Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-catalyzed intramolecular rearrangement of vinylidenecyclopropanes through C-C bond activation

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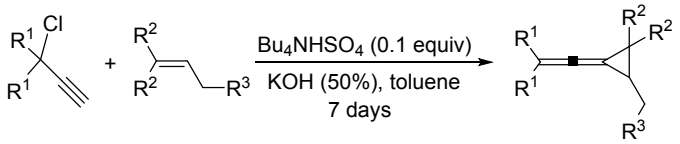
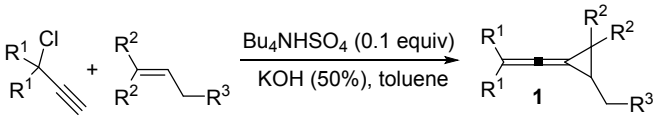
CONTENTS

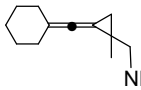
General remarks. ^{1}H and ^{13}C NMR spectra were recorded at 400 (or 300) MHz, respectively. HRMS spectra were recorded by EI or ESI method. The employed solvents were dry up by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

General Procedure for the Preparation of Substrates 1a-1g, 1j-1p and 1r.



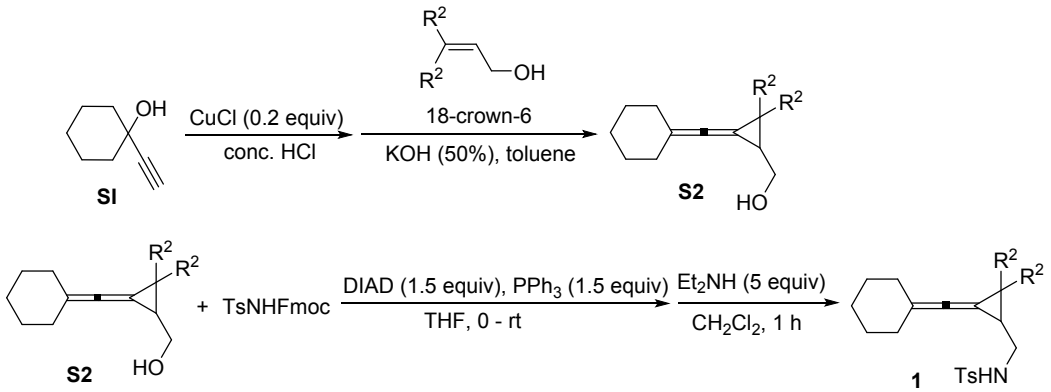
Under an argon atmosphere, to a solution of alkene (10.0 mmol, 1.0 equiv) and Bu_4NHSO_4 (1 mmol, 0.1 equiv) in toluene (30.0 mL) and 50% KOH water solution (30.0 mL) was added dropwise an alkyne (20.0 mmol, 2.0 equiv) over 30 min at room temperature. After the resulting mixtures were stirred for 7 days, the solvent was extracted with CH_2Cl_2 (3×20.0 mL). The combined organic layers were washed with a saturated aqueous solution of NaCl and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 30:1) afforded the corresponding VDCP[1,2,3] products **1a-1g**, **1j-1p** and **1r**.[4]



entry[a]	R^1, R^1	R^3	**1**, yield/%[b]
1	-$(CH_2)_5$-	4-$MeC_6H_4SO_2NH$	**1a**, 14
2	-$(CH_2)_5$-	4-$BrC_6H_4SO_2NH$	**1b**, 10
3	-$(CH_2)_5$-	2-$ClC_6H_4SO_2NH$	**1c**, 12
4	-$(CH_2)_5$-	2-$NO_2C_6H_4SO_2NH$	**1d**, 15
5	-$(CH_2)_5$-	$C_6H_4SO_2NH$	**1e**, 25
6	-$(CH_2)_5$-	$MeSO_2NH$	**1f**, 16
7	-$(CH_2)_5$-	CF_3SO_2NH	**1g**, 20
8	Me, Me	4-$MeC_6H_4SO_2NH$	**1j**, 13
9	Me, Me	CF_3SO_2NH	**1k**, 12
10	-$(CH_2)_6$-	CF_3SO_2NH	**1l**, 20
11	-$(CH_2)_6$-	4-$MeC_6H_4SO_2NH$	**1m**, 25
12	-$(CH_2)_4$-	4-$MeC_6H_4SO_2NH$	**1n**, 10
13	-$(CH_2)_6$-	C_6H_4CONH	**1o**, 20
14	-$(CH_2)_6$-	CF_3CONH	**1p**, 13
15			**1r**, 4

[a]To a solution of alkene (20.0 mmol, 1.0 equiv) and Bu_4NHSO_4 (2 mmol, 0.1 equiv) in toluene (30.0 mL) and 50% KOH water solution (30.0 ml) was added dropwise an alkyne (40.0 mmol, 2.0 equiv) over 30 min at room temperature. [b]Isolated yields

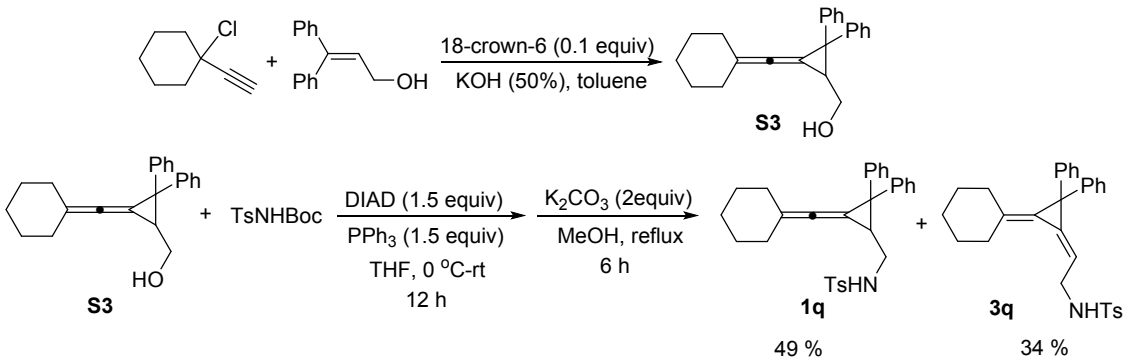
General Procedure for the Preparation of Substrates 1h and 1i.



A three-necked flask containing copper(I) chloride (40 mmol, 0.2 equiv) and conc. HCl (100.0 mL) was cooled to 0 °C. Then, alkynol **S1** (200 mmol, 1 equiv) was added dropwise to the above flask and warmed up to rt naturally. After three hours, the mixture was extracted with n-pentane (6.0 mL x 3). The organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Then under an argon atmosphere, the residue (40 mmol, 2.0 equiv) was added slowly to a three-necked flask containing 18-crown-6 (2 mmol, 0.1 equiv) and alkene (20 mmol, 1 equiv) in toluene (60.0 mL) and 50% KOH water solution (60.0 mL). After the resulting mixtures were stirred for 3 days, the solvent was extracted with CH_2Cl_2 (20.0 mL x 3). The combined organic layers were washed with a saturated aqueous solution of NaCl and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 30:1) afforded the corresponding products **S2**.

Under an argon atmosphere, to a solution of **S2** (2.0 mmol, 1.0 equiv), PPh_3 (3 mmol, 1.5 equiv) and TsNHFmoc (3 mmol, 1.5 equiv) in anhydrous THF (10.0 mL) was added dropwise DIAD (3 mmol, 1.5 equiv) over 20 min at 0 °C. After the resulting mixtures were stirred for 10 h, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate 30:1) afforded the corresponding products. Then the product was stirred in the Et_2NH (4 mL) solution of CH_2Cl_2 (20 mL). The solvent was removed under reduced pressure after 1 h, then giving the desired products **1h** and **1i**.[5]

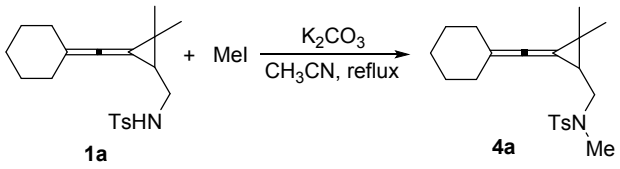
General Procedure for the Preparation of Substrates 1q.



Under an argon atmosphere, to a solution of alkene (10.0 mmol, 1.0 equiv) and 18-crown-6 (1 mmol, 0.1 equiv) in toluene (30.0 mL) and 50% KOH water solution (30.0) was added dropwise the alkyne (20.0 mmol, 2.0 equiv) over 30 min at room temperature. After the resulting mixtures were stirred for 7 days, the solvent was extracted with then CH_2Cl_2 (3×20.0 mL). The combined organic layers were washed with a saturated aqueous solution of NaCl and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 30:1) afforded the corresponding products **S3**.

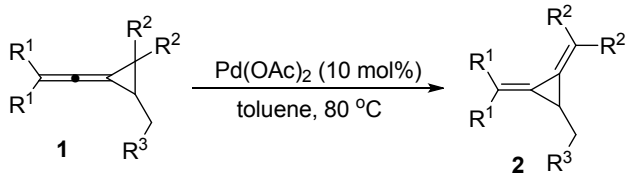
Under an argon atmosphere, to a solution of **S3** (2.0 mmol, 1.0 equiv), PPh_3 (3 mmol, 1.5 equiv) and TsNHBoc (3 mmol, 1.5 equiv) in anhydrous THF (10.0 mL) was added dropwise DIAD (3 mmol, 1.5 equiv) over 20 min at 0 °C. After the resulting mixtures were stirred for 10 h, the solvent was removed under reduced pressure and the residue was extracted with then CH_2Cl_2 (3×20.0 mL). The combined organic layers were washed with a saturated aqueous solution of NaCl and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the corresponding products. Then the product was refluxed for 2 h in the MeOH (10 mL) with K_2CO_3. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 30:1) afforded the corresponding product **1q**.[5]

General Procedure for the Preparation of Substrates 4a.



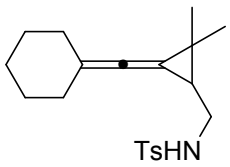
Under an argon atmosphere, to a solution of **1a** (0.4 mmol, 1.0 equiv), K_2CO_3 (0.6 mmol, 1.5 equiv) in anhydrous CH_3CN (4.0 mL) was added MeI (0.6 mmol, 1.5 equiv). After the resulting mixtures were stirred for 10 h under reflux, the solvent was removed under reduced pressure and the residue was extracted with then CH_2Cl_2 (3×10.0 mL). The combined organic layers were washed with a saturated aqueous solution of NaCl and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) afforded the corresponding products **4a**.[6]

General Procedure for the Pd-catalyed Reaction of VDCPs.

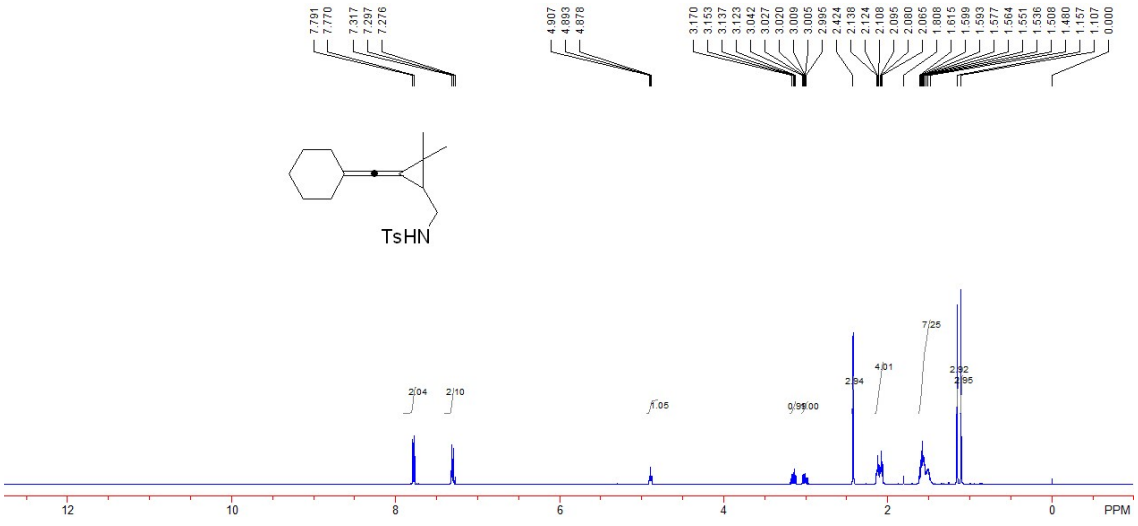


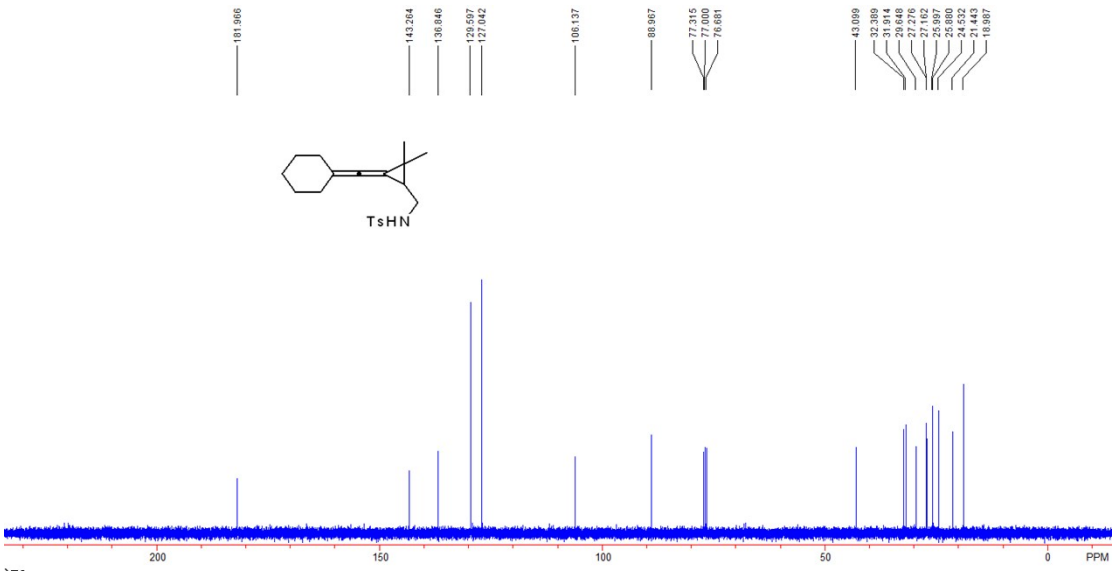
To a dried 25 mL Schlenk tube was added $Pd(OAc)_2$ (10 mol%), then the tube was evacuated and filled with Ar for 3 times. Compound **1** (0.2 mmol, 1.0 equiv) and 2.0 mL solvent was added. After the resulting mixtures were stirred for 10 h at 80 °C, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the corresponding products **2a**-**2m**.

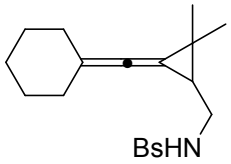
Spectroscopic Data and Charts of Compounds 1a-1l



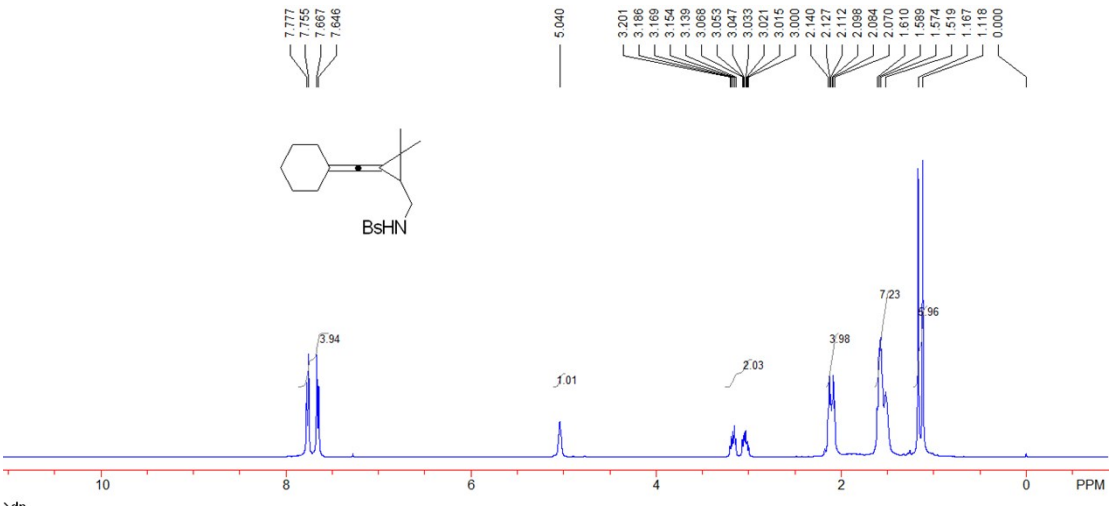
N-((3-(cyclohexylidenemethylene)-2,2-dimethylcyclopropyl)methyl)-4-methylbenzene-sulfonamide **1a**: Yield: 990 mg, 14%; A white solid, Mp: 129-131 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.51-1.62 (m, 7H, CH, $3CH_2$), 2.07-2.15 (m, 4H, $2CH_2$), 2.42 (s, 3H, CH_3), 3.09 (t, J = 6.0 Hz, 2H, CH_2), 4.40 (br, 1H, NH), 7.31 (d, J = 8.0 Hz, 2H, Ar), 7.75 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.4, 24.5, 25.9, 26.0, 27.2, 27.3, 29.6, 31.9, 32.4, 43.1, 89.0, 106.1, 127.0, 129.6, 136.8, 143.3, 182.0. IR (CH_2Cl_2) ν 3273, 2926, 2852, 1651, 1598, 1446, 1345, 1328, 1306, 1158, 1092, 995, 922, 897, 815, 802, 751, 660 cm^{-1}. MS (ESI) *m/z* 363 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{20}H_{31}N_2O_2S$: 363.2101, Found: 363.2104.

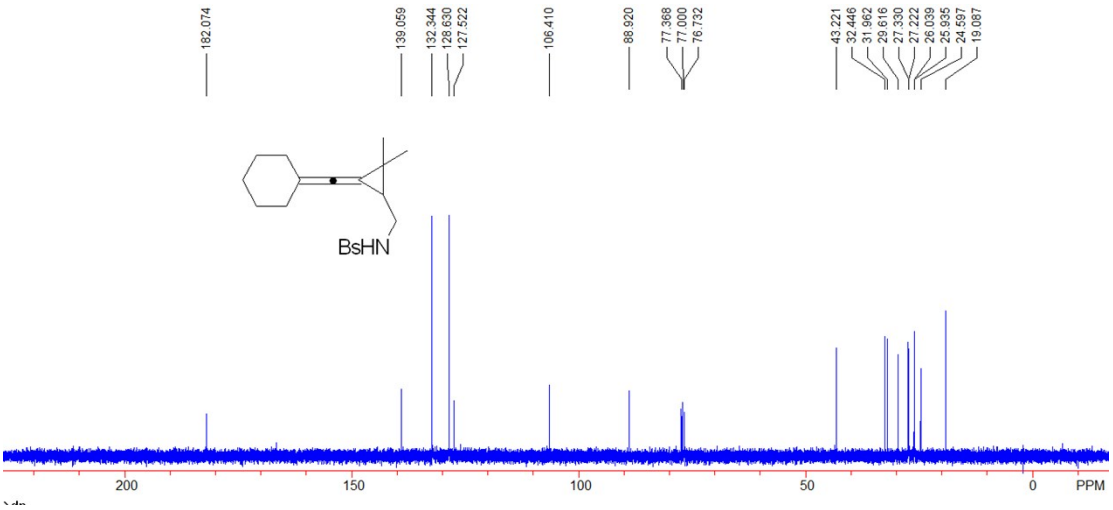


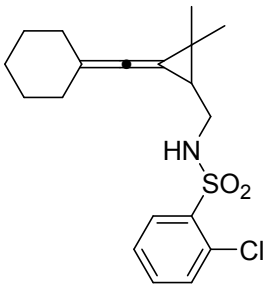




4-Bromo-*N*-((3-(cyclohexylidenemethylene)-2,2-dimethylcyclopropyl)methyl)benzene-sulfonamide **1b**: Yield: 780 mg, 10%; A white solid, Mp: 105-107 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.52-1.61 (m, 7H, CH, $3CH_2$), 2.07-2.14 (m, 4H, $2CH_2$), 3.00-3.10 (m, 1H, CH_2), 3.10-3.20 (m, 1H, CH_2), 5.04 (br, 1H, NH), 7.66 (d, J = 8.0 Hz, 2H, Ar), 7.77 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 24.6, 25.9, 26.0, 27.2, 27.3, 29.6, 32.0, 32.4, 43.2, 88.9, 106.4, 127.5, 128.6, 132.3, 139.1, 182.1. IR (CH_2Cl_2) ν 3280, 2926, 2852, 1651, 1598, 1446, 1345, 1329, 1306, 1158, 1092, 995, 922, 898, 815, 802, 751, 660 cm^{-1}. MS (ESI) *m/z* 427 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{19}H_{28}BrN_2O_2S$: 427.1049, Found: 427.1050.

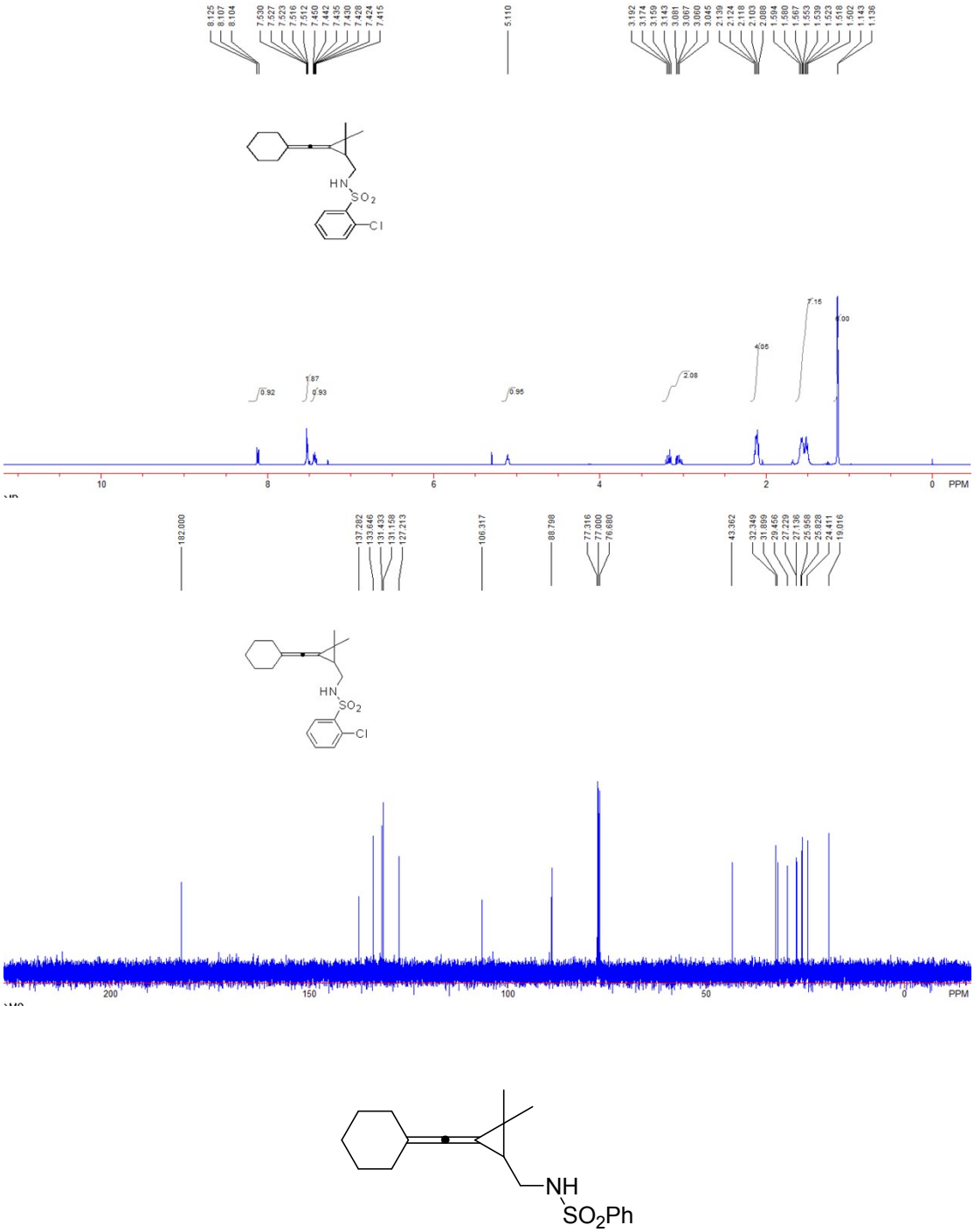






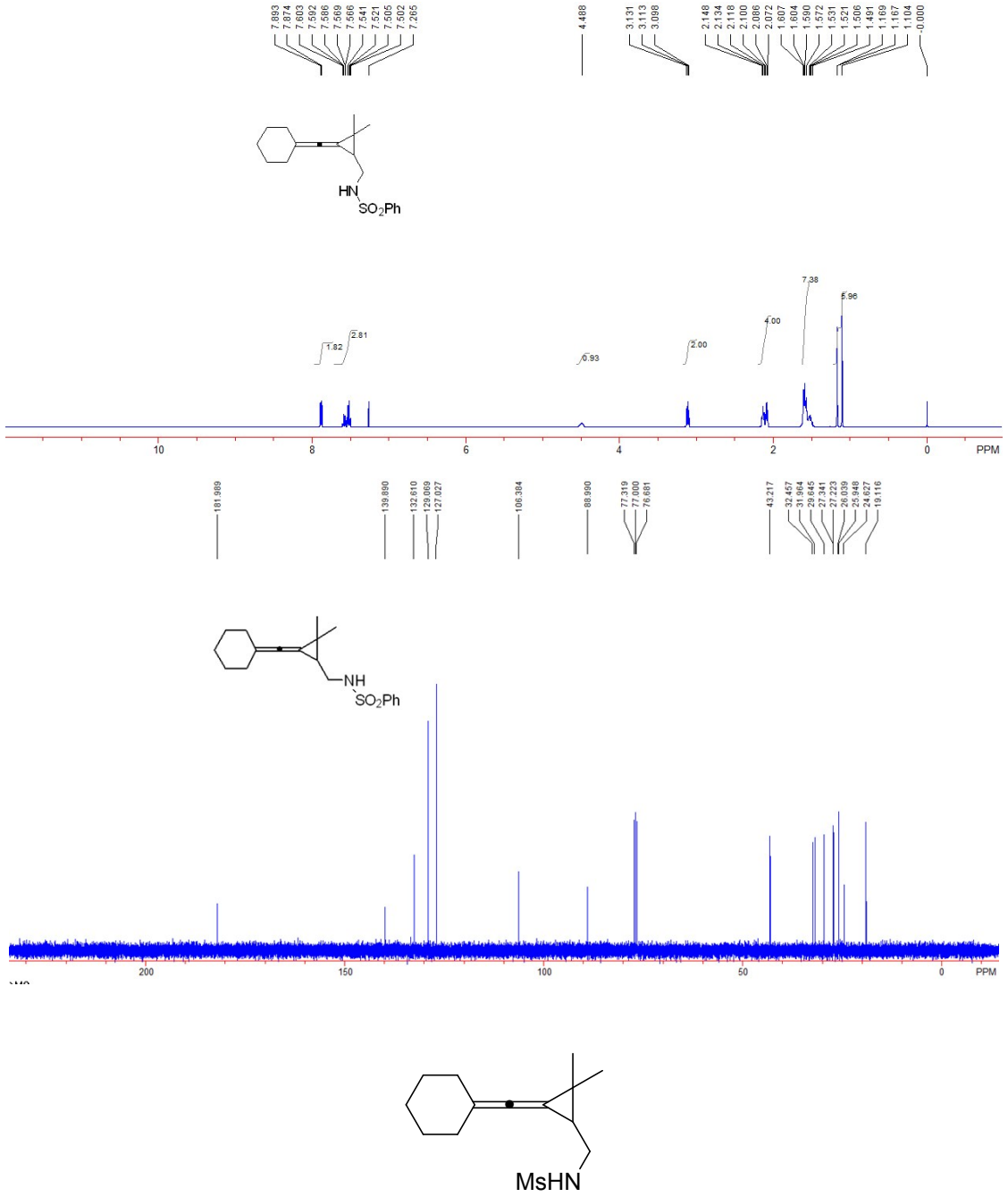
2-Chloro-*N*-((3-(cyclohexylidenemethylene)-2,2-dimethylcyclopropyl)methyl)benzenesulfonamide **1c**: Yield: 906 mg, 12%; A white solid, Mp: 121-123 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.136 (s, 3H, CH_3), 1.143 (s, 3H, CH_3), 1.50-1.59 (m, 7H, CH, $3CH_2$), 2.09-2.14 (m, 4H, $2CH_2$), 3.05-3.19 (m, 2H, CH_2), 5.11 (br, 1H, NH), 7.42-7.45 (m, 1H, Ar), 7.51-7.53 (m, 2H, Ar), 8.12 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 24.4, 25.8, 26.0, 27.1, 27.2, 29.5, 31.9, 32.3, 43.4, 88.8, 106.3, 127.2, 131.2, 131.4, 133.6, 137.3, 182.0. IR (Neat) ν 3306, 2924, 2853, 2006, 1578, 1453, 1436, 1333,

1163, 1129, 1044, 987, 851, 822, 760, 748 cm^{-1}. MS (ESI) *m/z* 383 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{19}H_{28}ClN_2O_2S$: 383.1555, Found: 383.1556.



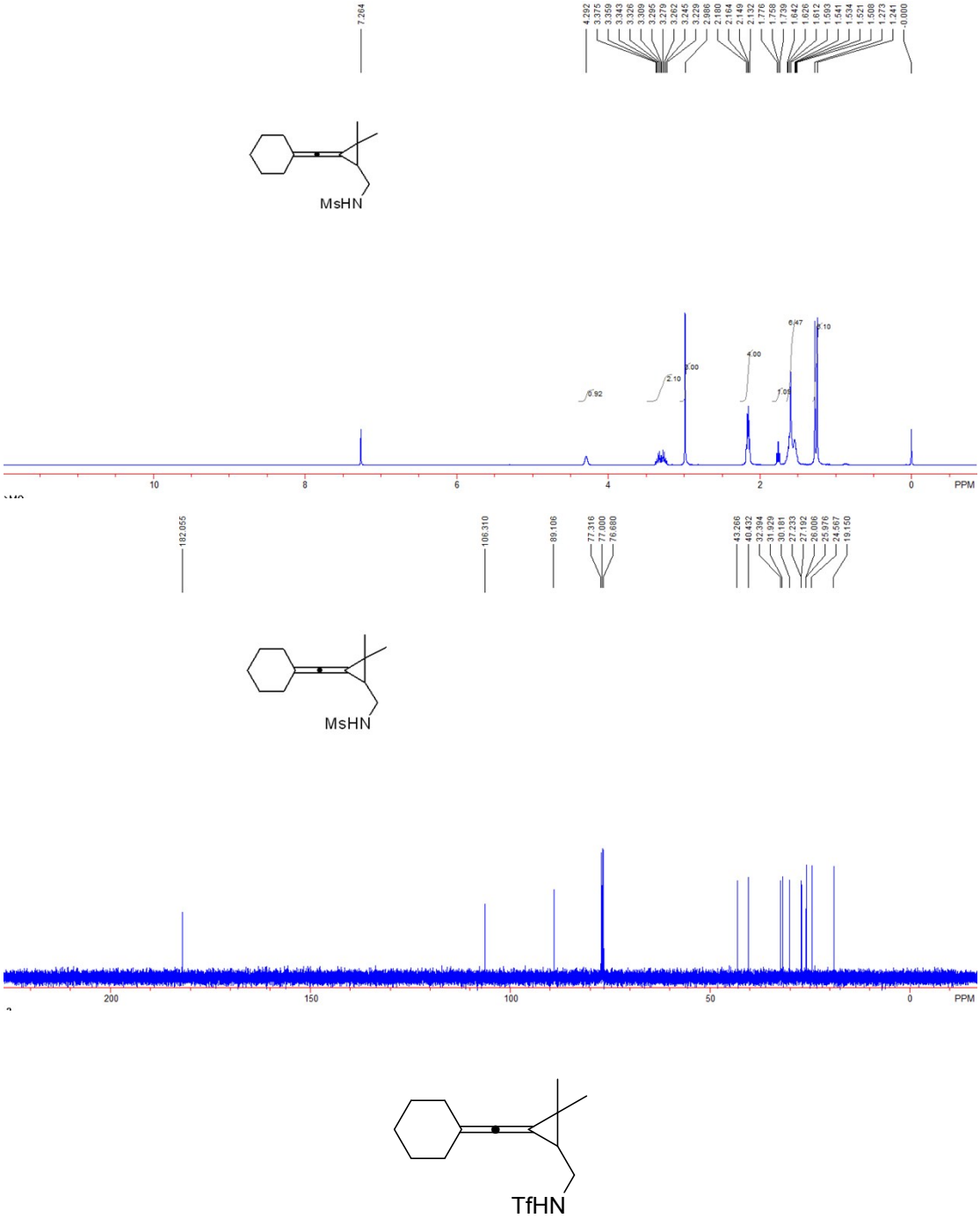
N-((3-(cyclohexylidenemethylene)-2,2-dimethylcyclopropyl)methyl)benzenesulfonamide **1d**: Yield: 1.60 g, 24%; A white solid, Mp: 127-129 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.49-1.61 (m, 7H, CH, $3CH_2$), 2.07-2.15 (m, 4H, $2CH_2$), 3.11 (t, J = 6 Hz, 2H, CH_2), 4.49 (br, 1H, NH), 7.50-7.61 (m, 3H, Ar), 7.88 (d, J = 7.6 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 24.7, 26.0, 26.1, 27.3, 27.4, 29.7, 32.0, 32.5, 43.2, 89.0, 106.4,

127.1, 129.1, 132.6, 139.9, 182.0. IR (CH_2Cl_2) ν 3279, 2924, 2853, 2006, 1447, 1418, 1325, 1161, 1123, 1094, 1061, 822, 755, 719, 689 cm^{-1}. MS (ESI) *m/z* 349 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{19}H_{29}N_2O_2S$: 349.1944, Found: 349.1949.



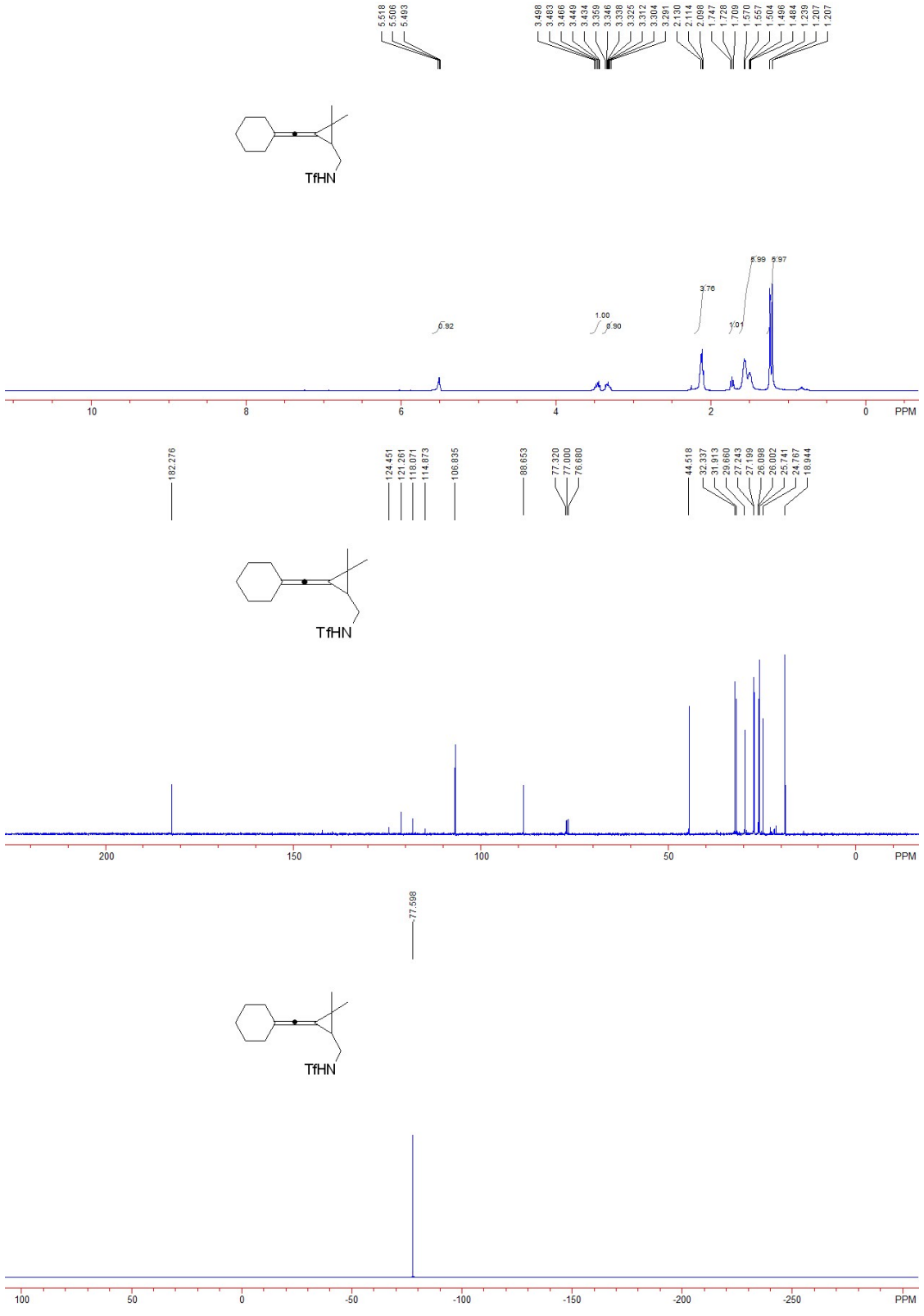
N-((3-(cyclohexylidenemethylene)-2,2-dimethylcyclopropyl)methyl)methanesulfonamide **1f**: Yield: 886 mg, 16%; A white solid, Mp: 95-87 ^oC. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.49-1.66 (m, 6H, $3CH_2$), 1.76 (t, J = 7.6 Hz, 1H, CH), 2.13-2.18 (m, 4H, $2CH_2$), 2.99 (s, 3H, CH_3), 3.23-3.38 (m, 2H, CH_2), 4.29 (br, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.2, 24.6, 25.98, 26.01, 27.19, 27.23, 30.2, 31.9, 32.4, 40.4, 43.3, 89.1, 106.3,

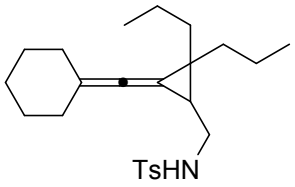
182.1. IR (Neat) ν 3285, 2924, 2853, 2006, 1435, 1410, 1314, 1149, 1123, 1062, 968, 850, 824, 755 cm^{-1}. MS (ESI) *m/z* 287 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{14}H_{27}N_2O_2S$: 287.1788, Found: 287.1791.



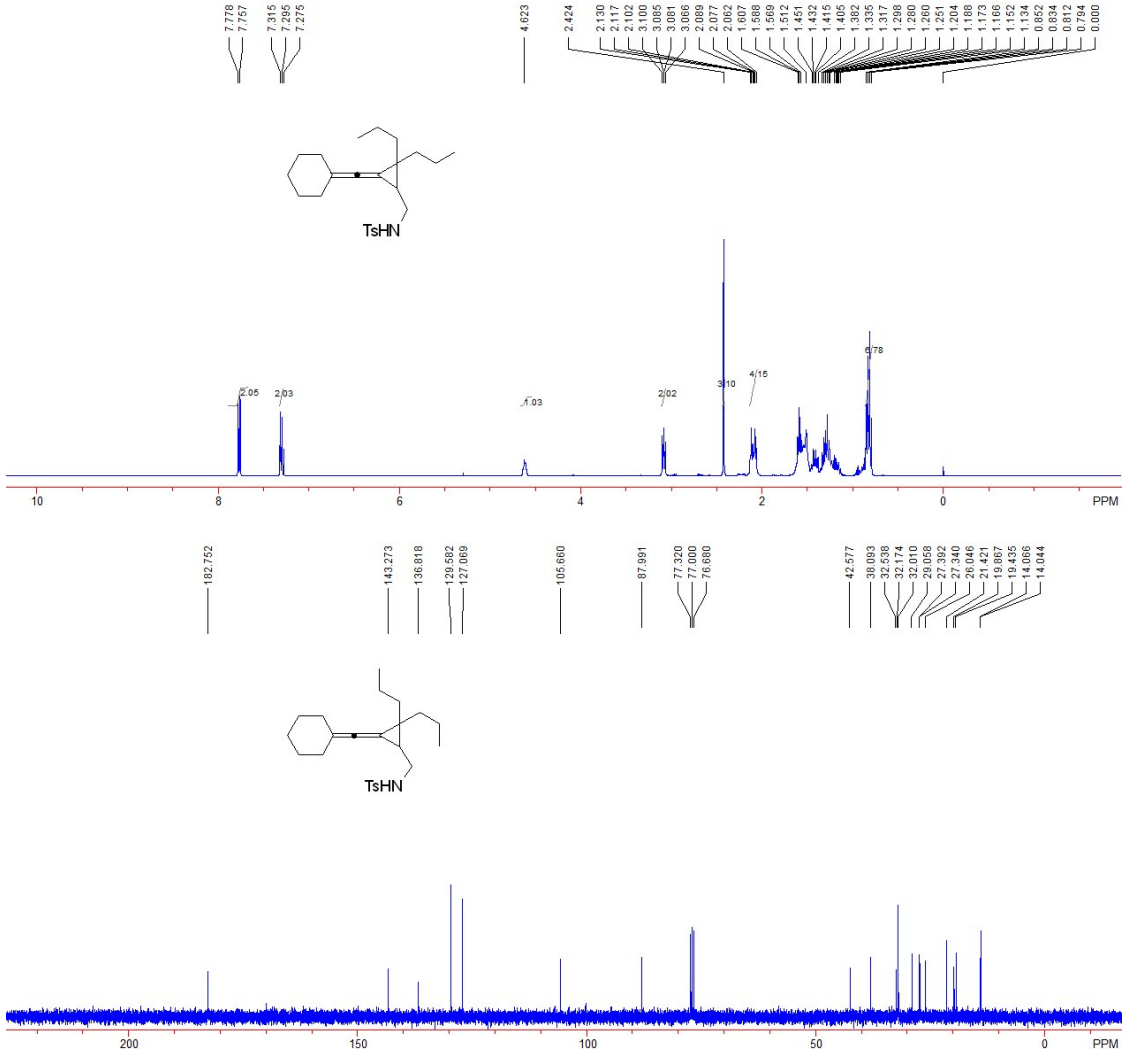
N-((3-(cyclohexylidenemethylene)-2,2-dimethylcyclopropyl)methyl)-1,1,1-trifluoromethane-sulfonamide **1k**: Yield: 1.32 g, 20%; A yellow oli. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.21 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.48-1.57 (m, 6H, $3CH_2$), 1.73 (t, J = 7.6 Hz, 1H, CH), 2.10-2.13 (m, 4H, $2CH_2$), 3.29-3.50 (m, 2H, CH_2), 5.51 (br, 1H, NH). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -77.60. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 24.8, 25.7, 26.0, 26.1, 27.20, 27.24, 29.7, 31.9,

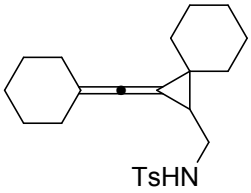
32.3, 44.5, 88.7, 106.8, 119.7 (q, J = 319.0 Hz), 182.3. IR (Neat) ν 3305, 2929, 2856, 2010, 1701, 1435, 1370, 1229, 1185, 1145, 1052, 988, 850, 827 cm^{-1}. MS (%) (EI) *m/z* 323 (M^{+}+1, 20), 190 (32), 161 (70), 148 (30), 119 (46), 105 (55), 91 (100), 81 (50), 69 (43), 55 (28), 41 (44). HRMS (EI) calcd. for $C_{14}H_{20}NO_2F_3S$: 323.1167, Found: 323.1161.



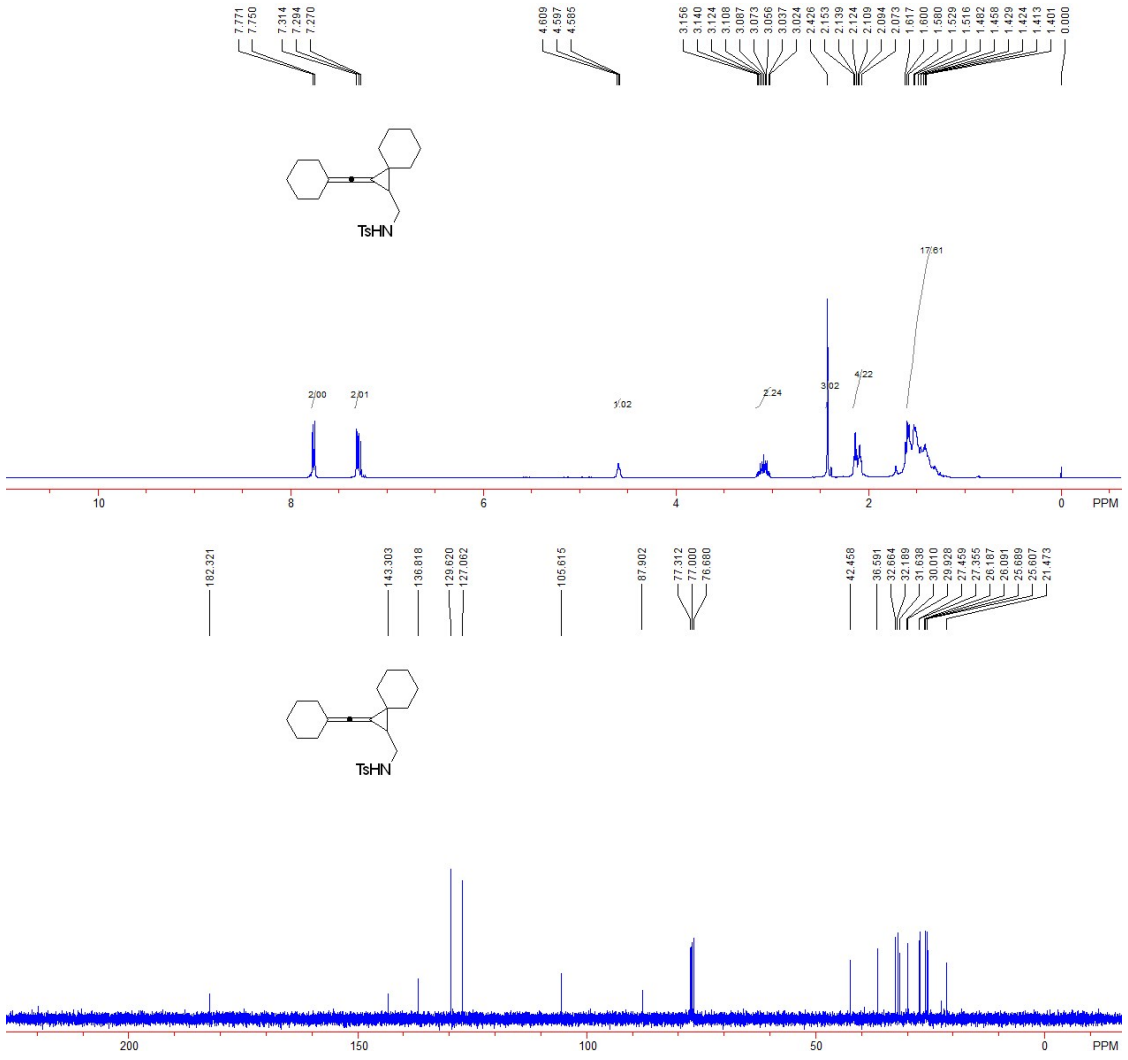


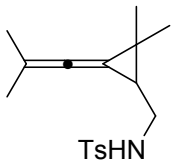
N-((3-(cyclohexylidenemethylene)-2,2-dipropylcyclopropyl)methyl)-4-methylbenzene-sulfonamide **1h**: Yield: 122 mg, 42%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.81 (t, *J* = 7.2 Hz, 3H, CH_3), 0.84 (t, *J* = 7.2 Hz, 3H, CH_3), 1.16-1.61 (m, 15H, 1CH, 7CH_2), 2.06-2.12 (m, 4H, 2CH_2), 2.43 (s, 3H, CH_3), 3.09 (t, *J* = 6.0 Hz, 2H, CH_2), 4.64 (br, 1H, NH), 7.30 (d, *J* = 8.0 Hz, 2H, Ar), 7.77 (d, *J* = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.04, 14.07, 19.4, 19.9, 21.4, 26.1, 27.3, 27.4, 29.1, 32.0, 32.2, 32.5, 38.1, 42.6, 88.0, 105.7, 127.1, 129.6, 136.8, 143.3, 182.8. IR (CH_2Cl_2) ν 3277, 2954, 2927, 2870, 2008, 1716, 1598, 1446, 1223, 1158, 1120, 1093, 1059, 1018, 911, 850 cm^{-1}. MS (ESI) m/z 402 $(M+H)^+$. HRMS (ESI) calcd. for $C_{24}H_{36}NO_2S$: 402.2461, Found: 402.2459.



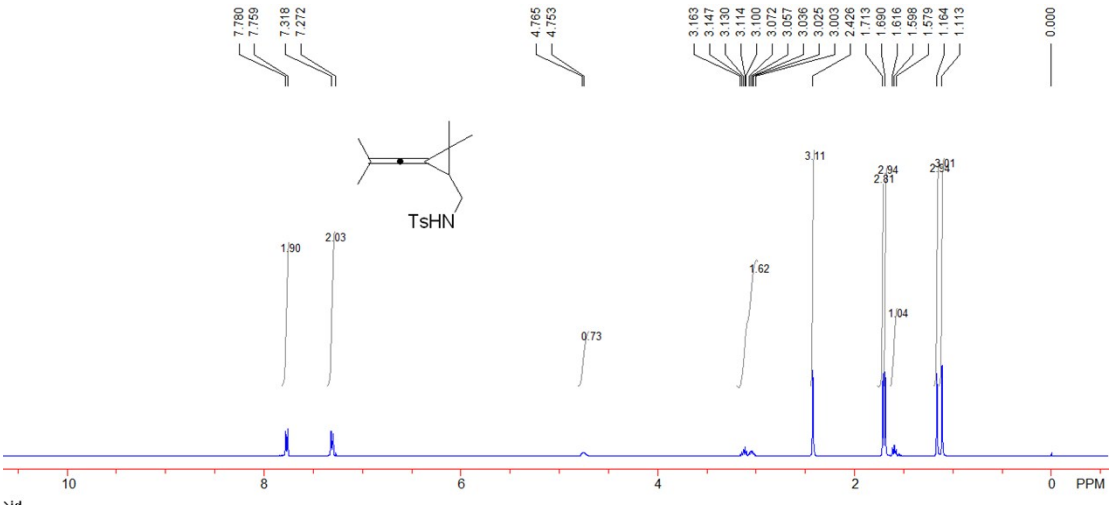


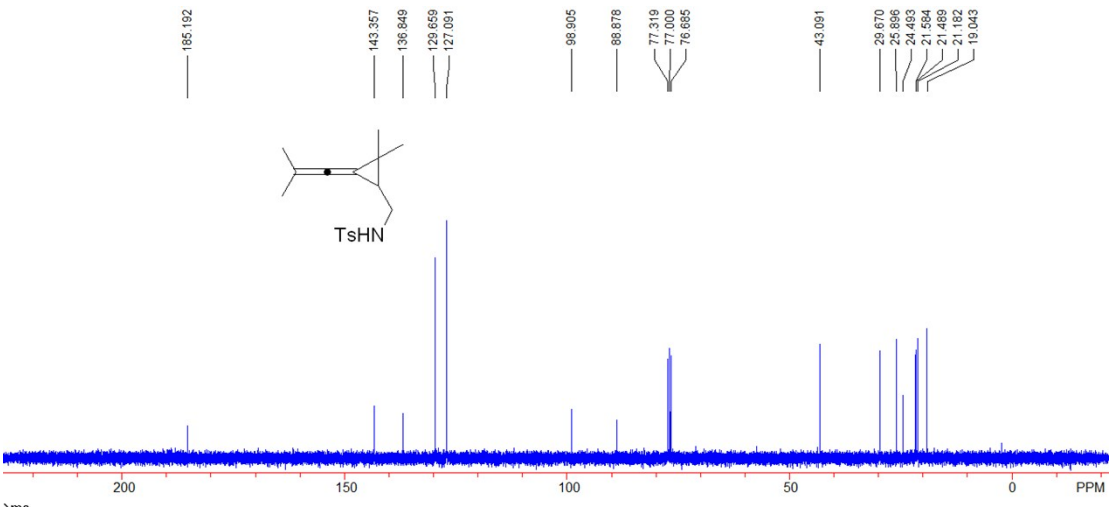
N-((2-(cyclohexylidenemethylene)spiro[2.5]octan-1-yl)methyl)-4-methylbenzene-sulfonamide **1i**: Yield: 139 mg, 17%; A yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.40-1.62 (m, 17H, $8CH_2$, 1CH), 2.07-2.15 (m, 4H, $2CH_2$), 2.43 (s, 3H, CH_3), 3.02-3.16 (m, 2H, CH_2), 4.60 (br, 1H, NH), 7.30 (d, *J* = 8.0 Hz, 2H, Ar), 7.76 (d, *J* = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 21.5, 25.6, 25.7, 26.1, 26.2, 27.4, 27.5, 29.9, 30.0, 31.6, 32.2, 32.7, 36.6, 42.5, 87.9, 105.6, 127.1, 129.6, 136.8, 143.3, 182.3. IR (CH_2Cl_2) ν 3277, 2924, 2850, 2007, 1716, 1598, 1445, 1325, 1305, 1158, 1094, 1071, 813, 665 cm^{-1}. MS (ESI) *m/z* 386 $(M+H)^+$. HRMS (ESI) calcd. for $C_{23}H_{32}NO_2S$: 386.2147, Found: 386.2148.

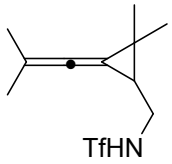




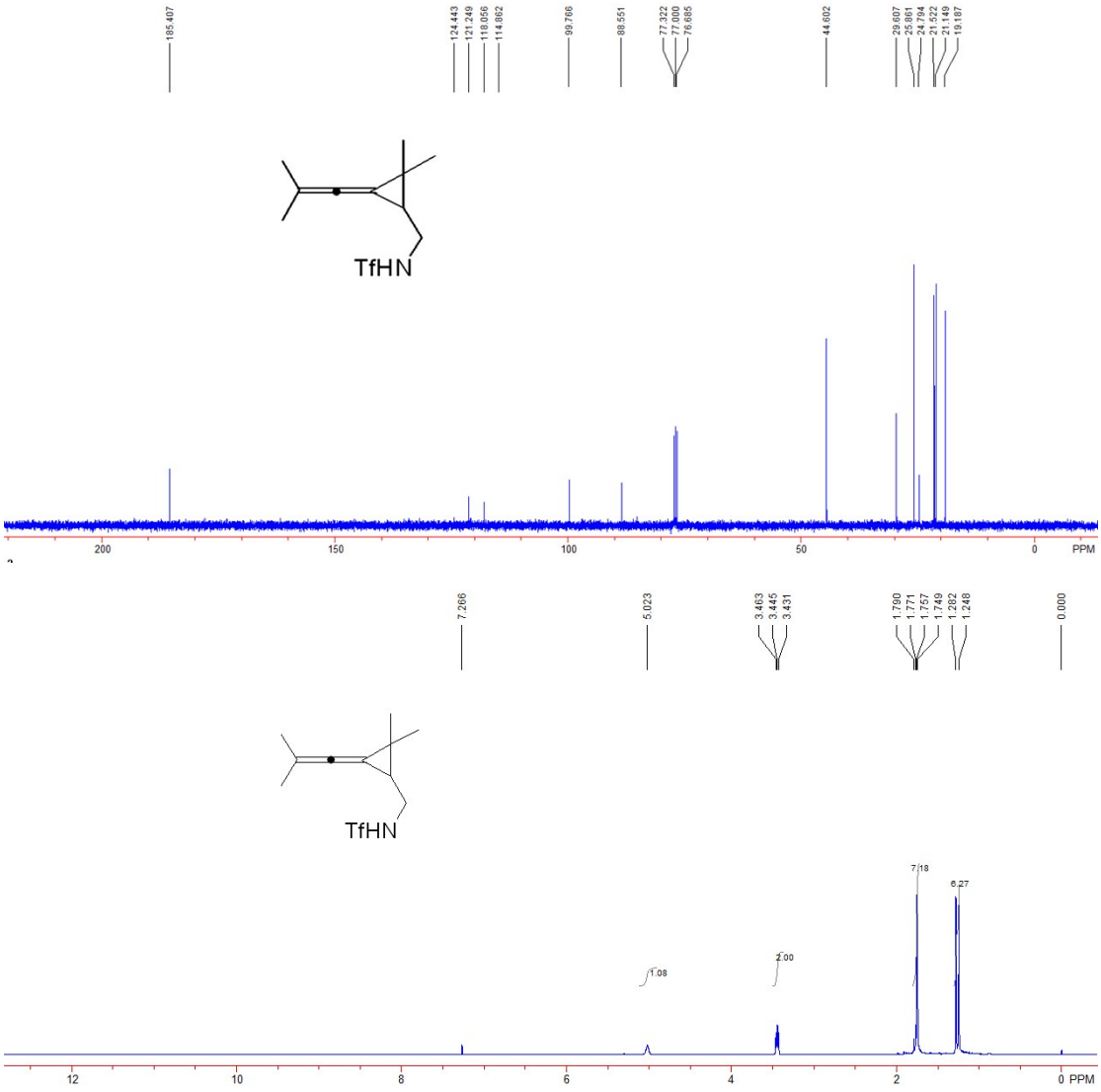
N-((2,2-dimethyl-3-(2-methylprop-1-en-1-ylidene)cyclopropyl)methyl)-4-methylbenzene-sulfonamide **1j**: Yield: 0.910 g, 13%; A white solid, Mp: 85-87 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.11 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.60 (t, J = 7.6 Hz, 1H, CH), 1.69 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.04-3.15 (m, 2H, CH_2), 4.76 (br, 1H, NH), 7.31 (d, J = 8.0 Hz, 2H, Ar), 7.70 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.2, 21.5, 21.6, 24.5, 25.9, 29.7, 43.1, 88.9, 98.9, 127.1, 129.7, 136.8, 143.4, 185.2. IR (CH_2Cl_2) ν 3279, 2976, 2908, 2862, 2009, 1598, 1446, 1325, 1158, 1123, 1094, 1056, 814, 633 cm^{-1}. MS (ESI) *m/z* 323 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{17}H_{27}N_2O_2S$: 323.1788, Found: 323.179.

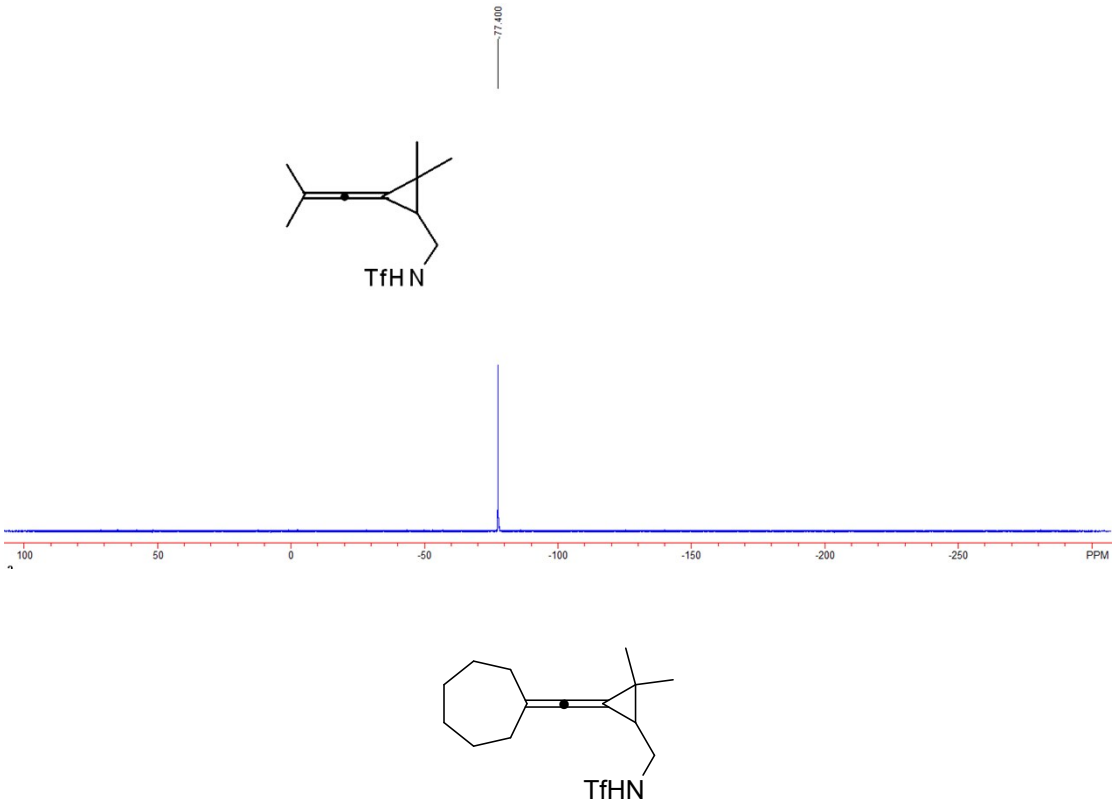




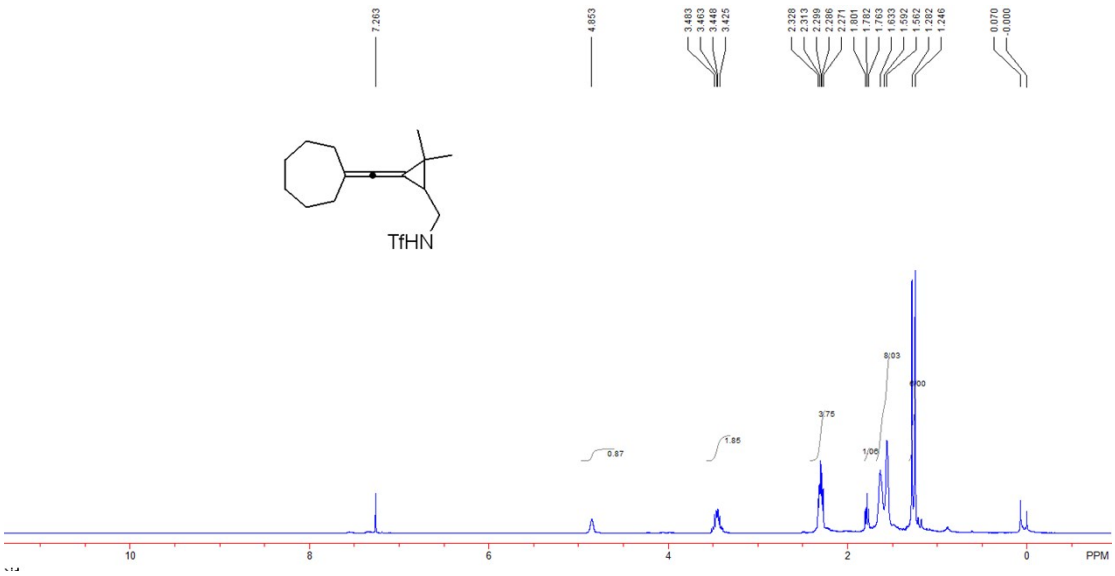


N-((2,2-dimethyl-3-(2-methylprop-1-en-1-ylidene)cyclopropyl)methyl)-1,1,1-trifluoromethanesulfonamide 1k:Yield: 640 mg, 11%; A yellow solid, Mp: 76-78 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.75-1.79 (m, 7H, CH, $2CH_3$), 3.45 (t, J = 5.6 Hz, 2H, CH_2), 5.02 (br, 1H, NH). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -77.40. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.2, 21.1, 21.5, 24.8, 25.9, 29.6, 44.6, 88.6, 99.8, 119.7 (q, J = 319.0 Hz), 185.4. IR (Neat) ν 3303, 2915, 2010, 1666, 1439, 1370, 1229, 1187, 1144, 1048, 854, 805, 685 cm^{-1}. MS(%) (EI) *m/z* 283 (M^+, 5), 216 (27), 150 (19), 121 (100), 105 (25), 91 (35), 77 (24), 69 (22), 41 (18). HRMS (ESI) calcd. for $C_{11}H_{16}F_3NO_2S$: 283.0854, Found: 283.0850.





N-((3-(cycloheptylidenemethylene)-2,2-dimethylcyclopropyl)methyl)-1,1,1-trifluoromethane-sulfonamide **1l**: Yield: 792 mg, 19%; A yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.56-1.63 (m, 8H, $4CH_2$), 1.78 (t, J = 8.0 Hz, 1H, CH), 2.27-2.33 (m, 4H, $2CH_2$), 3.43-3.48 (m, 2H, CH_2), 4.85 (br, 1H, NH). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -77.35. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 19.2, 24.9, 25.9, 28.3, 28.5, 29.5, 29.6, 29.7, 33.0, 33.5, 44.6, 88.2, 109.1, 119.7 (q, J = 319.5), 185.2. IR (Neat) ν 3304, 2926, 2854, 2005, 1710, 1441, 1374, 1260, 1191, 1147, 1053, 803 cm^{-1}. MS (%) (EI) *m/z* 337 (M^+, 10%), 231 (45), 216 (30), 204 (74), 191 (40), 175 (61), 162 (58), 149 (85), 105 (100), 91 (81), 69 (69), 55 (44). HRMS (EI) calcd. for $C_{15}H_{22}F_3NO_2S$: 337.1323, Found: 337.1321.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1.763
1.633
1.592
1.562
1.262
1.246
0.070
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1.85
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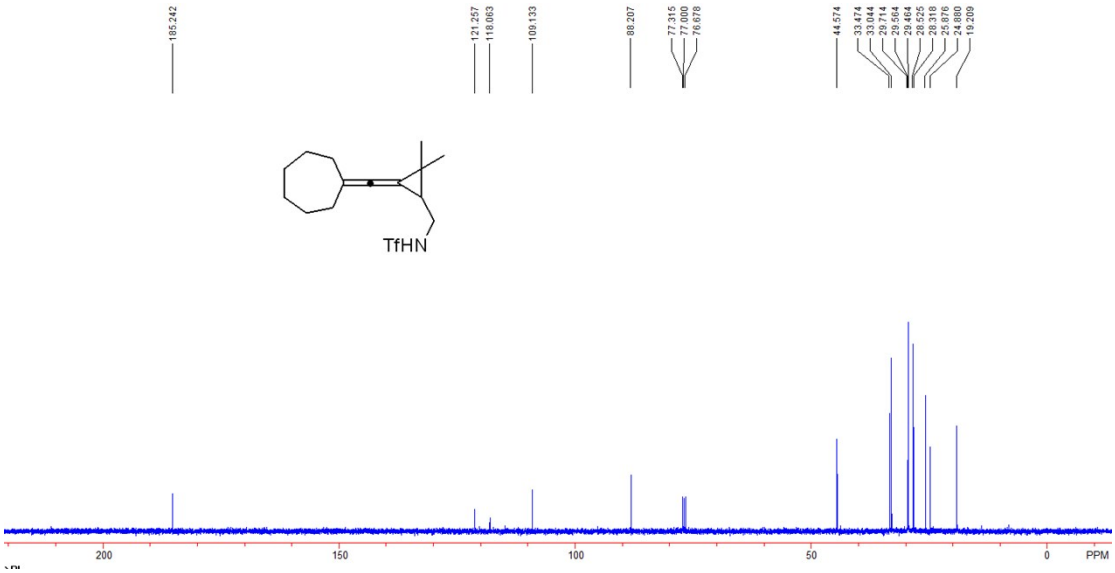
1.05
8.03
4.00
10
8
6
4
2
0
PPM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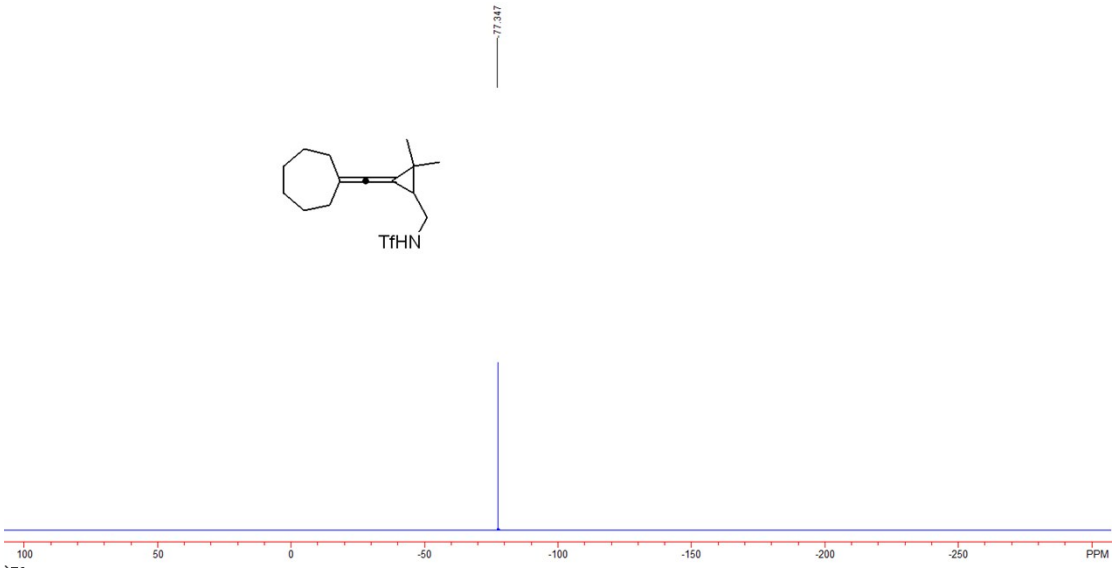
PPM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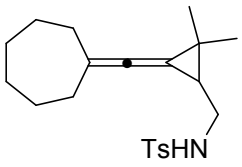
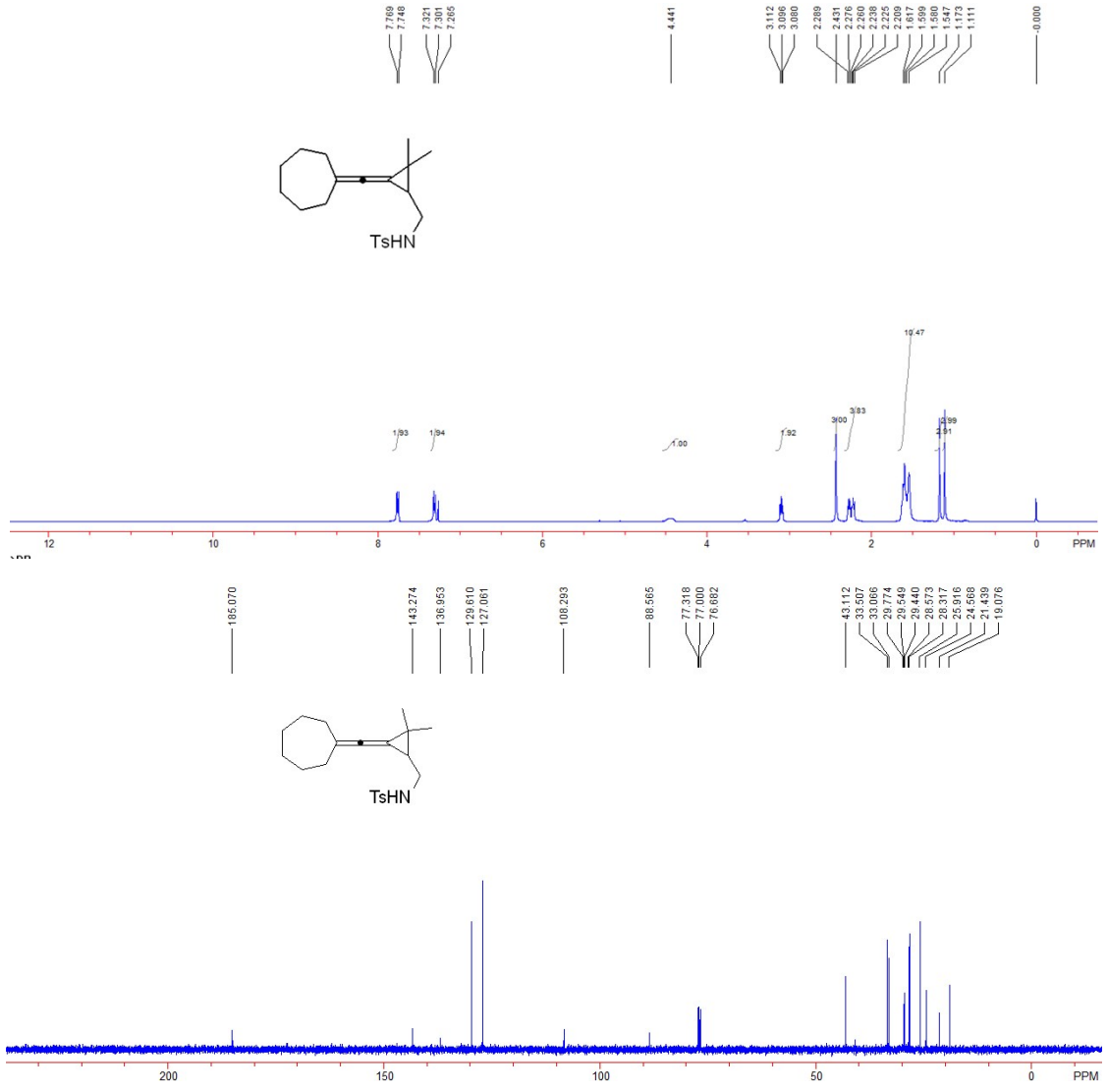
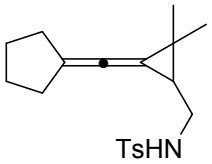
PPM

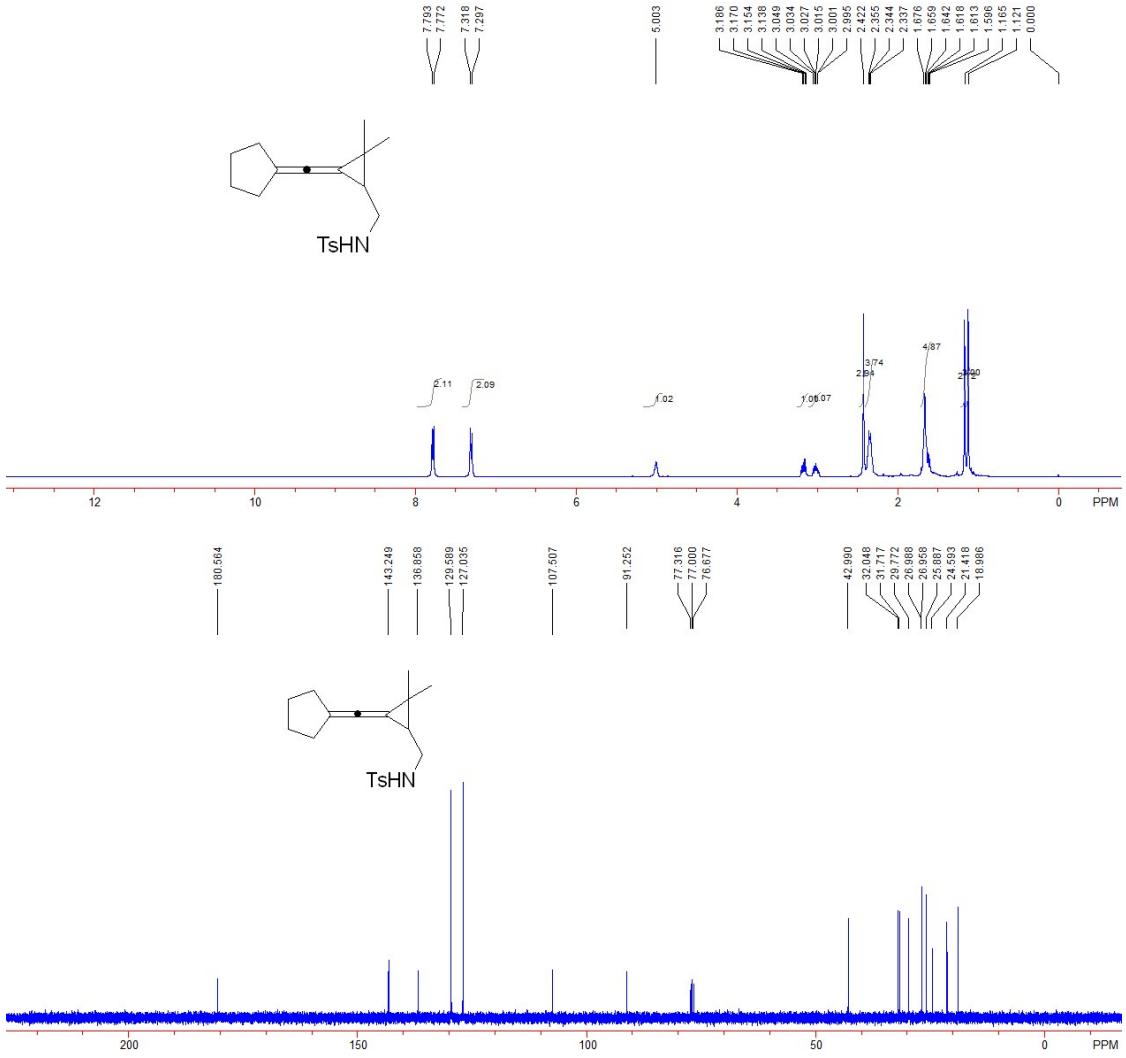


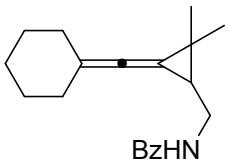
N-((3-(cycloheptylidenemethylene)-2,2-dimethylcyclopropyl)methyl)-4-methylbenzene-sulfonamide **1m**: Yield: 1.80 g, 25%; A white solid, Mp: 125-127 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.09 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.52-1.59 (m, 9H, CH, 4CH_2), 2.19-2.27 (m, 4H, 2CH_2), 2.41 (s, 3H, CH_3), 3.07 (t, *J* = 6.4 Hz, 2H, CH_2), 4.22 (br, 1H, NH), 7.29 (d, *J* = 8.0 Hz, 2H, Ar), 7.74 (d, *J* = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1, 21.5, 24.6, 26.0, 28.4, 28.6, 29.5, 29.6, 29.8, 33.1, 33.6, 41.0, 88.6, 108.3, 127.1, 129.7, 137.0, 143.3, 185.1. IR (Neat) ν 3278, 2921, 2850, 1998, 1598, 1496, 1441, 1323, 1157, 1121, 1094, 1085, 1018, 834, 813, 706 cm^{-1}. MS (ESI) *m/z* 360 $(M+H)^+$. HRMS (ESI) calcd. for $C_{21}H_{30}NO_2S$: 360.1992, Found: 360.1992.



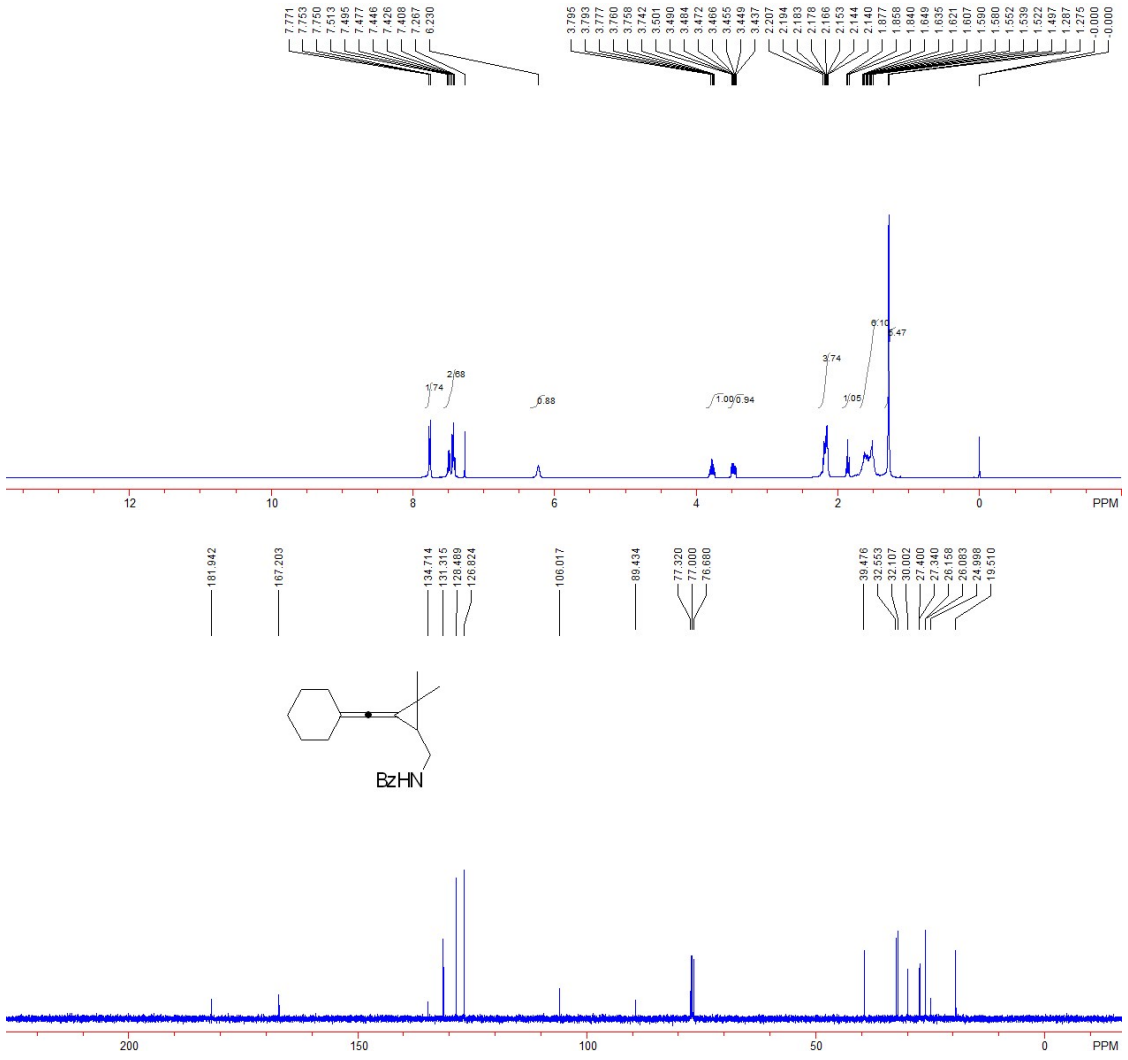


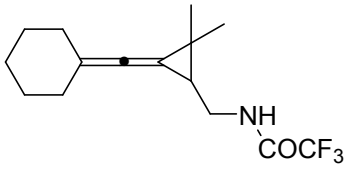
N-((3-(cyclopentylidenemethylene)-2,2-dimethylcyclopropyl)methyl)-4-methylbenzene-sulfonamide **1n**: Yield: 660 mg, 10%; A white solid, Mp: 140-142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.08 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.56-1.64 (m, 5H, CH, $2CH_2$), 2.30-2.32 (m, 4H, $2CH_2$), 2.38 (s, 3H, CH_3), 2.94-3.16 (m, 2H, CH_2), 4.97 (br, 1H, NH), 7.27 (d, J = 8.0 Hz, 2H, Ar), 7.74 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 21.4, 24.6, 25.9, 26.96, 26.99, 29.8, 31.7, 32.0, 43.0, 91.3, 107.5, 127.0, 129.6, 136.9, 143.2, 180.6. IR (Neat) ν 3277, 2951, 2864, 2006, 1597, 1434, 1324, 1288, 1156, 1121, 1093, 1059, 1036, 813, 706, 660 cm^{-1}. MS (ESI) *m/z* 332 $(M+H)^+$. HRMS (ESI) calcd. for $C_{19}H_{26}NO_2S$: 332.1679, Found: 332.1679.



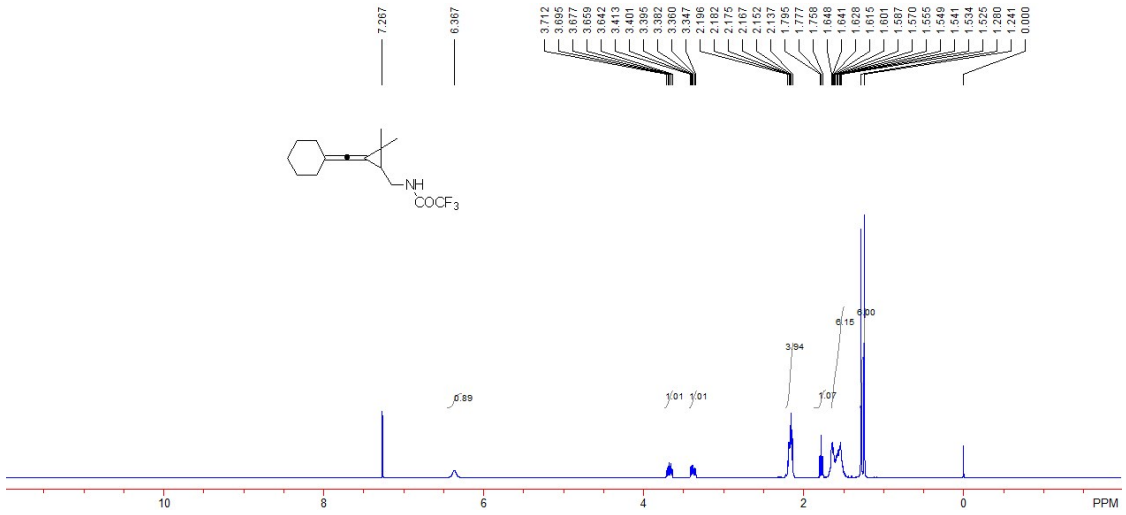


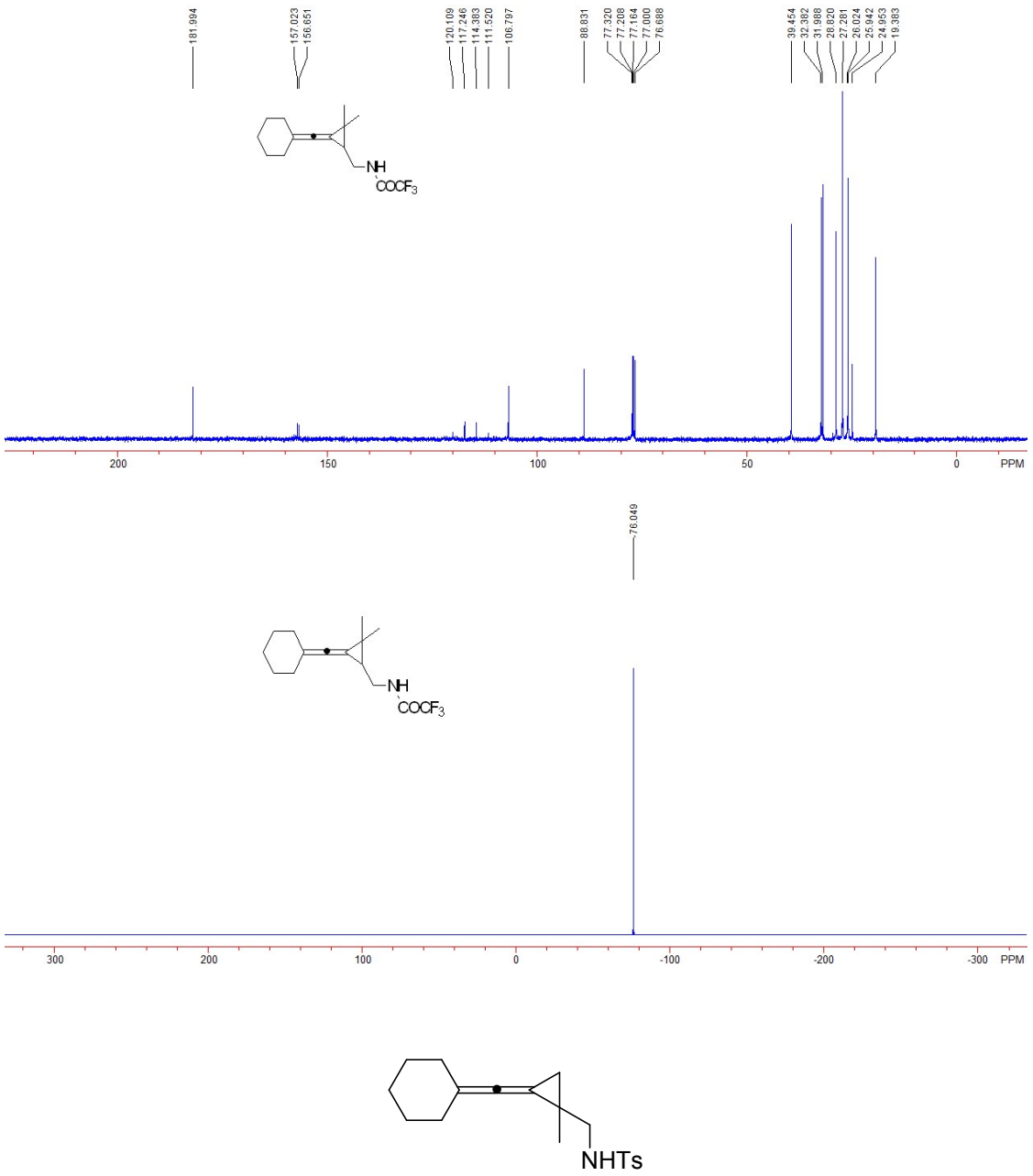
N-((3-(cyclohexylidenemethylene)-2,2-dimethylcyclopropyl)methyl)benzamide **1o**: Yield: 1.80 g, 25%; A white solid, Mp: 107-109 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.48-1.65 (m, 6H, $3CH_2$), 1.86 (t, *J* = 8.0 Hz, 1H, CH), 2.14-2.21 (m, 4H, $2CH_2$), 3.44-3.50 (m, 1H, CH_2), 3.74-3.81 (m, 1H, CH_2), 6.23 (br, 1H, NH), 7.40-7.51 (m, 3H, Ar), 7.76 (d, *J* = 7.2 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.5, 25.0, 26.1, 26.2, 27.3, 27.4, 30.0, 32.1, 32.6, 39.5, 89.4, 106.0, 126.8, 128.5, 131.3, 134.7, 167.2, 181.9. IR (Neat) ν 3311, 3065, 2923, 2853, 2832, 2006, 1636, 1603, 1578, 1488, 1446, 1369, 1315, 1290, 1263, 1242, 1120, 1072, 984, 964, 929, 891, 852, 799, 693 cm^{-1}. MS (ESI) *m/z* 296 $(M+H)^{+}$. HRMS (ESI) calcd. for $C_{20}H_{26}NO$: 296.2009, Found: 296.2008.



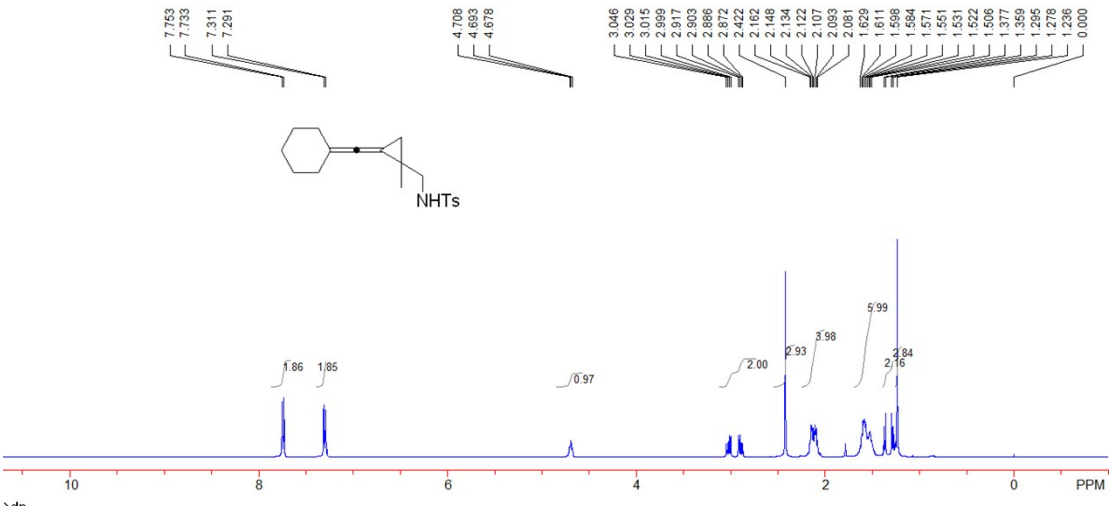


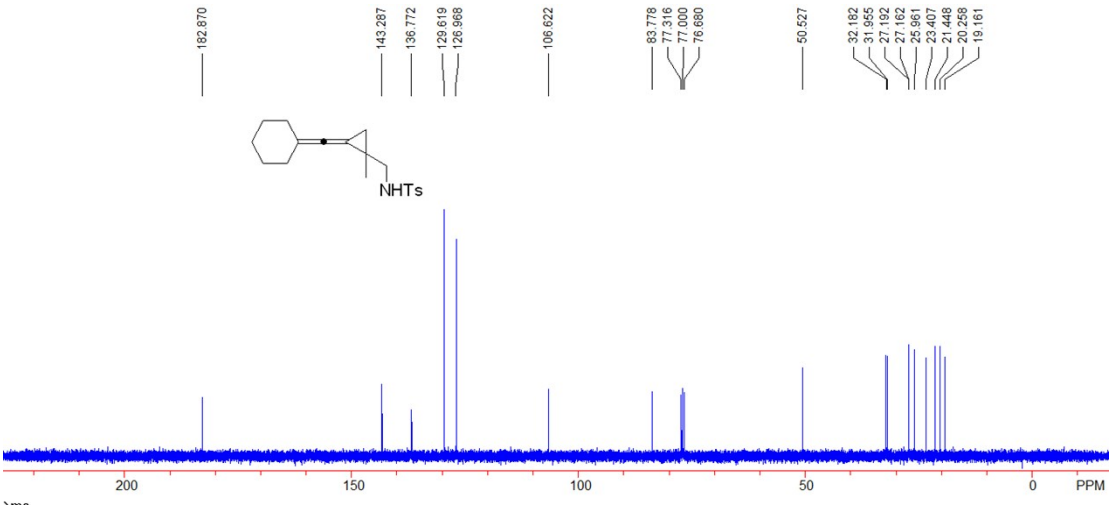
N-((3-(cyclohexylidenemethylene)-2,2-dimethylcyclopropyl)methyl)-2,2,2-trifluoroacetamide **1p**: Yield: 817 mg, 13%; A yellow solid, Mp: 98-100 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.53-1.65 (m, 6H, $3CH_2$), 1.78 (t, J = 7.6 Hz, 1H, CH), 2.14-2.20 (m, 4H, $2CH_2$), 3.35-3.41 (m, 1H, CH_2), 3.64-3.71 (m, 1H, CH_2), 6.37 (br, 1H, NH). ^{19}F NMR (376 MHz, $CDCl_3$): δ -76.05. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.4, 25.0, 25.9, 26.0, 27.3, 28.8, 32.0, 32.4, 39.5, 88.8, 106.8, 115.8 (q, J = 286.3 Hz), 156.8 (q, J = 37.2 Hz), 182.0. IR (Neat) ν 3305, 2925, 2854, 2007, 1707, 1552, 1447, 1370, 1345, 1204, 1178, 1158, 1122, 987, 849, 726 cm^{-1}. MS (%) (EI) *m/z* 287 (M^+, 12), 272 (9), 174 (14), 161 (45), 131 (33), 119 (36), 105 (48), 91 (100), 77 (47), 67 (29), 55 (23), 41 (39). HRMS (EI) calcd. for $C_{15}H_{20}NOF_3$: 287.1497, Found: 287.1500.

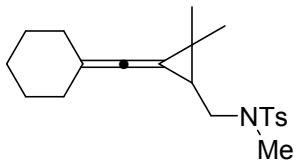




N-((2-(cyclohexylidenemethylene)-1-methylcyclopropyl)methyl)-4-methylbenzenesulfonamide **1r**: Yield: 210 mg, 4%; A white solid, Mp: 122-124 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.24 (s, 3H, CH_3), 1.29 (d, J = 6.8 Hz, 1H, CH), 1.37 (d, J = 6.8 Hz, 1H, CH), 1.51-1.63 (m, 6H, $3CH_2$), 2.08-2.16 (m, 4H, $2CH_2$), 2.42 (s, 3H, CH_3), 2.90 (dd, J_1 = 5.6 Hz, J_2 = 12.4 Hz, 1H, CH_2), 3.02 (dd, J_1 = 5.6 Hz, J_2 = 12.4 Hz, 1H, CH_2), 4.69 (t, J = 5.6 Hz, 1H, NH), 7.30 (d, J = 8.0 Hz, 2H, Ar), 7.74 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.2, 20.3, 21.4, 23.4, 26.0, 27.16, 27.19, 32.0, 32.2, 50.5, 83.8, 106.6, 127.0, 129.6, 136.8, 143.3, 182.9. IR (CH_2Cl_2) ν 3282, 2924, 2852, 2009, 2018, 1598, 1495, 1446, 1327, 1159, 1123, 1093, 1062, 842, 813 cm^{-1}. MS (ESI) *m/z* 349 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{19}H_{29}N_2O_2S$: 349.1944, Found: 349.1947.

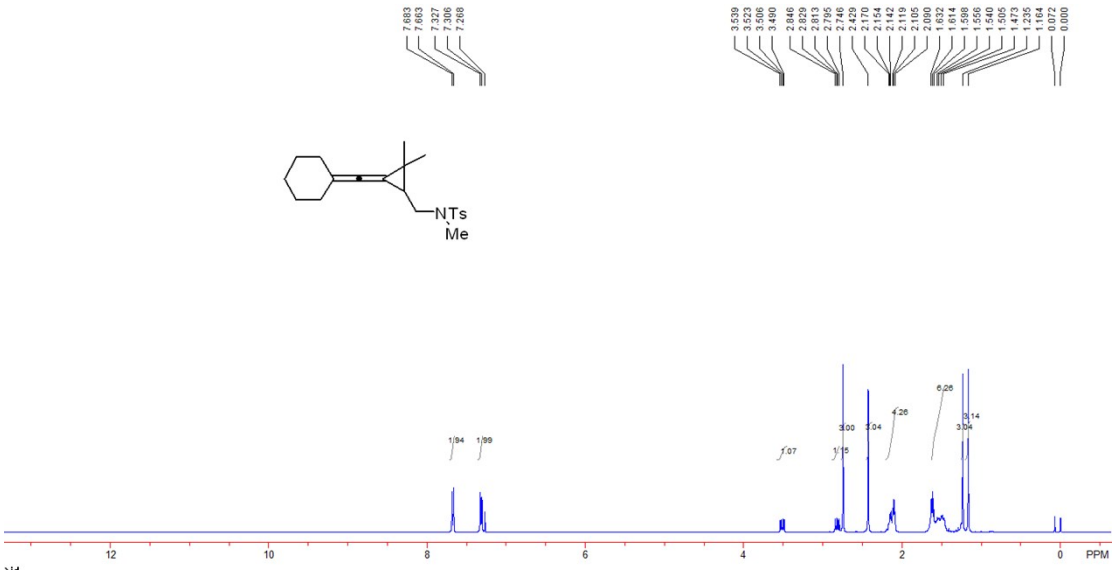


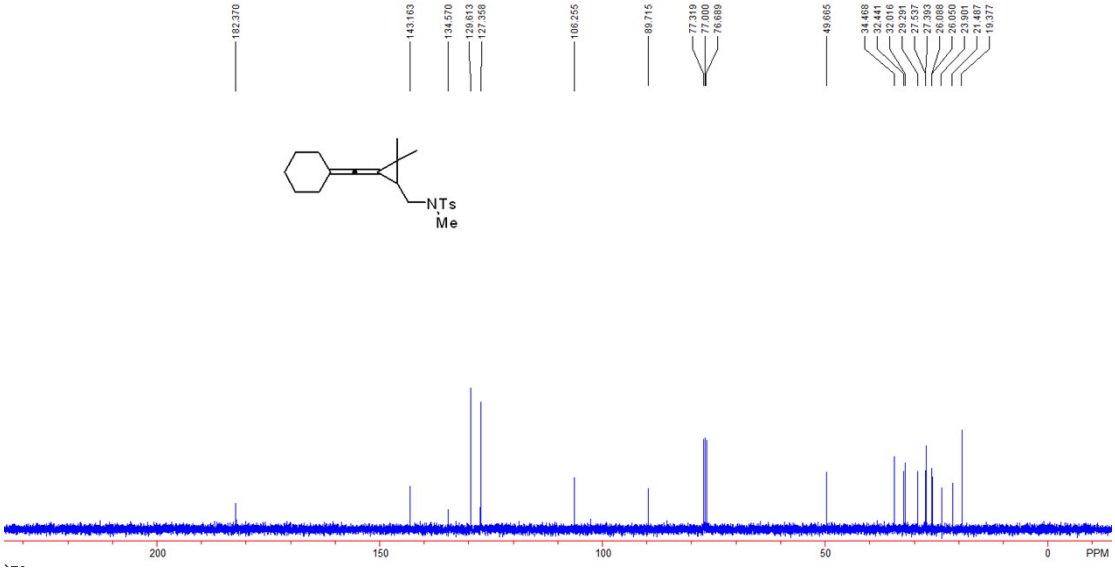


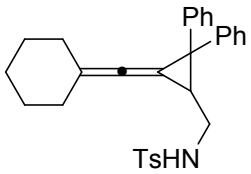


N-((3-(cyclohexylidenemethylene)-2,2-dimethylcyclopropyl)methyl)-N,4dimethylbenzene-sulfonamide **4a**: Yield: 80 mg, 56 %; A white solid, Mp: 129-131 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.16 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.47-1.63 (m, 7H, CH, $3CH_2$), 2.09-2.17 (m, 4H, $2CH_2$), 2.43 (s, 3H, CH_3), 2.75 (s, 3H, CH_3), 2.82 (dd, J_1 = 6.8 Hz, J_2 = 13.2 Hz, 1H, CH_2), 3.51 (dd, J_1 = 6.8 Hz, J_2 = 13.2 Hz, 1H, CH_2), 7.32 (d, J = 8.0 Hz, 2H, Ar), 7.67 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.4, 21.5, 23.9, 26.05, 26.09, 27.4, 27.5, 29.3, 32.0, 32.4, 34.5 49.7, 89.7, 106.3, 127.4, 129.6, 134.6, 143.2, 182.4. IR (CH_2Cl_2) ν 2922, 2852, 2007, 1597, 1447, 1341, 1304, 1191, 1161, 1119, 1088, 1018, 985, 939, 894, 814, 801, 744, 713, 701 cm^{-1}. MS (ESI) *m/z* 360 $(M+H)^+$. HRMS (ESI) calcd. for $C_{21}H_{30}NO_2S$: 360.1992, Found:

360.1997.

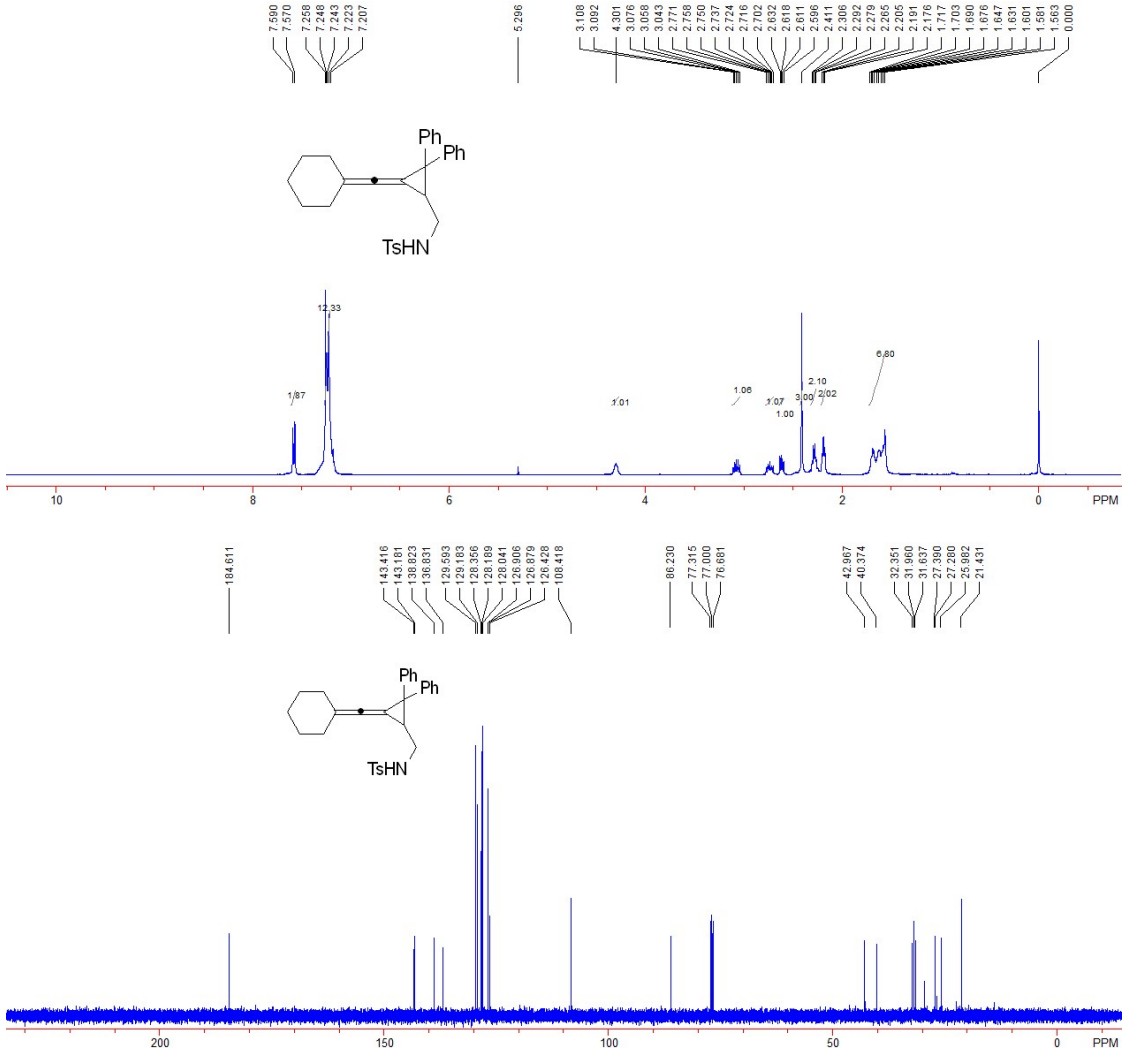


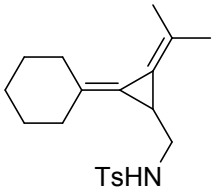




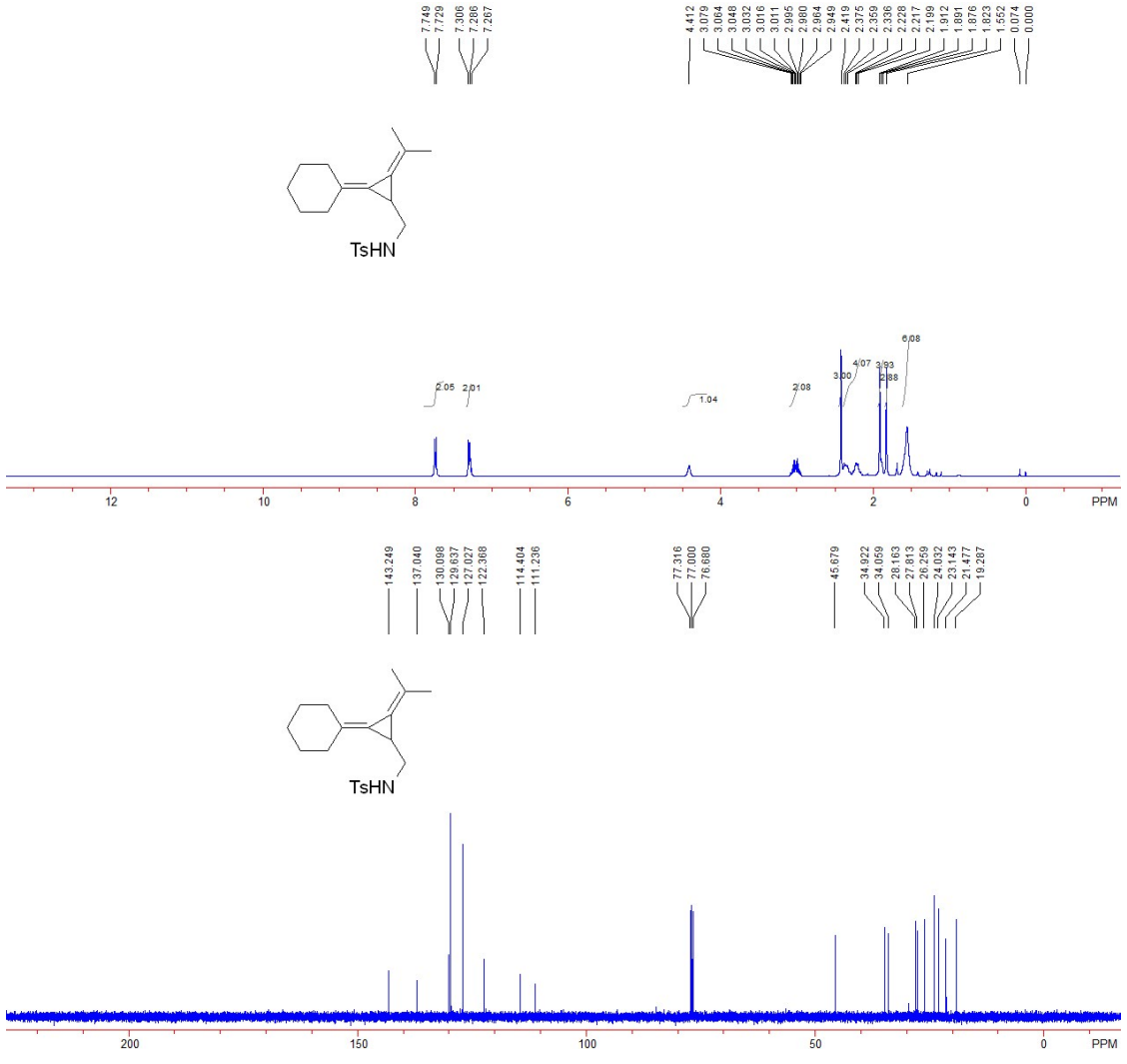
N-((3-(cyclohexylidenemethylene)-2,2-diphenylcyclopropyl)methyl)-4-methylbenzenesulfonamide **1q**: Yield: 222 mg, 49%; A white solid, Mp: 176-178 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.56-1.70 (m, 6H, $3CH_2$), 2.18-2.31 (m, 4H, $2CH_2$), 2.41 (s, 3H, CH_3), 2.60-2.63 (m, 1H, CH), 2.70-2.77 (m, 1H, CH_2), 3.04-3.11 (m, 1H, CH_2), 4.30 (br, 1H, NH), 7.18-7.26 (m, 12H, Ar), 7.58 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.4, 26.0, 27.3, 27.4, 31.6, 32.0, 32.4, 40.4, 43.0, 86.2, 108.4, 126.4, 126.88, 126.91, 128.0,

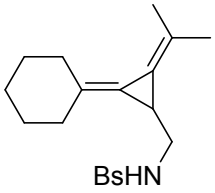
128.2, 128.4, 129.2, 129.6, 136.8, 138.8, 143.2, 143.4, 184.6. IR (CH_2Cl_2) ν 3283, 3056, 3024, 2928, 2853, 2011, 1598, 1492, 1445, 1409, 1328, 1161, 1093, 813 cm^{-1}. MS (ESI) *m/z* 470 $(M+H)^+$. HRMS (ESI) calcd. for $C_{30}H_{32}NO_2S$: 470.2148, Found: 470.2154.



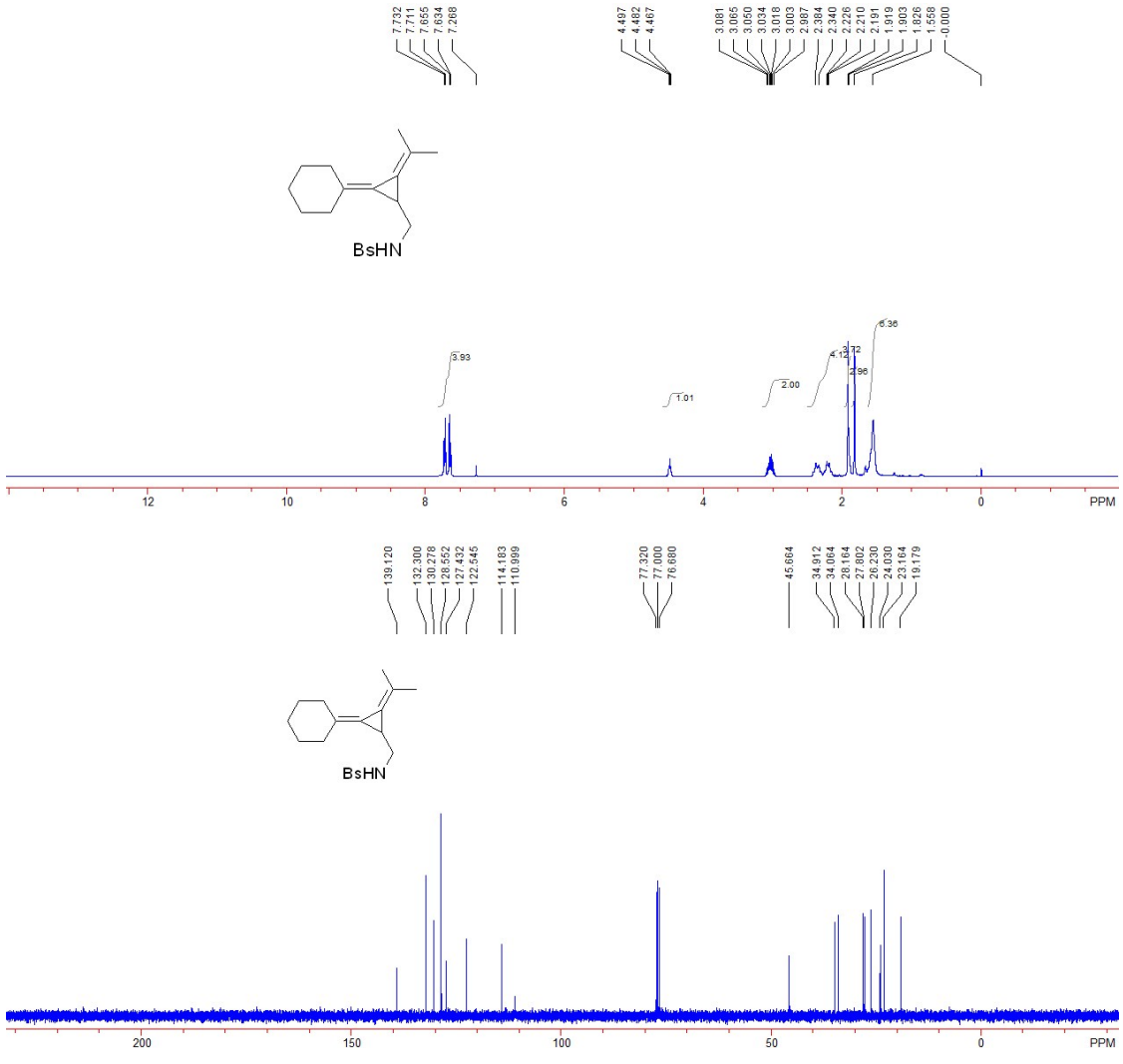


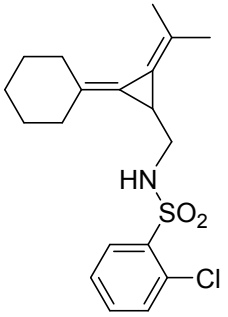
N-((2-cyclohexylidene-3-(propan-2-ylidene)cyclopropyl)methyl)-4-methylbenzenesulfona-mide **2a**: Yield: 40 mg, 76%; A white solid, Mp: 98-100 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.55 (br, 6H, $3CH_2$), 1.82 (s, 3H, CH_3), 1.89 (t, J = 6.0 Hz, 1H, CH), 1.91 (s, 3H, CH_3), 2.20-2.38 (m, 4H, $2CH_2$), 2.42 (s, 3H, CH_3), 2.97-3.08 (m, 2H, CH_2), 4.41 (br, 1H, NH), 7.30 (d, J = 8.0 Hz, 2H, Ar), 7.74 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.3, 21.5, 23.1, 24.0, 26.3, 27.8, 28.2, 34.1, 34.9, 45.7, 111.2, 114.4, 122.4, 127.0, 129.6, 130.1, 137.0, 143.3. IR (CH_2Cl_2) ν 3284, 2925, 2852, 1598, 1446, 1326, 1158, 1093, 1061, 835, 813, 706, 664 cm^{-1}. MS (ESI) *m/z* 346 $(M+H)^+$. HRMS (ESI) calcd. for $C_{20}H_{28}NO_2S$: 346.1835, Found: 346.1832.



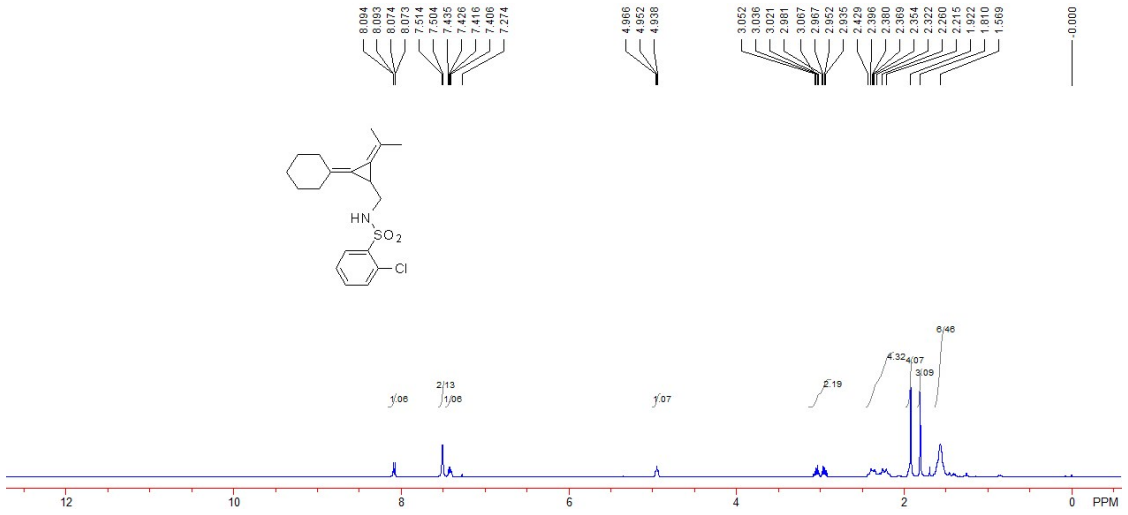


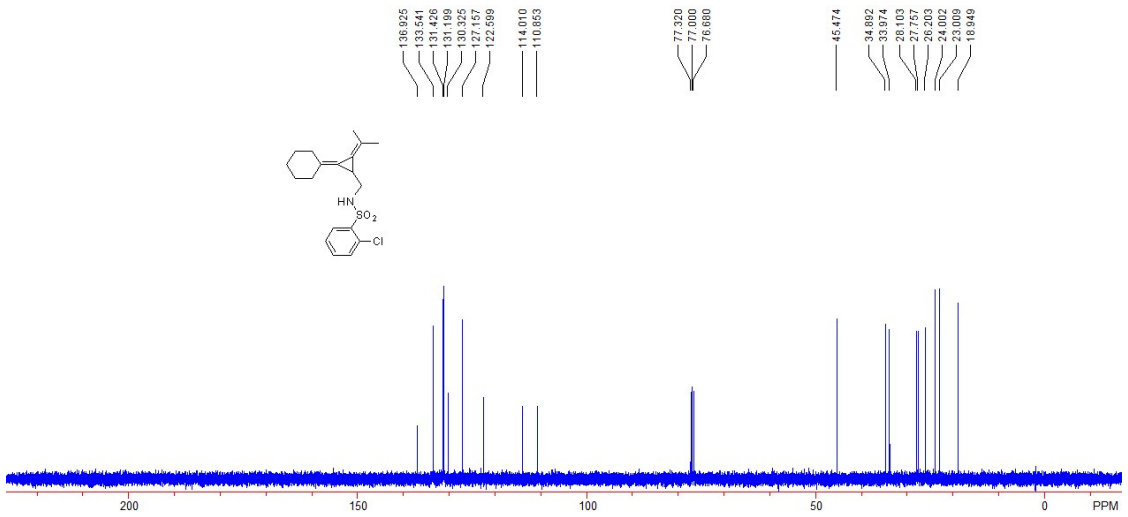
4-bromo-N-((2-cyclohexylidene-3-(propan-2-ylidene)cyclopropyl)methyl)benzenesulfon-amide **2b**: Yield: 69 mg, 84%; A white solid, Mp: 139-140 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.40-1.60 (m, 6H, $3CH_2$), 1.83 (s, 3H, CH_3), 1.90 (t, *J* = 6.4 Hz, 1H, CH), 1.92 (s, 3H, CH_3), 2.19-2.38 (m, 4H, $2CH_2$), 2.99-3.08 (m, 2H, CH_2), 4.48 (t, *J* = 6.0 Hz, 1H, NH), 7.64 (d, *J* = 8.0 Hz, 2H, Ar), 7.72 (d, *J* = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.2, 23.2, 24.0, 26.2, 27.8, 28.2, 34.0, 34.9, 45.7, 111.0, 114.2, 122.5, 127.4, 128.6, 130.3, 132.3, 139.1. IR (CH_2Cl_2) ν 3279, 2926, 2852, 1721, 1575, 1471, 1388, 1330, 1262, 1161, 1091, 1067, 1009, 819, 736, 703 cm^{-1}. MS (ESI) *m/z* 427 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{19}H_{28}BrN_2O_2S$: 427.1049, Found: 427.1042.

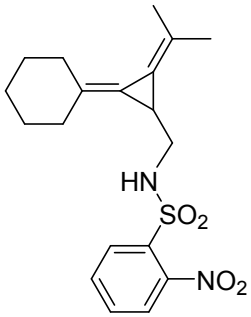




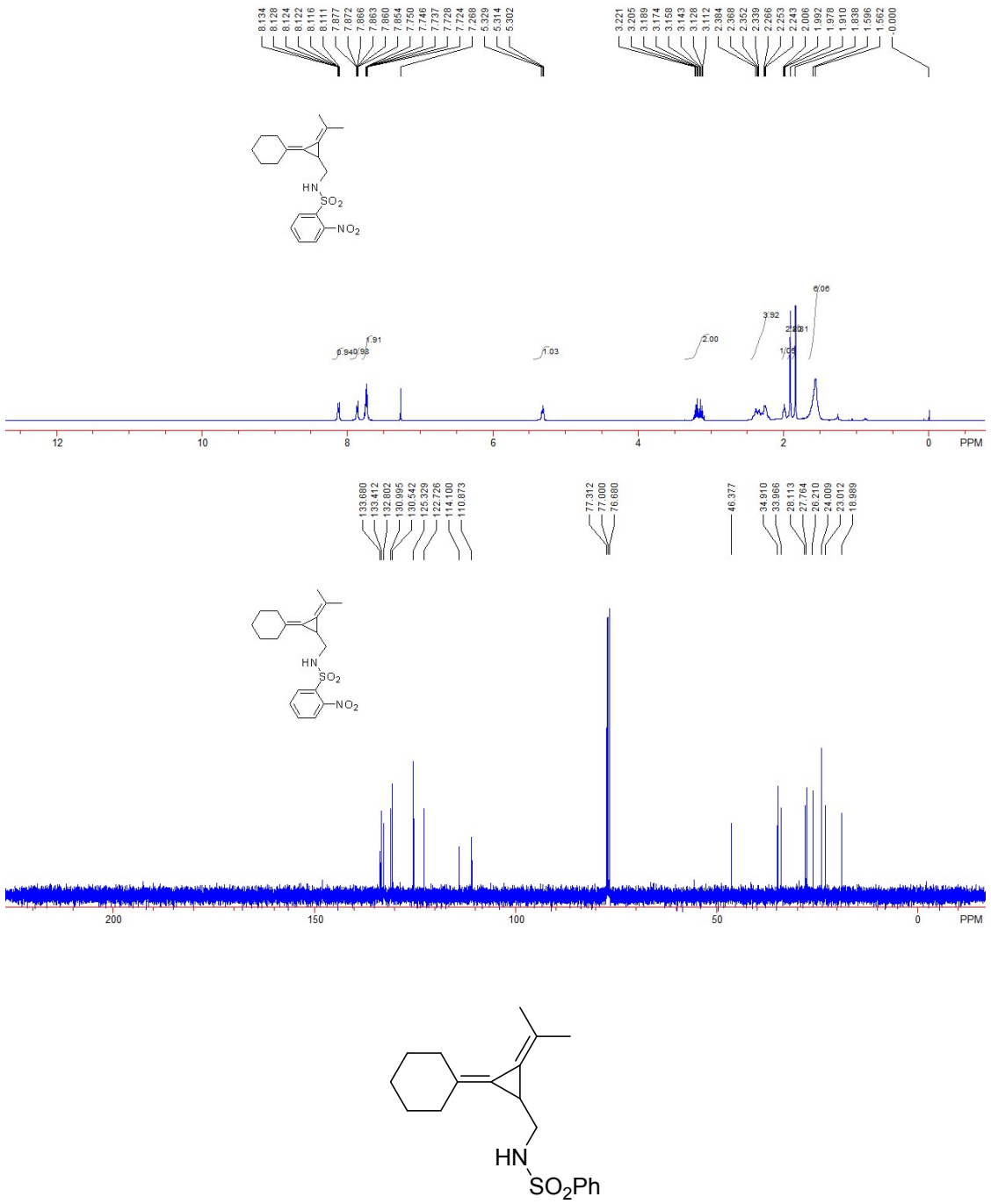
2-chloro-N-((2-cyclohexylidene-3-(propan-2-ylidene)cyclopropyl)methyl)benzenesulfonamide **2c**: Yield: 59 mg, 78%; A white solid, Mp: 176-178 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.57 (br, 6H, $3CH_2$), 1.81 (s, 3H, CH_3), 1.92 (br, 4H, CH, CH_3), 2.18-2.43 (m, 4H, $2CH_2$), 2.92-3.08 (m, 2H, CH_2), 4.95 (br, 1H, NH), 7.40-7.45 (m, 1H, Ar), 7.50-7.51 (m, 2H, Ar), 8.07-8.09 (m, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.9, 23.0, 24.0, 26.2, 27.7, 28.1, 33.9, 34.8, 45.4, 110.8, 114.0, 122.5, 127.1, 130.3, 131.2, 131.4, 133.5, 136.9. IR (Neat) ν 3308, 2927, 2853, 1728, 1653, 1577, 1453, 1435, 1404, 1335, 1258, 1161, 1130, 1111, 1042, 959, 804, 759, 749, 666 cm^{-1}. MS (ESI) *m/z* 383.2 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{19}H_{28}ClN_2O_2S$: 383.1555, Found: 383.1556.



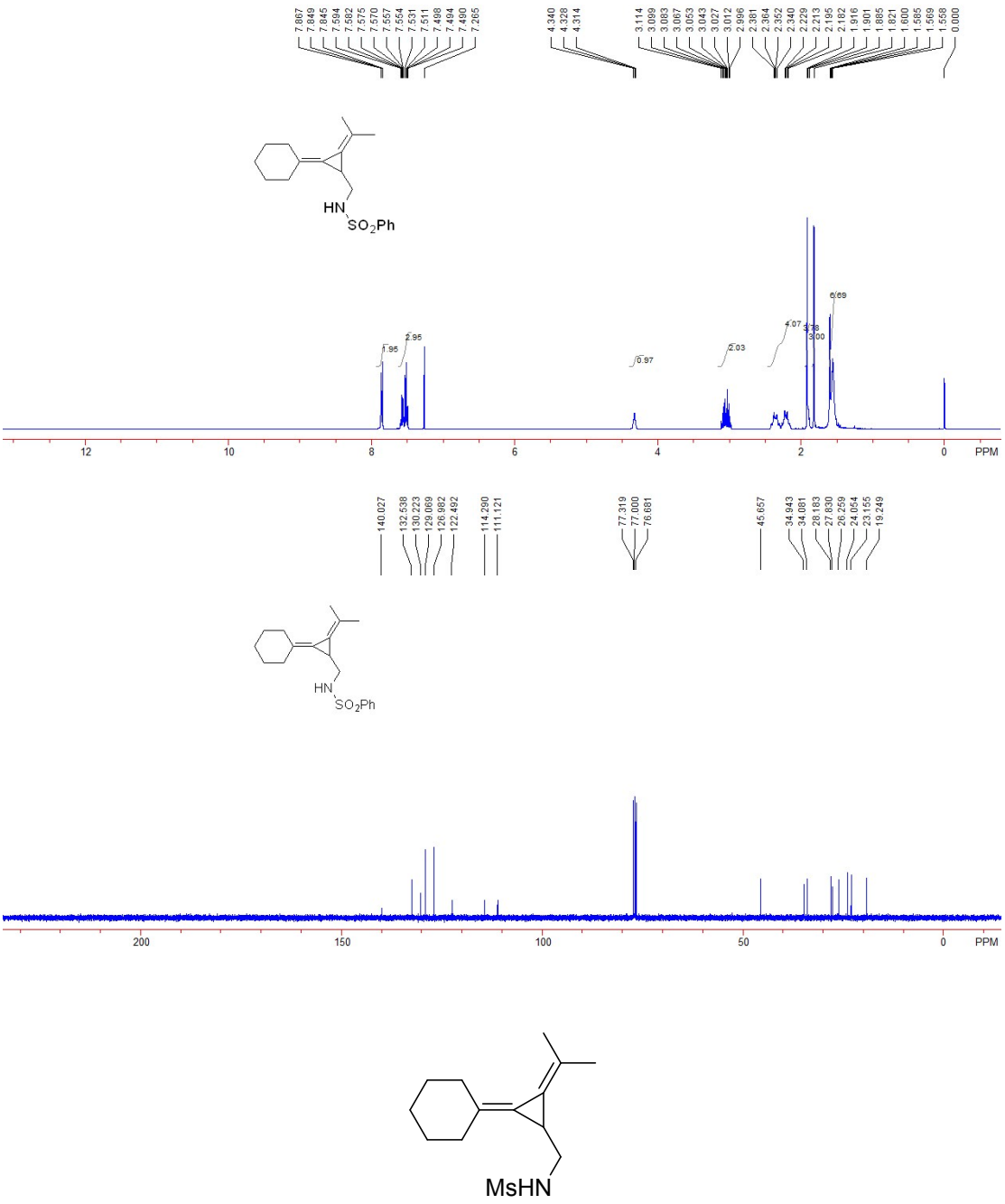




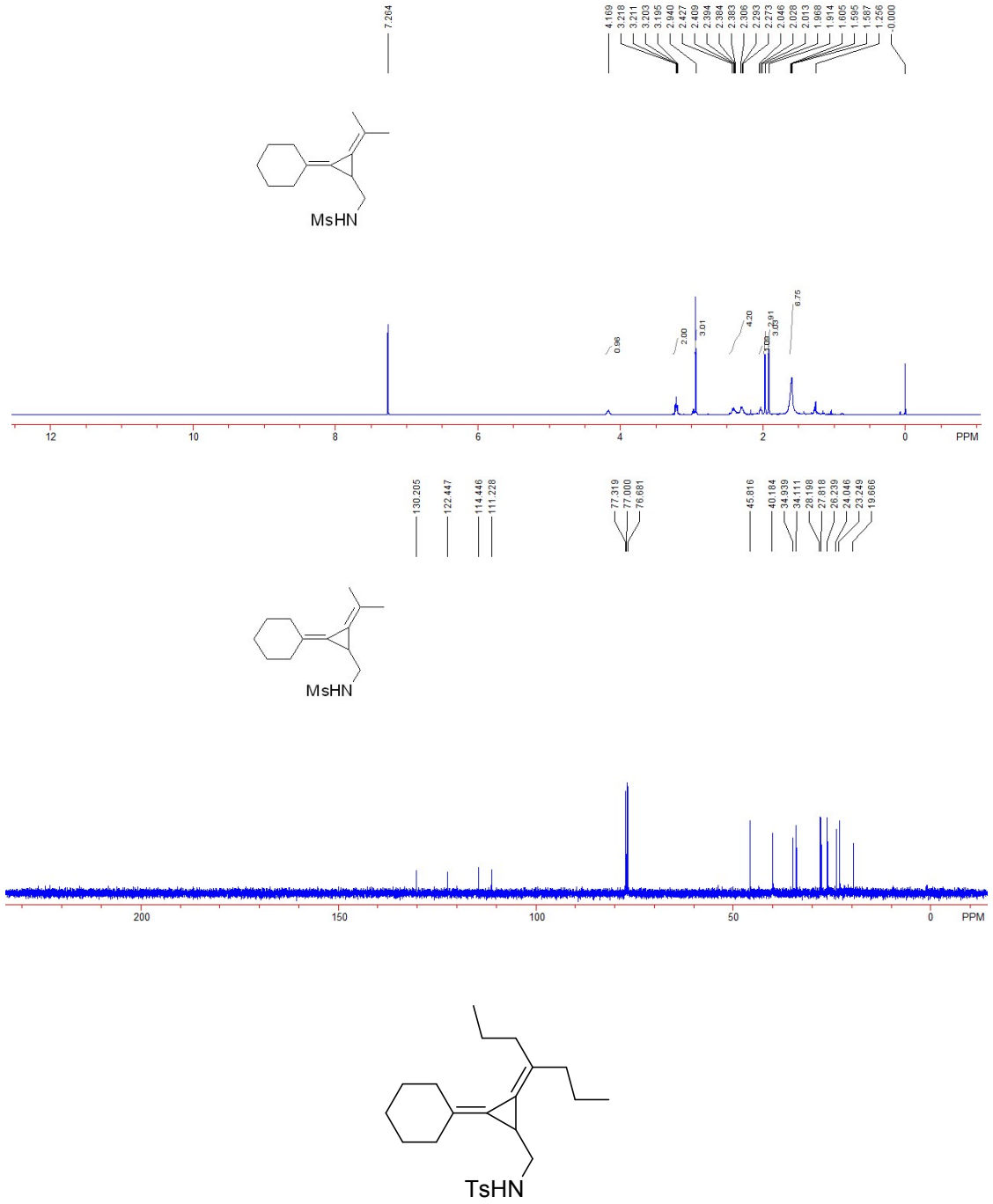
N-((2-cyclohexylidene-3-(propan-2-ylidene)cyclopropyl)methyl)-2-nitrobenzenesulfonamide **2d**: Yield: 69 mg, 86%; A yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.56-1.66 (m, 6H, $3CH_2$), 1.84 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.99 (t, *J* = 5.6 Hz, 1H, CH), 2.24-2.38 (m, 4H, $2CH_2$), 3.11-3.22 (m, 2H, CH_2), 5.31 (t, *J* = 5.6 Hz, 1H, NH), 7.72-7.76 (m, 2H, Ar), 7.85-7.88 (m, 1H, Ar), 8.11-8.13 (m, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 23.0, 24.0, 26.2, 27.8, 28.1, 34.0, 34.9, 46.4, 110.9, 114.1, 122.7, 125.3, 130.5, 131.0, 132.8, 133.4, 133.7. IR (Neat) ν 3344, 2926, 2853, 1731, 1652, 1593, 1539, 1441, 1407, 1346, 1264, 1166, 1124, 1060, 1022, 852, 782, 731, 702 cm^{-1}. MS (ESI) *m/z* 394.2 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{19}H_{28}N_3O_4S$: 394.1795, Found: 394.1793.



N-((2-cyclohexylidene-3-(propan-2-ylidene)cyclopropyl)methyl)benzenesulfonamide **2e**: Yield: 44 mg, 67%; A white solid, Mp: 109-111 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.56-1.60 (m, 6H, $3CH_2$), 1.82 (s, 3H, CH_3), 1.90 (t, J = 6.4 Hz, 1H, CH), 1.92 (s, 3H, CH_3), 2.16-2.39 (m, 4H, $2CH_2$), 2.98-3.11 (m, 2H, CH_2), 4.33 (br, 1H, NH), 7.49-7.59 (m, 3H, Ar), 7.86 (d, J = 7.2 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 19.2, 23.1, 24.0, 26.2, 27.8, 28.2, 34.0, 34.9, 45.6, 111.1, 114.3, 122.5, 126.9, 129.0, 130.2, 132.5, 140.0. IR (CH_2Cl_2) ν 3285, 2925, 2851, 1792, 1652, 1446, 1324, 1157, 1093, 1061, 1023, 851, 832, 753, 719, 688 cm^{-1}. MS (ESI) *m/z* 332 $(M+H)^+$. HRMS (ESI) calcd. for $C_{19}H_{26}NO_2S$: 332.1679, Found: 332.1683.



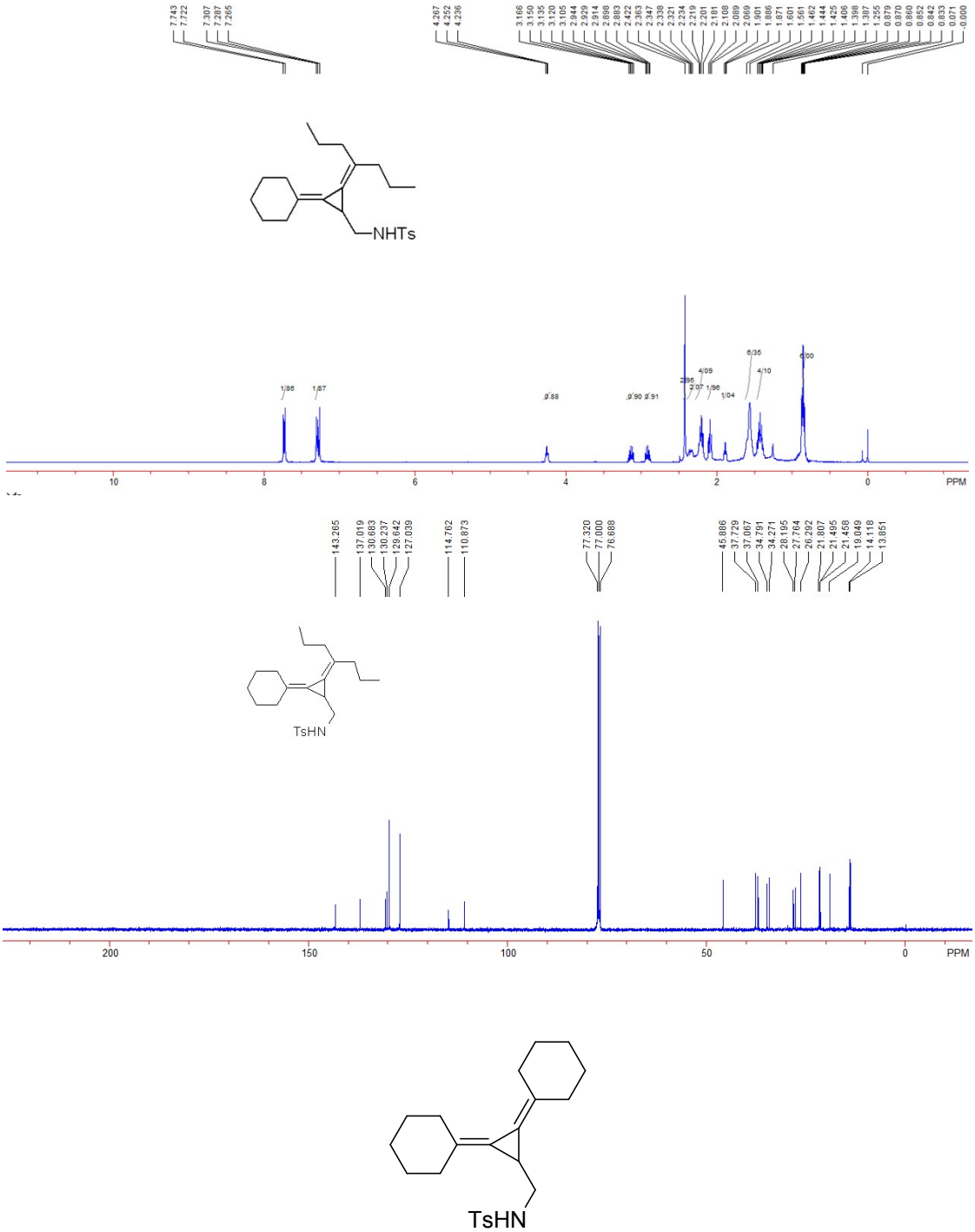
N-((2-cyclohexylidene-3-(propan-2-ylidene)cyclopropyl)methyl)methanesulfonamide **2f**: Yield: 30 mg, 56%; A white solid, Mp: 105-107 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.26 (br, 6H, $3CH_2$), 1.91 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.03 (t, J = 6.4 Hz, 1H, CH), 2.27-2.43 (m, 4H, $2CH_2$), 2.92 (s, 3H, CH_3), 3.20-3.23 (m, 2H, CH_2), 4.17 (br, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.7, 23.2, 24.0, 26.2, 27.8, 28.2, 34.1, 35.0, 40.2, 45.8, 111.2, 114.4, 122.4, 130.2. IR (CH_2Cl_2) ν 3309, 2926, 2852, 1734, 1652, 1571, 1452, 1453, 1334, 1253, 1161, 1130, 1110, 1061, 1041, 851, 748, 730 cm^{-1}. MS (ESI) *m/z* 287 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{14}H_{27}N_2O_2S$: 287.1788, Found: 287.1788.



N-((2-cyclohexylidene-3-(heptan-4-ylidene)cyclopropyl)methyl)-4-methylbenzenesulfonamide

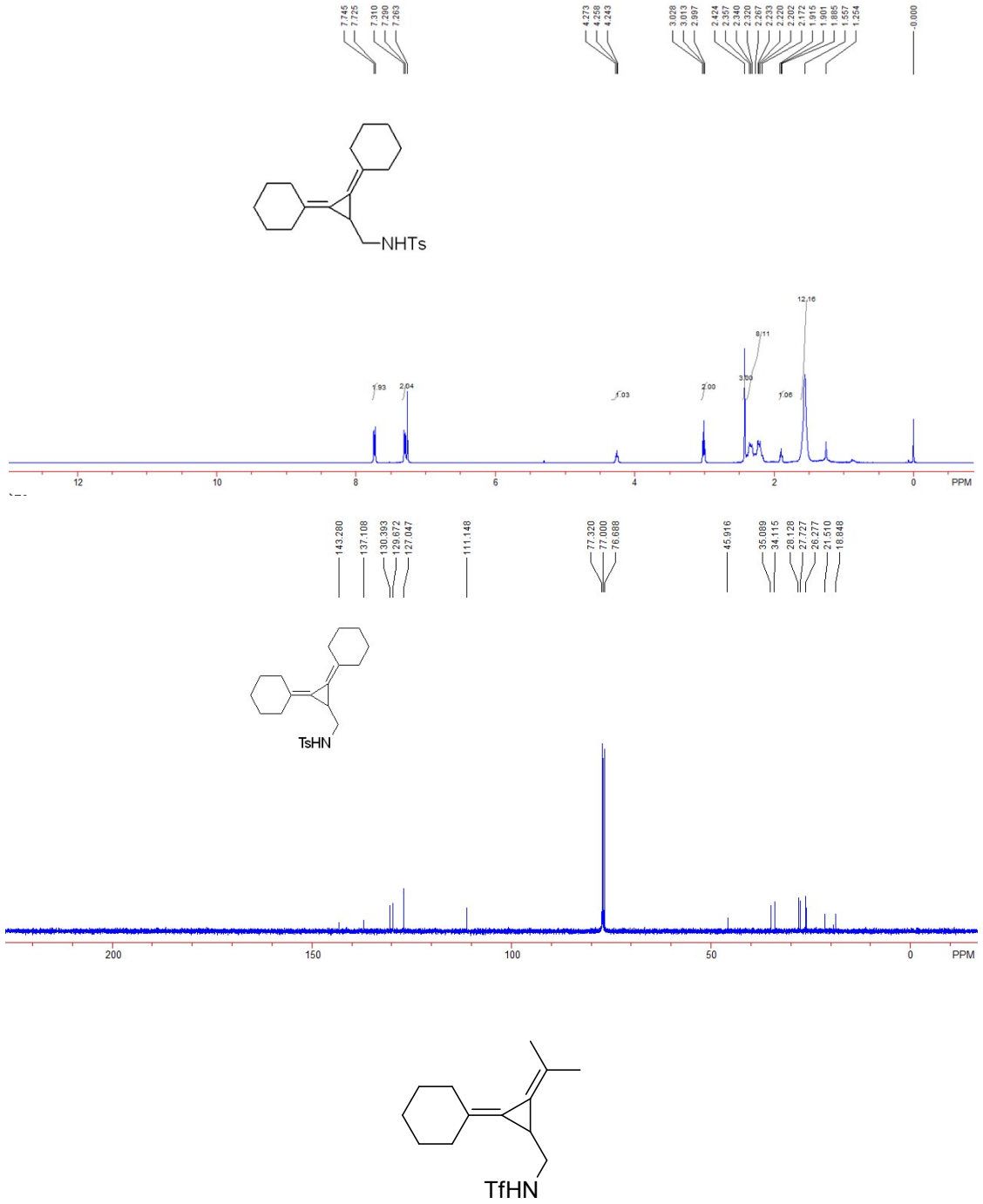
2g: Yield: 62 mg, 80%; A yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.83-0.87 (m, 6H, $3CH_2$), 1.39-1.46 (m, 4H, $2CH_2$), 1.56-1.60 (m, 6H, $3CH_2$), 1.89 (t, J = 6.0 Hz, 1H, CH), 2.09 (t, J = 8.0 Hz, 2H, CH_2), 2.18-2.23 (m, 4H, $2CH_2$), 2.32-2.36 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.88-2.94 (m, 1H, CH), 3.11-3.17 (m, 1H, CH), 4.25 (t, J = 6.0 Hz, 1H, NH), 7.30 (d, J = 8.0 Hz, 2H, Ar), 7.73 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.9, 14.1, 19.0, 21.46, 21.50, 21.8, 26.3, 27.8, 28.2, 34.3, 34.8, 37.1, 37.7, 45.9, 110.9, 114.8, 127.0, 129.6, 130.2, 130.7, 137.0, 143.2. IR (CH_2Cl_2) ν 3282, 2955, 2927, 2869, 1726, 1598, 1447, 1377, 1331, 1288, 1260,

1160, 1093, 1072, 1041, 813, 742, 706, 664 cm^{-1}. MS (ESI) *m/z* 402 $(M+H)^+$. HRMS (ESI) calcd. for $C_{24}H_{36}NO_2S$: 402.2461, Found: 402.2471.



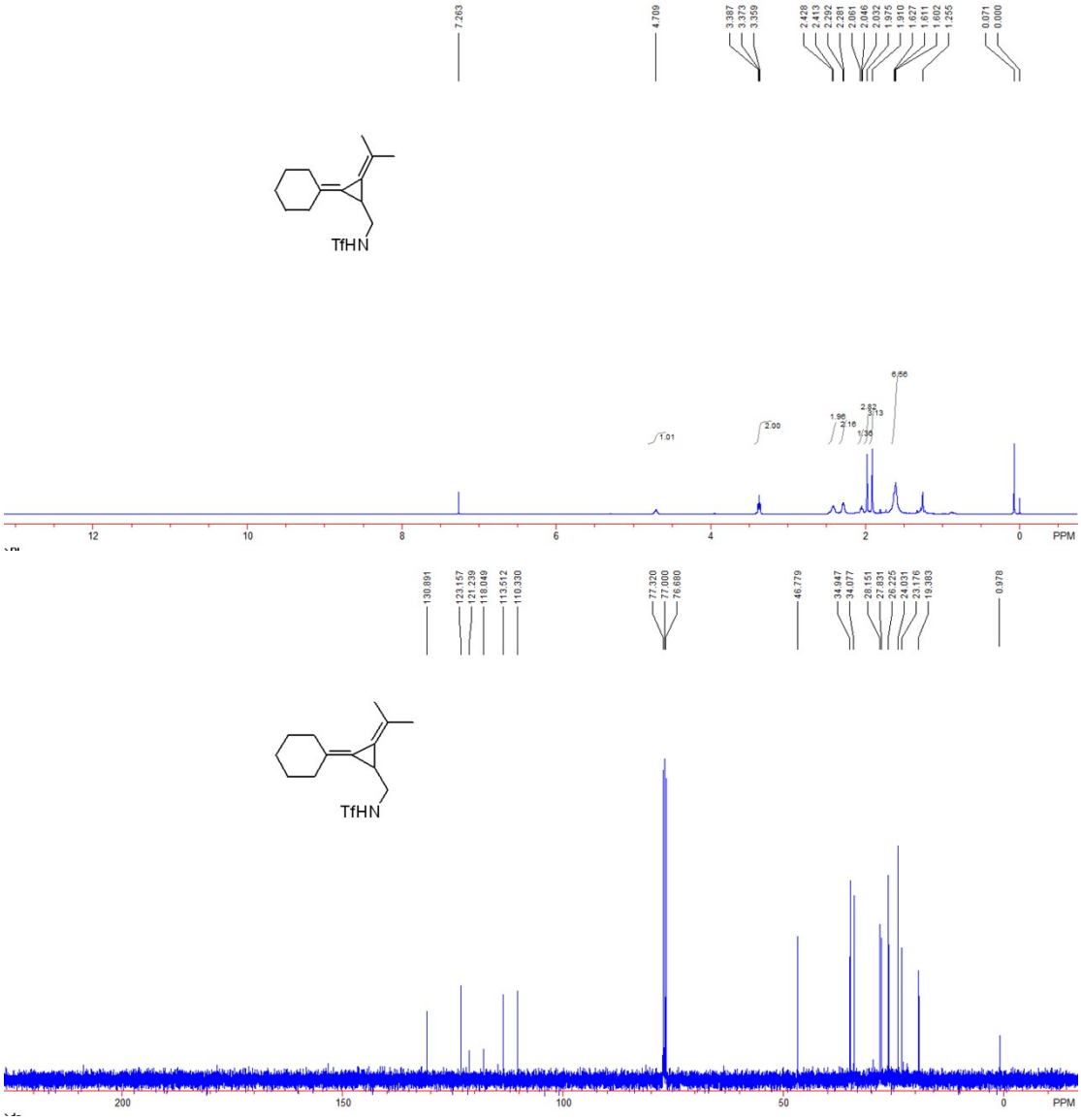
N-((2,3-dicyclohexylidenecyclopropyl)methyl)-4-methylbenzenesulfonamide **2h**: Yield: 48 mg, 62%; A white solid, Mp: 105-107 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.56 (br, 12H, $6CH_2$), 1.90 (t, J = 6.4 Hz, 1H, CH), 2.17-2.36 (m, 8H, $4CH_2$), 2.42 (s, 3H, CH_3), 3.01 (t, J = 6.4 Hz, 2H, CH_2), 4.26 (br, 1H, NH), 7.30 (d, J = 8.0 Hz, 2H, Ar), 7.74 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 18.8, 21.5, 26.3, 27.7, 28.1, 34.1, 35.1, 45.9, 111.1, 127.0, 129.7,

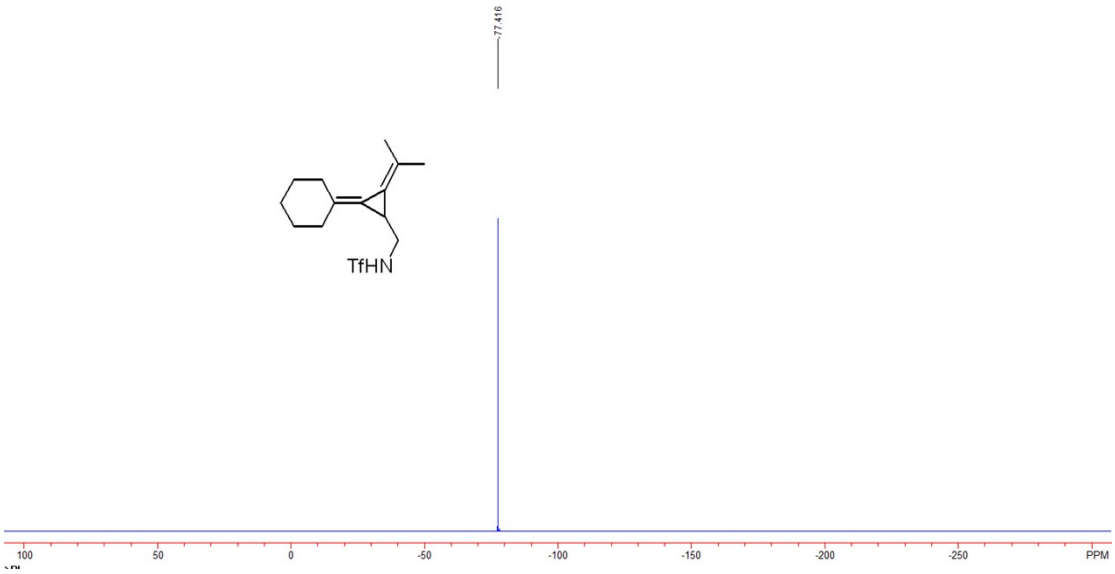
130.4, 137.1, 143.2. IR (CH_2Cl_2) ν 3269, 2926, 2853, 1743, 1446, 1313, 1260, 1229, 1152, 1095, 1038, 818, 676 cm^{-1}. MS (%) (ESI) *m/z* 386 $(M+H)^+$. HRMS (ESI) calcd. for $C_{23}H_{32}NO_2S$: 386.2148, Found: 386.2148.

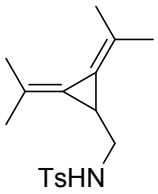


N-((2-cyclohexylidene-3-(propan-2-ylidene)cyclopropyl)methyl)-1,1,1-trifluoromethanesulfonamide **2i**: Yield: 50 mg, 78%; A yellow oil. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.60-1.63 (m, 6H, $3CH_2$), 1.91 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.05 (t, J = 6.0 Hz, 1H, CH), 2.28-2.29 (m, 2H, CH_2), 2.41-2.43 (m, 2H, CH_2), 3.36-3.39 (m, 2H, CH_2), 4.71 (br, 1H, NH). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -77.42. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 19.4,

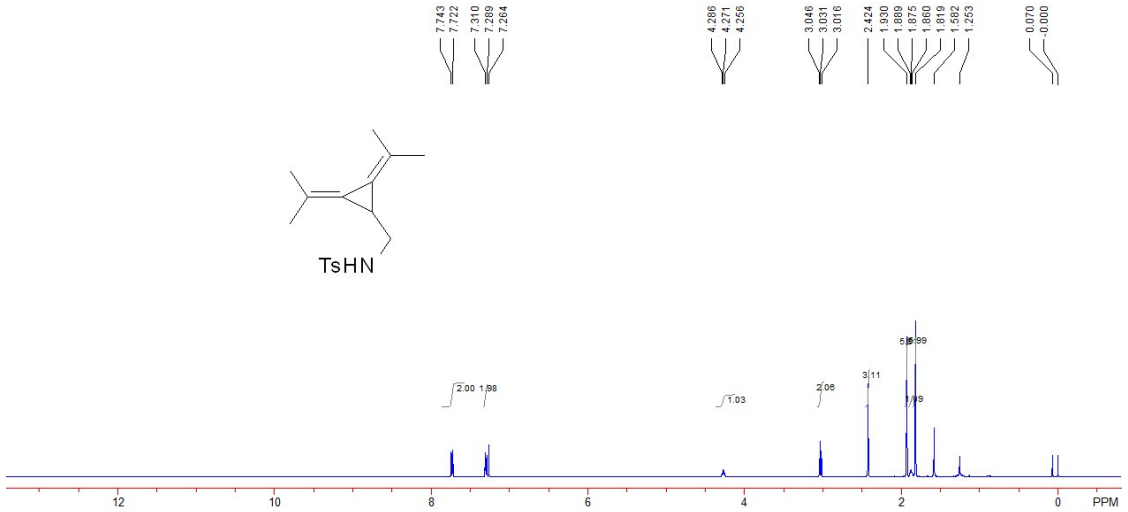
23.2, 24.0, 26.2, 27.8, 28.2, 34.1, 35.0, 46.8, 110.3, 113.5, 119.6 (q, J = 319.0 Hz), 123.2, 130.9. IR (CH_2Cl_2) ν 3313, 2929, 2855, 1734, 1653, 1448, 1370, 1229, 1185, 1057, 887, 838, 776, 742 cm^{-1}. MS (%) (ESI) *m/z* 324 (M^++1). HRMS (ESI) calcd. for $C_{14}H_{21}O_2NF_3S$: 324.1240, Found: 324.1239.

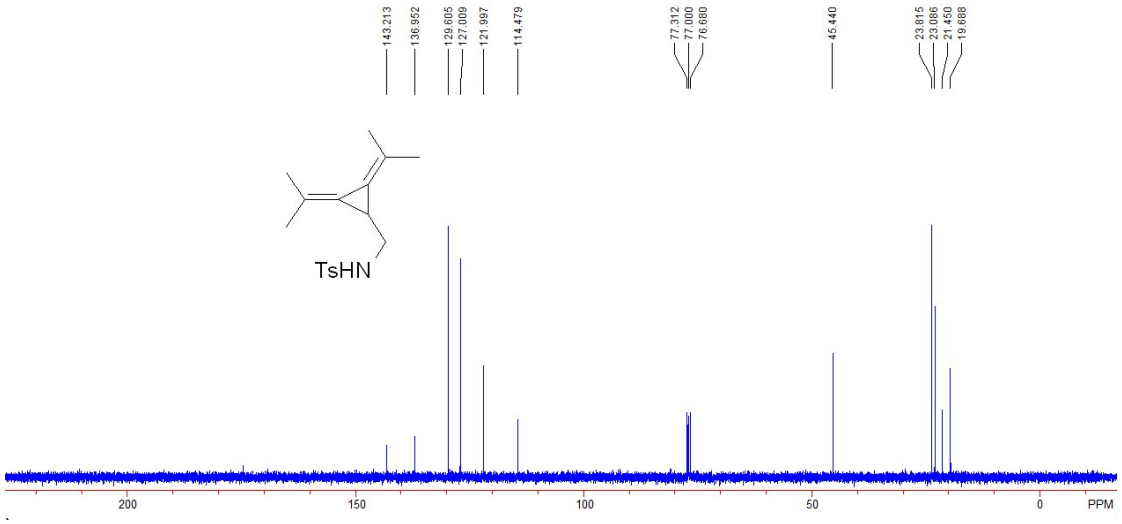


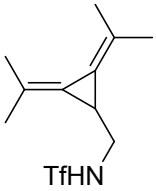




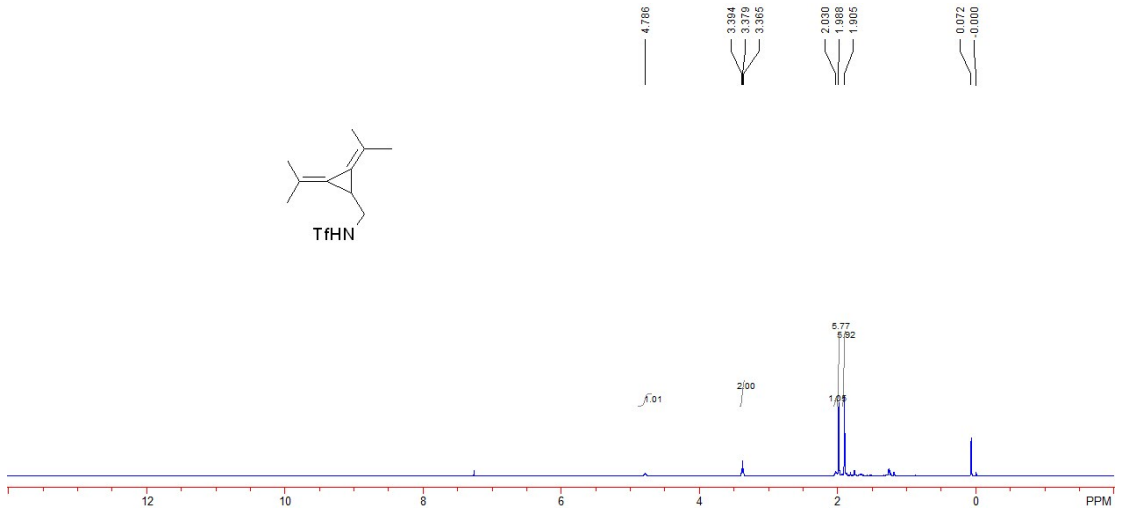
N-((2,3-di(propan-2-ylidene)cyclopropyl)methyl)-4-methylbenzenesulfonamide **2j**: Yield: 23 mg, 44%; A white solid, Mp: 116-118 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.82 (s, 6H, $2CH_3$), 1.87 (br, 1H, CH), 1.93 (s, 6H, $2CH_3$), 2.42 (s, 3H, CH_3), 3.03 (dd, J_1 = 6.0 Hz, J_2 = 6.0 Hz, 2H, CH_2), 4.27 (t, J = 6.0 Hz, 1H, NH), 7.30 (d, J = 8.4 Hz, 2H, Ar), 7.73 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 19.7, 21.5, 23.1, 23.8, 45.4, 114.5, 122.0, 127.0, 129.6, 137.0, 143.2. IR (CH_2Cl_2) ν 3288, 2922, 2851, 1656, 1598, 1442, 1327, 1159, 1094, 1063, 835, 813, 670 cm^{-1}. MS (%) (ESI) *m/z* 323 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{17}H_{27}N_2O_2S$: 323.1788, Found: 323.1787.

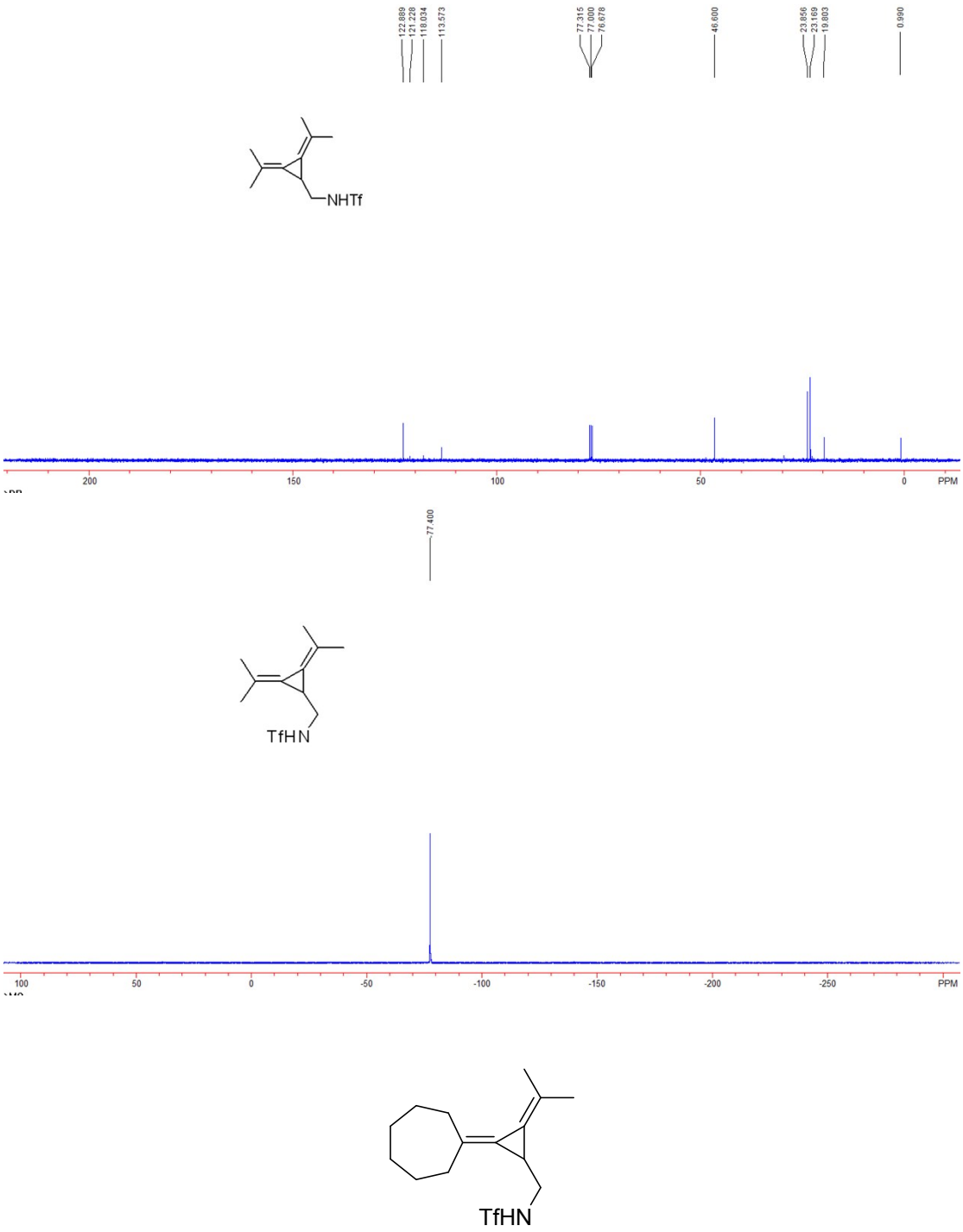






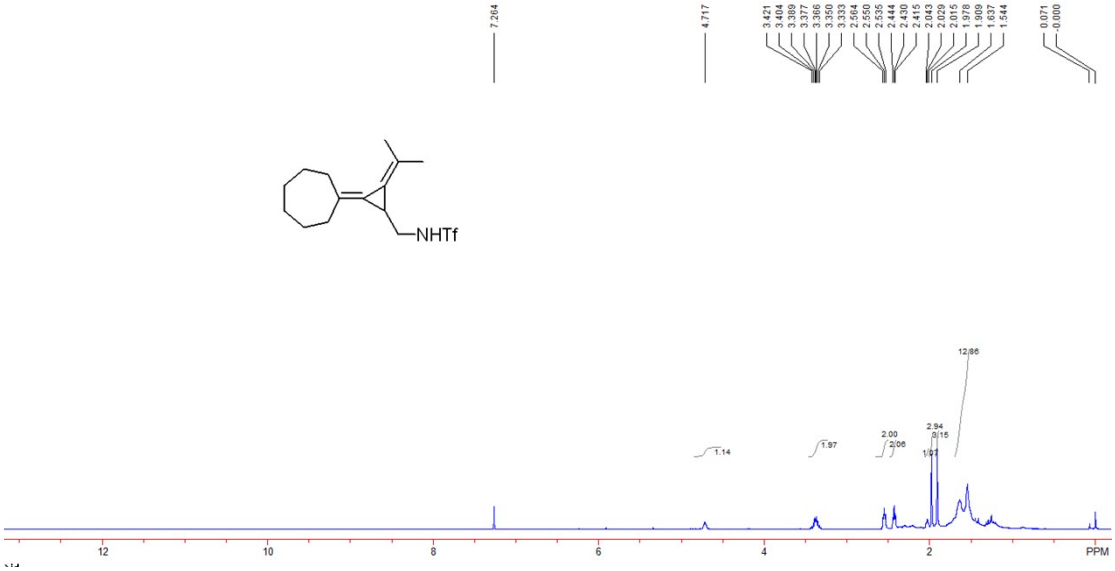
N-((2,3-di(propan-2-ylidene)cyclopropyl)methyl)-1,1,1-trifluoromethanesulfonamide **2k**: Yield: 24 mg, 44%; A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.91 (s, 6H, $2CH_3$), 1.99 (s, 6H, $2CH_3$), 2.03 (br, 1H, CH), 3.37-3.39 (m, 2H, CH_2), 4.79 (br, 1H, NH). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -77.44. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 19.8, 23.2, 23.9, 46.6, 113.6, 119.6 (q, J = 319.4 Hz), 122.9. IR (CH_2Cl_2) ν 3306, 2913, 1732, 1658, 1435, 1369, 1229, 1186, 1100, 1034, 899, 844, 800 cm^{-1}. MS (%) (EI) *m/z* 283 (M^+, 55), 154 (35), 139 (100), 134 (80), 133 (50), 119 (40), 98 (25). HRMS (EI) calcd. for $C_{11}H_{16}NO_2F_3S$: 283.0854, Found: 283.0857.

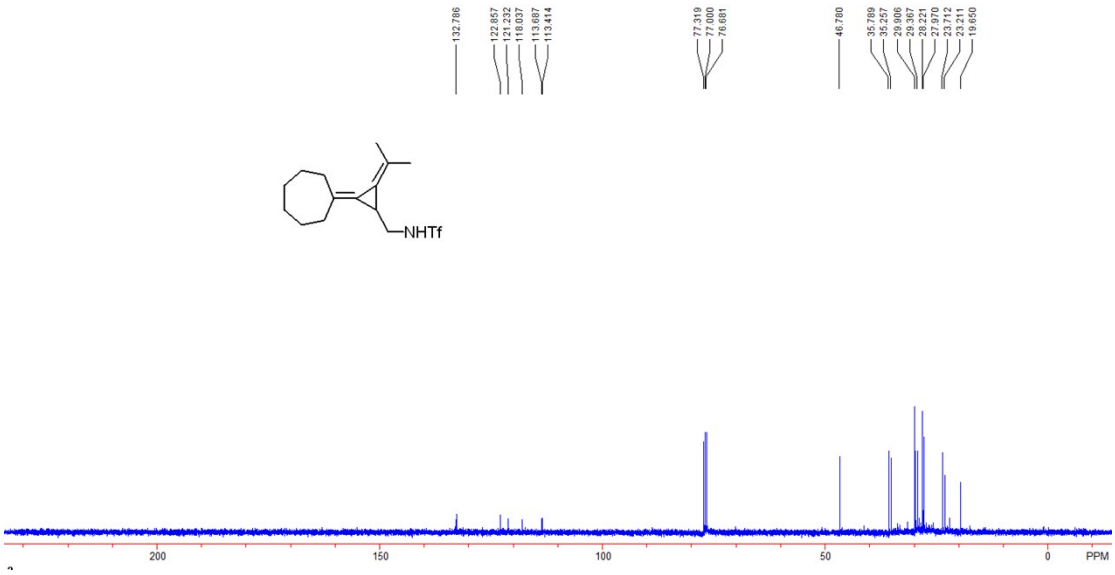


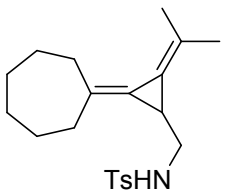


N-((2-cycloheptylidene-3-(propan-2-ylidene)cyclopropyl)methyl)-1,1,1-trifluoromethanesulfonamide **2l**: Yield: 7 mg, 10%; A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.54-1.64 (m, 8H, 4CH_2), 1.91 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.03 (t, J = 5.6 Hz, 1H, CH), 2.42-2.44 (m, 2H, CH_2), 2.54-2.56 (m, 2H, CH_2), 3.33-3.42 (m, 2H, CH_2), 4.72 (br, 1H, NH). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -77.38. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 19.7, 23.2, 23.7, 28.0, 28.2, 29.4, 29.9, 35.3, 35.8, 46.8, 113.4, 113.7, 119.6 (q, J = 319.5 Hz), 122.9, 132.8. IR (CH_2Cl_2) ν 3263, 2923, 2854, 1722, 1687, 1443, 1374, 1228, 1185, 1146, 1057, 801

cm^{-1}. MS (%) (EI) *m/z* 337 (M^+, 12), 231 (45), 204 (74), 191 (40), 175 (61), 162 (58), 149 (85), 119 (54), 105 (100), 91 (81), 77 (62), 69 (69), 55 (44). HRMS (EI) calcd. for $C_{15}H_{22}NO_2F_3S$: 337.1323, Found: 337.1319.

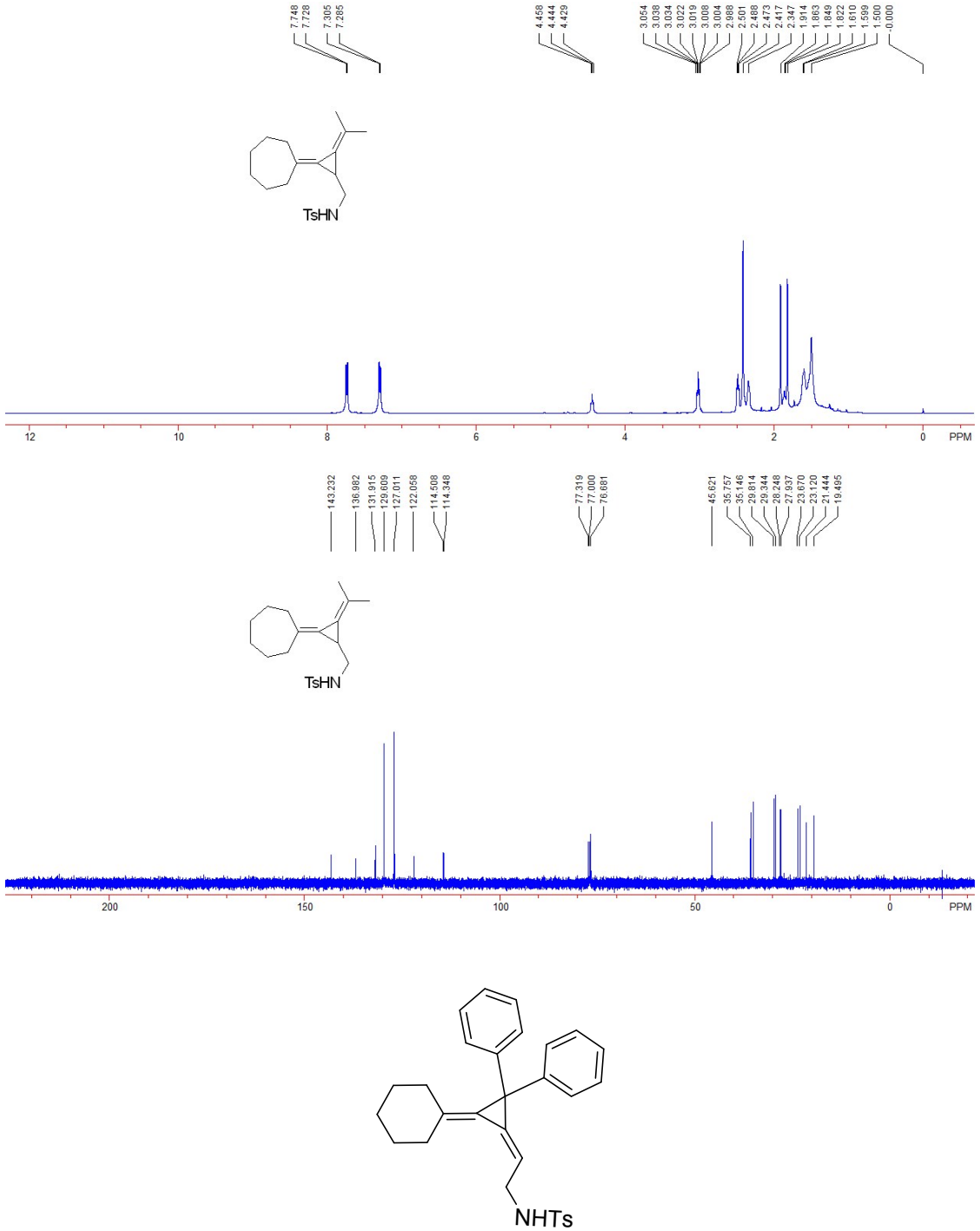






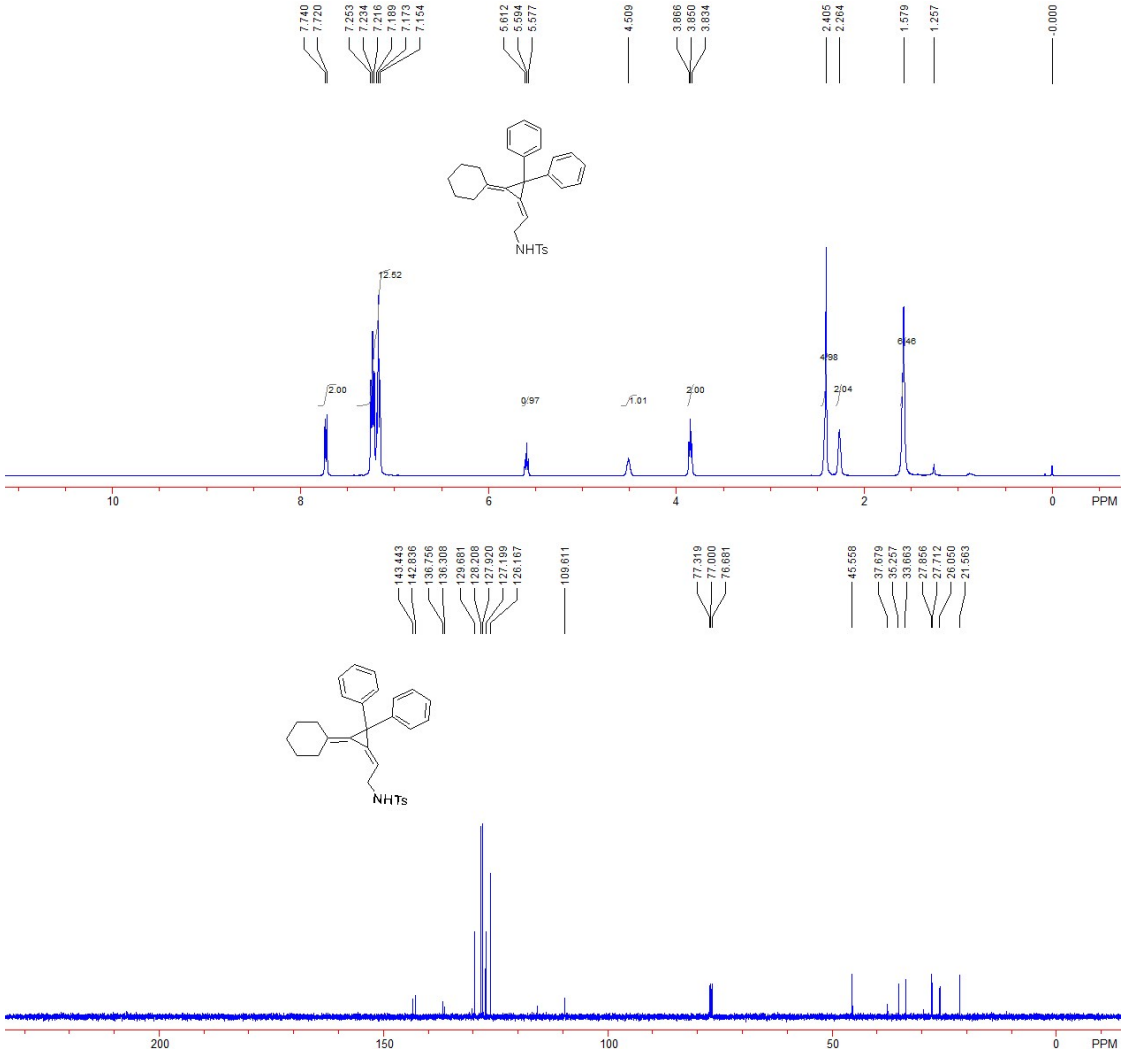
N-((2-cycloheptylidene-3-(propan-2-ylidene)cyclopropyl)methyl)-4-methylbenzenesulfonamide **2m**: Yield: 31 mg, 48%; A white solid, Mp: 106-108 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.50-1.61 (m, 8H, $4CH_2$), 1.82 (s, 3H, CH_3), 1.85 (t, J = 5.2 Hz, 1H, CH), 1.91 (s, 3H, CH_3), 2.35-2.50 (m, 4H, $2CH_2$), 2.47 (s, 3H, CH_3), 3.00-3.04 (m, 2H, CH_2), 4.44 (t, J = 6.0 Hz, 1H,

NH), 7.29 (d, J = 8.0 Hz, 2H, Ar), 7.74 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 19.5, 21.5, 23.2, 23.7, 28.0, 28.3, 29.4, 29.9, 35.2, 35.8, 45.7, 114.4, 114.5, 122.1, 127.0, 129.6, 132.0, 137.0, 143.3. IR (CH_2Cl_2) ν 3289, 2926, 2851, 1652, 1575, 1471, 1445, 1388, 1329, 1273, 1160, 1091, 1067, 1009, 819, 736, 703 cm^{-1}. MS (%) (ESI) *m/z* 360.2 $(M+H)^+$. HRMS (ESI) calcd. for $C_{21}H_{30}NO_2S$: 360.1992, Found: 360.1988.

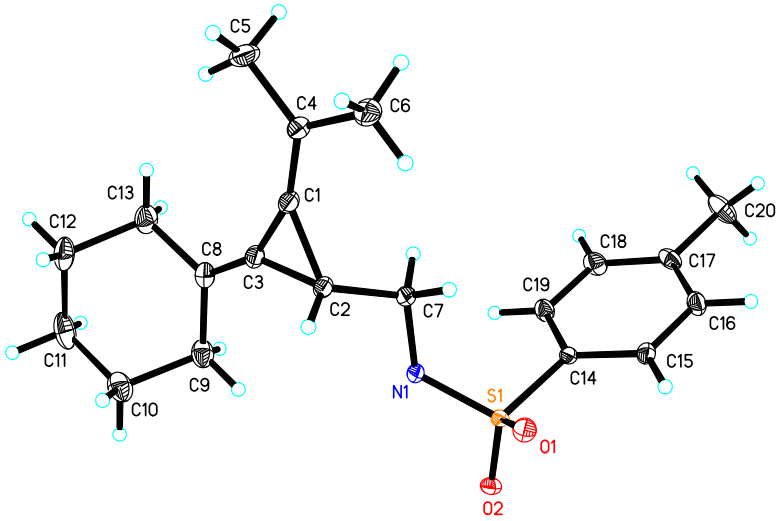


(E)-N-(2-(3-cyclohexylidene-2,2-diphenylcyclopropylidene)ethyl)-4-methylbenzenesulfonamide **3q**: Yield: 30 mg, 80%; A white solid, Mp: 135-137 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ

1.58 (br, 6H, $3CH_2$), 2.26 (br, 2H, CH_2), 2.41 (br, 5H, CH, $2CH_2$), 3.85 (t, J = 6.4 Hz, 2H, CH_2), 4.51 (br, 1H, NH), 5.59 (t, J = 6.8 Hz, 1H, CH), 7.15-7.25 (m, 12H, Ar), 7.73 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 21.6, 26.1, 27.7, 27.9, 33.7, 35.3, 37.7, 45.6, 109.6, 115.8, 126.2, 127.2, 127.9, 128.2, 129.7, 136.3, 136.8, 142.8, 143.4. IR (CH_2Cl_2) ν 3272, 3056, 2926, 2853, 1785, 1597, 1444, 1327, 1157, 1092, 1073, 1046, 978, 907, 813 cm^{-1}. MS (ESI) *m/z* 487 $(M+NH_4)^+$. HRMS (ESI) calcd. for $C_{30}H_{35}N_2O_2S$: 487.2414, Found: 487.2412.

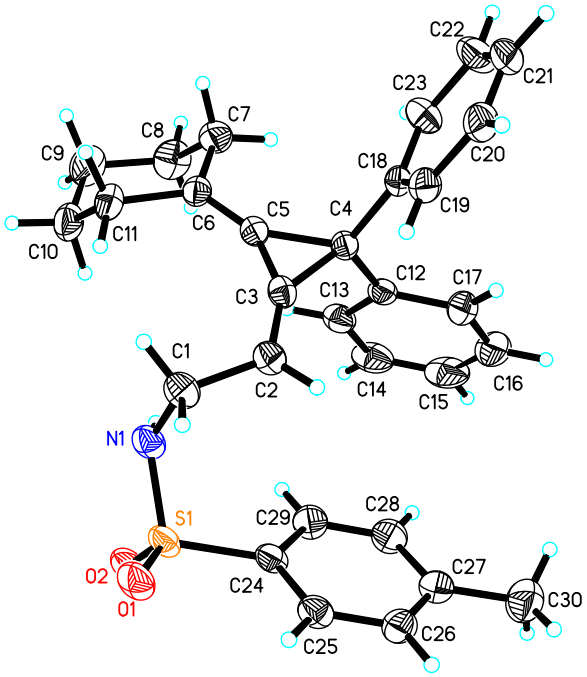


X-ray Crystal Data of Product 2a



The crystal data of **2a** have been deposited in CCDC with number 958985. Empirical formula: $C_{20}H_{26}NO_2S$, Formula weight: 344.48, Temperature: 140(2) K, Wavelength: 0.71073 Å, Crystal system: Triclinic, Space group: P-1, Unit cell dimensions: a = 8.6248(11) Å, α = 99.050(2)°; b = 9.8158(12) Å, β = 101.411(2)°; c = 11.6537(14) Å, γ = 96.596(2)°. Volume: 944.1(2) $Å^3$, Z = 2, Density (calculated): 1.212 Mg/m^3, F(000) = 370, Crystal size: 0.300 x 0.200 x 0.100 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0433, wR2 = 0.1264, R indices (all data): R1 = 0.0541, wR2 = 0.1398.

X-ray Crystal Data of Product 3q



The crystal data of **3q** have been deposited in CCDC with number 1031145. Empirical formula: $C_{20}H_{26}NO_2S$, Formula weight: 344.48, Temperature: 140(2) K, Wavelength: 0.71073 Å, Crystal system: Triclinic, Space group: P-1, Unit cell dimensions: a = 8.6248(11) Å, α = 99.050(2)°; b = 9.8158(12) Å, β = 101.411(2)°; c = 11.6537(14) Å, γ = 96.596(2)°. Volume: 944.1(2) $Å^3$, Z = 2, Density (calculated): 1.212 Mg/m^3, F(000) = 370, Crystal size: 0.300 x 0.200 x 0.100 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0433, wR2 = 0.1264, R indices (all data): R1 = 0.0541, wR2 = 0.1398.

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