Supporting Information

Rongalite as Sulfone Source: A Novel Copper-Catalyzed Sulfur Dioxide Anion Incorporation Process

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1. General information

All copper salts was purchased from Energy Chemical, 2'-iodochalcone derivatives were synthesized by the previous report.[1] Besides, all substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ^{1}H spectra were recorded in $CDCl_3$, CD_2Cl_2 and DMSO-d_6 on 600/400 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$, CD_2Cl_2 and DMSO-d_6 on 150/100 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. The X-ray crystal-structure determinations of **3b** was obtained on a Bruker SMART APEX CCD system.

2. General procedure for the synthesis of 3a-3aj using rongalite (3a as an example)

Under air atmosphere, a 38 mL oven dried reaction tube equipped with a magnetic stir bar was charged with the mixture of 2'-iodochalcone **1a** (0.2 mmol), rongalite **2** (0.6 mmol), $Cu(OTf)_2$ (20 mol %), 1,10-phen (24 mol %), Bu_4NCl (1.0 equiv.) and CH_3CN (2.0 mL). The mixture was stirred at 110 ^{o}C for 8 hours. After cooling to room temperature, the mixture was quenched with water (25 mL), extracted with EtOAc (3 × 50 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the products **3a**.

3. General procedure for the synthesis of 1-thiaflavanone sulfones using thiourea dioxide (3a as an example)

Under air atmosphere, a 38 mL oven dried reaction tube equipped with a magnetic stir bar was charged with the mixture of 2'-iodochalcone 1a (0.2 mmol), thiourea dioxide **2'** (0.4 mmol), $Cu(OTf)_2$ (20 mol %), 1,10-phen (24 mol %), Bu_4NCl (1.0 equiv.), NaOH (2.0 equiv.) and CH_3CN (2.0 mL). The mixture was stirred at 110 ^{o}C for 8 hours. After cooling to room temperature, the mixture was quenched with water (25 mL), extracted with EtOAc (3 × 50 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the products **3a**.

4. Preparation of 4-hydroxy-2-(p-tolyl)thiochromane 1,1-dioxide (4b)

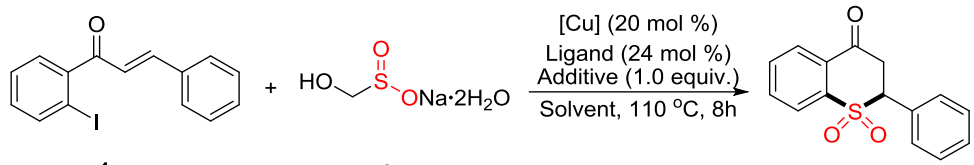
To a solution of 2-(p-tolyl)thiochroman-4-one 1,1-dioxide **3a** (1.0 mmol) in anhydrous ethanol (2.0 mL), sodium borohydride (0.55 mmol) was added portion-wise and stirred at room tempreature for 1h. After completion of reaction, solvent was evaporated under vacuum and treated with ice water. The aqueous layer was acidified (pH≈2) and extracted using ethyl acetate (3×10 mL). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over Na_2SO_4 and then concentrated. The crude reaction mixture was purified by column

chromatograohy using hexanes/ethyl acetate (5:1 v/v) as eluent gave 4-hydroxy-2-(p-tolyl)thiochromane 1,1-dioxide (**4b**).

5. Preparation of 2-(p-tolyl)-4H-thiochromen-4-one 1,1-dioxide (5b)

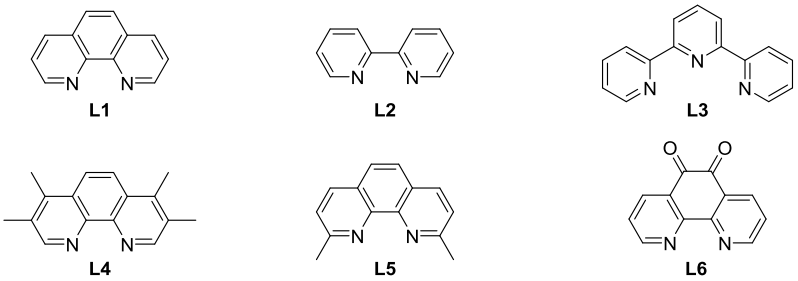
2-(p-tolyl)thiochroman-4-one 1,1-dioxide **3a** (0.5 mmol), diiodine (1.0 equiv.), H_2SO_4 (1.0 equiv.) and DMSO (3 mL) were added to a reaction tube (35 mL), the mixture was stirred at 100 °C overnight. Then the residue was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacou. The crude product was purified by a column chromatograohy to afford product **5b**.

6. Optimization of reaction conditions[a]



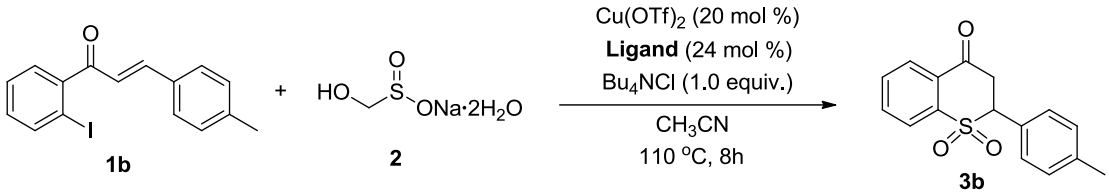
1a **2** **3a**

Entry	Cu salt	ligand	additive	solvent	Yield(%)[b]
1	$Cu(OAc)_2$	-	-	DMF	11
2	$Cu(OAc)_2$	-	-	DMSO	10
3	$Cu(OAc)_2$	-	-	CH_3CN	16
4	$Cu(OAc)_2$	-	-	Toluene	＜5
5	$Cu(OAc)_2$	-	-	NMP	Trace
6	$Cu(OAc)_2$	L1	-	CH_3CN	42
7	$Cu(OAc)_2$	L1	Bu_4NF	CH_3CN	51
8	$Cu(OAc)_2$	L1	Bu_4NCl	CH_3CN	67
9	$Cu(OAc)_2$	L1	Bu_4NBr	CH_3CN	56
10	$Cu(OAc)_2$	L1	Bu_4NI	CH_3CN	48
11	$Cu(OAc)_2$	L2	Bu_4NCl	CH_3CN	16
12	$Cu(OAc)_2$	L3	Bu_4NCl	CH_3CN	9
13	$Cu(OAc)_2$	L4	Bu_4NCl	CH_3CN	57
14	$Cu(OAc)_2$	L5	Bu_4NCl	CH_3CN	10
15	$Cu(OAc)_2$	L6	Bu_4NCl	CH_3CN	15
16	CuCl	L1	Bu_4NCl	CH_3CN	72
17	CuBr	L1	Bu_4NCl	CH_3CN	61
18	CuI	L1	Bu_4NCl	CH_3CN	55
19	$Cu(OTf)_2$	L1	Bu_4NCl	CH_3CN	76
20	$Cu(BF_4)_2$	L1	Bu_4NCl	CH_3CN	73
21	$Cu(OTf)_2$	L1	Bu_4NCl	CH_3CN	64
22	$Cu(OTf)_2$	L1	Bu_4NCl	CH_3CN	82
23	$Cu(OTf)_2$	L1	Bu_4NCl	CH_3CN	81
24	$Cu(OTf)_2$	L1	Bu_4NCl	CH_3CN	75



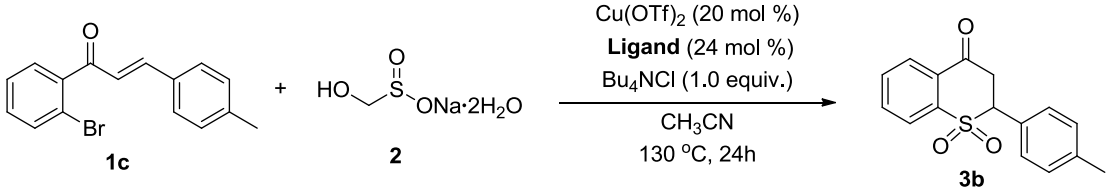
[a]Reaction conditions: **1a** (0.2 mmol), rongalite **2** (0.4 mmol), Cu catalyst (20 mol %), ligand (24 mol %), additive (1.0 equiv.), solvent (2.0 mL), 110 °C, 8h. [b]Isolated yield based on **1a**. [c]Using 1.0 equiv. of rongalite. [d]Using 3.0 equiv. of rongalite. [e]Using 4.0 equiv. of rongalite. [f]90 °C.

7. Further searching for potential ligands and brominated substrate testing



Entry	Ligand	Yield (%)	Entry	Ligand	Yield (%)
1	L1	72	9[d]	L14	trace
2	L7	8	10[d]	L15	52
3	L8	trace	11[e]	L16	trace
4	L9	trace	12[f]	L17	trace
5	L10	15	13[f]	L18	trace
6[c]	L11	10	14[f]	L19	trace
7[d]	L12	trace	15[f]	L20	trace
8[d]	L13	trace			

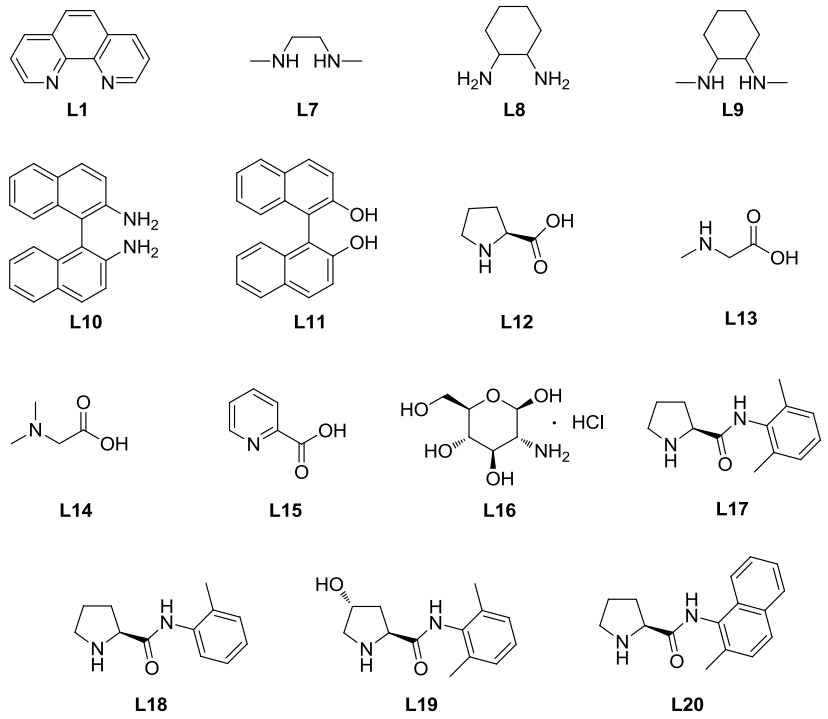
[a]Reaction conditions: **1b** (0.20 mmol), **2** (0.60 mmol), $Cu(OTf)_2$ (20 mol %), Ligand （24 mol %）, Bu_4NCl (1.0 equiv.), CH_3CN (2.0 mL), 110°C, 8h, under air. [b]Isolated yield based on **1b**. [c]With additional 0.40 mmol K_2CO_3. [d]With additional 0.048 mmol NaOH. [e]With additional 0.40 mmol KOAc. [f]With additional 0.20 mmol K_3PO_4.



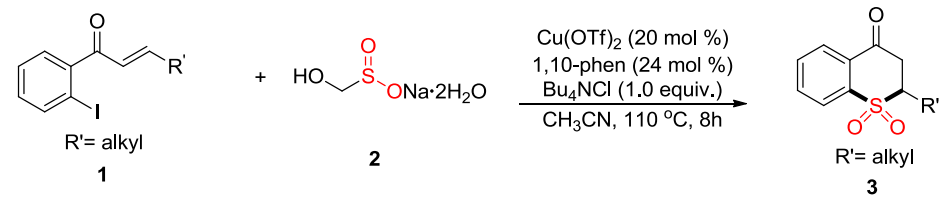
Entry	Ligand	Yield (%)	Entry	Ligand	Yield (%)
1	L1	14	9[d]	L14	trace
2	L7	trace	10[d]	L15	6
3	L8	trace	11[e]	L16	trace
4	L9	trace	12[f]	L17	trace
5	L10	trace	13[f]	L18	trace
6[c]	L11	trace	14[f]	L19	trace

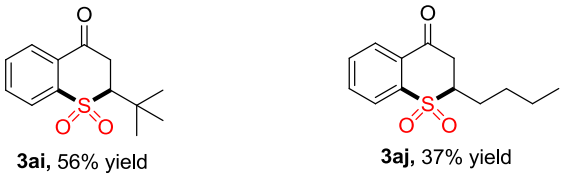
7[d]	L12	trace	15[f]	L20	trace
8[d]	L13	trace			

[a]Reaction conditions: **1c** (0.20 mmol), **2** (0.60 mmol), $Cu(OTf)_2$ (20 mol %), Ligand(24 mol %), Bu_4NCl (1.0 equiv.), CH_3CN (2.0 mL), 130°C, 24h, under air. [b]Isolated yield based on **1b**. [c]With additional 0.40 mmol K_2CO_3. [d]With additional 0.048 mmol NaOH. [e]With additional 0.40 mmol KOAc. [f]With additional 0.20 mmol K_3PO_4.



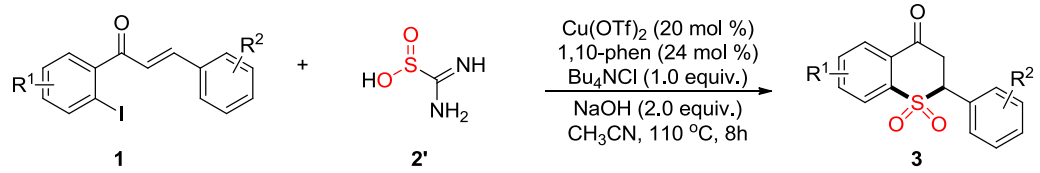
8. Synthesis of alkyl-substituted products 3ai and 3aj



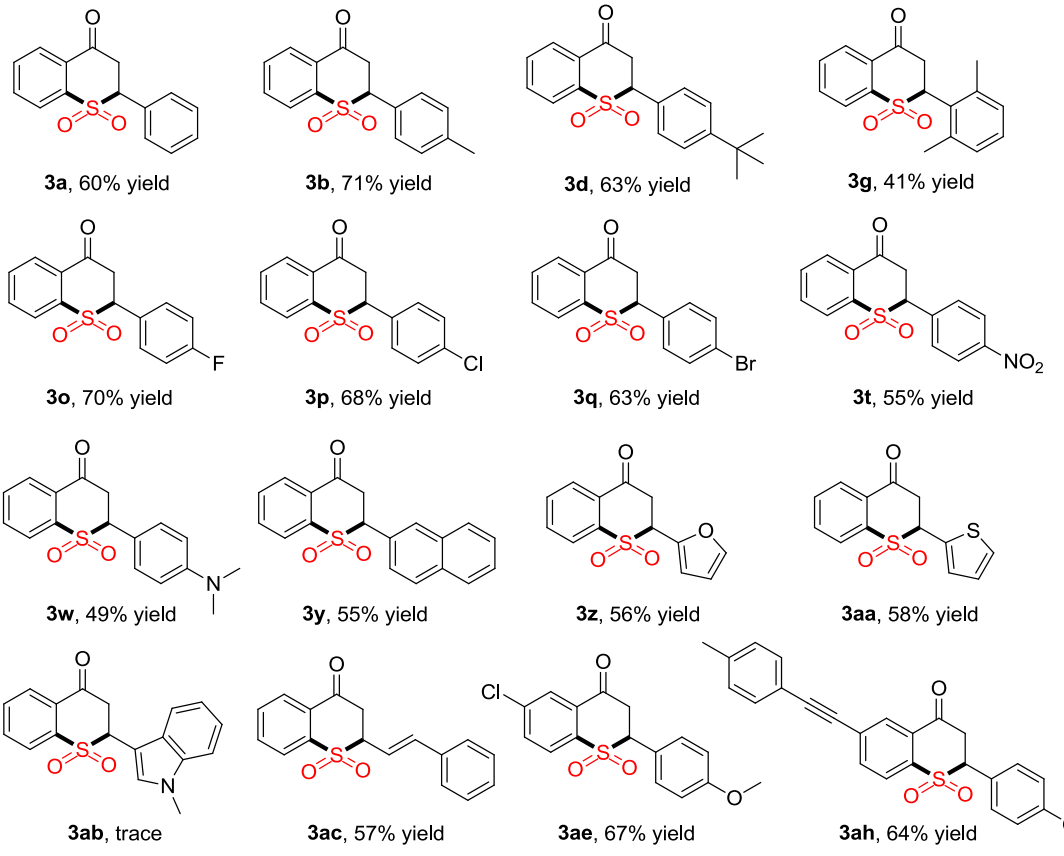


[a]Reaction conditions: **1** (0.20 mmol), **2** (0.6 mmol), $Cu(OTf)_2$ (20 mol %), 1,10-phen (24 mol %), Bu_4NCl (1.0 equiv.), CH_3CN (2.0 mL), 110 °C, 8 h. [b]Isolated yield based on **1**.

9. Synthesis of 1-thiaflavanone sulfones using thiourea dioxide



1 **2'** **3**



3a, 60% yield; **3b**, 71% yield; **3d**, 63% yield; **3g**, 41% yield

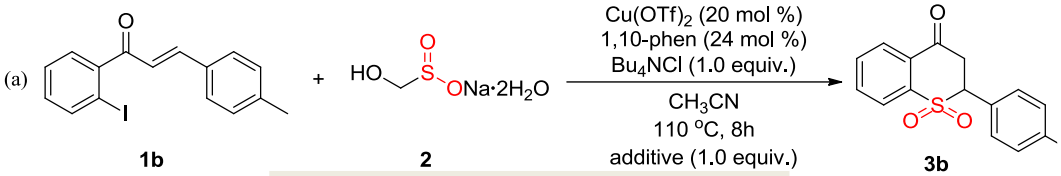
3o, 70% yield; **3p**, 68% yield; **3q**, 63% yield; **3t**, 55% yield

3w, 49% yield; **3y**, 55% yield; **3z**, 56% yield; **3aa**, 58% yield

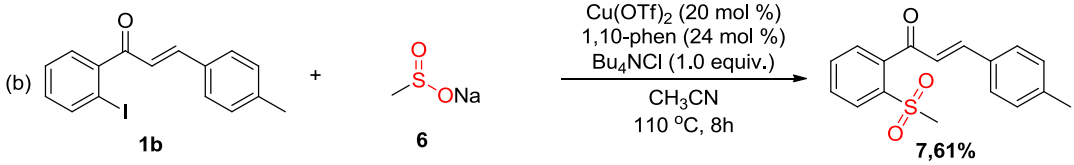
3ab, trace; **3ac**, 57% yield; **3ae**, 67% yield; **3ah**, 64% yield

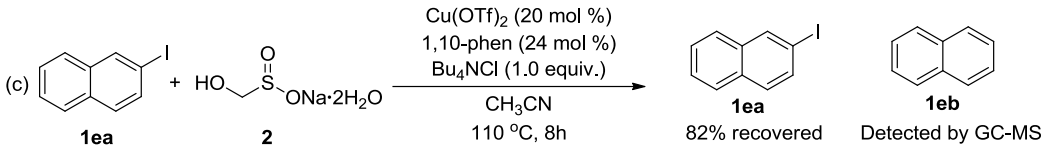
[a]Reaction conditions: **1** (0.20 mmol), **2'** (0.40 mmol), $Cu(OTf)_2$ (20 mol %), 1,10-phen (24 mol %), Bu_4NCl (1.0 equiv.), NaOH (2.0 equiv.), CH_3CN (2.0 mL), 110 °C, 8 h. [b]Isolated yield based on **1**.

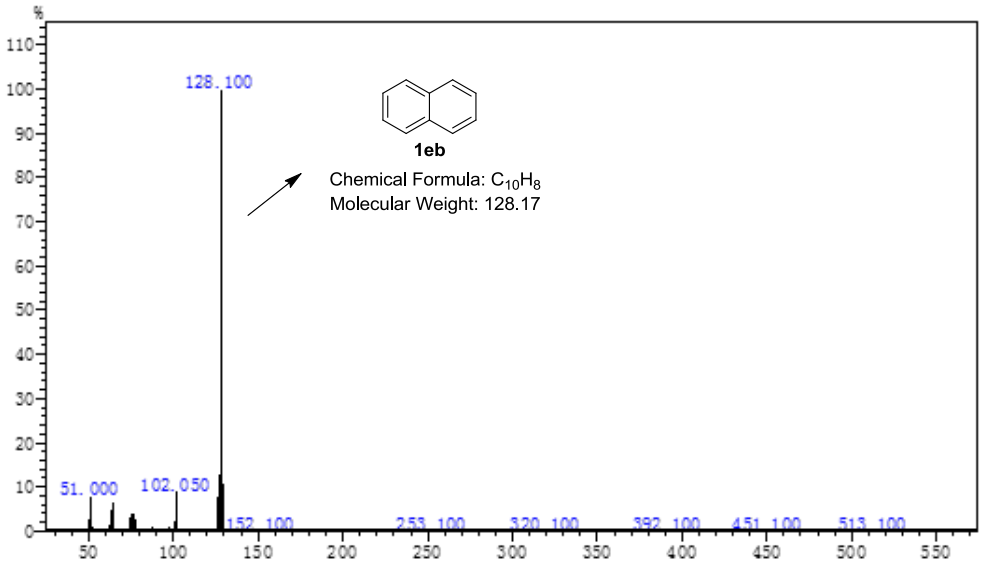
10. Control experiments

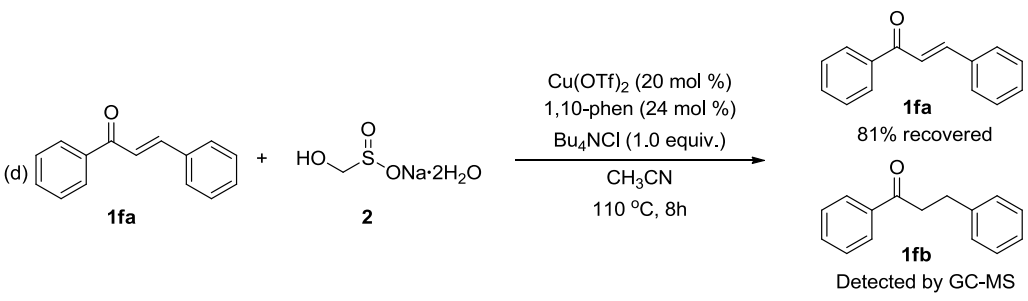


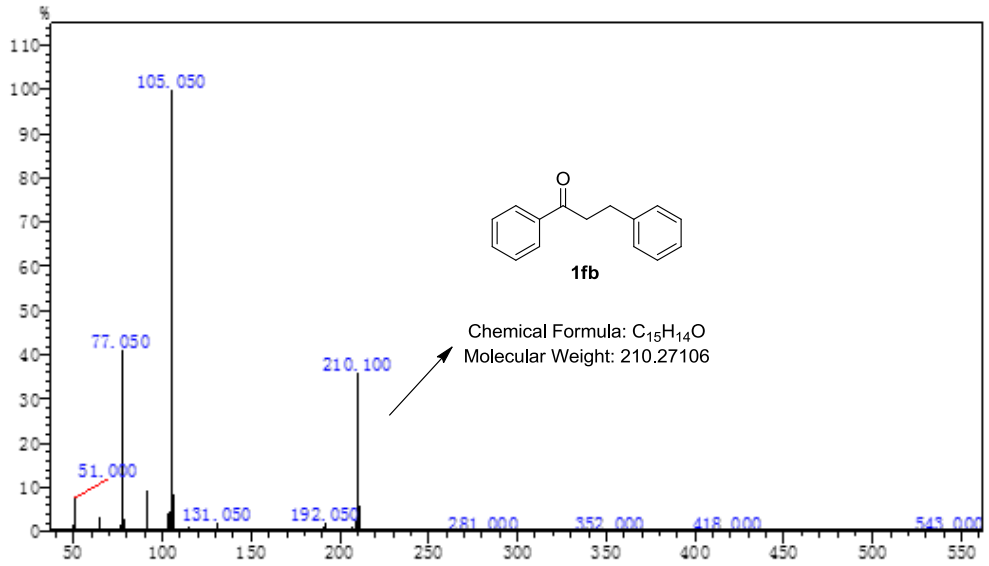
additive (1equiv)	yield of **3b**
TEMPO	71%
BHT	74%







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192.050
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418.000
543.000
1fb
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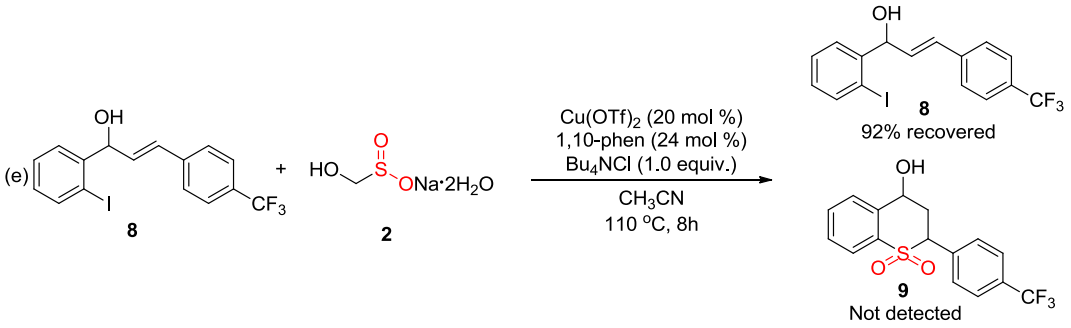
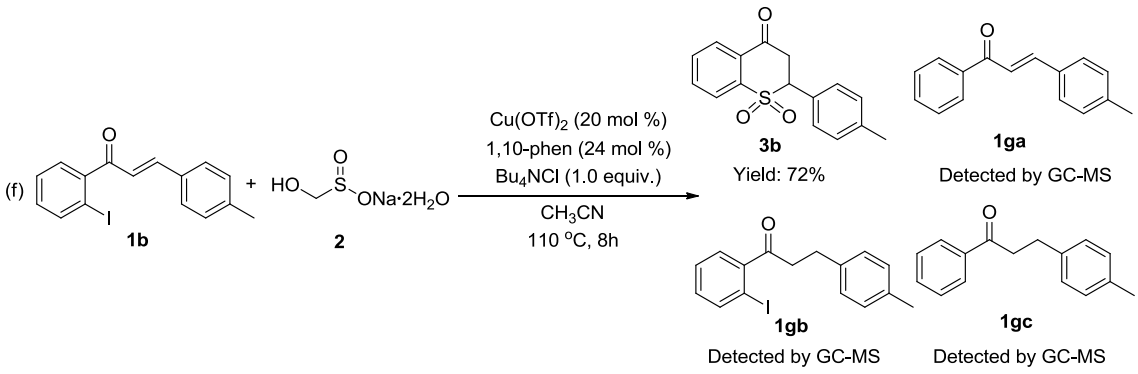
Molecular Weight: 210.27106


(e)
OH
CF3
8
HO
S
ONa·2H2O
2
Cu(OTf)2 (20 mol %)
1,10-phen (24 mol %)
Bu4NCl (1.0 equiv.)
CH3CN
110 °C, 8h
8
92% recovered
9
Not detected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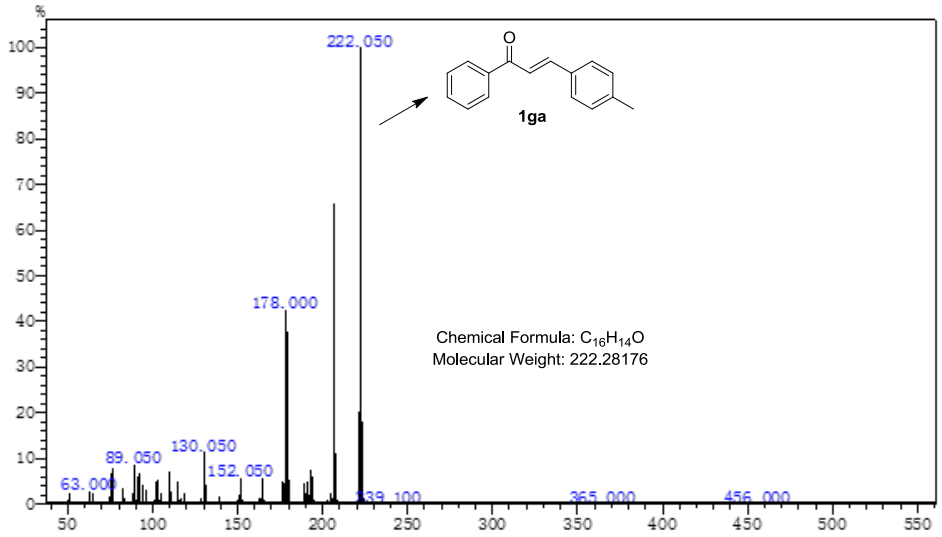
1b
HO
S
ONa·2H2O
2
Cu(OTf)2 (20 mol %)
1,10-phen (24 mol %)
Bu4NCl (1.0 equiv.)
CH3CN
110 °C, 8h
3b
Yield: 72%
1ga
Detected by GC-MS
1gb
Detected by GC-MS
1gc
Detected by GC-MS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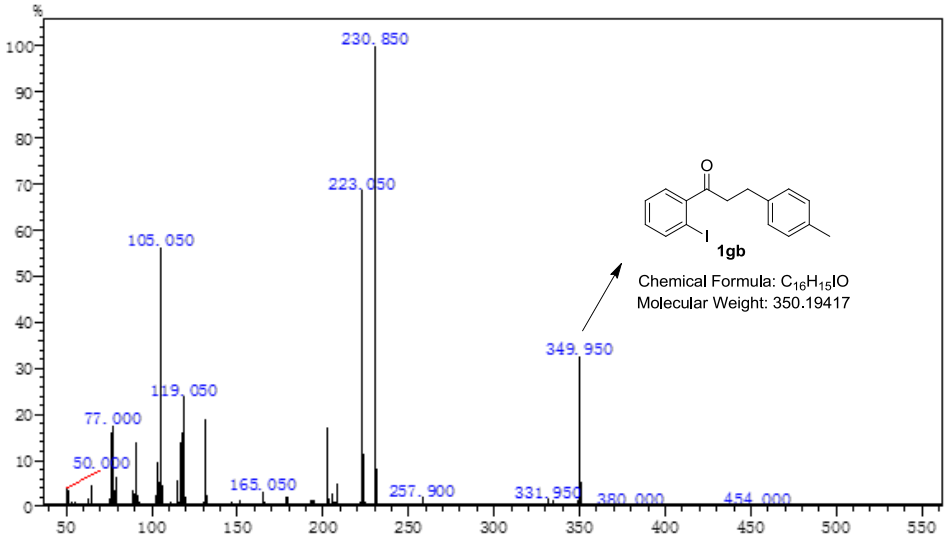
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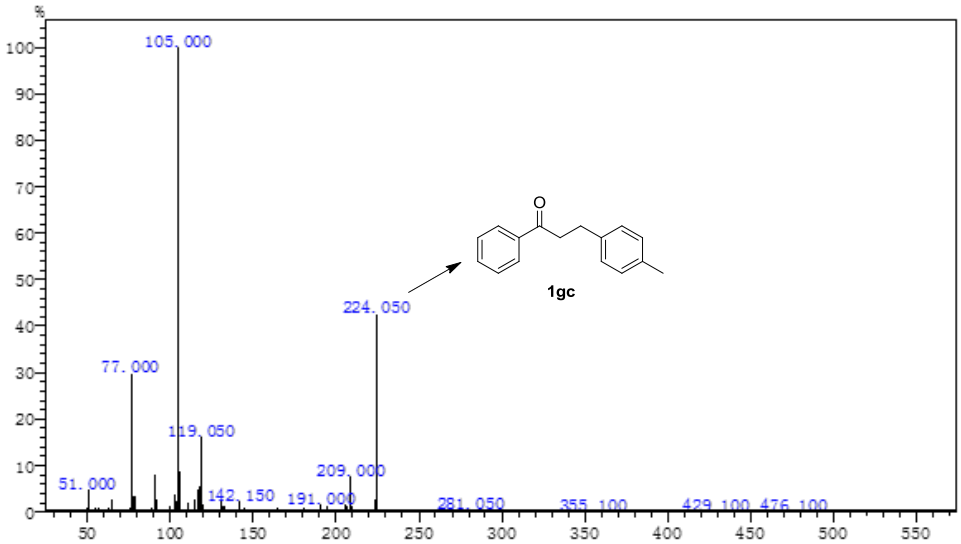
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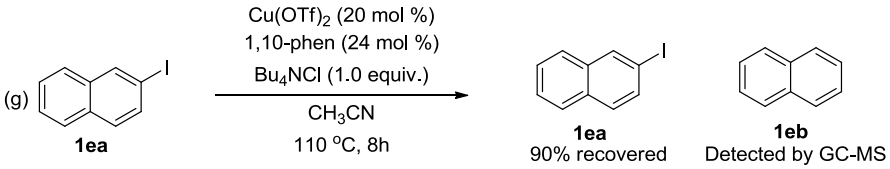
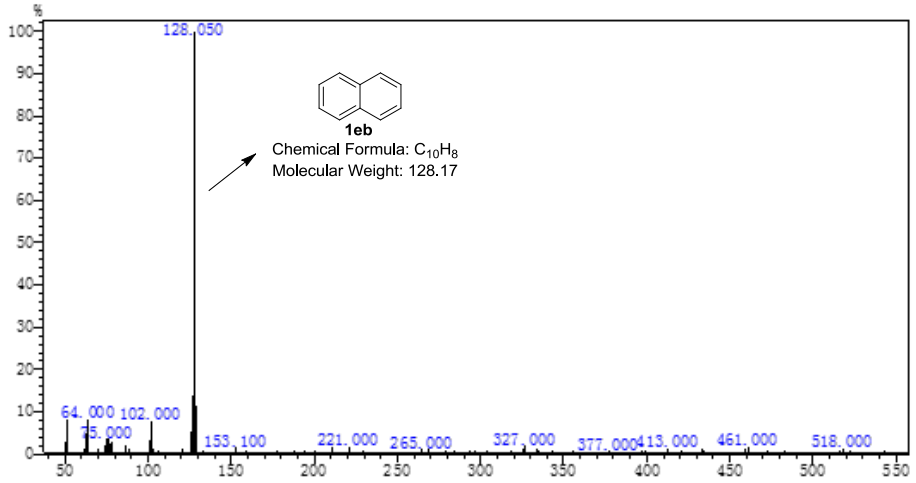

(g)
1ea
Cu(OTf)2 (20 mol %)
1,10-phen (24 mol %)
Bu4NCl (1.0 equiv.)
CH3CN
110 °C, 8h
1ea
90% recovered
1eb
Detected by GC-MS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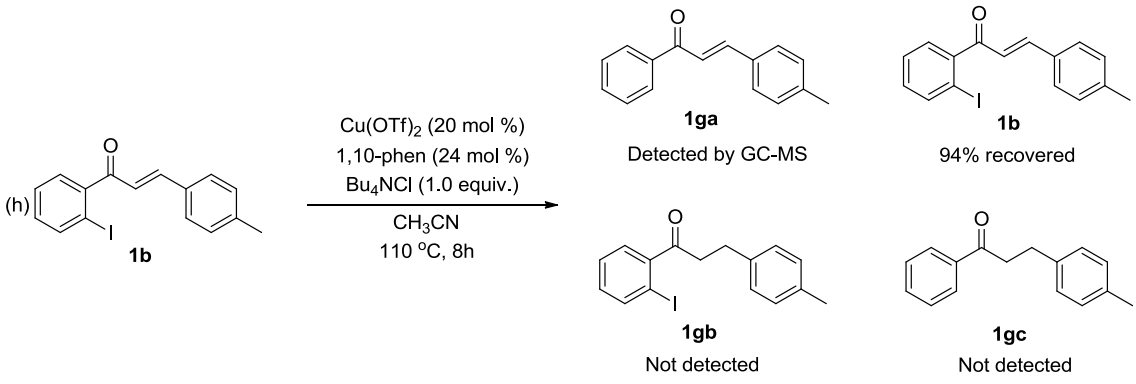
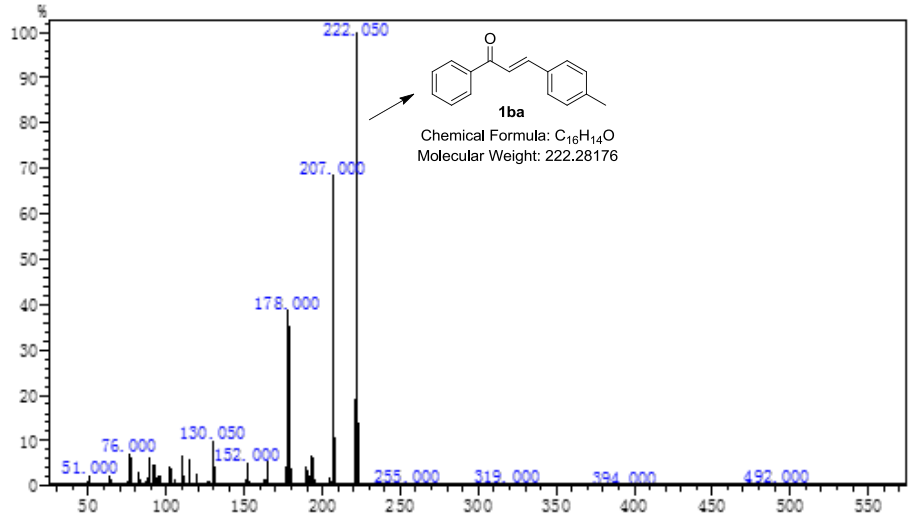

(h)
1b
Cu(OTf)2 (20 mol %)
1,10-phen (24 mol %)
Bu4NCl (1.0 equiv.)
CH3CN
110 °C, 8h
1ga
Detected by GC-MS
1b
94% recovered
1gb
Not detected
1gc
Not detected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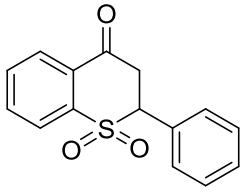
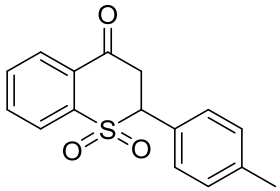
11. Characterization data for compounds



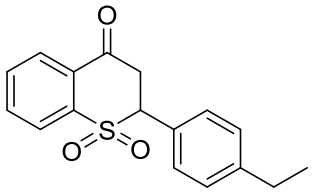
2-phenylthiochroman-4-one 1,1-dioxide (3a):

Yield 82%; 44.6 mg; white solid; mp 157–160 ℃; R_f 0.51 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.11 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.62 – 7.31 (m, 5H), 4.88 (dd, *J* = 12.6, 3.0 Hz, 1H), 3.91 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.35 (dd, *J* = 17.4, 3.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=190.9, 141.4, 135.1, 133.4, 130.5, 130.0, 129.9, 129.1, 128.7, 128.0, 124.4, 63.9, 43.0. HRMS (ESI) m/z calcd for $C_{15}H_{12}O_3SNa^+$ $(M+Na)^+$ 295.0399, found 295.0399.



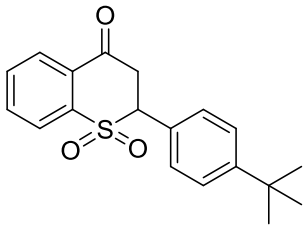
2-(p-tolyl)thiochroman-4-one 1,1-dioxide (3b):

Yield 77%; 44.1 mg; white solid; mp 201–202 ℃; R_f 0.46 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, $CDCl_3$) δ =8.15 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 4.84 (dd, *J* = 12.6, 3.0 Hz, 1H), 3.93 (dd, *J* = 17.4, 12.6 Hz, 1H), 3.38 (dd, *J* = 17.4, 3.0 Hz, 1H), 2.38 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ=191.2, 141.6, 140.3, 135.2, 133.5, 130.6, 130.0, 129.8, 128.8, 125.0, 124.6, 63.9, 43.2, 21.4. HRMS (ESI) m/z calcd for $C_{16}H_{14}O_3SNa^+$ $(M+Na)^+$ 309.0556, found 309.0555.



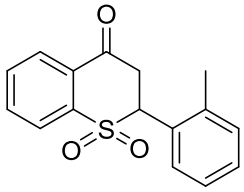
2-(4-ethylphenyl)thiochroman-4-one 1,1-dioxide (3c):

Yield 80%; 48.0 mg; white solid; mp 149–152 ℃; R_f 0.36 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.11 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 4.85 (dd, *J* = 12.6, 2.4 Hz, 1H), 3.90 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.34 (dd, *J* = 17.4, 2.4 Hz, 1H), 2.66 (q, *J* = 7.8 Hz, 2H), 1.23 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=191.1, 146.2, 141.5, 135.1, 133.3, 130.5, 129.8, 128.6, 125.1, 124.4, 63.7, 43.1, 28.6, 15.4. HRMS (ESI) m/z calcd for $C_{17}H_{16}O_3SNa^+$ $(M+Na)^+$ 323.0712, found 323.0716.



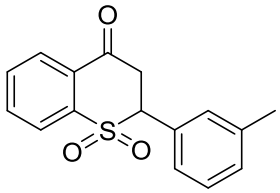
2-(4-(tert-butyl)phenyl)thiochroman-4-one 1,1-dioxide (3d):

Yield 76%; 49.9 mg; yellow solid; mp 152–153 ℃; R_f 0.32 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.12 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.98 (t, *J* = 7.2 Hz, 1H), 7.91 (t, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 5.59 (d, *J* = 10.8 Hz, 1H), 3.98 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.25 (dd, *J* = 18.0, 2.4 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (150 MHz, DMSO-*d6*) δ=191.3, 152.0, 141.2, 135.3, 133.7, 130.5, 129.9, 128.2, 125.7, 125.6, 123.8, 62.0, 42.6, 34.5, 31.1. HRMS (ESI) m/z calcd for $C_{19}H_{20}O_3SNa^+$ $(M+Na)^+$ 351.1025, found 351.1025.



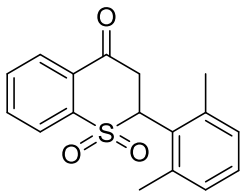
2-(o-tolyl)thiochroman-4-one 1,1-dioxide (3e):

Yield 72%; 41.2 mg; yellow solid; mp 222–225 ℃; R_f 0.48 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.14 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.98 (t, *J* = 7.2 Hz, 1H), 7.91 (t, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 16.2, 9.0 Hz, 3H), 5.99 – 5.84 (m, 1H), 4.04 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.24 – 3.09 (m, 1H), 2.48 (d, *J* = 27.0 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.4, 141.4, 139.1, 135.2, 133.6, 130.6, 130.6, 129.3, 129.2, 128.2, 127.6, 126.3, 123.7, 58.3, 43.2, 19.6. HRMS (ESI) m/z calcd for $C_{16}H_{14}O_3SNa^+$ $(M+Na)^+$ 309.0556, found 309.0555.



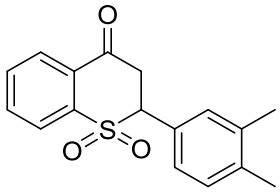
2-(m-tolyl)thiochroman-4-one 1,1-dioxide (3f):

Yield 81%; 46.3 mg; white solid; mp 136–138 ℃; R_f 0.40 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.13 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 1H), 7.98 (t, *J* = 7.2 Hz, 1H), 7.91 (t, *J* = 7.2 Hz, 1H), 7.32 (dd, *J* = 36.0, 9.6 Hz, 4H), 5.59 (d, *J* = 12.6 Hz, 1H), 4.02 (dd, *J* = 16.8, 13.8 Hz, 1H), 3.27 (d, *J* = 17.4 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.2, 141.3, 138.0, 135.3, 133.7, 130.7, 130.4, 130.1, 128.6, 128.6, 128.2, 127.4, 123.8, 62.3, 42.6, 21.0. HRMS (ESI) m/z calcd for $C_{16}H_{14}O_3SNa^+$ $(M+Na)^+$ 309.0556, found 309.0555.



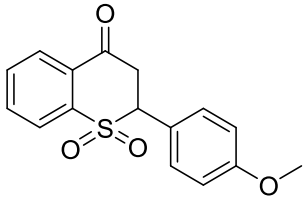
2-(2,6-dimethylphenyl)thiochroman-4-one 1,1-dioxide (3g):

Yield 74%; 44.4 mg; white solid; mp 157-160 ℃; R_f 0.36 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.13 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.96 (t, *J* = 7.2 Hz, 1H), 7.90 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.18 – 7.08 (m, 2H), 5.96 (d, *J* = 12.6 Hz, 1H), 4.34 (dd, *J* = 16.8, 13.8 Hz, 1H), 3.35 (d, *J* = 16.8 Hz, 1H), 2.69 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.1, 142.2, 140.9, 139.6, 135.0, 133.5, 131.0, 130.3, 129.0, 128.8, 128.2, 126.1, 123.3, 60.1, 42.8, 22.1, 21.4. HRMS (ESI) m/z calcd for $C_{17}H_{17}O_3S^+$ $(M+H)^+$ 301.0892, found 301.0896.



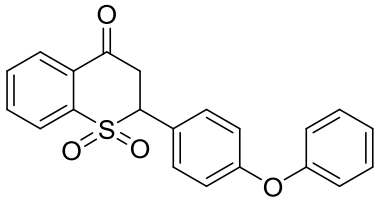
2-(3,4-dimethylphenyl)thiochroman-4-one 1,1-dioxide (3h):

Yield 78%; 46.8 mg; white solid; mp 172–174 ℃; R_f 0.35 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.12 (d, *J* = 7.2 Hz, 1H), 8.05 (d, *J* = 6.6 Hz, 1H), 7.97 (s, 1H), 7.90 (d, *J* = 6.6 Hz, 1H), 7.31 (s, 1H), 7.24 (s, 2H), 5.52 (d, *J* = 12.6 Hz, 1H), 4.09 – 3.88 (m, 1H), 3.24 (d, *J* = 17.4 Hz, 1H), 2.26 (s, 6H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.3, 141.3, 137.9, 136.6, 135.3, 133.6, 131.1, 130.4, 129.7, 128.2, 127.6, 125.9, 123.8, 62.1, 42.7, 19.4, 19.2. HRMS (ESI) m/z calcd for $C_{17}H_{16}O_3SNa^+$ $(M+Na)^+$ 323.0712, found 323.0716.



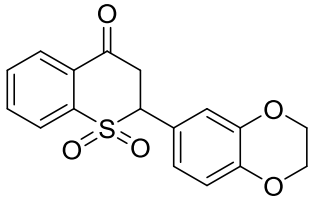
2-(4-methoxyphenyl)thiochroman-4-one 1,1-dioxide (3i):

Yield 84%; 50.7 mg; white solid; mp 210–212 ℃; R_f 0.45 (EtOAc/petroleum ether = 1:2); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.13 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 1H), 7.98 (d, *J* = 6.0 Hz, 1H), 7.90 (d, *J* = 6.6 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 5.55 (d, *J* = 12.0 Hz, 1H), 4.09 – 3.91 (m, 1H), 3.79 (s, 3H), 3.26 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.3, 160.2, 141.3, 135.3, 133.6, 131.5, 130.4, 128.2, 123.8, 120.3, 114.2, 61.8, 55.2, 42.7. HRMS (ESI) m/z calcd for $C_{16}H_{14}O_4SNa^+$ $(M+Na)^+$ 325.0505, found 325.0505.



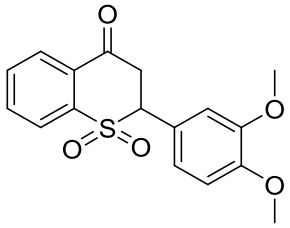
2-(4-phenoxyphenyl)thiochroman-4-one 1,1-dioxide (3j):

Yield 80%; 58.3 mg; yellow oil; R_f 0.36 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.14 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.97 (t, *J* = 7.8 Hz, 1H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 4H), 5.63 (d, *J* = 12.6 Hz, 1H), 4.02 (dd, *J* = 17.4, 13.8 Hz, 1H), 3.30 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.1, 158.1, 155.8, 141.2, 135.3, 133.7, 132.0, 130.4, 130.2, 128.2, 124.1, 123.8, 123.1, 119.4, 118.1, 61.7, 42.7. HRMS (ESI) m/z calcd for $C_{21}H_{16}O_4SNa^+$ $(M+Na)^+$ 387.0662, found 387.0665.



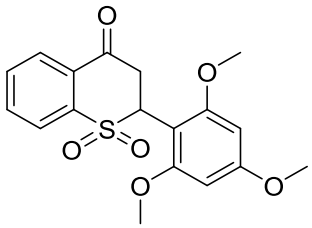
2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)thiochroman-4-one 1,1-dioxide (3k):

Yield 88%; 58.1 mg; yellow solid; mp 234–237 ℃; R_f 0.42 (EtOAc/petroleum ether = 1:2); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.11 (d, *J* = 7.2 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 7.97 (t, *J* = 7.2 Hz, 1H), 7.89 (t, *J* = 6.6 Hz, 1H), 7.05 (s, 1H), 6.97 (dd, *J* = 18.6, 7.8 Hz, 2H), 5.49 (d, *J* = 12.6 Hz, 1H), 4.27 (s, 4H), 4.04 – 3.88 (m, 1H), 3.24 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.3, 144.6, 143.4, 141.3, 135.3, 133.7, 130.4, 128.2, 123.8, 123.2, 121.3, 118.8, 117.2, 64.2, 64.1, 61.8, 42.7. HRMS (ESI) m/z calcd for $C_{17}H_{14}O_5SNa^+$ $(M+Na)^+$ 353.0454, found 353.0454.



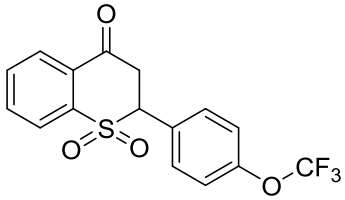
2-(3,4-dimethoxyphenyl)thiochroman-4-one 1,1-dioxide (3l):

Yield 82%; 54.5 mg; yellow solid; mp 210–212 ℃; R_f 0.42 (EtOAc/petroleum ether = 1:1); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.11 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.98 (t, *J* = 7.2 Hz, 1H), 7.90 (t, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 26.4, 14.4 Hz, 3H), 5.61 – 5.40 (m, 1H), 4.03 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.79 (d, *J* = 7.8 Hz, 6H), 3.25 (dd, *J* = 18.0, 2.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.4, 149.8, 148.6, 141.3, 135.3, 133.6, 130.5, 128.2, 123.8, 122.9, 120.7, 113.6, 111.7, 62.1, 55.7, 55.6, 42.9. HRMS (ESI) m/z calcd for $C_{17}H_{16}O_5SNa^+$ $(M+Na)^+$ 355.0611, found 355.0614.



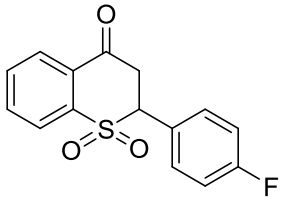
2-(2,4,6-trimethoxyphenyl)thiochroman-4-one 1,1-dioxide (3m):

Yield 79%; 57.2 mg; yellow solid; mp 170–171 ℃; R_f 0.39 (EtOAc/petroleum ether = 1:1); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.10 (d, *J* = 6.6 Hz, 1H), 7.90 (d, *J* = 6.0 Hz, 1H), 7.85 (dd, *J* = 14.4, 6.6 Hz, 2H), 6.32 (s, 1H), 6.17 (s, 1H), 5.57 (s, 1H), 3.81 (s, 3H), 3.77 (s, 4H), 3.61 (dd, *J* = 18.0, 3.6 Hz, 1H), 3.37 (s, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.1, 161.9, 160.0, 159.8, 141.7, 134.2, 133.1, 131.6, 127.4, 123.4, 99.4, 91.5, 56.6, 56.3, 55.4, 54.5, 41.5. HRMS (ESI) m/z calcd for $C_{18}H_{18}O_6SNa^+$ $(M+Na)^+$ 385.0716, found 385.0716.



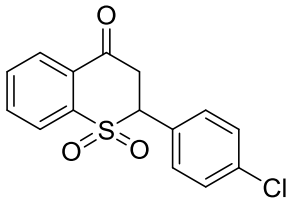
2-(4-(trifluoromethoxy)phenyl)thiochroman-4-one 1,1-dioxide (3n):

Yield 81%; 57.7 mg; white solid; mp 149–150 ℃; R_f 0.35 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.15 (d, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.99 (t, *J* = 6.6 Hz, 1H), 7.92 (t, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 5.76 (d, *J* = 12.6 Hz, 1H), 4.19 – 3.91 (m, 1H), 3.35 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.9, 149.3, 141.0, 135.4, 133.8, 132.3, 130.5, 128.2, 127.9, 123.9, 121.2, 120.1 (q, *J* = 255.0 Hz, $^1J_{CF}$), 61.6, 42.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ= -57.74 (s, 3F). HRMS (ESI) m/z calcd for $C_{16}H_{11}F_3O_4SNa^+$ $(M+Na)^+$ 379.0222, found 379.0933.



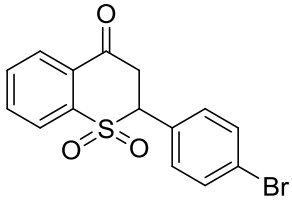
2-(4-fluorophenyl)thiochroman-4-one 1,1-dioxide (3o):

Yield 74%; 42.9 mg; yellow oil; R_f 0.29 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.13 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 1H), 7.99 (t, *J* = 6.6 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.60 (s, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 5.68 (d, *J* = 12.6 Hz, 1H), 4.14 – 3.92 (m, 1H), 3.28 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.0, 162.9 (d, *J* = 244.5 Hz, $^1J_{CF}$), 141.0, 135.4, 133.8, 132.4 (d, *J* = 7.5 Hz, $^3J_{CF}$), 130.4, 128.3, 124.9, 123.9, 115.7(d, *J* = 22.5 Hz, $^2J_{CF}$), 61.5, 42.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ= -110.59 (s, 1F). HRMS (ESI) m/z calcd for $C_{15}H_{11}FO_3SNa^+$ $(M+Na)^+$ 313.0305, found 313.0305.



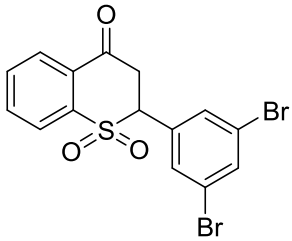
2-(4-chlorophenyl)thiochroman-4-one 1,1-dioxide (3p):

Yield 77%; 47.1 mg; yellow solid; mp 162-164 ℃; R_f 0.45 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.16 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.84 (dd, *J* = 10.8, 4.2 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.51 – 7.38 (m, 4H), 4.86 (dd, *J* = 12.6, 3.0 Hz, 1H), 3.91 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.38 (dd, *J* = 17.4, 3.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=190.6, 141.3, 136.4, 135.3, 133.7, 131.3, 130.5, 129.5, 129.0, 126.6, 124.6, 63.4, 43.1. HRMS (ESI) m/z calcd for $C_{15}H_{11}ClO_3SNa^+$ $(M+Na)^+$ 329.0010, found 329.0009.



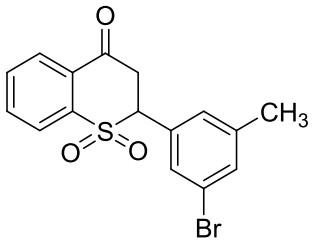
2-(4-bromophenyl)thiochroman-4-one 1,1-dioxide (3q):

Yield 84%; 58.8 mg; yellow solid; mp 155–157 ℃; R_f 0.41 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.13 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.85 (dd, *J* = 12.6, 2.4 Hz, 1H), 3.88 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.35 (dd, *J* = 17.4, 3.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=190.5, 141.2, 135.2, 133.6, 132.4, 131.5, 130.4, 128.8, 127.0, 124.6, 124.5, 63.4, 42.9. HRMS (ESI) m/z calcd for $C_{15}H_{11}BrO_3SNa^+$ $(M+Na)^+$ 372.9504, found 372.9504.



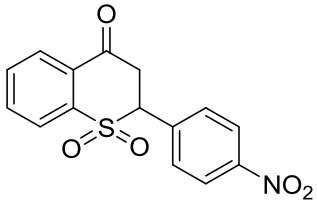
2-(3,5-dibromophenyl)thiochroman-4-one 1,1-dioxide (3r):

Yield 80%; 68.5 mg; white solid; mp 211-214 ℃; R_f 0.32 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-d_6) δ=8.20 – 8.05 (m, 2H), 8.01 (d, *J* = 12.6 Hz, 2H), 7.93 (dd, *J* = 18.0, 10.8 Hz, 1H), 7.78 (s, 2H), 5.71 (d, *J* = 12.6 Hz, 1H), 4.12 (dd, *J* = 17.4, 13.8 Hz, 1H), 3.33 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ=190.6, 140.6, 135.5, 134.6, 134.0, 133.0, 132.1, 130.3, 128.4, 123.9, 122.7, 61.2, 41.9. HRMS (ESI) m/z calcd for $C_{15}H_{10}Br_2O_3SNa^+$ $(M+Na)^+$ 450.8610, found 450.8609.



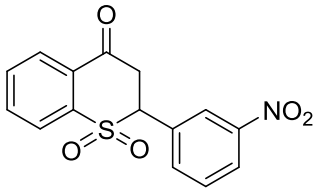
2-(3-bromo-5-methylphenyl)thiochroman-4-one 1,1-dioxide (3s):

Yield 77%; 56.1 mg; white solid; mp 189–194 ℃; R_f 0.35 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.10 (dd, *J* = 28.8, 6.6 Hz, 2H), 7.98 (s, 1H), 7.91 (d, *J* = 6.0 Hz, 1H), 7.55 (d, *J* = 24.6 Hz, 2H), 7.39 (s, 1H), 5.63 (d, *J* = 12.0 Hz, 1H), 4.21 – 3.91 (m, 1H), 3.30 (d, *J* = 17.4 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.8, 141.0, 140.7, 135.3, 133.8, 132.8, 130.9, 130.4, 129.9, 129.9, 128.3, 123.8, 121.7, 61.7, 42.4, 20.6. HRMS (ESI) m/z calcd for $C_{16}H_{13}BrO_3SNa^+$ $(M+Na)^+$ 386.9661, found 386.9663.



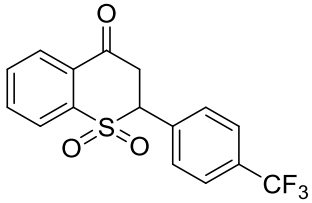
2-(4-nitrophenyl)thiochroman-4-one 1,1-dioxide (3t):

Yield 69%; 43.8 mg; yellow solid; mp 196–197 ℃; R_f 0.42 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.34 (d, *J* = 7.2 Hz, 2H), 8.14 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 6.6 Hz, 1H), 8.00 (d, *J* = 6.6 Hz, 1H), 7.95 (d, *J* = 6.6 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 5.91 (d, *J* = 12.6 Hz, 1H), 4.28 – 3.96 (m, 1H), 3.37 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.6, 148.2, 140.8, 135.8, 135.5, 134.0, 131.7, 130.4, 128.3, 123.8, 123.7, 61.8, 42.1. HRMS (ESI) m/z calcd for $C_{15}H_{11}NO_5SNa^+$ $(M+Na)^+$ 340.0250, found 340.0246.

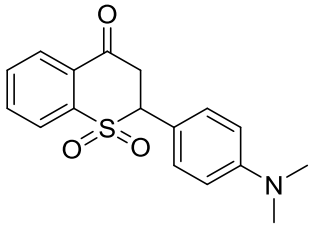


2-(3-nitrophenyl)thiochroman-4-one 1,1-dioxide (3u):

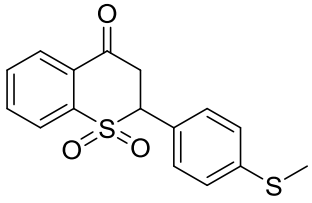
Yield 74%; 46.9 mg; yellow solid; mp 201–202 ℃; R_f 0.44 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.51 – 8.32 (m, 2H), 8.14 (d, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 6.6 Hz, 2H), 7.95 (t, *J* = 7.2 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 5.92 (d, *J* = 12.6 Hz, 1H), 4.17 (dd, *J* = 16.8, 13.8 Hz, 1H), 3.40 (s, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.6, 147.9, 140.7, 136.8, 135.5, 134.0, 130.8, 130.4, 128.4, 124.8, 124.5, 123.9, 61.5, 42.1. HRMS (ESI) m/z calcd for $C_{15}H_{11}NO_5SNa^+$ $(M+Na)^+$ 340.0250, found 340.0252.



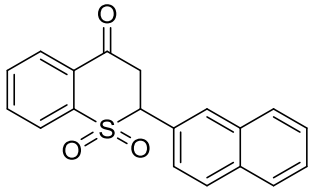
2-(4-(trifluoromethyl)phenyl)thiochroman-4-one 1,1-dioxide (3v):
Yield 79%; 53.7 mg; white solid; mp 160–162 ℃; R_f 0.38 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.15 (d, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 8.00 (t, *J* = 7.2 Hz, 1H), 7.92 (t, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 7.2 Hz, 2H), 5.84 (d, *J* = 12.6 Hz, 1H), 4.11 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.37 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.8, 140.9, 135.4, 133.9, 133.3, 131.2, 130.5, 130.0 (q, *J* = 31.5 Hz, $^2J_{CF}$), 128.3, 125.6, 124.0 (q, *J* = 270.0 Hz, $^1J_{CF}$), 123.8, 62.0, 42.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ= -62.92 (s, 3F). HRMS (ESI) m/z calcd for $C_{16}H_{11}F_3O_3SNa^+$ $(M+Na)^+$ 363.0273, found 363.0275.



2-(4-(dimethylamino)phenyl)thiochroman-4-one 1,1-dioxide (3w):
Yield 86%; 54.2 mg; yellow solid; mp 213–217 ℃; R_f 0.28 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.11 (d, *J* = 7.2 Hz, 1H), 8.05 (d, *J* = 7.2 Hz, 1H), 7.96 (t, *J* = 6.6 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 7.8 Hz, 2H), 5.40 (d, *J* = 12.0 Hz, 1H), 4.06 – 3.79 (m, 1H), 3.20 (d, *J* = 17.4 Hz, 1H), 2.93 (s, 6H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.5, 151.0, 141.5, 135.2, 133.4, 130.8, 130.4, 128.1, 123.8, 114.9, 112.0, 62.1, 42.9, 40.3. HRMS (ESI) m/z calcd for $C_{17}H_{18}NO_3S^+$ $(M+H)^+$ 316.1002, found 316.1003.

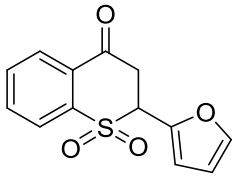


2-(4-(methylthio)phenyl)thiochroman-4-one 1,1-dioxide (3x):
Yield 81%; 51.5 mg; white soild; mp 146–149 ℃; R_f 0.25 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.00 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 5.46 (d, *J* = 12.0 Hz, 1H), 3.88 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.15 (d, *J* = 16.8 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.1, 141.1, 140.3, 135.3, 133.7, 130.6, 130.4, 128.2, 125.7, 124.8, 123.8, 62.0, 42.5, 14.4. HRMS (ESI) m/z calcd for $C_{16}H_{14}O_3S_2Na^+$ $(M+Na)^+$ 341.0277, found 341.0278.



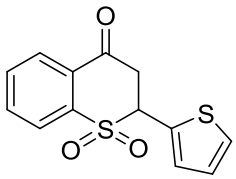
2-(naphthalen-2-yl)thiochroman-4-one 1,1-dioxide (3y):

Yield 82%; 52.8 mg; yellow solid; mp 197–199 ℃; R_f 0.43 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.18 (s, 2H), 8.12 (d, *J* = 6.6 Hz, 1H), 8.00 (d, *J* = 22.8 Hz, 4H), 7.91 (d, *J* = 6.6 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.59 (s, 2H), 5.84 (d, *J* = 12.0 Hz, 1H), 4.33 – 4.09 (m, 1H), 3.44 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.2, 141.2, 135.3, 133.7, 133.2, 132.7, 130.5, 129.9, 128.3, 128.2, 128.1, 127.6, 127.5, 127.1, 126.7, 126.2, 123.8, 62.5, 42.7. HRMS (ESI) m/z calcd for $C_{19}H_{14}O_3SNa^+$ $(M+Na)^+$ 345.0556, found 345.0552.



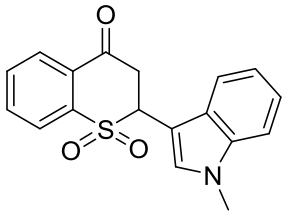
2-(furan-2-yl)thiochroman-4-one 1,1-dioxide (3z):

Yield 83%; 43.5 mg; yellow solid; mp 148–150 ℃; R_f 0.44 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.12 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.97 (t, *J* = 7.2 Hz, 1H), 7.90 (t, *J* = 7.2 Hz, 1H), 7.78 (s, 1H), 6.72 (s, 1H), 6.57 (s, 1H), 5.79 (d, *J* = 7.8 Hz, 1H), 3.77 (dd, *J* = 18.0, 10.8 Hz, 1H), 3.50 (dd, *J* = 18.0, 3.0 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.2, 144.9, 143.3, 140.4, 135.3, 133.9, 130.5, 128.2, 123.9, 112.5, 111.4, 57.7, 41.1. HRMS (ESI) m/z calcd for $C_{13}H_{10}O_4SNa^+$ $(M+Na)^+$ 285.0192, found 285.0192.



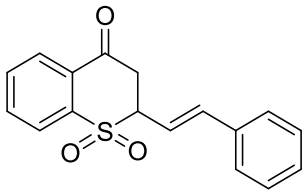
2-(thiophen-2-yl)thiochroman-4-one 1,1-dioxide (3aa):

Yield 80%; 44.5 mg; yellow solid; mp 111–113 ℃; R_f 0.38 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.12 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.99 (t, *J* = 7.2 Hz, 1H), 7.91 (t, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 4.2 Hz, 1H), 7.34 (s, 1H), 7.17 (s, 1H), 5.96 (d, *J* = 10.2 Hz, 1H), 3.85 (dd, *J* = 17.4, 12.6 Hz, 1H), 3.45 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.3, 140.6, 135.4, 133.9, 130.5, 130.0, 129.8, 128.6, 128.3, 127.4, 124.0, 58.6, 43.7. HRMS (ESI) m/z calcd for $C_{13}H_{10}O_3S_2Na^+$ $(M+Na)^+$ 300.9964, found 300.9963.



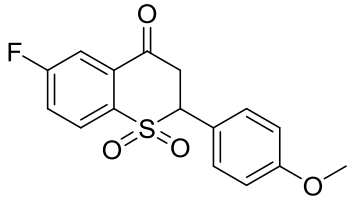
2-(1-methyl-1H-indol-3-yl)thiochroman-4-one 1,1-dioxide (3ab):

Yield 75%; 48.8 mg; white solid; mp 218–219 ℃; R_f 0.36 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.15 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.98 (t, *J* = 7.2 Hz, 1H), 7.90 (t, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.63 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 5.91 (d, *J* = 11.4 Hz, 1H), 3.97 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.83 (s, 3H), 3.34 (d, *J* = 16.8 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d6*) δ=191.5, 141.7, 136.5, 135.2, 133.5, 130.8, 130.6, 128.2, 127.5, 124.0, 121.9, 119.7, 119.6, 110.0, 101.8, 56.2, 43.4, 32.8. HRMS (ESI) m/z calcd for $C_{18}H_{15}NO_3SNa^+$ $(M+Na)^+$ 348.0665, found 348.0668.



(E)-2-styrylthiochroman-4-one 1,1-dioxide (3ac):

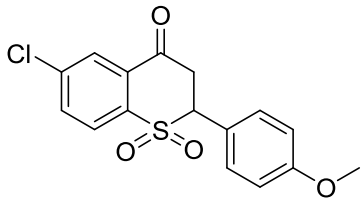
Yield 77%; 45.9 mg; yellow solid; mp 132–135 ℃; R_f 0.52 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.08 (dd, *J* = 15.6, 7.8 Hz, 2H), 7.97 (t, *J* = 7.2 Hz, 1H), 7.88 (t, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.26 (m, 3H), 6.93 (d, *J* = 16.2 Hz, 1H), 6.36 (dd, *J* = 16.2, 7.8 Hz, 1H), 5.14 (s, 1H), 3.63 (dd, *J* = 18.0, 11.4 Hz, 1H), 3.36 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.6, 140.9, 138.4, 135.3, 135.3, 133.7, 130.5, 128.8, 128.2, 126.9, 123.8, 116.5, 61.3, 42.1. HRMS (ESI) m/z calcd for $C_{17}H_{14}O_3SNa^+$ $(M+Na)^+$ 321.0556, found 321.0557.



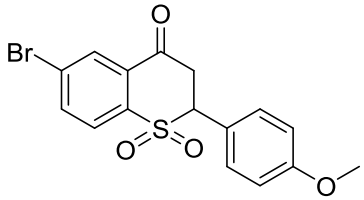
6-fluoro-2-(4-methoxyphenyl)thiochroman-4-one 1,1-dioxide (3ad):

Yield 81%; 51.8 mg; yellow solid; mp 165–167 ℃; R_f 0.31 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.16 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 5.55 (d, *J* = 12.6 Hz, 1H), 4.13 – 3.95 (m, 1H), 3.79 (s, 3H), 3.29 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d6*) δ=190.3, 164.5 (d, *J* = 253.5 Hz, $^1J_{CF}$), 160.3, 137.7, 133.5 (d, *J* = 7.5 Hz, $^3J_{CF}$), 131.5, 127.5 (d, *J* = 9.0 Hz, $^3J_{CF}$), 122.5 (d, *J* = 22.5 Hz, $^2J_{CF}$), 120.1, 114.6 (d, *J* = 22.5 Hz,

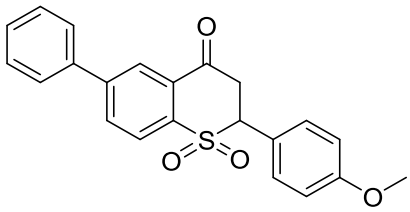
$^{2}J_{CF}$), 114.2, 61.9, 55.2, 42.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ= -102.15 (s, 1F). HRMS (ESI) m/z calcd for $C_{16}H_{13}FO_4SNa^+$ $(M+Na)^+$ 343.0411, found 343.0414.



6-chloro-2-(4-methoxyphenyl)thiochroman-4-one 1,1-dioxide (3ae):
Yield 80%; 53.8 mg; yellow solid; mp 111–113 ℃; R_f 0.35 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.19 – 7.97 (m, 3H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.68 – 5.46 (m, 1H), 4.01 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.79 (s, 3H), 3.28 (dd, *J* = 17.4, 2.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.2, 160.3, 139.9, 138.7, 135.0, 132.1, 131.5, 127.6, 126.3, 119.9, 114.2, 61.9, 55.2, 42.7. HRMS (ESI) m/z calcd for $C_{16}H_{13}ClO_4SNa^+$ $(M+Na)^+$ 359.0115, found 359.0115.

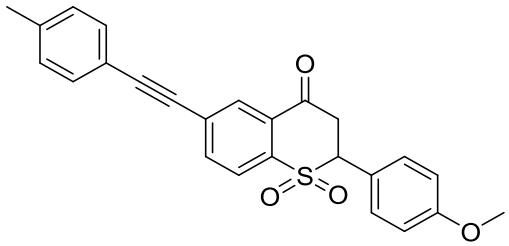


6-bromo-2-(4-methoxyphenyl)thiochroman-4-one 1,1-dioxide (3af):
Yield 82%; 62.3 mg; white solid; mp 186–187 ℃; R_f 0.36 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.17 (s, 2H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 6.6 Hz, 2H), 7.04 (d, *J* = 6.6 Hz, 2H), 5.55 (d, *J* = 12.6 Hz, 1H), 4.11 – 3.93 (m, 1H), 3.79 (s, 3H), 3.26 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.1, 160.2, 140.2, 137.8, 132.0, 131.4, 130.5, 127.4, 126.2, 119.9, 114.2, 61.8, 55.2, 42.7. HRMS (ESI) m/z calcd for $C_{16}H_{13}BrO_4SK^+$ $(M+K)^+$ 418.9350, found 418.9349.

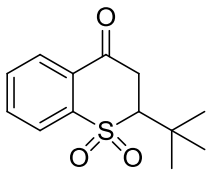


2-(4-methoxyphenyl)-6-phenylthiochroman-4-one 1,1-dioxide (3ag):
Yield 78%; 59.0 mg; yellow solid; mp 192–194 ℃; R_f 0.40 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.30 (s, 1H), 8.23 (d, *J* = 6.0 Hz, 1H), 8.13 (d, *J* = 6.6 Hz, 1H), 7.77 (d, *J* = 4.8 Hz, 2H), 7.54 (s, 2H), 7.48 (d, *J* = 6.6 Hz, 3H), 7.04 (d, *J* = 6.6 Hz, 2H), 5.54 (d, *J* = 12.6 Hz, 1H), 4.01 (t, *J* = 15.0 Hz, 1H), 3.79 (s, 3H), 3.29 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=191.2, 160.2, 144.9, 139.9, 137.5, 133.1, 131.5, 131.0, 129.3, 129.1, 127.1, 125.7, 124.8, 120.3,

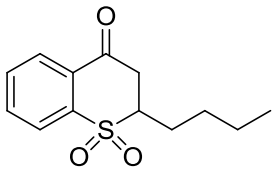
114.2, 61.9, 55.2, 42.8. HRMS (ESI) m/z calcd for $C_{22}H_{18}O_4SNa^+$ $(M+Na)^+$ 401.0818, found 401.0817.



2-(4-methoxyphenyl)-6-(p-tolylethynyl)thiochroman-4-one 1,1-dioxide (3ah):
Yield 74%; 61.6 mg; yellow solid; mp 195–198 ℃; R_f 0.38 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.13 (s, 1H), 8.06 (s, 2H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 5.56 (d, *J* = 12.6 Hz, 1H), 4.00 (dd, *J* = 17.4, 13.2 Hz, 1H), 3.79 (s, 3H), 3.25 (d, *J* = 17.4 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=190.6, 160.2, 140.3, 139.7, 137.1, 131.8, 131.5, 130.8, 130.3, 129.5, 127.7, 124.6, 120.1, 118.2, 114.2, 93.8, 86.6, 61.8, 55.2, 42.7, 21.2. HRMS (ESI) m/z calcd for $C_{25}H_{20}O_4SNa^+$ $(M+Na)^+$ 439.0975, found 439.0977.

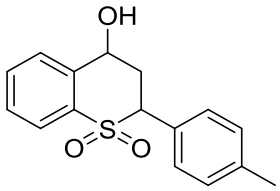


2-(tert-butyl)thiochroman-4-one 1,1-dioxide (3ai):
Yield 56%; 28.3 mg; white solid; mp 99.8-101.2 °C; R_f 0.27 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.99 (dt, *J* = 13.8, 6.6 Hz, 2H), 7.80 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.72 – 7.65 (m, 1H), 3.55 (d, *J* = 12.6 Hz, 1H), 3.47 (ddd, *J* = 17.4, 12.6, 4.8 Hz, 1H), 3.25 (dd, *J* = 17.4, 2.4 Hz, 1H), 1.30 (d, *J* = 3.6 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=192.1, 143.31, 134.92, 133.00, 130.13, 127.96, 123.42, 67.41, 40.17, 35.16, 28.44. HRMS (ESI) m/z calcd for $C_{13}H_{16}O_3SNa^+$ $(M+Na)^+$ 275.0712, found 275.0712.



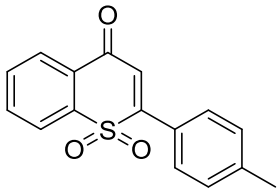
2-butylthiochroman-4-one 1,1-dioxide (3aj):
Yield 37%; 18.6 mg; yellow oil; R_f 0.27 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.08 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.03 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.82 (td, *J* = 7.6, 1.2 Hz, 1H), 7.73 (td, J = 7.6, 1.2 Hz, 1H), 3.63 (ddd, *J* = 13.6, 8.8, 4.4 Hz, 1H), 3.36 (dd, *J* = 17.6, 3.6 Hz, 1H), 3.24 (dd, J = 17.6, 10.4 Hz, 1H), 2.24 (ddd, *J* = 14.8, 10.4, 5.2 Hz, 1H), 1.71–1.32 (m, 5H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C

NMR (150 MHz, $CDCl_3$) δ=190.7, 141.04, 135.02, 133.27, 130.46, 128.42, 124.12, 58.95, 42.00, 28.20, 25.76, 22.36, 13.78. HRMS (ESI) m/z calcd for $C_{13}H_{16}O_3SNa^+$ $(M+Na)^+$ 275.0712, found 275.0712.



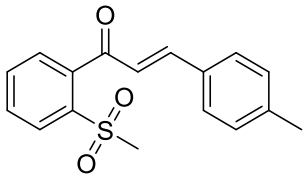
4-hydroxy-2-(p-tolyl)thiochromane 1,1-dioxide (4b):

Yield 99%; 285.2 mg; white solid; mp 164–166 ℃; R_f 0.54 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=7.91 – 7.75 (m, 2H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 6.17 (d, *J* = 6.6 Hz, 1H), 5.08 (s, 1H), 4.99 (d, *J* = 13.2 Hz, 1H), 2.88 (dd, *J* = 25.2, 12.6 Hz, 1H), 2.54 (t, *J* = 20.4 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=140.5, 138.5, 138.1, 132.5, 130.1, 129.1, 128.4, 128.3, 127.3, 123.2, 66.3, 62.0, 36.5, 20.9. HRMS (ESI) m/z calcd for $C_{16}H_{17}O_3S^+$ $(M+H)^+$ 289.0893, found 289.0892.



2-(p-tolyl)-4H-thiochromen-4-one 1,1-dioxide (5b):

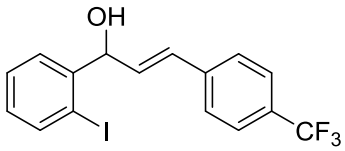
Yield 91%; 129.2 mg; yellow solid; mp 123–125 ℃; R_f 0.47 (EtOAc/petroleum ether = 1:8); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ=8.12 (dd, *J* = 16.8, 7.8 Hz, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.04 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ=177.9, 151.1, 142.1, 140.9, 135.4, 133.6, 129.8, 128.5, 128.4, 128.0, 127.6, 125.6, 123.4, 21.0. HRMS (ESI) m/z calcd for $C_{16}H_{13}O_3S^+$ $(M+H)^+$ 285.0580, found 285.0573.



(E)-1-(2-(methylsulfonyl)phenyl)-3-(p-tolyl)prop-2-en-1-one (7):

Yield 61%; 36.6 mg; yellow solid; mp 83–86 ℃; R_f 0.30 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.14 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 16.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 16.2 Hz, 1H), 3.30 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=195.9, 148.8, 142.0, 140.6, 139.2, 133.3, 131.4,

130.3, 130.2, 129.9, 128.9, 128.4, 125.7, 46.3, 21.7. HRMS (ESI) m/z calcd for $C_{17}H_{17}O_3S^+$ $(M+H)^+$ 301.0893, found 301.0891.



(E)-1-(2-iodophenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (8):
White solid; mp 100–103 ℃; R_f 0.25 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.82 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 3H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 16.2 Hz, 1H), 6.38 (dd, *J* = 16.2, 5.4 Hz, 1H), 5.63 (d, *J* = 5.4 Hz, 1H), 2.65 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=144.2, 140.2, 139.8, 132.5, 129.9, 129.7, 129.1, 128.0, 127.0, 126.4 (q, *J* = 271.5 Hz, $^1J_{CF}$), 125.7, 98.4, 77.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ= -62.52 (s, 3F). MS (EI) m/z calcd for $C_{16}H_{12}F_3IO^{\cdot+}$ $(M)^{\cdot+}$ 403.99, found 403.90.

12. Crystallographic data and molecular structure of compounds 3a

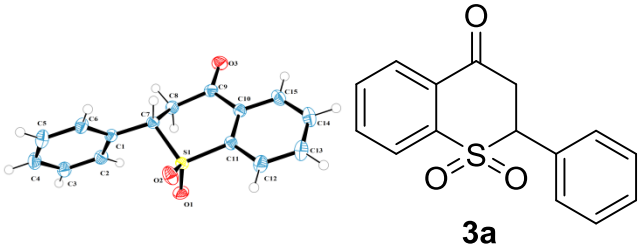


Figure 1. X-ray crystal structure of **3a**

Crystal Data for Compound **3a**: CCDC 1973077 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

```
Bond precision:  C-C = 0.0023 A          Wavelength=0.71073

Cell:          a=10.049(3)       b=10.240(3)       c=13.391(4)
               alpha=76.934(4)   beta=77.667(4)    gamma=71.574(4)
Temperature:   150 K

                Calculated                Reported
Volume          1258.3(6)                 1258.4(7)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C15 H12 O3 S              C15 H12 O3 S
Sum formula     C15 H12 O3 S              C15 H12 O3 S
Mr              272.31                    272.31
Dx,g cm-3       1.437                     1.437
Z               4                         4
Mu (mm-1)       0.257                     0.257
F000            568.0                     568.0
F000'           568.77
h,k,lmax        14,15,19                  14,15,19
Nref            8625                      7696
Tmin,Tmax       0.950,0.962               0.514,0.746
Tmin'           0.950

Correction method= # Reported T Limits: Tmin=0.514 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.892          Theta(max)= 31.852

R(reflections)= 0.0634( 6575)     wR2(reflections)= 0.1778( 7696)

S = 1.185                 Npar= 344
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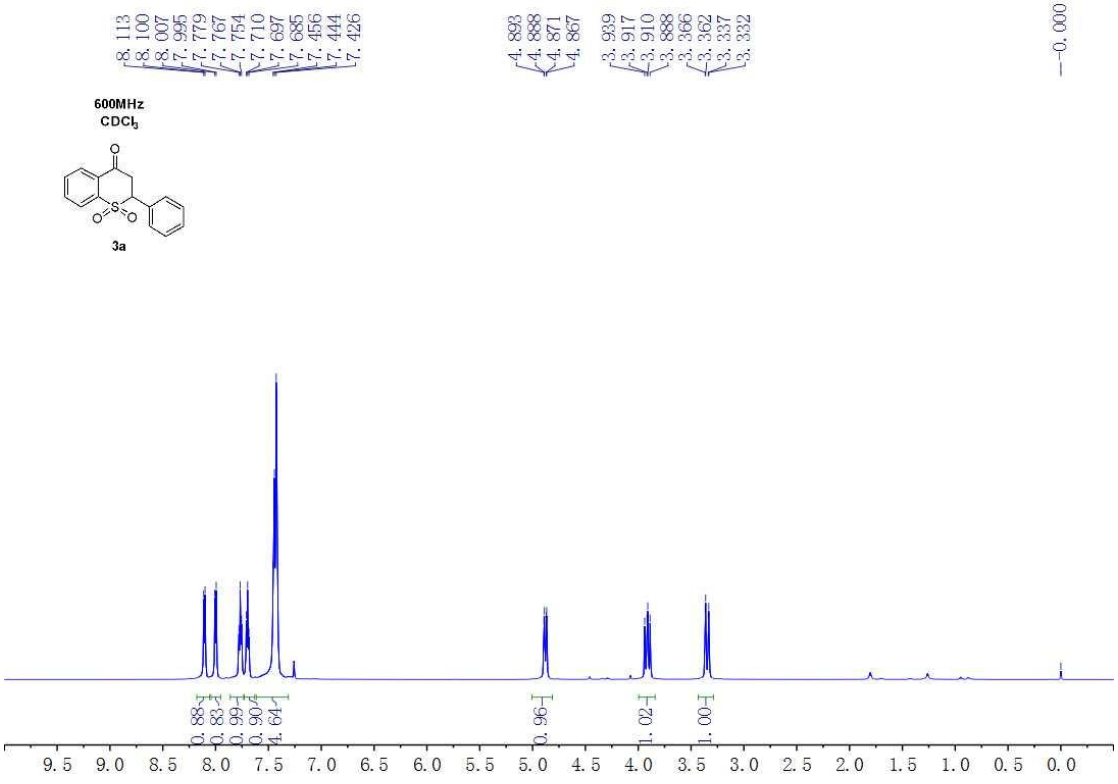
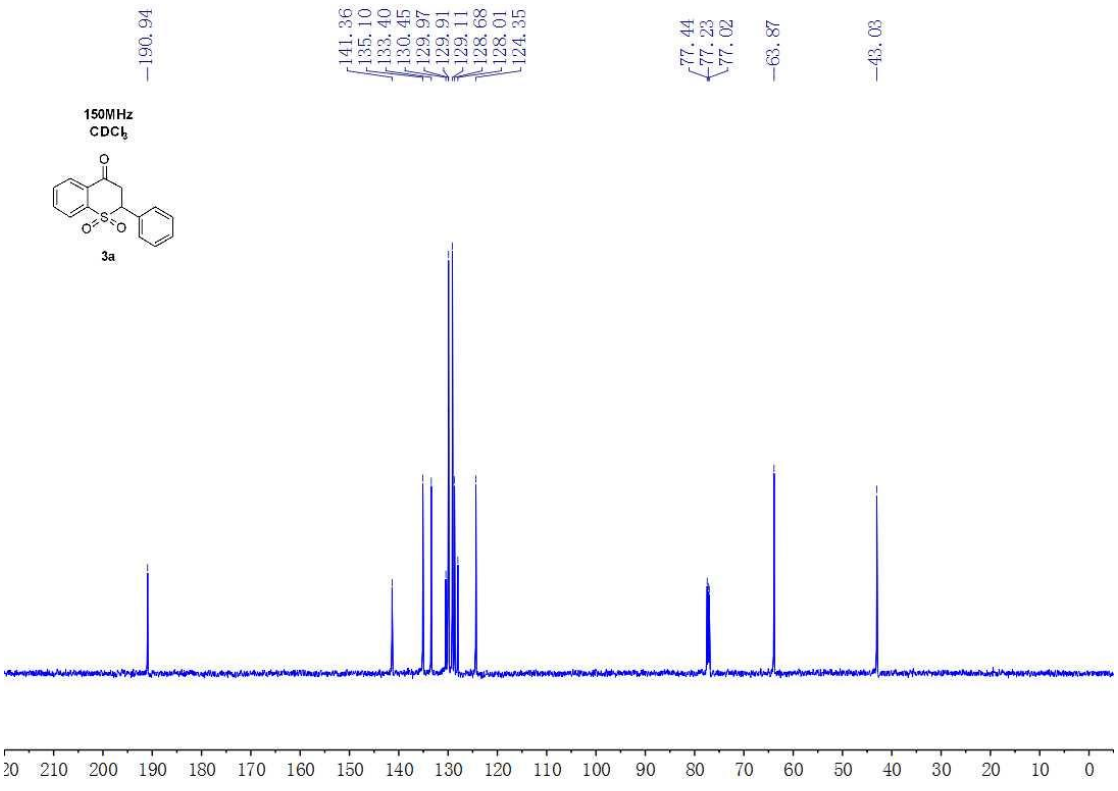
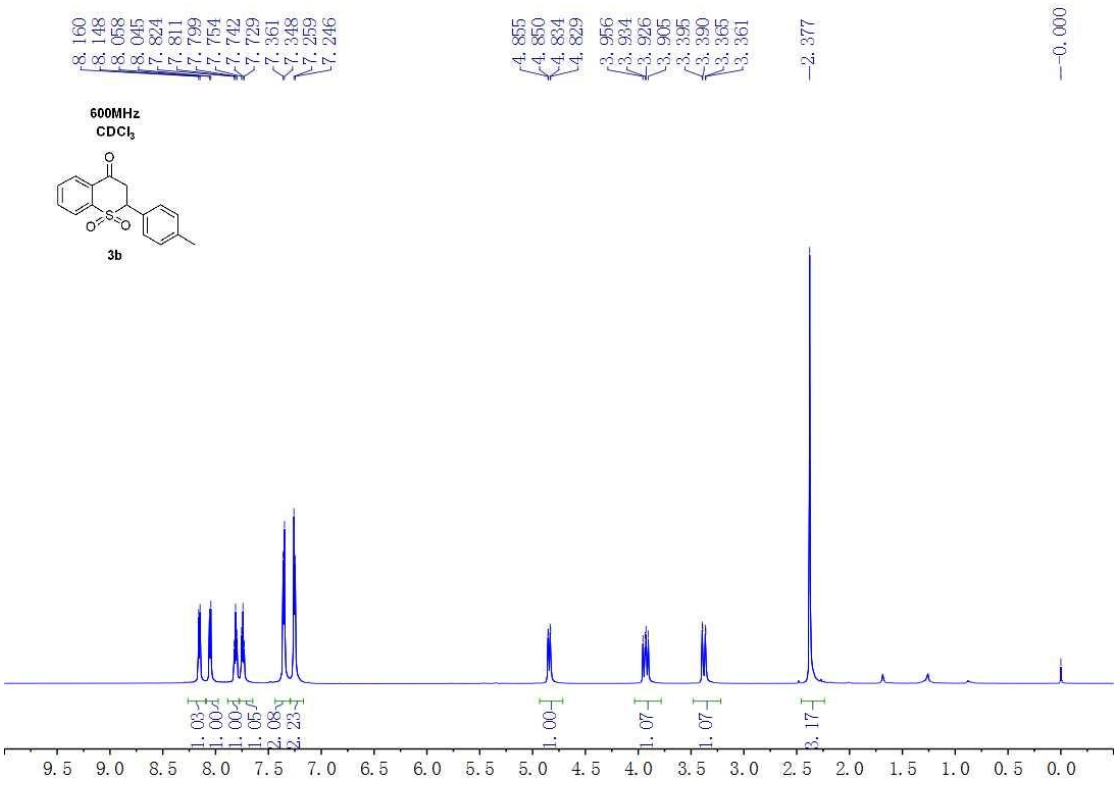
13. references

1. Sangeetha, S.; Muthupandi, P.; Sekar, G. *Org. Lett.* **2015**, *17*, 6006.

14.^{1}H and ^{13}C NMR spectra for all compounds



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1.00
1.00
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2.23
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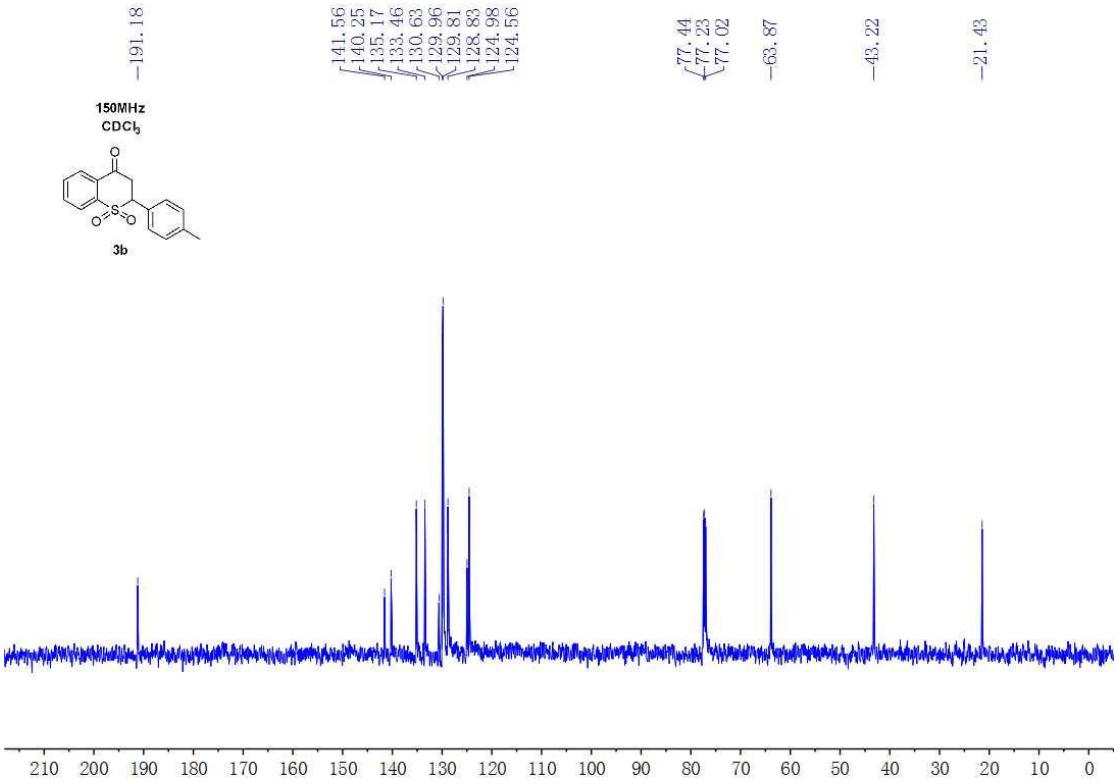
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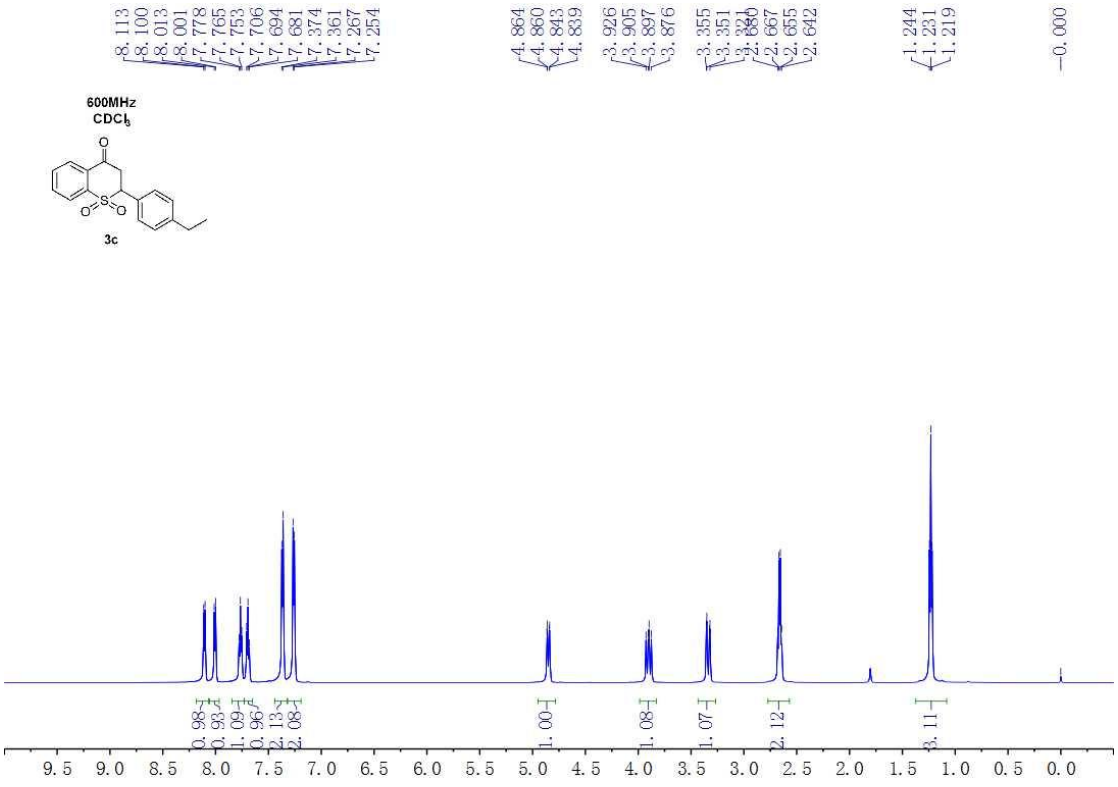
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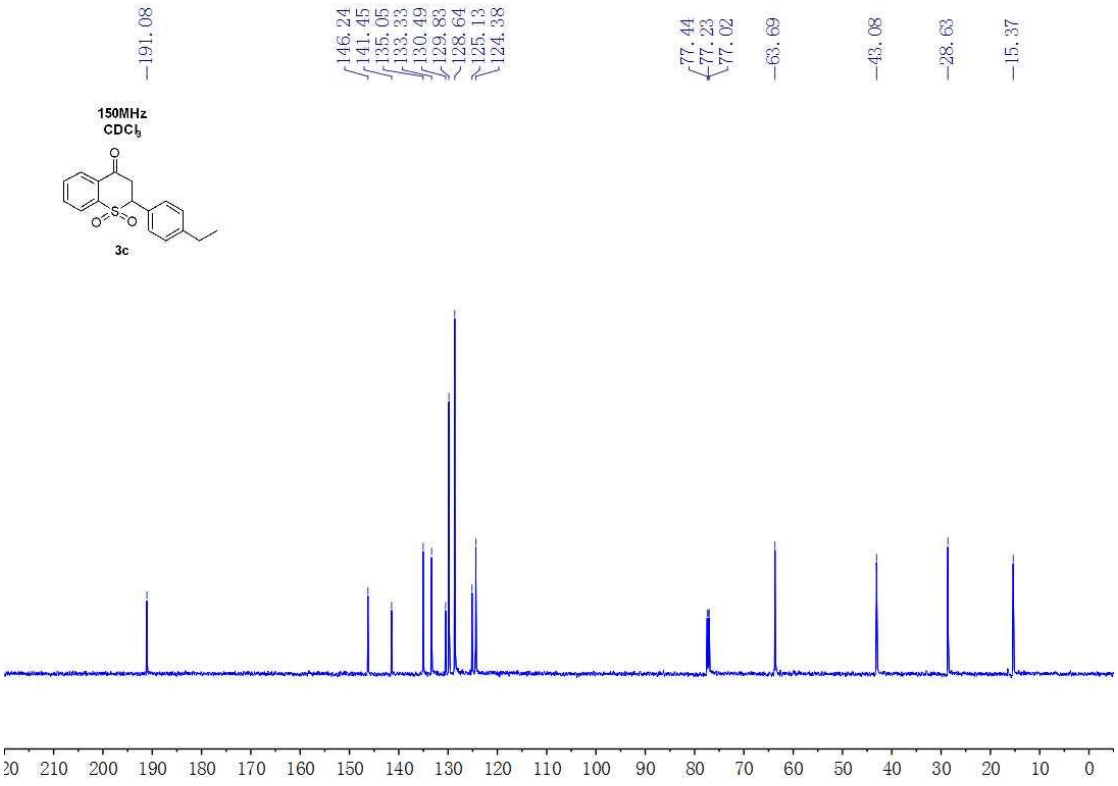
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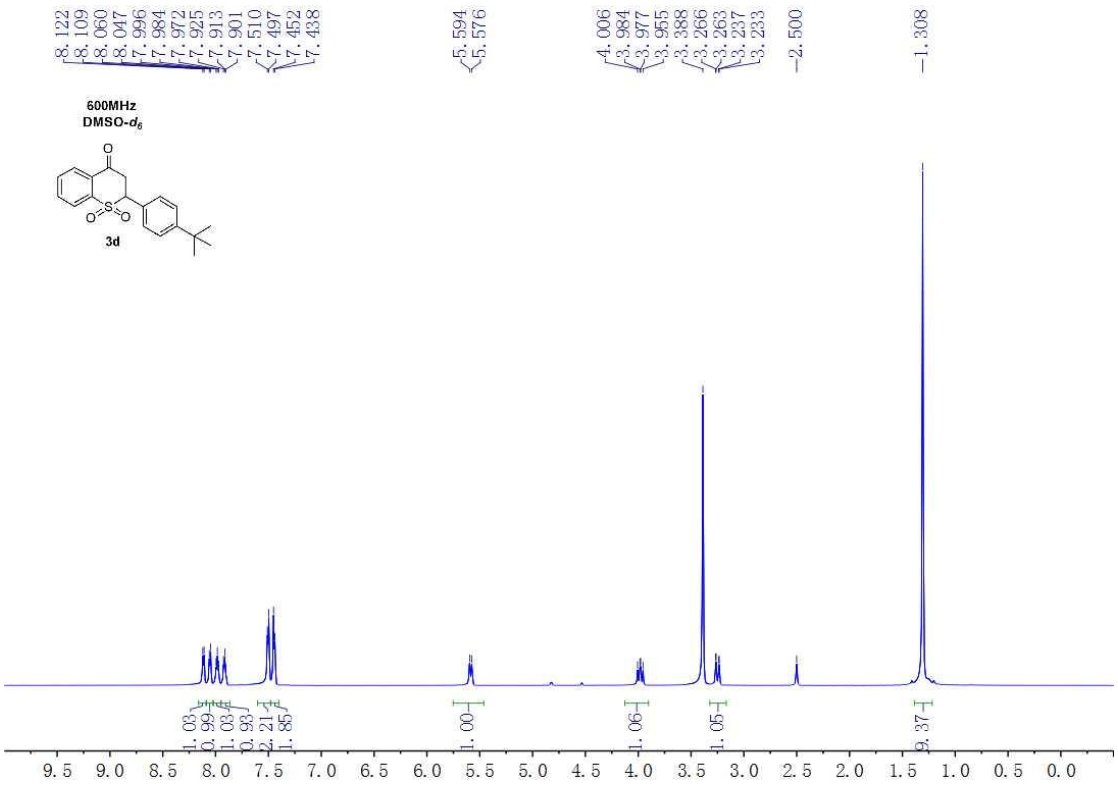
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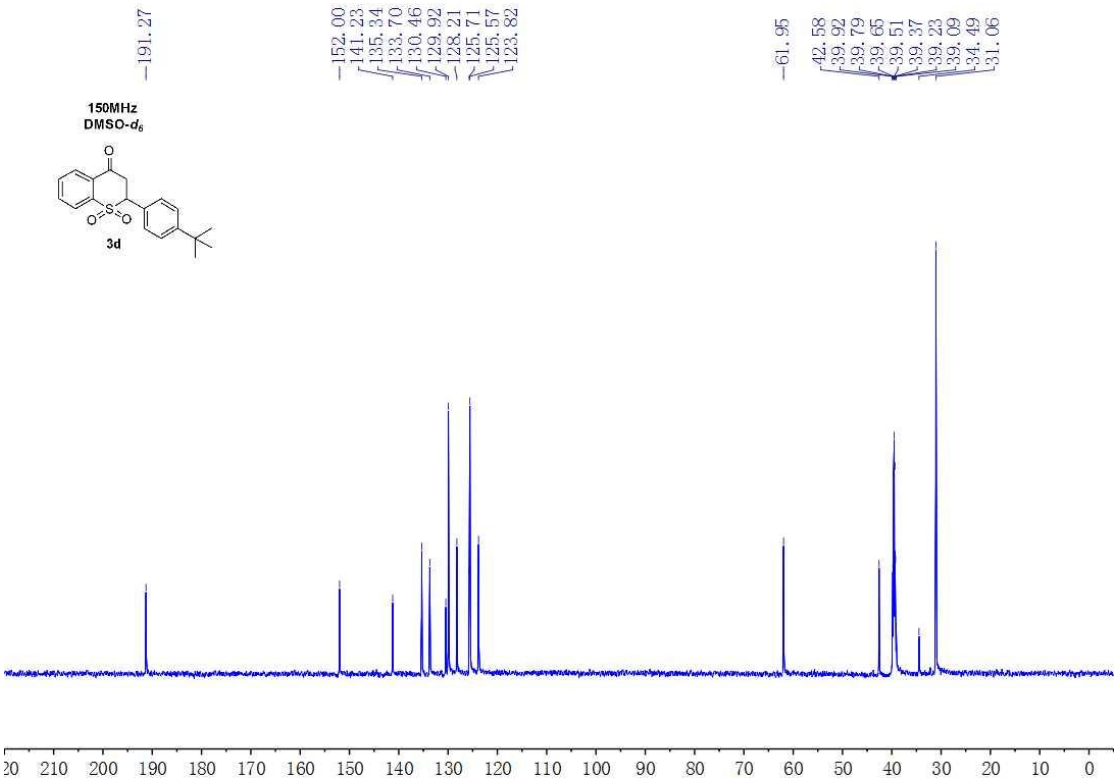
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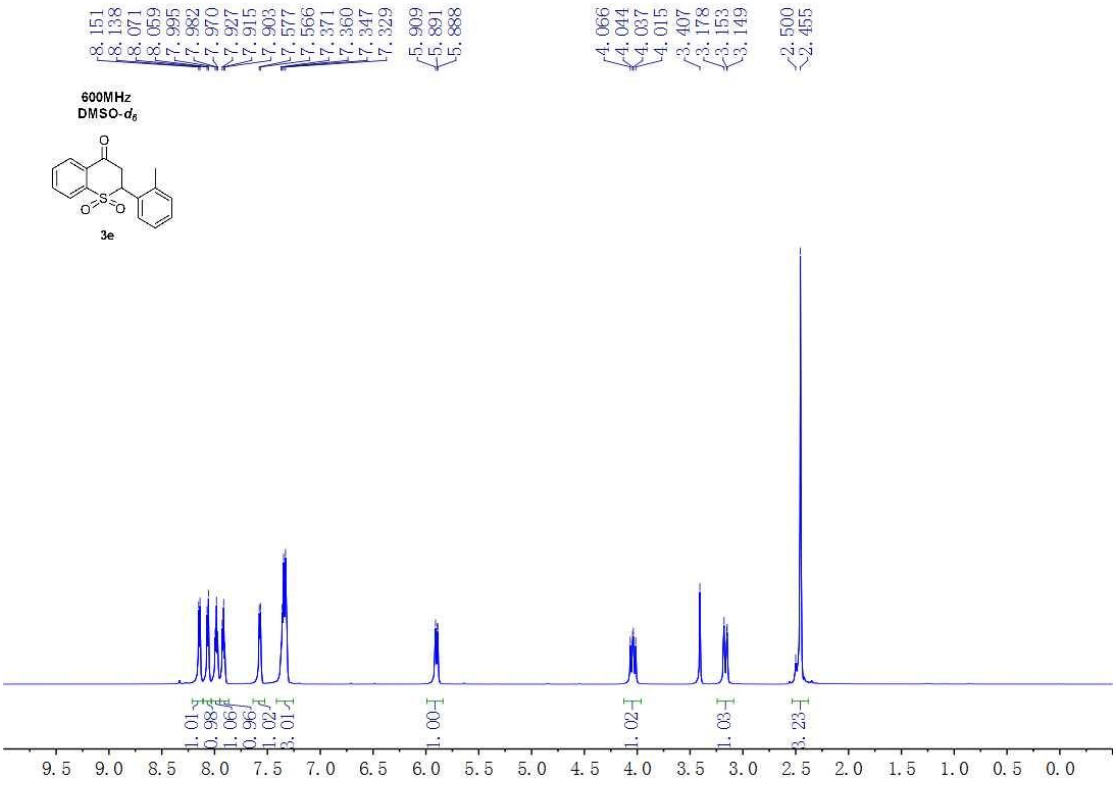
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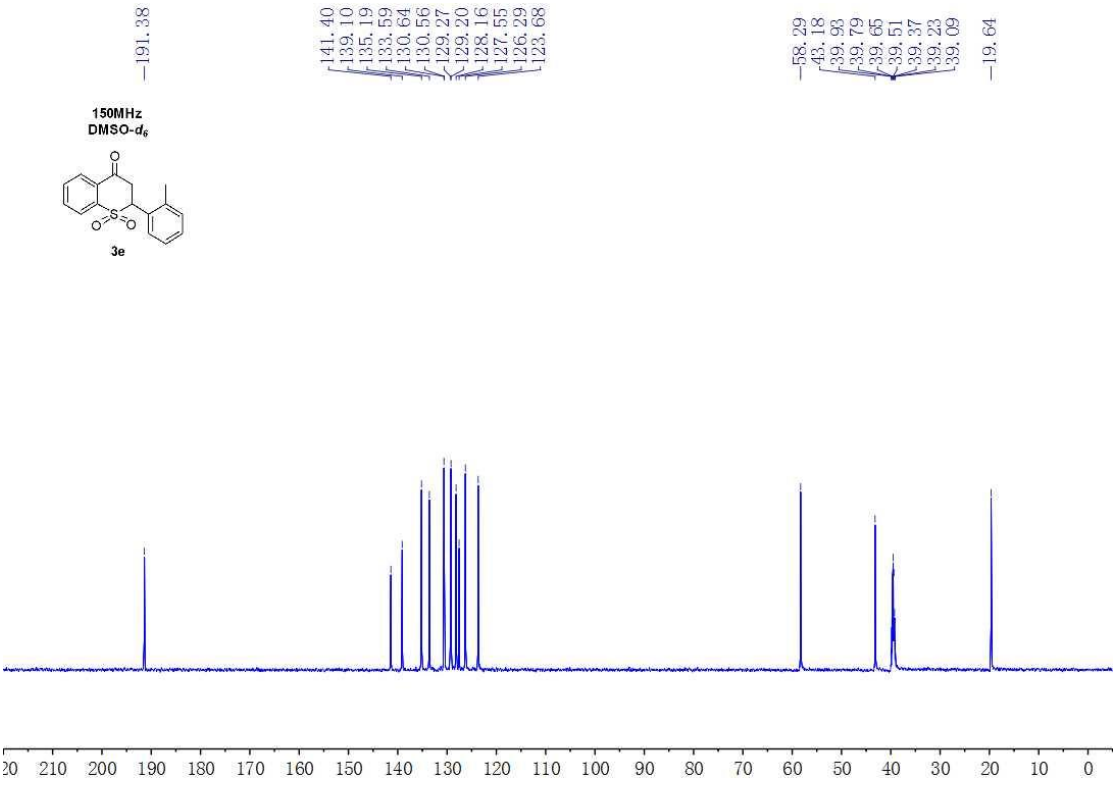
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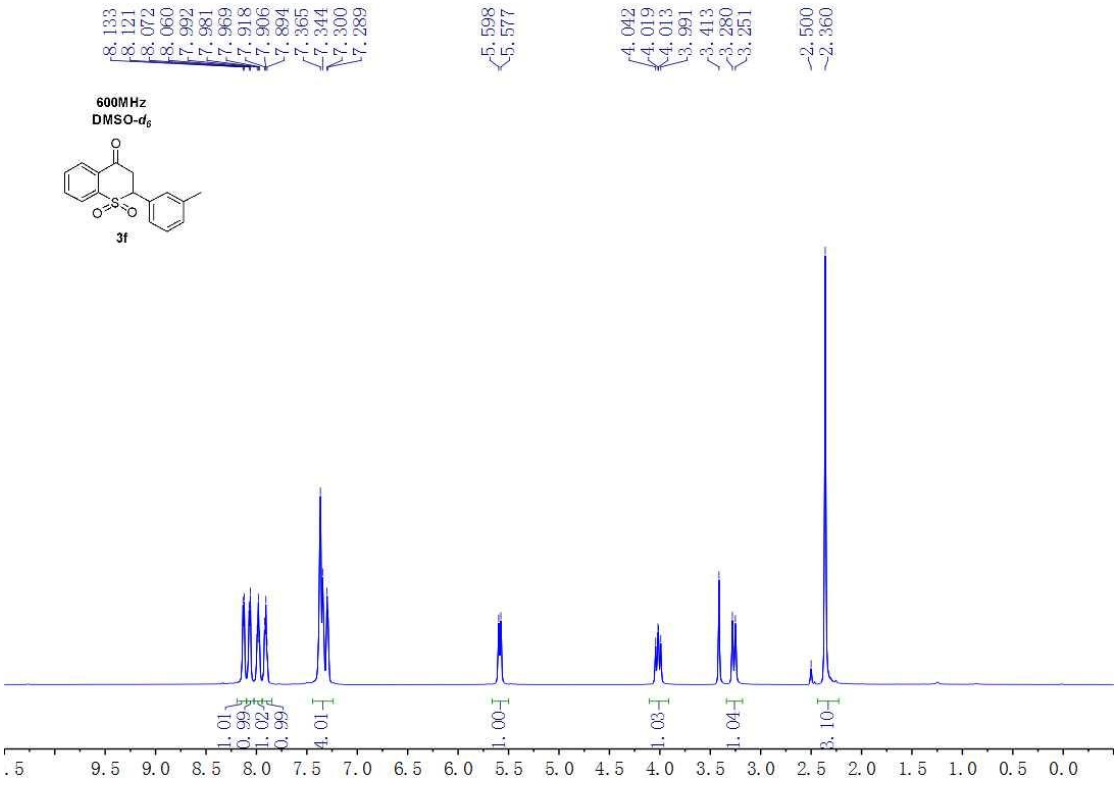
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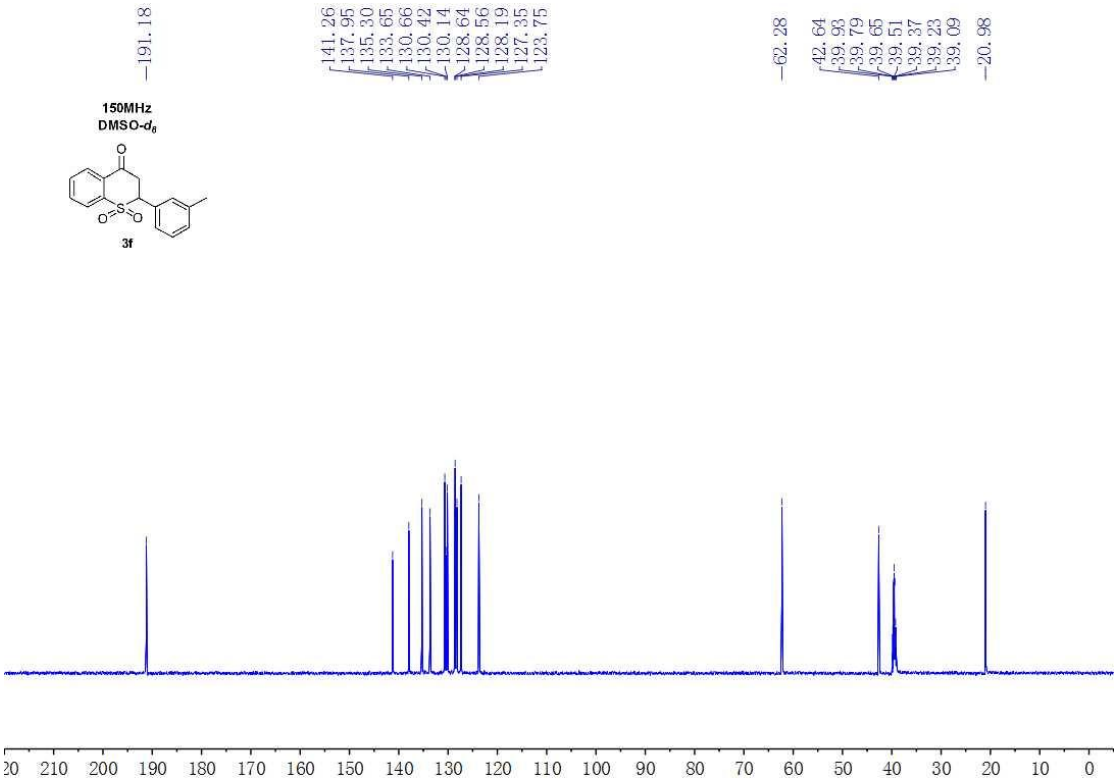
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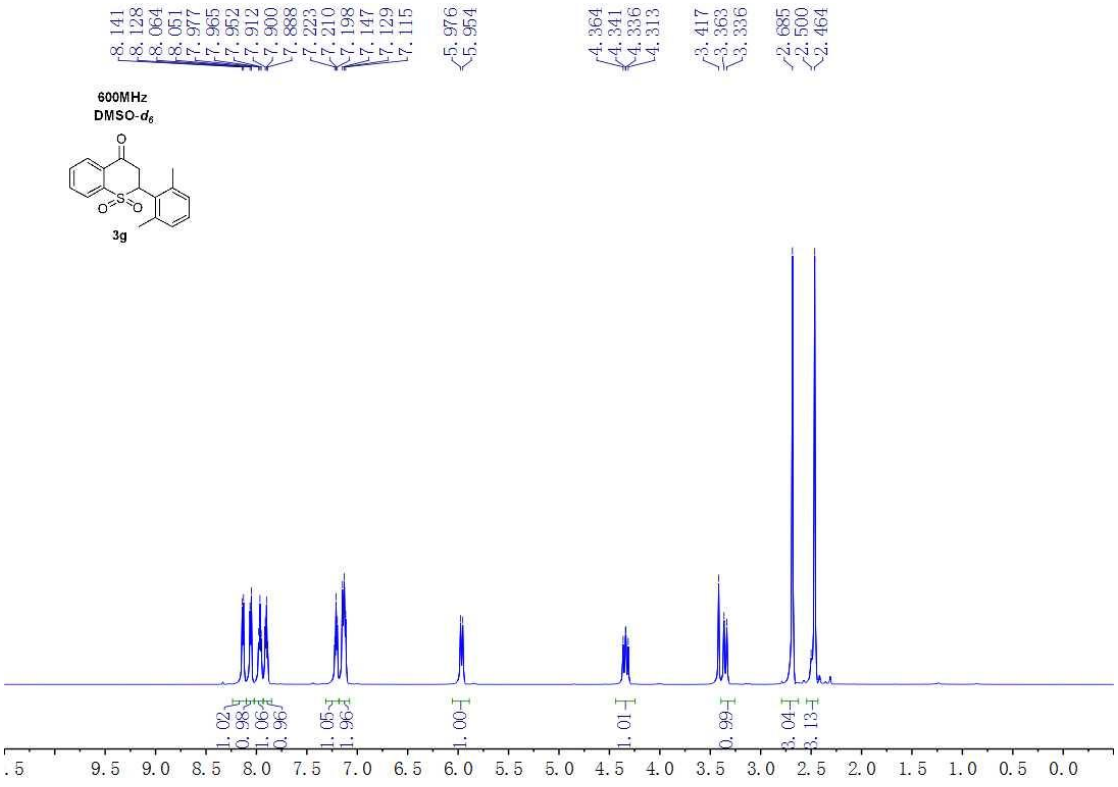
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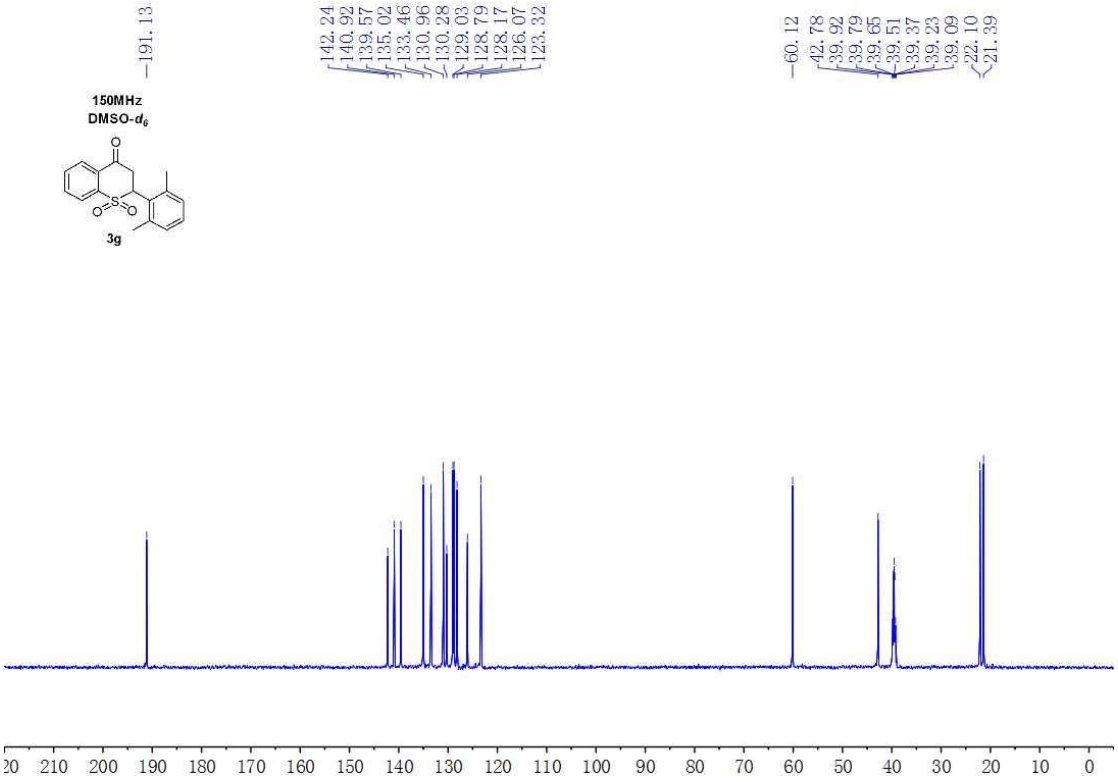
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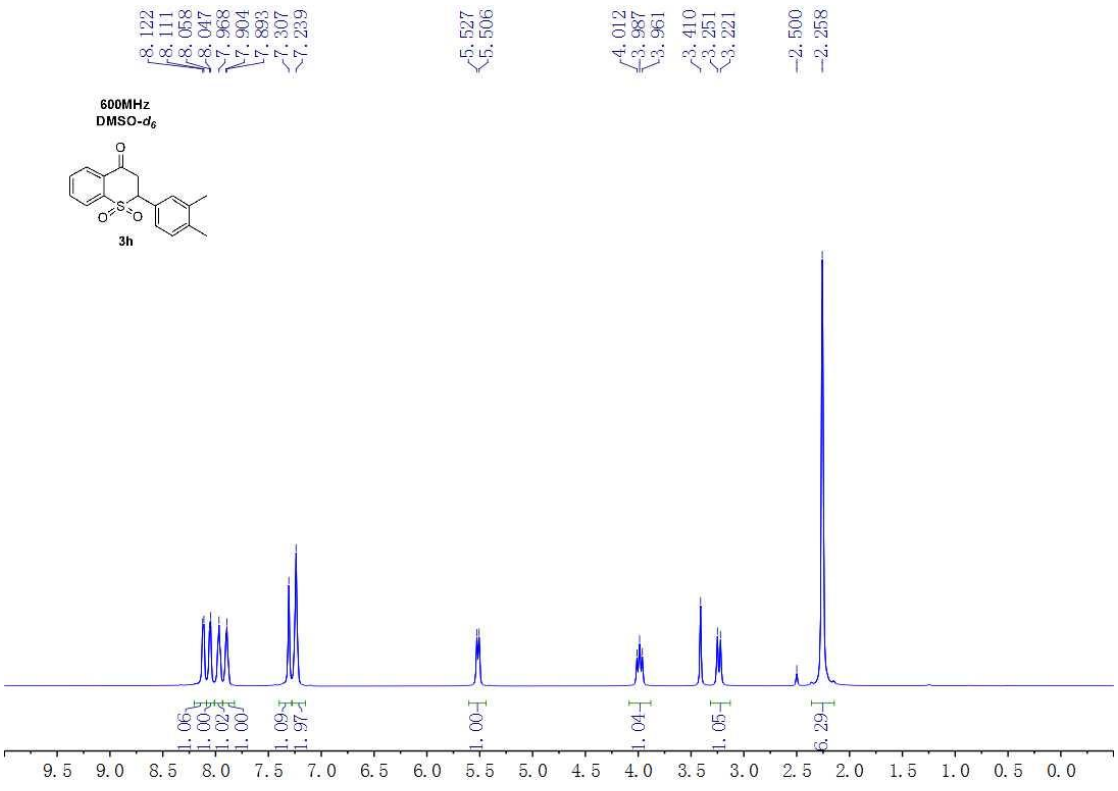
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3.410
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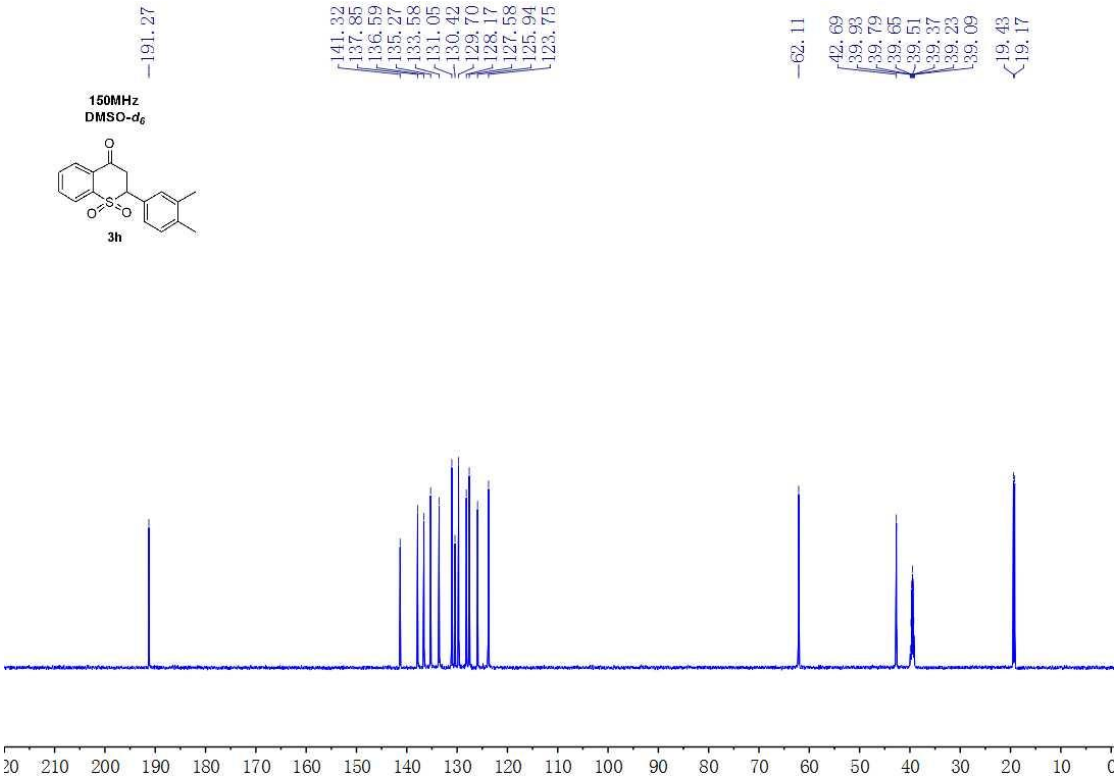
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42.69
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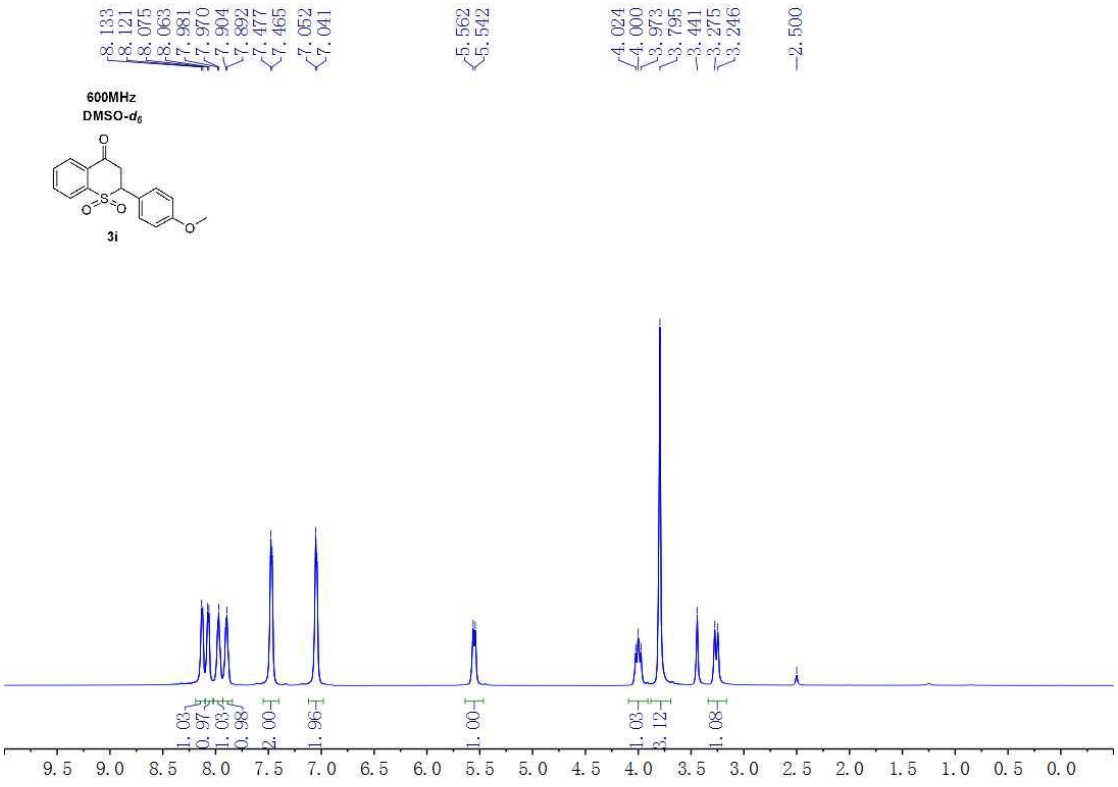
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5.562
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4.000
3.973
3.795
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1.03
0.98
2.00
1.96
1.00
1.03
3.12
1.08
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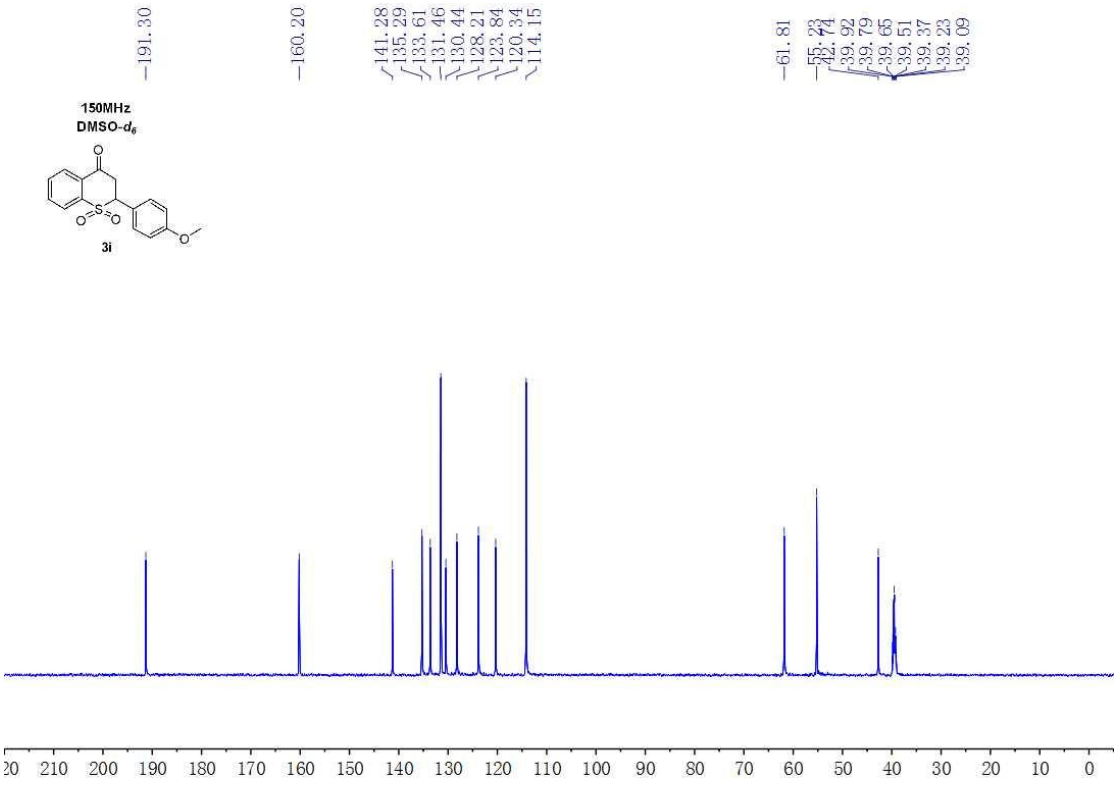
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39.79
39.65
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39.09
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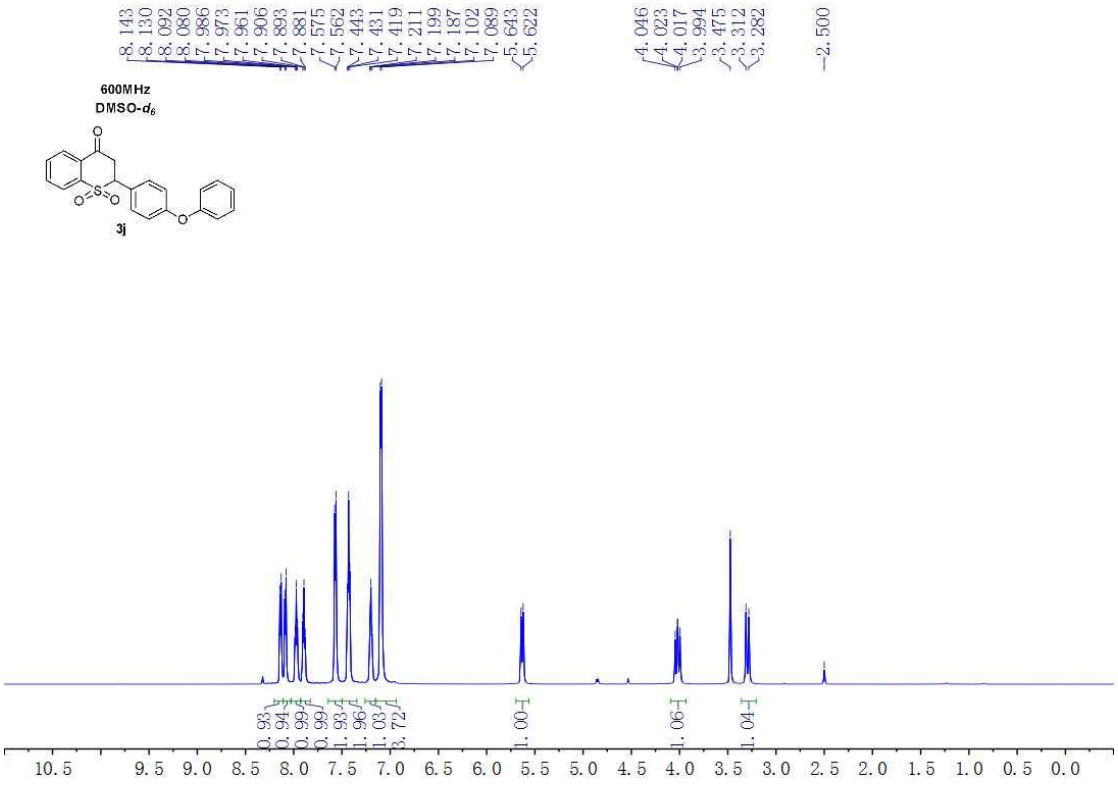
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7.443
7.431
7.419
7.211
7.199
7.187
7.102
7.089
5.643
5.622
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4.023
4.017
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3.475
3.312
3.282
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600MHz
DMSO-d_6
3j
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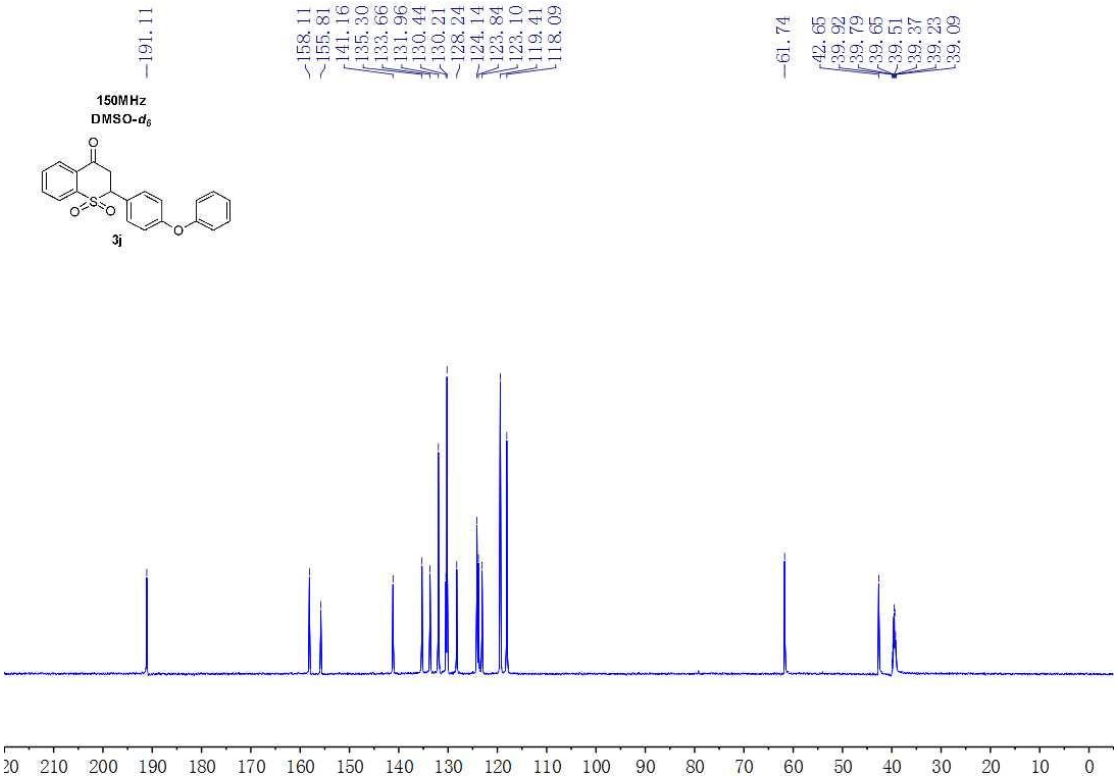
0.94
0.99
0.99
1.93
1.96
1.03
3.72
1.00
1.06
1.04
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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124.14
123.84
123.10
119.41
118.09
61.74
42.65
39.92
39.79
39.65
39.51
39.37
39.23
39.09
150MHz
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3j
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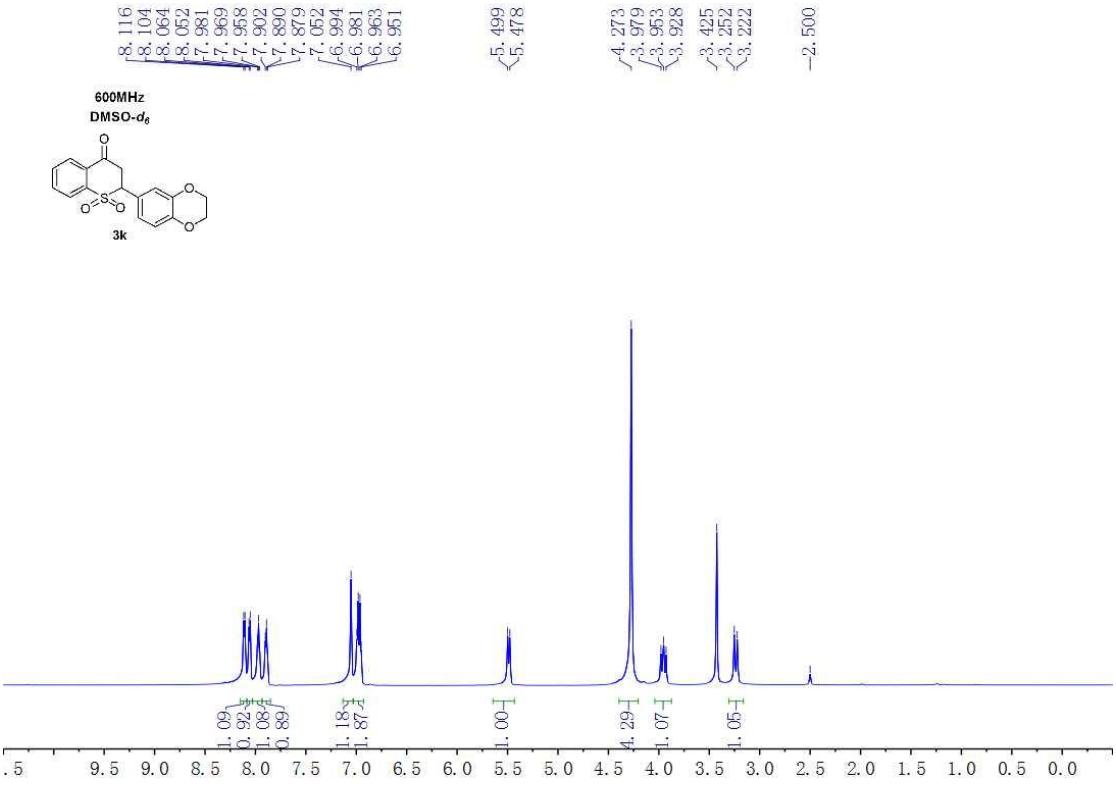
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6.981
6.963
6.951
5.499
5.478
4.273
3.979
3.953
3.928
3.425
3.252
3.222
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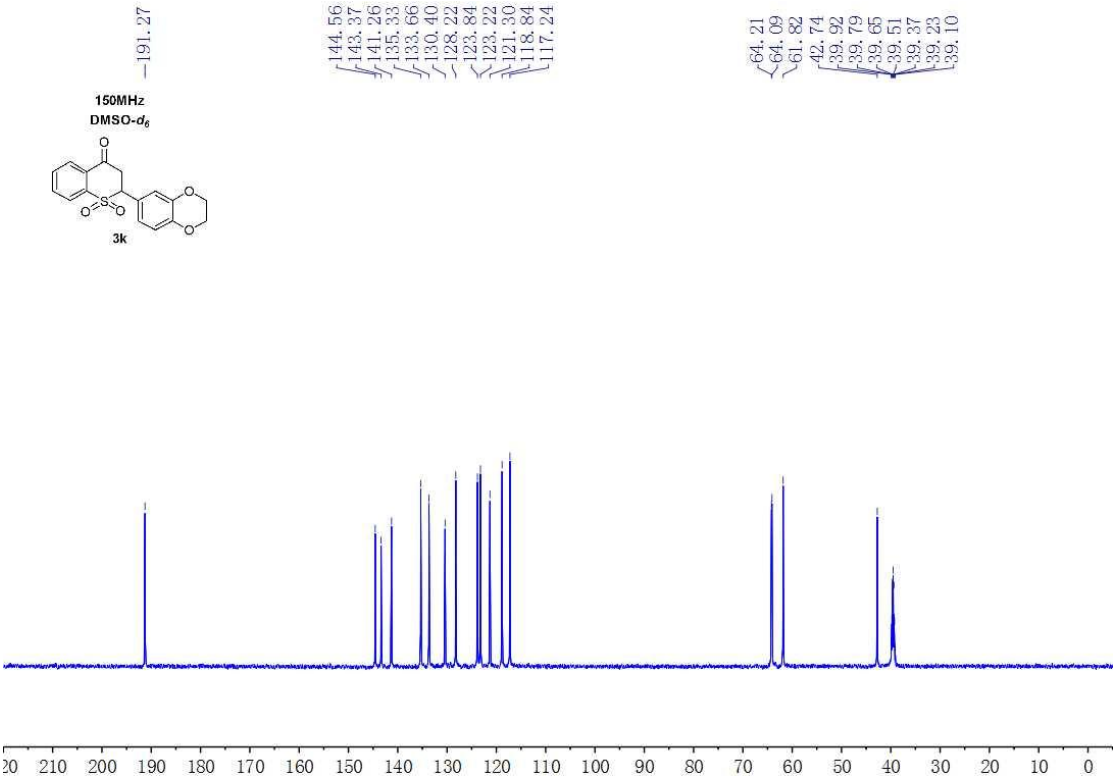
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121.30
118.84
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39.23
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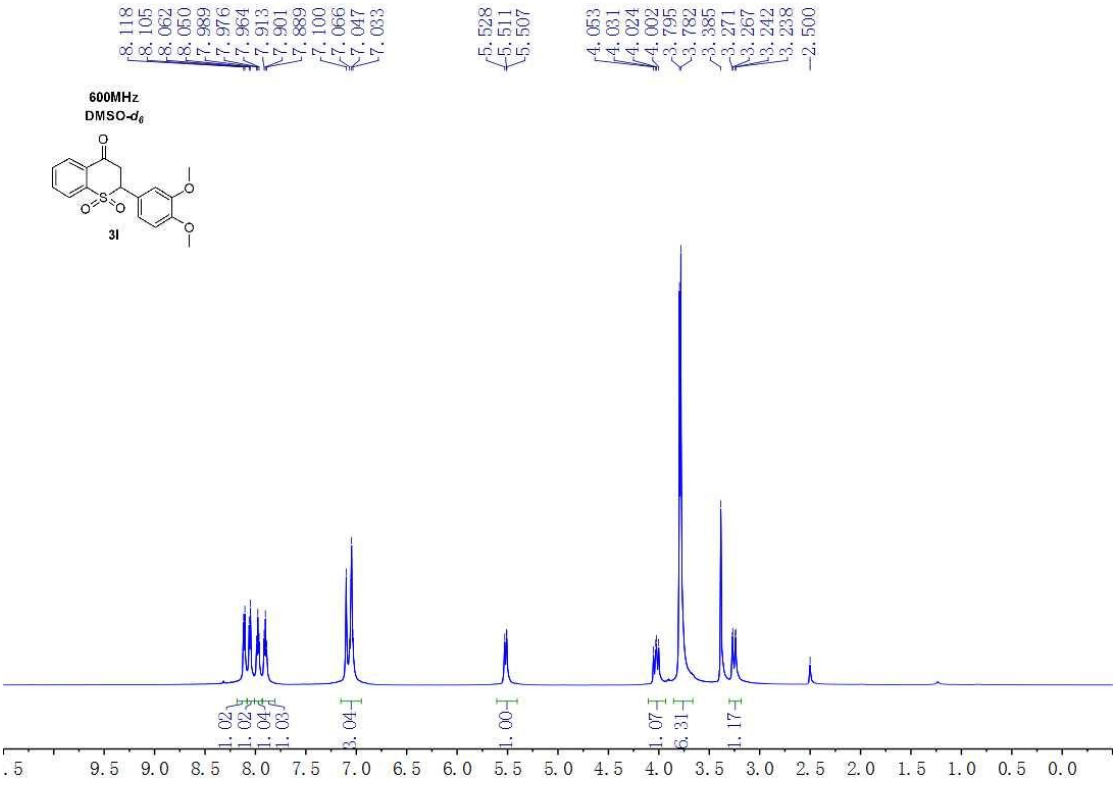
150MHz
DMSO-d_6
3k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7.889
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7.047
7.033
5.528
5.511
5.507
4.053
4.031
4.024
4.002
3.795
3.782
3.385
3.271
3.267
3.242
3.238
2.500
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1.03
3.04
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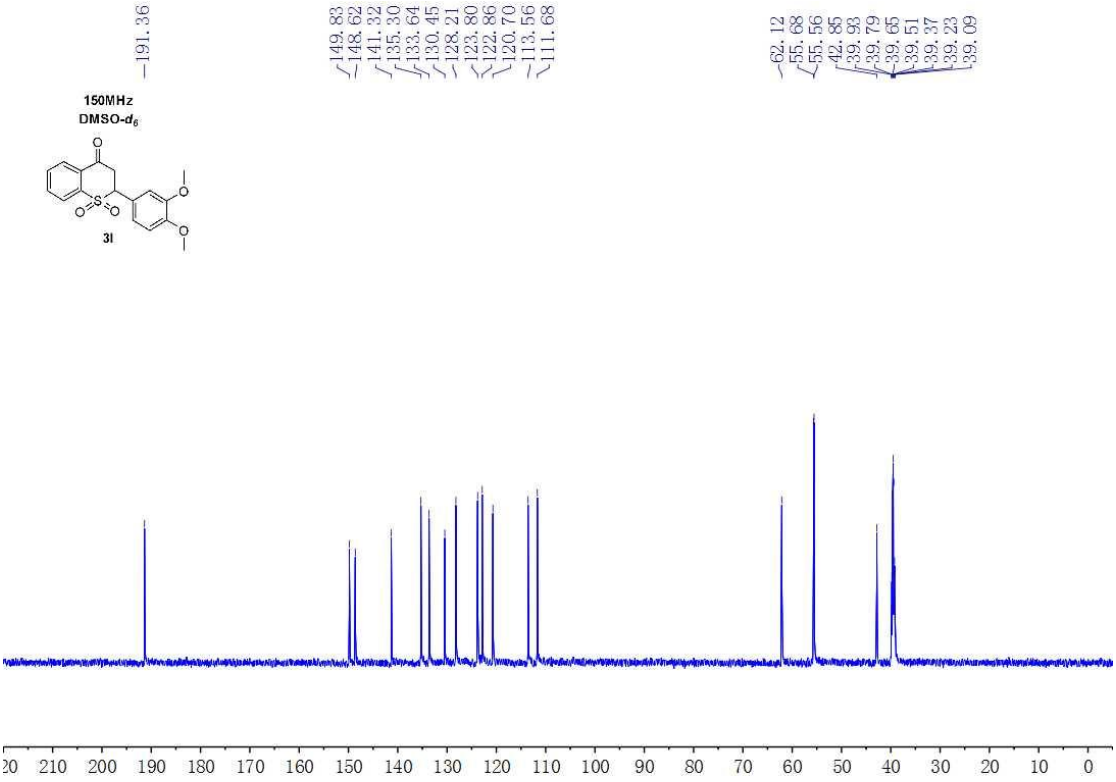
1.17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62.12
55.68
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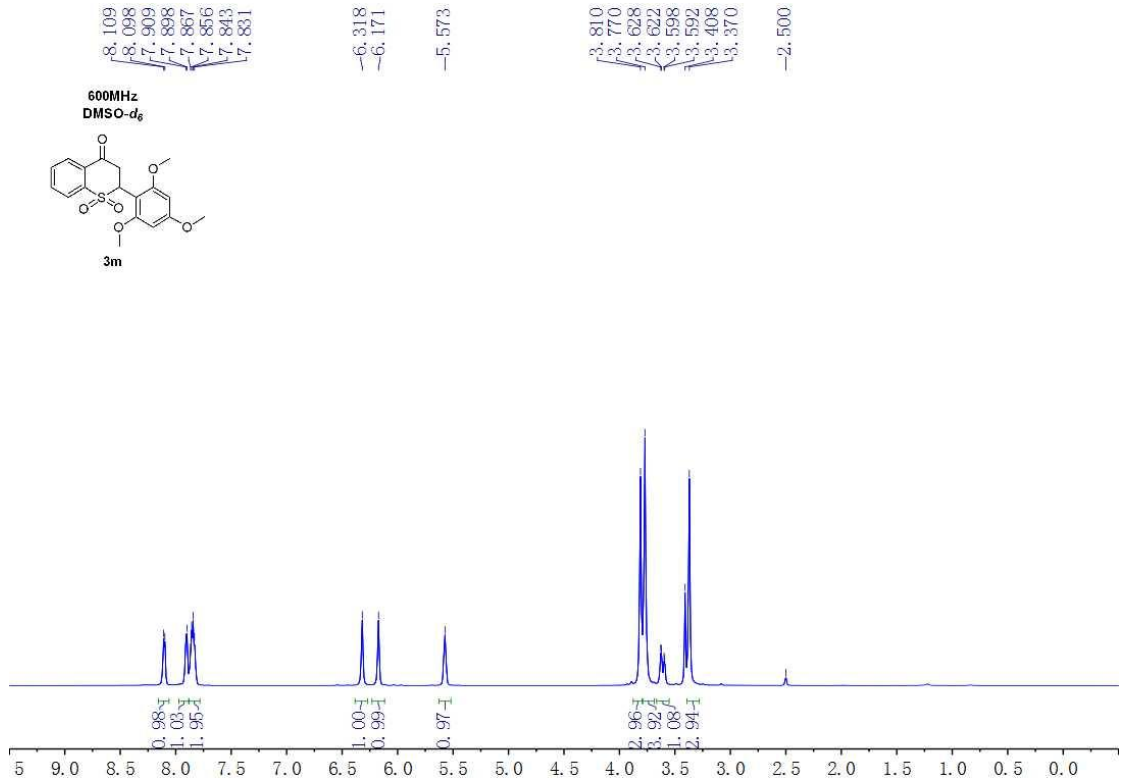
39.23
39.09
150MHz
DMSO-d_6
3l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3.598
3.592
3.408
3.370
2.500
600MHz
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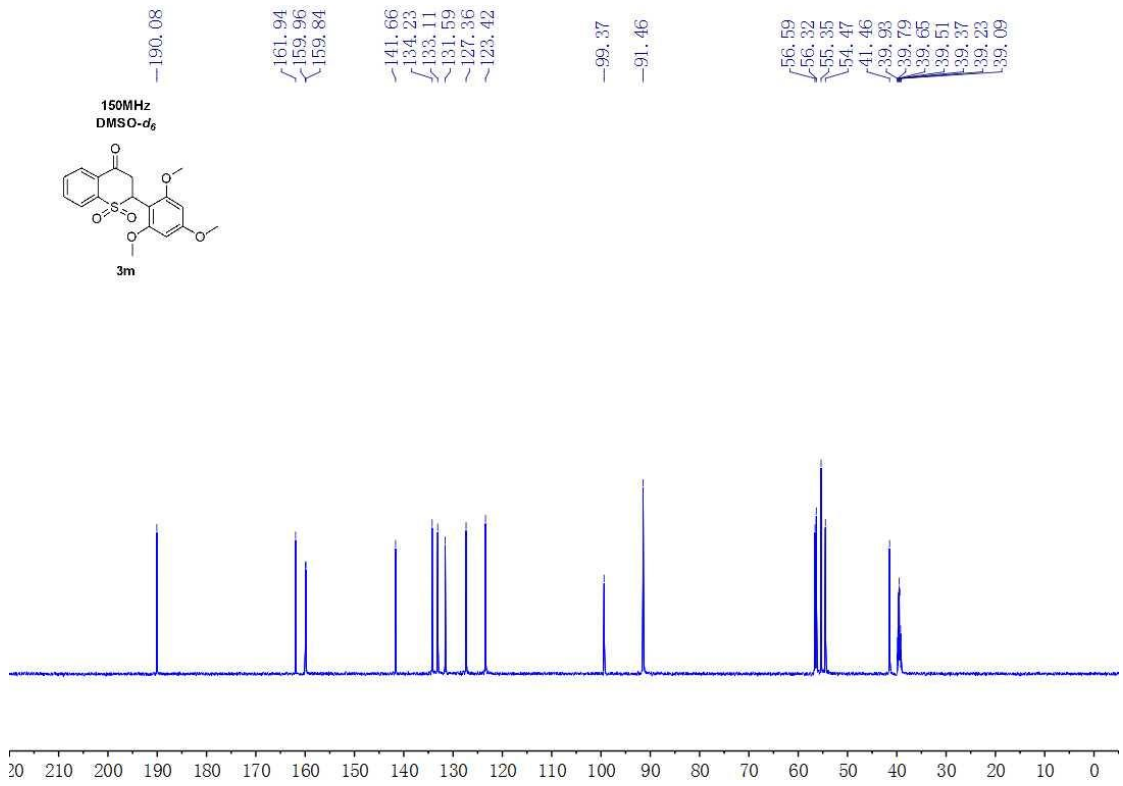
1.08
2.94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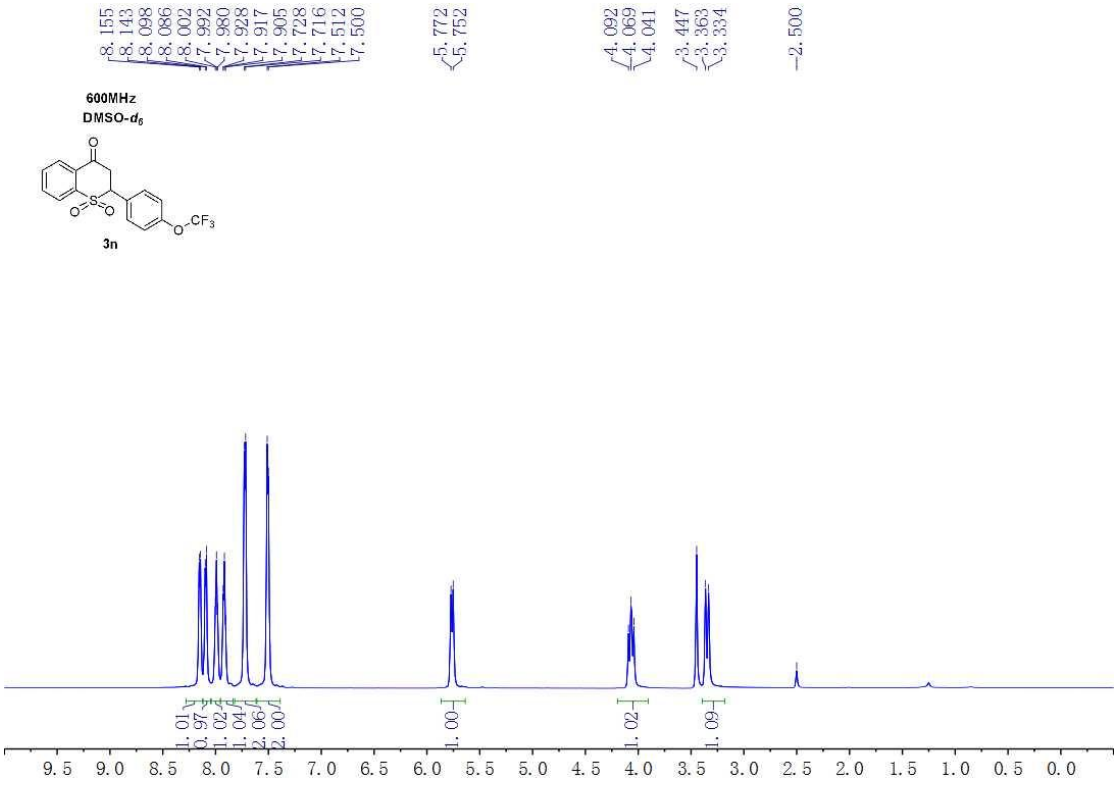
DMSO-d_6
3m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5.752
4.092
4.069
4.041
3.447
3.363
3.334
2.500
600MHz
DMSO-d6
3n
1.01
0.97
1.02
1.04
2.06
2.00
1.00
1.02
1.09
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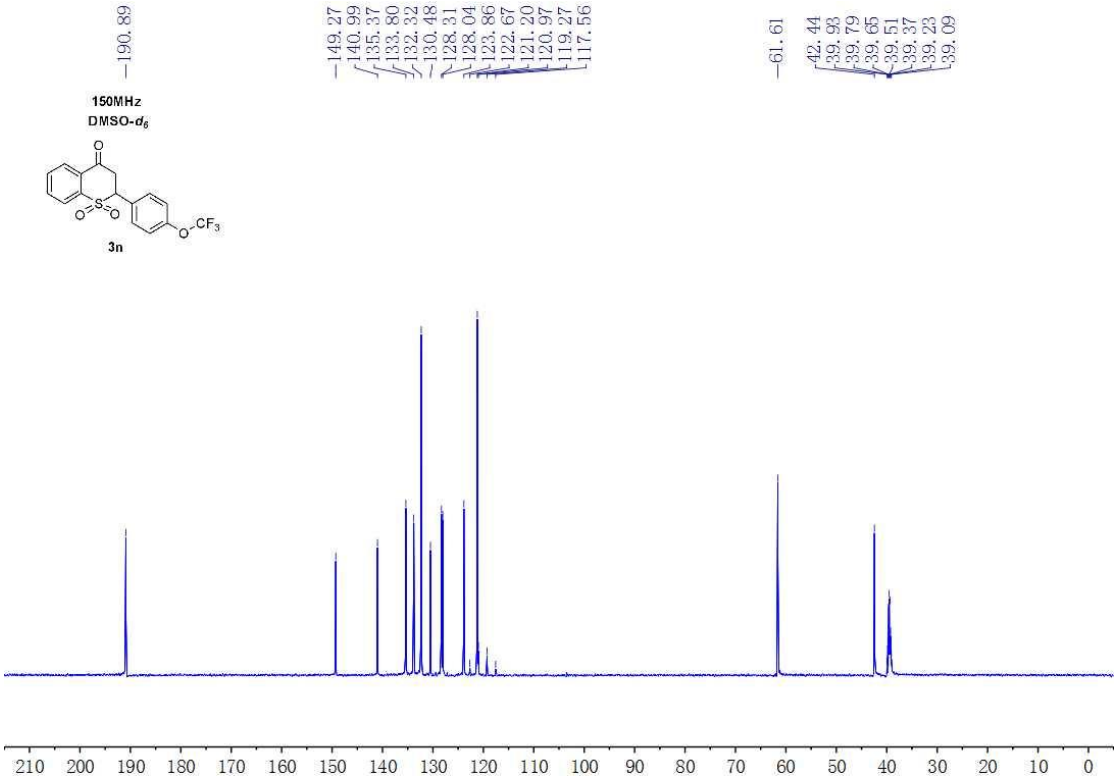
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122.67
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120.97
119.27
117.56
61.61
42.44
39.93
39.79
39.65
39.51
39.37
39.23
39.09
150MHz
DMSO-d6
3n
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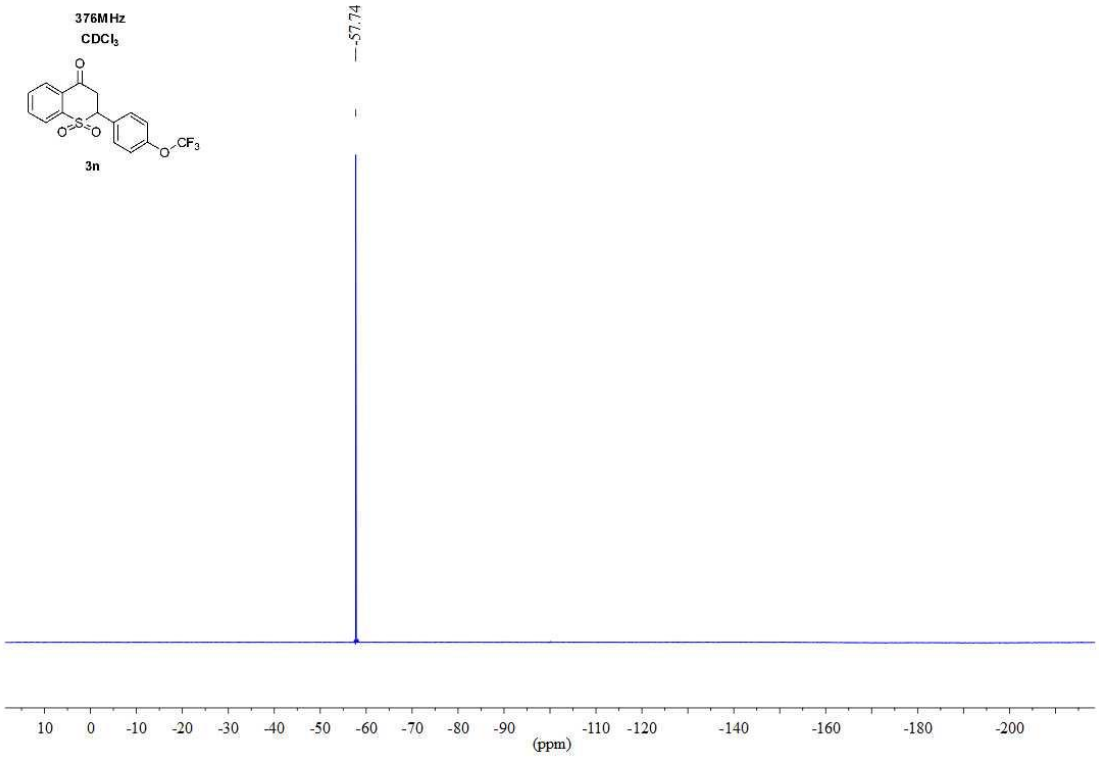
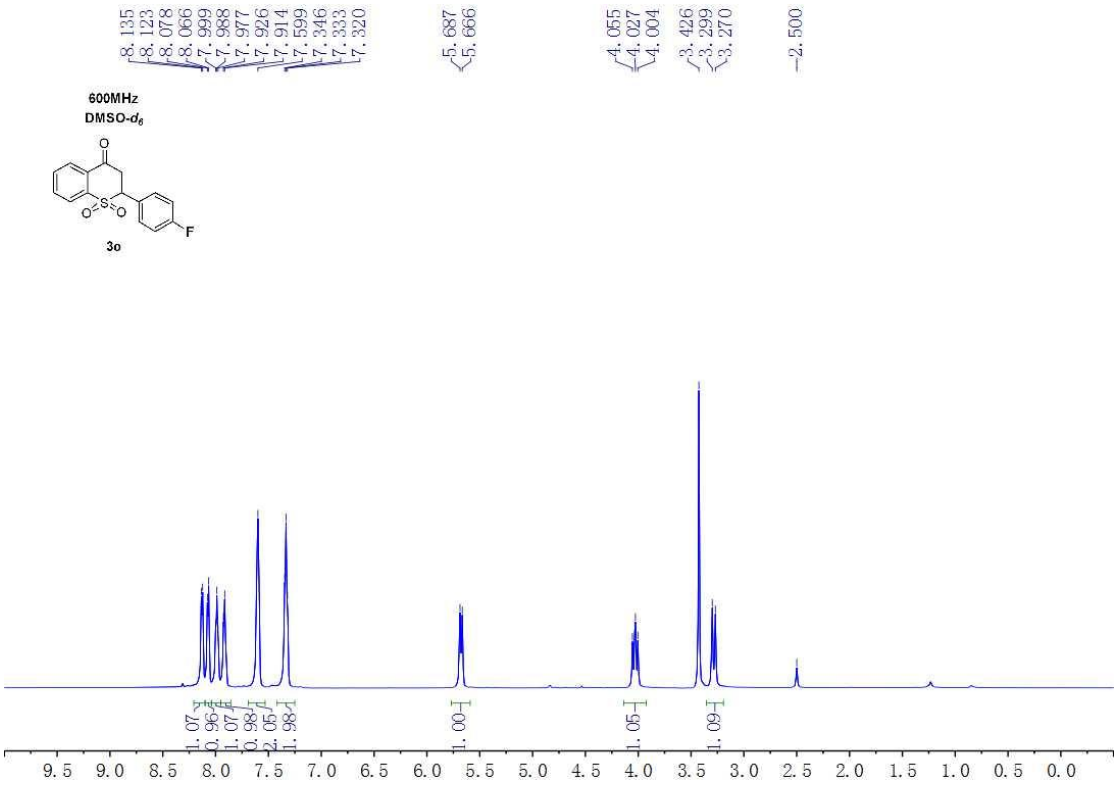
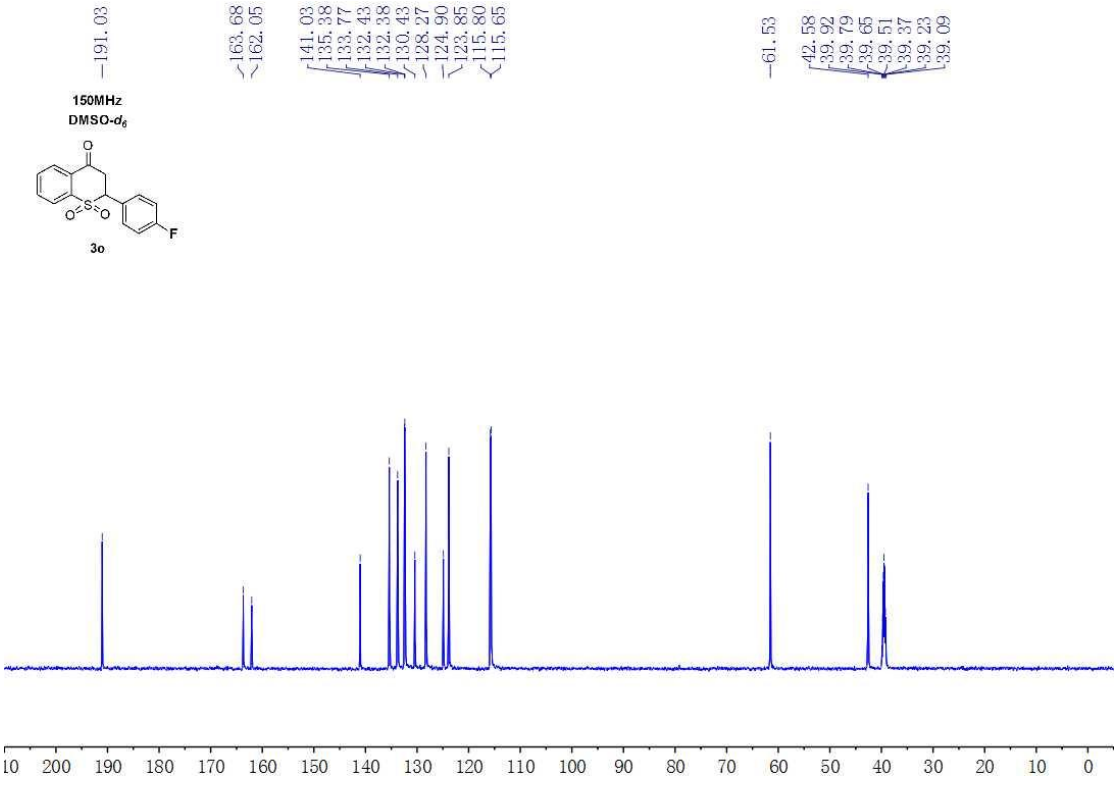
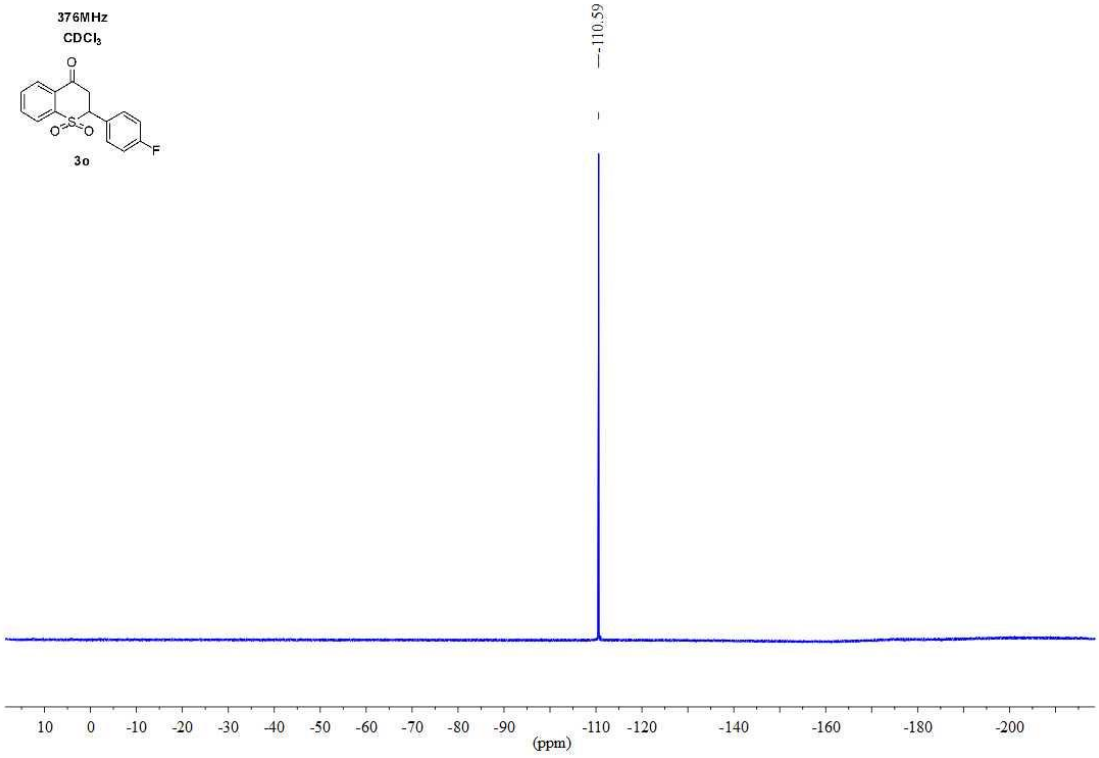


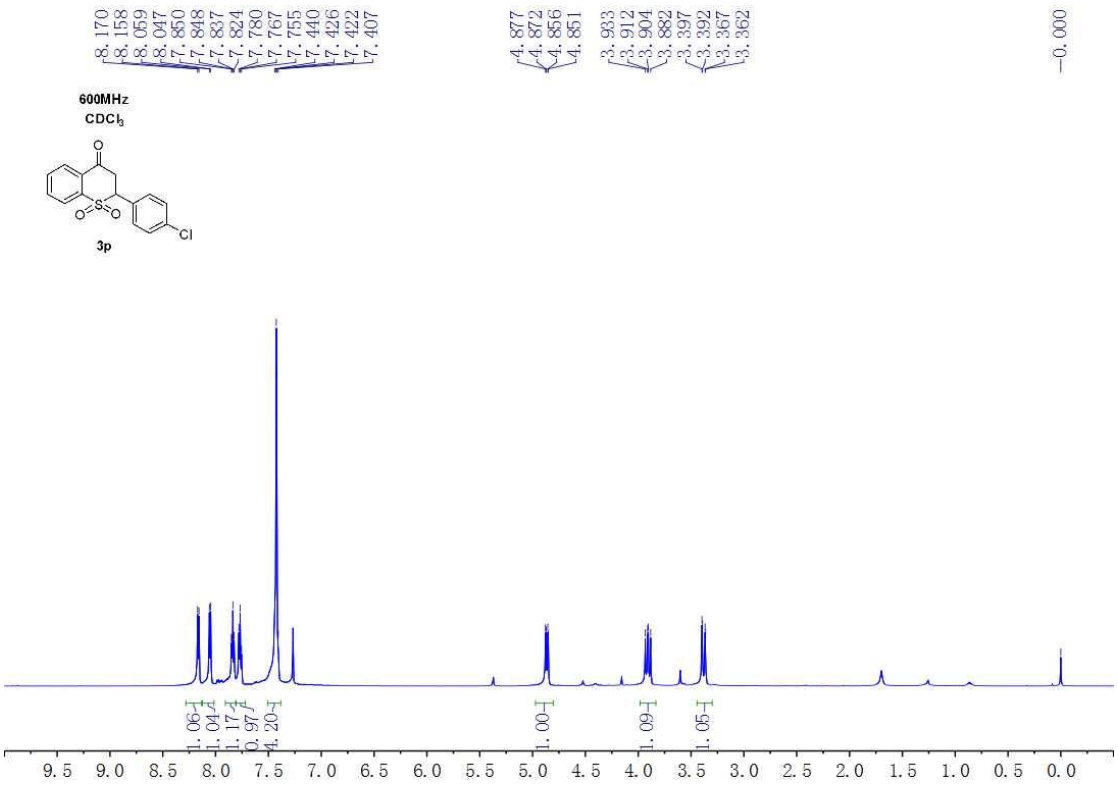
^{19}F NMR spectra (376 MHz，$CDCl_3$) of **3n**







^{19}F NMR spectra (376 MHz，$CDCl_3$) of **3o**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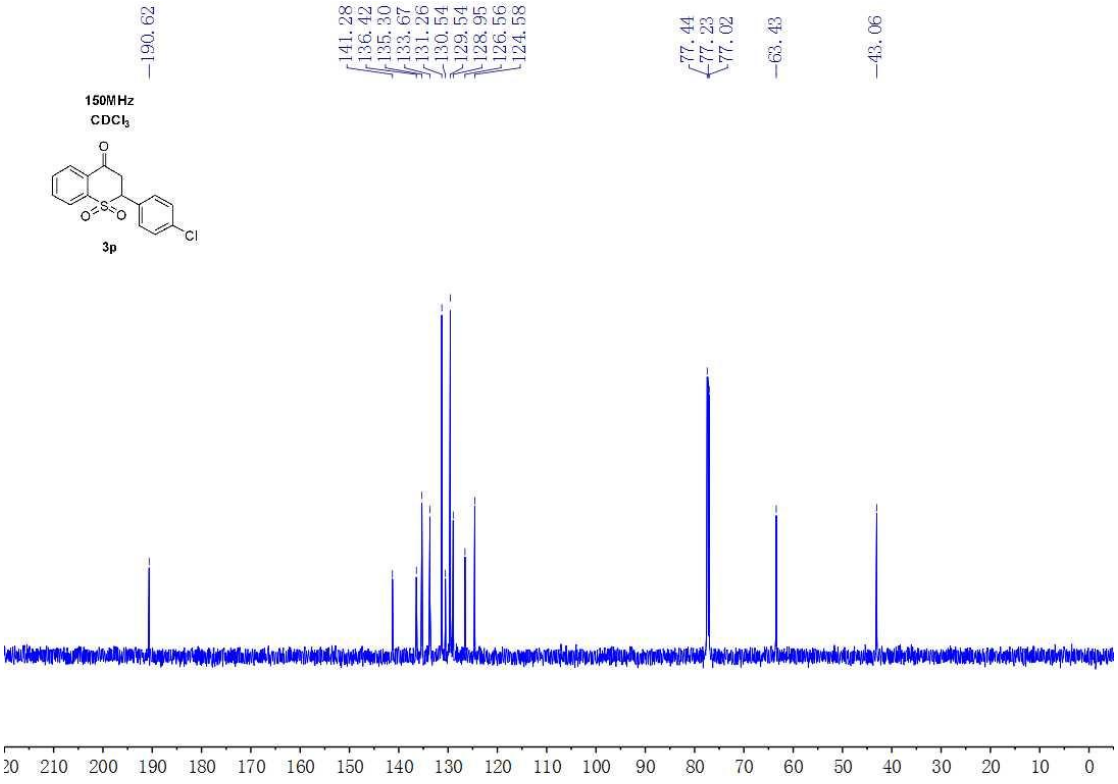
7.426
7.422
7.407
4.877
4.872
4.856
4.851
3.933
3.912
3.904
3.882
3.397
3.392
3.367
3.362
0.000
600MHz
CDCl3
3p
1.06
1.04
1.17
0.97
4.20
1.00
1.09
1.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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129.54
128.95
126.56
124.58
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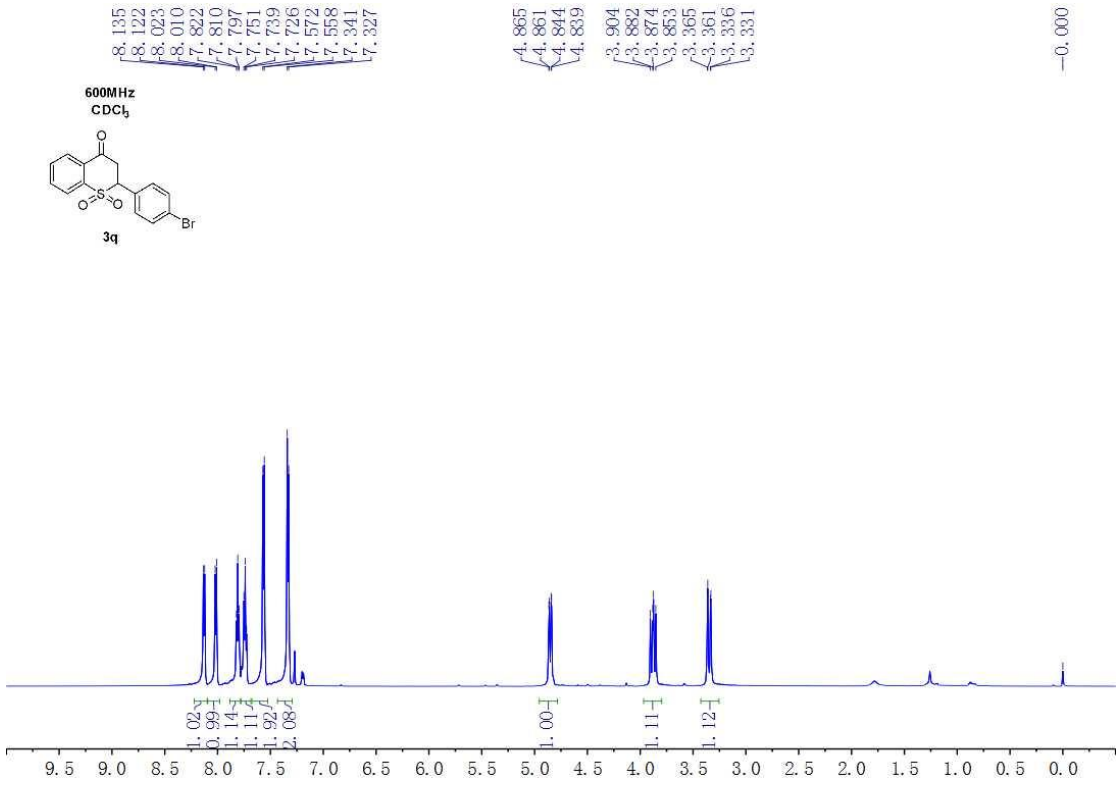
77.23
77.02
63.43
43.06
150MHz
CDCl3
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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4.861
4.844
4.839
3.904
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3.365
3.361
3.336
3.331
0.000
600MHz
CDCl3
Br
3q
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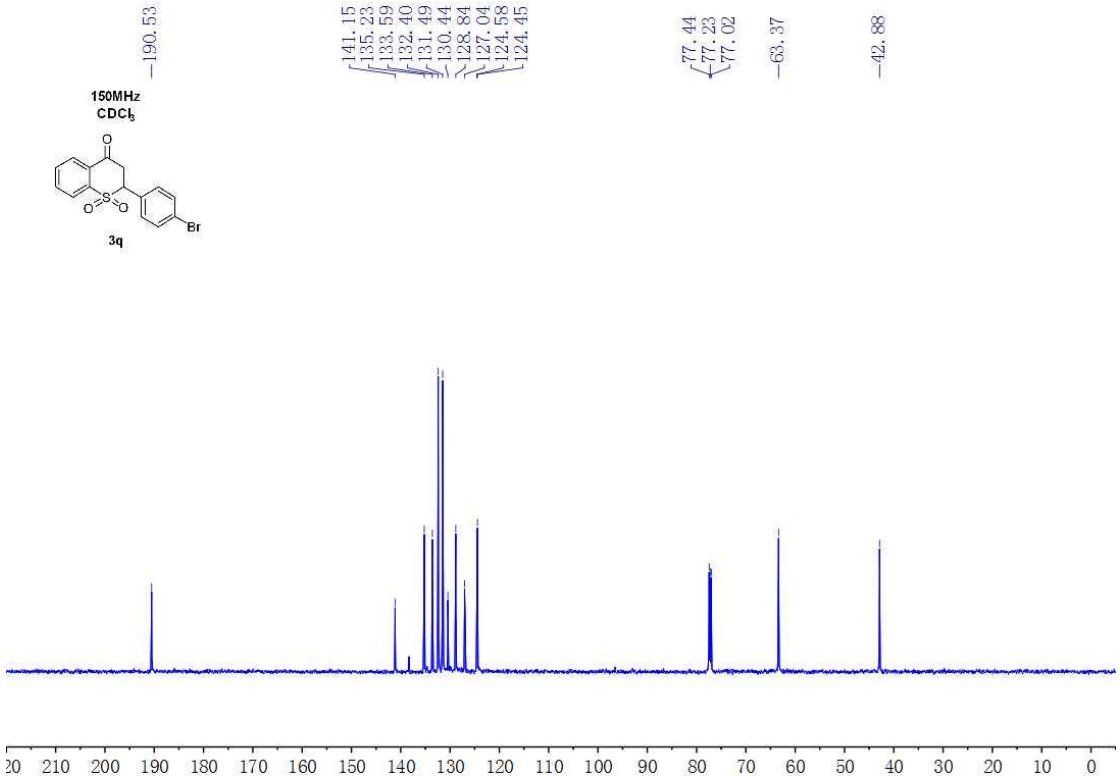
0.99
1.14
1.11
1.92
2.08
1.00
1.11
1.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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127.04
124.58
124.45
77.44
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77.02
63.37
42.88
150MHz
CDCl3
Br
3q
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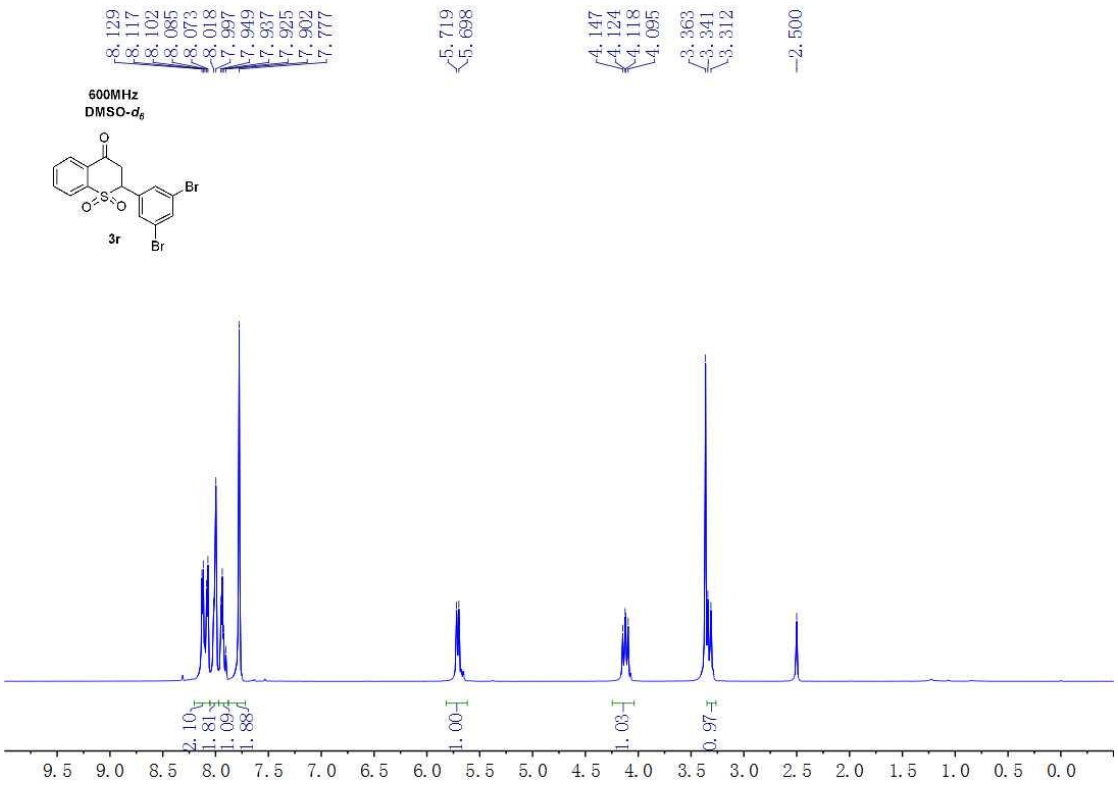
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7.925
7.902
7.777
5.719
5.698
4.147
4.124
4.118
4.095
3.363
3.341
3.312
2.500
600MHz
DMSO-d_6
Br
Br
3r
2.10
1.81
1.09
1.88
1.00
1.03
0.97
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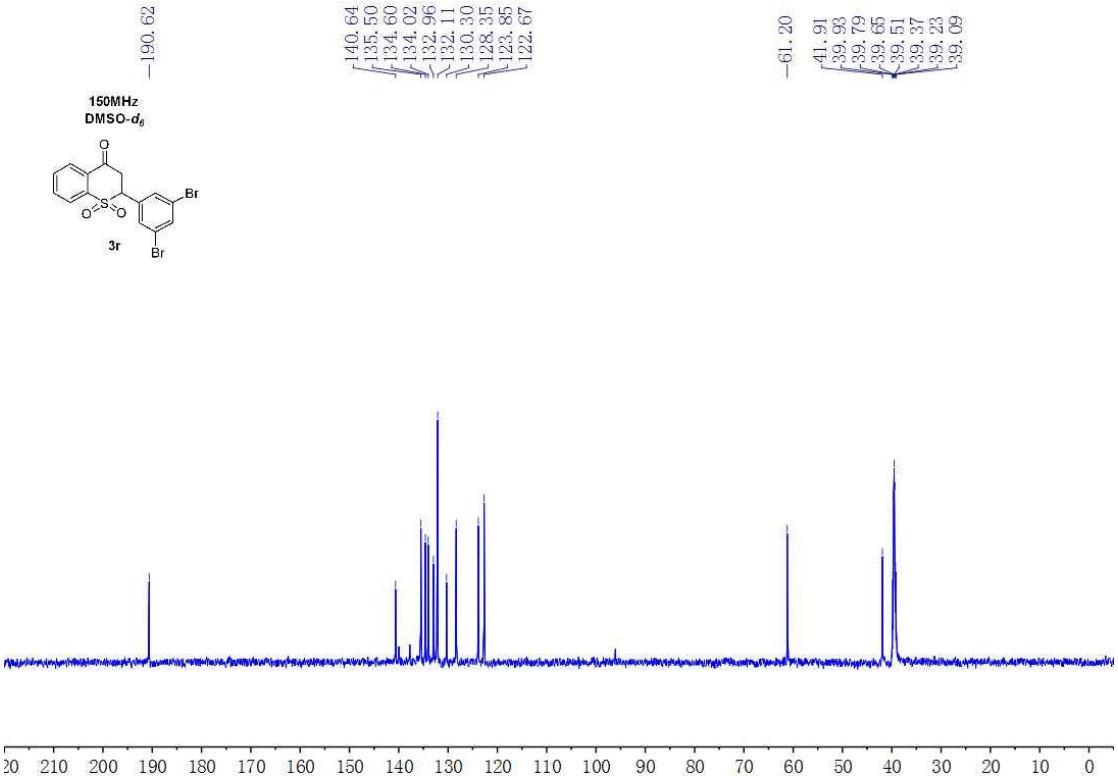
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134.60
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132.96
132.11
130.30
128.35
123.85
122.67
61.20
41.91
39.93
39.79
39.65
39.51
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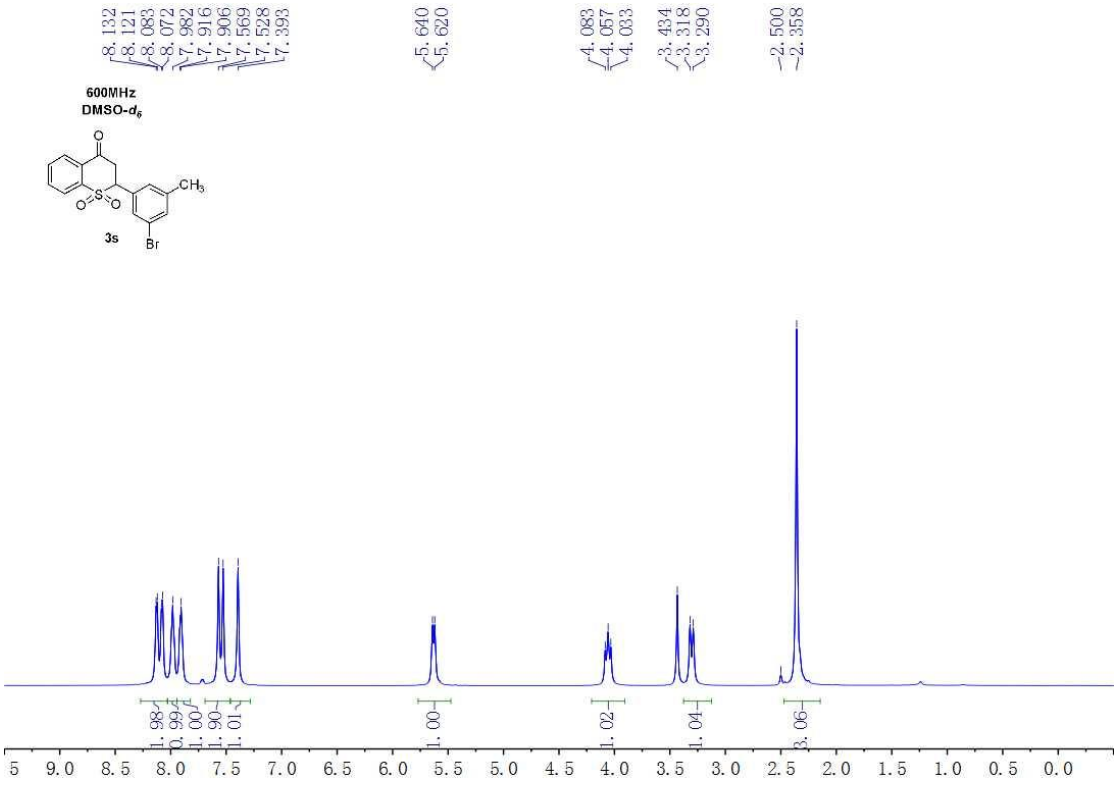
150MHz
DMSO-d_6
Br
Br
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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4.083
4.057
4.033
3.434
3.318
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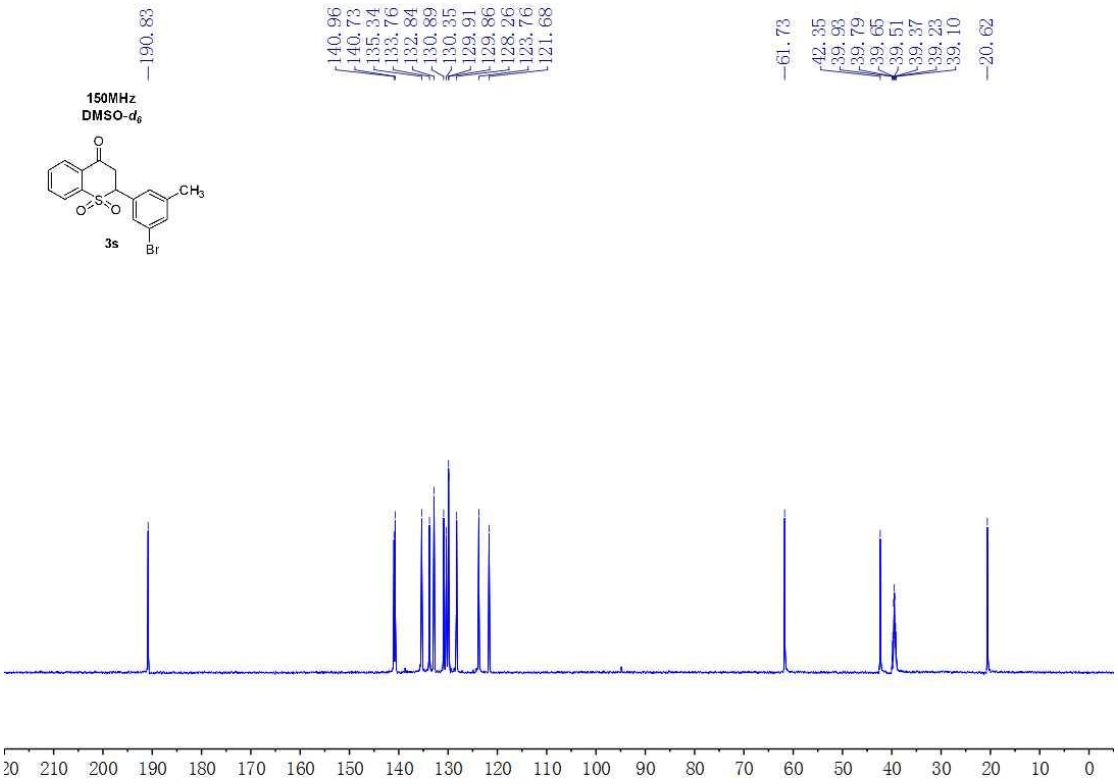
1.04
3.06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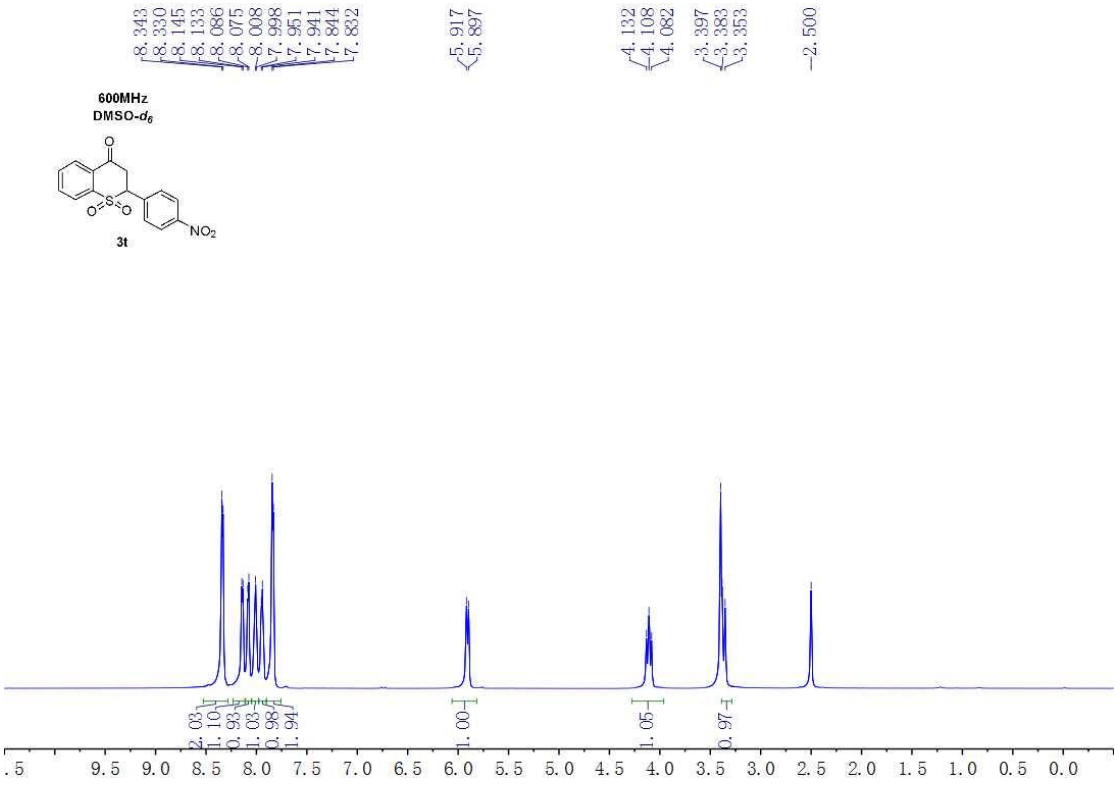
150MHz
DMSO-d_6
3s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4.132
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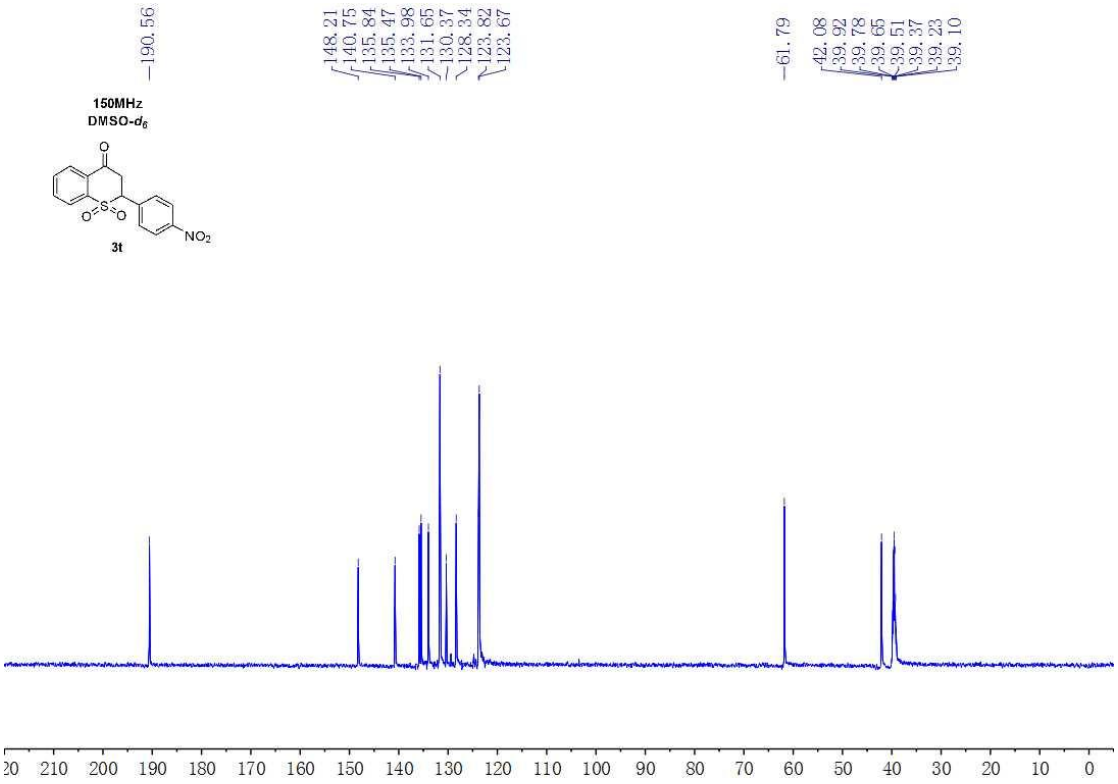
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130.37
128.34
123.82
123.67
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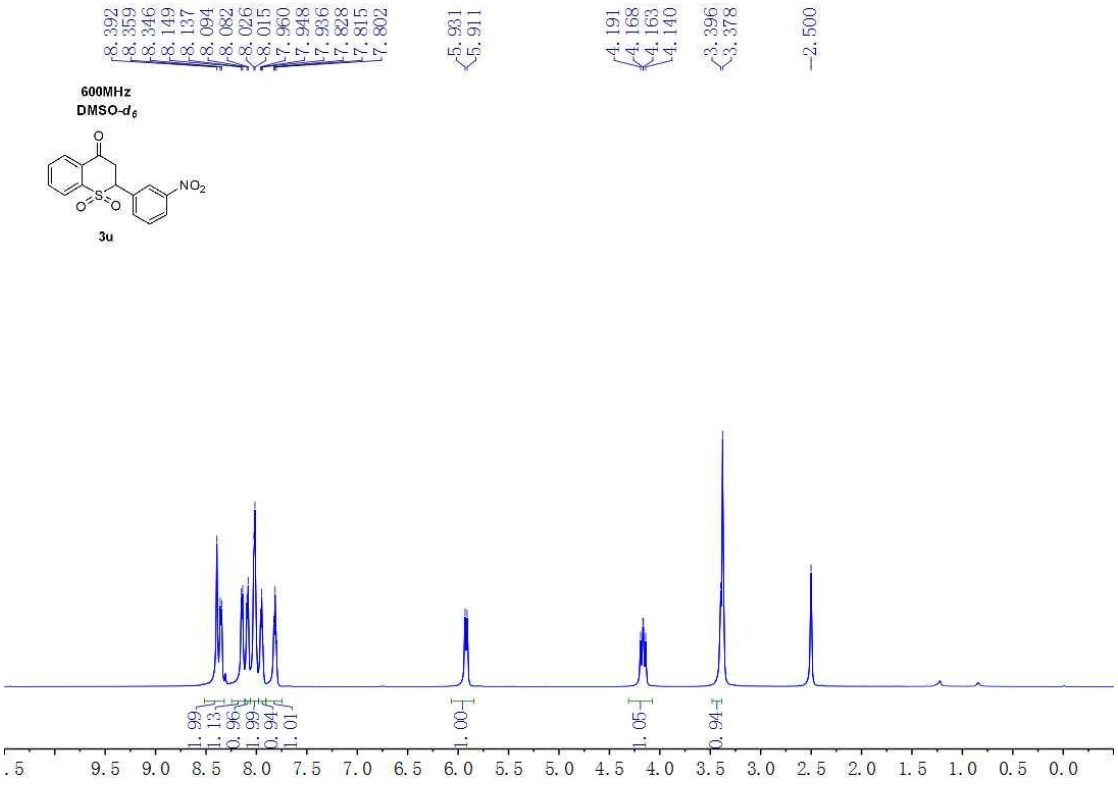
39.51
39.37
39.23
39.10
150MHz
DMSO-d_6
3t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8.026
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7.948
7.936
7.828
7.815
7.802
5.931
5.911
4.191
4.168
4.163
4.140
3.396
3.378
2.500
600MHz
DMSO-d_6
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0.94
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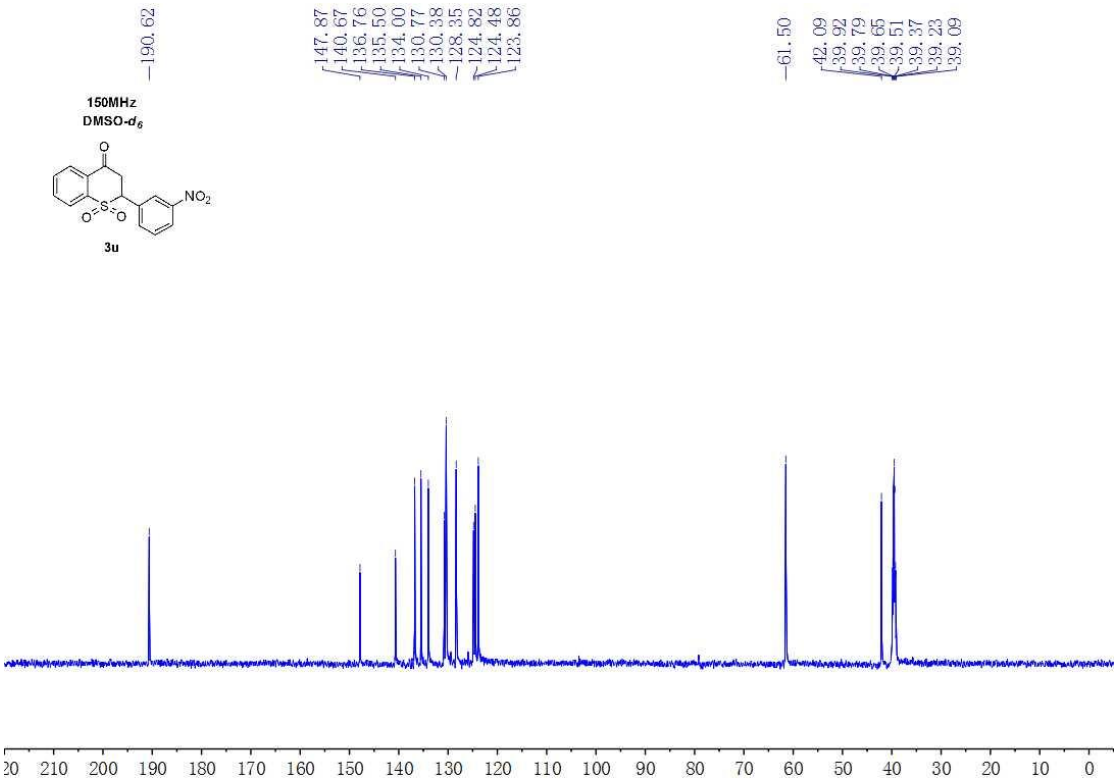
1.05
0.94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61.50
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39.65
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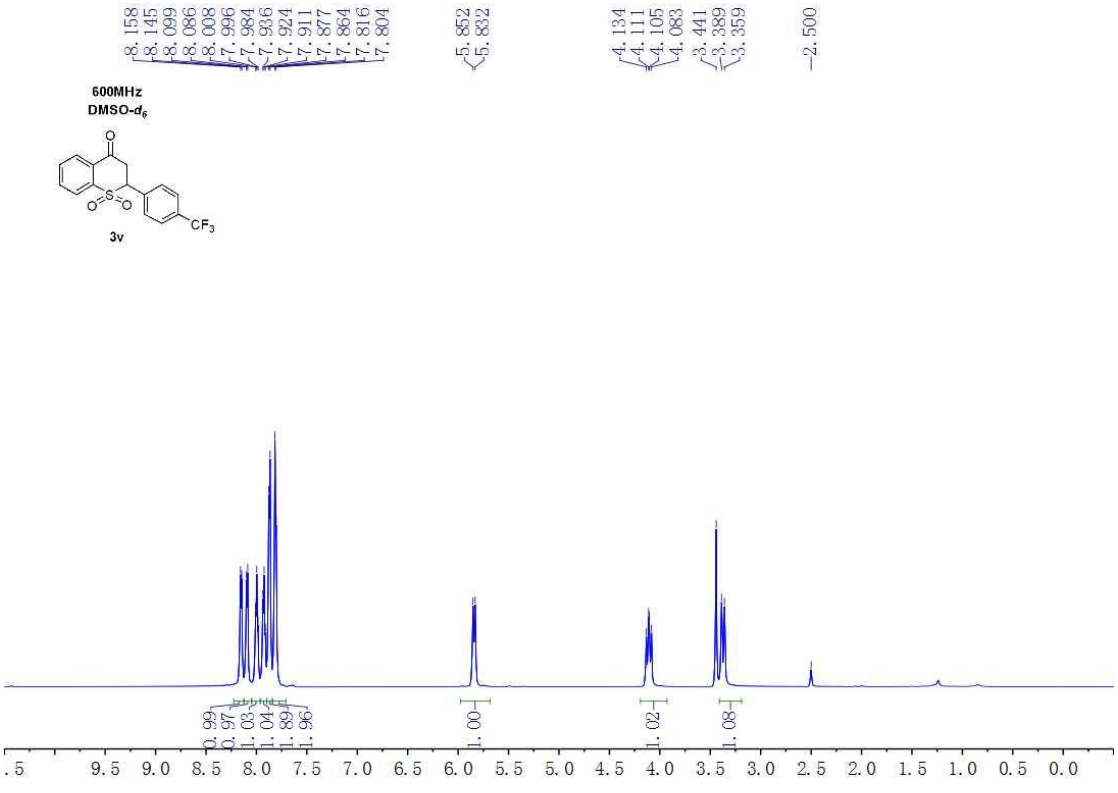
39.37
39.23
39.09
150MHz
DMSO-d_6
NO_2
3u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8.099
8.086
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7.984
7.936
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7.911
7.877
7.864
7.816
7.804
5.852
5.832
4.134
4.111
4.105
4.083
3.441
3.389
3.359
2.500
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DMSO-d_6
3v
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1.89
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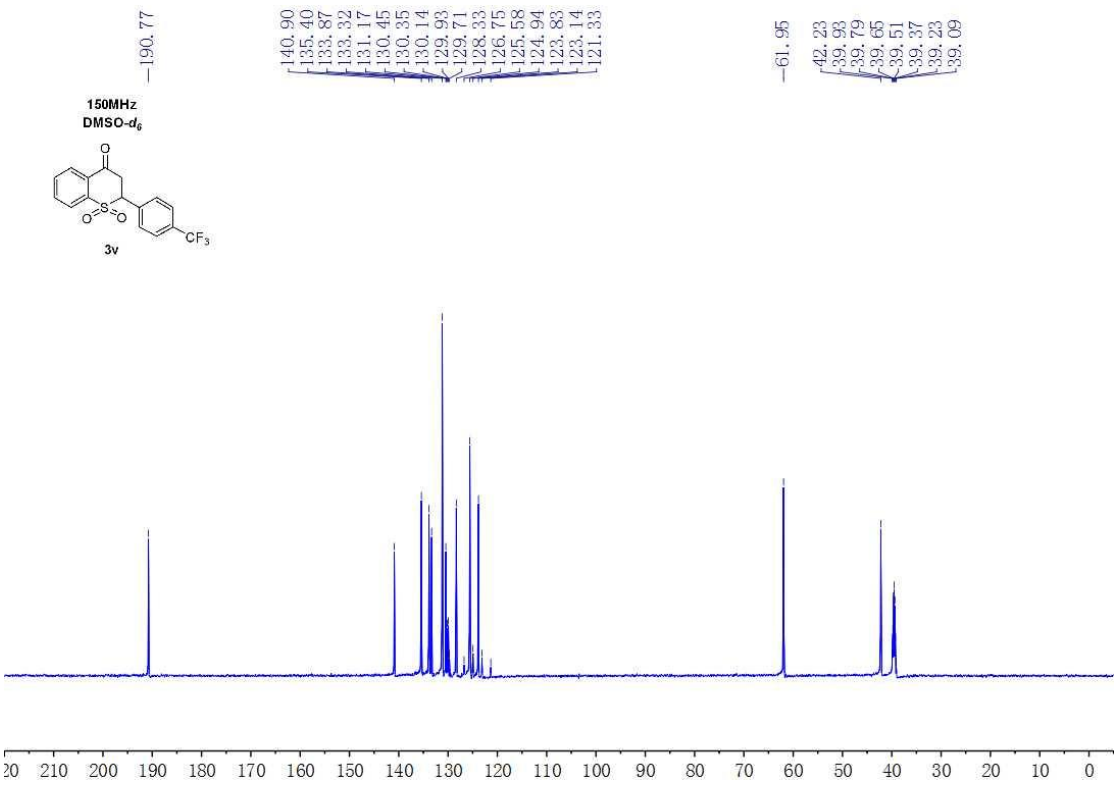
1.00
1.02
1.08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124.94
123.83
123.14
121.33
61.95
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39.79
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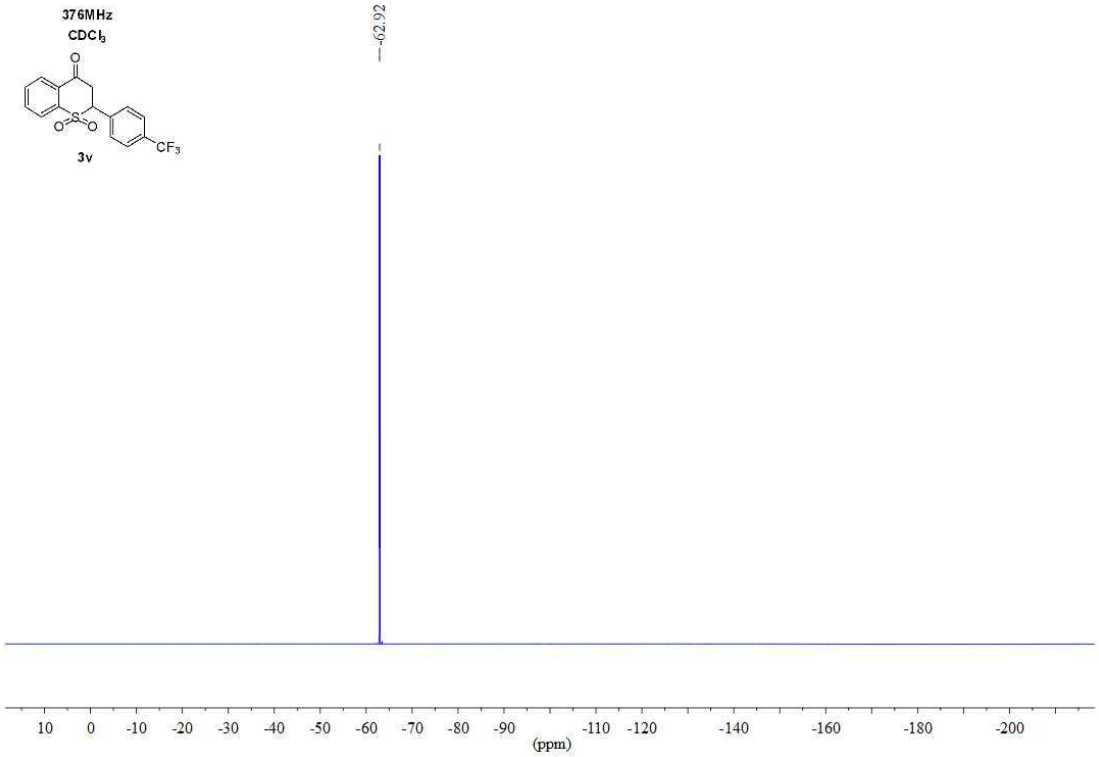
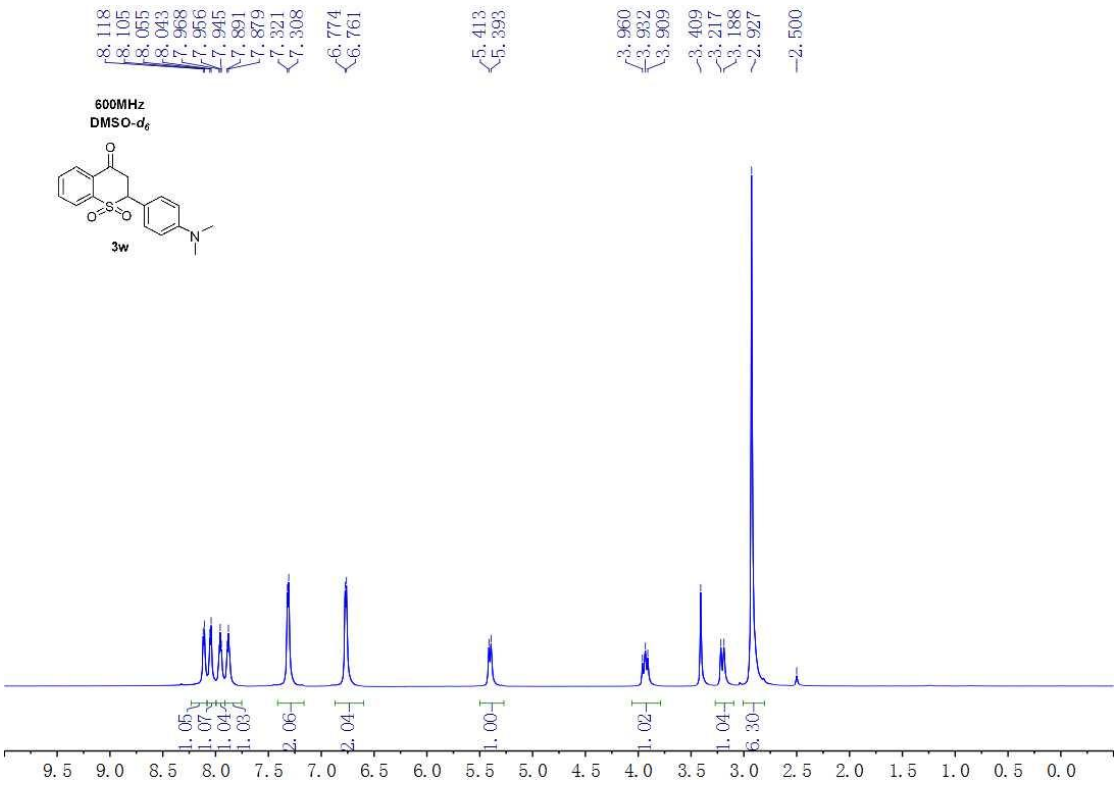
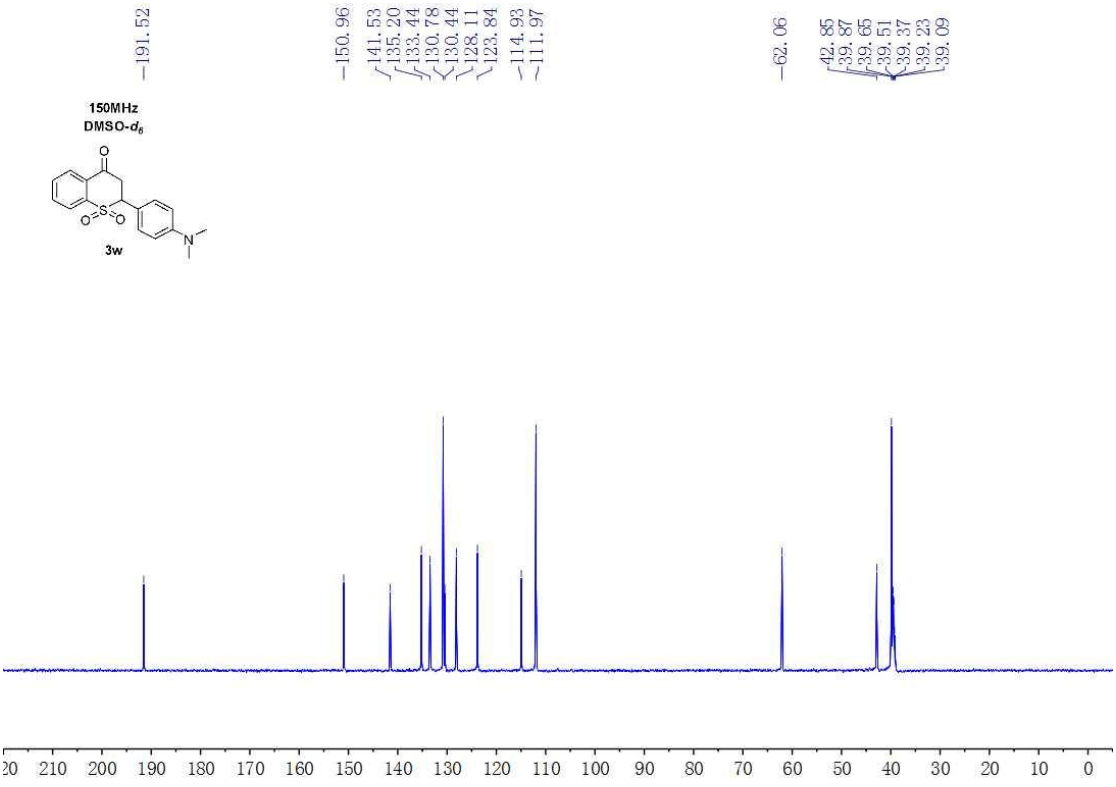
39.51
39.37
39.23
39.09
150MHz
DMSO-d_6
3v



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

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150.96
141.53
135.20
133.44
130.78
130.44
128.11
123.84
114.93
111.97
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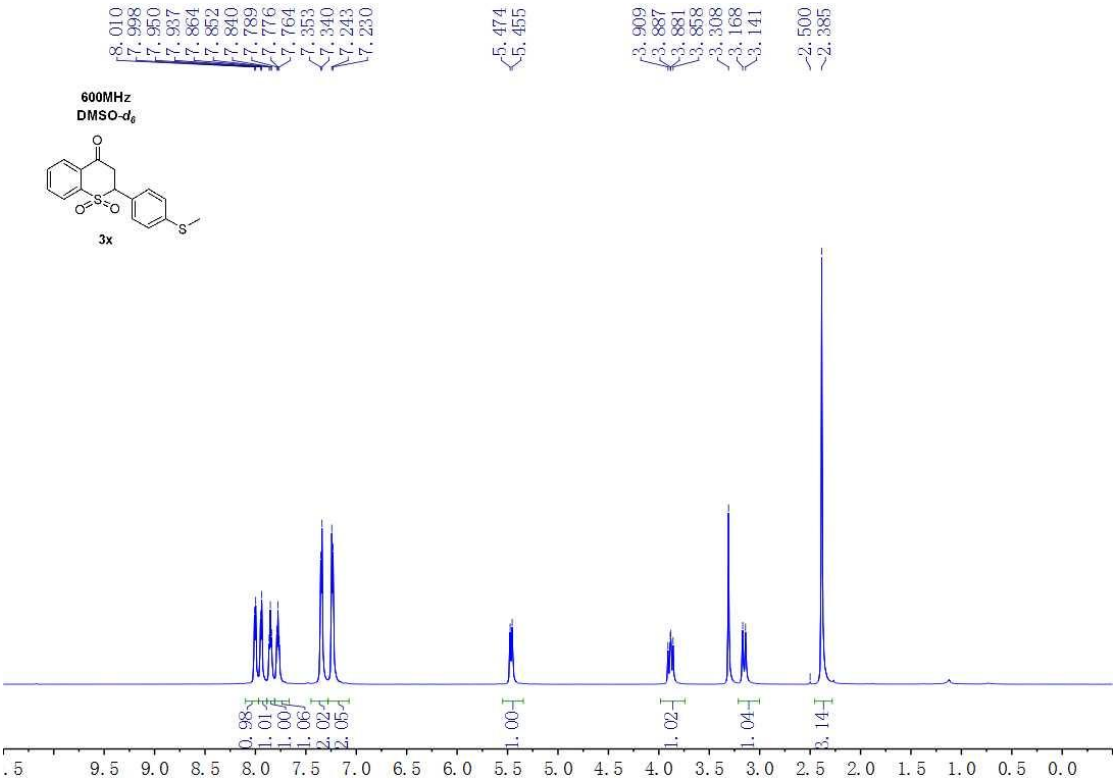
39.87
39.65
39.51
39.37
39.23
39.09
150MHz
DMSO-d_6
3w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7.950
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7.789
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7.764
7.353
7.340
7.243
7.230
5.474
5.455
3.909
3.887
3.881
3.858
3.308
3.168
3.141
2.500
2.385
600MHz
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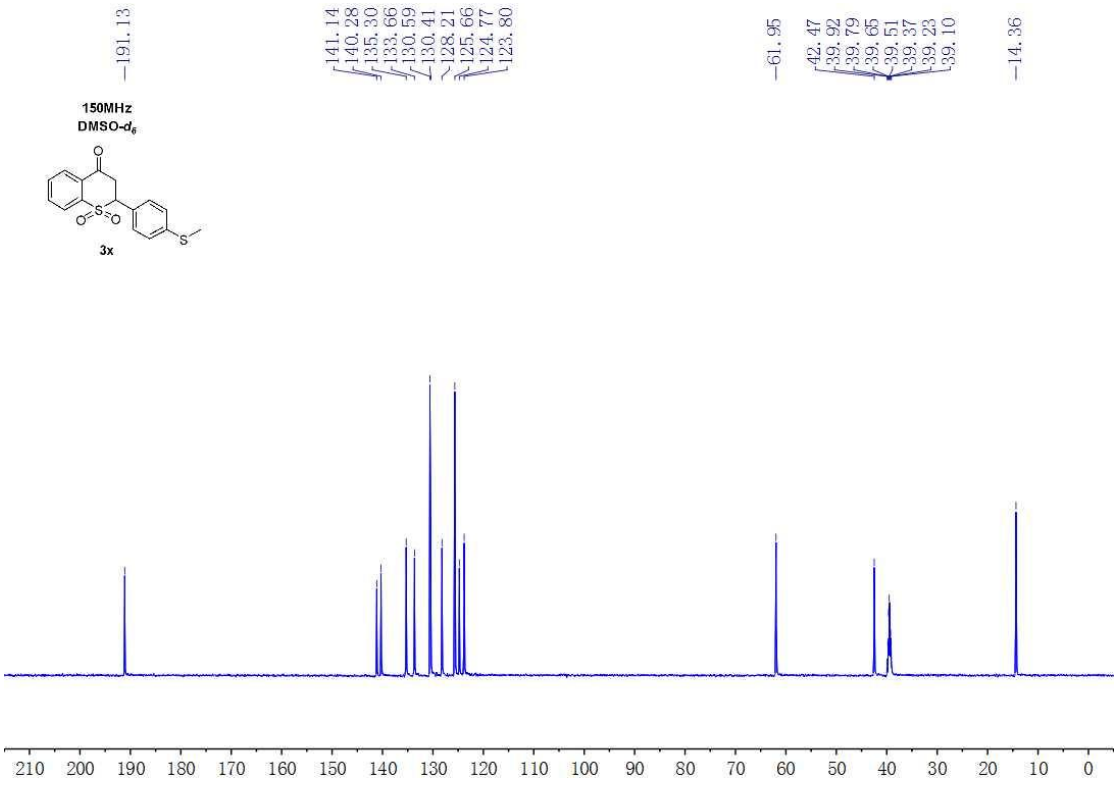
2.02
2.05
1.00
1.02
1.04
3.14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140.28
135.30
133.66
130.59
130.41
128.21
125.66
124.77
123.80
61.95
42.47
39.92
39.79
39.65
39.51
39.37
39.23
39.10
14.36
150MHz
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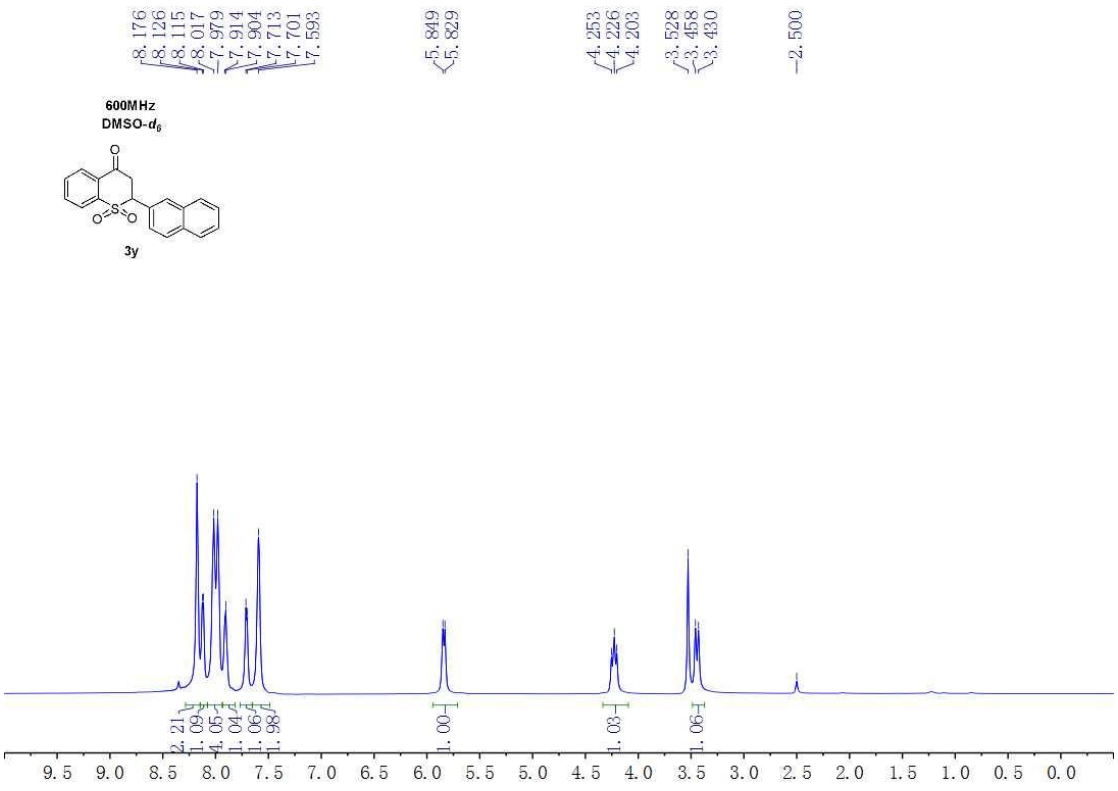
3x
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.914
7.904
7.713
7.701
7.593
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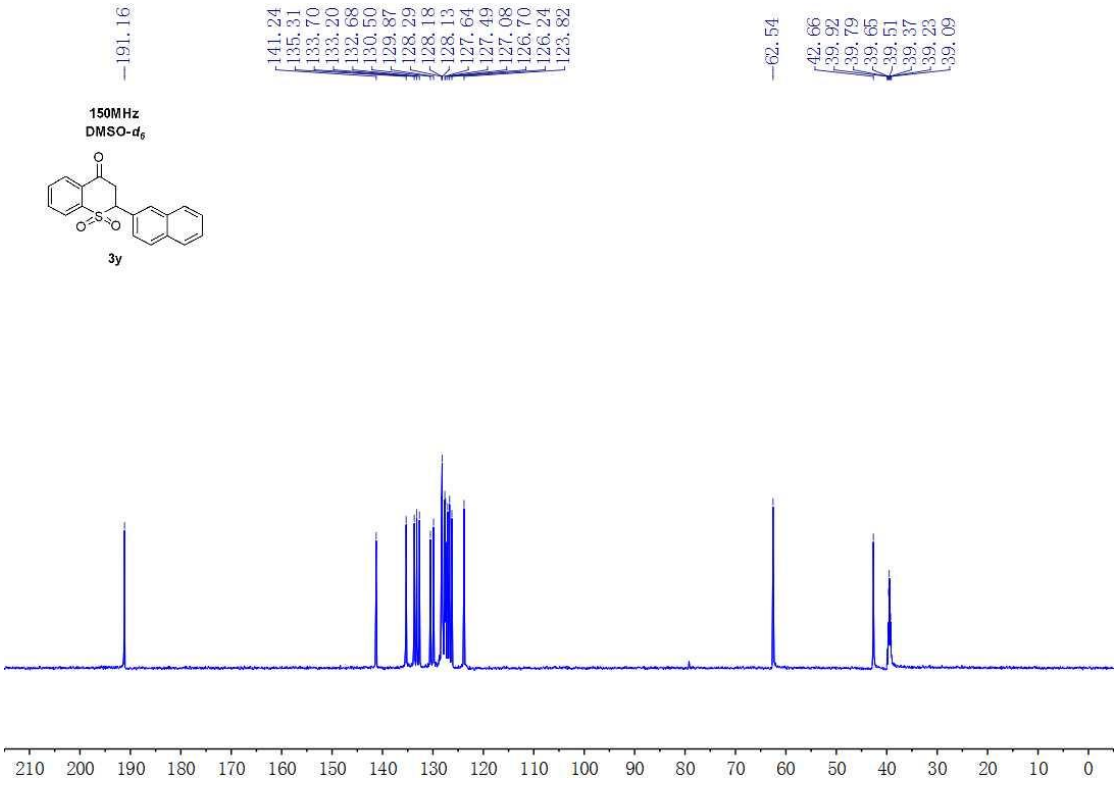
5.829
4.253
4.226
4.203
3.528
3.458
3.430
2.500
600MHz
DMSO-d_6
3y
2.21
1.09
4.05
1.04
1.06
1.98
1.00
1.03
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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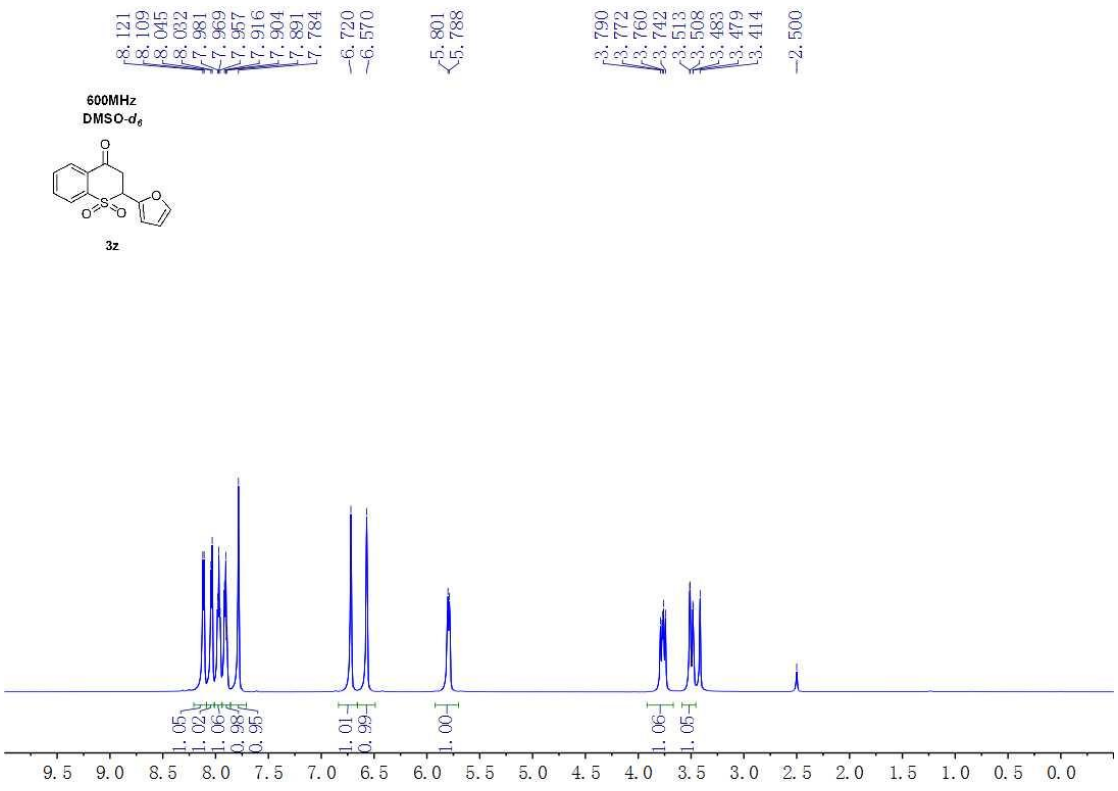
133.70
133.20
132.68
130.50
129.87
128.29
128.18
128.13
127.64
127.49
127.08
126.70
126.24
123.82
62.54
42.66
39.92
39.79
39.65
39.51
39.37
39.23
39.09
150MHz
DMSO-d6
3y
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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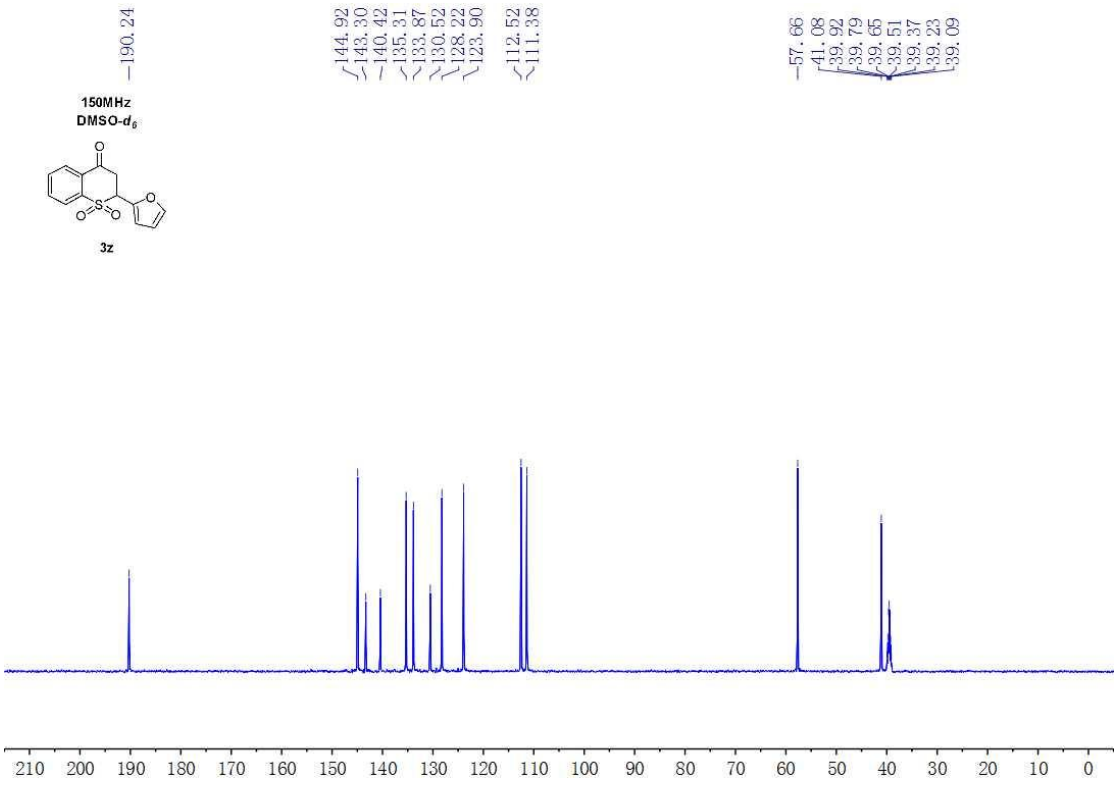
8.109
8.045
8.032
7.981
7.969
7.957
7.916
7.904
7.891
7.784
6.720
6.570
5.801
5.788
3.790
3.772
3.760
3.742
3.513
3.508
3.483
3.479
3.414
2.500
600MHz
DMSO-d6
3z
1.05
1.02
1.06
0.98
0.95
1.01
0.99
1.00
1.06
1.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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140.42
135.31
133.87
130.52
128.22
123.90
112.52
111.38
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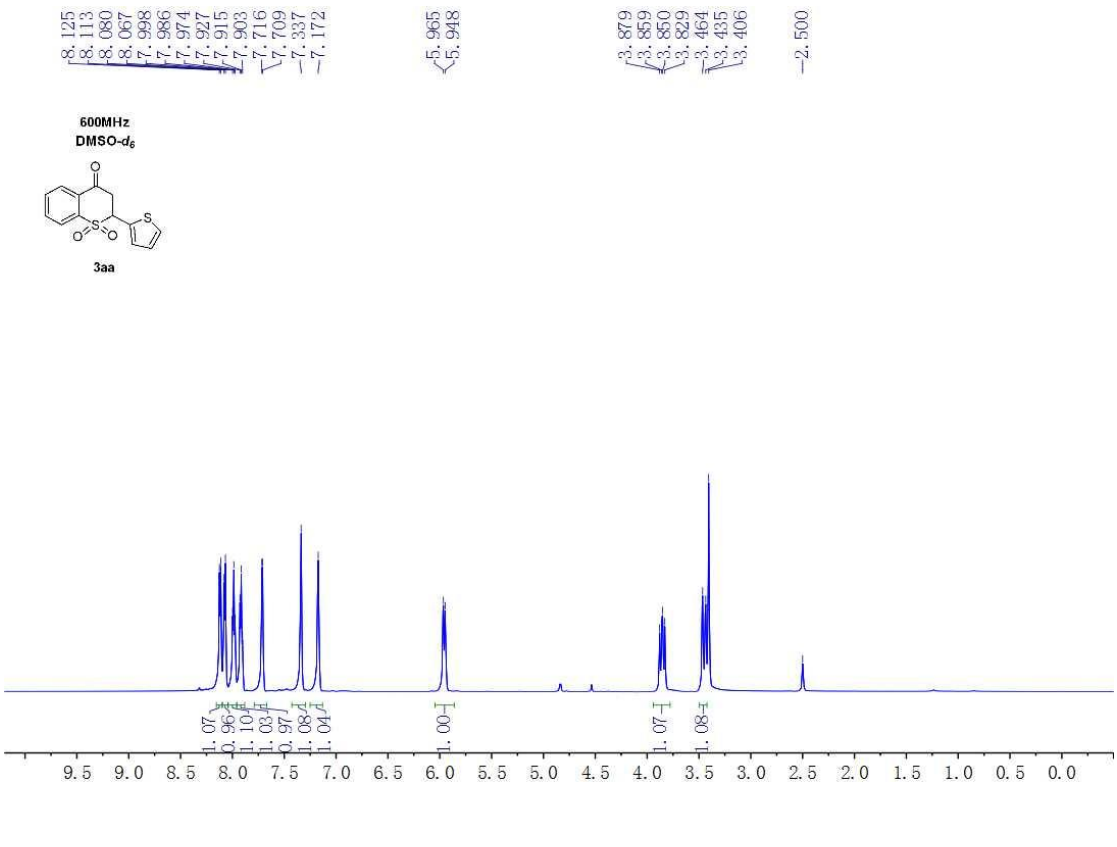
39.79
39.65
39.51
39.37
39.23
39.09
150MHz
DMSO-d6
3z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7.986
7.974
7.927
7.915
7.903
7.716
7.709
7.337
7.172
5.965
5.948
3.879
3.859
3.850
3.829
3.464
3.435
3.406
2.500
600MHz
DMSO-d6
3aa
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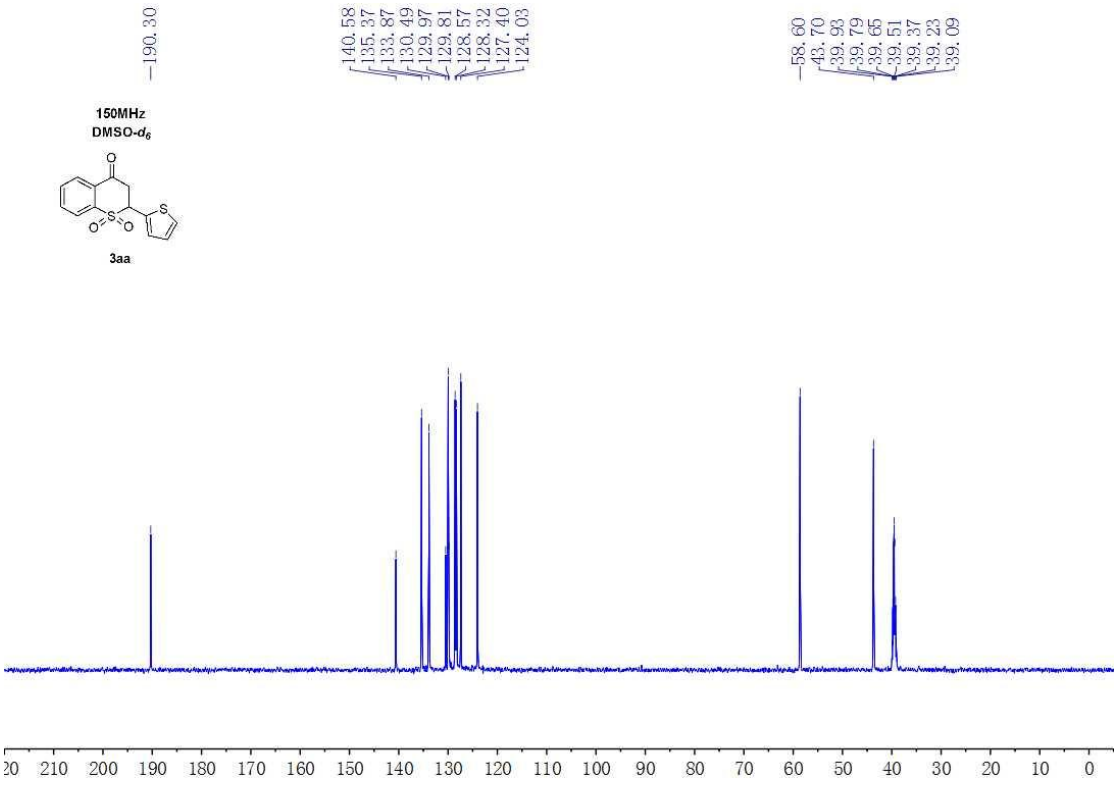
0.96
1.10
1.03
0.97
1.08
1.04
1.00
1.07
1.08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129.97
129.81
128.57
128.32
127.40
124.03
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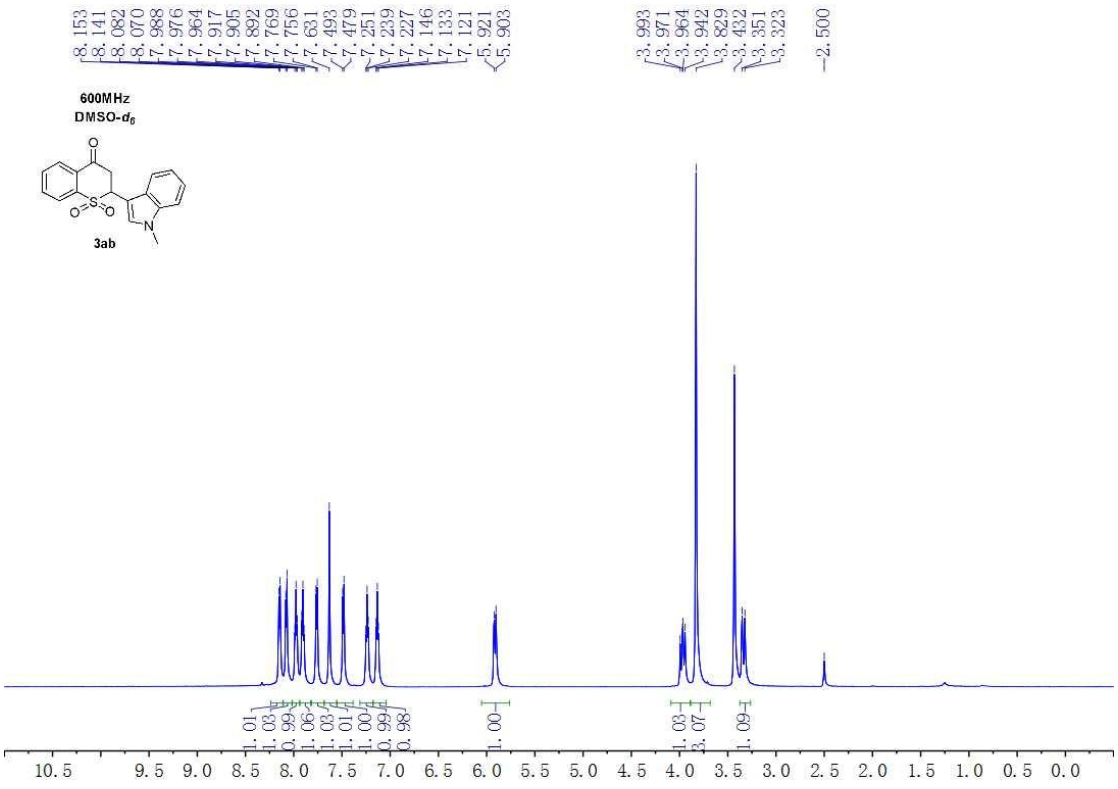
43.70
39.93
39.79
39.65
39.51
39.37
39.23
39.09
150MHz
DMSO-d_6
3aa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7.917
7.905
7.892
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7.756
7.631
7.493
7.479
7.251
7.239
7.227
7.146
7.133
7.121
5.921
5.903
3.993
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3.942
3.829
3.432
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3.323
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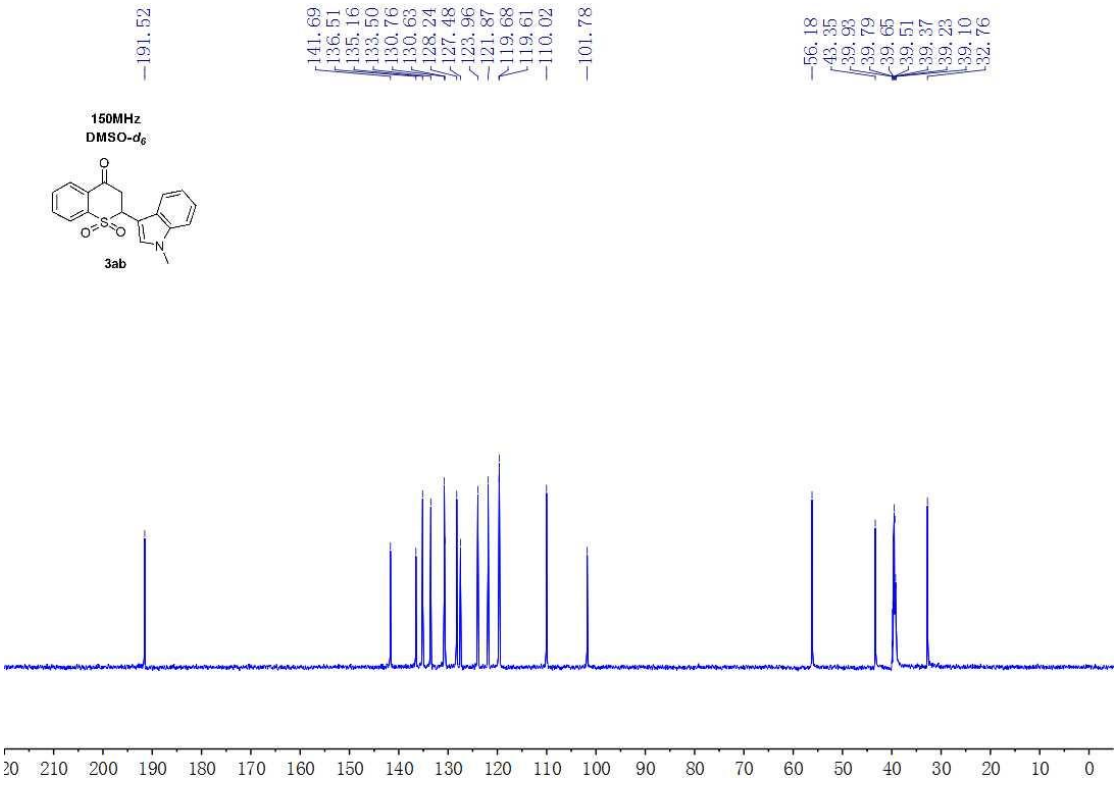
600MHz
DMSO-d_6
3ab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130.63
128.24
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123.96
121.87
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119.61
110.02
101.78
56.18
43.35
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39.65
39.51
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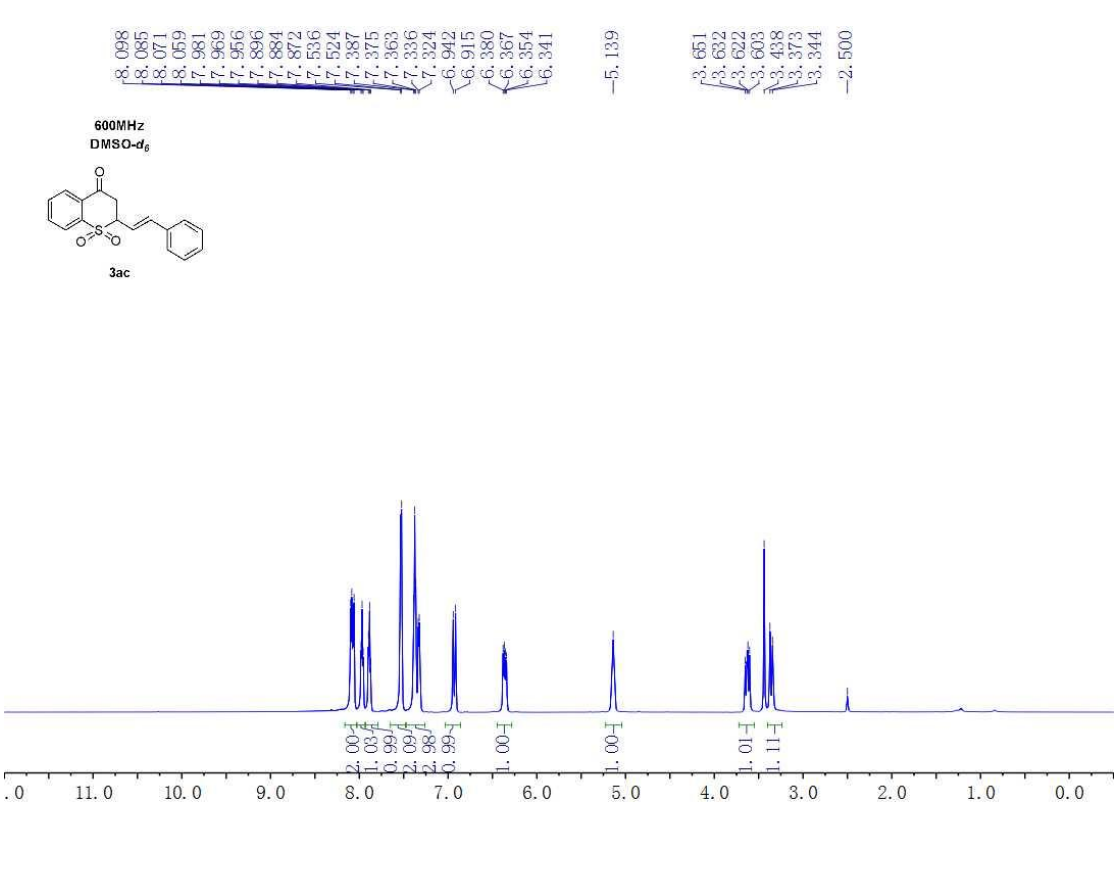
39.23
39.10
32.76
150MHz
DMSO-d6
3ab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7.872
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7.524
7.387
7.375
7.363
7.336
7.324
6.942
6.915
6.380
6.367
6.354
6.341
5.139
3.651
3.632
3.622
3.603
3.438
3.373
3.344
2.500
600MHz
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2.09
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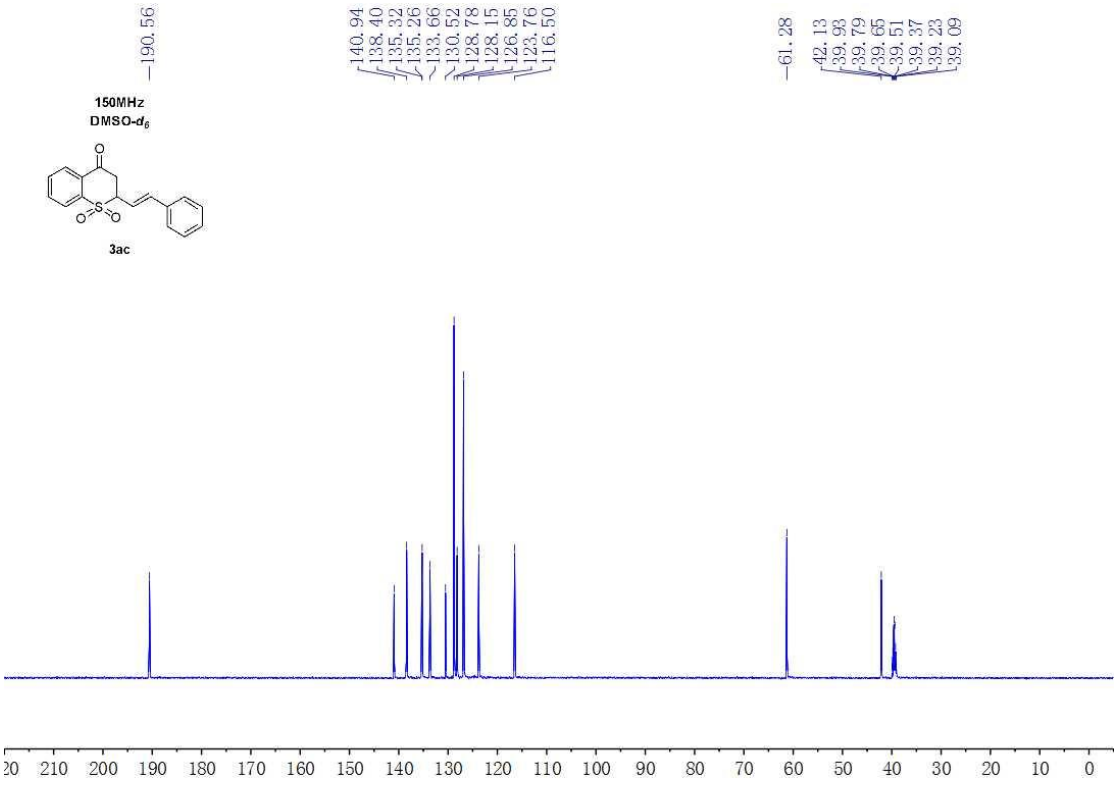
0.99
1.00
1.00
1.01
1.11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39.79
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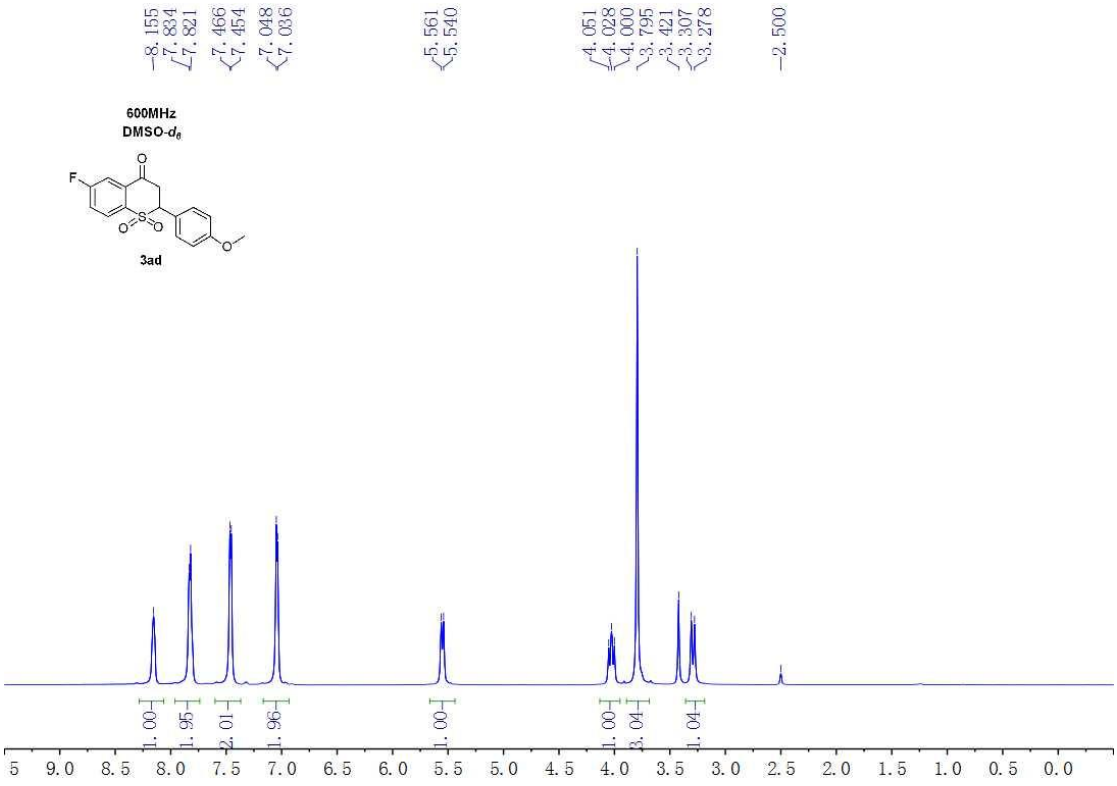
39.51
39.37
39.23
39.09
150MHz
DMSO-d_6
3ac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7.036
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4.028
4.000
3.795
3.421
3.307
3.278
2.500
600MHz
DMSO-d_6
F
O
3ad
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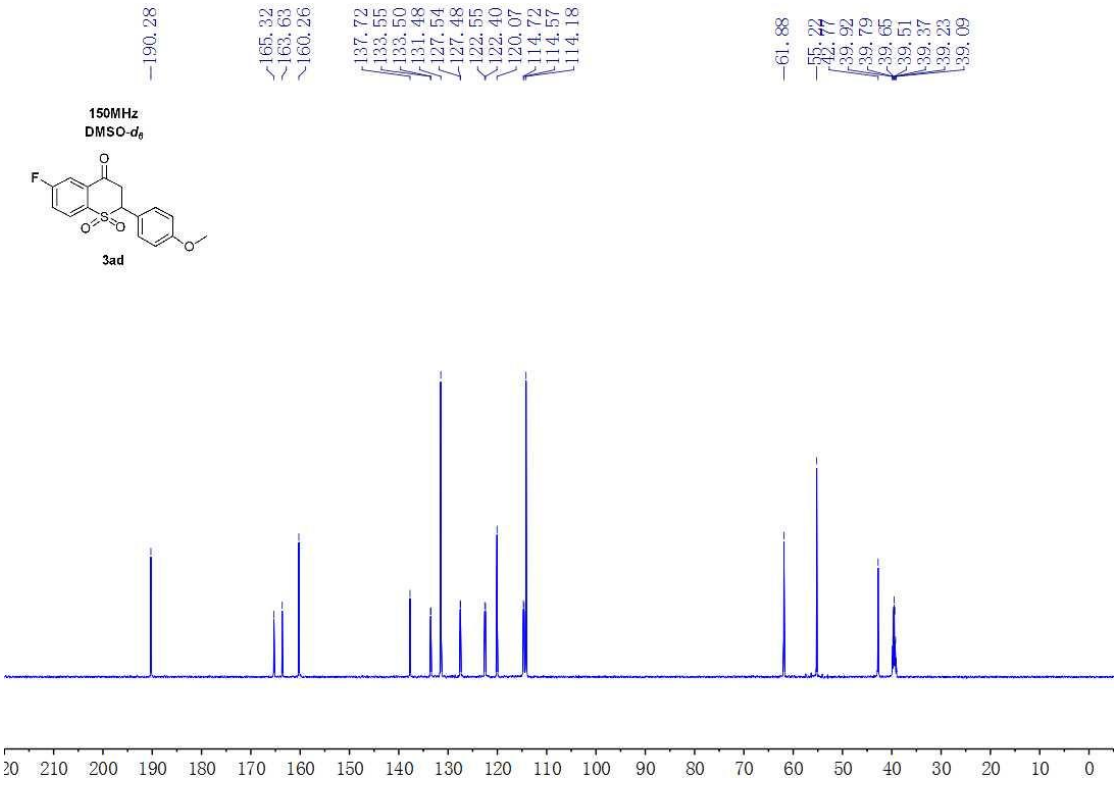
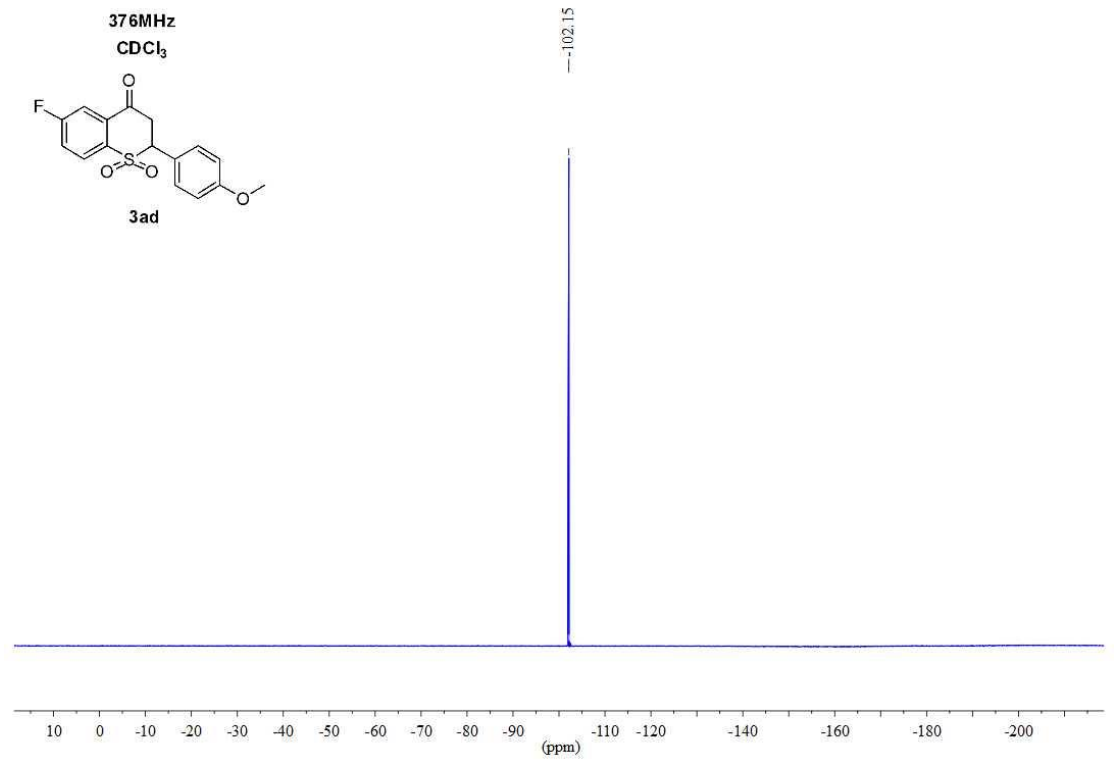
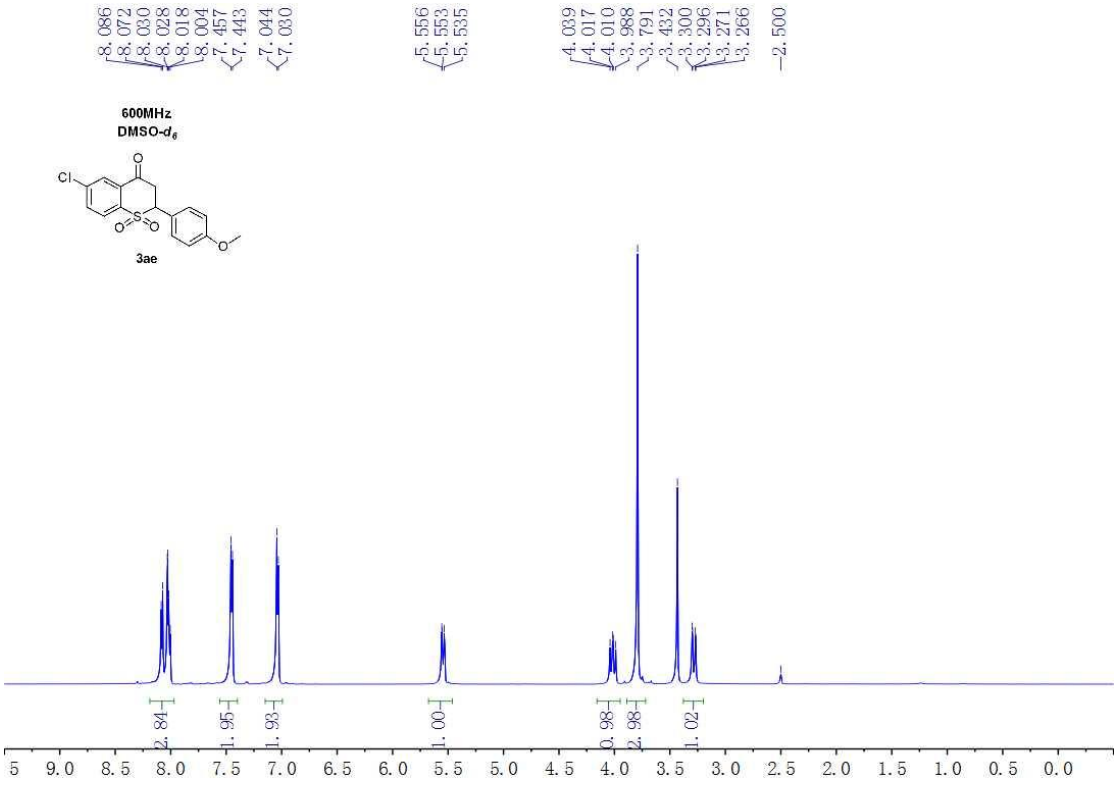
1.95
2.01
1.96
1.00
1.00
3.04
1.04





^{19}F NMR spectra (376 MHz，$CDCl_3$) of **3ad**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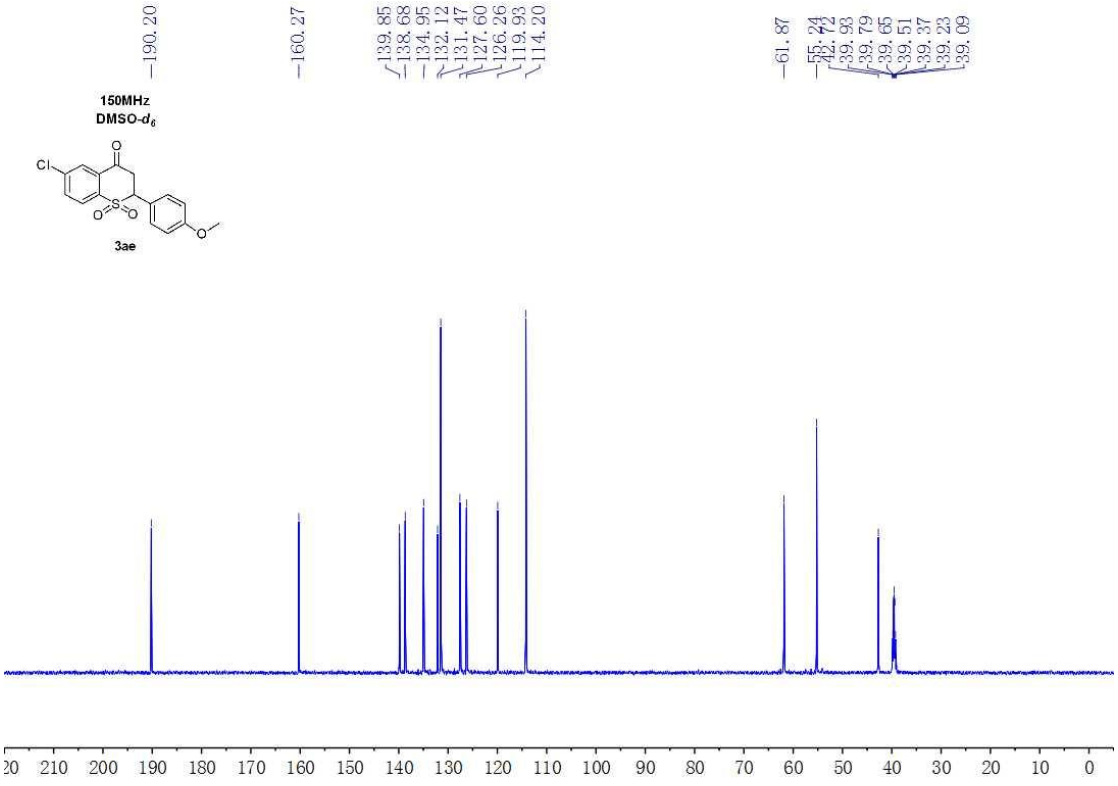
8.018
8.004
7.457
7.443
7.044
7.030
5.556
5.553
5.535
4.039
4.017
4.010
3.988
3.791
3.432
3.300
3.296
3.271
3.266
2.500
600MHz
DMSO-d_6
Cl
O
S
O
O
3ae
2.84
1.95
1.93
1.00
0.98
2.98
1.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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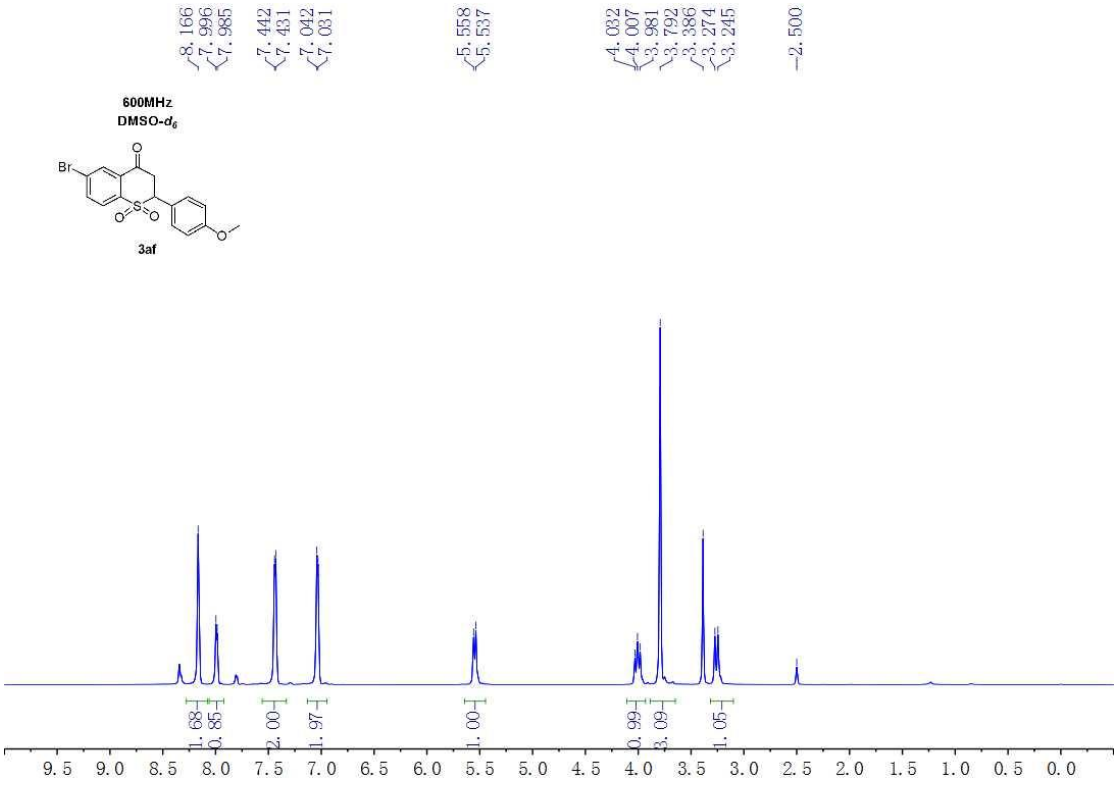
134.95
132.12
131.47
127.60
126.26
119.93
114.20
61.87
55.24
42.72
39.93
39.79
39.65
39.51
39.37
39.23
39.09
150MHz
DMSO-d_6
Cl
O
S
O
O
3ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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4.007
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3.792
3.386
3.274
3.245
2.500
600MHz
DMSO-d_6
Br
O
S
O
O
3af
1.68
0.85
2.00
1.97
1.00
0.99
3.09
1.05
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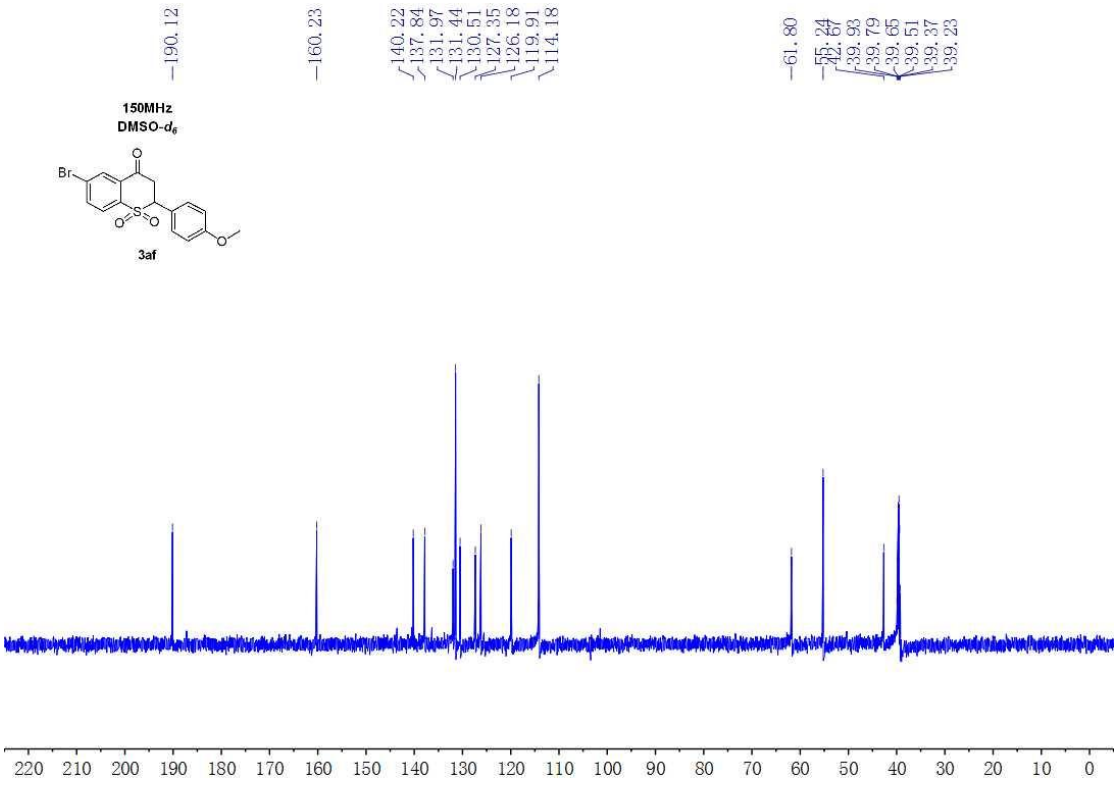
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137.84
131.97
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130.51
127.35
126.18
119.91
114.18
61.80
55.24
42.67
39.93
39.79
39.65
39.51
39.37
39.23
150MHz
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Br
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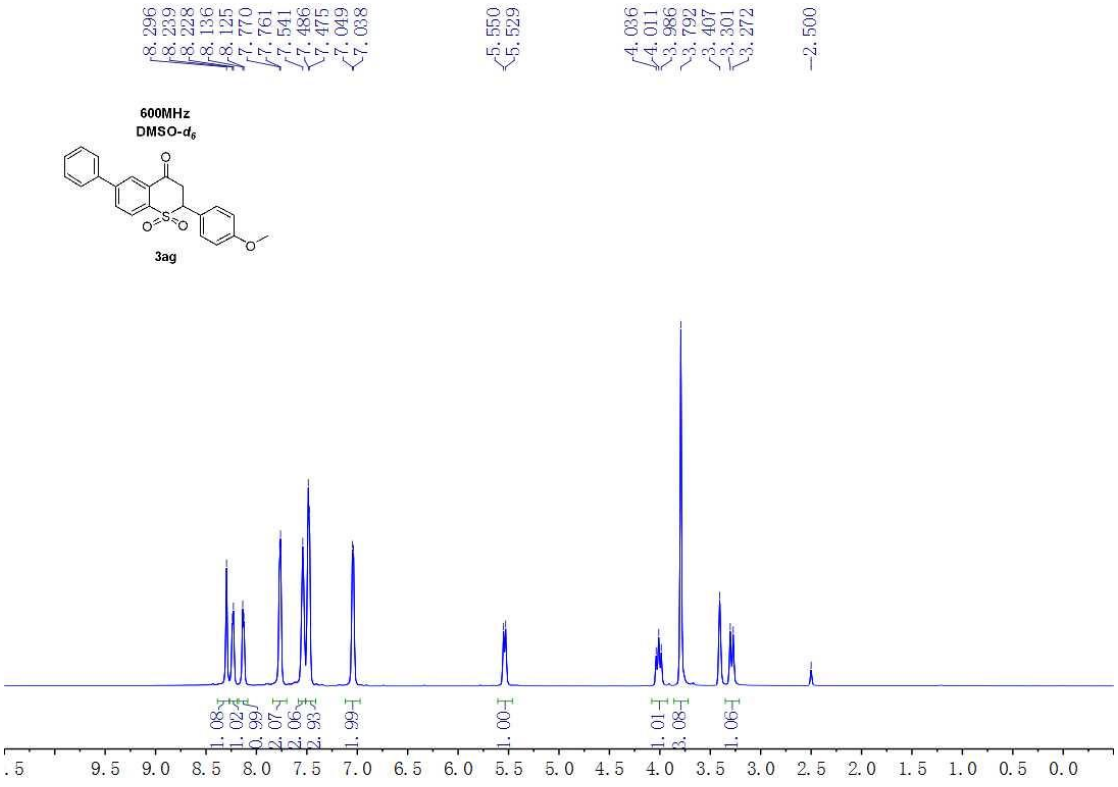
S
O
O
3af
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.049
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5.550
5.529
4.036
4.011
3.986
3.792
3.407
3.301
3.272
2.500
600MHz
DMSO-d_6
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1.02
0.99
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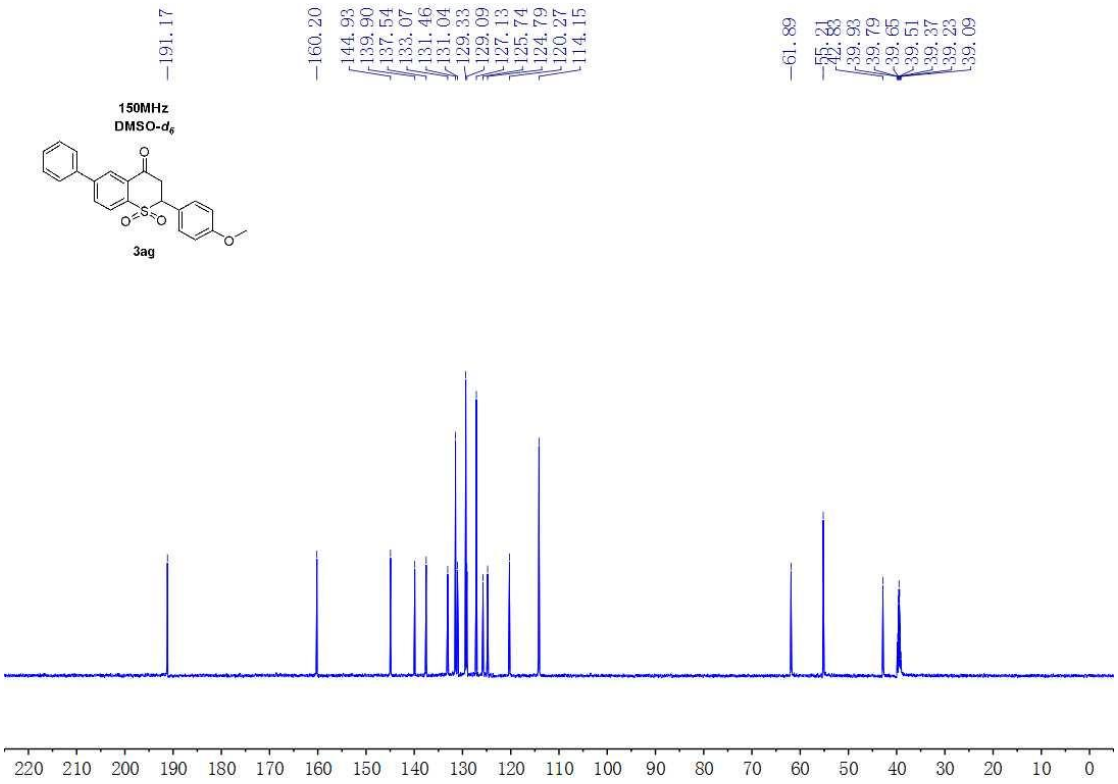
1.99
1.00
1.01
3.08
1.06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131.46
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129.09
127.13
125.74
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120.27
114.15
61.89
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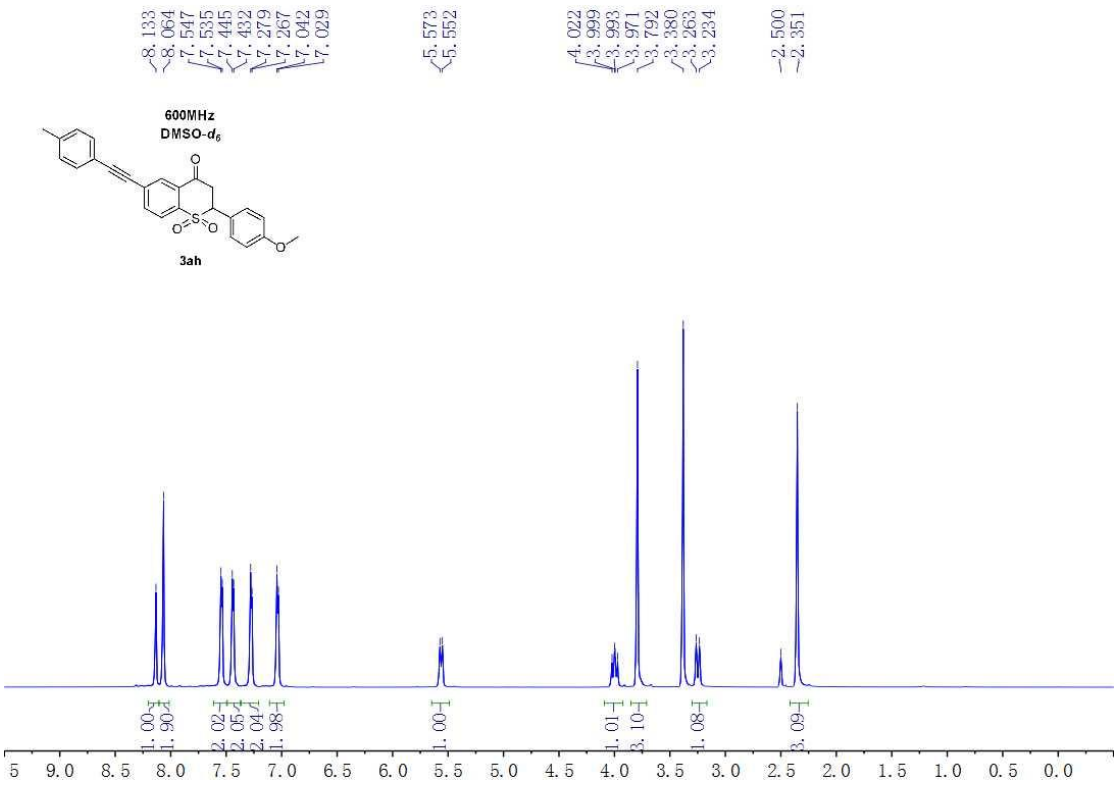
39.23
39.09
150MHz
DMSO-d_6
3ag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7.445
7.432
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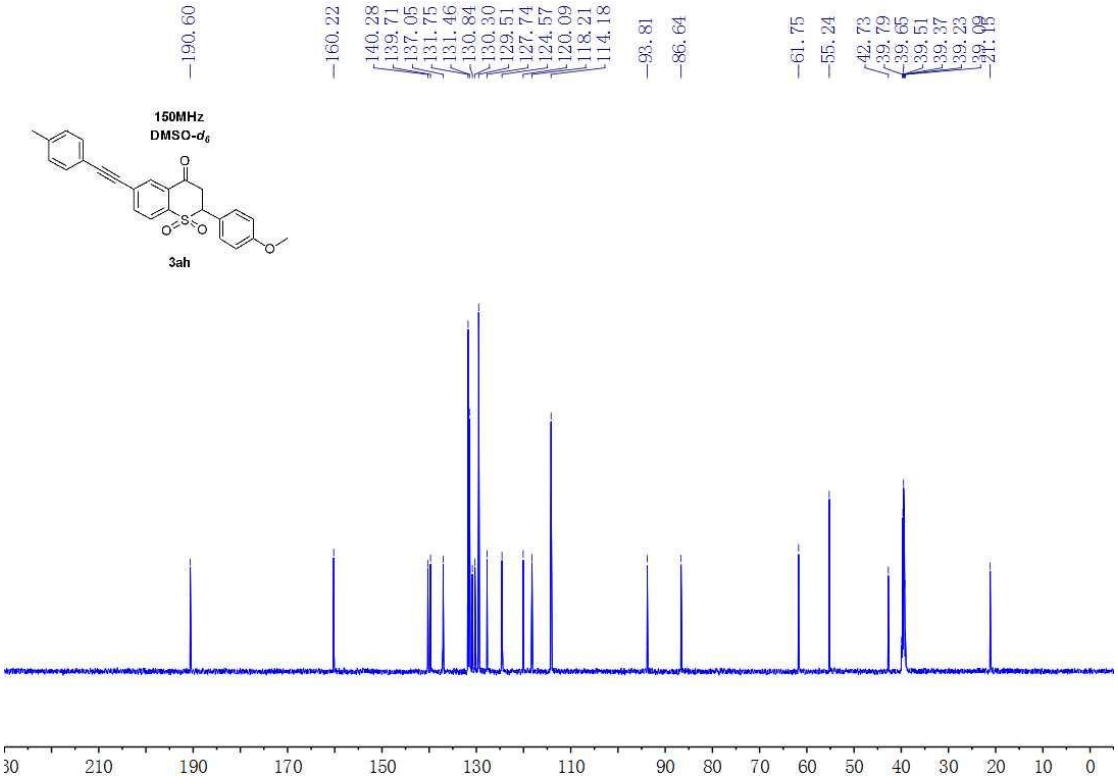
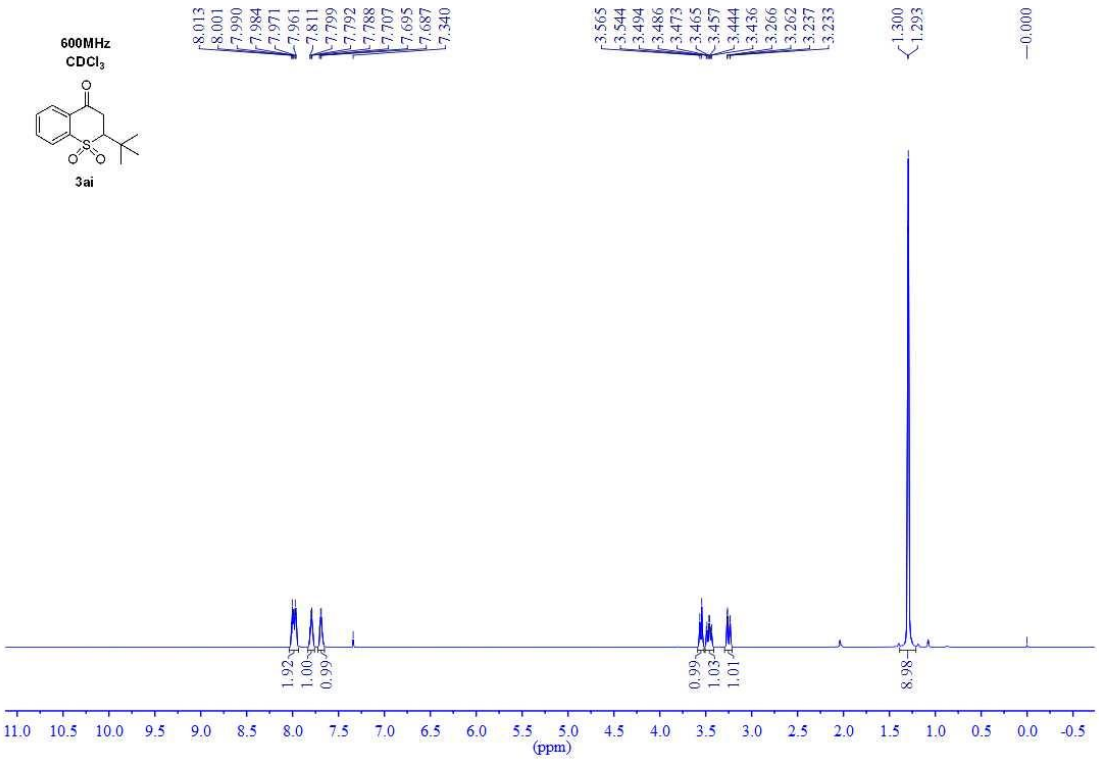
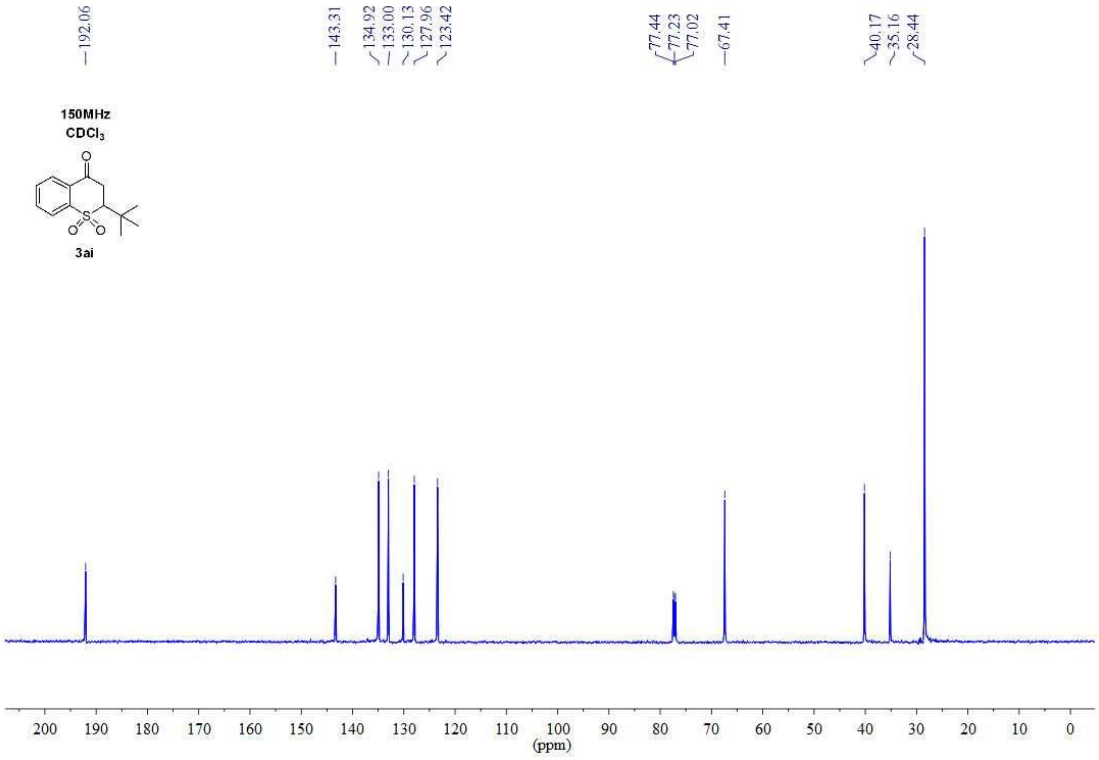
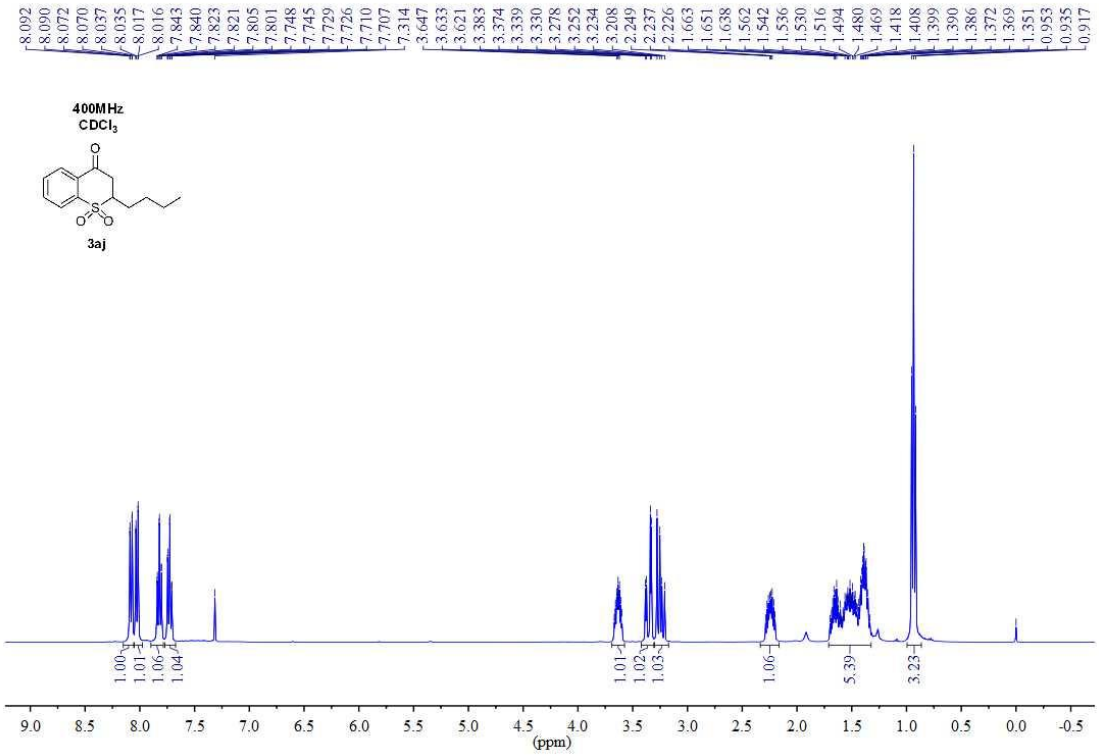
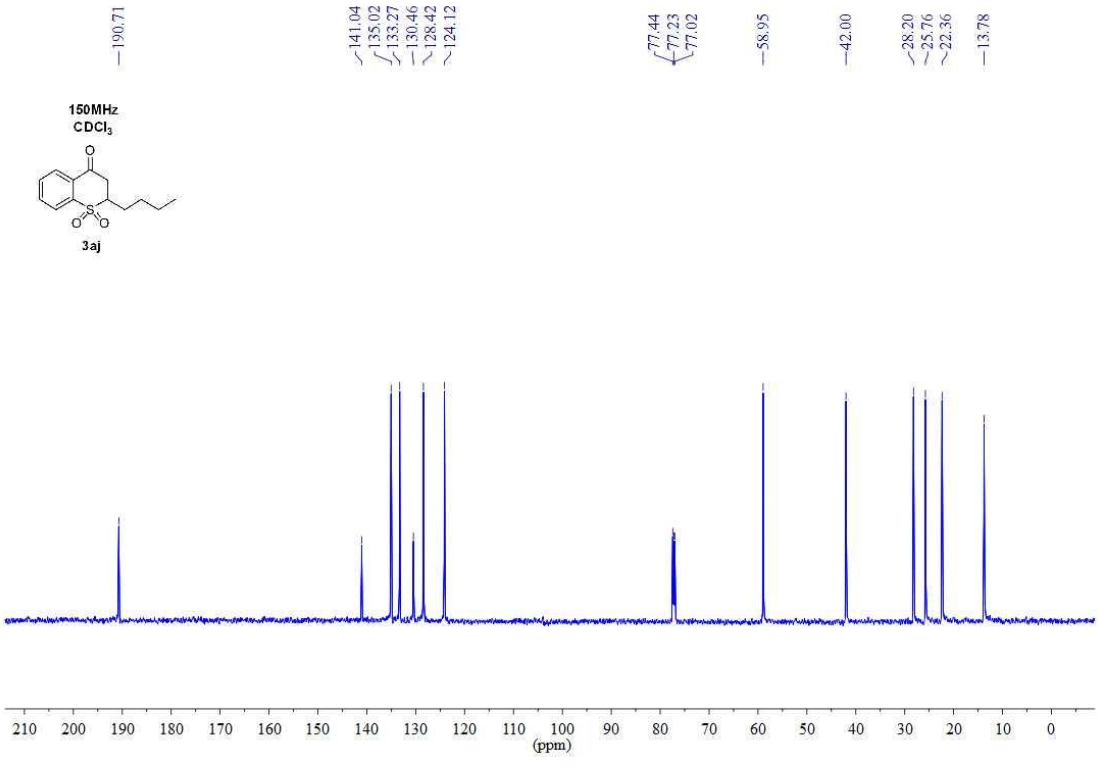
7.267
7.042
7.029
5.573
5.552
4.022
3.999
3.993
3.971
3.792
3.380
3.263
3.234
2.500
2.351
600MHz
DMSO-d_6
3ah
1.00
1.90
2.02
2.05
2.04
1.98
1.00
1.01
3.10
1.08
3.09

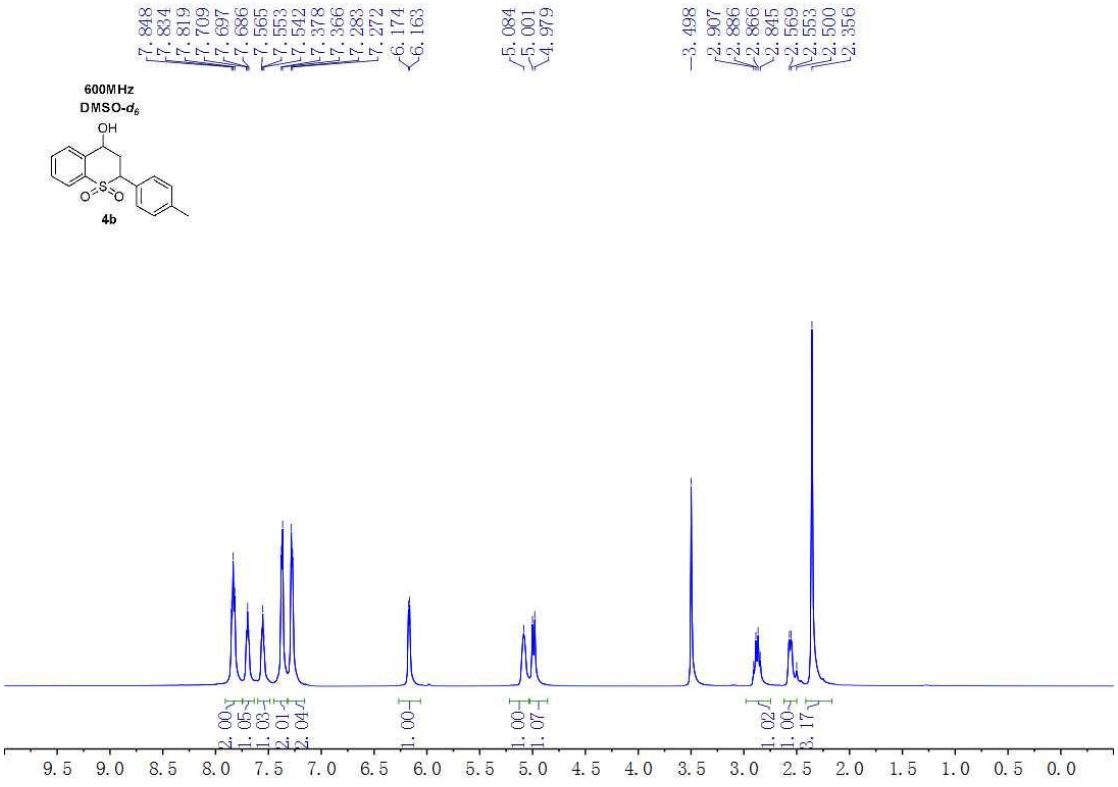

190.60
160.22
140.28
139.71
137.05
131.75
131.46
130.84
130.30
129.51
127.74
124.57
120.09
118.21
114.18
93.81
86.64
61.75
55.24
42.73
39.79
39.65
39.51
39.37
39.23
21.15
150MHz
DMSO-d_6
3ah

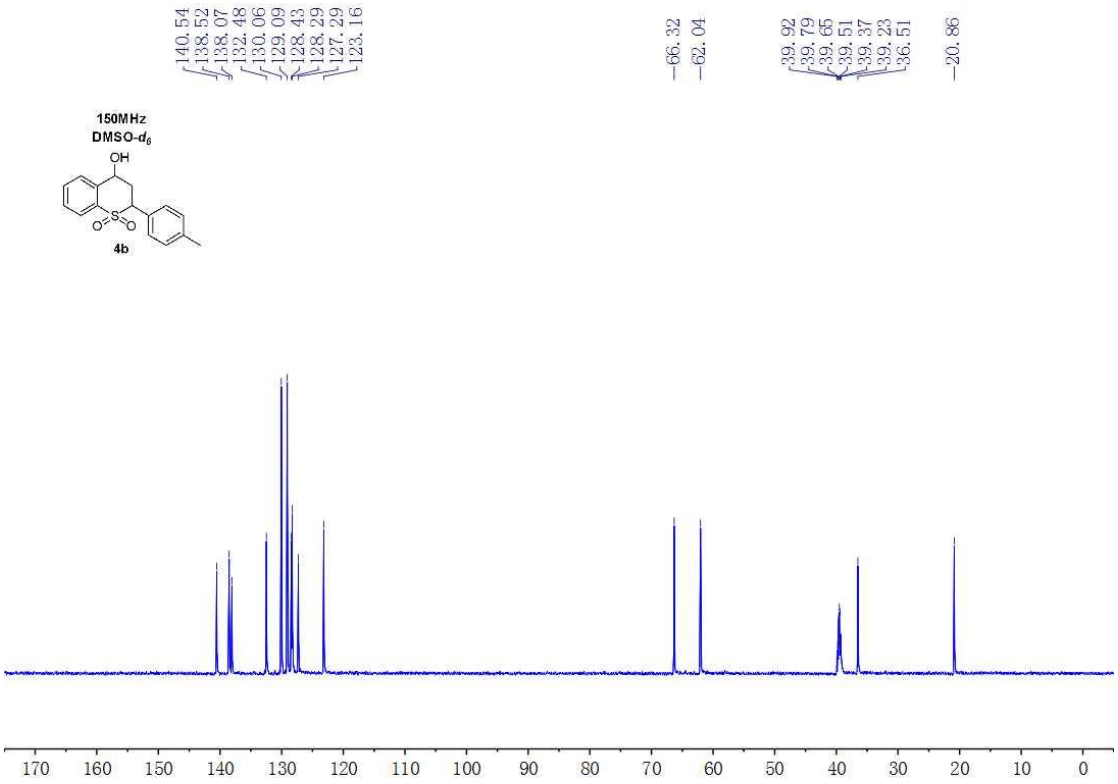

600MHz
CDCl3
3ai
8.013
8.001
7.990
7.984
7.971
7.961
7.811
7.799
7.792
7.788
7.707
7.695
7.687
7.340
3.565
3.544
3.494
3.486
3.473
3.465
3.457
3.444
3.436
3.266
3.262
3.237
3.233
1.300
1.293
0.000
1.92
1.00
0.99
0.99
1.03
1.01
8.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
(ppm)

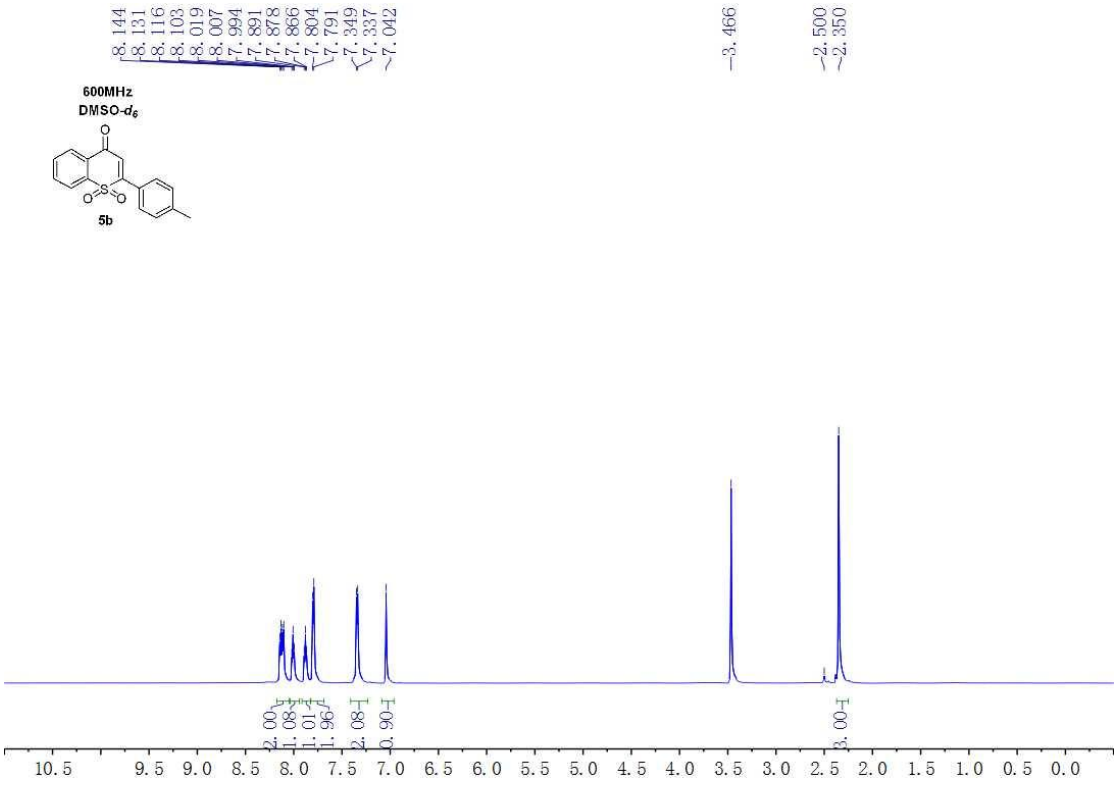

192.06
143.31
134.92
133.00
130.13
127.96
123.42
77.44
77.23
77.02
67.41
40.17
35.16
28.44
150MHz
CDCl3
3ai
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

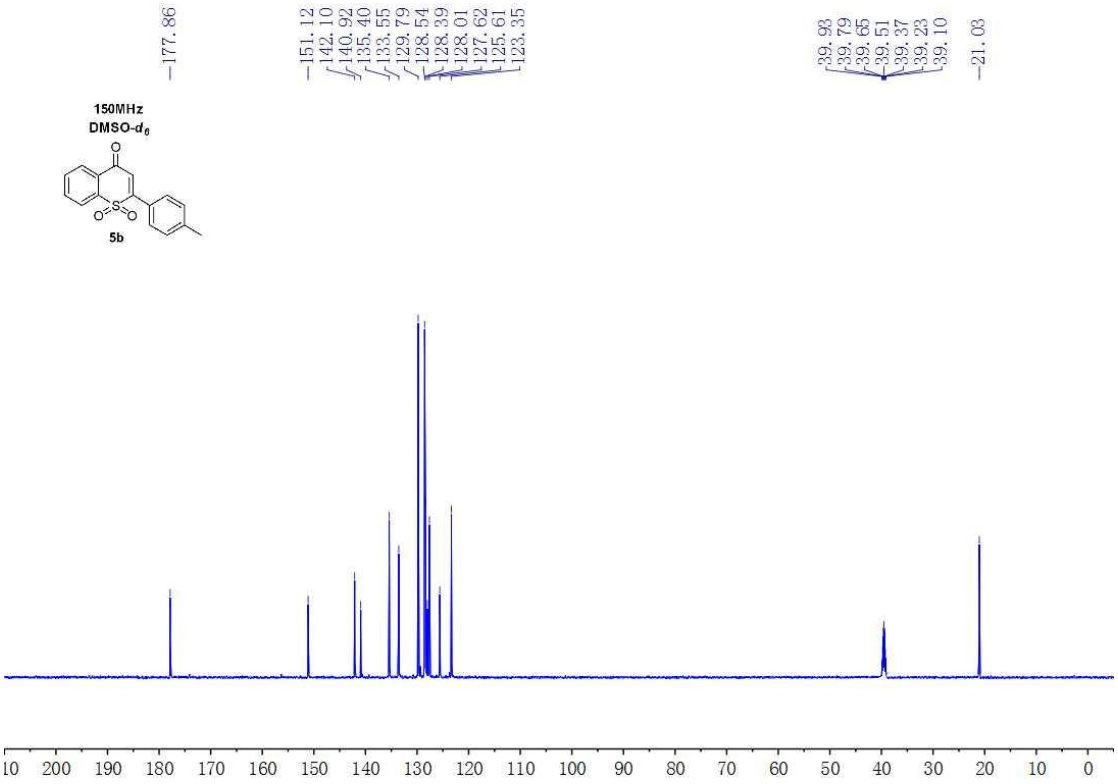

8.092
8.090
8.072
8.070
8.037
8.035
8.017
8.016
7.843
7.840
7.823
7.821
7.805
7.801
7.748
7.745
7.729
7.726
7.710
7.707
7.314
3.647
3.633
3.621
3.383
3.374
3.339
3.330
3.278
3.252
3.234
3.208
2.249
2.237
2.226
1.663
1.651
1.638
1.562
1.542
1.536
1.530
1.516
1.494
1.480
1.469
1.418
1.408
1.399
1.390
1.386
1.372
1.369
1.351
0.953
0.935
0.917
400MHz
CDCl3
3aj
1.00
1.01
1.06
1.04
1.01
1.02
1.03
1.06
5.39
3.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
(ppm)

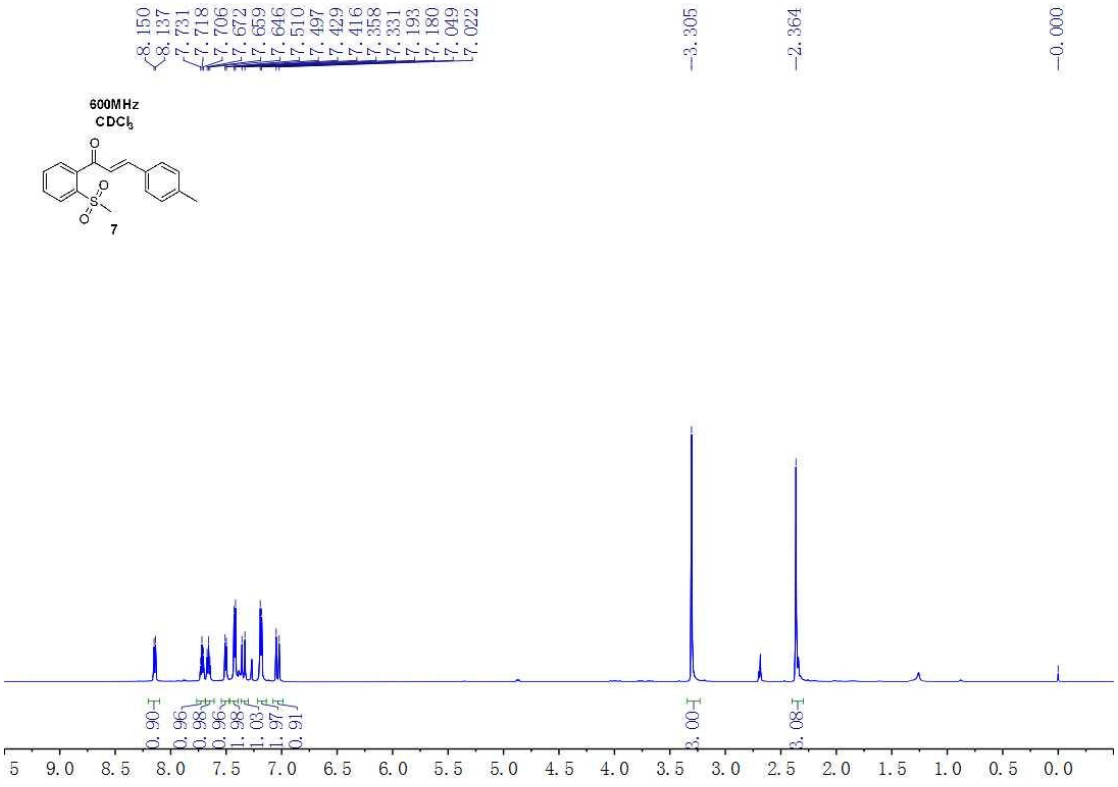

190.71
141.04
135.02
133.27
130.46
128.42
124.12
77.44
77.23
77.02
58.95
42.00
28.20
25.76
22.36
13.78
150MHz
CDCl3
3aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

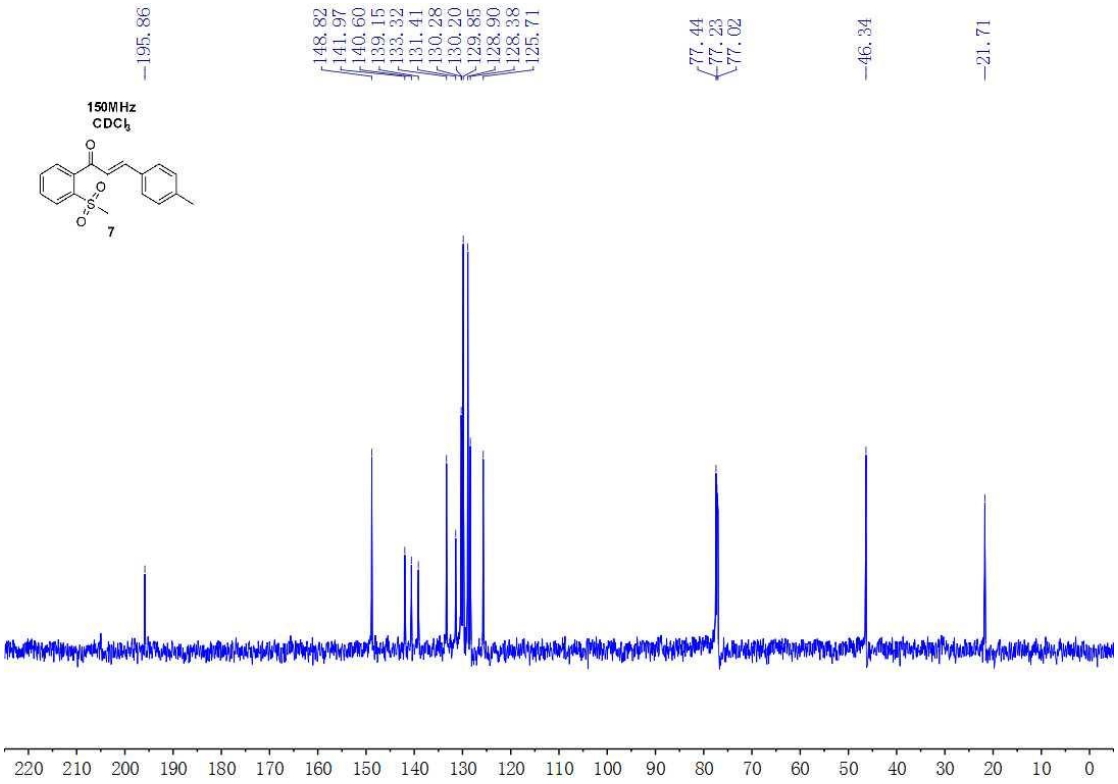

7.848
7.834
7.819
7.709
7.697
7.686
7.565
7.553
7.542
7.378
7.366
7.283
7.272
6.174
6.163
5.084
5.001
4.979
3.498
2.907
2.886
2.866
2.845
2.569
2.553
2.500
2.356
600MHz
DMSO-d_6
OH
O
S
O
4b
2.00
1.05
1.03
2.01
2.04
1.00
1.00
1.07
1.02
1.00
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

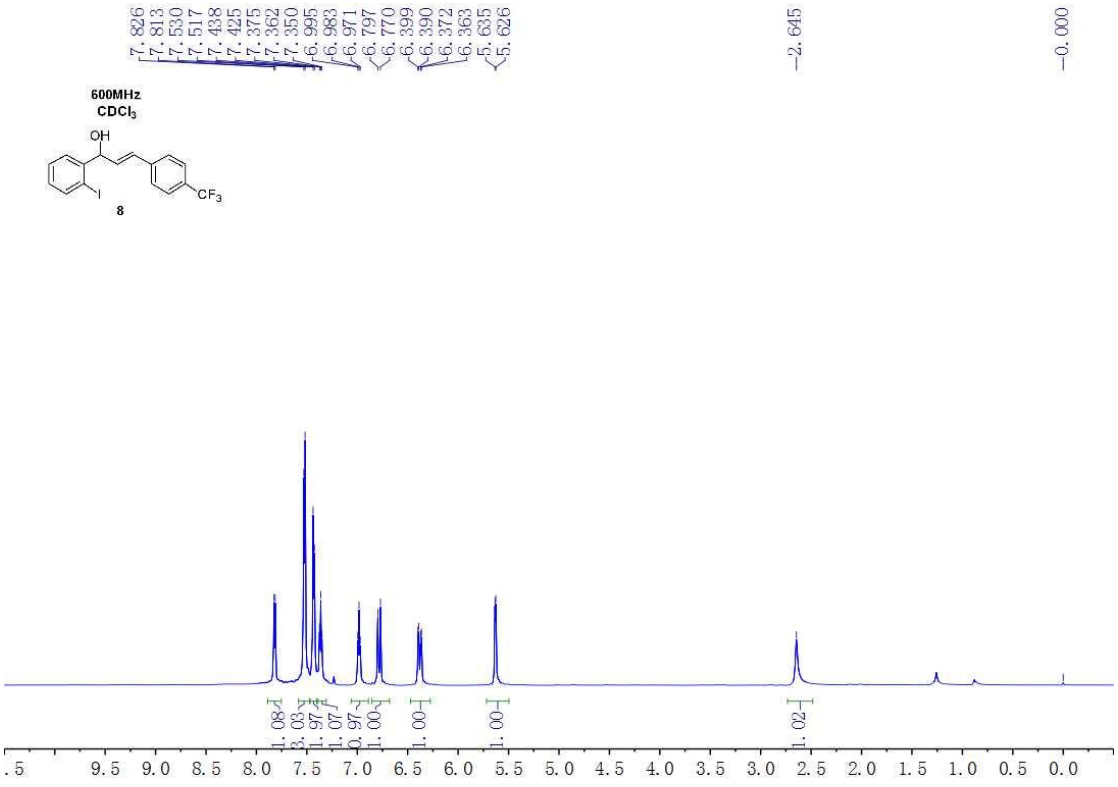

140.54
138.52
138.07
132.48
130.06
129.09
128.43
128.29
127.29
123.16
66.32
62.04
39.92
39.79
39.65
39.51
39.37
39.23
36.51
20.86
150MHz
DMSO-d_6
OH
O
S
O
4b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

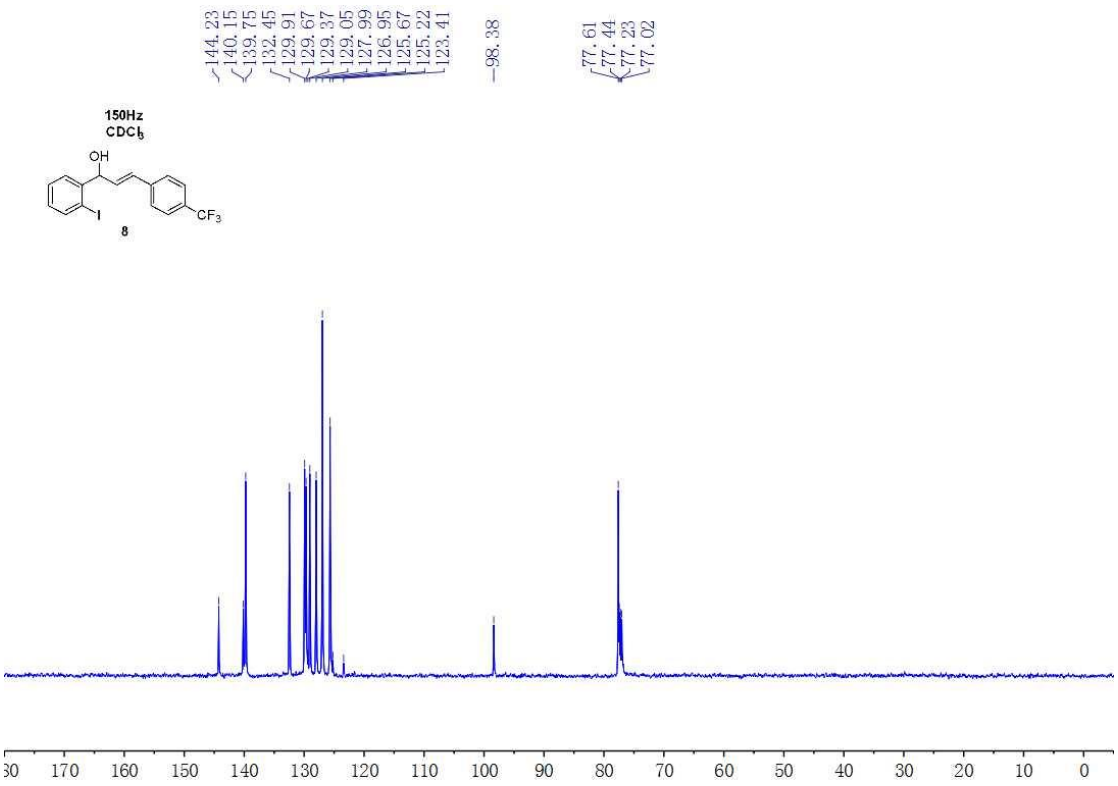

8.144
8.131
8.116
8.103
8.019
8.007
7.994
7.891
7.878
7.866
7.804
7.791
7.349
7.337
7.042
3.466
2.500
2.350
600MHz
DMSO-d_6
5b
2.00
1.08
1.01
1.96
2.08
0.90
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

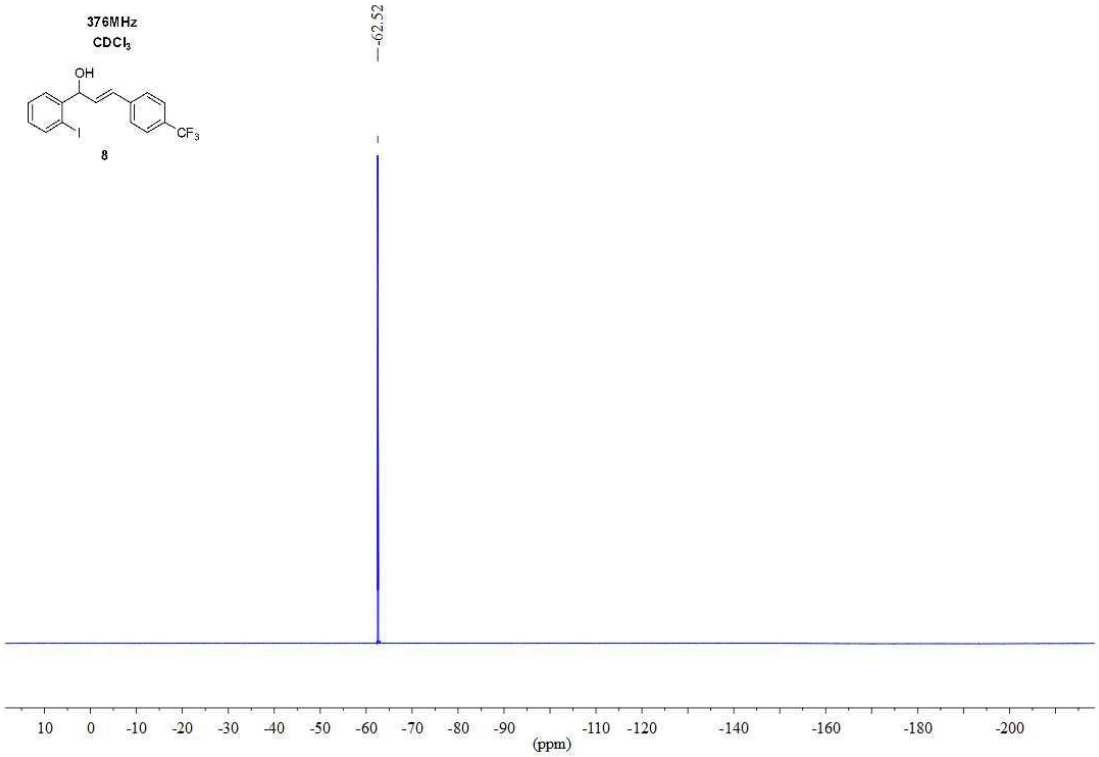

177.86
151.12
142.10
140.92
135.40
133.55
129.79
128.54
128.39
128.01
127.62
125.61
123.35
39.93
39.79
39.65
39.51
39.37
39.23
39.10
21.03
150MHz
DMSO-d_6
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.150
8.137
7.731
7.718
7.706
7.672
7.659
7.646
7.510
7.497
7.429
7.416
7.358
7.331
7.193
7.180
7.049
7.022
3.305
2.364
0.000
600MHz
CDCl3
7
0.90
0.96
0.98
0.96
1.98
1.03
1.97
0.91
3.00
3.08


195.86
148.82
141.97
140.60
139.15
133.32
131.41
130.28
130.20
129.85
128.90
128.38
125.71
77.44
77.23
77.02
46.34
21.71
150MHz
CDCl3
7


7.826
7.813
7.530
7.517
7.438
7.425
7.375
7.362
7.350
6.995
6.983
6.971
6.797
6.770
6.399
6.390
6.372
6.363
5.635
5.626
2.645
0.000
600MHz
CDCl3
OH
I
CF3
8
1.08
3.03
1.97
1.07
0.97
1.00
1.00
1.00
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


144.23
140.15
139.75
132.45
129.91
129.67
129.37
129.05
127.99
126.95
125.67
125.22
123.41
98.38
77.61
77.44
77.23
77.02
150Hz
CDCl3
OH
I
CF3
8
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



^{19}F NMR spectra (376 MHz，$CDCl_3$) of **8**