Rh(II)-Catalyzed Chemoselective Oxidative Amination and Cyclization Cascade of 1-(Arylethynyl)cycloalkyl)methyl Sulfamates

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Supporting Information

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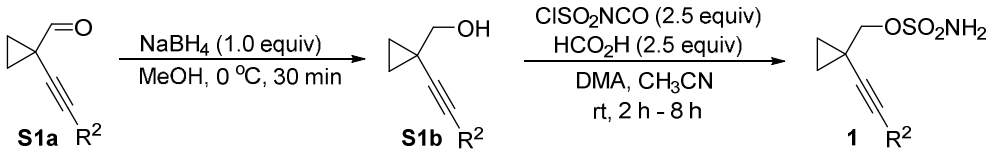
(A) General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 400 and 100 MHz, respectively. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), coupling constants in Hertz (Hz) and integration. Mass and High resolution mass spectra (HRMS) spectra were recorded by EI or ESI method. The employed solvents were dry up by standard methods when necessary. Commercially obtained reagents were used without further purification. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure, and the silica gel was heated at 120 ^{o}C for 2 h before use. All reactions were conducted with anhydrous solvents in oven-dried and nitrogen- or argon-charged glassware. Anhydrous solvents were purified by passage through activated alumina using a Glass Contours solvent purification system unless otherwise noted. Solvents for workup, extraction and column chromatography were used as received from commercial suppliers. $PhI(O_2C^tBu)_2$ and $PhI(OAc)_2$ were dried under vacuum for 12 hours prior to use. Rhodium catalysts were purchased from Sigma-Aldrich and used as received. Some products contain trace of impurity because they are sensitive to ambient water and air during the purification process.

(B) General Procedure for the Preparation of Substrates.

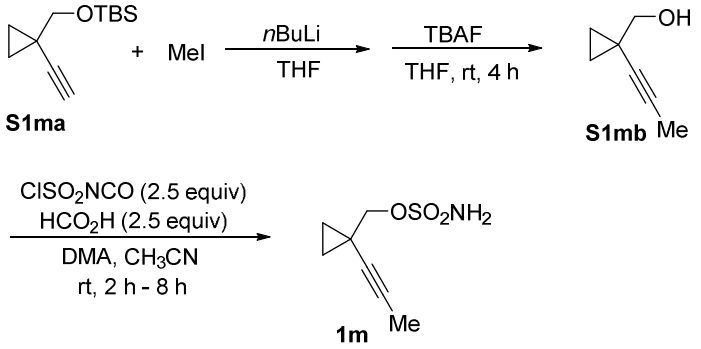
The substrates 1 were prepared according to Scheme S1:[1]



Scheme S1

The substrates **S1a** and **S1b** were synthesized according to the previously reported procedure.[2] To an oven dried round bottom flask equipped with stirring bar and a septum was added neat $ClSO_2NCO$ (2.5 mmol, 2.5 equiv) under an argon atmosphere. The flask was cooled to 0 °C followed by the dropwise addition of formic acid (2.5 mmol, 2.5 equiv). Then the resulting white mass was warmed to rt. After stirring for 12 h, the mixture was cooled to 0 °C and dried CH_3CN (5 mL) was added. Then, a solution of alcohol (1.0 mmol, 1.0 equiv) in DMA (1.0 mL/mmol alcohol) was added dropwise. Transfer of the alcohol was made quantitative with an additional 0.5 mL of DMA. The resulting white suspension was stirred for 10 min at 0 °C and warmed to room temperature. After that time TLC indicated usually complete consumption of the starting material. The reaction mixture was then diluted with a saturated aq. $NaHCO_3$ at 0 °C (dropwise, slowly) and extracted with DCM (3×10.0 mL). The combined organic extracts were washed with saturated aq. NaCl (20 mL), dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 4:1) provided the desired sulfamates **1**.

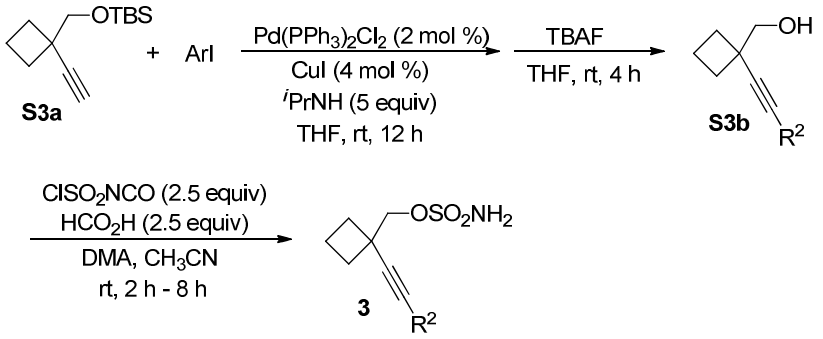
The substrate 1m was prepared according to Scheme S2:



Scheme S2

The substrate **S1ma** was synthesized according to the previously reported procedure.[2] To a dried Schlenk tube was added the substrate **S1ma** (5.0 mmol, 1.0 equiv) in 5 mL dried THF. Then, ^{n}BuLi (2.4 M in hexane, 5.5 mmol, 1.1 equiv) was added dropwise to the solution at -78 ^{o}C. After stirring at this temperature for 1 h, MeI (6.0 mmol, 1.2 equiv) was added. One hour later, the reaction mixture was then diluted with a saturated aq. $NaHCO_3$ (20 mL) and extracted with EA (3 × 10.0 mL). The combined organic extracts were washed with saturated aq. NaCl (20 mL), dried over Na_2SO_4 and concentrated in vacuo. The residual in 50 mL of flask was added TBAF 5.0 ml (1.0 M in THF) and the solution was stirred at rt for 4 h. The reaction mixture was then diluted with H_2O (20 mL) and extracted with DCM (3 × 10.0 mL). The combined organic extracts were washed with saturated aq. NaCl (20 mL), dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 1:1) provided the desired product **s1mb**. To an oven dried round bottom flask equipped with a stirring bar and a septum was added neat $ClSO_2NCO$ (2.5 mmol, 2.5 equiv) under an argon atmosphere. The flask was cooled to 0 °C followed by the dropwise addition of formic acid (2.5 mmol, 2.5 equiv). Then the resulting white mass was warmed to rt. After stirring for 12 h, the mixture was cooled to 0 °C and dried CH_3CN (5.0 mL) was added. Then, a solution of alcohol (1.0 mmol, 1.0 equiv) in DMA (1.0 mL/mmol alcohol) was added dropwise. Transfer of the alcohol was made quantitative with an additional 0.5 mL of DMA. The resulting white suspension was stirred for 10 min at 0 ^{o}C and warmed to room temperature. After that time TLC indicated usually complete consumption of the starting material. The reaction mixture was then diluted with a saturated aq. $NaHCO_3$ at 0 °C (dropwise, slowly) and extracted with DCM (3 × 10.0 mL). The combined organic extracts were washed with saturated aq. NaCl (20 mL), dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 4:1) provided the desired sulfamate **1m**.

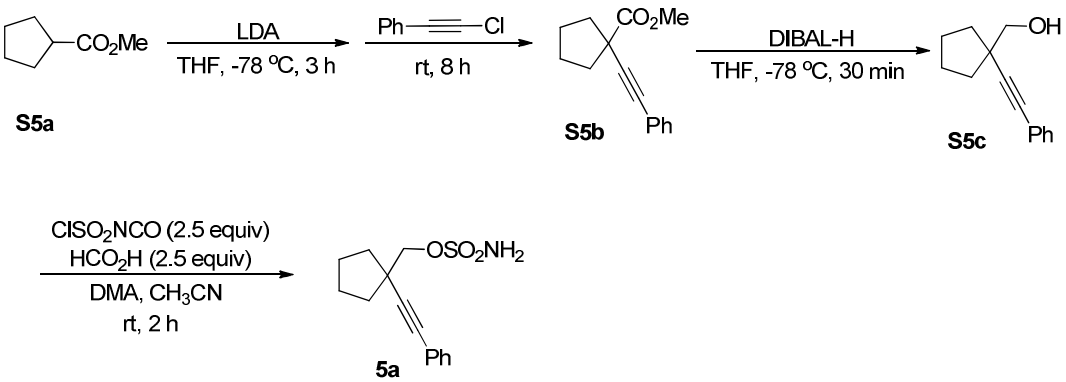
The substrates 3 were prepared according to Scheme S3:[3]



Scheme S3

The substrates **S3a** and **S3b** were synthesized according to the previously reported procedure.[2] To an oven dried round bottom flask equipped with a stirring bar and a septum was added neat $ClSO_2NCO$ (2.5 mmol, 2.5 equiv) under an argon atmosphere. The flask was cooled to 0 °C followed by the dropwise addition of formic acid (2.5 mmol, 2.5 equiv). Then the resulting white mass was warmed to rt. After stirring for 12 h, the mixture was cooled to 0 °C and dried CH_3CN (5 mL) was added. Then, a solution of alcohol (1.0 mmol, 1.0 equiv) in DMA (1.0 mL/mmol alcohol) was added dropwise. Transfer of the alcohol was made quantitative with an additional 0.5 mL of DMA. The resulting white suspension was stirred for 10 min at 0 ^oC and warmed to room temperature. After that time TLC indicated usually complete consumption of the starting material. The reaction mixture was then diluted with a saturated aq. $NaHCO_3$ at 0 °C (dropwise, slowly) and extracted with DCM (3 × 10.0 mL). The combined organic extracts were washed with saturated aq. NaCl (20 mL), dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 4:1) provided the desired sulfamate **3**.

The substrates 5a and 7a were prepared according to Scheme S4:



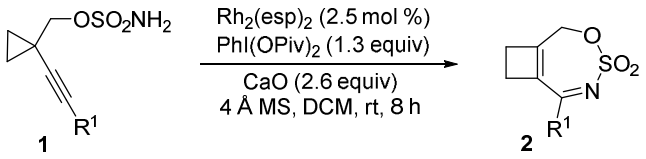
Scheme S4

The compound **S5a** was prepared according to the previously reported procedure.[4] To an oven dried round bottom flask equipped with a stirring bar and a septum was added neat $ClSO_2NCO$ (2.5 mmol, 2.5 equiv) under an argon atmosphere. The flask was cooled to 0 °C followed by the dropwise addition of formic acid (2.5 mmol, 2.5 equiv). Then the resulting white mass was warmed to rt. After stirring for 12 h, the mixture was cooled to 0 °C and dried CH_3CN (5 mL) was added. Then, a solution of **S5c** (1.0 mmol, 1.0 equiv) in DMA (1.0 mL/mmol alcohol) was added dropwise. Transfer of the alcohol was made quantitative with an additional 0.5 mL of DMA. The resulting white suspension was stirred for 10 min at 0 ^oC and warmed to room temperature. After that time TLC indicated usually complete consumption of the starting material. The reaction mixture was then diluted with a saturated aq. $NaHCO_3$ at 0 °C (dropwise, slowly) and extracted with DCM (3 × 10.0 mL). The combined organic extracts were washed with saturated aq. NaCl (20 mL), dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 4:1) provided the desired sulfamate **5a**. Substrate **7a** was prepared in the same way as that of **5a**.

The substrate 9a were prepared according to the previous reference.[5]

(C) General Procedure for the $Rh_2(esp)_2$-catalyed alkyl migration reaction.

The products 2a-2l were prepared according to Scheme S5:

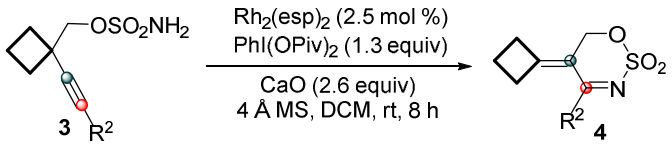


Scheme S5

To a 25 mL flame and vacuum dried Schlenk tube was added **1** (0.2 mmol, 1equiv), $Rh_2(esp)_2$ (2.5 mol %), CaO (0.52 mmol, 2.6 equiv) and dried 4 Å MS 50 mg. The tube was evacuated and backfilled with Ar for 3 times. Then 2 mL dried dichloromethane was added at rt. $PhI(OPiv)_2$ (0.26 equiv) in DCM 2 mL was added to the reaction dropwise. The reaction flask was then stirred at rt for 8 h. The reaction was filtered over Celite and the solids were washed with dichloromethane and ethyl acetate. The volatiles were removed under reduced pressure and the residue was purified by chromatography on silica gel quickly (eluent: petroleum ether/ethyl acetate 4:1) to give the desired product.

When the reaction scale was extended to 1.0 mmol in this case following the same procedure, **2a** was obtained in 180 mg; yield: 72%.

The products 4a-4l were prepared according to Scheme S6:



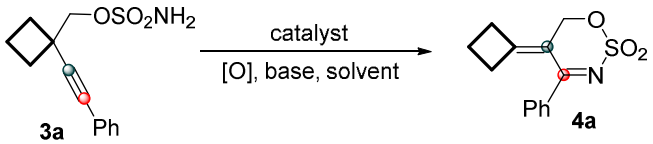
Scheme S6

To a 25 mL flame and vacuum dried Schlenk tube was added **3** (0.2 mmol, 1.0 equiv), $Rh_2(esp)_2$ (2.5 mol %), CaO (0.52 mmol, 2.6 equiv) and dried 4 Å MS (50 mg). The reaction tube was evacuated and backfilled with Ar for 3 times. Then 2 mL of dried dichloromethane was added at rt. $PhI(OPiv)_2$ (0.26 equiv) in DCM (2 mL) was added to the reaction dropwise at 0 ^oC and then the reaction mixture was warmed to rt. The reaction flask was then stirred at rt for 8 h. The reaction mixture was filtered over Celite and the solids were washed with dichloromethane and ethyl acetate. The volatiles were removed under reduced pressure and the residue was purified by a

chromatography on silica gel quickly (eluent: petroleum ether/ethyl acetate 4:1) to give the desired product **4**.

When the reaction scale was extended to 1.0 mmol in this case following the same procedure, **4a** was obtained in 105 mg; yield: 40%.

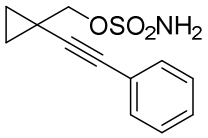
Table S1. Optimization of the Reaction Conditions[a]



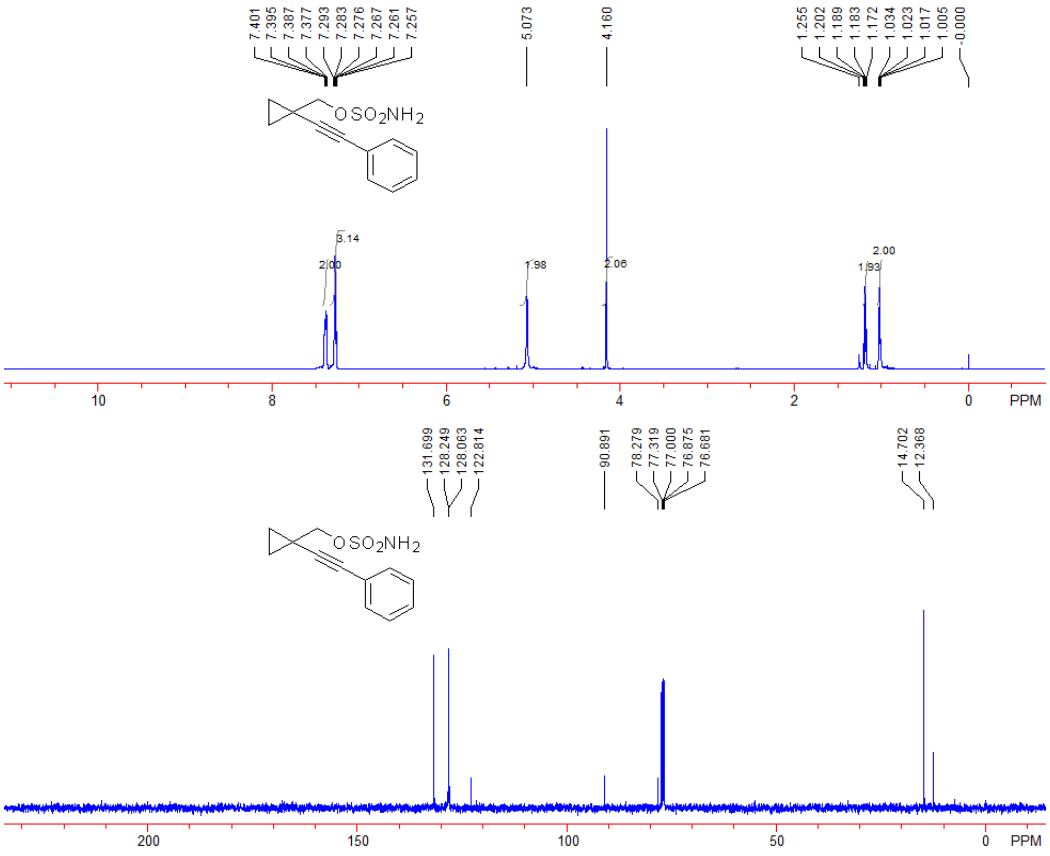
entry	cat. (mol %)	oxidant	base	solvent	yield (%)[b]
1	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	MgO	DCM	46
2	$Rh_2(oct)_4$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	MgO	DCM	<5
3	$Rh_2(OAc)_4$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	MgO	DCM	<5
4	$Rh_2(OPiv)_4$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	MgO	DCM	<5
5	$Rh_2(TFA)_4$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	MgO	DCM	<5
6	$Rh_2(esp)_2$ (2.5)	PhIO (1.3 equiv)	MgO	DCM	<5
7	$Rh_2(esp)_2$ (2.5)	$PhI(OAc)_2$ (1.3 equiv)	MgO	DCM	<5
8	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	CaO	DCM	48
9[d]	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	K_2CO_3	DCM	<5
10	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	NEt_3	DCM	<5
11[e]	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	LiO^tBu	DCM	<5
12	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	CaO	toluene	30
13	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	CaO	benzene	11
14[c]	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	CaO	Et_2O	<5
15	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	CaO	chlorobenzene	34
16	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	CaO	fluorobenzene	32
17[c]	$Rh_2(esp)_2$ (2.5)	$PhI(OPiv)_2$ (1.3 equiv)	CaO	DCM	53 (48)[d]

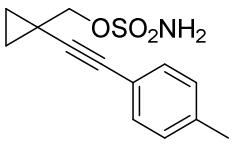
[a]Unless otherwise specified, all reactions were carried out using **3** (0.2 mmol), oxidant (0.26 mmol), $Rh_2(esp)_2$ (2.5 mol %) and base (0.52 mmol) in solvent (4.0 mL), rt, 8 h, 0.05 M in solvent unless otherwise specified. [b]The yield was determined by ^1H NMR spectroscopic data using mesitylene as an internal standard. [c]50 mg 4 Å MS was added. [d]Isolated yield.

(G) Spectroscopic Data of Substrates and Products

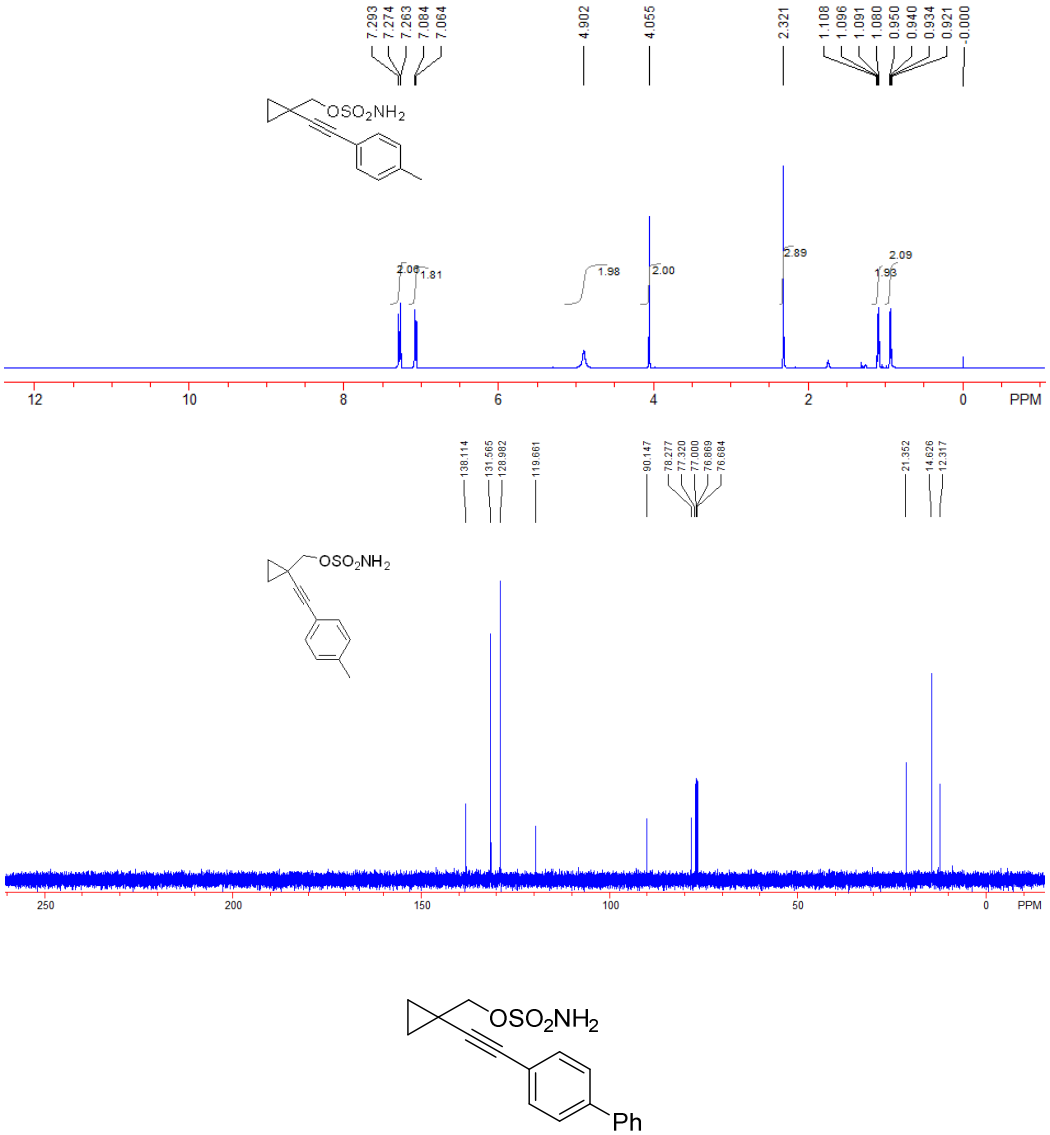


(1-(phenylethynyl)cyclopropyl)methyl sulfamate **1a**: Yield: 138 mg, 55%; A yellow solid, Mp: 50-52 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.01-1.03 (m, 2H, CH_2), 1.17-1.20 (m, 2H, CH_2), 4.16 (s, 2H, CH_2), 5.07 (br, 2H, NH_2), 7.26-7.29 (m, 3H, Ar), 7.38-7.40 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.4, 14.7, 76.9, 78.3, 90.9, 122.8, 128.1, 128.2, 131.7. IR (EtOH) ν 3387, 3294, 3142, 2223, 1596, 1546, 1490, 1452, 1440, 1343, 1304, 1266, 1166, 1068, 1033, 922, 787, 753, 689 cm^{-1}. MS (ESI) *m/z* 269 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{12}H_{17}N_2O_3S$: 269.0960, Found: 269.0960.



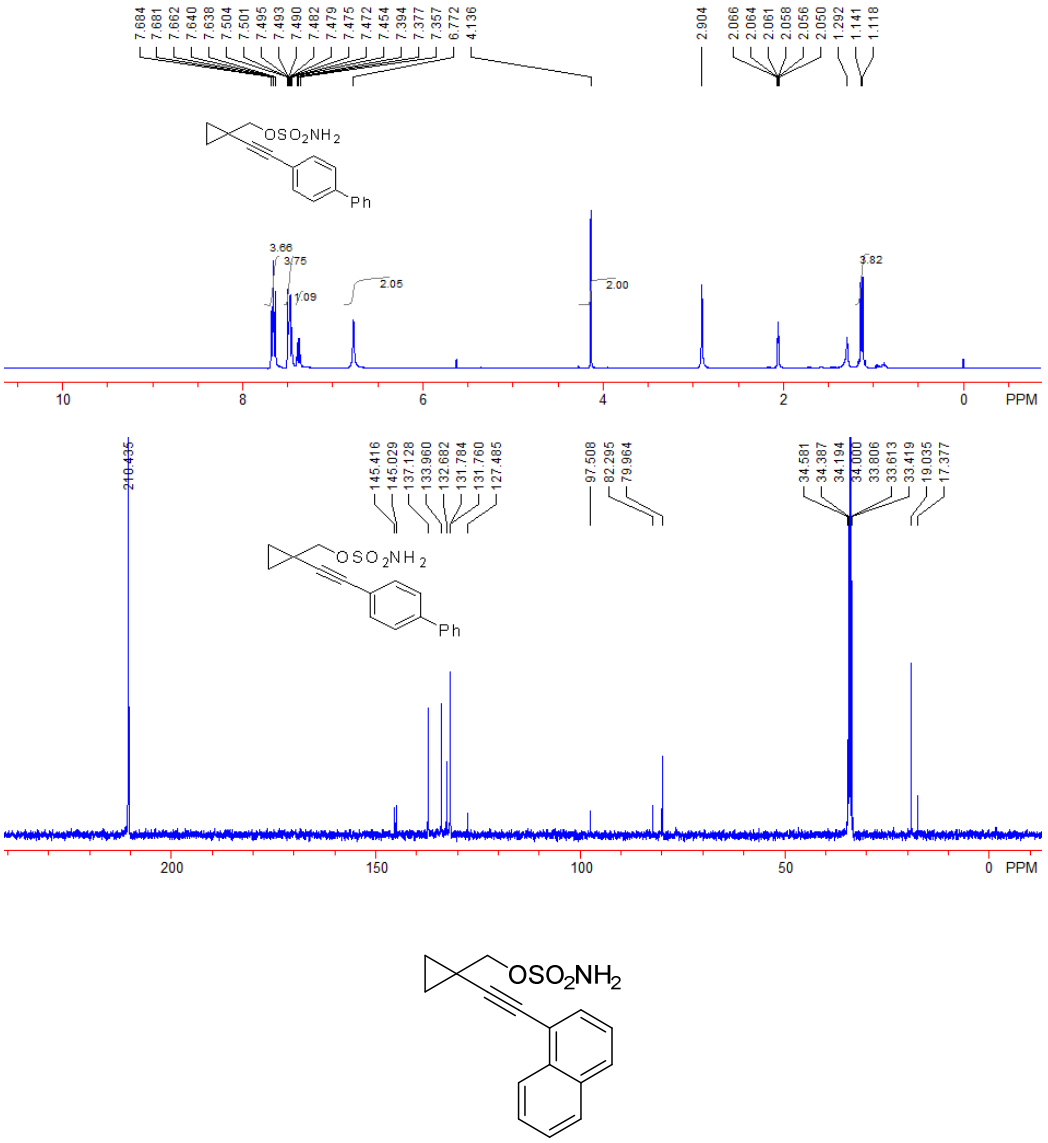


(1-(p-tolylethynyl)cyclopropyl)methyl sulfamate **1b**: Yield: 196 mg, 74%; A white solid, Mp: 56-58 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.92-0.95 (m, 2H, CH_2), 1.08-1.11 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 4.06 (s, 2H, CH_2), 4.90 (br, 2H, NH_2), 7.07 (d, J = 8.0 Hz, 2H, Ar), 7.28 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.3, 14.6, 21.4, 76.7, 78.3, 90.1, 119.7, 129.0, 131.6, 138.1. IR (EtOH) ν 3432, 3317, 3255, 3201, 2953, 2922, 2850, 2228, 1682, 1612, 1509, 1424, 1346, 1072, 816 cm^{-1}. MS (ESI) *m/z* 283 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{13}H_{19}N_2O_3S$: 283.1111, Found: 283.1110.



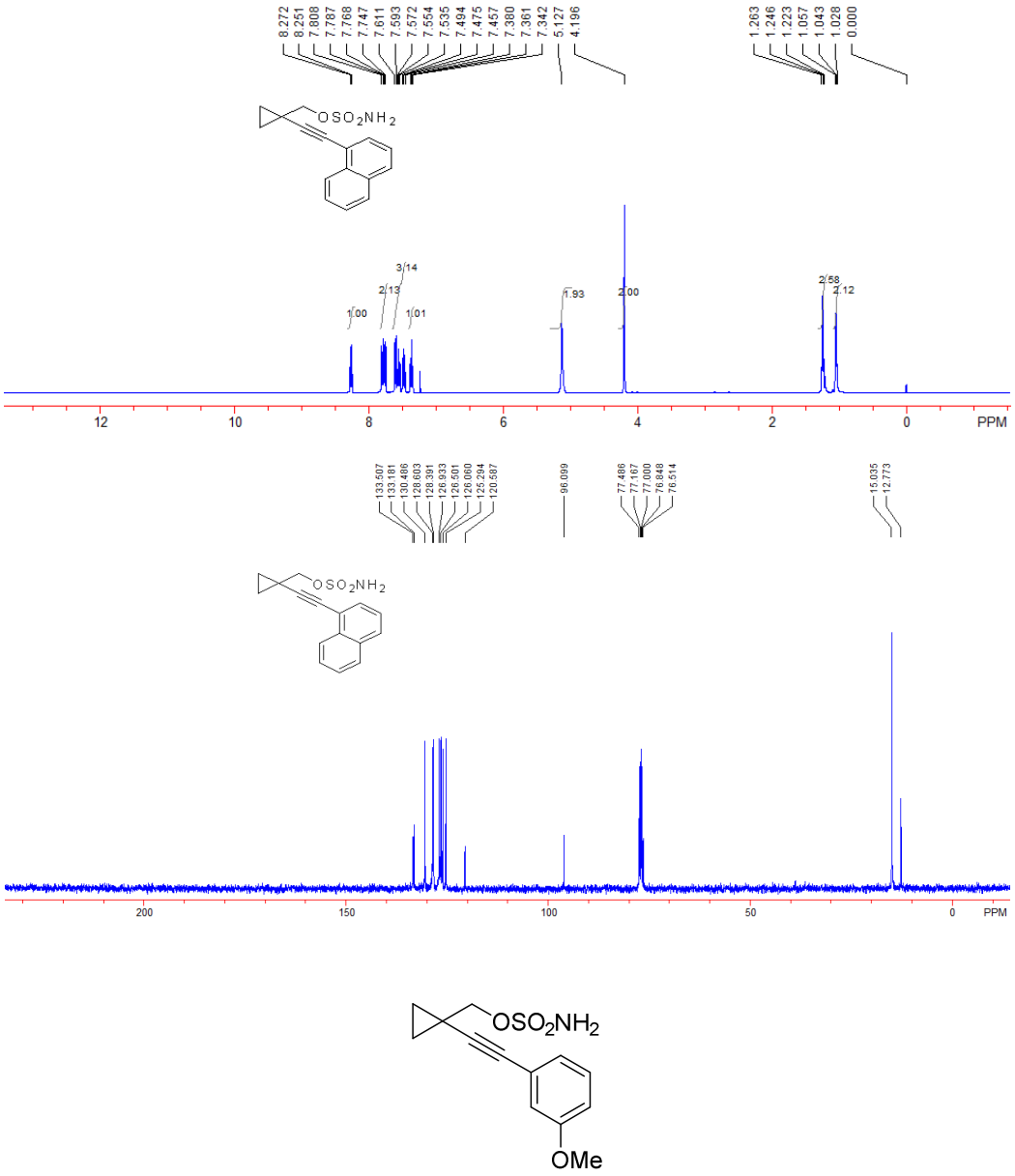
(1-([1,1'-biphenyl]-4-ylethynyl)cyclopropyl)methyl sulfamate **1c**: Yield: 260 mg, 80%; A white solid, Mp: 131-133 ^{o}C; ^{1}H NMR (CD_3COCD_3, 400 MHz, TMS) δ 1.12-1.14 (m, 4H, $2CH_2$), 4.14 (s, 2H, CH_2), 6.77 (br, 2H, NH_2), 7.36-7.39 (m, 1H, Ar), 7.45-7.50 (m, 4H, Ar), 7.64-7.68 (m, 4H, Ar).

^{13}C NMR (CD_3COCD_3, 100 MHz, TMS) δ 17.4, 19.0, 80.0, 82.3, 97.5, 127.5, 131.76, 131.78, 132.7, 134.0, 137.1, 145.0, 145.4. IR (EtOH) ν 3253, 3188, 3057, 2928, 2225, 1606, 1487, 1413, 1396, 1384, 1363, 1262, 1172, 1062, 1036, 1016, 983, 953, 925, 848, 802, 767, 717, 695 cm^{-1}. MS (ESI) *m/z* 328 $(M+H)^+$. HRMS (ESI) calcd. for $C_{18}H_{18}NO_3S$: 328.1002, Found: 328.1003.

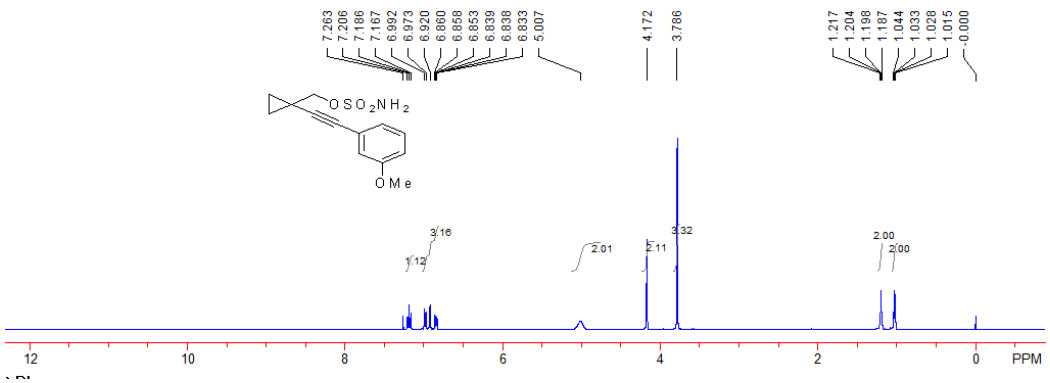


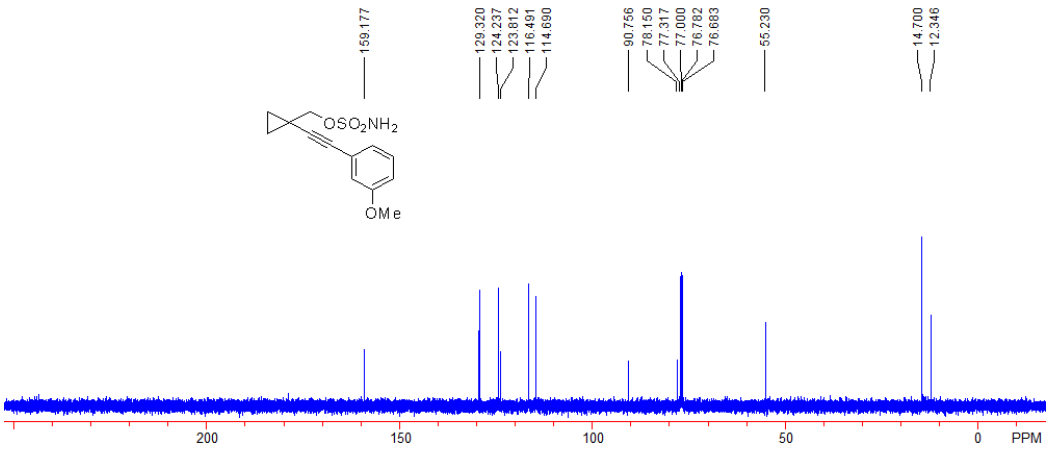
(1-(naphthalen-1-ylethynyl)cyclopropyl)methyl sulfamate **1d**: Yield: 229 mg, 76%; A white solid, Mp: 102-104 ^oC; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.03-1.06 (m, 2H, CH_2), 1.22-1.26 (m, 2H, CH_2), 4.20 (s, 2H, CH_2), 5.13 (br, 2H, NH_2), 7.34-7.38 (m, 1H, Ar), 7.46-7.61 (m, 3H, Ar), 7.75-7.81 (m, 2H, Ar), 8.25-8.27 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.8, 15.0, 76.5, 77.5, 96.1, 120.6, 125.3, 126.1, 126.5, 126.9, 128.4, 128.6, 130.5, 133.2, 133.5. IR (EtOH) ν 3372, 3268, 3151, 3054, 2974, 2220, 1585, 1506, 1439, 1366, 1303, 1263, 1179, 1116, 1067, 1035,

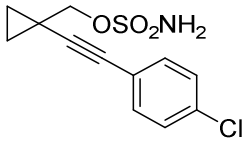
1015, 922, 799, 772, 739, 707, 686 cm^{-1}. MS (ESI) *m/z* 302 $(M+H)^+$. HRMS (ESI) calcd. for $C_{16}H_{16}NO_3S$: 302.0845, Found: 302.0849.



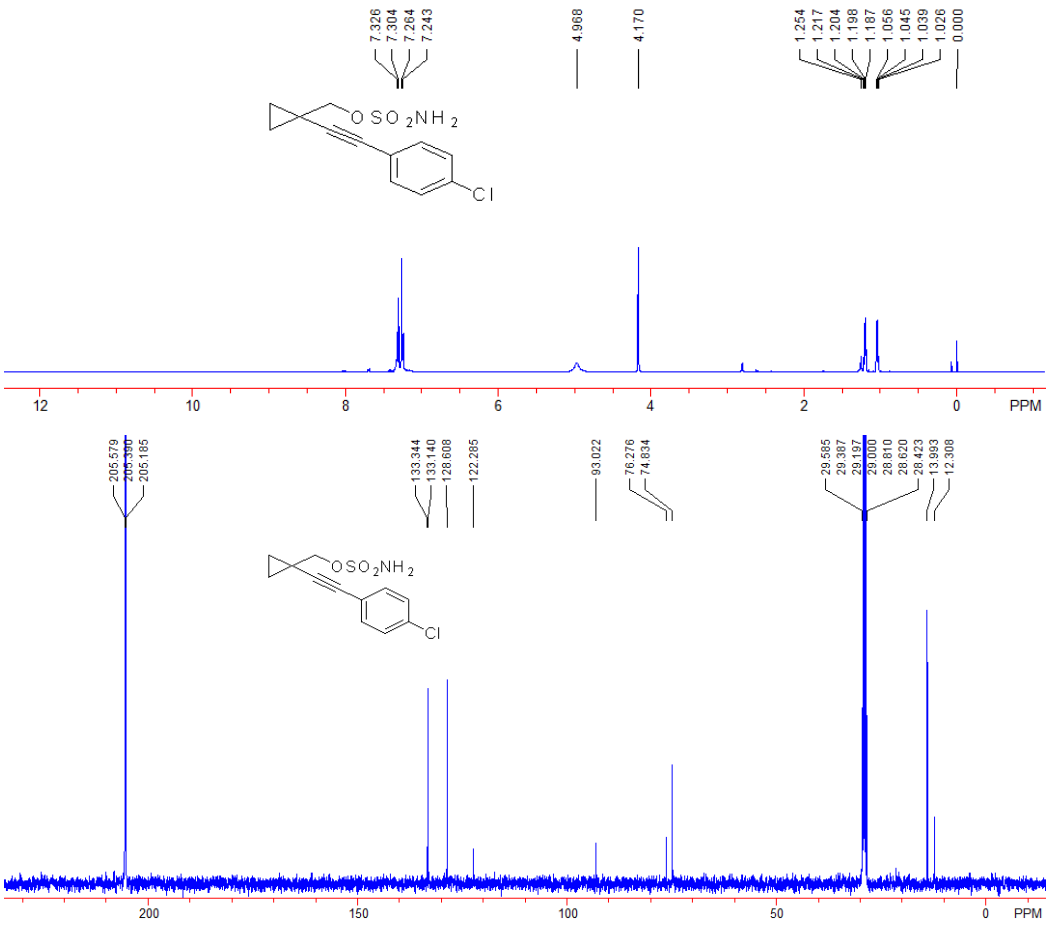
(1-((3-methoxyphenyl)ethynyl)cyclopropyl)methyl sulfamate **1e**: Yield: 212 mg, 75%; White solid, Mp: 77-79 ^oC; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.02-1.04 (m, 2H, CH_2), 1.19-1.22 (m, 2H, CH_2), 3.79 (s, 3H, CH_3), 4.17 (s, 2H, CH_2), 5.01 (br, 2H, NH_2), 6.83-6.86 (m, 1H, Ar), 6.92 (s, 1H, Ar), 6.97-6.99 (m, 1H, Ar), 7.17-7.21 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.3, 14.7, 55.2, 76.7, 78.2, 90.8, 114.7, 116.5, 123.8, 124.2, 129.3, 159.2. IR (EtOH) ν 3359, 3263, 3093, 2225, 1887, 1623, 1559, 1488, 1359, 1167, 1092, 1027, 1014, 933, 820, 795, 703 cm^{-1}. MS (ESI) *m/z* 299 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{13}H_{19}N_2O_4S$: 299.1060, Found: 299.1063.

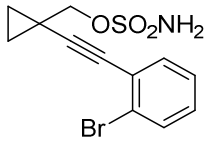




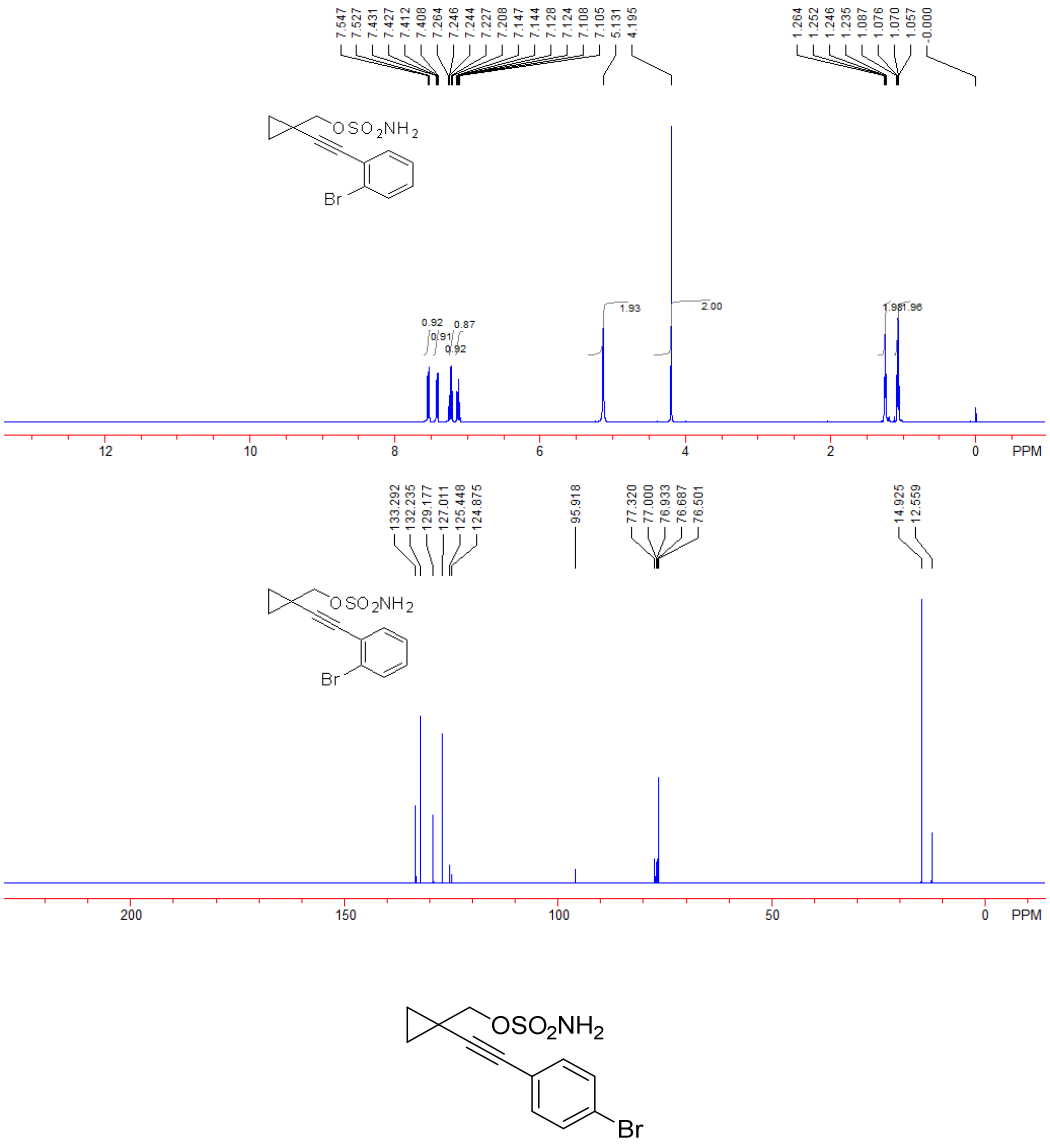


(1-((4-chlorophenyl)ethynyl)cyclopropyl)methyl sulfamate **1f**: Yield: 218 mg, 77%; A white solid, Mp: 56-58 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.03-1.06 (m, 2H, CH_2), 1.19-1.22 (m, 2H, CH_2), 4.17 (s, 2H, CH_2), 4.97 (br, 2H, NH_2), 7.25 (d, J = 8.8 Hz, 2H, Ar), 7.31 (d, J = 8.8 Hz, 2H, Ar). ^{13}C NMR (CD_3COCD_3, 100 MHz, TMS) δ 12.3, 14.0, 74.8, 76.3, 93.0, 122.3, 128.6, 133.1, 133.3. IR (EtOH) ν 3359, 3263, 3093, 2225, 1887, 1623, 1559, 1488, 1359, 1167, 1092, 1027, 1014, 933, 820, 795, 703 cm^{-1}. MS (ESI) *m/z* 286 $(M+H)^+$. HRMS (ESI) calcd. for $C_{12}H_{13}ClNO_3S$: 286.0299, Found: 286.0295.

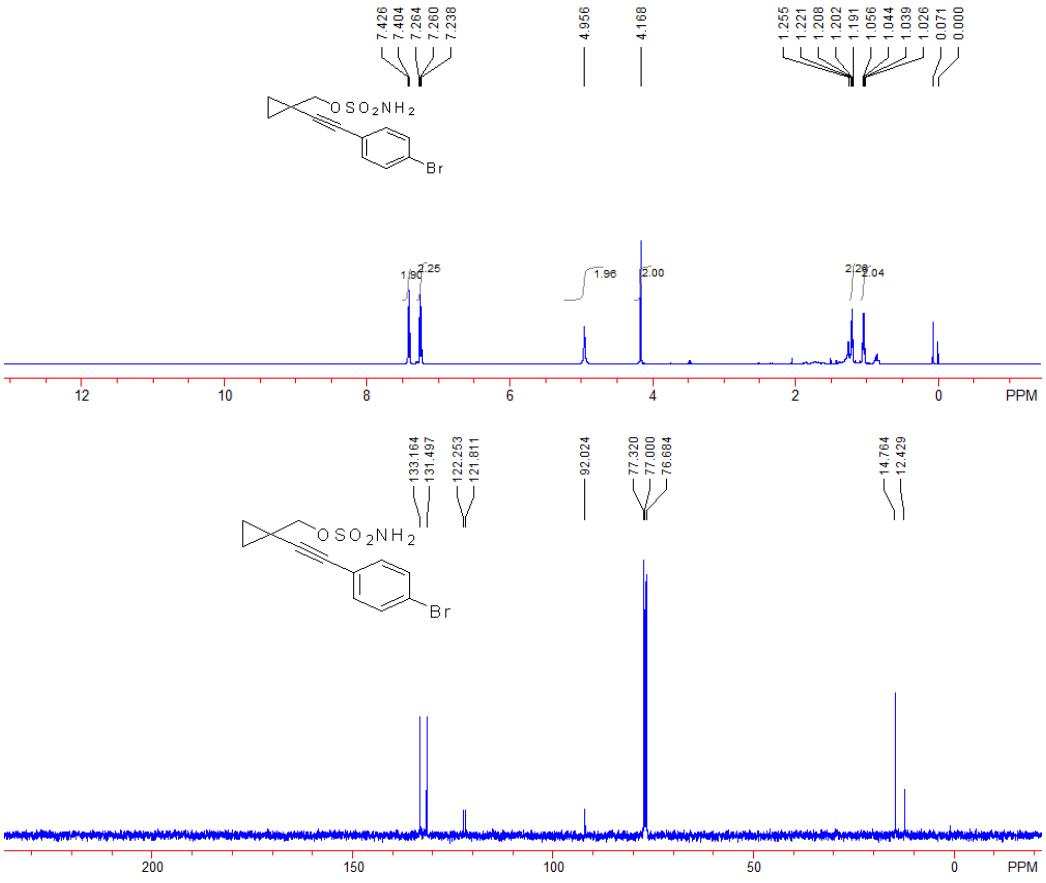


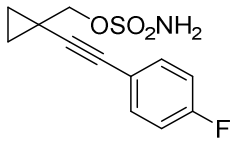


(1-((2-bromophenyl)ethynyl)cyclopropyl)methyl sulfamate **1g**: Yield: 262 mg, 79%; A yellow solid, Mp: 79-81 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.06-1.09 (m, 2H, CH_2), 1.24-1.26 (m, 2H, CH_2), 4.20 (s, 2H, CH_2), 5.13 (br, 2H, NH_2), 7.11-7.15 (m, 1H, Ar), 7.21-7.25 (m, 1H, Ar), 7.41-7.43 (m, 1H, Ar), 7.53-7.55 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.6, 14.9, 76.5, 76.9, 95.9, 124.9, 125.4, 127.0, 129.2, 132.2, 133.3. IR (EtOH) ν 3371, 3272, 3098, 2956, 2923, 2852, 2220, 1548, 1485, 1358, 1167, 1070, 1027, 1011, 950, 822, 794 cm^{-1}. MS (ESI) *m/z* 347 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{12}H_{16}BrN_2O_3S$: 347.0060, Found: 347.0058.

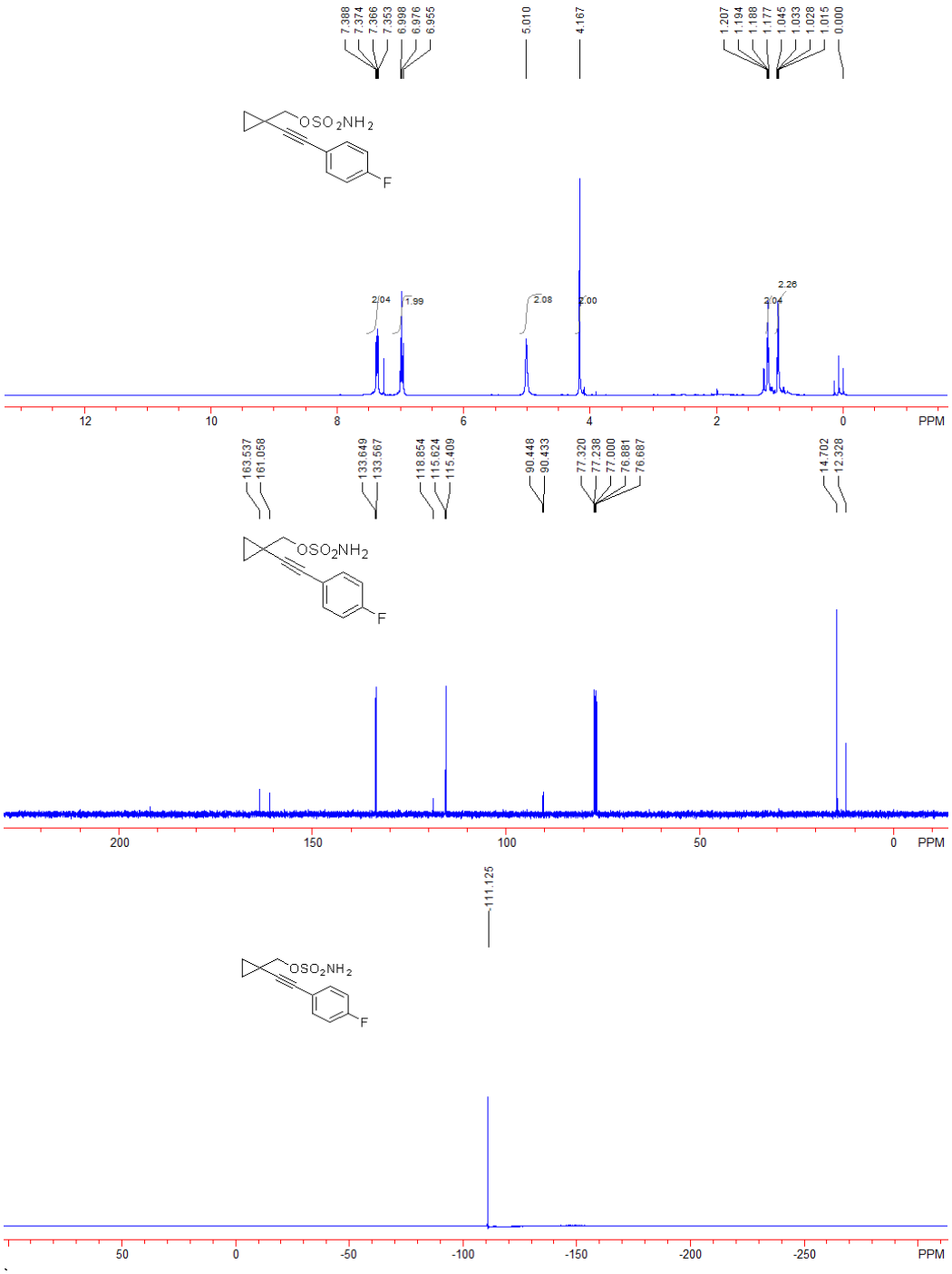


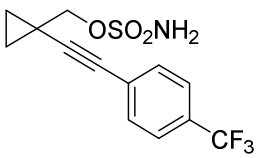
(1-((4-bromophenyl)ethynyl)cyclopropyl)methyl sulfamate **1h**: Yield: 215 mg, 65%; A yellow solid, Mp: 84-86 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.03-1.06 (m, 2H, CH_2), 1.19-1.22 (m, 2H, CH_2), 4.17 (s, 2H, CH_2), 4.96 (br, 2H, NH_2), 7.25 (d, J = 8.8 Hz, 2H, Ar), 7.41 (d, J = 8.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.4, 14.8, 92.0, 121.8, 122.3, 131.5, 133.2. IR (EtOH) ν 3403, 3291, 3090, 3015, 2977, 2894, 2224, 1557, 1529, 1471, 1433, 1341, 1173, 1045, 1025, 973, 927, 814, 791, 753, 710, 682 cm^{-1}. MS (ESI) *m/z* 352 $(M+Na)^+$. HRMS (ESI) calcd. for $C_{12}H_{12}BrNO_3SNa$: 351.9613, Found: 351.9610.





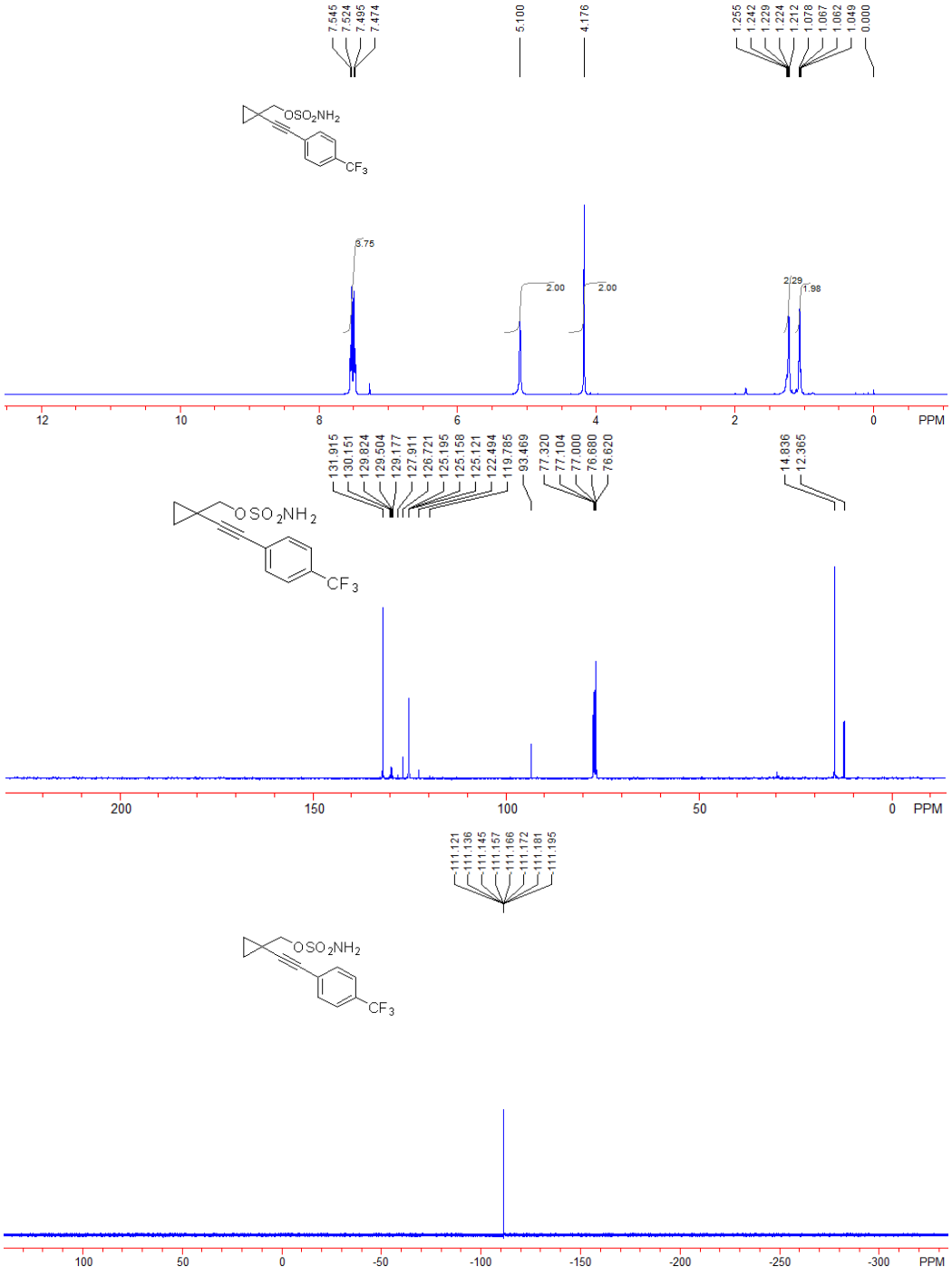
(1-((4-fluorophenyl)ethynyl)cyclopropyl)methyl sulfamate **1i**: Yield: 154 mg, 57%; A white solid, Mp: 107-109 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.02-1.05 (m, 2H, CH_2), 1.18-1.21 (m, 2H, CH_2), 4.17 (s, 2H, CH_2), 5.01 (br, 2H, NH_2), 6.96-7.00 (m, 2H, Ar), 7.35-7.39 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.3, 14.7, 76.9, 77.2, 90.4 (d, J = 1.5 Hz), 115.5 (d, J = 21.5 Hz), 118.9, 133.6 (d, J = 8.2 Hz), 162.3 (d, J = 247.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ, -111.1. IR (EtOH) ν 3200, 2938, 2899, 2816, 2224, 1597, 1491, 1464, 1442, 1305, 1180, 1059, 1010, 975, 925, 897, 826, 793, 755, 691 cm^{-1}. MS (ESI) *m/z* 287 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{12}H_{16}FN_2O_3S$: 287.0860, Found: 287.0860.

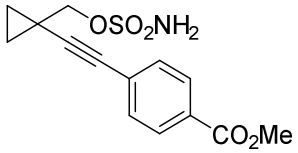




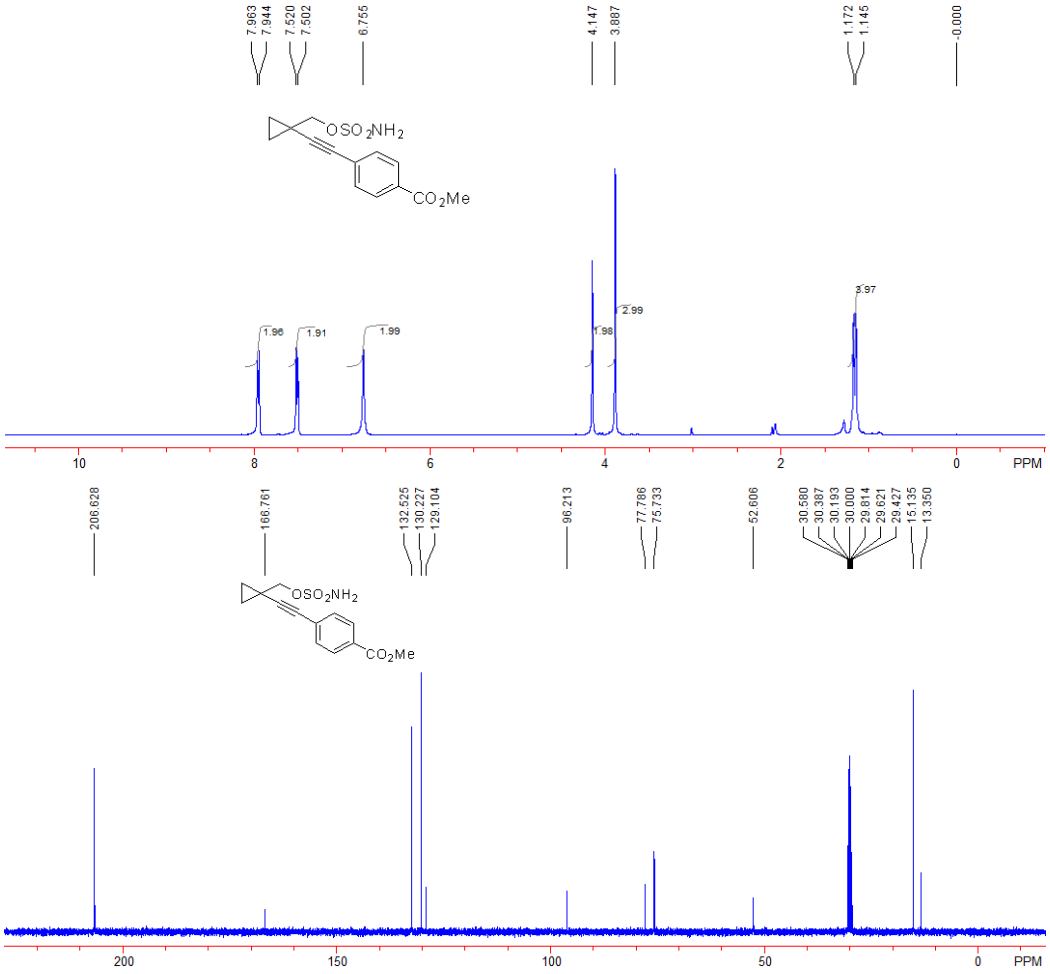
(1-((4-(trifluoromethyl)phenyl)ethynyl)cyclopropyl)methyl sulfamate **1j**: Yield: 177 mg, 55%; A white solid, Mp: 90-92 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.05-1.08 (m, 2H, CH_2), 1.21-1.26

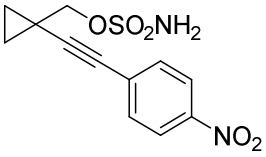
(m, 2H, CH_2), 4.18 (s, 2H, CH_2), 5.10 (br, 2H, NH_2), 7.47-7.55 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.4, 14.8, 76.6, 77.1, 93.5, 122.5, 123.8 (q, J = 270.9 Hz), 125.1 (q, J = 3.7 Hz), 126.7 (q, J = 1.5 Hz), 129.7 (q, J = 32 Hz), 131.9. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -111.1-(-111.2) (m). IR (EtOH) ν 3358, 3278, 2961, 2922, 2858, 2225, 1615, 1551, 1324, 1165, 1129, 1105, 1067, 1035, 1016, 961, 840, 818 cm^{-1}. MS (ESI) *m/z* 337 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{13}H_{16}F_3N_2O_3S$: 337.0828, Found: 337.0830.



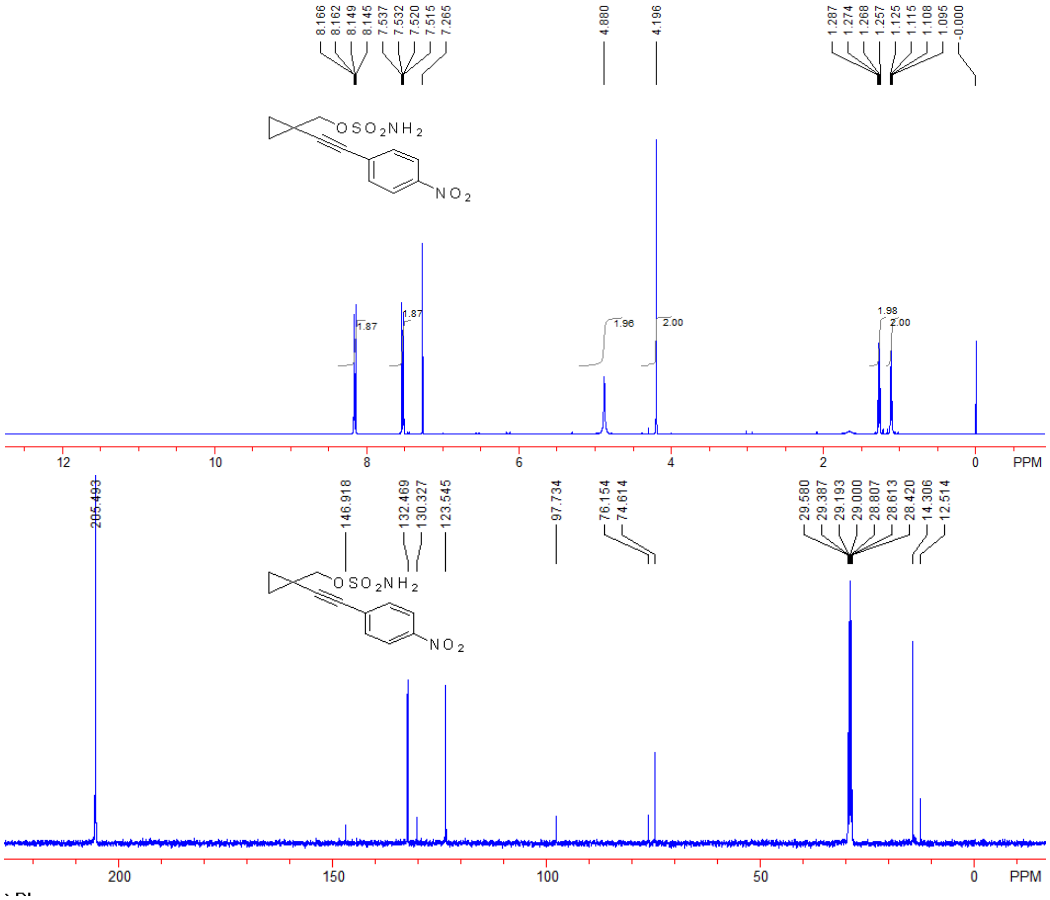


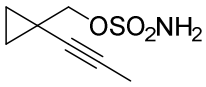
methyl 4-((1-((sulfamoyloxy)methyl)cyclopropyl)ethynyl)benzoate **1k**: Yield: 267 mg, 86%; A white solid, Mp: 153-155 ^{o}C; ^{1}H NMR ($(CD_3)_2CO$, 400 MHz, TMS) δ 1.15-1.17 (m, 4H, $2CH_2$), 3.89 (s, 3H, CH_3), 4.15 (s, 2H, CH_2), 6.76 (br, 2H, NH_2), 7.51 (d, J = 7.2 Hz, 2H, Ar), 7.95 (d, J = 7.2 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.4, 15.1, 52.6, 75.7, 77.8, 96.2, 129.1, 130.2, 132.5, 166.8. IR (EtOH) ν 3315, 3235, 3126, 3018, 2956, 2920, 2847, 2219, 1697, 1604, 1578, 1437, 1406, 1386, 1368, 1309, 1290, 1283, 1247, 1169, 1110, 1097, 1071, 1037, 1016, 966, 948, 909, 876, 861, 810, 779, 770 cm^{-1}. MS (ESI) *m/z* 327 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{14}H_{19}N_2O_5S$: 327.1009, Found: 327.1010.





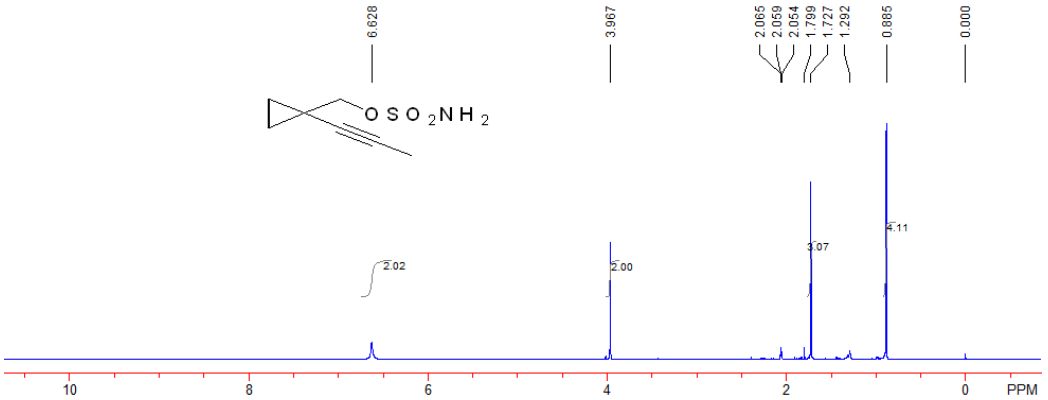
(1-((4-nitrophenyl)ethynyl)cyclopropyl)methyl sulfamate **1l**: Yield: 237 mg, 80%; A yellow solid, Mp: 120-122 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10-1.13 (m, 2H, CH_2), 1.26-1.29 (m, 2H, CH_2), 4.20 (s, 2H, CH_2), 4.88 (br, 2H, NH_2), 7.52-7.54 (m, 2H, Ar), 8.15-8.17 (m, 2H, Ar). ^{13}C NMR (CD_3COCD_3, 100 MHz, TMS) δ 12.5, 14.3, 74.6, 76.2, 97.7, 123.5, 130.3, 132.5, 146.9. IR (EtOH) ν 3387, 3346, 3259, 3121, 2226, 1592, 1503, 1460, 1446, 1427, 1385, 1340, 1309, 1284, 1179, 1110, 1030, 963, 952, 921, 884, 855, 815, 785, 750, 691 cm^{-1}. MS (EI) *m/z* 296 $(M)^{+}$. HRMS (EI) calcd. for $C_{12}H_{12}N_2O_5S$: 296.0467, Found: 296.0472.

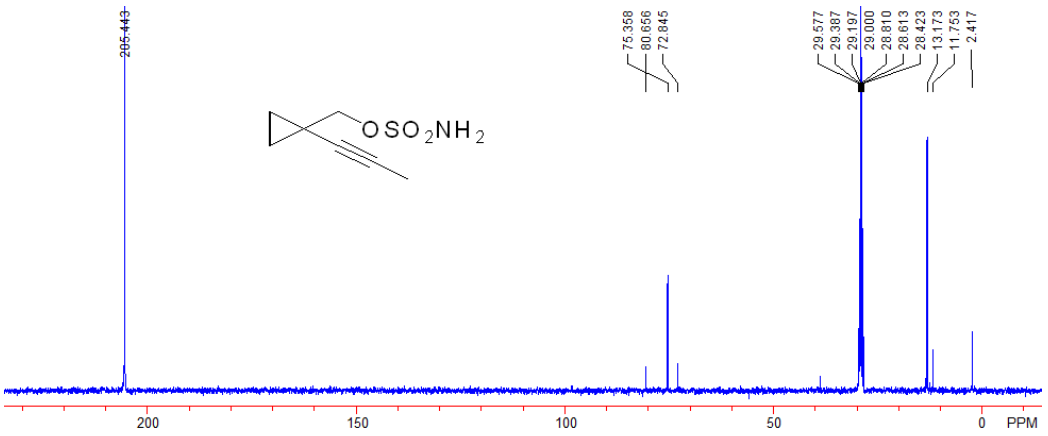


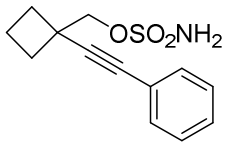


(1-(prop-1-yn-1-yl)cyclopropyl)methyl sulfamate **1m**: Yield: 330 mg, 87%; A yellow solid, Mp:

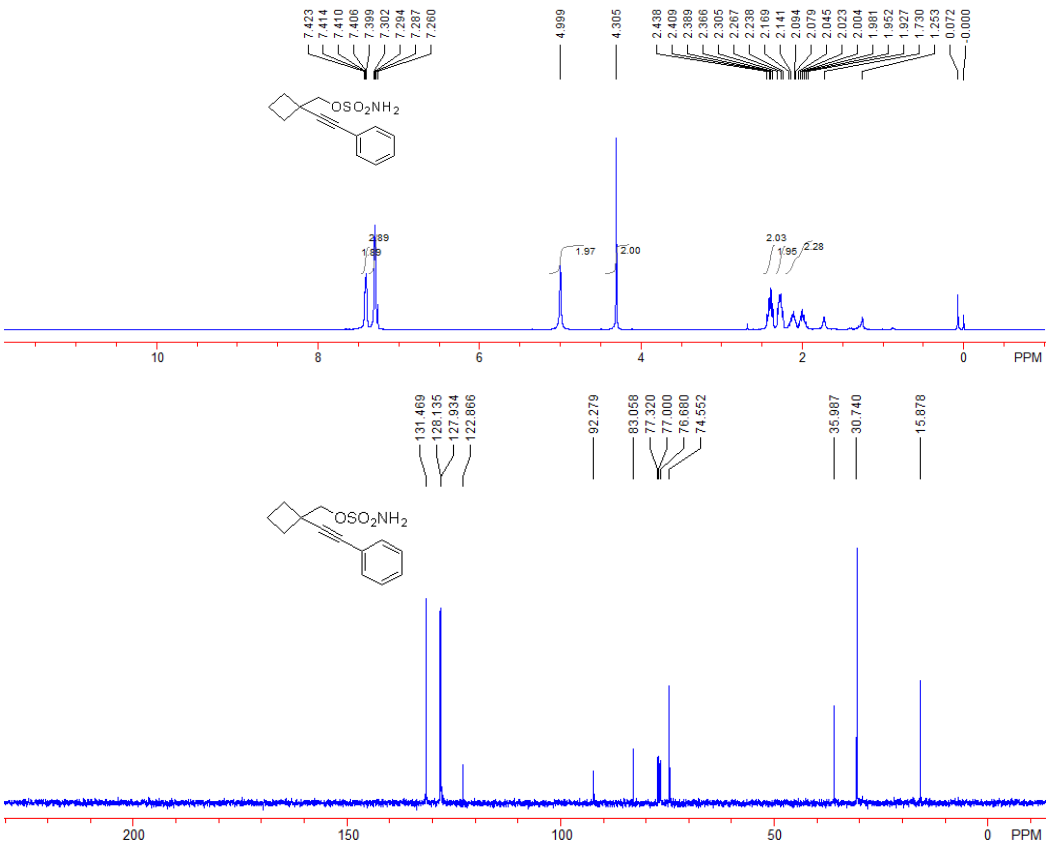
70-72 °C; ^{1}H NMR (CD_3COCD_3, 400 MHz, TMS) δ 0.89 (s, 4H, $2CH_2$), 1.73 (s, 3H, CH_3), 3.97 (s, 2H, CH_2), 6.63 (br, 2H, NH_2). ^{13}C NMR (CD_3COCD_3, 100 MHz, TMS) δ 2.4, 11.8, 13.2, 72.8, 75.4, 80.7. IR (EtOH) ν 3361, 3269, 2959, 2920, 1338, 1167, 1027, 938, 925, 899, 834, 822, 690 cm^{-1}. MS (ESI) *m/z* 188 $(M-H)^-$. HRMS (DART) calcd. for $C_7H_{10}NO_3S$: 188.0387, Found: 188.0384.

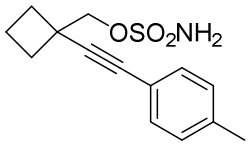




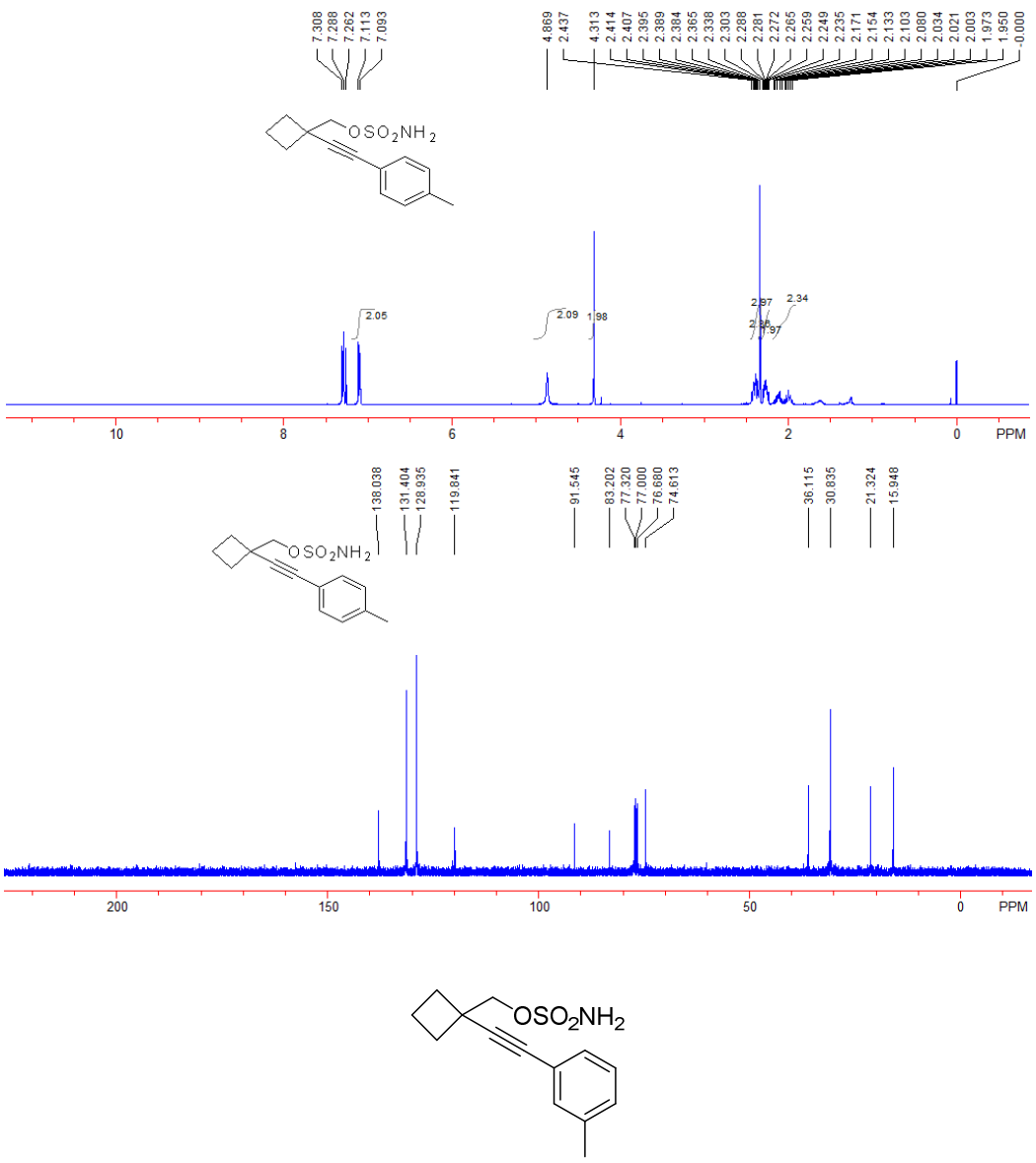


(1-(phenylethynyl)cyclobutyl)methyl sulfamate **3a**: Yield: 218 mg, 82%; A white solid, Mp: 54-56 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.93-2.17 (m, 2H, CH_2), 2.24-2.31 (m, 2H, CH_2), 2.37-2.44 (m, 2H, CH_2), 4.31 (s, 2H, CH_2), 5.00 (br, 2H, NH_2), 7.26-7.30 (m, 3H, Ar), 7.40-7.42 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 15.9, 30.7, 36.0, 74.6, 83.1, 92.3, 122.9, 127.9, 128.1, 131.5. IR (EtOH) ν 3380, 3285, 2989, 2947, 1556, 1491, 1442, 1362, 1179, 980, 926, 829, 782, 756, 691 cm^{-1}. MS (ESI) *m/z* 288 $(M+Na)^+$. HRMS (ESI) calcd. for $C_{13}H_{15}NO_3SNa$: 288.0665, Found: 288.0665.

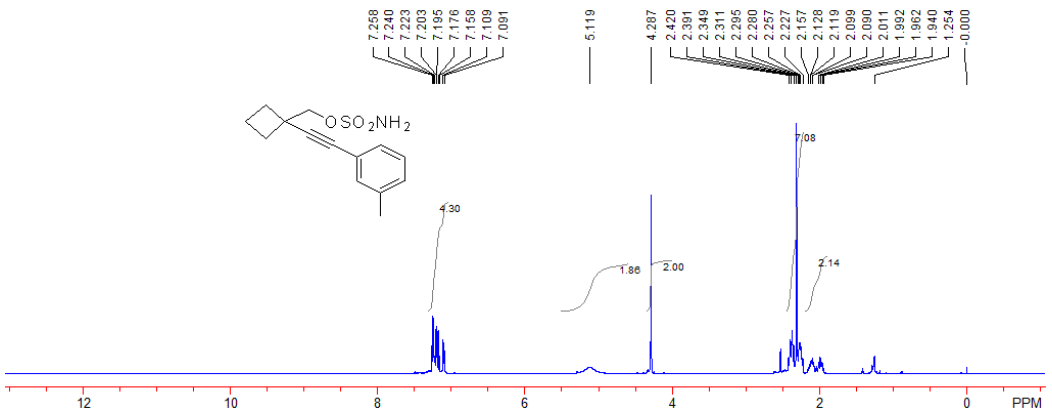


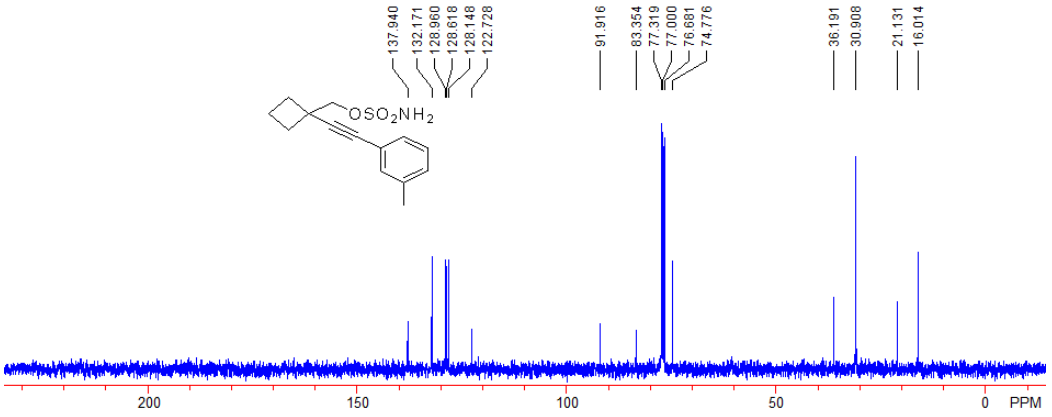


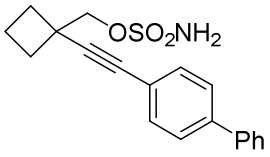
(1-(p-tolylethynyl)cyclobutyl)methyl sulfamate **3b**: Yield: 213 mg, 76%; A white solid, Mp: 65-67 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95-2.17 (m, 2H, CH_2), 2.24-2.30 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.37-2.44 (m, 2H, CH_2), 4.31 (s, 2H, CH_2), 4.87 (br, 2H, NH_2), 7.10 (d, J = 8.0 Hz, 2H, Ar), 7.29 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 15.9, 21.3, 30.8, 36.1, 74.6, 83.2, 91.5, 119.8, 128.9, 131.4, 138.0. IR (EtOH) ν 3369, 3283, 2989, 2947, 2855, 2222, 1599, 1556, 1484, 1456, 1362, 1242, 1178, 1090, 1043, 980, 923, 821, 782 cm^{-1}. MS (ESI) *m/z* 297 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{14}H_{21}N_2O_3S$: 297.1267, Found: 297.1267.



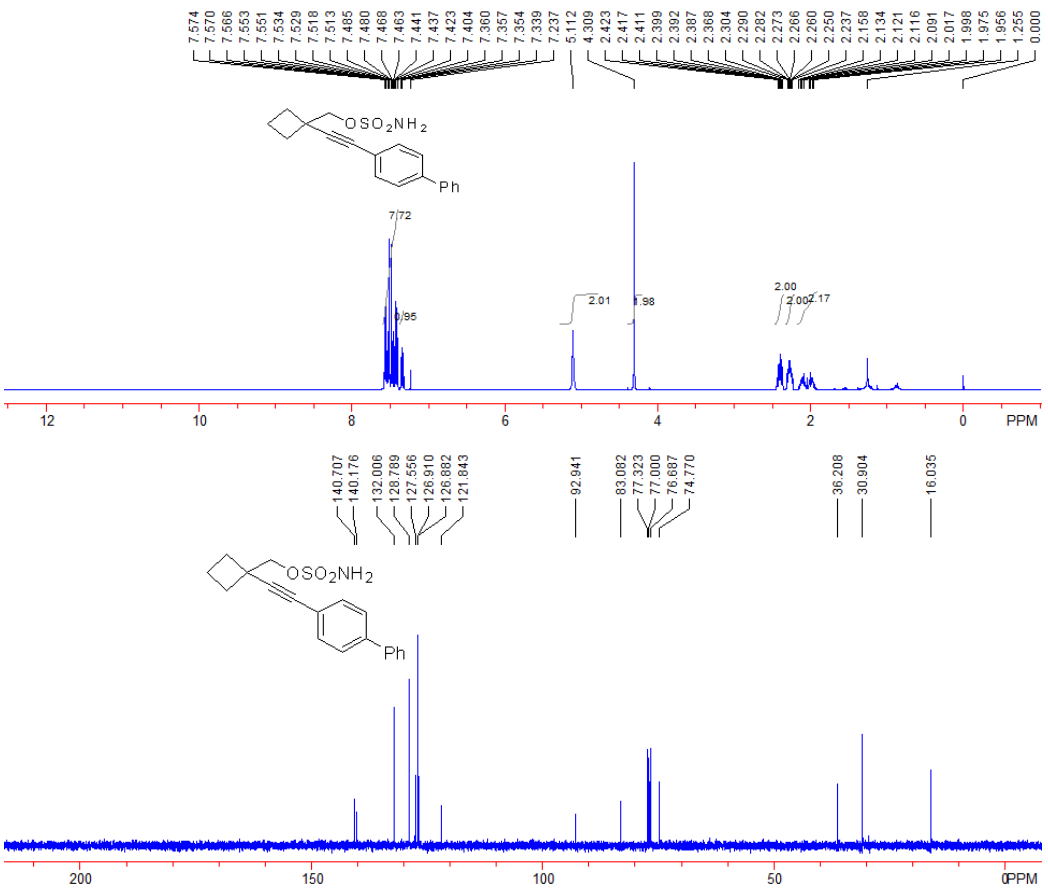
1-((3-methoxyphenyl)ethynyl)cyclobutyl)methyl sulfamate **3c**: Yield: 229 mg, 82%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.94-2.16 (m, 2H, CH_2), 2.23-2.42 (m, 4H, $2CH_2$), 3.30 (s, 3H, CH_3), 4.29 (s, 2H, CH_2), 5.12 (br, 2H, NH_2), 7.09-7.26 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.0, 21.1, 30.9, 36.2, 74.8, 83.4, 91.9, 122.7, 128.1, 128.6, 129.0, 132.2, 137.9. IR (EtOH) ν 3369, 3285, 2947, 2222, 1599, 1484, 1456, 1363, 1178, 1043, 981, 924, 879, 821, 782, 691 cm^{-1}. MS (ESI) *m/z* 297 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{14}H_{21}N_2O_3S$: 297.1267, Found: 297.1267.

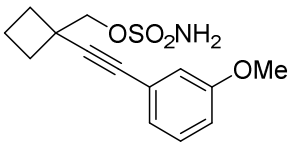




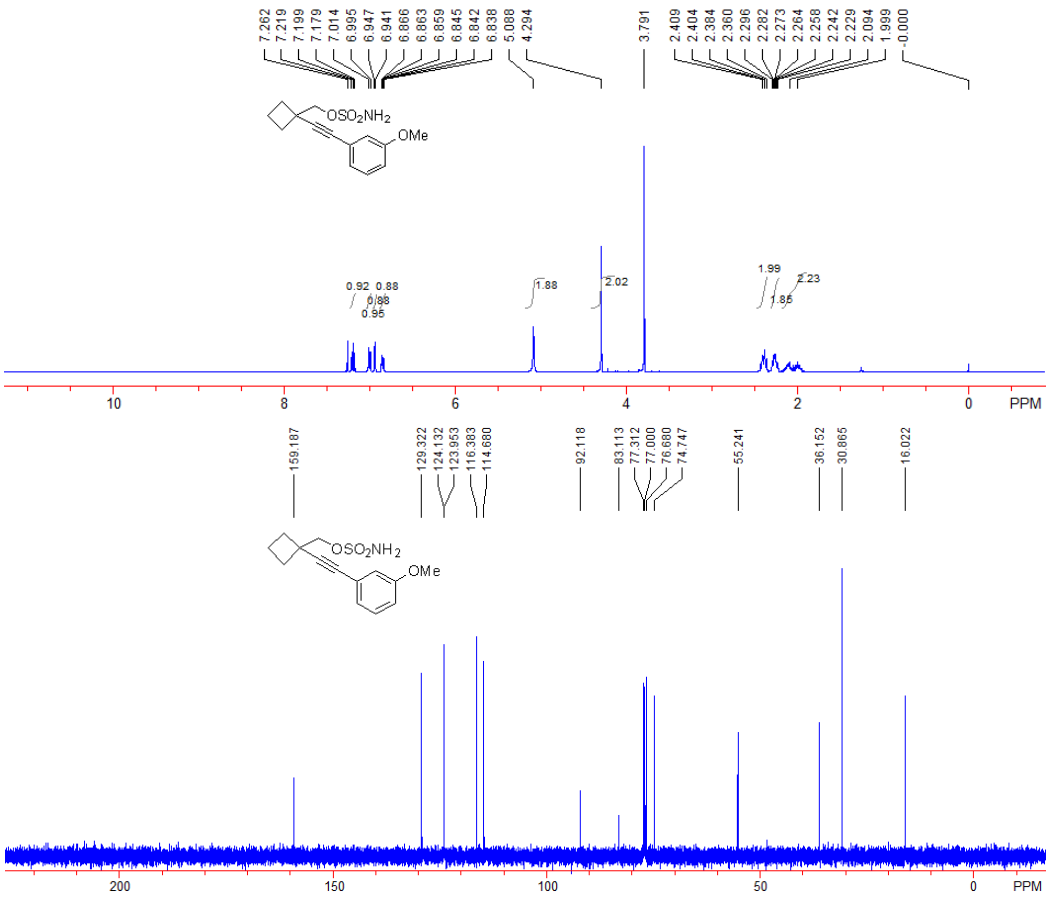


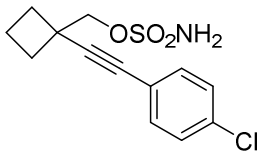
(1-([1,1'-biphenyl]-4-ylethynyl)cyclobutyl)methyl sulfamate **3d**: Yield: 235 mg, 69%; A white solid, Mp: 137-139 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.96-2.16 (m, 2H, CH_2), 2.24-2.30 (m, 2H, CH_2), 2.37-2.42 (m, 2H, CH_2), 4.31 (s, 2H, CH_2), 5.11 (br, 2H, NH_2), 7.24-7.36 (m, 1H, Ar), 7.40-7.57 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.0, 30.9, 36.2, 74.8, 83.1, 92.9, 121.8, 126.88, 126.91, 127.6, 128.8, 132.0, 140.2, 140.7. IR (EtOH) ν 3369, 3283, 2989, 2947, 2855, 2222, 1599, 1556, 1484, 1362, 1178, 1090, 980, 923, 821, 782, 745, 691 cm^{-1}. MS (ESI) *m/z* 359 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{19}H_{23}N_2O_3S$: 359.1424, Found: 359.1424.



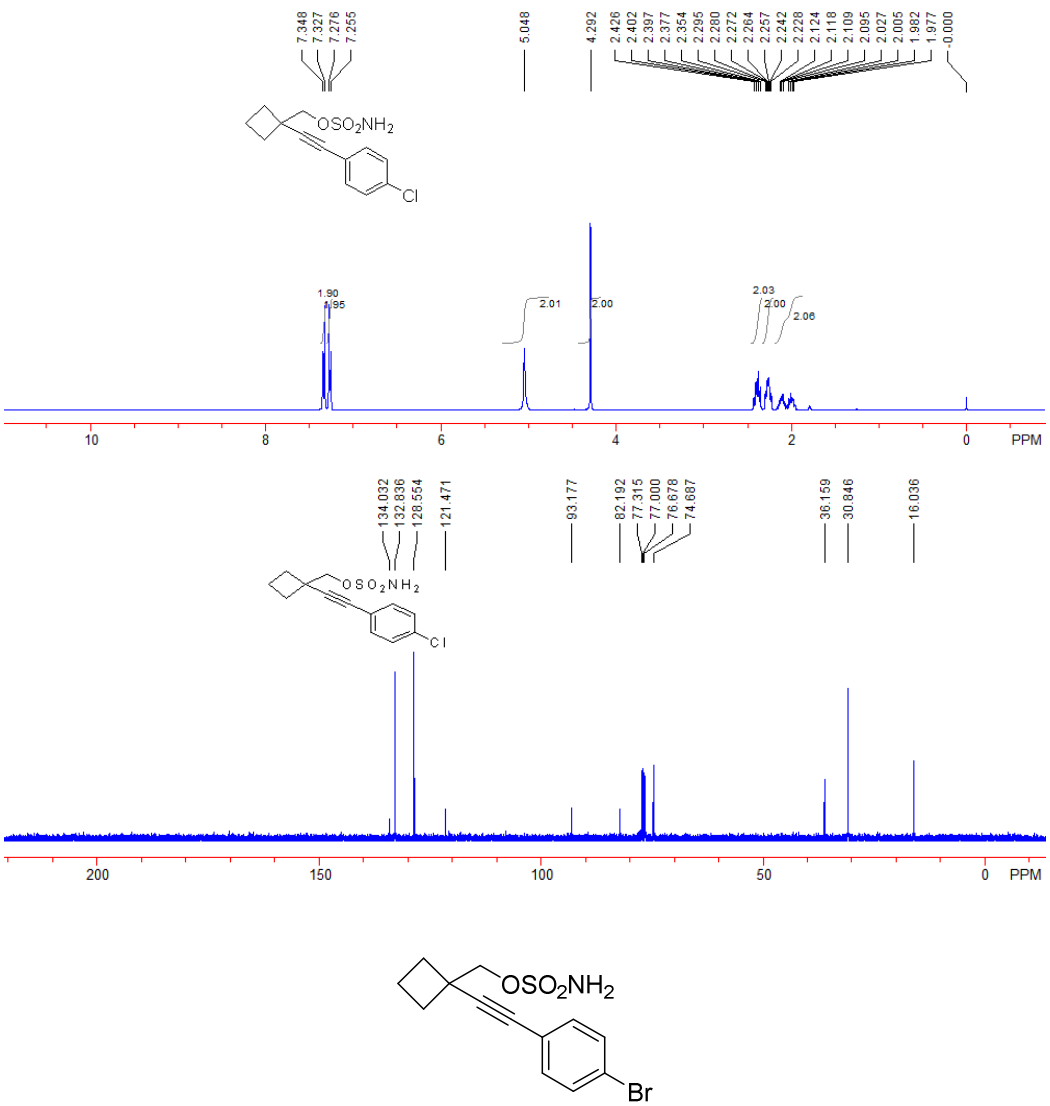


(1-((3-methoxyphenyl)ethynyl)cyclobutyl)methyl sulfamate **3e**: Yield: 315 mg, 84%; A white soild, Mp: 83-85 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95-2.16 (m, 2H, CH_2), 2.23-2.30 (m, 2H, CH_2), 2.36-2.43 (m, 2H, CH_2), 3.79 (s, 3H, CH_3), 4.29 (s, 2H, CH_2), 5.09 (br, 2H, NH_2), 6.84-6.87 (m, 1H, Ar), 6.94-6.95 (m, 1H, Ar), 7.00-7.01 (m, 1H, Ar), 7.18-7.22 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.0, 30.9, 36.2, 55.2, 74.7, 83.1, 92.1, 114.7, 116.4, 124.0, 124.1, 129.3, 159.2. IR (EtOH) ν 3367, 3274, 2969, 2944, 2832, 2222, 1711, 1596, 1574, 1481, 1464, 1428, 1362, 1316, 1282, 1265, 1205, 1178, 1132, 1041, 980, 923, 876, 853, 820, 781, 686 cm^{-1}. MS (ESI) *m/z* 313 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{14}H_{21}N_2O_4S$: 313.1222, Found: 313.1222.

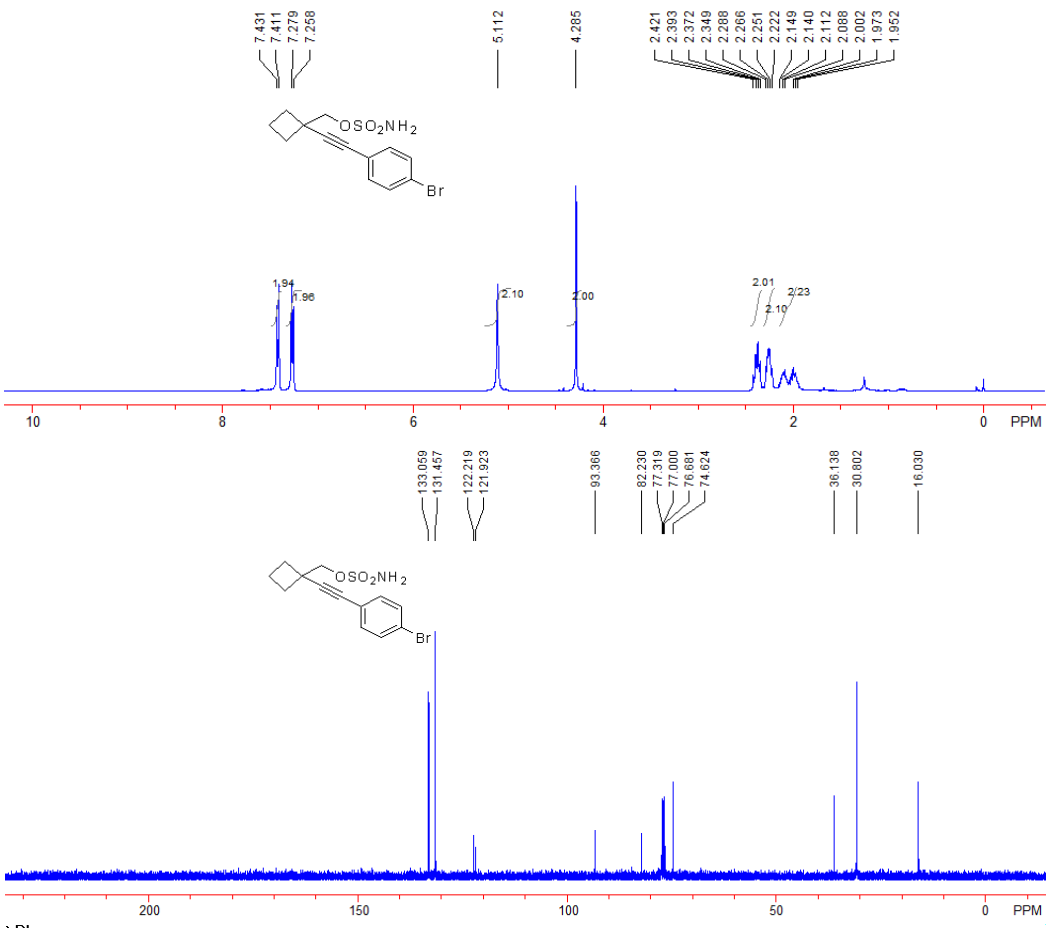


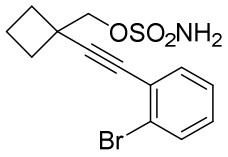


(1-((4-chlorophenyl)ethynyl)cyclobutyl)methyl sulfamate **3f**: Yield: 258 mg, 86%; A yellow solid, Mp: 85-87 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.98-2.12 (m, 2H, CH_2), 2.23-2.30 (m, 2H, CH_2), 2.35-2.43 (m, 2H, CH_2), 4.29 (s, 2H, CH_2), 5.05 (br, 2H, NH_2), 7.26 (d, J = 8.4 Hz, 2H, Ar), 7.33 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.0, 30.8, 36.2, 74.7, 82.2, 93.2, 121.5, 128.6, 132.8, 134.0. IR (EtOH) ν 3372, 3272, 3113, 3002, 2961, 2886, 2225, 1592, 1550, 1506, 1459, 1361, 1345, 1330, 1307, 1283, 1183, 1109, 968, 926, 858, 834, 780, 750, 691 cm^{-1}. MS (ESI) *m/z* 317 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{13}H_{18}ClN_2O_3S$: 317.0721, Found: 317.0722.

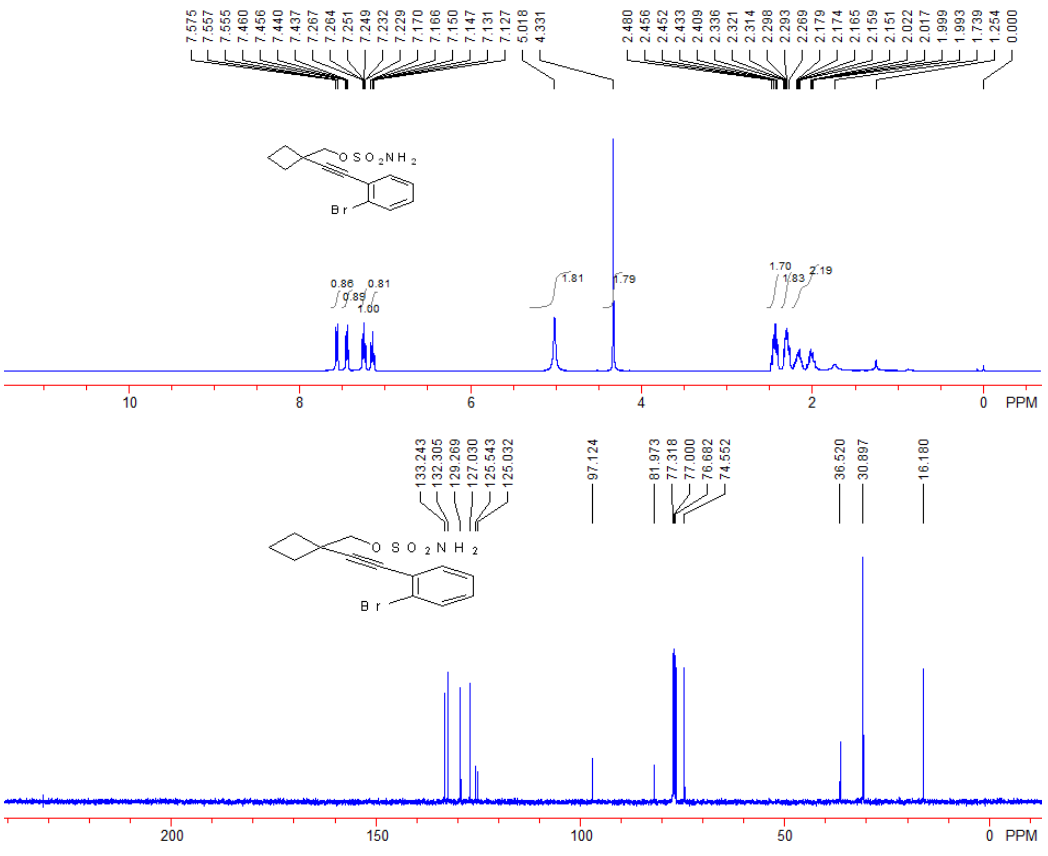


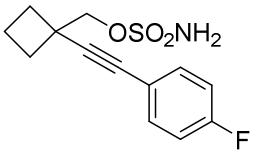
(1-((4-bromophenyl)ethynyl)cyclobutyl)methyl sulfamate **3g**: Yield: 277 mg, 81%; A white soild, Mp: 112-114 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95-2.15 (m, 2H, CH_2), 2.22-2.29 (m, 2H, CH_2), 2.35-2.42 (m, 2H, CH_2), 4.29 (s, 2H, CH_2), 5.11 (br, 2H, NH_2), 7.26 (d, J = 8.4 Hz, 2H, Ar), 7.42 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.0, 30.8, 36.1, 74.6, 82.2, 93.4, 121.9, 122.2, 131.5, 133.1. IR (EtOH) ν 3386, 3288, 2992, 2947, 2220, 1553, 1485, 1363, 1183, 1096, 1069, 1010, 981, 929, 824, 785, 703 cm^{-1}. MS (ESI) *m/z* 361 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{13}H_{18}BrN_2O_3S$: 361.0216, Found: 361.0215.



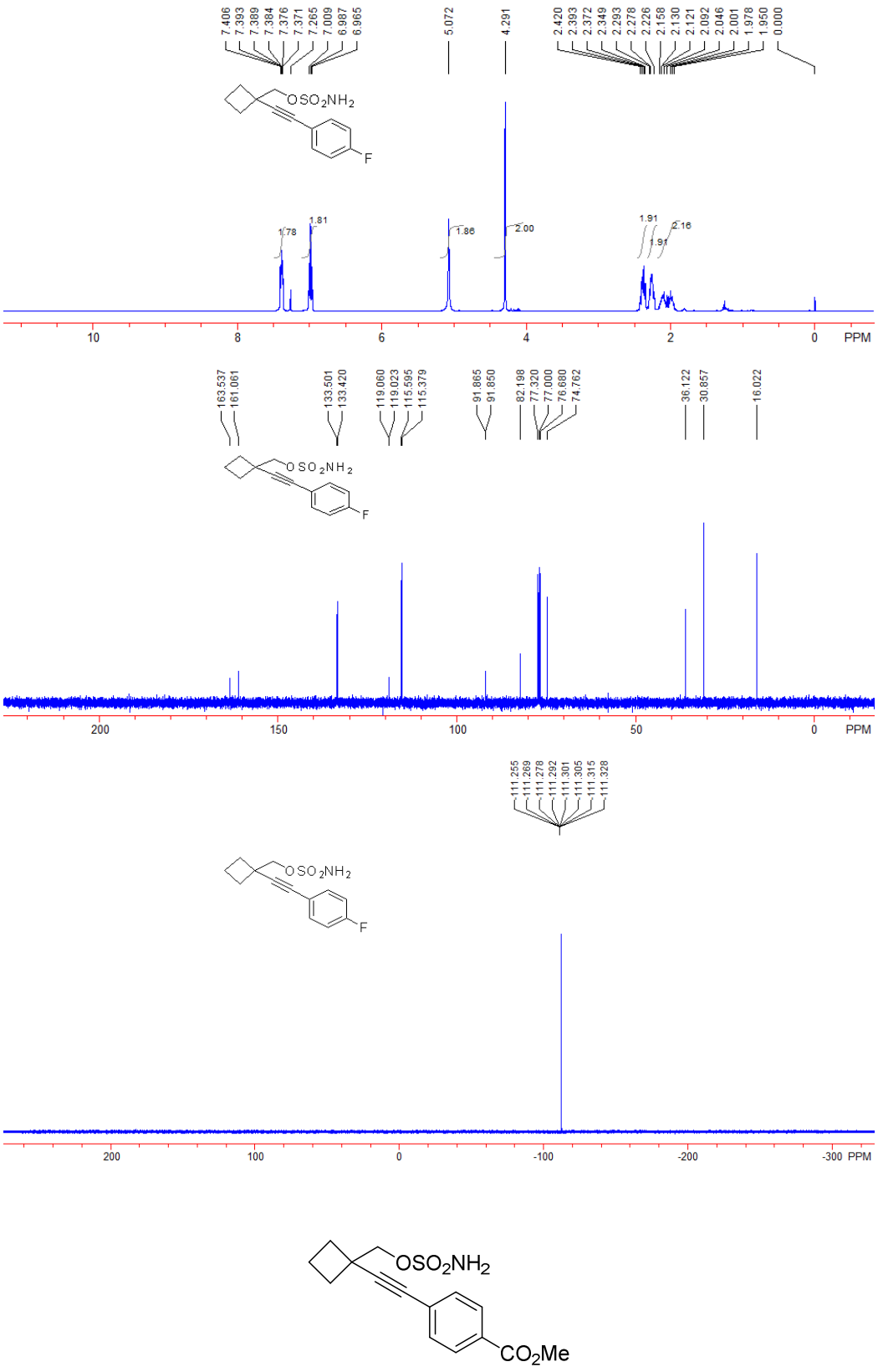


(1-((2-bromophenyl)ethynyl)cyclobutyl)methyl sulfamate **3h**: Yield: 269 mg, 78%; A white solid, Mp: 108-110 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.74-2.18 (m, 2H, CH_2), 2.27-2.34 (m, 2H, CH_2), 2.41-2.48 (m, 2H, CH_2), 4.33 (s, 2H, CH_2), 5.02 (br, 2H, NH_2), 7.13-7.17 (m, 1H, Ar), 7.23-7.27 (m, 1H, Ar), 7.44-7.46 (m, 1H, Ar), 7.56-7.58 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.2, 30.9, 36.5, 74.6, 82.0, 97.1, 125.0, 125.5, 127.0, 129.3, 132.3, 133.2. IR (EtOH) ν 3385, 3293, 2992, 2948, 2881, 2228, 1559, 1469, 1432, 1364, 1182, 1065, 982, 927, 831, 754 cm^{-1}. MS (ESI) *m/z* 361 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{13}H_{18}BrN_2O_3S$: 361.0216, Found: 361.0217.



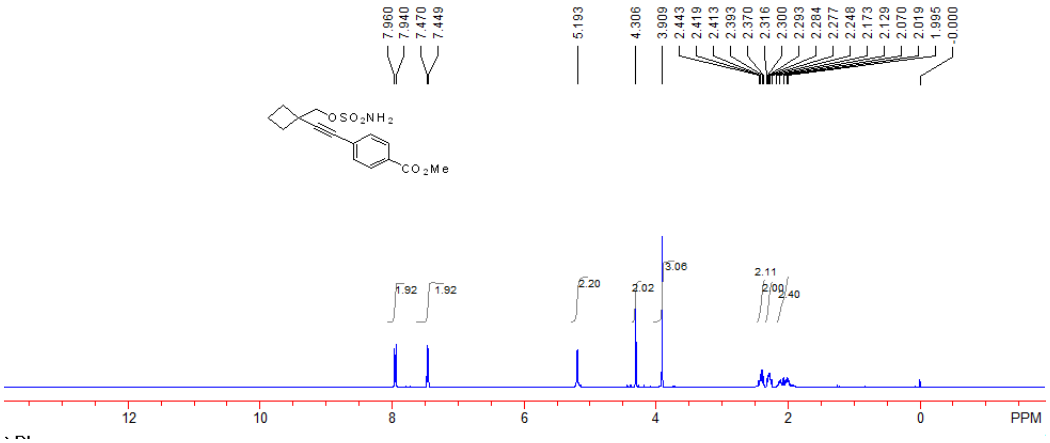


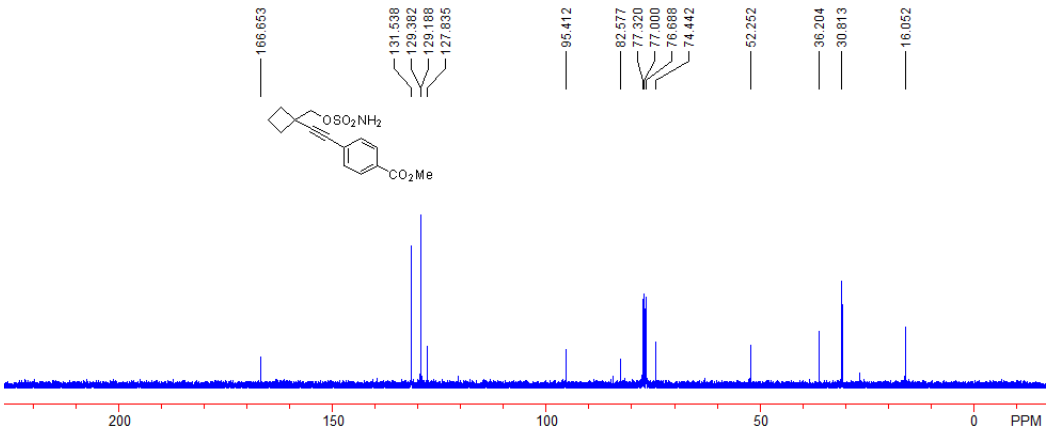
((1-((4-fluorophenyl)ethynyl)cyclobutyl)methyl sulfamate **3i**: Yield: 208 mg, 70%; A yellow solid, Mp: 64-66 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95-2.16 (m, 2H, CH_2), 2.23-2.29 (m, 2H, CH_2), 2.35-2.42 (m, 2H, CH_2), 4.29 (s, 2H, CH_2), 5.07 (br, 2H, NH_2), 6.97-7.01 (m, 2H, Ar), 7.37-7.41 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.0, 30.9, 36.1, 74.7, 82.2, 91.9 (d, J = 1.5 Hz), 115.4 (d, J = 21.6 Hz), 119.0 (d, J = 3.7 Hz), 133.4 (d, J = 8.1 Hz), 162.3 (d, J = 247.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ, -111.26-(-111.33) (m). IR (EtOH) ν 3385, 3287, 2989, 2948, 2884, 2860, 1675, 1600, 1555, 1506, 1457, 1361, 1230, 1181, 1156, 1092, 978, 927, 834, 752 cm^{-1}. MS (ESI) *m/z* 301 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{13}H_{18}FN_2O_3S$: 301.1017, Found: 301.1017.

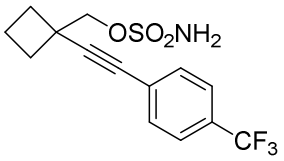


(1-((4-bromophenyl)ethynyl)cyclobutyl)methyl sulfamate **3j**: Yield: 265 mg, 82%; A white solid, Mp: 125-127 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.00-2.17 (m, 2H, CH_2), 2.25-2.32 (m, 2H,

CH_2), 2.39-2.44 (m, 2H, CH_2), 3.91 (s, 3H, CH_3), 4.31 (s, 2H, CH_2), 5.19 (br, 2H, NH_2), 7.46 (d, J = 8.0 Hz, 2H, Ar), 7.95 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.1, 30.8, 36.2, 52.3, 74.4, 82.6, 95.4, 127.8, 129.2, 129.4, 131.5, 166.7. IR (EtOH) ν 3374, 3343, 2992, 2951, 2886, 2850, 2220, 1703, 1604, 1437, 1366, 1309, 1290, 1276, 1176, 1109, 1017, 984, 923, 858, 826, 769, 696 cm^{-1}. MS (ESI) *m/z* 341 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{15}H_{21}N_2O_5S$: 341.1166, Found: 341.1167.

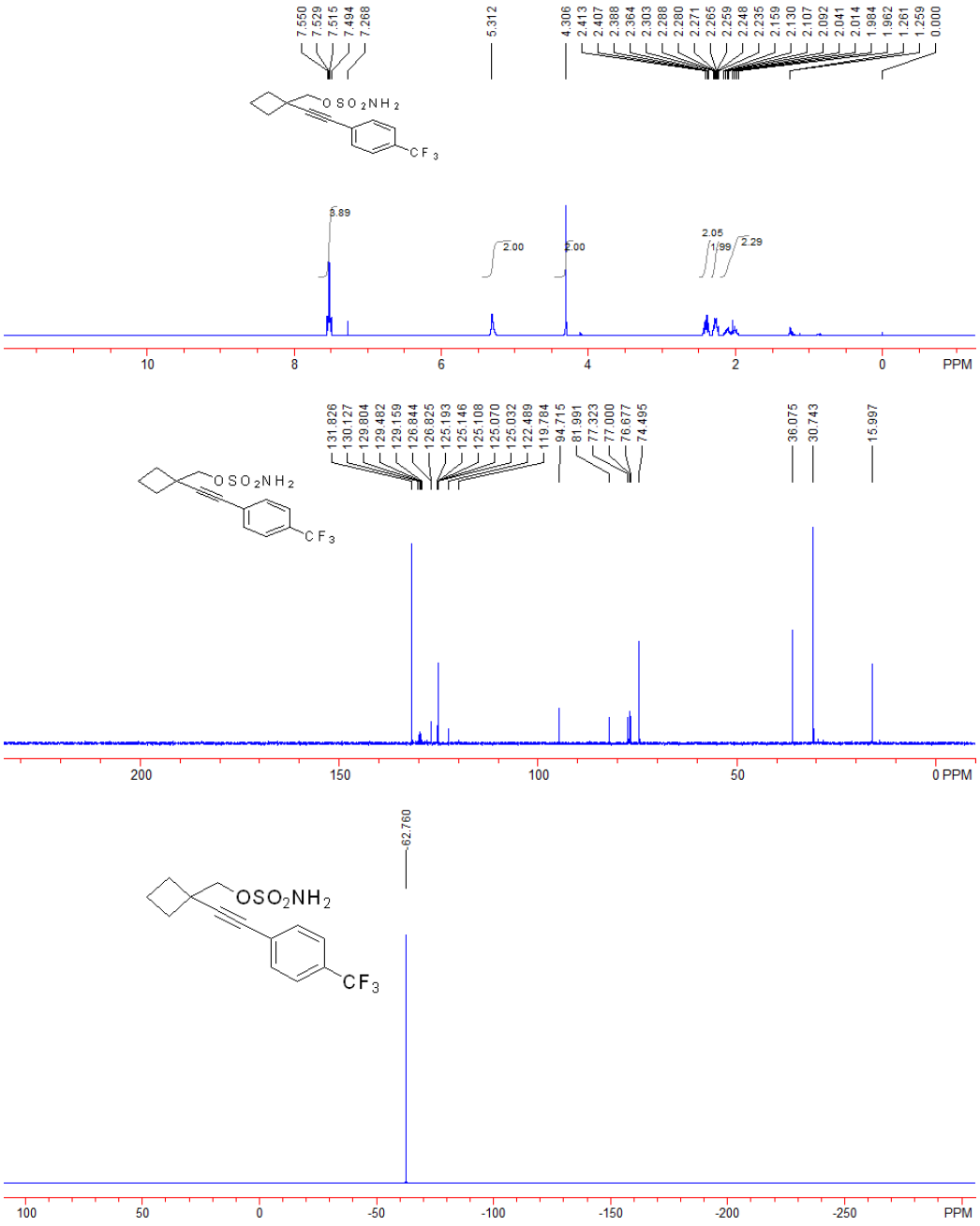


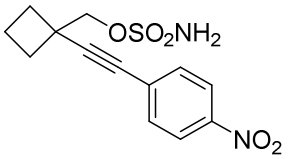




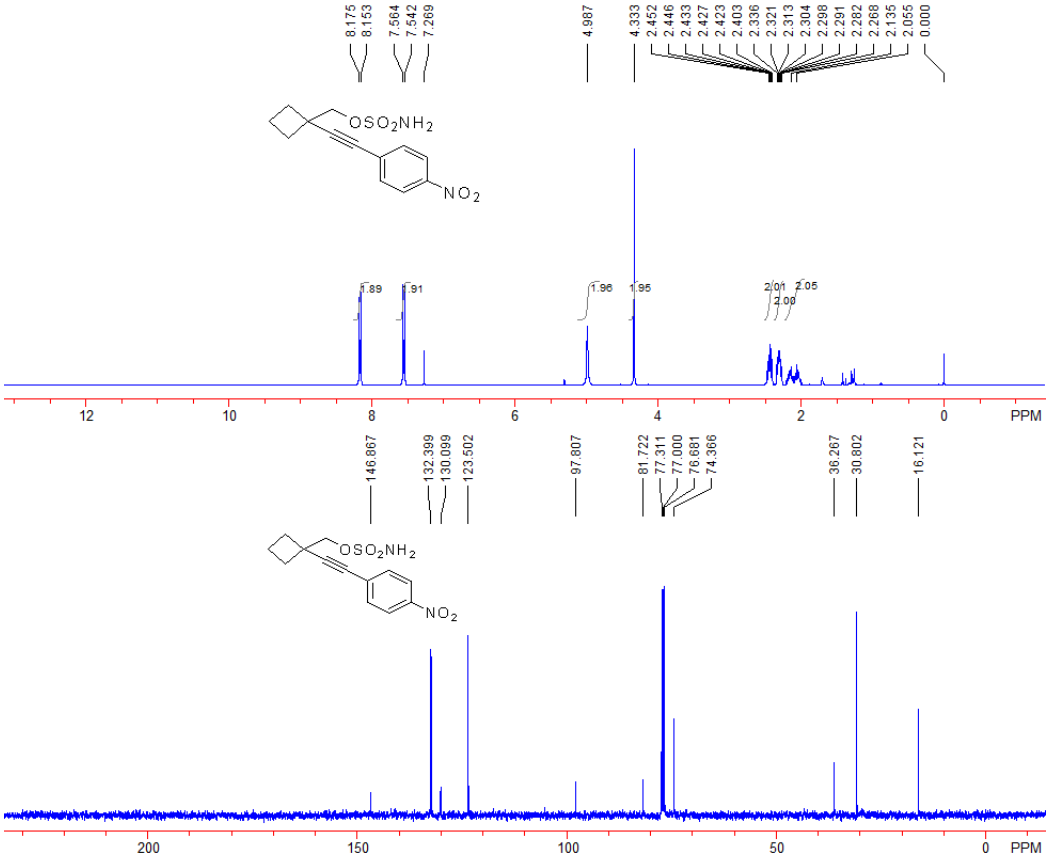
(1-((4-(trifluoromethyl)phenyl)ethynyl)cyclobutyl)methyl sulfamate **3k**: Yield: 234 mg, 71%; A yellow solid, Mp: 94-96 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.96-2.16 (m, 2H, CH_2), 2.24-2.30 (m, 2H, CH_2), 2.36-2.41 (m, 2H, CH_2), 4.31 (s, 2H, CH_2), 5.31 (br, 2H, NH_2), 7.49-7.55 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.0, 30.7, 36.1, 74.5, 77.3, 82.0, 94.7, 123.8 (q,

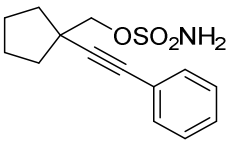
J = 270.4 Hz), 125.1 (q, J = 3.8 Hz), 126.8 (q, J = 1.9 Hz), 129.6 (q, J = 32.2 Hz), 131.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -62.8 (s). IR (EtOH) ν 3374, 3282, 2995, 2974, 2953, 2222, 1614, 1367, 1323, 1166, 1132, 1104, 1065, 1015, 982, 879, 840, 752 cm^{-1}. MS (ESI) *m/z* 351 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{14}H_{18}F_3N_2O_3S$: 351.0990, Found: 351.0990.





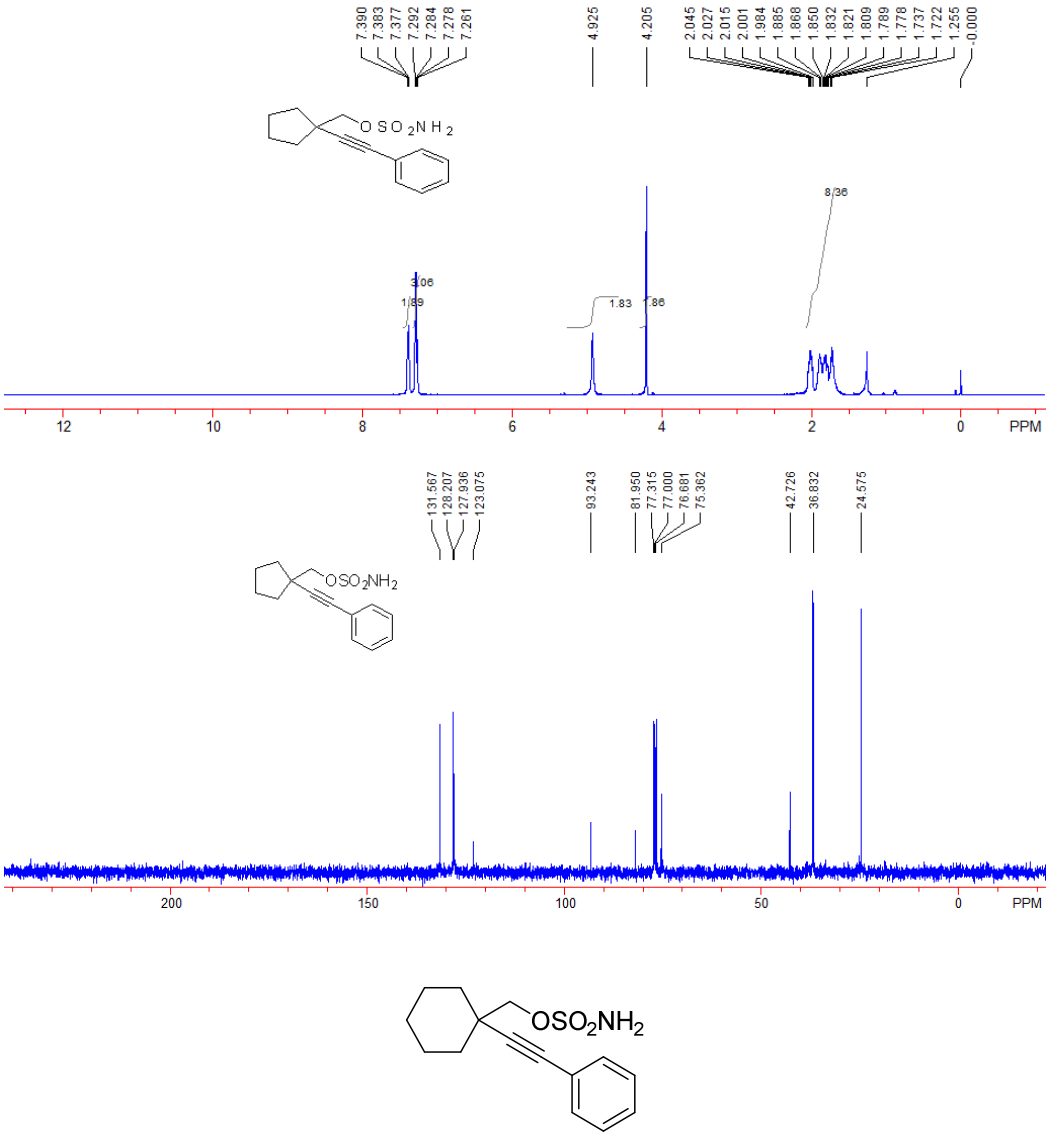
(1-((4-nitrophenyl)ethynyl)cyclobutyl)methyl sulfamate **3l**: Yield: 256 mg, 83%; A yellow solid, Mp: 130-132 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.06-2.14 (m, 2H, CH_2), 2.27-2.34 (m, 2H, CH_2), 2.40-2.45 (m, 2H, CH_2), 4.33 (s, 2H, CH_2), 4.99 (s, 2H, NH_2), 7.55 (d, J = 8.8 Hz, 2H, Ar), 8.16 (d, J = 8.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.1, 30.8, 36.3, 74.4, 81.7, 97.8, 123.5, 130.1, 132.4, 146.9. IR (EtOH) ν 3370, 3271, 3113, 3000, 2953, 2889, 2225, 1706, 1592, 1504, 1458, 1360, 1342, 1307, 1283, 1222, 1181, 1109, 968, 926, 857, 832, 779, 750, 691 cm^{-1}. MS (ESI) *m/z* 328 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{13}H_{18}N_3O_5S$: 328.0967, Found: 328.0967.





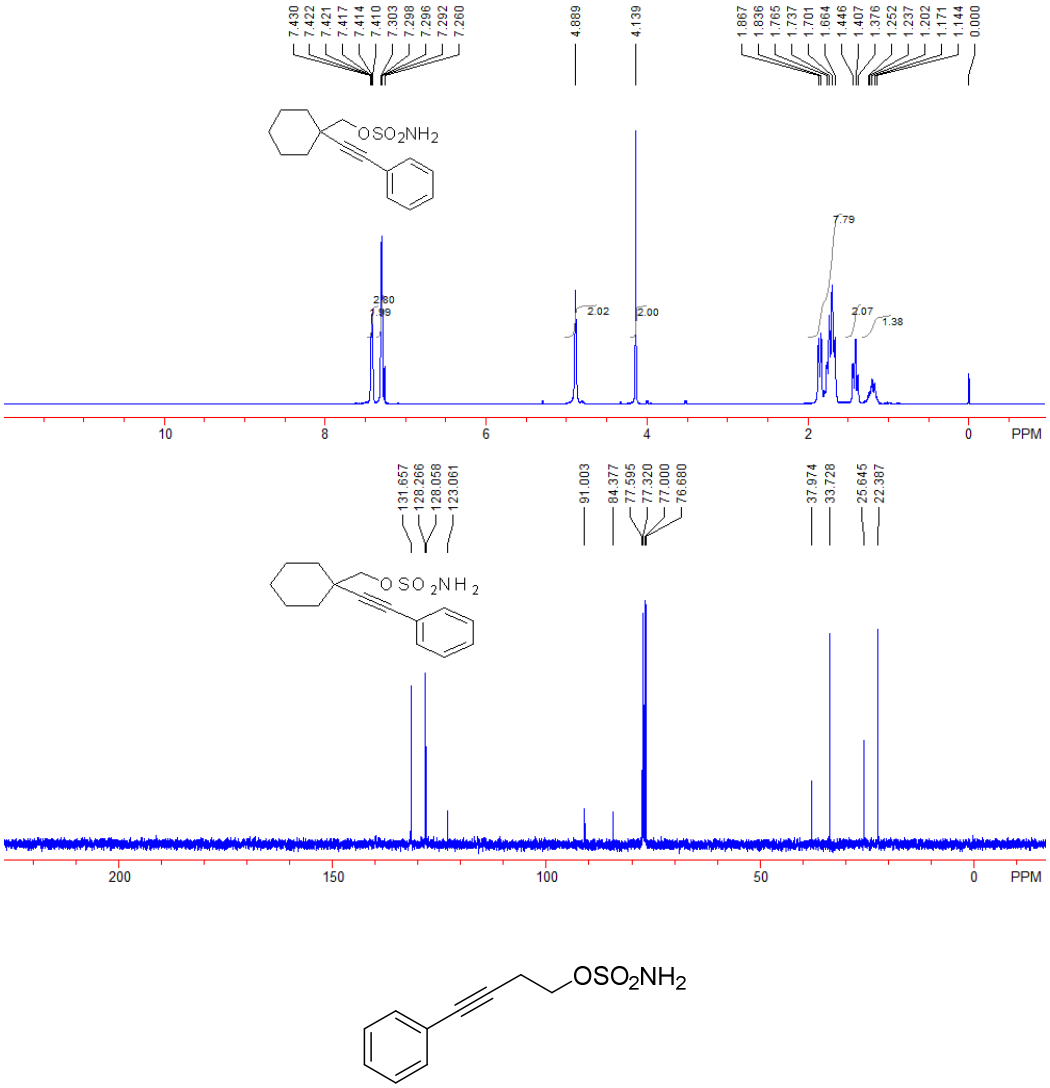
(1-(phenylethynyl)cyclopentyl)methyl sulfamate **5a**: Yield: 187 mg, 67%; A colorless oil; ^{1}H NMR

($CDCl_3$, 400 MHz, TMS) δ 1.72-2.05 (m, 8H, $4CH_2$), 4.21 (s, 2H, CH_2), 4.93 (br, 2H, NH_2), 7.26-7.29 (m, 3H, Ar), 7.38-7.39 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 24.6, 36.8, 42.7, 75.4, 82.0, 93.2, 123.1, 127.9, 128.2, 131.6. IR (EtOH) ν 3383, 3283, 2958, 2870, 1555, 1490, 1443, 1361, 1179, 1014, 979, 919, 820, 755, 691 cm^{-1}. MS (ESI) *m/z* 297 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{14}H_{21}N_2O_3S$: 297.1267, Found: 297.1267.

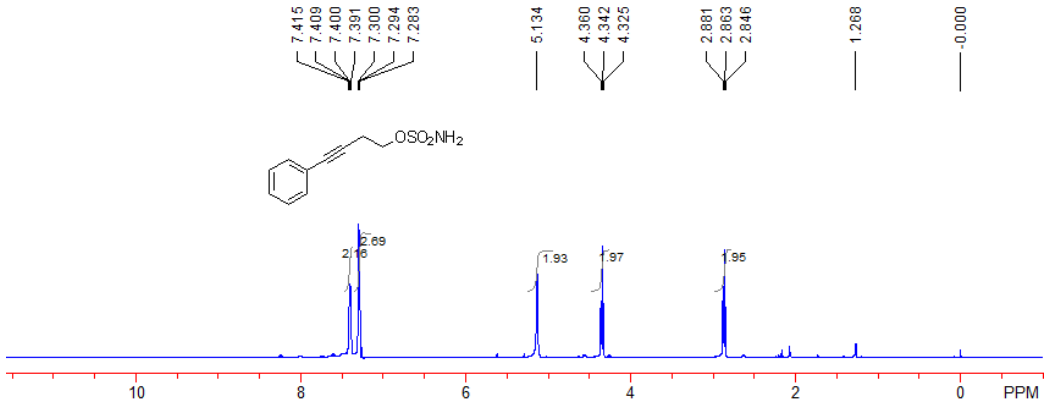


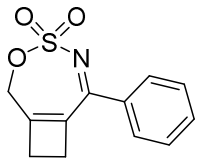
(1-(phenylethynyl)cyclohexyl)methyl sulfamate **7a**: Yield: 217 mg, 74%; A colorless oil; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.14-1.25 (m, 1H, CH_2), 1.38-1.45 (m, 2H, CH_2), 1.66-1.87 (m, 7H, $4CH_2$), 4.14 (s, 2H, CH_2), 4.89 (br, 2H, NH_2), 7.26-7.30 (m, 3H, Ar), 7.41-7.43 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 22.4, 25.6, 33.7, 38.0, 77.6, 84.4, 91.0, 123.1, 128.1, 128.3, 131.7. IR (EtOH) ν 3382, 3279, 2928, 2855, 1722, 1597, 1556, 1489, 1443, 1363, 1181, 1069, 1028, 984,

915, 825, 784, 755, 737, 690 cm^{-1}. MS (ESI) *m/z* 294 $(M+H)^+$. HRMS (ESI) calcd. for $C_{15}H_{20}NO_3S$: 294.1158, Found: 294.1156.

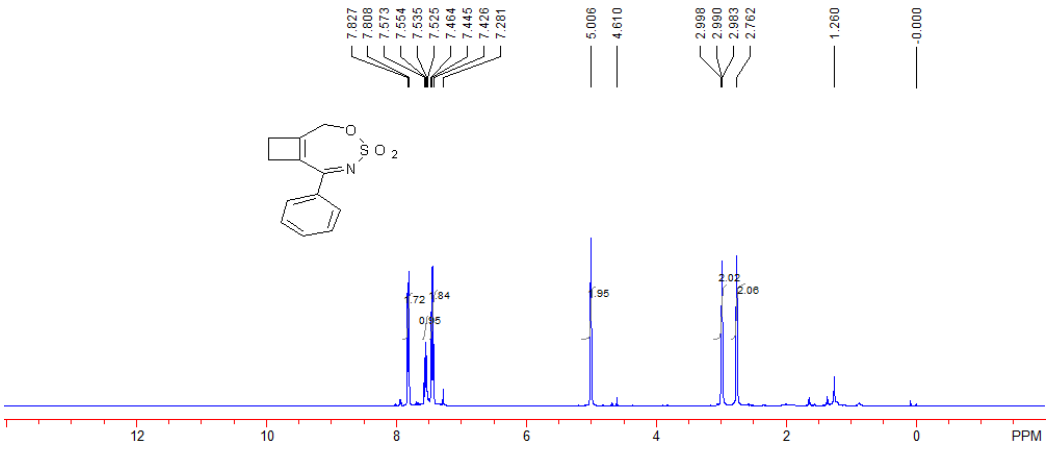


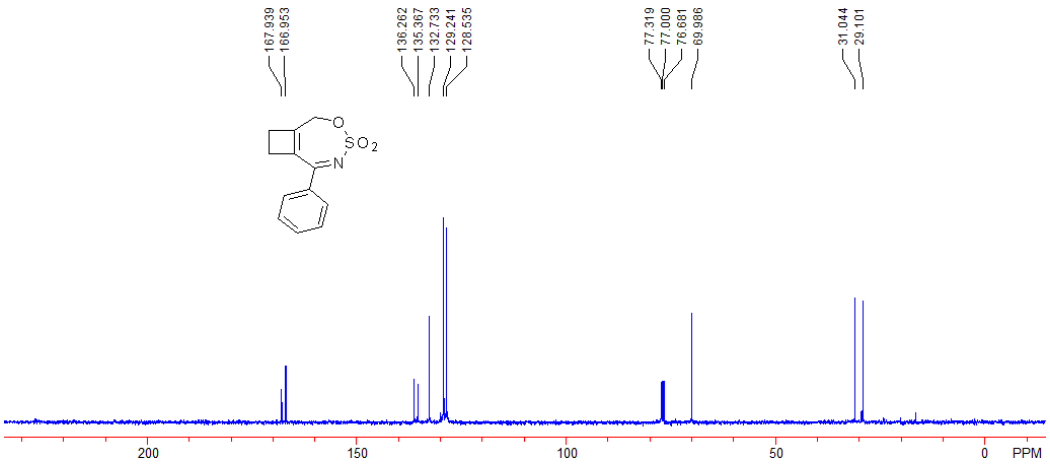
4-phenylbut-3-yn-1-yl sulfamate **9a** (a known compound):[5] Yield: 182 mg, 81%; A colorless oil; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.86 (t, *J* = 6.8 Hz, CH_2), 4.34 (t, *J* = 6.8 Hz, CH_2), 5.13 (br, 2H, NH_2), 7.28-7.30 (m, 3H, Ar), 7.39-7.42 (m, 2H, Ar).

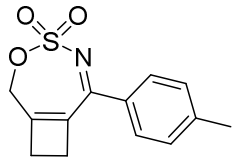




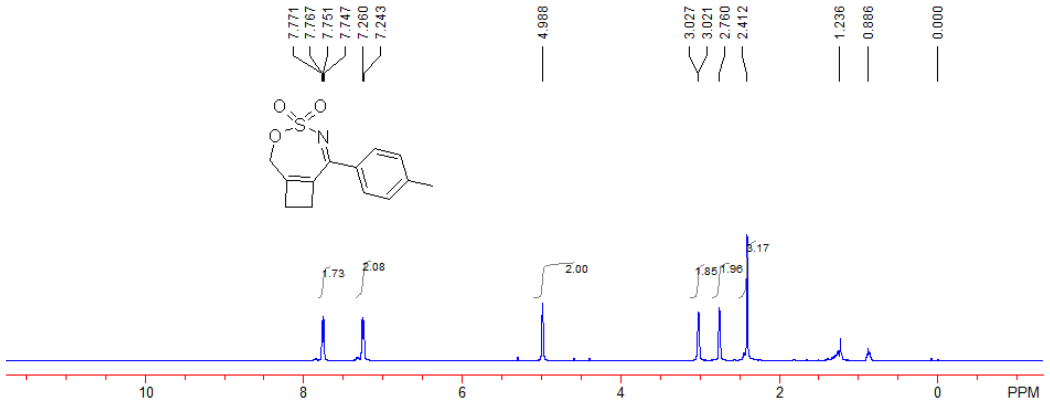
6-phenyl-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2a**: Yield: 38.0 mg, 80%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.76 (s, 2H, CH_2), 2.99 (m, 2H, CH_2), 5.01 (s, 2H, CH_2), 7.43-7.46 (m, 2H, Ar), 7.53-7.57 (m, 1H, Ar), 7.81-7.83 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.1, 31.0, 67.0, 128.5, 129.2, 132.7, 135.4, 136.3, 167.0, 167.9. IR (EtOH) ν 2956, 2921, 2862, 1596, 1563, 1182, 1043, 776, 697 cm^{-1}. MS (ESI) *m/z* 250 $(M+H)^+$. HRMS (ESI) calcd. for $C_{12}H_{12}NO_3S$: 250.0532, Found: 250.0533.

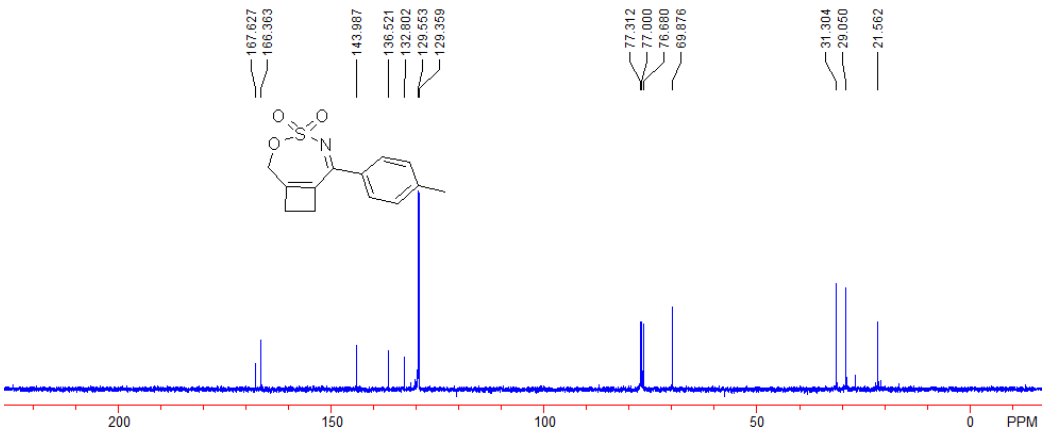


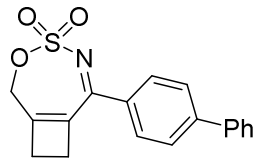




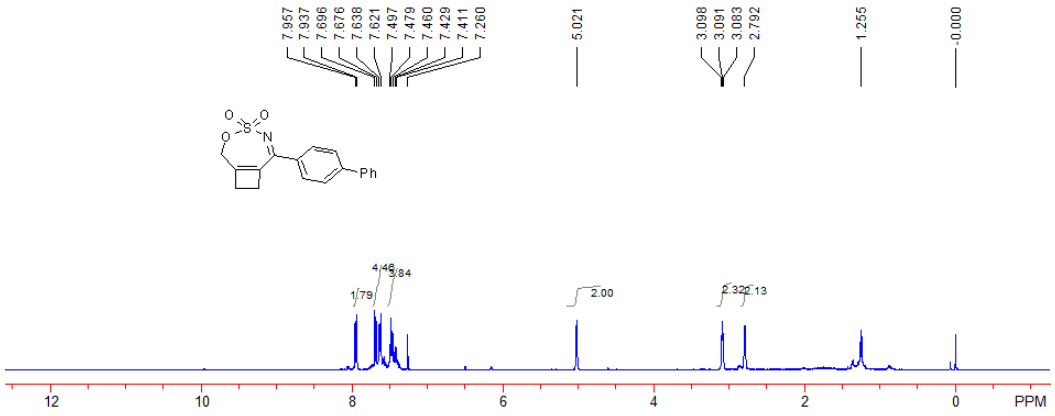
6-(p-tolyl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2b**: Yield: 43.5 mg, 82%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.41 (s, 3H, CH_3), 2.76 (s, 2H, CH_2), 3.02-3.03 (m, 2H, CH_2), 5.00 (s, 2H, CH_2), 7.24-7.26 (m, 2H, Ar), 7.75-7.77 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 29.1, 31.3, 69.9, 129.4, 129.6, 132.8, 136.5, 144.0, 166.4, 167.6. IR (EtOH) ν 2964, 2922, 2847, 1644, 1532, 1347, 1171, 935, 912, 832, 808, 791, 730 cm^{-1}. MS (ESI) *m/z* 264 $(M+H)^+$. HRMS (ESI) calcd. for $C_{13}H_{14}NO_3S$: 264.0694, Found: 264.0694.

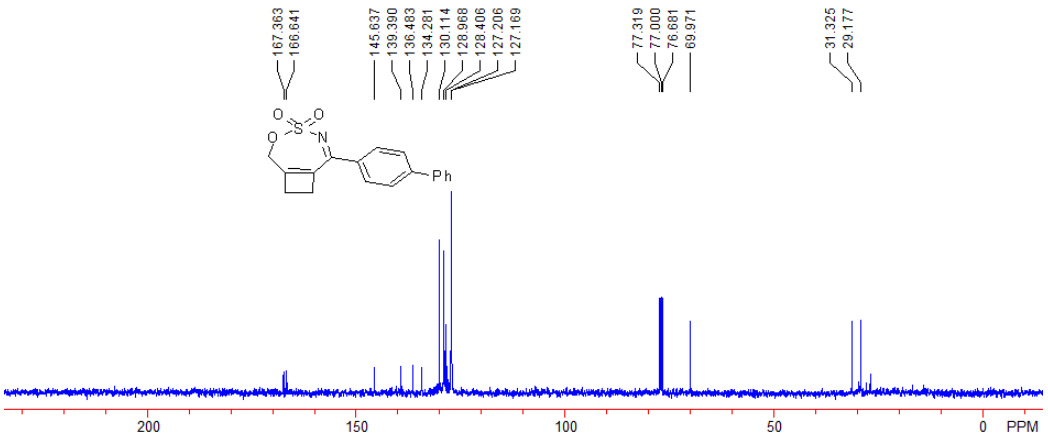


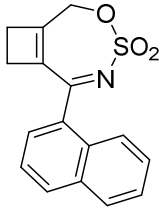




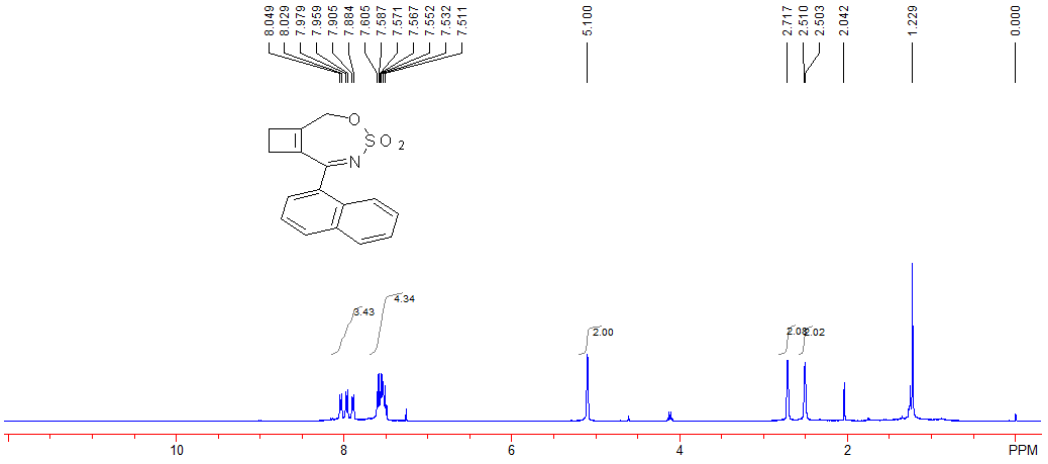
6-([1,1'-biphenyl]-4-yl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene-4,4-dioxide **2c**: Yield: 54.6 mg, 84%; A white solid, Mp: 135-137 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.79 (s, 2H, CH_2), 3.08-3.10 (m, 2H, CH_2), 5.02 (s, 2H, CH_2), 7.41-7.50 (m, 4H, Ar), 7.62-7.70 (m, 4H, Ar), 7.94-7.96 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.2, 31.3, 70.0, 127.17, 127.21, 128.4, 129.0, 130.1, 134.3, 136.5, 139.4, 145.6, 166.6, 167.4. IR (EtOH) ν 3031, 2923, 2848, 1623, 1603, 1563, 1525, 1361, 1317, 1303, 1254, 1174, 1162, 1006, 989, 852, 821, 759, 731, 696 cm^{-1}. MS (ESI) *m/z* 325 $(M+H)^+$. HRMS (ESI) calcd. for $C_{18}H_{15}NO_3S$: 325.0773, Found: 325.0773.

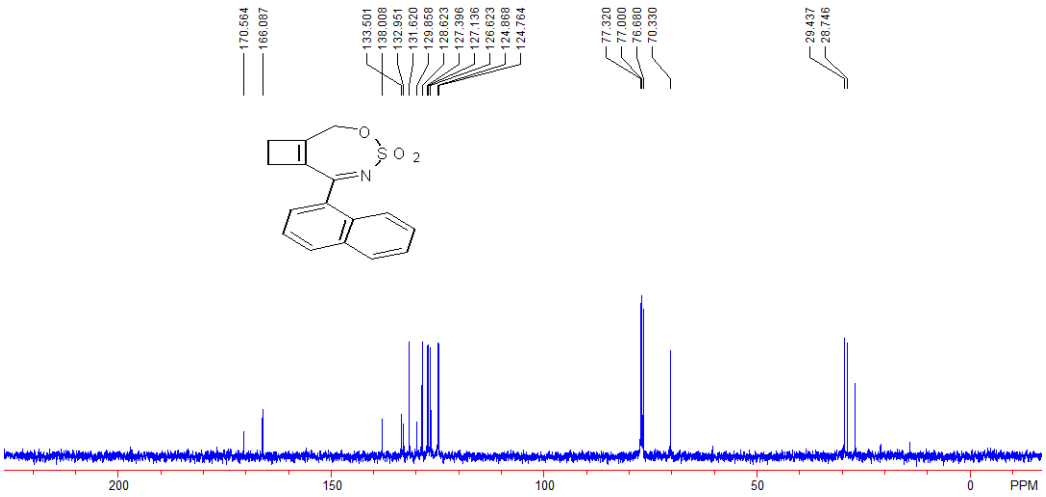


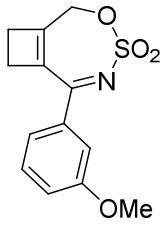




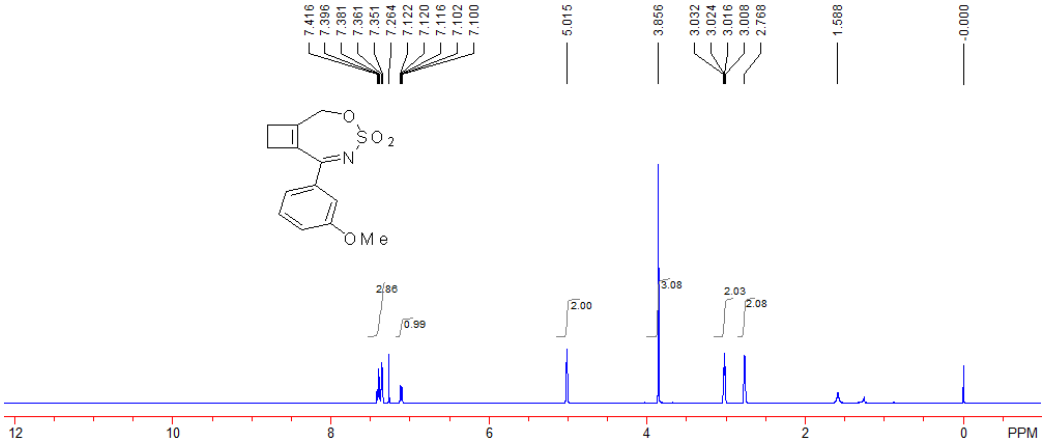
6-(naphthalen-1-yl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2d** (containing trace of ethyl acetate): Yield: 43.0 mg, 72%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.50-2.51 (m, 2H, CH_2), 2.72 (s, 2H, CH_2), 5.10 (s, 2H, CH_2), 7.51-7.61 (m, 4H, Ar), 7.88-8.05 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 28.7, 29.4, 70.3, 124.8, 124.9, 126.6, 127.1, 127.4, 128.6, 129.9, 131.6, 133.0, 133.5, 138.0, 166.1, 170.6. IR (EtOH) ν 3051, 2922, 2847, 1626, 1541, 1364, 1243, 1171, 1108, 980, 907, 829, 776 cm^{-1}. MS (ESI) *m/z* 300 $(M+H)^+$. HRMS (ESI) calcd. for $C_{16}H_{14}NO_3S$: 300.0694, Found: 300.0694.

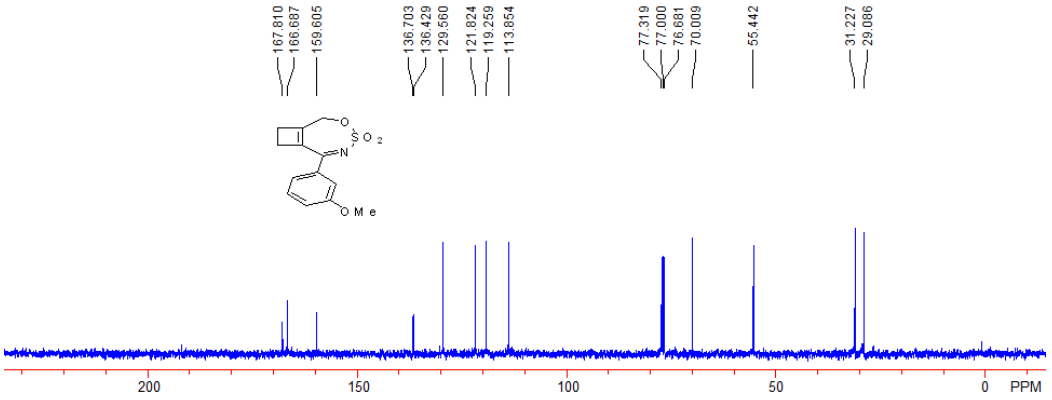


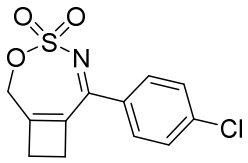




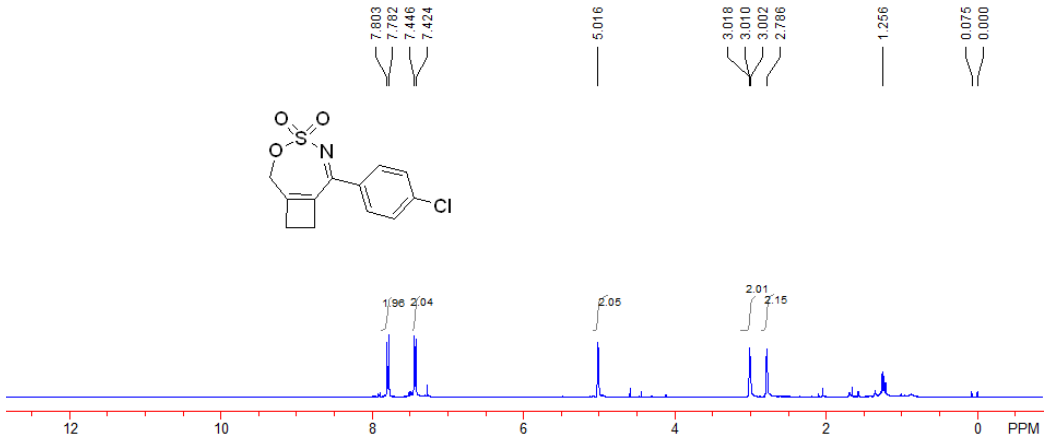
6-(3-methoxyphenyl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2e**: Yield: 48.0 mg, 86%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.77 (s, 2H, CH_2), 3.01-3.03 (m, 2H, CH_2), 3.86 (s, 3H, CH_3), 5.02 (s, 2H, CH_2), 7.10-7.12 (m, 1H, Ar), 7.35-7.42 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.1, 31.2, 55.4, 70.0, 113.9, 119.3, 121.8, 129.6, 136.4, 136.7, 159.6, 166.7, 167.8. IR (EtOH) ν 3000, 2920, 2850, 1620, 1578, 1525, 1434, 1374, 360, 1350, 1309, 1263, 1169, 1159, 1045, 984, 878, 837, 803, 786, 777, 743, 715, 687 cm^{-1}. MS (ESI) *m/z* 280 $(M+H)^+$. HRMS (ESI) calcd. for $C_{13}H_{14}NO_4S$: 280.0638, Found: 280.0639.

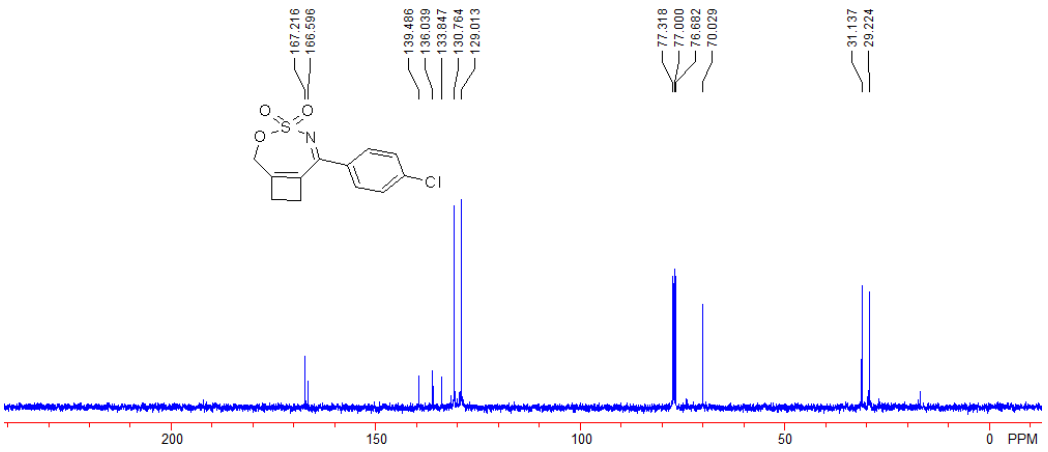


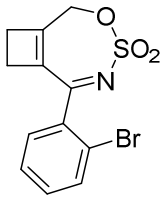




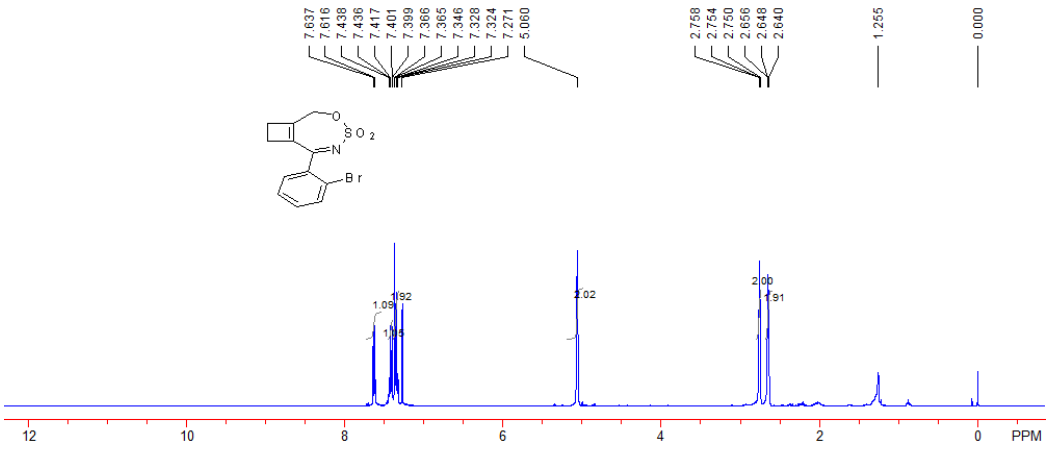
6-(4-chlorophenyl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2f**: Yield: 44.6 mg, 79%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.79 (s, 2H, CH_2), 3.00-3.02 (m, 2H, CH_2), 5.02 (s, 2H, CH_2), 7.43 (d, J = 8.4 Hz, 2H, Ar), 7.79 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.2, 31.1, 70.0, 129.0, 130.8, 133.8, 136.0, 139.5, 166.6, 167.2. IR (EtOH) ν 2971, 2930, 2855, 1624, 1583, 1570, 1526, 1360, 1308, 1296, 1251, 1172, 1073, 1009, 987, 928, 894, 841, 809, 759, 723, 693 cm^{-1}. MS (ESI) *m/z* 284 $(M+H)^+$. HRMS (ESI) calcd. for $C_{12}H_{11}ClNO_3S$: 284.0143, Found: 284.0143.

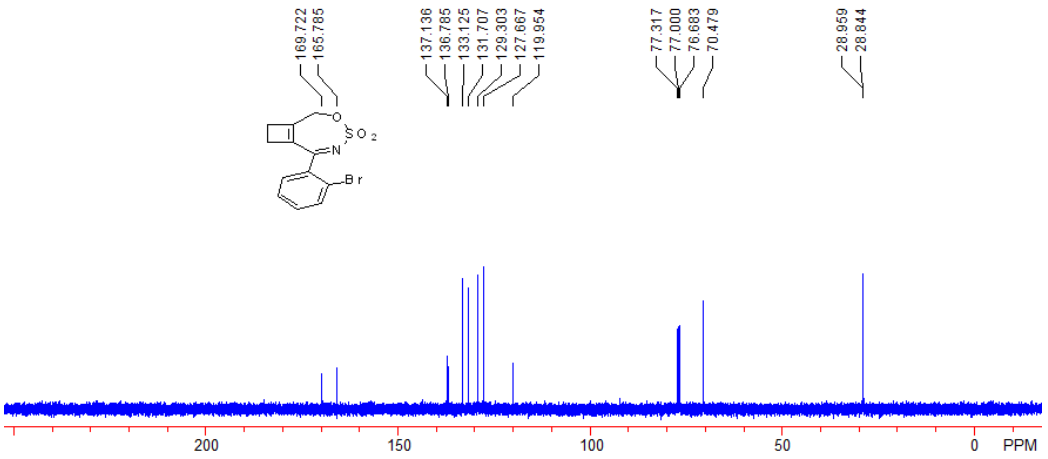


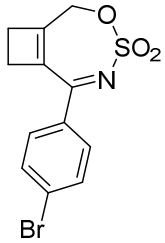




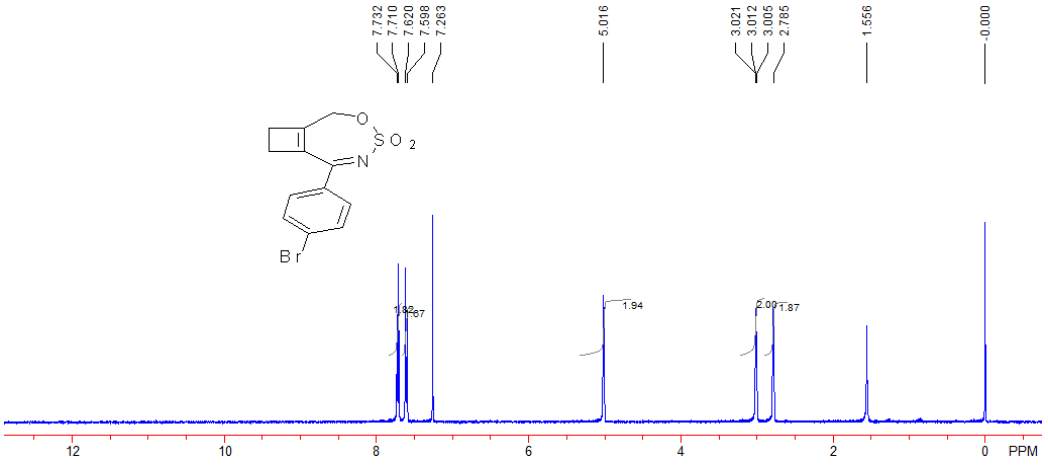
6-(2-bromophenyl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2g**: Yield: 53.6 mg, 82%; A yellow solid; Mp: 70-72 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.64-2.66 (m, 2H, CH_2), 2.75-2.76 (m, 2H, CH_2), 5.06 (s, 2H, CH_2), 7.32-7.37 (m, 2H, Ar), 7.40-7.44 (m, 1H, Ar), 7.62 (d, J = 8.4 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 28.8, 29.0, 70.5, 120.0, 127.7, 129.3, 131.7, 133.1, 136.8, 137.1, 165.8, 169.7. IR (EtOH) ν 2992, 2953, 2865, 1586, 1557, 1470, 1433, 1365, 1278, 1066, 1045, 1026, 973, 937, 888, 812, 709 cm^{-1}. MS (ESI) *m/z* 328 $(M+H)^+$. HRMS (ESI) calcd. for $C_{12}H_{11}BrNO_3S$: 327.9638, Found: 327.9638.

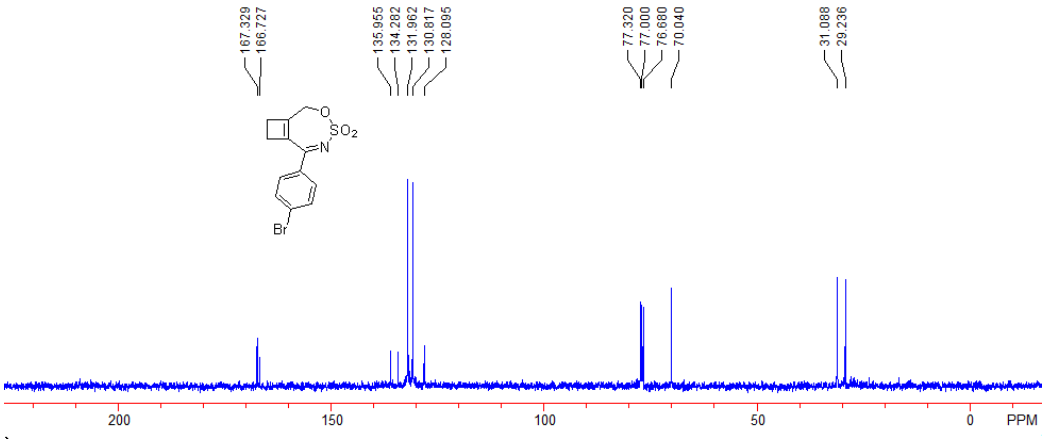


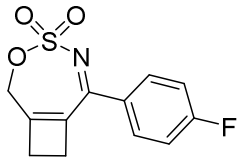




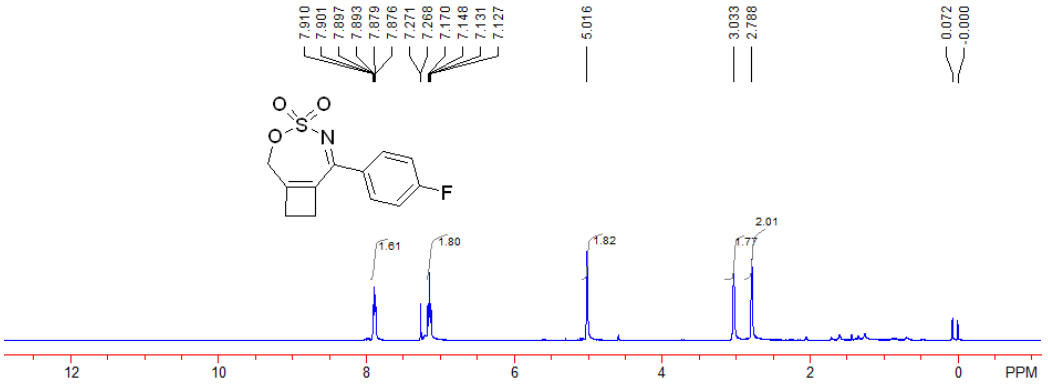
6-(4-bromophenyl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2h**: Yield: 49.7 mg, 76%; A white solid; Mp: 110-112 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.79 (m, 2H, CH_2), 3.00-3.02 (m, 2H, CH_2), 5.02 (s, 2H, CH_2), 7.60 (d, *J* = 8.8 Hz, 2H, Ar), 7.72 (d, *J* = 8.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.2, 31.1, 70.0, 128.1, 130.8, 132.0, 134.3, 136.0, 166.7, 167.3. IR (EtOH) ν 2979, 2930, 1624, 1584, 1525, 1394, 1360, 1309, 1251, 1173, 1073, 1009, 987, 928, 842, 787, 759, 694 cm^{-1}. MS (ESI) *m/z* 328 $(M+H)^+$. HRMS (ESI) calcd. for $C_{12}H_{11}BrNO_3S$: 327.9638, Found: 327.9638.

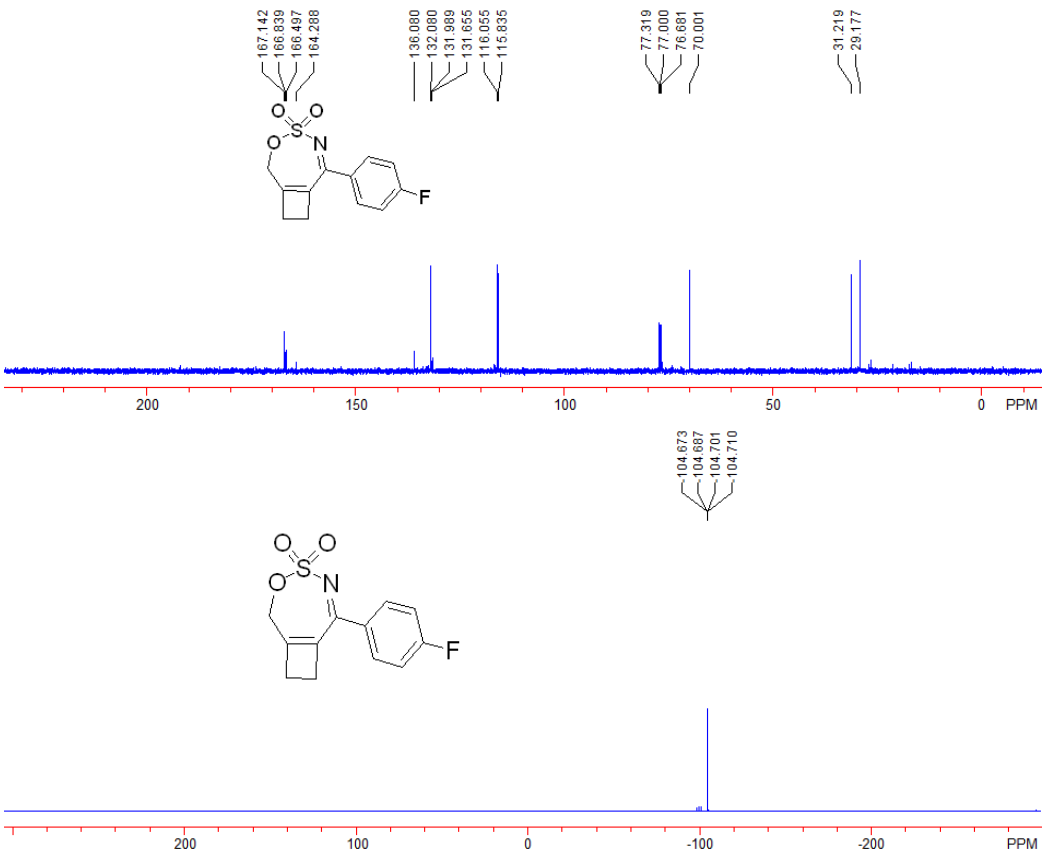


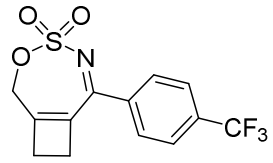




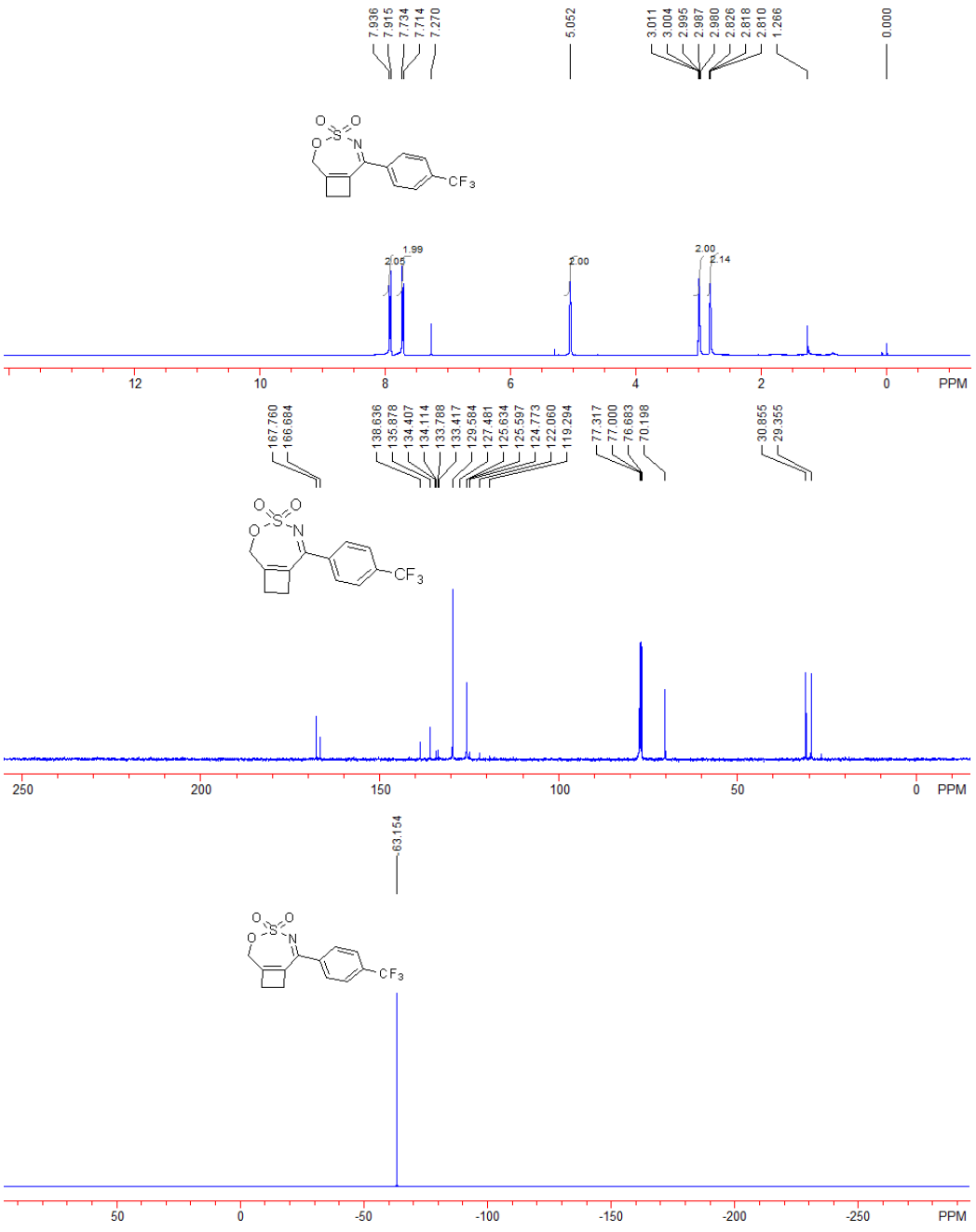
6-(4-fluorophenyl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2i**: Yield: 41.1 mg, 77%; A yellow solid; Mp: 70-72 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.79 (s, 2H, CH_2), 3.03 (s, 2H, CH_2), 5.02 (s, 2H, CH_2), 7.13-7.17 (m, 2H, Ar), 7.88-7.91 (m, 2H, Ar),. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.2, 31.2, 70.0, 115.9 (d, J = 22 Hz), 131.7, 132.0 (d, J = 9.1 Hz), 136.1, 165.6 (d, J = 255.1 Hz), 166.5, 167.1. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ (-104.67)-(-104.71) (m). IR (EtOH) ν 2959, 2915, 2846, 1598, 1526, 1504, 1361, 1311, 1176, 1155, 1086, 988, 907, 851, 797, 759, 728, 691 cm^{-1}. MS (EI) *m/z* 267 $(M+H)^+$. HRMS (EI) calcd. for $C_{12}H_{10}NO_3FS$: 267.0365, Found: 267.0363.

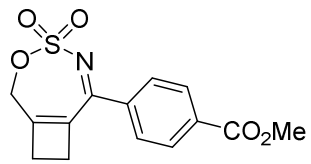






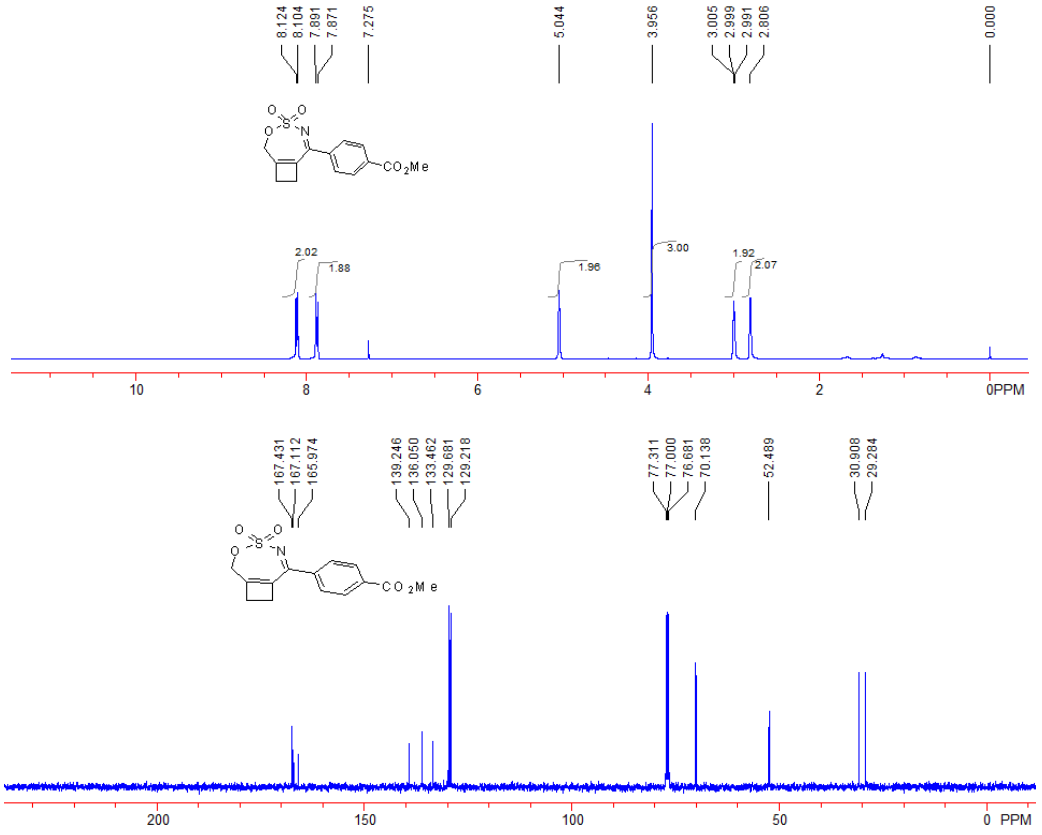
6-(4-fluorophenyl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2j**: Yield: 45.9 mg, 72%; A yellow solid; Mp: 70-72 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.81-2.83 (m, 2H, CH_2), 2.98-3.01 (m, 2H, CH_2), 5.05 (s, 2H, CH_2), 7.72 (d, J = 8.0 Hz, 2H, Ar), 7.92 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.4, 30.9, 70.2, 123.4 (q, J = 274.5 Hz), 125.6 (q, J = 3.8 Hz), 129.6, 134.0 (q, J = 33.4 Hz), 135.9, 138.6, 166.7, 167.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -63.2 (s). IR (EtOH) ν 2951, 2856, 1725, 1647, 1608, 1355, 1163, 935, 844, 810, 791, 746, 690 cm^{-1}. MS (EI) *m/z* 318 $(M+H)^+$. HRMS (EI) calcd. for $C_{13}H_{11}F_3NO_3S$: 318.0406, Found: 318.0408.

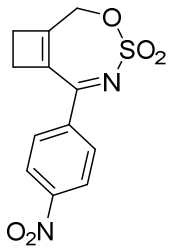




methyl 4-(4,4-dioxido-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-dien-6-yl)benzoate **2k**: Yield: 48.6 mg, 78%; A white solid, Mp: 140-142 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.81 (s, 2H, CH_2), 2.99-3.01 (m, 2H, CH_2), 3.96 (s, 3H, CH_3), 5.04 (s, 2H, CH_2), 7.88 (d, J = 8.0 Hz, 2H, Ar),

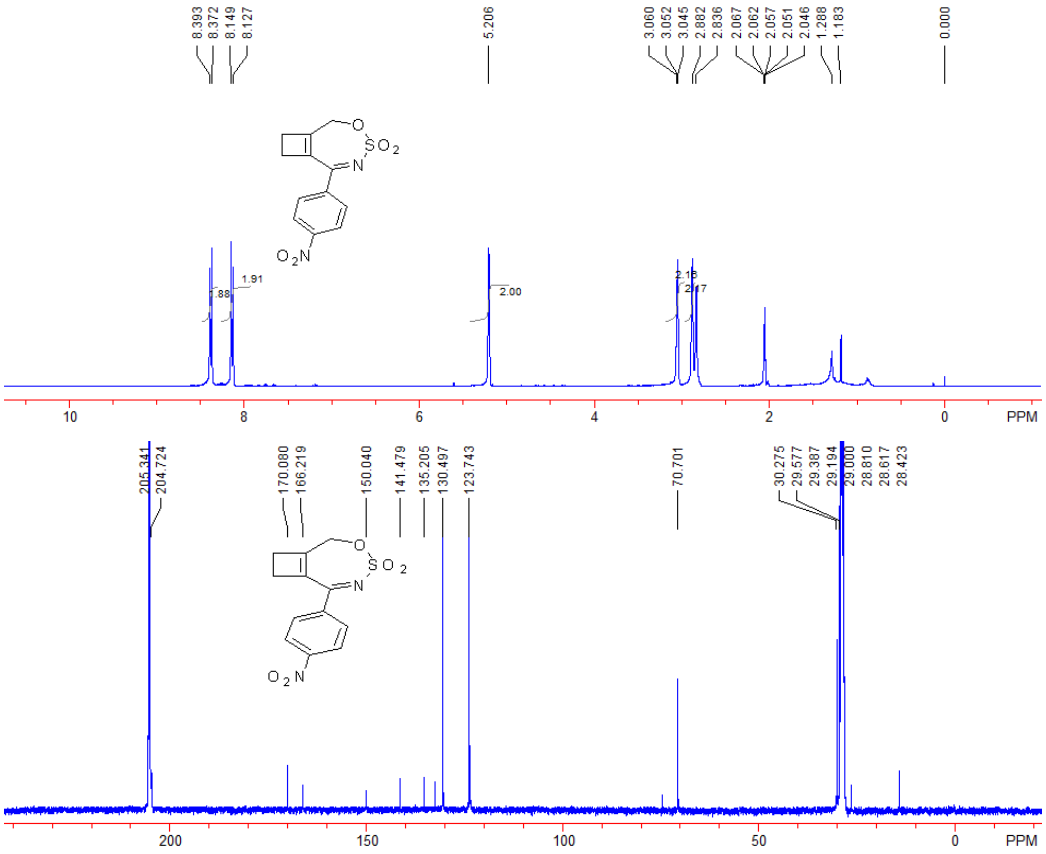
8.11 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.3, 30.9, 52.5, 70.1, 129.2, 129.7, 133.5, 136.1, 139.2, 166.0, 167.1, 167.4. IR (EtOH) ν 2953, 2850, 1720, 1530, 1437, 1370, 1278, 1189, 1108, 1010, 963, 915, 817, 780, 730, 708 cm^{-1}. MS (ESI) *m/z* 308 $(M+H)^+$. HRMS (ESI) calcd. for $C_{14}H_{14}NO_5S$: 308.0587, Found: 308.0588.

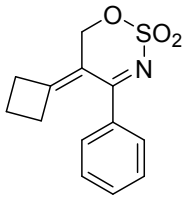




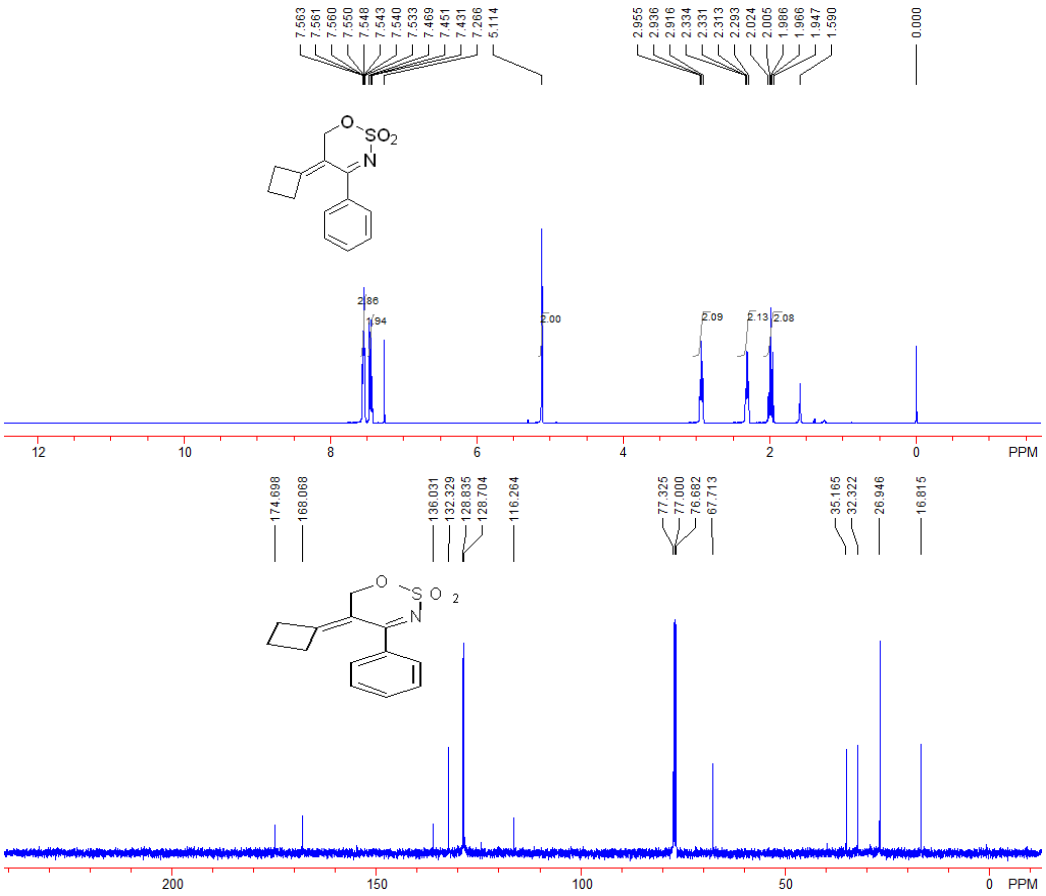
6-(4-(trifluoromethyl)phenyl)-3-oxa-4-thia-5-azabicyclo[5.2.0]nona-1(7),5-diene 4,4-dioxide **2l**: Yield: 48.6 mg, 83%; A yellow solid; Mp: 110-112 ^{o}C; ^{1}H NMR ($CD_3C(O)CD_3$, 400 MHz, TMS) δ 2.88 (s, 2H, CH_2), 3.05-3.06 (m, 2H, CH_2), 5.21 (s, 2H, CH_2), 8.13 (d, J = 8.8 Hz, 2H, Ar), 8.38 (d, J = 8.8 Hz, 2H, Ar). ^{13}C NMR ($CD_3C(O)CD_3$, 100 MHz, TMS) δ 30.3, 70.7, 123.7, 130.5, 135.2, 141.5, 150.0, 166.2, 170.1. IR (EtOH) ν 3001, 2965, 2868, 1647, 1532, 1360, 1341, 1176, 946, 918, 867, 814, 772, 726, 711cm^{-1}. MS (ESI) *m/z* 295 $(M+H)^+$. HRMS (DART) calcd. for $C_{12}H_{11}N_2O_5S$:

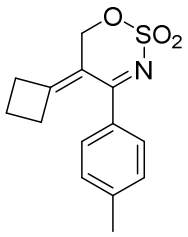
295.0383, Found: 295.0381.



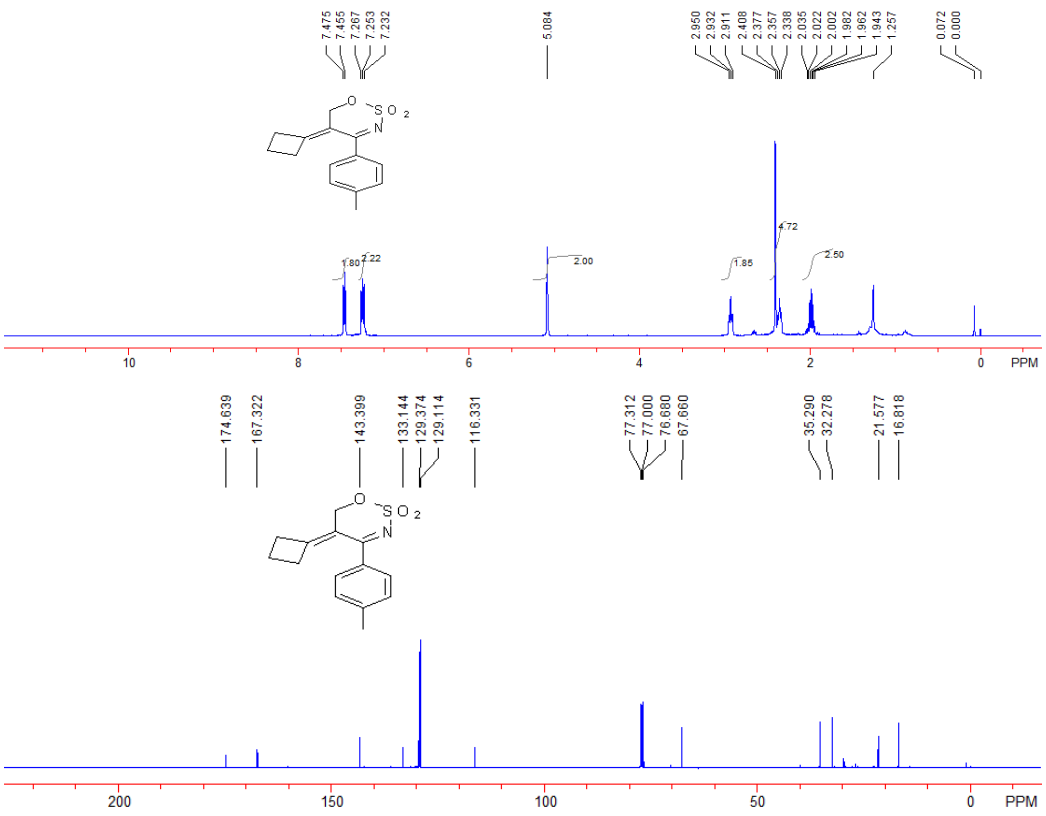


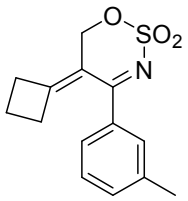
5-cyclobutylidene-4-phenyl-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4a**: Yield: 25.0 mg, 48%; A white solid, Mp: 80-82 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95-2.02 (m, 2H, CH_2), 2.29-2.33 (m, 2H, CH_2), 2.92-2.96 (m, 2H, CH_2), 5.11 (s, 2H, CH_2), 7.43-7.47 (m, 2H, Ar), 7.54-7.56 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.8, 26.9, 32.3, 35.2, 67.7, 116.3, 128.7, 128.8, 132.3, 136.0, 168.1, 174.7. IR (EtOH) ν 2927, 2855, 1734, 1637, 1607, 1345, 1173, 945, 854, 810, 791, 743, 690 cm^{-1}. MS (ESI) *m/z* 264 $(M+H)^+$. HRMS (ESI) calcd. for $C_{13}H_{14}NO_3S$: 264.0694, Found: 264.0692.



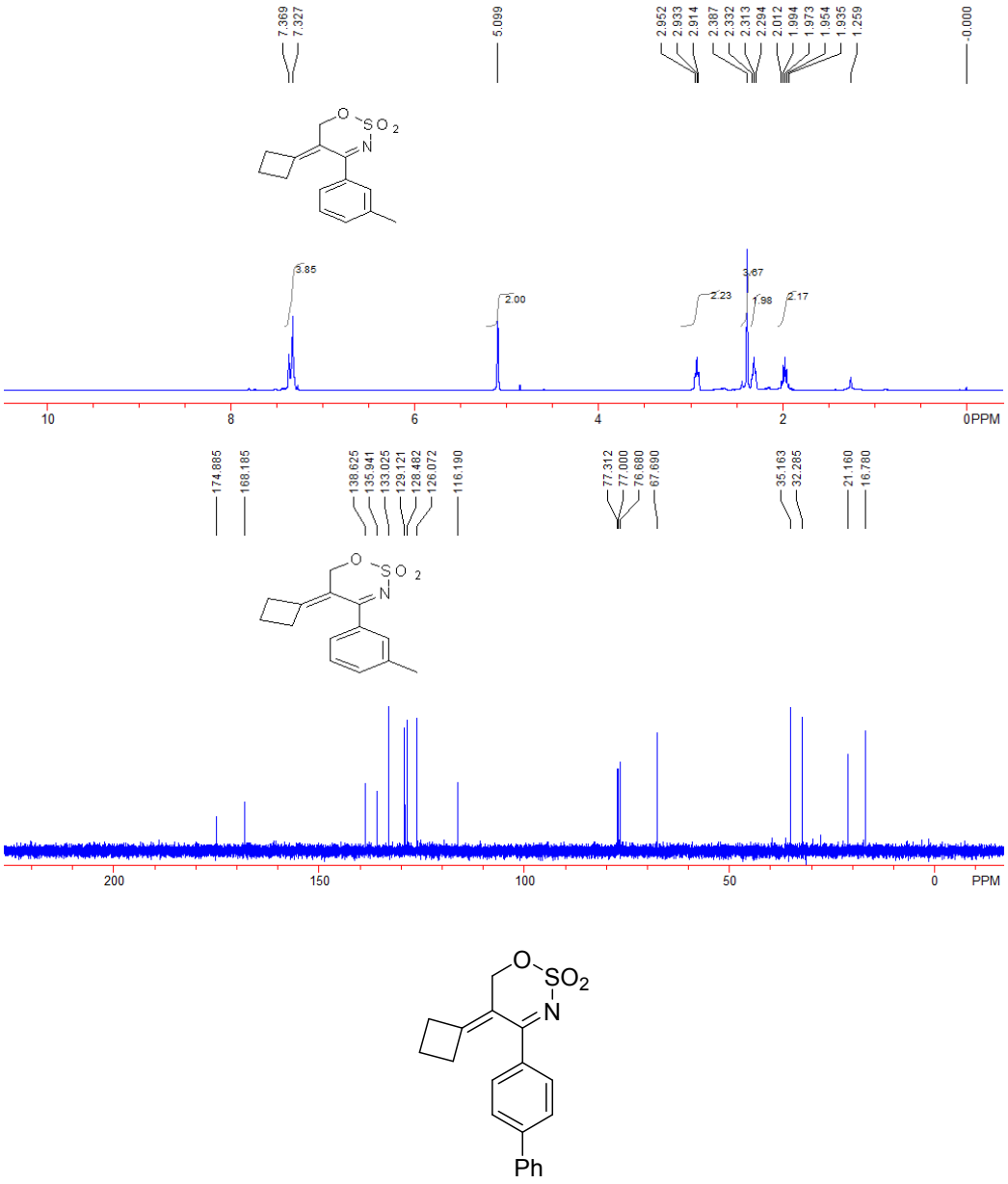


5-cyclobutylidene-4-phenyl-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4b**: Yield: 22.0 mg, 41%; A yellow soild, Mp: 83-85 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95-2.04 (m, 2H, CH_2), 2.34-2.38 (m, 2H, CH_2), 2.41 (s, 3H, CH_3), 2.92-2.95 (m, 2H, CH_2), 5.08 (s, 2H, CH_2), 7.24 (d, J = 8.0 Hz, 2H, Ar), 7.46 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.8, 21.6, 32.3, 35.3, 67.7, 116.3, 129.1, 129.4, 133.1, 143.4, 167.3, 174.6. IR (EtOH) ν 2921, 2851, 1724, 1647, 1608, 1345, 1173, 935, 854, 810, 791, 743, 690 cm^{-1}. MS (ESI) *m/z* 278 $(M+H)^+$. HRMS (DART) calcd. for $C_{14}H_{16}NO_3S$: 278.0851, Found: 278.0852.

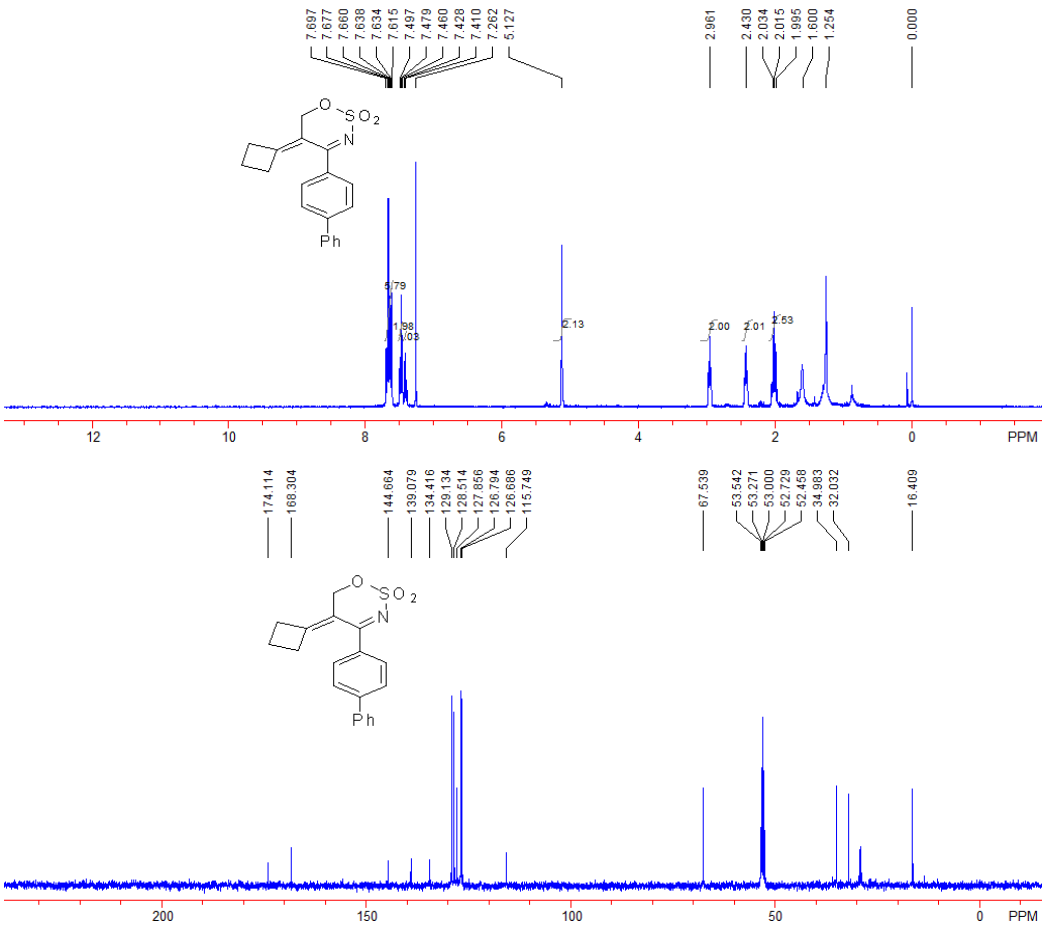


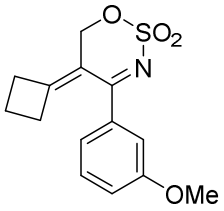


5-cyclobutylidene-3-phenyl-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4c**: Yield: 21.0 mg, 40%; A white solid, Mp: 86-88 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.94-2.01 (m, 2H, CH_2), 2.29-2.33 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.91-2.95 (m, 2H, CH_2), 5.10 (s, 2H, CH_2), 7.33-7.37 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.8, 21.2, 32.3, 35.2, 67.7, 116.2, 126.1, 128.5, 129.1, 133.0, 135.9, 138.6, 168.2, 174.9. IR (EtOH) ν 2959, 2923, 2850, 1665 1649, 1538, 1367, 1184, 913, 804, 792, 742 cm^{-1}. MS (ESI) *m/z* 278 $(M+H)^+$. HRMS (DART) calcd. for $C_{14}H_{16}NO_3S$: 278.0851, Found: 278.0852.

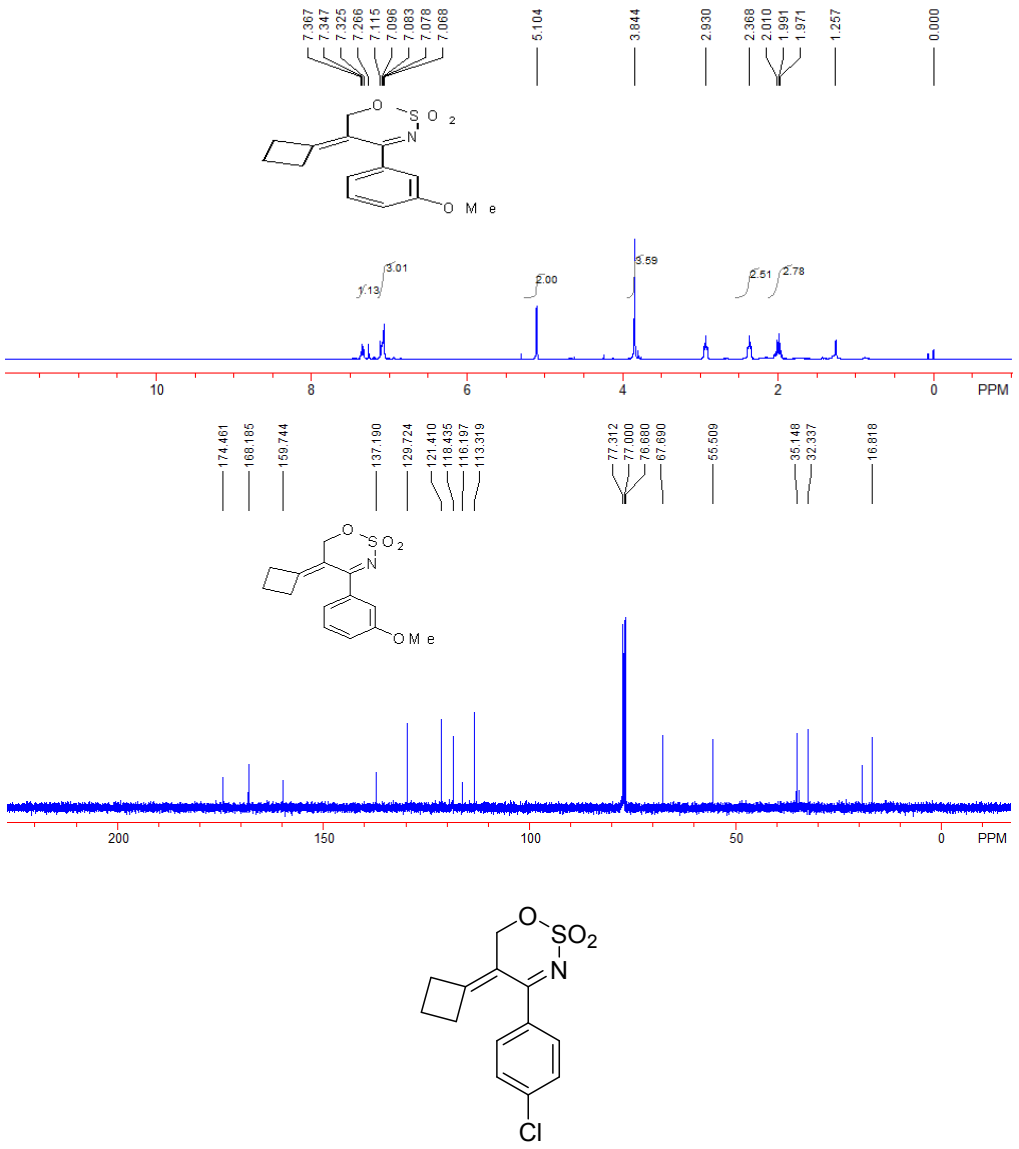


5-cyclobutylidene-4-phenyl-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4d**: Yield: 28.0 mg, 42%; A white solid, Mp: 120-122 ^{o}C (containing some petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.00-2.03 (m, 2H, CH_2), 2.42-2.44 (m, 2H, CH_2), 2.95-2.97 (m, 2H, CH_2), 5.13 (s, 2H, CH_2), 7.41-7.50 (m, 3H, Ar), 7.62-7.70 (m, 6H, Ar). ^{13}C NMR (CD_2Cl_2, 100 MHz, TMS) δ 16.4, 32.0, 35.0, 67.5, 115.7, 126.7, 126.8, 127.9, 128.5, 129.1, 134.4, 139.1, 144.7, 168.3, 174.1. IR (EtOH) ν 2959, 2923, 2850, 1665, 1649, 1538, 1367, 1184, 913, 804, 792, 742 cm^{-1}. MS (ESI) *m/z* 340 $(M+H)^+$. HRMS (DART) calcd. for $C_{19}H_{18}NO_3S$: 340.0997, Found: 340.0988.

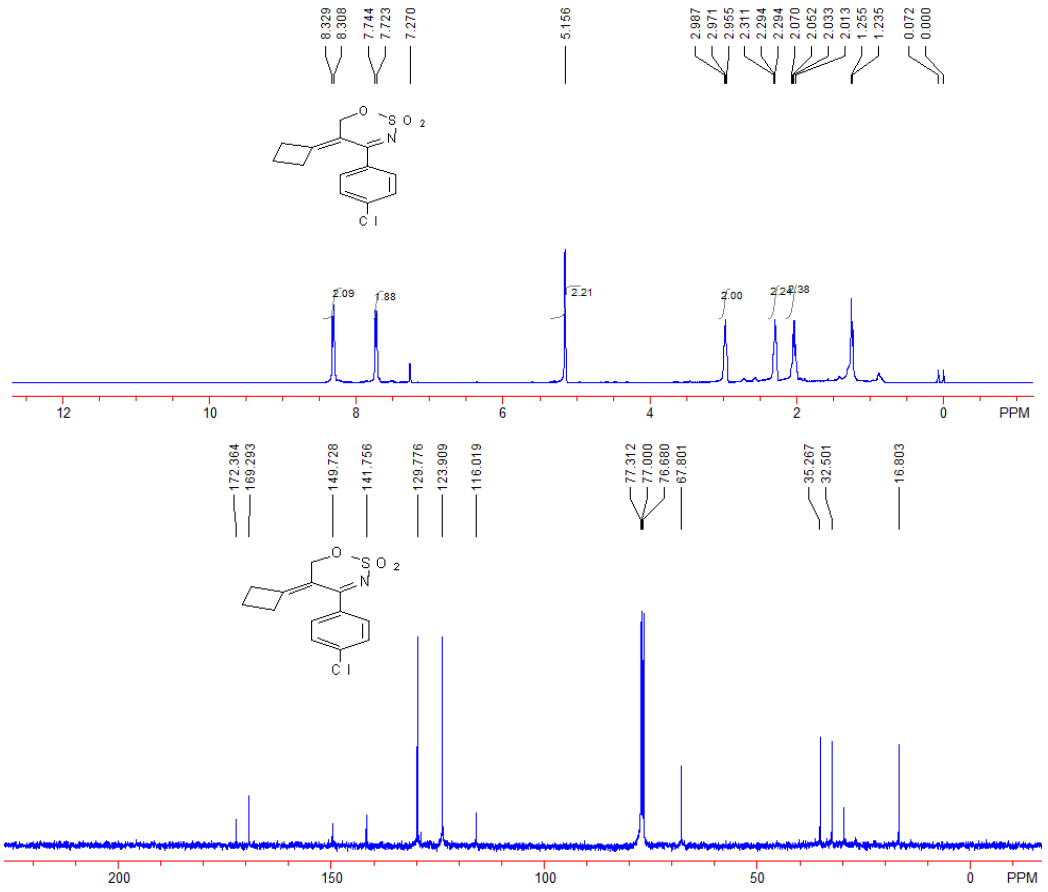


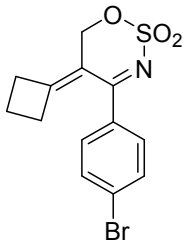


5-cyclobutylidene-4-phenyl-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4e**: Yield: 23.4 mg, 40%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.97-2.01 (m, 2H, CH_2), 2.35-2.38 (m, 2H, CH_2), 2.91-2.93 (m, 2H, CH_2), 5.11 (s, 2H, CH_2), 7.07-7.11 (m, 3H, Ar), 7.27-7.35 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.8, 32.3, 35.1, 55.5, 67.7, 113.3, 116.2, 118.4, 121.4, 129.7, 137.2, 159.7, 168.2, 174.5. IR (EtOH) ν 2961, 2920, 2850, 1538, 1366, 1349, 1260, 1179, 1041, 836, 799, 738, 675 cm^{-1}. MS (ESI) *m/z* 294 $(M+H)^+$. HRMS (DART) calcd. for $C_{14}H_{16}NO_4S$: 294.0800, Found: 294.0802.

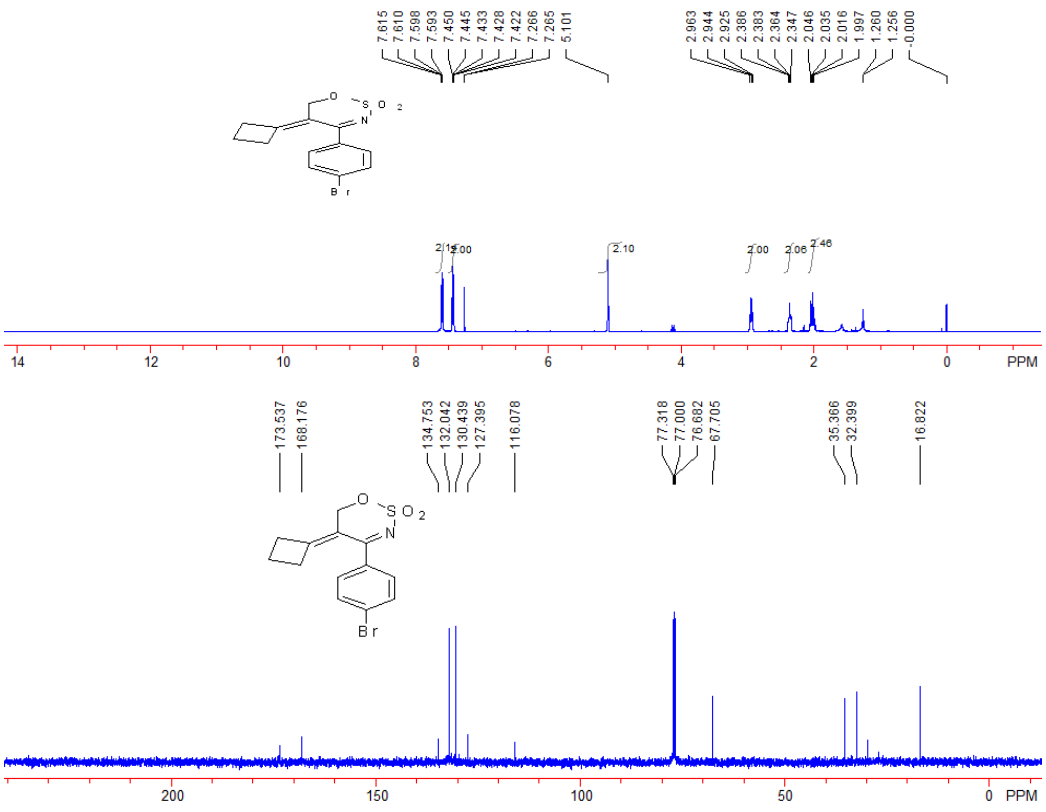


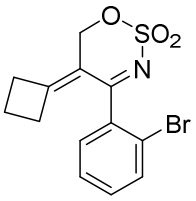
4-(4-bromophenyl)-5-cyclobutylidene-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4f**: Yield: 27.0 mg, 46%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.01-2.07 (m, 2H, CH_2), 2.30-2.31 (m, 2H, CH_2), 2.96-2.99 (m, 2H, CH_2), 5.16 (s, 2H, CH_2), 7.73 (d, J = 8.4 Hz, 2H, Ar), 8.31 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.8, 32.5, 35.3, 67.8, 116.0, 123.9, 129.8, 141.8, 149.7, 169.3, 172.4. IR (EtOH) ν 2959, 2923, 2850, 1640, 1522, 1370, 1180, 936, 910, 868, 814, 729, 711 cm^{-1}. MS (ESI) *m/z* 341 $(M+H)^+$. HRMS (DART) calcd. for $C_{13}H_{13}BrNO_3S$: 341.9794, Found: 341.9792.



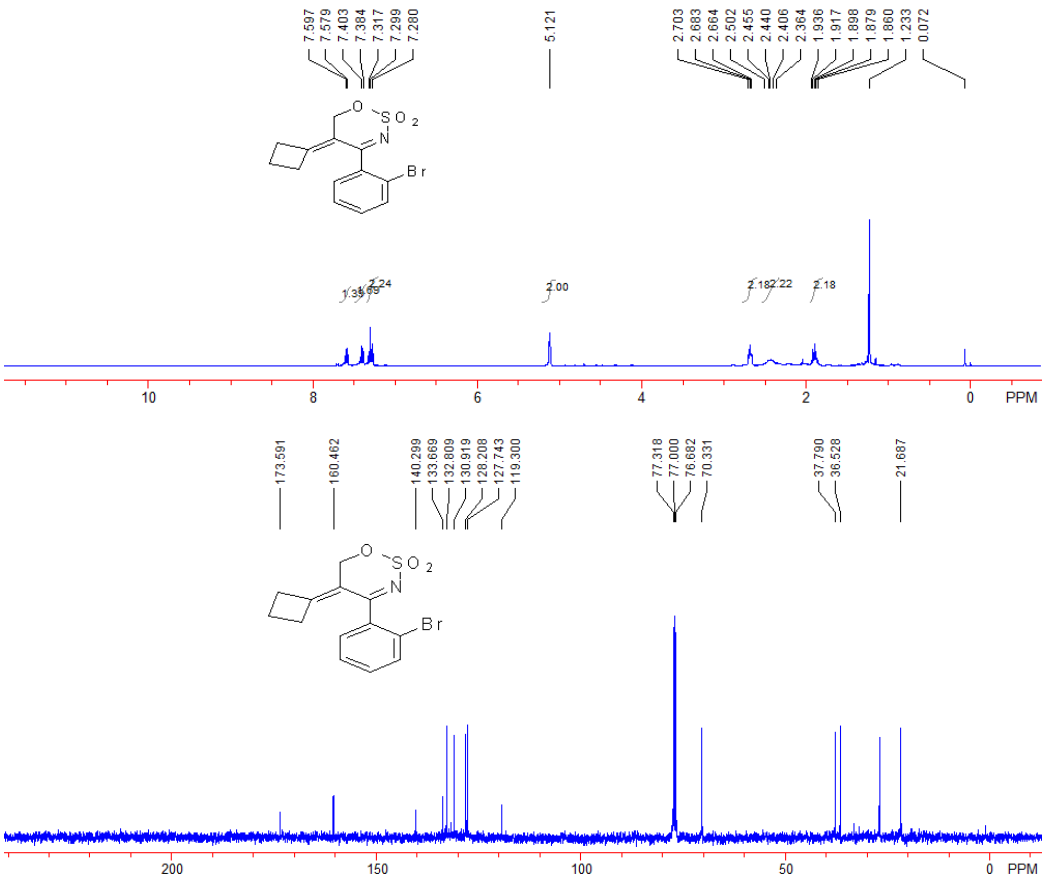


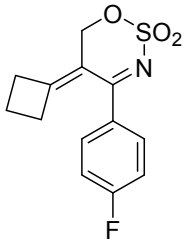
4-(4-bromophenyl)-5-cyclobutylidene-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4g** (containing trace amount of ethyl acetate): Yield: 32.0 mg, 47%; A white solid, Mp: 110-112 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.97-2.05 (m, 2H, CH_2), 2.34-2.36 (m, 2H, CH_2), 2.93-2.96 (m, 2H, CH_2), 5.10 (s, 2H, CH_2), 7.43 (d, J = 8.0 Hz, 2H, Ar), 7.60 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.8, 32.4, 35.4, 67.7, 116.1, 127.4, 130.4, 132.0, 134.8, 168.2, 173.5. IR (EtOH) ν 2964, 2920, 2850, 1646, 1585, 1534, 1486, 1366, 1173, 1069, 935, 909, 809, 729, 709, 691 cm^{-1}. MS (ESI) *m/z* 341 $(M+H)^+$. HRMS (DART) calcd. for $C_{13}H_{13}BrNO_3S$: 341.9794, Found: 341.9792.



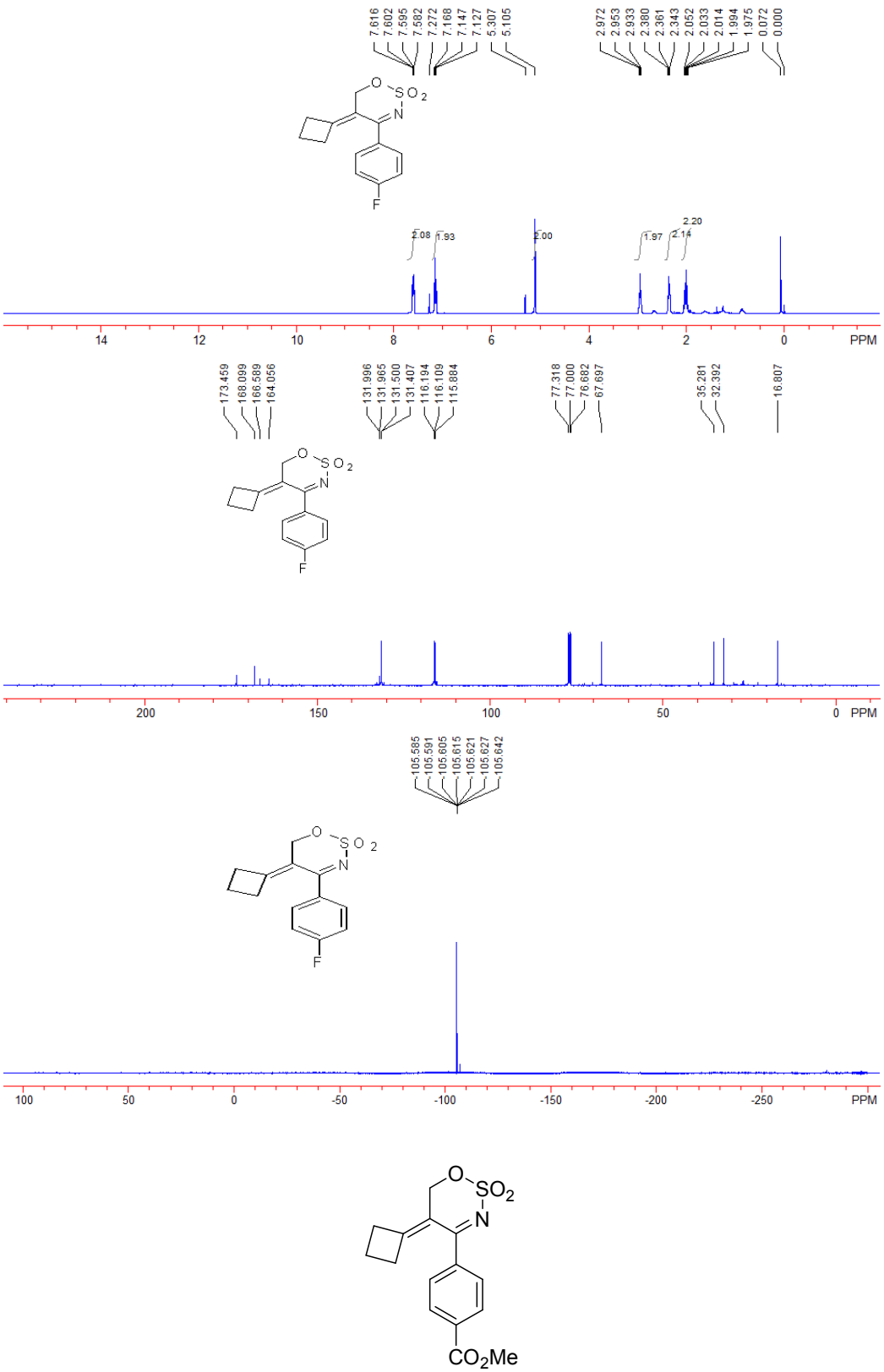


4-(4-bromophenyl)-5-cyclobutylidene-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4h**: Yield: 23.0 mg, 34%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.86-1.94 (m, 2H, CH_2), 2.36-2.50 (m, 2H, CH_2), 2.93-2.96 (m, 2H, CH_2), 5.12 (s, 2H, CH_2), 7.28-7.32 (m, 2H, Ar), 7.38-7.40 (m, 1H, Ar), 7.58-7.60 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 36.5, 37.8, 70.3, 119.3, 127.7, 128.2, 130.9, 132.8, 133.7, 140.3, 160.5, 173.6. IR (EtOH) ν 2964, 2875, 1699, 1624, 1551, 1369, 1288, 1178, 1083, 1022, 990, 904, 868, 818, 770, 752, 733, 711, 685 cm^{-1}. MS (ESI) *m/z* 341 $(M+H)^+$. HRMS (DART) calcd. for $C_{13}H_{13}BrNO_3S$: 341.9794, Found: 341.9792.



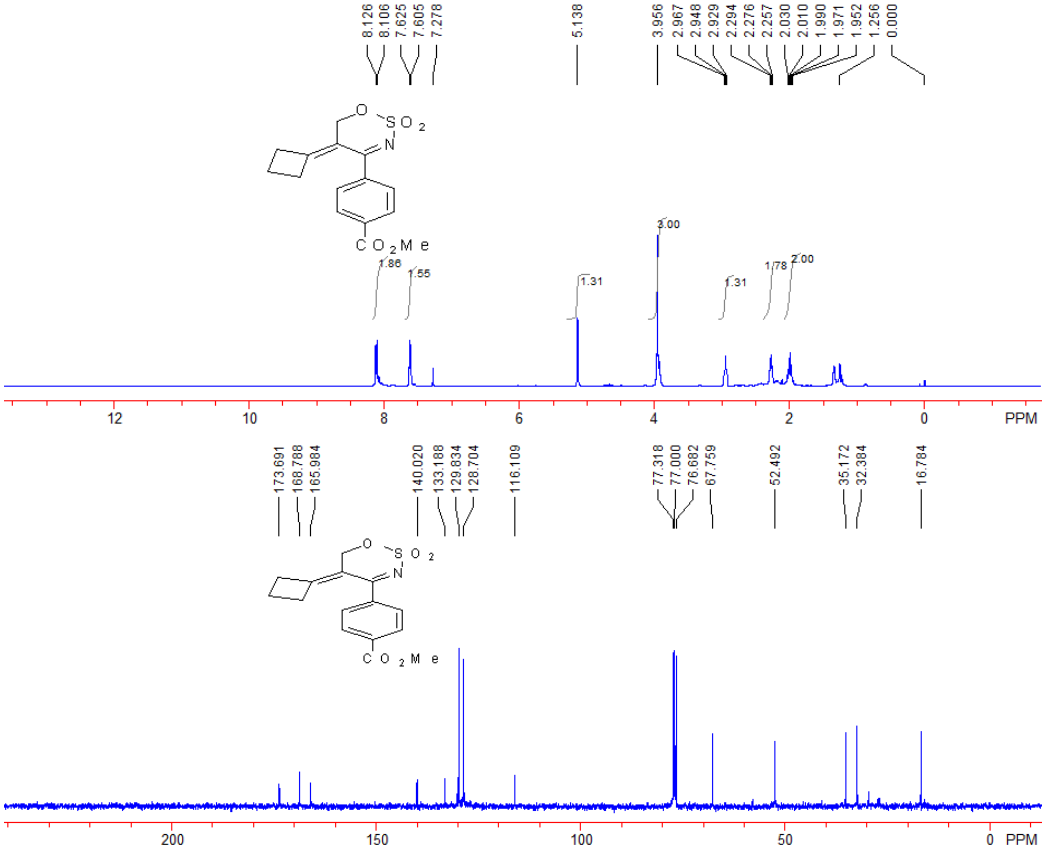


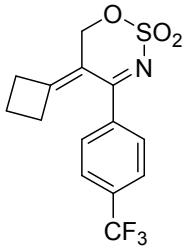
5-cyclobutylidene-4-phenyl-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4i** (containing trace of CH_2Cl_2): Yield: 27.5 mg, 49%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.98-2.05 (m, 2H, CH_2), 2.34-2.38 (m, 2H, CH_2), 2.93-2.97 (m, 2H, CH_2), 5.12 (s, 2H, CH_2), 7.13-7.17 (m, 2H, Ar), 7.58-7.62 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.8, 32.4, 35.3, 67.7, 116.0 (d, J = 22.5 Hz), 116.2, 131.5 (d, J = 9.3 Hz), 132.0 (d, J = 3.1 Hz), 165.3 (d, J = 253.3 Hz), 168.1, 173.5. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ (-105.59)-(-105.64) (m). IR (EtOH) ν 2964, 2920, 2850, 1646, 1585, 1534, 1486, 1366, 1173, 1099, 1011, 935, 909, 809, 729, 691 cm^{-1}. MS (ESI) *m/z* 282 $(M+H)^+$. HRMS (ESI) calcd. for $C_{13}H_{13}FNO_3S$: 282.0600, Found: 282.0604.



5-cyclobutylidene-4-phenyl-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4j**: Yield: 26.3 mg, 41%; A white solid, Mp: 100-102 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95-2.03 (m, 2H, CH_2),

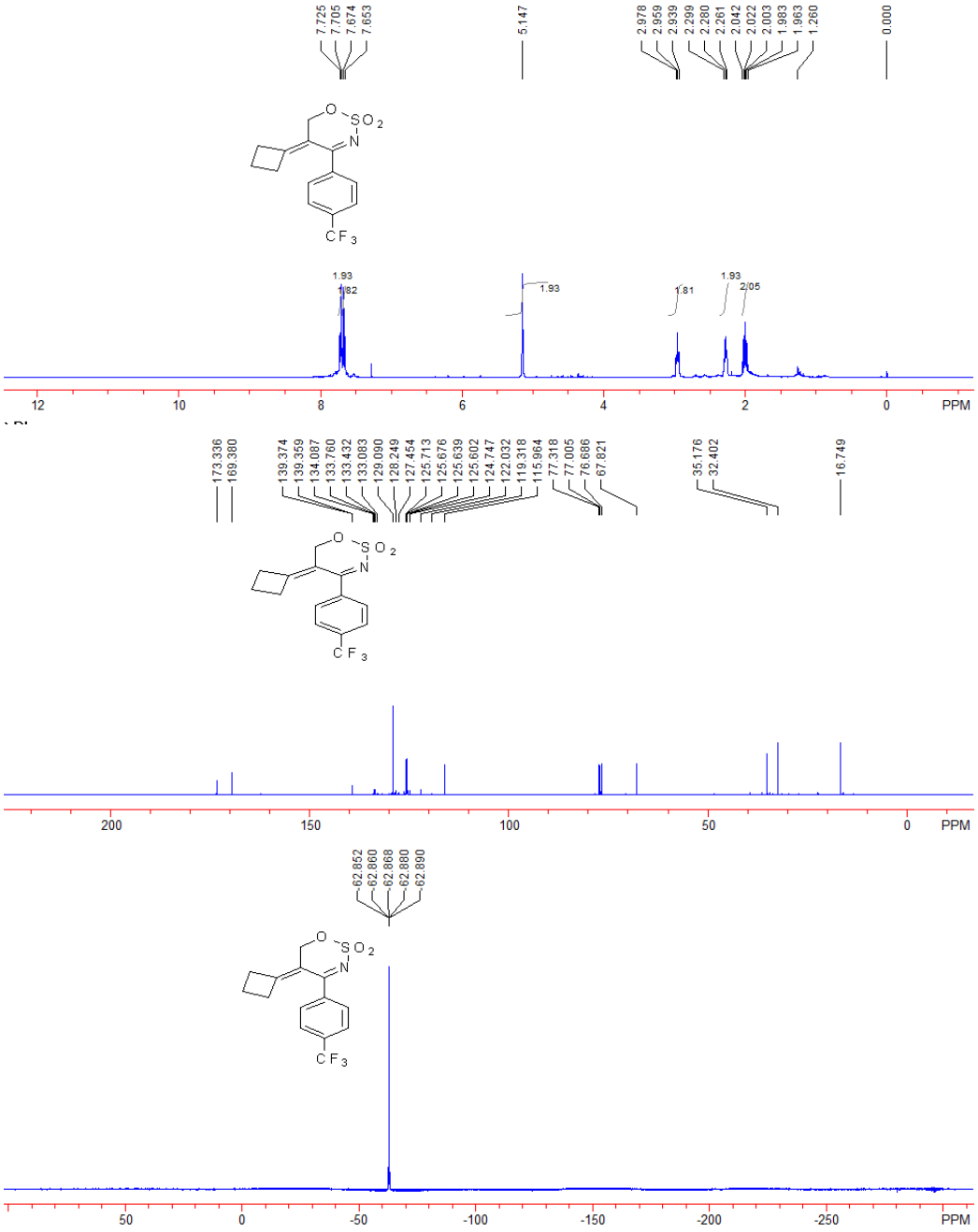
2.26-2.29 (m, 2H, CH_2), 2.93-2.97 (m, 2H, CH_2), 3.96 (s, 3H, CH_3), 5.14 (s, 2H, CH_2), 7.61 (d, J = 8.0 Hz, 2H, Ar), 8.11 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.8, 32.4, 35.2, 67.8, 116.1, 128.7, 129.8, 133.2, 140.0, 166.0, 168.8, 173.7. IR (EtOH) ν 2953, 2923, 2850, 1721, 1540, 1436, 1370, 1277, 1179, 1108, 1019, 961, 912, 815, 779, 730, 708 cm^{-1}. MS (ESI) *m/z* 322 $(M+H)^+$. HRMS (DART) calcd. for $C_{15}H_{16}NO_5S$: 322.0744, Found: 322.0740.

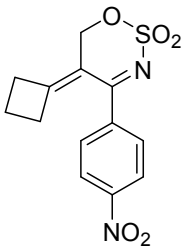




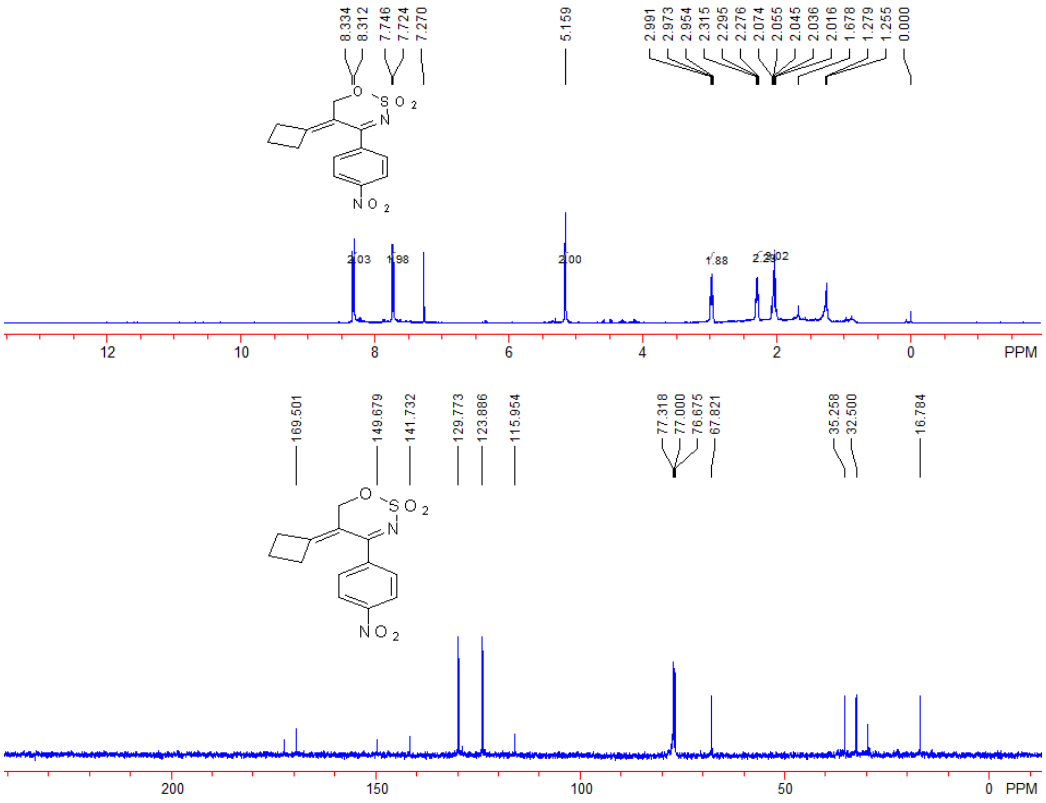
5-cyclobutylidene-4-(4-(trifluoromethyl)phenyl)-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4k**: Yield: 29.7 mg, 45%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.96-2.04 (m, 2H, CH_2), 2.26-2.30 (m, 2H, CH_2), 2.94-2.98 (m, 2H, CH_2), 5.15 (s, 2H, CH_2), 7.65-7.73 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.7, 32.4, 35.2, 67.8, 116.0, 123.4 (q, J = 271.5 Hz), 125.6 (q, J = 3.7 Hz), 129.1, 133.6 (q, J = 32.8 Hz), 119.4 (q, J = 1.5 Hz), 169.4, 173.3. ^{19}F NMR (376 MHz,

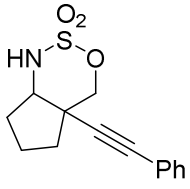
$CDCl_3$, $CFCl_3$) δ (-63.85)-(-62.89) (m). IR (EtOH) ν 2966, 2930, 1643, 1540, 1370, 1320, 1173, 1125, 1065, 938, 860, 816, 731, 690 cm^{-1}. MS (ESI) *m/z* 332 $(M+H)^+$. HRMS (DART) calcd. for $C_{14}H_{13}F_3NO_3S$: 332.0563, Found: 332.0559.



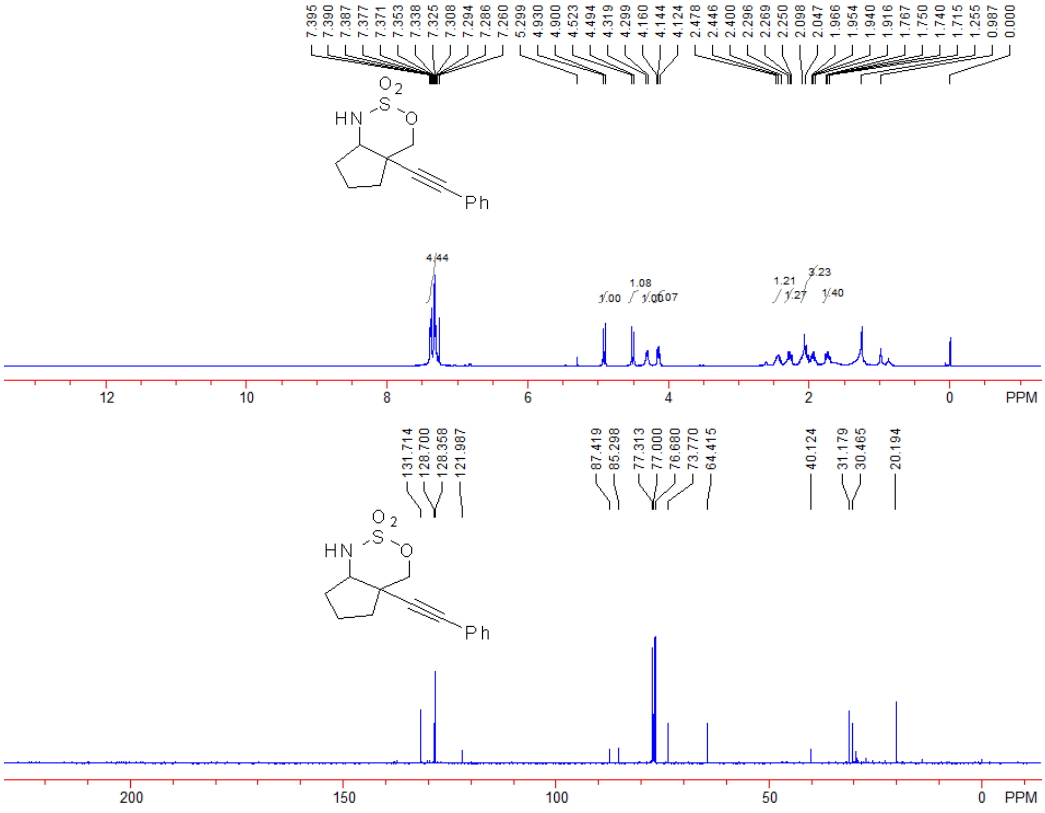


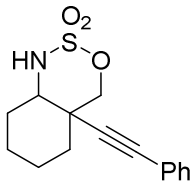
5-cyclobutylidene-4-phenyl-5,6-dihydro-1,2,3-oxathiazine 2,2-dioxide **4l**: Yield: 27.7 mg, 45%; A yellow solid, Mp: 90-92 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.02-2.07 (m, 2H, CH_2), 2.28-2.32 (m, 2H, CH_2), 2.95-2.99 (m, 2H, CH_2), 5.16 (s, 2H, CH_2), 7.73 (d, *J* = 8.8 Hz, 2H, Ar), 8.32 (d, *J* = 8.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.8, 32.5, 35.3, 67.8, 116.0, 123.9, 129.8, 141.7, 149.7, 169.5. IR (EtOH) ν 3111, 2964, 2861, 1640, 1522, 1370, 1342, 1178, 936, 908, 867, 814, 770, 726, 711 cm^{-1}. MS (ESI) *m/z* 309 $(M+H)^+$. HRMS (DART) calcd. for $C_{13}H_{13}N_2O_5S$: 309.0540, Found: 309.0536.





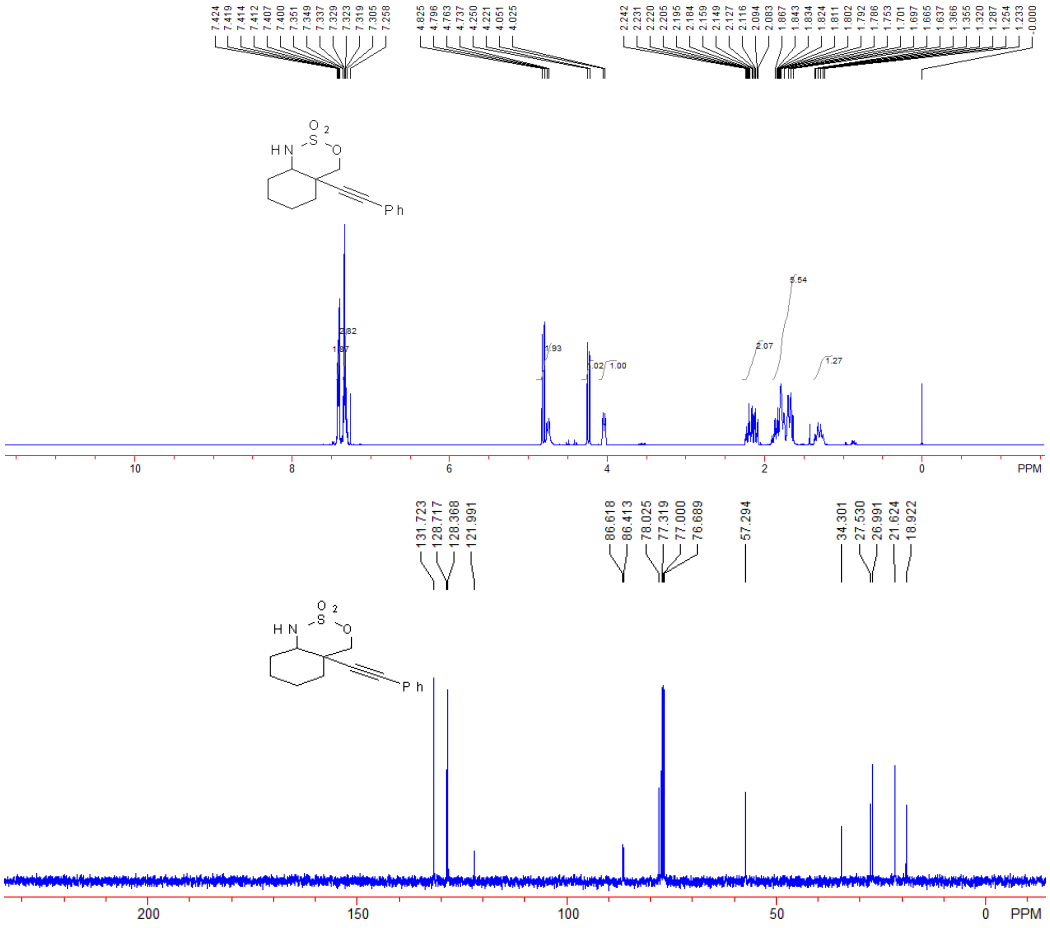
4a-(phenylethynyl)octahydrobenzo[d][1,2,3]oxathiazine 2,2-dioxide **6a**: Yield: 18.8 mg, 34%; A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.72-1.77 (m, 1H, CH_2), 1.92-2.10 (m, 3H, $2CH_2$), 2.25-2.30 (m, 1H, CH_2), 2.40-2.48 (m, 1H, CH_2), 4.12-4.16 (m, 1H, CH), 4.30-4.32 (m, 1H, NH), 4.51 (d, J = 12.0 Hz, 1H, CH_2), 4.92 (d, J = 12.0 Hz, 1H, CH_2), 7.29-7.40 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.2, 30.5, 31.2, 40.1, 64.4, 73.8, 85.3, 87.4, 122.0, 128.4, 128.7, 131.7. IR (EtOH) ν 3271, 2952, 2923, 2852, 1723, 1583, 1422, 1364, 1261, 1186, 1100, 1050, 974, 960, 916, 778, 756, 690 cm^{-1}. MS (ESI) *m/z* 278 $(M+H)^+$. HRMS (ESI) calcd. for $C_{14}H_{16}NO_3S$: 278.0851, Found: 278.0850.



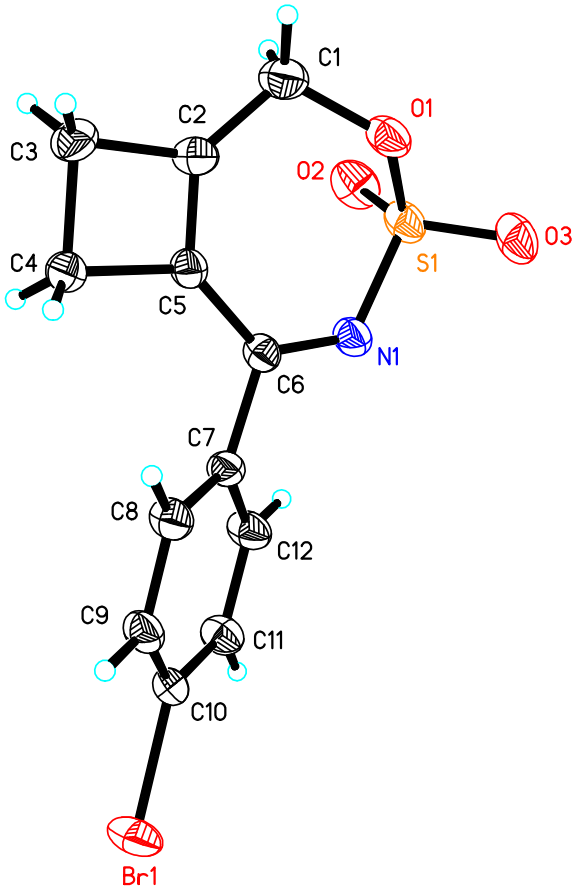


4a-(phenylethynyl)octahydrobenzo[d][1,2,3]oxathiazine 2,2-dioxide **8a**: Yield: 37.1 mg, 64%; A white solid, Mp: 124-126 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23-1.37 (m, 1H, CH_2), 1.64-1.87 (m, 5H, $3CH_2$), 2.08-2.24 (m, 2H, CH_2), 4.03 (d, J = 10.4 Hz, 1H, CH), 4.24 (d, J = 11.6 Hz, 1H, CH_2), 4.75 (d, J = 10.4 Hz, 1H, NH), 4.81 (d, J = 11.6 Hz, 1H, CH_2), 7.31-7.35 (m, 3H, Ar),

7.40-7.42 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.9, 21.6, 27.0, 27.5, 34.3, 57.3, 76.0, 86.4, 86.6, 122.0, 128.4, 128.7, 131.7. IR (EtOH) ν 3279, 2951, 2927, 2852, 1723, 1583, 1422, 1364, 1261, 1186, 1100, 1050, 979, 960, 916, 779, 756, 690 cm^{-1}. MS (ESI) *m/z* 292 $(M+H)^+$. HRMS (ESI) calcd. for $C_{15}H_{18}NO_3S$: 292.1002, Found: 292.1002.

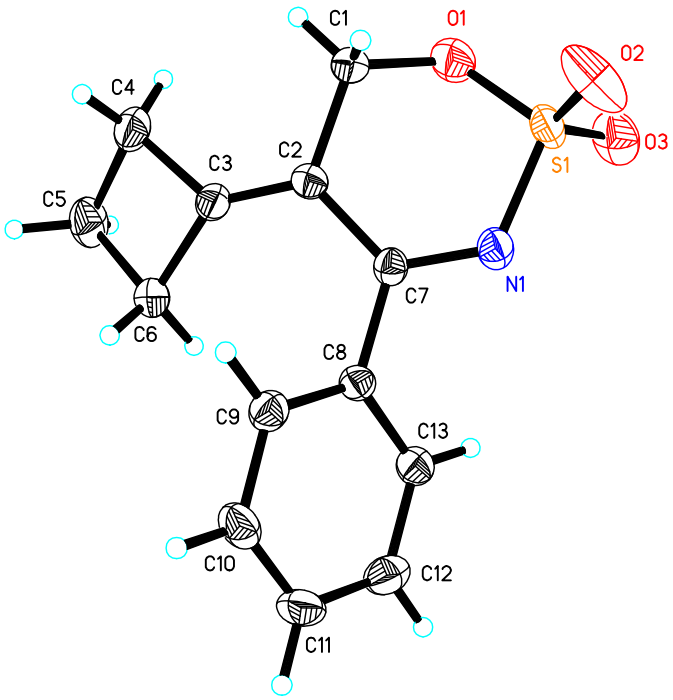


X-ray Crystal Data of Product 2h



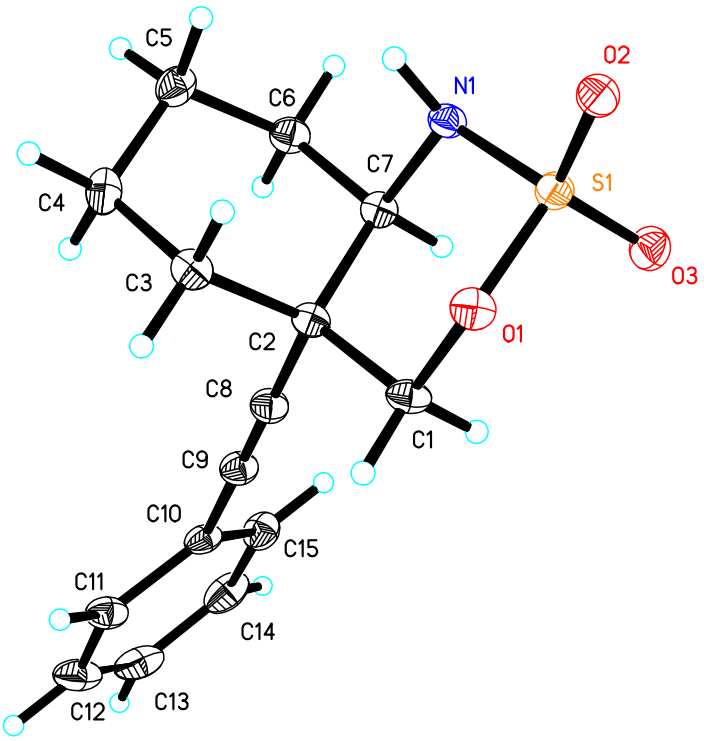
The crystal data of **2h** have been deposited in CCDC with number 1510152. Empirical formula: $C_{12}H_{10}BrNO_3S$, Formula weight: 328.18, Crystal system: Triclinic, Space group: P -1, Unit cell dimensions: a = 12.1801(15) Å, α = 89.100(3)°; b = 14.4847(18) Å, β = 82.956(3)°; c = 15.6426(19) Å, γ = 66.053(2)°. Volume: 2501.4(5) $Å^3$, Z = 8, Density (calculated): 1.743 Mg/m^3, F(000) = 1312, Crystal size: 0.200 x 0.160 x 0.130 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0495, wR2 = 0.1080.

X-ray Crystal Data of Product 4a



The crystal data of **4a** have been deposited in CCDC with number 1500320. Empirical formula: $C_{13}H_{13}NO_3S$, Formula weight: 263.30, Crystal system: Orthorhombic, Space group: P 21 21 21, Unit cell dimensions: a = 5.4587(10) Å, α = 90°; b = 9.1326(16) Å, β = 90°; c = 24.374(4) Å, γ = 90°. Volume: 1215.1(4) $Å^3$, Z = 4, Density (calculated): 1.439 Mg/m^3, F(000) = 552, Crystal size: 0.200 x 0.160 x 0.120 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0584, wR2 = 0.1617.

X-ray Crystal Data of Product 8a



The crystal data of **8a** have been deposited in CCDC with number 1477721. Empirical formula: $C_{15}H_{17}NO_3S$, Formula weight: 291.35, Crystal system: Monoclinic, Space group: P 1 21/c 1, Unit cell dimensions: a = 8.7197(19) Å, α = 90°; b = 18.932(4) Å, β = 101.498(4)°; c = 8.9238(19) Å, γ = 90°. Volume: 1443.6(5) $Å^3$, Z = 4, Density (calculated): 1.341 Mg/m^3, F(000) = 616, Crystal size: 0.2 x 0.15 x 0.12 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0499, wR2 = 0.1137.

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