Supporting Information

Generation of sulfones from *β*-sulfinyl esters under redox-neutral conditions

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Contents

1. General Information

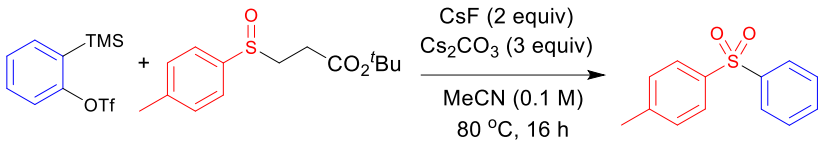
^{1}H NMR spectra were recorded on Varian 400 MHz spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra were recorded on Varian 400 (100 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line for $CDCl_3$ at 77 ppm. High resolution mass spectra were obtained on a Thermo Scientific LTQ Orbitrap XL and Thermo Scientific DS II mass spectrometers. Single crystal data were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. Flash column chromatography was performed on silica gel (particle size 200–400 mesh ASTM). Analytical thin-layer chromatography (TLC) was carried out using commercial silica gel plates, and spots were detected with UV light (254 nm).

Materials: Materials were purchased from Sigma-Aldrich, Energy Chemicals, Bidepharmatech, Adamas, and used as received. In general, the starting substrates **1**[1] and **2**[2] was prepared following the reported literatures. **2h'**[3], **5**[4] and **2a-^{18}O**[5] were synthesized following related literatures. Compounds The structure of **3a** was confirmed by means of X-ray crystallography. CCDC 2326446 contains the supplementary crystallography data of **3a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

2. General experimental procedure

To a 10 ml round bottom flask equipped with a magnetic stir bar was added CsF (0.4 mmol) and Cs_2CO_3 (0.6 mmol). Then RB flask was evacuated and backfilled with nitrogen and dissolved in CH_3CN (2.0 ml) under nitrogen atmosphere. To the stirring solution, *β*-sulfinyl esters **2** (0.4 mmol) was added followed by the addition of aryne precursor **1** (0.2 mmol). Then the reaction mixture was heated at 80 °C for 16 hours. The reaction mixture was diluted with CH_2Cl_2 and filtered off. The filtrate was evaporated under vacuum and the crude compounds were purified by column chromatography. Purified products were characterized through NMR and Mass analysis.

3. General experimental procedure for scale-up reaction



1a 5 mmol

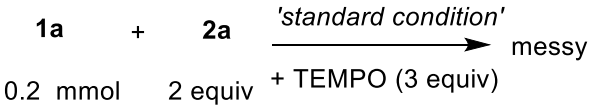
2a 10 mmol

3a 836.3 mg 72% yield

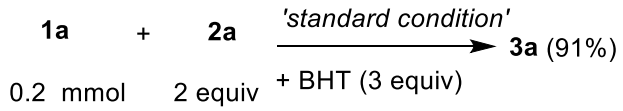
To a 100 ml round bottom flask equipped with a magnetic stir bar was added CsF (10 mmol) and Cs_2CO_3 (15 mmol). Then RB flask was evacuated and backfilled with nitrogen and dissolved in CH_3CN (50 ml) under nitrogen atmosphere. To the stirring solution, *β*-sulfinyl esters **2a** (10 mmol) was added followed by the addition of aryne precursor **1a** (5 mmol). Then the reaction mixture was heated at 80 °C for 16 hours. The reaction mixture was diluted with CH_2Cl_2 and filtered off. The filtrate was evaporated under vacuum and the crude compounds were purified by column chromatography to give 836.3 mg product **3a** as yellowish solid.

4. Control experiments

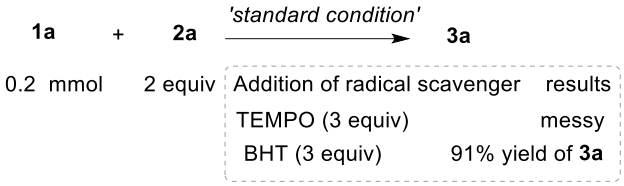
4.1 Free radical trapping experiments



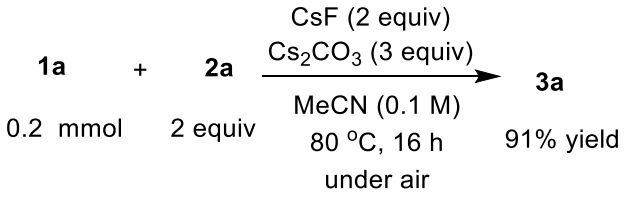
To a 10 ml round bottom flask equipped with a magnetic stir bar was added CsF (0.4 mmol) and Cs_2CO_3 (0.6 mmol). Then RB flask was evacuated and backfilled with nitrogen and dissolved in CH_3CN (2.0 ml) under nitrogen atmosphere. To the stirring solution, TEMPO (0.6 mmol) and *β*-sulfinyl esters **2a** (0.4 mmol) was added followed by the addition of aryne precursor **1a** (0.2 mmol). Then the reaction mixture was heated at 80 °C for 16 hours. The TLC analysis shown the reaction was messy.



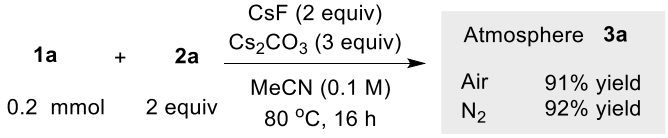
To a 10 ml round bottom flask equipped with a magnetic stir bar was added CsF (0.4 mmol) and Cs_2CO_3 (0.6 mmol). Then RB flask was evacuated and backfilled with nitrogen and dissolved in CH_3CN (2.0 ml) under nitrogen atmosphere. To the stirring solution BHT (0.6 mmol) and *β*-sulfinyl esters **2a** (0.4 mmol) was added followed by the addition of aryne precursor **1a** (0.2 mmol). Then the reaction mixture was heated at 80 °C for 16 hours. The reaction mixture was diluted with CH_2Cl_2 and filtered off. The filtrate was evaporated under vaccum and the crude compounds were purified by column chromatography, [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3a** as a colorless liquid (42.3 mg, 91%).



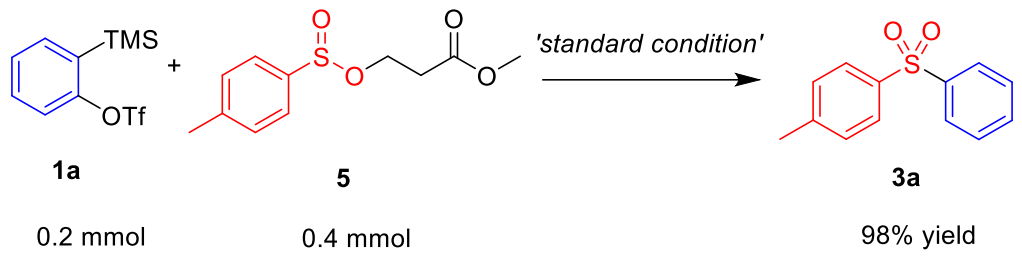
4.2 Reaction conducted under air



To a 10 ml round bottom flask equipped with a magnetic stir bar was added CsF (0.4 mmol) and Cs_2CO_3 (0.6 mmol) and dissolved in CH_3CN (2.0 ml) under air. To the stirring solution *β*-sulfinyl esters **2a** (0.4 mmol) was added followed by the addition of aryne precursor **1a** (0.2 mmol). Then the reaction mixture was heated at 80 °C for 16 hours. The reaction mixture was diluted with CH_2Cl_2 and filtered off. The filtrate was evaporated under vaccum and the crude compounds were purified by column chromatography, [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3a** as a colorless liquid (42.3 mg, 91%).



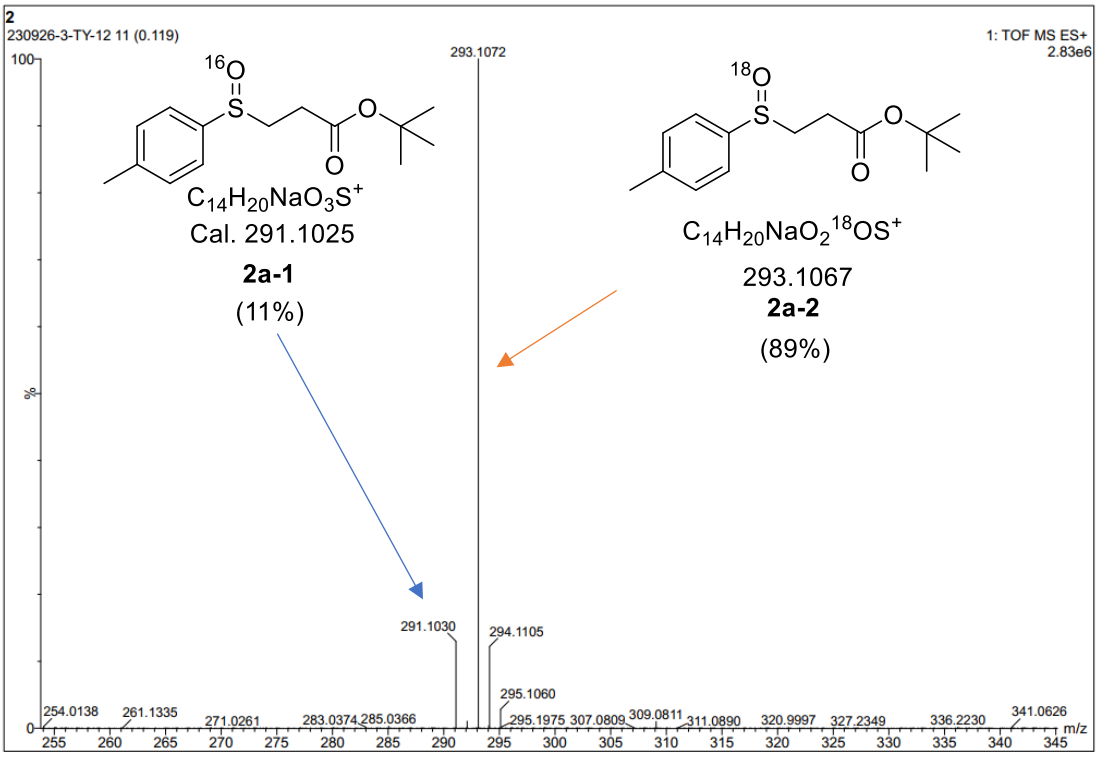
4.3 Using **5** as starting material

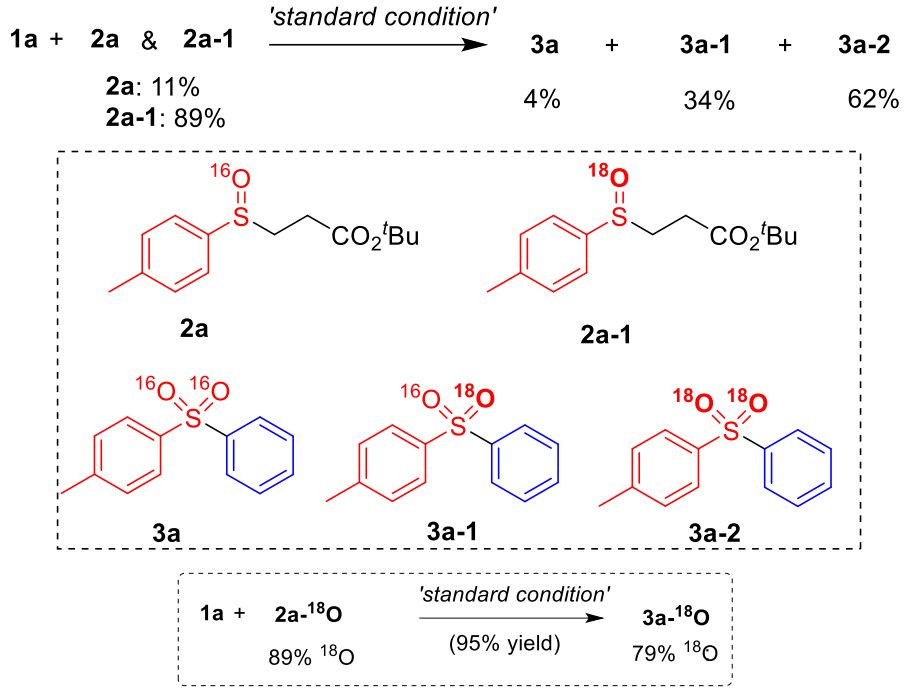


To a 10 ml round bottom flask equipped with a magnetic stir bar was added CsF (0.4 mmol) and Cs_2CO_3 (0.6 mmol) and dissolved in CH_3CN (2.0 ml) under air. To the stirring solution **5**[4] (0.4 mmol) was added followed by the addition of aryne precursor **1a** (0.2 mmol). Then the reaction mixture was heated at 80 °C for 16 hours. The reaction mixture was diluted with CH_2Cl_2 and filtered off. The filtrate was evaporated under vaccum and the crude compounds were purified by column chromatography, [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3a** as a colorless liquid (45.5 mg, 98%).

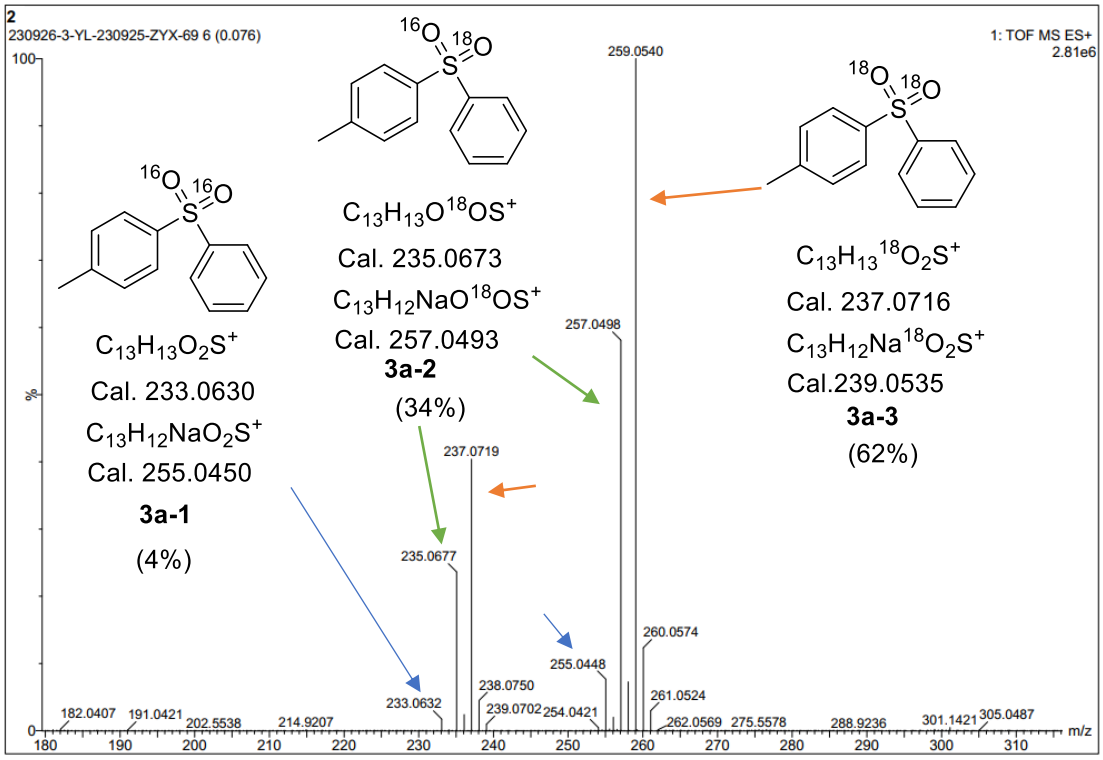
4.4 Copies of HRMS Spectra of Compounds **2a, 2a-1, 3a, 3a-1** and **3a-2**

HRMS Spectra of **2a** & **2a-1**

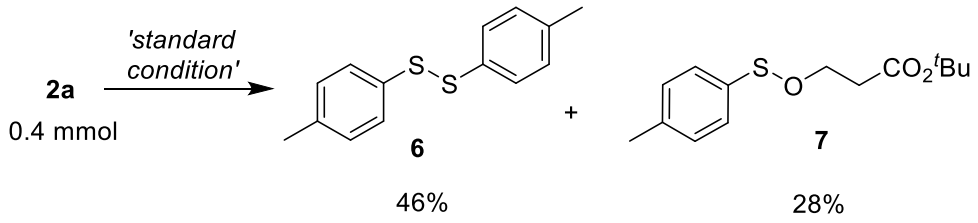




HRMS of **3a, 3a-1** and **3a-2**

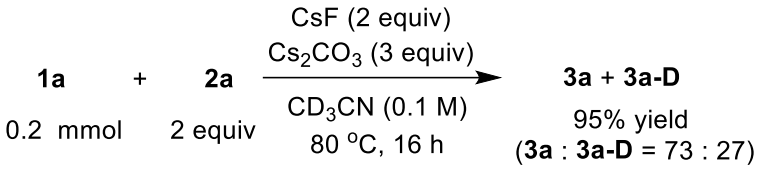


4.5 Treated **2a** alone under standard condition



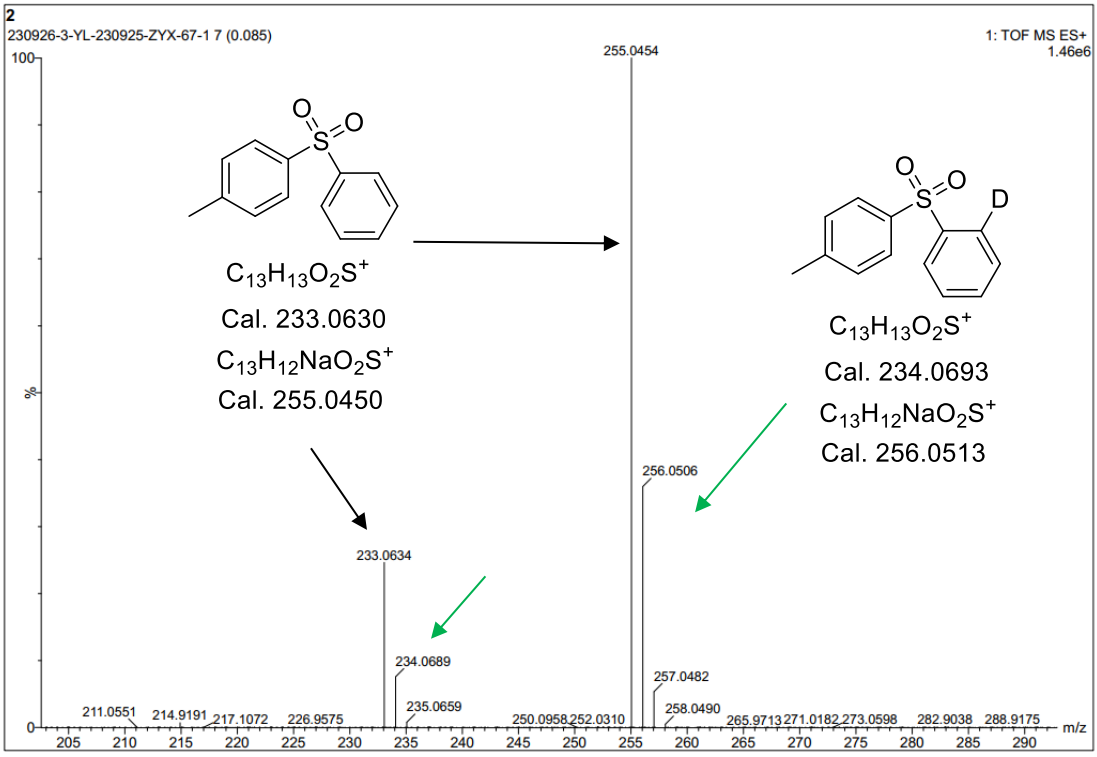
To a 10 ml round bottom flask equipped with a magnetic stir bar was added CsF (0.4 mmol) and Cs_2CO_3 (0.6 mmol) and dissolved in CH_3CN (2.0 ml) under air. To the stirring solution **2a** (0.4 mmol) was added. Then the reaction mixture was heated at 80 ºC for 16 hours. The reaction mixture was diluted with CH_2Cl_2 and filtered off. The filtrate was evaporated under vaccum and the crude compounds were purified by column chromatography, [Hexane] to give **6** as a colorless liquid (23.0 mg, 46%). [Hexane /Ethyl acetate = 5:1 (v/v)] to give **7** as a colorless liquid (30.0 mg, 28%).

4.6 Experimental procedure for deuterium labelled reaction

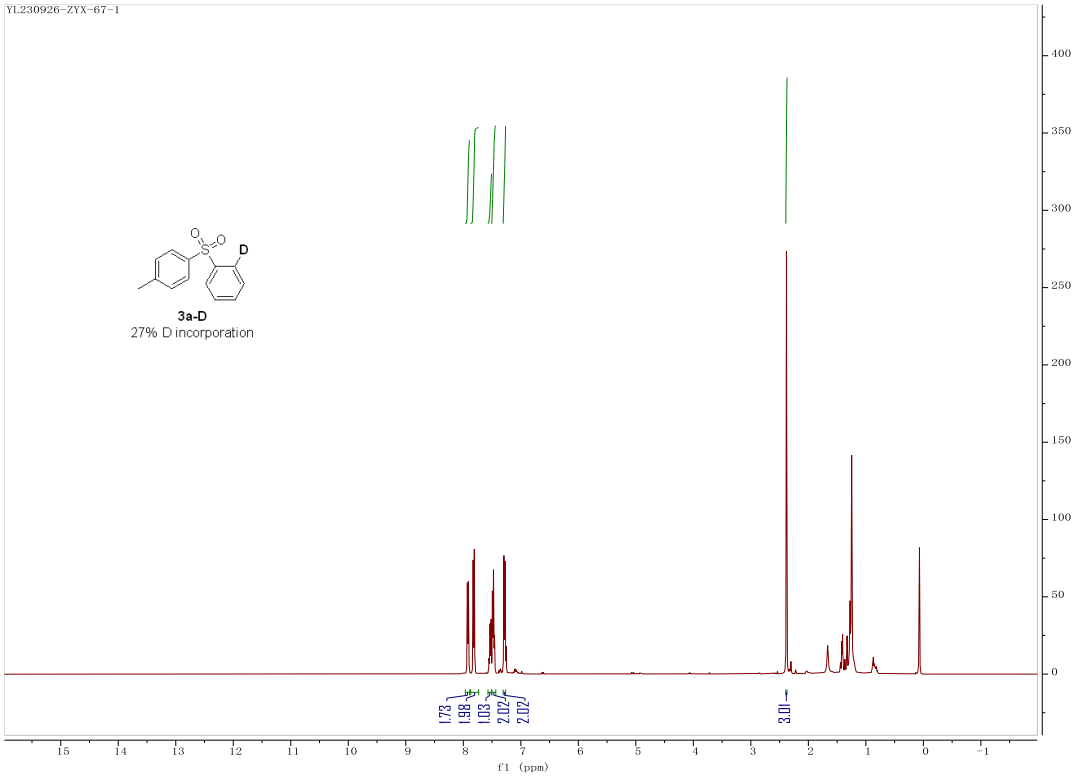


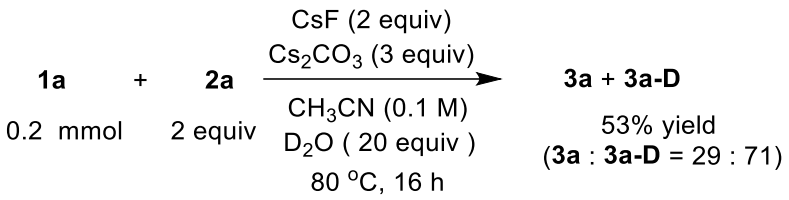
To a 10 ml round bottom flask equipped with a magnetic stir bar was added CsF (0.4 mmol) and Cs_2CO_3 (0.6 mmol). Then RB flask was evacuated and backfilled with nitrogen and dissolved in CD_3CN (2.0 ml) under nitrogen atmosphere. To the stirring solution, *β*-sulfinyl esters **2a** (0.4 mmol) was added followed by the addition of aryne precursor **1a** (0.2 mmol). Then the reaction mixture was heated at 80 ºC for 16 hours. The reaction mixture was diluted with CH_2Cl_2 and filtered off. The filtrate was evaporated under vaccum and the crude compounds were purified by column chromatography, [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3a-D** as a colorless liquid (44.3 mg, 95%) characterized through NMR and HRMS analysis showed 27% deuterium incorporation in the respective product **3a-D**.

HRMS Spectra of **3a** & **3a-D**



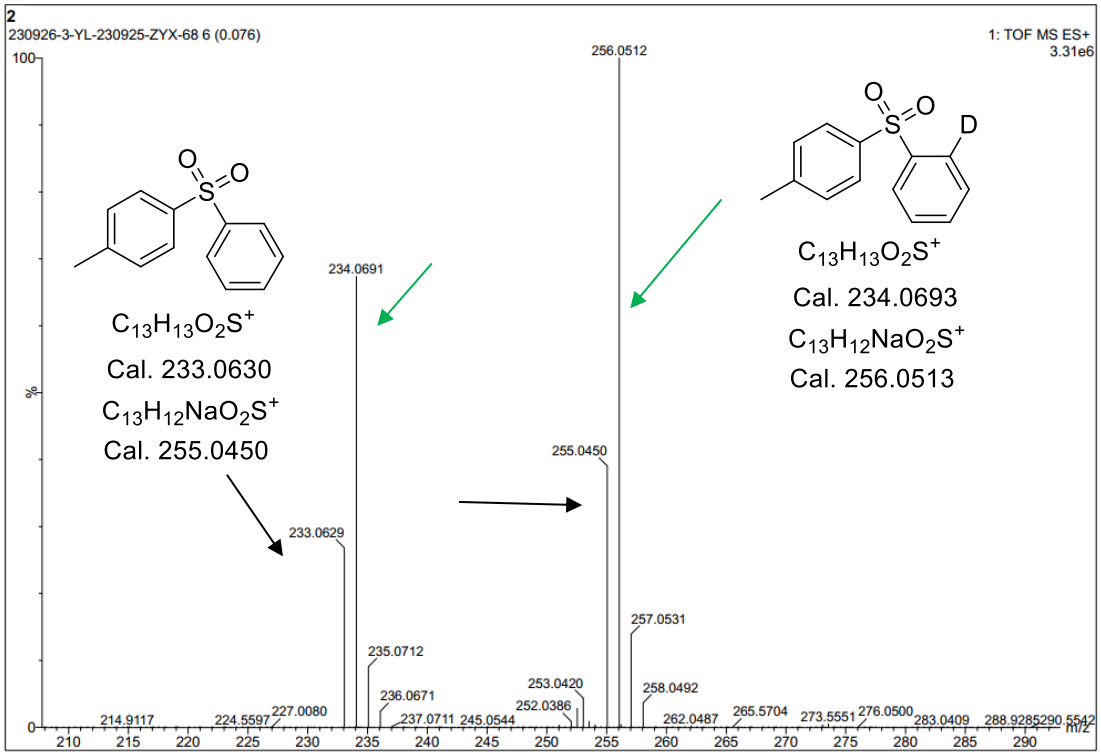
^{1}H NMR Spectra of **3a** & **3a-D** (400 MHz, $CDCl_3$)



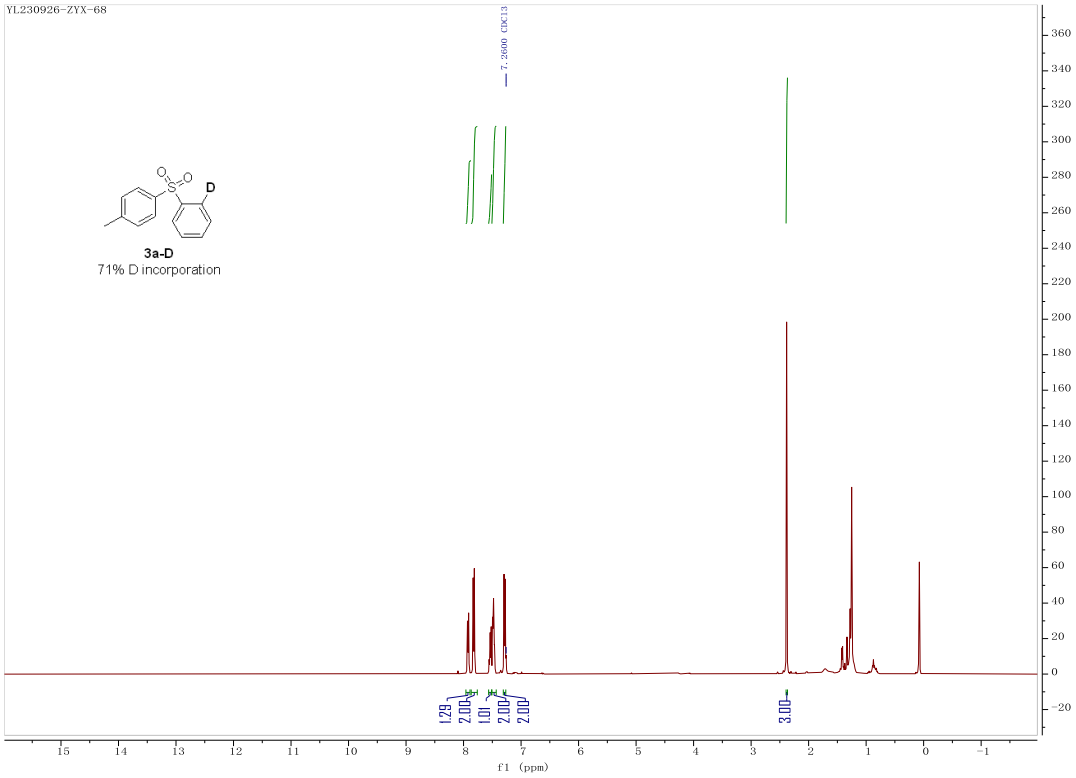


To a 10 ml round bottom flask equipped with a magnetic stir bar was added CsF (0.4 mmol) and Cs_2CO_3 (0.6 mmol). Then RB flask was evacuated and backfilled with nitrogen and dissolved in CH_3CN (2.0 ml) under nitrogen atmosphere. To the stirring solution, D_2O (4 mmol) and *β*-sulfinyl esters **2a** (0.4 mmol) was added followed by the addition of aryne precursor **1a** (0.2 mmol). Then the reaction mixture was heated at 80 °C for 16 hours. The reaction mixture was diluted with CH_2Cl_2 and filtered off. The filtrate was evaporated under vaccum and the crude compounds were purified by column chromatography, [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3a-D** as a colorless liquid (24.7 mg, 53%) Purified products were characterized through NMR and HRMS analysis showed 71% deuterium incorporation in the respective product **3a-D**.

HRMS Spectra of **3a** & **3a-D**

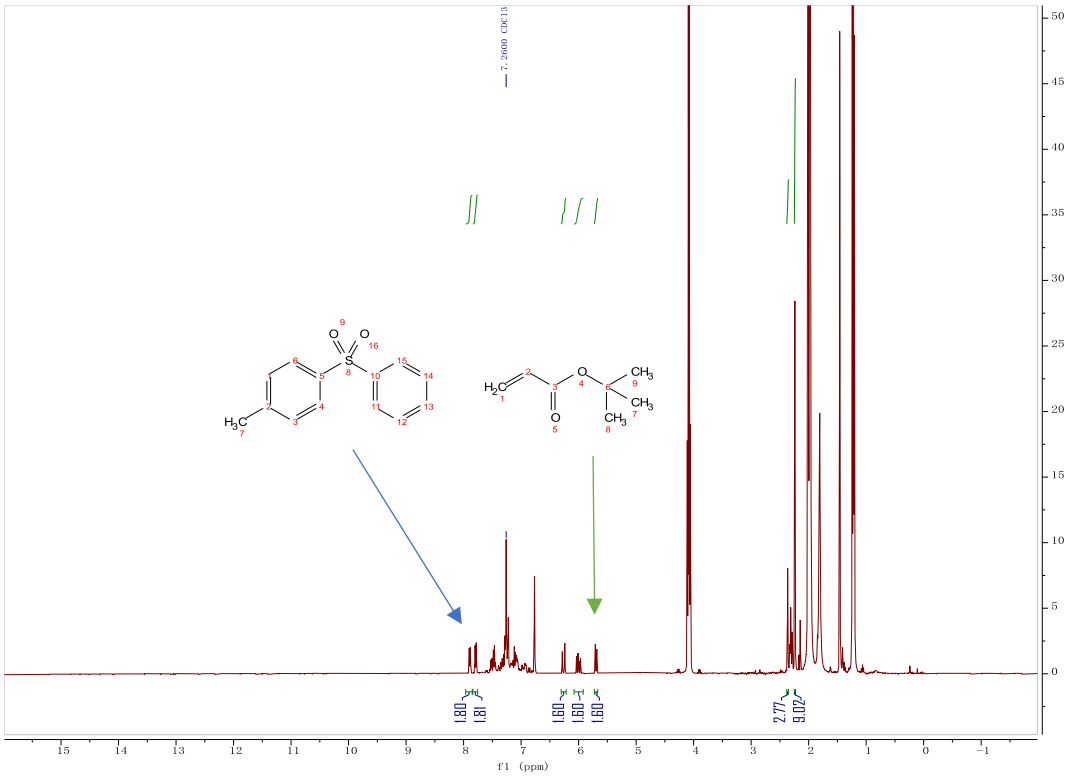


^{1}H NMR Spectra of **3a** & **3a-D** (400 MHz, $CDCl_3$)



5. Crude NMR of template reaction

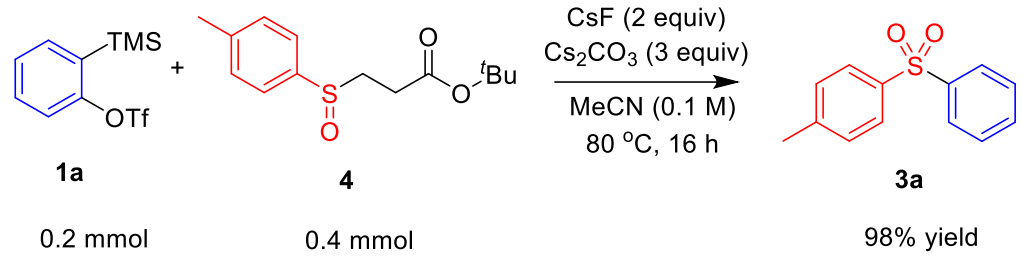
Crude NMR of template reaction using mesitylene as internal standard:



Suggested that 40% of *tert*-butyl acrylate was recovered.

6. X-ray crystallographic data of 3aa

The compound for X-ray crystallography of **3a** is obtained using the template reaction as shown below. The sample for X-ray crystallography is prepared by slowly evaporation of $CDCl_3$ at room tempreture.



1a 0.2 mmol

4 0.4 mmol

3a 98% yield

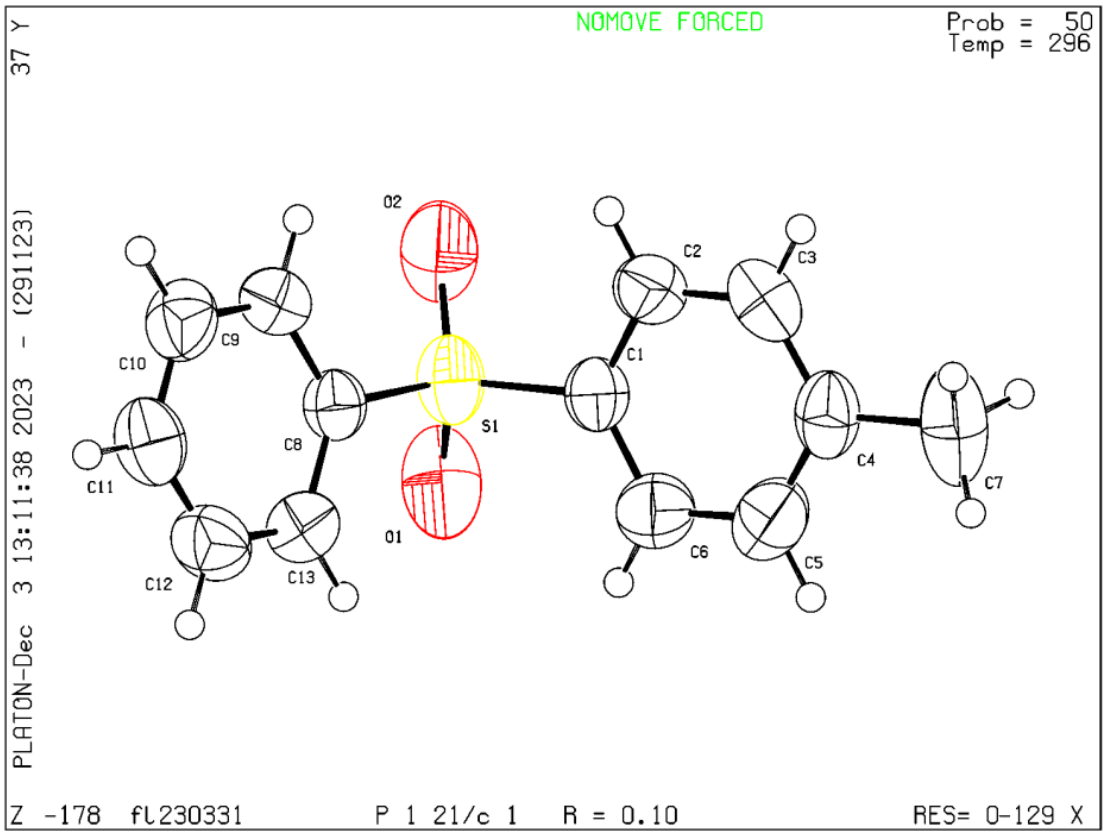


Figure S1. ORTEP diagram of **3a** with thermal ellipsoids shown at 50% probability. The structure of **3a** was determined by the X-ray diffraction. Recrystallized from dichloromethane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2326446.

Table 1. Crystal data and structure refinement for 3a (CCDC 2326446).

Identification code	**3a**
Empirical formula	$C_{13}H_{12}O_2S$
Formula weight	232.29
Temperature/K	295.64(10)
Crystal system	monoclinic

Space group	$P2_1/c$
a/Å	13.0408(8)
b/Å	7.8341(5)
c/Å	11.5786(8)
α/°	90
β/°	95.948(6)
γ/°	90
Volume/Å^3	1176.54(13)
Z	4
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	2.296
F(000)	488.0
Crystal size/mm^3	0.16 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	13.202 to 133.184
Index ranges	-15 ≤ h ≤ 15, -3 ≤ k ≤ 9, -13 ≤ l ≤ 13
Reflections collected	7411
Independent reflections	2068 [R_{int} = 0.0752, R_{sigma} = 0.0448]
Data/restraints/parameters	2068/0/147
Goodness-of-fit on F^2	1.945
Final R indexes [I>=2σ (I)]	R_1 = 0.0981, wR_2 = 0.2493
Final R indexes [all data]	R_1 = 0.1050, wR_2 = 0.2639
Largest diff. peak/hole / e Å^{-3}	0.82/-0.54

Crystal structure determination of 3a (CCDC 2326446)

Crystal Data for $C_{13}H_{12}O_2S$ (*M* =232.29 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 13.0408(8) Å, *b* = 7.8341(5) Å, *c* = 11.5786(8) Å, *β* = 95.948(6), *V* = 1176.54(13) Å^3, *Z* = 4, *T* = 295.64(10) K, μ(Cu Kα) = 2.296 mm^{-1}, *Dcalc* = 1.311 g/cm^3, 7411 reflections measured (13.202° ≤ 2Θ ≤ 133.184°), 2068 unique (R_{int} = 0.0752, R_{sigma} = 0.0448) which were used in all calculations. The final R_1 was 0.0981 (I > 2σ(I)) and wR_2 was 0.2639 (all data).

Refinement model description

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3aa (CCDC 2326446). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	2699.8(6)	3327.0(11)	6806.7(8)	65.9(5)
O1	2265(2)	1685(3)	6500(4)	95.7(12)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3aa (CCDC 2326446). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	2693(2)	3918(5)	7983(2)	93.9(10)
C1	2064(2)	4858(4)	5871(3)	56.2(8)
C2	2058(3)	6545(4)	6205(3)	64.4(10)
C3	1552(3)	7733(5)	5481(4)	71.8(11)
C4	1057(3)	7281(5)	4420(3)	65.8(9)
C5	1096(3)	5593(6)	4094(4)	77.8(11)
C6	1596(3)	4366(5)	4804(4)	72.4(10)
C7	486(4)	8584(7)	3642(5)	103.8(18)
C8	3984(2)	3334(3)	6454(3)	51.6(8)
C9	4719(3)	4223(4)	7153(3)	61.4(9)
C10	5730(3)	4189(4)	6906(4)	70.2(10)
C11	5989(3)	3290(4)	5962(4)	68.5(10)
C12	5250(3)	2432(5)	5272(3)	74.1(11)
C13	4247(3)	2430(4)	5505(3)	65.9(9)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3aa (CCDC 2326446). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	51.8(7)	69.0(7)	78.1(8)	19.8(4)	13.2(4)	4.0(3)
O1	65.2(19)	66.6(17)	154(3)	30.1(15)	7.7(18)	-11.7(11)
O2	81(2)	140(3)	64.0(18)	25.8(17)	25.9(14)	32.8(19)
C1	44.8(16)	61.3(17)	62.8(19)	1.8(14)	6.7(13)	2.3(13)
C2	62(2)	67(2)	64(2)	-9.2(15)	8.3(16)	3.2(14)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa (CCDC 2326446). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	69(2)	59.0(19)	90(3)	-0.9(17)	20.5(19)	12.5(16)
C4	46.8(17)	83(2)	69(2)	16.7(18)	13.4(14)	9.7(16)
C5	67(2)	96(3)	69(2)	1.5(19)	-4.5(18)	0.4(19)
C6	72(2)	62.5(19)	81(3)	-7.5(17)	-2.0(18)	-4.9(16)
C7	70(3)	129(4)	116(4)	50(3)	24(2)	37(3)
C8	50.9(18)	50.5(16)	53.3(18)	6.7(12)	5.4(13)	3.3(11)
C9	64(2)	57.3(17)	63(2)	-8.5(14)	5.6(15)	3.6(14)
C10	55(2)	63.1(19)	90(3)	0.0(18)	-4.3(17)	-6.7(15)
C11	57(2)	70(2)	82(3)	13.2(17)	20.1(18)	4.3(14)
C12	80(3)	82(3)	63(2)	-4.5(18)	19.4(18)	12(2)
C13	65(2)	68(2)	63(2)	-5.8(16)	-2.3(15)	0.3(15)

Table 4 Bond Lengths for 3aa (CCDC 2326446).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.435(3)	C4	C7	1.506(5)
S1	O2	1.439(3)	C5	C6	1.383(6)
S1	C1	1.764(3)	C8	C9	1.378(5)
S1	C8	1.764(3)	C8	C13	1.379(5)
C1	C2	1.378(5)	C9	C10	1.379(5)
C1	C6	1.375(5)	C10	C11	1.372(6)
C2	C3	1.375(5)	C11	C12	1.364(6)
C3	C4	1.373(6)	C12	C13	1.363(5)
C4	C5	1.378(6)			

Table 5 Bond Angles for 3aa (CCDC 2326446).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	118.8(2)	C3	C4	C7	121.2(4)
O1	S1	C1	108.00(17)	C5	C4	C7	121.1(4)
O1	S1	C8	107.77(17)	C4	C5	C6	122.2(4)
O2	S1	C1	108.31(17)	C1	C6	C5	118.5(3)
O2	S1	C8	108.48(17)	C9	C8	S1	119.0(3)
C8	S1	C1	104.62(14)	C9	C8	C13	120.8(3)
C2	C1	S1	119.7(3)	C13	C8	S1	120.2(2)
C6	C1	S1	119.9(3)	C8	C9	C10	119.4(3)
C6	C1	C2	120.4(3)	C11	C10	C9	119.7(3)
C3	C2	C1	119.6(4)	C12	C11	C10	120.2(4)
C4	C3	C2	121.5(4)	C13	C12	C11	121.3(4)
C3	C4	C5	117.7(3)	C12	C13	C8	118.7(3)

Table 6 Torsion Angles for 3aa (CCDC 2326446).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C1	C2	C3	-179.3(3)	C2	C1	C6	C5	-1.8(6)
S1	C1	C6	C5	179.5(3)	C2	C3	C4	C5	-1.0(6)
S1	C8	C9	C10	177.9(3)	C2	C3	C4	C7	178.7(4)
S1	C8	C13	C12	-178.6(3)	C3	C4	C5	C6	1.2(6)
O1	S1	C1	C2	157.4(3)	C4	C5	C6	C1	0.2(7)
O1	S1	C1	C6	-23.9(4)	C6	C1	C2	C3	2.0(6)
O1	S1	C8	C9	-145.1(3)	C7	C4	C5	C6	-178.5(4)
O1	S1	C8	C13	33.5(3)	C8	S1	C1	C2	-88.0(3)
O2	S1	C1	C2	27.5(4)	C8	S1	C1	C6	90.7(3)

Table 6 Torsion Angles for 3aa (CCDC 2326446).

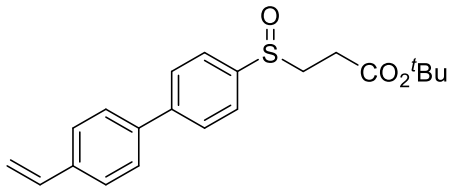
A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	S1	C1	C6	-153.7(3)	C8	C9	C10	C11	0.8(5)
O2	S1	C8	C9	-15.3(3)	C9	C8	C13	C12	0.1(5)
O2	S1	C8	C13	163.3(3)	C9	C10	C11	C12	-0.1(6)
C1	S1	C8	C9	100.1(3)	C10	C11	C12	C13	-0.7(6)
C1	S1	C8	C13	-81.2(3)	C11	C12	C13	C8	0.7(6)
C1	C2	C3	C4	-0.6(6)	C13	C8	C9	C10	-0.8(5)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa (CCDC 2326446).

Atom	*x*	*y*	*z*	U(eq)
H2	2393.22	6878.39	6917.58	77
H3	1544.86	8868.73	5714.29	86
H5	776.16	5268.07	3372.76	93
H6	1614.44	3234.53	4564.95	87
H7A	-169.15	8818.62	3917.66	156
H7B	379.85	8145.83	2864.72	156
H7C	882.77	9616.13	3648.76	156
H9	4534.24	4840.6	7785.58	74
H10	6234.71	4773.01	7377.21	84
H11	6670.67	3265.19	5792.03	82
H12	5433.67	1836.39	4629.6	89
H13	3749.09	1831.44	5033.96	79

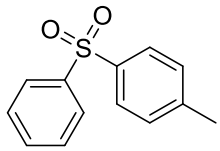
7. Analytical data of starting substrates and products

***tert*-butyl 3-((4'-vinyl-[1,1'-biphenyl]-4-yl)sulfinyl)propanoate (2h')**



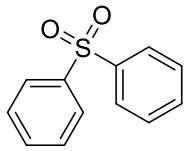
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 2:1 (v/v)] to give **2h'** as a white solid (528 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.23 (d, *J* = 10.9 Hz, 1H), 3.15 (ddd, *J* = 13.4, 8.4, 6.8 Hz, 1H), 2.91 (ddd, *J* = 13.7, 8.3, 5.9 Hz, 1H), 2.72 (ddd, *J* = 17.3, 8.3, 6.8 Hz, 1H), 2.43 (ddd, *J* = 17.2, 8.4, 5.8 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 143.4, 141.8, 138.8, 137.3, 136.1, 127.6, 127.2, 126.8, 124.5, 114.5, 81.3, 51.3, 27.9, 27.1. HRMS (ESI) calcd for $C_{21}H_{24}O_3NaS^+$ m/z [M + H]$^+$: 379.1344; found: 379.1347.

1-Methyl-4-(phenylsulfonyl)benzene (3a) [6]



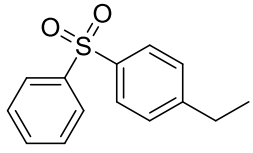
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3a** as a pale yellow solid (42.7 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.0 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.44 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.0, 138.7, 133.1, 130.0, 129.3, 127.8, 127.6, 21.7.

Sulfonyldibenzene (3b) [7]



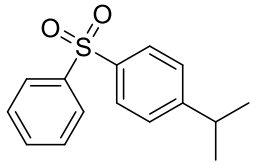
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3b** as a white solid (31.7 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 4H), 7.55 (t, *J* = 7.1 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 133.2, 129.3, 127.6.

1-ethyl-4-(phenylsulfonyl)benzene (3c) [8]



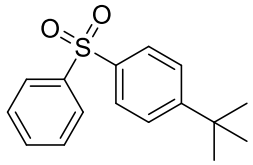
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3c** as a white solid (47.7 mg, 97%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.9 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.43 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.67 (q, *J* = 7.5 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 141.9, 138.7, 133.0, 129.2, 128.8, 127.8, 127.5, 28.8, 15.1.

1-isopropyl-4-(phenylsulfonyl)benzene (3d) [9]



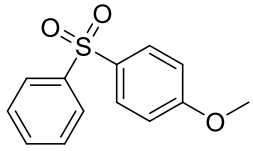
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3d** as a white solid (51.0 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.50 (dt, *J* = 14.7, 6.9 Hz, 3H), 7.34 (d, *J* = 8.2 Hz, 2H), 2.93 (hept, *J* = 7.0 Hz, 1H), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 142.0, 139.4, 133.1, 129.8, 127.9, 127.6, 127.5, 34.2, 23.6.

1-(*tert*-butyl)-4-(phenylsulfonyl)benzene (3e) [10]



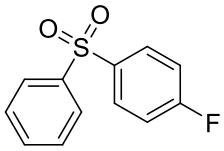
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3e** as a white solid (45.5 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.59 – 7.43 (m, 5H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 142.0, 138.6, 133.1, 129.3, 127.7, 127.6, 126.4, 35.3, 31.1.

1-methoxy-4-(phenylsulfonyl)benzene (3f) [10]



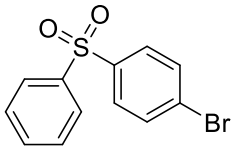
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3f** as a white solid (43.2 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.82 (m, 4H), 7.57 – 7.42 (m, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 142.4, 133.2, 132.9, 129.9, 129.2, 127.3, 114.6, 55.7.

1-fluoro-4-(phenylsulfinyl)benzene (3g) [11]



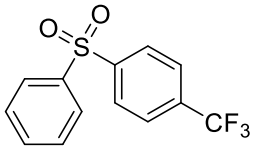
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3g** as a white solid (36.4 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 4H), 7.61 – 7.54 (m, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.17 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (d, *J* = 255.8 Hz), 141.6, 137.8, 133.4, 130.6 (d, *J* = 9.5 Hz), 129.5, 127.7, 116.72 (d, *J* = 22.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.2.

1-bromo-4-(phenylsulfonyl)benzene (3h) [11]



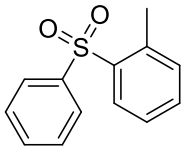
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3h** as a colorless liquid (53.5 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.8, 133.5, 132.7, 129.54, 129.3, 128.5, 127.7.

1-(phenylsulfonyl)-4-(trifluoromethyl)benzene (3i) [12]



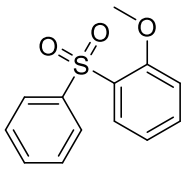
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3i** as a colorless liquid (45.8 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 7.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 140.7, 134.9 (q, *J* = 32.9 Hz), 133.9, 129.7, 128.3, 128.0, 126.5 (q, *J* = 3.9 Hz), 123.2 (q, *J* = 271.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2.

1-methyl-2-(phenylsulfonyl)benzene (3j) [13]



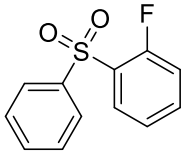
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3j** as a white solid (29.8 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.46-7.51 (m, 3H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 138.9, 138.1, 133.7, 133.1, 132.7, 129.5, 129.1, 127.7, 126.5, 20.3.

1-methoxy-2-(phenylsulfonyl)benzene (3k) [14]



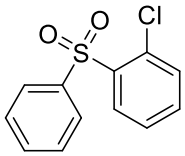
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3k** as a white solid (24.3 mg, 49%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.1 Hz, 2H), 7.54 (q, *J* = 9.7, 8.7 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 141.6, 135.7, 133.0, 129.9, 128.6, 128.5, 120.6, 112.6, 55.9.

1-fluoro-2-(phenylsulfonyl)benzene (3l) [15]



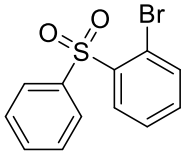
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3l** as a white solid (34.5 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 1H), 8.00 (d, *J* = 6.8 Hz, 2H), 7.64 – 7.47 (m, 4H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (d, *J* = 255.9 Hz), 141.4, 136.1 (d, *J* = 8.4 Hz), 133.8, 129.8, 129.6 (d, *J* = 13.9 Hz), 129.4, 128.2 (d, *J* = 2.0 Hz), 124.7 (d, *J* = 3.8 Hz), 117.4 (d, *J* = 21.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.6.

1-chloro-2-(phenylsulfonyl)benzene (3m) [16]



Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3m** as a white solid (34.4 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 7.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 5.7 Hz, 1H), 7.52 – 7.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.5, 134.8, 133.6, 133.0, 132.2, 131.1, 129.0, 128.6, 127.4.

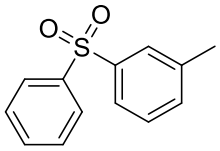
1-bromo-2-(phenylsulfonyl)benzene (3n) [17]



Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3n** as a yellowish solid (49.1 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 2H), 7.67 – 7.47 (m, 5H), 7.43 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 135.7, 134.7, 133.5, 131.5, 128.9, 128.7, 128.0,

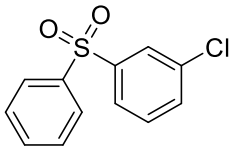
121.3.

1-methyl-3-(phenylsulfonyl)benzene (3o) [9]



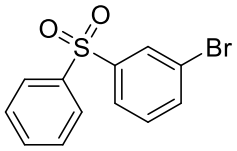
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3o** as a white solid (37.2 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.74 (d, *J* = 5.4 Hz, 2H), 7.60-7.45 (m, 3H), 7.40-7.34 (m, 2H), 2.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 141.5, 139.7, 134.1, 133.2, 129.4, 129.3, 128.1, 127.8, 125.0, 21.5.

1-chloro-3-(phenylsulfinyl)benzene (3p) [18]



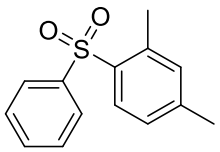
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3p** as a white solid (32.7 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 3H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.44 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.0, 135.6, 133.7, 133.4, 130.7, 129.5, 127.9, 127.8, 125.8.

1-bromo-3-(phenylsulfonyl)benzene (3q) [8]



Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3q** as a colorless liquid (50.5 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.94 (d, *J* = 7.3 Hz, 2H), 7.87 (d, *J* = 6.9 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 140.9, 136.3, 133.7, 130.9, 130.5, 129.5, 127.8, 126.3, 124.0.

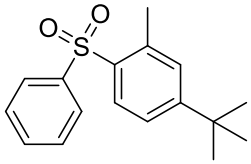
2,4-dimethyl-1-(phenylsulfonyl)benzene (3r) [19]



Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3r** as a white solid (46.3 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.54 (t, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H),

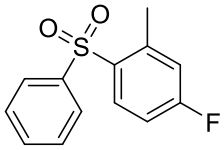
7.18 (d, J = 8.1 Hz, 1H), 7.02 (s, 1H), 2.38 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 141.6, 137.8, 135.9, 133.5, 132.9, 129.66, 129.0, 127.5, 127.2, 21.4, 20.1.

4-(tert-butyl)-2-methyl-1-(phenylsulfonyl)benzene (3s) [20]



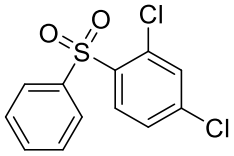
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3s** as a white solid (39.2 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.85 (d, J = 7.0 Hz, 2H), 7.55 (d, J = 7.3 Hz, 1H), 7.50 (d, J = 7.8 Hz, 3H), 7.15 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 141.5, 139.0, 135.8, 133.8, 132.6, 130.7, 129.0, 127.1, 125.8, 34.8, 31.2, 19.2.

4-fluoro-2-methyl-1-(phenylsulfonyl)benzene (3t) [21]



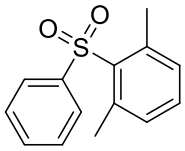
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3t** as a colorless liquid (31.5 mg, 63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, J = 8.8, 5.8 Hz, 1H), 7.84 (d, J = 7.1 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.07 (t, J = 8.3 Hz, 1H), 6.93 (d, J = 9.2 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (J = 254 Hz), 141.6 (J = 9.1 Hz), 141.2, 133.3, 132.4 (J = 9.3 Hz), 129.2, 127.7, 119.7 (J = 22.3 Hz), 113.6 (J = 21.9 Hz), 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.8.

2,4-dichloro-1-(phenylsulfonyl)benzene (3u) [19]



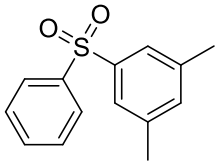
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3u** as a colorless liquid (43.6 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.48 – 7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.8, 137.1, 134.0, 133.8, 132.7, 131.9, 129.1, 128.6, 127.7.

1,3-dimethyl-2-(phenylsulfonyl)benzene (3v) [22]



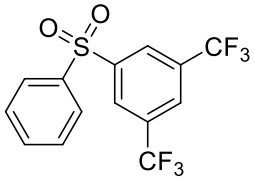
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3v** as a white solid (28.0 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 2.63 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 140.3, 136.8, 132.9, 132.8, 131.6, 129.1, 126.4, 23.0.

1,3-dimethyl-5-(phenylsulfonyl)benzene (3w) [23]



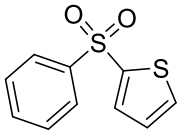
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3w** as a white solid (35.5 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 6.7 Hz, 2H), 7.59 – 7.45 (m, 5H), 7.16 (s, 1H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 141.3, 139.4, 135.0, 133.1, 129.3, 127.7, 125.2, 21.32.

1-(phenylsulfonyl)-3,5-bis(trifluoromethyl)benzene (3x) [24]



Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3x** as a colorless liquid (53.1 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 2H), 8.05 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.70 – 7.63 (m, 1H), 7.62 – 7.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.8, 134.5, 133.4 (q, *J* = 34.7 Hz), 130.0, 128.2 (q, *J* = 4.0 Hz), 127.0 (dt, *J* = 7.1, 3.5 Hz), 126.9 (q, *J* = 274.7 Hz). ^{19}F NMR (376 MHz, $cdcl_3$) δ -62.9.

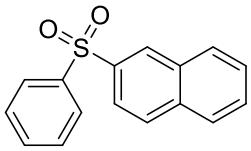
2-(phenylsulfonyl)thiophene (3y) [25]



Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3y** as a white solid (41.7 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 3.9 Hz, 1H), 7.64 (d, *J* = 5.0 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1,

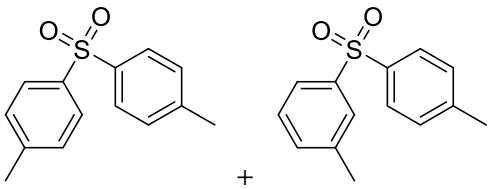
142.1, 134.0, 133.5, 133.4, 129.4, 128.0, 127.4.

2-(phenylsulfonyl)naphthalene (3z) [10]



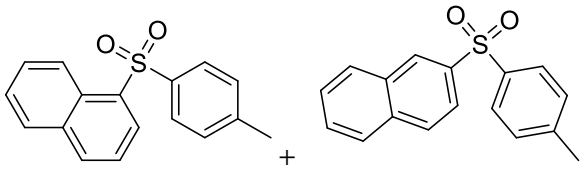
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **3z** as a colorless liquid (49.4 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.05-7.96 (m, 3H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.66 – 7.59 (m, 2H), 7.56 – 7.46 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 138.4, 135.1, 133.3, 132.3, 129.8, 129.5, 129.4, 129.3, 129.2, 128.0, 127.8, 127.7, 122.8.

A mixture of 4,4'-sulfonylbis(methylbenzene) (4b) and 1-methyl-3-tosylbenzene (4b') [26]



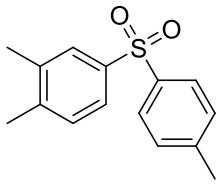
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give a mixture of **4b** and **4b'** as a white solid (35.5 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 6H), 7.75 – 7.68 (m, 2H), 7.39 – 7.31 (m, 2H), 7.30 – 7.23 (m, 6H), 2.38 (s, 6H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 144.0, 141.8, 139.5, 139.1, 138.8, 133.9, 130.0, 129.9, 129.2, 127.9, 127.8, 127.6, 124.7, 21.7, 21.6, 21.4.

A mixture of 1-tosylnaphthalene (4c) and 2-tosylnaphthalene (4c') [27, 28]



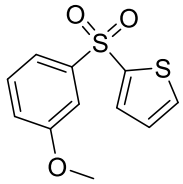
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give a mixture of **4c** and **4c'** as a white solid (34.9 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.5 Hz, 1H), 8.56 (s, 1H), 8.50 (d, *J* = 7.4 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 7.1 Hz, 1H), 7.93 – 7.81 (m, 9H), 7.66 – 7.49 (m, 5H), 7.32 – 7.22 (m, 4H), 2.38 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.1, 138.9, 138.8, 138.7, 136.30, 135.1, 135.0, 134.3, 132.3, 130.0, 129.8, 129.7, 129.4, 129.1, 129.1, 128.9, 128.5, 128.4, 128.0, 127.8, 127.7, 127.5, 126.9, 124.5, 124.5, 122.7, 21.6, 21.6.

1,2-dimethyl-4-tosylbenzene (4d)[29]



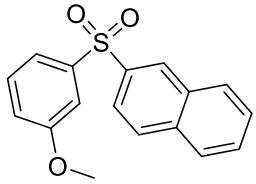
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give-as a white solid (47.3 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 2.30 (s, 2H), 2.20 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.6, 139.1, 139.0, 138.0, 130.3, 129.8, 128.2, 127.5, 125.0, 21.5, 19.9, 19.8.

2-((3-methoxyphenyl)sulfonyl)thiophene (4ye) [30]



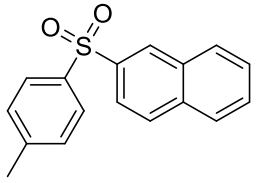
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **4ye** as a white solid (38.1 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 3.8 Hz, 1H), 7.64 (d, *J* = 5.1 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.48 (s, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.10 – 7.06 (m, 2H), 3.84 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 143.2, 142.9, 134.0, 133.5, 130.5, 127.9, 119.8, 119.6, 111.9.

2-((3-methoxyphenyl)sulfonyl)naphthalene (4ze) [28]



Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **4ze** as a white solid (56.5 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.86 (t, *J* = 7.0 Hz, 2H), 7.67-7.56 (m, 3H), 7.51 (s, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 142.7, 138.3, 135.0, 132.2, 130.4, 129.6, 129.4, 129.1, 129.0, 127.9, 127.6, 122.6, 120.0, 119.5, 112.3, 55.7.

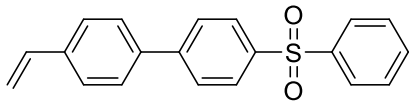
2-tosylnaphthalene (4f)[27]



Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)]

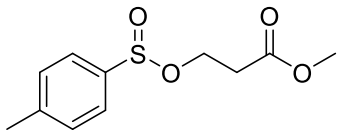
to give **4f** as a white solid (53.2 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.93 – 7.84 (m, 1H), 7.84 – 7.72 (m, 5H), 7.51 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 138.7, 138.6, 134.9, 132.2, 129.9, 129.5, 129.3, 129.0, 128.8, 127.9, 127.7, 127.5, 122.6, 21.5.

4-(phenylsulfonyl)-4'-vinyl-1,1'-biphenyl (3h')



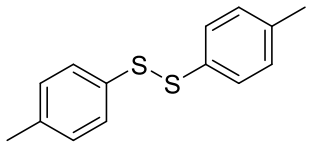
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **4f** as a white solid (56.6 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 4H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.52 (dt, *J* = 18.2, 9.1 Hz, 7H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.81 (d, *J* = 17.5 Hz, 1H), 5.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 141.7, 140.0, 138.3, 137.9, 136.0, 133.2, 129.3, 128.2, 127.6, 127.6, 127.4, 126.8, 114.8. HRMS (ESI) calcd for $C_{20}H_{16}O_2NaS^+$ m/z $[M + H]^+$: 343.0769; found: 343.0774.

methyl 3-((*p*-tolylsulfinyl)oxy)propanoate (5) [31]



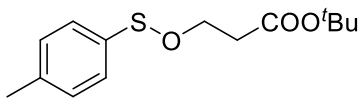
Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **4** as a colorless oil (203.0 mg, 42%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.26 - 4.20 (m, 1H), 3.87 – 3.77 (m, 1H), 3.63 (s, 3H), 2.59 (t, *J* = 6.4 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 142.9, 141.3, 129.8, 125.3, 59.5, 51.9, 34.8, 21.5.

1,2-di-*p*-tolyldisulfane (6) [32]



Purified by flash column chromatography (silica gel), [Hexane] to give **5** as a colorless solid (23.0 mg, 46%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 4H), 7.12 (d, *J* = 7.8 Hz, 4H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.56, 134.55, 129.92, 128.62, 21.20.

***tert*-butyl 3-((*p*-tolylthio)oxy)propanoate (7)** [32]

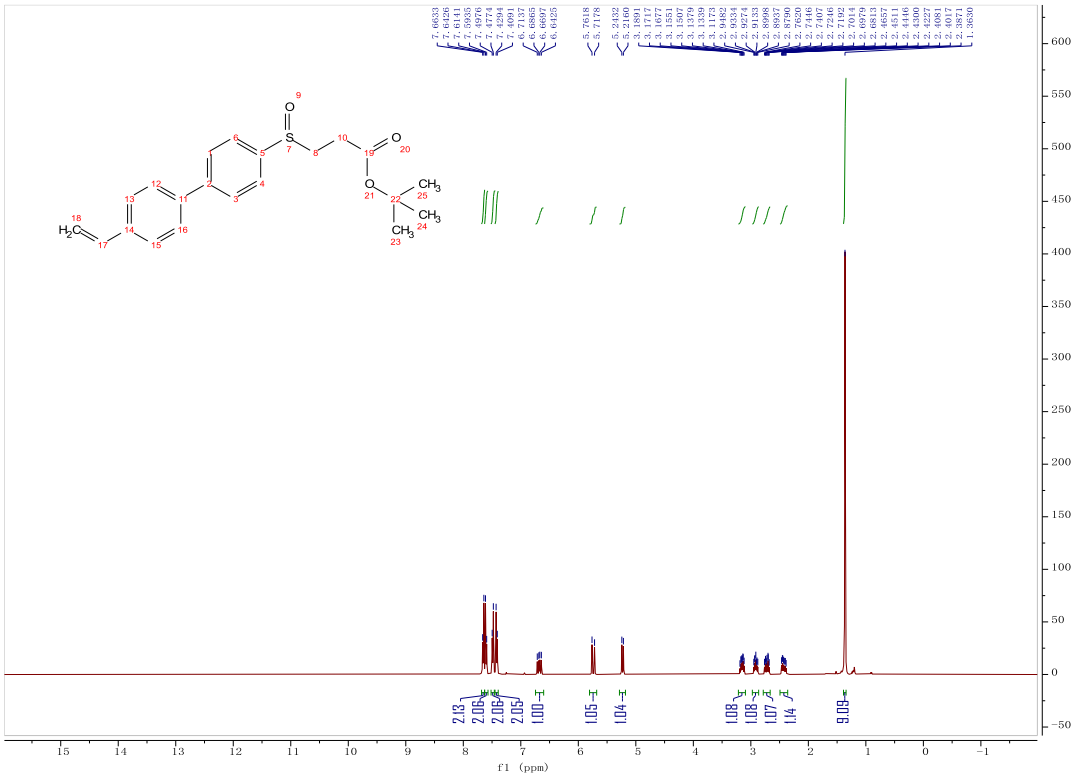


Purified by flash column chromatography (silica gel), [Hexane /Ethyl acetate = 5:1 (v/v)] to give **6** as a colorless oil (30.0 mg, 28%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 3.07 (t, *J* = 7.5 Hz, 2H), 2.50 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 136.8, 131.6, 131.1,

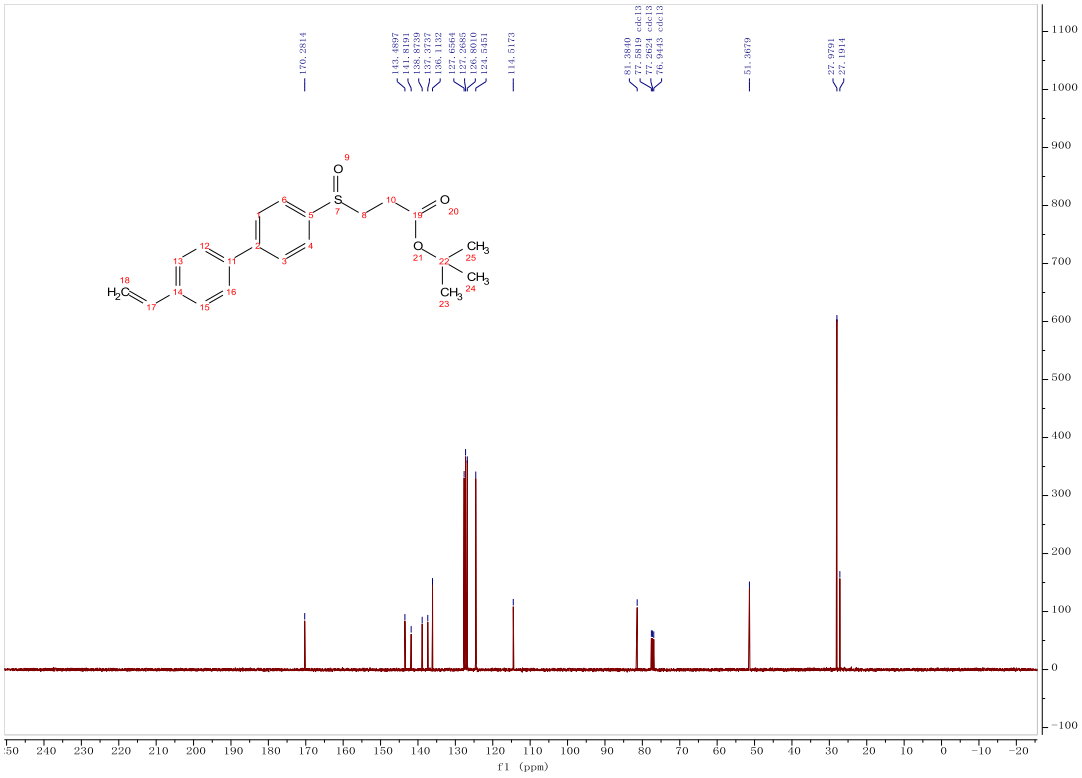
129.9, 81.0, 35.8, 30.1, 28.2, 21.2.

8. ^{1}H NMR ,^{13}C NMR and ^{19}F NMR spectra of starting substrates and products

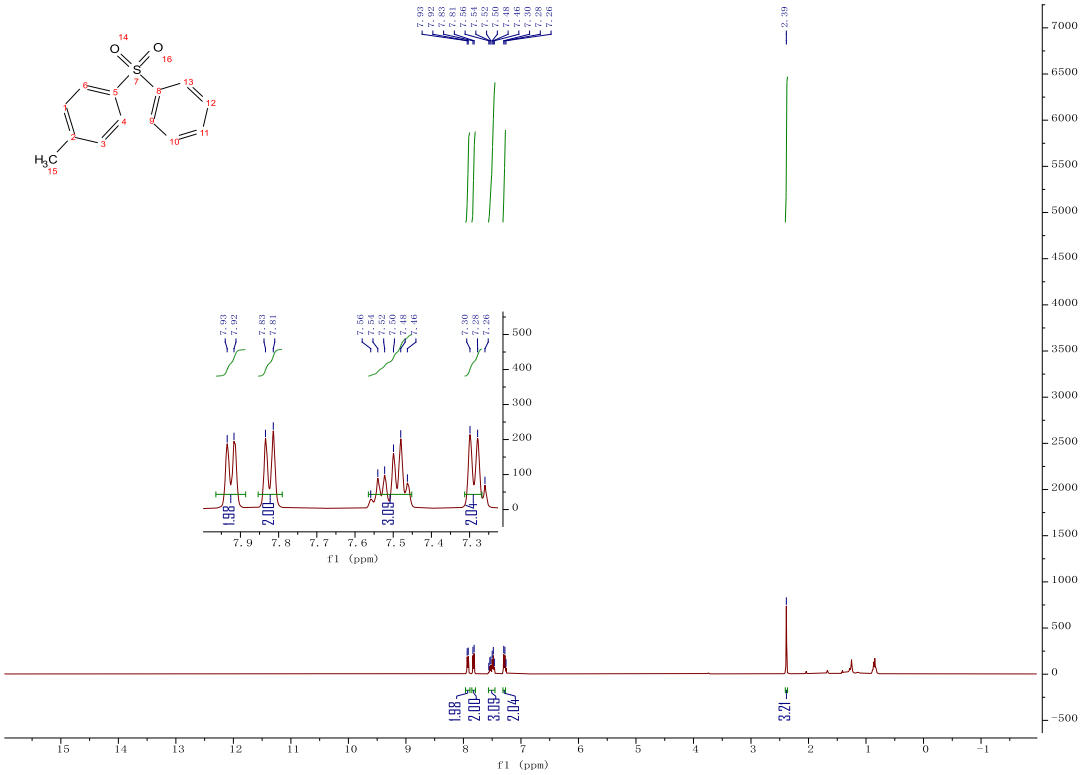
^{1}H NMR Spectra of **2h'** (400 MHz, $CDCl_3$)



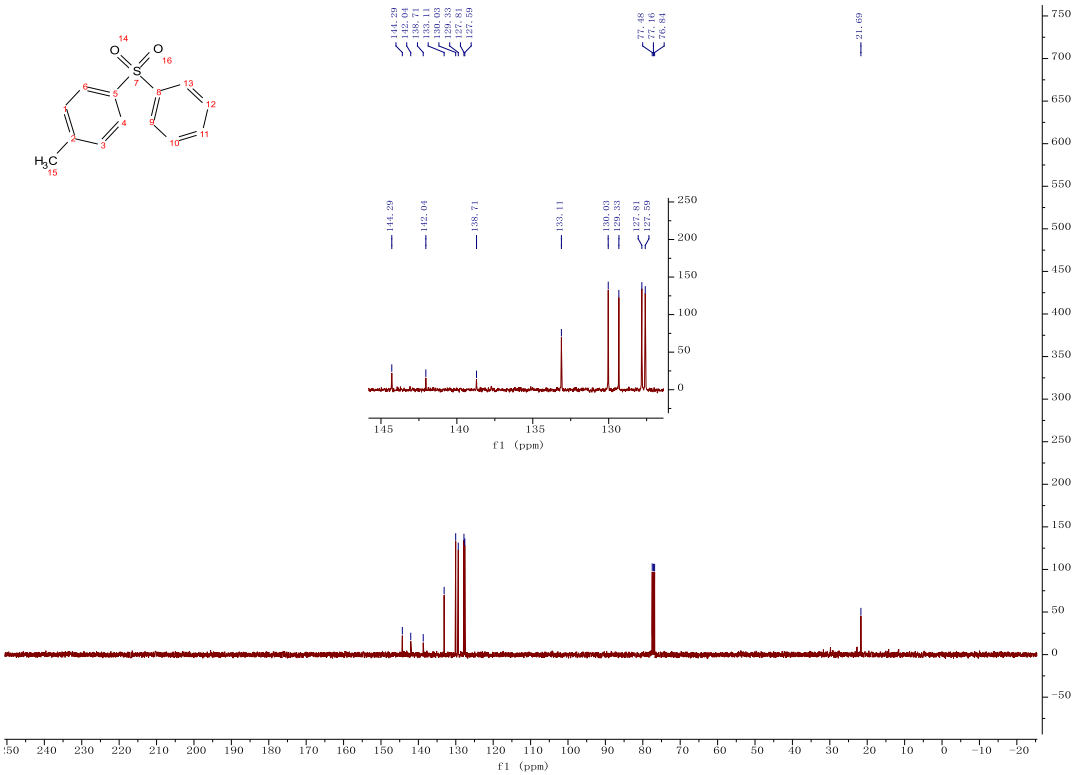
^{13}C NMR Spectra of **2h'** (100 MHz, $CDCl_3$)



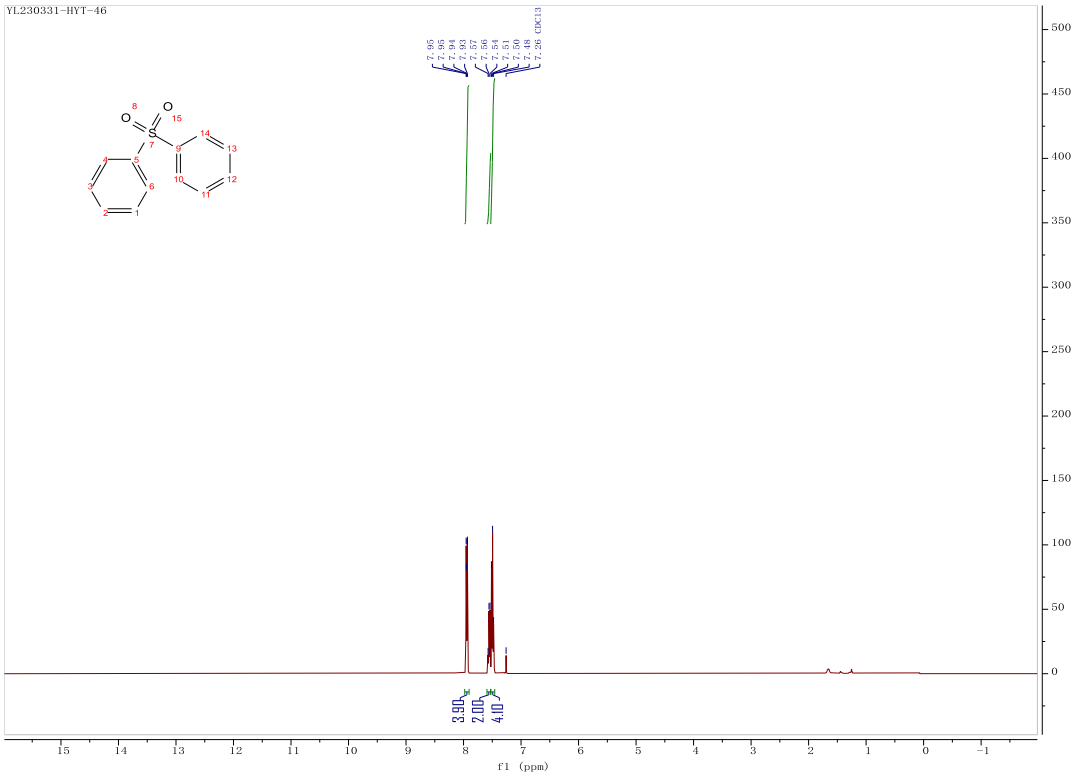
^{1}H NMR Spectra of **3a** (400 MHz, $CDCl_3$)



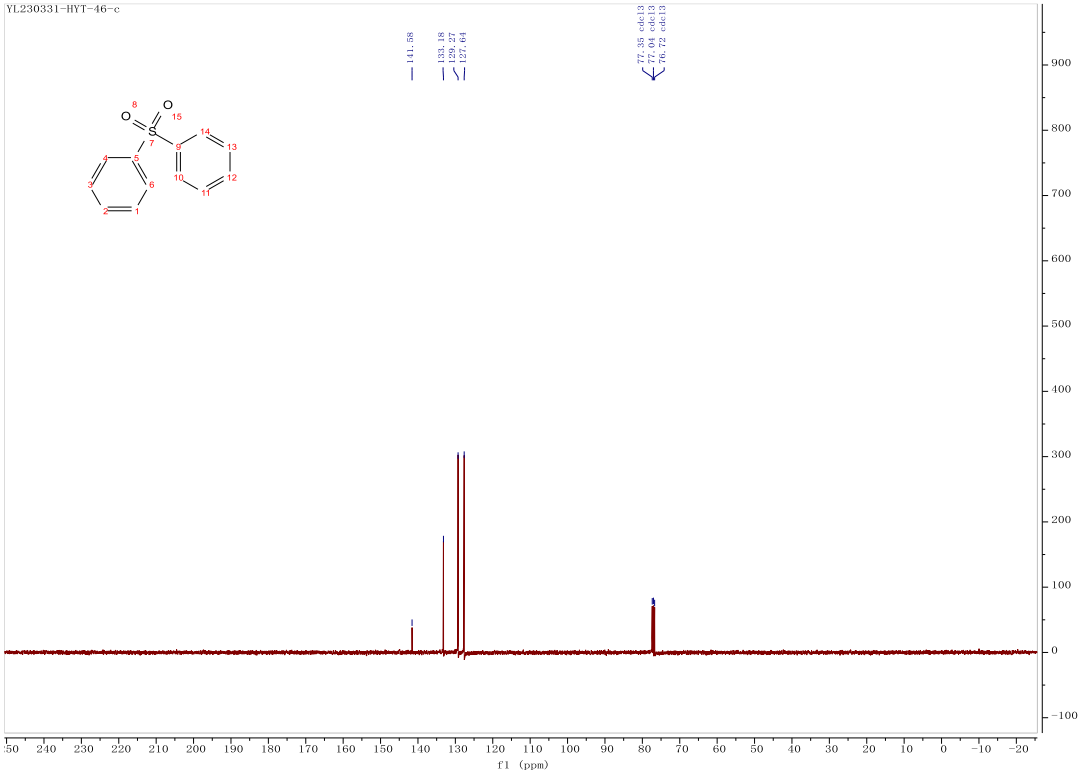
^{13}C NMR Spectra of **3a** (100 MHz, $CDCl_3$)



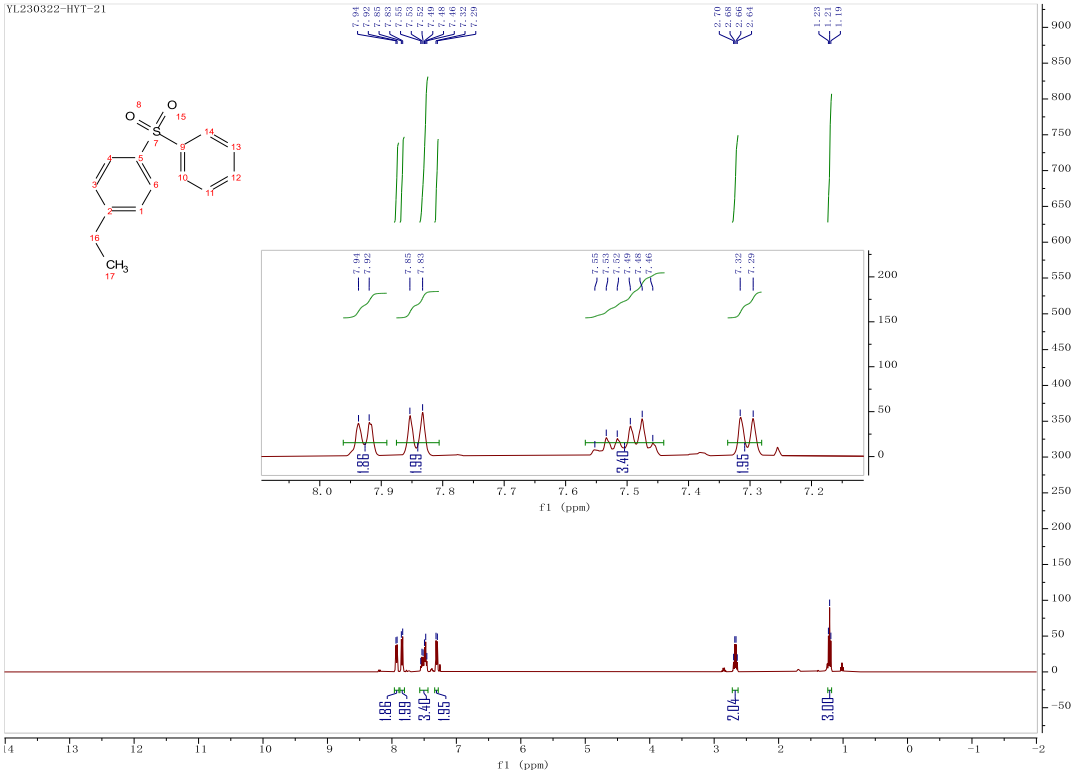
^{1}H NMR Spectra of **3b** (400 MHz, $CDCl_3$)



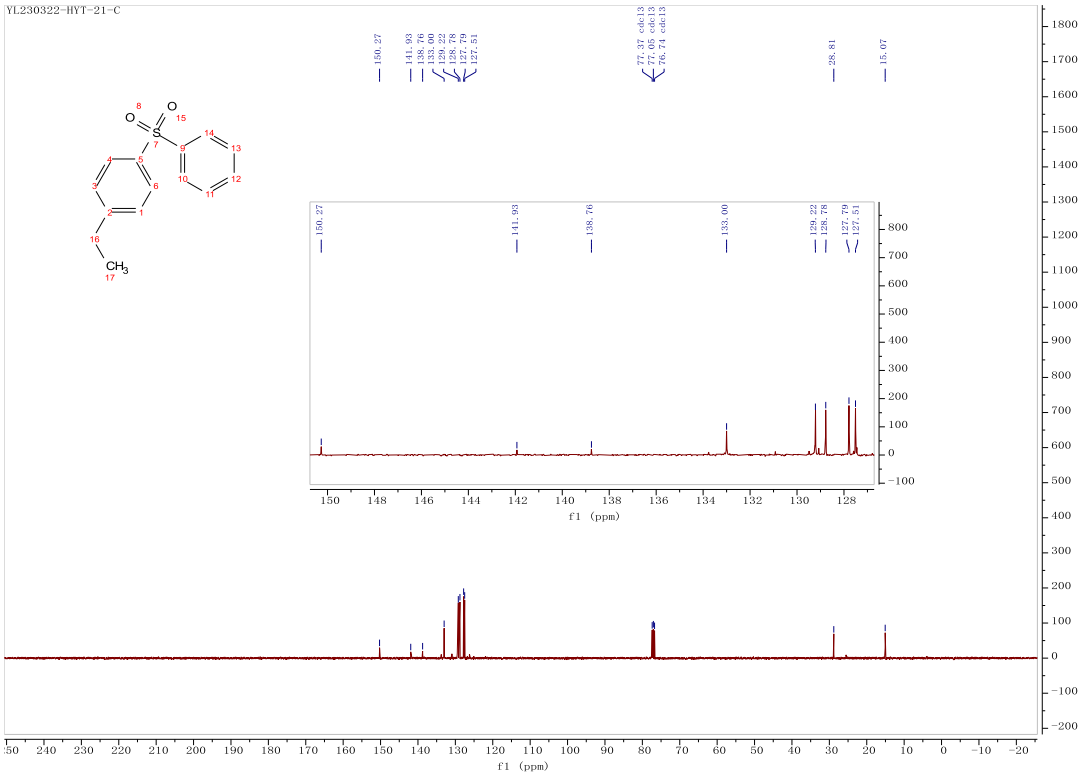
^{13}C NMR Spectra of **3b** (100 MHz, $CDCl_3$)



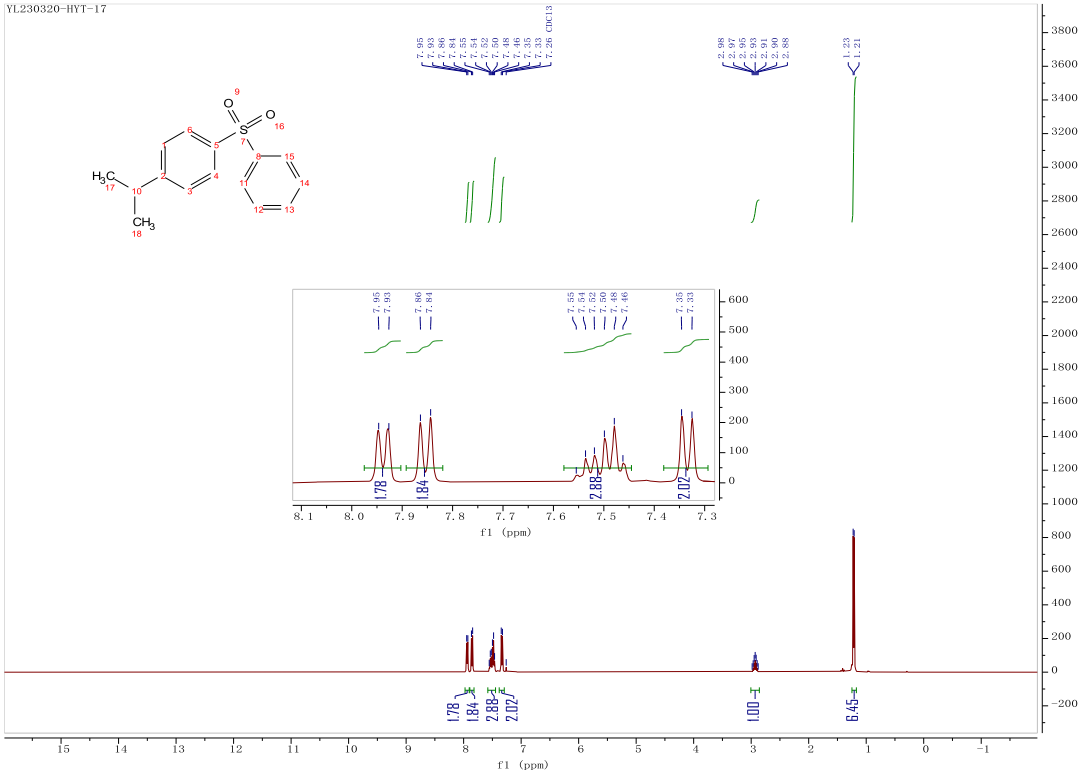
^{1}H NMR Spectra of **3c** (400 MHz, $CDCl_3$)



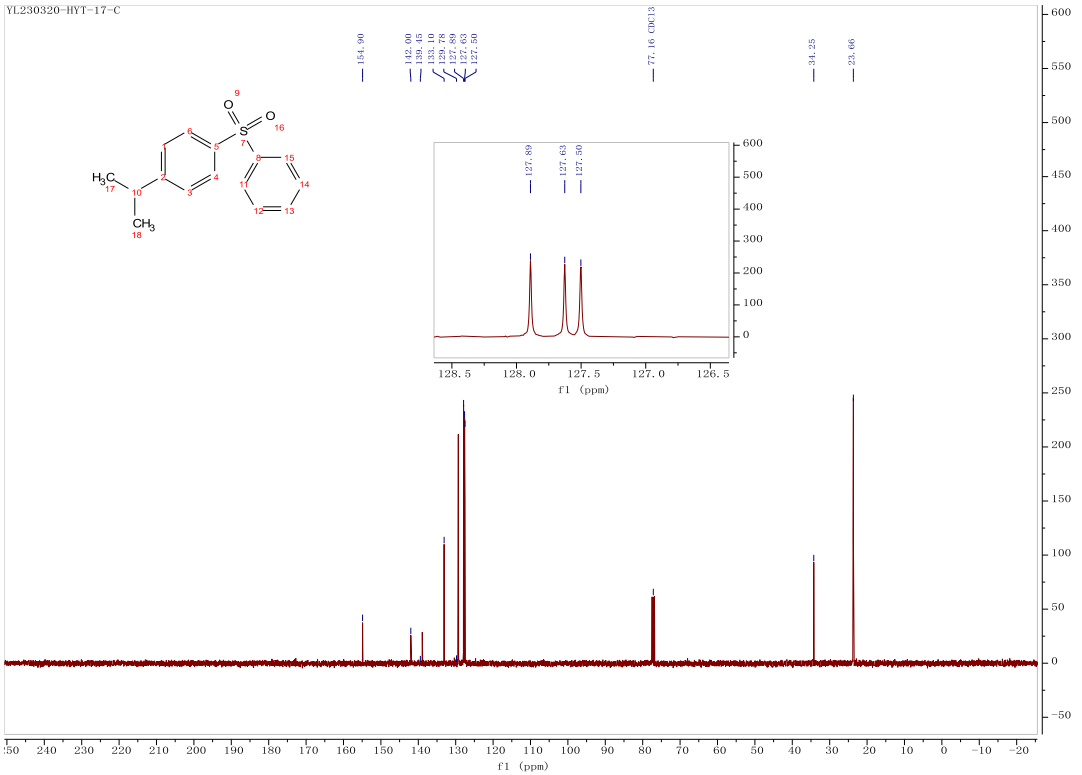
^{13}C NMR Spectra of **3c** (100 MHz, $CDCl_3$)



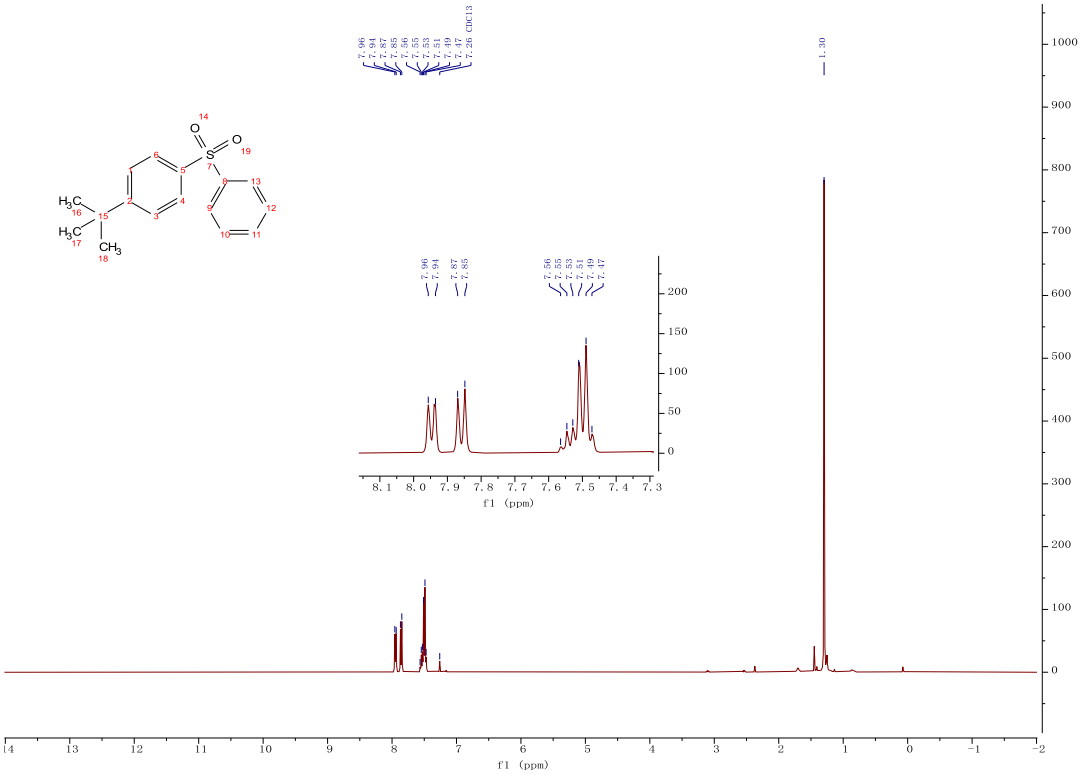
^{1}H NMR Spectra of **3d** (400 MHz, $CDCl_3$)



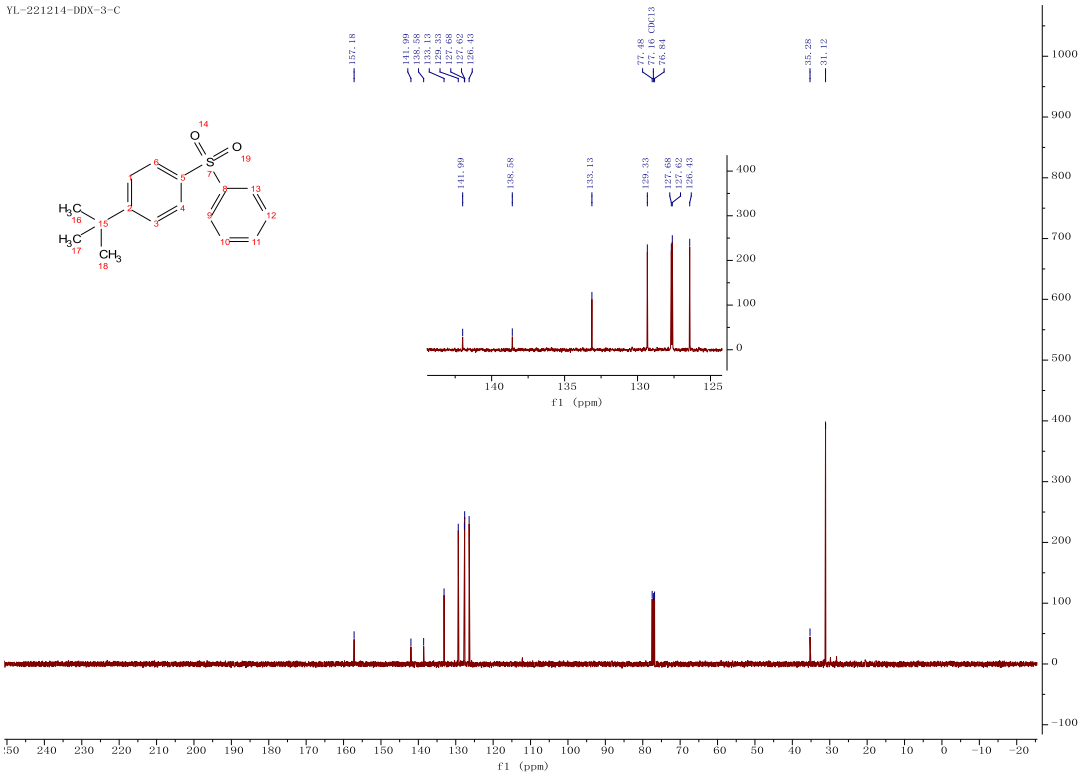
^{13}C NMR Spectra of **3d** (100 MHz, $CDCl_3$)



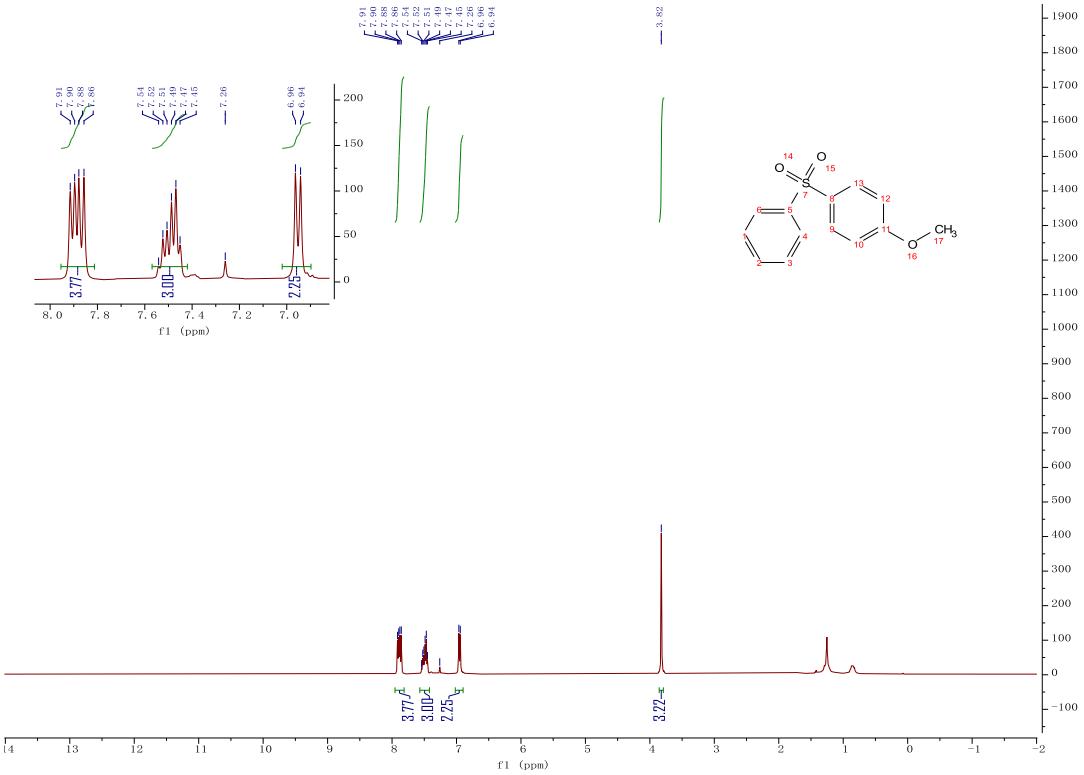
^{1}H NMR Spectra of **3e** (400 MHz, $CDCl_3$)



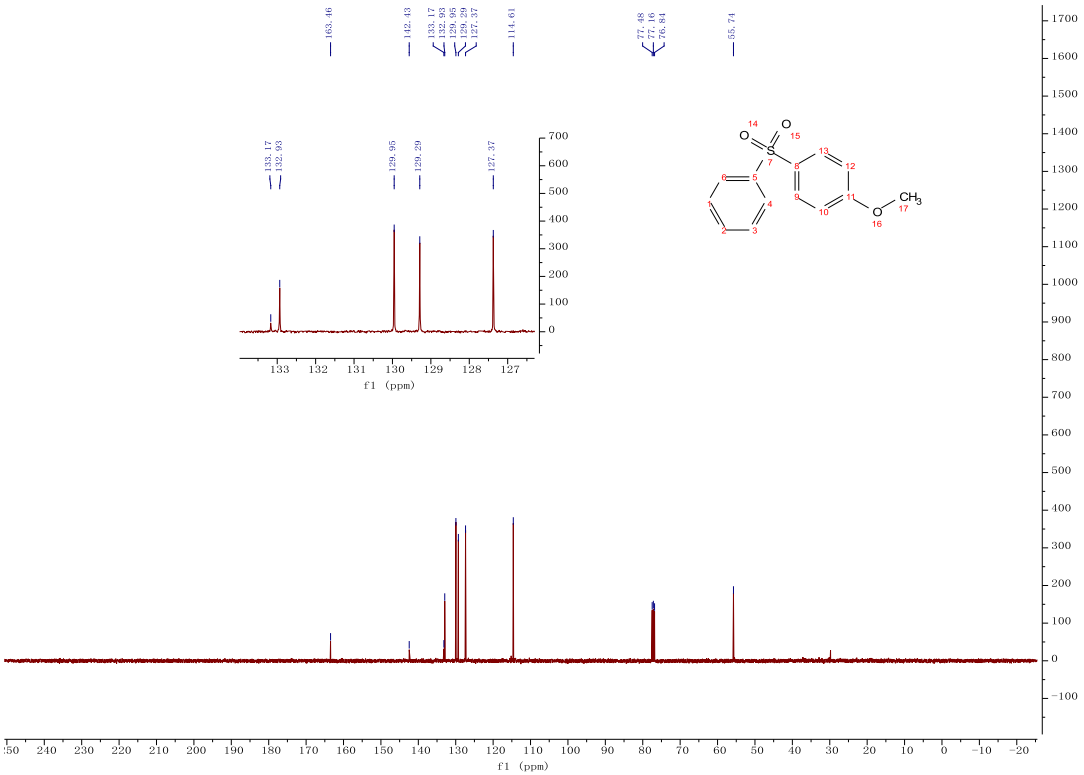
^{13}C NMR Spectra of **3e** (100 MHz, $CDCl_3$)



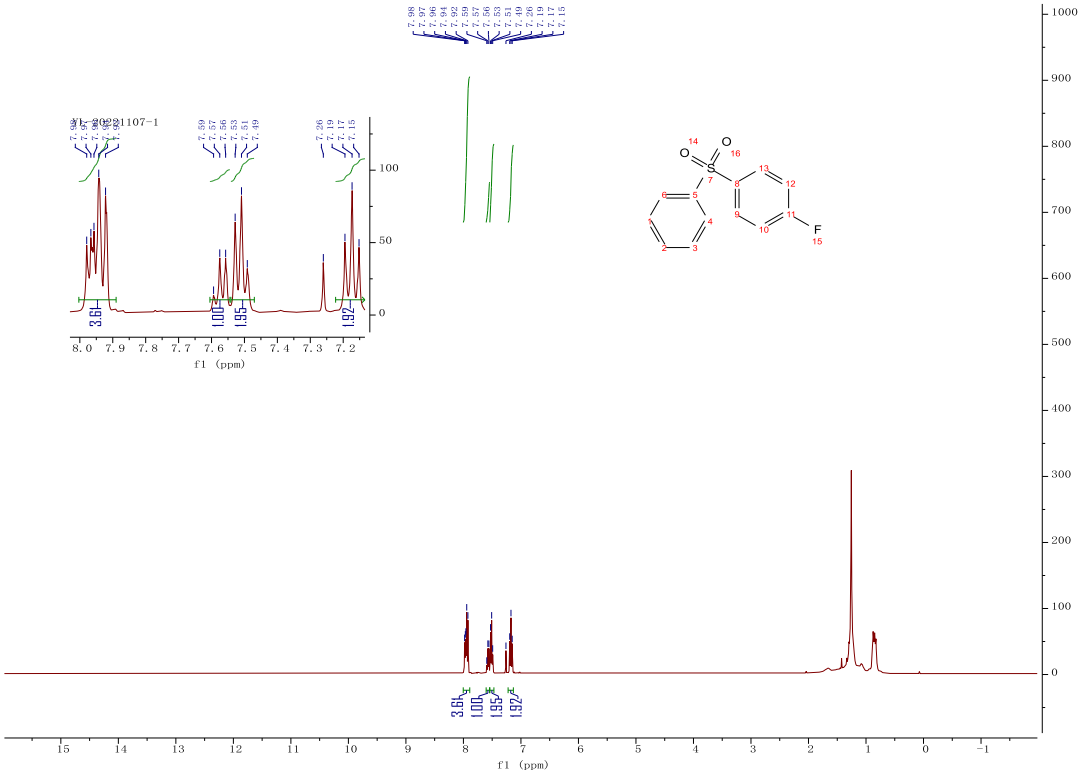
^{1}H NMR Spectra of **3f** (400 MHz, $CDCl_3$)



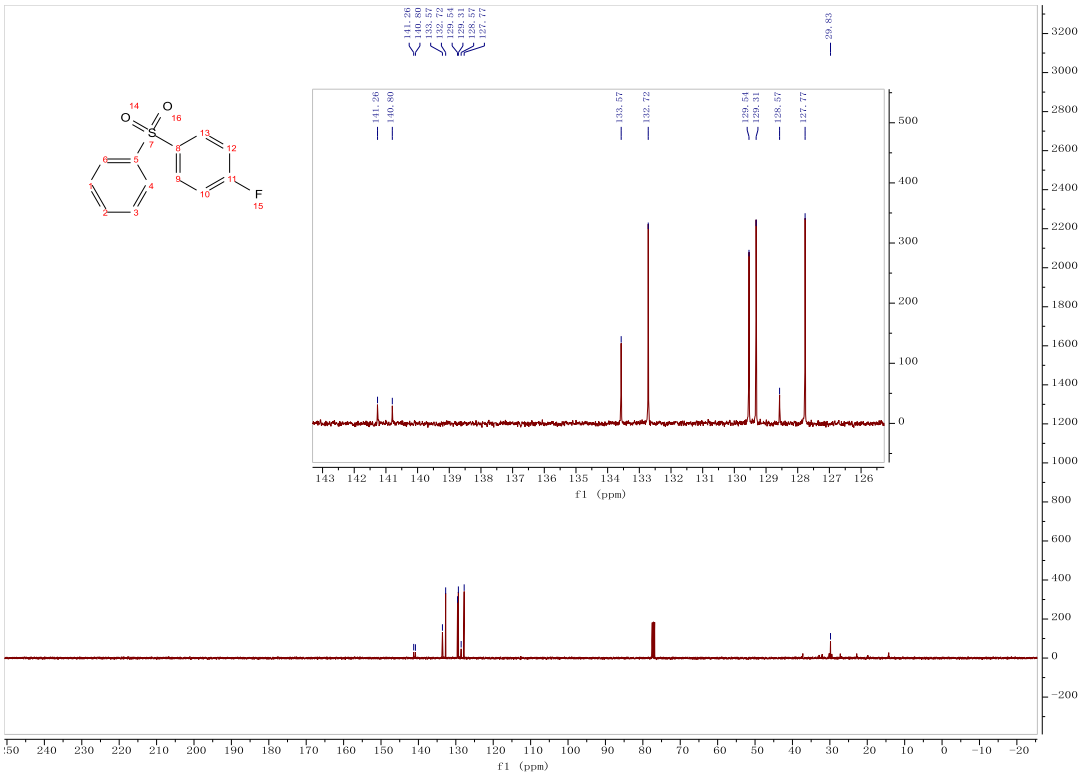
^{13}C NMR Spectra of **3f** (100 MHz, $CDCl_3$)



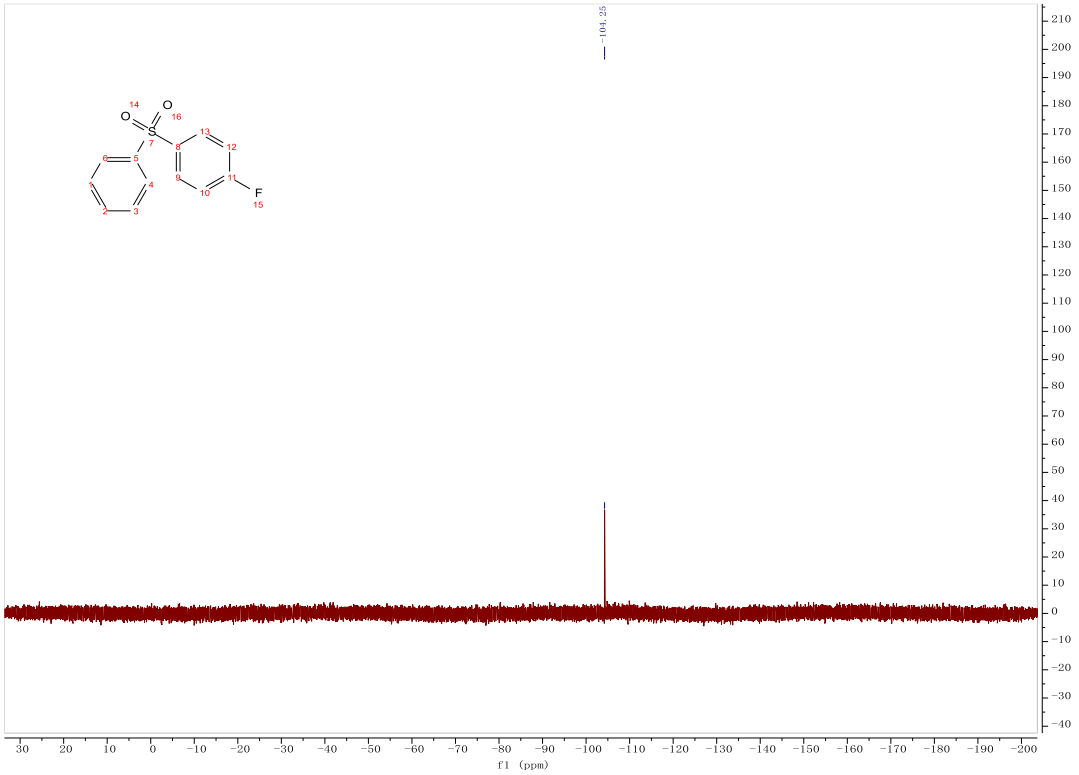
^{1}H NMR Spectra of **3g** (400 MHz, $CDCl_3$)



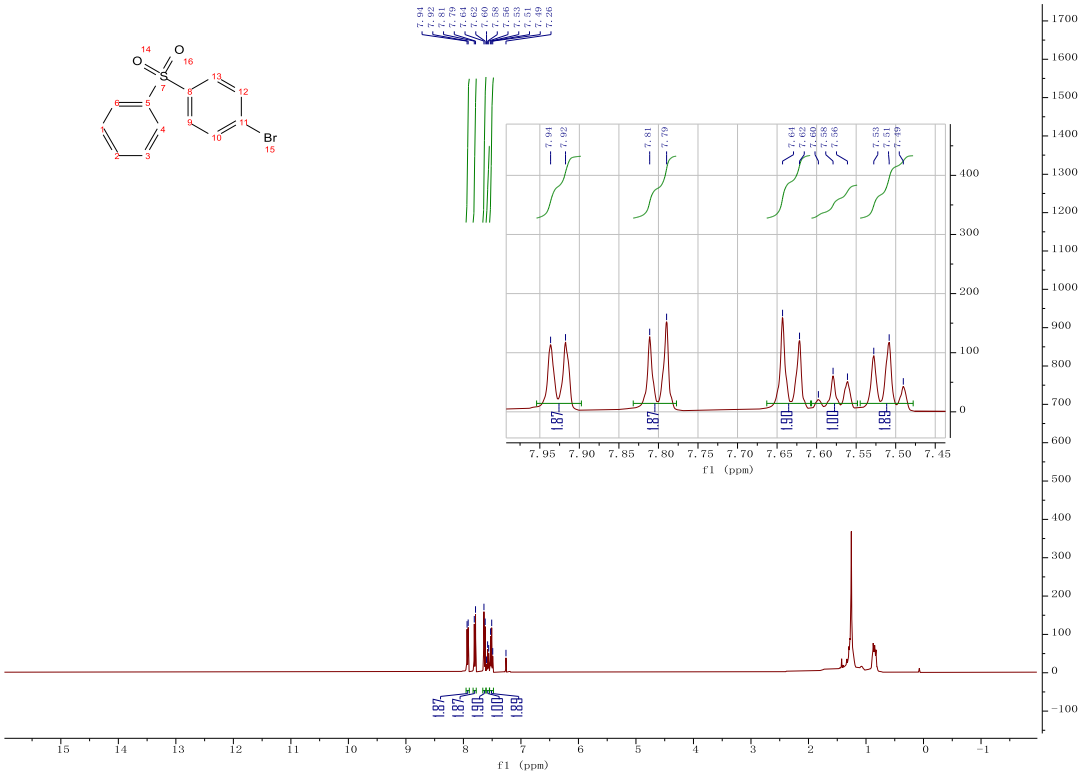
^{13}C NMR Spectra of **3g** (100 MHz, $CDCl_3$)



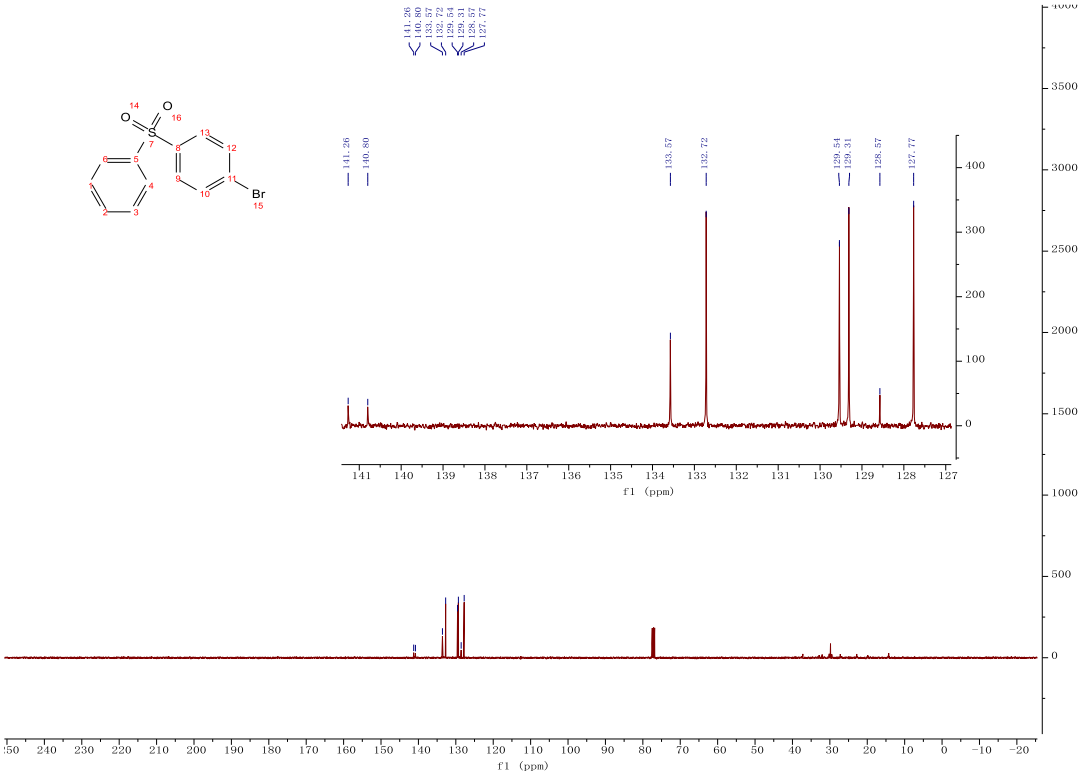
^{19}F NMR spectrum of **3g** (376 MHz, $CDCl_3$)



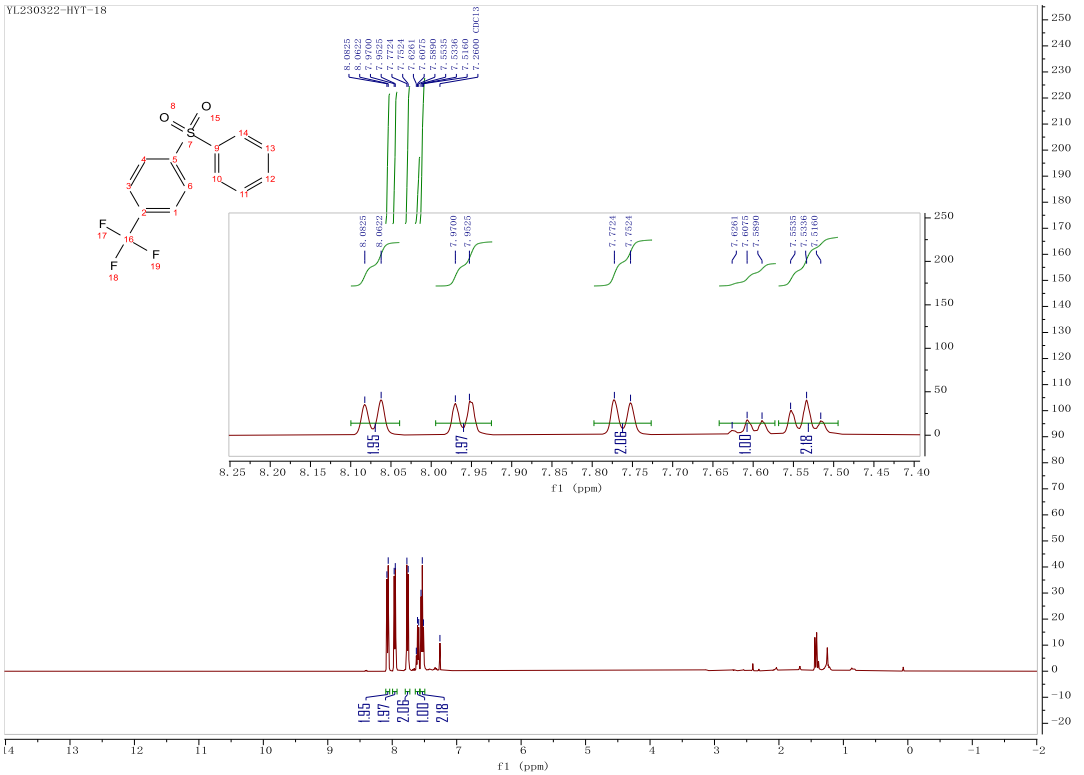
^{1}H NMR Spectra of **3h** (400 MHz, $CDCl_3$)



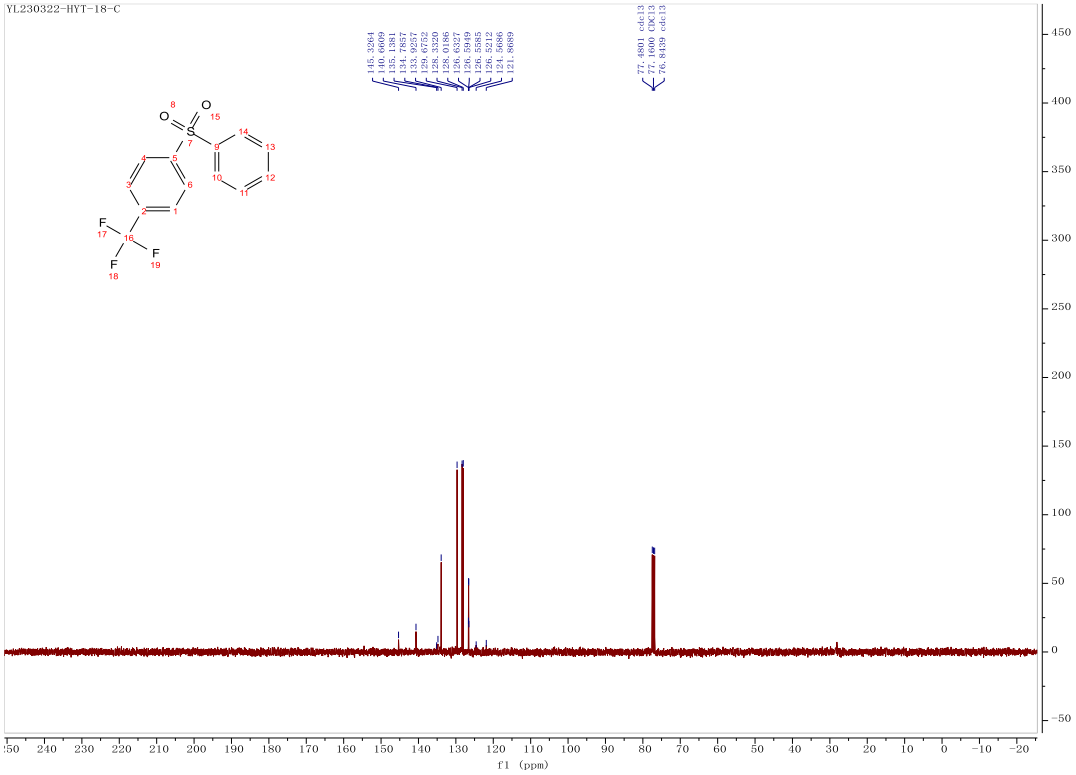
^{13}C NMR Spectra of **3h** (100 MHz, $CDCl_3$)



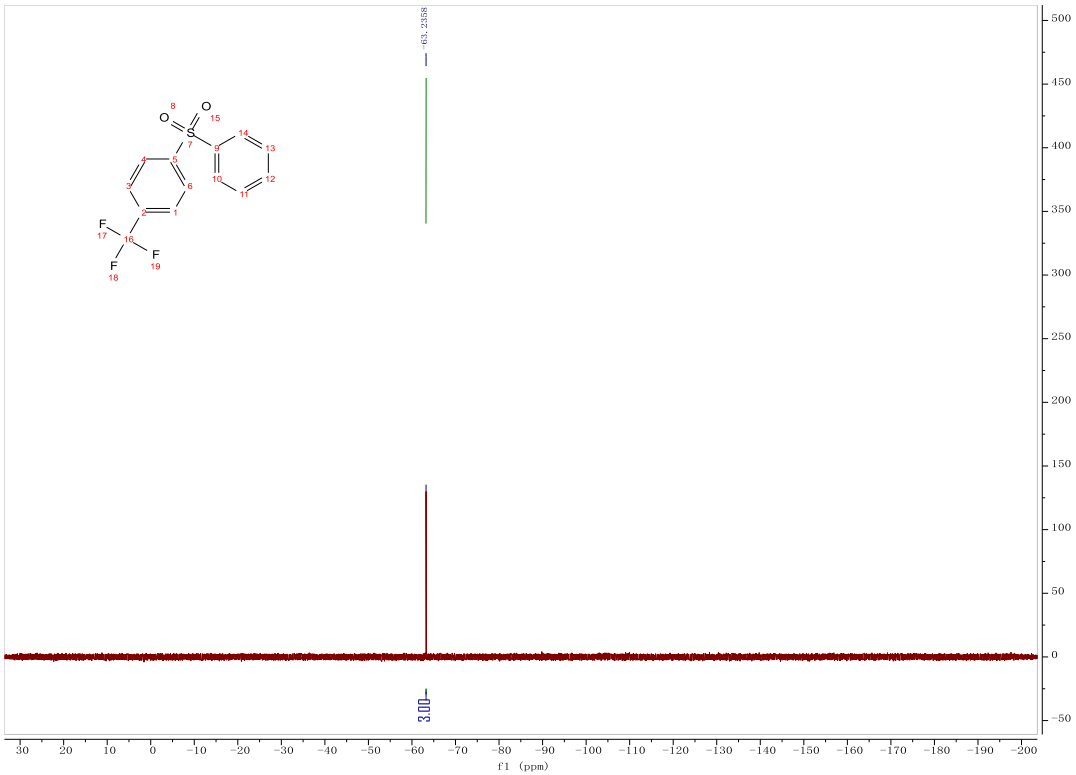
^{1}H NMR Spectra of **3i** (400 MHz, $CDCl_3$)



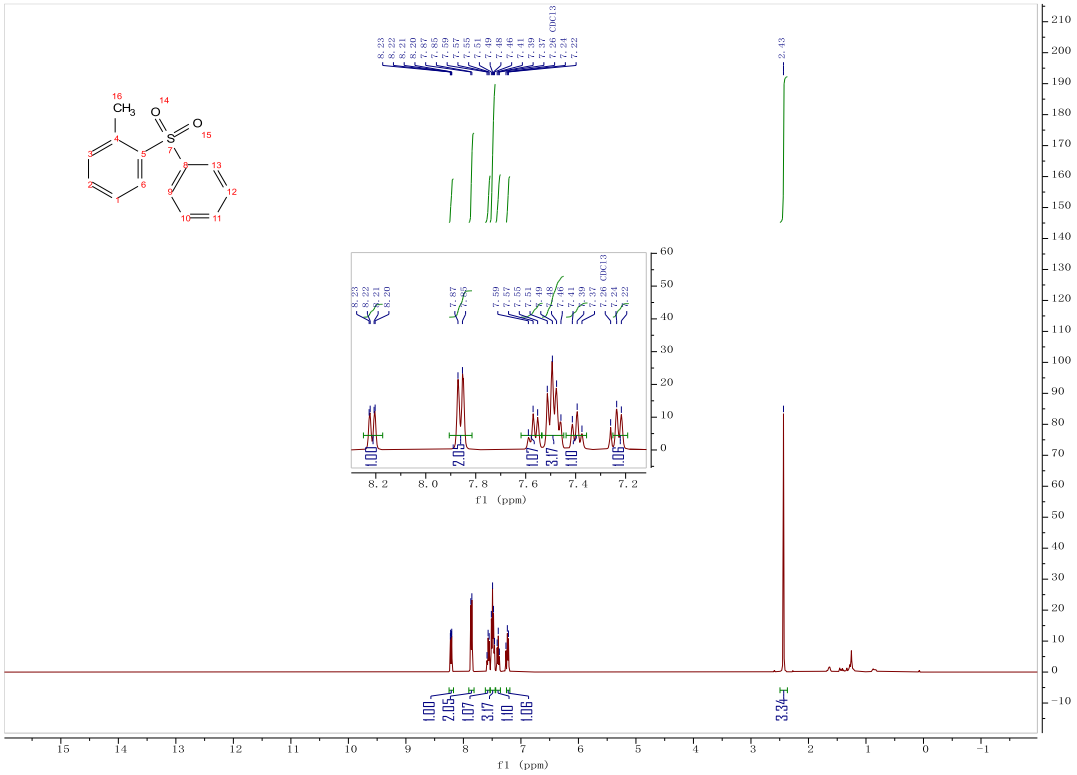
^{13}C NMR Spectra of **3i** (100 MHz, $CDCl_3$)



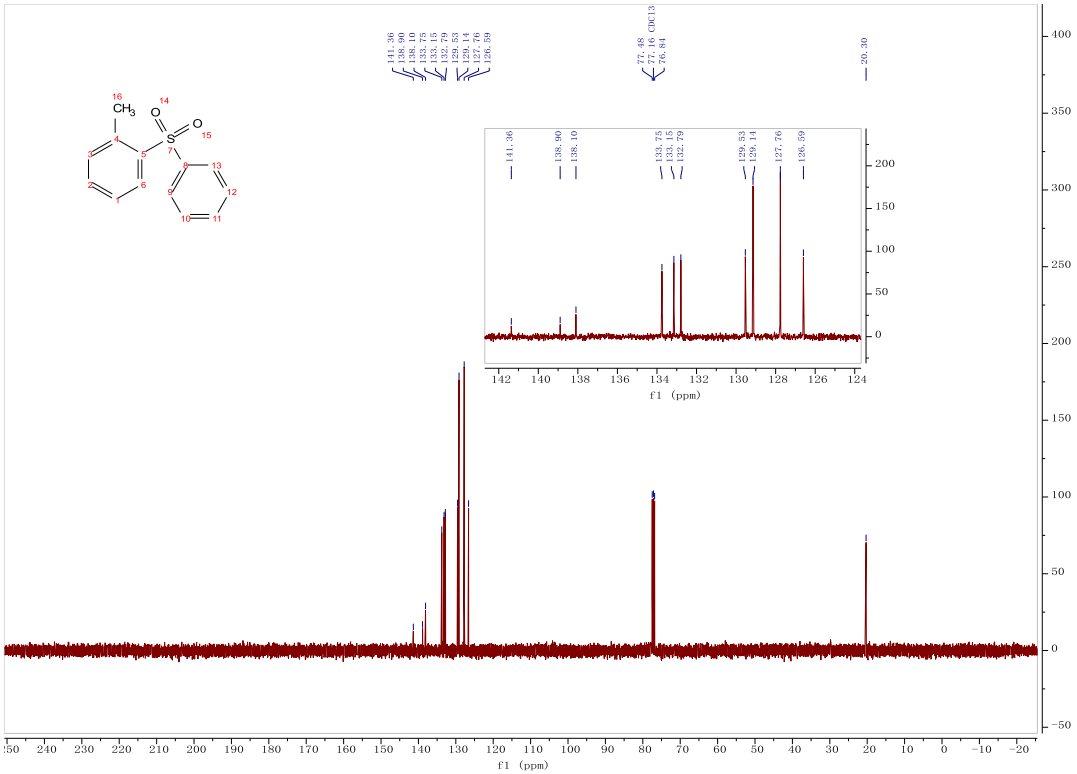
^{19}F NMR spectrum of **3i** (376 MHz, $CDCl_3$)



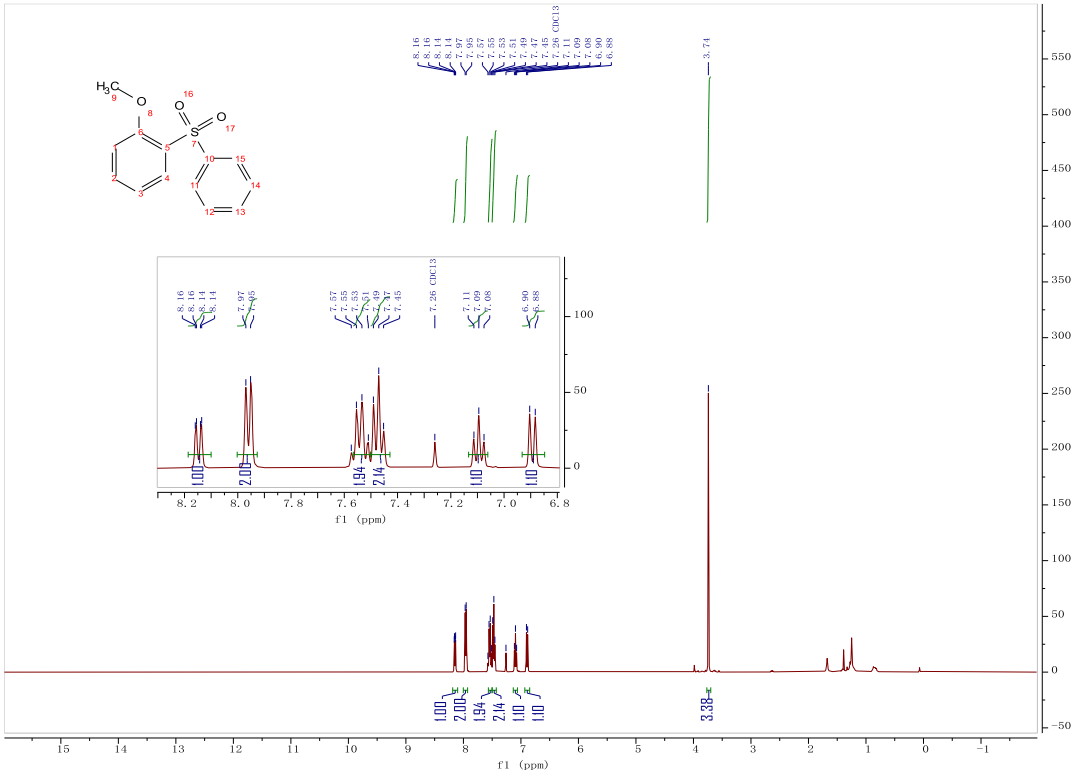
^{1}H NMR Spectra of **3j** (400 MHz, $CDCl_3$)



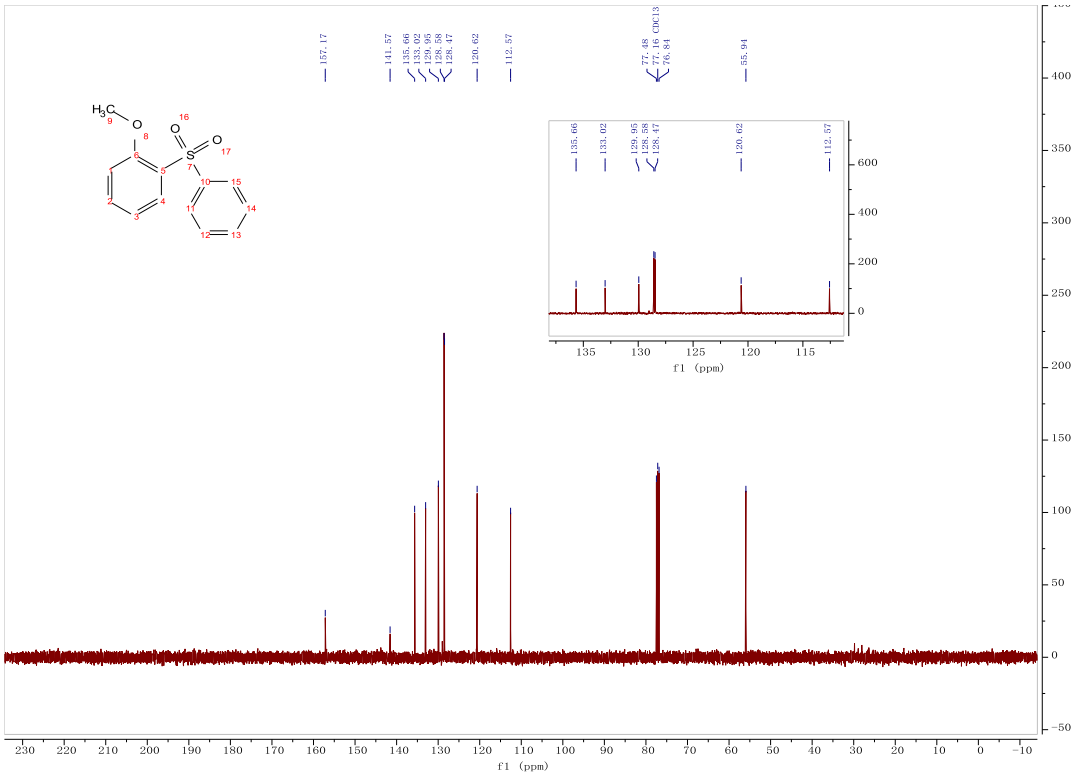
^{13}C NMR Spectra of **3j** (100 MHz, $CDCl_3$)



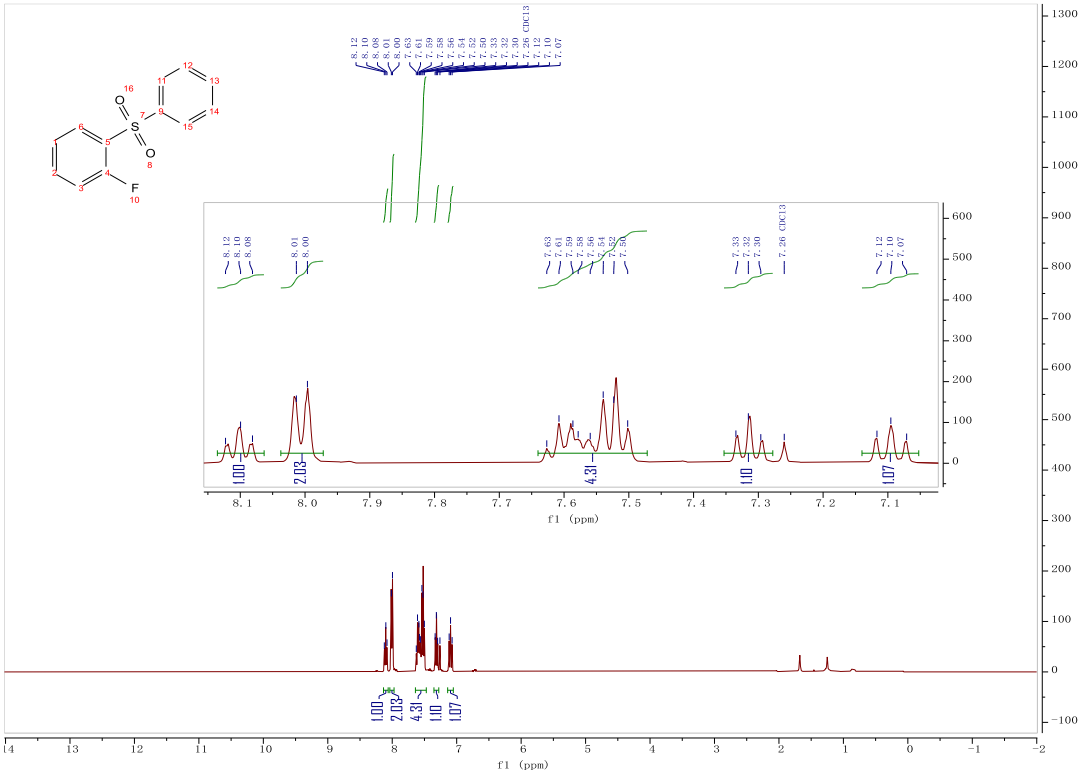
^{1}H NMR Spectra of **3k** (400 MHz, $CDCl_3$)



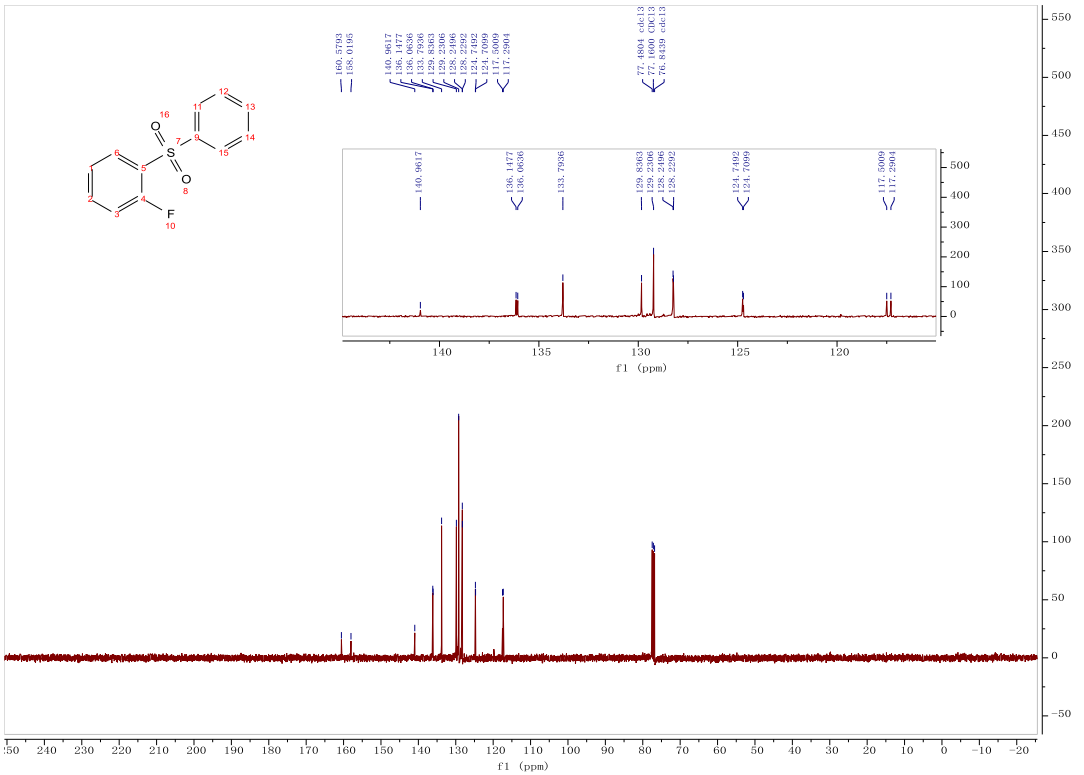
^{13}C NMR Spectra of **3k** (100 MHz, $CDCl_3$)



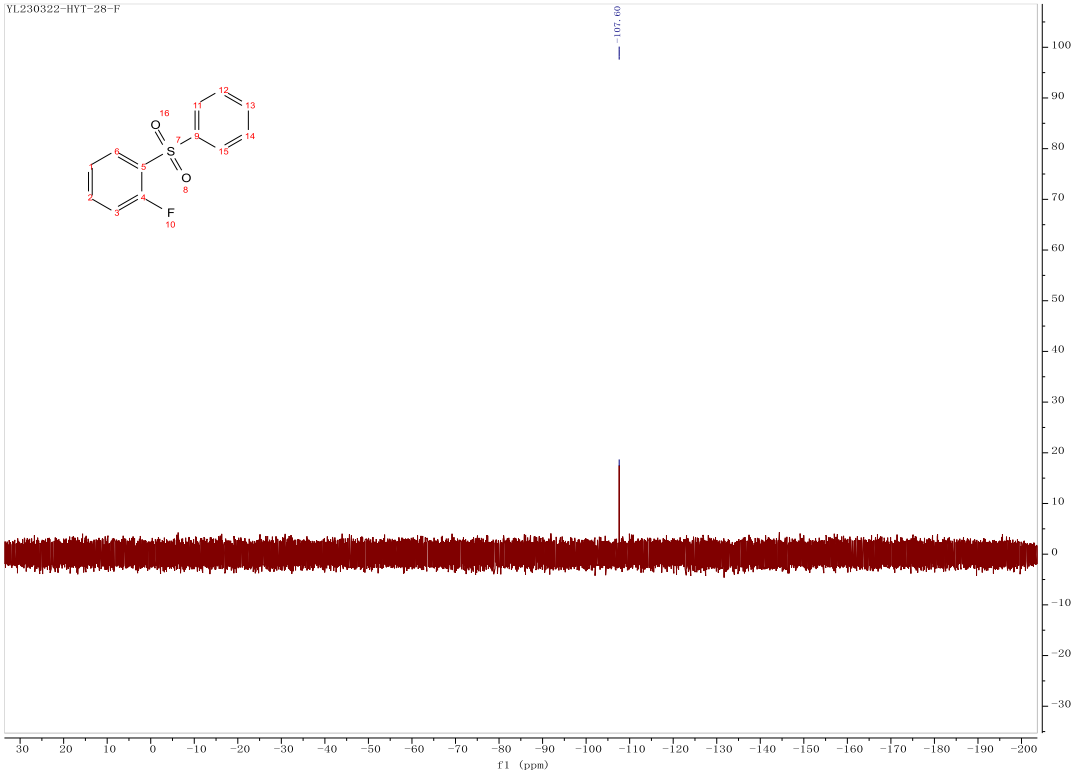
^{1}H NMR Spectra of **3l** (400 MHz, $CDCl_3$)



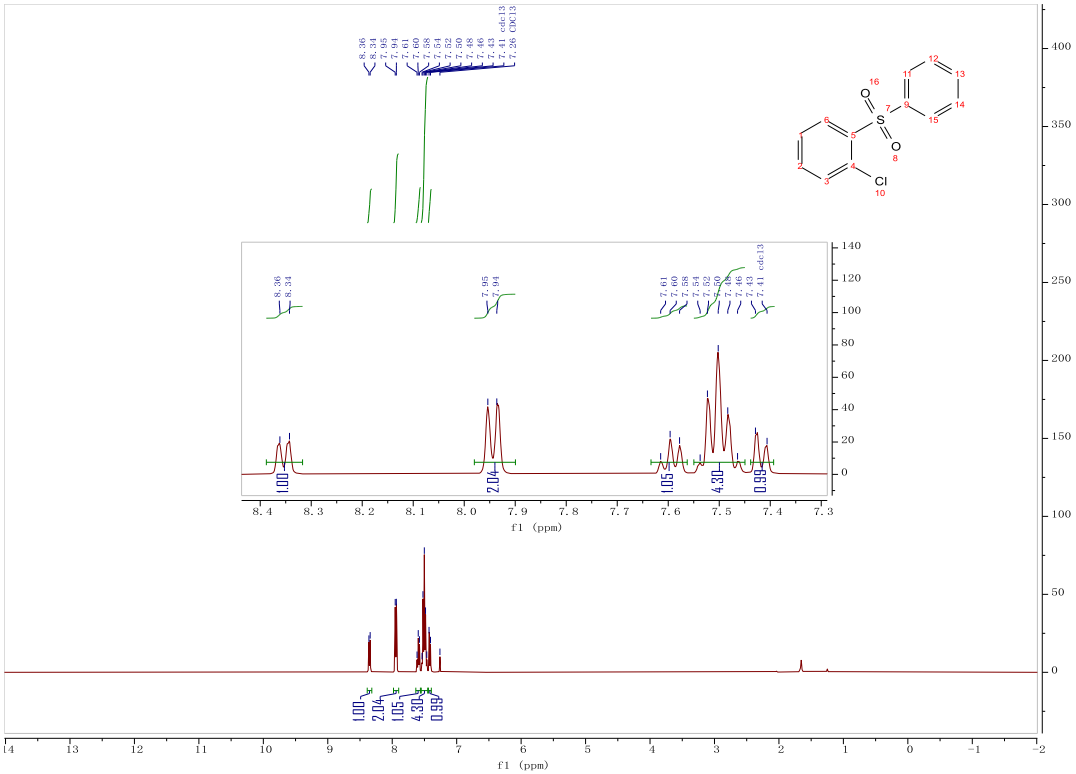
^{13}C NMR Spectra of **3l** (100 MHz, $CDCl_3$)



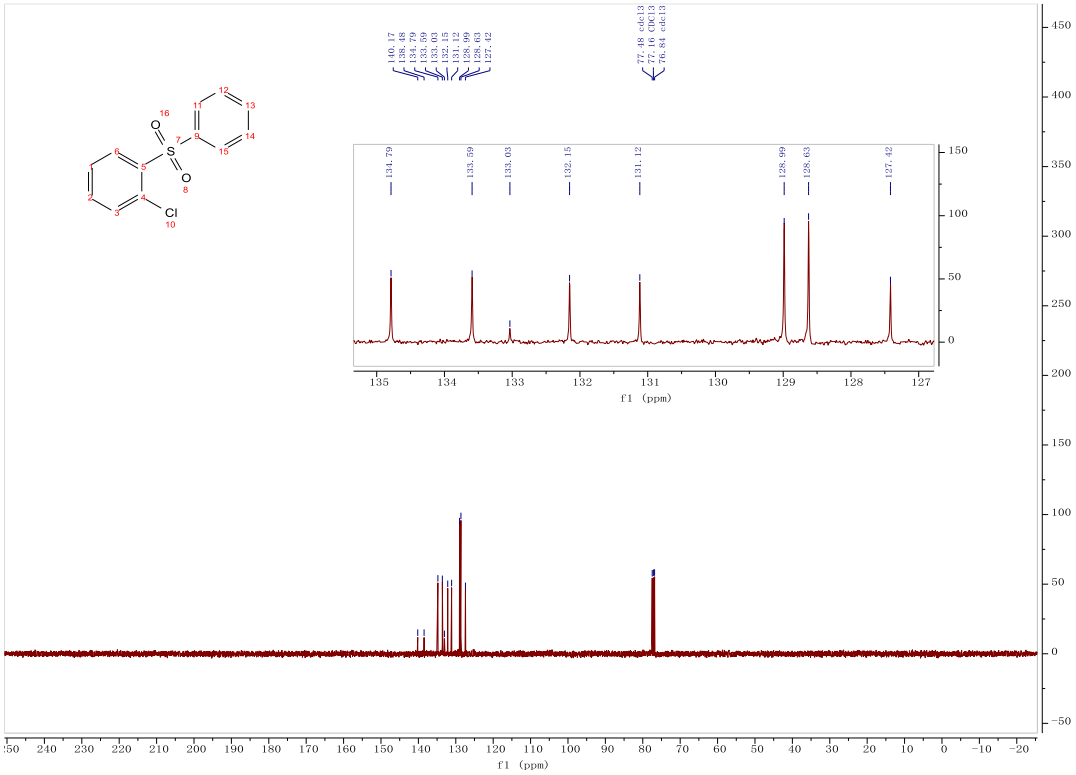
^{19}F NMR spectrum of **3l** (376 MHz, $CDCl_3$)



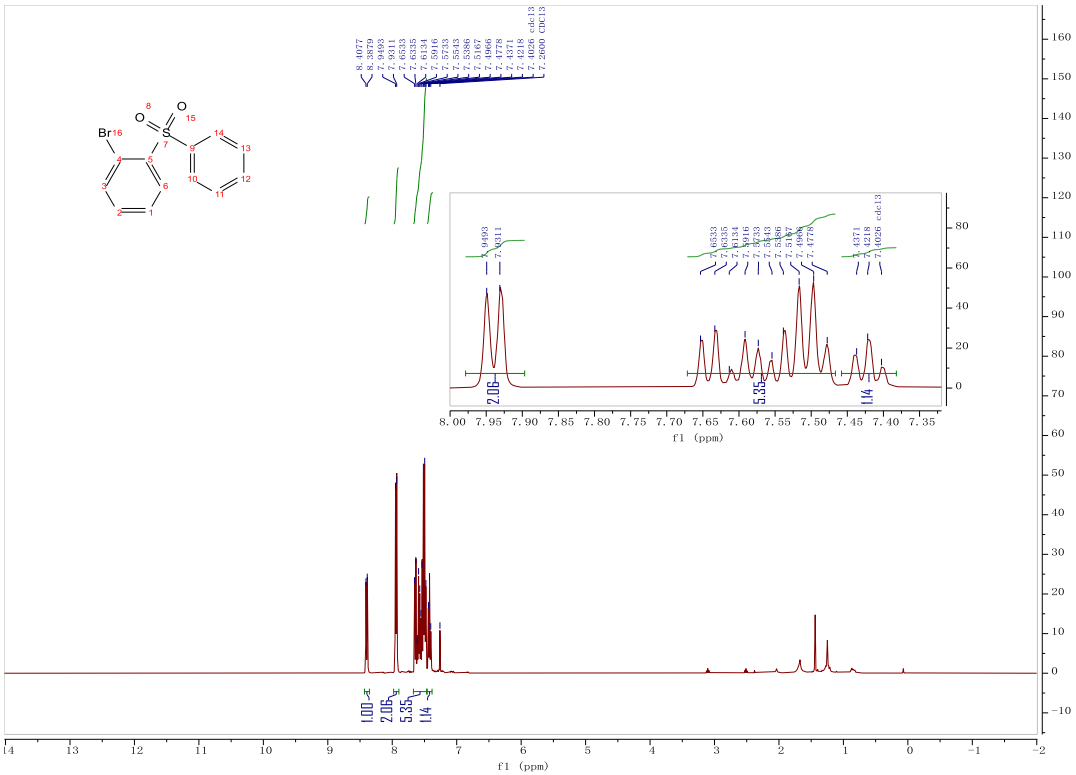
^{1}H NMR Spectra of **3m** (400 MHz, $CDCl_3$)



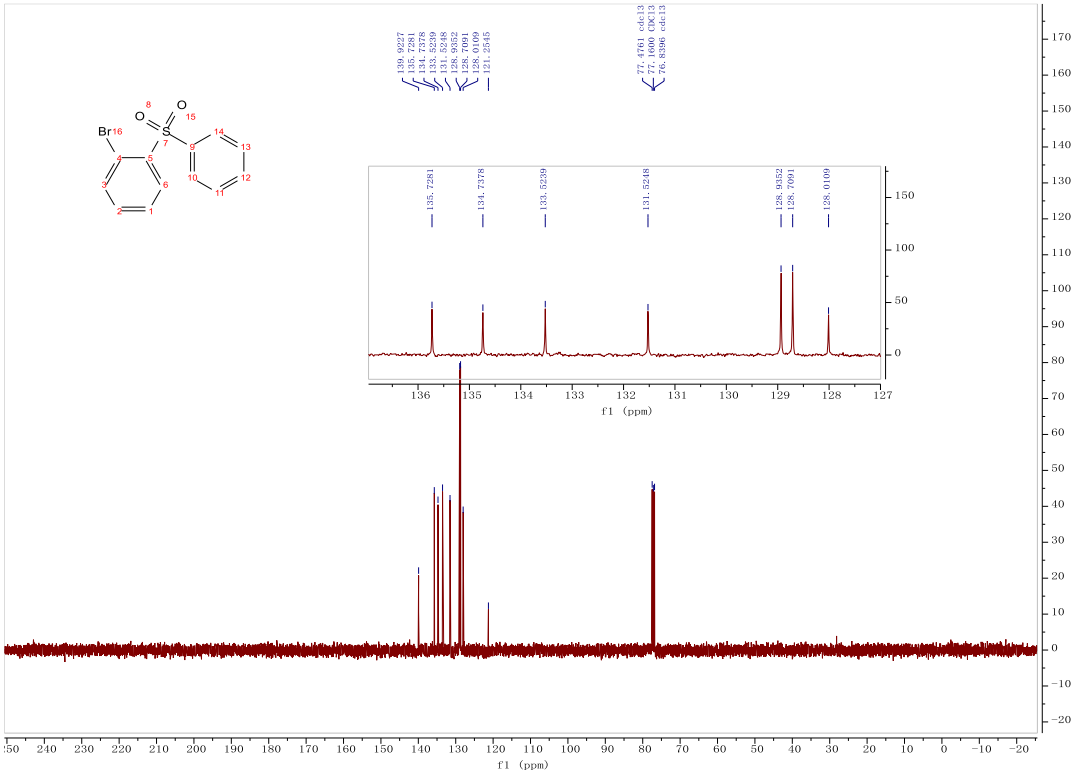
^{13}C NMR Spectra of **3m** (100 MHz, $CDCl_3$)



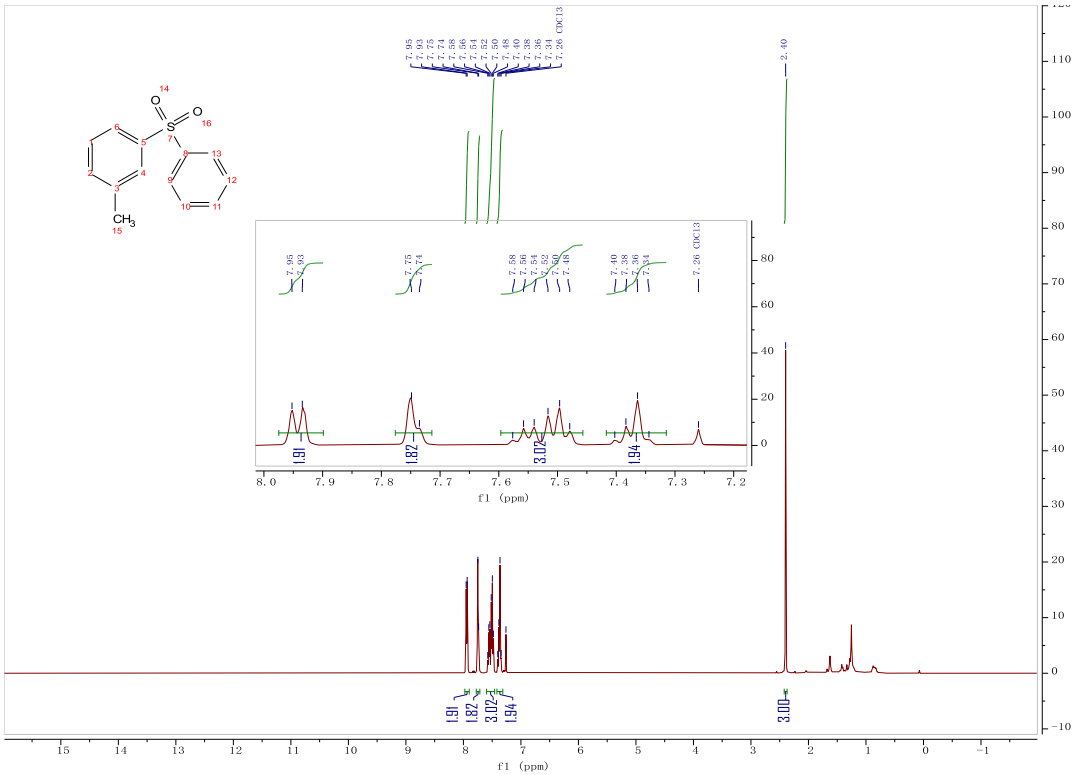
^{1}H NMR Spectra of **3n** (400 MHz, $CDCl_3$)



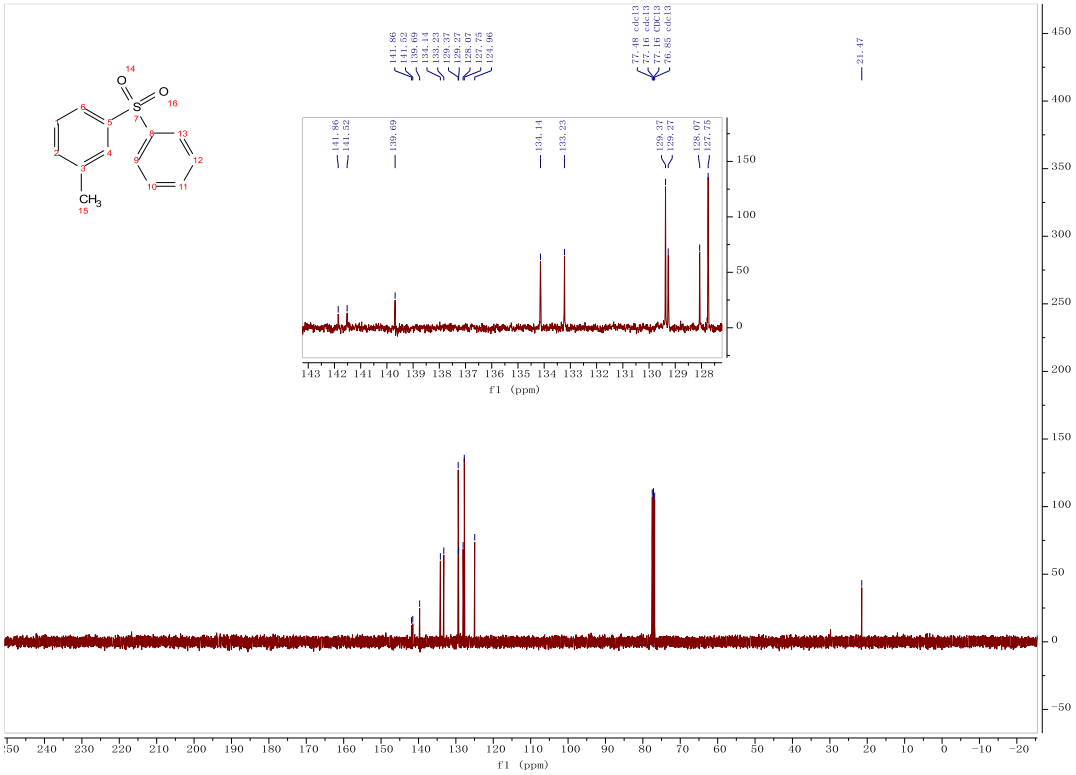
^{13}C NMR Spectra of **3n** (100 MHz, $CDCl_3$)



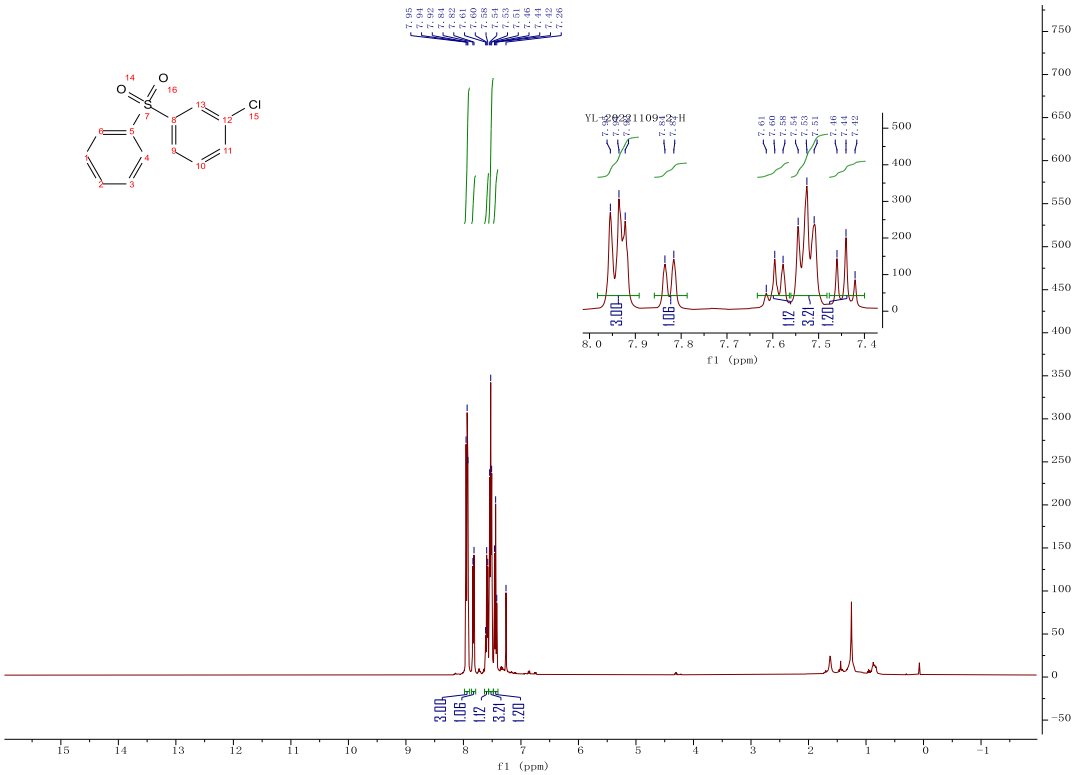
^{1}H NMR Spectra of **3o** (400 MHz, $CDCl_3$)



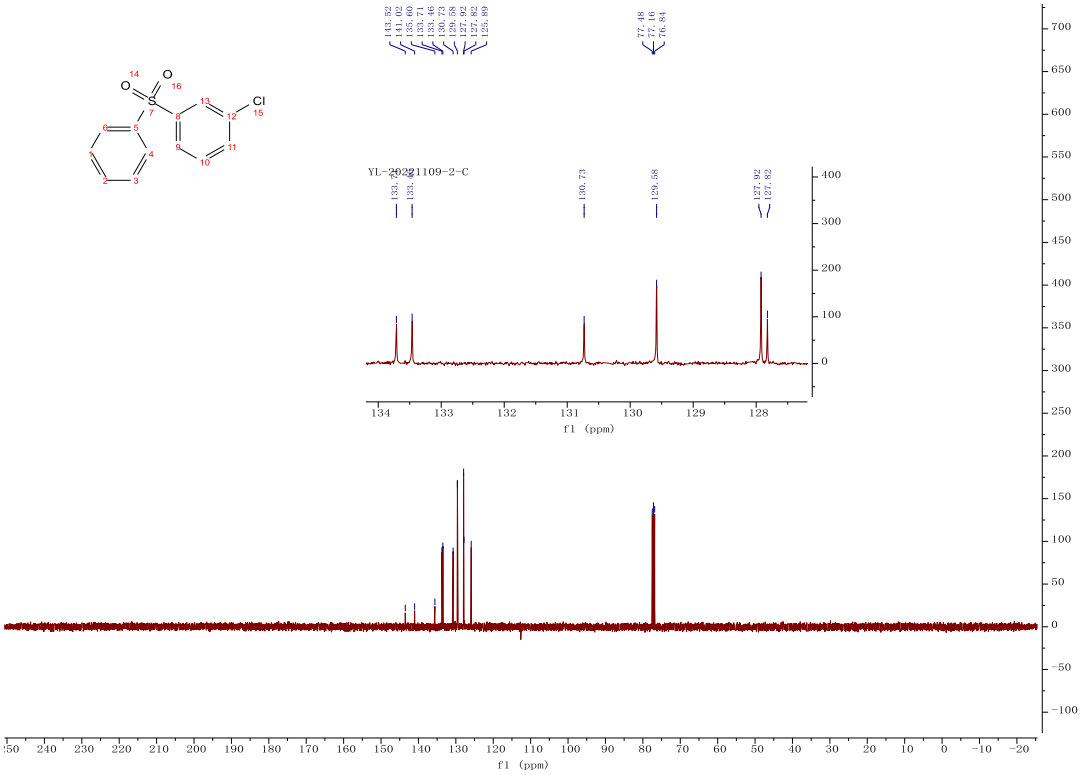
^{13}C NMR Spectra of **3o** (100 MHz, $CDCl_3$)



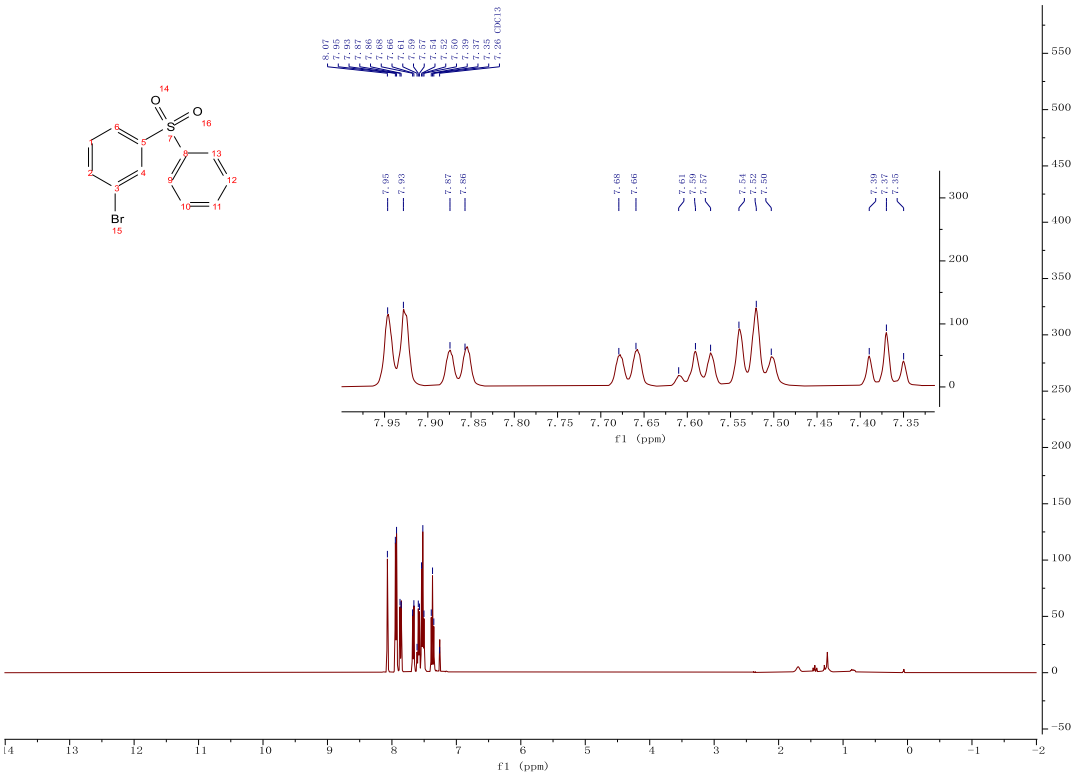
^{1}H NMR Spectra of **3p** (400 MHz, $CDCl_3$)



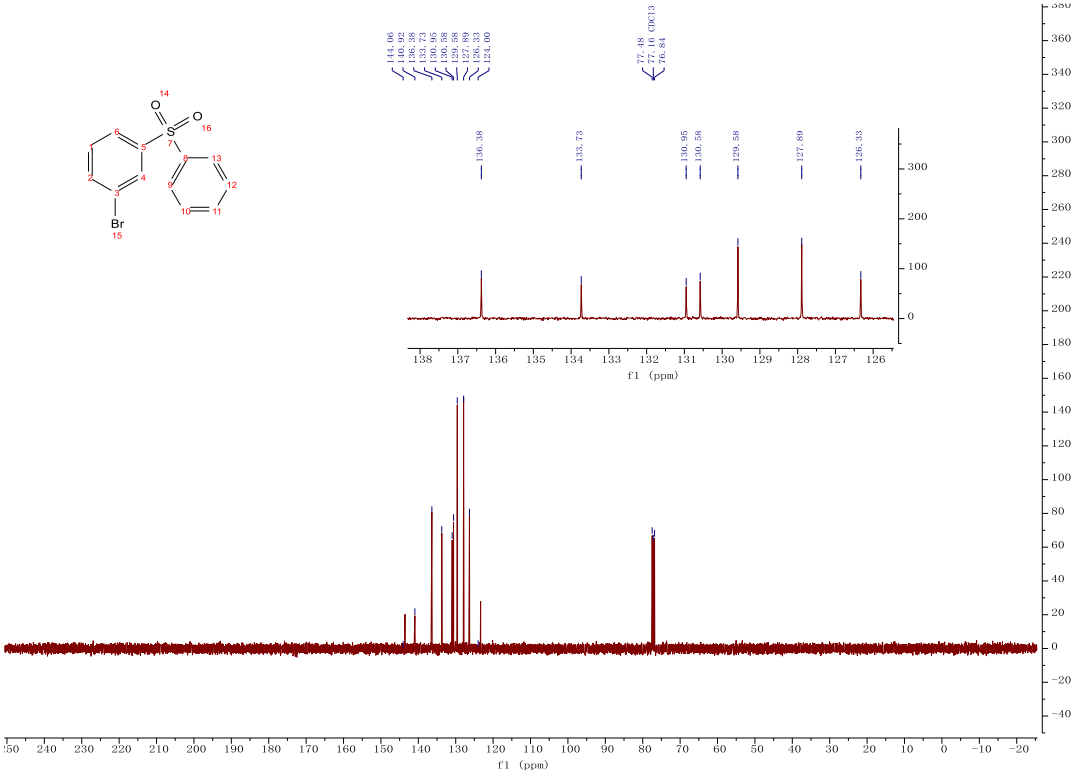
^{13}C NMR Spectra of **3p** (100 MHz, $CDCl_3$)



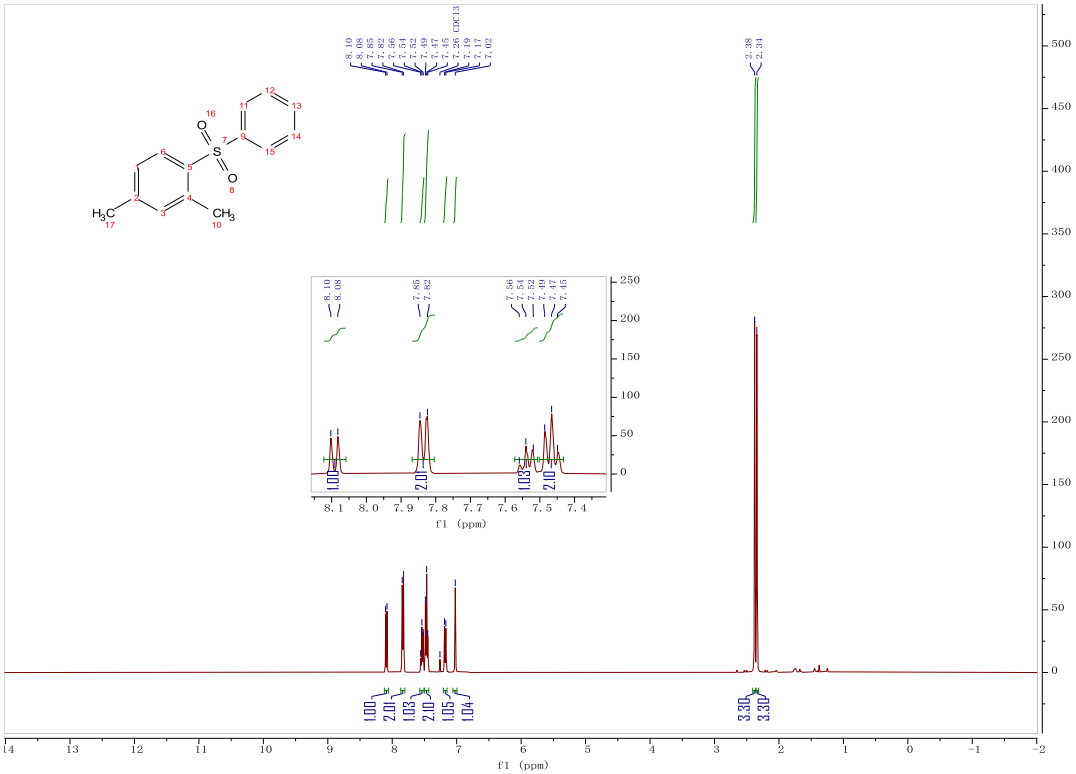
^{1}H NMR Spectra of **3q** (400 MHz, $CDCl_3$)



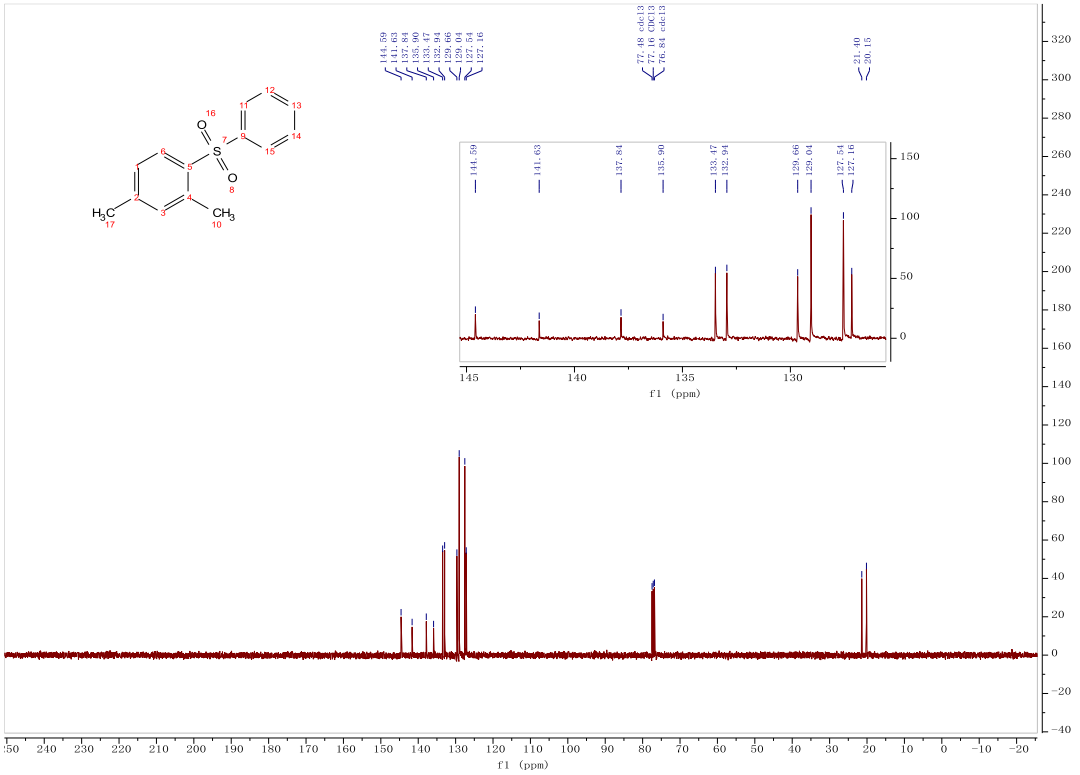
^{13}C NMR Spectra of **3q** (100 MHz, $CDCl_3$)



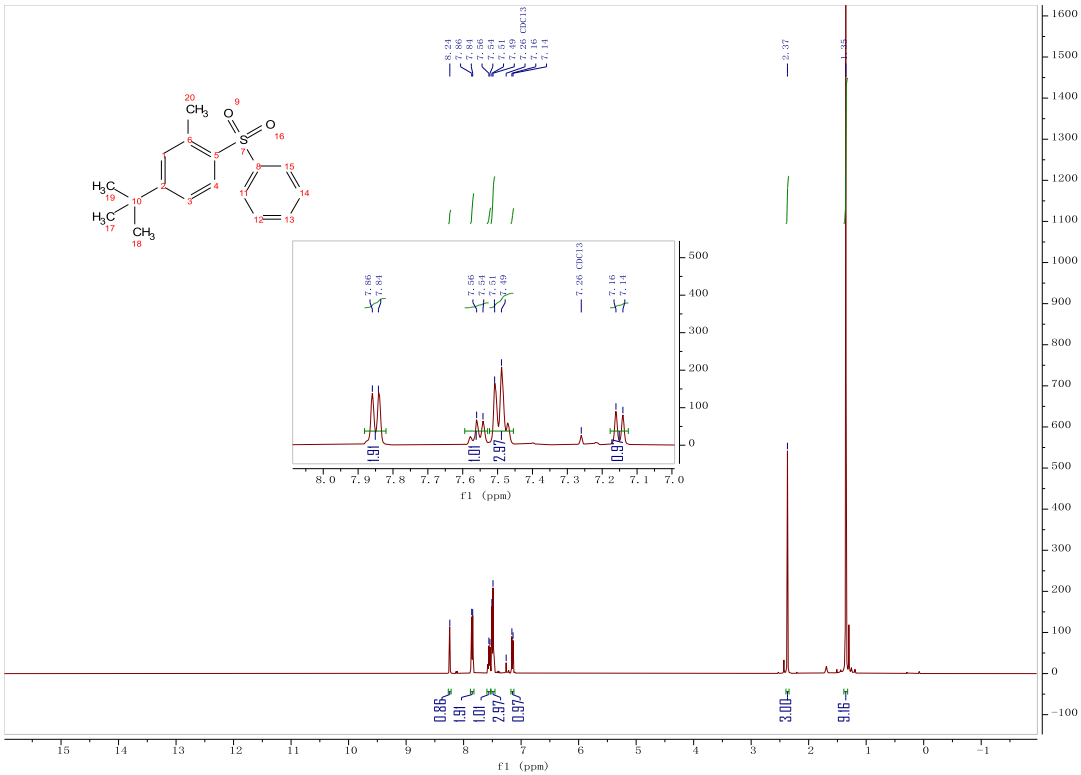
^{1}H NMR Spectra of **3r** (400 MHz, $CDCl_3$)



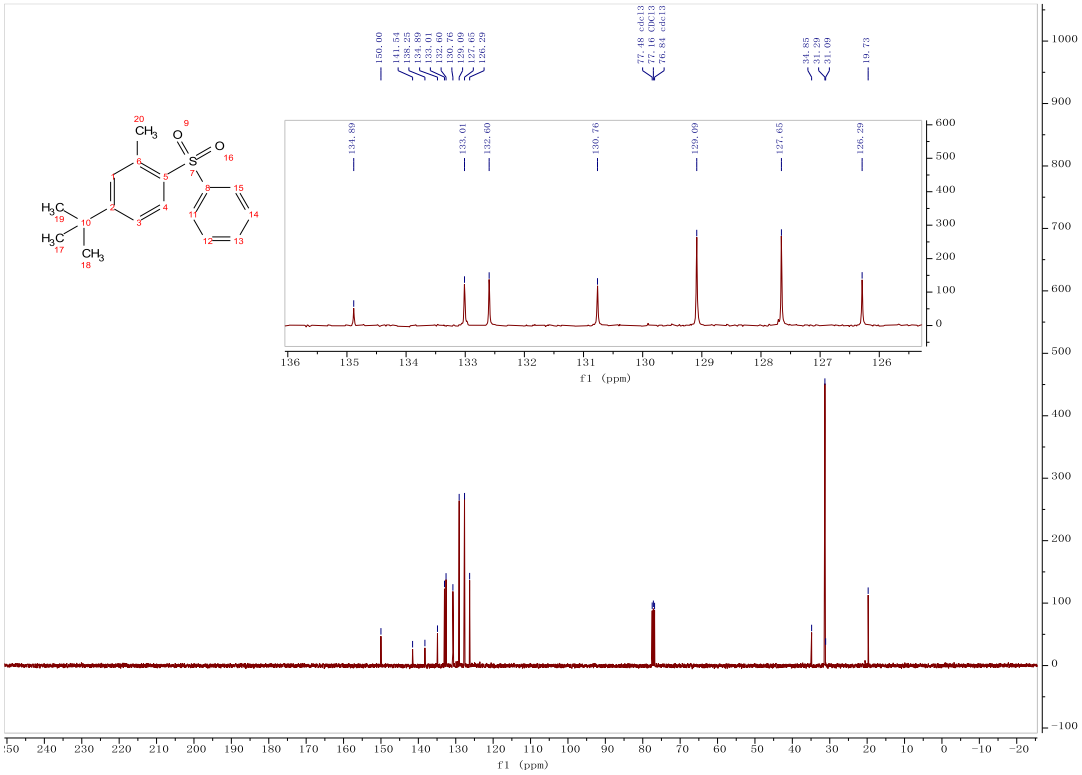
^{13}C NMR Spectra of **3r** (100 MHz, $CDCl_3$)



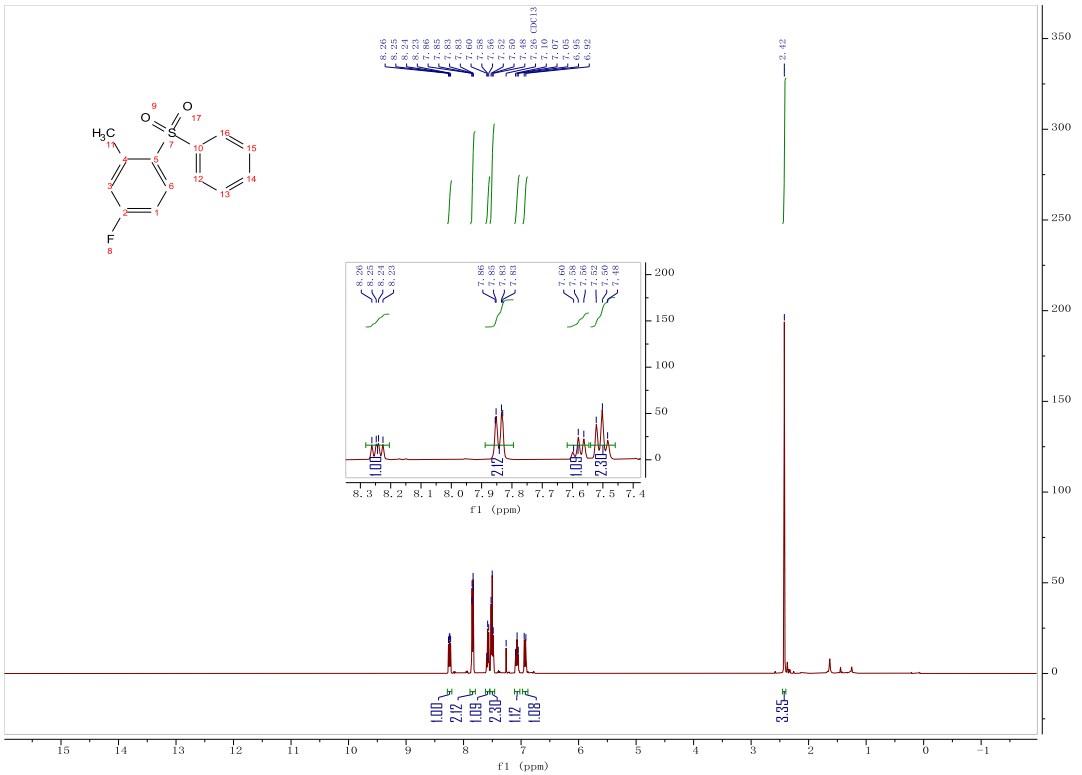
^{1}H NMR Spectra of **3s** (400 MHz, $CDCl_3$)



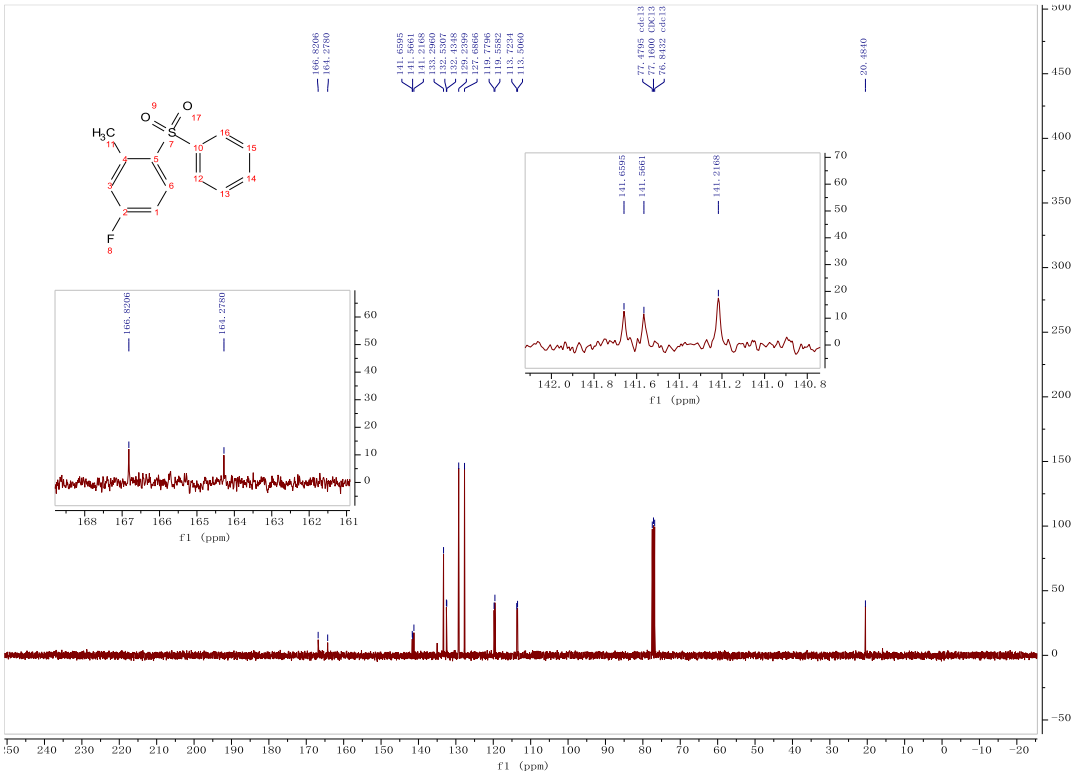
^{13}C NMR Spectra of **3s** (100 MHz, $CDCl_3$)



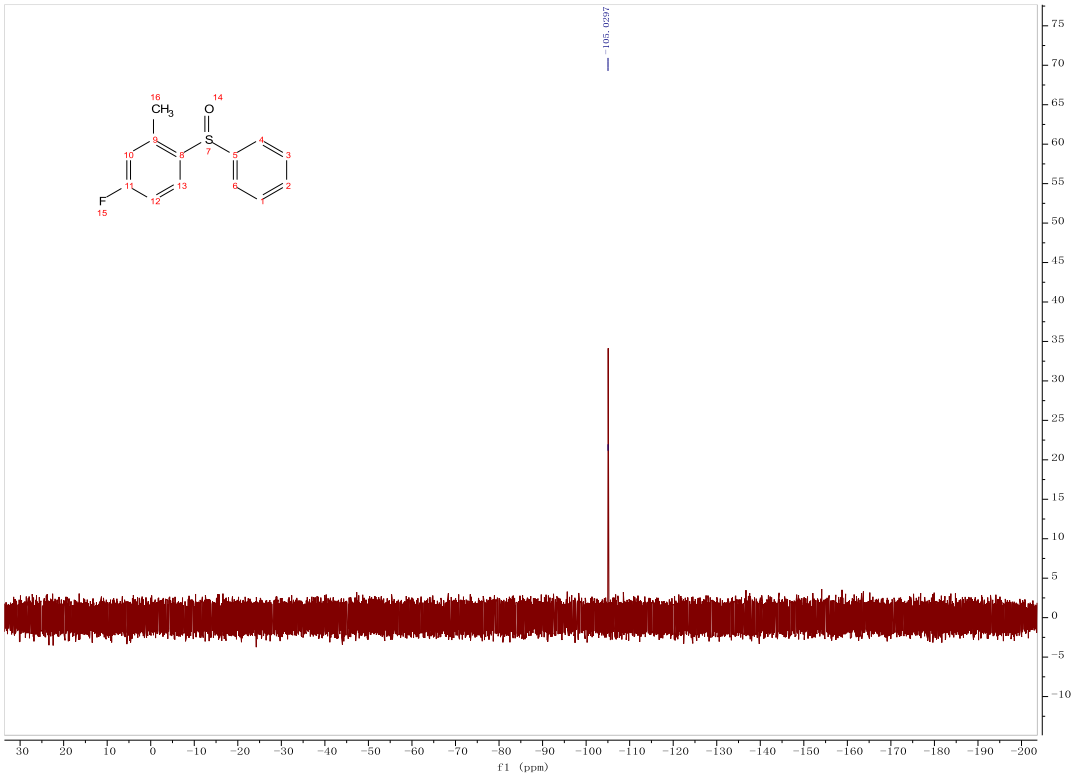
^{1}H NMR Spectra of **3t** (400 MHz, $CDCl_3$)



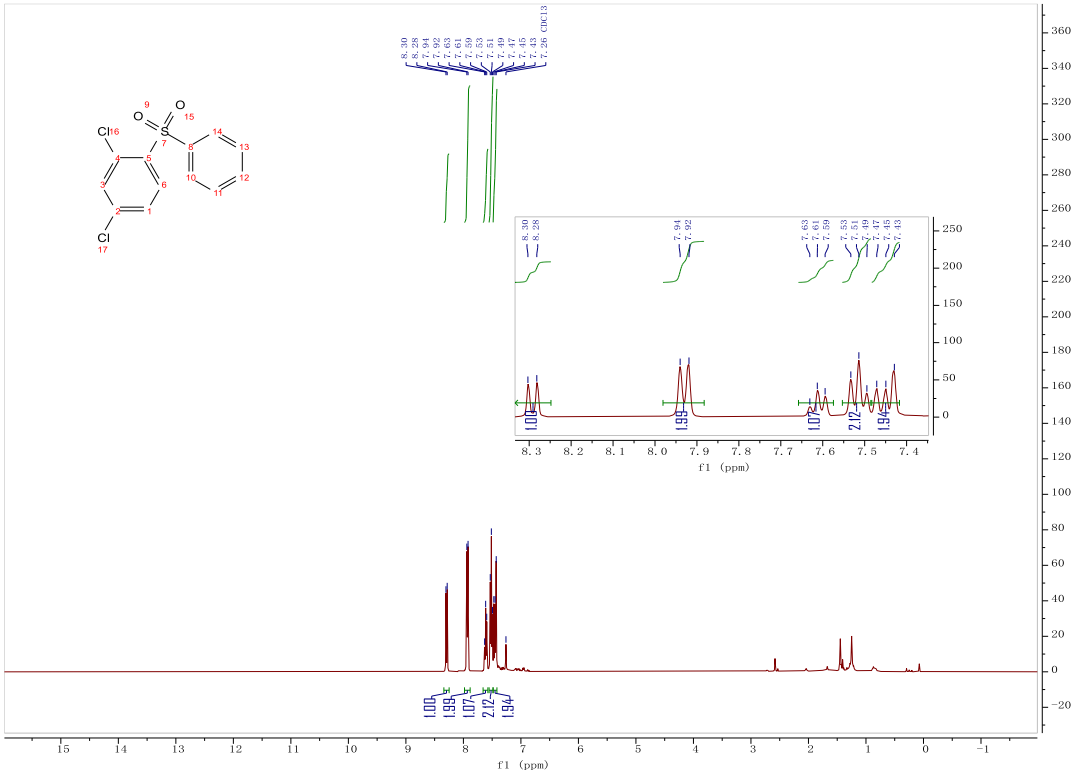
^{13}C NMR Spectra of **3t** (100 MHz, $CDCl_3$)



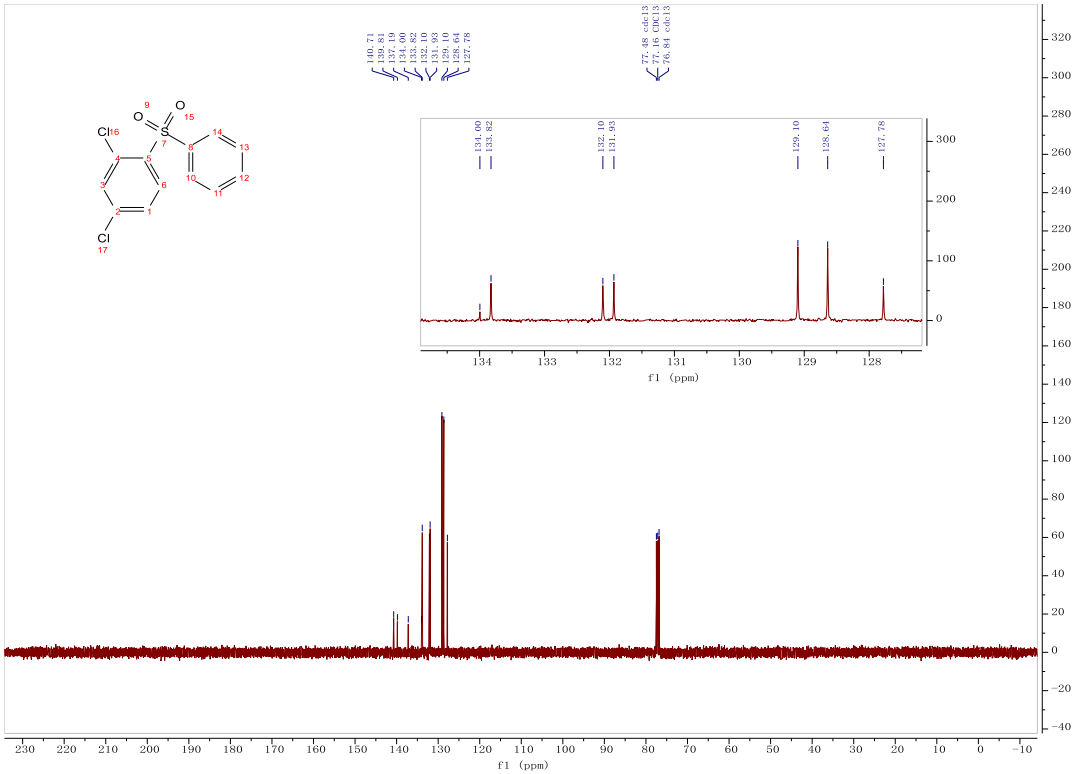
^{19}F NMR spectrum of **3t** (376 MHz, $CDCl_3$)



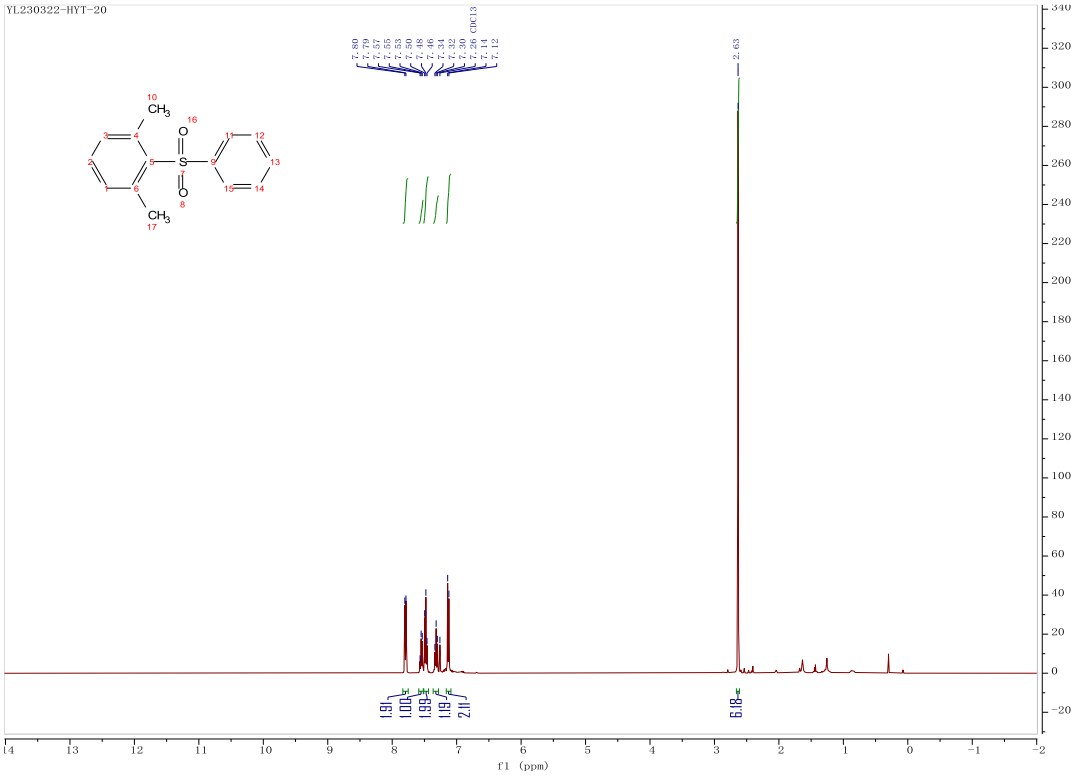
^{1}H NMR Spectra of **3u** (400 MHz, $CDCl_3$)



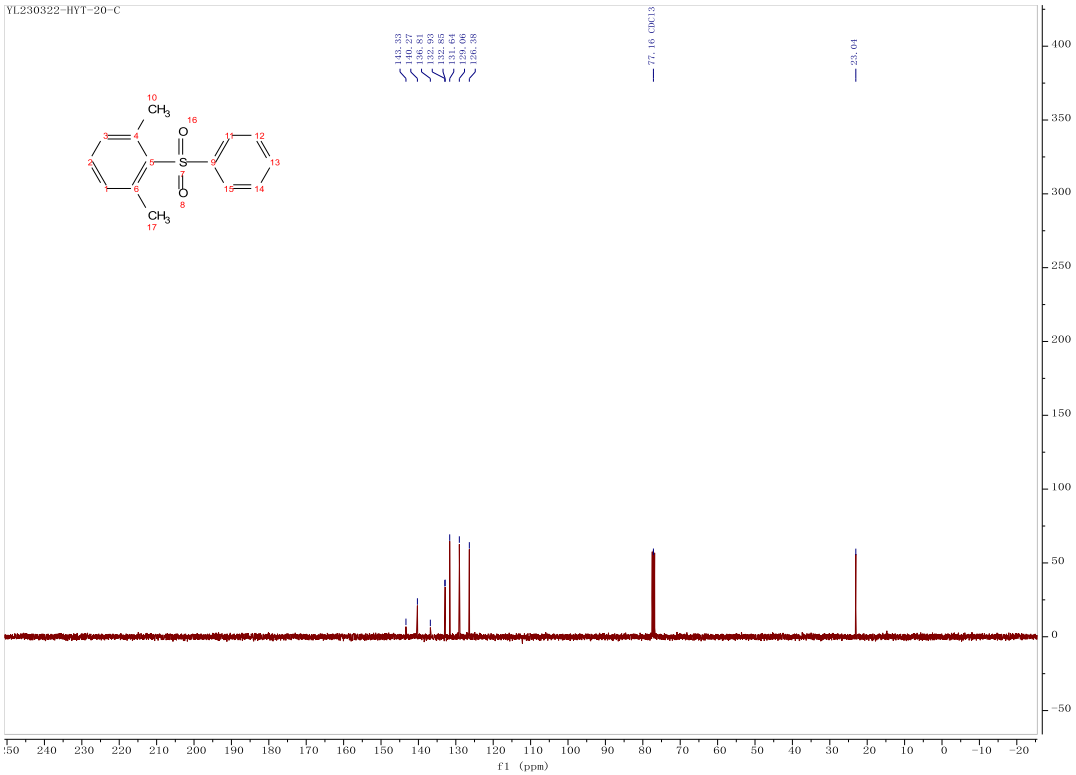
^{13}C NMR Spectra of **3u** (100 MHz, $CDCl_3$)



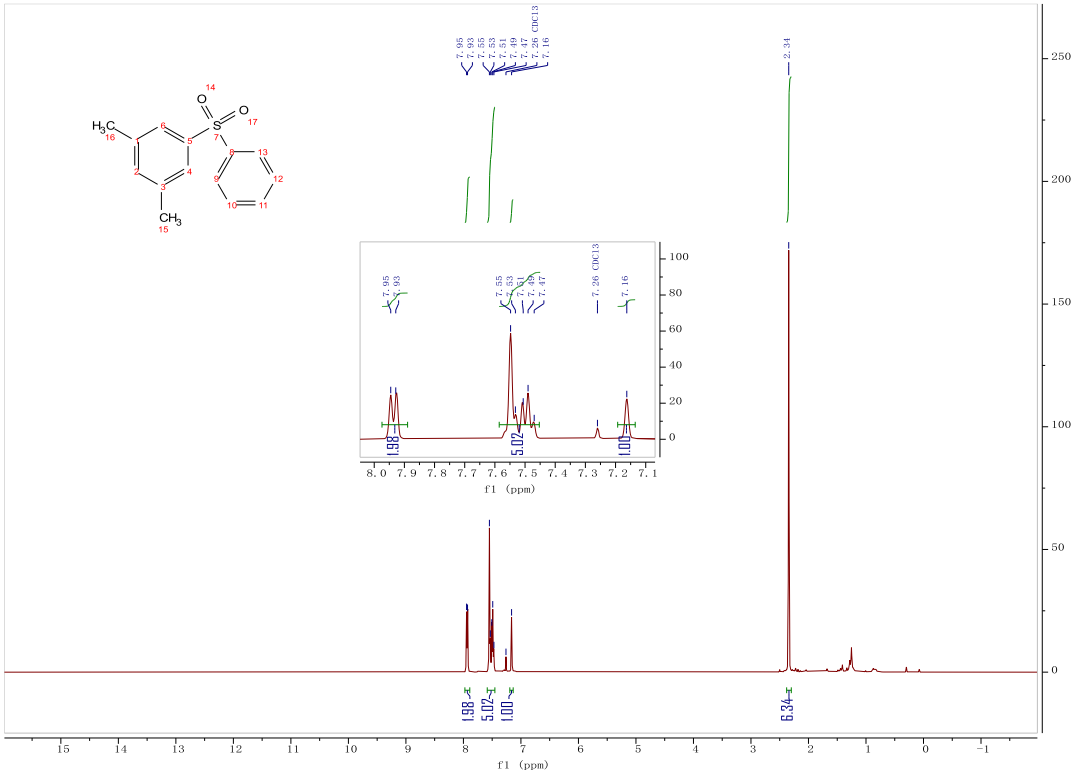
^{1}H NMR Spectra of **3v** (400 MHz, $CDCl_3$)



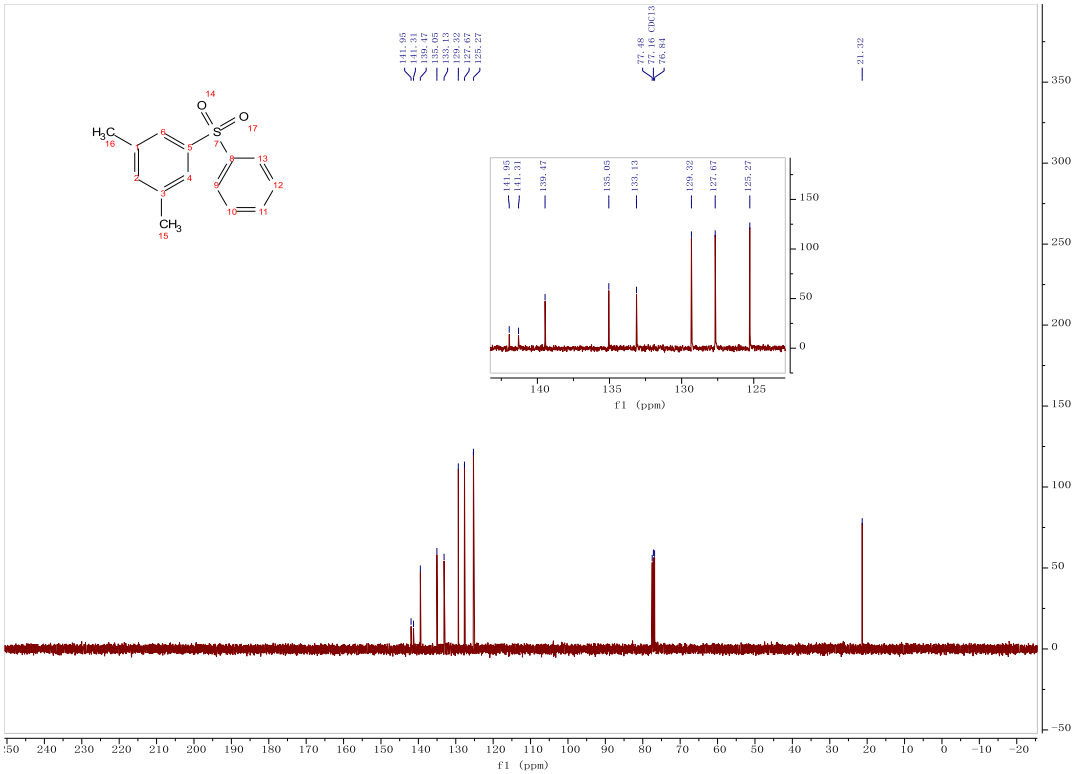
^{13}C NMR Spectra of **3v** (100 MHz, $CDCl_3$)



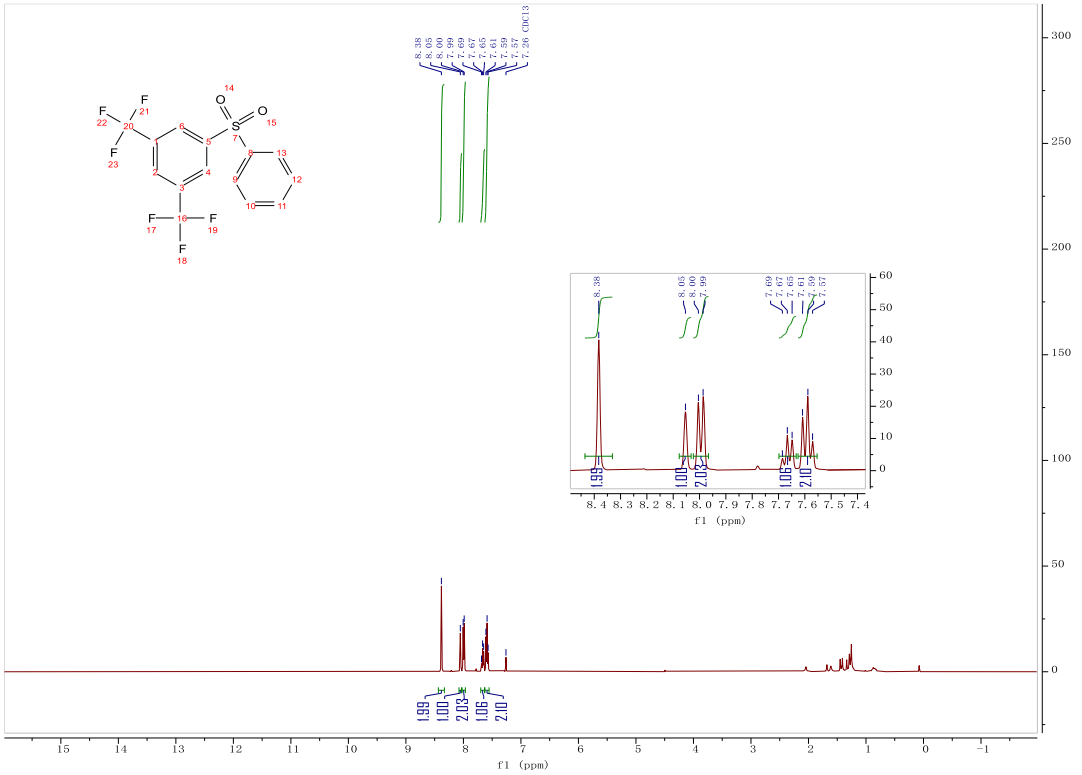
^{1}H NMR Spectra of **3w** (400 MHz, $CDCl_3$)



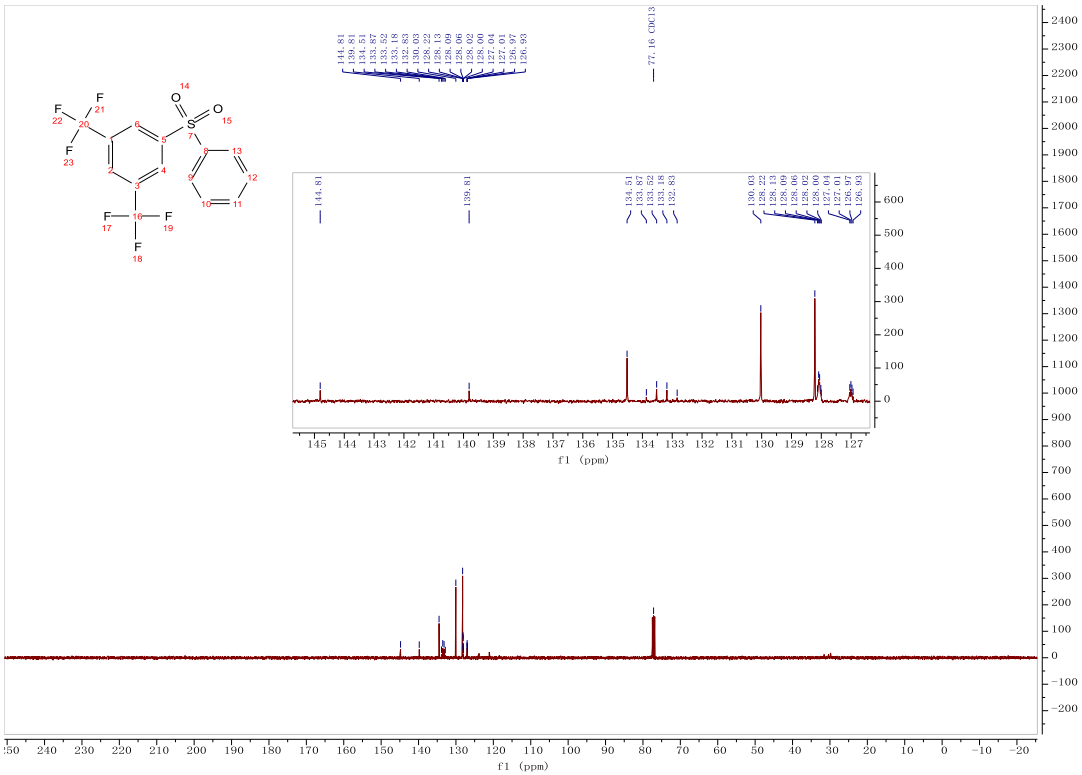
^{13}C NMR Spectra of **3w** (100 MHz, $CDCl_3$)



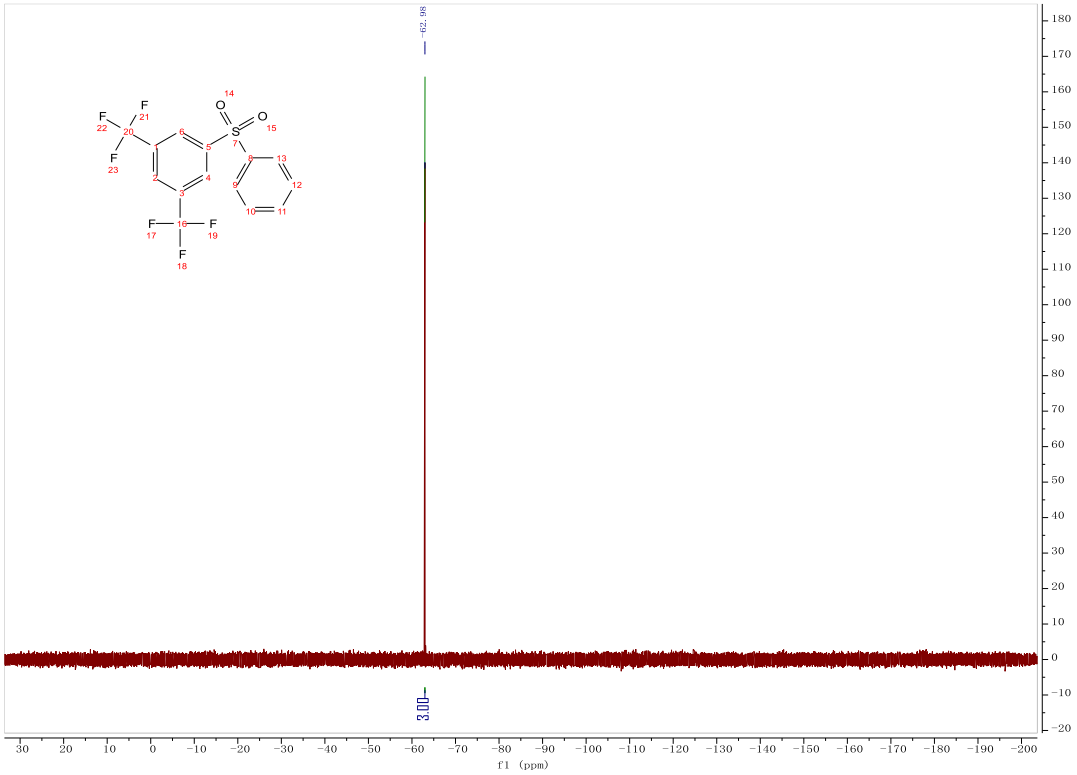
^{1}H NMR Spectra of **3x** (400 MHz, $CDCl_3$)



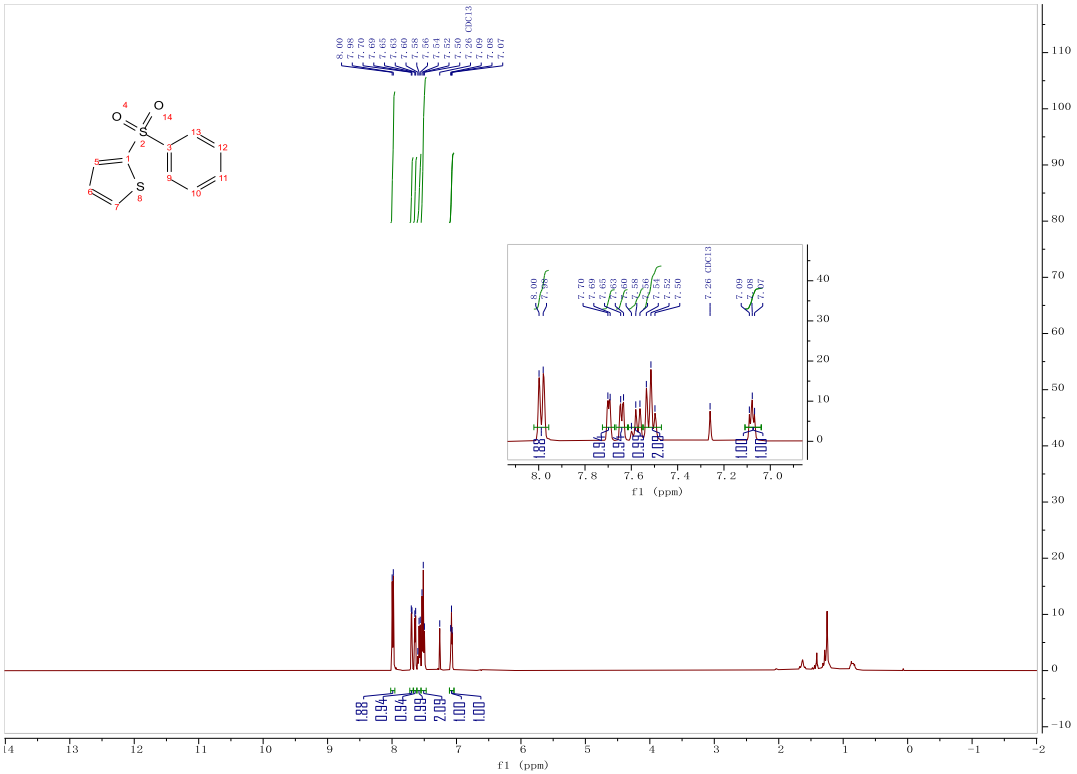
^{13}C NMR Spectra of **3x** (100 MHz, $CDCl_3$)



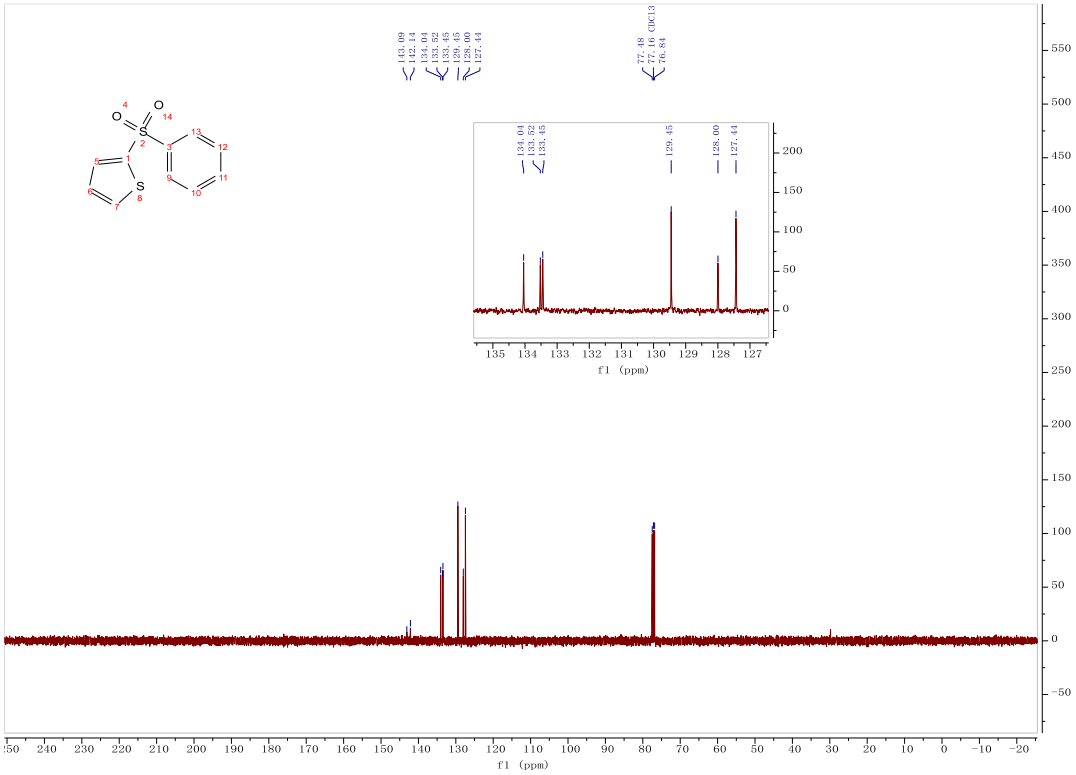
^{19}F NMR spectrum of **3x** (376 MHz, $CDCl_3$)



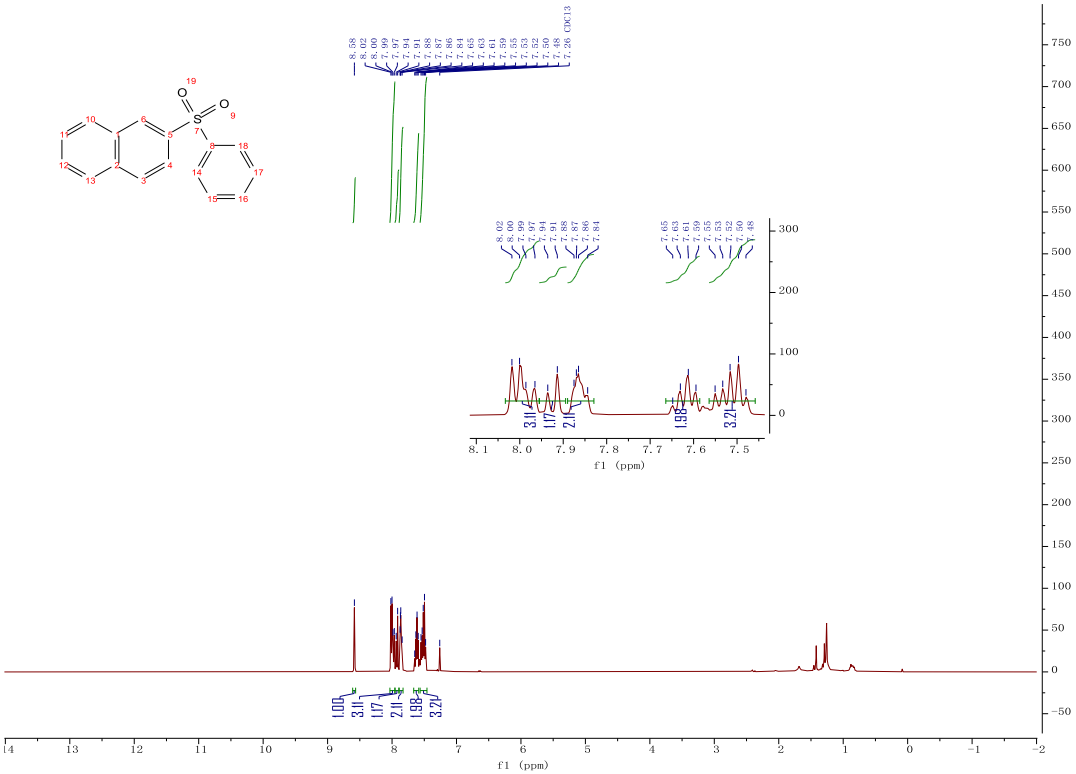
^{1}H NMR Spectra of **3y** (400 MHz, $CDCl_3$)



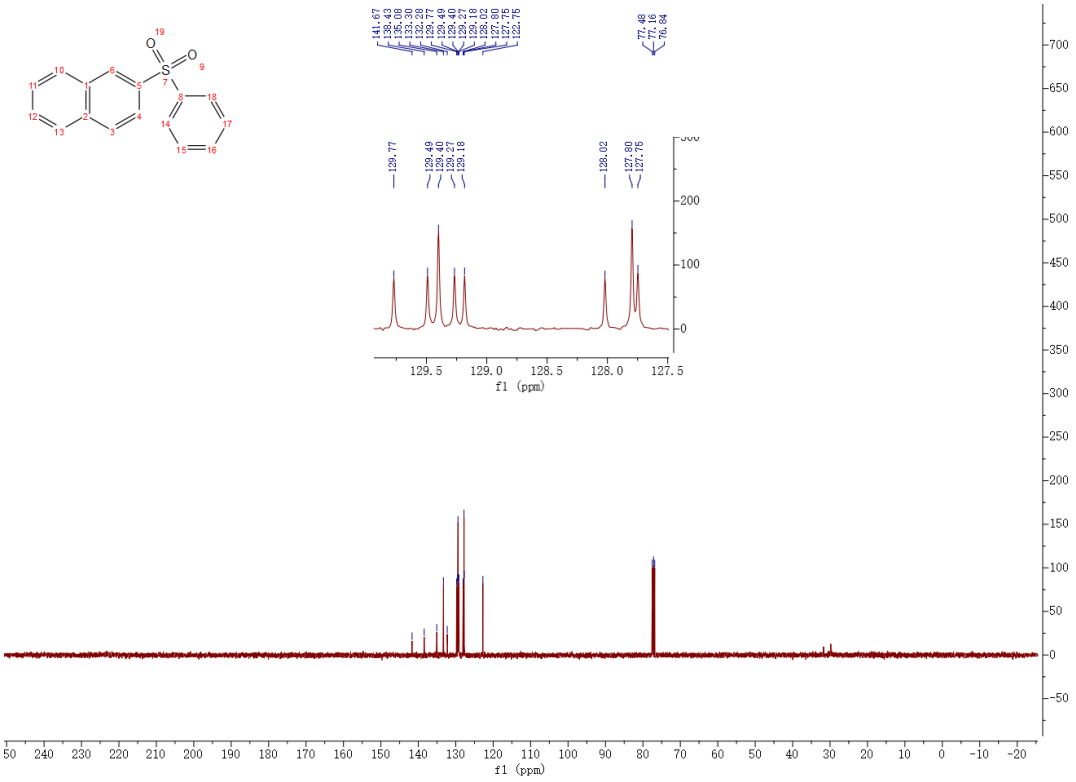
^{13}C NMR Spectra of **3y** (100 MHz, $CDCl_3$)



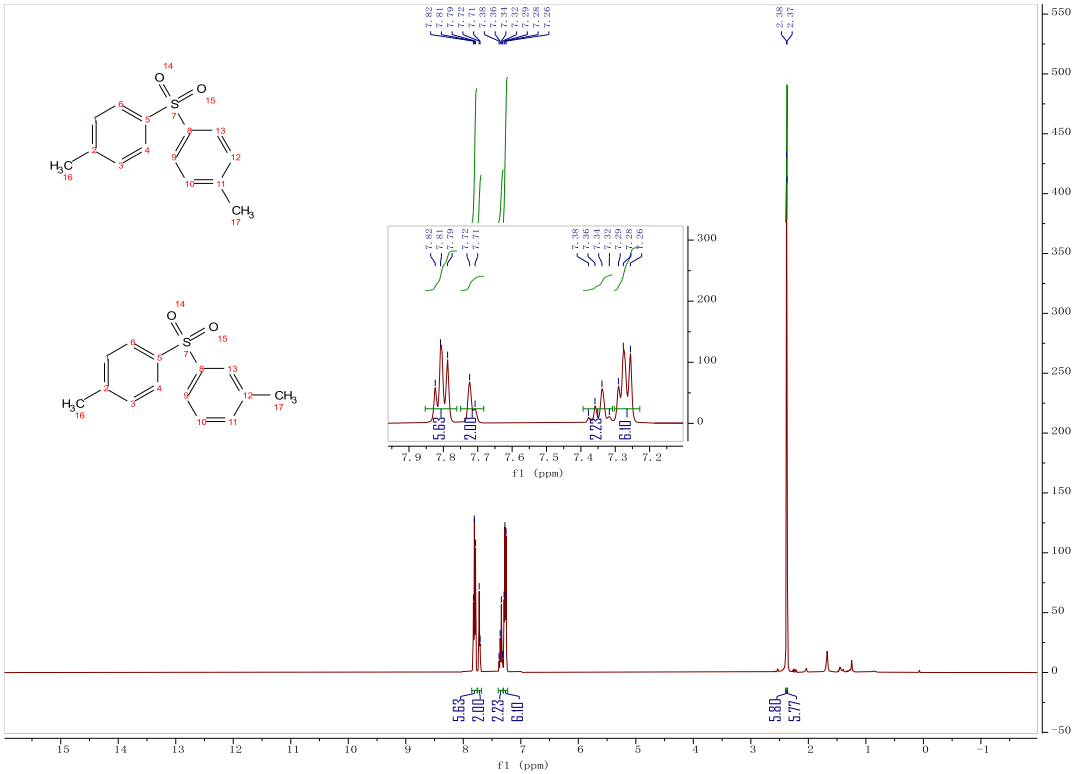
^{1}H NMR Spectra of **3z** (400 MHz, $CDCl_3$)



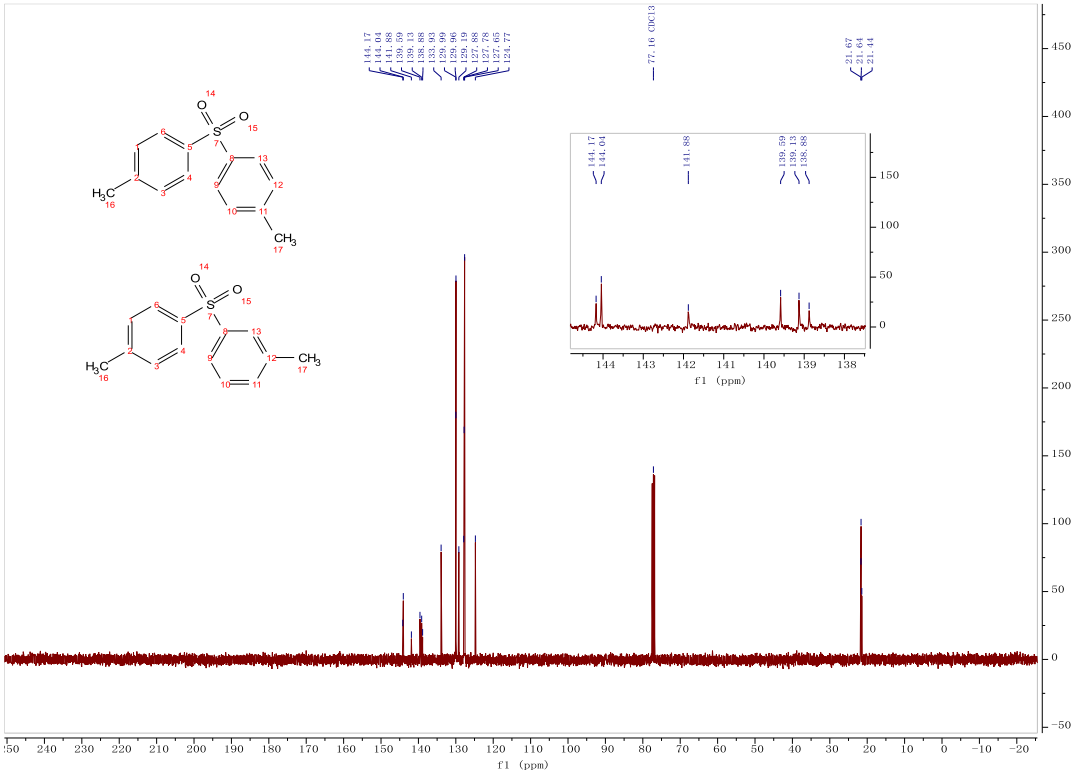
^{13}C NMR Spectra of **3z** (100 MHz, $CDCl_3$)



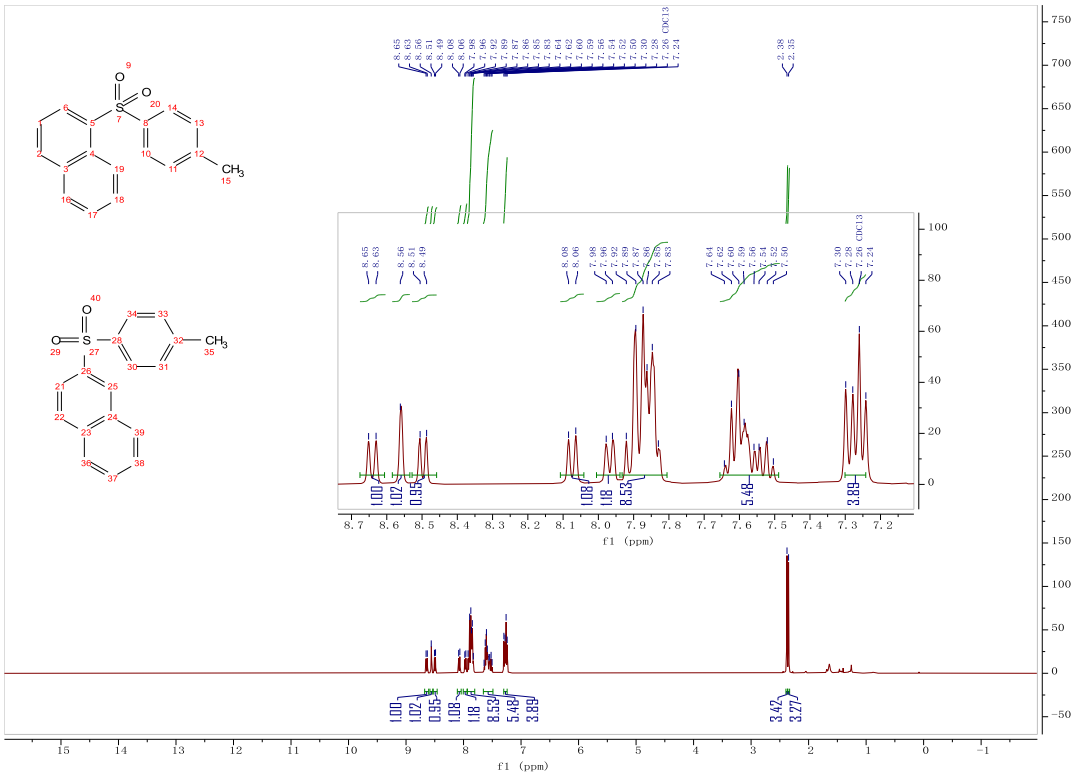
^{1}H NMR Spectra of mixture of **4b** and **4b'** (400 MHz, $CDCl_3$)



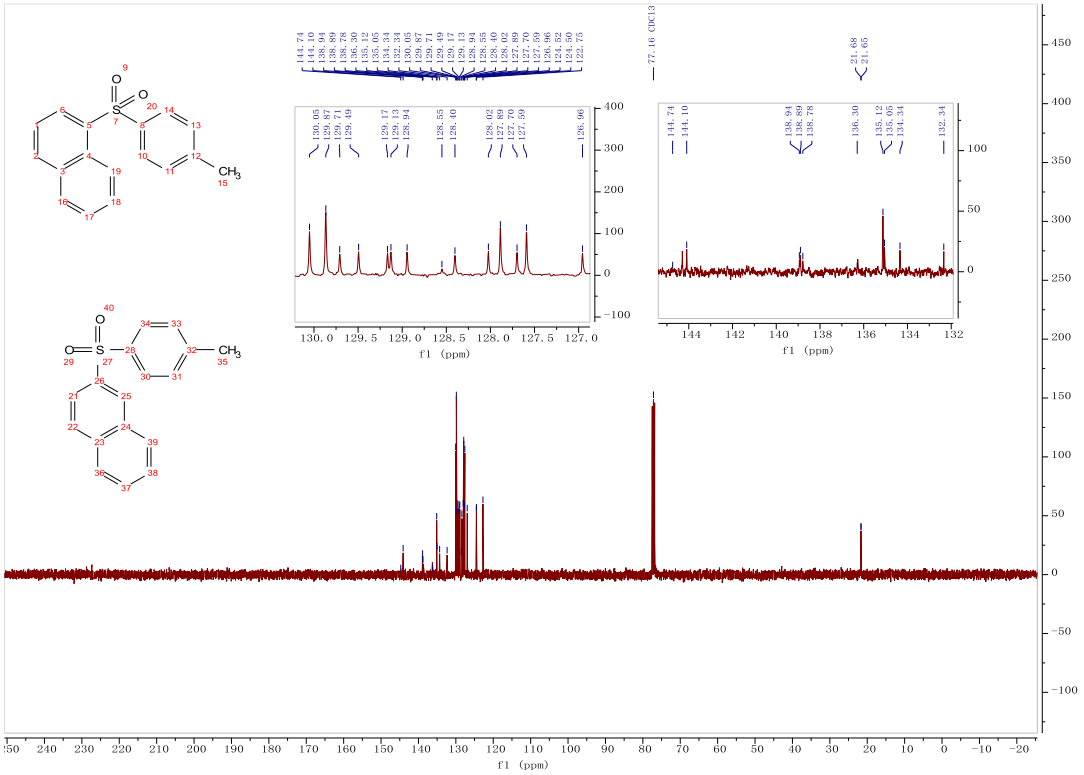
^{13}C NMR Spectra of mixture of **4b** and **4b'** (100 MHz, $CDCl_3$)



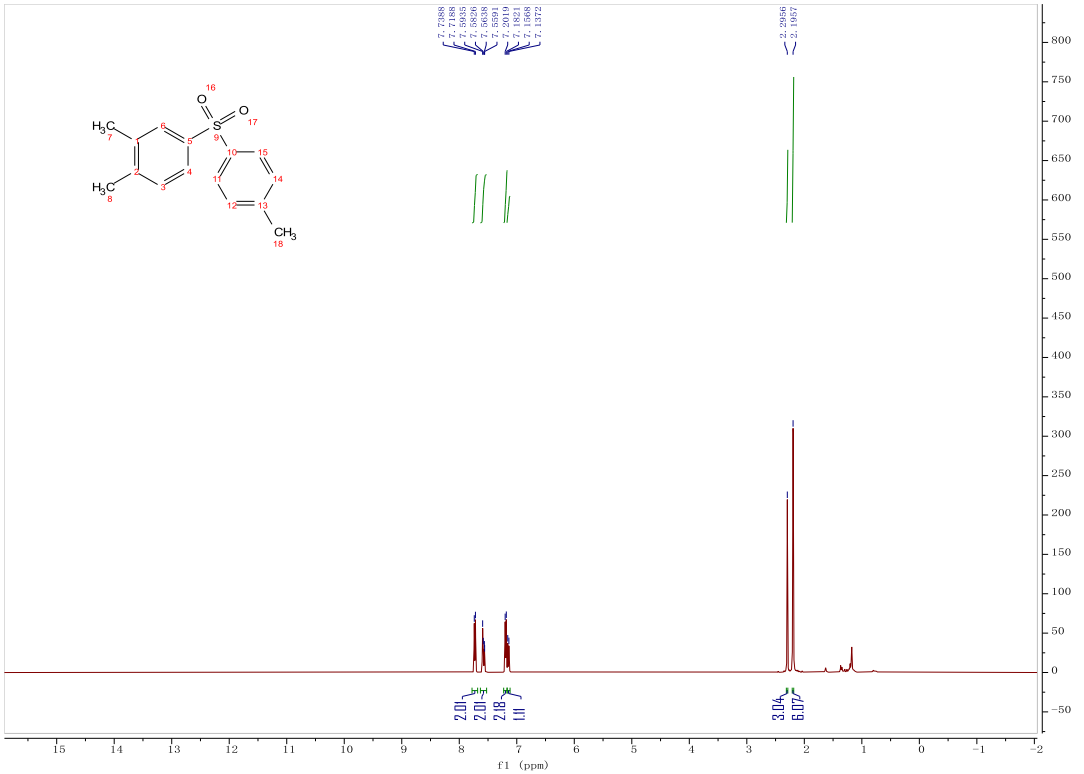
^{1}H NMR Spectra of mixture of **4c** and **4c'** (400 MHz, $CDCl_3$)



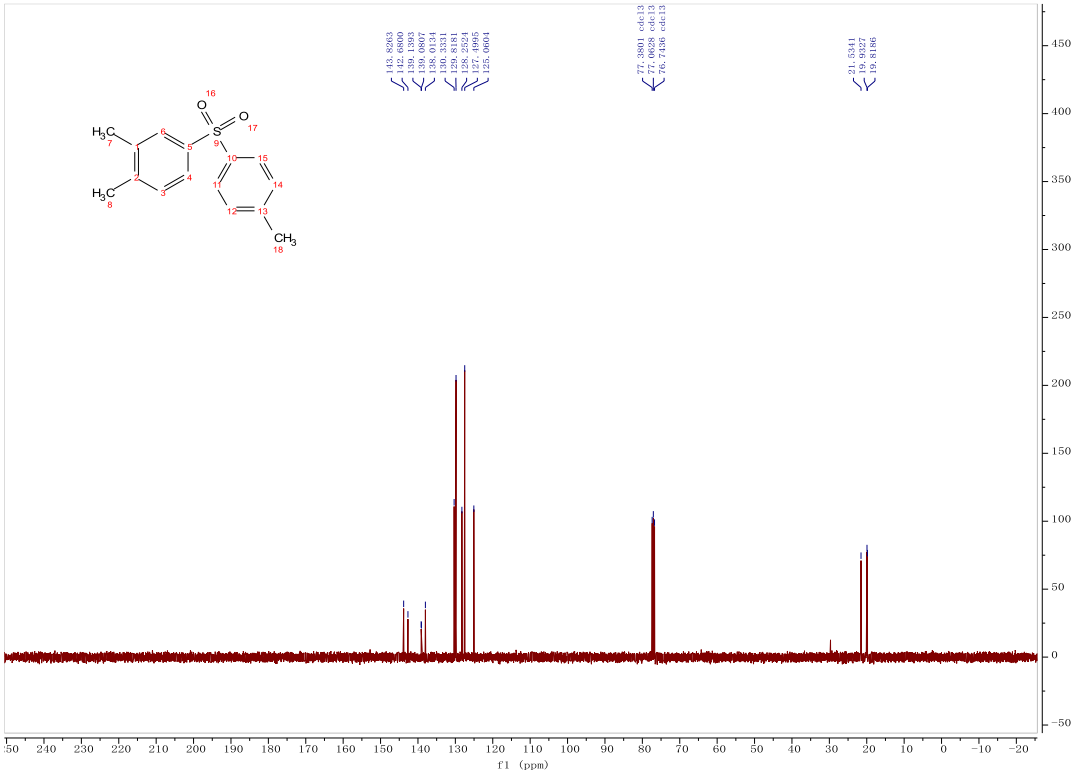
^{13}C NMR Spectra of mixture of **4c** and **4c'** (100 MHz, $CDCl_3$)



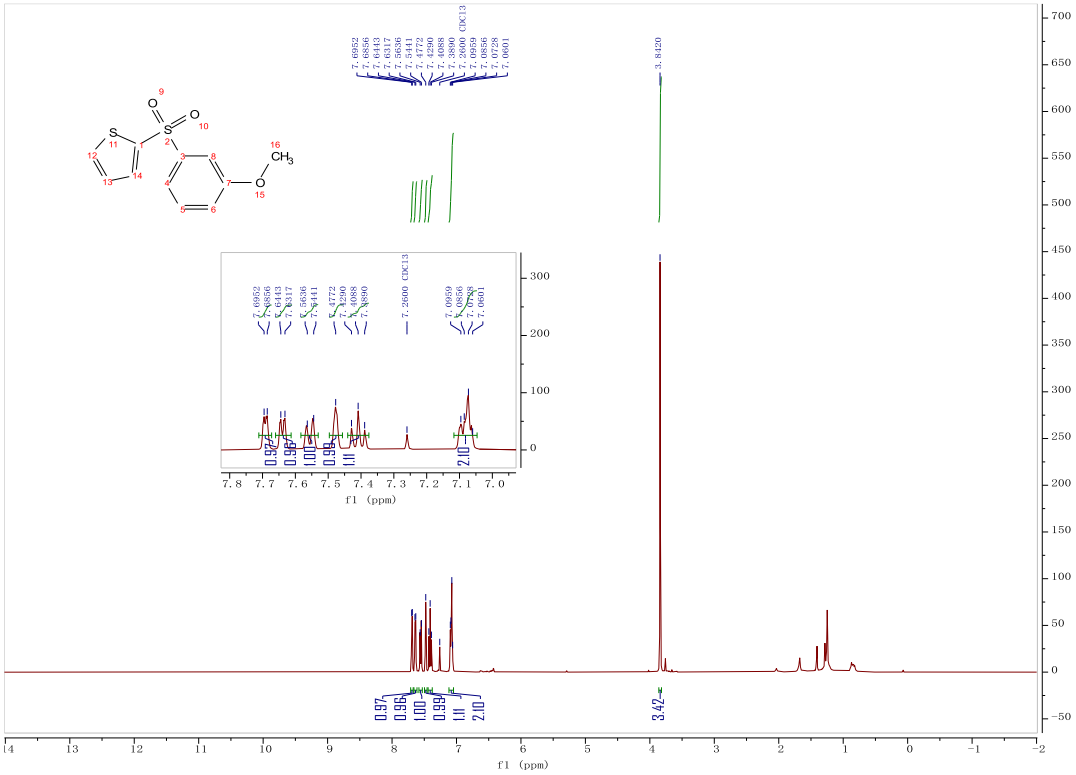
^{1}H NMR Spectra of mixture of **4d** (400 MHz, $CDCl_3$)



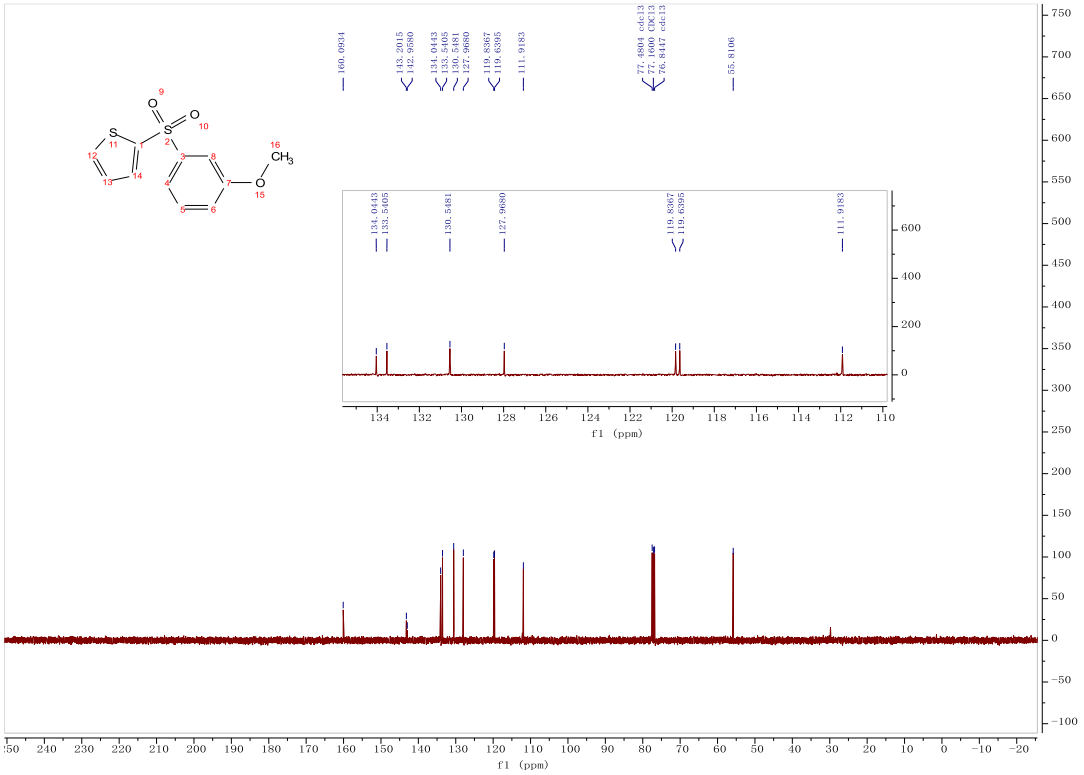
^{13}C NMR Spectra of mixture of **4d** (100 MHz, $CDCl_3$)



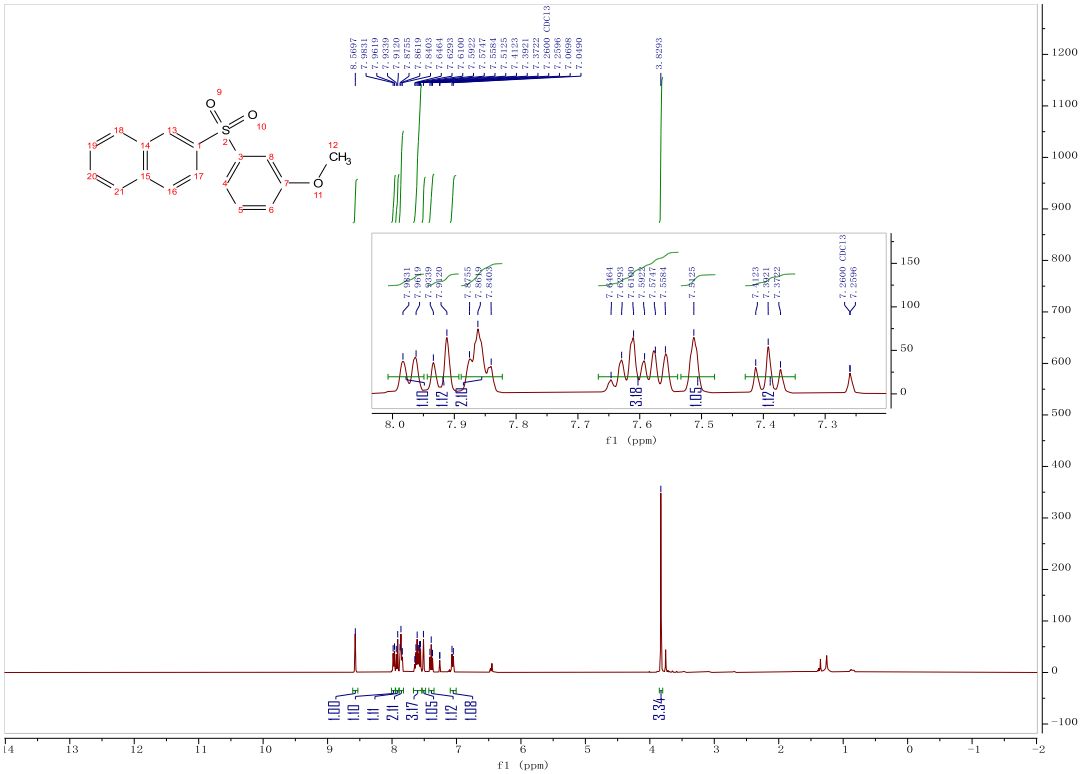
^{1}H NMR Spectra of **4ye** (400 MHz, $CDCl_3$)



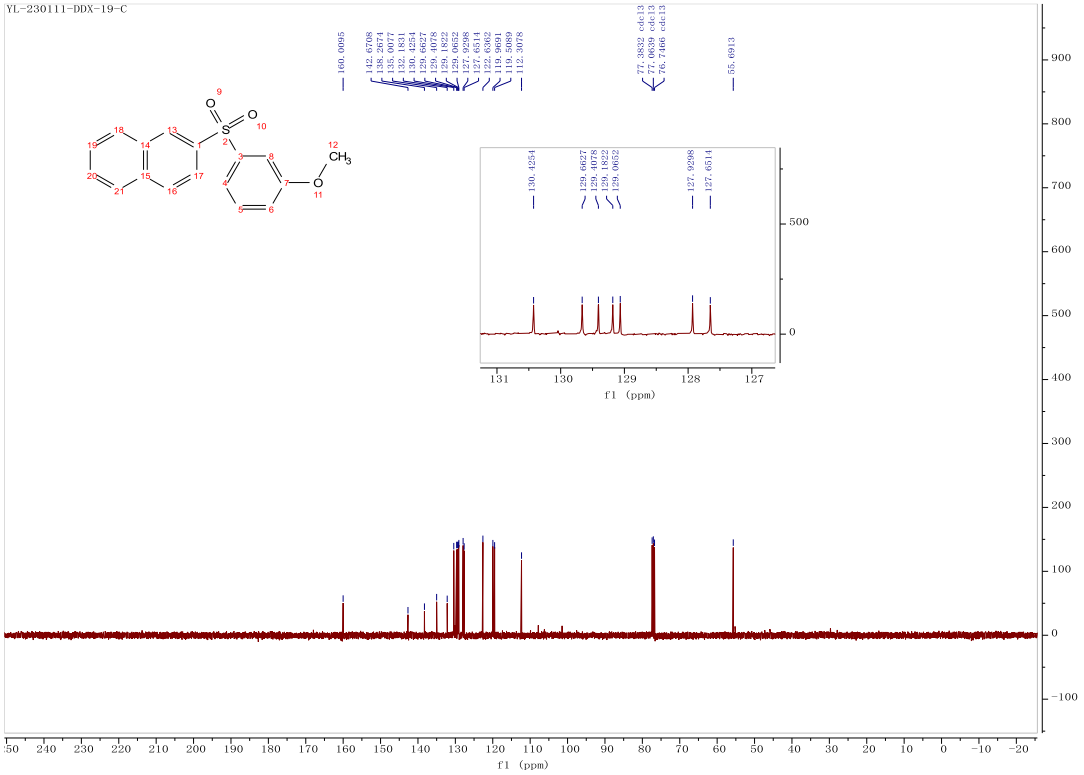
^{13}C NMR Spectra of **4ye** (100 MHz, $CDCl_3$)



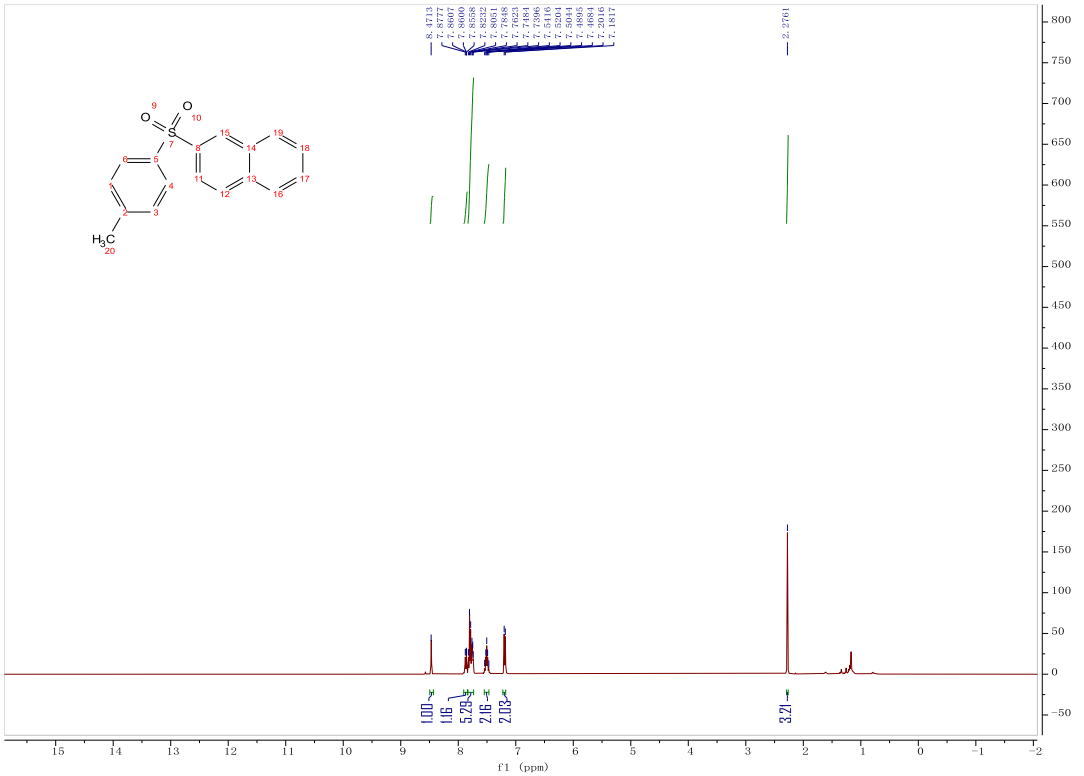
^{1}H NMR Spectra of **4ze** (400 MHz, $CDCl_3$)



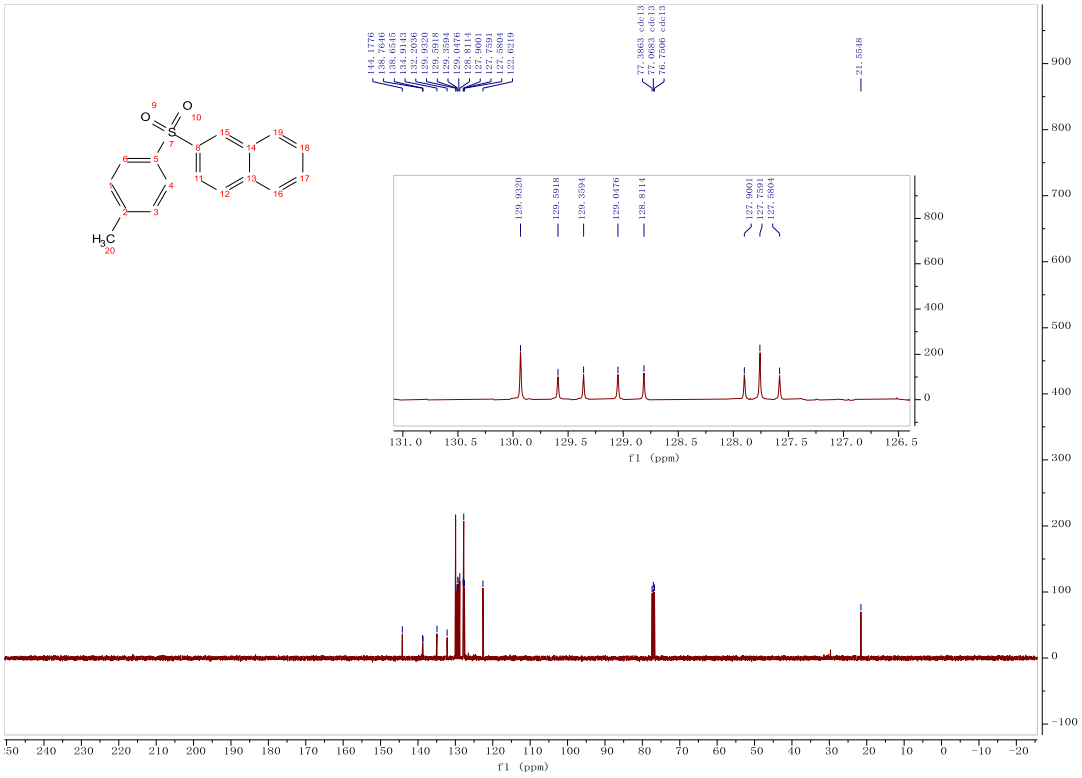
^{13}C NMR Spectra of **4ze** (100 MHz, $CDCl_3$)



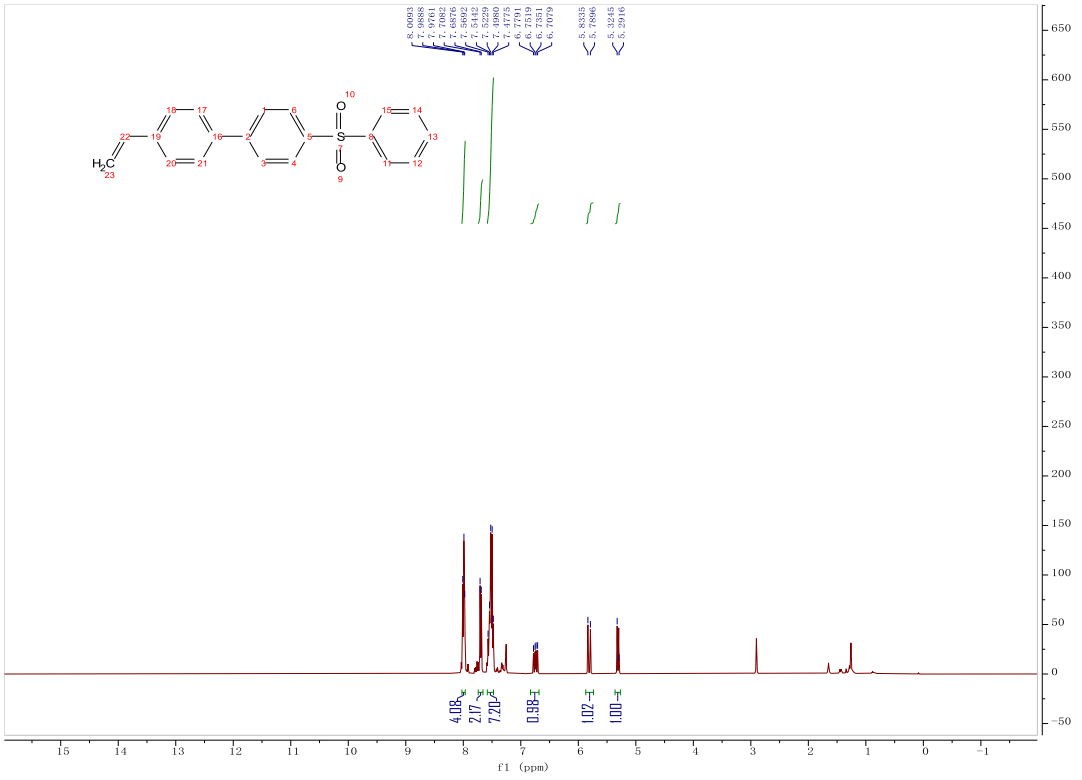
^{1}H NMR Spectra of **4f** (400 MHz, $CDCl_3$)



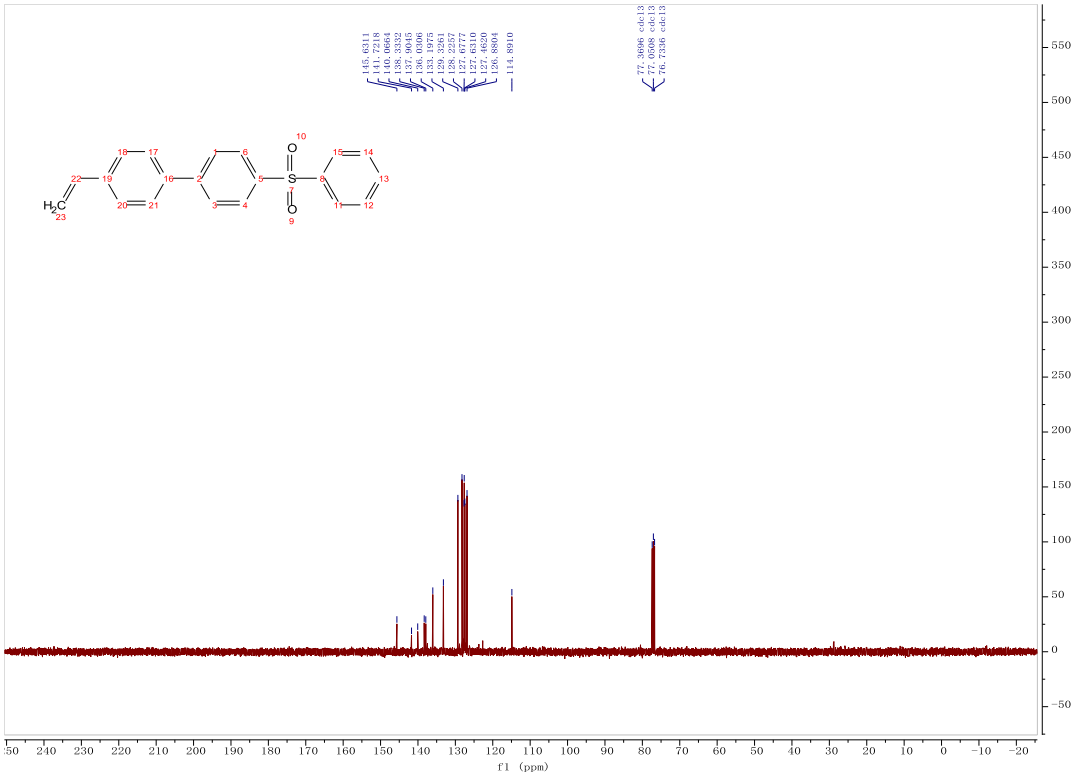
^{13}C NMR Spectra of **4f** (100 MHz, $CDCl_3$)



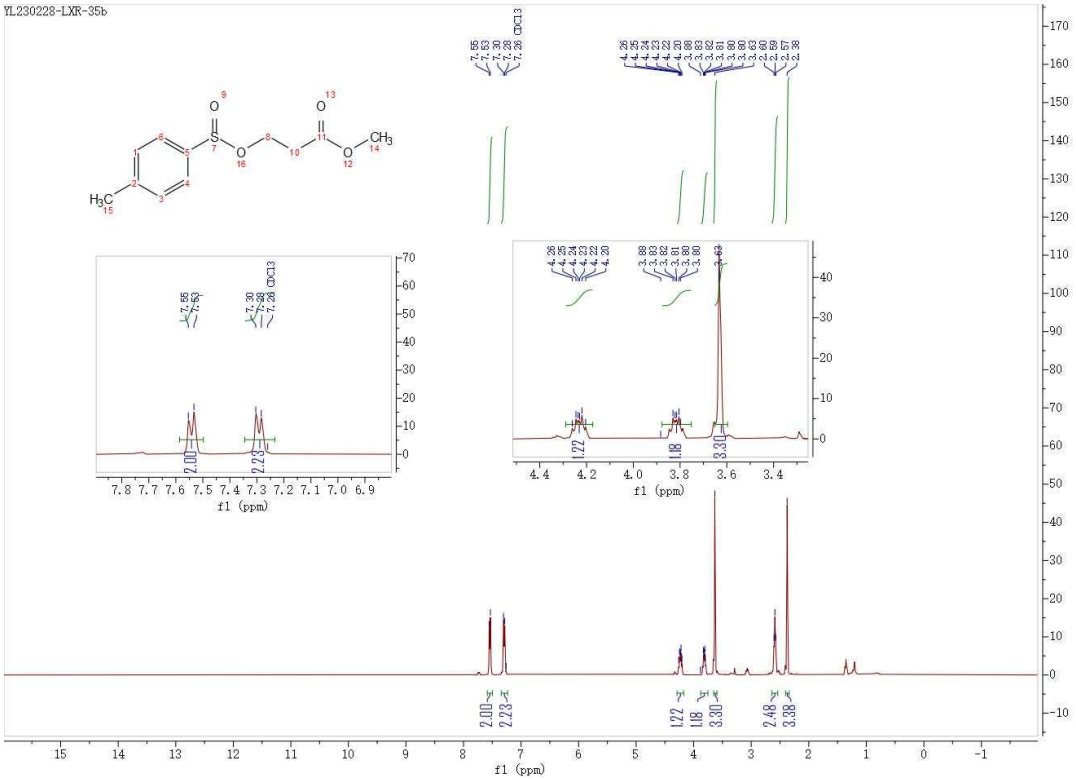
^{1}H NMR Spectra of **3h'** (400 MHz, $CDCl_3$)



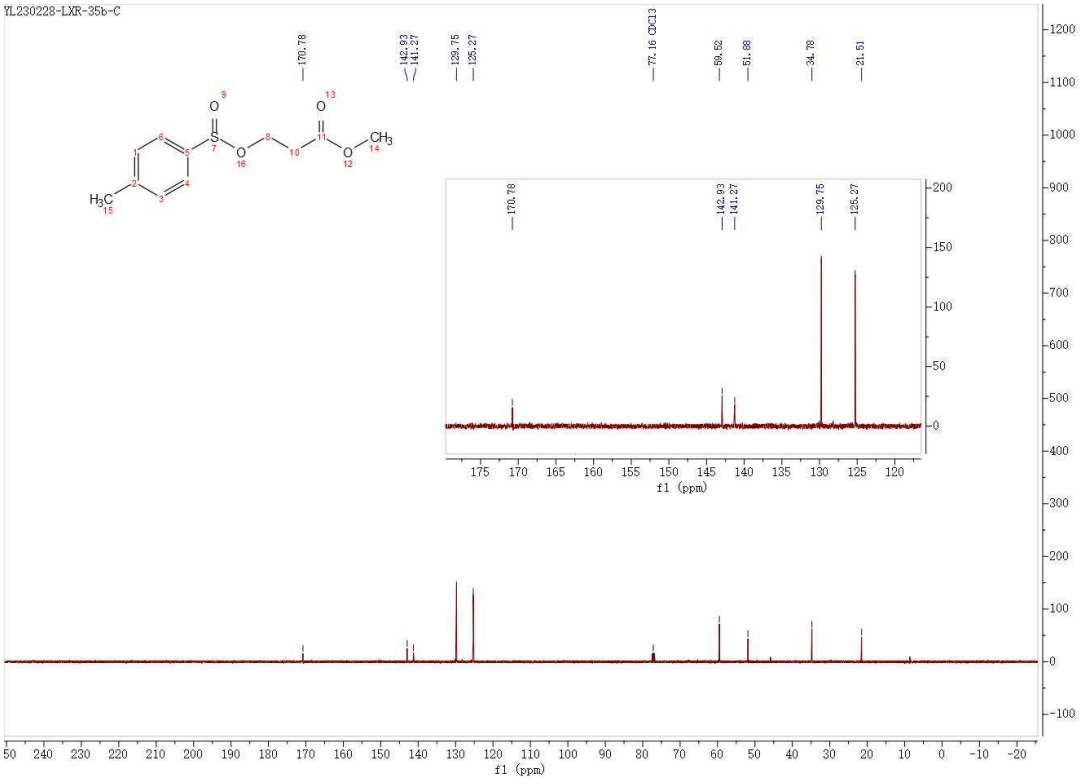
^{13}C NMR Spectra of **3h'** (100 MHz, $CDCl_3$)



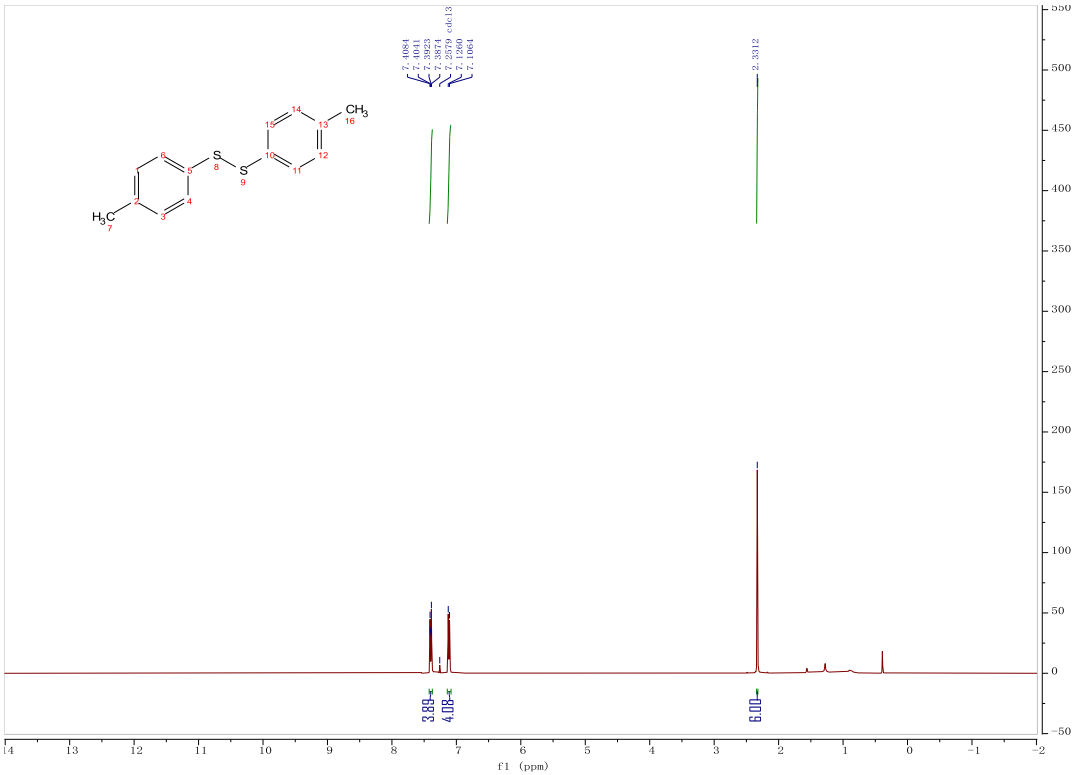
^{1}H NMR Spectra of **5** (400 MHz, $CDCl_3$)



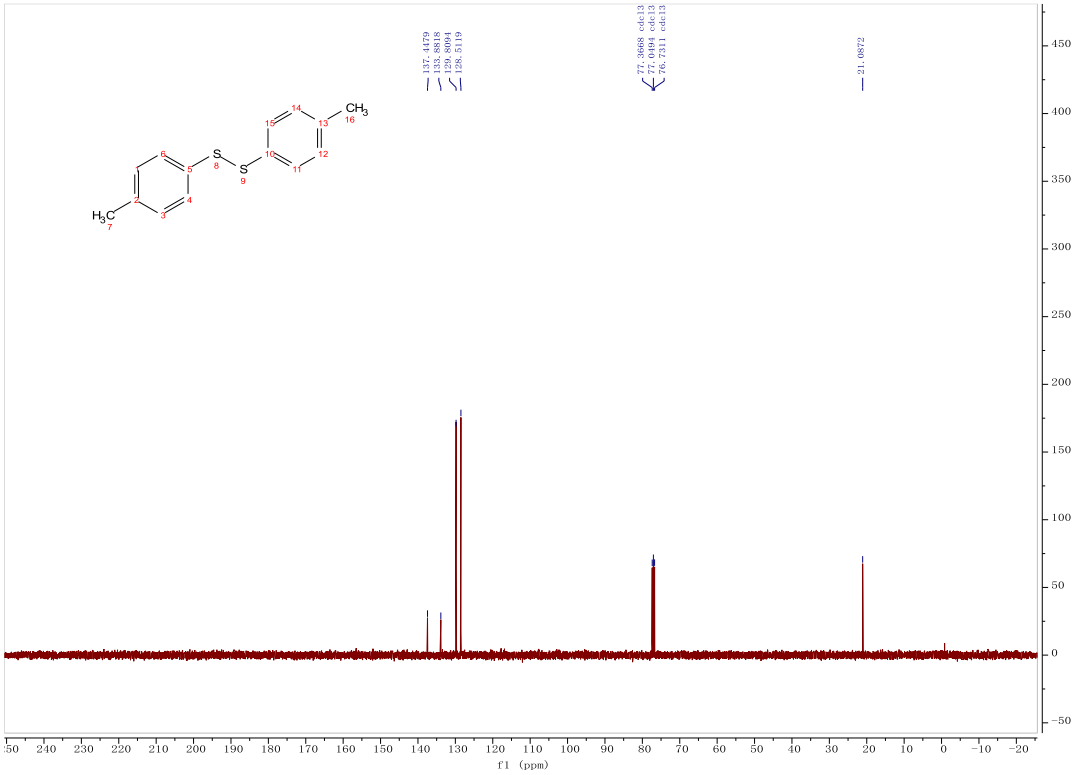
^{13}C NMR Spectra of **5** (100 MHz, $CDCl_3$)



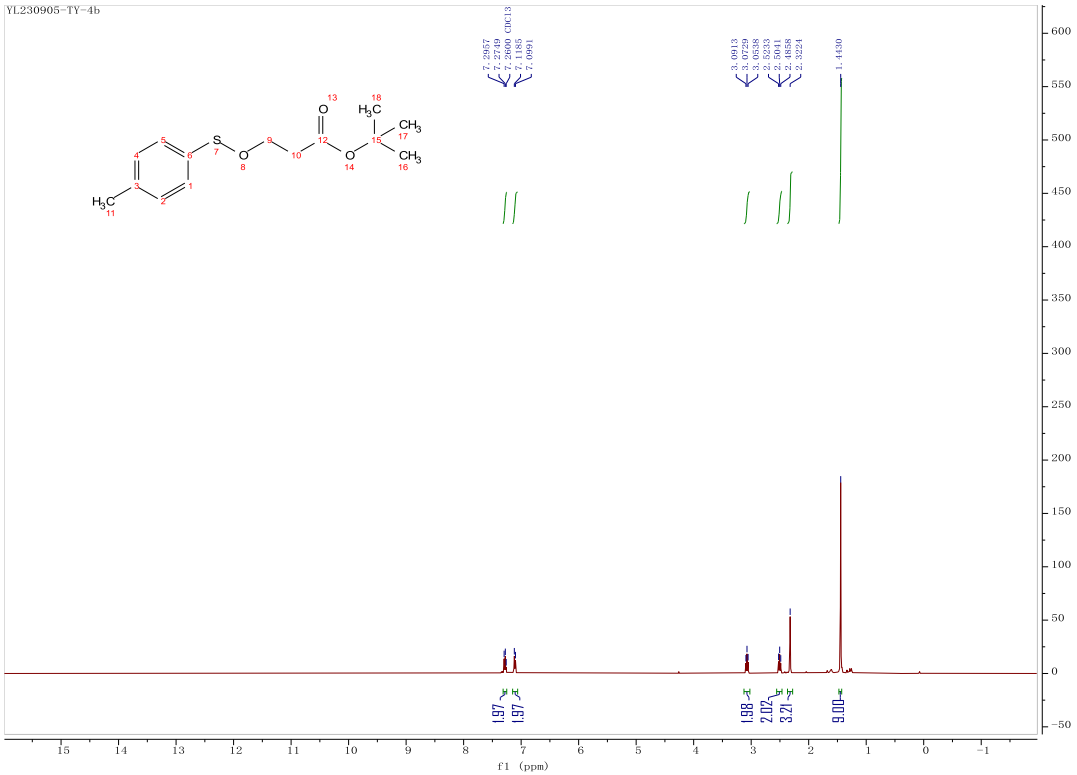
^{1}H NMR spectrum of 6 (400 MHz, $CDCl_3$)



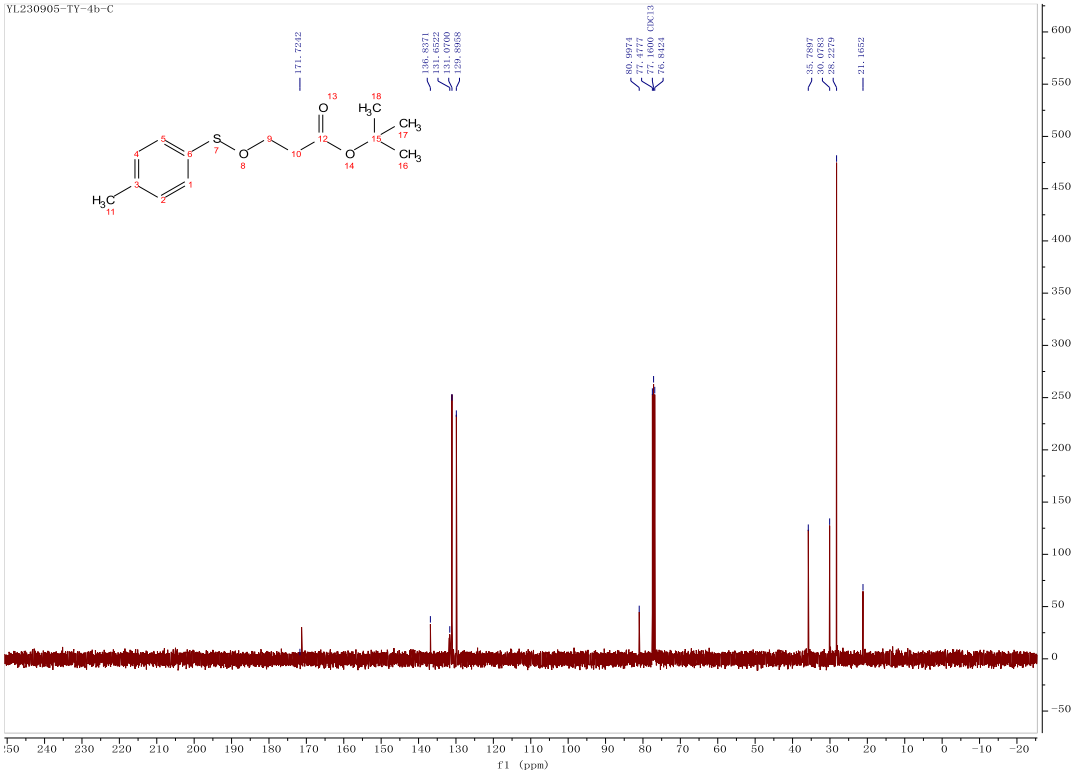
^{13}C NMR spectrum of 6 (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of 7 (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 7 (100 MHz, $CDCl_3$)



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