd, J_1 = 7.15 Hz, J_2 = 1.63 Hz, 1H), 2.44 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 147.0, 144.2, 140.1, 139.2, 132.7, 130.5, 129.7, 129.3, 127.7, 126.3, 125.9, 117.1, 116.5, 21.5, 21.4. HRMS (ESI) calcd. for $C_{21}H_{18}N_2O_2S$ $(M+H)^+$: 363.1162, found: 363.1164.

7-methoxy-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3ia)



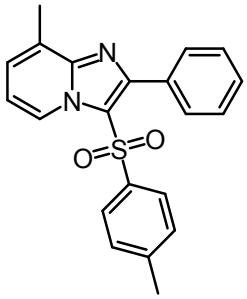
White solid (100.1 mg, 88%). mp. 159.2-160.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, J = 7.53 Hz, 1H), 7.79-7.73 (m, 2H), 7.53-7.42 (m, 5H), 7.13 (d, J = 8.28 Hz, 2H), 6.95 (d, J = 2.51 Hz, 1H), 6.71 (dd, J_1 = 7.65 Hz, J_2 = 2.38 Hz, 1H), 3.86 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 153.2, 148.7, 144.2, 139.4, 132.7, 130.5, 129.7, 129.3, 127.7, 127.2, 126.2, 116.5, 109.1, 95.5, 55.8, 21.5. HRMS (ESI) calcd. for $C_{21}H_{18}N_2O_3S$ $(M+H)^+$: 379.1111, found: 379.1109.

7-chloro-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3ja)[11]



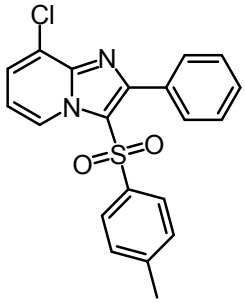
White solid (51.1 mg, 42%). mp. 179.5-180.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (d, J = 7.53 Hz, 1H), 7.71 (dd, J_1 = 7.53 Hz, J_2 = 6.02 Hz, 3H), 7.52-7.43 (m, 5H), 7.13 (d, J = 8.03 Hz, 2H), 7.03 (dd, J_1 = 7.28 Hz, J_2 = 1.51 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 146.4, 144.7, 138.8, 135.4, 132.2, 130.5, 129.8, 129.6, 127.9, 127.2, 126.4, 118.3, 116.9, 116.1, 21.5. HRMS (ESI) calcd. for $C_{20}H_{15}ClN_2O_2S$ $(M+H)^+$: 383.0616, found: 383.0620.

8-methyl-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3ka)



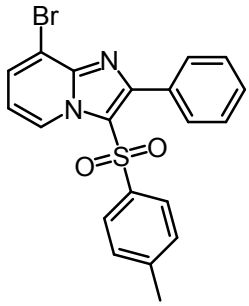
White solid (98.0 mg, 90%). mp. 161.5-162.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (d, J = 6.78 Hz, 1H), 7.76-7.69 (m, 2H), 7.52 (d, J = 8.03 Hz, 2H), 7.48-7.42 (m, 3H), 7.23 (d, J = 7.03 Hz, 1H), 7.13 (d, J = 8.03 Hz, 2H), 6.95 (t, J = 6.90 Hz, 1H), 2.63 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 146.8, 144.2, 139.2, 133.0, 130.6, 129.6, 129.2, 128.1, 127.8, 127.3, 126.4, 124.5, 118.1, 114.6, 21.5, 17.1. HRMS (ESI) calcd. for $C_{21}H_{18}N_2O_2S$ $(M+H)^+$: 363.1162, found: 363.1166.

8-chloro-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3la)



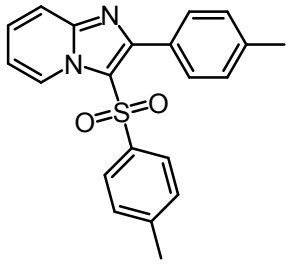
White solid (100.8 mg, 87%). mp. 151.7-152.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (d, J = 6.78 Hz, 1H), 7.72 (d, J = 6.27 Hz, 2H), 7.55-7.41 (m, 6H), 7.13 (d, J = 8.03 Hz, 2H), 7.00 (t, J = 7.15 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 144.7, 143.9, 138.7, 132.2, 130.7, 129.7, 129.5, 127.8, 127.3, 126.5, 125.5, 123.9, 119.8, 114.2, 21.5. HRMS (ESI) calcd. for $C_{20}H_{15}ClN_2O_2S$ $(M+H)^+$: 383.0616, found: 383.0619.

8-bromo-2-phenyl-3-tosylimidazo[1,2-a]pyridine (3ma)



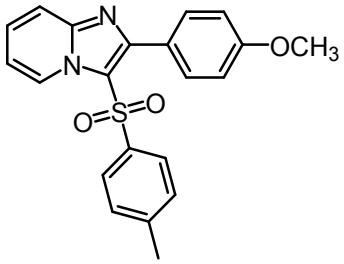
White solid (68.6 mg, 53%). mp. 180.4-181.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (d, J = 7.03 Hz, 1H), 7.74-7.67 (m, 3H), 7.51-7.42 (m, 5H), 7.13 (d, J = 8.28 Hz, 2H), 6.93 (t, J = 7.28 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 144.7, 144.4, 138.7, 132.3, 130.8, 129.7, 129.5, 127.8, 126.5, 126.1, 119.8, 114.5, 112.0, 21.5. HRMS (ESI) calcd. for $C_{20}H_{15}BrN_2O_2S$ $(M+H)^+$: 427.0110, found: 427.0107.

2-(p-tolyl)-3-tosylimidazo[1,2-a]pyridine (3na)



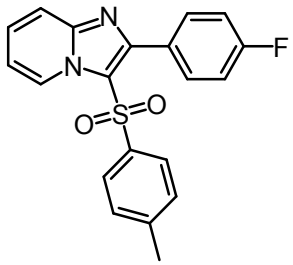
White solid (100.6 mg, 92%). mp. 188.4-189.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (dt, J_1 = 7.02 Hz, J_2 = 1.14 Hz, 1H), 7.70 (dt, J_1 = 9.00 Hz, J_1 = 1.14 Hz, 1H), 7.66 (d, J = 8.09 Hz, 2H), 7.54 (d, J = 8.39 Hz, 2H), 7.43 (ddd, J_1 = 8.96 Hz, J_2 = 6.98 Hz, J_3 = 1.30 Hz, 1H), 7.29-7.25 (m, 2H), 7.15 (d, J = 7.93 Hz, 2H), 7.03 (td, J_1 = 6.94 Hz, J_2 = 1.22 Hz, 1H), 2.44 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 146.5, 144.4, 139.4, 139.1, 130.5, 129.7, 129.6, 128.5, 126.8, 126.4, 117.9, 117.5, 114.5, 21.5. HRMS (ESI) calcd. for $C_{21}H_{18}N_2O_2S$ $(M+H)^+$: 363.1162, found: 363.1163.

2-(4-methoxyphenyl)-3-tosylimidazo[1,2-a]pyridine (3oa)



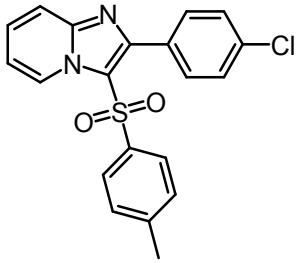
White solid (101.8 mg, 90%). mp. 137.2-138.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (d, J = 7.03 Hz, 1H), 7.74 (d, J = 8.78 Hz, 2H), 7.69 (d, J = 9.03 Hz, 1H), 7.53 (d, J = 8.28 Hz, 2H), 7.43 (t, J = 7.65 Hz, 1H), 7.14 (d, J = 8.03 Hz, 2H), 7.06-6.96 (m, 3H), 3.89 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 152.7, 146.6, 144.3, 139.1, 132.0, 129.7, 128.5, 126.8, 126.3, 124.9, 117.8, 117.2, 114.4, 113.3, 55.3, 21.5. HRMS (ESI) calcd. for $C_{21}H_{18}N_2O_3S$ $(M+H)^+$: 379.1111, found: 379.1109.

2-(4-fluorophenyl)-3-tosylimidazo[1,2-a]pyridine (3pa)



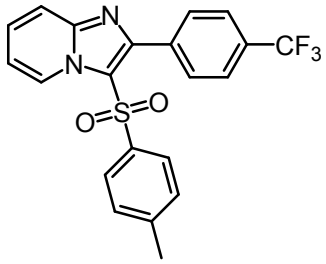
White solid (100.2 mg, 91%). mp. 171.3-172.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (d, J = 7.03 Hz, 1H), 7.79-7.74 (m, 2H), 7.70 (d, J = 9.03 Hz, 1H), 7.52 (d, J = 8.28 Hz, 2H), 7.49-7.43 (m, 1H), 7.20-7.12 (m, 4H), 7.06 (td, J_1 = 6.90, J_2 = 1.25 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 162.4, 151.7, 146.6, 144.5, 139.0, 132.6, 132.5, 129.8, 128.7, 128.6, 126.8, 126.3, 118.0, 117.8, 115.0, 114.8, 114.7, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.86. HRMS (ESI) calcd. for $C_{20}H_{15}FN_2O_2S$ $(M+H)^+$: 367.0911, found: 367.0915.

2-(4-chlorophenyl)-3-tosylimidazo[1,2-a]pyridine (3qa)



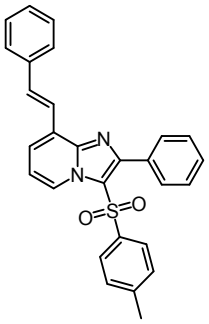
White solid (95 mg, 83%). mp. 177.8-178.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (d, J = 6.78 Hz, 1H), 7.76-7.68 (m, 3H), 7.53 (d, J = 8.03 Hz, 2H), 7.49-7.41 (m, 3H), 7.17 (d, J = 8.03 Hz, 2H), 7.06 (t, J = 6.78 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 146.6, 144.6, 138.9, 135.6, 131.9, 131.1, 129.8, 128.7, 128.1, 126.8, 126.4, 118.0, 117.9, 114.7, 21.5. HRMS (ESI) calcd. for $C_{20}H_{15}ClN_2O_2S$ $(M+H)^+$: 383.0616, found: 383.0620.

3-tosyl-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3ra)



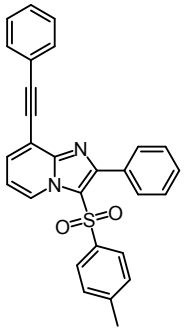
White (22.9 mg, 18%). mp. 201.9-202.2 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (d, J = 7.03 Hz, 1H), 7.89 (d, J = 8.03 Hz, 2H), 7.75-7.70 (m, 3H), 7.54 (d, J = 8.28 Hz, 2H), 7.51-7.45 (m, 1H), 7.17 (d, J = 8.03 Hz, 2H), 7.09 (td, J_1 = 6.96, J_2 = 1.13 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 146.7, 144.8, 138.7, 136.3, 131.3, 131.0, 129.9, 128.8, 126.8, 126.4, 125.5, 124.7, 122.8, 118.3, 118.1, 114.9, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.64. HRMS (ESI) calcd. for $C_{21}H_{15}F_3N_2O_2S$ $(M+H)^+$: 417.0879, found: 417.0881.

(E)-2-phenyl-8-styryl-3-tosylimidazo[1,2-a]pyridine (7)



White (90.1 mg, 73%). mp. 175.8-176.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (d, J = 6.6 Hz, 1H), 7.89-7.78 (m, 3H), 7.63-7.56 (m, 4H), 7.53 (d, J = 8.3 Hz, 2H), 7.51-7.46 (m, 3H), 7.38-7.32 (m, 2H), 7.30-7.24 (m, 1H), 7.13 (d, J = 8.1 Hz, 2H), 7.05 (t, J = 7.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 145.2, 144.4, 139.0, 136.9, 134.2, 132.9, 130.8, 129.7, 129.3, 128.7, 128.4, 127.8, 127.4, 127.2, 126.4, 124.9, 124.4, 122.3, 118.1, 114.7, 21.6. HRMS (ESI) calcd. for $C_{28}H_{22}N_2O_2S$ $(M+H)^+$: 451.1475, found: 451.1477.

2-phenyl-8-(phenylethynyl)-3-tosylimidazo[1,2-a]pyridine (9)



White (79.0 mg, 88%). mp. 151.6-152.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (dd, J_1 = 6.97 Hz, J_2 = 0.98 Hz, 1H), 7.82-7.77 (m, 2H), 7.65 (dd, J_1 = 7.21 Hz, J_2 = 0.98 Hz, 1H), 7.63-7.58 (m, 2H), 7.52-7.43 (m, 5H), 7.37-7.31 (m, 3H), 7.12 (d, J = 8.07 Hz, 2H), 7.04 (t, J = 7.09 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 146.2, 144.5, 138.8, 132.5, 132.1, 131.9, 130.9, 129.7, 129.4, 129.1, 128.3, 127.7, 126.4, 122.4, 118.6, 114.3, 114.1, 96.9, 83.4, 21.6. HRMS (ESI) calcd. for $C_{28}H_{20}N_2O_2S$ $(M+H)^+$: 449.1318, found: 449.1323.

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8. ^{1}H, ^{13}C and ^{19}F NMR Spectra

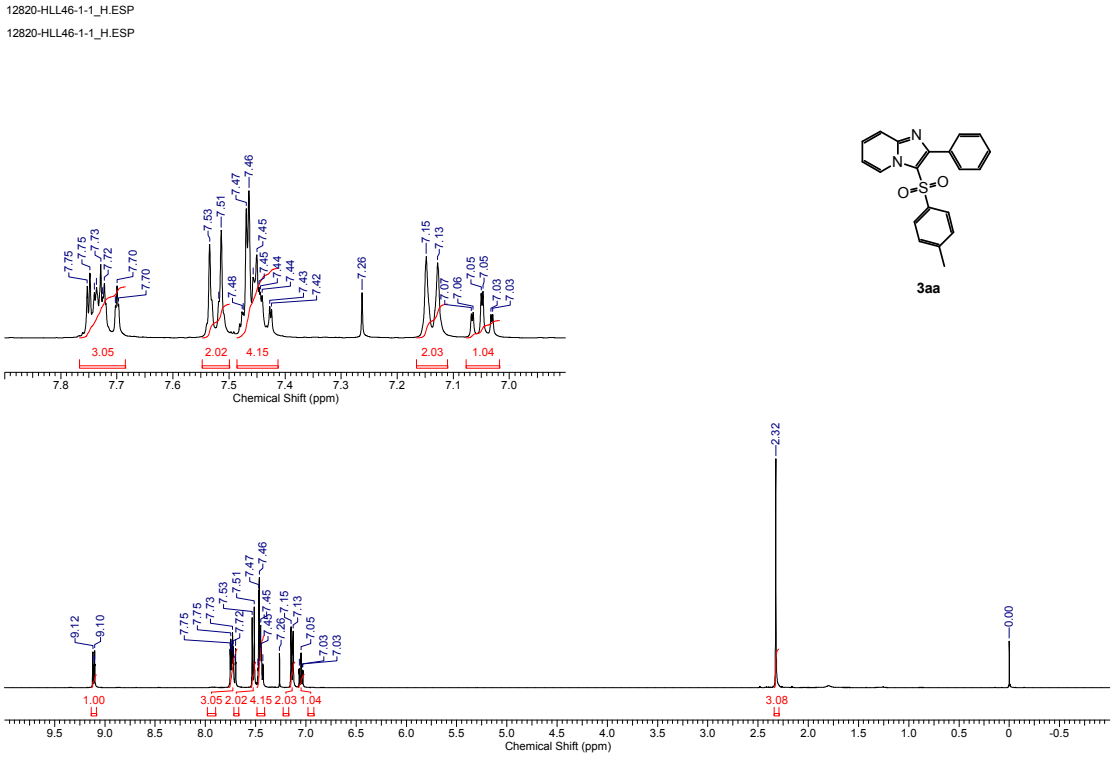

Figure S7. ^{1}H NMR spectrum of compound **3aa**

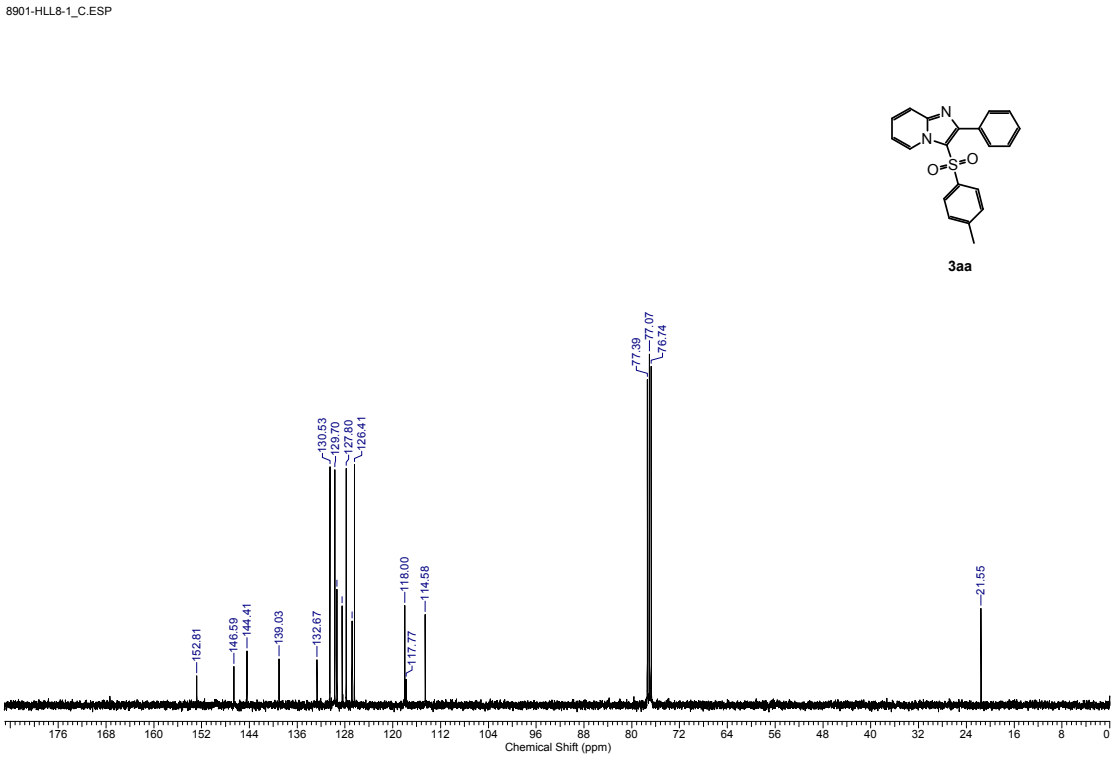

Figure S8. ^{13}C NMR spectrum of compound **3aa**

749-HLL97-1_H.ESP
749-HLL97-1_H.ESP

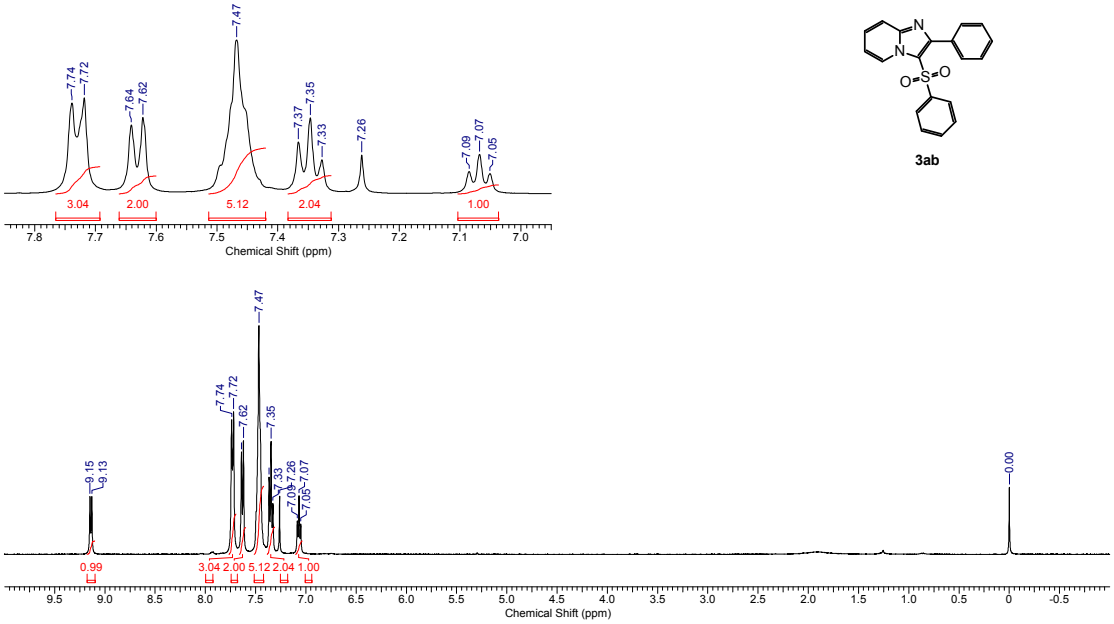

Figure S9. ^{1}H NMR spectrum of compound **3ab**

2021-HLL97-1-1_C.esp

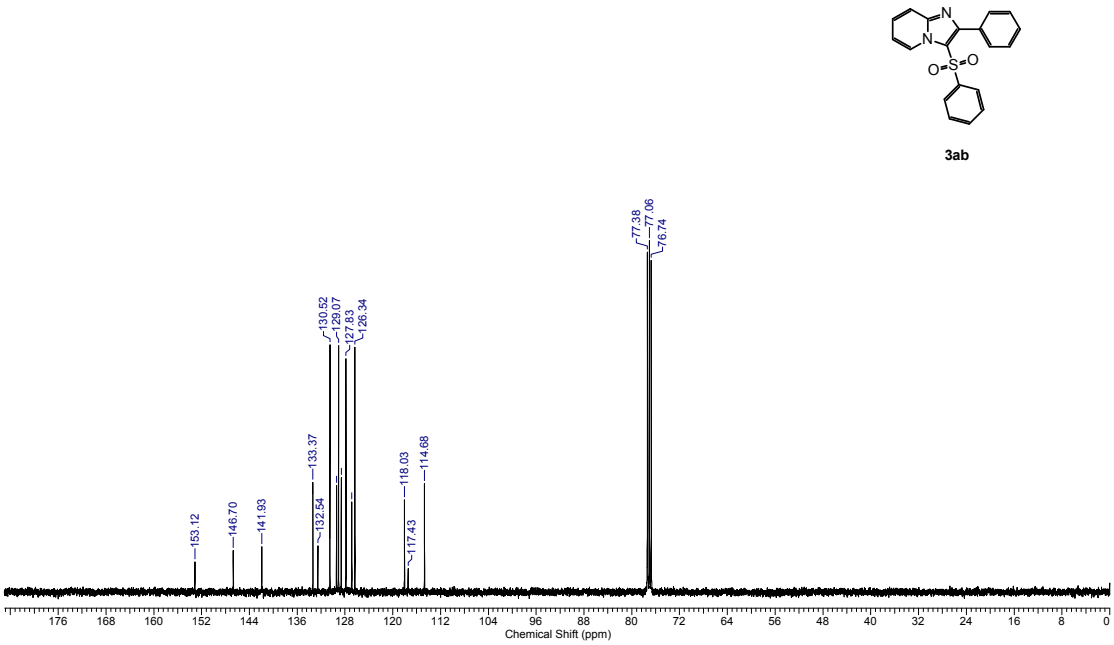

Figure S10. ^{13}C NMR spectrum of compound **3ab**

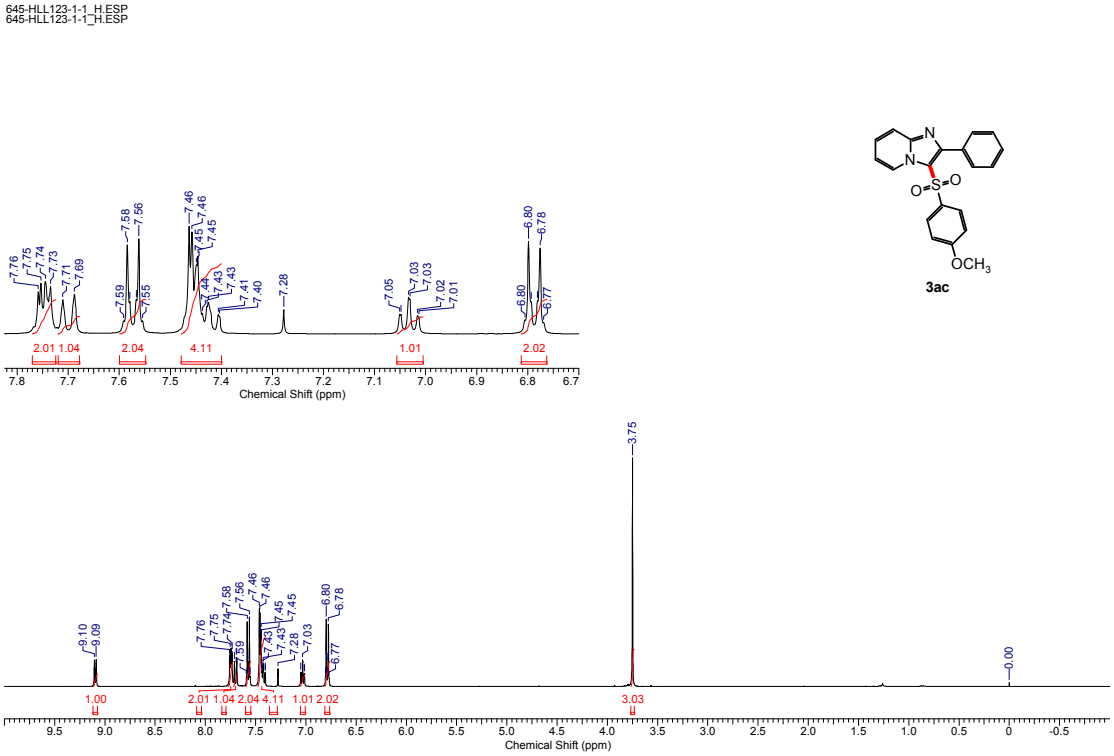

Figure S11. ^{1}H NMR spectrum of compound **3ac**

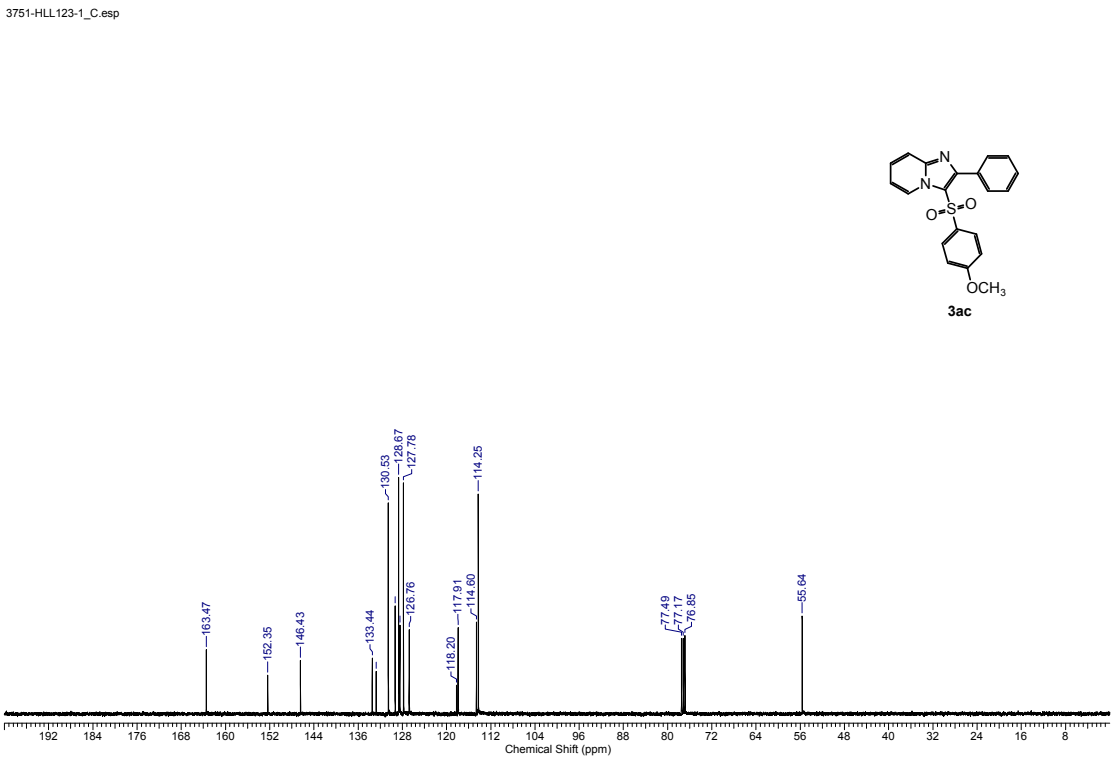

Figure S12. ^{13}C NMR spectrum of compound **3ac**

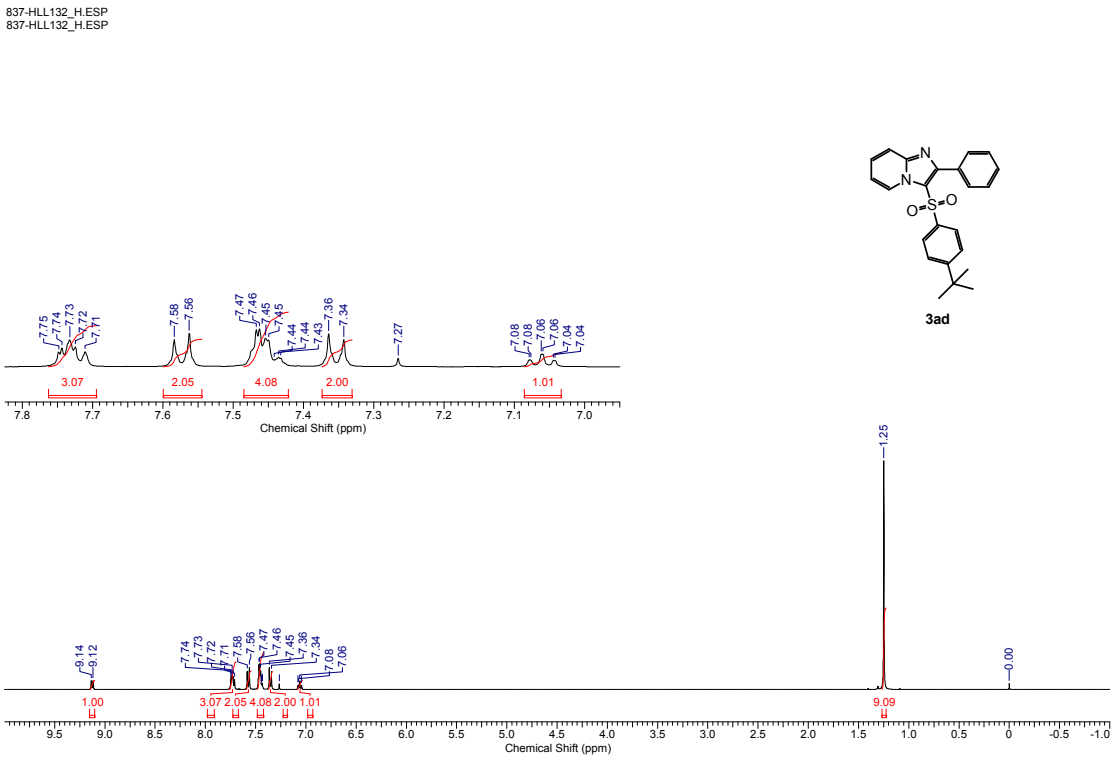

Figure S13. ^{1}H NMR spectrum of compound **3ad**

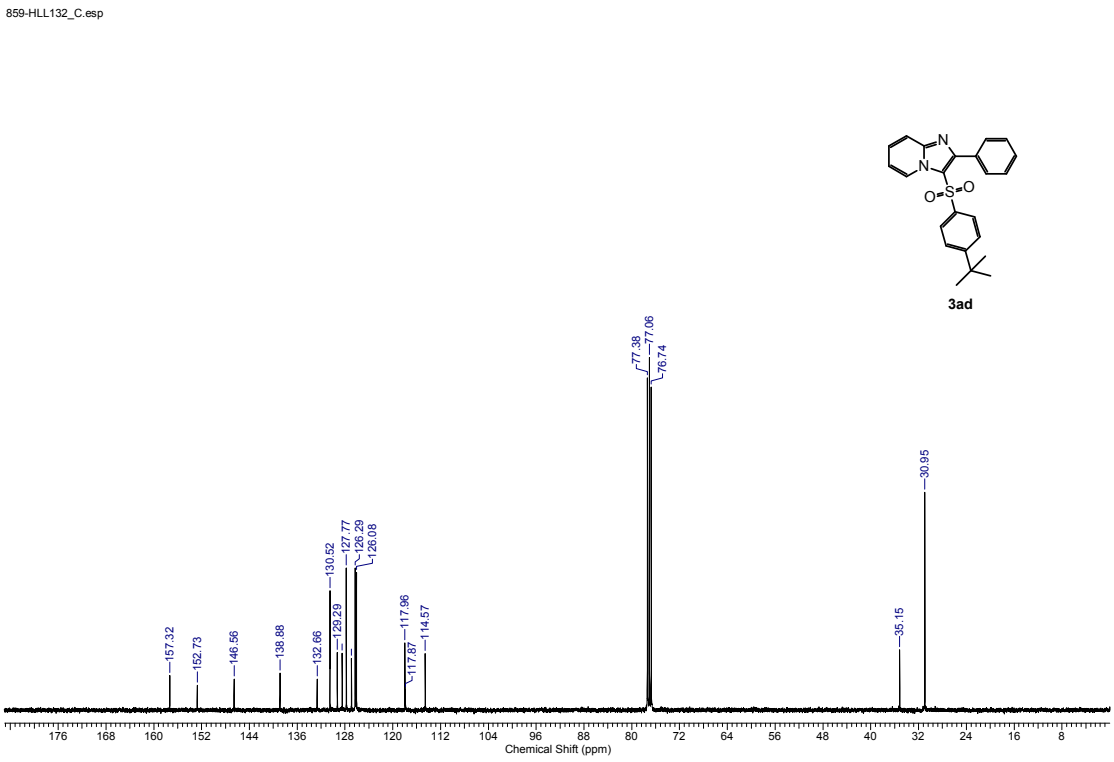

Figure S14 ^{13}C NMR spectrum of compound **3ad**

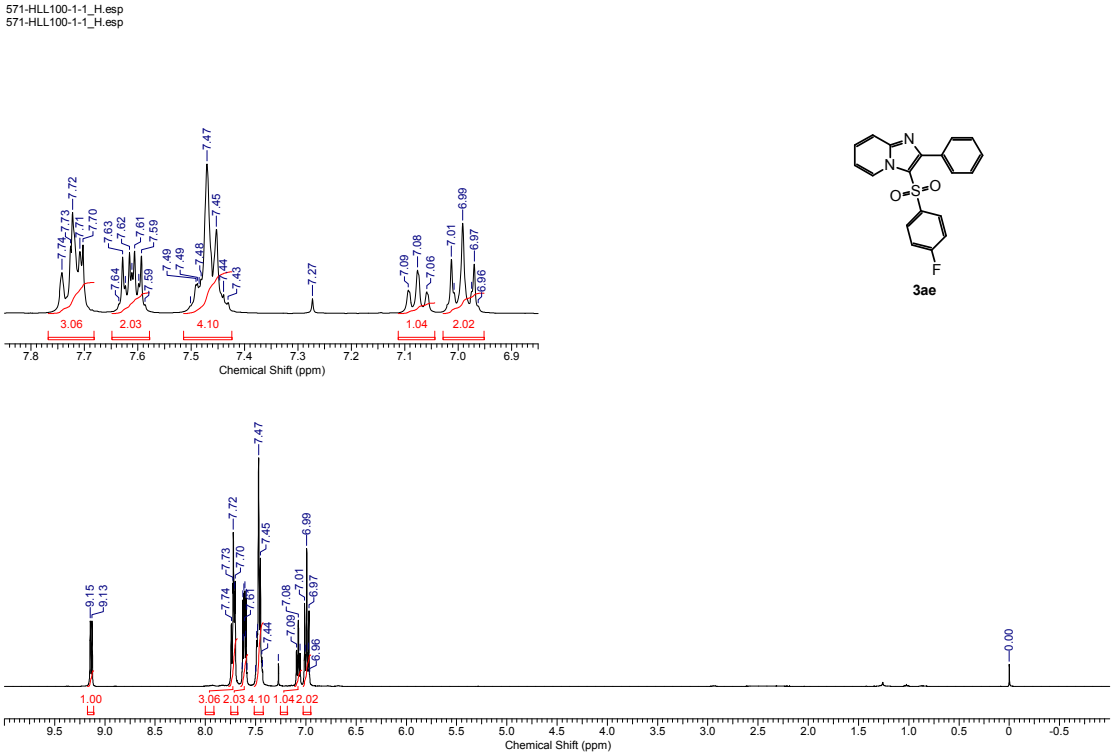

Figure S15. ^{1}H NMR spectrum of compound **3ae**

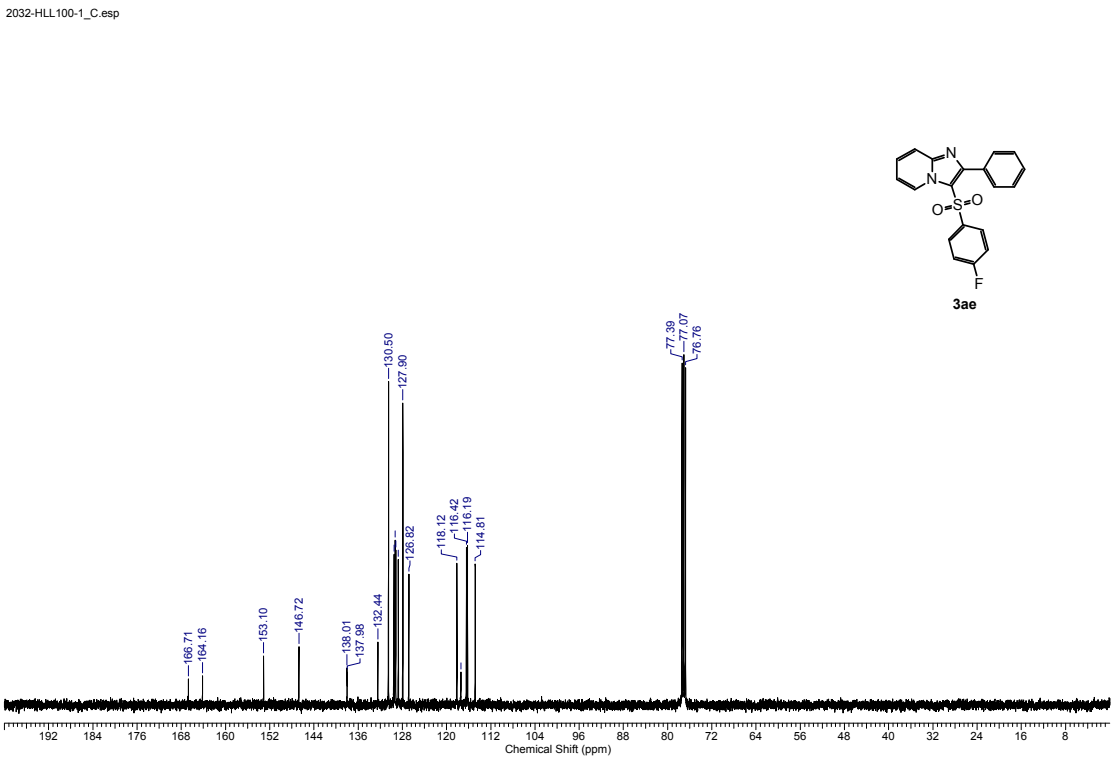

Figure S16. ^{13}C NMR spectrum of compound **3ae**

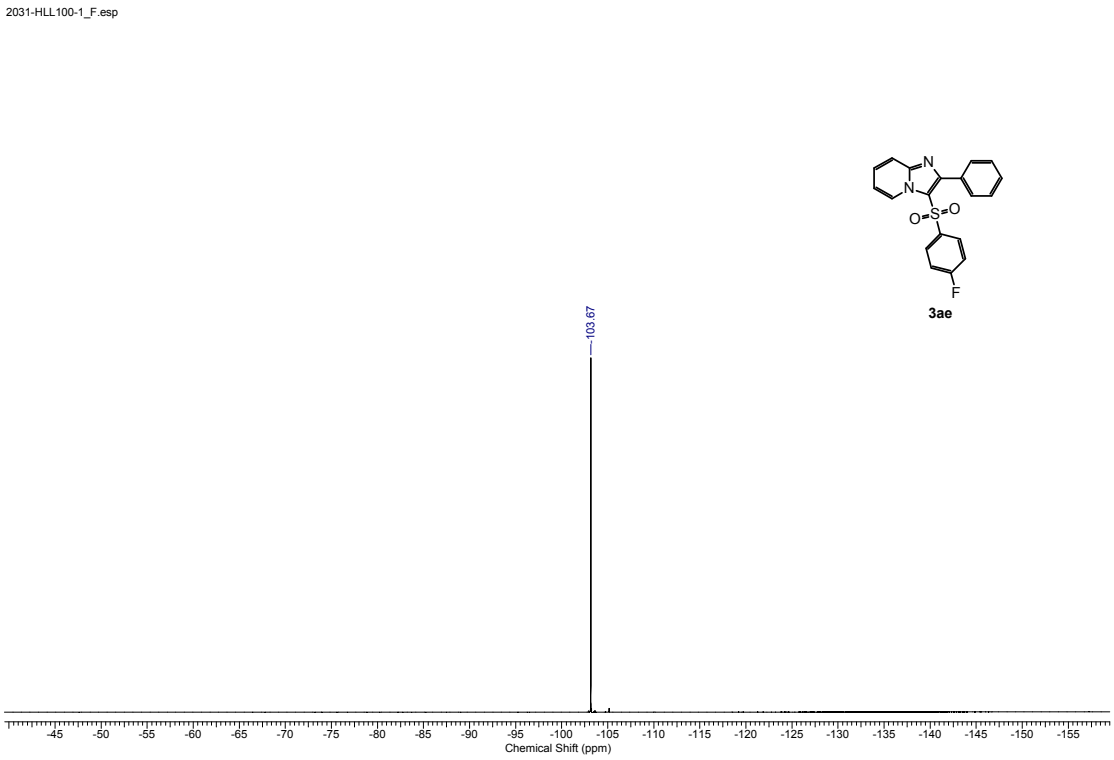

Figure S17. ^{19}F NMR spectrum of compound **3ae**

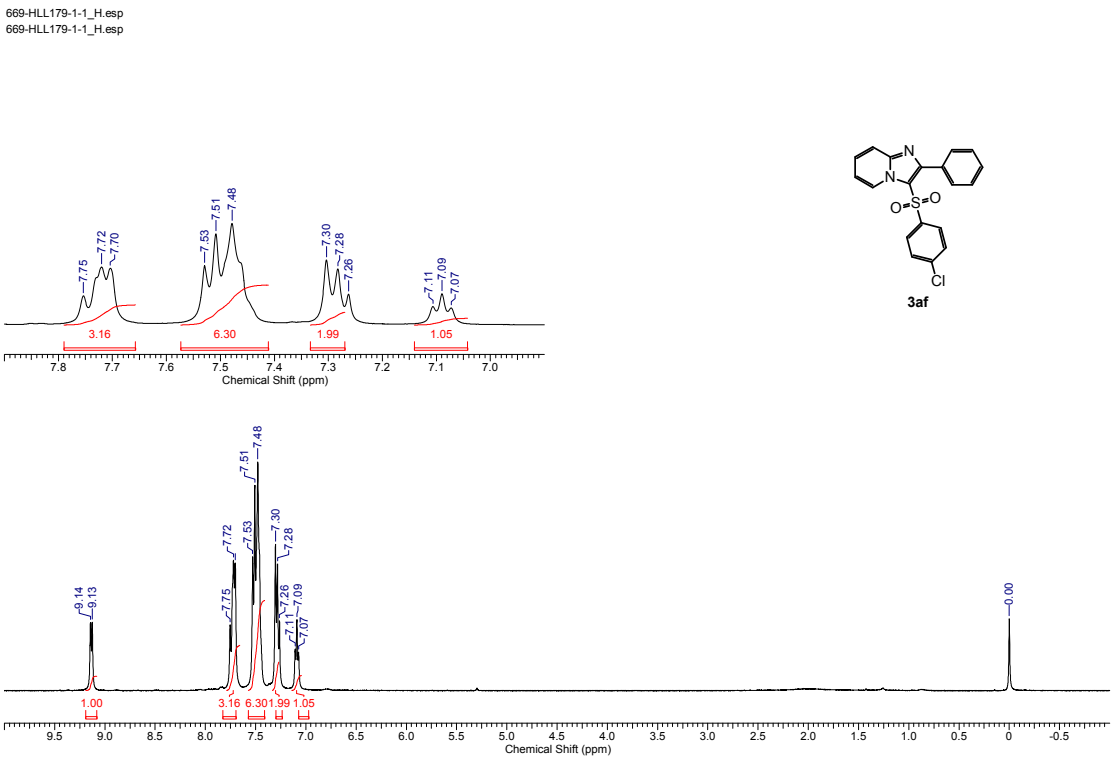

Figure S18. ^{1}H NMR spectrum of compound **3af**

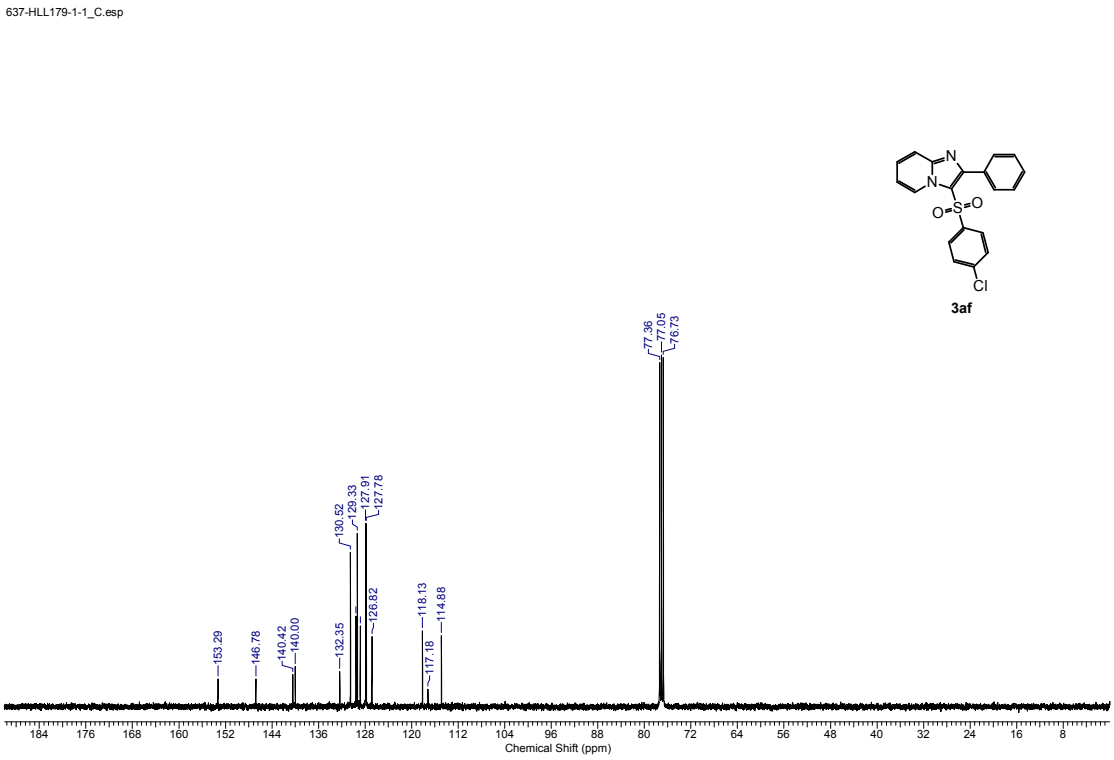

Figure S19. ^{13}C NMR spectrum of compound **3af**

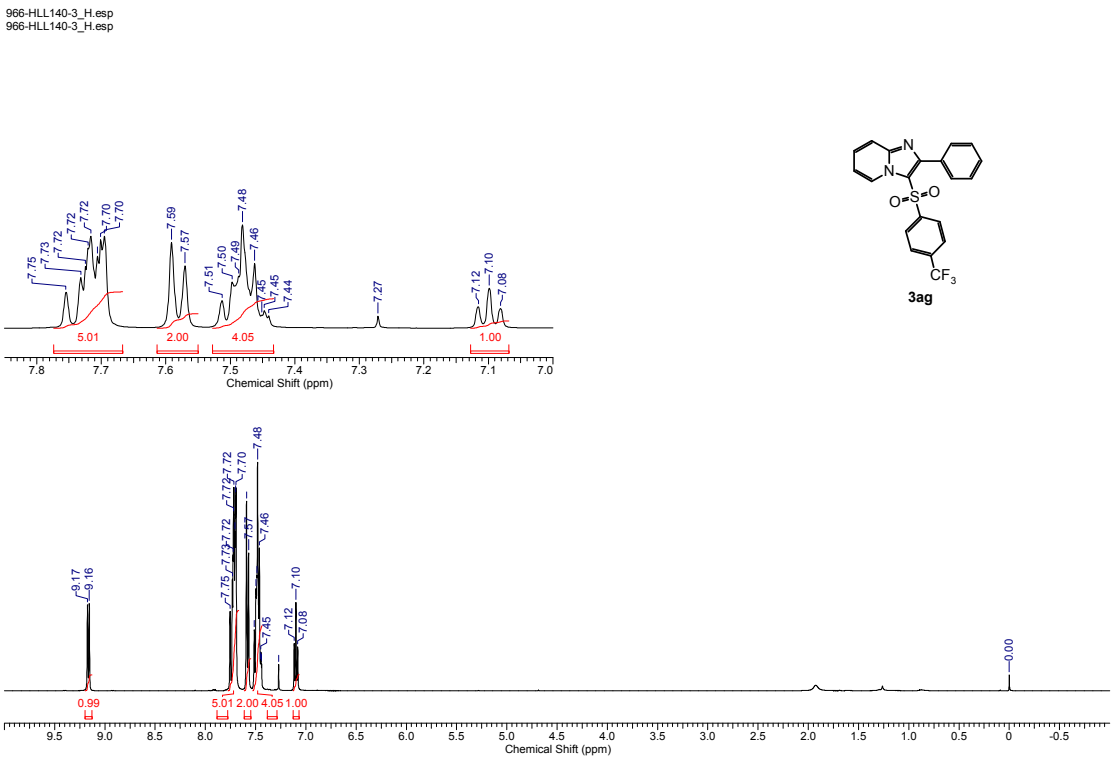

Figure S20. ^{1}H NMR spectrum of compound **3ag**

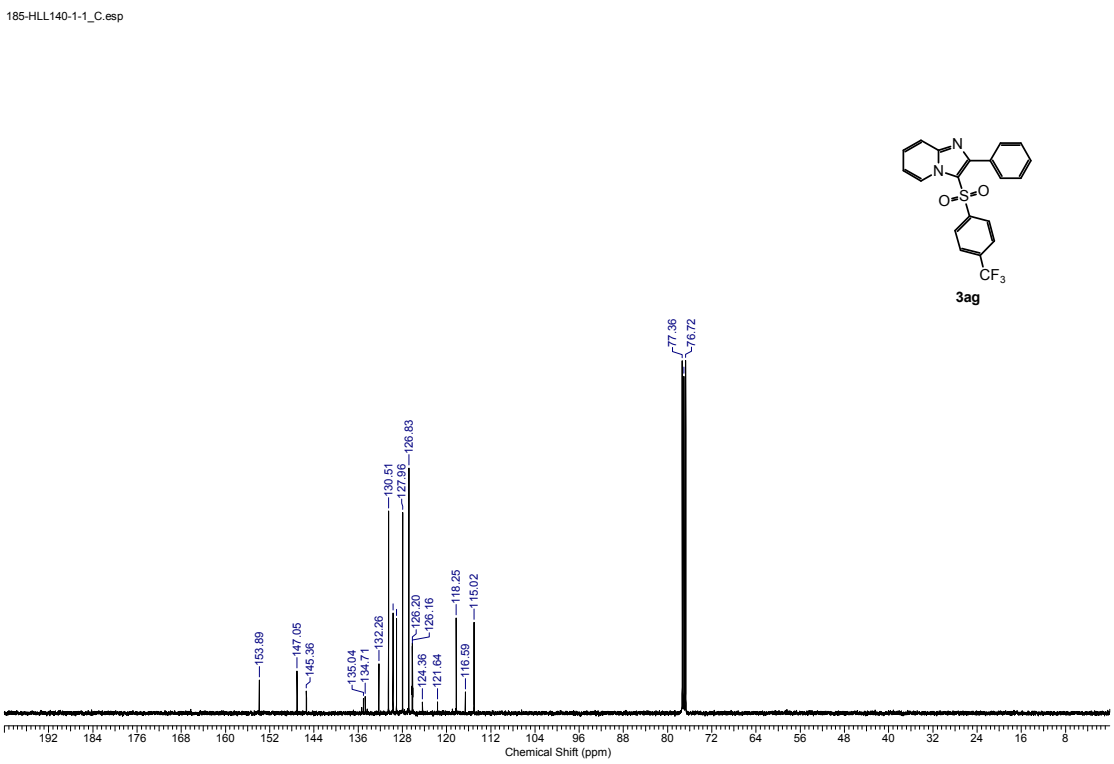

Figure S21. ^{13}C NMR spectrum of compound **3ag**

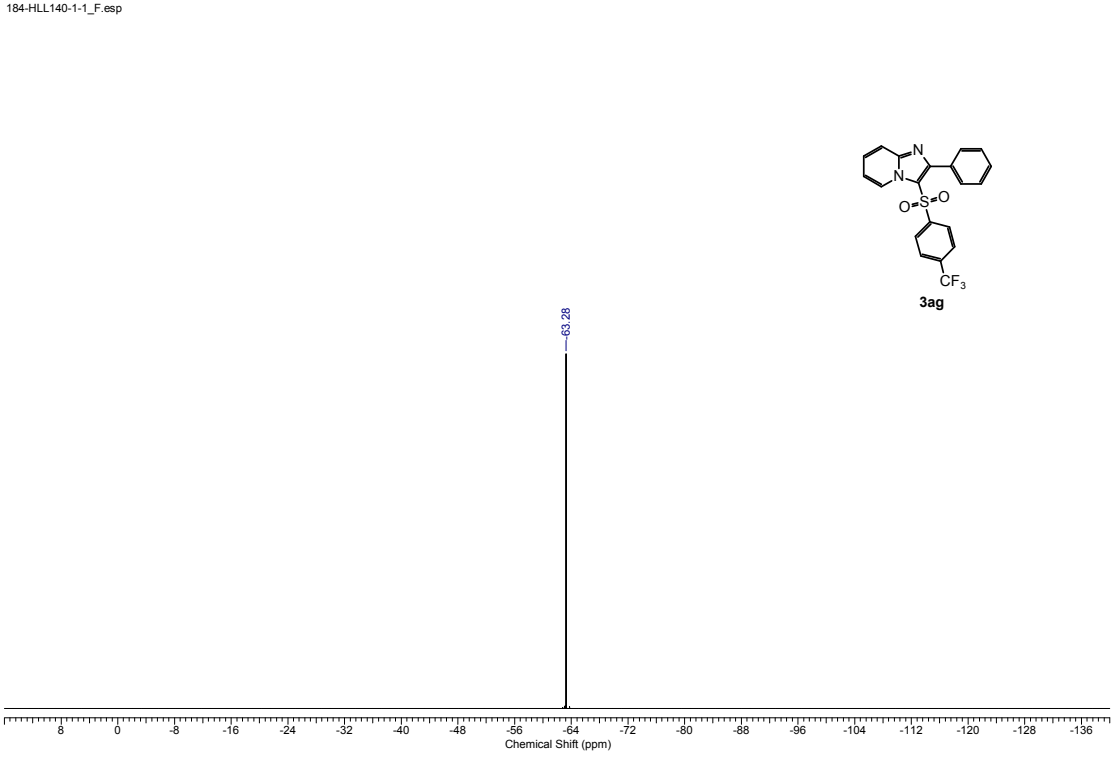

Figure S22. ^{19}F NMR spectrum of compound **3ag**

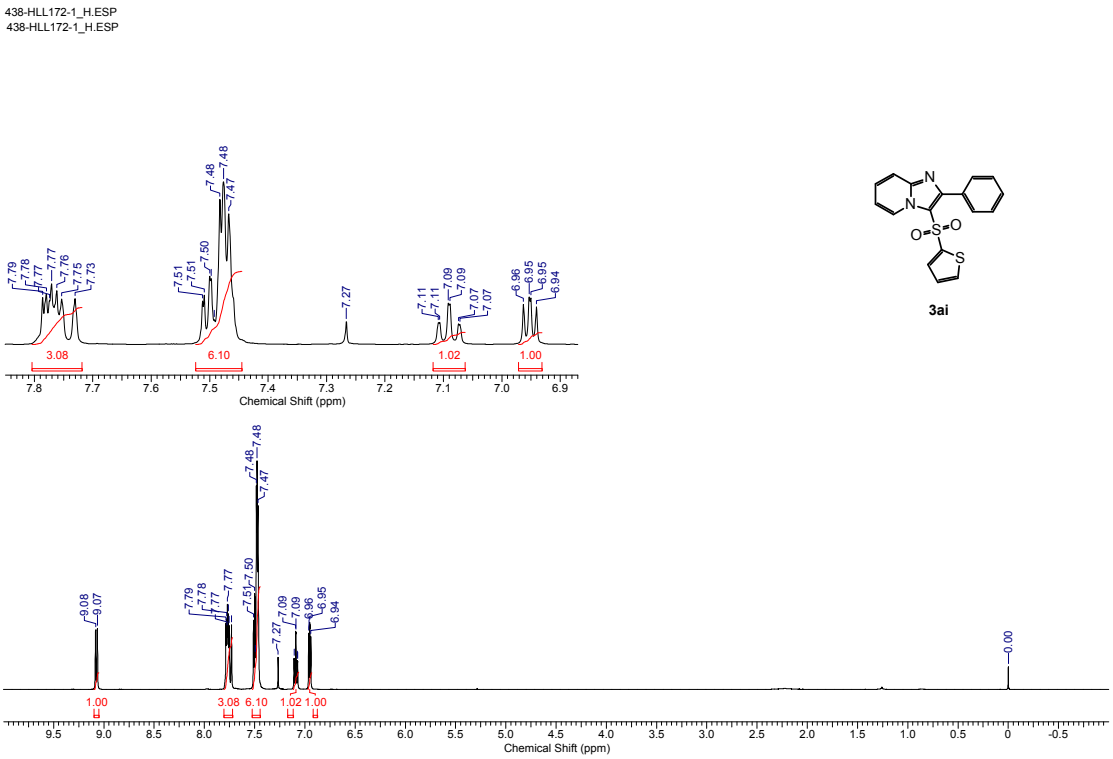

Figure S23. ^{1}H NMR spectrum of compound **3ai**

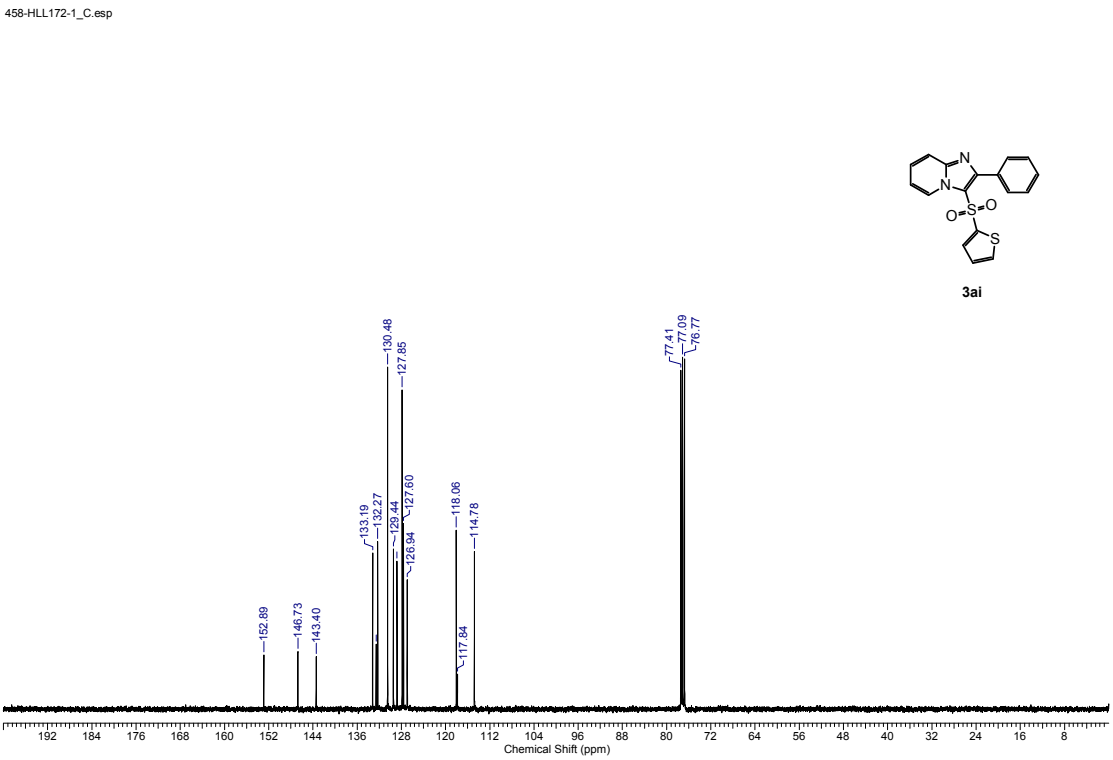

Figure S24. ^{13}C NMR spectrum of compound **3ai**

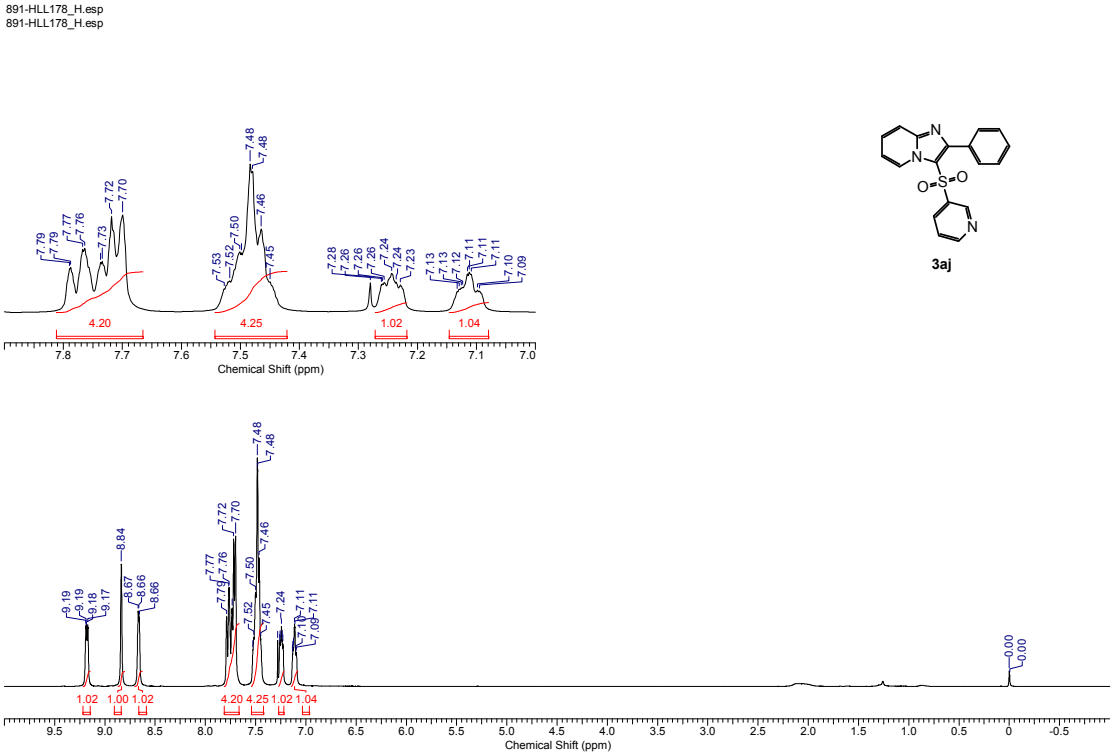

Figure S25. ^{1}H NMR spectrum of compound **3aj**

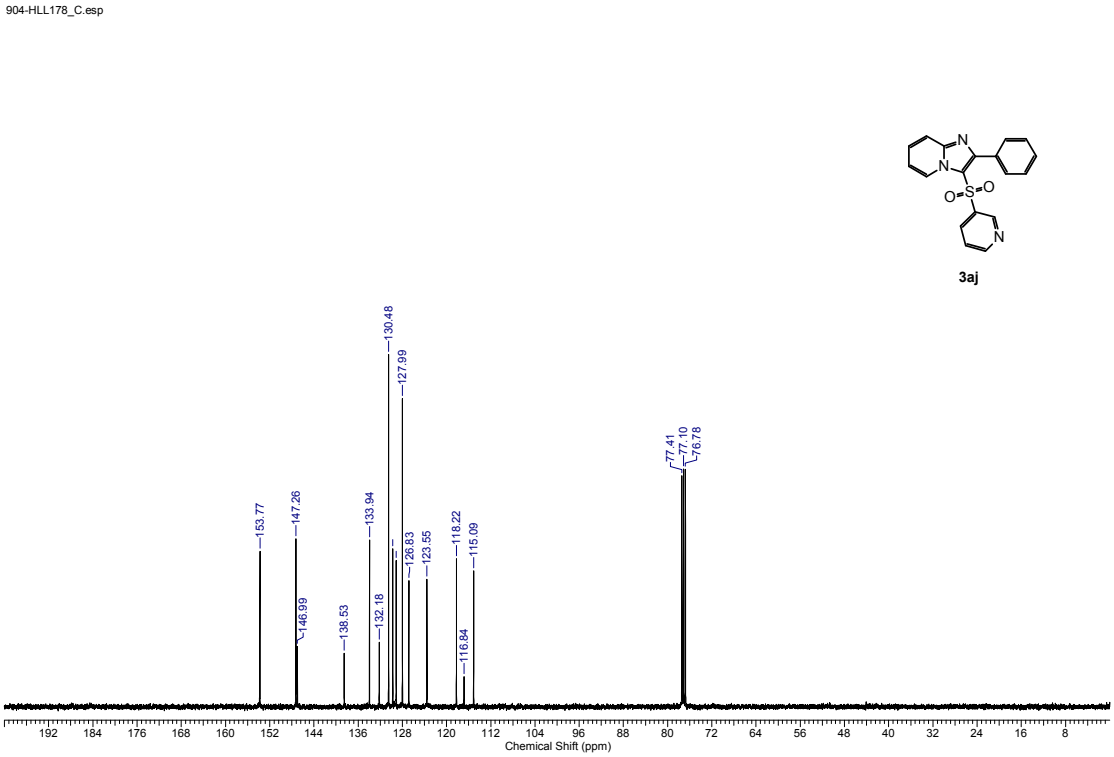

Figure S26. ^{13}C NMR spectrum of compound **3aj**

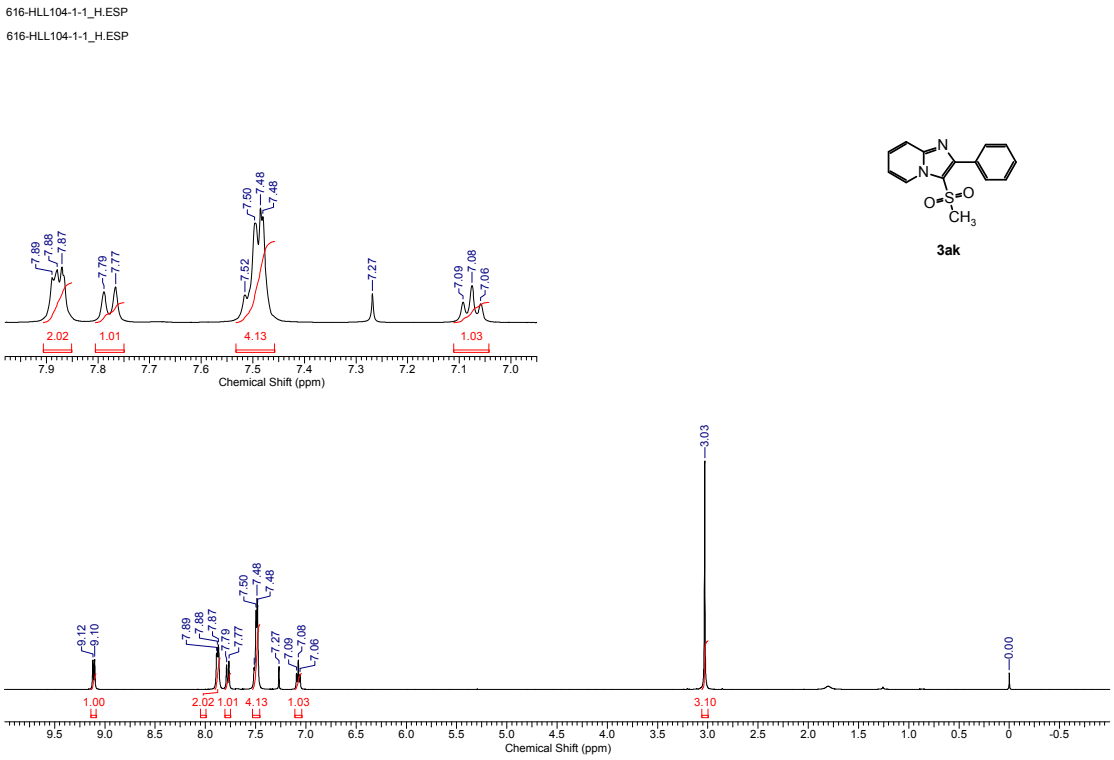

Figure S27. ^{1}H NMR spectrum of compound **3ak**

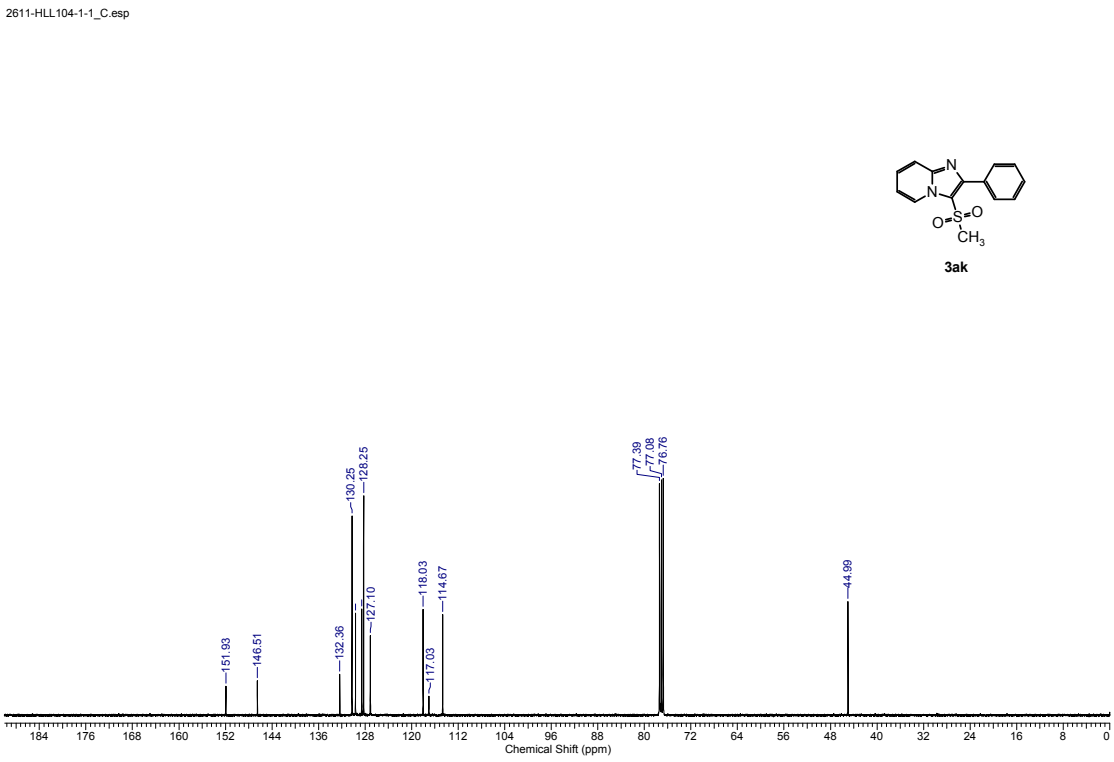

Figure S28. ^{13}C NMR spectrum of compound **3ak**

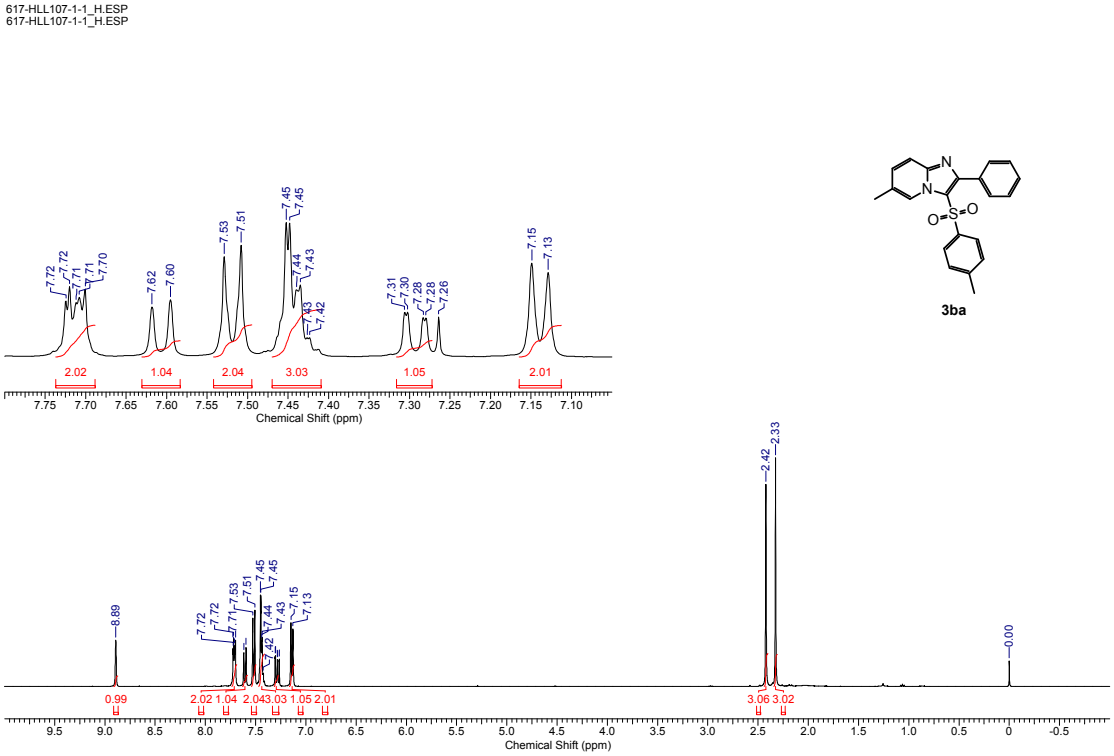

Figure S29. ^{1}H NMR spectrum of compound **3ba**

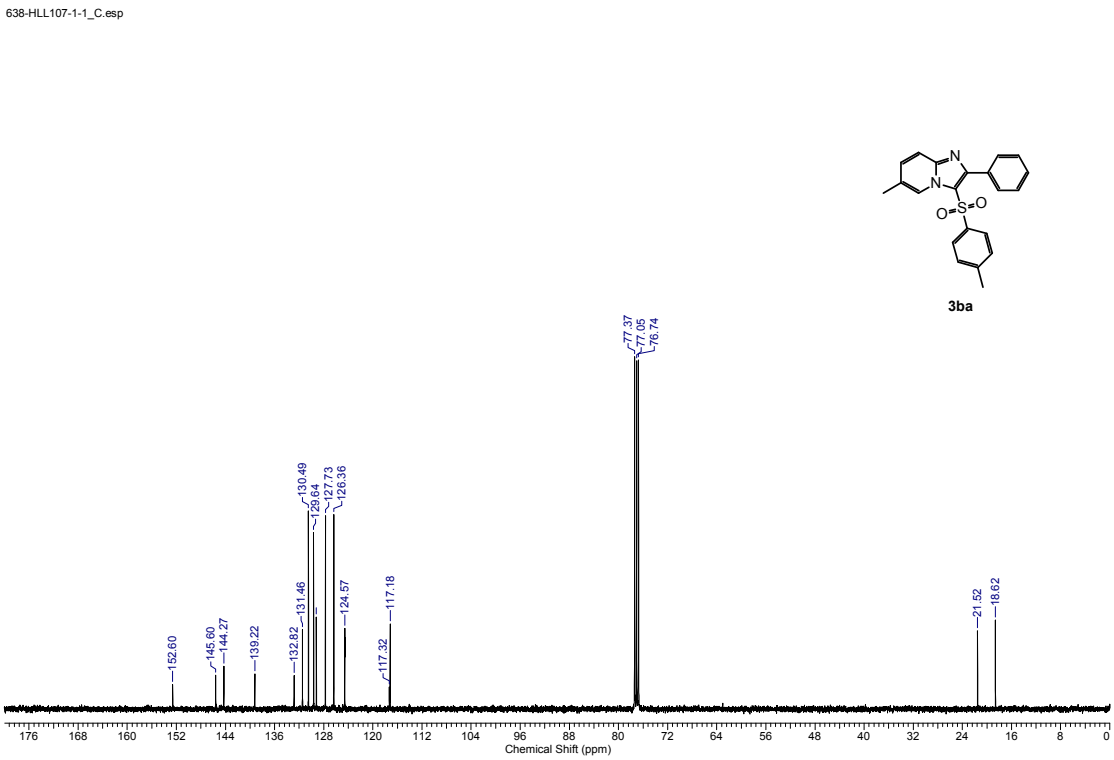

Figure S30. ^{13}C NMR spectrum of compound **3ba**

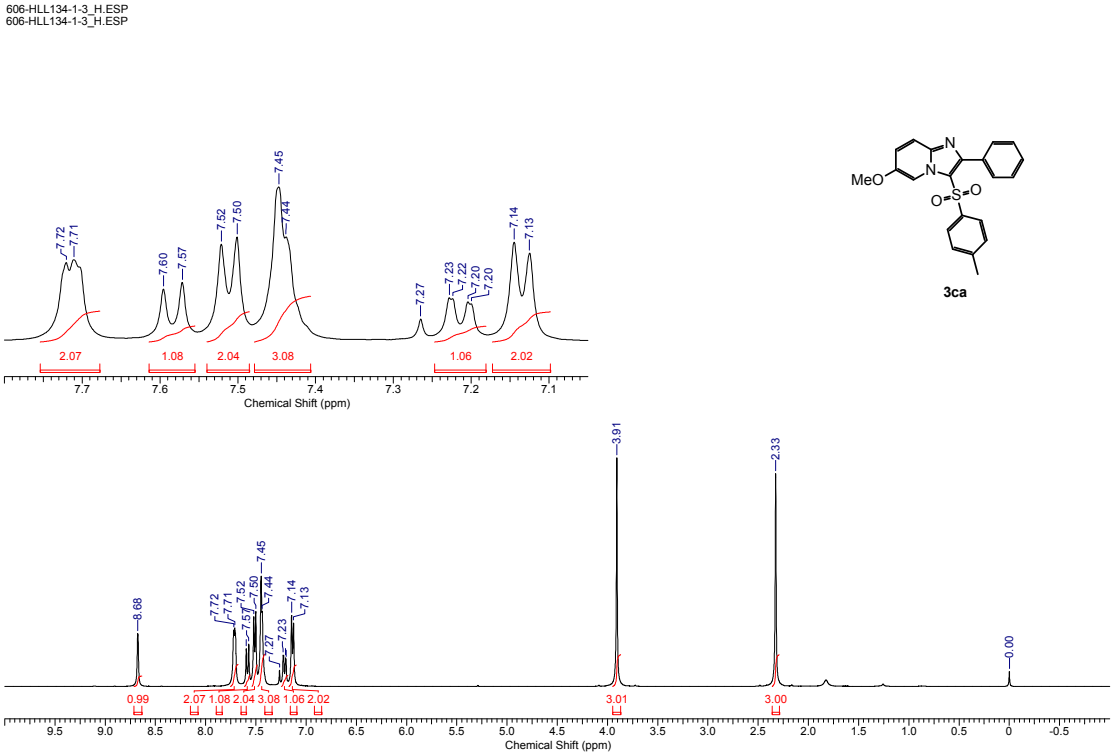

Figure S31. ^{1}H NMR spectrum of compound **3ca**

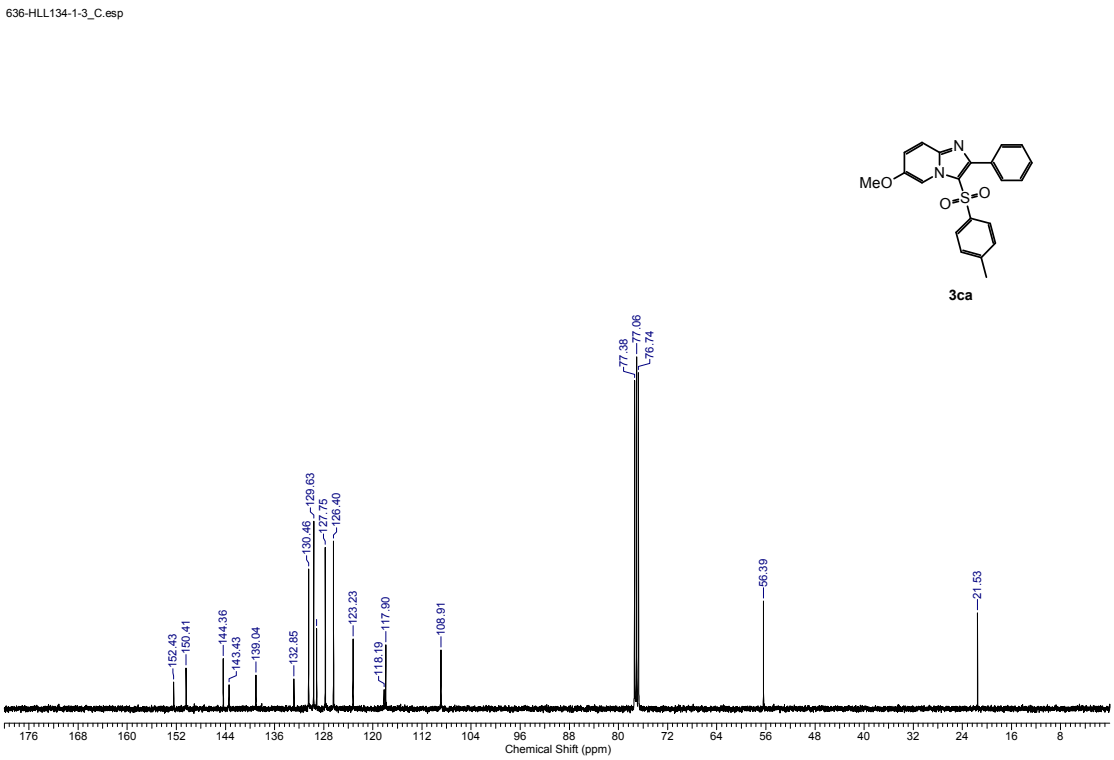

Figure S32. ^{13}C NMR spectrum of compound **3ca**

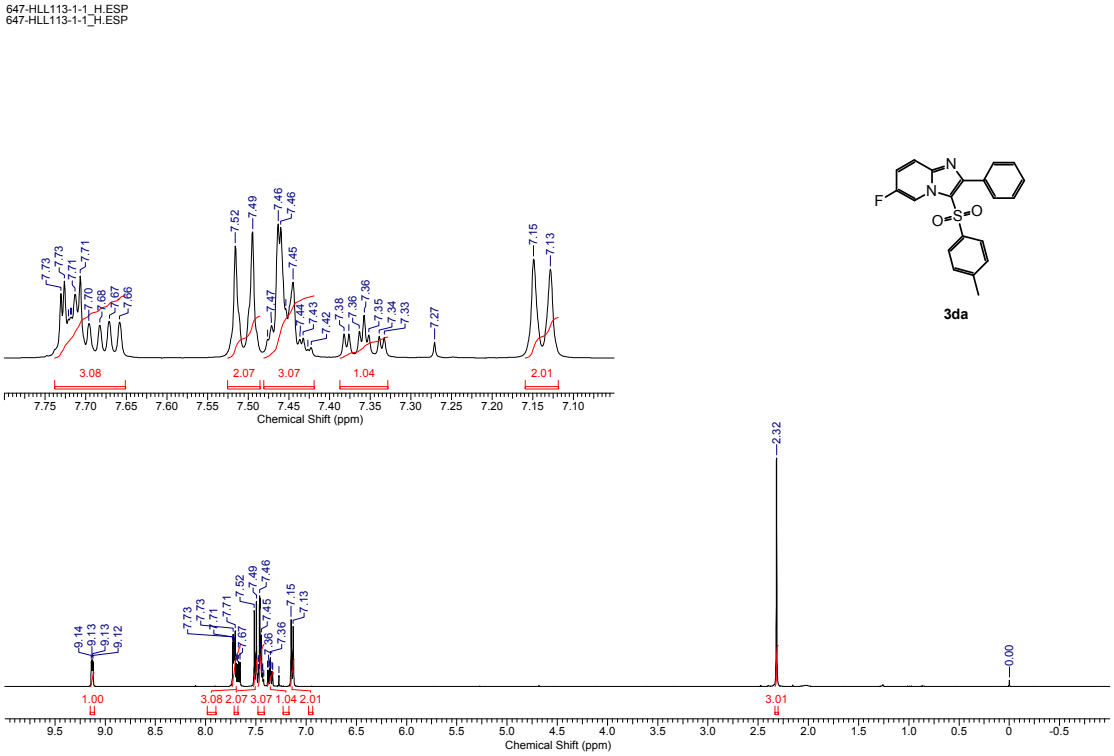

Figure S33. ^{1}H NMR spectrum of compound **3da**

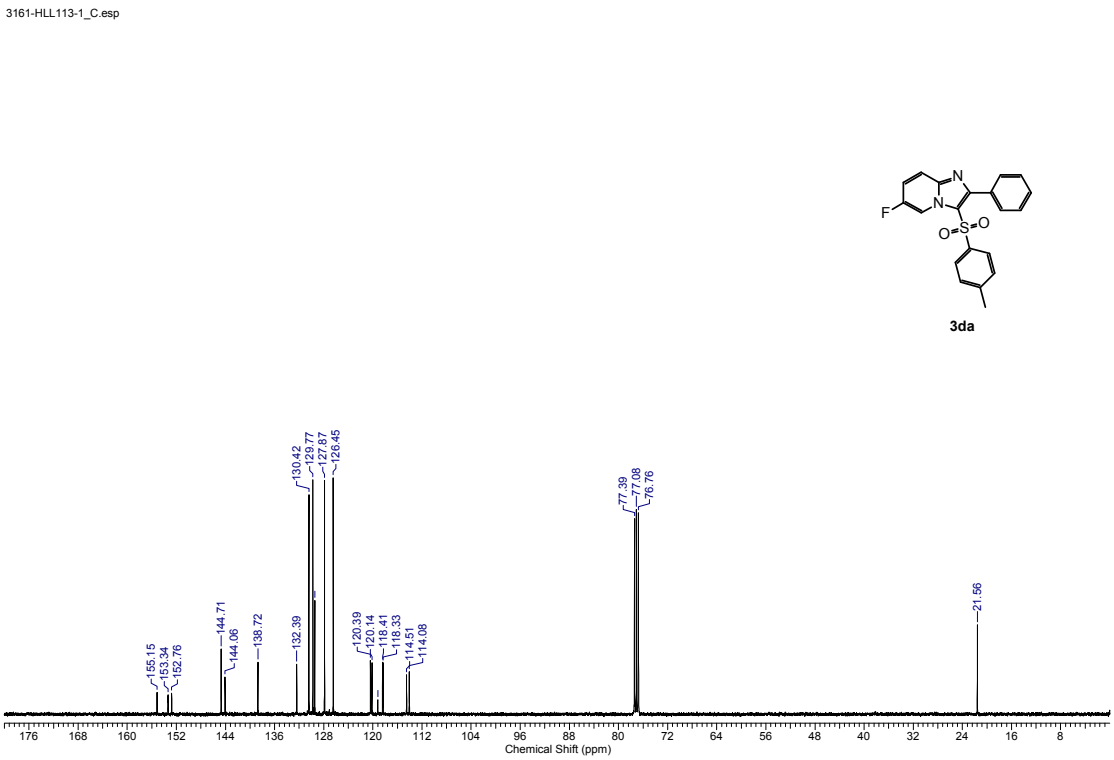

Figure S34. ^{13}C NMR spectrum of compound **3da**

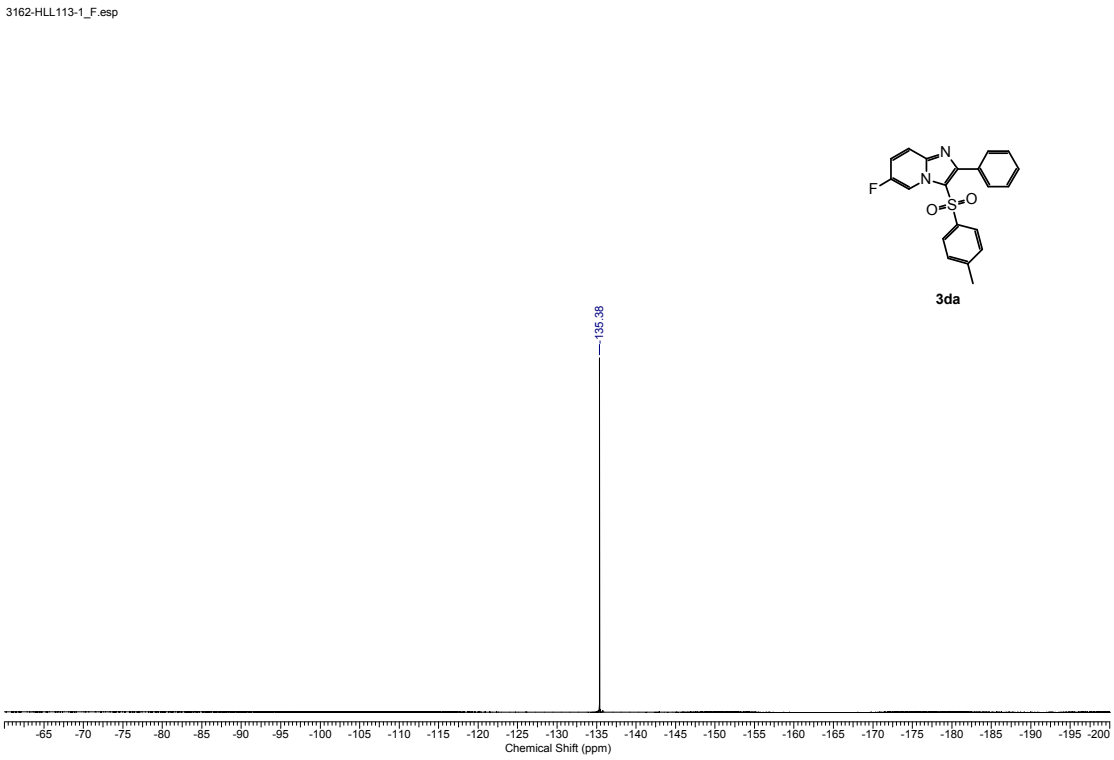

Figure S35. ^{19}F NMR spectrum of compound **3da**

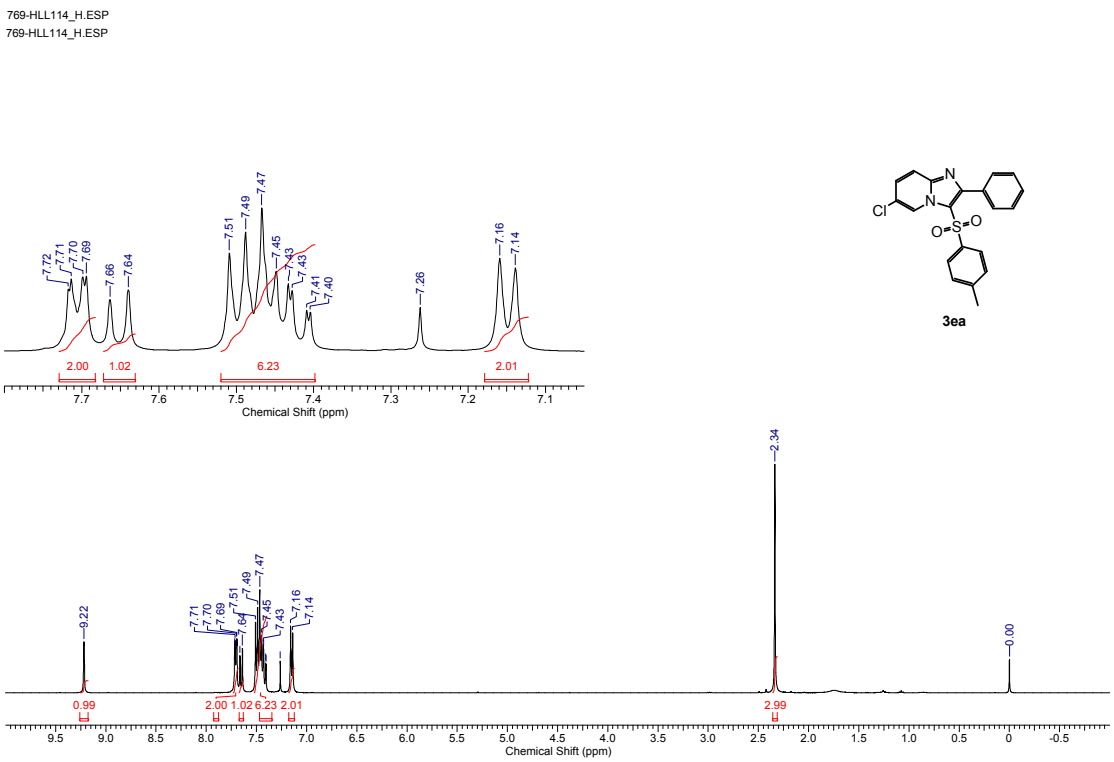

Figure S36. ^{1}H NMR spectrum of compound **3ea**

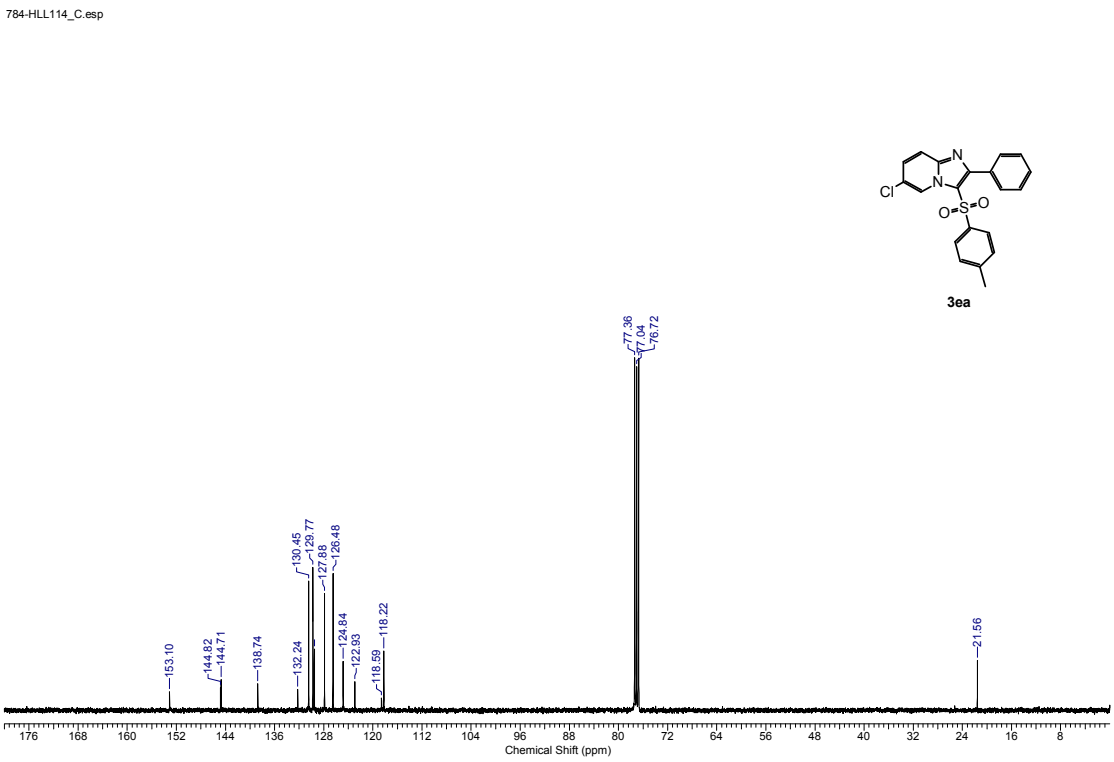

Figure S37. ^{13}C NMR spectrum of compound **3ea**

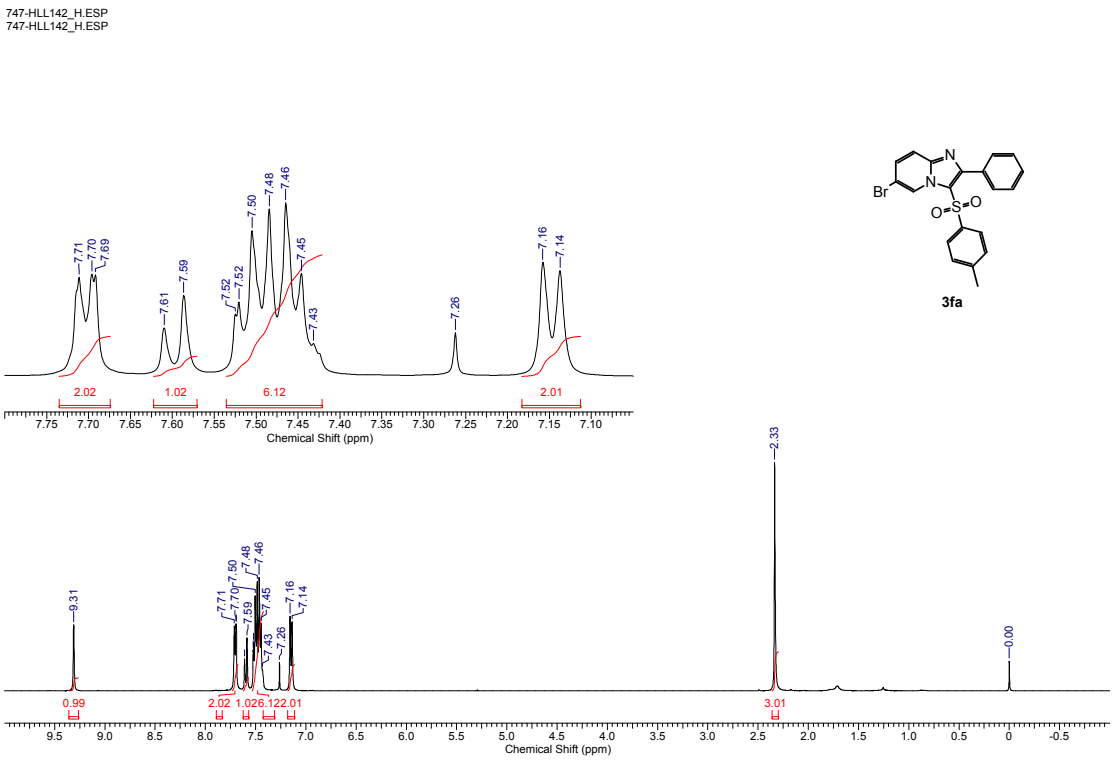

Figure S38. ^{1}H NMR spectrum of compound **3fa**

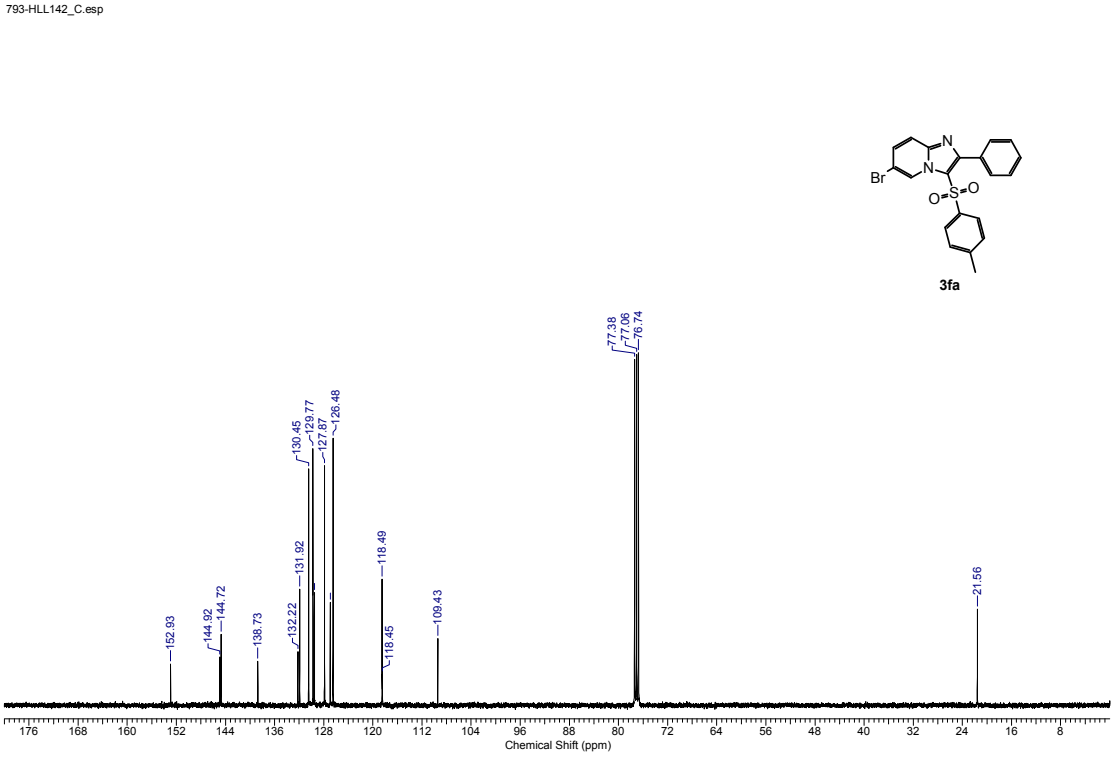

Figure S39. ^{13}C NMR spectrum of compound **3fa**

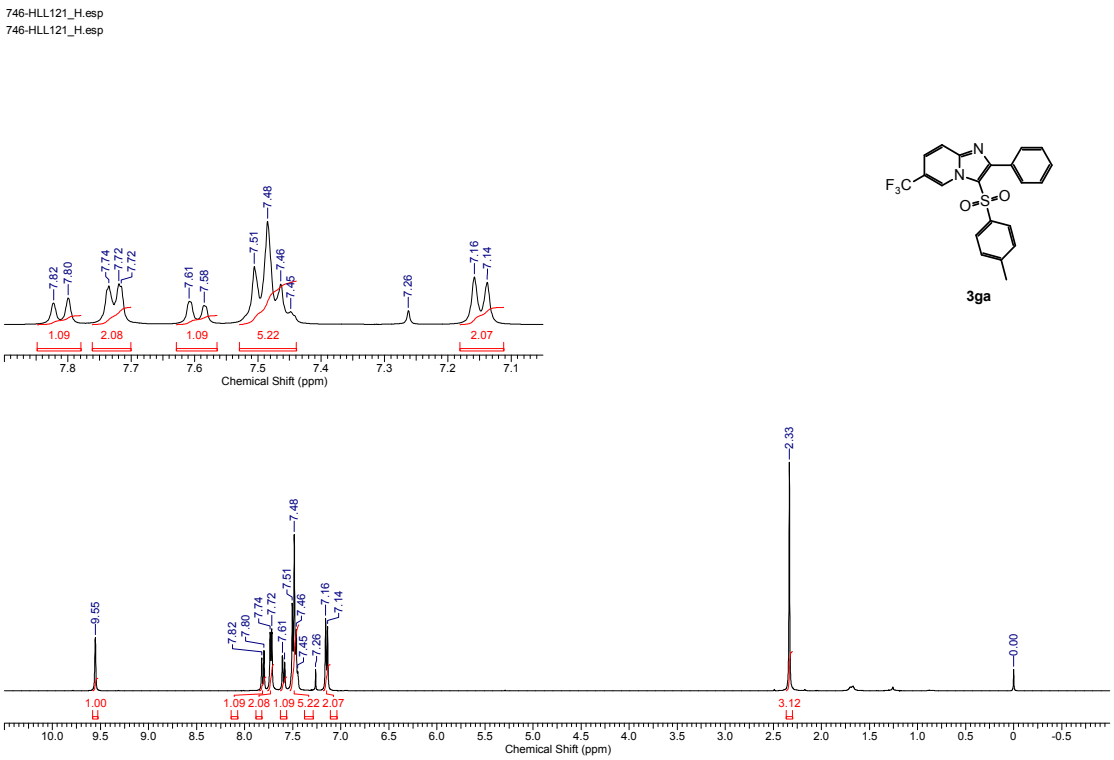

Figure S40. ^{1}H NMR spectrum of compound **3ga**

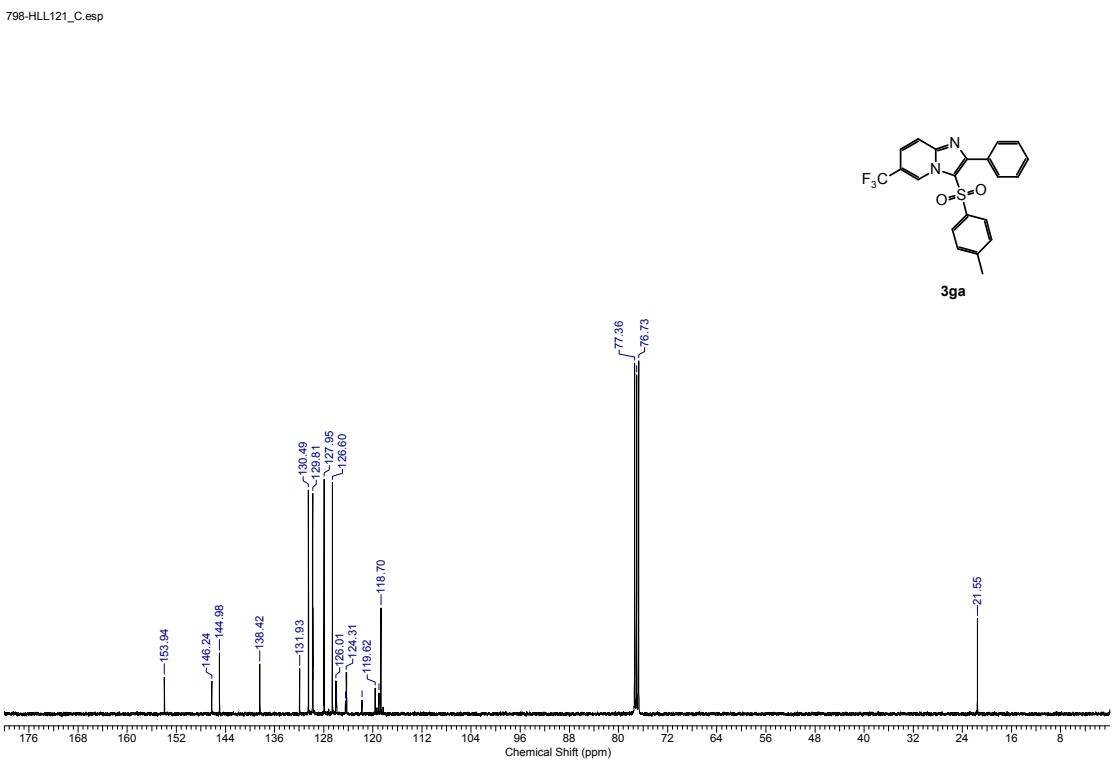

Figure S41. ^{13}C NMR spectrum of compound **3ga**

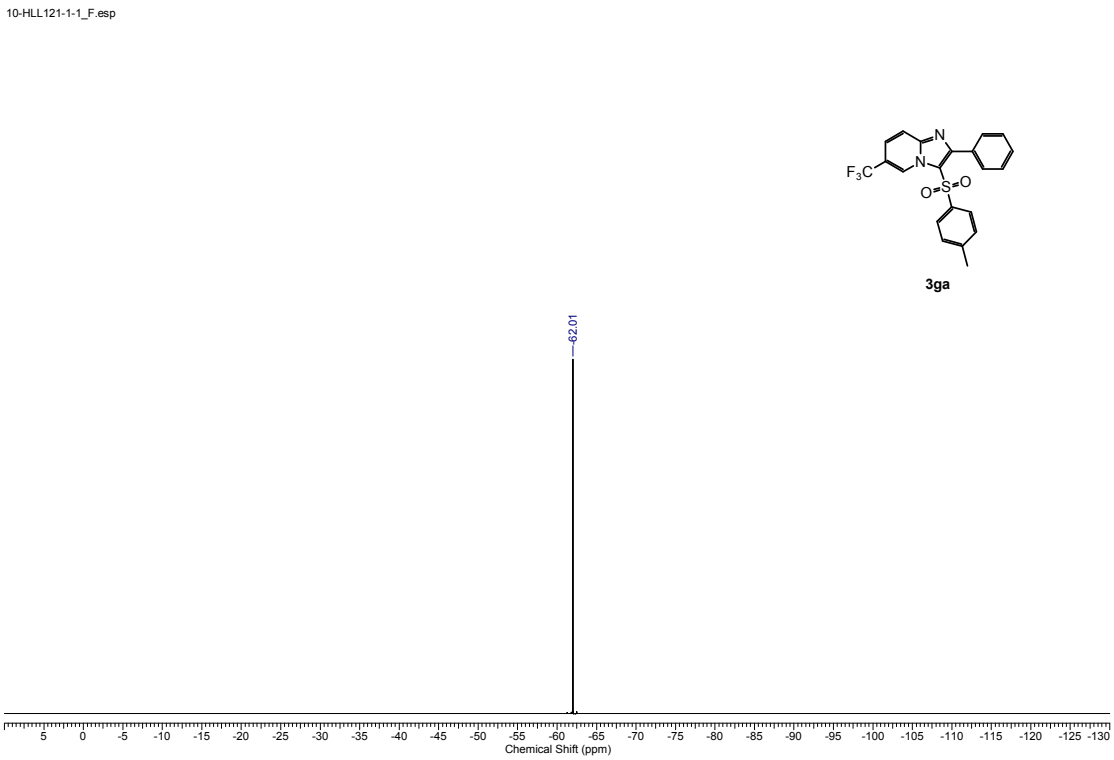

Figure S42. ^{19}F NMR spectrum of compound **3ga**

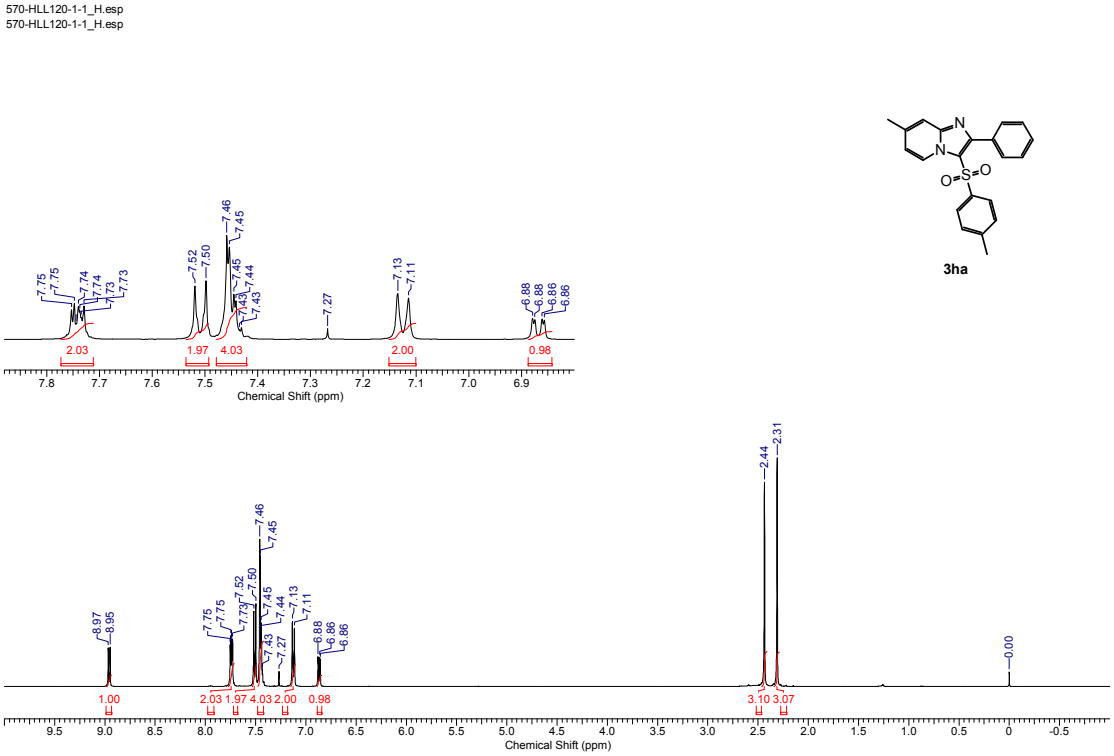

Figure S43. ^{1}H NMR spectrum of compound **3ha**

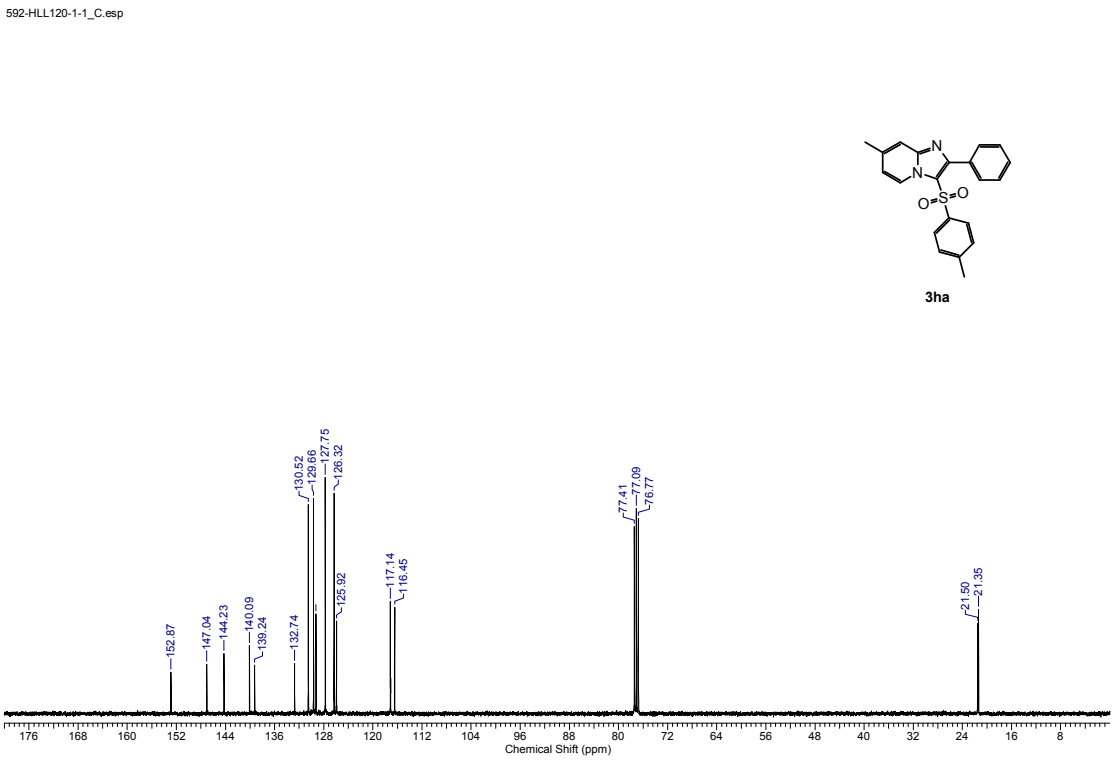

Figure S44. ^{13}C NMR spectrum of compound **3ha**

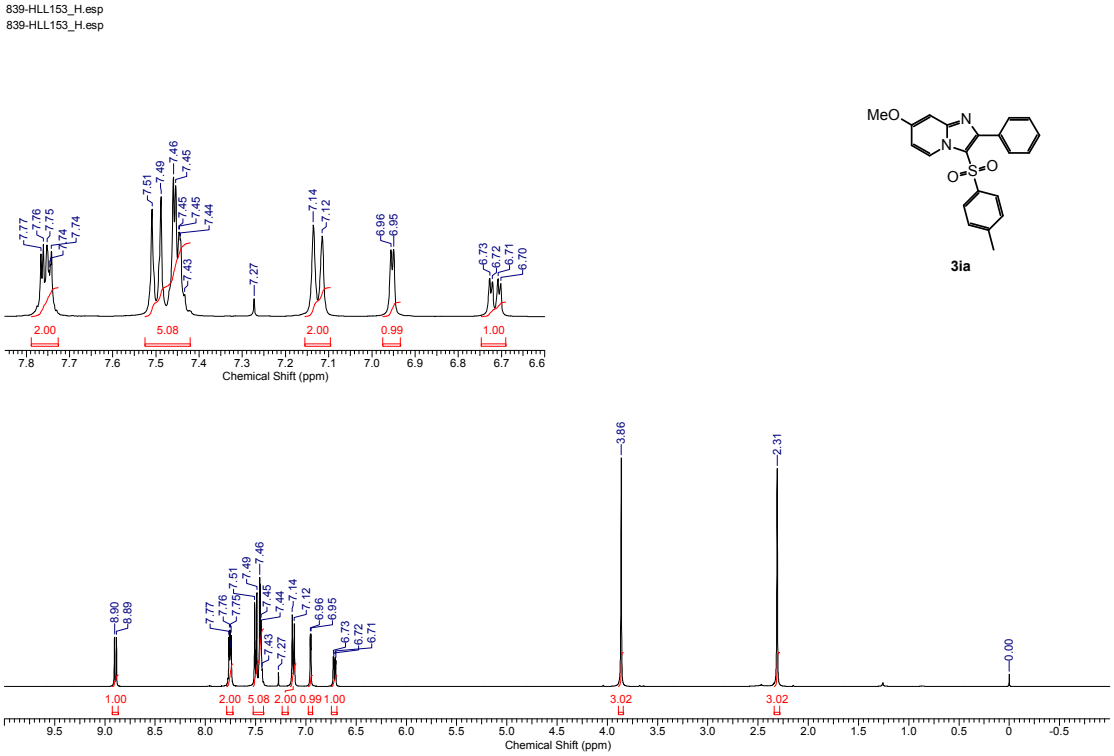

Figure S45. ^{1}H NMR spectrum of compound **3ia**

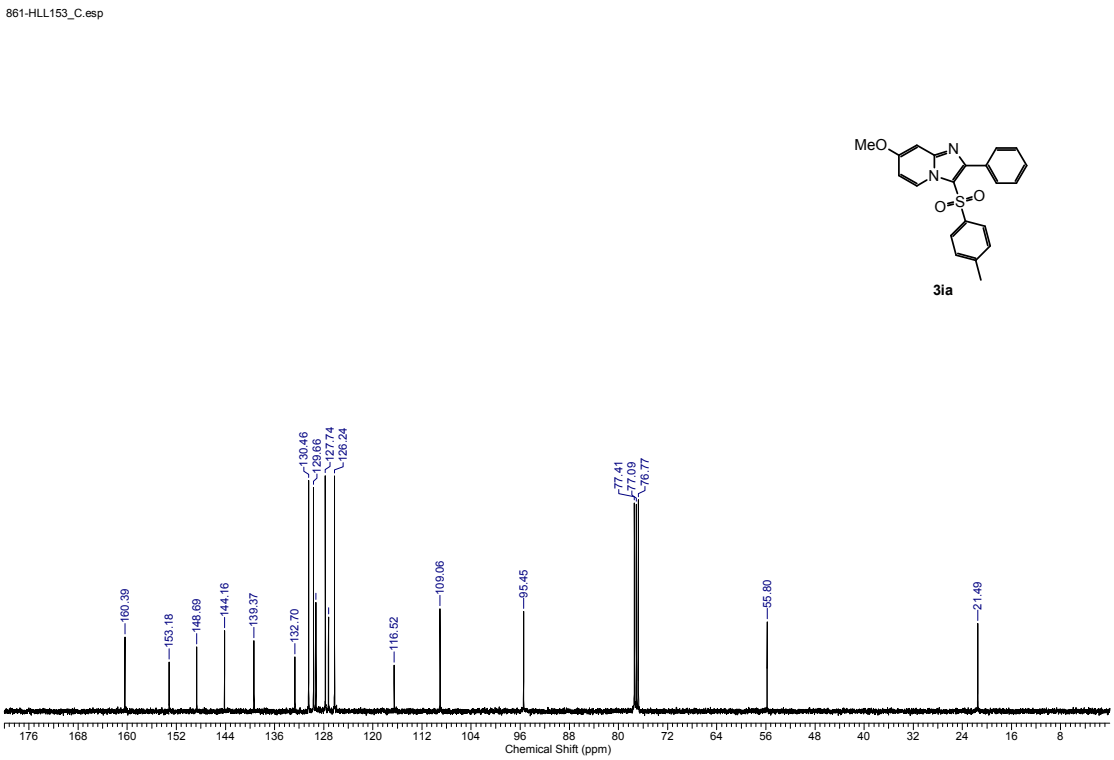

Figure S46. ^{13}C NMR spectrum of compound **3ia**

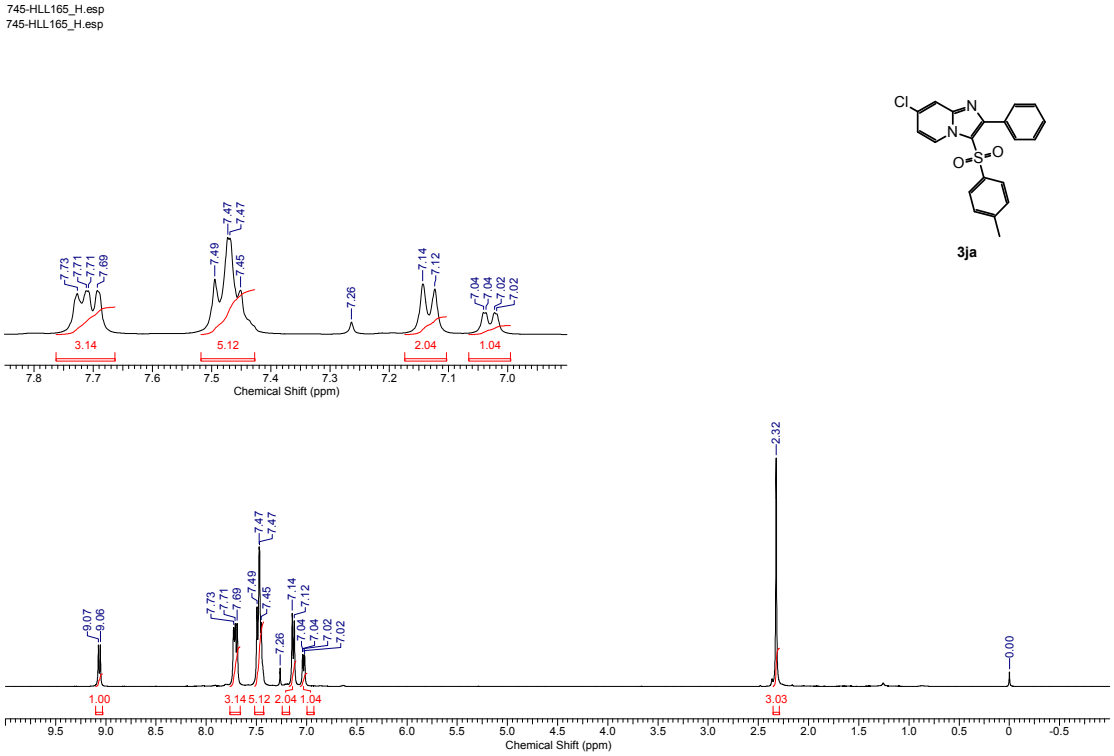

Figure S47. ^{1}H NMR spectrum of compound **3ja**

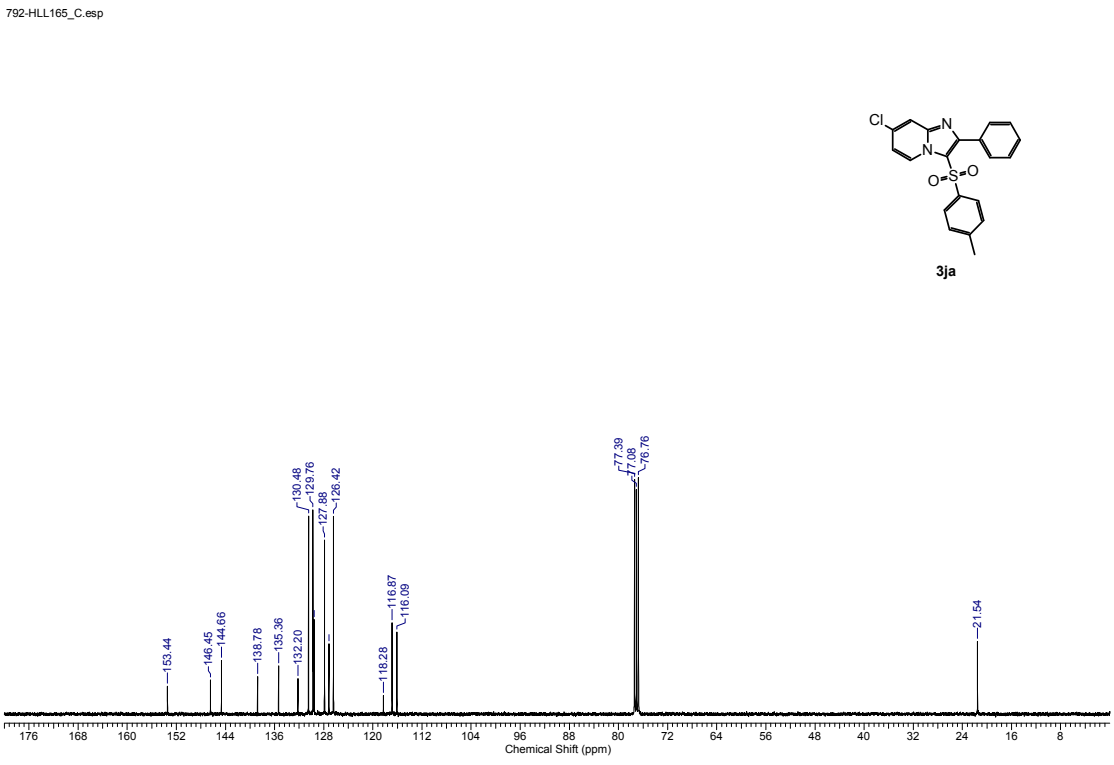

Figure S48. ^{13}C NMR spectrum of compound **3ja**

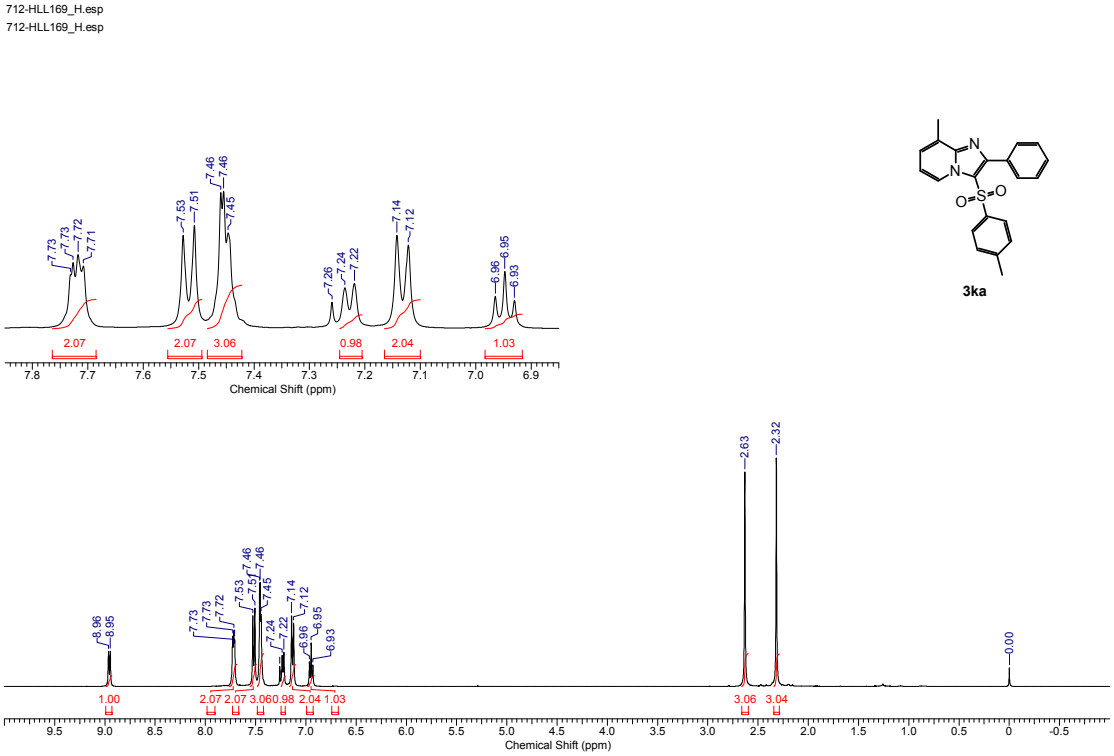

Figure S49. ^{1}H NMR spectrum of compound **3ka**

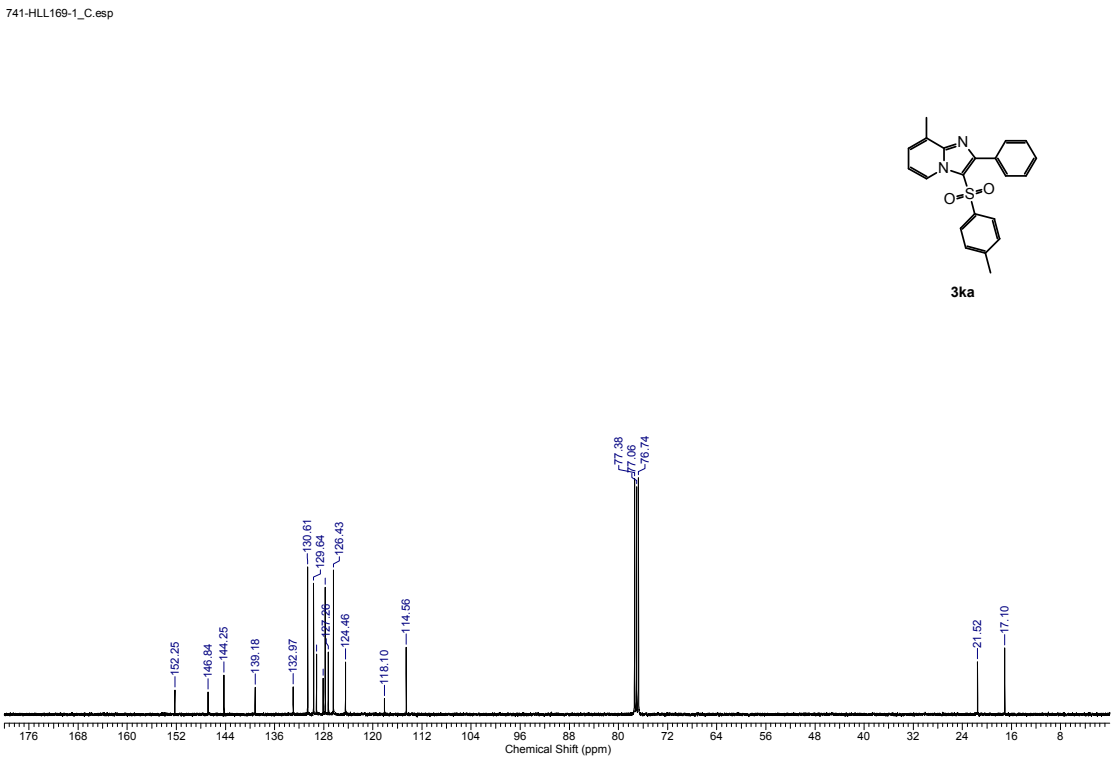

Figure S50. ^{13}C NMR spectrum of compound **3ka**

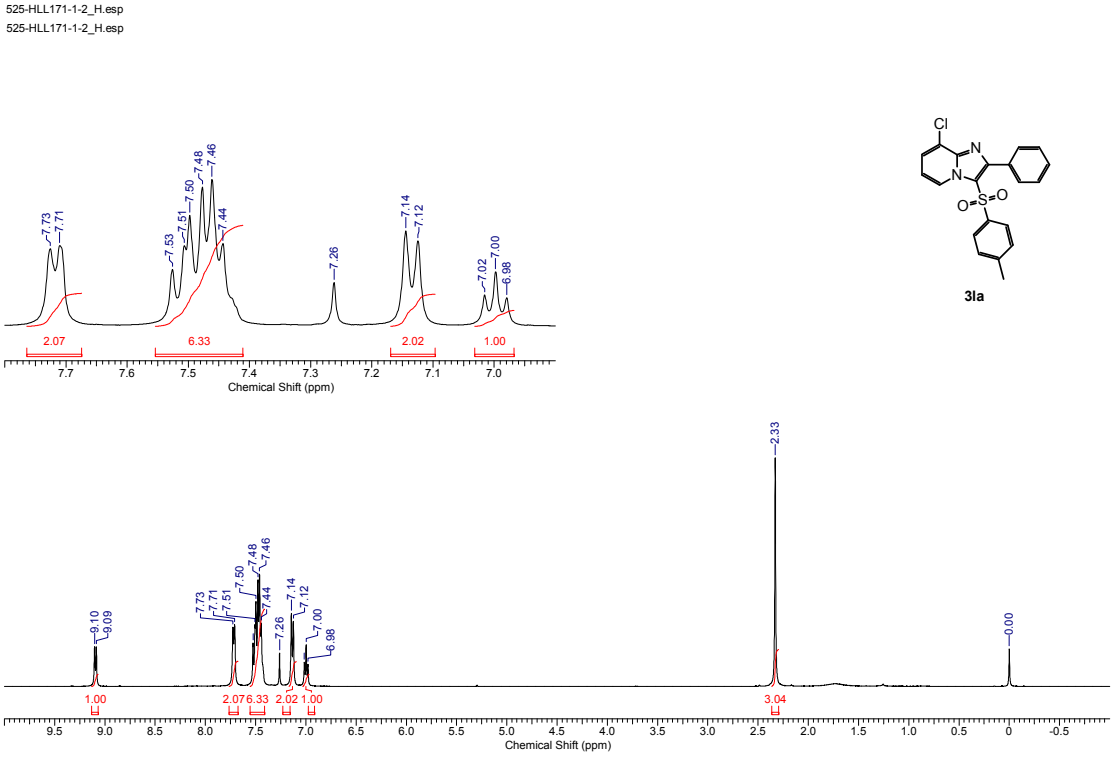

Figure S51. ^{1}H NMR spectrum of compound **3la**

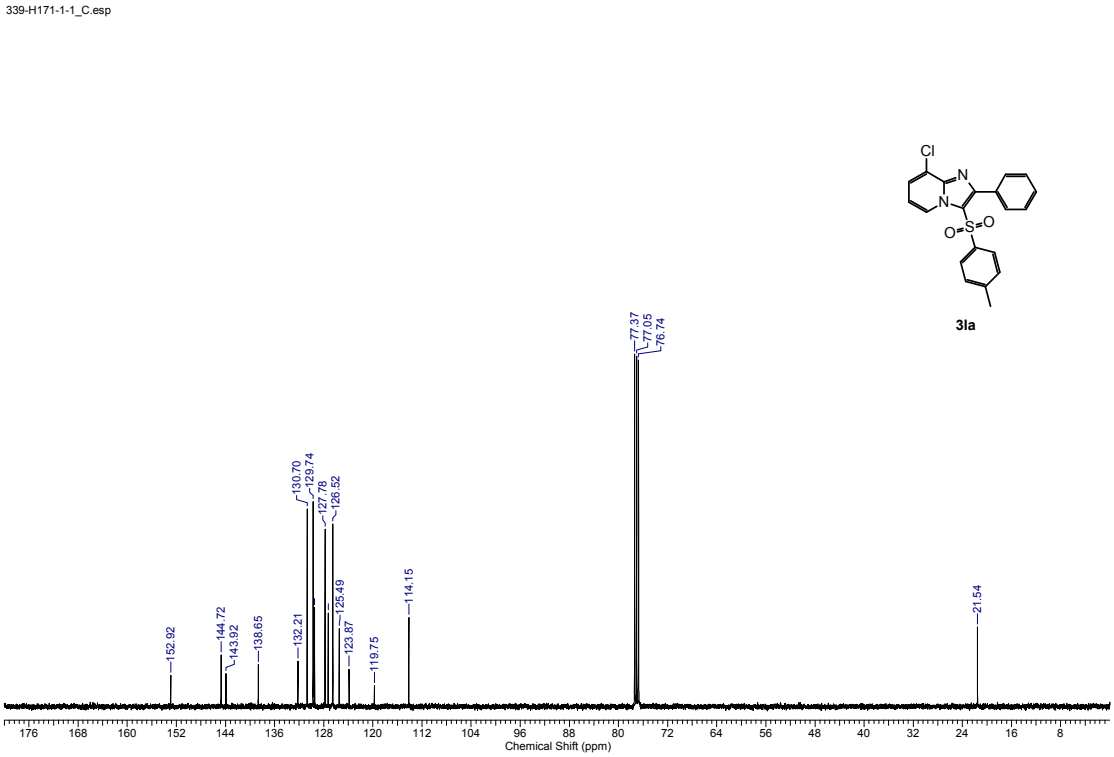

Figure S52. ^{13}C NMR spectrum of compound **3la**

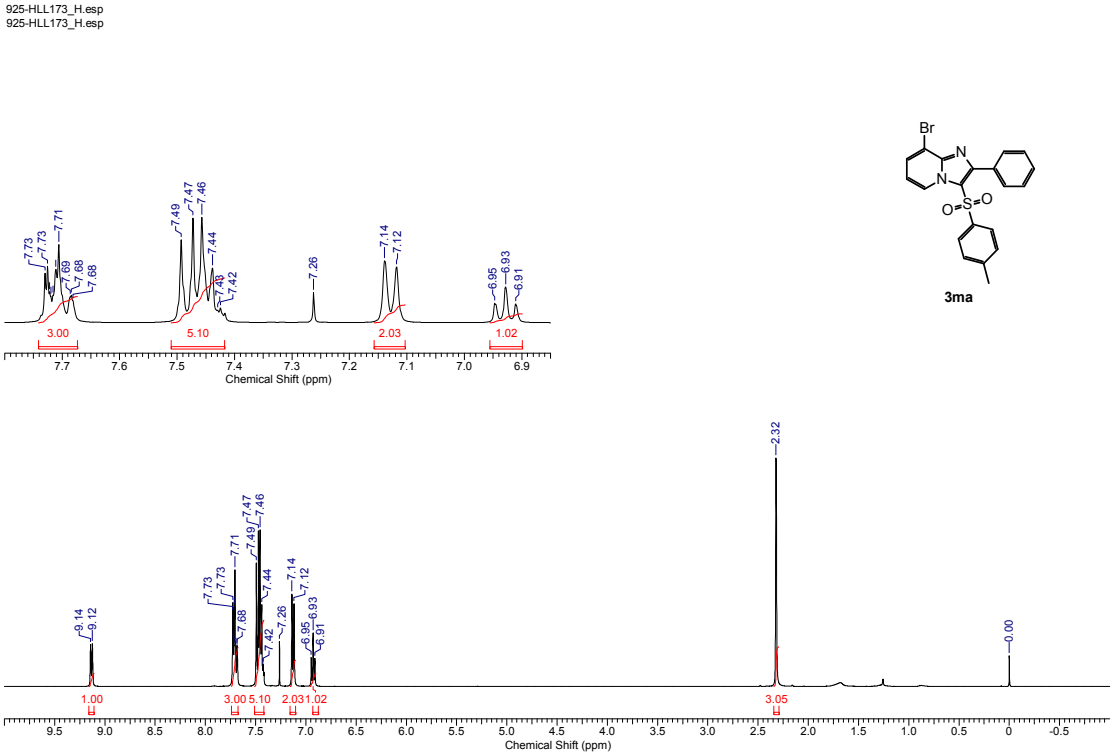

Figure S53. ^{1}H NMR spectrum of compound **3ma**

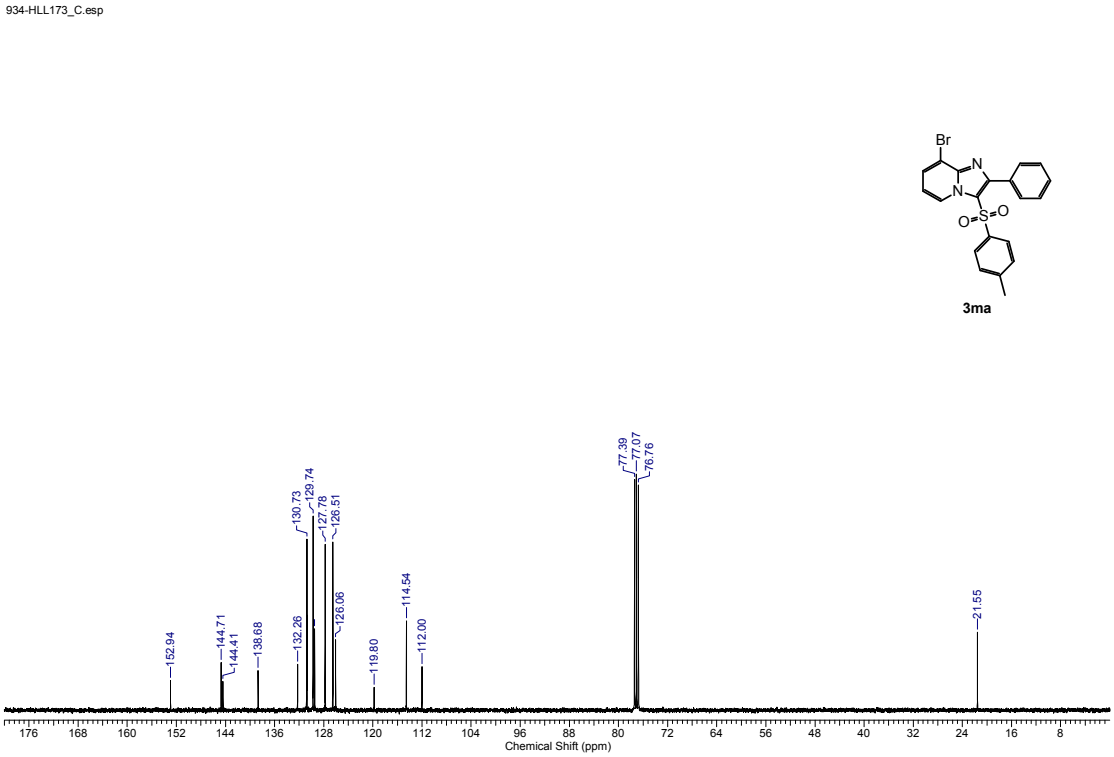

Figure S54. ^{13}C NMR spectrum of compound **3ma**

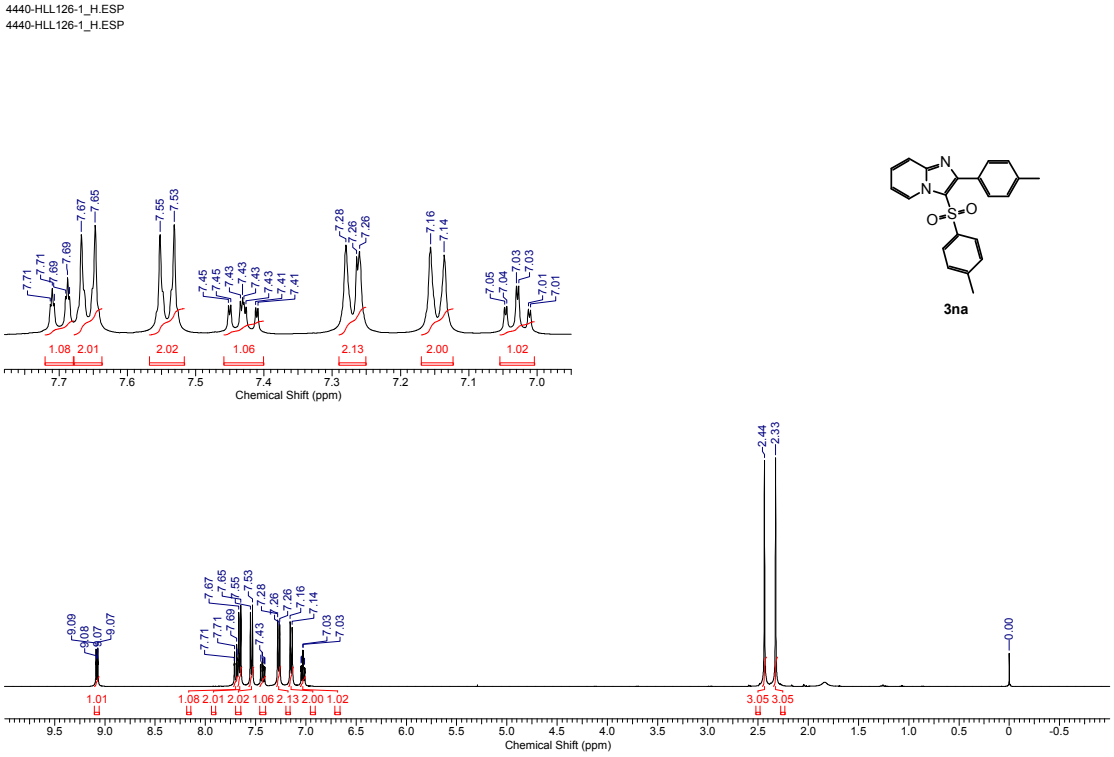

Figure S55. ^{1}H NMR spectrum of compound **3na**

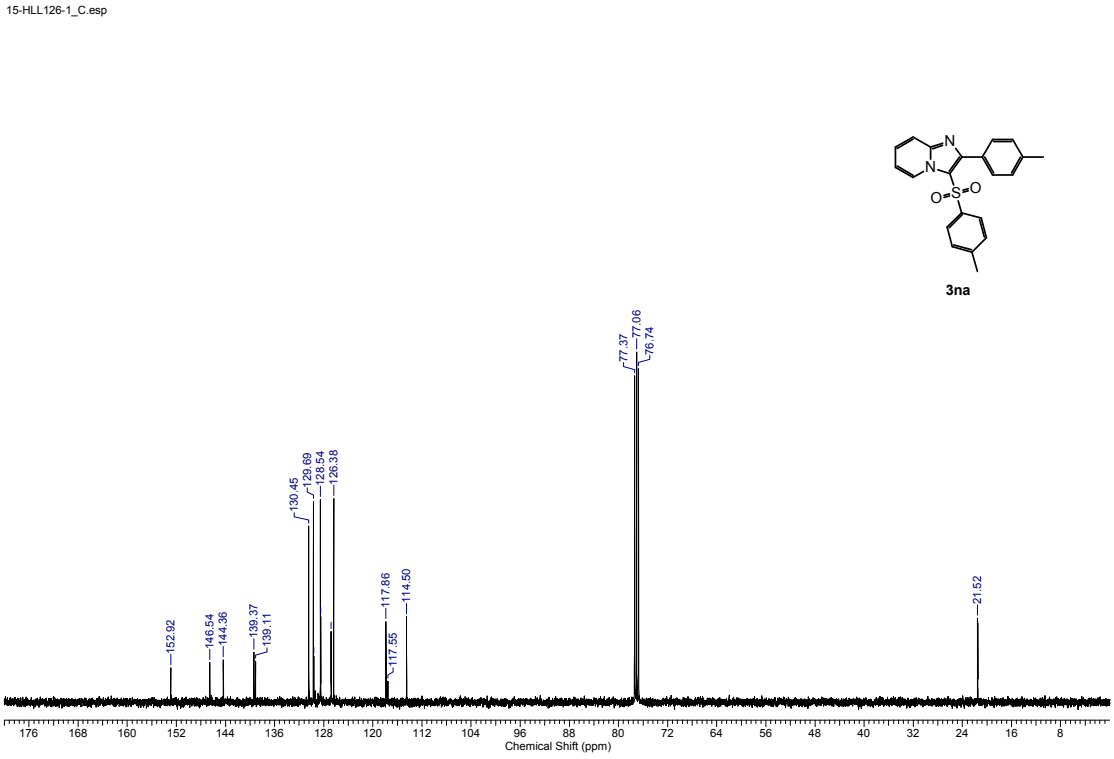

Figure S56. ^{13}C NMR spectrum of compound **3na**

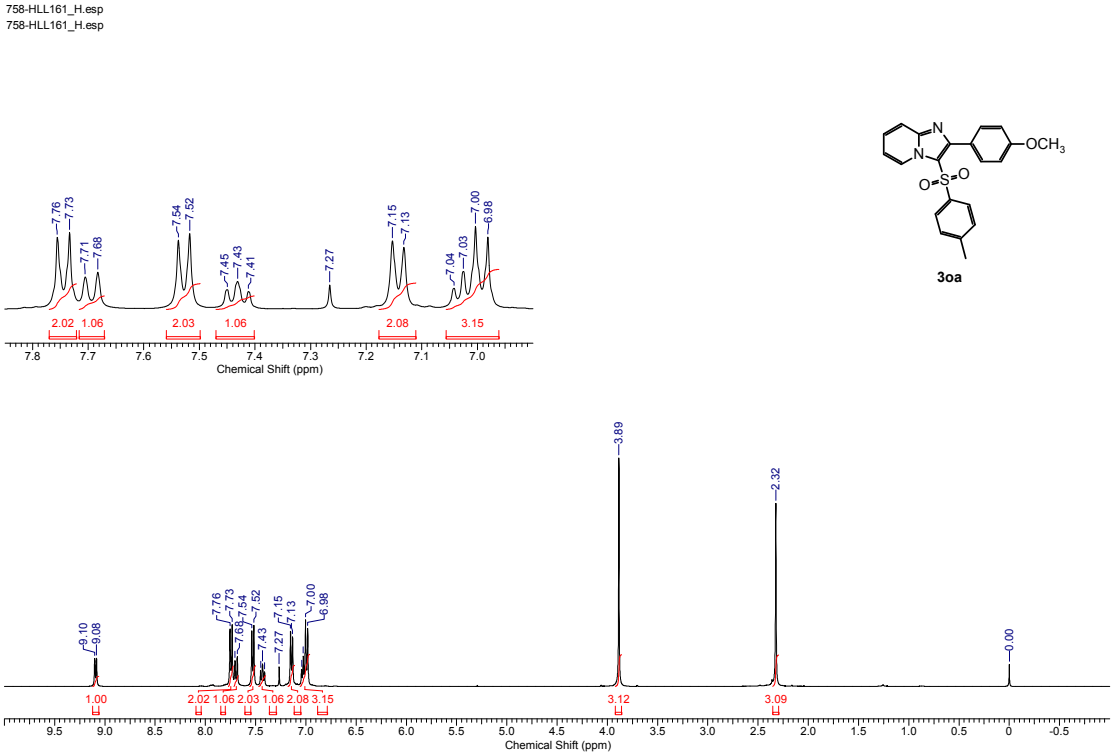

Figure S57. ^{1}H NMR spectrum of compound **3oa**

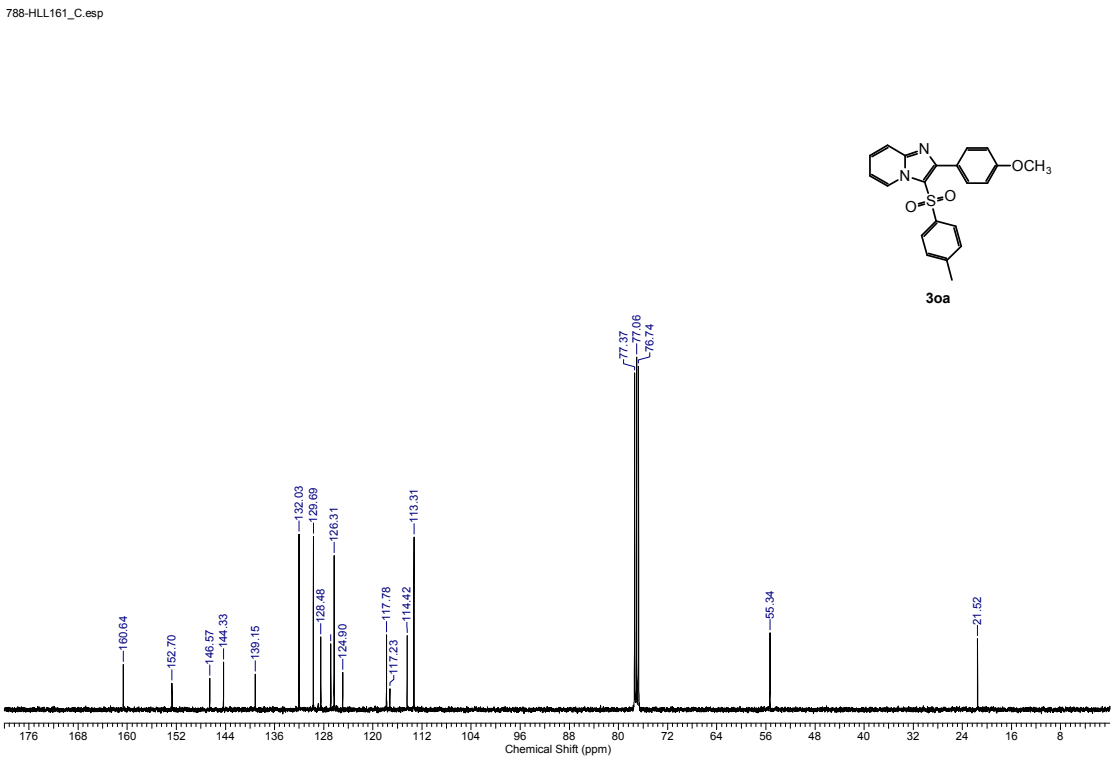

Figure S58. ^{13}C NMR spectrum of compound **3oa**

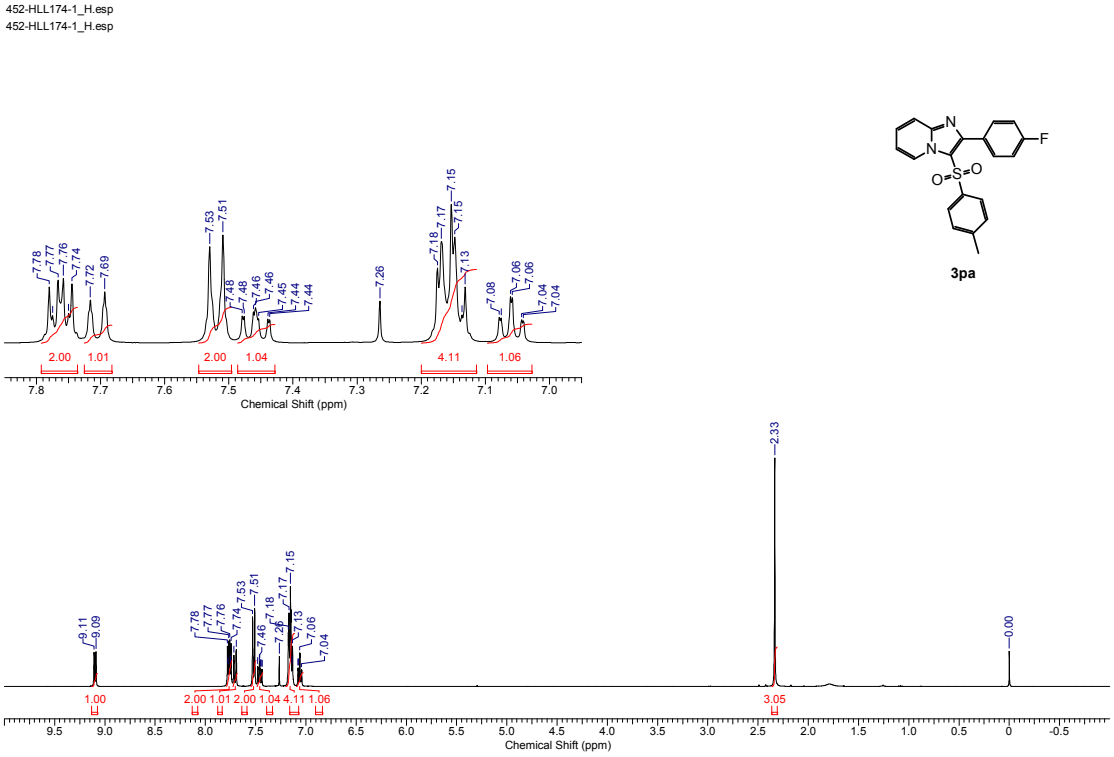

Figure S59. ^{1}H NMR spectrum of compound **3pa**

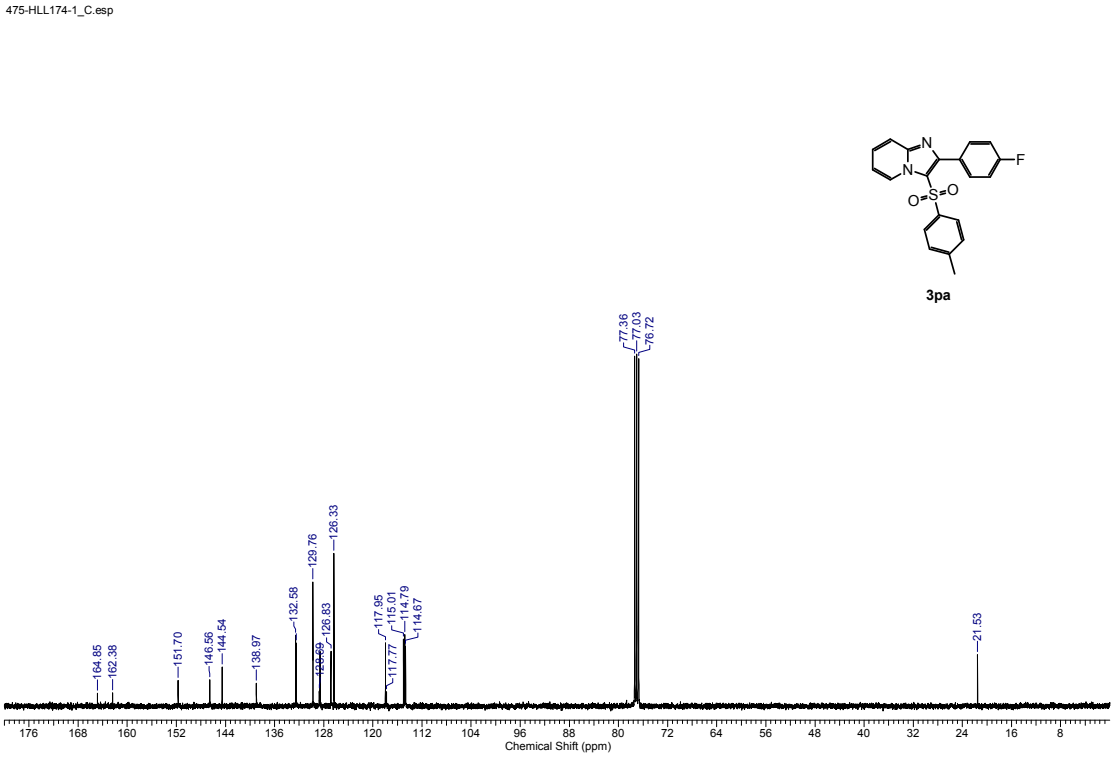

Figure S60. ^{13}C NMR spectrum of compound **3pa**

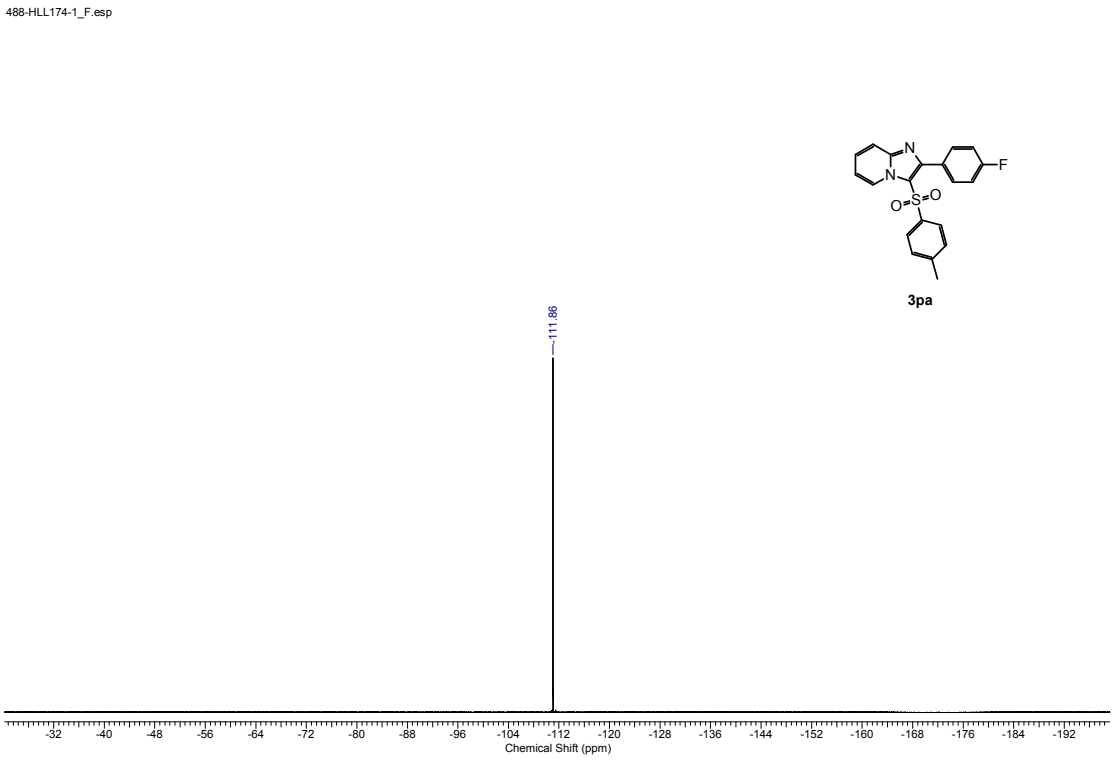

Figure S61. ^{19}F NMR spectrum of compound **3pa**

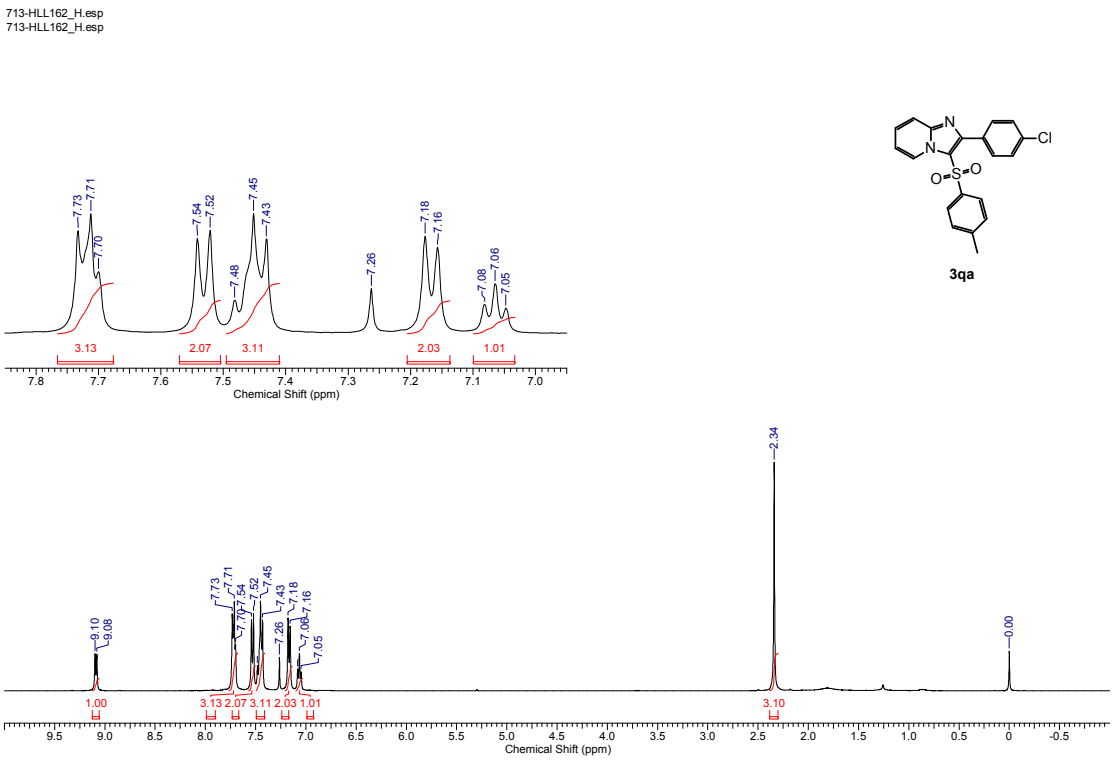

Figure S62. ^{1}H NMR spectrum of compound **3qa**

740-HLL162_C.esp

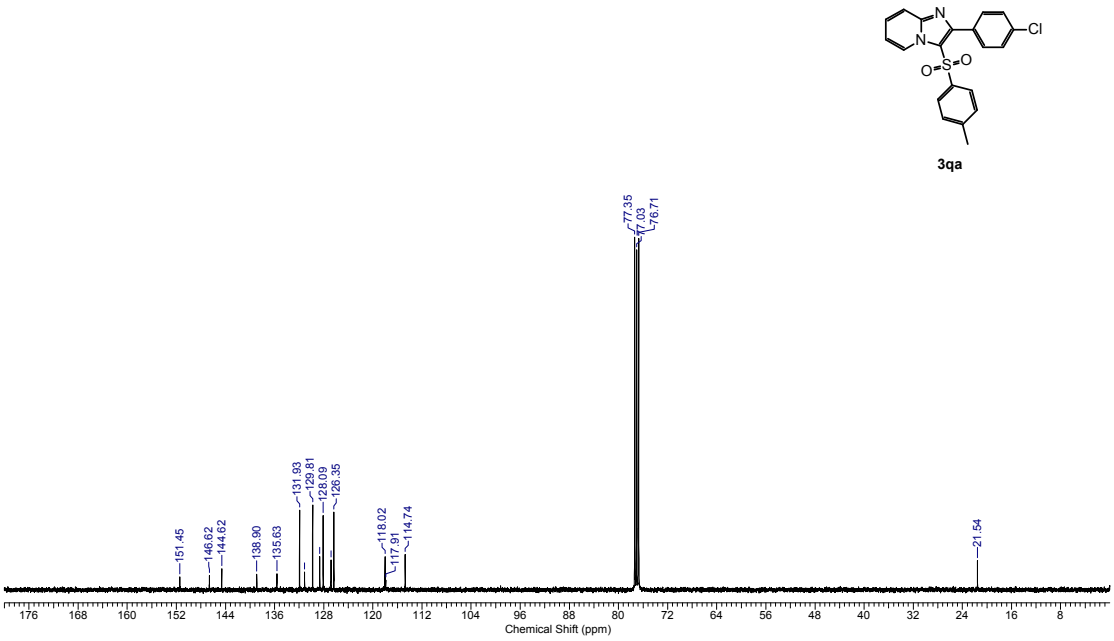

Figure S63. ^{13}C NMR spectrum of compound **3qa**

982-HLL163-1_H.ESP
982-HLL163-1_H.ESP

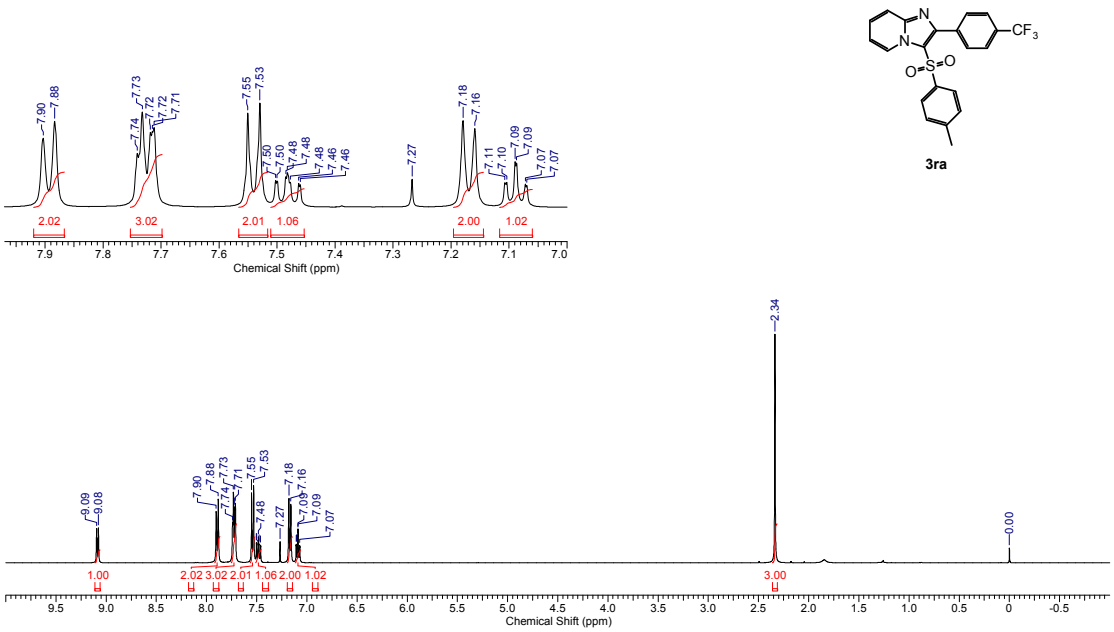

Figure S64. ^{1}H NMR spectrum of compound **3ra**

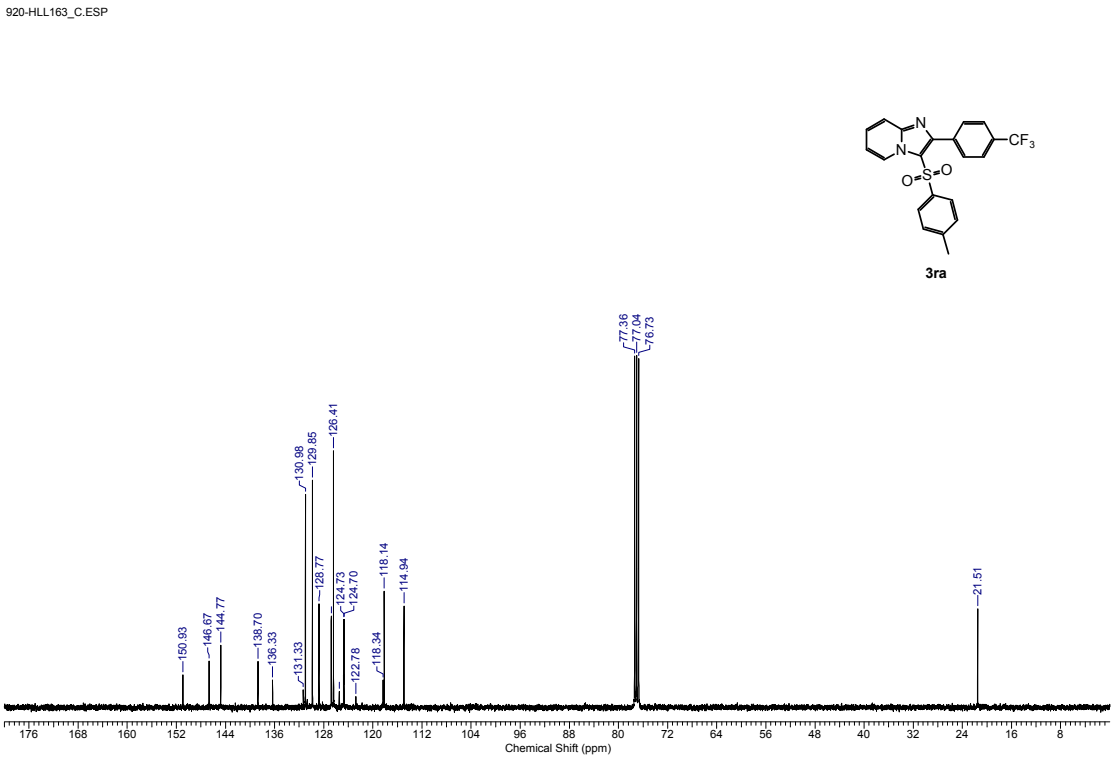

Figure S65. ^{13}C NMR spectrum of compound **3ra**

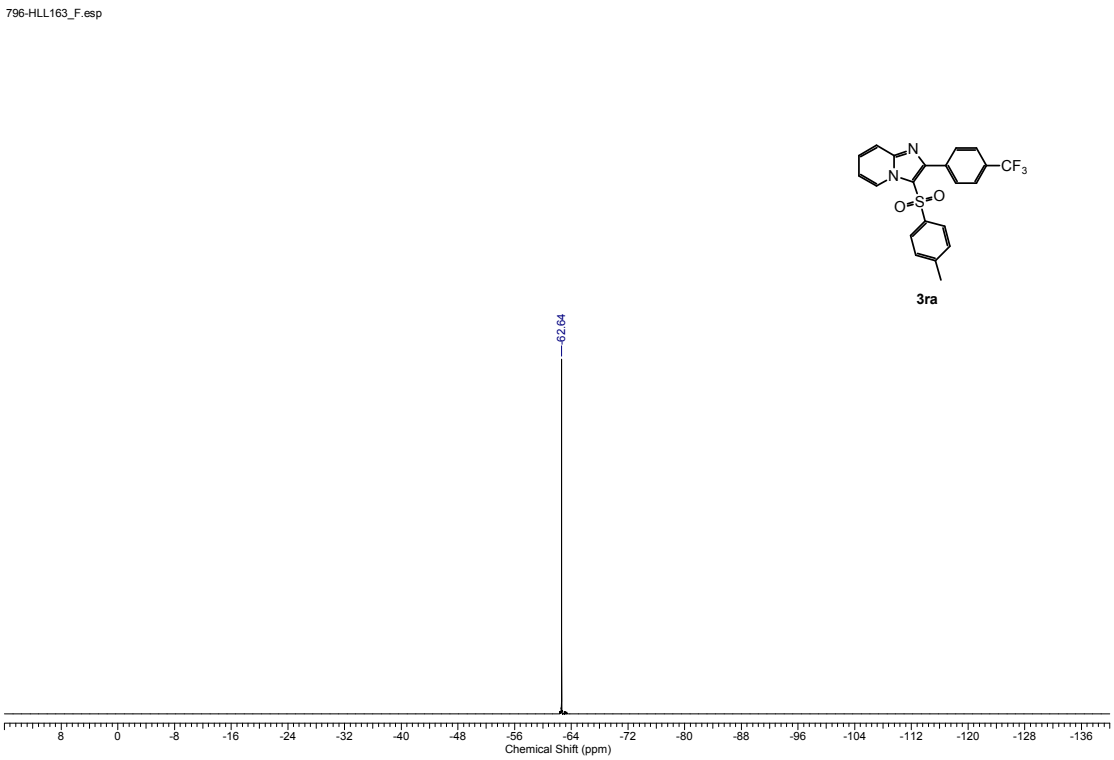

Figure S66. ^{19}F NMR spectrum of compound **3ra**

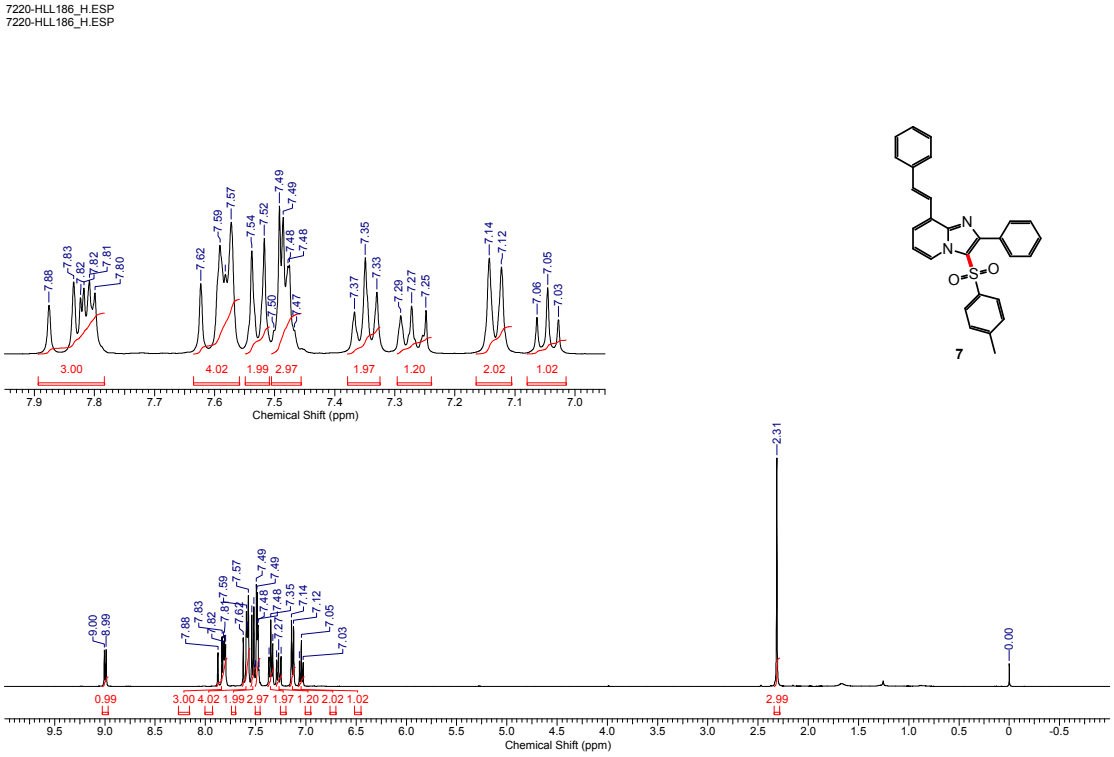

Figure S67. ^{1}H NMR spectrum of compound **7**

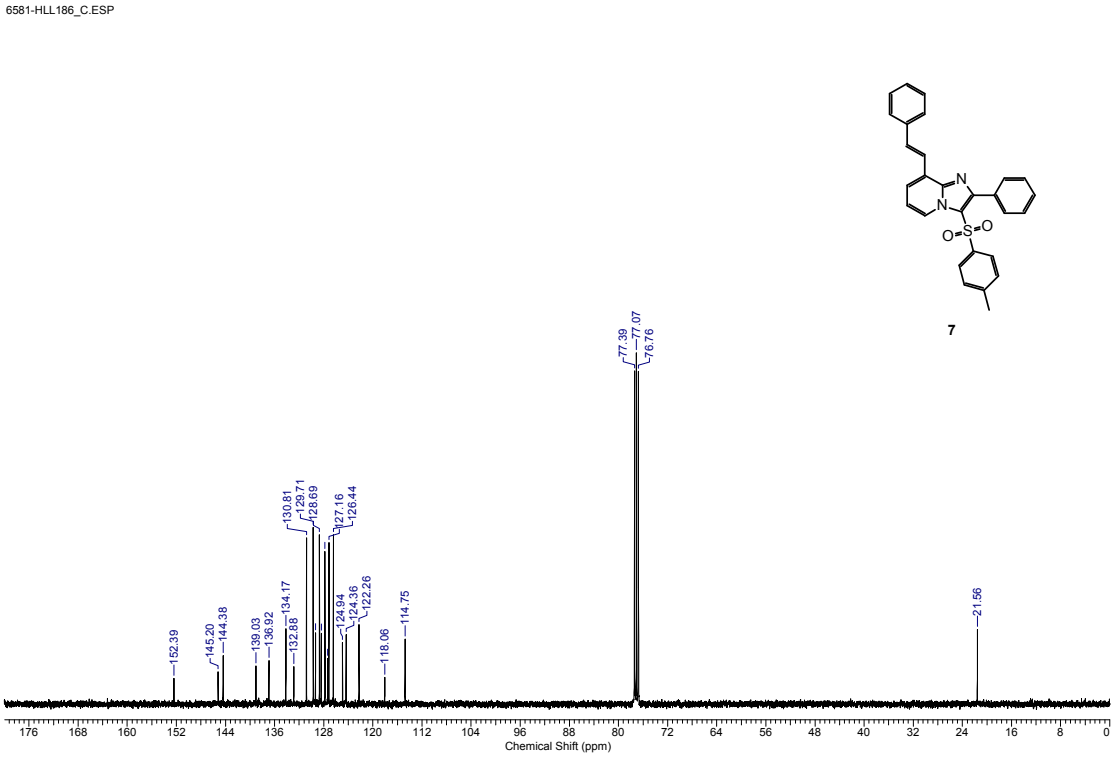

Figure S68. ^{13}C NMR spectrum of compound **7**

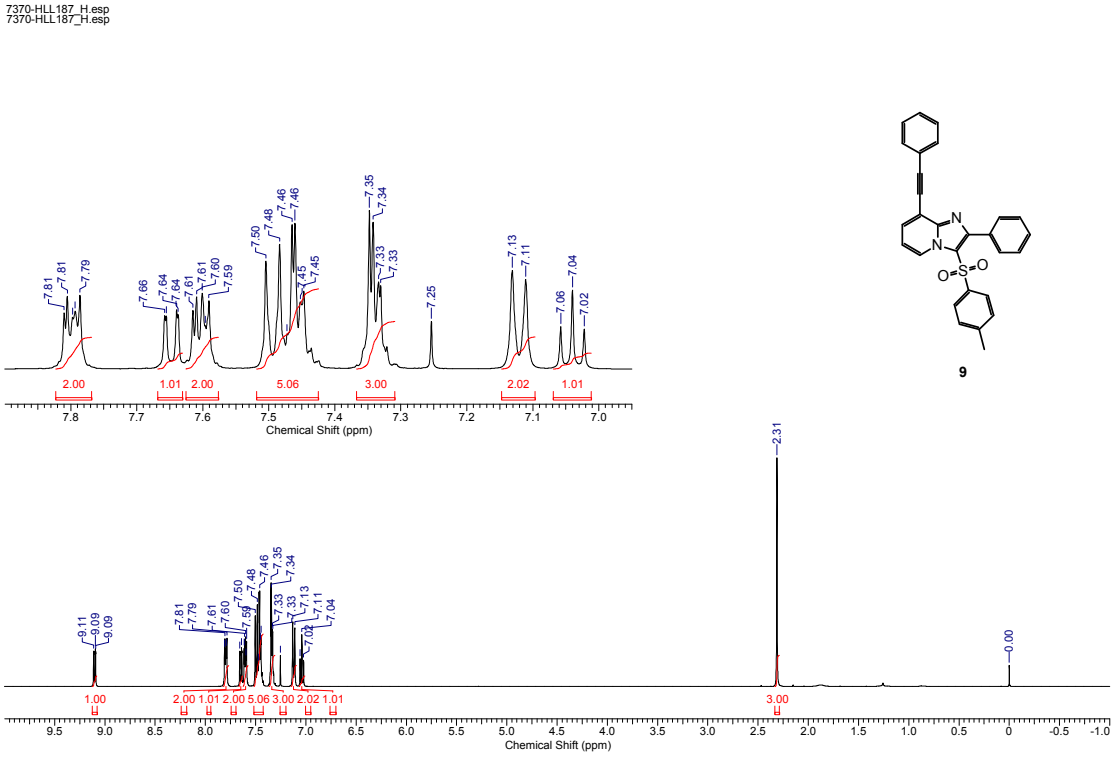

Figure S69. ^{1}H NMR spectrum of compound **9**

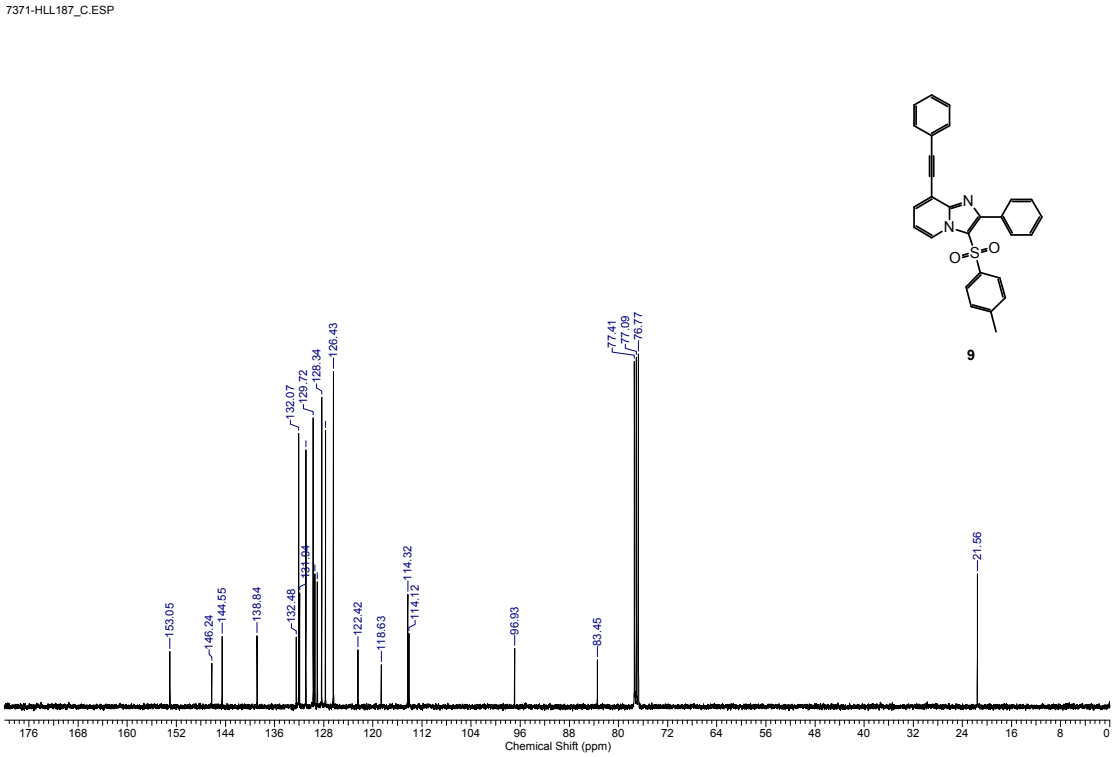

Figure S70. ^{13}C NMR spectrum of compound **9**

9. X-Ray Crystallographic Data

The structure of **3aa**, **3ad**, **3ca**, **3da** and **3na** were determined by the X-ray diffraction. Recrystallized from dichloromethane. Further information can be found in the CIF file. These crystals were deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2003750 (**3aa**), 2046849 (**3ad**), 2046836 (**3ca**), 2046840 (**3da**) and 2046841 (**3na**).

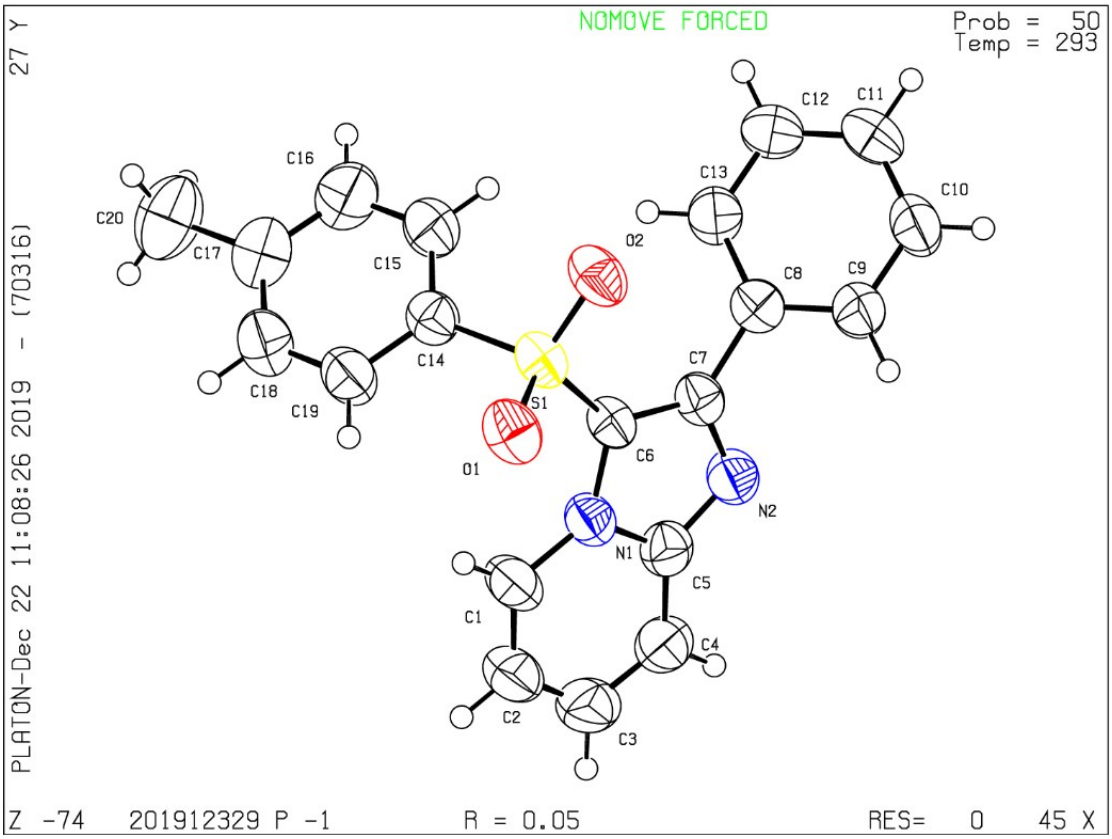

Figure S71. X-ray structure of compound **3aa** (CCDC 2003750)

Table S2. Crystal data and structure refinement for **3aa.**

Identification code	201912329
Empirical formula	$C_{20}H_{16}N_2O_2S$
Formula weight	348.41
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.2243(9)
b/Å	9.2775(13)
c/Å	11.9174(11)
α/°	109.972(11)
β/°	100.537(9)
γ/°	108.093(11)

Volume/Å^3	862.17(19)
Z	2
ρ_{calc}g/cm^3	1.342
μ/mm^{-1}	1.794
F(000)	364.0
Crystal size/mm^3	0.15 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/˚	8.342 to 141.842
Index ranges	-11 ≤ h ≤ 10, -11 ≤ k ≤ 11, -9 ≤ l ≤ 14
Reflections collected	6330
Independent reflections	3249 [R_{int} = 0.0318, R_{sigma} = 0.0509]
Data/restraints/parameters	3249/0/228
Goodness-of-fit on F^2	1.035
Final R indexes [I > = 2σ (I)]	R_1 = 0.0487, wR_2 = 0.1260
Final R indexes [all data]	R_1 = 0.0651, wR_2 = 0.1408
Largest diff. peak/hole / e Å^{-3}	0.28/-0.29

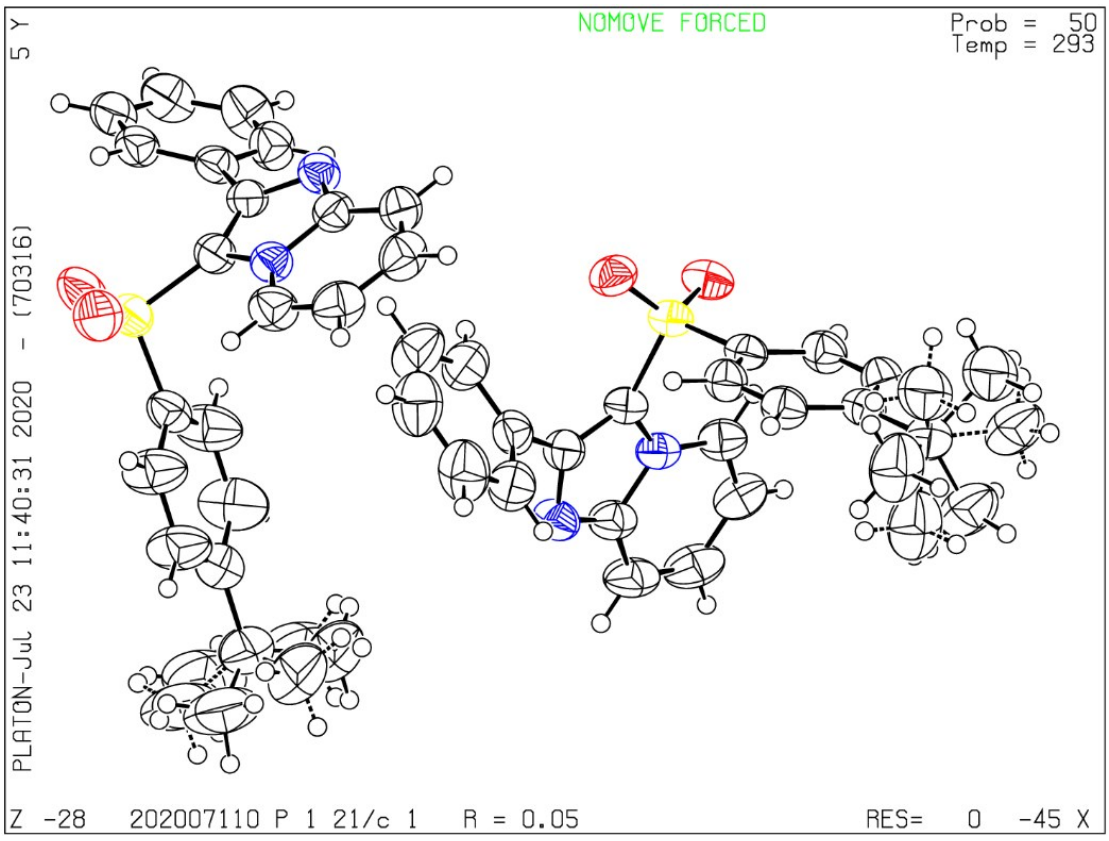

Figure S72. X-ray structure of compound **3ad** (CCDC 2046849)

Table S3. Crystal data and structure refinement for **3ad.**

Identification code	202007110

Empirical formula	$C_{23}H_{22}N_2O_2S$
Formula weight	390.48
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.5438(7)
b/Å	18.4815(6)
c/Å	13.4134(4)
α/°	90
β/°	107.063(4)
γ/°	90
Volume/Å^3	4157.6(3)
Z	8
ρ_{calc}g/cm^3	1.248
μ/mm^{-1}	1.541
F(000)	1648.0
Crystal size/mm^3	0.22 × 0.14 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.118 to 134.152
Index ranges	-20 ≤ h ≤ 17, -14 ≤ k ≤ 22, -16 ≤ l ≤ 15
Reflections collected	17564
Independent reflections	7412 [R_{int} = 0.0364, R_{sigma} = 0.0460]
Data/restraints/parameters	7412/108/536
Goodness-of-fit on F^2	1.027
Final R indexes [I > = 2σ (I)]	R_1 = 0.0541, wR_2 = 0.1396
Final R indexes [all data]	R_1 = 0.0827, wR_2 = 0.1675
Largest diff. peak/hole / e Å^{-3}	0.50/-0.31

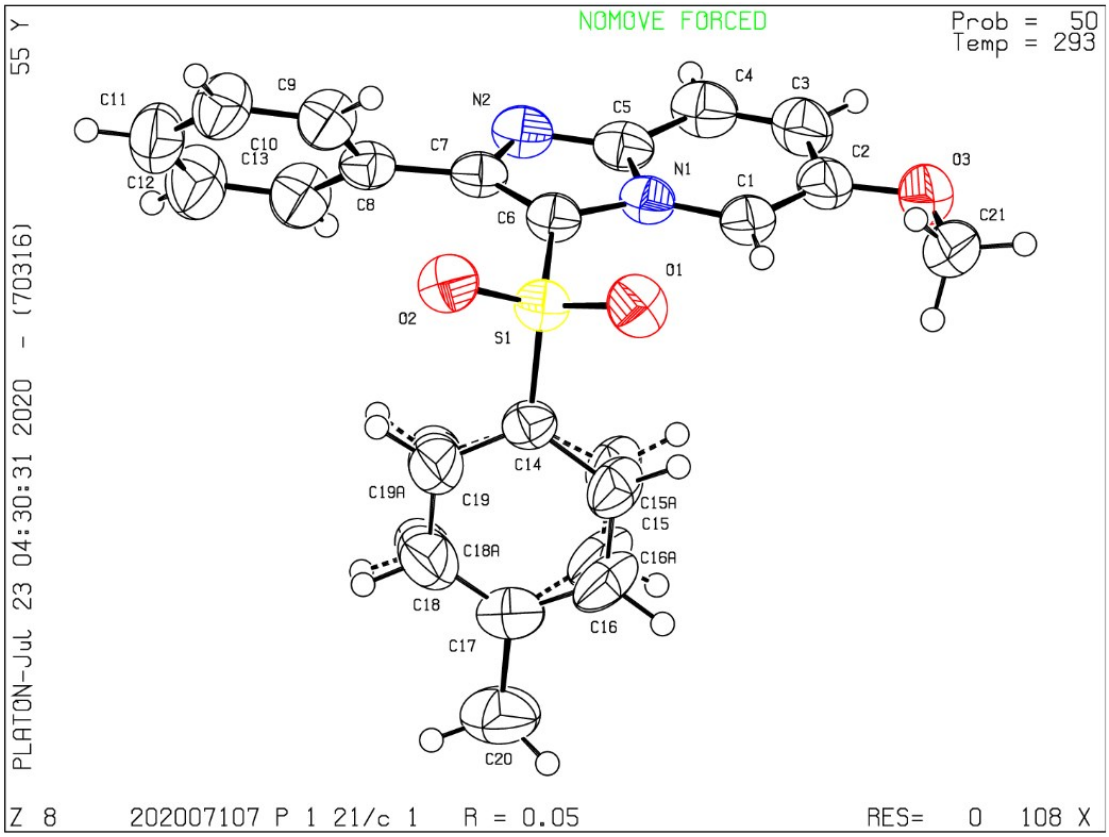

Figure S73. X-ray structure of compound **3ca** (CCDC 2046836)

Table S4. Crystal data and structure refinement for **3ca.**

Identification code	202007107
Empirical formula	$C_{21}H_{18}N_2O_3S$
Formula weight	378.43
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.29236(19)
b/Å	14.5610(4)
c/Å	15.4305(3)
α/°	90
β/°	91.003(2)
γ/°	90
Volume/Å^3	1862.87(8)
Z	4
ρ_{calc}g/cm^3	1.349
μ/mm^{-1}	1.745
F(000)	792.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	8.35 to 134.156
Index ranges	-9 ≤ h ≤ 9, -17 ≤ k ≤ 16, -18 ≤ l ≤ 9
Reflections collected	6802
Independent reflections	3322 [R_{int} = 0.0283, R_{sigma} = 0.0393]
Data/restraints/parameters	3322/0/248
Goodness-of-fit on F^2	1.036
Final R indexes [I > = 2σ (I)]	R_1 = 0.0458, wR_2 = 0.1209
Final R indexes [all data]	R_1 = 0.0580, wR_2 = 0.1319
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.29

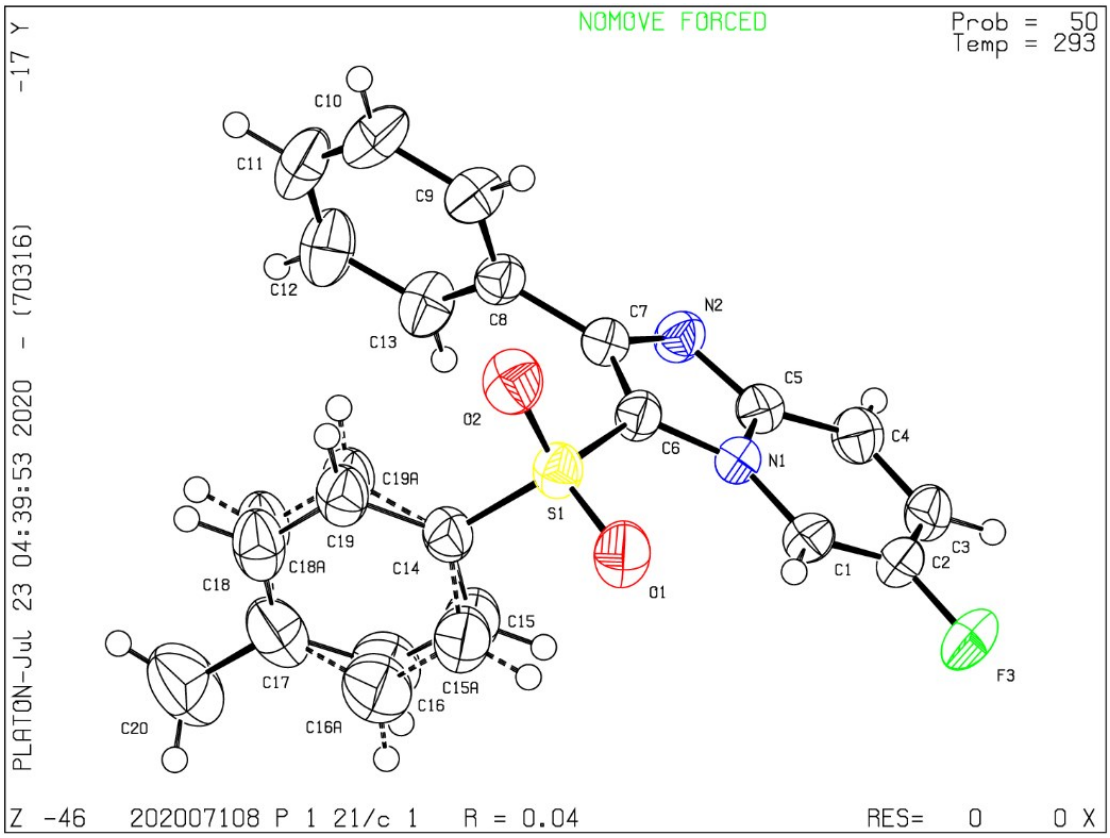

Figure S74. X-ray structure of compound **3da** (CCDC 2046840)

Table S5. Crystal data and structure refinement for **3da.**

Identification code	202007108
Empirical formula	$C_{20}H_{15}FN_2O_2S$
Formula weight	366.40
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.7672(3)

b/Å	12.5717(3)
c/Å	10.2914(3)
α/°	90
β/°	100.758(2)
γ/°	90
Volume/Å^3	1749.90(7)
Z	4
ρ_{calc}g/cm^3	1.391
μ/mm^{-1}	1.881
F(000)	760.0
Crystal size/mm^3	0.21 × 0.14 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.604 to 134.126
Index ranges	-9 ≤ h ≤ 16, -12 ≤ k ≤ 15, -12 ≤ l ≤ 12
Reflections collected	6568
Independent reflections	3126 [R_{int} = 0.0284, R_{sigma} = 0.0351]
Data/restraints/parameters	3126/0/237
Goodness-of-fit on F^2	1.055
Final R indexes [I > = 2σ (I)]	R_1 = 0.0436, wR_2 = 0.1146
Final R indexes [all data]	R_1 = 0.0530, wR_2 = 0.1252
Largest diff. peak/hole / e Å^{-3}	0.30/-0.30

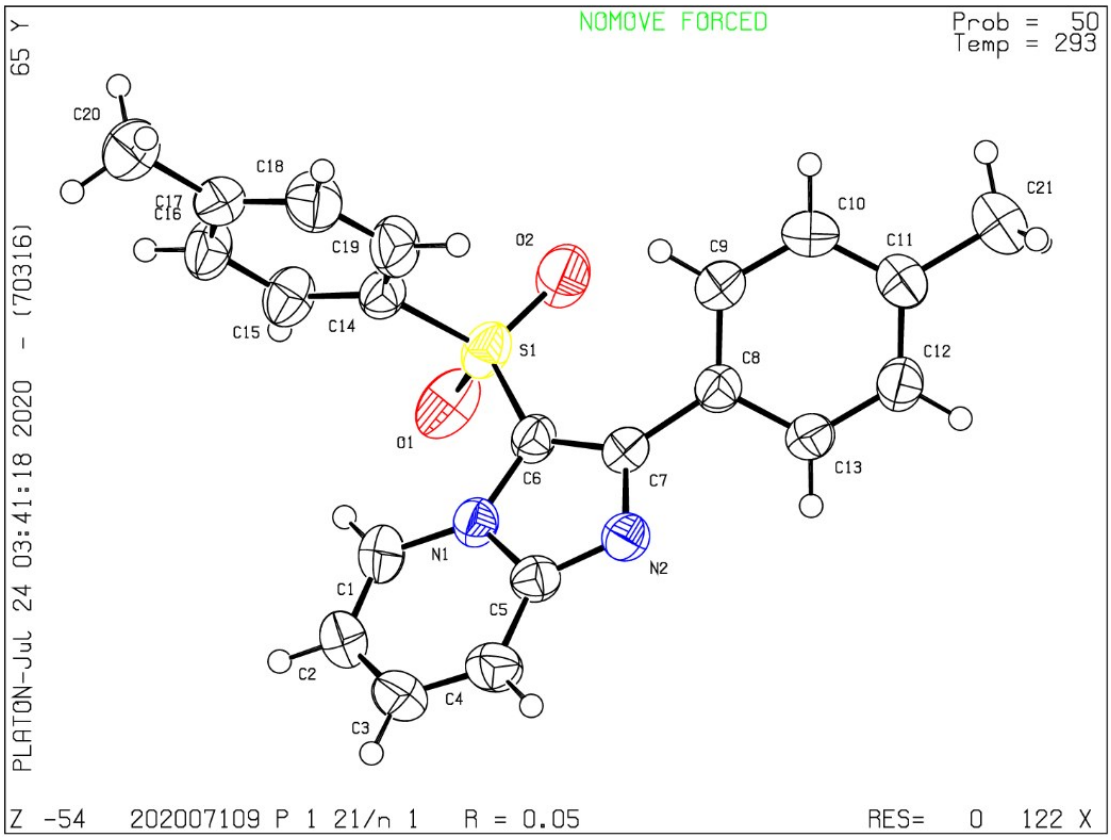

Figure S75. X-ray structure of compound **3na** (CCDC 2046841)

Table S6. Crystal data and structure refinement for **3na.**

Identification code	202007109
Empirical formula	$C_{21}H_{18}N_2O_2S$
Formula weight	362.43
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.3338(3)
b/Å	15.3970(4)
c/Å	12.9510(3)
α/°	90
β/°	93.887(3)
γ/°	90
Volume/Å^3	1856.95(8)
Z	4
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	1.685
F(000)	760.0
Crystal size/mm^3	0.19 × 0.15 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.934 to 134.132
Index ranges	-11 ≤ h ≤ 9, -18 ≤ k ≤ 16, -15 ≤ l ≤ 15
Reflections collected	6984
Independent reflections	3308 [R_{int} = 0.0310, R_{sigma} = 0.0404]
Data/restraints/parameters	3308/0/237
Goodness-of-fit on F^2	1.043
Final R indexes [I > = 2σ (I)]	R_1 = 0.0484, wR_2 = 0.1238
Final R indexes [all data]	R_1 = 0.0606, wR_2 = 0.1360
Largest diff. peak/hole / e Å^{-3}	0.19/-0.31