Modular Access to Diarylmethyl Sulfonamides via Visible Light-Promoted Cross-Coupling Reactions

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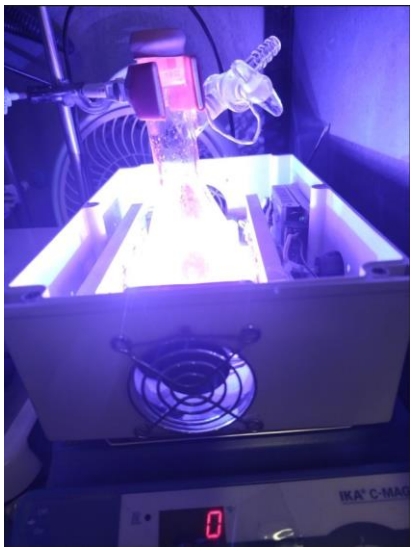
(A) General Information

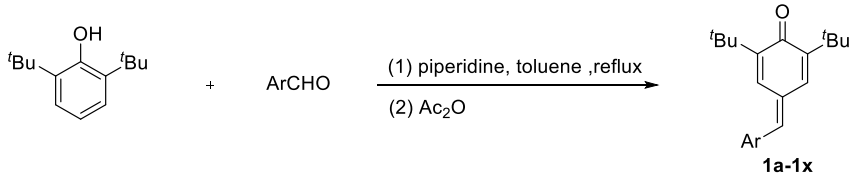
All reactions and manipulations which are sensitive to moisture or air were performed under inert atmosphere of argon. All chemicals were purchased from J&K, Acros and Aldrich, and were used as received. Anhydrous CH_2Cl_2, EA, THF, DME, DMSO, DMF and MeCN were freshly distilled from calcium hydride. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 and chemical shifts are reported in δ (ppm) referenced to residual undeuterated solvent signal for ^{1}H NMR (7.26 ppm) and ^{13}C NMR (77.00 ppm). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. HRMS spectra were recorded on a Waters Acquity UPLC/Xevo TQD-MS-MS quadrupole mass spectrometer. The light source for the photocatalytic reaction is manufactured by GeAo chemistry with a power of 40 W, a broad band source (450–465 nm). A fan was used to maintain the reaction temperature at room temperature (about 25-30 ℃). The reactions were carried out in a borosilicate glass vessel and the distance from the light source to the irradiation vessel is about 1 cm.

Photoreactor (GeAo) (small scale)



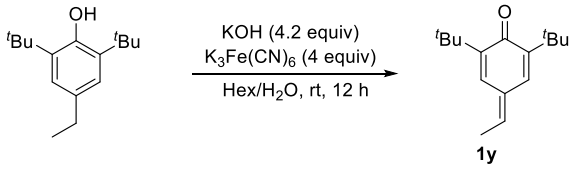
Photoreactor (GeAo) (large scale)

(B) General procedure for the synthesis of *p*-QMs 1.



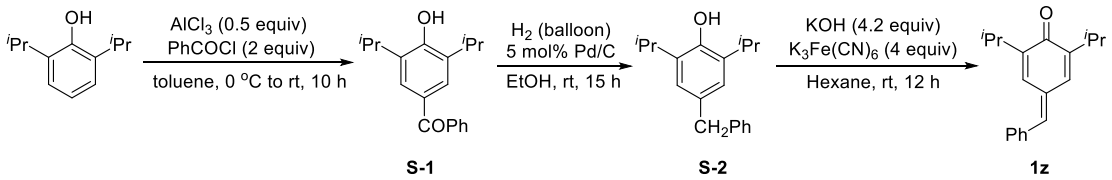
1a-1x

Substrates **1a-1x** were synthesized according to the reported literature.[1-3] In a Dean-Stark apparatus, to a mixture solution of 2,6-di-*tert*-butylphenol (5.0 mmol, 1.0 eq.) and the corresponding aromatic aldehyde (5.5 mmol, 1.1 eq.) in 30 mL toluene was heated with an oil bath to reflux. Then piperidine (10.0 mmol, 2.0 eq.) was added dropwise and the reaction mixture was continued to reflux for 24 h. after cooling the reaction mixture just below the boiling point of toluene, acetic anhydride (10.0 mmol, 2.0 eq.) was added and the reaction mixture was stirred for another 1 h at the same temperature. Then the reaction mixture was poured into ice water (100 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue were purified by flash column chromatography (petroleum ether/ethyl acetate) affording the desired products *p*-QMs **1a-1x**.



1y

Substrate **1y** was synthesized according to the reported literature.[4] To a solution of 2,6-di-*tert*-butyl-4-ethylphenol (2.4 g, 10 mmol) in hexane (30 mL) was added a solution of $K_3Fe(CN)_6$ (13.2 g, 40.0 mmol) and KOH (2.4 g, 42.0 mmol) in water (30 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 6 h. The combined organic layer was washed with saturated brine and extracted with ethyl acetate (20 mL x 3), and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Then the product **1y** was obtained by recrystallization from CH_2Cl_2 and hexane (1.4 g, 59% yield, yellow solid).



S-1 **S-2** **1z**

Substrate **1z** was synthesized according to the reported literature.[5] To a solution of propofol (1.8 g, 10.0 mmol) in anhydrous toluene in ice-water bath was added benzoyl chloride (2.6 g, 18.0 mmol). Then $AlCl_3$ (535.0 mg, 4.0 mmol) was added in three batches. And the reaction mixture was raised to room temperature and stirred overnight, after complete consumption of starting

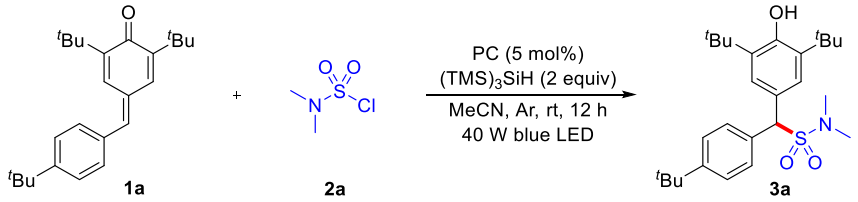
material, solvent was concentrated under reduced pressure and the residue were purified by flash column chromatography to afford product **S-1**.

To a solution of **S-1** in anhydrous ethanol (30 mL) was added 10% Pd/C (534 mg, 5 mol%), and then stirred at room temperature for 5 h under hydrogen atmosphere (balloon). Filtered through a pad of celite, and solvent was concentrated under reduced pressure and the residue was purified by flash column chromatography to afford product **S-2**.

To a solution of **S-2** in hexane (30 mL) was added $K_3Fe(CN)_6$ (13.2 g, 40.0 mmol) and KOH (2.4 g, 42.0 mmol) sequently under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 h. The combined organic layer was washed with saturated brine and extracted with ethyl acetate (20 mL x 3), and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure and the residue was purified by flash column chromatography to afford product **1z** (1.8 g, 67% yield for three steps).

(C) Optimization of the reaction conditions.

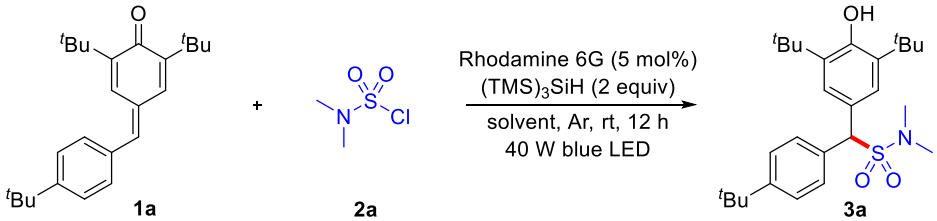
Table S1. Photocatalyst screening[a]



Entry	PC	Yield (%)[b]
1	Eosin Y	41
2	Rose Bengal	46
3	Rhodamine 6G	76
4	4CzIPN	50
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	35
6	$[Ru(bpy)_3](PF_6)_2$	0

[a]**1a** (0.1 mmol), **2a** (0.2 mmol), PC (5 mol%), $(TMS)_3SiH$ (2 equiv), MeCN (1 mL), 40 W blue LED (450-465 nm), Ar, rt (25-30 °C), 12 h. [b]Isolated yield.

Table S2. Solvent screening[a]

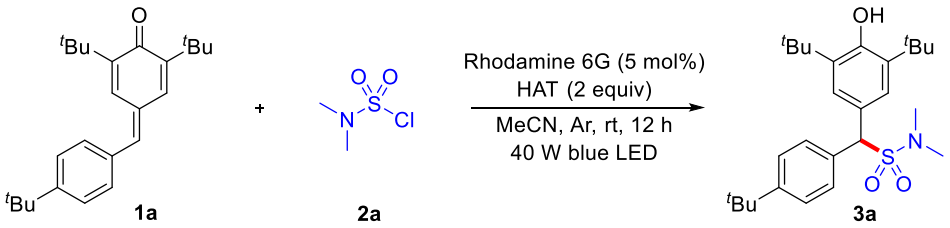


Entry	Solvent	Yield (%)[b]
1	MeCN	76
2	CH_2Cl_2	15

3	THF	64
4	EA	43
5	DME	58
6	DMF	20
7	DMSO	0

[a]**1a** (0.1 mmol), **2a** (0.2 mmol), Rhodamine 6G (5 mol%), $(TMS)_3SiH$ (2 equiv), Solvent (1 mL), 40 W blue LED (450-465 nm), Ar, rt (25-30 °C), 12 h. [b]Isolated yield.

Table S3. Halogen atom transfer (HAT) reagent screening[a]

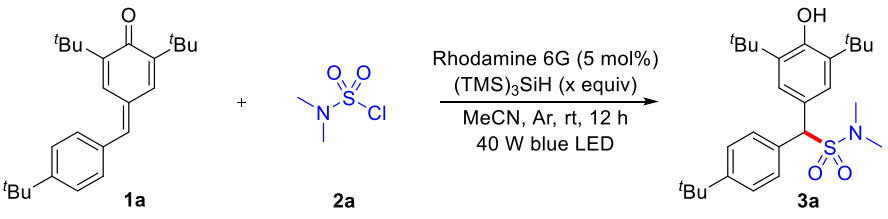


1a **2a** **3a**

Entry	HAT (2 equiv)	Yield (%)[b]
1	$(TMS)_3SiH$	76
2	Et_3SiH	0
3	Me_2EtSiH	0
4	$^{i}Pr_3SiH$	0
5	$^{t}BuMe_2SiH$	0
6	Bn_3SiH	18
7	$PhMe_2SiH$	17
8	$^{i}PrNEt$	0
9	Et_3N	0
10	$Py{\bullet}BH_3$	11
11	BPh_4Na	0

[a]**1a** (0.1 mmol), **2a** (0.2 mmol), Rhodamine 6G (5 mol%), HAT (2 equiv), MeCN (1 mL), 40 W blue LED (450-465 nm), Ar, rt (25-30 °C), 12 h. [b]Isolated yield.

Table S4. The equivalent of halogen atom transfer (HAT) reagent screening[a]

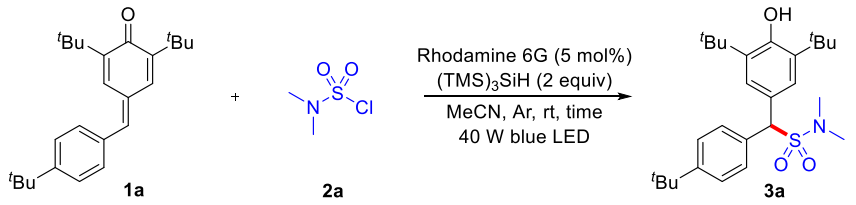


1a **2a** **3a**

Entry	x (equiv)	Yield (%)[b]
1	2	76
2	3	78
3	5	66

[a]**1a** (0.1 mmol), **2a** (0.2 mmol), Rhodamine 6G (5 mol%), $(TMS)_3SiH$ (x equiv), MeCN (1 mL), 40 W blue LED (450-465 nm), Ar, rt (25-30 °C). [b]Isolated yield.

Table S5. Reaction time screening[a]

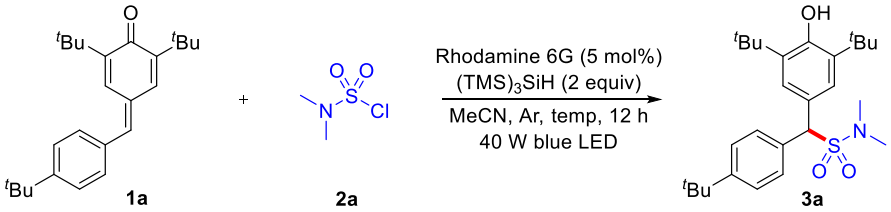


1a **2a** **3a**

Entry	Time (h)	Yield (%)[b]
1	6	70
2	12	76
3	24	58
4	36	31
5	48	32

[a]**1a** (0.1 mmol), **2a** (0.2 mmol), Rhodamine 6G (5 mol%), $(TMS)_3SiH$ (2 equiv), MeCN (1 mL), 40 W blue LED (450-465 nm), Ar, rt (25-30 °C). [b]Isolated yield.

Table S6. Temperature screening[a]

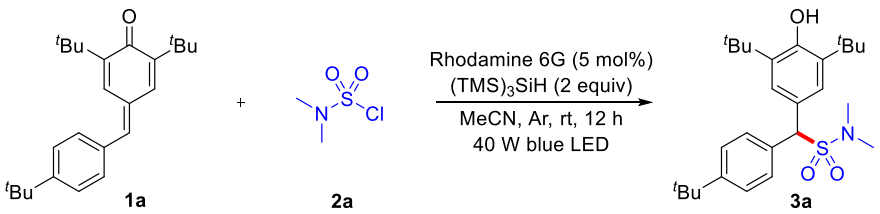


1a **2a** **3a**

Entry	Temp (°C)	Yield (%)[b]
1	0	47
2	10	65
3	rt (25-30)	76
4	50	53

[a]**1a** (0.1 mmol), **2a** (0.2 mmol), Rhodamine 6G (5 mol%), $(TMS)_3SiH$ (2 equiv), MeCN (1 mL), 40 W blue LED (450-465 nm), Ar. [b]Isolated yield.

Table S7. Control experiments[a]



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

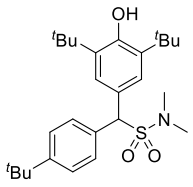
Entry	Control experiments	Yield (%)[b]
1	none	76
2	Without PC	0
3	Without $(TMS)_3SiH$	0
4	Air	0
5	Without light	0

[a]**1a** (0.1 mmol), **2a** (0.2 mmol), Rhodamine 6G (5 mol%), $(TMS)_3SiH$ (2 equiv), MeCN (1 mL), 40 W blue LED (450-465 nm), Ar, rt (25-30 ^oC).12 h. [b]Isolated yield.

(D) General procedure for synthesis of diarylmethyl sulfonamides

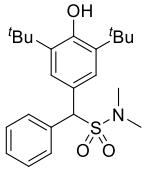
To an 8 mL vial equipped with a magnetic stir bar was added **1** (0.1 mmol), sulfamoyl chlorides (0.2 mmol), $(TMS)_3SiH$ (49.8 mg, 0.2 mmol), Rhodamine 6G (2.4 mg, 5.0 mol%) and MeCN (1 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon 40 W blue LED (450–465 nm) at room temperature for 12 h. The solvent was concentrated in vacuo and the residue was purified by a column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to provide the desired product **3**.

1-(4-(*tert*-butyl)phenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3a)



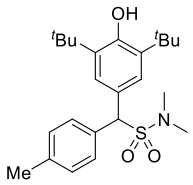
White solid, mp 135–136 ^oC, 34.9 mg, 76% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 5.27 (s, 1H), 5.24 (s, 1H), 2.58 (s, 6H), 1.44 (s, 18H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.0 (C), 151.3 (C), 136.0 (C), 131.8 (C), 129.1 (CH), 126.4 (CH), 125.7 (CH), 124.9 (C), 71.6 (CH), 37.8 (CH_3), 34.5 (C), 34.4 (C), 31.2 (CH_3), 30.2 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{41}NO_3SNa$: 482.2699; Found: 482.2691.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-phenylmethanesulfonamide (3b)



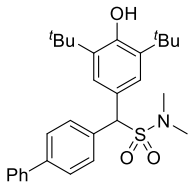
White solid, mp 172–173 ^oC, 32.6 mg, 81% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 7.2 Hz, 1H), 7.43 (s, 2H), 7.41-7.33 (m, 3H), 5.28 (s, 1H), 5.27 (s, 1H), 2.59 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.1 (C), 136.0 (C), 134.9 (C), 129.4 (CH), 128.7 (CH), 128.3 (CH), 126.3 (CH), 124.7 (C), 71.8 (CH), 37.8 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{33}NO_3SNa$: 426.2073; Found: 426.2077.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-(*p*-tolyl)methanesulfonamide (3c)



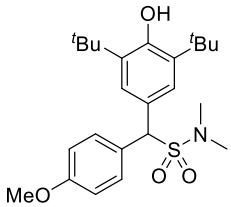
White solid, mp 157–158 ^oC, 32.1 mg, 77% yield. R_f = 0.35 (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.26 (s, 1H), 5.24 (s, 1H), 2.59 (s, 6H), 2.34 (s, 3H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.0 (C), 138.1 (C), 136.0 (C), 131.9 (C), 129.4 (CH), 129.3 (CH), 126.3 (CH), 124.9 (C), 71.6 (CH), 37.9 (CH_3), 34.4 (C), 30.2 (CH_3), 21.1 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{36}NO_3S$: 418.2410; Found: 418.2406.

1-([1,1'-biphenyl]-4-yl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3d)



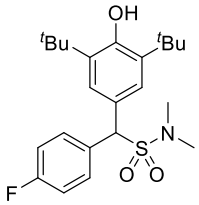
Yellow solid, mp 165–166 °C, 38.3 mg, 80% yield. R_f = 0.35 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 8.0 Hz, 2H), 7.64-7.85 (m, 4H), 7.48 (s, 2H), 7.46-7.42 (m, 2H), 7.38-7.34 (m, 1H), 5.34 (s, 1H), 5.30 (s, 1H), 2.64 (s, 6H), 1.47 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.1 (C), 141.1 (C), 140.4 (C), 136.2 (C), 133.9 (C), 129.9 (CH), 128.8 (CH), 127.5 (CH), 127.4 (CH), 127.0 (CH), 126.4 (CH), 124.8 (CH), 71.7 (CH), 37.9 (CH_3), 34.4 (C), 30.3 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{38}NO_3S$: 480.2567; Found: 480.2568.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3e)



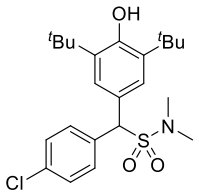
Yellow solid, mp 153–154 °C, 32.0 mg, 74% yield. R_f = 0.25 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 8.8 Hz, 2H), 7.41 (s, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.26 (s, 1H), 5.22 (s, 1H), 3.80 (s, 3H), 2.59 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.5 (C), 154.0 (C), 136.0 (C), 130.7 (CH), 127.0 (C), 126.3 (CH), 125.0 (C), 114.1 (CH), 71.2 (CH), 55.3 (CH_3), 37.9 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{36}NO_3S$: 434.2360; Found: 434.2366.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(4-fluorophenyl)-*N*,*N*-dimethylmethanesulfonamide (3f)



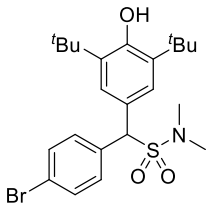
White solid, mp 168–169 °C, 28.2 mg, 67% yield. R_f = 0.35 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66-7.63 (m, 2H), 7.39 (s, 2H), 7.10-7.05 (m, 2H), 5.30 (s, 1H), 5.25 (s, 1H), 2.60 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.6 (d, *J* = 249.5 Hz) (C), 154.2 (C), 136.2 (C), 131.2 (d, *J* = 8.1 Hz) (C), 130.8 (d, *J* = 4.0 Hz) (CH), 126.3 (CH), 124.5 (CH), 115.6 (d, *J* = 21.2 Hz) (C), 71.0 (CH), 37.8 (CH_3), 34.4 (C), 30.2 (CH_3). ^{19}F NMR(376 MHz, $CDCl_3$) δ: -113.7. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{32}FNO_3SNa$: 444.1979; Found: 444.1977.

1-(4-chlorophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3g)



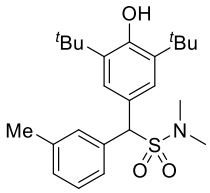
White solid, mp 180–181 °C, 33.2 mg, 76% yield. R_f = 0.4 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62-7.60 (m, 2H), 7.38-7.35 (m, 4H), 5.31 (s, 1H), 5.24 (s, 1H), 2.60 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.2 (C), 136.2 (C), 134.3 (C), 133.5 (C), 130.8 (CH), 128.9 (CH), 126.3 (CH), 124.3 (C), 71.1 (CH), 37.8 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{32}NClO_3SNa$: 460.1684; Found: 460.1693.

1-(4-bromophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3h)



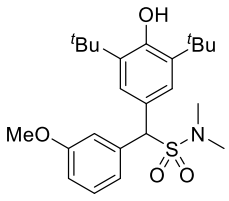
White solid, mp 177–178 °C, 34.6 mg, 72% yield. R_f = 0.45 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (q, *J* = 8.4 Hz, 4H), 7.37 (s, 2H), 5.30 (s, 1H), 5.22 (s, 1H), 2.60 (s, 6H), 1.43 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.2 (C), 136.2 (C), 134.0 (C), 131.8 (CH), 131.1 (CH), 126.3 (CH), 124.2 (C), 122.5 (C), 71.2 (CH), 37.9 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{33}BrNO_3S$: 482.1359; Found: 482.1352.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-(*m*-tolyl)methanesulfonamide (3i)



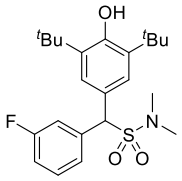
White solid, mp 155–156 °C, 32.9 mg, 79 % yield. R_f = 0.35 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 8.0 Hz, 1H), 7.19 (s, 2H), 7.11-7.07 (m, 1H), 7.03-6.96 (m, 1H), 5.35 (s, 1H), 5.06 (s, 1H), 2.43 (s, 6H), 2.24 (s, 3H), 1.23 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.0 (C), 136.1 (C), 136.0 (C), 133.6 (C), 130.8 (CH), 128.5 (CH), 128.0 (CH), 126.5 (CH), 126.4 (CH), 124.5 (C), 66.8 (CH), 37.9 (CH_3), 34.4 (C), 30.2 (CH_3), 20.1 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{36}NO_3S$: 418.2410; Found: 418.2406.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(3-methoxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3j)



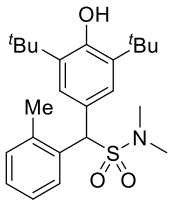
White solid, mp 143–144 °C, 36.4 mg, 84% yield. R_f = 0.25 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (s, 2H), 7.24-7.16 (m, 3H), 6.81-6.78 (m, 1H), 5.20 (s, 3H), 5.16 (s, 3H), 3.75 (s, 3H), 2.53 (s, 6H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.6 (C), 154.1 (C), 136.3 (C), 136.0 (C), 129.6 (CH), 126.3 (CH), 124.6 (C), 121.8 (CH), 114.9 (CH), 114.0 (CH), 71.7 (CH), 55.2 (CH_3), 37.8 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{36}NO_3S$: 434.2360; Found: 434.2368.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(3-fluorophenyl)-*N*,*N*-dimethylmethanesulfonamide (3k)



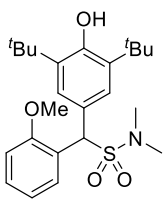
White solid, mp 174–175 °C, 35.8 mg, 85% yield. R_f = 0.35 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.32 (m, 5H), 7.05-7.00 (m, 1H), 5.31 (s, 1H), 5.25 (s, 1H), 2.61 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.7 (d, *J* = 247.5 Hz) (C), 154.3 (C), 137.3 (d, *J* = 7.1 Hz) (C), 130.1 (d, *J* = 9.1 Hz) (CH), 126.3 (CH), 125.2 (d, *J* = 3.0 Hz) (CH), 124.2 (C), 116.5 (d, *J* = 22.2 Hz) (CH), 115.3 (d, *J* = 21.2 Hz) (CH), 71.3 (CH), 37.8 (CH_3), 34.4 (C), 30.2 (CH_3). ^{19}F NMR(376 MHz, $CDCl_3$) δ: -112.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{32}FNO_3SNa$: 444.1979; Found: 444.1977.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-(*o*-tolyl)methanesulfonamide (3l)



White solid, mp 145–146 °C, 32.5 mg, 78 % yield. R_f = 0.35 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.0 Hz, 1H), 7.20 (s, 2H), 7.12-7.06 (m, 1H), 7.04-6.97 (m, 1H), 5.36 (s, 1H), 5.09 (s, 1H), 2.44 (s, 6H), 2.25 (s, 3H), 1.24 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.0 (C), 136.0 (C), 135.9 (C), 133.6 (C), 130.8 (CH), 128.4 (CH), 128.0 (CH), 126.6 (CH), 126.4 (CH), 124.4 (C), 66.7 (CH), 37.8 (CH_3), 34.3 (C), 30.2 (CH_3), 20.1 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{35}NO_3SNa$: 440.2230; Found: 440.2242.

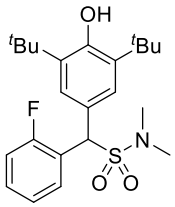
1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(2-methoxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3m)



White solid, mp 149–150 °C, 35.5 mg, 82 % yield. R_f = 0.25 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 8.8 Hz, 2H), 7.41 (s, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.26 (s, 1H), 5.22 (s, 1H), 3.80 (s, 3H), 2.59 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.5 (C), 153.8 (C), 135.8 (C), 129.9 (CH), 129.2 (CH), 126.6 (CH), 125.1 (C), 123.6 (C), 120.8 (CH), 110.8 (CH), 61.7 (CH),

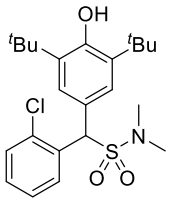
55.7 (CH_3), 37.8 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{36}NO_3S$: 434.2360; Found: 434.2351.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(2-fluorophenyl)-*N*,*N*-dimethylmethanesulfonamide (3n)



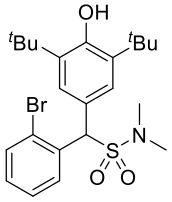
White solid, mp 167–168 °C, 34.1 mg, 81% yield. R_f = 0.4 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (t, *J* = 7.6 Hz, 1H), 7.43 (s, 2H), 7.33-7.28 (m, 1H), 7.23-7.19 (m, 1H), 7.11-7.06 (m, 1H), 5.74 (s, 1H), 5.28 (s, 1H), 2.64 (s, 3H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.3 (*J* = 247.5 Hz) (C), 159.0 (C), 154.2 (C), 136.2 (C), 130.3 (*J* = 2.0 Hz) (CH), 129.8 (*J* = 9.1 Hz) (CH), 126.5 (CH), 124.4 (*J* = 3.0 Hz) (CH), 122.8 (*J* = 14.1 Hz) (C), 115.5 (*J* = 23.2 Hz) (CH), 62.0 (*J* = 4.0 Hz) (CH), 37.3 (CH_3), 34.4 (C), 30.2 (CH_3). ^{19}F NMR(376 MHz, $CDCl_3$) δ: -118.1. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{32}FNO_3SNa$: 444.1979; Found: 444.1967.

1-(2-chlorophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3o)



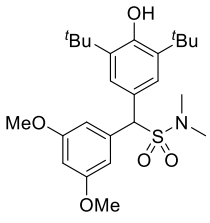
White solid, mp 160–161 °C, 31.5 mg, 72% yield. R_f = 0.35 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 2H), 7.22-7.20 (m, 1H), 7.17-7.13 (m, 1H), 7.08-7.04 (m, 1H), 5.80 (s, 1H), 5.08 (s, 1H), 2.46 (s, 6H), 1.24 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.1 (C), 136.1 (C), 134.2 (C), 133.2 (C), 130.2 (CH), 129.8 (CH), 129.3 (CH), 127.2 (CH), 126.4 (CH), 124.3 (C), 66.2 (CH), 37.8 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{32}ClNO_3SNa$: 460.1684; Found: 460.1674.

1-(2-bromophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3p)



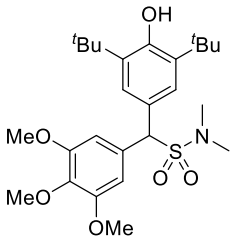
White solid, mp 159–160 °C, 36.1 mg, 75% yield. R_f = 0.5 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44 (s, 2H), 7.38 (td, *J* = 7.6, 1.6 Hz, 1H), 7.17 (td, *J* = 7.6, 1.6 Hz, 1H), 5.60 (s, 1H), 5.27 (s, 1H), 2.65 (s, 6H), 1.43 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.1 (C), 136.0 (C), 134.9 (C), 133.2 (CH), 130.3 (CH), 129.6 (CH), 127.8 (CH), 126.4 (CH), 125.2 (C), 124.3 (C), 69.0 (CH), 37.8 (CH_3), 34.3 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{33}BrNO_3S$: 482.1359; Found: 482.1367.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(3,5-dimethoxyphenyl)-*N*,*N*-dimethylmethanesulfonamide (3q)



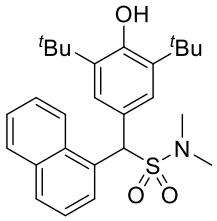
White solid, mp 154–155 °C, 43.1 mg, 93% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (s, 2H), 6.85 (d, *J* = 2.4 Hz, 2H), 6.42 (t, *J* = 2.4 Hz, 1H), 5.28 (s, 1H), 5.17 (s, 1H), 3.80 (s, 6H), 2.62 (s, 6H), 1.43 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.7 (C), 154.1 (C), 136.9 (C), 136.0 (C), 126.3 (CH), 124.5 (C), 107.5 (CH), 100.4 (CH), 71.7 (CH), 55.3 (CH_3), 37.9 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{37}NO_5SNa$: 486.2285; Found: 486.2287.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-(3,4,5-trimethoxyphenyl)methanesulfonamide (3r)



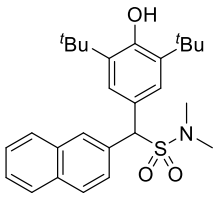
White solid, mp 172–173 °C, 42.9 mg, 87% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (s, 2H), 6.94 (s, 2H), 5.31 (s, 1H), 5.17 (s, 1H), 3.89 (s, 6H), 3.83 (s, 3H), 2.61 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.2 (C), 153.1 (C), 137.9 (C), 136.1 (C), 130.2 (C), 126.3 (CH), 124.5 (C), 106.6 (CH), 71.7 (CH), 60.8 (CH_3), 56.1 (CH_3), 37.9 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{40}NO_6S$: 494.2571; Found: 494.2567.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-(naphthalen-1-yl)methanesulfonamide (3s)



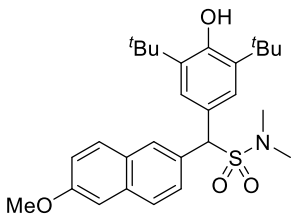
White solid, mp 151–152 °C, 38.1 mg, 84% yield. R_f = 0.45 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, J = 7.2 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.89-7.83 (m, 2H), 7.60-7.55 (m, 2H), 7.51-7.48 (m, 3H), 6.19 (s, 1H), 5.25 (s, 1H), 2.58 (s, 6H), 1.42 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.1 (C), 136.0 (C), 134.1 (C), 131.3 (C), 130.8 (C), 129.3 (CH), 128.8 (CH), 127.1 (CH), 126.7 (CH), 126.6 (CH), 125.6 (CH), 125.4 (CH), 124.8 (CH), 122.2 (C), 66.0 (CH), 37.9 (CH_3), 34.3 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{36}NO_3S$: 454.2410; Found: 454.2407.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-(naphthalen-2-yl)methanesulfonamide (3t)



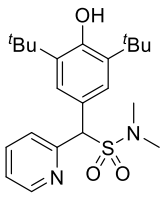
Yellow solid, mp 109–110 °C, 34.9 mg, 77% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (s, 1H), 7.89-7.83 (m, 4H), 7.54 (s, 2H), 7.51-7.49 (m, 2H), 5.50 (s, 1H), 5.31 (s, 1H), 2.64 (s, 6H), 1.47 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.1 (C), 136.1 (C), 133.2 (C), 132.9 (C), 132.4 (C), 128.8 (CH), 128.3 (CH), 128.1 (CH), 127.5 (CH), 126.9 (CH), 126.4 (CH), 126.4 (CH), 126.3 (CH), 124.8 (C), 72.0 (CH), 37.9 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{36}NO_3S$: 454.2410; Found: 454.2416.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(6-methoxynaphthalen-2-yl)-*N*,*N*-dimethylmethanesulfonamide (3u)



White solid, mp 197–198 °C, 40.1 mg, 83% yield. R_f = 0.4 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 1.6 Hz, 1H), 7.81-7.74 (m, 3H), 7.49 (s, 2H), 7.15 (dd, J = 8.8, 2.0 Hz, 1H), 7.11 (d, J = 2.8 Hz, 1H), 5.42 (s, 1H), 5.28 (s, 1H), 3.92 (s, 3H), 2.60 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.0 (C), 154.0 (C), 136.0 (C), 134.2 (C), 129.9 (CH), 129.6 (C), 128.7 (C), 128.7 (CH), 127.4 (CH), 127.2 (CH), 126.4 (CH), 124.9 (C), 119.2 (CH), 105.4 (CH), 71.8 (CH), 55.3 (CH_3), 37.9 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{38}NO_4S$: 484.2516; Found: 484.2501.

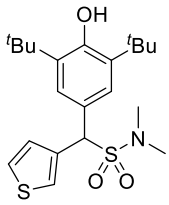
1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-(pyridin-2-yl)methanesulfonamide (3v)



White solid, mp 144–145 °C, 30.3 mg, 75% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59 (dt, J = 4.0, 0.8 Hz, 1H),

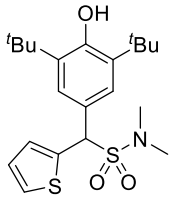
7.89-7.87 (m, 1H), 7.73 (td, *J* = 7.6, 2.0 Hz, 1H), 7.52 (s, 2H), 7.25-7.23 (m, 1H), 5.59 (s, 1H), 5.28 (s, 1H), 2.62 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.0 (C), 154.3 (C), 149.2 (CH), 136.9 (CH), 136.1 (C), 126.7 (CH), 124.1 (CH), 123.7 (C), 123.1 (CH), 73.9 (CH), 37.8 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{33}N_2O_3S$: 405.2206; Found: 405.2211.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-(thiophen-3-yl)methanesulfonamide (3w)



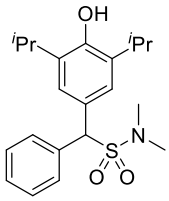
Yellow solid, mp 162–163 °C, 32.7 mg, 80% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.47 (m, 1H), 7.39-7.38 (m, 3H), 7.34-7.32 (m, 1H), 5.41 (s, 1H), 5.29 (s, 1H), 2.59 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.2 (C), 136.1 (C), 134.9 (C), 128.5 (CH), 126.5 (CH), 125.8 (CH), 124.9 (CH), 124.3 (C), 67.5 (CH), 37.7 (CH_3), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{33}N_2O_3S$: 410.1818; Found: 410.1808.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*,*N*-dimethyl-1-(thiophen-2-yl)methanesulfonamide (3x)



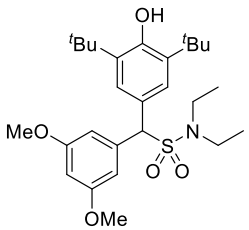
White solid, mp 164–165 °C, 33.5 mg, 82% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.47 (m, 1H), 7.39-7.38 (m, 3H), 7.34-7.32 (m, 1H), 5.41 (s, 1H), 5.29 (s, 1H), 2.58 (s, 6H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.2 (C), 136.2 (C), 134.9 (C), 128.5 (CH), 126.5 (CH), 125.8 (CH), 125.0 (CH), 124.4 (C), 67.5 (CH), 37.7 (CH_3), 34.4 (C), 30.3 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{33}N_2O_3S$: 410.1818; Found: 410.1812.

1-(4-hydroxy-3,5-diisopropylphenyl)-*N*,*N*-dimethyl-1-phenylmethanesulfonamide (3z)



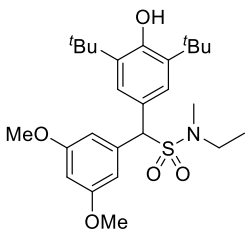
Yellow oil, 16.9 mg, 45% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67-7.65 (m, 2H), 7.39-7.31 (m, 5H), 5.41 (s, 1H), 5.29 (s, 1H), 4.92 (s, 1H), 3.18-3.11 (m, 2H), 2.60 (s, 6H), 1.27-1.26 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.3 (C)，134.9 (C)，134.0 (C)，129.5 (CH)，128.7 (CH)，128.3 (CH)，126.0 (CH)，125.0 (C)，71.8 (CH)，37.9 (CH_3)，27.3 (CH)，27.0 (CH_3). HRMS (ESI) m/z: $[M-H]^+$ calcd for $C_{21}H_{29}NO_3S$: 374.1793; Found: 374.1756.

1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(3,5-dimethoxyphenyl)-*N*,*N*-diethylmethanesulfonamide (4a)



White solid, mp 142–143 °C, 38.3 mg, 78% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (s, 1H), 6.84 (d, *J* = 2.4 Hz, 2H), 6.41 (t, *J* = 2.4 Hz, 1H), 5.25 (s, 1H), 5.06 (s, 1H), 3.79 (s, 6H), 3.09-3.03 (m, 4H), 1.44 (s, 18H), 1.00 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.7 (C), 153.9 (C), 137.4 (C), 135.9 (C), 126.4 (CH), 125.1 (C), 107.7 (CH), 100.4 (CH), 73.5 (CH), 55.3 (CH_3), 42.3 (CH_2), 34.3 (C), 30.2 (CH_3), 14.5 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{42}NO_5S$: 492.2778; Found: 492.2786.

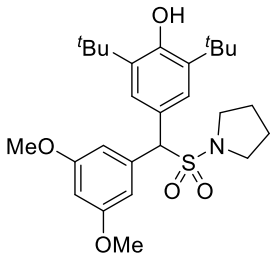
1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-(3,5-dimethoxyphenyl)-*N*-ethyl-*N*-methylmethanesulfonamide (4b)



White solid, mp 117–118 °C, 39.1 mg, 82% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (s, 2H), 6.84 (d,

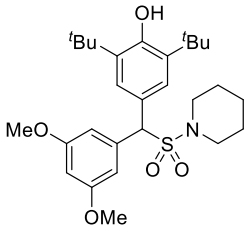
J = 2.0 Hz, 1H), 6.41 (t, *J* = 2.4 Hz, 1H), 5.26 (s, 1H), 5.12 (s, 1H), 3.80 (s, 6H), 3.00-2.67 (m, 2H), 2.61 (s, 3H), 1.43 (s, 18H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.7 (C), 154.0 (C), 137.1 (C), 135.9 (C), 126.4 (CH), 124.8 (C), 107.6 (CH), 100.4 (CH), 72.4 (CH), 55.3 (CH_3), 45.2 (CH_2), 34.4 (C), 34.2 (CH_3), 30.2 (CH_3), 13.7 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{40}NO_5S$: 478.2622; Found: 478.2626.

2,6-di-*tert*-butyl-4-((3,5-dimethoxyphenyl)(pyrrolidin-1-ylsulfonyl)methyl)phenol (4c)



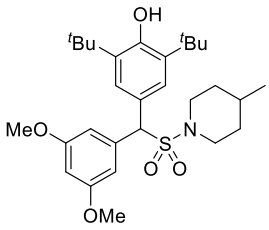
White solid, mp 142–143 °C, 36.2 mg, 74% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (s, 2H), 6.86 (d, *J* = 2.4 Hz, 1H), 6.41 (t, *J* = 2.0 Hz, 1H), 5.26 (s, 1H), 5.23 (s, 1H), 3.80 (s, 6H), 3.17-3.12 (m, 2H), 3.09-3.03 (m, 2H), 1.72-1.64 (m, 4H), 1.43 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.7 (C), 154.0 (C), 137.2 (C), 135.9 (C), 126.4 (CH), 124.9 (C), 107.6 (CH), 100.4 (CH), 71.7 (CH), 55.3 (CH_2), 48.3 (CH_2), 34.4 (C), 30.2 (CH_3), 25.8 (CH_2). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{40}NO_5S$: 490.2622; Found: 490.2622.

2,6-di-*tert*-butyl-4-((3,5-dimethoxyphenyl)(piperidin-1-ylsulfonyl)methyl)phenol (4d)



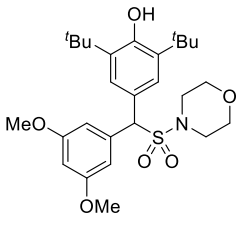
White solid, mp 119–120 °C, 38.2 mg, 76% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (s, 2H), 6.84 (d, *J* = 2.4 Hz, 2H), 6.41 (t, *J* = 2.4 Hz, 1H), 5.26 (s, 1H), 5.08 (s, 1H), 3.04-2.93 (m, 4H), 1.44 (s, 18H), 1.41-1.31 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.7 (C), 154.1 (C), 137.1 (C), 136.0 (C), 126.5 (CH), 124.8 (C), 107.7 (CH), 100.4 (CH), 72.6 (CH), 55.4 (CH_3), 47.1 (CH_2), 34.4 (CH_2), 30.3 (CH_3), 25.7 (CH_2), 23.8 (CH_2). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{42}NO_5S$: 504.2778; Found: 504.2780.

2,6-di-*tert*-butyl-4-((3,5-dimethoxyphenyl)((4-methylpiperidin-1-yl)sulfonyl)methyl)phenol (4e)



White solid, mp 112–113 °C, 41.9 mg, 81% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (s, 2H), 6.83 (d, *J* = 2.4 Hz, 2H), 6.41 (t, *J* = 2.4 Hz, 2H), 5.25 (s, 1H), 5.08 (s, 1H), 3.80 (s, 6H), 3.67-3.58 (m, 2H), 2.45 (td, *J* = 12.0, 2.4 Hz, 1H), 2.29 (td, *J* = 12.4, 2.8 Hz, 1H), 1.44 (s, 18H), 1.31-1.23 (m, 2H), 1.06-0.92 (m, 3H), 0.85 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.7 (C), 154.1 (C), 137.1 (C), 136.0 (C), 126.4 (CH), 124.8 (C), 107.7 (CH), 100.5 (CH), 72.7 (CH), 55.3 (CH_3), 46.5 (CH_2), 46.4 (CH_2), 34.4 (C), 34.0 (CH_2), 33.9 (CH_2), 30.4 (CH), 30.3 (CH_3), 21.5 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{44}NO_5S$: 518.2935; Found: 518.2939.

2,6-di-*tert*-butyl-4-((3,5-dimethoxyphenyl)(morpholinosulfonyl)methyl)phenol (4f)



White solid, mp 167–168 °C, 38.9 mg, 77% yield. R_f = 0.45 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (s, 2H), 6.83 (d, *J* = 2.4 Hz, 2H), 6.43 (t, *J* = 2.4 Hz, 1H), 5.29 (s, 1H), 5.10 (s, 1H), 3.80 (s, 6H), 3.51 (q, *J* = 5.2 Hz, 4H), 3.04-3.01 (m, 4H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.8 (C), 154.2 (C), 136.5 (C), 136.1 (C), 126.4 (CH), 124.3 (C), 107.7 (CH), 100.5 (CH), 72.8 (CH), 66.8 (CH_2), 55.4 (CH_3), 46.4 (CH_2), 34.4 (C), 30.2 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{40}O_6S$: 506.2571; Found: 506.2577.

(E) Synthetic application

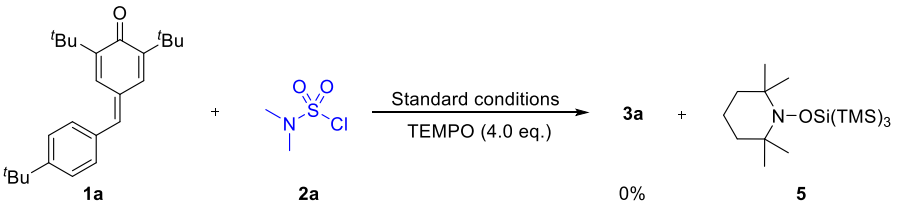
(1) Procedure for the Synthesis of 3q at 1.0 mmol Scale.

To an 50 mL vial equipped with a magnetic stir bar was added **1q** (356.0 mg, 1.0 mmol), *N*,*N*-dimethylsulfamoyl chloride **2a** (288.0 mg, 2.0 mmol), $(TMS)_3SiH$ (498.0 mg, 2.0 mmol), Rhodamine 6G (24.0 mg, 5.0 mol%) and MeCN (10 mL) under nitrogen atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon 40 W blue LED (450–465 nm) at room temperature for 24 h. The solvent was concentrated in vacuo and the residue was purified by a column chromatography on silica gel with petroleum ether/ethyl acetate (6:1) as eluent to provide the desired product **3q** as a white solid (416.7 mg, 90% yield).

(2) Sunlight driven experiment

To an 8 mL vial equipped with a magnetic stir bar was added **1q** (70.8 mg, 0.2 mmol), *N*,*N*-dimethylsulfamoyl chloride **2a** (57.2 mg, 0.4 mmol), $(TMS)_3SiH$ (99.6 mg, 0.4 mmol), Rhodamine 6G (4.8 mg, 5.0 mol%) and MeCN (2 mL) under nitrogen atmosphere and sealed with PTFE cap. The reaction mixture was stirred upon sunlight irradiation under argon atmosphere for 12 h. Then the solvent was concentrated in vacuo and the residue was purified by a column chromatography on silica gel with petroleum ether/ethyl acetate (6:1) as eluent to provide the desired product **3q** as a white solid (68.7 mg, 74% yield).

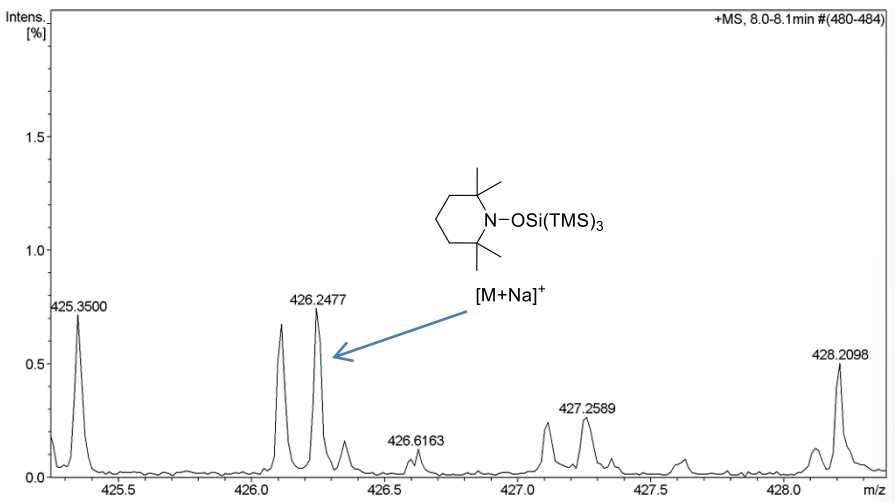
(F) Radical trapping experiment with TEMPO



1a **2a** **3a** 0% **5**

Dected by ESI-HRMS (m/z)
$[M+Na]^+$ calcd: 426.2470
found: 426.2477

To an 8 mL vial equipped with a magnetic stir bar was added **1a** (35.0 mg, 0.1 mmol), *N*,*N*-dimethylsulfamoyl chloride **2a** (28.6 mg, 0.2 mmol), $(TMS)_3SiH$ (49.8 mg, 0.2 mmol), Rhodamine 6G (2.4 mg, 5.0 mol%), TEMPO (62.4 mg, 0.4 mmol) and MeCN (1.0 mL) under nitrogen atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon 40 W blue LED (450–465 nm) at room temperature for 12 h. HRMS (ESI) m/z: compound **5**, $[\mathbf{5}+Na]^+$ calcd for $C_{18}H_{45}ONSiNa$: 240.2470; Found: 240.2477.



(G) Stern-Volmer fluorescence quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 1.25 μM Rhodamine 6G, in degassed dry MeCN at room temperature. The solutions were irradiated at 347 nm and fluorescence was measured from 357 nm to 684 nm. Control experiments showed that the excited state Rhodamine 6G* was mainly quenched by **1a**.

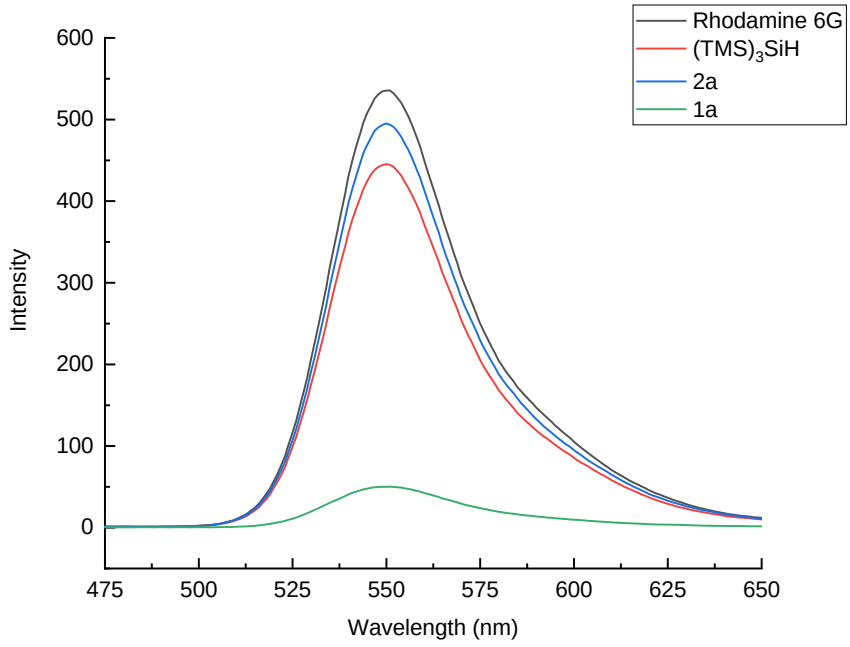


Figure S1. Fluorescence quenching of excited Rhodamine 6G with **1a**, **2a**, $(TMS)_3SiH$ in MeCN (excitation wavelength: 347 nm). Rhodamine 6G (1.25 μM) in MeCN (black line), Rhodamine 6G (1.25 μM) with **1a** (1.0 mM) in MeCN (green line), Rhodamine 6G (1.25 μM) with **2a** (1.0 mM) in MeCN (blue line), Rhodamine 6G (1.25 μM) with $(TMS)_3SiH$ (1.0 mM) in MeCN (red line).

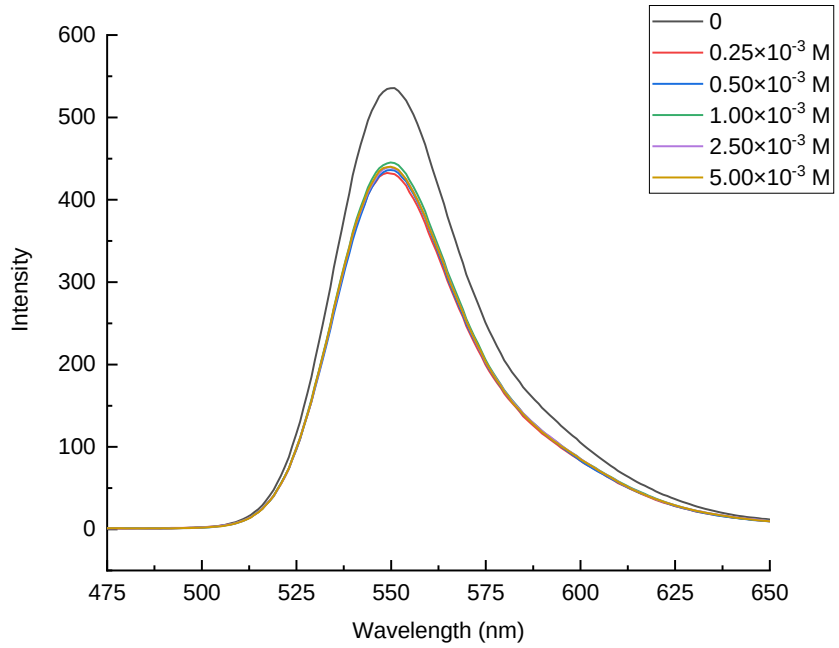


Figure S2. Luminescence quenching of Rhodamine 6G by $(TMS)_3SiH$ (10^{-3} M).

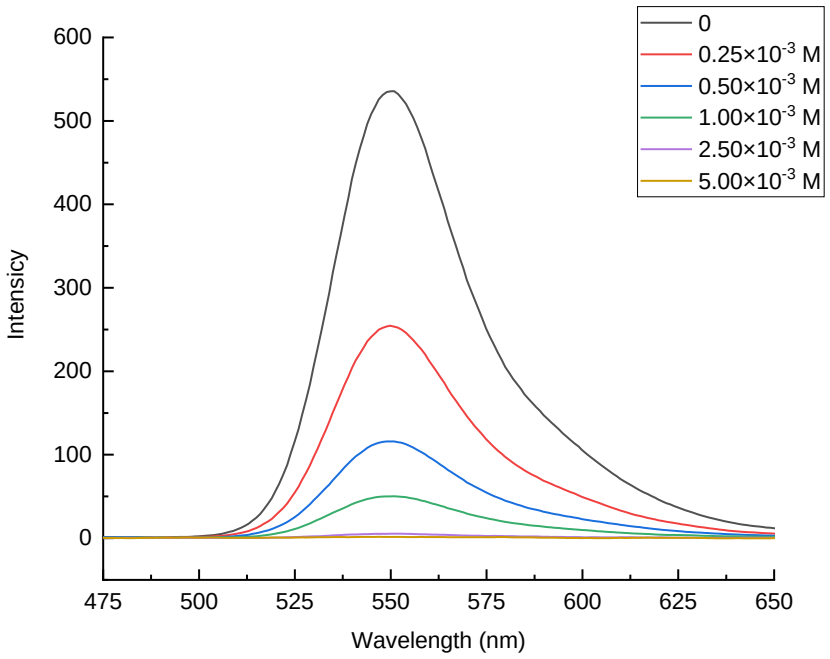


Figure S3. Luminescence quenching of Rhodamine 6G by **1a** (10^{-3} M)

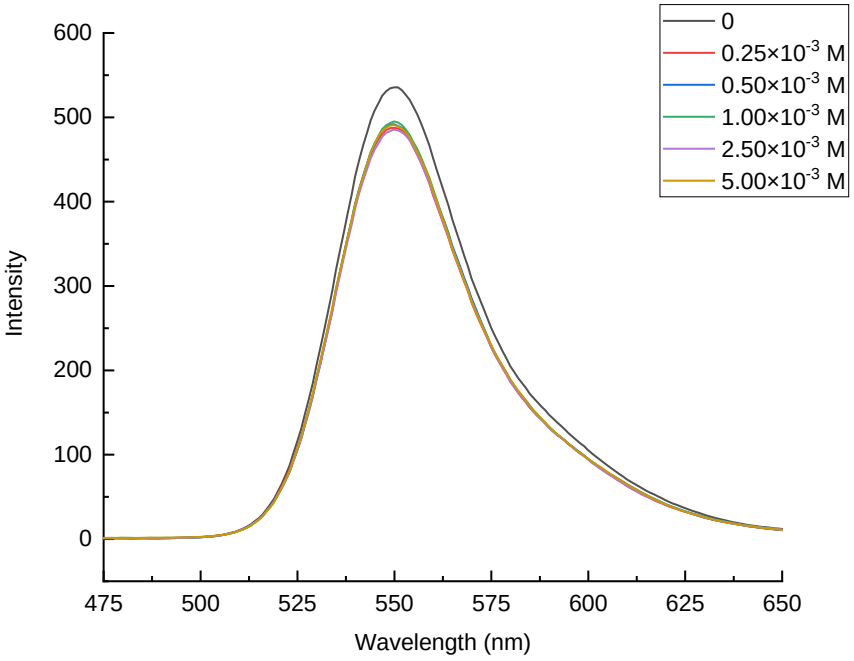


Figure S4. Luminescence quenching of Rhodamine 6G by **2a** (10^{-3} M).

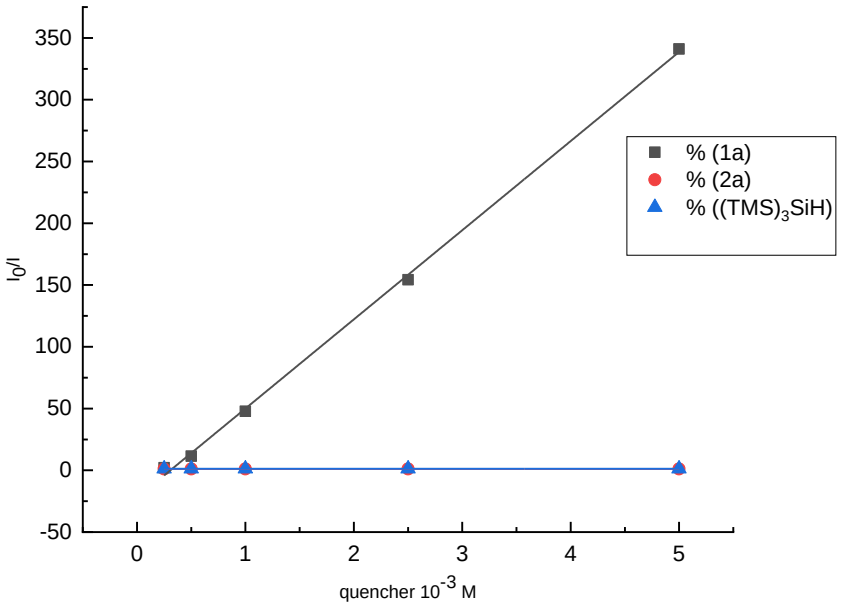
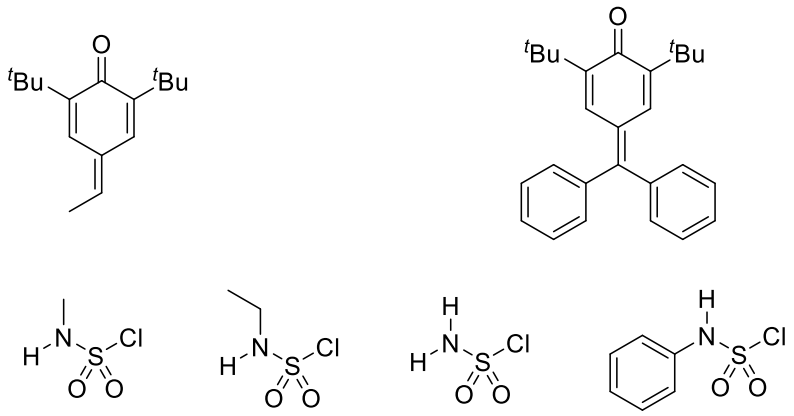


Figure S5. Stern-Volmer plots of Rhodamine 6G and three quenchers. I_0 and I are luminescence intensities in the absence and presence of the indicated concentrations (10^{-3} M) of the corresponding quencher.

These results suggested that the excited photocatalyst Rhodamine 6G was primarily quenched by **1a**, while **2a** and $(TMS)_3SiH$ showed much less effect.

(H) Unsuccessful examples



References:

[1] Yan, Y.; Li, H.; Xie, F.; Lu, W.; Zhang, Z.; Jing, L.; Han, P. Electrochemical Reductive Carboxylation of *para*-Quinone Methides with CO_2. *Adv. Synth. Catal.* **2023**, *365*, 3830-3836

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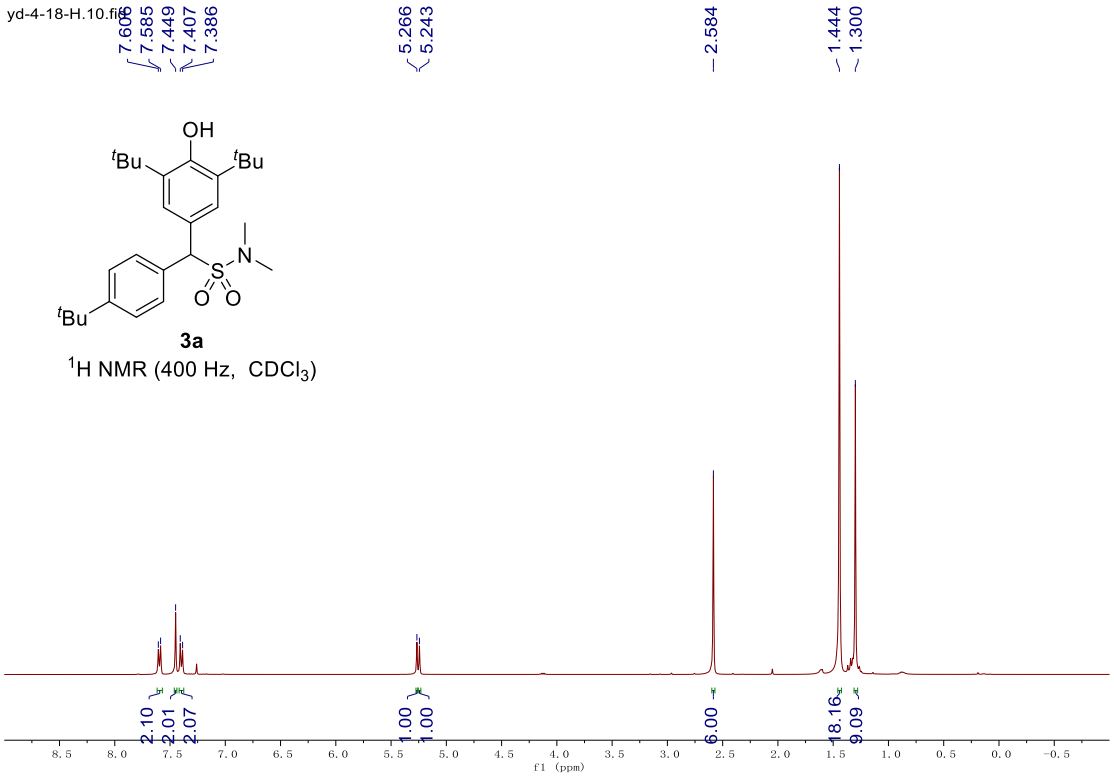
[3] Dong, N.; Zhang, Z.-P.; Xue, X.-S.; Li, X.; Cheng, J.-P. Phosphoric Acid Catalyzed Aasymmetric 1,6-Conjugate Addition of Thioacetic Acid to *para*-Quinone Methides. *Angew. Chem. Int. Ed*. **2016**, *55*, 1460-1464.

[4] Luo, C.; Lu, W.-h.; Wang, G.-q.; Zhang, Z.-b.; Li, H.-q.; Han, P.; Yang, D.; Jing, L.-h.; Wang, C. Photocatalytic Synthesis of Diarylmethyl Silanes via 1,6-Conjugate Addition of Silyl Radicals to *p*-Quinone Methides. *J. Org. Chem.* **2022**, *87*, 3567-3576.

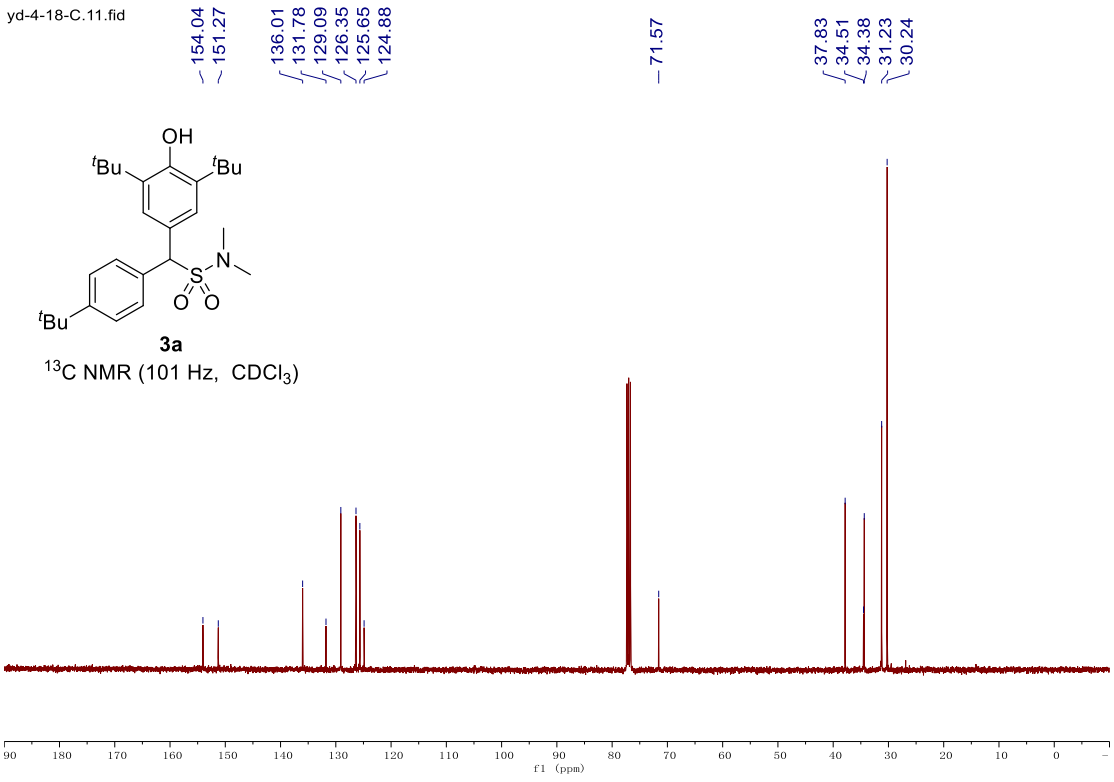
[5] Zhu, J.; Xu, M.; Gong, B.; Lin, A.; Gao, S. (*Z*)-Selective Synthesis of Bromofluoroalkenes via the $TMSCF_2Br$-Mediated Tandem Reaction with *para*-Quinone Methides. *Org. Lett.* **2023**, *25*, 3271-3275.

(I) NMR Spectra of New Compounds



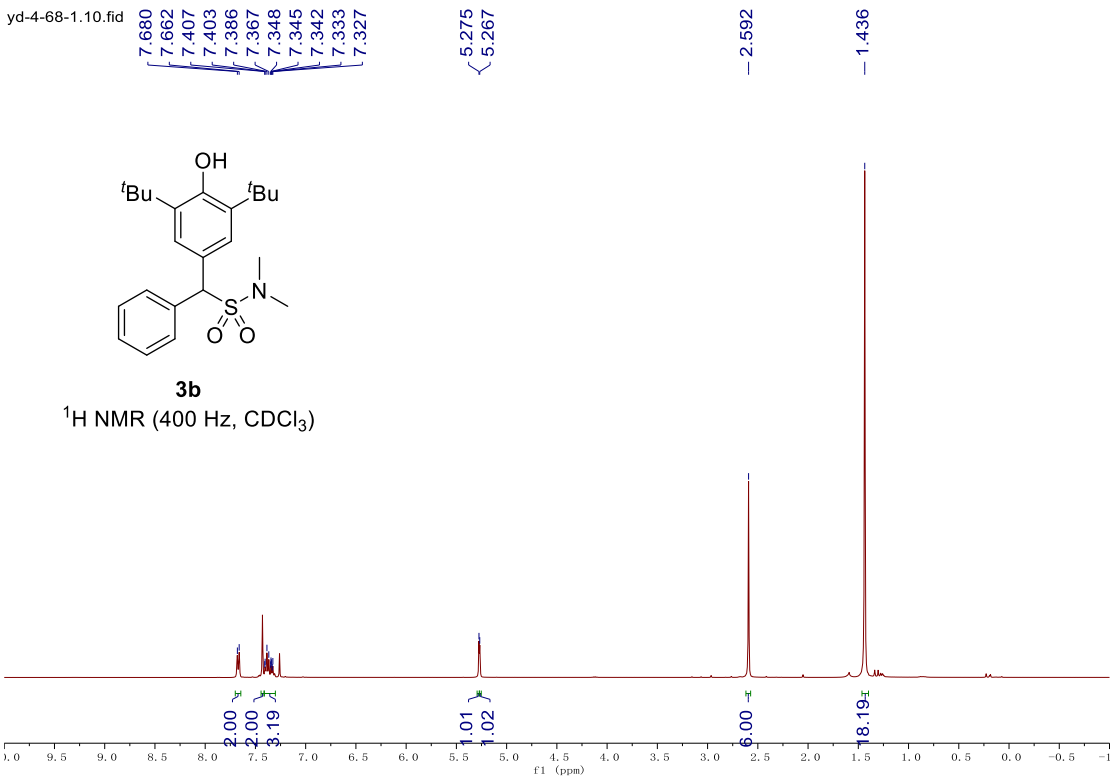
3a

^{1}H NMR (400 Hz, $CDCl_3$)



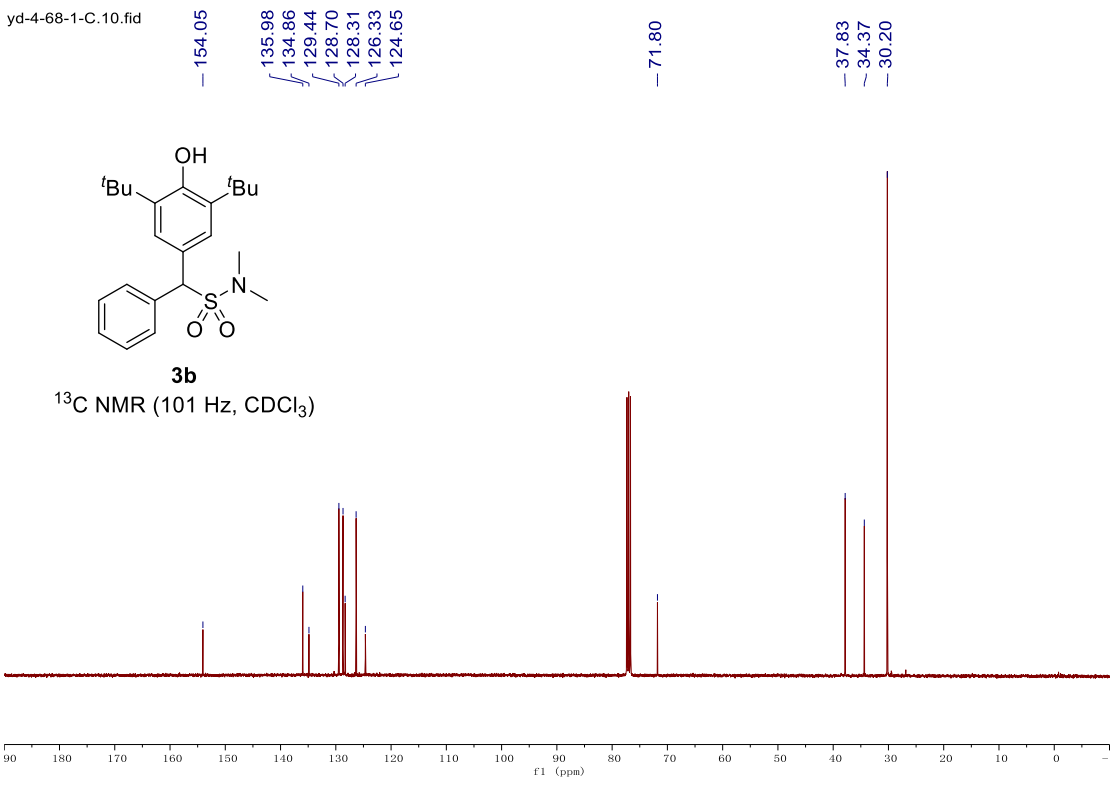
3a

^{13}C NMR (101 Hz, $CDCl_3$)



3b

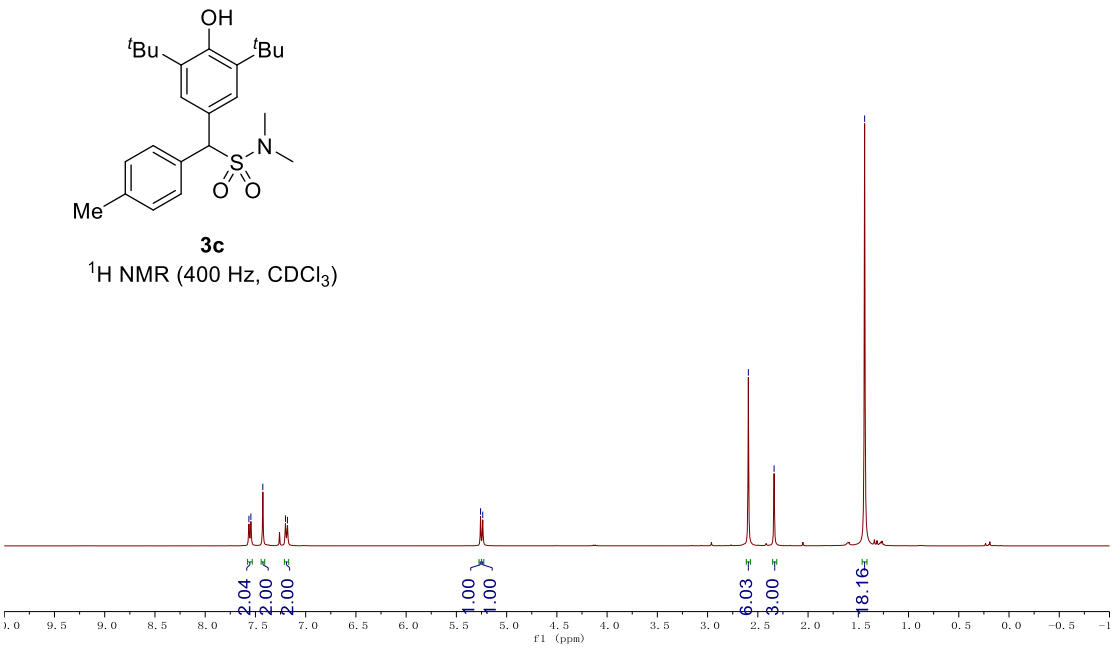
^{1}H NMR (400 Hz, $CDCl_3$)



3b

^{13}C NMR (101 Hz, $CDCl_3$)

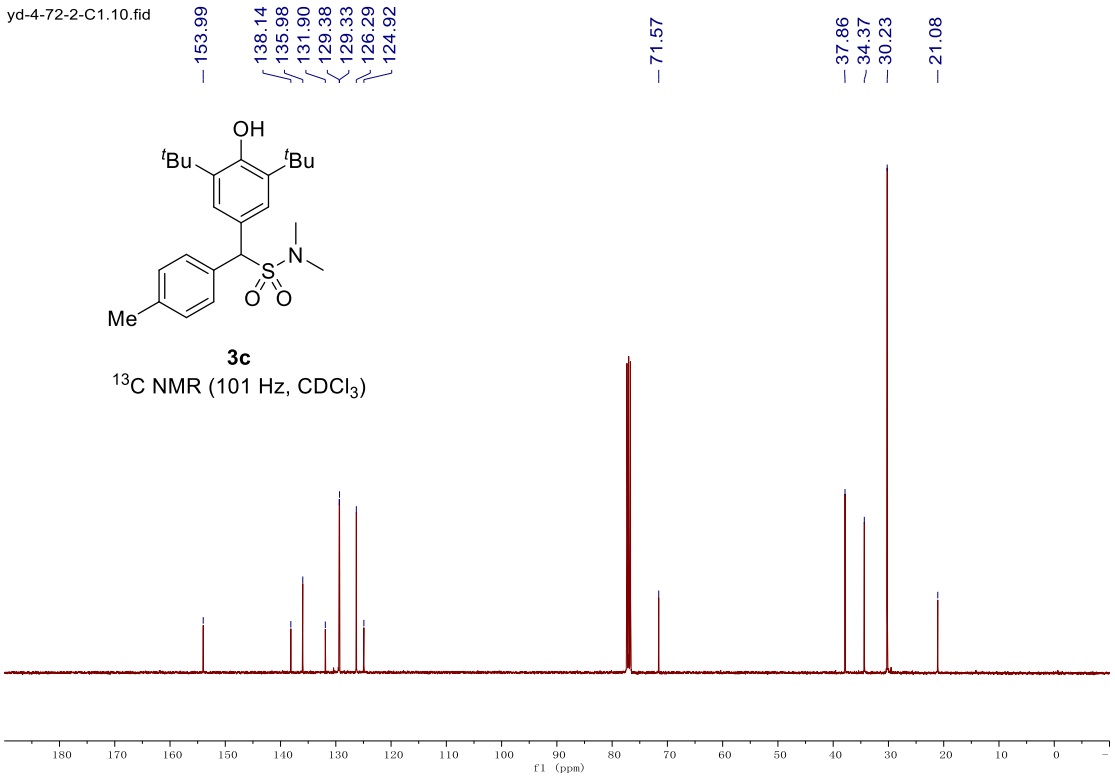
yd-4-72-2-H2.10.fid



3c

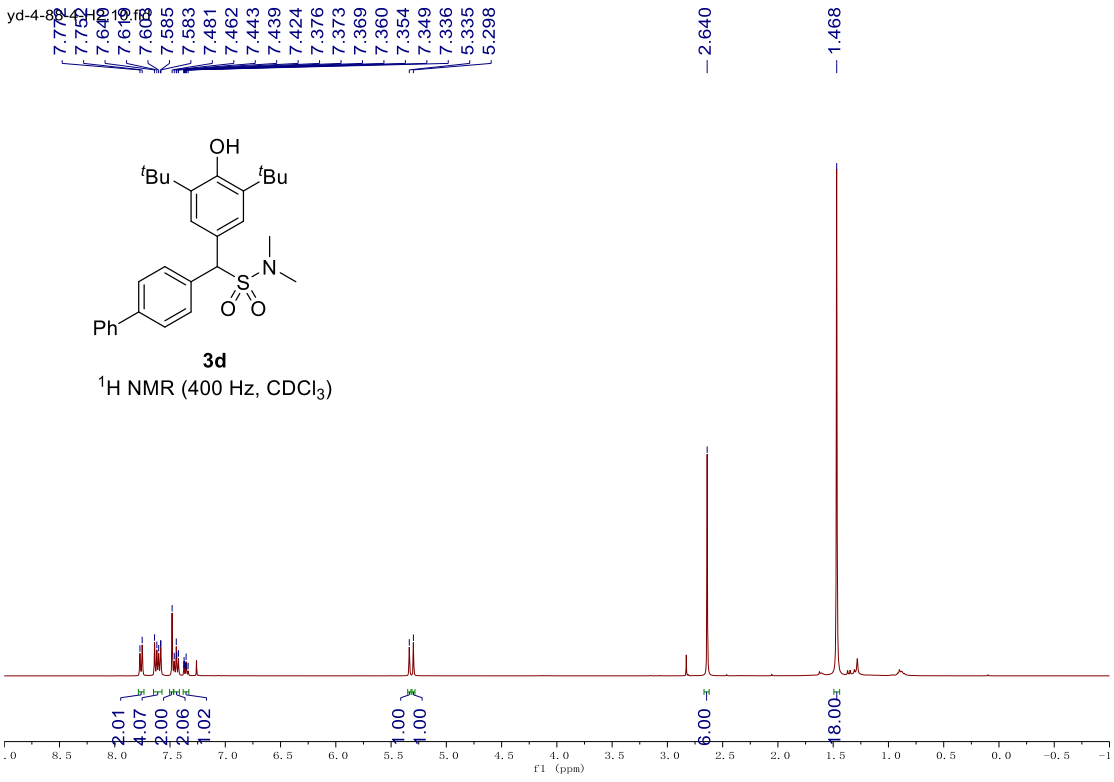
^{1}H NMR (400 Hz, $CDCl_3$)

yd-4-72-2-C1.10.fid



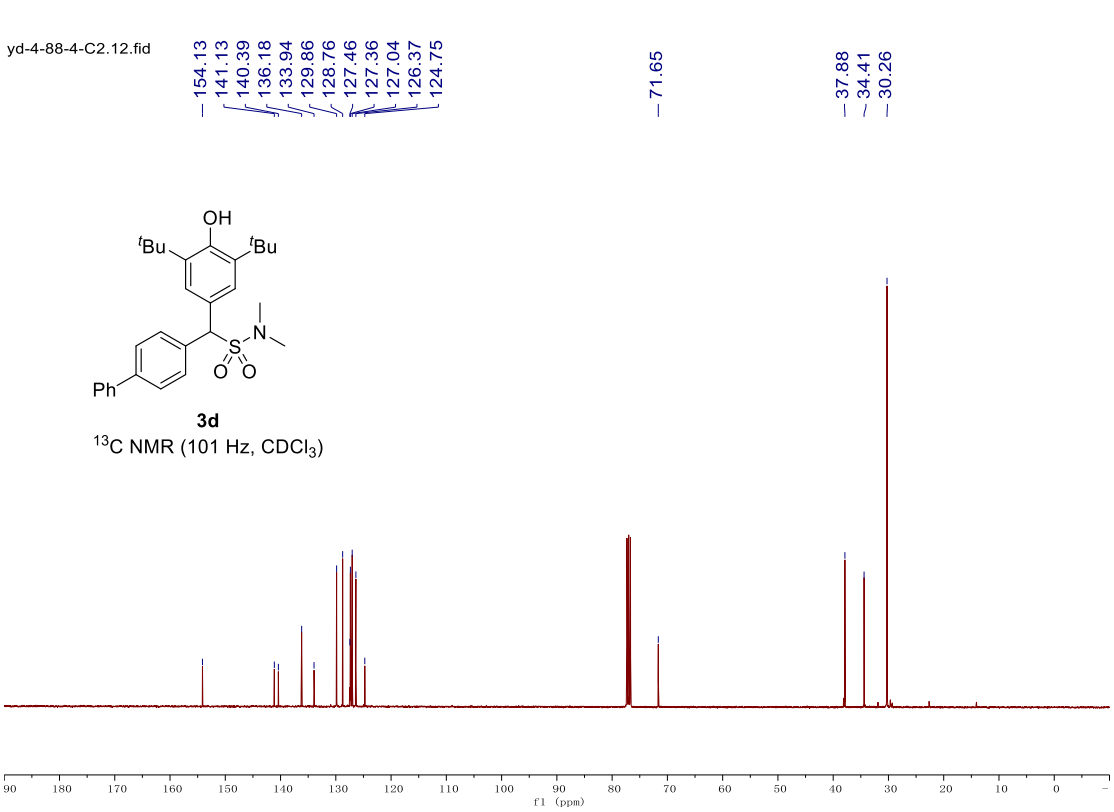
3c

^{13}C NMR (101 Hz, $CDCl_3$)



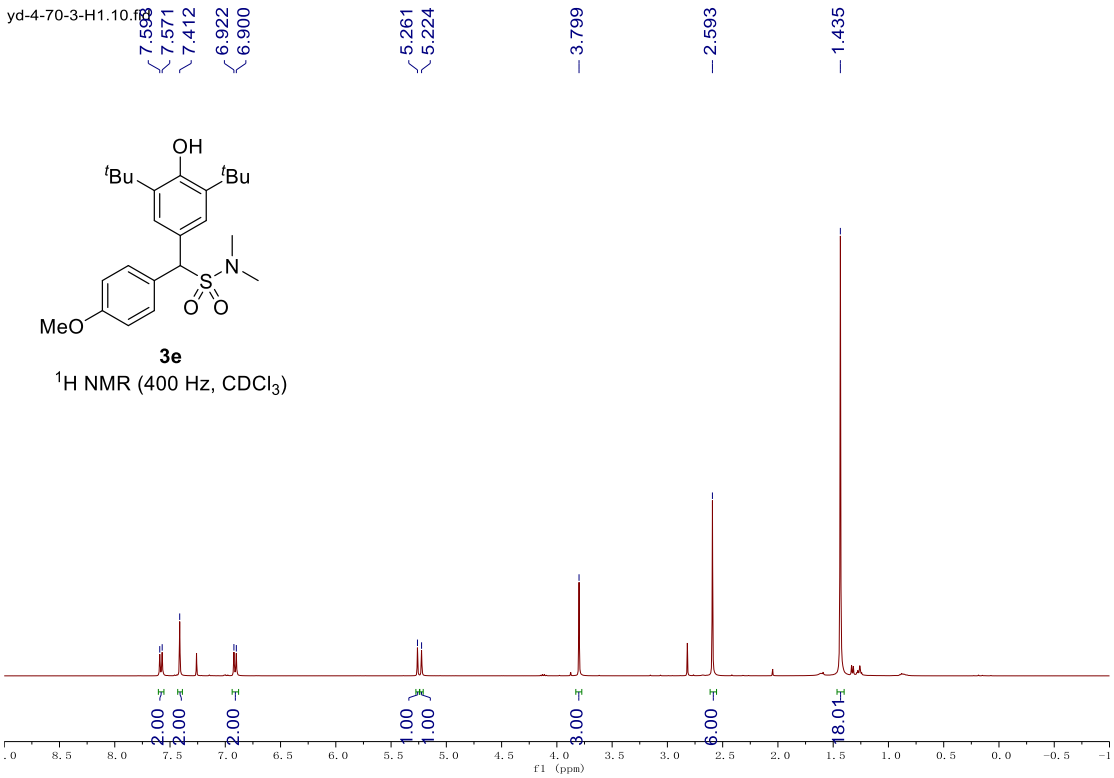
3d

^{1}H NMR (400 Hz, $CDCl_3$)



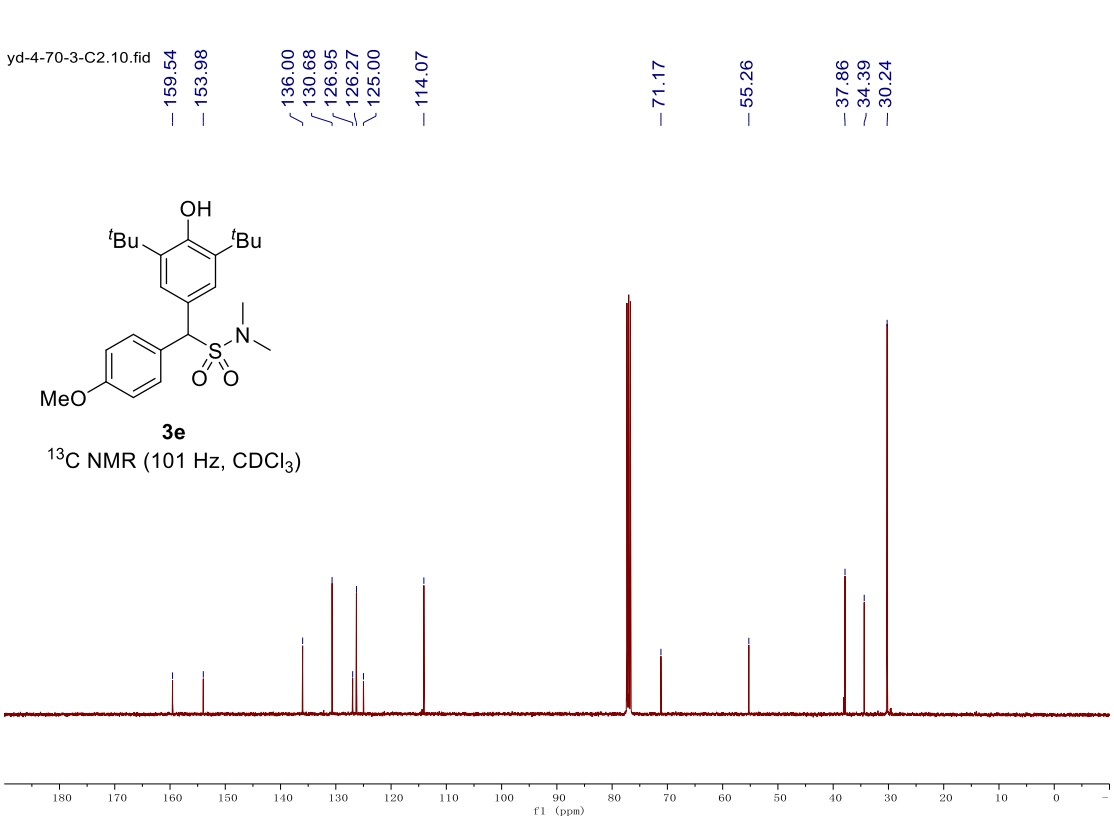
3d

^{13}C NMR (101 Hz, $CDCl_3$)



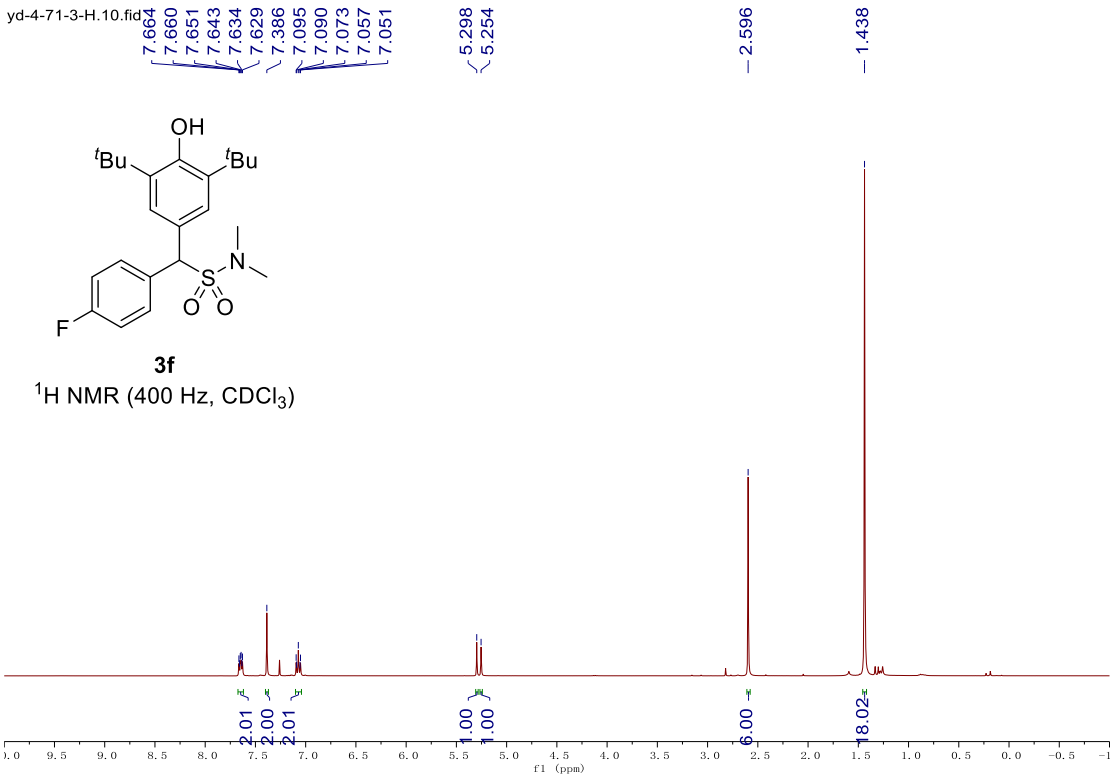
3e

^{1}H NMR (400 Hz, $CDCl_3$)



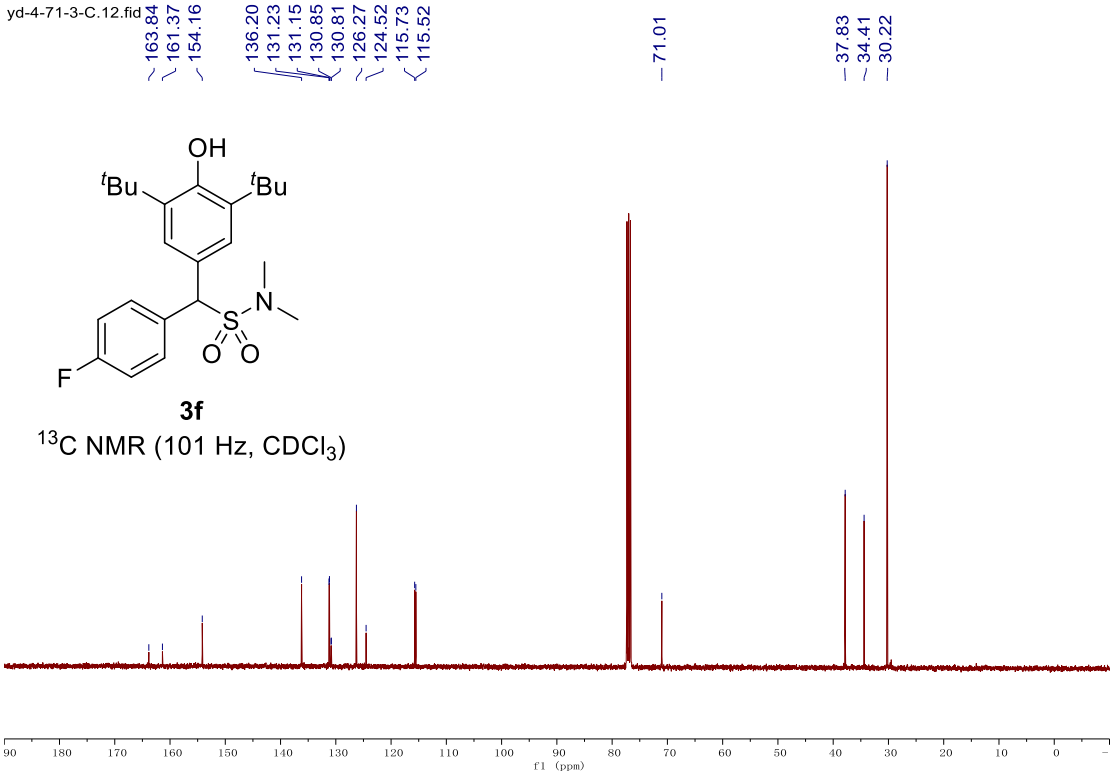
3e

^{13}C NMR (101 Hz, $CDCl_3$)



3f

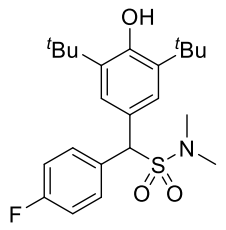
^{1}H NMR (400 Hz, $CDCl_3$)



3f

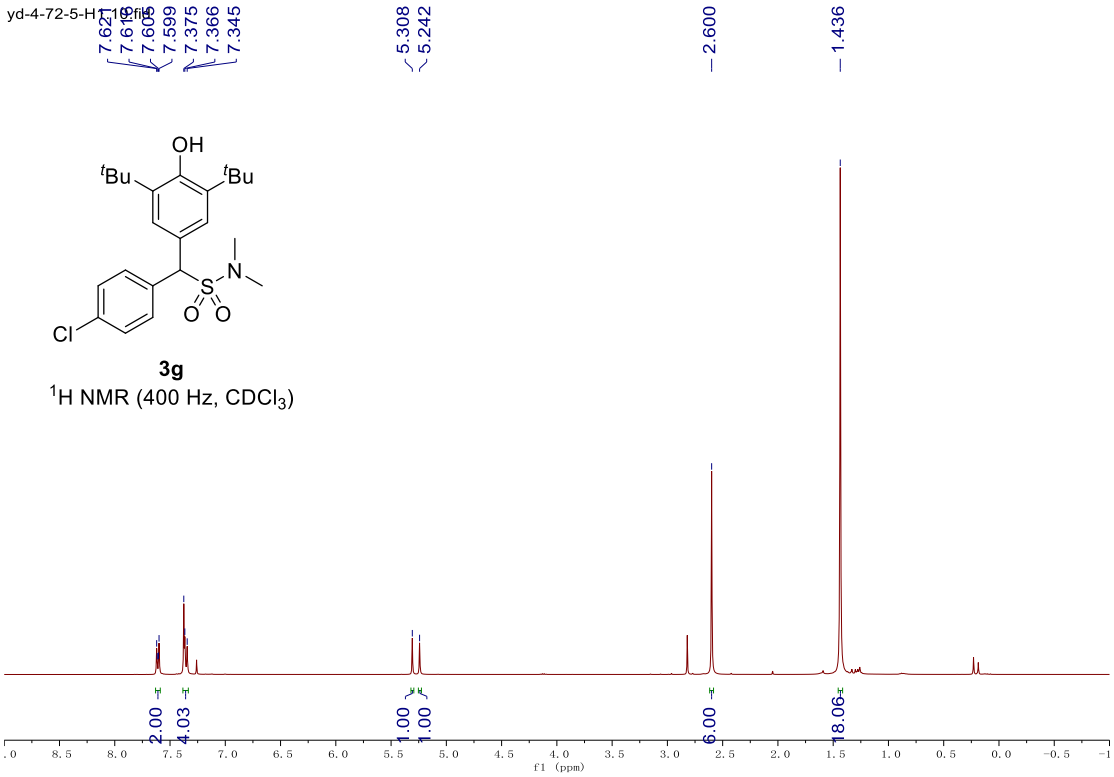
^{13}C NMR (101 Hz, $CDCl_3$)

yd-4-71-3-F.10.fid



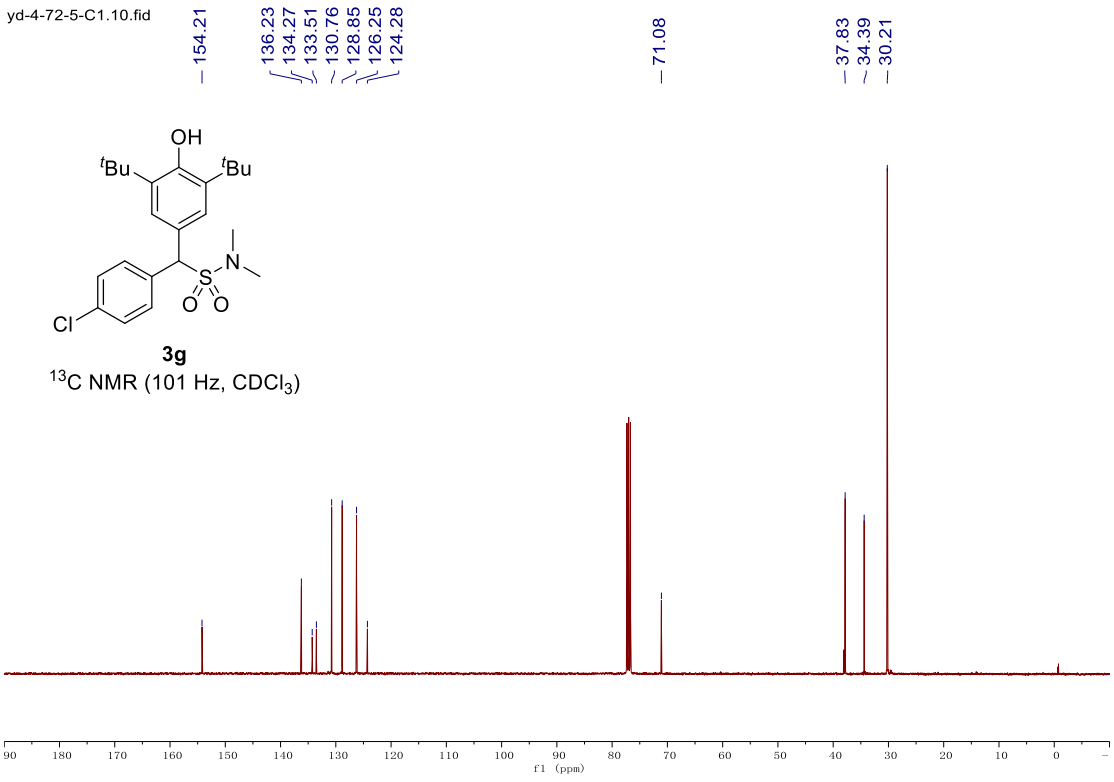
3f

^{19}F NMR (376 Hz, $CDCl_3$)



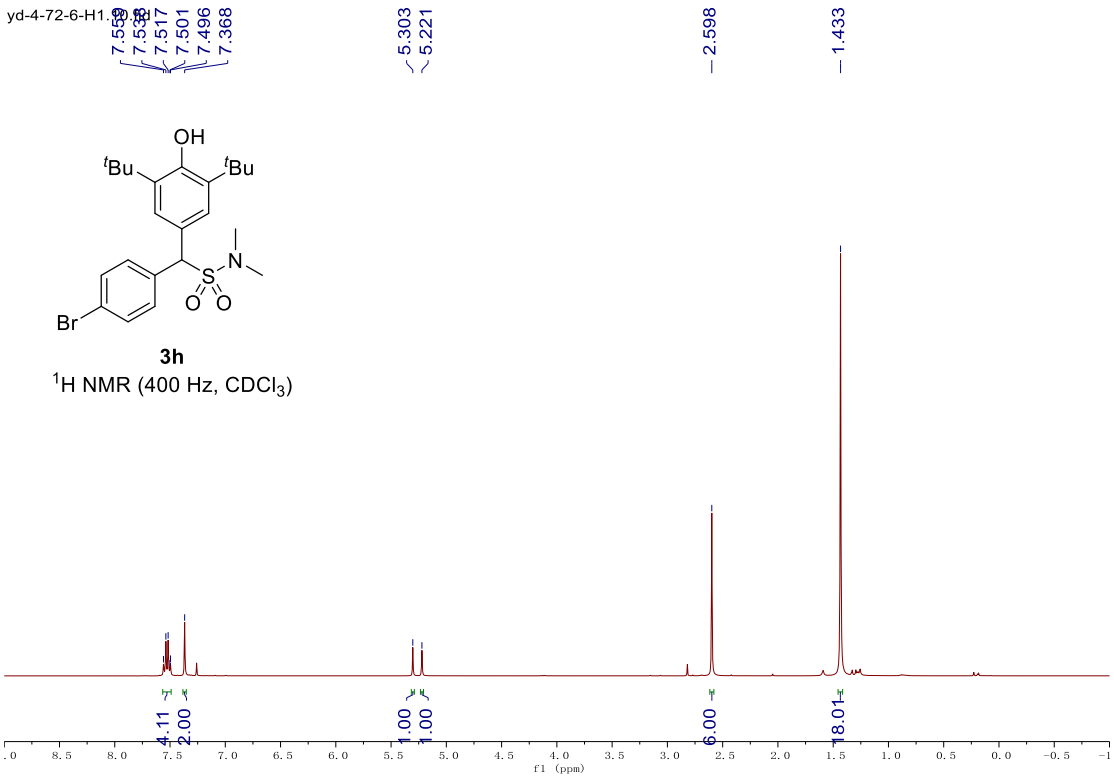
3g

^{1}H NMR (400 Hz, $CDCl_3$)



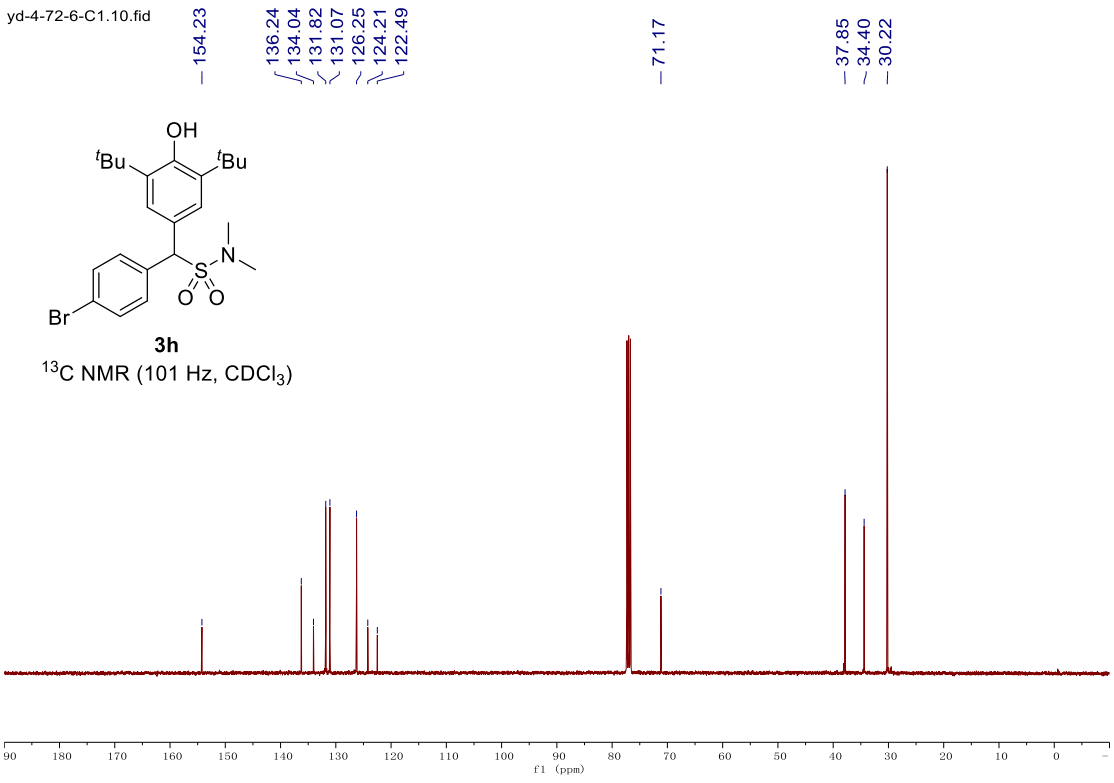
3g

^{13}C NMR (101 Hz, $CDCl_3$)



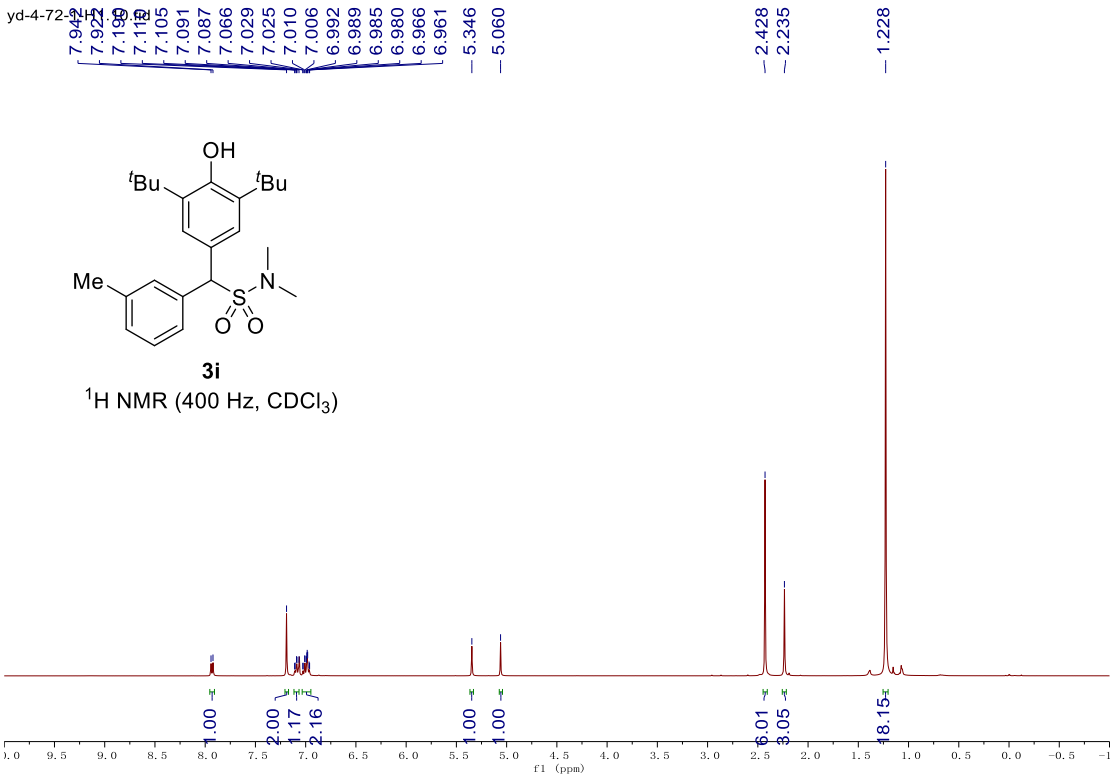
3h

^{1}H NMR (400 Hz, $CDCl_3$)



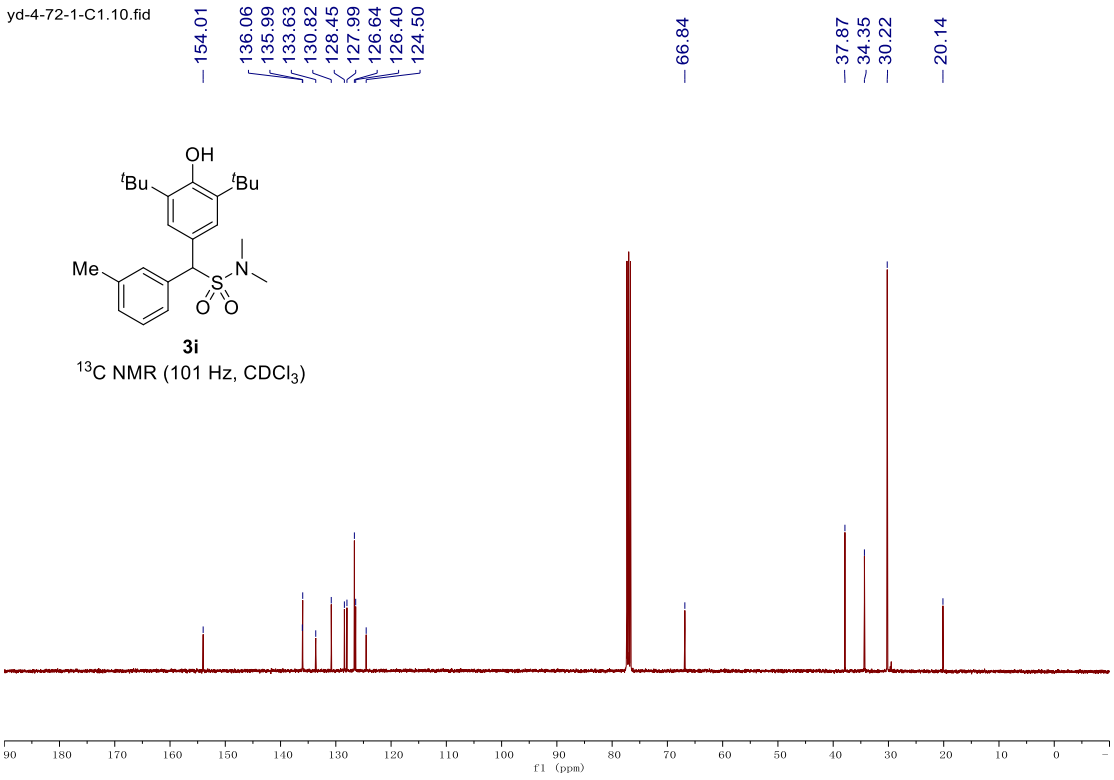
3h

^{13}C NMR (101 Hz, $CDCl_3$)



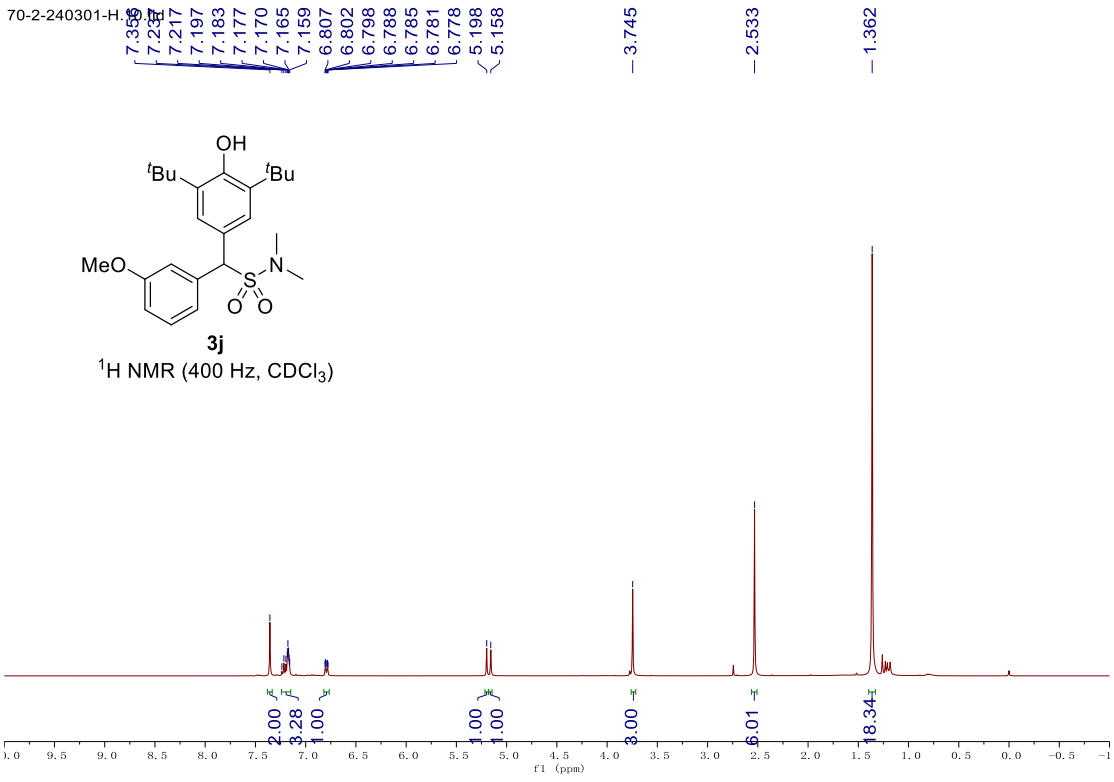
3i

^{1}H NMR (400 Hz, $CDCl_3$)



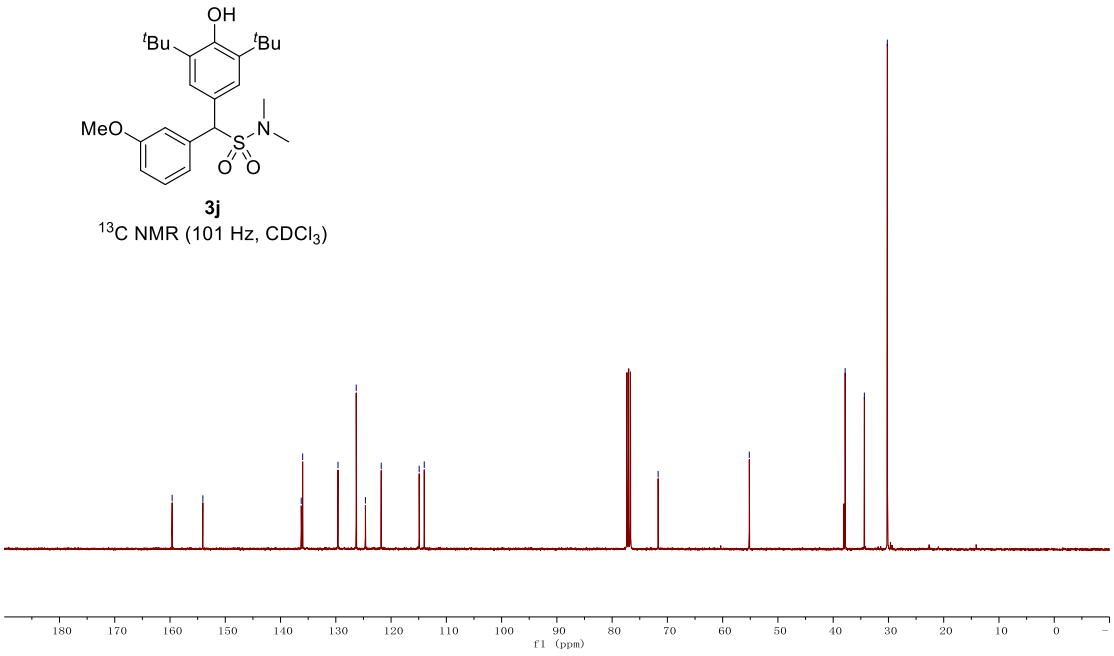
3i

^{13}C NMR (101 Hz, $CDCl_3$)



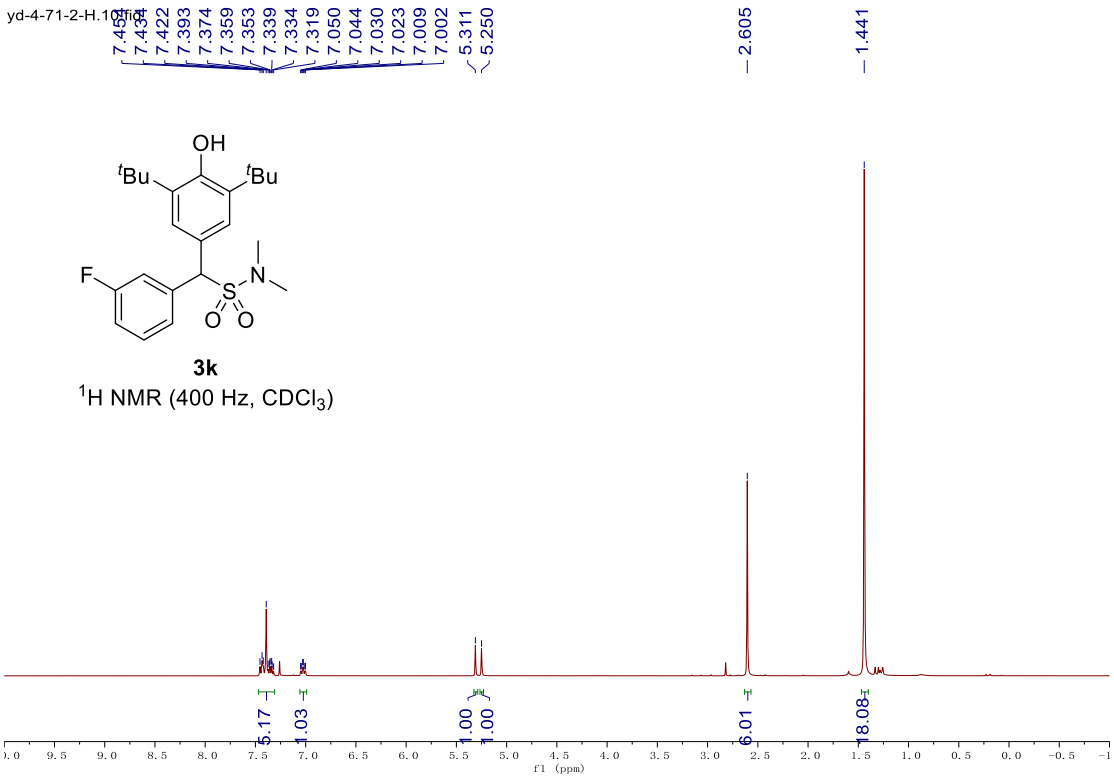
3j

^{1}H NMR (400 Hz, $CDCl_3$)



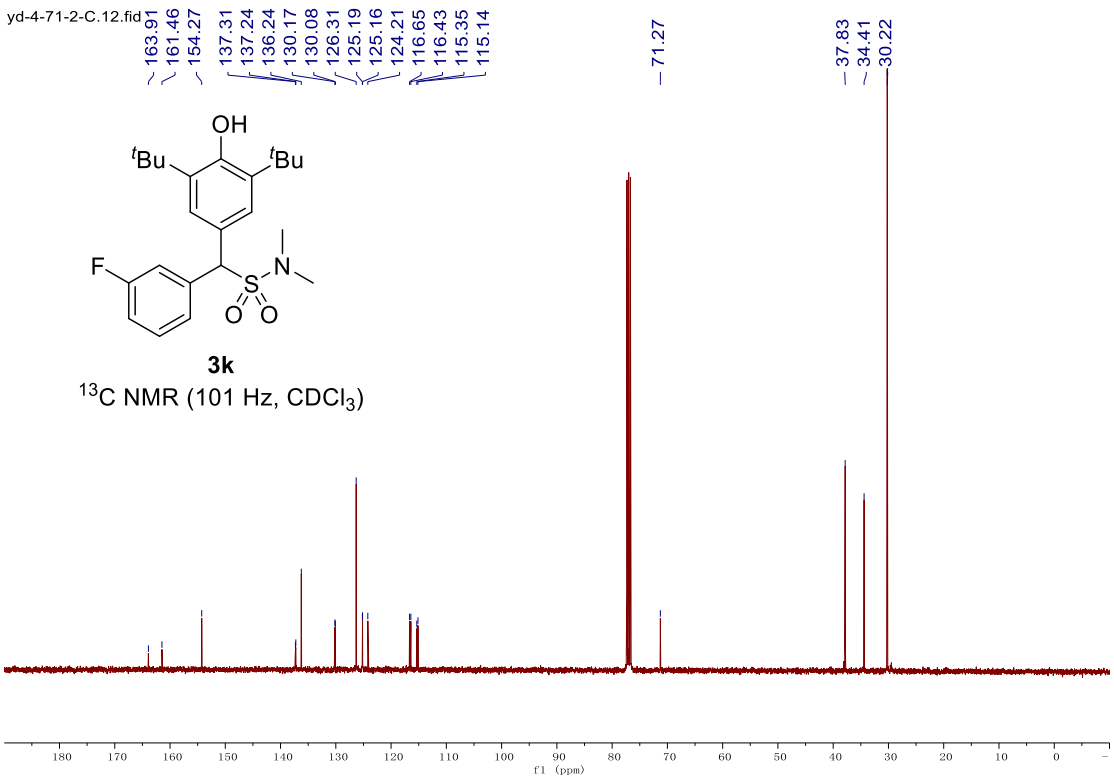
3j

^{13}C NMR (101 Hz, $CDCl_3$)



3k

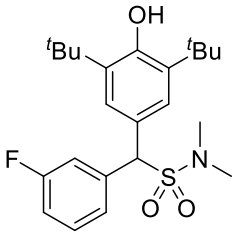
^{1}H NMR (400 Hz, $CDCl_3$)



3k

^{13}C NMR (101 Hz, $CDCl_3$)

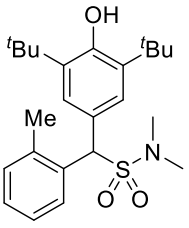
yd-4-71-2-F.10.fid



3k

^{19}F NMR (376 Hz, $CDCl_3$)

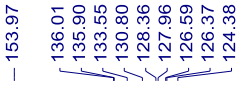
yd-4-68-2-H.10.fid

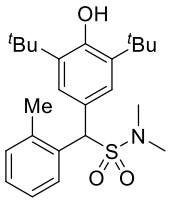


3l

^{1}H NMR (400 Hz, $CDCl_3$)

yd-4-68-2-C.12.fid

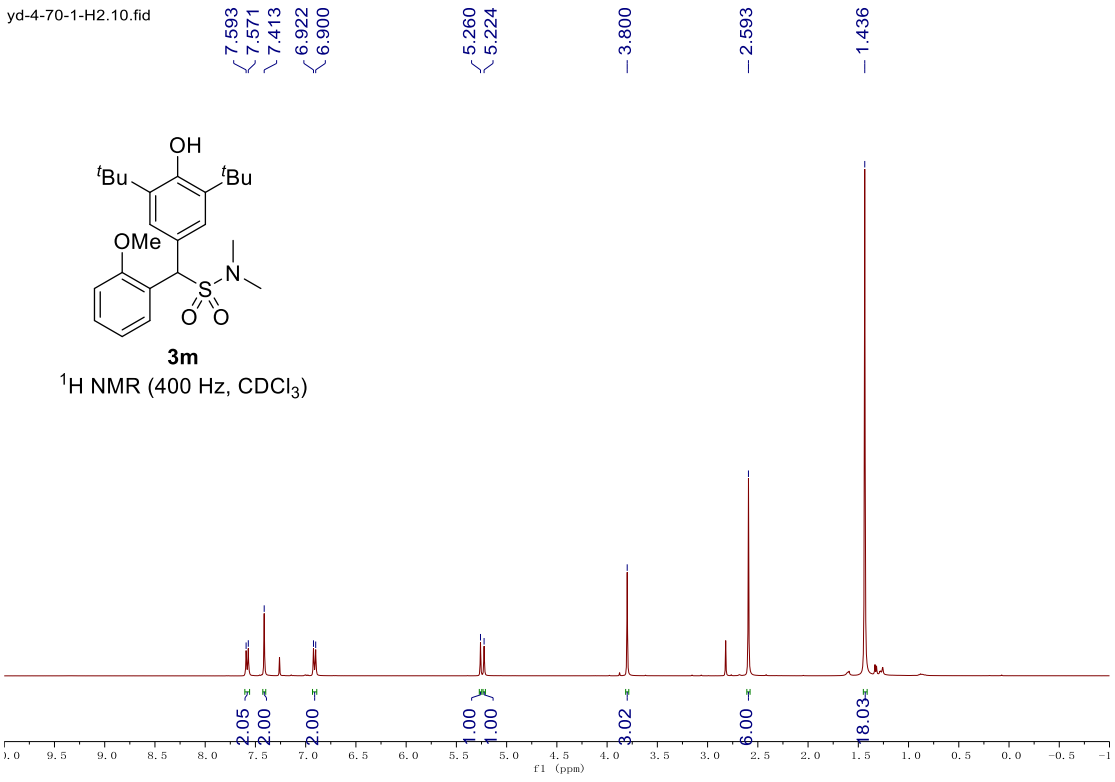




3l

^{13}C NMR (101 Hz, $CDCl_3$)

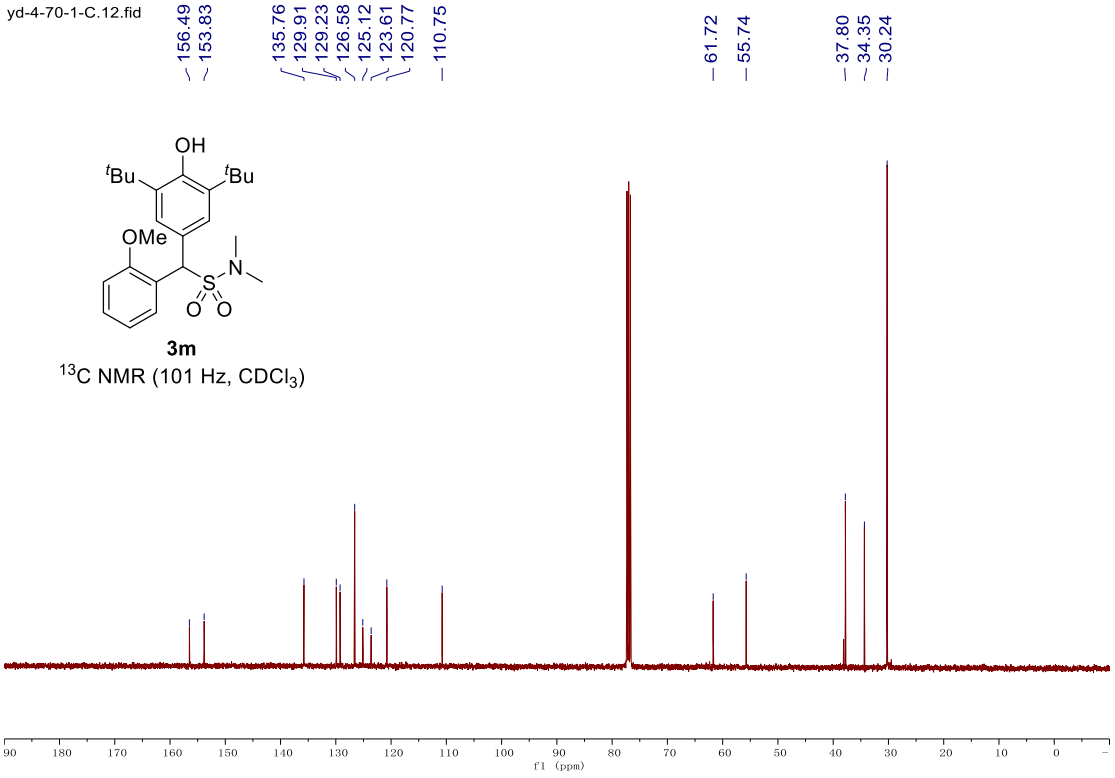
yd-4-70-1-H2.10.fid



3m

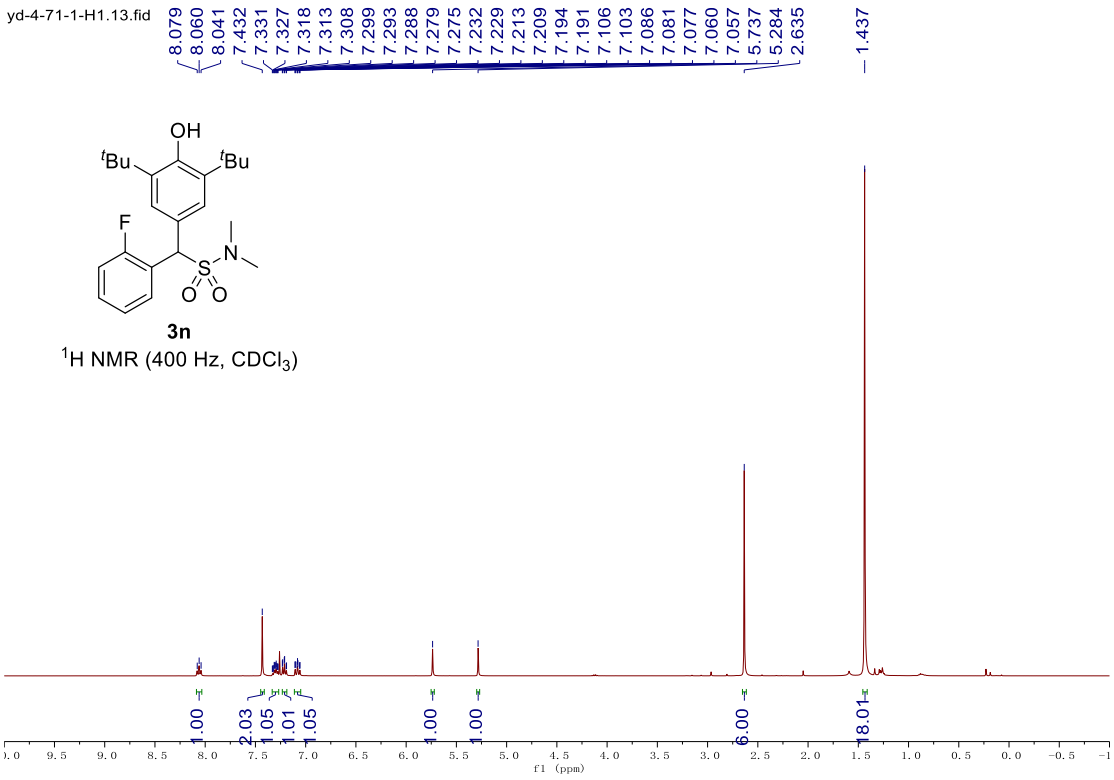
^{1}H NMR (400 Hz, $CDCl_3$)

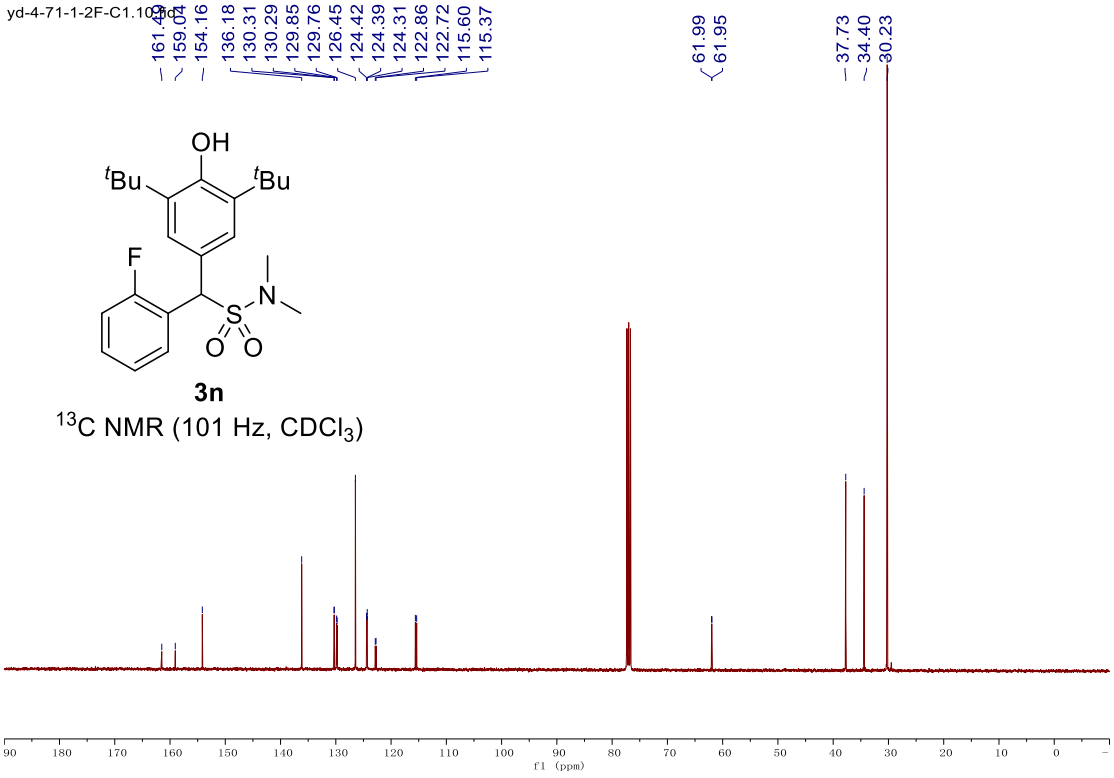
yd-4-70-1-C.12.fid



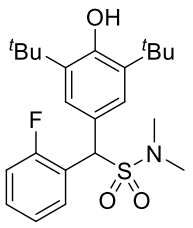
3m

^{13}C NMR (101 Hz, $CDCl_3$)


yd-4-71-1-H1.13.fid
8.079
8.060
8.041
7.432
7.331
7.327
7.318
7.313
7.308
7.299
7.293
7.288
7.279
7.275
7.232
7.229
7.213
7.209
7.194
7.191
7.106
7.103
7.086
7.081
7.077
7.060
7.057
5.737
5.284
2.635
1.437
OH
tBu
tBu
F
N
S
O
O
3n
1H NMR (400 Hz, CDCl3)
1.00
2.03
1.05
1.01
1.05
1.00
1.00
6.00
18.01
f1 (ppm)

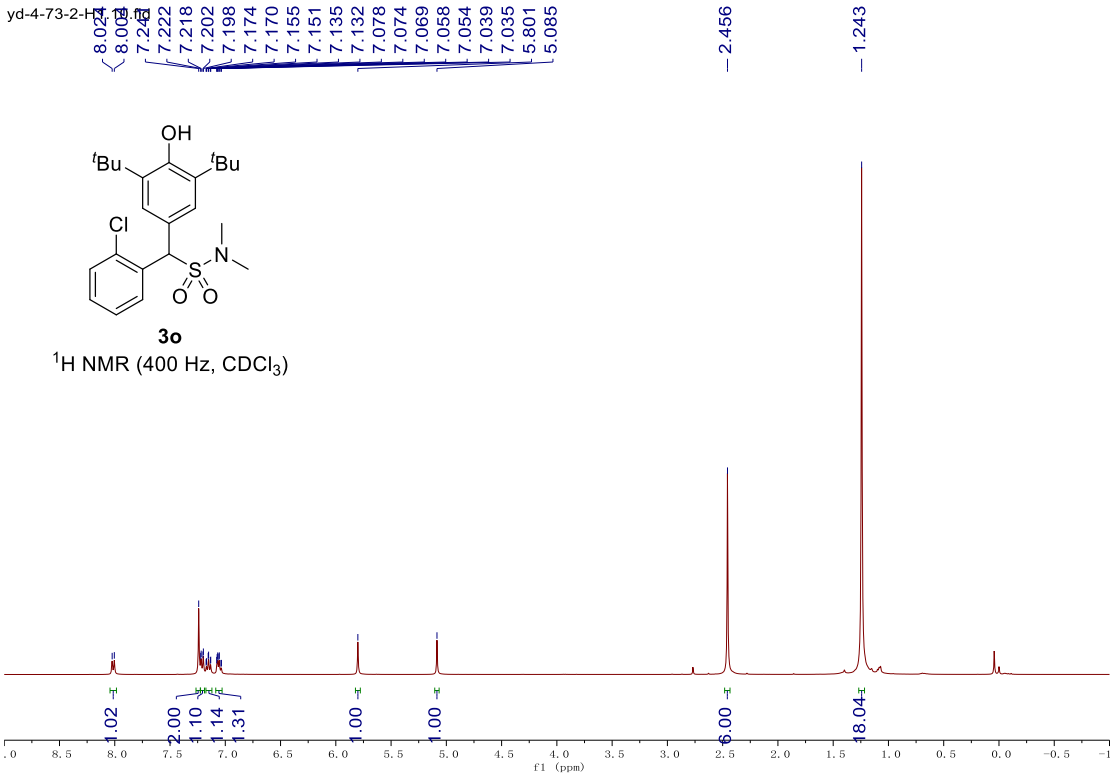

yd-4-71-1-2F-C1.10.fid
161.43
159.04
154.16
136.18
130.31
130.29
129.85
129.76
126.45
124.42
124.39
124.31
122.86
122.72
115.60
115.37
61.99
61.95
37.73
34.40
30.23
OH
tBu
tBu
F
N
S
O
O
3n
13C NMR (101 Hz, CDCl3)
f1 (ppm)

yd-4-71-1-F.10.fid



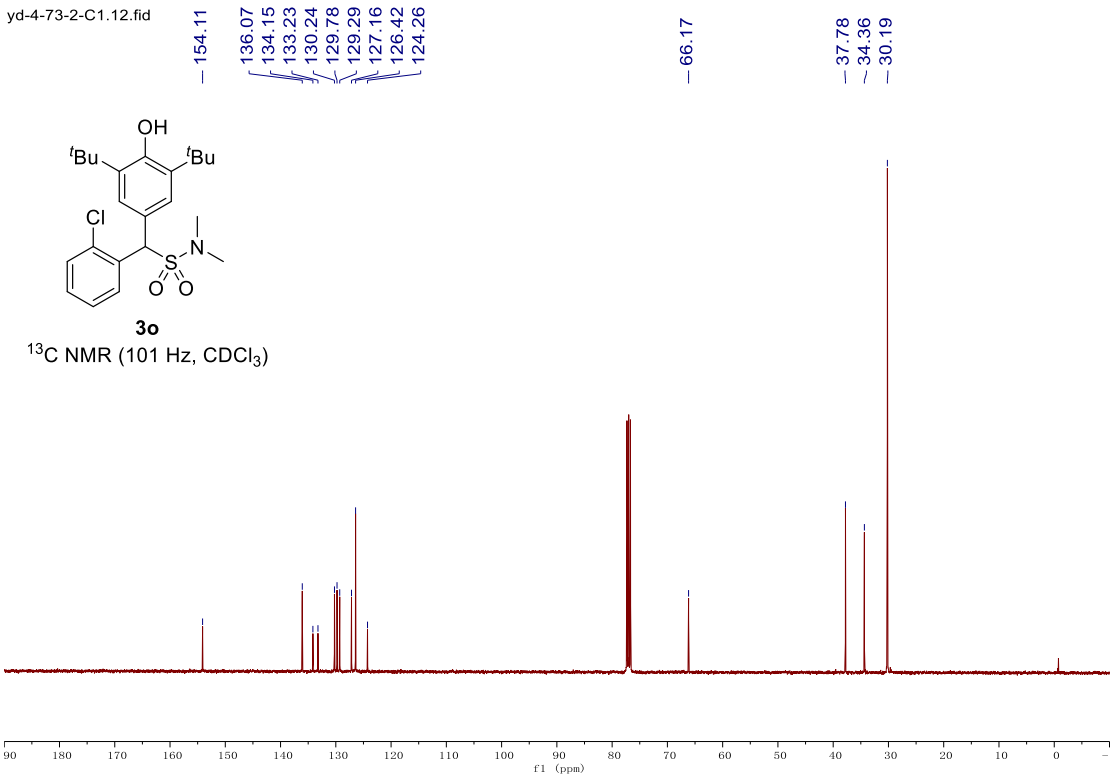
3n

^{19}F NMR (376 Hz, $CDCl_3$)



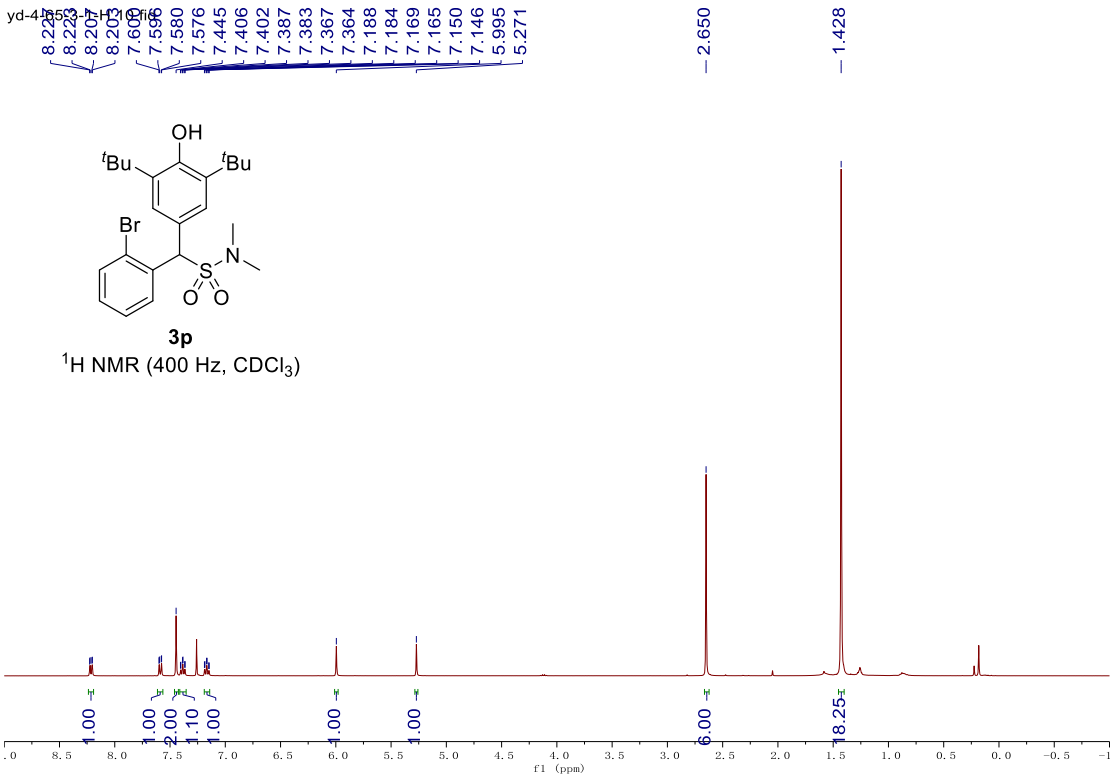
3o

^{1}H NMR (400 Hz, $CDCl_3$)



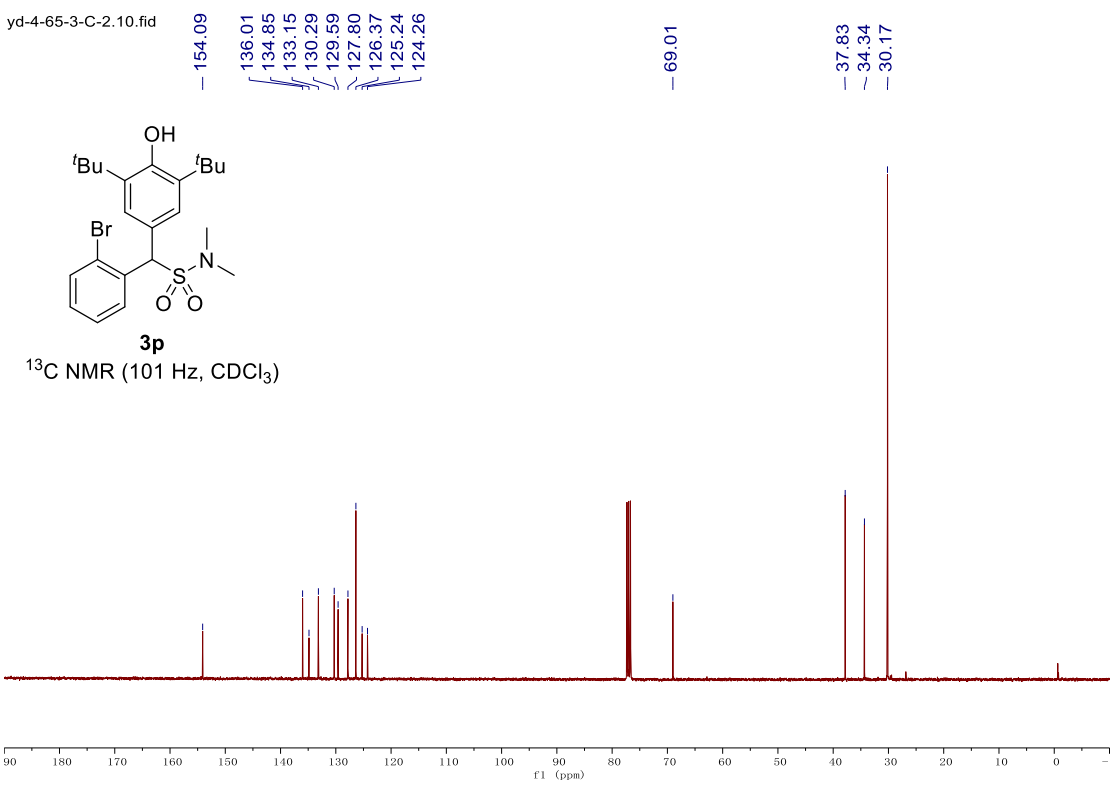
3o

^{13}C NMR (101 Hz, $CDCl_3$)



3p

^{1}H NMR (400 Hz, $CDCl_3$)

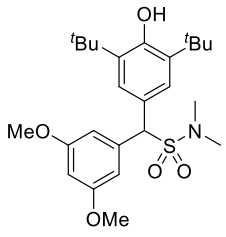


3p

^{13}C NMR (101 Hz, $CDCl_3$)

yd-4-67-4-H.10.fid

7.430 6.854 6.848 6.424 6.419 6.413 5.282 5.175 3.801 2.624 1.435

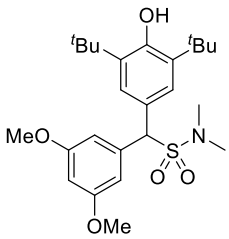


3q

^{1}H NMR (400 Hz, $CDCl_3$)

yd-4-67-4-C.12.fid

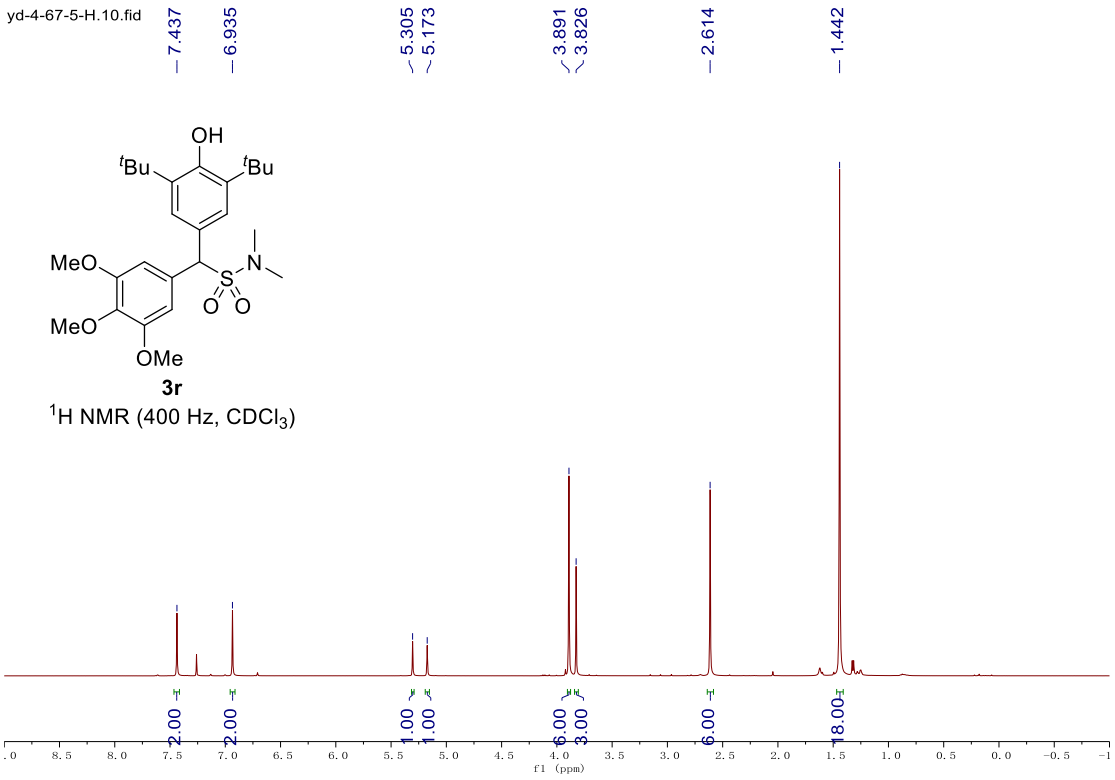
160.72 154.10 136.86 135.95 126.31 124.53 107.49 100.41 71.68 55.33 37.90 34.37 30.21



3q

^{13}C NMR (101 Hz, $CDCl_3$)

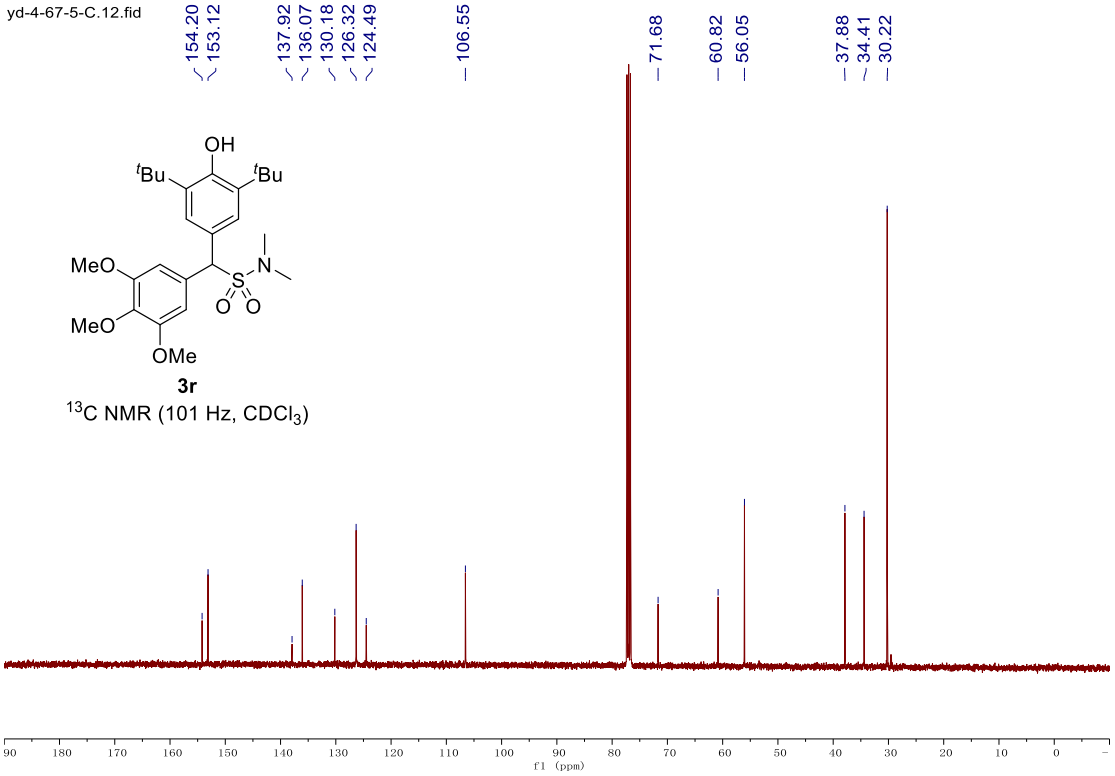
yd-4-67-5-H.10.fid



3r

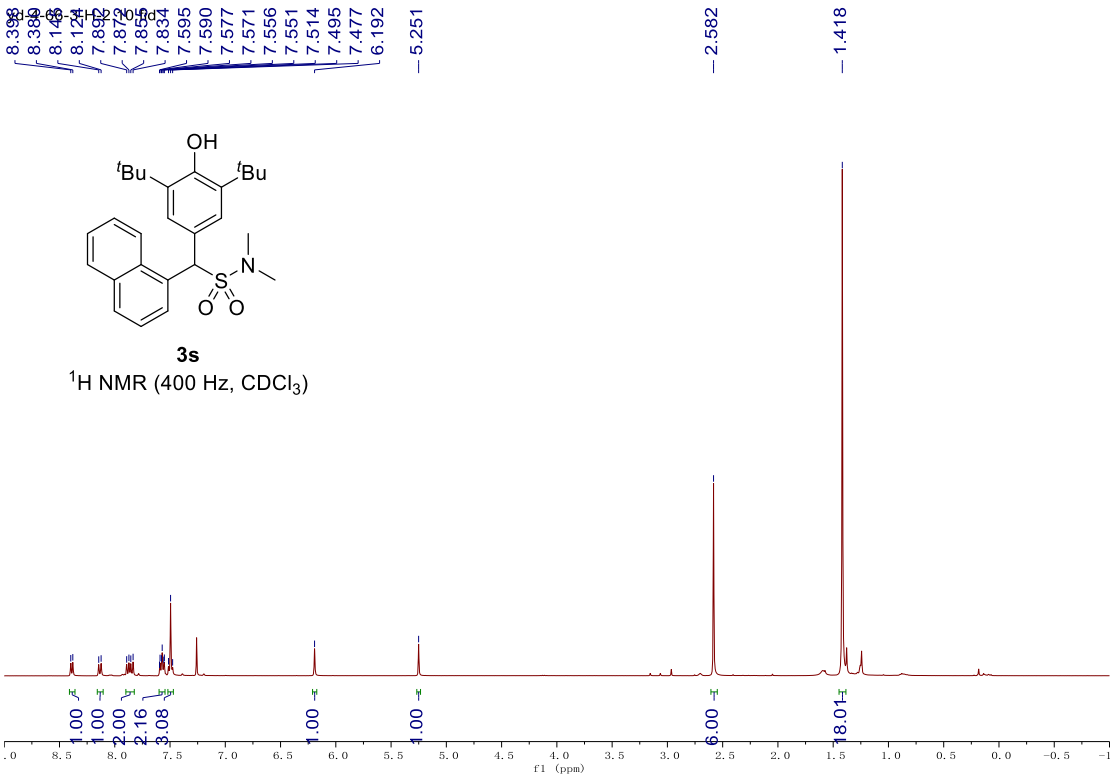
^{1}H NMR (400 Hz, $CDCl_3$)

yd-4-67-5-C.12.fid



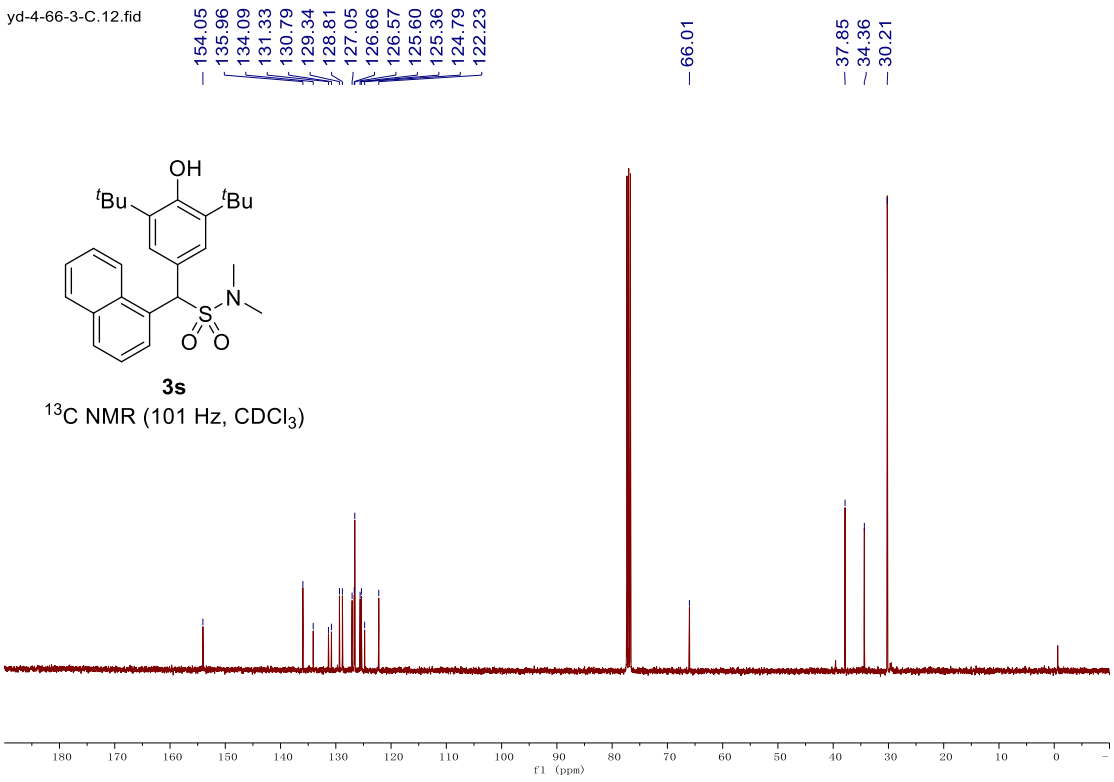
3r

^{13}C NMR (101 Hz, $CDCl_3$)



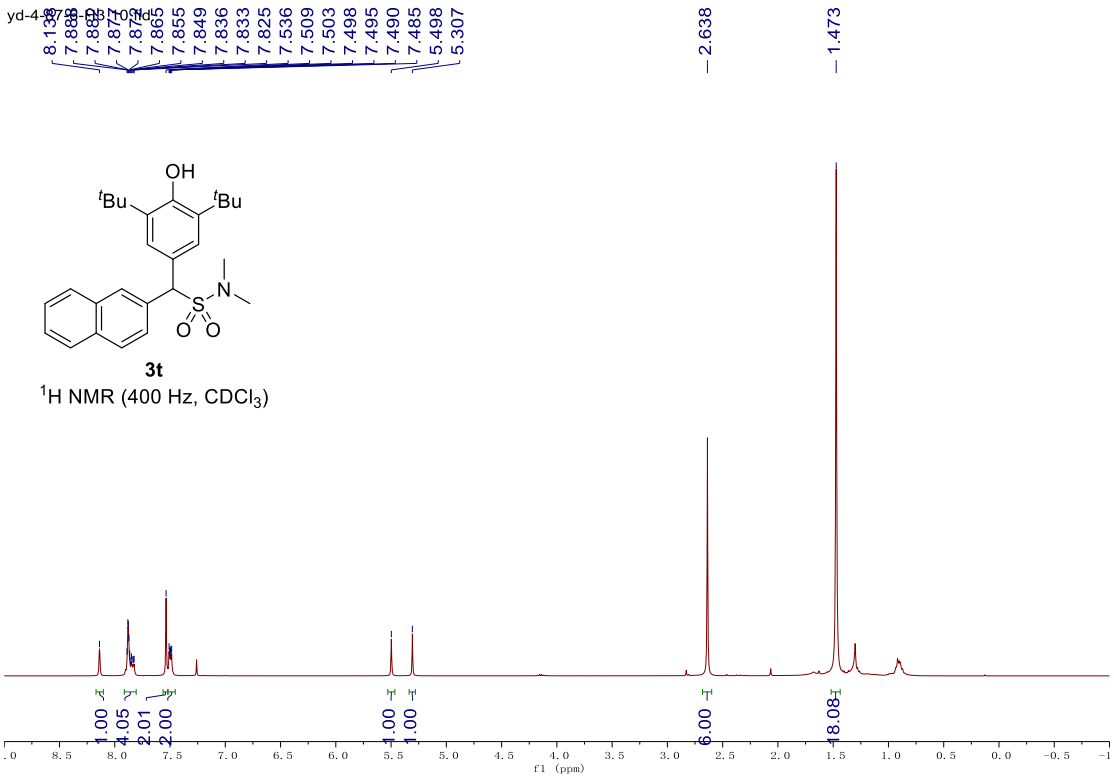
3s

^{1}H NMR (400 Hz, $CDCl_3$)



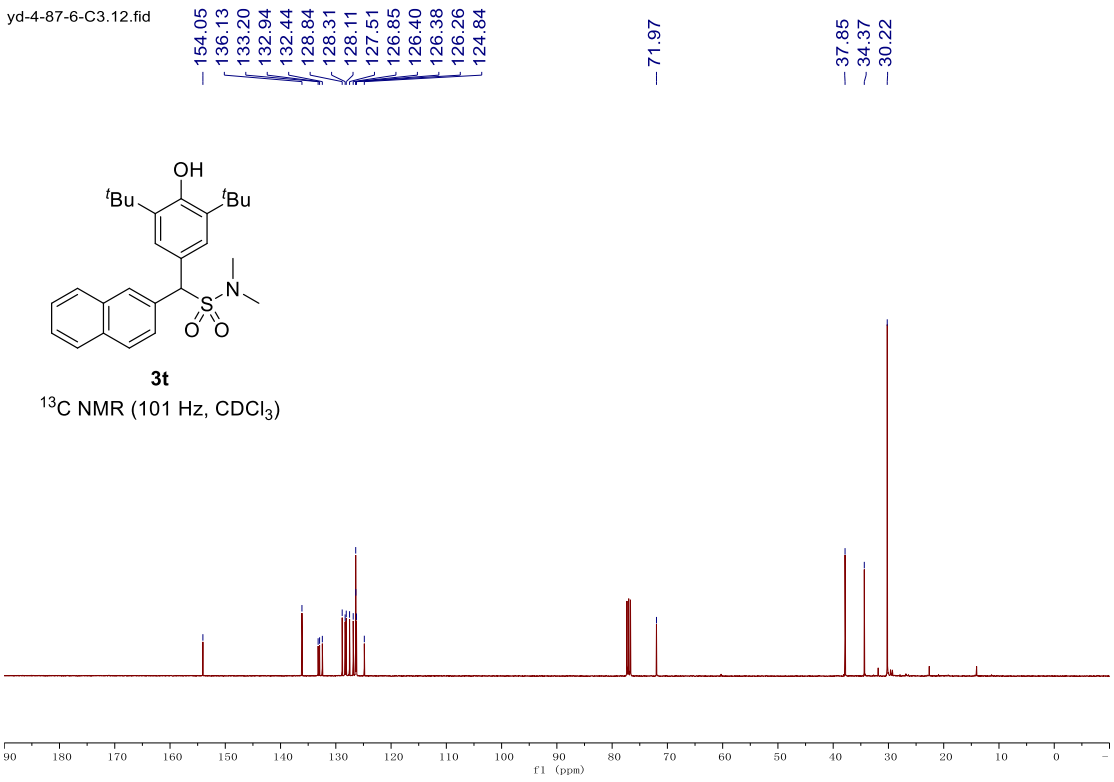
3s

^{13}C NMR (101 Hz, $CDCl_3$)



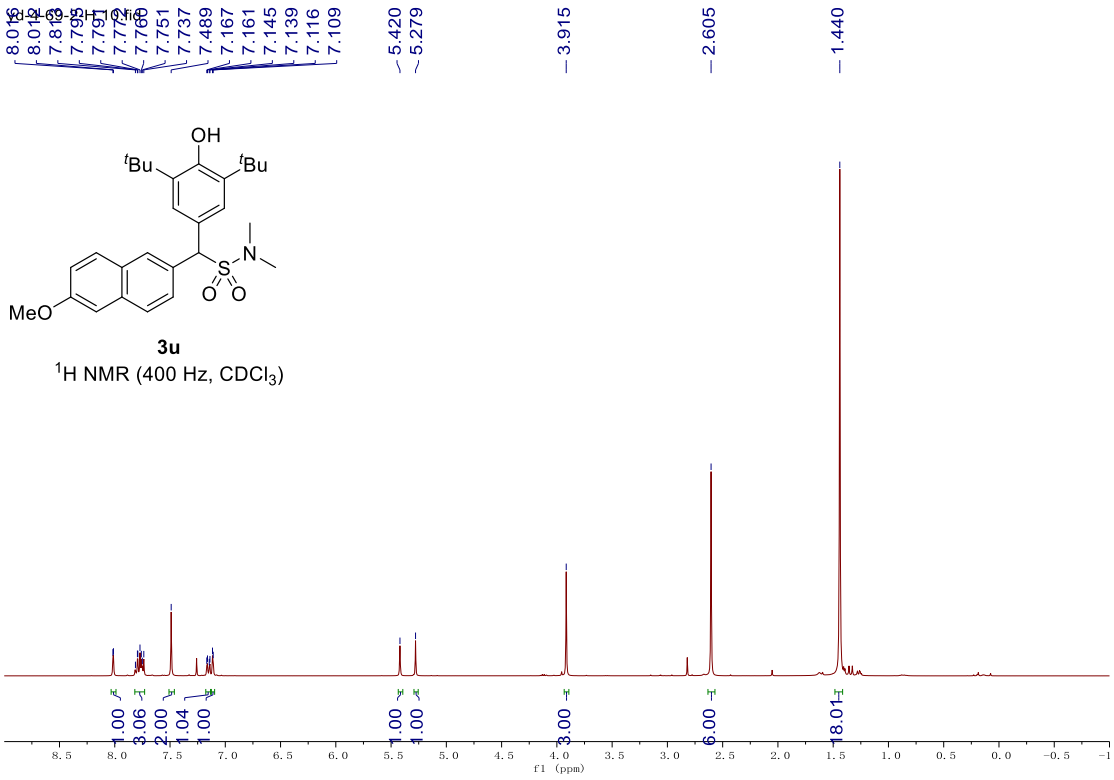
3t

^{1}H NMR (400 Hz, $CDCl_3$)



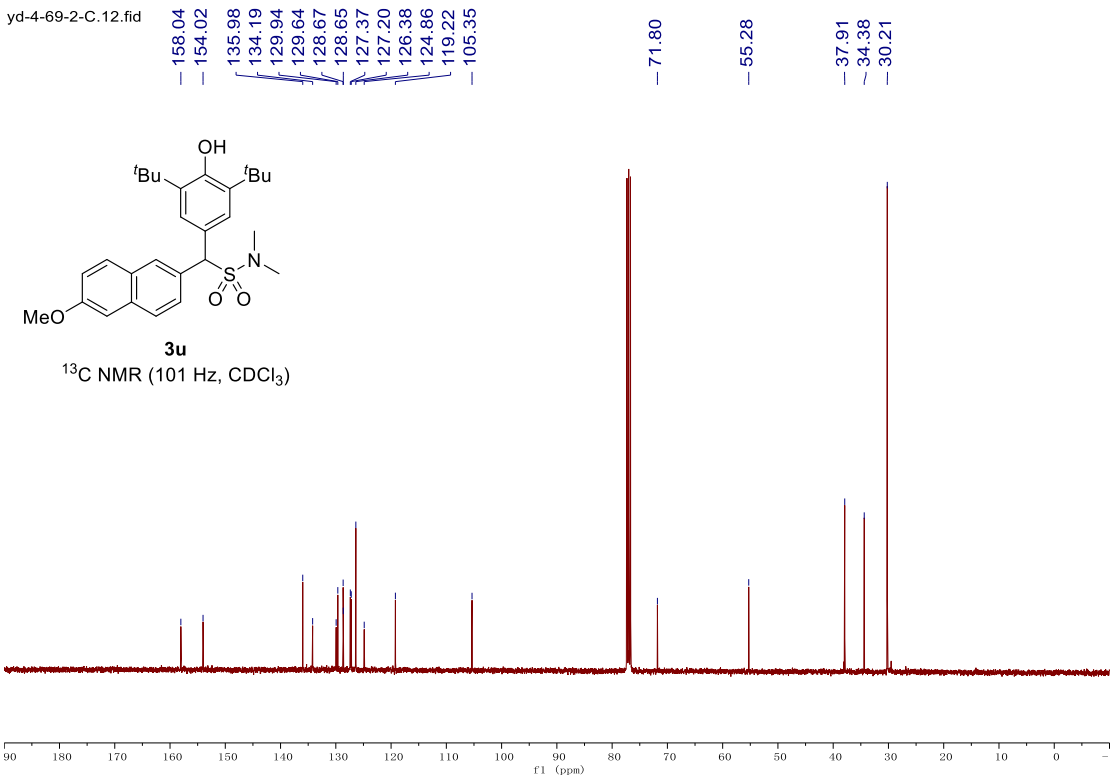
3t

^{13}C NMR (101 Hz, $CDCl_3$)



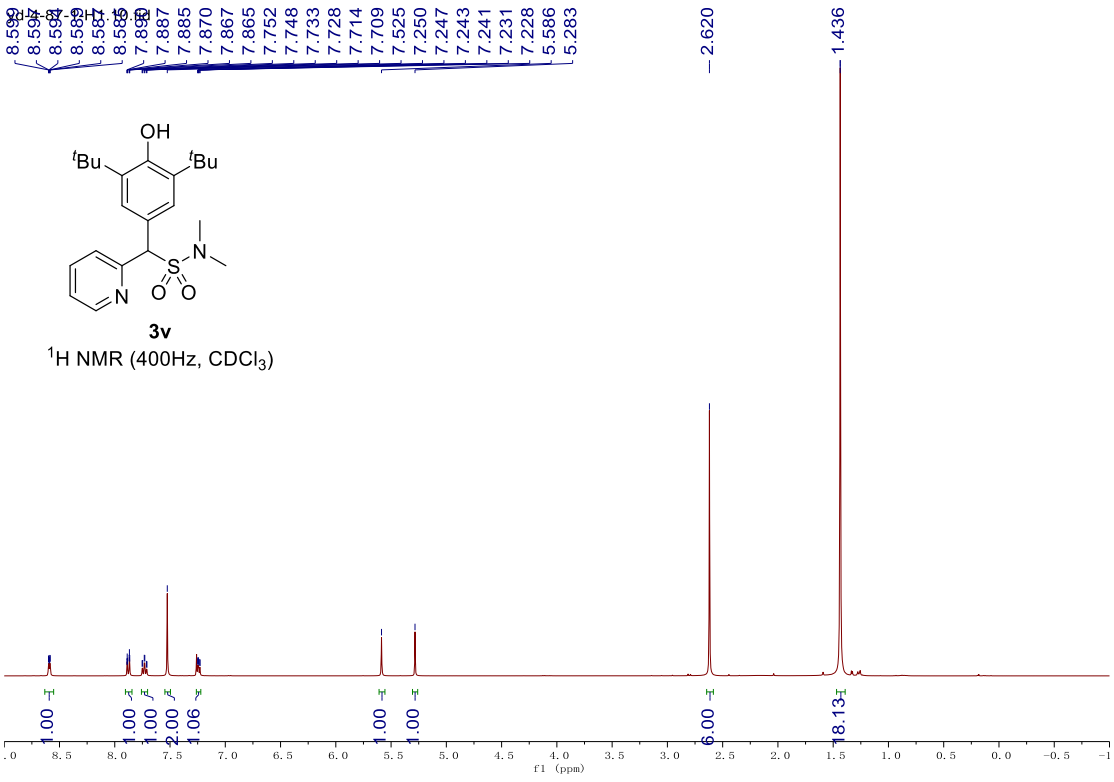
3u

^{1}H NMR (400 Hz, $CDCl_3$)



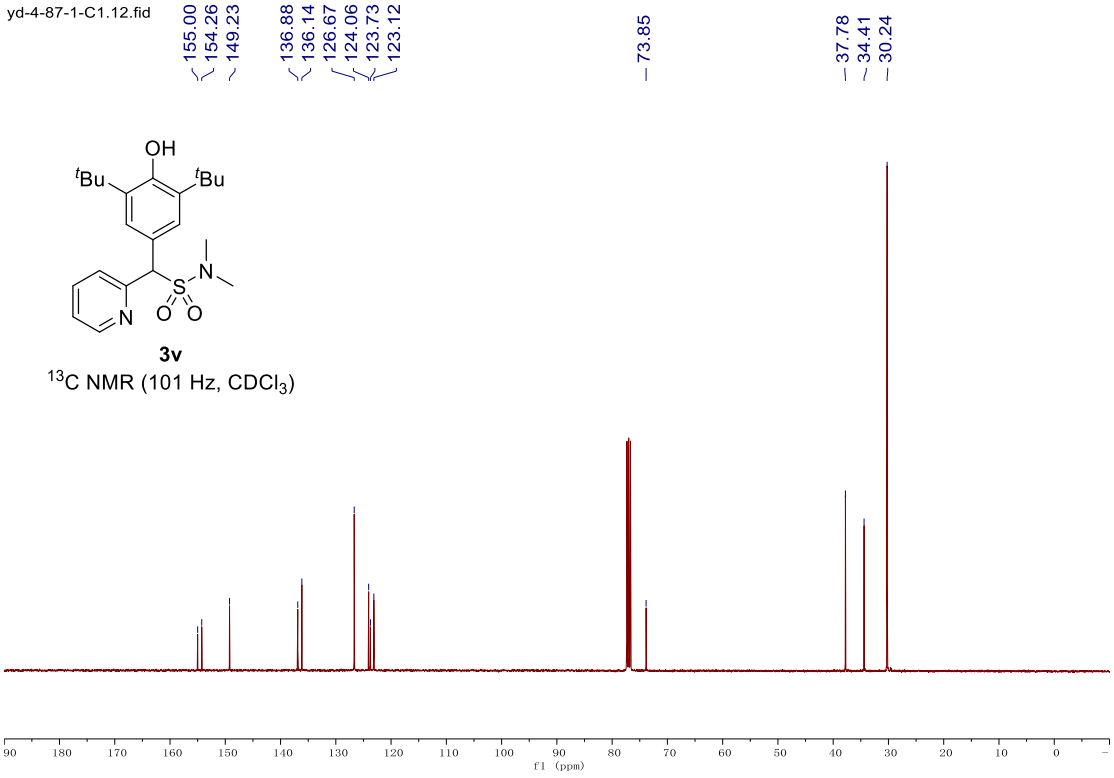
3u

^{13}C NMR (101 Hz, $CDCl_3$)



3v

^{1}H NMR (400Hz, $CDCl_3$)

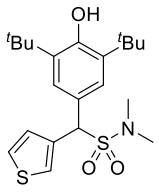


3v

^{13}C NMR (101 Hz, $CDCl_3$)

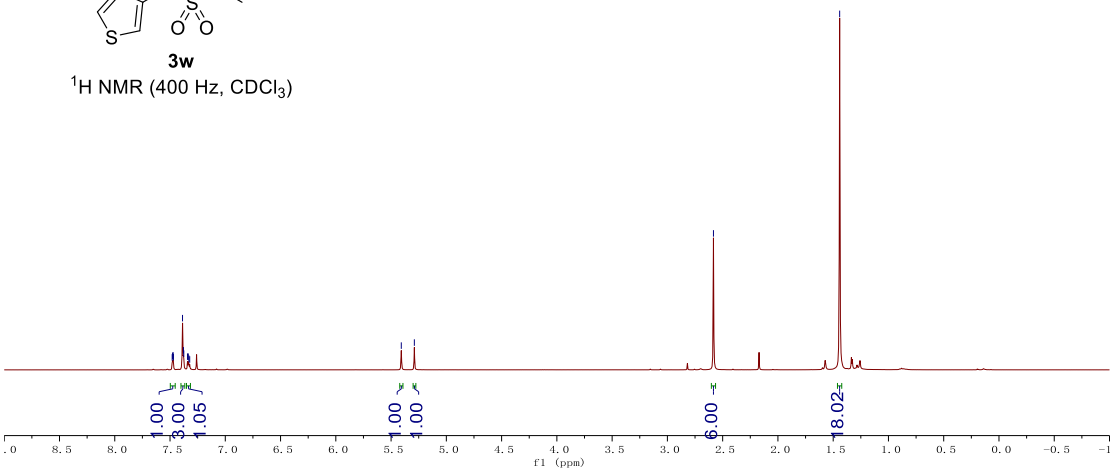
yd-4-82-1-H1.12.fid

7.480 7.477 7.472 7.469 7.387 7.379 7.375 7.342 7.335 7.329 7.322 5.408 5.289 2.583 1.441



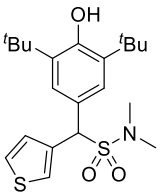
3w

^{1}H NMR (400 Hz, $CDCl_3$)



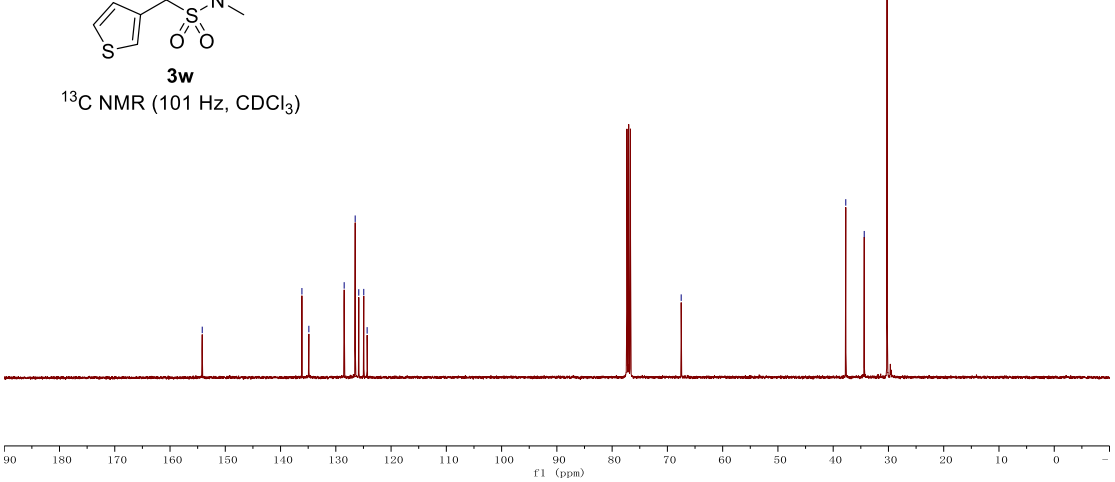
yd-4-82-1-C1.12.fid

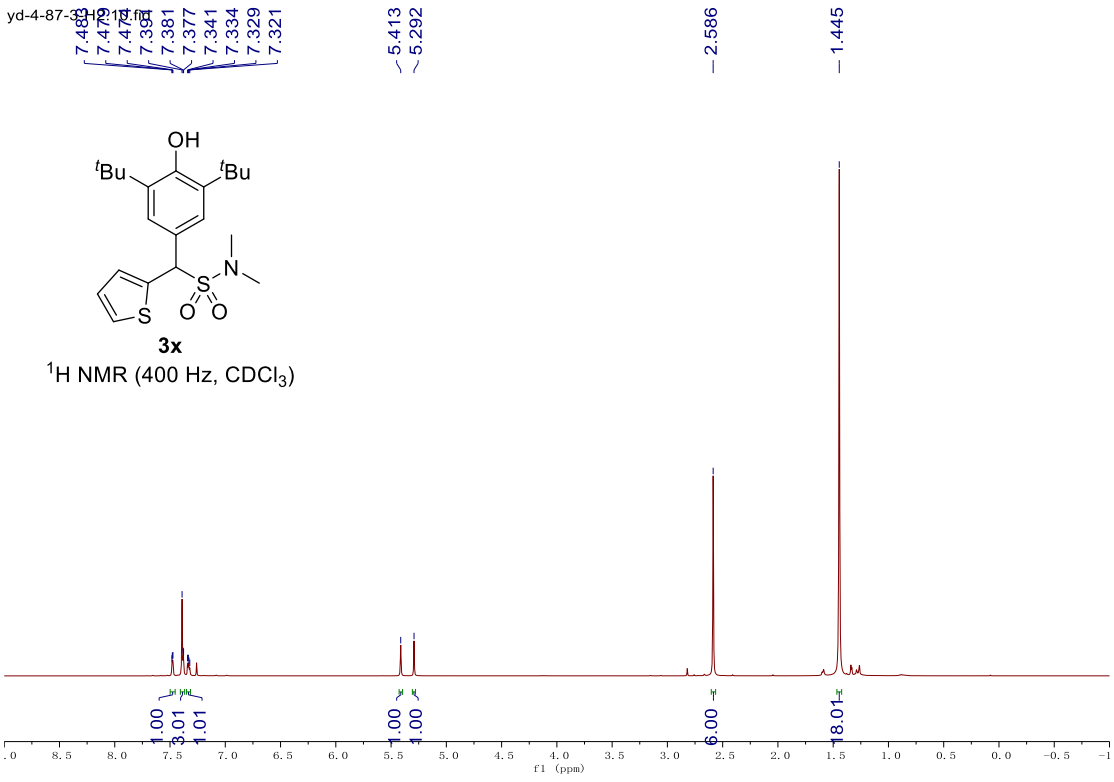
154.17 136.13 134.88 128.49 126.50 125.84 124.94 124.33 67.50 37.72 34.38 30.24



3w

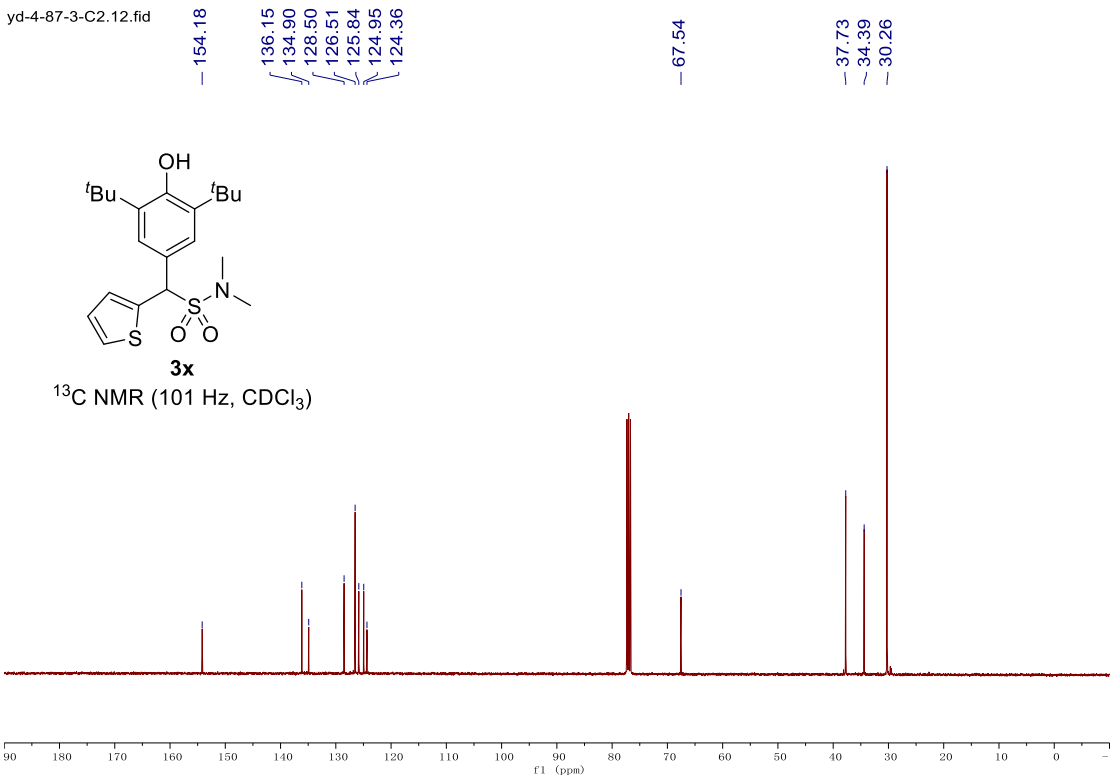
^{13}C NMR (101 Hz, $CDCl_3$)





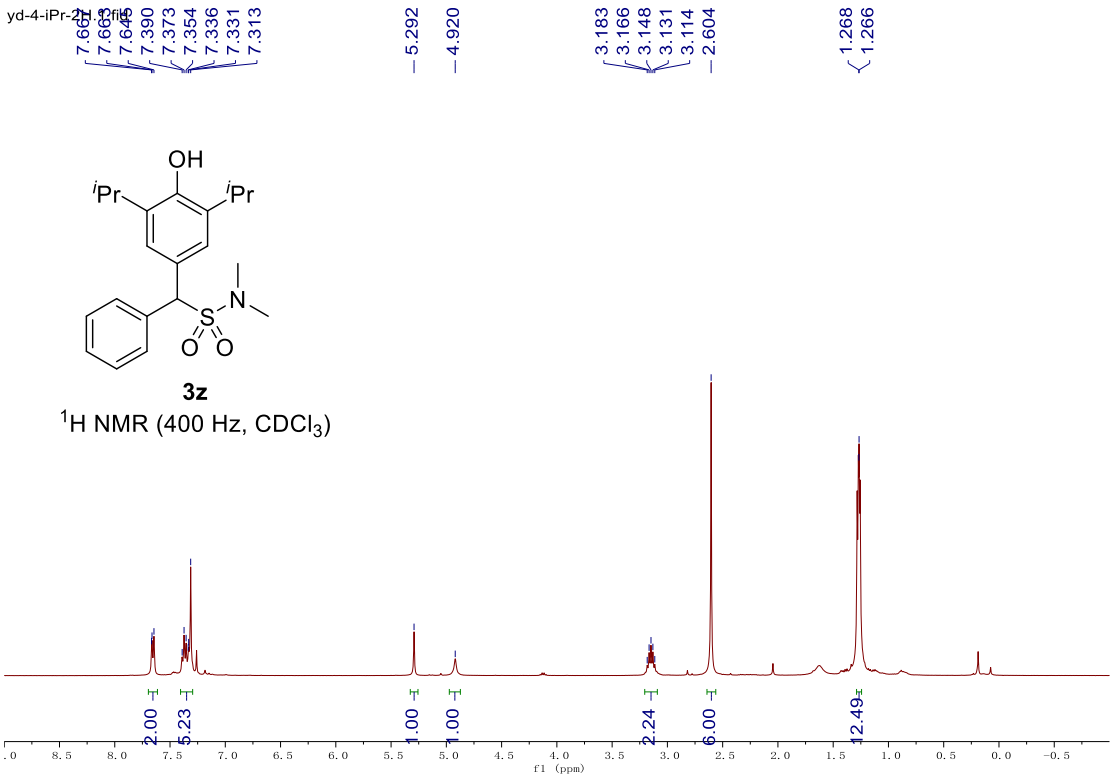
3x

^{1}H NMR (400 Hz, $CDCl_3$)



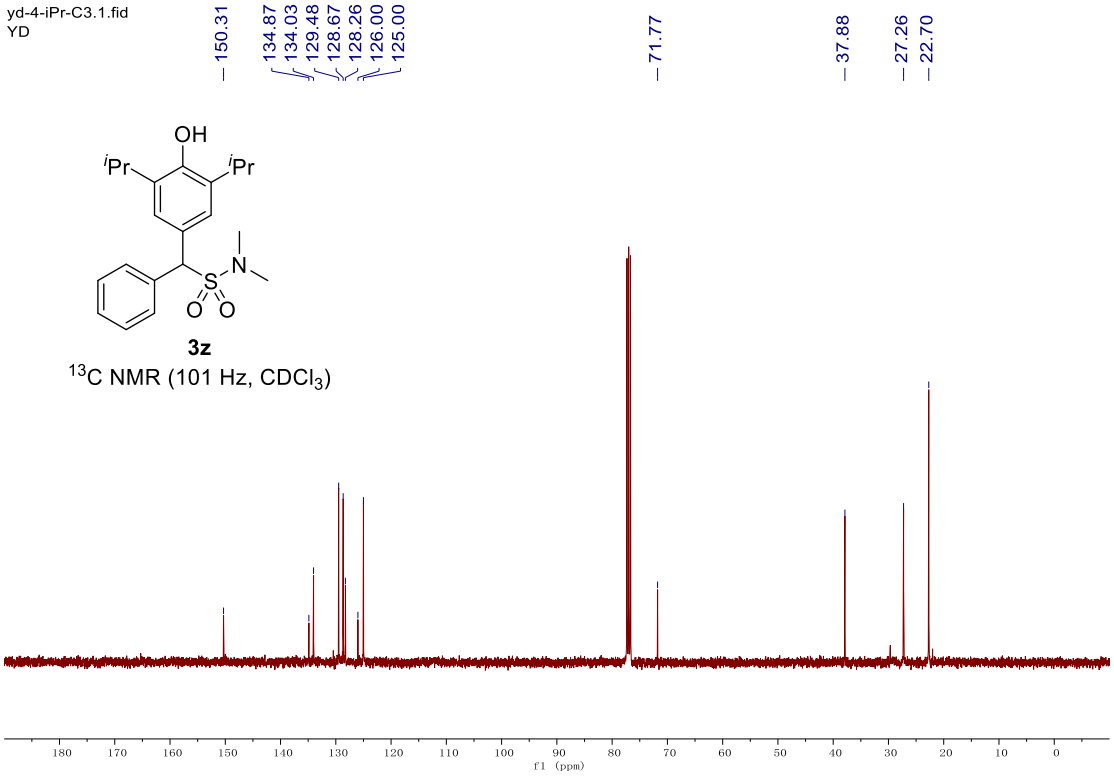
3x

^{13}C NMR (101 Hz, $CDCl_3$)



3z

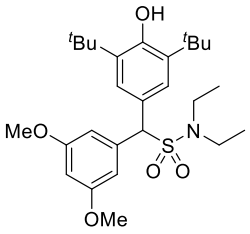
^{1}H NMR (400 Hz, $CDCl_3$)



3z

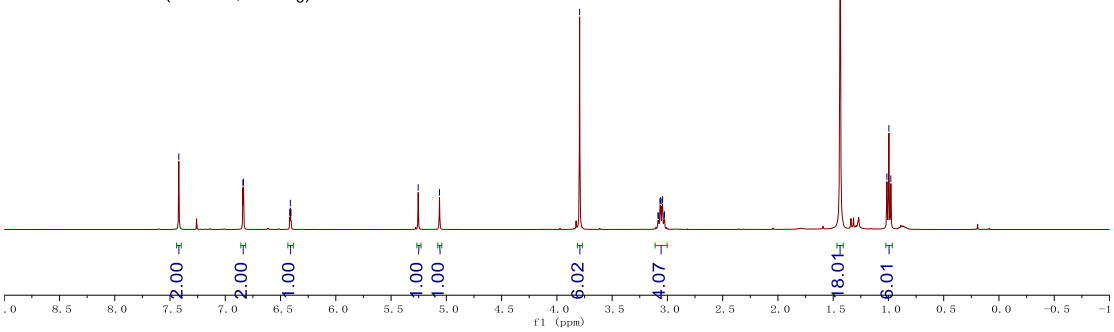
^{13}C NMR (101 Hz, $CDCl_3$)

yd-4-75-8-H1.10.fid

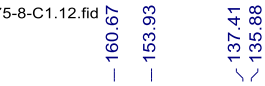


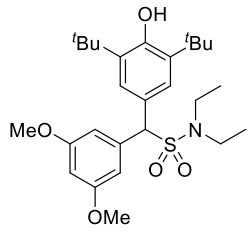
4a

^{1}H NMR (400 Hz, $CDCl_3$)



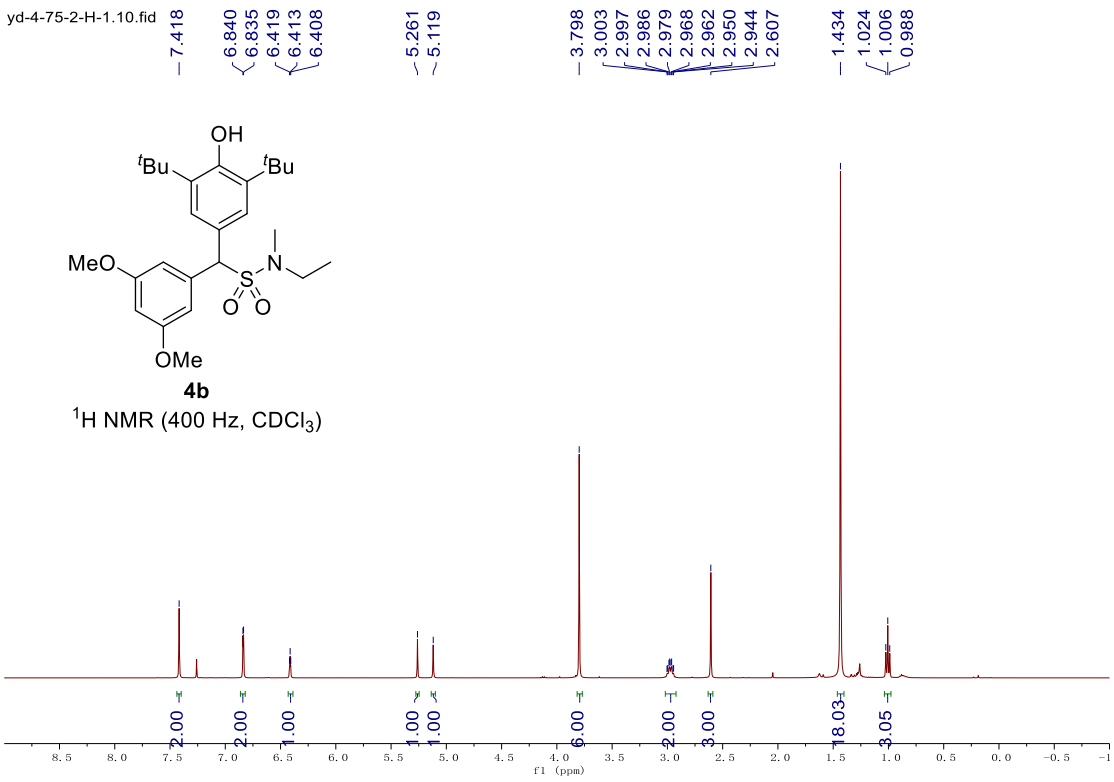
yd-4-75-8-C1.12.fid





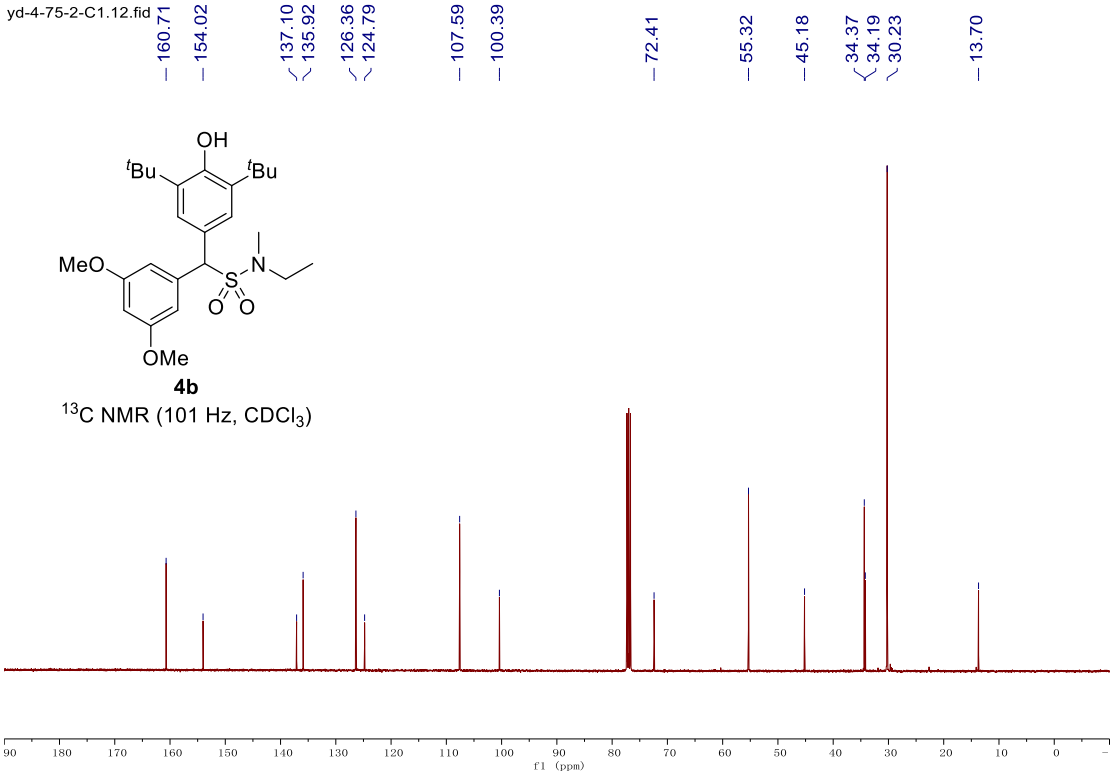
4a

^{13}C NMR (101 Hz, $CDCl_3$)



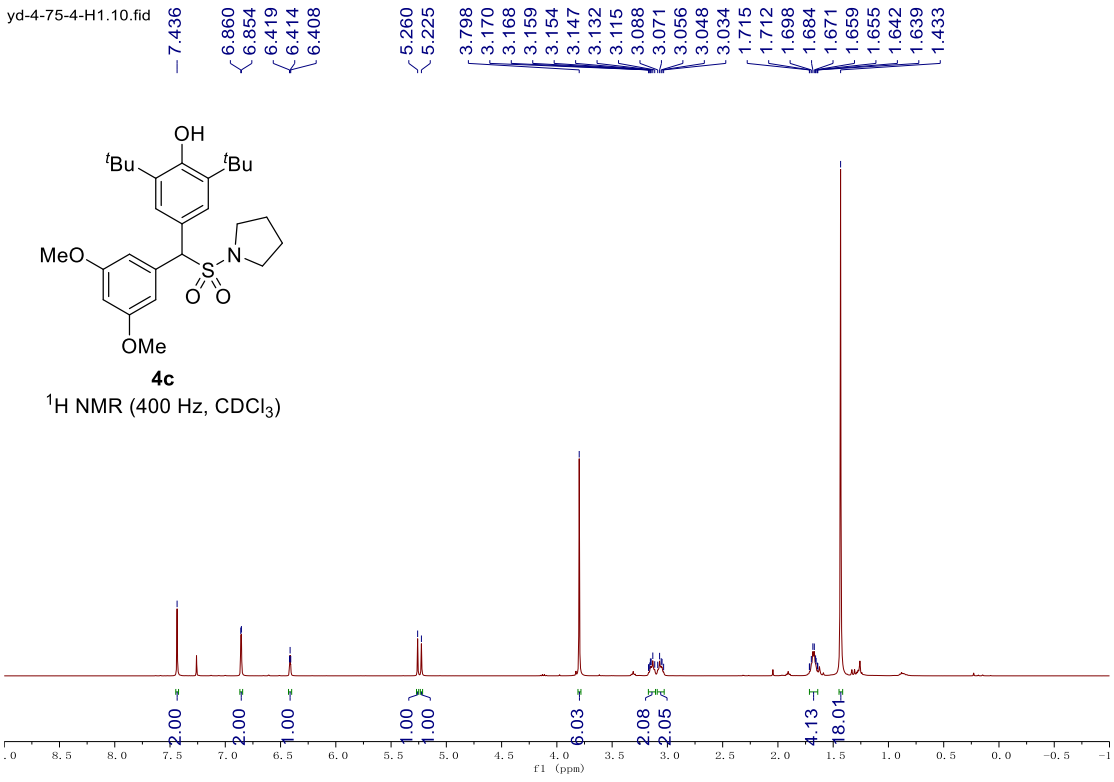
4b

^{1}H NMR (400 Hz, $CDCl_3$)



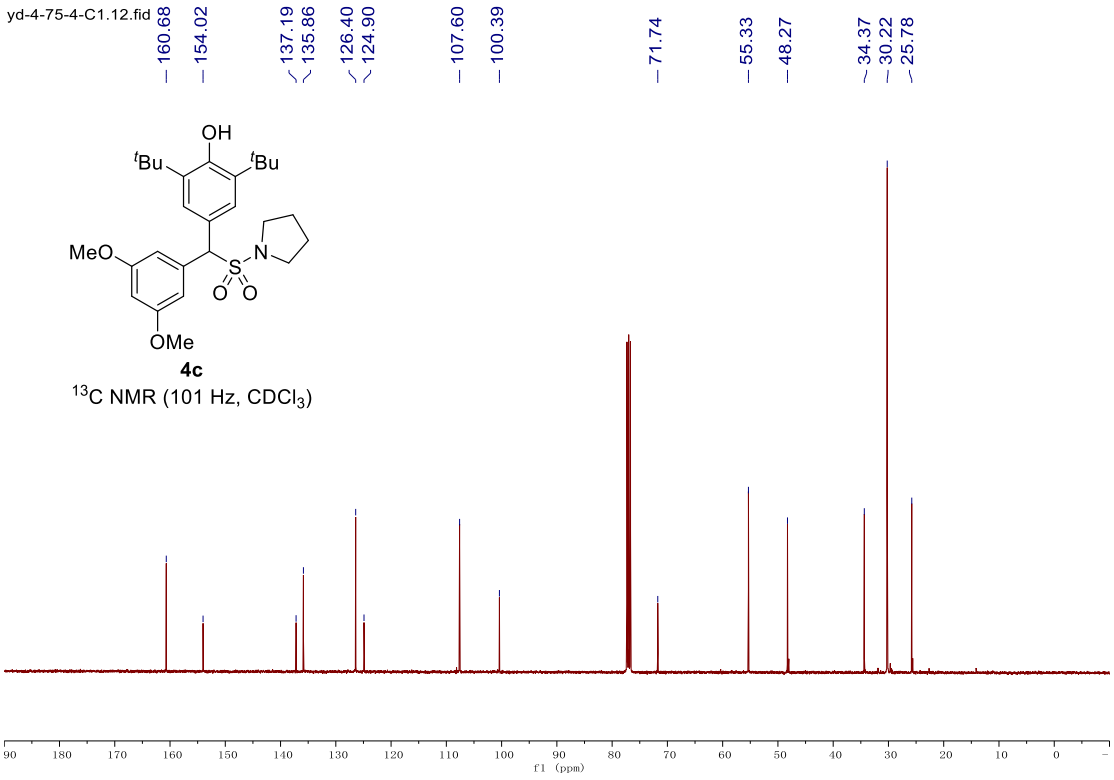
4b

^{13}C NMR (101 Hz, $CDCl_3$)



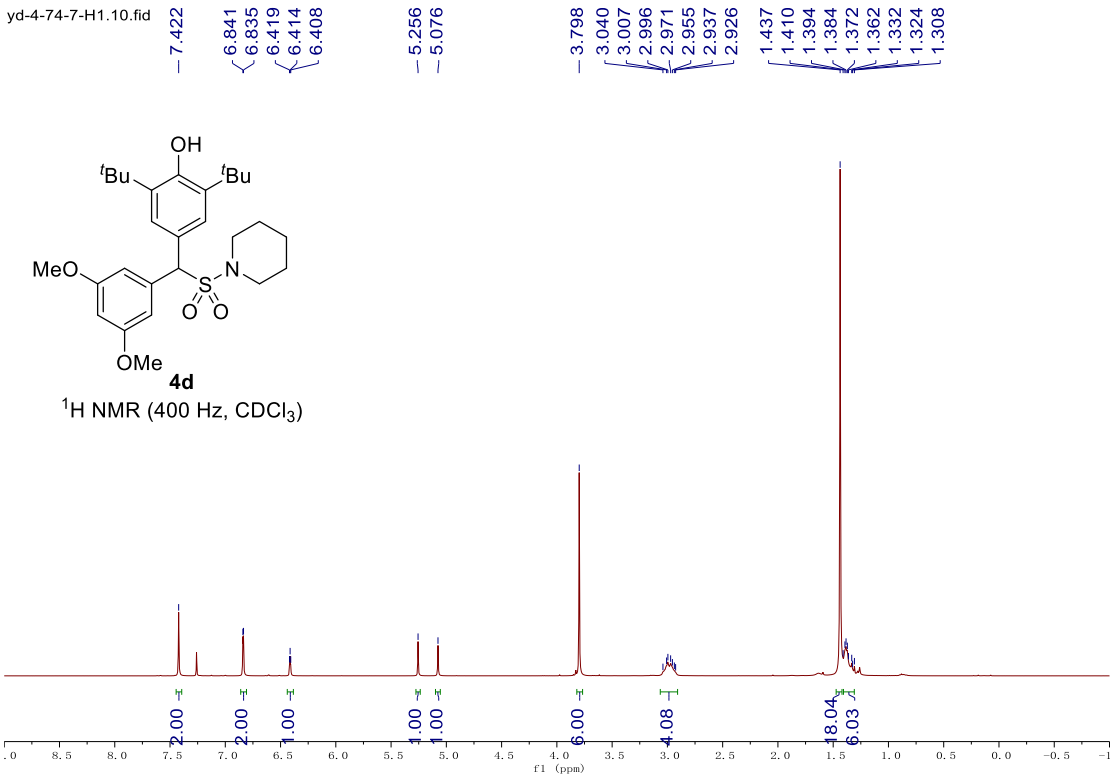
4c

^{1}H NMR (400 Hz, $CDCl_3$)



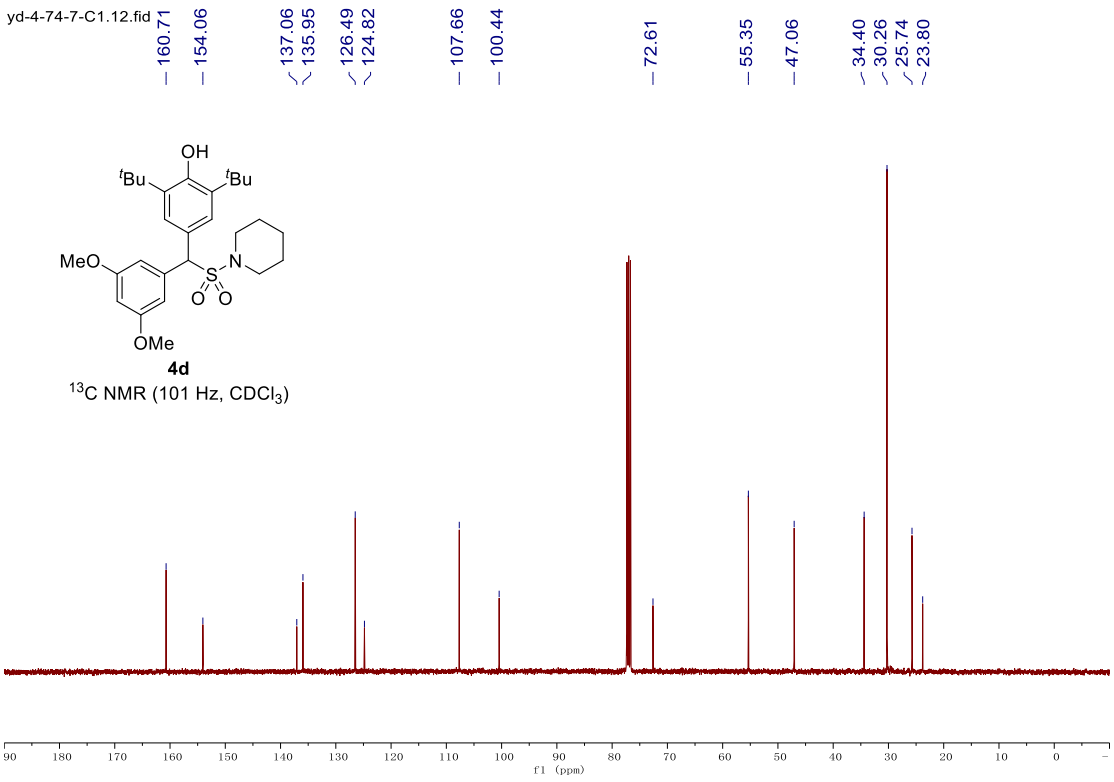
4c

^{13}C NMR (101 Hz, $CDCl_3$)



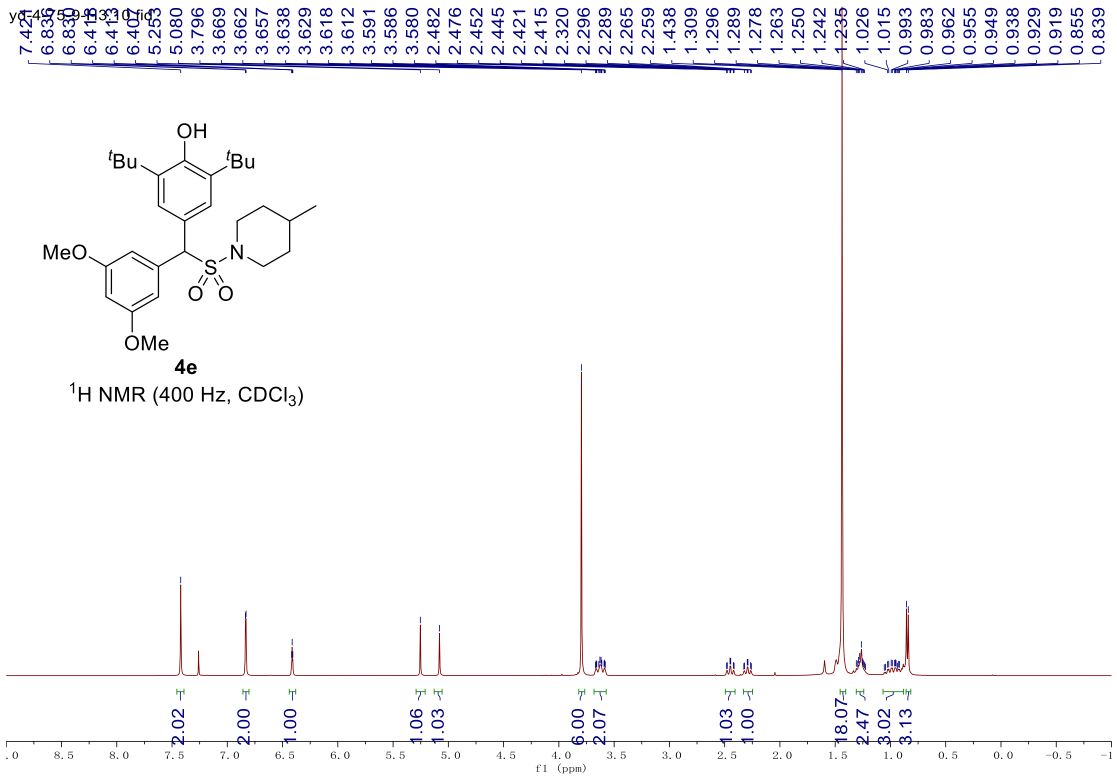
4d

^{1}H NMR (400 Hz, $CDCl_3$)



4d

^{13}C NMR (101 Hz, $CDCl_3$)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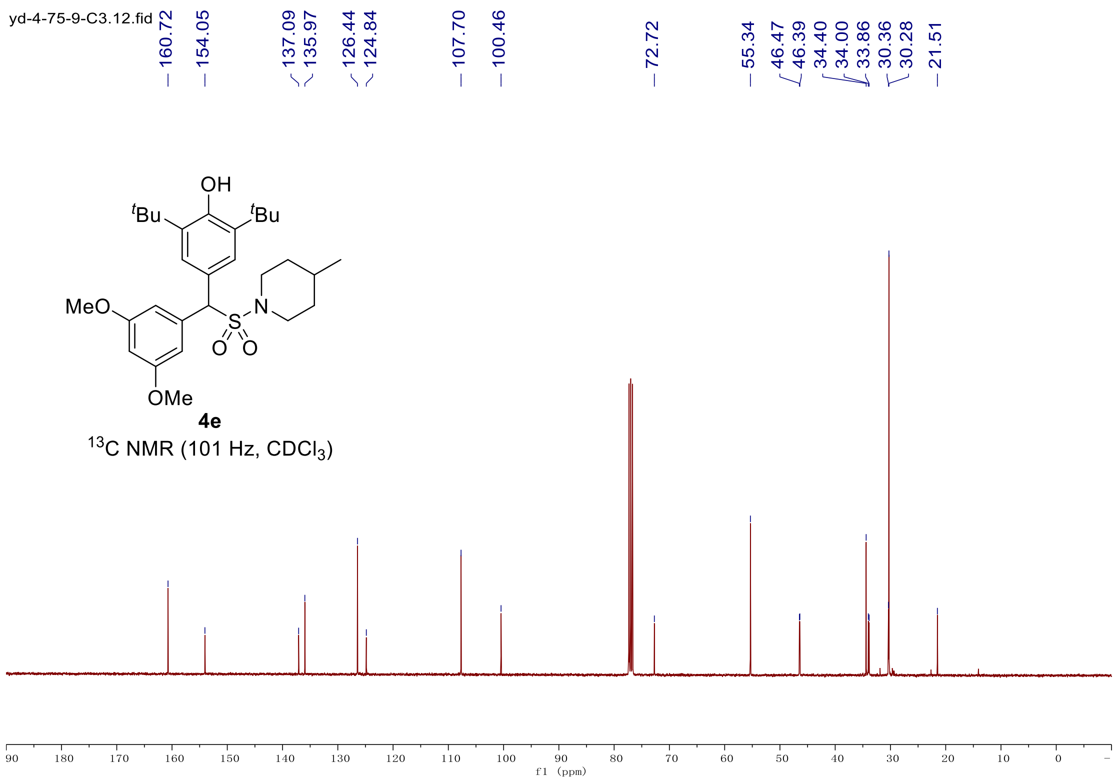
3.669
3.662
3.657
3.638
3.629
3.618
3.612
3.591
3.586
3.580
2.482
2.476
2.452
2.445
2.421
2.415
2.320
2.296
2.289
2.265
2.259
1.438
1.309
1.296
1.289
1.278
1.263
1.250
1.242
1.026
1.015
0.993
0.983
0.962
0.955
0.949
0.938
0.929
0.919
0.855
0.839
OH
tBu
tBu
MeO
S
N
O
O
OMe
4e
1H NMR (400 Hz, CDCl3)
2.02
2.00
1.00
1.06
1.03
6.00
2.07
1.03
1.00
18.07
2.47
3.02
3.13
f1 (ppm)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160.72
154.05
137.09
135.97
126.44
124.84
107.70
100.46
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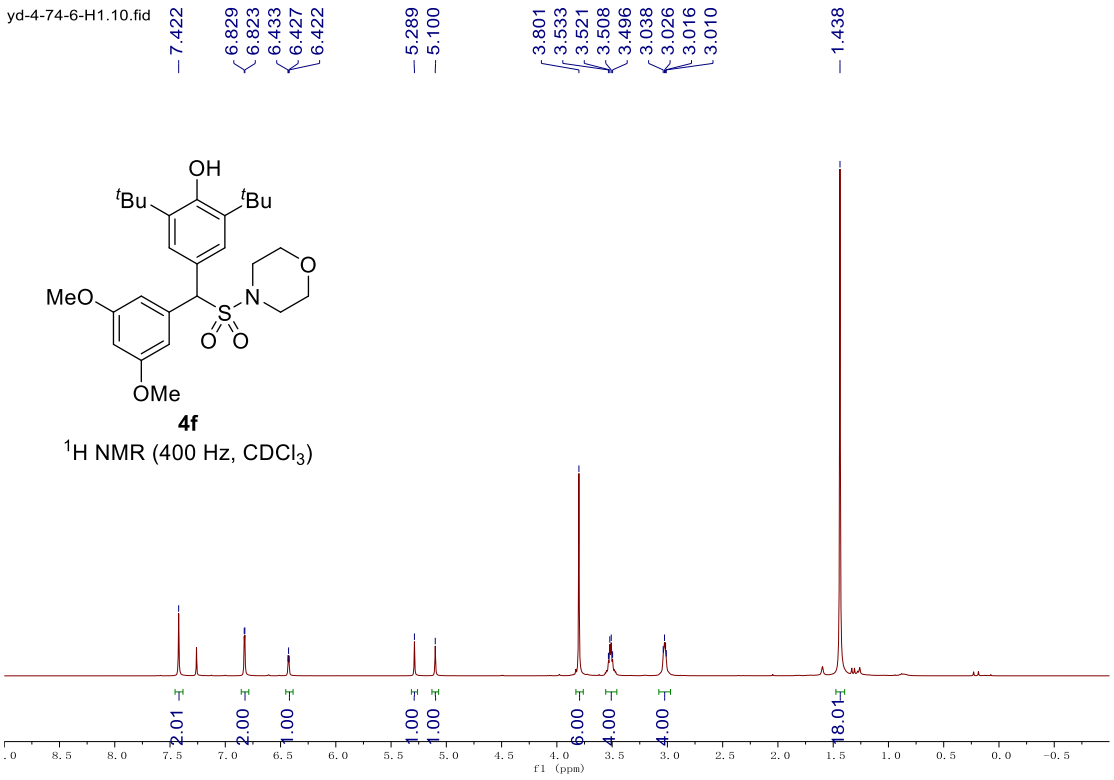
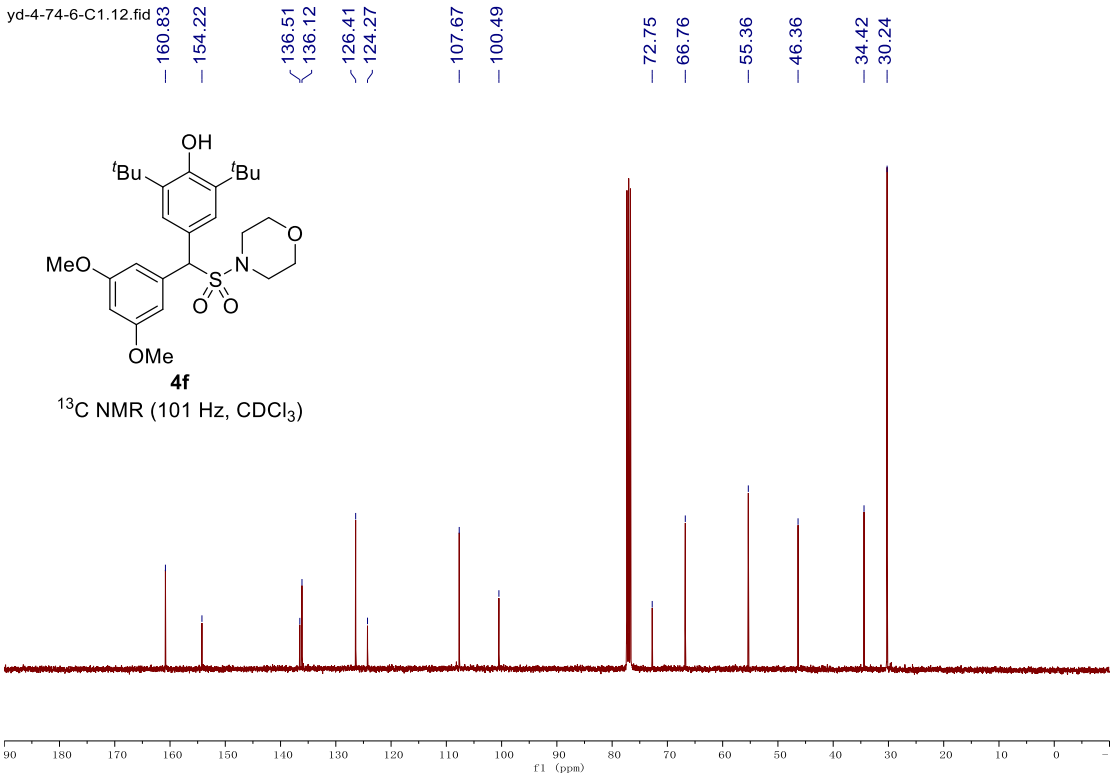
46.47
46.39
34.40
34.00
33.86
30.36
30.28
21.51
OH
tBu
tBu
MeO
S
N
O
O
OMe
4e
13C NMR (101 Hz, CDCl3)
f1 (ppm)



4f

^{1}H NMR (400 Hz, $CDCl_3$)



4f

^{13}C NMR (101 Hz, $CDCl_3$)