Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoredox- or metal-catalyzed three-component reaction of 1-(allyloxy)-2-(1-arylvinyl)benzenes, potassium metabisulfite, and cycloketone oxime esters: synthesis of cyanoalkylsulfonylated benzoxepines

Nengneng Zhou,* Sixin Wu, Kaimo Kuang, Ziqin Xia, Qiankun Xu, and Man Zhang

Key Laboratory of Functionalized Molecular Solids, Ministry of Education, Anhui Key Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, China.

E-mail: zhounn@ahnu.edu.cn

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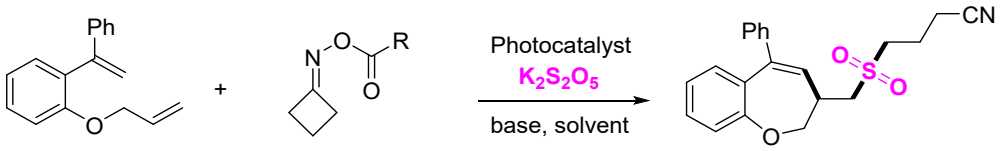
General Information:

All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts, solvents were obtained from commercial suppliers. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. High resolution mass spectra were obtained on a high–resolution mass spectrometer in the ESI or APCI mode. All substrates **1** and cycloketone oxime esters **2** were synthesized according to the literature.[1,2]

Detailed Optimization of Reaction Conditions

Table S1 Optimization of reaction conditions [a]



1a

2a, R = *p*-$CF_3C_6H_4$ **2a-2**, R = C_6F_5
2a-1, R = *p*-$NO_2C_6H_4$ **2a-3**, R = C_6H_5

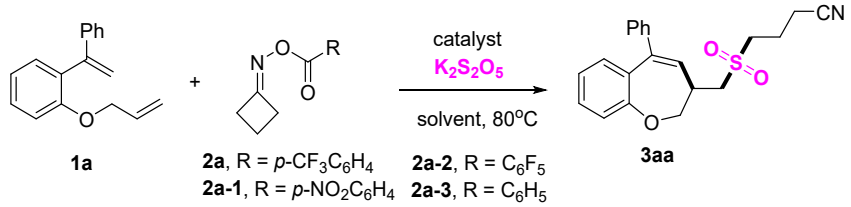
3aa

entry	photocatalyst	base	solvent	yield(%)[b]
1	*fac*-Ir(ppy)$_3$	-	MeCN	16
2	Ru(bpy)$_3$(PF$_6$)$_2$	-	MeCN	27
3	Eosin Y	-	MeCN	36
4[c]	Eosin Y	-	MeCN	34
5[d]	Eosin Y	-	MeCN	15
6	Eosin Y	Na_2HPO_4	MeCN	56
7	Eosin Y	Na_2CO_3	MeCN	24
8	Eosin Y	Et_3N	MeCN	5
9	Eosin Y	2,6-Lutidine	MeCN	82
10	Eosin Y	2,6-Lutidine	DCM	53
11	Eosin Y	2,6-Lutidine	THF	41
12	Eosin Y	2,6-Lutidine	DMF	12
13	Eosin Y	2,6-Lutidine	DMSO	15
14[e]	Eosin Y	2,6-Lutidine	MeCN	65
15[f]	Eosin Y	2,6-Lutidine	MeCN	74
16[g]	Eosin Y	2,6-Lutidine	MeCN	76
17[h]	Eosin Y	2,6-Lutidine	MeCN	68
18[i]	Eosin Y	2,6-Lutidine	MeCN	42
19	-	2,6-Lutidine	MeCN	0
20[j]	Eosin Y	2,6-Lutidine	MeCN	0

[a] Reaction condition: **1a** (0.1 mmol), **2a** (0.15 mmol), $K_2S_2O_5$ (0.2 mmol), base (0.3 mmol), photocatalyst (2 mol%), solvent (1 mL), 12 W blue LED under Ar at 80 °C for 12 h. [b] Isolated yield.

[c] $Na_2S_2O_5$. [d] DABSO. [e] 60 °C. [f] 100°C. [g] **2a-1**. [h] **2a-2**. [i] **2a-3**. [j] In the dark.

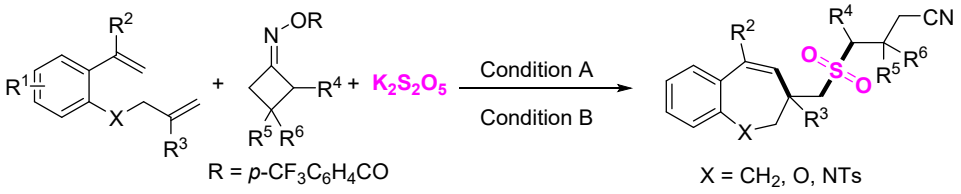
Table S2 Optimization of reaction conditions [a]



entry	catalyst	solvent	yield(%)[b]
1	CuCl	MeCN	48
2	$Cu(OAc)_2$	MeCN	10
3	$FeCl_2$	MeCN	77
4	$Fe(acac)_2$	MeCN	36
5	$FeCl_3$	MeCN	47
6	$NiCl_2$·glyme	MeCN	56
7[c]	$FeCl_2$	MeCN	55
8[d]	$FeCl_2$	MeCN	35
9	$FeCl_2$	DCM	58
10	$FeCl_2$	THF	23
11	$FeCl_2$	toluene	31
12	$FeCl_2$	DMF	0
13	$FeCl_2$	DMSO	0
14[e]	$FeCl_2$	MeCN	75
15[f]	$FeCl_2$	MeCN	57
16[g]	$FeCl_2$	MeCN	37
17[h]	$FeCl_2$	MeCN	62
18[i]	$FeCl_2$	MeCN	48

[a] Reaction condition: **1a** (0.1 mmol), **2a** (0.15 mmol), $K_2S_2O_5$ (0.2 mmol), catalyst (10 mol%), solvent (1 mL), at 80 °C for 36 h under Ar atmosphere. [b] Isolated yield. [c] $Na_2S_2O_5$. [d] DABSO. [e] **2a-1**. [f] **2a-2**. [g] **2a-3**. [h] 60 °C. [i]100°C.

General procedures for synthesis Cyanoalkylsulfonylated benzoxepines 3

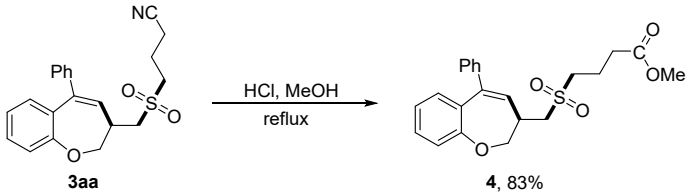


Condition A: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), cyclobutanone *O*-acyl oximes **2** (1.5 equiv, 0.15 mmol), 2,6-Lutidine (3.0 equiv, 0.3 mmol), Eosin Y (5 mol%), $K_2S_2O_5$ (2.0 equiv, 0.2 mmol). The flask was evacuated and backfilled with Ar

for 3 times. 1 mL MeCN was added with syringe under Ar. The tube was stirred exposing to 12 W blue LED light at 80 °C for 12 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 1:1, v/v) to afford the desired products **3**.

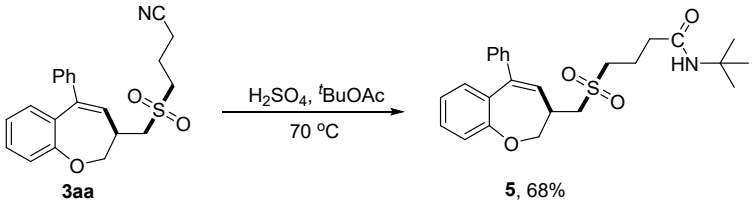
Condition B: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), cyclobutanone *O*-acyl oximes **2** (1.5 equiv, 0.15 mmol), $K_2S_2O_5$ (2.0 equiv, 0.2 mmol), $FeCl_2$ (10 mol%). The flask was evacuated and backfilled with Ar for 3 times. 1 mL MeCN was added with syringe under Ar. The tube was then sealed and the mixture was stirred at 80 °C for 36 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 1:1, v/v) to afford the desired products **3**.

Derivatization



3aa **4**, 83%

To a Schlenk tube were added **3aa** (73.4 mg, 0.2 mmol), 2 mL conc. HCl and 2 mL MeOH. Then the mixture was heated at 70 °C and stirred overnight under reflux. After cooling to room tempertrue, the reaction mixture was quenched with 10 mL H_2O, and extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by flash chromatography (petroleum ether/ethylacetate 1:1) to afford the desired product **4** in 83 % yield (66.4 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.31 (m, 3H), 7.25-7.20 (m, 3H), 7.12-7.10 (m, 1H), 7.00-6.93 (m, 2H), 6.07 (d, *J* = 5.6 Hz, 1H), 4.54 (dd, *J* = 11.2 Hz, *J* = 6.4 Hz, 1H), 4.36 (dd, *J* = 11.2 Hz, *J* = 4.0 Hz, 1H), 3.68 (s, 3H), 3.46-3.39 (m, 1H), 3.27-3.16 (m, 2H), 3.13-3.09 (m, 2H), 2.54 (t, *J* = 6.8 Hz, 2H), 2.21-2.13 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.5, 158.7, 142.9, 141.8, 132.0, 130.2, 130.0, 129.0, 128.9, 128.2, 127.4, 123.3, 121.2, 76.9, 54.2, 53.1, 51.9, 36.1, 31.9, 17.6 ppm. APCI-HRMS: m/z Calcd for $C_{22}H_{24}O_5S+H^+$: 401.1417, found 401.1411.

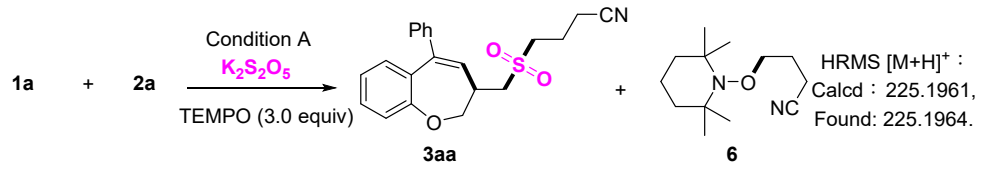


3aa **5**, 68%

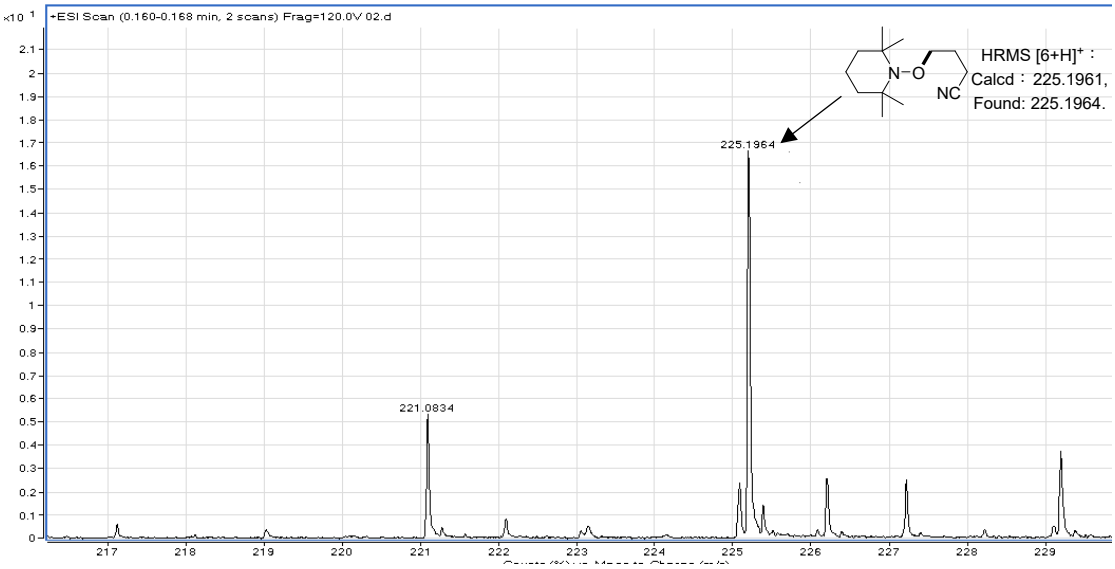
To a 10 mL Schlenk were sequentially added **3aa** (73.4 mg, 0.2 mmol, 1.0 equiv.), tert-butyl acetate (2 mL) and conc. H_2SO_4 (4 drops). The reaction mixture was stirred at 70 °C overnight. After cooling to room temperature, the reaction mixture was quenched with $NaHCO_3$ aq. and extracted with DCM (15 mL × 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel chromatography (petroleum ether/ethylacetate 1:1) to afford the desired product **5** in 68% yield (60.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.31 (m, 3H), 7.26-7.20 (m, 3H),

7.12-7.10 (m, 1H), 7.00-6.93 (m, 2H), 6.08 (d, J = 5.6 Hz, 1H), 4.53 (dd, J = 11.2 Hz, J = 6.4 Hz, 1H), 4.37 (dd, J = 11.2 Hz, J = 4.0 Hz, 1H), 3.44-3.37 (m, 1H), 3.26-3.16 (m, 2H), 3.11 (t, J = 7.2 Hz, 2H), 2.32 (t, J = 6.8 Hz, 2H), 2.20-2.12 (m, 2H), 1.33 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 158.6, 142.8, 141.1, 132.0, 130.2, 130.2, 129.0, 128.9, 128.2, 127.4, 123.3, 121.2, 77.2, 54.2, 53.0, 51.4, 36.0, 34.7, 28.7, 18.4 ppm. APCI-HRMS: m/z Calcd for $C_{25}H_{31}NO_4S$+H^+: 442.2047, found 442.2050.

Trapping experiment with TEMPO



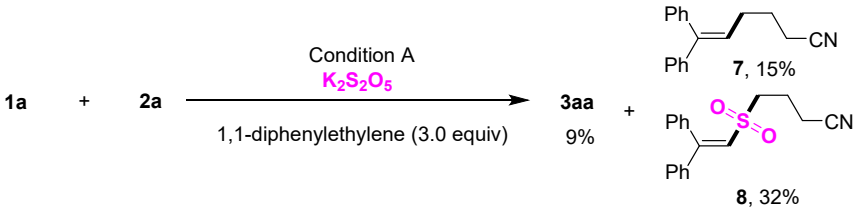
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), cyclobutanone *O*-acyl oximes **2** (1.5 equiv, 0.15 mmol), 2,6-Lutidine (3.0 equiv, 0.3 mmol), Eosin Y (5 mol%), $K_2S_2O_5$ (2.0 equiv, 0. 2 mmol), TEMPO (3.0 equiv). The flask was evacuated and backfilled with Ar for 3 times. 1 mL MeCN was added with syringe under Ar. The tube was stirred exposing to 12 W blue LED light at room temperature. However, product **3aa** could not be detected, the intermediate **6** was formed, suggesting that this transformation proceeds through a radical pathway.



Trapping experiment with BHT

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), cyclobutanone *O*-acyl oximes **2** (1.5 equiv, 0.15 mmol), 2,6-Lutidine (3.0 equiv, 0.3 mmol), Eosin Y (5 mol%), $K_2S_2O_5$ (2.0 equiv, 0. 2 mmol), BHT (3.0 equiv). The flask was evacuated and backfilled with Ar for 3 times. 1 mL MeCN was added with syringe under Ar. The tube was stirred exposing to 12 W blue LED light at room temperature. However, product **3aa** could not be detected.

Trapping experiment with 1,1-diphenylethene



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a** (0.2 mmol), cyclobutanone *O*-acyl oxime **2a** (1.5 equiv, 0.3 mmol), 2,6-Lutidine (3.0 equiv, 0.6 mmol), Eosin Y (5 mol%), $K_2S_2O_5$ (2.0 equiv, 0. 4 mmol), 1,1-diphenylethene (3.0 equiv). The flask was evacuated and backfilled with Ar for 3 times. 2 mL MeCN was added with syringe under Ar. The tube was stirred exposing to 12 W blue LED light at room temperature. After the reaction finished, the residue was concentrated in vacuo, then purified by column chromatography to afford **7** (7.4 mg, 15%) and **8** (19.9 mg, 32%). *6,6-diphenylhex-5-enenitrile (7).* Yellow oil; (7.4 mg, 15%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.36 (m, 2H), , 7.33 (d, *J* = 6.8 Hz, 1H), 7.27-7.20 (m, 5H), 7.17-7.14 (m, 2H), 6.01 (t, *J* = 7.2 Hz, 2H), 2.32-2.23 (m, 4H), 1.83-1.76 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 142.1, 139.6, 129.6, 128.3, 128.1, 127.2, 127.2, 127.1, 126.6, 119.5, 28.7, 25.7, 16.6 ppm. 4-((2,2-diphenylvinyl)sulfonyl)butanenitrile (***8***). Yellow oil; (19.9 mg, 32%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.42 (m, 4H), 7.39-7.36 (m, 4H), 7.29-7.27 (m, 2H), 6.79 (s, 1H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.12-2.05 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.7, 138.7, 135.3, 130.7, 129.7, 129.6, 128.7, 128.324, 128.304, 125.6, 118.1, 52.7, 18.7, 16.1 ppm.

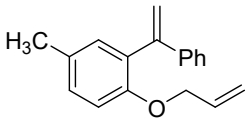
Reference:

[1] a) A.-R. Li, H.-M. Chen, P.-Y. Chen, J.-C. Tsai, L.-Y. Chen, E.-C. Wang, Y.-T. Huang, Y.-C. Wei, P.-J. Lu, *J. Chin. Chem. Soc*, **2008**, *55*, 923-932; b) K.-S. Huang, S.-R. Li, Y.-F. Wang, Y.-L. Lin, Y.-H. Chen, T.-W. Tsai, C.-H. Yang, E.-C. Wang, *J. Chin. Chem. Soc,* **2005**, *52*, 159-167.

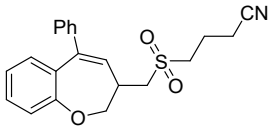
[2] (a) T. Nishimura, Y. Nishiguchi, Y. Maeda, S. Uemura, *J. Org. Chem.* 2004, **69**, 5342. (b) Y.-R. Gu, X.-H. Duan, L. Yang, L.-N. Guo, *Org. Lett.* 2017, **19**, 5908.

B. Zhao, H. Tan, C. Chen, N. Jiao, N. and Z. Shi, *Chin. J. Chem.* 2018, **36**, 995.

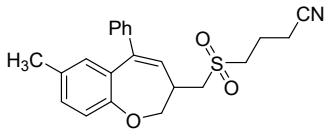
Characterization data of compounds



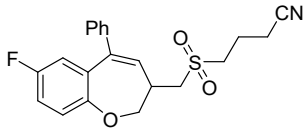
*1-(allyloxy)-4-methyl-2-(1-phenylvinyl)benzene (**1b**).* Yellow solid; mp: 40-41°C; R_f = 0.46 (petroleum ether/ethyl acetate 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.23 (m, 5H), 7.10-7.08 (m, 2H), 6.79-6.77 (m, 1H), 5.66 (d, *J* = 1.6 Hz, 2H), 5.64-5.56 (m, 1H), 5.71-5.62 (m, 2H), 5.32 (d, *J* = 1.6 Hz, 1H), 5.01-4.97 (m, 2H), 4.31-4.29 (m, 2H), 2.31 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9, 147.4, 141.5, 133.2, 131.9, 131.4, 130.1, 129.2, 127.9, 127.2, 126.5, 116.4, 115.4, 113.0, 69.3, 20.5 ppm. ESI-HRMS: m/z Calcd for $C_{18}H_{18}O+H^+$: 251.1430, found 251.1438.



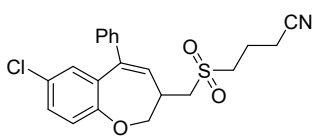
4-(((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3aa)***. Yellow solid; (*hv*: 30.1 mg, 82%; *iron*: 28.3 mg, 77%); mp: 50-51 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.33 (m, 3H), 7.25-7.21 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.00-6.94 (m, 2H), 6.05 (d, *J* = 5.6 Hz, 1H), 4.45 (dd, *J* = 11.2 Hz, *J* = 6.4 Hz, 1H), 4.33 (dd, *J* = 11.2 Hz, *J* = 4.0 Hz, 1H), 3.44-3.39 (m, 1H), 3.30-3.20 (m, 2H), 3.16 (t, *J* = 7.6 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.28-2.20 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 142.8, 141.4, 132.1, 129.8, 129.7, 129.1, 128.9, 127.5, 123.3, 121.1, 118.0, 76.4, 55.1, 52.1, 36.3, 18.2, 16.4 ppm. APCI-HRMS: m/z Calcd for $C_{21}H_{21}NO_3S+H^+$: 368.1315, found 368.1307.



4-(((7-methyl-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3ba)***. White solid; (*hv*: 30.9 mg, 81%; *iron*: 28.2 mg, 74%); mp: 61-62 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.32 (m, 3H), 7.26-7.24 (m, 2H), 7.05-7.00 (m, 2H), 6.74 (d, *J* = 2.0 Hz, 1H), 6.05 (d, *J* = 5.6 Hz, 1H), 4.49 (dd, *J* = 11.2 Hz, *J* = 6.8 Hz, 1H), 4.33 (dd, *J* = 11.2 Hz, *J* = 4.0 Hz, 1H), 3.42-3.34 (m, 1H), 3.23-3.21 (m, 2H), 3.15 (t, *J* = 7.2 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.28-2.21 (m, 2H), 2.16 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.3, 142.6, 141.6, 132.9, 132.1, 129.9, 129.8, 129.5, 128.7, 128.2, 127.5, 121.0, 118.0, 77.4, 55.0, 52.0, 35.8, 20.7, 18.1, 16.3 ppm. APCI-HRMS: m/z Calcd for $C_{22}H_{23}NO_3S+H^+$: 382.1471, found 382.1468.

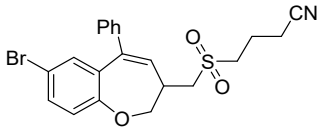


4-(((7-fluoro-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3ca)***. White solid; (*hv*: 30.3 mg, 78%; *iron*: 24.3 mg, 63%); mp: 63-64 °C; R_f = 0.45 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.33 (m, 3H), 7.25-7.23 (m, 2H), 7.09-7.05 (m, 1H), 6.95-6.90 (m, 1H), 6.66-6.63 (m, 1H), 6.11 (d, *J* = 5.6 Hz, 1H), 4.52 (dd, *J* = 11.6 Hz, *J* = 6.4 Hz, 1H), 4.32 (dd, *J* = 11.6 Hz, *J* = 4.0 Hz, 1H), 3.45-3.38 (m, 1H), 3.29-3.20 (m, 2H), 3.19-3.16 (m, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.30-2.23 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.4 (d, *J* = 241.9 Hz), 154.6, 142.0, 140.6 (d, *J* = 1.9 Hz), 131.5 (d, *J* = 7.8 Hz), 130.8, 130.5, 128.6 (d, *J* = 31.0 Hz), 127.8, 122.3 (d, *J* = 8.5 Hz), 118.0, 117.8, 115.7 (d, *J* = 23.1 Hz), 76.9, 54.9, 52.1, 36.0, 18.1, 16.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -119.3 ppm. APCI-HRMS: m/z Calcd for $C_{21}H_{20}FNO_3S+H^+$: 386.1221, found 386.1216.

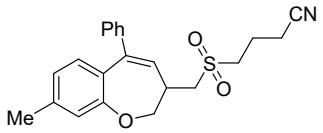


4-(((7-chloro-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3da)***. White solid; (*hv*: 29.3 mg, 73%; *iron*: 23.3 mg, 58%); mp: 61-62 °C; R_f = 0.45 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.33 (m, 3H), 7.24-7.17 (m, 3H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 2.8 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 4.55 (dd, *J* = 11.6 Hz, *J* = 6.4 Hz, 1H), 4.32 (dd, *J* = 11.6 Hz, *J* = 4.0 Hz, 1H), 3.46-3.38 (m, 1H), 3.30-3.22 (m, 2H), 3.18 (t, *J* = 7.2

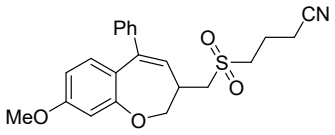
Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.30-2.23 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.2, 142.0, 140.5, 131.5, 131.4, 131.0, 128.9, 128.7, 128.6, 128.5, 127.8, 122.6, 118.0, 76.8, 54.9, 52.1, 36.0, 18.2, 16.4. ppm. APCI-HRMS: m/z Calcd for $C_{21}H_{20}ClNO_3S+H^+$: 402.0925, found 402.0922.



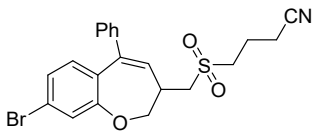
*4-(((7-bromo-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3ea**).* White solid; (*hv*: 32.5 mg, 73%; *iron*: 33.4 mg, 75%); mp: 61-62 °C; R_f = 0.45 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.31 (m, 4H), 7.24-7.22 (m, 2H), 7.06 (d, *J* = 2.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 4.54 (dd, *J* = 11.2 Hz, *J* = 6.4 Hz, 1H), 4.31 (dd, *J* = 11.2 Hz, *J* = 4.0 Hz, 1H), 3.45-3.37 (m, 1H), 3.28-3.21 (m, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.29-2.22 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.7, 142.0, 140.5, 134.4, 132.0, 131.9, 131.1, 128.7, 128.5, 127.9, 123.0, 118.0, 116.2, 76.9, 54.9, 52.1, 36.0, 18.2, 16.4. ppm. APCI-HRMS: m/z Calcd for $C_{21}H_{20}BrNO_3S+H^+$: 446.0420, found 446.0417.



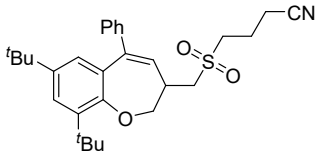
*4-(((8-methyl-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3fa**).* White solid; (*hv*: 30.1 mg, 79%; *iron*: 28.5 mg, 75%); mp: 55-56 °C; R_f = 0.55 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.31 (m, 3H), 7.24-7.22 (m, 3H), 6.93 (s, 1H), 6.82-6.77 (m, 2H), 5.97 (d, *J* = 5.6 Hz, 1H), 4.54 (dd, *J* = 11.2 Hz, *J* = 6.0 Hz, 1H), 4.30 (dd, *J* = 11.2 Hz, *J* = 3.6 Hz, 1H), 3.44-3.40 (m, 1H), 3.32-3.27 (m, 1H), 3.23-3.15 (m, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 2.29-2.22 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 143.1, 141.3, 139.5, 131.9, 129.1, 128.8, 128.2, 127.3, 126.5, 124.1, 121.6, 118.0, 75.8, 55.1, 52.1, 36.4, 20.9, 18.2, 16.3 ppm. APCI-HRMS: m/z Calcd for $C_{24}H_{22}O_3S+H^+$: 382.1471, found 382.1479.



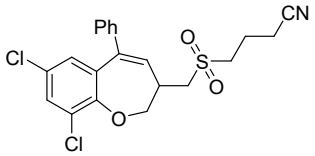
*4-(((8-methoxy-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3ga**).* White solid; (*hv*: 29.8 mg, 75%; *iron*: 26.2 mg, 66%); mp: 56-57 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.31 (m, 3H), 7.24-7.21 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.66 (d, *J* = 2.8 Hz, 1H), 5.87 (d, *J* = 5.6 Hz, 1H), 4.58 (dd, *J* = 11.6 Hz, *J* = 5.2 Hz, 1H), 4.31 (dd, *J* = 11.6 Hz, *J* = 3.2 Hz, 1H), 3.80 (s, 3H), 3.47-3.41 (m, 1H), 3.36-3.30 (m, 1H), 3.22-3.16 (m, 3H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.30-2.22 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.149, 160.131, 143.4, 141.1, 133.1, 128.9, 128.2, 128.0, 127.3, 121.6, 118.1, 109.4, 106.0, 75.2, 55.4, 55.2, 52.1, 36.7, 18.2, 16.4. ppm. APCI-HRMS: m/z Calcd for $C_{22}H_{23}NO_4S+H^+$: 398.1421, found 398.1420.



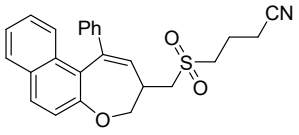
4-(((8-bromo-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3ha)***. White solid; (*hv*: 33.8 mg, 76%; *iron*: 30.7 mg, 69%); mp: 61-62 °C; R_f = 0.45 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.32 (m, 3H), 7.28 (d, *J* = 2.0 Hz, 2H), 7.23-7.20 (m, 2H), 7.10 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.06 (d, *J* = 5.6 Hz, 1H), 4.56 (dd, *J* = 11.2 Hz, *J* = 5.6 Hz, 1H), 4.31 (dd, *J* = 11.2 Hz, *J* = 3.6 Hz, 1H), 3.46-3.39 (m, 1H), 3.32-3.27 (m, 1H), 3.23-3.16 (m, 3H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.30-2.23 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.3, 142.4, 140.6, 133.2, 130.5, 128.8, 128.6, 128.4, 127.7, 126.5, 124.4, 122.0, 118.0, 76.3, 54.9, 52.1, 36.3, 18.2, 16.4 ppm. APCI-HRMS: m/z Calcd for $C_{21}H_{20}BrNO_3S+H^+$: 446.0420, found 446.0417.



4-(((7,9-di-tert-butyl-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3ia)***. Yellow solid; (*hv*: 12.4 mg, 26%; *iron*: 0%); mp: 75-76 °C; R_f = 0.45 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.29 (m, 3H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.23-7.21 (m, 2H), 6.77 (d, *J* = 2.4 Hz, 1H), 5.93 (d, *J* = 5.2 Hz, 1H), 4.49 (dd, *J* = 11.6 Hz, *J* = 5.6 Hz, 1H), 4.27 (dd, *J* = 11.6 Hz, *J* = 4.0 Hz, 1H), 3.51-3.45 (m, 1H), 3.35-3.30 (m, 1H), 3.25-3.17 (m, 3H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.31-2.24 (m, 2H), 1.44 (s, 9H), 1.13 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.5, 144.4, 144.3, 142.2, 140.4, 129.7, 129.1, 128.9, 128.0, 127.9, 127.2, 123.7, 118.0, 75.6, 55.7, 52.1, 36.8, 35.3, 344, 31.3, 30.8, 18.2, 16.4 ppm. ESI-HRMS: m/z Calcd for $C_{29}H_{37}NO_3S+NH_4^+$: 497.2832, found 497.2837.

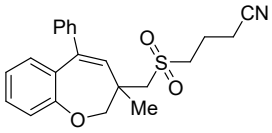


4-(((7,9-dichloro-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3ja)***. White solid; (*hv*: 29.1 mg, 67%; *iron*: 18.3 mg, 42%) mp: 72-73 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.34 (m, 4H), 7.25-7.23 (m, 2H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.23 (d, *J* = 5.6 Hz, 1H), 4.56 (dd, *J* = 10.8 Hz, *J* = 8.4 Hz, 1H), 4.49 (dd, *J* = 10.8 Hz, *J* = 5.2 Hz, 1H), 3.38-3.30 (m, 1H), 3.28-3.16 (m, 4H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.31-2.24 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.1, 140.9, 140.4, 134.4, 131.1, 129.7, 129.3, 128.9, 128.6, 128.5, 128.1, 128.1, 118.0, 79.4, 54.5, 52.0, 34.8, 18.1, 16.4 ppm. APCI-HRMS: m/z Calcd for $C_{21}H_{19}Cl_2O_3S+H^+$: 436.0535, found 436.0530.

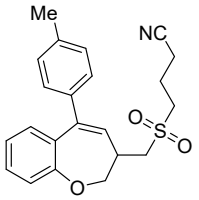


4-(((1-phenyl-3,4-dihydronaphtho[2,1-b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3ka)***. Yellow solid; (*hv*: 38.4 mg, 92%; *iron*: 37.9 mg, 91%); mp: 188-189 °C; R_f = 0.30 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88-7.81 (m, 2H), 7.38-7.15 (m, 9H), 6.56 (d, *J* = 5.2 Hz, 1H), 4.69 (dd, *J* = 10.4 Hz, *J* = 6.0 Hz, 1H), 4.40 (t, *J* = 10.4 Hz, 1H), 3.30-3.23 (m, 2H), 3.12-3.05 (m, 2H), 3.05-2.94 (m, 1H), 2.58 (t, *J* = 6.8 Hz, 2H), 2.22-2.15 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.3, 141.4, 141.0, 132.1, 131.9, 130.7, 130.2, 128.7, 128.3, 127.7, 127.2,

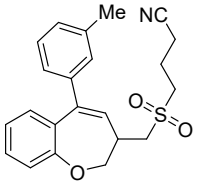
126.8, 126.7, 126.0, 124.8, 121.9, 118.0, 83.7, 54.5, 51.5, 32.7, 18.0, 16.4 ppm. APCI-HRMS: m/z Calcd for $C_{25}H_{23}NO_3S+H^+$: 418.1471, found 418.1477.



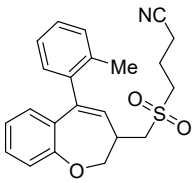
*4-(((3-methyl-5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3la**).* White solid; (*hv*: 35.1 mg, 92%; *iron*: 33.1 mg, 87%); mp: 50-51 °C; R_f = 0.60 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.31 (m, 3H), 7.23-7.16 (m, 3H), 7.08-7.06 (m, 1H), 6.92-6.86 (m, 2H), 5.80 (d, *J* = 2.0 Hz, 1H), 4.55 (dd, *J* = 12.0 Hz, *J* = 2.0 Hz, 1H), 3.93 (d, *J* = 12.0 Hz, 1H), 3.37 (dd, *J* = 50.4 Hz, *J* = 14.0 Hz, 2H), 3.22-3.10 (m, 2H), 2.63-2.49 (m, 2H), 2.24-2.17 (m, 2H), 1.47 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 144.2, 138.0, 136.4, 132.9, 129.1, 129.0, 128.2, 127.3, 127.2, 122.9, 120.3, 118.1, 76.8, 60.4, 53.6, 44.3, 22.9, 18.2, 16.3 ppm. APCI-HRMS: m/z Calcd for $C_{22}H_{23}NO_3S+H^+$: 382.1471, found 382.1469.



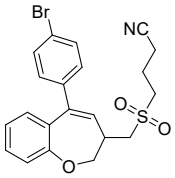
*4-(((5-(p-tolyl)-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3ma**).* White solid; (*hv*: 33.1 mg, 87%; *iron*: 32.8 mg, 86%); mp: 56-57 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.20 (m, 1H), 7.16-7.09 (m, 5H), 6.98-6.97 (m, 2H), 6.03 (d, *J* = 5.6 Hz, 1H), 4.53 (dd, *J* = 11.2 Hz, *J* = 5.6 Hz, 1H), 4.33 (dd, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 3.42-3.37 (m, 1H), 3.29-3.19 (m, 2H), 3.16 (t, *J* = 8.2 Hz, 2H), 2.62 (t, *J* = 8.2 Hz, 2H), 2.37 (s, 3H), 2.28-2.21 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 141.3, 139.8, 137.2, 132.0, 130.0, 129.3, 129.0, 128.9, 128.7, 123.3, 121.1, 118.0, 76.8, 55.0, 52.0, 36.1, 21.1, 18.1, 16.3 ppm. APCI-HRMS: m/z Calcd for $C_{22}H_{23}NO_3S+H^+$: 382.1471, found 382.1465.



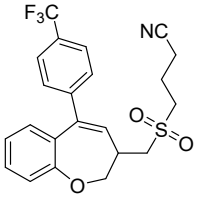
*4-(((5-(m-tolyl)-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3na**).* White solid; (*hv*: 30.9 mg, 81%; *iron*: 27.8 mg, 73%); mp: 70-71 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.20 (m, 2H), 7.15-7.12 (m, 2H), 7.06-7.03 (m, 2H), 6.02 (d, *J* = 5.6 Hz, 1H), 4.55 (dd, *J* = 11.2 Hz, *J* = 5.6 Hz, 1H), 4.33 (dd, *J* = 11.2 Hz, *J* = 4.0 Hz, 1H), 3.45-3.38 (m, 1H), 3.31-3.20 (m, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 2.29-2.22 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 142.8, 141.5, 137.9, 132.2, 129.7, 129.6, 129.5, 129.0, 128.2, 128.1, 125.9, 123.3, 121.1, 118.0, 76.4, 55.1, 52.0, 36.3, 21.4, 18.2, 16.3 ppm. APCI-HRMS: m/z Calcd for $C_{22}H_{23}NO_3S+H^+$: 382.1471, found 382.1476.



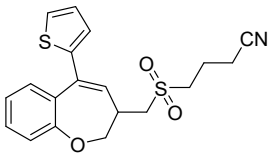
*4-(((5-(o-tolyl)-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3oa**).* White solid; (*hv*: 32.8 mg, 86%; *iron*: 29.3 mg, 77%); mp: 51-52 °C; R_f = 0.55 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.07 (m, 7H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.71-6.69 (m, 1H), 5.88 (d, *J* = 5.6 Hz, 1H), 4.64 (dd, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 4.23 (dd, *J* = 12.0 Hz, *J* = 2.4 Hz, 1H), 3.52-3.46 (m, 1H), 3.45-3.40 (m, 1H), 3.22-3.18 (m, 3H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.30-2.23 (m, 2H), 2.03 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0, 142.9, 140.3, 136.0, 131.6, 130.6, 130.0, 129.6, 128.8, 127.4, 127.4, 125.9, 123.1, 120.6, 118.0, 72.7, 55.3, 52.3, 37.6, 19.5, 18.2, 16.3. ppm. APCI-HRMS: m/z Calcd for $C_{22}H_{23}NO_3S+H^+$: 382.1471, found 382.1462.



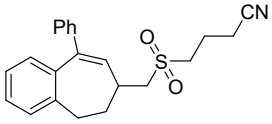
*4-(((5-(4-bromophenyl)-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3pa**).* White solid; (*hv*: 33.8 mg, 76%; *iron*: 31.6 mg, 71%); mp: 61-62 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.46 (m, 2H), 7.25-7.22 (m, 1H), 7.14-7.10 (m, 3H), 7.02-6.98 (m, 1H), 6.92-6.90 (m, 1H), 6.06 (d, *J* = 5.6 Hz, 1H), 4.54 (dd, *J* = 11.2 Hz, *J* = 6.4 Hz, 1H), 4.33 (dd, *J* = 11.2 Hz, *J* = 4.0 Hz, 1H), 3.45-3.38 (m, 1H), 3.30-3.18 (m, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.30-2.22 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 141.7, 140.4, 131.8, 131.4, 130.5, 130.2, 129.4, 129.3, 123.5, 121.6, 121.3, 118.0, 76.7, 55.0, 52.1, 36.1, 18.1, 16.4 ppm. APCI-HRMS: m/z Calcd for $C_{21}H_{20}BrNO_3S+H^+$: 446.0420, found 446.0412.



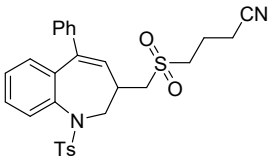
*4-(((5-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3qa**).* White solid; (*hv*: 32.6 mg, 75%; *iron*: 23.9 mg, 55%); mp: 61-62 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.28-7.23 (m, 1H), 7.14-7.12 (m, 1H), 7.02-6.98 (m, 1H), 6.88-6.85 (m, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 4.57 (dd, *J* = 11.6 Hz, *J* = 6.0 Hz, 1H), 4.34 (dd, *J* = 11.6 Hz, *J* = 4.0 Hz, 1H), 3.50-3.43 (m, 1H), 3.32-3.20 (m, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.30-2.23 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.8, 146.5, 140.3, 131.8, 131.1, 129.6 (q, *J* = 32.7 Hz), 129.5, 129.2, 129.0, 125.2 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 273.2 Hz), 123.5, 121.3, 118.0, 76.4, 54.9, 52.1, 36.3, 18.2, 16.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -62.4 ppm. APCI-HRMS: m/z Calcd for $C_{20}H_{20}F_3NO_3S+H^+$: 436.1189, found 436.1197.



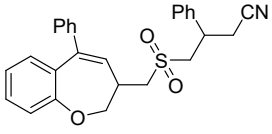
*4-(((5-(thiophen-2-yl)-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3ra**)*. Yellow solid; (*hv*: 25.4 mg, 68%; *iron*: 18.7 mg, 50%); mp: 70-71 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.25 (m, 3H), 7.14-7.08 (m, 2H), 7.01-6.99 (m, 1H), 6.94 (d, *J* = 3.6 Hz, 1H), 6.27 (d, *J* = 5.4 Hz, 1H), 4.50-4.42 (m, 2H), 3.38-3.30 (m, 1H), 3.26-3.20 (m, 1H), 3.17-3.12 (m, 3H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.28-2.21 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.6, 144.2, 135.0, 131.2, 130.6, 129.7, 128.8, 127.2, 126.7, 125.0, 123.9, 121.7, 118.0, 79.3, 54.9, 51.9, 34.9, 18.2, 16.4 ppm. APCI-HRMS: m/z Calcd for $C_{19}H_{19}NO_3S$+H^+: 374.0879, found 374.0875.



*4-(((9-phenyl-6,7-dihydro-5H-benzo[7]annulen-7-yl)methyl)sulfonyl)butanenitrile (**3ta**)*. White solid; (*hv*: 33.6 mg, 92%; *iron*: 34.7 mg, 95%); mp: 92-93 °C; R_f = 0.50 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.19 (m, 8H), 7.04-7.02 (m, 2H), 6.27 (d, *J* = 6.4 Hz, 1H), 3.25 (dd, *J* = 14.0 Hz, *J* = 5.2 Hz, 1H), 3.08-3.02 (m, 3H), 2.82-2.71 (m, 2H), 2.68-2.63 (m, 1H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.48-2.39 (m, 1H), 2.25-2.17 (m, 2H), 2.11-2.03 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9, 141.2, 141.0, 139.4, 129.5, 128.7, 128.6, 128.2, 128.1, 127.8, 127.6, 126.4, 118.1, 58.5, 51.2, 42.3, 31.7, 31.6, 18.0, 16.3 ppm. APCI-HRMS: m/z Calcd for $C_{22}H_{23}NO_2S$+H^+: 366.1522, found 366.1523.

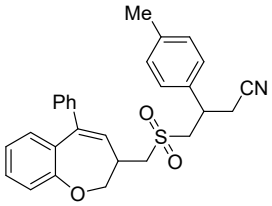


*4-(((5-phenyl-1-tosyl-2,3-dihydro-1H-benzo[b]azepin-3-yl)methyl)sulfonyl)butanenitrile (**3ua**)*. Yellow solid; (*hv*: 28.1 mg, 54%; *iron*: 29.6 mg, 57%); mp: 81-82 °C; R_f = 0.30 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.47 (m, 3H), 7.36-7.18 (m, 5H), 7.01-6.93 (m, 5H), 6.11 (d, *J* = 5.6 Hz, 1H), 4.44 (s, 1H), 4.13 (s, 1H), 3.28-3.20 (m, 1H), 3.16-3.03 (m, 4H), 2.61-2.57 (m, 2H), 2.25 (s, 3H), 2.22-2.16 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.3, 137.5, 130.8, 129.4, 128.9, 128.6, 128.0, 127.9, 127.8, 127.2, 118.1, 77.20, 55.0, 51.7, 32.3, 21.4, 18.0, 16.2 ppm. APCI-HRMS: m/z Calcd for $C_{28}H_{28}N_2O_4S_2$+H^+: 521.1563, found 521.1560.

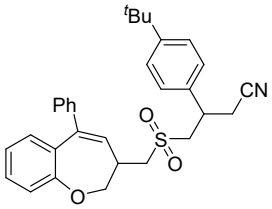


*3-phenyl-4-(((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile (**3ab**)*. White solid; (*hv*: 24.4 mg, 55%; *iron*: 22.1 mg, 50%); (dr = 1.17:1); mp: 66-67 °C; R_f = 0.75 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.24 (m, 8H), 7.22-7.17 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.99-6.91 (m, 2H), 5.94 (d, *J* = 5.6 Hz, 0.43H), 5.88 (d, *J* = 5.6 Hz, 0.50H), 4.43-4.38 (m, 1H), 4.27-4.18 (m, 1H), 3.75-3.70 (m, 1H), 3.50-3.40 (m, 1H), 3.32-3.25 (m, 1H), 3.03-2.88 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 158.6, 142.8, 142.7, 141.4,

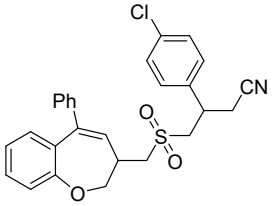
141.3, 138.8, 132.111, 132.078, 129.9, 129.8, 129.594, 129.570, 129.134, 129.114, 128.9, 128.8, 128.7, 128.3, 127.5, 127.2, 123.410, 123.367, 121.212, 117.165, 76.6, 57.8, 57.7, 55.9, 55.8, 36.3, 36.2, 36.1, 24.580, 24.558 ppm. APCI-HRMS: m/z Calcd for $C_{27}H_{25}NO_3S+H^+$: 444.1628, found 444.1622.



4-(((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)-3-(p-tolyl)butanenitrile ***(3ac)***. White solid; (*hv*: 23.8 mg, 52%; *iron*: 23.3 mg, 51%); (dr = 1.14:1); mp: 70-71 °C; R_f = 0.76 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.30 (m, 3H), 7.22-7.16 (m, 7H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.99-6.90 (m, 2H), 5.90 (d, *J* = 5.6 Hz, 0.43H), 5.83 (d, *J* = 5.6 Hz, 0.5H), 4.43-4.38 (m, 1H), 4.27-4.17 (m, 1H), 3.71-3.66 (m, 1H), 3.43 (d, *J* = 7.2 Hz, 1H), 3.29-3.23 (m, 1H), 3.00-2.81 (m, 4H), 2.31 (s, 1.4H), 2.28 (s, 1.6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 158.6, 142.7, 141.3, 141.2, 138.6, 135.6, 132.1, 132.0, 130.2, 130.1, 129.8, 129.6, 129.1, 128.8, 128.230, 128.210, 127.4, 127.011, 126.987, 123.4, 123.3, 121.2, 121.1, 117.2, 76.3, 57.9, 57.7, 55.7, 55.7, 36.4, 36.1, 36.0, 35.9, 24.7, 24.6, 21.0 ppm. APCI-HRMS: m/z Calcd for $C_{28}H_{27}NO_3S+H^+$: 458.1784, found 458.1789.

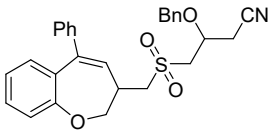


3-(4-(tert-butyl)phenyl)-4-(((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitr-ile ***(3ad)***. White solid; (*hv*: 26.4 mg, 53%; *iron*: 24.5 mg, 49%); (dr = 3.5:1); mp: 77-78 °C; R_f = 0.78 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.0 Hz, 2H), 7.32-7.30 (m, 3H), 7.23-7.19 (m, 5H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.99-6.89 (m, 2H), 5.90-5.88 (m, 1H), 4.43-4.37 (m, 1H), 4.24-4.14 (m, 1H), 3.73-3.68 (m, 1H), 3.49-3.39 (m, 2H), 3.32-3.25 (m, 1H), 2.98-2.77 (m, 4H), 1.30 (s, 2H), 1.26 (s, 7H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.8, 158.6, 151.8, 142.9, 142.7, 141.3, 141.2, 135.5, 132.1, 132.0, 129.839, 129.768, 129.6, 129.0, 128.8, 128.210, 128.184, 127.4, 126.835, 126.8, 126.4, 123.3, 123.2, 121.115, 121.093, 117.2, 77.2, 76.6, 76.3, 57.8, 55.7, 55.6, 36.3, 36.2, 35.9, 34.5, 31.3, 31.2, 24.5, 24.4 ppm. APCI-HRMS: m/z Calcd for $C_{31}H_{33}NO_3S+H^+$: 500.2254, found 500.2250.

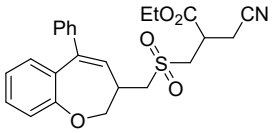


3-(4-chlorophenyl)-4-(((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3ae)***. White solid; (*hv*: 29.1 mg, 61%; *iron*: 25.3 mg, 53%); mp: 71-72 °C; R_f = 0.65 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.30 (m, 5H), 7.24-7.16 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.99-6.91 (m, 2H), 5.97-5.93 (m, 1H), 4.491-4.43 (m, 1H), 4.28-4.21 (m,

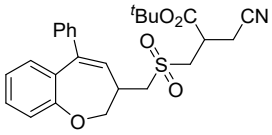
1H), 3.76-3.70 (m, 1H), 3.49-3.29 (m, 3H), 3.14-2.98 (m, 2H), 2.95-2.86 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 158.6, 142.7, 141.6, 141.5, 137.3, 137.2, 134.7, 132.1, 129.702, 129.666, 129.6, 129.5, 129.2, 128.8, 128.5, 128.3, 128.2, 127.499, 127.467, 123.4, 123.3, 121.1, 116.9, 76.2, 76.1, 57.5, 57.3, 56.1, 36.440, 36.382, 35.5, 35.4, 24.5 ppm. APCI-HRMS: m/z Calcd for $C_{27}H_{24}ClNO_3S+H^+$: 478.1238, found 478.1236.



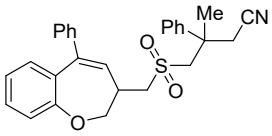
3-(benzyloxy)-4-(((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3af)***. White solid; (*hv*: 27.4 mg, 58%; *iron*: 25.1 mg, 53%); (dr = 1:1); mp: 64-65 °C; R_f = 0.65 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.25 (m, 8H), 7.23-7.19 (m, 3H), 7.11-7.08 (m, 1H), 7.00-6.92 (m, 2H), 5.93-5.82 (m, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.60-4.54 (m, 1H), 4.43-4.33 (m, 2H), 4.27-4.19 (m, 1H), 3.52-3.45 (m, 1H), 3.37-3.12 (m, 4H), 2.85-2.79 (m, 1H), 2.69-2.62 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 142.9, 142.7, 141.2, 141.0, 135.7, 132.0, 130.0, 129.9, 128.9, 128.855, 128.761, 128.7, 128.4, 128.3, 128.2, 127.4, 123.3, 121.2, 115.8, 76.8, 73.1, 73.0, 70.2, 58.0, 57.8, 56.7, 56.6, 36.0, 22.7 ppm. APCI-HRMS: m/z Calcd for $C_{28}H_{27}NO_4S+H^+$: 474.1734, found 474.1728.



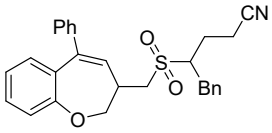
ethyl 3-cyano-2-((((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)methyl)propanoate ***(3ag)***. White solid; (*hv*: 16.7 mg, 38%; *iron*: 15.8 mg, 36%); (dr = 1.13:1); mp: 51-52 °C; R_f = 0.65 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.32 (m, 3H), 7.25-7.21 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.00-6.93 (m, 2H), 6.07-6.04 (m, 1H), 4.58-4.52 (m, 1H), 4.37-4.32 (m, 1H), 4.29-4.23 (m, 2H), 3.72-3.67 (m, 1H), 3.45-3.37 (m, 2H), 3.35-3.26 (m, 3H), 3.02-2.99 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.4, 158.7, 142.8, 141.5, 132.125, 132.093, 129.8, 129.7, 129.6, 129.1, 128.9, 128.2, 127.5, 123.4, 121.2, 121.1, 116.4, 76.4, 62.8, 56.1, 56.0, 53.2, 53.1, 36.3, 36.2, 35.818, 35.779, 19.5, 14.0 ppm. ESI-HRMS: m/z Calcd for $C_{24}H_{25}NO_5S+H^+$: 440.1526, found 440.1525.



tert-butyl 3-cyano-2-((((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)methyl)propanoate ***(3ah)***. White solid; (*hv*: 21.0 mg, 45%; *iron*: 21.5 mg, 46%); (dr = 1.22:1); mp: 51-52 °C; R_f = 0.65 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.32 (m, 2H), 7.25-7.21 (m, 2H), 7.13-7.11 (m, 1H), 7.00-6.93 (m, 2H), 6.07-6.05 (m, 1H), 4.58-4.53 (m, 1H), 4.37-4.32 (m, 1H), 3.68-3.63 (m, 1H), 3.46-3.41 (m, 1H), 3.37-3.22 (m, 4H), 2.97-2.94 (m, 2H), 1.50 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 168.3, 158.732, 158.677, 142.8, 141.5, 132.118, 132.091, 129.837, 129.769, 129.7, 129.1, 128.9, 128.2, 127.4, 123.4, 123.3, 121.2, 121.1, 116.5, 84.1, 76.5, 56.1, 56.0, 53.3, 53.2, 36.6, 36.5, 36.3, 36.2, 27.9, 27.8, 19.8, 19.7 ppm. ESI-HRMS: m/z Calcd for $C_{26}H_{29}NO_5S+NH_4^+$: 485.2110, found 485.2104.



3-methyl-3-phenyl-4-(((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)butanenitrile ***(3ai)***. White solid; (*hv*: 22.4 mg, 49%; *iron*: 21.5 mg, 47%); mp: 66-67 °C; R_f = 0.75 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.32 (m, 3H), 7.23-7.18 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.99-6.90 (m, 2H), 5.84 (d, *J* = 5.6 Hz, 1H), 4.33-4.27 (m, 1H), 4.20-4.15 (m, 1H), 3.48-3.37 (m, 2H), 3.27-3.17 (m, 3H), 2.71-2.51 (m, 2H), 1.80 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5, 142.7, 141.127, 141.062, 132.0, 129.908, 129.870, 129.3, 129.2, 129.0, 128.8, 128.2, 127.4, 125.7, 125.6, 123.3, 121.2, 117.3, 76.8, 63.690, 63.665, 56.5, 56.4, 39.9, 35.9, 35.8, 28.8, 28.7, 26.4, 26.3 ppm. APCI-HRMS: m/z Calcd for $C_{28}H_{27}NO_3S+H^+$: 458.1784, found 458.1780.



5-phenyl-4-(((5-phenyl-2,3-dihydrobenzo[b]oxepin-3-yl)methyl)sulfonyl)pentanenitrile ***(3aj)***. White solid; (*hv*: 18.7 mg, 41%; *iron*: 20.6 mg, 45%); (dr = 1:1); mp: 59-60 °C; R_f = 0.75 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.29 (m, 6H), 7.28-7.20 (m, 5H), 7.12-7.09 (m, 1H), 6.98-6.94 (m, 2H), 6.00-5.91 (m, 1H), 4.51-4.45 (m, 1H), 4.29-4.22 (m, 1H), 3.41-3.30 (m, 3H), 3.13-2.93 (m, 2H), 2.89-2.83 (m, 1H), 2.68-2.57 (m, 1H), 2.50-2.42 (m, 1H), 2.37-2.26 (m, 1H), 2.04-1.98 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 143.0, 141.2, 135.6, 132.1, 130.1, 129.3, 129.007, 128.983, 128.9, 128.2, 127.7, 127.4, 123.2, 121.1, 118.4, 76.3, 63.0, 62.9, 53.3, 53.0, 36.2, 35.3, 35.2, 23.4, 15.5 ppm. ESI-HRMS: m/z Calcd for $C_{28}H_{27}NO_3S+NH_4^+$: 475.2050, found 475.2042.


7.318
7.313
7.301
7.297
7.293
7.285
7.281
7.246
7.237
7.227
7.097
7.080
6.789
6.783
6.771
6.766
6.665
5.661
5.644
5.632
5.619
5.612
5.607
5.600
5.587
5.575
5.563
5.321
5.317
5.015
5.011
5.007
5.003
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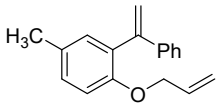
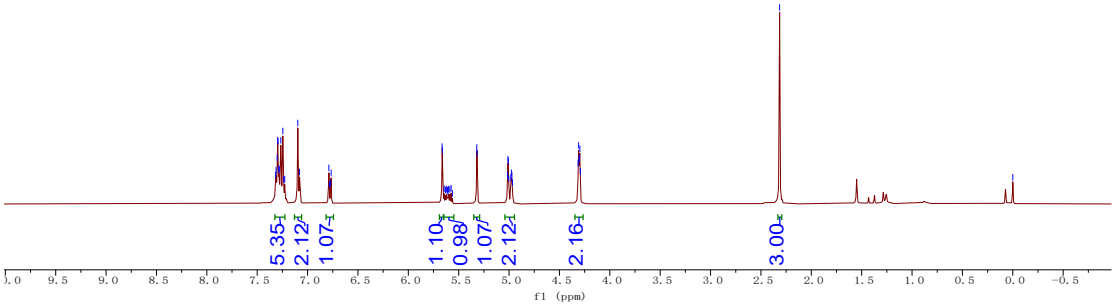
4.293
2.314
-0.000


H3C
Ph
O

1b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1.07
2.12
2.16
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f1 (ppm)


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147.391
141.499
133.190
131.929
131.384
130.128
129.202
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127.174
126.462
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115.359
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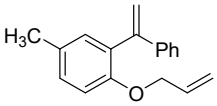
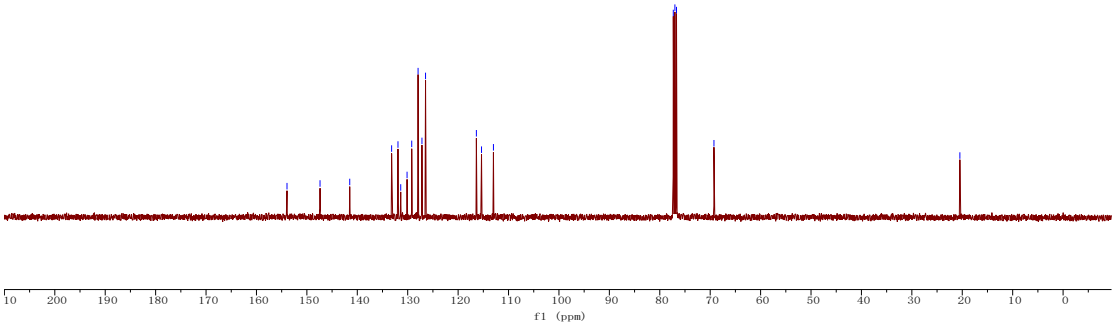
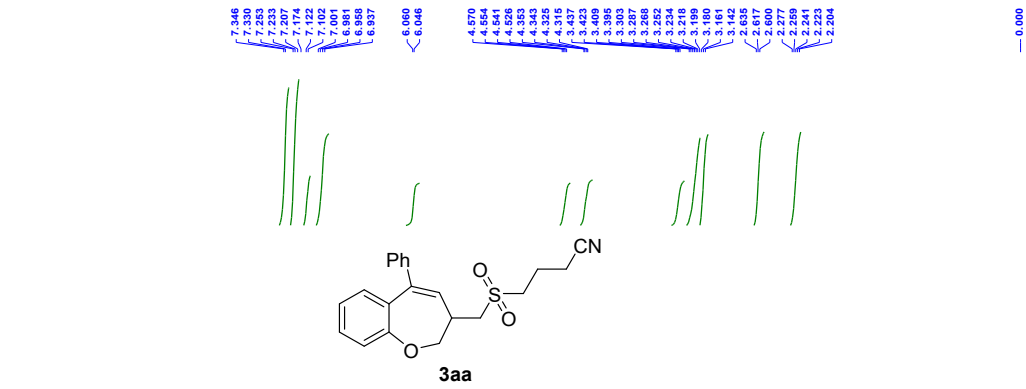
77.316
77.000
76.683
69.254
20.473


H3C
Ph
O

1b


f1 (ppm)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7.122
7.102
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6.937
6.060
6.046
4.570
4.554
4.541
4.526
4.353
4.343
4.325
4.315
3.437
3.423
3.409
3.395
3.303
3.287
3.268
3.252
3.234
3.218
3.199
3.180
3.161
3.142
2.635
2.617
2.600
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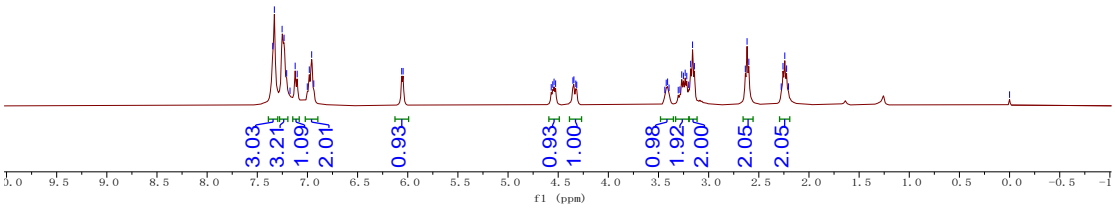
2.259
2.241
2.223
2.204
0.000
Ph
O
S
O
CN
O

3aa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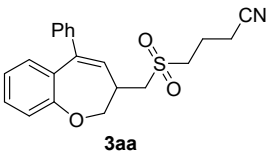
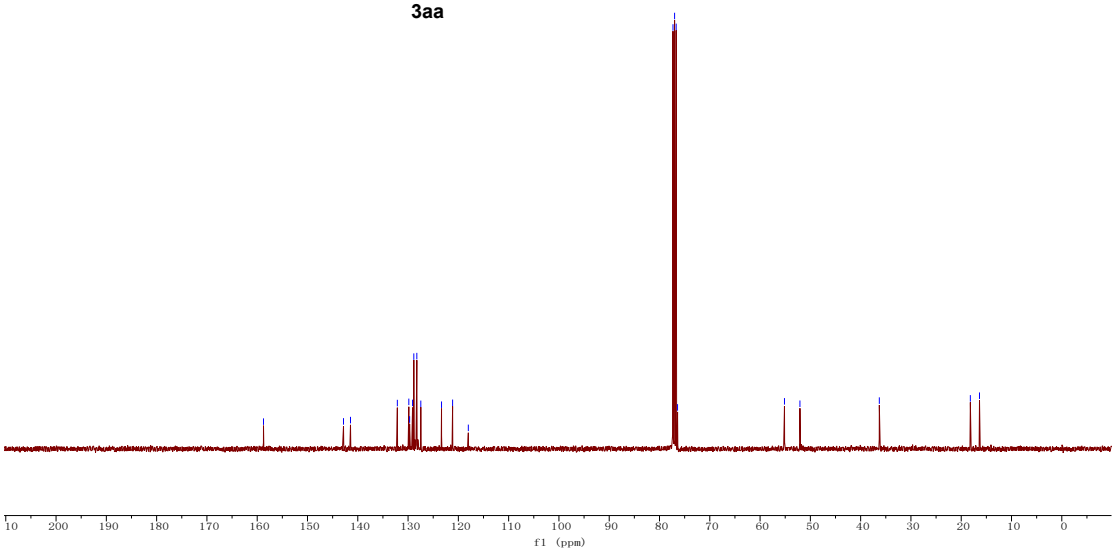
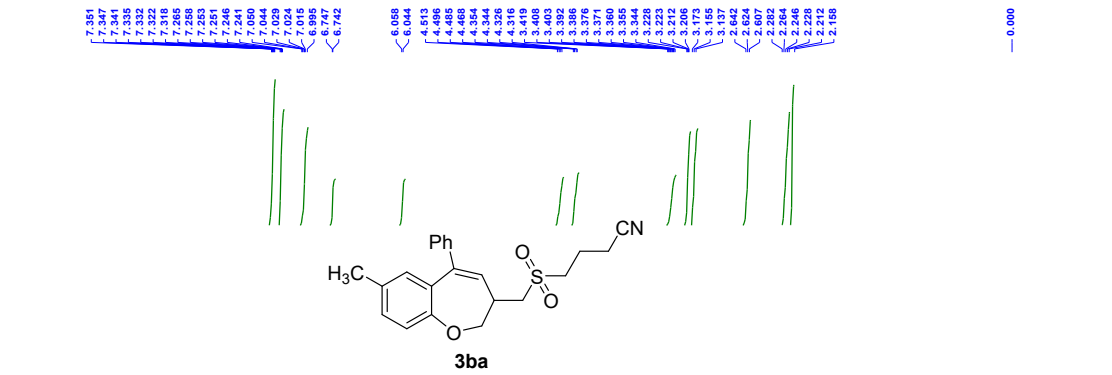
0.93
1.00
0.98
1.92
2.00
2.05
2.05
f1 (ppm)


158.748
142.039
141.449
132.132
129.850
129.691
129.107
128.857
128.288
127.466
123.346
121.143
118.017
77.317
77.000
76.682
76.409
55.147
52.074
36.287
18.186
16.366


Ph
O
S
O
CN
O

3aa


f1 (ppm)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7.253
7.251
7.246
7.241
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7.044
7.029
7.024
7.015
6.995
6.747
6.742
6.058
6.044
4.513
4.496
4.485
4.466
4.354
4.344
4.326
4.316
3.419
3.408
3.403
3.392
3.386
3.376
3.371
3.360
3.355
3.344
3.228
3.223
3.212
3.206
3.173
3.155
3.137
2.642
2.624
2.607
2.282
2.264
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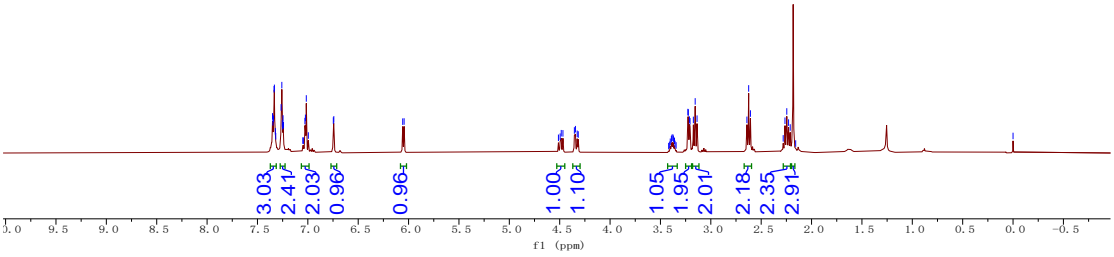
2.228
2.212
2.158
0.000
Ph
CN
O
S
O
H3C
O

3ba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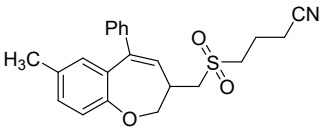
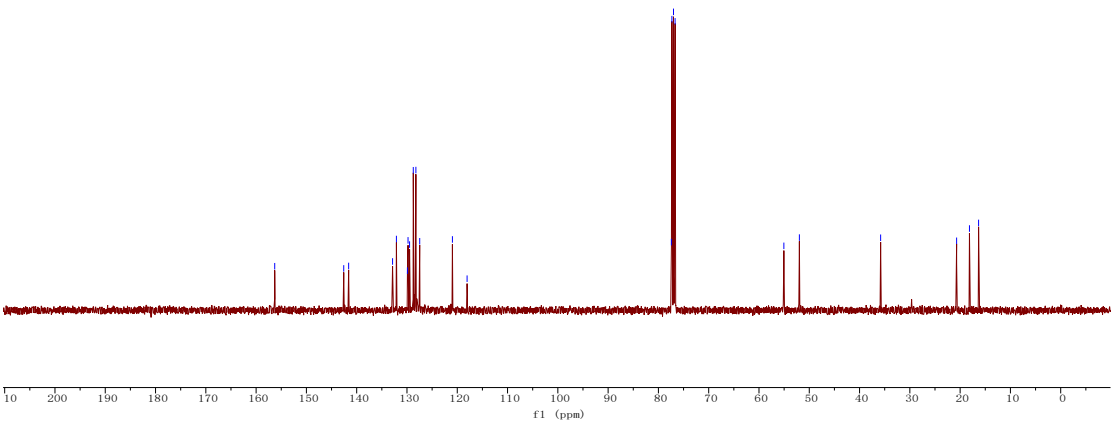
0.96
1.00
1.10
1.05
1.95
2.01
2.18
2.35
2.91
f1 (ppm)


156.301
142.576
141.599
132.865
132.101
129.913
129.789
129.484
128.746
128.228
127.468
120.963
118.046
77.415
77.319
77.000
76.683
55.052
51.966
35.809
20.700
18.144
16.328


Ph
CN
O
S
O
H3C
O

3ba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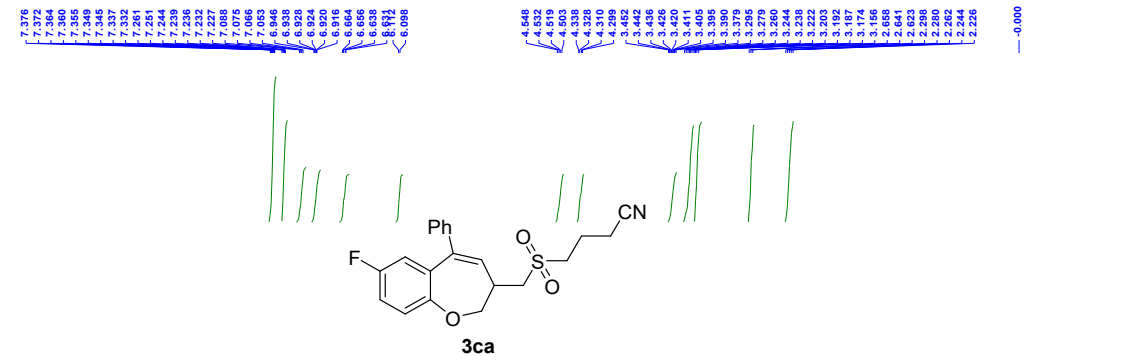
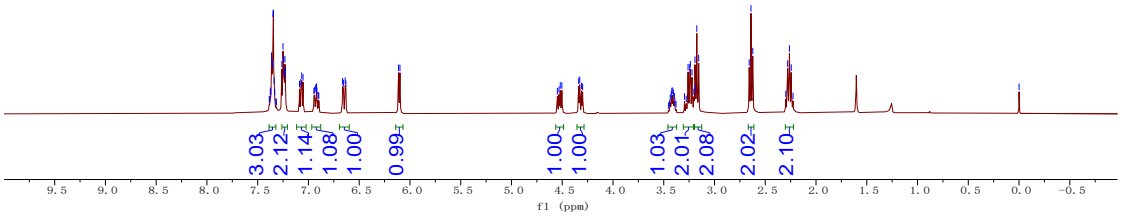

Ph
F
O
S
O
CN
O

3ca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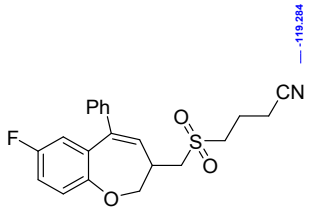
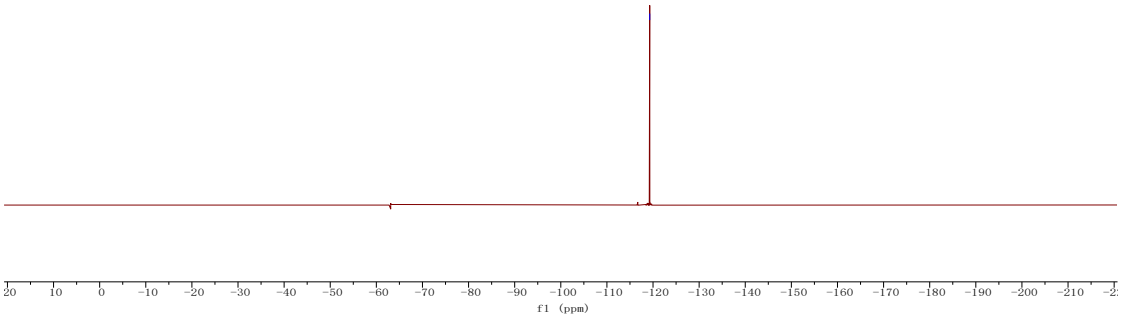
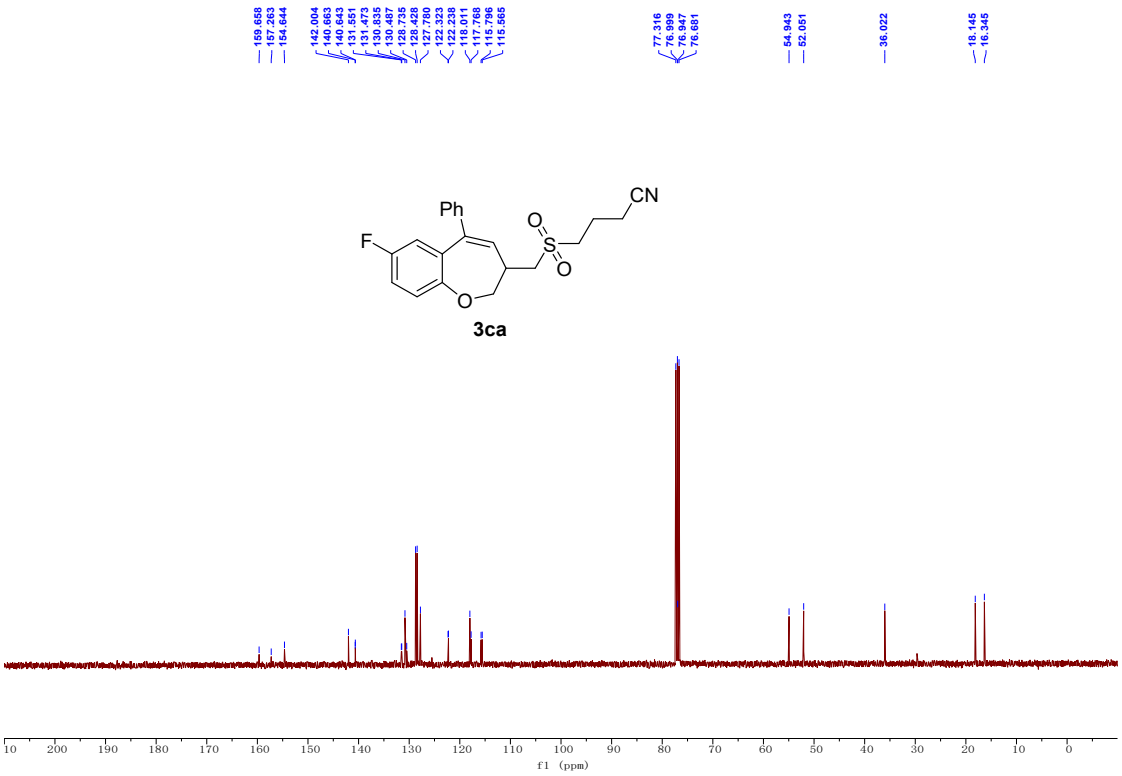
1.00
0.99
1.00
1.00
1.03
2.01
2.08
2.02
2.10
f1 (ppm)


Ph
F
O
S
O
CN
O

3ca


f1 (ppm)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140.643
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131.473
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128.735
128.428
127.780
122.323
122.238
118.101
117.768
115.796
115.565
77.316
76.999
76.947
76.681
54.943
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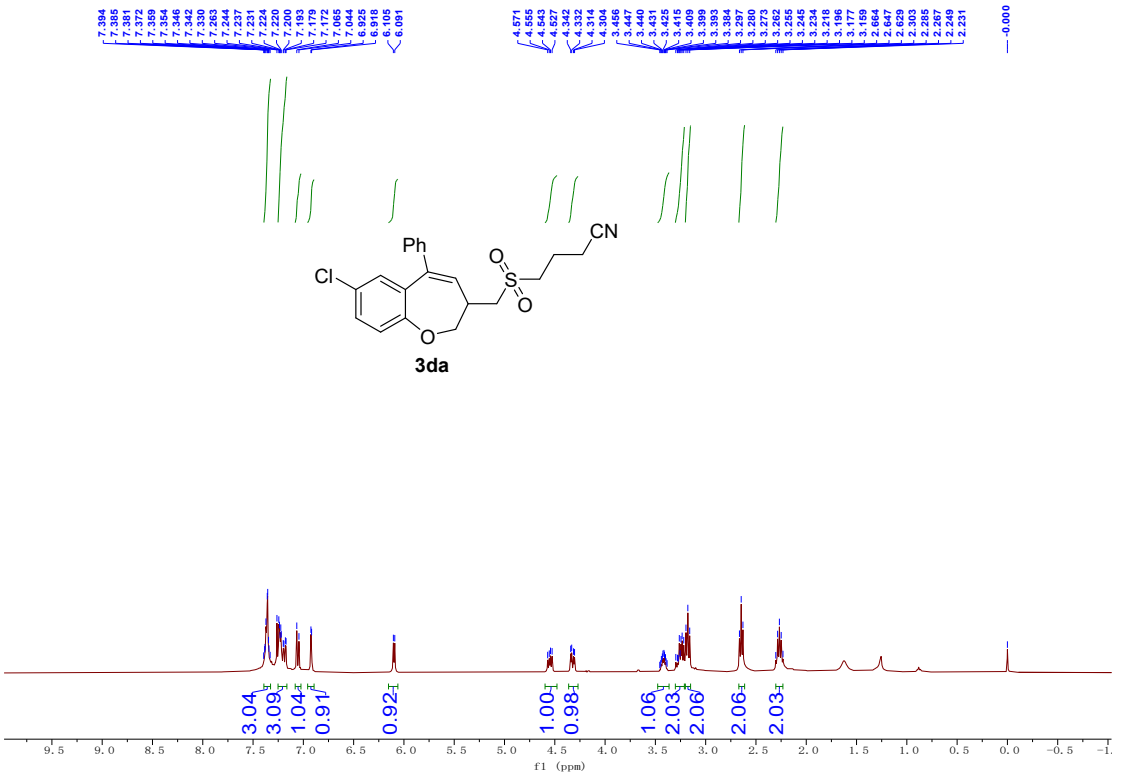
36.022
18.145
16.345
Ph
F
O
S
O
CN
O
3ca
f1 (ppm)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7.283
7.244
7.237
7.231
7.224
7.220
7.200
7.193
7.179
7.172
7.066
7.044
6.925
6.918
6.105
6.091
4.571
4.555
4.543
4.527
4.342
4.332
4.314
4.304
3.466
3.447
3.440
3.431
3.425
3.415
3.409
3.399
3.393
3.384
3.297
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3.273
3.262
3.255
3.245
3.234
3.218
3.196
3.177
3.159
2.664
2.647
2.629
2.303
2.285
2.267
2.249
2.231
-0.000
Ph
Cl
O
S
O
CN
O
3da
3.04
3.09
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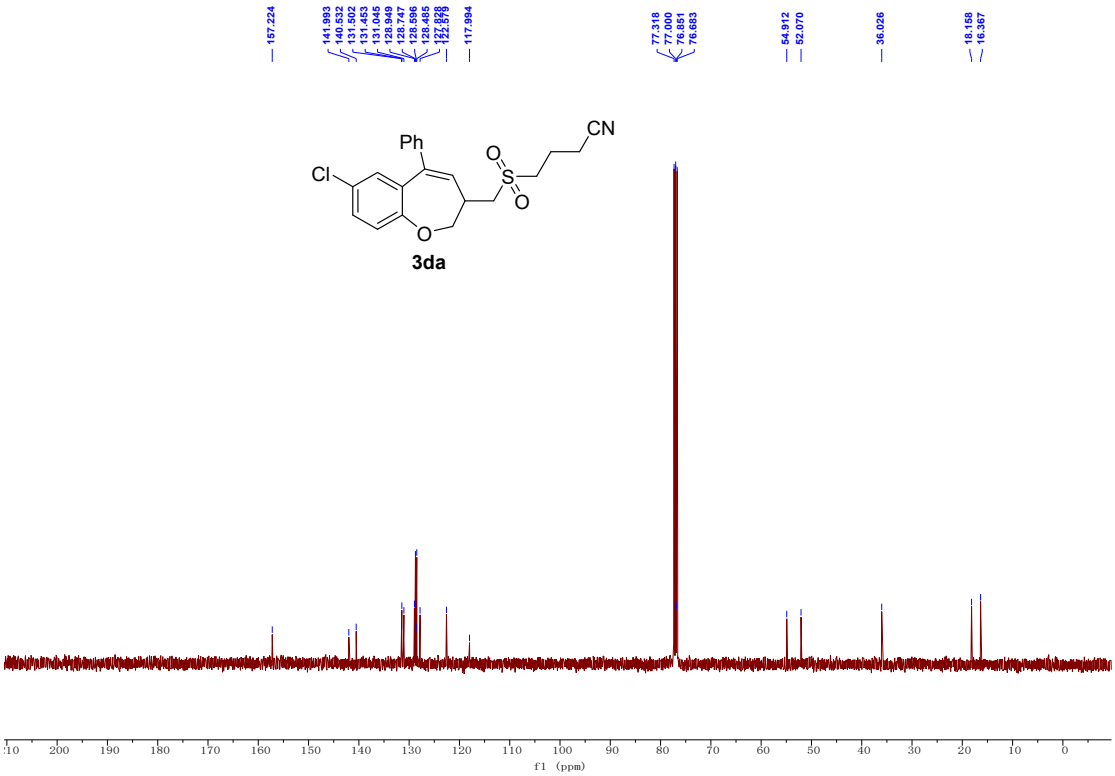
0.92
1.00
0.98
1.06
2.03
2.06
2.06
2.03
f1 (ppm)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128.747
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128.485
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77.318
77.000
76.851
76.683
54.912
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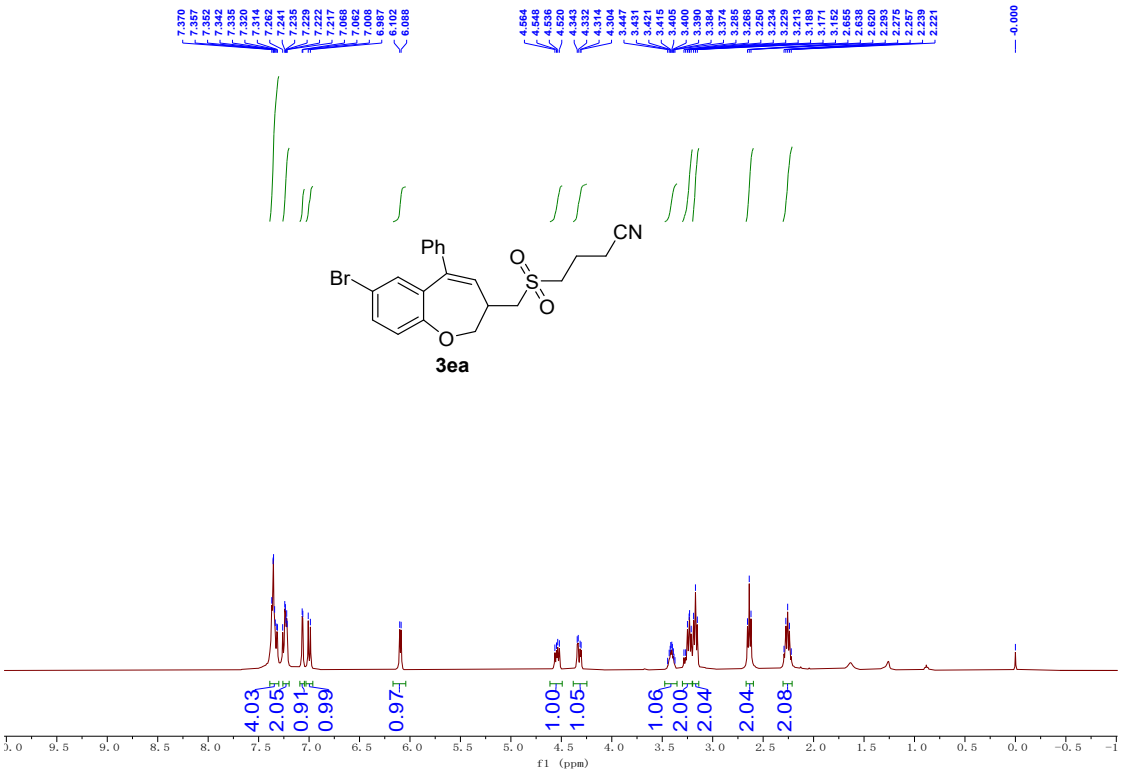
36.026
18.158
16.587
Ph
Cl
O
S
O
CN
O
3da
f1 (ppm)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7.062
7.008
6.997
6.103
6.088
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4.536
4.520
4.343
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4.314
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3.250
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3.171
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2.638
2.620
2.293
2.275
2.257
2.239
2.221
-0.000
Ph
Br
O
S
O
CN
O
3ea
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0.97
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1.05
1.06
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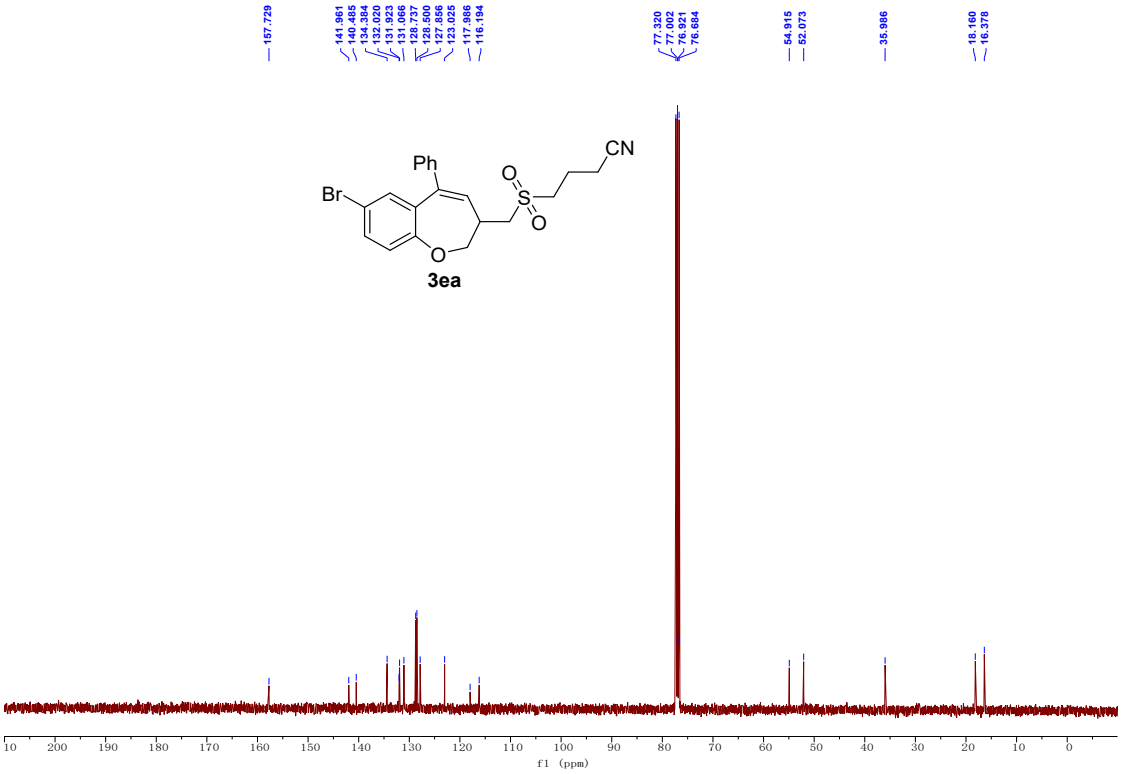
2.04
2.04
2.08
f1 (ppm)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116.194
77.320
77.002
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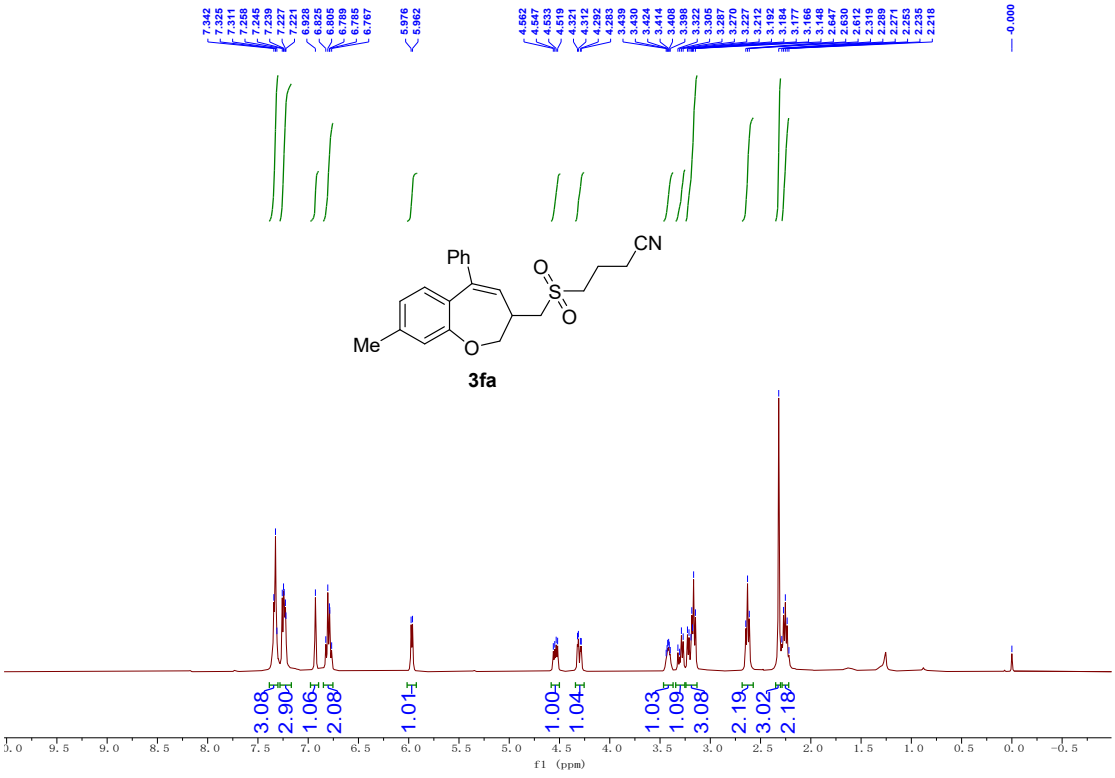
16.378
Ph
Br
O
S
O
CN
O
3ea
f1 (ppm)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6.785
6.767
5.976
5.962
4.662
4.647
4.633
4.619
4.321
4.312
4.292
4.283
3.439
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3.398
3.322
3.305
3.287
3.270
3.227
3.212
3.192
3.184
3.177
3.166
3.148
2.647
2.630
2.612
2.319
2.289
2.271
2.253
2.235
2.218
-0.000
Ph
O
S
O
CN
Me
O
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2.90
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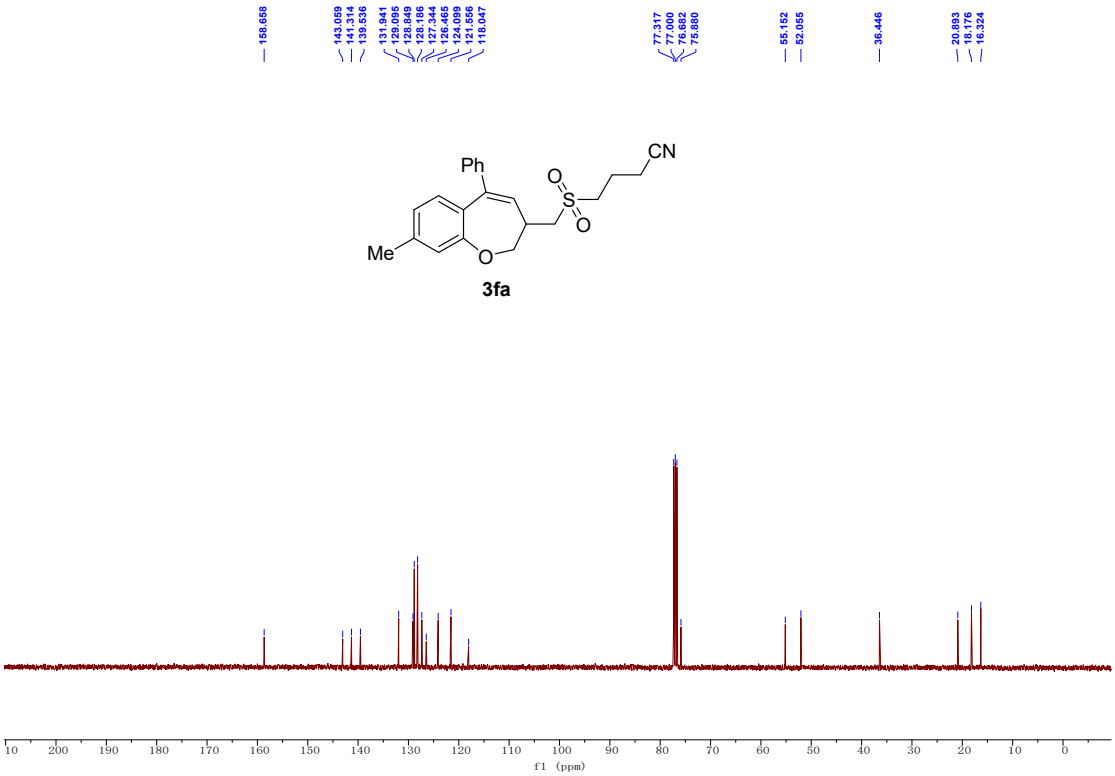
1.00
1.04
1.03
1.09
3.08
2.19
3.02
2.18
f1 (ppm)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128.186
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124.099
121.556
118.047
77.317
77.000
76.682
75.880
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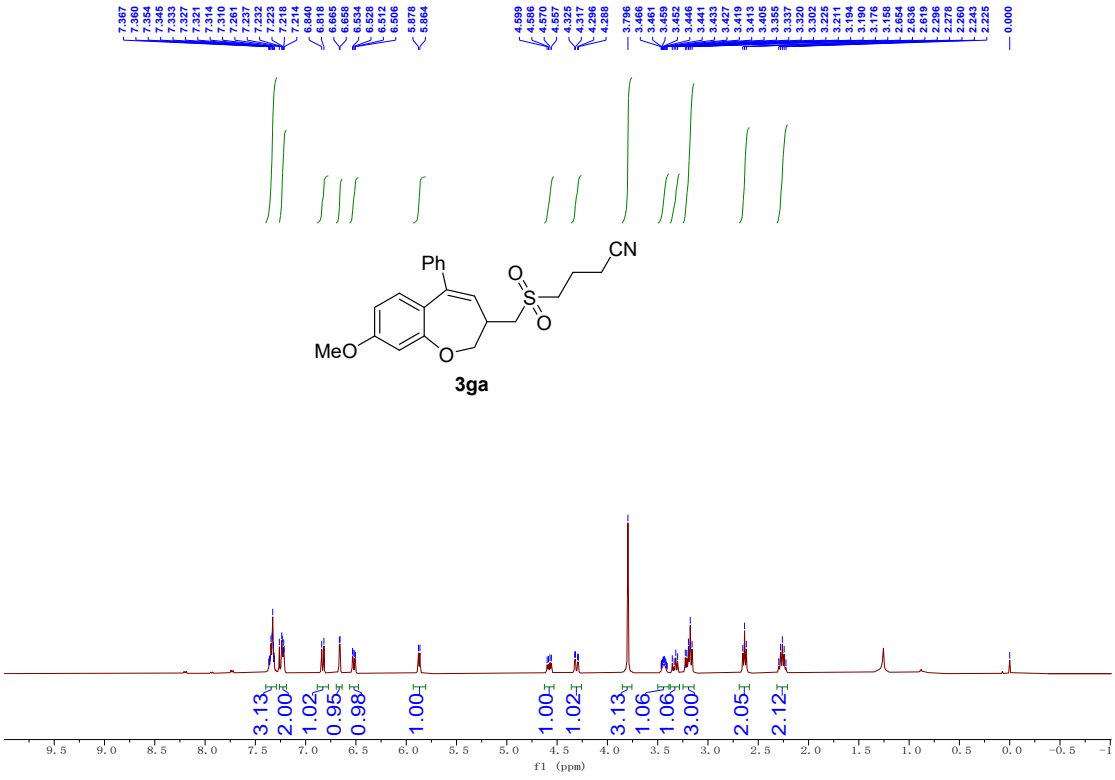
Ph
CN
O
S
O
Me
O
f1 (ppm)

3fa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7.237
7.232
7.223
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7.214
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6.628
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6.506
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5.864
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4.570
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3.194
3.190
3.176
3.168
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Ph
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S
O
MeO
O
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0.95
0.98
1.00
1.00
1.02
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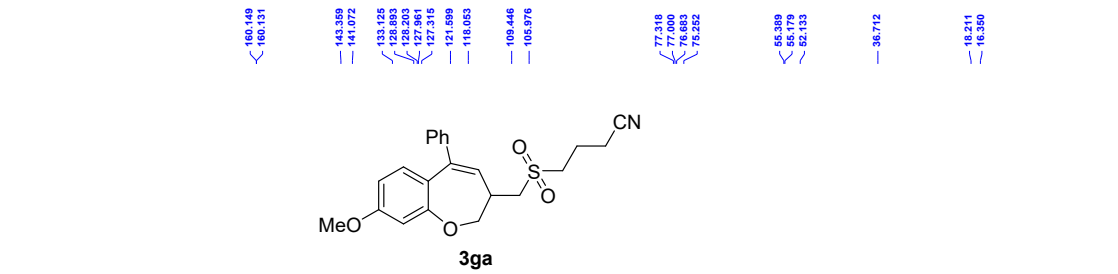
1.06
1.06
3.00
2.05
2.12
f1 (ppm)

3ga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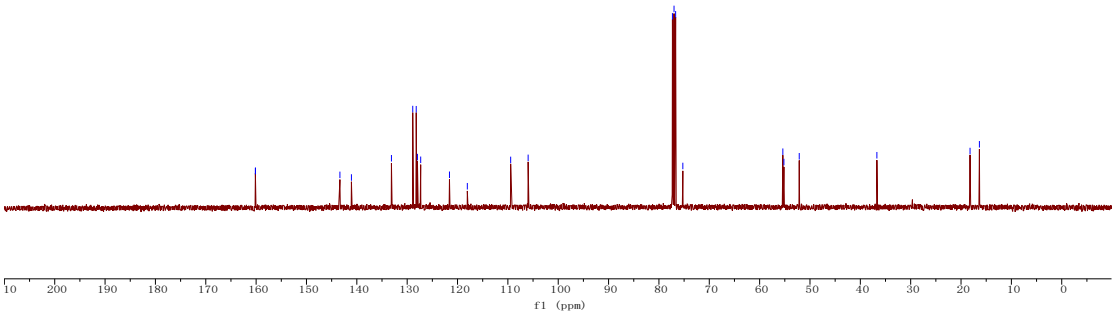
77.318
77.000
76.683
75.252
55.389
55.179
52.133
36.712
18.211
16.350

Ph
CN
O
S
O
MeO
O

3ga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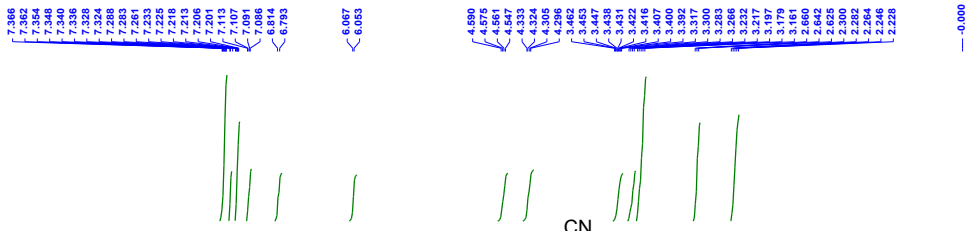
f1 (ppm)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7.225
7.218
7.213
7.206
7.201
7.113
7.107
7.091
7.086
6.814
6.793
6.067
6.053
4.590
4.576
4.561
4.547
4.333
4.324
4.305
4.296
3.462
3.455
3.447
3.438
3.431
3.422
3.416
3.407
3.400
3.392
3.317
3.300
3.283
3.266
3.232
3.217
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2.228
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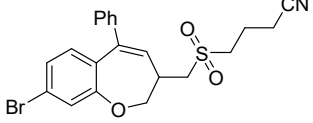
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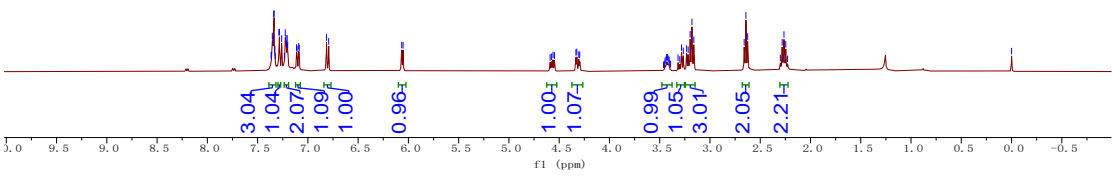
S
O
Br
O

3ha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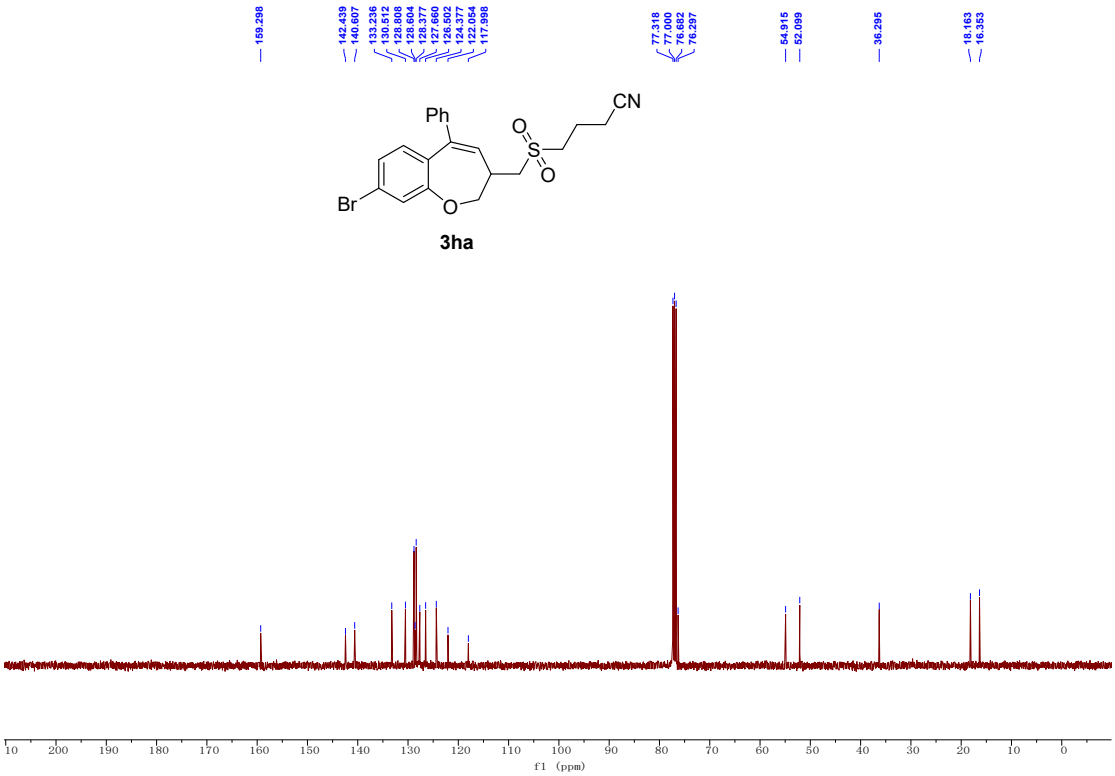
1.07
0.99
1.05
3.01
2.05
2.21
f1 (ppm)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128.604
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126.502
124.377
122.054
117.998
77.318
77.000
76.682
76.297
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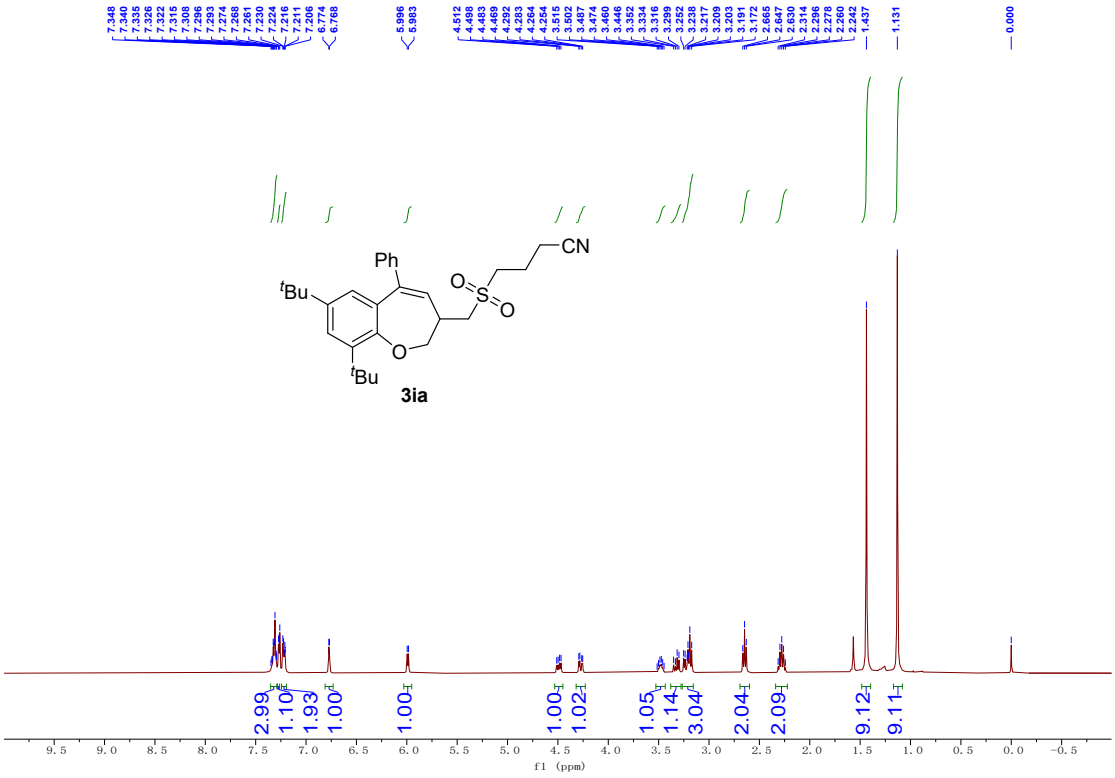
36.295
18.163
16.353
Ph
CN
O
S
O
Br
O
f1 (ppm)

3ha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7.296
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7.268
7.261
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7.224
7.216
7.211
7.206
6.774
6.768
5.996
5.983
4.512
4.498
4.483
4.469
4.282
4.268
4.264
4.254
3.515
3.502
3.487
3.474
3.460
3.446
3.352
3.334
3.316
3.299
3.252
3.238
3.217
3.209
3.203
3.191
3.172
2.665
2.647
2.630
2.314
2.296
2.278
2.260
2.242
1.437
1.131
0.000
Ph
CN
tBu
O
S
O
O
tBu
2.99
1.10
1.93
1.00
1.00
1.00
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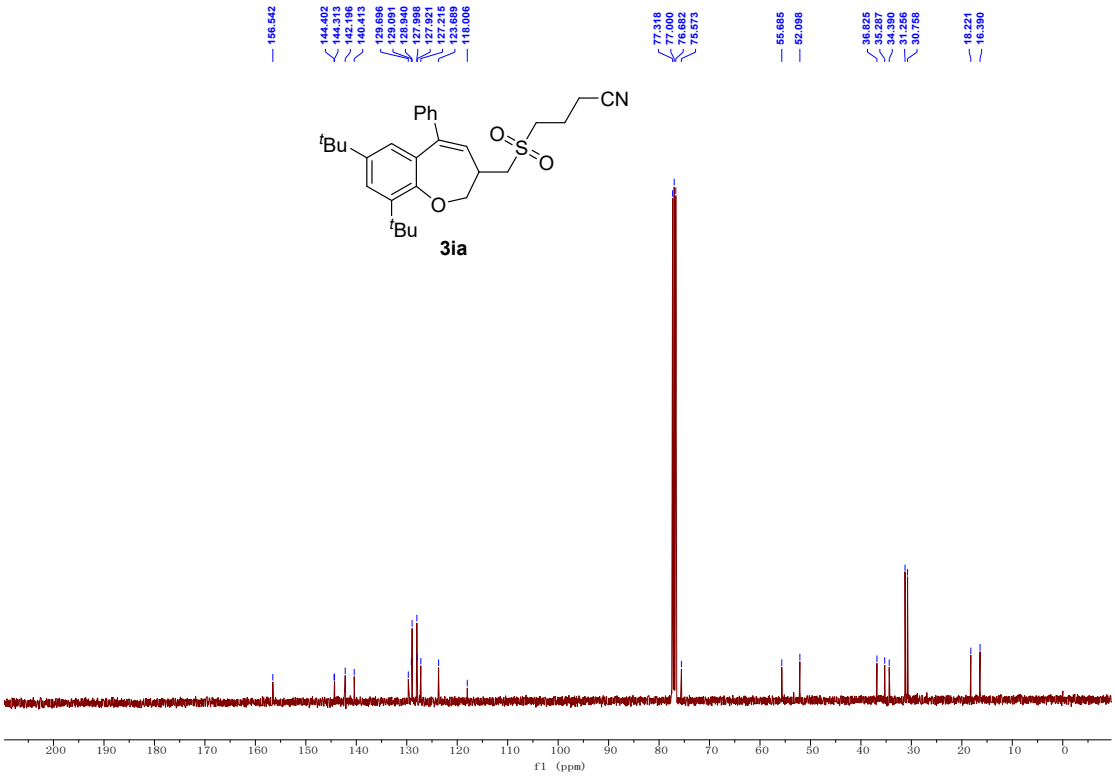
1.05
1.14
3.04
2.04
2.09
9.12
9.11
f1 (ppm)

3ia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144.313
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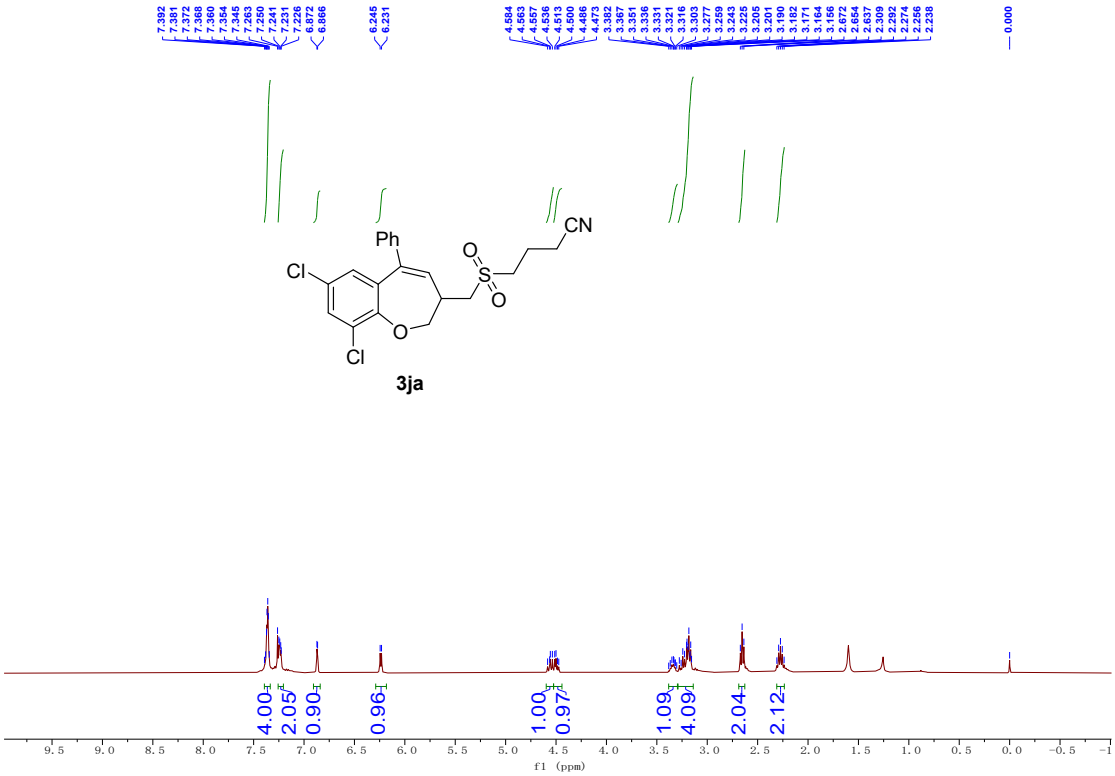
128.940
127.998
127.921
127.215
123.689
118.006
77.318
77.000
76.682
75.573
55.685
52.098
36.825
35.287
34.390
31.256
30.758
18.221
16.390
Ph
CN
O
S
O
tBu
O
tBu
3ia
f1 (ppm)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7.263
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7.241
7.231
7.226
6.872
6.866
6.245
6.231
4.584
4.563
4.557
4.536
4.513
4.500
4.486
4.473
3.382
3.367
3.351
3.336
3.331
3.321
3.316
3.303
3.277
3.259
3.243
3.225
3.205
3.201
3.190
3.182
3.171
3.164
3.156
2.672
2.654
2.637
2.309
2.292
2.274
2.256
2.238
0.000
Ph
CN
Cl
O
S
O
O
Cl
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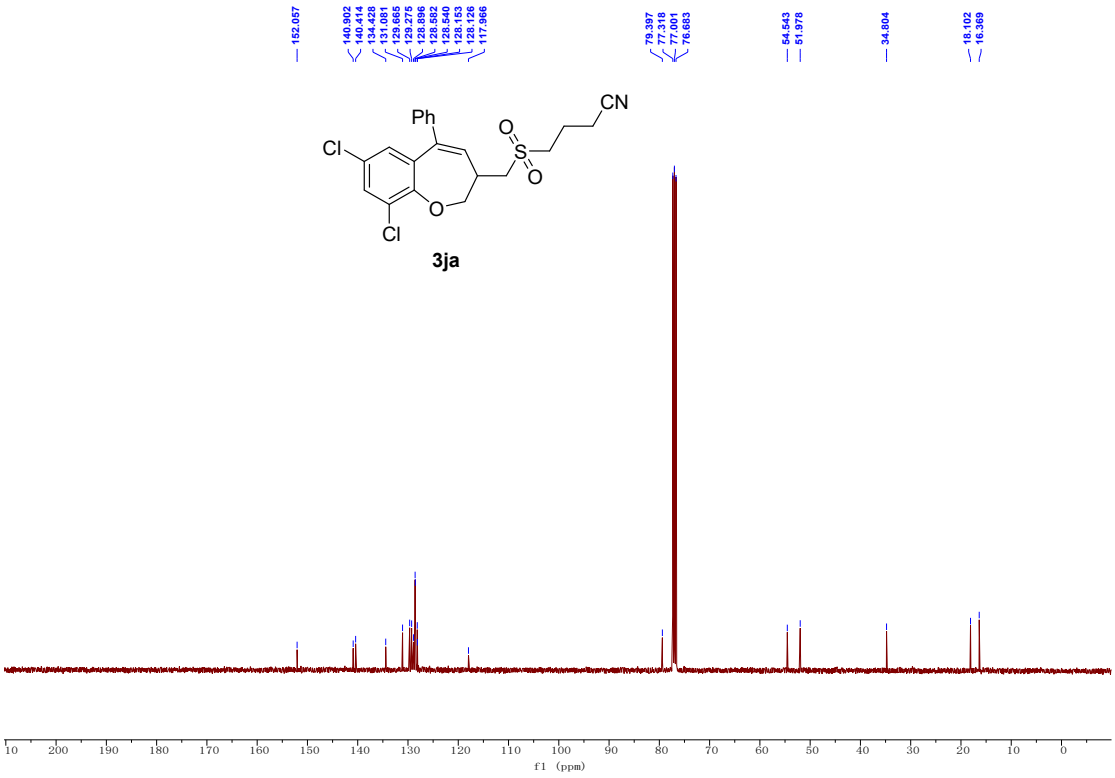
0.96
1.00
0.97
1.09
4.09
2.04
2.12
f1 (ppm)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128.153
128.126
117.966
79.397
77.316
77.001
76.683
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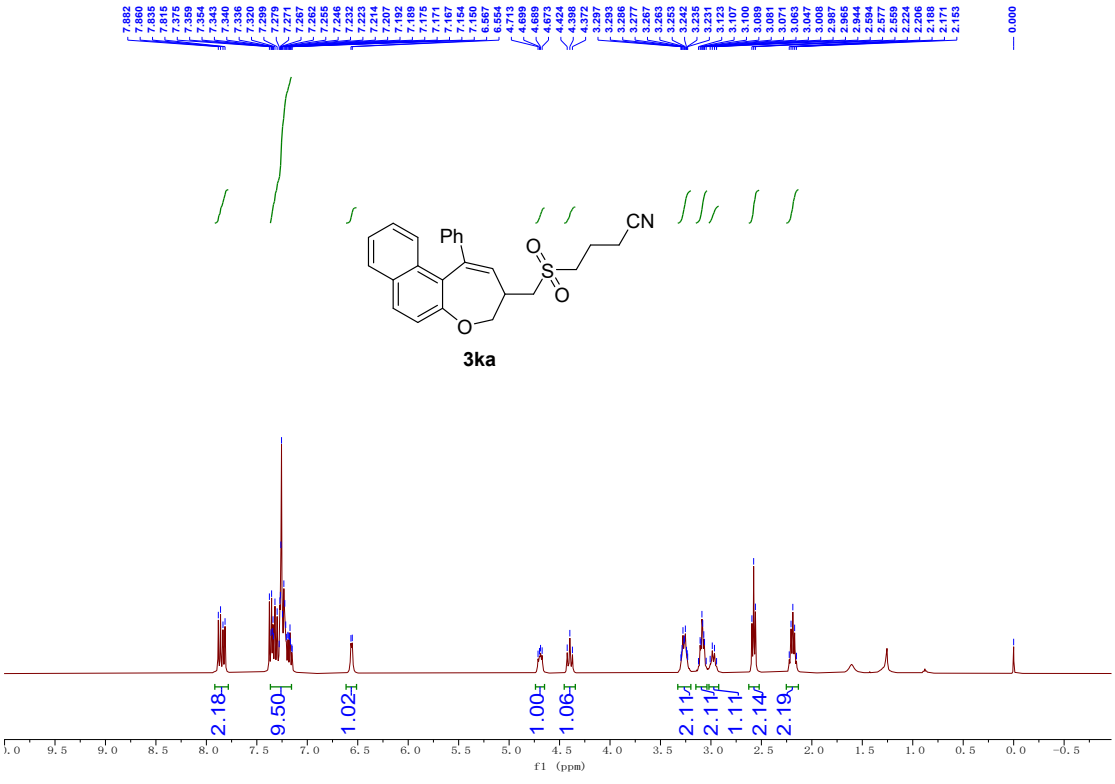
18.102
16.369
Ph
Cl
Cl
O
S
O
O
CN
3ja
f1 (ppm)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7.343
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7.336
7.320
7.299
7.279
7.271
7.267
7.262
7.255
7.246
7.232
7.223
7.214
7.207
7.192
7.189
7.175
7.171
7.167
7.154
7.150
6.567
6.554
4.713
4.699
4.689
4.673
4.424
4.398
4.372
3.297
3.293
3.286
3.277
3.267
3.263
3.253
3.242
3.235
3.231
3.123
3.107
3.100
3.089
3.081
3.071
3.063
3.047
3.008
2.987
2.965
2.944
2.894
2.577
2.559
2.224
2.206
2.188
2.171
2.153
0.000
Ph
O
S
O
O
CN
3ka
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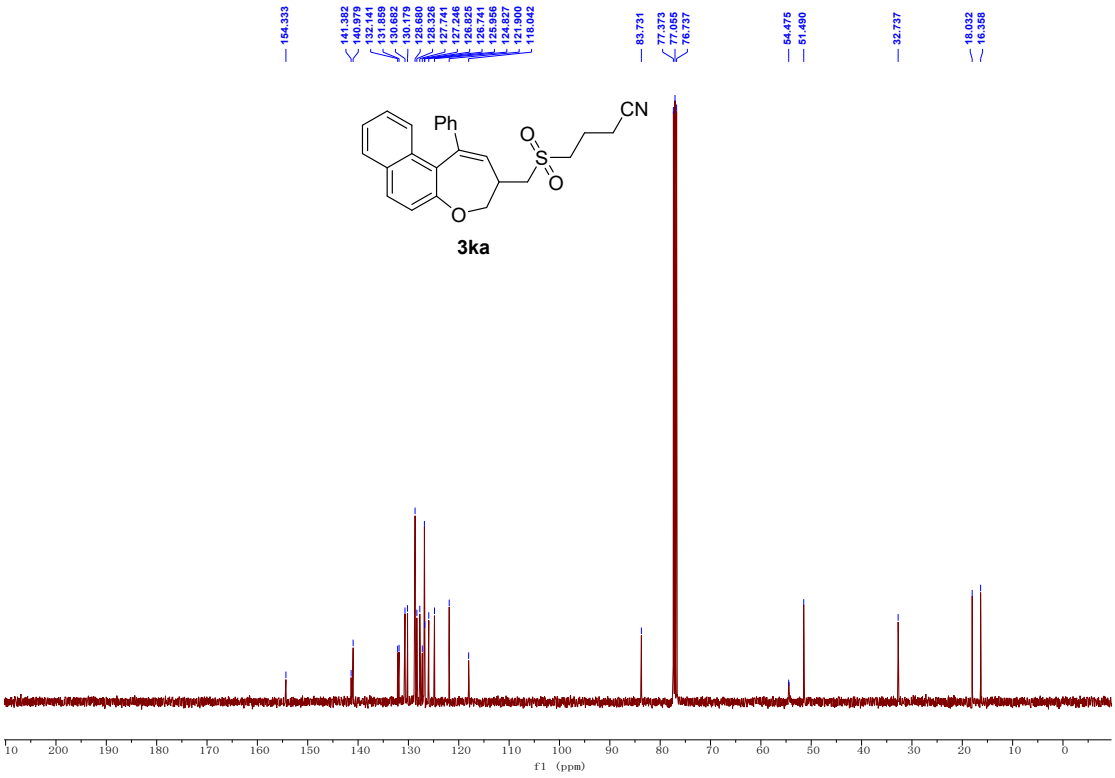
1.02
1.00
1.06
2.11
2.11
1.11
2.14
2.19
f1 (ppm)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130.173
128.680
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127.741
127.246
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126.741
125.956
124.257
121.900
118.042
83.731
77.373
77.055
76.737
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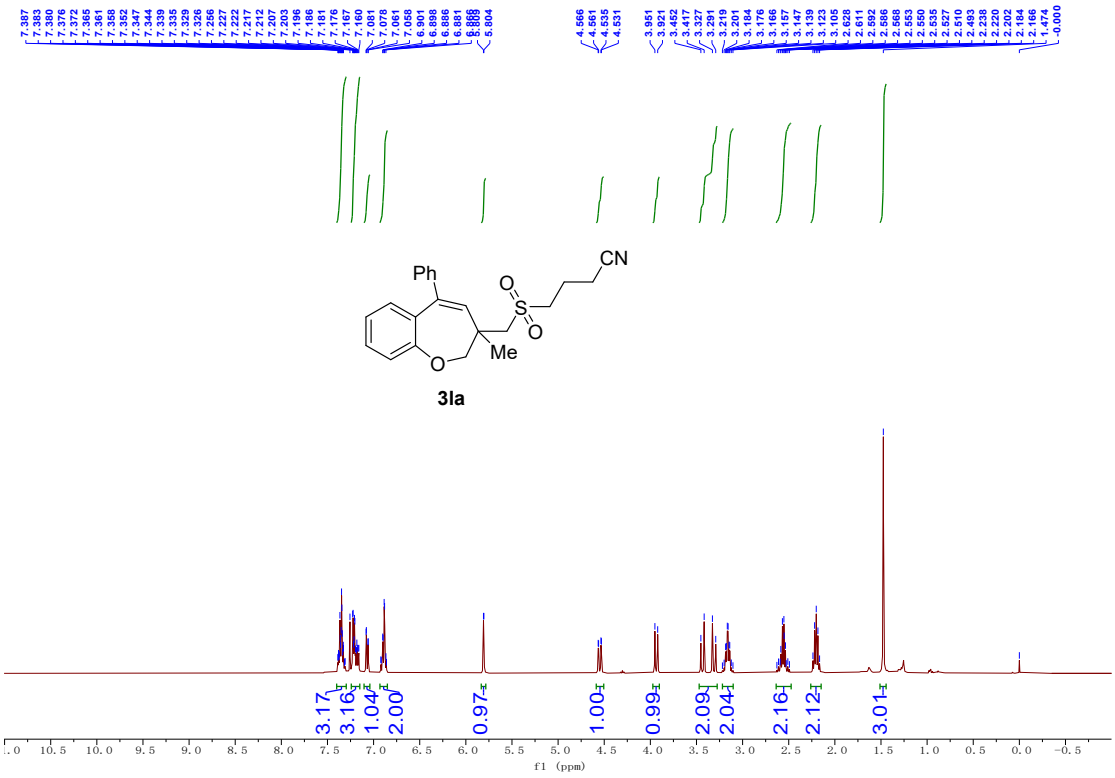
51.490
32.737
18.032
16.358
Ph
O
S
O
CN
O
3ka
f1 (ppm)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7.344
7.339
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7.329
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7.256
7.227
7.222
7.217
7.212
7.207
7.203
7.198
7.186
7.181
7.176
7.167
7.160
7.081
7.078
7.061
7.058
6.901
6.898
6.886
6.881
6.806
6.804
4.566
4.561
4.535
4.531
3.951
3.921
3.452
3.417
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3.219
3.201
3.184
3.176
3.166
3.157
3.147
3.139
3.123
3.105
2.628
2.611
2.592
2.586
2.568
2.553
2.550
2.535
2.527
2.510
2.493
2.238
2.220
2.202
2.184
2.166
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0.000
Ph
O
S
O
CN
O
Me
3la
3.17
3.16
1.04
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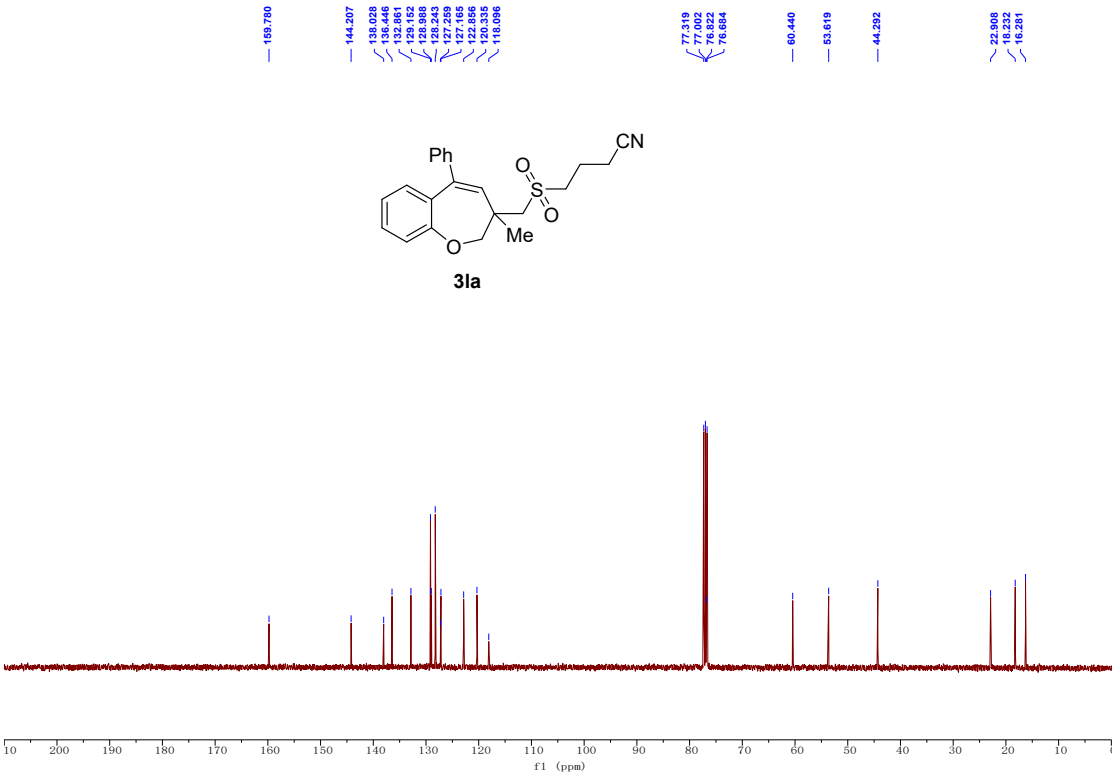
0.97
1.00
0.99
2.09
2.04
2.16
2.12
3.01
f1 (ppm)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122.856
120.335
118.096
77.319
77.002
76.822
76.684
60.440
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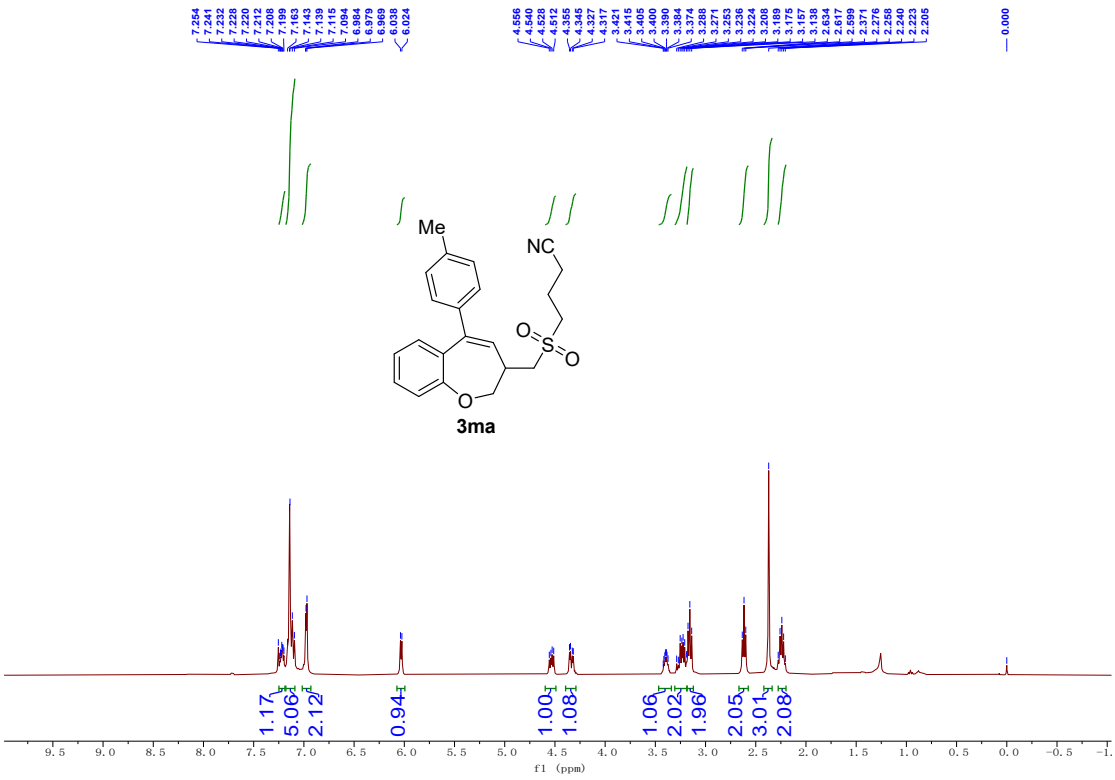
22.908
18.232
16.281
Ph
O
S
O
CN
Me
O
3la
f1 (ppm)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7.208
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7.143
7.139
7.115
7.094
6.984
6.979
6.969
6.038
6.024
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4.540
4.528
4.512
4.355
4.346
4.327
4.317
3.421
3.415
3.405
3.400
3.390
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3.224
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3.157
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2.617
2.599
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2.276
2.258
2.240
2.223
2.205
0.000
Me
NC
O
S
O
O
3ma
1.17
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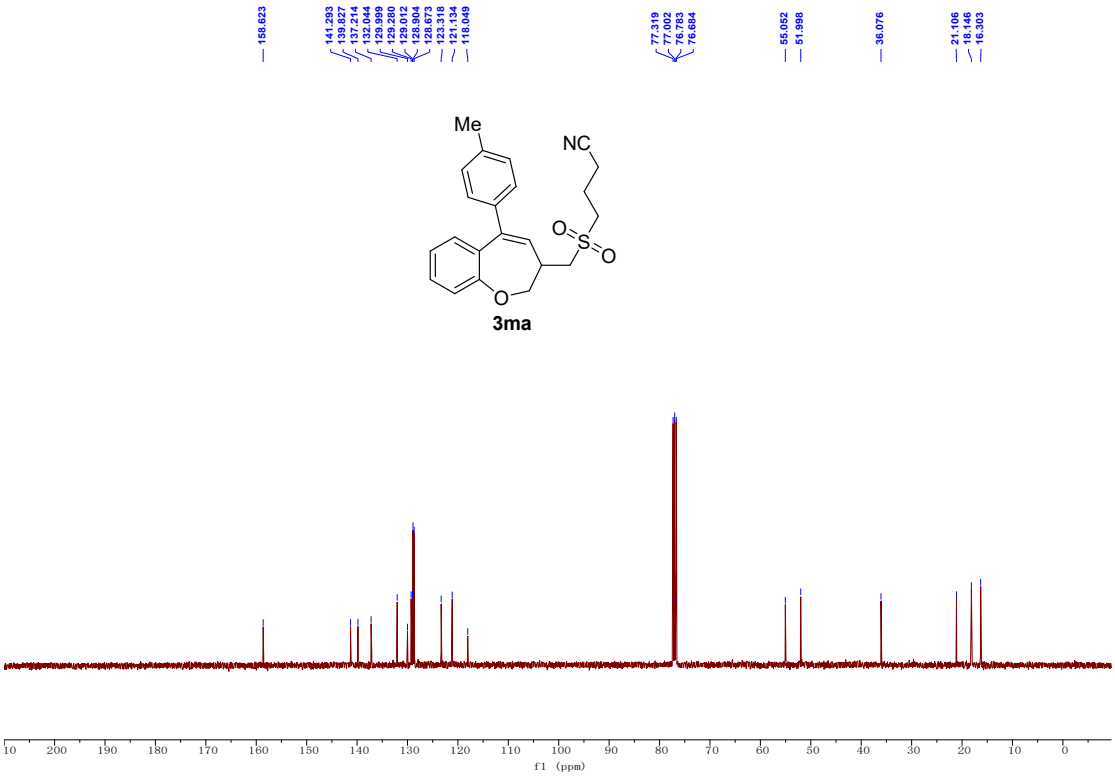
1.00
1.08
1.06
2.02
1.96
2.05
3.01
2.08
f1 (ppm)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77.002
76.783
76.684
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21.106
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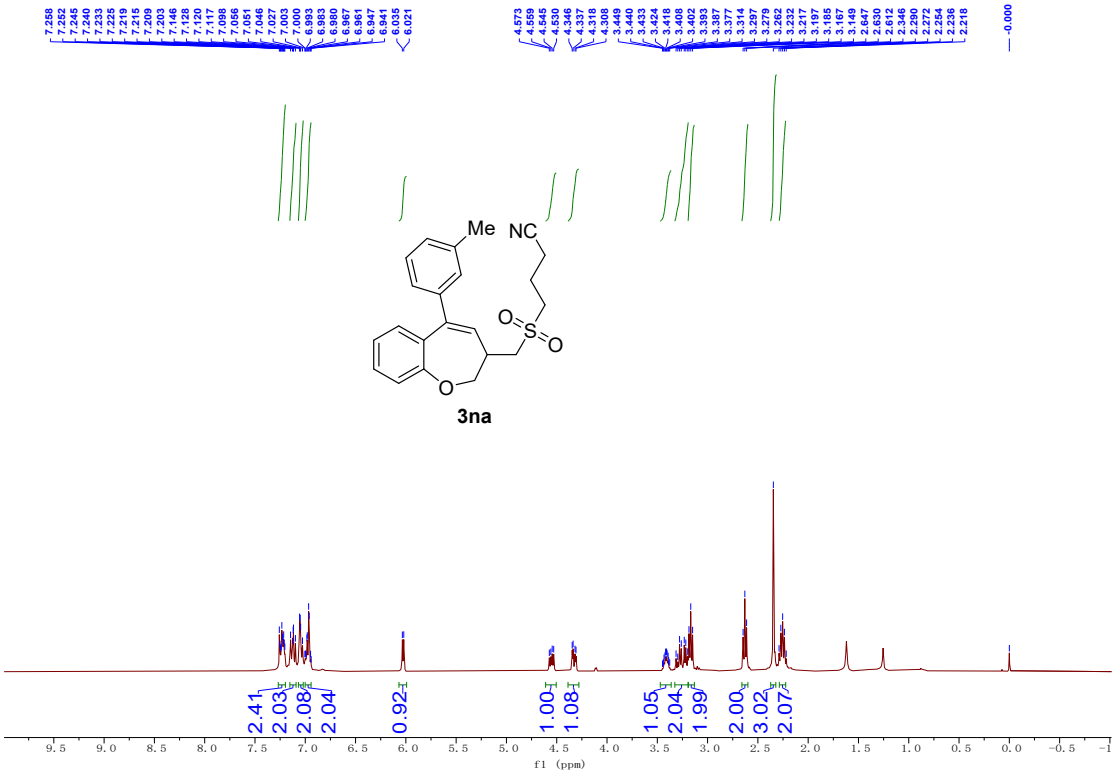
Me
NC
O
S
O
O
3ma
f1 (ppm)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7.120
7.117
7.098
7.056
7.051
7.046
7.027
7.003
7.000
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6.967
6.961
6.947
6.941
6.035
6.021
4.573
4.559
4.545
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4.337
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3.424
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3.408
3.402
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3.232
3.217
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3.185
3.167
3.149
2.647
2.630
2.612
2.346
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2.254
2.236
2.218
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Me
NC
O
S
O
O
3na
2.41
2.03
2.08
2.04
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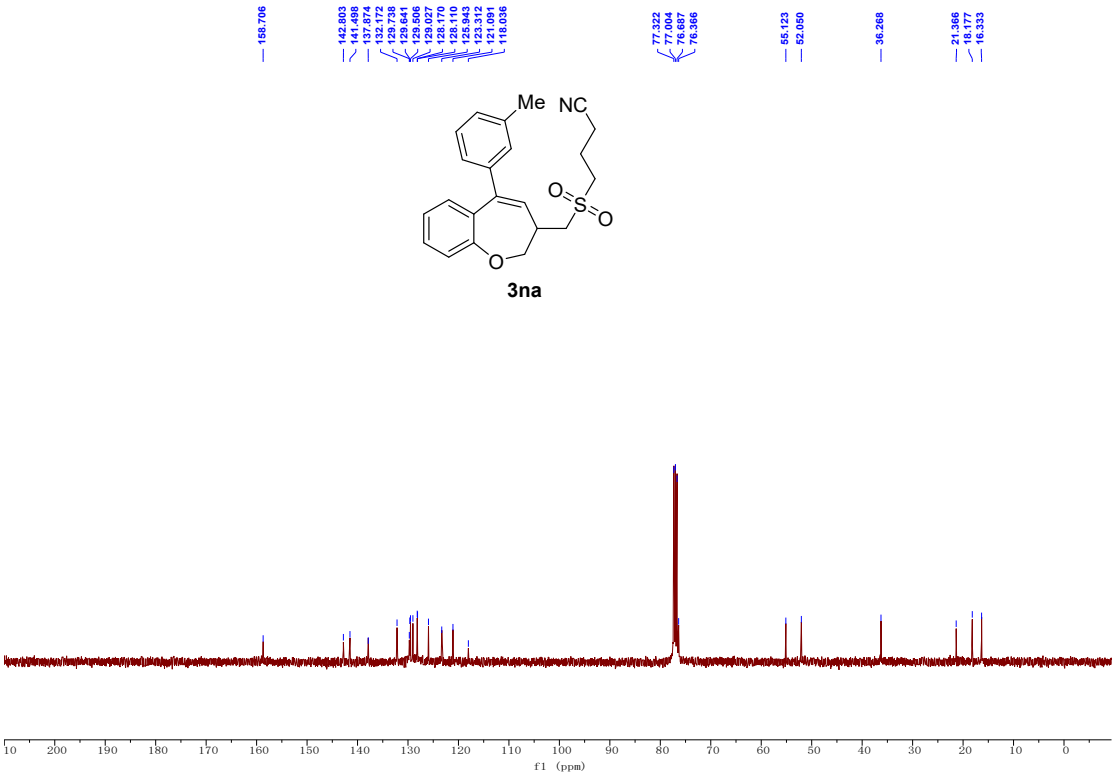
1.00
1.08
1.05
2.04
1.99
2.00
3.02
2.07
f1 (ppm)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125.943
123.312
121.091
118.036
77.322
77.004
76.687
76.366
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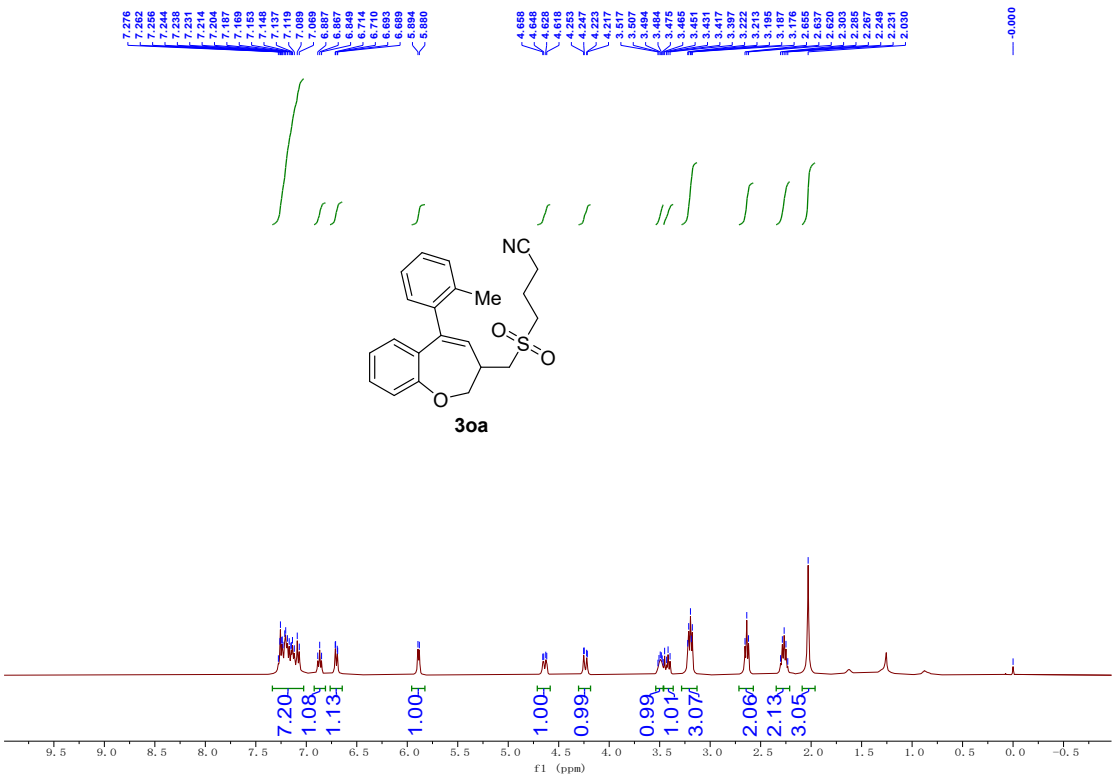
36.288
21.366
18.377
16.333
Me
NC
O
S
O
O
3na
f1 (ppm)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5.894
5.880
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4.648
4.628
4.618
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4.223
4.217
3.517
3.507
3.494
3.484
3.475
3.465
3.451
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3.397
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3.176
2.655
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2.285
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NC
Me
O
S
O
O
3oa
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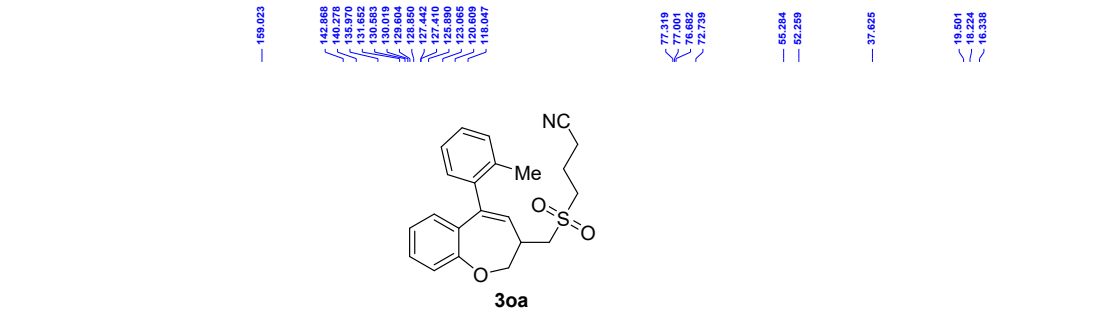
2.13
3.05
f1 (ppm)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123.065
120.609
118.047
77.319
77.001
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18.224
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NC
Me
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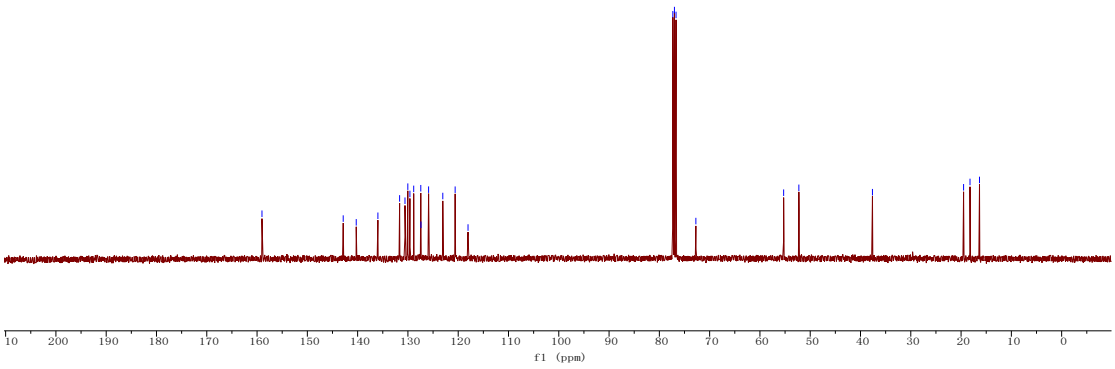
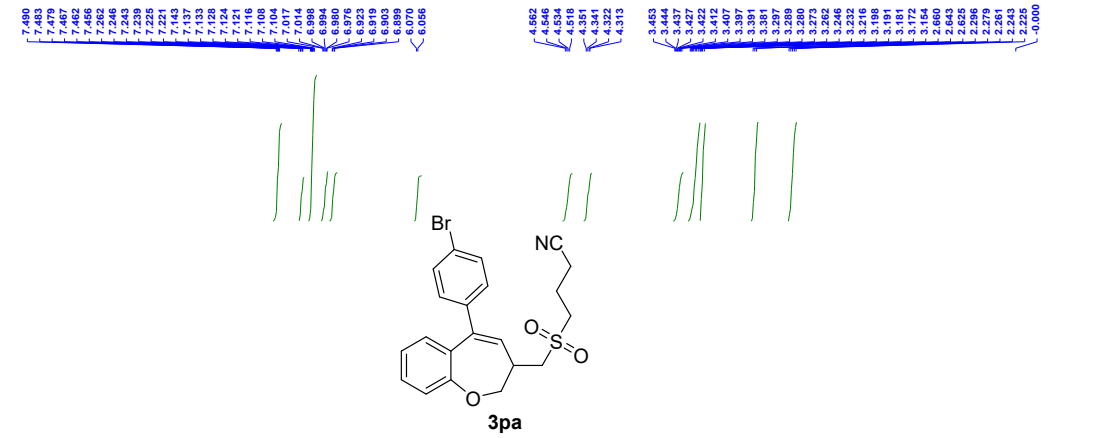
S
O
O

3oa


f1 (ppm)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7.246
7.243
7.239
7.225
7.221
7.143
7.137
7.133
7.128
7.124
7.121
7.116
7.108
7.104
7.017
7.014
6.998
6.994
6.980
6.976
6.923
6.919
6.903
6.899
6.070
6.056
4.562
4.546
4.534
4.518
4.351
4.341
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3.453
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3.422
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3.407
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3.172
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2.660
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2.279
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Br
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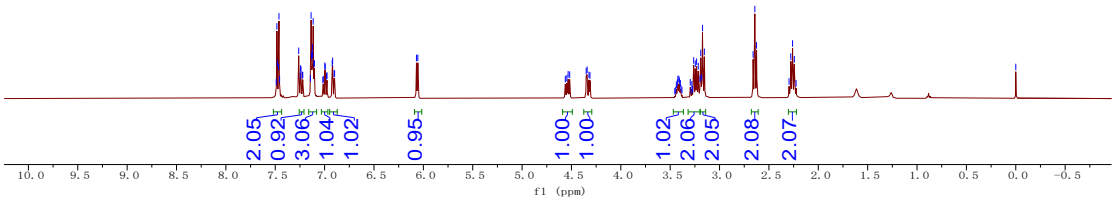
S
O
O

3pa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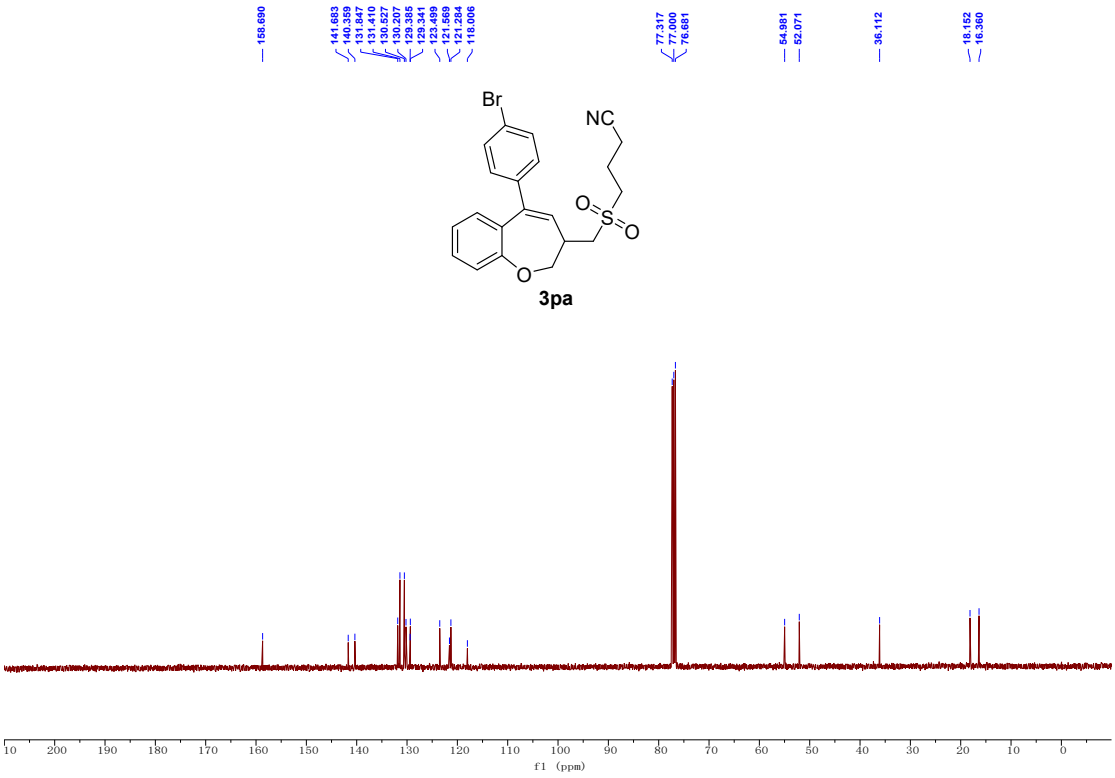
2.05
2.08
2.07
f1 (ppm)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77.317
77.000
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36.112
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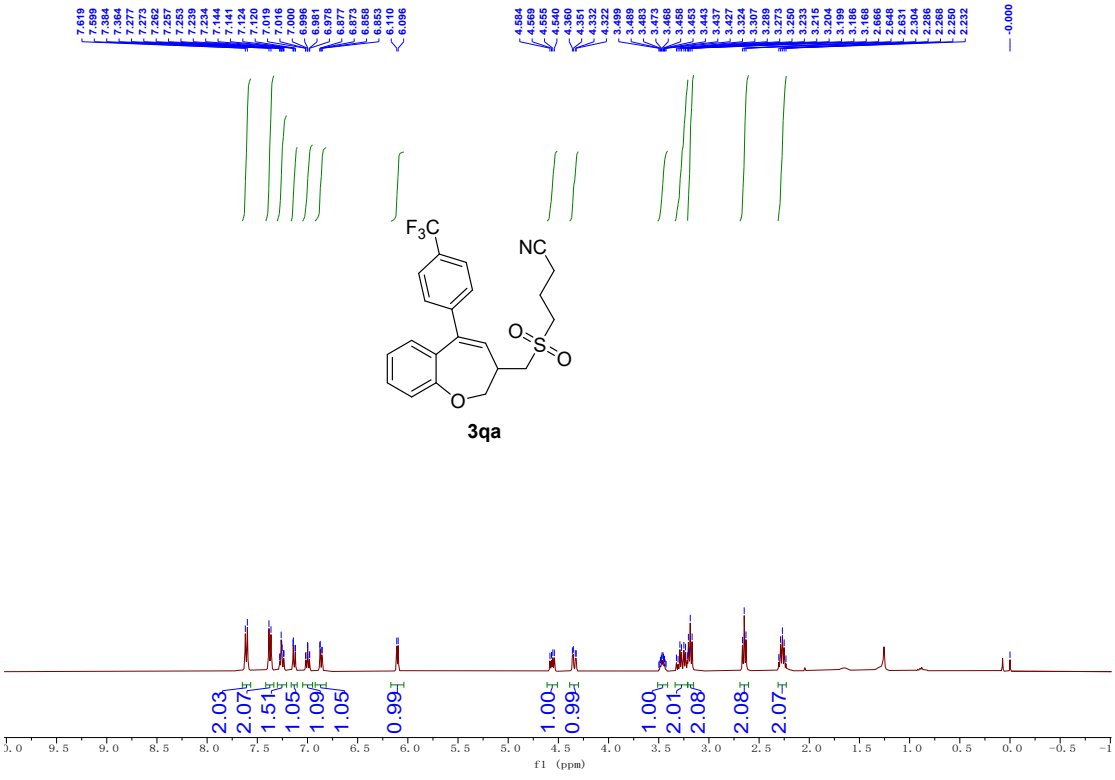
O
S
O
O
3pa
f1 (ppm)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7.384
7.364
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7.273
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7.257
7.253
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7.234
7.144
7.141
7.124
7.120
7.019
7.016
7.000
6.996
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6.877
6.873
6.858
6.853
6.110
6.096
4.584
4.569
4.555
4.540
4.360
4.351
4.332
4.322
3.499
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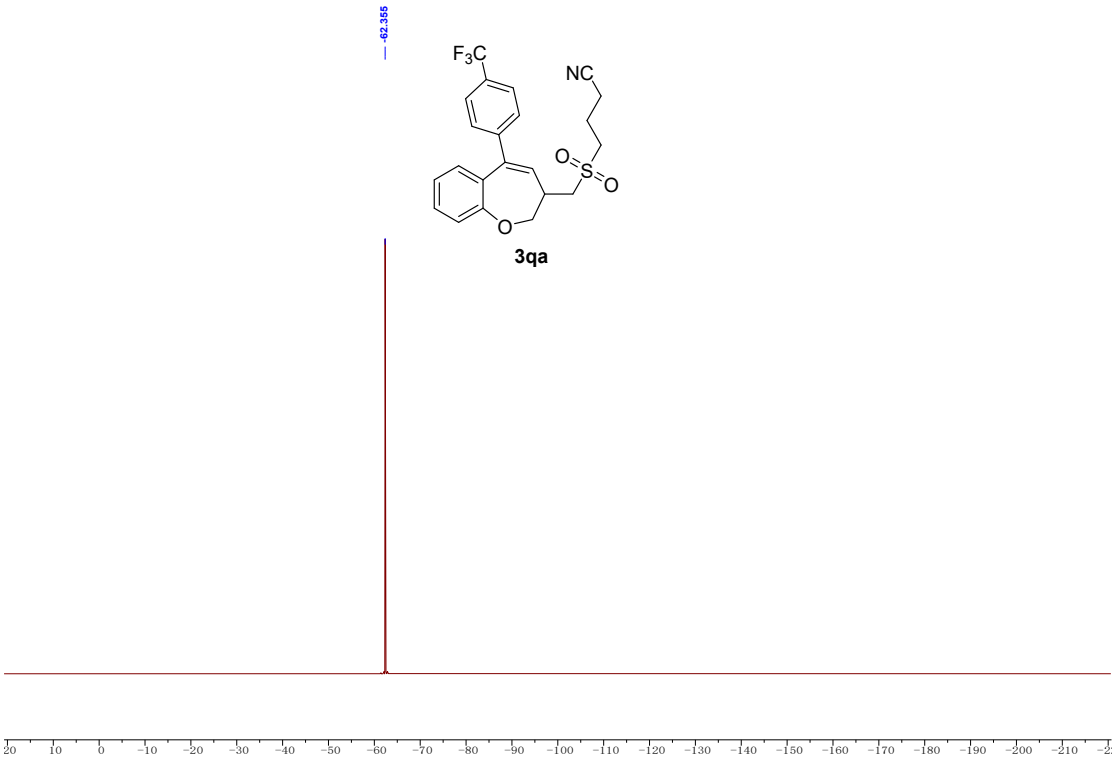
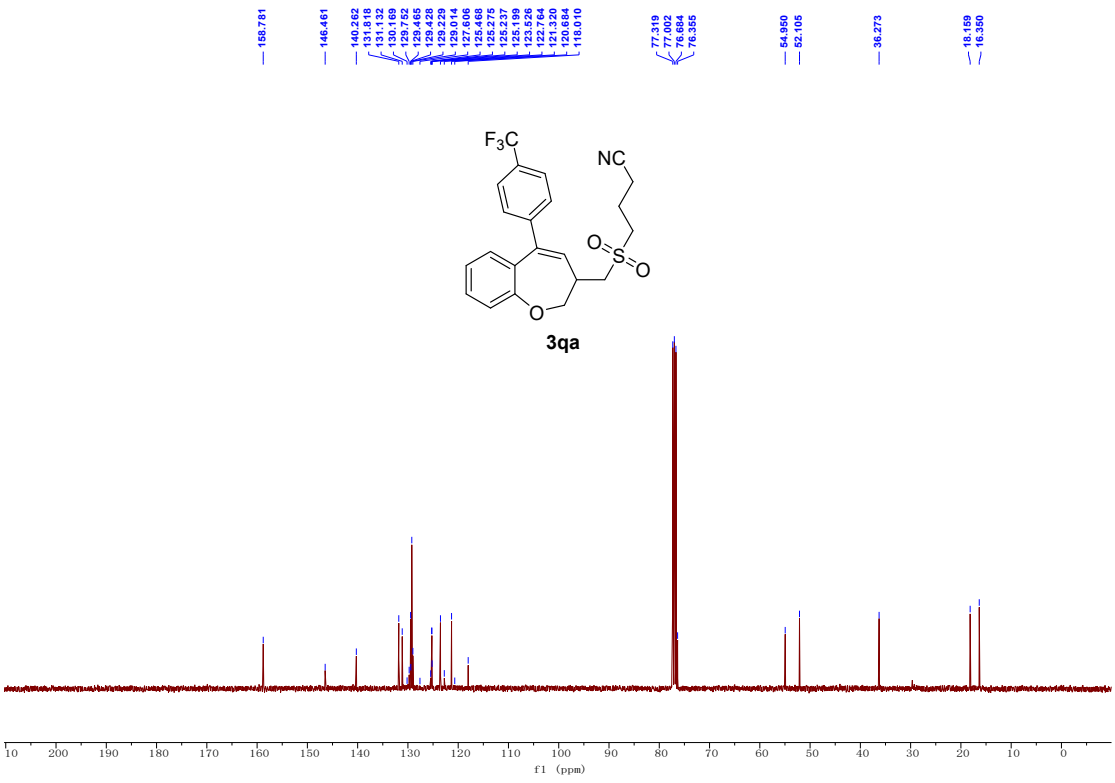
3.483
3.473
3.468
3.463
3.443
3.437
3.427
3.324
3.307
3.289
3.273
3.250
3.233
3.215
3.204
3.199
3.186
3.168
2.666
2.648
2.631
2.304
2.286
2.268
2.250
2.232
-0.000
F3C
NC
O
S
O
O
3qa
2.03
2.07
1.51
1.05
1.09
1.05
0.99
1.00
0.99
1.00
2.01
2.08
2.08
2.07
f1 (ppm)


-62.355
F3C
NC
O
S
O
O
3qa
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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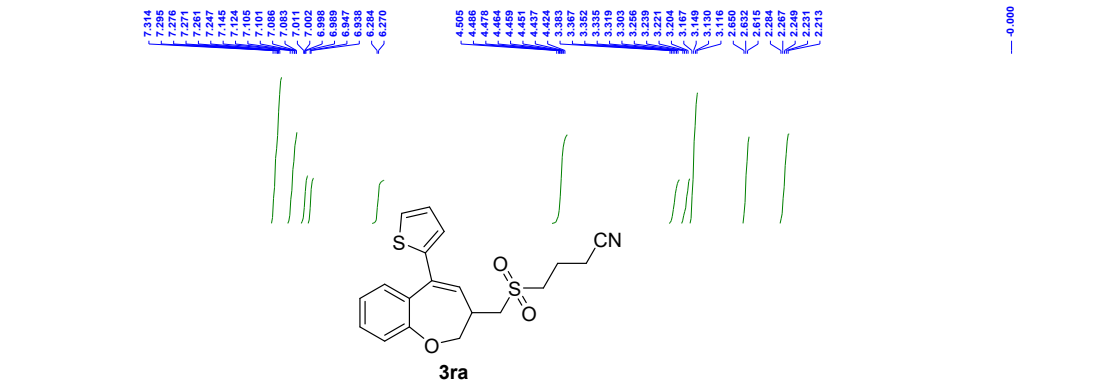
140.262
131.016
131.132
130.169
129.752
129.465
129.428
129.229
129.014
127.606
125.496
125.275
125.237
125.199
123.526
122.764
121.320
120.684
118.010
77.319
77.002
76.684
76.355
54.950
52.105
36.273
18.159
16.350
F3C
NC
O
S
O
O
3qa
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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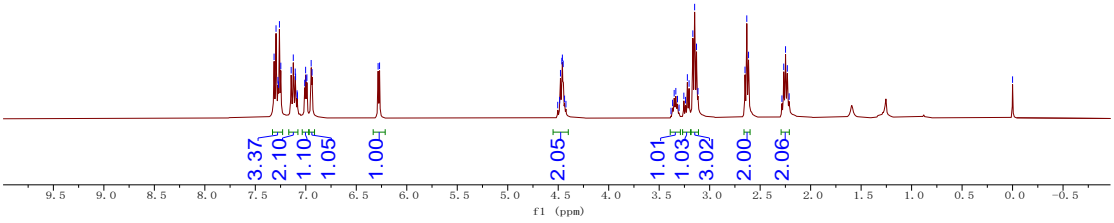
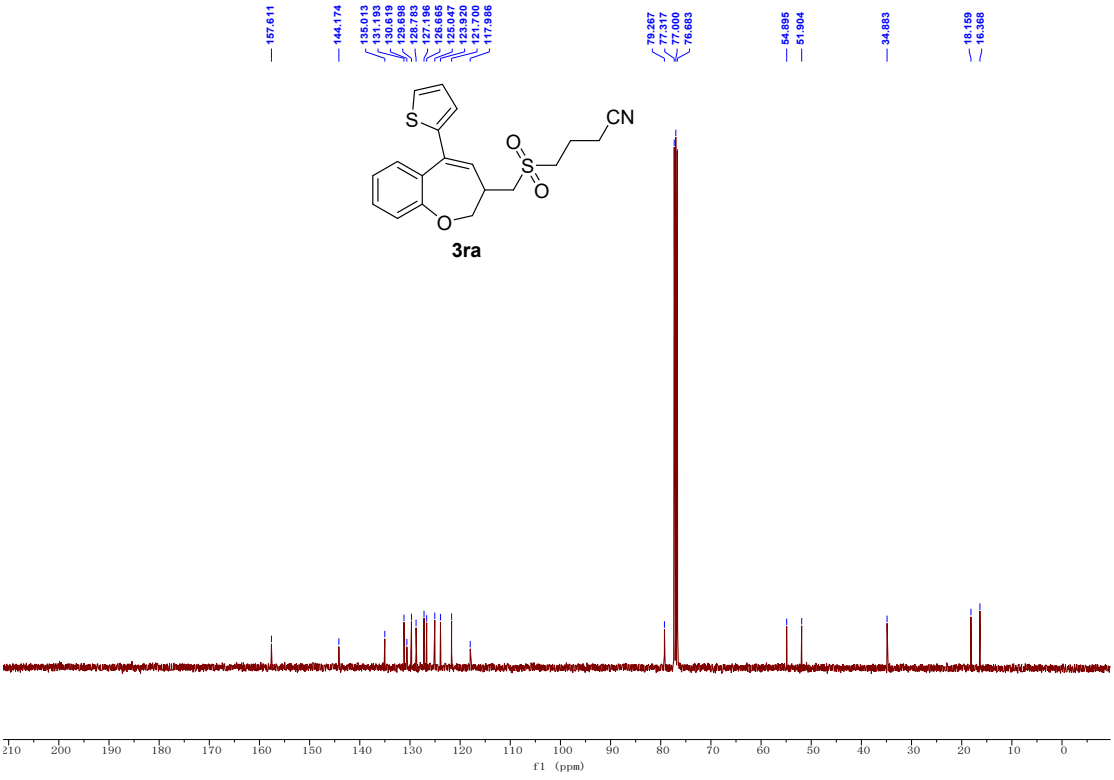
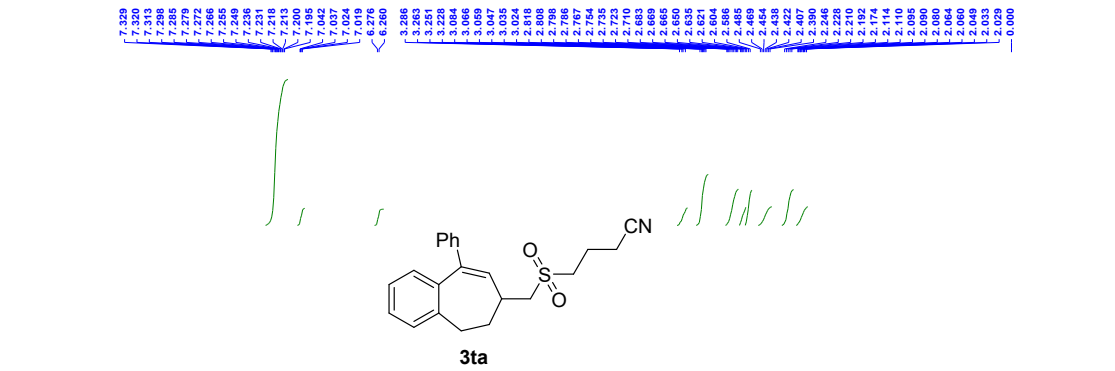
7.295
7.276
7.271
7.261
7.247
7.145
7.124
7.105
7.101
7.086
7.083
7.011
7.002
6.998
6.989
6.947
6.938
6.284
6.270
4.505
4.486
4.478
4.464
4.459
4.451
4.437
4.434
4.383
3.367
3.352
3.335
3.319
3.303
3.256
3.239
3.221
3.204
3.167
3.149
3.130
3.116
2.650
2.632
2.615
2.598
2.267
2.249
2.231
2.213
-0.000
S
O
S
O
CN
O

3ra

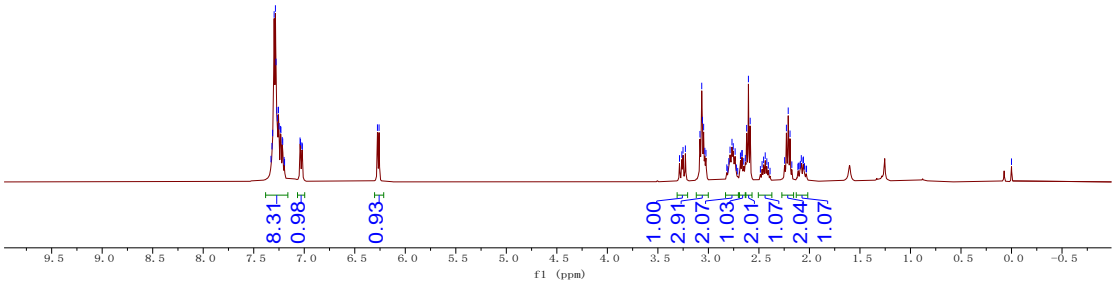

3.37
2.10
1.10
1.05
1.00
2.05
1.01
1.03
3.02
2.00
2.06
f1 (ppm)

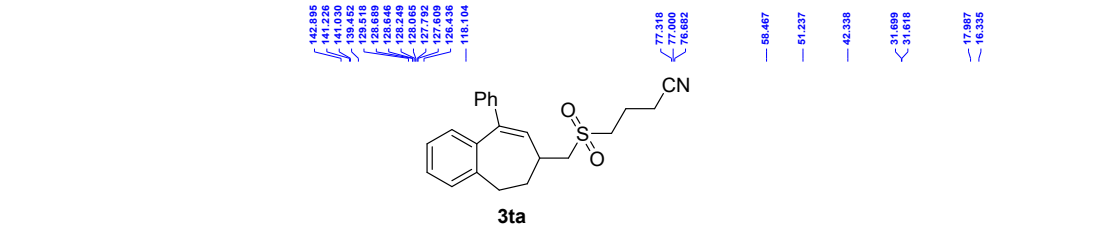

157.611
144.174
135.013
131.193
130.619
129.698
128.783
127.196
126.665
125.047
123.920
121.700
117.986
79.267
77.317
77.000
76.683
54.895
51.904
34.883
18.159
16.368
S
O
S
O
CN
O
f1 (ppm)

3ra

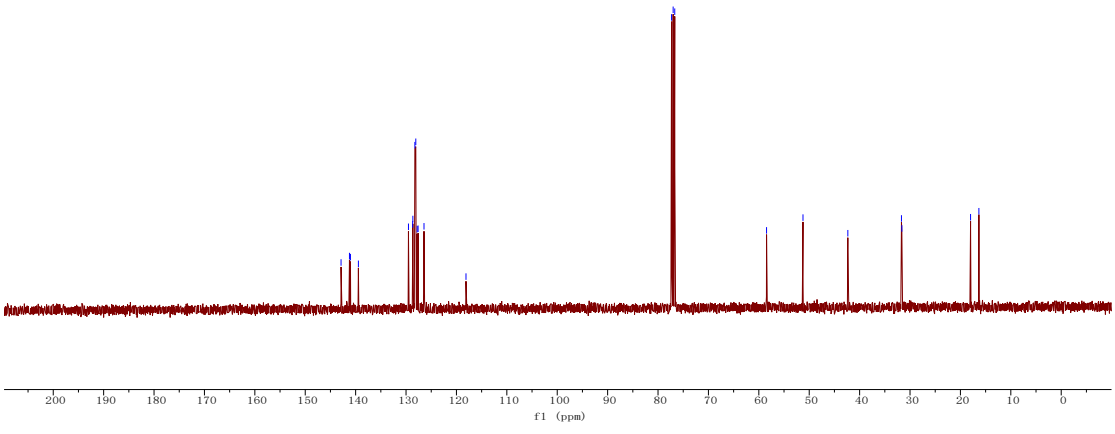

Ph
O
S
O
CN

3ta


8.31
0.98
0.93
1.00
2.91
2.07
1.03
2.01
1.07
2.04
1.07
f1 (ppm)


Ph
O
S
O
CN

3ta


f1 (ppm)


7.516
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7.338
7.319
7.307
7.299
7.272
7.263
7.255
7.238
7.219
7.201
7.183
7.010
6.990
6.982
6.966
6.947
6.928
6.127
6.113
4.439
4.132
3.276
3.254
3.236
3.217
3.197
3.165
3.149
3.124
3.106
3.087
3.071
3.046
3.035
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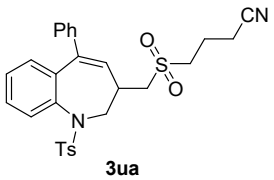
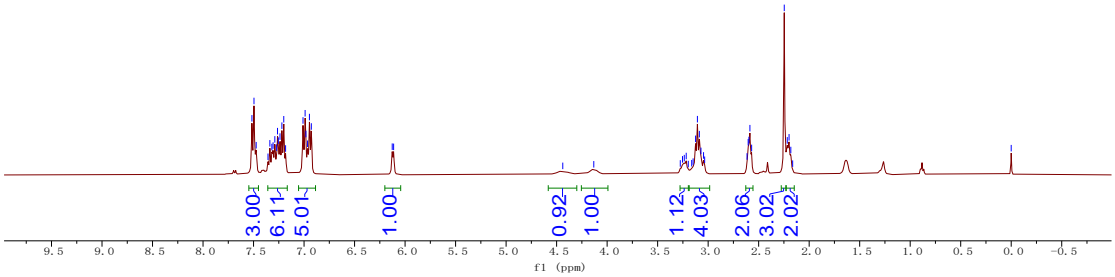
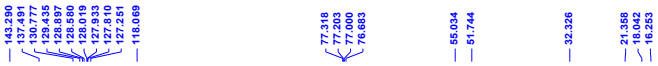
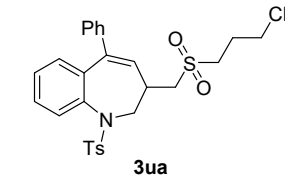
2.596
2.587
2.570
2.247
2.217
2.199
2.182
2.163
0.000


Ph
O
S
O
CN
N
Ts

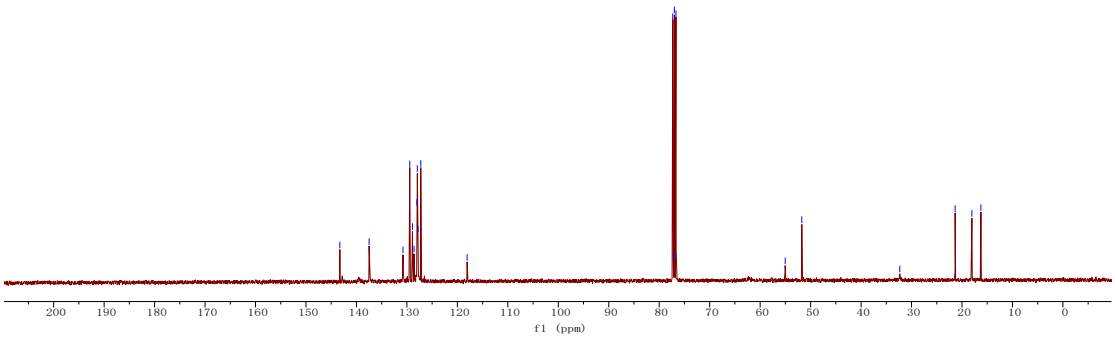
3ua

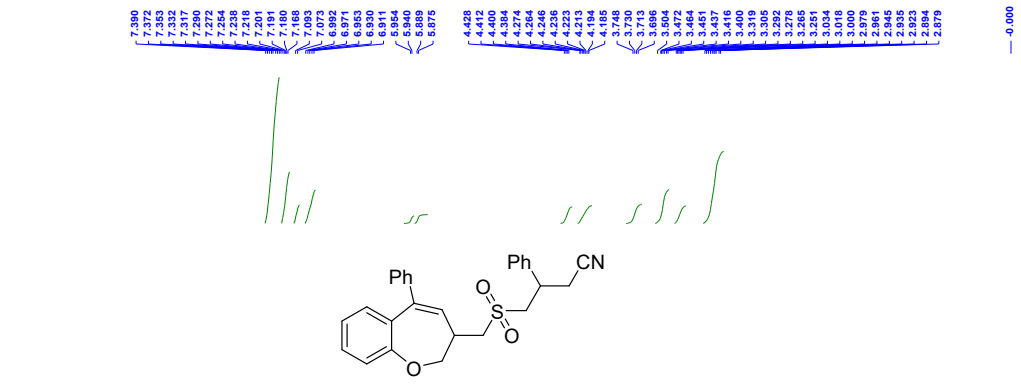

3.00
6.11
5.01
1.00
0.92
1.00
1.12
4.03
2.06
3.02
2.02
f1 (ppm)


143.290
137.491
130.777
129.435
128.897
128.580
128.019
127.933
127.810
127.251
118.069
77.318
77.203
77.000
76.683
55.034
51.744
32.326
21.358
18.042
16.253

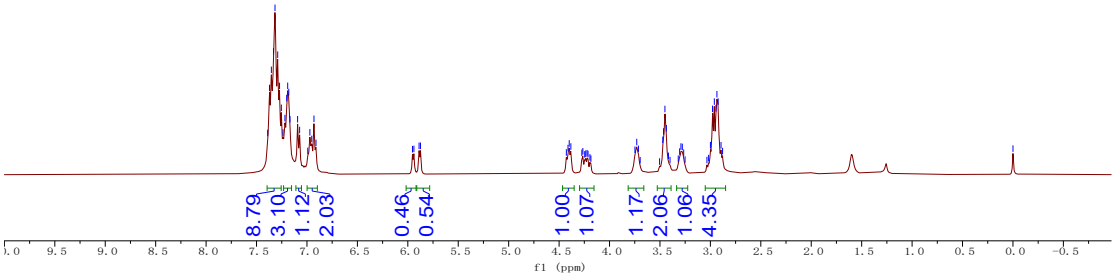

Ph
O
S
O
CN
N
Ts

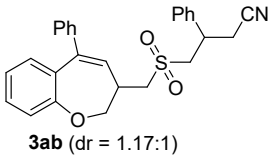
3ua


f1 (ppm)

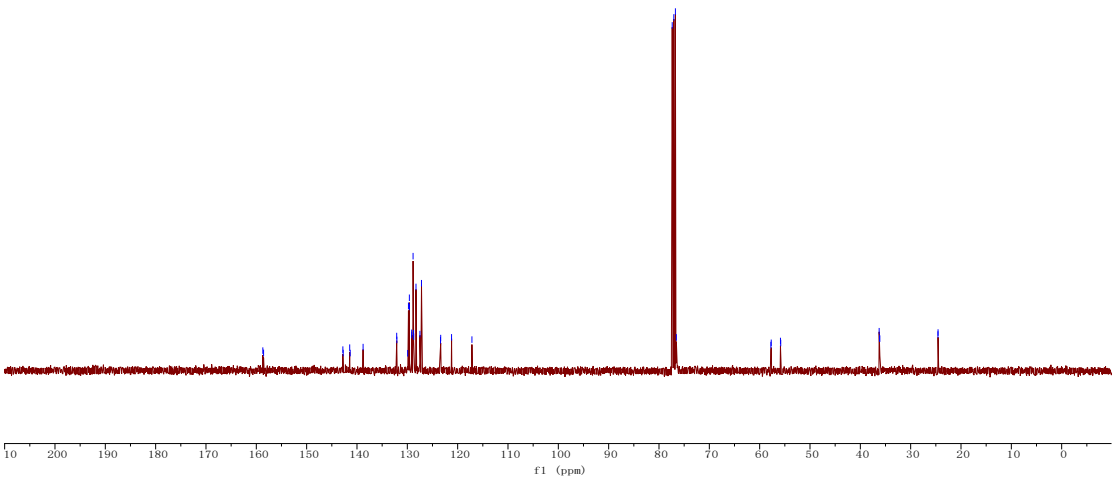


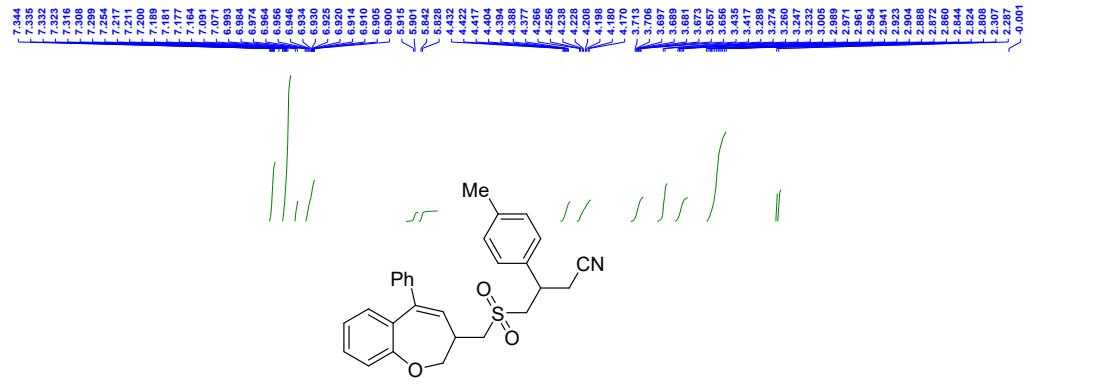
3ab (dr = 1.17:1)



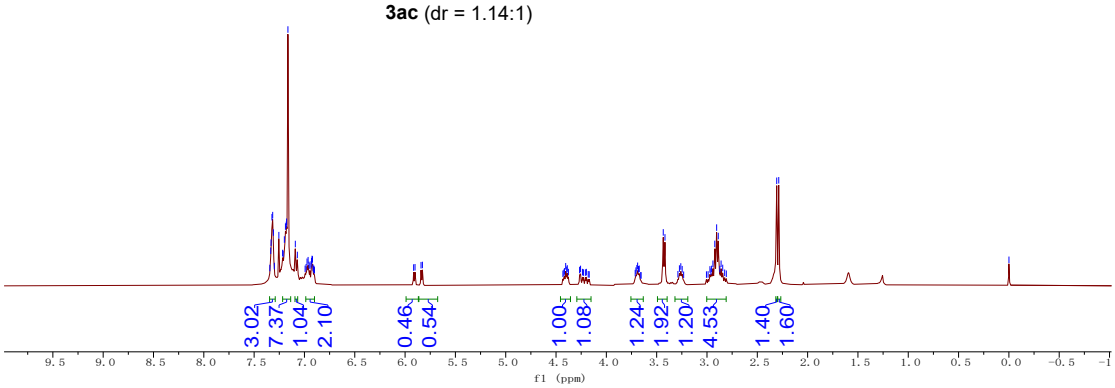


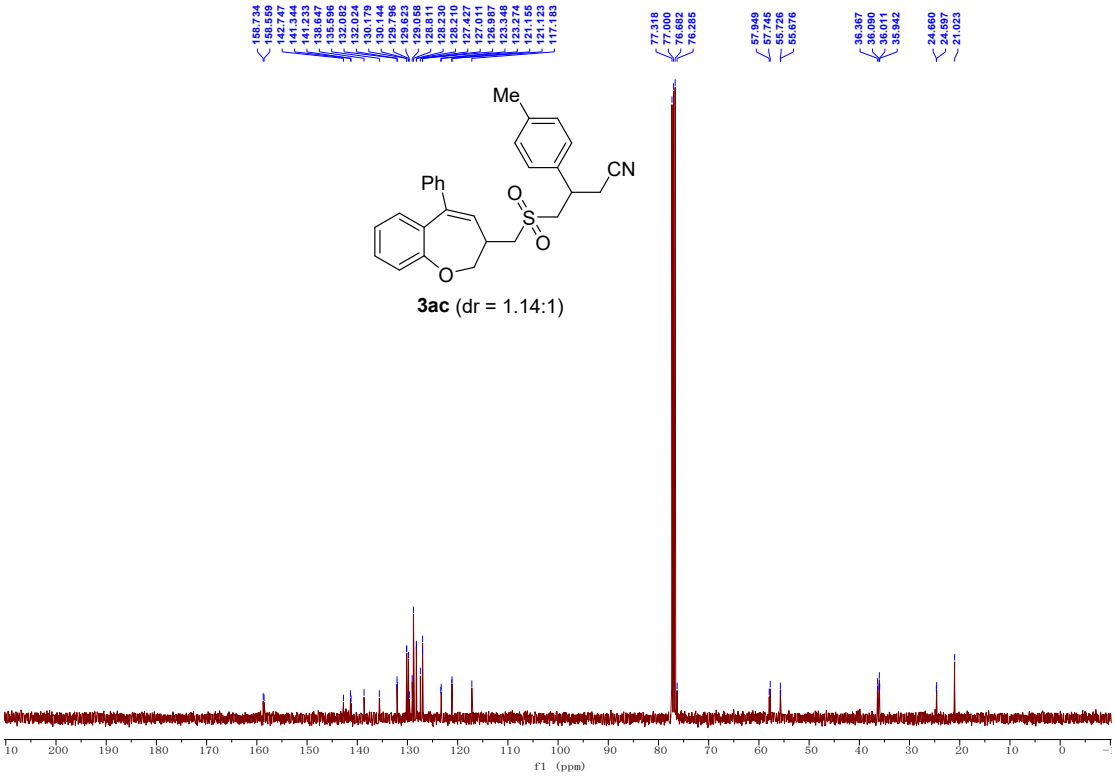
3ab (dr = 1.17:1)



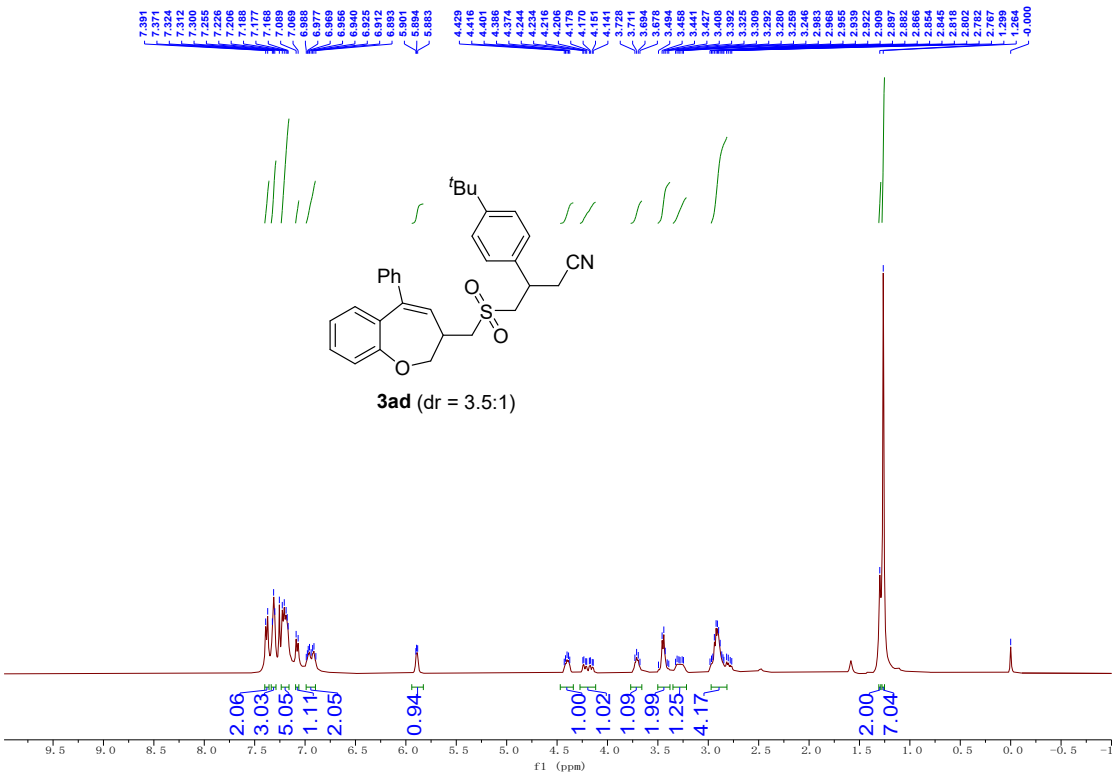


3ac (dr = 1.14:1)

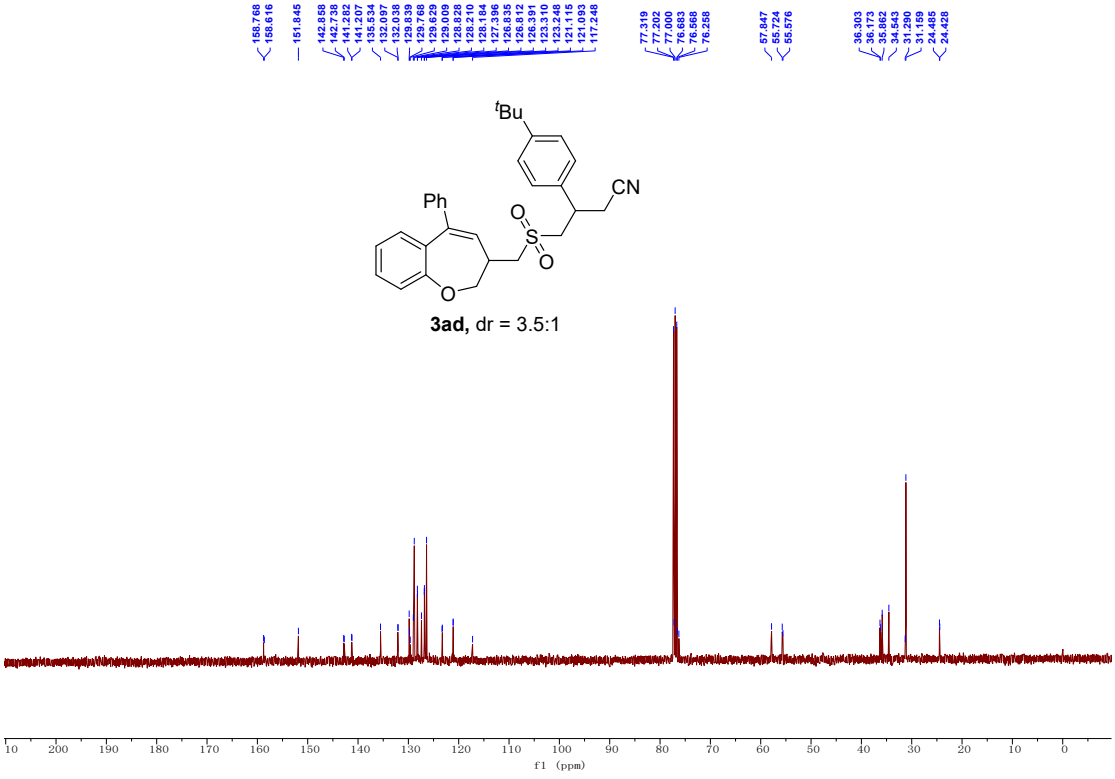




3ac (dr = 1.14:1)



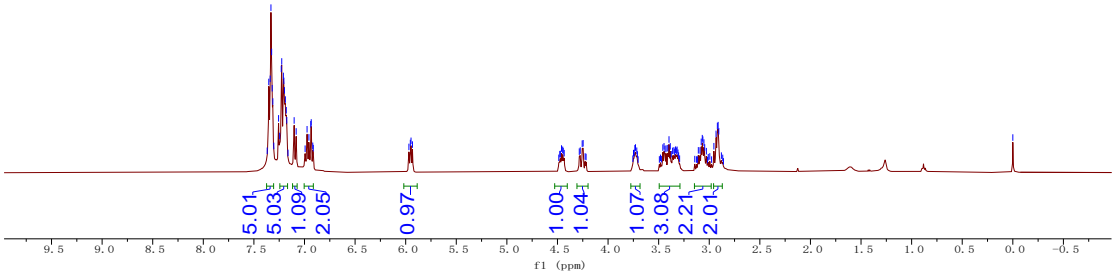
3ad (dr = 3.5:1)

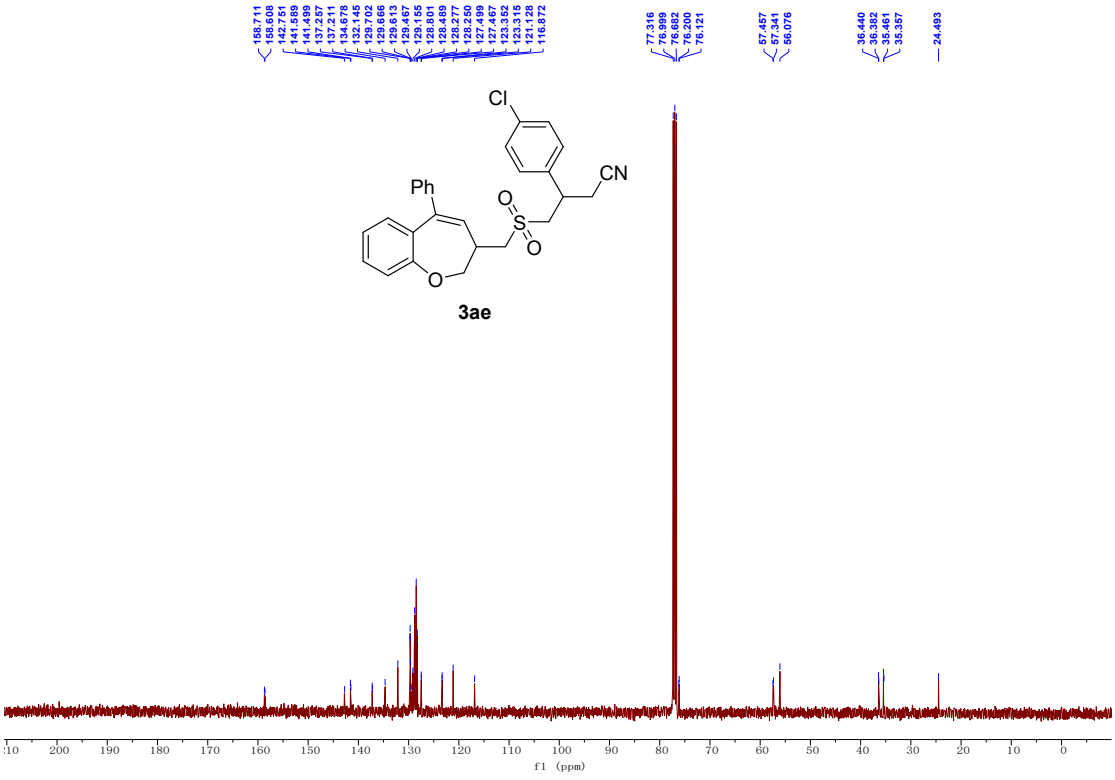


3ad, dr = 3.5:1

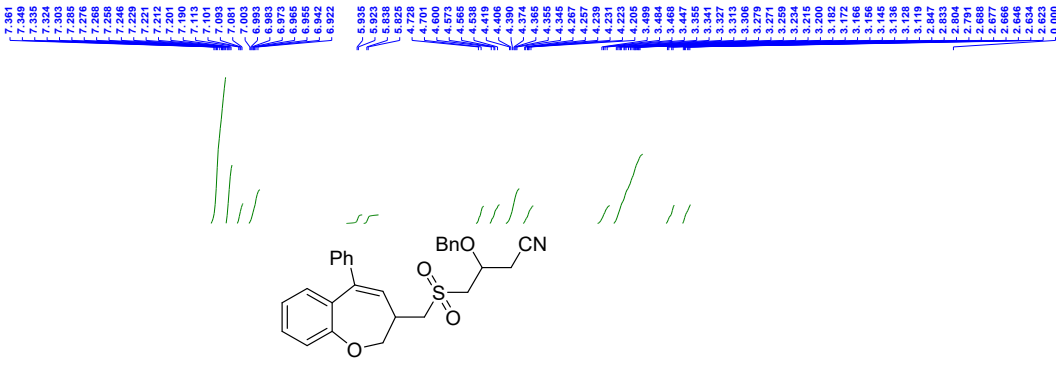

Cl
CN
Ph
O
S
O
O

3ae

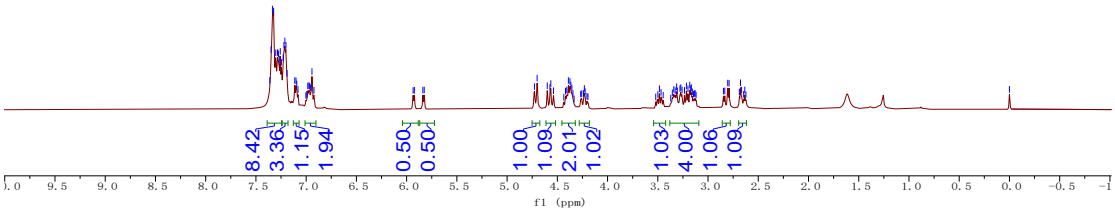

5.01
5.03
1.09
2.05
0.97
1.00
1.04
1.07
3.08
2.21
2.01
f1 (ppm)

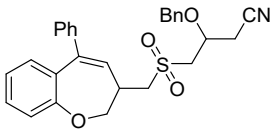

Cl
CN
Ph
O
S
O
O
f1 (ppm)

3ae

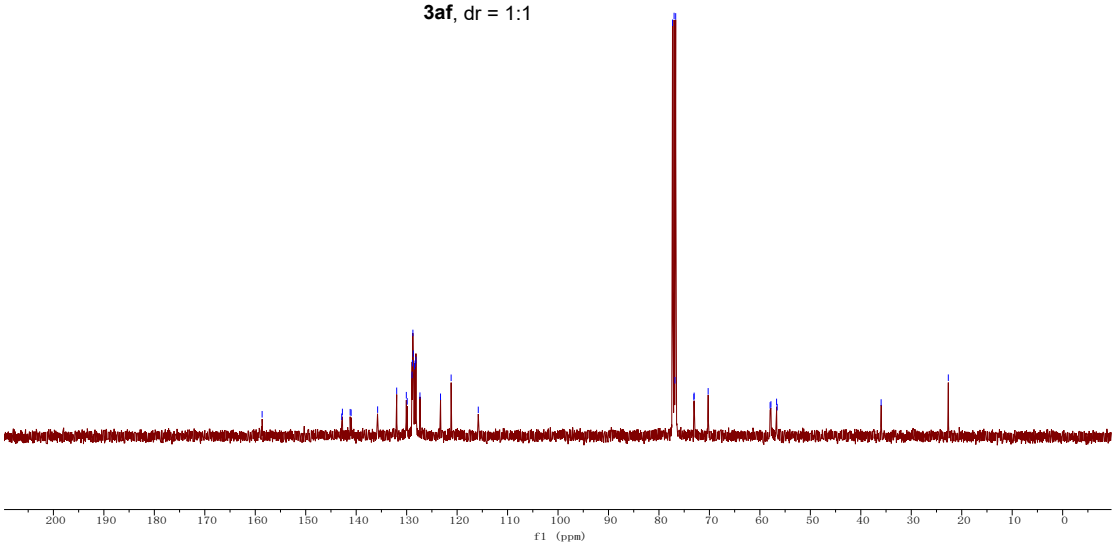


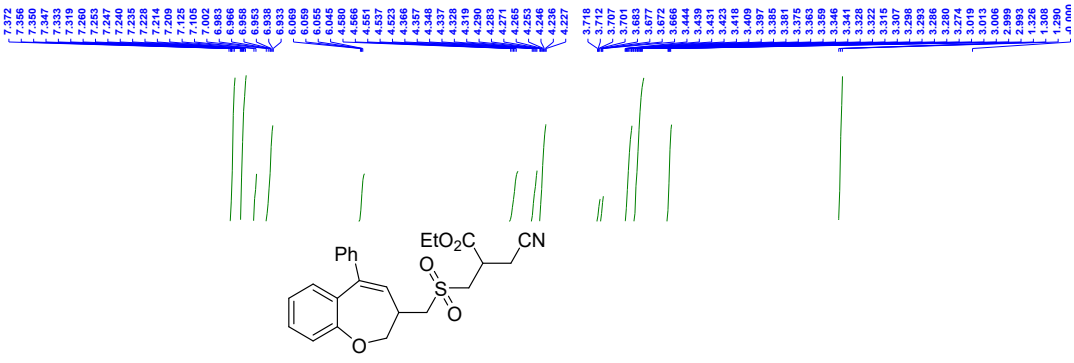
3af, dr = 1:1



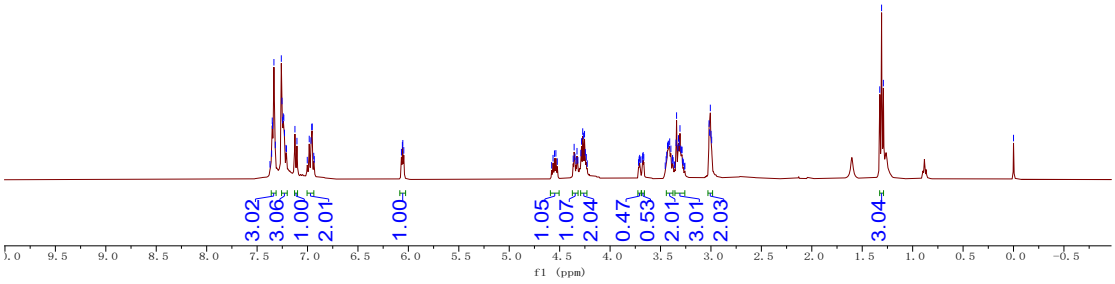


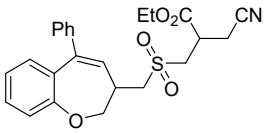
3af, dr = 1:1



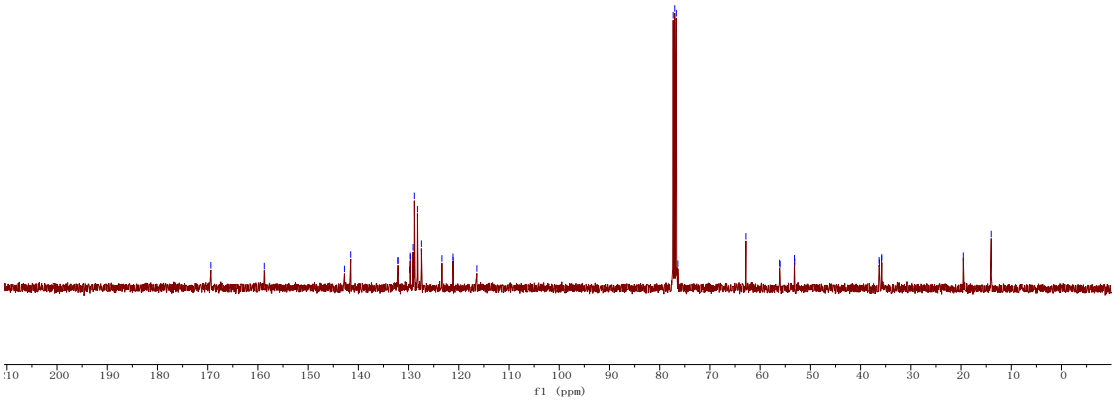


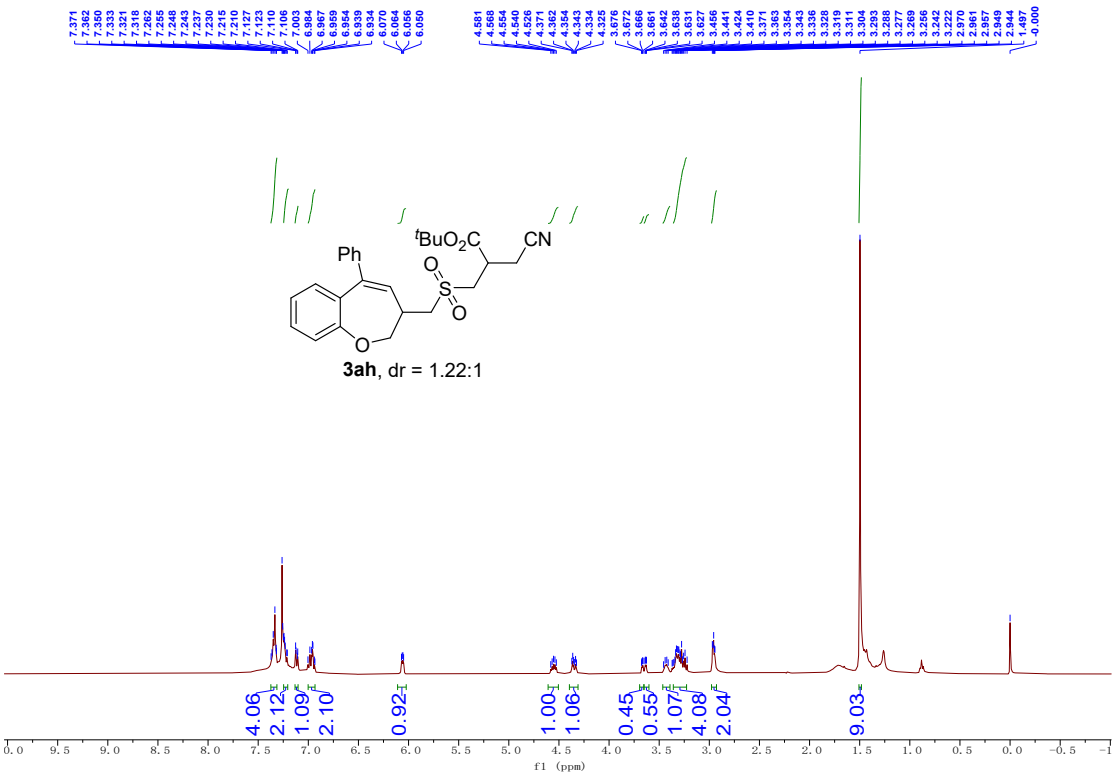
3ag, dr = 1.13:1



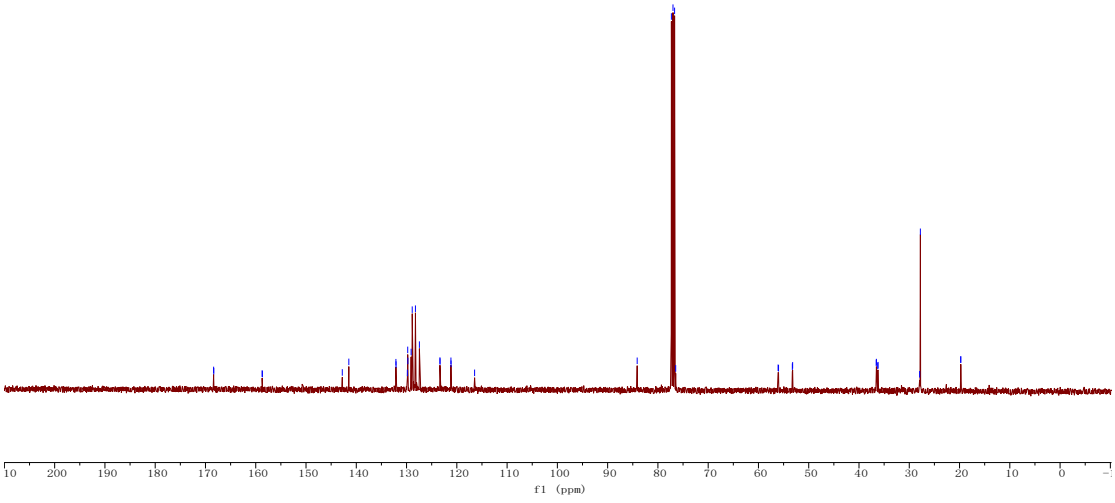


3ag, dr = 1.13:1

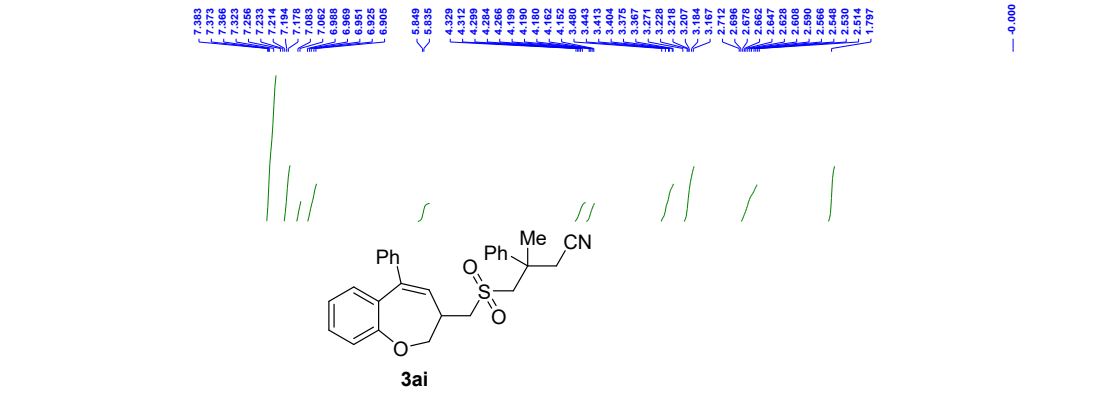




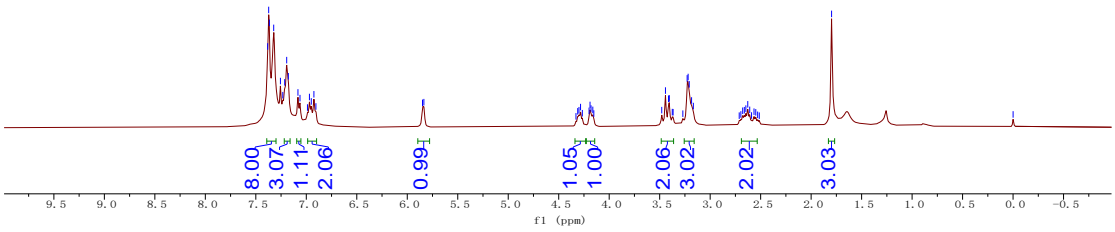
3ah, dr = 1.22:1

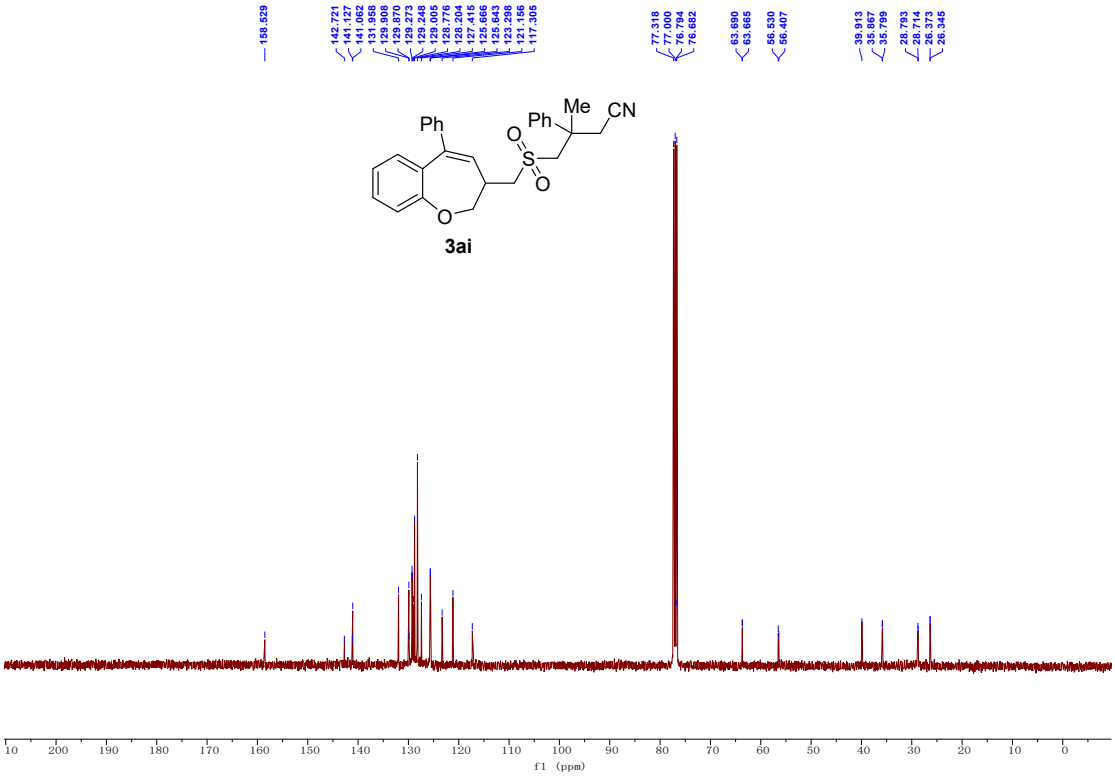


3ah, dr = 1.22:1

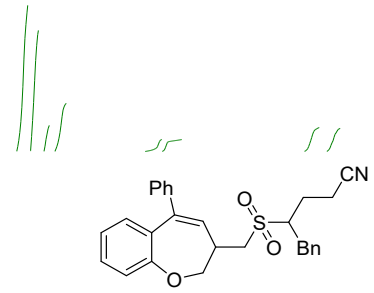

Ph
Me
CN
Ph
O
S
O
O

3ai

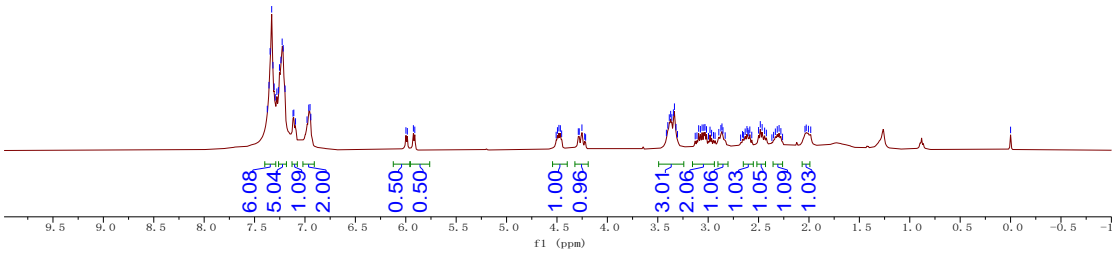

8.00
3.07
1.11
2.06
0.99
1.05
1.00
2.06
3.02
2.02
3.03
f1 (ppm)

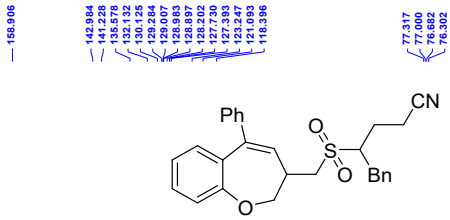

Ph
Me
CN
Ph
O
S
O
O
f1 (ppm)

3ai

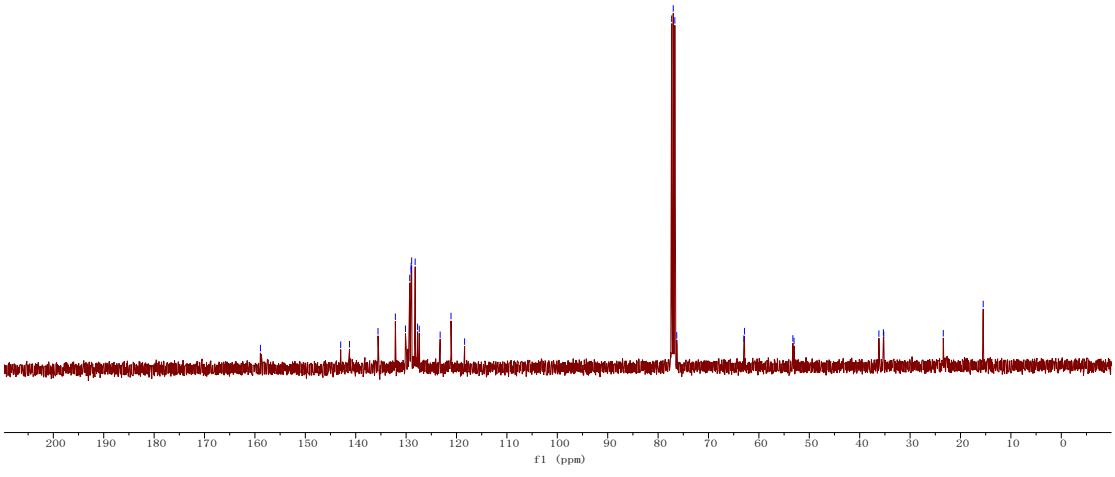


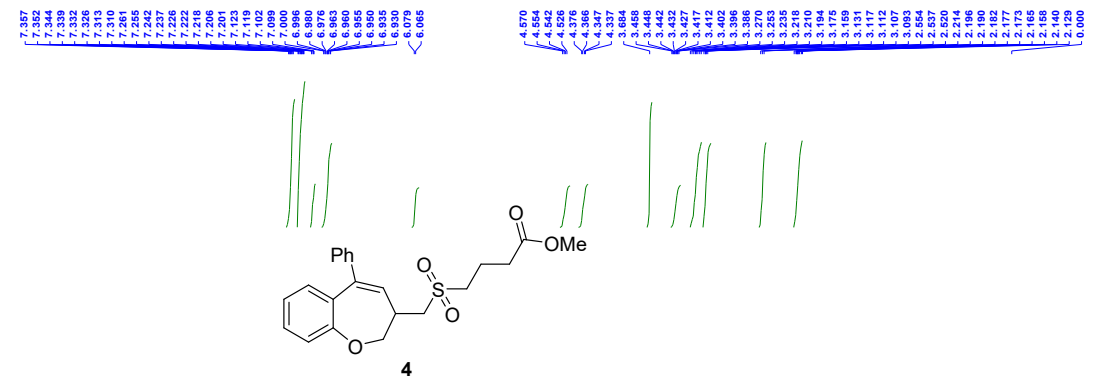
3aj, dr = 1:1





3aj, dr =1:1

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7.352
7.344
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7.242
7.237
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7.206
7.201
7.123
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7.102
7.099
7.000
6.996
6.980
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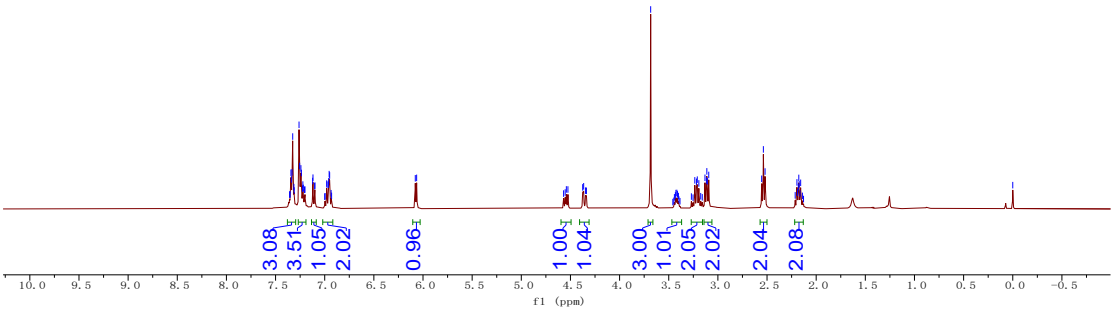
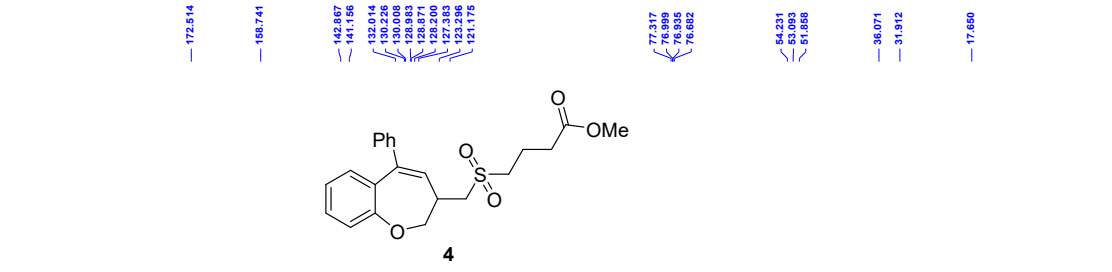
2.177
2.173
2.165
2.158
2.140
2.129
0.000
Ph
O
OMe
O
S
O
O

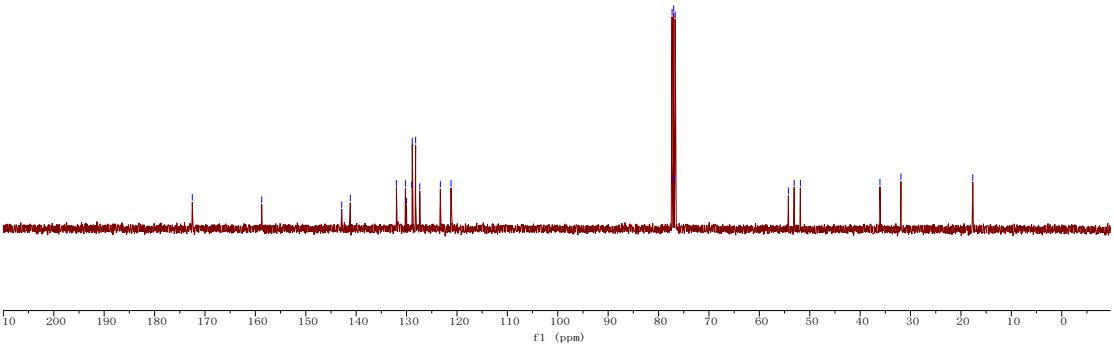
4

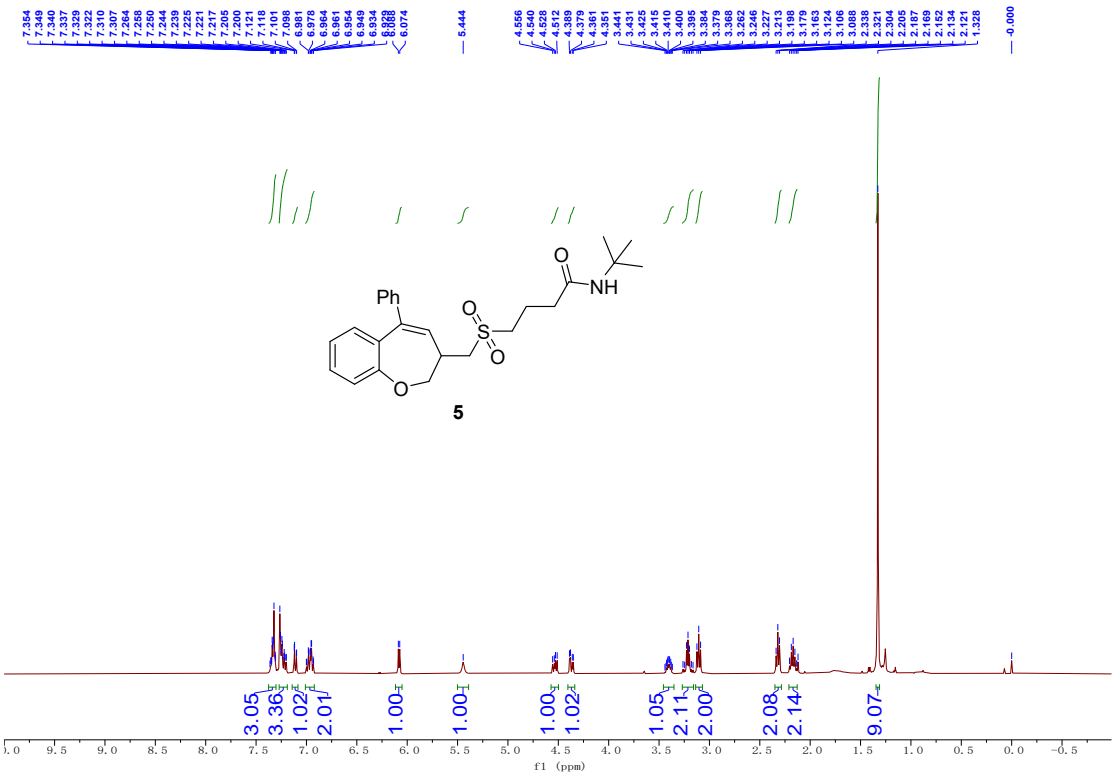

3.08
3.51
1.05
2.02
0.96
1.00
1.04
3.00
1.01
2.05
2.02
2.04
2.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

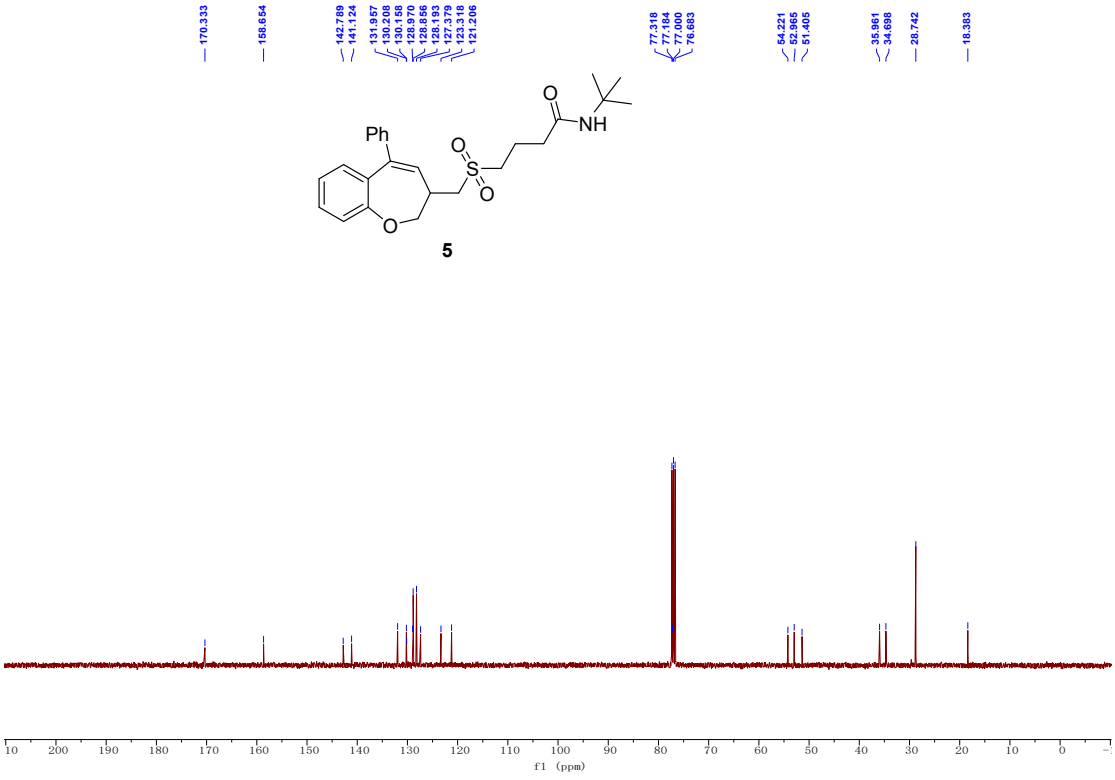

172.514
158.741
142.867
141.156
132.014
130.226
130.008
128.983
128.871
127.500
127.383
123.296
121.175
77.317
76.999
76.935
76.682
64.231
53.093
51.858
36.071
31.912
17.650

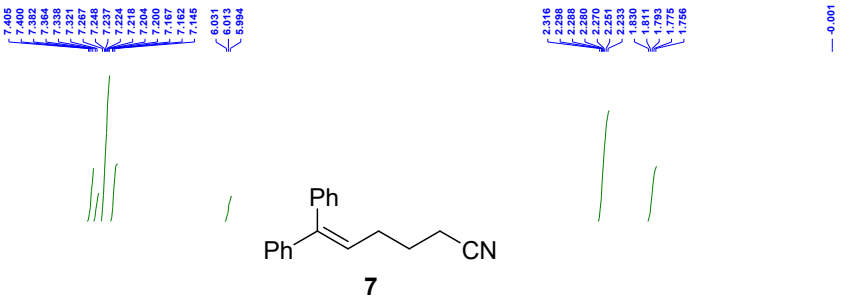
O
OMe
Ph
O
S
O
O

4

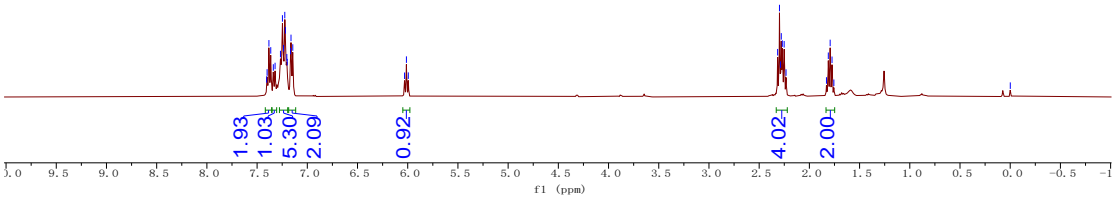

10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.354
7.349
7.340
7.337
7.329
7.322
7.310
7.300
7.264
7.258
7.250
7.244
7.239
7.225
7.221
7.217
7.205
7.200
7.121
7.118
7.101
7.098
6.981
6.978
6.964
6.961
6.954
6.949
6.934
6.074
5.444
4.556
4.540
4.528
4.512
4.389
4.379
4.361
4.351
3.444
3.431
3.425
3.415
3.410
3.400
3.395
3.384
3.373
3.365
3.262
3.246
3.227
3.213
3.198
3.179
3.163
3.124
3.106
3.088
2.338
2.321
2.304
2.205
2.187
2.169
2.152
2.134
2.121
1.328
-0.000
Ph
O
NH
S
O
O
O
5
3.05
3.36
1.02
2.01
1.00
1.00
1.00
1.02
1.05
2.11
2.00
2.08
2.14
9.07
f1 (ppm)

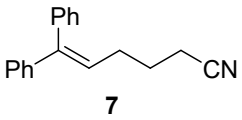

170.333
158.654
142.789
141.124
131.957
130.208
130.158
128.970
128.866
128.553
127.379
123.318
121.206
77.318
77.184
77.000
76.683
64.221
52.965
51.405
35.961
34.698
28.742
18.383
Ph
O
NH
S
O
O
O
5
f1 (ppm)


7.405
7.400
7.392
7.364
7.338
7.321
7.267
7.248
7.237
7.224
7.214
7.204
7.200
7.167
7.162
7.145
6.031
6.013
5.994
2.316
2.298
2.288
2.280
2.270
2.251
2.233
1.830
1.811
1.793
1.775
1.756
-0.001
Ph
Ph
CN

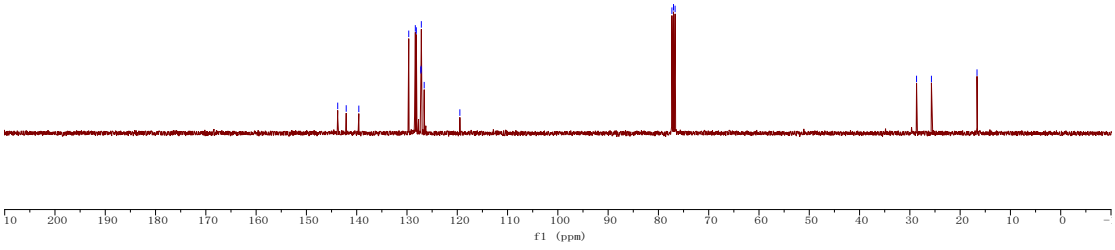
7


1.93
1.03
5.30
2.09
0.92
4.02
2.00
f1 (ppm)

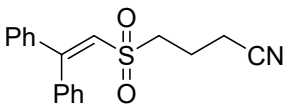

143.776
142.086
139.579
129.649
128.342
128.142
127.228
127.098
127.147
126.577
119.485
77.319
77.000
76.684
28.668
25.710
16.643


Ph
Ph
CN

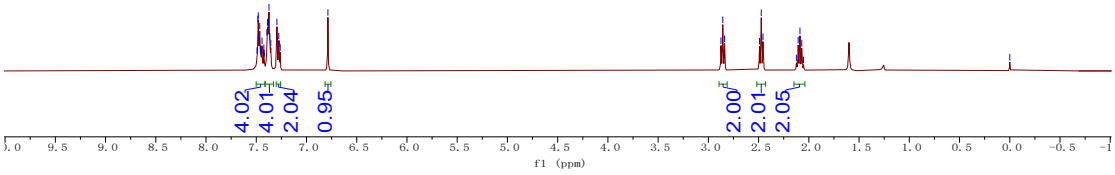
7


f1 (ppm)

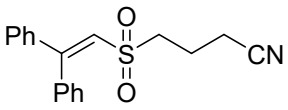

7.492
7.484
7.480
7.474
7.465
7.457
7.452
7.442
7.430
7.424
7.421
7.394
7.388
7.384
7.378
7.373
7.364
7.355
7.295
7.289
7.276
7.271
7.262
6.787
2.875
2.857
2.838
2.491
2.474
2.456
2.124
2.106
2.088
2.070
2.053
0.000


Ph
Ph
O
S
O
CN

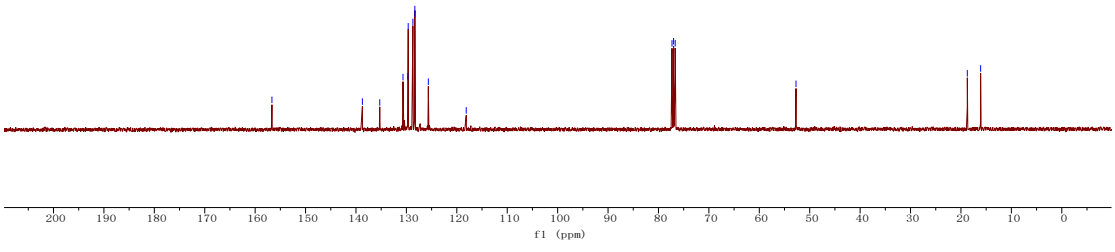
8


4.02
4.01
2.04
0.95
2.00
2.01
2.05
f1 (ppm)


166.673
138.732
135.286
130.674
129.720
129.642
128.712
128.324
128.304
125.649
118.133
77.318
77.000
76.682
52.722
18.738
16.098


Ph
Ph
O
S
O
CN

8


f1 (ppm)