Supporting Information

Metal-free Oxysulfonylation and Aminosulfonylation of alkenyl oximes: Synthesis of Sulfonylated Isoxazolines and Cyclic Nitrones

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Contents

1. Optimization of reaction conditions

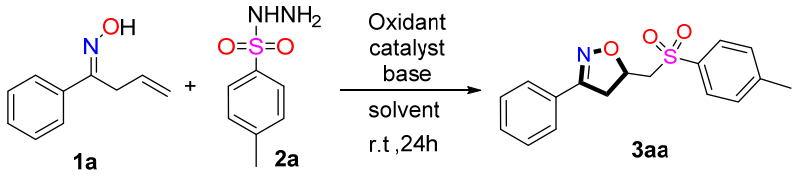


Table S1. Oxysulfonylation of alkenyl oximes **1a** with **2a** under different conditions.[a]

Entry	Catalyst	Oxidant	Base	Solvent	Yield [b] (%)
1	TBAI	TBHP	NaOAc	DCE	24
2	TBAI	$K_2S_2O_8$	NaOAc	DCE	trace
3	TBAI	DTBP	NaOAc	DCE	trace
4	TBAI	BPO	NaOAc	DCE	trace
5	TBAI	TBHP	Na_2CO_3	DCE	trace
6	TBAI	TBHP	K_2CO_3	DCE	N.R.
7	TBAI	TBHP	KOH	DCE	trace
8	TBAI	TBHP	NaOMe	DCE	21
9	TBAI	TBHP	DBU	DCE	trace
10	TBAI	TBHP	KF	DCE	24
11	TBAI	TBHP	$NaHCO_3$	DCE	30
12	TBAI	TBHP	$NaHCO_3$	MeCN	20
13	TBAI	TBHP	$NaHCO_3$	THF	28
14	TBAI	TBHP	$NaHCO_3$	DMSO	N.R.
15	TBAI	TBHP	$NaHCO_3$	DMF	N.R.
16	TBAI	TBHP	$NaHCO_3$	toluene	31
17	TBAI	TBHP	$NaHCO_3$	acetone	trace
18	TBAI	TBHP	$NaHCO_3$	Diox	36
19	NaI	TBHP	$NaHCO_3$	Diox	74
20	TEAI	TBHP	$NaHCO_3$	Diox	trace
21	MnI_2	TBHP	$NaHCO_3$	Diox	83

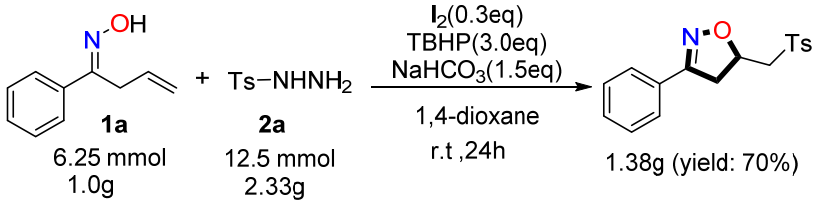
22	FeI_2	TBHP	$NaHCO_3$	Diox	47
23	ZnI_2	TBHP	$NaHCO_3$	Diox	trace
24	NIS	TBHP	$NaHCO_3$	Diox	87
25	I_2	TBHP	$NaHCO_3$	Diox	91
26	I_2	TBHP	none	Diox	44
27	none	TBHP	$NaHCO_3$	Diox	N.R.
28[c]	I_2	TBHP	$NaHCO_3$	Diox	86
29[d]	I_2	TBHP	$NaHCO_3$	Diox	77.
30[e]	I_2	TBHP	$NaHCO_3$	Diox	82
31[f]	I_2	TBHP	$NaHCO_3$	Diox	79
32[g]	I_2	TBHP	$NaHCO_3$	Diox	trace
33	KI	TBHP	$NaHCO_3$	Diox	80
34	KI	$PhI(OAc)_2$	$NaHCO_3$	Diox	N.R
35	I_2	TBHP	Na_2CO_3	Diox	20
36	I_2	TBHP	K_2CO_3	Diox	trace
37	I_2	TBHP	NaOAc	Diox	49
38	I_2	TBHP	KF	Diox	45
39	I_2	TBHP	DBU	Diox	trace
40	I_2	TBHP	$NaHCO_3$	DCE	75
41	I_2	TBHP	$NaHCO_3$	MeCN	81
42	I_2	TBHP	$NaHCO_3$	THF	83
43	I_2	TBHP	$NaHCO_3$	toluene	61
44	I_2	TBHP	$NaHCO_3$	EtOH	55

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol, 2.0 equiv), oxidant (0.75 mmol, 3.0 equiv), catalyst (0.3 equiv), base (1.5 equiv), solvent (2.0 mL), under argon and stirred at room temperature for 24 h. TBHP= tert-butylhydroperoxide (70% solution in water); TEAB= Tetraethylammonium bromide. BPO= Benzoyl peroxide [b]Isolated yield based on **1a**. [c] Reaction was proceeded under 70°C. [d]2.0 equiv. of TBHP was used. [e]1.8 equiv. of **2a**

was used. [f]0.2 equiv. of I_2 was used. [g]Reaction system was open to air.

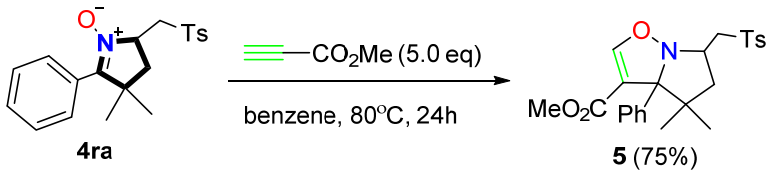
2. Expansion Reactions

(1) Gram scale experiment to synthesis compound **3aa**.



A 100 mL flask equipped with a magnetic stir bar was charged with β,γ-unsaturated ketoxime **1a** (6.25 mmol, 1.0 g) and *p*-Toluenesulfonyl hydrazide **2a** (12.5 mmol, 2.33 g). Then, I_2 (0.24 g), $NaHCO_3$ (0.8 g), and TBHP (2.4 g, 70% solution in water), 1,4-dioxane (50 ml) were added to this system. Hereafter, the reaction tube was vacuumed and charged with argon and stirred at room temperature for 24 h. Then, the reaction mixture was filtered and evaporated to obtain crude product. The residue was purified by column chromatography (ethyl acetate: petroleum ether= 1: 10, v/v) to afford the desired product **3aa** 1.38g (70% yield) as a white solid.

(2) The [3+2] cycloaddition of cyclic nitrone **4ra** with methyl propiolate.[1]

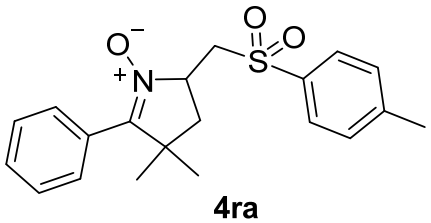


The compound **3ra** (89.4 mg, 0.25 mmol) was mixed with methyl propiolate (105mg, 1.25 mmol) using benzene as solvent in a 50 mL flask. The mixture was heated for 24 h at 80°C. After removal of solvent, the residue was purified by silica gel chromatography (ethyl acetate: petroleum ether= 1: 15, v/v) to give 83 mg of product **5** (75%) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 7.7 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.23 – 7.15 (m, 2H), 7.15 – 7.09 (m, 1H), 3.83 – 3.63 (m, 5H), 3.31 (dd, J = 13.4, 9.9 Hz, 1H), 2.39 (s, 3H), 1.95 (dd, J = 12.9, 5.0 Hz, 1H), 1.64 – 1.49 (m, 1H), 1.25 (s, 3H), 0.71 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 155.5, 145.0, 143.9, 136.9, 130.0, 127.9, 127.8, 126.9, 126.8, 111.9, 83.0, 61.4, 60.0, 51.6, 45.4, 44.1, 27.7, 27.2, 21.7. HRMS-ESI

(m/z): $[M+H]^+$ calcd for: $C_{24}H_{28}NO_5S^+$, 442.1683; found: 442.1688. IR (KBr): υ = 2962.9, 1711.2, 1613.5, 1439.9, 1315.5, 1149.9, 768.1, 671.7, 510.9 cm^{-1}.

3. X-ray diffraction data for 4ra.

The crystals of **3ai** was obtained by crystallization from a solution in acetone/petroleum ether after purification by column chromatography.



4ra

Chemical Formula: $C_{20}H_{23}NO_3S$

Figure S1. ORTEP drawing of compound **4ra**.

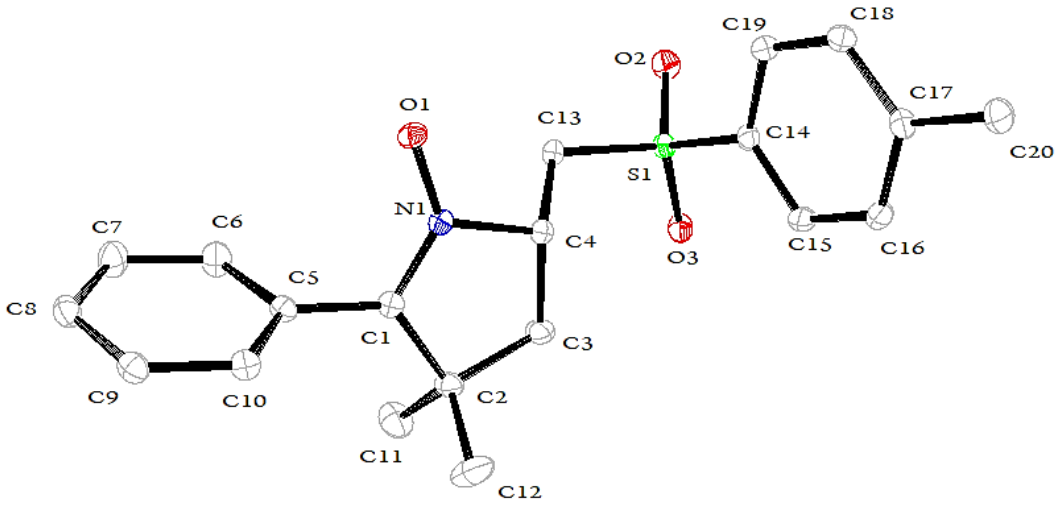


Table S2. Crystal data and structure refinement for **4ra**.

Identification code	4ra
Empirical formula	$C_{20}H_{23}NO_3S$
Formula weight	357.45
Temperature/K	113
Crystal system	orthorhombic
Space group	P b c a

a/Å	10.1298(3)
b/Å	18.7025(5)
c/Å	19.0521(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3609.47(17)
Z	8
ρ_{calc}g/ cm^3	1.316
μ/mm^{-1}	0.198
F (000)	1520
Crystal size/mm^3	0.32×0.24×0.22
Radiation	MoK\a (λ = 0.71073)
2Θ range for data collection/°	2.1630 to 33.0000
Index ranges	-13 ≤ h ≤ 13, -24≤ k ≤ 24, -25 ≤ l ≤ 25
Reflections collected	55619
Independent reflections	4310 [$R_{(int)}$ = 0.0558, $R_{(sigma)}$ = 0.0271]
Data/restraints/parameters	4310 /0/230
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.0400, wR2 = 0.0977
Final R indexes [all data]	R1 = 0.0483, wR2 = 0.1037
Largest diff. peak/hole / e Å^{-3}	0.35 / -0.40
Flack parameter	n/a

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4ra**. Ueq is defined as 1/3 of the trace of the orthogonalized.

Atom	*x*	*y*	*z*	Ueq
S1	5056.3(3)	3001.3(2)	8499.9(2)	20.25(11)

O1	2201.3(10)	4474.3(5)	7428.9(5)	23.6(2)
O2	5242.6(11)	3224.9(6)	9217.1(6)	29.5(3)
O3	6189.2(10)	2753.8(6)	8111.2(6)	27.1(3)
N1	3101.0(12)	4182.2(6)	7040.3(6)	19.0(3)
C1	3442.9(14)	4357.7(8)	6405.5(8)	21.0(3)
C2	4514.3(15)	3879.9(9)	6115.1(8)	25.2(3)
C3	4881.7(17)	3412.2(9)	6756.4(8)	30.9(4)
C4	3832.5(14)	3545.6(7)	7318.2(7)	20.2(3)
C5	2851.6(14)	4989.2(8)	6061.0(7)	21.3(3)
C6	3175.8(18)	5666.9(9)	6305.8(9)	31.9(4)
C7	2636.3(19)	6272.7(9)	6006.9(9)	34.3(4)
C8	1766.6(16)	6209.4(8)	5451.8(8)	27.0(3)
C9	1448.8(15)	5538.1(8)	5195.8(8)	25.4(3)
C10	1984.0(15)	4927.0(8)	5499.0(8)	23.9(3)
C11	5699.7(18)	4327.2(11)	5883.3(11)	42.8(5)
C12	3995(2)	3432.3(11)	5503.6(10)	44.9(5)
C13	4346.6(14)	3734.2(7)	8044.7(7)	20.3(3)
C14	3860.6(14)	2317.9(7)	8475.6(7)	20.0(3)
C15	4015.4(16)	1757.6(8)	8004.4(8)	25.3(3)
C16	3085.8(16)	1213.2(8)	7990.6(8)	26.4(3)
C17	1998.1(15)	1225.9(8)	8436.3(8)	23.3(3)
C18	1862.4(16)	1795.4(8)	8902.8(8)	25.1(3)
C19	2787.0(15)	2340.9(8)	8927.2(8)	23.6(3)
C20	1001.7(18)	6314(9)	8417.1(9)	32.4(4)

Table S4. Anisotropic Displacement Parameters ($Å^2×10^3$) for **4ra.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U11	U22	U33	U23	U13	U12

S1	18.38(19)	19.44(19)	22.9(2)	1.96(13)	-1.39(13)	0.06(13)
O1	18.1(5)	26.0(5)	26.7(5)	-1.3(4)	4.7(4)	4.0(4)
O2	31.1(6)	31.6(6)	25.7(6)	-0.3(5)	-7.0(5)	-3.6(5)
O3	18.4(5)	25.3(5)	37.6(6)	5.1(5)	5.0(5)	2.1(4)
N1	15.7(6)	18.8(6)	22.4(6)	-0.6(5)	-0.5(5)	0.4(5)
C1	19.1(7)	22.3(7)	21.6(7)	-0.4(5)	-2.1(6)	-0.7(6)
C2	23.1(7)	32.1(8)	20.5(7)	-0.6(6)	0.3(6)	5.6(6)
C3	33.4(9)	34.9(9)	24.2(8)	1.5(7)	4.9(7)	13.8(7)
C4	20.0(7)	18.8(6)	21.7(7)	0.8(5)	-1.2(6)	1.1(5)
C5	20.2(7)	24.0(7)	19.8(7)	1.5(5)	0.7(6)	-0.8(6)
C6	35.7(9)	28.0(8)	32.1(8)	-1.4(7)	-12.0(7)	-3.1(7)
C7	41.8(10)	22.8(8)	38.1(9)	-0.3(7)	-6.9(8)	-4.2(7)
C8	27.0(8)	26.0(7)	27.9(8)	7.5(6)	3.4(6)	1.1(6)
C9	21.3(7)	30.9(8)	23.9(7)	3.0(6)	-2.0(6)	0.4(6)
C10	22.0(7)	24.3(7)	25.3(7)	-0.1(6)	-2.1(6)	-2.0(6)
C11	28.1(9)	53.5(12)	46.8(11)	13.0(9)	10.4(8)	5.7(8)
C12	45.0(11)	53.4(12)	36.3(10)	-20.5(9)	-11.2(9)	19.5(9)
C13	19.9(7)	17.6(6)	23.5(7)	0.9(5)	-1.8(6)	0.5(5)
C14	20.1(7)	18.9(7)	21.1(7)	2.5(5)	-0.4(6)	0.9(5)
C15	25.1(8)	24.9(7)	26.0(7)	-1.6(6)	7.5(6)	0.3(6)
C16	30.2(8)	20.0(7)	29.1(8)	-3.6(6)	5.5(6)	-1.3(6)
C17	22.8(8)	20.9(7)	26.0(7)	4.2(6)	0.5(6)	-0.5(6)
C18	22.7(8)	26.0(7)	26.7(8)	1.0(6)	6.2(6)	0.2(6)
C19	25.5(8)	23.1(7)	22.2(7)	-1.3(6)	2.7(6)	2.0(6)
C20	33.5(9)	24.8(8)	39.0(9)	-0.2(7)	8.5(7)	-6.9(7)

Table S5. Bond lengths for **4ra.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å

S1	O2	1.4414(11)	C4	C13	1.5203(19)
S1	O3	1.4421(11)	C5	C6	1.390(2)
S1	C13	1.7743(14)	C5	C10	1.390(2)
S1	C14	1.7614(15)	C6	C7	1.381(2)
O1	N1	1.2950(15)	C7	C8	1.381(2)
N1	C1	1.3002(19)	C8	C9	1.385(2)
N1	C4	1.4989(18)	C9	C10	1.391(2)
C1	C2	1.511(2)	C14	C15	1.389(2)
C1	C5	1.478(2)	C14	C19	1.387(2)
C2	C3	1.548(2)	C16	C17	1.391(2)
C2	C11	1.529(2)	C17	C18	1.394(2)
C2	C12	1.528(2)	C17	C20	1.502(2)
C3	C4	1.529(2)	C18	C19	1.386(2)

Table S6. Bond angles for **4ra**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	O3	120.07(8)	C13	C4	C3	115.92(13)
O2	S1	C13	107.00(7)	C6	C5	C1	118.95(13)
O2	S1	C14	108.99(7)	C6	C5	C10	118.95(14)
O3	S1	C13	108.62(7)	C10	C5	C1	122.10(13)
O3	S1	C14	107.51(7)	C7	C6	C5	121.08(15)
C14	S1	C13	105.61(7)	C6	C7	C8	119.86(15)
O1	N1	C1	127.79(12)	C7	C8	C9	119.70(15)
O1	N1	C4	118.75(11)	C8	C9	C10	120.54(14)
C1	N1	C4	113.41(12)	C5	C10	C9	119.85(14)
N1	C1	C2	112.50(13)	C4	C13	S1	113.87(10)
N1	C1	C5	120.46(13)	C15	C14	S1	119.14(11)
C5	C1	C2	126.95(13)	C19	C14	S1	120.02(11)
C1	C2	C3	102.58(12)	C19	C14	C15	120.84(14)
C1	C2	C11	110.27(14)	C16	C15	C14	119.31(14)

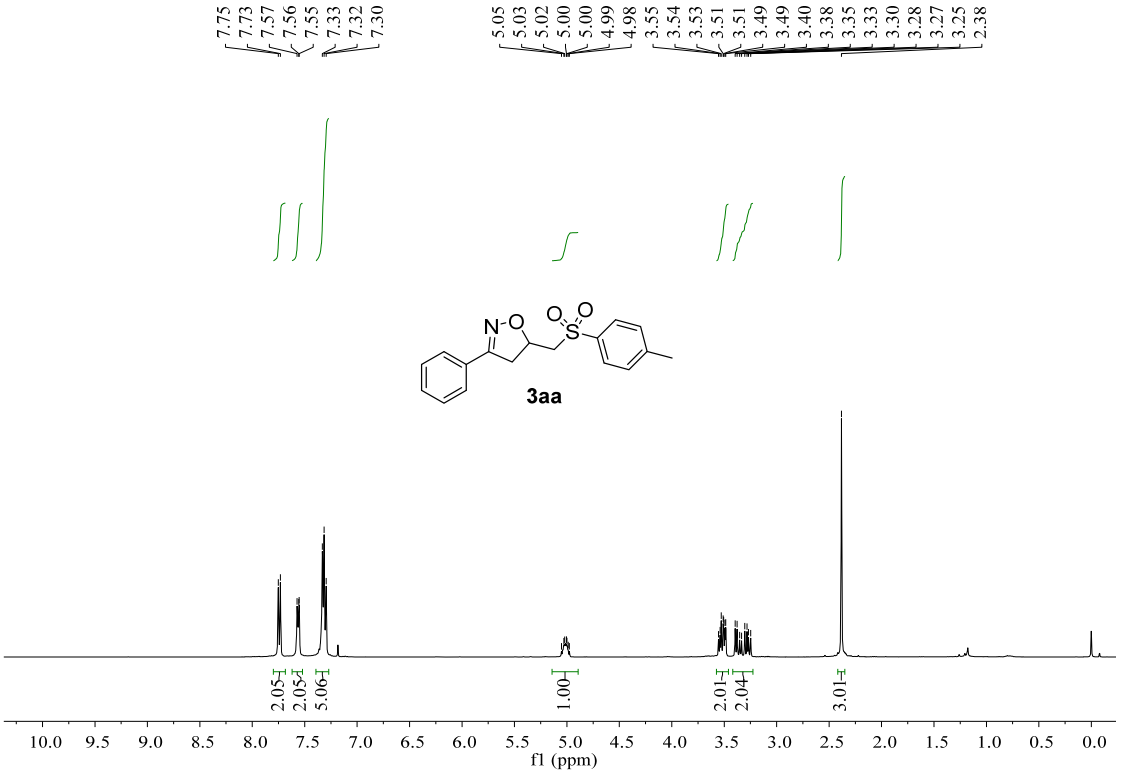
C1	C2	C12	110.86(13)	C15	C16	C17	120.90(14)
C11	C2	C3	110.39(14)	C16	C17	C18	118.70(14)
C12	C2	C3	112.02(15)	C16	C17	C20	120.30(14)
C12	C2	C11	110.48(15)	C18	C17	C20	120.99(14)
C4	C3	C2	107.05(12)	C19	C18	C17	121.15(14)
N1	C4	C3	103.06(11)	C18	C19	C14	119.09(14)
N1	C4	C13	107.85(11)				

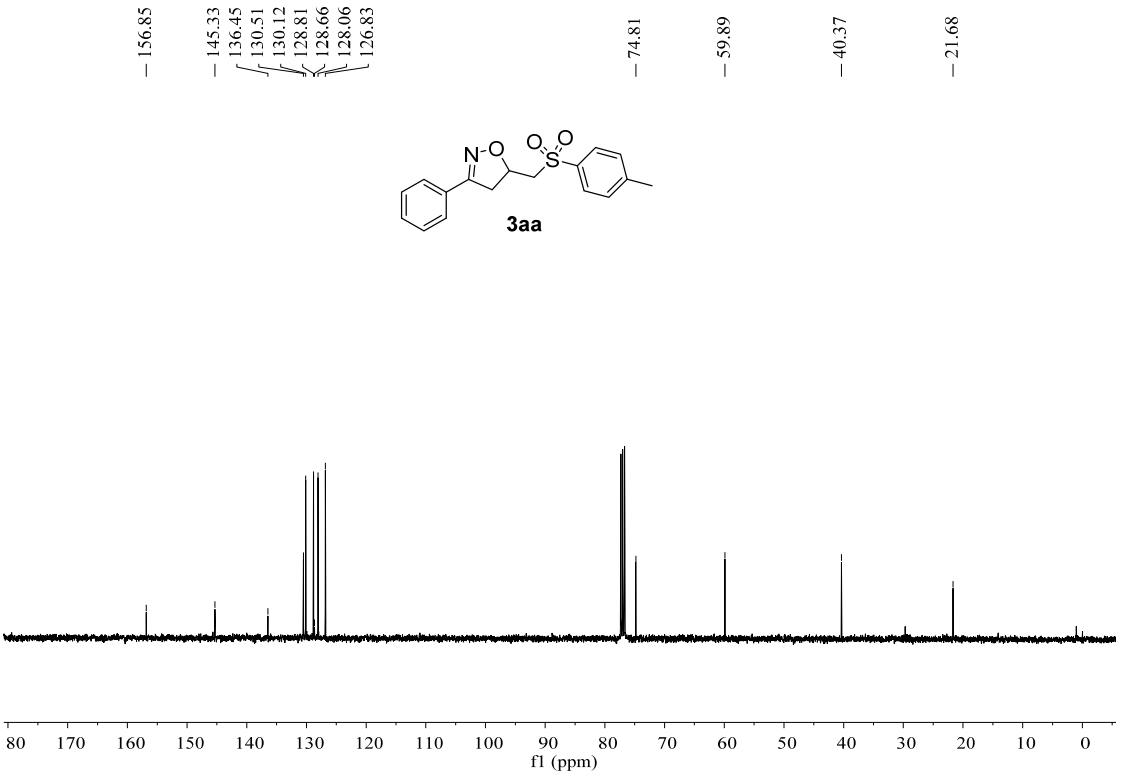
Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4ra.**

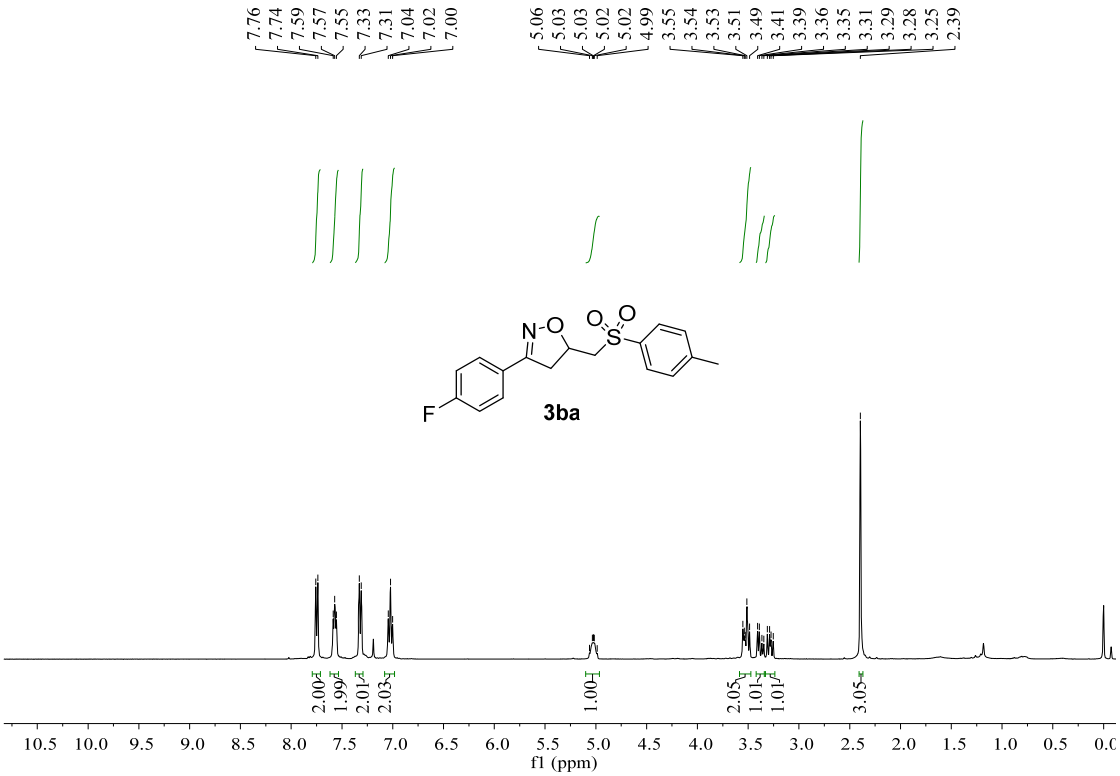
Atom	*x*	*y*	*z*	Ueq
H3A	0.489554	0.290064	0.662312	0.037
H3B	0.576591	0.354521	0.693515	0.037
H4	0.322472	0.312541	0.734864	0.024
H6	0.377851	0.571411	0.668504	0.038
H7	0.286264	0.673196	0.618253	0.041
H8	0.138816	0.662457	0.524670	0.032
H9	0.086039	0.549469	0.480985	0.030
H10	0.175722	0.446814	0.532250	0.029
H11A	0.544039	0.463792	0.549269	0.064
H11B	0.641398	0.400946	0.573145	0.064
H11C	0.600469	0.462109	0.627708	0.064
H12A	0.322754	0.315516	0.565843	0.067
H12B	0.468866	0.310570	0.534270	0.067
H12C	0.373663	0.374886	0.511747	0.067
H13A	0.360888	0.392766	0.832765	0.024
H13B	0.501821	0.411589	0.799860	0.024
H15	0.475022	0.174721	0.769477	0.030

H16	0.319330	0.082636	0.767254	0.032
H18	0.112307	0.180988	0.920922	0.030
H19	0.268720	0.272530	0.924878	0.028
H20A	0.116764	0.032760	0.800738	0.049
H20B	0.011157	0.083417	0.838553	0.049
H20C	0.107572	0.034461	0.884576	0.049

4. Copies of ^{1}H and ^{13}C NMR Spectra.



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7.00
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5.02
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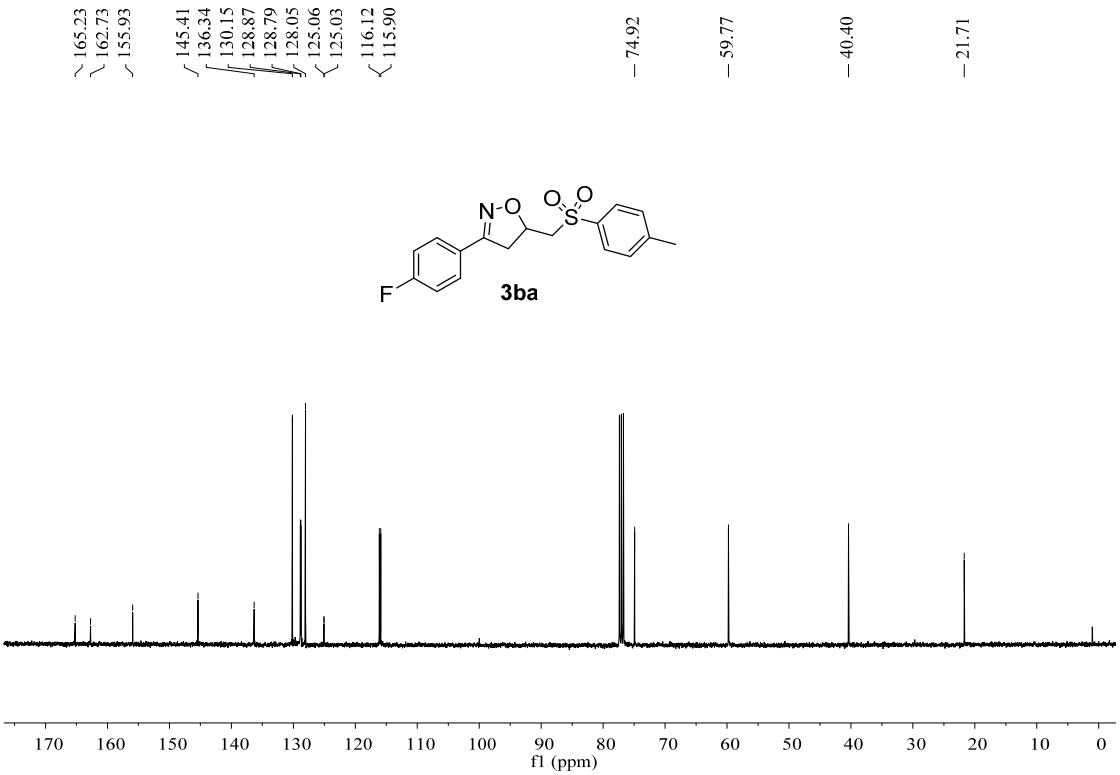
f1 (ppm)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155.93
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136.34
130.15
128.87
128.79
128.05
125.06
125.03
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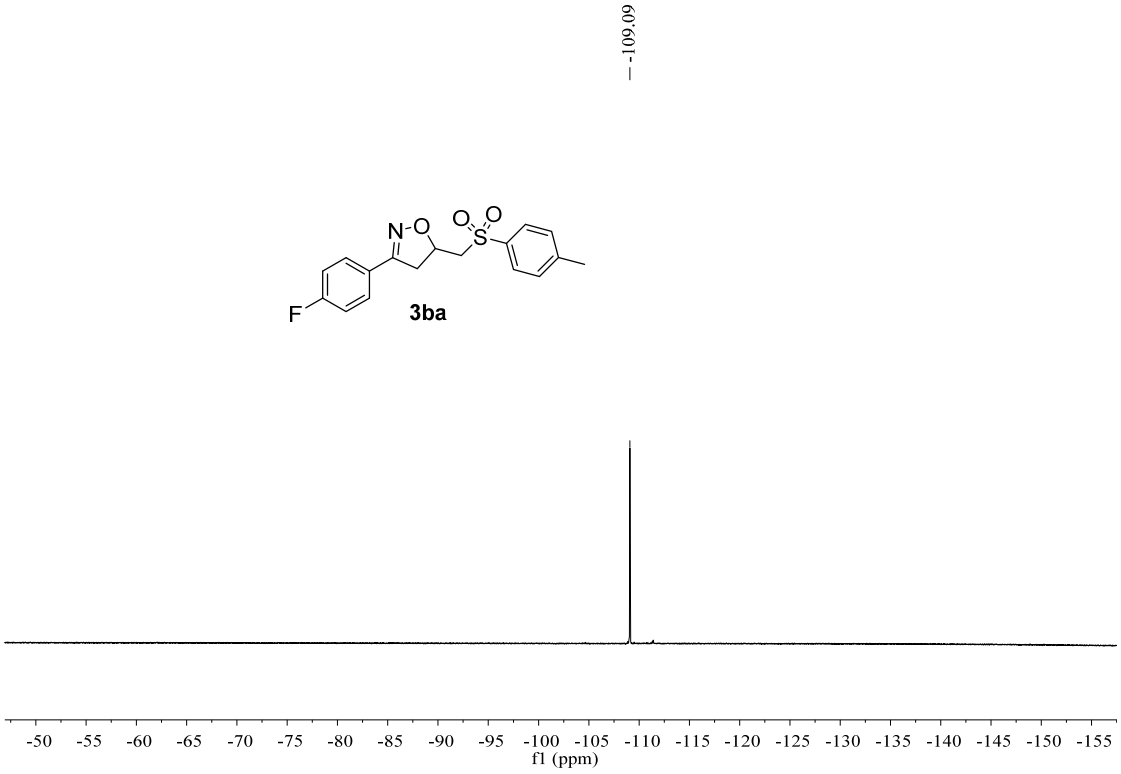
115.90
74.92
59.77
40.40
21.71
N
O
O
O
S
F
3ba
f1 (ppm)


-109.09
3ba
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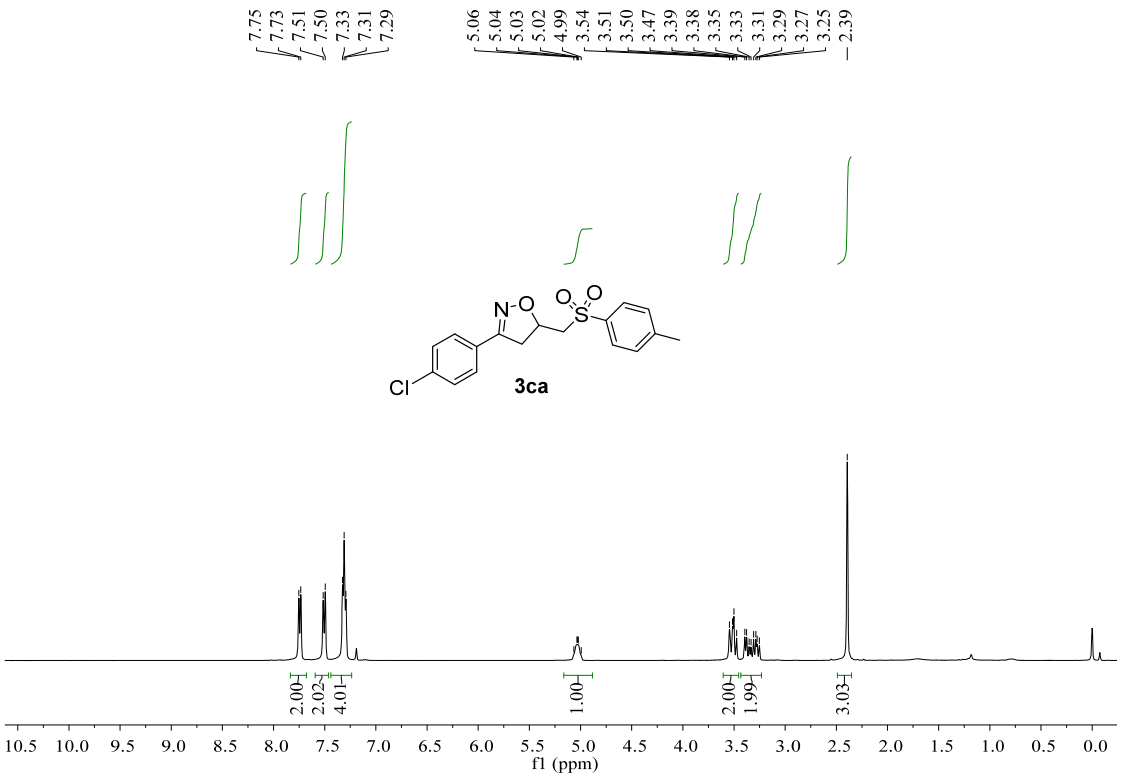
f1 (ppm)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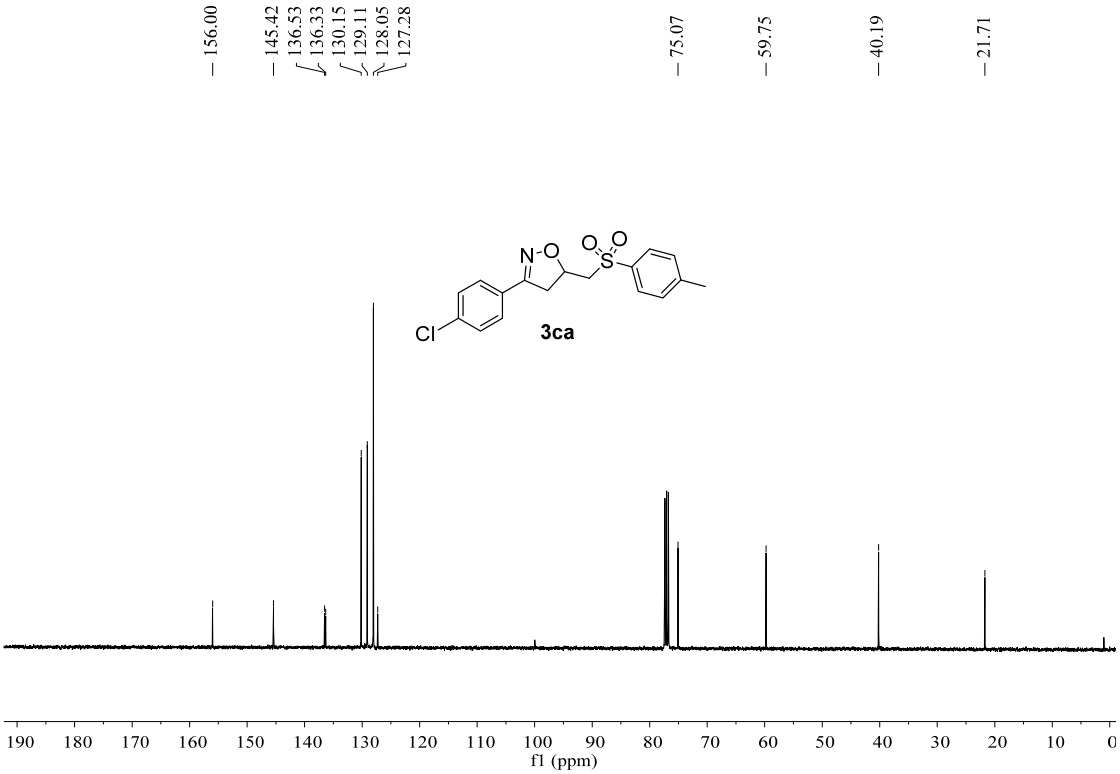
7.29
5.06
5.04
5.03
5.02
4.99
3.54
3.51
3.50
3.47
3.39
3.38
3.35
3.33
3.31
3.29
3.27
3.25
2.39
3ca
2.00
2.02
4.01
1.00
2.00
1.99
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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21.71
Cl
3ca
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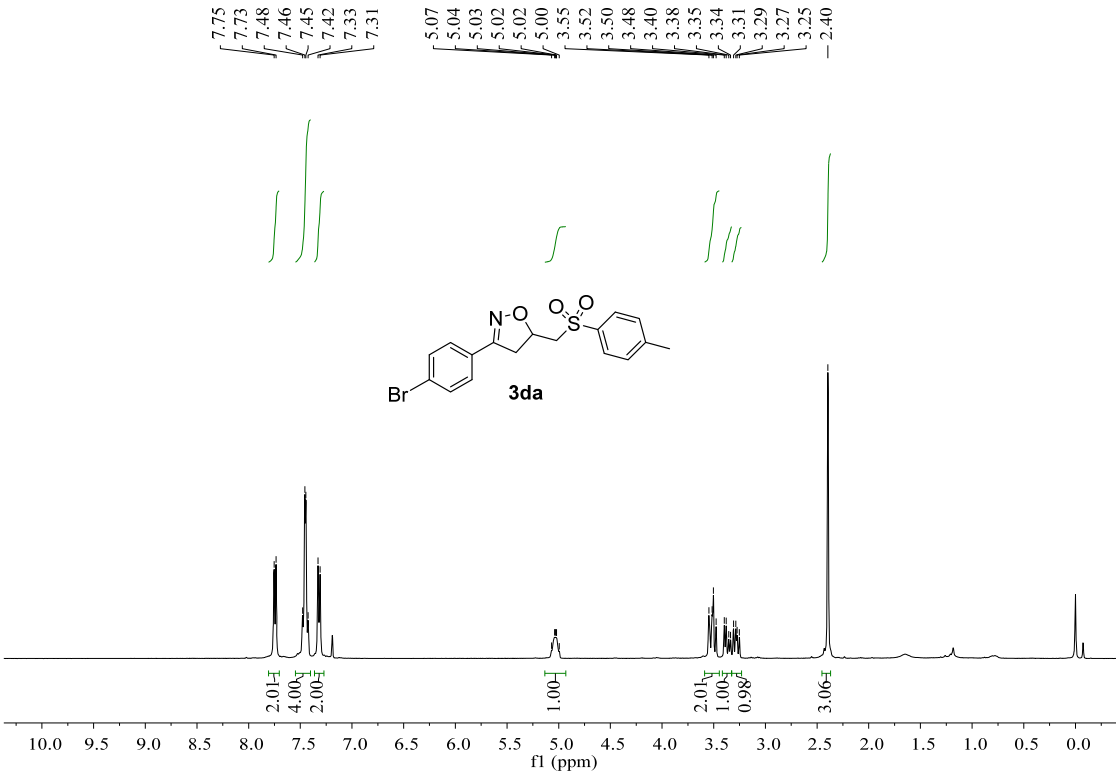
f1 (ppm)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7.31
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5.04
5.03
5.02
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5.00
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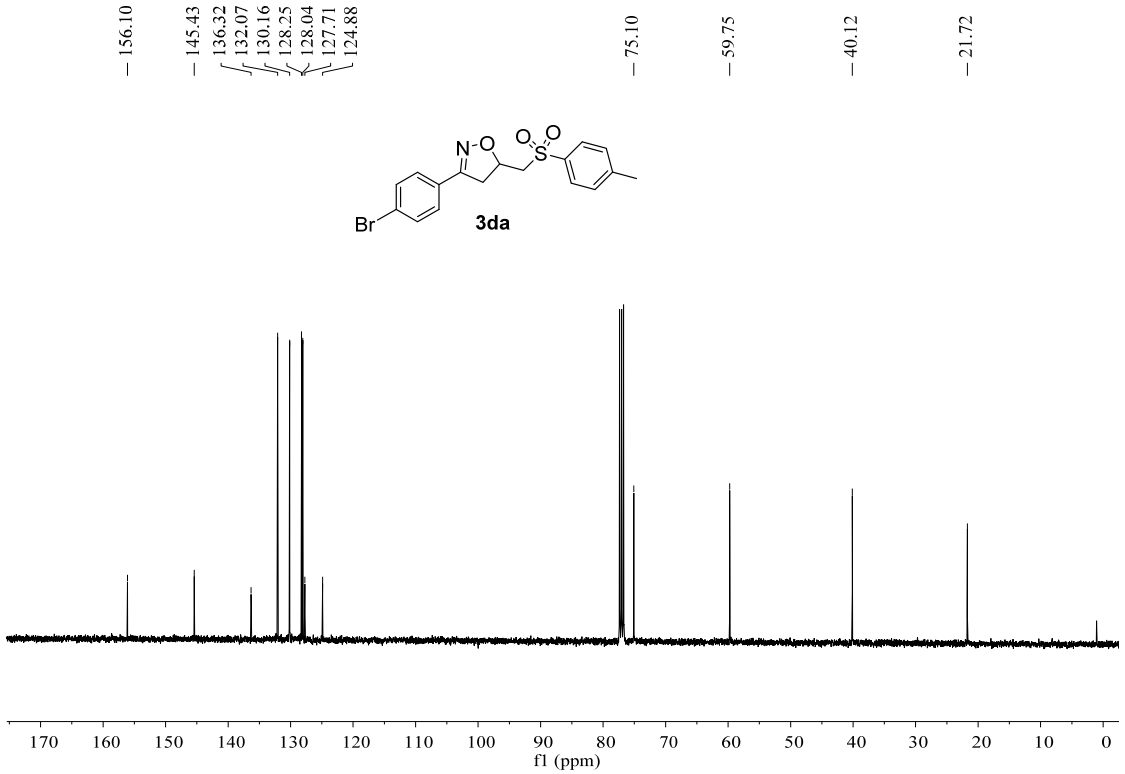
3.52
3.50
3.48
3.40
3.38
3.35
3.34
3.31
3.29
3.27
3.25
2.40
Br
3da
2.01
4.00
2.00
1.00
2.01
1.00
0.98
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.71
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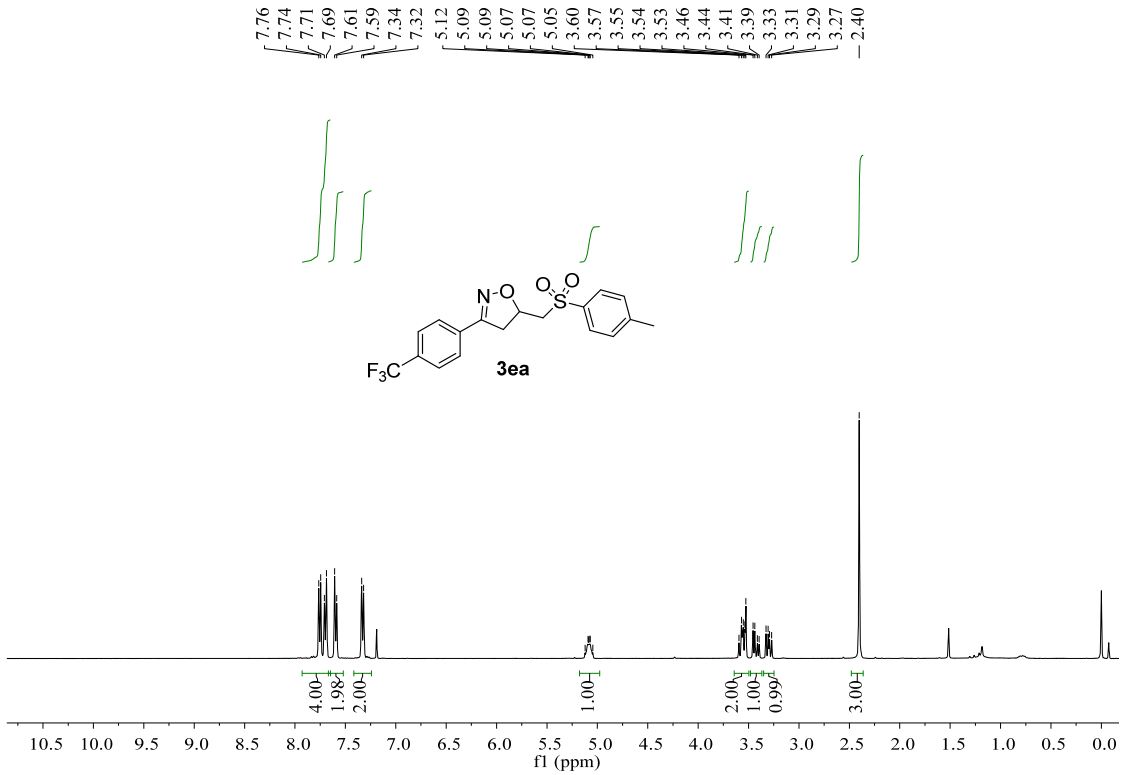
40.12
21.72
Br
3da
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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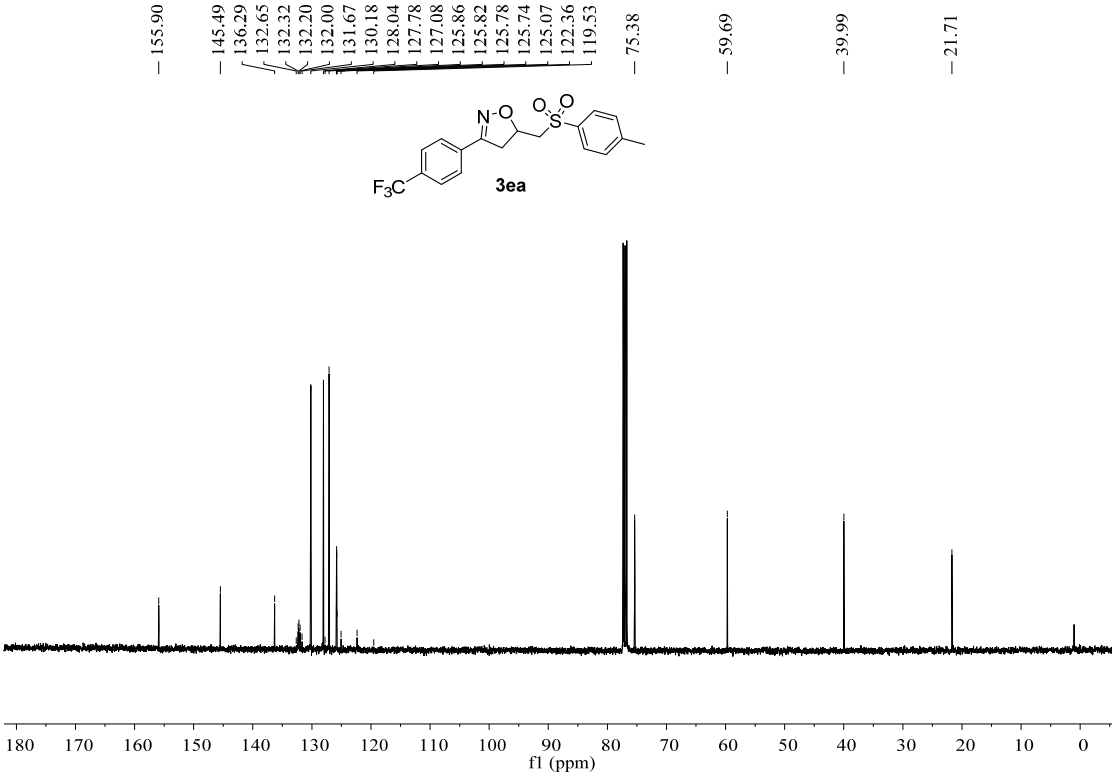
7.32
5.12
5.09
5.09
5.07
5.07
5.05
3.60
3.57
3.55
3.54
3.53
3.46
3.44
3.41
3.39
3.33
3.31
3.29
3.27
2.40
F3C
3ea
4.00
1.98
2.00
1.00
2.00
1.00
0.99
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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131.67
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128.04
127.78
127.08
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125.82
125.78
125.74
125.07
122.36
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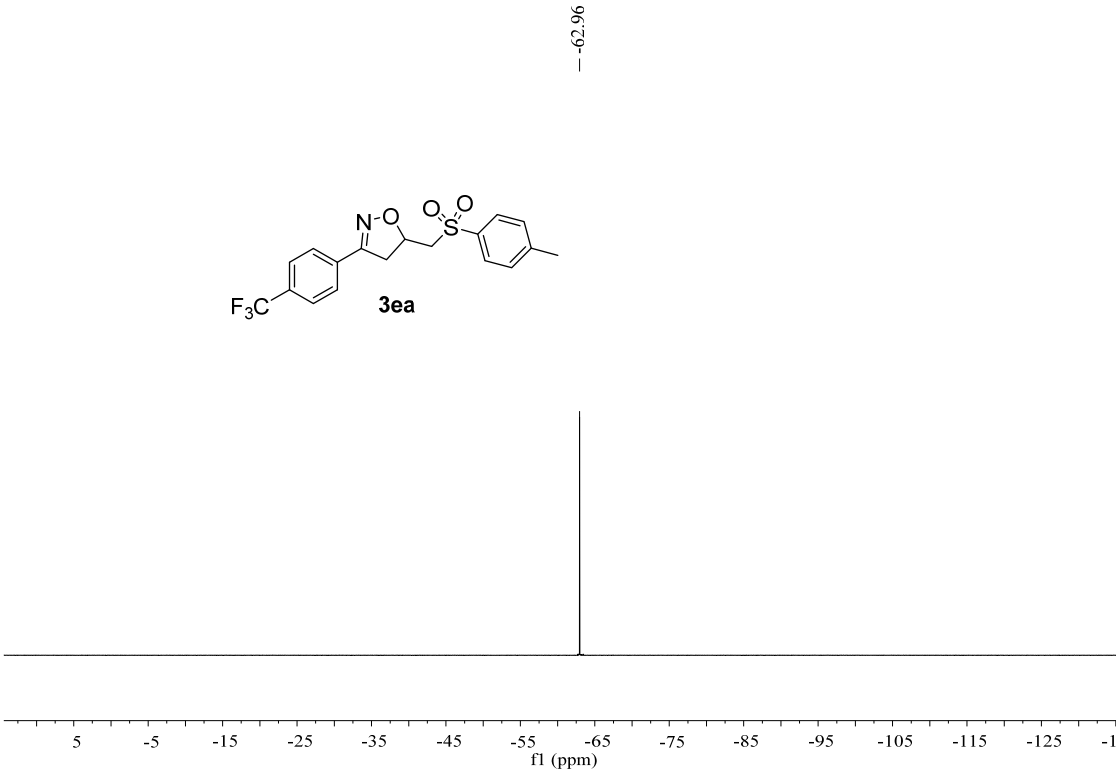
59.69
39.99
21.71
3ea
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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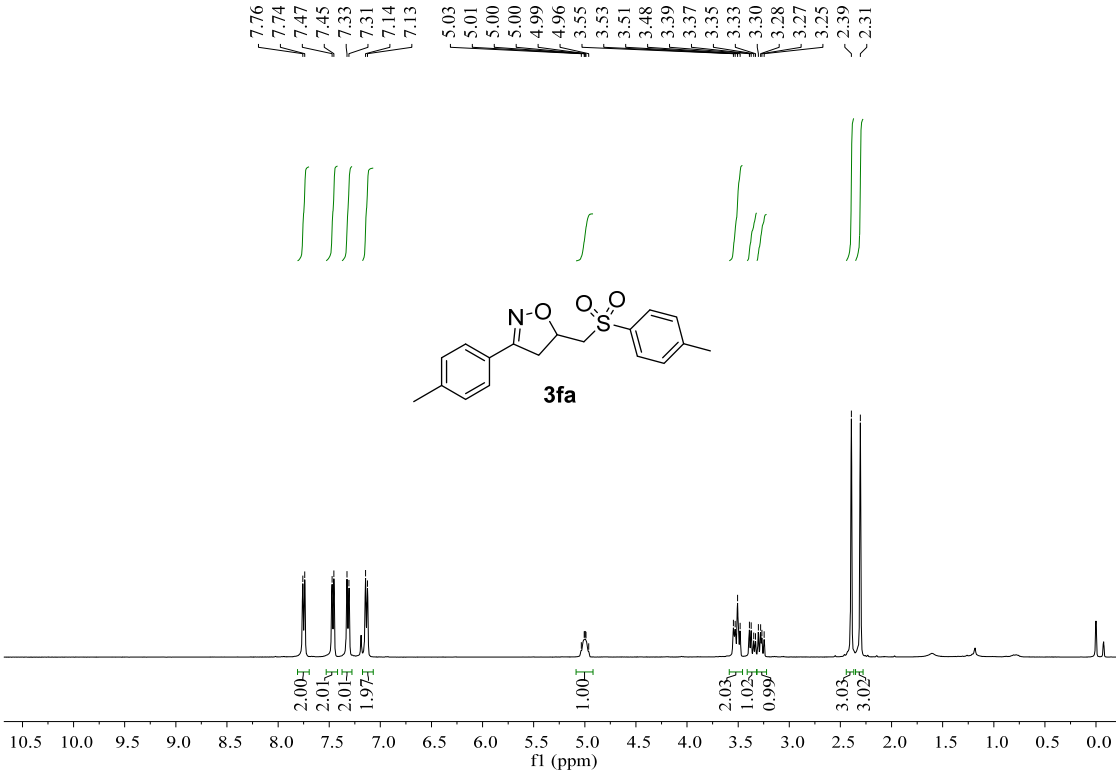
3ea
5 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95 -105 -115 -125 -1
f1 (ppm)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7.31
7.14
7.13
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5.00
5.00
4.99
4.96
3.55
3.53
3.51
3.48
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3.37
3.35
3.33
3.30
3.28
3.27
3.25
2.39
2.31
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2.01
1.97
1.00
2.03
1.02
0.99
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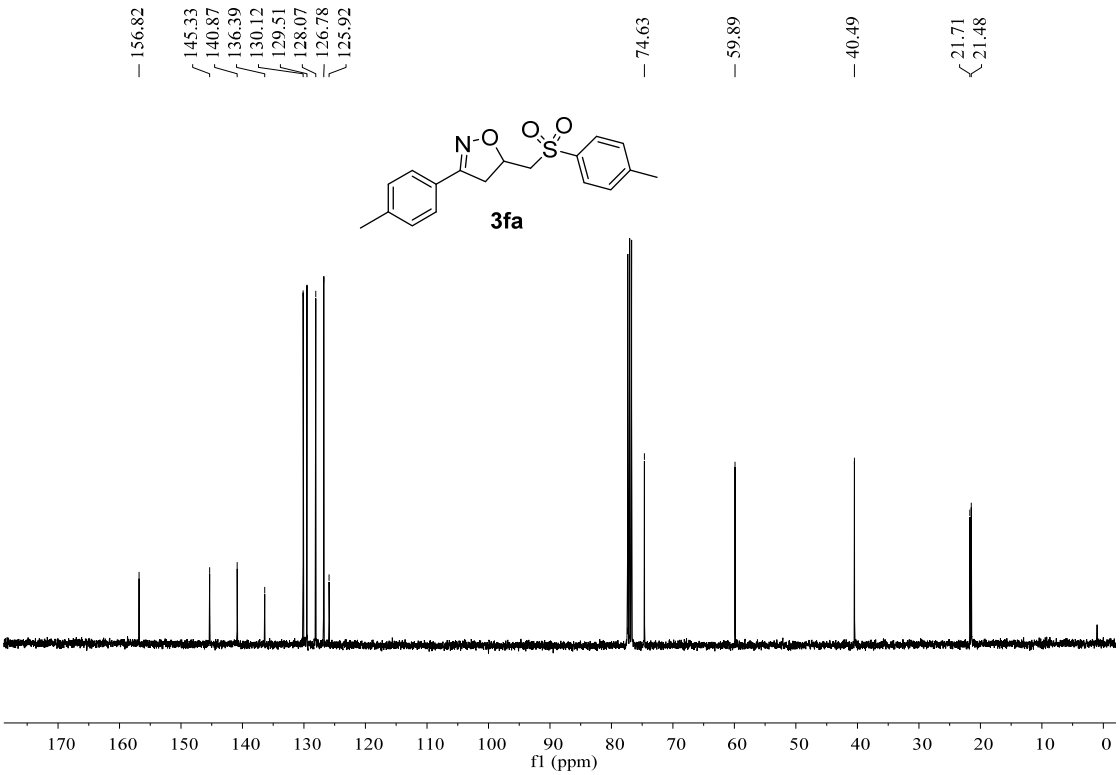
3.02
f1 (ppm)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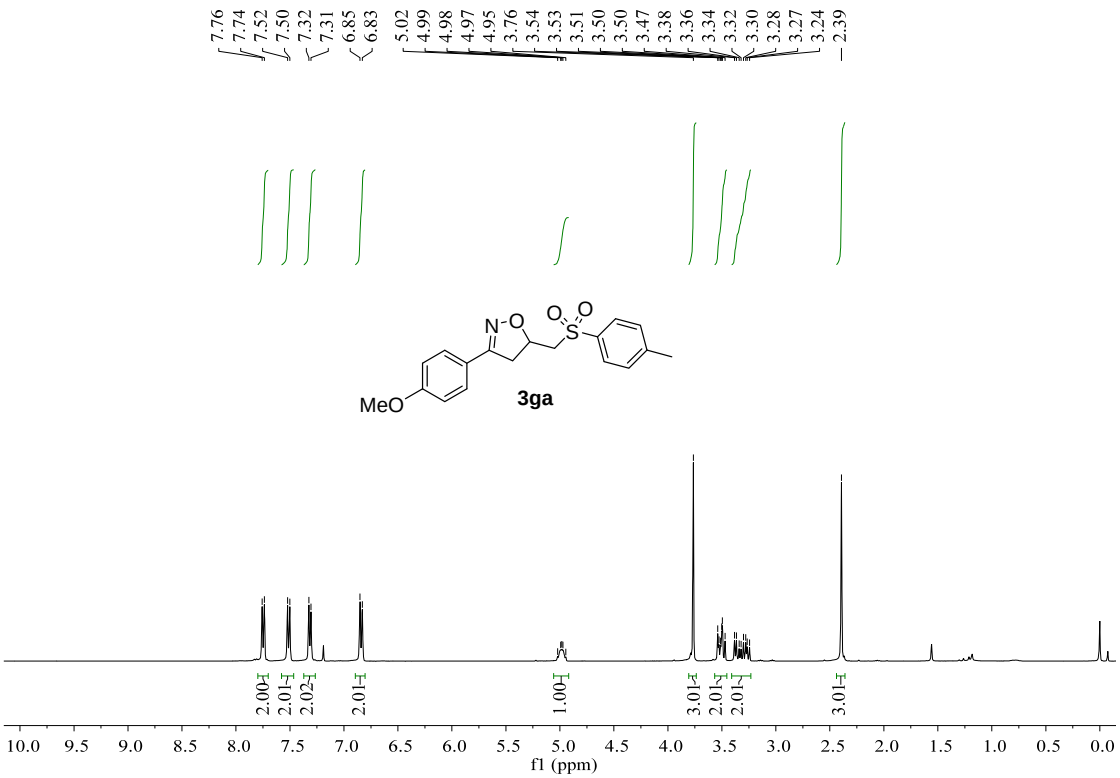
74.63
59.89
40.49
21.71
21.48
3fa
f1 (ppm)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4.98
4.97
4.95
3.76
3.54
3.53
3.51
3.50
3.50
3.47
3.38
3.36
3.34
3.32
3.30
3.28
3.27
3.24
2.39
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1.00
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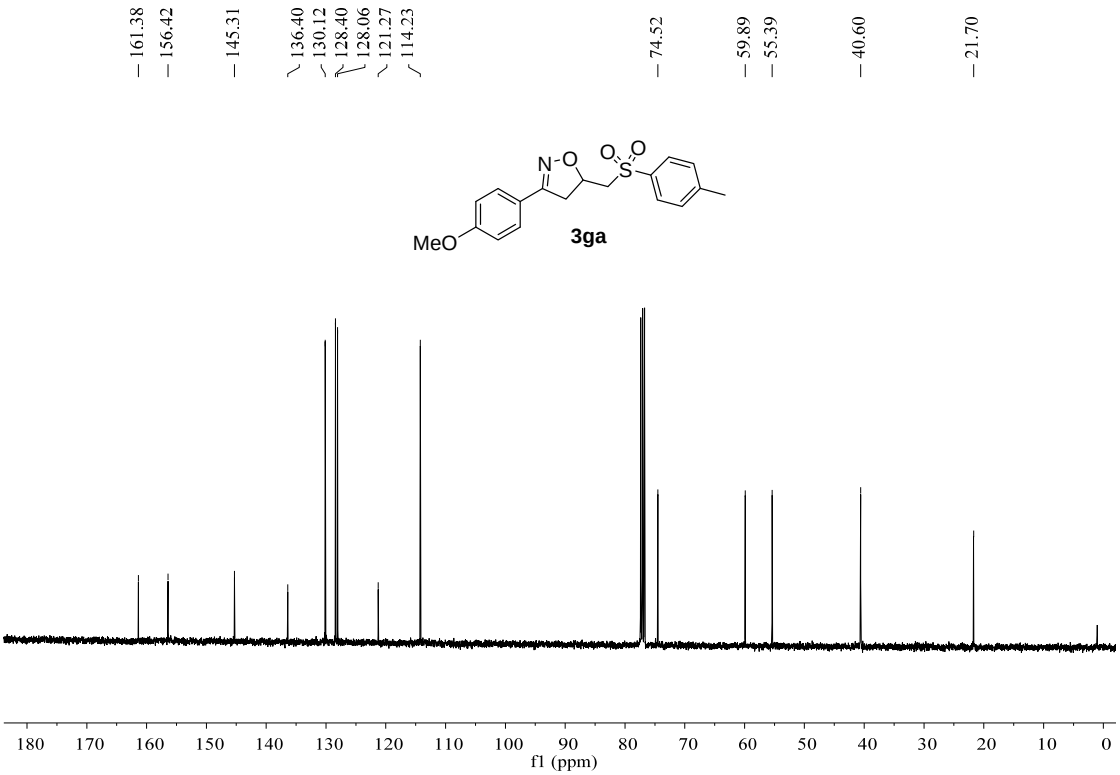
2.01
2.01
3.01
f1 (ppm)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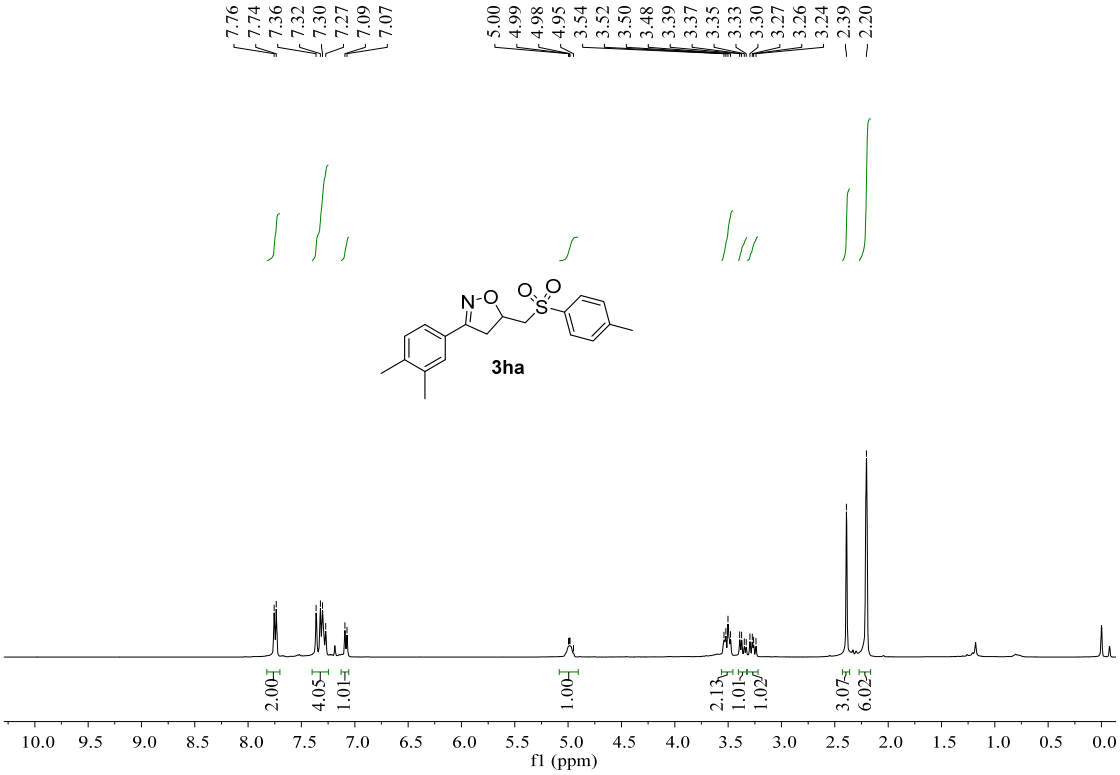
MeO
3ga
f1 (ppm)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3.52
3.50
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3.39
3.37
3.35
3.33
3.30
3.27
3.26
3.24
2.39
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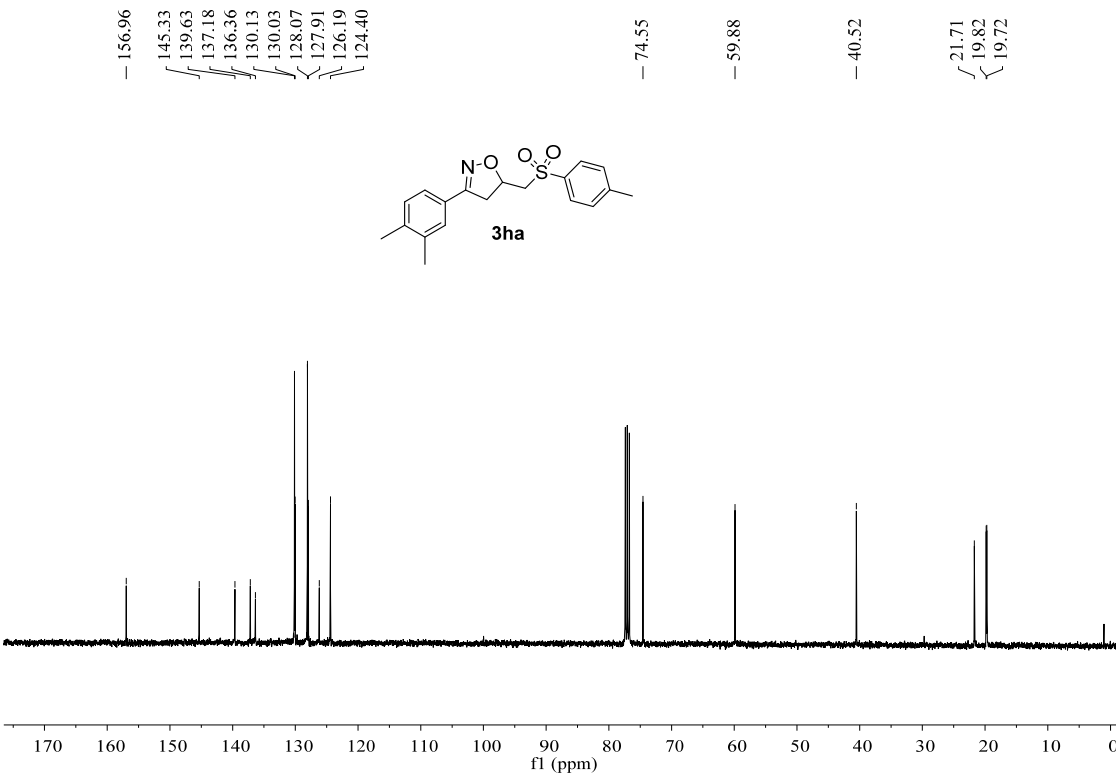
1.02
3.07
6.02
f1 (ppm)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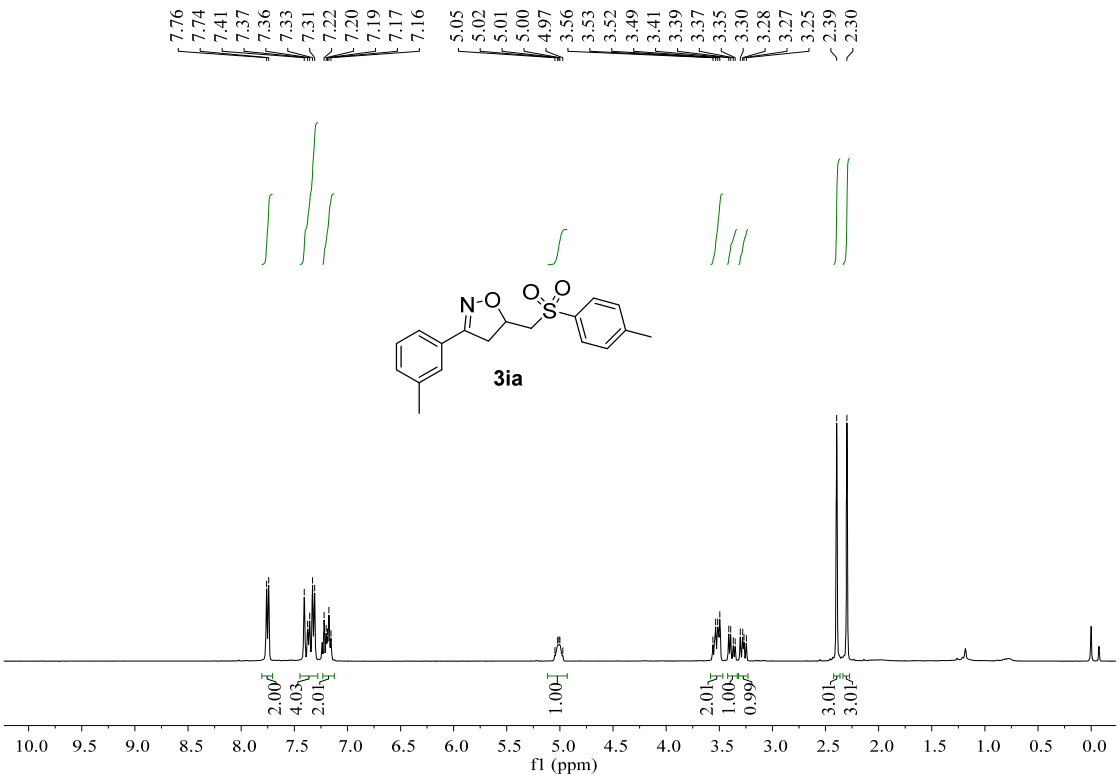
40.52
21.71
19.82
19.72
3ha
f1 (ppm)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5.02
5.01
5.00
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3.28
3.27
3.25
2.39
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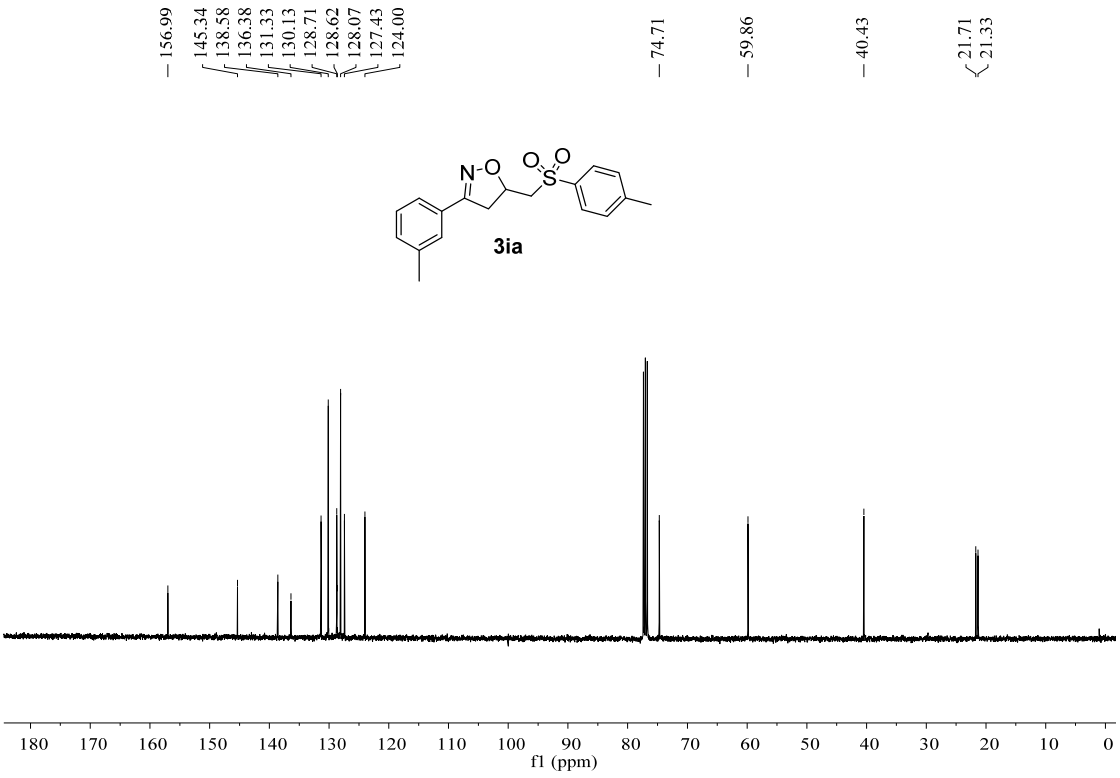
f1 (ppm)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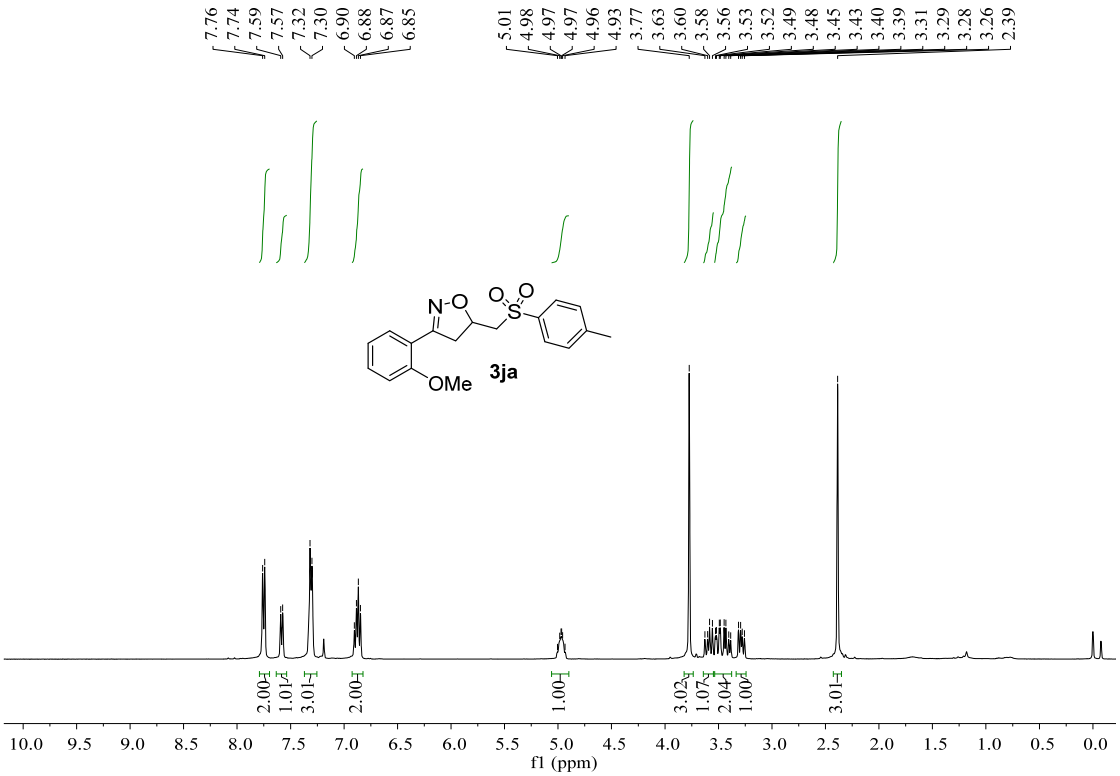
21.71
21.33
3ia
f1 (ppm)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3.28
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2.39
N
O
O
O
S
OMe
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3.01
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3.02
1.07
2.04
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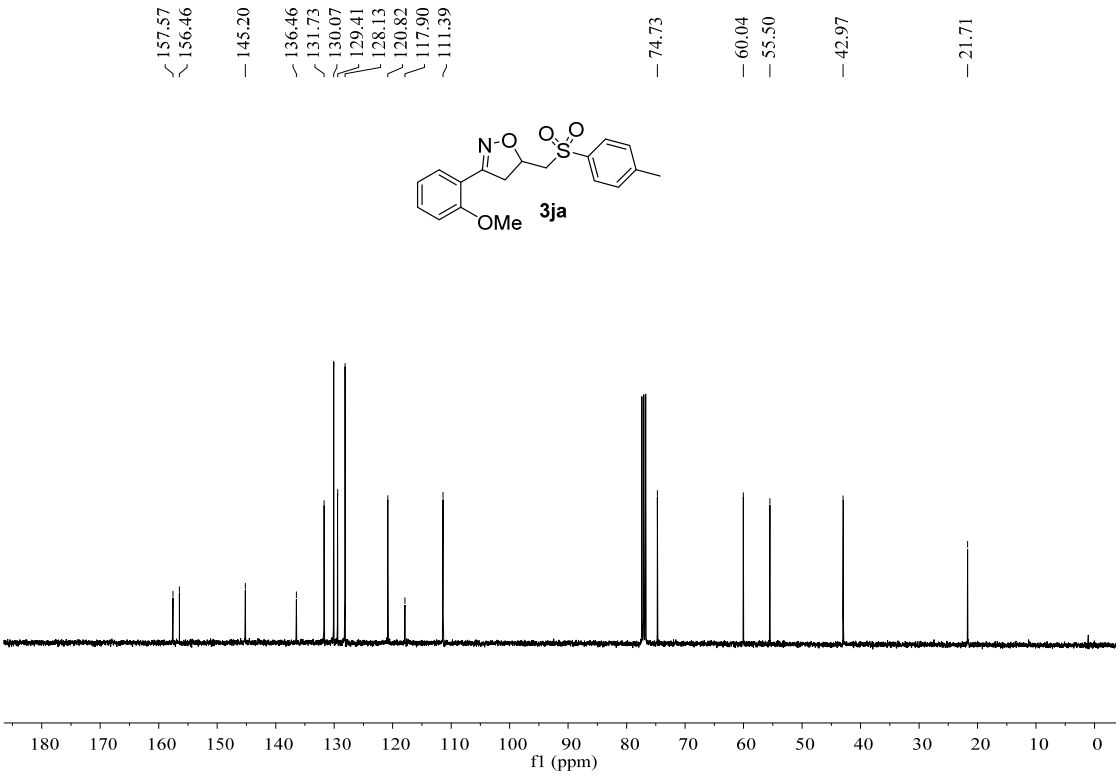
3.01
f1 (ppm)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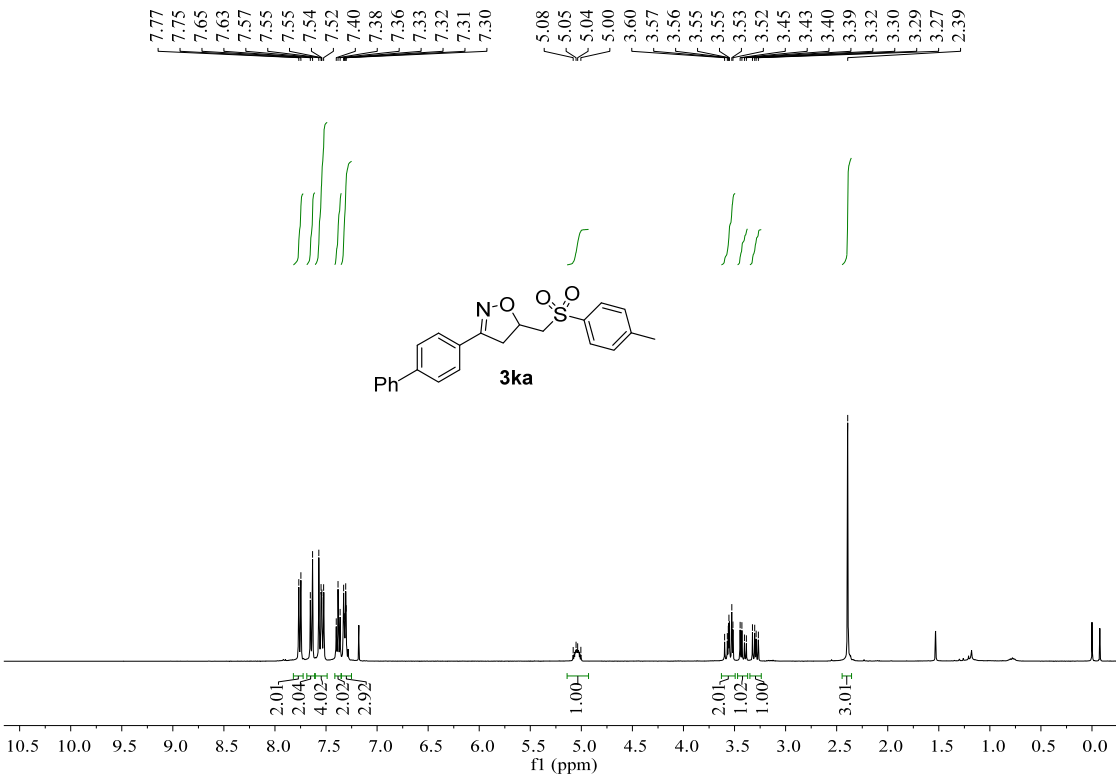
21.71
N
O
O
O
S
OMe
3ja
f1 (ppm)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7.31
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5.05
5.04
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3.29
3.27
2.39
N
O
O
O
S
Ph
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2.04
4.02
2.02
2.92
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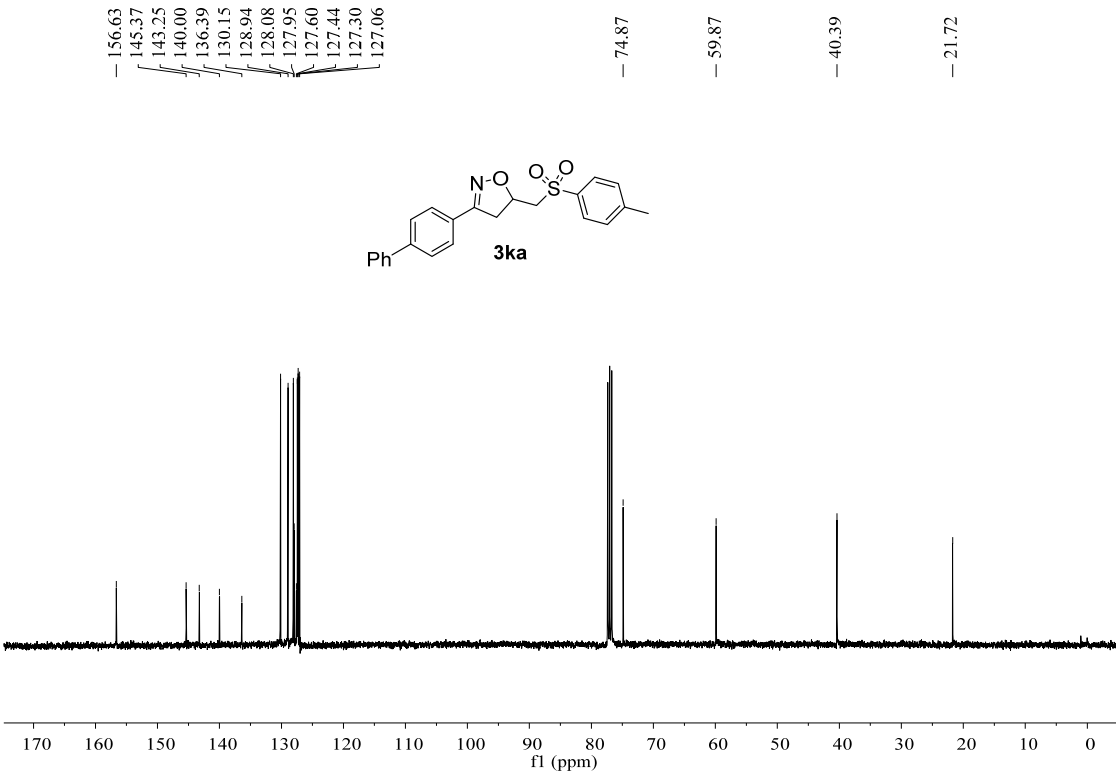
2.01
1.02
1.00
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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74.87
59.87
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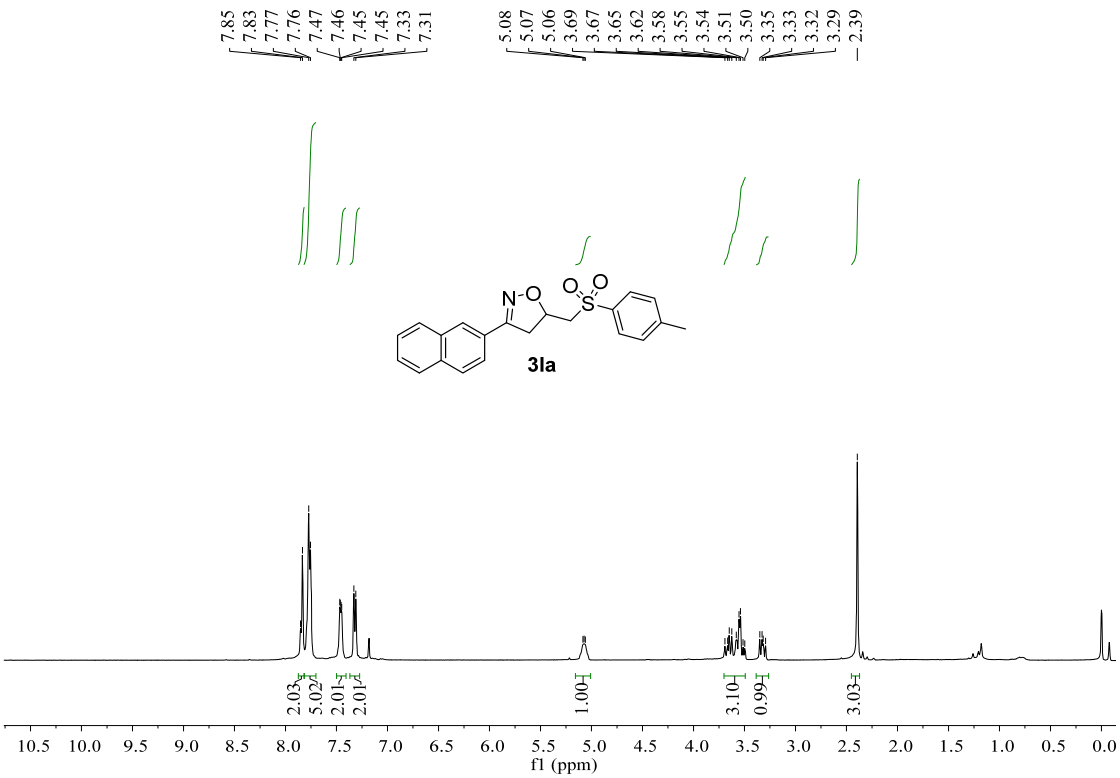
N
O
O
O
S
Ph
3ka
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.32
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2.01
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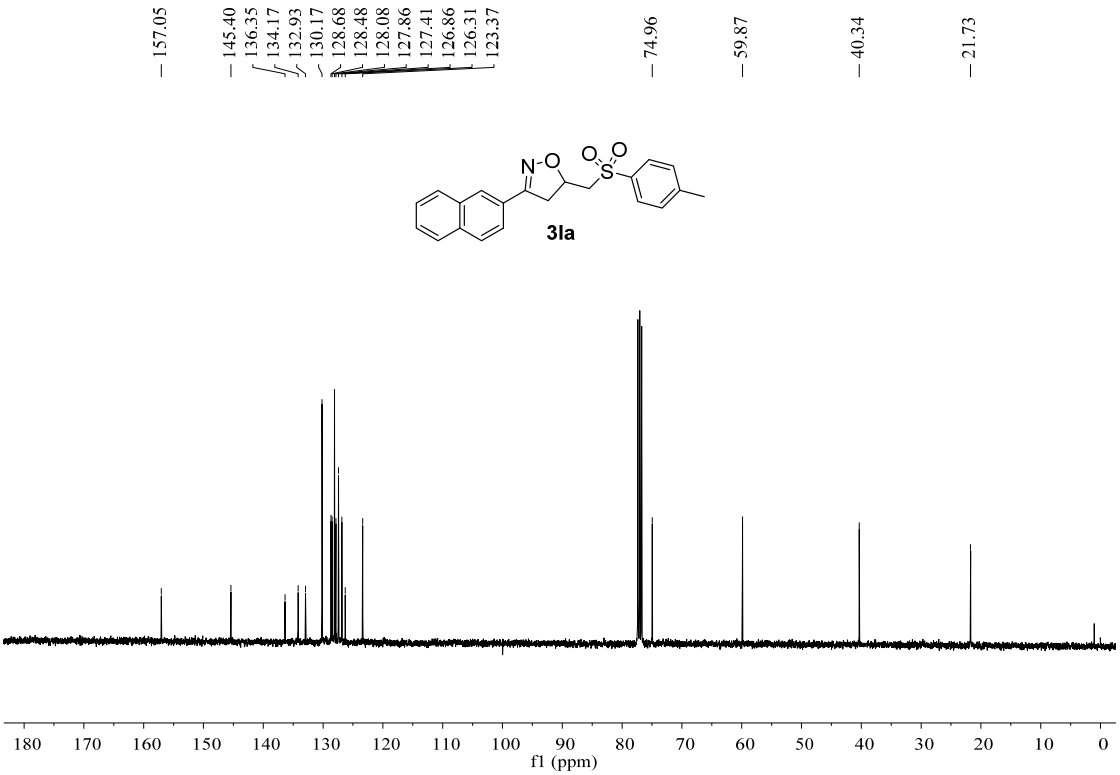
3.03
f1 (ppm)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59.87
40.34
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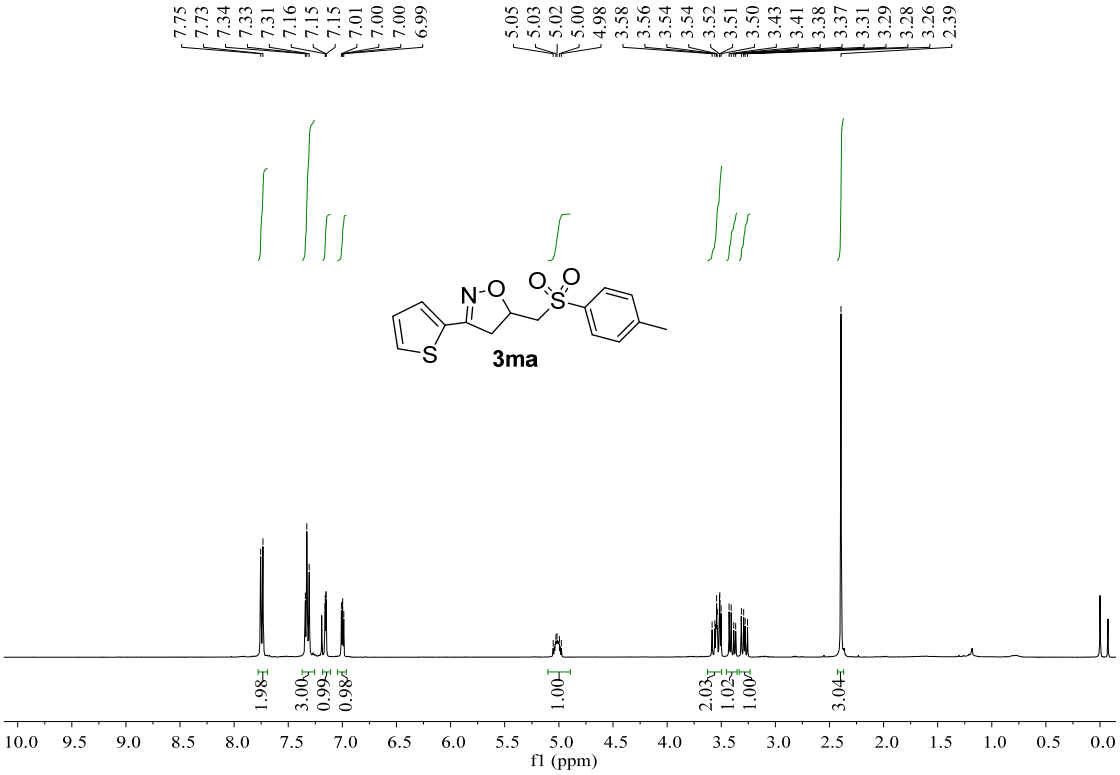
3la
f1 (ppm)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3.28
3.26
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1.02
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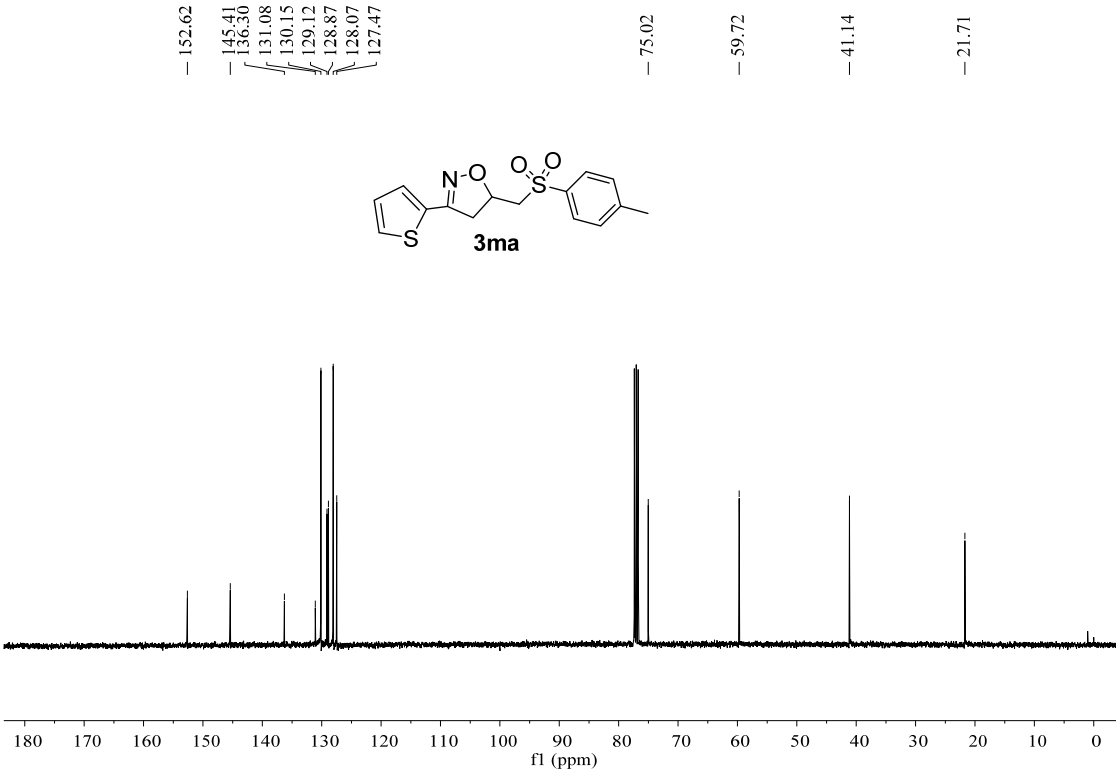
3.04
f1 (ppm)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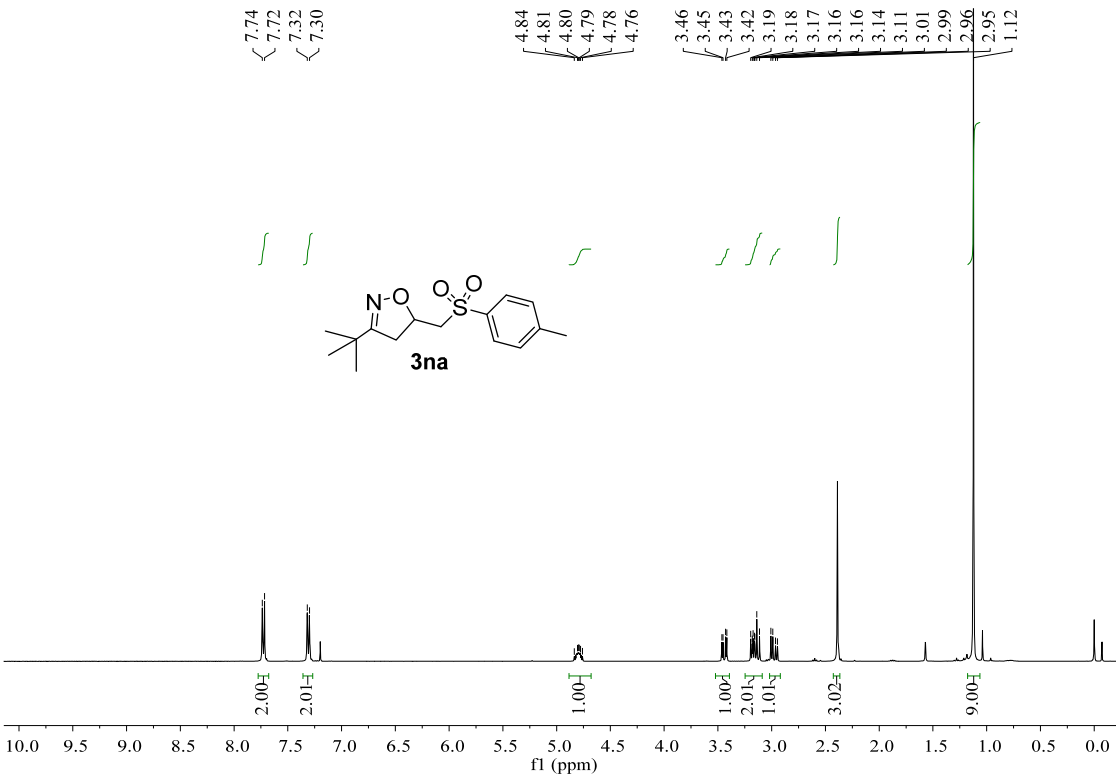
75.02
59.72
41.14
21.71
3ma
f1 (ppm)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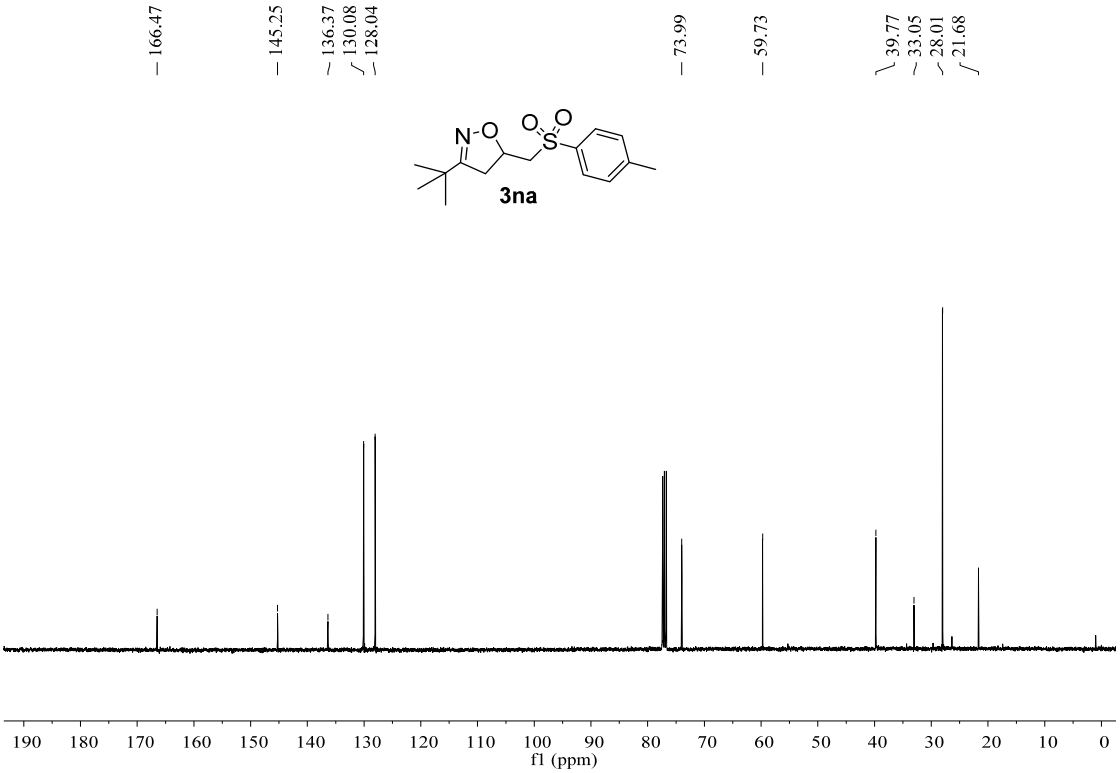
9.00
f1 (ppm)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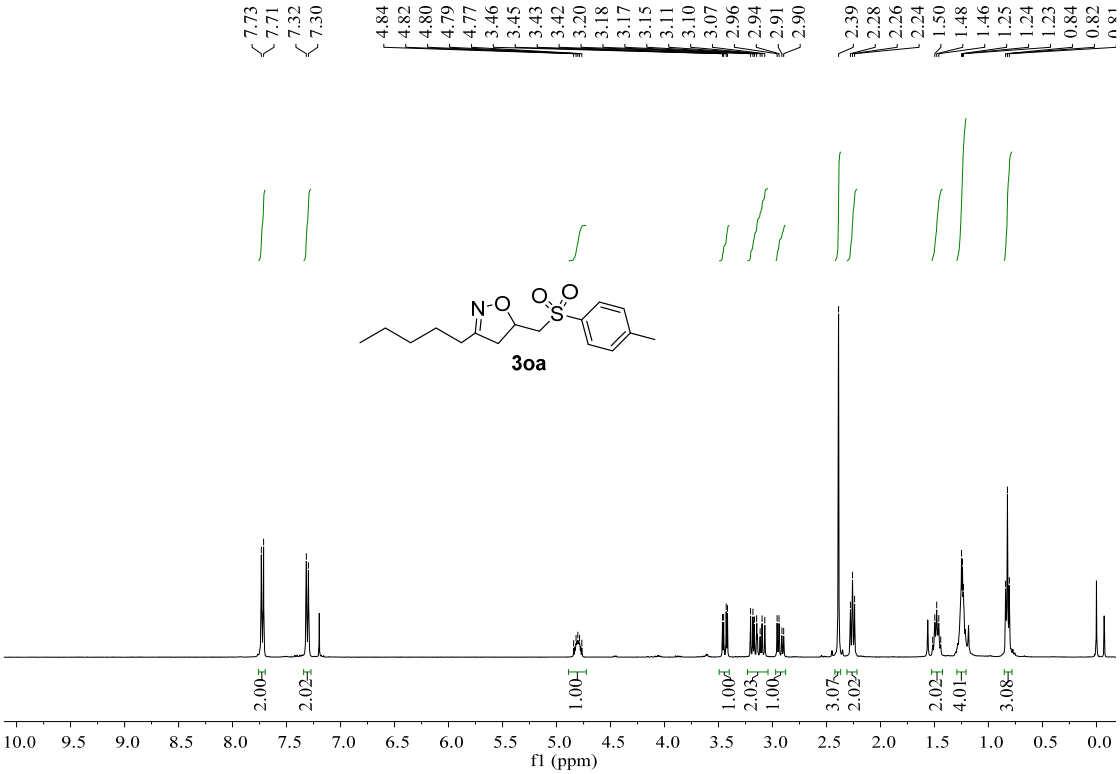
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7.71
7.32
7.30
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4.82
4.80
4.79
4.77
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3.45
3.43
3.42
3.20
3.18
3.17
3.15
3.11
3.10
3.07
2.96
2.94
2.91
2.90
2.39
2.28
2.26
2.24
1.50
1.48
1.46
1.25
1.24
1.23
0.84
0.82
3oa
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2.03
1.00
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2.02
2.02
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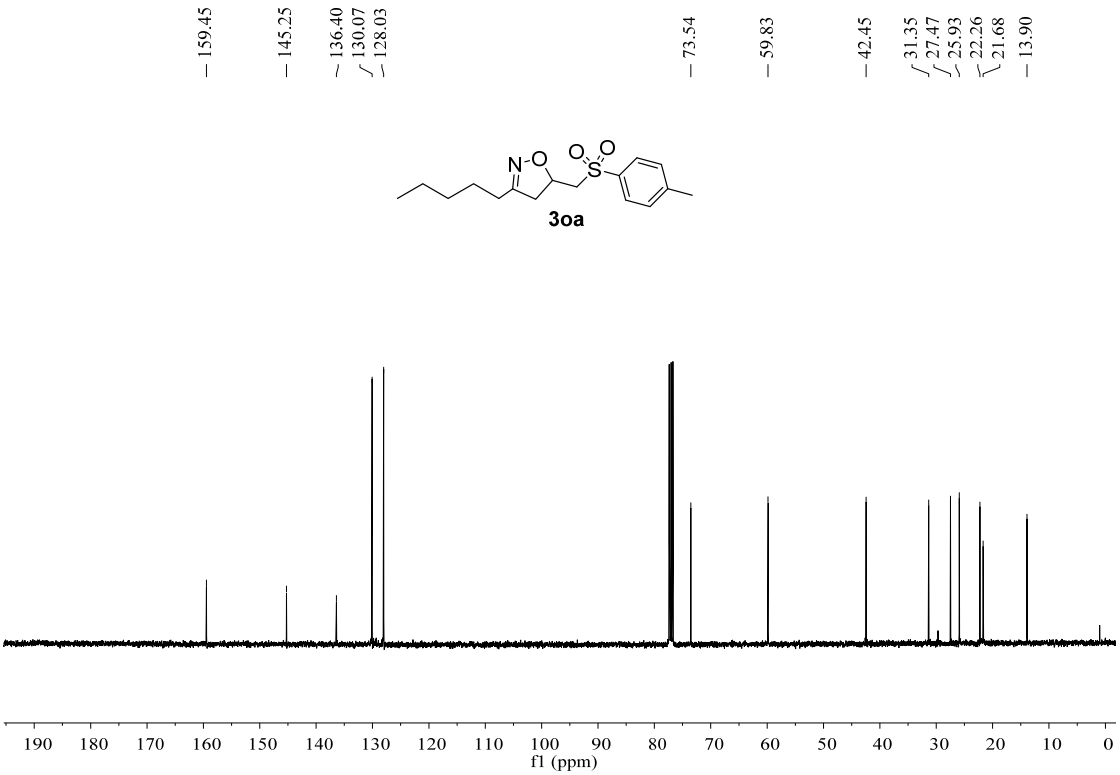
3.08
f1 (ppm)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22.26
21.68
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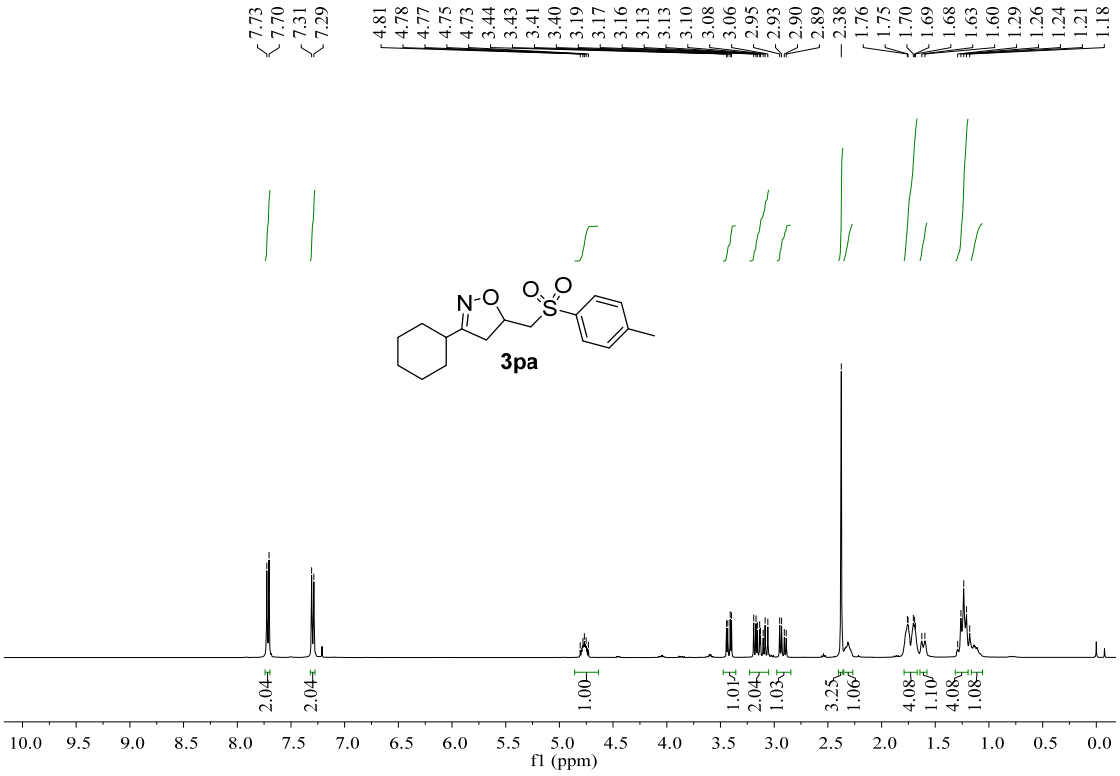
f1 (ppm)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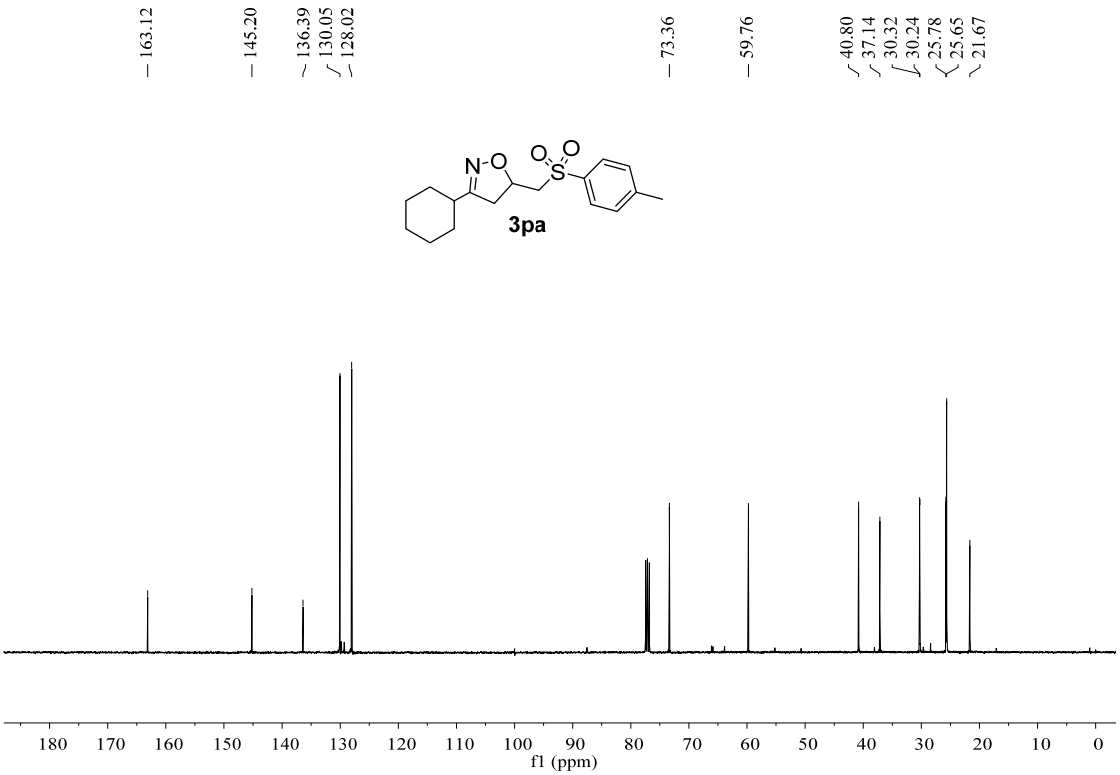
3.41
3.40
3.19
3.17
3.16
3.13
3.13
3.10
3.08
3.06
2.95
2.93
2.90
2.89
2.38
1.76
1.75
1.70
1.69
1.68
1.63
1.60
1.29
1.26
1.24
1.21
1.18
3pa
2.04
2.04
1.00
1.01
2.04
1.03
3.25
1.06
4.08
1.10
4.08
1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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40.80
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21.67
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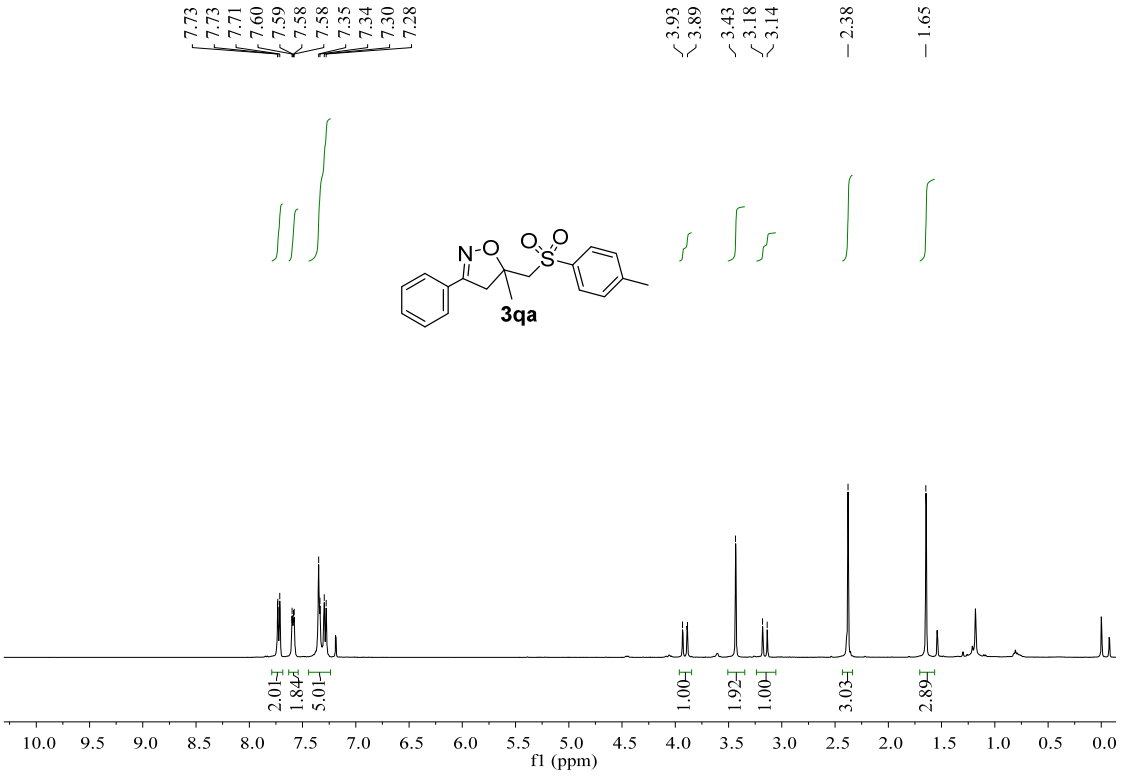
f1 (ppm)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3.89
3.43
3.18
3.14
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5.01
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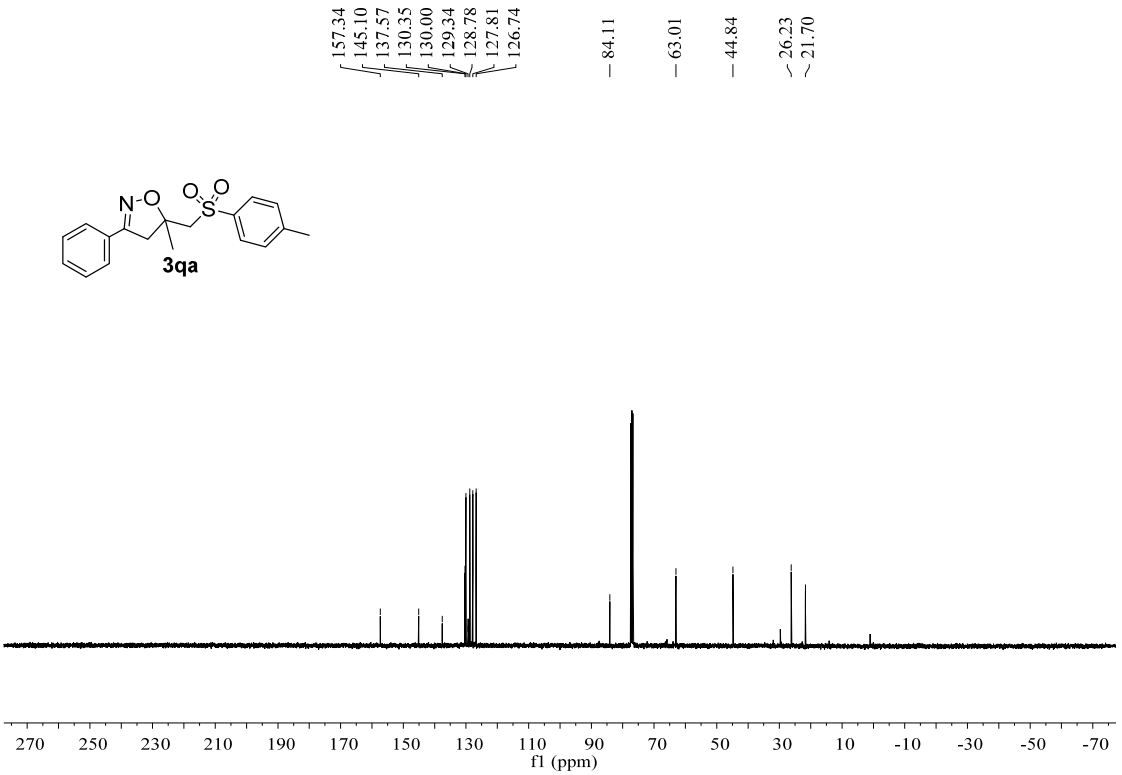
1.00
3.03
2.89
f1 (ppm)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44.84
26.23
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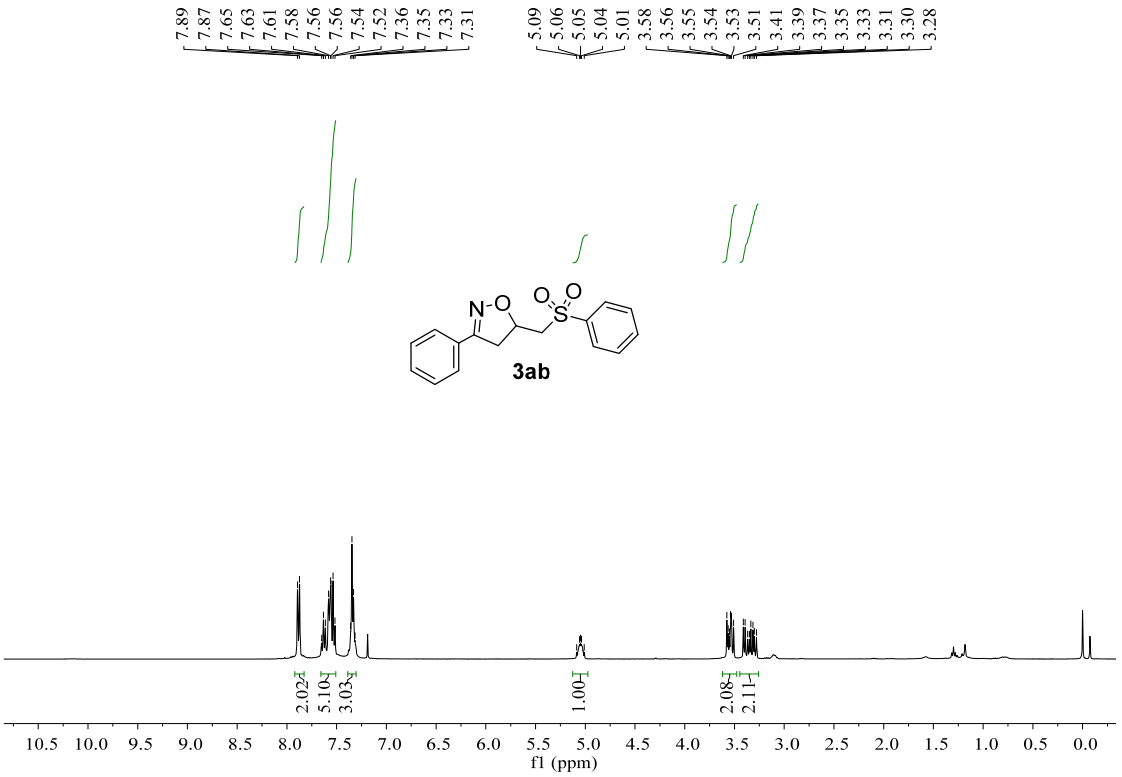
3qa
f1 (ppm)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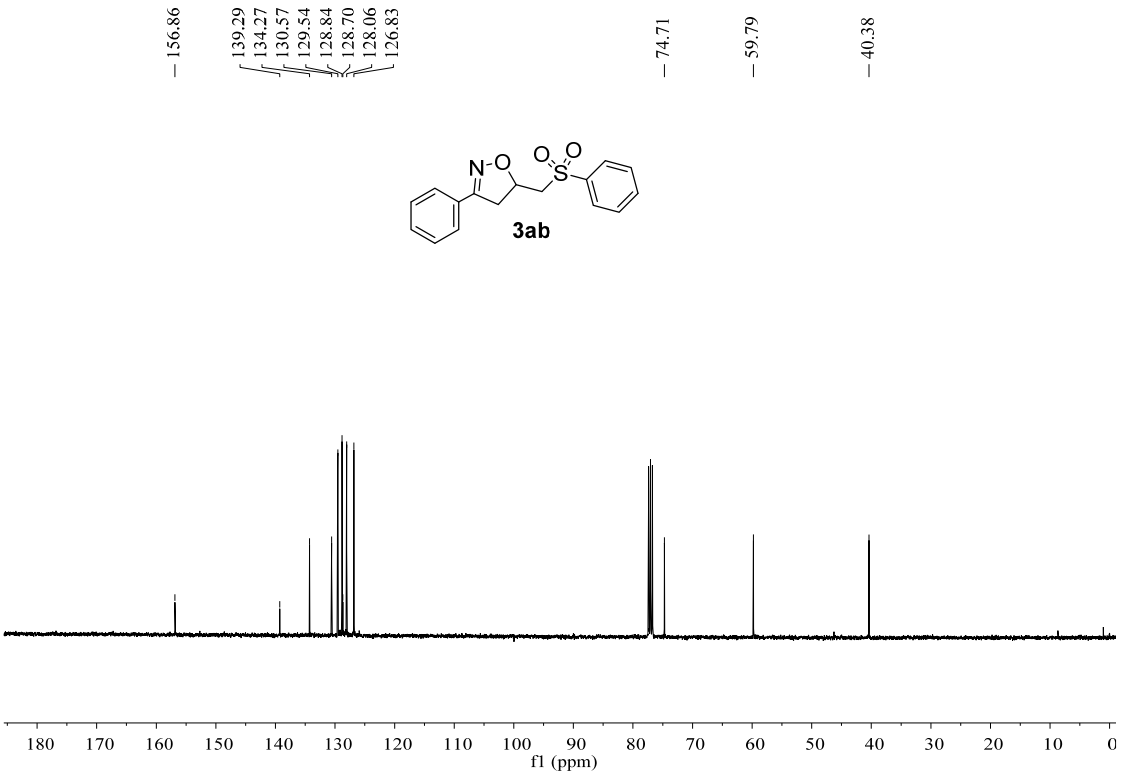
7.35
7.33
7.31
5.09
5.06
5.05
5.04
5.01
3.58
3.56
3.55
3.54
3.53
3.51
3.41
3.39
3.37
3.35
3.33
3.31
3.30
3.28
3ab
2.02
5.10
3.03
1.00
2.08
2.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.06
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74.71
59.79
40.38
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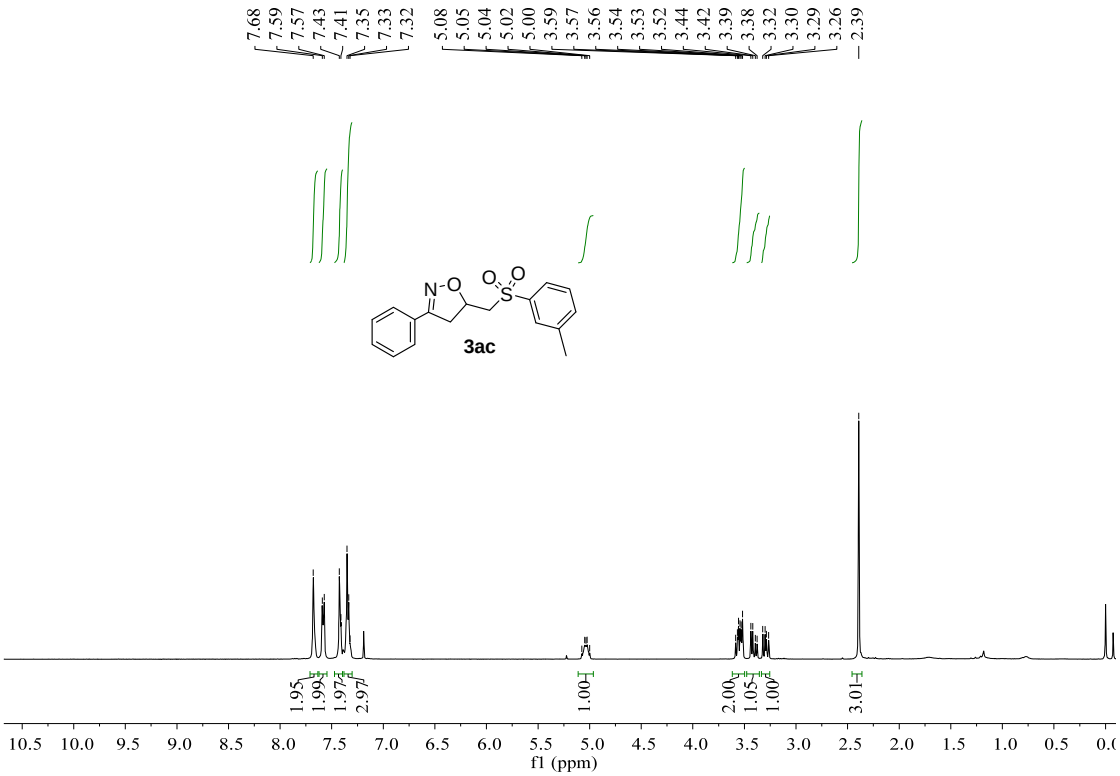
f1 (ppm)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7.57
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7.41
7.35
7.33
7.32
5.08
5.05
5.04
5.02
5.00
3.59
3.57
3.56
3.54
3.53
3.52
3.44
3.42
3.39
3.38
3.32
3.30
3.29
3.26
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3ac
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1.99
1.97
2.97
1.00
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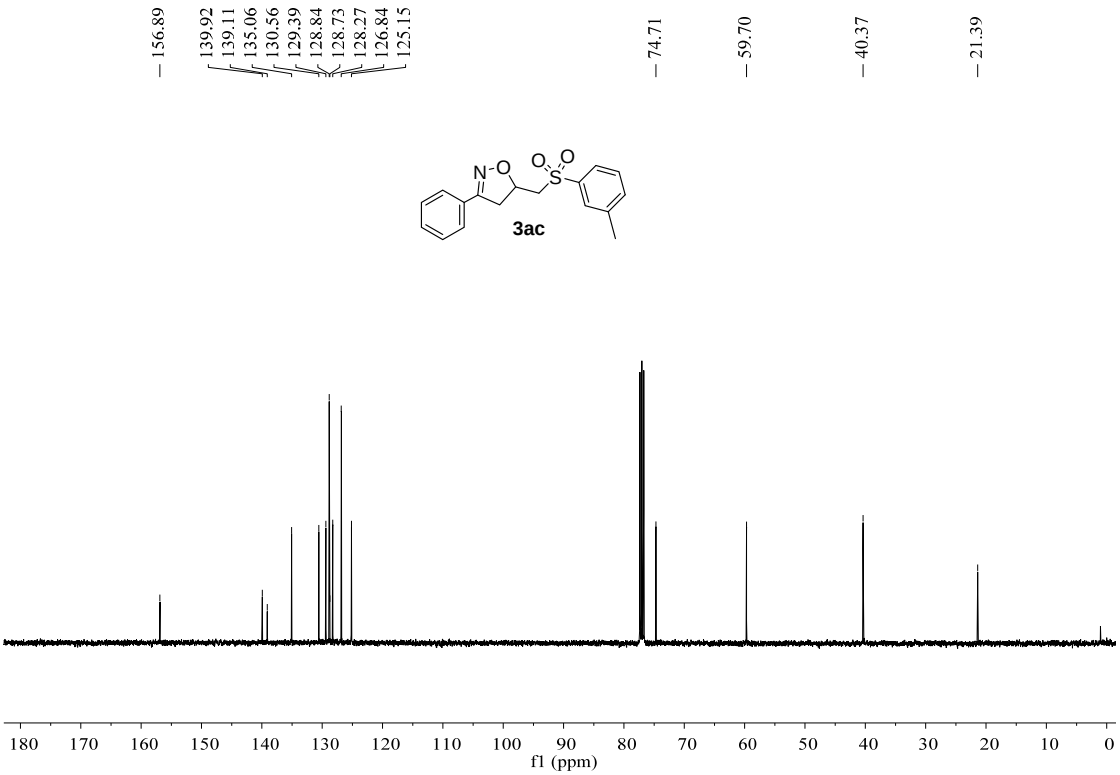
1.00
3.01
f1 (ppm)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139.92
139.11
135.06
130.56
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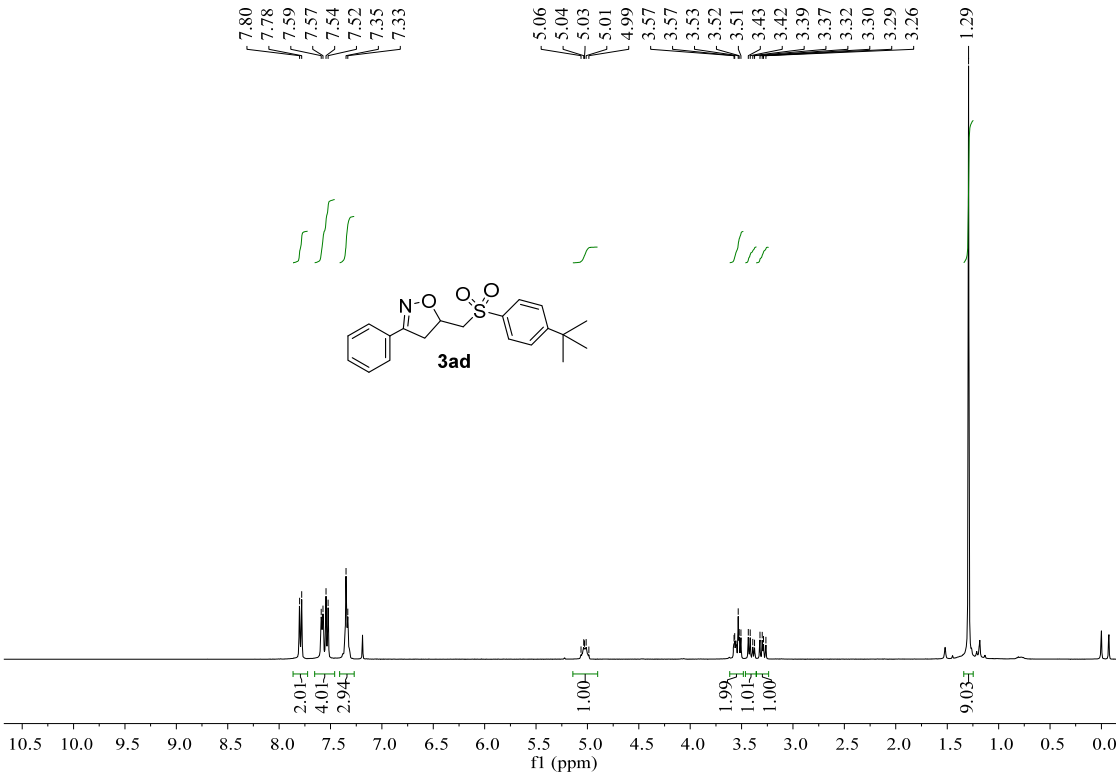
128.27
126.84
125.15
74.71
59.70
40.37
21.39
3ac
f1 (ppm)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7.33
5.06
5.04
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5.01
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3.57
3.53
3.52
3.51
3.43
3.42
3.39
3.37
3.32
3.30
3.29
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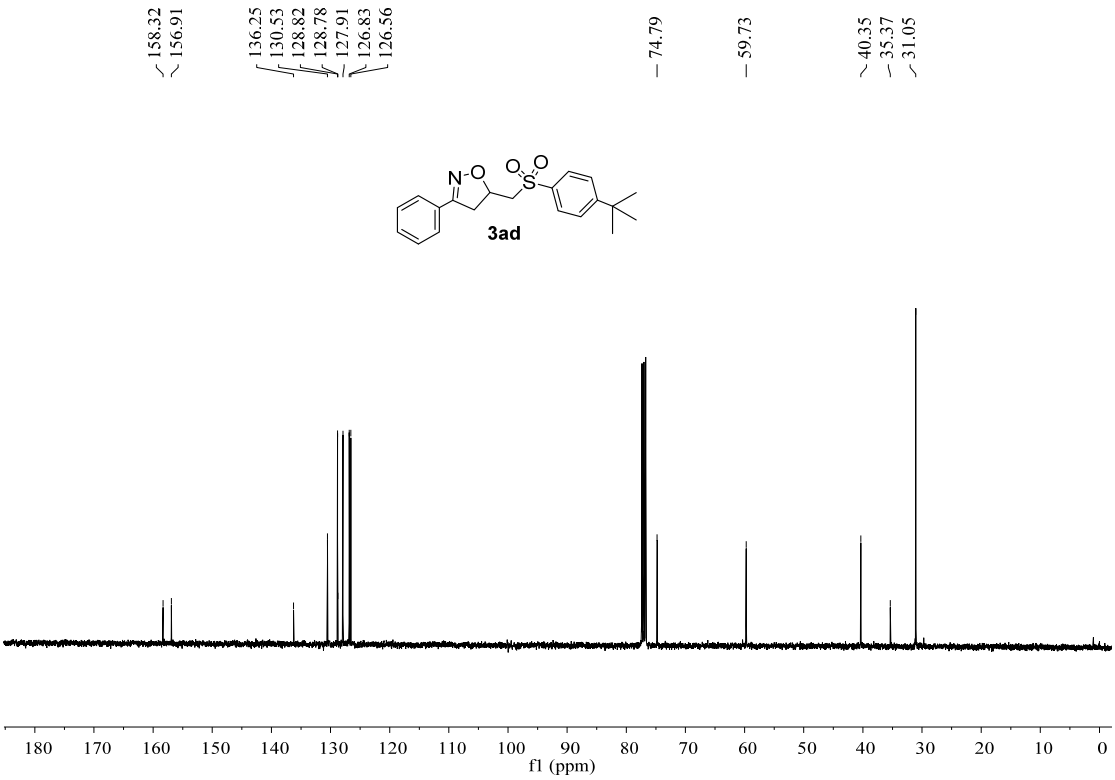
4.01
2.94
1.00
1.99
1.01
1.00
9.03
f1 (ppm)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136.25
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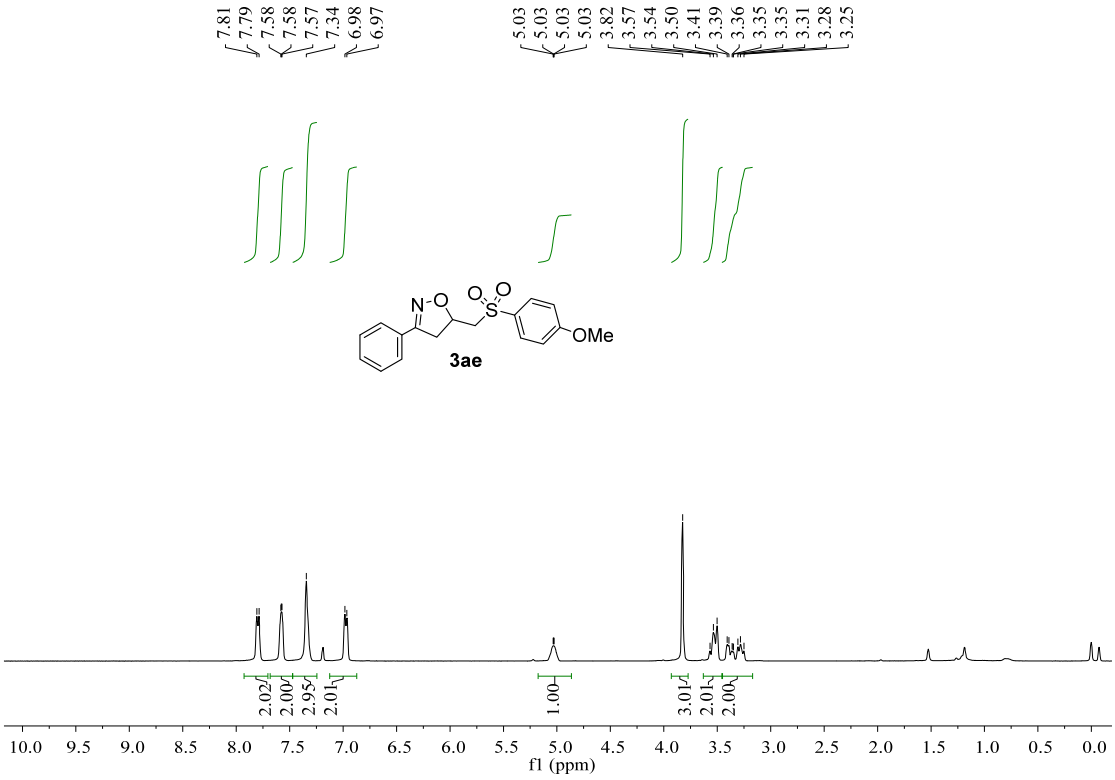
128.82
128.78
127.91
126.83
126.56
74.79
59.73
40.35
35.37
31.05
3ad
f1 (ppm)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7.58
7.58
7.57
7.34
6.98
6.97
5.03
5.03
5.03
5.03
3.82
3.57
3.54
3.50
3.41
3.39
3.36
3.35
3.35
3.31
3.28
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3ae
2.02
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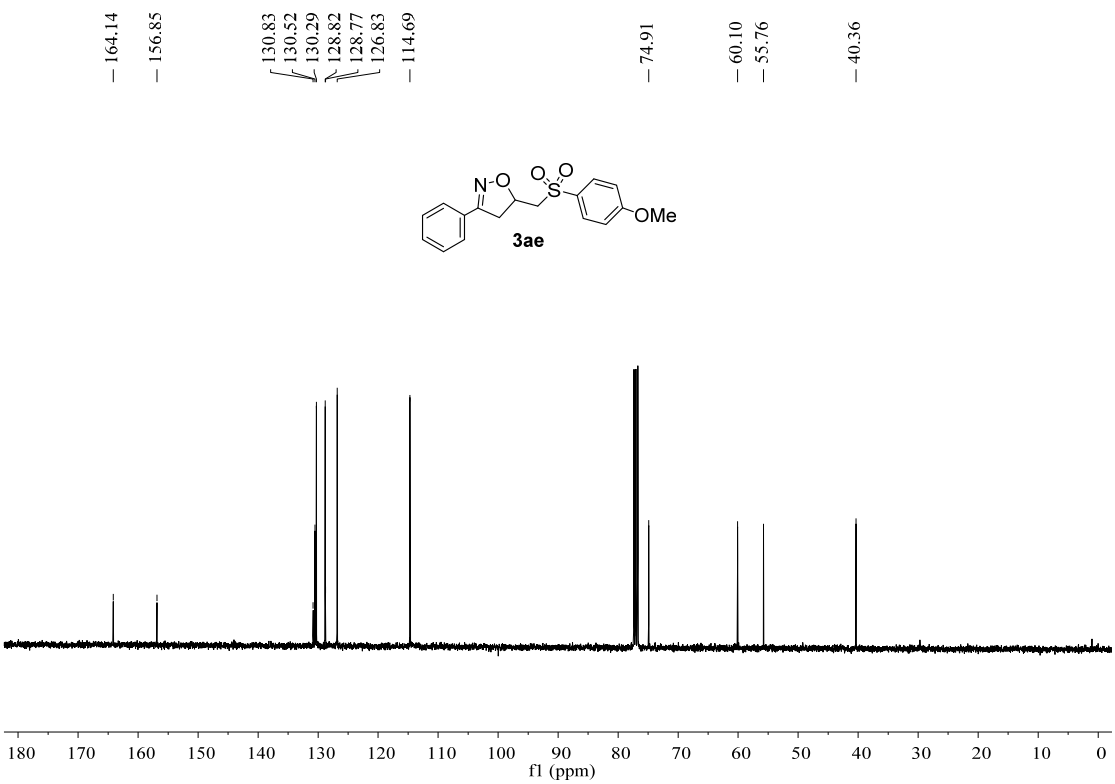
2.95
2.01
1.00
3.01
2.01
2.00
f1 (ppm)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156.85
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130.52
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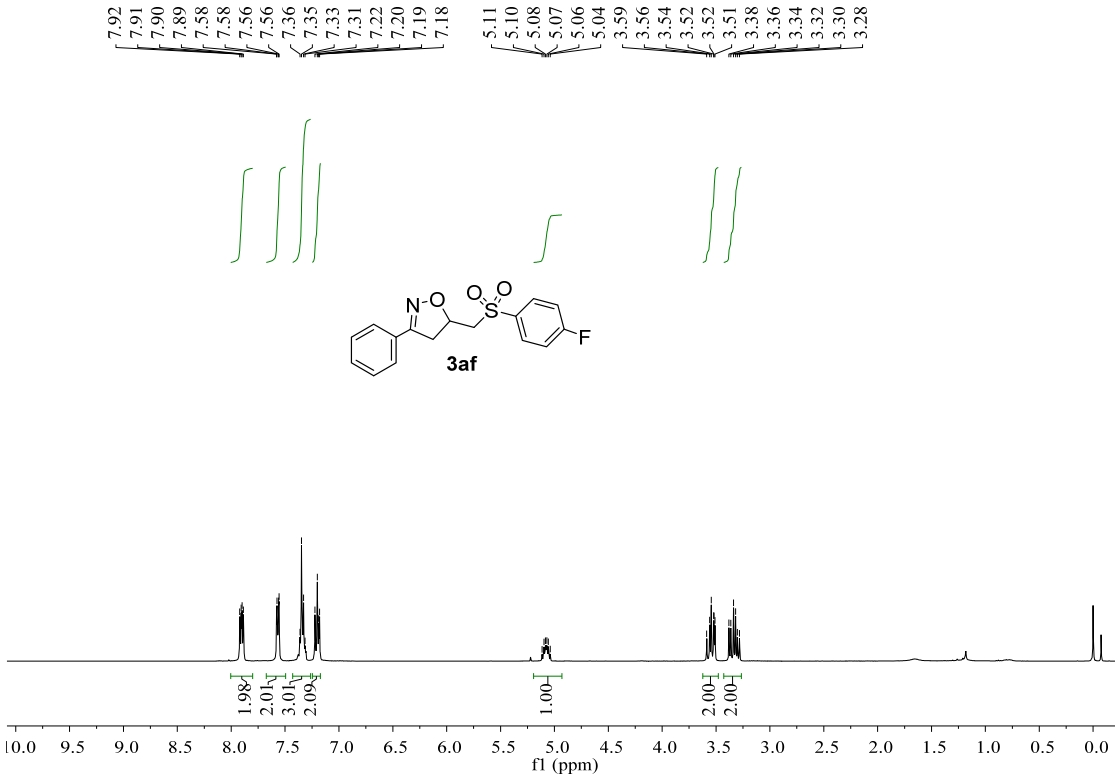
60.10
55.76
40.36
OMe
3ae
f1 (ppm)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7.58
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7.56
7.36
7.35
7.33
7.31
7.22
7.20
7.19
7.18
5.11
5.10
5.08
5.07
5.06
5.04
3.59
3.56
3.54
3.52
3.52
3.51
3.38
3.36
3.34
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3af
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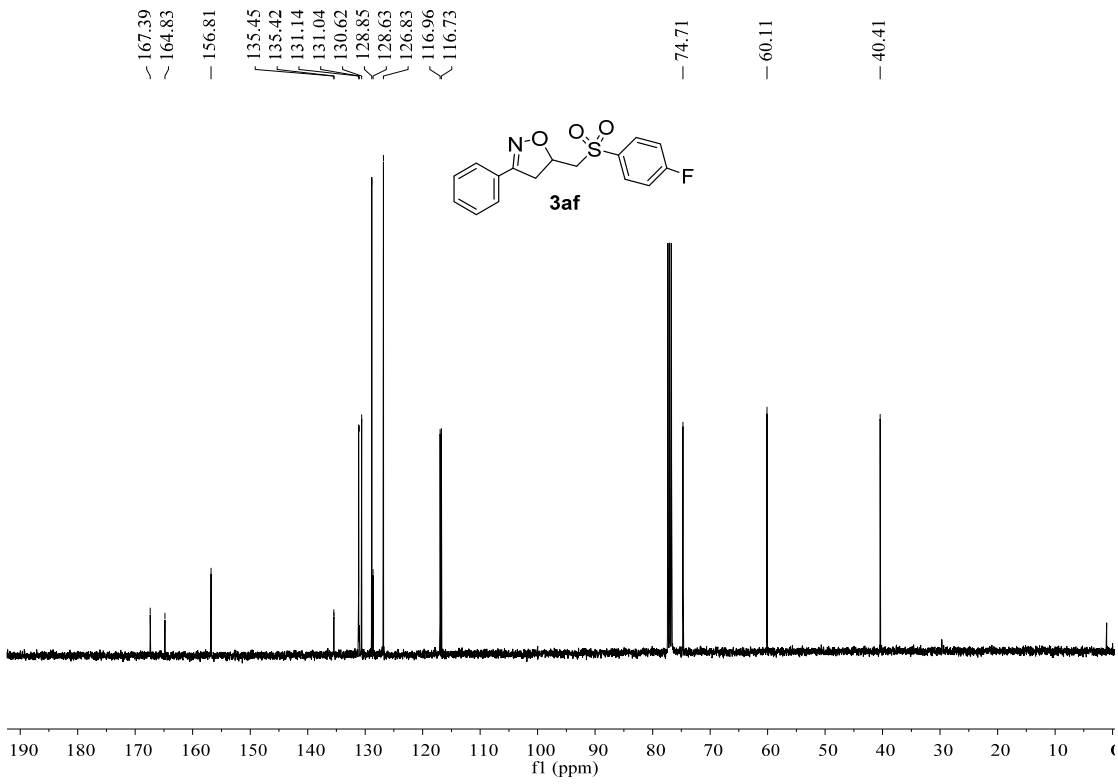
3.01
2.09
1.00
2.00
2.00
f1 (ppm)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131.14
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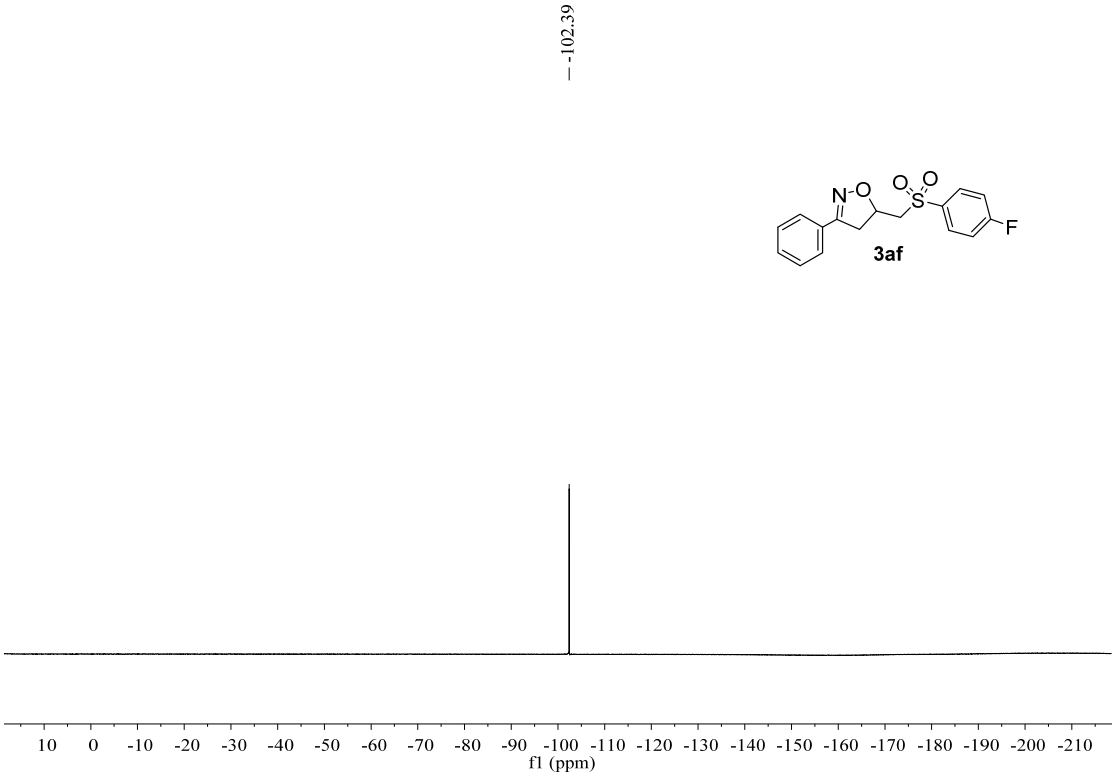
116.96
116.73
74.71
60.11
40.41
3af
f1 (ppm)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3af
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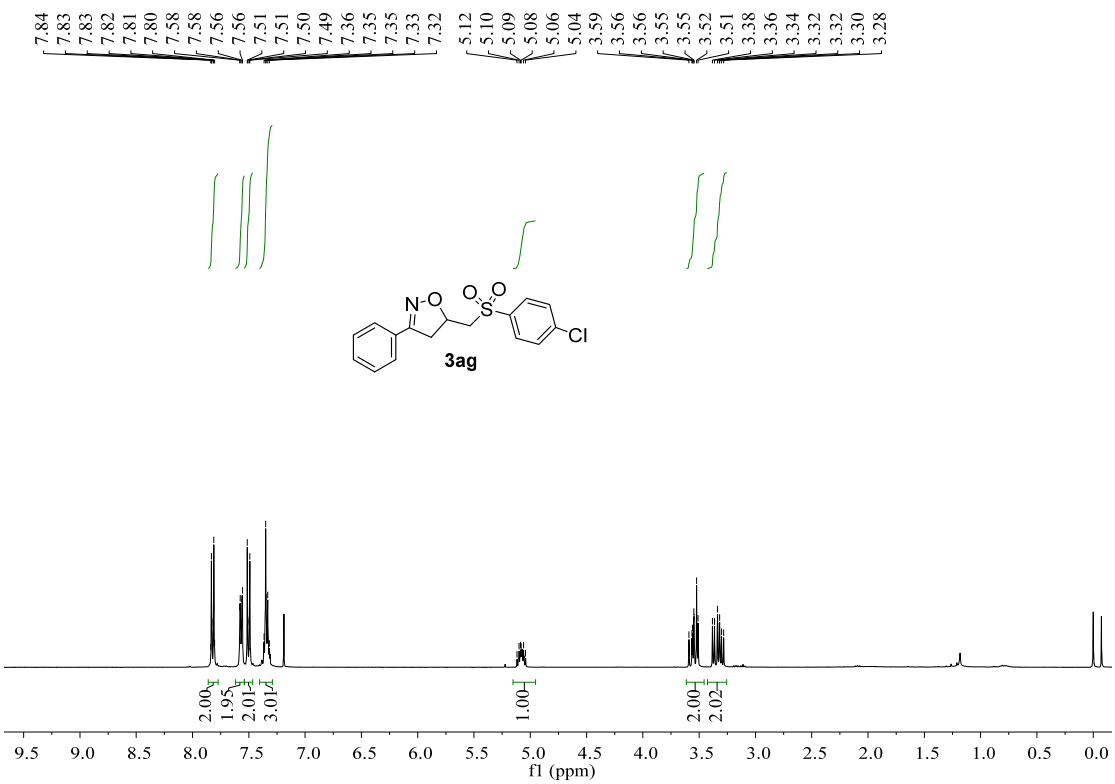
f1 (ppm)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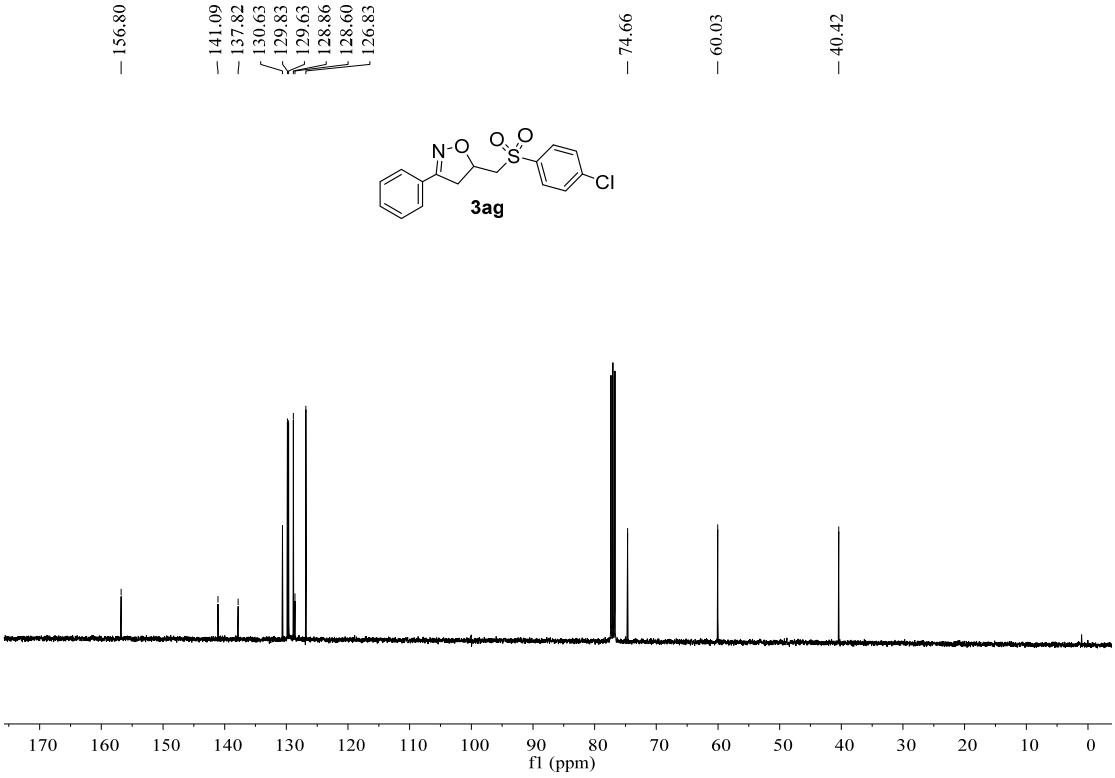
5.12 5.10 5.09 5.08 5.06 5.04
3.59 3.56 3.56 3.55 3.55 3.52 3.51 3.38 3.36 3.34 3.32 3.32 3.30 3.28
3ag
2.00 1.95 2.01 3.01 1.00 2.00 2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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74.66
60.03
40.42
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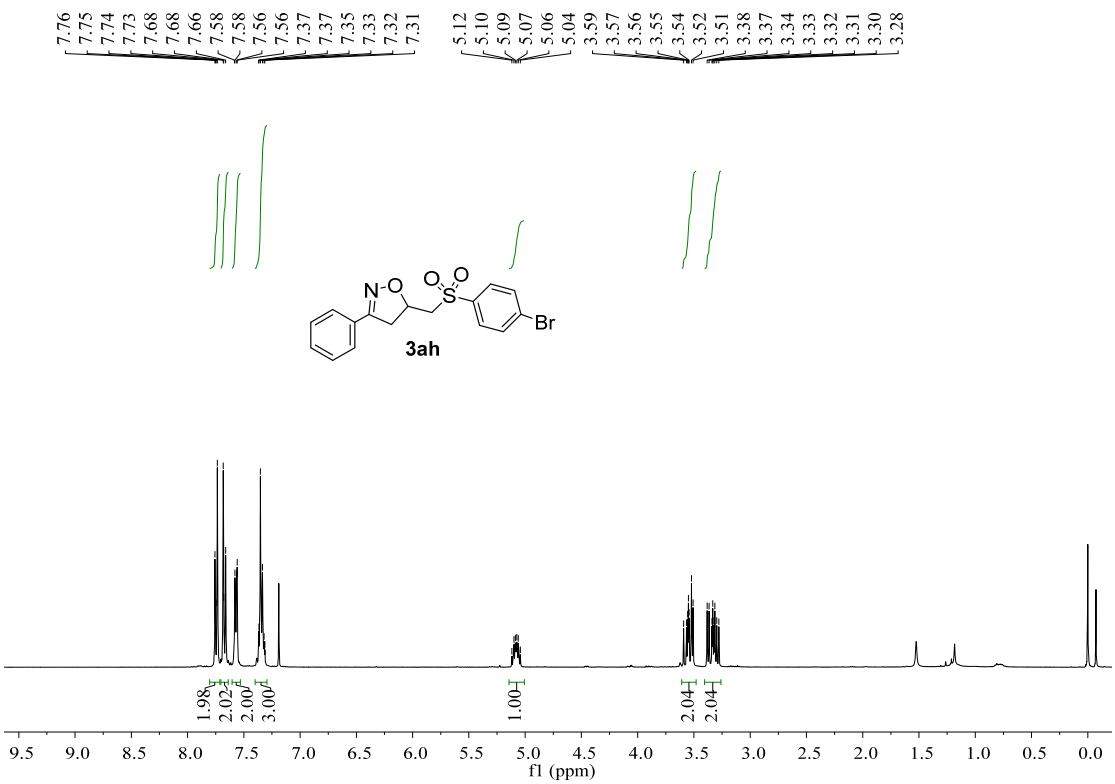
O
O
O
S
Cl
3ag
f1 (ppm)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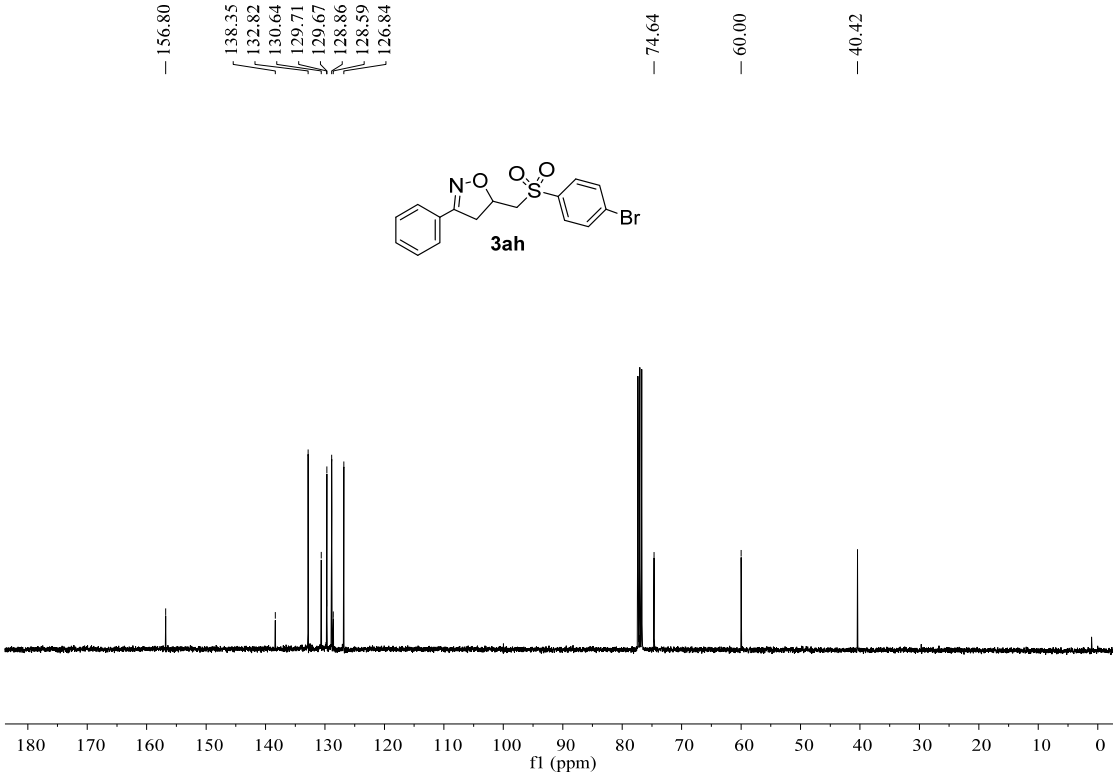
7.56
7.37
7.37
7.35
7.33
7.32
7.31
5.12
5.10
5.09
5.07
5.06
5.04
3.59
3.57
3.56
3.55
3.54
3.52
3.51
3.38
3.37
3.34
3.33
3.32
3.31
3.30
3.28
N
O
O
O
S
Br
3ah
1.98
2.02
2.00
3.00
1.00
2.04
2.04
f1 (ppm)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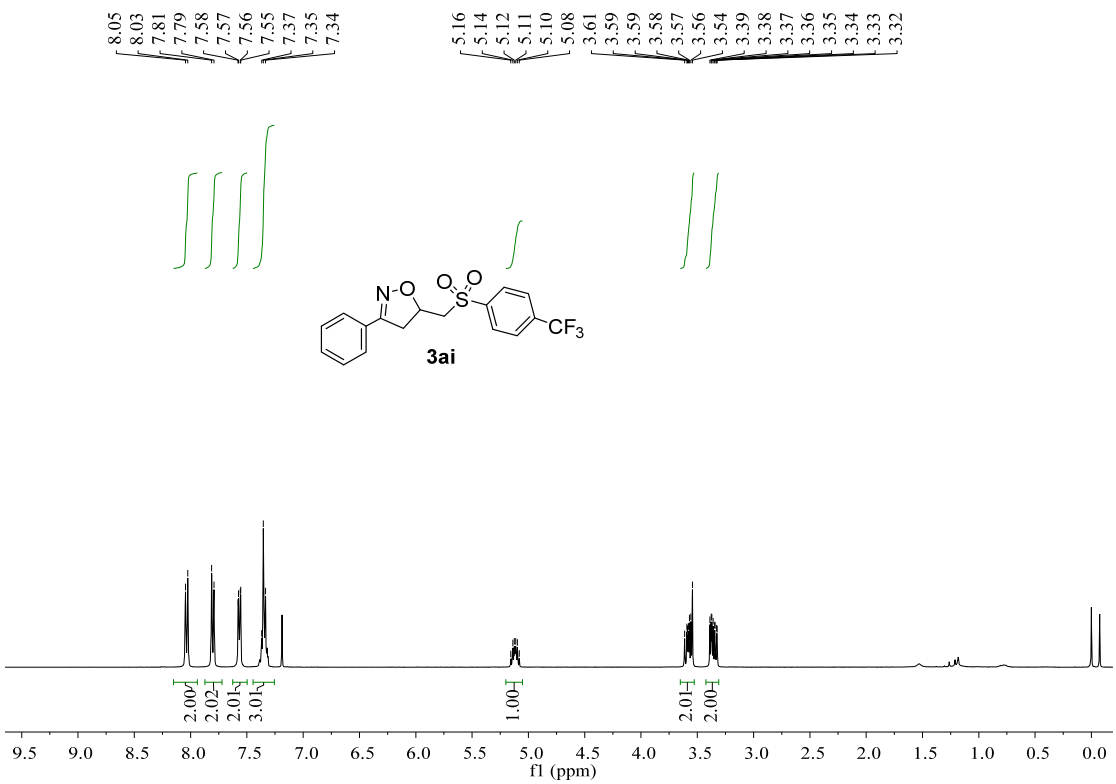
128.59
126.84
74.64
60.00
40.42
N
O
O
S
O
Br
3ah
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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5.12
5.11
5.10
5.08
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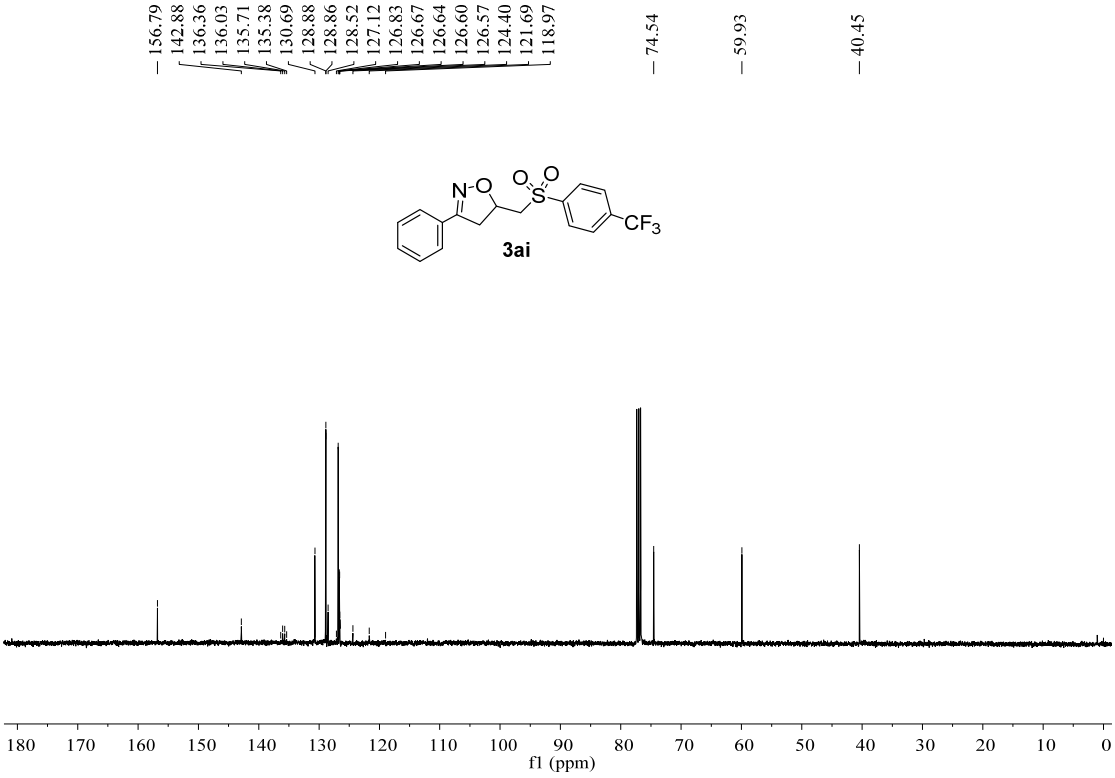
3.59
3.58
3.57
3.56
3.54
3.39
3.38
3.37
3.36
3.35
3.34
3.33
3.32
N
O
O
S
O
CF3
3ai
2.00
2.02
2.01
3.01
1.00
2.01
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.12
126.83
126.67
126.64
126.60
126.57
124.40
121.69
118.97
74.54
59.93
40.45
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O
O
O
S
CF3
3ai
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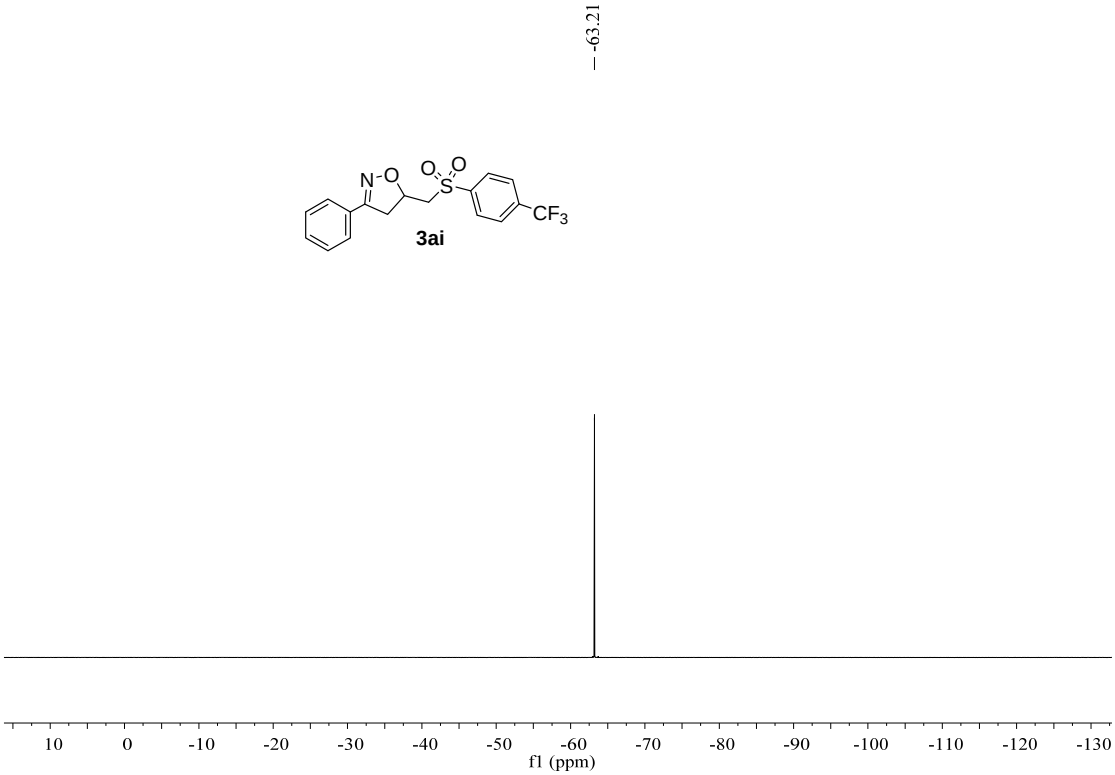
f1 (ppm)


-63.21
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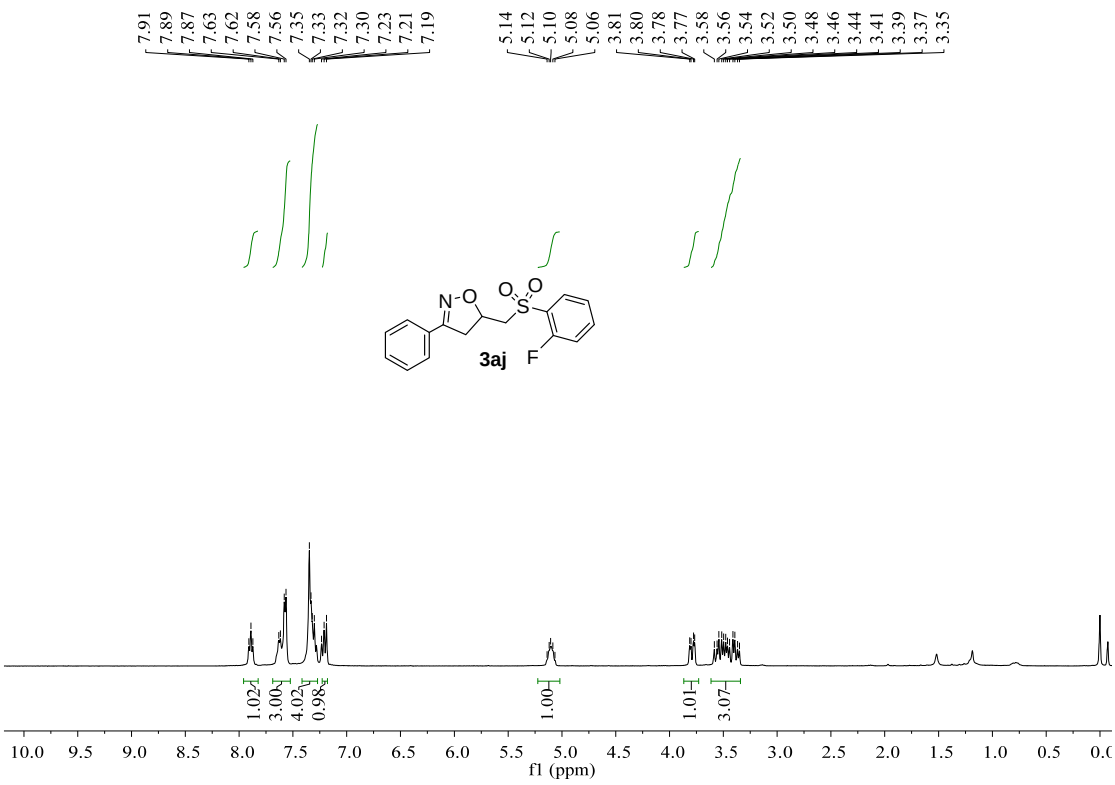
f1 (ppm)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7.32
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7.21
7.19
5.14
5.12
5.10
5.08
5.06
3.81
3.80
3.78
3.77
3.58
3.56
3.54
3.52
3.50
3.48
3.46
3.44
3.41
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3.37
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3aj
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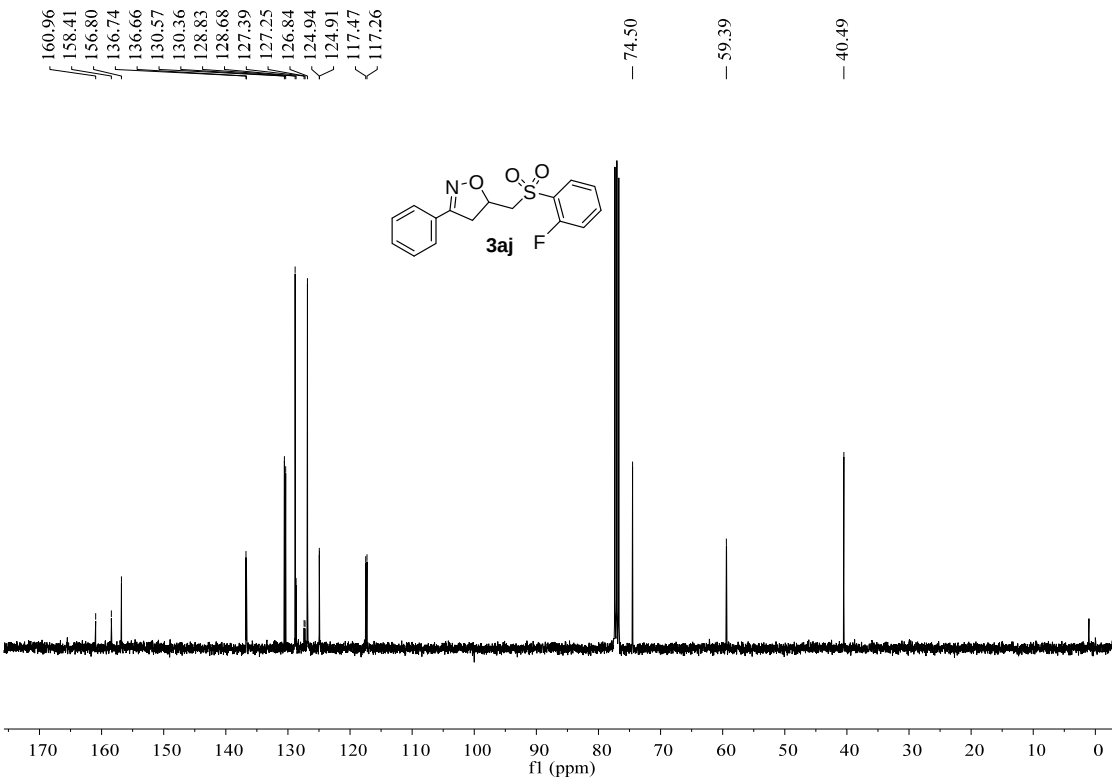
3.00
4.02
0.98
1.00
1.01
3.07
f1 (ppm)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74.50
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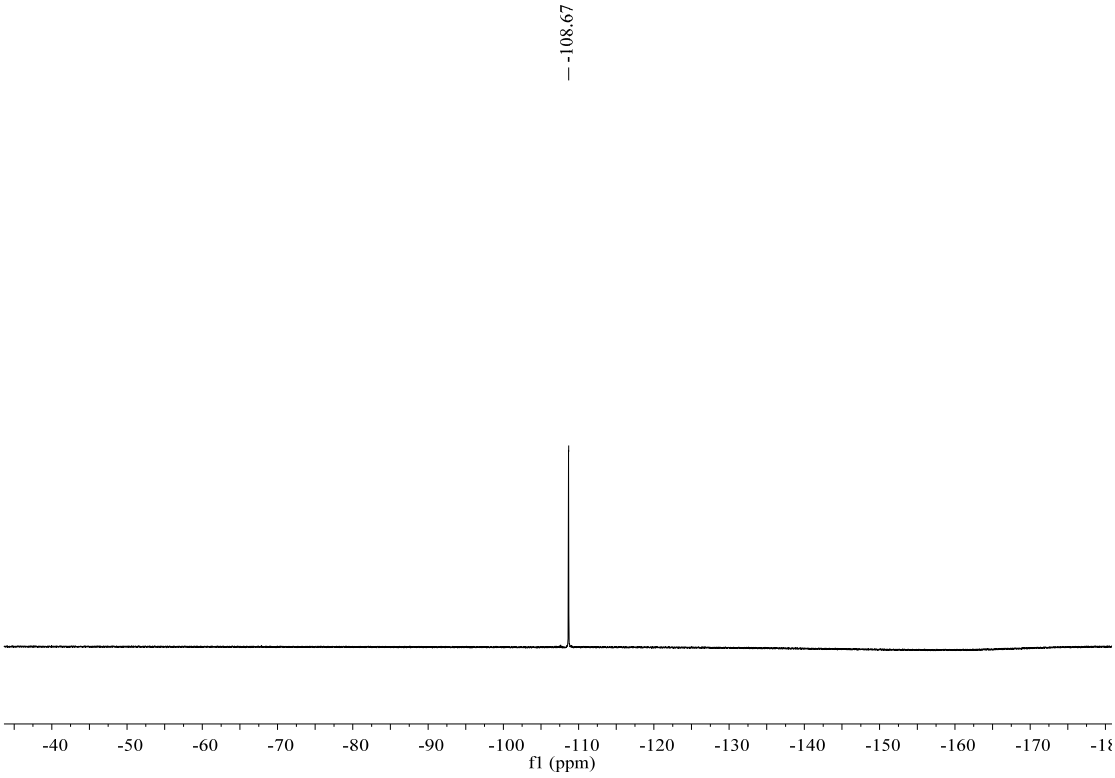
40.49
3aj
f1 (ppm)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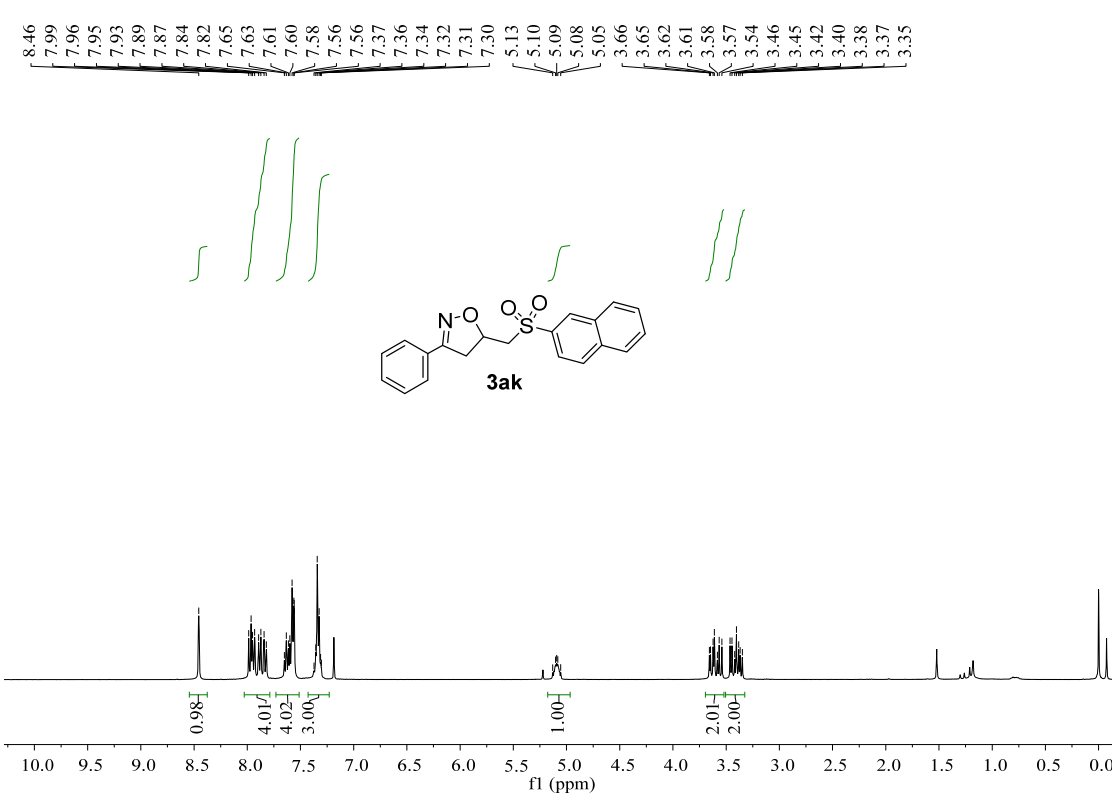
-120
-130
-140
-150
-160
-170
f1 (ppm)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3.57
3.54
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3.45
3.42
3.40
3.38
3.37
3.35
N
O
O
O
S
3ak
0.98
4.01
4.02
3.00
1.00
2.01
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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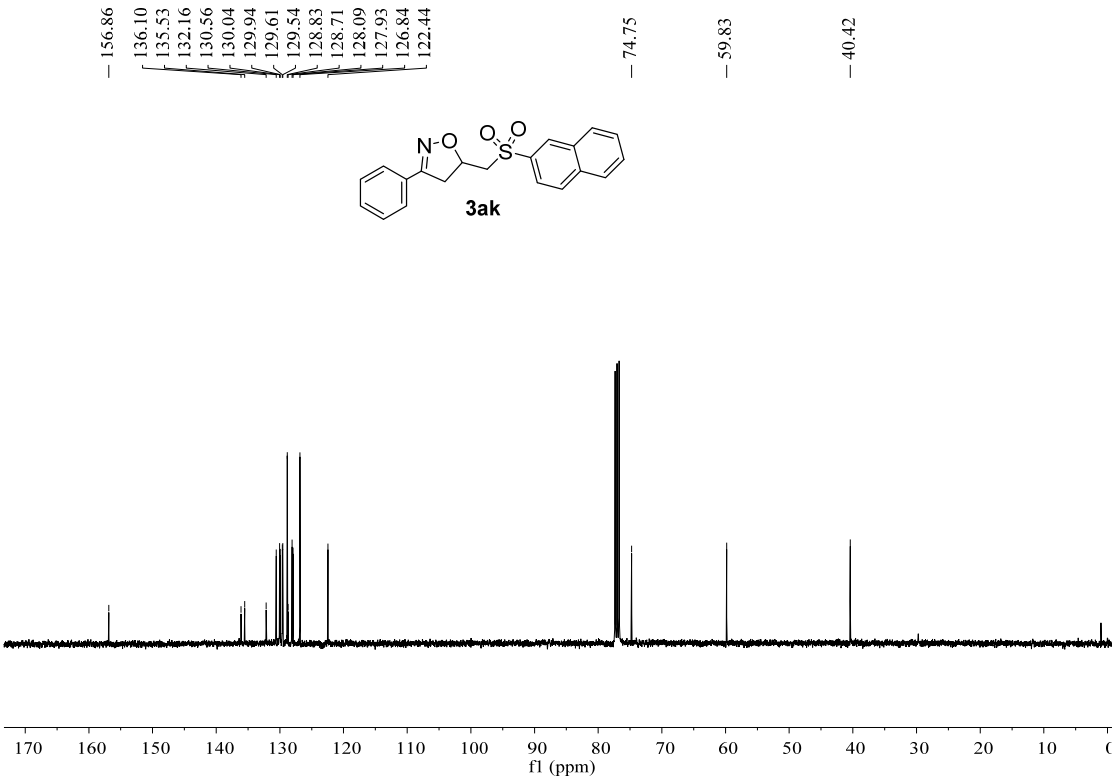
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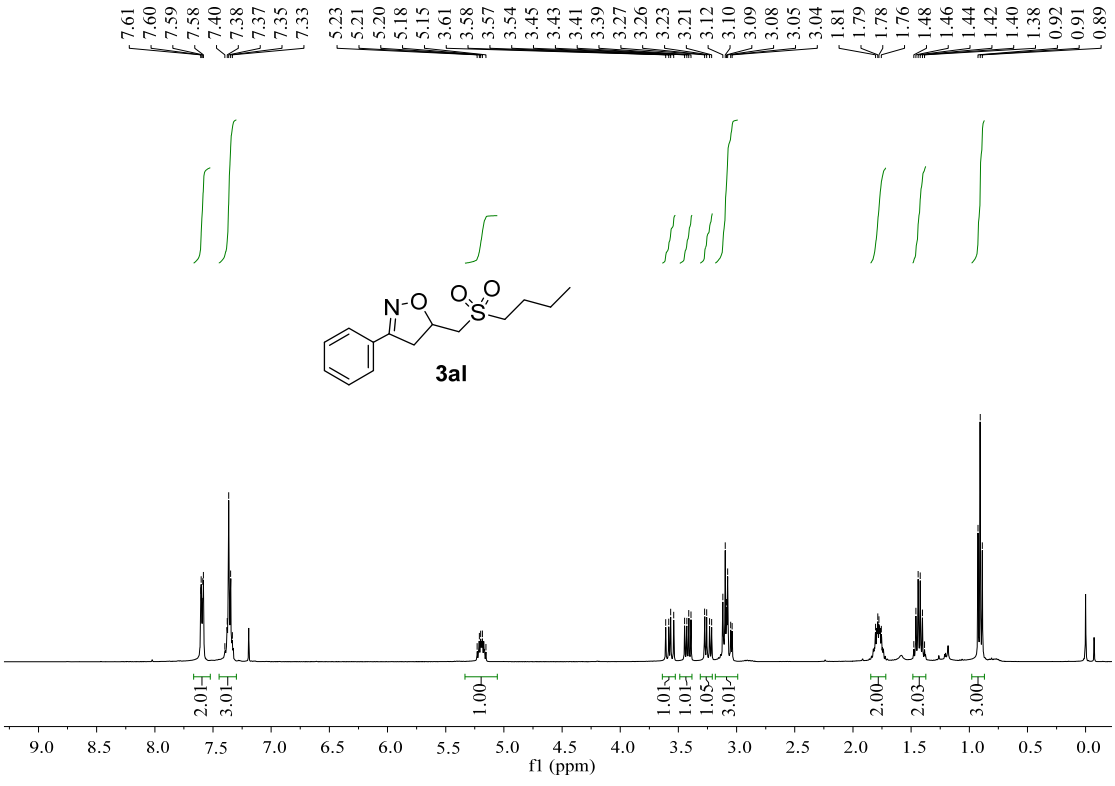
f1 (ppm)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3.58
3.57
3.54
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3.43
3.41
3.39
3.27
3.26
3.23
3.21
3.12
3.10
3.09
3.08
3.05
3.04
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1.79
1.78
1.76
1.48
1.46
1.44
1.42
1.40
1.38
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0.91
0.89
3al
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3.01
1.00
1.01
1.01
1.05
3.01
2.00
2.03
3.00
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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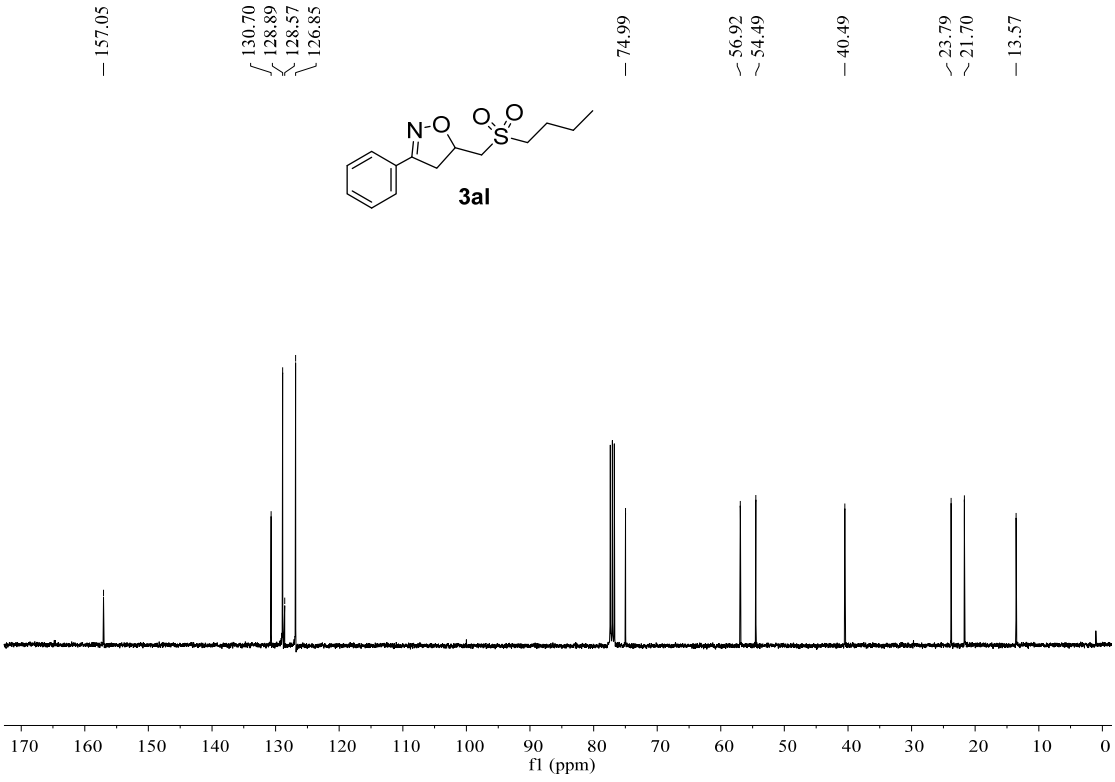
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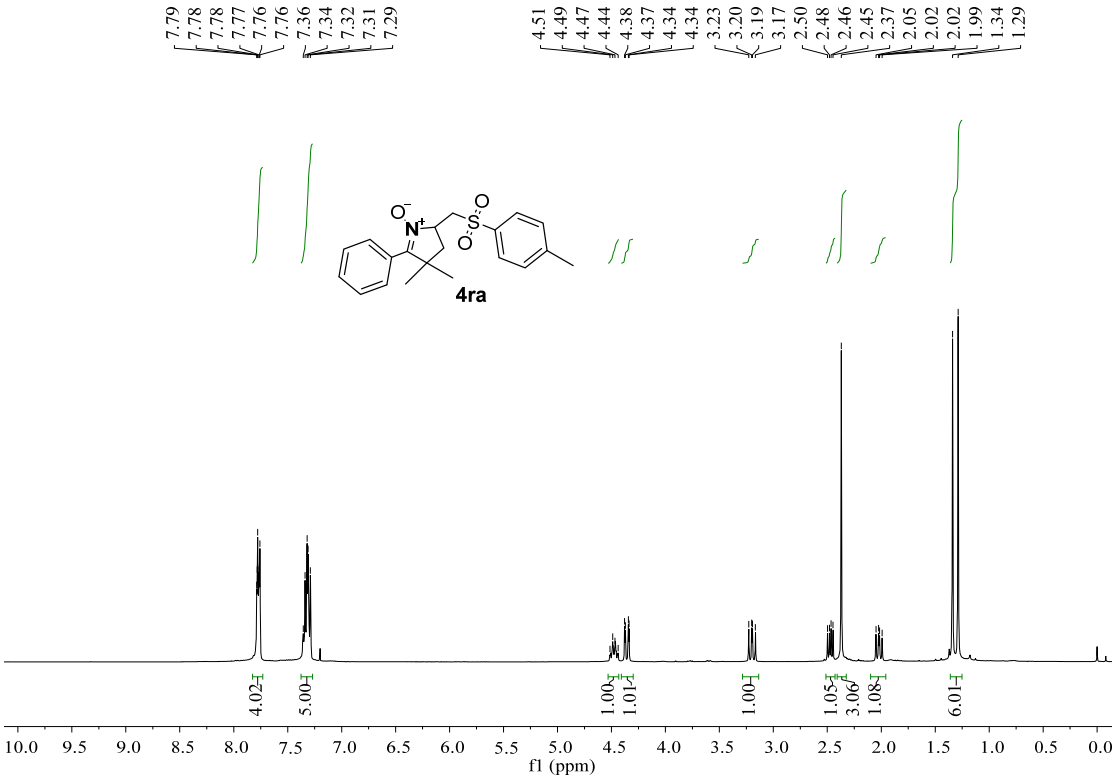
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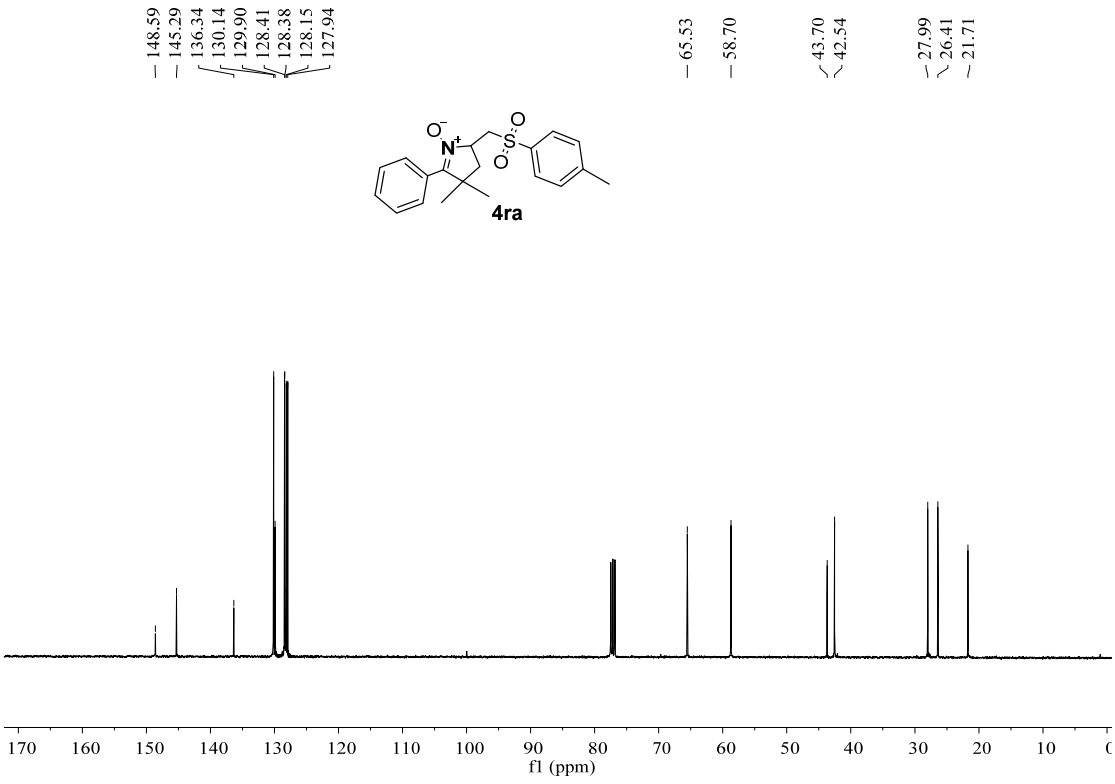
4.49
4.47
4.44
4.38
4.37
4.34
4.34
3.23
3.20
3.19
3.17
2.50
2.48
2.46
2.45
2.37
2.05
2.02
2.02
1.99
1.34
1.29
4ra
4.02
5.00
1.00
1.01
1.00
1.05
3.06
1.08
6.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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26.41
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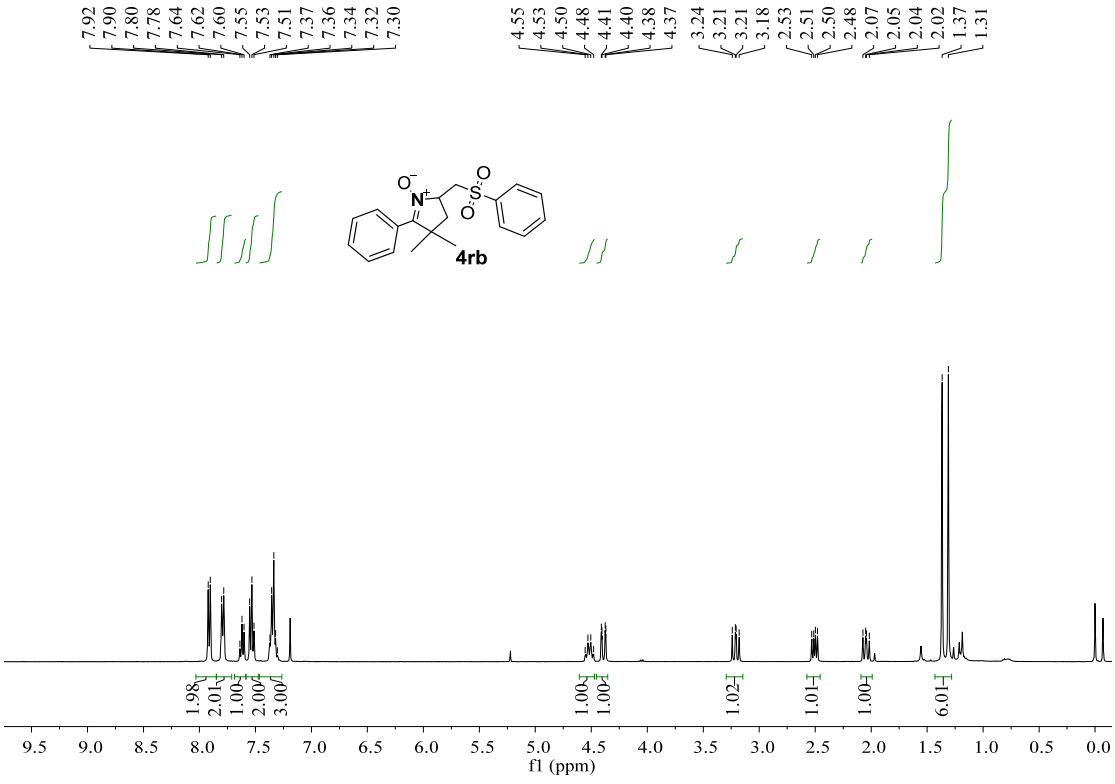
f1 (ppm)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4.53
4.50
4.48
4.41
4.40
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4.37
3.24
3.21
3.21
3.18
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2.51
2.50
2.48
2.07
2.05
2.04
2.02
1.37
1.31
4rb
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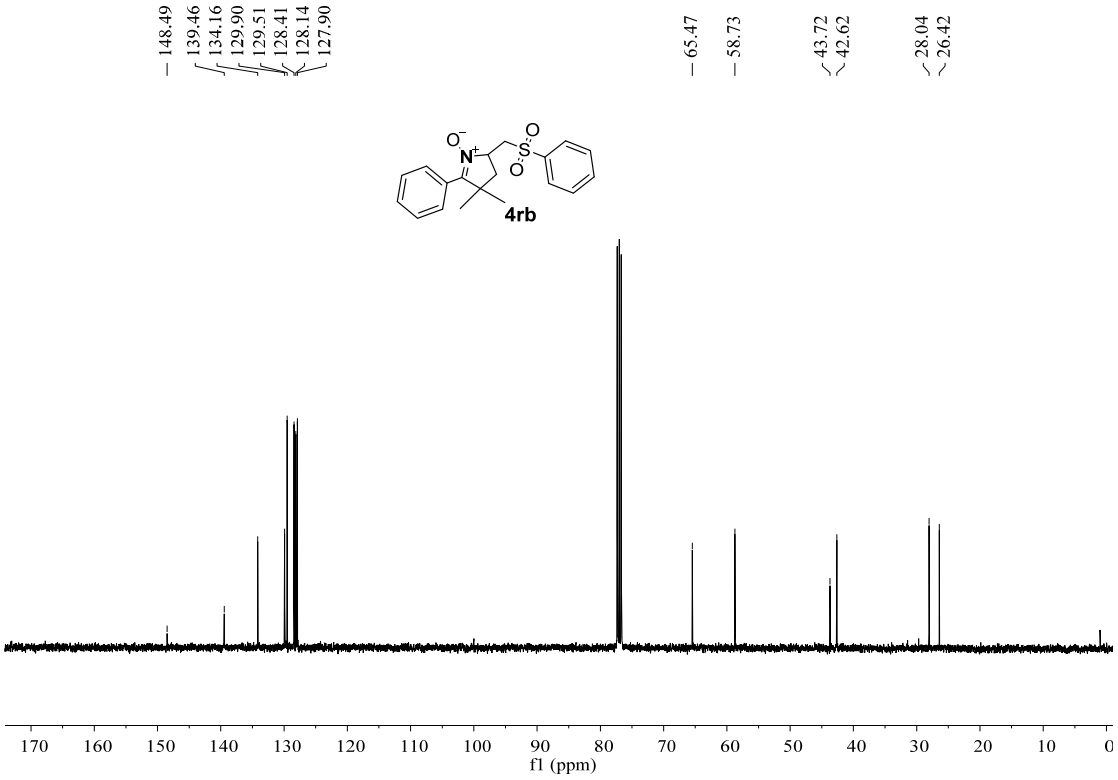
f1 (ppm)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127.90
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26.42
4rb
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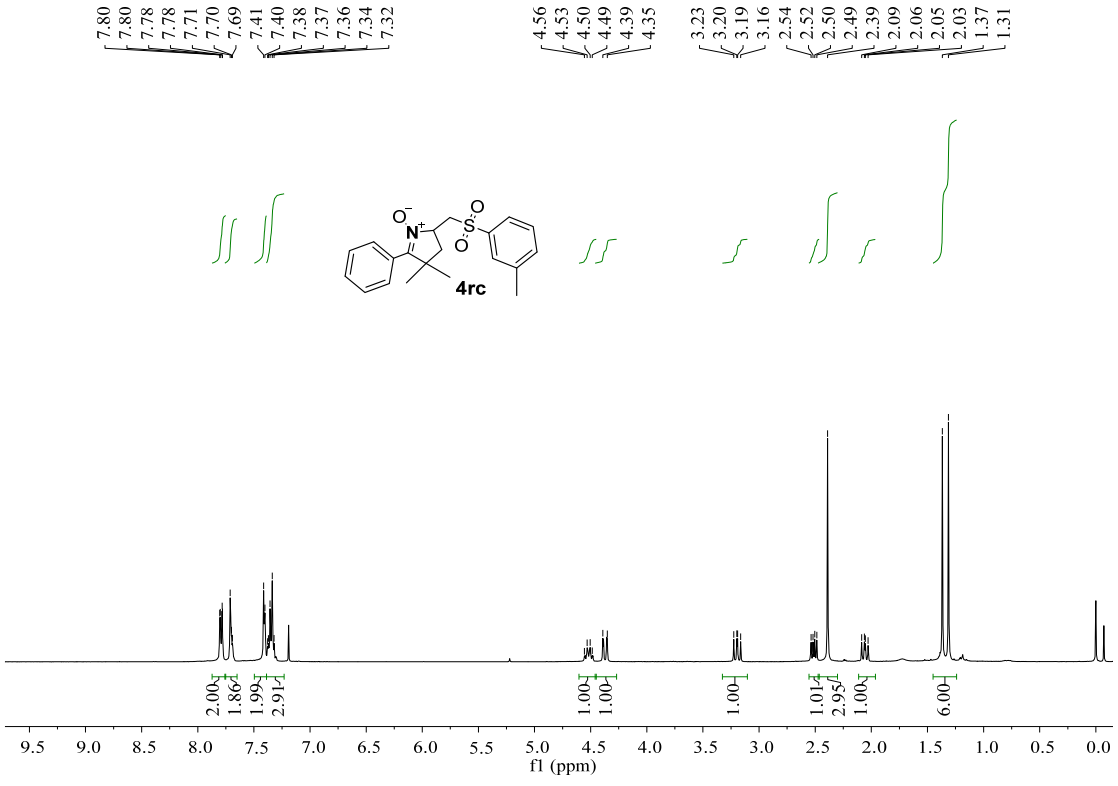
f1 (ppm)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7.36
7.34
7.32
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4.53
4.50
4.49
4.39
4.35
3.23
3.20
3.19
3.16
2.54
2.52
2.50
2.49
2.39
2.09
2.06
2.05
2.03
1.37
1.31
4rc
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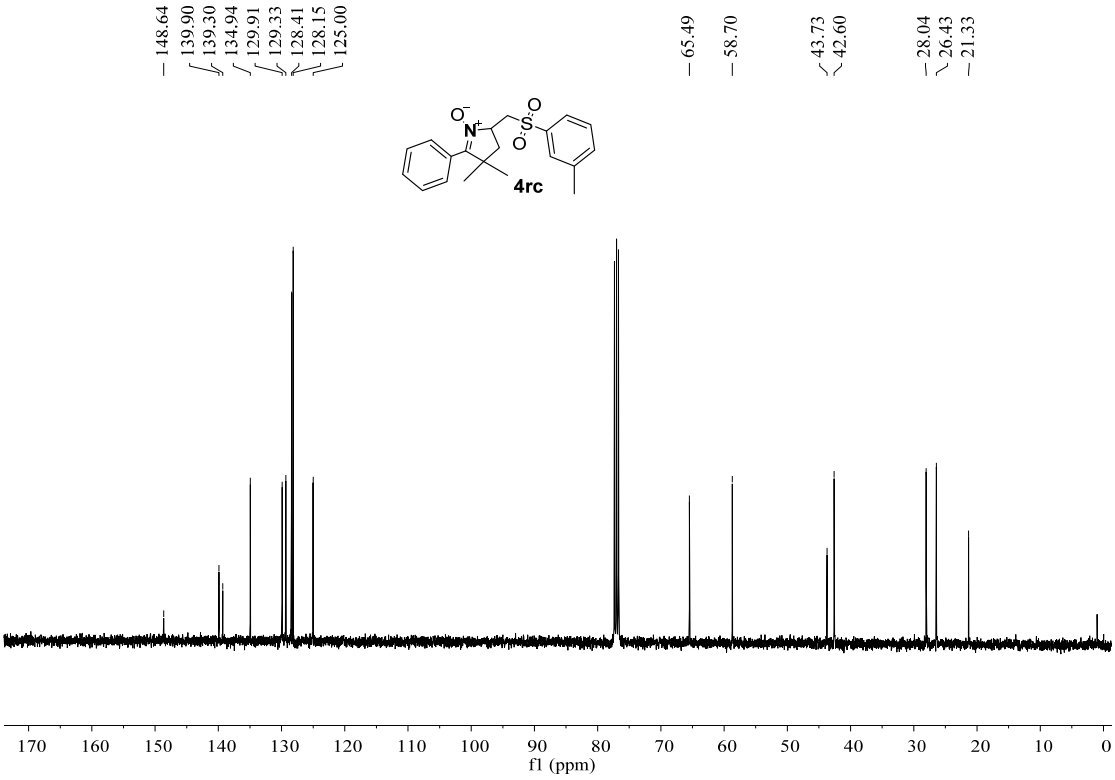
1.86
1.99
2.91
1.00
1.00
1.00
1.01
2.95
1.00
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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42.60
28.04
26.43
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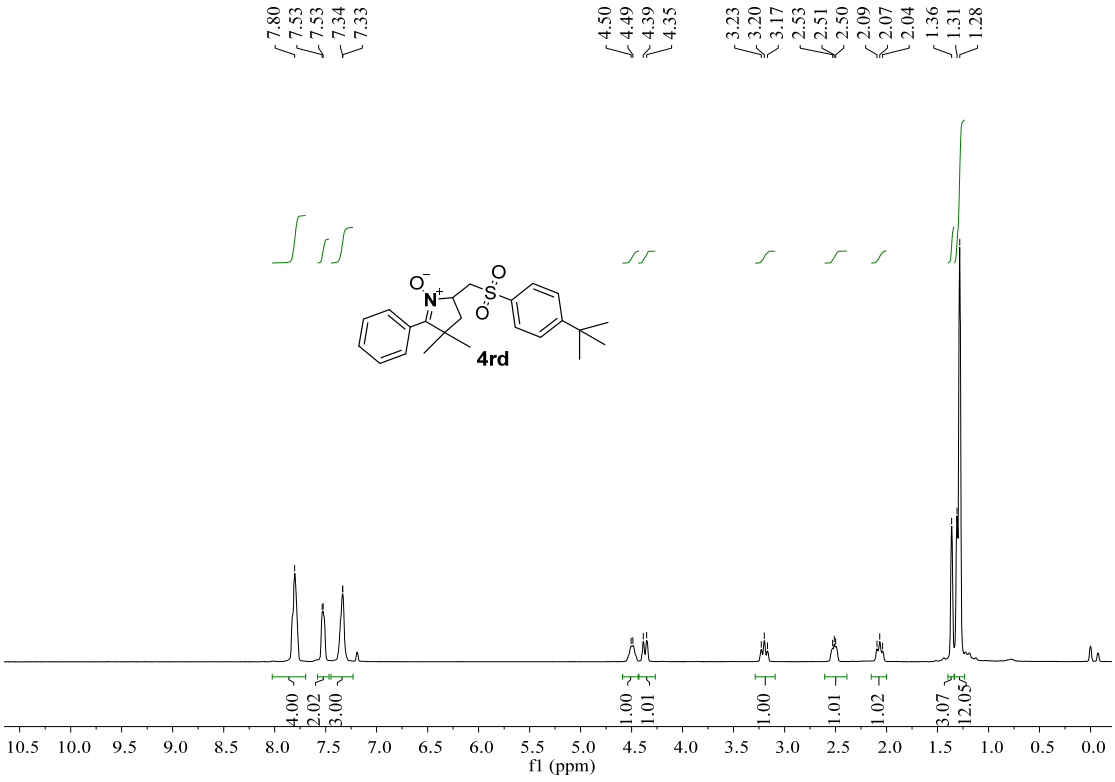
4rc
f1 (ppm)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7.34
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4.49
4.39
4.35
3.23
3.20
3.17
2.53
2.51
2.50
2.09
2.07
2.04
1.36
1.31
1.28
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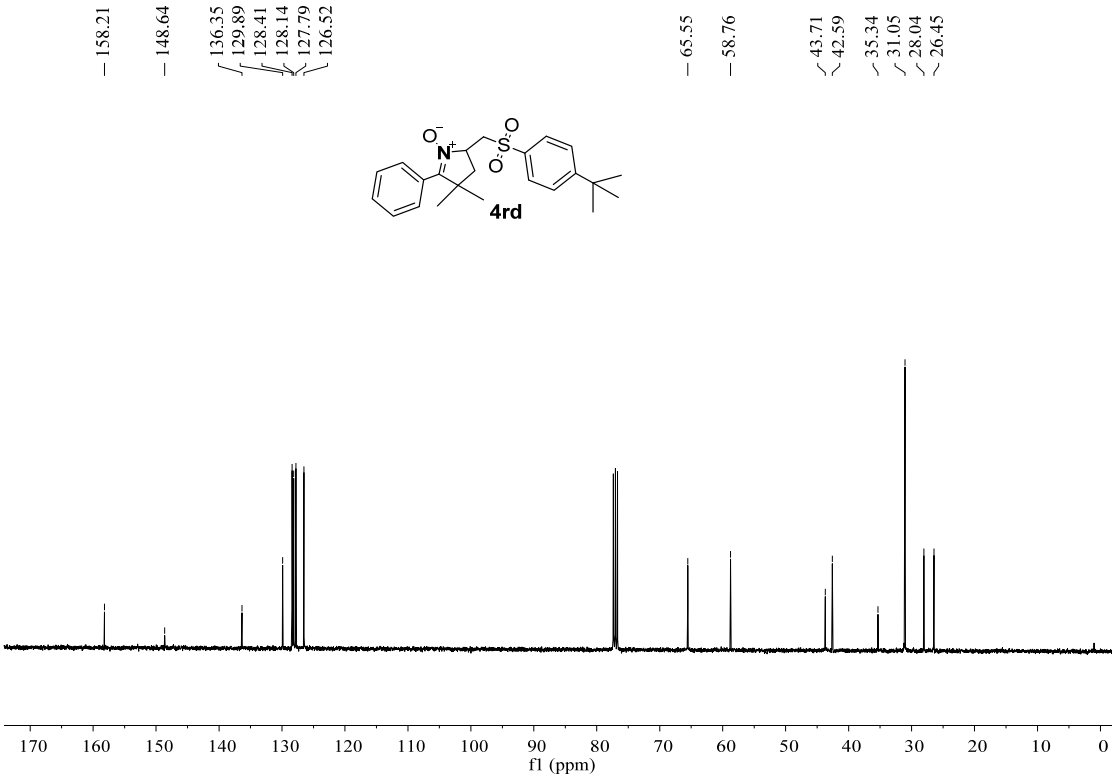
1.02
3.07
12.05
f1 (ppm)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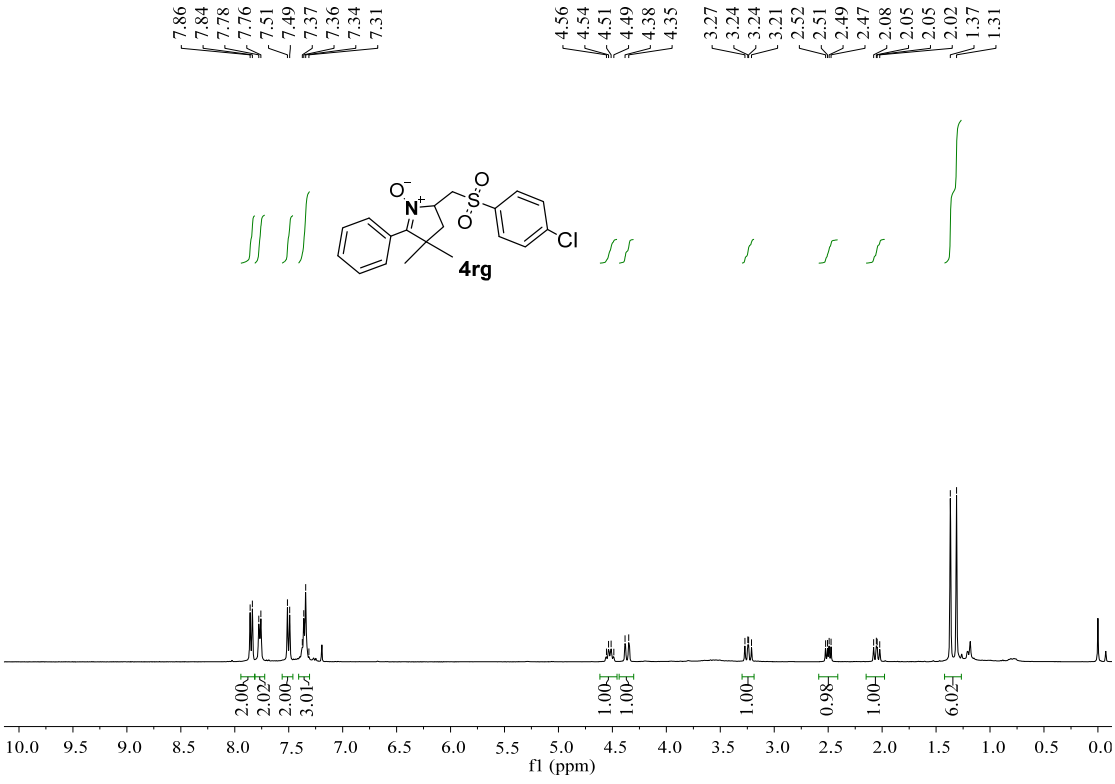
31.05
28.04
26.45
4rd
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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4.56
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4.35
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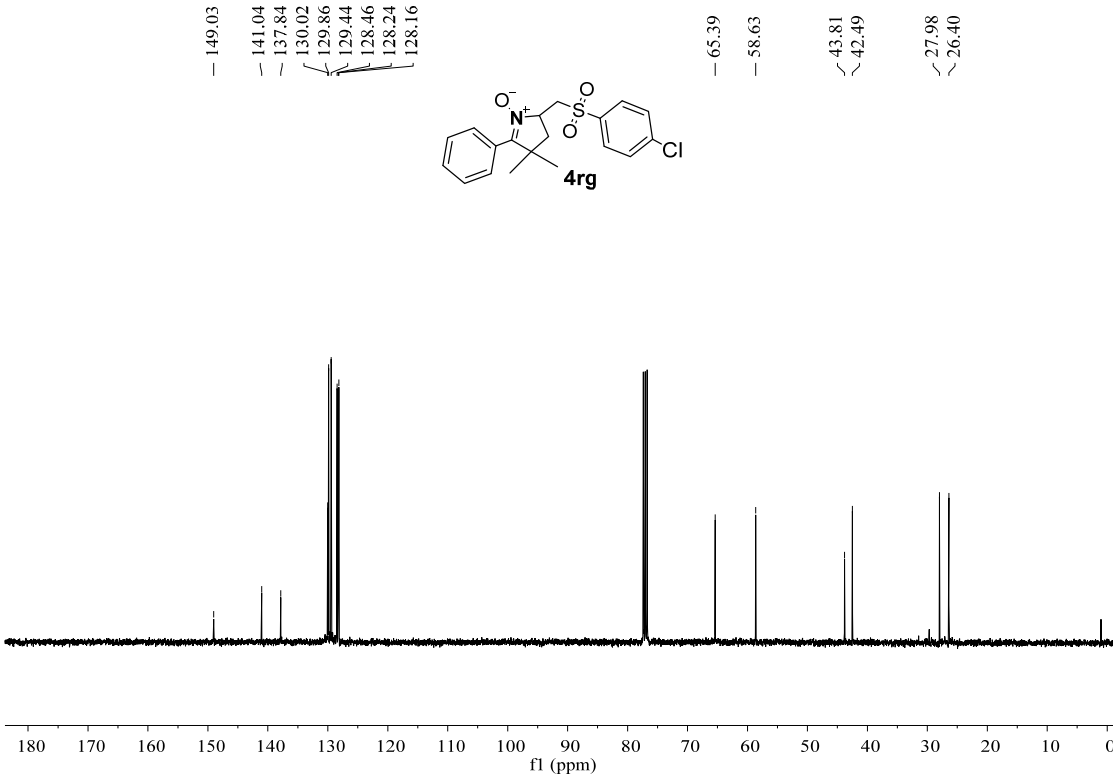
2.05
2.02
1.37
1.31
Cl
4rg
2.00
2.02
2.00
3.01
1.00
1.00
1.00
0.98
1.00
6.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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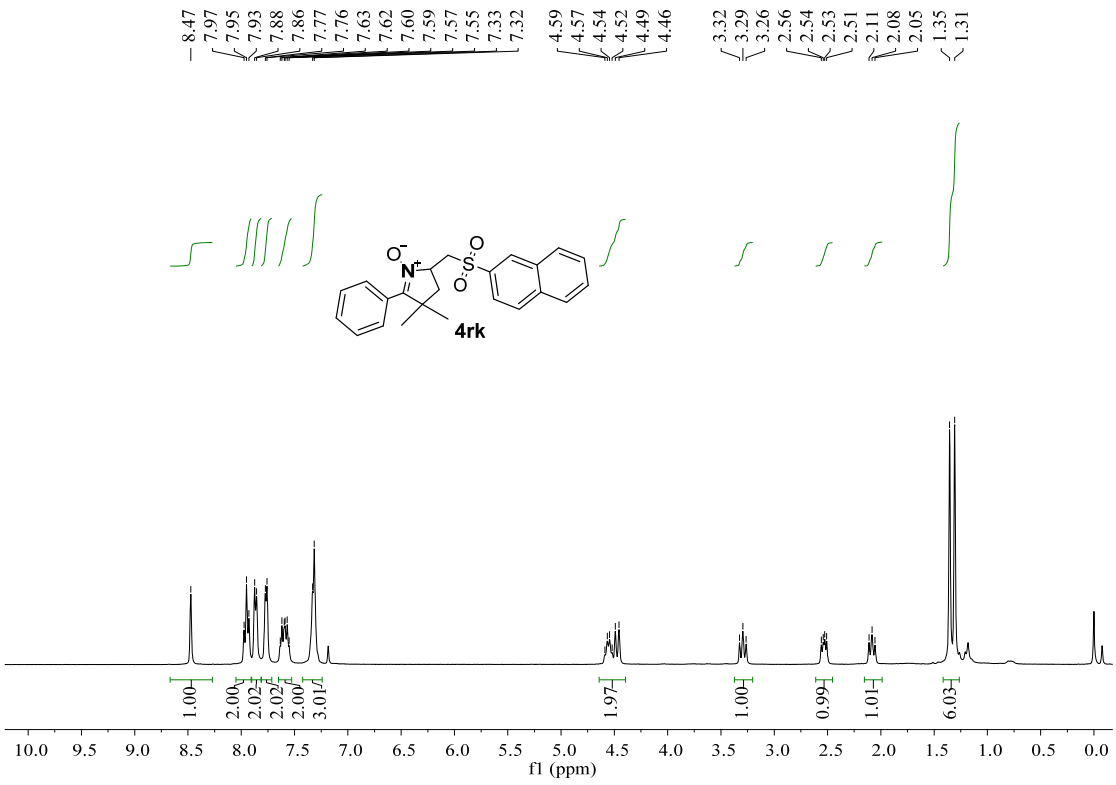
Cl
4rg
f1 (ppm)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2.05
1.35
1.31
4rk
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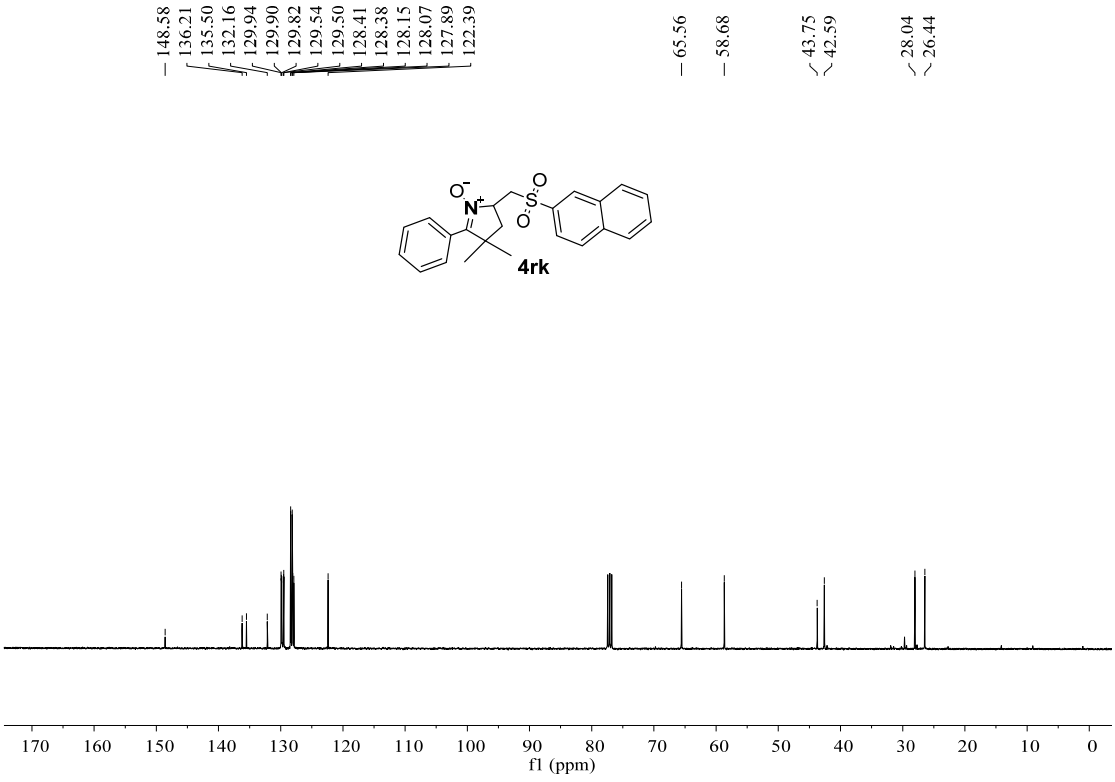
f1 (ppm)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127.89
122.39
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26.44
4rk
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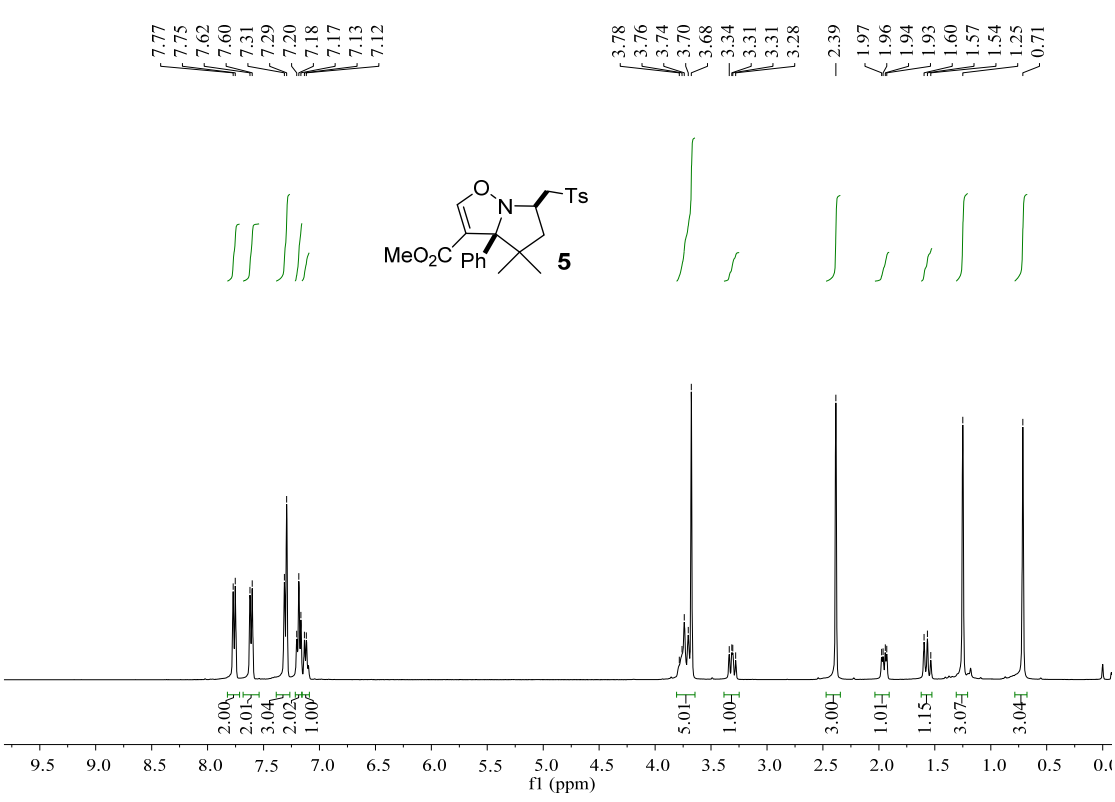
f1 (ppm)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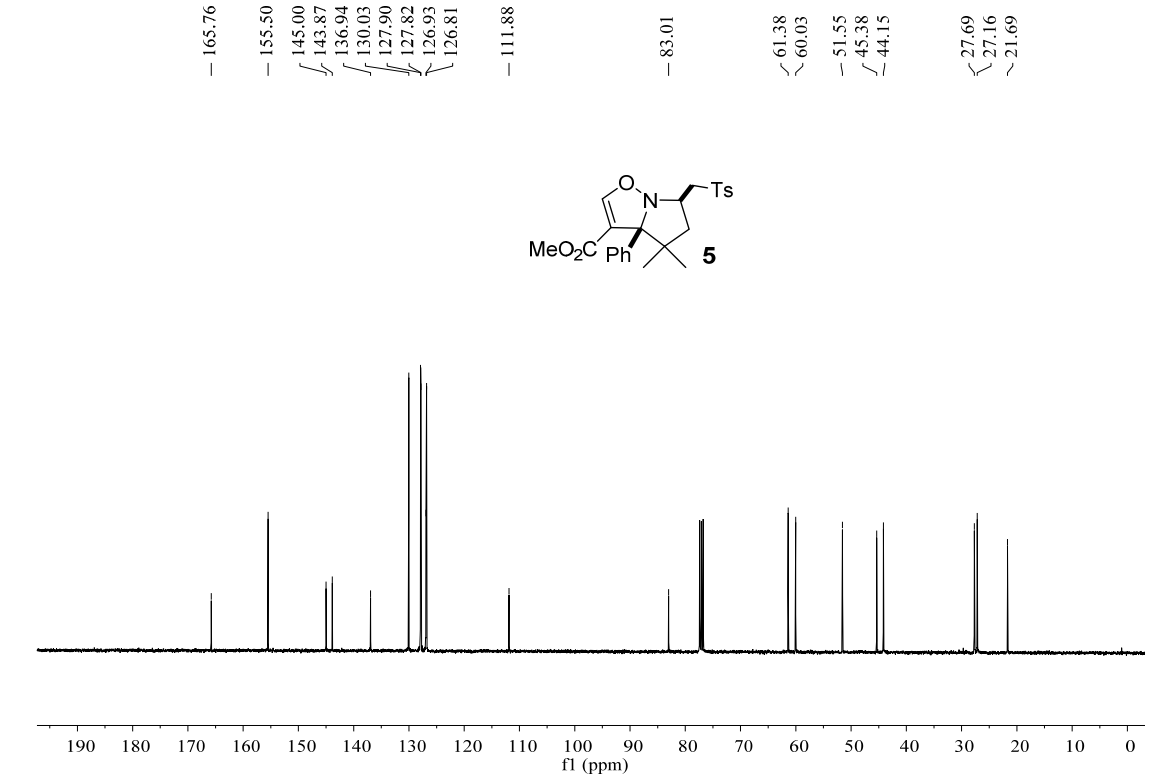
3.31
3.31
3.28
2.39
1.97
1.96
1.94
1.93
1.60
1.57
1.54
1.25
0.71
Ts
MeO2C
Ph
5
2.00
2.01
3.04
2.02
1.00
5.01
1.00
3.00
1.01
1.15
3.07
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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83.01
61.38
60.03
51.55
45.38
44.15
27.69
27.16
21.69
Ts
MeO2C
Ph
5
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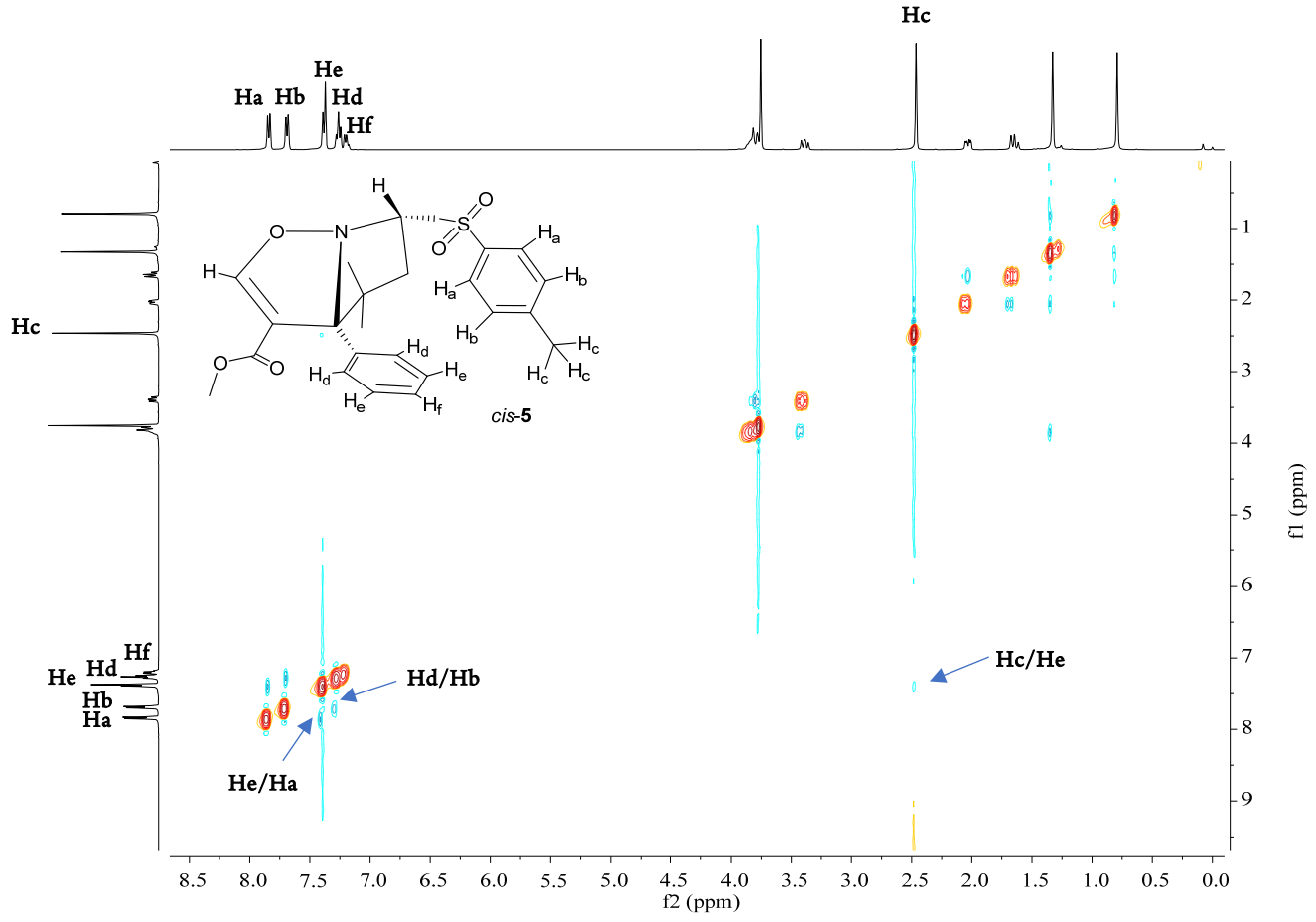
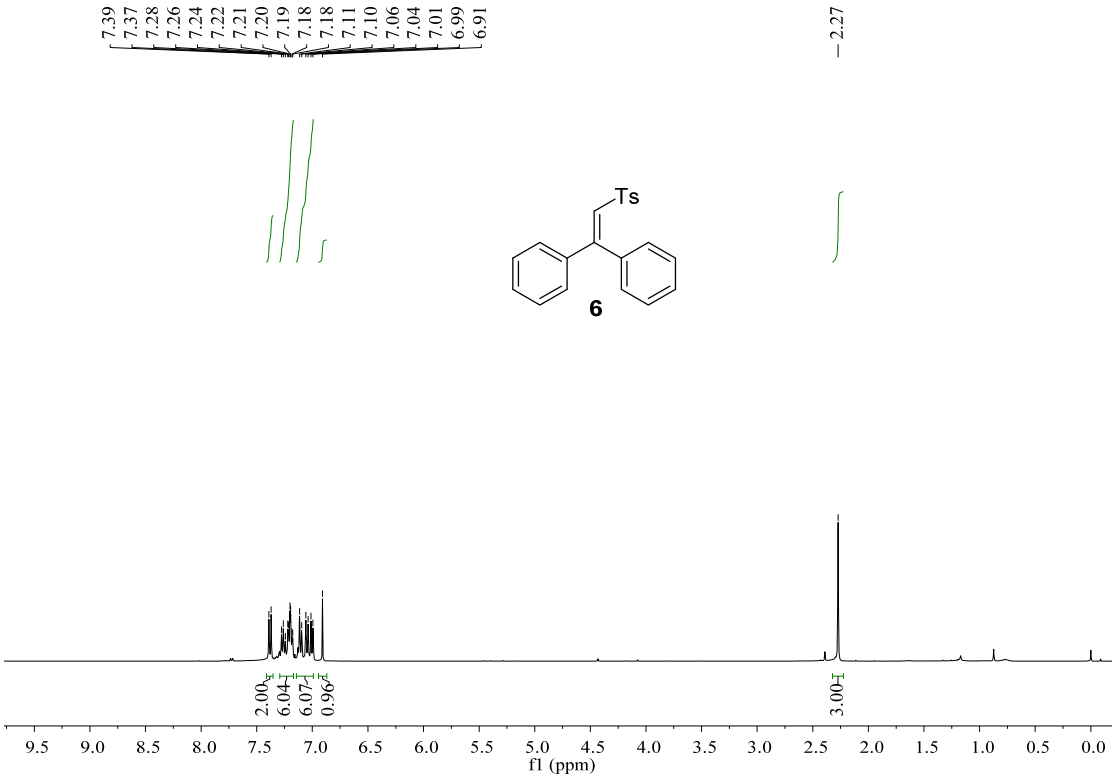
f1 (ppm)


Hc
He
Ha Hb Hd
Hf
Hc
Hf
He Hd
Hb
Ha
Hd/Hb
He/Ha
Hc/He
cis-5
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
f2 (ppm)
f1 (ppm)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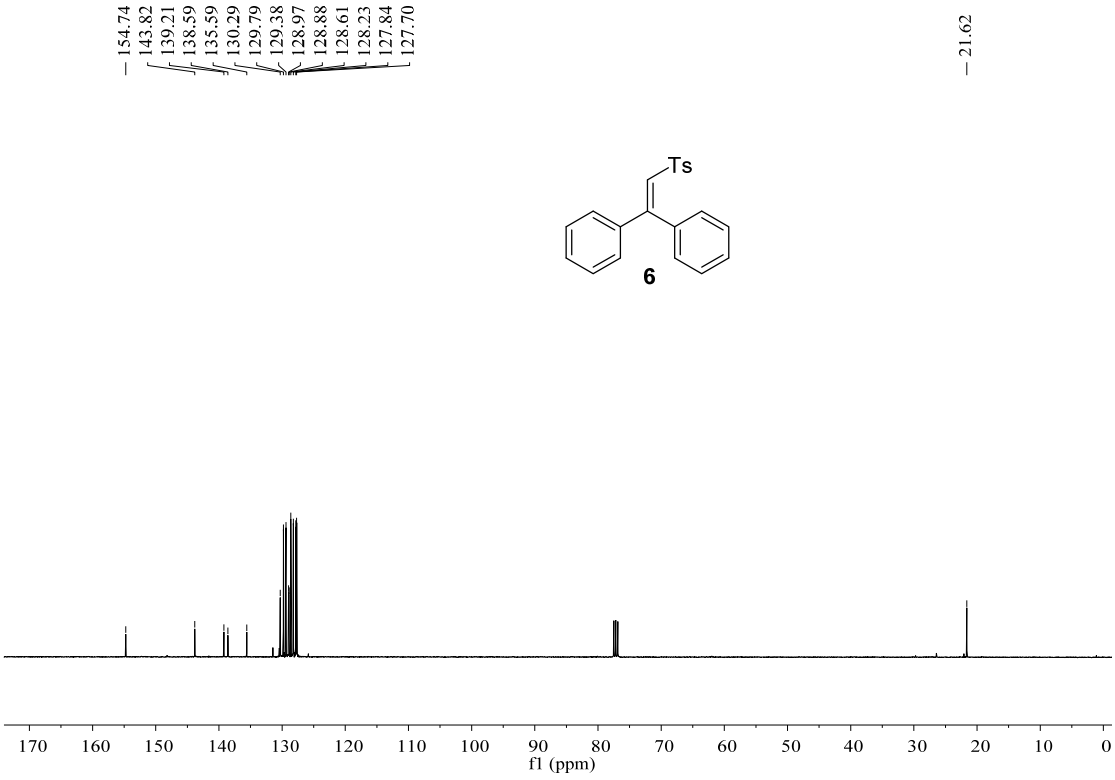
7.11
7.10
7.06
7.04
7.01
6.99
6.91
2.27
Ts
6
2.00
6.04
6.07
0.96
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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21.62
Ts
6
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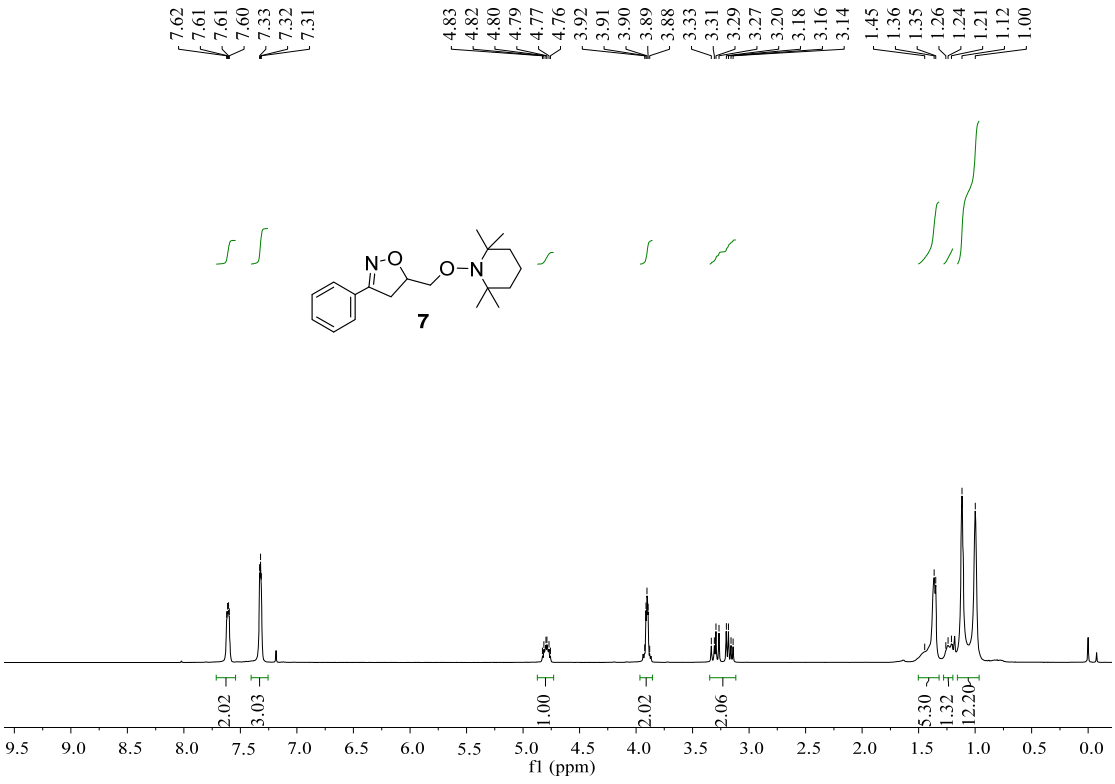
f1 (ppm)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4.76
3.92
3.91
3.90
3.89
3.88
3.33
3.31
3.29
3.27
3.20
3.18
3.16
3.14
1.45
1.36
1.35
1.26
1.24
1.21
1.12
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N-O
O-N
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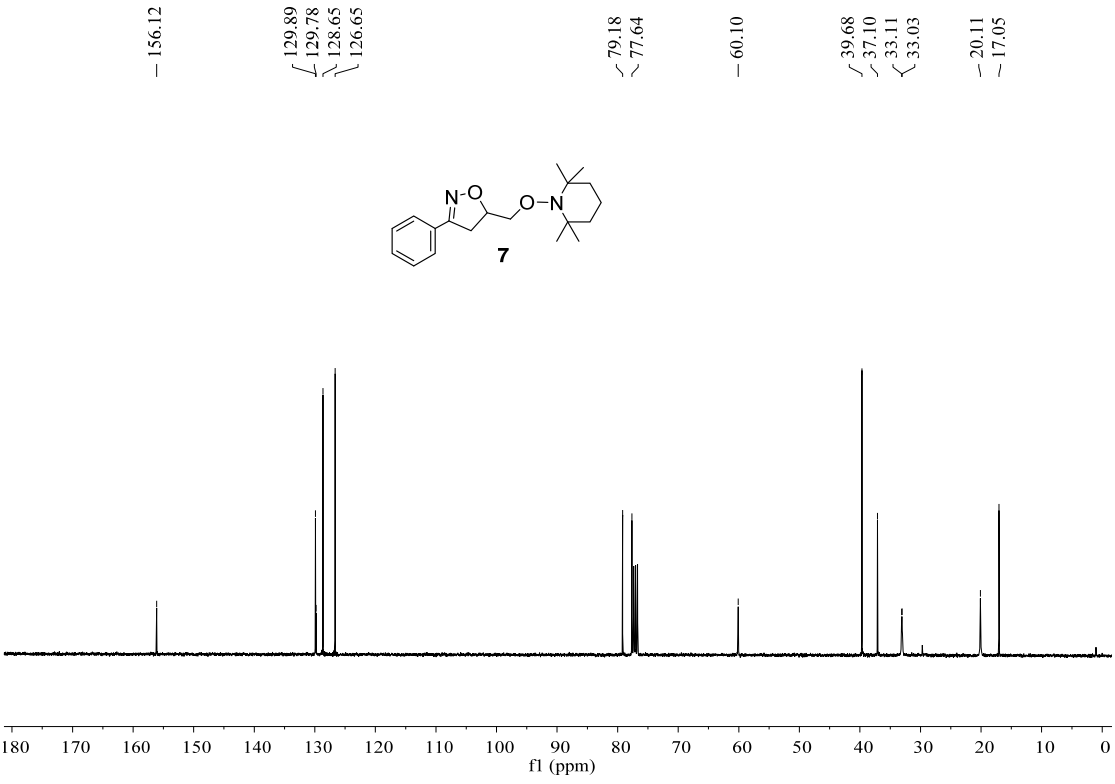
1.32
12.20
f1 (ppm)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60.10
39.68
37.10
33.11
33.03
20.11
17.05
N-O
O-N
7
f1 (ppm)

5. References

1. Hyun-Suk, Y.; Eunsu, S.; Seunghoon, S. *Chem. Eur. J.* **2011,** *17,* 1764.