Supporting Information

Cobalt Single-Atom Catalyst at PPM Level Reduces Sulfonyl Chlorides to Sulfinate Esters

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Table of Contents

SI-1 Experimental section

Materials and Instrumentation

Powder X-ray diffraction (PXRD) data were collected on an Ultima IV automated multipurpose X-ray diffractometer using Cu-Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific Nexsa X-ray photoelectron spectrometer using Mg as the exciting source. The NMR experiments were carried out on Bruker AV-400 (400 MHz) or JEOL-500 (500 MHz) spectrometers. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.16 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet, and J, coupling constant in Hz. The Brunauer-Emmett-Teller (BET) specific surface area was calculated based on the N_2 adsorption isotherms at 77 K on the BSD-660 gas adsorption instrument. The pore size distribution was derived from the adsorption branch of N_2 adsorption isotherms using the non-local density functional theory (NLDFT) method and assuming a slit pore model. The surface morphologies and element distribution analyses were performed on a Tecnai G2 F20 transmission electron microscope (TEM) with an energy dispersive spectrometer (EDS). High-resolution mass spectrometry (HRMS) was obtained on an Exactive Plus LC-MS (ESI) mass spectrometer with the use of a quadrupole analyzer or an Agilent 1290-6545XT mass spectrometer with a QTOF analyzer. The metal element content was obtained using an Optima 8000 inductively coupled plasma-optical emission spectrometry (ICP-OES). Raman spectra were collected by a Confocal LabRam HR800 spectrometer (HORIBA Jobin Yvon, France). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) images were collected using a Themis Z (Thermo Fisher Scientific) at 300 kV. The collection half-angle for HAADF imaging is set to 60-200 mrad.

XAFS measurements and analysis details

Data reduction, data analysis, and EXAFS fitting were performed and analyzed with the Athena and Artemis programs of the Demeter data analysis packages[1] that utilize the FEFF6 program[2] to fit the EXAFS data. The energy calibration of the sample was conducted through a standard Co foil, which, as a reference, was simultaneously measured. A linear function was subtracted from the pre-edge region, then the edge jump was normalized using Athena software. The $\chi^{(k)}$ data were isolated by subtracting a smooth, third-order polynomial approximating the absorption background of an isolated atom. The k^2-weighted $\chi^{(k)}$ data were Fourier transformed after applying a Hanning window function

($\Delta k = 1.0$). For EXAFS modeling, the global amplitude EXAFS (CN, R, σ^2 and ΔE_0) were obtained by nonlinear fitting, with least-squares refinement, of the EXAFS equation to the Fourier-transformed data in R-space, using Artemis software, EXAFS of the Co foil was fitted and the obtained amplitude reduction factor S_0^2 value (0.748) was set in the EXAFS analysis to determine the coordination numbers (CNs) in sample.

Synthesis of Co_1Zn_{20}@BMOF[3]

In a typical procedure, $Co(NO_3)_2 \cdot 6H_2O$ (0.09 mmol, 26.5 mg) and $Zn(NO_3)_2 \cdot 6H_2O$ (1.80 mmol, 539.0 mg) were dissolved in 15 mL of methanol to form a clear solution, which was subsequently injected into 15 mL of a clear methanol solution containing 2-methylimidazole (7.50 mmol, 616.0 mg). The mixed solution was then heated in a reactor (50 mL) at 120 ºC for 4 hours. The as-obtained purple suspension was centrifuged and washed with methanol several times and dried at 80 ºC for 24 hours to obtain the Co_1Zn_{20}@BMOF sample.

Synthesis of M_1Zn_{20}@BMOF (M = Cu, Ni, Mn, or Fe)

In a typical procedure, metal salt ($Cu(NO_3)_2 \cdot 2.5H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, or $FeCl_3 \cdot 6H_2O$; 0.09 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (1.80 mmol, 539.0 mg) were dissolved in 15 mL of methanol to form a clear solution, which was subsequently injected into 15 mL of a clear methanol solution containing 2-methylimidazole (7.50 mmol, 616.0 mg). The mixed solution was then heated in a reactor (50 mL) at 120 ºC for 4 hours. The as-obtained suspension was centrifuged and washed with methanol several times and dried at 80 ºC for 24 hours to obtain the M_1Zn_{20}@BMOF sample.

Synthesis of Co_1Zn_5@BMOF[3]

In a typical procedure, $Co(NO_3)_2 \cdot 6H_2O$ (0.37 mmol, 109.0 mg) and $Zn(NO_3)_2 \cdot 6H_2O$ (1.5 mmol, 446.0 mg) were dissolved in 15 mL of methanol to form a clear solution, which was subsequently injected into 15 mL of a clear methanol solution containing 2-methylimidazole (7.50 mmol, 616.0 mg). The mixed solution was then heated in a reactor (50 mL) at 120 ºC for 4 hours. The as-obtained purple suspension was centrifuged and washed with methanol several times and dried at 80 ºC for 24 hours to obtain the Co_1Zn_5@BMOF sample.

Synthesis of ZIF-67[3]

In a typical procedure, $Co(NO_3)_2 \cdot 6H_2O$ (1.87 mmol, 546.0 mg) was dissolved in 15 mL of methanol to form a clear solution, which was subsequently injected into 15 mL of a clear methanol solution containing 2-methylimidazole (7.50 mmol, 616.0 mg). The mixed solution was then heated in a reactor

(50 mL) at 120 ºC for 4 hours. The as-obtained purple suspension was centrifuged and washed with methanol several times and dried at 80 ºC for 24 hours to obtain the ZIF-67 sample.

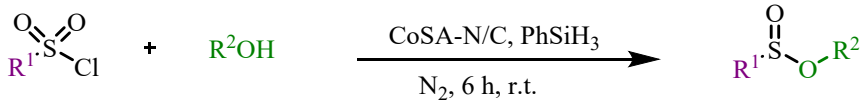
Synthesis of ZIF-8[3]

In a typical procedure, $Zn(NO_3)_2 \cdot 6H_2O$ (1.87 mmol, 558.0 mg) was dissolved in 15 mL of methanol to form a clear solution, which was subsequently injected into 15 mL of a clear methanol solution containing 2-methylimidazole (7.50 mmol, 616.0 mg). The mixed solution was then heated in a reactor (50 mL) at 120 ºC for 4 hours. The as-obtained white suspension was centrifuged and washed with methanol several times and dried at 80 ºC for 24 hours to obtain the ZIF-8 sample.

Synthesis of CoSA-N/C

The powder of Co_1Zn_{20}@BMOF was placed in a tube furnace and then heated to 900 ºC at a heating rate of 5 ºC/min under flowing argon gas. The samples were pyrolyzed at 900 ºC for 3 hours and then naturally cooled to room temperature to obtain the CoSA-N/C. M-NC (M = Cu, Ni, Mn, or Fe), NC, Co NPs, and Co_5-N/C were obtained using a similar procedure.

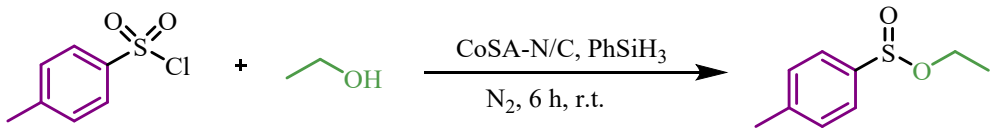
General procedure for the synthesis of sulfinate esters



1 **2** **3**

In a microwave reaction tube (10 mL) equipped with a stirring bar, **1** (0.25 mmol), 50 μL CoSA-N/C ink (0.2 mg, 0.42 ppm is calculated by dividing the Co element in content CoSA-N/C by the volume of **2**, and 1.14× 10^{-2} mol% based on Co sites; add 20 mg CoSA-N/C to 5 mL alcohol and ultrasonicated for 10 minutes to obtain an ink with evenly dispersed CoSA-N/C) was added. The tube was evacuated and flushed with N_2 three times. **2** (4 mL) and $PhSiH_3$ (47 μL, 0.38 mmol) were injected into the tube *via* a syringe or pipette. The reaction mixture was stirred for 6 h at room temperature. The mixture was concentrated in vacuo, and the crude product was subjected to flash column chromatography on silica gel to yield the desired product.

Decagram-scale synthesis



1g **2a** **3g**

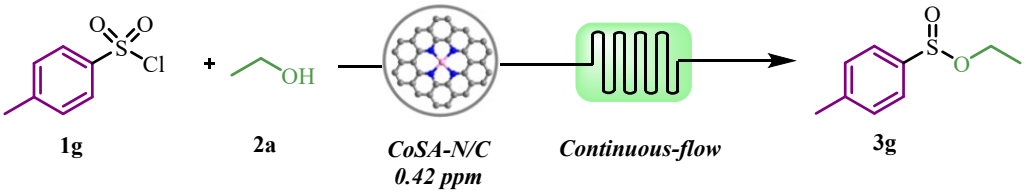
In an eggplant-shaped flask (1000 mL) equipped with a stirring bar, **1g** (10.00 g, 52.5 mmol), and CoSA-N/C (42.0 mg, 0.42 ppm, and 1.14× 10^{-2} mol% based on Co sites) were added. The flask was

evacuated and flushed with N_2 three times. **2a** (840 mL) and $PhSiH_3$ (10 mL, 78.75 mmol) were injected into the flask. The reaction mixture was stirred for 24 h. After completion, the catalyst was collected by filtration and washed with MeOH. The mixture was concentrated in vacuo, and the crude product was subjected to flash column chromatography on silica gel to yield the desired product. Then the colorless oil was obtained.

Cycle procedure

In an eggplant-shaped flask (1000 mL) equipped with a stirring bar, **1g** (10.00 g, 52.5 mmol), and CoSA-N/C (42.0 mg, 0.42 ppm, and 1.14×10^{-2} mol% based on Co sites) were added. The flask was evacuated and flushed with N_2 three times. **2a** (840 mL) and $PhSiH_3$ (10 mL, 78.75 mmol) were injected into the flask. The reaction mixture was stirred for 24 h. After completion, CoSA-N/C was collected by filtration, and **2a** was obtained using a distillation apparatus. The recovered **2a** and CoSA-N/C were put into the next cycle.

Continuous-flow reaction procedure



Add **1g** (10.00 g, 52.5 mmol), CoSA-N/C (42.0 mg, 0.42 ppm, and 1.14×10^{-2} mol% based on Co sites), **2a** (840 mL), and a stir bar to the mobile phase bottle, then degas with N_2 for 20 minutes. The inlet and outlet of the peristaltic pump were connected to the mobile phase bottle, and the peristaltic pump was started at a speed of 80 $mL\cdot min^{-1}$ to remove air from the tube. $PhSiH_3$ (10 mL, 78.75 mmol) was added to the mobile phase bottle with a syringe, then a N_2 balloon was inserted into the hole in the cap of the mobile phase bottle. In the continuous-flow setup, the tubing inner diameter is 1/8 inch (approximately 3.175 mm), and the conduit volume is 10 mL. Therefore, at a flow rate of 80 mL/min, the theoretical residence time is approximately 7.5 seconds (retention time = conduit volume/flow rate).

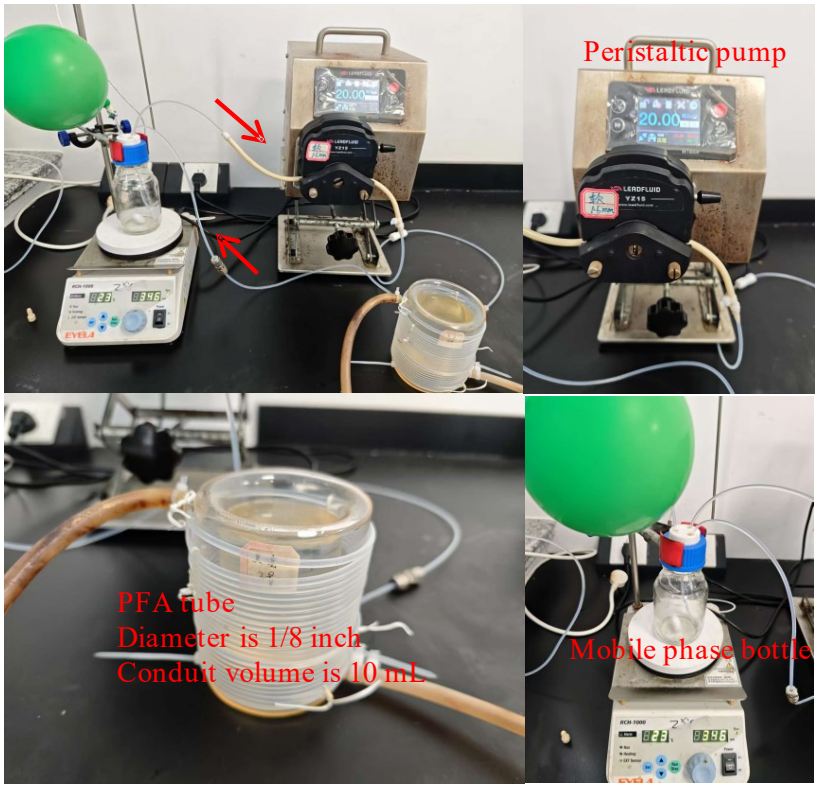
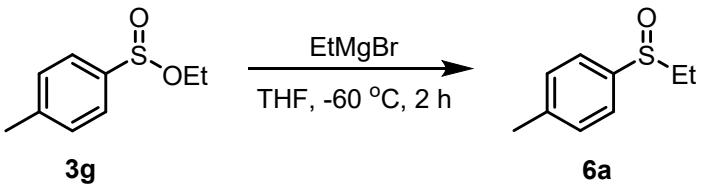


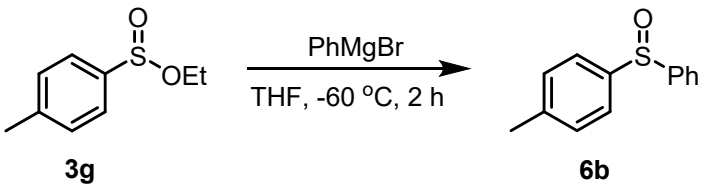
Fig.S1 The continuous-flow reaction setups.

Transformations of sulfinate ester



3g **6a**

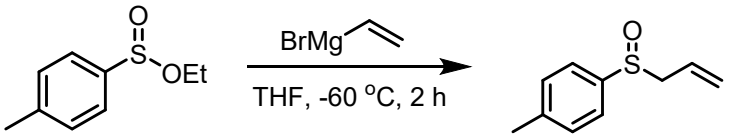
The microwave reaction tube (10 mL) equipped with a stirring bar was evacuated and flushed with N_2 three times. **3g** (97.0 mg, 0.50 mmol), tetrahydrofuran (THF, 3 mL), and ethylmagnesium bromide (EtMgBr, 1.0 mol/L in THF, 600 μL) were injected into the tube. The reaction mixture was stirred at -60 °C for 2 hours. After completion, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The filtrate was concentrated and subjected to flash column chromatography on silica gel to obtain the target product **6a** (yellow oil, 53.2 mg, 63% yield).



3g **6b**

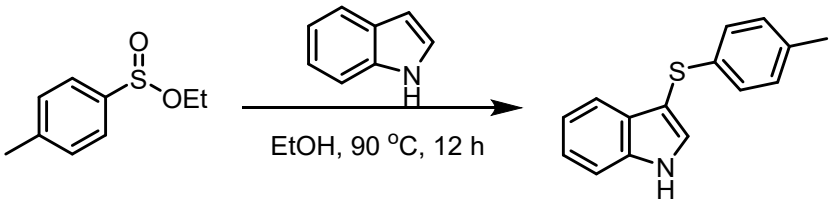
The microwave reaction tube (10 mL) equipped with a stirring bar was evacuated and flushed with N_2 three times. **3g** (97.0 mg, 0.50 mmol), THF (3 mL), and phenylmagnesium bromide (PhMgBr, 1.0 mol/L in THF, 600 μL) were injected into the tube. The reaction mixture was stirred at -60 °C for 2

hours. After completion, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The filtrate was concentrated and subjected to flash column chromatography on silica gel to obtain the target product **6b** (yellow oil, 55.6 mg, 51% yield).



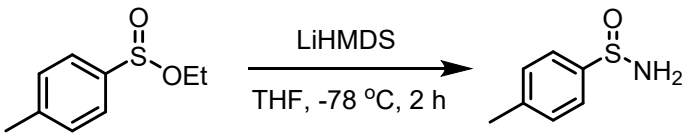
3g **6c**

The microwave reaction tube (10 mL) equipped with a stirring bar was evacuated and flushed with N_2 three times. **3g** (97.0 mg, 0.50 mmol), THF (3 mL), and vinylmagnesium bromide (1.0 mol/L in THF, 600 μL) were injected into the tube. The reaction mixture was stirred at -60 °C for 2 hours. After completion, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The filtrate was concentrated and subjected to flash column chromatography on silica gel to obtain the target product **6c** (colorless oil, 49.8 mg, 54% yield).



3g **6d**

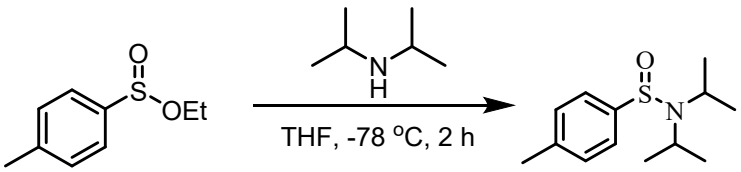
The microwave reaction tube (10 mL) equipped with a stirring bar was evacuated and flushed with N_2 three times. **3g** (97.0 mg, 0.50 mmol), indole (87.9 mg, 0.75 mmol), and EtOH (6 mL) were added to the tube. The reaction mixture was stirred at 90 °C for 12 hours.[4] After completion, the mixture was extracted with ethyl acetate. The filtrate was concentrated and subjected to flash column chromatography on silica gel to obtain the target product **6d** (colorless oil, 62.0 mg, 52% yield).



3g **6e**

The microwave reaction tube (10 mL) equipped with a stirring bar was evacuated and flushed with N_2 three times. **3g** (192.0 mg, 1.00 mmol), THF (4 mL), and lithium bis(trimethylsilyl)amide (LiHMDS, 1.5 mL, 1.0 mol/L in THF) were injected into the tube. The reaction mixture was stirred at -78 °C for

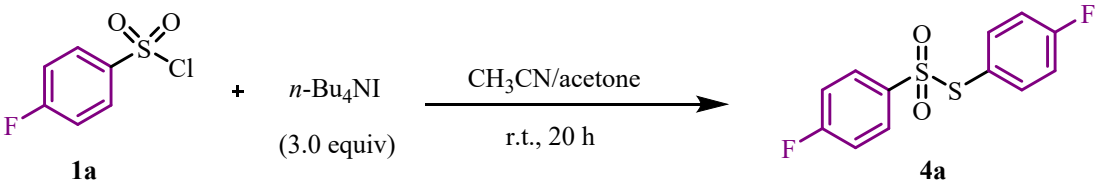
2 hours. After completion, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The filtrate was concentrated and subjected to flash column chromatography on silica gel to obtain the target product **6e** (white solid, 87.3 mg, 56% yield).



3g **6f**

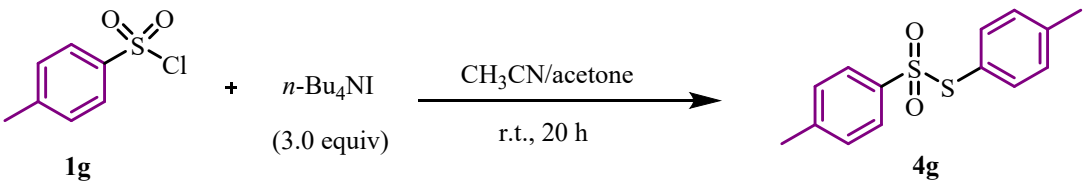
The microwave reaction tube (10 mL) equipped with a stirring bar was evacuated and flushed with N_2 three times. **3g** (192.0 mg, 1.00 mmol), diisopropylamine (800 μL), and THF (4 mL) were injected into the tube. The reaction mixture was stirred at -78 °C for 2 hours. After completion, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The filtrate was concentrated and subjected to flash column chromatography on silica gel to obtain the target product **6f** (colorless oil, 98.6 mg, 46% yield).

Synthesis of by-products[5]



1a **4a**

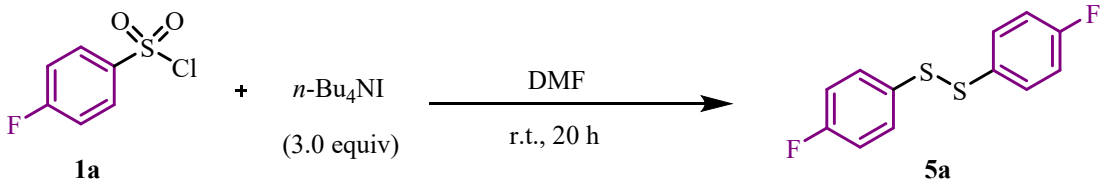
The solution of *n*-Bu_4NI (1.11 g, 3.0 mmol) in CH_3CN/acetone (2.5/0.5 mL) was slowly added to a solution of sulfonyl chloride (**1a**, 0.20 g, 1.0 mmol) in CH_3CN/acetone (2.5/0.5 mL) by a syringe. After stirring at room temperature for 20 hours, the solvents were evaporated. The mixture was concentrated in vacuo, and the desired pure product was purified using silica gel chromatography (PE : EA = 20 : 1) to give **4a** as a yellow oil (100 mg, 70% yield).



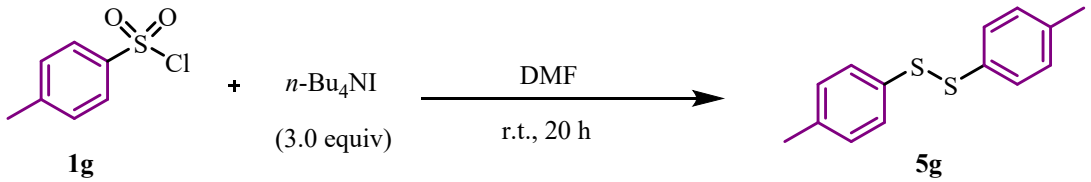
1g **4g**

The solution of *n*-Bu_4NI (1.11 g, 3.0 mmol) in CH_3CN/acetone (2.5/0.5 mL) was slowly added to a solution of sulfonyl chloride (**1g**, 0.19 g, 1.0 mmol) in CH_3CN/acetone (2.5/0.5 mL) by a syringe. After stirring at room temperature for 20 hours, the solvents were evaporated. The mixture was

concentrated in vacuo, and the desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **4g** as a colorless oil (103 mg, 74% yield).



The solution of *n*-Bu_4NI (1.11 g, 3.0 mmol) in DMF (3.0 mL) was slowly added to a solution of sulfonyl chloride (**1a**, 0.20 g, 1.0 mmol) in DMF (3.0 mL) by a syringe. After stirring at room temperature for 20 hours, the reaction mixture was extracted with Et_2O. The organic phase was washed with H_2O and brine, dried by Na_2SO_4, concentrated in vacuo. The crude product was purified using silica gel chromatography (PE: EA = 50: 1) to give **5a** as a white solid (94 mg, 74% yield).



The solution of *n*-Bu_4NI (1.11 g, 3.0 mmol) in DMF (3.0 mL) was slowly added to a solution of sulfonyl chloride (**1g**, 0.19 g, 1.0 mmol) in DMF (3.0 mL) by a syringe. After stirring at room temperature for 20 hours, the reaction mixture was extracted with Et_2O. The organic phase was washed with H_2O and brine, dried by Na_2SO_4, concentrated in vacuo. The crude product was purified using silica gel chromatography (PE: EA = 50: 1) to give **5g** as a white solid (98 mg, 79% yield).

E-factor calculation

The E-factor is defined as the mass ratio of total waste generated to the target product obtained, providing a practical metric for the rapid assessment of process waste, as established in prior literature.[6] For the model reaction, the total mass of the isolated product (**3g**) was 7.8 g. The total waste was calculated from the mass difference of the inputs and the incorporated product, comprising loss **1g**, **2a**, and $PhSiH_3$. This yields an E-factor of 4.8 $g_{waste}/g_{product}$ for this synthesis.

EcoScale calculation

The EcoScale calculation is an essential component of green metrics in organic synthesis, offering a quantitative evaluation of a reaction's environmental impact and efficiency. This calculation is performed by summing individual penalties assigned to various reaction parameters, as reported previously[6]. For the given reaction, penalties were attributed as follows: yield penalty of 8, cost of

components penalty of 0, safety penalty of 5, technical setup of 0, temperature/time of 1, and workup and purification of 10. With an ideal reaction scoring 100, the EcoScale value for this synthesis was calculated as 76 (100-24), categorizing it as excellent (>75). This result underscores the reaction's alignment with green chemistry principles, balancing high yield, reasonable costs, and minimal environmental and operational impact.

SI-2 Figures and tables of the characterization of catalysts and synthesis of sulfinate esters

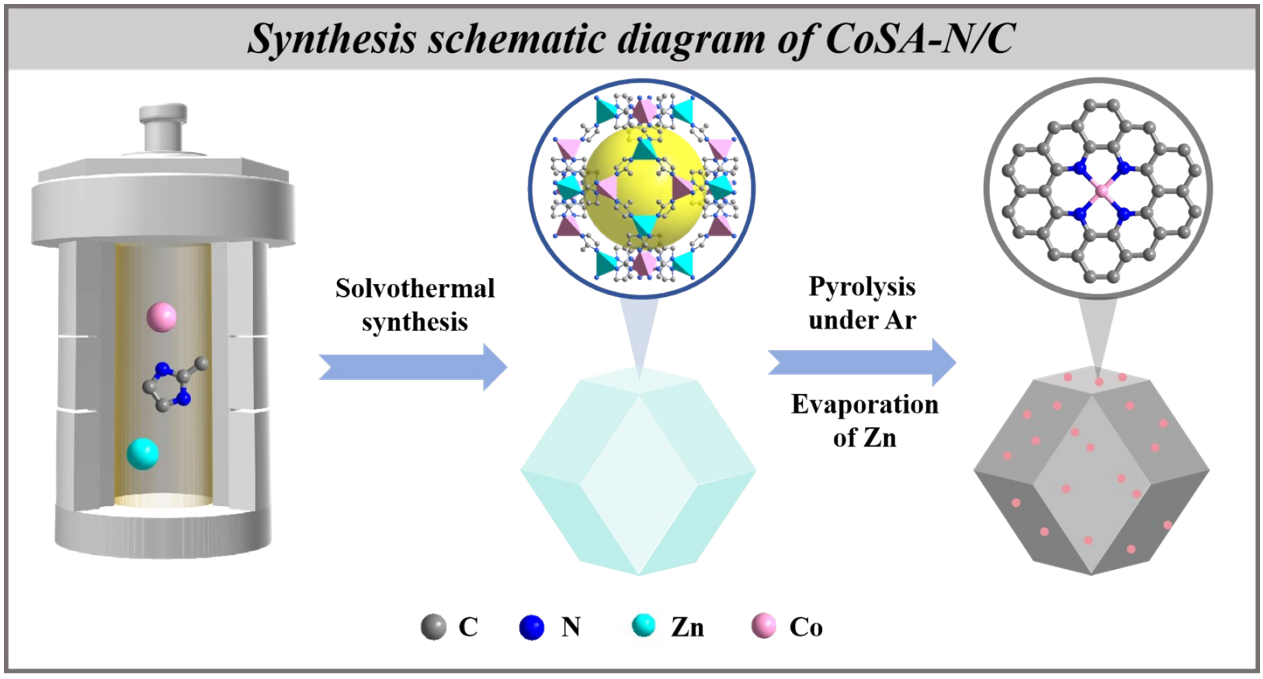


Fig.S2 Synthesis of CoSA-N/C.

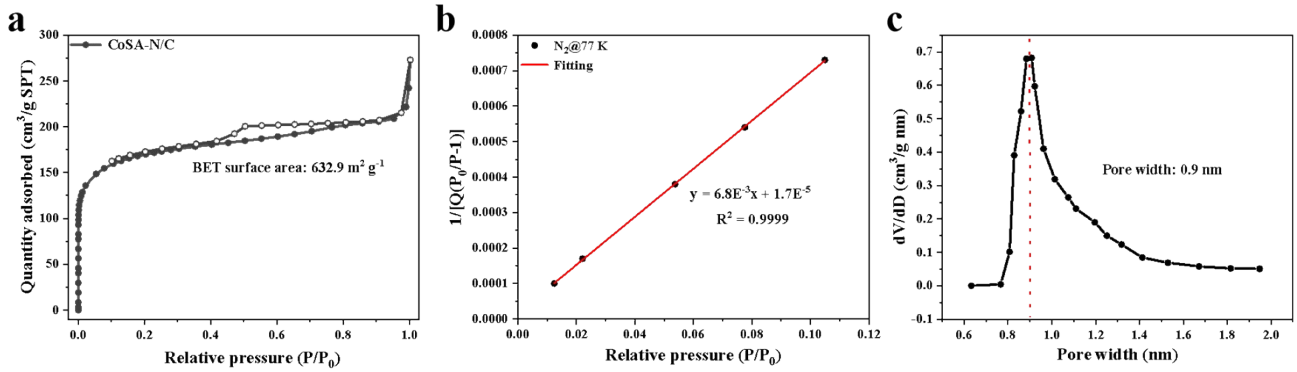


Fig.S3 (a) The N_2 adsorption-desorption isotherm of CoSA-N/C at 77 K; (b) BET calculation plot for CoSA-N/C based on its N_2 adsorption isotherm at 77 K; (c) Pore sizes evaluated by Horvath-Kawazoe mode from N_2 isotherms at 77 K.

Table S1 The data of ICP-OES results

M (g)	V0 (mL)	Element	C1 (mg/L)	Cx (mg/kg)	W (%)
0.0209	10	Co	17.6370	8438.7560	0.8439
0.0209	10	Co	17.7590	8497.1292	0.8497
0.0209	10	Co	17.6060	8423.9234	0.8424
0.0209	10	Zn	92.2380	44133.0144	4.4133
0.0209	10	Zn	92.5340	44274.6411	4.4275
0.0209	10	Zn	91.8720	43957.8947	4.3958

M: the weight of the sample; **V0**: The constant volume of the sample; **C1**: elemental concentration in sample solution; **Cx** and **W**: elemental content in sample;

Fig.S4 Gas chromatography mass spectrometry (GC-MS) confirmed the formation of siloxanes after the reaction.

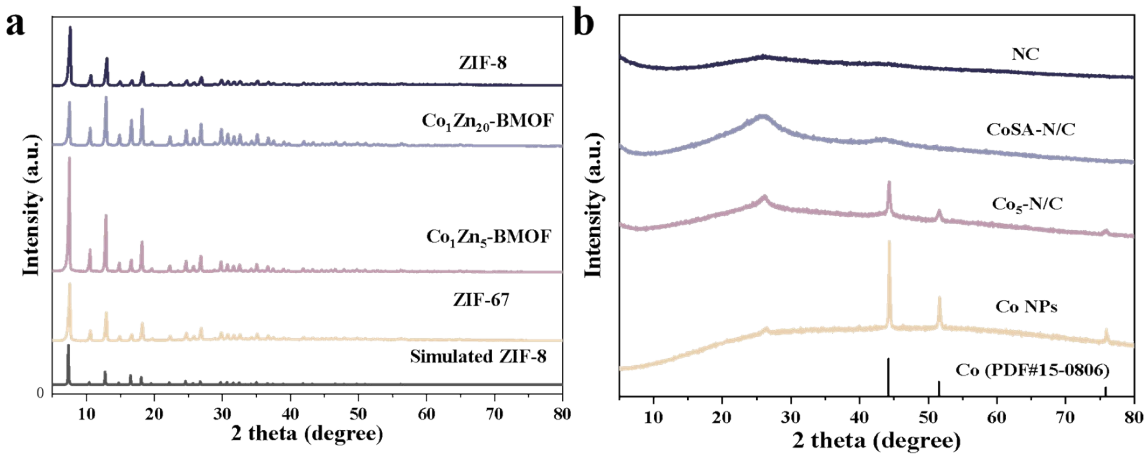


Fig.S5 The PXRD patterns of MOF precursors (a) and pyrolyzed materials(b).

The PXRD patterns of the synthesized MOF precursors align closely with the simulated pattern, confirming their phase purity and structural integrity (Fig.S5a). Subsequent pyrolysis yielded the NC and CoSA-N/C materials, whose PXRD patterns exhibit featureless profiles indicative of an amorphous carbon structure and the absence of crystalline phases (Fig.S5b). In contrast, the patterns for the Co NPs and Co_5-N/C materials show distinct diffraction peaks, confirming the presence of crystalline metallic cobalt nanoparticles (Fig.S5b).

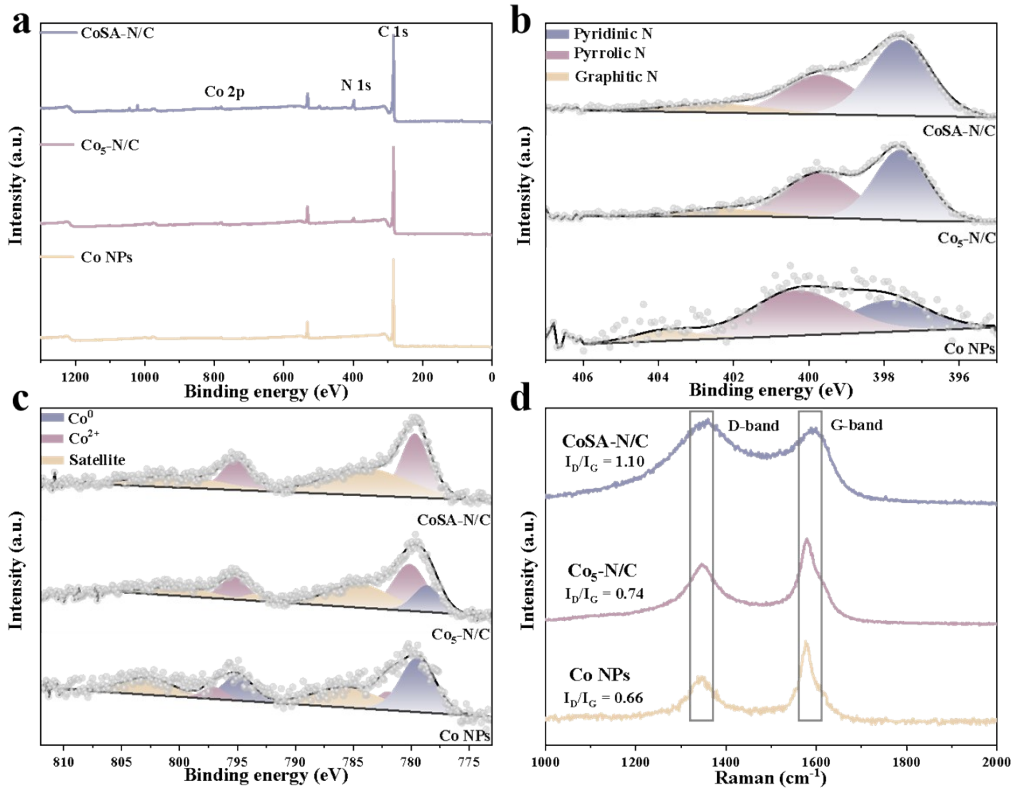
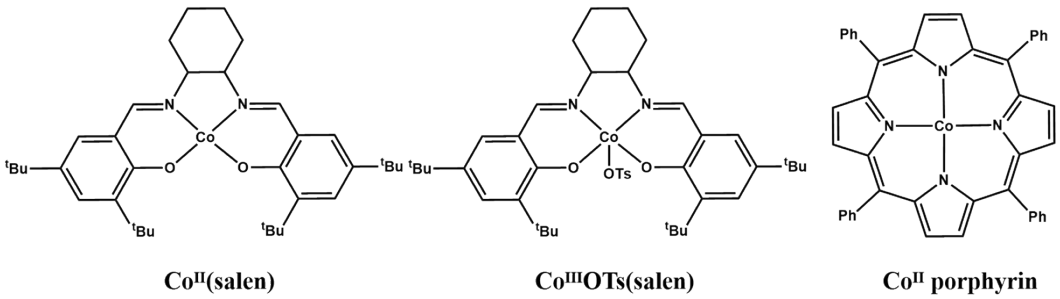


Fig.S6 The XPS survey (a), N 1s (b), and Co 2p (c) XPS spectra of Co NPs, Co_5-N/C, and CoSA-N/C; (d) The Raman spectra of Co NPs, Co_5-N/C, and CoSA-N/C.

CoSA-N/C has the highest content of pyridinic N and no Co^0 exist.



Co^{II}(salen) $Co^{III}OTs$(salen) Co^{II} porphyrin

Fig.S7 Co^{II}(salen), $Co^{III}OTs$(salen), and Co^{II} porphyrin.

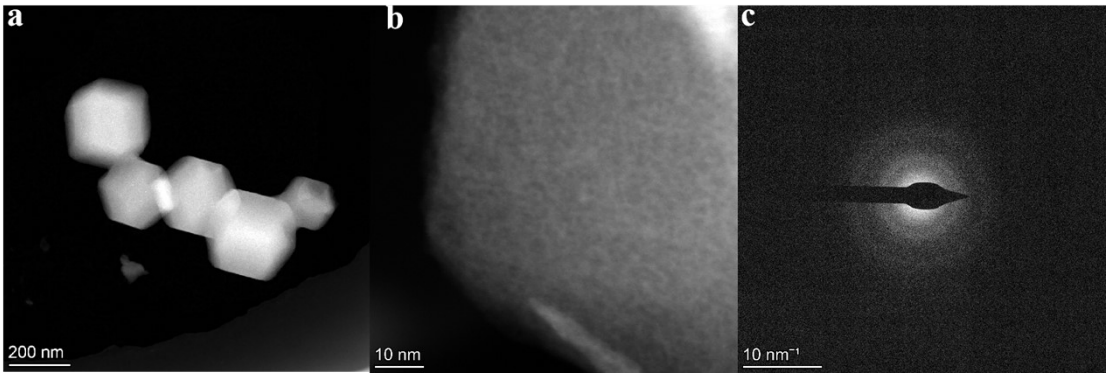


Fig.S8 (a) The TEM image of CoSA-N/C; (b) The HRTEM image of CoSA-N/C; (c) The selected area electron diffraction (SAED) image of CoSA-N/C.

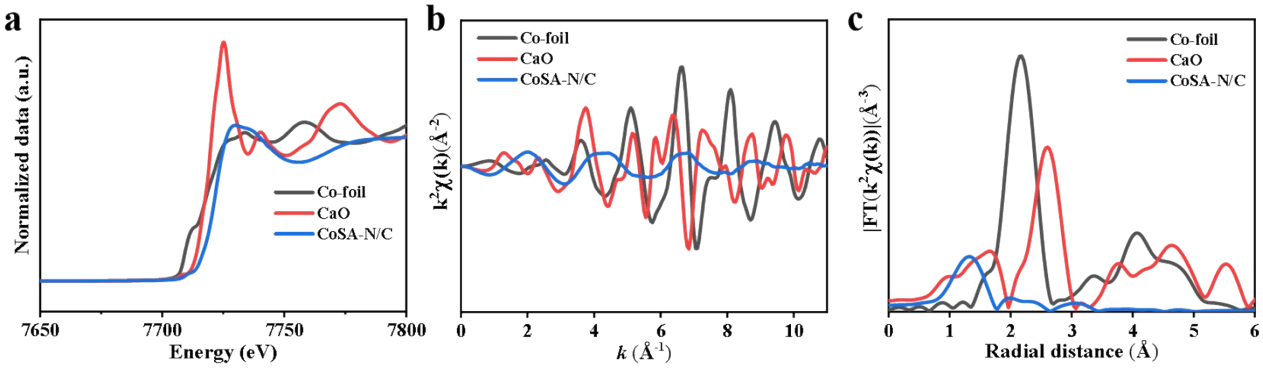


Fig.S9 (a) Normalised Co K-edge X-ray near absorption near edge spectra of the sample and reference materials; the corresponding Co K-edge Extended X-ray Absorption Fine Structure (EXAFS) shown in k^2 weighted (b) k-space and (c) R-space.

In the E-space plot, a preliminary analysis of the average oxidation state range is provided for reference. Generally, the K-edge is analyzed by comparing the absorption edge positions-a shift toward higher energy suggests a higher oxidation state. It can be inferred that the oxidation state of Co in CoSA-N/C is likely higher than that in CoO. The k-space data are primarily used to assess data quality. The oscillatory signal of the sample appears smooth and periodic, indicating acceptable data quality. Based on the R-space plot and fitting results, the sample exhibits a coordination environment dominated by Co-N bonds in the first coordination shell. No significant signals corresponding to Co-Co scattering were detected, suggesting the absence of notable cobalt aggregation.

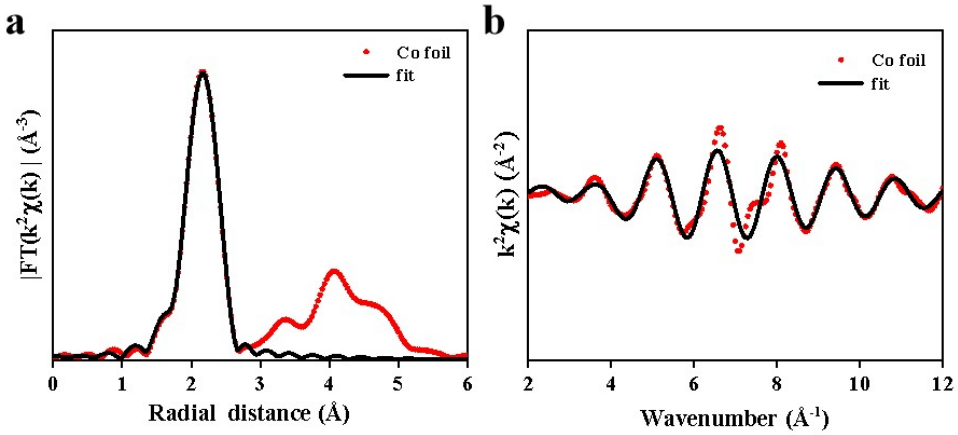


Fig.S10 The Co K-edge EXAFS (red) and fitting (black) of the Co foil shown in k^2 weighted (a) k-space and (b) R-space.

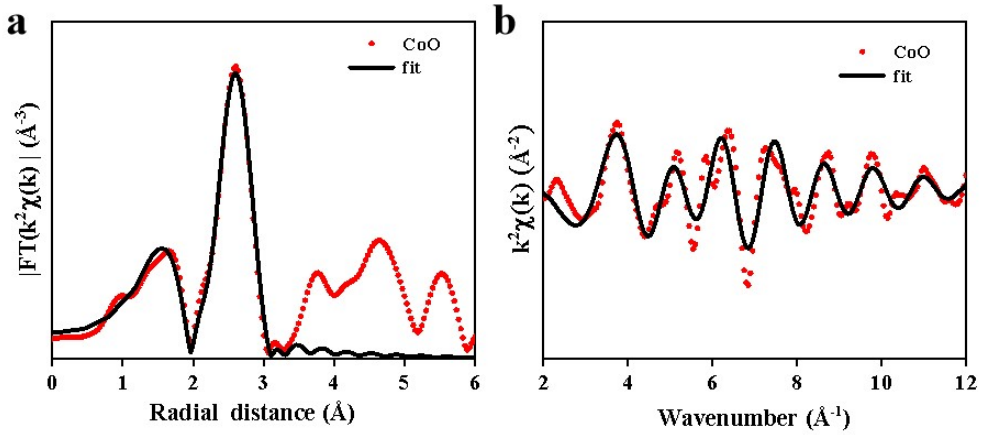


Fig.S11 The Co K-edge EXAFS (red) and fitting (black) of the CoO shown in k^2 weighted (a) k-space and (b) R-space.

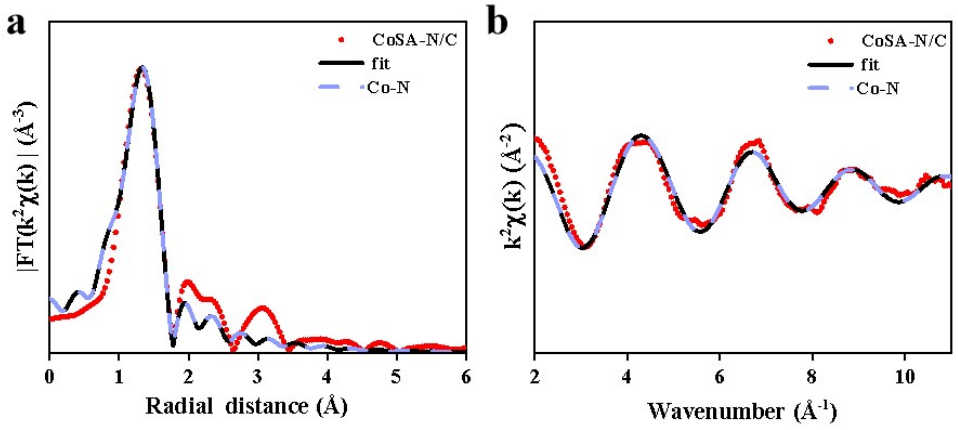
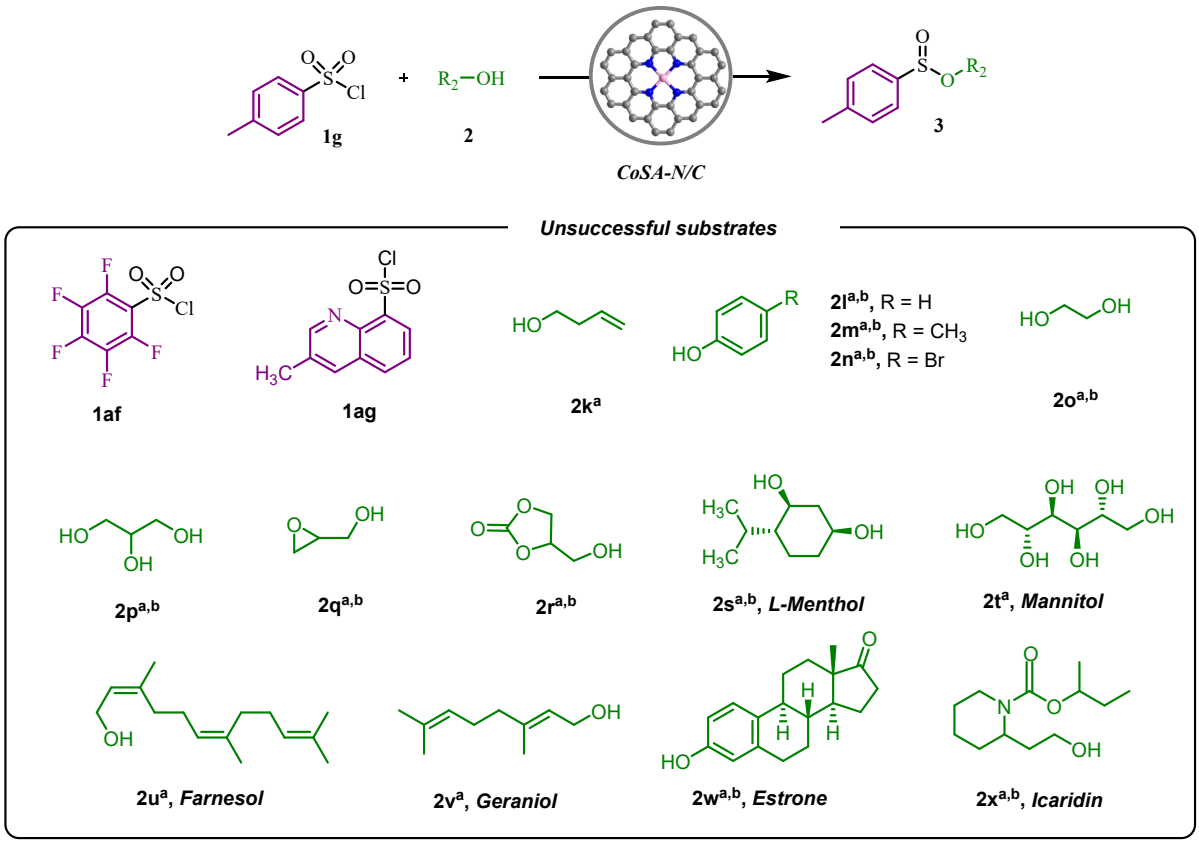


Fig.S12 The Co K-edge EXAFS (red) and fitting (black) of the CoSA-N/C shown in k^2 weighted (a) k-space and (b) R-space.

The fitting curves fit well with the experimental curves, indicating that the results in Table S5 are reliable.



[a]Reaction conditions: **1g** (0.25 mmol), $PhSiH_3$ (1.5 equiv.), CoSA-N/C (2 mg, 0.1 mol%, 4.2 ppm), and **2** (4 mL) at room temperature under a N_2 atmosphere for 6 h; [b]CH_2Cl_2 as the solvent (4 mL) with **2** (100 equiv.).

Scheme S1 Unsuccessful substrates.

The majority of alcohol and phenol substrates (**2k**-**2x**) failed to undergo the desired transformation. **2k** bearing an olefinic group may be disfavored due to competing reactivity or coordination. Phenolic compounds (**2l**-**2n**) exhibited no conversion, likely a result of their relatively low nucleophilicity. Polyols (**2o**-**2p**) likewise remained unreactive, and even partially protected derivatives (**2q**-**2r**) did not yield the corresponding sulfinate esters. We speculate that high viscosity of these substrates may impede mass transfer under the reaction conditions. Furthermore, various natural product-derived alcohols, which are typically solid or highly viscous liquids (**2s**-**2x**), have been proved unsuitable for this conversion.

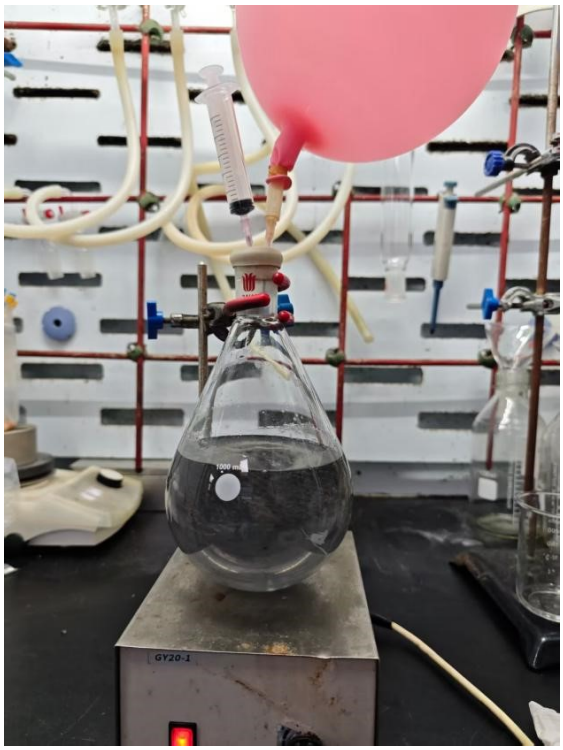


Fig.S13 The decagram-scale reaction setup.

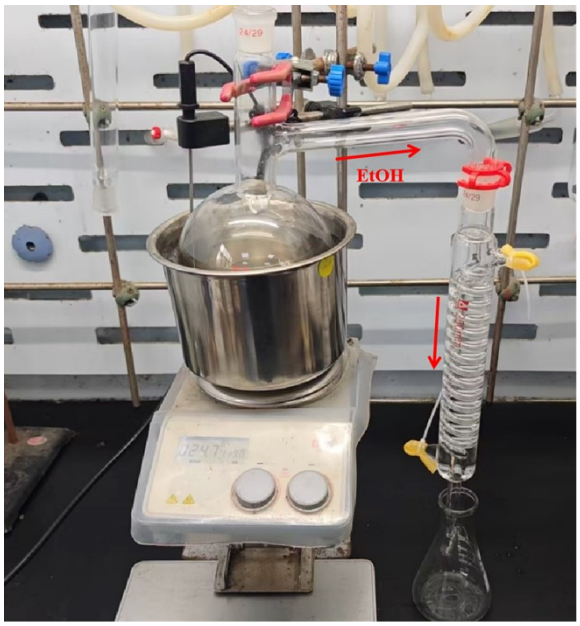


Fig.S14 The distillation setup for the recovery of ethanol.

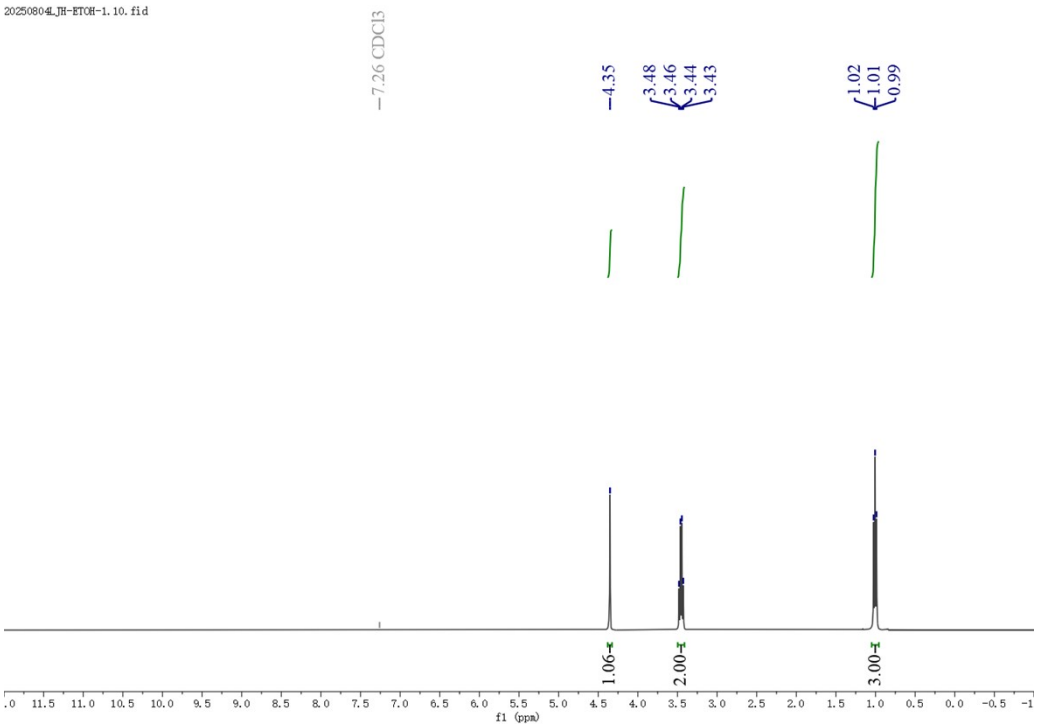


Fig.S15 The crude ^{1}H NMR spectrum of recovered ethanol by distillation.

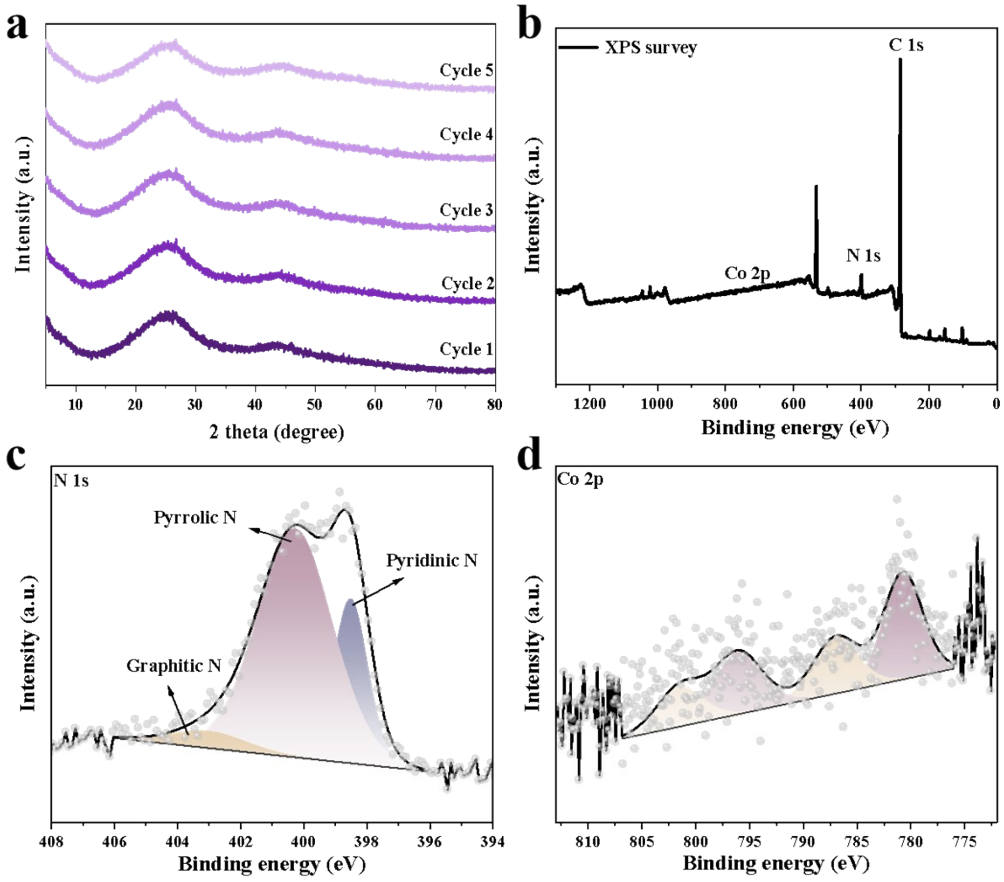


Fig.S16 (a) The PXRD patterns of recovered CoSA-N/C; (b-d) The XPS spectra of recovered CoSA-N/C.

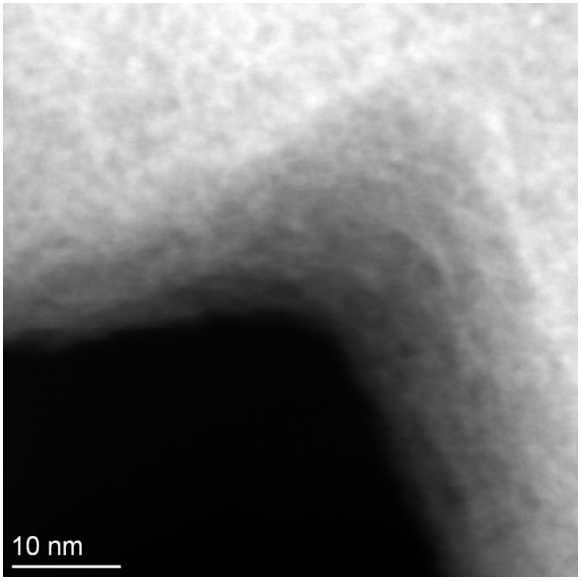
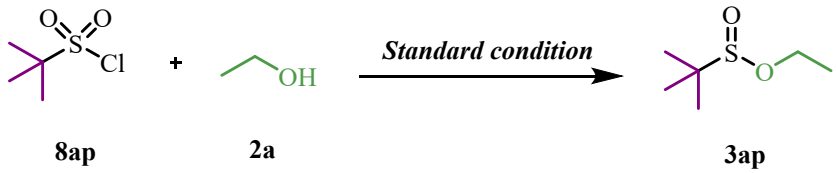


Fig.S17 The HRTEM image of recovered CoSA-N/C.



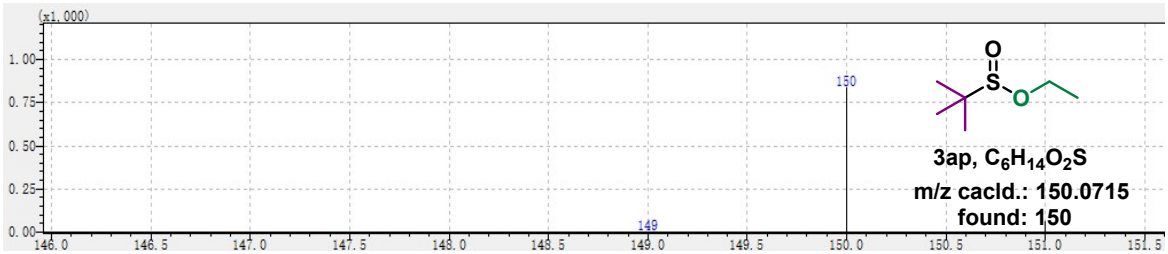


Fig.S18 The GC-MS spectrum of the crude reaction mixture of **3ap** from **8ap**.

We used gas chromatography-mass spectrometry (GC-MS) to detect the system with **8ap** as the starting substrate and further found the existence of the target product **3ap** after reaction.

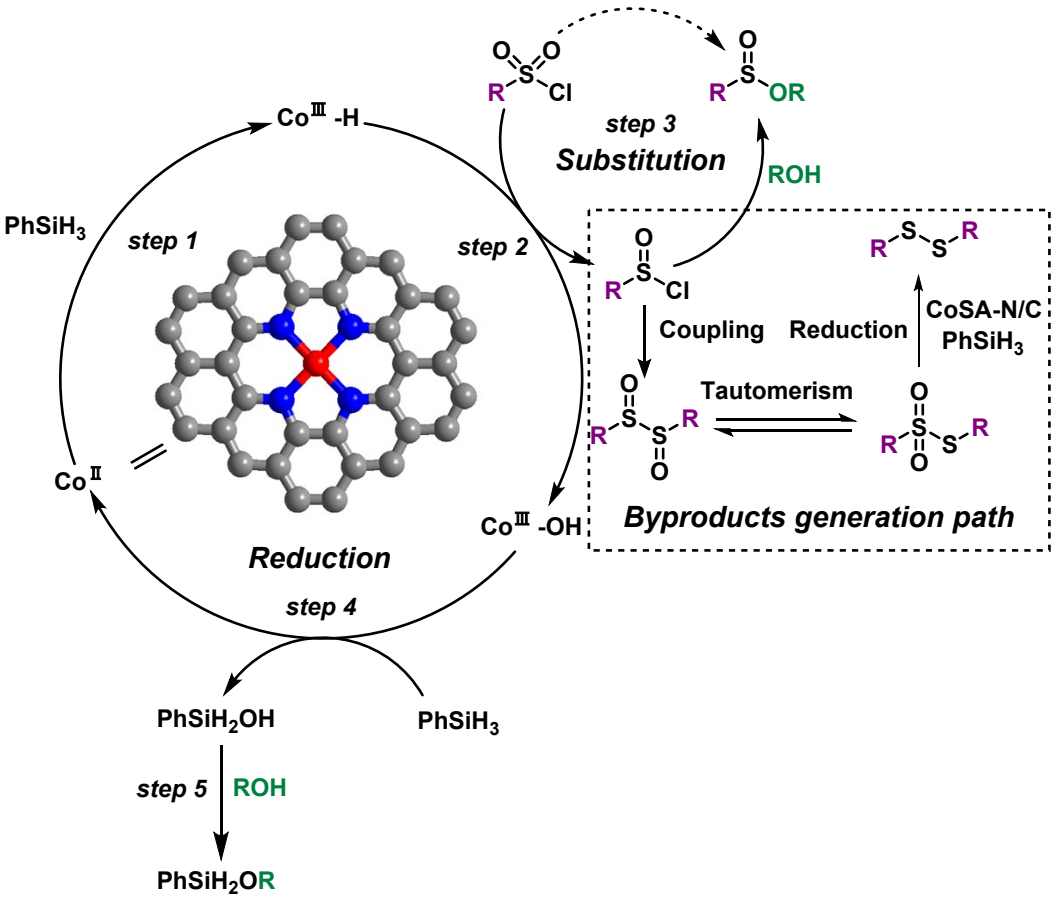
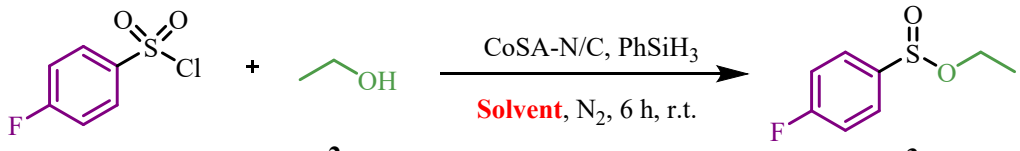


Fig.S19 The possible mechanism.

The high reactivity of the sulfinyl chloride intermediate leads to a competition between the desired alcohol substitution pathway and an alternative coupling pathway (Fig. S19). In the latter, sulfinyl chloride species undergo coupling to form an unstable disulfoxide, which tautomerizes to the more stable thiosulfonate (**4**). Subsequently, **4** can then undergo a catalyst-mediated reduction analogous to the main pathway, yielding disulfide (**5**).

SI-3 Tables of optimization of reaction conditions and coordination parameters of catalysts

Table S2 ptimization of solvents.



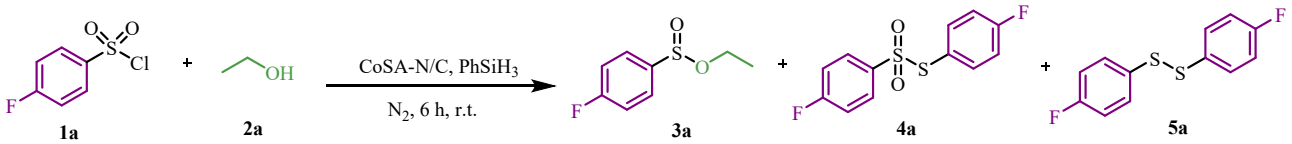
1a **2a** **3a**

Entry	Solvent	Yield (%)[a]
1	EtOH	73[b]
2	DCM	10
3	1,4-dioxane	10
4	EA	3
5	CH_3CN	3
6	DMF	4
7	DMSO	2

[a]Reaction conditions: 0.25 mmol **1a**, 1.5 equiv. $PhSiH_3$, 10 equiv. **2a**, 0.2 mg (0.42 ppm) CoSA-N/C, and 4 mL solvent at room temperature under a N_2 atmosphere for 6 h.[b]4 mL **2a.** Yield was determined by ^{19}F NMR with CF_3OPh as the internal standard.

Among all solvents, ethanol has the highest yield of **3a**. In addition, ethanol also exhibits greener properties compared to other organic solvents.

Table S3 Optimization of reaction conditions.



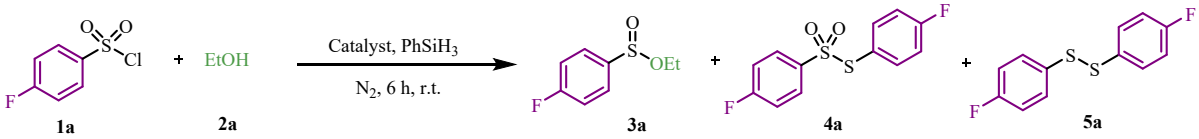
1a **2a** **3a** **4a** **5a**

Entry	Deviation from the standard conditions	Yield of 3a (%)[a]	Yield of 4a (%)[a]	Yield of 4a (%)[a]
1	none	77	trace	trace
2	Ph_3SiH instead of $PhSiH_3$	58	7	trace
3	Ph_2SiH_2 instead of $PhSiH_3$	68	6	trace
4	HCOONa instead of $PhSiH_3$	0	trace	trace
5	HBpin instead of PhSiH3	0	17	trace
6	without reductant	0	0	0
7	0.25 mol/L **1a** (1 mL **2a**)	43	trace	trace
8	0.125 mol/L **1a** (2 mL **2a**)	64	trace	trace
9	0.042 mol/L **1a** (6 mL **2a**)	32	trace	trace
10	Air	0	15	trace
11	reaction for 1 h	20	trace	trace
12	reaction for 3 h	69	7	trace
13	reaction for 10 h	53	6	10
14	0.5 equiv. PhSiH3	31	11	trace
15	2.0 equiv. PhSiH3	86	7	trace

Standard conditions: 0.25 mmol **1a**, 1.5 equiv. $PhSiH_3$, 0.2 mg (0.42 ppm) CoSA-N/C, and 4 mL **2a** at room temperature under a N_2 atmosphere for 6 h. [a]Yield was determined by ^{19}H NMR with CF_3OPh as the internal standard.

Table S3 shows that the reductant and inert atmosphere are necessary for this reaction (Entries 6 and 10). The optimal reaction time was determined to be 6 hours. Shorter or longer durations may result in insufficient conversion or overreduction of **1a**, respectively (Entries 11-13). Insufficient amounts of reductant led to a low conversion of **1a**, but excessive reductant did not enhance the reaction yield (Entries 14-15).

Table S4 Investigation on catalytic activity of Fe- or Mn-N/C



1a 2a 3a 4a 5a

Entry	Catalyst	3a (%)	4a (%)	5a (%)
1	Mn-N/C (5 mg)	64	9	trace
2	Fe-N/C (5 mg)	57	trace	trace
3	recycle Mn-N/C (5 mg)	52	trace	trace
4	recycle Fe-N/C (5 mg)	45	trace	trace
5	Mn-N/C (0.2 mg)	36	trace	trace
6	Fe-N/C (0.2 mg)	32	trace	trace

[a]Standard conditions: 0.25 mmol **1a**, 1.5 equiv. $PhSiH_3$, catalyst, and 4 mL **2a** at room temperature under a N_2 atmosphere for 6 h. Yield was determined by ^{19}F NMR with CF_3OPh as the internal standard.

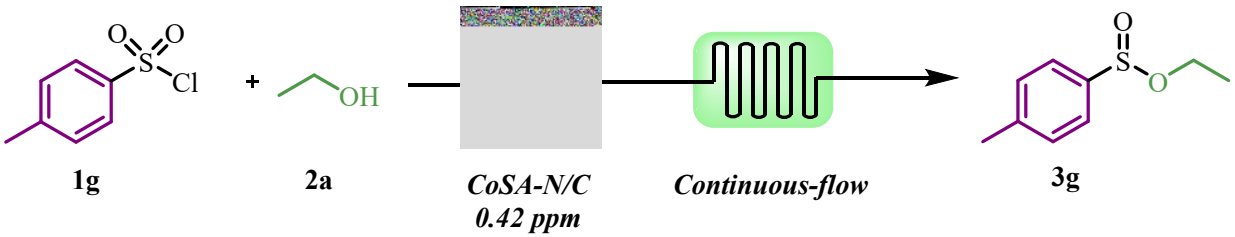
Recyclic experiments demonstrated a significant decrease in reaction activity (Table S4), which is likely attributable to the leaching of metal species. Fe and Mn atoms tend to form clusters or nanoparticles during pyrolysis or under reaction conditions, which are susceptible to etching by acidic components in the system, leading to inferior stability. Therefore, considering the balance between catalytic activity and structural stability, CoSA-N/C was used as the optimal catalyst in this system.

Table S5 EXAFS fitting parameters at the Co *K*-edge for various samples.

Sample	Shell	CNa	R(Å)b	σ 2(Å2)c	∆ E0(eV)d	K-range/Å-1	R-range/Å	R factor
Co foil	Co-Co	12*	2.49±0.01	0.0064±0.0002	8.2±0.1	3.0-12.0	1.0-3.0	0.0011
CoO	Co-O	6.0±1.0	2.10±0.01	0.0113±0.0029	-3.5±0.3	3.3-12.2	1.0-3.1	0.0082
	Co-Co	11.7±1.0	3.00±0.01	0.0087±0.0008				
Co	Co-N	4.0±0.6	1.88±0.01	0.0050±0.0019	-9.8±0.9	2.5-10.5	1.0-2.0	0.0088

[a]*CN*, coordination number; [b]*R*, the distance between absorber and backscatter atoms; [c]σ^2, Debye-Waller factor, Debye-Waller factor to account for both thermal and structural disorders; [d]ΔE_0, inner potential correction; *R* factor indicates the goodness of the fit. $S0^2$ was fixed to 0.748, accourding to the experimental EXAFS fit of Co foil by fixing *CN* as the known crystallographic value. * This value was fixed during EXAFS fitting. Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as CN ± 20%; R ± 1%; σ2 ± 20%; ΔE0 ± 20%. A reasonable range of EXAFS fitting parameters: $0.700 < S_0^2 < 1.000$; $CN > 0$; $\sigma^2 > 0$ Å^2; $|\Delta E_0| < 15$ eV; *R* factor < 0.02.

Table S6 Optimization for the continuous-flow reaction.



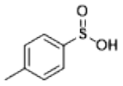
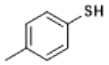
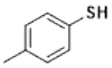
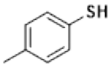
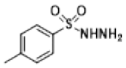
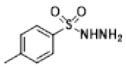
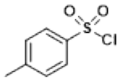
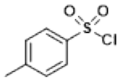
Concentration of 1g	Flow rate (mL/min)	Reaction time (h)	Yield (%)[a]	TOF ($^{-1}$h)
0.06 mol / L	80	1	78	6842
0.12 mol / L	80	1	24	4189
0.12 mol / L	80	4	43	1886
0.06 mol / L	40	1	38	3339
0.06 mol / L	120	1	65	5702
0.06 mol / L	160	1	50	4365
0.06 mol / L	80	2	68	2989

Reaction conditions: 5.25 mmol (1.0 g) **1g**, 1.5 equiv. $PhSiH_3$, 4.2 mg (0.01 mol%, 0.42 ppm) CoSA-N/C, and **2a** at room temperature under a N_2 atmosphere.[a]Isolated yield

By optimizing the concentration of **1g** and flow rate, the optimal substrate concentration is 0.06 mol/L, as higher concentrations lead to a significant drop in yield. The optimal flow rate and total reaction time are 80 mL/min and 1 hour, respectively. Under these conditions, the TOF reaches 6842 h^{-1}.

The marked improvement in reaction efficiency under continuous-flow conditions can be attributed to several key factors. Firstly, the turbulent flow regime generated by high-speed circulation enhances mass transfer, thereby boosting overall catalytic efficiency. Secondly, continuous circulation ensures sustained and dynamic contact between the solid catalyst and liquid reactants. This not only facilitates substrate diffusion but also improves the utilization of active sites. Moreover, the flow system enables the timely removal of reaction by-products (*e.g.*, siloxanes derived from $PhSiH_3$), preventing their accumulation on the catalyst surface or within pores. Collectively, these advantages lead to the significantly shortened reaction time and higher TOF observed.

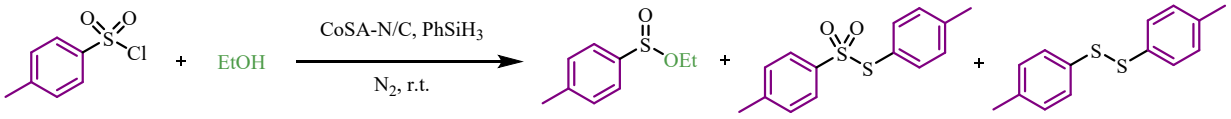
Table S7 Comparison of the existing synthetic methods for sulfinate esters.

Sulfur substrate	Catalyst	Additive	Drive form	Solvent	TOF (h^{-1})	E-factor	Ref.
	—	ethyl 2-isocyanoacetate	r.t.	CH_2Cl_2 (Toxic solvents)	—	30.0	7
	Homogeneous $Ni(ClO_4)_2$	2,2'-bipyridine, $LiClO_4$	Electricity	CH_3CN (Toxic solvents)	0.77	7.5	8
	—	$^{n}Bu4NBF_4$	Electricity	CH_2Cl_2 (Toxic solvents)	—	58.2	9
	Heterogeneous Co/N-SiO_2-AC	K_2CO_3	60 ℃	Ethanol (green solvent)	2.5	14.4	10
	—	$NaHSO_3$	80 ℃	Ethanol (green solvent)	—	38.7	11
	Cu(OTf)2	—	80 ℃	Ethanol (green solvent)	4.6	19.5	12
	—	$CH_2(OH)SO_2Na$	80 ℃	Ethanol (green solvent)	—	127.7	13
	**CoSA-N/C**	**$PhSiH_3$**	**r.t.**	**Ethanol (green solvent)**	**1183**	**4.8**	**This work**

r.t. : Room temperature

A systematic comparison with prior sulfinate ester syntheses is presented in Table S7. The comparison is structured across multiple criteria, including substrate type, catalyst type, additive requirement, solvent greenness, TOF, E-factor, and reaction driving mode. The analysis clearly highlights the safety, efficiency, and waste-minimization benefits of our single-atom catalysis approach.

Table S8 Control experiment on factors affecting by-products formation.



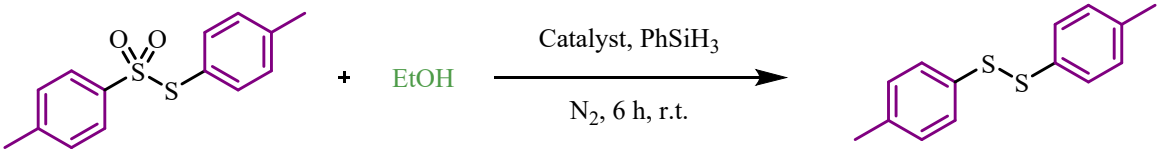
1g **2a** **3g** **4g** **5g**

Entry	Reaction time (h)	2a (mL)	3a (%)	4a (%)	5a (%)
1	6	4	84	trace	trace
2	3	1	21	50	trace
3	6	1	26	28	36

Reaction conditions: 0.25 mmol **1g**, 1.5 equiv. $PhSiH_3$, 0.2 mg CoSA-N/C (0.01 mol%) and **2a** at room temperature under a N_2 atmosphere. Yield was isolated yield.

The influence of reaction conditions on by-product formation was systematically investigated (Table S8). Control experiments identified the concentration of sulfonyl chloride (**1g**) as the primary factor governing thiosulfonate (**4g**) formation, with higher concentrations favoring its generation (Entry 2). Extending the reaction time led to a decrease in **4g** yield alongside an increase in disulfide (**5g**) yield, indicating that **5g** formation is time-dependent (Entry 3).

Table S9 Controlled experiments on the formation mechanism of **5g**



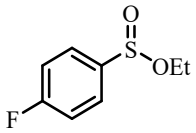
4g **2a** **5g**

Entry	Catalyst	5g (%)
1	CoSA-N/C (0.2 mg)	76
2	None	trace

Reaction conditions: 0.25 mmol **4g**, 1.5 equiv. $PhSiH_3$, and 4 mL **2a** at room temperature under a N_2 atmosphere for 6 h. Yield was isolated yield.

The proposed formation mechanism of **5g** was validated (Table S9). Under standard catalytic conditions, **4g** was efficiently converted to **5g** in 76% yield (Entry 1). In contrast, no reaction occurred in the absence of the CoSA-N/C catalyst (Entry 2). This result confirms that **4g** indeed undergoes a similar catalyst-dependent reduction process to form **5g**.

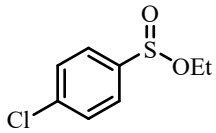
SI-4 Analytic data of products



Ethyl 4-fluorobenzenesulfinate (**3a**)[14]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3a** as a colorless oil (33.2 mg, 71% yield).

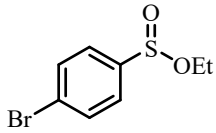
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 2H), 7.25 – 7.19 (m, 2H), 4.14 – 4.08 (m, 1H), 3.77 – 3.70 (m, 1H), 1.31 – 1.26 (t, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -107.0.



Ethyl 4-chlorobenzenesulfinate (**3b**)[15]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3b** as a colorless oil (48.1 mg, 94% yield).

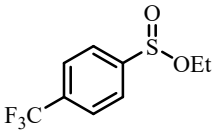
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 4.09 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.71 (dq, *J* = 10.0, 7.1 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H).



Ethyl 4-bromobenzenesulfinate (**3c**)[14]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3c** as a colorless oil (46.4 mg, 75% yield).

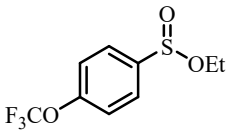
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 4.12 – 4.05 (m, 1H), 3.75 – 3.66 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).



Ethyl 4-(trifluoromethyl)benzenesulfinate (**3d**)[15]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3d** as a yellow oil (43.8 mg, 74% yield).

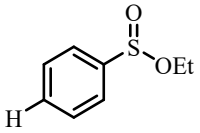
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (q, *J* = 8.2 Hz, 4H), 4.24 – 4.06 (m, 1H), 3.82 – 3.69 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.0.



Ethyl 4-(trifluoromethoxy)benzenesulfinate (**3e**)[15]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3e** as a colorless oil (56.4 mg, 89% yield).

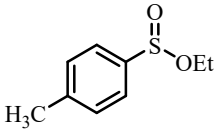
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.13 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.75 (dq, *J* = 9.9, 7.0 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.8.



Ethyl benzenesulfinate (**3f**)[14]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3f** as a yellow oil (30.4 mg, 71% yield).

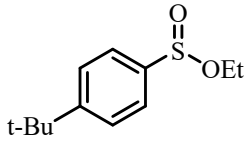
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.52 (dd, *J* = 5.3, 2.0 Hz, 3H), 4.15 – 4.03 (m, 1H), 3.75 – 3.66 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).



Ethyl 4-methylbenzenesulfinate (**3g**)[14]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3g** as a yellow oil (38.6 mg, 84% yield).

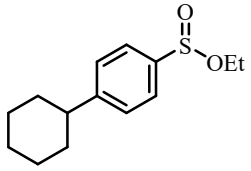
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.07 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.69 (dq, *J* = 10.0, 7.1 Hz, 1H), 2.40 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).



Ethyl 4-(*tert*-butyl)benzenesulfinate (**3h**)[16]

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3h** as a yellow oil (46.6 mg, 83% yield)

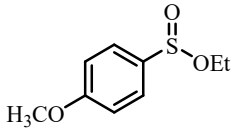
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 4.11 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.74 (dq, *J* = 10.0, 7.1 Hz, 1H), 1.34 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H).



Ethyl 4-cyclohexylbenzenesulfinate (**3i**)

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3i** as a colorless oil (55.3 mg, 88% yield).

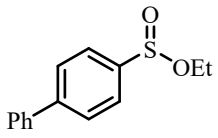
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.13 – 4.07 (m, 1H), 3.77 – 3.71 (m, *J* = 10.0, 7.1 Hz, 1H), 2.58 – 2.53 (m, *J* = 11.6, 8.1, 3.4 Hz, 1H), 1.96 – 1.69 (m, 6H), 1.45 – 1.36 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 152.7, 142.2, 127.6, 125.3, 61.1, 44.7, 34.3, 26.8, 26.1, 15.7. **HRMS (ESI)** calcd. For $C_{14}H_{21}O_2S^+$ $(M+H)^+$: 253.1257, found: 253.1252. **IR (neat, cm^{-1}):** 2923 (s), 2851 (w), 1595 (w), 1448 (w), 1385 (w), 1131 (s), 1004 (m), 881 (s), 824 (m), 709 (m), 592 (m), 462 (w).



Ethyl 4-methoxybenzenesulfinate (**3j**)[16]

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3j** as a yellow oil (47.4 mg, 95% yield).

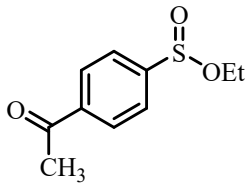
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 4.08 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.86 (s, 3H), 3.72 (dq, *J* = 10.0, 7.1 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H).



Ethyl [1,1'-biphenyl]-4-sulfinate (**3k**)[16]

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3k** as a yellow oil (54.6 mg, 89% yield).

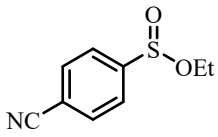
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.74 (m, 4H), 7.64 – 7.58 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 4.22 – 4.10 (m, 1H), 3.81 – 3.77 (m, dq, *J* = 10.0, 7.1 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).



Ethyl 4-acetylbenzenesulfinate (**3l**)

The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **3l** as a white solid (36.6 mg, 69% yield).

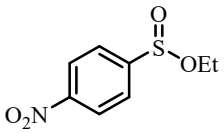
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 4.12 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.72 (dq, *J* = 10.0, 7.1 Hz, 1H), 2.62 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.1, 149.2, 139.8, 128.9, 125.7, 61.7, 26.8, 15. 6. **HRMS (ESI)** calcd. For $C_{10}H_{13}O_3S^+$ (M+H) $^+$: 213.0580, found: 213.0577. **IR (neat, cm^{-1}):** 2923 (s), 2853 (m), 1692 (m), 1594 (w), 1463 (w), 1398 (w), 1261 (w), 1135 (w), 866 (w), 698 (w), 500 (w).



Ethyl 4-cyanobenzenesulfinate (**3m**)[16]

The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **3m** as a yellow oil (39.3 mg, 81% yield).

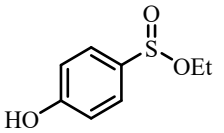
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 4H), 4.16 (dq, *J* = 9.9, 7.1 Hz, 1H), 3.77 (dq, *J* = 9.9, 7.1 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H).



Ethyl 4-nitrobenzenesulfinate (**3n**)

The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **3n** as a yellow oil (48.8 mg, 91% yield).

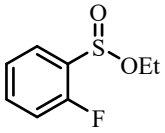
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H), 4.20 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.80 (dq, *J* = 10.0, 7.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.2, 150.1, 126.7, 124.2, 62.4, 15.6. **HRMS (ESI)** calcd. For $C_{10}H_8NO_4S^+$ $(M+H)^+$: 216.0325, found: 216.0323. **IR (neat, cm^{-1}):** 2953 (w), 2923 (s), 2853 (w), 1529 (s), 1349 (s), 1183 (s), 996 (m), 915 (m), 854 (w), 745 (w), 611 (m), 463 (m).



Ethyl 4-hydroxybenzenesulfinate (**3o**)

The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **3o** as a colorless oil (44.6 mg, 93% yield).

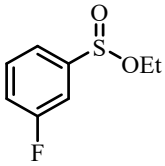
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (m, *J* = 8.7, 2.1 Hz, 2H), 7.07 – 6.91 (m, 2H), 4.18 – 4.02 (m, 1H), 3.75 – 3.80 (dq, *J* = 9.6, 6.9, 2.2 Hzm, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.13, 134.94, 127.25, 116.15, 61.27, 15.55. **HRMS (ESI)** calcd. For $C_8H_9O_3S^-$ $(M-H)^-$: 185.0278, found: 185.0267. **IR (neat, cm^{-1}):** 2923 (s), 2853 (m), 1706 (w), 1583 (m), 1496 (w), 1375 (w), 1284 (m), 1133 (s), 1075 (m), 835 (m), 670 (w), 586 (w), 518 (w).



Ethyl 2-fluorobenzenesulfinate (**3p**)[15]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3p** as a colorless oil (39.4 mg, 84% yield).

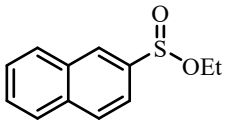
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.83 (m, 1H), 7.58 – 7.49 (m, 1H), 7.34 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.16 – 7.12 (m, 1H), 4.17 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.84 (dq, *J* = 10.0, 7.1 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.4.



Ethyl 3-fluorobenzenesulfinate (**3q**)[15]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3q** as a colorless oil (34.4 mg, 73% yield).

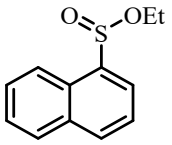
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.43 (m, 3H), 7.31 – 7.22 (m, 1H), 4.19 – 4.12 (m, 1H), 3.79 – 3.72 (m, 1H), 1.32 (td, *J* = 7.1, 1.3 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -109.9.



Ethyl naphthalene-2-sulfinate (**3r)**[16]

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3r** as a colorless oil (49.9 mg, 91% yield).

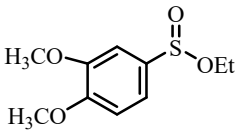
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 1.7 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.92 – 7.87 (m, 1H), 7.70 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.59 (ddd, *J* = 6.8, 4.1, 1.7 Hz, 2H), 4.15 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.72 (dq, *J* = 10.0, 7.0 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H).



Ethyl naphthalene-1-sulfinate (**3s**)[14]

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3s** as a colorless oil (44.6 mg, 81% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.68 – 7.54 (m, 3H), 4.16 (dq, *J* = 9.9, 7.1 Hz, 1H), 3.60 (dq, *J* = 9.9, 7.0 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H).

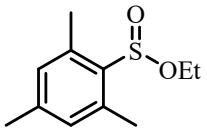


Ethyl 3,4-dimethoxybenzenesulfinate (**3t**)

The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **3t** as a colorless oil (37.8 mg, 66% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 4.06 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.91 (d, *J* = 5.7 Hz, 6H), 3.70 (dq, *J* = 10.0, 7.1 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

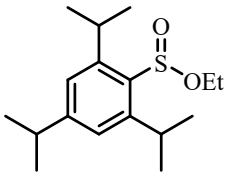
^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.2, 149.6, 136.7, 118.8, 110.9, 107.3, 78.6 – 75.2 (m), 60.7, 56.2, 15.7. **HRMS (ESI)** calcd. For $C_{10}H_{15}O_4S^+$ (M+H) $^+$: 231.0686, found: 231.0690. **IR (neat, cm^{-1}):** 2923 (m), 2852 (w), 1583 (w), 1505 (s), 1462 (m), 1319 (m), 1259 (s), 1234 (s), 1130 (s), 1019 (m), 662 (w), 619 (m), 555 (w), 539 (w).



Ethyl 2,4,6-trimethylbenzenesulfinate (**3u**)[16]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3u** as a yellow oil (43.3 mg, 82% yield).

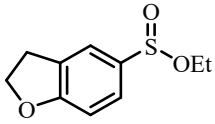
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.85 (s, 2H), 4.19 – 4.09 (m, 2H), 2.59 (s, 6H), 2.28 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).



Ethyl 2,4,6-triisopropylbenzenesulfinate (**3v**)

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3v** as a colorless oil (52.2 mg, 71% yield).

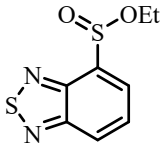
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.09 (s, 2H), 4.25 (dq, *J* = 10.0, 7.1 Hz, 1H), 4.12 (dq, *J* = 10.0, 7.1 Hz, 1H), 4.04 (dq, *J* = 6.8 Hz, 2H), 2.88 (dq, *J* = 7.0 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.31 – 1.22 (m, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.8, 148.8, 138.2, 122.7, 78.7 – 75.4 (m), 65.2, 34.5, 28.2, 24.3 (d, *J* = 14.9 Hz), 23.7, 16.0. **HRMS (ESI)** calcd. For $C_{17}H_{29}O_2S^+$ (M+H) $^+$: 297.1883, found: 297.1880. **IR (neat, cm^{-1}):** 2963 (w), 1599 (w), 1463 (w), 1264 (m), 1191 (w), 1007 (w), 598 (w), 732 (s), 703 (m), 581 (w).



Ethyl 2,3-dihydrobenzofuran-5-sulfinate (**3w**)

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3w** as a colorless oil (43.5 mg, 82% yield).

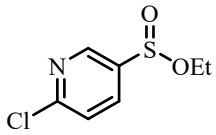
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (m, *J* = 1.4 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.87 (dd, *J* = 8.3 Hz, 1H), 4.65 (t, *J* = 8.8 Hz, 2H), 4.08 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.74 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.26 (t, *J* = 8.8 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.6, 136.6, 128.5, 126.5, 122.1 (d, J = 4.8 Hz), 109.7, 78.4 – 74.8 (m), 72.2, 60.7, 29.3, 15.7. **HRMS (ESI)** calcd. For $C_{10}H_{13}O_3S^+$ (M+H) $^+$: 213.0580, found: 213.0582. **IR (neat, cm^{-1}):** 2923 (m), 2853 (m), 1601 (w), 1484 (s), 1354 (w), 1204 (s), 1185 (m), 1109 (m), 980 (m), 819 (w), 693 (w) ,602 (s), 558 (m), 525 (m).



Ethyl benzo[*c*][1,2,5]thiadiazole-4-sulfinate (**3x**)

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3x** as a yellow oil (48.9 mg, 86% yield).

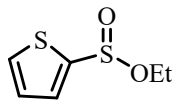
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.8, 5.4 Hz, 2H), 7.76 (dd, *J* = 8.7, 7.0 Hz, 1H), 4.41 – 4.17 (m, 1H), 3.86 (dq, *J* = 9.9, 7.0 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.3, 150.4, 136.7, 128.6, 127.4, 125.3, 63.2, 15.6. **HRMS (ESI)** calcd. For $C_8H_9N_2O_2S_2^+$ (M+H) $^+$: 229.0100, found: 229.0098. **IR (neat, cm^{-1}):** 2923 (m), 2853 (w), 1721 (w), 1519 (w), 1456 (w), 1313 (w), 1272 (w), 1130 (s), 1006 (w), 829 (m), 754 (m), 626 (w), 508 (w).



Ethyl 6-chloropyridine-3-sulfinate (**3y**)

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3y** as a colorless oil (37.7 mg, 73% yield).

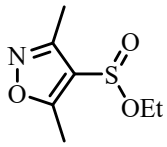
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 2.5 Hz, 1H), 7.99 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 4.19 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.85 (dq, *J* = 9.9, 7.1 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.2, 147.5, 140.4, 136.0, 125.0, 62.6, 15.7. **HRMS (ESI)** calcd. For $C_7H_9ClNO_2S^+$ (M+H) $^+$: 206.0037, found: 203.0039. **IR (neat, cm^{-1}):** 2921 (s), 2852 (m), 1646 (w), 1463 (w), 1376 (w), 1135 (w), 1221 (w), 697 (w), 582 (w), 489 (w).



Ethyl thiophene-2-sulfinate (**3z**)[16]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3z** as a colorless oil (27.3 mg, 62% yield).

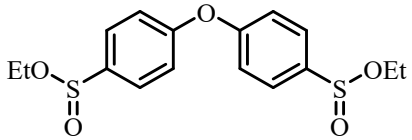
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 4.9 Hz, 1H), 7.47 (d, *J* = 3.8 Hz, 1H), 7.14 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.19 (dq, *J* = 10.0, 7.1 Hz, 1H), 3.86 (dq, *J* = 10.0, 7.1 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H).



Ethyl 3,5-dimethylisoxazole-4-sulfinate (**3aa**)

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3aa** as a colorless oil (31.2 mg, 66% yield).

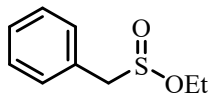
^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.18 (dd, *J* = 9.9, 7.1 Hz, 1H), 3.93 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.57 (s, 3H), 2.37 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 171.5, 157.5, 118.6, 62.2, 15.6, 12.0, 10.7. **HRMS (ESI)** calcd. For $C_7H_{12}NO_3S^+$ (M+H) $^+$: 190.0532, found: 190.0533. **IR (neat, cm^{-1}):** 2923 (s), 2853 (m), 1723 (w), 1691 (w), 1591 (w), 1438 (w), 1262 (m), 1121 (m), 1029 (w), 724 (w), 694 (w), 541 (m), 507 (w).



Diethyl 4,4'-oxydibenzenesulfinate (**3ab**)

The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **3ab** as a white solid (54.7 mg, 61% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.3 Hz, 4H), 7.16 (d, *J* = 8.4 Hz, 4H), 4.14 (dq, *J* = 10.0, 7.1 Hz, 2H), 3.80 (dq, *J* = 10.0, 7.0 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.4, 140.3, 127.5, 119.4, 61.4, 15.6. **HRMS (ESI)** calcd. For $C_{16}H_{19}O_5S_2^+$ (M+H) $^+$: 355.0668, found: 355.0681. **IR (neat, cm^{-1}):** 2924 (w), 2853 (w), 1723 (w), 1577 (m), 1329 (w), 1242 (s), 1133 (s), 1077 (m), 1009 (m), 891 (m), 699 (m), 587 (w), 494 (w).

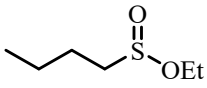


Ethyl phenylmethanesulfinate (**3ac**)

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3ac** as a colorless oil (19.9 mg, 43% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 5H), 4.16 – 4.04 (m, 2H), 4.03 – 3.91 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 130.5, 129.1, 128.8, 128.3, 65.2, 64.6, 15.8. **HRMS (ESI)** calcd. For $C_9H_{13}O_2S_2^+$ (M+H) $^+$: 185.0631, found: 185.0629. **IR (neat, cm^{-1}):**

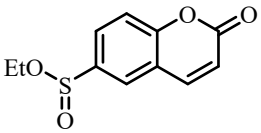
2923 (m), 2853 (w), 1719 (m), 1601 (w), 1495 (w), 1453 (w), 1376 (w), 1314 (w), 1133 (s), 1108 (s), 1027 (m), 912 (w), 851 (w), 696 (s), 499 (m).



Ethyl butane-1-sulfinate (**3ad**)[16]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3ad** as a colorless oil (15.5 mg, 41% yield).

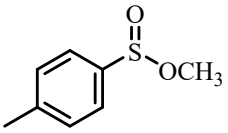
^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.16 – 4.02 (m, 2H), 2.81 – 2.64 (m, 2H), 1.71 – 1.62 (m, 2H), 1.49 – 1.39 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H).



Ethyl 2-oxo-2H-chromene-6-sulfinate (**3ae**)

The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **3ae** as a white solid (49.2 mg, 83% yield).

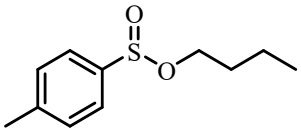
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.85 – 7.75 (m, 2H), 7.48 (d, *J* = 8.6 Hz, 1H), 6.53 (d, *J* = 9.4 Hz, 1H), 4.30 – 4.03 (m, 1H), 3.81 – 3.67 (m, 1H), 1.31 (t, *J* = 8.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.7, 156.2, 142.7, 141.2, 128.5, 125.4, 119.1, 118.1, 118.0, 61.7, 15.6. **HRMS (ESI)** calcd. For $C_{11}H_{11}O_4S^+$ $(M+H)^+$: 239.0373, found : 239.0374. **IR (neat, cm^{-1}) :** 2923 (s), 2853 (m), 1733 (s), 1596 (m), 1464 (w), 1370 (m), 1260 (w), 1180 (w), 1135 (s), 893 (w), 821 (m), 738 (w), 697 (w), 609 (m), 505 (m), 482 (m).



Methyl 4-methylbenzenesulfinate (**3af**)[14]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3af** as a colorless oil (38.7 mg, 90% yield).

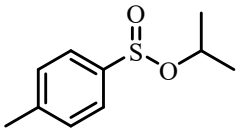
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.30 (m, 2H), 3.45 (s, 3H), 2.42 (s, 3H).



Butyl 4-methylbenzenesulfinate (**3ag**)[17]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3ag** as a yellow oil (48.8 mg, 92% yield).

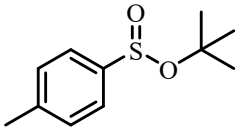
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 4.01 (dq, *J* = 10.1, 6.5 Hz, 1H), 3.60 (dq, *J* = 10.0, 6.6 Hz, 1H), 2.41 (s, 3H), 1.63 – 1.56 (m, 2H), 1.37 – 1.31 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).



Isopropyl 4-methylbenzenesulfinate (**3ah**)[14]

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3ah** as a colorless oil (33.6 mg, 68% yield).

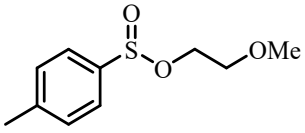
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.59 (heptet, *J* = 6.3 Hz, 1H), 2.41 (s, 3H), 1.38 (d, *J* = 6.2 Hz, 3H), 1.24 (d, *J* = 6.4 Hz, 3H).



tert-Butyl 4-methylbenzenesulfinate (**3ai**)[14]

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **3ai** as a yellow oil (27.7 mg, 52% yield).

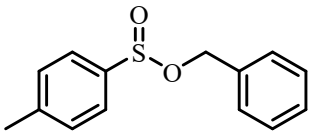
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H), 1.55 (s, 9H).



2-Methoxyethyl 4-methylbenzenesulfinate (**3aj**)[17]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3aj** as a yellow oil (33.6 mg, 63% yield).

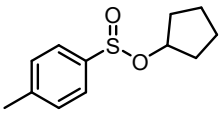
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.14 (ddd, *J* = 11.2, 5.9, 3.6 Hz, 1H), 3.68 (ddd, *J* = 11.2, 5.9, 3.7 Hz, 1H), 3.56 – 3.53 (m, 2H), 3.34 (s, 3H), 2.41 (s, 3H).



Benzyl 4-methylbenzenesulfinate (**3ak**)[14]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3ak** as a colorless oil (85.7 mg, 35% yield).

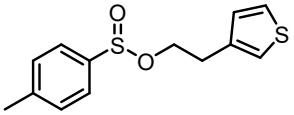
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.26 (m, 7H), 5.03 (d, *J* = 11.3 Hz, 1H), 4.56 (d, *J* = 11.4 Hz, 1H), 2.43 (s, 3H).



cyclopentyl 4-methylbenzenesulfinate (**3al**)

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3al** as a colorless oil (38.6 mg, 69% yield).

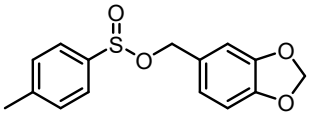
^{1}H NMR (500 MHz, Chloroform-d) δ 7.58 (dd, J = 8.2, 1.6 Hz, 2H), 7.33 - 7.30 (m, 2H), 4.83 - 4.78 (m, 1H), 2.41 (s, 3H), 1.88 (dq, J = 6.0, 1.7 Hz, 2H), 1.73 - 1.70 (m, 4H), 1.60 - 1.49 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.80, 142.56, 129.76, 125.22, 80.86, 34.26, 33.89, 23.44 (d, J = 2.4 Hz), 21.63. **HRMS (ESI)** calcd. For $C_{12}H_{17}O_2S^+$ $(M+H)^+$: 225.0944, found : 225.0947. **IR (neat, cm^{-1})** : 2923 (s), 2852 (w), 1599 (w), 1462 (m), 1319 (m), 1135 (w), 866 (w), 662 (w), 592 (m), 539 (w).



2-(thiophen-3-yl)ethyl 4-methylbenzenesulfinate (**3am**)

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **3am** as a colorless oil (21.3 mg, 32% yield).

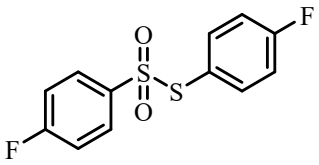
^{1}H NMR (500 MHz, Chloroform-d) δ 7.52 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.24 (dd, J = 5.0, 3.0 Hz, 1H), 7.00 - 6.97 (m, 1H), 6.90 (dd, J = 5.0, 1.3 Hz, 1H), 4.25 - 4.21 (m, 1H), 3.81 - 3.78 (m, 1H), 2.96 (t, J = 6.9 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 142.86, 141.61, 137.65, 129.83, 128.37, 125.74, 125.35, 121.96, 64.17, 30.83, 21.64. **HRMS (ESI)** calcd. For $C_{13}H_{15}O_2S_2^+$ $(M+H)^+$: 267.0508, found : 267.0503. **IR (neat, cm^{-1})**: 2923 (s), 2853 (w), 1519 (w), 1462 (m), 1313 (w), 1130 (s), 1029 (w), 908 (m), 829 (m), 734 (m), 626 (w), 541 (w).



benzo[d][1,3]dioxol-5-ylmethyl 4-methylbenzenesulfinate (**3an**), from Piperonyl alcohol

The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **3an** as a colorless oil (38.4 mg, 53% yield).

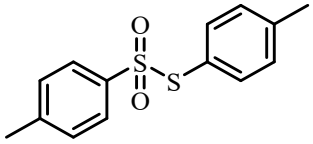
^{1}H NMR (500 MHz, Chloroform-d) δ 7.62 (d, J = 8.0 Hz, 2H), 7.37 - 7.30 (m, 2H), 6.76 - 6.72 (m, 3H), 5.95 (d, J = 1.0 Hz, 2H), 4.92 (dd, J = 11.1, 0.9 Hz, 1H), 4.45 (dd, J = 11.1, 0.9 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 147.96, 143.00, 141.68, 129.90, 129.30, 125.46, 122.81, 109.41, 108.35, 101.32, 65.83, 21.66. **HRMS (ESI)** calcd. For $C_{15}H_{15}O_4S^+$ $(M+H)^+$: 231.0686, found : 231.0690. **IR (neat, cm^{-1})**: 2923 (s), 2853 (m), 1591 (w), 1463 (w), 1354 (w), 1204 (s), 1007 (w), 936 (m), 819 (w), 703 (m), 581 (w), 525 (m).



S-(4-fluorophenyl) 4-fluorobenzenesulfonothioate (**4a**)[5]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **4a** as a yellow oil (100 mg, 70% yield).

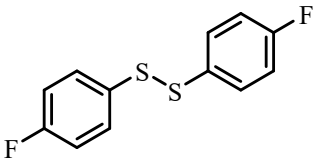
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.54 (m, 2H), 7.40 – 7.32 (m, 2H), 7.16 – 7.01 (m, 4H).



S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**4g**)[5]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **4g** as a colorless oil (103 mg, 74% yield).

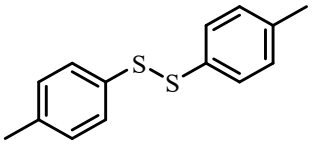
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.19 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.37 (s, 3H).



1,2-bis(4-fluorophenyl)disulfane (**5a**)[5]

The desired pure product was purified using silica gel chromatography (PE: EA = 50: 1) to give **5a** as a white solid (94 mg, 74% yield).

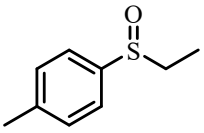
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 4H), 7.01 (t, *J* = 8.6 Hz, 4H).



1,2-di-p-tolyldisulfane (**5g**)[5]

The desired pure product was purified using silica gel chromatography (PE: EA = 50: 1) to give **5g** as a white solid (98 mg, 79% yield).

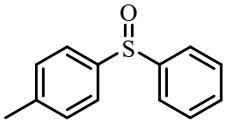
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.3 Hz, 4H), 7.12 (d, *J* = 8.0 Hz, 4H), 2.33 (s, 6H).



1-(Ethylsulfinyl)-4-methylbenzene (**6a**)[18]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **6a** as a yellow oil (53.2 mg, 63% yield).

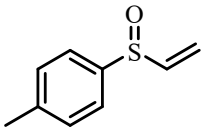
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.85 (dq, *J* = 13.6, 7.1 Hz, 1H), 2.73 (dq, *J* = 13.6, 7.1 Hz, 1H), 2.39 (s, 3H), 1.16 (t, *J* = 7.4 Hz, 3H).



1-Methyl-4-(phenylsulfinyl)benzene (**6b**)[19]

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **6b** as a yellow oil (55.6 mg, 51% yield).

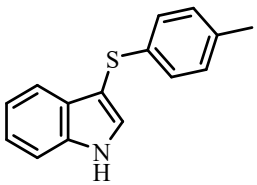
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 – 7.58 (m, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 2H), 2.35 (s, 3H).



1-Methyl-4-(vinylsulfinyl)benzene (**6c**)[20]

The desired pure product was purified using silica gel chromatography (PE: EA = 20: 1) to give **6c** as a colorless oil (49.8 mg, 54% yield).

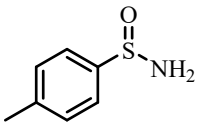
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.56 (dd, *J* = 16.4, 9.6 Hz, 1H), 6.16 (d, *J* = 16.5 Hz, 1H), 5.86 (d, *J* = 9.6 Hz, 1H), 2.38 (s, 3H).



1-(*p*-Tolylthio)naphthalen-2-ol (**6d**)[4]

The desired pure product was purified using silica gel chromatography (PE: EA = 10: 1) to give **6d** as a colorless oil (62.3 mg, 52% yield).

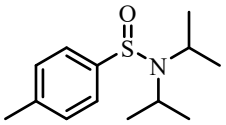
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (br s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 2.6 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 2.24 (s, 3H).



4-Methylbenzenesulfinamide (**6e**)[21]

The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **6e** as a white solid (87.3 mg, 56% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.41 (s, 2H), 2.40 (s, 3H).

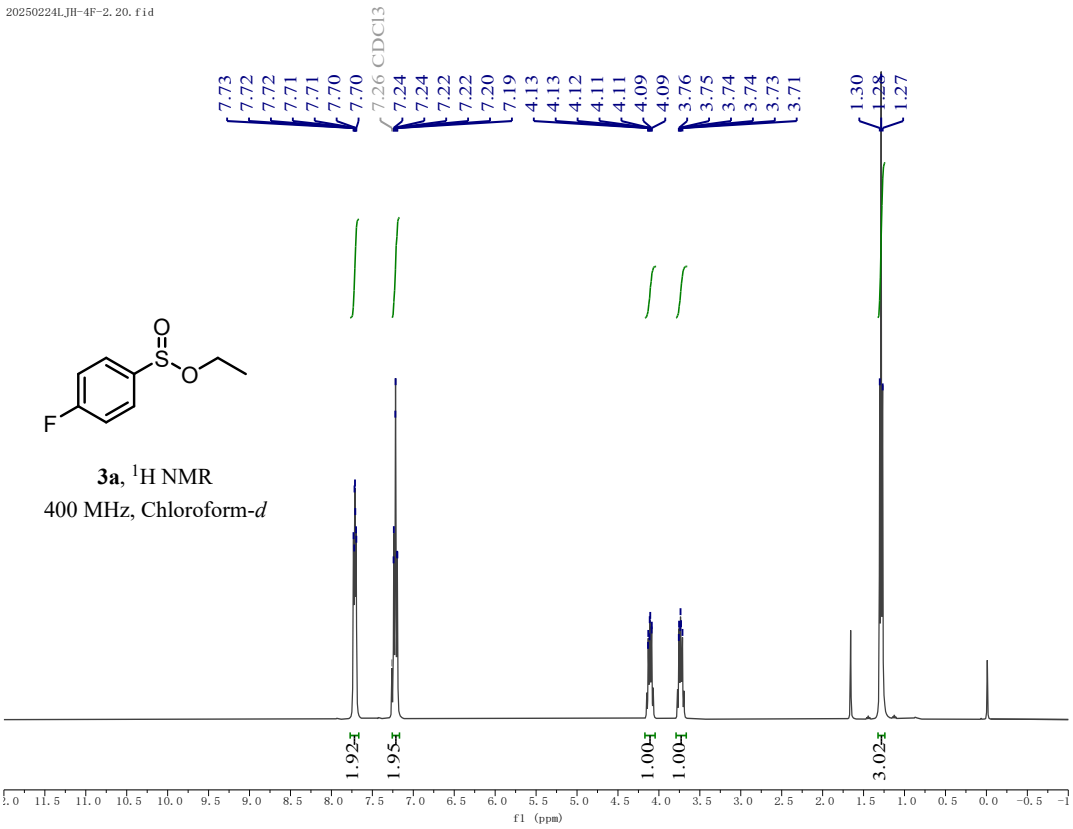


N, *N*-diisopropyl-4-methylbenzenesulfinamide (**6f**)[22]

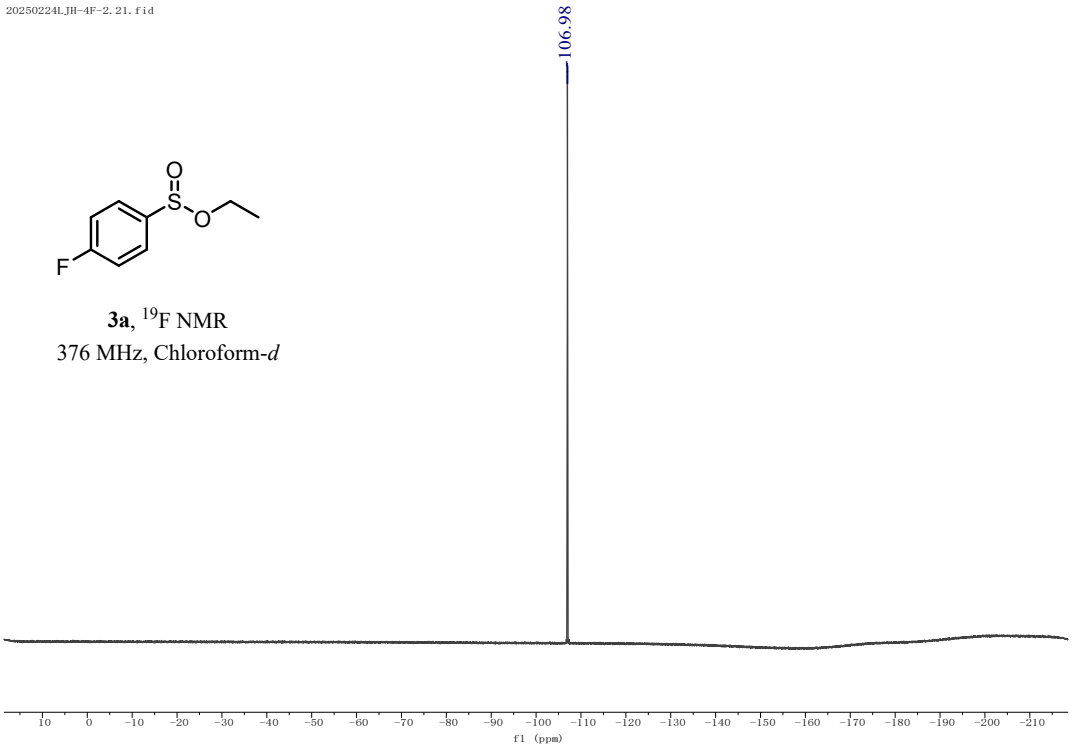
The desired pure product was purified using silica gel chromatography (PE: EA = 5: 1) to give **6f** as a colorless oil (98.6 mg, 46% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 3.54 (heptet, *J* = 6.7 Hz, 2H), 2.40 (s, 3H), 1.40 (d, *J* = 6.8 Hz, 6H), 1.11 (d, *J* = 6.7 Hz, 6H).

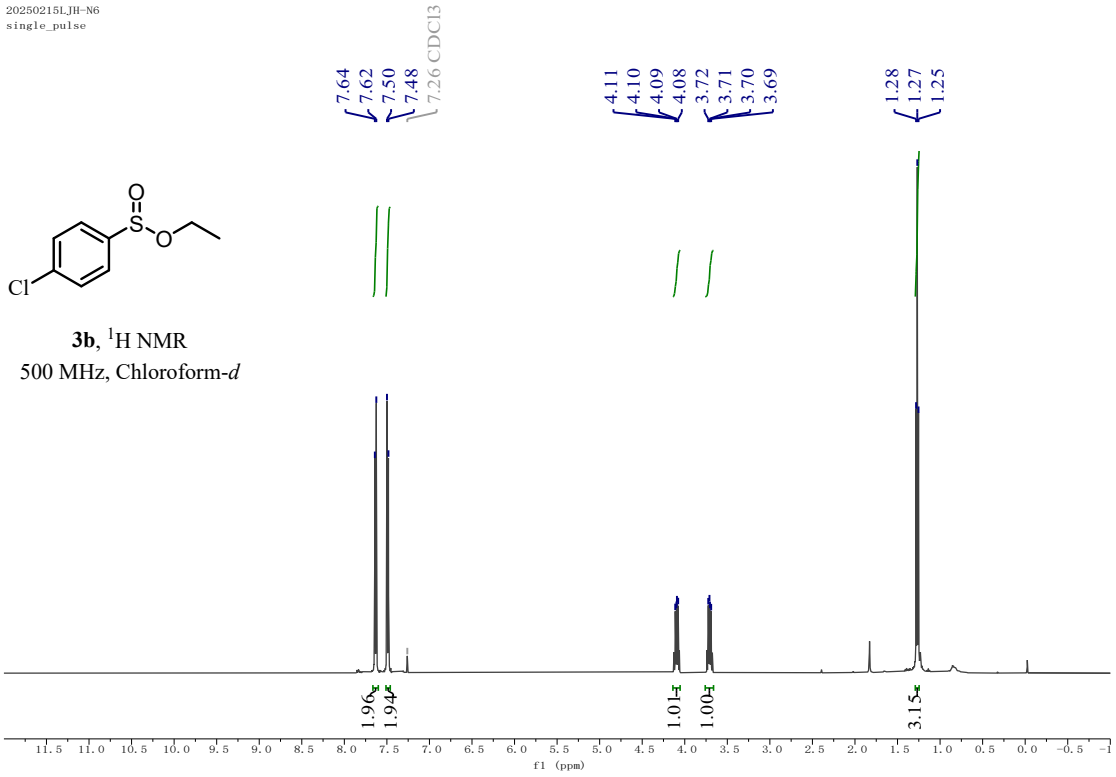
SI-5 NMR spectra



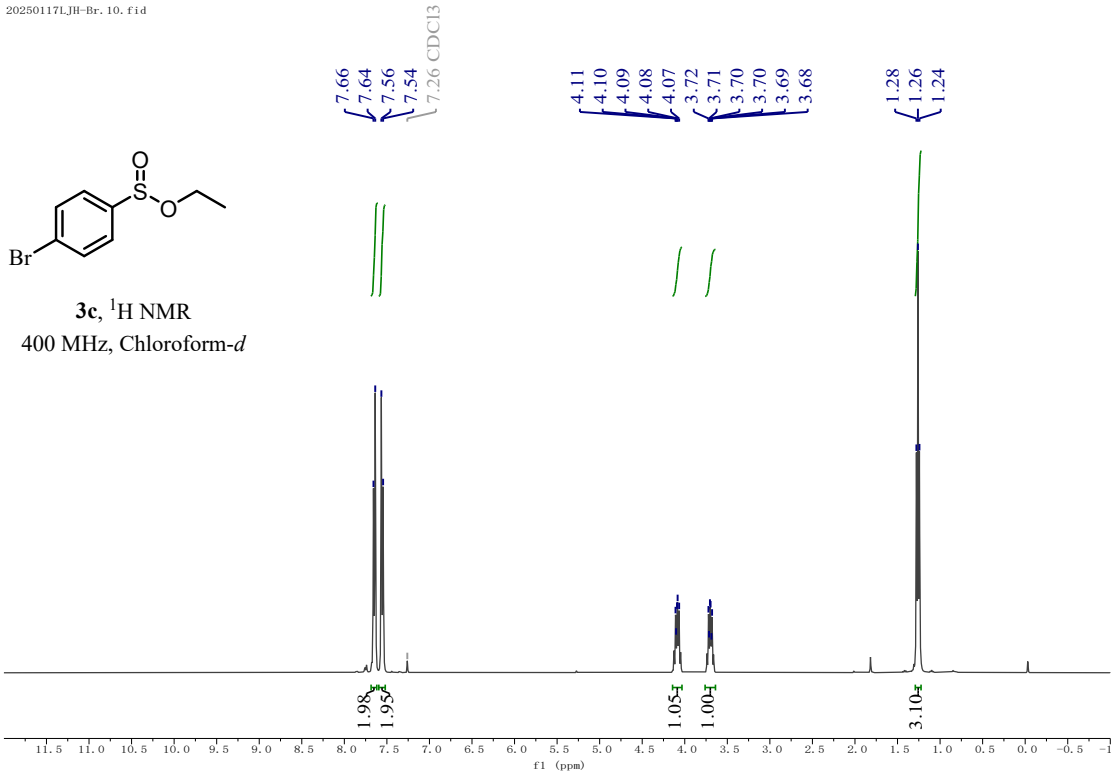
3a, ^{1}H NMR
400 MHz, Chloroform-*d*



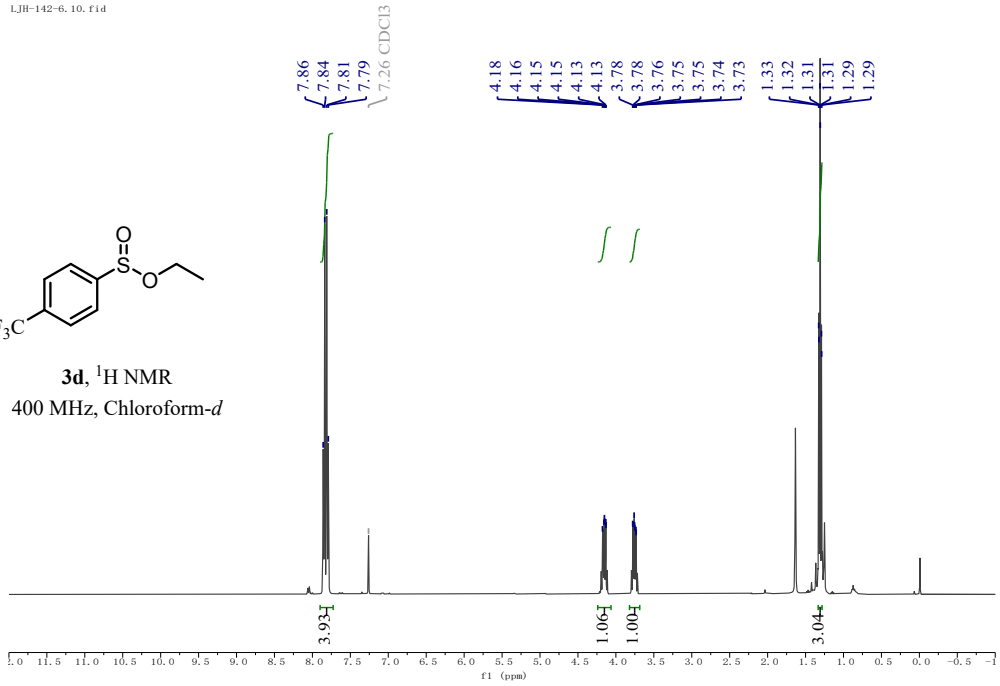
3a, ^{19}F NMR
376 MHz, Chloroform-*d*



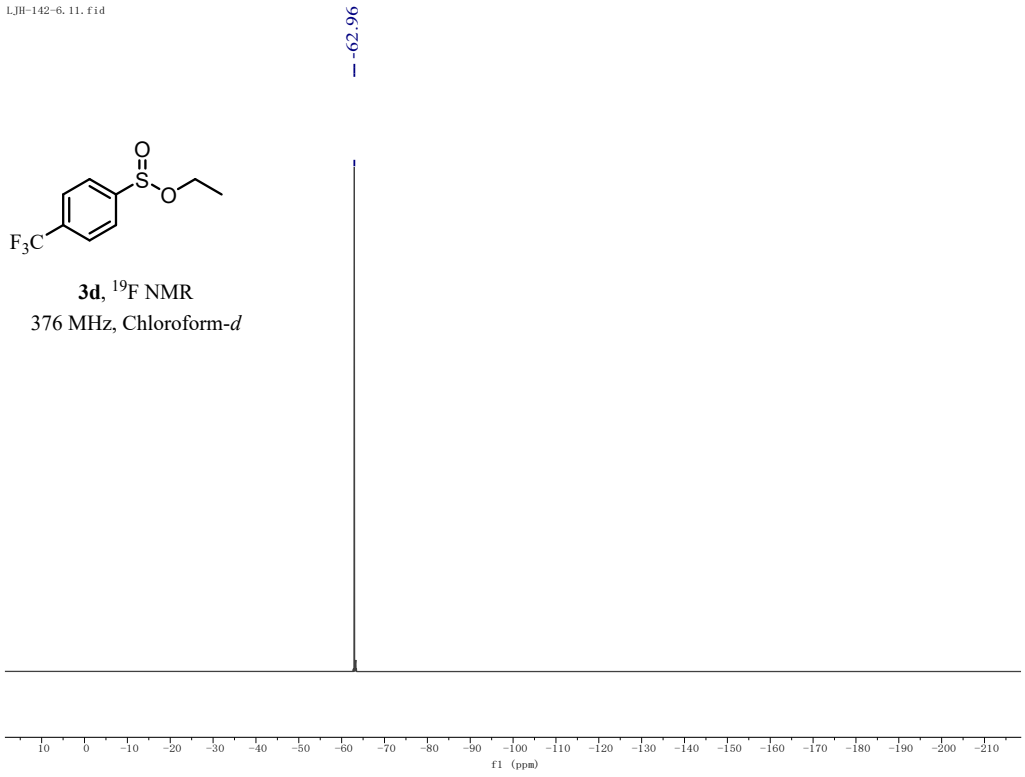
3b, ^{1}H NMR
500 MHz, Chloroform-*d*



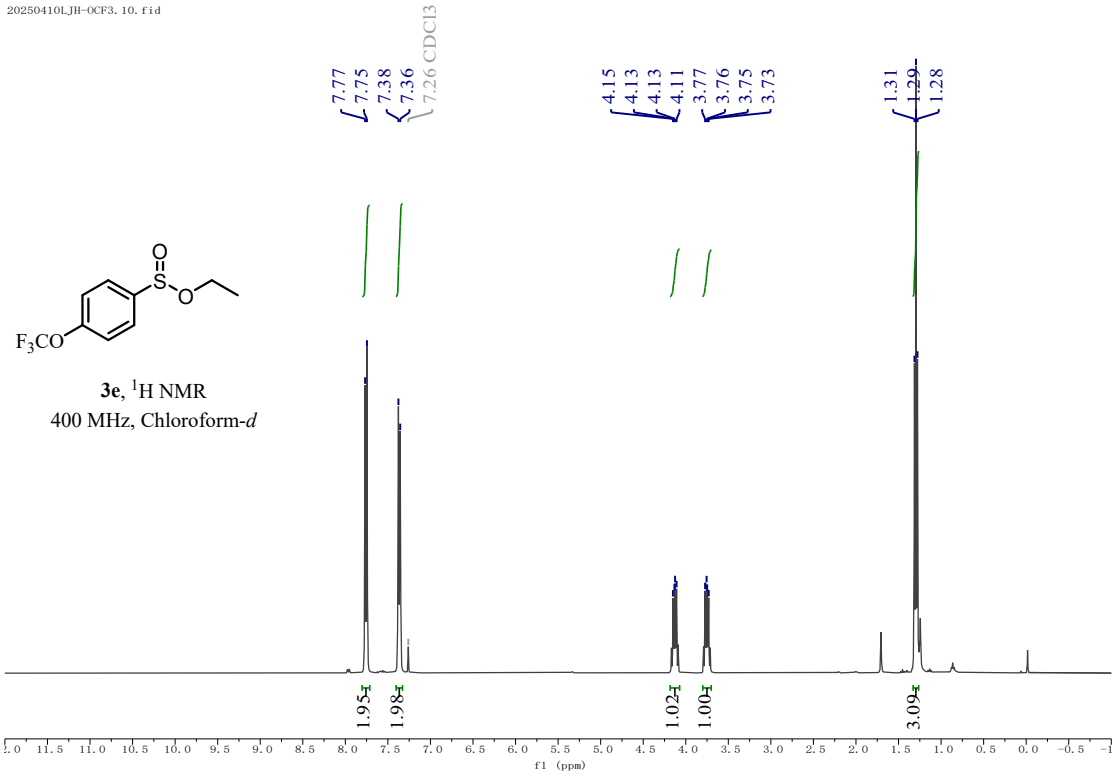
3c, ^{1}H NMR
400 MHz, Chloroform-*d*



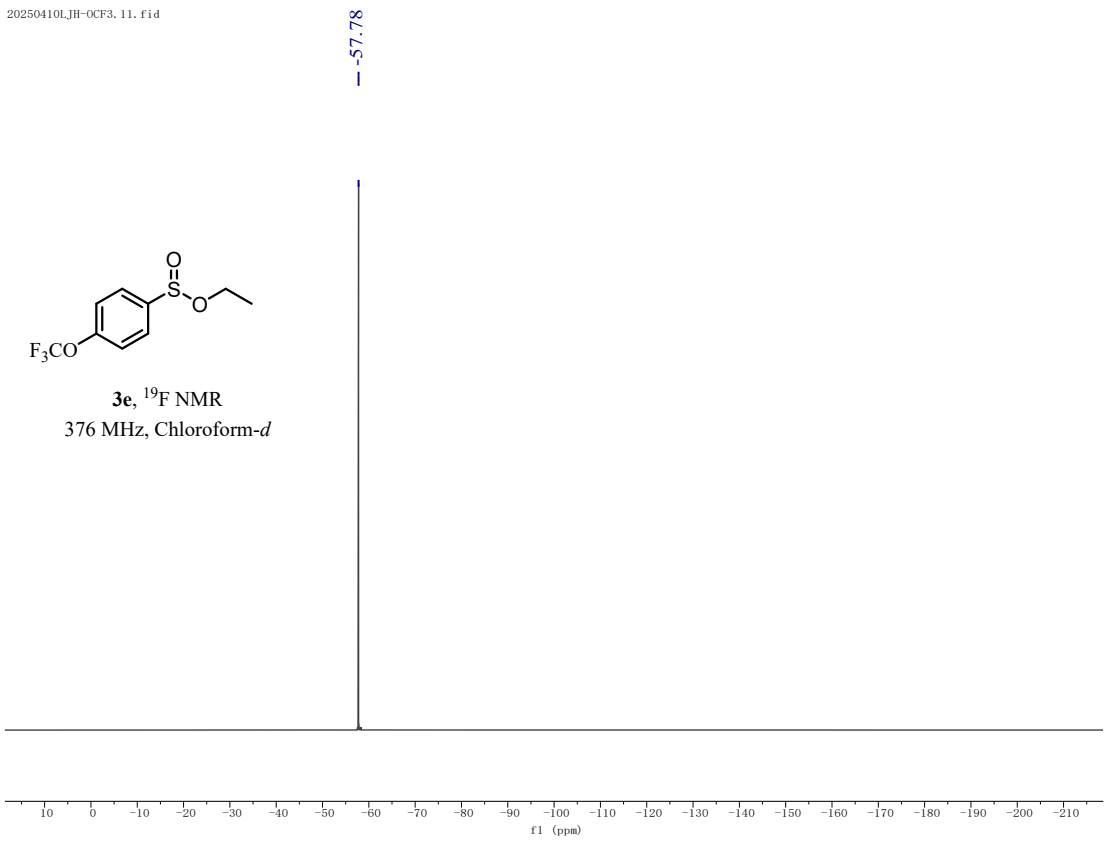
3d, ^{1}H NMR
400 MHz, Chloroform-*d*



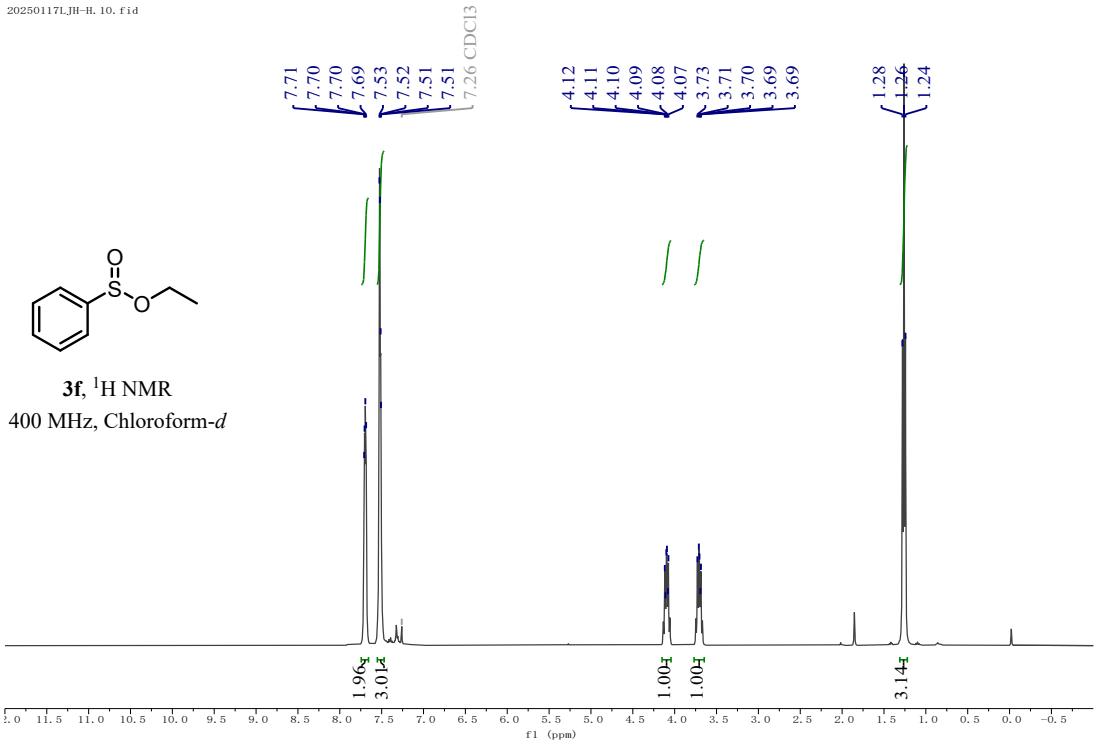
3d, ^{19}F NMR
376 MHz, Chloroform-*d*



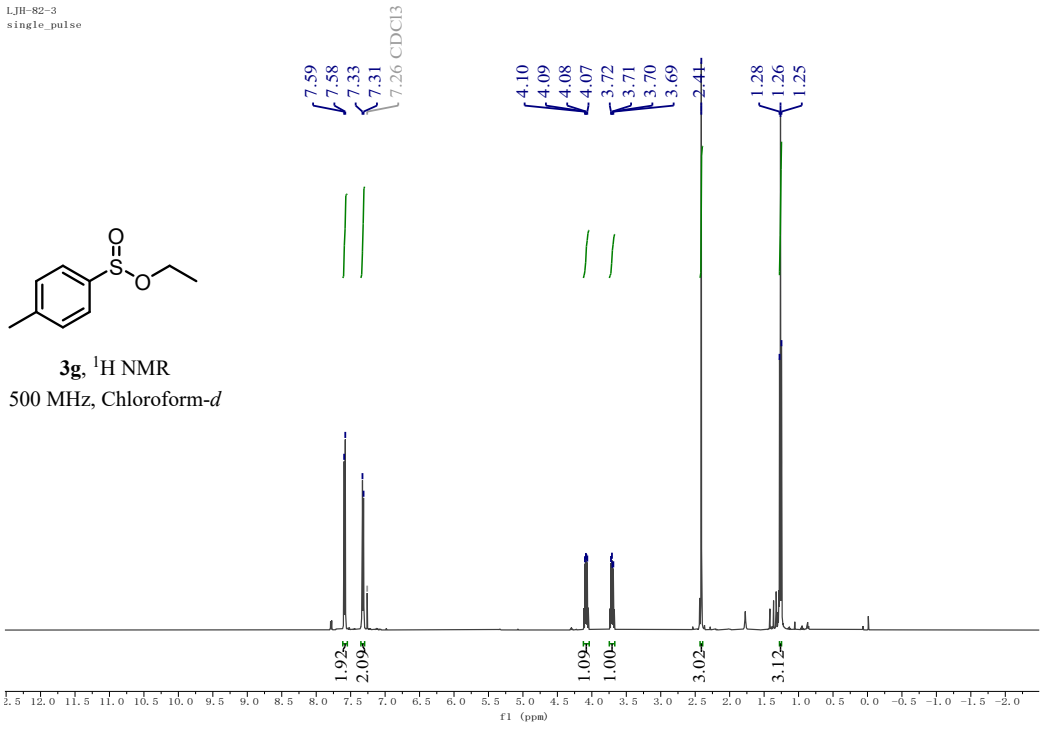
3e, ^{1}H NMR
400 MHz, Chloroform-*d*



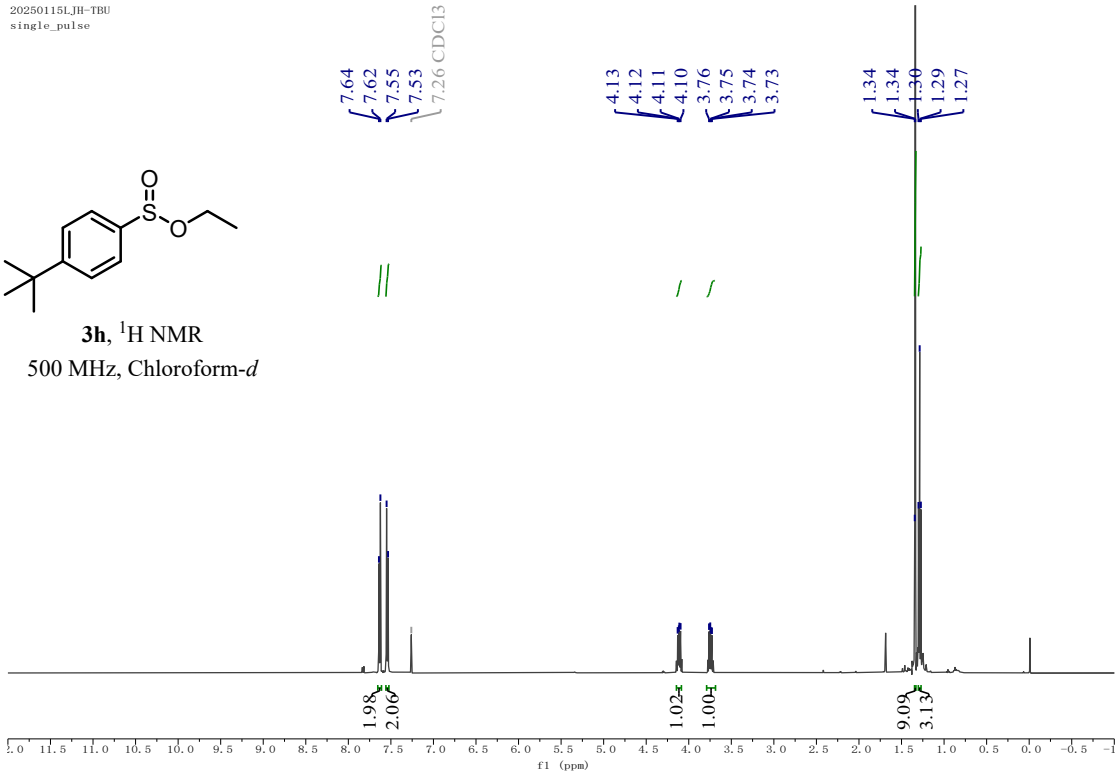
3e, ^{19}F NMR
376 MHz, Chloroform-*d*



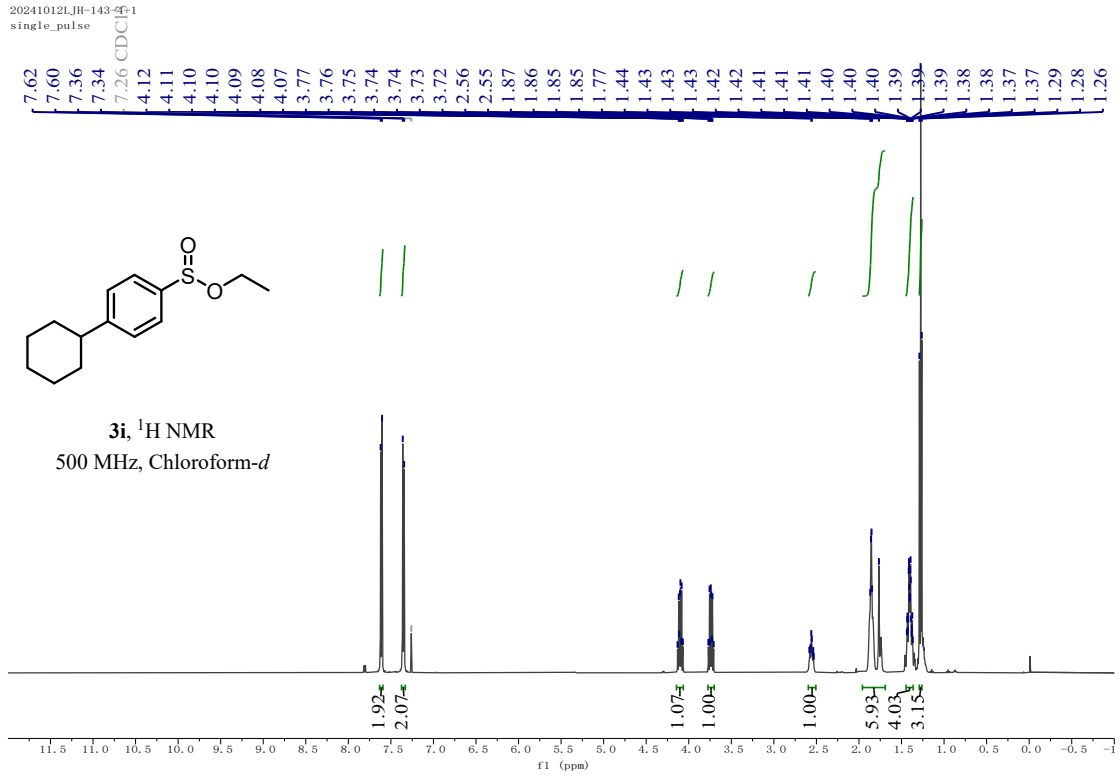
3f, ^{1}H NMR
400 MHz, Chloroform-*d*



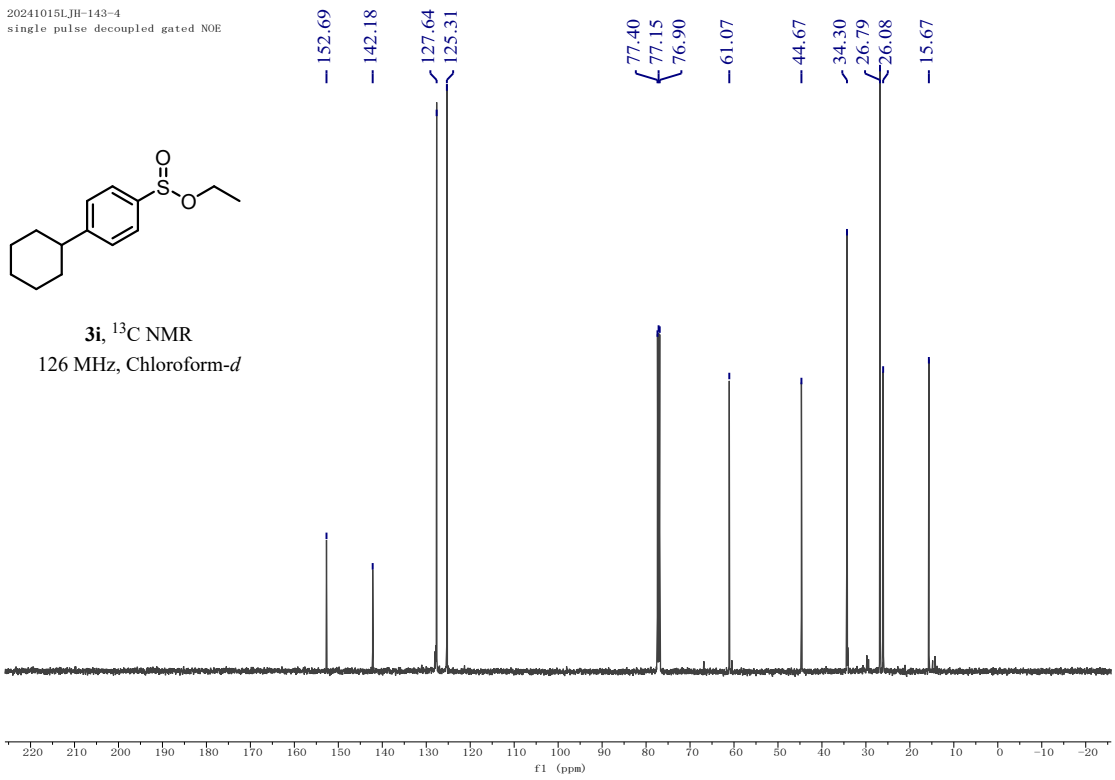
3g, ^{1}H NMR
500 MHz, Chloroform-*d*



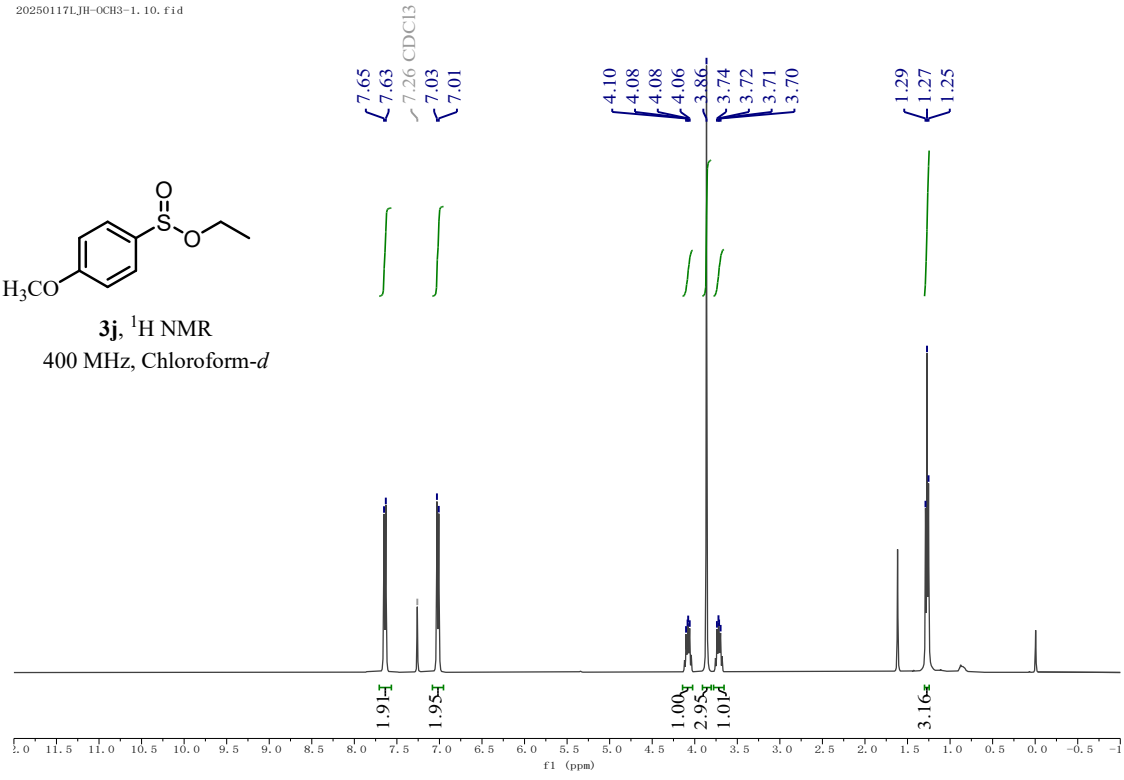
3h, ^{1}H NMR
500 MHz, Chloroform-*d*



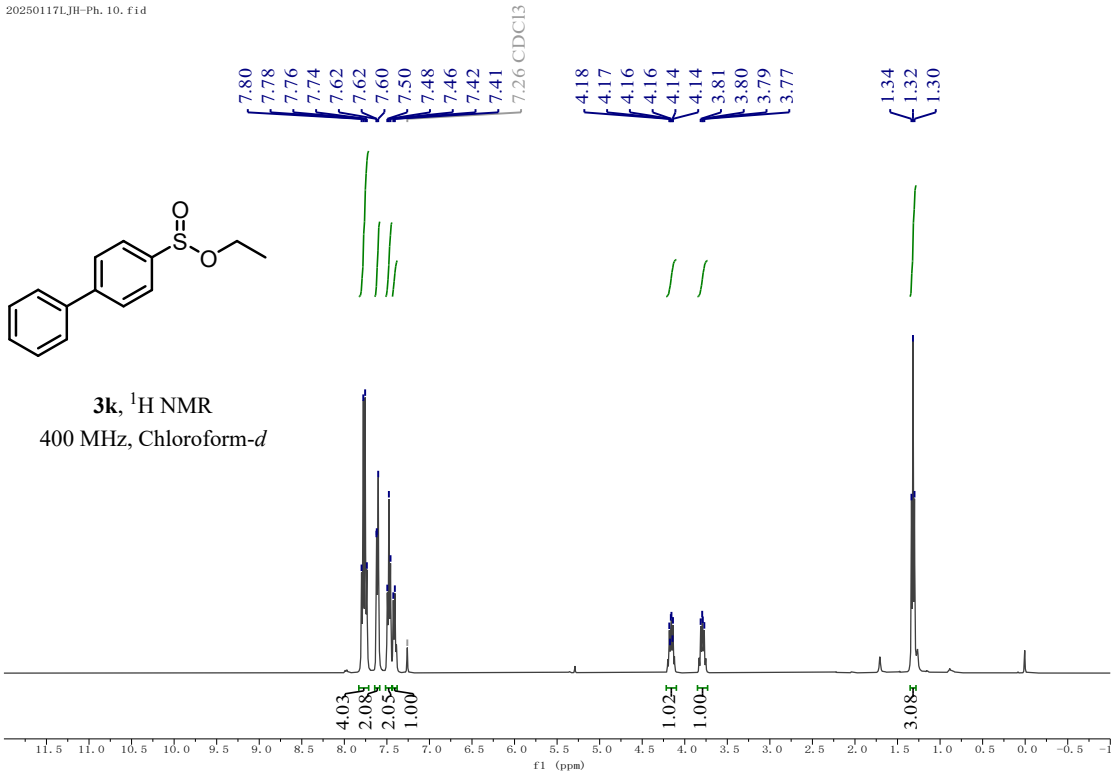
3i, ^{1}H NMR
500 MHz, Chloroform-*d*



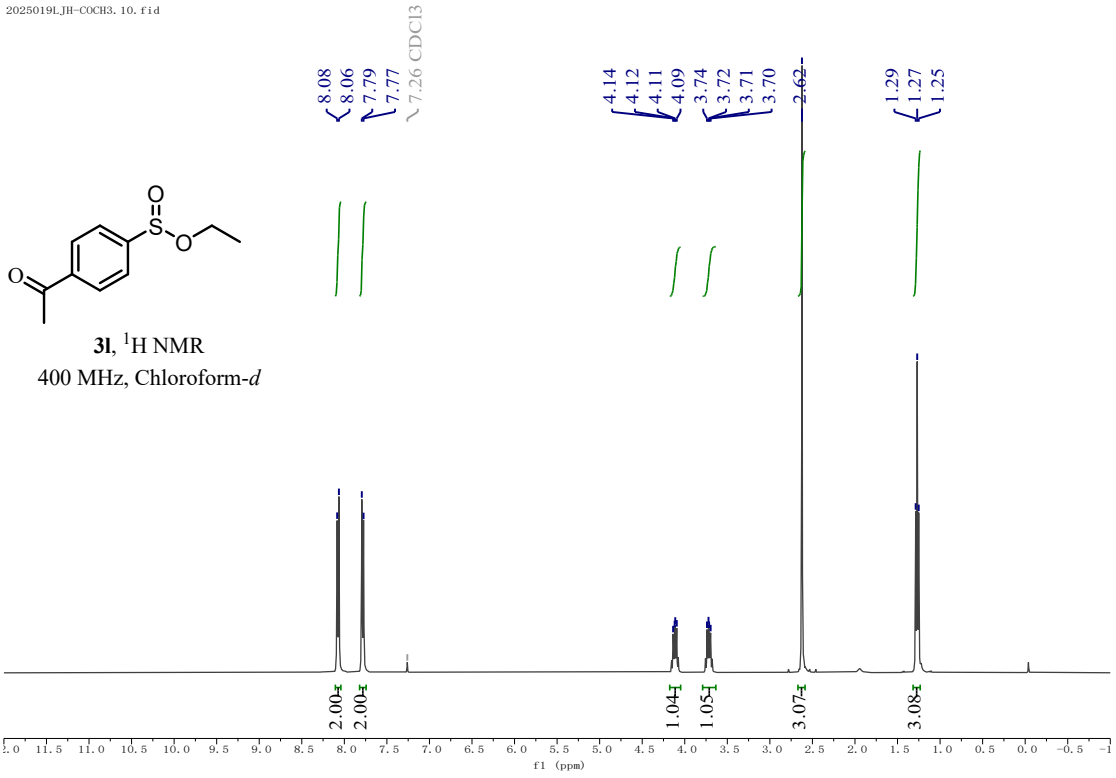
3i, ^{13}C NMR
126 MHz, Chloroform-*d*



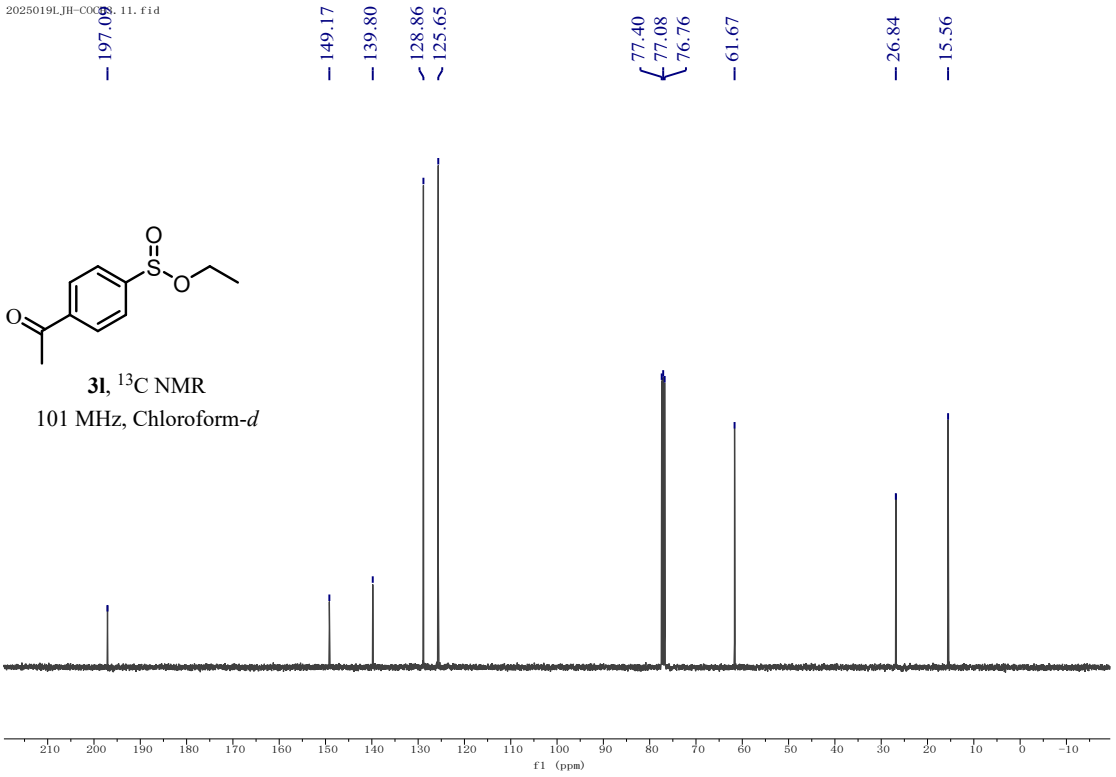
3j, ^{1}H NMR
400 MHz, Chloroform-*d*



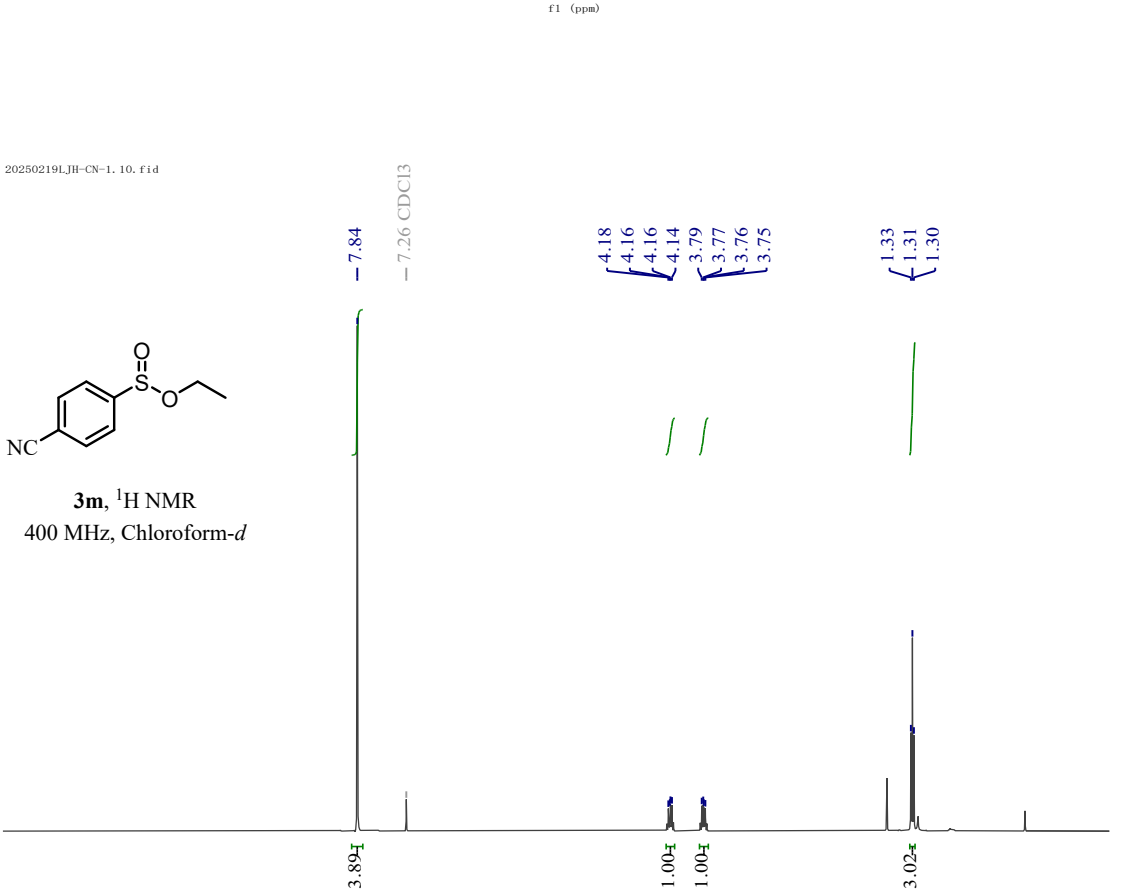
3k, ^{1}H NMR
400 MHz, Chloroform-*d*



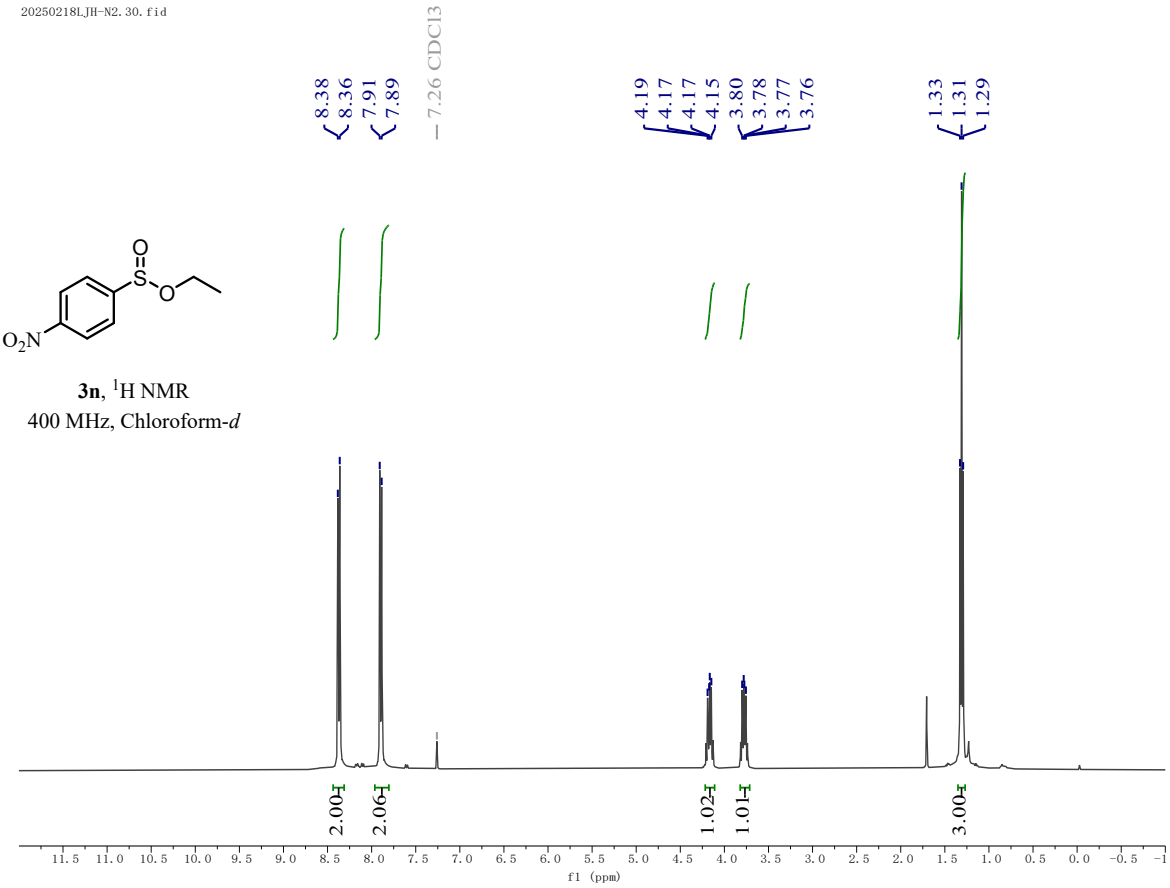
3l, ^{1}H NMR
400 MHz, Chloroform-*d*



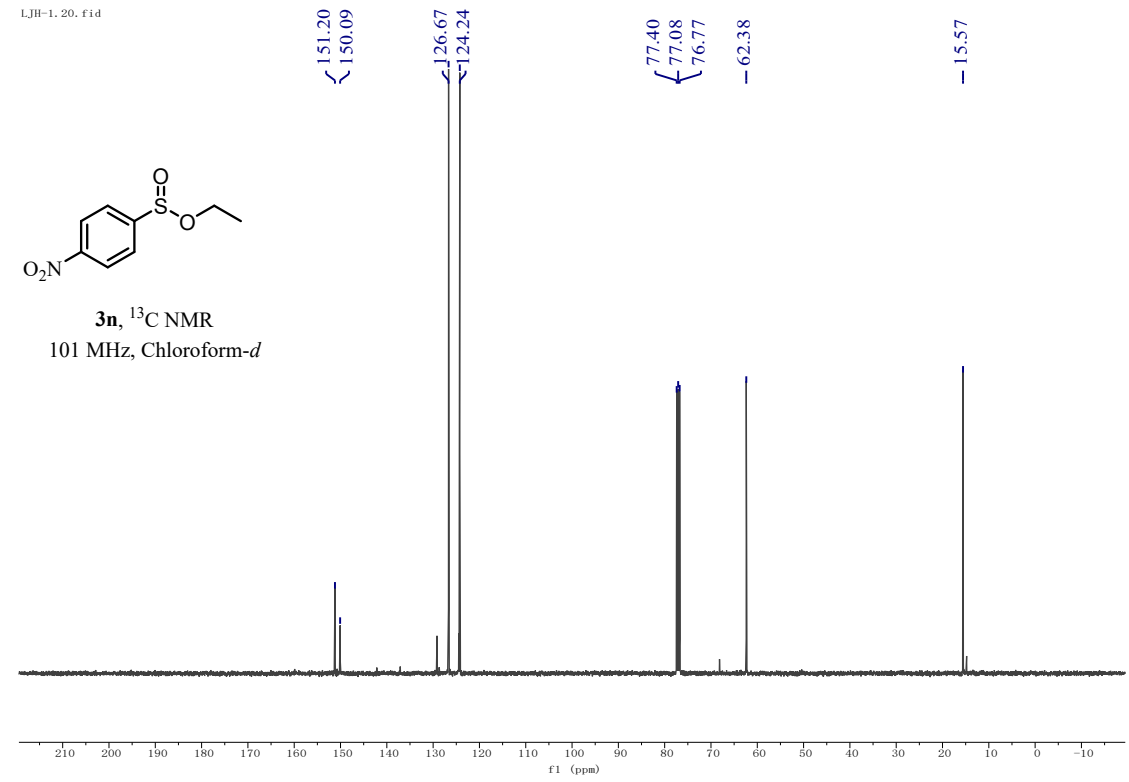
3l, ^{13}C NMR
101 MHz, Chloroform-*d*



3m, ^{1}H NMR
400 MHz, Chloroform-*d*



3n, ^{1}H NMR
400 MHz, Chloroform-*d*



3n, ^{13}C NMR
101 MHz, Chloroform-*d*

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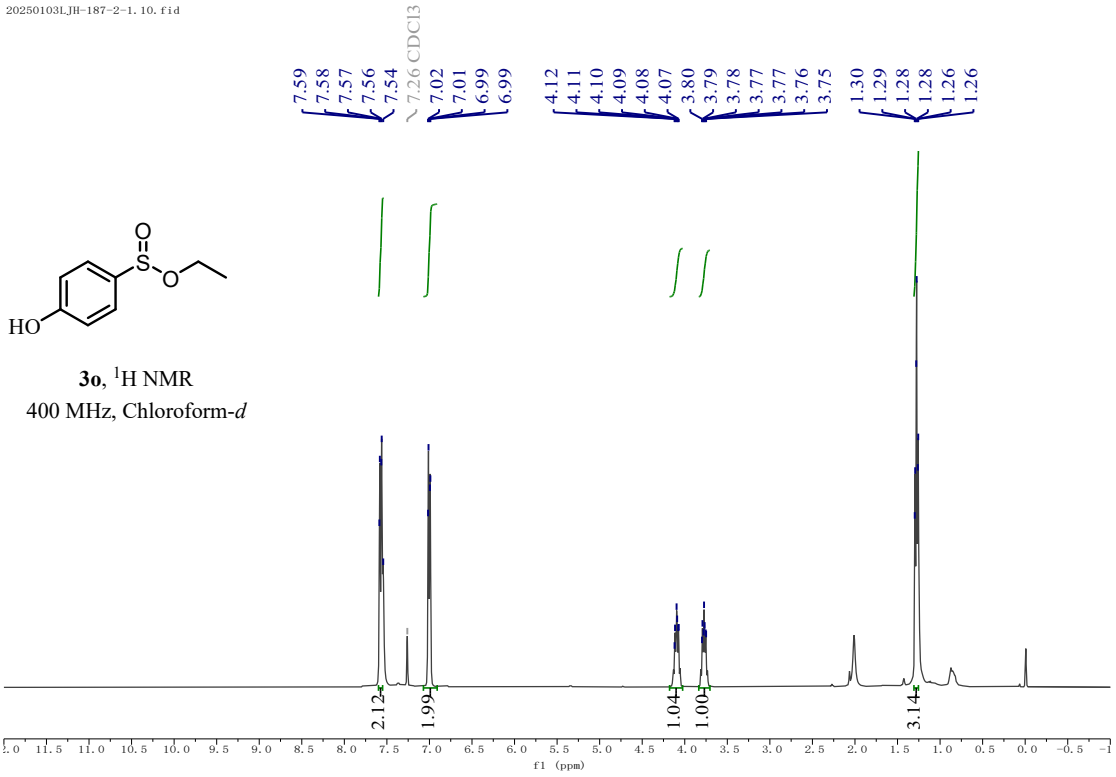

3o, ^{1}H NMR
400 MHz, Chloroform-*d*

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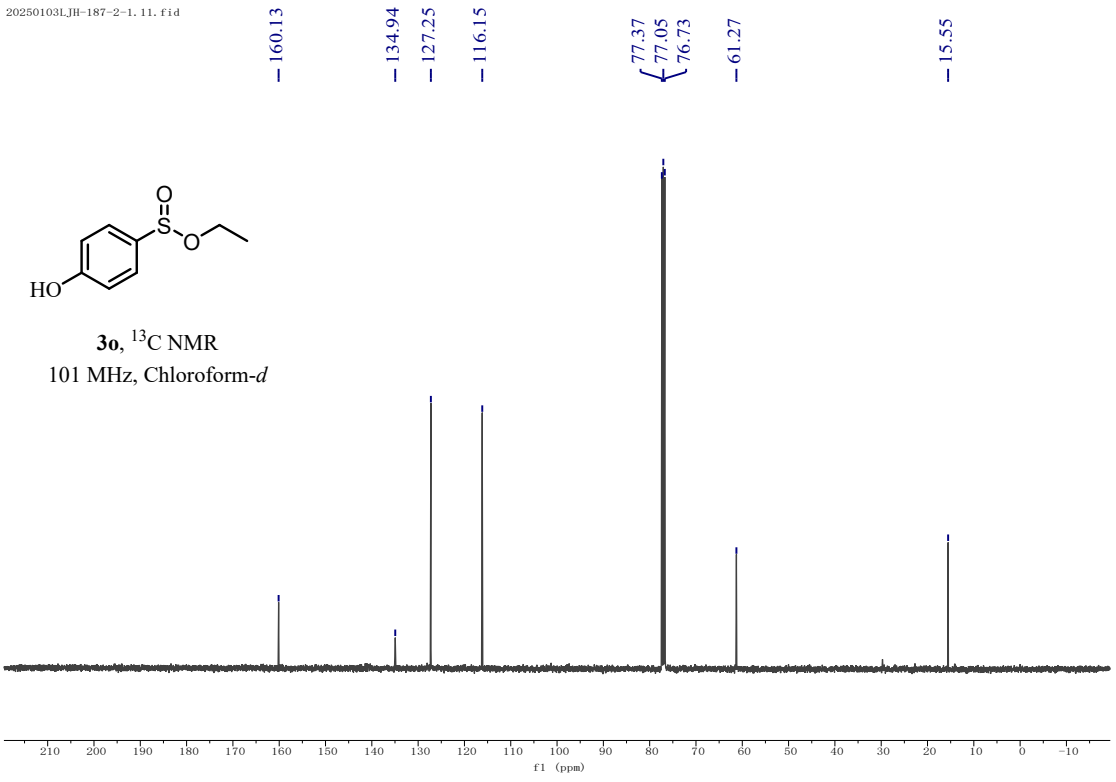
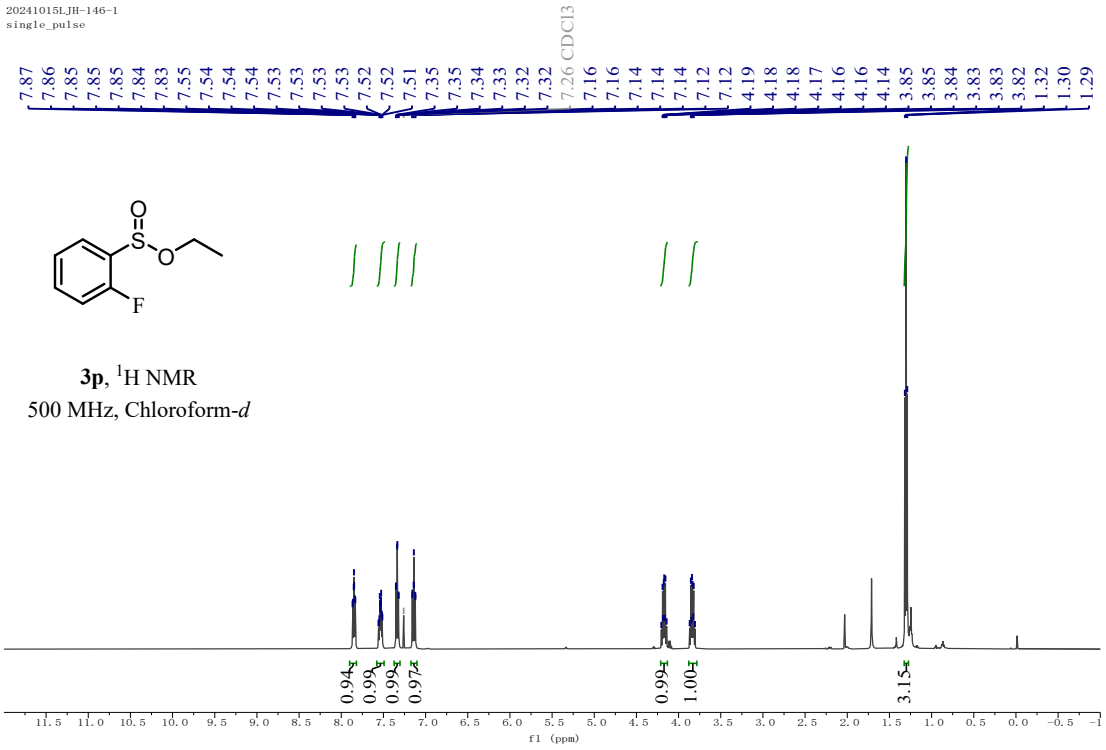
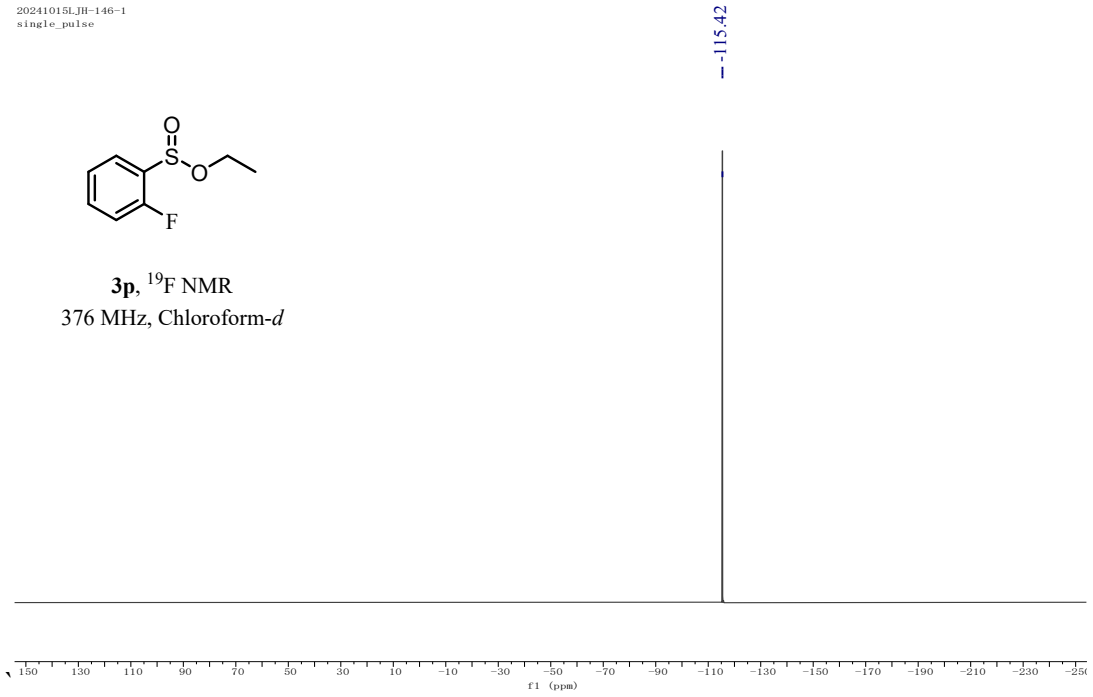


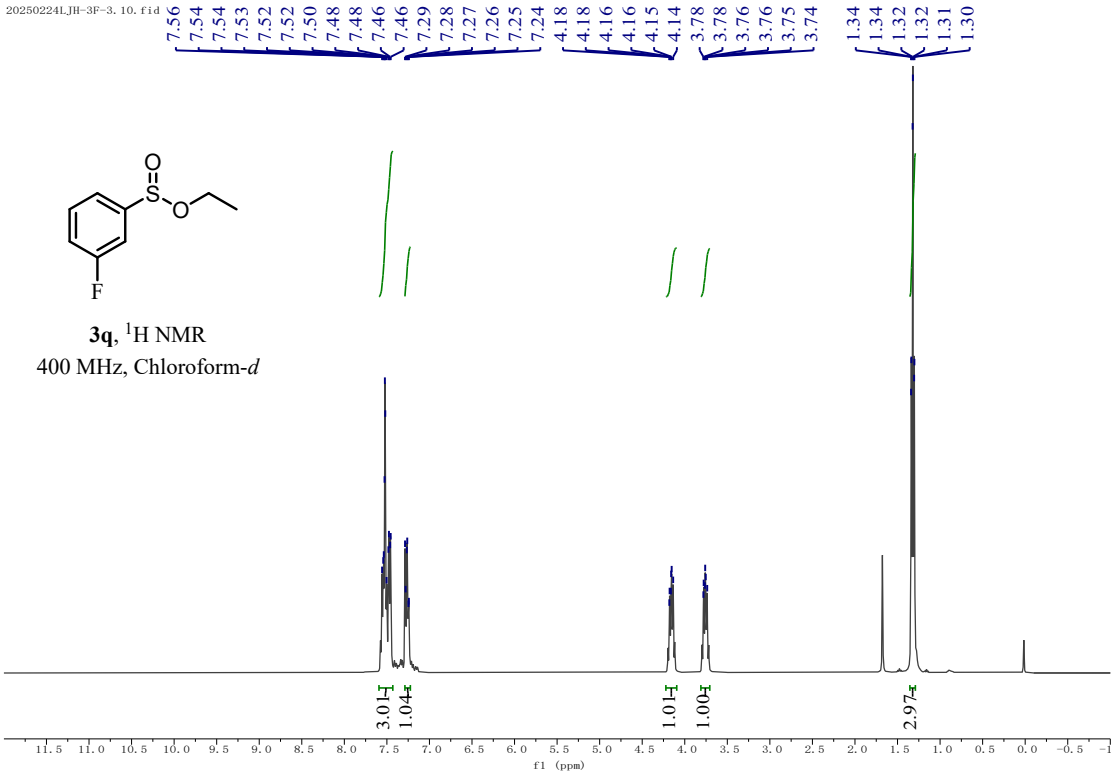
3o, ^{13}C NMR
101 MHz, Chloroform-*d*



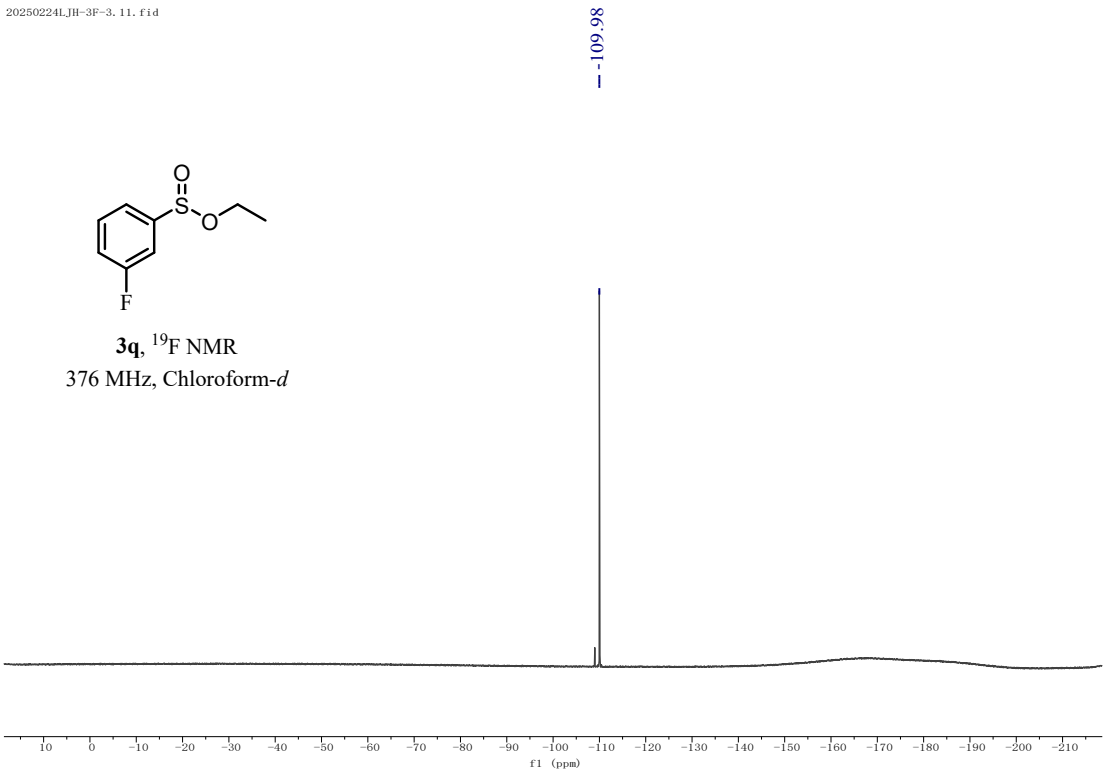
3p, ^{1}H NMR
500 MHz, Chloroform-*d*



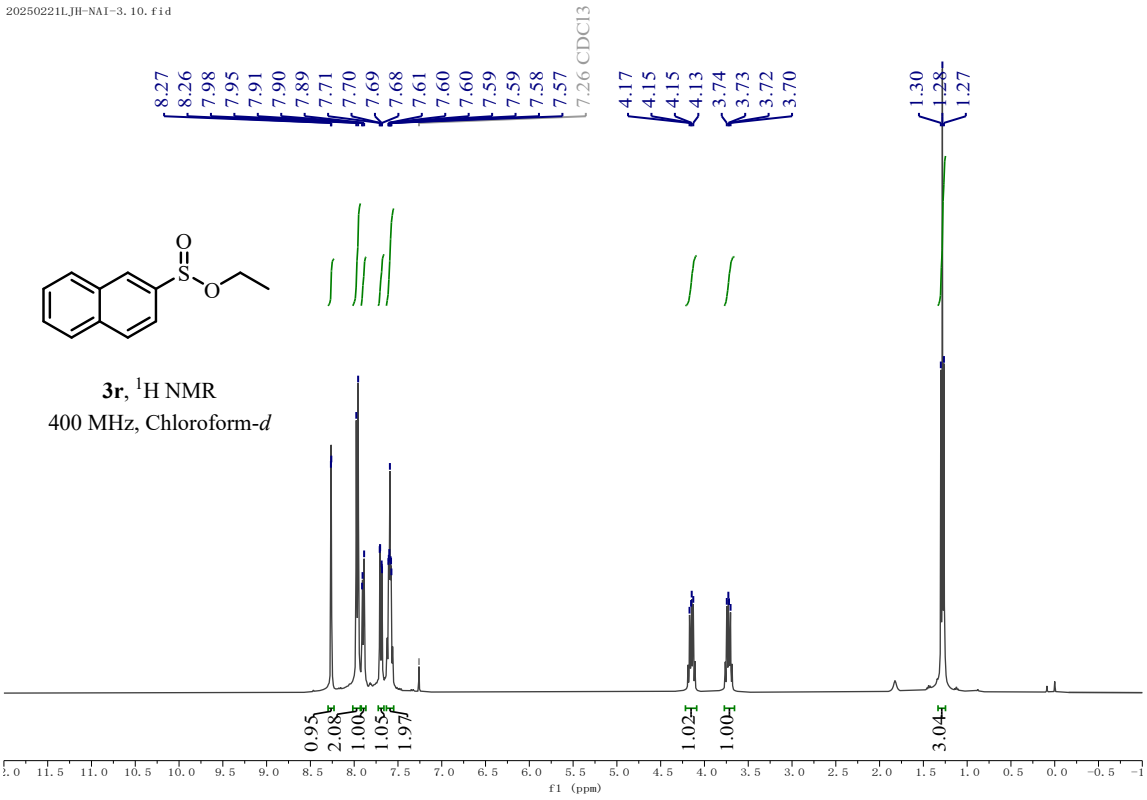
3p, ^{19}F NMR
376 MHz, Chloroform-*d*



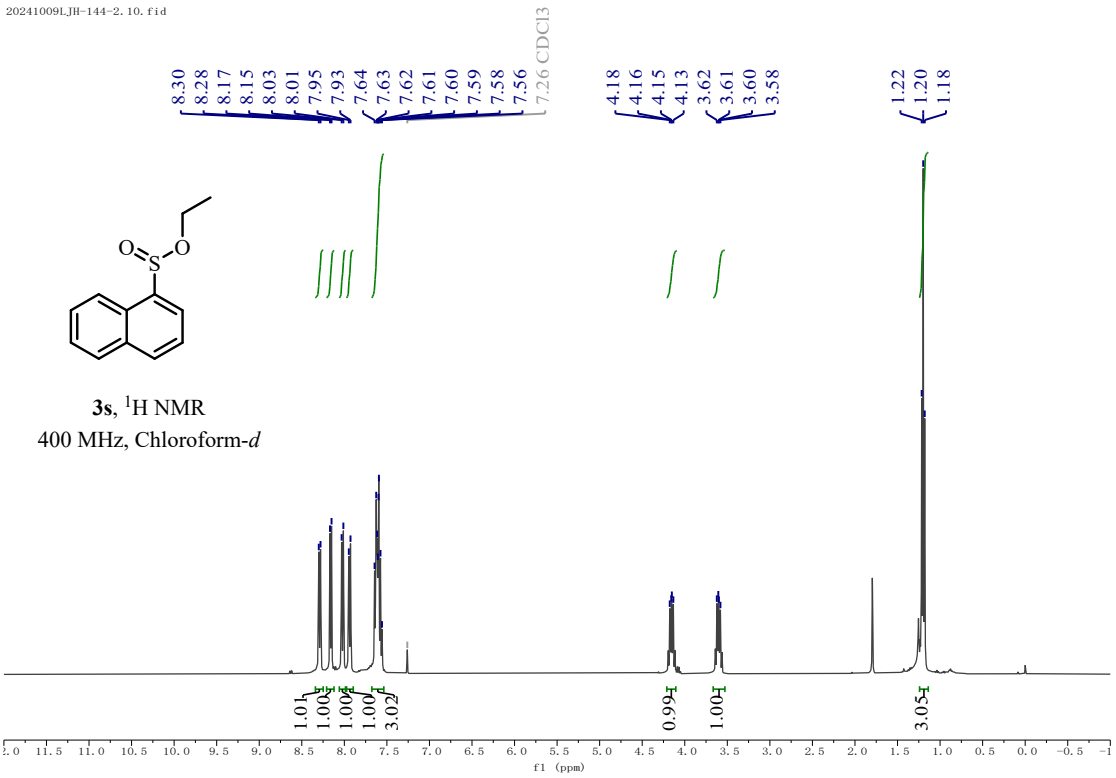
3q, ^{1}H NMR
400 MHz, Chloroform-*d*



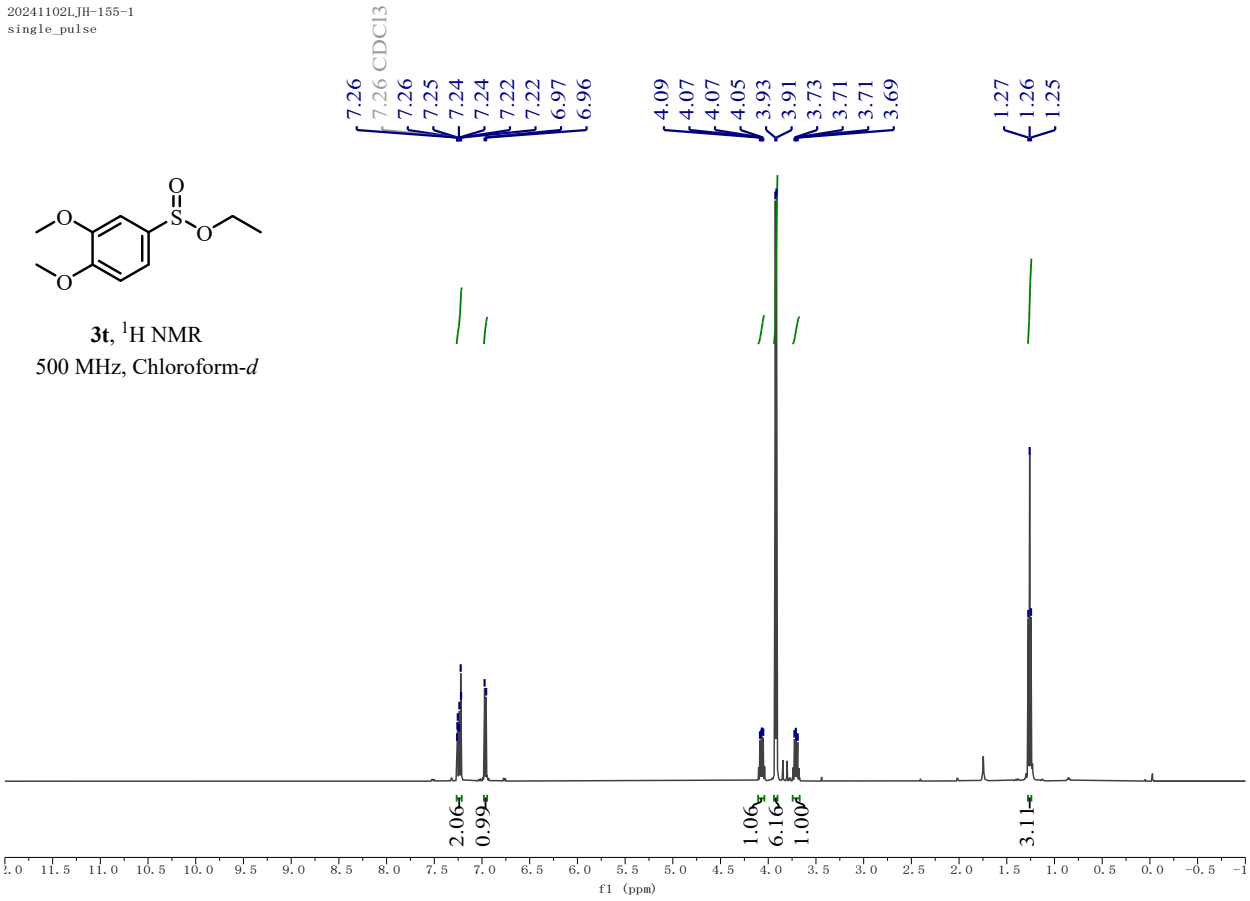
3q, ^{19}F NMR
376 MHz, Chloroform-*d*



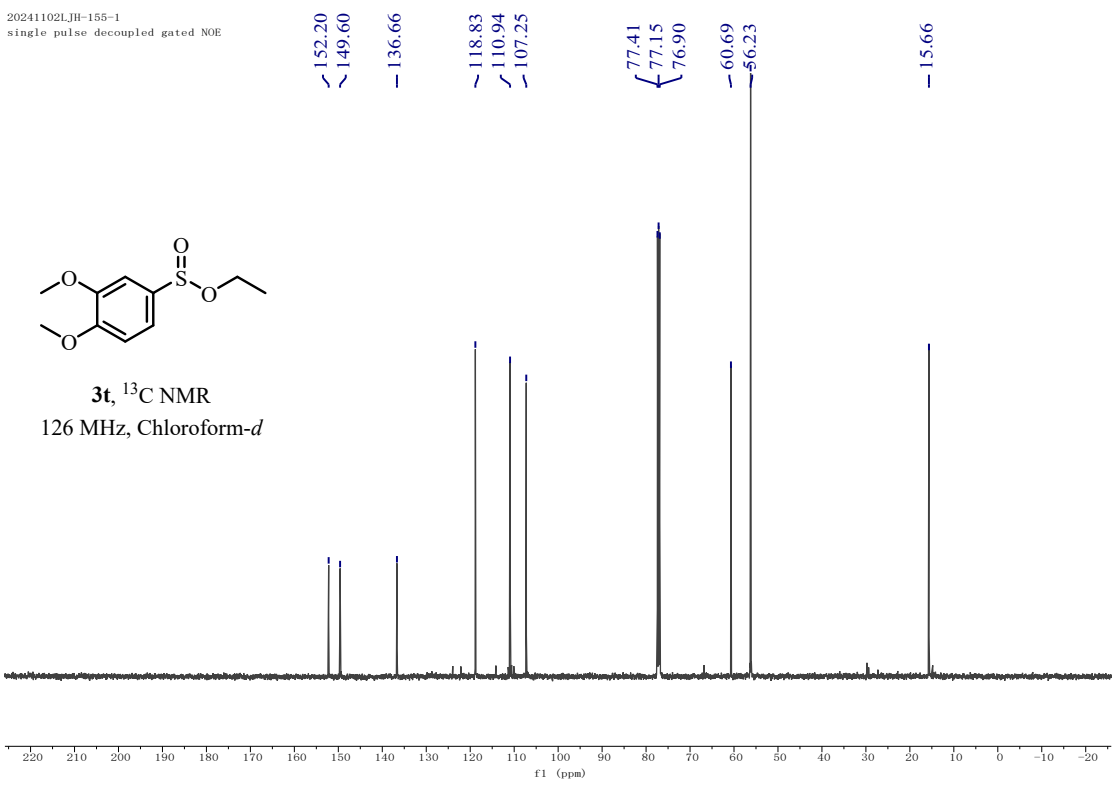
3r, ^{1}H NMR
400 MHz, Chloroform-*d*



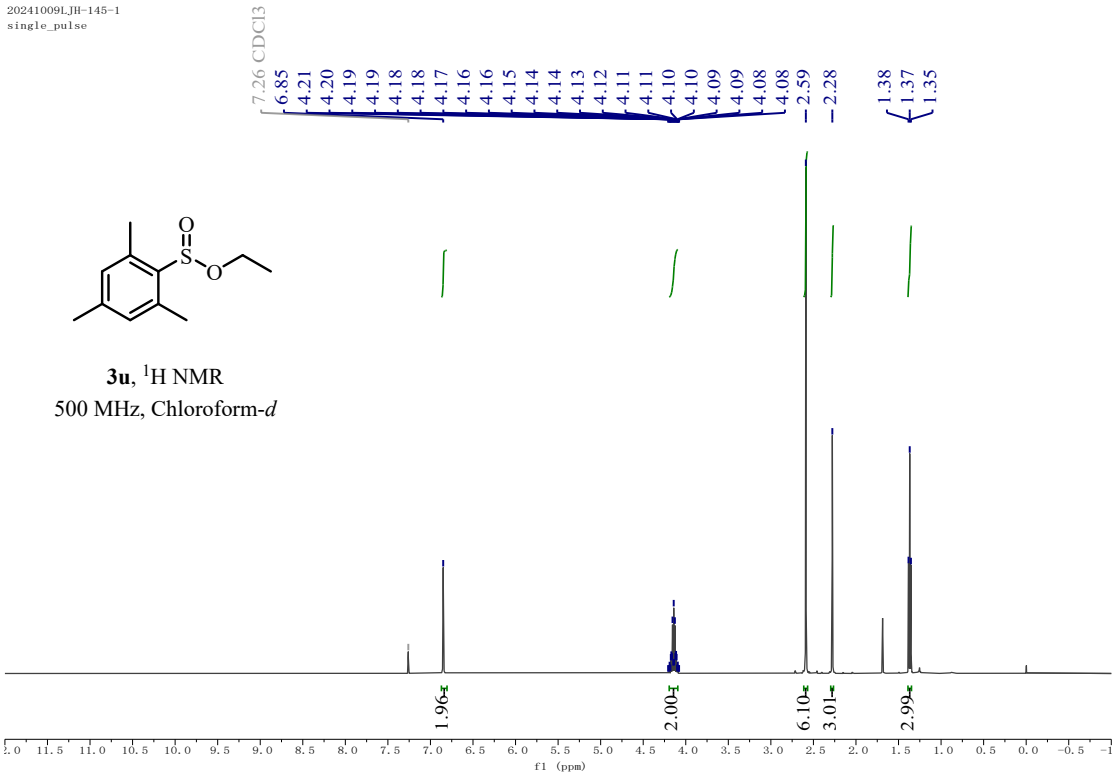
3s, ^{1}H NMR
400 MHz, Chloroform-*d*



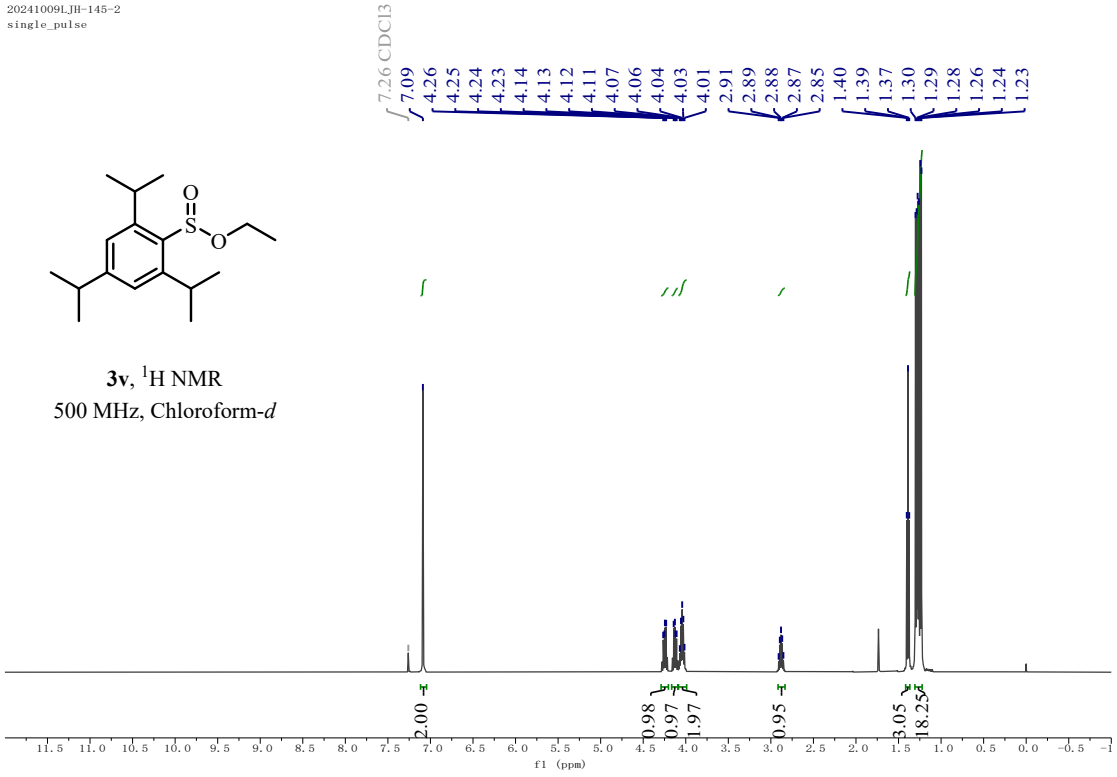
3t, ^{1}H NMR
500 MHz, Chloroform-*d*



3t, ^{13}C NMR
126 MHz, Chloroform-*d*



3u, ^{1}H NMR
500 MHz, Chloroform-*d*



3v, ^{1}H NMR
500 MHz, Chloroform-*d*

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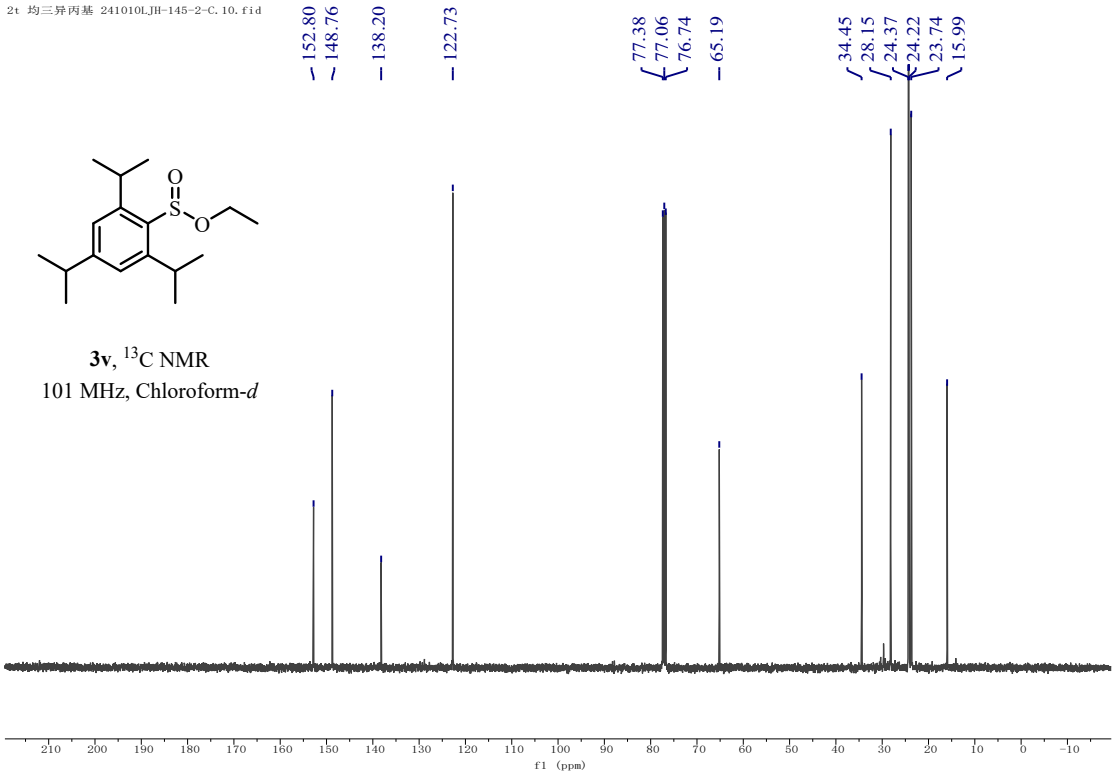

3v, ^{13}C NMR
101 MHz, Chloroform-*d*

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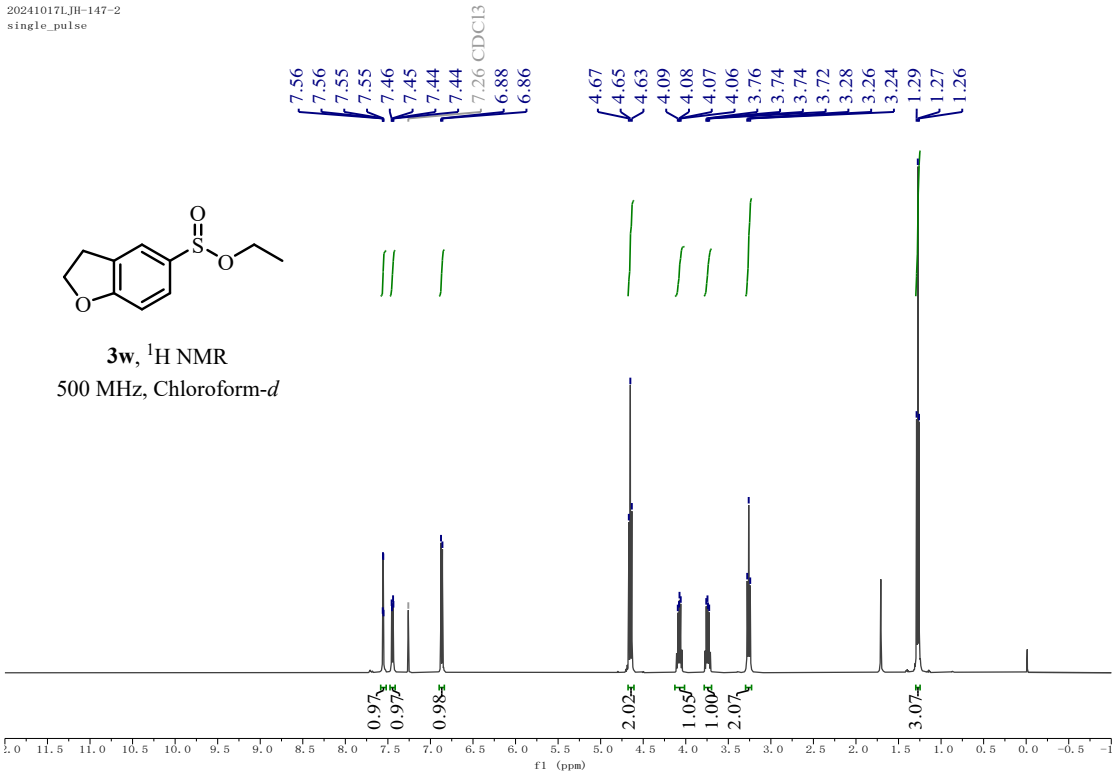
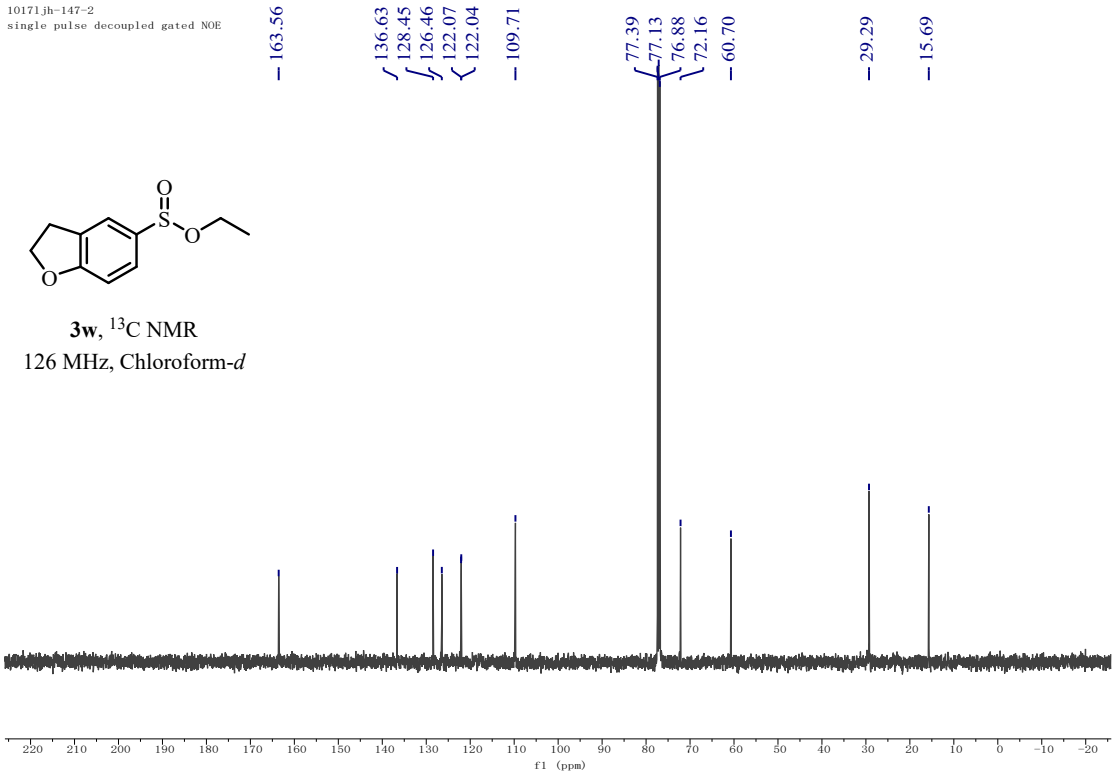
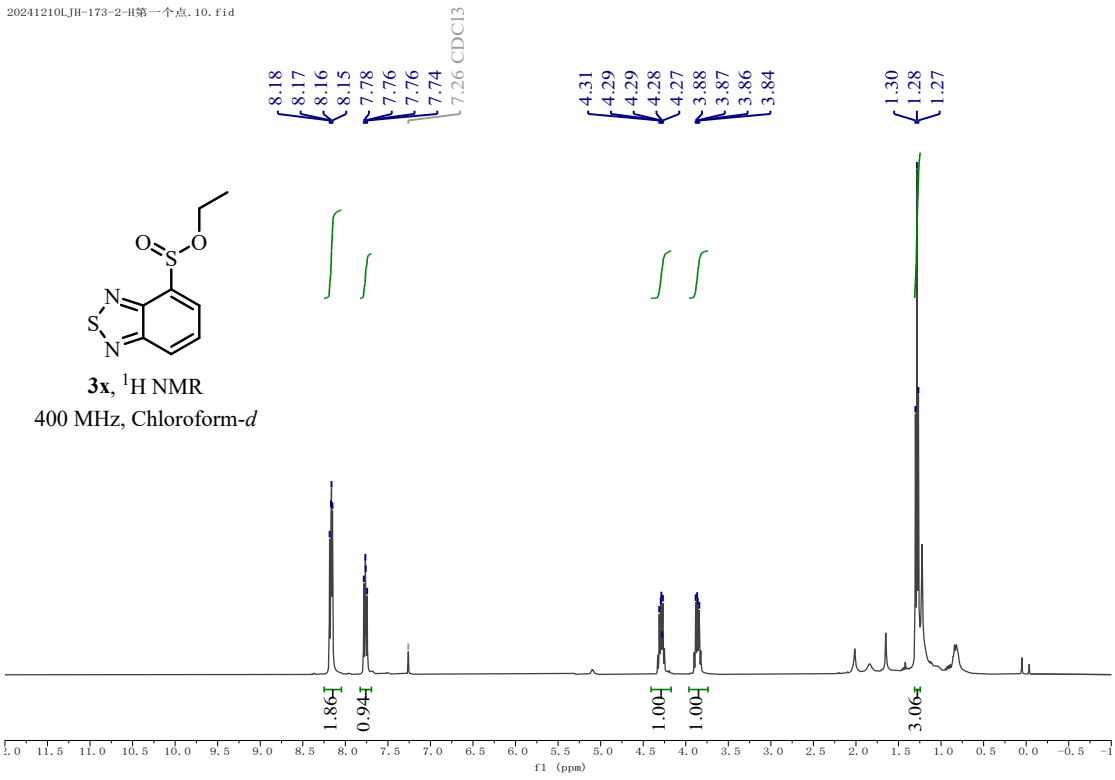
single_pulse



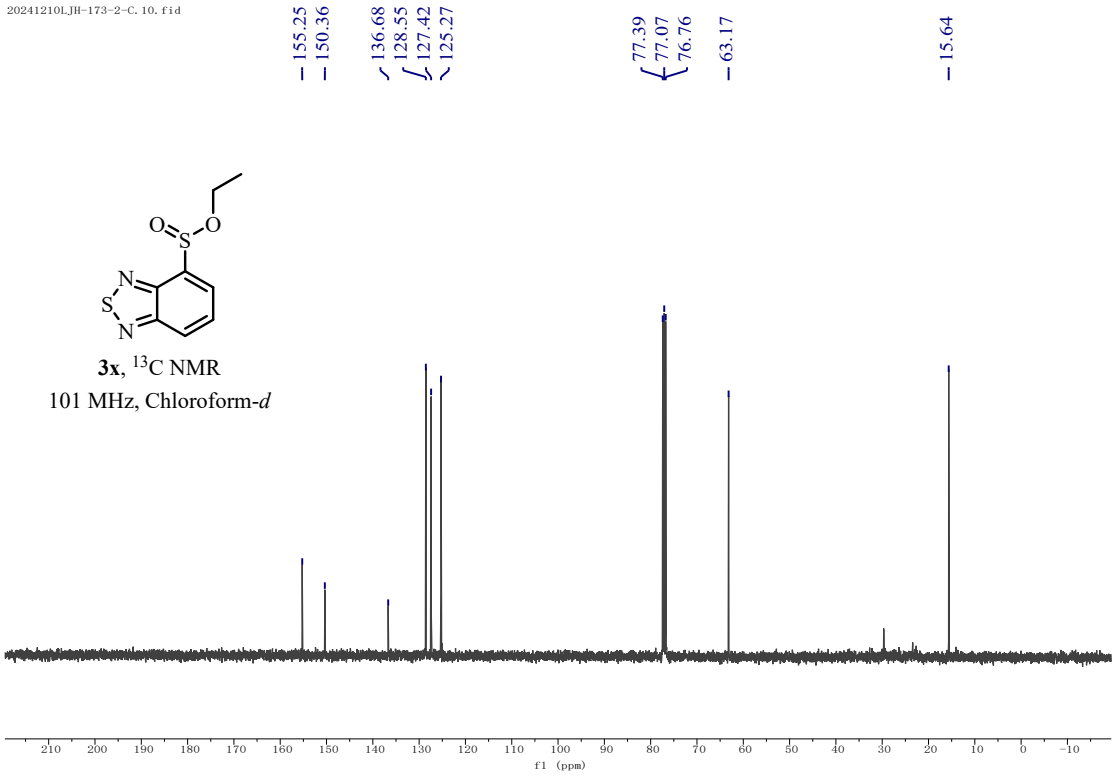
3w, ^{1}H NMR
500 MHz, Chloroform-*d*



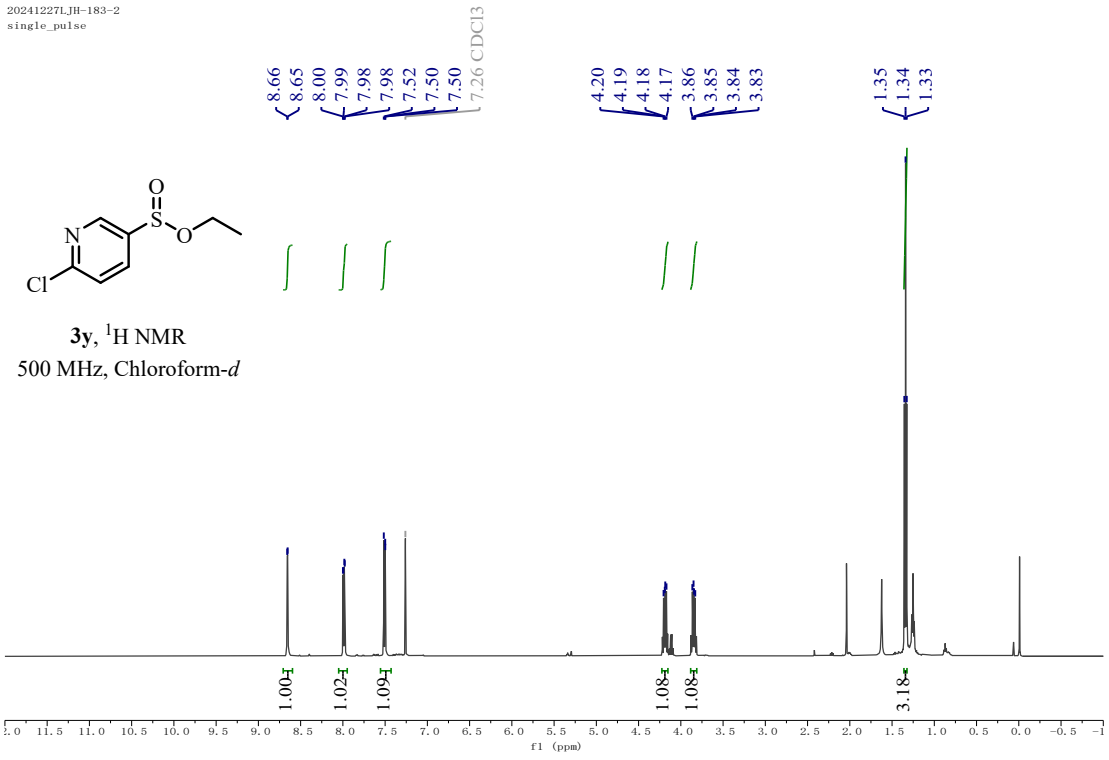
3w, ^{13}C NMR
126 MHz, Chloroform-*d*



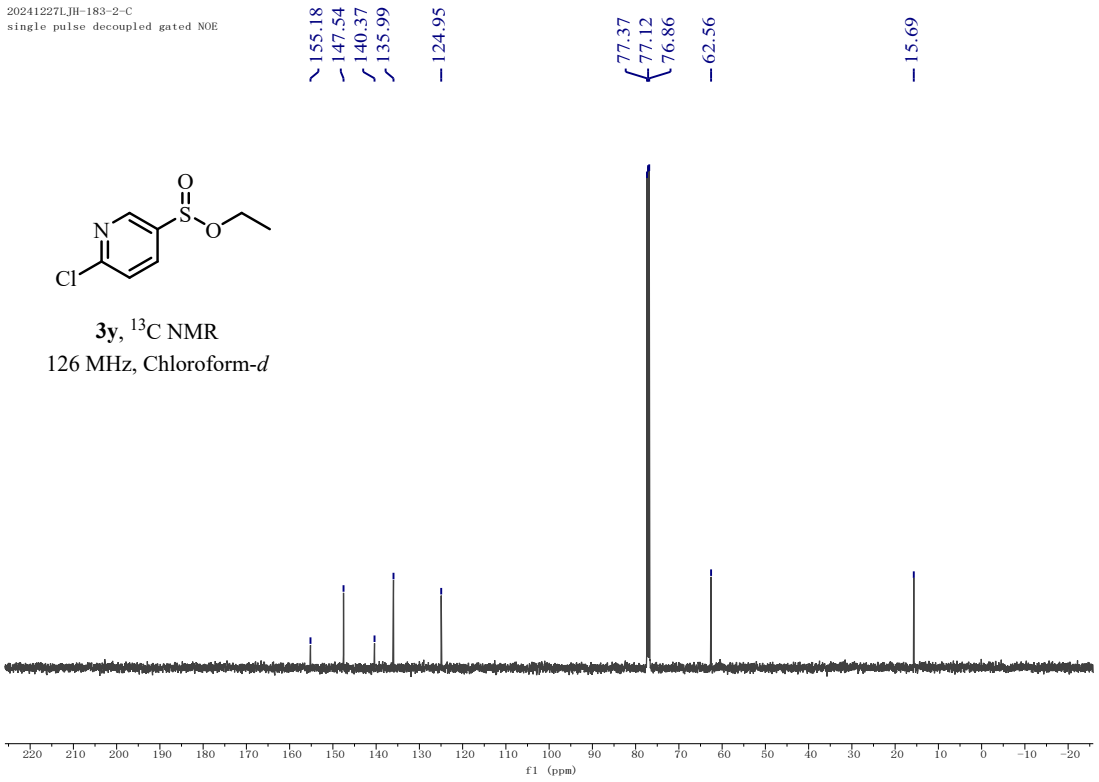
3x, ^{1}H NMR
400 MHz, Chloroform-*d*



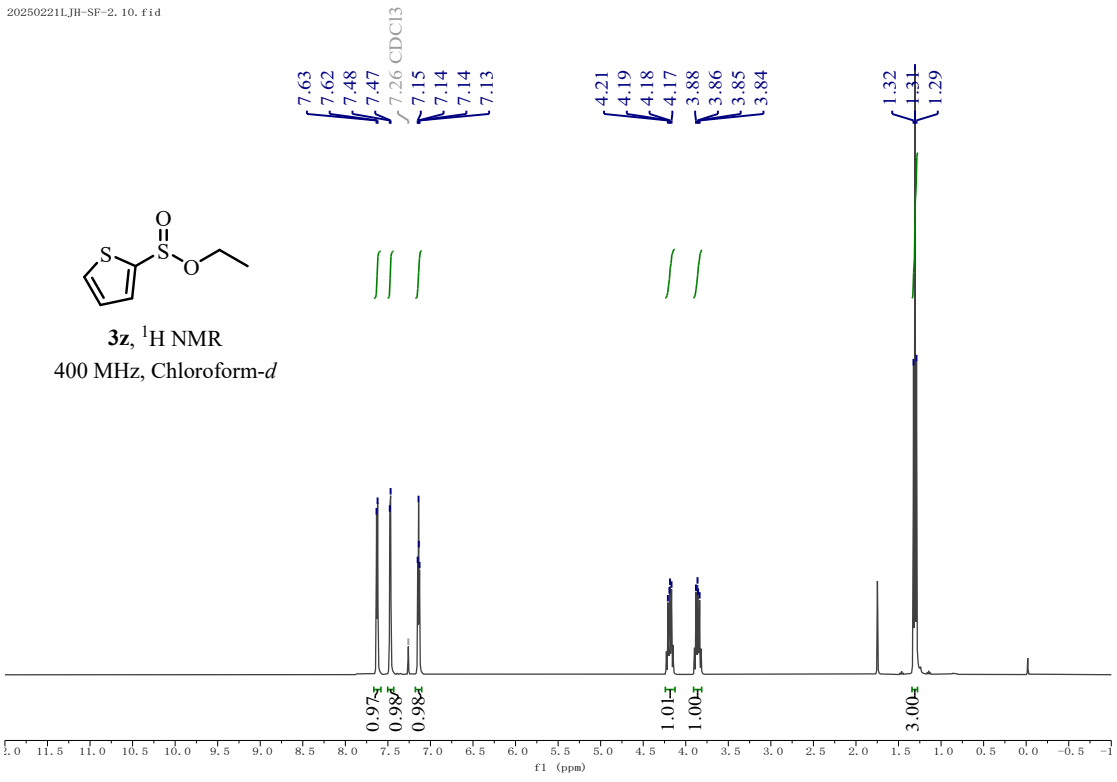
3x, ^{13}C NMR
101 MHz, Chloroform-*d*



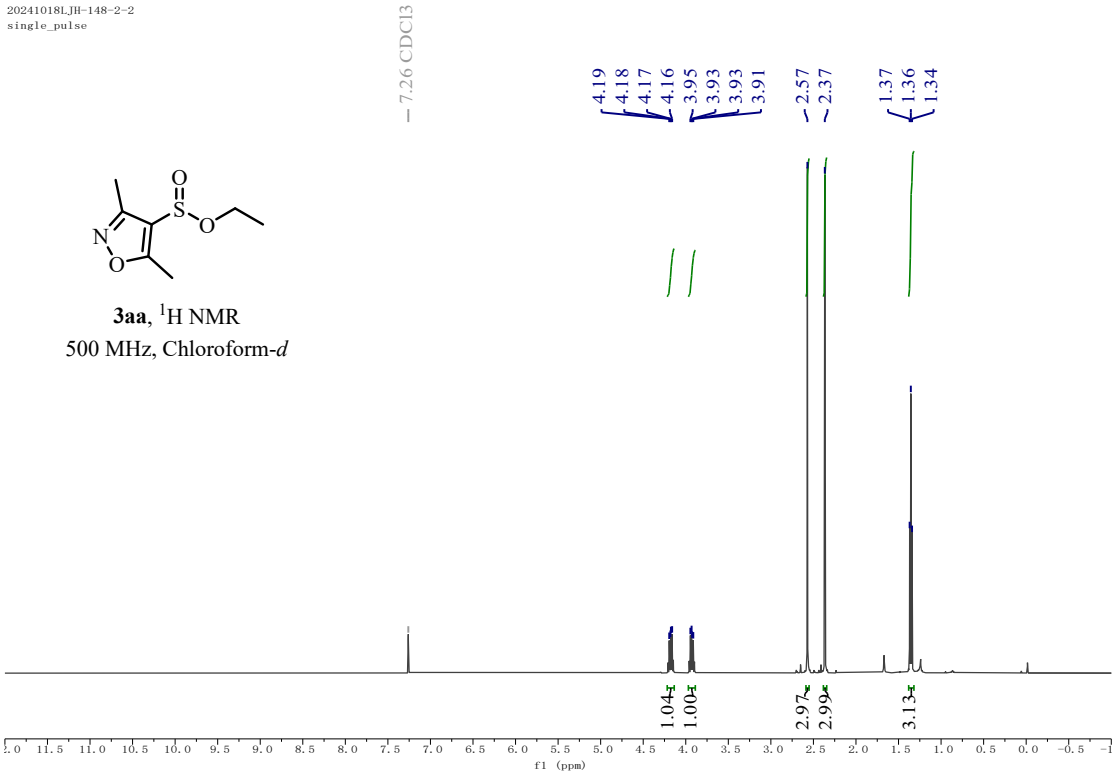
3y, ^{1}H NMR
500 MHz, Chloroform-*d*



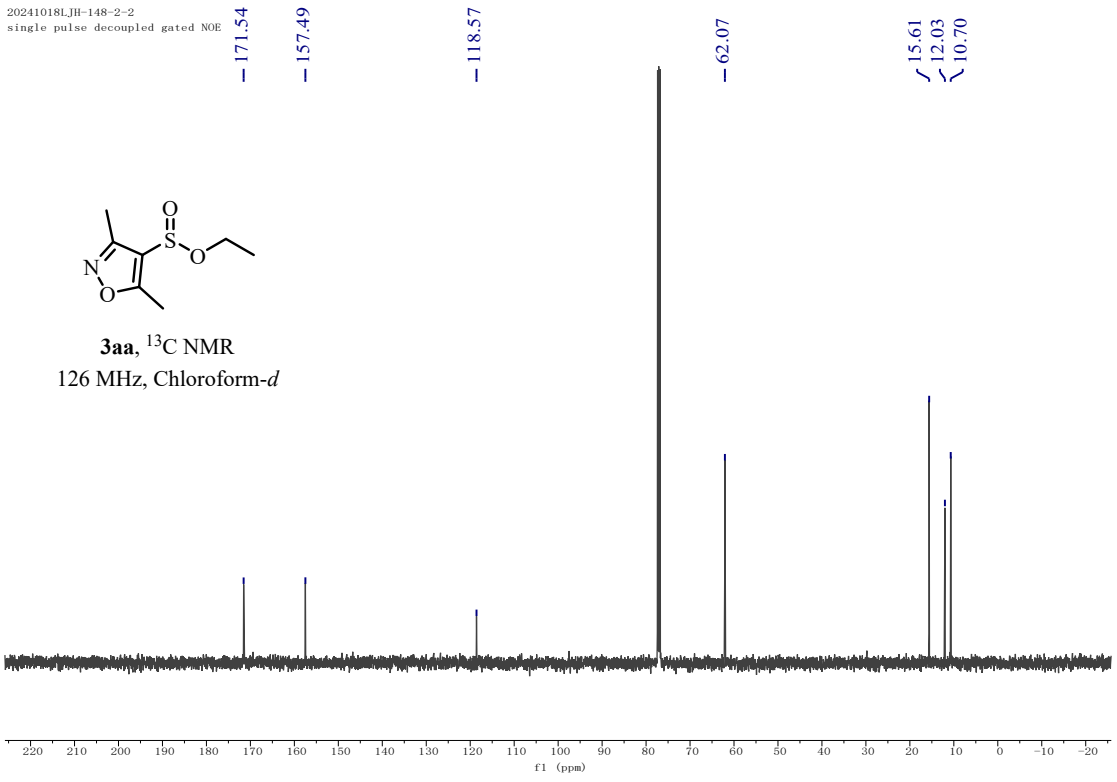
3y, ^{13}C NMR
126 MHz, Chloroform-*d*



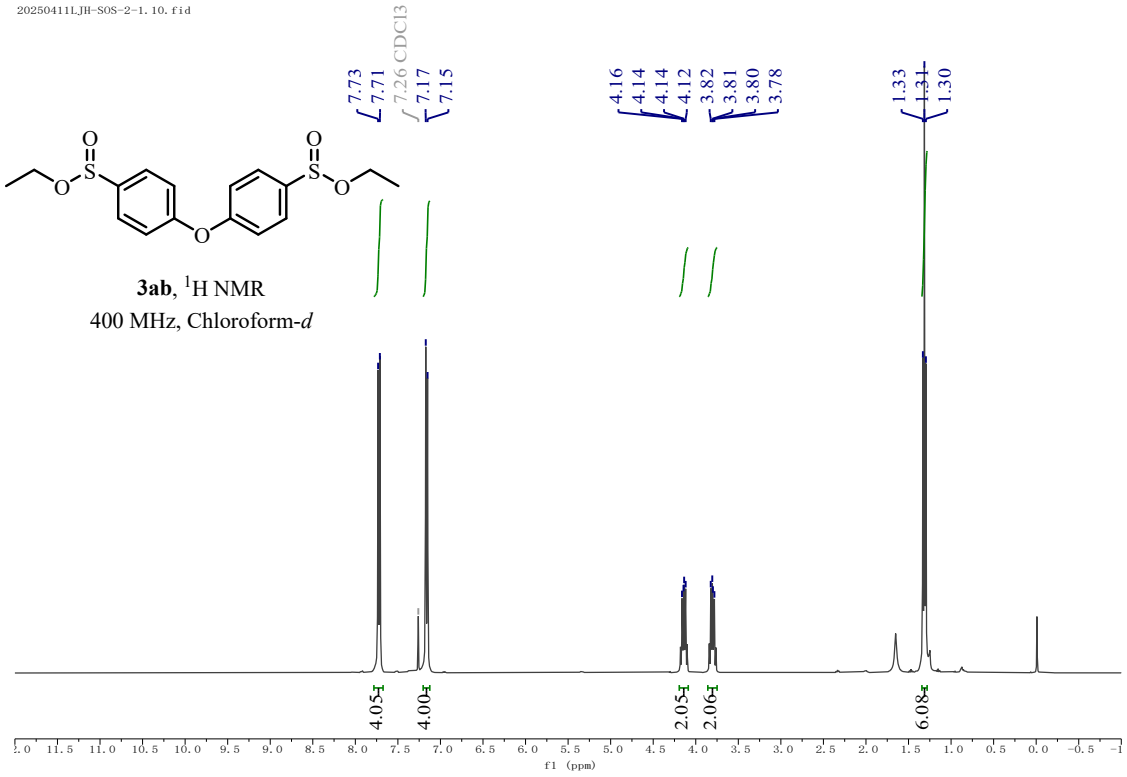
3z, ^{1}H NMR
400 MHz, Chloroform-*d*



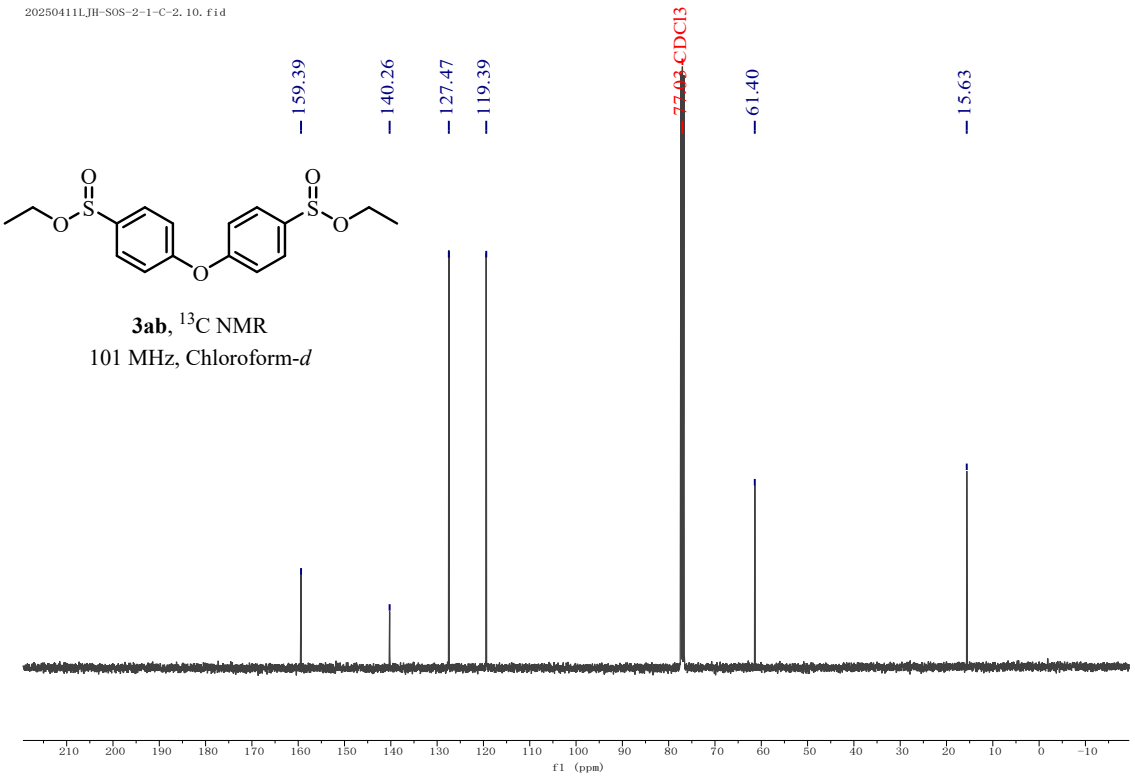
3aa, ^{1}H NMR
500 MHz, Chloroform-*d*



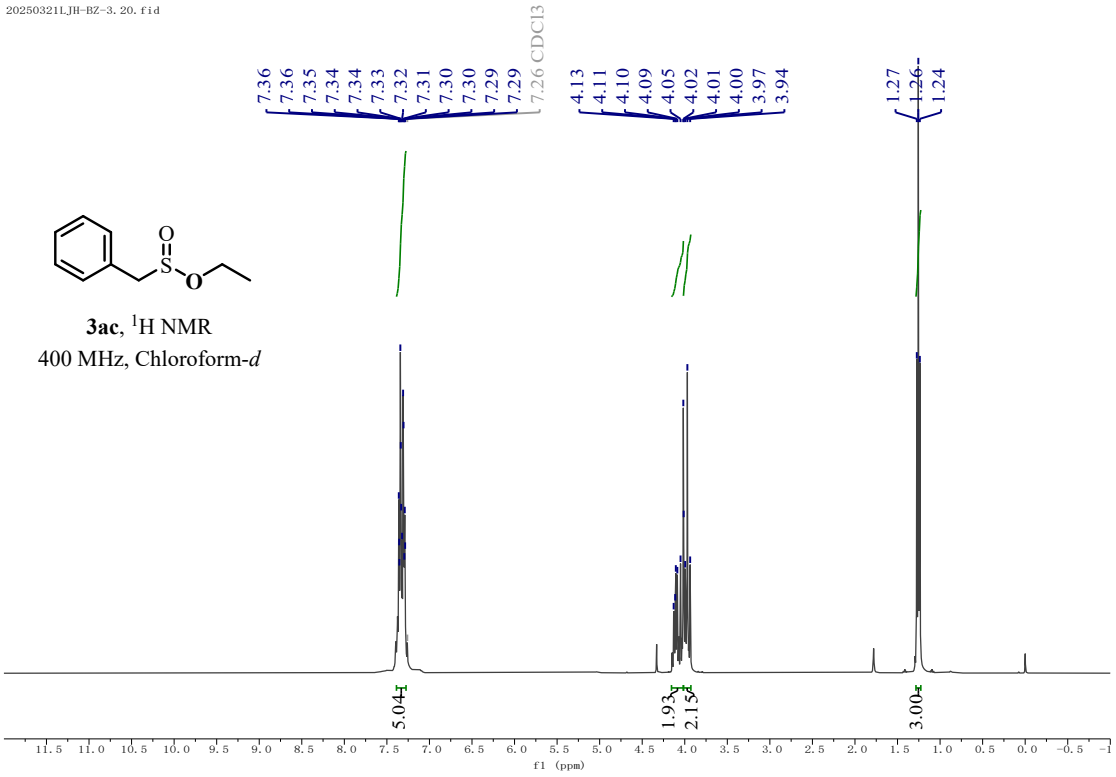
3aa, ^{13}C NMR
126 MHz, Chloroform-*d*



3ab, ^{1}H NMR
400 MHz, Chloroform-*d*



3ab, ^{13}C NMR
101 MHz, Chloroform-*d*



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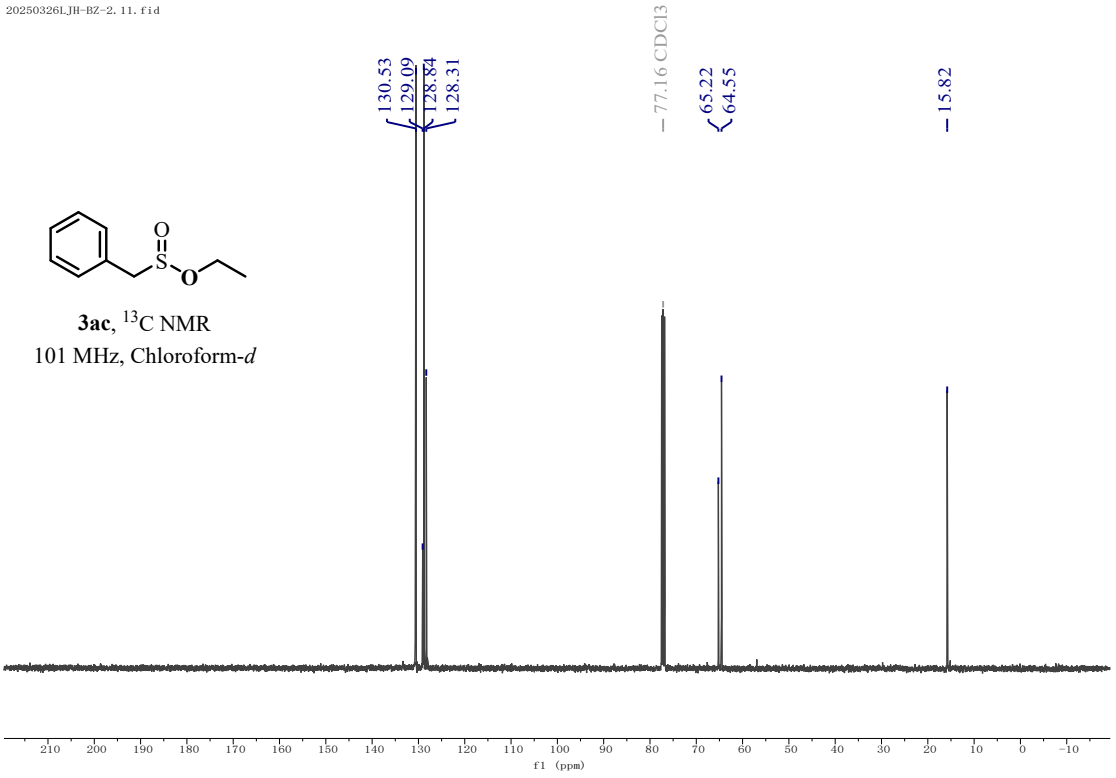
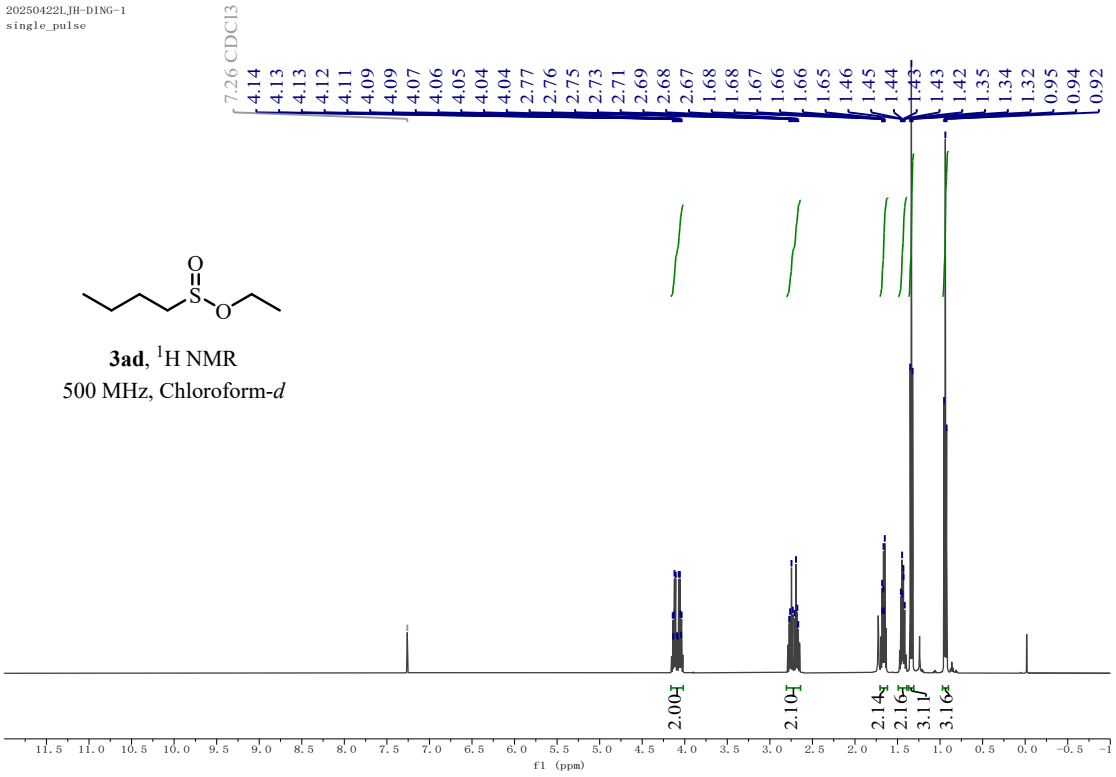
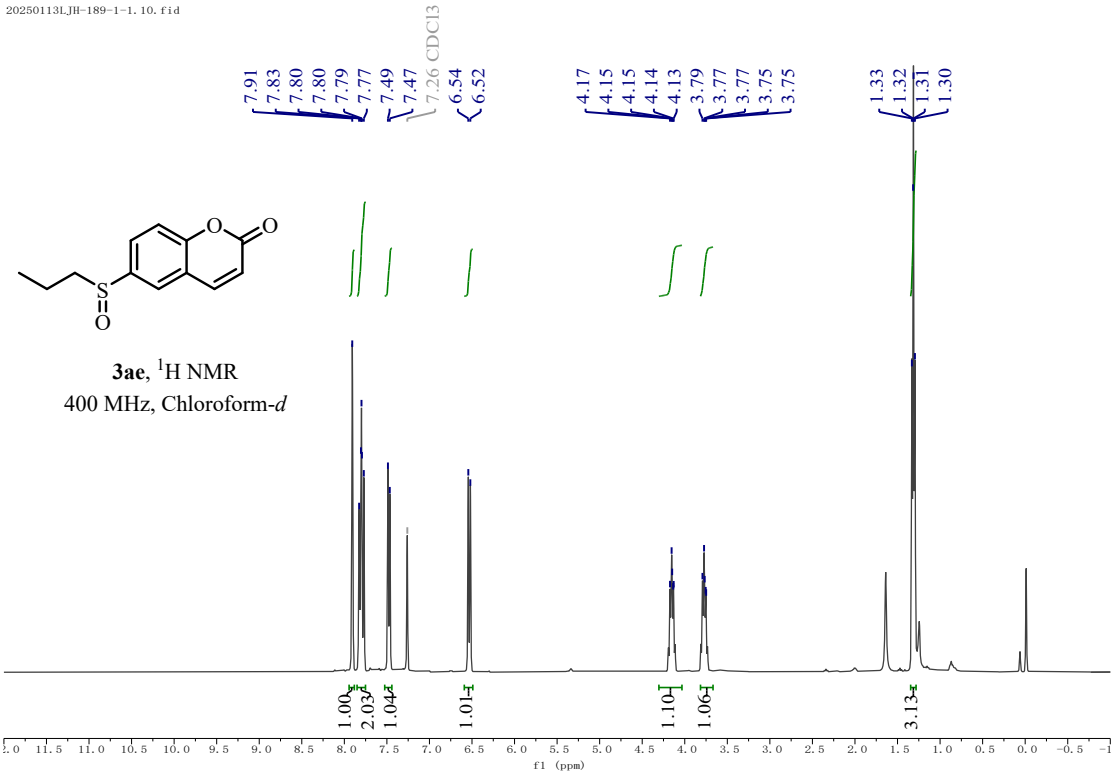
400 MHz, Chloroform-*d*



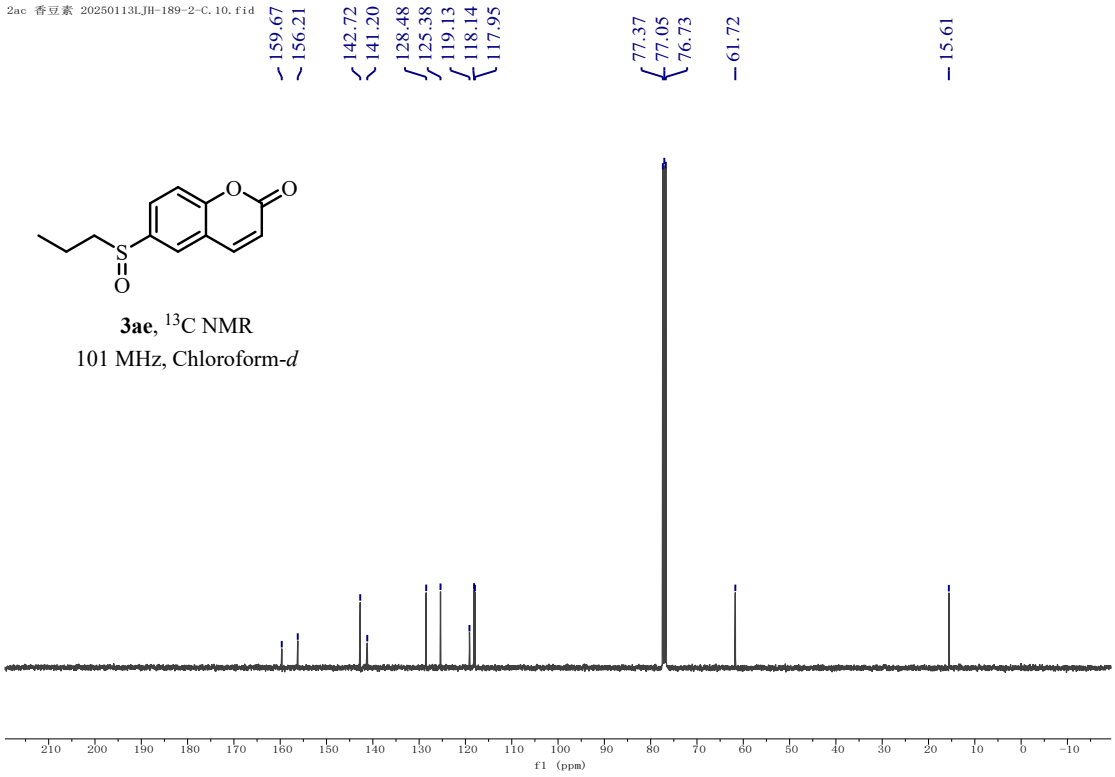
3ac, ^{13}C NMR
101 MHz, Chloroform-*d*



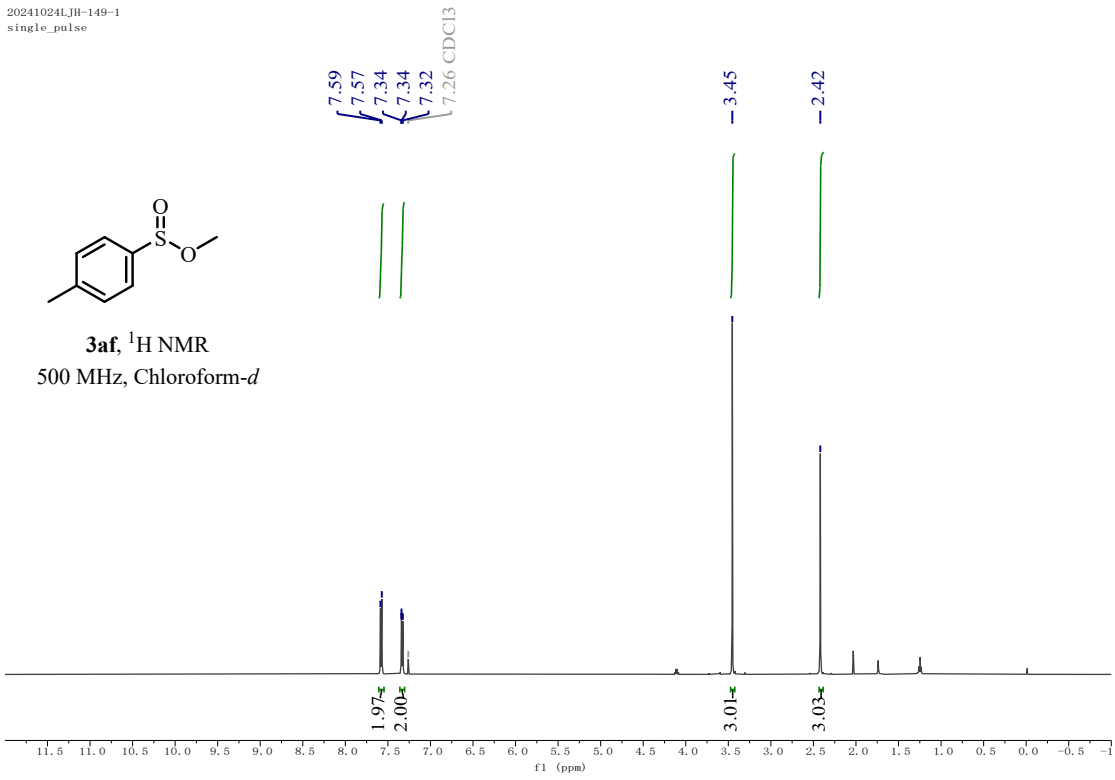
3ad, ^{1}H NMR
500 MHz, Chloroform-*d*



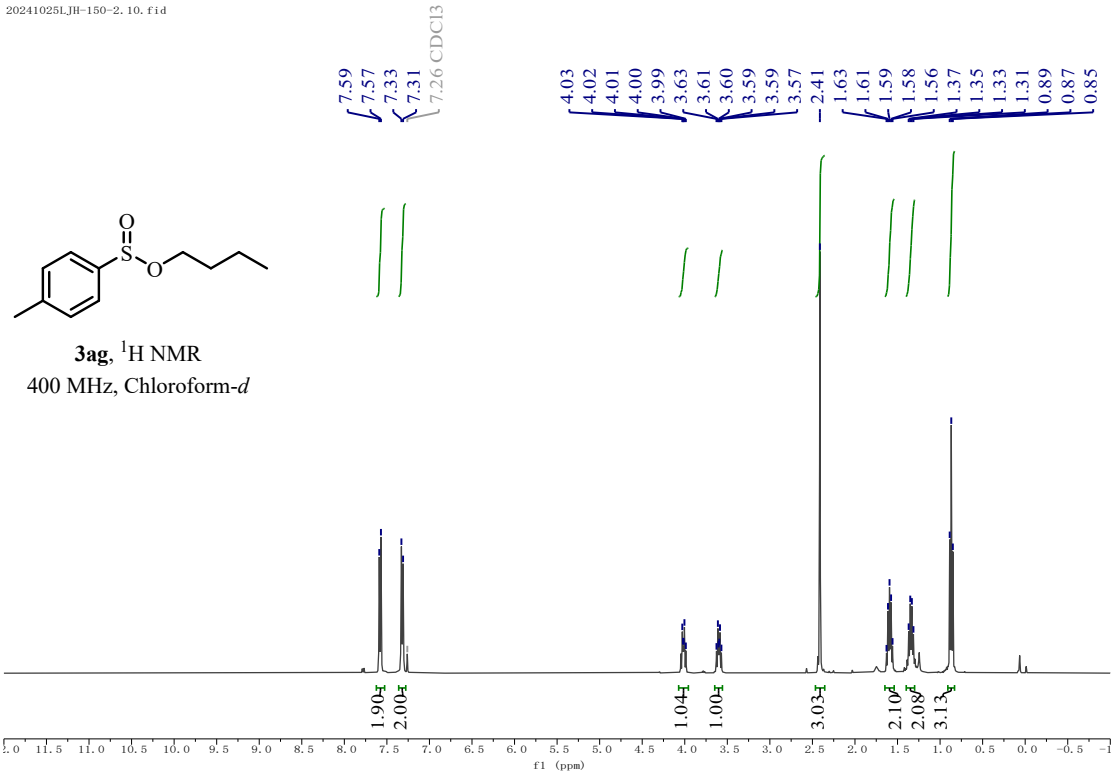
3ae, ^{1}H NMR
400 MHz, Chloroform-*d*



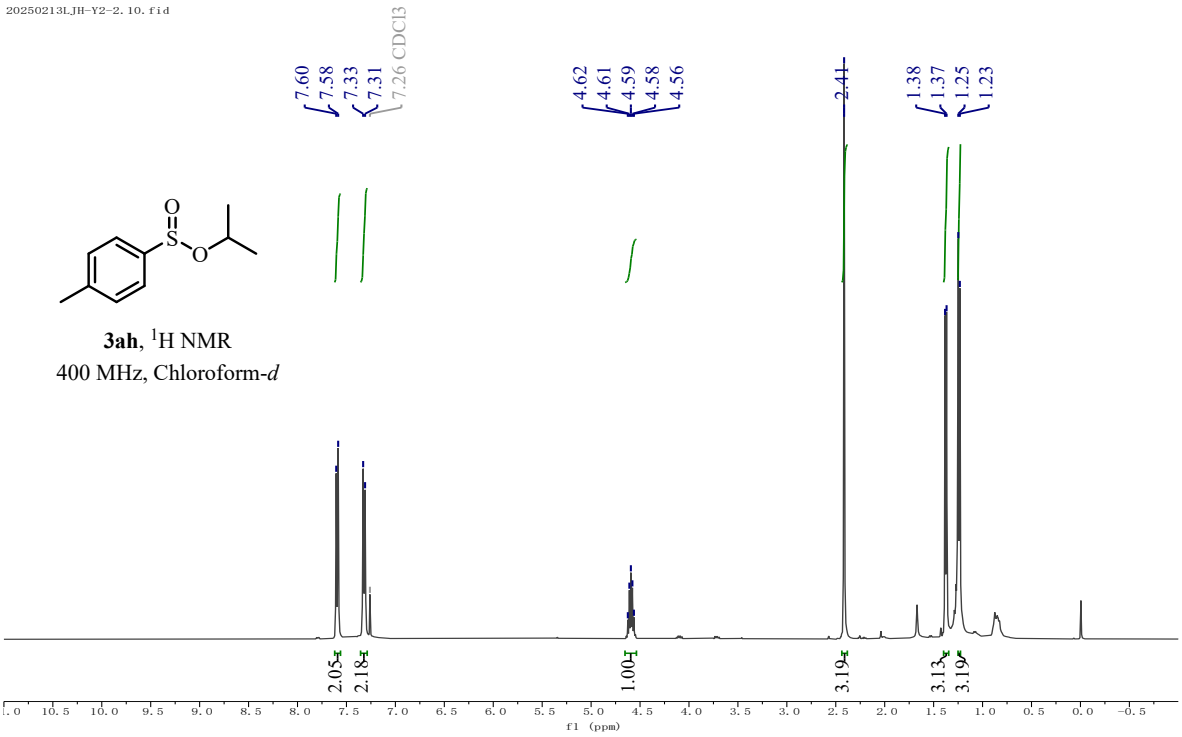
3ae, ^{13}C NMR
101 MHz, Chloroform-*d*



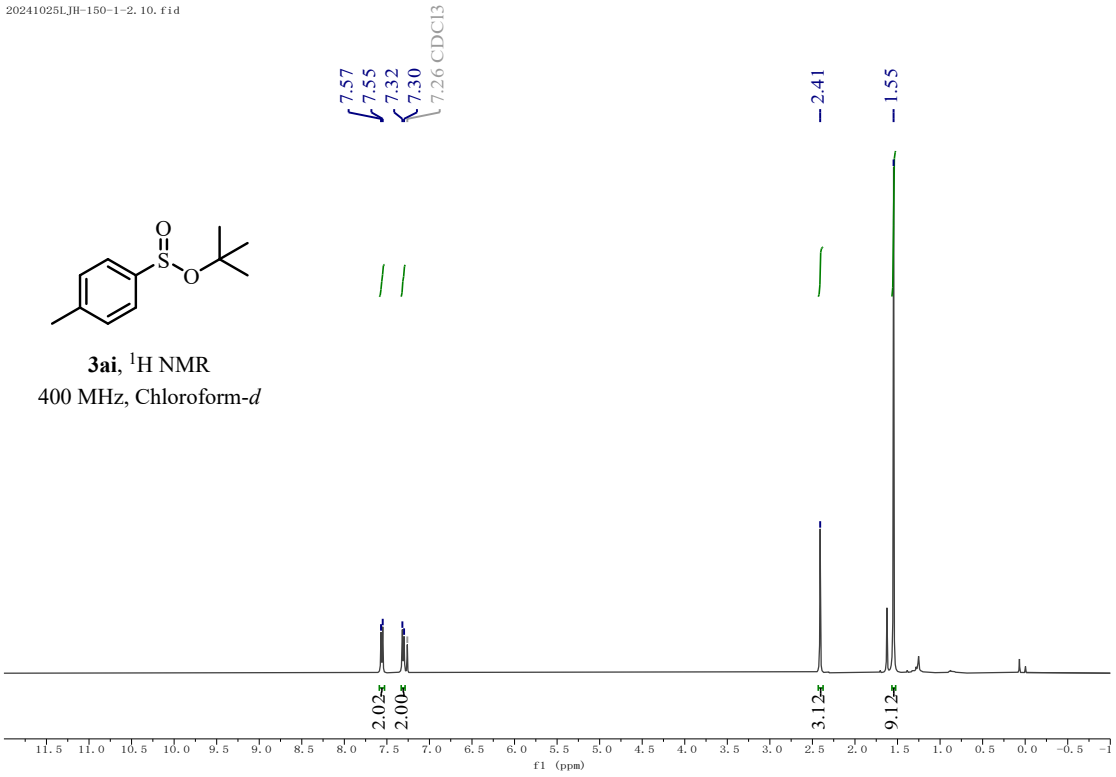
3af, ^{1}H NMR
500 MHz, Chloroform-*d*



3ag, ^{1}H NMR
400 MHz, Chloroform-*d*



3ah, ^{1}H NMR
400 MHz, Chloroform-*d*



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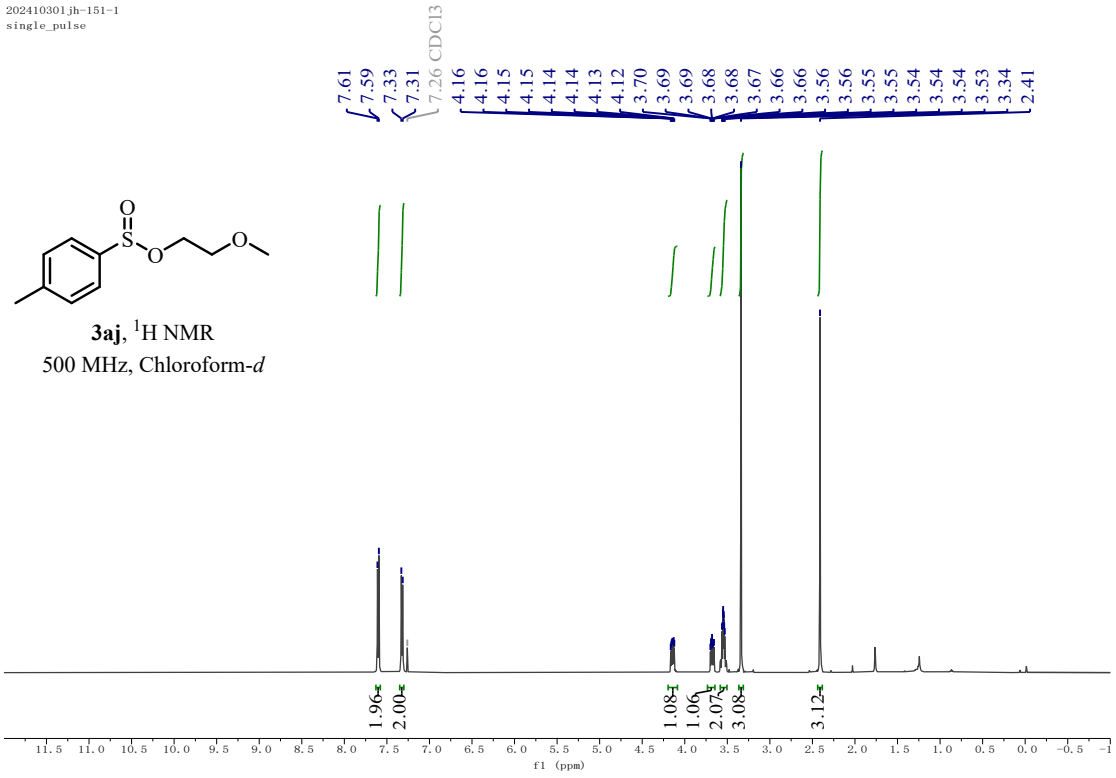
400 MHz, Chloroform-*d*



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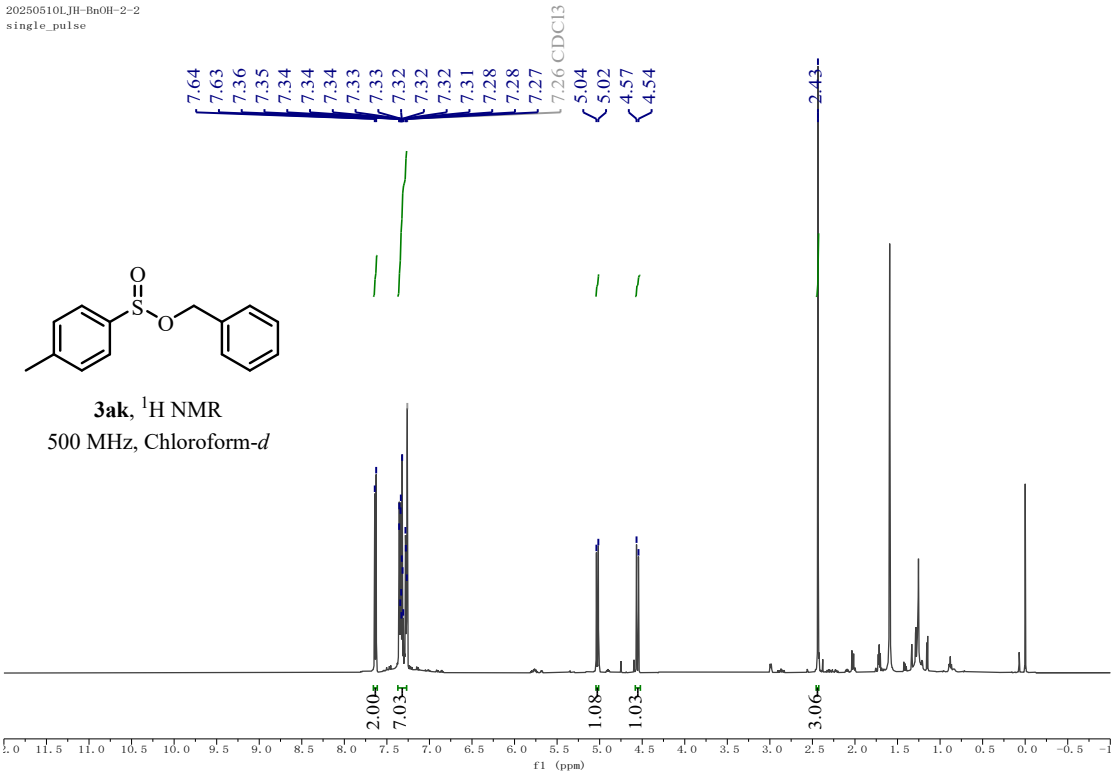
500 MHz, Chloroform-*d*



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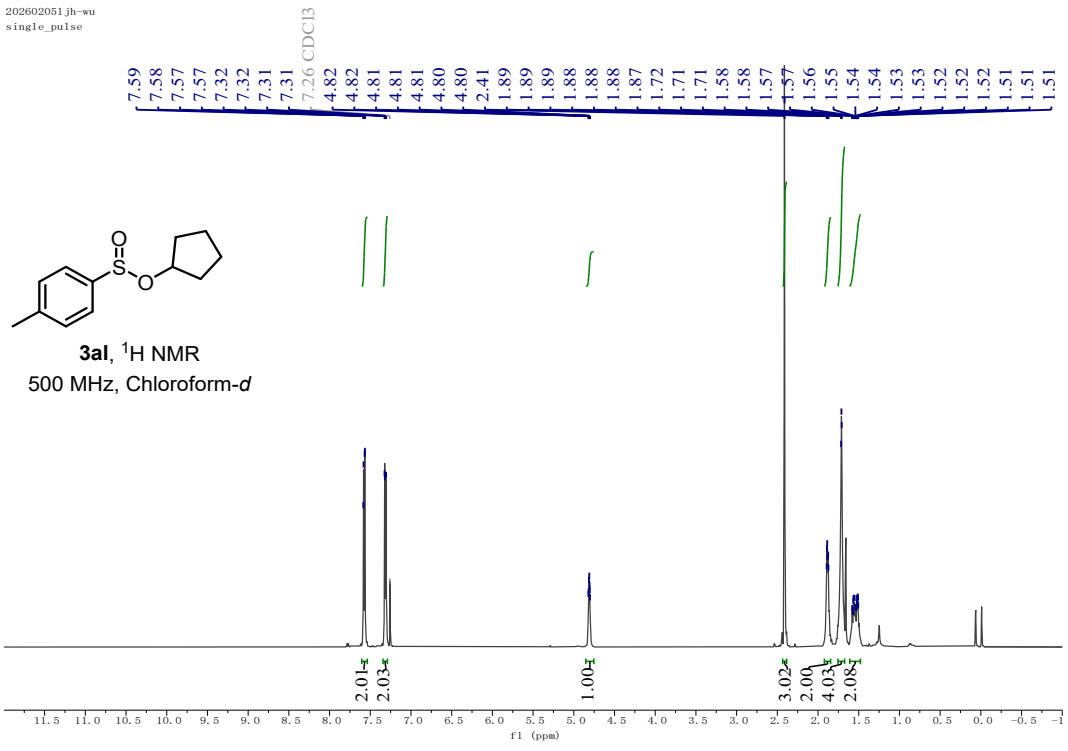
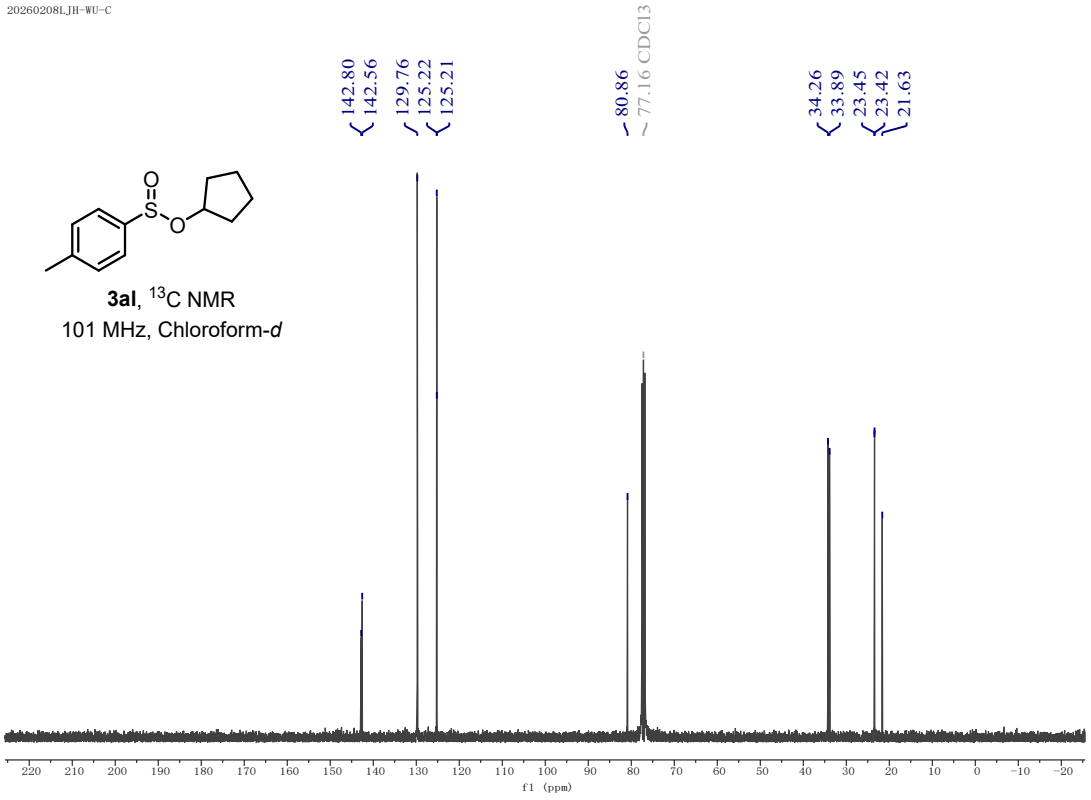
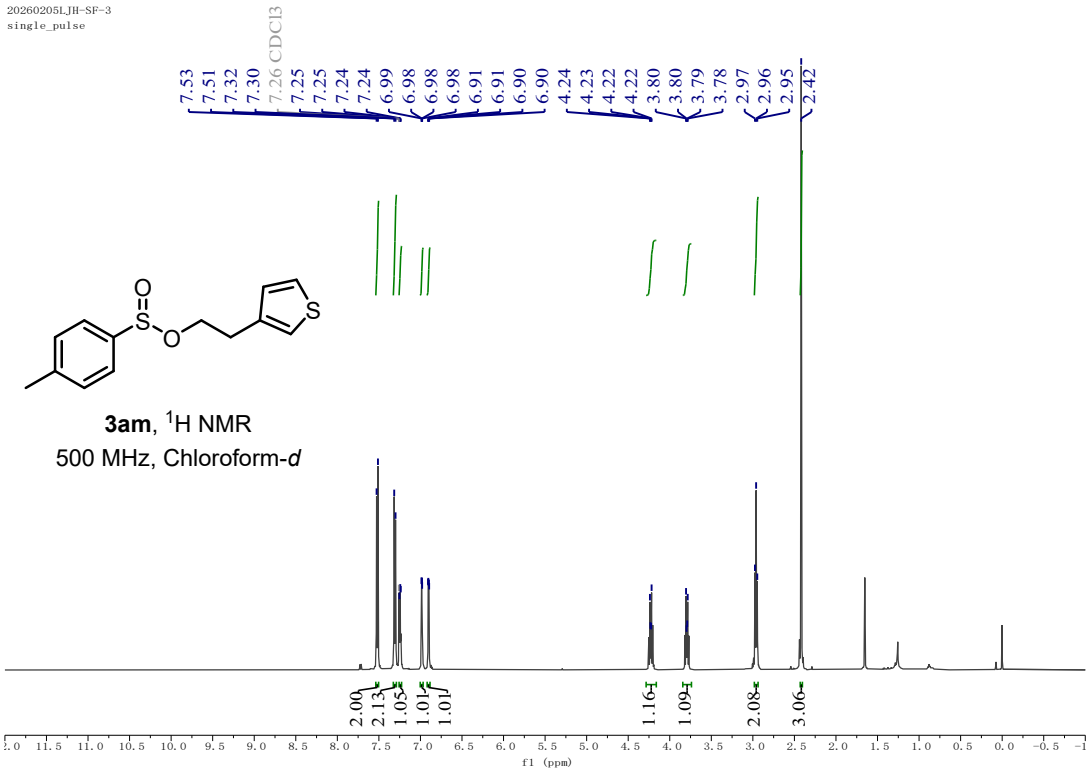
500 MHz, Chloroform-*d*



3al, ^{1}H NMR
500 MHz, Chloroform-*d*


20260208LJH-WU-C
142.80
142.56
129.76
125.22
125.21
80.86
77.16 CDCl3
34.26
33.89
23.45
23.42
21.63
3al, 13C NMR
101 MHz, Chloroform-d
f1 (ppm)


20260205LJH-SF-3
single_pulse
7.53
7.51
7.32
7.30
7.26 CDCl3
7.25
7.25
7.24
7.24
6.99
6.98
6.98
6.98
6.91
6.91
6.90
6.90
4.24
4.23
4.22
4.22
3.80
3.80
3.79
3.78
2.97
2.96
2.95
2.42
2.00
2.13
1.05
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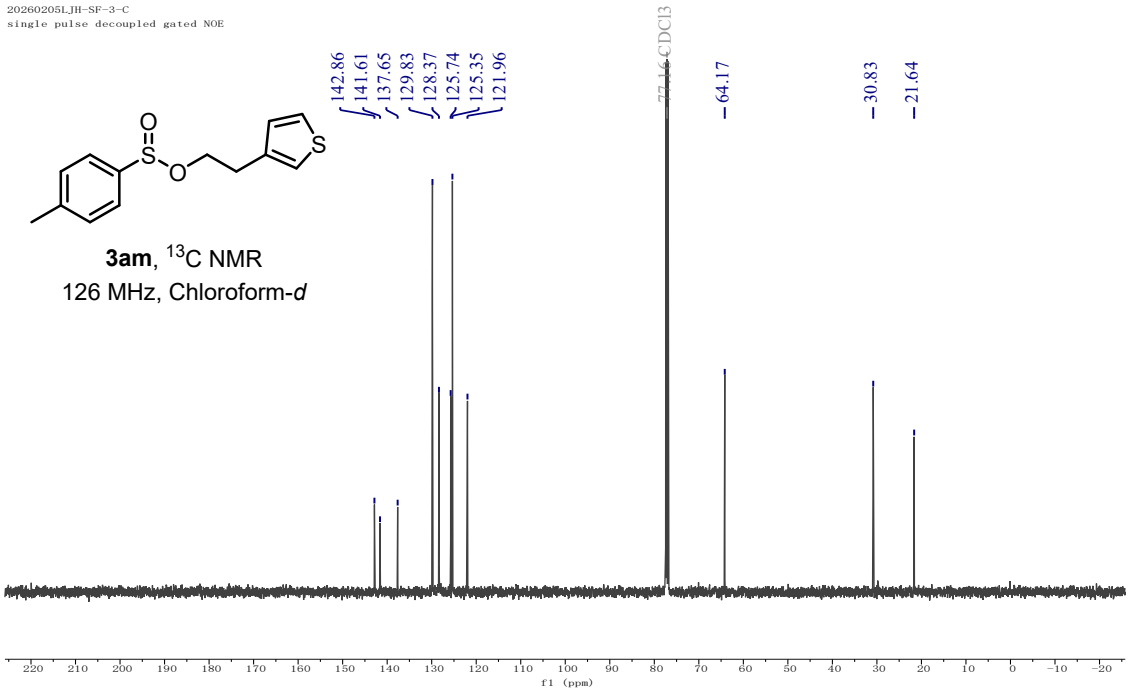
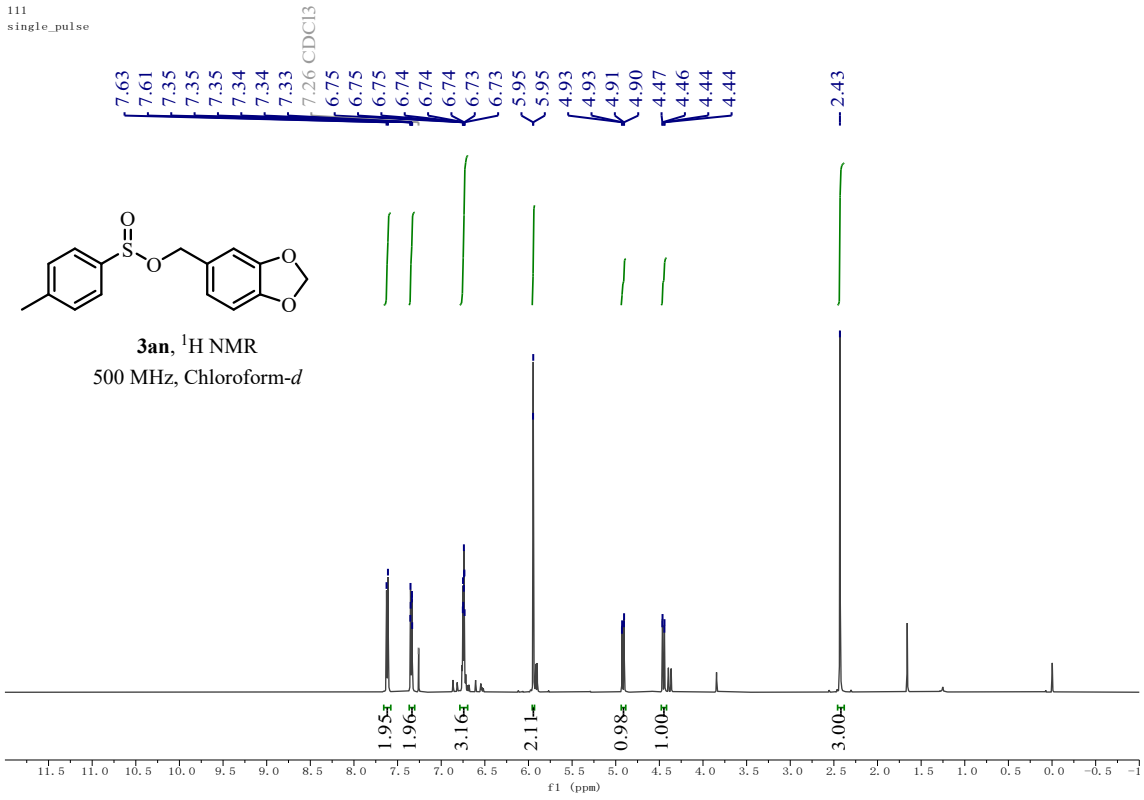
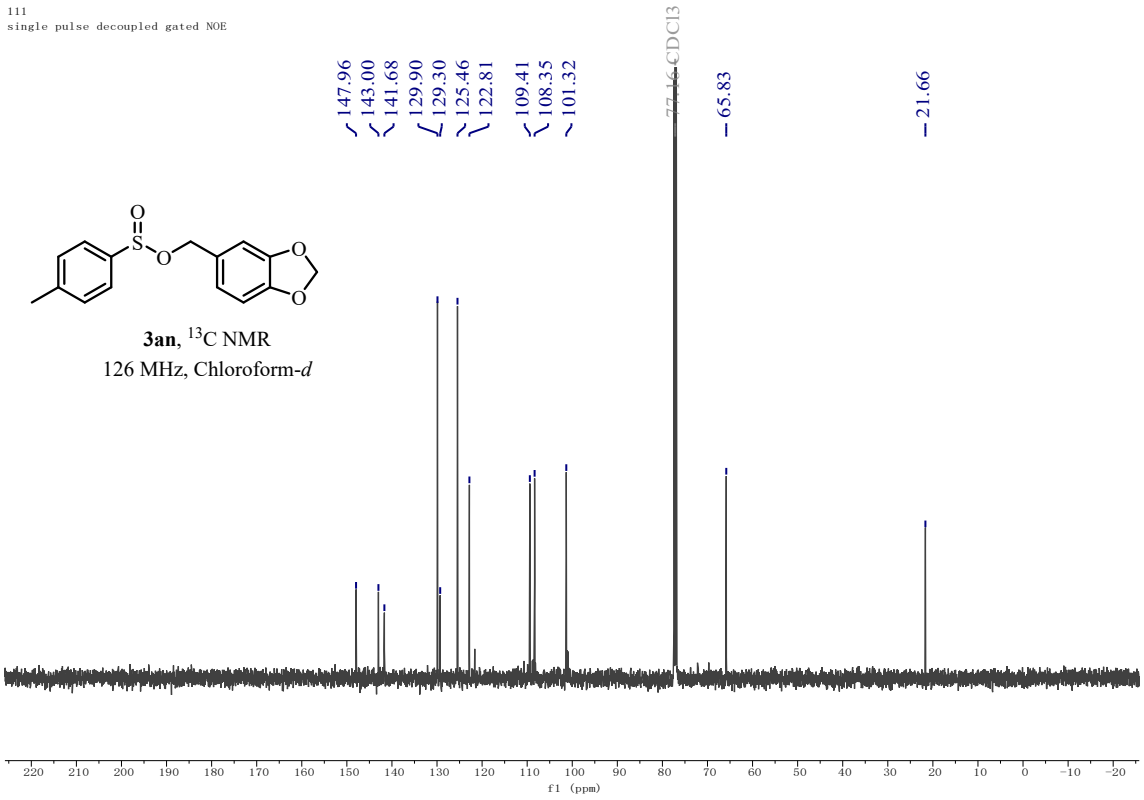
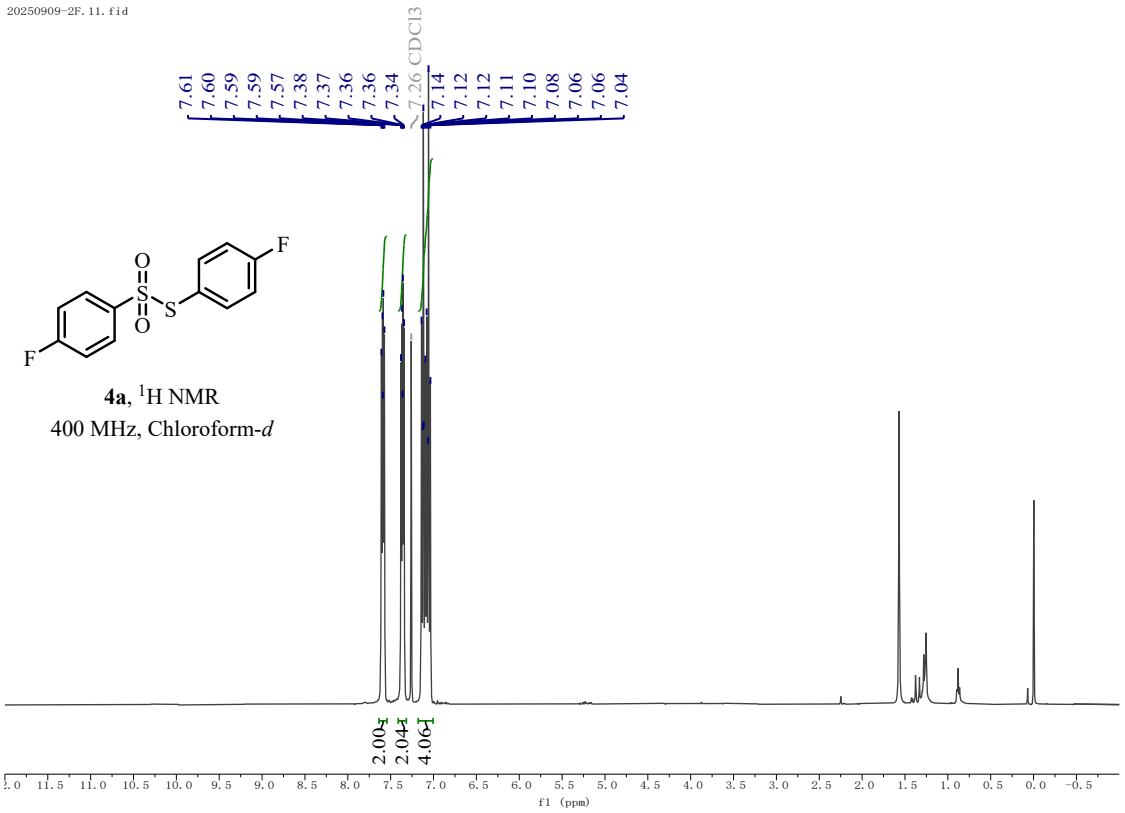
1.01
1.16
1.09
2.08
3.06
3am, 1H NMR
500 MHz, Chloroform-d
f1 (ppm)


20260205LJH-SF-3-C
single pulse decoupled gated NOE
142.86
141.61
137.65
129.83
128.37
125.74
125.35
121.96
77.16 CDCl3
64.17
30.83
21.64
3am, 13C NMR
126 MHz, Chloroform-d
f1 (ppm)


111
single_pulse
7.63
7.61
7.35
7.35
7.35
7.34
7.34
7.33
7.26 CDCl3
6.75
6.75
6.75
6.74
6.74
6.74
6.73
6.73
5.95
5.95
4.93
4.93
4.91
4.90
4.47
4.46
4.44
4.44
2.43
1.95
1.96
3.16
2.11
0.98
1.00
3.00
3an, 1H NMR
500 MHz, Chloroform-d
f1 (ppm)

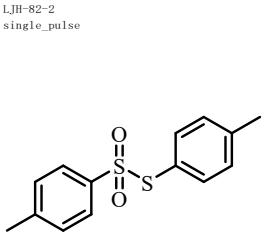


3an, ^{13}C NMR
126 MHz, Chloroform-*d*



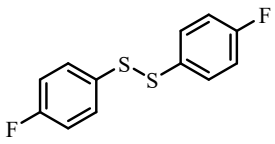
4a, ^{1}H NMR
400 MHz, Chloroform-*d*

LJH-82-2
single_pulse



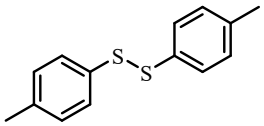
4b, ^{1}H NMR
500 MHz, Chloroform-*d*

20250909-1F. 10. fid



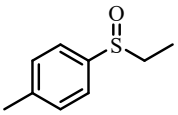
5a, ^{1}H NMR
400 MHz, Chloroform-*d*

LJH-82-1 1
single_pulse

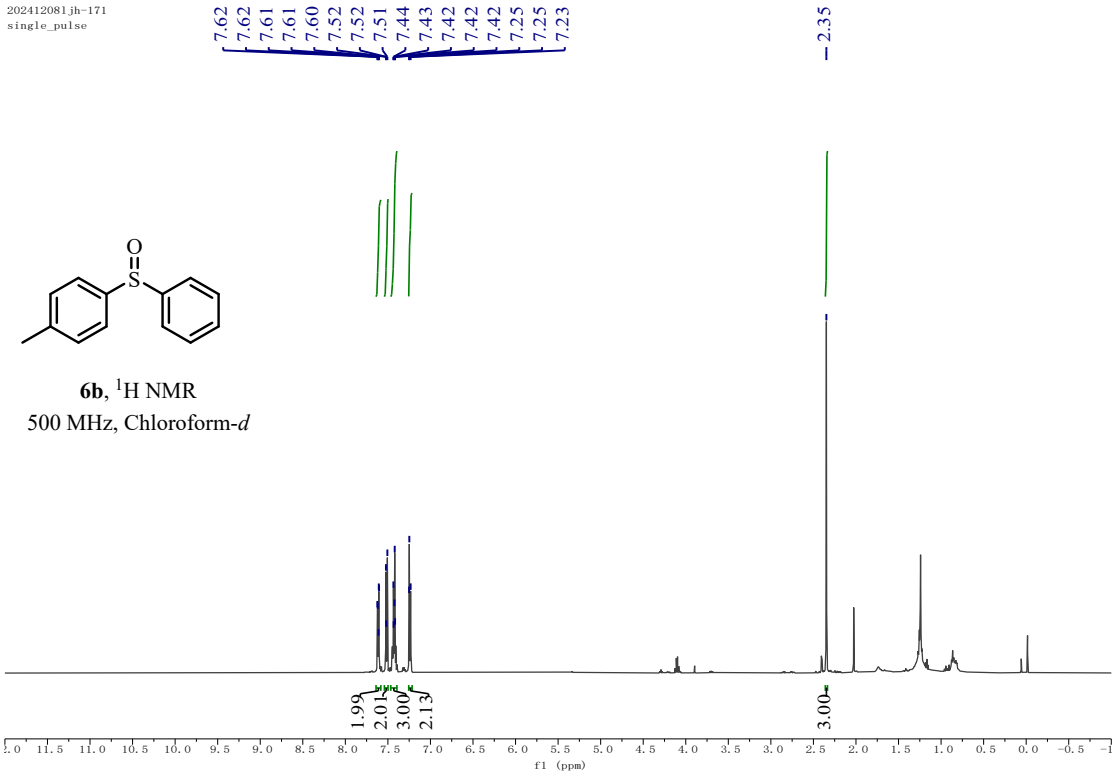


5b, ^{1}H NMR
500 MHz, Chloroform-*d*

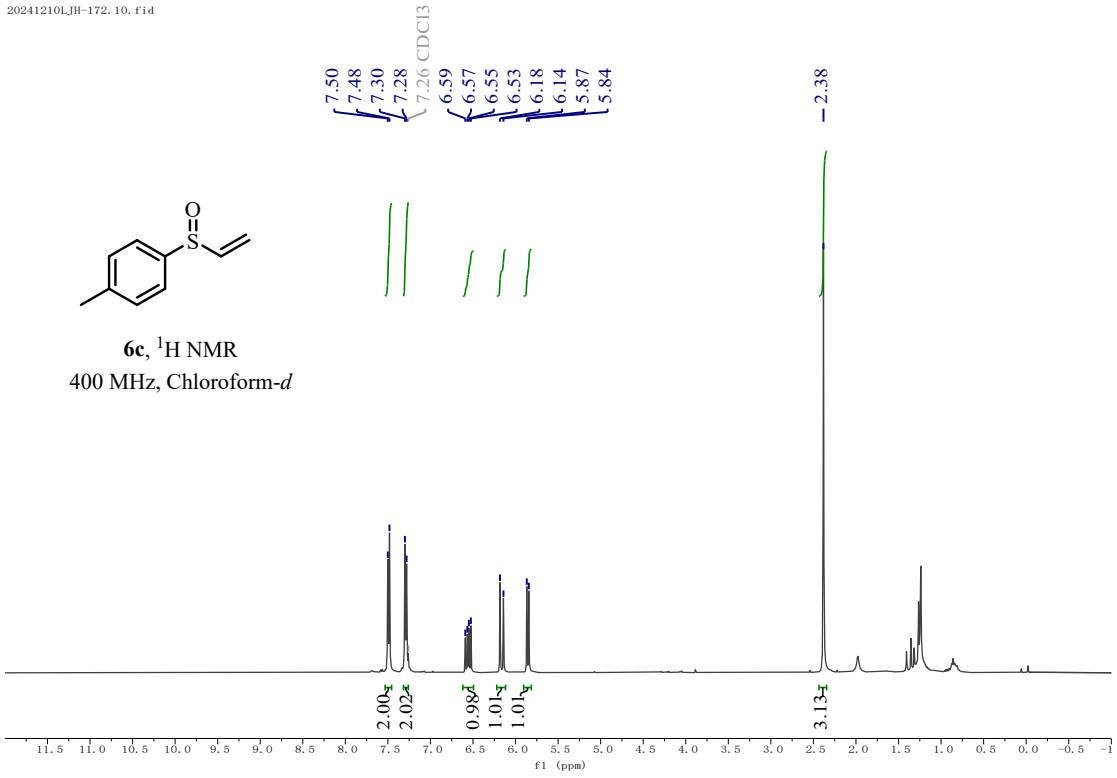
20241206LJH-170.10.fid



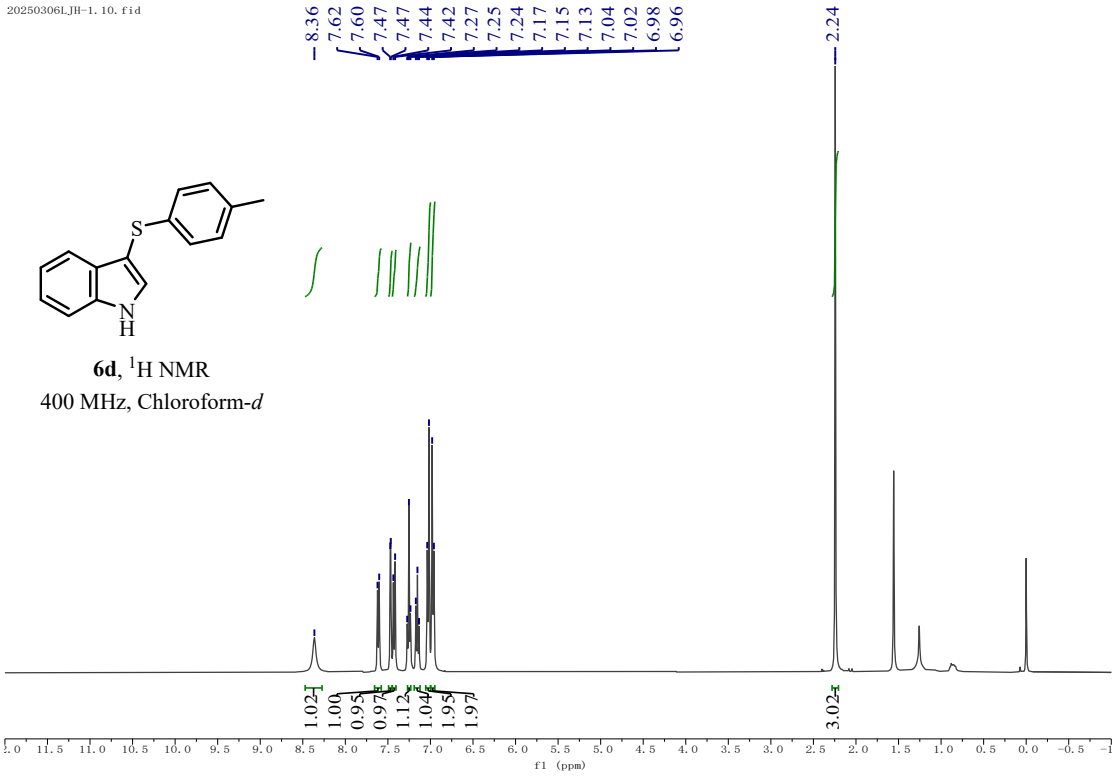
6a, ^{1}H NMR
400 MHz, Chloroform-*d*



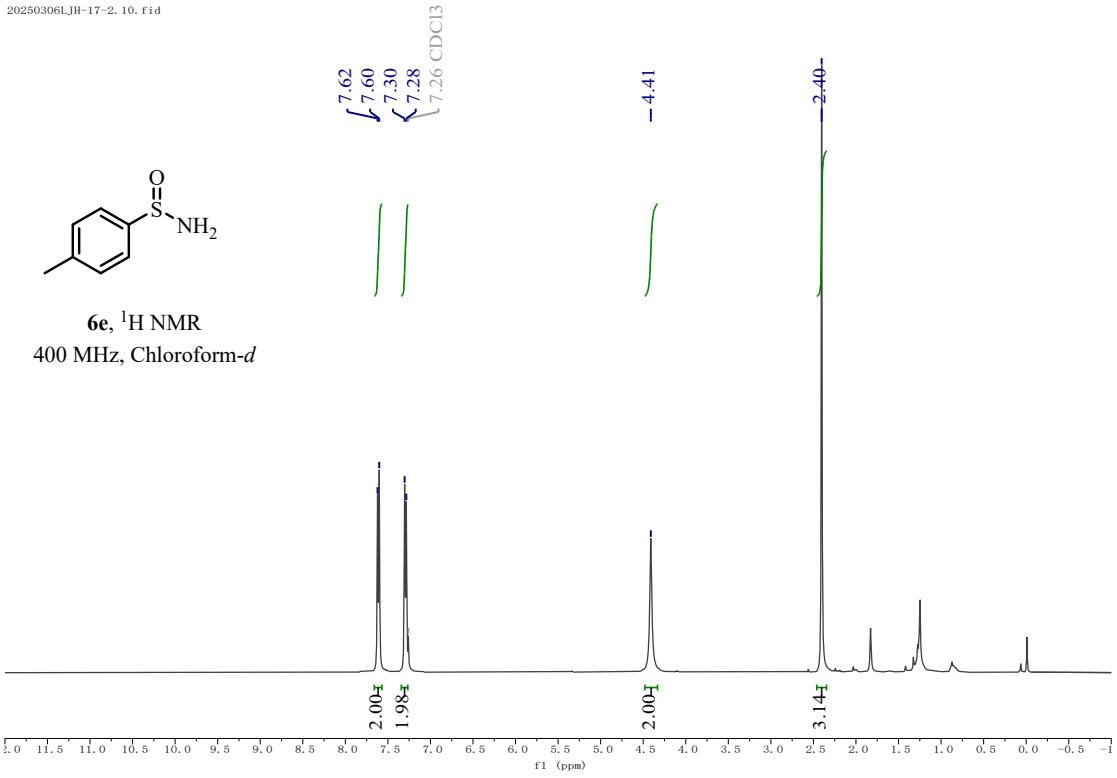
6b, ^{1}H NMR
500 MHz, Chloroform-*d*



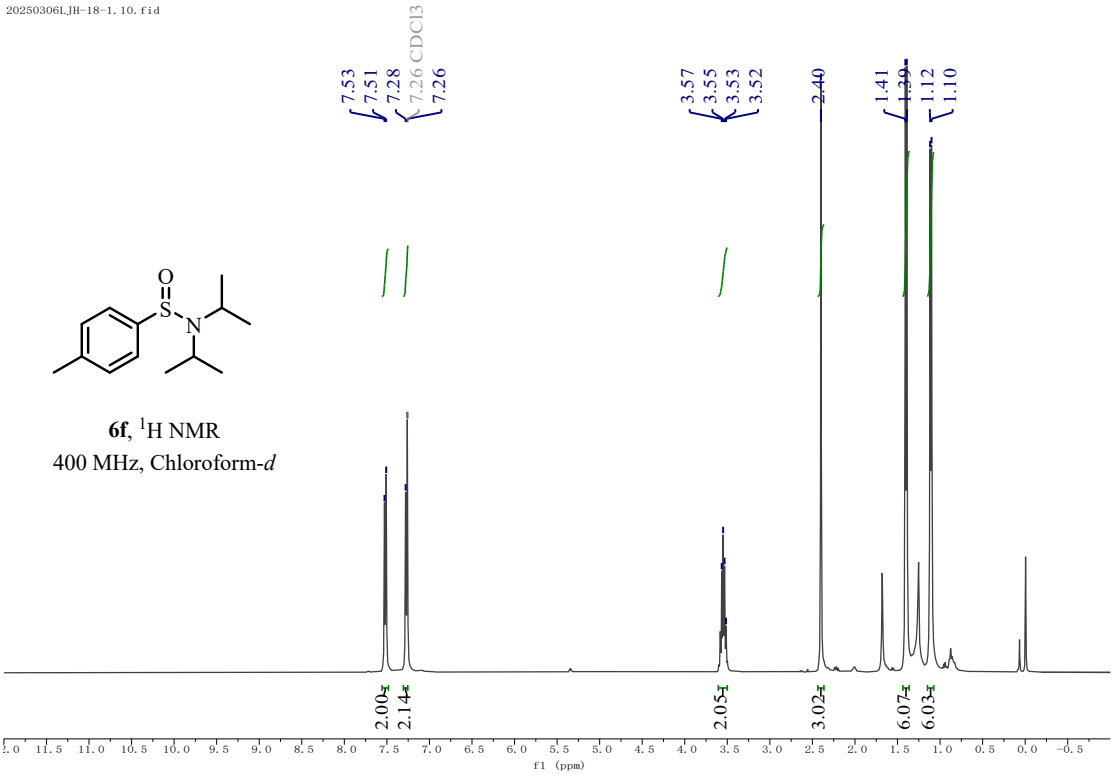
6c, ^{1}H NMR
400 MHz, Chloroform-*d*



6d, ^{1}H NMR
400 MHz, Chloroform-*d*



6e, ^{1}H NMR
400 MHz, Chloroform-*d*



6f, ^{1}H NMR
400 MHz, Chloroform-*d*

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