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Supplementary Information

Visible Light-Induced Sulfonylation with Sulfinates as Closed-Shell Radical Acceptors

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General Information

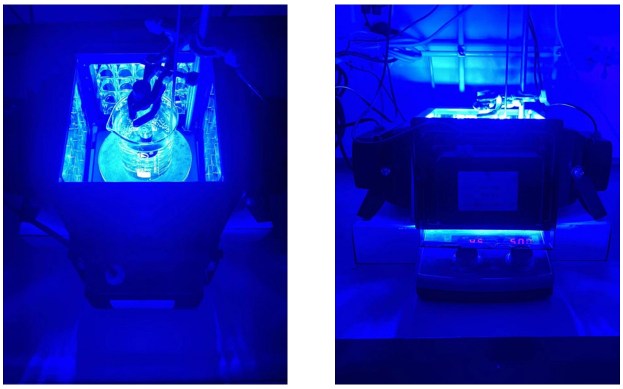
All reactions were performed under argon using flame-dried glassware unless otherwise noted. DMSO was distilled over CaH_2 and rigorously degassed by freeze/pump/thaw. All reagents and starting materials were commercially available and used without further purification unless indicated otherwise. Thin layer chromatographies were carried out on GF254 plates (0.25 mm layer thickness). Flash chromatographies were performed with 200 – 300 mesh silica gels. Reactions were monitored by TLC and visualized by $KMnO_4$ stain. Yields reported were for isolated, spectroscopically pure compounds.

^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker Avance 400 or 600 MHz spectrophotometers. Chemical shifts (δ) were expressed in ppm., and *J*-values are given in Hz. Chemical shifts in ^1H NMR spectra was reported in parts per million on the δ scale from an internal standard of residual chloroform (7.26 ppm). Data for ^{13}C NMR spectra were presented in terms of chemical shift in ppm from the central peak of $CDCl_3$ (77.16ppm). ^1H NMR data was presented as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, br s = broad singlet), coupling constant in Herts (Hz), and integration.

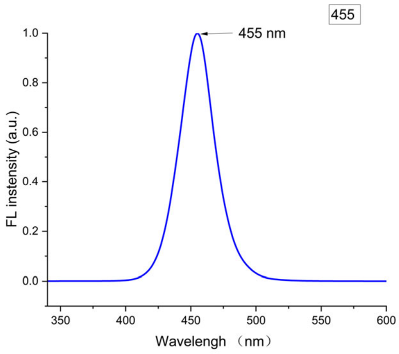
HR-ESI-MS were taken on Agilent 6540 Q-TOF spectrometer. UV-Vis measurements were carried out on a Hitachi UV-1900 UV-Visible spectrophotometer. EPR spectra were recorded by an ADANI SPINSCAN X spectrometer. Cyclic voltammetry studies were carried out on a CHI 760E electrochemical workstation (Shanghai CH Instruments Co., China). The emission spectra were recorded in a Hitachi F-7000 fluorescence spectrometer.

General Procedures for Photochemical Sulfonylation

To an oven dried 10.0 mL glass tube with a magnetic stirring bar was charged with aryl halide (0.20 mmol, 1.0 equiv.), sodium sulfinate (0.40 mmol, 2.0 equiv.), photocatalyst (0.02 mmol, 10 mol%), Cs_2CO_3 (0.40 mmol, 2.0 equiv.), and TBAI (0.5 mmol, 2.5 equiv.). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMSO (2.0 mL) were carefully added to the reaction tube under Argon. The resulting mixture was stirred for 12 hours under four 35 W blue LED lamps (the distance was about 7.0 cm) irradiation at 45 °C unless noted otherwise. After irradiating for the indicated time, the reaction was diluted with water. The aqueous phase was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether) on silica gel to afford the product.



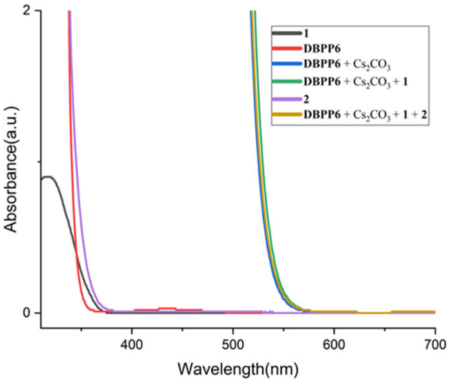
Supplementary Figure 1. Experimental setup for Photocatalyzed Sulfonylation with Sulfinate as Radical Acceptors Enabled by Phenolate Photocatalysis



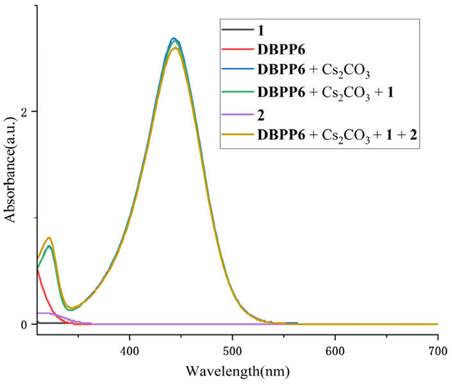
Supplementary Figure 2. Emission spectra of the 35 W blue LED lamp.

Supplementary Note 1. UV-Vis Spectroscopic Measurements

The UV-Vis absorption spectra of DMSO solutions (0.05 M or 0.0001M) of 4-acetylbenzene bromide **1**, sodium *p*-toluenesulfinate **2**, and **DBPP6** with Cs_2CO_3 were recorded on Hitachi UV-1900 UV-Visible spectrophotometer (1 mm short light path cuvettes have been employed in order to avoid fast signal saturation). The absorption of DMSO solution of **1** (black line), and **2** (purple line) is about 380 nm. The colorless solution of **DBPP6** (red line) was immediately turned to a primrose yellow color upon addition of Cs_2CO_3 (blue line), and no new color change after **1** or both **1** and **2** was added to the solution of the phenolate anion of **DBPP6** (green and brown line), indicating that no EDA ground state association occurred and the photon-absorbing ability of the phenolate anion in the visible spectral region was responsible for triggering the aryl radical from its halide.



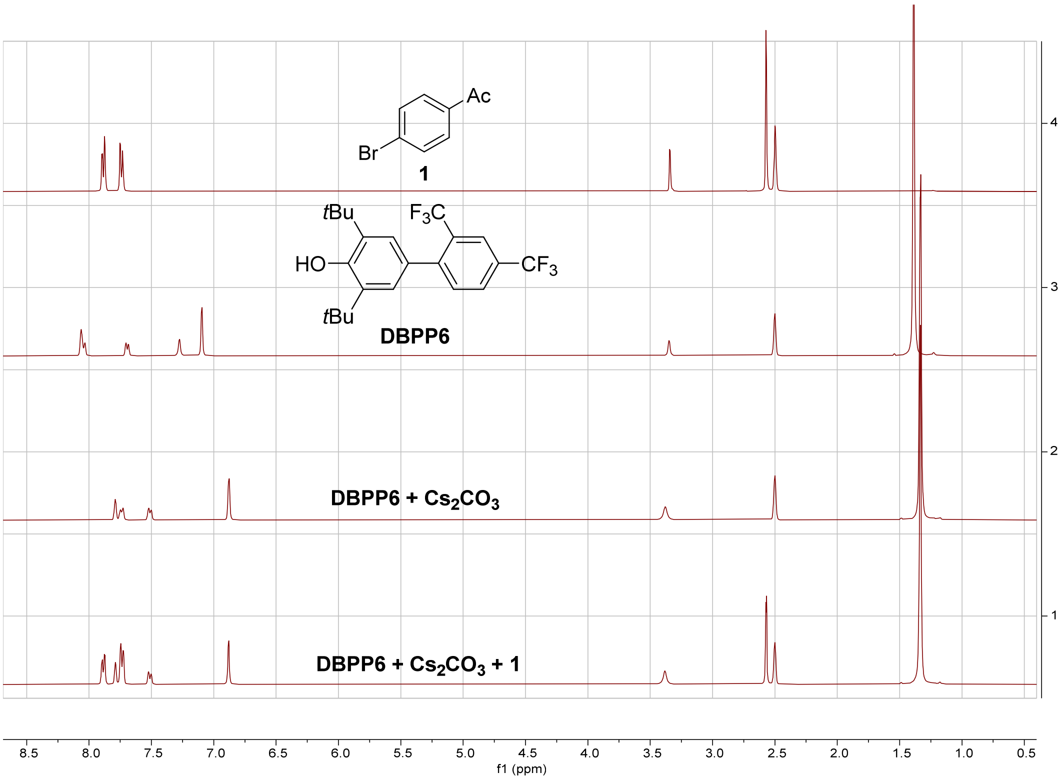
Supplementary Figure 3. UV-Vis absorption spectra (0.05 M in DMSO)



Supplementary Figure 4. UV-Vis absorption spectra (0.0001 M in DMSO)

Supplementary Note 2. ^{1}H NMR Spectroscopic Studies

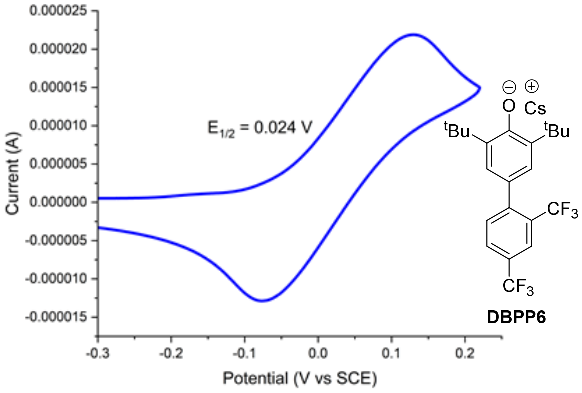
The ^{1}H NMR analysis was made on the DMSO-*d*6 solutions (0.1 M) of **1**, **DBPP6**, mixture of **DBPP6** and Cs_2CO_3, mixture of **DBPP6**, Cs_2CO_3 and **1**. Under these conditions, **DBPP6** was completely deprotonated by Cs_2CO_3, and no significant peak shifting of hydrogens were observed after **1** was added to the solution of the phenolate anion of **DBPP6**. On the contrary, in the previously reported cases, the formation of an EDA complex between the reaction components is typically accompanied by a significant shift of the signals.[1, 2] Altogether, the possible formation of an EDA complex between **1** and the phenolate anion of **DBPP6** can be reasonably excluded.



Supplementary Figure 5. Comparison of ^{1}H NMR spectra of **1**, **DBPP6**, mixtures of DBPP6 and Cs_2CO_3, mixtures of **DBPP6**, Cs_2CO_3 and **1** in DMSO-*d*6.

Supplementary Note 3. Electrochemical Measurements

Tetrabutylammonium hexafluorophosphate (34.9 mg, 0.09 mmol) was added to a 0.003 M solution of the phenolate anion of **DBPP6** (generated in situ by the deprotonation of **DBPP6** with 1.1 equiv. Cs_2CO_3) in 3.0 mL of dry DMSO. The resulting solution was vigorously bubbled with N_2 for 5 minutes prior to the measurement. The oxidation potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate.



Supplementary Figure 6. The cyclic voltammogram of the phenolate anion of **DBPP6** vs SCE in DMSO at 0.1 V/s.

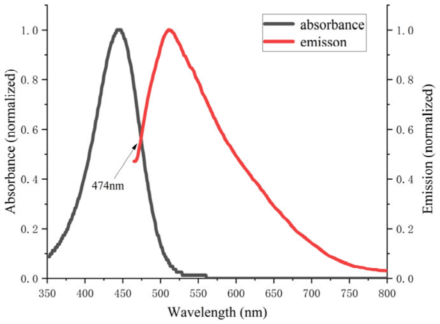
With this data in hand we calculated the redox potential of the excited phenolate anion of **DBPP6** employing the following equation[3]:

$$E_{1/2}(\mathbf{DBPP6}^{\bullet}/\mathbf{DBPP6}^{-*}) = E_{1/2}(\mathbf{DBPP6}^{\bullet}/\mathbf{DBPP6}^{-}) - E_{0\text{-}0}(\mathbf{DBPP6}^{-*}/\mathbf{DBPP6}^{-})$$

$E_{1/2}(\mathbf{DBPP6}^{\bullet}/\mathbf{DBPP6}^{-})$ = 0.02 V vs SCE. $E_{0\text{-}0}(\mathbf{DBPP6}^{-*}/\mathbf{DBPP6}^{-})$, the excited state energy of the phenolate anion of **DBPP6**, was estimated from the intersection of the normalized absorbance and emission spectra. This corresponds to 474 nm, which translates into an $E_{0\text{-}0}(\mathbf{DBPP6}^{-*}/\mathbf{DBPP6}^{-})$ of 2.62 eV for the phenolate anion of **DBPP6**.

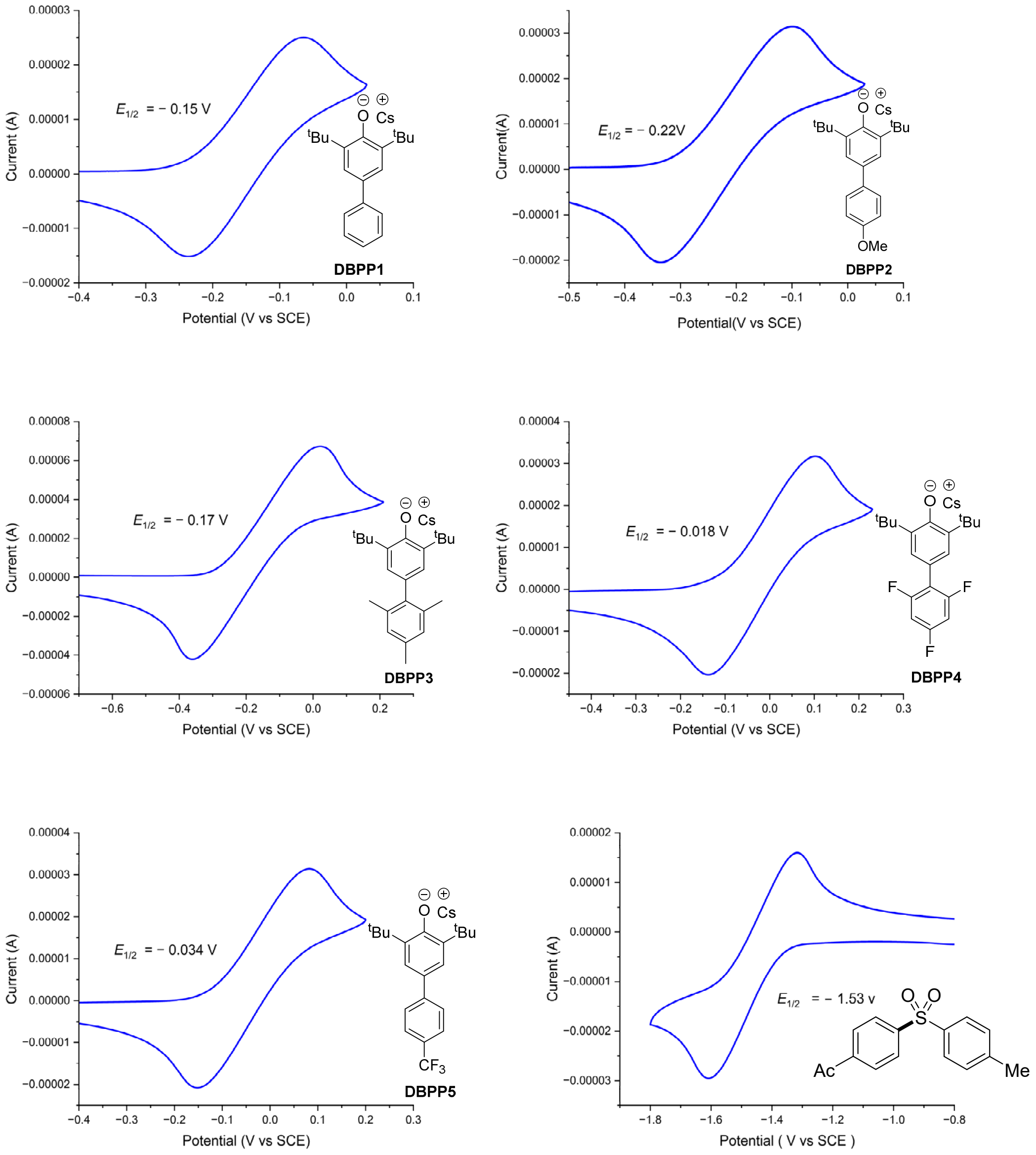
$$E_{1/2}(\mathbf{DBPP6}^{\bullet}/\mathbf{DBPP6}^{-*}) = E_{1/2}(\mathbf{DBPP6}^{\bullet}/\mathbf{DBPP6}^{-}) - E_{0\text{-}0}(\mathbf{DBPP6}^{-*}/\mathbf{DBPP6}^{-})$$

$$= 0.02 - 2.62 = -2.60 \text{ V vs. SCE}$$



Supplementary Figure 7. Normalized absorption and emission spectra of the phenolate anion of **DBPP6** in dry DMSO (5×10^{-5} M), the intersect wavelength was considered to be 474 nm.

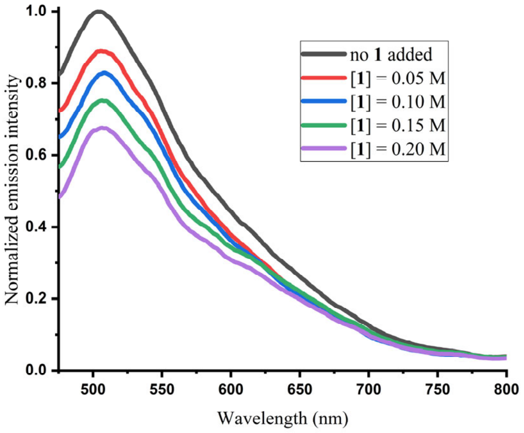
The cyclic voltammetry of target product **3** and phenolate photocatalyst **DBPP** were also carried out. Tetrabutylammonium hexafluorophosphate (34.9 mg, 0.09 mmol) was respectively added to a 0.003M solution of the phenolate anion of **DBPP** (generated in situ by the deprotonation of **DBPP** with 1.1 equiv. Cs_2CO_3) or **3** in 3.0 mL of dry DMSO. The resulting solution was vigorously bubbled with N_2 for 5 minutes prior to the measurement. The oxidation/reduction potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a SCE at 0.1 V/s scan rate.



Supplementary Figure 8. The cyclic voltammogram of **3** and the phenolate anion of **DBPP** vs SCE in DMSO at 0.1 V/s.

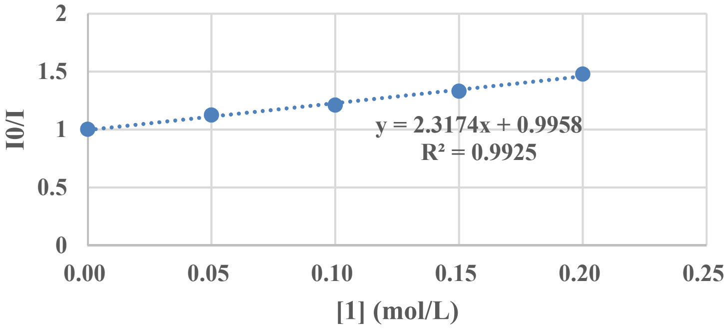
Supplementary Note 4. Steady-State Luminescence Quenching Studies

The samples were prepared by mixing the phenolate anion of **DBPP6** (5×10^{-5} M, freshly prepared in situ by the deprotonation of **DBPP6** with 1.1 equiv. Cs_2CO_3) with the required amount of 4-acetylbenzene bromide **1** in a total volume of 1.0 mL of dry DMSO (rigorously degassed by freeze/pump/thaw) in a 10 × 10 mm light path quartz fluorescence cuvette under an argon atmosphere. The samples were vigorously bubbled with dry argon for 5 minutes prior to the measurement. The excitation wavelength was fixed at 445 nm, the emission light was acquired from 475 nm to 800 nm.



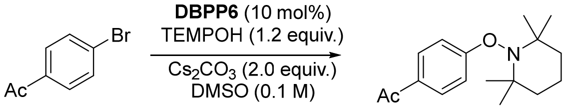
Supplementary Figure 9. Quenching of the phenolate anion of **DBPP6** emission (5×10^{-5} M in DMSO) in the presence of increasing amounts of **1**.

The Stern-Volmer plot shows a linear correlation between the amounts of **1** and the ratio I_0/I.



Supplementary Figure 10. Stern-Volmer quenching plot.

Supplementary Note 5. Radical Trapping Experiments

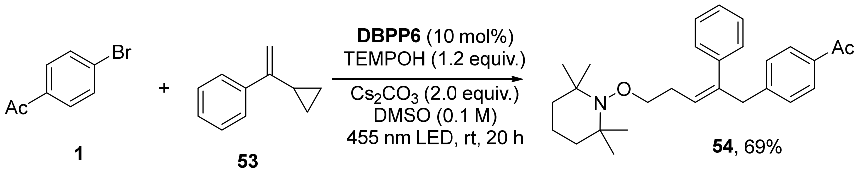


1

52, 57%

To an oven dried 10.0 mL glass tube with a magnetic stirring bar was charged with 4-acetylbenzene bromide **1** (39.8 mg, 0.2 mmol), **DBPP6** (8.5 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.40 mmol), and TEMPOH (37.7 mg, 0.24 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMSO (2.0 mL) were carefully added to the reaction tube under Argon. The resulting mixture was stirred for 20 hours under four 35 W blue LED lamps (the distance was about 7.0 cm) irradiation at room temperature. Irradiation was stopped and the reaction was diluted with water. The aqueous phase was extracted with ethyl acetate (25 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether = 1:50) on silica gel to afford **52** (31.6 mg, 57% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 – 7.47 (m, 2H), 7.25 (br, 2H), 2.54 (s, 3H), 1.73 – 1.54 (m, 5H), 1.52 – 1.37 (m, 1H), 1.24 (s, 6H), 0.99 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 167.7, 130.2, 130.0, 113.9, 60.7, 39.7, 32.4, 26.3, 20.5, 17.0. HR-ESI-MS (m/z): calcd. for $C_{17}H_{26}NO_2$ $[M + H]^+$, 276.1958, found 276.1954.

Supplementary Note 6. Radical Clock Experiments

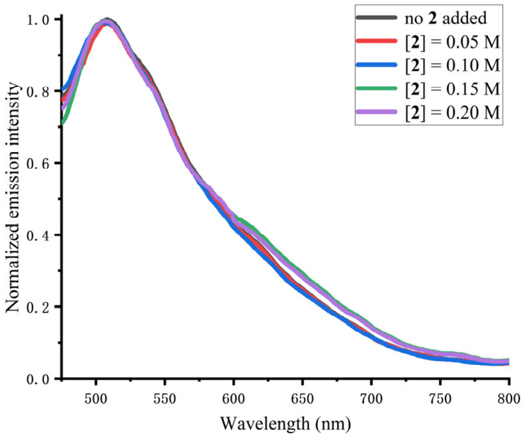


To an oven dried 10.0 mL glass tube with a magnetic stirring bar was charged with 4-acetylbenzene bromide **1** (39.8 mg, 0.20 mmol), (1-cyclopropylvinyl)benzene **53** (144.3mg, 1.0 mmol), **DBPP6** (8.5 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.40 mmol), and TEMPOH (37.7 mg, 0.24 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMSO (2.0 mL) were carefully added to the reaction tube under Argon. The resulting mixture was stirred for 20 hours under four 35W blue LED lamps (the distance was about 7.0 cm) irradiation at room temperature. Irradiation was stopped and the reaction was diluted with water. The aqueous phase was extracted with ethyl acetate (25 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether = 1:100) on silica gel to afford **54** (57.7 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.30 Hz, 1H), 7.49 – 6.99 (m, 4H), 6.06 (t, *J* = 7.34 Hz, 1H), 4.76 – 3.52 (m, 2H), 3.18 – 2.15 (m, 3H), 1.55 – 1.33 (m, 2H), 1.16 (s, 4H), 1.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 145.8, 142.6, 138.0, 135.1, 128.6, 128.45, 128.37, 128.3, 128.2, 126.8, 126.2, 75.8, 59.8, 39.6, 36.0, 33.1, 28.8, 26.5, 20.2, 17.1. HR-ESI-MS (m/z): calcd. for $C_{28}H_{38}NO_2$ $[M + H]^+$, 420.2897, found 420.2899.

Supplementary Note 7. Mechanism Experiments for Excluding the Formation of Sulfonyl Radicals

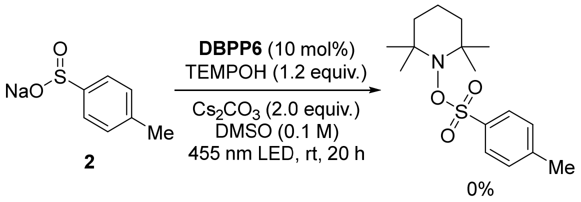
Steady-State Luminescence Quenching Studies of 2

The samples were prepared by mixing the phenolate anion of **DBPP6** (5×10^{-5} M, freshly prepared in situ by the deprotonation of **DBPP6** with 1.1 equiv. Cs_2CO_3) with the required amount of sodium *p*-toluenesulfinate **2** in a total volume of 1.0 mL of dry DMSO (rigorously degassed by freeze/pump/thaw) in a 10 × 10 mm light path quartz fluorescence cuvette under an argon atmosphere. The samples were vigorously bubbled with dry argon for 5 minutes prior to the measurement. The excitation wavelength was fixed at 445 nm, the emission light was acquired from 475 nm to 800 nm. Experimental results showed that the excited **DBPP6**$^-$ could not be quenched by *p*-toluenesulfinate **2**.



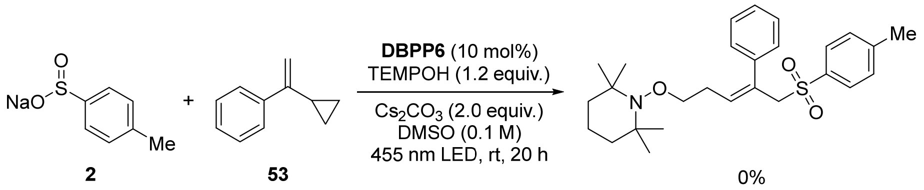
Supplementary Figure 11. Quenching of the phenolate anion of **DBPP6** emission (5×10^{-5} M in DMSO) in the presence of increasing amounts of **2**.

Radical Trapping Experiments



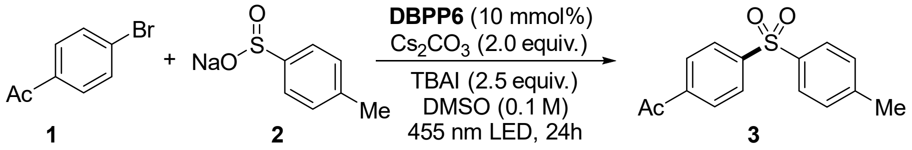
To an oven dried 10.0 mL glass tube with a magnetic stirring bar was charged with sodium *p*-toluenesulfinate **2** (35.6 mg, 0.20 mmol), **DBPP6** (8.5 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.40 mmol), and TEMPOH (37.7 mg, 0.24 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMSO (2.0 mL) were carefully added to the reaction tube under Argon. The resulting mixture was stirred for 20 hours under four 35W blue LED lamps (the distance was about 7.0 cm) irradiation at room temperature. No desired product was detected.

Radical Clock Experiments

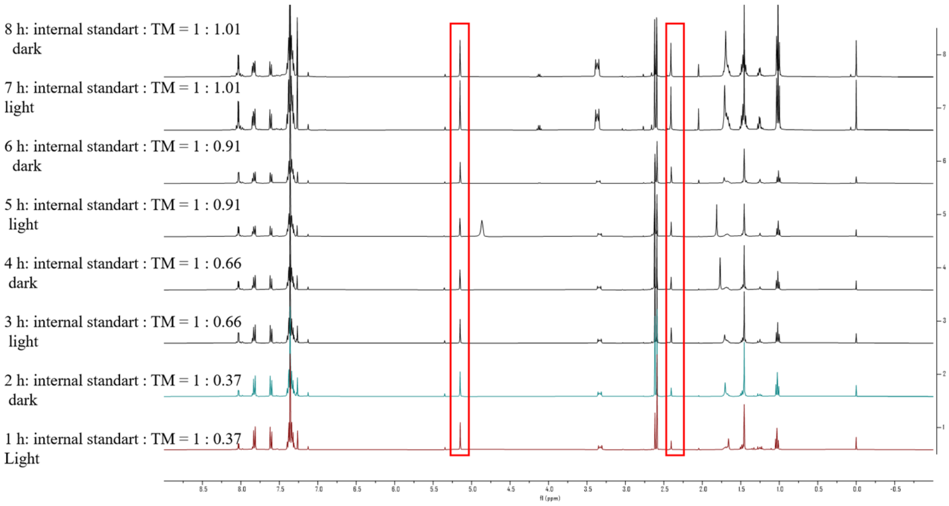


To an oven dried 10.0 mL glass tube with a magnetic stirring bar was charged with sodium *p*-toluenesulfinate **2** (35.6 mg, 0.20 mmol), **DBPP6** (8.5 mg, 0.02 mmol), (1-cyclopropylvinyl)benzene **53** (144.3mg, 1.0 mmol), Cs_2CO_3 (131.2 mg, 0.40 mmol), and TEMPOH (37.7 mg, 0.24 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMSO (2.0 mL) were carefully added to the reaction tube under Argon. The resulting mixture was stirred for 20 hours under four 35W blue LED lamps (the distance was about 7.0 cm) irradiation at room temperature. No desired product was detected.

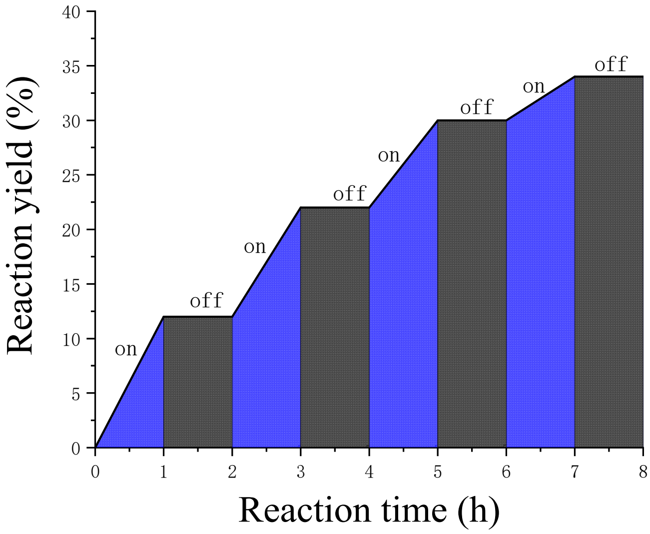
Supplementary Note 8. Light-dark Interval Experiments



The light-dark interval experiments were performed according the general procedure with 0.2 mmol 4-acetylbenzene bromide **1**. The yield of **3** was determined by ^{1}H NMR using diphenylacetonitrile as an internal standard. An aliquot was taken out of the reaction system via syringe for every 1 hour was achieved. The whole process was performed under argon with glass tube. The NMR spectra revealed that a radical chain process was not the major reaction pathway, while it could not be completely ruled out at the current stage.



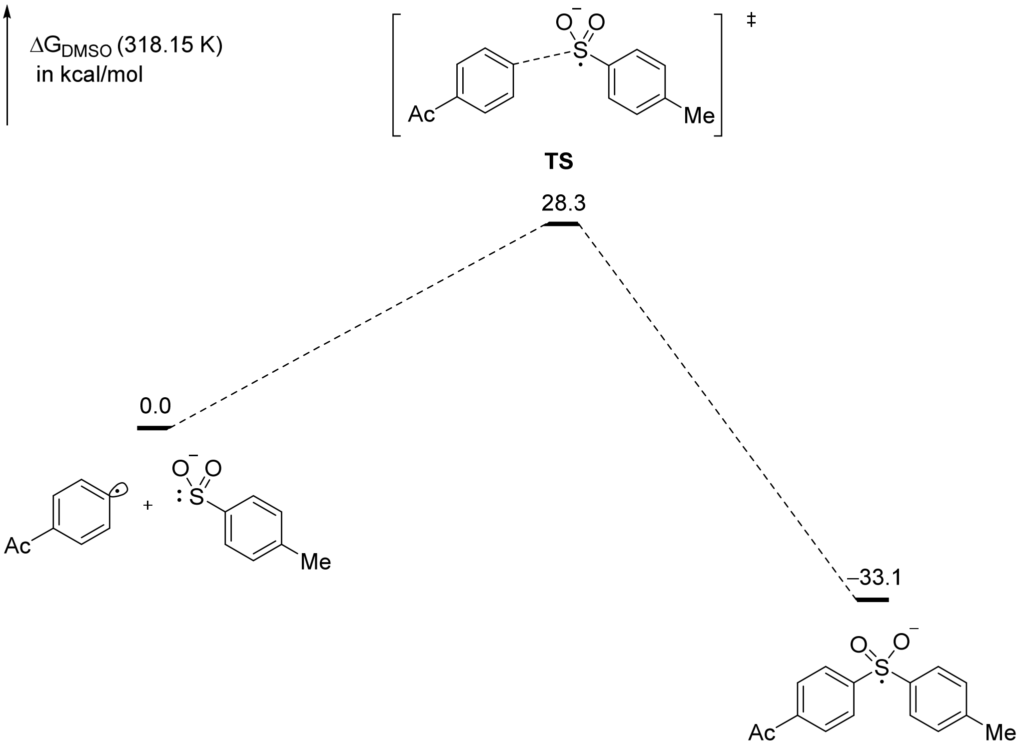
Supplementary Figure 12. The yields of NMR from the light-dark interval experiments. Yields were inferred by area integration ratio.



Supplementary Figure 13. Light dark interval experiment of compound **3** yield changing with time.

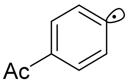
Supplementary Note 9. Density Functional Theory (DFT) Calculations

DFT calculations were performed with the Gaussian 16 software package, A.03 version.[5] B3LYP functional including Grimme empirical dispersion correction (GD3BJ)[6] with split-valence basis sets 6-31+G(d, p)[7-9] were used for the geometry optimizations in the gas phase. Harmonic vibrational frequency calculations were performed for the stationary point to determine whether it is the transition structure and to derive the thermochemical corrections for free energies. The transition state has only one imaginary frequency. Intrinsic reaction coordinates (IRC) calculations at the same level verified the connectivity of located intermediates and transition states. Based on the optimized structure, the single point energies were calculated at M06-2X[10] /def2-TZVP[11] level in solution-phase with DMSO as the solvent using the SMD[12] solvation model. The reported free energy in solution includes Gibbs free energy correction at temperature of 318.15 K.



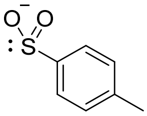
Supplementary Figure 10. Cartesian (Å) Coordinates and Energies of Optimized Structures

Cartesian Coordinates for the Stationary Points



0 2

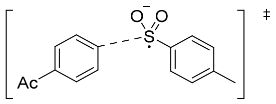
C	-1.87976	1.31117	0.00009
C	-0.48068	1.20471	0.00005
C	0.13987	-0.05551	-0.00003
C	-0.64622	-1.22111	-0.00009
C	-2.04316	-1.13942	-0.00007
C	-2.58734	0.12902	0.00001
C	1.63043	-0.20866	0.00001
O	2.14318	-1.3201	0.00019
C	2.49572	1.03718	-0.00014
H	-2.36544	2.28189	0.00015
H	0.11422	2.11211	0.00014
H	-0.14369	-2.18297	-0.00014
H	-2.65546	-2.03577	-0.00012
H	2.29392	1.65326	-0.88335
H	2.29462	1.65291	0.88347
H	3.54319	0.73512	-0.00059



-1 1

C	0.32264	-1.20489	0.08945
C	1.71774	-1.20345	0.00042
C	2.43732	0.	-0.03706
C	1.71774	1.20345	0.00041
C	0.32264	1.20489	0.08944
C	-0.37901	0.	0.13589
S	-2.23743	0.	0.34097

O	-2.61251	-1.29286	-0.39477
O	-2.61252	1.29287	-0.39475
C	3.94813	0.	-0.09338
H	-0.24346	-2.13269	0.08496
H	2.25826	-2.14819	-0.05247
H	2.25825	2.14819	-0.05249
H	-0.24347	2.13269	0.08494
H	4.32834	-0.88613	-0.61411
H	4.32834	0.88622	-0.61395
H	4.38959	-0.00009	0.91285

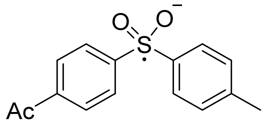


TS

-1 2

C	-2.6485	-0.78805	-0.9351
C	-3.07296	0.21358	-0.03745
C	-2.15907	0.67198	0.93519
C	-0.86794	0.14495	0.99395
C	-0.45316	-0.85314	0.11115
C	-1.35769	-1.31063	-0.85315
C	-4.44448	0.74964	-0.14293
C	-4.889	1.82631	0.8445
O	-5.247	0.3639	-0.99642
H	-3.35539	-1.13913	-1.68248
H	-2.45517	1.44444	1.64155
H	-0.17396	0.53404	1.74103
H	-1.04094	-2.09492	-1.53981
H	-4.81686	1.46643	1.87662
H	-4.25533	2.71647	0.76518

H	-5.92337	2.09401	0.62213
C	2.75421	1.37497	-1.38989
C	3.06767	2.1664	-0.26867
C	2.91234	1.59028	0.99743
C	2.45108	0.28182	1.15868
C	2.0971	-0.46278	0.02586
C	2.28938	0.07261	-1.25886
S	1.70497	-2.20491	0.21753
O	1.21242	-2.85449	-1.0545
O	1.28759	-2.57849	1.61918
C	3.54075	3.59087	-0.43487
H	2.8746	1.79381	-2.38758
H	3.15943	2.17429	1.88229
H	2.33849	-0.15789	2.14377
H	2.03111	-0.52481	-2.12634
H	4.34772	3.66641	-1.17456
H	2.7305	4.25045	-0.77432
H	3.91724	3.99483	0.51095



-1 2

C	-2.48833	-0.00373	1.15645
C	-1.3252	-0.74426	1.19787
C	-0.70674	-1.16467	-0.00805
C	-1.27791	-0.7829	-1.25385
C	-2.43789	-0.0432	-1.28331
C	-3.09536	0.37794	-0.08268
H	-2.95302	0.28291	2.09481
H	-0.88445	-1.0338	2.14607
H	-0.79945	-1.10475	-2.17311

H	-2.89465	0.23323	-2.22781
C	-4.31419	1.14751	-0.16336
O	-4.84138	1.4821	-1.25449
C	-4.99491	1.58026	1.13581
H	-5.89814	2.13773	0.87855
H	-5.27176	0.71921	1.75867
H	-4.34208	2.22056	1.74419
C	2.02685	-0.50542	0.0216
C	2.43458	0.04618	-1.19883
C	2.40748	0.098	1.22677
C	3.22639	1.19271	-1.20531
H	2.13412	-0.43318	-2.12386
C	3.19982	1.24314	1.2027
H	2.08604	-0.34294	2.16383
C	3.62461	1.81098	-0.00966
H	3.54313	1.61622	-2.15594
H	3.49683	1.70592	2.14151
O	1.11531	-2.62556	-1.22572
O	1.07	-2.55629	1.34846
C	4.51227	3.03189	-0.02361
H	5.57188	2.75884	0.07635
H	4.40598	3.59064	-0.95921
H	4.27242	3.70956	0.80298
S	0.87706	-1.88555	0.03823

Supplementary Note 10. Quantum Yield Measurements

The quantum yield for the model reaction was measured by using Melchiorre's procedure.[1]

Determination of the Photon Flux:

A standard ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in Handbook of Photochemistry. The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex $Fe(phen)_3^{2+}$ formed are related to moles of photons absorbed.

The solutions were prepared and stored in dark:

1. Potassium ferrioxalate solution: 589.5 mg of potassium ferrioxalate (commercially available from Alfa Aesar), and 278 μL of sulfuric acid (96%) were added to a 100 mL volumetric flask, and filled to the mark with water (HPLC grade).

2. Phenantroline solution: 0.2% by weight of 1,10-phenanthroline in water (200 mg in 100 mL volumetric flask).

3. Buffer solution: to a 100 mL volumetric flask, 4.94 g of NaOAc and 1 mL of sulfuric acid (96%) were added and filled to the mark with water (HPLC grade).

Procedure: 1 mL of the actinometer solution was added to a quartz cuvette (l = 10 mm). The cuvette was placed 10 cm away from the light source and irradiated at λ = 450 nm (emission slit width at 10.0 nm) at 45 ℃. This procedure was repeated 3 times, quenching the reactions after different time intervals: 10, 15, 20, and 25 seconds.

The actinometer measurements were done as follows:

1. After irradiation, the actinometer solution was removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. This flask was filled to the mark with water (HPLC grade).

2. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.

The moles of Fe^{2+} formed for each sample are determined according to the Beer's

Law:

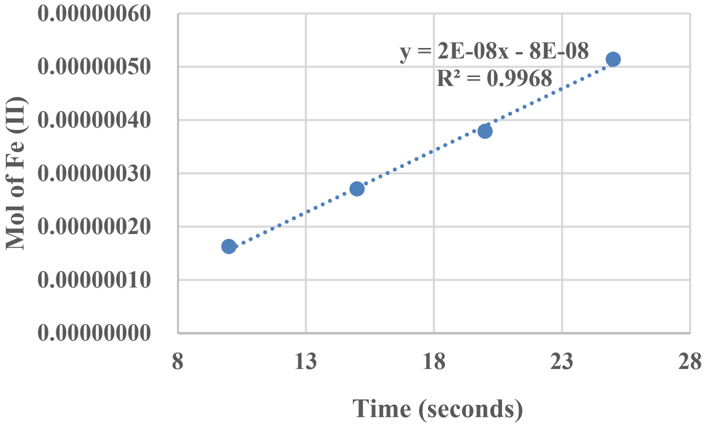
$$mol\ \mathrm{Fe}^{2+} = \frac{\mathrm{V}_1\ \cdot \mathrm{V}_1\ \cdot \Delta\mathrm{A}\ (510\ \mathrm{nm})}{10^3 \cdot \mathrm{V}_1\ \cdot \mathrm{l} \cdot \varepsilon\ (510\ \mathrm{nm})}$$

Where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), ΔA (510 nm) the optical difference in absorbance between the irradiated solution and the one stored in the dark, ε (510 nm) is that of the complex $\mathrm{Fe(phen)_3}^{2+}$ (11100 L mol^{-1} cm^{1}).

The moles of Fe^{2+} formed (x) are plotted as a function of time (t). The slope of this line was correlated to the moles of incident photons by unit of time ($q^0_{n,p}$) by the use of the following Equation:

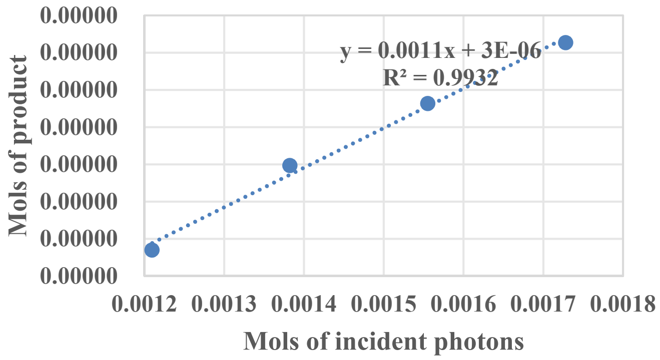
$$\Phi\ (\lambda)\ = \frac{\mathrm{dx/dt}}{\mathrm{q_{n,p}}^0[1 - 10^{-A(\lambda)}]}$$

Where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe^{2+} at 450 nm is 0.9 and the absorbance A(λ) of the actinometer at λ = 450 nm was measured by UV/Vis spectroscopy to be 0.27. $q^0_{n,p}$, which is the photon flux, was determined to be 4.80×10^{-8} einstein s^{-1} .



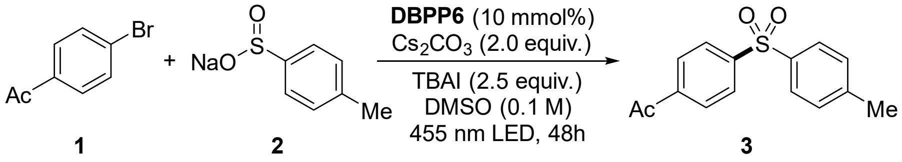
Supplementary Figure 15. The moles of Fe^{2+} formed are related to time (t).

The measurements for the reaction under study were done as follows: the moles of product **3** formed were determined by ^{1}H NMR spectroscopy. The moles of product per unit of time are related to the number of photons absorbed. The photons absorbed are correlated to the number of incident photons by the use of the equation displayed in the previous point. According to equation the slope (dx/dt) is equal to: $\Phi \cdot (1-10^{-A(450\ \mathrm{nm})}) \cdot q^0_{n,p}$, where Φ is the quantum yield to be determined and the absorption A(450 nm) of the reaction was determined by UV/Vis spectroscopy to be more than 4, thus $(1-10^{-A(450\ \mathrm{nm})}) > 1 - 10^{-4} = 0.9999$ (approximated to 1). The calculation yields the quantum yield (Φ) of the photoreaction = 0.0011.

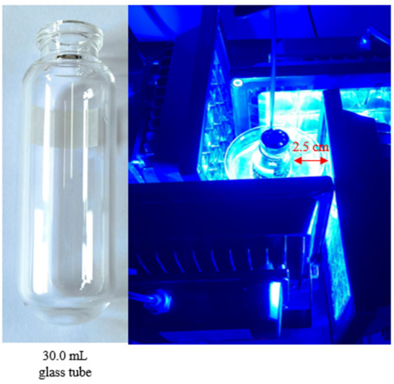


Supplementary Figure 16. The moles of product (**3**) per unit of time are related to the number of photons absorbed.

Supplementary Note 11. Gram-Scale Synthesis of Compound 3



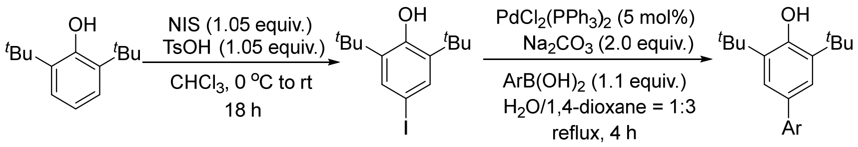
To an oven dried 30.0 mL glass tube with a magnetic stirring bar was charged with 4-acetylbenzene bromide **1** (398 mg, 2.0 mmol), sodium *p*-toluenesulfinate **2** (712 mg, 2.0 mmol), **DBPP6** (85 mg, 0.2 mmol), Cs_2CO_3 (1.31 g, 4.0 mmol), and TBAI (1.84 g, 5 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMSO (20.0 mL) were carefully added to the reaction tube under Argon. The resulting mixture was stirred for 48 hours under four 35W blue LED lamps (the distance was about 2.5 cm) irradiation at 45℃. After irradiating for the indicated time, the reaction was diluted with water. The aqueous phase was extracted with ethyl acetate (45 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether = 50/1 ~ 5/1) on silica gel to afford the product **3** (448.7 mg, 82% yield) as a white solid.



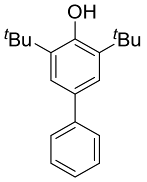
Supplementary Figure 17. Experimental setup for Gram-Scale Synthesis of Compound **3**

Synthesis of Photocatalysts

The catalyst was prepared following the general procedure reported by our own group.[4]

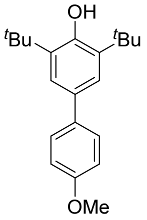


3,5-Di-*tert*-butyl-[1,1'-biphenyl]-4-ol (DBPP1)[4]



DBPP1 was prepared according to the general procedure reported on 5.0 mmol scale of 2,6-dibutylphenol. The crude product was purified by flash column chromatography (acetone/petroleum ether = 1/100) to give 1.09 g of **DBPP1** (77% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.53 (m, 2H), 7.46 – 7.38 (m, 4H), 7. 33 – 7.28 (m, 1H), 5.27 (s, 1H), 1.50 (s, 18H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.5, 142.3, 136.2, 132.6, 128.6, 127.0, 126.4, 124.1, 34.5, 30.4. HR-ESI-MS (m/z): calcd. for $C_{20}H_{25}O$ $[M - H]^-$, 281.1911, found 281.1910.

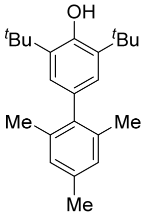
3,5-Di-*tert*-butyl-4'-methoxy-[1,1'-biphenyl]-4-ol (DBPP2)[4]



DBPP2 was prepared according to the general procedure reported on 5.0 mmol scale of 2,6-dibutylphenol. The crude product was purified by flash column chromatography (acetone/petroleum ether = 1/100) to give 1.17 g of **DBPP2** (75% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 – 7.44 (m, 2H), 7.35 (s, 2H), 7.00 – 6.93 (m, 2H), 5.22 (s, 1H), 3.85 (s, 3H), 1.49 (s, 18H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 158.5, 153.1, 136.1, 134.9,

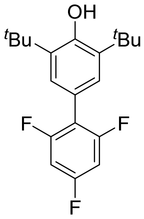
132.3, 128.0, 123.7, 114.1, 55.4, 34.5, 30.4. HR-ESI-MS (m/z): calcd. for $C_{21}H_{27}O_2$ [M – H]$^-$, 311.2017, found 311.2019.

3,5-Di-*tert*-butyl-2',4',6'-trimethyl-[1,1'-biphenyl]-4-ol (DBPP3)[13]



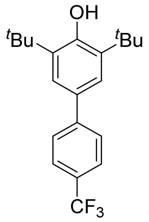
DBPP3 was prepared according to the general procedure reported on 5.0 mmol scale of 2,6-dibutylphenol. The crude product was purified by flash column chromatography (acetone/petroleum ether = 1/100) to give 748 mg of **DBPP3** (46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 2H), 6.91 (s, 2H), 5.15 (s, 1H), 2.33 (s, 3H), 2.04 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 140.0, 136.6, 136.2, 135.5, 131.6, 128.0, 125.8, 34.4, 30.5, 21.0. HR-ESI-MS (m/z): calcd. for $C_{23}H_{31}O$ [M – H]$^-$, 323.2380, found 323.2378.

3,5-Di-*tert*-butyl-2',4',6'-trifluoro-[1,1'-biphenyl]-4-ol (DBPP4)



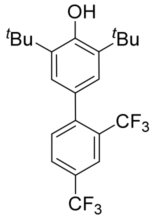
DBPP4 was prepared according to the general procedure reported on 5.0 mmol scale of 2,6-dibutylphenol. The crude product was purified by flash column chromatography (acetone/petroleum ether = 1/100) to give 624 mg of **DBPP4** (37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (m, 2H), 6.74 (t, J = 8.3 Hz, 2H), 5.35 (s, 1H), 1.46 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (m), 159.1 (m), 153.9, 135.7, 127.1, 119.2,100.4 (m), 34.4, 30.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.6 (t, J = 5.7 Hz, 1F), -111.2 (d, J = 5.8 Hz, 2F). HR-ESI-MS (m/z): calcd. for $C_{20}H_{22}F_3O$ [M – H]$^-$, 335.1628, found 335.1629.

3,5-Di-*tert*-butyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-ol (DBPP5) [14]



DBPP5 was prepared according to the general procedure reported on 5.0 mmol scale of 2,6-dibutylphenol. The crude product was purified by flash column chromatography (acetone/petroleum ether = 1/100) to give 1.26 g of **DBPP5** (72% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 – 7.61 (m, 4H), 7.40 (d, *J* = 1.4 Hz, 2H), 5.36 (s, 1H), 1.50 (s, 18H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.3, 145.7, 136.5, 131.1, 128.4 (q, *J* = 32.2 Hz), 127.1, 125.6 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 270.0 Hz), 123.1, 34.5, 30.3. ^{19}F NMR (376 MHz, CDCl$_3$) δ -62.2 (s, 3F). HR-ESI-MS (m/z): calcd. for $C_{21}H_{24}F_3O$ [M – H]$^-$, 349.1785, found 349.1784.

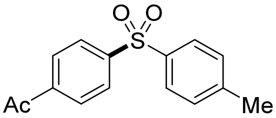
3,5-Di-*tert*-butyl-2',4'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-ol (DBPP6)



DBPP6 was prepared according to the general procedure reported on 5.0 mmol scale of 2,6-dibutylphenol. The crude product was purified by flash column chromatography (acetone/petroleum ether = 1/100) to give1.42 g of **DBPP6** (68% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 2H), 5.35 (s, 1H), 1.46 (s, 18H).^{13}C NMR (100 MHz, CDCl$_3$) δ 154.0, 146.3, 135.4, 133.1, 129.5, 129.3 (q, *J* = 30.4 Hz), 129.2 (q, *J* = 30.2 Hz), 128.0 (d, *J* = 3.2), 123.7 (q, *J* = 270.6), 123.6 (d, *J* = 1.0 Hz), 123.5 (q, *J* = 272.6 Hz), 123.4 (m) , 34.4, 30.3. ^{19}F NMR (376 MHz, CDCl$_3$) δ -57.1 (s, 3F), -62.6 (s, 3F),. HR-ESI-MS (m/z) calcd. for $C_{22}H_{24}F_6O$ [M – H]$^-$: 417.1659, found: 417.1661.

Identification of Sulfonylation Products

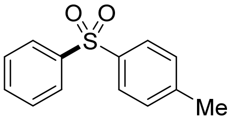
1-(4-Tosylphenyl)ethan-1-one. (3)[15]



3

Prepared according to the general procedure A using 4-acetylbenzene bromide **1** (39.8 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **3** as a colorless solid (48.9 mg, 89% yield) (m.p. = 146.1–148.5 °C).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.98 (m, 4H), 7.87 – 7.80 (m, 2H), 7.36 – 7.29 (m, 2H), 2.62 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 145.8, 144.8, 140.2, 137.8, 130.1, 129.1, 127.9, 127.8, 26.9, 21.6. HR-ESI-MS (m/z): calcd. for $C_{15}H_{15}O_3S$ $[M + H]^+$, 275.0736, found 275.0741.

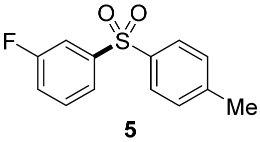
1-Methyl-4-(phenylsulfonyl)benzene. (4)[16]



4

Prepared according to the general procedure A using iodobenzene (22 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **4** as a colorless solid (36.8 mg, 79% yield) (m.p. = 126.2–128.5 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.2, 142.0, 138.6, 133.0, 129.9, 129.2, 127.7, 127.5, 21.6. HR-ESI-MS (m/z): calcd. for $C_{13}H_{16}NO_2S$ $[M + NH_4]^+$, 250.0896 , found 250.0897.

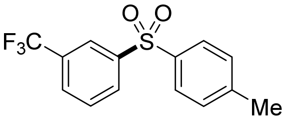
1-Fluoro-3-tosylbenzene. (5)[17]



5

Prepared according to the general procedure A using 1-fluoro-3-iodobenzene (23 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **5** as a colorless solid (m.p. = 98.7–100.4 °C) (41.0 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.74 – 7.70 (m, 1H), 7.64 – 7.58 (m, 1H), 7.53 – 7.43 (m, 1H), 7.32 (m, 2H), 7.26 – 7.21 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 252.1 Hz), 144.7, 144.1 (d, *J* = 6.4 Hz), 138.0, 131.1 (d, *J* = 7.6 Hz), 130.1, 127.9, 123.3 (d, *J* = 3.3 Hz), 120.3 (d, *J* = 21.3 Hz), 114.9 (d, *J* = 24.3 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.3 (s, 1F). HR-ESI-MS (m/z): calcd. for $C_{13}H_{11}FO_2S$ $[M + H]^+$, 251.0537, found 251.0539.

1-Tosyl-3-(trifluoromethyl)benzene. (6)[17]

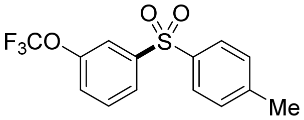


6

Prepared according to the general procedure A using 1-trifluoromethyl-3-iodobenzene (29 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **6** as a colorless solid (46.2 mg, 77% yield) (m.p. = 98.3–99.6 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.13 – 8.08 (m, 1H), 7.87 – 7.83 (m, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.3, 137.6, 132.5 – 131.4 (m), 130.8, 130.2, 130.1, 129.7 (q, *J* = 3.5 Hz), 127.9, 124.5 (q, *J* = 3.8 Hz), 121.8, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). HR-ESI-MS (m/z): calcd. for $C_{14}H_{11}F_3O_2S$ [M + H]$^+$, 301.0505, found 301.0508.

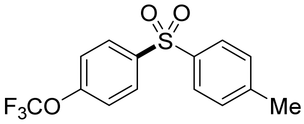
1-Tosyl-3-(trifluoromethoxy)benzene. **(7)**



7

Prepared according to the general procedure A using 1-trifluoromethoxy-3-iodobenzene (31 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **7** as a colorless powder (57.6 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 4H), 7.54 (t, *J* = 8.1 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (d, *J* = 2.0 Hz), 144.8, 144.2, 137.8, 130.9, 130.2, 127.9, 125.8, 122.1(d, *J* = 257.5 Hz), 121.5, 120.1, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.0 (s, 3F). HR-ESI-MS (m/z): calcd. for $C_{14}H_{12}F_3O_3S$ [M + H]$^+$, 317.0454, found 317.0457.

1-Tosyl-4-(trifluoromethoxy)benzene. **(8)**

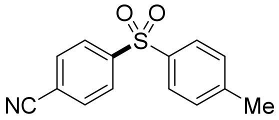


8

Prepared according to the general procedure A using 1-trifluoromethoxy-3-iodobenzene (31 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **8** as a colorless powder (53.7 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.28 (m, 4H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 144.6, 140.4, 138.1, 130.1, 129.7, 127.8, 121.06, 120.2 (d, *J* = 258.1 Hz), 21.6. ^{19}F

NMR (376 MHz, $CDCl_3$) δ -57.7 (s, 3F). HR-ESI-MS (m/z): calcd. for $C_{14}H_{12}F_3O_3S$ $[M + H]^+$, 317.0454, found 317.0456.

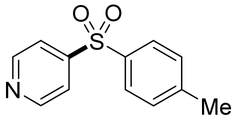
4-Tosylbenzonitrile. **(9)**[17]



9

Prepared according to the general procedure A using 4-bromobenzonitrile (23 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **9** as a colorless solid (37.6 mg, 74% yield) (m.p. = 136.4–137.8 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.12 (m, 2H), 7.88 – 7.78 (m, 3H), 7.67 – 7.63 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 143.9, 137.2, 136.1, 131.4, 131.1, 130.3, 128.0, 117.1, 113.9, 21.7. HR-ESI-MS (m/z): calcd. for $C_{14}H_{12}NO_2S$ $[M + H]^+$, 258.0583, found 258.0583.

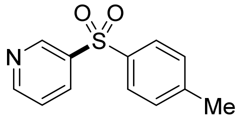
4-Tosylpyridine. **(10)**[18]



10

Prepared according to the general procedure A using 3-iodopyridine (21 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **10** as a colorless solid (39.1 mg, 84% yield) (m.p. = 136.2–137.6 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 6.1 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.76 – 7.73 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 149.1, 144.4, 135.7, 129.3, 127.2, 119.5, 20.6. HR-ESI-MS (m/z): calcd. for $C_{12}H_{12}NO_2S$ $[M + H]^+$, 234.0583, found 234.0584.

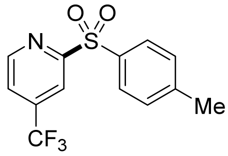
3-Tosylpyridine. **(11)**[19]



11

Prepared according to the general procedure A using 3-iodopyridine (41 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **11** as a colorless solid (40.5 mg, 87% yield) (m.p. = 160.3–161.8 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.77 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.23 – 8.18 (m, 1H), 7.88 – 7.83 (m, 2H), 7.44 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 148.6, 145.0, 138.7, 137.8, 135.1, 130.2, 127.9, 123.8, 21.6. HR-ESI-MS (m/z): calcd. for $C_{12}H_{12}NO_2S$ [M + H]$^+$, 234.0583, found 234.0586.

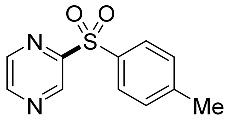
2-Tosyl-4-(trifluoromethyl)pyridine. **(12)**



12

Prepared according to the general procedure A using 2-bromo-4-(trifluoromethyl)pyridine (25 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **12** as a colorless powder (42.7 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.9 Hz, 1H), 8.41 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 5.0 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 151.6, 140.6 (q, *J* = 35.3 Hz), 134.9, 130.0, 129.3, 123.3, 122.5 (d, *J* = 3.5 Hz), 120.6, 118.0 (t, *J* = 3.7 Hz), 21.7. ^{19}F NMR (376 MHz, CDCl3) δ -64.7 (s, 3F). HR-ESI-MS (m/z) calcd. for $C_{13}H_{10}F_3NO_2S$ [M + H]$^+$: 302.0457, found: 302.0454.

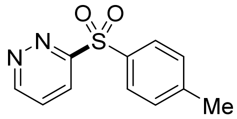
2-(Phenylsulfonyl)pyrazine. **(13)**



13

Prepared according to the general procedure A using 2-iodopyrazine (20 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **13** as a colorless powder (41.9 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, J = 1.5 Hz, 1H), 8.76 (d, J = 2.4 Hz, 1H), 8.65 – 8.62 (m, 1H), 7.96 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 147.7, 145.7, 144.6, 143.0, 135.1, 130.1, 129.1, 21.7. HR-ESI-MS (m/z) calcd. for $C_{11}H_{11}N_2O_2S$ $[M + H]^+$: 235.0536, found: 235.0535.

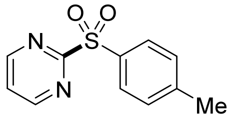
3-Tosylpyridazine. **(14)**



14

Prepared according to the general procedure A using 3-bromopyridazine (20 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **14** as a colorless powder (37.1 mg, 79% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.29 (dd, J = 5.1, 1.6 Hz, 1H), 8.29 (dd, J = 8.5, 1.6 Hz, 1H), 8.01 (d, J = 8.1 Hz, 2H), 7.72 (dd, J = 8.5, 5.1 Hz, 1H), 7.36 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9, 152.8, 145.8, 134.8, 130.0, 129.4, 128.0, 124.6, 21.7. HR-ESI-MS (m/z) calcd. for $C_{11}H_{11}N_2O_2S$ $[M + H]^+$: 235.0536, found: 235.0534.

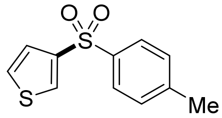
2-Tosylpyrimidine. **(15)**



15

Prepared according to the general procedure A using 2-iodopyrimidine (20 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **15** as a colorless powder (40.8 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.9 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 4.9 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 158.7, 145.6, 134.4, 129.9, 129.7, 123.2, 21.8. HR-ESI-MS (m/z) calcd. for $C_{11}H_{11}N_2O_2S$ $[M + H]^+$: 235.0536, found: 235.0538.

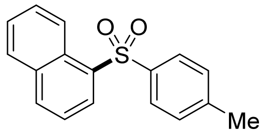
3-Tosylthiophene. **(16)**[20]



16

Prepared according to the general procedure A using 3-iodothiophene (42 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **16** as a colorless solid (43.3 mg, 91% yield) (m.p. = 130.5–132.4 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 3.1, 1.3 Hz, 1H), 7.87 – 7.82 (m, 2H), 7.37 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.35 – 7.28 (m, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.4, 138.7, 131.2, 129.9, 128.3, 127.5, 125.8, 21.6. HR-ESI-MS (m/z) calcd. for $C_{12}H_{12}NO_2S$ $[M + H]^+$: 234.0583, found: 234.0587.

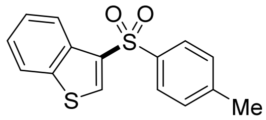
1-Tosylnaphthalene. **(17)**[21]



17

Prepared according to the general procedure A using 1-iodonaphthalene (21 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **17** as a colorless solid (50.8 mg, 81% yield) (m.p. = 101.4–103.7 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 7.6 Hz, 1H), 8.50 (dd, J = 7.4, 1.3 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.63 – 7.51 (m, 3H), 7.26 (d, J = 8.1 Hz, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 138.8, 136.2, 135.0, 134.2, 129.8, 129.0, 128.5, 128.3, 127.5, 126.8, 124.43, 124.39, 21.5. HR-ESI-MS (m/z) calcd. for $C_{17}H_{15}O_2S$ [M + H]$^+$: 283.0787, found: 283.0788.

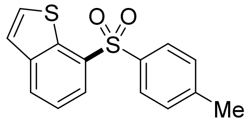
3-Tosylbenzo[*b*]thiophene. **(18)**[20]



18

Prepared according to the general procedure A using 3-bromo-1-benzothiophene (26 μL, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **18** as a colorless oil (38.6 mg, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.20 (dd, J = 8.1, 1.1 Hz, 1H), 7.92 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.1 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.44 – 7.39 (m, 1H), 7.29 (d, J = 8.1 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.4, 140.6, 138.3, 135.6, 135.4, 133.6, 129.9, 127.5, 125.8, 125.7, 123.1, 122.9, 21.6. HR-ESI-MS (m/z) calcd. for $C_{15}H_{13}O_2S_2$ [M + H]$^+$: 289.0351, found: 289.0357.

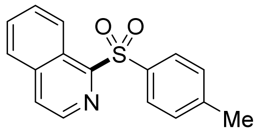
7-Tosylbenzo[*b*]thiophen. **(19)**



19

Prepared according to the general procedure A using 7-bromo-1-benzothiophene (42.6 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **19** as a colorless powder (47.8 mg, 83% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.6 Hz, 1H), 8.02 – 7.93 (m, 3H), 7.58 (d, J = 5.5 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 5.5 Hz, 1H), 7.27 (d, J = 5.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.8, 137.9, 136.7, 135.4, 129.7, 129.2, 128.5, 127.7, 125.5, 124.5, 123.5, 21.6. HR-ESI-MS (m/z) calcd. for $C_{15}H_{13}O_2S_2$ $[M + H]^+$: 289.0351, found: 289.0356.

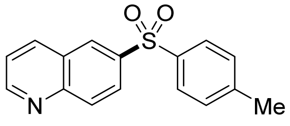
1-Tosylisoquinoline. **(20)**[18]



20

Prepared according to the general procedure A using 1-bromoisoquinoline (41.6 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **20** as a colorless solid (X = I, 50.5 mg, 89% yield; X = Br, 48.7 mg, 86% yield; X = Cl, 39.7 mg, 70% yield) (m.p. = 177.2–178.5 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 9.20 – 9.14 (m, 1H), 8.44 (d, J = 5.5 Hz, 1H), 8.01 – 7.96 (m, 2H), 7.94 – 7.89 (m, 1H), 7.82 – 7.76 (m, 3H), 7.36 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 144.8, 140.6, 137.8, 136.0, 131.1, 129.6, 129.3, 129.2, 127.6, 125.4, 125.0, 124.3, 21.7. HR-ESI-MS (m/z) calcd. for $C_{16}H_{14}NO_2S$ $[M + H]^+$: 284.0740, found: 284.0740.

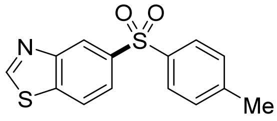
6-Tosylquinoline. **(21)**[21]



21

Prepared according to the general procedure A using 6-iodoquinoline (51.0 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **21** as a colorless solid (53.3 mg, 94% yield) (m.p. = 137.3–139.1 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 6.2 Hz, 1H), 8.57 (d, *J* = 2.1 Hz, 1H), 8.30 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.19 (d, *J* = 8.9 Hz, 1H), 8.08 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.54 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 149.4, 144.6, 139.7, 138.1, 137.4, 131.3, 130.1, 128.8, 127.9, 127.4, 126.4, 122.6, 21.6. HR-ESI-MS (m/z) calcd. for $C_{16}H_{14}NO_2S$ $[M + H]^+$: 284.0740, found: 284.0739.

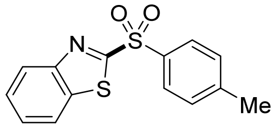
5-Tosylbenzo[*d*]thiazole. **(22)**[22]



22

Prepared according to the general procedure A using 5-bromobenzothiazole (42.8 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **22** as a colorless solid (39.9 mg, 69% yield) (m.p. = 165.7–167.2 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.72 (d, *J* = 1.7 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 1.8 Hz, 1H), 7.92 – 7.84 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 153.0, 144.4, 140.6, 138.7, 138.5, 130.0, 127.8, 123.7, 123.4, 123.0, 21.6. HR-ESI-MS (m/z) calcd. for $C_{14}H_{12}NO_2S_2$ $[M + H]^+$: 290.0304, found: 290.0305.

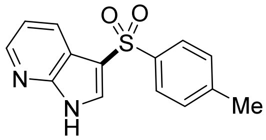
2-Tosylbenzo[*d*]thiazole. (23)[18]



23

Prepared according to the general procedure A using 2-bromo-1,3-benzothiazole (48.2 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **23** as a colorless solid (X = I, 49.8 mg, 86% yield; X = Br, 48.2 mg, 82% yield; X = Cl, 43.3 mg, 75% yield) (m.p. = 129.7–131.6 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.3 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 2H), 8.00 – 7.90 (m, 1H), 7.61 – 7.49 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 152.9, 145.9, 137.0, 135.5, 130.2, 129.0, 127.8, 127.5, 125.5, 122.2, 21.8. HR-ESI-MS (m/z) calcd. for $C_{14}H_{12}NO_2S_2$ $[M + H]^+$: 290.0304, found: 290.0304.

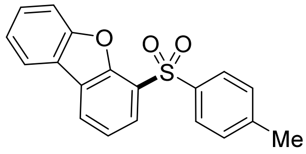
3-Tosyl-1*H*-pyrrolo[2,3-*b*]pyridine. (24)



24

Prepared according to the general procedure A using 3-iodo-7-azaindole (48.8 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:3) on silica gel to afford product **24** as a colorless powder (43.0 mg, 79% yield). ^1H NMR (600 MHz, Acetone-d_6) δ 8.37 (d, *J* = 6.3 Hz, 1H), 8.28 – 8.23 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.27 (dd, *J* = 8.0, 4.7 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 148.6, 145.1, 143.5, 141.0, 131.0, 129.7, 127.6, 126.7, 118.0, 116.1, 116.0, 20.5. HR-ESI-MS (m/z) calcd. for $C_{14}H_{14}N_2O_2S$ $[M + H]^+$: 273.0692, found: 273.0689.

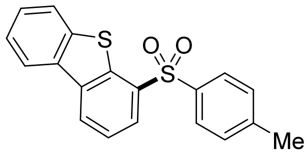
4-Tosyldibenzo[*b*,*d*]furan. (25)



25

Prepared according to the general procedure A using 4-iododibenzofuran (59 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **25** as a colorless solid (47.7 mg, 74% yield) (m.p. = 184.1–185.8 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 4H), 7.94 – 7.91 (m, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.42 – 7.33 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 144.5, 138.3, 129.7, 128.3, 128.2, 126.6, 126.5, 126.1, 125.9, 123.6, 122.8, 122.7, 120.8, 112.3, 21.6. HR-ESI-MS (m/z) calcd. for $C_{19}H_{14}O_3S$ $[M + H]^+$: 323.0736, found: 323.0738.

4-Tosyldibenzo[*b*,*d*]thiophene. (26)

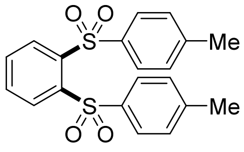


26

Prepared according to the general procedure A using 4-iododibenzothiophene (62 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **26** as a colorless powder (56.1 mg, 83% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.9 Hz, 1H), 8.21 – 8.14 (m, 1H), 8.16 – 8.09

(m, 1H), 8.02 – 7.94 (m, 2H), 7.92 – 7.85 (m, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.55 – 7.42 (m, 2H), 7.30 – 7.23 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 140.2, 138.0, 137.8, 137.5, 135.5, 133.9, 129.8, 127.8, 127.7, 127.4, 126.0, 124.89, 124.88, 122.6, 121.8, 21.6. HR-ESI-MS (m/z) calcd. for $C_{19}H_{15}O_2S_2$ [M + H]$^+$: 339.0508, found: 339. 0510.

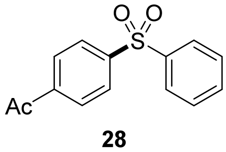
1,2-Ditosylbenzene. **(27)**



27

Prepared according to the general procedure A using 1-chloro-2-iodobenzene (47 mg, 0.2 mmol), sodium *p*-toluenesulfinate **2** (71.2 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:5) on silica gel to afford product **27** as a colorless powder (43.2 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.88 – 7.83 (m, 4H), 7.80 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.29 (d, *J* = 8.1 z, 4H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 140.6, 138.6, 133.8, 133.1, 129.4, 128.2, 21.7. HR-ESI-MS (m/z) calcd. for $C_{20}H_{19}O_4S_2$[M + H]$^+$: 387.0719, found: 387.0722.

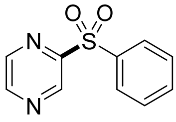
1-(4-(Phenylsulfonyl)phenyl)ethan-1-one. **(28)**[23]



28

Prepared according to the general procedure A using 1-bromo-4-acetyl-benzene **1** (39.8 mg, 0.2 mmol), sodium benzenesulfinate (65.6 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **28** as a colorless solid (44.3 mg, 85% yield) (m.p. = 135.2–137.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 4H), 7.98 – 7.94 (m, 2H), 7.63 – 7.58 (m, 1H), 7.56 – 7.50 (m, 2H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 145.5, 140.8, 140.4, 133.7, 129.5, 129.1, 128.0, 127.9, 26.9. HR-ESI-MS (m/z) calcd. for $C_{14}H_{13}O_3S$[M + H]$^+$: 261.0580, found: 261.0580.

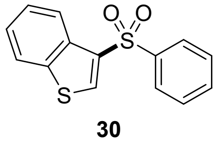
2-(Phenylsulfonyl)pyrazine. **(29)**



29

Prepared according to the general procedure A using 2-iodopyrazine (20 μL, 0.2 mmol), sodium benzenesulfinate (65.6 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **29** as a colorless powder (33.1 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, J = 1.5 Hz, 1H), 8.77 (d, J = 2.3 Hz, 1H), 8.65 (s, 1H), 8.15 – 8.05 (m, 2H), 7.71 – 7.63 (m, 1H), 7.58 (t, J = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 147.8, 144.6, 143.1, 138.1, 134.4, 129.4, 129.1. HR-ESI-MS (m/z): calcd. for $C_{10}H_9N_2O_2S$ [M + H]$^+$, 221.0379, found 221.0381.

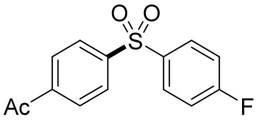
3-(Phenylsulfonyl)benzo[*b*]thiophene. **(30)**



30

Prepared according to the general procedure A using 3-bromo-1-benzothiophene (26 μL, 0.2 mmol), sodium benzenesulfinate (65.6 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:5) on silica gel to afford product **30** as a colorless powder (33.5 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.24 – 8.17 (m, 1H), 8.06 – 8.01 (m, 2H), 7.90 – 7.83 (m, 1H), 7.56 – 7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.6, 135.9, 135.2, 133.6, 133.4, 129.3, 127.4, 125.9, 125.8, 123.1, 123.0. HR-ESI-MS (m/z) calcd. for $C_{14}H_{10}O_2S_2$ $[M + H]^+$: 275.0195, found: 275.0196.

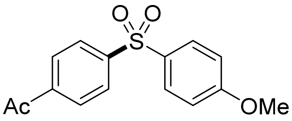
1-(4-((4-Fluorophenyl)sulfonyl)phenyl)ethan-1-one. **(31)**



31

Prepared according to the general procedure A using 4-acetylbenzene bromide **1** (39.8 mg, 0.2 mmol), sodium 4-fluorobenzenesulfinate (72.8 mg, 0.4 mmol), **DBPP6** (8.3mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **31** as a colorless powder (37.8 mg, 68% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.93 (m, 6H), 7.25 – 7.16 (m, 2H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 165.7 (d, J = 255.5 Hz), 145.3, 140.5, 136.9 , 130.7 (d, J = 9.6 Hz), 129.2, 127.9, 116.9 (d, J = 22.7 Hz), 26.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.2 (s, F). HR-ESI-MS (m/z) calcd. for $C_{14}H_{12}FO_3S$ $[M + H]^+$: 279.0486, found: 279.0489.

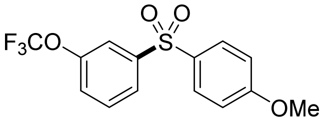
1-(4-((4-Methoxyphenyl)sulfonyl)phenyl)ethan-1-one. **(32)**[15]



32

Prepared according to the general procedure A using 4-acetylbenzene bromide **1** (39.8 mg, 0.2 mmol), sodium 4-methoxybenzenesulfinate (72.6 mg, 0.4 mmol) (21 μL, 0.2 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **32** as a colorless solid (45.8 mg, 79% yield) (m.p. = 130.3–132.0 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 4H), 7.91 – 7.85 (m, 2H), 7.02 – 6.91 (m, 2H), 3.84 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 163.8, 146.2, 140.1, 132.2, 130.1, 129.0, 127.6, 114.7, 55.7, 26.9. HR-ESI-MS (m/z) calcd. for $C_{15}H_{15}O_4S$ $[M + H]^+$: 291.0686, found: 291.0683.

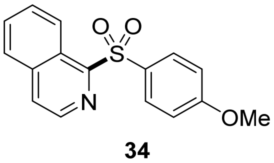
1-((4-Methoxyphenyl)sulfonyl)-3-(trifluoromethoxy)benzene. **(33)** [24]



33

Prepared according to the general procedure A using 3-(trifluoromethoxy)iodobenzene (31 μL, 0.2 mmol), sodium 4-methoxybenzenesulfinate (72.6 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **33** as a colorless oil (48.1 mg, 76% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 3H), 7.77 (s, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.02 – 6.97 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 149.4 (d, *J* = 1.5 Hz), 144.6, 132.1, 130.9, 130.1, 125.6, 125.1, 120.3 (d, *J* = 257.6), 119.9, 114.8, 55.7. ^{19}F NMR (376 MHz, CDCl3) δ -58.0 (s, 3F). HR-ESI-MS (m/z) calcd. for $C_{14}H_{12}FO_3S$ $[M + H]^+$: 279.0486, found: 279.0489.

1-((4-Methoxyphenyl)sulfonyl)isoquinoline. **(34)**

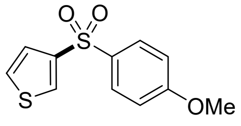


34

Prepared according to the general procedure A using 1-bromoisoquinoline (41.6 mg, 0.2 mmol), sodium 4-methoxybenzenesulfinate (72.6 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol), and in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **34** as a colorless powder (48.4 mg, 81% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.25 – 9.07 (m, 1H), 8.43 (d, *J* = 5.5 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.94 – 7.88 (m, 1H), 7.82 – 7.75 (m, 3H), 7.03

(d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 157.6, 140.5, 137.8, 131.5, 131.1, 130.3, 129.2, 127.5, 125.5, 124.9, 124.2, 114.2, 55.7. HR-ESI-MS (m/z) calcd. for $C_{16}H_{14}NO_3S$ [M + H]$^+$: 300.0689, found: 300.0683.

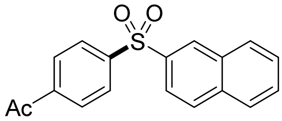
3-((4-Methoxyphenyl)sulfonyl)thiophene. (35)



35

Prepared according to the general procedure A using 3-iodothiophene (42 mg, 0.2 mmol), sodium 4-methoxybenzenesulfinate (72.6 mg, 0.4mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **35** as a colorless powder (35.6 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.32 – 7.28 (m, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 142.8, 133.1, 130.8, 129.7, 128.2, 125.7, 114.5, 55.7. HR-ESI-MS (m/z) calcd. for $C_{11}H_{10}O_3S_2$ [M + H]$^+$: 255.0144, found: 255.0142

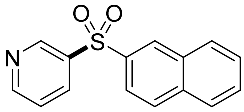
1-(4-(Naphthalen-2-ylsulfonyl)phenyl)ethan-1-one. (36)



36

Prepared according to the general procedure A using 4-acetylbenzene bromide **1** (39.8, 0.2 mmol), sodium naphthalene-2-sulfinate (72.8 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **36** as a colorless powder (44.6 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.13 – 8.01 (m, 4H), 8.03 – 7.92 (m, 2H), 7.94 – 7.81 (m, 2H), 7.70 – 7.58 (m, 2H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 145.4, 140.3, 137.5, 135.2, 132.2, 129.9, 129.6, 129.55, 129.50, 129.1, 128.1, 128.0, 127.9, 122.5, 26.9. HR-ESI-MS (m/z) calcd. for $C_{18}H_{15}O_3S$ $[M + H]^+$: 311.0736, found: 311.0732.

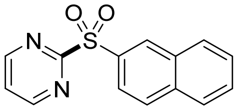
3-(Naphthalen-2-ylsulfonyl)pyridine. **(37)**



37

Prepared according to the general procedure A using 3-iodopyridine (41 mg, 0.2 mmol), sodium naphthalene-2-sulfinate (72.8 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **37** as a colorless powder (38.2 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 2.3 Hz, 1H), 8.78 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.61 (d, *J* = 1.9 Hz, 1H), 8.30 – 8.23 (m, 1H), 8.04 – 7.93 (m, 2H), 7.92 – 7.83 (m, 2H), 7.72 – 7.57 (m, 2H), 7.49 – 7.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 148.8, 138.4, 137.5, 135.3, 135.2, 132.2, 130.1, 129.58, 129.55, 129.5, 128.0, 127.9, 123.9, 122.4. HR-ESI-MS (m/z) calcd. for $C_{15}H_{12}NO_2S$ $[M + H]^+$: 270.0583 found: 270.0578.

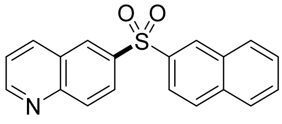
2-(Naphthalen-2-ylsulfonyl)pyrimidine. **(38)**



38

Prepared according to the general procedure A using 2-iodopyrimidine (20 μL, 0.2 mmol), sodium naphthalene-2-sulfinate (72.8 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **38** as a colorless powder (40.0 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.9 Hz, 2H), 8.74 (d, *J* = 1.8 Hz, 1H), 8.11 – 8.04 (m, 1H), 8.00 (t, *J* = 7.7 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.47 (t, *J* = 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 158.8, 135.7, 134.4, 132.1, 131.8, 129.6, 129.4, 128.0, 127.7, 123.9, 123.3. HR-ESI-MS (m/z) calcd. for $C_{14}H_{11}N_2O_2S$ $[M + H]^+$: 271.0536, found: 271.0531.

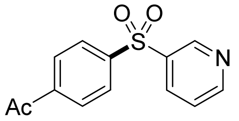
6-(Naphthalen-2-ylsulfonyl)quinoline. **(39)**



39

Prepared according to the general procedure A using 5-iodoquinoline (51.0 mg, 0.2 mmol), sodium naphthalene-2-sulfinate (72.8 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **39** as a colorless powder (40.2 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 – 9.00 (m, 1H), 8.68 – 8.61 (m, 2H), 8.34 – 8.27 (m, 1H), 8.22 – 8.09 (m, 2H), 8.02 – 7.98 (m, 1H), 7.96 – 7.85 (m, 3H), 7.63 (tt, *J* = 8.6, 6.1 Hz, 2H), 7.53 (dd, *J* = 8.4, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 149.5, 139.4, 137.9, 137.4, 135.1, 132.2, 131.4, 129.8, 129.5, 129.46, 129.44, 129.1, 128.0, 127.8, 127.4, 126.5, 122.7. HR-ESI-MS (m/z) calcd. for $C_{19}H_{14}NO_2S$ $[M + H]^+$: 320.0742, found: 320.0742.

1-(4-(Pyridin-3-ylsulfonyl)phenyl)ethan-1-one. **(40)**[15]

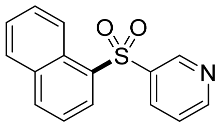


40

Prepared according to the general procedure A using 4-acetylbenzene bromide **1** (39.8, 0.2 mmol), sodium pyridine-3-sulfinate (66.0 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **40** as a colorless solid (38.6 mg, 74% yield) (m.p. = 139.3–140.3 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.2 – 9.1 (m, 1H), 8.9 – 8.8 (m, 1H), 8.2 (d, *J* = 8.2 Hz, 1H), 8.1 – 8.0 (m, 4H), 7.5 (dd, *J* = 8.9, 4.9 Hz, 1H), 2.6 (s, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 196.5, 154.1, 148.9, 144.5, 140.8, 137.6, 135.4, 129.3, 128.2, 124.0, 26.9. HR-ESI-MS (m/z) calcd. for $C_{13}H_{12}NO_3S$ $[M + H]^+$: 262.0532, found: 262.0535.

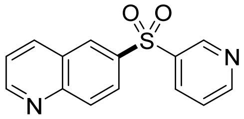
3-(Naphthalen-1-ylsulfonyl)pyridine. **(41)**



41

Prepared according to the general procedure A using 1-iodonaphthalene (21μL, 0.2 mmol), sodium pyridine-3-sulfinate (71.2 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **41** as a colorless powder (40.4 mg, 75% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, J = 2.4 Hz, 1H), 8.73 (dd, J = 4.9, 1.5 Hz, 1H), 8.62 (d, J = 8.5 Hz, 1H), 8.56 (dd, J = 7.3, 1.3 Hz, 1H), 8.28 – 8.21 (m, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.68 – 7.52 (m, 3H), 7.41 (dd, J = 8.1, 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 148.5, 138.4, 135.9, 135.0, 134.9, 134.3, 130.5, 129.3, 128.8, 128.3, 127.2, 124.5, 123.9, 123.7. HR-ESI-MS (m/z) calcd. for $C_{15}H_{12}NO_2S$ $[M + H]^+$: 270.0583, found: 270.0588.

6-(Pyridin-3-ylsulfonyl)quinoline. **(42)**

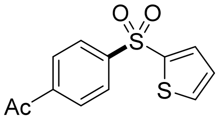


42

Prepared according to the general procedure A using 5-iodoquinoline (51.0 mg, 0.2 mmol), sodium pyridine-3-sulfinate (71.2 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **42** as a colorless powder (32.4 mg, 60% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.24 – 9.19 (m, 1H), 9.07 (dd, J = 4.3, 1.8 Hz, 1H), 8.80 (dd, J =

4.8, 1.6 Hz, 1H), 8.61 (d, *J* = 2.1 Hz, 1H), 8.35 – 8.21 (m, 3H), 8.11 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.57 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.51 – 7.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.7, 149.7, 148.9, 138.5, 137.9, 137.4, 135.4, 131.8, 129.6, 127.4, 126.2, 124.0, 122.9. HR-ESI-MS (m/z) calcd. for $C_{14}H_{11}N_2O_2S$ $[M + H]^+$: 271.0536, found: 271.0533.

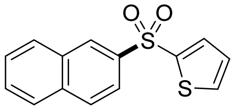
1-(4-(Thiophen-2-ylsulfonyl)phenyl)ethan-1-one. **(43)**[15]



43

Prepared according to the general procedure A using 4-acetylbenzene bromide **1** (39.8, 0.2 mmol), sodium thiophene-2-sulfinate (68.1 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **43** as a colorless solid (43.1mg, 81% yield) (m.p. = 132.0–133.3 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08(m, 4H), 7.74 –7.69 (m, 2H), 7.14 – 7.08 (m, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 145.8, 142.1, 140.4, 134.7, 134.1, 129.1, 128.1, 127.7, 26.9. HR-ESI-MS (m/z) calcd. for $C_{12}H_{11}O_3S_2$ $[M + H]^+$: 267.0144, found: 267.0146.

2-(Naphthalen-2-ylsulfonyl)thiophene. **(44)**

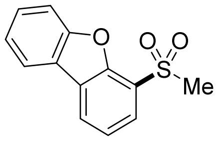


44

Prepared according to the general procedure A using 2-iodonaphthalene (21 μL, 0.2 mmol), sodium thiophene-2-sulfinate (68.1 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **44** as a colorless powder (37.9 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.02 – 7.86 (m, 4H), 7.78 – 7.72 (m, 1H), 7.69

– 7.58 (m, 3H), 7.12 – 7.05 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.1, 138.9, 135.1, 133.9, 133.4, 132.2, 129.7, 129.5, 129.2, 128.7, 128.0, 127.9, 127.7, 122.4. HR-ESI-MS (m/z) calcd. for $C_{14}H_{11}O_2S_2$ [M + H]$^+$: 275.0195, found: 275.0198.

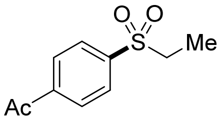
3-(Methylsulfonyl)dibenzo[*b*,*d*]furan. (45)



45

Prepared according to the general procedure A using 4-iododibenzofuran (59 mg, 0.2 mmol), sodium methanesulfinate (40.8 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **45** as a colorless powder (40.8 mg, 83% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.29 – 8.17 (m, 1H), 8.07 – 7.97 (m, 2H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 3.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.5, 151.7, 128.6, 126.6, 126.5, 126.3, 124.5, 123.9, 122.9, 122.7, 121.0, 112.4, 43.7. HR-ESI-MS (m/z) calcd. for $C_{13}H_{11}O_3S$ [M + H]$^+$: 247.0423, found: 247.0421.

1-(4-(Ethylsulfonyl)phenyl)ethan-1-one. (46)[15]

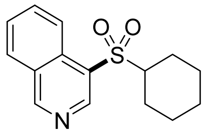


46

Prepared according to the general procedure A using 4-acetylbenzene bromide **1** (39.8 mg, 0.2 mmol), sodium ethanesulfinate (46.4 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **46** as a colorless solid (36.9 mg, 87% yield) (m.p. = 106.9–108.7 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 – 8.10 (m, 2H), 8.05 – 7.99 (m, 2H), 3.16 (q, *J* = 7.5 Hz, 2H), 2.68 (s, 3H), 1.30 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 196.7, 142.3, 140.9, 129.0, 128.7, 50.5, 27.0, 7.4. HR-ESI-MS (m/z) calcd. for $C_{10}H_{13}O_3S$ $[M + H]^+$: 213.0580, found: 213.0581.

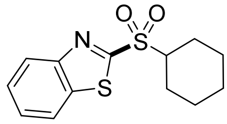
4-(Cyclohexylsulfonyl)isoquinoline. **(47)**



47

Prepared according to the general procedure A using 4-bromoisoquinoline (21 μL, 0.2 mmol), sodium cyclohexanesulfinate (68.0 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **47** as a colorless powder (46.7 mg, 85% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 9.13 (s, 1H), 8.75 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.98 – 7.87 (m, 1H), 7.78 (t, J = 7.6 Hz, 1H), 3.11 (tt, J = 12.2, 3.5 Hz, 1H), 2.02 (d, J = 12.8 Hz, 2H), 1.95 – 1.83 (m, 2H), 1.69 – 1.53 (m, 3H), 1.28 – 1.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 147.4, 133.0, 132.2, 129.0, 128.7, 128.5, 127.2, 123.9, 63.9, 25.2, 25.03, 25.00. HR-ESI-MS (m/z) calcd. for $C_{15}H_{18}NO_2S$ $[M + H]^+$: 276.1053, found: 276.1054.

2-(Cyclohexylsulfonyl)benzo[*d*]thiazole. **(48)**

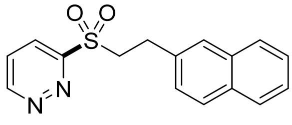


48

Prepared according to the general procedure A using 2-bromo-1,3-benzothiazole (48.2 mg, 0.2 mmol), sodium cyclohexanesulfinate (68.0 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:15) on silica gel to afford product **48** as a colorless powder (52.8 mg, 94% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.19 (m, 1H), 8.06 – 7.95 (m, 1H), 7.69 –

7.55 (m, 2H), 3.48 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.24 – 2.12 (m, 2H), 1.98 – 1.84 (m, 2H), 1.74 – 1.52 (m, 3H), 1.41 – 1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 153.0, 137.0, 127.9, 127.6, 125.5, 122.3, 63.0, 25.1, 25.0, 25.0. HR-ESI-MS (m/z) calcd. for $C_{13}H_{16}NO_2S_2$ $[M + H]^+$: 282.0617, found: 282.0617.

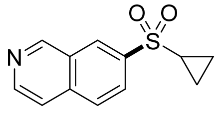
3-((2-(Naphthalen-2-yl)ethyl)sulfonyl)pyridazine. **(49)**



49

Prepared according to the general procedure A using 3-bromopyridazine (20 μL, 0.2 mmol), sodium 2-(naphthalen-2-yl)ethane-1-sulfinate (96.9 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:10) on silica gel to afford product **49** as a colorless powder (38.7 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (dd, *J* = 5.1, 1.7 Hz, 1H), 8.13 (dd, *J* = 8.5, 1.6 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.83 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.61 – 7.53 (m, 1H), 7.54 – 7.45 (m, 1H), 7.39 – 7.35 (m, 2H), 4.08 – 4.00 (m, 2H), 3.67 – 3.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 153.4, 133.9, 133.0, 131.2, 129.0, 128.1, 128.0, 127.0, 126.8, 126.0, 125.5, 124.4, 123.0, 52.8, 25.9. HR-ESI-MS (m/z) calcd. for $C_{16}H_{15}N_2O_2S$ $[M + H]^+$: 299.0849, found: 299.0847.

7-(Cyclopropylsulfonyl)isoquinoline. **(50)**

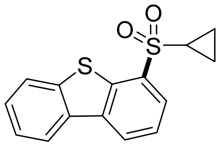


50

Prepared according to the general procedure A using 5-iodoquinoline (51.0 mg, 0.2 mmol), sodium cyclopropanesulfinate (50.8 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:20) on silica gel to afford product **50** as a colorless powder (31.2 mg, 67% yield). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.73 (d, *J* = 5.8 Hz, 1H), 8.66 – 8.52 (m, 1H), 8.11 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 5.7 Hz, 1H), 2.59 – 2.47 (m, 1H), 1.47 – 1.36 (m, 2H), 1.16 – 1.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 145.9, 139.4, 137.6, 128.9, 128.4, 127.2, 120.4, 32.9, 29.7, 6.2. HR-ESI-MS (m/z) calcd. for $C_{12}H_{12}NO_2S$ $[M + H]^+$: 234.0583, found: 234.0581.

4-(Cyclopropylsulfonyl)dibenzo[*b*,*d*]thiophene. (51)



51

Prepared according to the general procedure A using 4-iododibenzothiophene (62 mg, 0.2 mmol), sodium cyclopropanesulfinate (50.8 mg, 0.4 mmol), **DBPP6** (8.3 mg, 0.02 mmol), Cs_2CO_3 (131.2 mg, 0.4 mmol), and TBAI (184.5 mg, 0.5 mmol) in DMSO (2.0 mL). The reaction was purified by column chromatography (acetone/petroleum ether = 1:30) on silica gel to afford product **51** as a colorless powder (36.9 mg, 64% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.9 Hz, 1H), 8.25 – 8.16 (m, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.94 – 7.88 (m, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.60 – 7.48 (m, 2H), 2.71 (t, *J* = 4.8 Hz, 1H), 1.69 (s, 1H), 1.47 (dd, *J* = 4.9, 2.3 Hz, 2H), 1.01 (dd, *J* = 8.0, 2.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.0, 134.5, 134.0, 127.9, 127.4, 126.2, 125.0, 124.8, 122.6, 121.8, 32.4, 5.7. HR-ESI-MS (m/z) calcd. for $C_{15}H_{13}O_2S_2$ $[M + H]^+$: 289.0351, found: 289.0350.

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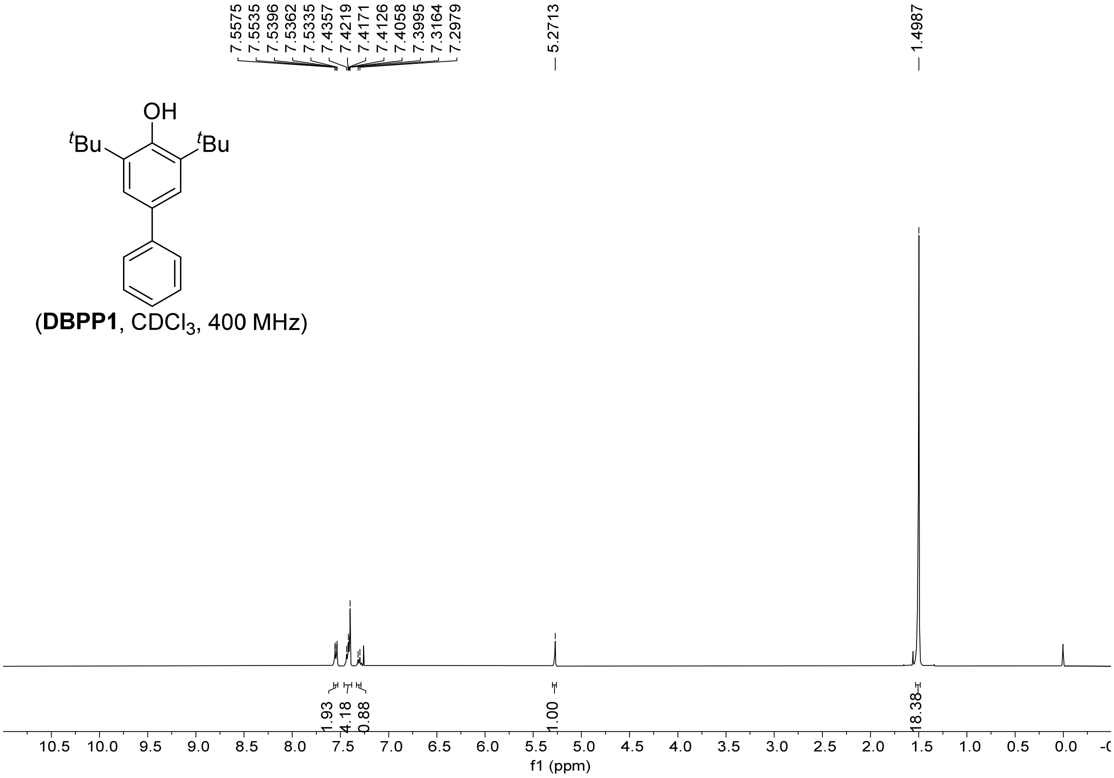
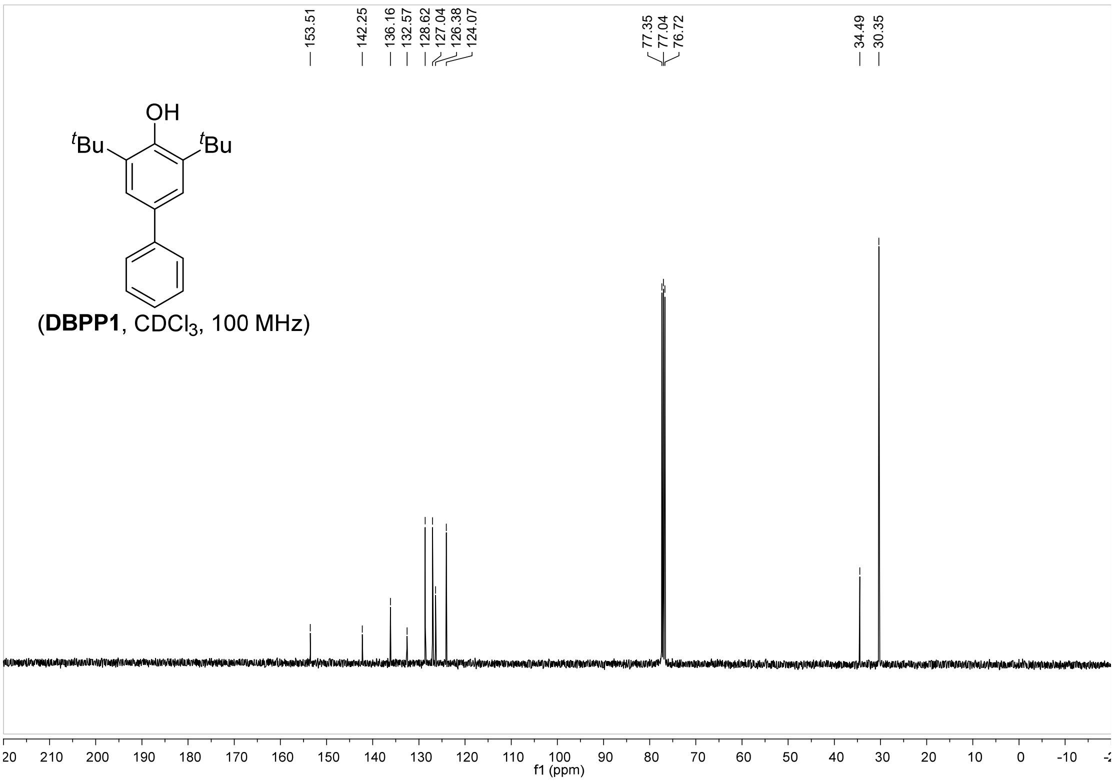
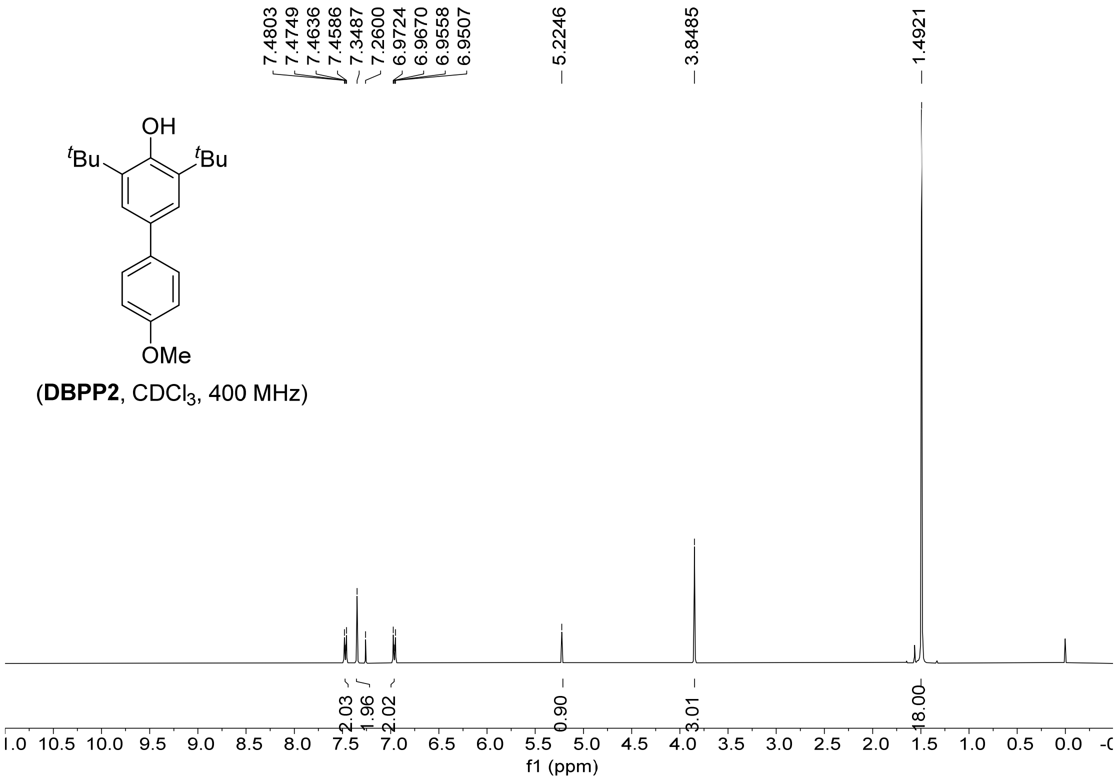
Copies of NMR Spectra



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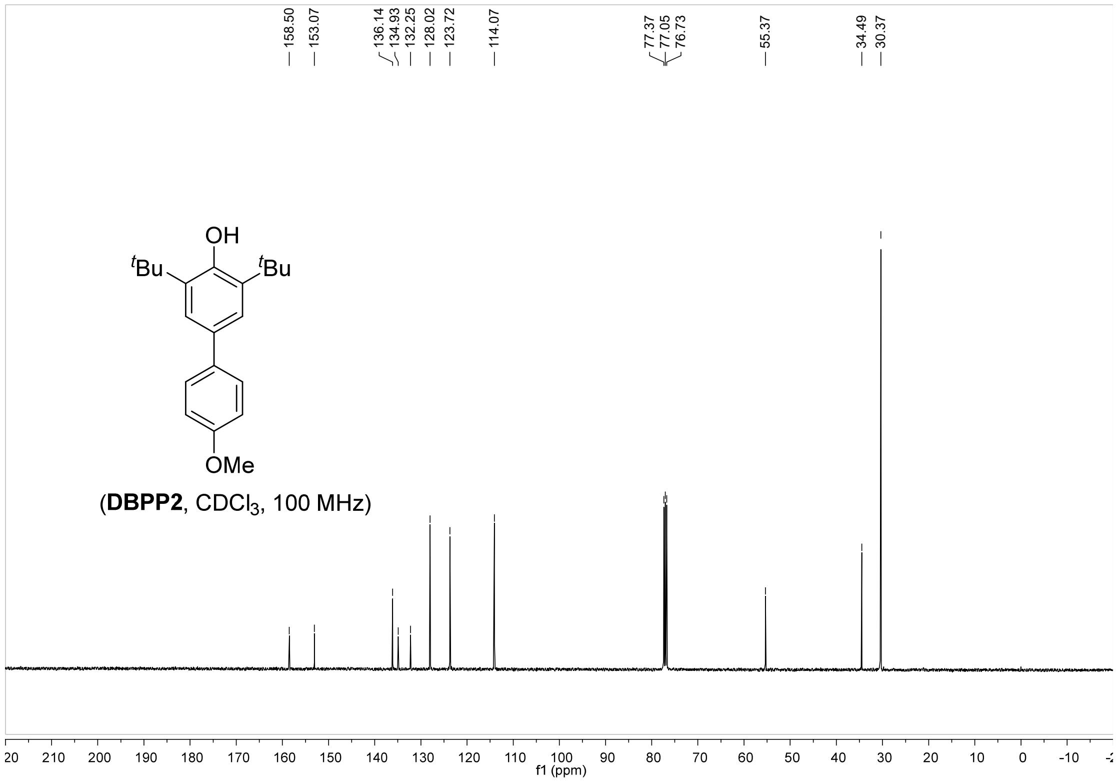
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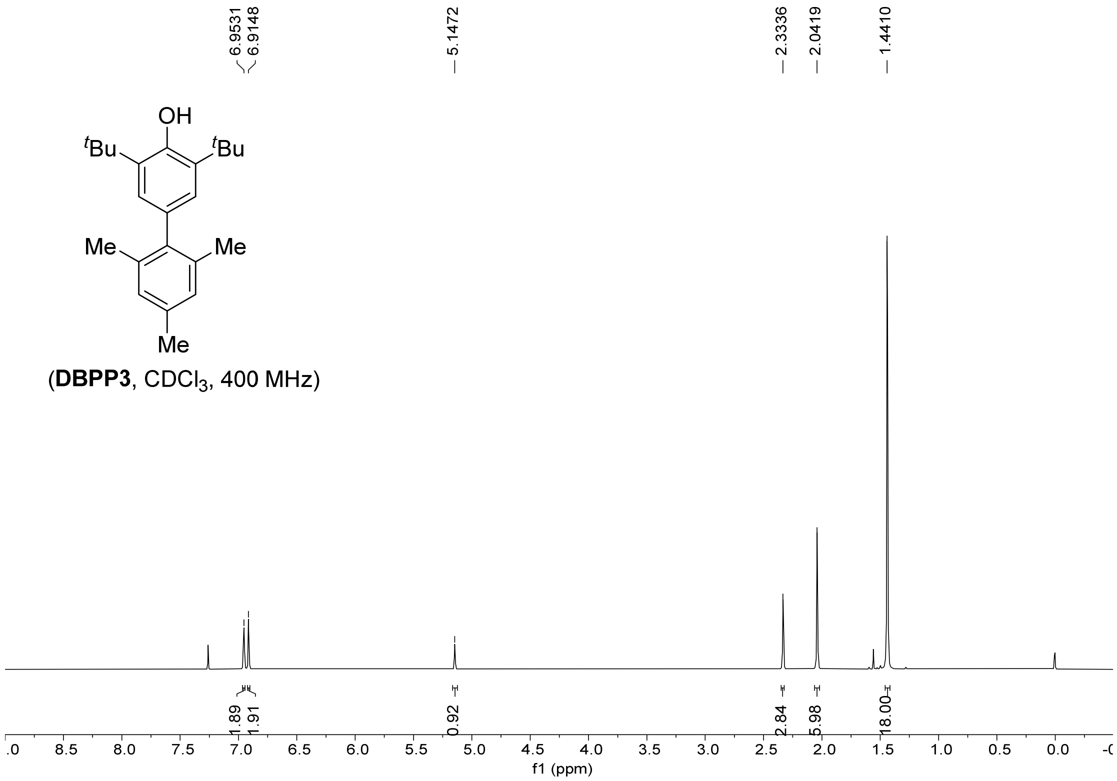
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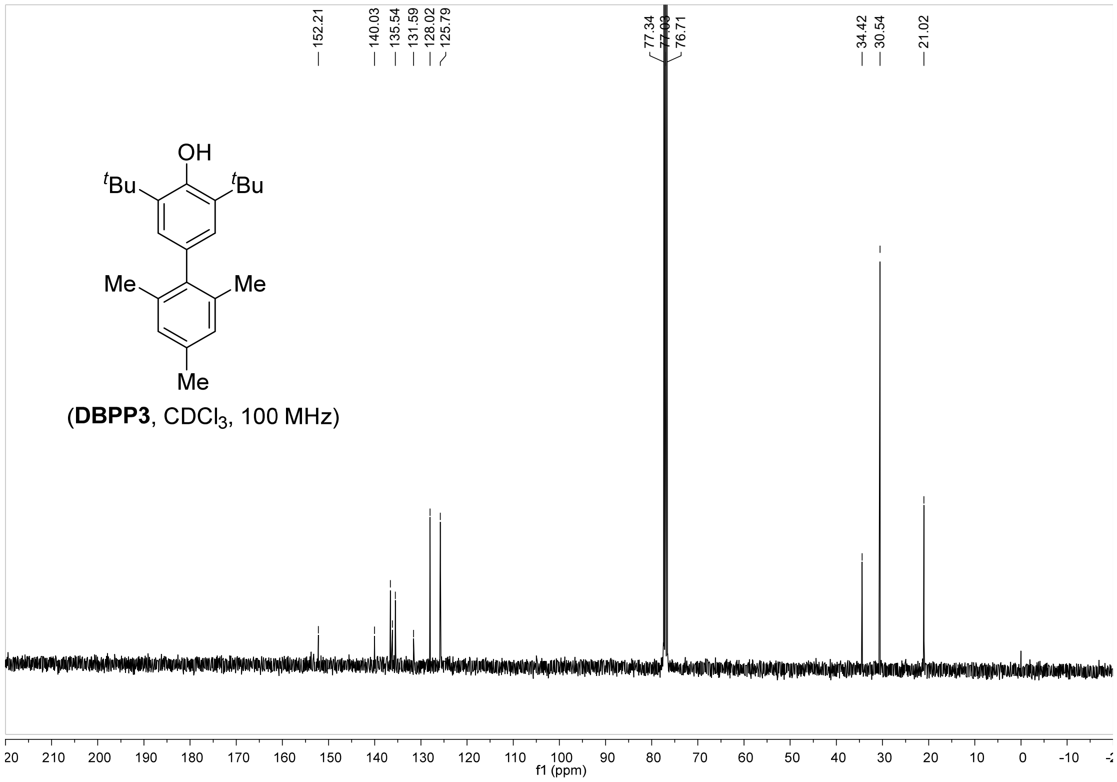
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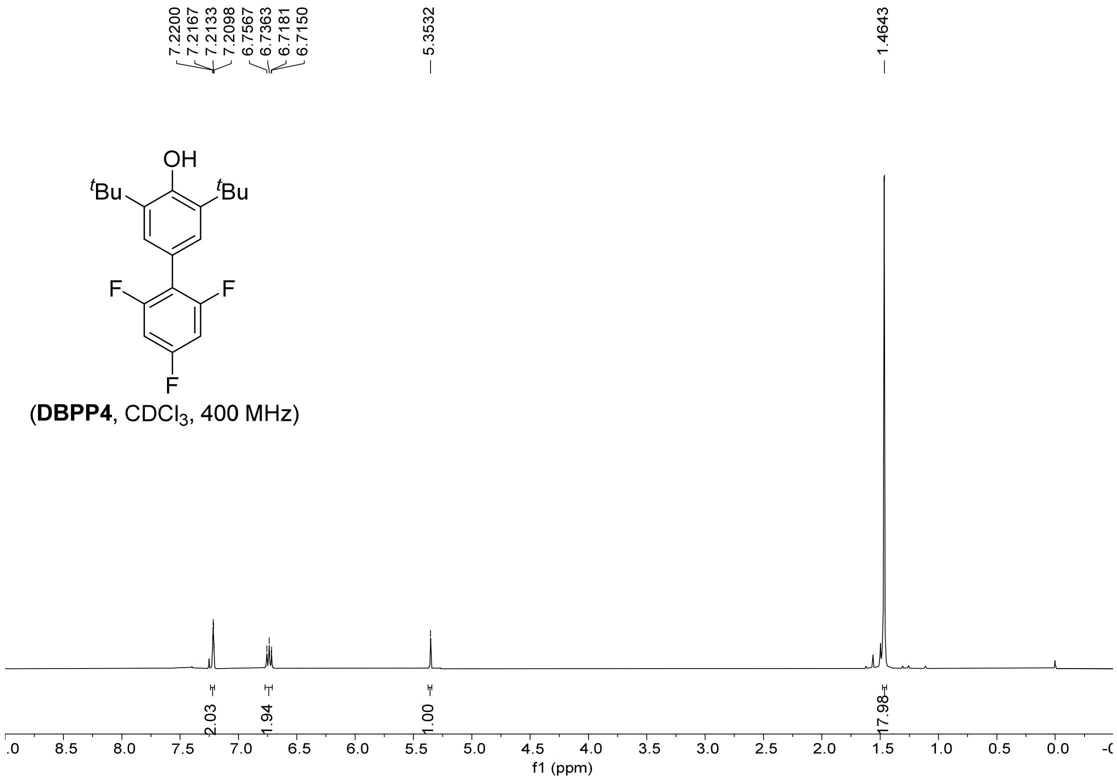
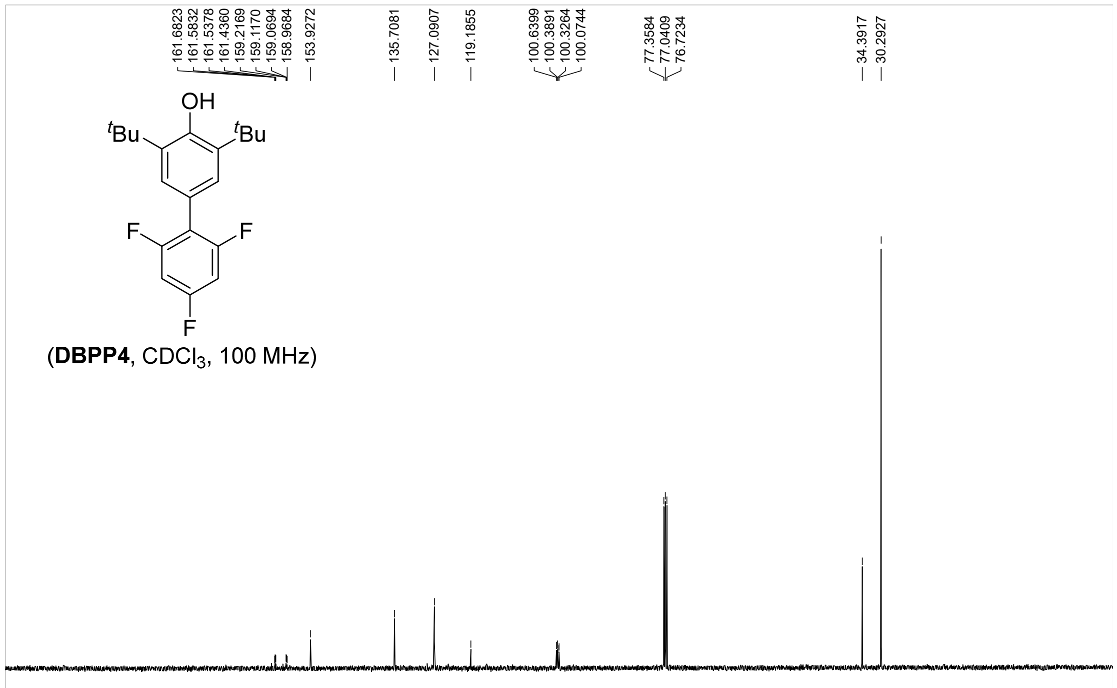
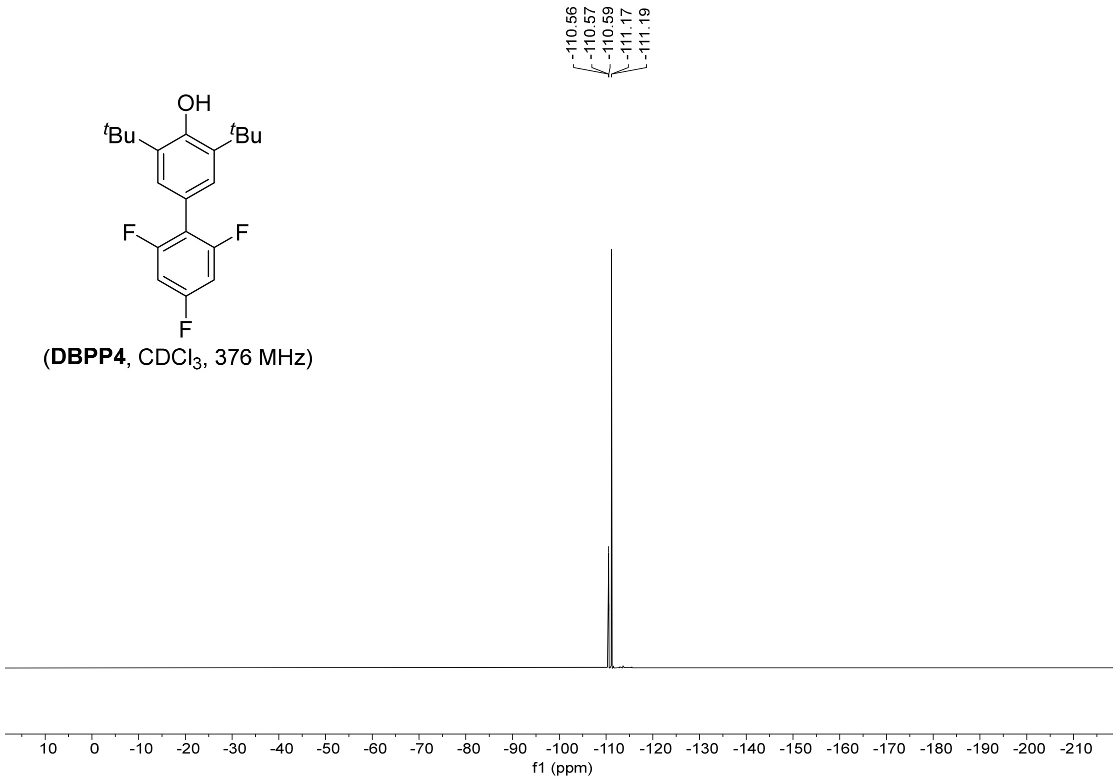
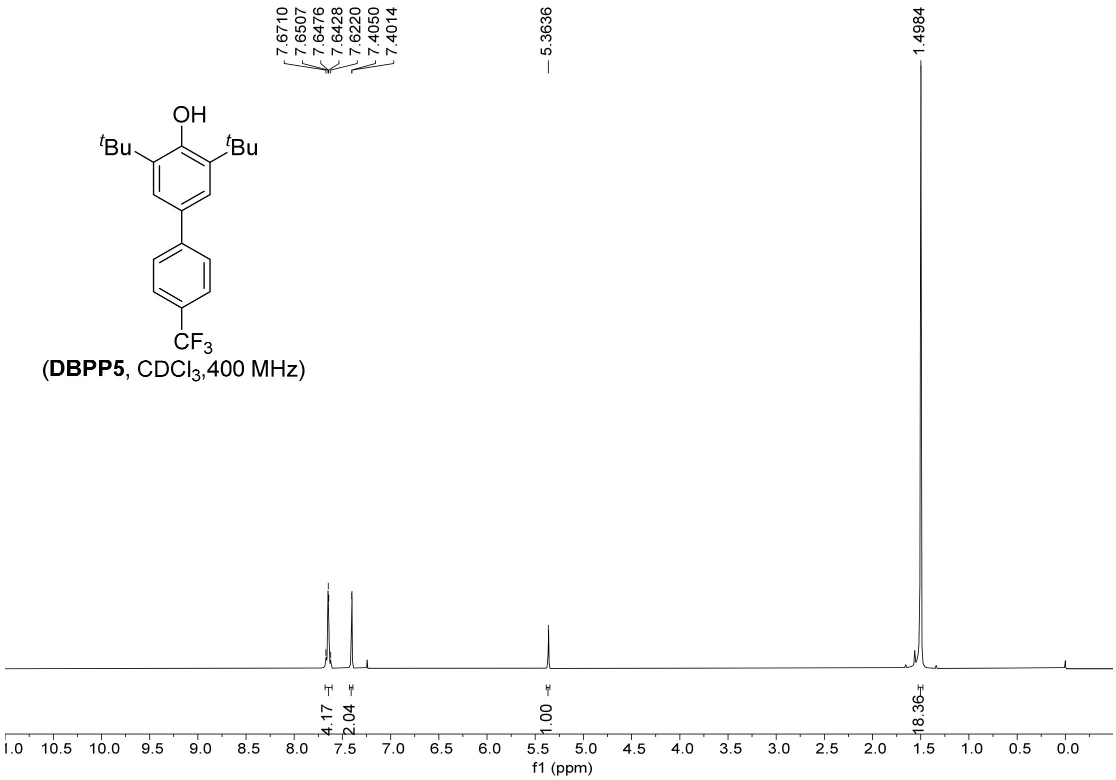
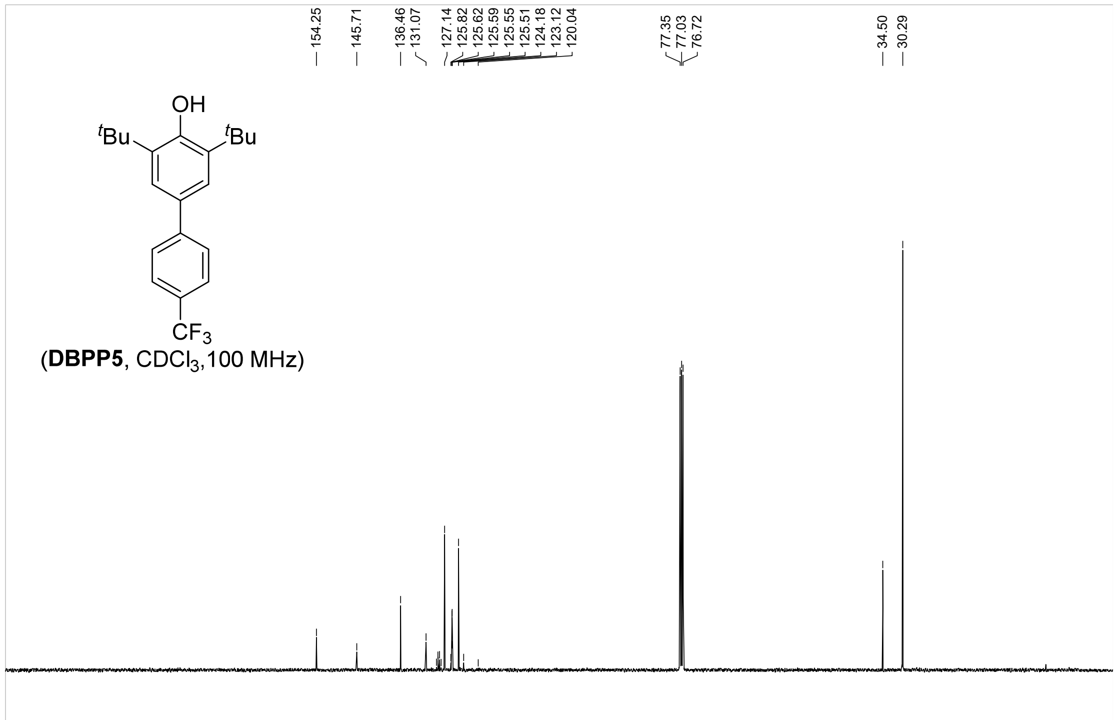
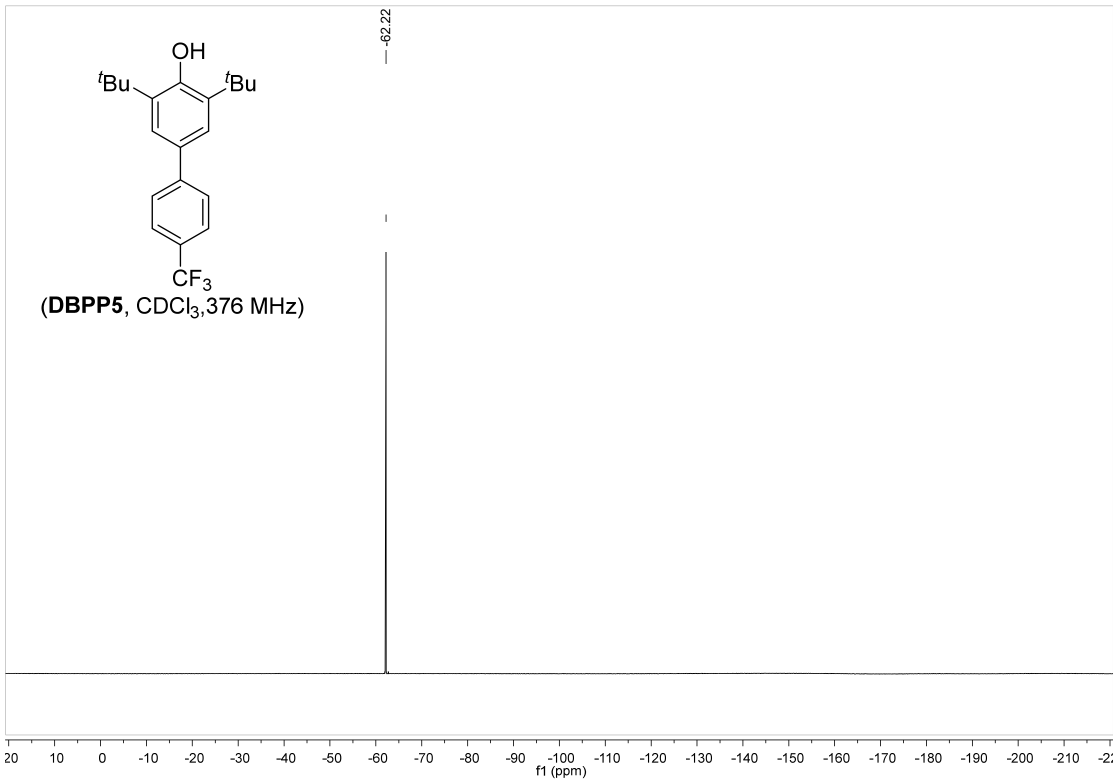

7.2200
7.2167
7.2133
7.2098
6.7567
6.7363
6.7181
6.7150
5.3532
1.4643
OH
tBu
tBu
F
F
F
(DBPP4, CDCl3, 400 MHz)
2.03
1.94
1.00
17.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


161.6823
161.5832
161.5378
161.4360
159.2169
159.1170
159.0694
158.9684
153.9272
135.7081
127.0907
119.1855
100.6399
100.3891
100.3264
100.0744
77.3584
77.0409
76.7234
34.3917
30.2927
OH
tBu
tBu
F
F
F
(DBPP4, CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-110.56
-110.57
-110.59
-111.17
-111.19
OH
^{t}Bu
^{t}Bu
F
F
F
(**DBPP4**, $CDCl_3$, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.6710
7.6507
7.6476
7.6428
7.6220
7.4050
7.4014
5.3636
1.4984
OH
tBu
tBu
CF3
(DBPP5, CDCl3,400 MHz)
4.17
2.04
1.00
18.36
1.0
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
f1 (ppm)


154.25
145.71
136.46
131.07
127.14
125.82
125.62
125.59
125.55
125.51
124.18
123.12
120.04
77.35
77.03
76.72
34.50
30.29
OH
tBu
tBu
CF3
(DBPP5, CDCl3,100 MHz)
20
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)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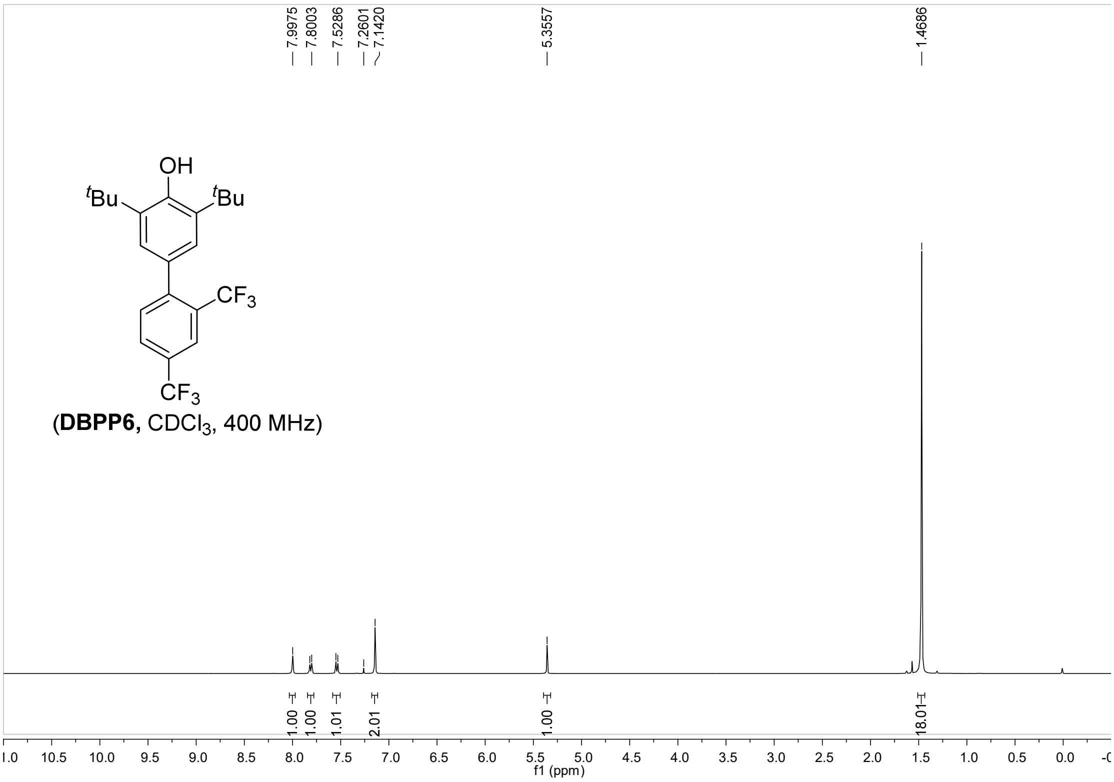
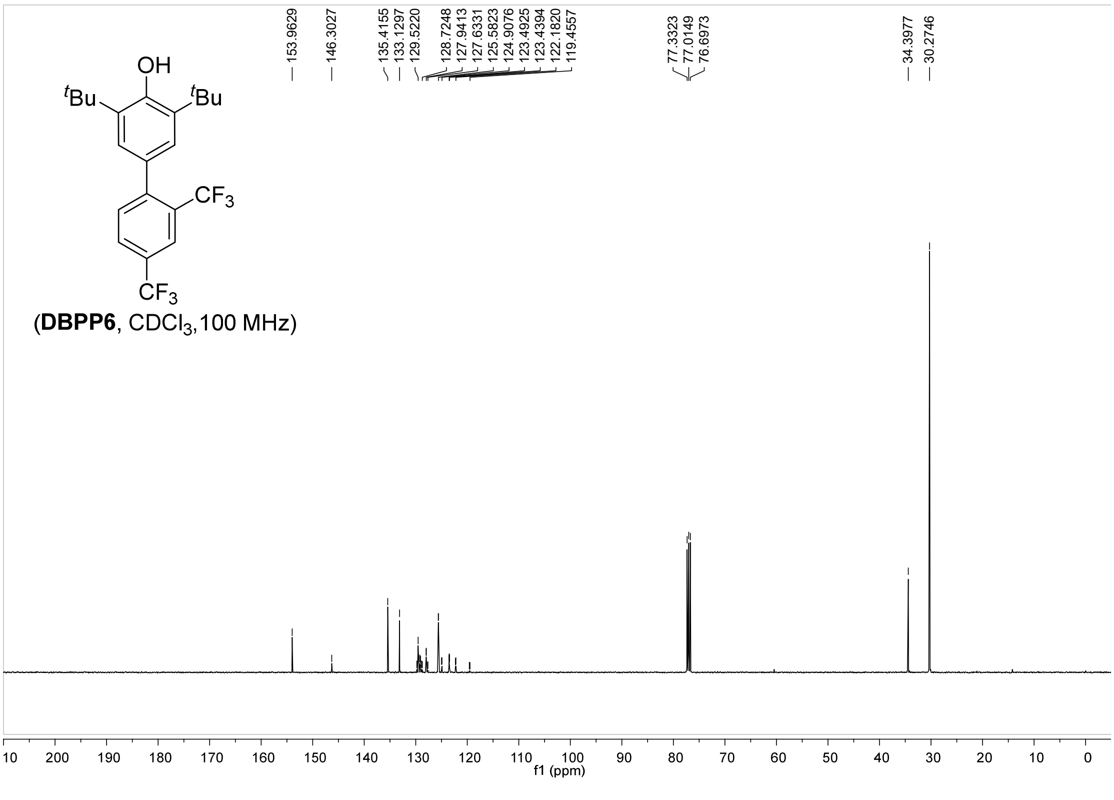
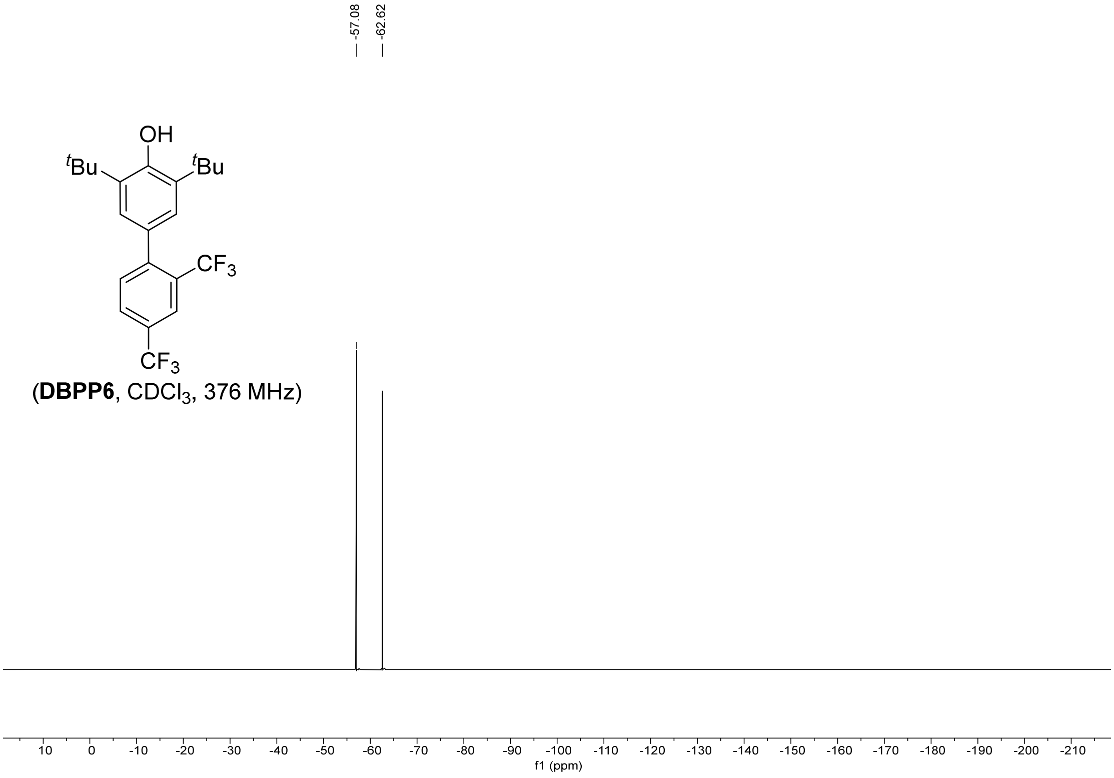
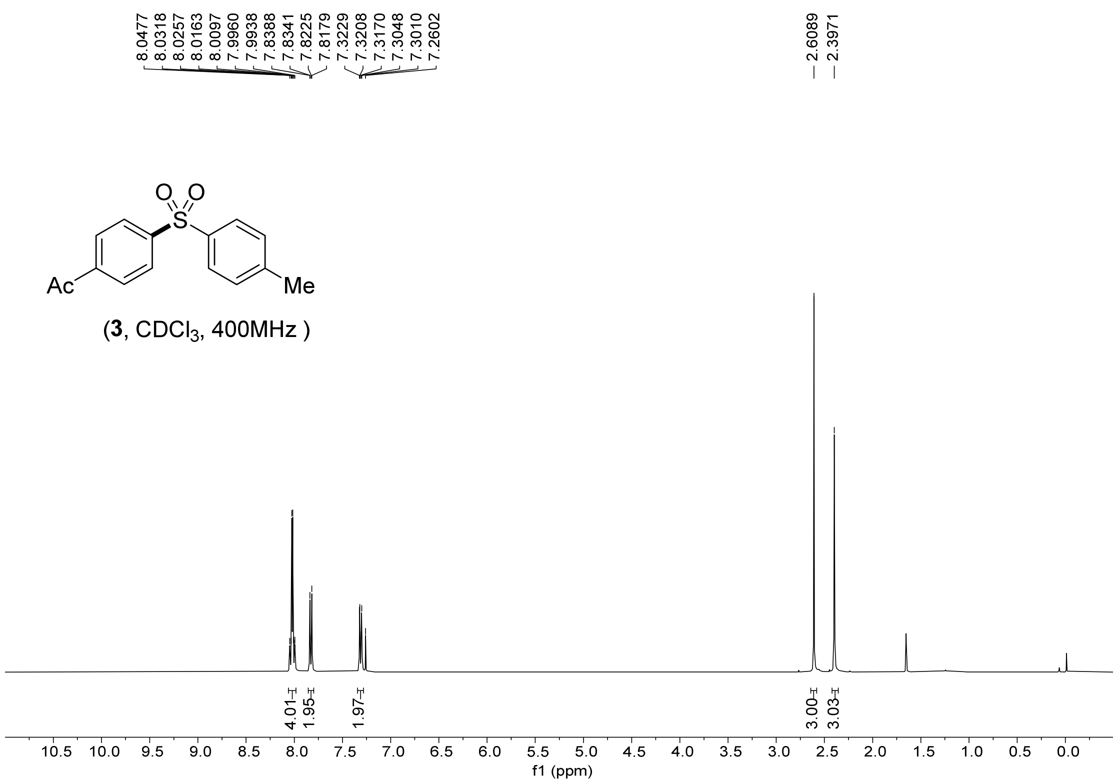

7.9975
7.8003
7.5286
7.2601
7.1420
5.3557
1.4686
OH
ᵗBu
ᵗBu
CF₃
CF₃
(DBPP6, CDCl₃, 400 MHz)
1.00
1.00
1.01
2.01
1.00
18.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

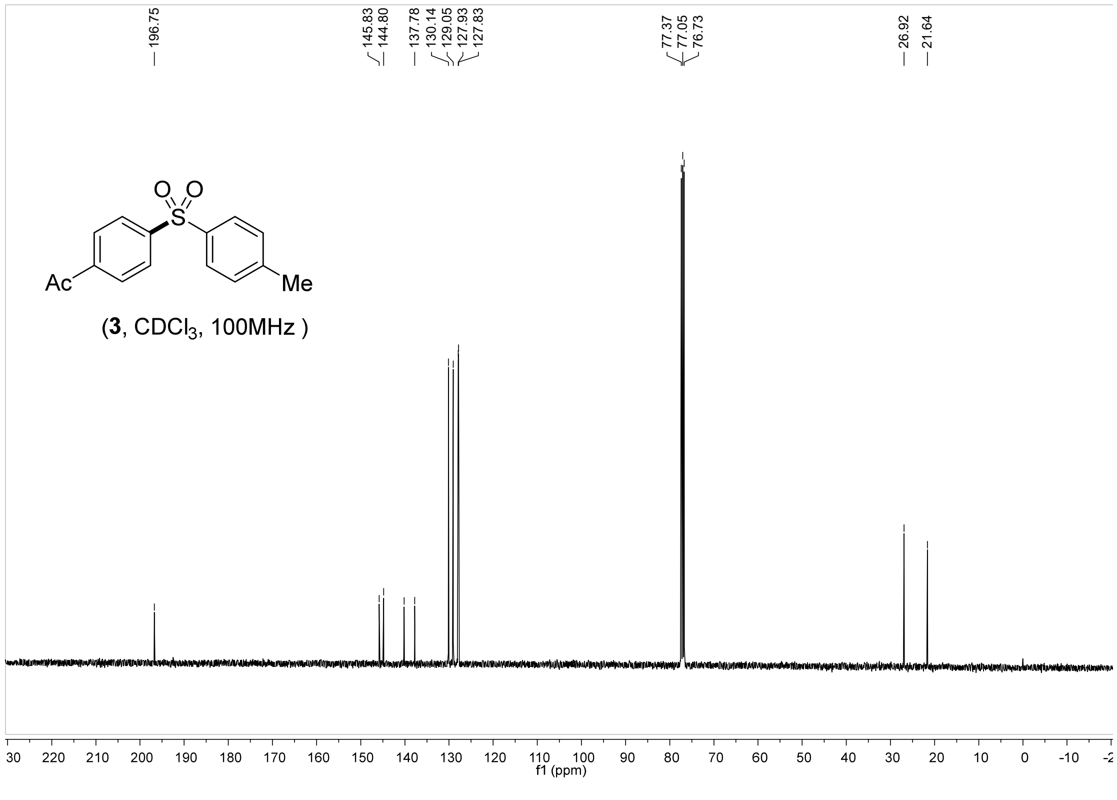

153.9629
146.3027
135.4155
133.1297
129.5220
128.7248
127.9413
127.6331
125.5823
124.9076
123.4925
123.4394
122.1820
119.4557
77.3323
77.0149
76.6973
34.3977
30.2746
OH
ᵗBu
ᵗBu
CF₃
CF₃
(DBPP6, CDCl₃,100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



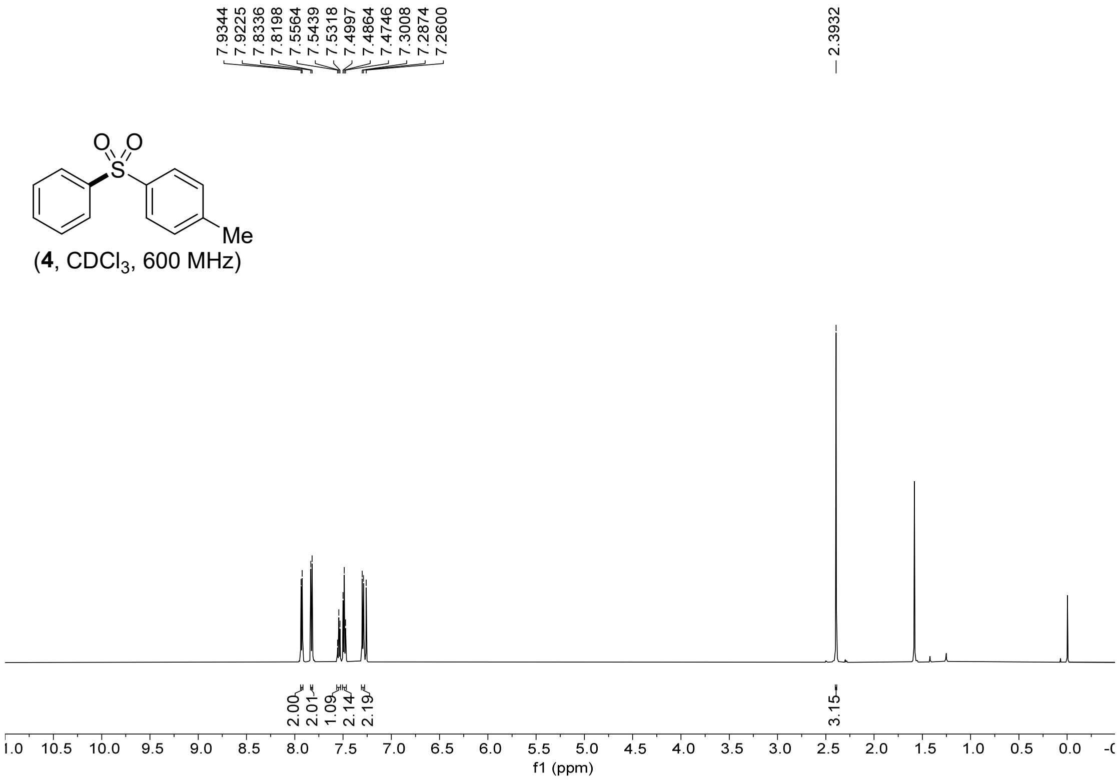
(**DBPP6**, $CDCl_3$, 376 MHz)

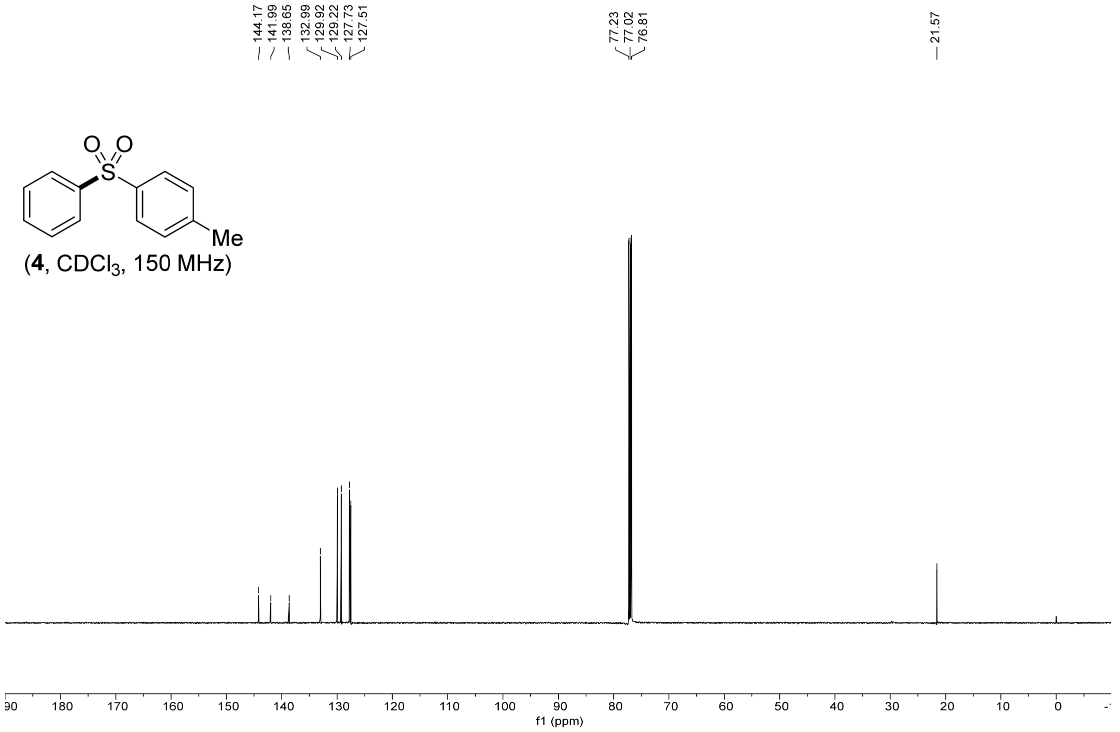


(**3**, $CDCl_3$, 400MHz)



(**3**, $CDCl_3$, 100MHz)


(**4**, $CDCl_3$, 600 MHz)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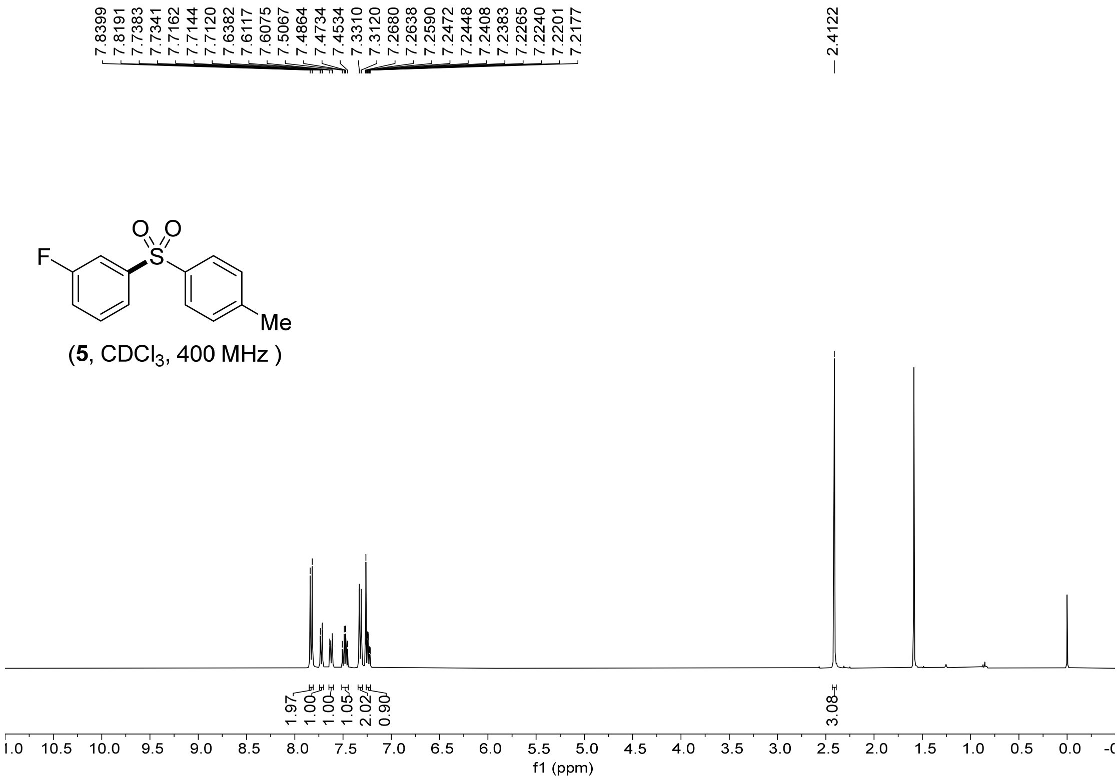
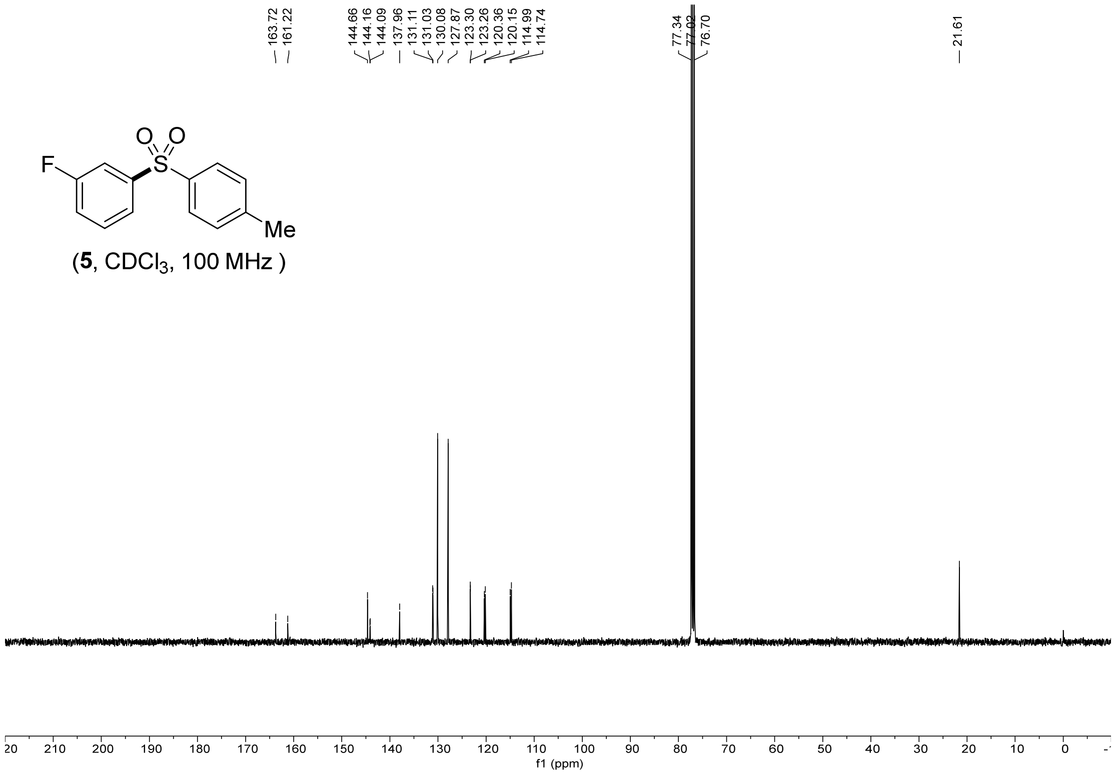
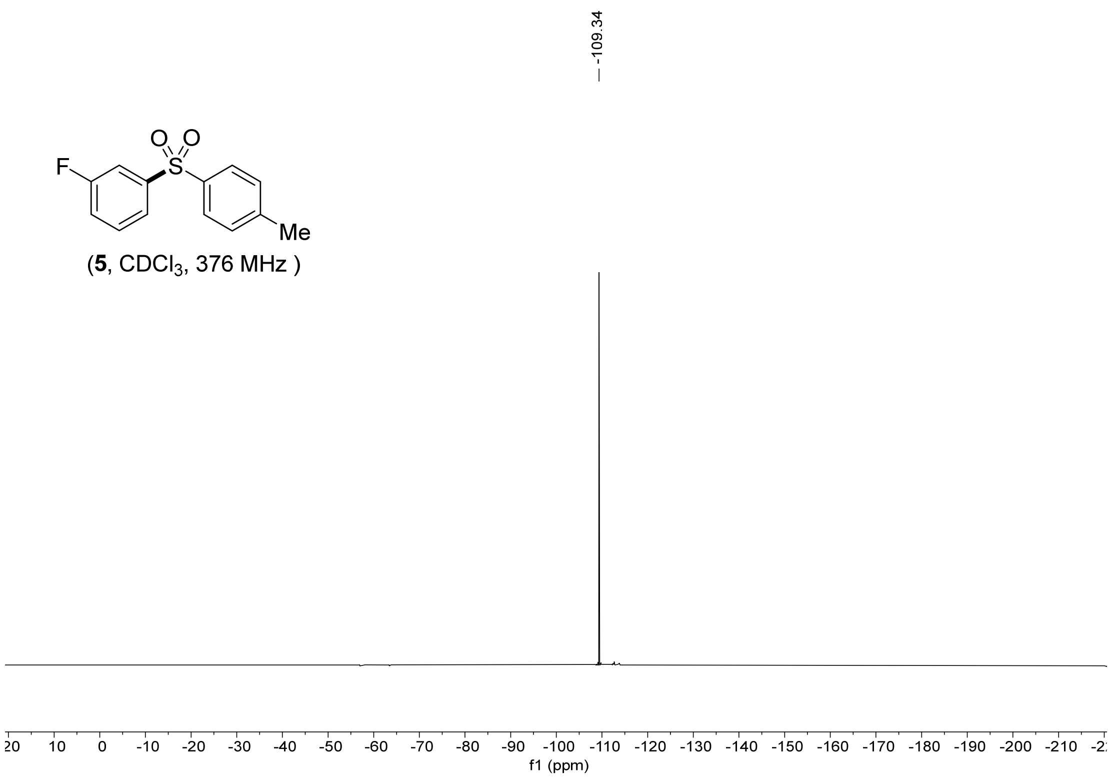
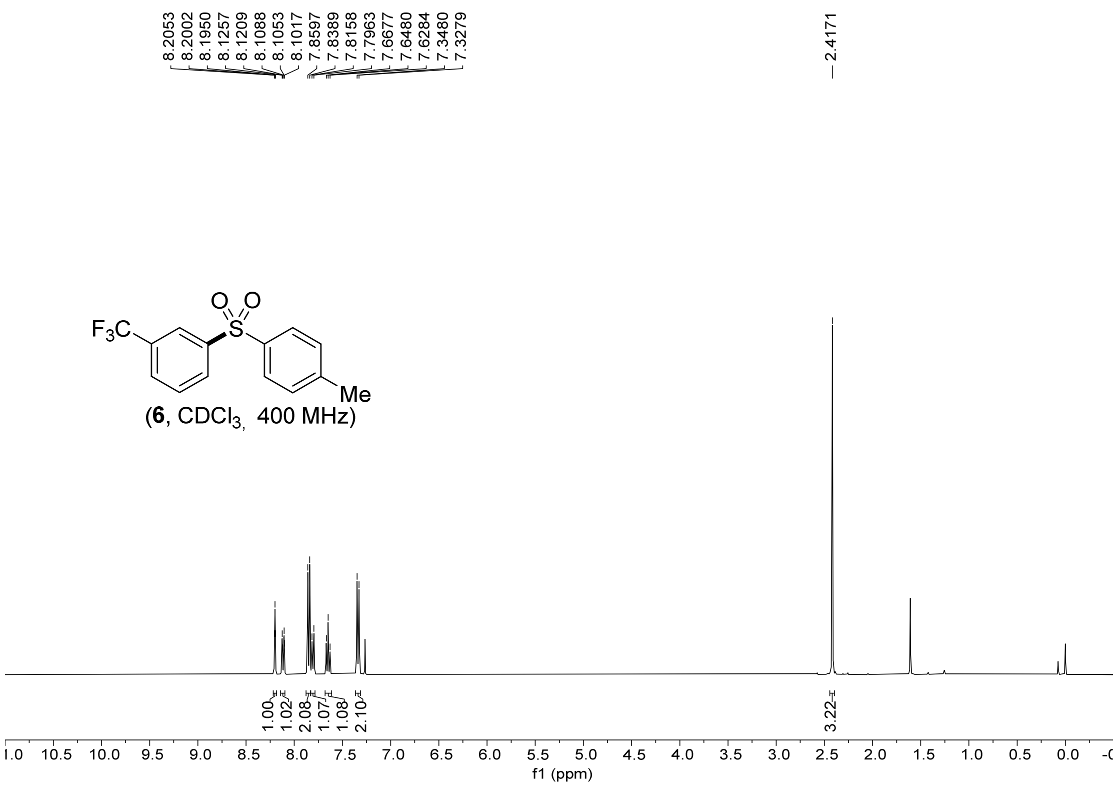
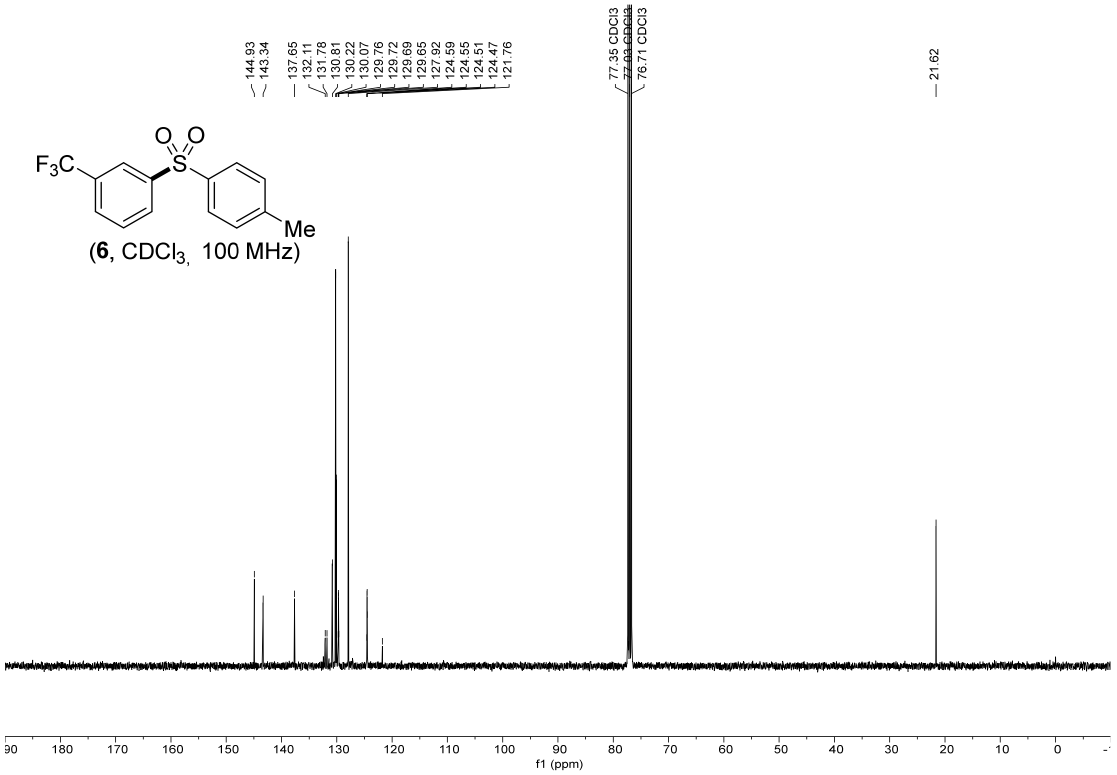
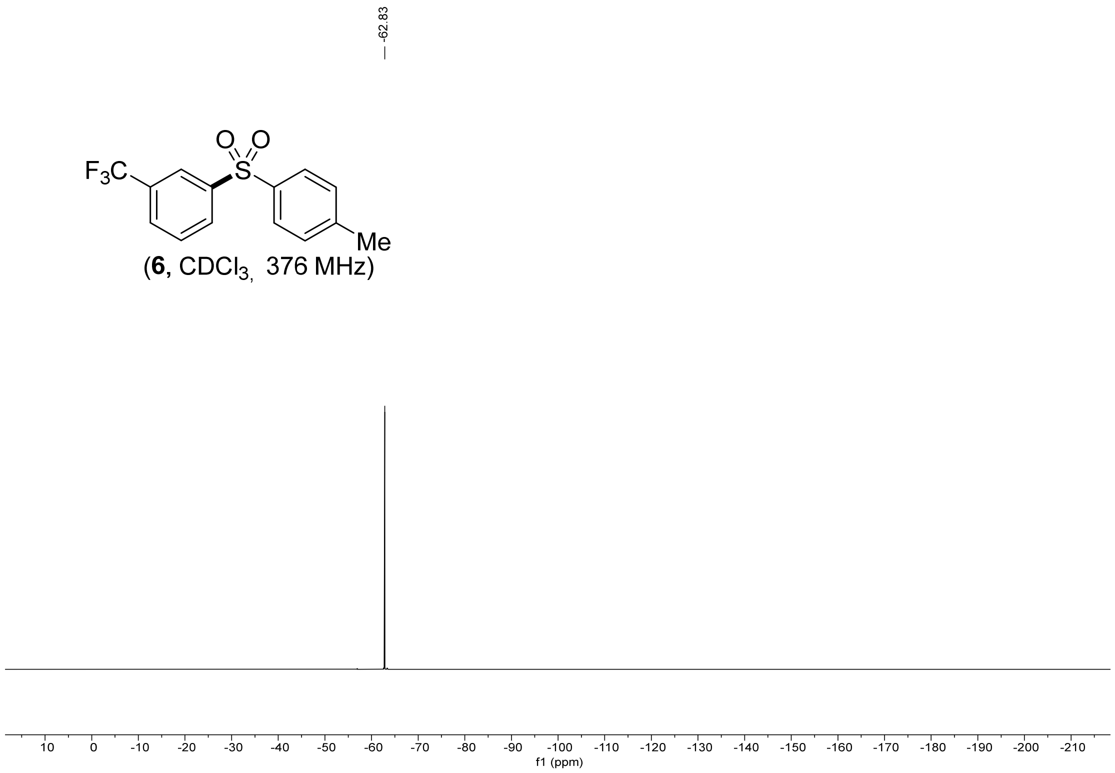

7.8399
7.8191
7.7383
7.7341
7.7162
7.7144
7.7120
7.6382
7.6117
7.6075
7.5067
7.4864
7.4734
7.4534
7.3310
7.3120
7.2680
7.2638
7.2590
7.2472
7.2448
7.2408
7.2383
7.2265
7.2240
7.2201
7.2177
2.4122
O
O
F
S
Me
(5, CDCl3, 400 MHz)
1.97
1.00
1.00
1.05
2.02
0.90
3.08
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
f1 (ppm)


163.72
161.22
144.66
144.16
144.09
137.96
131.11
131.03
130.08
127.87
123.30
123.26
120.36
120.15
114.99
114.74
77.34
77.02
76.70
21.61
O
O
F
S
Me
(5, CDCl3, 100 MHz)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


(**5**, $CDCl_3$, 376 MHz)


8.2053
8.2002
8.1950
8.1257
8.1209
8.1088
8.1053
8.1017
7.8597
7.8389
7.8158
7.7963
7.6677
7.6480
7.6284
7.3480
7.3279
2.4171
F3C
O
O
S
Me
(6, CDCl3, 400 MHz)
1.00
1.02
2.08
1.07
1.08
2.10
3.22
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
-0
f1 (ppm)


144.93
143.34
137.65
132.11
131.78
130.81
130.22
130.07
129.76
129.72
129.69
129.65
127.92
124.59
124.55
124.51
124.47
121.76
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
21.62
F3C
O
O
S
Me
(6, CDCl3, 100 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



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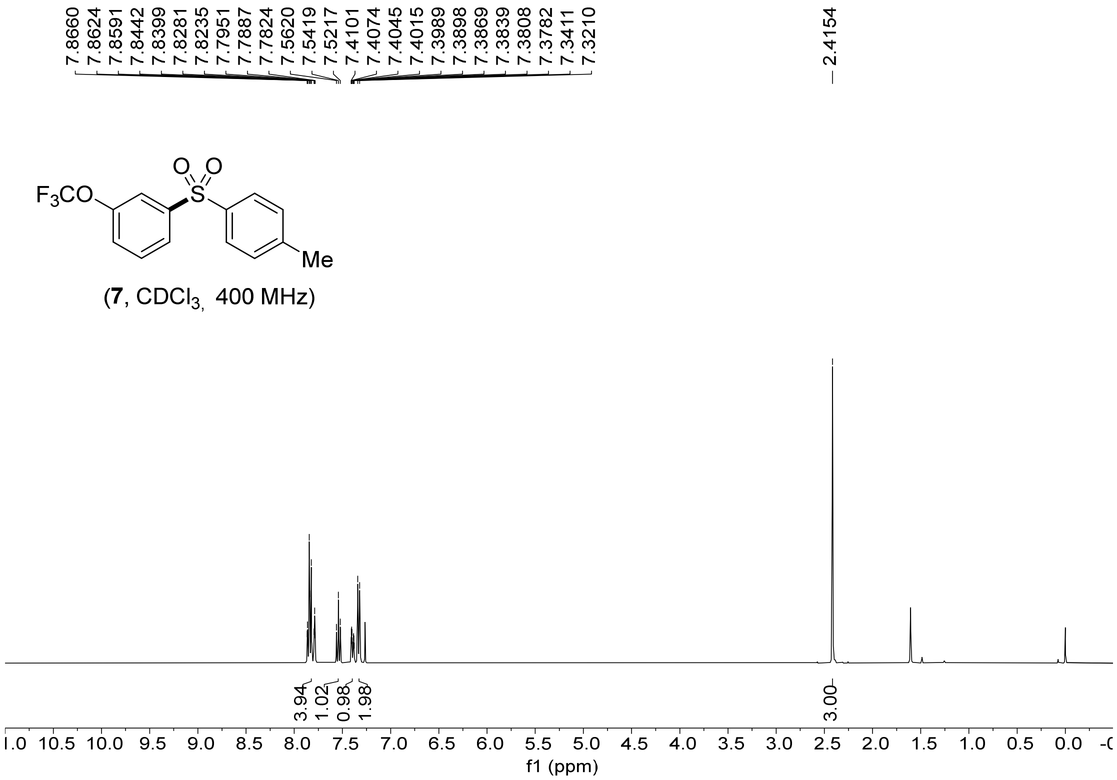

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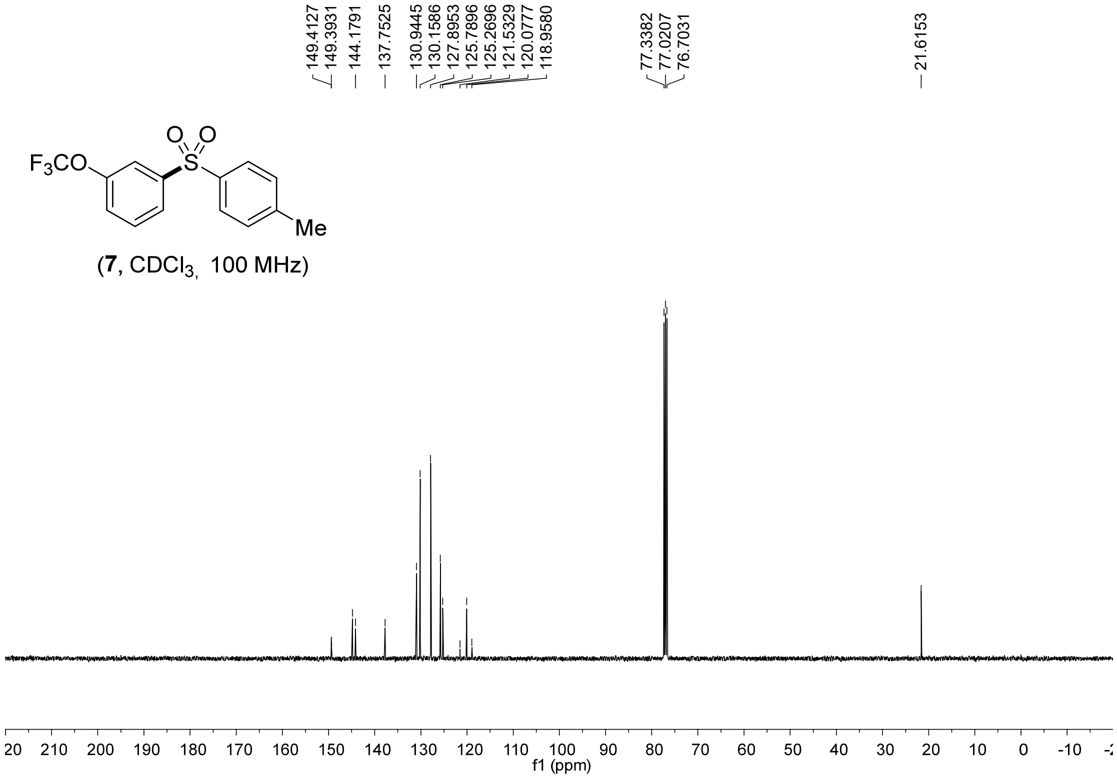

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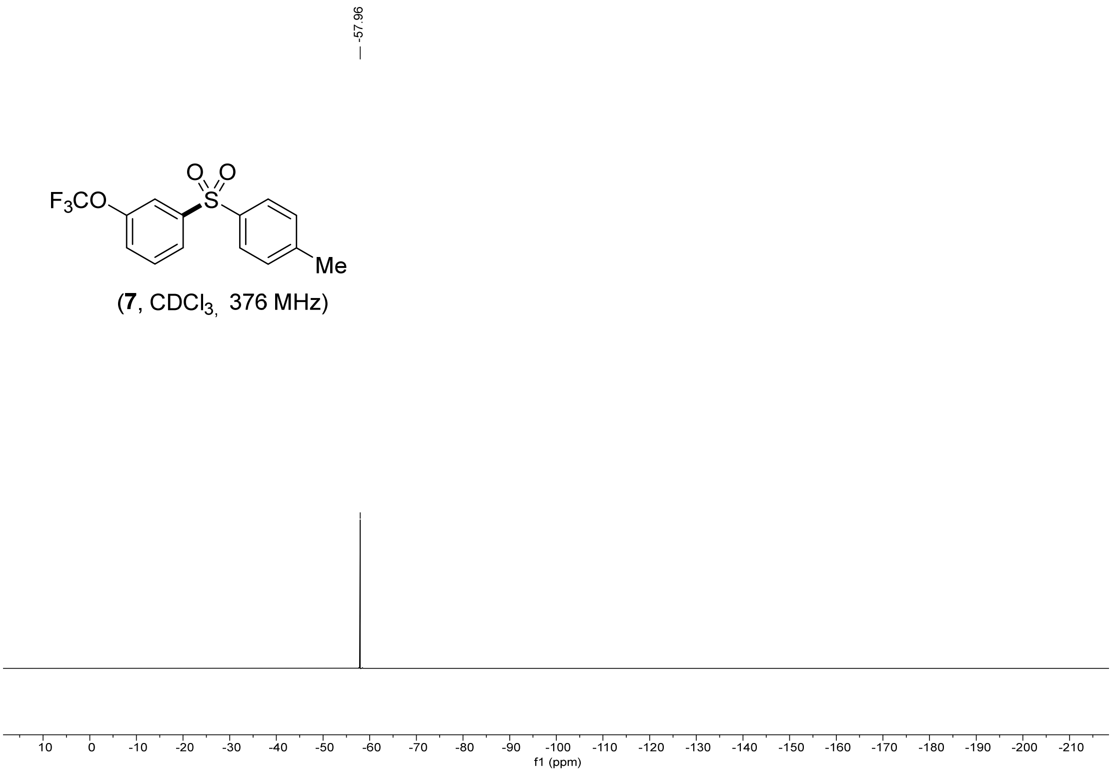
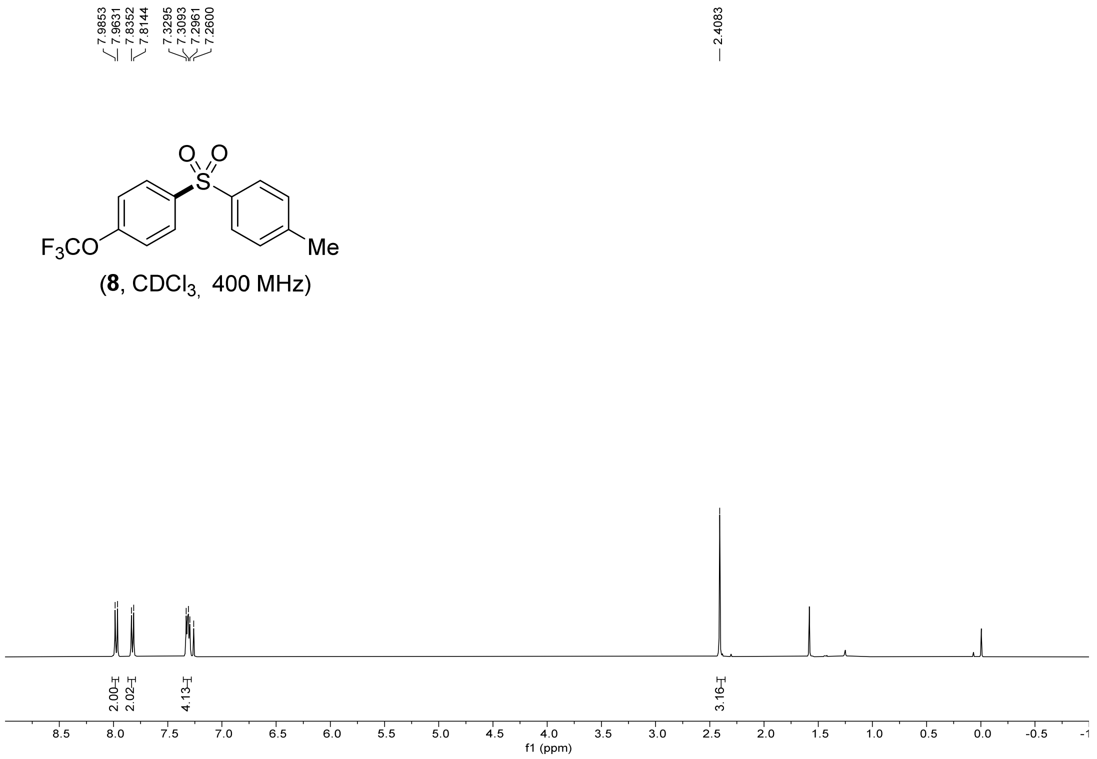
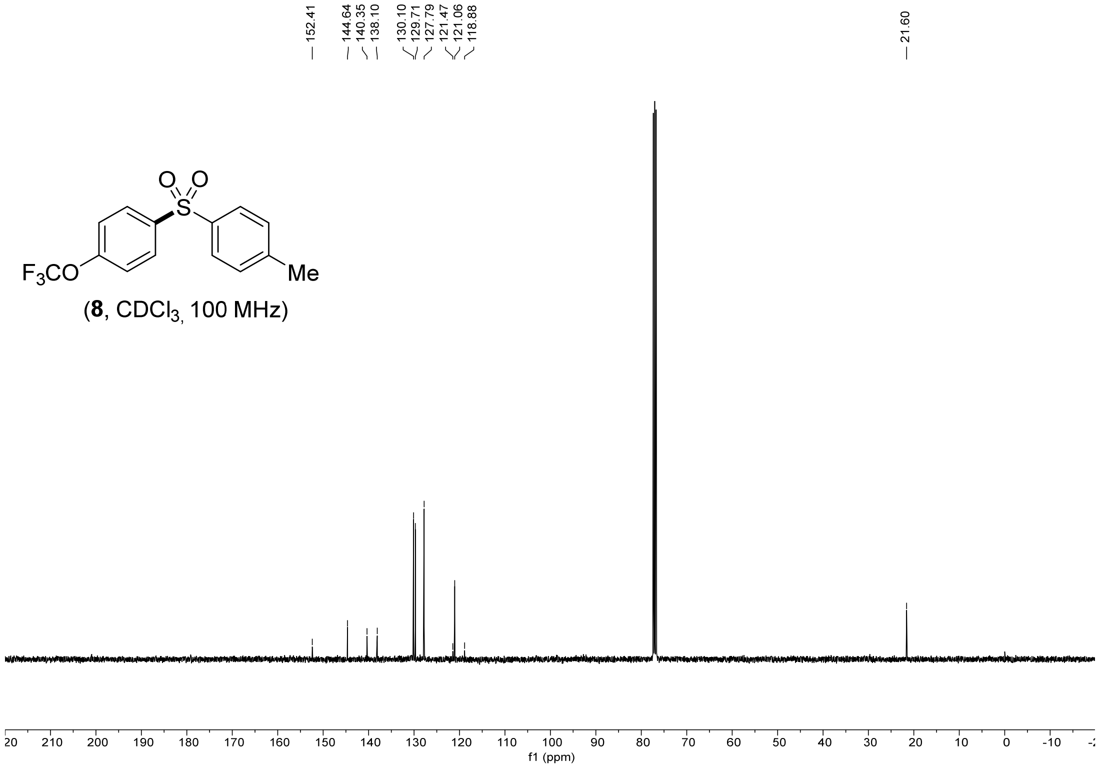
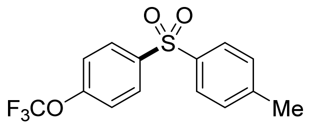


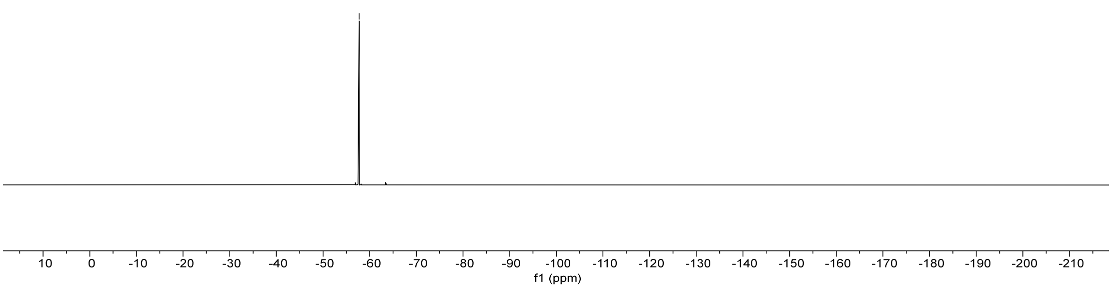
(**7**, $CDCl_3$, 376 MHz)

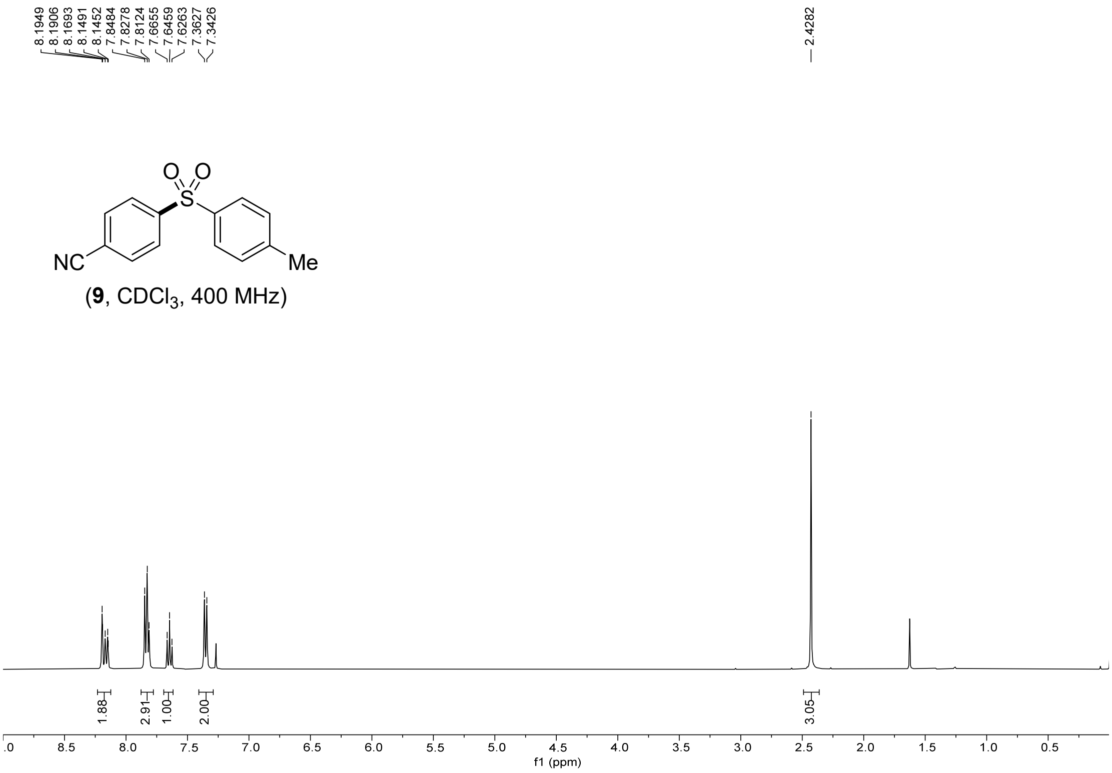

7.9853
7.9631
7.8352
7.8144
7.3295
7.3093
7.2961
7.2600
2.4083
F3CO
Me
(8, CDCl3, 400 MHz)
2.00
2.02
4.13
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

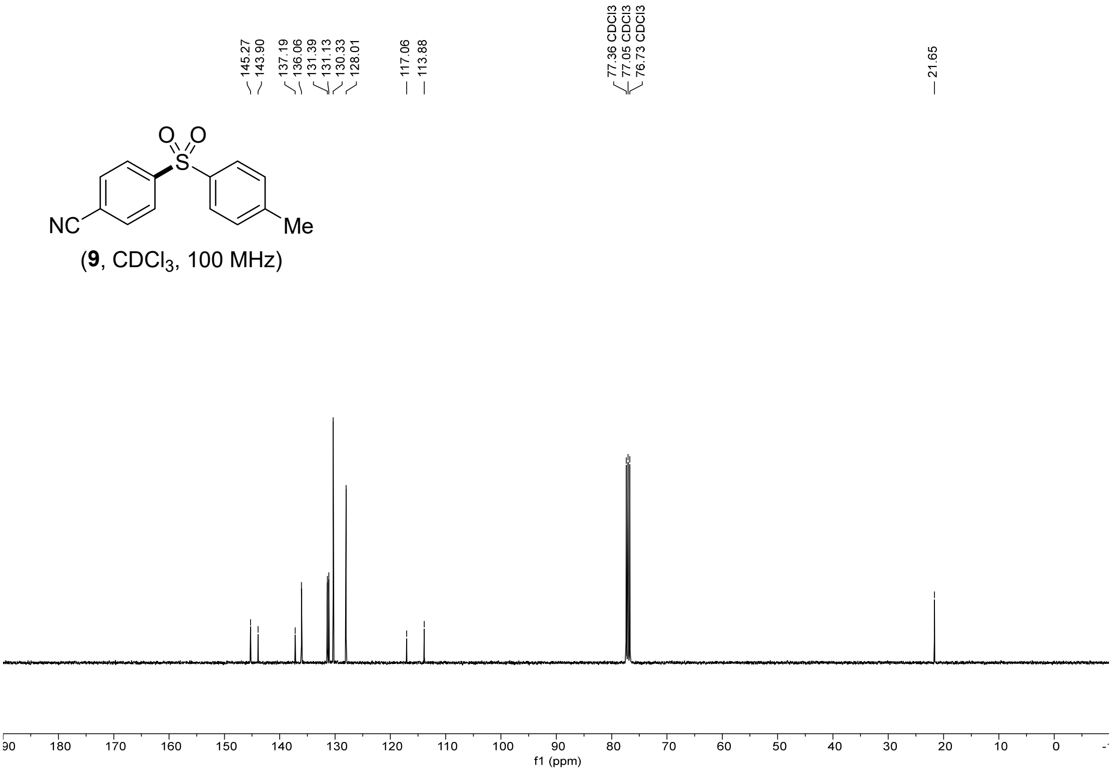

152.41
144.64
140.35
138.10
130.10
129.71
127.79
121.47
121.06
118.88
21.60
F3CO
Me
(8, CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

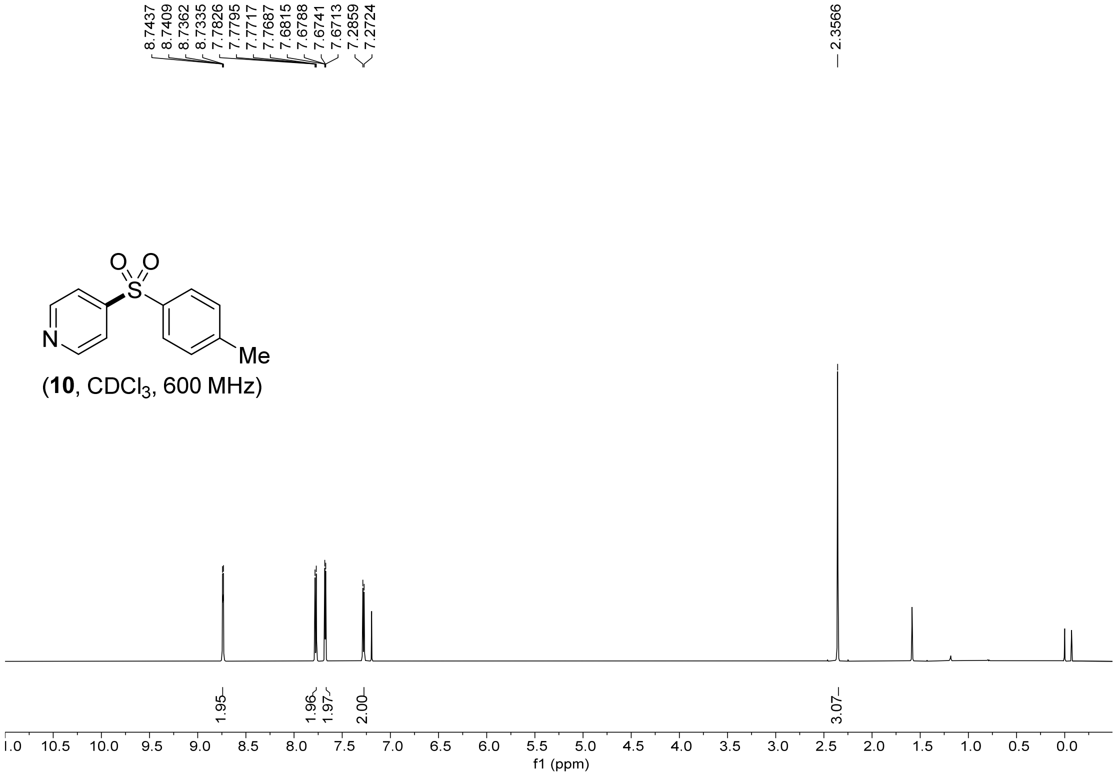


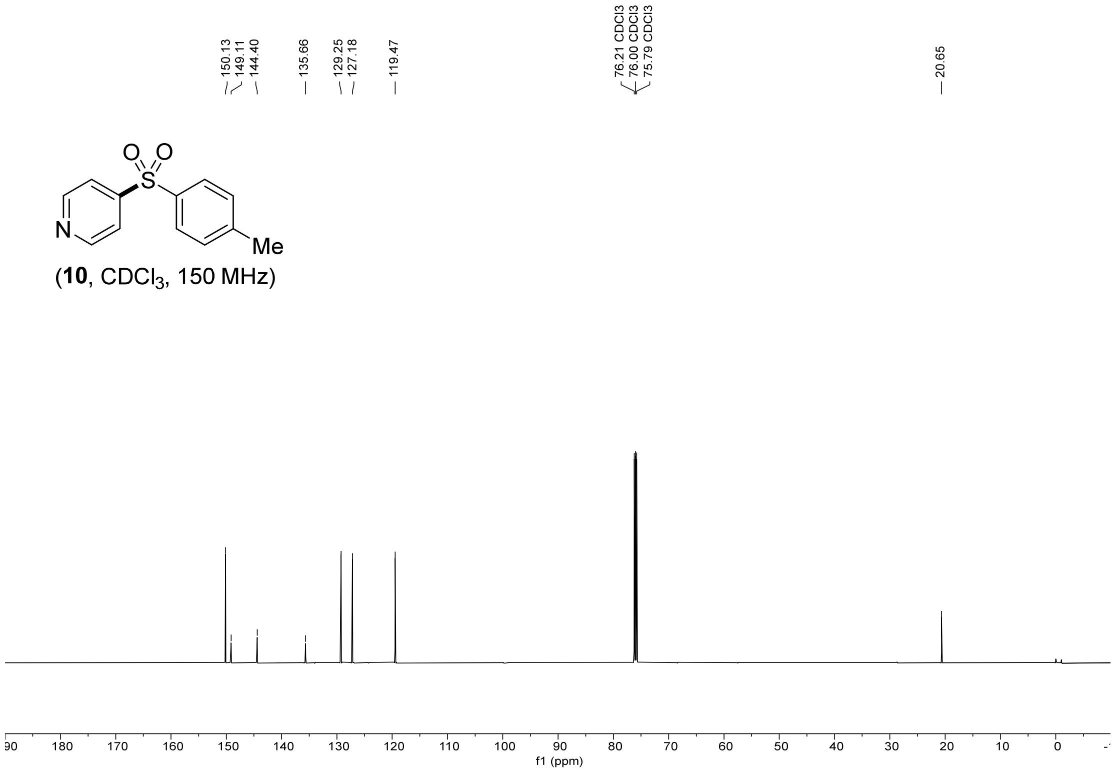
(**8**, $CDCl_3$, 376 MHz)

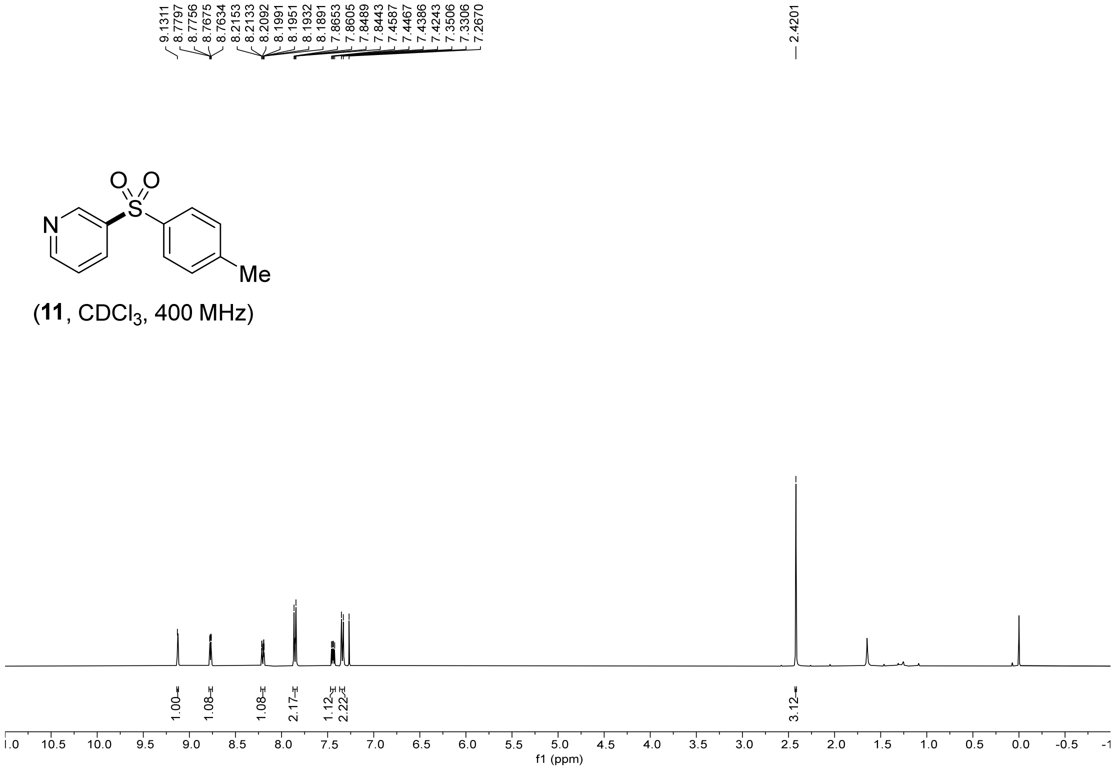


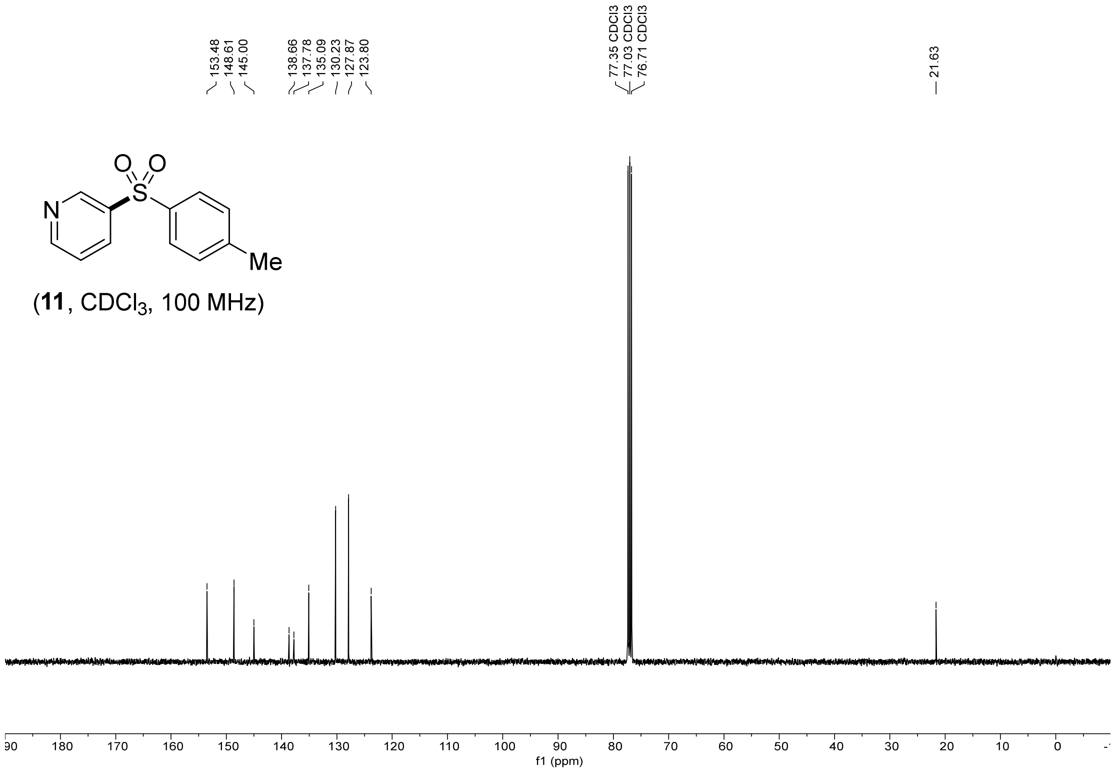

8.1949
8.1906
8.1693
8.1491
8.1452
7.8484
7.8278
7.8124
7.6655
7.6459
7.6263
7.3627
7.3426
2.4282
NC
Me
O
O
S
(**9**, $CDCl_3$, 400 MHz)
1.88
2.91
1.00
2.00
3.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

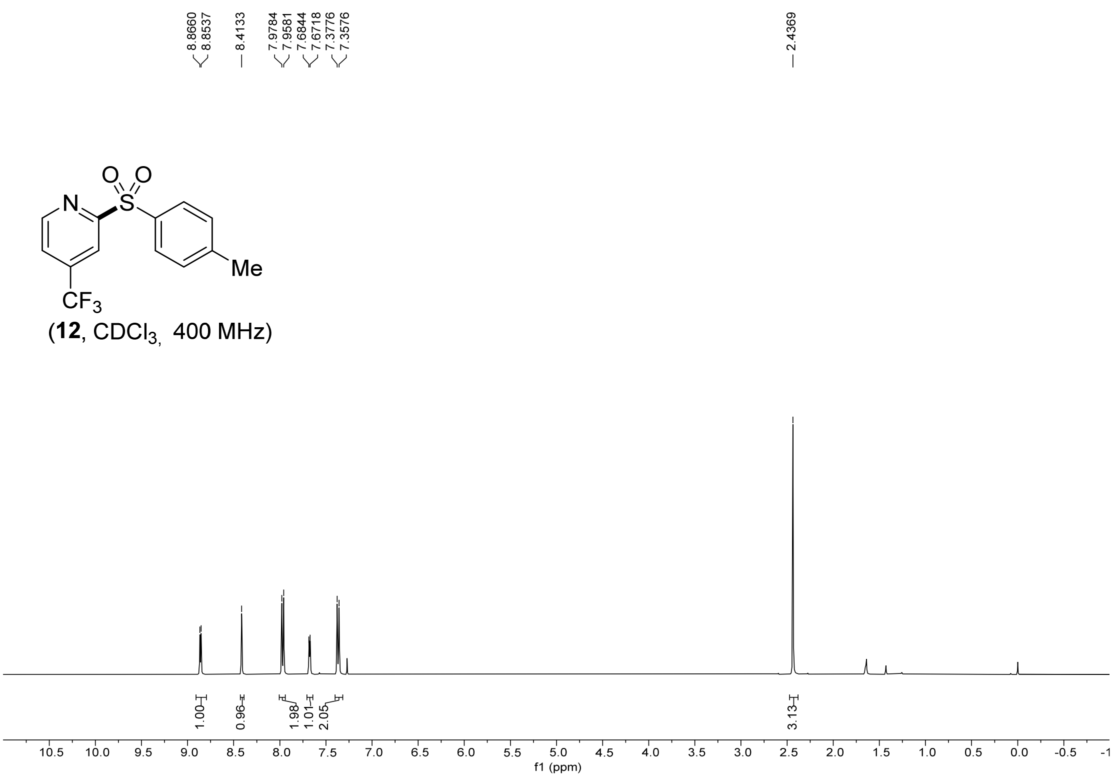

145.27
143.90
137.19
136.06
131.39
131.13
130.33
128.01
117.06
113.88
77.36 CDCl3
77.05 CDCl3
76.73 CDCl3
21.65
NC
Me
O
O
S
(**9**, $CDCl_3$, 100 MHz)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


(**10**, $CDCl_3$, 600 MHz)

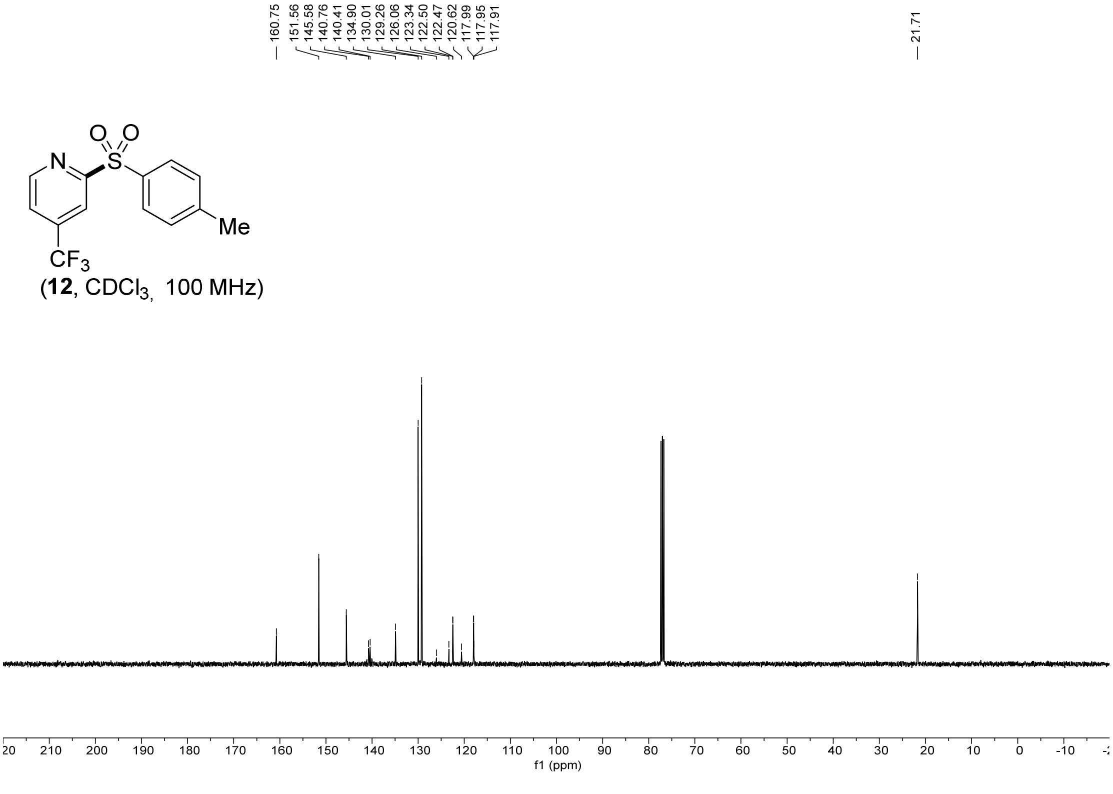

(**10**, $CDCl_3$, 150 MHz)


(**11**, $CDCl_3$, 400 MHz)

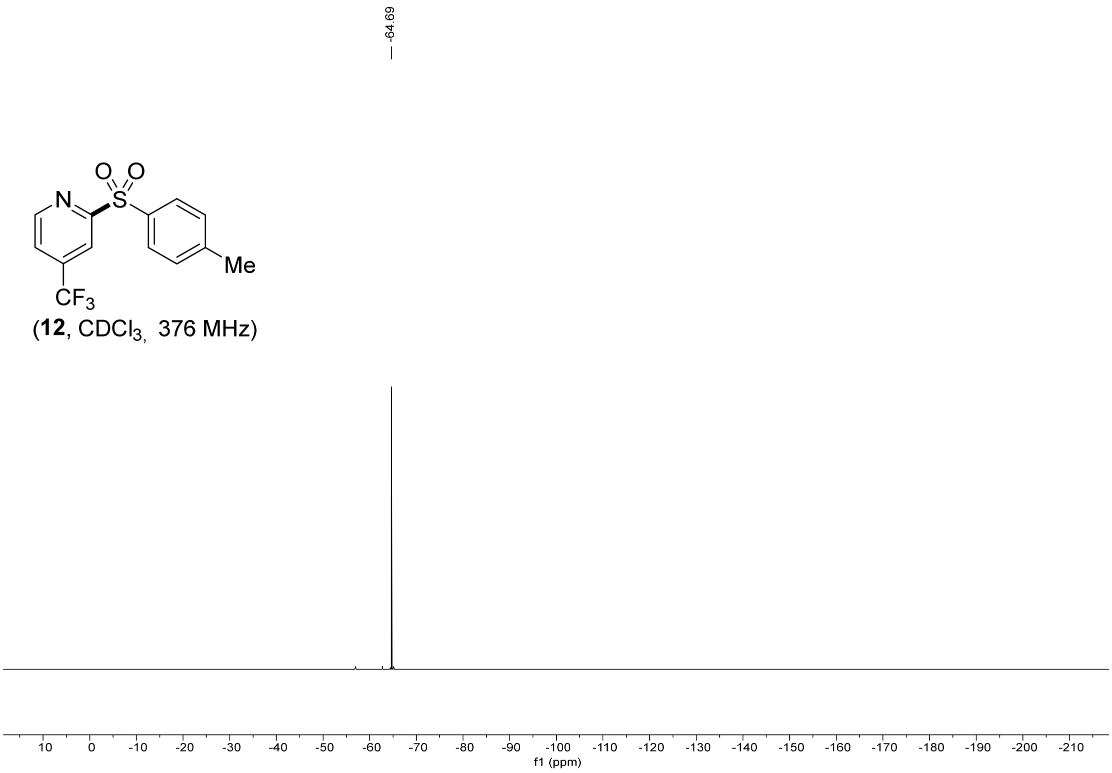

(**11**, $CDCl_3$, 100 MHz)

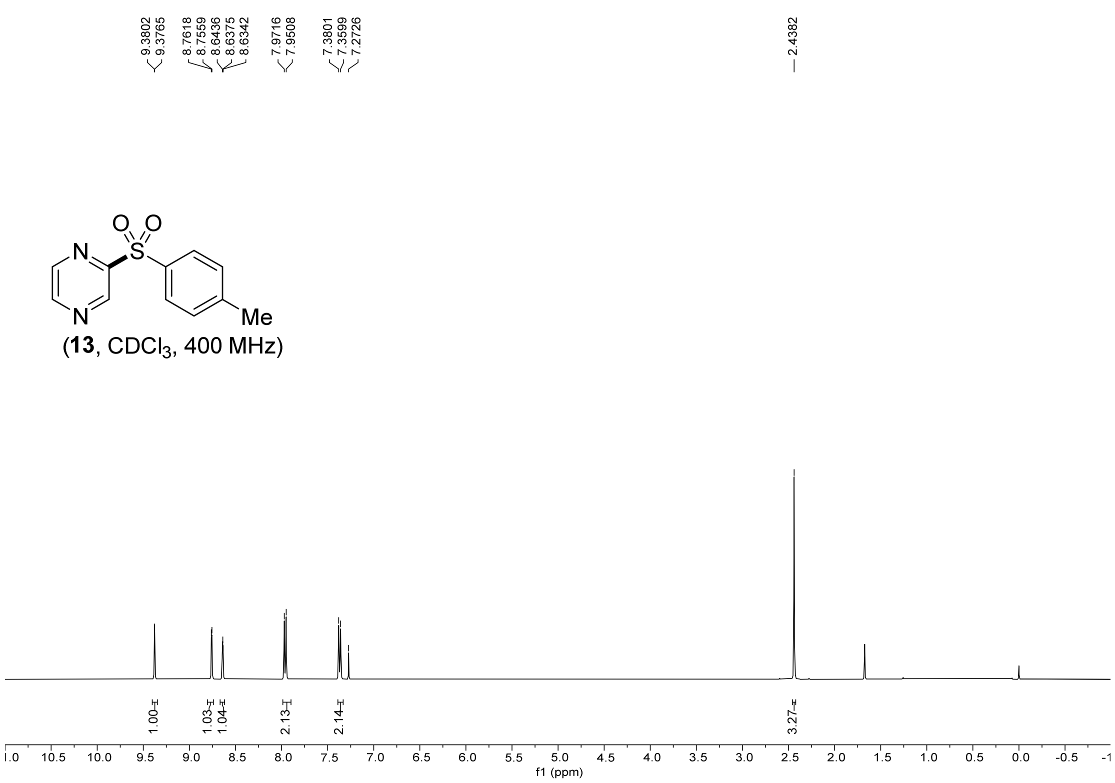


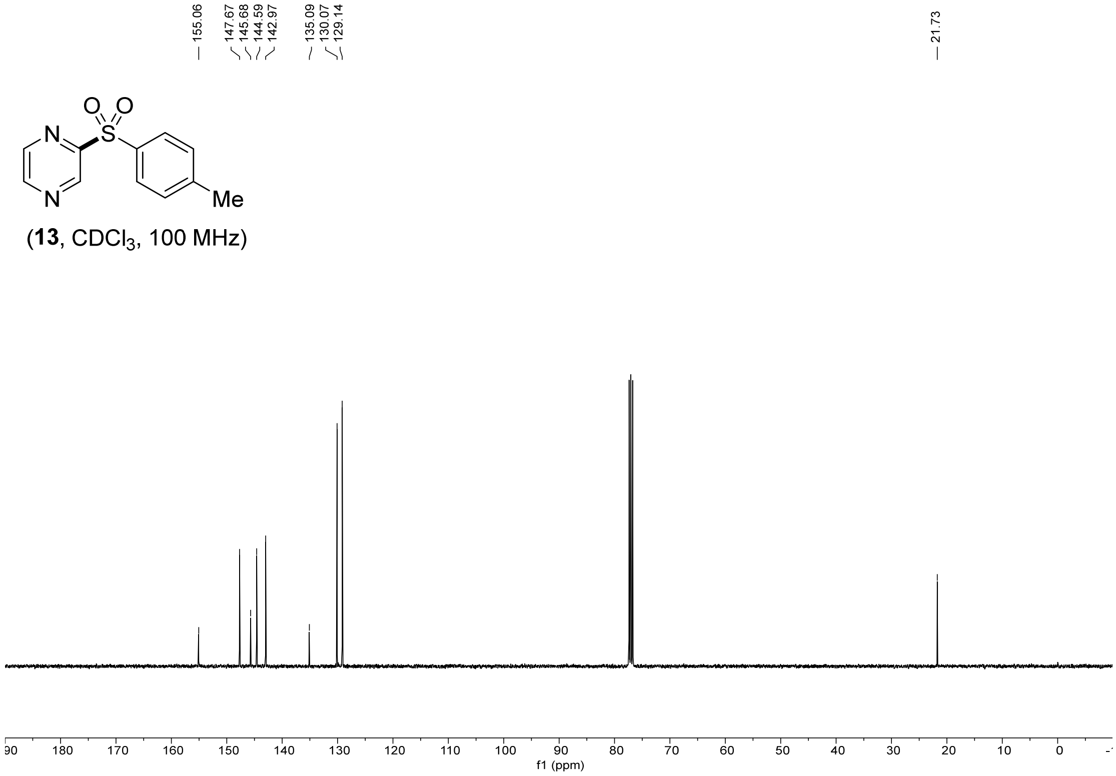
(**12**, $CDCl_3$, 400 MHz)

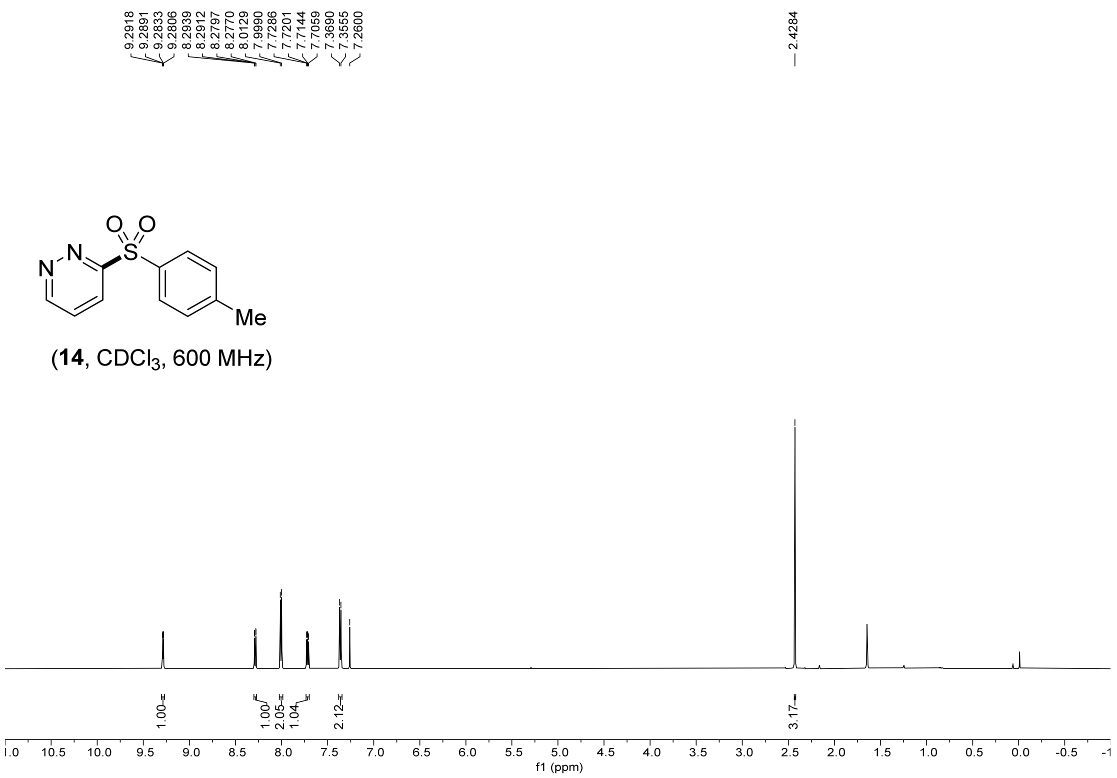


(**12**, $CDCl_3$, 100 MHz)

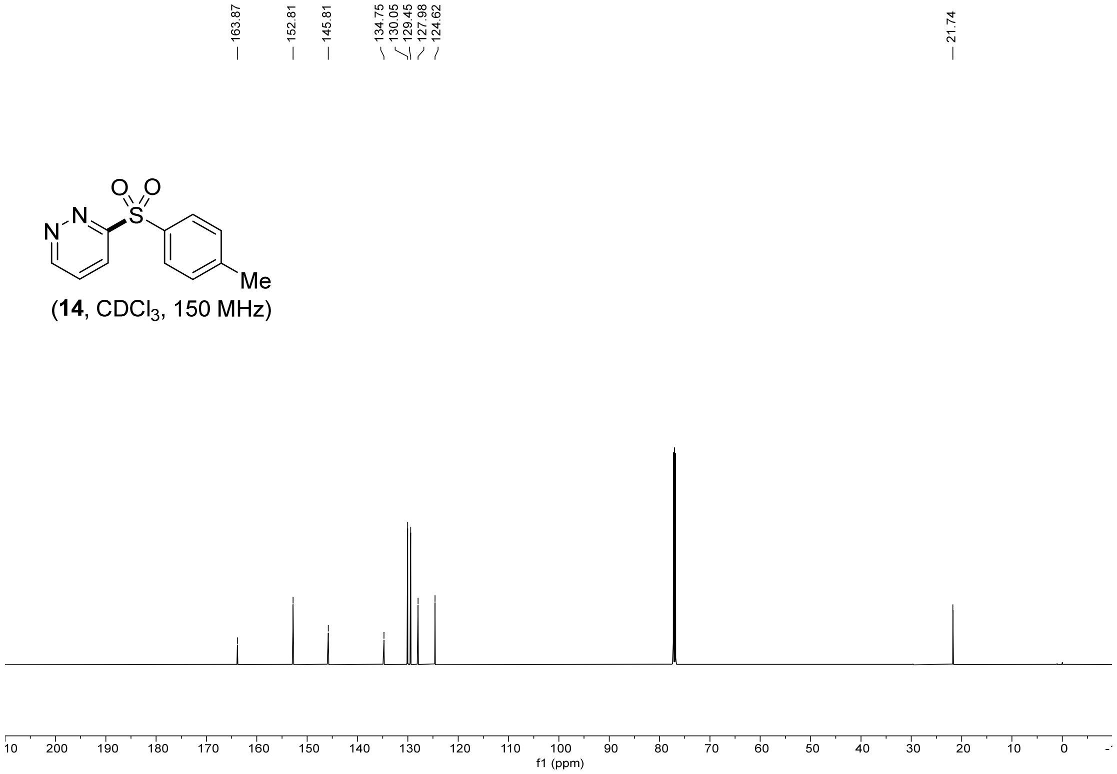

(**12**, $CDCl_3$, 376 MHz)


(**13**, $CDCl_3$, 400 MHz)

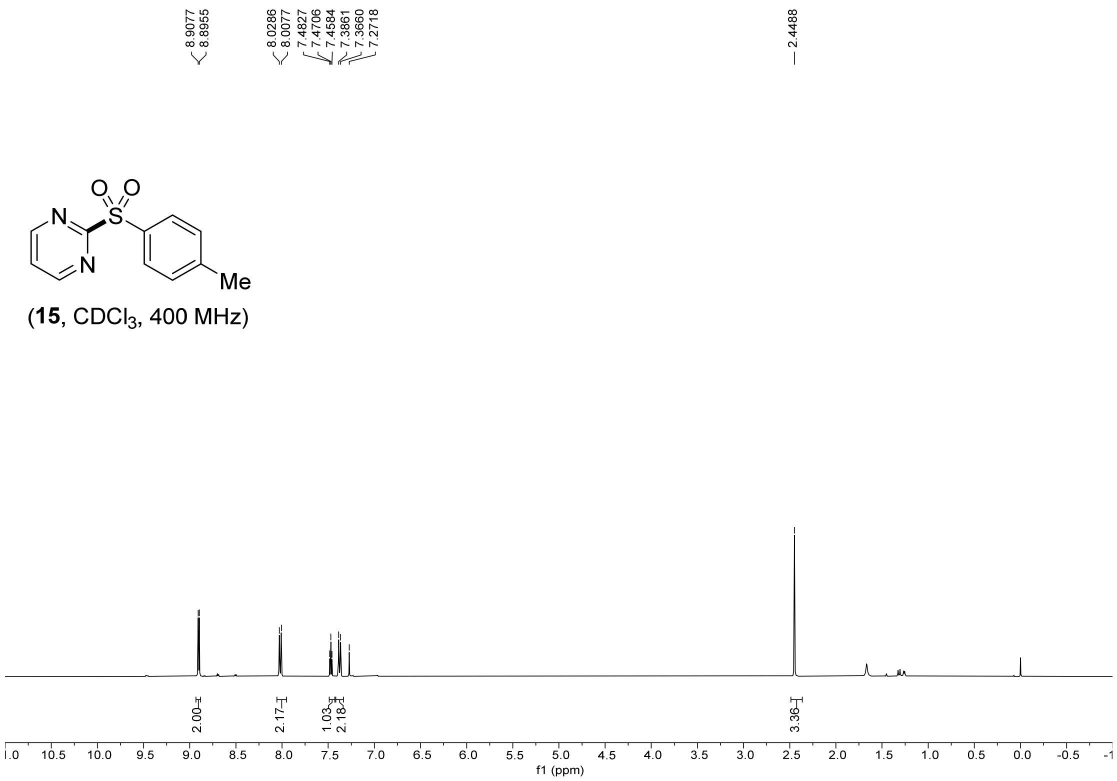

(**13**, $CDCl_3$, 100 MHz)

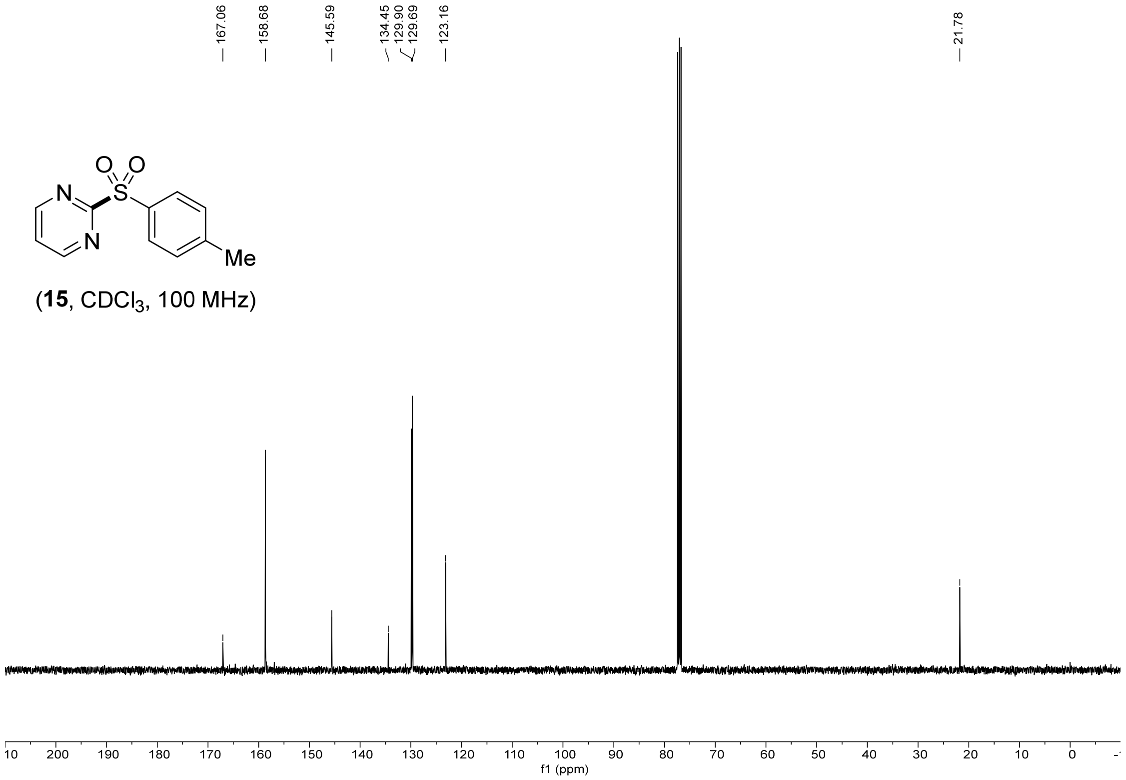


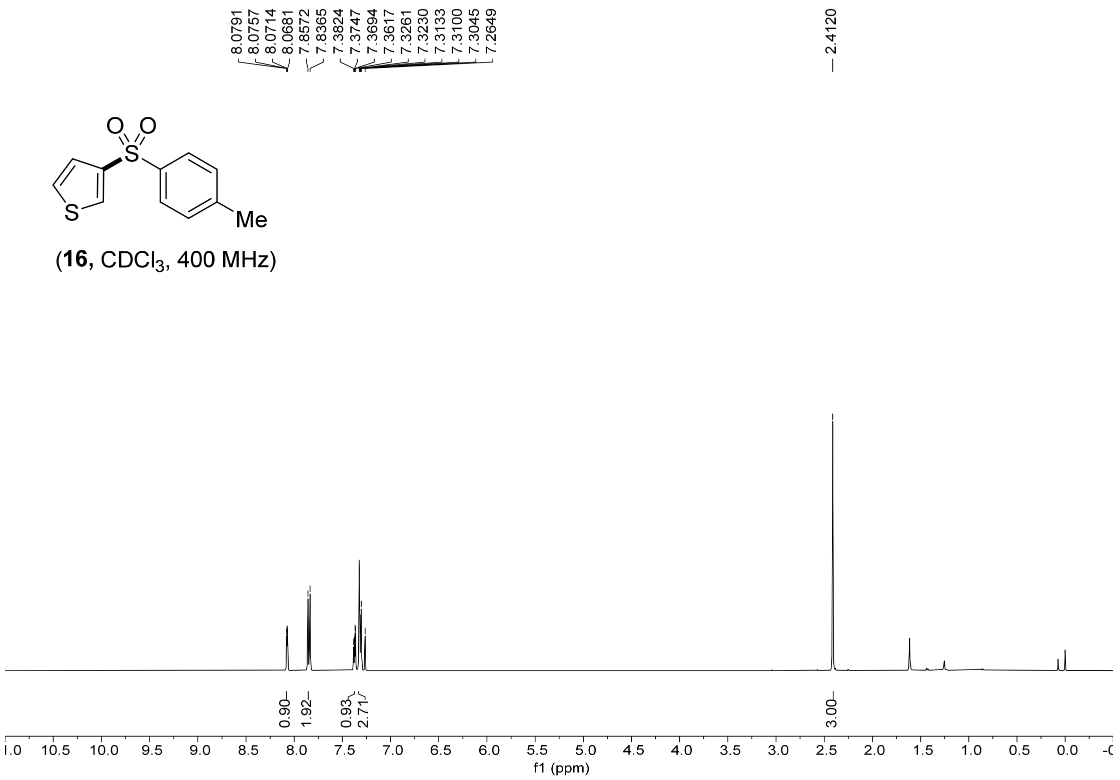
(**14**, $CDCl_3$, 600 MHz)



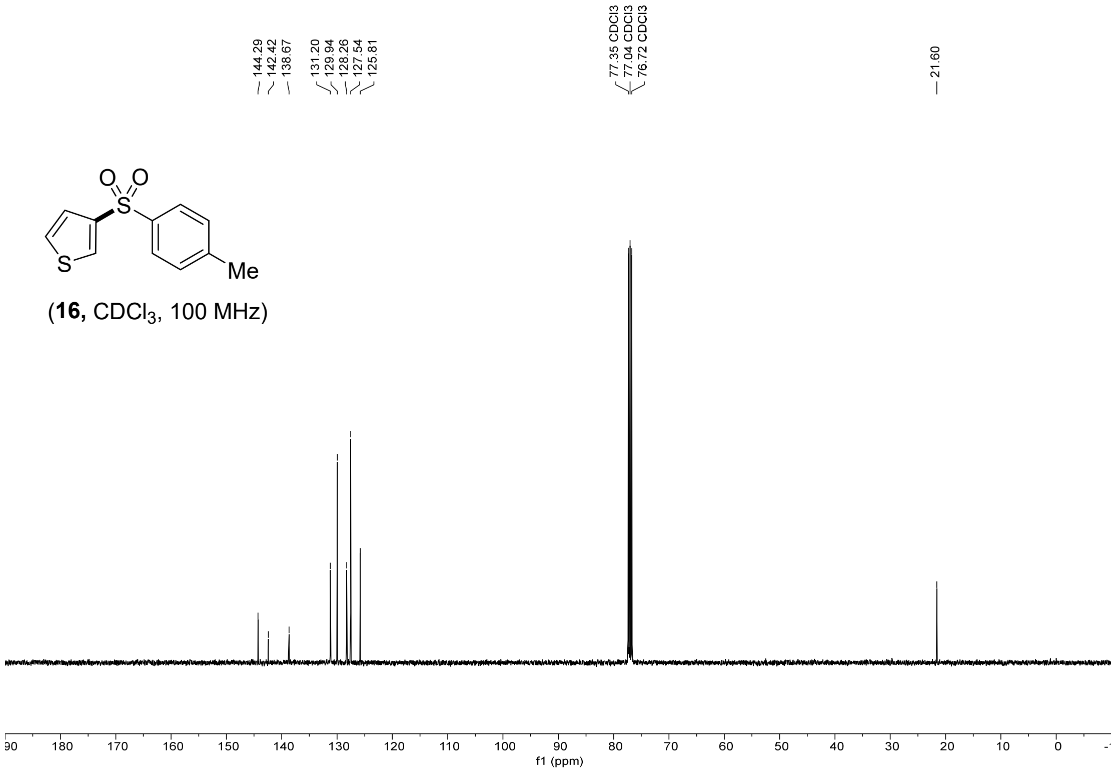
(**14**, $CDCl_3$, 150 MHz)


8.9077
8.8955
8.0286
8.0077
7.4827
7.4706
7.4584
7.3861
7.3660
7.2718
2.4488
O
O
N
S
N
Me
(**15**, CDCl$_3$, 400 MHz)
2.00
2.17
1.03
2.18
3.36
1.0
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
-0.5
-1
f1 (ppm)

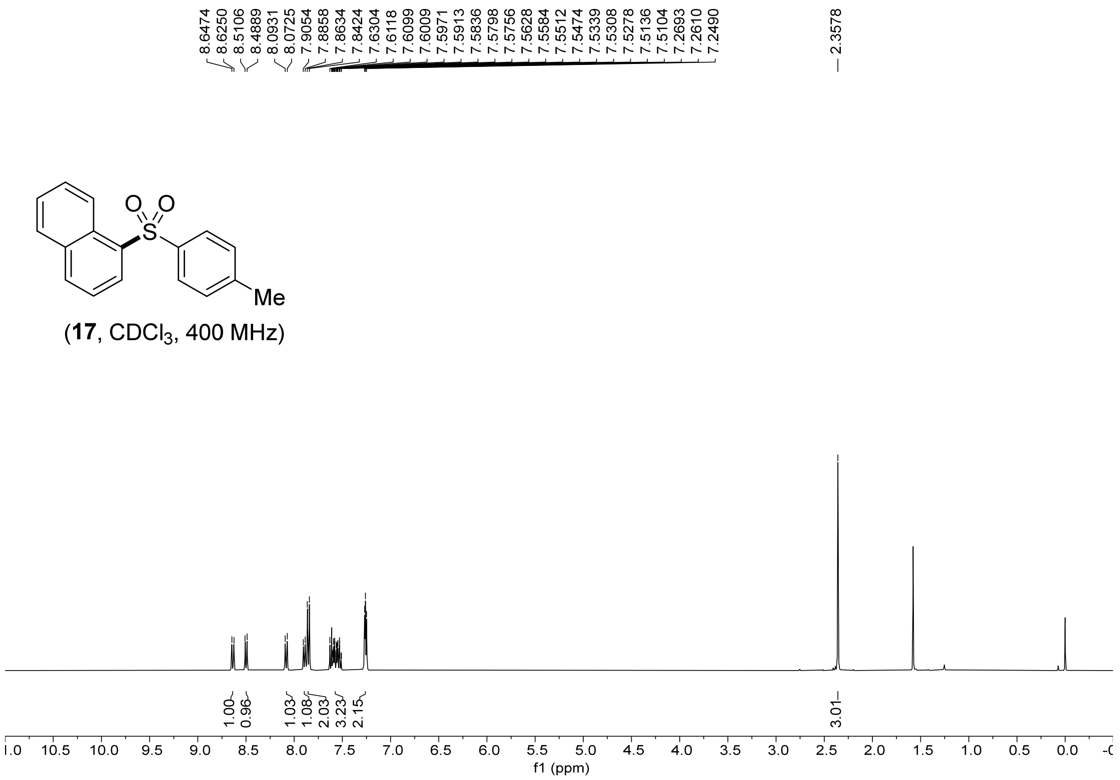

167.06
158.68
145.59
134.45
129.90
129.69
123.16
21.78
O
O
N
S
N
Me
(**15**, CDCl$_3$, 100 MHz)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

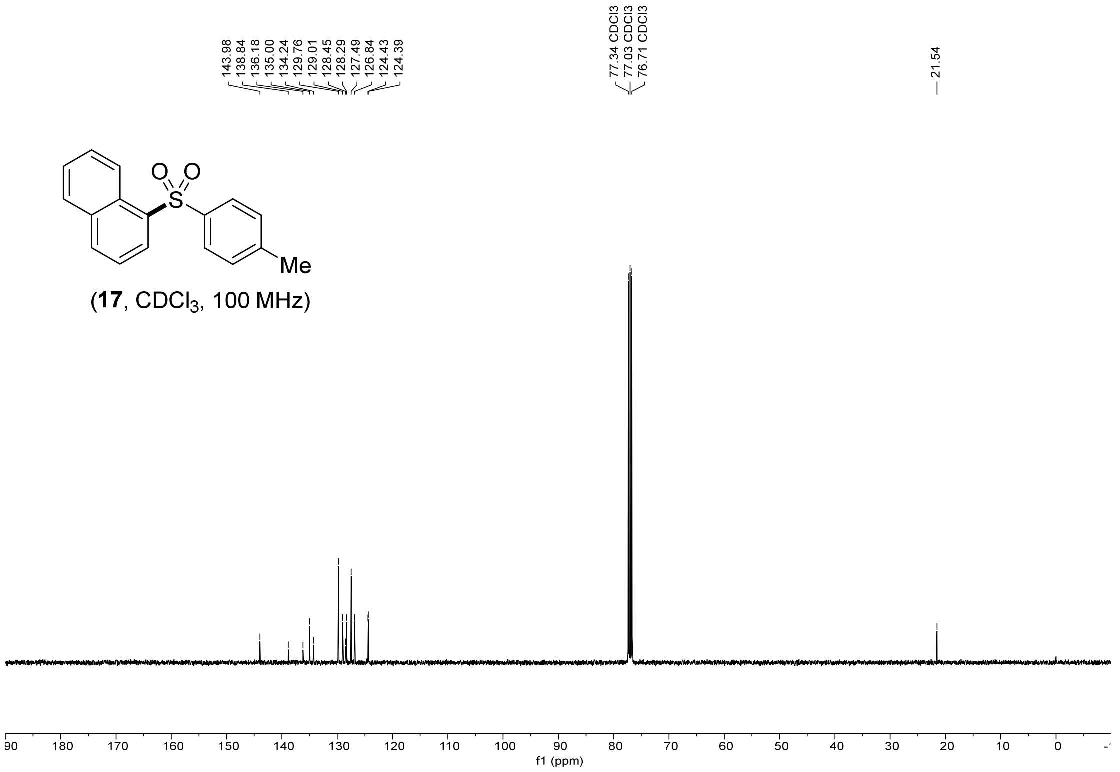


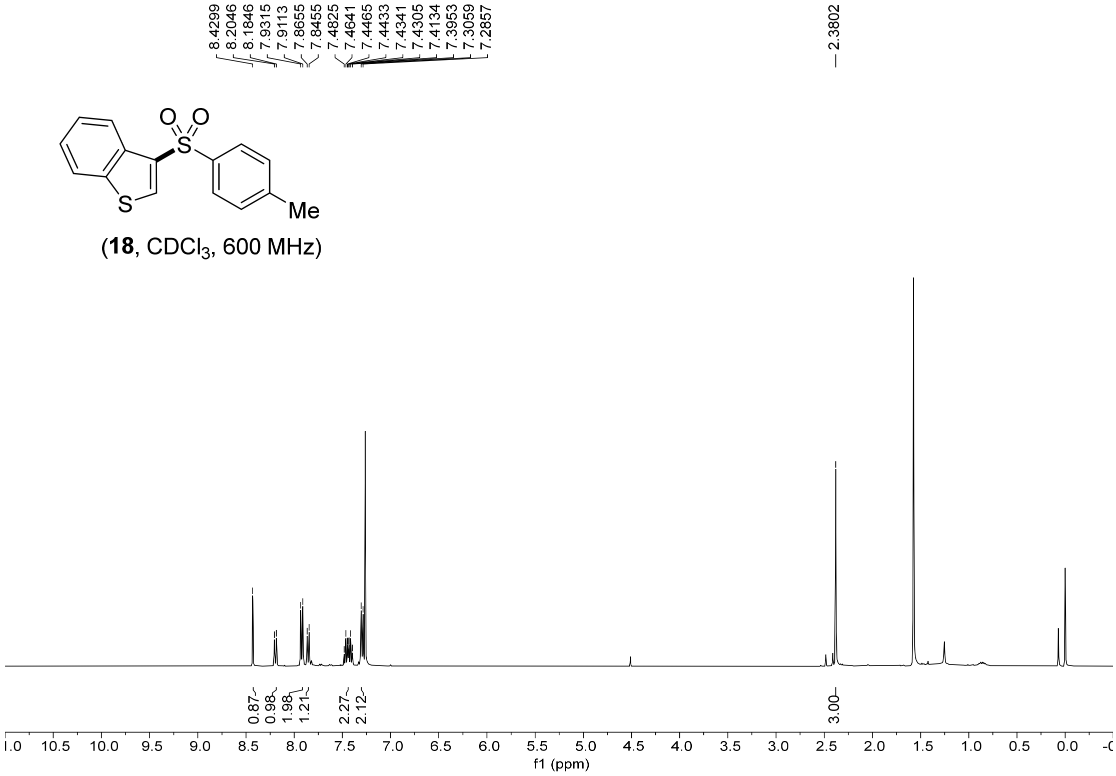
(**16,** $CDCl_3$, 400 MHz)

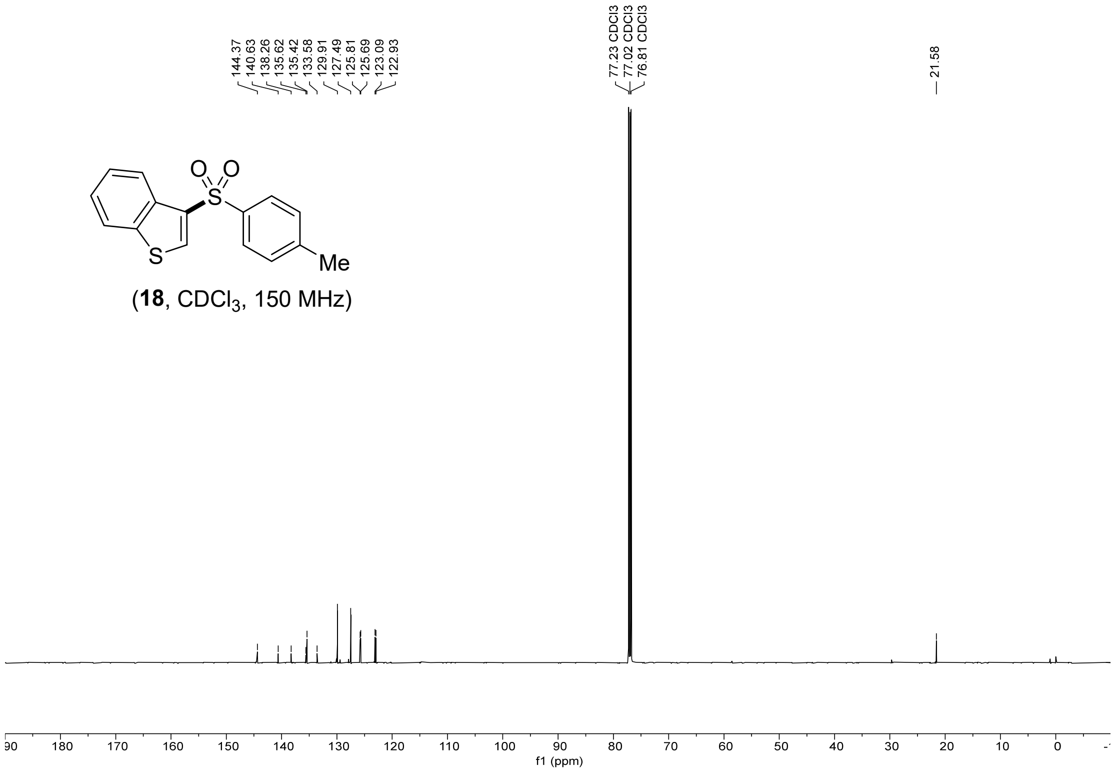


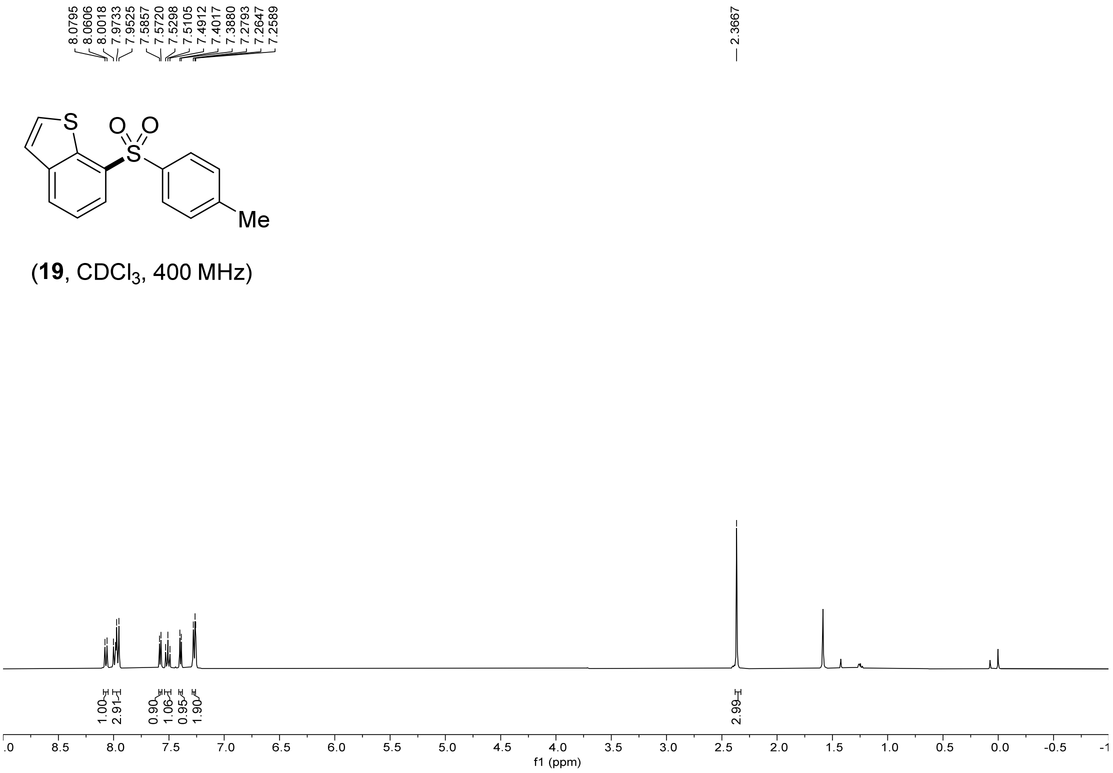
(**16,** $CDCl_3$, 100 MHz)


8.6474
8.6250
8.5106
8.4889
8.0931
8.0725
7.9054
7.8858
7.8634
7.8424
7.6304
7.6118
7.6099
7.6009
7.5971
7.5913
7.5836
7.5798
7.5756
7.5628
7.5584
7.5512
7.5474
7.5339
7.5308
7.5278
7.5136
7.5104
7.2693
7.2610
7.2490
2.3578
O
O
S
Me
(17, CDCl3, 400 MHz)
1.00
0.96
1.03
1.08
2.03
3.23
2.15
3.01
1.0
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
f1 (ppm)

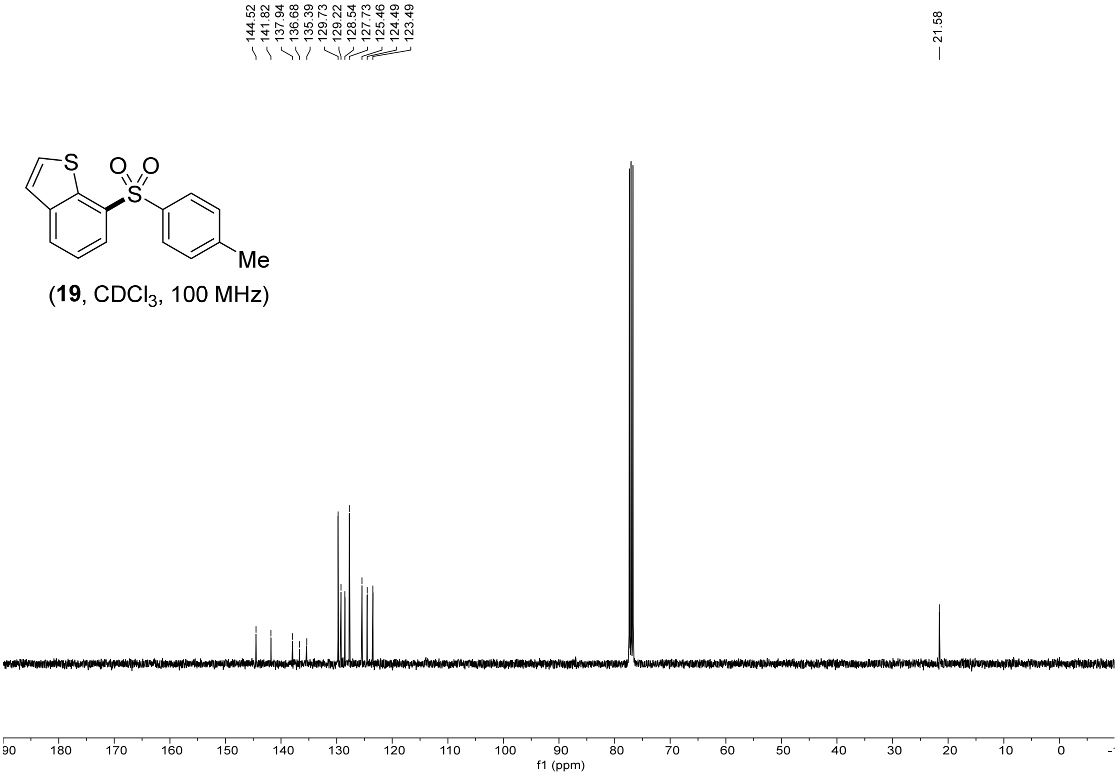

143.98
138.84
136.18
135.00
134.24
129.76
129.01
128.45
128.29
127.49
126.84
124.43
124.39
77.34 CDCl3
77.03 CDCl3
76.71 CDCl3
21.54
O
O
S
Me
(17, CDCl3, 100 MHz)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


(**18**, CDCl$_3$, 600 MHz)

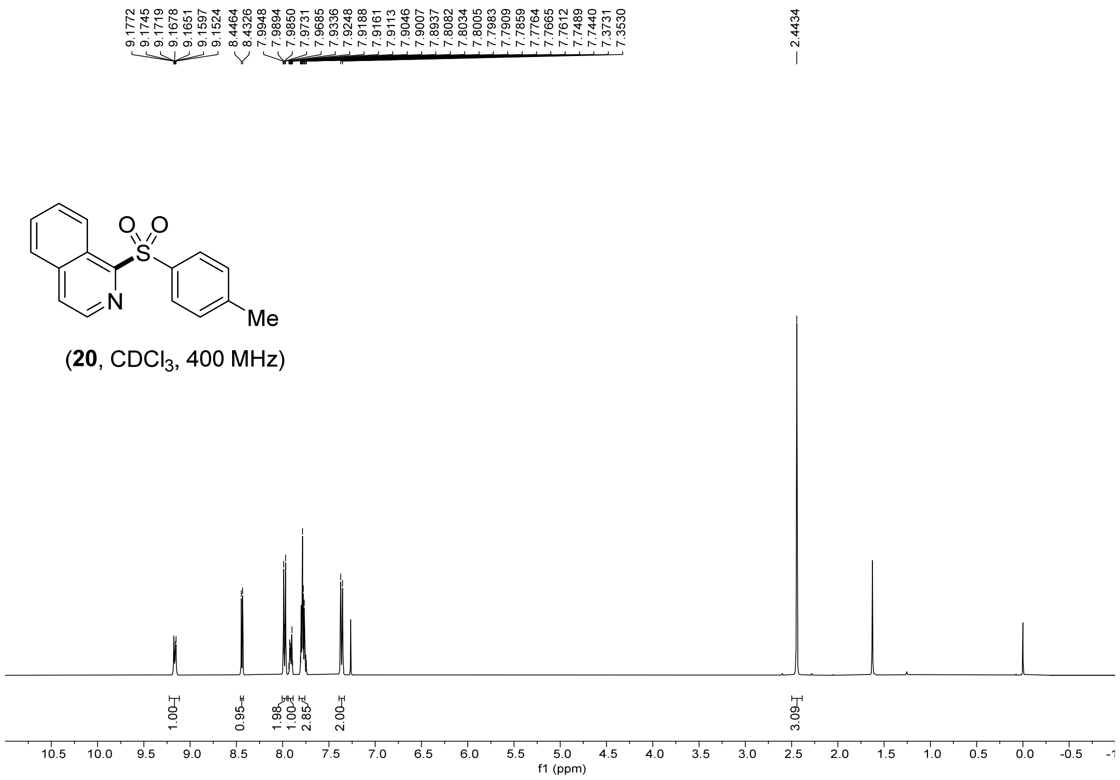

(**18**, CDCl$_3$, 150 MHz)

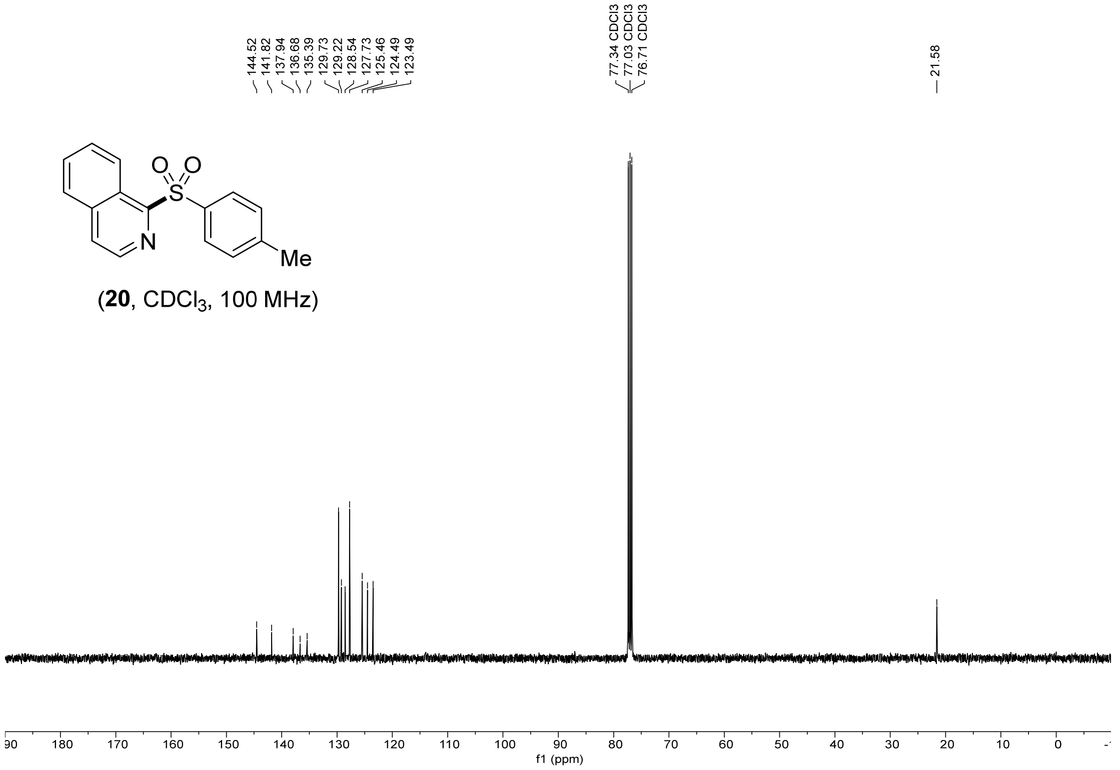


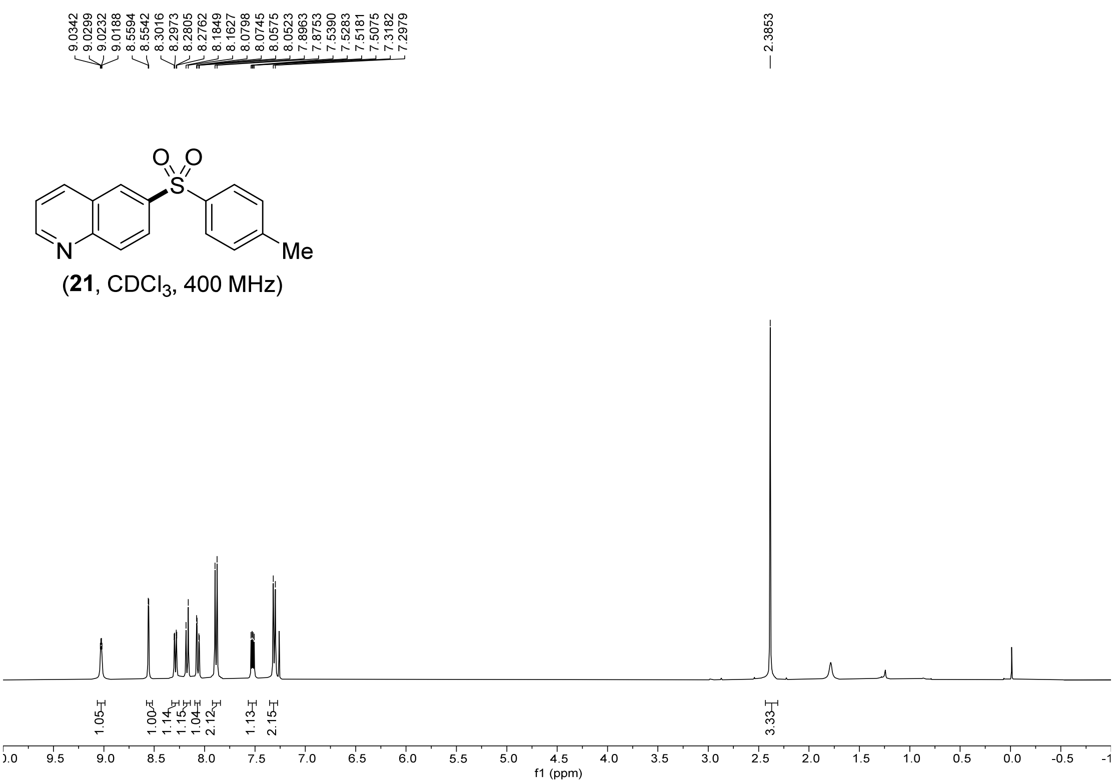
(**19**, $CDCl_3$, 400 MHz)

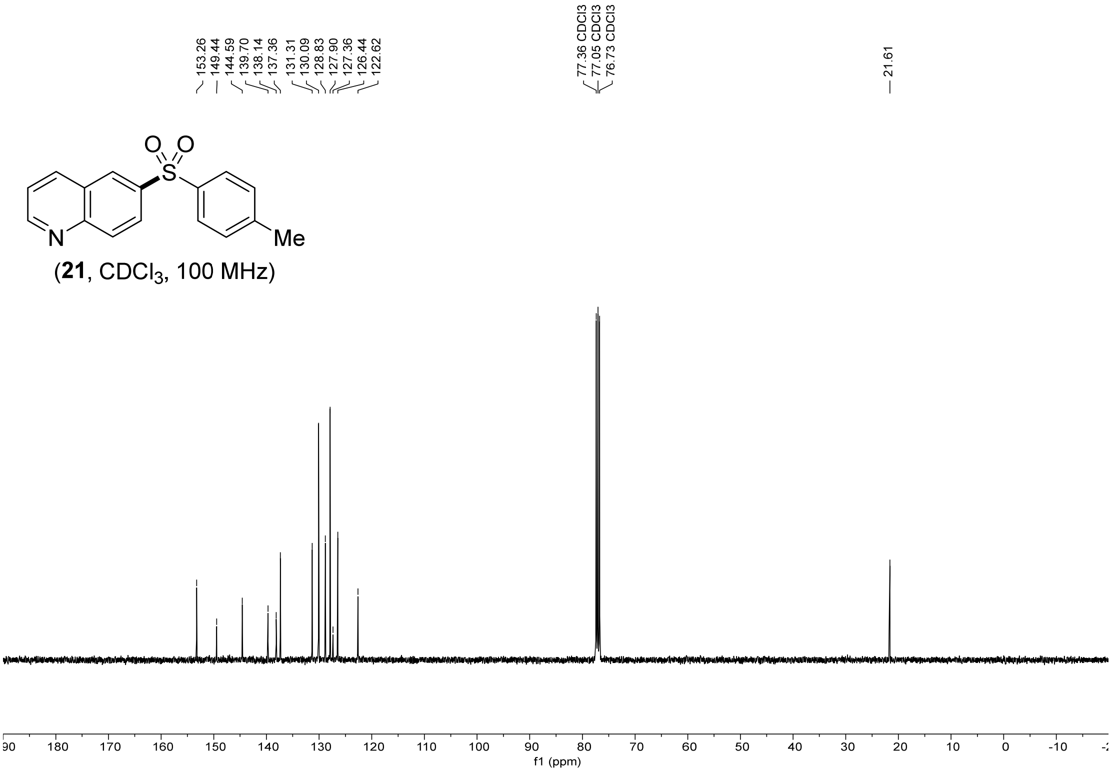


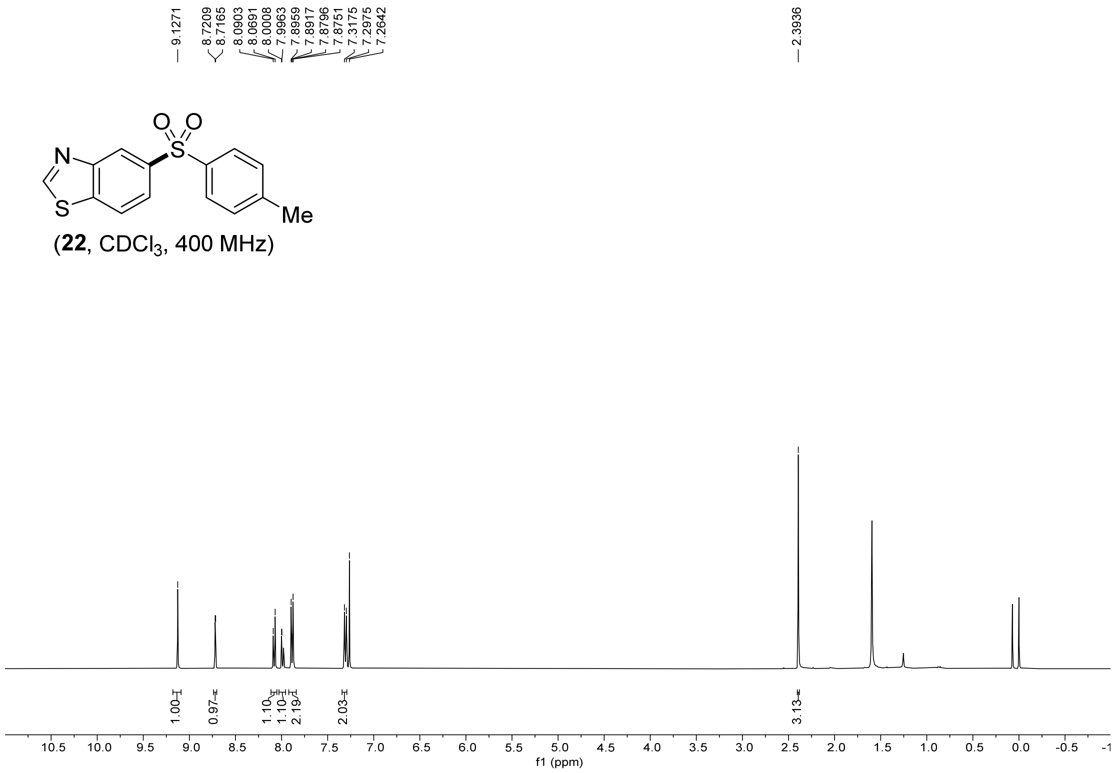
(**19**, $CDCl_3$, 100 MHz)


(**20**, CDCl$_3$, 400 MHz)

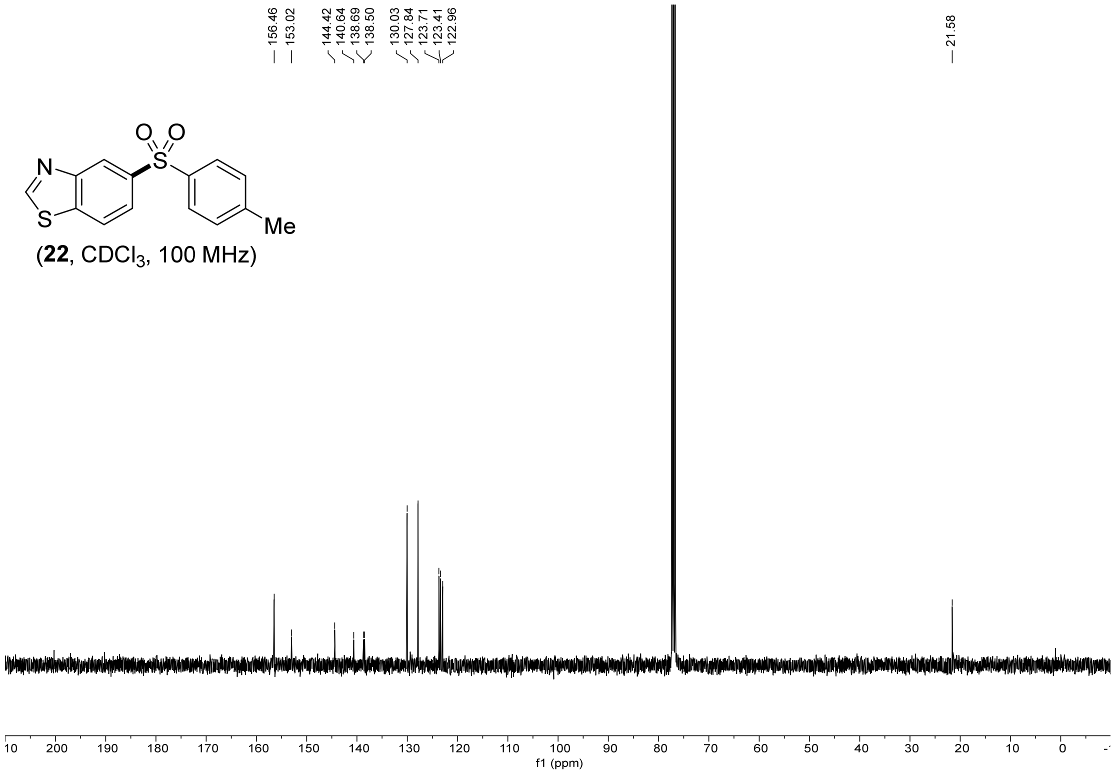

(**20**, CDCl$_3$, 100 MHz)


9.0342
9.0299
9.0232
9.0188
8.5594
8.5542
8.3016
8.2973
8.2805
8.2762
8.1849
8.1627
8.0798
8.0745
8.0575
8.0523
7.8963
7.8753
7.5390
7.5283
7.5181
7.5075
7.3182
7.2979
2.3853
O
O
S
N
Me
(21, CDCl3, 400 MHz)
1.05
1.00
1.14
1.15
1.04
2.12
1.13
2.15
3.33
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
-0.5
-1
f1 (ppm)

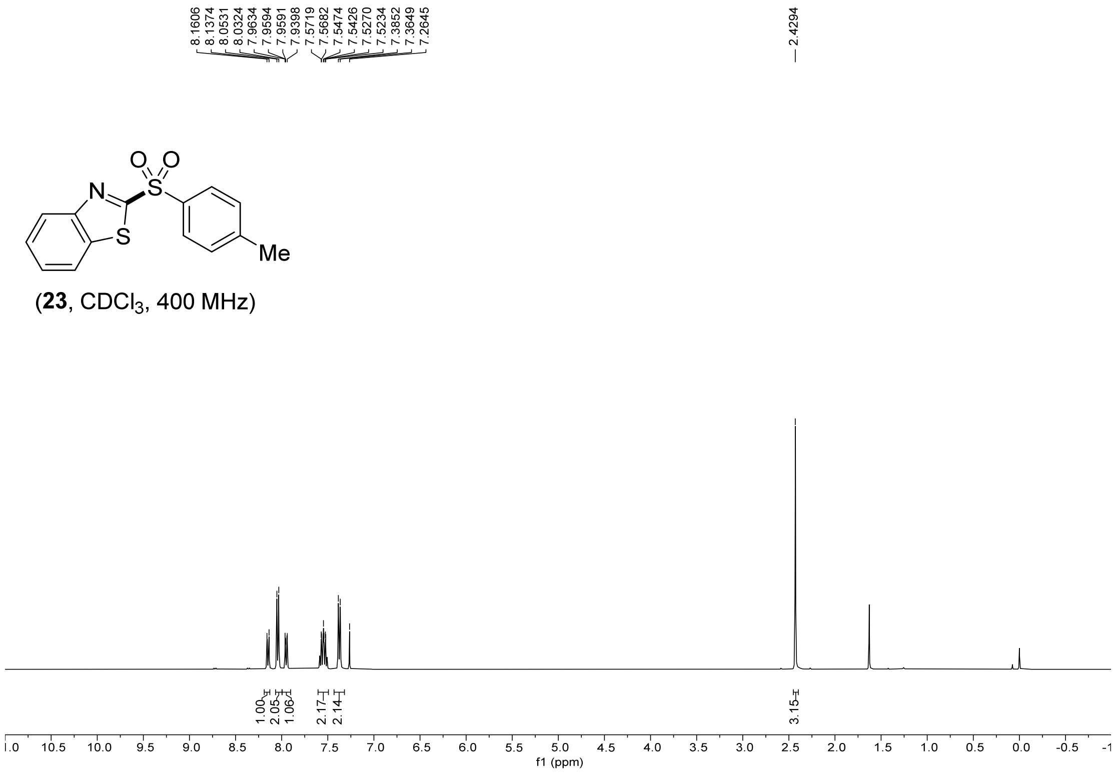

153.26
149.44
144.59
139.70
138.14
137.36
131.31
130.09
128.83
127.90
127.36
126.44
122.62
77.36 CDCl3
77.05 CDCl3
76.73 CDCl3
21.61
O
O
S
N
Me
(21, CDCl3, 100 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

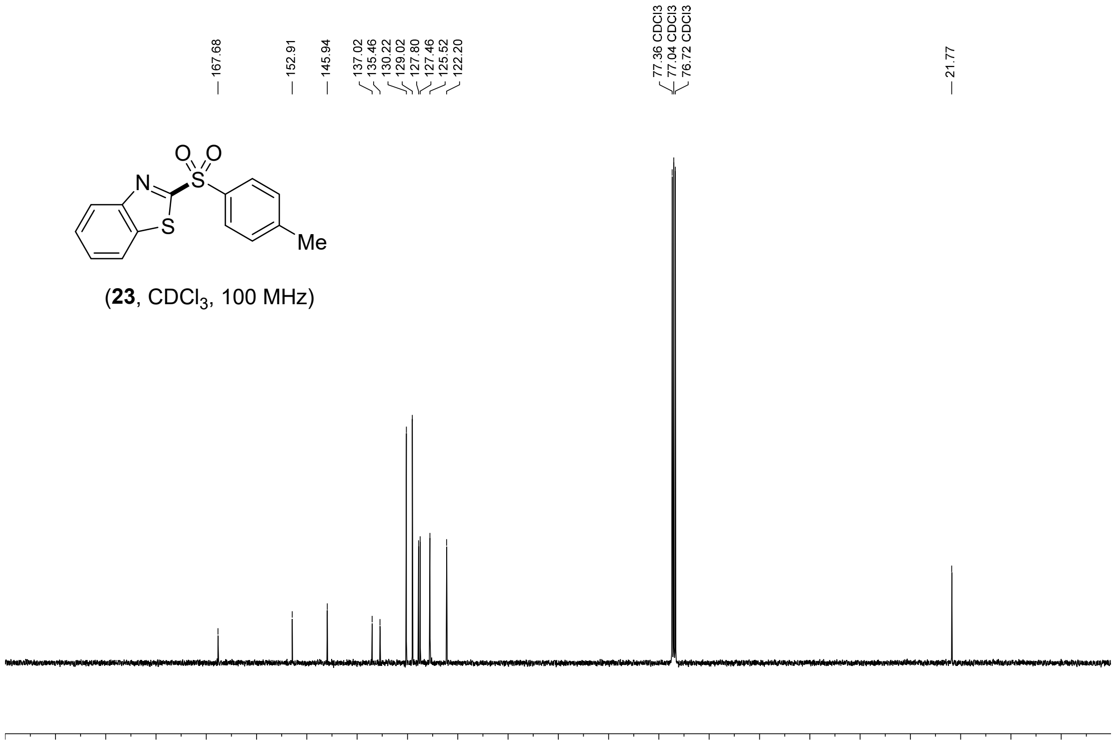


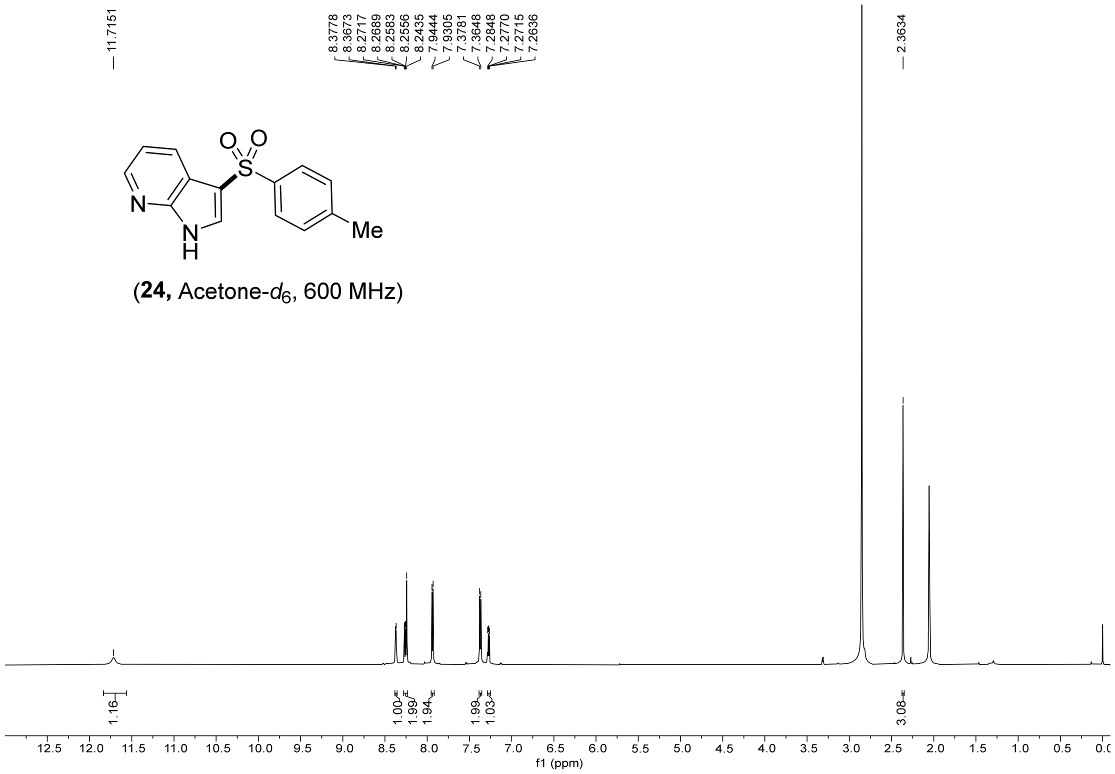
(**22**, CDCl$_3$, 400 MHz)



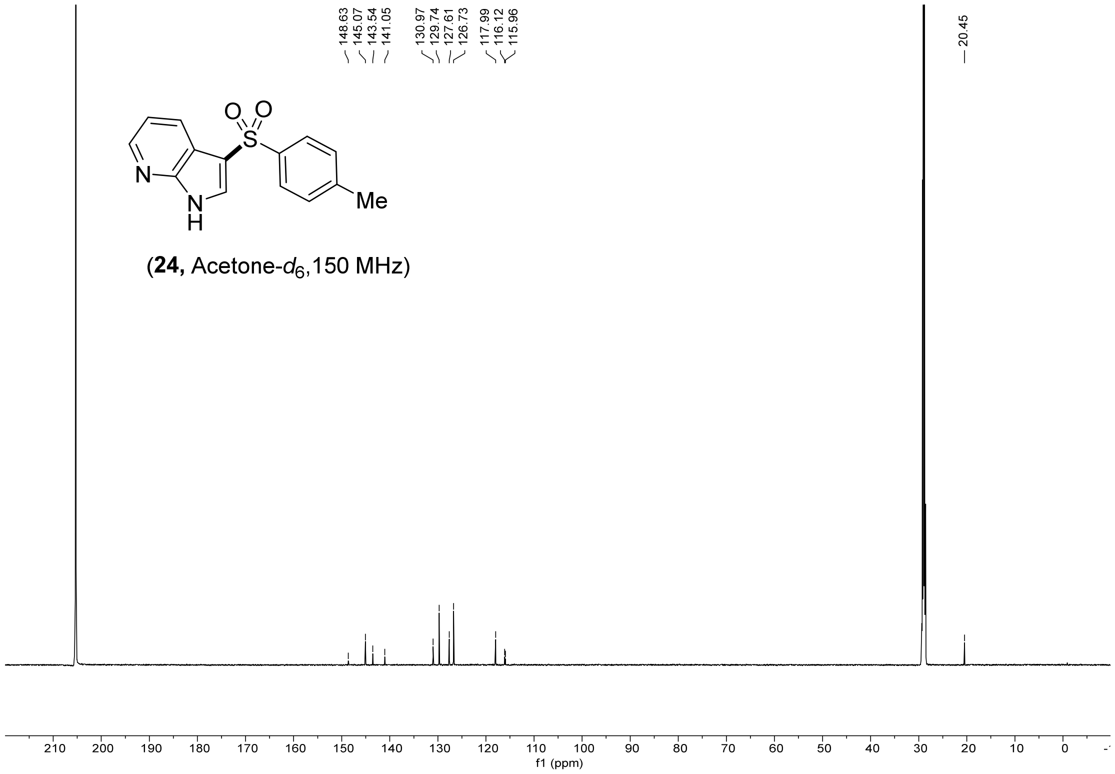
(**22**, CDCl$_3$, 100 MHz)


(**23**, $CDCl_3$, 400 MHz)

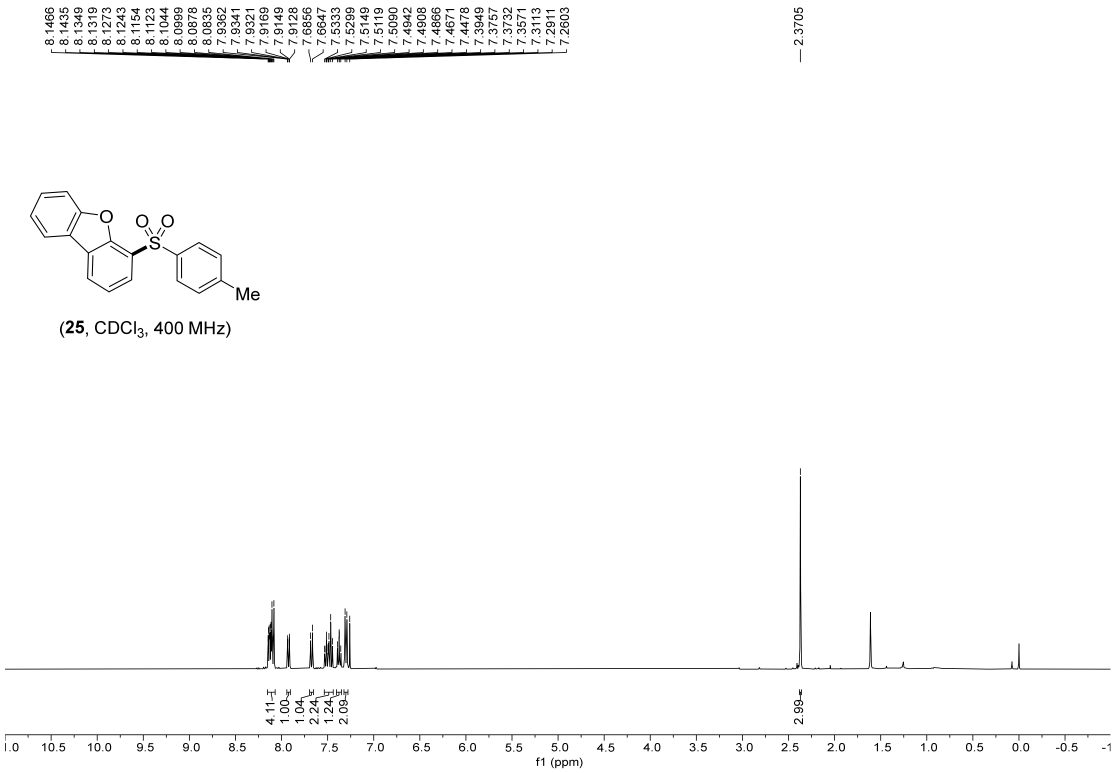

(**23**, $CDCl_3$, 100 MHz)



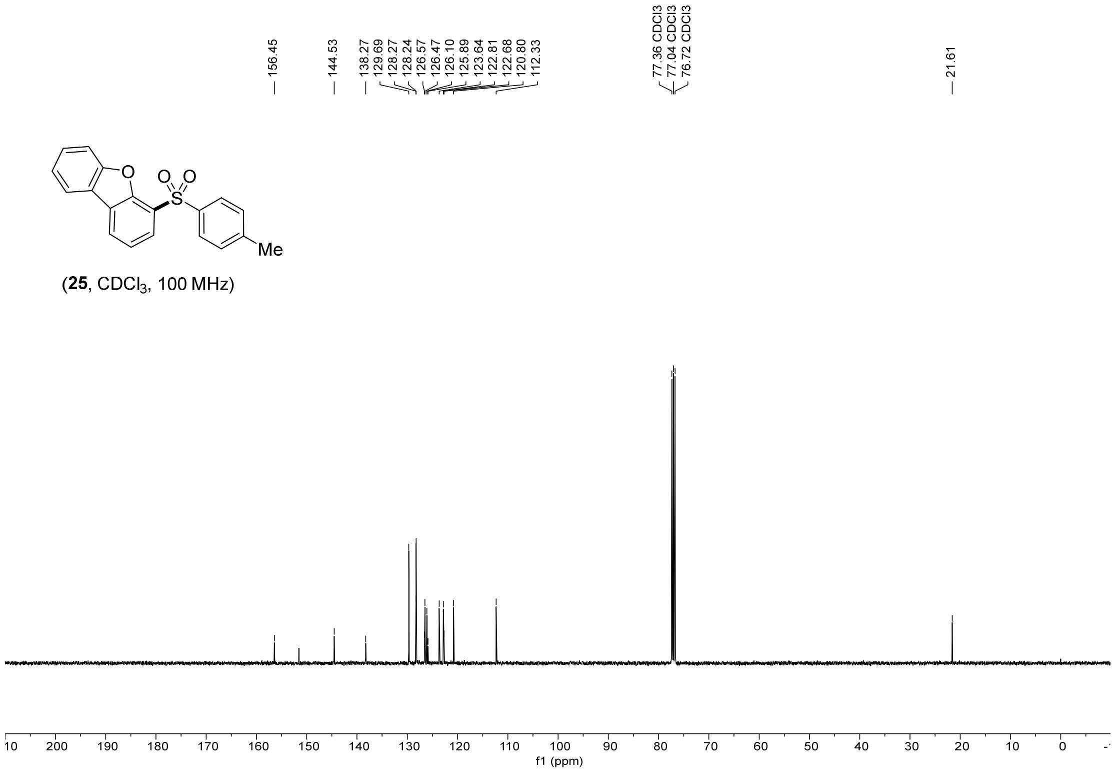
(**24,** Acetone-*d*$_6$, 600 MHz)



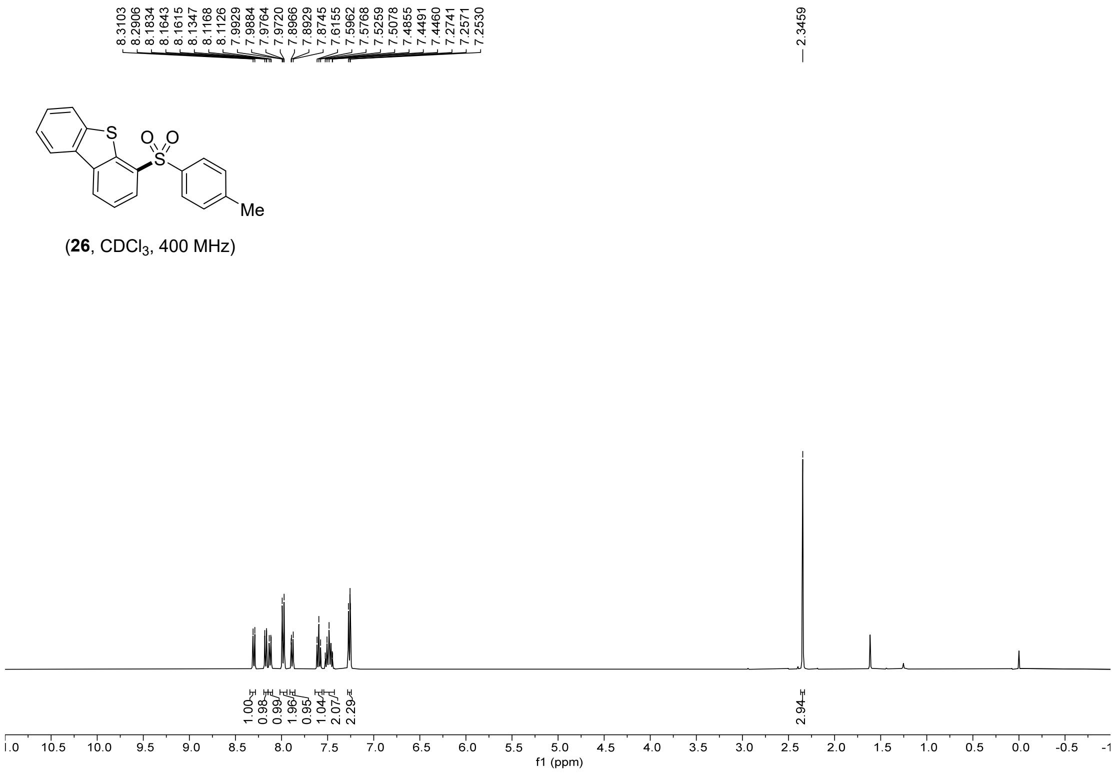
(**24,** Acetone-*d*$_6$,150 MHz)



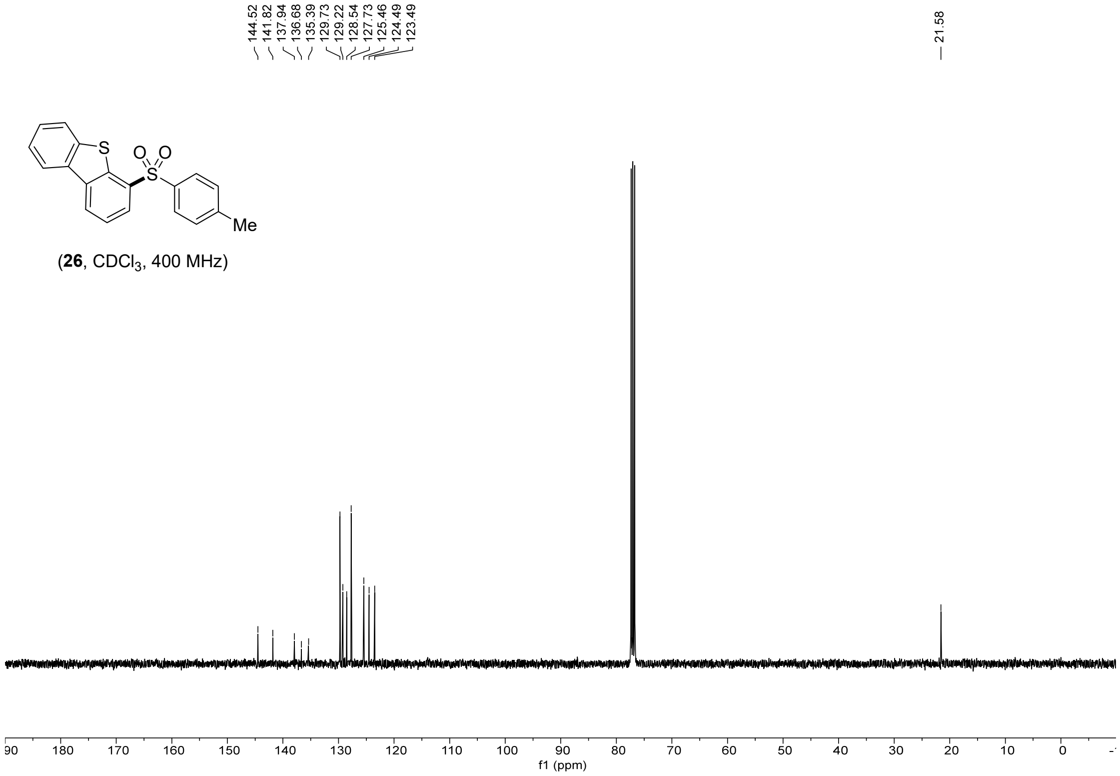
(**25**, $CDCl_3$, 400 MHz)



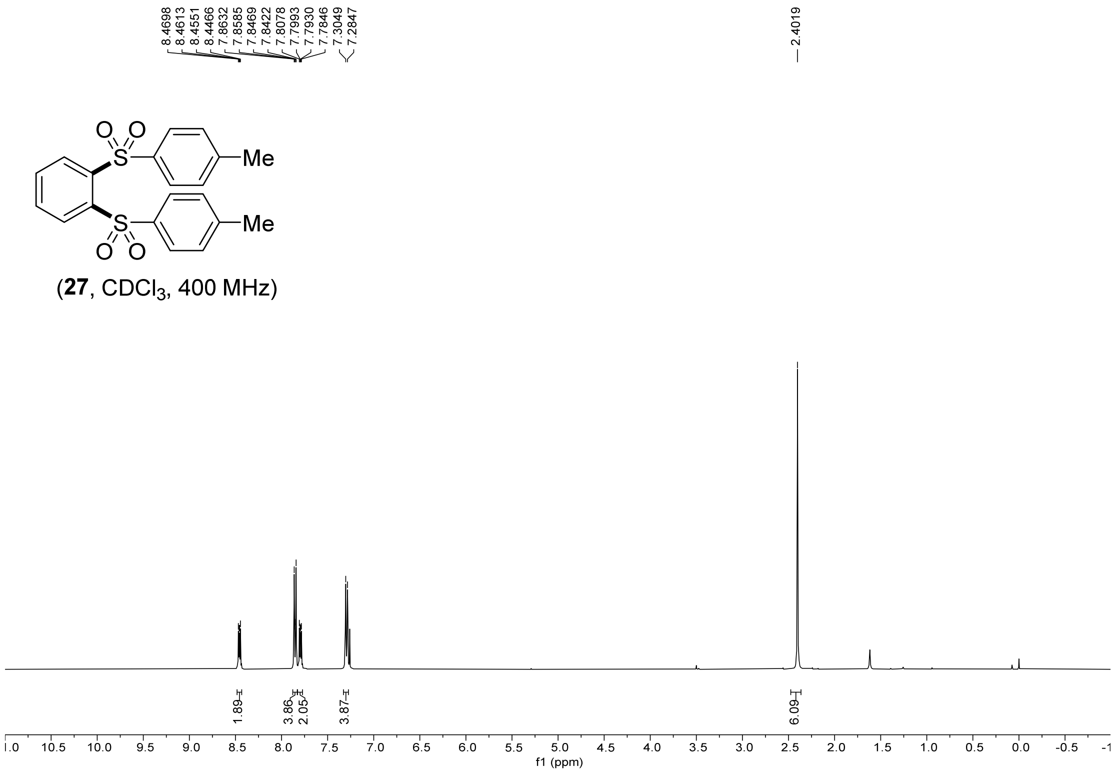
(**25**, $CDCl_3$, 100 MHz)

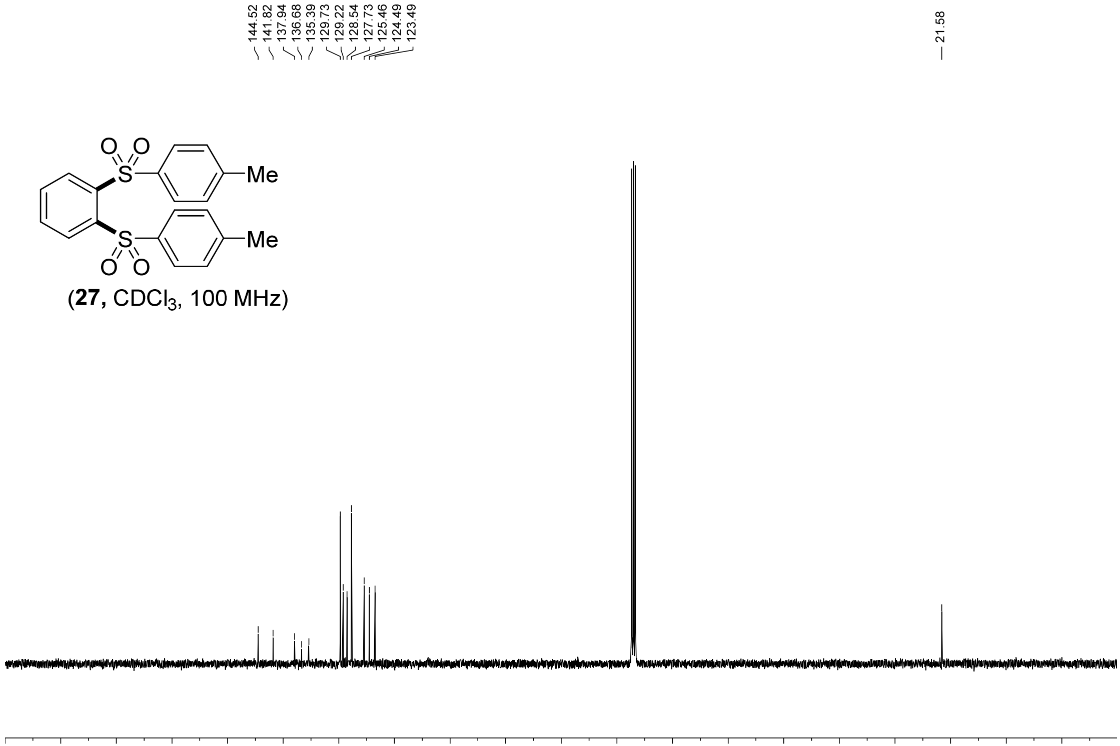


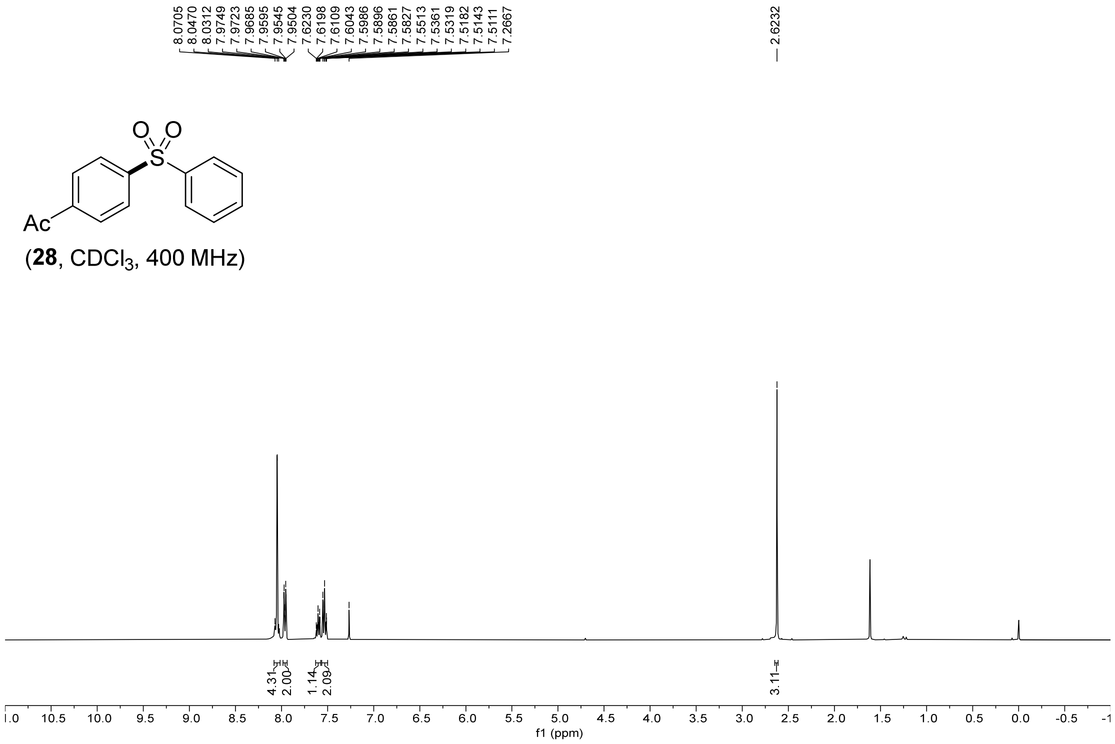
(**26**, CDCl$_3$, 400 MHz)

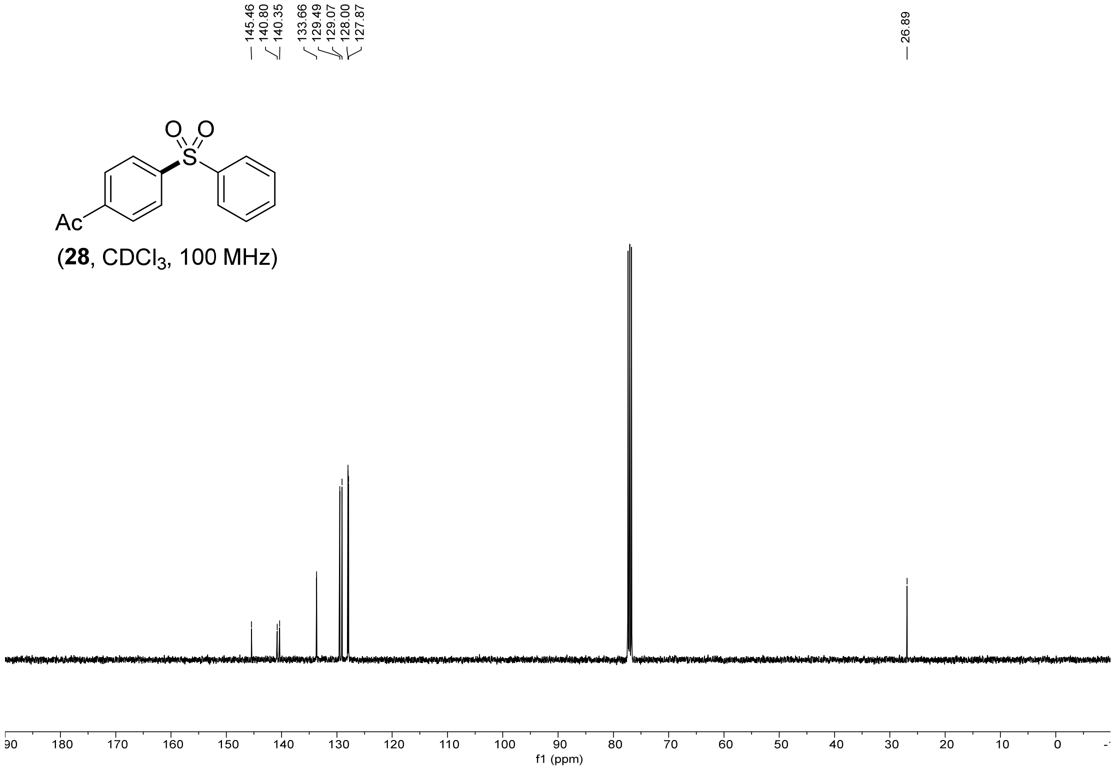


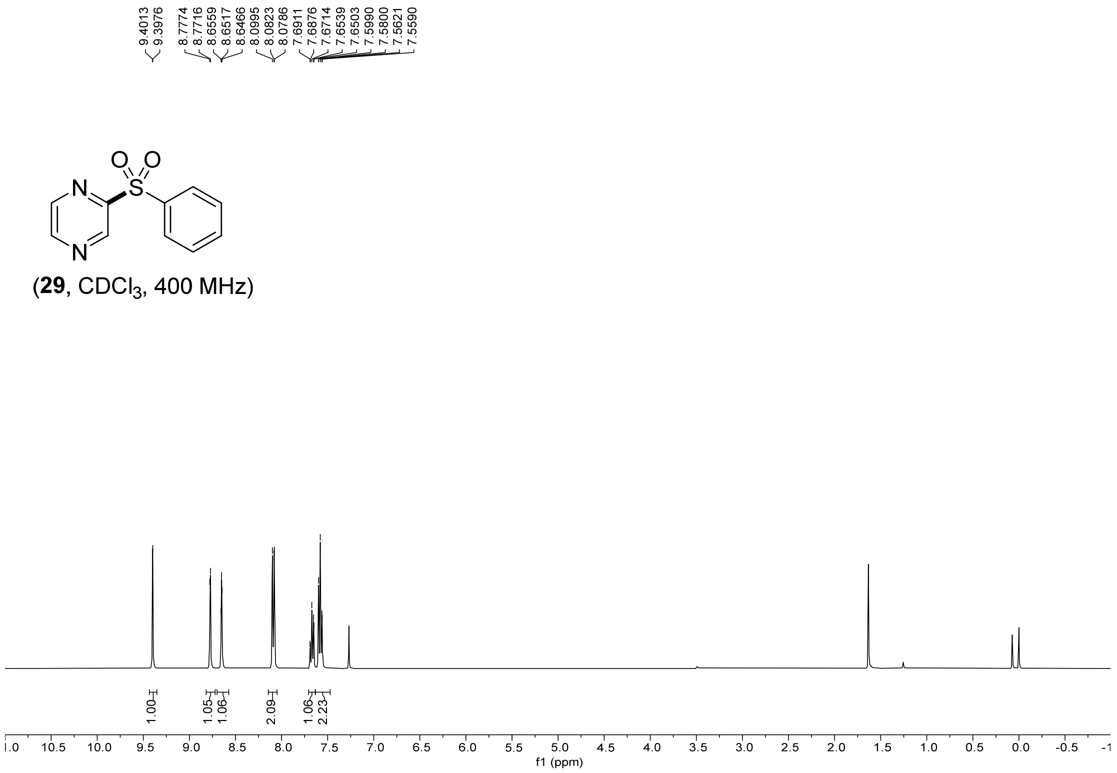
(**26**, CDCl$_3$, 400 MHz)


8.4698
8.4613
8.4551
8.4466
7.8632
7.8585
7.8469
7.8422
7.8078
7.7993
7.7930
7.7846
7.3049
7.2847
2.4019
Me
Me
(**27**, CDCl$_3$, 400 MHz)
1.89
3.86
2.05
3.87
6.09
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
-0.5
f1 (ppm)

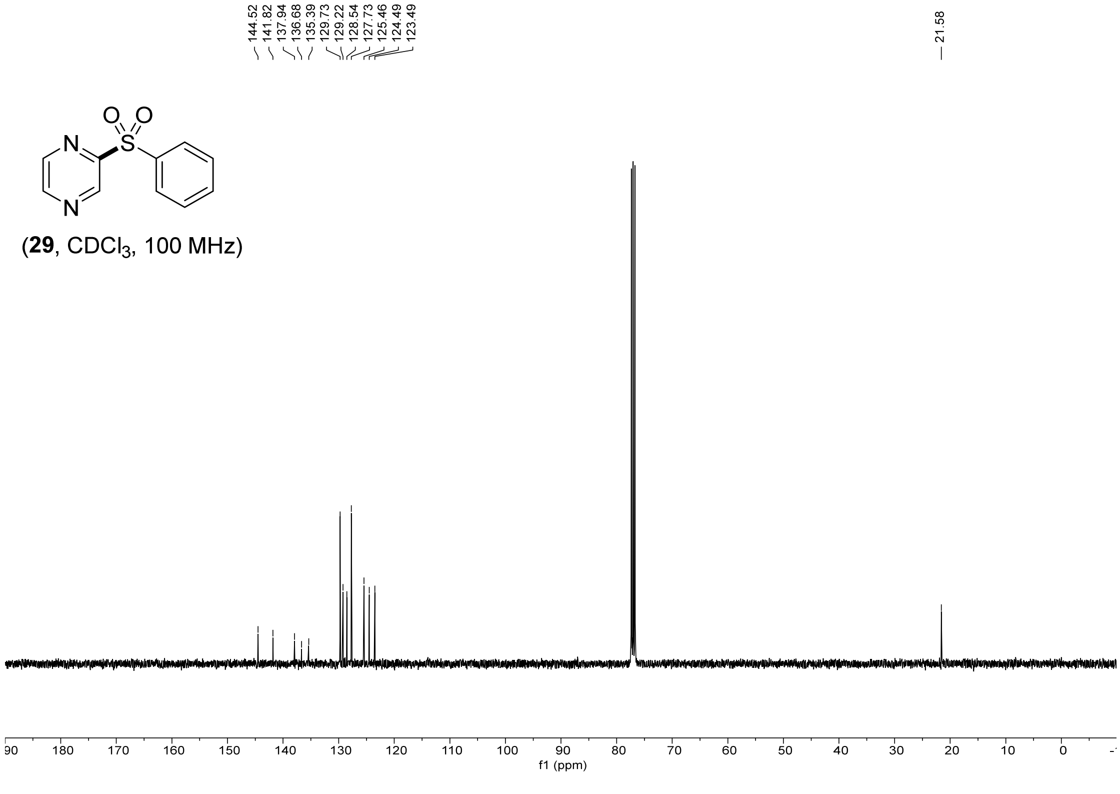

144.52
141.82
137.94
136.68
135.39
129.73
129.22
128.54
127.73
125.46
124.49
123.49
21.58
Me
Me
(**27,** CDCl$_3$, 100 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


(**28**, $CDCl_3$, 400 MHz)

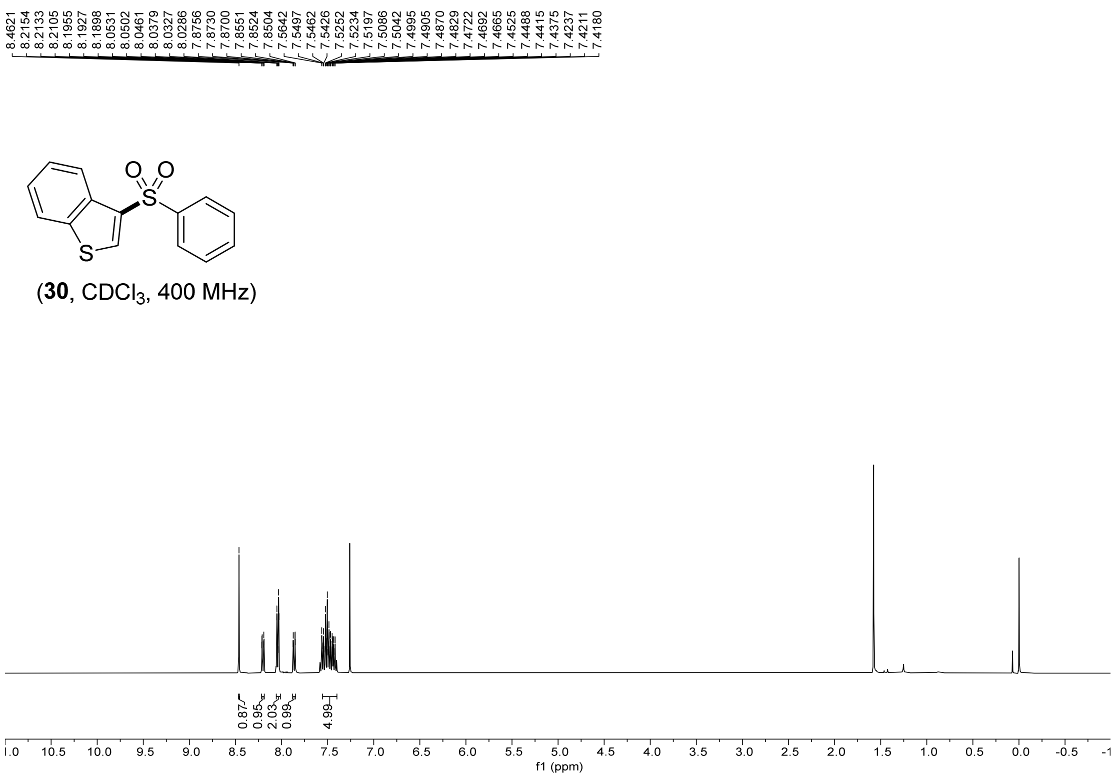

(**28**, $CDCl_3$, 100 MHz)



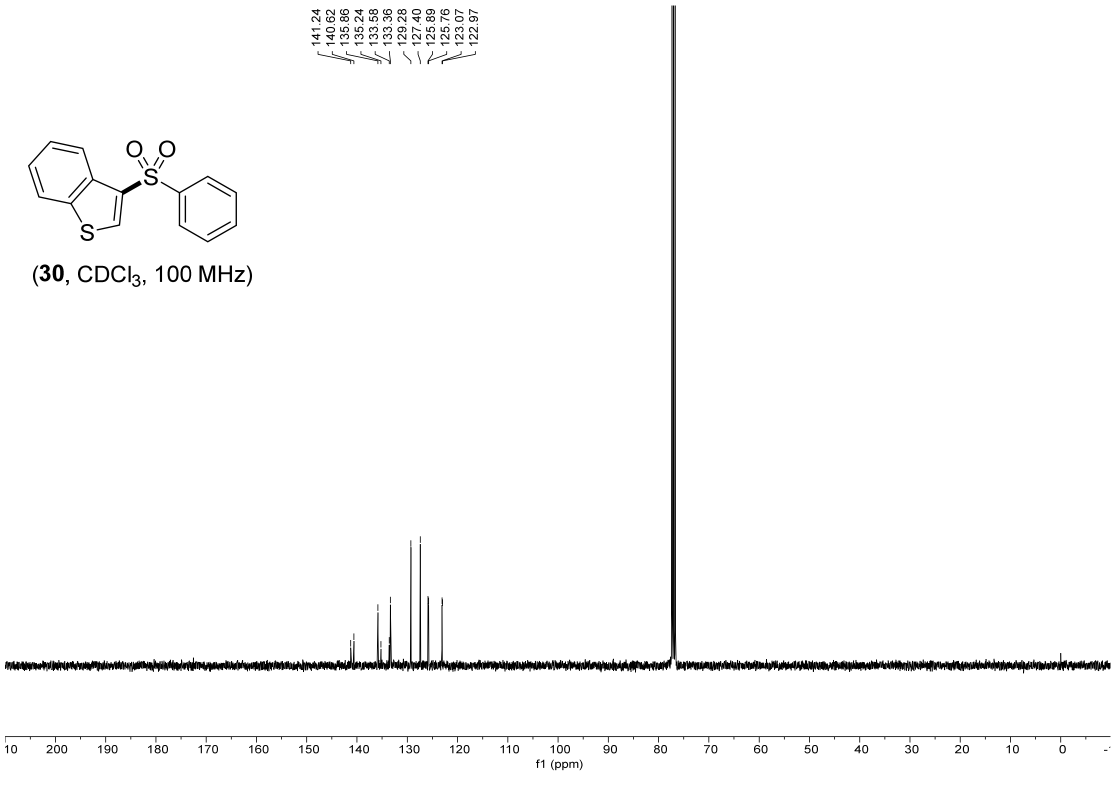
(**29**, CDCl$_3$, 400 MHz)



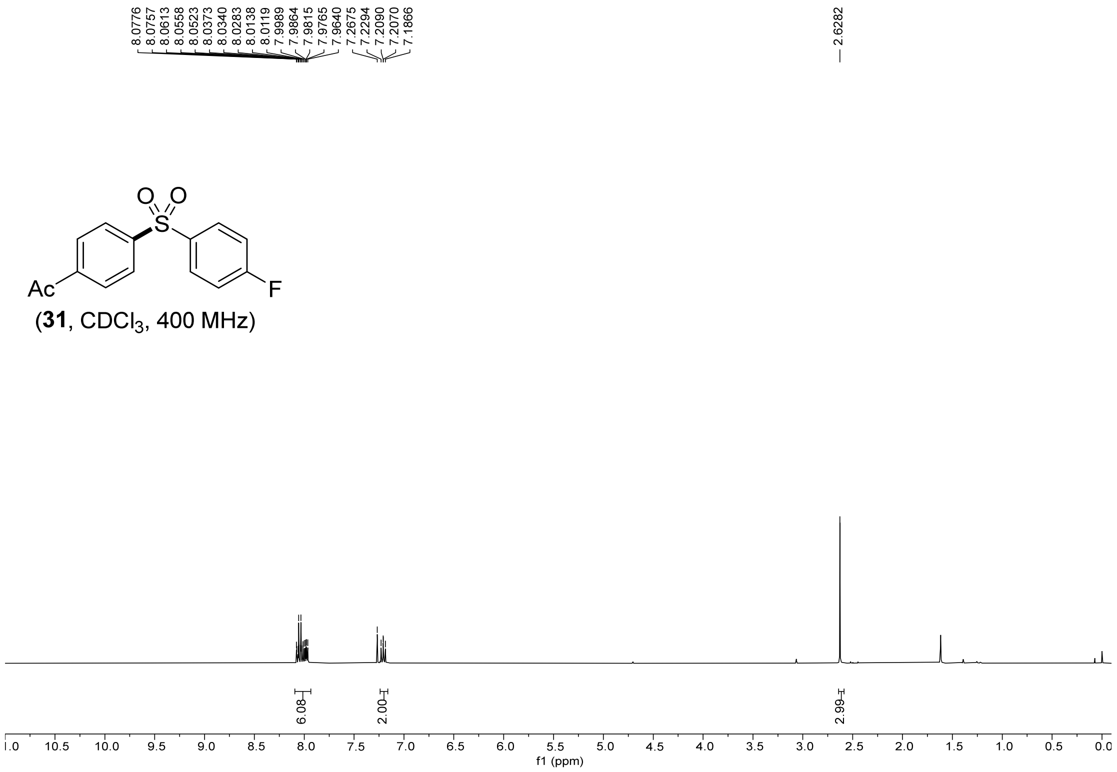
(**29**, CDCl$_3$, 100 MHz)



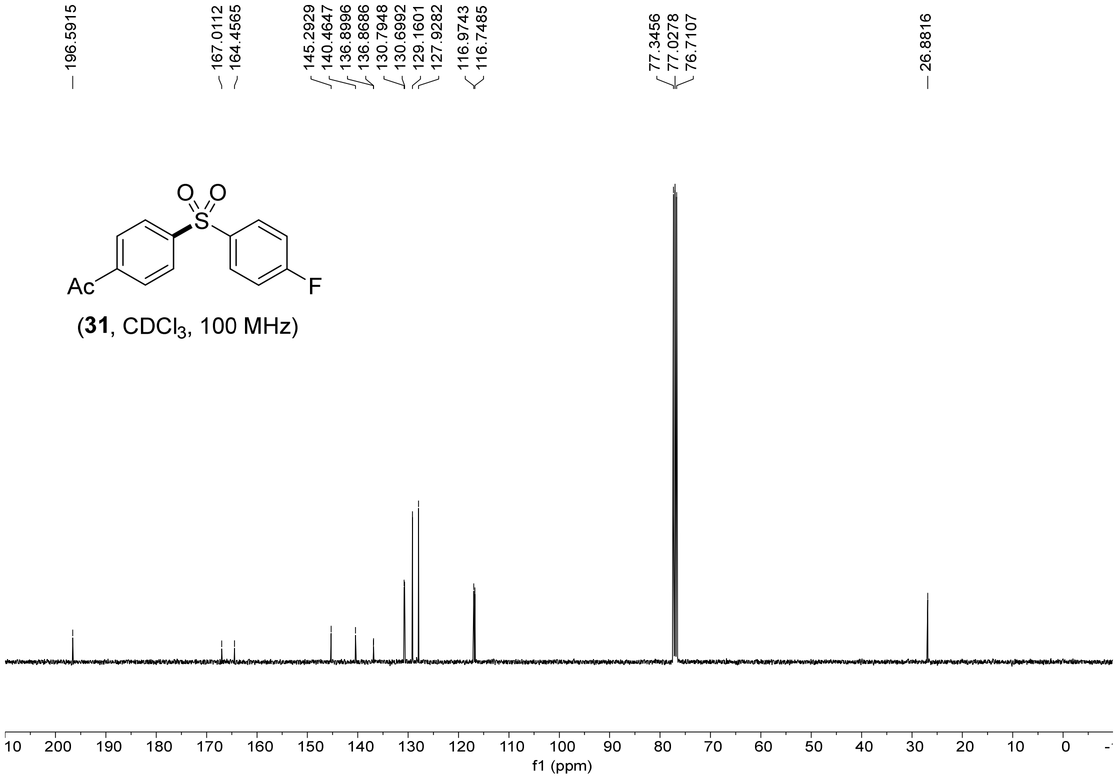
(**30**, CDCl$_3$, 400 MHz)



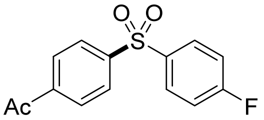
(**30**, CDCl$_3$, 100 MHz)



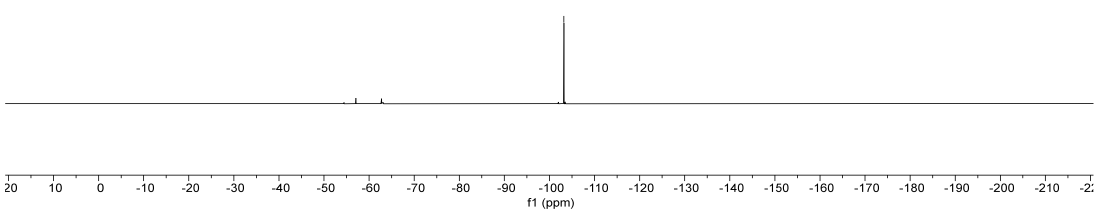
(**31**, $CDCl_3$, 400 MHz)

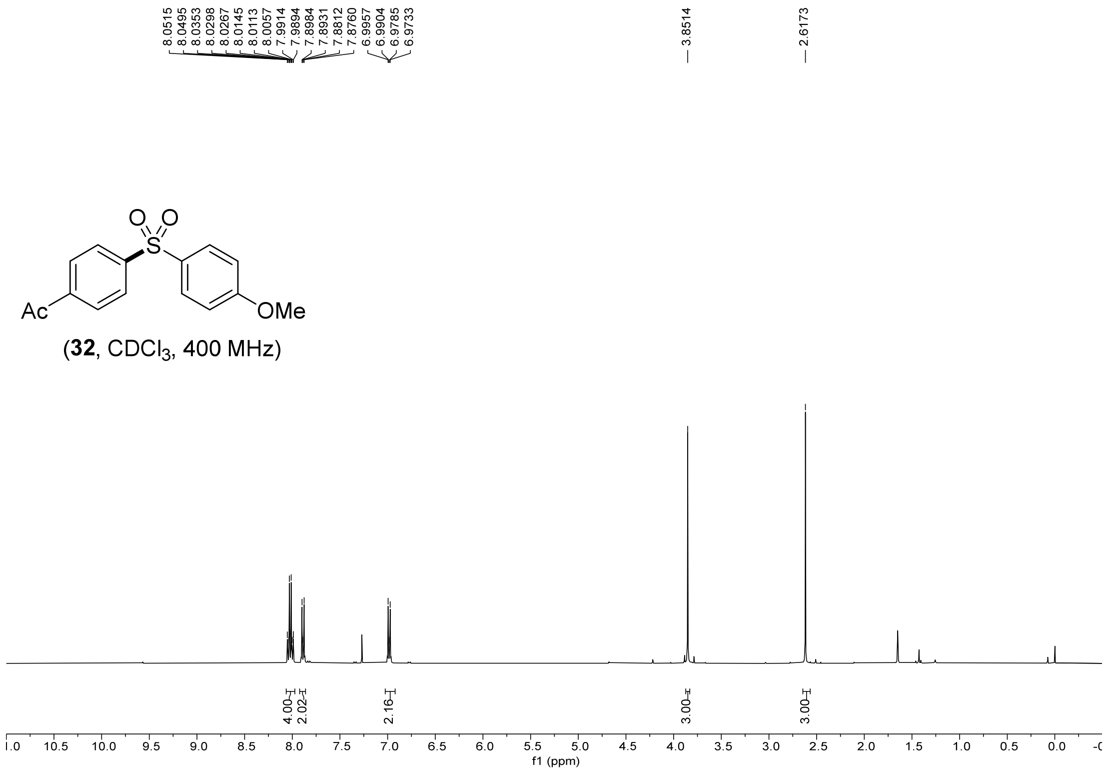


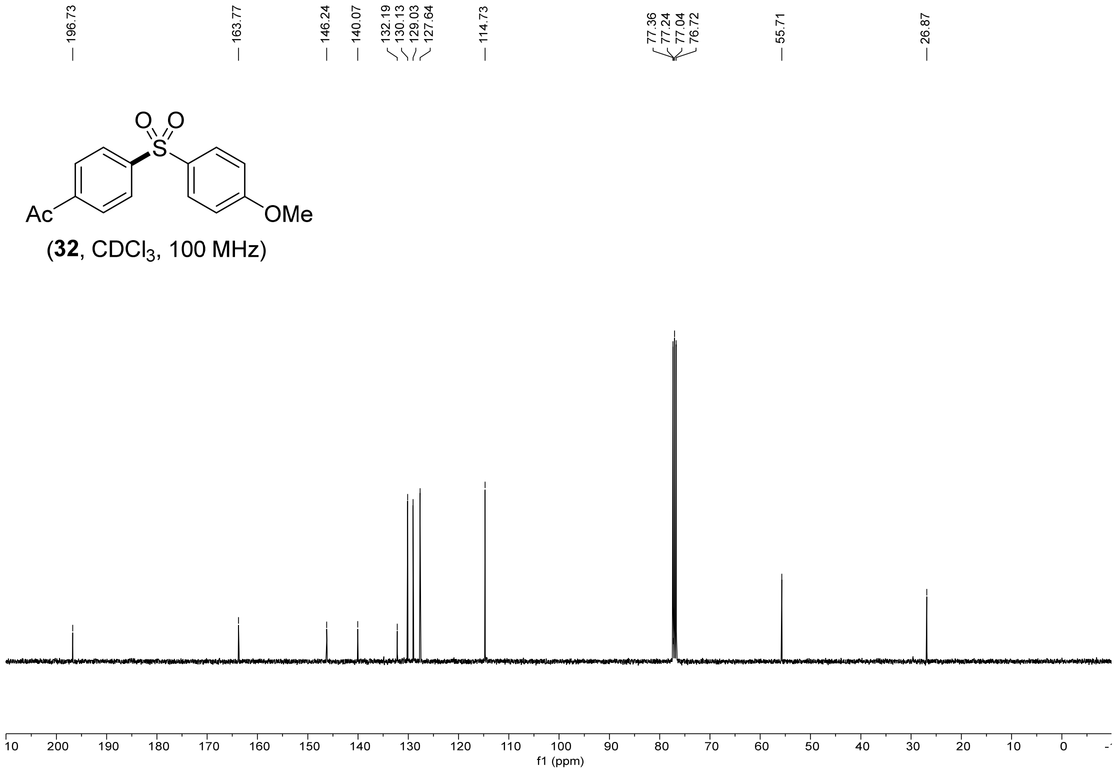
(**31**, $CDCl_3$, 100 MHz)

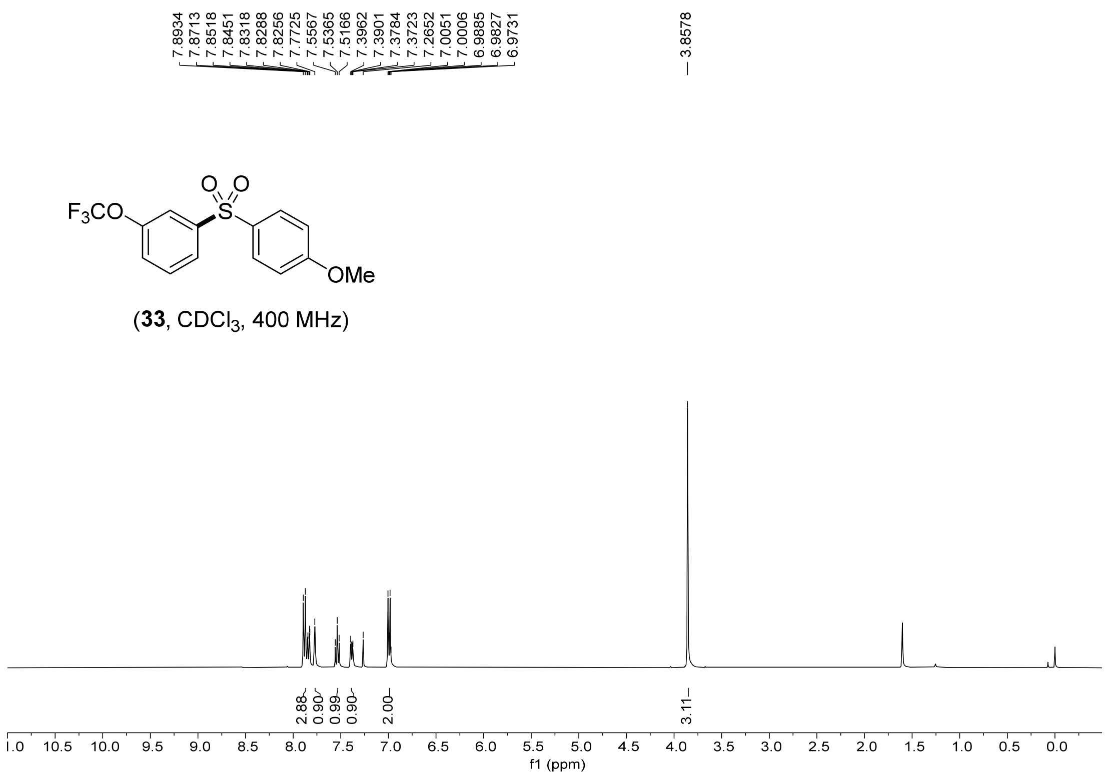


(**31**, $CDCl_3$, 376 MHz)

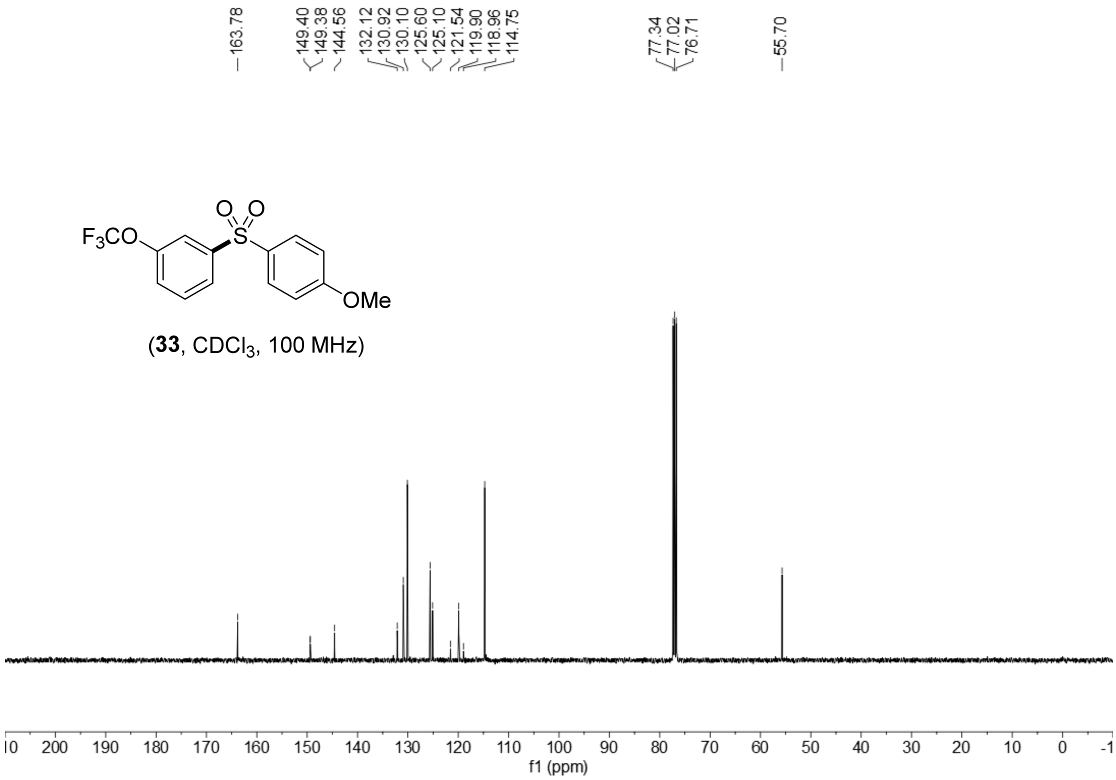



(**32**, $CDCl_3$, 400 MHz)

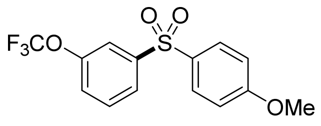

(**32**, $CDCl_3$, 100 MHz)



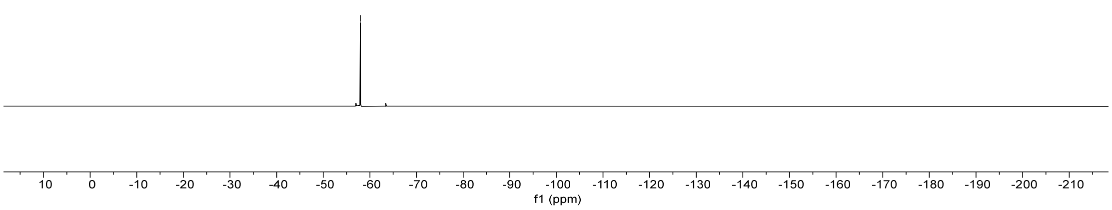
(**33**, $CDCl_3$, 400 MHz)

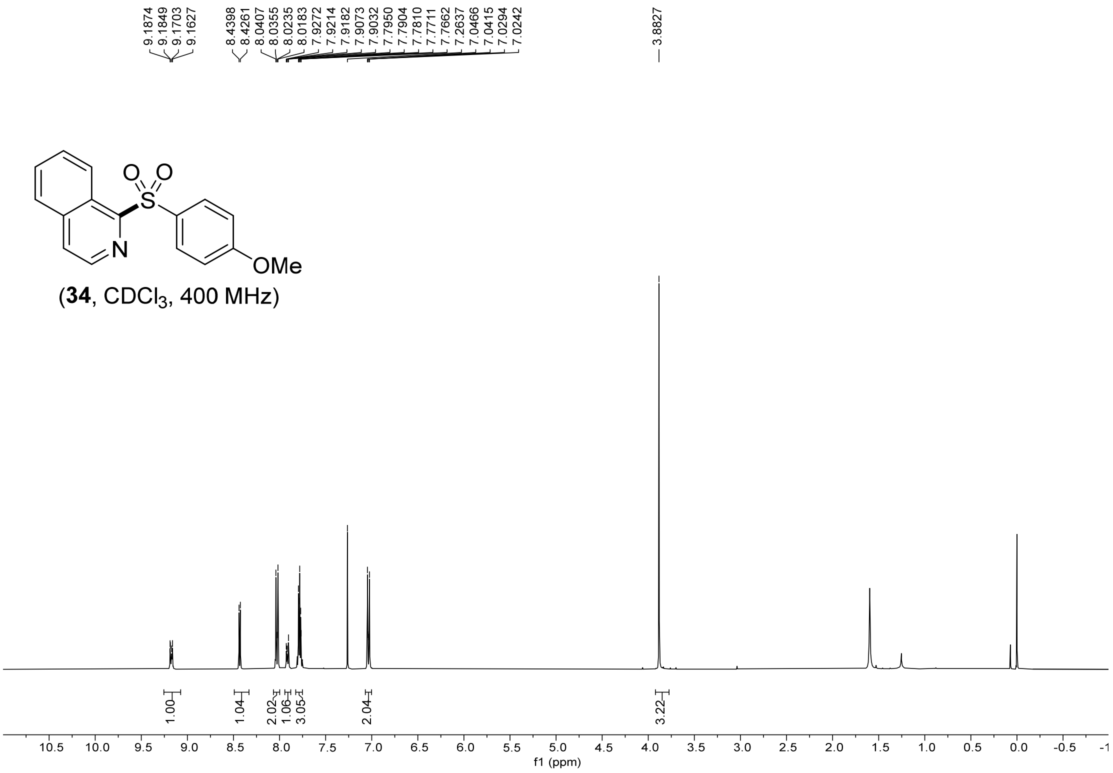


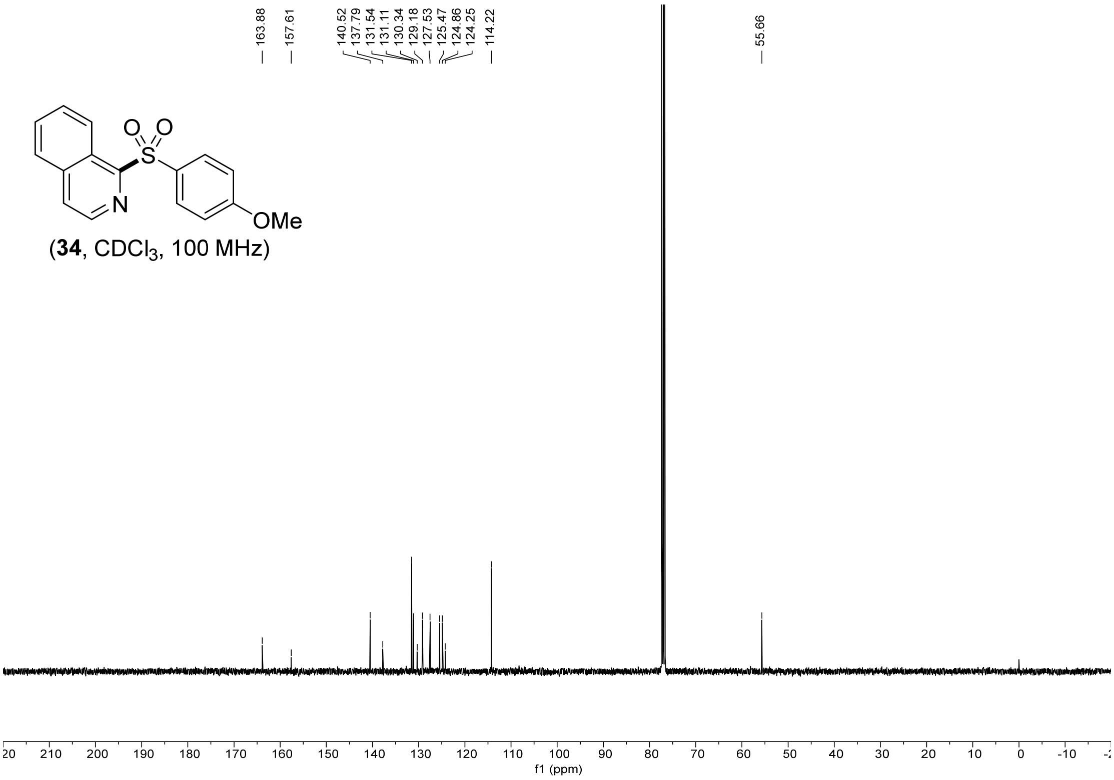
(**33**, $CDCl_3$, 100 MHz)

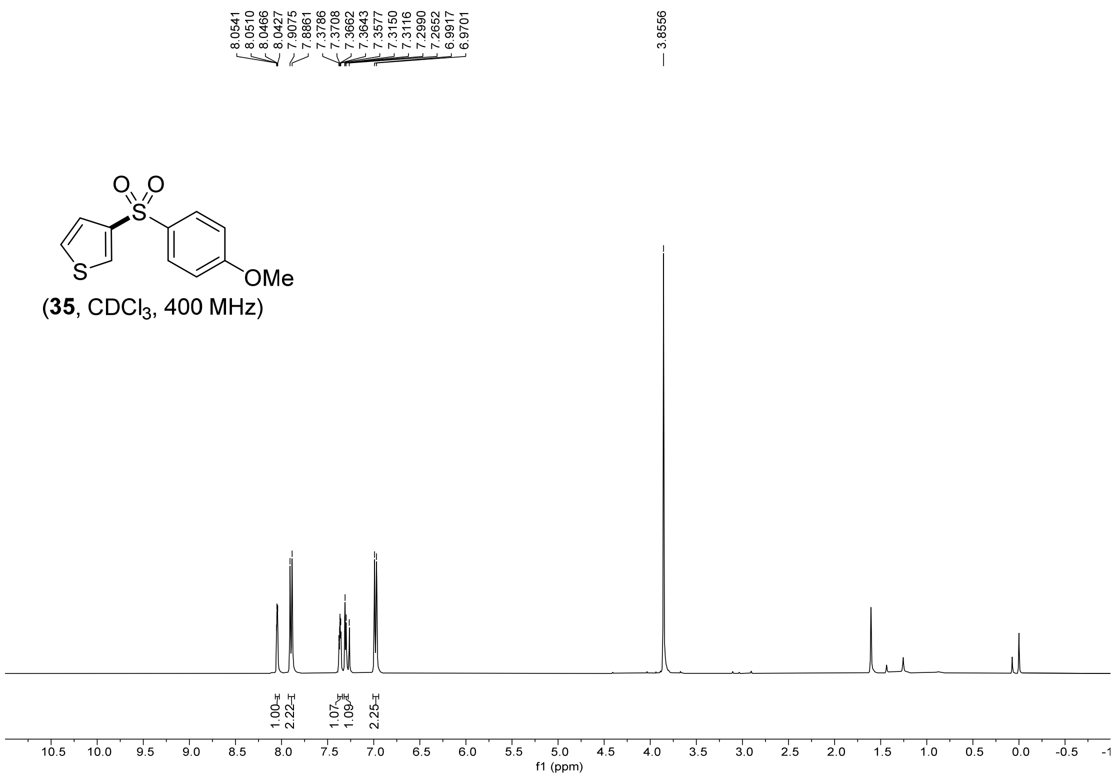


(**33**, $CDCl_3$, 376 MHz)

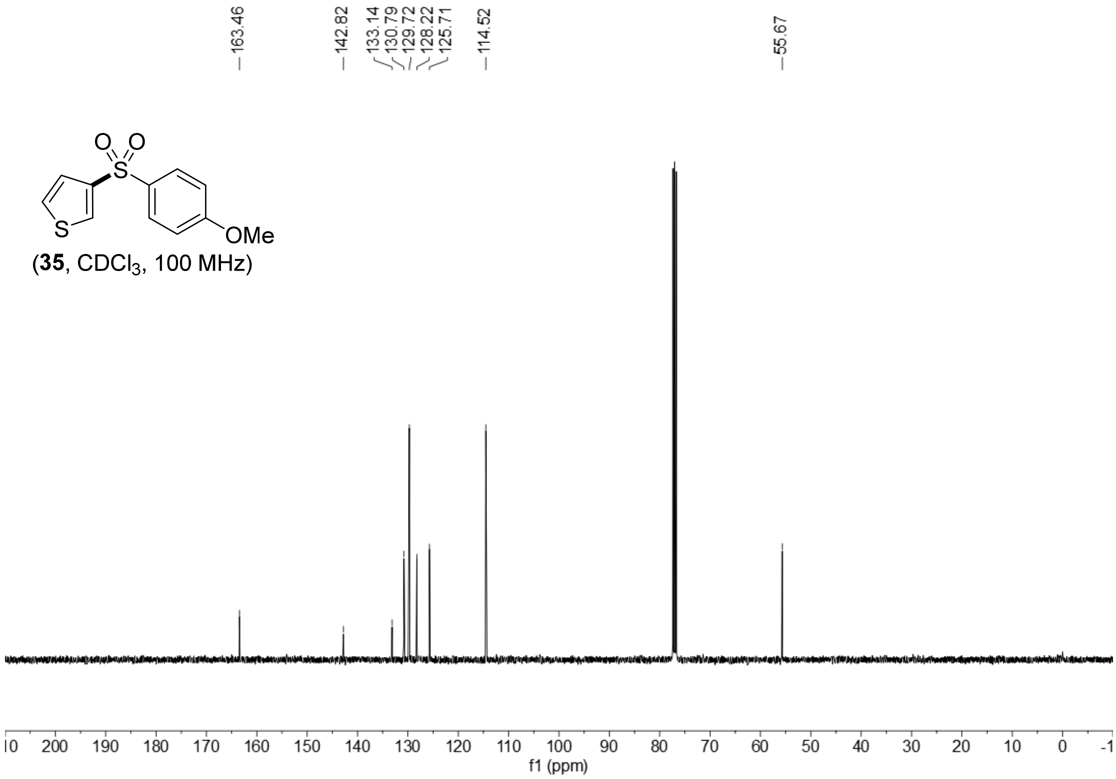



(**34**, $CDCl_3$, 400 MHz)

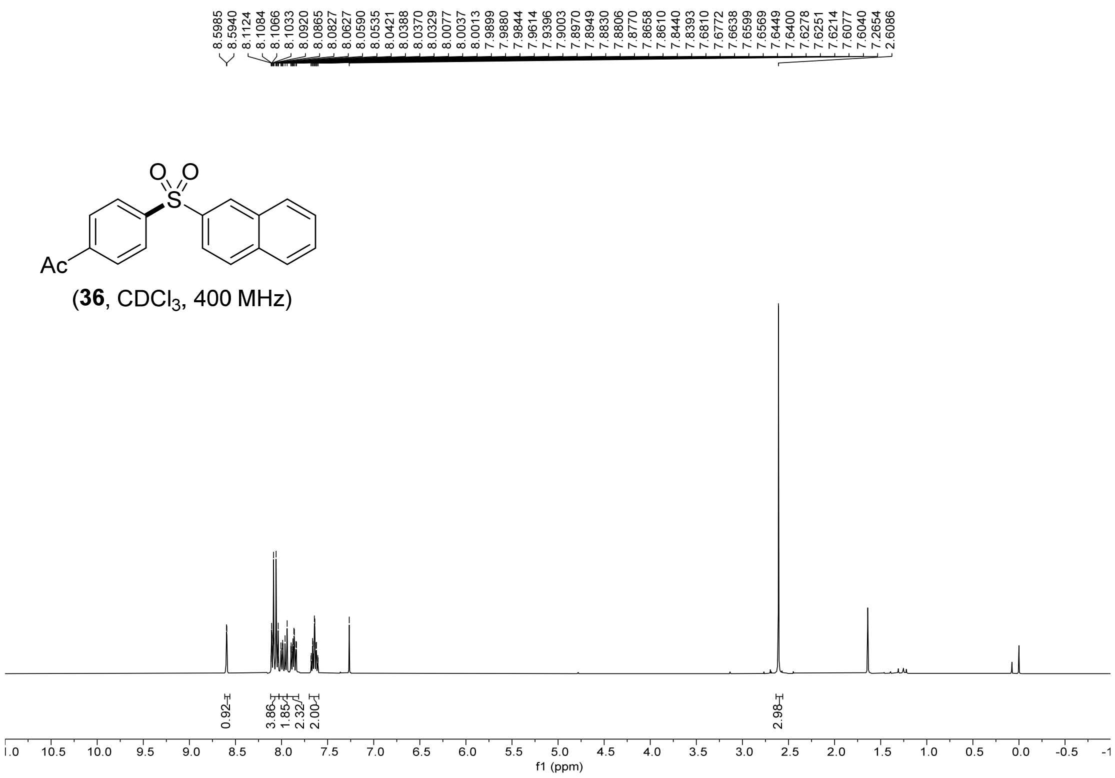

(**34**, $CDCl_3$, 100 MHz)



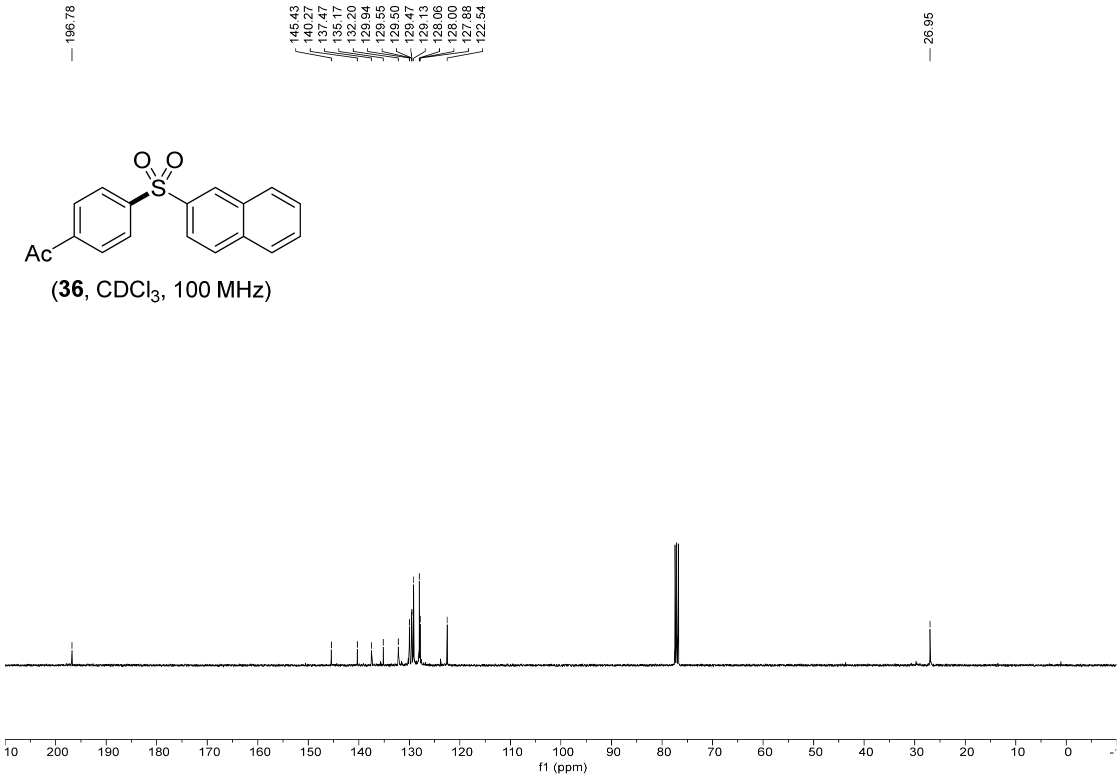
(**35**, CDCl$_3$, 400 MHz)



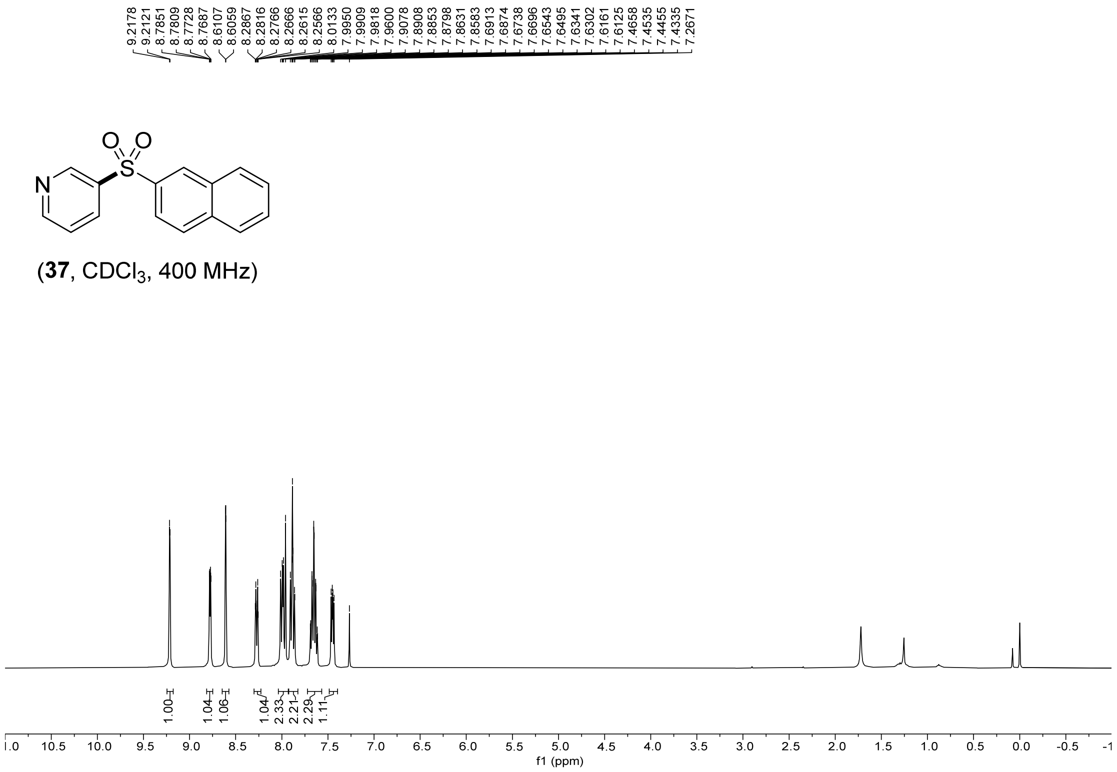
(**35**, CDCl$_3$, 100 MHz)



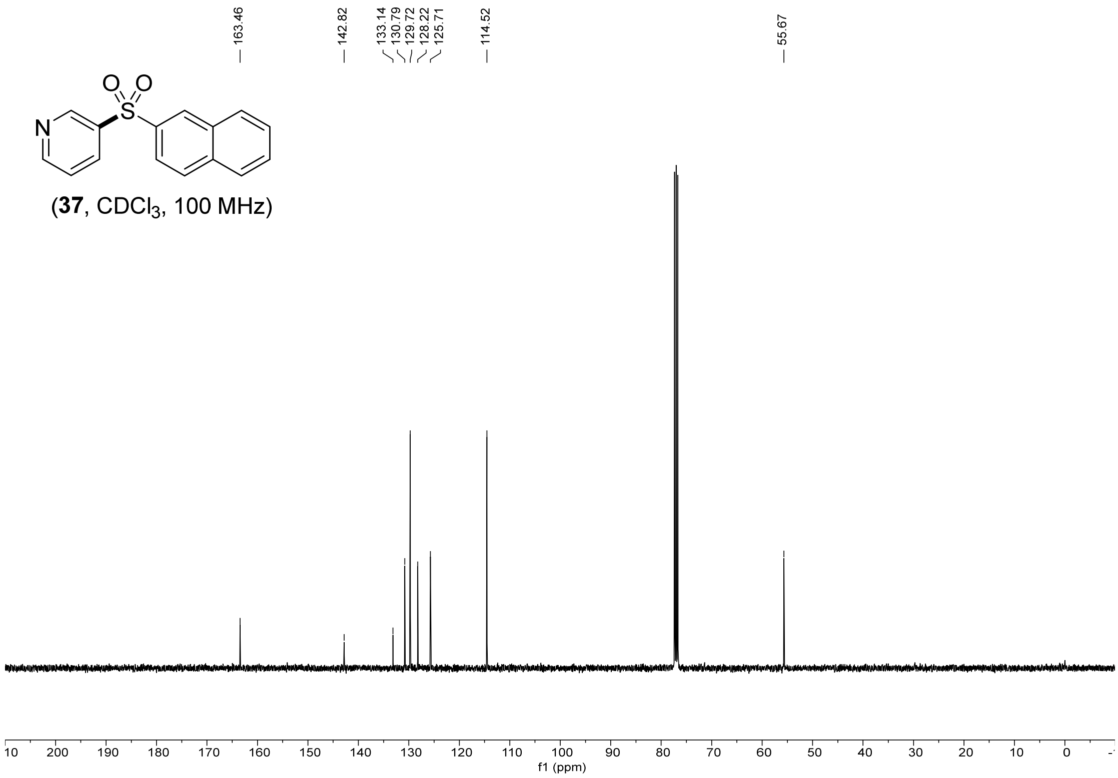
(**36**, CDCl$_3$, 400 MHz)



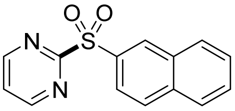
(**36**, CDCl$_3$, 100 MHz)



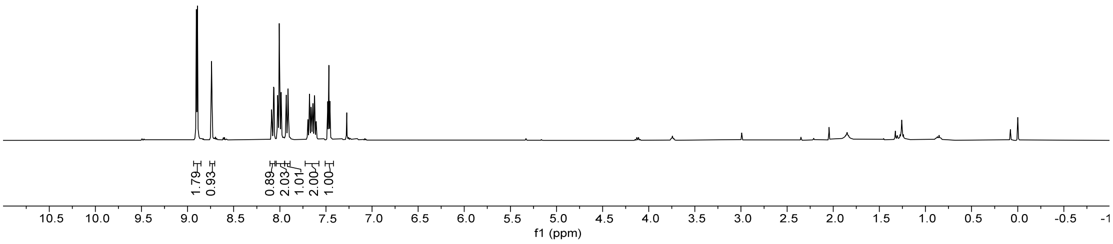
(**37**, CDCl$_3$, 400 MHz)

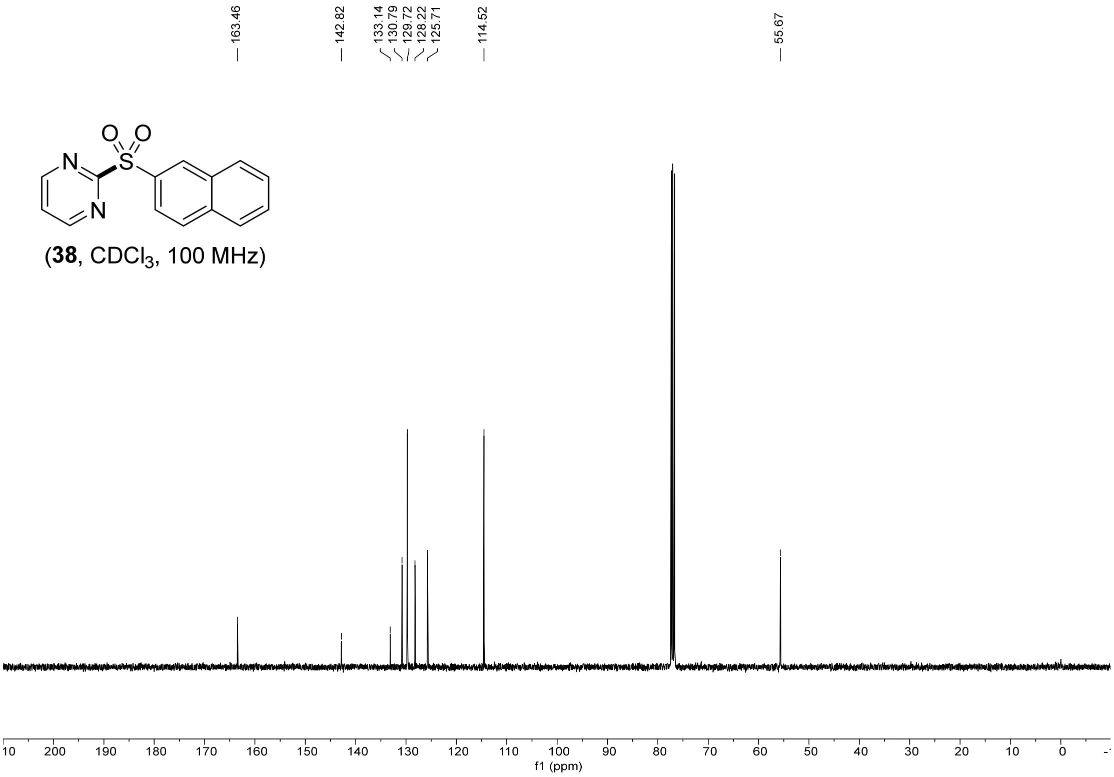


(**37**, CDCl$_3$, 100 MHz)

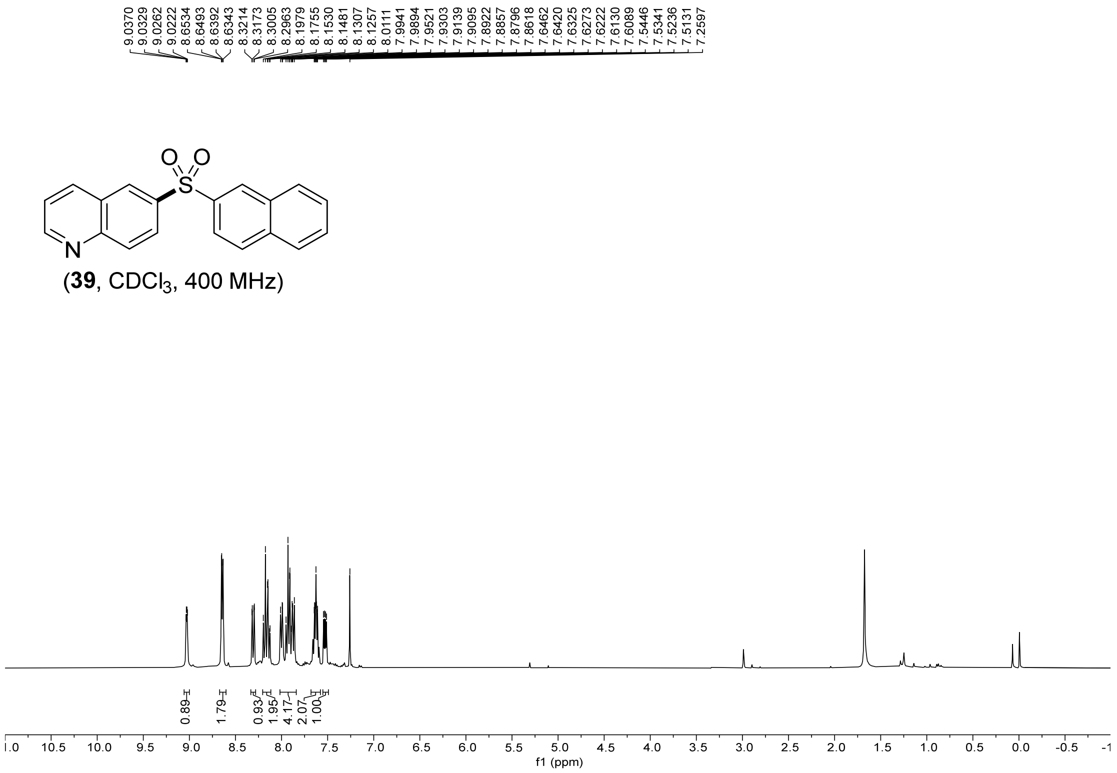


(**38**, CDCl$_3$, 400 MHz)

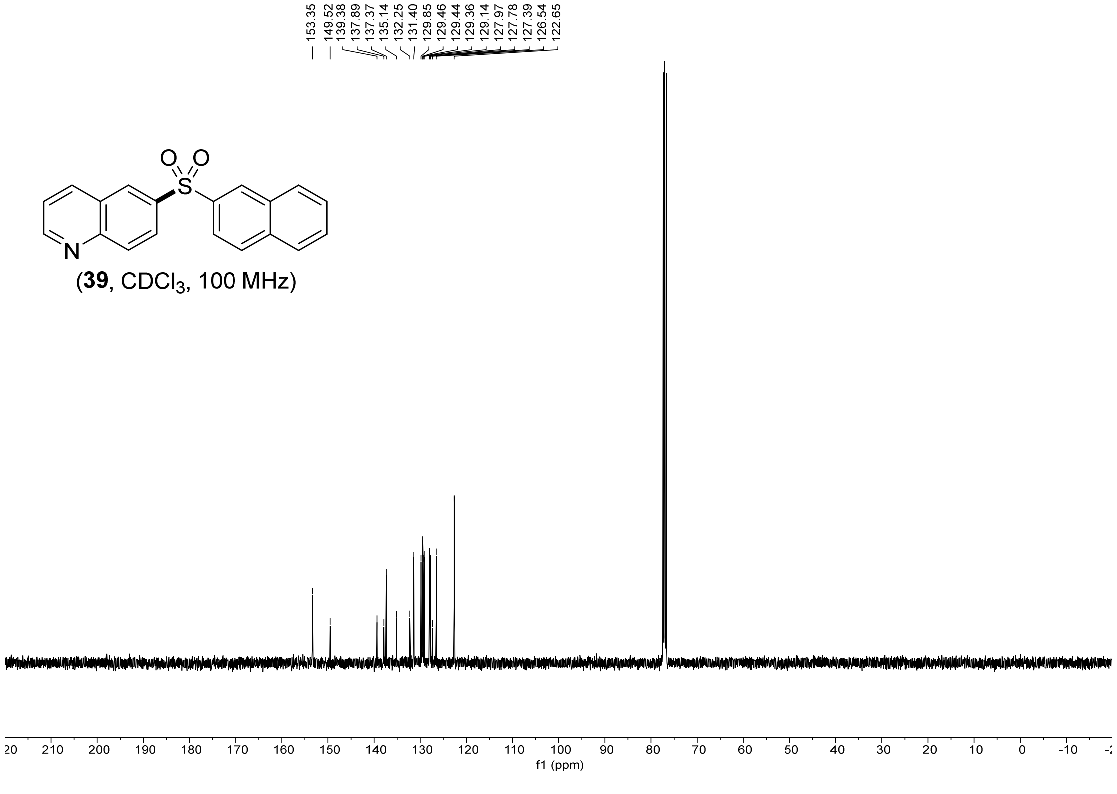




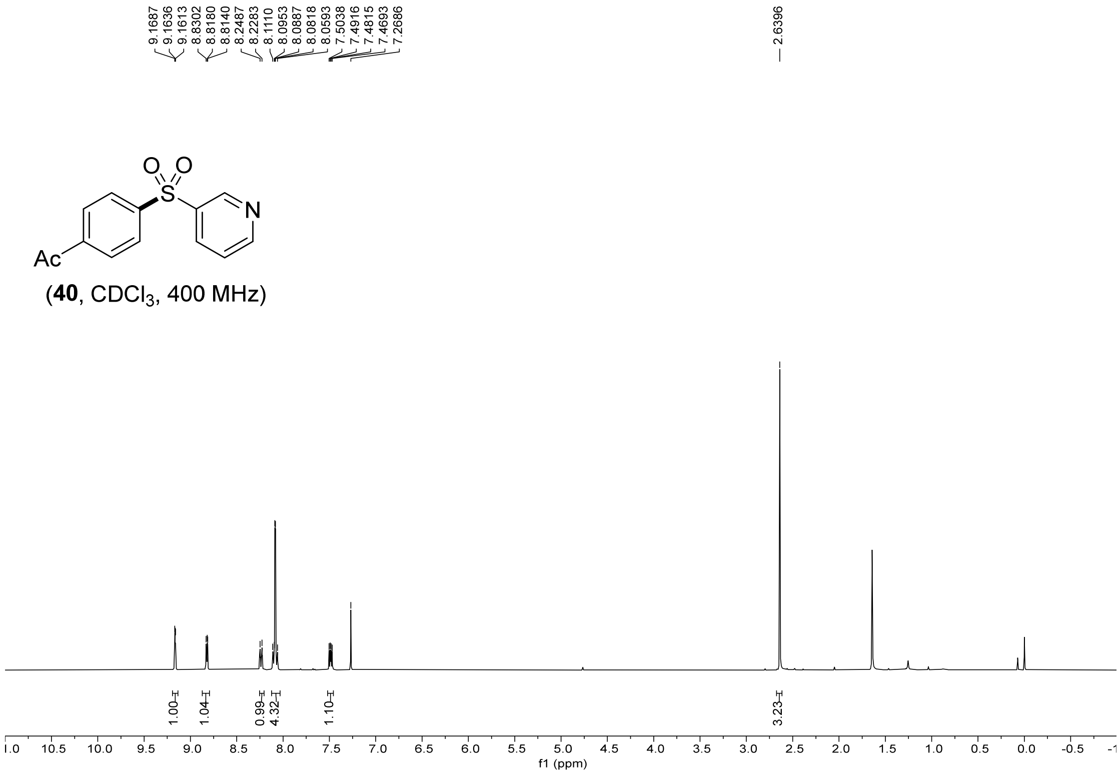
(**38**, CDCl$_3$, 100 MHz)

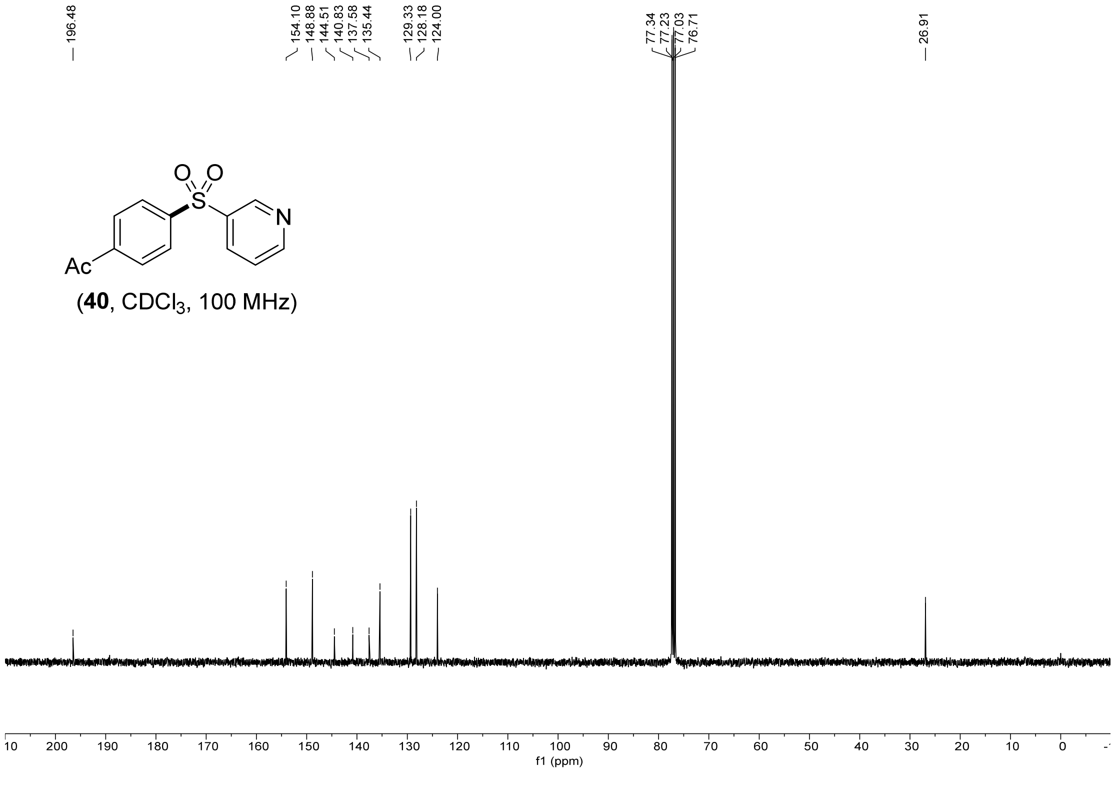


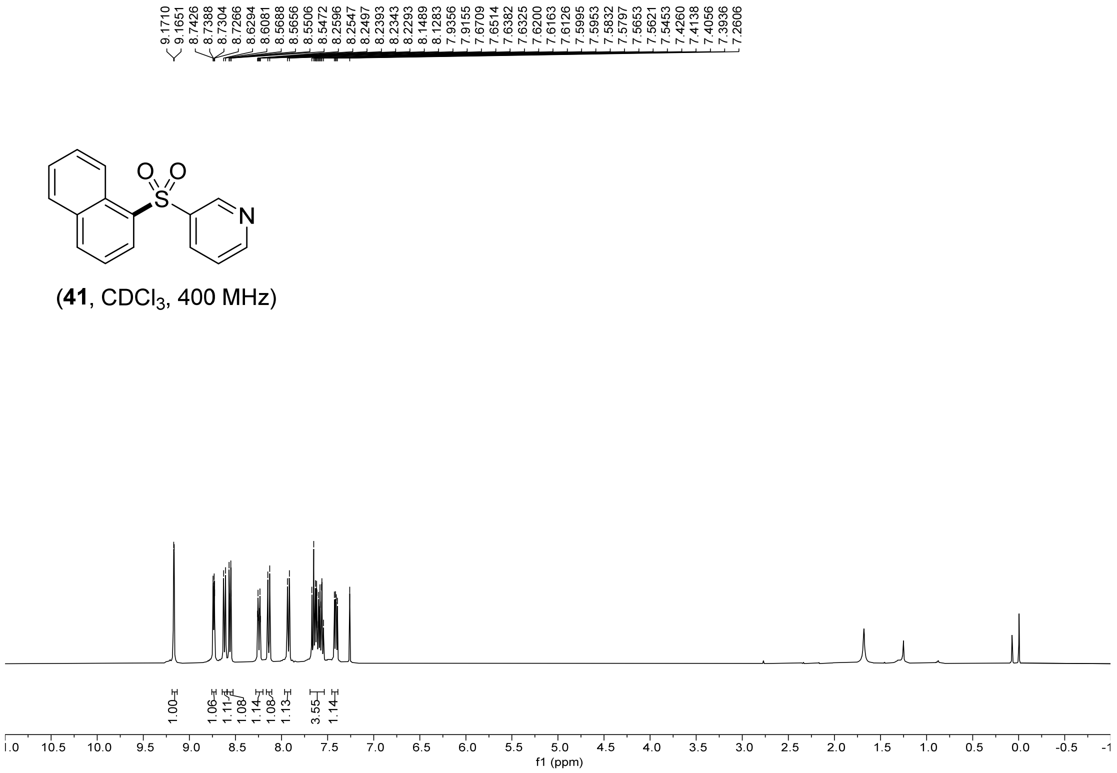
(**39**, $CDCl_3$, 400 MHz)



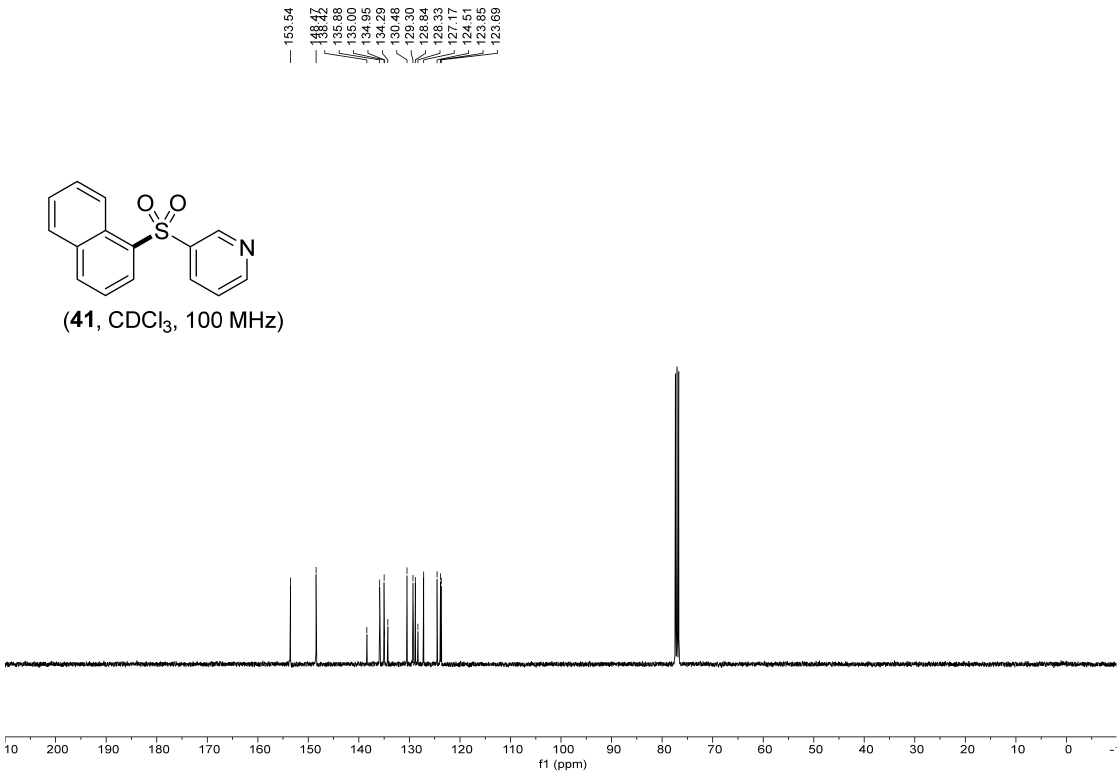
(**39**, $CDCl_3$, 100 MHz)


9.1687
9.1636
9.1613
8.8302
8.8180
8.8140
8.2487
8.2283
8.1110
8.0953
8.0887
8.0818
8.0593
7.5038
7.4916
7.4815
7.4693
7.2686
2.6396
O
O
S
N
Ac
(40, CDCl$_3$, 400 MHz)
1.00
1.04
0.99
4.32
1.10
3.23
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
-0.5
-1
f1 (ppm)

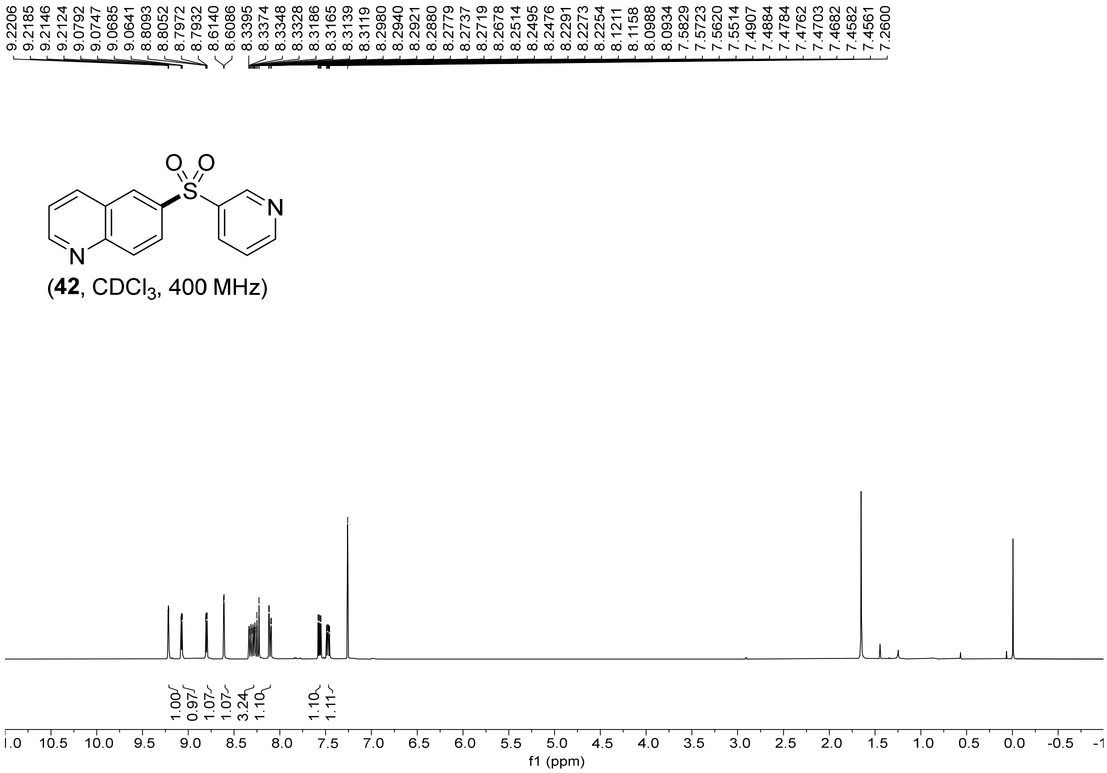

196.48
154.10
148.88
144.51
140.83
137.58
135.44
129.33
128.18
124.00
77.34
77.23
77.03
76.71
26.91
O
O
S
N
Ac
(40, CDCl$_3$, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



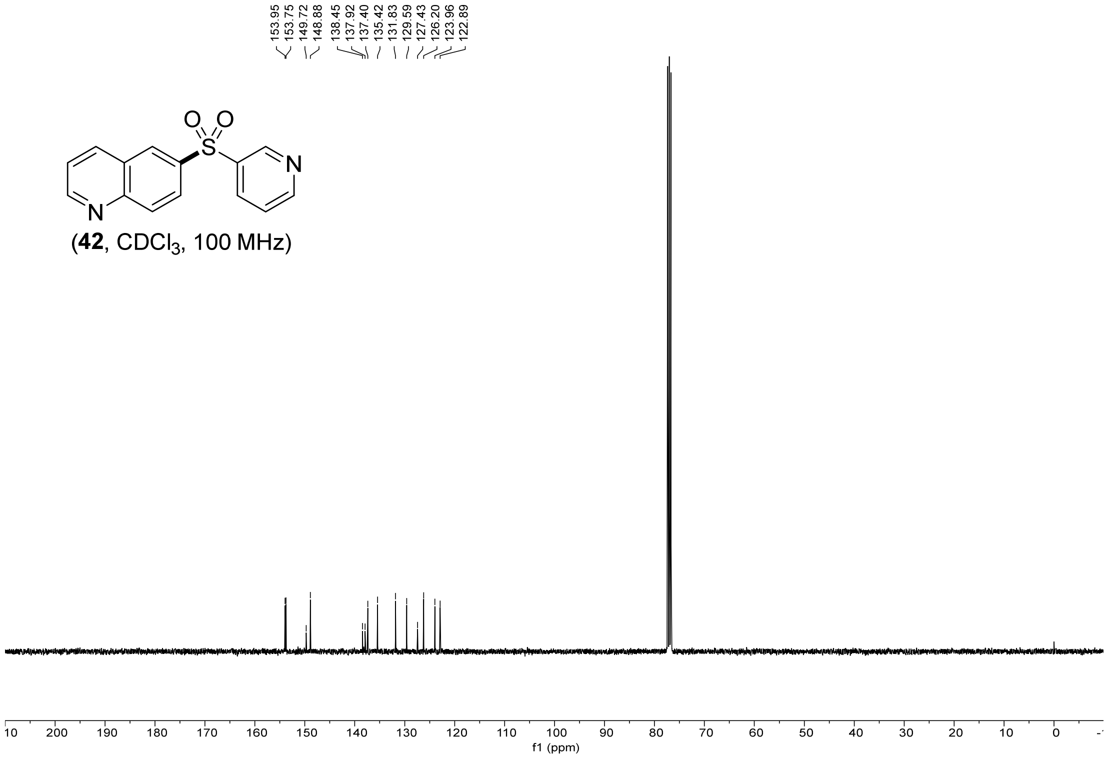
(**41**, $CDCl_3$, 400 MHz)



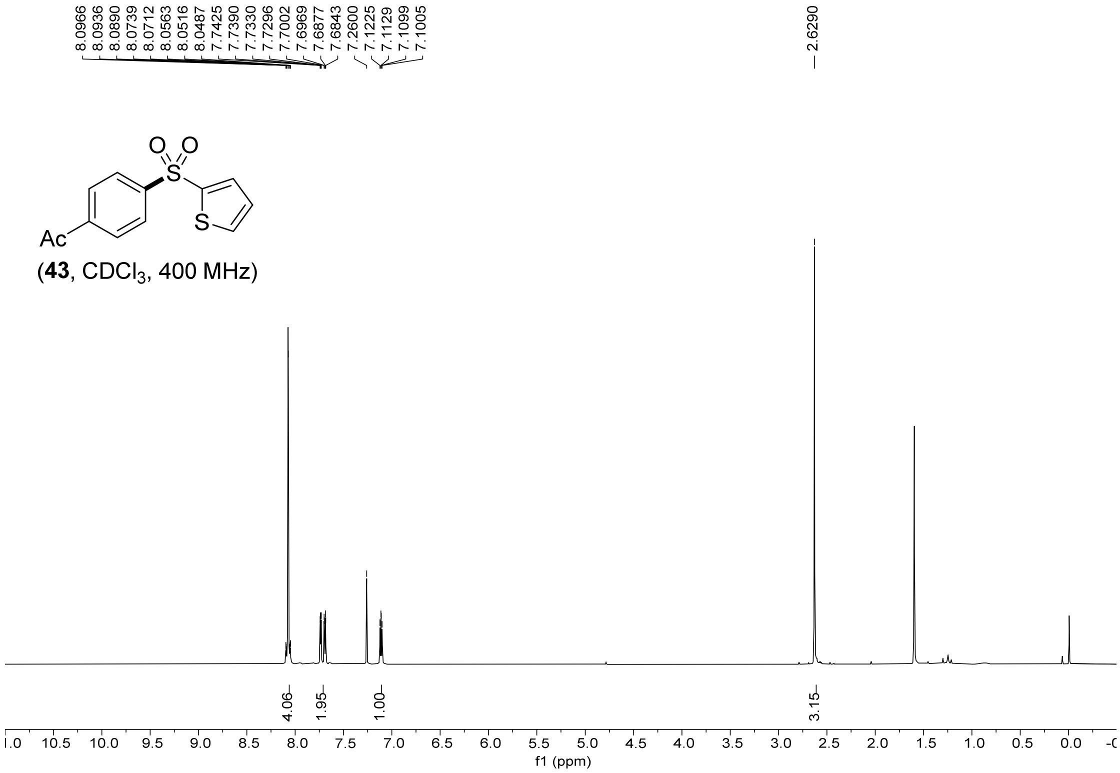
(**41**, $CDCl_3$, 100 MHz)



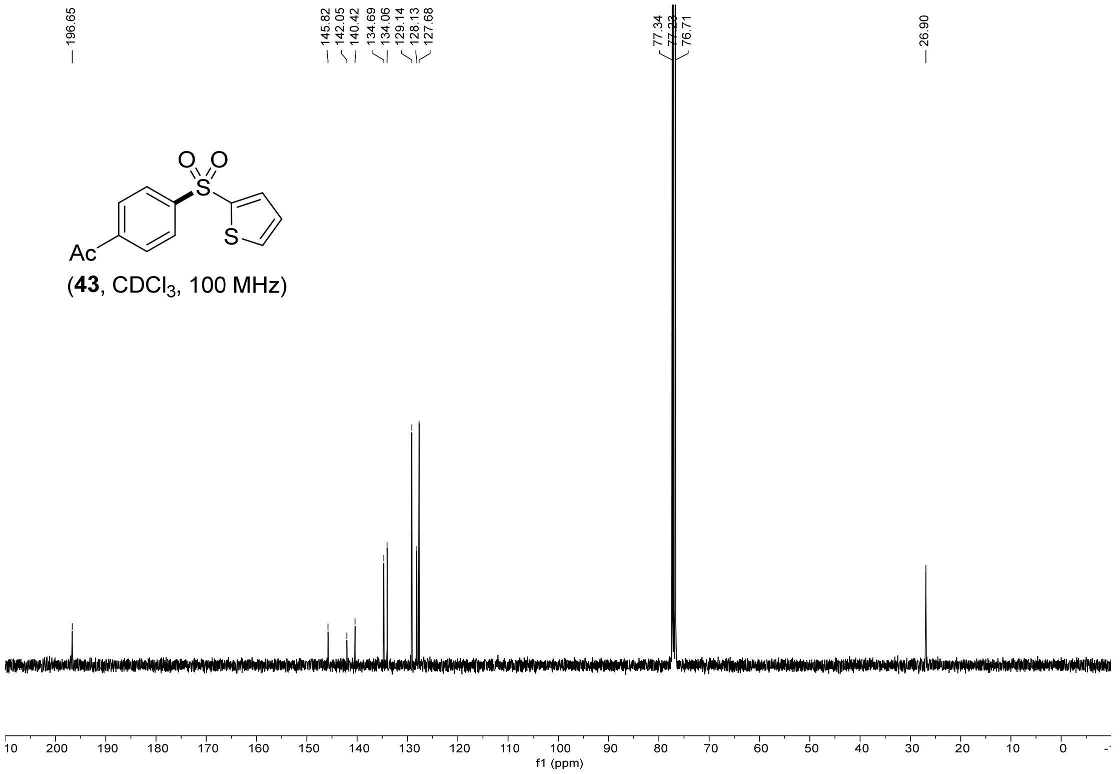
(**42**, $CDCl_3$, 400 MHz)



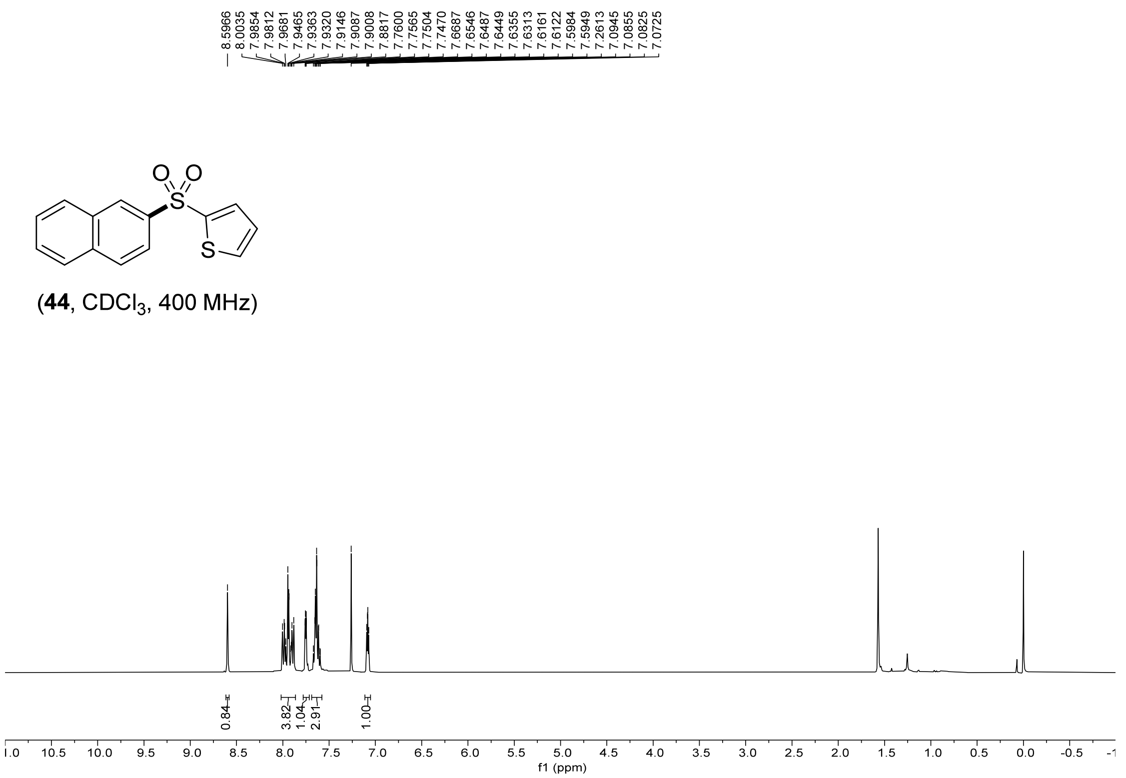
(**42**, $CDCl_3$, 100 MHz)



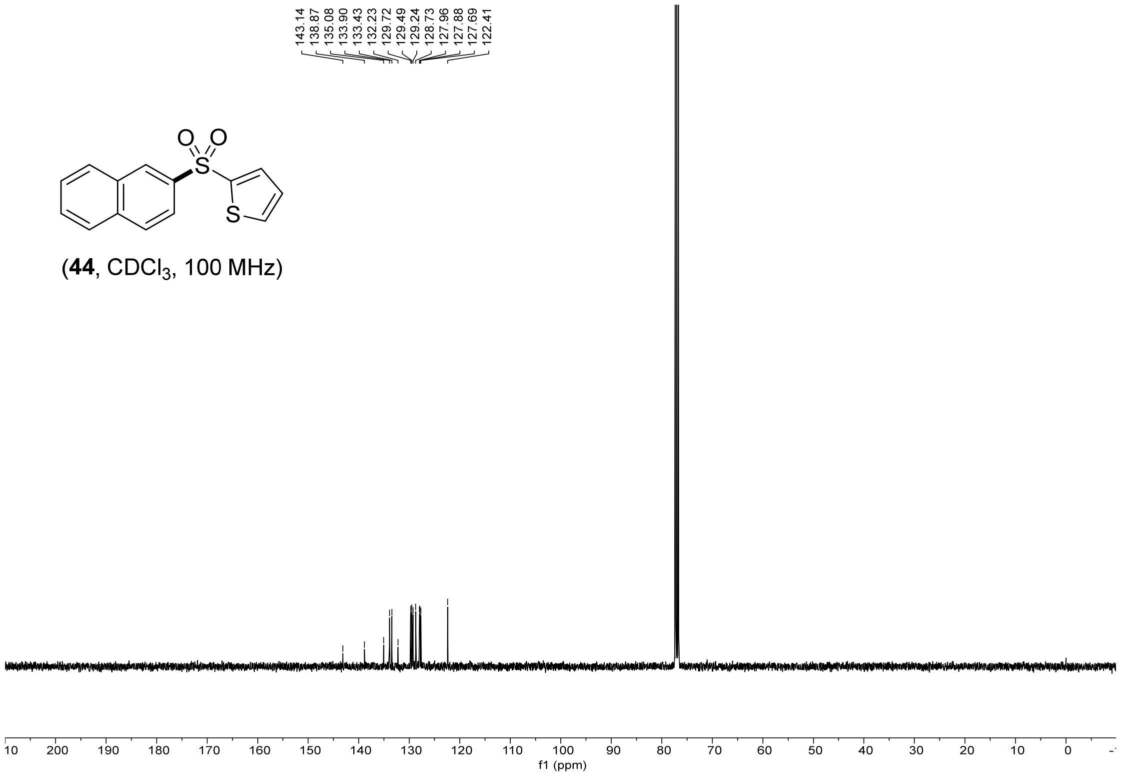
(**43**, $CDCl_3$, 400 MHz)



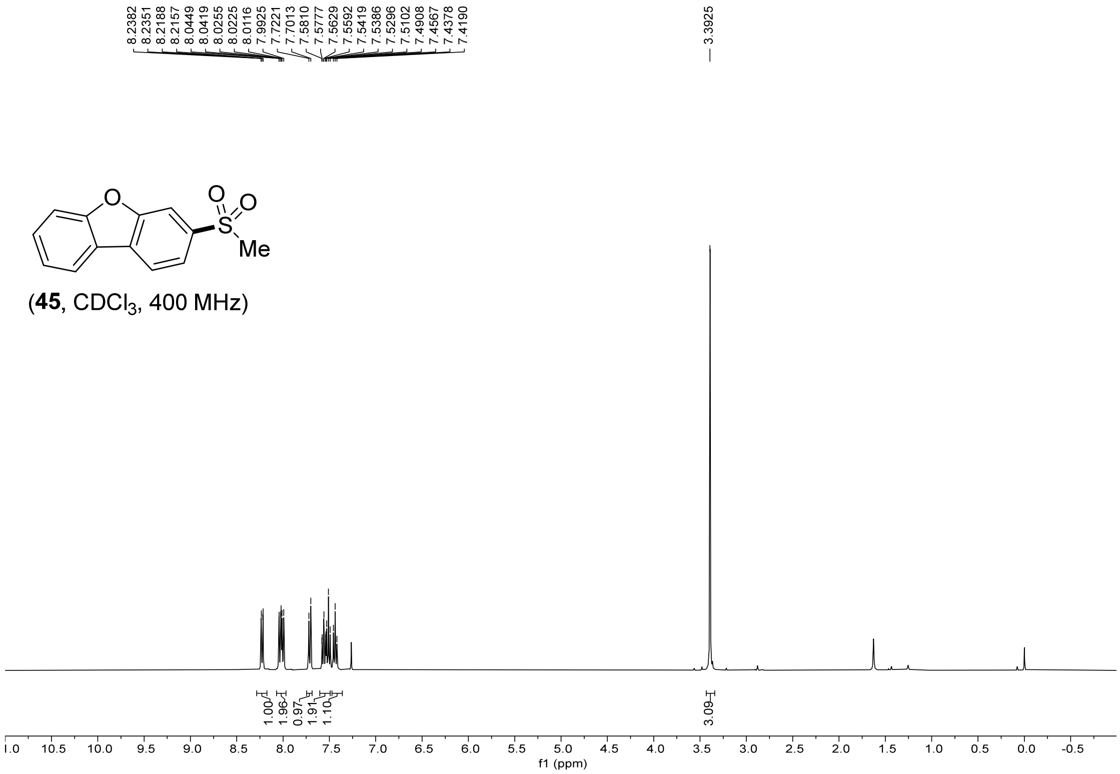
(**43**, $CDCl_3$, 100 MHz)



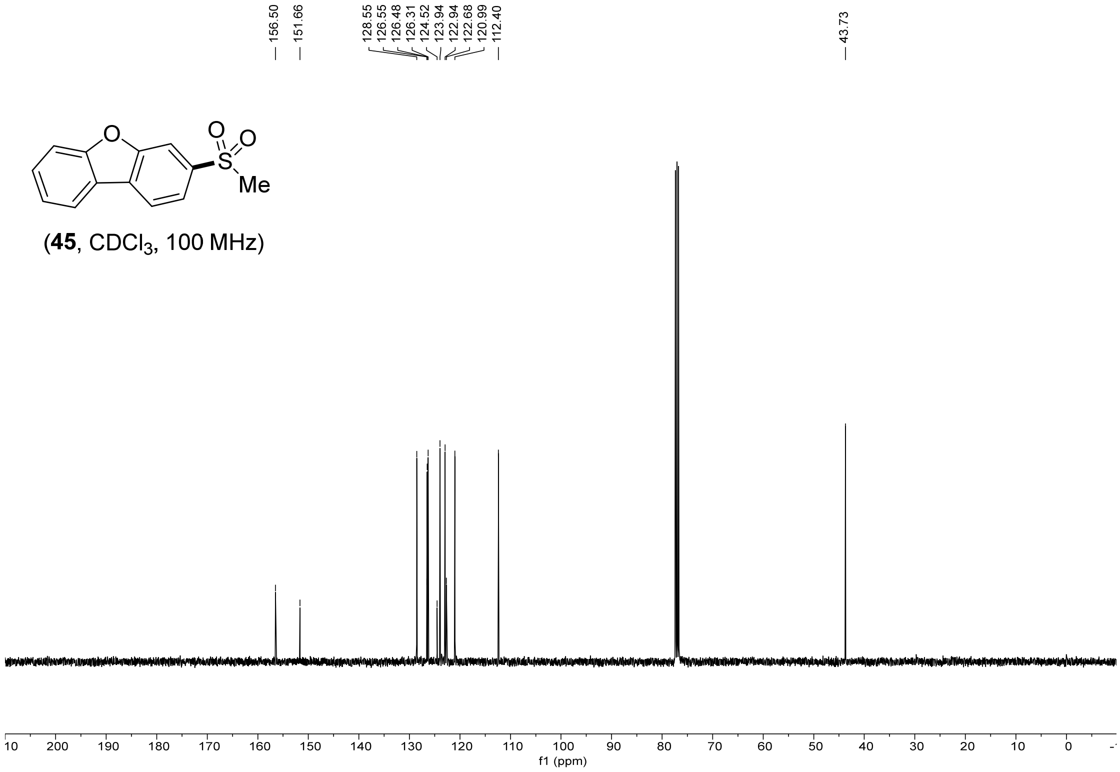
(**44**, $CDCl_3$, 400 MHz)



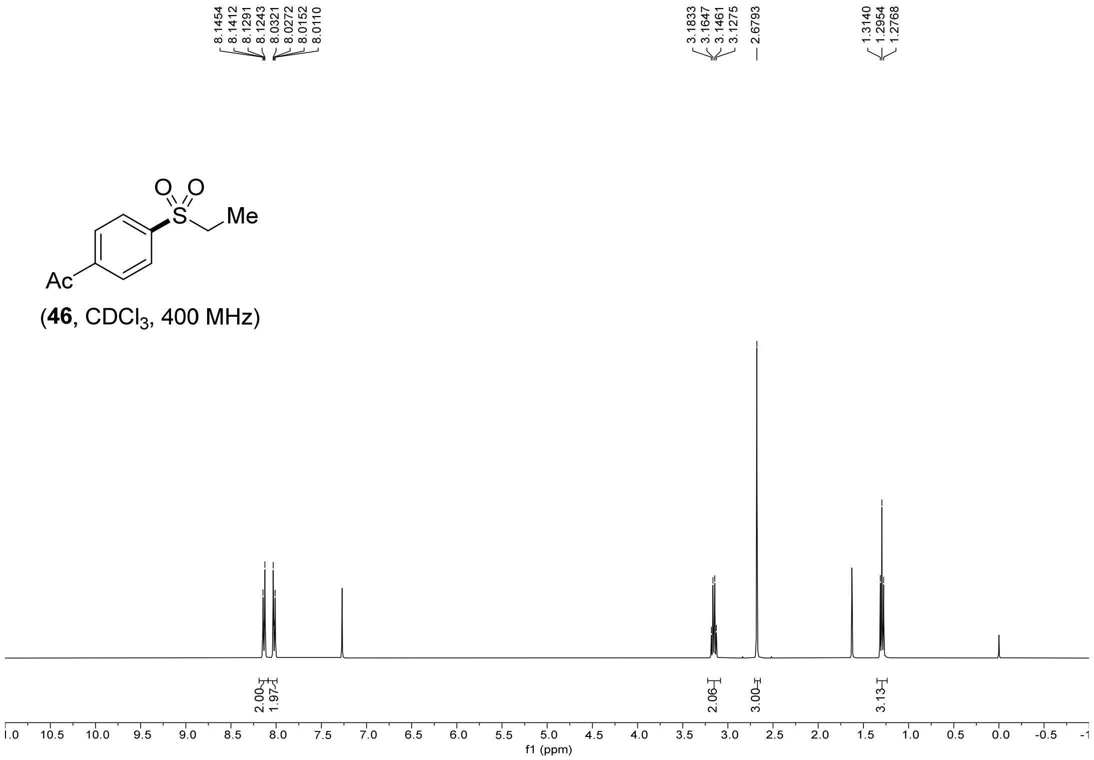
(**44**, $CDCl_3$, 100 MHz)

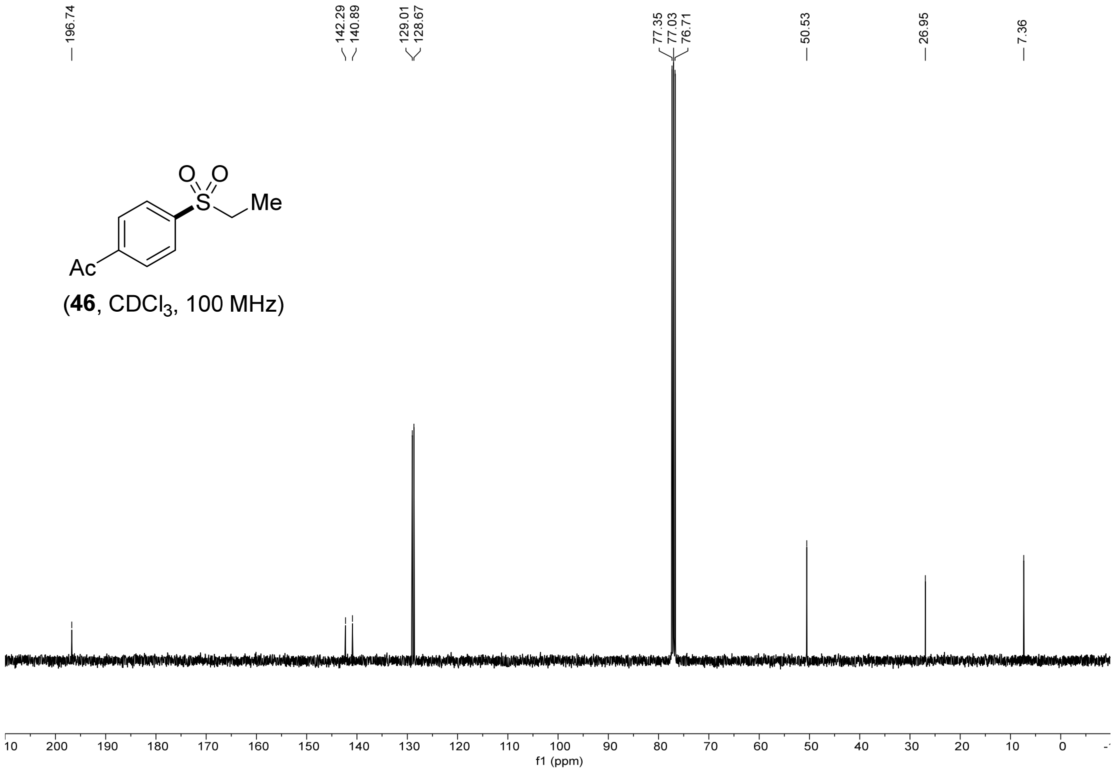


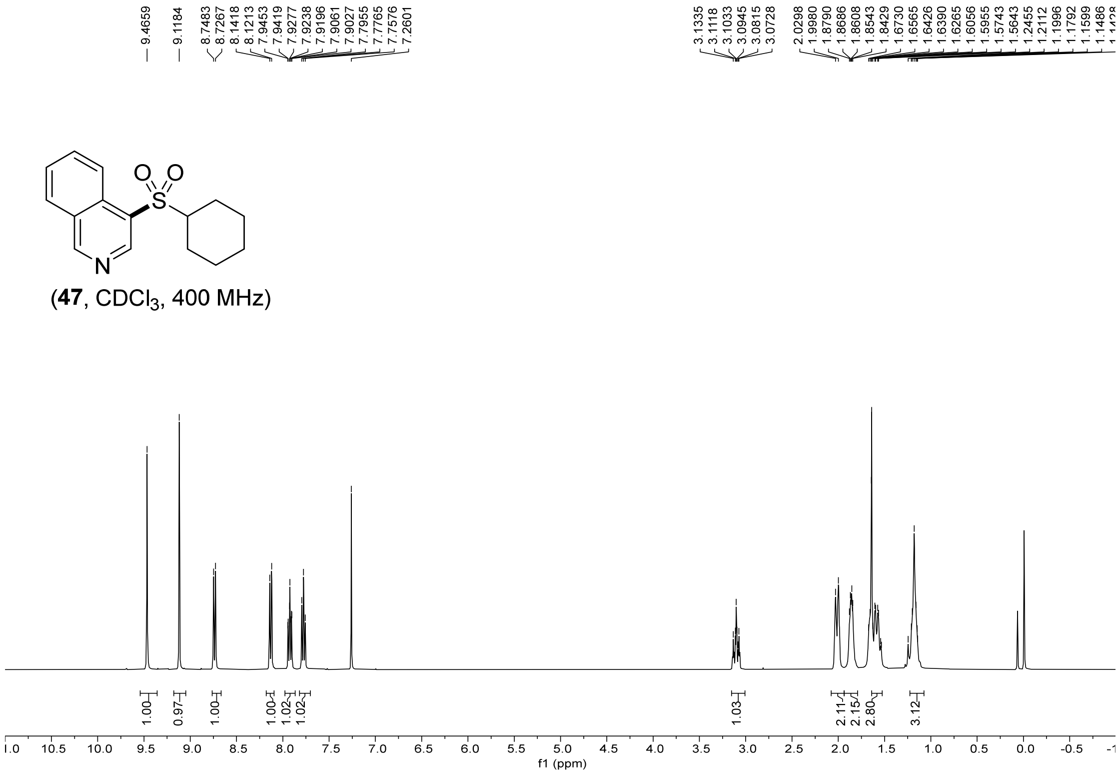
(**45**, CDCl$_3$, 400 MHz)



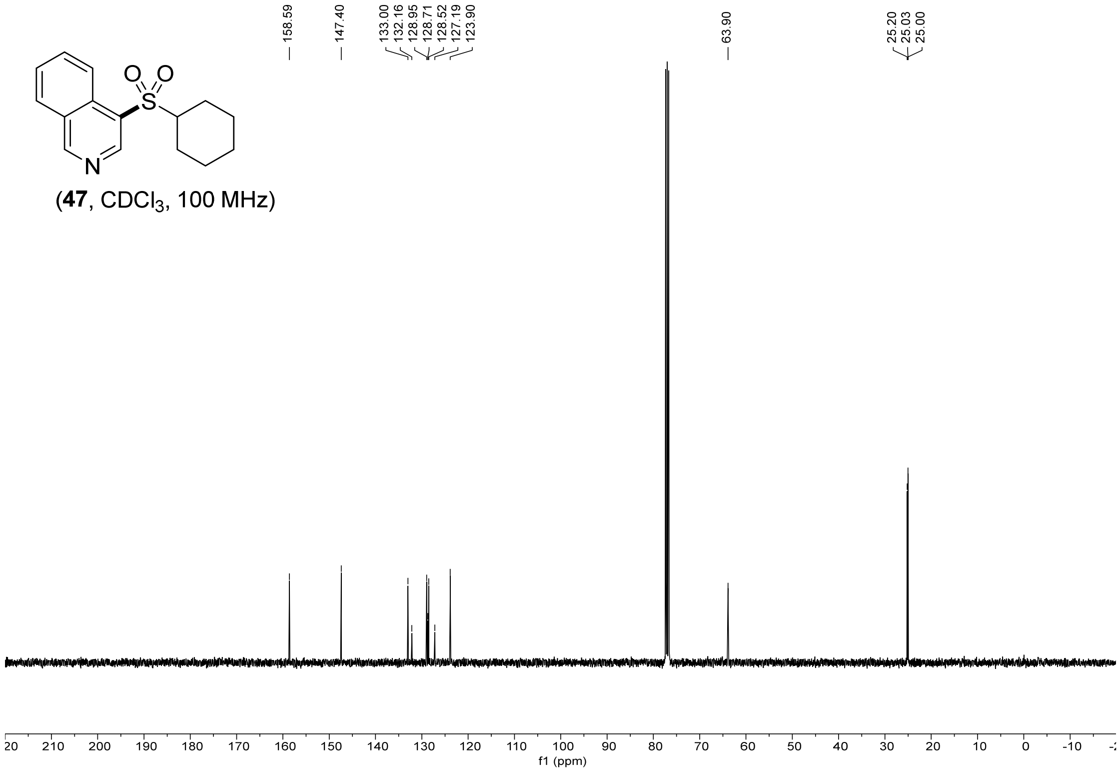
(**45**, CDCl$_3$, 100 MHz)


8.1454
8.1412
8.1291
8.1243
8.0321
8.0272
8.0152
8.0110
3.1833
3.1647
3.1461
3.1275
2.6793
1.3140
1.2954
1.2768
Me
Ac
(**46**, $CDCl_3$, 400 MHz)
2.00
1.97
2.06
3.00
3.13
f1 (ppm)

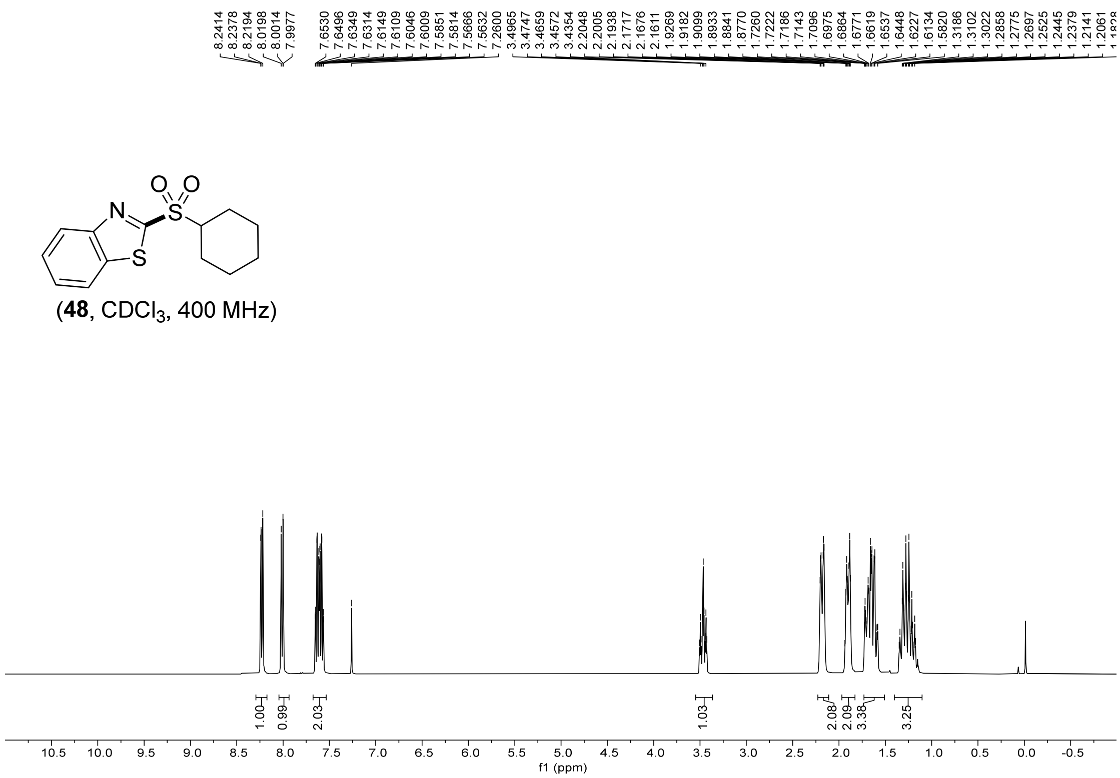

196.74
142.29
140.89
129.01
128.67
77.35
77.03
76.71
50.53
26.95
7.36
Me
Ac
(**46**, $CDCl_3$, 100 MHz)
f1 (ppm)



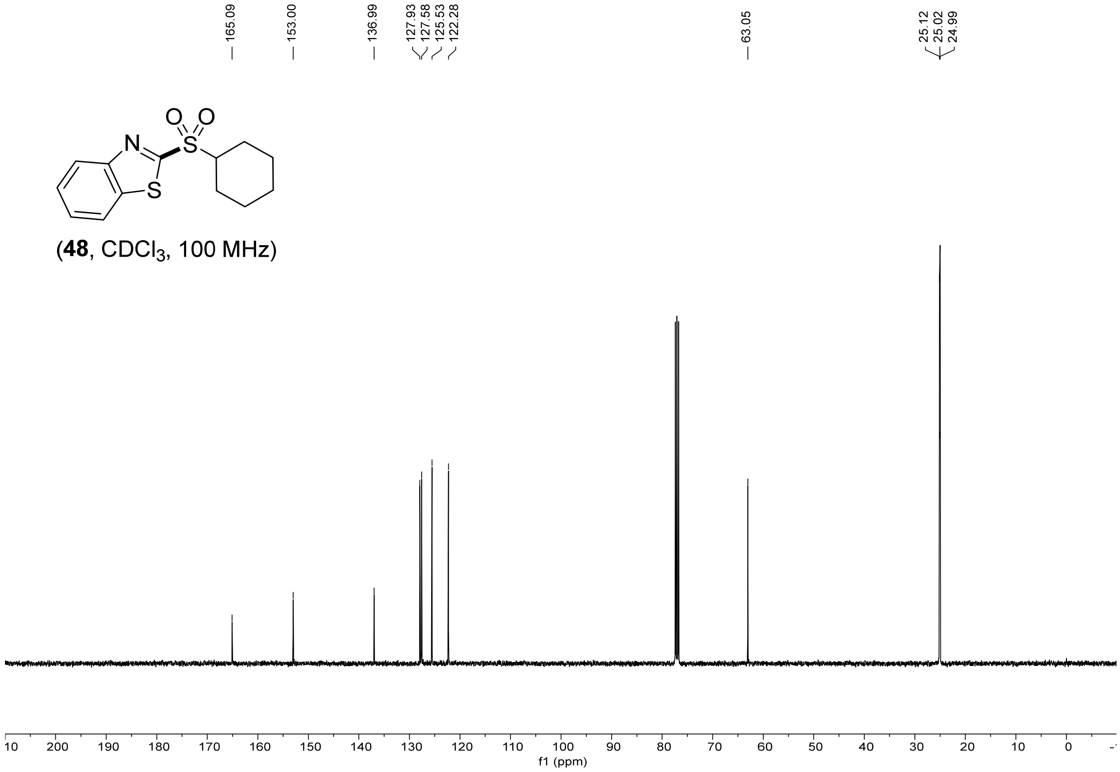
(**47**, $CDCl_3$, 400 MHz)



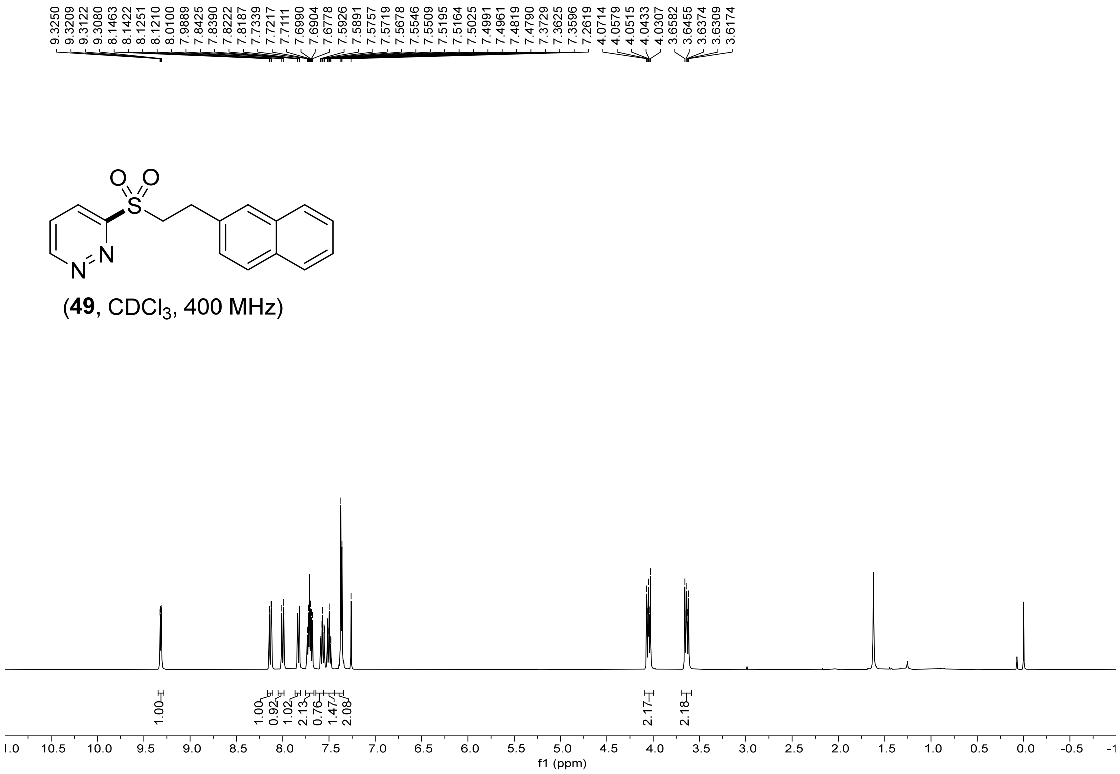
(**47**, $CDCl_3$, 100 MHz)

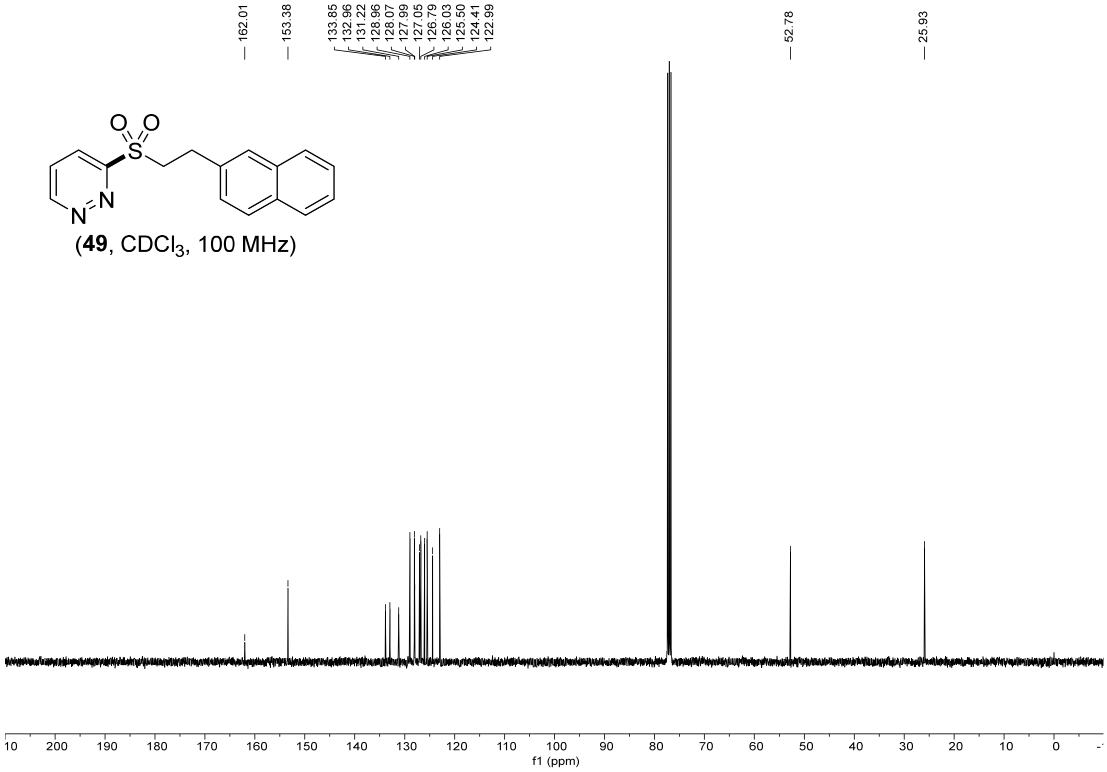


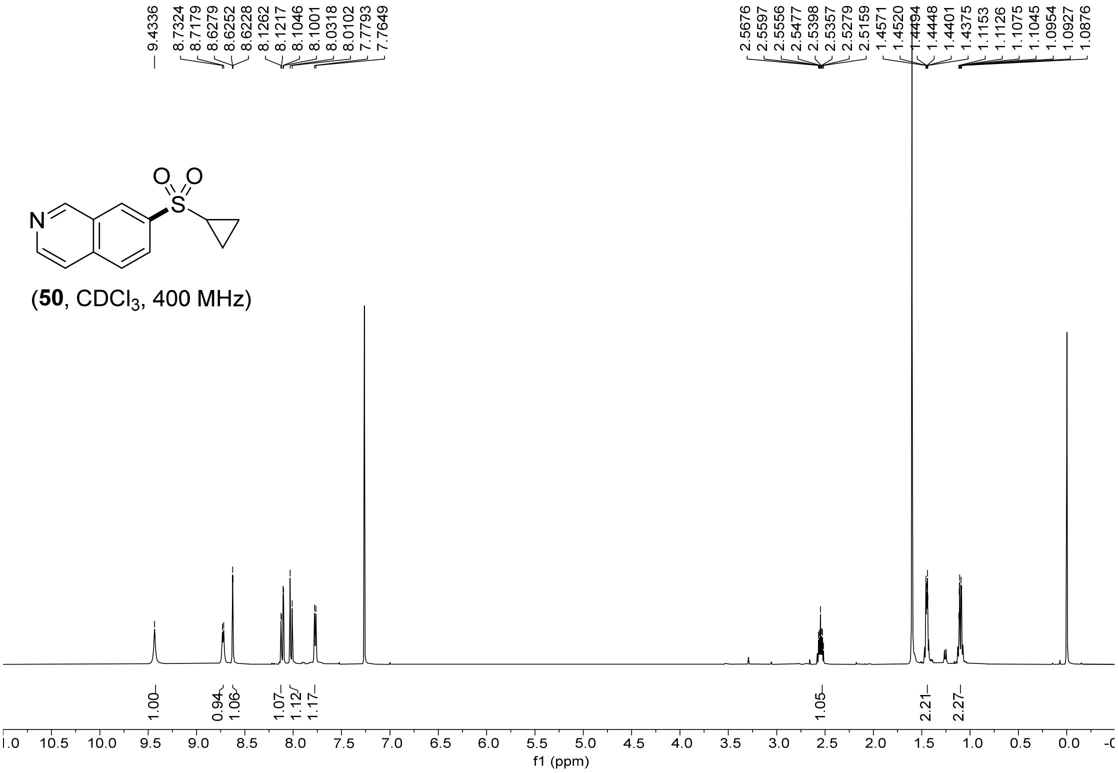
(**48**, CDCl$_3$, 400 MHz)



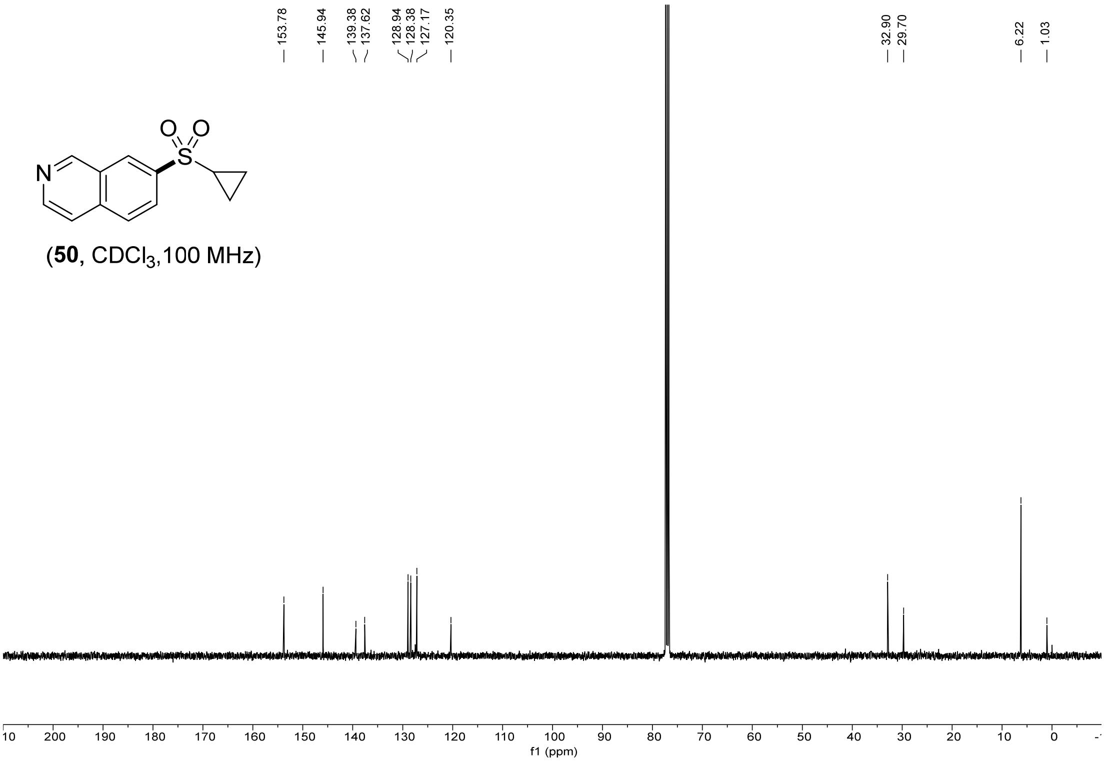
(**48**, CDCl$_3$, 100 MHz)


(**49**, $CDCl_3$, 400 MHz)

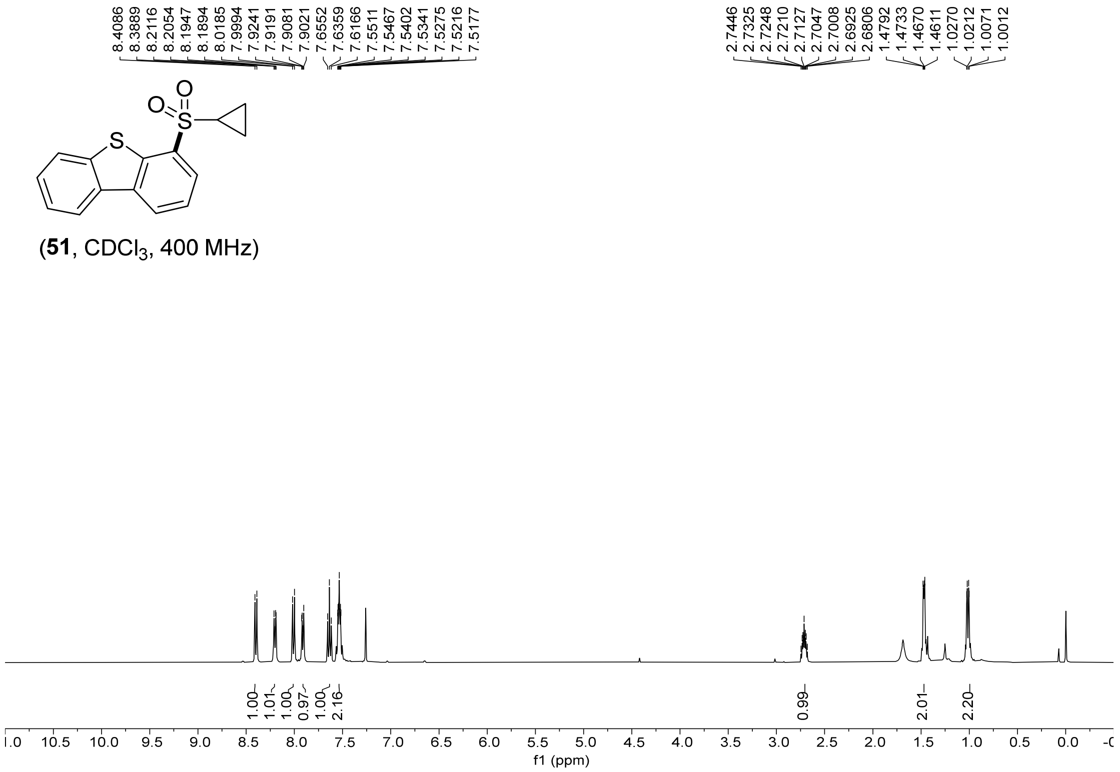

(**49**, $CDCl_3$, 100 MHz)



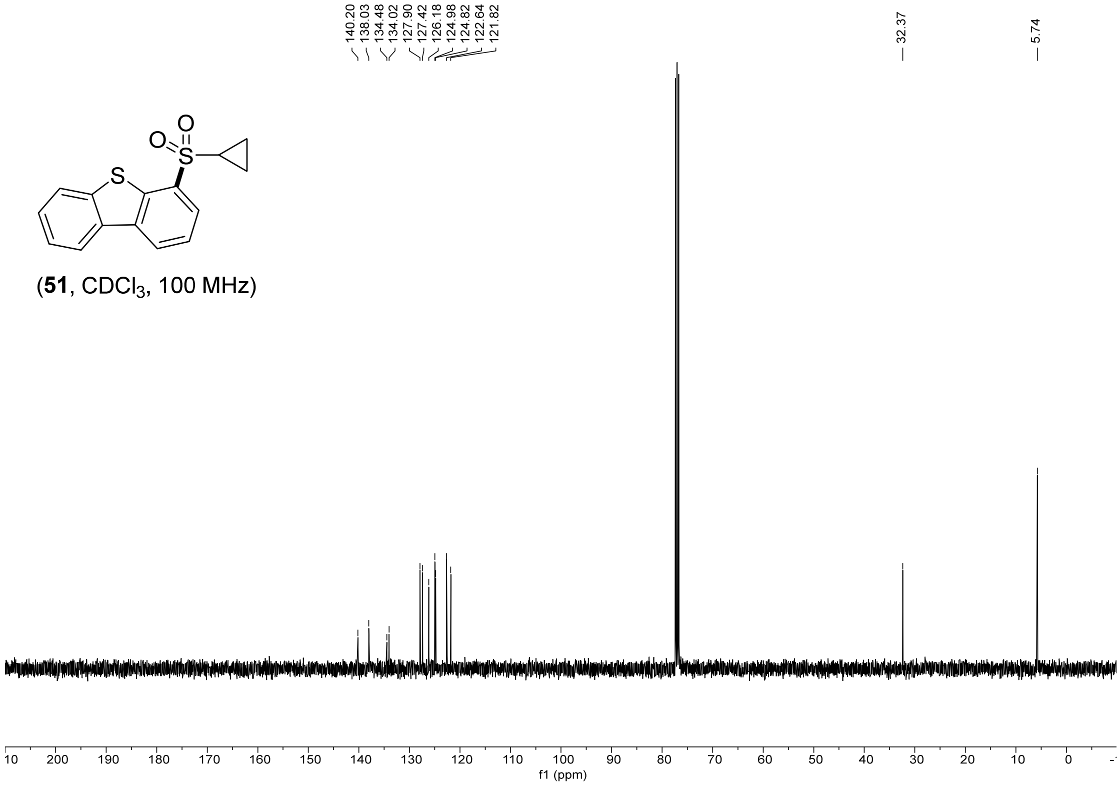
(**50**, $CDCl_3$, 400 MHz)



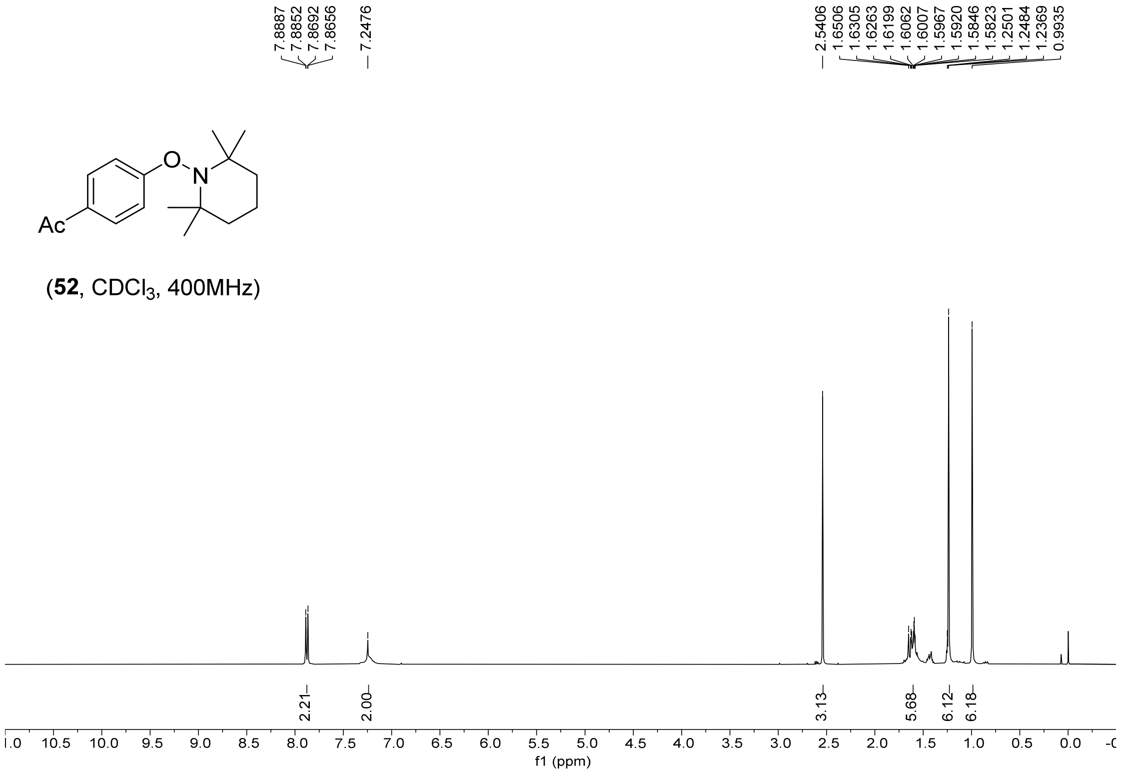
(**50**, $CDCl_3$,100 MHz)



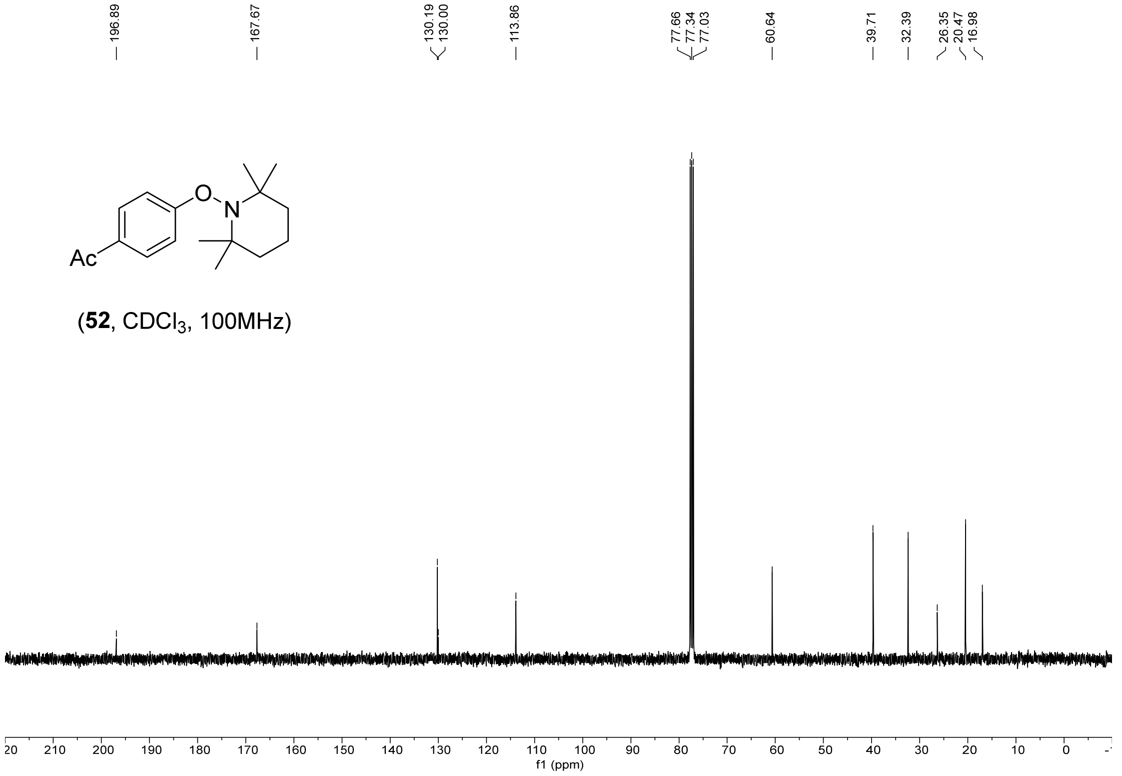
(**51**, CDCl$_3$, 400 MHz)



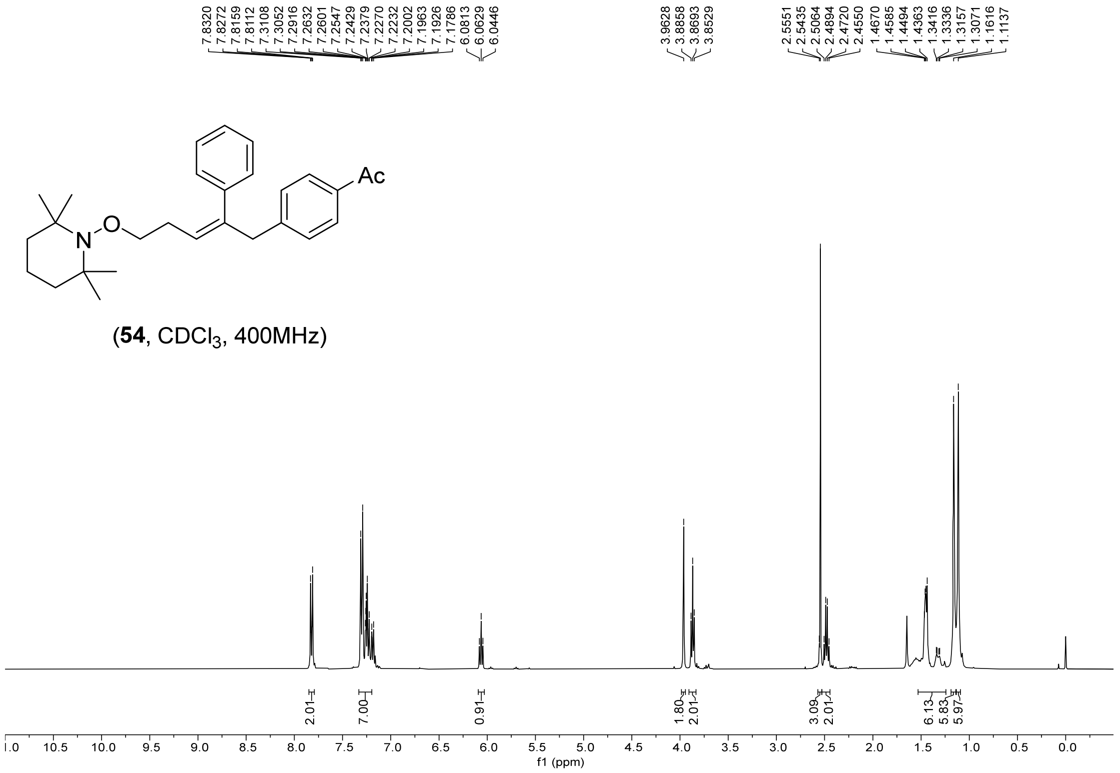
(**51**, CDCl$_3$, 100 MHz)

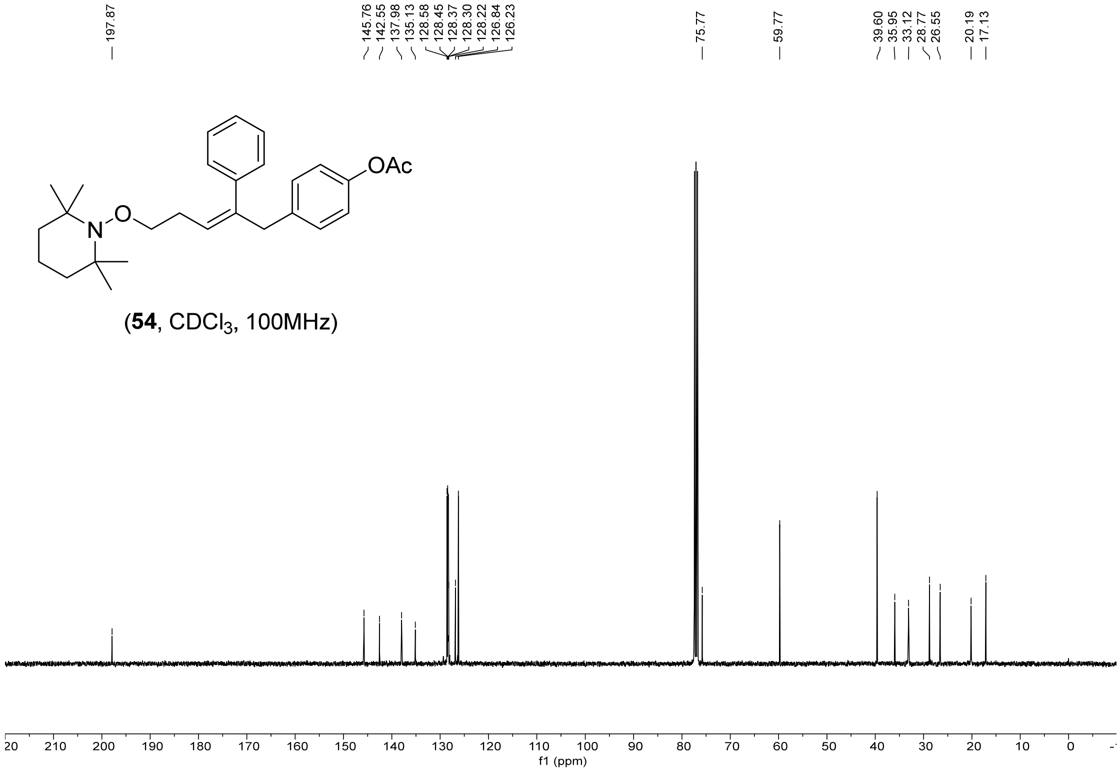


(**52**, $CDCl_3$, 400MHz)



(**52**, $CDCl_3$, 100MHz)


7.8320
7.8272
7.8159
7.8112
7.3108
7.3052
7.2916
7.2632
7.2601
7.2547
7.2429
7.2379
7.2270
7.2232
7.2002
7.1963
7.1926
7.1786
6.0813
6.0629
6.0446
3.9628
3.8858
3.8693
3.8529
2.5551
2.5435
2.5064
2.4894
2.4720
2.4550
1.4670
1.4585
1.4494
1.4363
1.3416
1.3336
1.3157
1.3071
1.1616
1.1137
Ac
N
O
(54, CDCl3, 400MHz)
2.01
7.00
0.91
1.80
2.01
3.09
2.01
6.13
5.83
5.97
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
f1 (ppm)


197.87
145.76
142.55
137.98
135.13
128.58
128.45
128.37
128.30
128.22
126.84
126.23
75.77
59.77
39.60
35.95
33.12
28.77
26.55
20.19
17.13
OAc
N
O
(54, CDCl3, 100MHz)
220
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)