Supporting Information for

Efficient 2-Sulfolmethyl Quinoline Formation from 2-Methylquinolines and Sodium Sulfinates under Transition-Metal Free Conditions

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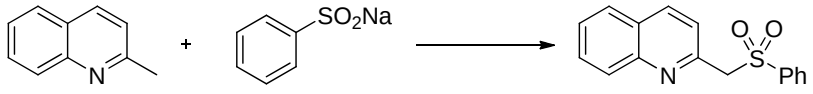
General information:

All experiments were carried out under an atmosphere of air. Flash column chromatography was performed over silica gel 48-75 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at Institute of Chemistry, Chinese Academy of Sciences. The structures of known compounds were further corroborated by comparing their NMR data and MS data with those of literature. Reagents were used as received or prepared by our laboratory.

Optimization of reaction conditions

Table S1. Optimization of reaction conditions [a]



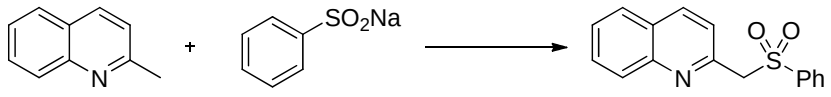
1a **2a** **3a**

Entry	Additives	Oxidant	Solvent	Yield[b] [%]
1	I_2	TBHP	DMSO:AcOH (1:1)	60
2	NIS	TBHP	DMSO:AcOH (1:1)	32
3	TBAI	TBHP	DMSO:AcOH (1:1)	61
4	CuI	TBHP	DMSO:AcOH (1:1)	23
5	NaI	TBHP	DMSO:AcOH (1:1)	73
6	NH_4I	TBHP	DMSO:AcOH (1:1)	83
7	KI	TBHP	DMSO:AcOH (1:1)	92
8	KI	TBP	DMSO:AcOH (1:1)	55
9	KI	Oxone	DMSO:AcOH (1:1)	53
10	KI	$K_2S_2O_8$	DMSO:AcOH (1:1)	34
11	KI	H_2O_2	DMSO:AcOH (1:1)	70
12	KI	O_2	DMSO:AcOH (1:1)	62
13	KI	TBHP	DMSO	1
14	KI	TBHP	AcOH	46
15	KI	TBHP	PhCl	2
16	KI	TBHP	anisole	3
17	KI	TBHP	toluene	0
18	KI	TBHP	DMSO:AcOH (2:1)	81
19	KI	TBHP	DMSO:AcOH (1:2)	83
20[c]	KI	TBHP	DMSO:AcOH (1:1)	77
21[d]	KI	TBHP	DMSO:AcOH (1:1)	84
22[e]	KI	TBHP	DMSO:AcOH (1:1)	72

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.25 mmol), catalyst (0.5 mmol, for I_2 0.25 mmol), oxidant (0.5 mmol), solvent (1.6 mL), 80 °C, 16 h under air. [b] GC yield based on **1a**. [c] 40 °C. [d] KI (0.25 mmol). [e] 0.25 mmol TBHP.

Optimization of reaction conditions under oxygen atmosphere

Table S2. Optimization of reaction conditions under oxygen atmosphere [a]

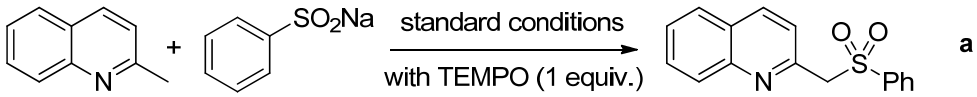


1a **2a** **3a**

Entry	Additives	Solvent	Yield[b] [%]
1	NIS	DMSO:AcOH (1:1)	30
2	TBAI	DMSO:AcOH (1:1)	45
3	CuI	DMSO:AcOH (1:1)	20
4	KI	DMSO:AcOH (1:1)	62
5	KI	DMSO	2
6	KI	AcOH	3
7	KI	PhCl	2
8	KI	anisole	3
9	KI	toluene	0
10	KI	DMSO:AcOH (2:1)	42
11	KI	DMSO:AcOH (1:2)	35
12[c]	KI	DMSO:AcOH (1:1)	51
13[d]	KI	DMSO:AcOH (1:1)	80
14[e]	KI	DMSO:AcOH (1:1)	65

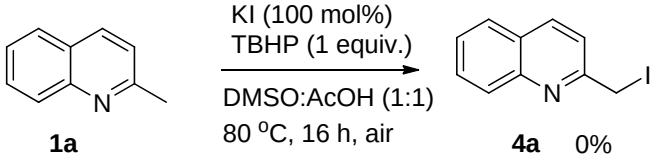
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.25 mmol), catalyst (0.5 mmol, for I_2 0.25 mmol), solvent (1.6 mL), 80 °C, 16 h under O_2. [b] GC yield based on **1a**. [c] 100 °C. [d] TBHP (0.25 mmol). [e] 24 h.

General procedure for the control experiments:



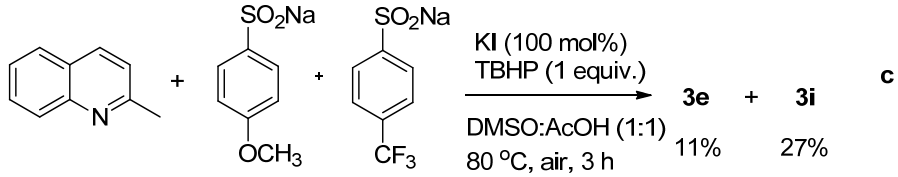
1a **2a** **3a** 0% **a**

A 10 mL oven-dried reaction vessel was charged with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol), KI (83.3 mg, 0.5 mmol), 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (78 mg, 0.5 mmol), 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol), acetic acid (0.8 mL) and DMSO (0.8 mL) under air. Finally TBHP (75 μL, 0.5 mmol) was slowly added to the reaction vessel by syringe. The resulting solution was stirred at 80 °C for 16 h, and no desired product **3a** was observed.



1a **4a** 0% **b**

A 10 mL oven-dried reaction vessel was charged with KI (83.3 mg, 0.5 mmol), 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol), acetic acid (0.8 mL) and DMSO (0.8 mL) under air. Finally TBHP (75 μL, 0.5 mmol) was slowly added to the reaction vessel by syringe. The resulting solution was stirred at 80 ^{o}C for 16 h, and no 2-(iodomethyl)quinoline was observed.

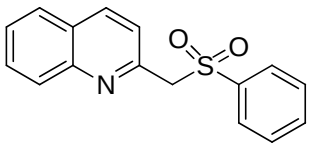


A 10 mL oven-dried reaction vessel was charged with sodium 4-methoxybenzenesulfinate (**2e**, 38.8 mg, 0.2 mmol), sodium 4-(trifluoromethyl)benzenesulfinate (**2i**, 46.4 mg, 0.2 mmol), KI (33.3 mg, 0.2 mmol), 2-methylquinoline (**1a**, 27 μL, 0.2 mmol), acetic acid (0.8 mL) and DMSO (0.8 mL) under air. Finally TBHP (30 μL, 0.2 mmol) was slowly added to the reaction vessel by syringe. The resulting solution was stirred at 80 ^{o}C for 3 h, and C-H sulfenylation products **3e** and **3i** were determined by GC in ratio 1:2.5.

General procedure: (3a):

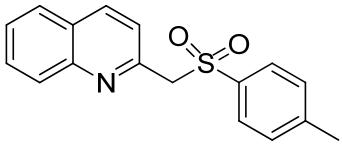
A 10 mL oven-dried reaction vessel was charged with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol), KI (83.3 mg, 0.5 mmol), 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol), acetic acid (0.8 mL) and DMSO (0.8 mL) under air. Finally TBHP (75 μL, 0.5 mmol) was slowly added to the reaction vessel by syringe. The resulting solution was stirred at 80 ^{o}C for 16 h. The volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3a** as white solid; yield: 129.8 mg (92%), mp 122-124 ^{o}C.

2-((Phenylsulfonyl)methyl)quinoline (3a, CAS: 65492-27-5)[1]



^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (d, J = 8.4 Hz, 1H), 7.83-7.81 (m, 2H), 7.68-7.66 (m, 3H), 7.60-7.53 (m, 3H), 7.43-7.39 (m, 2H), 4.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.2, 147.7, 138.3, 136.7, 133.7, 129.7, 129.1, 128.8, 128.4, 127.5, 127.2, 127.0, 122.6, 65.2.

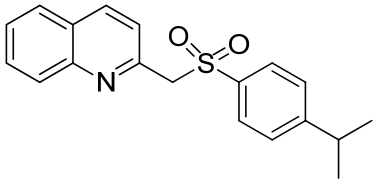
2-(Tosylmethyl)quinoline (3b, CAS: 69722-31-2)[2]



The reaction was conducted with sodium 4-methylbenzenesulfinate (**2b**, 222.5 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3b** as red solid; yield: 148 mg (90%), mp 161.1-162.5 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (d, J = 8.2 Hz, 1H), 7.88-7.81 (m, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.60-7.55 (m, 4H), 7.21 (d, J = 7.4 Hz, 2H), 4.72 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.3, 147.7, 144.6, 136.6, 135.4, 129.6, 129.4, 129.0, 128.3, 127.4, 127.2, 126.9, 122.5, 65.2, 21.4.

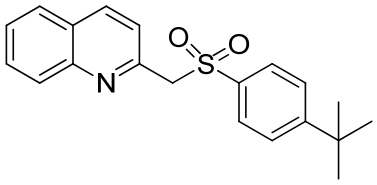
2-(((4-*iso*-Propylphenyl)sulfonyl)methyl)quinoline (3c)



The reaction was conducted with sodium 4-*iso*-propylbenzenesulfinate (**2c**, 257 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3c** as yellow solid; yield: 124 mg (76%), mp 106.4-107.2 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.16 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.60-7.52 (m, 4H), 7.23 (d, J = 8.0 Hz, 2H), 4.72 (s, 2H), 2.95-2.88 (m, 1H), 1.22-1.20 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.4, 149.4, 147.8, 136.7, 135.5, 129.7, 129.1, 128.6, 127.5, 127.3, 127.0, 126.9, 122.7, 65.3, 34.2, 23.5; HRMS calcd. for: $C_{19}H_{19}NO_2SNa$ $[M+Na]^+$ 348.1028, found 348.1022.

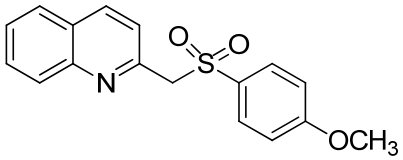
2-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)quinoline (3d)



The reaction was conducted with sodium 4-(*tert*-butyl)benzenesulfinate (**2d**, 275 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3d** as red solid; yield: 115.7 mg (68%), mp 151.2-153.4 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 8.3 Hz, 2H), 7.68-7.53 (m, 5H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.72 (s, 2H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 157.6, 149.4, 147.8, 136.7, 135.2, 129.6, 129.1, 128.3, 127.5, 127.2, 127.0, 125.8, 122.7, 65.3, 35.1, 30.9; HRMS calcd. for: $C_{20}H_{21}NO_2SNa$ $[M+Na]^+$ 362.1185, found 362.1179.

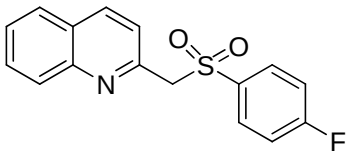
2-(((4-Methoxyphenyl)sulfonyl)methyl)quinoline (3e)



The reaction was conducted with sodium 4-methoxybenzenesulfinate (**2e**, 242.5 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3e** as yellow solid; yield: 142 mg (90%), mp 149.1-150.8 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): *δ* 8.17 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.70-7.66 (m, 1H), 7.60-7.53 (m, 4H), 6.87-6.83 (m, 2H), 4.72 (s, 2H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): *δ* 163.8, 149.5, 147.7, 136.9, 130.7, 129.8, 129.8, 129.1, 127.5, 127.3, 127.1, 122.7, 114.1, 65.4, 55.6; HRMS calcd. for: $C_{17}H_{15}NO_3SNa$ $[M+Na]^+$ 336.0664, found 336.0661.

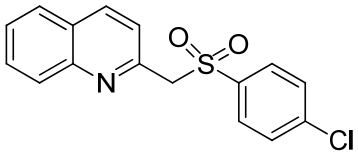
2-(((4-Fluorophenyl)sulfonyl)methyl)quinoline (3f)



The reaction was conducted with sodium 4-fluorobenzenesulfinate (**2f**, 227.5 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3f** as yellow solid; yield: 100.1 mg (62%), mp 125.8-128.1 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.19 (d, J = 8.2 Hz, 1H), 7.83-7.81 (m, 2H), 7.70-7.55 (m, 5H), 7.07 (t, J = 8.4 Hz, 2H), 4.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 166.9 (J = 255 Hz), 149.3, 147.9, 136.9, 131.5, 131.4, 130.0, 129.2, 127.6, 127.4, 127.2, 122.7, 116.1 (J = 22.6 Hz), 65.4; HRMS calcd. for: $C_{16}H_{13}FNO_2S$ $[M+H]^+$ 302.0645, found 302.0646.

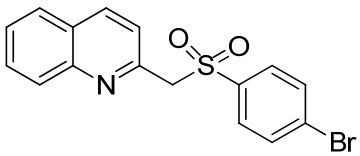
2-(((4-Chlorophenyl)sulfonyl)methyl)quinoline (3g)[3]



The reaction was conducted with sodium 4-chlorobenzenesulfinate (**2g**, 247.5 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3g** as white solid; yield: 112 mg (71%), mp 147.8-148.9 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.19 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.60-7.56 (m, 4H), 7.37 (d, J = 8.2 Hz, 2H), 4.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.1, 147.9, 140.5, 137.0, 130.1, 130.0, 130.0, 129.2, 129.2, 127.6, 127.4, 127.3, 122.7, 65.3.

2-(((4-Bromophenyl)sulfonyl)methyl)quinoline (3h)

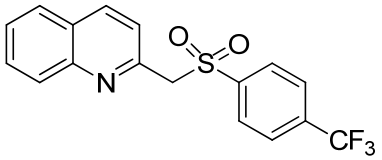


The reaction was conducted with sodium 4-bromobenzenesulfinate (**2h**, 302.5 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3h** as white solid; yield: 130 mg (72%), mp 134.8-135.9 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.19 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.70 (t, J

= 7.6 Hz, 1H), 7.60-7.48 (m, 6H), 4.72 (s, 2H); ^{13}C NMR (100 MHz, CDCl3, ppm): δ 149.1, 147.9, 137.5, 137.0, 132.2, 130.1, 130.0, 129.2, 129.1, 127.6, 127.4, 127.3, 122.7, 65.3. HRMS calcd. for: $C_{16}H_{13}BrNO_2S$ $[M+H]^+$ 361.9844, found 361.9842.

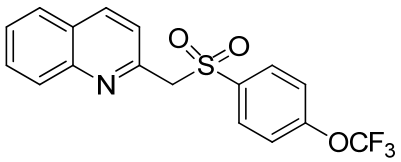
2-(((4-(Trifluoromethyl)phenyl)sulfonyl)methyl)quinoline (3i)



The reaction was conducted with sodium 4-(trifluoromethyl)benzenesulfinate (**2i**, 290 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3i** as white solid; yield: 82.5 mg (47%), mp 180.5-181.4 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.21 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 9.6 Hz, 3H), 7.70-7.65 (m, 3H), 7.62-7.55 (m, 2H), 4.76 (s, 2H); ^{13}CNMR (100 MHz, $CDCl_3$, ppm): δ 148.8, 147.8, 141.7, 137.1, 135.4 (q, J = 73.0 Hz), 130.1, 129.3, 129.0, 127.6, 127.4, 127.3, 123.1 (q, J = 271.0 Hz), 125.9 (q, J = 36.9 Hz), 122.6, 65.1; HRMS calcd. for: $C_{17}H_{13}F_3NO_2S$ $[M+H]^+$ 352.0613, found 352.0611.

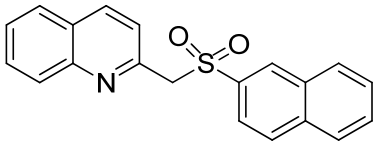
2-(((4-(Trifluoromethoxy)phenyl)sulfonyl)methyl)quinoline (3j)



The reaction was conducted with sodium 4-(trifluoromethoxy)benzenesulfinate (**2j**, 310 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3j** as dark solid; yield: 130 mg (71%), mp 141.8-143.2 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.20 (d, J = 8.4 Hz, 1H), 7.84-7.54 (m, 7H), 7.21 (d, J = 8.2 Hz, 2H), 4.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.0, 149.1, 147.8, 137.0, 136.5, 130.9, 130.0, 129.1, 127.5, 127.3, 127.26, 120.2 (q, J = 258 Hz), 122.6, 120.6, 65.3; HRMS calcd. for: $C_{17}H_{13}F_3NO_3S$ $[M+H]^+$ 368.0562, found 368.0561.

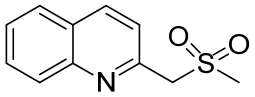
2-((Naphthalen-2-ylsulfonyl)methyl)quinoline (3k)



The reaction was conducted with sodium naphthalene-2-sulfinate (**2k**, 267.5 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3k** as yellow solid; yield: 85 mg (51%), mp 170.1-171.6 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.29 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.89-7.80 (m, 4H), 7.74 (d, J = 8.4 Hz, 1H), 7.66-7.51 (m, 6H), 4.81 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.4, 147.9, 136.8, 135.6, 135.4, 132.1, 130.5, 129.8, 129.4, 129.2, 129.18, 129.1, 127.9, 127.5, 127.4, 127.4, 127.1, 123.1, 122.7, 65.4; HRMS calcd. for: $C_{20}H_{15}NO_2SNa$ $[M+Na]^+$ 356.0715, found 356.0714.

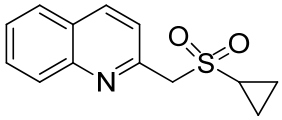
2-((Methylsulfonyl)methyl)quinoline (3l, CAS: 19499-11-7)[4]



The reaction was conducted with sodium methanesulfinate (**2l**, 127.5 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give **3l** as yellow solid; yield: 55 mg (50%), mp 187.8-191.5 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.24 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1H), 7.62-7.59 (m, 2H), 4.61 (s, 2H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 150.0, 148.0, 137.4, 130.1, 129.2, 127.7, 127.5, 127.3, 122.8, 63.7, 40.1.

2-((Cyclopropylsulfonyl)methyl)quinoline (3m)

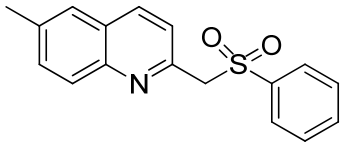


The reaction was conducted with sodium cyclopropanesulfinate (**2m**, 160 mg, 1.25 mmol) and 2-methylquinoline (**1a**, 67.5 μL, 0.5 mmol). The residue was purified by column chromatography

(silica gel, petroleum ether/ethyl acetate = 7:1) to give **3m** as yellow solid; yield: 69 mg (56%), mp 118-120 ^{o}C

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.22 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.66-7.57 (m, 2H), 4.68 (s, 2H), 2.47-2.40 (m, 1H), 1.13-1.10 (m, 2H), 0.97-0.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 149.9, 147.9, 137.0, 130.0, 129.2, 127.6, 127.4, 127.1, 122.7, 63.0, 29.3, 4.9; HRMS calcd. for: $C_{13}H_{14}NO_2S$ $[M+H]^+$ 248.0739, found 248.0739.

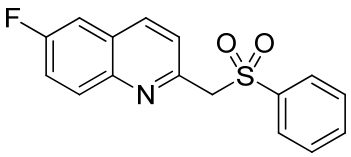
6-Methyl-2-((phenylsulfonyl)methyl)quinoline (3n)



The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 2,6-dimethylquinoline (**1b**, 78.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **3n** as white solid; yield: 127.7 mg (86%), mp 132.5-133.7 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.07 (d, J = 8.4 Hz, 1H), 7.72-7.64 (m, 3H), 7.57-7.48 (m, 4H), 7.40 (t, J = 7.6 Hz, 2H), 4.71 (s, 2H), 2.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 148.2, 146.4, 138.3, 137.1, 136.1, 133.6, 132.1, 128.8, 128.79, 128.5, 127.3, 126.3, 122.6, 65.2, 21.5; HRMS calcd. for: $C_{17}H_{15}NO_2SNa$ $[M+Na]^+$ 320.0715, found 320.0713.

6-Fluoro-2-((phenylsulfonyl)methyl)quinoline (3o)

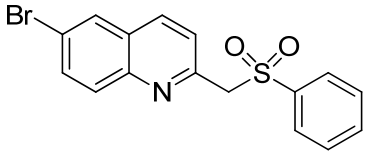


The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 6-fluoro-2-methylquinoline (**1c**, 80.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give **3o** as white solid; yield: 112.8 mg (75%), mp 161-162.5^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.13 (d, J = 8.4 Hz, 1H), 7.83 (m, 1H), 7.67 (d, J = 7.6 Hz,

2H), 7.59 (m, 2H), 7.43 (m, 4H), 4.72 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 160.7 (d, J = 248 Hz), 148.5, 144.9, 138.1, 136.2, 133.8, 131.6 (d, J = 9.3 Hz), 128.9, 128.4, 127.9 (d, J = 10.4 Hz), 123.4, 120.1 (d, J = 25.8 Hz), 110.5 (d, J = 21.7 Hz), 65.0; HRMS calcd. for: $C_{16}H_{12}FNO_2SNa$ $[M+Na]^+$ 324.0465, found 324.0463.

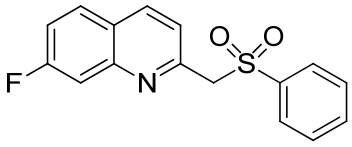
6-Bromo-2-((phenylsulfonyl)methyl)quinoline (3p)



The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 6-bromo-2-methylquinoline (**1d**, 111 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **3p** as yellow solid; yield: 157 mg (84%), mp 164.3-166.5 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (d, J = 8.4 Hz, 1H), 7.98 (s, 1H), 7.74-7.65 (m, 4H), 7.61-7.56 (m, 2H), 7.42 (t, J = 7.6 Hz, 2H), 4.71 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 149.7, 146.3, 138.2, 135.7, 133.7, 133.2, 130.8, 129.5, 128.9, 128.4, 128.3, 123.5, 121.0, 65.1; HRMS calcd. for: $C_{16}H_{13}BrNO_2S$ $[M+H]^+$ 361.9844, found 361.9841.

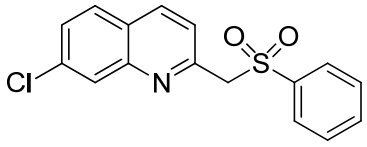
7-Fluoro-2-((phenylsulfonyl)methyl)quinoline (3q)



The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 7-fluoro-2-methylquinoline (**1e**, 80.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give **3q** as yellow solid; yield: 141.5 mg (94%), mp 141.9-142.8 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (d, J = 8.4 Hz, 1H), 7.84-7.80 (m, 1H), 7.67 (d, J = 7.8 Hz, 2H), 7.61-7.56 (m, 2H), 7.46-7.41 (m, 3H), 7.34 (t, J = 7.5 Hz, 1H), 4.72 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 163.1 (d, J = 269.3 Hz), 150.3, 148.6 (d, J = 12.6 Hz), 138.2, 136.6, 133.7, 129.5 (d, J = 9.9 Hz), 128.8, 128.3, 124.2, 122.0 (d, J = 2.4 Hz), 117.6 (d, J = 25.4 Hz), 112.6 (d, J = 20.3 Hz), 64.9; HRMS calcd. for: $C_{16}H_{13}FNO_2S$ $[M+H]^+$ 302.0645, found 302.0645.

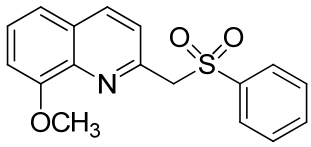
7-Chloro-2-((phenylsulfonyl)methyl)quinoline (3r)



The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 7-chloro-2-methylquinoline (**1f**, 89 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give **3r** as white solid; yield: 143 mg (90%), mp 135.6-136.8 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.15 (d, J = 8.4 Hz, 1H), 7.83 (s, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.62-7.58 (m, 2H), 7.51-7.49 (m, 1H), 7.43 (t, J = 7.7 Hz, 2H), 4.72 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 150.3, 148.0, 138.2, 136.5, 135.5, 133.7, 128.9, 128.7, 128.7, 128.3, 128.0, 125.5, 122.8, 65.0; HRMS calcd. for: $C_{16}H_{13}ClNO_2S$ $[M+H]^+$ 318.0350, found 318.0349.

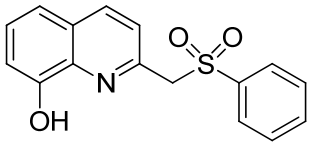
8-Methoxy-2-((phenylsulfonyl)methyl)quinoline (3s)



The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 8-methoxy-2-methylquinoline (**1g**, 86.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) to give **3s** as white solid; yield: 144 mg (92%), mp 142-143 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.13 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 7.4 Hz, 2H), 7.63-7.55 (m, 2H), 7.48-7.37 (m, 4H), 7.02 (d, J = 7.6 Hz, 1H), 4.84 (s, 2H), 3.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.2, 147.9, 139.8, 138.4, 136.8, 133.6, 128.9, 128.5, 128.48, 127.3, 123.1, 119.3, 108.3, 65.1, 56.0; HRMS calcd. for: $C_{17}H_{15}NO_3SNa$ $[M+Na]^+$ 336.0664, found 336.0660.

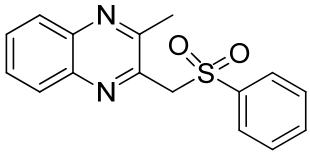
2-((Phenylsulfonyl)methyl)quinolin-8-ol (3t)



The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 2-methylquinolin-8-ol (**1h**, 79.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give **3t** as yellow solid; yield: 113.6 mg (76%), mp 157.6-159.8 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (d, J = 8.4 Hz, 1H), 7.66-7.56 (m, 4H), 7.47-7.32 (m, 5H), 7.11 (d, J = 7.5 Hz, 1H), 4.71 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 151.8, 147.2, 138.2, 137.6, 137.2, 133.9, 128.9, 128.5, 128.45, 127.6, 123.5, 117.7, 110.5, 64.7; HRMS calcd. for: $C_{16}H_{13}NO_3SNa$ $[M+Na]^+$ 322.0508, found 322.0507.

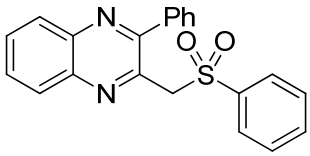
2-Methyl-3-((phenylsulfonyl)methyl)quinoxaline (3u)



The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 2,3-dimethylquinoxaline (**1i**, 79 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **3u** as white solid; yield: 74.6 mg (50%), mp 199-201 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.01 (d, J = 8.2 Hz, 1H), 7.74-7.62 (m, 6H), 7.50-7.44 (m, 2H), 4.82 (s, 2H), 2.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.1, 144.3, 141.6, 140.7, 138.1, 134.0, 130.6, 129.4, 129.1, 128.8, 128.7, 128.4, 62.1, 23.1. HRMS calcd. for: $C_{16}H_{14}N_2O_2SNa$ $[M+Na]^+$ 321.0614, found 326.0611.

2-Phenyl-3-((phenylsulfonyl)methyl)quinoxaline (3v)

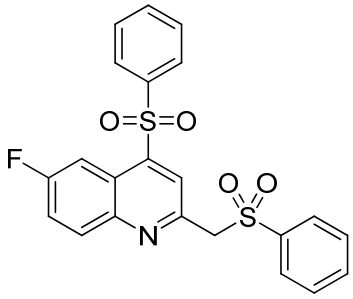


The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 2-methyl-3-phenylquinoxaline (**1j**, 110 mg, 0.5 mmol). The residue was purified by column

chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **3v** as white solid; yield: 124.2 mg (69%), mp 140-142 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.13 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.78 (m, 2H), 7.62 (m, 5H), 7.47 (m, 5H), 4.91 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.4, 143.4, 141.3, 140.9, 138.9, 137.5, 133.8, 131.0, 130.3, 129.2, 129.2, 129.2, 129.0, 128.9, 128.7, 128.6, 61.1. HRMS calcd. for: $C_{21}H_{16}N_2O_2SNa$ $[M+Na]^+$ 383.0825, found 383.0827.

6-Fluoro-4-(phenylsulfonyl)-2-((phenylsulfonyl)methyl)quinoline (3w)



The reaction was conducted with sodium benzenesulfinate (**2a**, 205 mg, 1.25 mmol) and 4-chloro-6-fluoro-2-methylquinoline (**1k**, 97.5 mg, 0.5 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give **3w** as yellow solid; yield: 163 mg (37%), mp 173-175 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.32-8.28 (m, 2H), 8.02-7.96 (m, 3H), 7.71-7.44 (m, 9H), 4.79 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 161.8 (d, J = 252 Hz), 148.4, 146.4, 145.3, 139.7, 138.2, 134.3, 134.2, 133.2, 133.1, 123.5, 129.7, 129.3, 128.4, 128.1, 123.9, 121.3 (d, J = 26 Hz), 108.4 (d, J = 26 Hz,), 64.8; HRMS calcd. for: $C_{22}H_{16}ClFNO_4S_2Na$ $[M+Na]^+$ 464.0397, found 464.0396.

References:

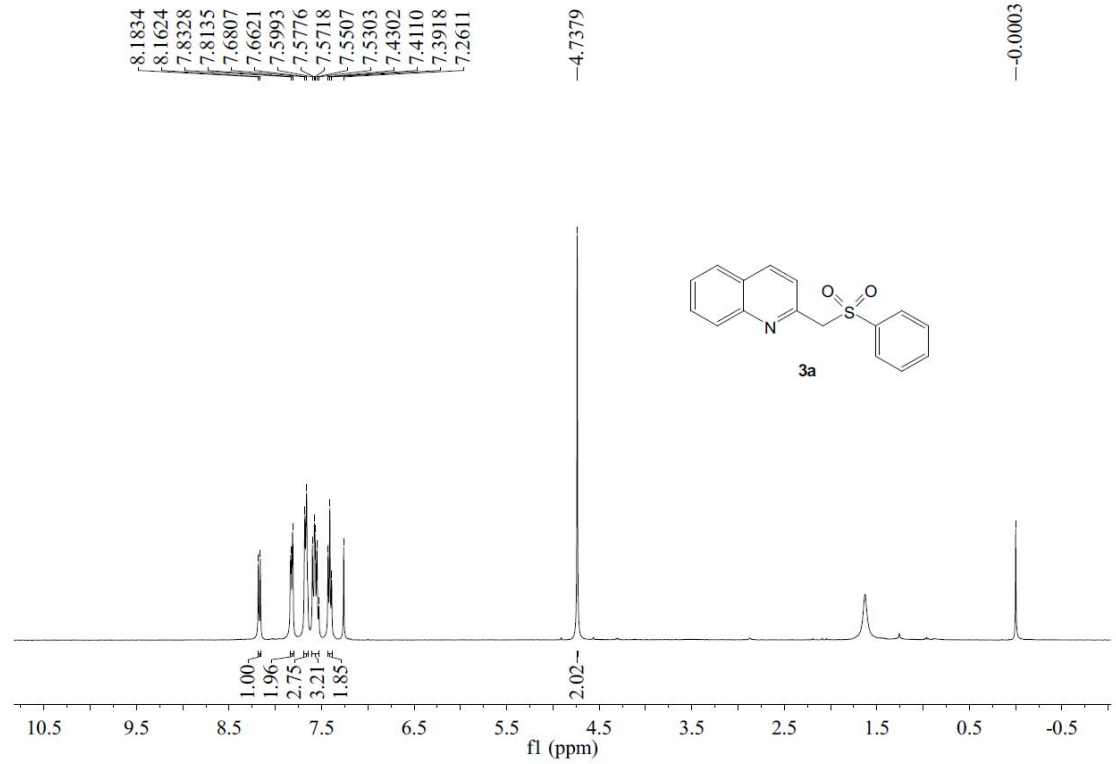
[1] D. W. Wang, X. B. Wang, D. S. Wang, S. Duo, S. M. Lu, Y. G. Zhou, Y. X. Li, *J. Org. Chem*. **2009**, *74*, 2780.

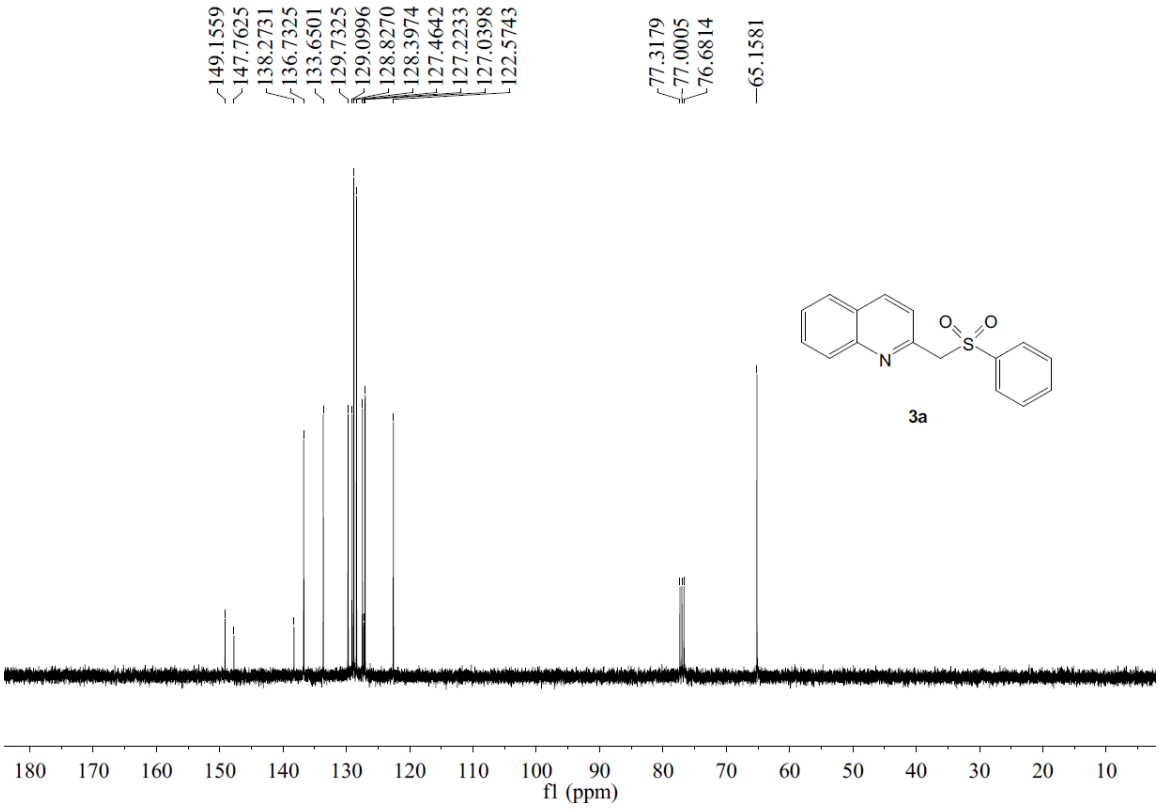
[2] E. B. Kbott, *J. Chem. Soc.* **1955**, 949.

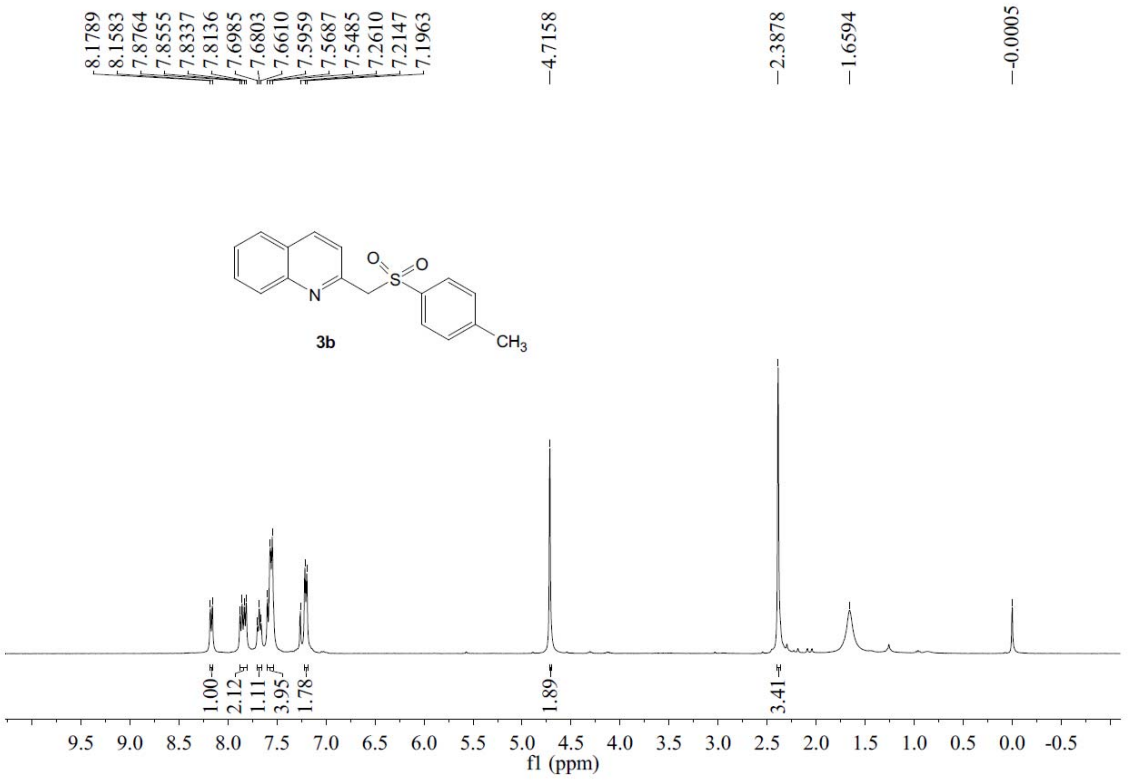
[3] I. Masayuki, K. Hideki, M. Satoru, EP 1466898 A1, 2002.

[4] J. E. Douglass, M. A. Gebhart, *J. Heterocycl. Chem.* **1990**, *27*, 1433.

^{1}H and ^{13}C NMR spectra of products



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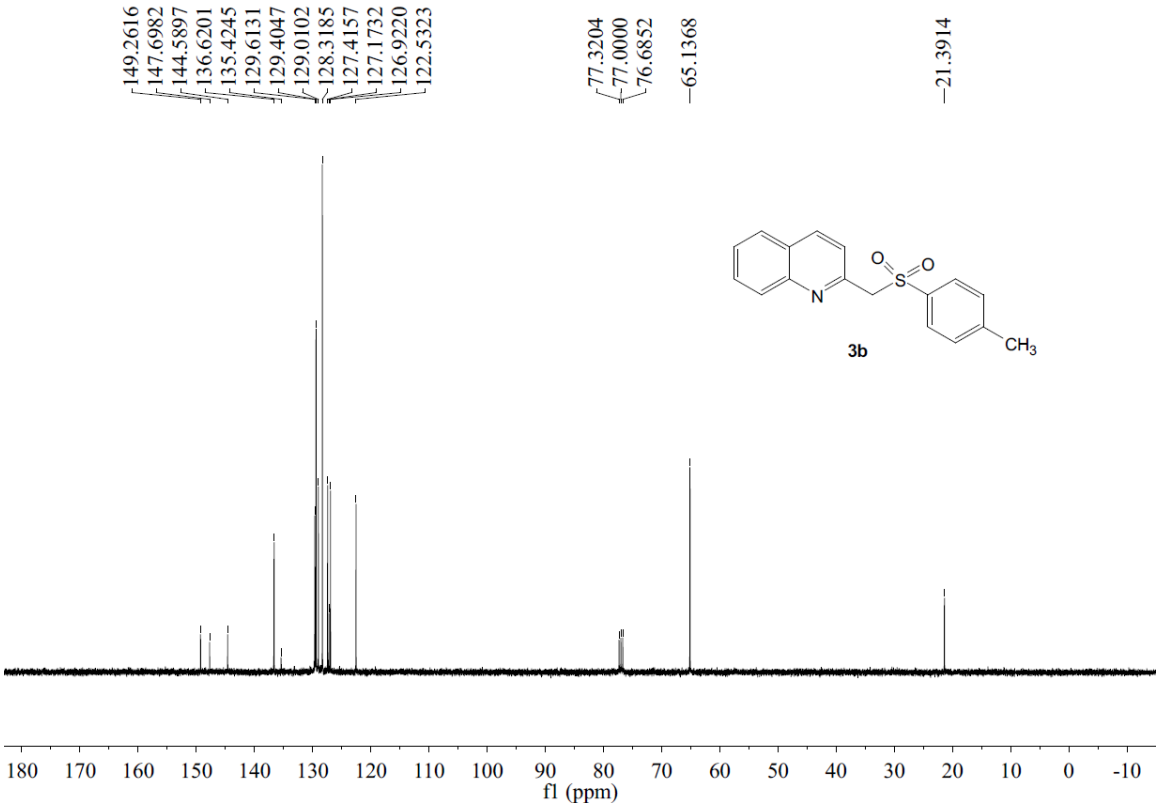
1.6594
0.0005
3b
1.00
2.12
1.11
3.95
1.78
1.89
3.41
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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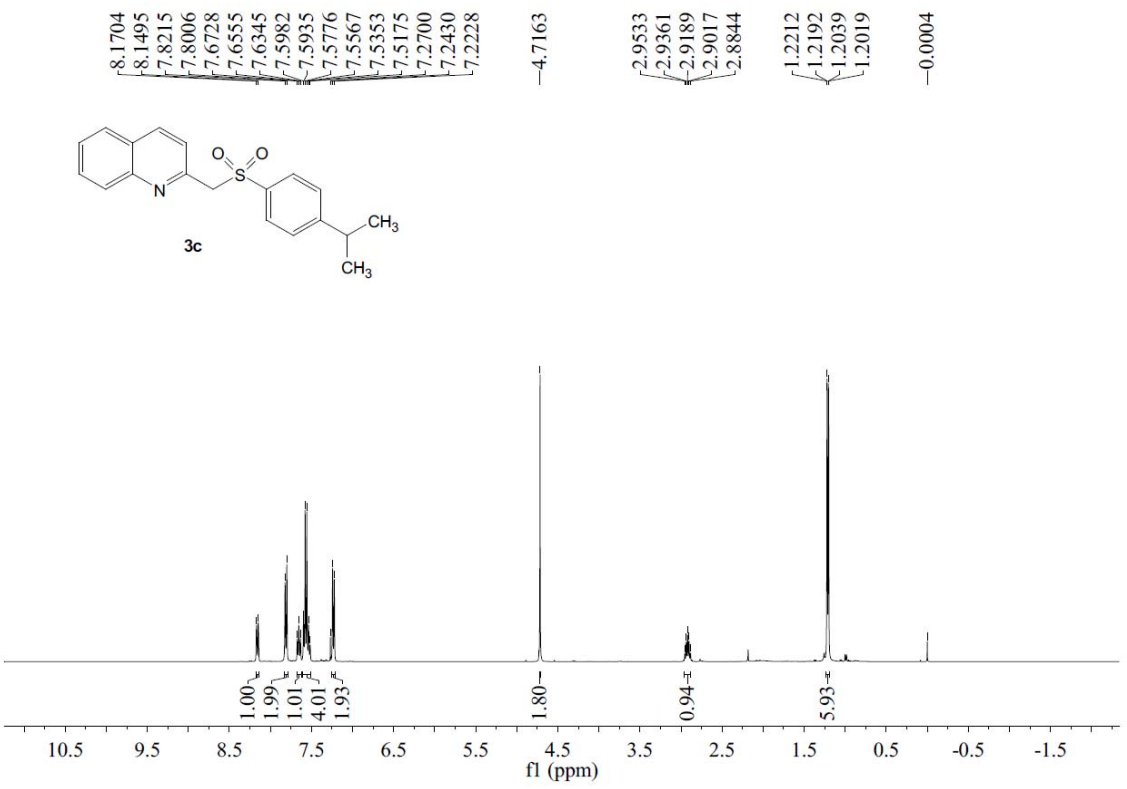
f1 (ppm)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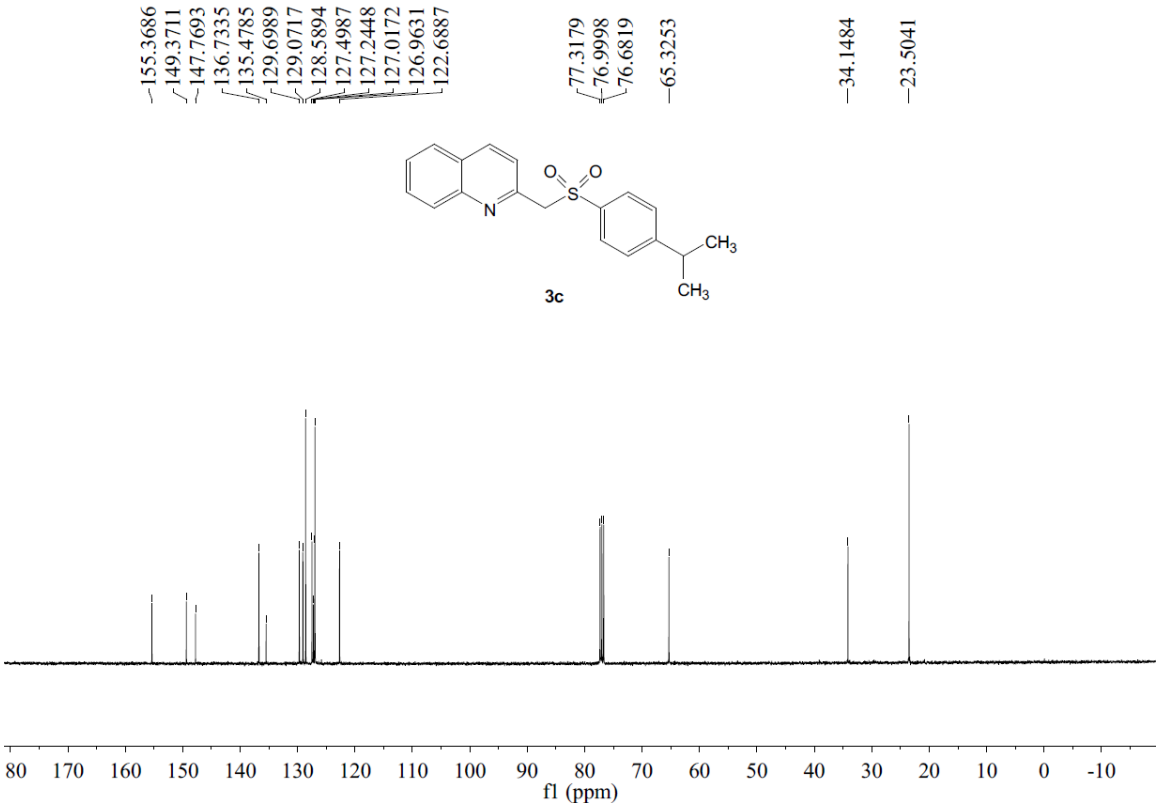
f1 (ppm)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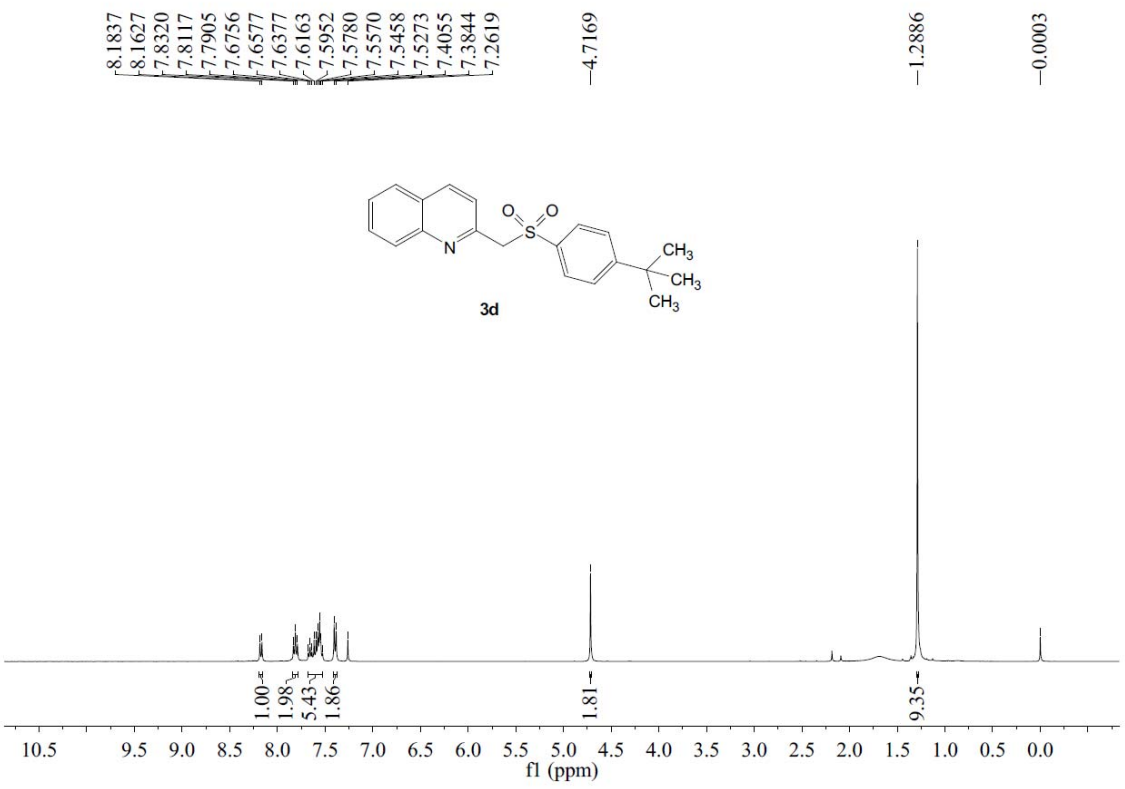
f1 (ppm)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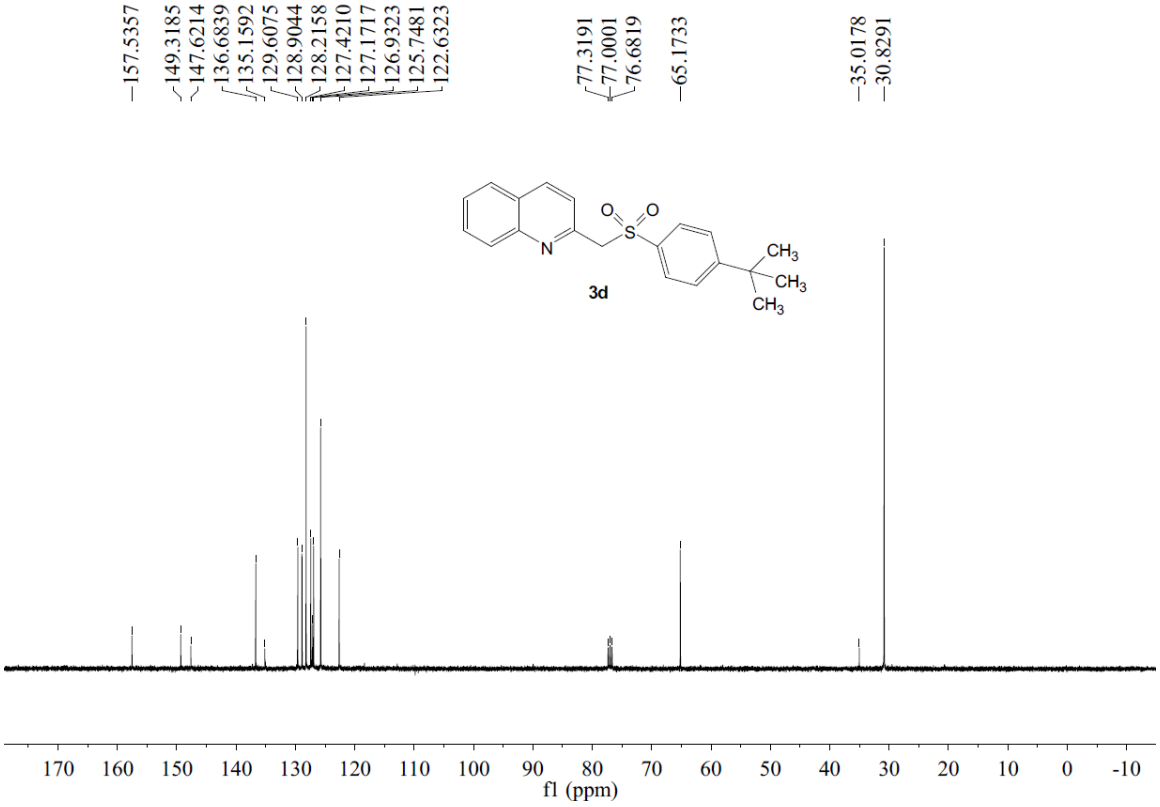
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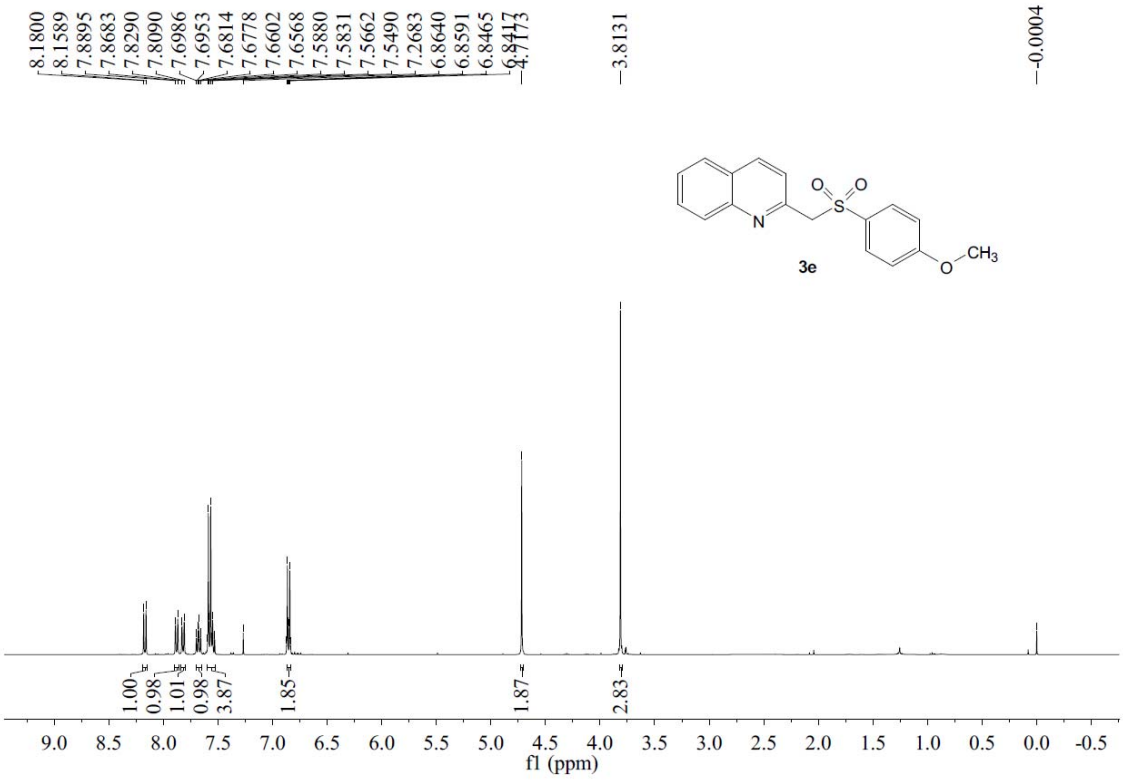
f1 (ppm)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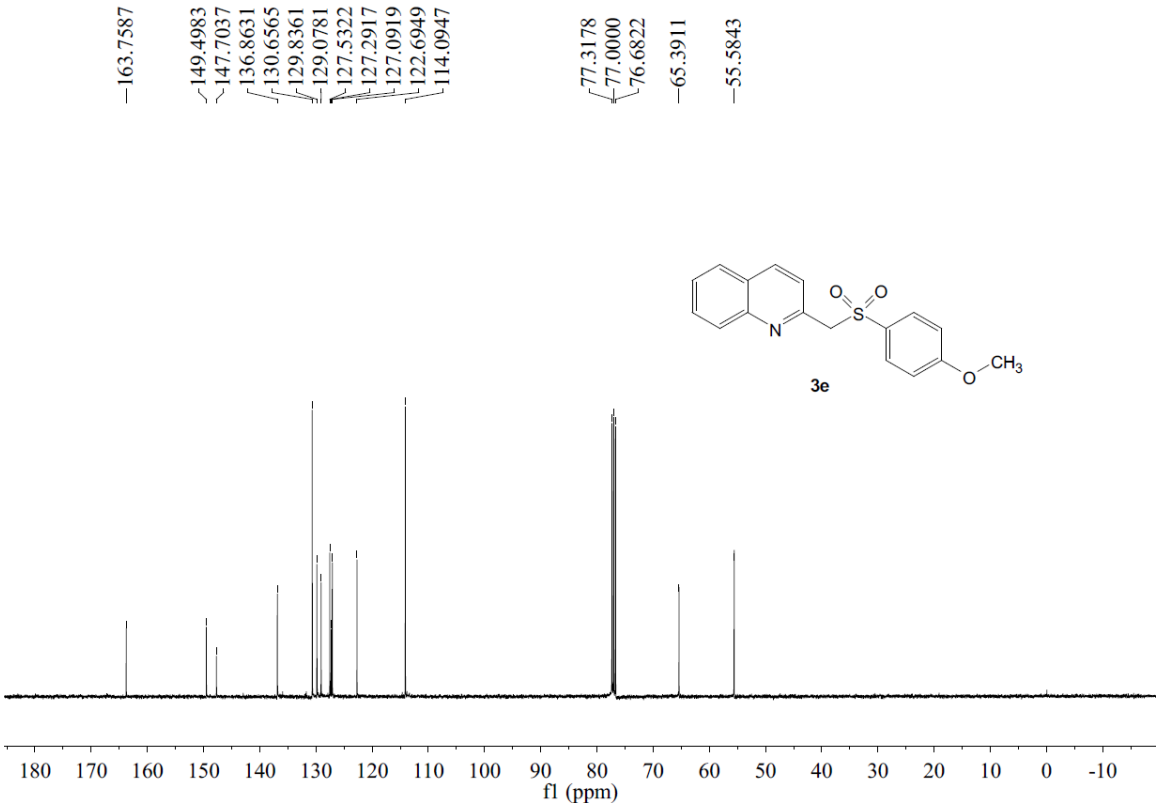
4.7173
3.8131
0.0004
3e
1.00
0.98
1.01
0.98
3.87
1.85
1.87
2.83
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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114.0947
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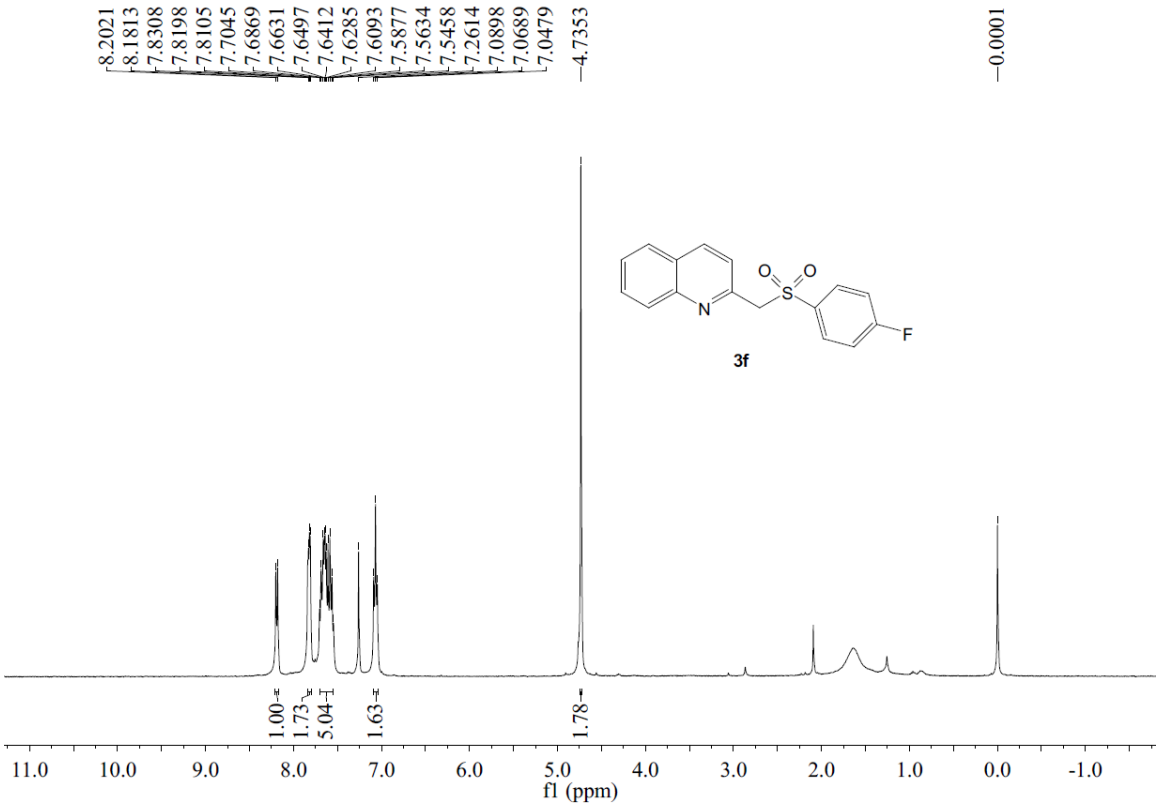
3e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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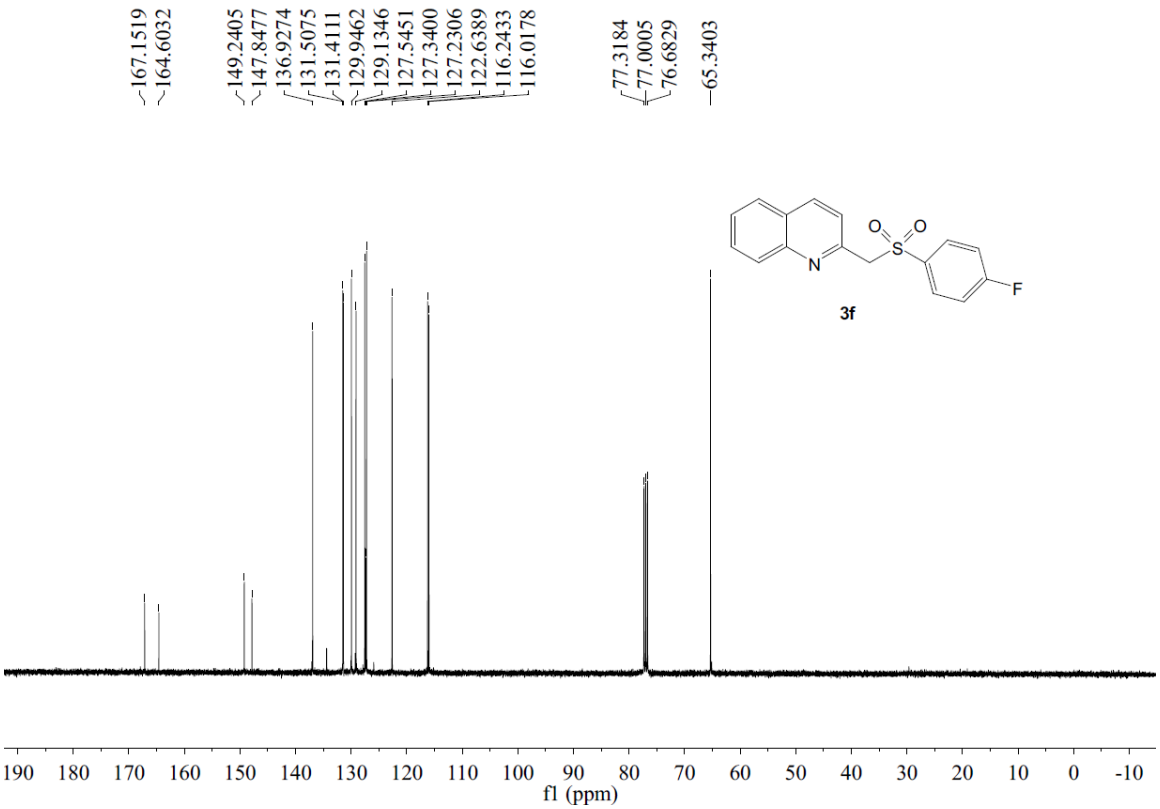
7.6412
7.6285
7.6093
7.5877
7.5634
7.5458
7.2614
7.0898
7.0689
7.0479
4.7353
0.0001
3f
1.00
1.73
5.04
1.63
1.78
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)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127.3400
127.2306
122.6389
116.2433
116.0178
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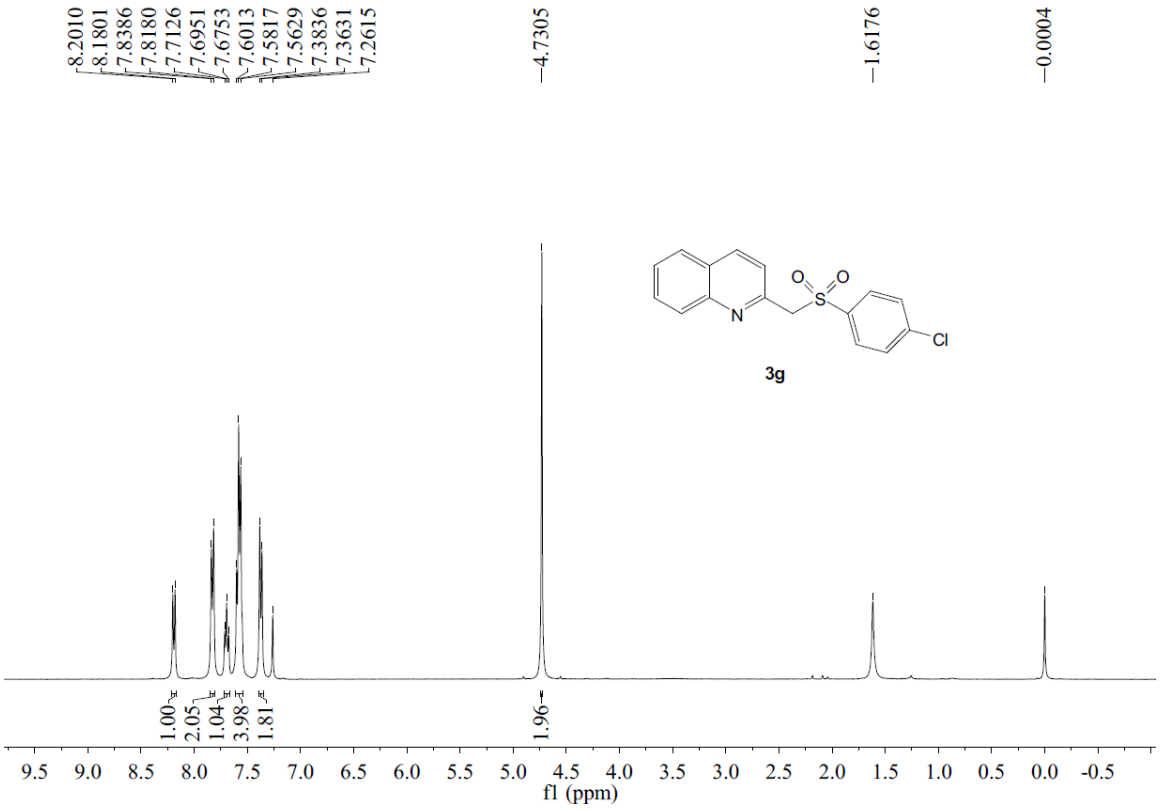
76.6829
65.3403
3f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.6753
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7.3836
7.3631
7.2615
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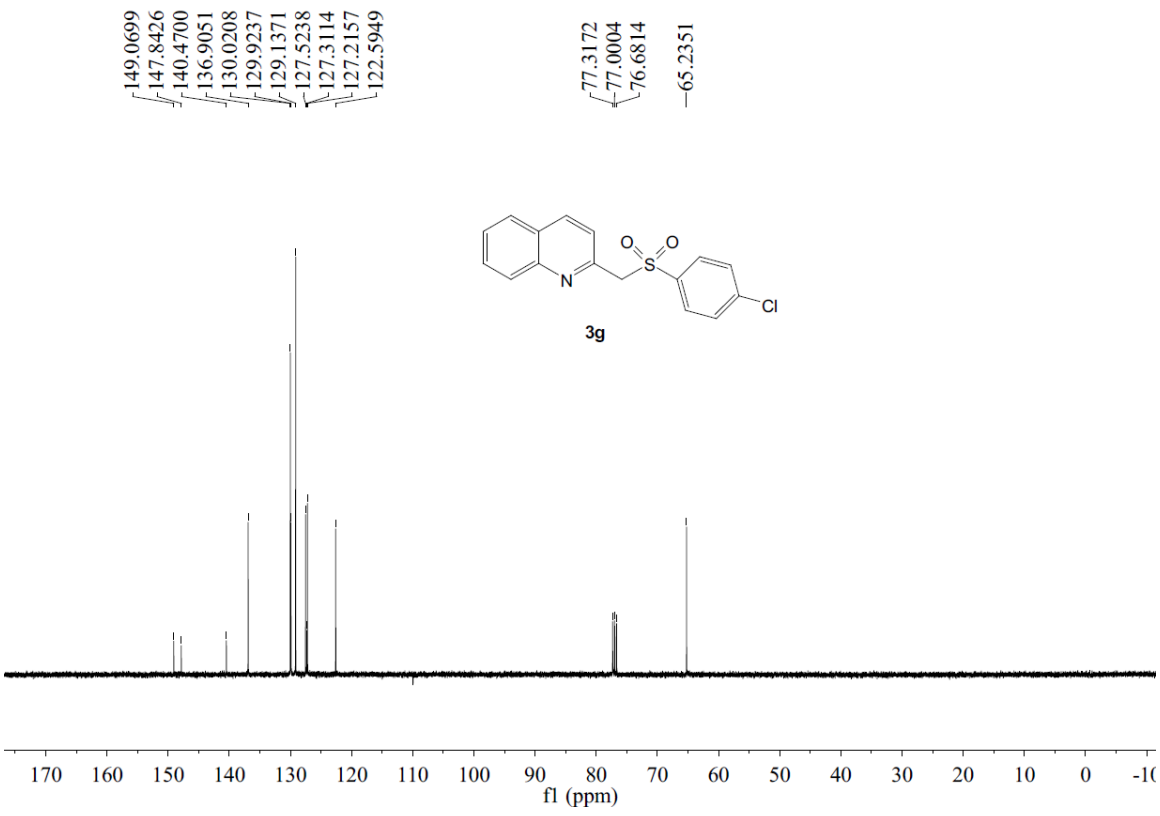
0.0004
1.00
2.05
1.04
3.98
1.81
1.96
3g
f1 (ppm)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129.9237
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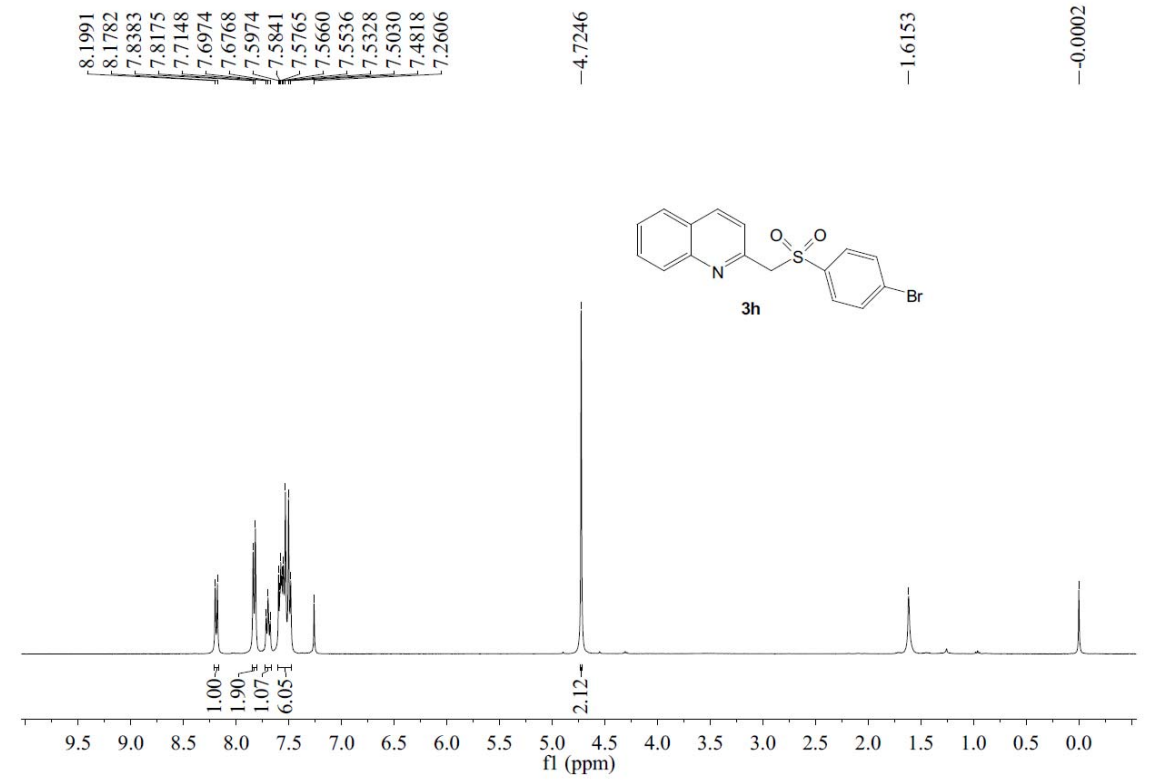
127.2157
122.5949
77.3172
77.0004
76.6814
65.2351
3g
f1 (ppm)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7.5765
7.5660
7.5536
7.5328
7.5030
7.4818
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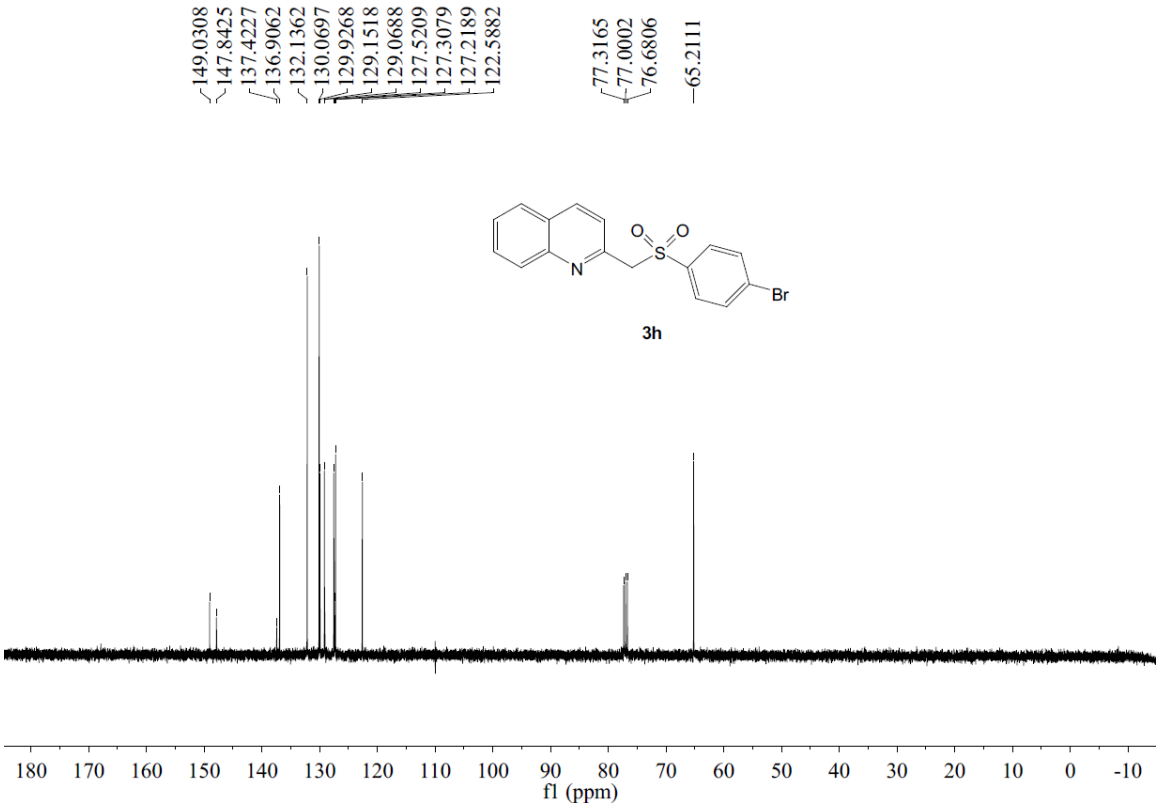
1.6153
0.0002
3h
1.00
1.90
1.07
6.05
2.12
fl (ppm)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129.9268
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127.3079
127.2189
122.5882
77.3165
77.0002
76.6806
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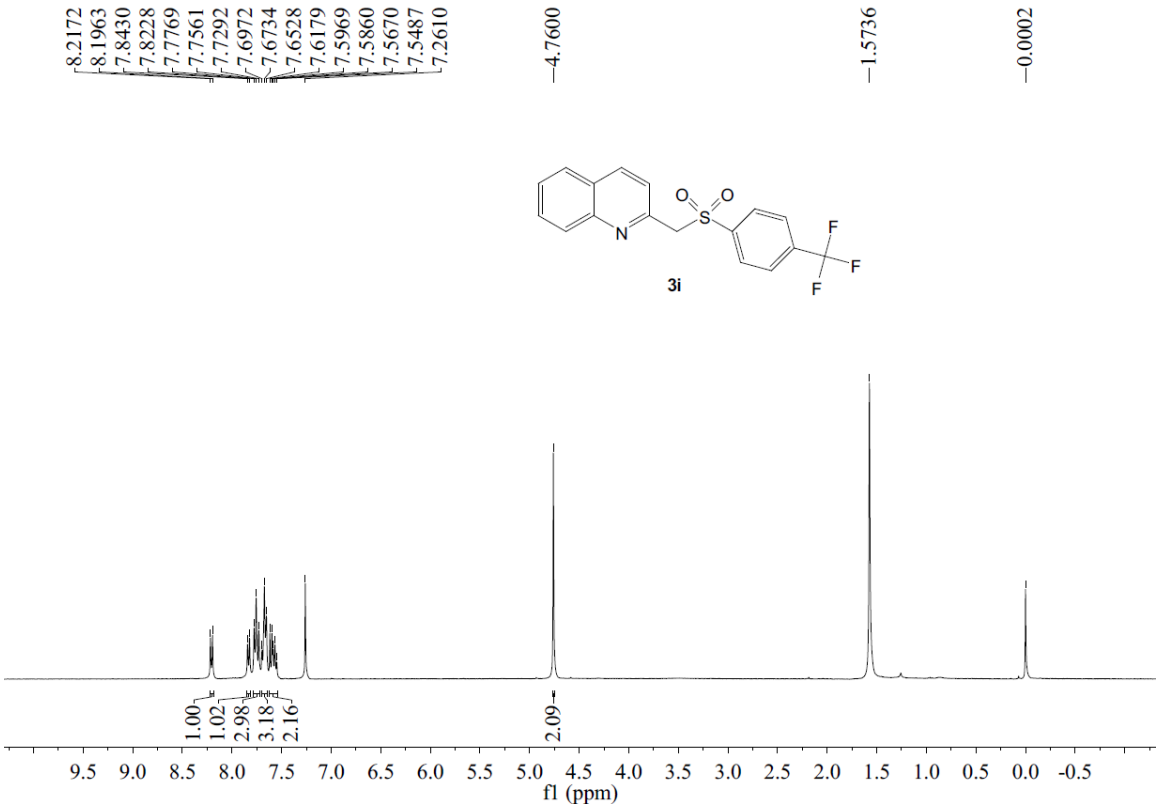
3h
fl (ppm)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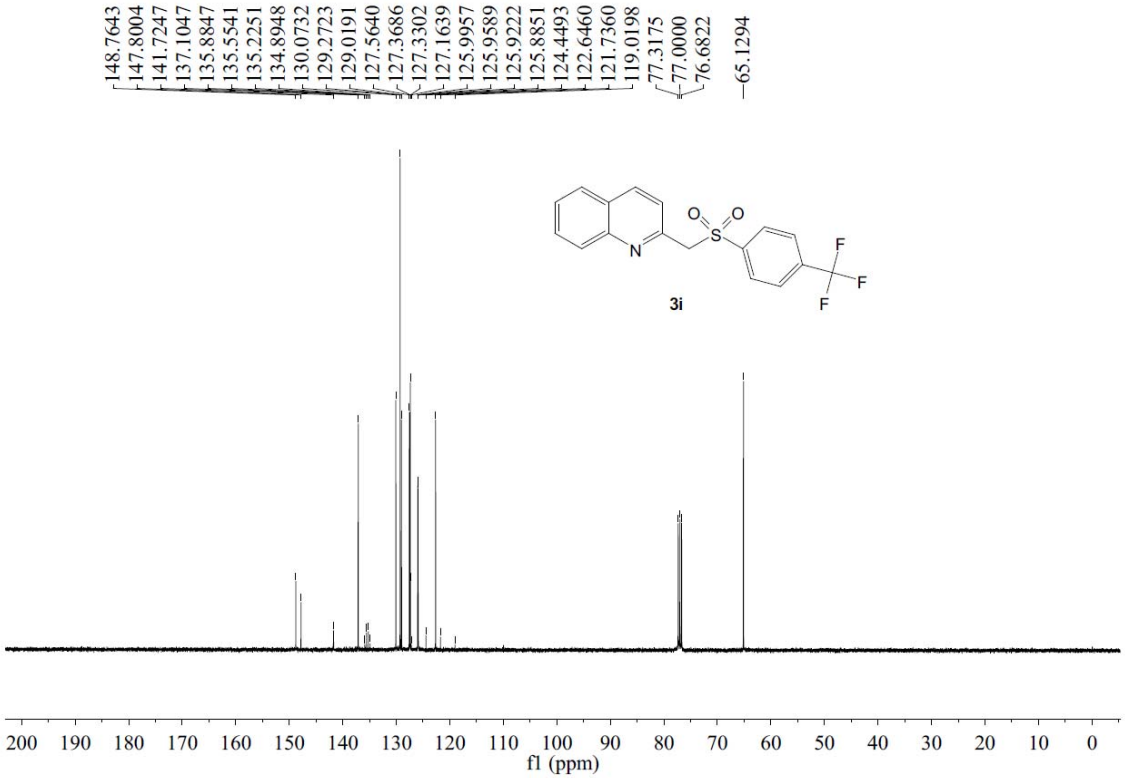
7.6528
7.6179
7.5969
7.5860
7.5670
7.5487
7.2610
4.7600
1.5736
0.0002
3i
1.00
1.02
2.98
3.18
2.16
2.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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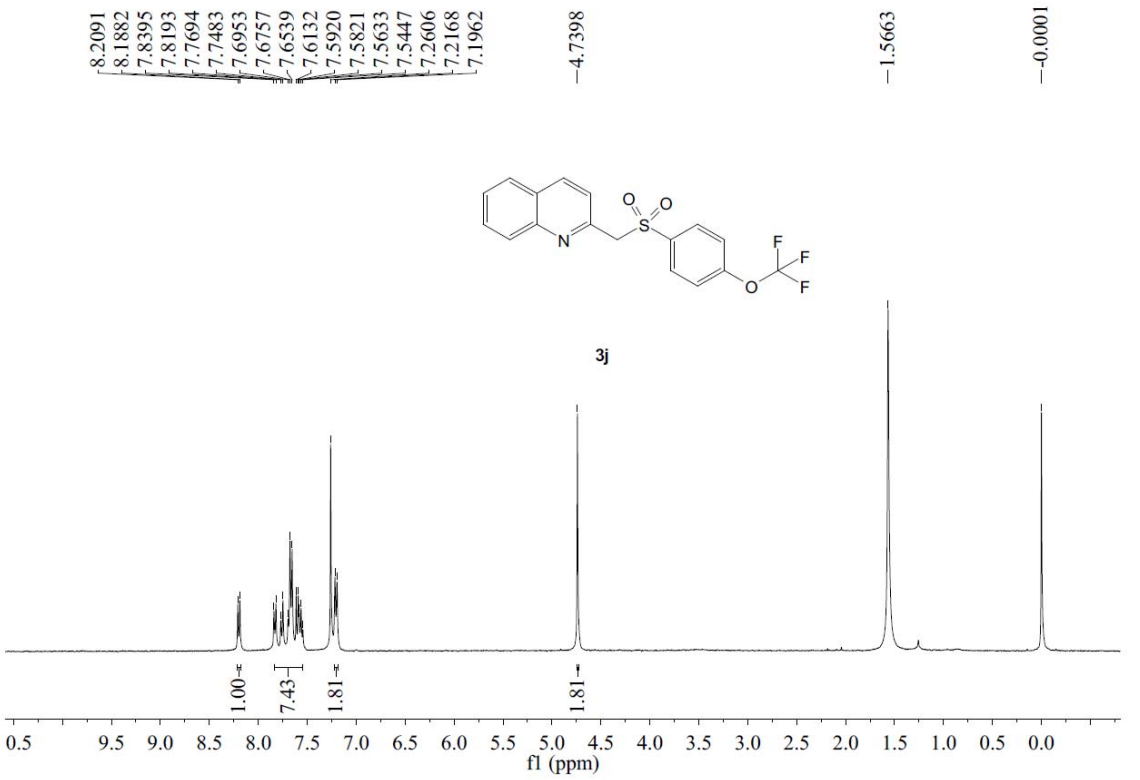
127.5640
127.3686
127.3302
127.1639
125.9957
125.9589
125.9222
125.8851
124.4493
122.6460
121.7360
119.0198
77.3175
77.0000
76.6822
65.1294
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.7483
7.6953
7.6757
7.6539
7.6132
7.5920
7.5821
7.5633
7.5447
7.2606
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4.7398
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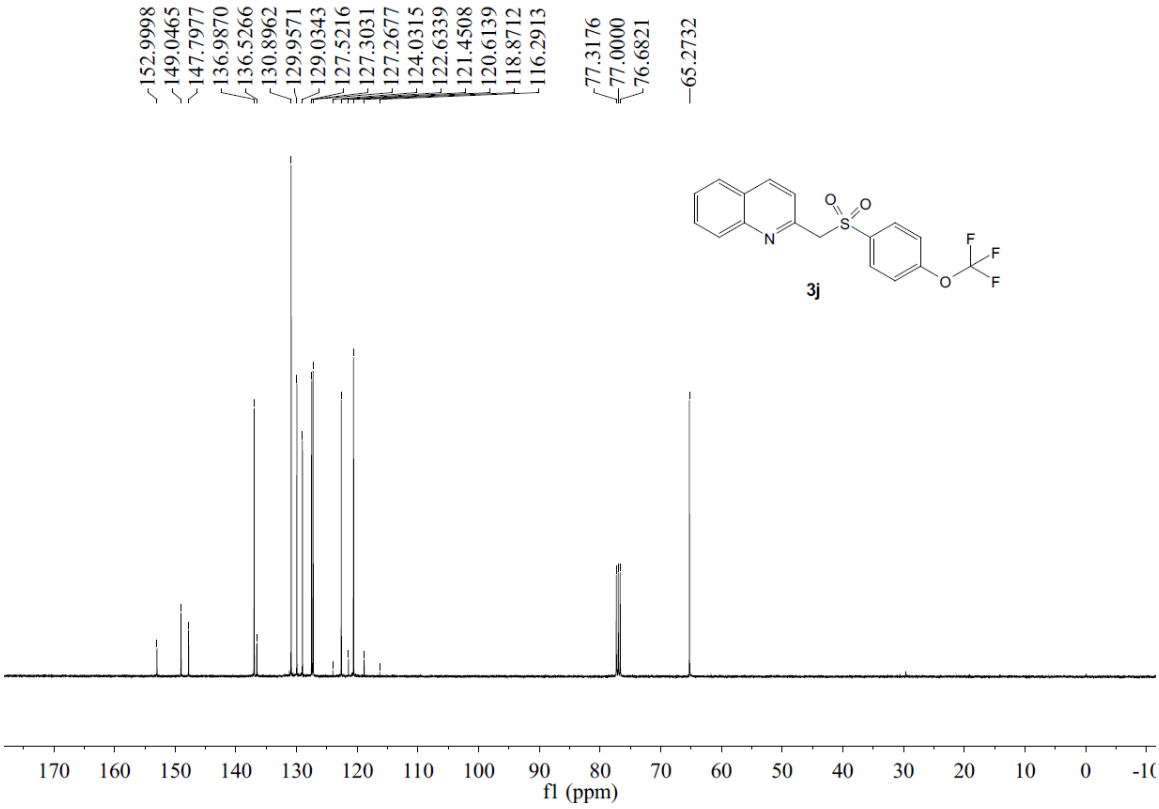
3j
1.00
7.43
1.81
1.81
fl (ppm)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147.7977
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127.3031
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124.0315
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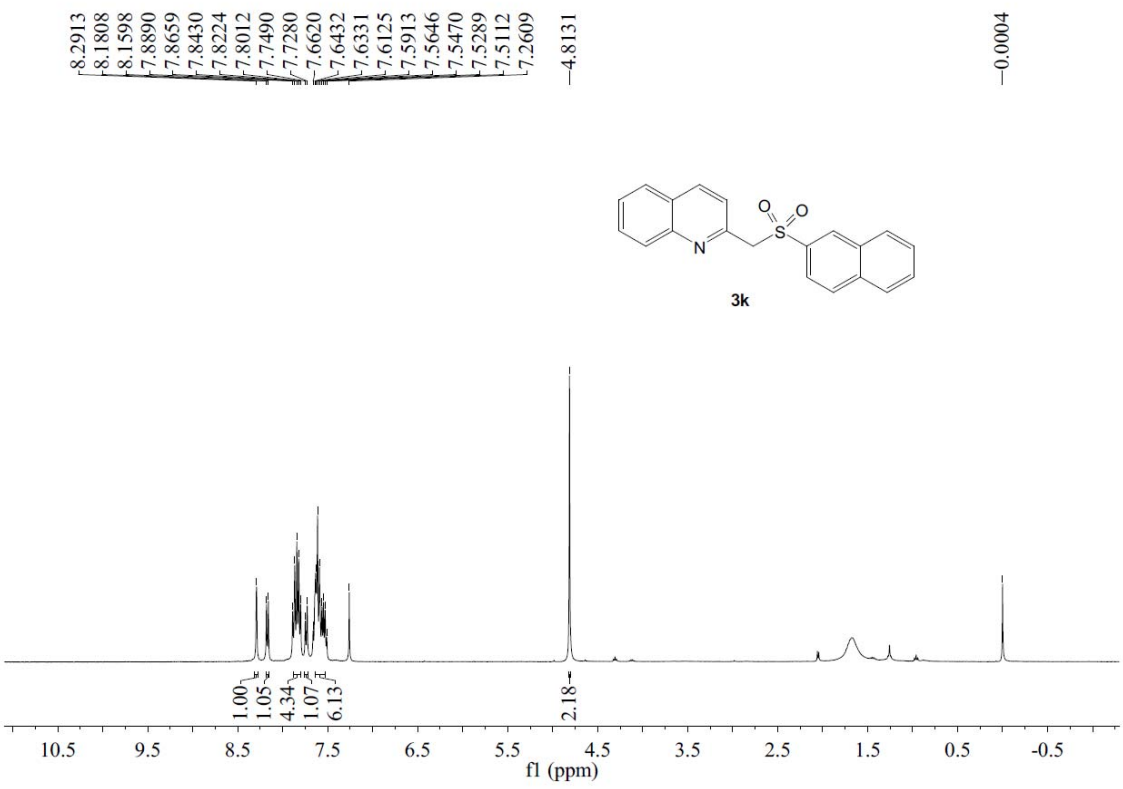
118.8712
116.2913
77.3176
77.0000
76.6821
65.2732
3j
fl (ppm)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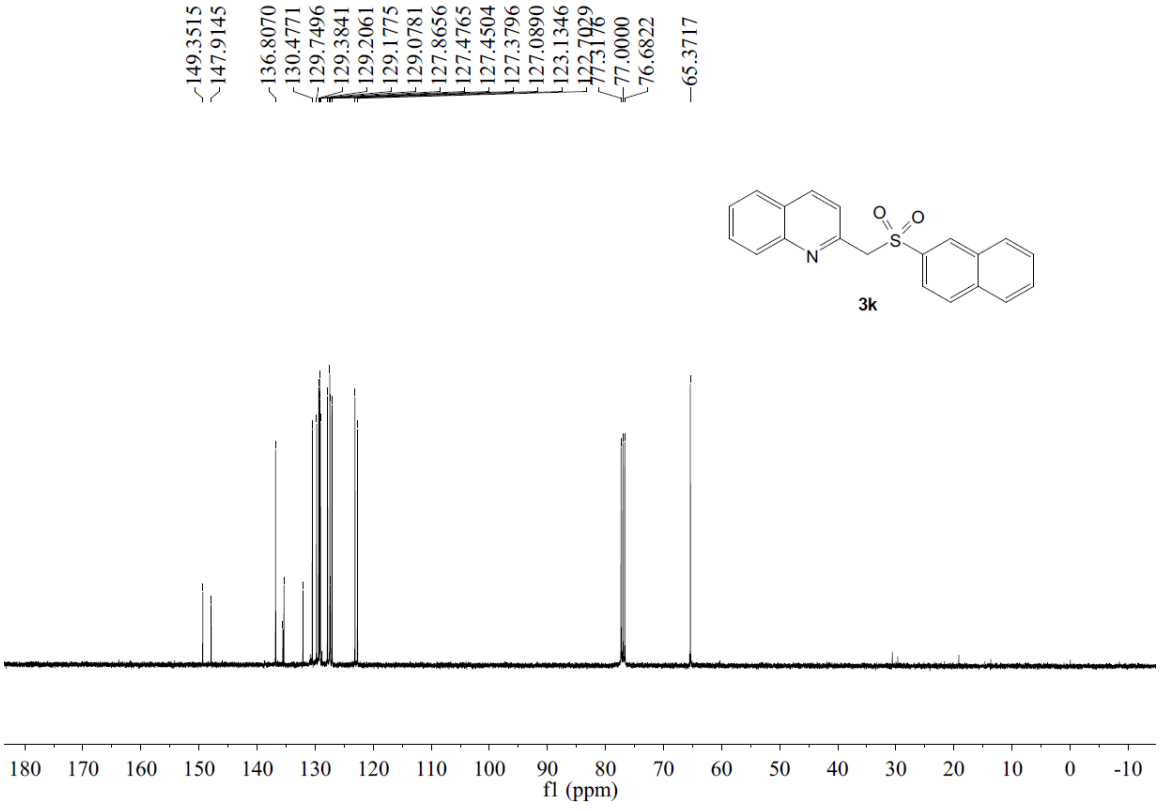
7.6331
7.6125
7.5913
7.5646
7.5470
7.5289
7.5112
7.2609
4.8131
0.0004
3k
1.00
1.05
4.34
1.07
6.13
2.18
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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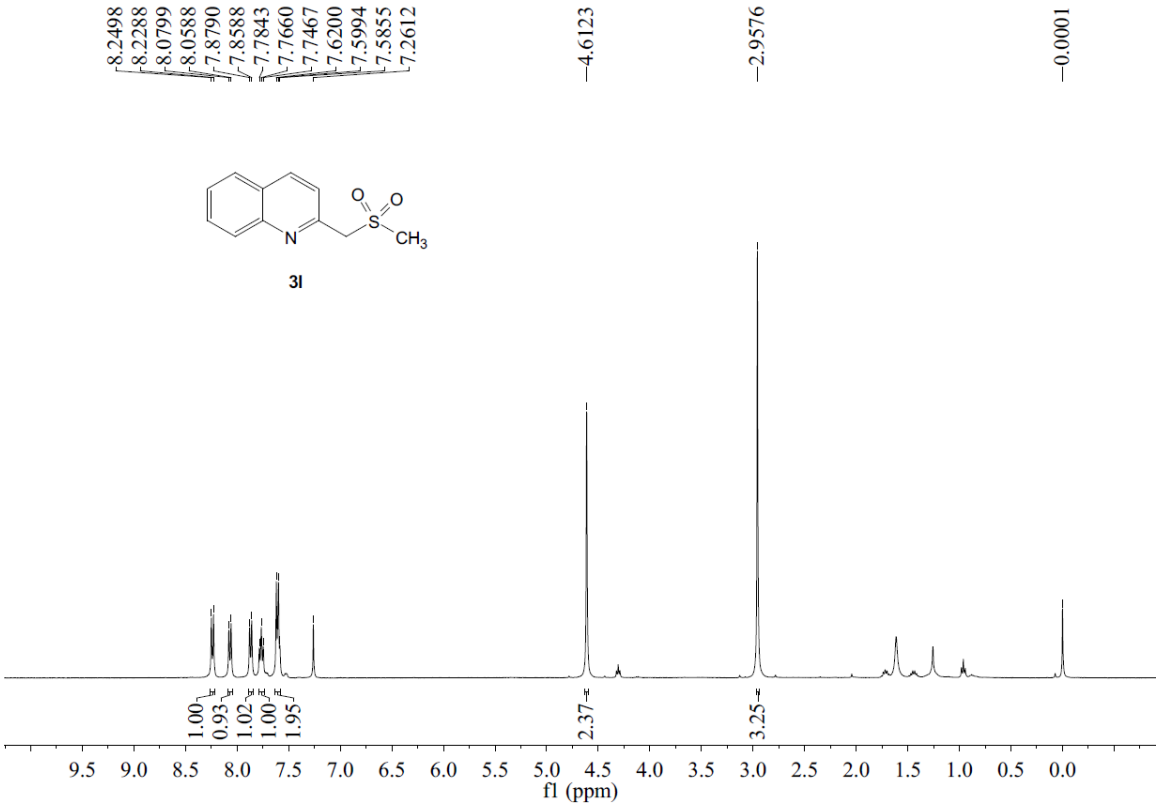
127.3796
127.0890
123.1346
122.7029
77.3176
77.0000
76.6822
65.3717
3k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.7467
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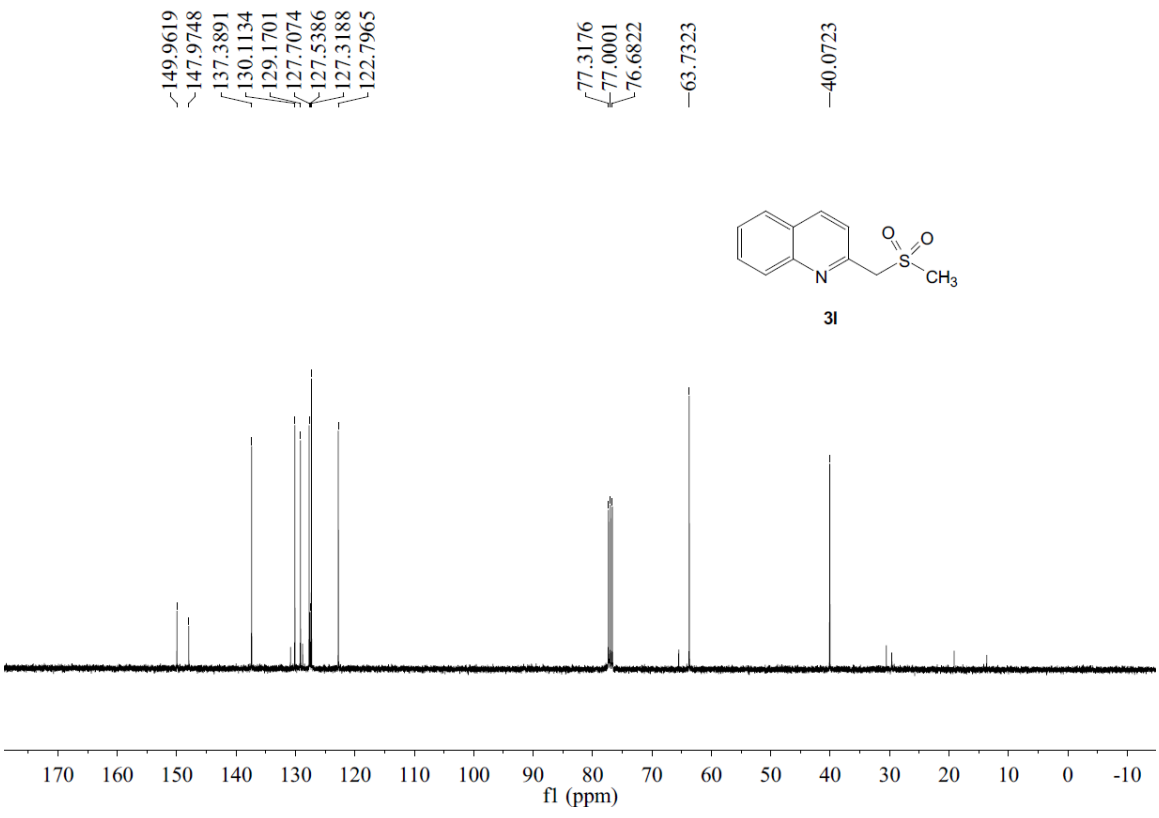
7.5994
7.5855
7.2612
4.6123
2.9576
0.0001
3I
1.00
0.93
1.02
1.00
1.95
2.37
3.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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63.7323
40.0723
3I
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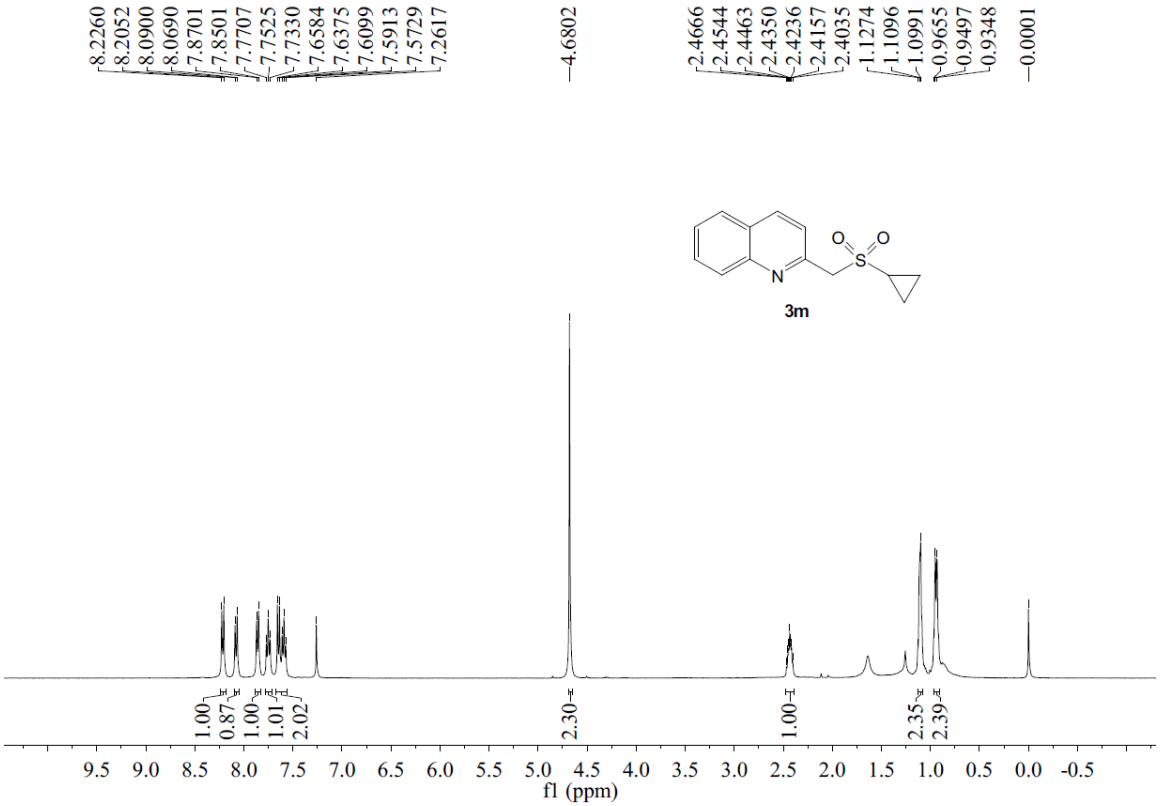
f1 (ppm)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7.7707
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7.7330
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7.6375
7.6099
7.5913
7.5729
7.2617
4.6802
2.4666
2.4544
2.4463
2.4350
2.4236
2.4157
2.4035
1.1274
1.1096
1.0991
0.9655
0.9497
0.9348
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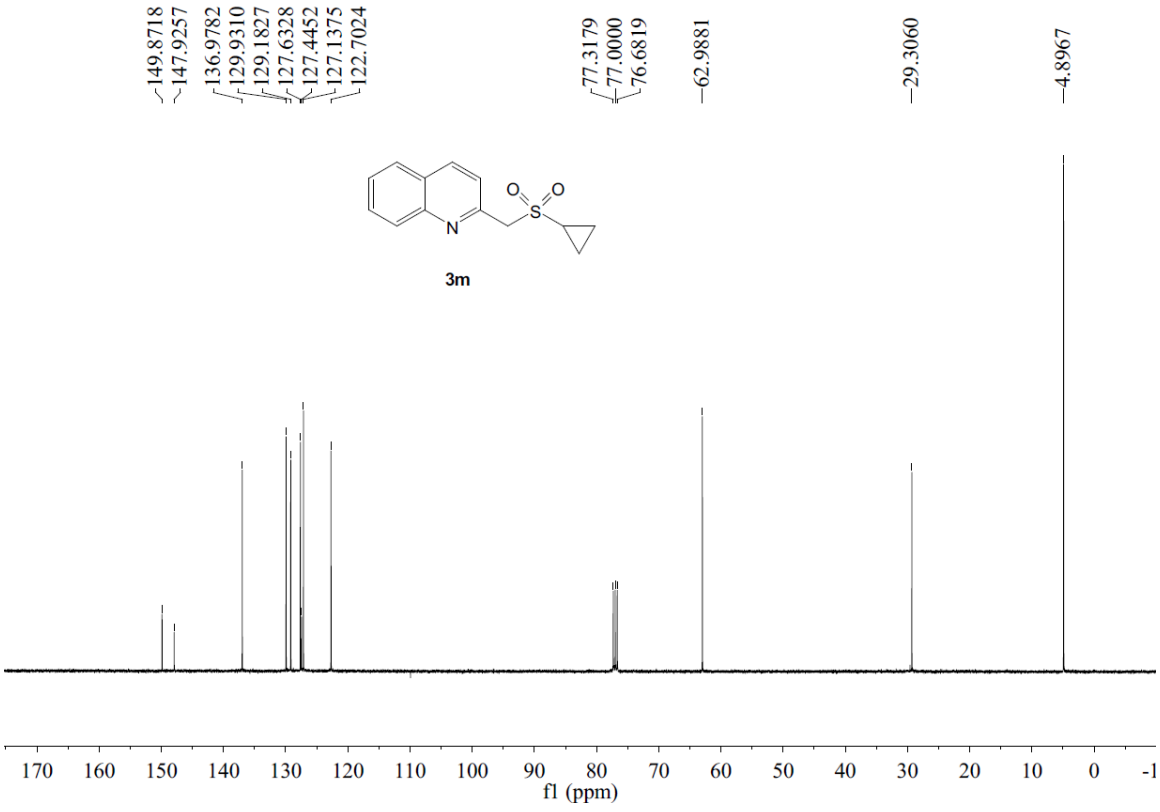
O
O
S
N
3m
1.00
0.87
1.00
1.01
2.02
2.30
1.00
2.35
2.39
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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S
N
3m
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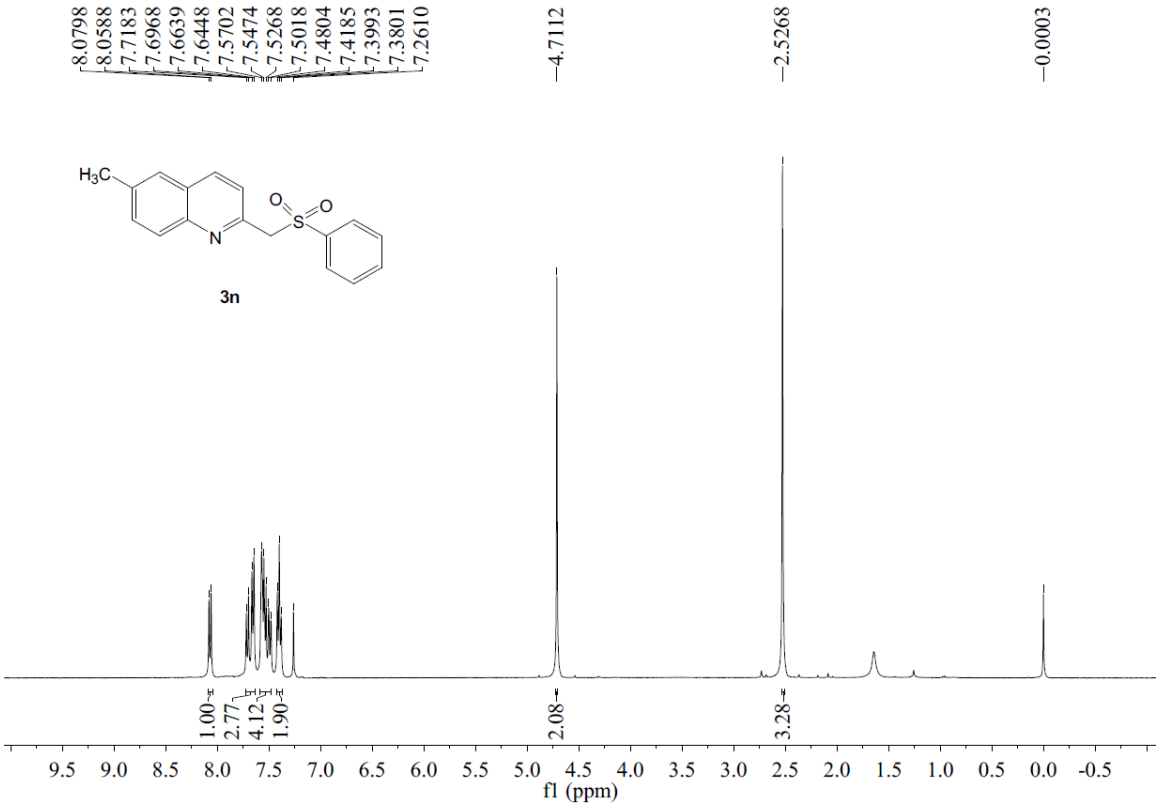
f1 (ppm)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7.4185
7.3993
7.3801
7.2610
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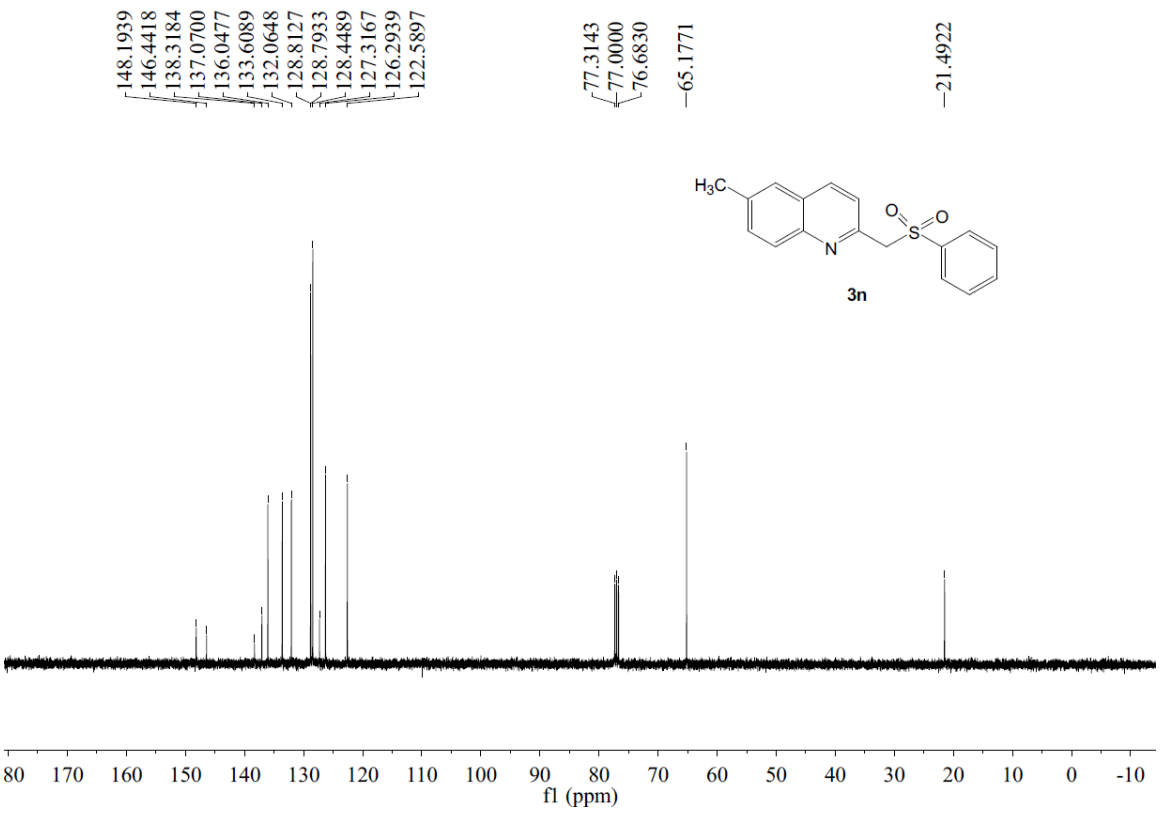
2.5268
0.0003
H3C
N
O
S
O
3n
1.00
2.77
4.12
1.90
2.08
3.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.5897
77.3143
77.0000
76.6830
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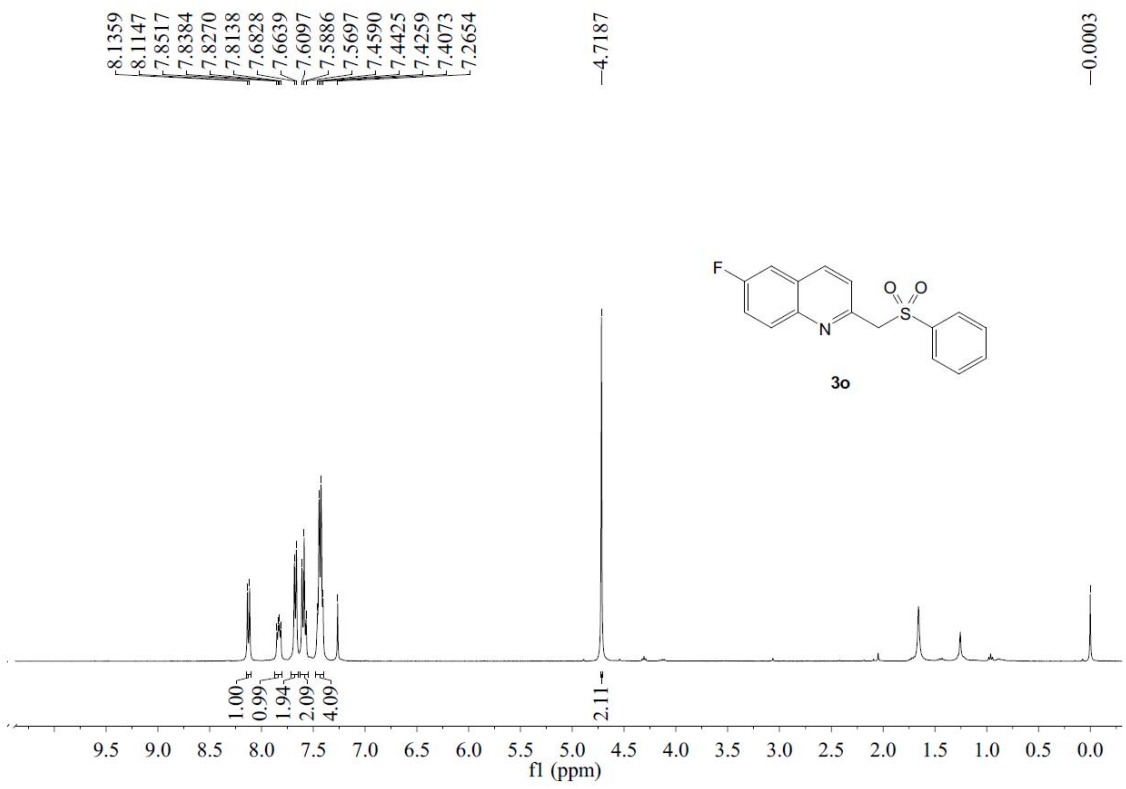
H3C
N
O
S
O
3n
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.4590
7.4425
7.4259
7.4073
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4.7187
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F
O
O
S
N
3o
1.00
0.99
1.94
2.09
4.09
2.11
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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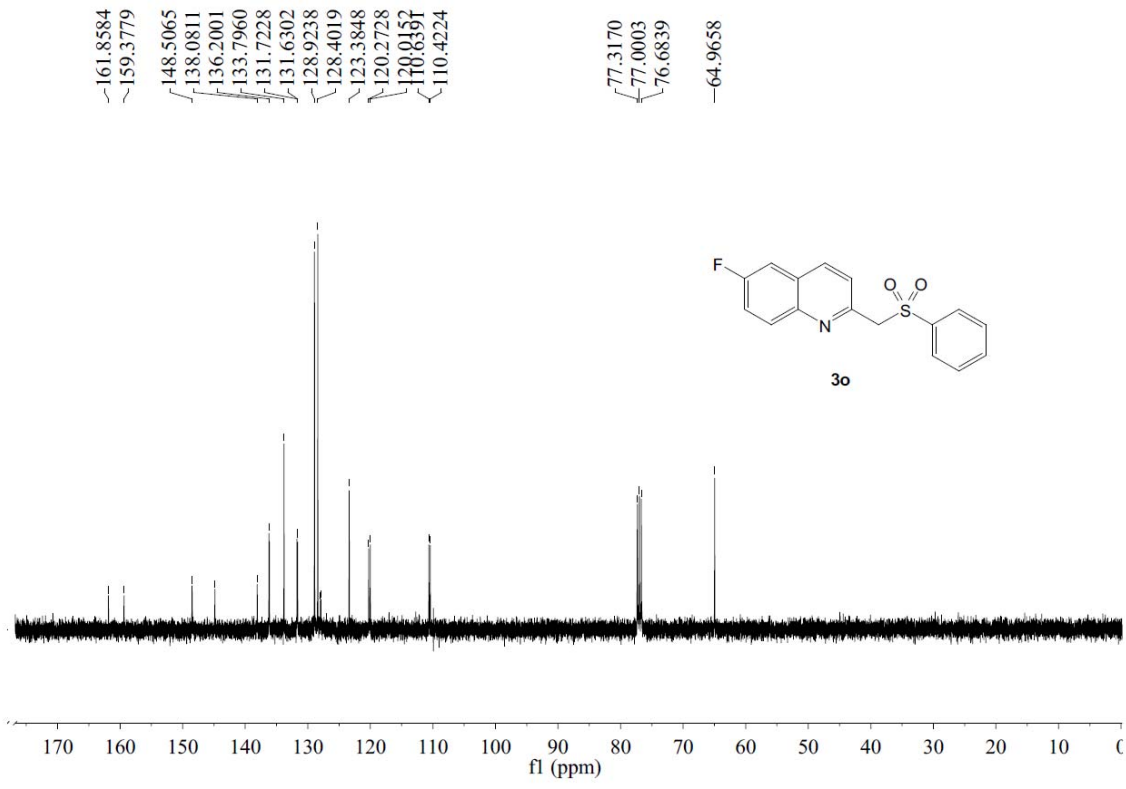
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77.3170
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O
S
N
3o
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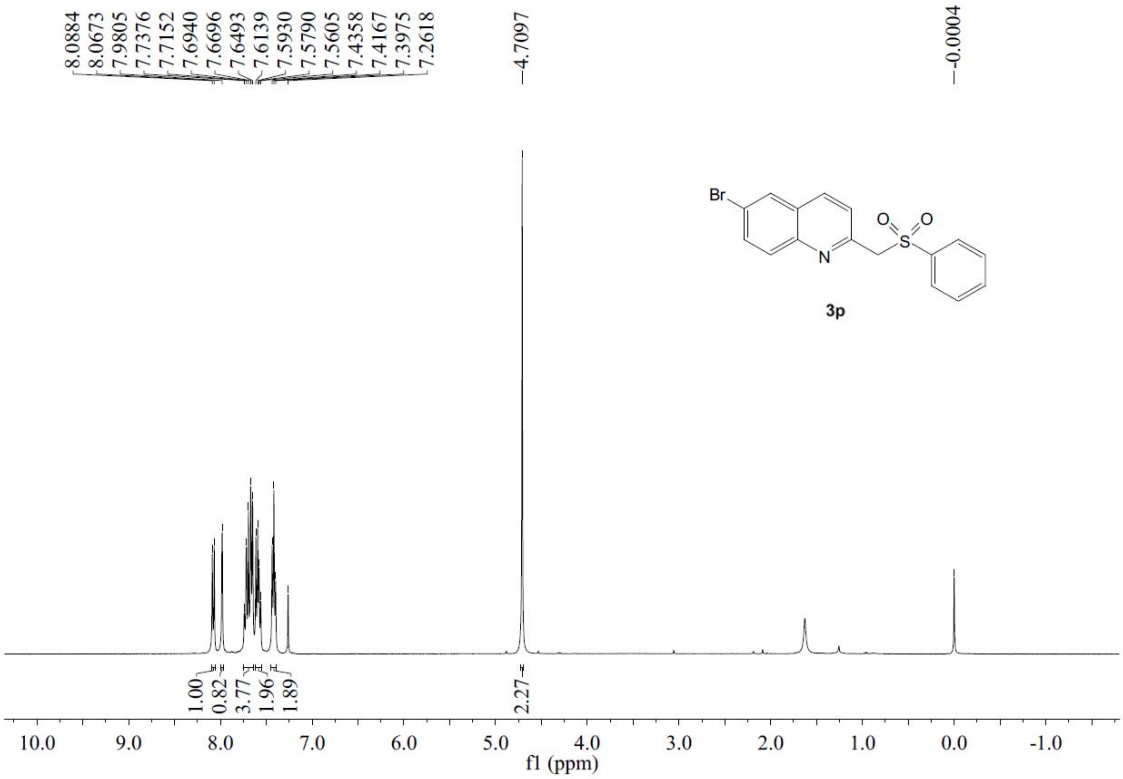
f1 (ppm)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O
O
S
N
3p
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1.89
2.27
10.0
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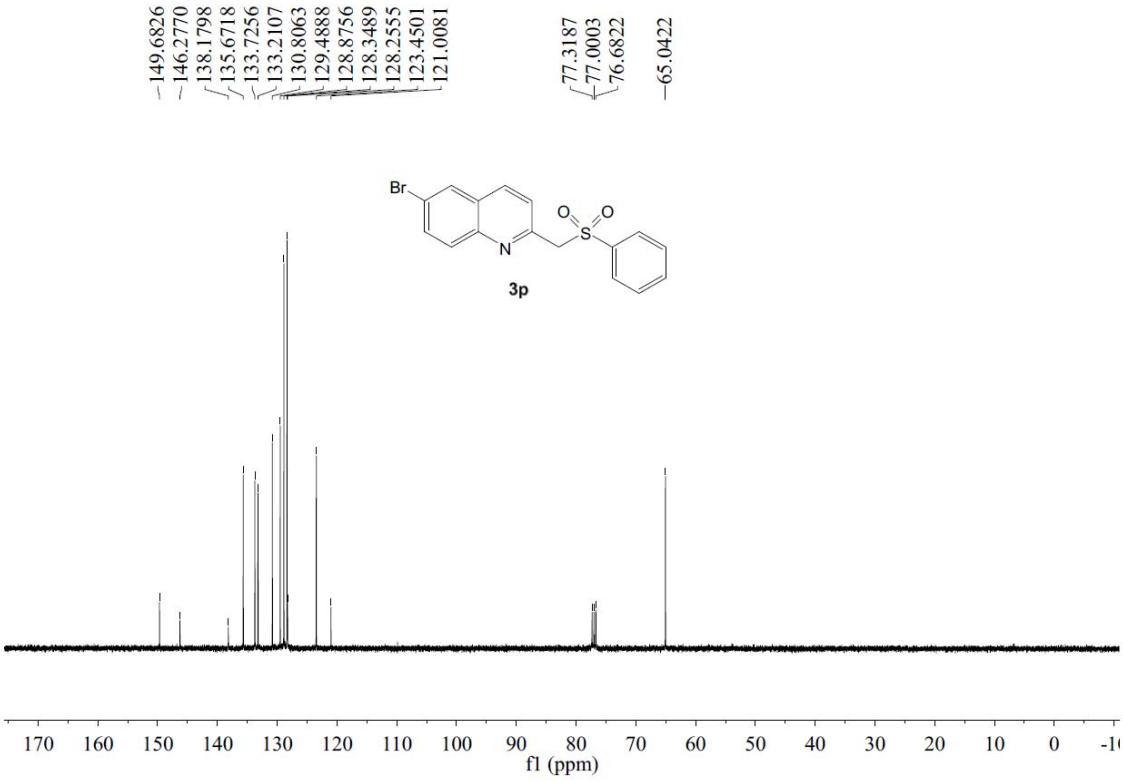
f1 (ppm)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123.4501
121.0081
77.3187
77.0003
76.6822
65.0422
Br
O
O
S
N
3p
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120
110
100
90
80
70
60
50
40
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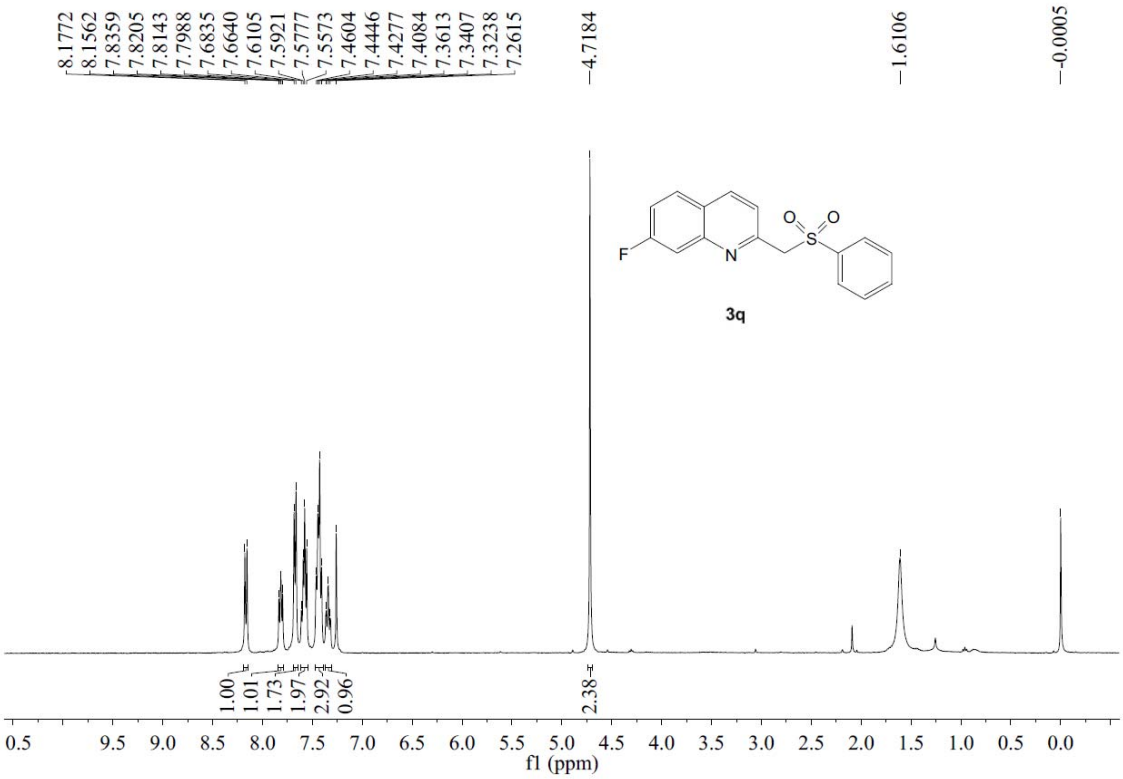
10
0
f1 (ppm)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7.5777
7.5573
7.4604
7.4446
7.4277
7.4084
7.3613
7.3407
7.3238
7.2615
4.7184
1.6106
0.0005
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O
O
S
3q
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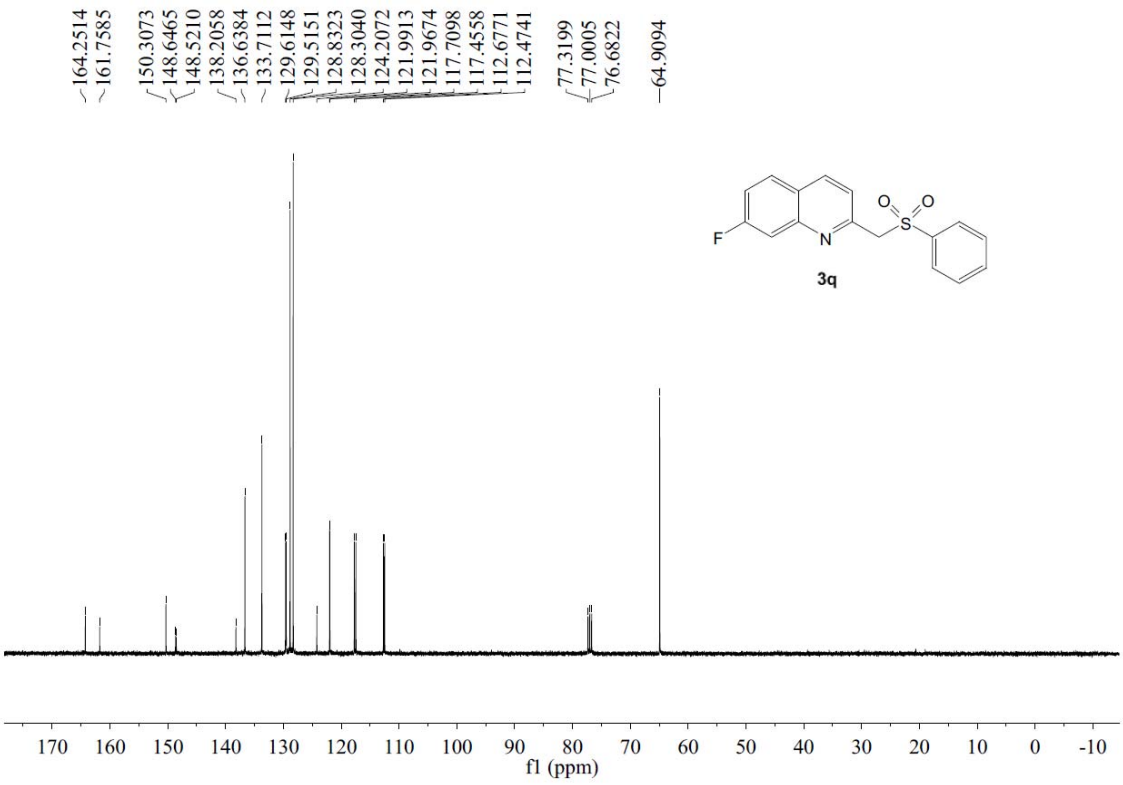
2.38
fl (ppm)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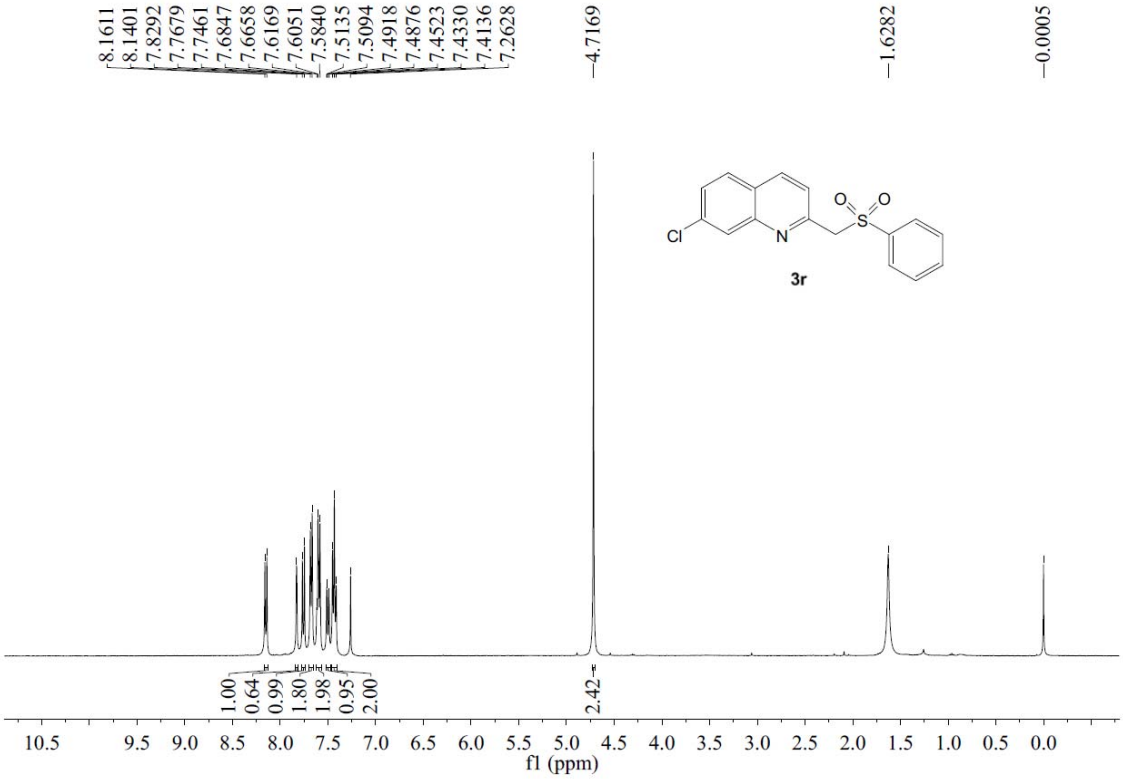
F
N
O
O
S
3q
fl (ppm)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Cl
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O
S
O
3r
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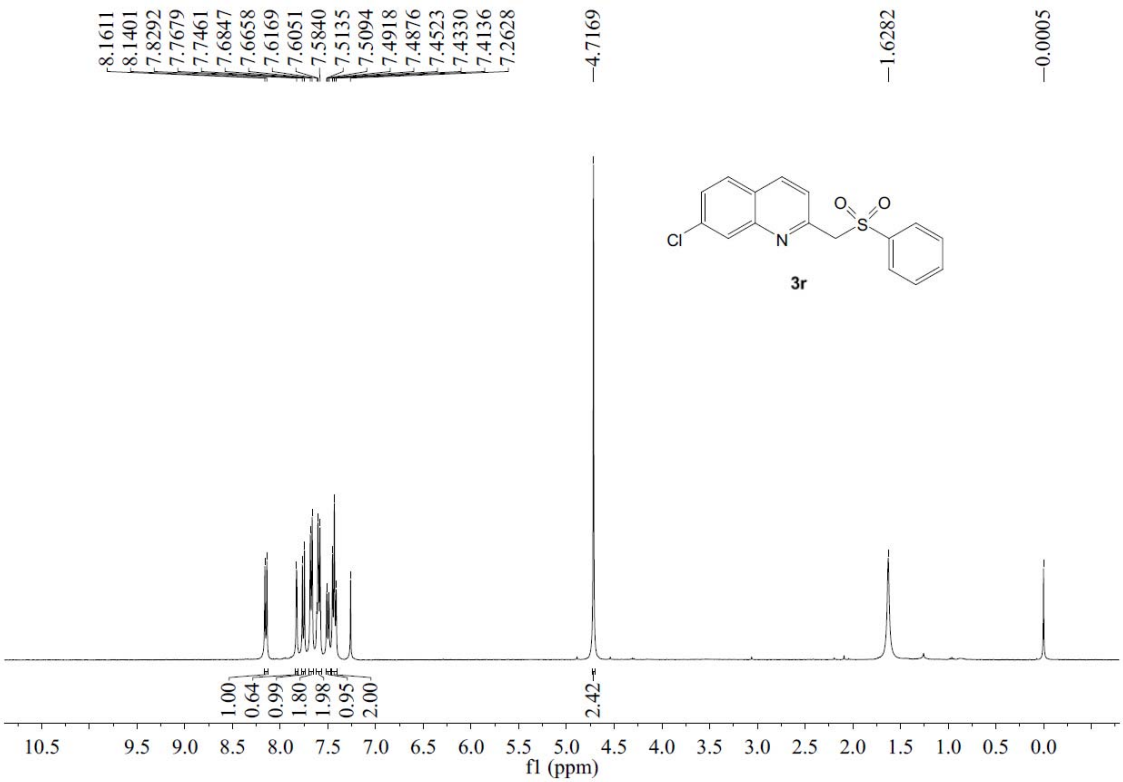
2.00
2.42
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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8.1401
7.8292
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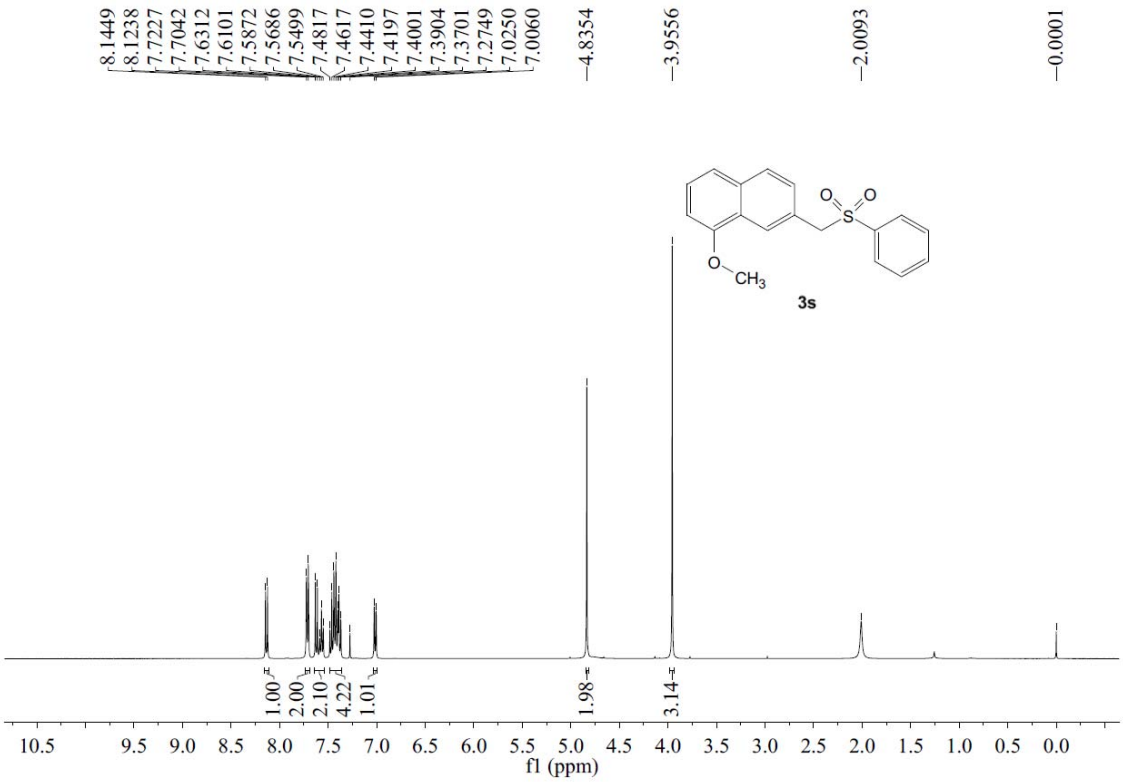
7.7461
7.6847
7.6658
7.6169
7.6051
7.5840
7.5135
7.5094
7.4918
7.4876
7.4523
7.4330
7.4136
7.2628
4.7169
1.6282
0.0005
Cl
N
O
S
O
3r
1.00
0.64
0.99
1.80
1.98
0.95
2.00
2.42
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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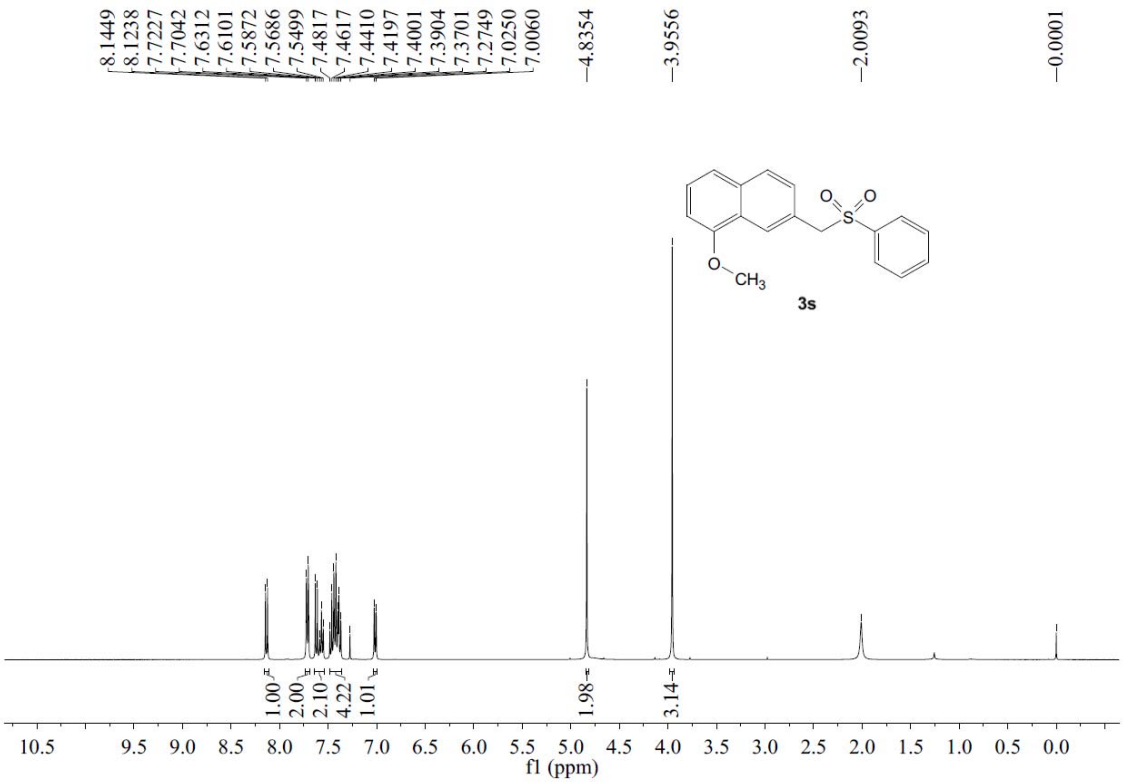
7.7042
7.6312
7.6101
7.5872
7.5686
7.5499
7.4817
7.4617
7.4410
7.4197
7.4001
7.3904
7.3701
7.2749
7.0250
7.0060
4.8354
3.9556
2.0093
0.0001
O
S
O
O
CH3
3s
1.00
2.00
2.10
4.22
1.01
1.98
3.14
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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8.1238
7.7227
7.7042
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7.5872
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7.5499
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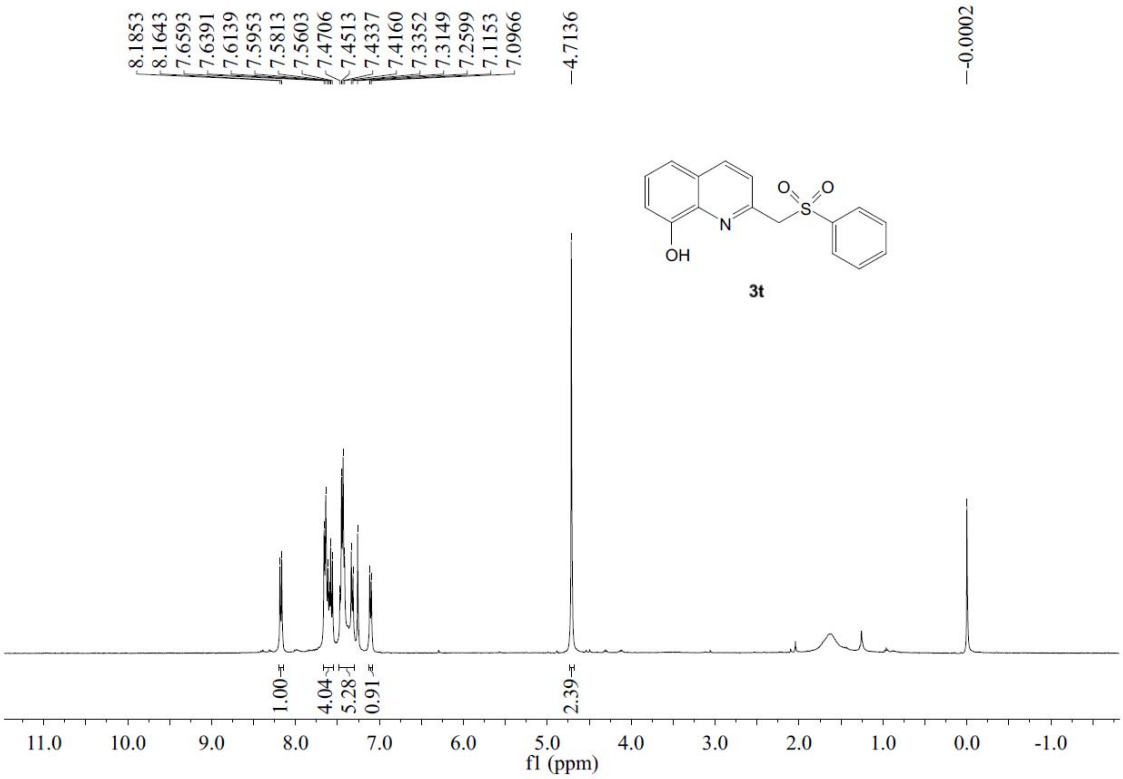
7.4617
7.4410
7.4197
7.4001
7.3904
7.3701
7.2749
7.0250
7.0060
4.8354
3.9556
2.0093
0.0001
O
S
O
O
CH3
3s
1.00
2.00
2.10
4.22
1.01
1.98
3.14
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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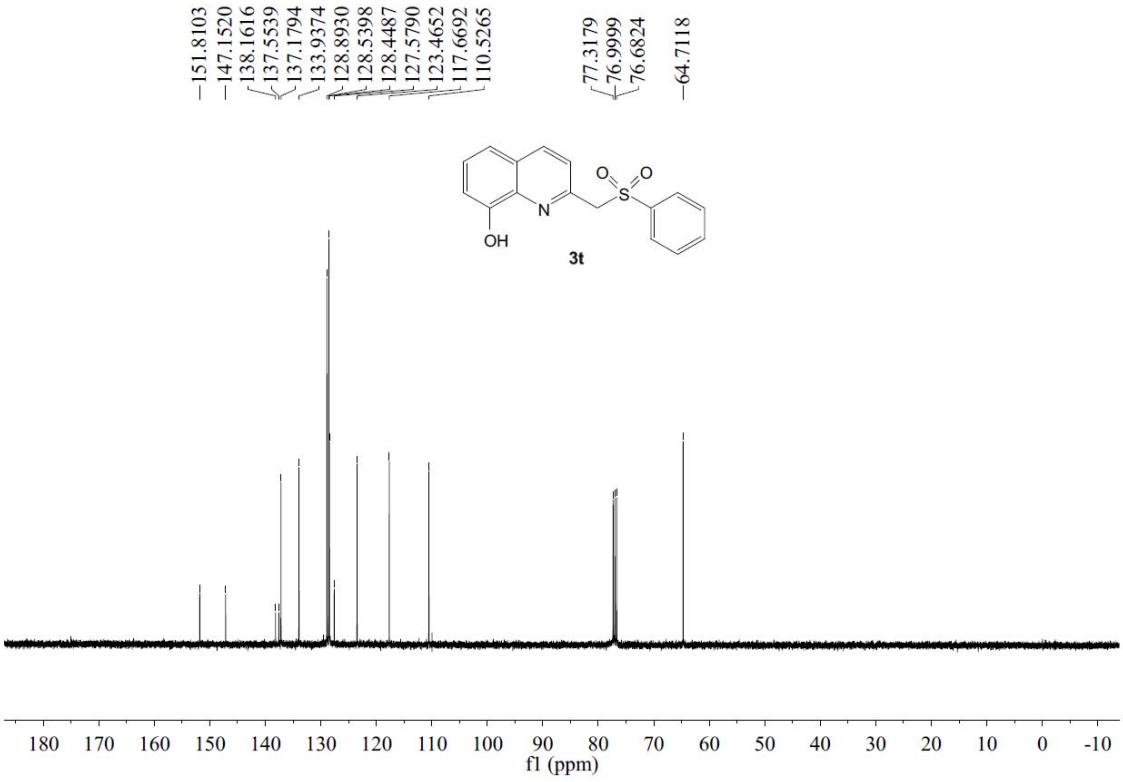
7.6593
7.6391
7.6139
7.5953
7.5813
7.5603
7.4706
7.4513
7.4337
7.4160
7.3352
7.3149
7.2599
7.1153
7.0966
4.7136
0.0002
O
O
S
N
OH
3t
1.00
4.04
5.28
0.91
2.39
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)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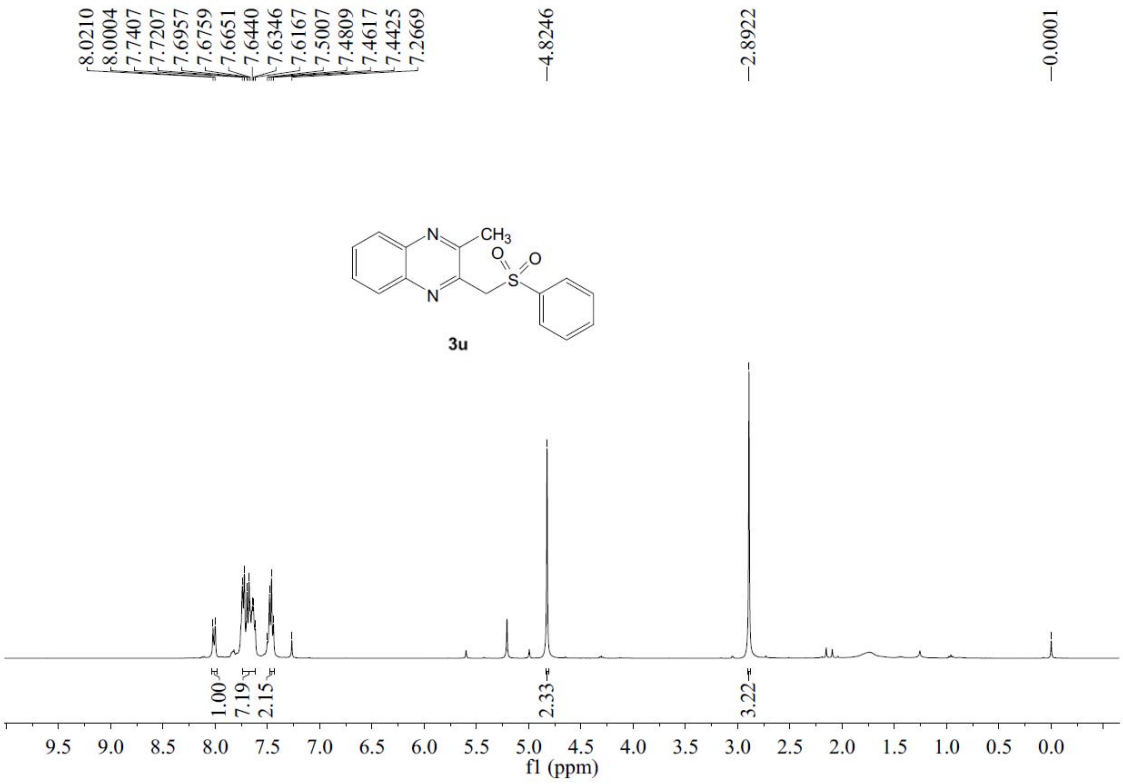
147.1520
138.1616
137.5539
137.1794
133.9374
128.8930
128.5398
128.4487
127.5790
123.4652
117.6692
110.5265
77.3179
76.9999
76.6824
64.7118
O
O
S
N
OH
3t
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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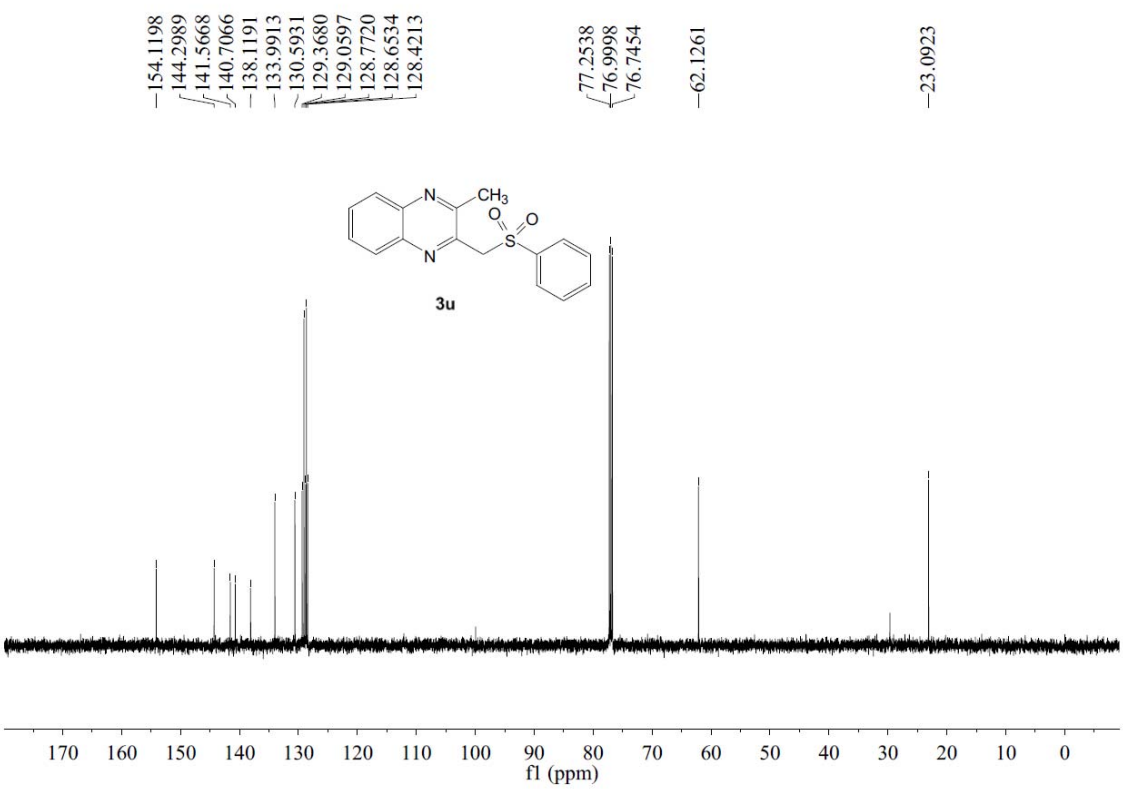
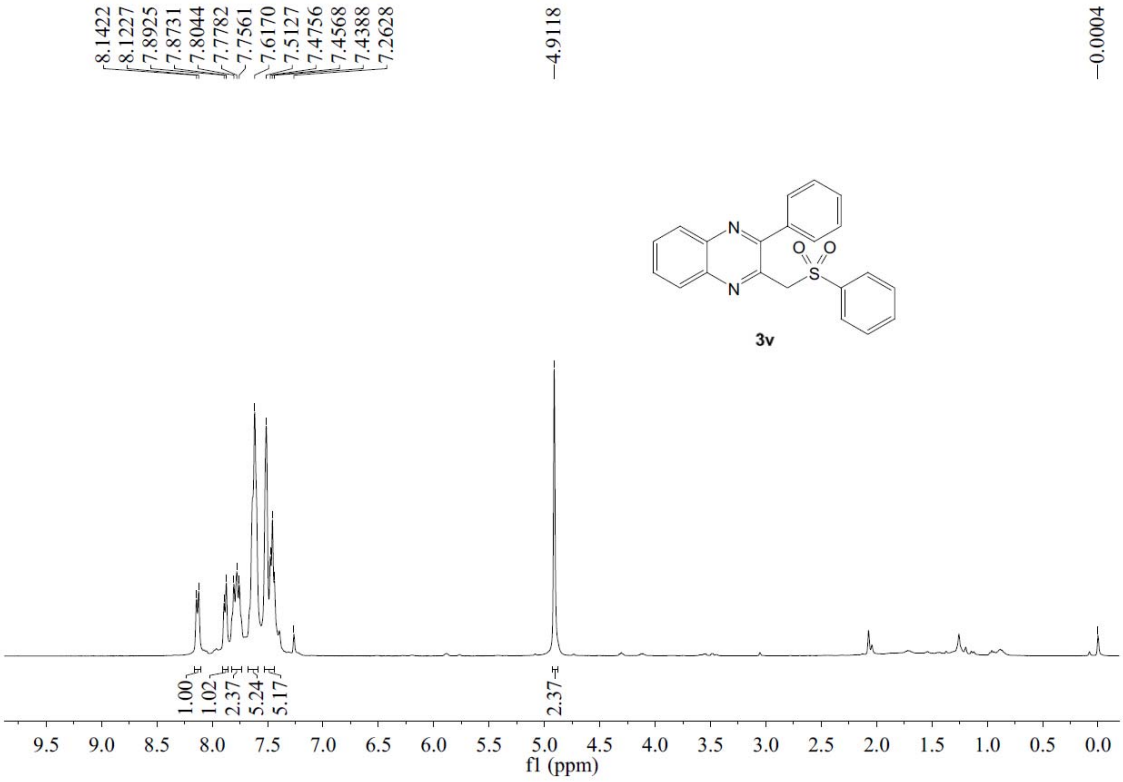
8.0004
7.7407
7.7207
7.6957
7.6759
7.6651
7.6440
7.6346
7.6167
7.5007
7.4809
7.4617
7.4425
7.2669
4.8246
2.8922
0.0001
3u
1.00
7.19
2.15
2.33
3.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.1198
144.2989
141.5668
140.7066
138.1191
133.9913
130.5931
129.3680
129.0597
128.7720
128.6534
128.4213
77.2538
76.9998
76.7454
62.1261
23.0923
3u
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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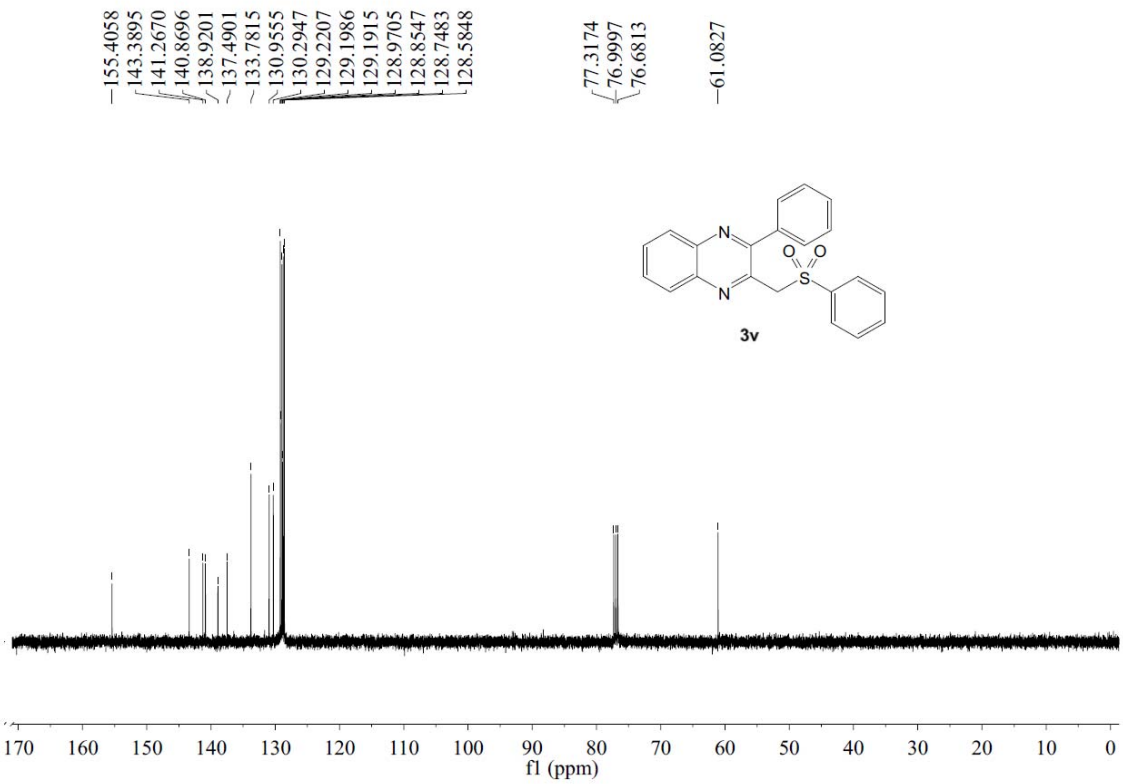
8.1227
7.8925
7.8731
7.8044
7.7782
7.7561
7.6170
7.5127
7.4756
7.4568
7.4388
7.2628
4.9118
0.0004
3v
1.00
1.02
2.37
5.24
5.17
2.37
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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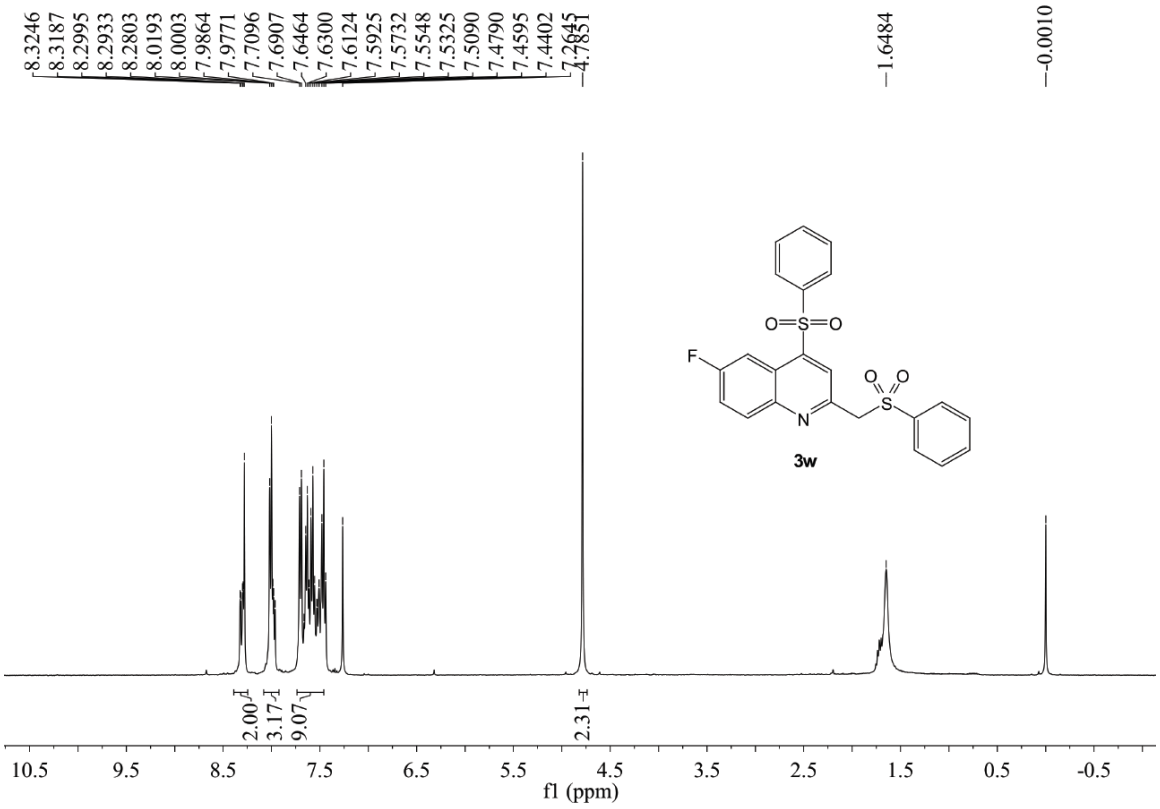
143.3895
141.2670
140.8696
138.9201
137.4901
133.7815
130.9555
130.2947
129.2207
129.1986
129.1915
128.9705
128.8547
128.7483
128.5848
77.3174
76.9997
76.6813
61.0827
3v
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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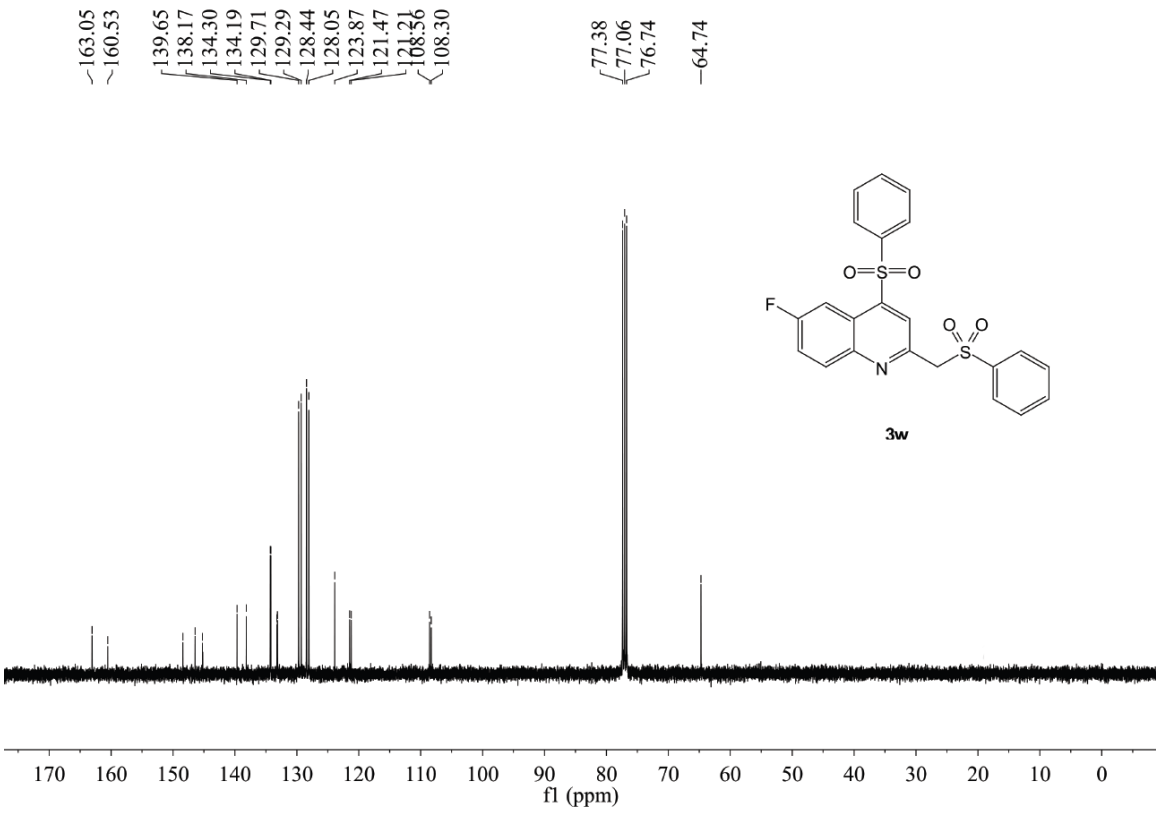
8.3187
8.2995
8.2933
8.2803
8.0193
8.0003
7.9864
7.9771
7.7096
7.6907
7.6464
7.6300
7.6124
7.5925
7.5732
7.5548
7.5325
7.5090
7.4790
7.4595
7.4402
7.2645
7.2631
4.7851
1.6484
0.0010
2.00
3.17
9.07
2.31
3w
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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160.53
139.65
138.17
134.30
134.19
129.71
129.29
128.44
128.05
123.87
121.47
121.21
108.56
108.30
77.38
77.06
76.74
64.74
3w
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)