Supporting Information

Copper-Catalyzed Sulfonamidation of Enol Silyl Ether via SO_2 Insertion towards the Synthesis of β-Keto Sulfonamides

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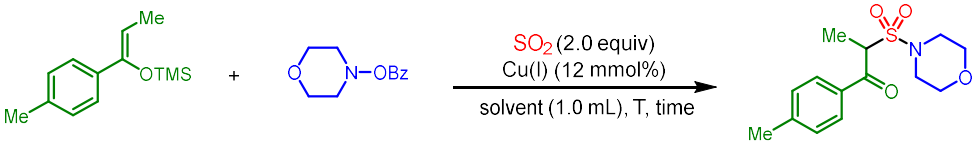
1. General information

Unless otherwise noted, all commercially available reagents were obtained from commercial suppliers and used without further purification. Unless otherwise noted, all catalytic reactions were carried out using standard techniques in an argon atmosphere glovebox (Vigor, SGI800-750TS-F). The substrates and reagents for catalytic reactions were degassed and stored in the glovebox, unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Thin Layer Chromatography analysis was performed on silica gel coated glass plates (0.25 mm) with fluorescence indicator UV254. Column chromatography was conducted with silica gel (200-300 mesh) at room temperature and under elevated pressure.

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded at 400 MHz, 376 MHz and 100 MHz, respectively in $CDCl_3$ using TMS as an internal reference with chemical shift values reported in ppm. ^{1}H NMR was reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (J values) in Hz and integration. Chemical shifts (δ) were reported with respect to the corresponding solvent residual peak at 7.26 ppm for $CDCl_3$ for ^{1}H NMR. ^{13}C NMR spectra were reported in ppm using the central peak of $CDCl_3$ (77.16 ppm). High-resolution mass spectrometric measurements were provided by the Department of The State Key Laboratory of Biotherapy, Sichuan University. The molecular ion $[M+H]^+$ and $[M+Na]^+$ are given in m/z units.

2. Optimization of the Reaction Condition.



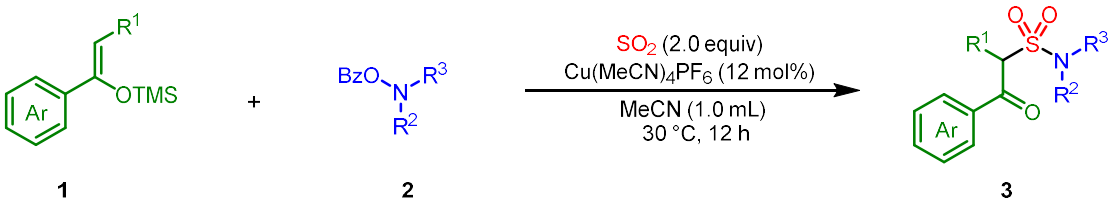
1a, 0.2 mmol **2a** **3a**

Entry	Cat.Cu	T (°C)	Solvent	Time (h)	SO_2 source	3a Yield[a] (%)
1	-	60	MeCN	12	SOgen	0
2	Cu(OAc)	60	MeCN	12	SOgen	47
3	CuOTf	60	MeCN	12	SOgen	74
4	CuCl	60	MeCN	12	SOgen	29
5	CuBr	60	MeCN	12	SOgen	41
6	CuCN	60	MeCN	12	SOgen	60
7	Copper(I) thiophene-2-carboxylate	60	MeCN	12	SOgen	51
8	$Cu(MeCN)_4PF_6$	60	MeCN	12	SOgen	84
9	$Cu(MeCN)_4PF_6$	50	MeCN	12	SOgen	83
10	$CuSO_4$	30	MeCN	12	SOgen	1
11	$Cu(OAc)_2$	30	MeCN	12	SOgen	16
12	$Cu(OTf)_2$	30	MeCN	12	SOgen	58
13	$CuCl_2$	30	MeCN	12	SOgen	24
14	$CuBr_2$	30	MeCN	12	SOgen	15
15	CuF_2	30	MeCN	12	SOgen	7
16	$Cu(MeCN)_4PF_6$	40	MeCN	12	SOgen	91
17	**$Cu(MeCN)_4PF_6$**	**30**	**MeCN**	**12**	SOgen	**91**
18	$Cu(MeCN)_4PF_6$	18	MeCN	12	SOgen	68
19[b]	$Cu(MeCN)_4PF_6$	30	MeCN	12	SOgen	8
20[c]	$Cu(MeCN)_4PF_6$	30	MeCN	12	SOgen	30
21[d]	$Cu(MeCN)_4PF_6$	30	MeCN	12	SOgen	84
22	$Cu(MeCN)_4PF_6$	30	DMF	12	SOgen	30
23	$Cu(MeCN)_4PF_6$	30	EtOAc	12	SOgen	12
24	$Cu(MeCN)_4PF_6$	30	DCM	12	SOgen	33
25	$Cu(MeCN)_4PF_6$	30	Cyclohexane	12	SOgen	trace
26	$Cu(MeCN)_4PF_6$	30	Toluene	12	SOgen	27
27	$Cu(MeCN)_4PF_6$	30	THF	12	SOgen	11
28	$Cu(MeCN)_4PF_6$	30	1,4-Dioxane	12	SOgen	8
29	$Cu(MeCN)_4PF_6$	30	EtOH	12	SOgen	20
30	$Cu(MeCN)_4PF_6$	30	MeCN	1	SOgen	48
31	$Cu(MeCN)_4PF_6$	30	MeCN	3	SOgen	75
32	$Cu(MeCN)_4PF_6$	30	MeCN	6	SOgen	85
33[e]	$Cu(MeCN)_4PF_6$	30	MeCN	12	DABSO	6
34[e]	$Cu(MeCN)_4PF_6$	30	MeCN	12	$Na_2S_2O_5$	3
35[e]	$Cu(MeCN)_4PF_6$	30	MeCN	12	$K_2S_2O_5$	3
36[e]	$Cu(MeCN)_4PF_6$	30	MeCN	12	TsCl	N.D.

[a]Yield was determined by GC of the crude mixture using *n*-hexadecane as an internal standard.

[b]3 mol% of the catalyst was used. [c]6 mol % of the catalyst was used. [d]9 mol% of the catalyst was used. [e]The reaction was set up in a 4 mLvial.

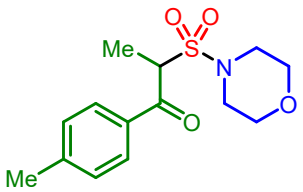
3. General procedure for the synthesis of β-carbonylsulfonamide 3



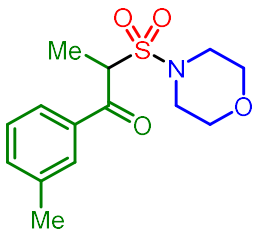
1 **2** **3**

In the glovebox, compound **1** (0.2 mmol, 1.0 equiv.), compound **2** (0.6 mmol, 3.0 equiv.), $Cu(MeCN)_4PF_6$ (9.0 mg, 12.0 mol%) were added into chamber B with a magnetic stirring bar, followed by addition of MeCN (1.0 mL). Tetrabromothiophene S,S-dioxides (172.7 mg, 2.0 equiv.) , 4- methylphenylene (64 μL, 2.4 equiv.) was added to chamber B with a magnetic stirring bar, followed by addition of tetradecane (1.0 mL). The two chamber system was sealed and removed out of the glovebox. The chamber A was allowed to stir at 100 ℃ using heating mantle with 600-800 rpm stirring speed for 10 min. Then chamber B was heated to 30 °C in heat block. After 12 hours, two chamber was cooled to room temperature. Upon completion, the reaction mixture was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford pure products **3**.

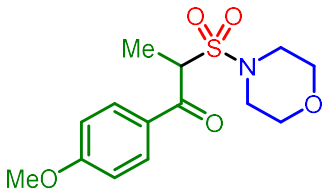
4. Characterization data of products 3



2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-one (3a)
Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (55.3 mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.12 (q, J = 6.9 Hz, 1H), 3.69 – 3.59 (m, 4H), 3.40 – 3.27 (m, 4H), 2.43 (s, 3H), 1.65 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ192.8, 145.6, 133.6, 129.8, 129.4, 67.1, 63.0, 47.2, 21.9, 13.6. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_4S$ 320.0927; found: 320.0926.

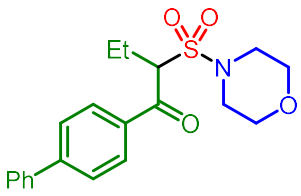


2-(morpholinosulfonyl)-1-(m-tolyl)propan-1-one (3b)
Prepared by the general procedure, isolated as colourless oil using petroleum ether/ethyl acetate (7:1) as eluent (51.7 mg, 87%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.73 (m, 2H), 7.47 – 7.37 (m, 2H), 5.14 (q, *J* = 6.9 Hz, 1H), 3.71 – 3.60 (m, 4H), 3.42 – 3.29 (m, 4H), 2.43 (s, 3H), 1.66 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.6, 139.0, 136.2, 135.2, 129.6, 128.9, 126.5, 67.1, 63.0, 47.2, 21.5, 13.7. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_4S$ 320.0927; found: 320.0926.

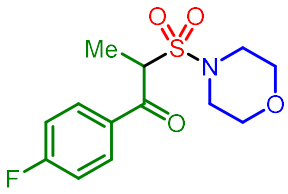


1-(4-methoxyphenyl)-2-(morpholinosulfonyl)propan-1-one (3c) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (3:1) as eluent (58.9 mg, 94%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.08 (q, *J* = 6.9 Hz, 1H), 3.87 (s,

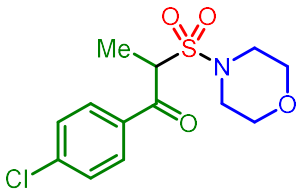
3H), 3.72 – 3.56 (m, 4H), 3.44 – 3.24 (m, *J* = 4.5 Hz, 4H), 1.63 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.2, 164.4, 131.5, 128.8, 114.0, ,66.8, 62.5, 55.5, 47.0, 13.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_5S$ 336.0876; found: 336.0881.



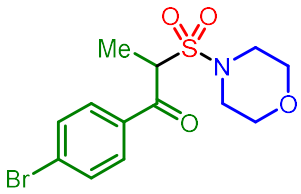
1-([1,1'-biphenyl]-4-yl)-2-(morpholinosulfonyl)butan-1-one (3d)
Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (59.8 mg, 80%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.08 (m, 2H), 7.77 – 7.71 (m, 2H), 7.66 – 7.61 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H), 5.03 (dd, *J* = 10.8, 3.7 Hz, 1H), 3.71 – 3.60 (m, 4H), 3.42 – 3.28 (m, 4H), 2.45 – 2.31 (m, 1H), 2.26 – 2.14 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.9, 147.0, 139.6, 135.9, 129.7, 129.2, 128.7, 127.7, 127.4, 69.7, 67.1, 47.2, 22.3, 11.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}NO_4S$ 374.1421; found: 374.1412.



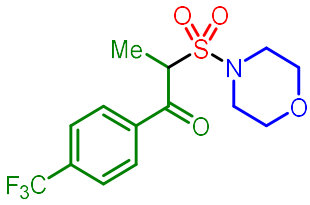
1-(4-fluorophenyl)-2-(morpholinosulfonyl)propan-1-one (3e)
Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (4:1) as eluent (56.7 mg, 94%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.02 (m, 2H), 7.17 (t, *J* = 8.5 Hz, 2H), 5.09 (q, *J* = 6.9 Hz, 1H), 3.70 – 3.59 (m, 4H), 3.41 – 3.27 (m, 4H), 1.64 (d, *J* = 6.9 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.82(s, 1F). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.8, 166.4 (d, J = 258.4 Hz), 132.5 (d, J = 2.9 Hz), 132.1 (d, J = 9.7 Hz), 116.2 (d, J = 22.1 Hz), 67.0, 63.1, 47.2, 13.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{16}FNNaO_4S$ 324.0676; found: 324.0672.



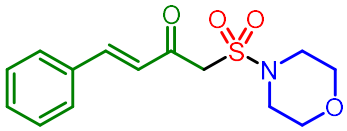
1-(4-chlorophenyl)-2-(morpholinosulfonyl)propan-1-one (3f)
Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (4:1) as eluent (56.6 mg, 89%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 5.08 (q, *J* = 6.9 Hz, 1H), 3.72 – 3.60 (m, 4H), 3.40 – 3.27 (m, 4H), 1.65 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.2, 141.0, 134.4, 130.7, 129.3, 67.0, 63.2, 47.3, 13.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{16}ClNNaO_4S$ 340.0381; found: 340.0377.



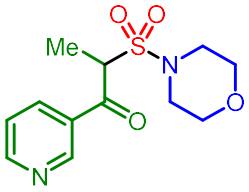
1-(4-bromophenyl)-2-(morpholinosulfonyl)propan-1-one (3g)
Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (4:1) as eluent (68.2 mg, 94%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.67 – 7.61 (m, 2H), 5.07 (q, *J* = 6.9 Hz, 1H), 3.69 – 3.60 (m, 4H), 3.39 – 3.26 (m, 4H), 1.63 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.4, 134.8, 132.3, 130.7, 129.8, 67.0, 63.1, 47.2, 13.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}BrNO_4S$ 362.0056; found: 362.0053.



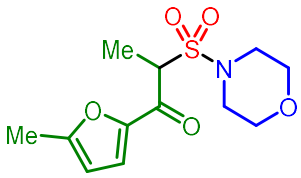
2-(morpholinosulfonyl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (3h) Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (42.9 mg, 61%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 5.13 (q, *J* = 6.9 Hz, 1H), 3.73 – 3.62 (m, 4H), 3.43 – 3.29 (m, 4H), 1.67 (d, *J* = 6.9 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.29(s, 3F). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.8, 138.8, 135.4 (q, J = 33.0 Hz), 129.7, 126.1 (q, J = 3.7 Hz),123.5 (q, J = 273.9 Hz), 67.1, 63.6, 47.4, 13.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{16}F_3NNaO_4S$ 374.0644; found: 374.0645.



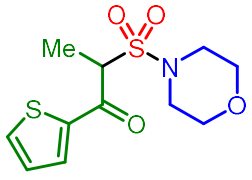
(E)-1-(morpholinosulfonyl)-4-phenylbut-3-en-2-one (3i) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (2:1) as eluent (36.6 mg, 62%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, J = 16.0 Hz, 1H), 7.60 (dd, J = 7.6, 1.7 Hz, 2H), 7.49 – 7.36 (m, 3H), 6.98 (d, J = 16.0 Hz, 1H), 4.25 (s, 2H), 3.76 – 3.70 (m, 4H), 3.38 – 3.31 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.0, 146.6, 133.6, 131.4,129.0, 128.9, 124.8, 66.4, 59.6, 46.1. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{17}NNaO_4S$ 318.0770; found: 318.0772.



2-(morpholinosulfonyl)-1-(pyridin-3-yl)propan-1-one (3j) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (1:1) as eluent (28.4mg, 50%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.22 (s, 1H), 8.81 (s, 1H), 8.35 – 8.23 (m, 1H), 7.50 – 7.42 (m, 1H), 5.09 (q, *J* = 6.9 Hz, 1H), 3.71 – 3.60 (m, 4H), 3.42 – 3.27 (m, *J* = 4.7 Hz, 4H), 1.66 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.6, 154.4, 150.5, 136.6, 131.5, 123.8, 67.1, 63.5, 47.3, 13.2. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{16}N_2NaO_4S$ 307.0723; found: 307.0730.

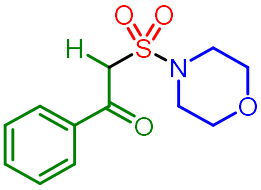


1-(5-methylfuran-2-yl)-2-(morpholinosulfonyl)propan-1-one (3k) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (4:1) as eluent (51.8 mg, 90%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 3.5 Hz, 1H), 6.24 (d, *J* = 3.4 Hz, 1H), 4.82 (q, *J* = 6.8 Hz, 1H), 3.69 – 3.59 (m, 4H), 3.41 – 3.26 (m, 4H), 2.41 (s, 3H), 1.61 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.1, 158.9, 149.7, 121.4, 109.3, 66.0, 62.4, 46.1, 13.3 (d, *J* = 2.0 Hz), 12.0. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{17}NNaO_5S$ 310.0720; found: 310.0714.



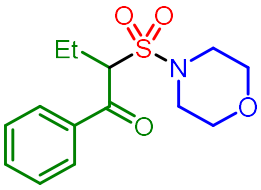
2-(morpholinosulfonyl)-1-(thiophen-2-yl)propan-1-one (3l) Prepared by the general procedure, isolated as colourless oil using petroleum ether/ethyl acetate (5:1) as eluent (28.3 mg, 49%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 3.9 Hz, 1H), 7.76 (d, *J* = 4.9 Hz, 1H), 7.23 – 7.16 (m, 1H), 4.89 (q, *J* = 7.0 Hz, 1H), 3.70 – 3.60 (m, 4H), 3.41 – 3.28 (m, 4H), 1.67 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.5,

143.4, 136.3, 134.6, 128.9, 67.0, 65.0, 47.2, 13.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{15}NNaO_4S_2$ 312.0335; found: 312.0337.



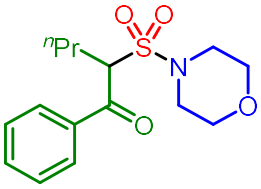
2-(morpholinosulfonyl)-1-phenylethan-1-one (3m)

Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (32.8 mg, 61%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 4.57 (s, 2H), 3.76 – 3.69 (m, 4H), 3.40 – 3.30 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.2, 135.8, 134.6, 129.5, 129.1, 66.7, 57.3, 46.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_4S$ 292.0614; found: 292.0612.



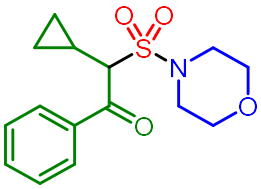
2-(morpholinosulfonyl)-1-phenylbutan-1-one (3n)

Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (6:1) as eluent (50.6 mg, 85%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 4.98 (dd, *J* = 10.8, 3.7 Hz, 1H), 3.68 – 3.56 (m, 4H), 3.39 – 3.25 (m, 4H), 2.42 – 2.27 (m, 1H), 2.23 – 2.13(m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.5, 137.3, 134.3, 129.1,129.0, 69.6, 67.0, 47.1, 22.3, 11.8. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_4S$ 320.0927; found: 320.0923.



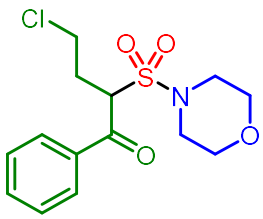
2-(morpholinosulfonyl)-1-phenylpentan-1-one (3o)

Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (7:1) as eluent (50.4 mg, 81%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 5.06 (dd, *J* = 10.9, 3.4 Hz, 1H), 3.68 – 3.58 (m, 4H), 3.39 – 3.25 (m, 4H), 2.39 – 2.26 (m, 1H), 2.13 – 2.02 (m, 1H), 1.35 – 1.22 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.5, 137.1, 134.3, 129.1, 129.0, 68.0, 67.0, 47.2, 30.6, 20.6, 14.0. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{21}NNaO_4S$ 334.1083; found: 334.1084.



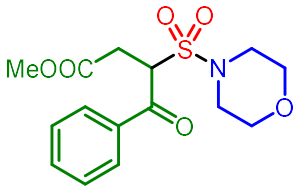
2-cyclopropyl-2-(morpholinosulfonyl)-1-phenylethan-1-one (3p)

Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (30.9 mg, 50%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 2H), 7.66 – 7.59 (m, 1H), 7.54 – 7.46 (m, 2H), 4.26 (d, J = 10.1 Hz, 1H), 3.76 – 3.63 (m, 4H), 3.56 – 3.37 (m, 4H), 1.66 – 1.54 (m, 1H), 0.91 – 0.77 (m, 2H), 0.74 – 0.62 (m, 1H), 0.32 – 0.20 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.6, 136.6, 134.2, 129.0, 72.8, 67.2, 47.12, 9.9, 5.2, 4.7. HRMS (ESI/Q-TOF) m/z: [M+Na]+ calcd for $C_{15}H_{19}NNaO_4S$ 332.0927; found: 332.0925.



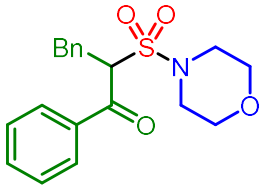
4-chloro-2-(morpholinosulfonyl)-1-phenylbutan-1-one (3q)

Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (54.4 mg, 82%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 5.41 (dd, *J* = 9.9, 3.9 Hz, 1H), 3.79 – 3.67(m, 1H), 3.63 – 3.54 (m, 4H), 3.45 – 3.35 (m, 1H), 3.33 – 3.21 (m, 4H), 2.86 – 2.75 (m, 1H), 2.61 – 2.50 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.3, 136.7, 134.6, 129.2, 129.2, 66.9, 64.8, 47.0, 41.8, 31.1. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{18}ClNNaO_4S$ 354.0537; found: 354.0542.



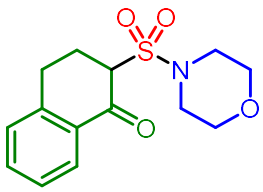
methyl 3-(morpholinosulfonyl)-4-oxo-4-phenylbutanoate (3r)

Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (2:1) as eluent (49.8 mg, 73%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.03 (m, 2H), 7.67 – 7.61 (m, 1H), 7.57 – 7.49 (m, 2H), 5.50 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.64 (s, 3H), 3.61 – 3.56 (m, 4H), 3.48 (dd, *J* = 17.2, 10.9 Hz, 1H), 3.28 – 3.20 (m, 4H), 3.14 (dd, *J* = 17.2, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.1, 170.5, 136.5, 134.4, 129.3, 129.0, 66.8, 63.6, 52.6, 46.9, 33.1. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{19}NNaO_6S$ 364.0825; found: 364.0826.



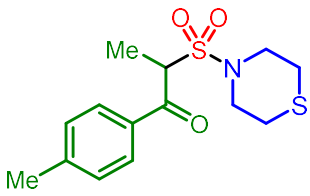
2-(morpholinosulfonyl)-1,3-diphenylpropan-1-one (3s)

Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (4:1) as eluent (44.6 mg, 62%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7,75 (m, 2H), 7.57 – 7.50 (m, 1H), 7.43 – 7.37 (m, 2H), 7.23 – 7.10 (m, 5H), 5.29 (dd, *J* = 11.5, 3.1 Hz, 1H), 3.69 – 3.58 (m, 5H), 3.45 (dd, *J* = 13.1, 3.0 Hz, 1H), 3.42 – 3.28 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.0, 137.2, 136.2, 134.2, 129.0, 129.0, 128.9, 128.8, 127.3, 69.4, 67.0, 47.2, 34.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{21}NNaO_4S$ 382.1083; found: 382.1082.

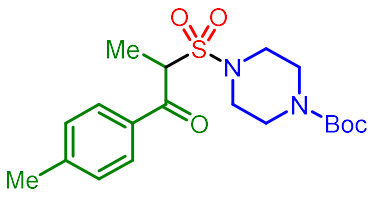


2-(morpholinosulfonyl)-3,4-dihydronaphthalen-1(2H)-one (3t)

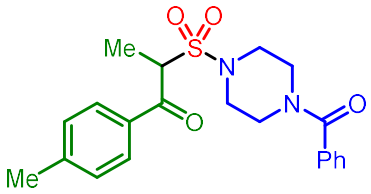
Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (4:1) as eluent (54.4 mg, 92%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.01 (m, 1H), 7.56 – 7.49 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 4.03 (t, *J* = 5.0 Hz, 1H), 3.79 – 3.68 (m, 4H), 3.54 – 3.33 (m, 5H), 2.98 – 2.88 (m, 1H), 2.82 – 2.72 (m, 1H), 2.62 – 2.52 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.0, 144.0, 134.7, 131.8, 129.2, 128.1, 127.2, 67.0, 65.8, 46.5, 26.3, 25.6. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{17}NNaO_4S$ 318.0770; found: 318.0773.



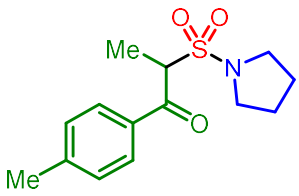
2-(thiomorpholinosulfonyl)-1-(p-tolyl)propan-1-one (3u) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (15:1) as eluent (62.1 mg, 99%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.09 (q, J = 6.9 Hz, 1H), 3.67 – 3.43 (m, 4H), 2.68 – 2.53 (m, 4H), 2.43 (s, 3H), 1.62 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.5, 145.4, 133.4, 129.6, 129.2, 62.8, 49.0, 27.8, 21.7, 13.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_3S_2$ 336.0699; found: 336.0697.



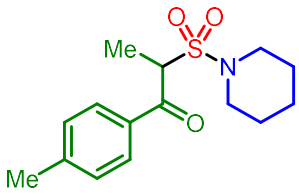
tert-butyl 4-((1-oxo-1-(p-tolyl)propan-2-yl)sulfonyl) piperazine-1-carboxylate (3v) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (77.8 mg, 98%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.11 (q, J = 6.9 Hz, 1H), 3.45-3.33 (m, 4H), 3.33-3.19 (m, 4H), 2.41 (s, 3H), 1.62 (d, J = 6.9 Hz, 3H), 1.43 (s, 9H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.6, 154.2, 145.4, 133.4, 129.5, 129.2, 80.2, 62.8, 46.7, 43.9, 28.2, 21.6, 13.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{28}N_2NaO_5S$ 419.1611; found: 419.1612.



2-((4-benzoylpiperazin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3w) Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (63.3 mg, 79%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.33 (m, 5H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.13 (q, *J* = 6.9 Hz, 1H), 3.73 (s, 2H), 3.39 (s, 6H), 2.42 (s, 3H), 1.64 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.8, 170.6, 145.7, 135.1, 133.5, 130.2, 129.8, 129.4, 128.7, 127.1, 63.1, 48.2, 47.1, 42.7, 21.9, 21.8, 13.6. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{24}N_2NaO_4S$ 423.1349; found: 423.1357.

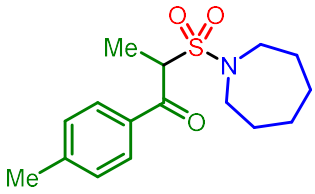


2-(pyrrolidin-1-ylsulfonyl)-1-(p-tolyl)propan-1-one (3x) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (6:1) as eluent (38.8 mg, 69%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 5.12 (q, J = 6.9 Hz, 1H), 3.44 – 3.27(m, 4H), 2.42 (s, 3H), 1.87 – 1.75 (m, 4H), 1.67 (d, J = 6.9 Hz, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.0, 145.0, 133.8, 129.5, 129.2, 62.9, 48.8, 25.8, 21.7, 13.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_3S$ 304.0978; found: 304.0976.

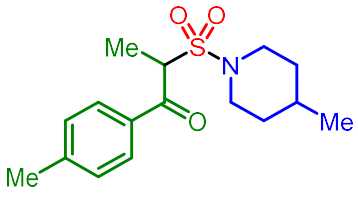


2-(piperidin-1-ylsulfonyl)-1-(p-tolyl)propan-1-one (3y) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (10:1) as eluent (33.1 mg, 56%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 5.08 (q, J = 6.9 Hz, 1H), 3.37 – 3.18 (m, 4H), 2.42

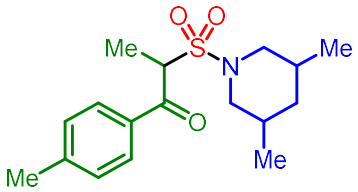
(s, 3H), 1.63 (d, J = 6.9 Hz, 3H), 1.60 – 1.48 (m, 6H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.9, 145.1, 133.7, 129.4, 129.3, 62.8, 47.9, 26.1, 23.7, 21.7, 13.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{21}NNaO_3S$ 318.1134; found: 318.1133.



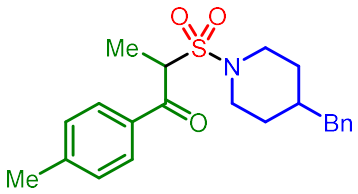
2-(azepan-1-ylsulfonyl)-1-(p-tolyl)propan-1-one (3z)
Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (15:1) as eluent (55.1 mg, 89%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.12 (q, *J* = 6.9 Hz, 1H), 3.38 – 3.18 (m, 4H), 2.42 (s, 3H), 1.75 – 1.61 (m, 7H), 1.61 – 1.50 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.1, 145.2, 133.9, 129.6, 129.4, 63.0, 50.0, 30.0, 26.8, 21.8, 13.7. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{23}NNaO_3S$ 332.1291; found: 332.1294.



2-((4-methylpiperidin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3aa) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (15:1) as eluent (37.8 mg, 61%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 5.09 (q, J = 6.9 Hz, 1H), 3.85-3.71 (m, 1H), 3.71-3.57 (m, 1H), 2.99-2.74 (m, 2H), 2.42 (s, 3H), 1.63 (d, J = 6.9 Hz, 3H), 1.62-1.53 (m, 2H), 1.53-1.39 (m, 1H), 1.25-1.06 (m, 2H), 0.91 (d, J = 6.6 Hz, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.9, 145.1, 133.7, 129.5, 129.3, 62.8, 47.3, 34.2, 30.3, 21.7, 21.6, 13.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{23}NNaO_3S$ 332.1291; found: 332.1295.

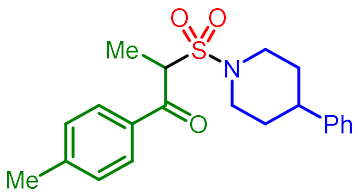


2-((3,5-dimethylpiperidin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3ab) Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (15:1) as eluent (52.4 mg, 81%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.09 (q, J = 6.9 Hz, 1H), 3.81-3.69 (m, 1H), 3.60-3.49 (m, 1H), 2.42 (s, 3H), 2.40-2.24 (m, 2H), 1.78-1.53 (m, 6H), 0.81 (dd, J = 17.5, 6.6 Hz, 6H), 0.63 (q, J = 12.1 Hz, 1H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.1, 145.2, 133.9, 129.6, 129.4, 63.0, 53.7 (d, *J* = 8.6 Hz), 41.8, 31.9, 21.8, 18.9 (d, *J* = 2.8 Hz), 13.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{26}NO_3S$ 324.1628; found: 324.1623.

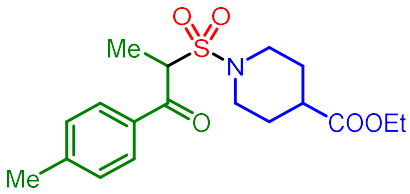


2-((4-benzylpiperidin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3ac) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (10:1) as eluent (45.5 mg, 59%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.15 (m, 4H), 7.15 – 7.08 (m, 1H), 7.08 – 6.98 (m, 2H), 5.01 (q, *J* = 6.9 Hz, 1H), 3.76 – 3.52 (m, 2H), 2.81 – 2.65 (m, 2H), 2.43 (d, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 1.61 – 1.47 (m, 6H), 1.24 – 1.06 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.0, 145.2, 139.9, 133.8, 129.6, 129.4, 129.2, 128.4, 126.2, 62.9, 47.4, 42.9, 37.6, 32.4, 21.8, 13.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{28}NO_3S$ 386.1784;

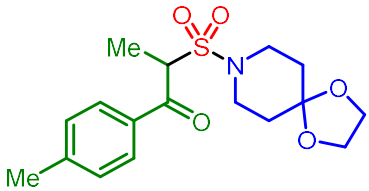
found: 386.1777.



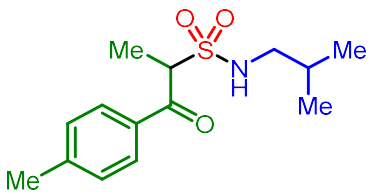
2-((4-phenylpiperidin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3ad) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (10:1) as eluent (55.7 mg, 75%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, J = 8.2 Hz, 2H), 7.38-7.27 (m, 4H), 7.24-7.13 (m, 3H), 5.16 (q, J = 6.9 Hz, 1H), 4.03-3.92 (m, 1H), 3.86-3.75 (m, 1H), 3.11-2.90(m, 2H), 2.66-2.53 (m, 1H), 2.44 (s, 3H), 1.86-1.59 (m, 7H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.8, 145.2, 145.0, 133.7, 129.5, 129.3, 128.5, 126.7, 126.5, 62.8, 47.6, 42.0, 33.4(d, *J* = 7.7 Hz), 21.7, 13.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{26}NO_3S$ 372.1628; found: 372.1620.



ethyl 1-((1-oxo-1-(p-tolyl)propan-2-yl)sulfonyl) piperidine-4-carboxylate (3ae) Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (10:1) as eluent (60.3 mg, 82%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.09 (q, *J* = 6.9 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.80 – 3.58 (m, 2H), 3.06 – 2.90 (m, 2H), 2.47 – 2.34 (m, 4H), 1.95 – 1.83 (m, 2H), 1.78 – 1.64 (m, 2H), 1.62 (d, *J* = 6.9 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.0, 174.0, 145.4, 133.7, 129.7, 129.4, 63.0, 60.8 (d, *J* = 2.4 Hz), 46.4 (d, *J* = 4.4 Hz), 40.4, 28.4 (d, *J* = 5.9 Hz), 21.8 (d, *J* = 2.6 Hz), 14.3, 13.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{26}NO_5S$ 368.1526; found: 368.1518.

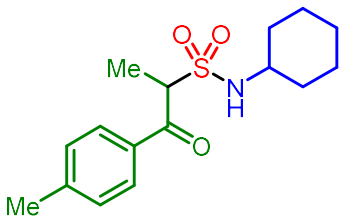


2-((1,4-dioxa-8-azaspiro[4.5]decan-8-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3af) Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (50.2 mg, 71%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.10 (q, J = 6.9 Hz, 1H), 3.93 (s, 4H), 3.50-3.34 (m, 4H), 2.41 (s, 3H), 1.76-1.64 (m, 4H), 1.62 (d, J = 6.9 Hz, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.6, 145.1, 133.6, 129.5, 129.2, 106.2, 64.4, 62.9, 45.2, 35.4, 21.7, 13.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{23}NNaO_5S$ 376.1189; found: 376.1185.

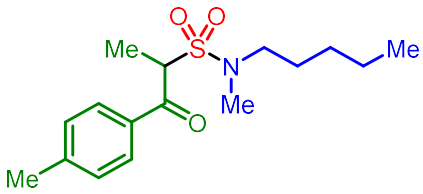


N-isobutyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3ag) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (3:1) as eluent (26.6 mg, 47%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, J = 16 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 5.08 (q, J = 7.0 Hz, 1H), 4.68 (br s, 1H), 3.08-2.91 (m, 2H), 2.42 (s, 3H), 1.81-1.70 (m, 1H), 1.67 (d, J = 7.0 Hz, 3H), 0.92 (dd, J = 6.7, 2.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.1, 145.4, 133.1, 129.6, 129.1, 62.5, 51.7, 29.4, 21.7, 19.7, 14.0. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for

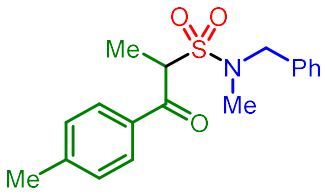
$C_{14}H_{21}NNaO_3S$ 306.1134; found: 306.1127.



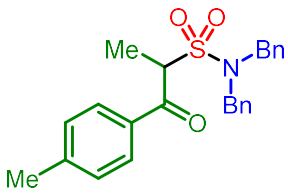
N-cyclohexyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3ah) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (10:1) as eluent (30.3 mg, 49%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.04 (q, *J* = 7.0 Hz, 1H), 4.46 – 4.39 (m, 1H), 3.36 – 3.23 (m, 1H), 2.43 (s, 3H), 2.05 – 1.92(m, 2H), 1.75 – 1.64 (m, 5H), 1.60 – 1.52 (m, 1H), 1.34 – 1.19 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.0, 145.5, 133.4, 129.7, 129.3, 63.0, 53.9, 35.2, 34.8, 25.3, 25.0, 25.0, 14.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{23}NNaO_3S$ 332.1285; found: 332.1291.



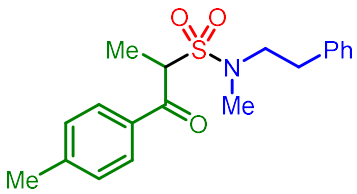
N-methyl-1-oxo-N-pentyl-1-(p-tolyl)propane-2-sulfonamide (3ai) Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (12 mg, 15.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (15:1) as eluent (57.9 mg, 93%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.11 (q, *J* = 6.9 Hz, 1H), 3.21 – 3.05 (m, 2H), 2.83 (s, 3H), 2.42 (s, 3H), 1.65 (d, *J* = 7.0 Hz, 3H), 1.57 – 1.45 (m, 2H), 1.33 – 1.20 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.1, 145.3, 133.8, 129.7, 129.4, 63.0, 51.2, 35.4, 28.6, 27.8, 22.4, 21.9, 14.1, 13.8. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{25}NNaO_3S$ 334.1447; found: 334.1450.



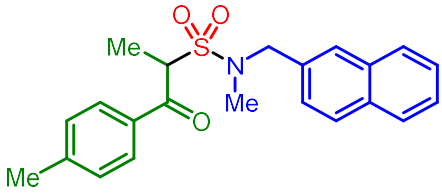
N-benzyl-N-methyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3aj) Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (57.7 mg, 87%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.15 (m, 7H), 5.17 (q, *J* = 7.0 Hz, 1H), 4.33 – 4.20 (m, 2H), 2.71 (s, 3H), 2.38 (s, 3H), 1.68 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.2, 145.4, 136.0, 133.8, 129.7, 129.4, 128.7, 128.3, 128.0, 63.3, 55.0, 35.4, 21.9, 13.9. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{21}NNaO_3S$ 354.1134; found: 354.1140.



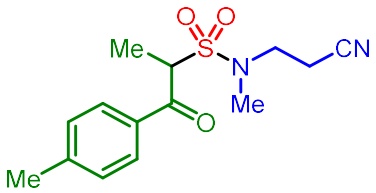
N,N-dibenzyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3ak) Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (12 mg, 15.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as colourless oil using petroleum ether/ethyl acetate (15:1) as eluent (77.4 mg, 95%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, J = 8.3 Hz, 2H), 7.31 – 7.23 (m, 12H), 5.01 (q, J = 7.0 Hz, 1H), 4.40 (s, 4H), 2.45 (s, 3H), 1.70 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.8, 145.1, 135.8, 133.4, 129.4, 129.2, 128.6, 128.4, 127.7, 63.9, 52.0, 21.7, 13.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{26}NO_3S$ 408.1628; found: 408.1619.



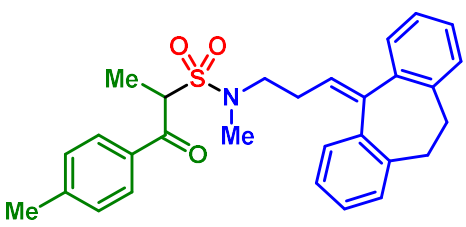
N-methyl-1-oxo-N-phenethyl-1-(p-tolyl)propane-2-sulfonamide (3al) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (15:1) as eluent (66.3 mg, 96%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 2H), 7.34 – 7.27 (m, 4H), 7.24 – 7.16 (m, 3H), 5.07 (q, *J* = 6.9 Hz, 1H), 3.44 – 3.35 (m, 2H), 2.91 – 2.82 (m, 5H), 2.43 (s, 3H), 1.63 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.8, 145.2, 138.3, 133.7, 129.6, 129.3, 128.9, 128.6, 126.6, 62.9, 52.8, 36.0, 35.4, 21.8, 13.7. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{24}NO_3S$ 346.1471; found: 346.1466.



N-methyl-N-(naphthalen-2-ylmethyl)-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3am) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (46.5 mg, 61%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.88 – 7.78 (m, 2H), 7.59 – 7.39 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.26 (q, *J* = 7.0 Hz, 1H), 4.93 – 4.77 (m, 2H), 2.76 (s, 3H), 2.44 (s, 3H), 1.80 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.3, 145.5, 133.9, 133.8, 131.7, 131.0, 129.7, 129.5, 129.0, 128.8, 127.3, 126.7, 126.1, 125.3, 123.5, 63.5, 52.9, 35.6, 21.9, 14.1. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NO_3S$ 382.1471; found: 382.1466.



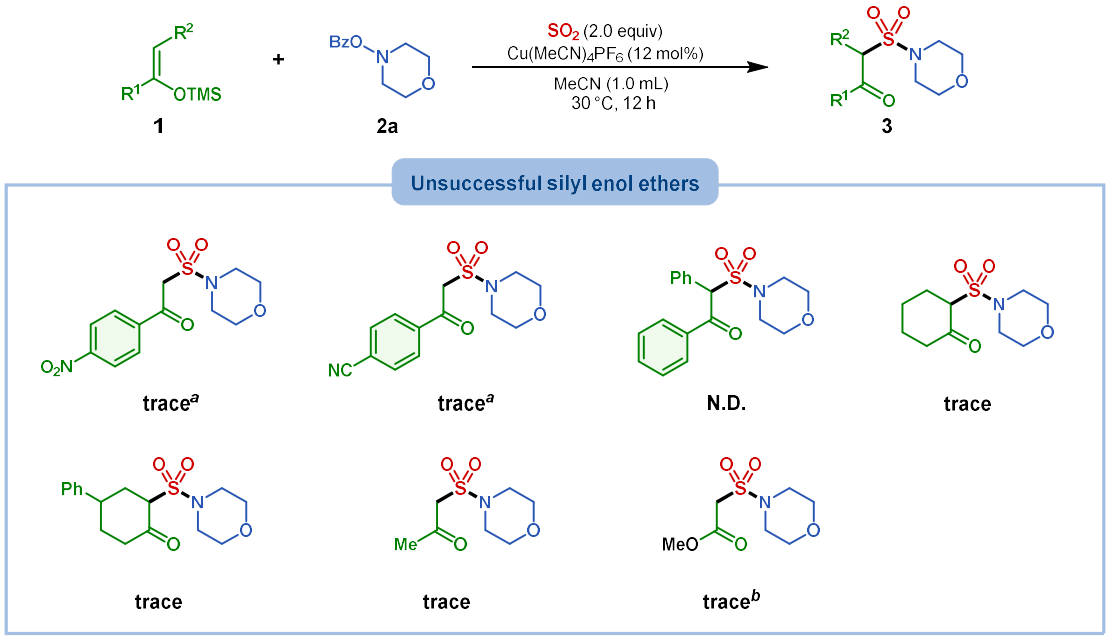
N-(2-cyanoethyl)-N-methyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3an) Prepared by the general procedure, $Cu(MeCN)_4PF_6$ (15 mg, 20.0 mol%) instead of $Cu(MeCN)_4PF_6$ (9 mg, 12.0 mol%), isolated as white solid using petroleum ether/ethyl acetate (2:1) as eluent (35.3 mg, 60%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.16 (q, *J* = 7.0 Hz, 1H), 3.50-3.36 (m, 2H), 2.98 (s, 3H), 2.59 (t, *J* = 6.9 Hz, 2H), 2.43 (s, 3H), 1.67 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.9, 145.9, 133.4, 129.9, 129.4, 117.6, 63.3, 47.4, 36.8, 21.9, 18.3, 13.9. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{18}N_2NaO_3S$ 317.0930; found: 317.0932.



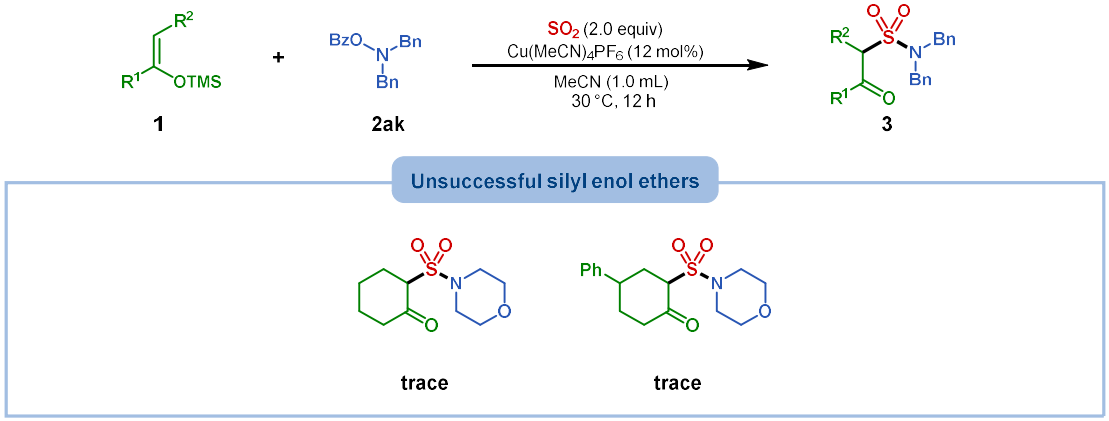
N-(3-(10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)propyl)-N-methyl-1-oxo-1-(p-tolyl) propane-2-sulfonamide (3ao) Prepared by the general procedure, isolated as colourless oil using petroleum ether/ethyl acetate (15:1) as eluent (57.5 mg, 61%).^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 (d, J = 8.2 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.23 – 7.06 (m, 6H), 7.06 – 6.99 (m, 1H), 5.78 (t, J = 7.4 Hz, 1H), 5.10 (q, J = 7.0 Hz, 1H), 3.49 – 3.13 (m, 4H), 3.02 – 2.86 (m, 1H), 2.83 – 2.66 (m, 4H), 2.43 (s, 3H), 2.41 – 2.29 (m, 2H), 1.64 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.0, 145.4, 145.2, 140.9, 139.8, 139.5, 137.1, 133.7, 130.1, 129.7, 129.4,

128.7, 128.2, 128.1, 127.7, 127.3, 126.9, 126.2, 125.9, 63.0, 50.9, 35.4, 33.8, 32.0, 28.4, 21.9, 13.7. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{32}NO_3S$ 474.2097; found: 474.2088.

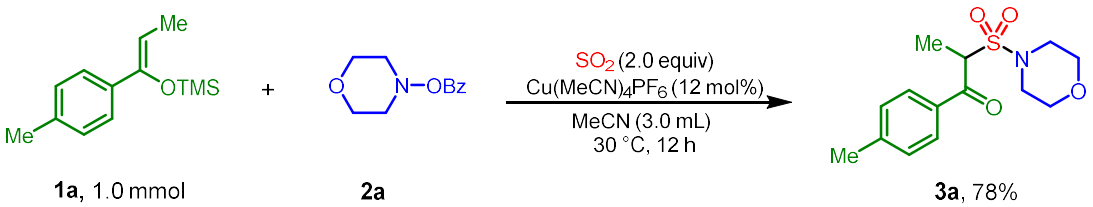
5. Unsuccessful silyl enol ethers



[a]The reaction substrate is unstable. [b]The reaction substrate is *tert*-butyl((1-methoxyvinyl)oxy)dimethylsilane.



6. Scale-up reaction

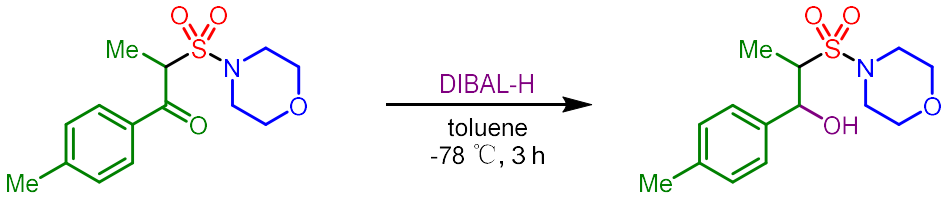


In the glovebox, compound **1a** (1.0 mmol, 1.0 equiv.), compound **2a** (3.0 mmol, 3.0 equiv.), $Cu(MeCN)_4PF_6$ (44.7 mg, 12.0 mol%) were added into chamber B with a magnetic stirring bar,

followed by addition of MeCN (3.0 mL). Tetrabromothiophene S,S-dioxides (863.4 mg, 2.0 equiv.) , 4- methylphenylene (320 μL, 2.4 equiv.) was added to chamber B with a magnetic stirring bar, followed by addition of tetradecane (3.0 mL). The two chamber system was sealed and removed out of the glovebox. The chamber A was allowed to stir at 100 ℃ using heating mantle with 600-800 rpm stirring speed for 10 min. Then chamber B was heated to 30 °C in heat block. After 12 hours, two chamber was cooled to room temperature. Upon completion, the reaction mixture was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford pure products **3a** (231 mg, 78%).

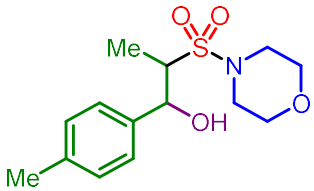
7. Transformations of β-carbonylsulfonamide

Transformation A of Product 3



3a **4**, 85%

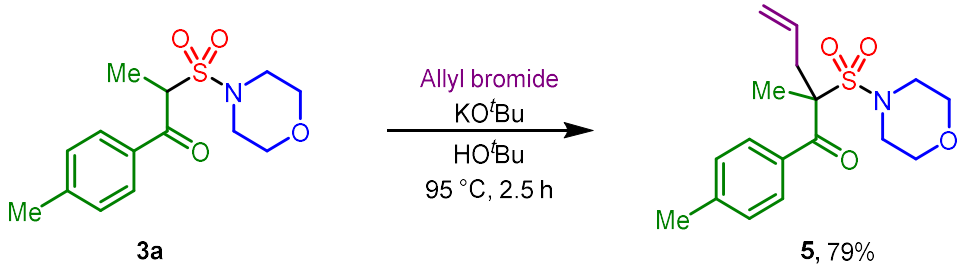
A mixture of compound **3a** (59.5 mg, 0.2 mmol) in toluene (3.0 mL) was added DIBAL-H (2.0 M in hexane, 1.2 mL, 2.4 mmol) dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 3 h. Upon completion, the mixture was slowly quenched with 2 N NaOH (aq) and extracted with ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford the corresponding product **4** (50.9 mg, 85%).[1]



2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-ol (4)

Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (2:1) as eluent (50.9 mg, 85%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.11 (m, 4H), 4.83 (d, *J* = 9.0 Hz, 1H), 4.02 (d, *J* = 1.5 Hz, 1H), 3.78 – 3.69 (m, 4H), 3.45 – 3.34 (m, 4H), 3.34 – 3.23 (m, 1H), 2.34 (s, 3H), 0.96 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.5, 137.0, 129.5, 127.0, 74.0, 67.0, 63.6, 46.4, 21.3, 13.0. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{21}NNaO_4S$ 322.1083; found: 322.1080.

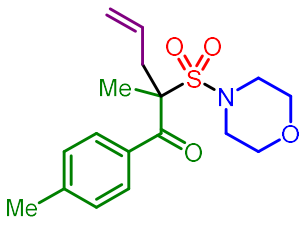
Transformation B of Product 3



3a **5**, 79%

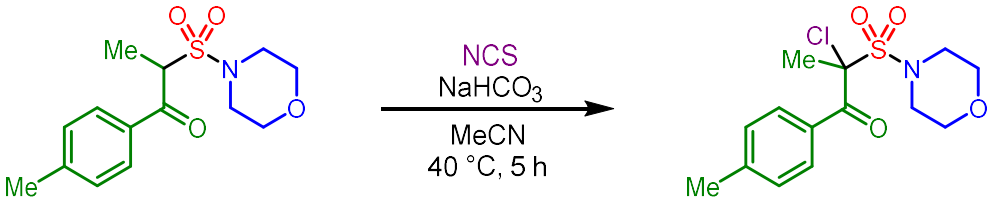
A mixture of compound **3a** (59.5 mg, 0.2 mmol), allyl bromide (0.3 mmol, 1.5 equiv.), potassium t-butoxide (0.3 mmol, 1.5 equiv.) in t-butyl alcohol (0.6 mL) was heated at reflux for

2.5 h under a nitrogen atmosphere. Upon completion, water was added, and the products were extracted with ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford the corresponding product **5** (53.3 mg, 79%).[2]



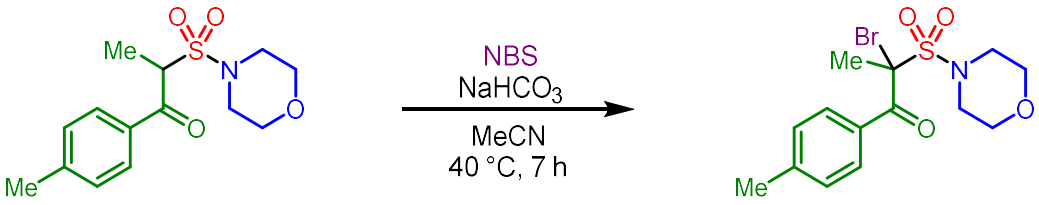
2-methyl-2-(morpholinosulfonyl)-1-(p-tolyl)pent-4-en-1-one (5) Prepared by the general procedure, isolated as yellow oil using petroleum ether/ethyl acetate (6:1) as eluent (53.3 mg, 79%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 5.53 – 5.36 (m, 1H), 5.15 – 4.99 (m, 2H), 3.77 – 3.60 (m, 4H), 3.45 – 3.25 (m, 5H), 2.57 (dd, J = 13.3, 8.3 Hz, 1H), 2.39 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ199.3, 142.9, 135.9, 131.0, 129.0, 128.9, 120.8, 76.3, 67.2, 47.9, 40.4, 21.7 (d, J = 2.9 Hz), 20.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{23}NNaO_4S$ 360.1240; found: 360.1244.

Transformation C of Product 3



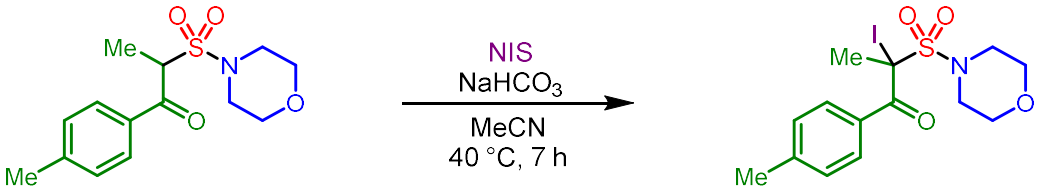
3a **6a**, 81%

A mixture of compound **3a** (59.5 mg, 0.2 mmol) and N-chlorosuccinimide (0.26 mmol, 1.3 equiv.) in MeCN (0.8 mL) was added saturated $NaHCO_3$ (0.2 mL).The reaction mixture was stirred at 40 °C for 5 h. Upon completion, water was added, and the products were extracted with DCM. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford the corresponding product **6a** (53.6 mg, 81%).[3]



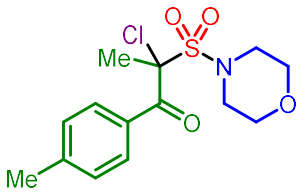
3a **6b**, 73%

A mixture of compound **3a** (59.5 mg, 0.2 mmol) and N-bromosuccinimide (0.26 mmol, 1.3 equiv.) in MeCN (0.8 mL) was added saturated $NaHCO_3$ (0.2 mL). The reaction mixture was stirred at 40 °C for 7 h. Upon completion, water was added, and the products were extracted with DCM. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford the corresponding product **6b** (54.7 mg, 73%).[3]



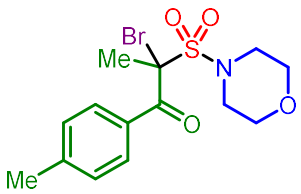
3a **6c**, 41%

A mixture of compound **3a** (59.5 mg, 0.2 mmol) and N-iodosuccinimide (0.26 mmol, 1.3 equiv.) in MeCN (0.8 mL) was added saturated $NaHCO_3$ (0.2 mL). The reaction mixture was stirred at 40 °C for 7 h. Upon completion, water was added, and the products were extracted with DCM. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford the corresponding product **6c** (35.0 mg, 41%).[3]



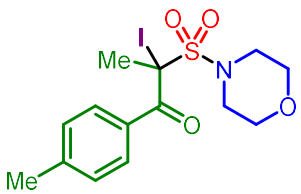
2-chloro-2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-one (6a)

Prepared by the general procedure, isolated as pale yellow solid using petroleum ether/ethyl acetate (10:1) as eluent (53.6 mg, 81%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.02 (m, 2H), 7.27 – 7.21 (m, 2H), 3.75 – 3.65 m, 4H), 3.52 – 3.39 (m, 4H), 2.40 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.7, 144.6, 132.0, 130.8, 128.9, 86.4, 67.1, 48.4, 26.8, 21.8. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{18}ClNNaO_4S$ 354.0537; found: 354.0541.



2-bromo-2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-one (6b)

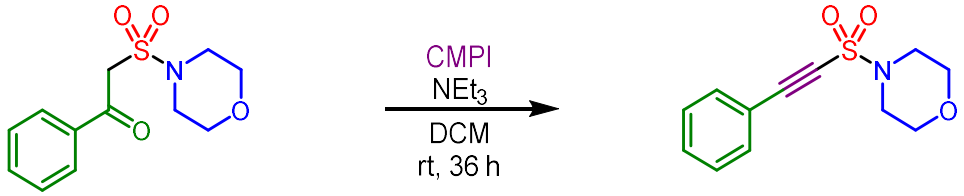
Prepared by the general procedure, isolated as pale yellow solid using petroleum ether/ethyl acetate (10:1) as eluent (54.7 mg, 73%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.03 (m, 2H), 7.25 – 7.19 (m, 2H), 3.74 – 3.64 (m, 4H), 3.54 – 3.40 (m, 4H), 2.40 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.5, 144.4, 132.3, 130.8, 128.9, 77.0, 67.1, 48.6, 27.9 (d, J = 3.8 Hz), 21.7 (d, J = 3.9 Hz). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{19}BrNO_4S$ 376.0213; found: 376.0208.



2-iodo-2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-one (6c)

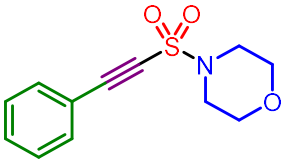
Prepared by the general procedure, isolated as brown solid using petroleum ether/ethyl acetate (10:1) as eluent (35.0 mg, 41%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.05 (m, 2H), 7.25 – 7.20 (m, 2H), 3.74 – 3.66 (m, 4H), 3.54 – 3.41 (m, 4H), 2.57 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.8, 144.2, 132.6, 130.9, 128.9, 67.2, 56.2, 49.0, 30.8, 21.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{19}INO_4S$ 424.0074; found: 424.0072.

Transformation D of Product 3



3l **7**, 70%

A mixture of compound **3l** (53.9 mg, 0.2 mmol) and 2-Chloro-1-methylpyridinium iodide (0.24 mmol, 1.2 equiv.) in DCM (2.0 mL) was added Et_3N (0.36 mmol, 1.8 equiv.) dropwise. The reaction mixture was stirred at room temperature for 36 h, then 1N NaOH (0.6 mL) was added. After 5 min, water was added , and the reaction mixture was extracted with DCM. The combined organic extracts were dried over anhydrous Na_2SO_4 and the residue was filtered through a short column of Al_2O_3 using DCM as eluent to afford the corresponding product **7** (35.4 mg, 70%).[4]

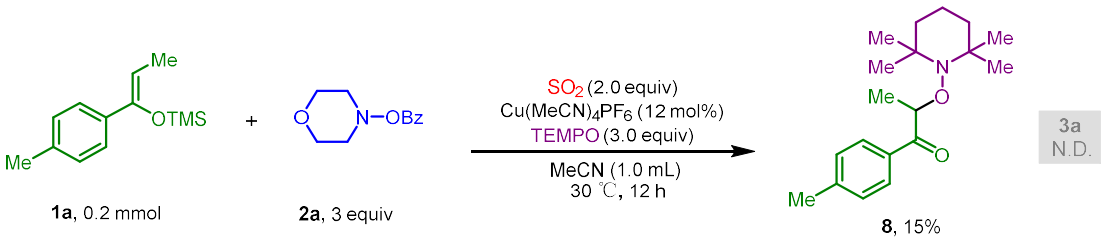


4-((phenylethynyl)sulfonyl)morpholine (7)

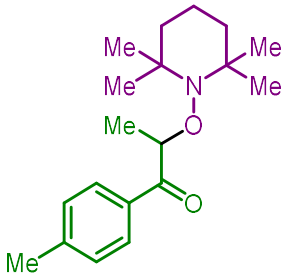
Prepared by the general procedure, isolated as white solid (35.4 mg, 70%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.56 (m, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.39 (m, 2H), 3.89 – 3.81 (m, 4H), 3.30 – 3.21 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 133.0, 131.6, 129.0, 118.0, 91.6, 79.3, 65.9, 46.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{13}NNaO_3S$ 274.0508; found: 274.0509.

8. Mechanistic Studies

Radical trapping experiments A

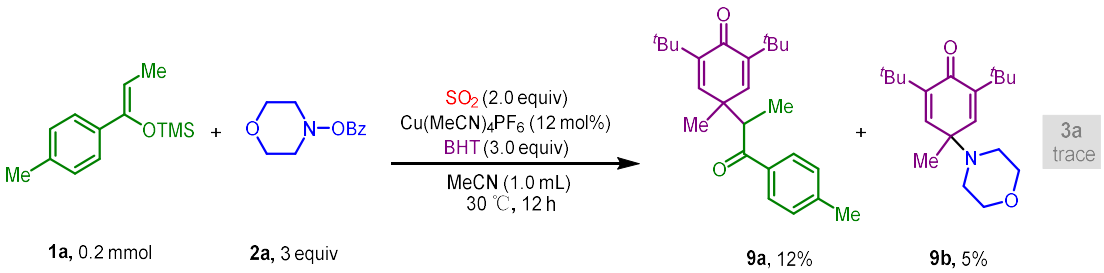


In the glovebox, compound **1a** (0.2 mmol, 1.0 equiv.), compound **2a** (0.6 mmol, 3.0 equiv.), $Cu(MeCN)_4PF_6$ (9.0 mg, 12.0 mol%), TEMPO (0.6 mmol, 3.0 equiv.) were added into chamber B with a magnetic stirring bar, followed by addition of MeCN (1.0 mL). Tetrabromothiophene S,S-dioxides (0.4 mmol, 172.7 mg) , 4- methylphenylene (0.48 mmol, 64 μL)was added to chamber A with a magnetic stirring bar, followed by addition of tetradecane (1.0 mL). The two chamber system was sealed and removed out of the glovebox. The chamber A was allowed to stir at 100 ℃ using heating mantle with 600-800 rpm stirring speed for 10 min. Then chamber B was heated to 30 °C in heat block. After 12 hours, two chamber was cooled to room temperature. TLC, GC and LC-MS analysis demonstrated the product **3a** is not founded. The TEMPO-adduct **5a** was detected by LC-MS. The reaction mixture was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford the TEMPO-adduct **8** (9.3 mg, 15%).



2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-1-(p-tolyl)propan-1-one (8) Prepared by the general procedure, isolated as colourless oil using petroleum ether/ethyl acetate (80:1) as eluent (9.3 mg, 15%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, J = 8.2 Hz, 2H), 7.31 – 7.21 (m, 2H), 4.98 (q, J = 7.1 Hz, 1H), 2.41 (s, 3H), 1.53 – 1.47 (m, 5H), 1.39 (s, 2H), 1.33 – 1.26 (m, 5H), 1.18 (s, 3H), 1.04 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.7, 144.0, 132.8, 129.5, 129.3, 86.6, 86.5, 59.8, 40.4, 21.9, 21.8, 20.5, 19.5, 19.5, 17.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{30}NO_2$ 304.2271; found: 304.2276.

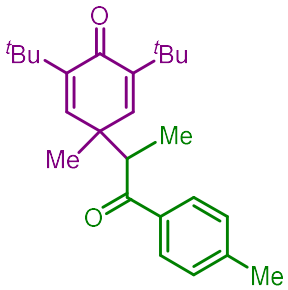
Radical trapping experiments B



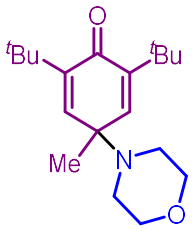
1a, 0.2 mmol **2a**, 3 equiv **9a**, 12% **9b**, 5%

In the glovebox, compound **1a** (0.2 mmol, 1.0 equiv.), compound **2a** (0.6 mmol, 3.0 equiv.), $Cu(MeCN)_4PF_6$ (9.0 mg, 12.0 mol%), BHT (0.6 mmol, 3.0 equiv.) were added into chamber B with a magnetic stirring bar, followed by addition of MeCN (1.0 mL). Tetrabromothiophene S,S-dioxides (0.4 mmol, 172.7 mg) , 4- methylphenylene (0.48 mmol, 64 μL)was added to chamber A with a magnetic stirring bar, followed by addition of tetradecane (1.0 mL). The two chamber system was sealed and removed out of the glovebox. The chamber A was allowed to stir at 100 ℃ using heating mantle with 600-800 rpm stirring speed for 10 min. Then chamber B was heated to 30 °C in heat block. After 12 hours, two chamber was cooled to room temperature. Upon completion, the reaction mixture was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford compound **9a** (8.9 mg, 12%) and compound **9b** (8.6 mg, 5%).

2,6-di-tert-butyl-4-methyl-4-(1-oxo-1-(p-tolyl)propan-2-yl)cyclohexa-2,5-dien-1-one (9a)



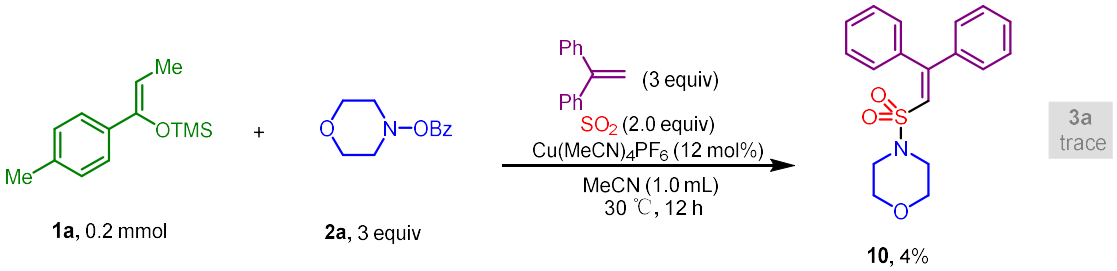
Prepared by the general procedure, isolated as pale oil using petroleum ether/ethyl acetate (50:1) as eluent (8.9 mg, 12%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 2.9 Hz, 1H), 6.43 (d, J = 2.9 Hz, 1H), 3.70 (q, J = 6.9 Hz, 1H), 2.42 (s, 3H), 1.23 (s, 9H), 1.19 – 1.16 (m, 12H), 1.02 (d, J = 7.0 Hz, 3H). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{35}O_2$ 367.2632; found: 367.2625.



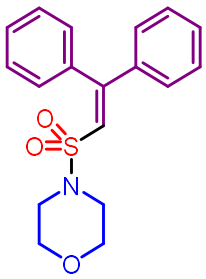
2,6-di-tert-butyl-4-methyl-4-morpholinocyclohexa-2,5-dien-1-one (9b)

Prepared by the general procedure, isolated as pale oil using petroleum ether/ethyl acetate (15:1) as eluent (8.6 mg, 5%).^{1}H NMR (400 MHz, Chloroform-*d*) 6.60 (s, 2H), 3.61 – 3.48 (m, 4H), 3.23 – 3.09 (m, 4H), 1.71 (s, 3H), 1.25 (s, 18H). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{32}NO_2$ 306.2428; found: 306.2427.

Radical trapping experiments C



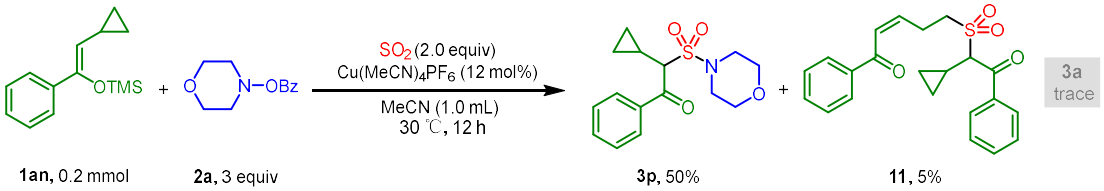
In the glovebox, compound **1a** (0.2 mmol, 1.0 equiv.), compound **2a** (0.6 mmol, 3.0 equiv.), $Cu(MeCN)_4PF_6$ (9.0 mg, 12.0 mol%), 1,1-Diphenylethylene (0.6 mmol, 3.0 equiv.) were added into chamber B with a magnetic stirring bar, followed by addition of MeCN (1.0 mL). Tetrabromothiophene S,S-dioxides (0.4 mmol, 172.7 mg) , 4- methylphenylene (0.48 mmol, 64 μL)was added to chamber A with a magnetic stirring bar, followed by addition of tetradecane (1.0 mL). The two chamber system was sealed and removed out of the glovebox. The chamber A was allowed to stir at 100 °C using heating mantle with 600-800 rpm stirring speed for 10 min. Then chamber B was heated to 30 °C in heat block. After 12 hours, two chamber was cooled to room temperature. Upon completion, the reaction mixture was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford compound **10** (7.5 mg, 4%).



4-((2,2-diphenylvinyl)sulfonyl)morpholine (10)

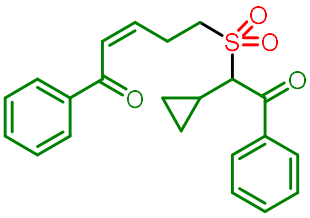
Prepared by the general procedure, isolated as pale oil using petroleum ether/ethyl acetate (5:1) as eluent (7.5 mg, 4%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 4H), 7.38 – 7.30 (m, 4H), 7.27 – 7.22 (m, 2H), 6.63 (s, 1H), 3.66 – 3.58 (m, 4H), 3.12 – 3.05 (m, 4H). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}NNaO_3S$ 352.0978; found: 352.0976.

Radical clock experiment



In the glovebox, compound **1an** (0.2 mmol, 1.0 equiv.), compound **2a** (0.6 mmol, 3.0 equiv.), $Cu(MeCN)_4PF_6$ (9.0 mg, 12.0 mol%) were added into chamber B with a magnetic stirring bar, followed by addition of MeCN (1.0 mL). Tetrabromothiophene S,S-dioxides (0.4 mmol, 172.7

mg) , 4- methylphenylene (0.48 mmol, 64 μL)was added to chamber A with a magnetic stirring bar, followed by addition of tetradecane (1.0 mL). The two chamber system was sealed and removed out of the glovebox. The chamber A was allowed to stir at 100 ℃ using heating mantle with 600-800 rpm stirring speed for 10 min. Then chamber B was heated to 30 °C in heat block. After 12 hours, two chamber was cooled to room temperature. Upon completion, the reaction mixture was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford compound **3p** (30.9 mg, 50%) and compound **11** (2.0 mg, 5%).



(Z)-5-((1-cyclopropyl-2-oxo-2-phenylethyl)sulfonyl)-1-phenylpent-2-en-1-one (11) Prepared by the general procedure, isolated as white solid using petroleum ether/ethyl acetate (5:1) as eluent (2.0 mg, 5%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.89 (m, 4H), 7.69 – 7.63 (m, 1H), 7.61 – 7.44 (m, 5H), 7.07 – 6.96 (m, 2H), 4.26 (d, J = 9.6 Hz, 1H), 3.68 – 3.57 (m, 1H), 3.55 – 3.42 (m, 1H), 3.01 – 2.84 (m, 2H), 1.00 – 0.80 (m, 3H), 0.80 – 0.71 (m, 1H), 0.47 – 0.32 (m, 1H). HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{22}NaO_4S$ 405.1131; found: 405.1134.

9. References

[1]Lv, H.; He, X.; Shen, L.; Zhang, X.; Lian, Z. *Adv. Synth. Cat*. 2022, *364*, 2729-2734.

[2] Han, B.; Yang, X. L.; Fang, R.; Yu, W.; Wang, C.; Duan, X. Y.; Liu, S. *Angew. Chem. Int. Ed*. 2012, *51*, 8816-8820.

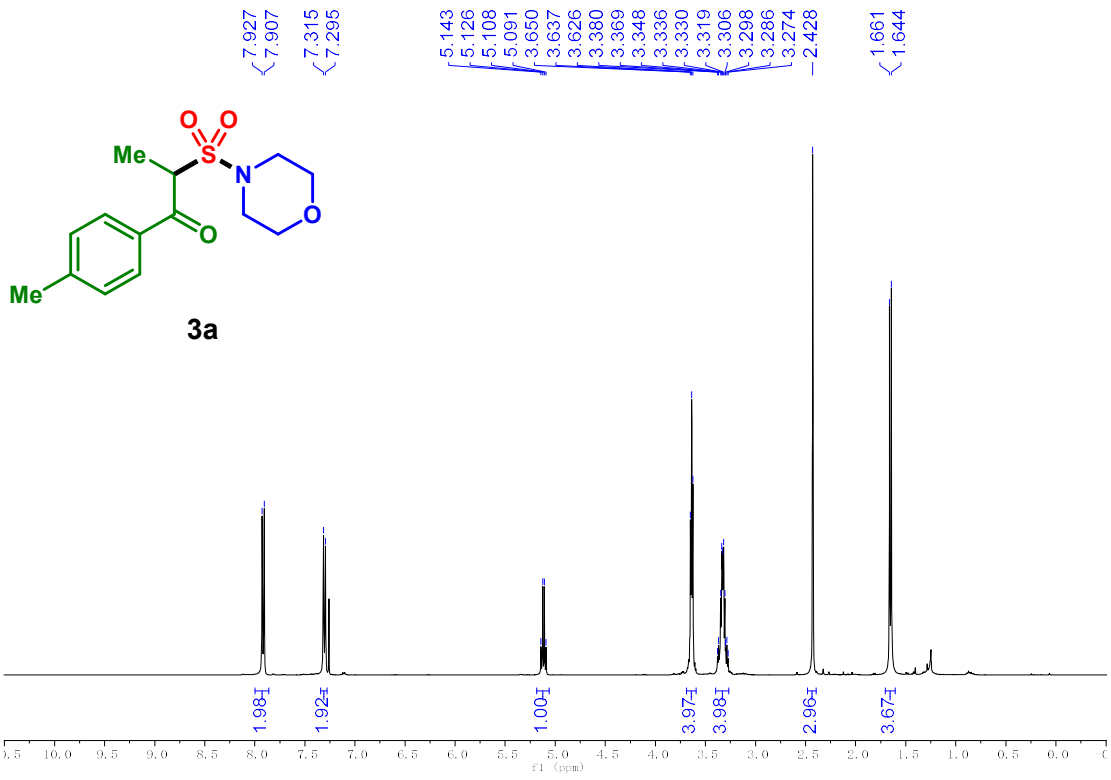
[3] Freihammer, P. M.; Detty, M. R. *J. Org. Chem.* 2000, *65*, 7203-7207.

[4] Leclercq, M.; Brienne, M. J. *Tetrahedron letters.* 1990, *31*, 3875-3878.

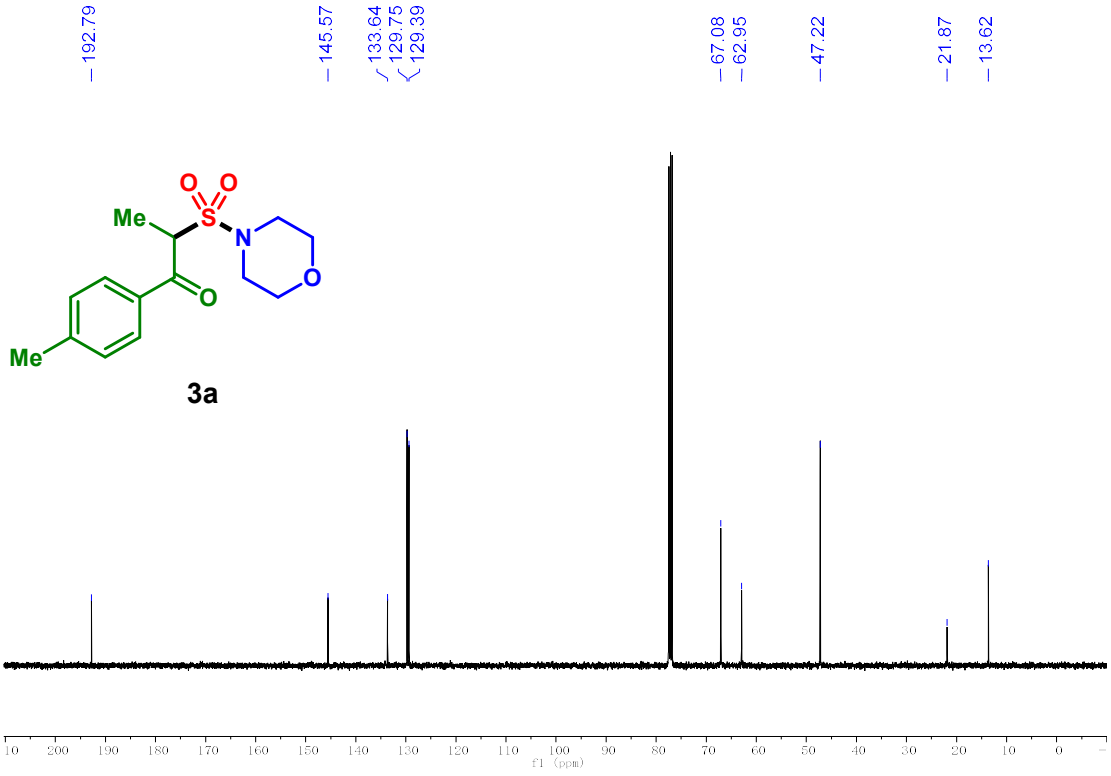
10. NMR Spectra

2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-one (3a)

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

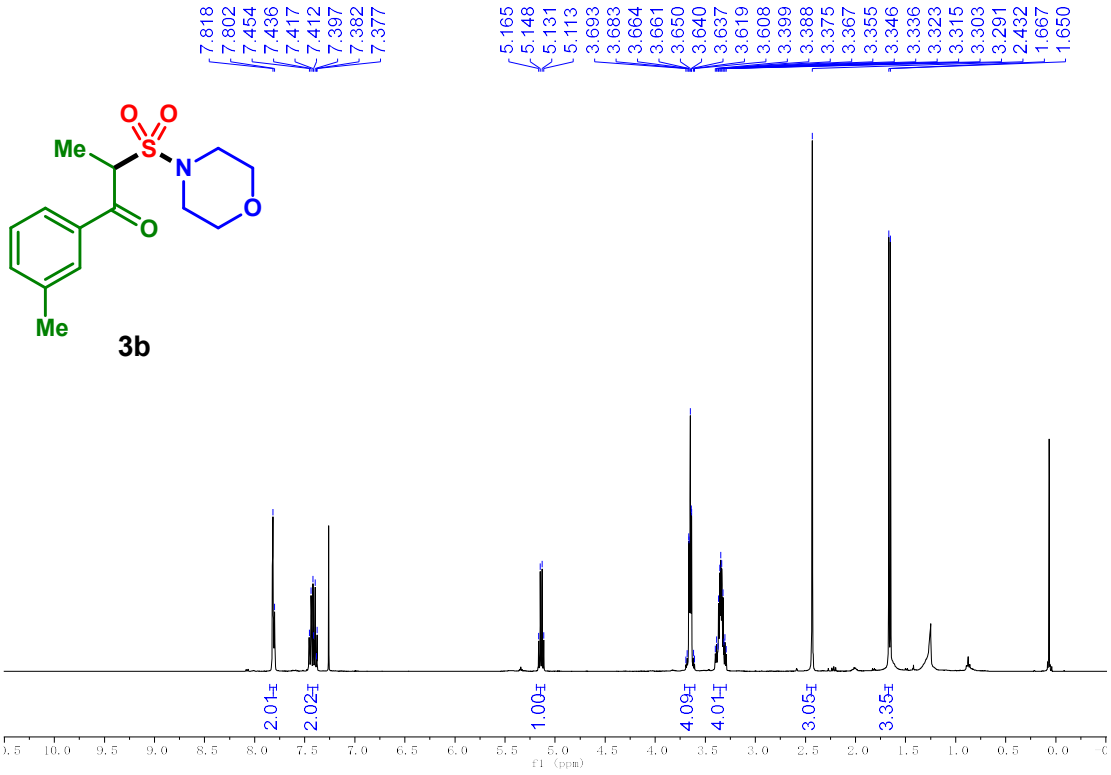


^{13}C NMR (100 MHz, $CDCl_3$)

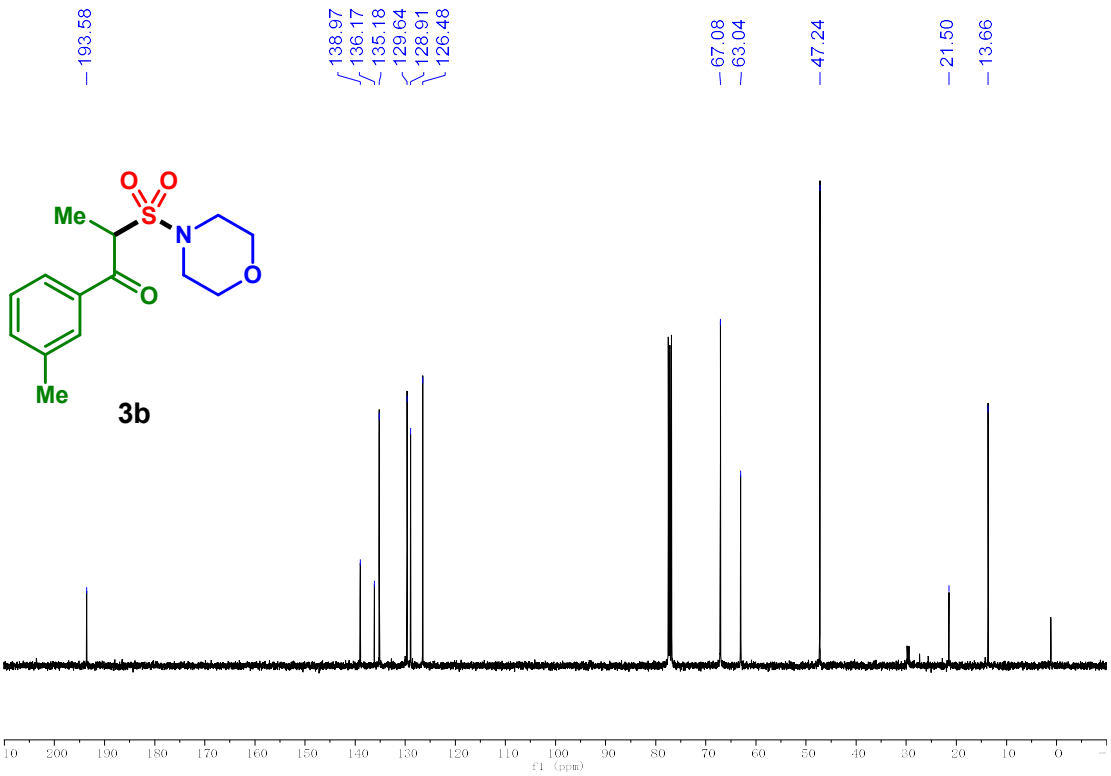


2-(morpholinosulfonyl)-1-(m-tolyl)propan-1-one (3b)

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

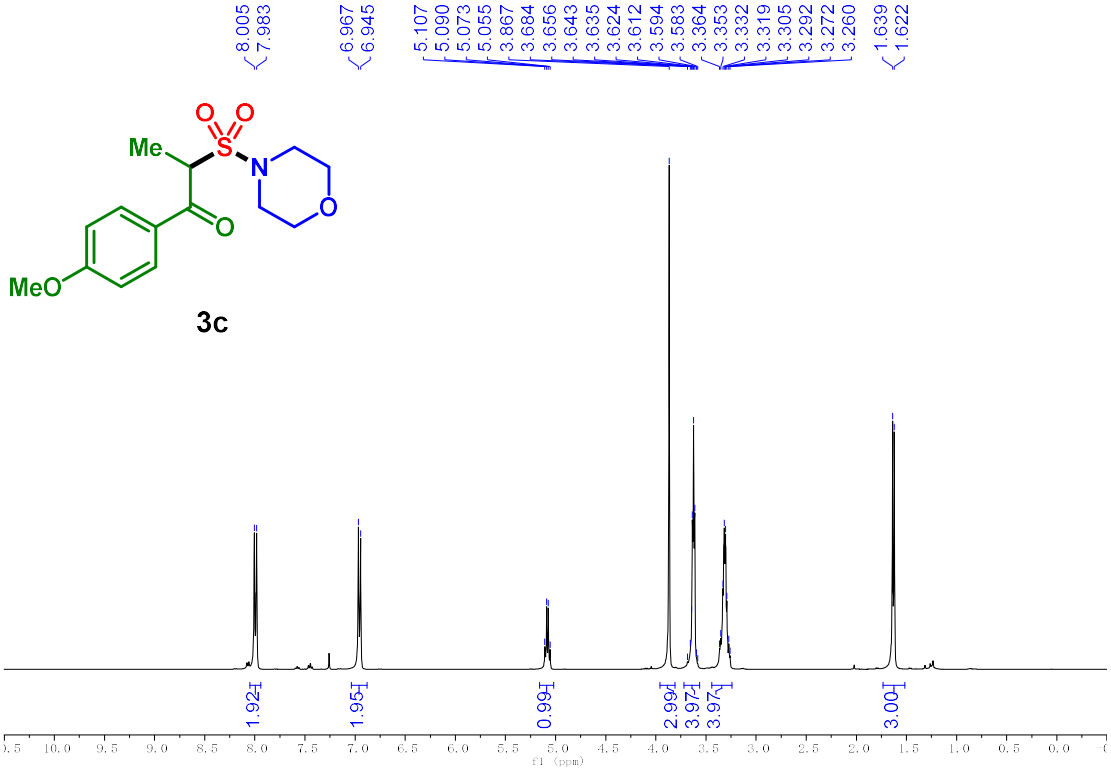


^{13}C NMR (100 MHz, $CDCl_3$)

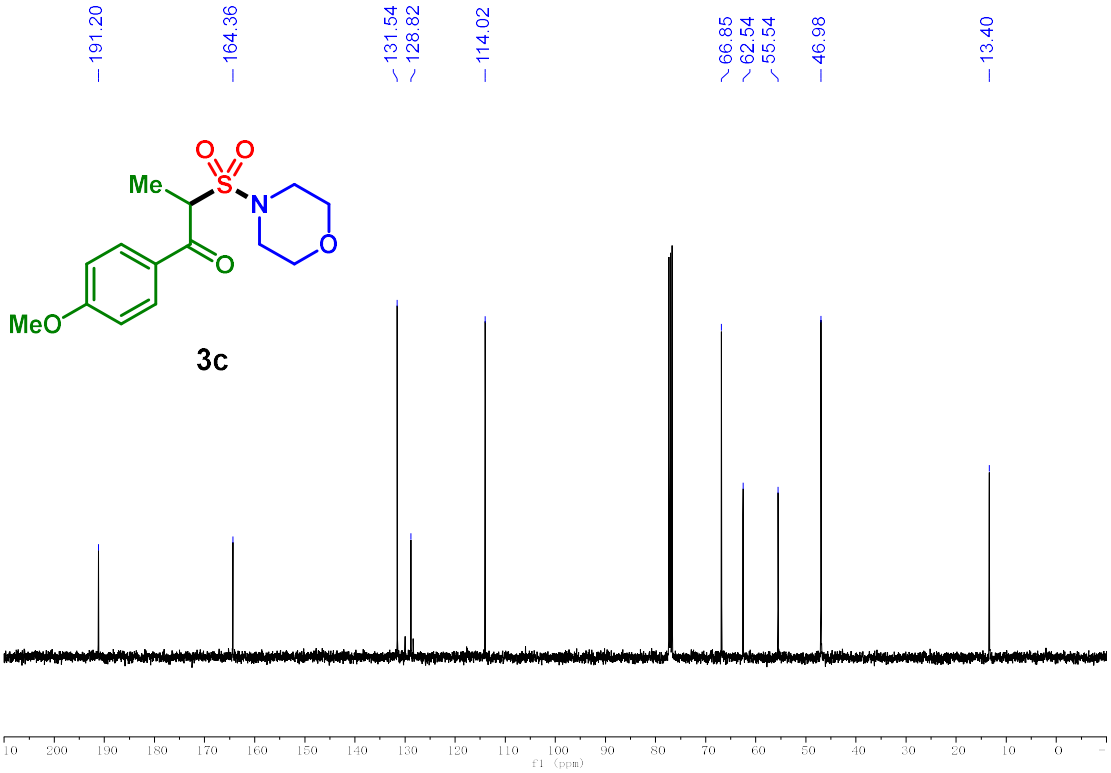


1-(4-methoxyphenyl)-2-(morpholinosulfonyl)propan-1-one (3c)

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

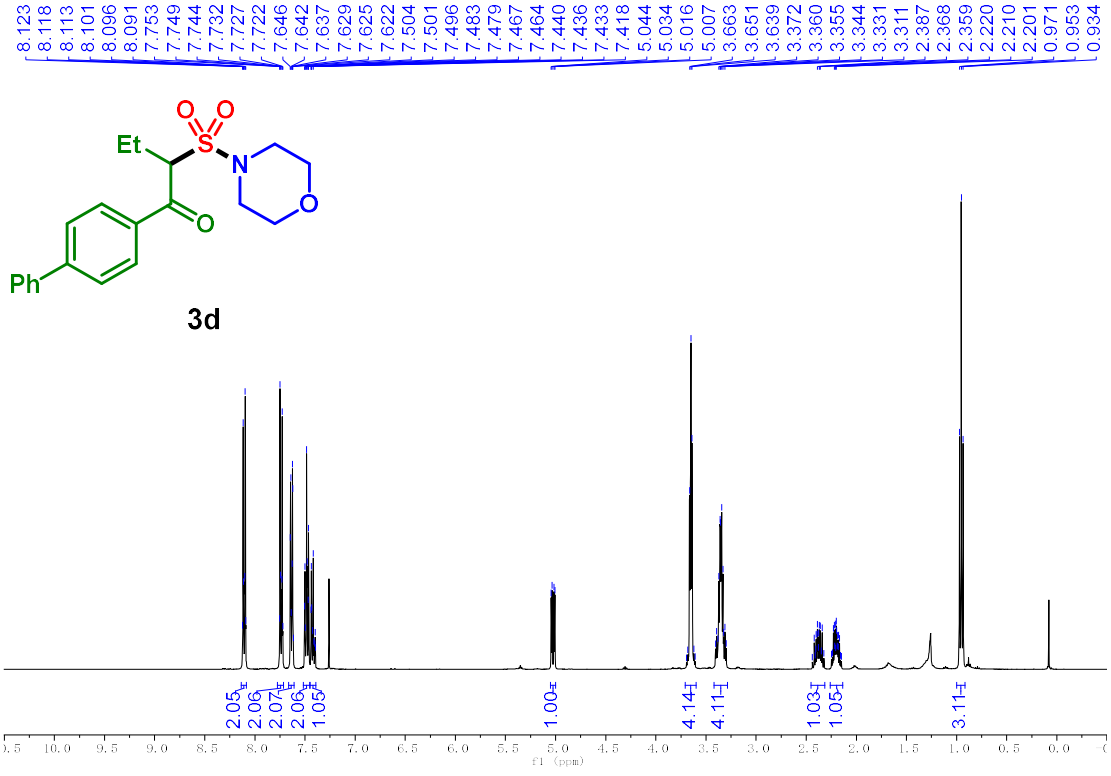


^{13}C NMR (100 MHz, $CDCl_3$)

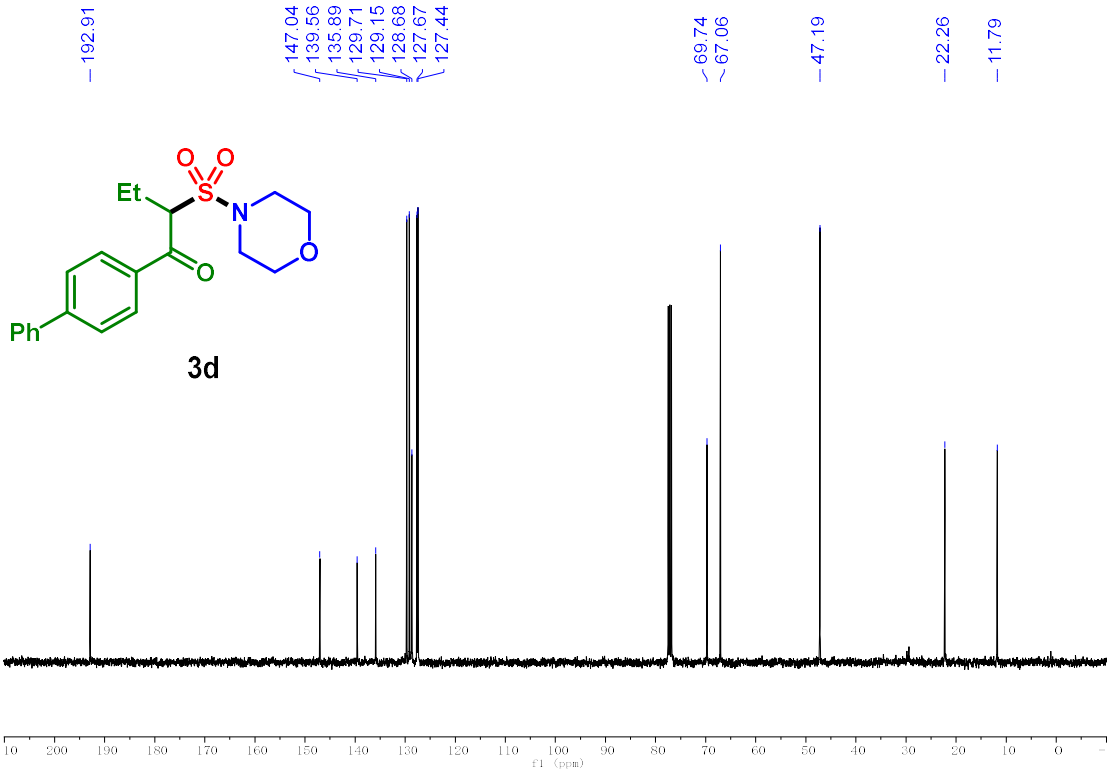


1-([1,1'-biphenyl]-4-yl)-2-(morpholinosulfonyl)butan-1-one (3d)

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

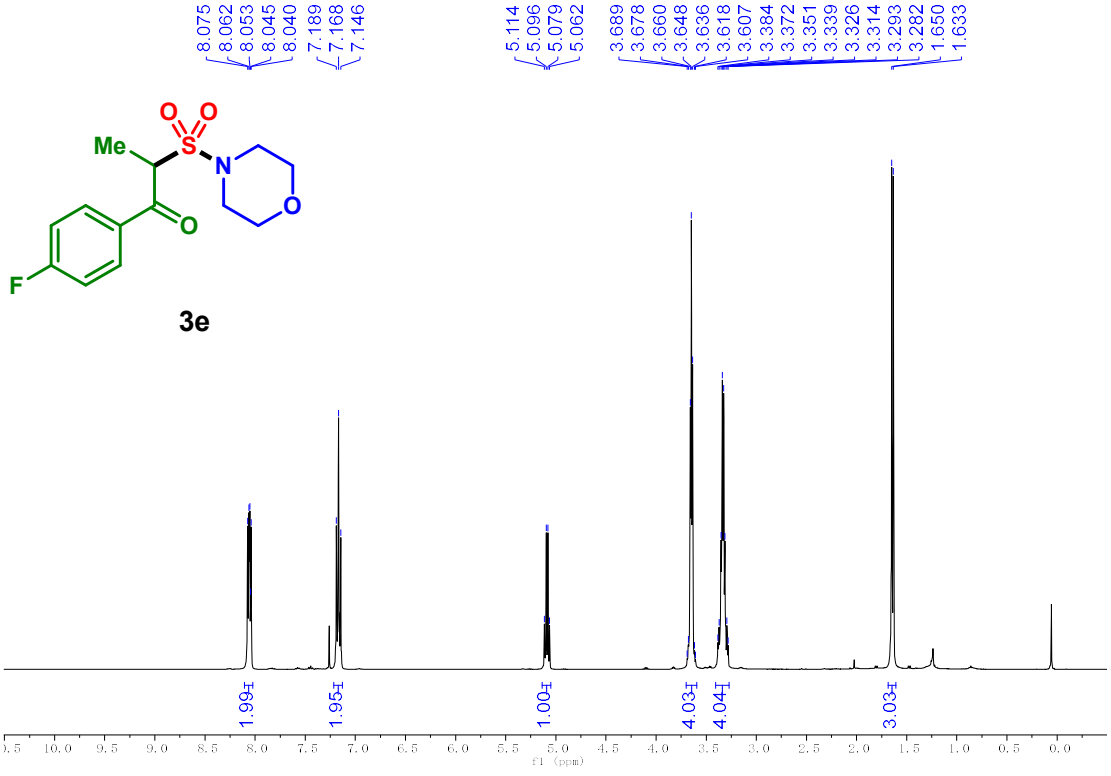


^{13}C NMR (100 MHz, $CDCl_3$)

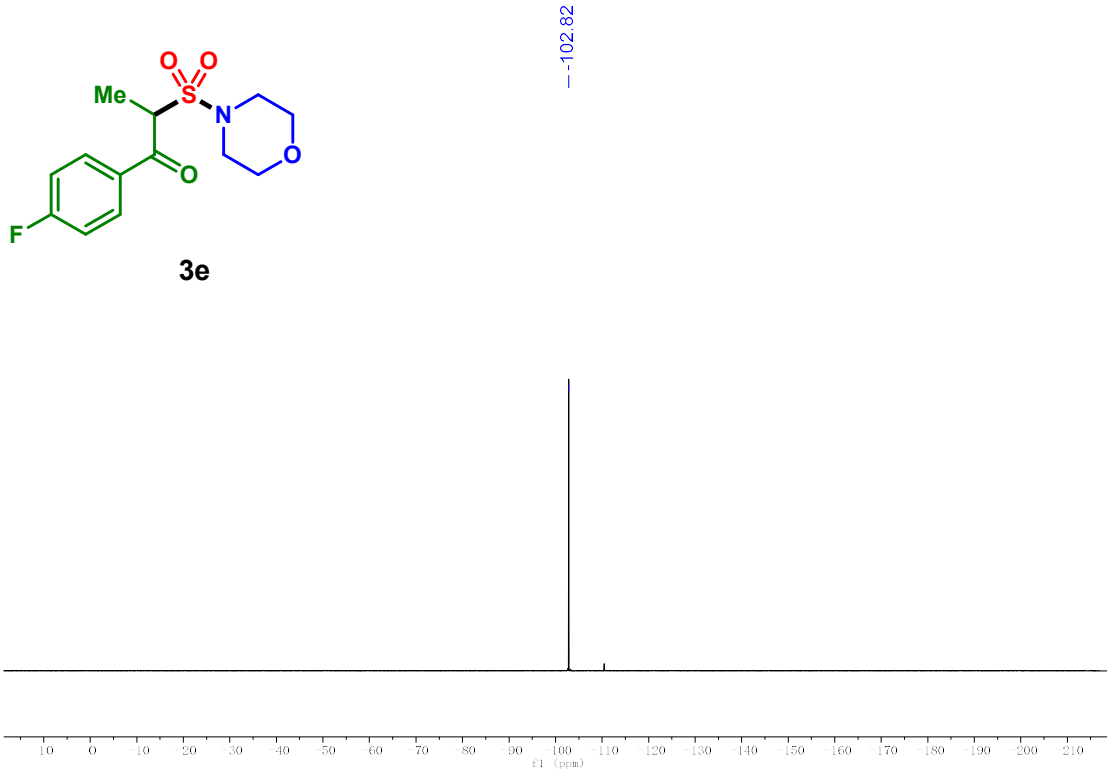


1-(4-fluorophenyl)-2-(morpholinosulfonyl)propan-1-one (3e)

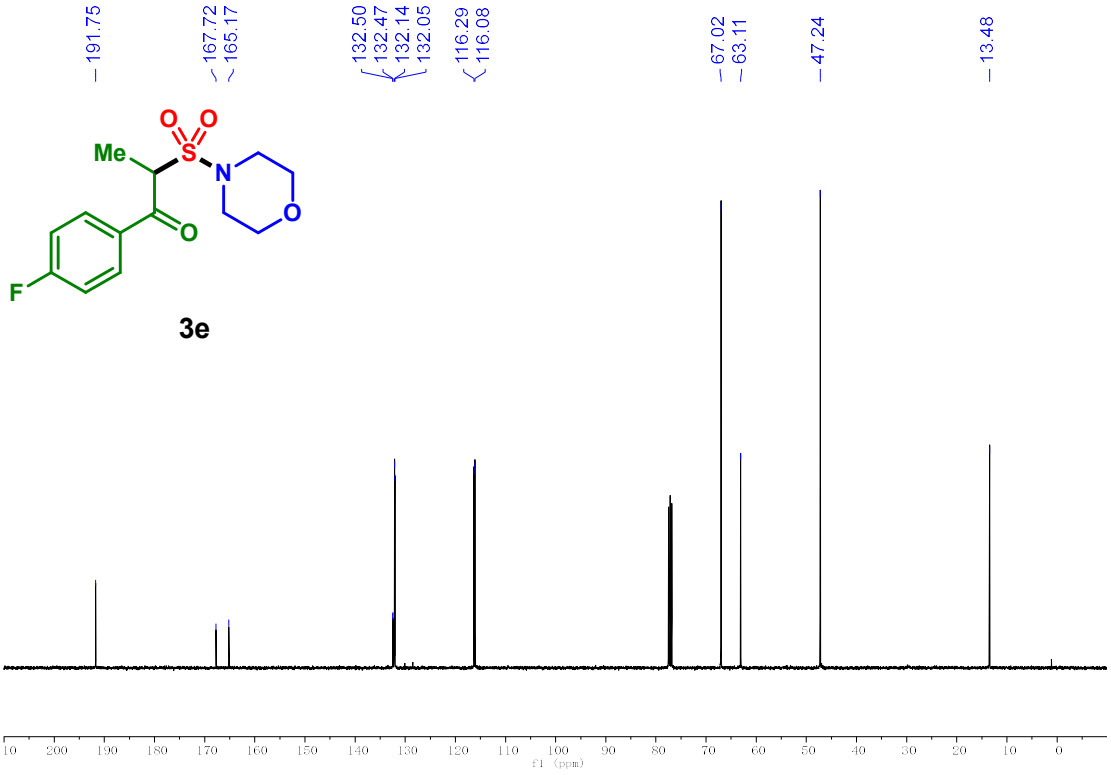
^{1}H NMR (400 MHz, $CDCl_3$)



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

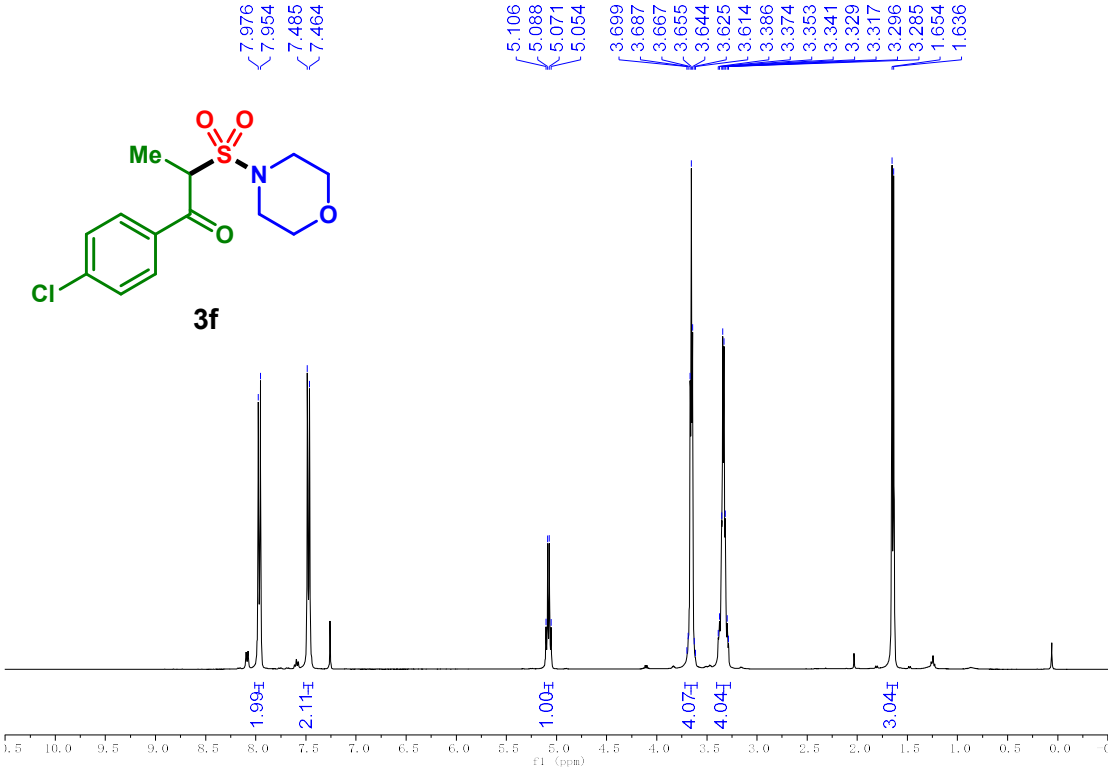


^{13}C NMR (100 MHz, $CDCl_3$)

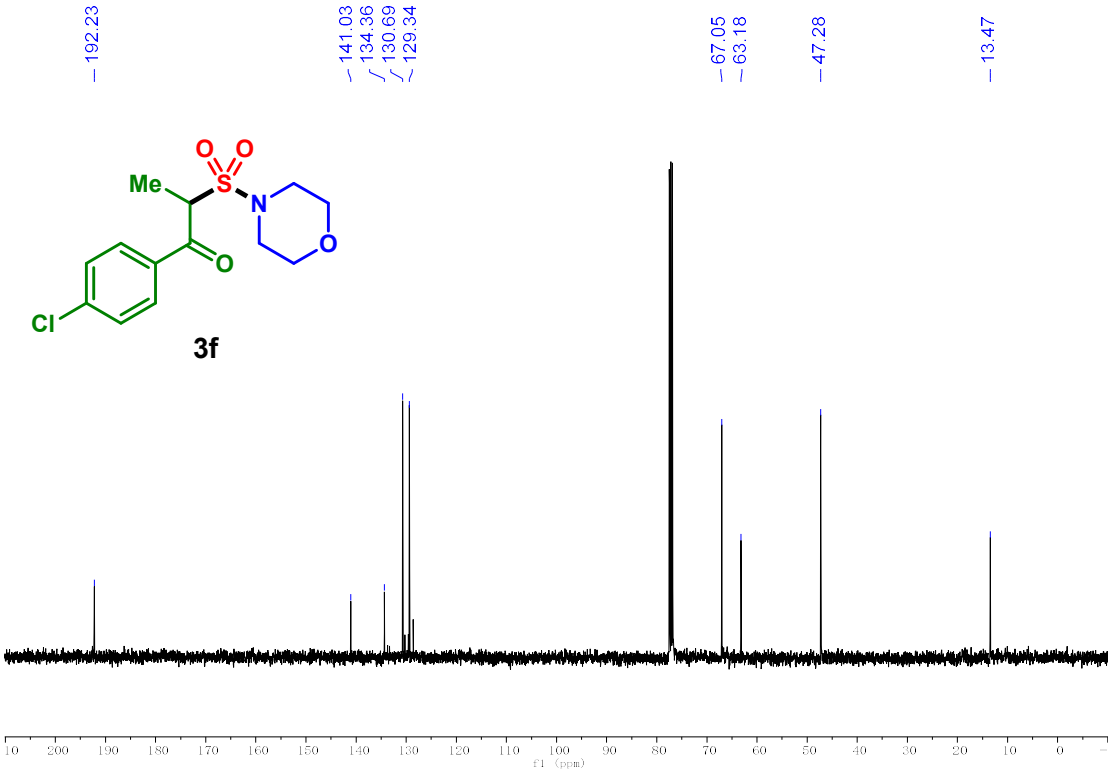


1-(4-chlorophenyl)-2-(morpholinosulfonyl)propan-1-one (3f)

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

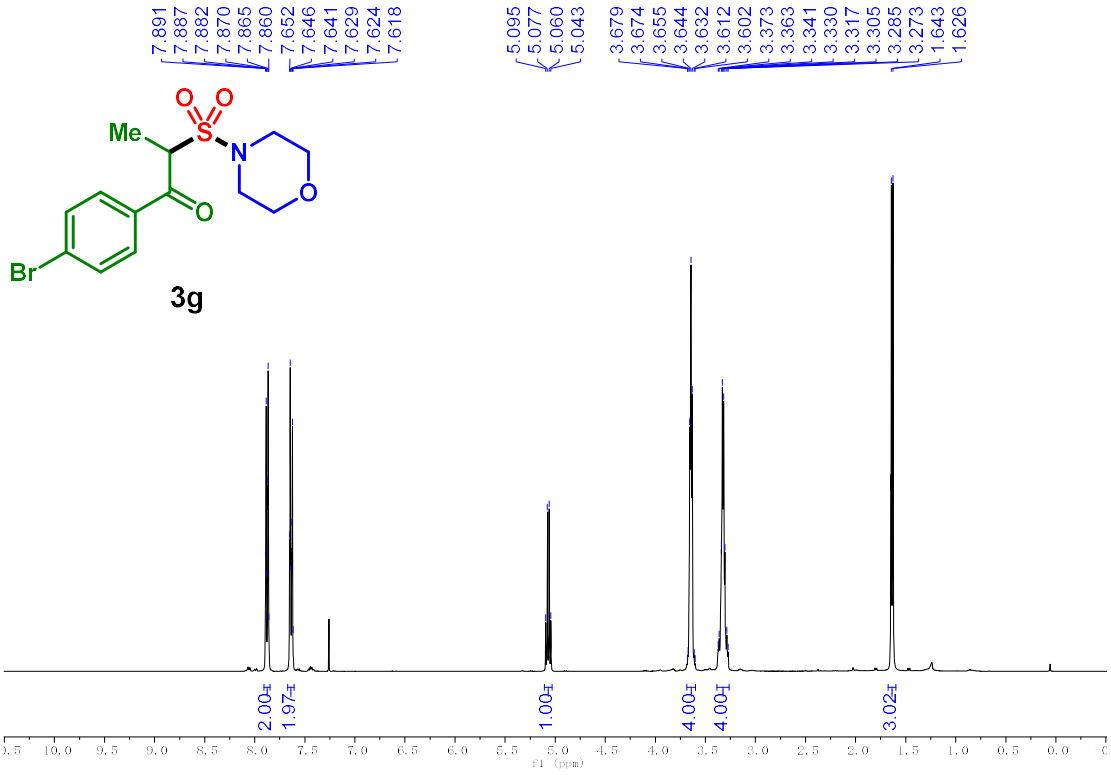


^{13}C NMR (100 MHz, $CDCl_3$)

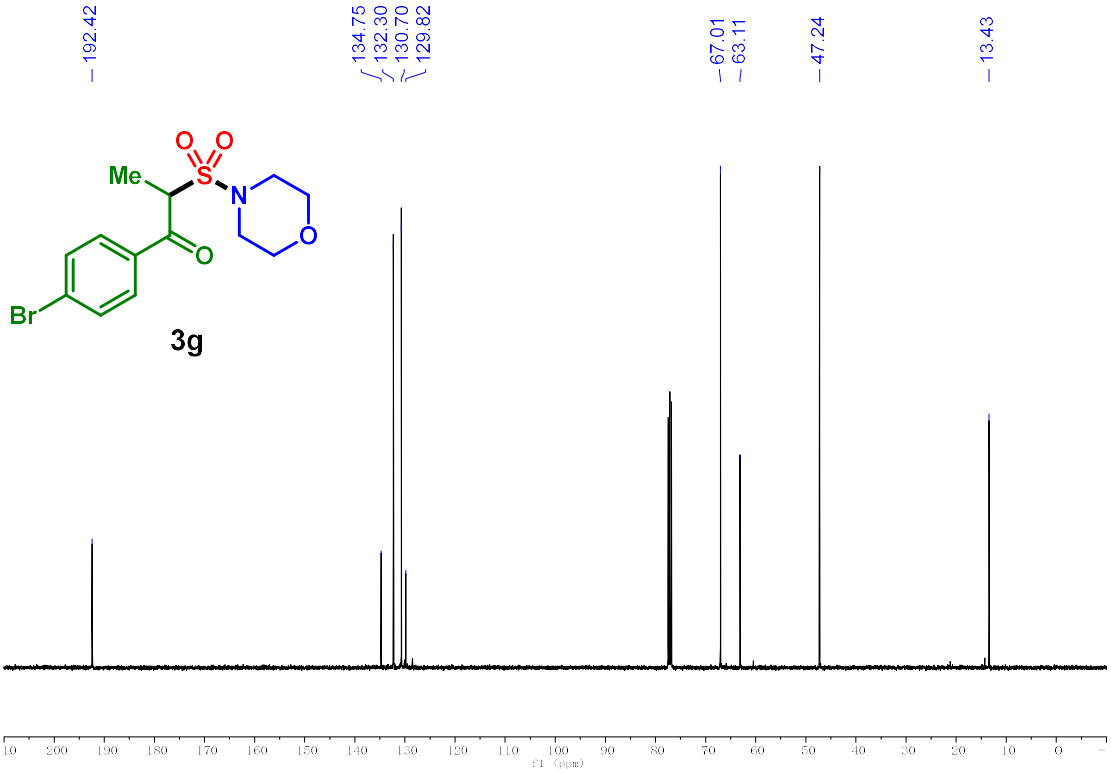


1-(4-bromophenyl)-2-(morpholinosulfonyl)propan-1-one (3g)

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

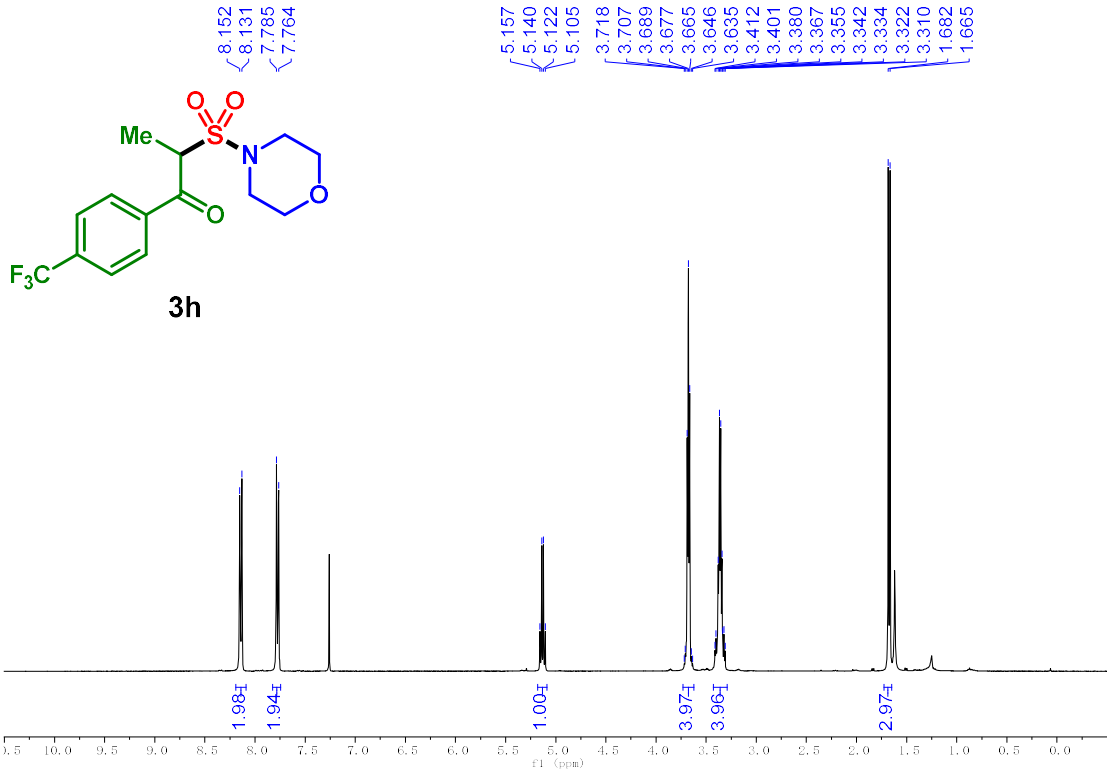


^{13}C NMR (100 MHz, $CDCl_3$)

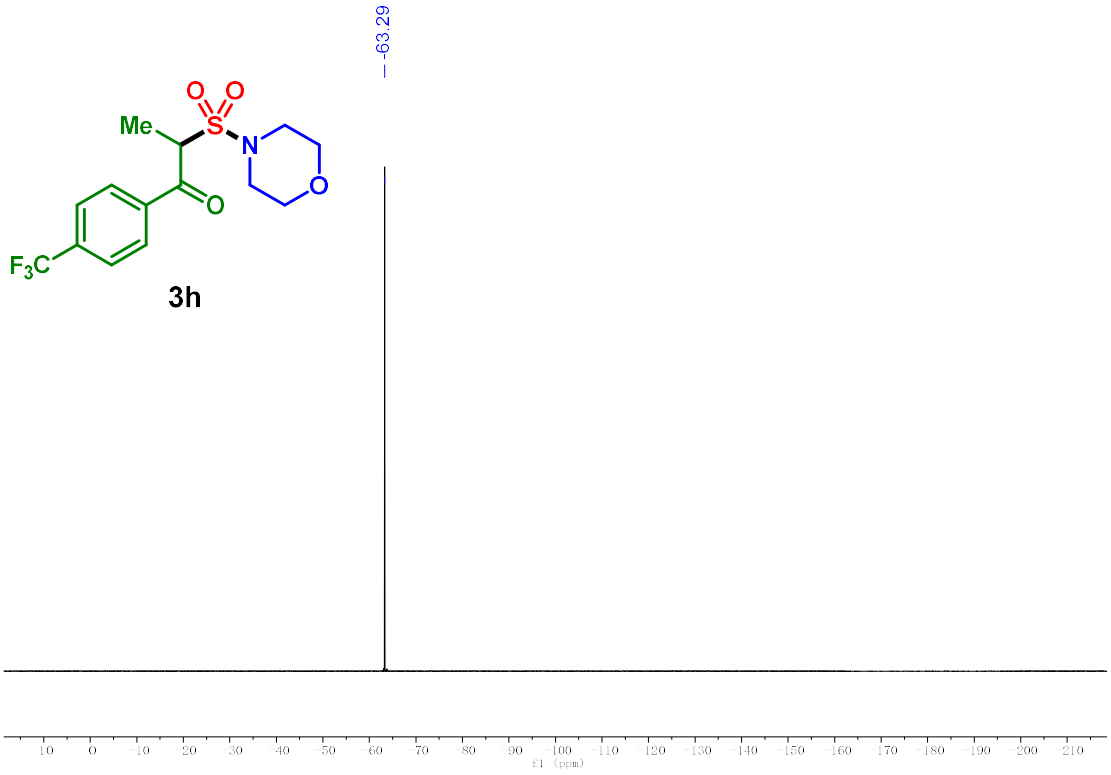


2-(morpholinosulfonyl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (3h)

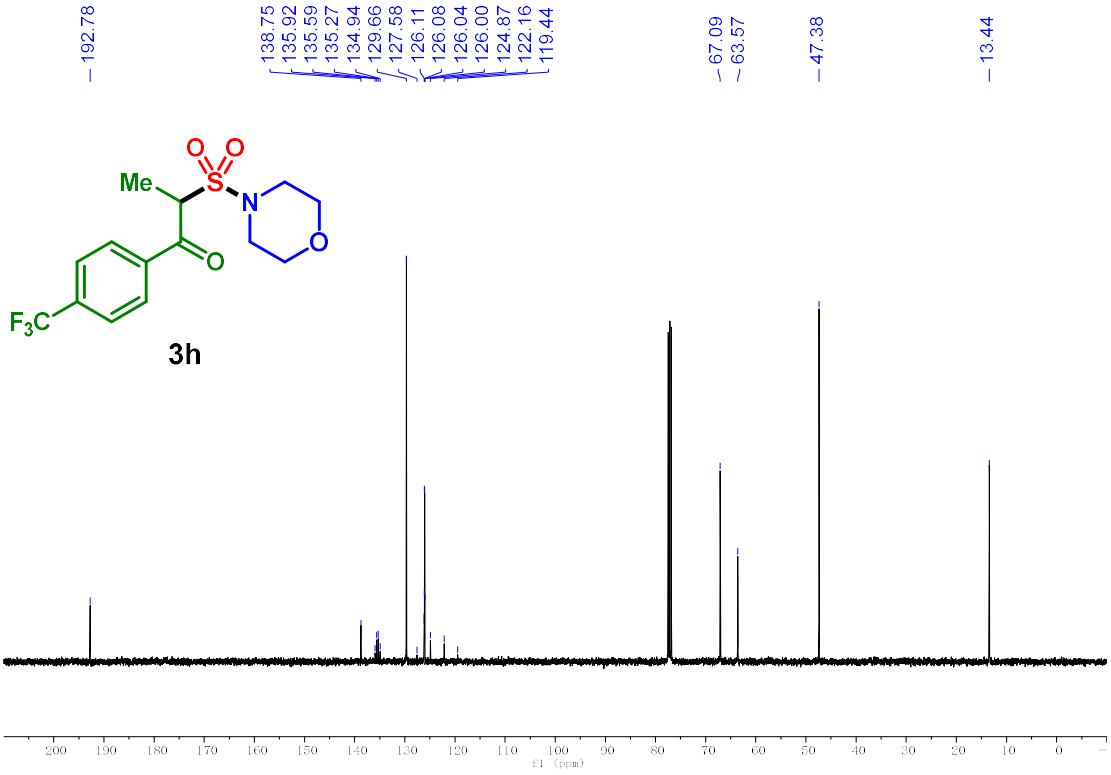
^{1}H NMR (400 MHz, $CDCl_3$)



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

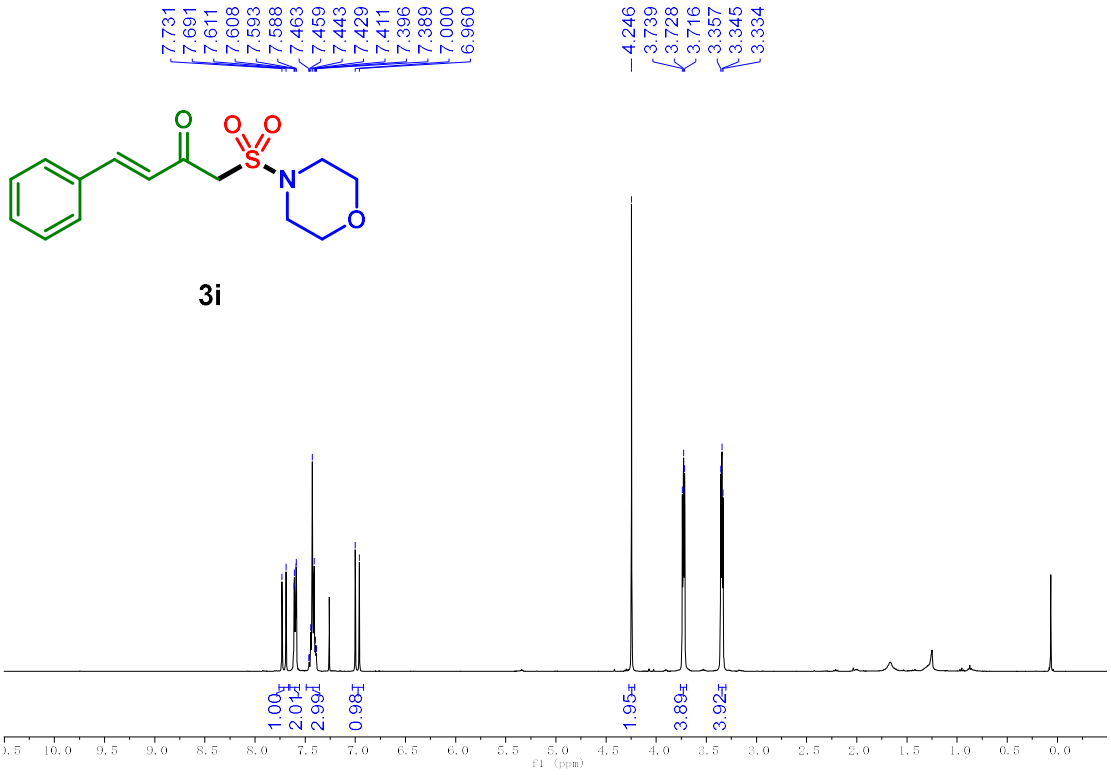


^{13}C NMR (100 MHz, $CDCl_3$)

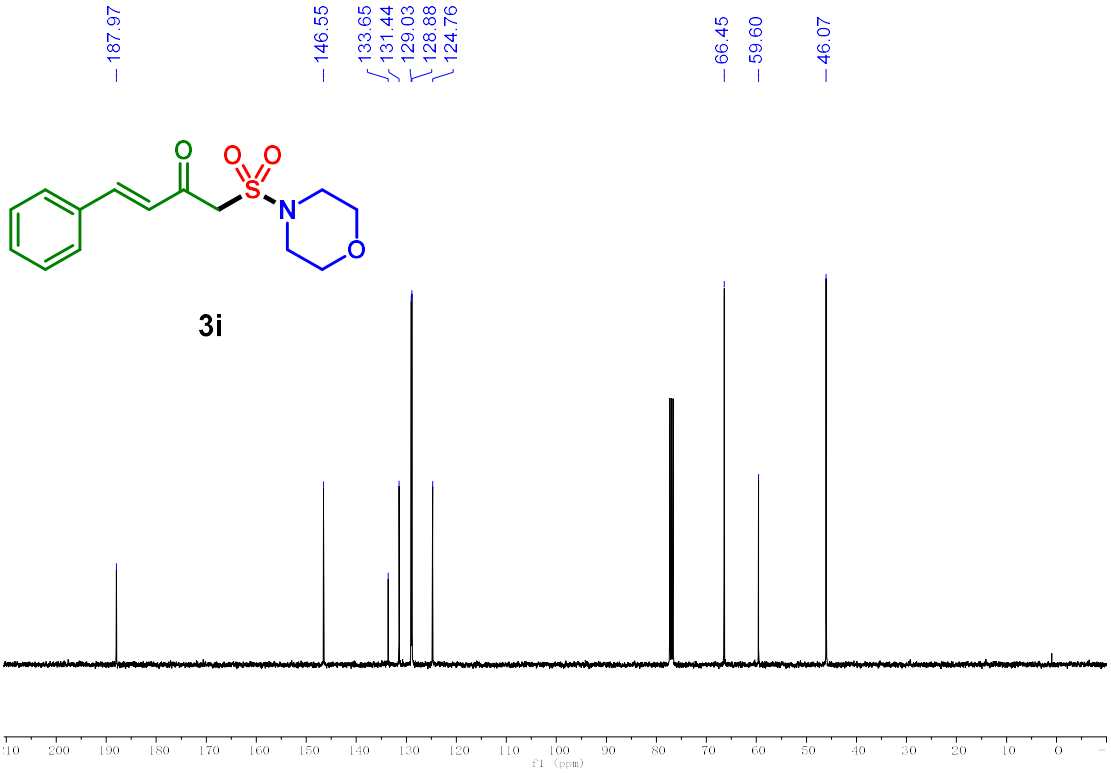


(E)-1-(morpholinosulfonyl)-4-phenylbut-3-en-2-one (3i)

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

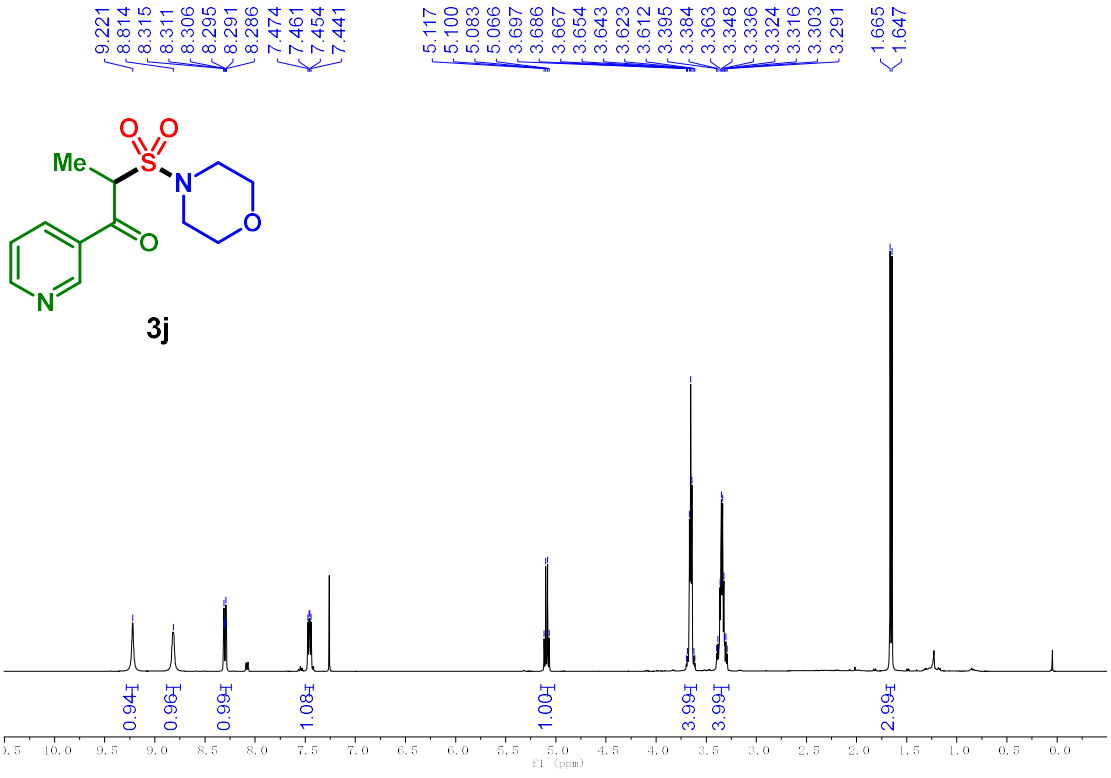


^{13}C NMR (100 MHz, $CDCl_3$)

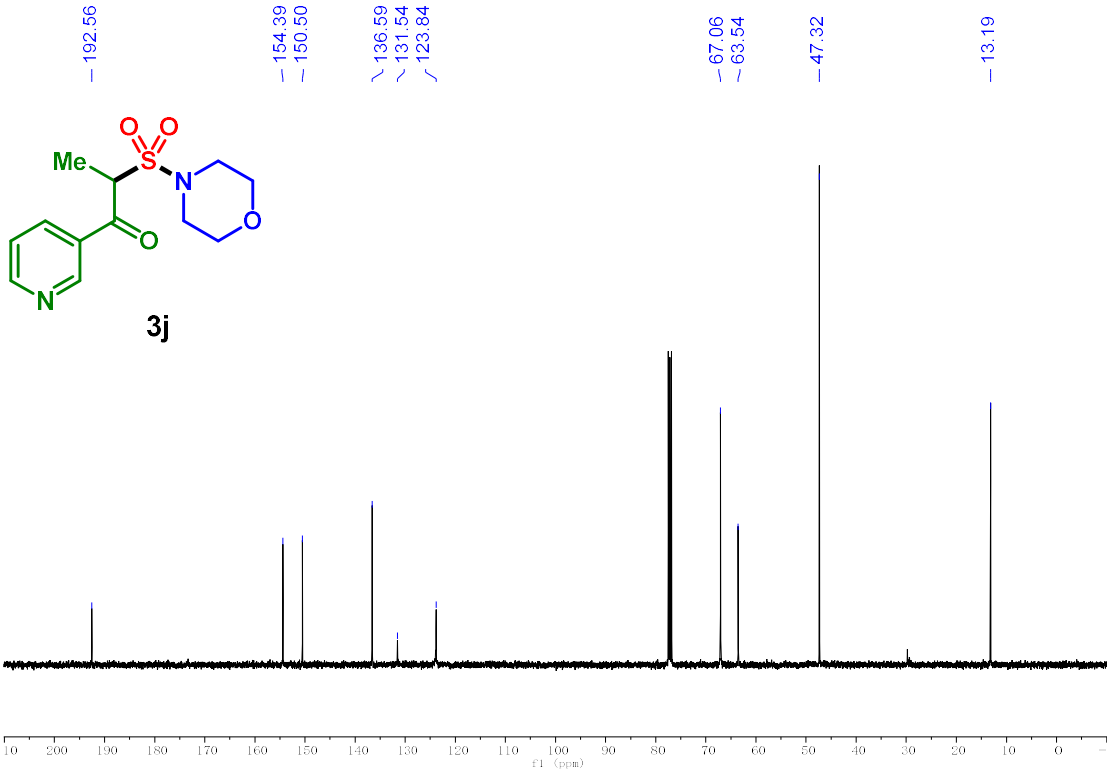


2-(morpholinosulfonyl)-1-(pyridin-3-yl)propan-1-one (3j)

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

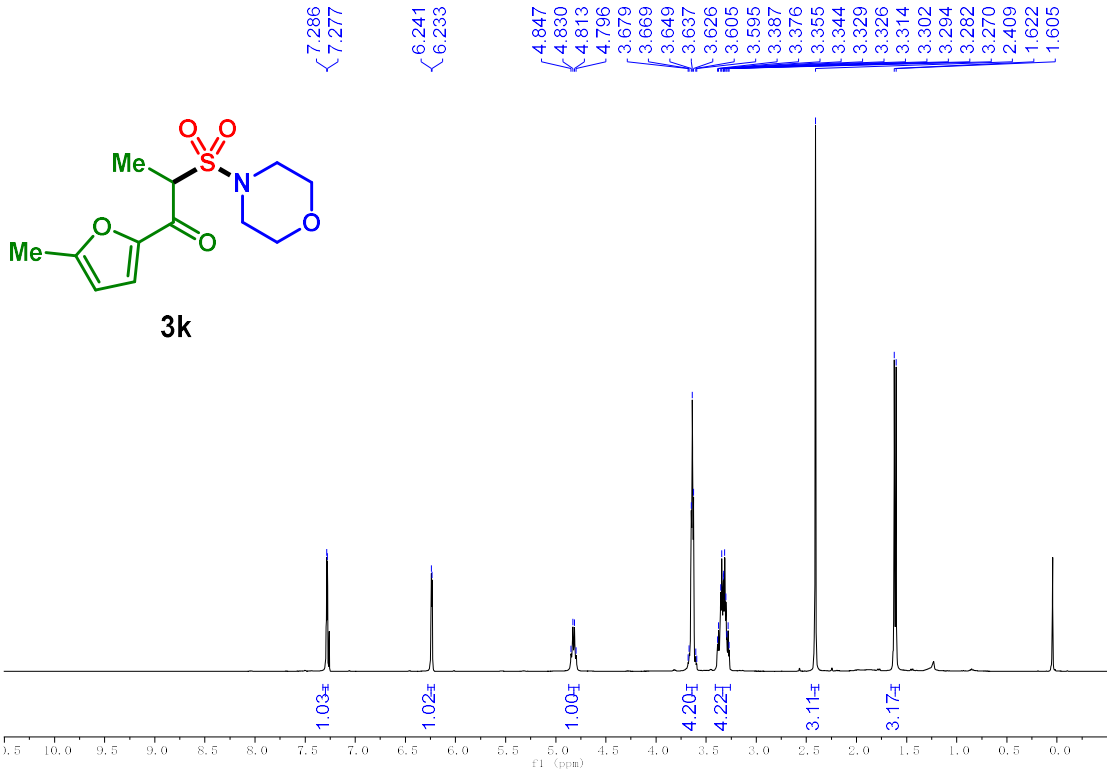


^{13}C NMR (100 MHz, $CDCl_3$)

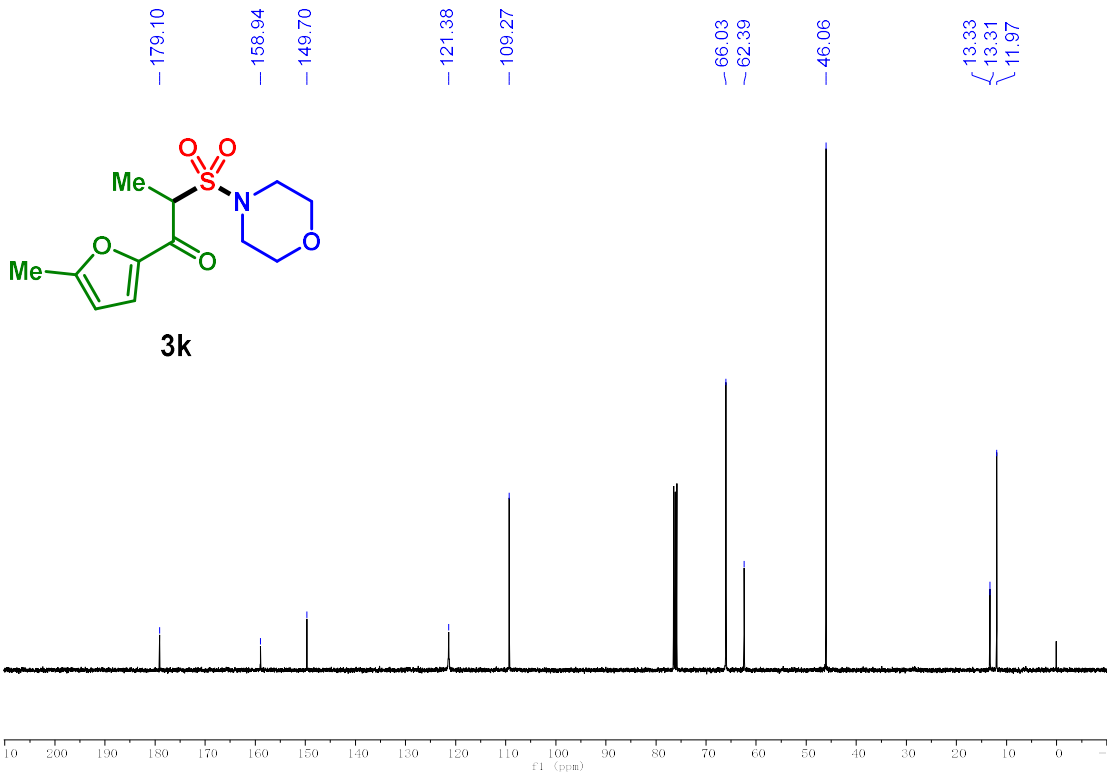


1-(5-methylfuran-2-yl)-2-(morpholinosulfonyl)propan-1-one (3k)

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

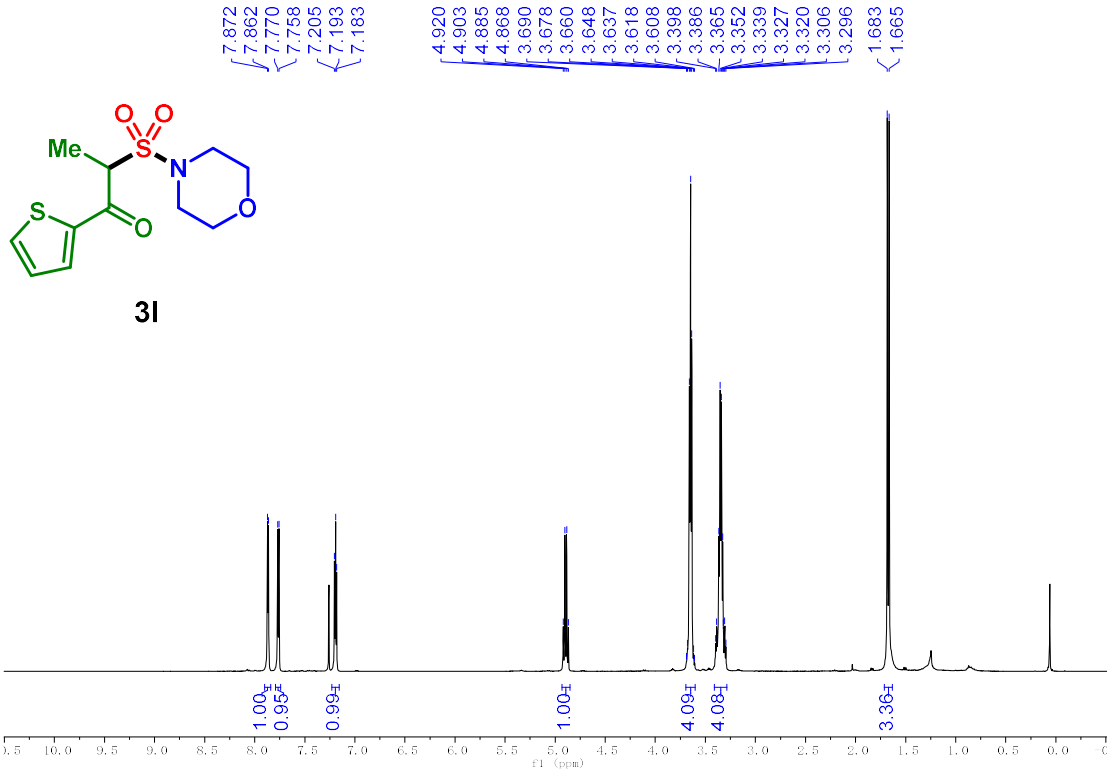


^{13}C NMR (100 MHz, $CDCl_3$)

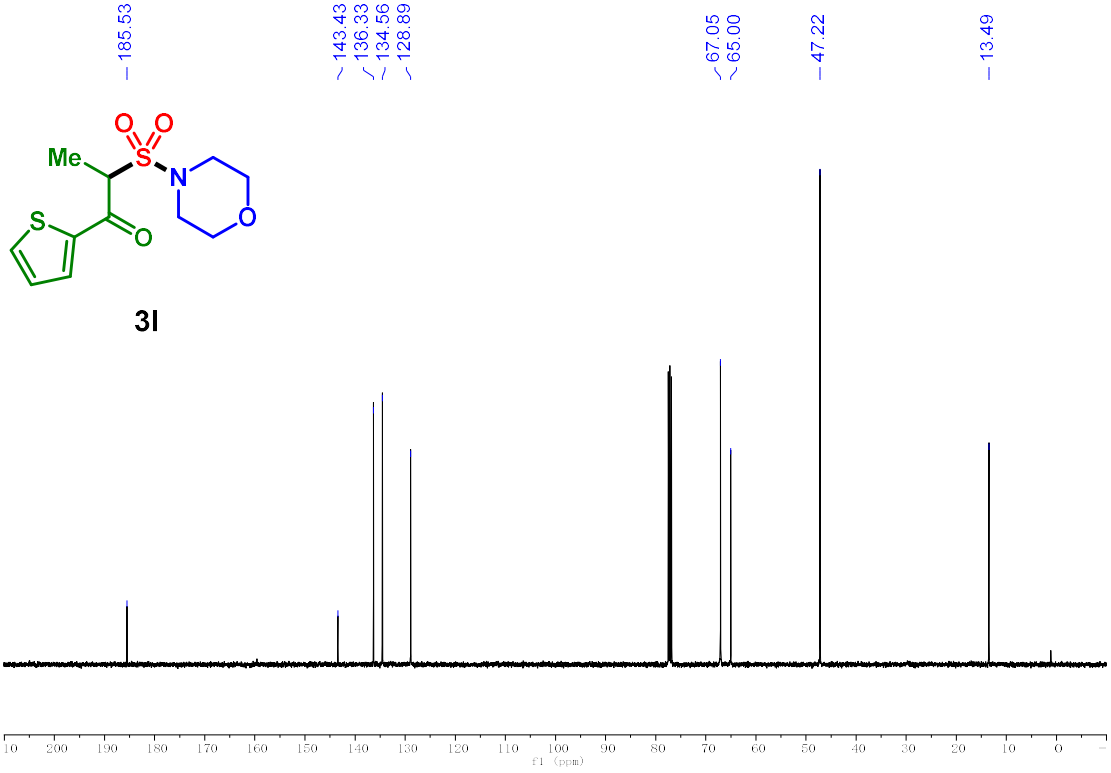


2-(morpholinosulfonyl)-1-(thiophen-2-yl)propan-1-one (3l)

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

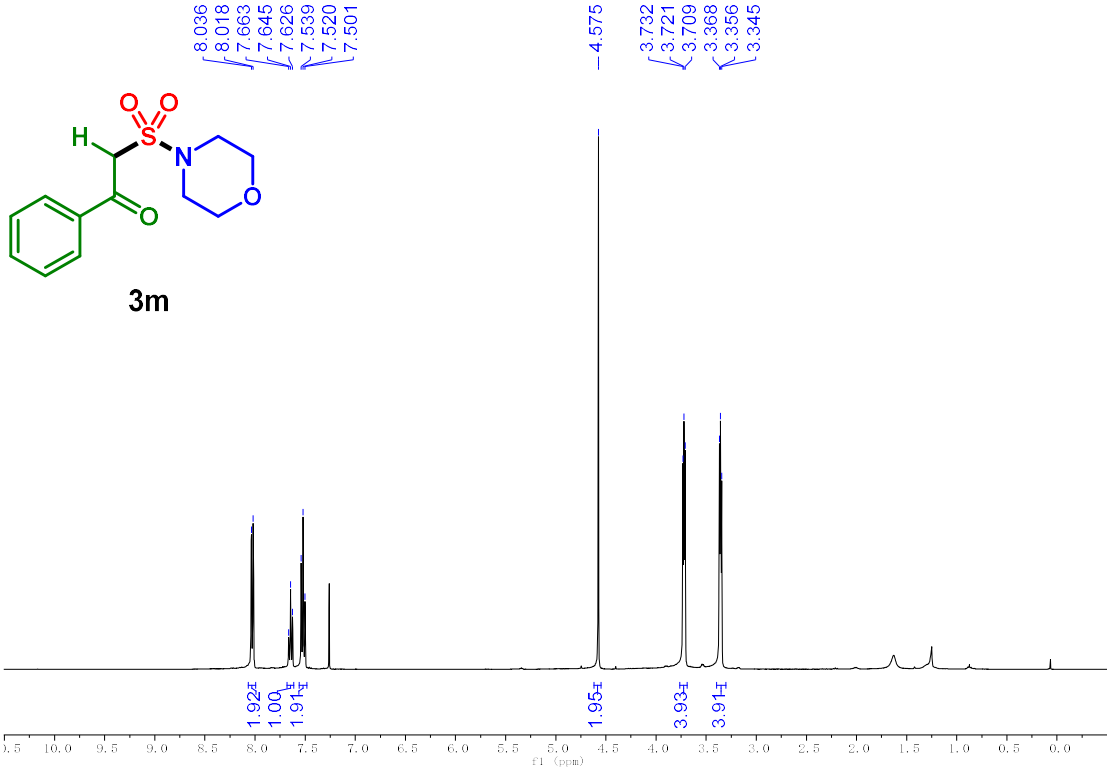


^{13}C NMR (100 MHz, $CDCl_3$)

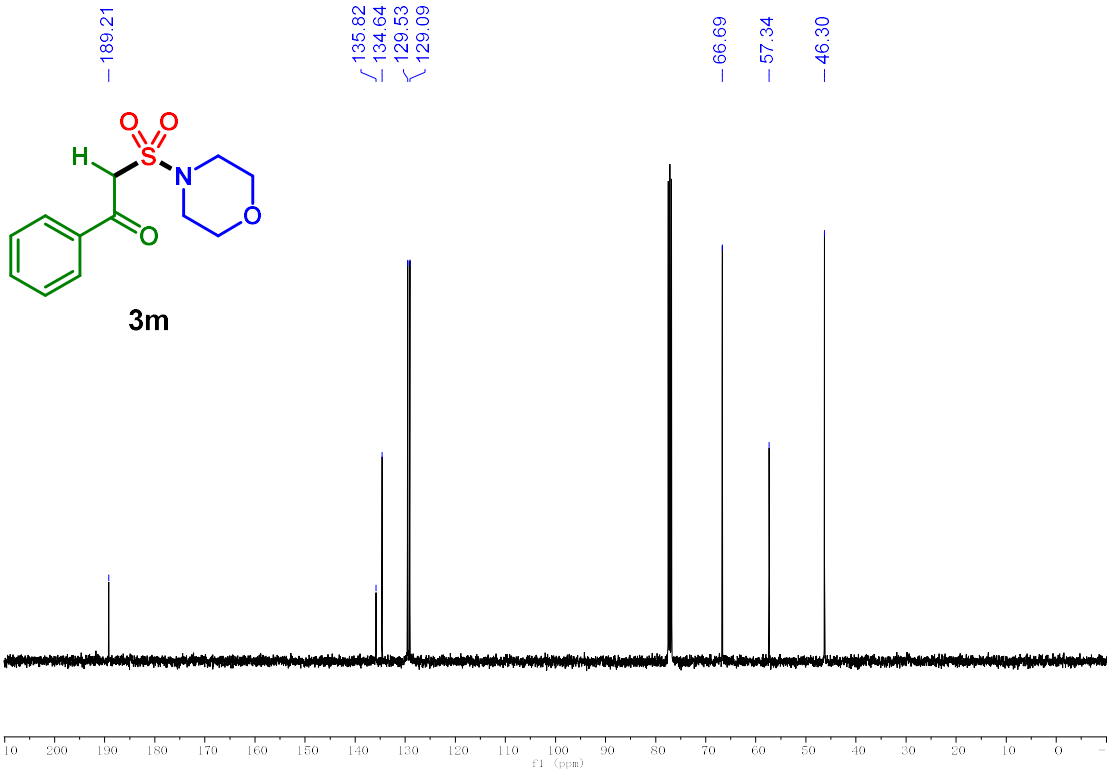


2-(morpholinosulfonyl)-1-phenylethan-1-one (3m)

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

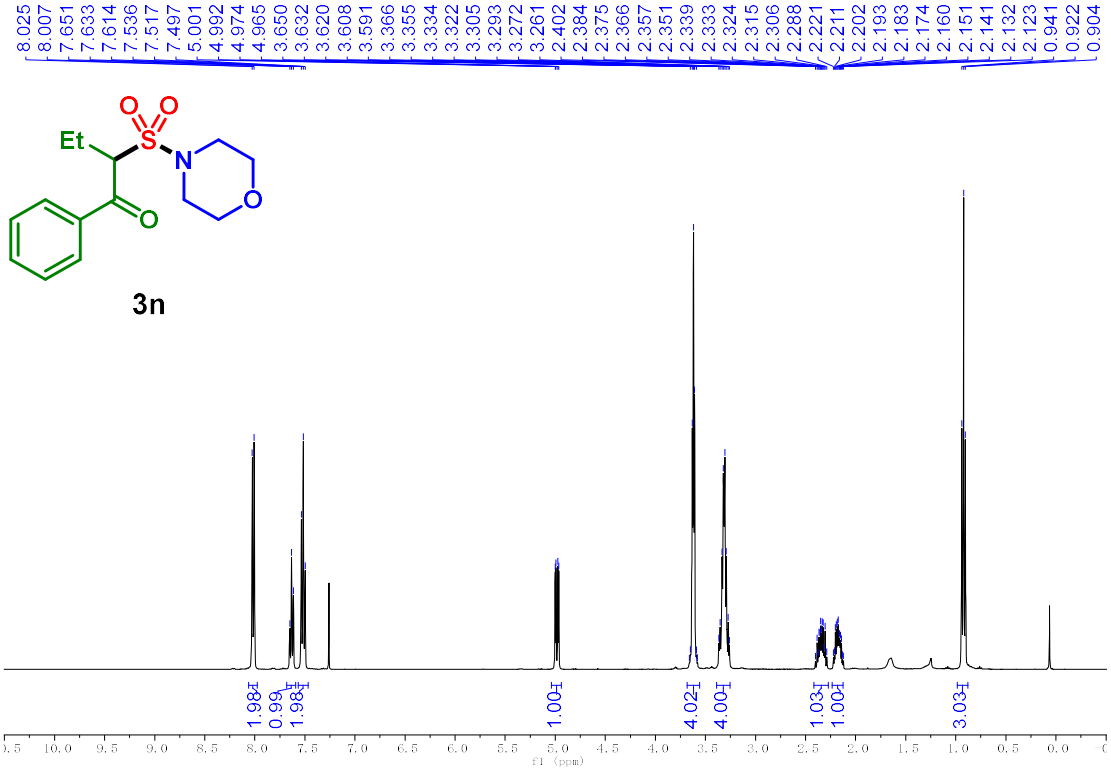


^{13}C NMR (100 MHz, $CDCl_3$)

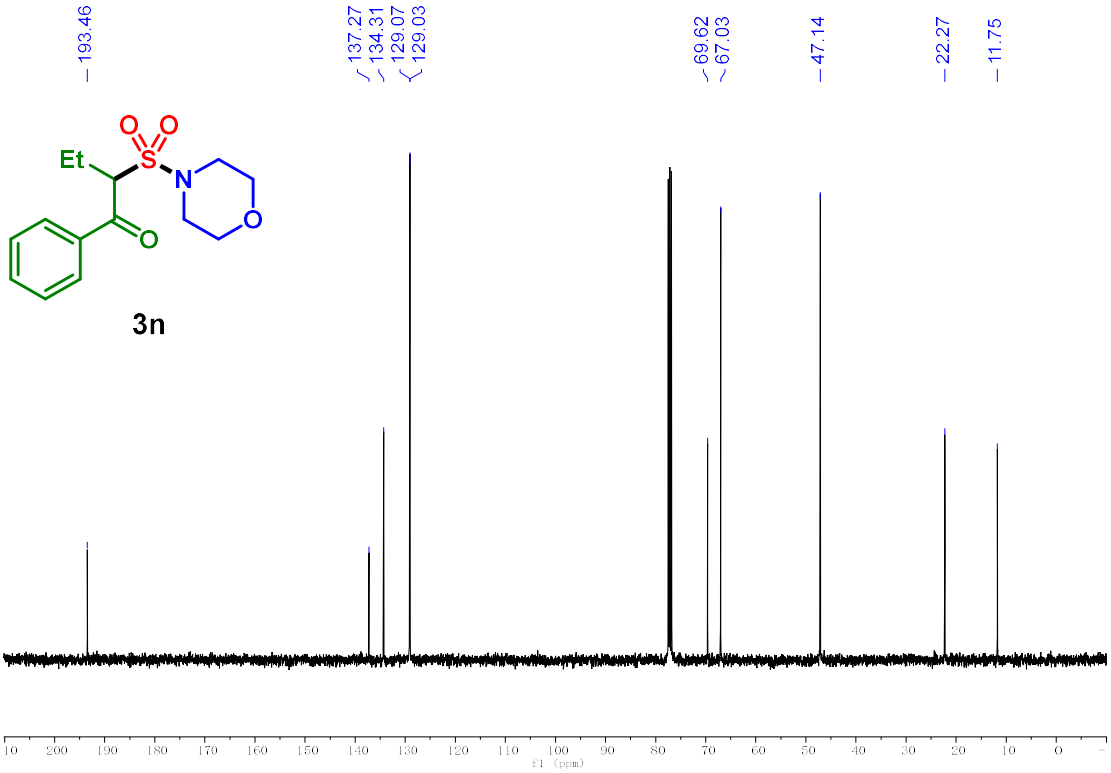


2-(morpholinosulfonyl)-1-phenylbutan-1-one (3n)

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

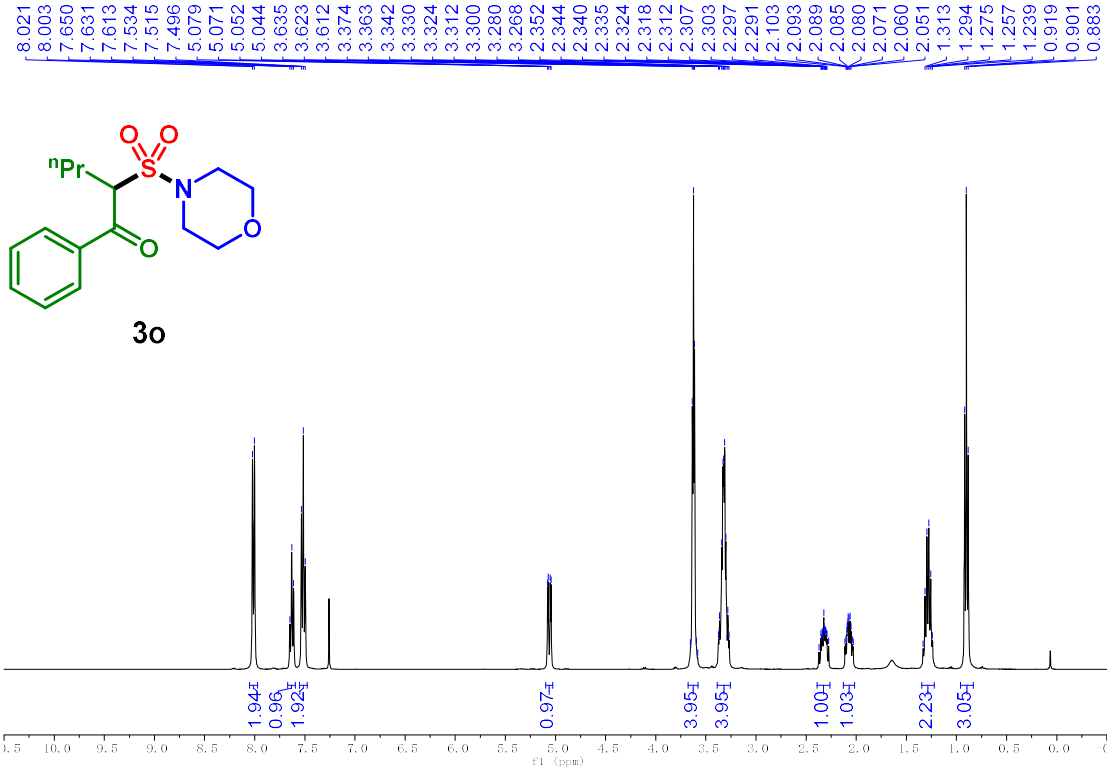


^{13}C NMR (100 MHz, $CDCl_3$)

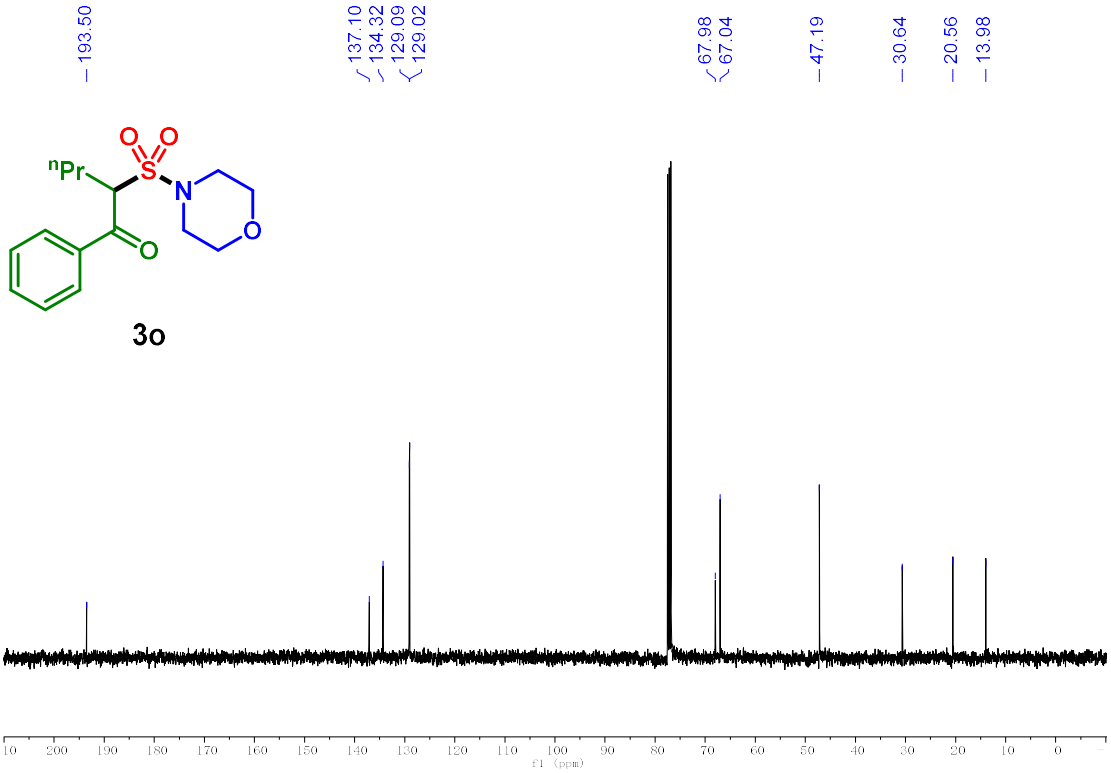


2-(morpholinosulfonyl)-1-phenylpentan-1-one (3o)

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

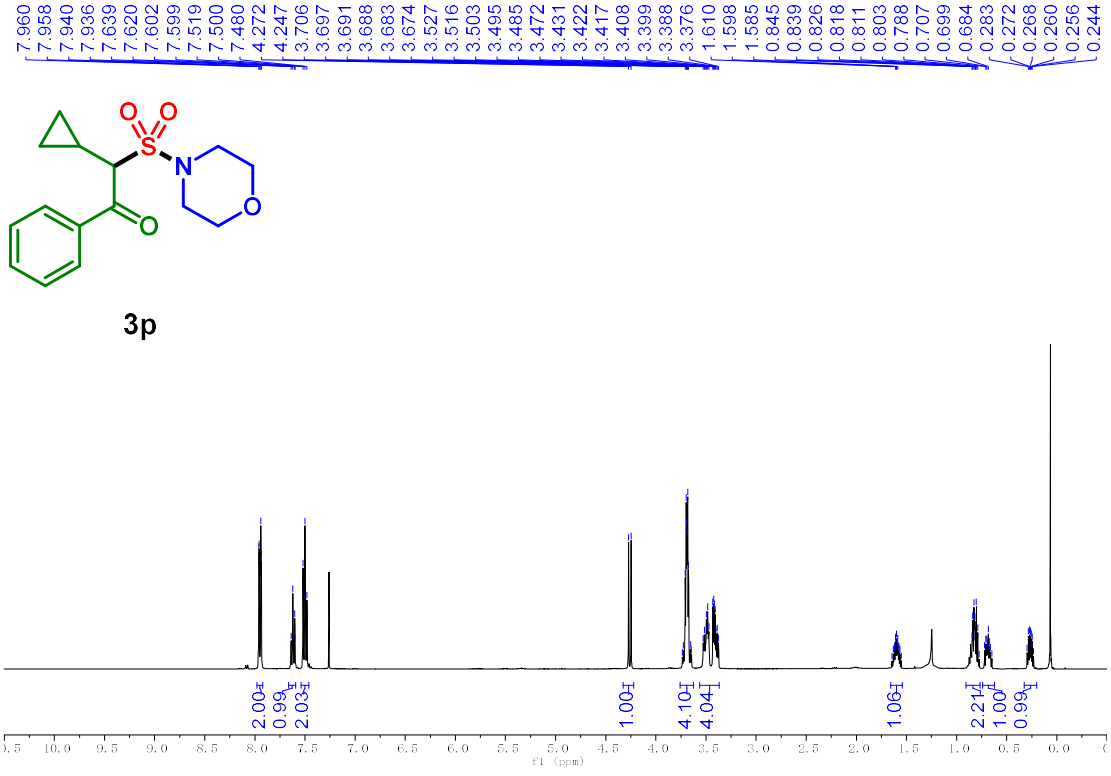


^{13}C NMR (100 MHz, $CDCl_3$)

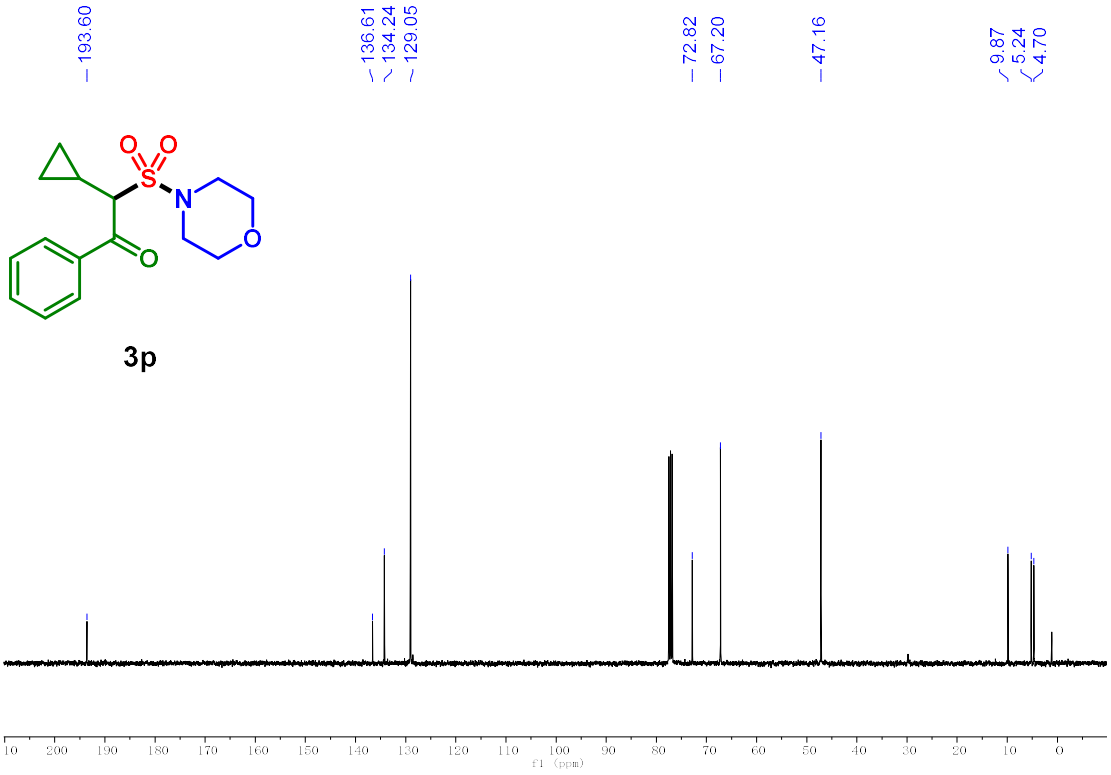


2-cyclopropyl-2-(morpholinosulfonyl)-1-phenylethan-1-one (3p)

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

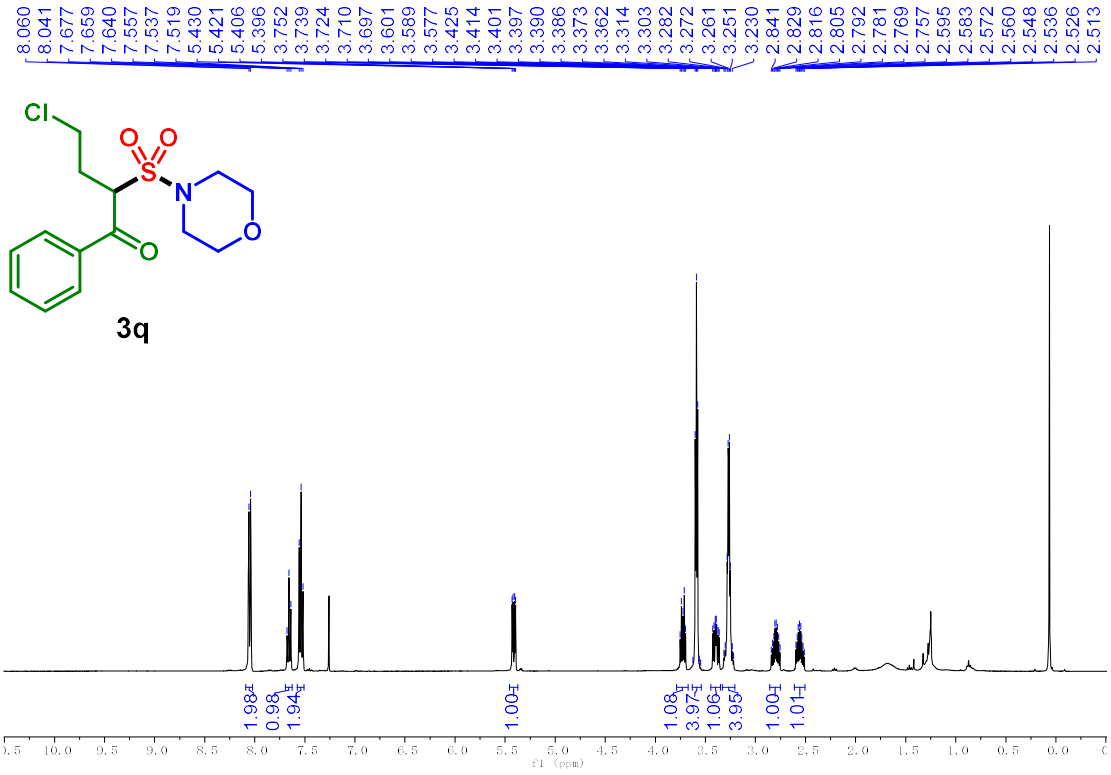


^{13}C NMR (100 MHz, $CDCl_3$)

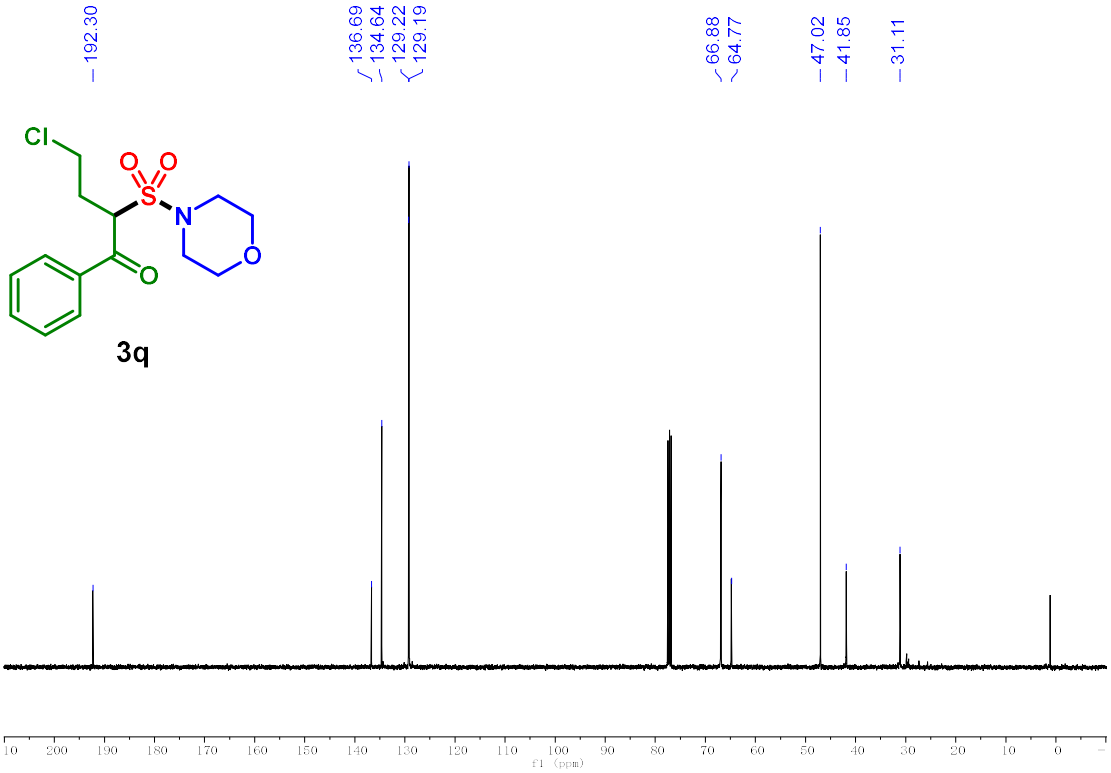


4-chloro-2-(morpholinosulfonyl)-1-phenylbutan-1-one (3q)

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

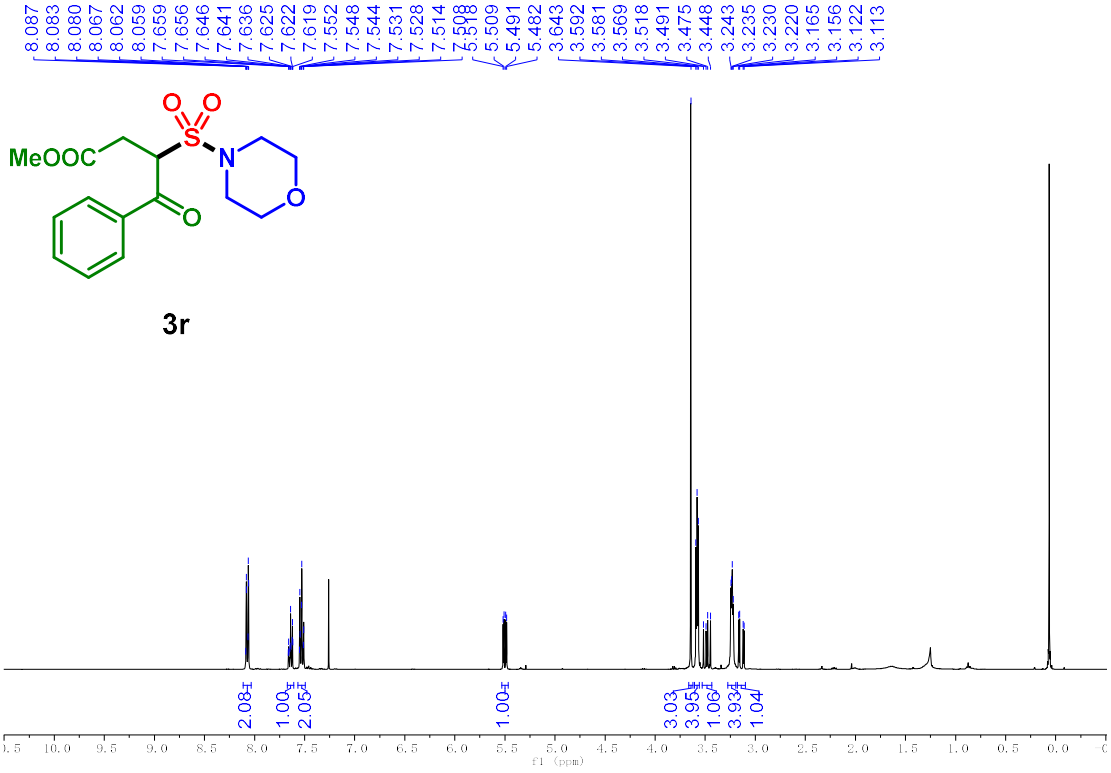


^{13}C NMR (100 MHz, $CDCl_3$)

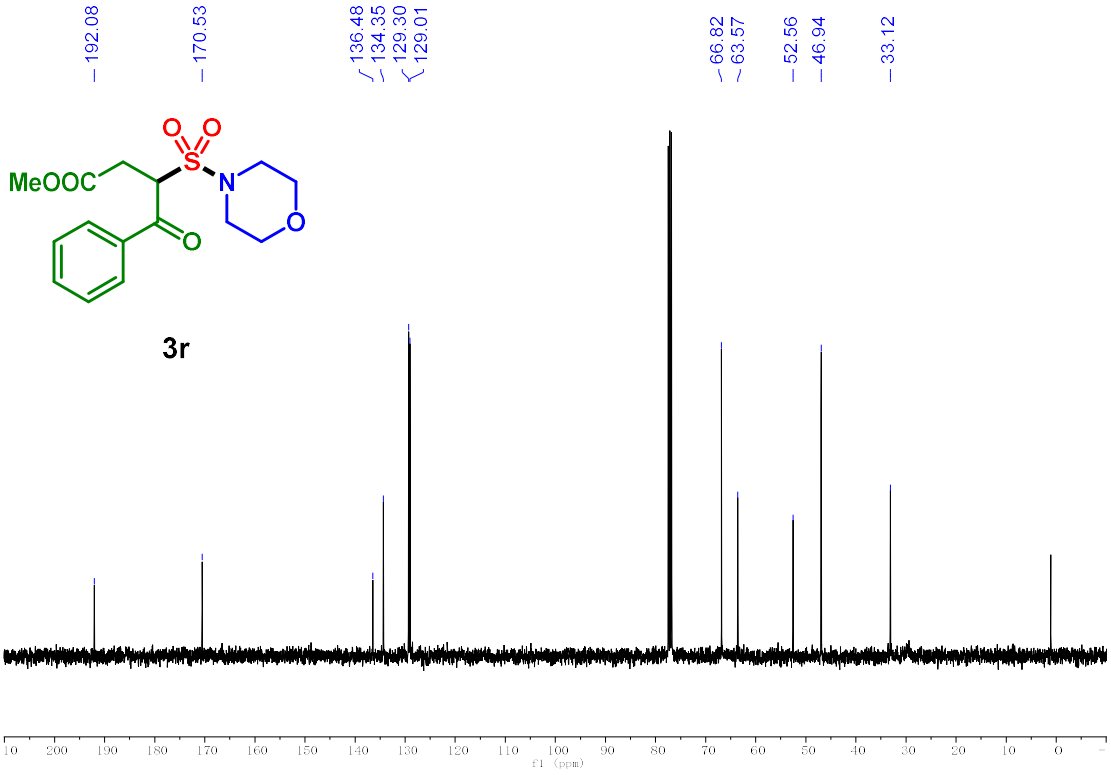


methyl 3-(morpholinosulfonyl)-4-oxo-4-phenylbutanoate (3r)

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

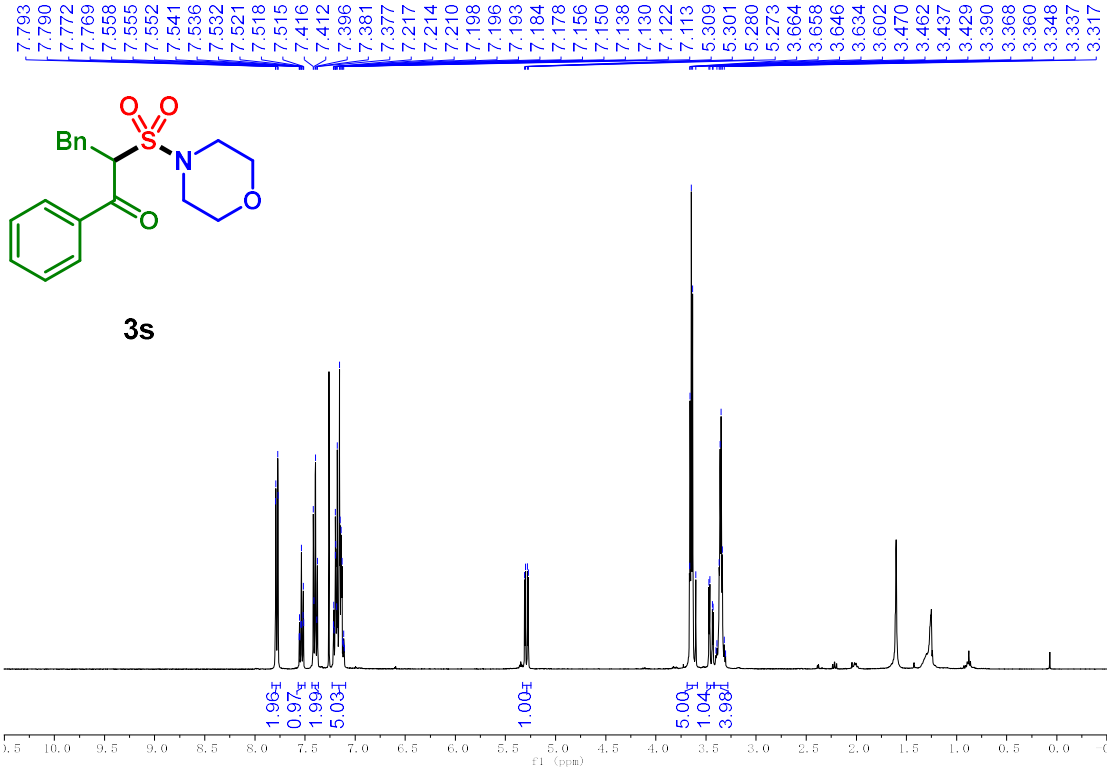


^{13}C NMR (100 MHz, $CDCl_3$)

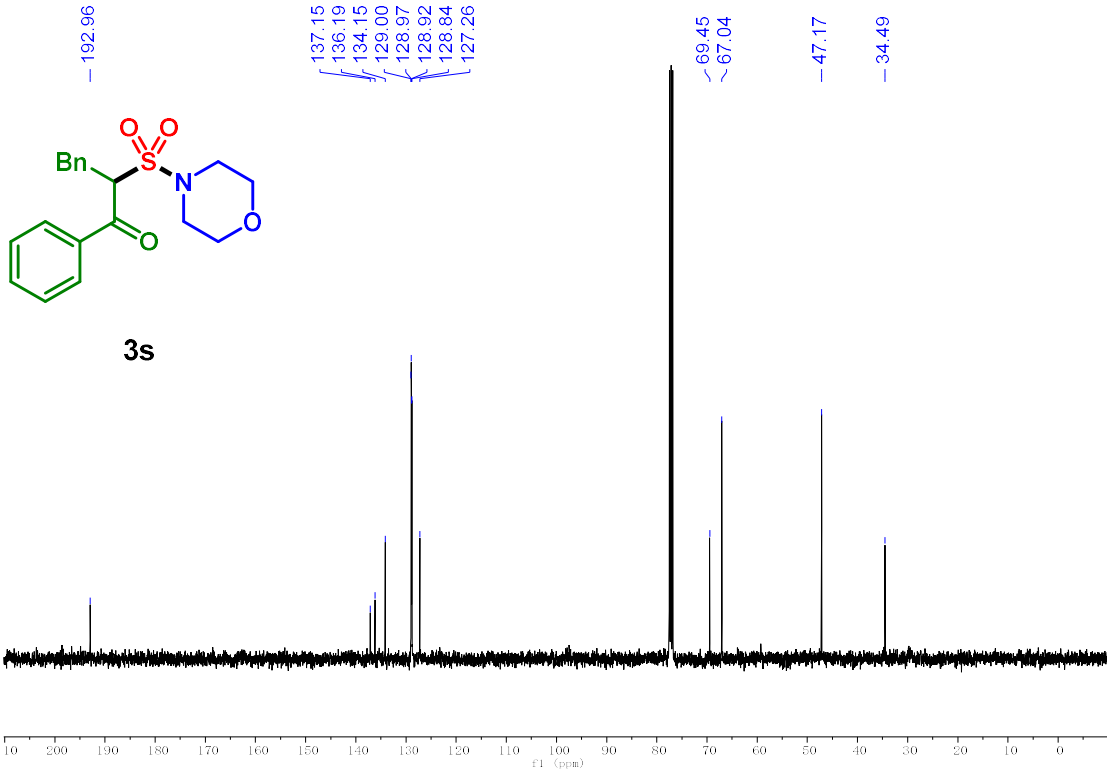


2-(morpholinosulfonyl)-1,3-diphenylpropan-1-one (3s)

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

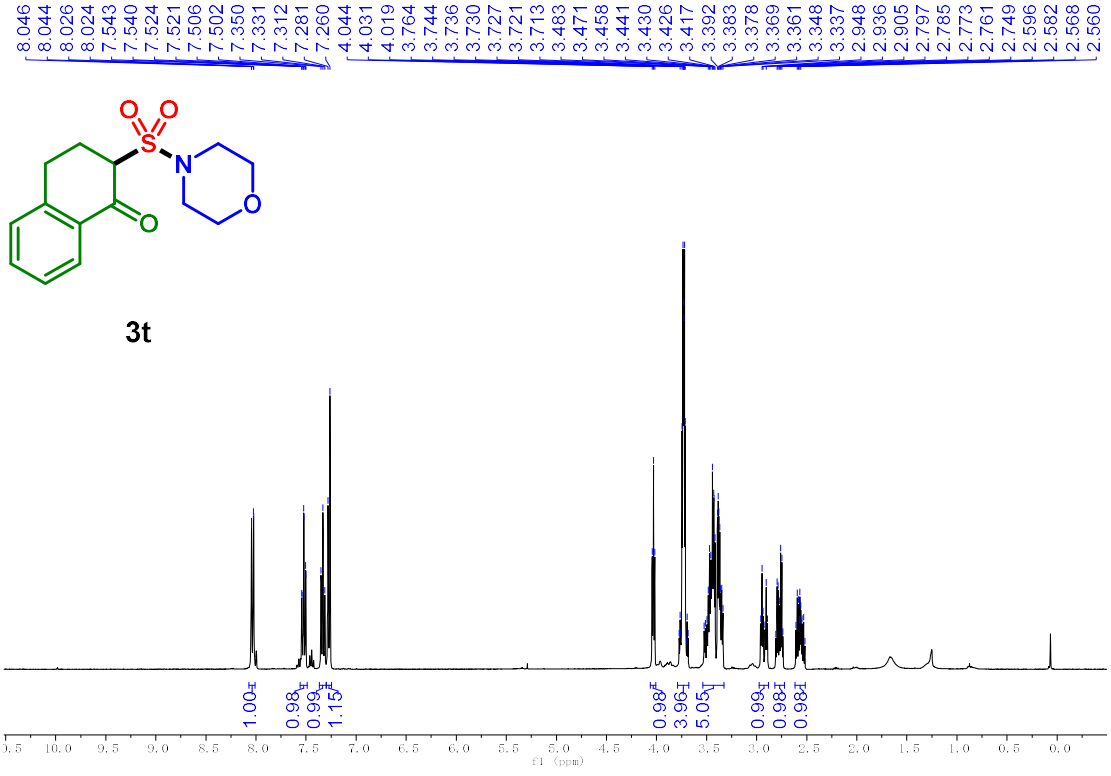


^{13}C NMR (100 MHz, $CDCl_3$)

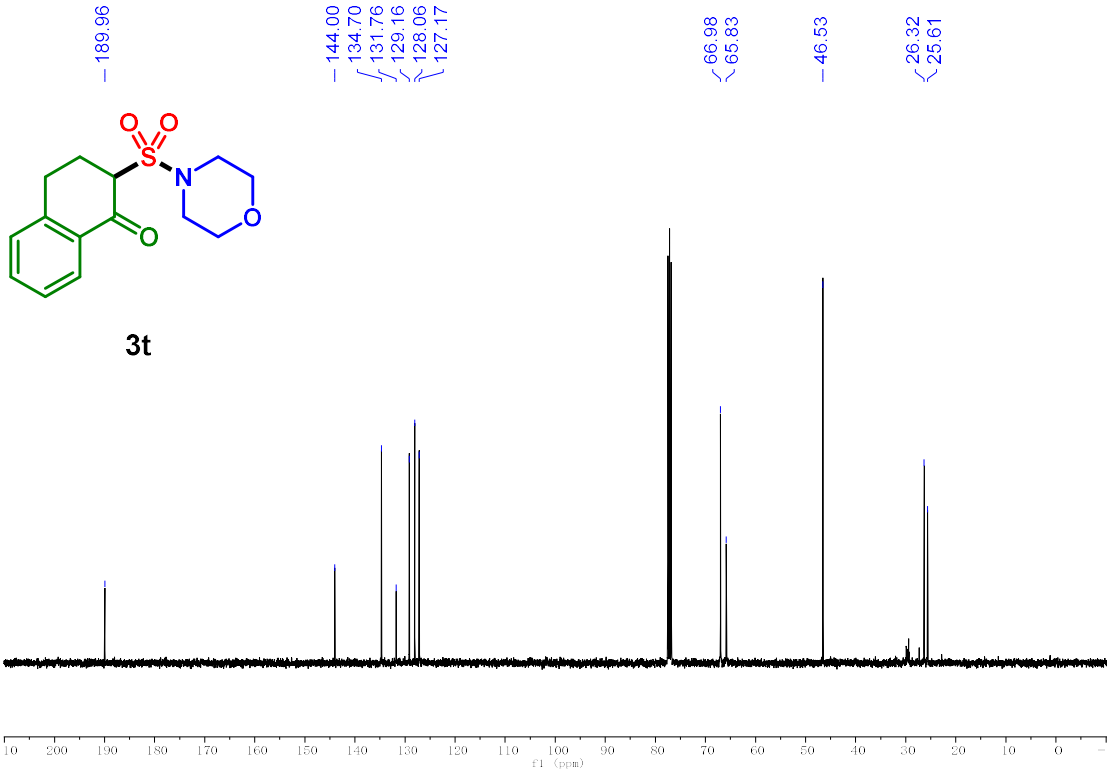


2-(morpholinosulfonyl)-3,4-dihydronaphthalen-1(2H)-one (3t)

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

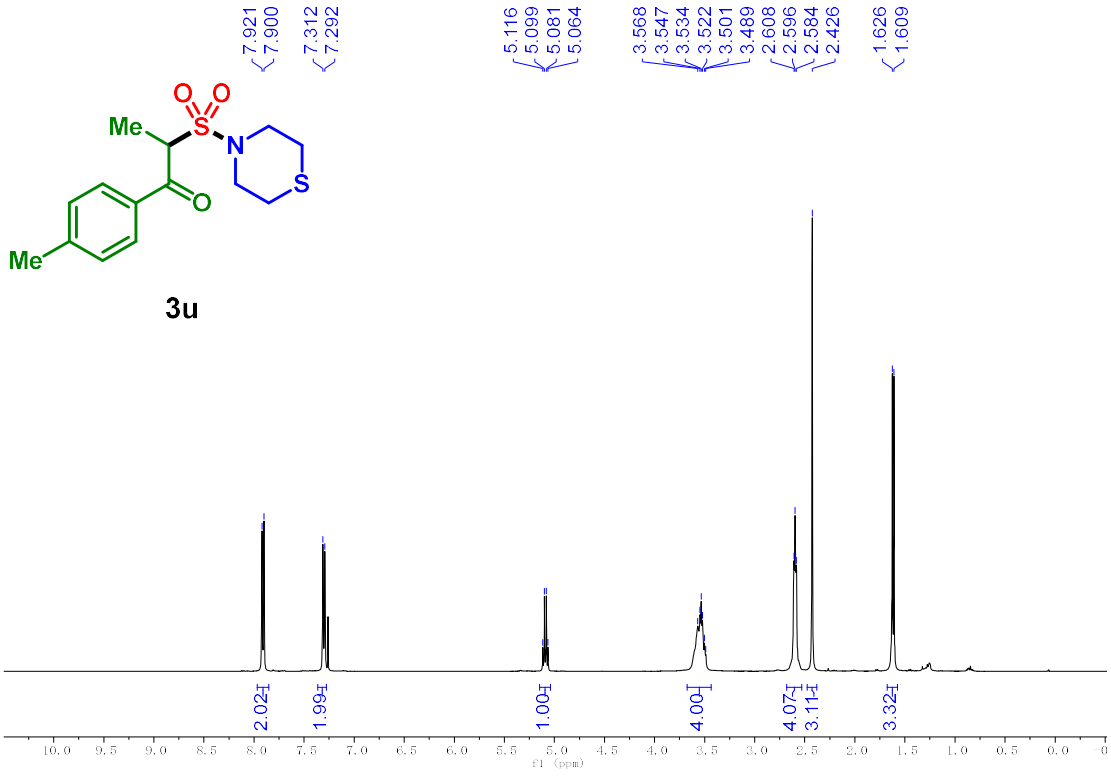


^{13}C NMR (100 MHz, $CDCl_3$)

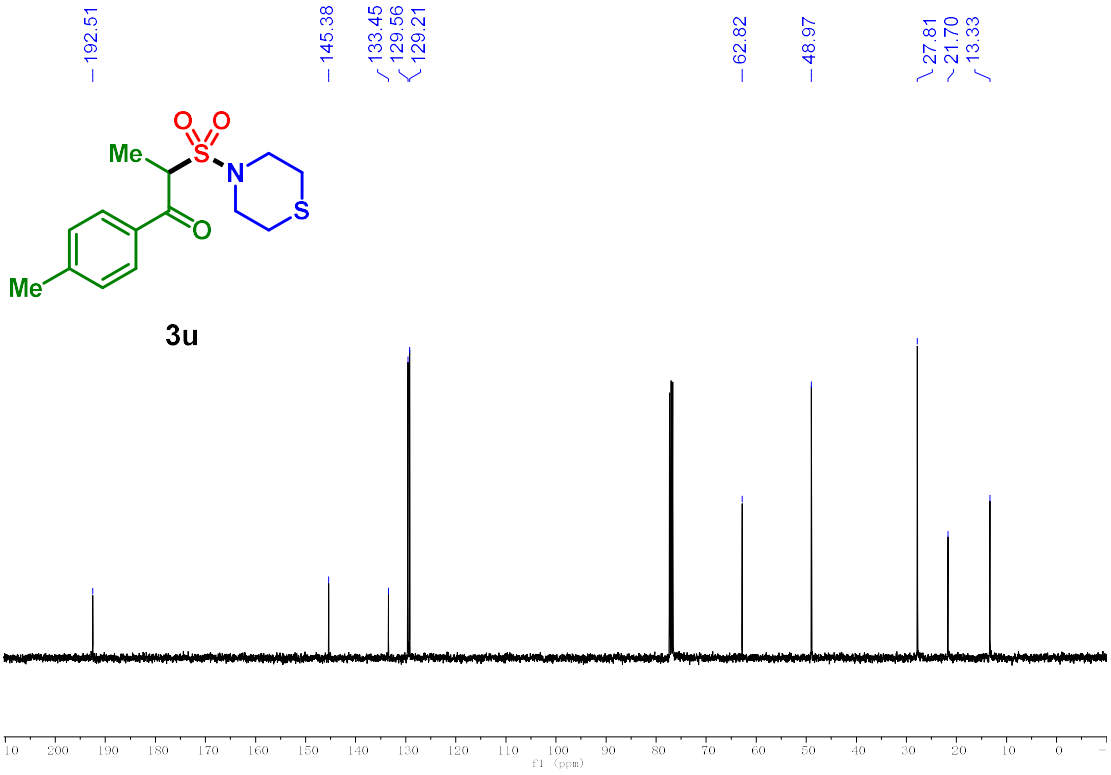


2-(thiomorpholinosulfonyl)-1-(p-tolyl)propan-1-one (3u)

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

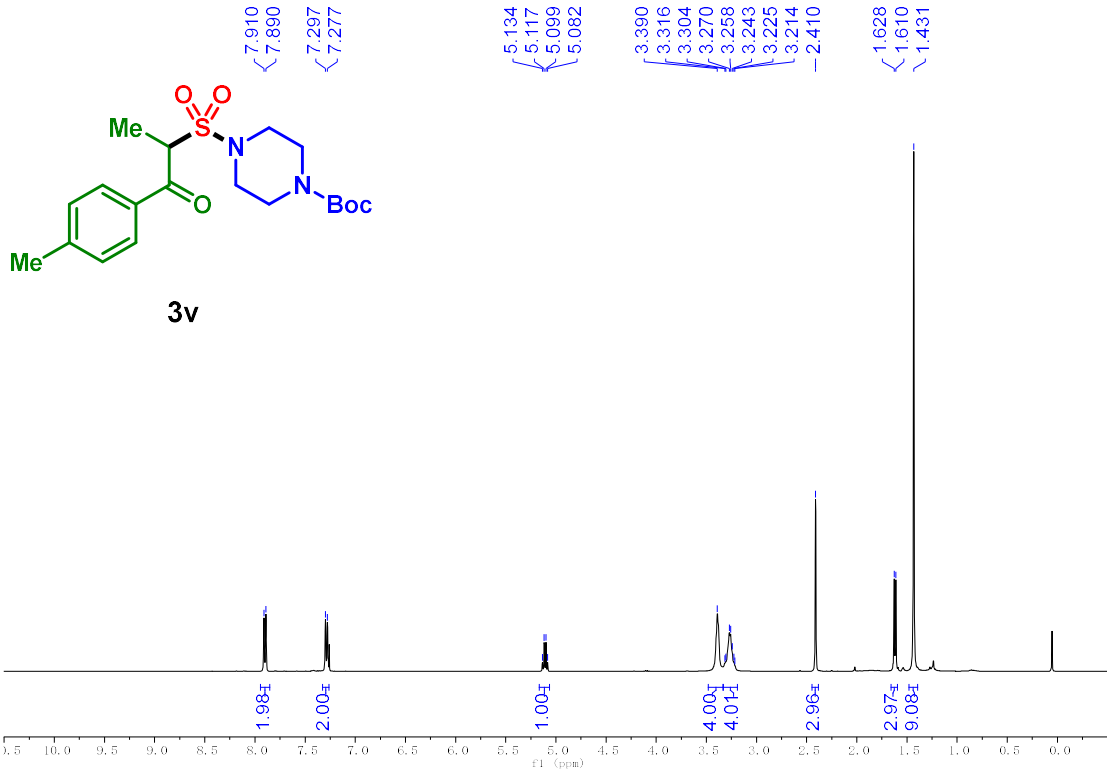


^{13}C NMR (100 MHz, $CDCl_3$)



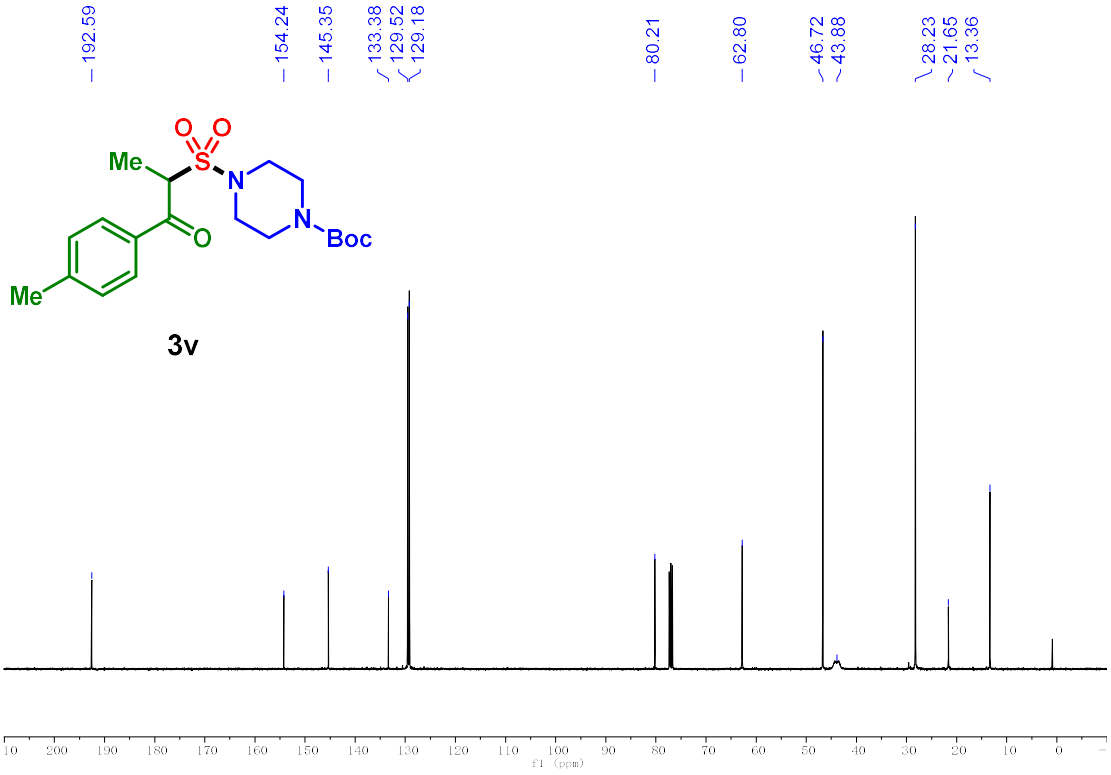
tert-butyl 4-((1-oxo-1-(p-tolyl)propan-2-yl)sulfonyl)piperazine-1-carboxylate (3v)

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



3v

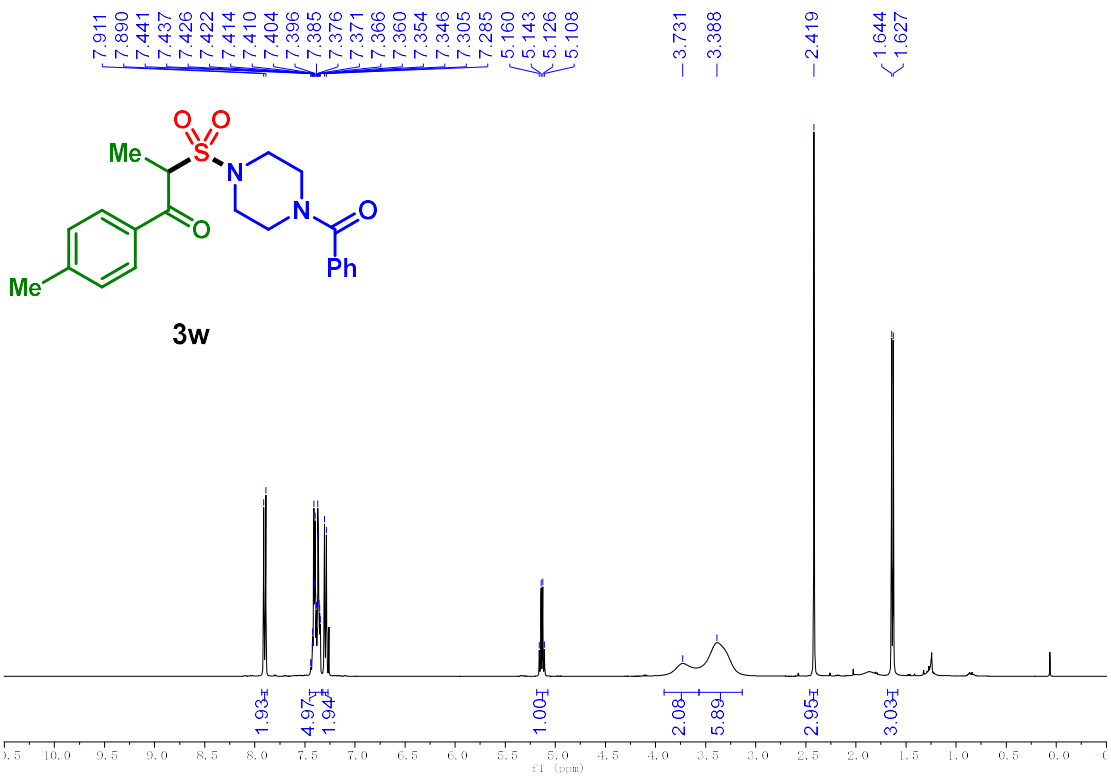
^{13}C NMR (100 MHz, $CDCl_3$)



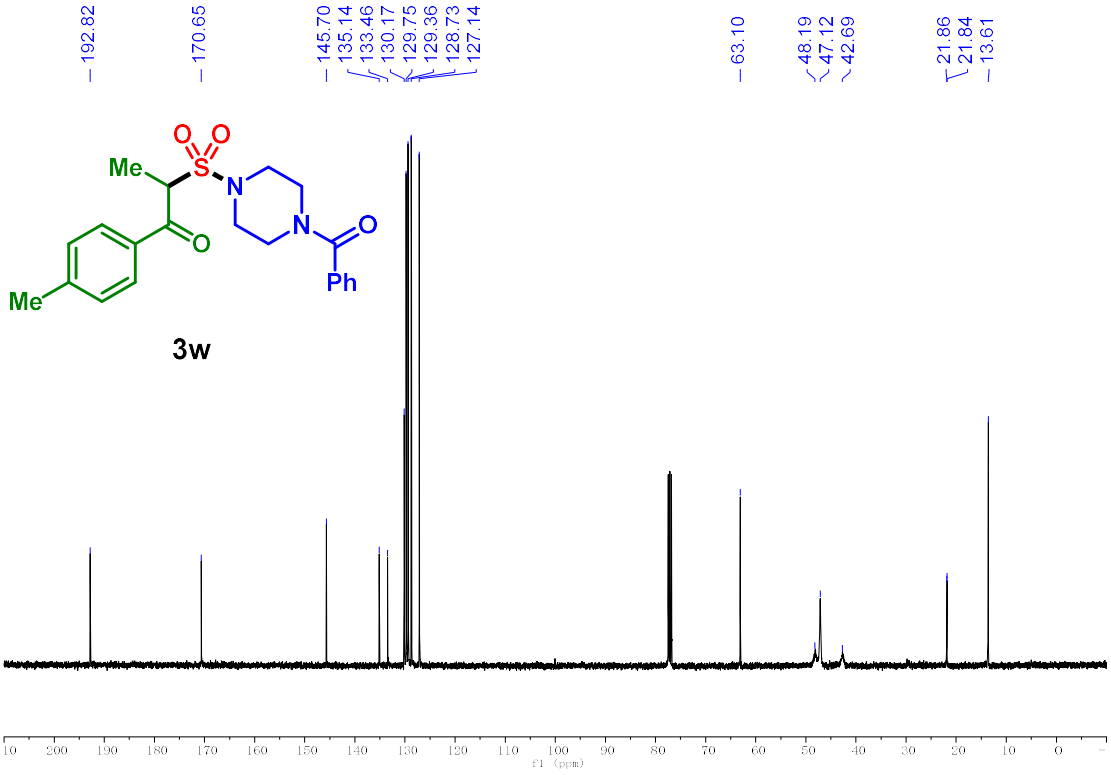
3v

2-((4-benzoylpiperazin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3w)

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

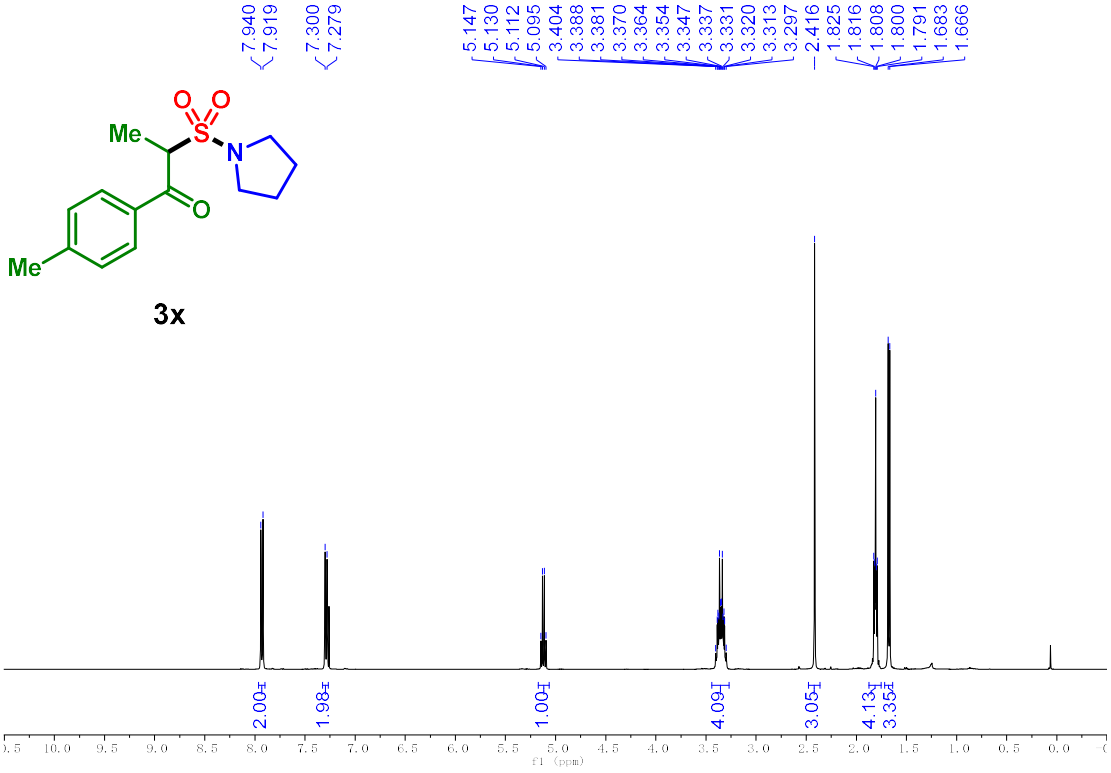


^{13}C NMR (100 MHz, $CDCl_3$)

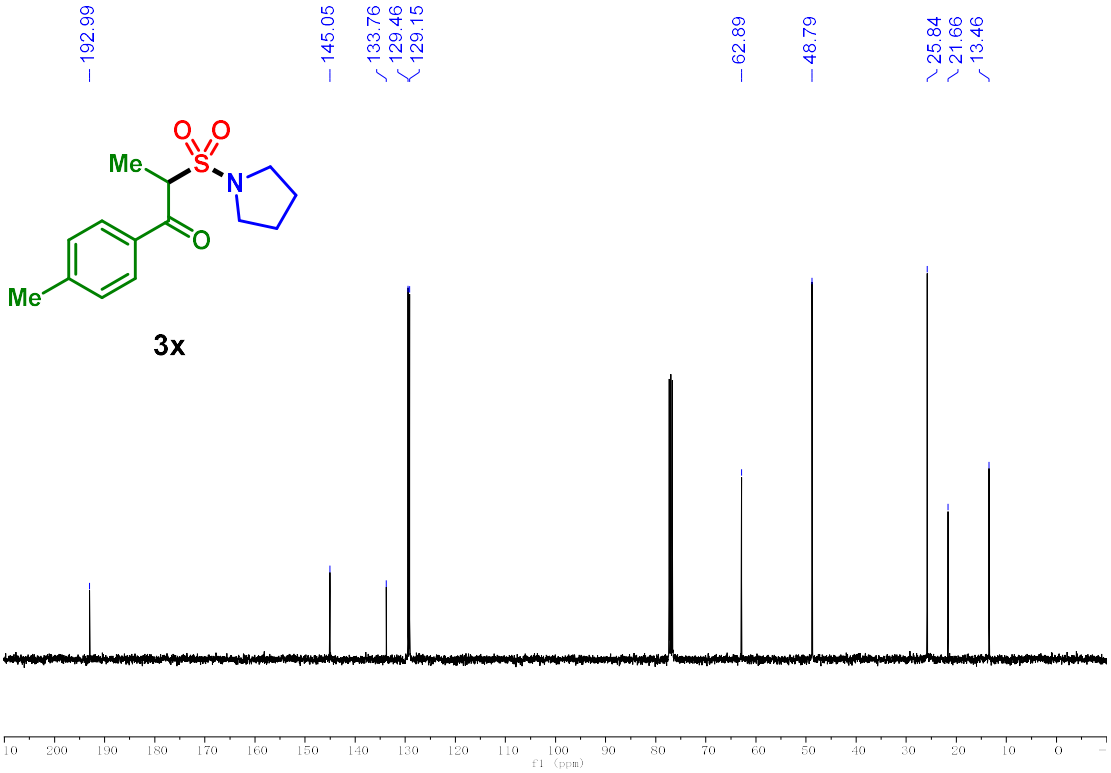


2-(pyrrolidin-1-ylsulfonyl)-1-(p-tolyl)propan-1-one (3x)

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

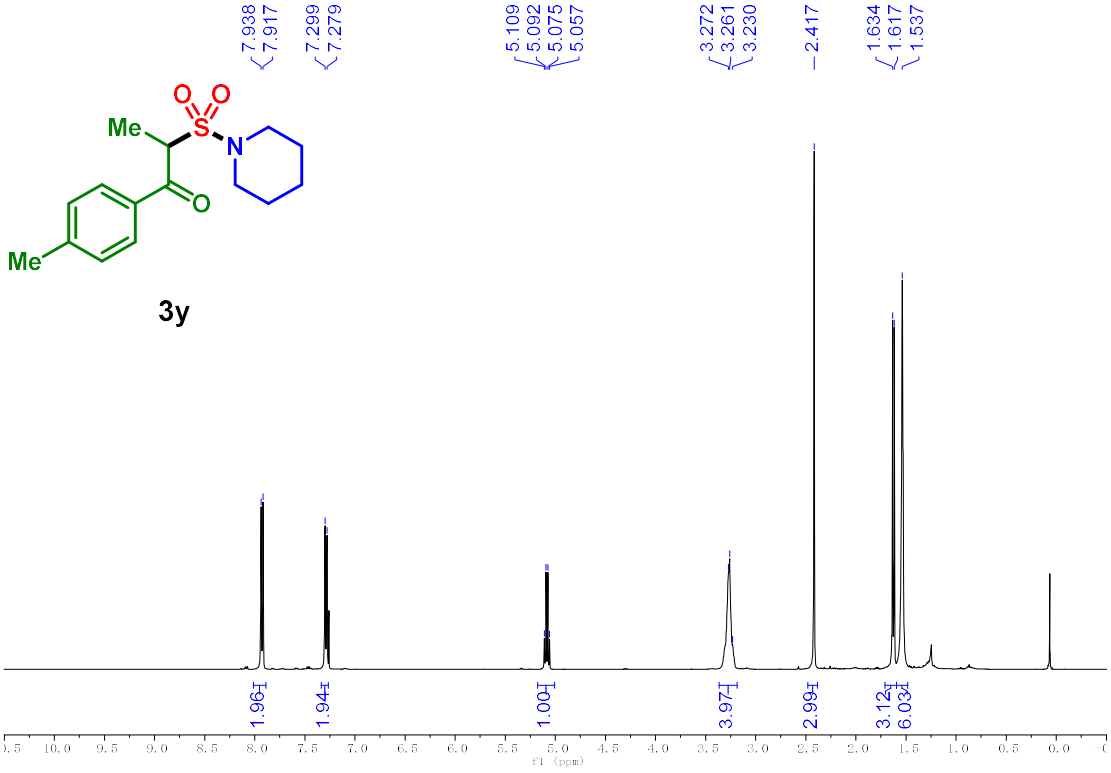


^{13}C NMR (100 MHz, $CDCl_3$)

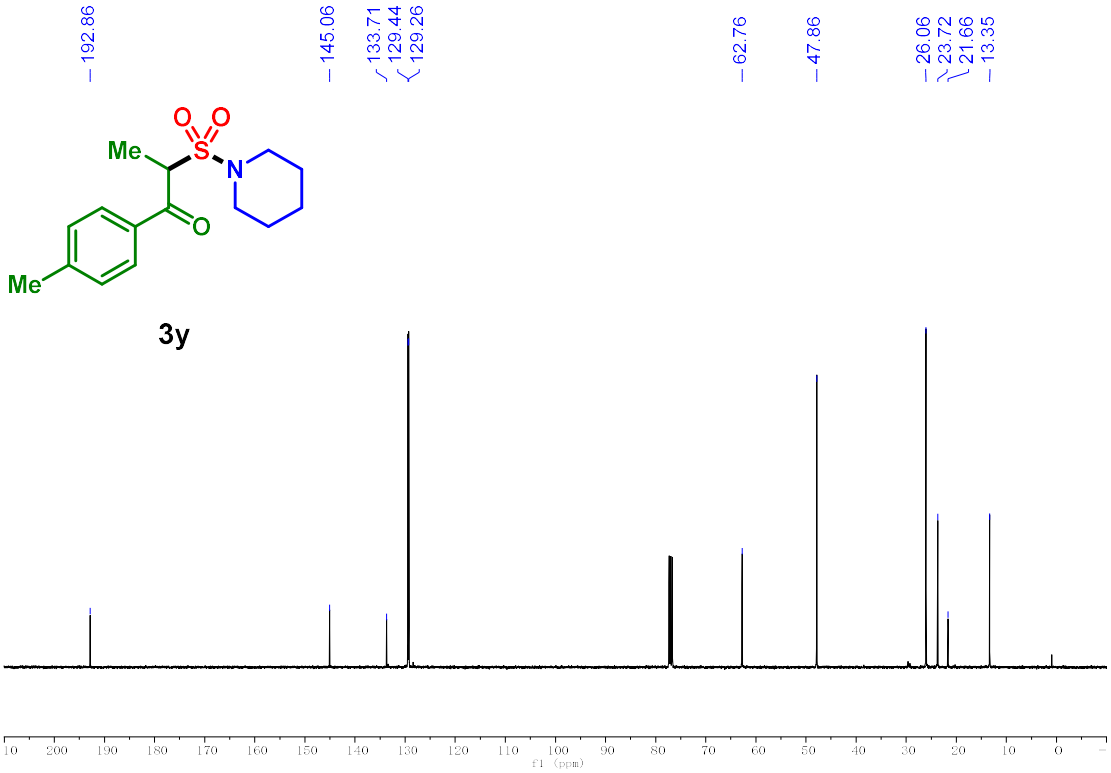


2-(piperidin-1-ylsulfonyl)-1-(p-tolyl)propan-1-one (3y)

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

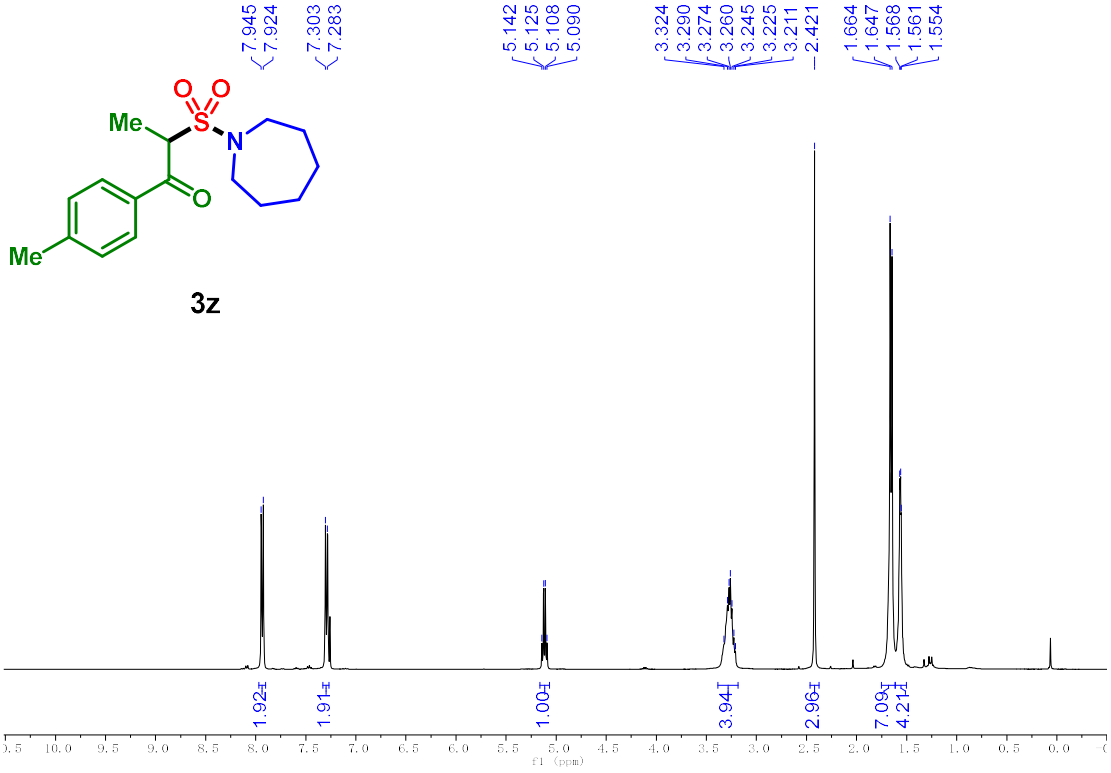


^{13}C NMR (100 MHz, $CDCl_3$)

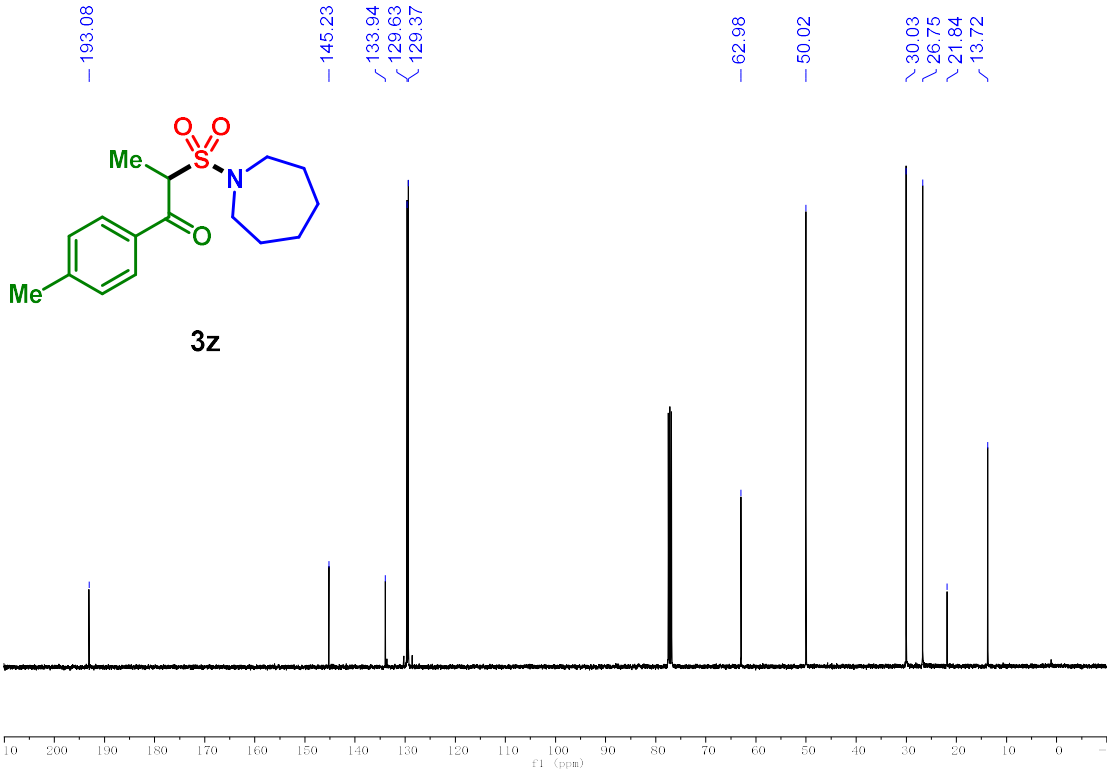


2-(azepan-1-ylsulfonyl)-1-(p-tolyl)propan-1-one (3z)

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

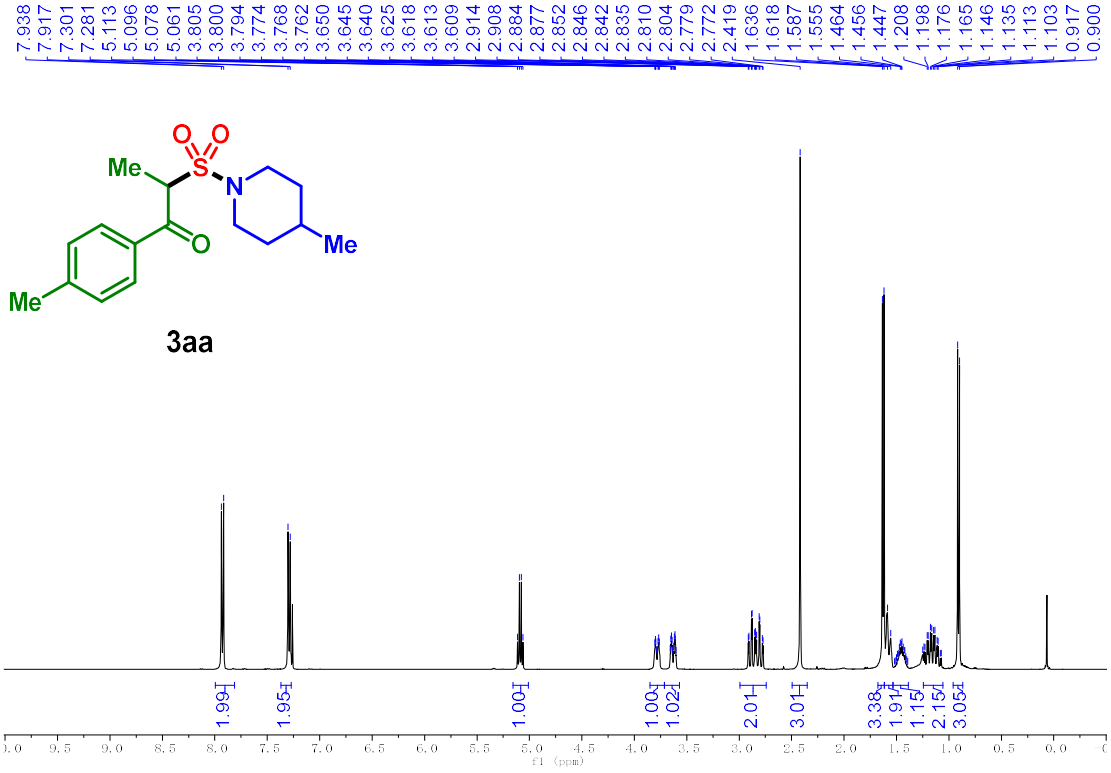


^{13}C NMR (100 MHz, $CDCl_3$)

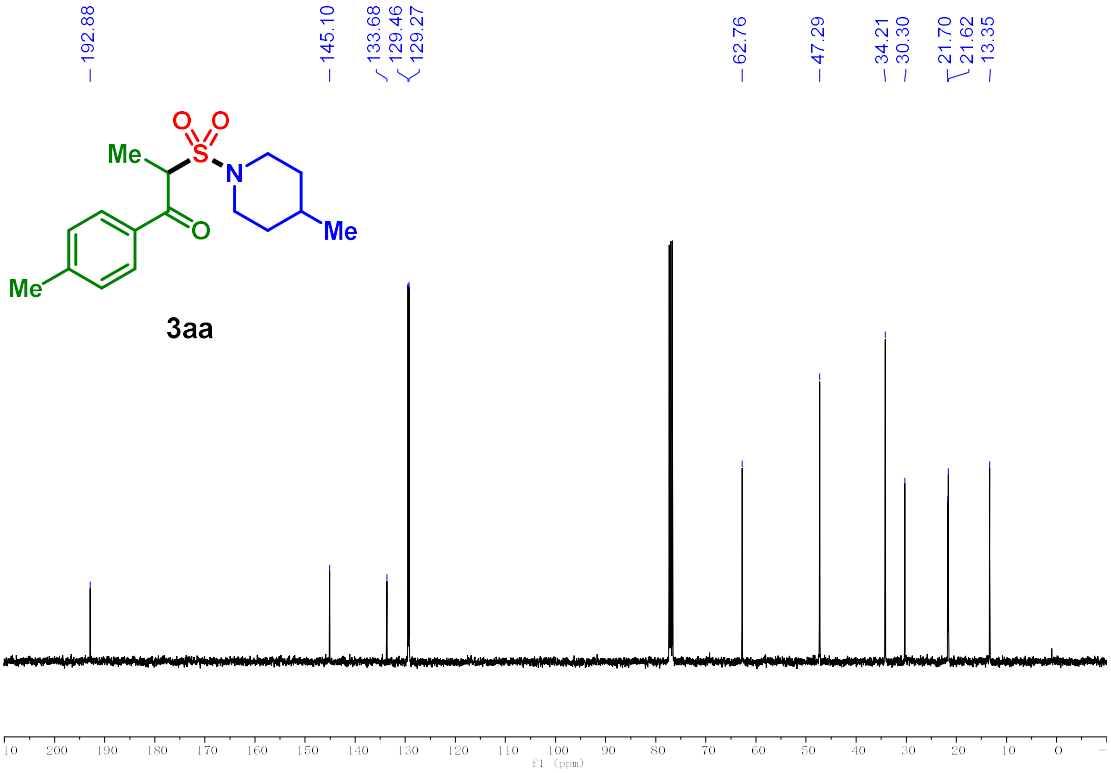


2-((4-methylpiperidin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3aa)

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

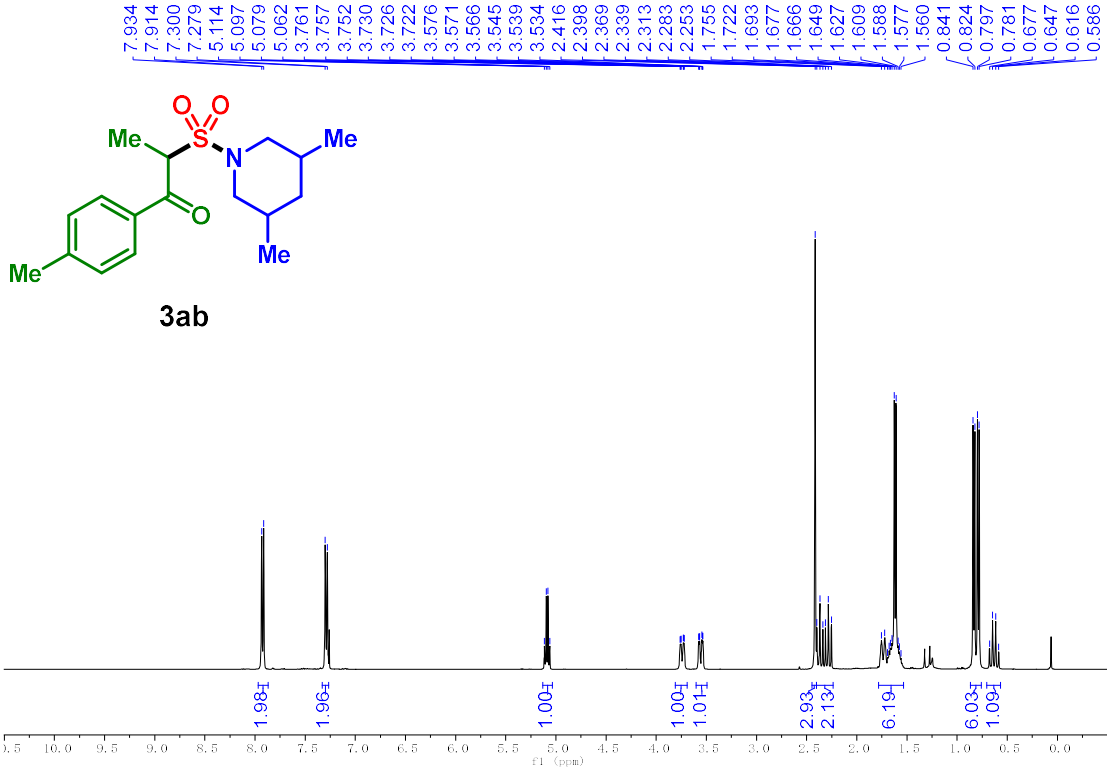


^{13}C NMR (100 MHz, $CDCl_3$)

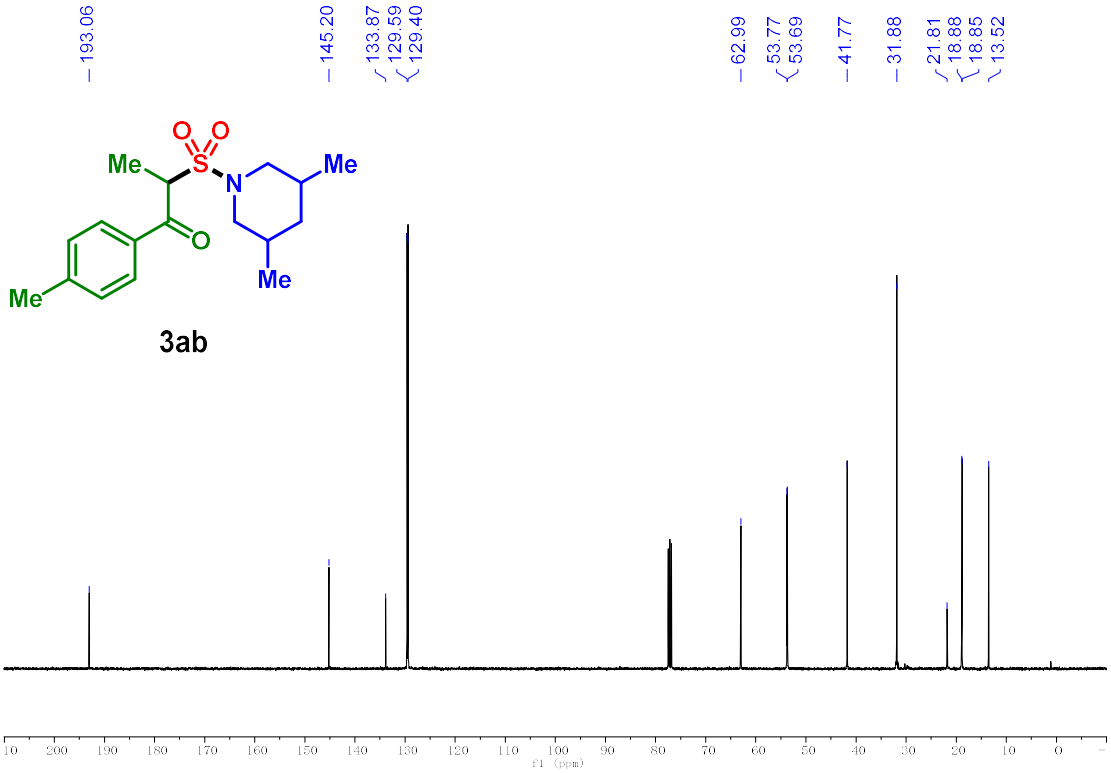


2-((3,5-dimethylpiperidin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3ab)

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

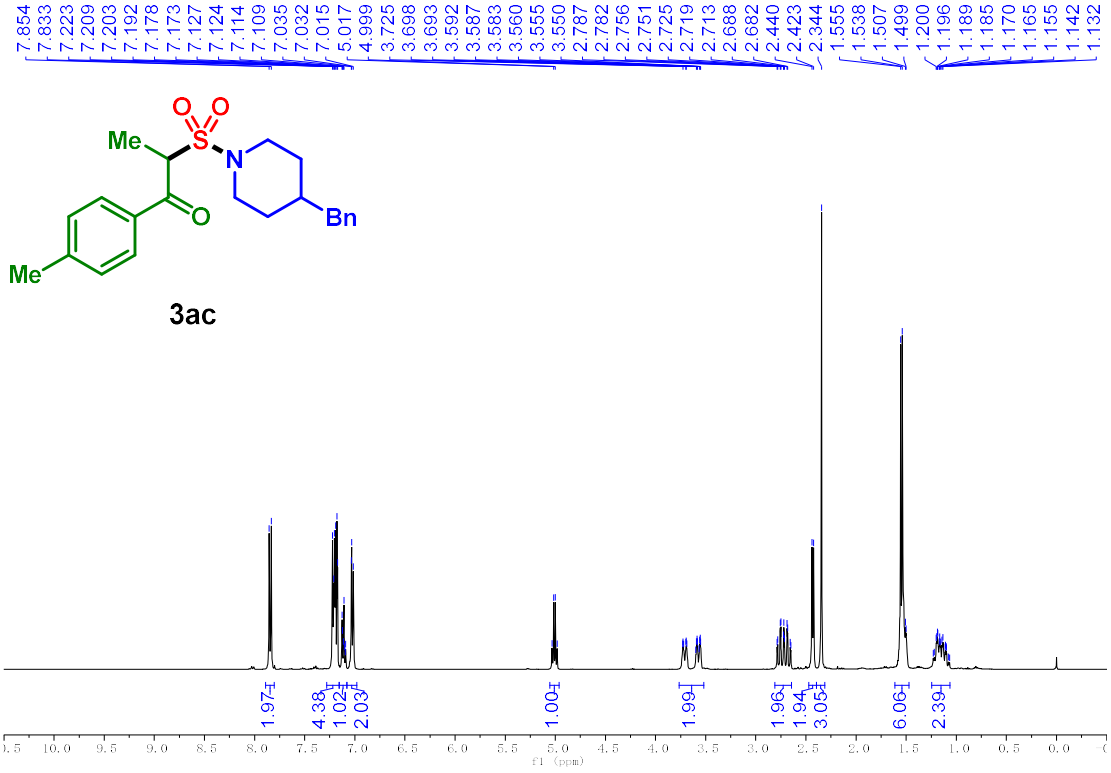


^{13}C NMR (100 MHz, $CDCl_3$)

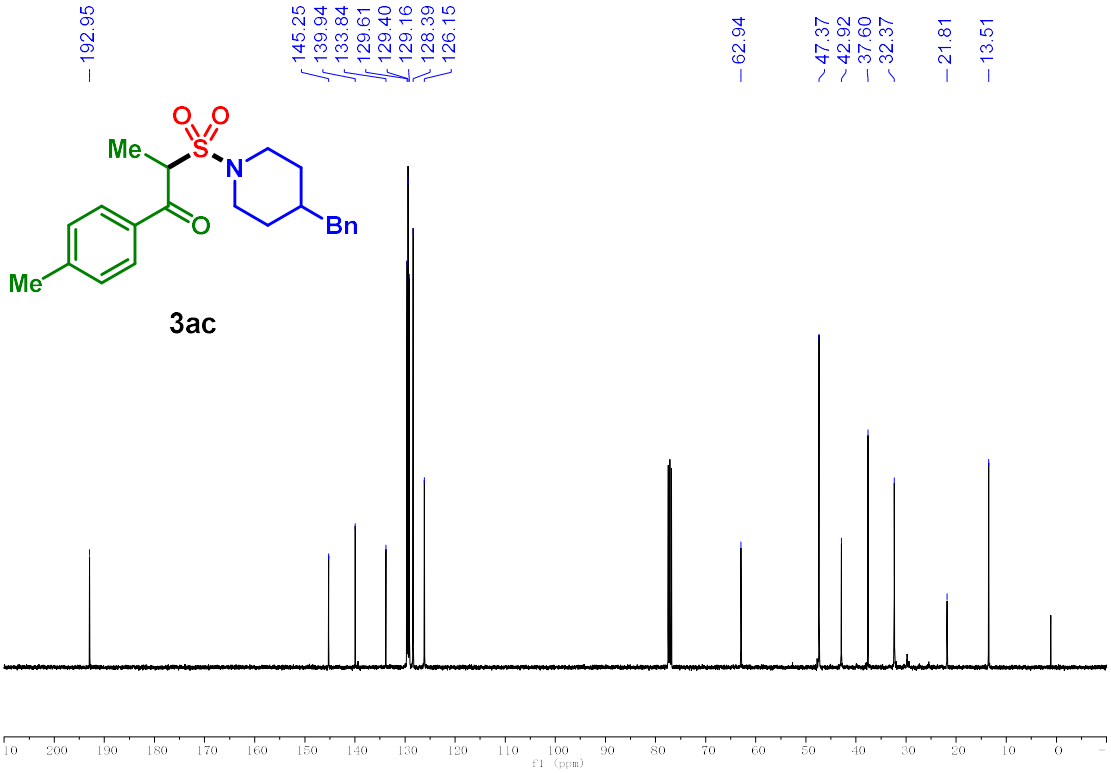


2-((4-benzylpiperidin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3ac)

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

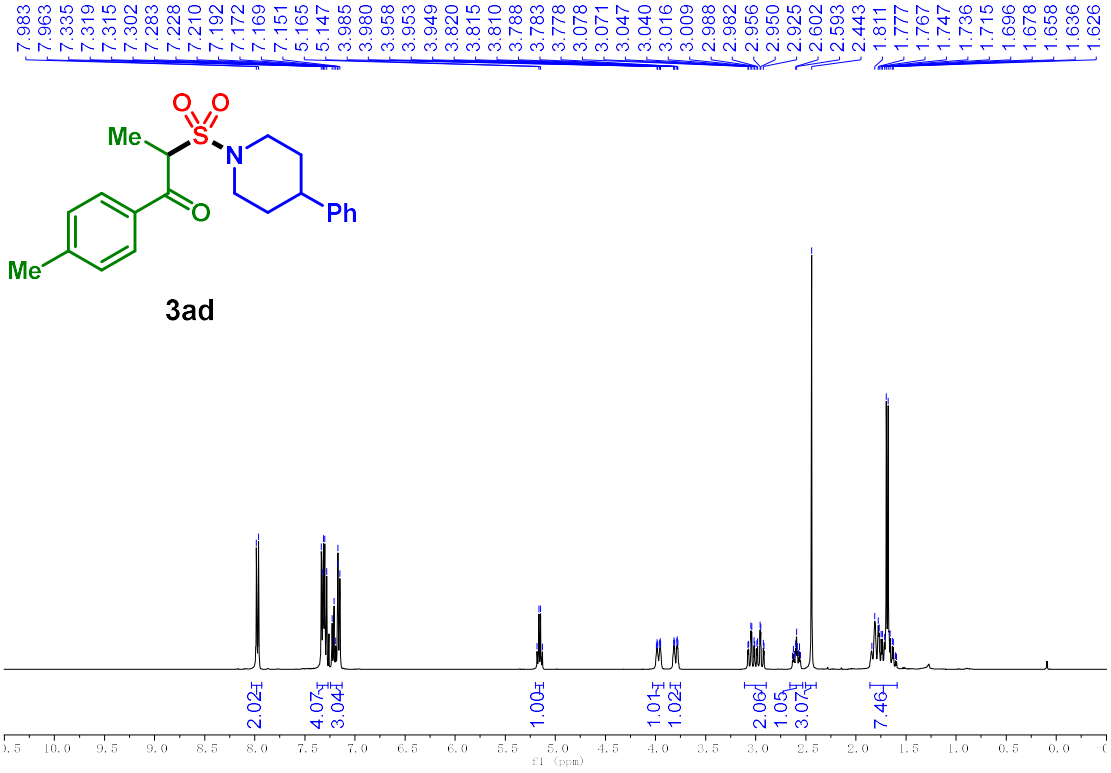


^{13}C NMR (100 MHz, $CDCl_3$)

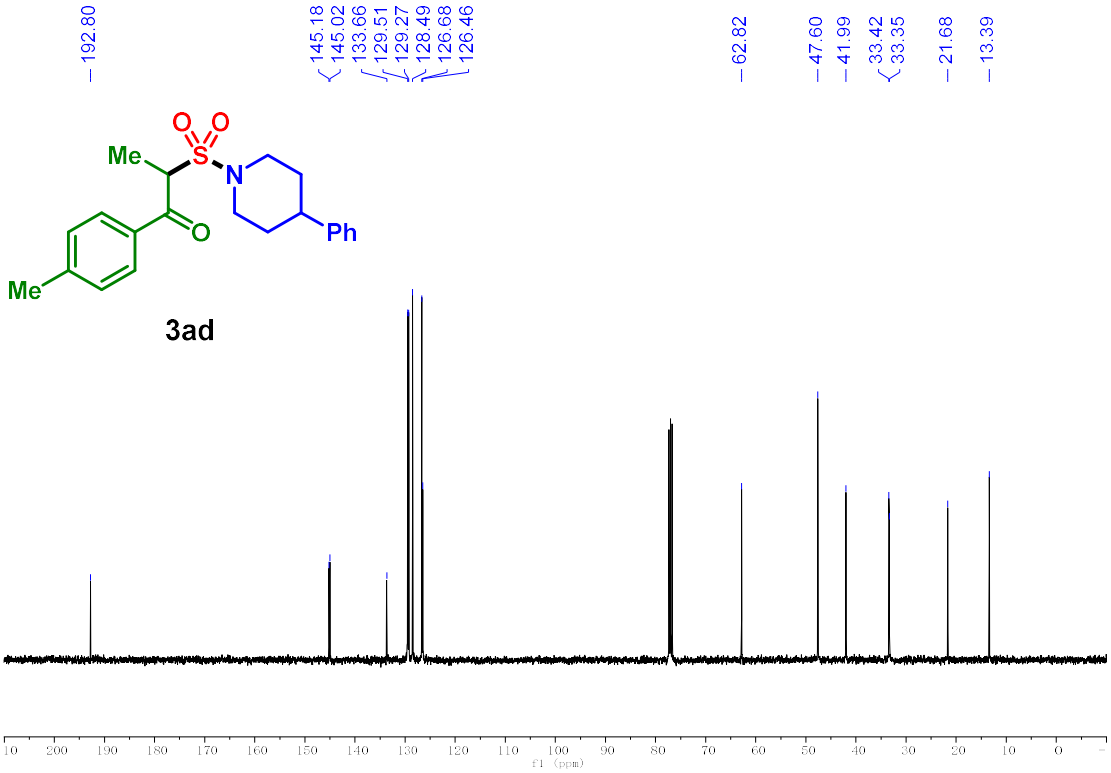


2-((4-phenylpiperidin-1-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3ad)

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

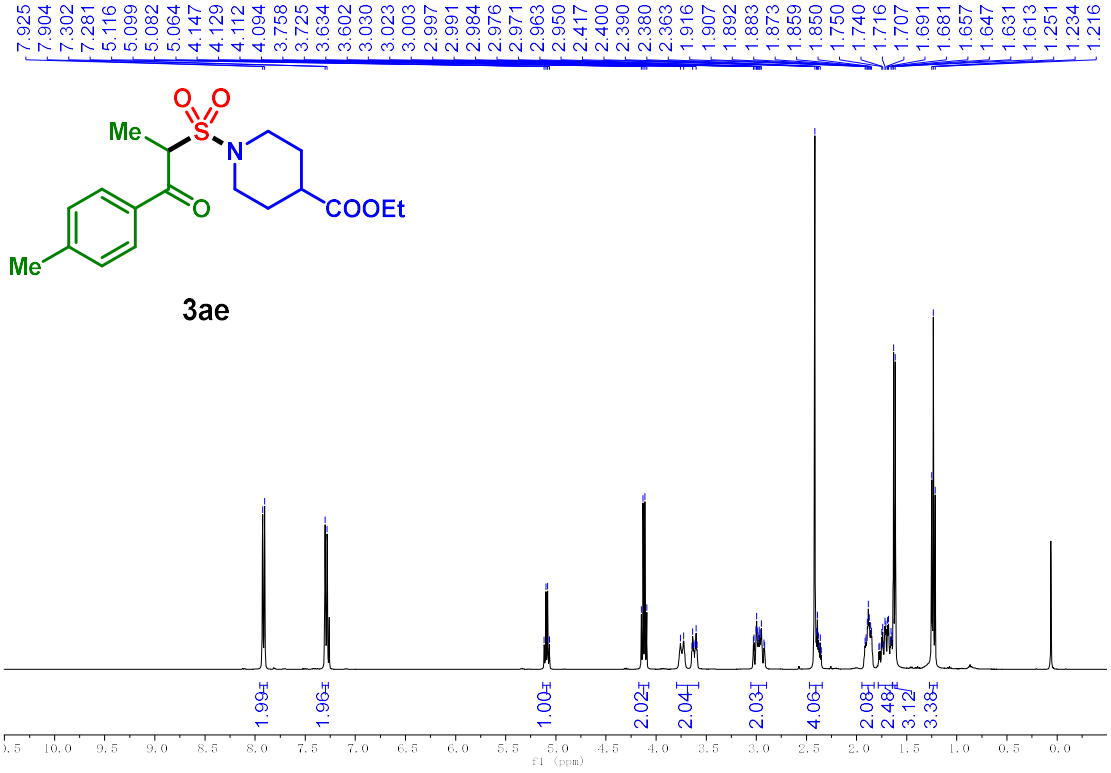


^{13}C NMR (100 MHz, $CDCl_3$)

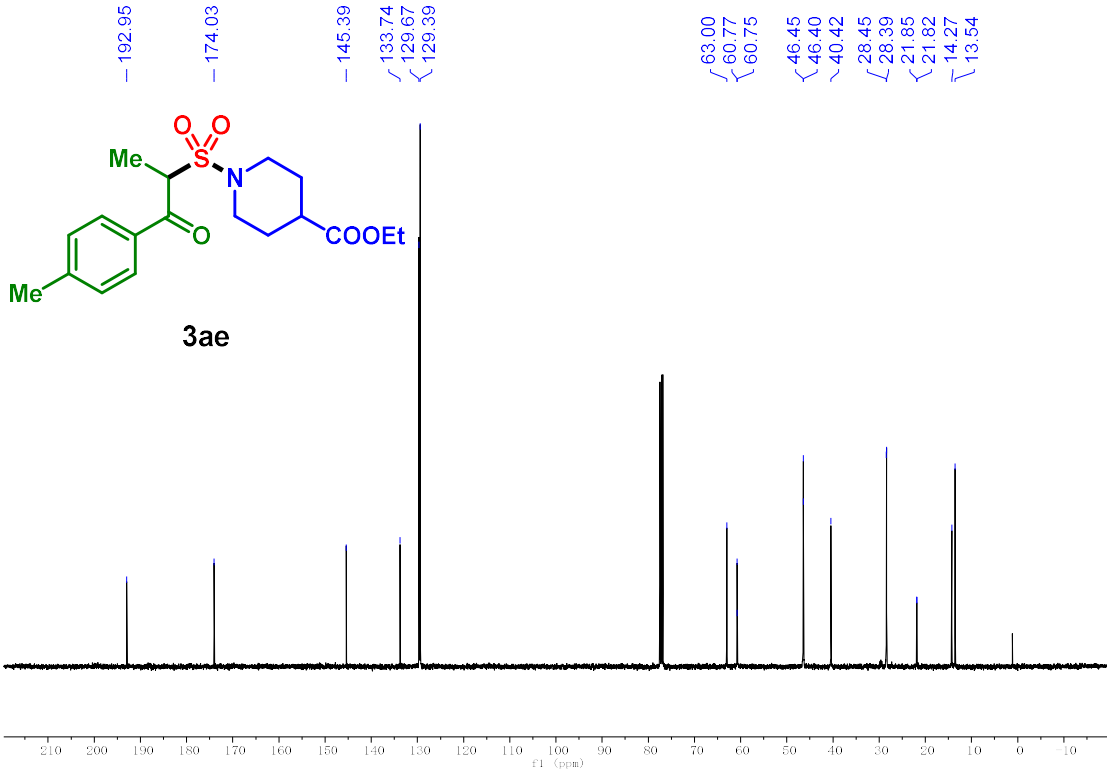


ethyl 1-((1-oxo-1-(p-tolyl)propan-2-yl)sulfonyl)piperidine-4-carboxylate (3ae)

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

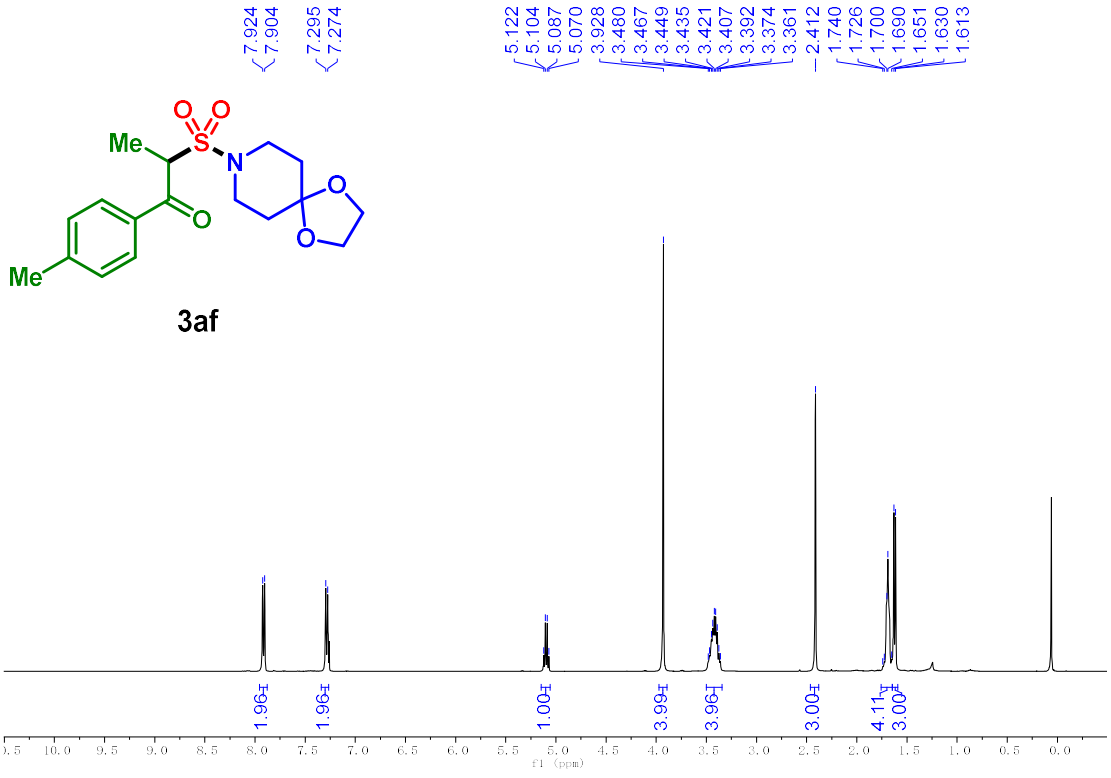


^{13}C NMR (100 MHz, $CDCl_3$)

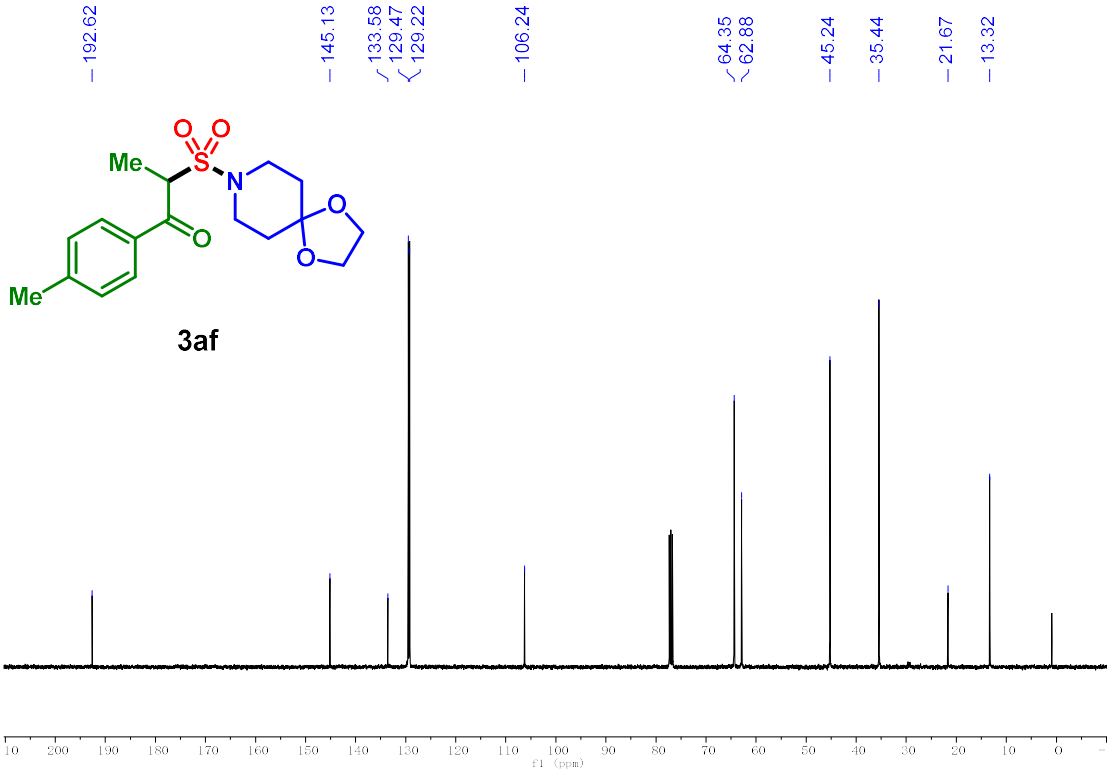


2-((1,4-dioxa-8-azaspiro[4.5]decan-8-yl)sulfonyl)-1-(p-tolyl)propan-1-one (3af)

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

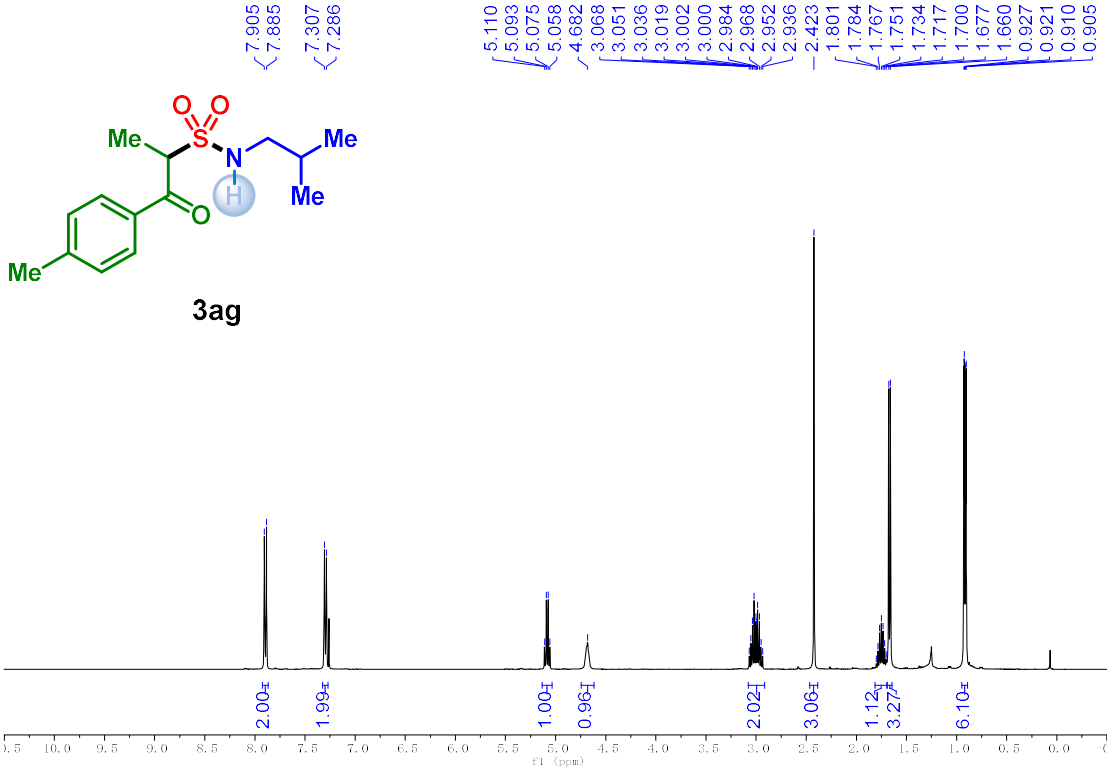


^{13}C NMR (100 MHz, $CDCl_3$)

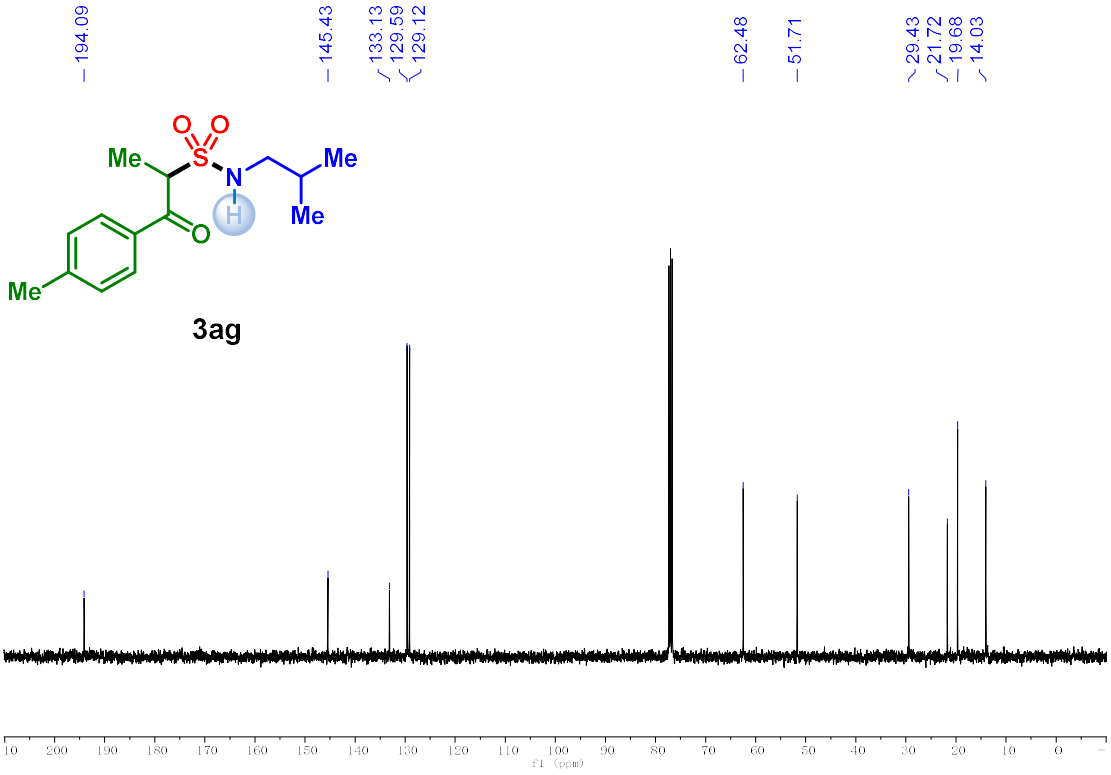


N-isobutyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3ag)

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

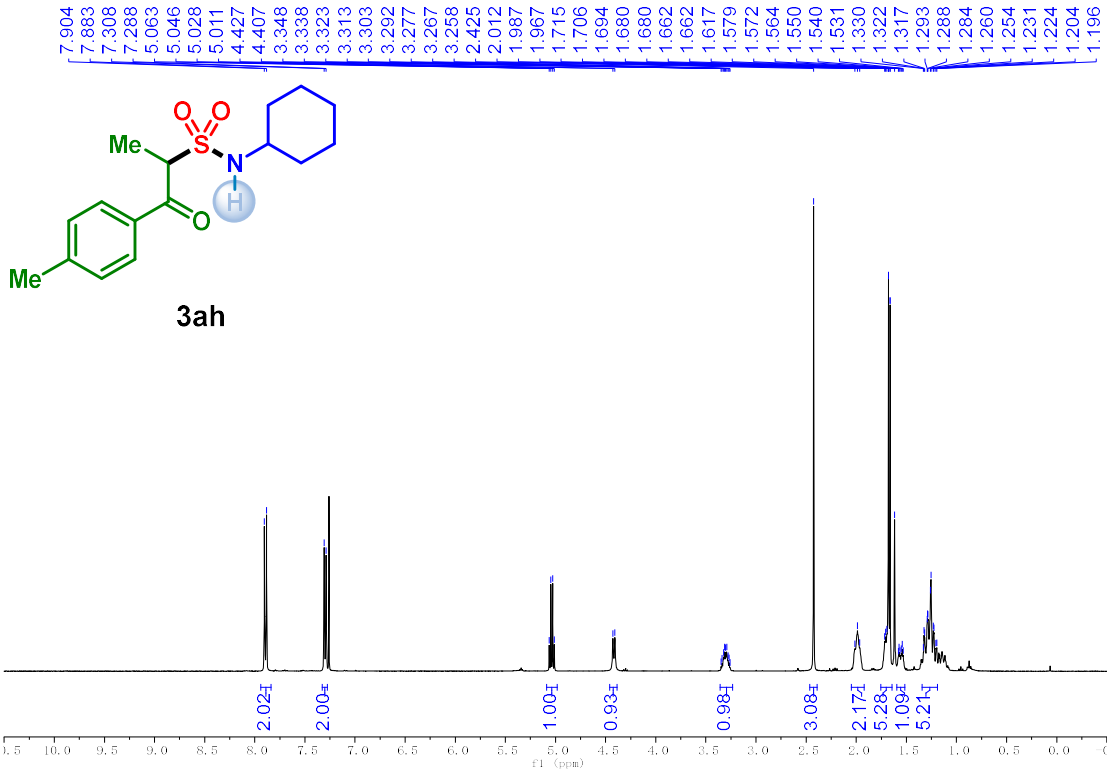


^{13}C NMR (100 MHz, $CDCl_3$)

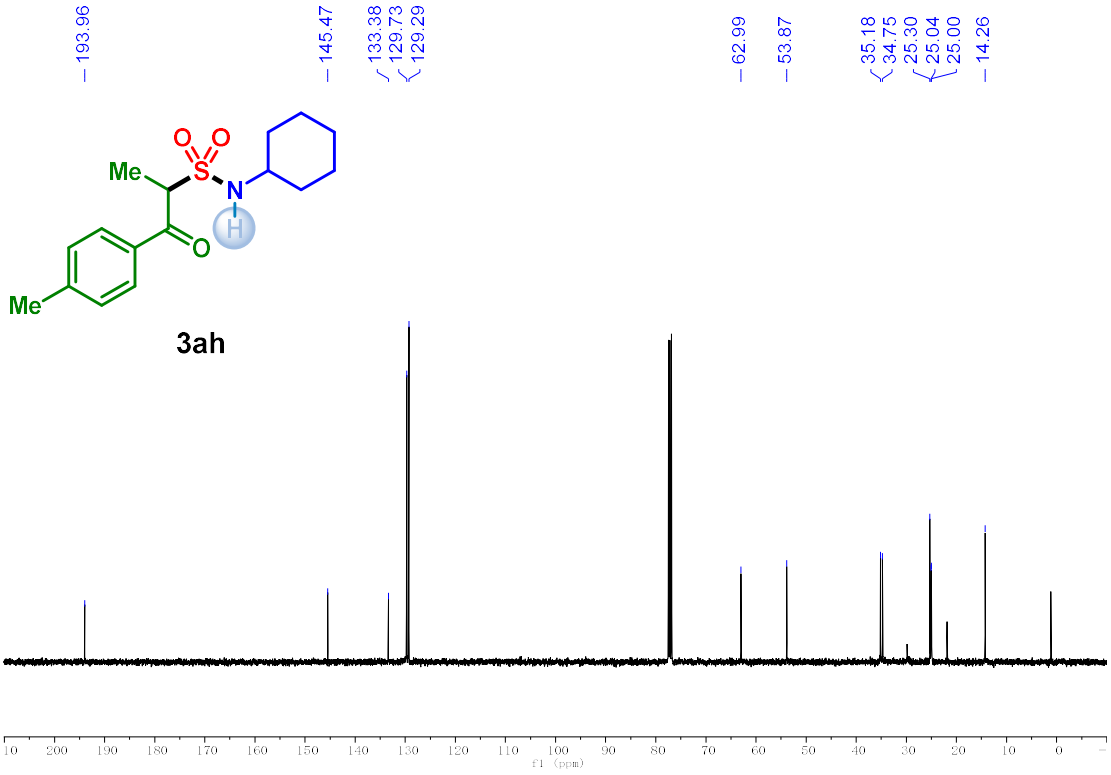


N-cyclohexyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3ah)

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

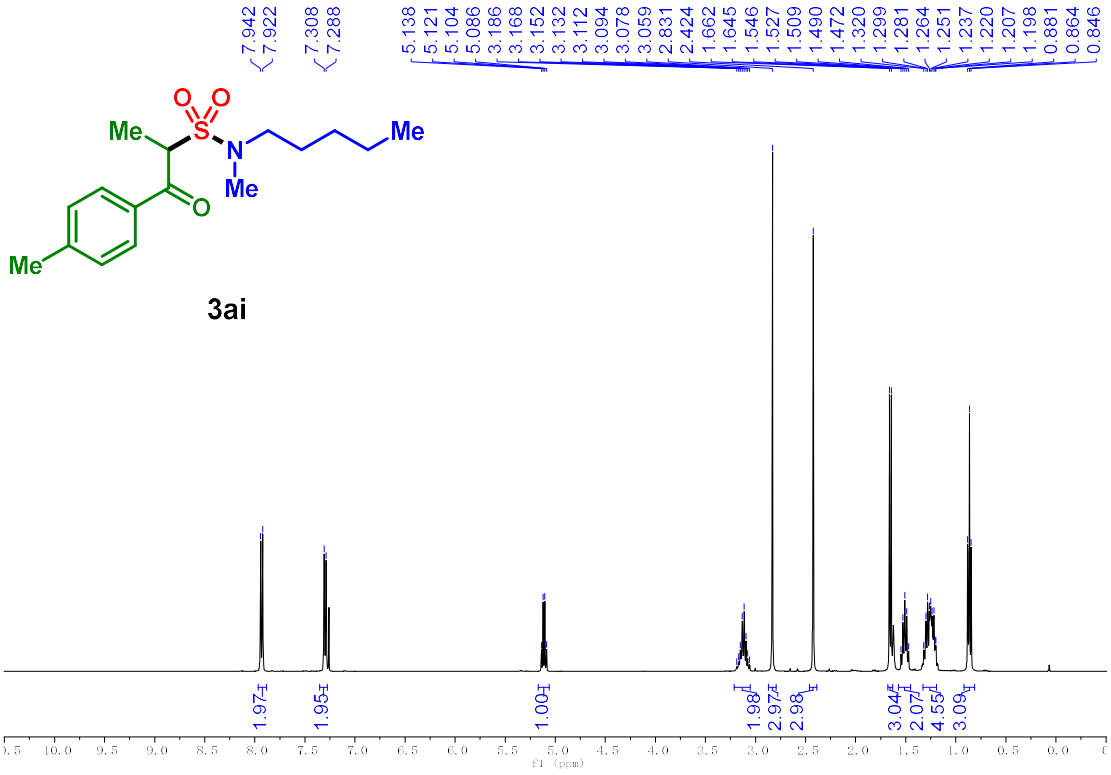


^{13}C NMR (100 MHz, $CDCl_3$)

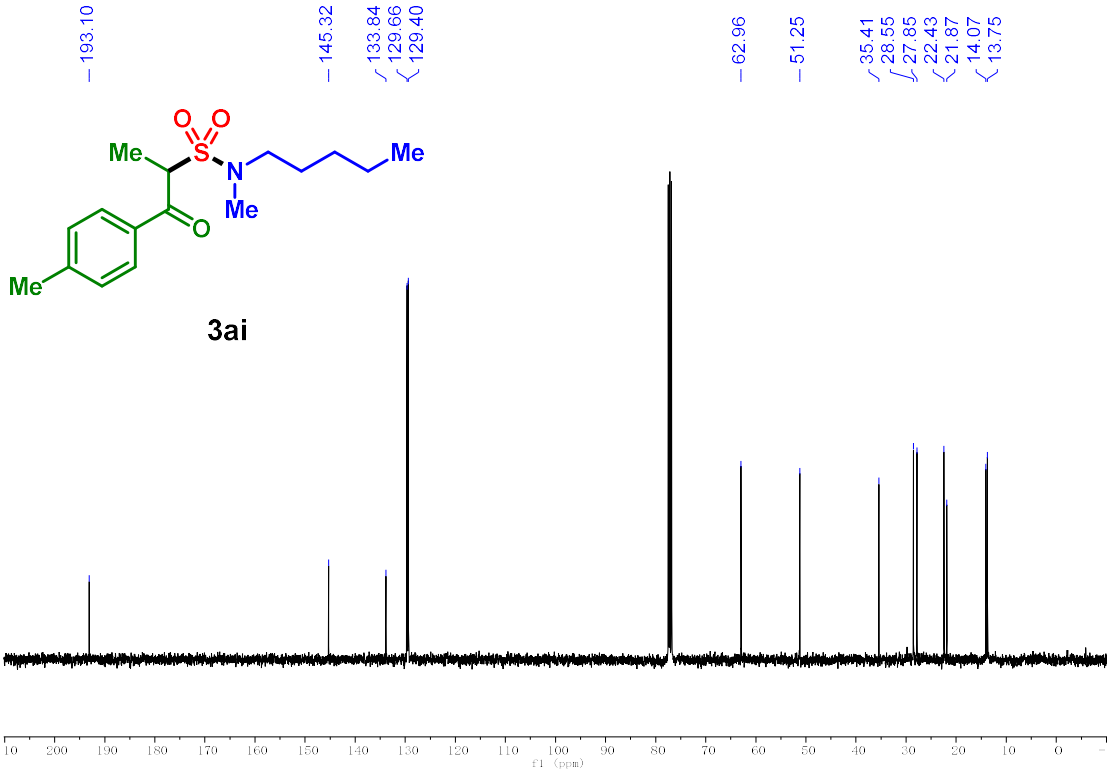


N-methyl-1-oxo-N-pentyl-1-(p-tolyl)propane-2-sulfonamide (3ai)

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

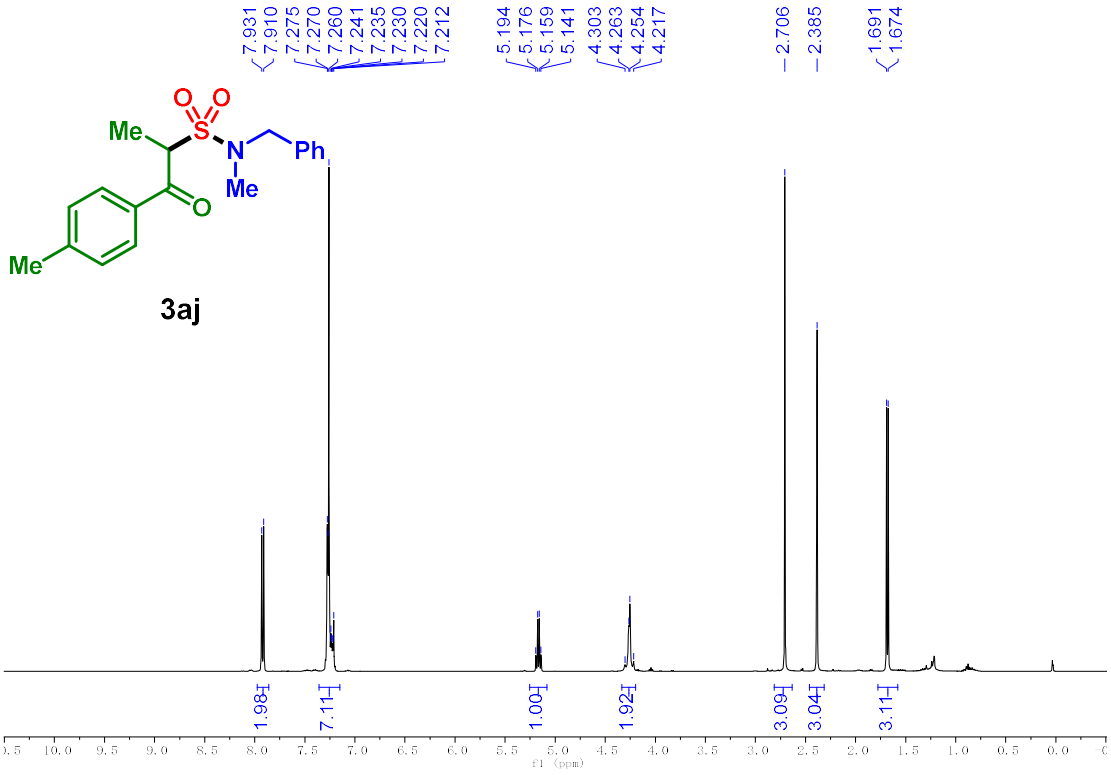


^{13}C NMR (100 MHz, $CDCl_3$)

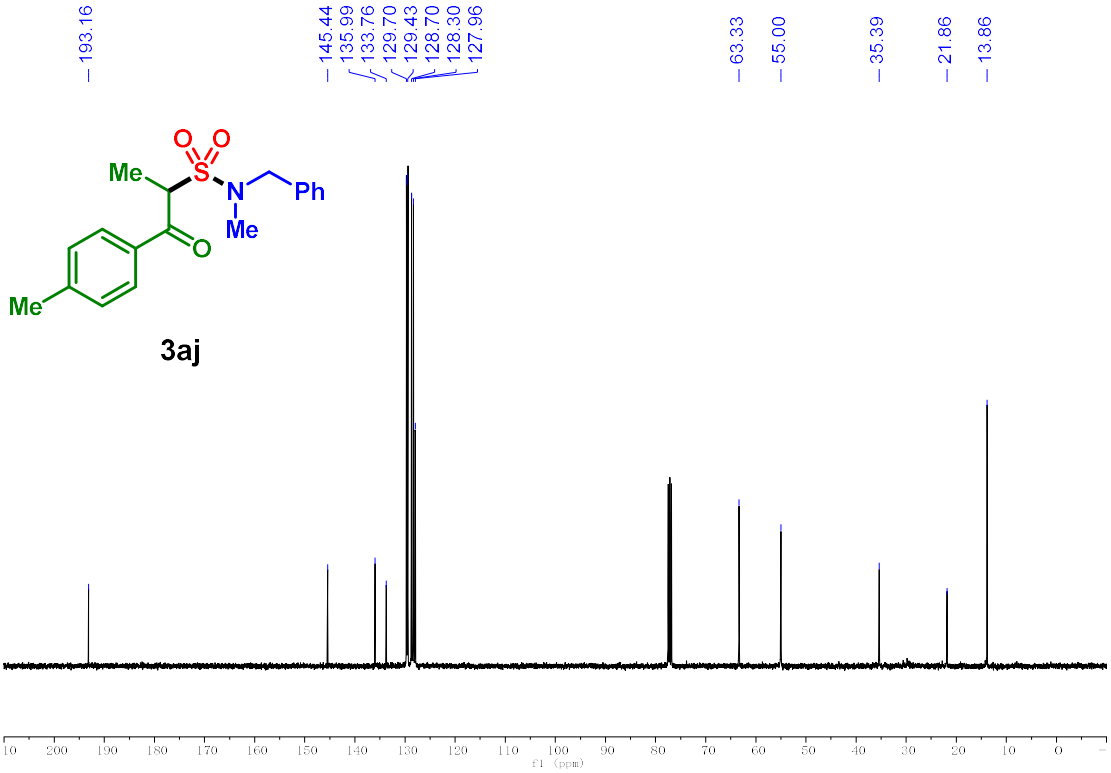


N-benzyl-N-methyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3aj)

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

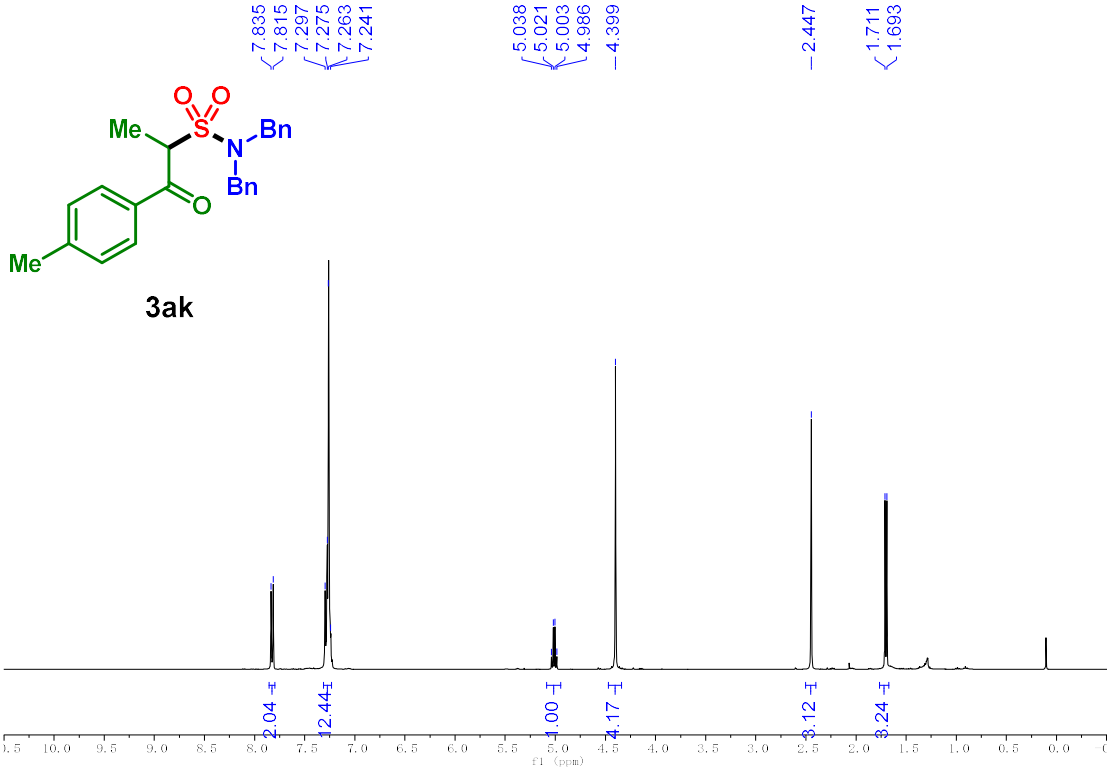


^{13}C NMR (100 MHz, $CDCl_3$)

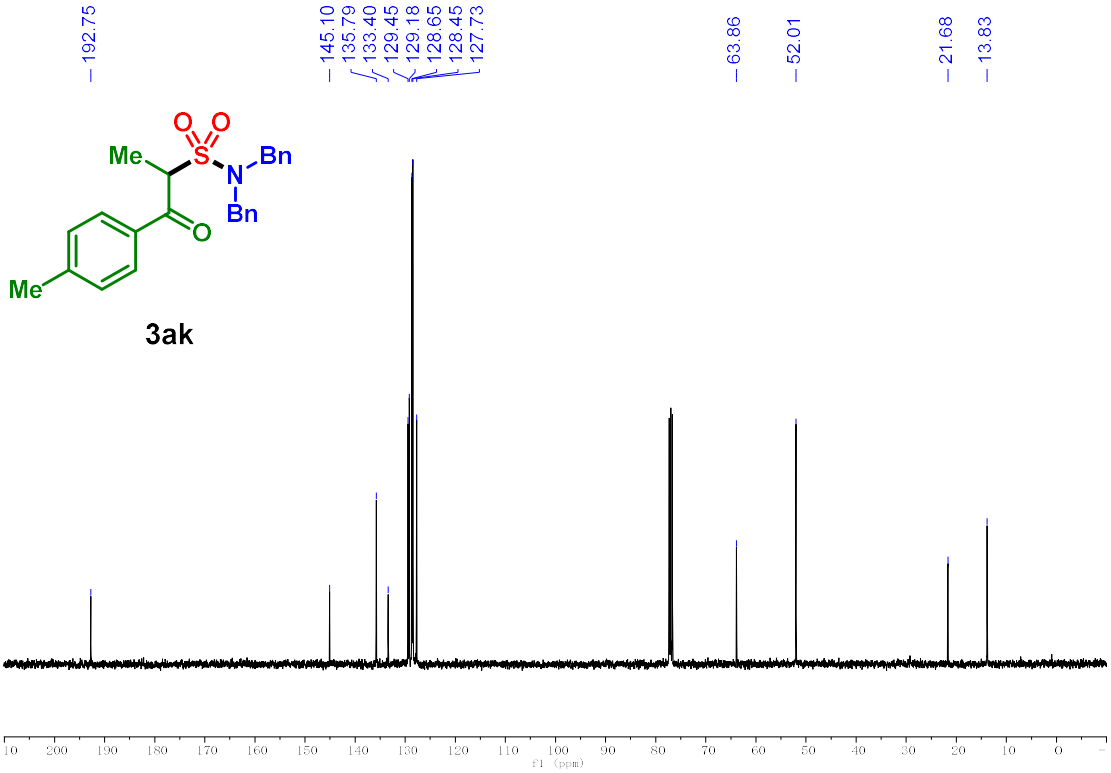


N,N-dibenzyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3ak)

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

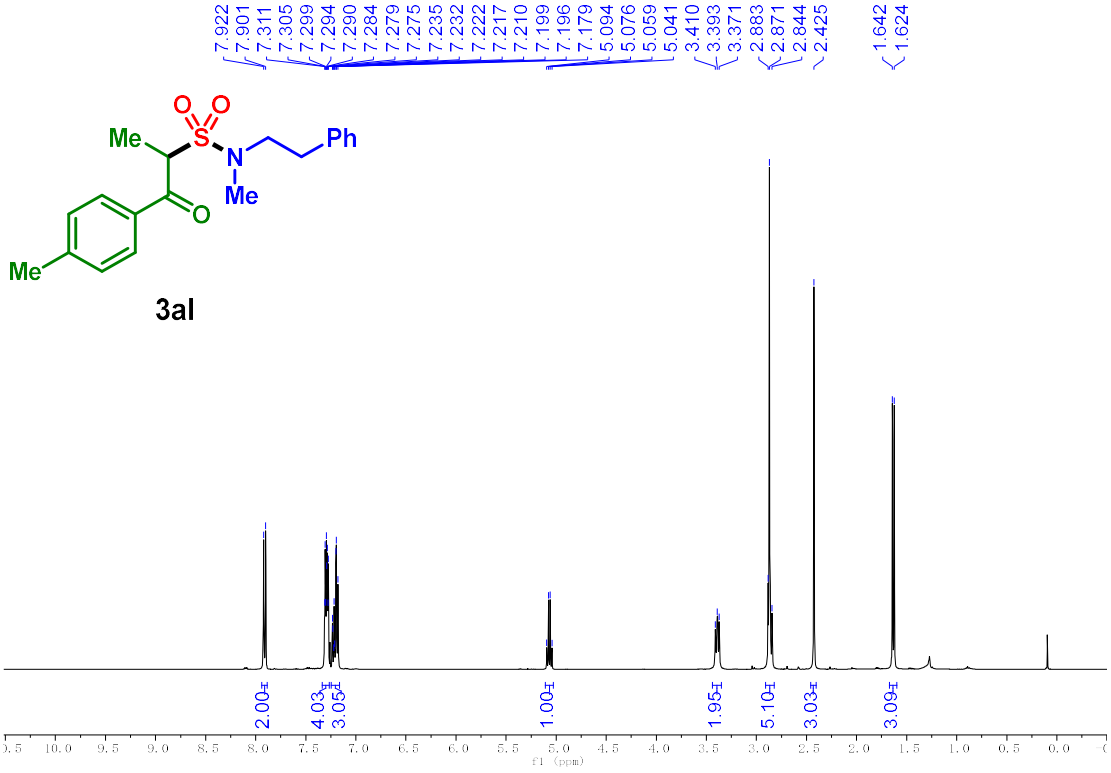


^{13}C NMR (100 MHz, $CDCl_3$)

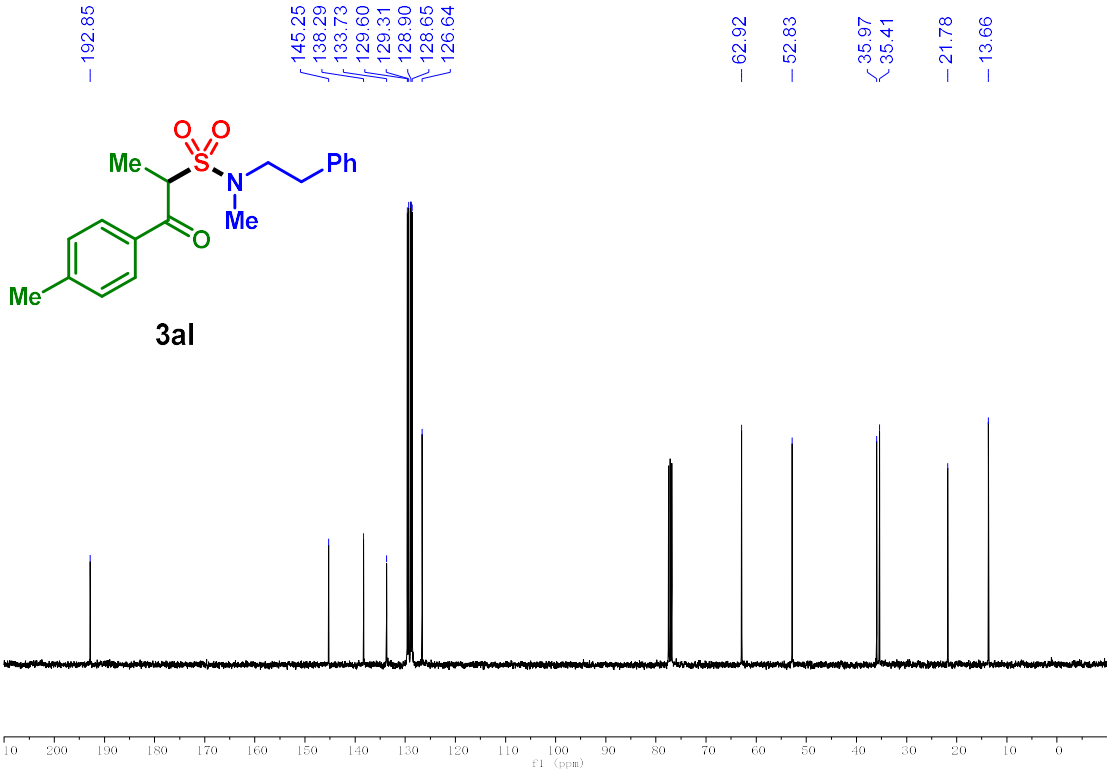


N-methyl-1-oxo-N-phenethyl-1-(p-tolyl)propane-2-sulfonamide (3al)

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

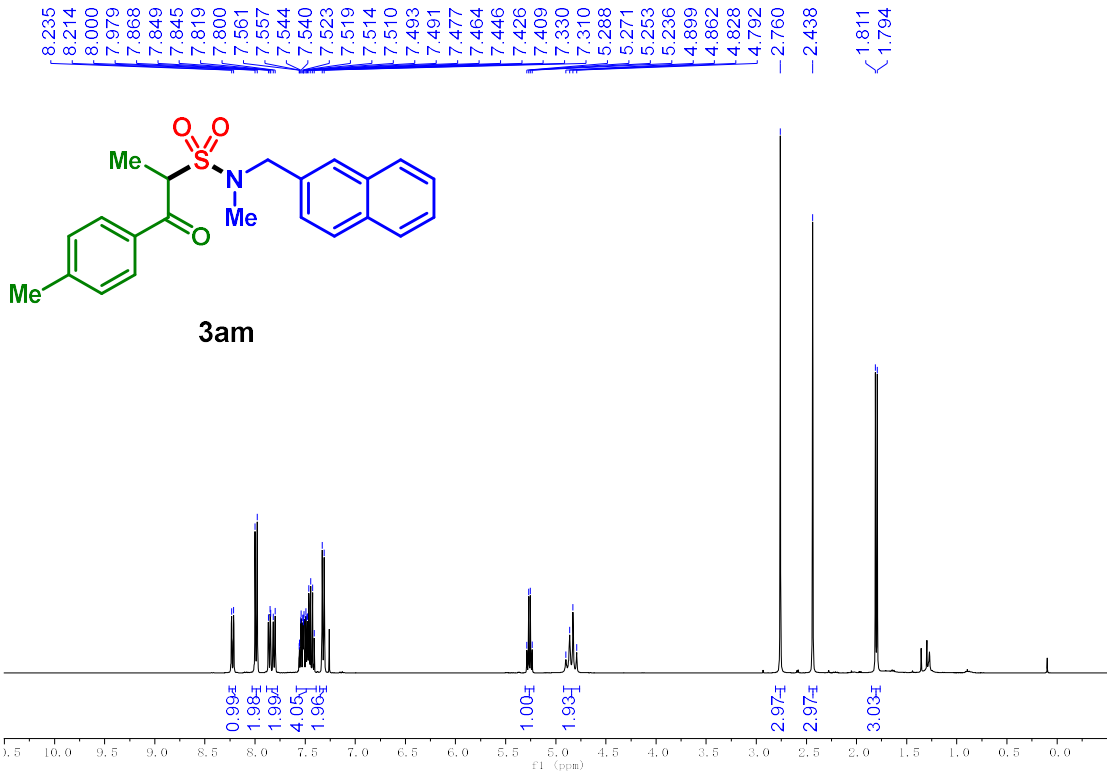


^{13}C NMR (100 MHz, $CDCl_3$)

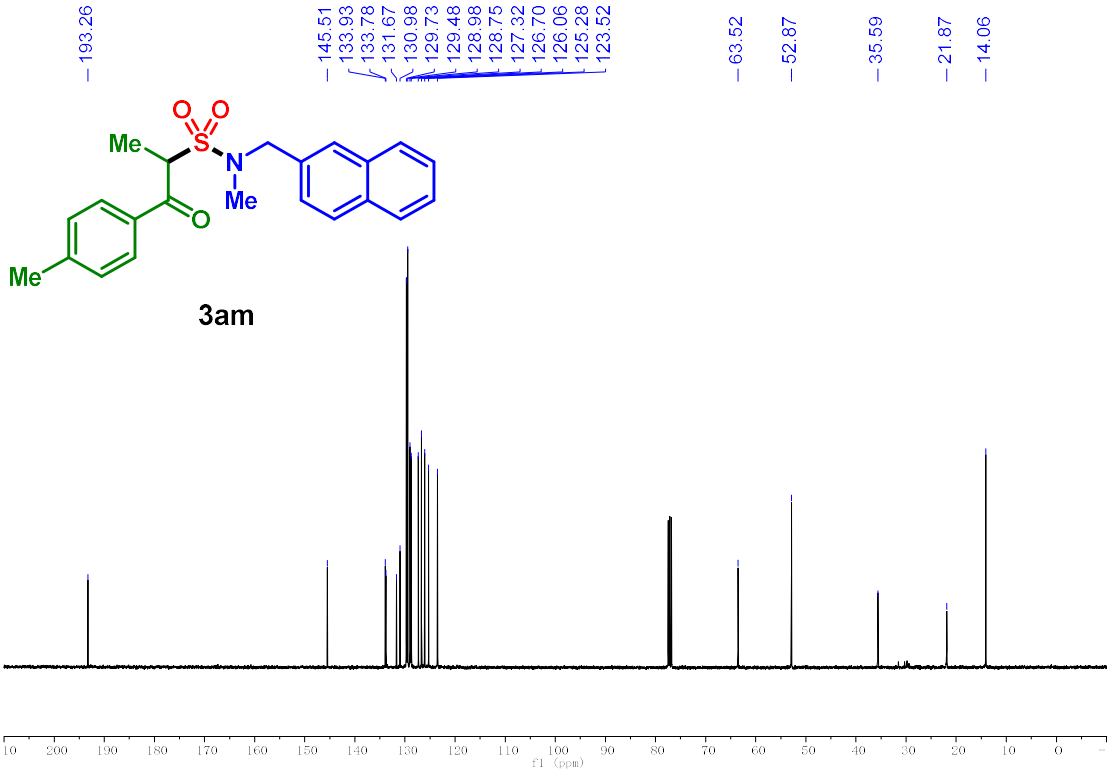


N-methyl-N-(naphthalen-2-ylmethyl)-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3am)

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

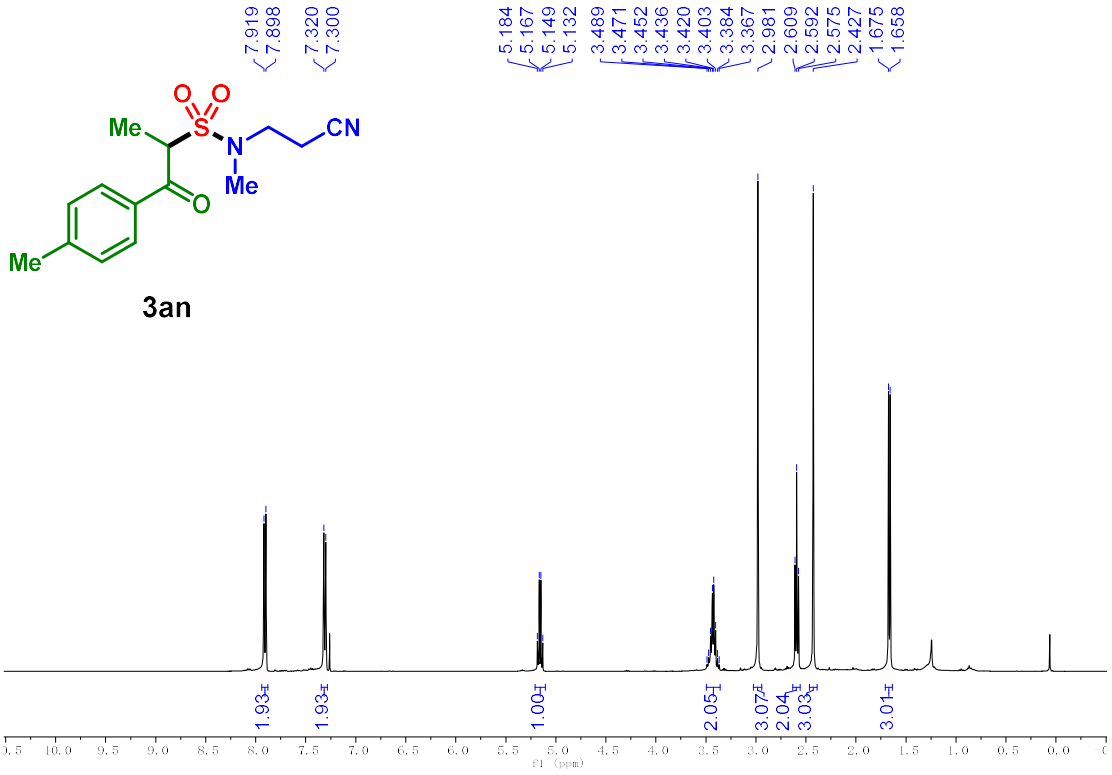


^{13}C NMR (100 MHz, $CDCl_3$)



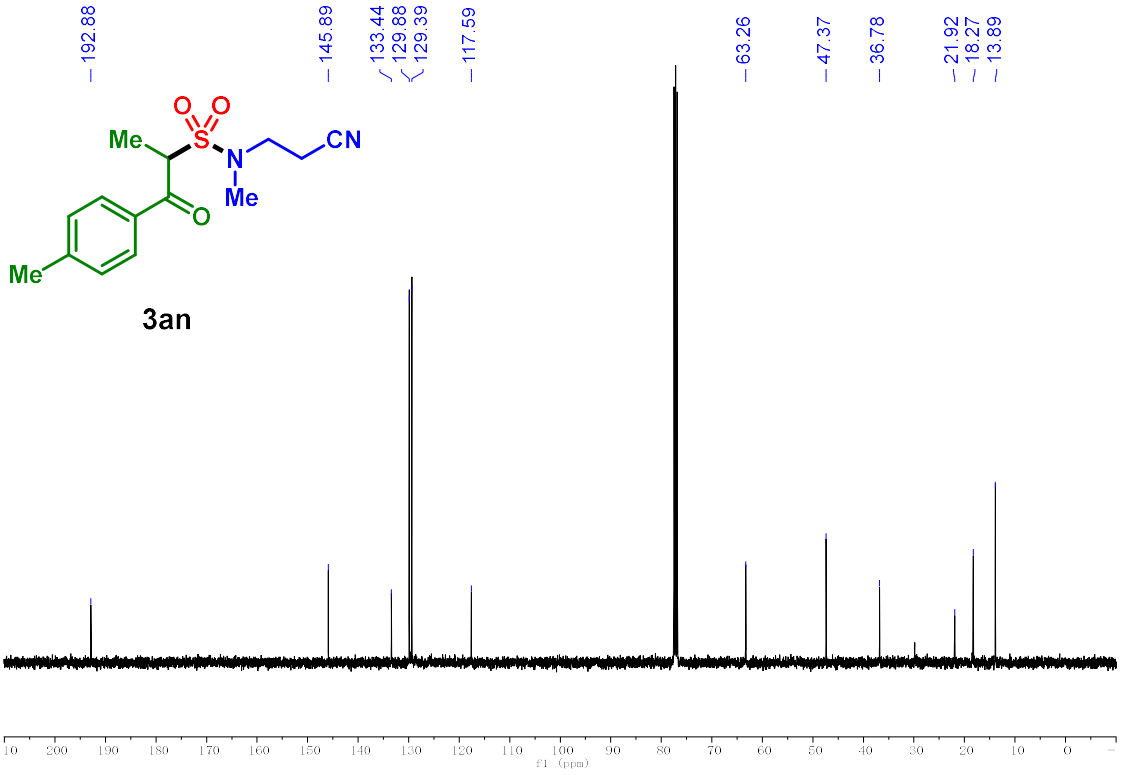
N-(2-cyanoethyl)-N-methyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3an)

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



3an

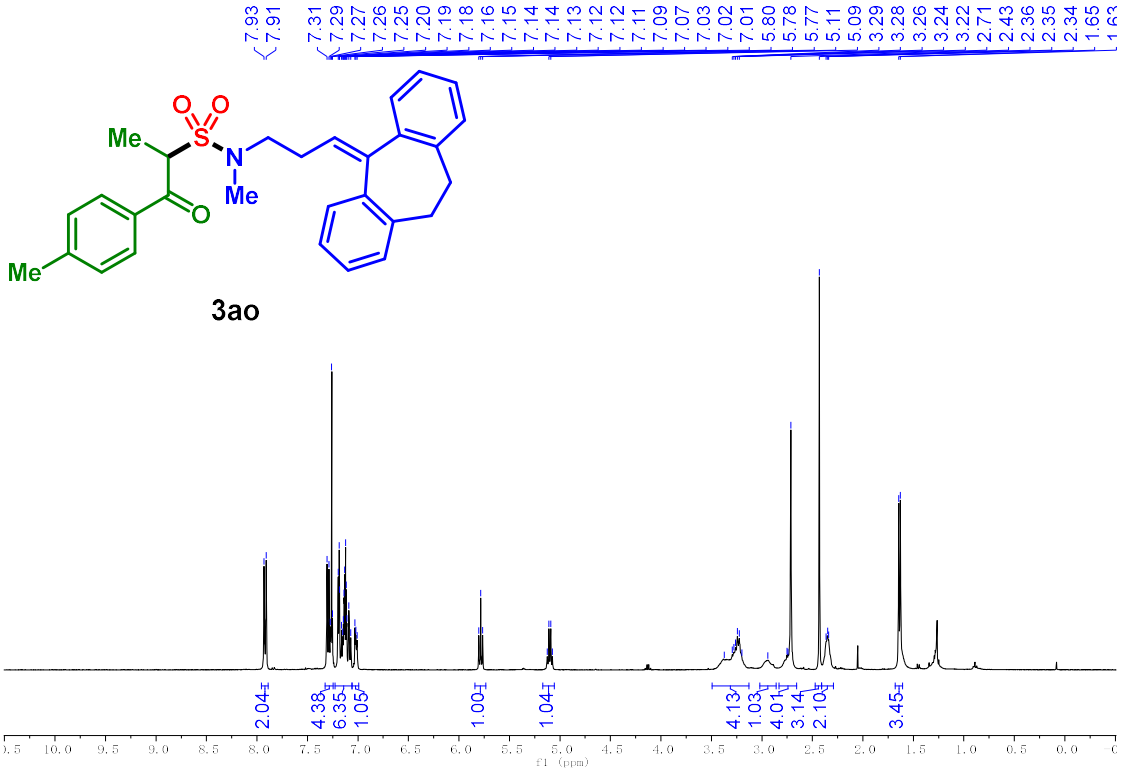
^{13}C NMR (100 MHz, $CDCl_3$)



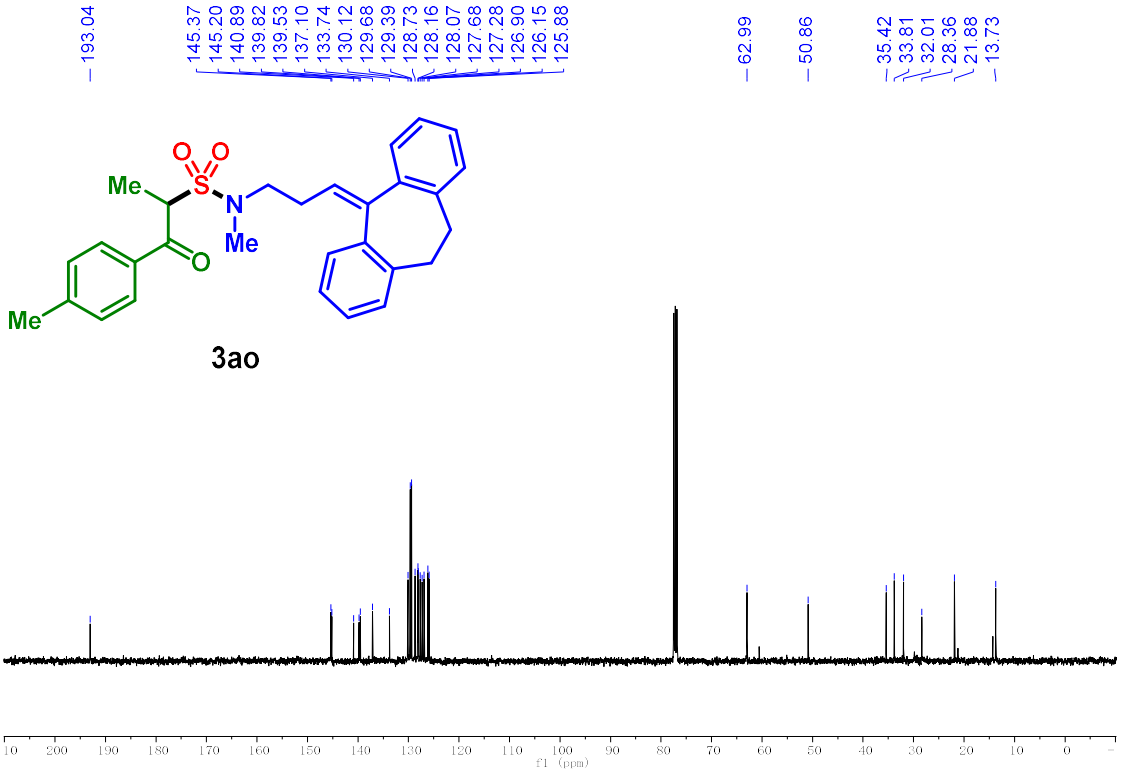
3an

N-(3-(10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)propyl)-N-methyl-1-oxo-1-(p-tolyl)propane-2-sulfonamide (3ao)

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

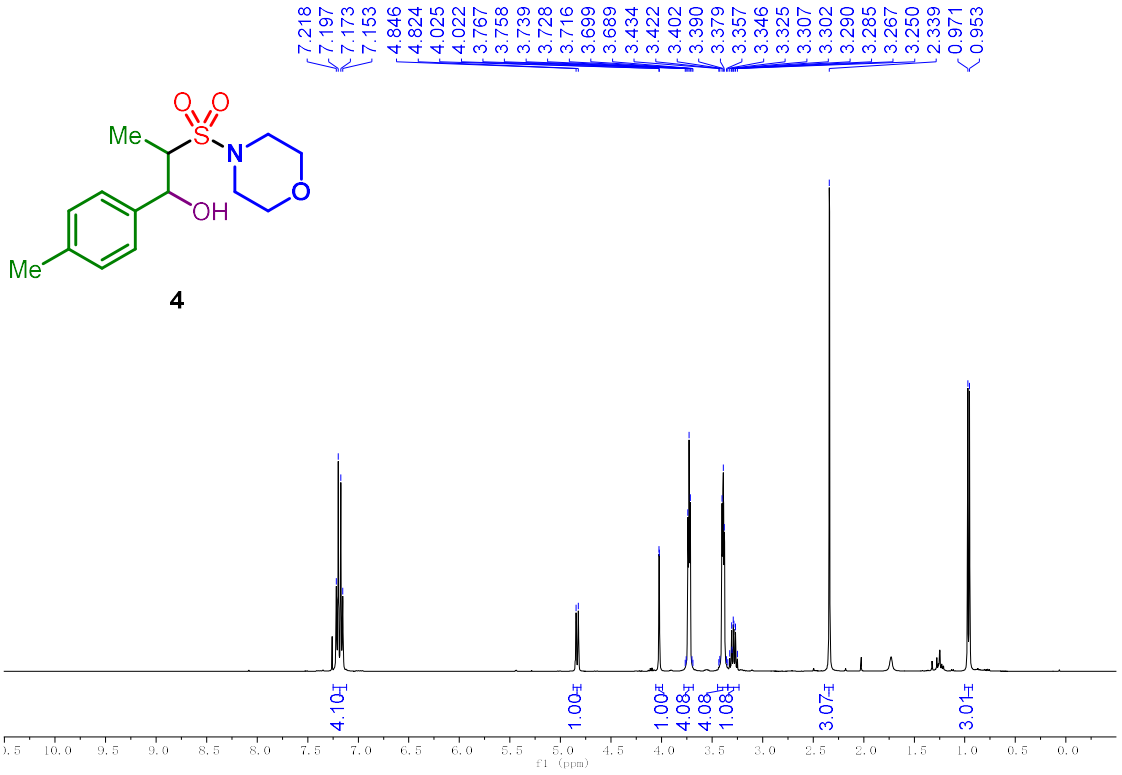


^{13}C NMR (100 MHz, $CDCl_3$)

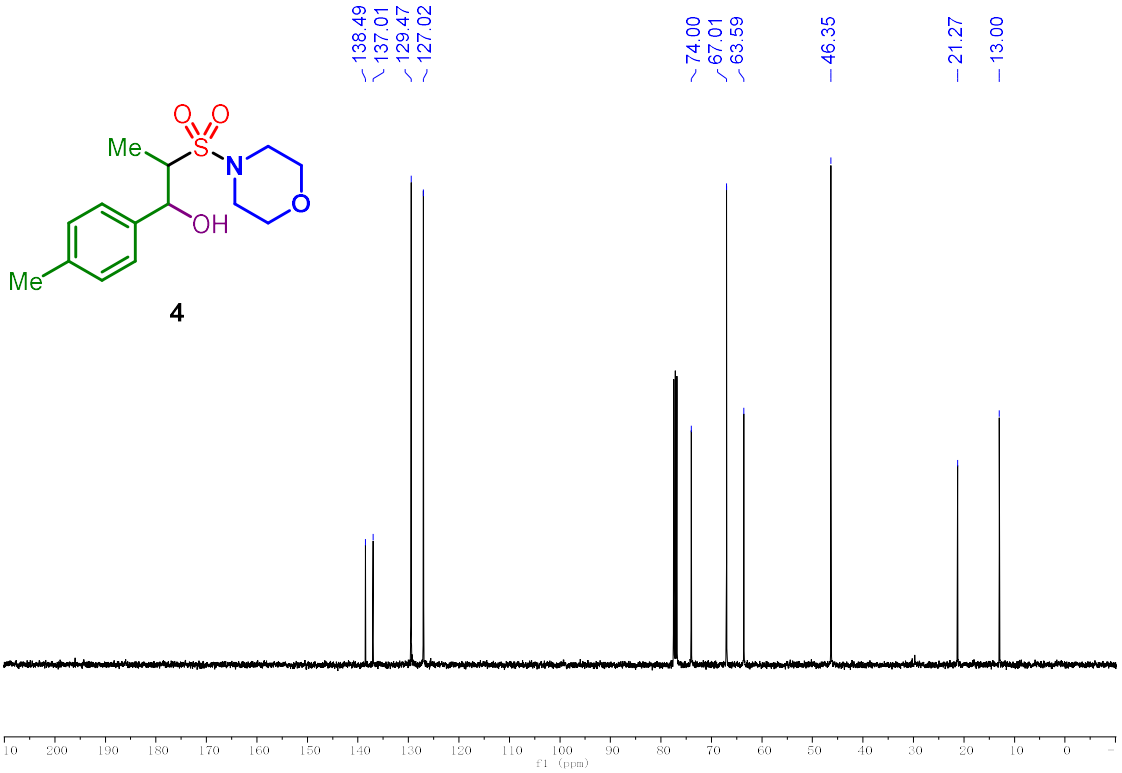


2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-ol (4)

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

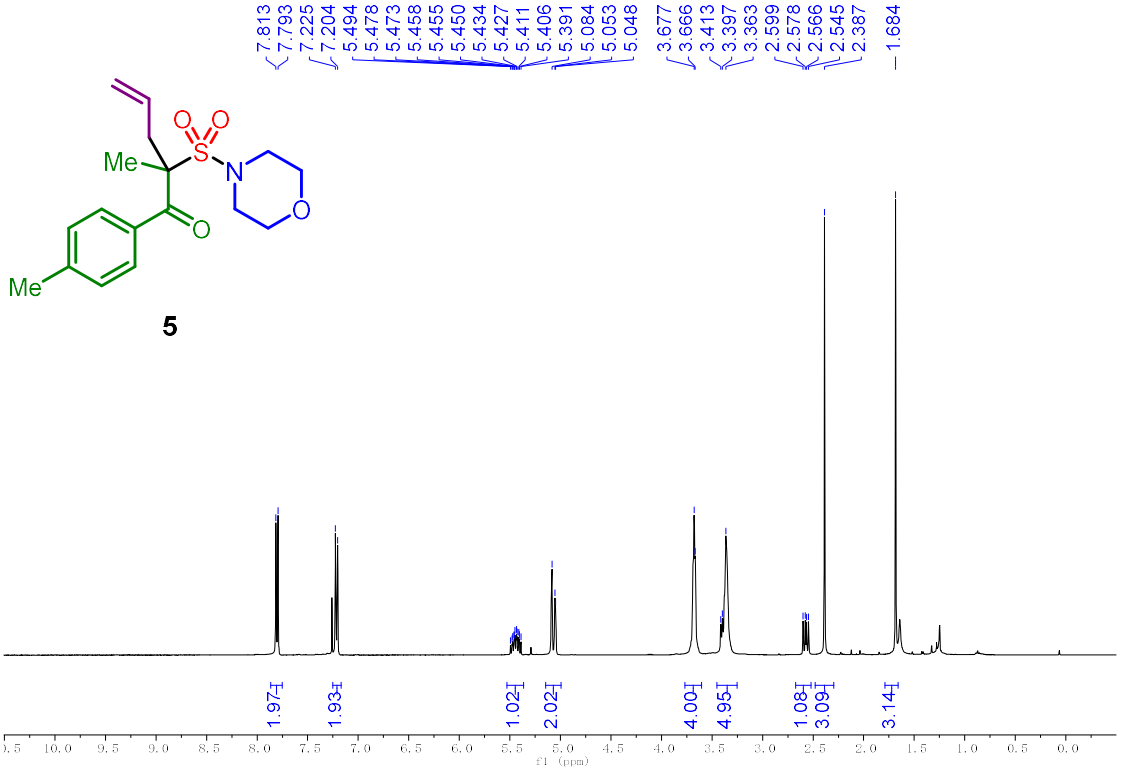


^{13}C NMR (100 MHz, $CDCl_3$)

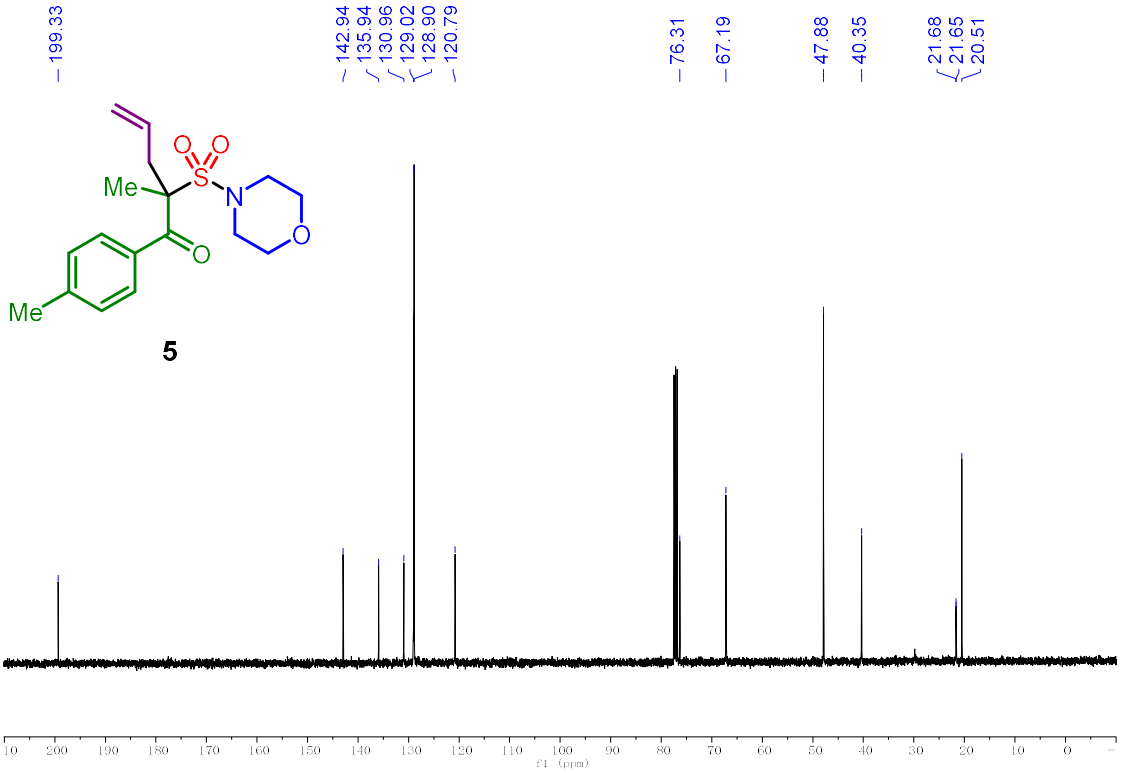


2-methyl-2-(morpholinosulfonyl)-1-(p-tolyl)pent-4-en-1-one (5)

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

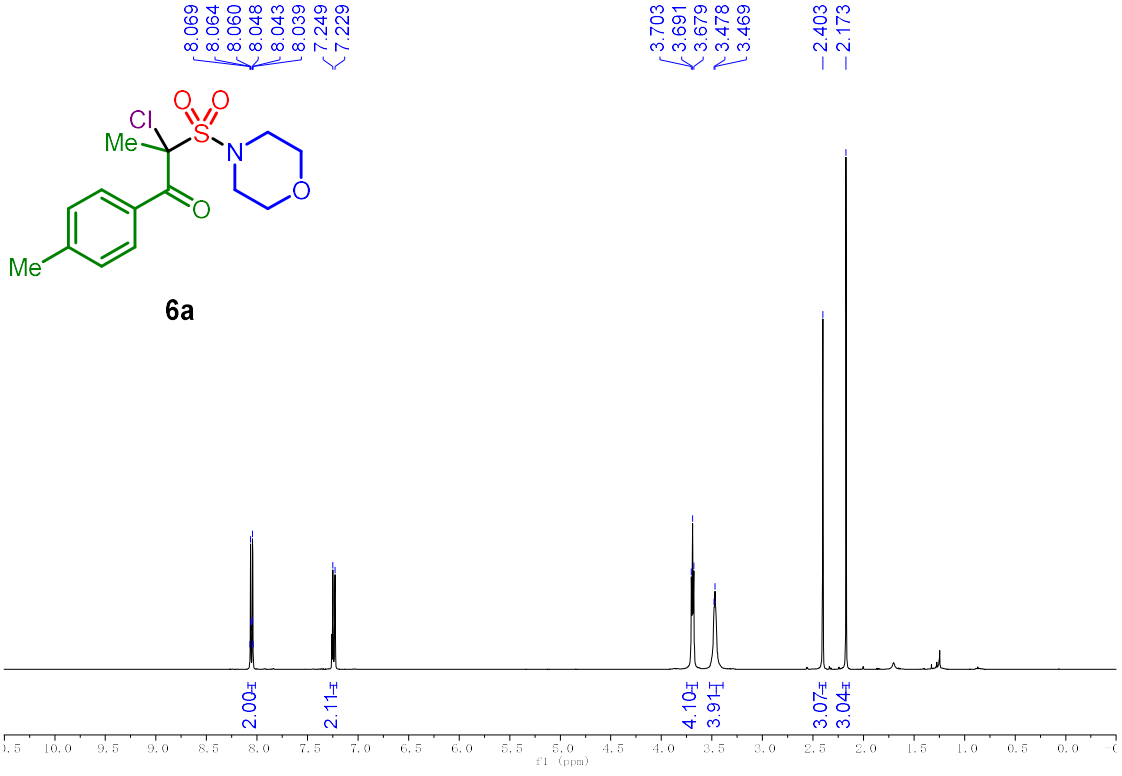


^{13}C NMR (100 MHz, $CDCl_3$)

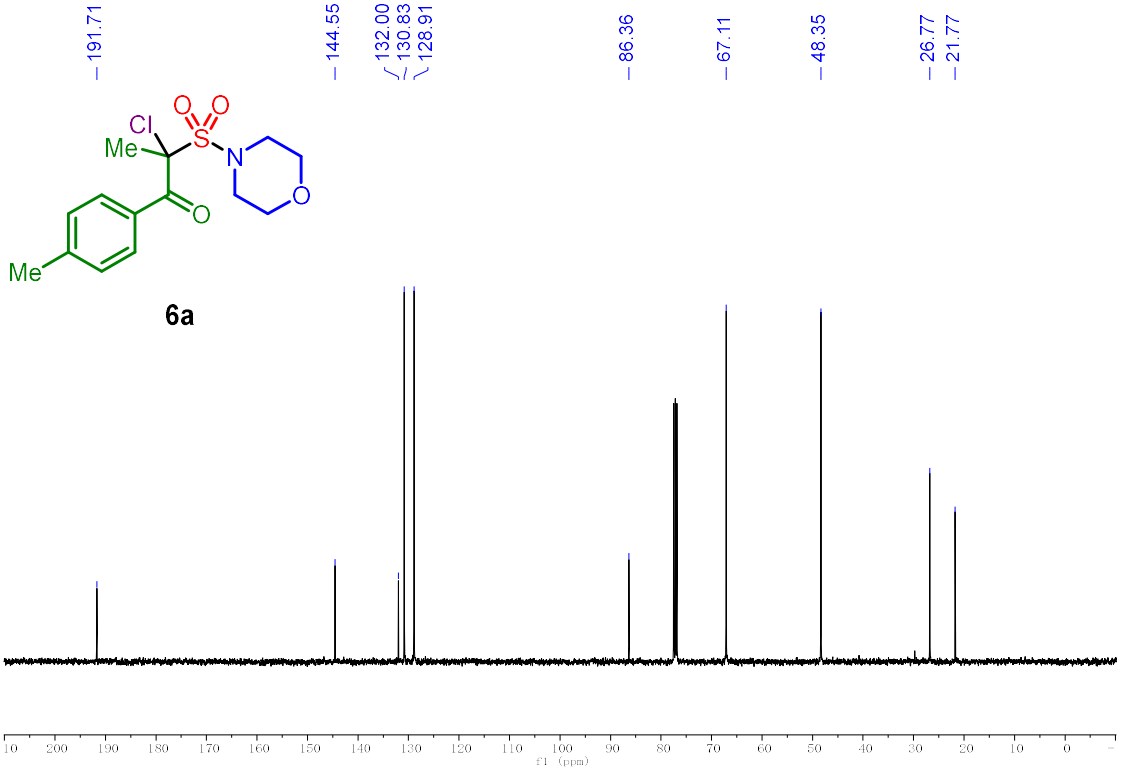


2-chloro-2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-one (6a)

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

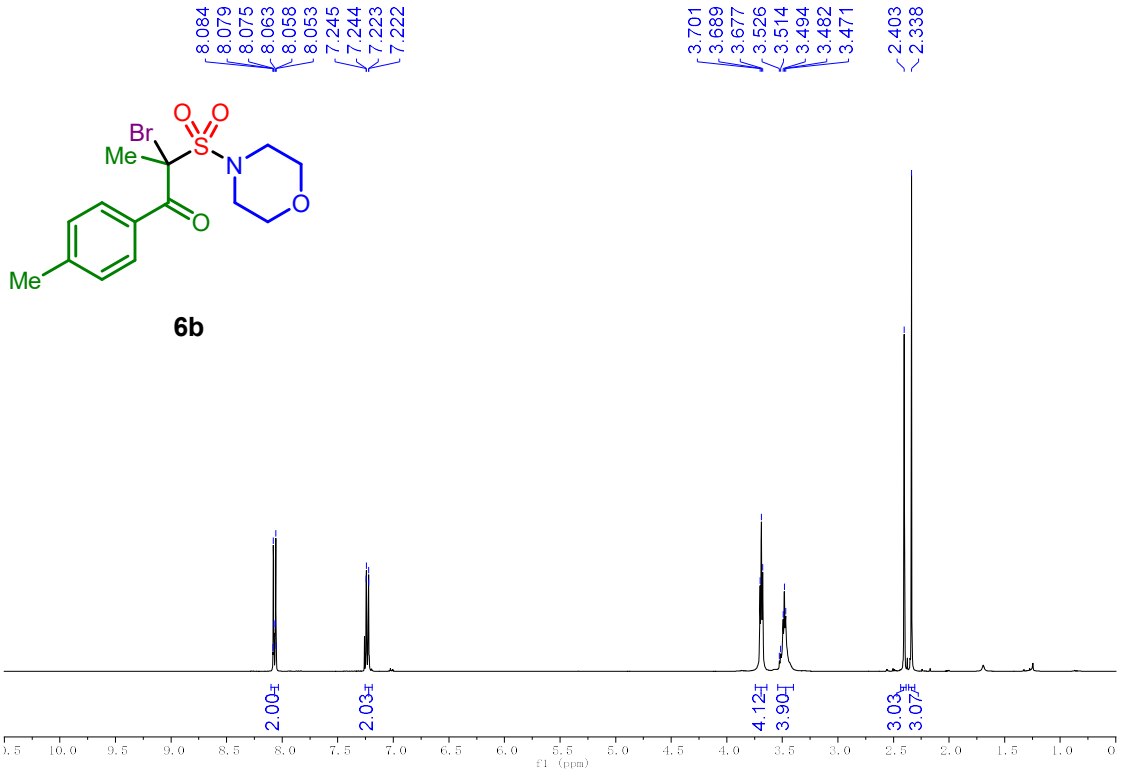


^{13}C NMR (100 MHz, $CDCl_3$)

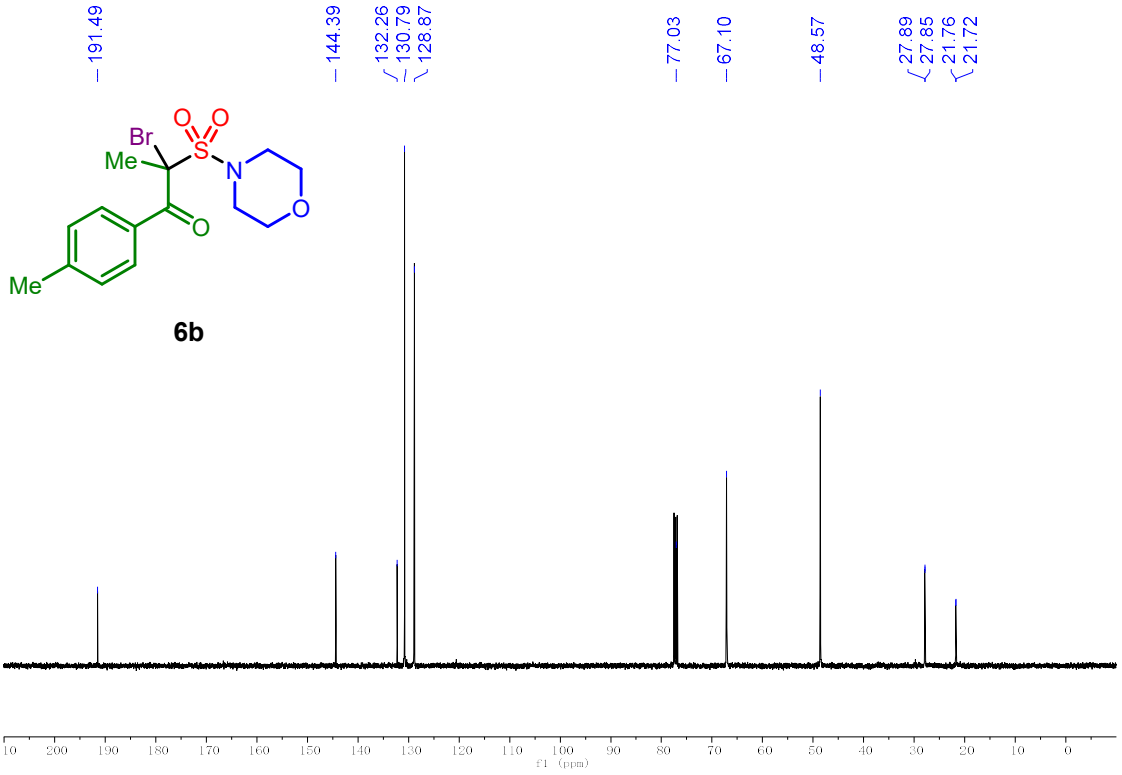


2-bromo-2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-one (6b)

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

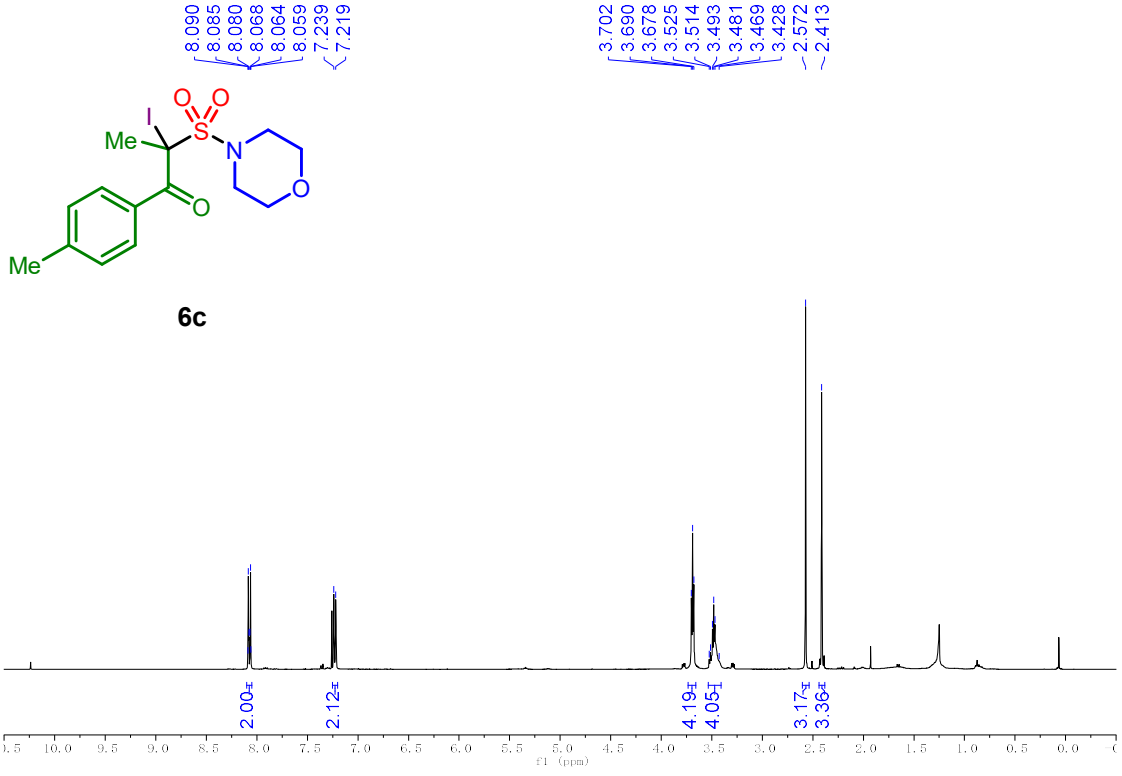


^{13}C NMR (100 MHz, $CDCl_3$)

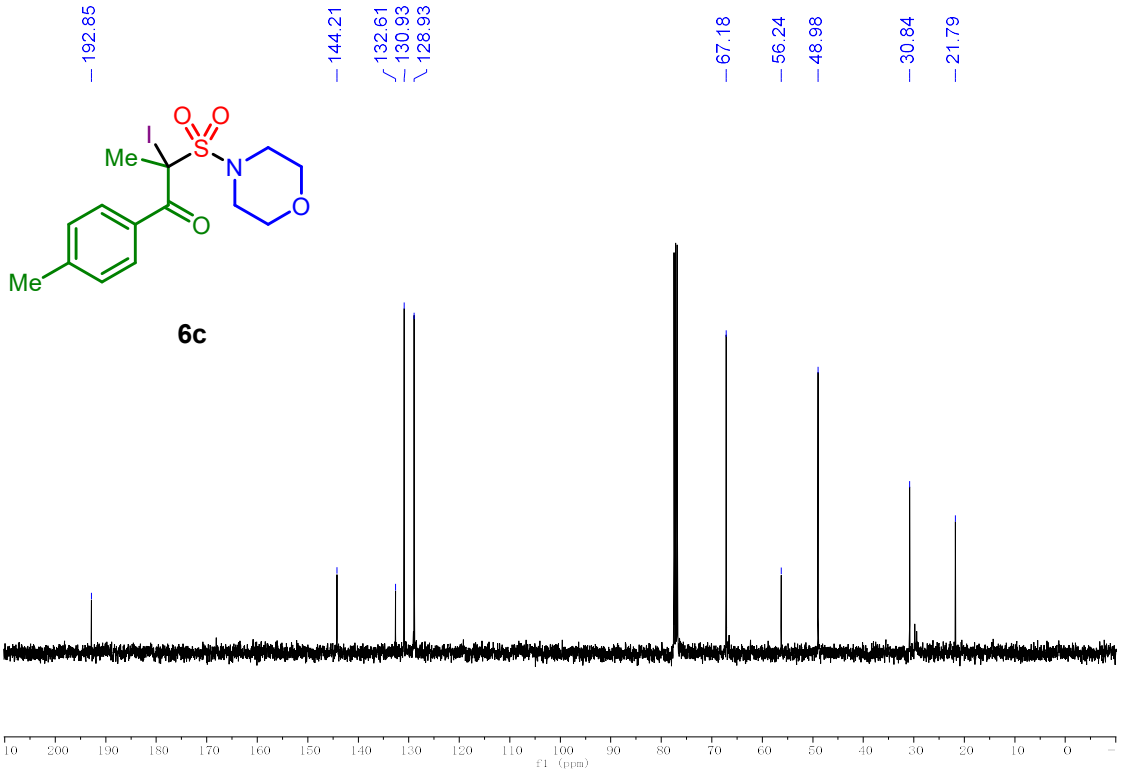


2-iodo-2-(morpholinosulfonyl)-1-(p-tolyl)propan-1-one (6c)

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

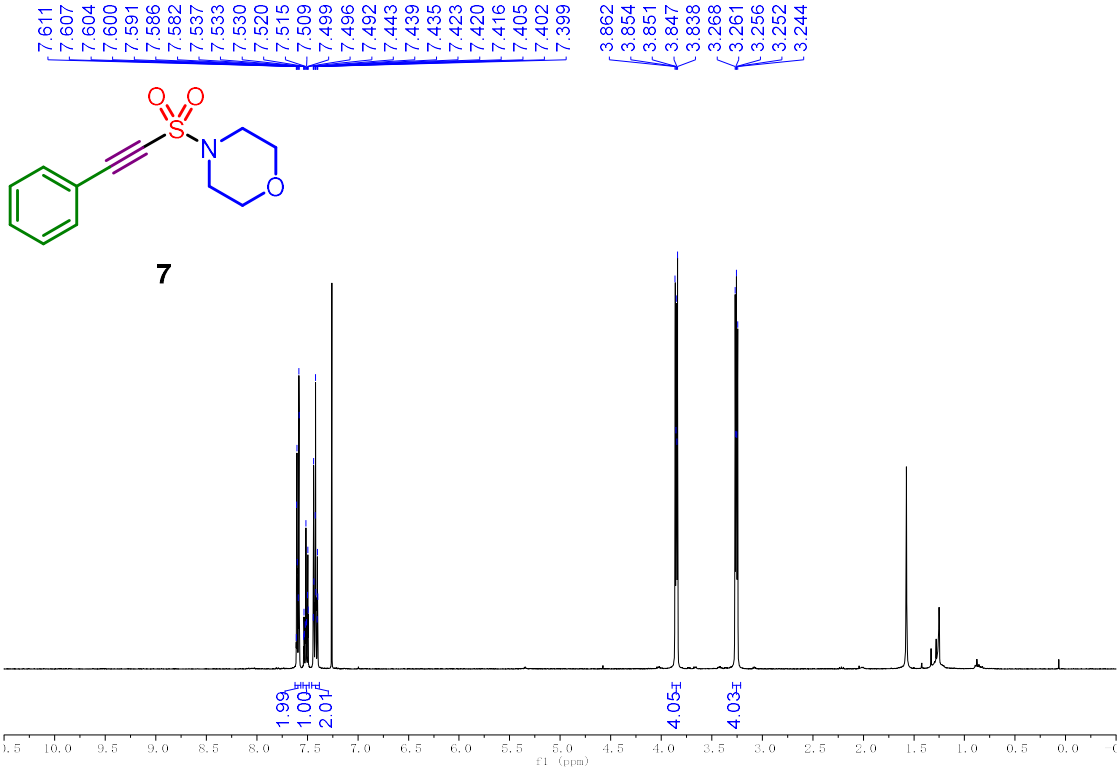


^{13}C NMR (100 MHz, $CDCl_3$)

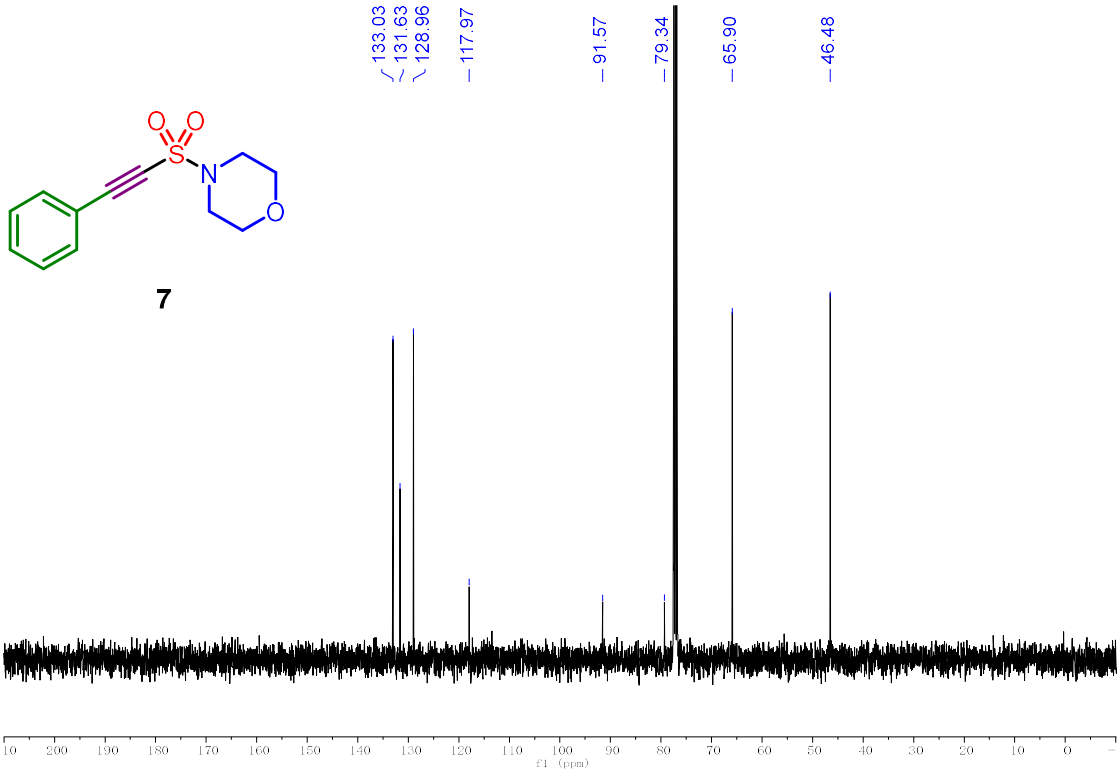


4-((phenylethynyl)sulfonyl)morpholine (7)

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

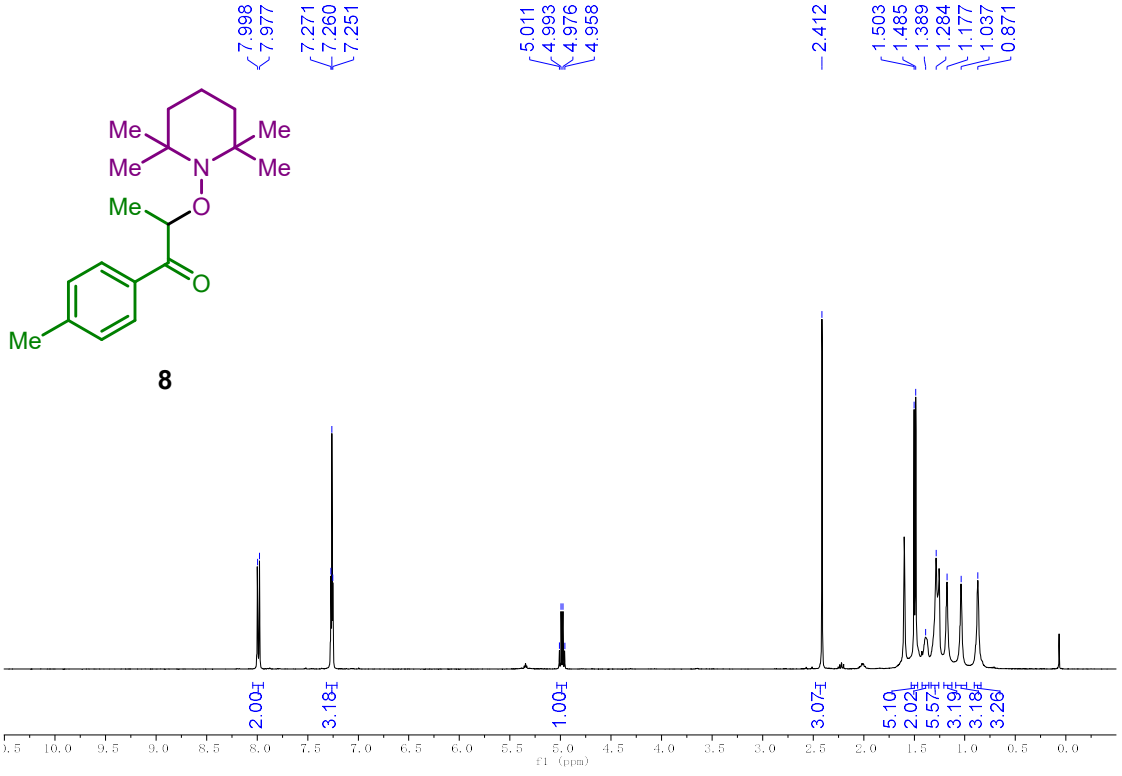


^{13}C NMR (100 MHz, $CDCl_3$)

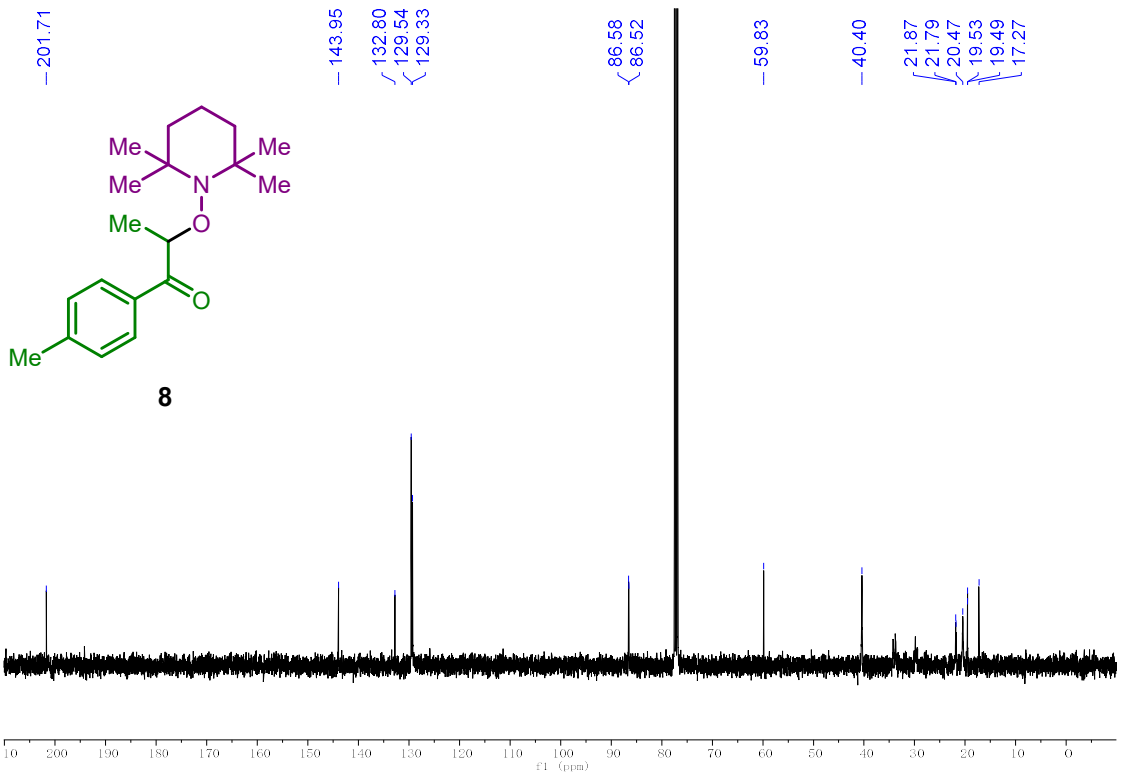


2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-1-(p-tolyl)propan-1-one (8)

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

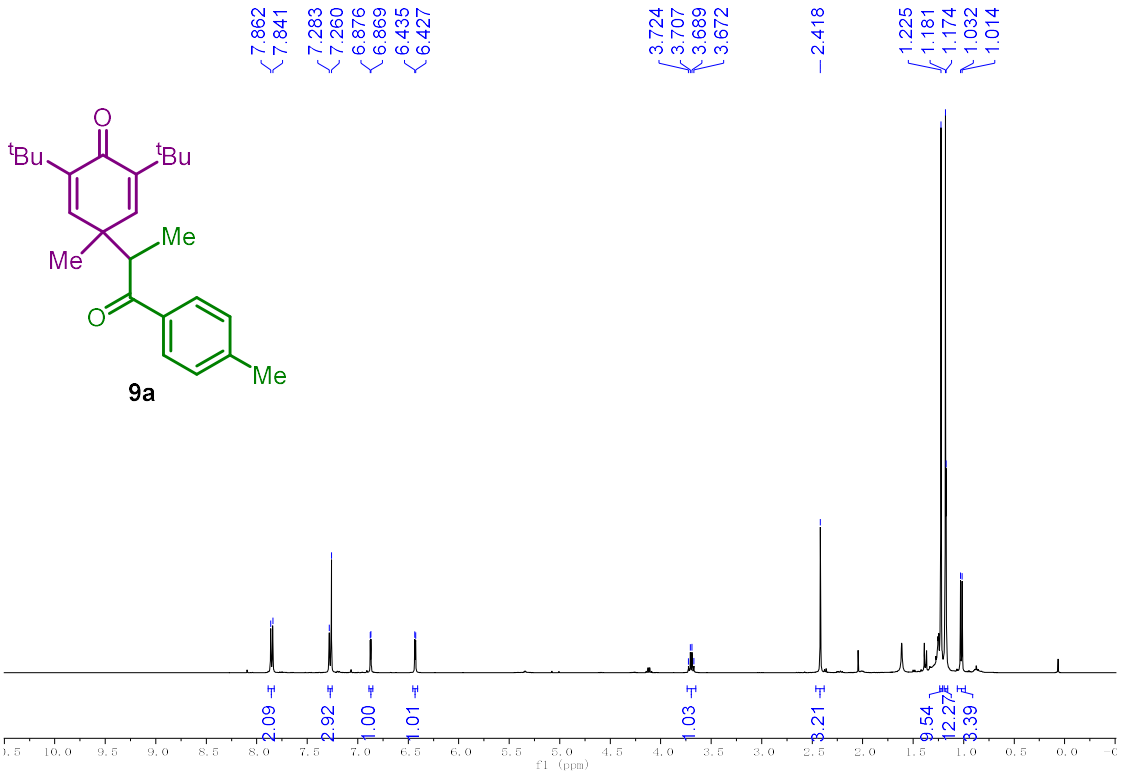


^{13}C NMR (100 MHz, $CDCl_3$)



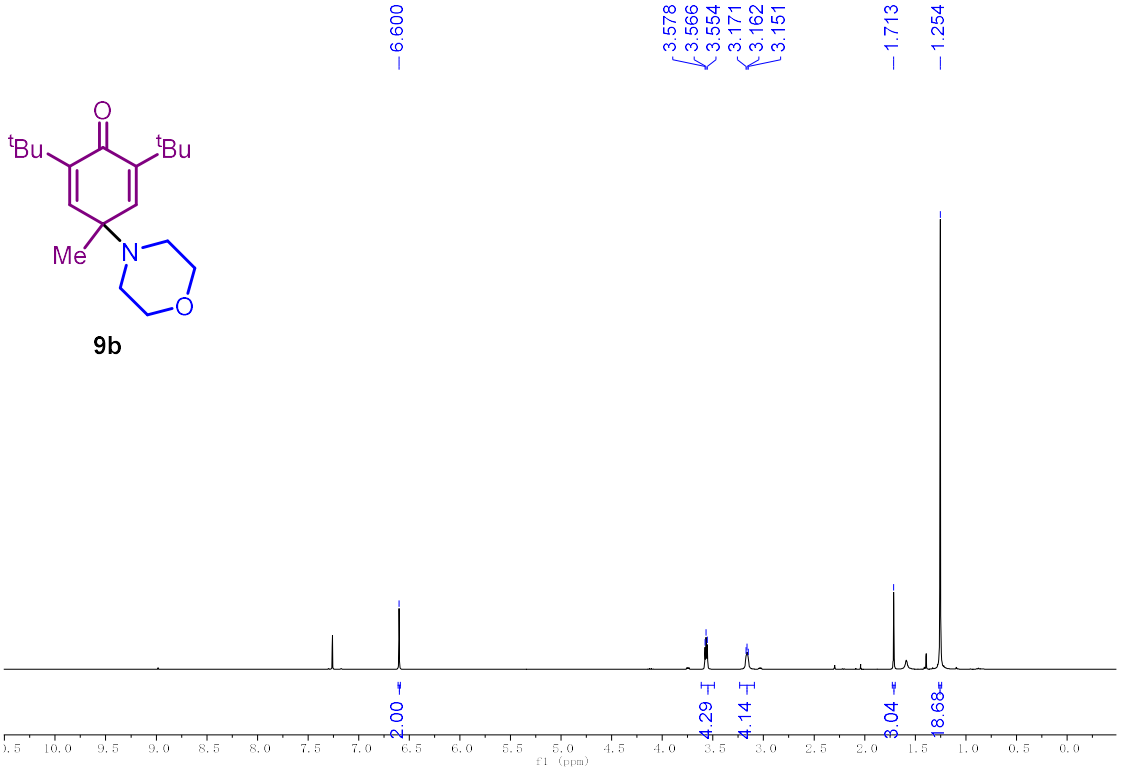
2,6-di-tert-butyl-4-methyl-4-(1-oxo-1-(p-tolyl)propan-2-yl)cyclohexa-2,5-dien-1-one (9a)

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



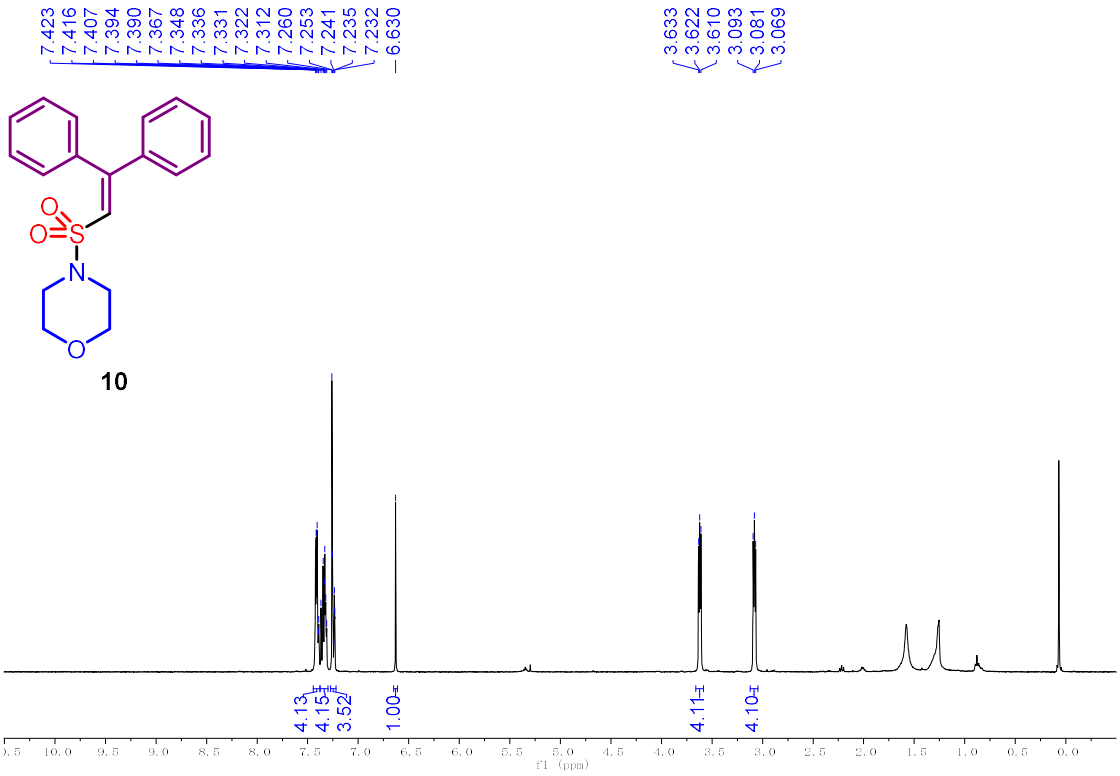
2,6-di-tert-butyl-4-methyl-4-morpholinocyclohexa-2,5-dien-1-one (9b)

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



4-((2,2-diphenylvinyl)sulfonyl)morpholine (10)

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



(Z)-5-((1-cyclopropyl-2-oxo-2-phenylethyl)sulfonyl)-1-phenylpent-2-en-1-one (11)

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