Supporting Information

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1. General

New compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, IR, MS, and HRMS. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz, ^{19}F NMR, 377 MHz). ^{1}H NMR chemical shifts were determined relative to Me_4Si (0.0 ppm) in $CDCl_3$ or the signals of residual undeuterated acetonitrile (1.94 ppm) in CD_3CN, undeuterated acetone (2.04 ppm) in acetone-d_6, or undeuterated nitromethane (4.33 ppm) in CD_3NO_2 as an internal standard. ^{13}C NMR chemical shifts were determined relative to $CDCl_3$ (77.0 ppm), CD_3CN (118.20 ppm), acetone-d_6 (29.80 ppm), or CD_3OD (49.00 ppm). ^{19}F NMR chemical shifts were determined relative to C_6F_6 (−164.9 ppm in $CDCl_3$ or −165.2 ppm in CD_3CN) as an external standard. Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. Mass spectra were obtained on a SHIMADZU GCMS-QP2010 mass spectrometer. High-resolution mass spectra were obtained on JEOL JMS-700 (magnetic sector type mass spectrometer) and JEOL JMS-T100LP mass spectrometers. Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. All reactions were carried out under nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F_{254} and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

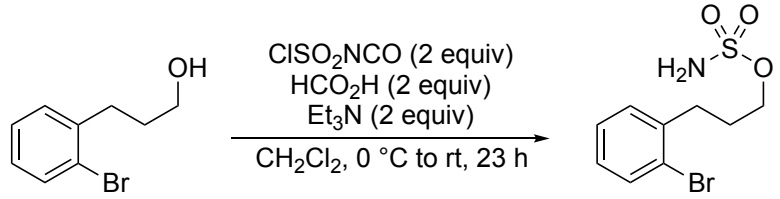
2. Materials

Sulfamate esters were prepared according to the reported procedures.[1–9] *N*-alkylsulfamide **10a** was prepared according to the reported procedure.[10] Dehydrated acetonitrile was used from a solvent purification system. Nitromethane was distilled over calcium sulfate before use. All other solvents and reagents were purchased and used as obtained.

3. Preparation of starting materials

Preparation of sulfamate esters

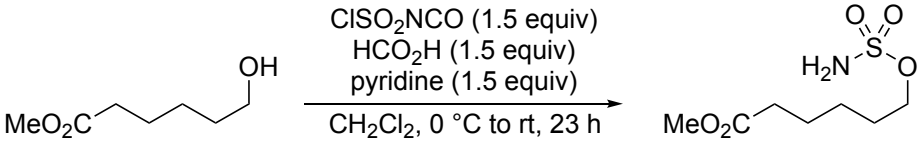
3-(2-bromophenyl)propyl sulfamate (1f)



According to the reported procedure,[4] the reaction using $ClSO_2NCO$ (1.4 mL, 16 mmol), formic acid (610 μL, 16 mmol), 3-(2-bromophenyl)propan-1-ol (1.71 g, 8.0 mmol), and Et_3N (2.8 mL, 20 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless liquid (1.51 g, 66% yield).

^1H NMR: (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.8 Hz, 1H), 7.28–7.17 (m, 2H), 7.12–7.01 (m, 1H), 5.13 (brs, 2H), 4.23 (t, J = 6.4 Hz, 2H), 2.85 (t, J = 8.4 Hz, 2H), 2.11–1.98 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.7, 132.9, 130.5, 128.0, 127.6, 124.3, 70.5, 32.0, 28.6; IR: (ATR) 3387, 3285, 1362, 1179, 1022, 1001, 978, 932, 806, 750 cm^{-1}; HRMS: (EI) calcd for ($C_9H_{12}BrNO_3S$) 292.9721 (M^+) found *m*/*z* 292.9725

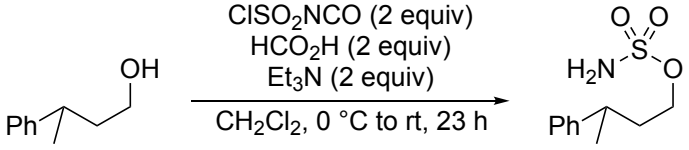
methyl 6-(sulfamoyloxy)hexanoate (1j)



According to the reported procedure,[7] the reaction using methyl 6-hydroxyhexanoate (1.48 g, 10 mmol), MeCN (18 mL), pyridine (1.2 mL, 15 mmol), $ClSO_2NCO$ (1.2 mL, 15 mmol), and formic acid (570 μL, 15 mmol) was carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (1.18 g, 52% yield).

mp: 44.0–44.4 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 4.90 (brs, 2H), 4.23 (t, J = 6.4 Hz, 2H), 3.68 (s, 3H), 2.35 (t, J = 7.2 Hz, 2H), 1.81–1.74 (m, 2H), 1.71–1.64 (m, 2H), 1.50–1.42 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 174.2, 70.9, 51.7, 33.7, 28.3, 24.9, 24.0; IR: (ATR) 3269, 2940, 1719, 1362, 1184, 916, 822 cm^{-1}; HRMS: (CI) calcd for ($C_7H_{16}NO_5S$) 226.0749 ([M+H]$^+$) found *m*/*z* 226.0745

3-phenylbutyl sulfamate (1o)

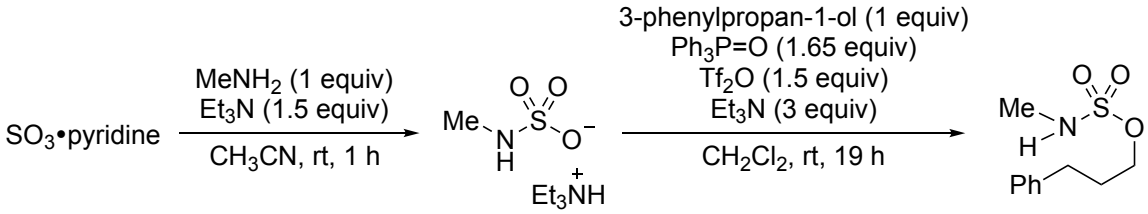


According to the reported procedure,[4] the reaction using $ClSO_2NCO$ (1.7 mL, 20 mmol), formic acid (760 μL, 20 mmol), 3-phenylbutan-1-ol (1.50 g, 10 mmol), and Et_3N (3.5 mL, 25 mmol) was

carried out. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless liquid (1.31 g, 57% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.39–7.14 (m, 5H), 4.53 (brs, 2H), 4.19–3.99 (m, 2H), 2.99–2.84 (m, 1H), 2.13–1.93 (m, 2H), 1.31 (d, J = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 145.4, 128.6, 127.0, 126.5, 69.8, 36.8, 36.1 22.2; IR: (ATR) 3370, 3283, 1358, 1177, 966, 930, 826, 764 cm^{-1}; HRMS: (EI) calcd for ($C_{10}H_{15}NO_3S$) 229.0773 (M^+) found *m/z* 229.0769.

3-phenylpropyl methylsulfamate (4)

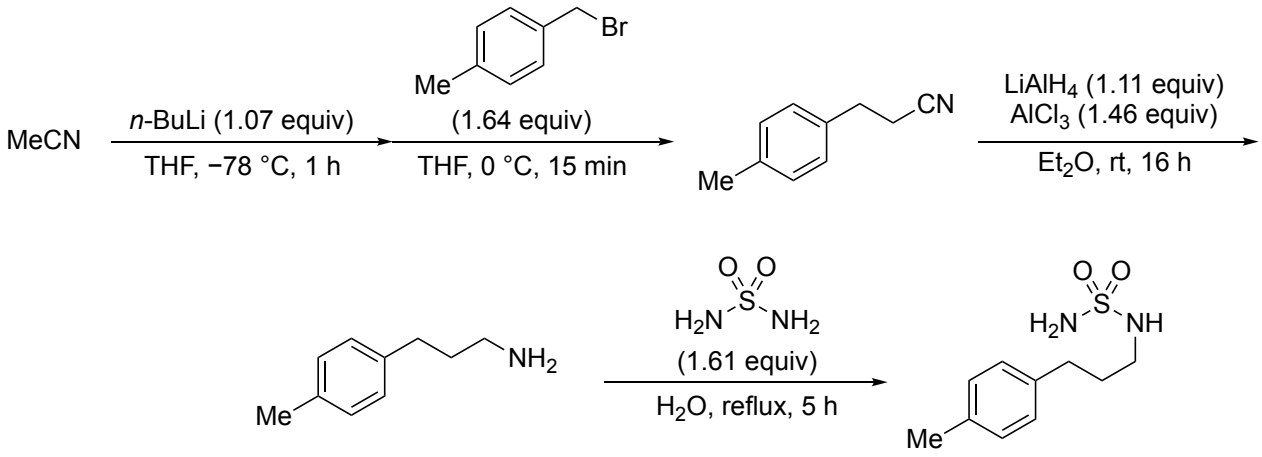


Following the reported procedure,[11] triethylammonium sulfamate salt was prepared using sulfur trioxide pyridine complex (SO_3•pyridine) (4.5 g, 30 mmol), acetonitrile (90 mL), $MeNH_2$ (2 M in THF, 15 mL, 30 mmol), and Et_3N (4.2 mL, 45 mmol). The obtained salt was used without further purification. According to the reported procedure,[11] a flame-dried round-bottom flask containing a magnetic stir bar was charged with triphenylphosphine oxide (9.18 g, 33 mmol) and CH_2Cl_2 (100 mL), and the flask was cooled to 0 °C. Trifluoromethanesulfonic anhydride (4.9 mL, 30 mmol) was then added to the cooled solution dropwise. The mixture was allowed to stir at 0 °C for 15 minutes. A solution of sulfamate salt in CH_2Cl_2 (20 mL) was then added, and the mixture was stirred for 15 minutes at 0 °C. A flame-dried round-bottom flask containing a magnetic stir bar was charged with Et_3N (8.4 mL, 60 mmol, 3.0 equiv) and CH_2Cl_2 (80 mL), and the mixture was cooled to −78 °C. The sulfamate salt solution was transferred dropwise to the Et_3N solution, and the resulting solution was stirred at −78 °C for 15 minutes. A solution of 3-phenylpropan-1-ol (2.7 mL, 20 mmol) in CH_2Cl_2 (20 mL) was then added to the Et_3N solution. Without removing the cooling bath, the solution was stirred for 18 h, during which time no additional ice was added and the mixture warmed to room temperature. The reaction was then diluted with 2 M HCl (50 mL) and H_2O (100 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 25 mL), and the collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (hexane/EtOAc = 70:30) to give the product as a colorless liquid (26% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.31–7.17 (m, 5H), 4.73 (br s, 1H), 4.12 (t, J = 6.0 Hz, 2H), 2.76 (d, J = 5.6 Hz, 3H), 2.73 (t, J = 7.8 Hz, 2H), 2.07–2.00 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 140.4, 128.4, 128.3, 126.1, 69.8, 31.5, 30.3, 30.0; IR: (ATR) 3319, 3306, 2953, 1342, 1171, 932, 860, 746, 700 cm^{-1}; HRMS: (CI) calcd for ($C_{10}H_{16}NO_3S$) 230.0851 ([M+H]$^+$) found *m/z* 230.0853

Preparation of *N*-alkylsulfamides

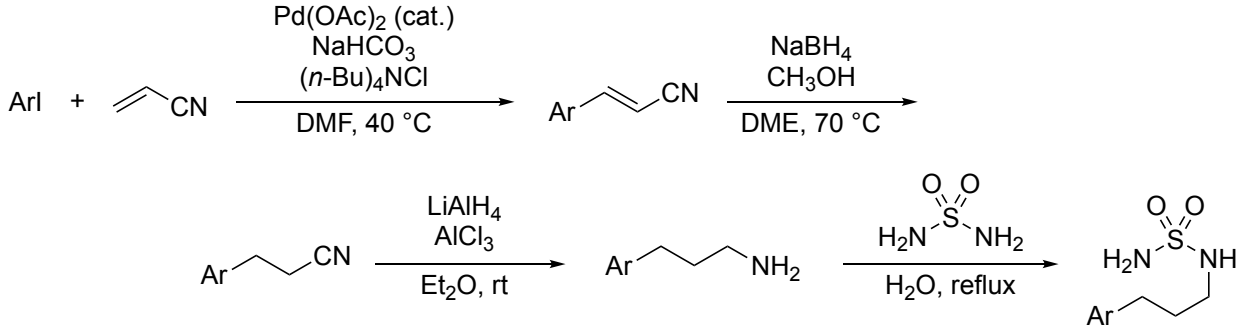
***N*-(3-(4-methylphenyl)propyl)sulfamide (10b)**



3-(4-Methylphenyl)propylamine was prepared following the reported procedure.[12,13] According to the reported procedure,[10] a round-bottom flask containing a magnetic stir bar was charged with sulfamide (3.91 g, 40.6 mmol), H_2O (25 mL), and 3-(4-methylphenyl)propylamine (3.77 g, 25.3 mmol). The mixture was refluxed for 5 h. Then, the mixture was cooled to room temperature, acidified with 2 M HCl aq. to pH 2, and cooled to 0 ºC. The solid that formed was filtered and then washed with ice water to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 50:50) gave the product as a white solid (2.52 g, 44% yield).

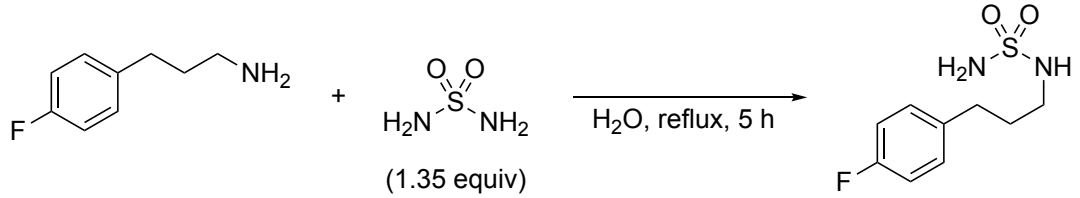
mp: 93.9–95.2 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.20–6.99 (m, 4H), 5.09 (brs, 2H), 5.00 (brs, 1H), 2.97 (dt, J = 7.2, 7.2 Hz, 2H), 2.62 (t, J = 7.2 Hz, 2H), 2.29 (s, 3H), 1.80 (tt, J = 7.2, 7.2 Hz, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 139.6, 136.1, 129.8, 129.1, 43.5, 32.9, 31.9, 20.9; IR: (ATR) 3348, 3265, 1435, 1341, 1317, 1152, 1076, 934, 808 cm^{-1}; HRMS: (EI) calcd for ($C_{10}H_{16}N_2O_2S$) 228.0932 (M^+), found *m*/*z* 228.0934

Typical procedure for the preparation of *N*-alkylsulfamides 10c–g



3-Arylpropylamines were prepared following the reported procedure.[13] According to the reported procedure,[10] a round-bottom flask containing a magnetic stir bar was charged with sulfamide, H_2O, and 3-arylpropylamine. The mixture was refluxed for 5 h. Then, the mixture was cooled to room temperature, acidified with 2 M HCl aq. to pH 2, and cooled to 0 ºC. The solid that formed was filtered and then washed with cold water. Furhter purification by flash column chromatography on silica gel gave the desired product.

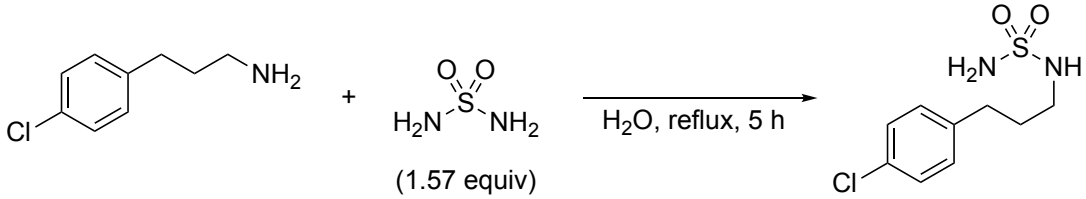
***N*-(3-(4-fluorophenyl)propyl)sulfamide (10c)**



According to the typical procedure, the reaction using sulfamide (1.17 g, 12.1 mmol), H_2O (8 mL), and 3-(4-fluorophenyl)propylamine (1.37 g, 8.95 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 50:50) gave the product as a white solid (0.685 g, 33% yield).

mp: 56.5–57.4 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.33–7.13 (m, 2H), 7.10–6.90 (m, 2H), 5.10 (brs, 2H), 5.03 (brs, 1H), 2.98 (dt, J = 7.2, 7.2 Hz, 2H), 2.65 (t, J = 7.2 Hz, 2H), 1.80 (tt, J = 7.2, 7.2 Hz, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 162.0 (d, J_{CF} = 239.6 Hz), 138.7 (d, J_{CF} = 3.3 Hz), 130.9 (d, J_{CF} = 8.2 Hz), 115.7 (d, J_{CF} = 21.4 Hz), 43.3, 32.4, 31.8; ^{19}F NMR: (377 MHz, CD_3CN) δ −120.1; IR: (ATR) 3314, 3267, 1512, 1437, 1331, 1238, 1150, 1069, 912, 812 cm^{-1}; HRMS: (EI) calcd for ($C_9H_{13}FN_2O_2S$) 232.0682 (M^+), found *m*/*z* 232.0682

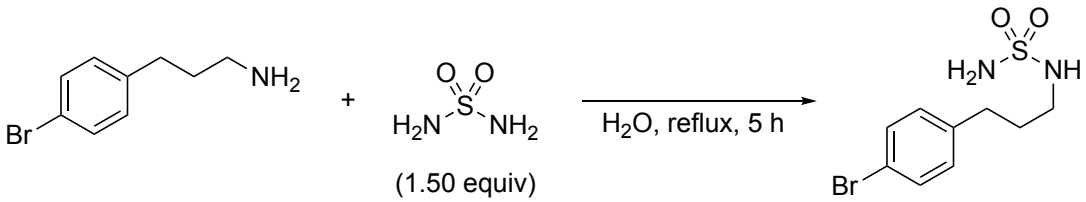
***N*-(3-(4-chlorophenyl)propyl)sulfamide (10d)**



According to the typical procedure, the reaction using sulfamide (2.65 g, 27.6 mmol), H_2O (18 mL), and 3-(4-chlorophenyl)propylamine (2.96 g, 17.5 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 50:50) gave the product as a white solid (2.00 g, 46% yield).

mp: 82.9–84.1 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.30 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 5.10 (brs, 2H), 5.03 (brs, 1H), 2.97 (dt, J = 7.2, 7.2 Hz, 2H), 2.65 (t, J = 7.2 Hz, 2H), 1.81 (tt, J = 7.2, 7.2 Hz, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 141.6, 131.8, 131.0, 129.1, 43.3, 32.6, 31.6; IR: (ATR) 3294, 3242, 1493, 1435, 1321, 1163, 1084, 928, 797 cm^{-1}; HRMS: (EI) calcd for ($C_9H_{13}ClN_2O_2S$) 248.0386 (M^+), found *m*/*z* 248.0384

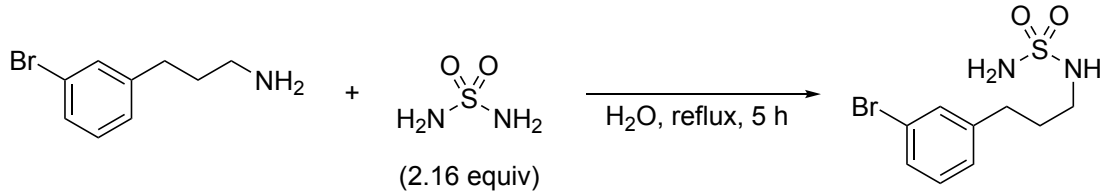
***N*-(3-(4-bromophenyl)propyl)sulfamide (10e)**



According to the typical procedure, the reaction using sulfamide (1.44 g, 15.0 mmol), H_2O (10 mL), and 3-(4-bromophenyl)propylamine (2.14 g, 10.0 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 80:20 to 40:60) gave the product as a white solid (1.77 g, 61% yield).

mp: 89.4–90.2 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.49–7.40 (m, 2H), 7.16 (d, J = 8.4 Hz, 2H), 5.10 (brs, 2H), 5.03 (brs, 1H), 2.97 (dt, J = 7.2, 7.2 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 1.80 (tt, J = 7.2, 7.2 Hz, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 142.1, 132.1, 131.4, 119.9, 43.3, 32.6, 31.5; IR: (ATR) 3302, 3248, 1487, 1435, 1319, 1163, 1084, 1072, 1011, 926, 791 cm^{-1}; HRMS: (EI) calcd for ($C_9H_{13}BrN_2O_2S$) 291.9881 (M^+), found m/z 291.9876

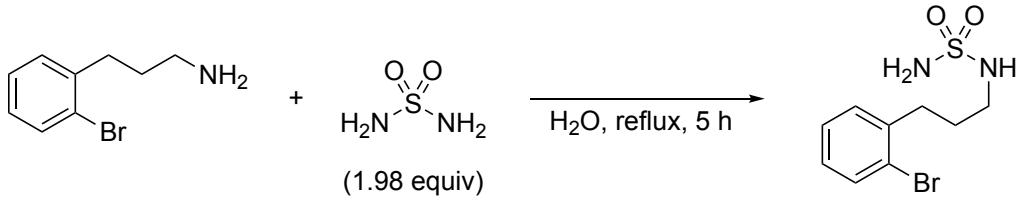
_N_-(3-(3-bromophenyl)propyl)sulfamide (10f)



According to the typical procedure, the reaction using sulfamide (3.87 g, 40.3 mmol), H_2O (20 mL), and 3-(3-bromophenyl)propylamine (4.00 g, 18.7 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 50:50) gave the product as a white solid (3.65 g, 67% yield).

mp: 74.2–76.4 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.42 (s, 1H), 7.39–7.31 (m, 1H), 7.30–7.12 (m, 2H), 5.11 (brs, 2H), 5.03 (brs, 1H), 2.98 (dt, J = 7.2, 7.2 Hz, 2H), 2.66 (t, J = 7.2 Hz, 2H), 1.81 (tt, J = 7.2, 7.2 Hz, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 145.5, 132.1, 131.1, 129.7, 128.3, 122.7, 43.3, 32.9, 31.5; IR: (ATR) 3381, 3252, 1566, 1551, 1437, 1327, 1148, 1059, 908, 891, 847, 787 cm^{-1}; HRMS: (CI) calcd for ($C_9H_{14}BrN_2O_2S$) 292.9959 ([M+H]$^+$), found m/z 292.9958

_N_-(3-(2-bromophenyl)propyl)sulfamide (10g)



According to the typical procedure, the reaction using sulfamide (3.90 g, 40.5 mmol), H_2O (20 mL), and 3-(2-bromophenyl)propylamine (4.39 g, 20.5 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 50:50) gave the product as a white solid (3.57 g, 59% yield).

mp: 48.5–49.8 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.57 (dd, J = 8.0, 0.8 Hz, 1H), 7.40–7.25 (m, 2H), 7.12 (ddd, J = 8.0, 6.8, 2.4 Hz, 1H), 5.12 (brs, 2H), 5.06 (brs, 1H), 3.03 (dt, J = 6.8, 6.8 Hz, 2H), 2.79 (t, J = 8.0 Hz, 2H), 1.83 (tt, J = 8.0, 6.8 Hz, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 141.8,

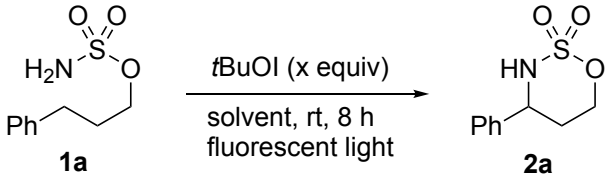
133.5, 131.5, 128.8, 128.6, 124.7, 43.4, 33.7, 30.2; IR: (ATR) 3335, 3291, 3254, 1439, 1323, 1163, 1070, 1024, 924, 737 cm^{-1}; HRMS: (CI) calcd for ($C_9H_{14}BrN_2O_2S$) 292.9959 ($[M+H]^+$), found *m*/*z* 292.9954

4. Effects of reaction parameters on the C−H amination

Effects of the loading amount of *t*BuOI and solvents on the amination of 1a

A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with NaI, 3-phenylpropyl sulfamate (**1a**) (0.2 mmol), and MeCN (1 mL). To the mixture, *t*BuOCl was added, and the mixture was stirred at room temperature for 8 h on the benchtop in the presence of a fluorescent light on the ceiling. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 5 mL), and extracted with Et_2O (3 x 10 mL). Collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^1H NMR spectroscopy. The results are summarized in Table S1.

Table S1



entry	x	solvent	yield (%)[a]	recovery of **1a** (%)[a]
1	1	MeCN	44	48
2	2	MeCN	84	5
3	2.2	MeCN	92	<5
5	2.2	acetone	68	21
6	2.2	CH_2Cl_2	62	<5
8	2.2	Et_2O	<5	90
4	2.2	$MeNO_2$	78	<5
7	2.2	*t*BuOH	61	13

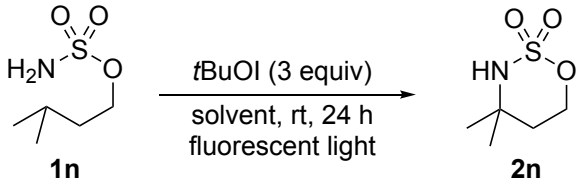
Reactions were performed on a 0.2 mmol scale. [a]Determined by ^1H NMR analysis.

Effects of solvents on the amination of 1n using *t*BuOI

A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with NaI (0.6 mmol), isopentyl sulfamate (**1n**) (0.2 mmol), and solvent (1 mL). To the mixture, *t*BuOCl (0.6 mmol) was added, and the mixture was stirred at room temperature for 24 h on the benchtop in the presence of a fluorescent light on the ceiling. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 5 mL), and extracted with Et_2O (3 x 10 mL). Collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by

^{1}H NMR spectroscopy. The results are summarized in Table S2.

Table S2



1n **2n**

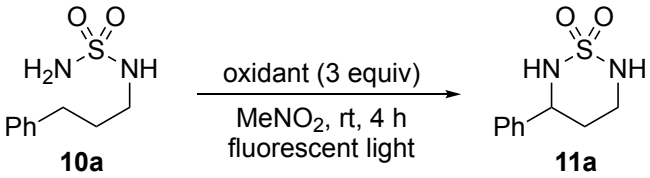
entry	solvent	yield (%)[a]	recovery of **1n** (%)[a]
1	CH_3CN	<5	5
2	acetone	0	35
3	Et_2O	0	71
4	CH_2Cl_2	<5	0
5	$MeNO_2$	25	14

Reactions were performed on a 0.2 mmol scale. [a]Determined by ^{1}H NMR analysis.

Effects of oxidants on the amination of 10a

A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with *N*-(3-phenylpropyl)sulfamide (**10a**) (0.2 mmol), and $MeNO_2$ (1 mL). To the mixture, oxidant (0.6 mmol) was added, and the mixture was stirred at room temperature for 4 h on the benchtop in the presence of a fluorescent light on the ceiling. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 5 mL), and extracted with Et_2O (3 x 10 mL). Collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy. The results are summarized in Table S3.

Table S3



10a **11a**

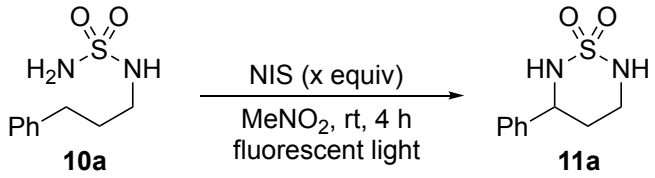
entry	oxidant	yield (%)[a]	recovery of **10a** (%)[a]
1	NIS	92	<5
2	DIH (1.5 equiv)	83	0
3	*t*BuOI	33	36
4	IPy_2BF_4	0	94
5	I_2	0	>95
6	NBS	51	29
7	NCS	0	>95

Reactions were performed on a 0.2 mmol scale. [a]Determined by ^{1}H NMR analysis.

Effects of the loading amount of NIS on the amination of 10a

A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with *N*-(3-phenylpropyl)sulfamide (**10a**) (0.2 mmol), NIS, and $MeNO_2$ (1 mL), and the mixture was stirred at room temperature for 4 h on the benchtop in the presence of a fluorescent light on the ceiling. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 5 mL), and extracted with Et_2O (3 x 10 mL). Collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^1H NMR spectroscopy. The results are summarized in Table S4.

Table S4



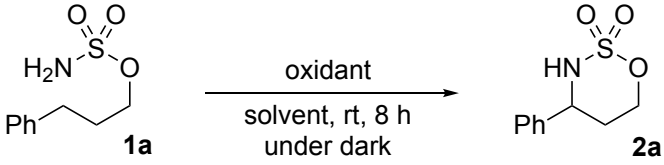
entry	x	yield (%)[a]	recovery of **10a** (%)[a]
1	3	92	<5
2	2.5	89	<5
3	2	77	8
4	1	42	52

Reactions were performed on a 0.2 mmol scale. [a]Determined by ^1H NMR analysis.

5. Experiments in the dark

A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with 3-phenylpropyl sulfamate (**1a**) (0.2 mmol), solvent (1 mL), and oxidant in the dark, and the mixture was stirred at room temperature for 8 h in the dark. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 5 mL), and extracted with Et_2O (3 x 10 mL). Collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^1H NMR spectroscopy. The results are summarized in Table S5.

Table S5



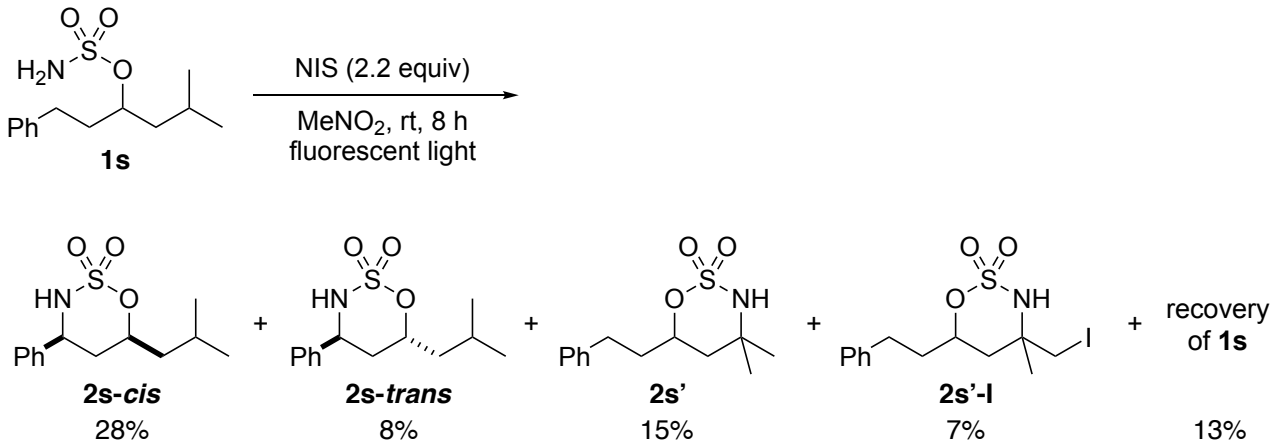
entry	oxidant	solvent	yield (%)[a]	recovery of **1a** (%)[a]
1	*t*BuOI (2.2 equiv)	MeCN	<5	84
2	NIS (3 equiv)	$MeNO_2$	<5	>95

Reactions were performed on a 0.2 mmol scale. [a]Determined by ^1H NMR analysis.

6. Competition experiments between benzilic and 3° C–H bonds

A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with NIS (248.6mg, 1.10 mmol), 5-methyl-1-phenylhexan-3-yl sulfamate (**1s**) (132.7 mg, 0.49 mmol), and $MeNO_2$ (2.5 mL), and the mixture was stirred at room temperature for 8 h on the benchtop in the presence of a fluorescent light on the ceiling. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 5 mL), and extracted with Et_2O (3 x 10 mL). Collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (hexane/EtOAc then hexane/CH_2Cl_2) to give **2s-*cis*** (colorless liquid, 37.1 mg, 28% yield) and the mixture (47.7 mg) containing **2s-*trans***, **2s'**, and **2s'-I**. Yields of **2s-*trans***, **2s'**, and **2s'-I** were determined by ^1H NMR analysis of the mixture.

The analytical data for these products were listed in the section of **Product data**.



7. NMR studies

^{1}H NMR monitoring of the mixture of sulfamate ester 1a and *t*BuOI: A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with NaI (60.1 mg, 0.40 mmol), 3-phenylpropyl sulfamate (**1a**) (43.5 mg, 0.20 mmol) and CD_3CN (1 mL). The flask was then placed in the dark, and *t*BuOCl (45 μL, 0.40 mmol*)* was added to the flask. After mixing for 30 min at room temperature in the dark, the mixture was transferred into an NMR tube. The resulting ^{1}H NMR spectra are shown in Figure S1. Subsequently, the mixture was exposed to ambient light. The resulting ^{1}H NMR spectra after 1 and 3 h are shown.

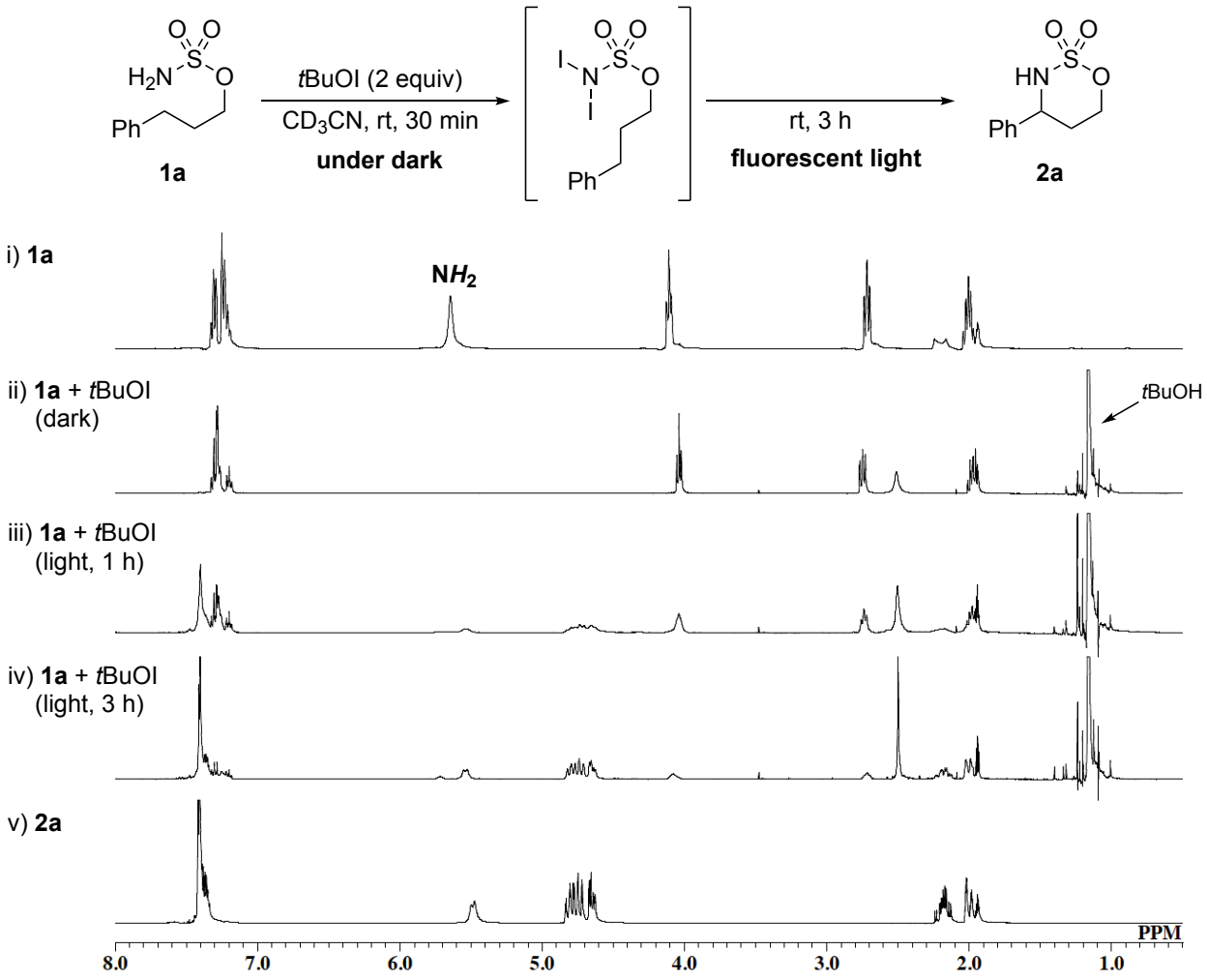


Figure S1. ^{1}H NMR spectra in CD_3CN: i) **1a**. ii) Mixture of **1a** and 2 equiv of *t*BuOI after stirring for 30 min in the dark. iii) Spectrum obtained 1 h after exposure to ambient light. iv) Spectrum obtained 3 h after exposure to ambient light. v) **2a**.

^{1}H NMR monitoring of the mixture of sulfamate ester 1a and NIS: A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with NIS (44.8 mg, 0.20 mmol), 3-phenylpropyl sulfamate (**1a**) (21.8 mg, 0.10 mmol) and CD_3NO_2 (1 mL) in the dark. After mixing for 1 h at room temperature in the dark, the mixture was transferred into an NMR tube. The resulting ^{1}H NMR spectra are shown in Figure S2. Subsequently, the mixture was exposed to ambient light. The resulting ^{1}H NMR spectrum after 2 h is shown.

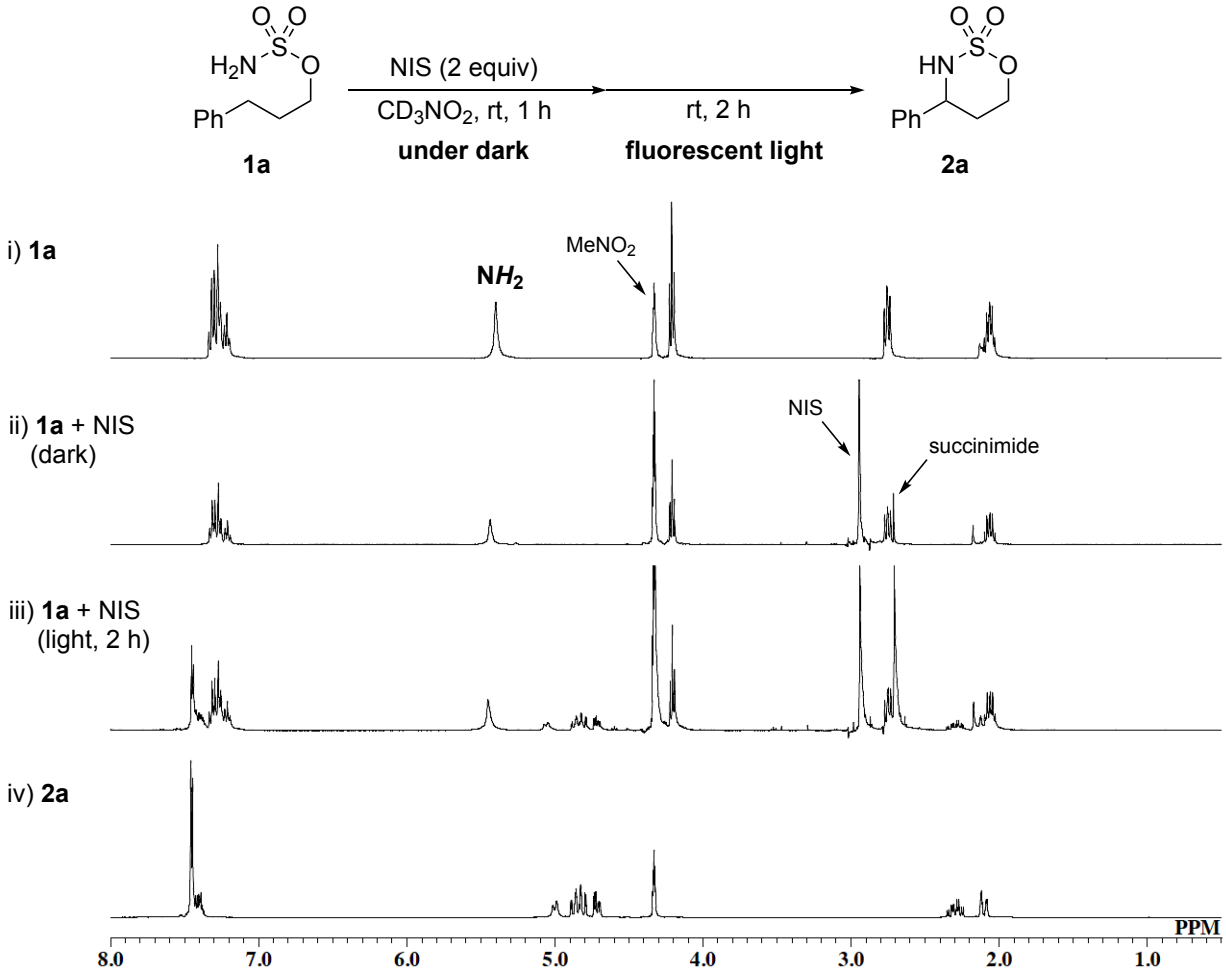


Figure S2. ^{1}H NMR spectra in CD_3NO_2: i) **1a**. ii) Mixture of **1a** and 2 equiv of NIS after stirring for 1 h in the dark. iii) Spectrum obtained 2 h after exposure to ambient light. iv) **2a**.

^{1}H NMR monitoring of the mixture of *N*-alkylsulfamide 10a and NIS: A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with NIS (45.1 mg, 0.20 mmol), *N*-(3-phenylpropyl)sulfamide (**10a**) (17.3 mg, 0.081 mmol) and CD_3NO_2 (1 mL) in the dark. After mixing for 1 h at room temperature in the dark, the mixture was transferred into an NMR tube. The resulting ^{1}H NMR spectra are shown in Figure S3. Subsequently, the mixture was exposed to ambient light. The resulting ^{1}H NMR spectrum after 1 h is shown.

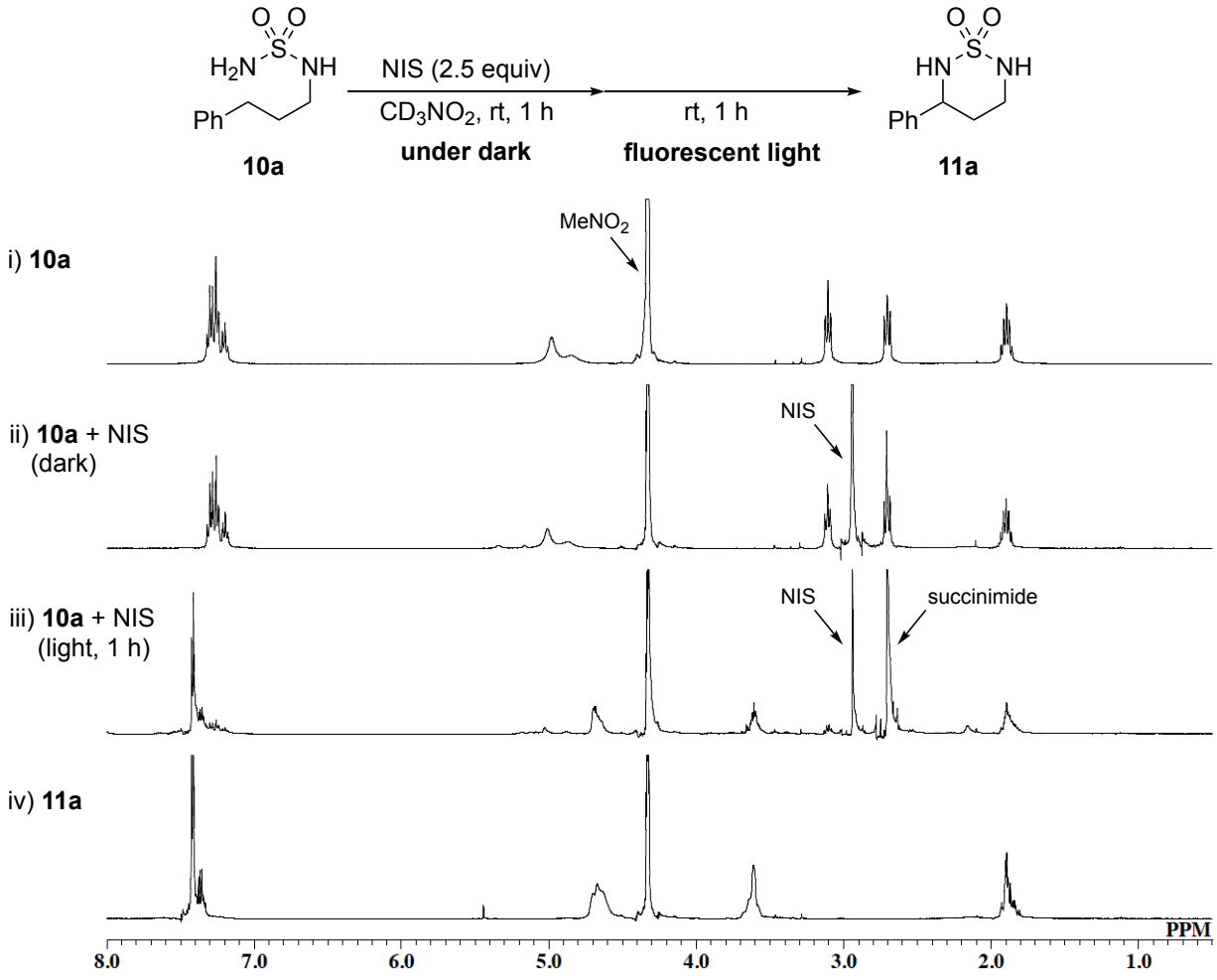


Figure S3. ^{1}H NMR spectra in CD_3NO_2: i) **10a**. ii) Mixture of **10a** and 2.5 equiv of NIS after stirring for 1 h in the dark. iii) Spectrum obtained 1 h after exposure to ambient light. iv) **11a**.

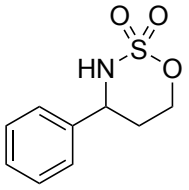
8. Intramolecular C−H amination of sulfamate esters

Typical procedure for the reaction under condition A (using *t*BuOI in MeCN): A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with NaI (1.1–1.5 mmol), sulfamate ester (0.5 mmol), and MeCN (2.5 mL). To the mixture, *t*BuOCl (1.1–1.5 mmol) was added, and the mixture was stirred at room temperature for the indicated time on the benchtop in the presence of a fluorescent light on the ceiling. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 5 mL), and extracted with Et_2O (3 x 10 mL). Collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel gave the product.

Typical procedure for the reaction under condition B (using NIS in $MeNO_2$): A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with NIS (1.5 mmol), sulfamate ester (0.5 mmol), and $MeNO_2$ (2.5 mL), and the mixture was stirred at room temperature for indicated time on the benchtop in the presence of a fluorescent light on the ceiling. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 5 mL), and extracted with Et_2O (3 x 10 mL). Collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel gave the product.

Product data

4-phenyl-1,2,3-oxathiazinane 2,2-dioxide (2a)



Condition A: According to the typical procedure, the reaction using NaI (165.1 mg, 1.50 mmol), MeCN (2.5 mL), 3-phenylpropyl sulfamate (107.7 mg, 0.50 mmol), and *t*BuOCl (123.1 mg, 1.50 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (94.8 mg, 89% yield).

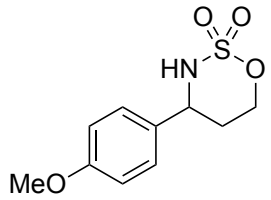
Gram-scale synthesis (Condition A): According to the typical procedure, the reaction using NaI (2.47 g, 16.5 mmol), MeCN (37.5 mL), 3-phenylpropyl sulfamate (1.61 g, 7.5 mmol), and *t*BuOCl (1.87 mL, 16.5 mmol) was conducted for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (1.33 g, 83% yield).

Condition B: According to the typical procedure, the reaction using 3-phenylpropyl sulfamate (103.2 mg, 0.48 mmol), $MeNO_2$ (2.5 mL), and NIS (337.6 mg, 1.50 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (85.9 mg, 84% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.47–7.33 (m, 5H), 4.93–4.83 (m, 2H), 4.67 (ddd, J = 11.2, 4.8, 1.2 Hz, 1H), 4.21 (brd, J = 8.8 Hz, 1H), 2.32–2.18 (m, 1H), 2.05 (dddd, J = 14.4, 2.4, 2.4, 2.4 Hz, 1H);
^{13}C NMR: (100 MHz, $CDCl_3$) δ 137.9, 129.1, 128.9, 126.2, 71.9, 58.9, 30.1

The analytical data for this compound were in excellent agreement with the reported data.[1]

4-(4-methoxyphenyl)-1,2,3-oxathiazinane 2,2-dioxide (2b)



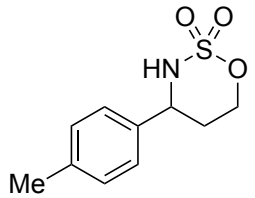
Condition A: According to the typical procedure , the reaction using NaI (165.7 mg, 1.11 mmol), MeCN (2.5 mL), 3-(4-methoxyphenyl)propyl sulfamate (122.6 mg, 0.50 mmol), and *t*BuOCl (124.9 mg, 1.15 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (102.2 mg, 84% yield).

Condition B: According to the typical procedure B, the reaction using 3-(4-methoxyphenyl)propyl sulfamate (117.7 mg, 0.48 mmol), $MeNO_2$ (2.5 mL), and NIS (335.0 mg, 1.49 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 60:40) gave the product as a colorless solid (109.9 mg, 90% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.31–7.24 (m, 2H), 6.95–6.87 (m, 2H), 4.90–4.76 (m, 2H), 4.68–4.60 (m, 1H), 4.30 (brd, *J* = 9.2 Hz, 1H), 3.81 (s, 3H), 2.32–2.16 (m, 1H), 2.03–1.94 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.9, 130.0, 127.6, 114.4, 71.8, 58.4, 55.3, 30.1

The analytical data for this compound were in excellent agreement with the reported data.[2]

4-(4-methylphenyl)-1,2,3-oxathiazinane 2,2-dioxide (2c)



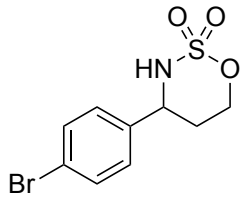
Condition A: According to the typical procedure, the reaction using NaI (187.4 mg, 1.25 mmol), MeCN (2.5 mL), 3-(4-methylphenyl)propyl sulfamate (110.3 mg, 0.48 mmol), and *t*BuOCl (139.3 mg, 1.28 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (93.3 mg, 85% yield).

Condition B: According to the typical procedure, the reaction using 3-(4-methylphenyl)propyl sulfamate (114.0 mg, 0.50 mmol), $MeNO_2$ (2.5 mL), and NIS (336.0 mg, 1.49 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (98.1 mg, 87% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.29–7.18 (m, 4H), 4.92–4.79 (m, 2H), 4.65 (ddd, *J* = 11.6, 4.8, 1.2 Hz, 1H), 4.27 (brd, *J* = 9.2 Hz, 1H), 2.36 (s, 3H), 2.31–2.15 (m, 1H), 2.04–1.96 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.9, 135.0, 129.8, 126.1, 71.8, 58.7, 30.2, 21.1

The analytical data for this compound were in excellent agreement with the reported data.[3]

4-(4-bromophenyl)-1,2,3-oxathiazinane 2,2-dioxide (2d)



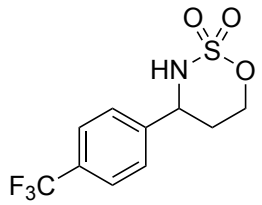
Condition A: According to the typical procedure, the reaction using NaI (187.4 mg, 1.25 mmol), MeCN (2.5 mL), 3-(4-bromophenyl)propyl sulfamate (146.7 mg, 0.50 mmol), and *t*BuOCl (144.6 mg, 1.33 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (115.4 mg, 79% yield).

Condition B: According to the typical procedure, the reaction using 3-(4-bromophenyl)propyl sulfamate (146.9 mg, 0.50 mmol), $MeNO_2$ (2.5 mL), and NIS (337.4 mg, 1.50 mmol) was conducted for 12 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (80.6 mg, 55% yield).

^{1}H NMR: (400 MHz, acetone-d_6) δ 7.62–7.52 (m, 2H), 7.51–7.40 (m, 2H), 6.40 (brd, J = 9.2 Hz, 1H), 4.91–4.64 (m, 3H), 2.29–2.08 (m, 2H); ^{13}C NMR: (100 MHz, acetone-d_6) δ 139.5, 132.5, 129.6, 122.4, 72.7, 59.3, 30.8

The analytical data for this compound were in excellent agreement with the reported data.[4]

4-(4-(trifluoromethyl)phenyl)-1,2,3-oxathiazinane 2,2-dioxide (2e)

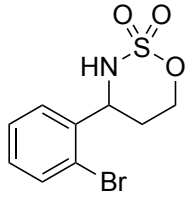


Condition A: According to the typical procedure, the reaction using NaI (189.8 mg, 1.27 mmol), MeCN (2.5 mL), 3-(4-(trifluoromethyl)phenyl)propyl sulfamate (140.4 mg, 0.50 mmol), and *t*BuOCl (141 μL, 1.25 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (91.6 mg, 66% yield).

^{1}H NMR: (400 MHz, CD_3CN) δ 7.72 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 5.60 (brd, J =10.0 Hz, 1H), 4.94–4.85 (m, 1H), 4.76 (ddd, J = 12.0, 12.0, 2.8 Hz, 1H), 4.66 (ddd, J = 12.0, 4.8, 2.0 Hz, 1H), 2.23–2.10 (m, 1H), 2.09–2.00 (m, 1H); ^{13}C NMR: (100 MHz, CD_3CN) δ 143.9, 130.5 (q, J = 32.1 Hz), 128.2, 126.5 (q, J = 4.1 Hz), 125.1 (q, J = 270.0 Hz), 73.2, 59.3, 30.3; ^{19}F NMR: (377 MHz, CD_3CN) δ −63.6

The analytical data for this compound were in excellent agreement with the reported data.[4]

4-(2-bromophenyl)-1,2,3-oxathiazinane 2,2-dioxide (2f)

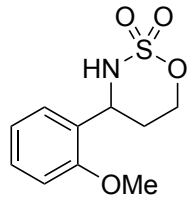


Condition A: According to the typical procedure, the reaction using NaI (165.7 mg, 1.11 mmol), MeCN (2.5 mL), 3-(2-bromophenyl)propyl sulfamate (145.3 mg, 0.49 mmol), and *t*BuOCl (124 μL, 1.1 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless liquid (108.6 mg, 75% yield).

Condition B: According to the typical procedure, the reaction using 3-(2-bromophenyl)propyl sulfamate (139.8 mg, 0.48 mmol), $MeNO_2$ (2.5 mL), and NIS (337.1 mg, 1.50 mmol) was conducted for 12 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless liquid (61.7 mg, 44% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63–7.57 (m, 1H), 7.50–7.32 (m, 2H), 7.28–7.17 (m, 1H), 5.24 (ddd, *J* = 12.0, 8.8, 2.4 Hz, 1H), 4.96–4.79 (m, 2H), 4.63 (ddd, *J* = 12.0, 5.2, 1.6 Hz, 1H), 2.27–2.11 (m, 1H), 2.02 (dddd, *J* = 14.8, 2.4, 2.4, 2.4 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 137.0, 133.5, 130.1, 128.3, 126.9, 123.0, 72.1, 58.5, 29.6; IR: (ATR) 3265, 1420, 1358, 1184, 1065, 1013, 908, 866, 822, 775, 754 cm^{-1}; HRMS: (EI) calcd for ($C_9H_{10}BrNO_3S$) 290.9565 (M^+) found *m*/*z* 290.9570

4-(2-methoxyphenyl)-1,2,3-oxathiazinane 2,2-dioxide (2g)

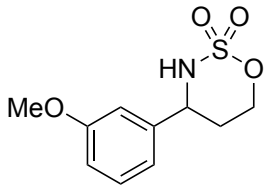


Condition A: According to the typical procedure, the reaction using NaI (165.1 mg, 1.10 mmol), MeCN (2.5 mL), 3-(2-methoxyphenyl)propyl sulfamate (122.7 mg, 0.50 mmol), and *t*BuOCl (121.5 mg, 1.12 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc =70:30) gave the product as a colorless solid (98.2 mg, 81% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.41–7.31 (m, 1H), 7.25–7.14 (m, 1H), 7.06–6.92 (m, 2H), 5.45 (brd, *J* = 10.8 Hz, 1H), 4.94–4.80 (m, 2H), 4.64–4.56 (m, 1H), 3.91 (s, 3H), 2.58–2.44 (m, 1H), 1.81–1.72 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 157.0, 130.0, 128.9, 125.6, 121.3, 111.3, 72.0, 59.1, 55.4, 28.9

The analytical data for this compound were in excellent agreement with the reported data.[14]

4-(3-methoxyphenyl)-1,2,3-oxathiazinane 2,2-dioxide (2h)

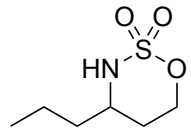


Condition A: According to the typical procedure, the reaction using NaI (167.1 mg, 1.11 mmol), MeCN (2.5 mL), 3-(3-methoxyphenyl)propyl sulfamate (125.1 mg, 0.51 mmol), and *t*BuOCl (124 μL, 1.10 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (91.0 mg, 75% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 1H), 6.95–6.83 (m, 3H), 4.91–4.78 (m, 2H), 4.65 (ddd, *J* = 11.6, 4.8, 1.6 Hz, 1H), 4.35 (brd, *J* = 9.2 Hz, 1H), 3.82 (s, 3H), 2.31–2.14 (m, 1H), 2.02 (dddd, *J* = 14.4, 2.4, 2.4, 2.4 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.1, 139.4, 130.2, 118.2, 114.3, 112.1, 71.8, 58.8, 55.3, 30.1

The analytical data for this compound were in excellent agreement with the reported data.[5]

4-propyl-1,2,3-oxathiazinane 2,2-dioxide (2i)

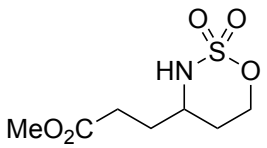


Condition A: According to the typical procedure, the reaction using NaI (226.1 mg, 1.51 mmol), MeCN (2.5 mL), hexyl sulfamate (90.4 mg, 0.50 mmol), and *t*BuOCl (165 μL, 1.58 mmol) was conducted for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 85:15) gave the product as a colorless liquid (54.1 mg, 60% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.81–4.62 (m, 1H), 4.61–4.41 (m, 1H), 3.91 (brs, 1H), 3.81–3.64 (m, 1H), 1.80–1.65 (m, 2H), 1.60–1.32 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 72.0, 55.7, 37.2, 29.9, 18.3, 13.6

The analytical data for this compound were in excellent agreement with the reported data.[4]

methyl 3-(2,2-dioxido-1,2,3-oxathiazinan-4-yl)propanoate (2j)

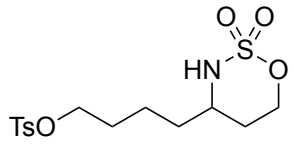


Condition A: According to the typical procedure, the reaction using NaI (224.6 mg, 1.50 mmol), MeCN (2.5 mL), methyl 6-(sulfamoyloxy)hexanoate (112.7 mg, 0.50 mmol), and *t*BuOCl (165 μL, 1.58 mmol) was conducted for 48 h. Purification by flash column chromatography on silica gel (CH_2Cl_2/Et_2O = 95:5) gave the product as a colorless solid (54.8 mg, 49% yield).

mp: 103.7–105.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.80–4.67 (m, 1H), 4.59–4.51 (m, 1H), 4.00 (brd, *J* = 10.8 Hz, 1H), 3.82–3.62 (m, 1H), 3.70 (s, 3H) 2.50 (t, *J* = 6.8 Hz, 2H), 2.01–1.90 (m, 1H),

1.88–1.72 (m, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 173.5, 71.7, 55.7, 52.0, 30.1, 29.6, 29.5; IR: (ATR) 1732, 1354, 1171, 1009, 872 cm^{-1}; HRMS: (CI) calcd for ($C_7H_{14}NO_5S$) 224.0593 ($[M+H]^+$) found *m*/*z* 224.0593

4-(2,2-dioxido-1,2,3-oxathiazinan-4-yl)butyl 4-methylbenzenesulfonate (2k)

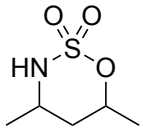


Condition A: According to the typical procedure, the reaction using NaI (225.0 mg, 1.50 mmol), MeCN (2.5 mL), 7-(tosyloxy)heptyl sulfamate (180.8 mg, 0.49 mmol), and *t*BuOCl (165 μL, 1.58 mmol) was conducted for 48 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 1:1 then CH_2Cl_2/Et_2O = 85:15) gave the product as a colorless liquid (92.6 mg, 52% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 4.75–4.62 (m, 1H), 4.53 (ddd, *J* = 11.6, 3.2, 3.2 Hz, 1H), 4.25 (brd, *J* = 10.8 Hz, 1H), 4.03 (t, *J* = 5.6 Hz, 2H), 3.71–3.52 (m, 1H), 2.46 (s, 3H), 1.77–1.56 (m, 4H), 1.56–1.29 (m, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 145.0, 132.7, 129.9, 127.8, 71.9, 70.1, 55.8, 34.1, 29.8, 28.1, 21.6, 21.1

The analytical data for this compound were in excellent agreement with the reported data.[10]

4,6-dimethyl-1,2,3-oxathiazinane 2,2-dioxide (2l)



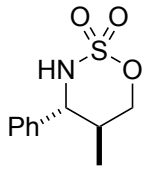
Condition A: According to the typical procedure, the reaction using NaI (225.4 mg, 1.50 mmol), MeCN (2.5 mL), pentan-2-yl sulfamate (87.1 mg, 0.52 mmol), and *t*BuOCl (165 μL, 1.58 mmol) was conducted for 24 h. The diastereomeric ratio of the product was determined by ^{1}H NMR analysis of the crude product (*cis*/*trans* = 58:42). Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless liquid (53.8 mg, 65% combined yield of isomers).

***cis*-isomer:** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.92–4.80 (m, 1H), 3.87–3.64 (m, 2H), 1.82 (ddd, *J* = 14.8, 2.4, 2.4 Hz, 1H), 1.44–1.30 (m, 1H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.27 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 80.6, 51.1, 39.1, 21.1, 20.9

The analytical data for this compound were in excellent agreement with the reported data.[6]

***trans*-isomer:** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.10–5.02 (m, 1H), 4.26 (brd, *J* = 6.0 Hz, 1H), 3.89–3.78 (m, 1H), 1.84 (ddd, *J* = 14.0, 8.8, 5.2 Hz, 1H), 1.69 (ddd, *J* = 14.0, 5.2, 3.2 Hz, 1H), 1.51 (d, *J* = 6.4 Hz, 3H), 1.47 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 78.6, 49.3, 35.9, 20.7, 19.6; HRMS: (EI) calcd for ($C_5H_{11}NO_3S$) 165.0460 (M^+) found *m*/*z* 165.0457

***trans*-5-methyl-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide (2m)**

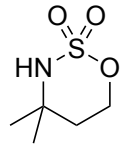


Condition B: According to the typical procedure, the reaction using 2-methyl-3-phenylpropyl sulfamate (117.5 mg, 0.51 mmol), $MeNO_2$ (2.5 mL), and NIS (337.4 mg, 1.50 mmol) was conducted for 8 h. The diastereomeric ratio of the product was determined by ^{1}H NMR analysis of the crude product (*cis*/*trans* = 1:>20). Purification by flash column chromatography on silica gel (hexane/EtOAc = 75:25) gave the product as a colorless solid (97.2 mg, 83% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.45–7.18 (m, 5H), 4.62 (brd, *J* = 8.8 Hz, 1H), 4.54–4.43 (m, 2H), 4.35 (dd, *J* = 10.8, 8.8 Hz, 1H), 2.44–2.28 (m, 1H), 0.70 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 137.0, 129.2, 129.1, 127.2, 76.6, 65.4, 33.9, 11.9

The analytical data for this compound were in excellent agreement with the reported data.[4]

4,4-dimethyl-1,2,3-oxathiazinane 2,2-dioxide (2n)

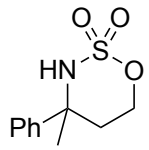


Condition B: According to the typical procedure, the reaction using isopentyl sulfamate (89.4 mg, 0.53 mmol), $MeNO_2$ (2.5 mL), and NIS (338.1 mg, 1.50 mmol) was conducted for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 75:25 then CH_2Cl_2/Et_2O = 95:5) gave the product as a colorless solid (49.8 mg, 42% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.70–4.66 (m, 2H), 4.16 (brs, 1H), 1.79–1.75 (m, 2H), 1.42 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 69.2, 56.4, 35.4, 28.1

The analytical data for this compound were in excellent agreement with the reported data.[3]

4-methyl-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide (2o)



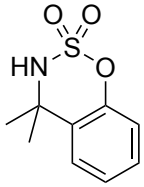
Condition A: According to the typical procedure, the reaction using NaI (165.3 mg, 1.10 mmol), MeCN (2.5 mL), 3-phenylbutyl sulfamate (112.4 mg, 0.49 mmol), and *t*BuOCl (123.1 mg, 1.13 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless solid (78.8 mg, 71% yield).

Condition B: According to the typical procedure, the reaction using 3-phenylbutyl sulfamate (113.7 mg, 0.50 mmol), $MeNO_2$ (2.5 mL), and NIS (337.9 mg, 1.50 mmol) was conducted for 8 h.

Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30 then CH_2Cl_2) gave the product as a colorless solid (84.8 mg, 75% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.49–7.42 (m, 2H), 7.42–7.34 (m, 2H), 7.34–7.28 (m, 1H), 4.79–4.58 (m, 3H), 2.51 (ddd, *J* = 14.8, 7.6, 3.2 Hz, 1H), 2.17 (ddd, *J* = 14.8, 7.6, 3.2 Hz, 1H), 1.64 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.3, 128.7, 127.8, 124.8, 69.2, 61.6, 33.4, 30.9; IR: (ATR) 3292, 3053, 3036, 2990, 2982, 1418, 1341, 1182, 1096, 974 cm^{-1}; HRMS: (EI) calcd for ($C_{10}H_{13}NO_3S$) 227.0616 (M^+) found *m*/*z* 227.0613

4,4-dimethyl-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (2p)

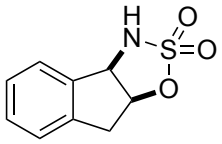


Condition B: According to the typical procedure, the reaction using 2-isopropylphenyl sulfamate (104.0 mg, 0.48 mmol), $MeNO_2$ (2.5 mL), and NIS (250.1 mg, 1.11 mmol) was conducted for 48 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 80:20) gave the product as a colorless solid (66.9 mg, 65% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30–7.15 (m, 3H), 6.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.92 (brs, 1H), 1.73 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 149.3, 129.2, 127.9, 126.4, 125.6, 119.1, 60.2, 30.7

The analytical data for this compound were in excellent agreement with the reported data.[4]

3,3a,8,8a-tetrahydroindeno[1,2-*d*][1,2,3]oxathiazole 2,2-dioxide (2q)

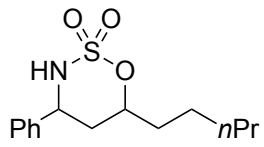


Condition A: According to the typical procedure, the reaction using NaI (187.6 mg, 1.25 mmol), MeCN (2.5 mL), 2,3-dihydro-1*H*-inden-2-yl sulfamate (105.7 mg, 0.50 mmol), and *t*BuOCl (141 μL, 1.50 mmol) was conducted for 8 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 60:40 then CH_2Cl_2/Et_2O = 95:5) gave the product as a colorless solid (53.1 mg, 50% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.44–7.17 (m, 4H), 5.52 (ddd, *J* = 6.4, 6.4, 2.4 Hz, 1H), 5.31 (dd, *J* = 6.4, 6.4 Hz, 1H), 4.58–4.48 (m, 1H), 3.54–3.40 (m, 2H); ^{13}C NMR: (100 MHz, CD_3OD) δ 141.1, 140.0, 130.4, 128.7, 126.7, 126.2, 87.7, 65.6, 38.5

The analytical data for this compound were in excellent agreement with the reported data.[7]

6-pentyl-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide (2r)



Condition A: According to the typical procedure, the reaction using NaI (166.2 mg, 1.11 mmol), MeCN (2.5 mL), 1-phenyloctan-3-yl sulfamate (142.5 mg, 0.50 mmol), and *t*BuOCl (124 μL, 1.50 mmol) was conducted for 8 h. The diastereomeric ratio of the product was determined by ^{1}H NMR analysis of the crude product (*cis*/*trans* = 59:41). Purification by flash column chromatography on silica gel (hexane/EtOAc = 85:15) gave the *cis*-isomer as a colorless solid (67.1 mg, 47% yield) and the *trans*-isomer as a colorless solid (42.8 mg, 30% yield).

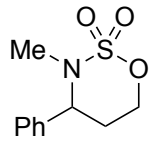
Condition B: According to the typical procedure, the reaction using 1-phenyloctan-3-yl sulfamate (138.8 mg, 0.49 mmol), $MeNO_2$ (2.5 mL), and NIS (339.9 mg, 1.51 mmol) was conducted for 8 h. The diastereomeric ratio of the product was determined by ^{1}H NMR analysis of the crude product (*cis*/*trans* = 73:27). Purification by flash column chromatography on silica gel (hexane/EtOAc = 85:15) gave the *cis*-isomer as a colorless solid (96.6 mg, 68% yield) and the *trans*-isomer as a colorless solid (26.3 mg, 19% yield).

***cis*-isomer:** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.44–7.23 (m, 5H), 4.90–4.83 (m, 1H), 4.79 (ddd, *J* = 12.0, 9.6, 2.8 Hz, 1H), 4.33 (brd, *J* = 9.6 Hz, 1H), 2.06 (ddd, *J* = 14.8, 3.2, 3.2 Hz, 1H), 1.91 (ddd, *J* = 18.4, 12.0, 12.0 Hz, 1H), 1.87–1.73 (m, 1H), 1.73–1.60 (m, 1H), 1.56–1.17 (m, 6H), 0.90 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.1, 129.0, 128.7, 126.3, 84.4, 58.2, 36.2, 35.1, 31.2, 24.1, 22.4, 13.9

The analytical data for this compound were in excellent agreement with the reported data.[8]

***trans*-isomer:** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 4.94–4.77 (m, 2H), 4.62 (brd, *J* = 8.4 Hz, 1H), 2.38 (ddd, *J* = 14.4, 8.8, 4.8 Hz, 1H), 2.25–2.13 (m, 1H), 2.09 (ddd, *J* = 14.4, 5.6, 4.4 Hz, 1H), 1.77–1.63 (m, 1H), 1.62–1.49 (m, 1H), 1.48–1.15 (m, 5H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.1, 128.9, 128.4, 126.3, 84.0, 55.2, 33.7, 33.5, 31.2, 25.1, 22.4, 13.9; IR: (ATR) 3250, 2928, 2857, 1348, 1182, 847, 752 cm^{-1}; HRMS: (CI) calcd for ($C_{14}H_{22}NO_3S$) 284.1320 ($[M+H]^+$) found *m*/*z* 284.1318

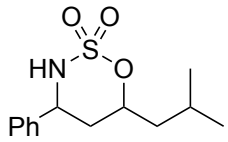
3-methyl-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide (5)



Condition A: According to the typical procedure, the reaction using NaI (65.9 mg, 0.44 mmol), MeCN (1.0 mL), 3-phenylpropyl methylsulfamate (47.0 mg, 0.20 mmol), and *t*BuOCl (50 μL, 0.44 mmol) was conducted for 8 h. The crude product was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard (54% yield, 31% rsm). Purification by flash column chromatography on silica gel (hexane/EtOAc = 70:30) gave the product as a colorless liquid (21.7 mg, 48% yield).

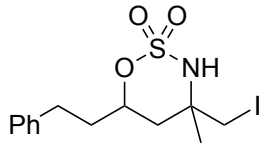
Condition B: According to the typical procedure, the reaction using 3-phenylpropyl methylsulfamate (47.5 mg, 0.21 mmol), $MeNO_2$ (1.0 mL), and NIS (137.4 mg, 0.61 mmol) was conducted for 8 h. The crude product was analyzed by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard (43% yield, 55% rsm).
^1H NMR: (400 MHz, $CDCl_3$) δ 7.46–7.30 (m, 5H), 4.83 (ddd, *J* = 13.6, 11.2, 2.4 Hz, 1H), 4.78 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.57 (ddd, *J* = 11.2, 5.2, 2.4 Hz, 1H), 2.58–2.41 (m, 1H), 2.50 (s, 3H), 1.90 (dddd, *J* = 14.4, 2.4, 2.4, 2.4 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 137.3, 129.1, 128.8, 127.4, 71.6, 64.1, 32.4, 27.8; IR: (ATR) 2928, 1379, 1354, 1192, 1167, 1013, 995, 872, 820, 783, 762 cm^{-1}; HRMS: (CI) calcd for ($C_{10}H_{14}NO_3S$) 228.0694 ($[M+H]^+$) found *m*/*z* 228.0695

6-isobutyl-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide (2s)



***cis*-isomer:** ^1H NMR: (400 MHz, $CDCl_3$) δ 7.46–7.29 (m, 5H), 5.00–4.91 (m, 1H), 4.81 (ddd, *J* = 12.0, 9.2, 2.8 Hz, 1H), 4.20 (brd, *J* = 9.2 Hz, 1H), 2.05 (ddd, *J* = 14.4, 2.8, 2.8 Hz, 1H) 1.96–1.72 (m, 3H), 1.44 (ddd, *J* = 14.0, 8.4, 4.0 Hz, 1H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.0, 129.1, 128.9, 126.3, 82.8, 58.2, 44.1, 36.6, 23.7, 22.9, 21.8
The analytical data for this compound were in excellent agreement with the reported data.[8]
***trans*-isomer:** ^1H NMR: (400 MHz, $CDCl_3$) δ 7.50–7.15 (m, 5H), 4.99–4.82 (m, 2H), 4.60 (brd, *J* = 8.4 Hz, 1H), 2.39 (ddd, *J* = 14.0, 8.8, 4.8 Hz, 1H), 2.21 (ddd, *J* = 14.0, 9.6, 5.2 Hz, 1H), 2.06 (ddd, *J* = 14.8, 5.6, 5.6 Hz, 1H), 1.93–1.87 (m, 1H), 1.47–1.39 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H) , 0.96 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.1, 129.0, 128.4, 126.3, 82.2, 55.2, 42.4, 33.9, 24.3, 22.9, 21.6; HRMS: (CI) calcd for ($C_{13}H_{20}NO_3S$) 270.1164 ($[M+H]^+$) found *m*/*z* 270.1166

4-(iodomethyl)-4-methyl-6-phenethyl-1,2,3-oxathiazinane 2,2-dioxide (2s'-I)

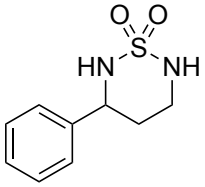


major isomer: mp: 107.8–108.2 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2H), 7.28–7.14 (m, 3H), 4.83 (dddd, *J* = 12.0, 8.8, 4.0, 2.0 Hz, 1H), 4.34 (brs, 1H), 3.38 (d, *J* = 10.4 Hz, 1H), 3.30 (d, *J* = 10.4 Hz, 1H), 2.92–2.82 (m, 1H), 2.81–2.71 (m, 1H), 2.18–2.06 (m, 1H), 1.98–1.86 (m, 2H), 1.63 (s, 3H), 1.53 (dd, *J* = 14.0, 2.0 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 140.2, 128.7, 128.5, 126.4, 80.0, 56.1, 39.1, 36.9, 30.7, 23.2, 20.3; IR: (ATR) 3246, 2922, 1356, 1163, 887, 762 cm^{-1}; HRMS: (EI) calcd for ($C_{13}H_{18}INO_3S$) 395.0052 (M^+) found *m*/*z* 395.0053

9. Intramolecular C−H amination of *N*-alkylsulfamides

Typical procedure: A heat-gun-dried reaction flask containing a magnetic stir bar was charged with NIS (1.25 mmol), *N*-alkylsulfamide (0.50 mmol), and $MeNO_2$ (2.5 mL). The mixture was stirred at room temperature for 4 h on the benchtop in the presence of a fluorescent light on the ceiling. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 15 mL), and the mixture was extracted with Et_2O (3 x 15 mL). Collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel gave the product.

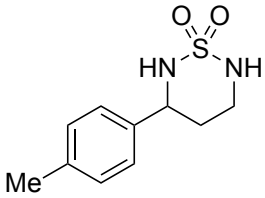
3-phenyl-1,2,6-thiadiazinane 1,1-dioxide (11a)



According to the typical procedure, the reaction using NIS (282.8 mg, 1.26 mmol), *N*-(3-phenylpropyl)sulfamide (106.1 mg, 0.50 mmol), and $MeNO_2$ (2.5 mL) was conducted. Purification by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 100:0 to 80:20) gave the product as a colorless solid (91.5 mg, 87% yield).

mp: 131.0–133.2 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.44–7.25 (m, 5H), 5.00 (brd, *J* = 8.0 Hz, 1H), 4.89–4.69 (m, 1H), 4.63 (ddd, *J* = 11.2, 8.0, 3.2 Hz, 1H), 3.61–3.38 (m, 2H), 1.84–1.64 (m, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 141.4, 129.5, 128.8, 127.4, 60.5, 44.9, 31.3; IR: (ATR) 3264, 1456, 1433, 1412, 1329, 1169, 1063, 808, 718 cm^{-1}; MS: (EI) *m*/*z* 212 (M^+, 10), 119 (58), 105 (61), 104 (100), 78 (23), 77 (27); HRMS: (EI) calcd for ($C_9H_{12}N_2O_2S$) 212.0619 (M^+), found *m*/*z* 212.0621

3-(4-methylphenyl)-1,2,6-thiadiazinane 1,1-dioxide (11b)

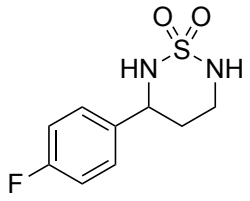


According to the typical procedure, the reaction using NIS (282.3 mg, 1.25 mmol), *N*-(3-(4-methylphenyl)propyl)sulfamide (114.0 mg, 0.50 mmol), and $MeNO_2$ (2.5 mL) was conducted. Purification by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 100:0 to 80:20) gave the product as a colorless solid (93.9 mg, 83% yield).

mp: 184.6–185.8 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.93 (brd, *J* = 7.6 Hz, 1H), 4.84–4.70 (m, 1H), 4.58 (ddd, *J* = 11.2, 8.0, 3.2 Hz, 1H), 3.61–3.39 (m, 2H), 2.32 (s, 3H), 1.83–1.64 (m, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 138.7, 138.5, 130.1, 127.3, 60.3, 45.0, 31.4, 20.9; IR: (ATR) 3233, 3156, 1450, 1404, 1339, 1161, 1043, 928, 754 cm^{-1}; MS: (EI) *m*/*z* 226 (M^+, 9), 133 (39), 119 (98), 118 (100), 91 (31); HRMS: (EI) calcd for

($C_{10}H_{14}N_2O_2S$) 226.0776 (M^+), found *m*/*z* 226.0772

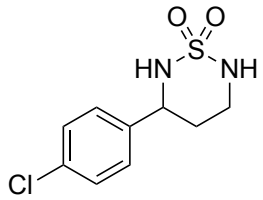
3-(4-fluorophenyl)-1,2,6-thiadiazinane 1,1-dioxide (11c)



According to the typical procedure, the reaction using NIS (282.4 mg, 1.26 mmol), *N*-(3-(4-fluorophenyl)propyl)sulfamide (114.2 mg, 0.49 mmol), and $MeNO_2$ (2.5 mL) was conducted. Purification by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 100:0 to 80:20) gave the product as a colorless solid (95.6 mg, 84% yield).

mp: 133.3–135.5 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.47–7.28 (m, 2H), 7.20–7.00 (m, 2H), 5.00 (brd, *J* = 8.0 Hz, 1H), 4.90–4.71 (m, 1H), 4.63 (ddd, *J* = 11.2, 8.0, 3.2 Hz, 1H), 3.61–3.35 (m, 2H), 1.86–1.64 (m, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 163.0 (d, J_{CF} = 242.9 Hz), 137.5 (d, J_{CF} = 3.3 Hz), 129.5 (d, J_{CF} = 8.2 Hz), 116.1 (d, J_{CF} = 21.4 Hz), 59.8, 44.9, 31.2; ^{19}F NMR: (377 MHz, CD_3CN) δ −116.8; IR: (ATR) 3237, 3154, 1510, 1450, 1404, 1337, 1227, 1159, 1067, 1042, 928, 831, 756 cm^{-1}; MS: (EI) *m*/*z* 230 (M^+, 6), 138 (21), 137 (46), 123 (64), 122 (100); HRMS: (EI) calcd for ($C_9H_{11}FN_2O_2S$) 230.0525 (M^+), found *m*/*z* 230.0524

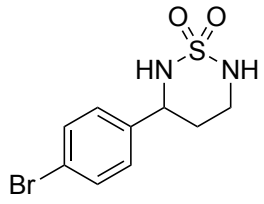
3-(4-chlorophenyl)-1,2,6-thiadiazinane 1,1-dioxide (11d)



According to the typical procedure, the reaction using NIS (284.3 mg, 1.26 mmol), *N*-(3-(4-chlorophenyl)propyl)sulfamide (123.3 mg, 0.50 mmol), and $MeNO_2$ (2.5 mL) was conducted. Purification by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 100:0 to 80:20) gave a solid, which was washed with cold mixed solvent of Et_2O/hexane (9:1) (3 x 2 mL) gave the product as a colorless solid (98.4 mg, 80% yield).

mp: 165.8–167.7 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.49–7.29 (m, 4H), 5.02 (brd, *J* = 8.0 Hz, 1H), 4.89–4.74 (m, 1H), 4.63 (ddd, *J* = 11.2, 8.0, 3.2 Hz, 1H), 3.60–3.39 (m, 2H), 1.84–1.61 (m, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 140.2, 134.0, 129.5, 129.2, 59.8, 44.8, 31.1; IR: (ATR) 3235, 3156, 1491, 1402, 1337, 1161, 1069, 1043, 1013, 926, 833, 760 cm^{-1}; MS: (EI) *m*/*z* 248 ($[M+2]^+$, 4), 246 (M^+, 10), 154 (21), 153 (46), 141 (31), 140 (45), 139 (98), 138 (100), 103 (21), 77 (26); HRMS: (EI) calcd for ($C_9H_{11}ClN_2O_2S$) 246.0230 (M^+), found *m*/*z* 246.0225

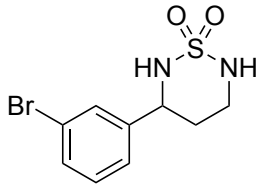
3-(4-bromophenyl)-1,2,6-thiadiazinane 1,1-dioxide (11e)



According to the typical procedure, the reaction using NIS (282.0 mg, 1.25 mmol), *N*-(3-(4-bromophenyl)propyl)sulfamide (145.9 mg, 0.50 mmol), and $MeNO_2$ (2.5 mL) was conducted. Purification by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 100:0 to 80:20) gave a solid, which was washed with cold mixed solvent of Et_2O/hexane (9:1) (3 x 2 mL) gave the product as a colorless solid (116.6 mg, 80% yield).

mp: 179.2–180.8 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.60–7.48 (m, 2H), 7.37–7.25 (m, 2H), 5.02 (brd, *J* = 8.0 Hz, 1H), 4.90–4.75 (m, 1H), 4.61 (ddd, *J* = 11.2, 8.0, 3.2, 1H), 3.60–3.40 (m, 2H), 1.86–1.62 (m, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 140.7, 132.5, 129.5, 122.1, 59.9, 44.8, 31.1; IR: (ATR) 3237, 3146, 1489, 1450, 1398, 1337, 1161, 1072, 1043, 1009, 947, 926, 829, 760 cm^{-1}; MS: (EI) *m*/*z* 292 ([M+2]$^+$, 14), 290 (M$^+$, 15), 199 (50), 198 (25), 197 (46), 185 (93), 184 (92), 183 (100), 182 (79), 119 (52), 104 (21), 103 (53), 102 (24), 77 (79), 76 (32), 75 (26), 70 (37), 51 (30), 50 (23); HRMS: (CI) calcd for ($C_9H_{12}BrN_2O_2S$) 290.9803 ([M+H]$^+$), found *m*/*z* 290.9810

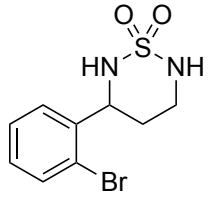
3-(3-bromophenyl)-1,2,6-thiadiazinane 1,1-dioxide (11f)



According to the typical procedure, the reaction using NIS (281.8 mg, 1.25 mmol), *N*-(3-(3-bromophenyl)propyl)sulfamide (145.8 mg, 0.50 mmol), and $MeNO_2$ (2.5 mL) was conducted. Purification by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 100:0 to 90:10) gave a solid, which was washed with cold mixed solvent of Et_2O/hexane (9:1) (3 x 2 mL) gave the product as a colorless solid (94.4 mg, 65% yield).

mp: 159.5–161.2 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.56 (dd, *J* = 1.6, 1.6 Hz, 1H), 7.50 (ddd, *J* = 7.6, 1.6, 1.6 Hz, 1H), 7.37 (ddd, *J* = 7.6, 1.6, 1.6 Hz, 1H), 7.31 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.04 (brd, *J* = 8.4 Hz, 1H), 4.88–4.77 (m, 1H), 4.63 (ddd, *J* = 11.6, 8.4, 3.2 Hz, 1H), 3.60–3.41 (m, 2H), 1.85–1.63 (m, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 143.9, 131.8, 131.5, 130.4, 126.4, 122.9, 59.9, 44.8, 31.2; IR: (ATR) 3244, 3138, 1408, 1337, 1161, 928, 766 cm^{-1}; MS: (EI) *m*/*z* 292 ([M+2]$^+$, 25), 290 (M$^+$, 26), 199 (40), 197 (39), 185 (89), 184 (81), 183 (100), 182 (62), 118 (21), 104 (25), 103 (43), 77 (70), 76 (28), 75 (21), 71 (25), 70 (23), 51 (25); HRMS: (EI) calcd for ($C_9H_{11}BrN_2O_2S$) 289.9725 (M$^+$), found *m*/*z* 289.9726

3-(2-bromophenyl)-1,2,6-thiadiazinane 1,1-dioxide (11g)

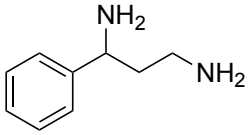


According to the typical procedure, the reaction using NIS (281.1 mg, 1.25 mmol), *N*-(3-(2-bromophenyl)propyl)sulfamide (146.2 mg, 0.50 mmol), and $MeNO_2$ (2.5 mL) was conducted. Purification by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 100:0 to 90:10) gave a solid, which was washed with cold mixed solvent of Et_2O/hexane (9:1) (3 x 2 mL) gave the product as a colorless solid (89.9 mg, 62% yield).

mp: 165.5–166.4 °C; ^{1}H NMR: (400 MHz, CD_3CN) δ 7.64 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56–7.34 (m, 2H), 7.33–7.19 (m, 1H), 5.14–4.95 (m, 2H), 4.94–4.78 (m, 1H), 3.65–3.39 (m, 2H), 1.86–1.60 (m, 2H); ^{13}C NMR: (100 MHz, CD_3CN) δ 139.9, 133.9, 130.7, 129.1, 128.7, 123.7, 59.8, 44.9, 30.4; IR: (ATR) 3246, 3213, 1445, 1408, 1337, 1161, 1036, 1026, 932, 816, 743 cm^{-1}; MS: (EI) *m*/*z* 292 ([M+2]$^+$, 9), 290 (M$^+$, 8), 264 (27), 262 (26), 211 (100), 199 (31), 198 (20), 197 (32), 185 (85), 184 (74), 183 (94), 182 (61), 119 (24), 118 (26), 104 (76), 103 (53), 102 (37), 91 (20), 77 (83), 76 (28), 75 (22), 71 (48), 51 (32); HRMS: (EI) calcd for ($C_9H_{11}BrN_2O_2S$) 289.9725 (M$^+$), found *m*/*z* 289.9727

10. Conversion of cyclic sulfamides to unprotected 1,3-diamines

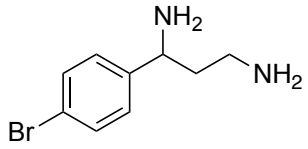
1-phenylpropane-1,3-diamine (12a)



According to the reported procedure,[15] a heat-gun-dried reaction flask containing a magnetic stir bar was charged with 3-phenyl-1,2,6-thiadiazinane 1,1-dioxide (106.0 mg, 0.50 mmol) and propane-1,3-diamine (1.5 mL) under nitrogen. The mixture was refluxed for 5 h. After cooling to room temperature, the mixture was diluted with 5 mL of $CHCl_3$ and 10 mL of water. The mixture was extracted with $CHCl_3$ (3 x 10 mL), and the combined organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the product as a yellow liquid (63.2 mg, 84% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.43–7.19 (m, 5H), 4.01 (dd, *J* = 6.8, 6.8 Hz, 1H), 2.79–2.66 (m, 2H), 1.88–1.72 (m, 2H), 1.45 (brs, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 146.5, 128.5, 127.0, 126.1, 54.4, 43.0, 39.6; IR: (ATR) 3354, 3287, 2928, 2864, 1601, 1493, 1454, 910, 764 cm^{-1}; HRMS: (DART) calcd for ($C_9H_{15}N_2$) 151.1235 ([M+H]$^+$), found *m*/*z* 151.1229

1-(4-bromophenyl)propane-1,3-diamine (12e)



According to the reported procedure,[15] a heat-gun-dried reaction flask containing a magnetic stir bar was charged with 3-(4-bromophenyl)-1,2,6-thiadiazinane 1,1-dioxide (145.8 mg, 0.50 mmol) and propane-1,3-diamine (1.5 mL) under nitrogen. The mixture was refluxed for 5 h. After cooling to room temperature, the mixture was diluted with 5 mL of $CHCl_3$ and 10 mL of water. The mixture was extracted with $CHCl_3$ (3 x 10 mL), and the combined organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the desired product as a yellow liquid (110.9 mg, 97% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.49–7.41 (m, 2H), 7.26–7.17 (m, 2H), 4.01 (dd, J = 6.8, 6.8 Hz, 1H), 2.78–2.65 (m, 2H), 1.84–1.69 (m, 2H), 1.38 (brs, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 145.4, 131.6, 128.0, 120.6, 53.8, 42.7, 39.4; IR: (ATR) 3364, 3281, 2922, 2851, 1589, 1485, 1406, 1070, 1009, 822 cm^{-1}; HRMS: (DART) calcd for ($C_9H_{14}BrN_2$) 229.0340 ($[M+H]^+$), found m/z 229.0334

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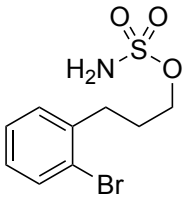
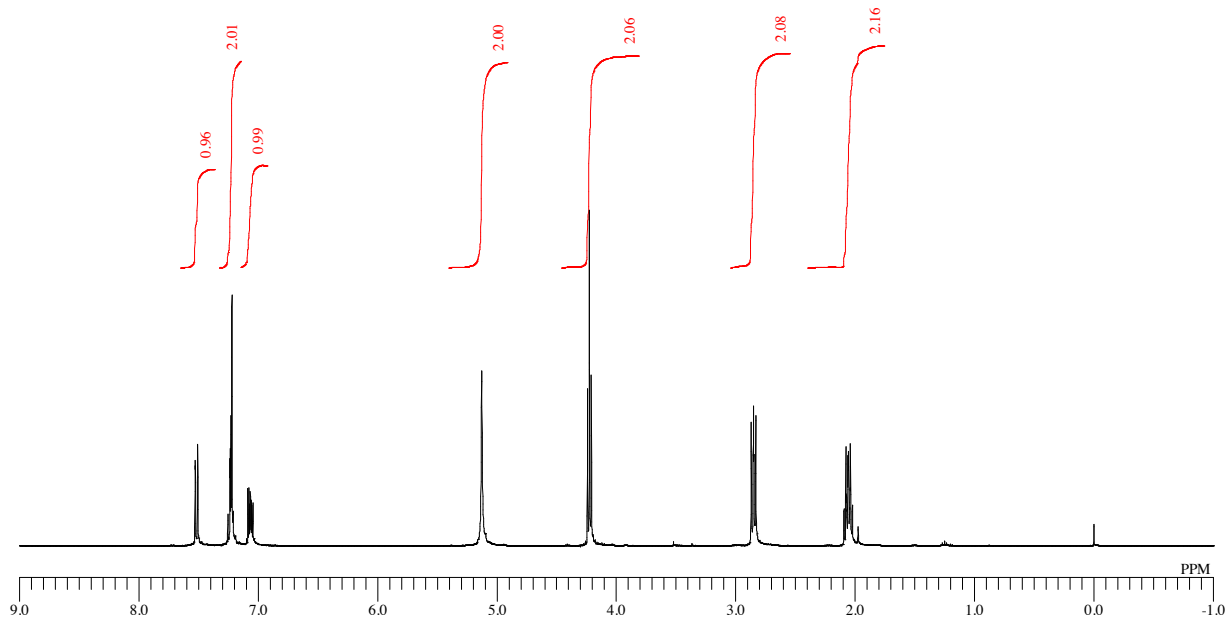
12. NMR spectra



1f

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



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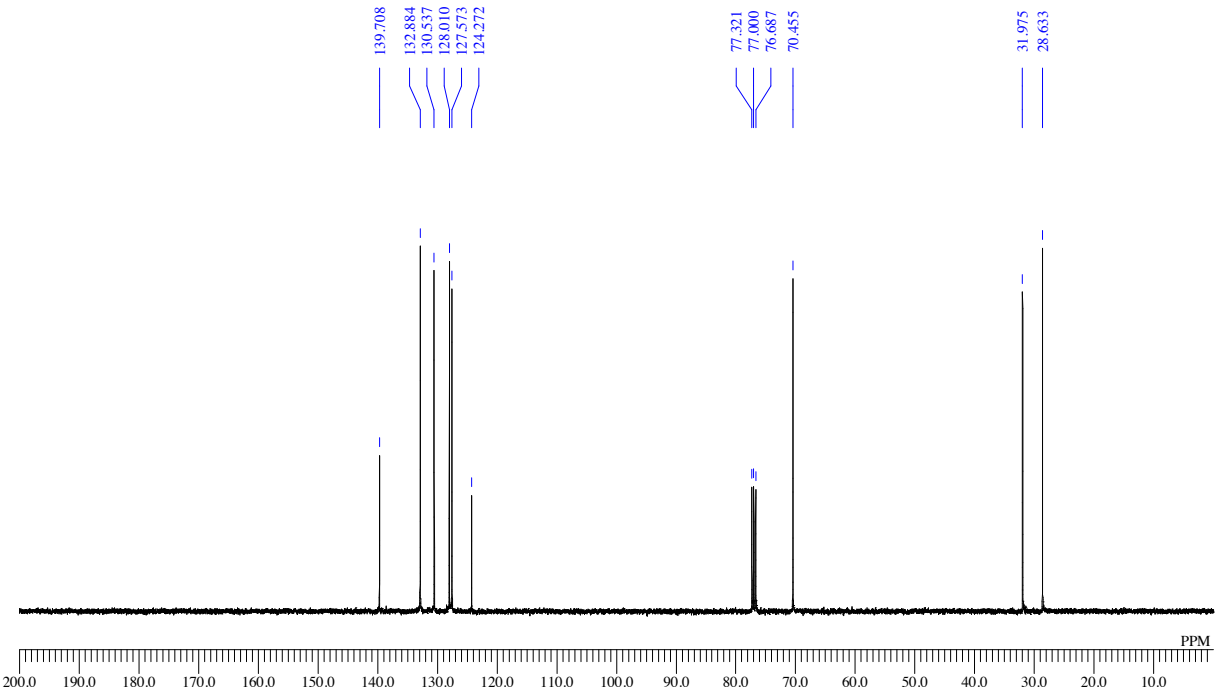
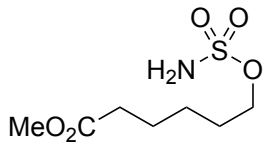
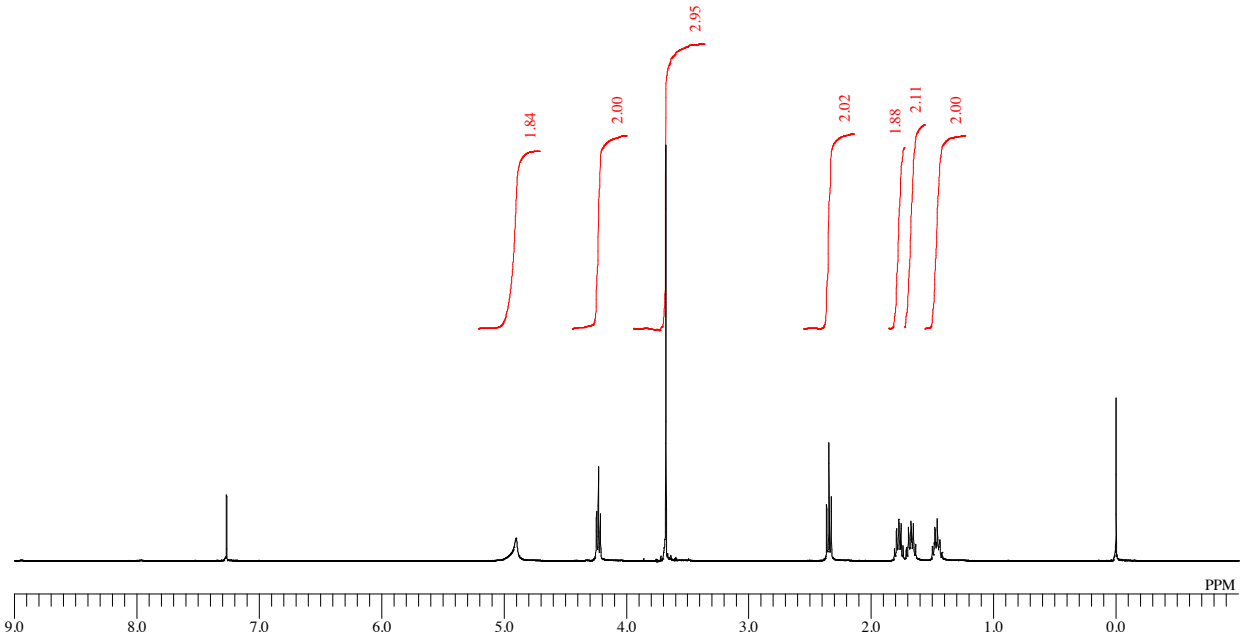


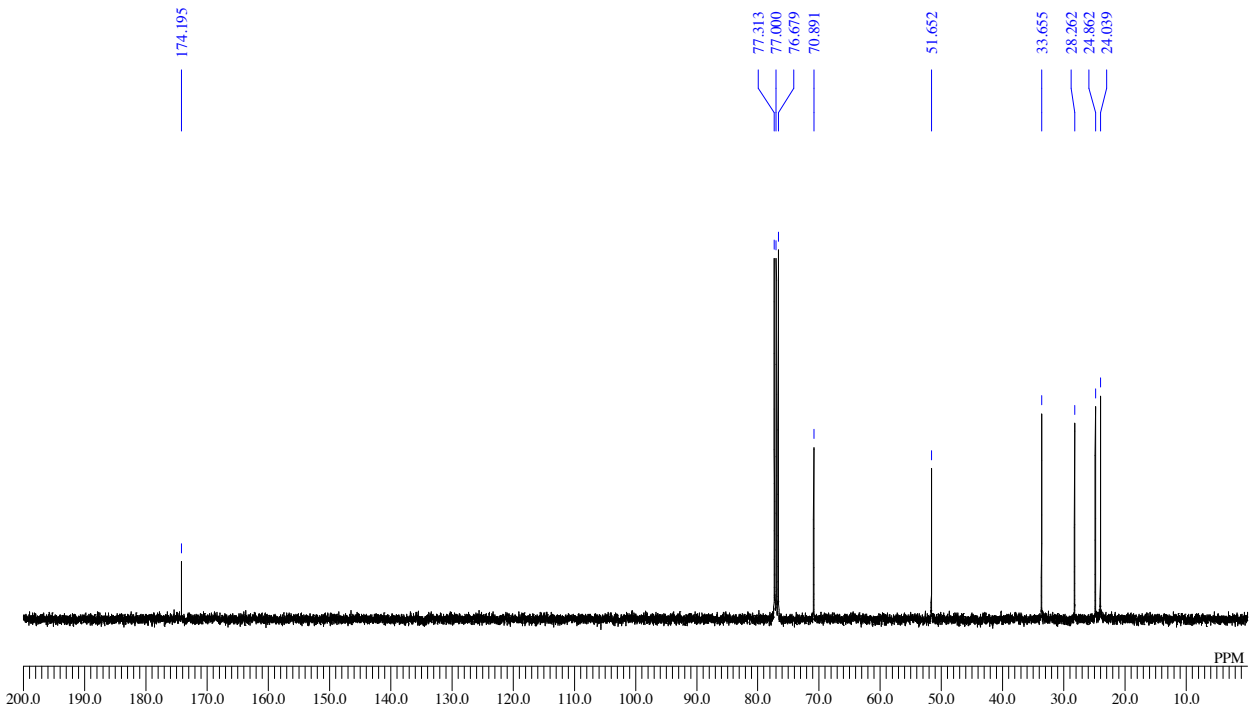


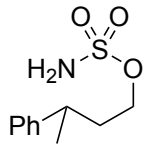
1j

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



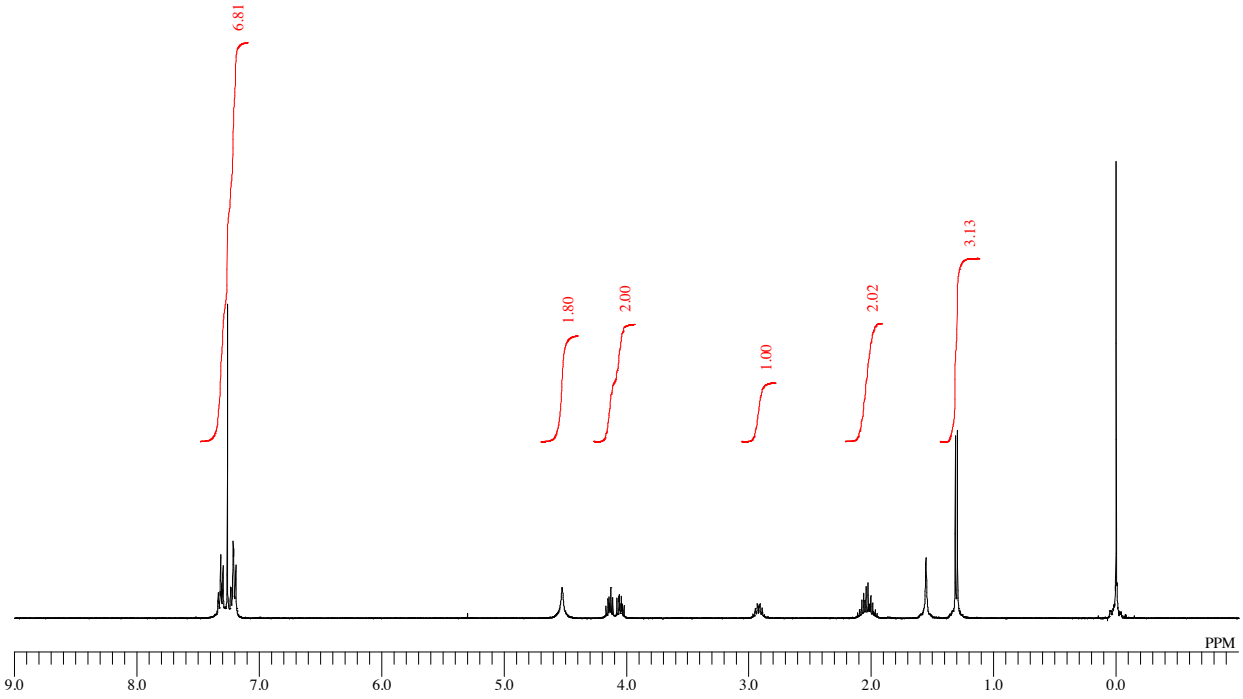
^{13}C NMR: (100 MHz, $CDCl_3$)



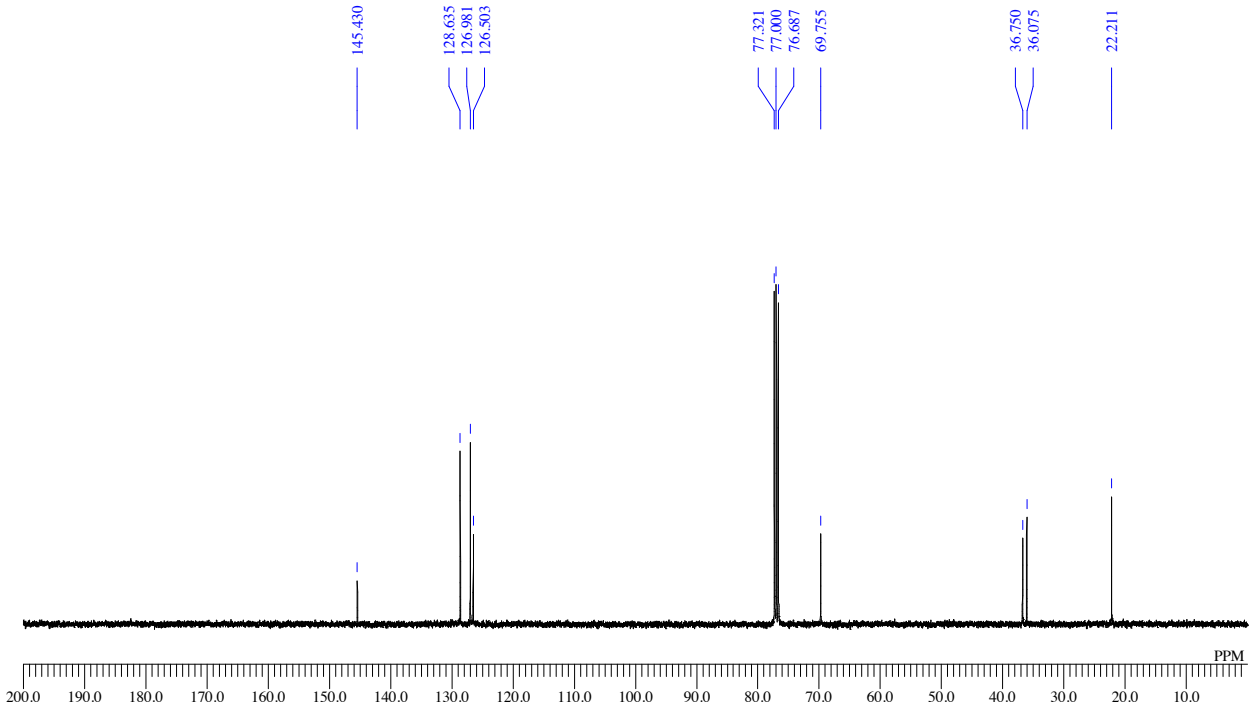


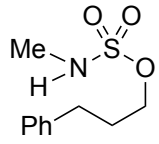
1o

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



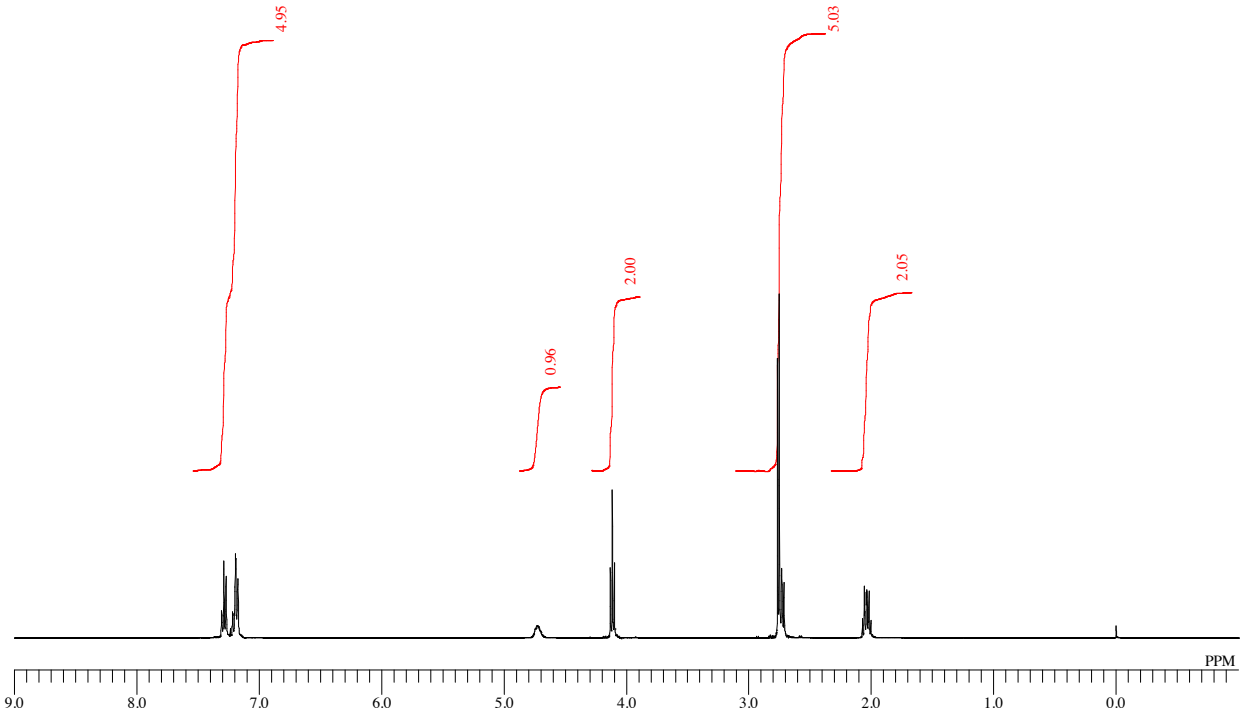
^{13}C NMR: (100 MHz, $CDCl_3$)



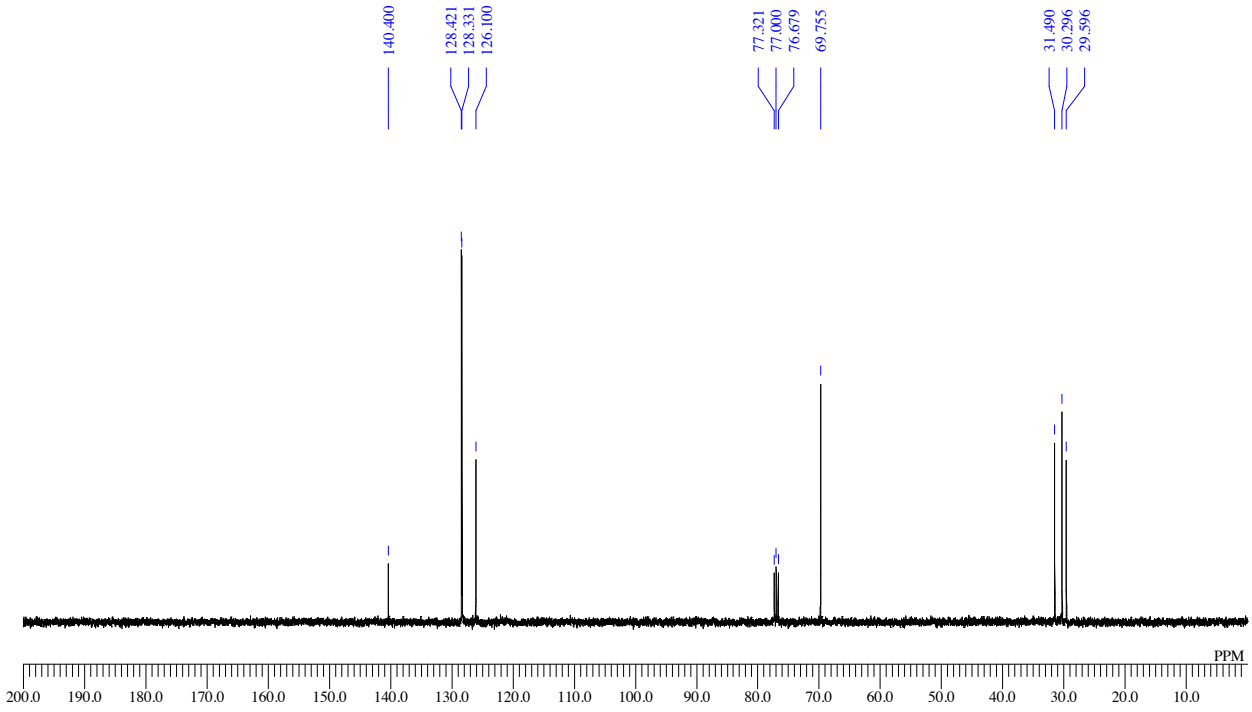


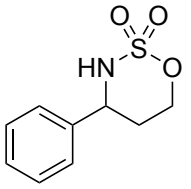
4

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



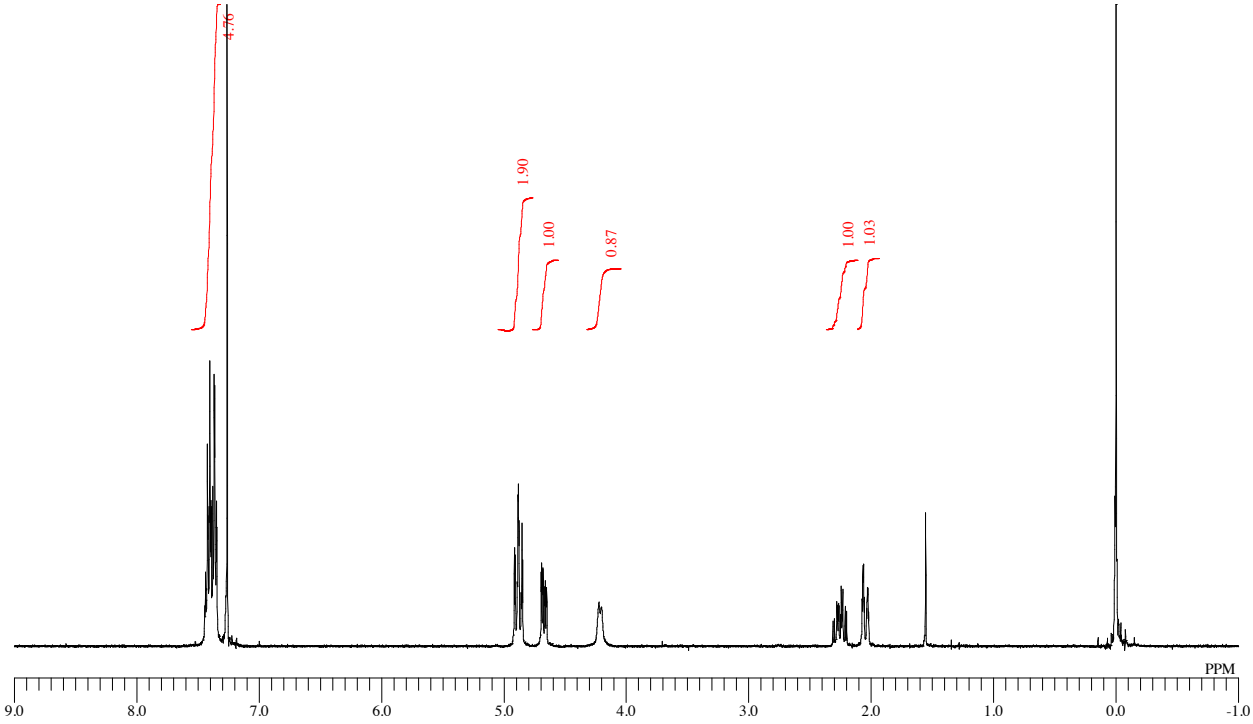
^{13}C NMR: (100 MHz, $CDCl_3$)



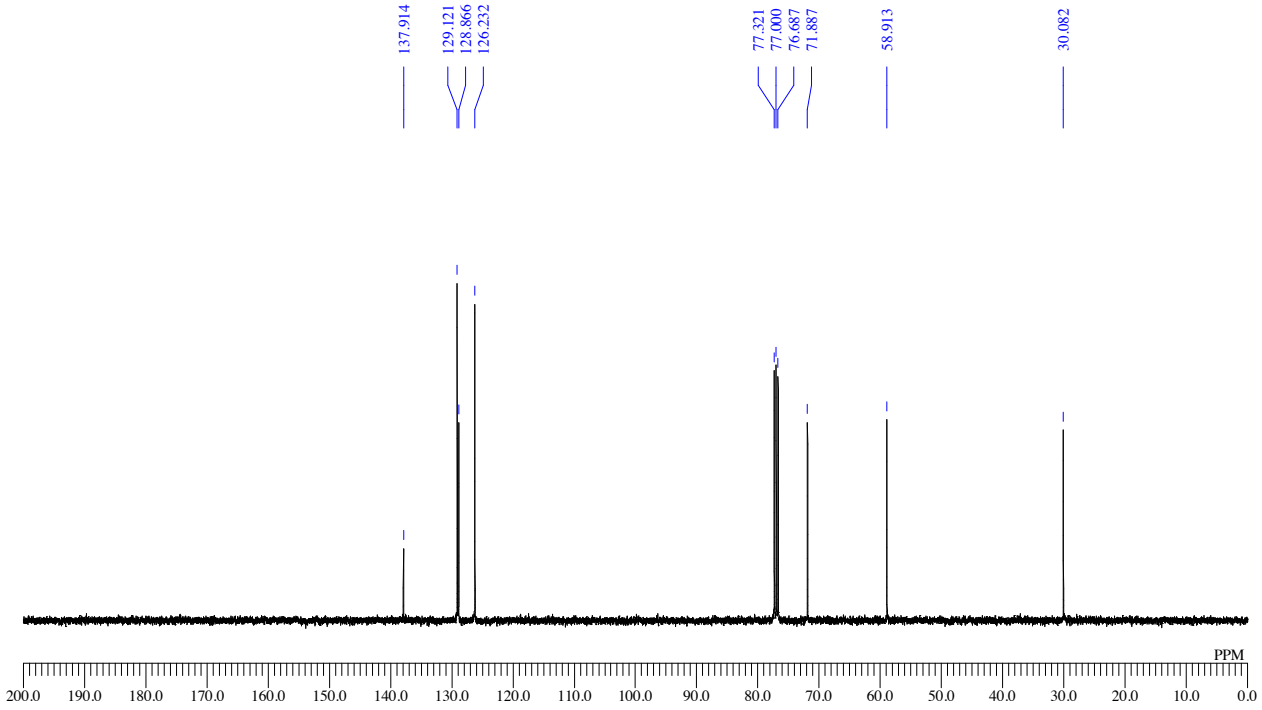


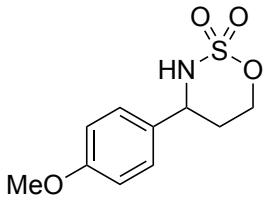
2a

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



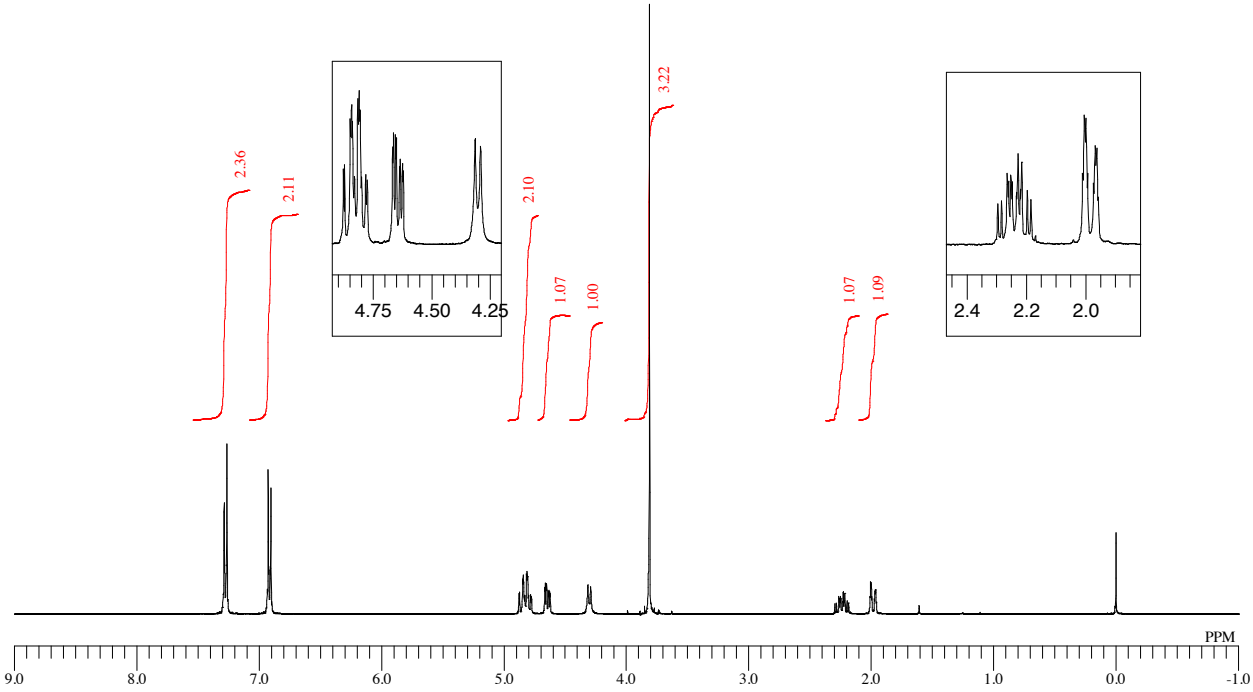
^{13}C NMR: (100 MHz, $CDCl_3$)



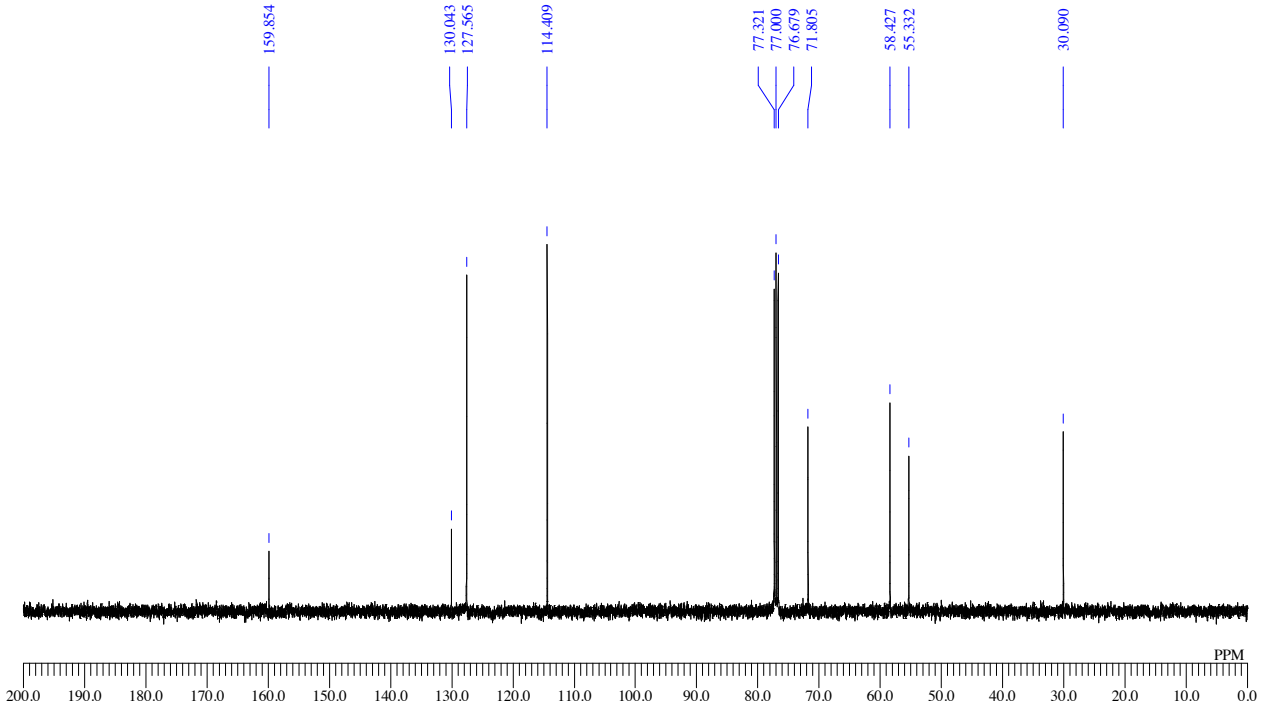


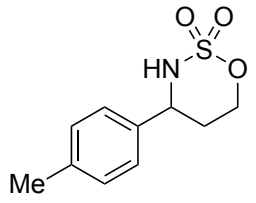
2b

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



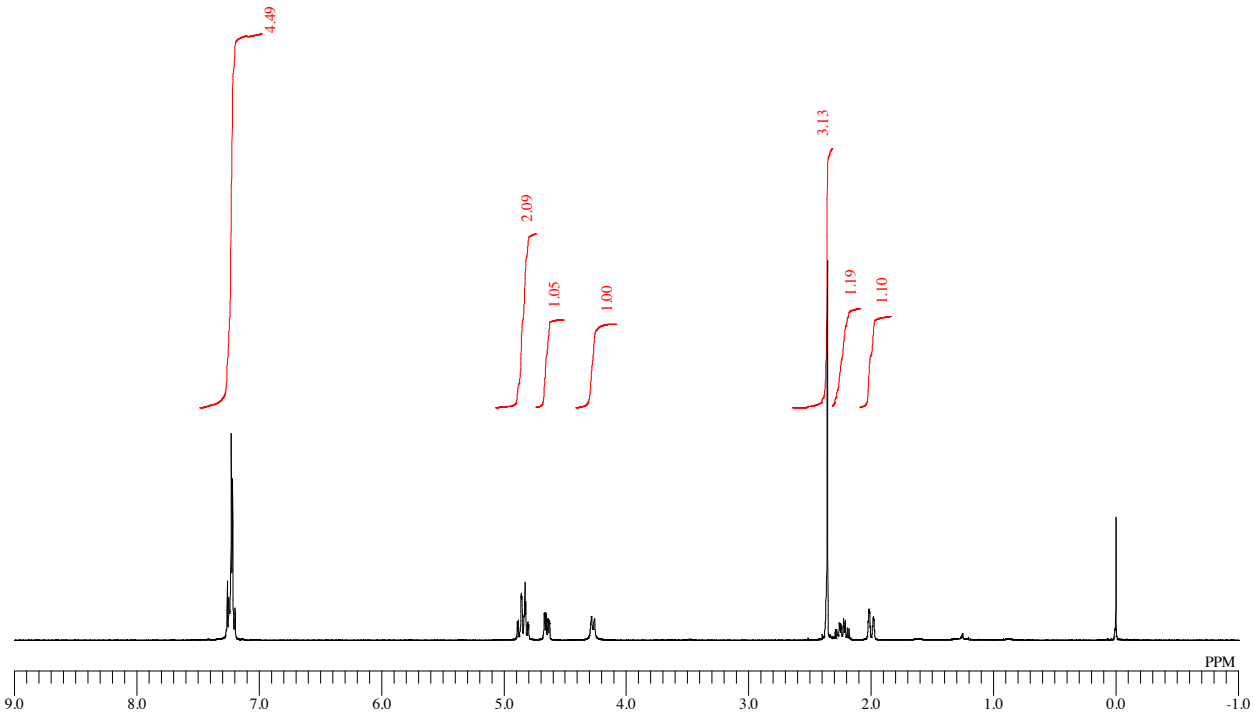
^{13}C NMR: (100 MHz, $CDCl_3$)



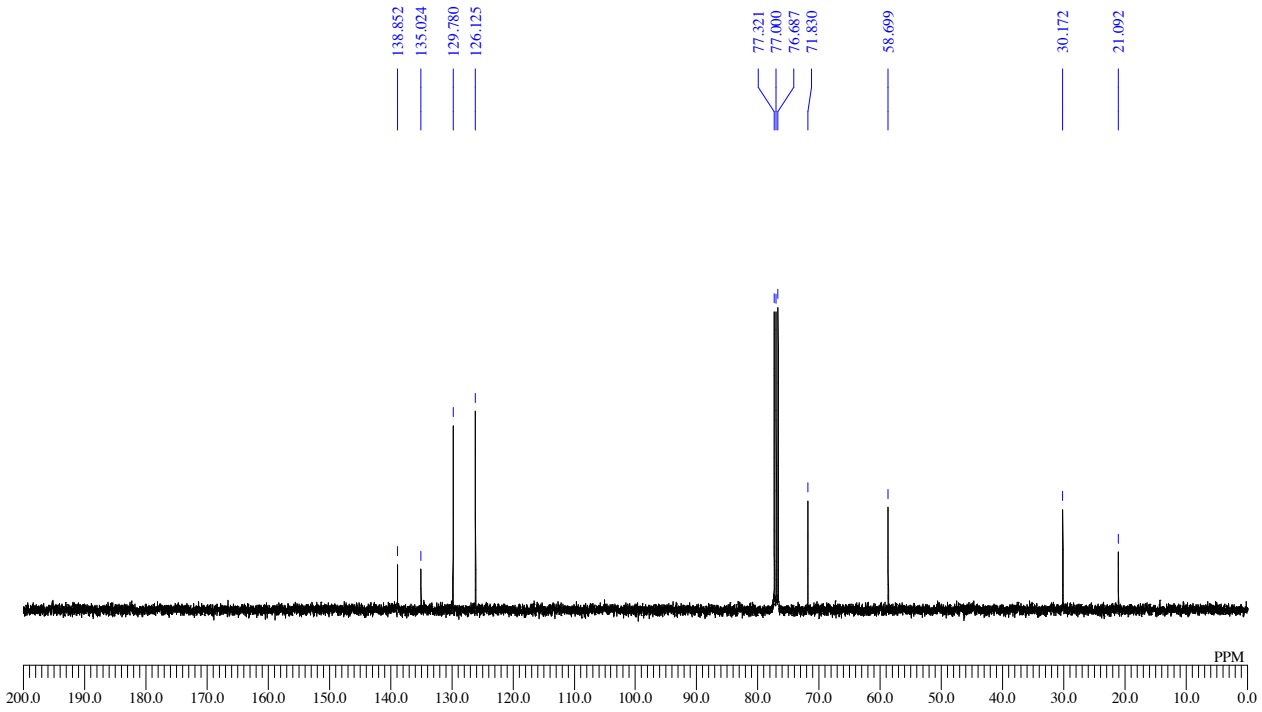


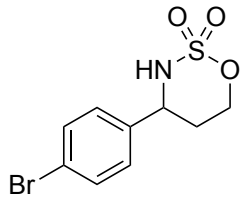
2c

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



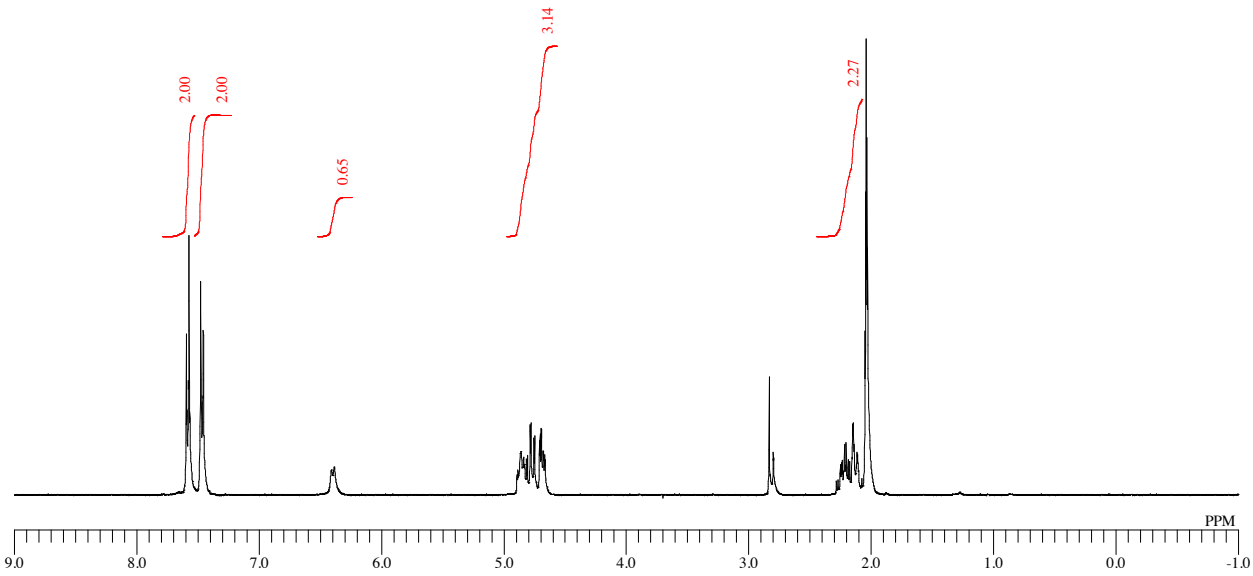
^{13}C NMR: (100 MHz, $CDCl_3$)



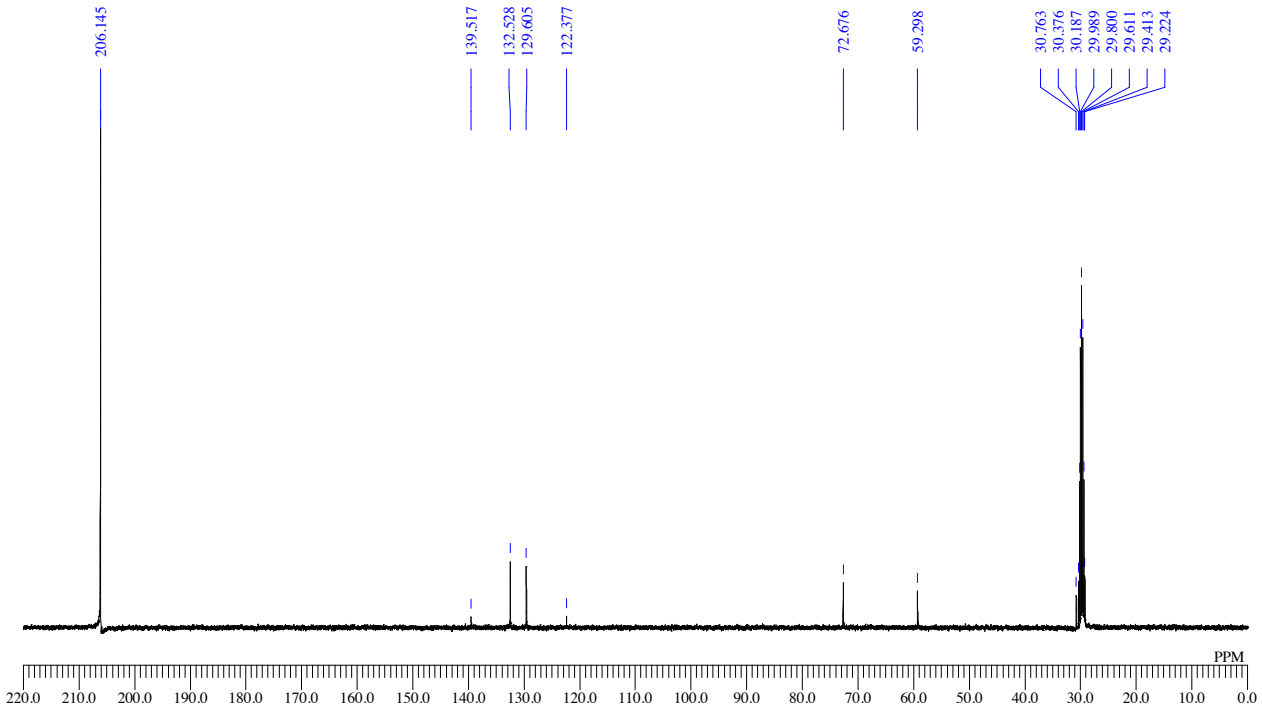


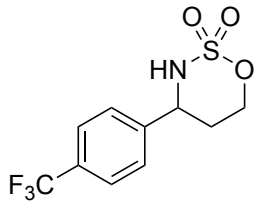
2d

^{1}H NMR: (400 MHz, acetone-d_6)



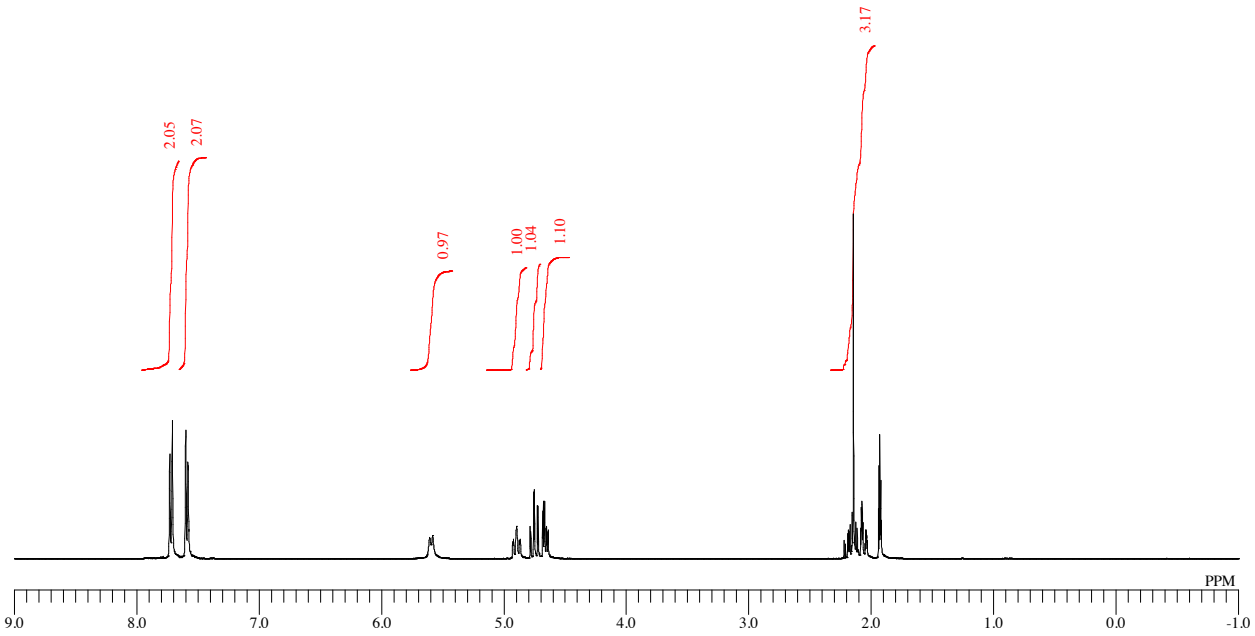
^{13}C NMR: (100 MHz, acetone-d_6)



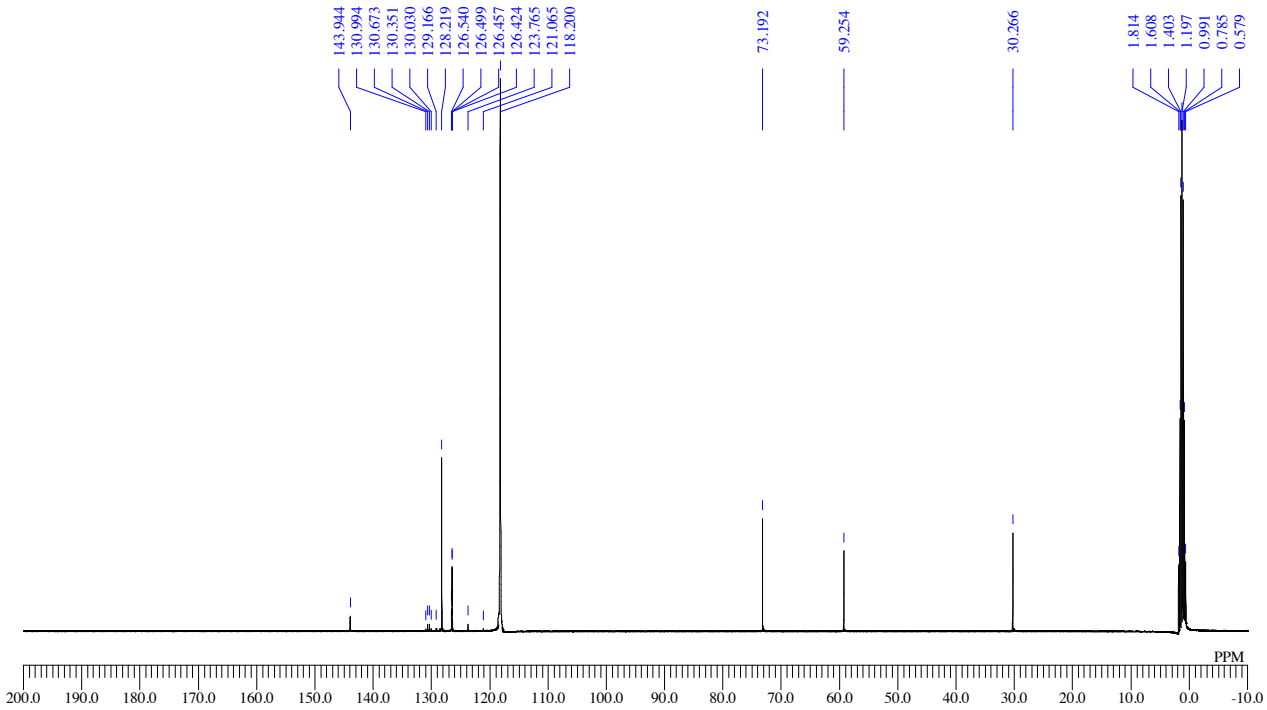


2e

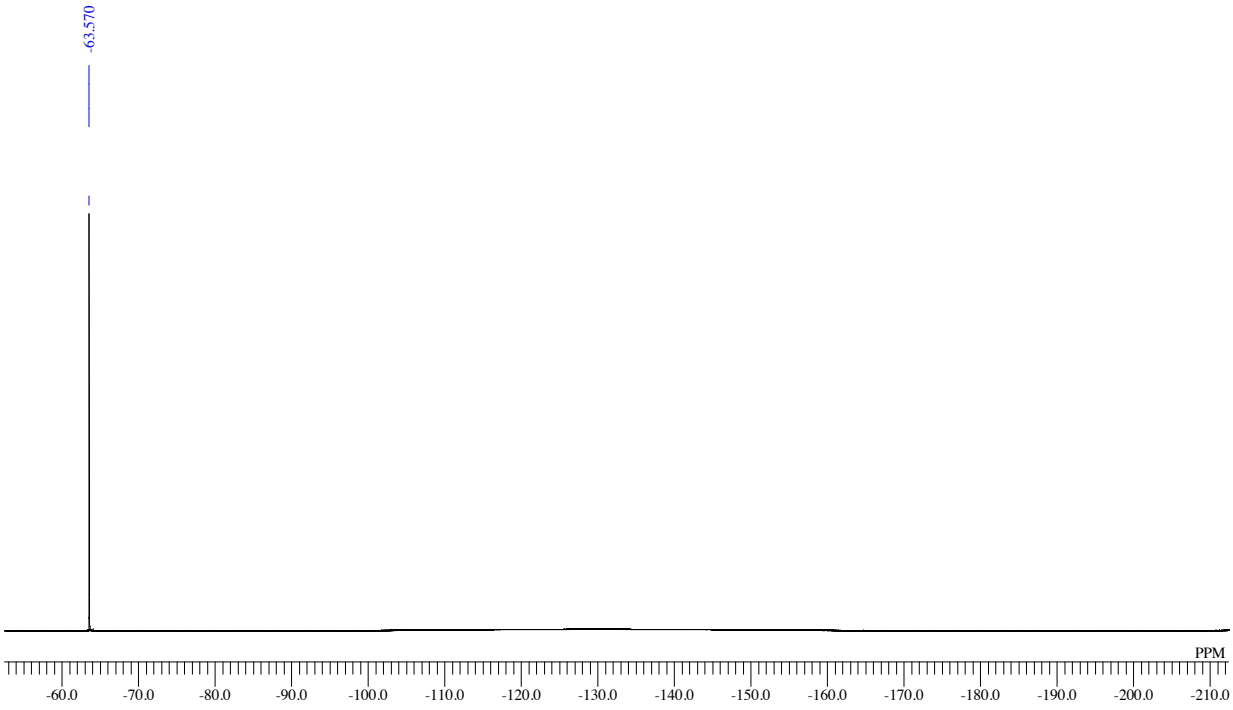
^{1}H NMR: (400 MHz, CD_3CN)

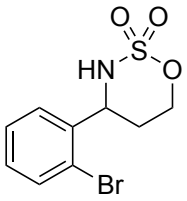


^{13}C NMR: (100 MHz, CD_3CN)



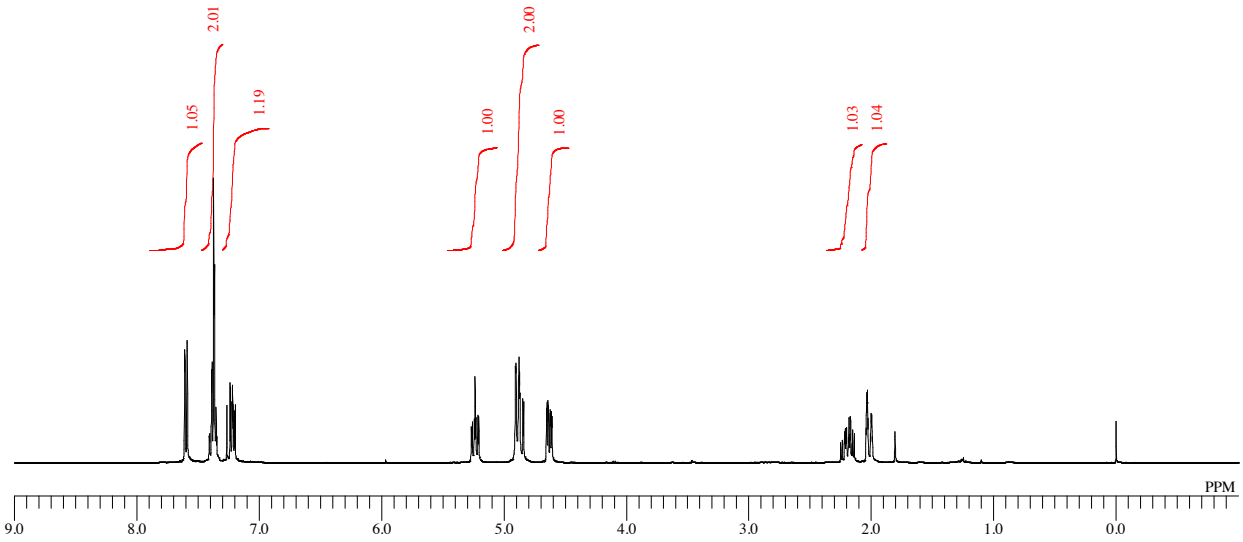
^{19}F NMR: (377 MHz, CD_3CN)



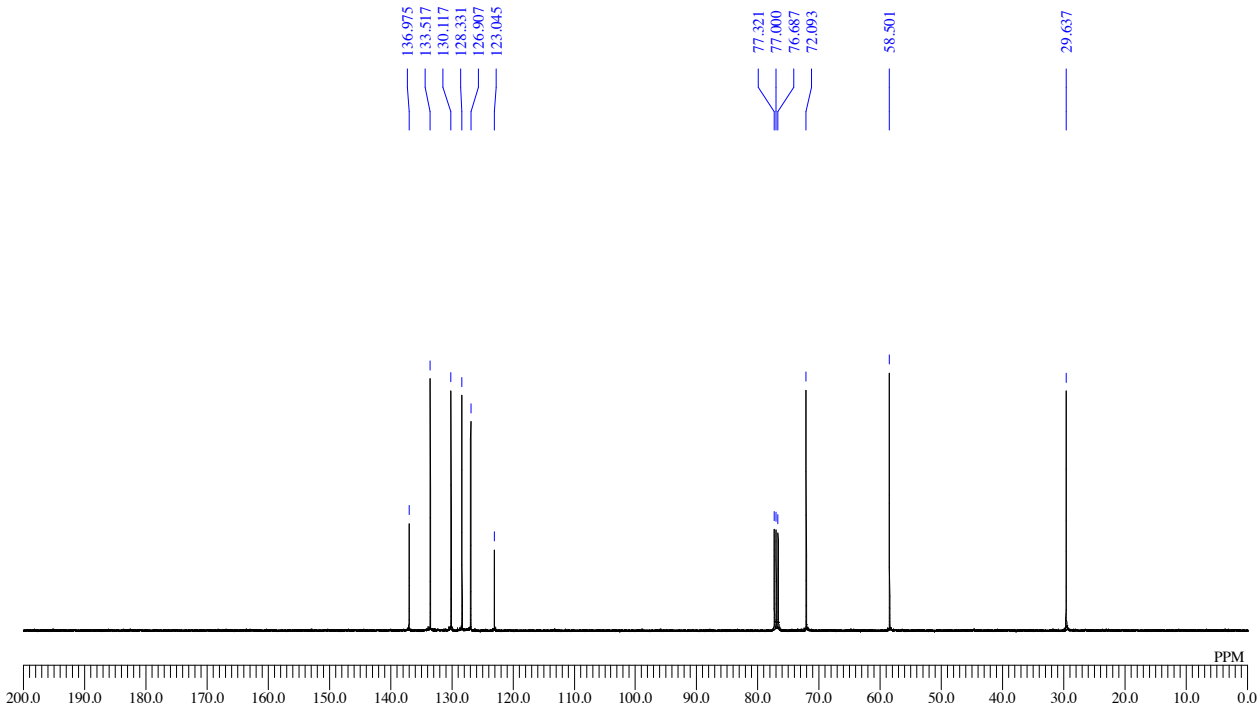


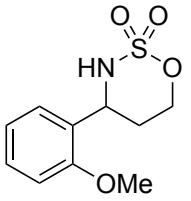
2f

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



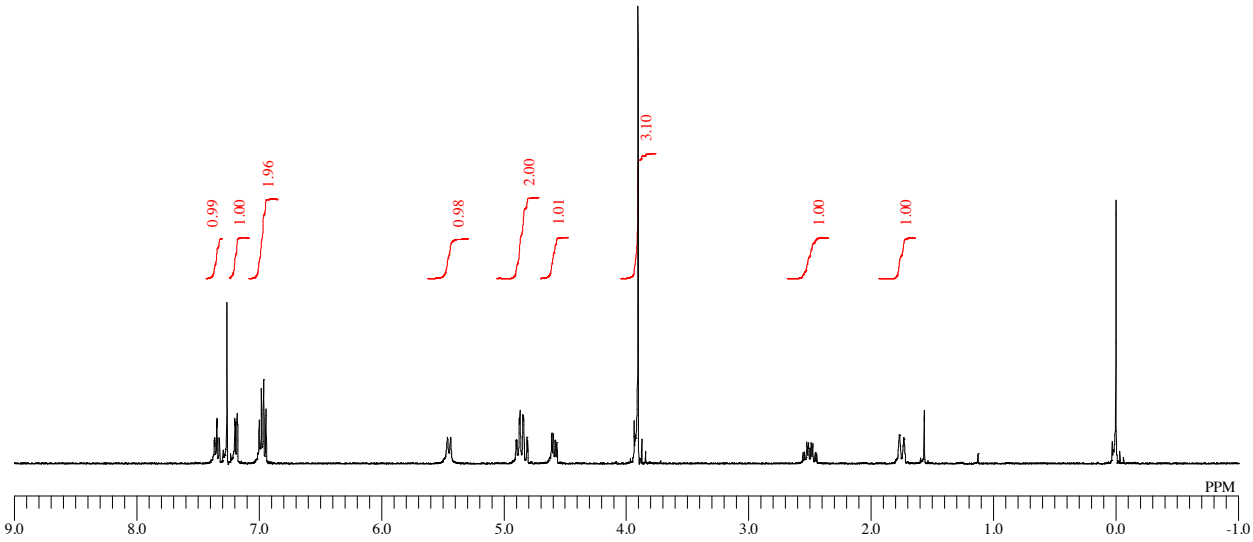
^{13}C NMR: (100 MHz, $CDCl_3$)



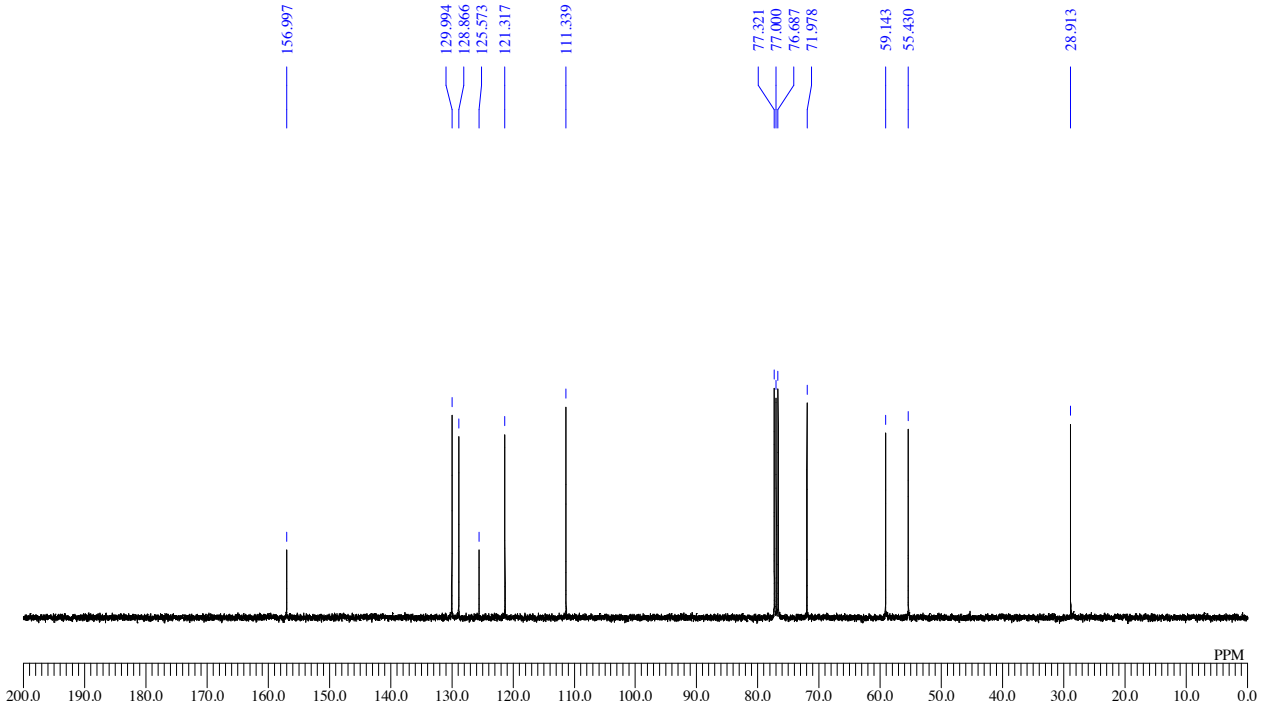


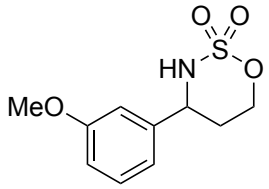
2g

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



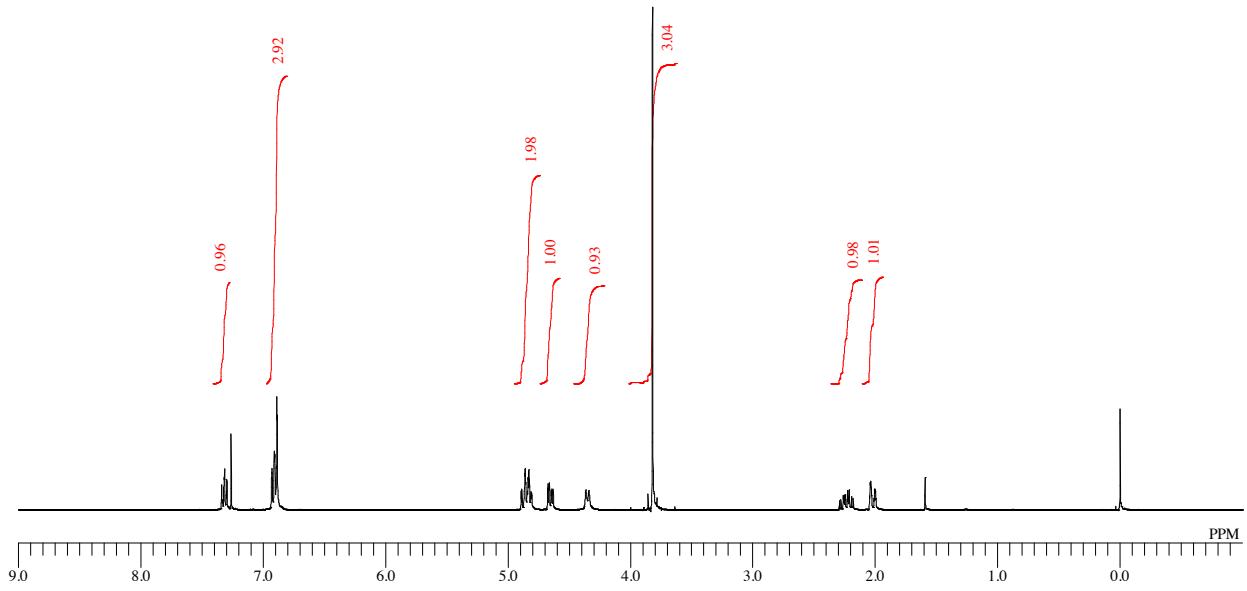
^{13}C NMR: (100 MHz, $CDCl_3$)



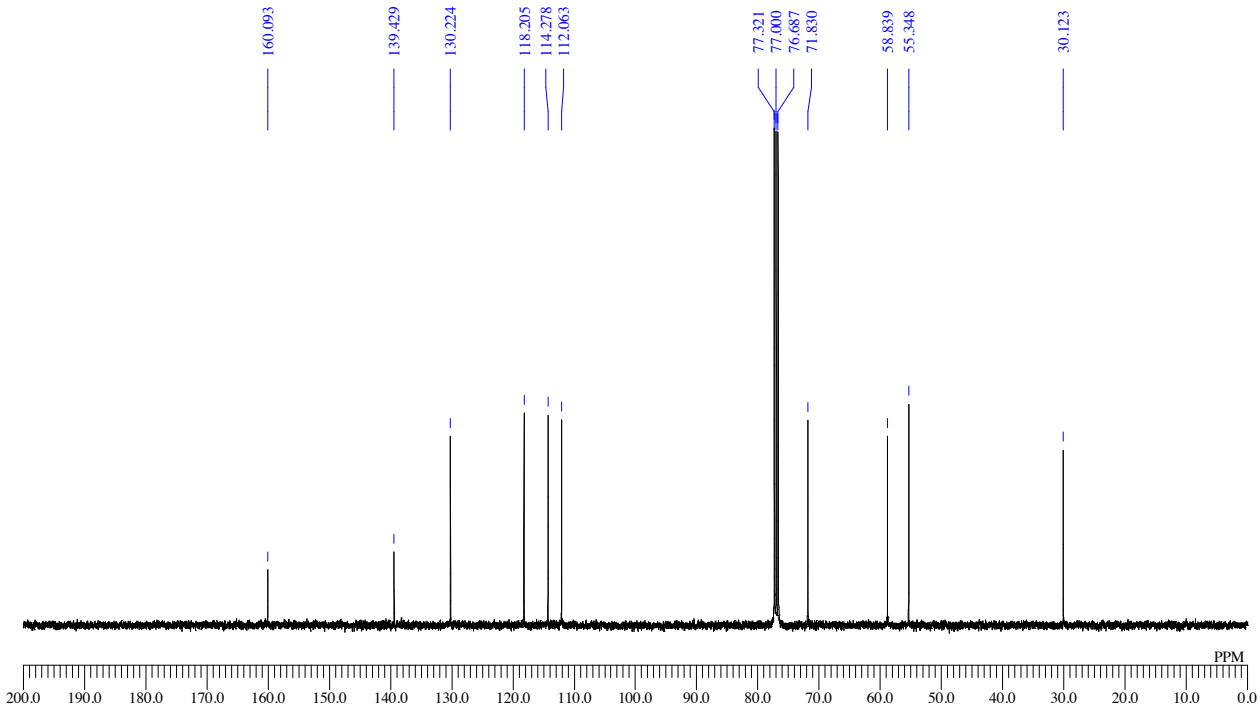


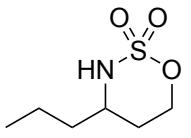
2h

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



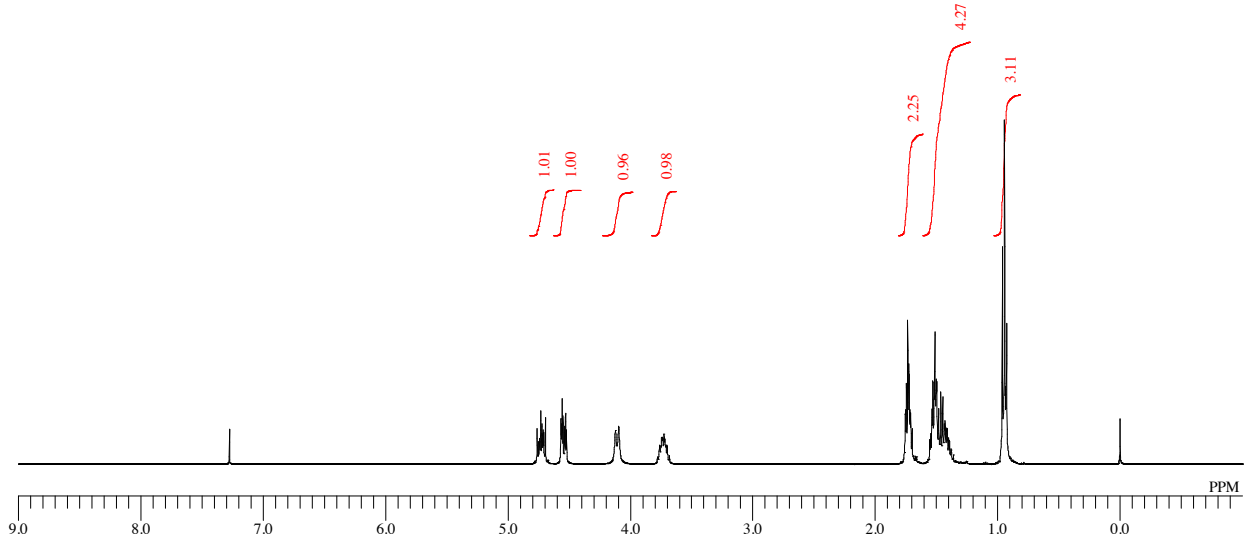
^{13}C NMR: (100 MHz, $CDCl_3$)



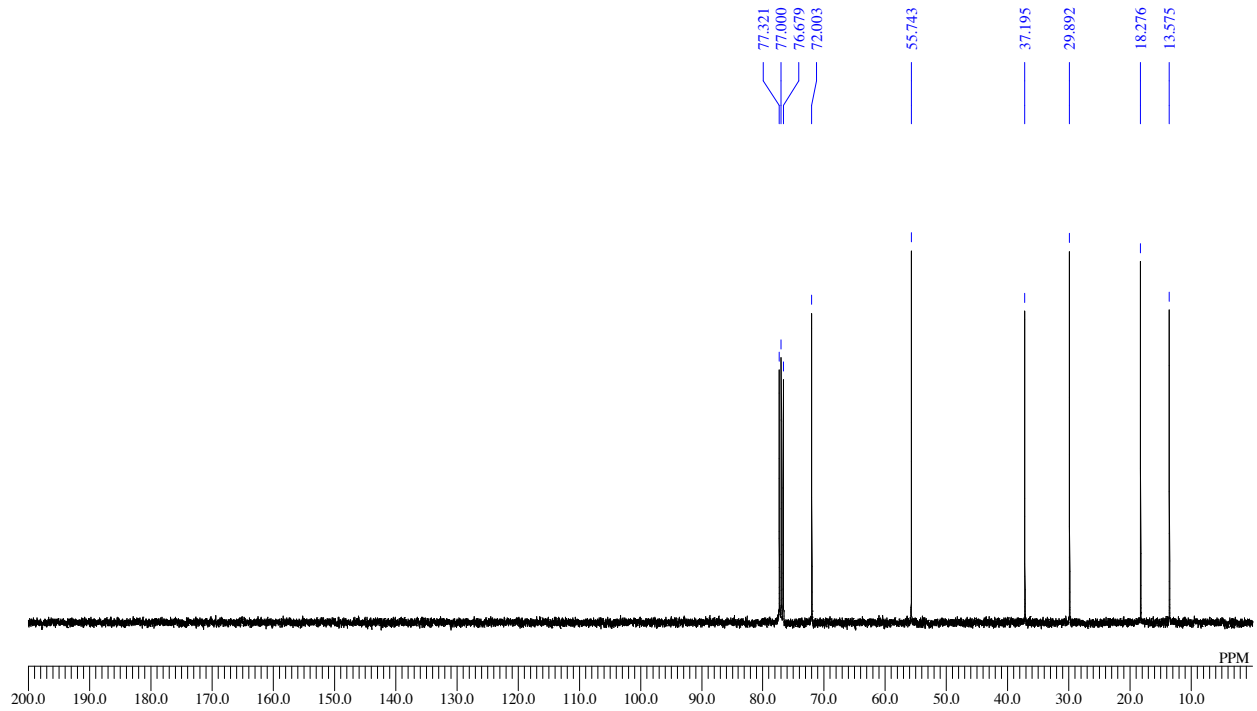


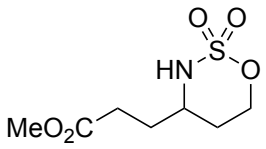
2i

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



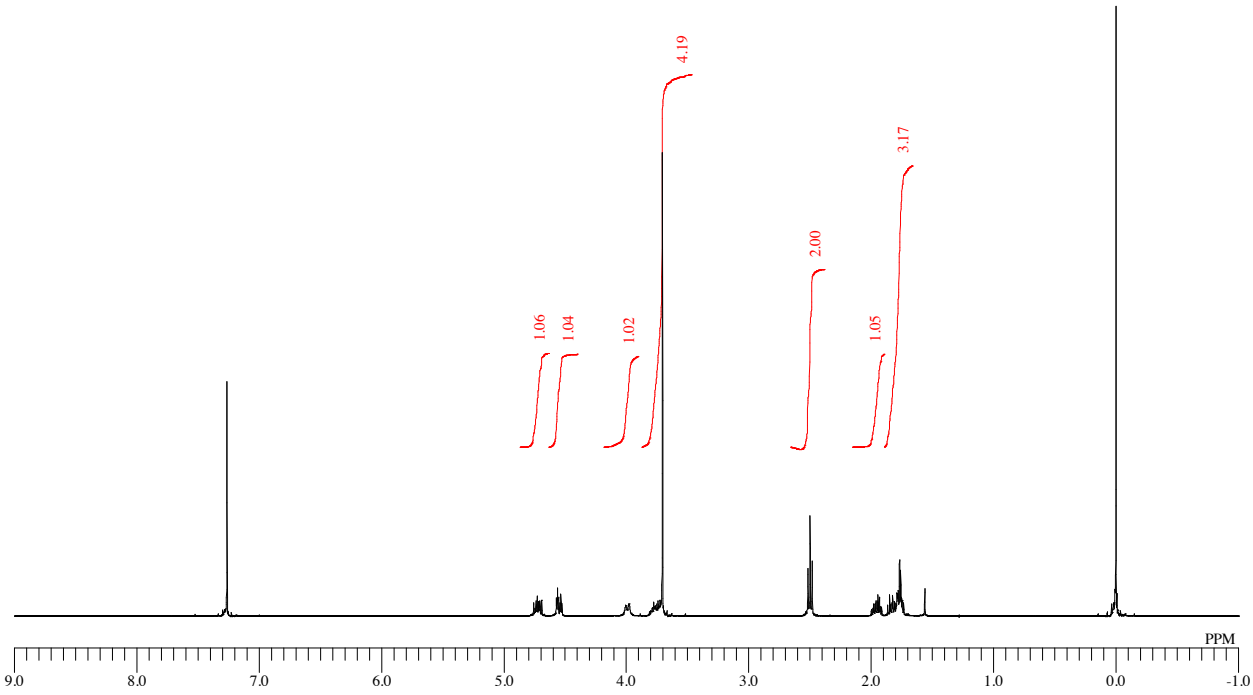
^{13}C NMR: (100 MHz, $CDCl_3$)



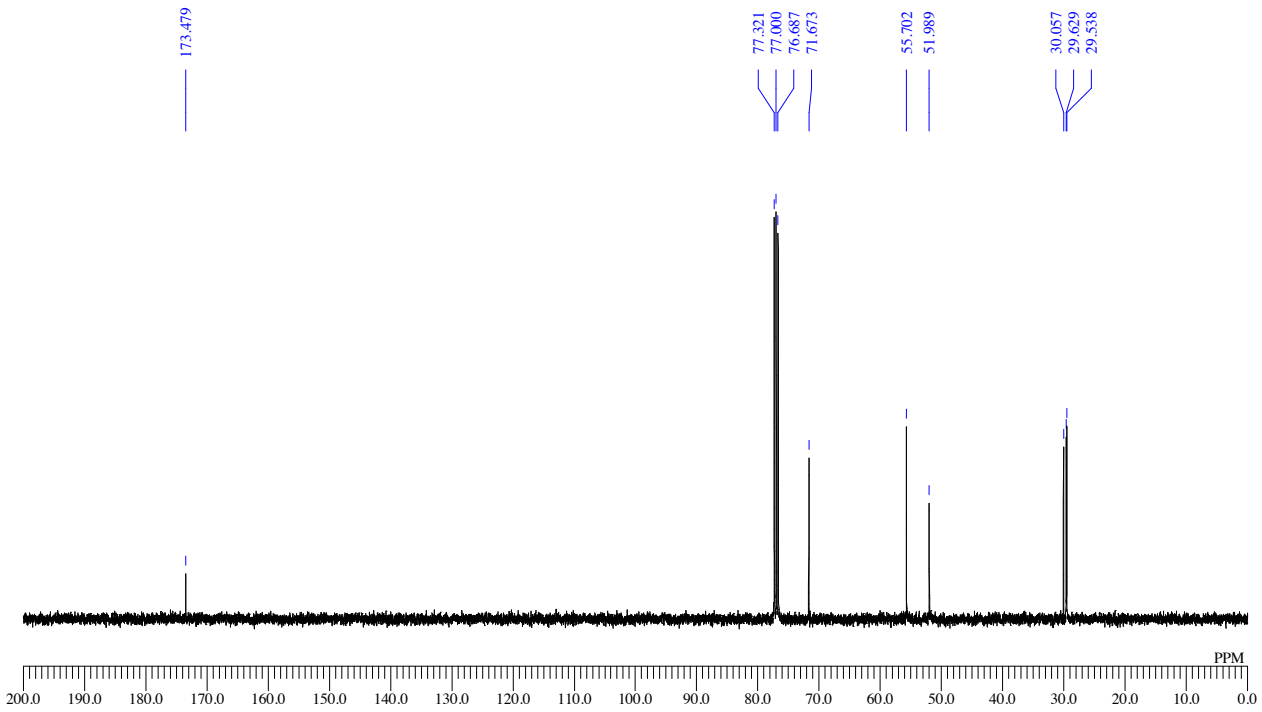


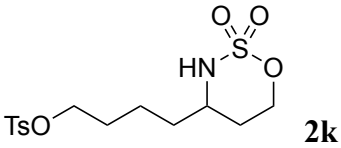
2j

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



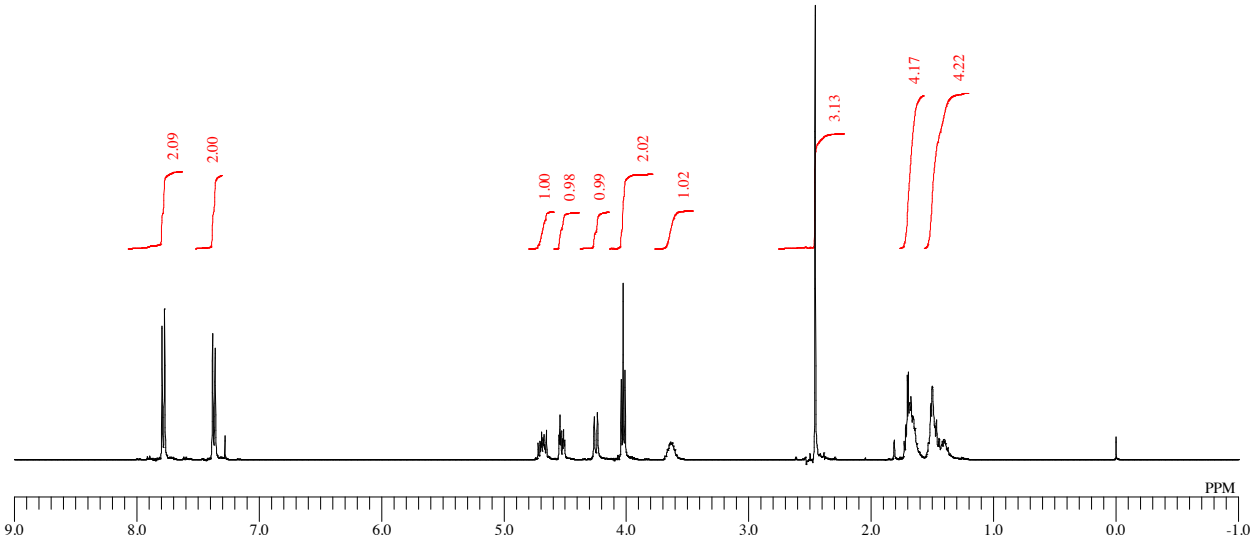
^{13}C NMR: (100 MHz, $CDCl_3$)



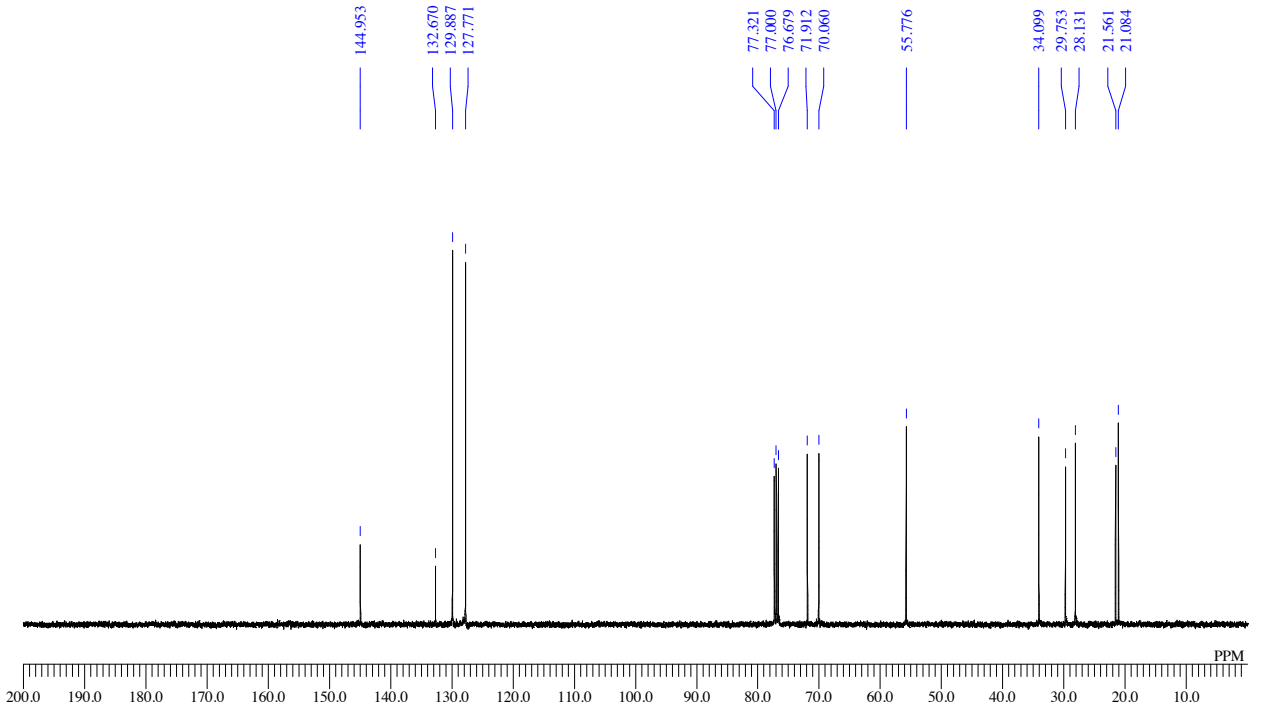


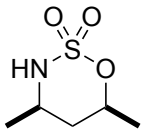
2k

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



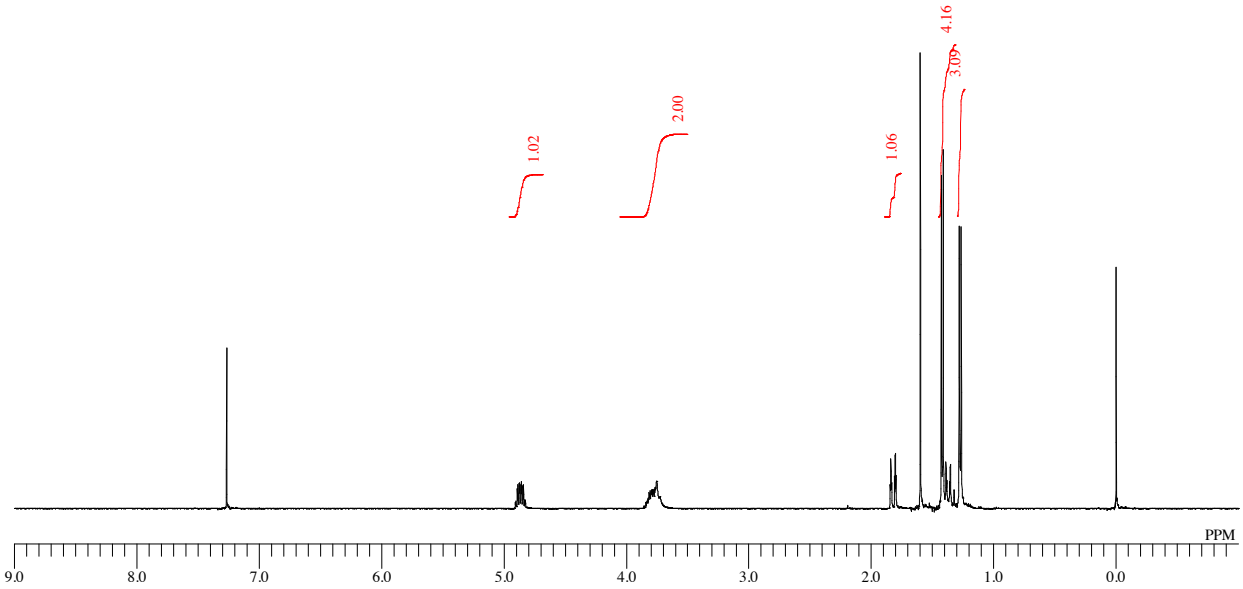
^{13}C NMR: (100 MHz, $CDCl_3$)



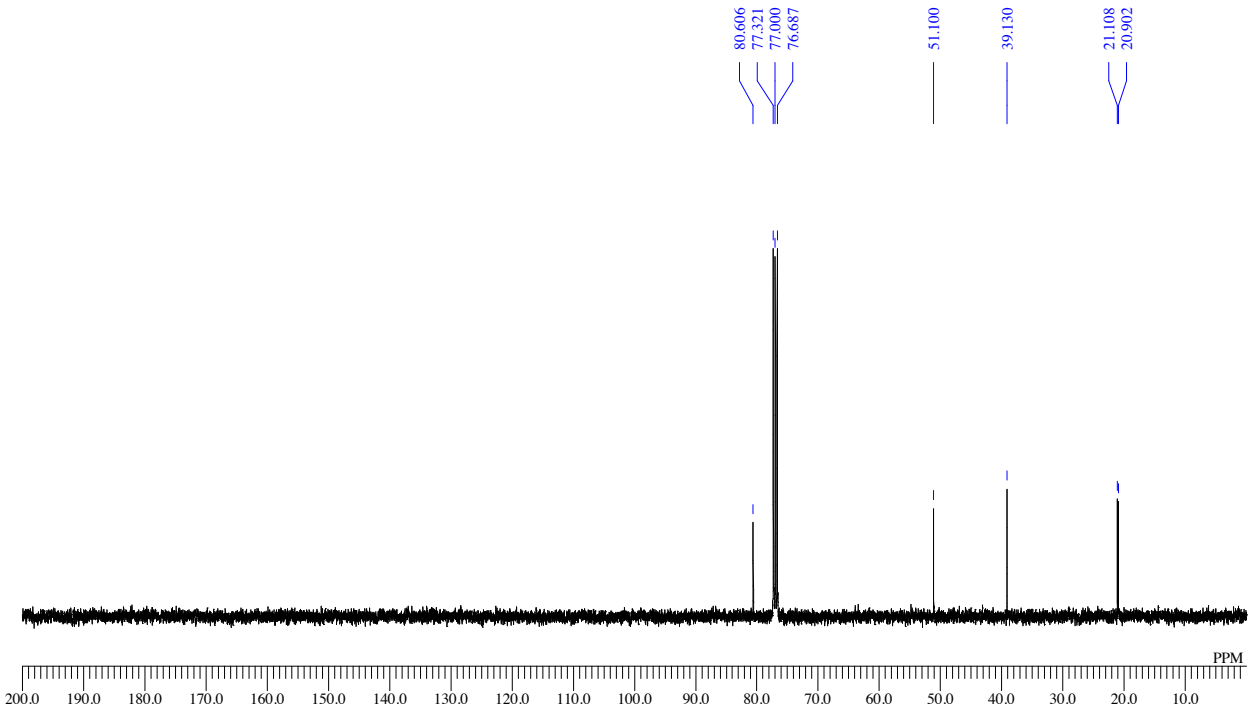


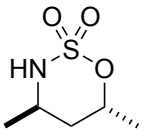
2l (*cis*-isomer)

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



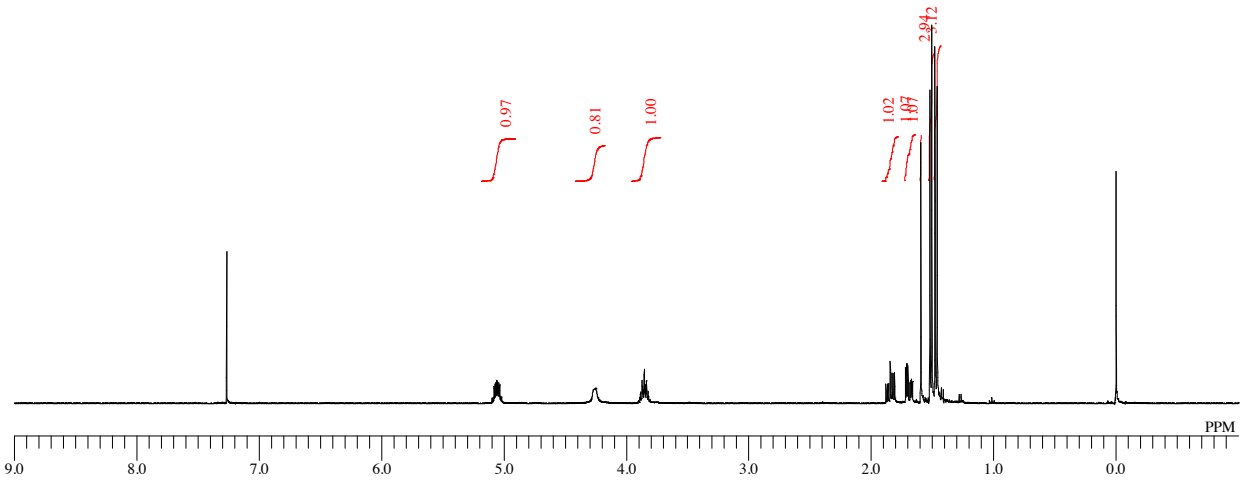
^{13}C NMR: (100 MHz, $CDCl_3$)



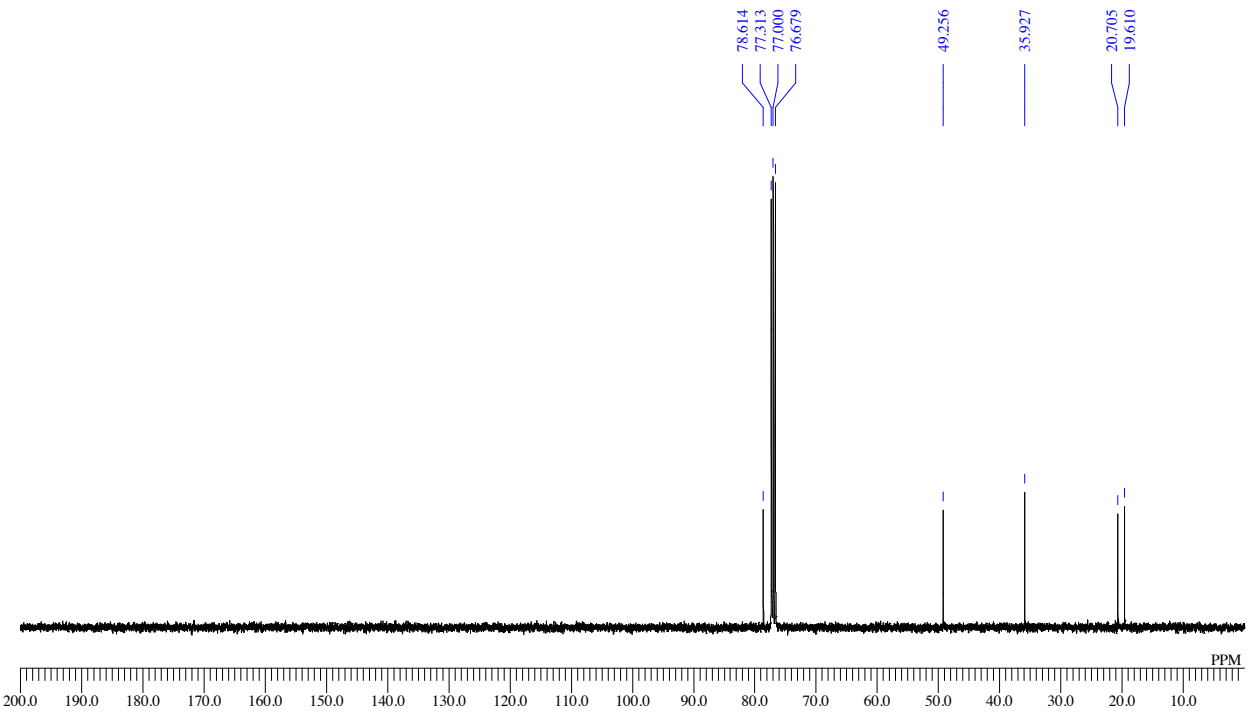


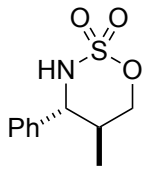
2l (*trans*-isomer)

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



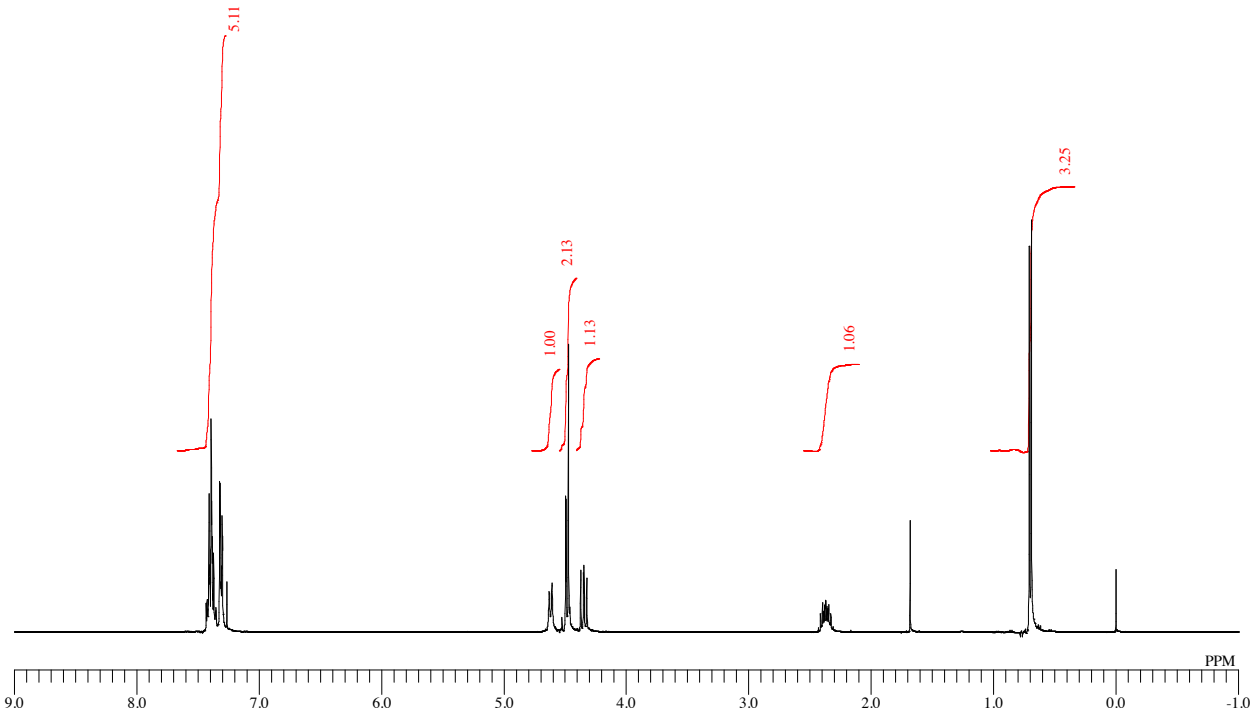
^{13}C NMR: (100 MHz, $CDCl_3$)



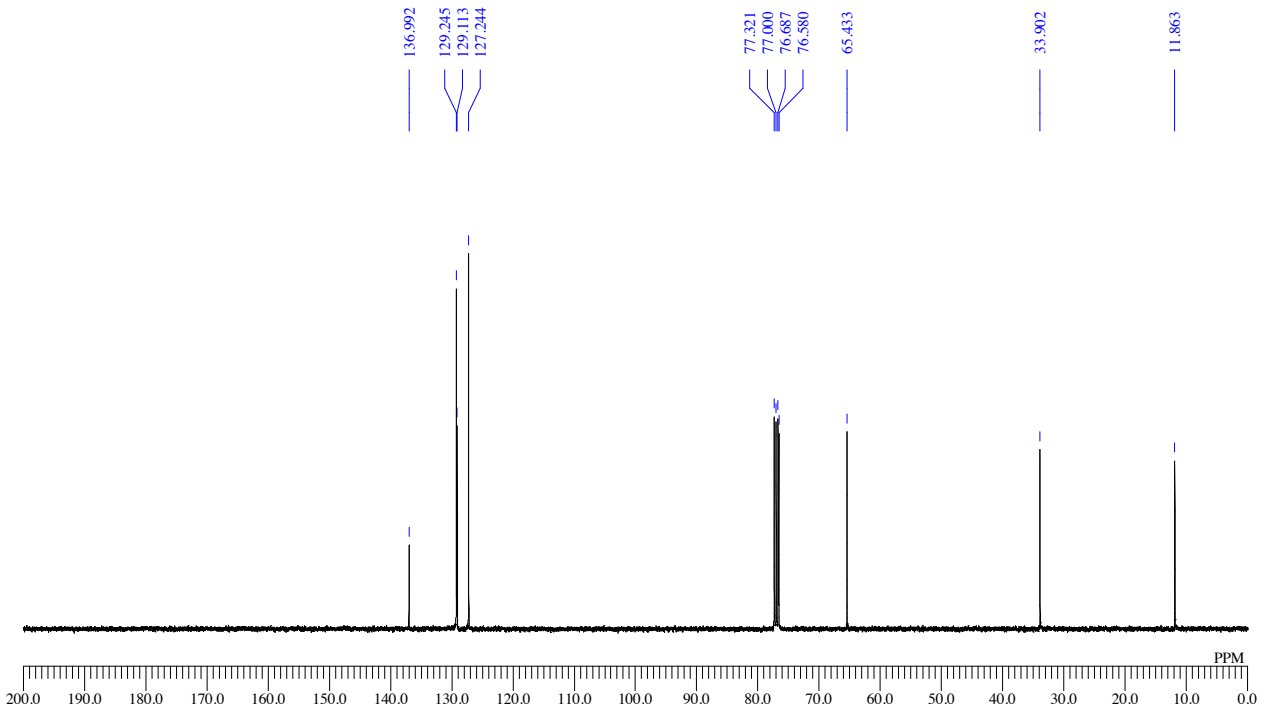


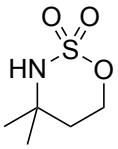
2m

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



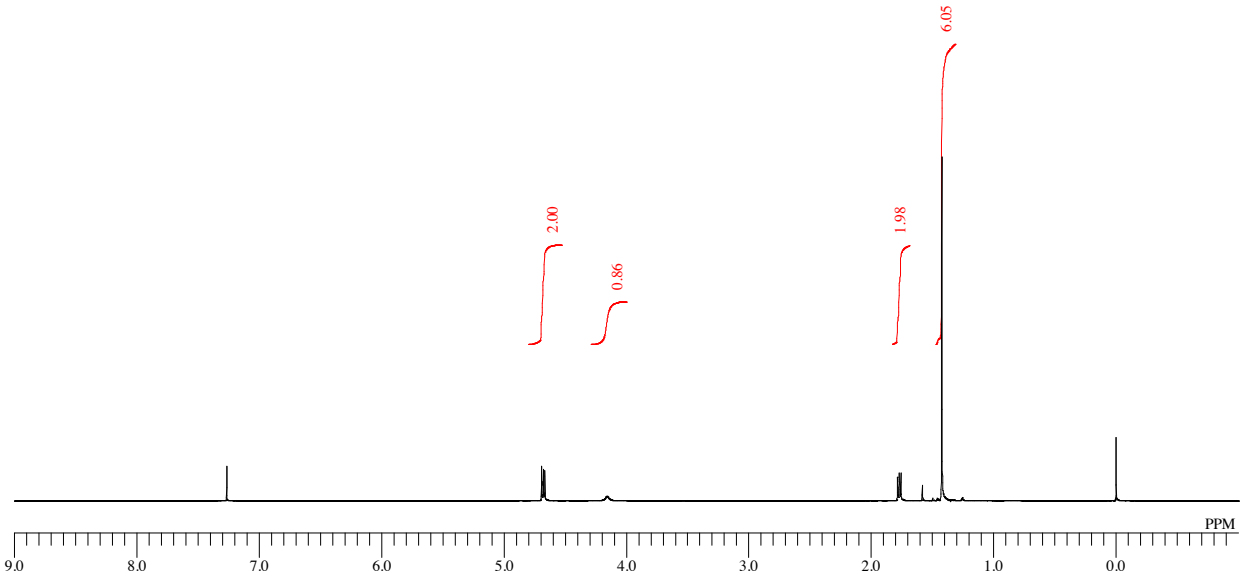
^{13}C NMR: (100 MHz, $CDCl_3$)



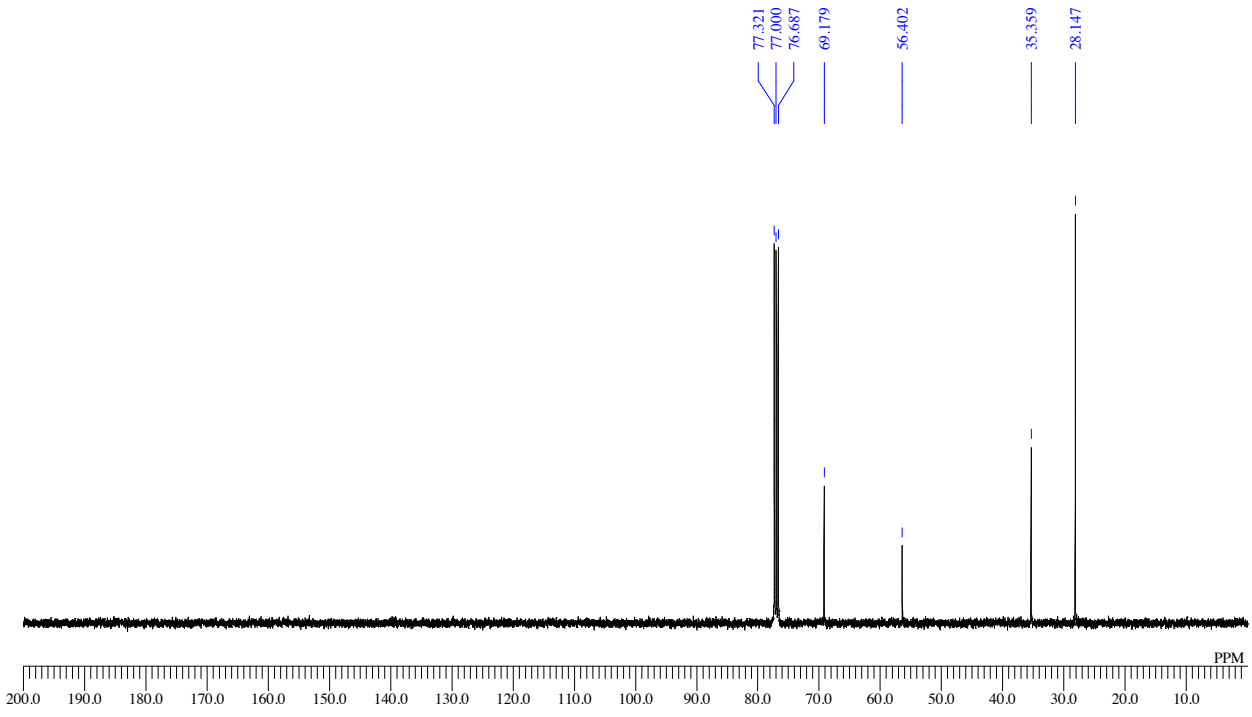


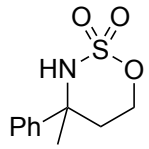
2n

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



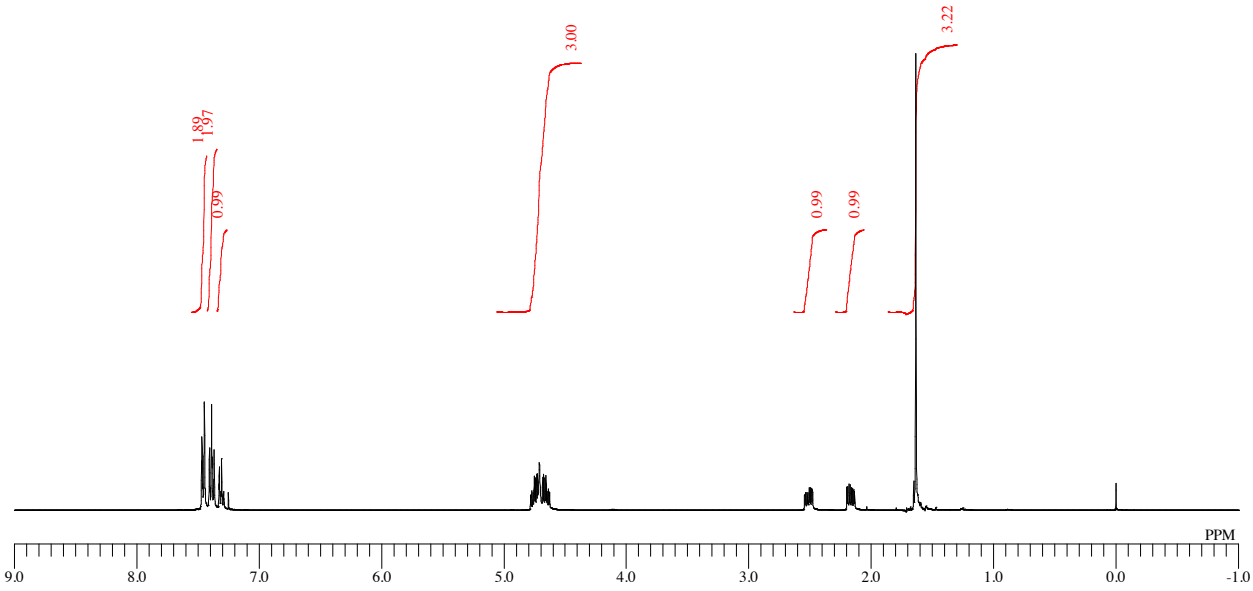
^{13}C NMR: (100 MHz, $CDCl_3$)



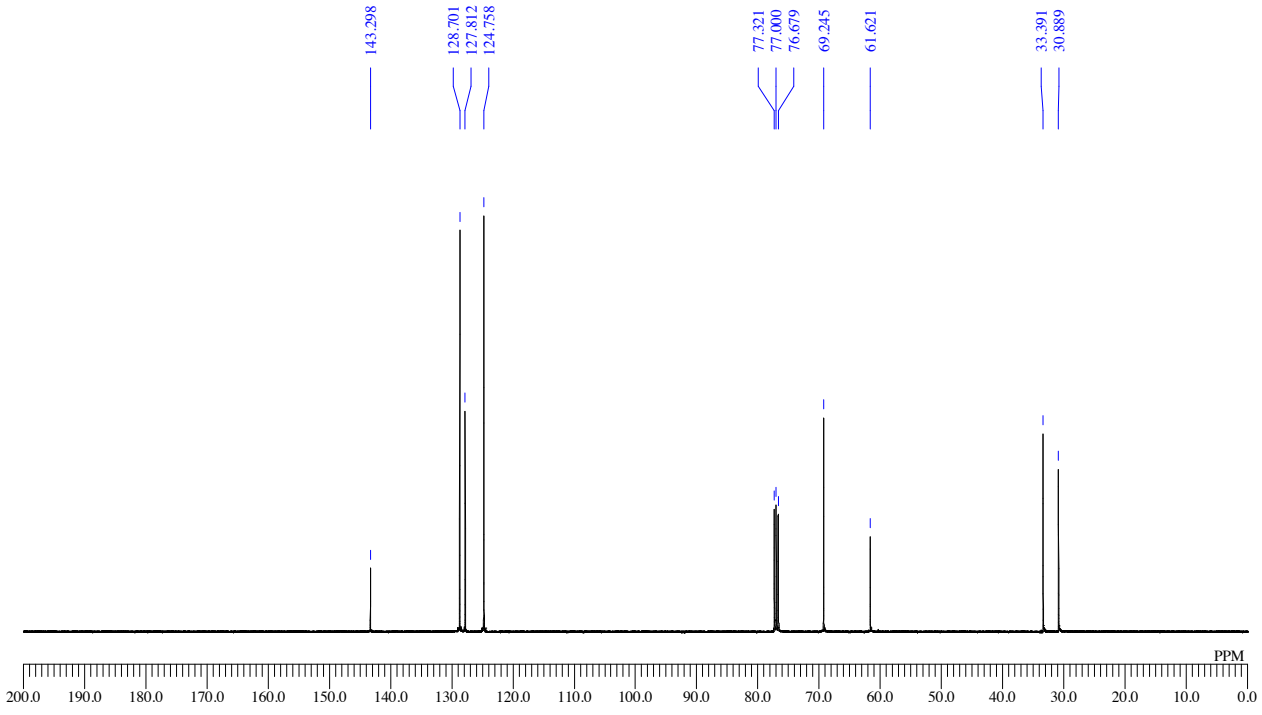


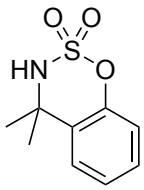
2o

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



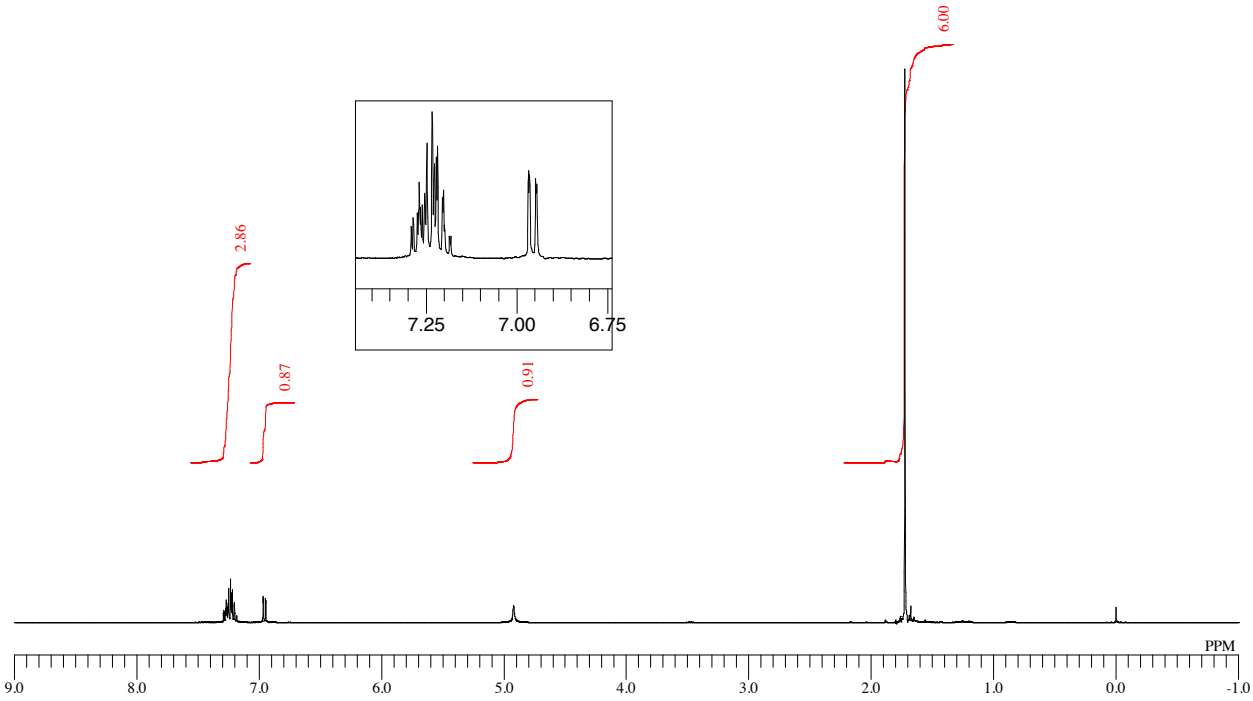
^{13}C NMR: (100 MHz, $CDCl_3$)



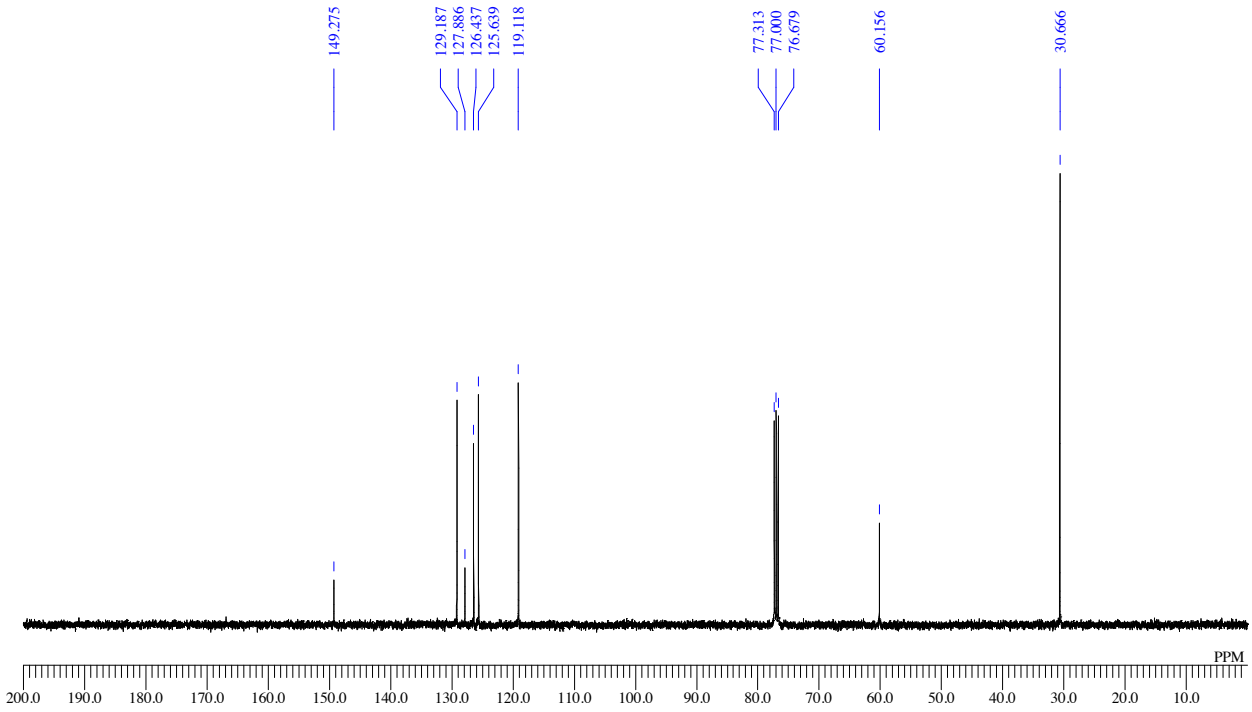


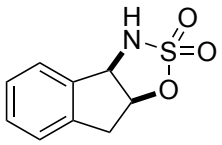
2p

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



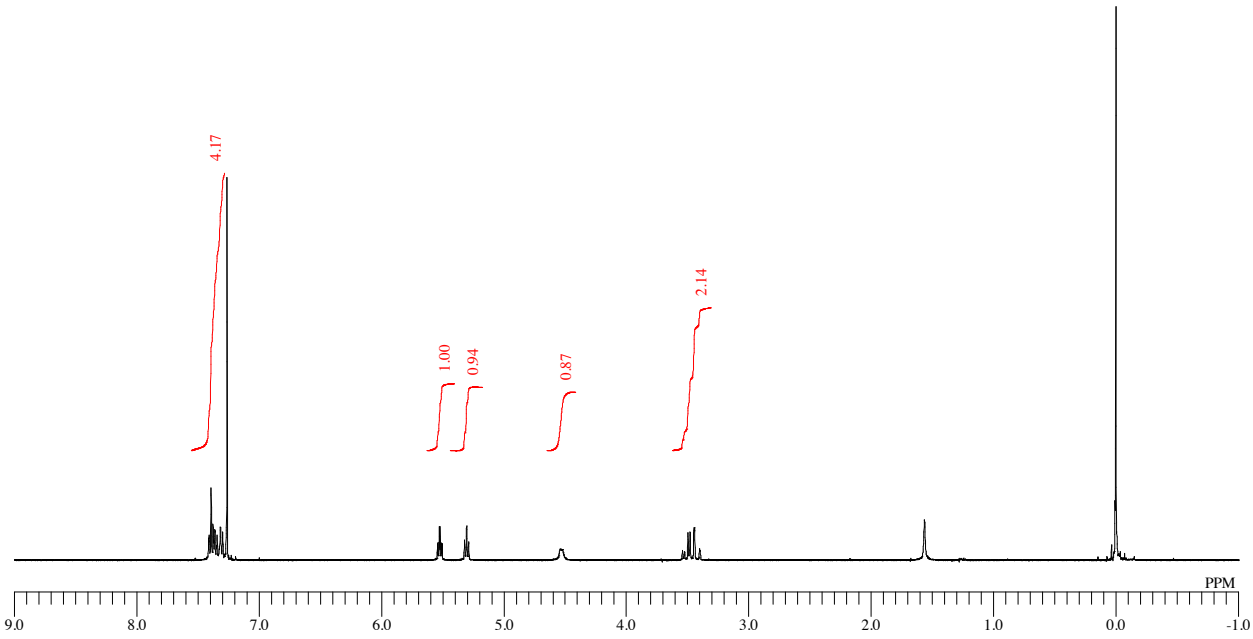
^{13}C NMR: (100 MHz, $CDCl_3$)



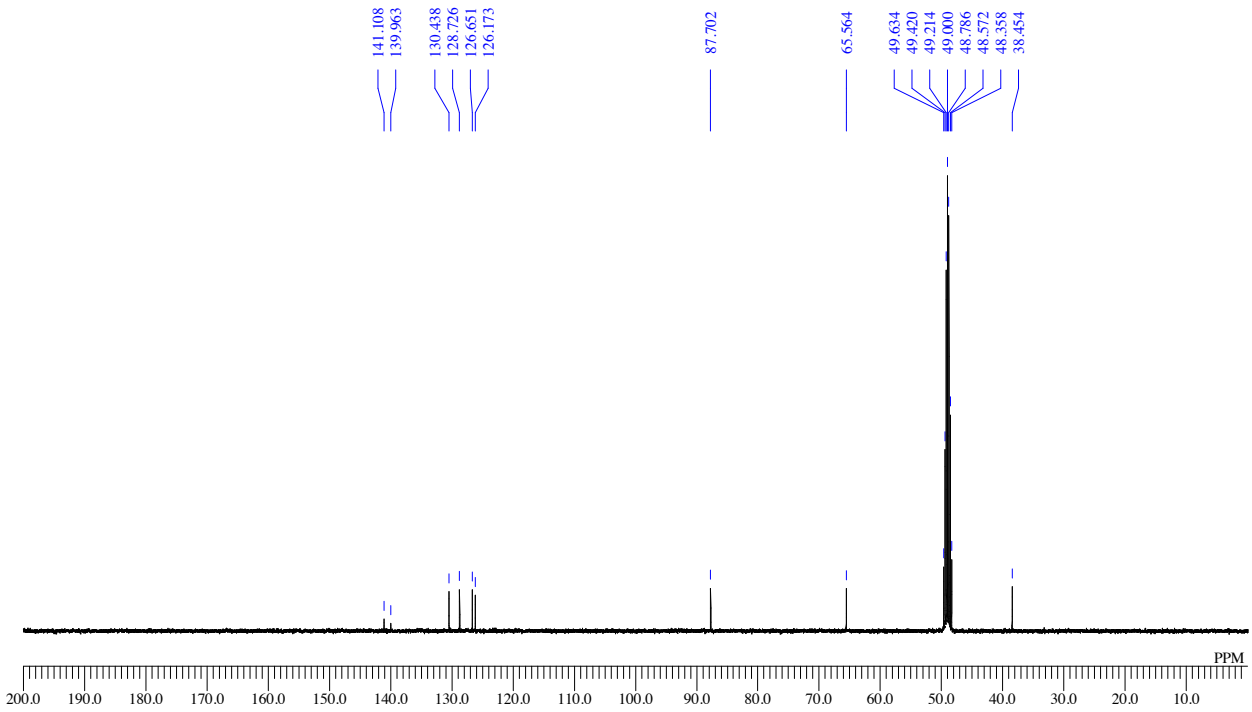


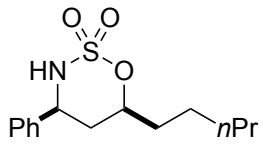
2q

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



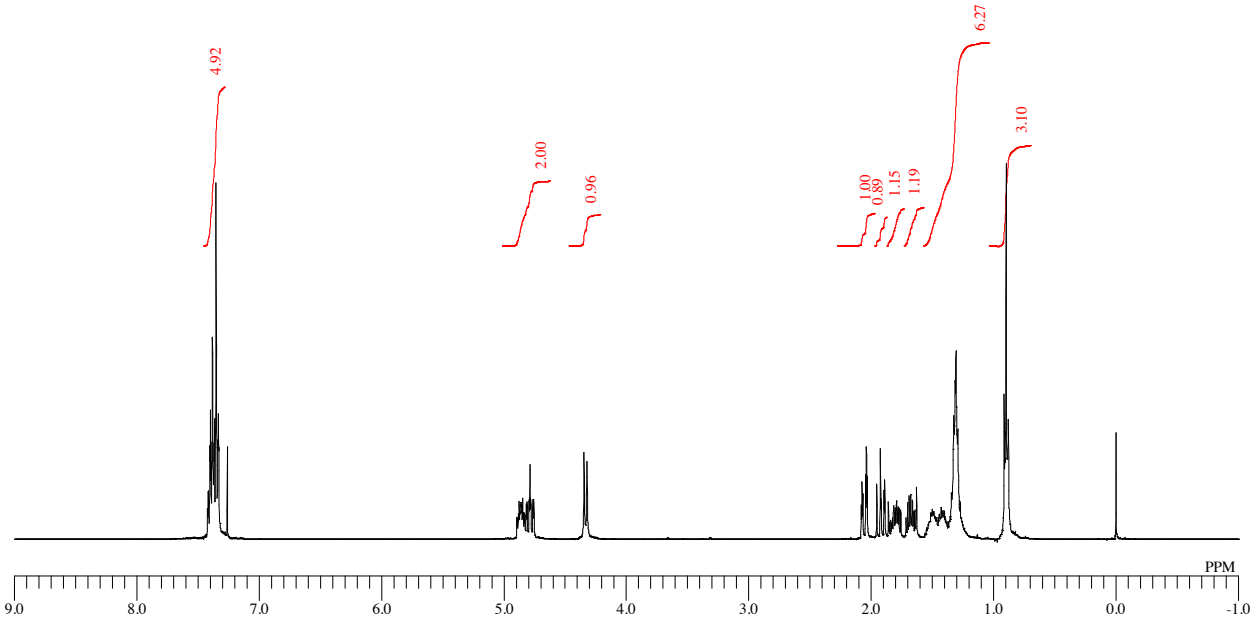
^{13}C NMR: (100 MHz, CD_3OD)



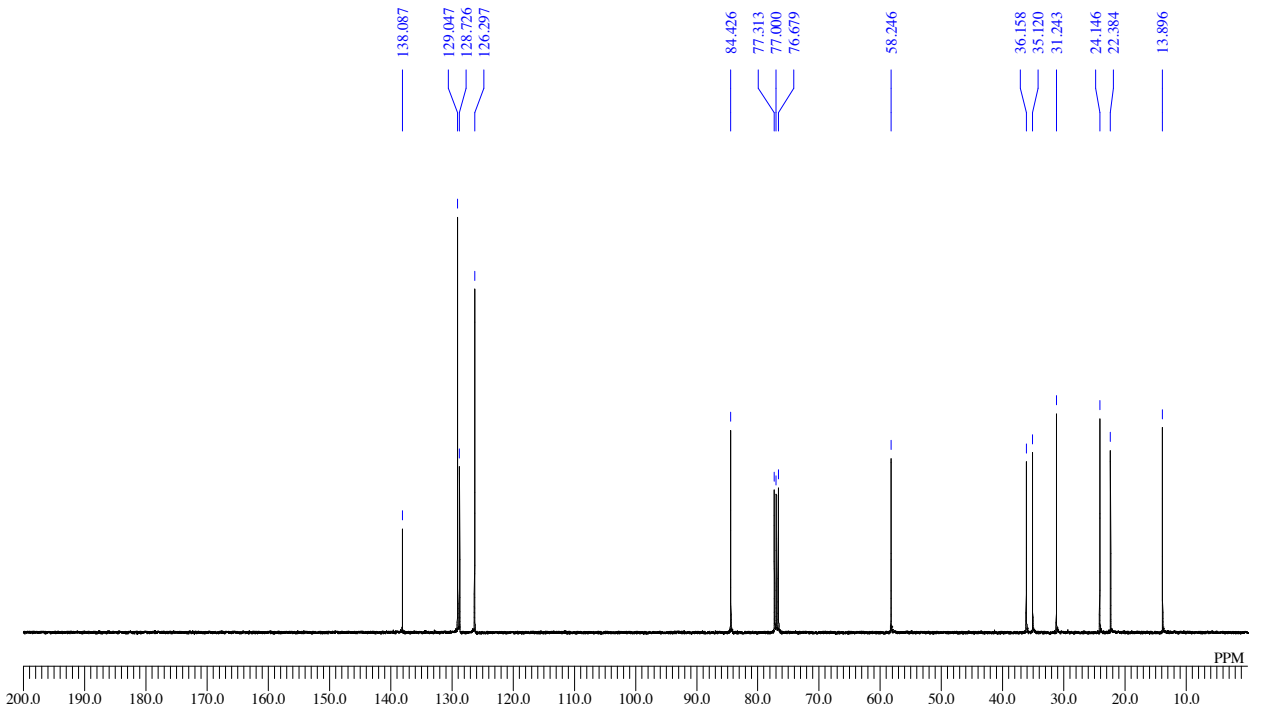


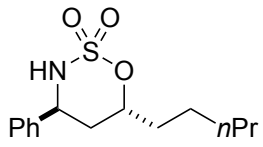
2r (*cis*-isomer)

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



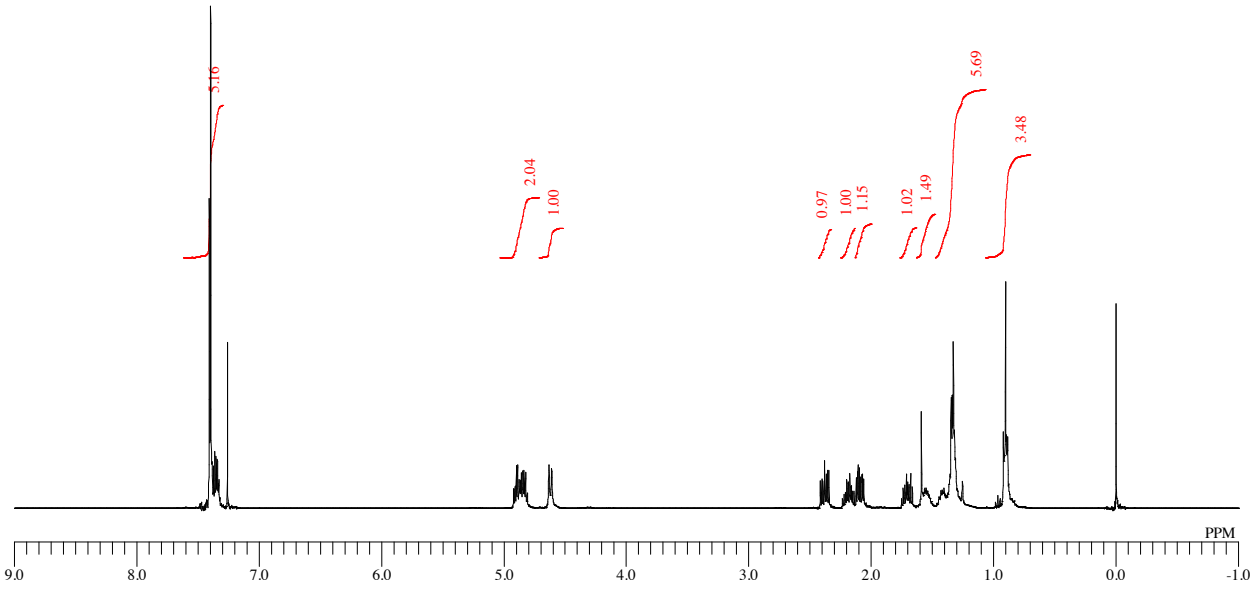
^{13}C NMR: (100 MHz, $CDCl_3$)



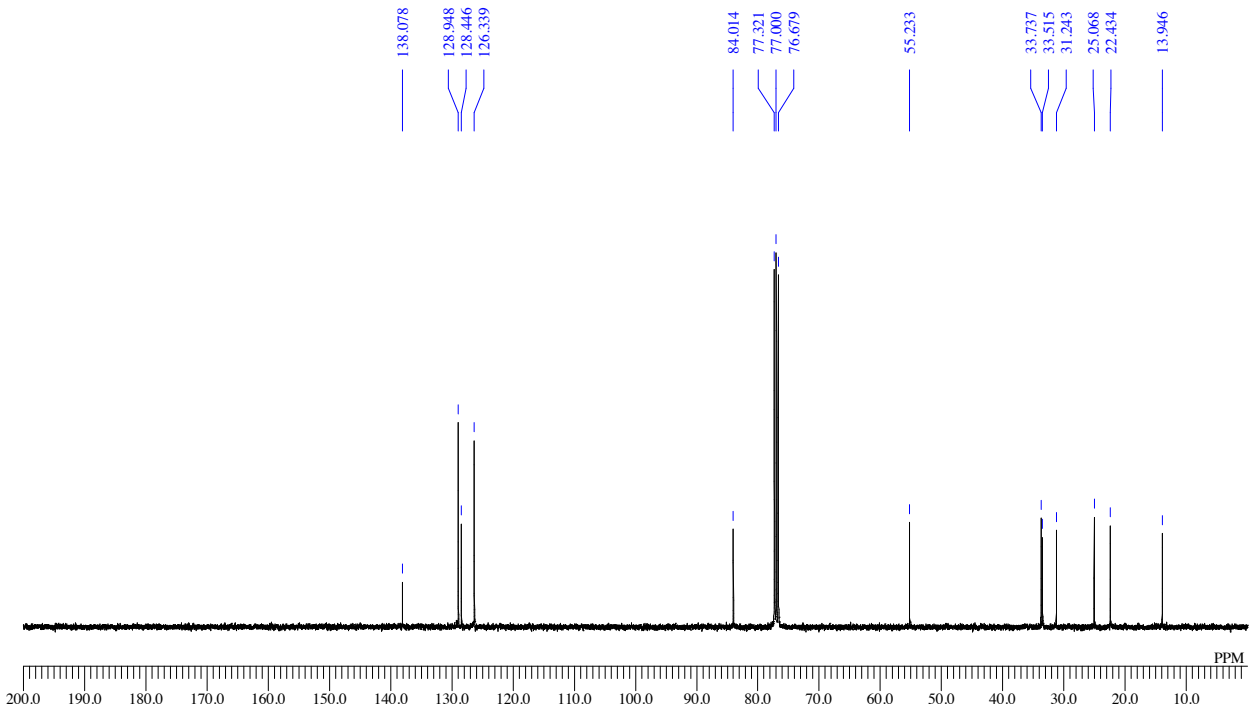


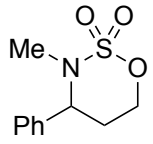
2r (*trans*-isomer)

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



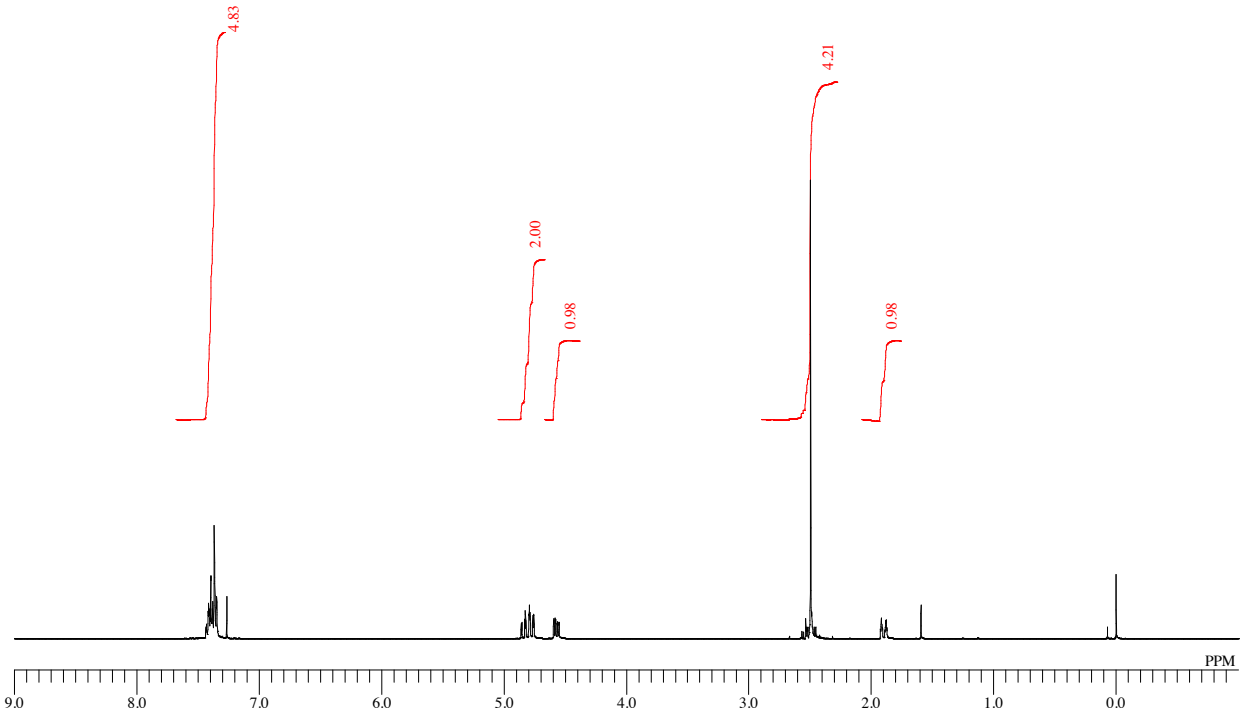
^{13}C NMR: (100 MHz, $CDCl_3$)



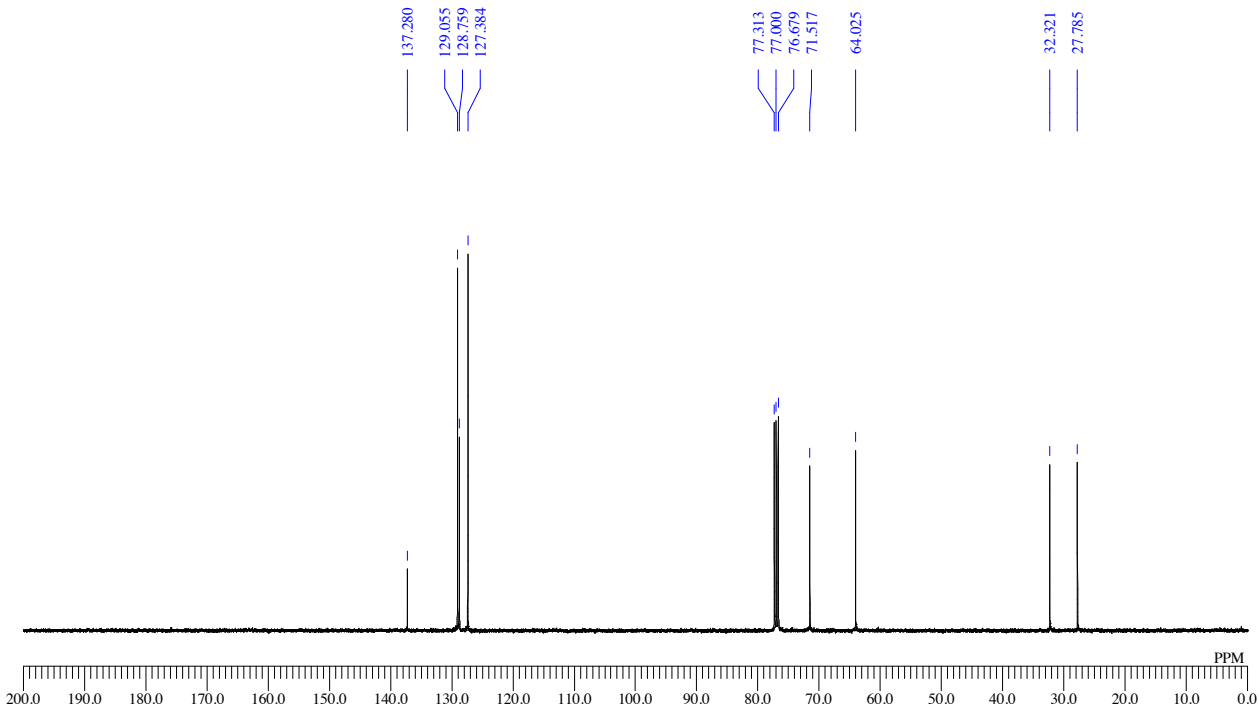


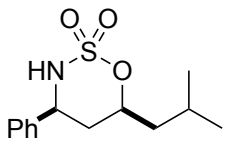
5

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



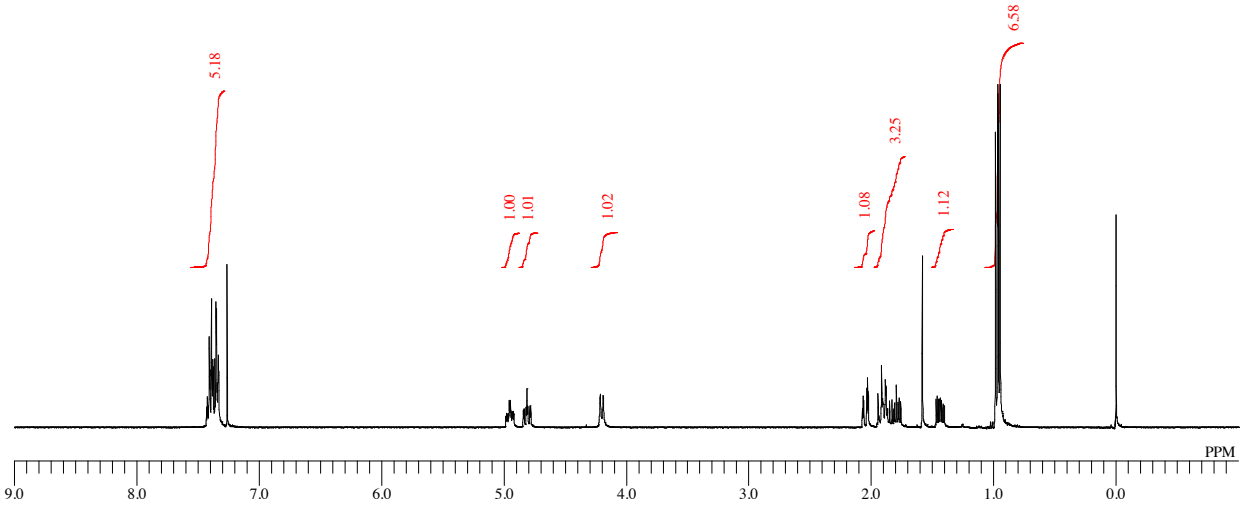
^{13}C NMR: (100 MHz, $CDCl_3$)



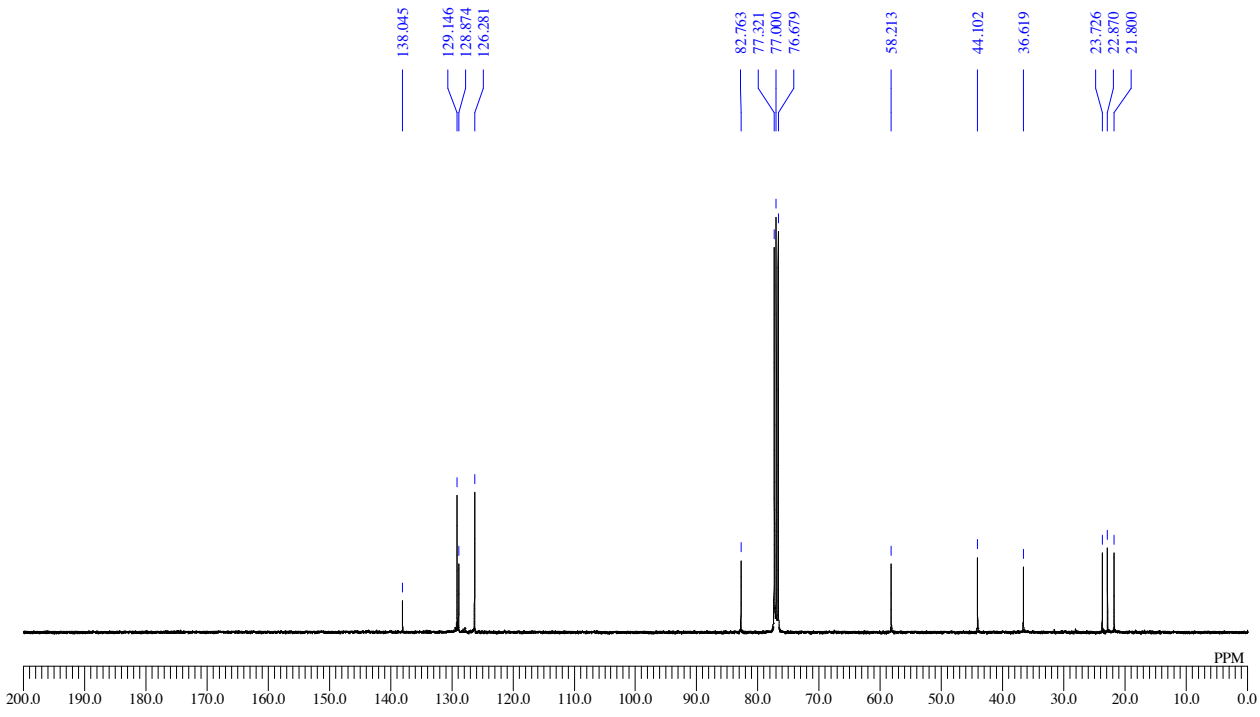


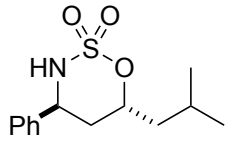
2s (*cis*-isomer)

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



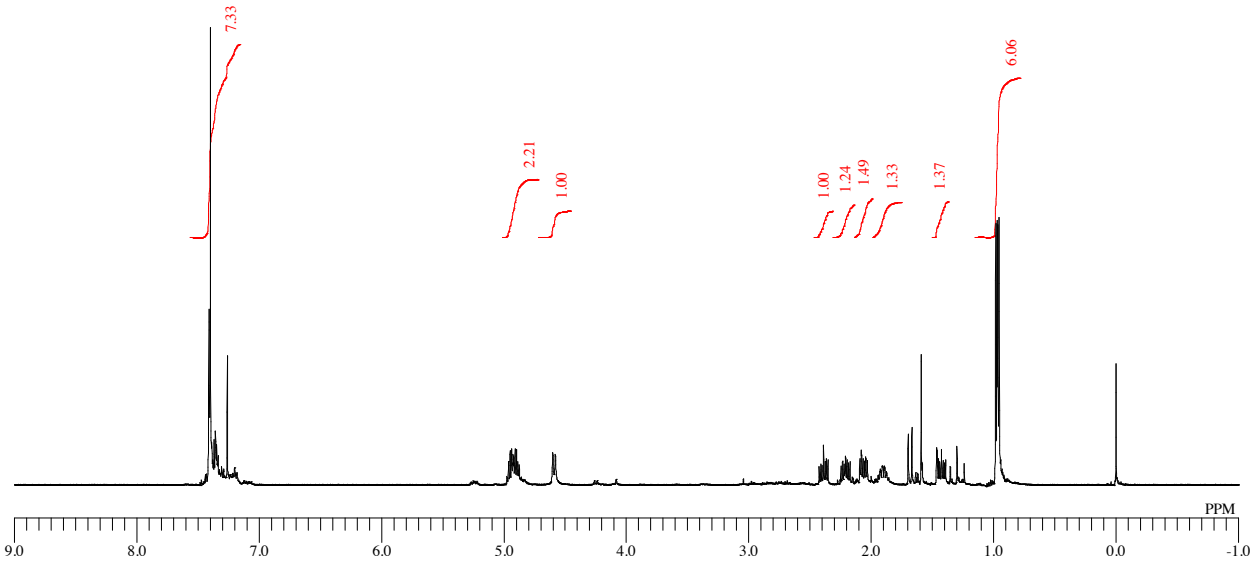
^{13}C NMR: (100 MHz, $CDCl_3$)



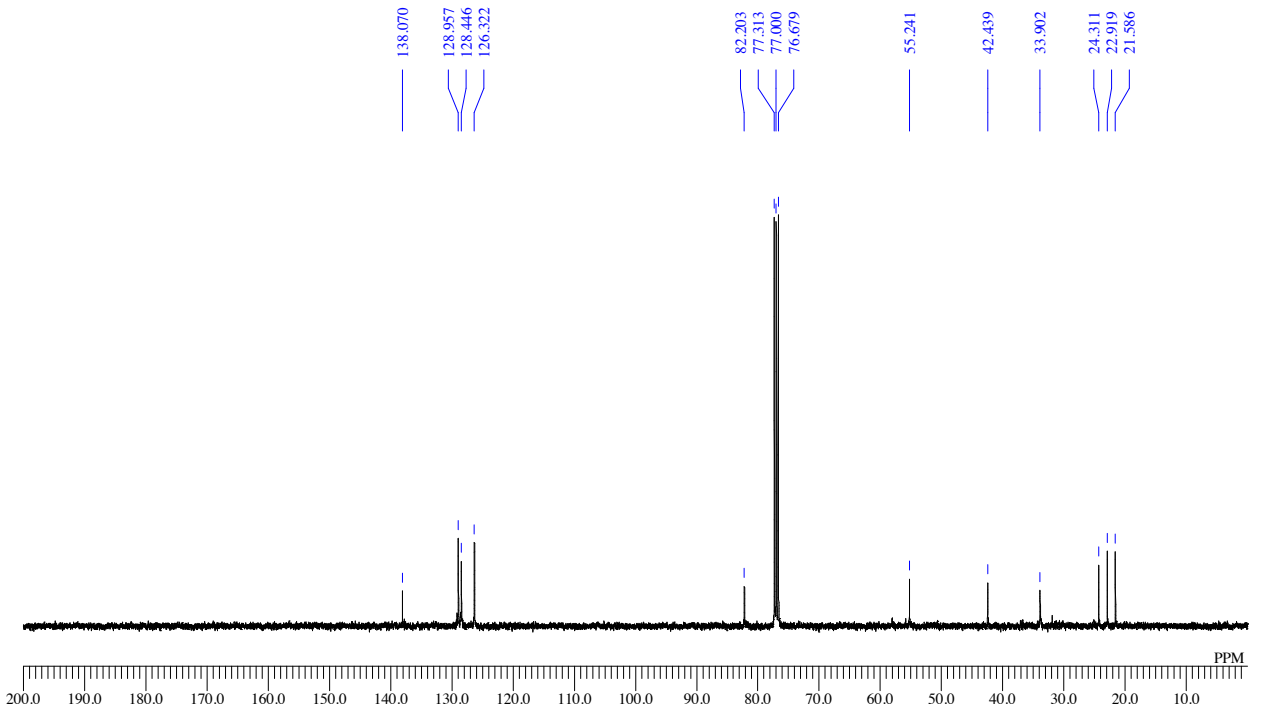


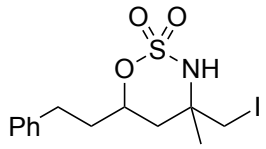
2s (*trans*-isomer)

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



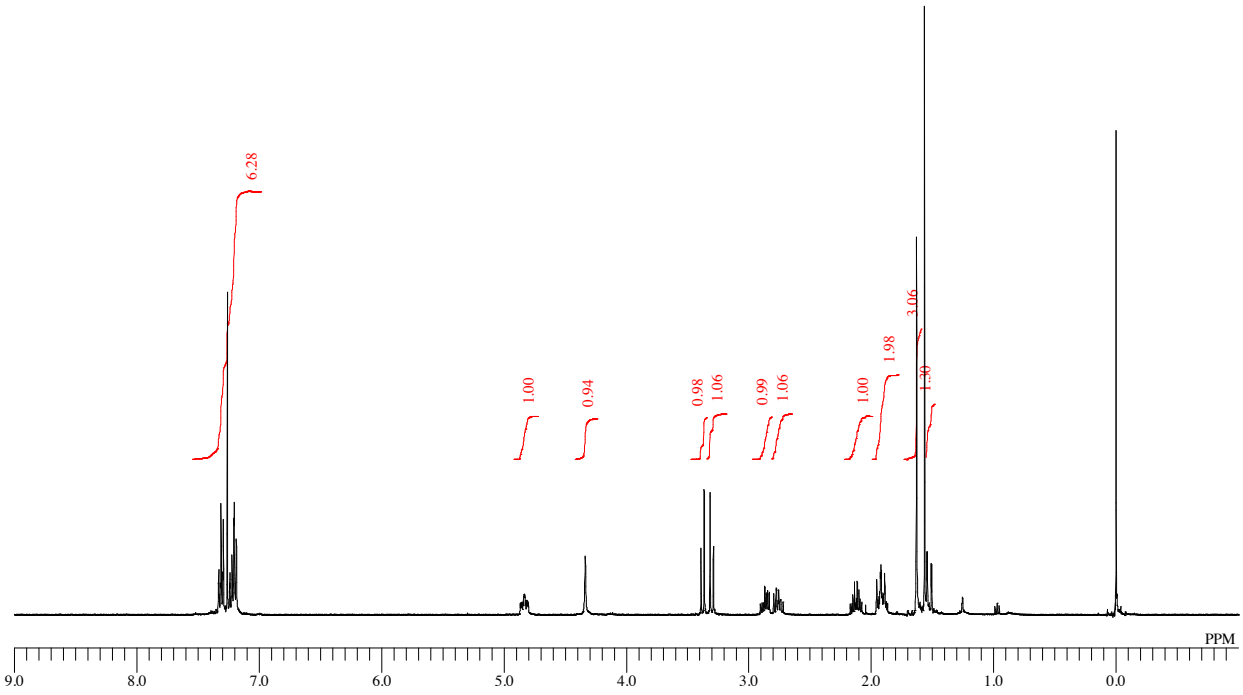
^{13}C NMR: (100 MHz, $CDCl_3$)



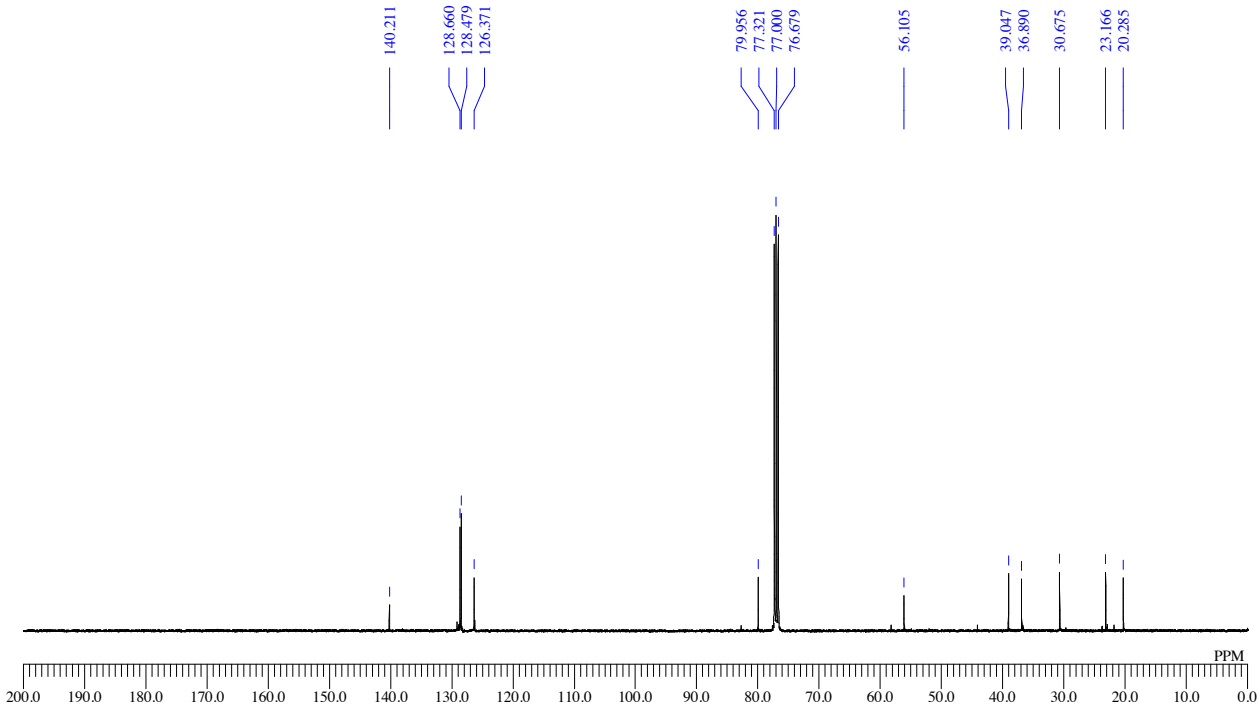


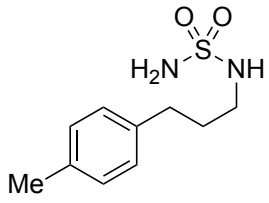
2s'-I

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



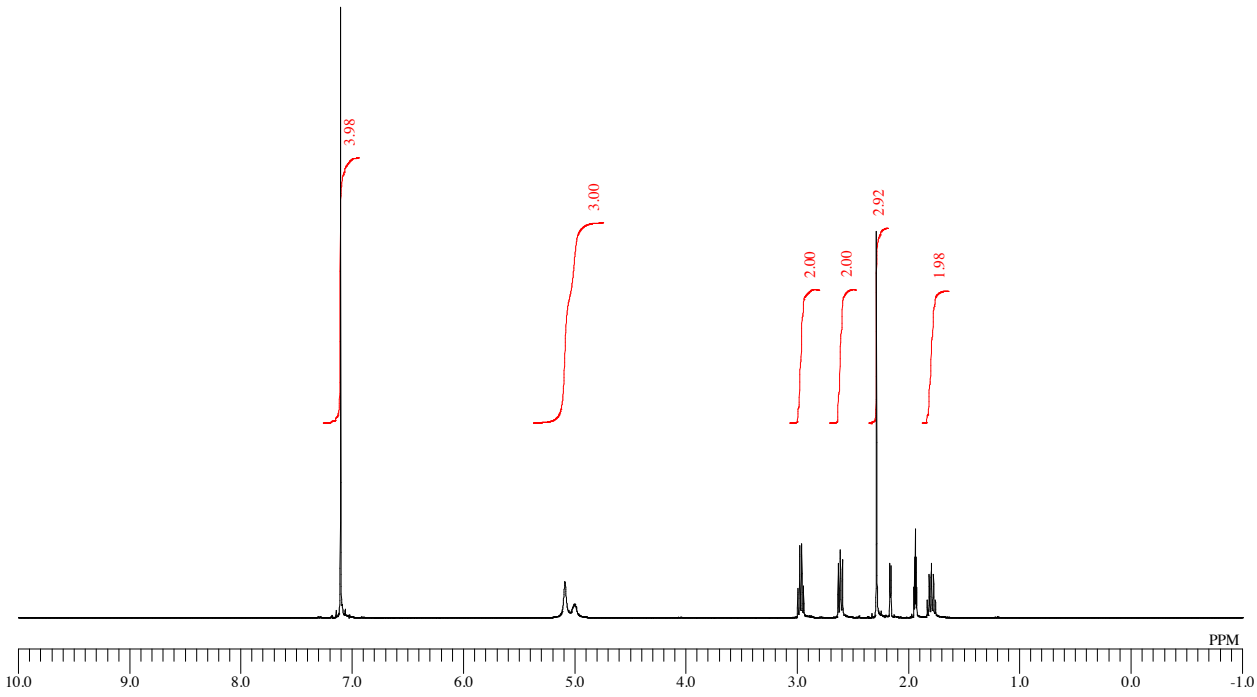
^{13}C NMR: (100 MHz, $CDCl_3$)



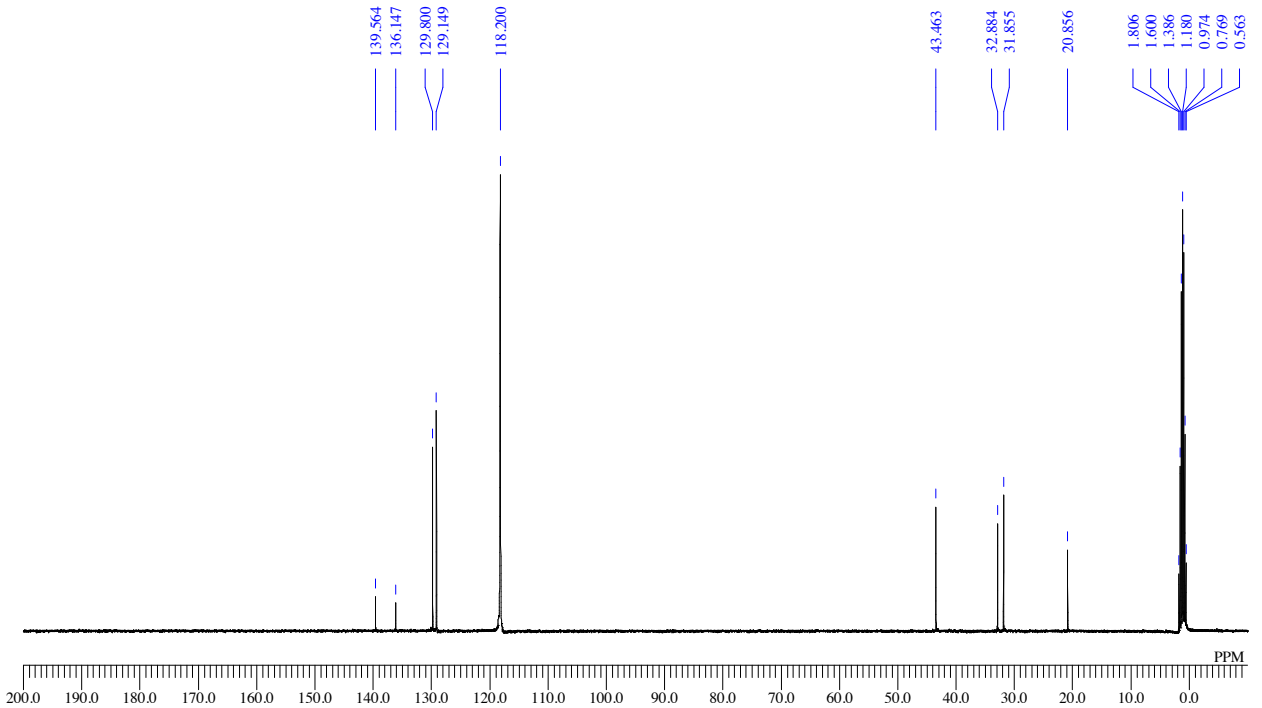


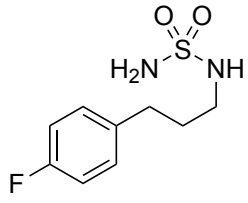
10b

^{1}H NMR: (400 MHz, CD_3CN)



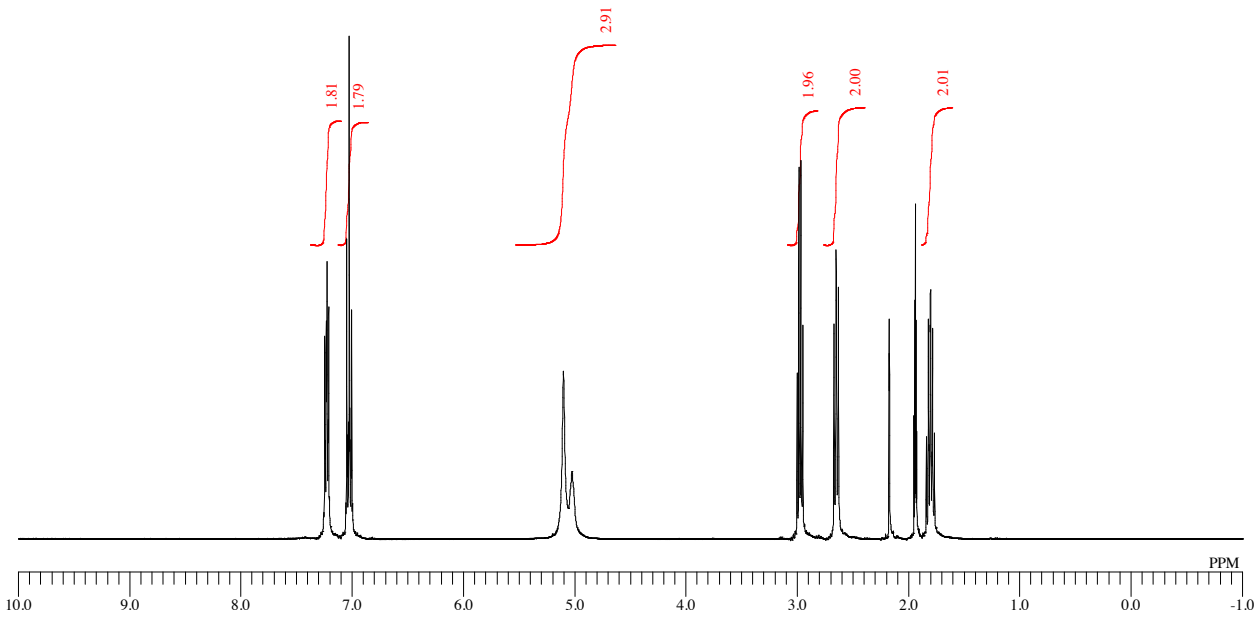
^{13}C NMR: (100 MHz, CD_3CN)



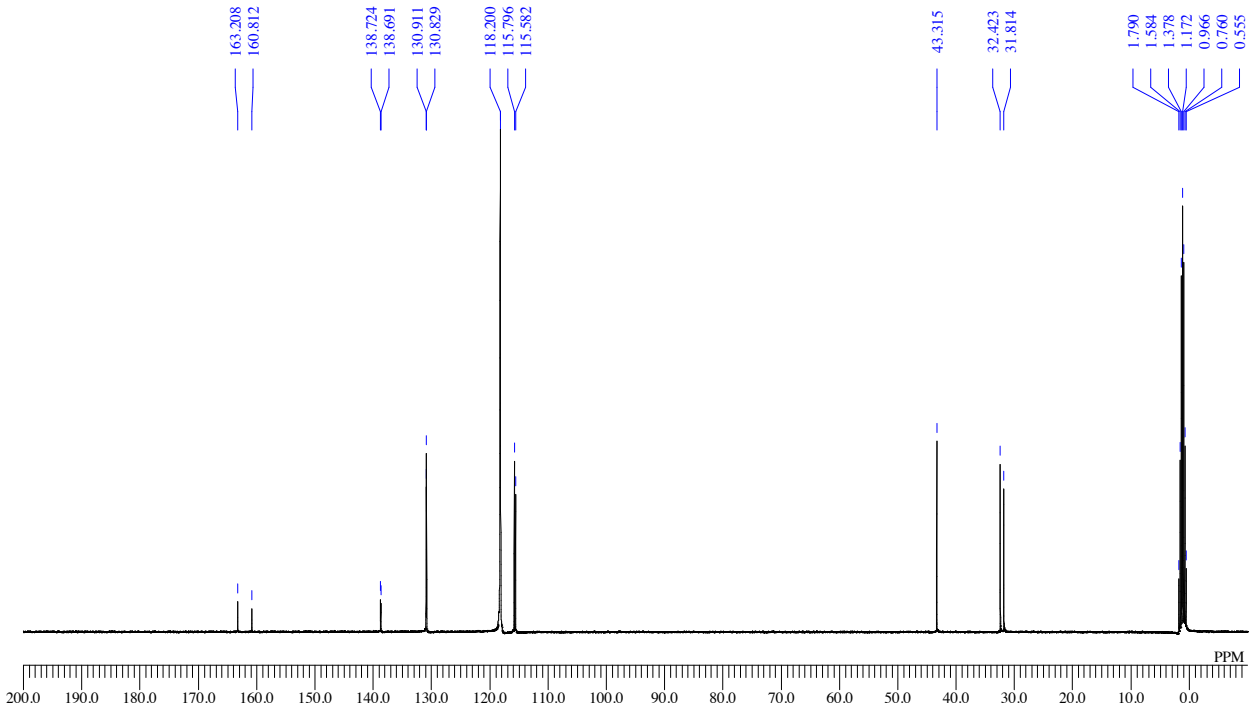


10c

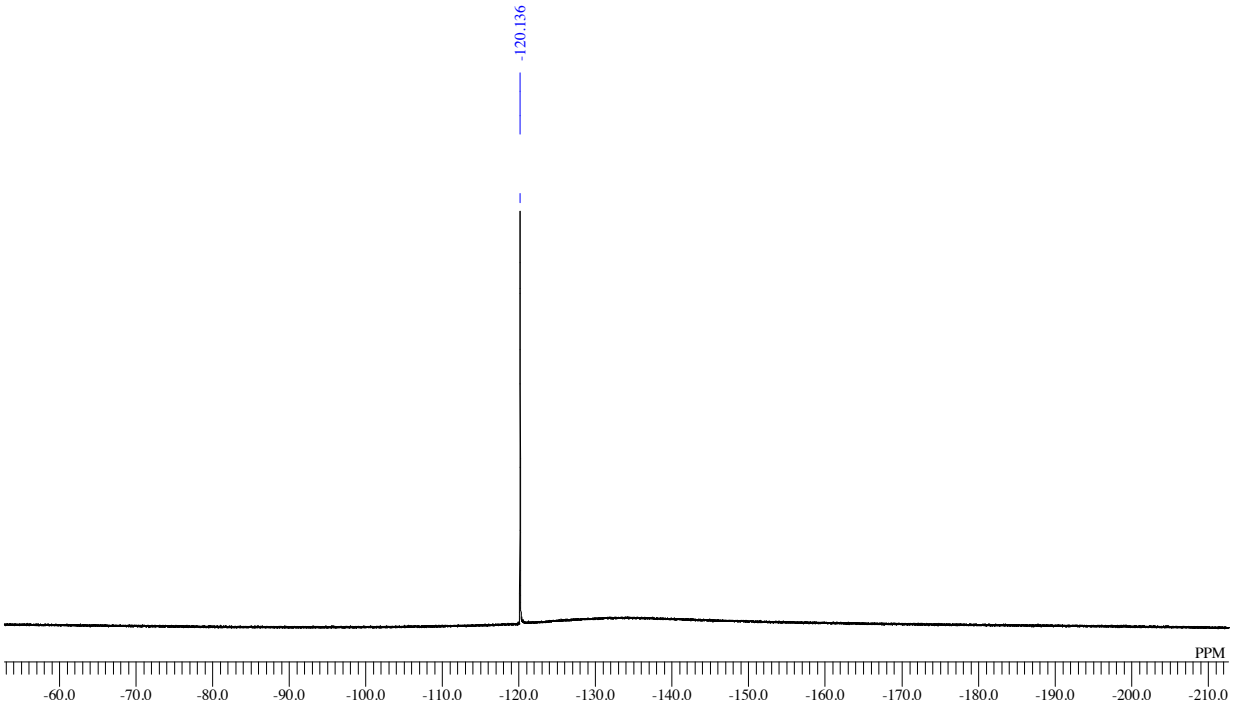
^{1}H NMR: (400 MHz, CD_3CN)

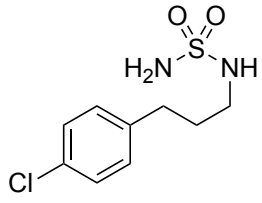


^{13}C NMR: (100 MHz, CD_3CN)



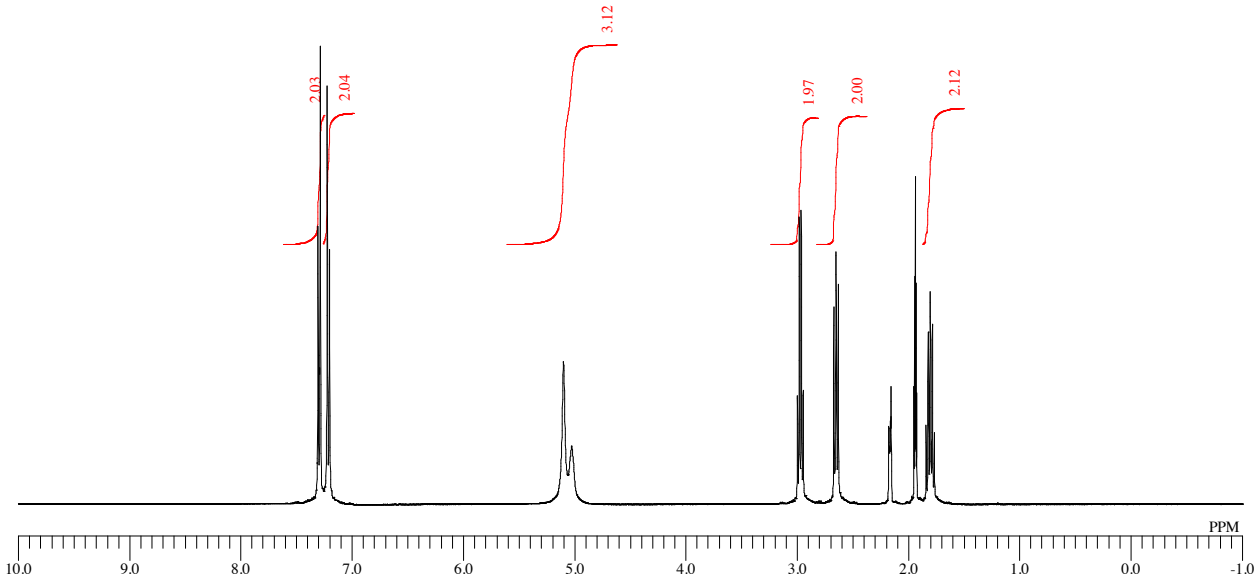
^{19}F NMR: (377 MHz, CD_3CN)



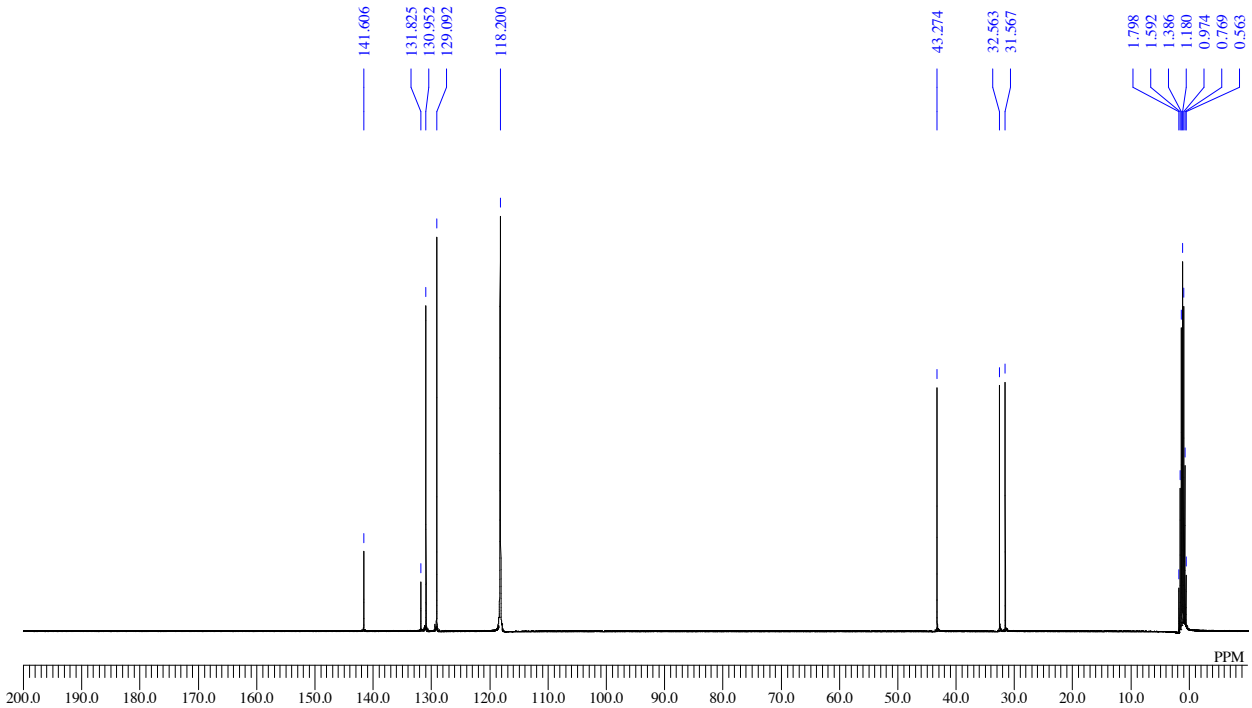


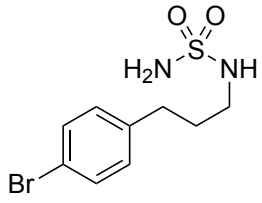
10d

^{1}H NMR: (400 MHz, CD_3CN)



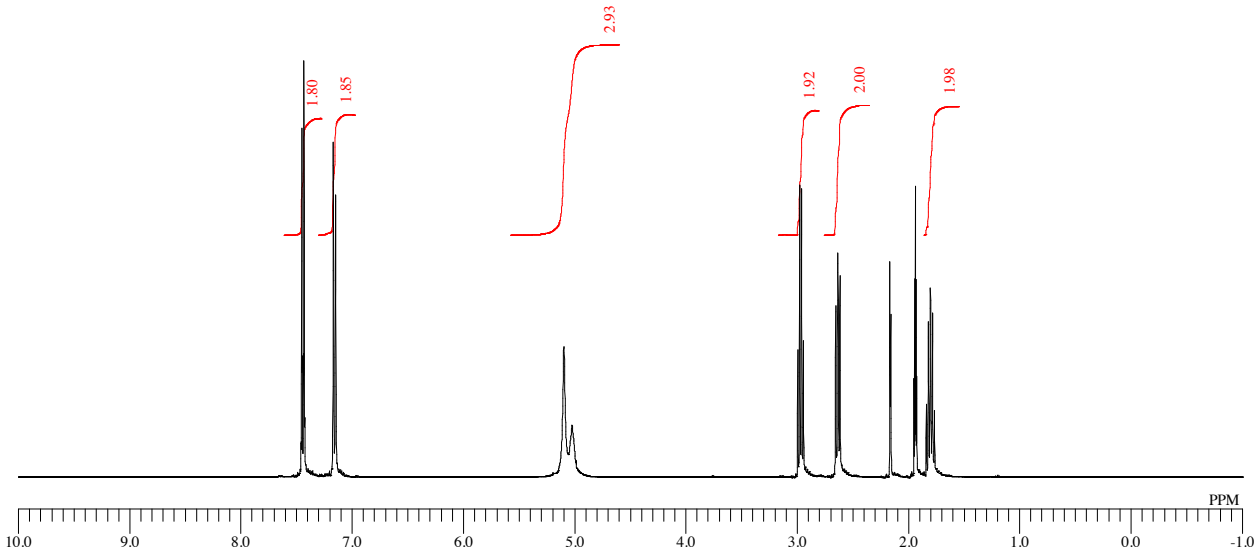
^{13}C NMR: (100 MHz, CD_3CN)



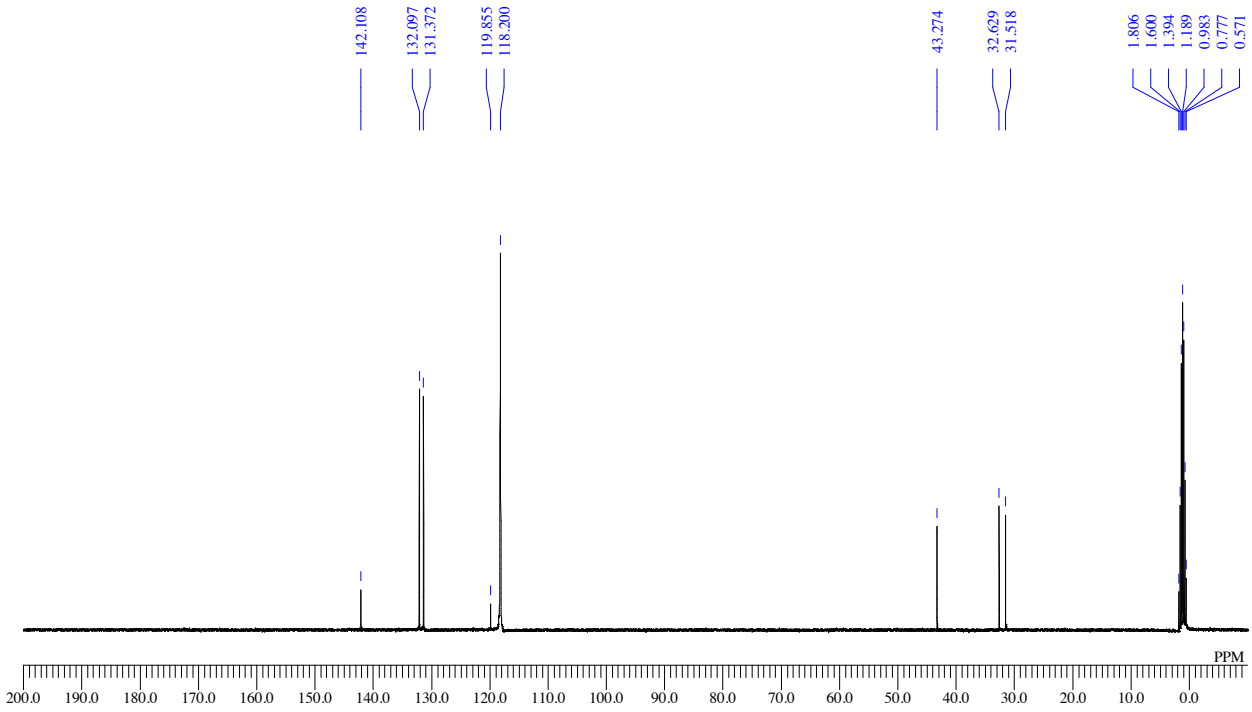


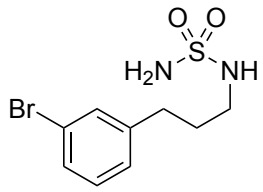
10e

^{1}H NMR: (400 MHz, CD_3CN)



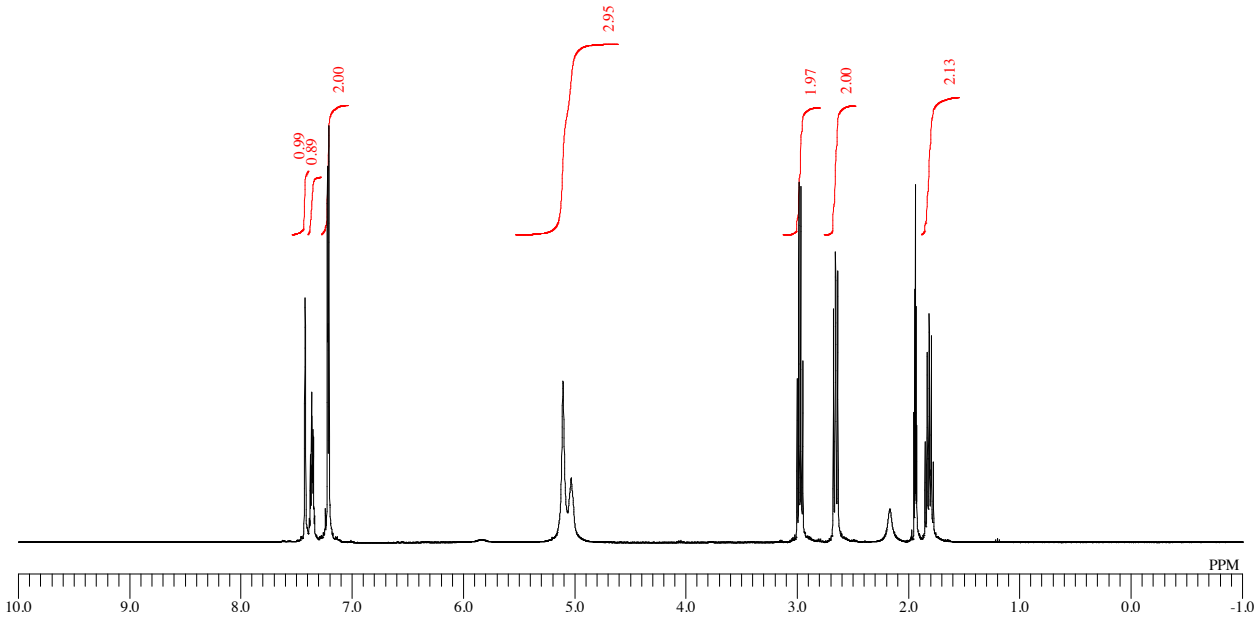
^{13}C NMR: (100 MHz, CD_3CN)



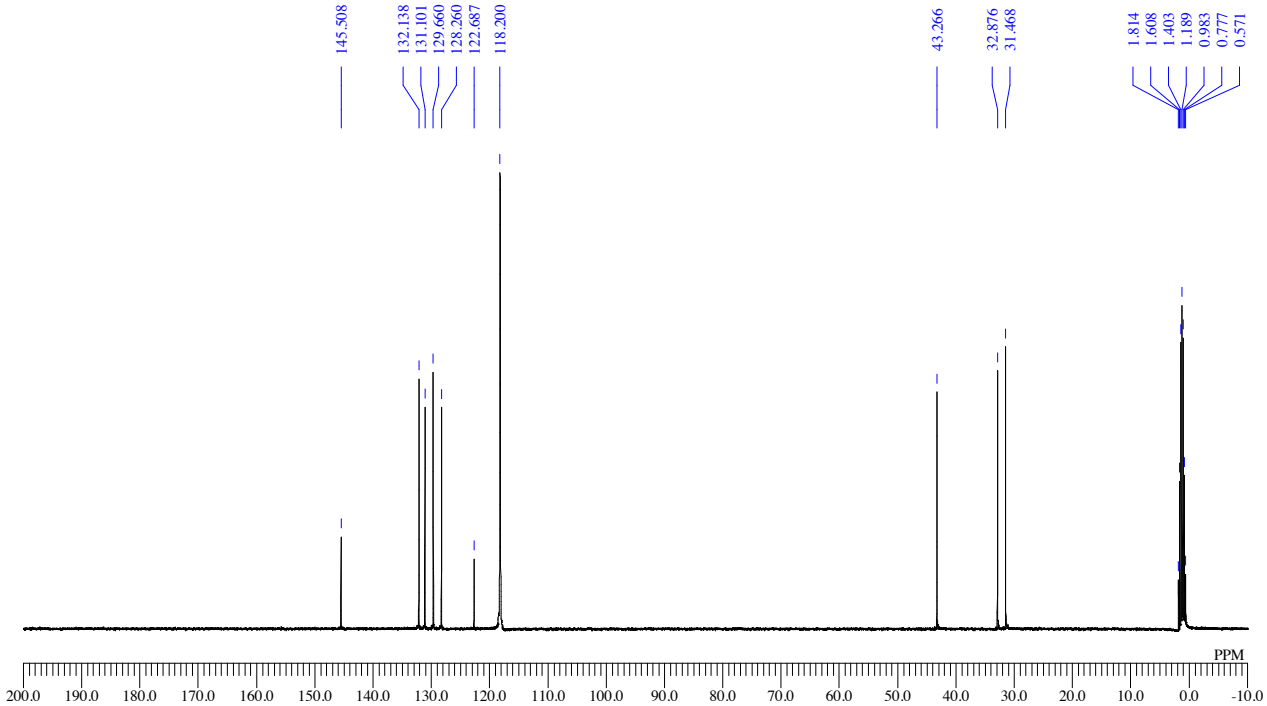


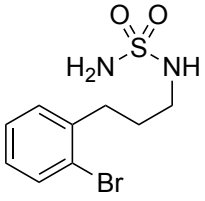
10f

^{1}H NMR: (400 MHz, CD_3CN)



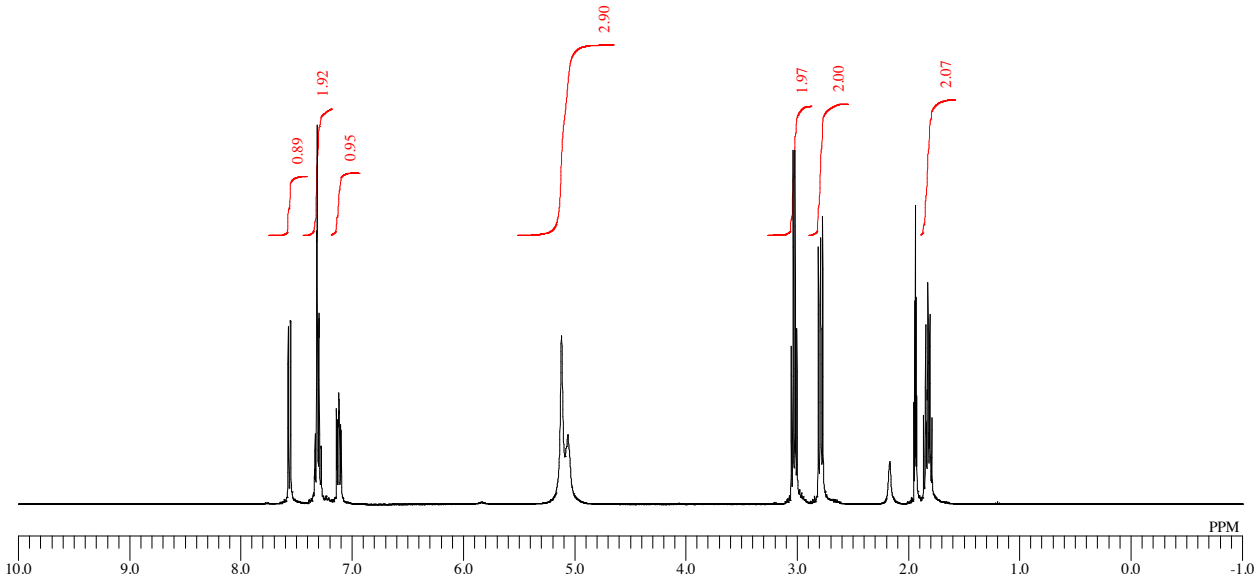
^{13}C NMR: (100 MHz, CD_3CN)



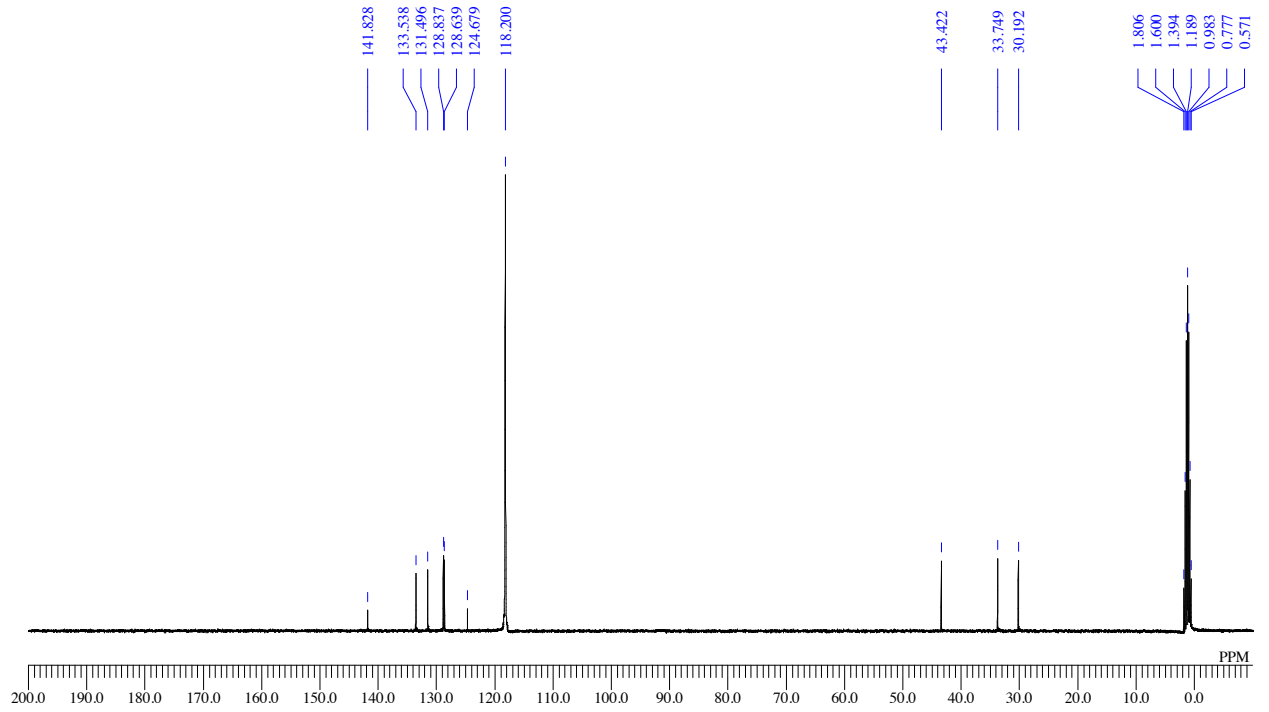


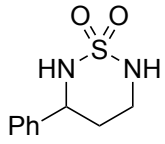
10g

^{1}H NMR: (400 MHz, CD_3CN)



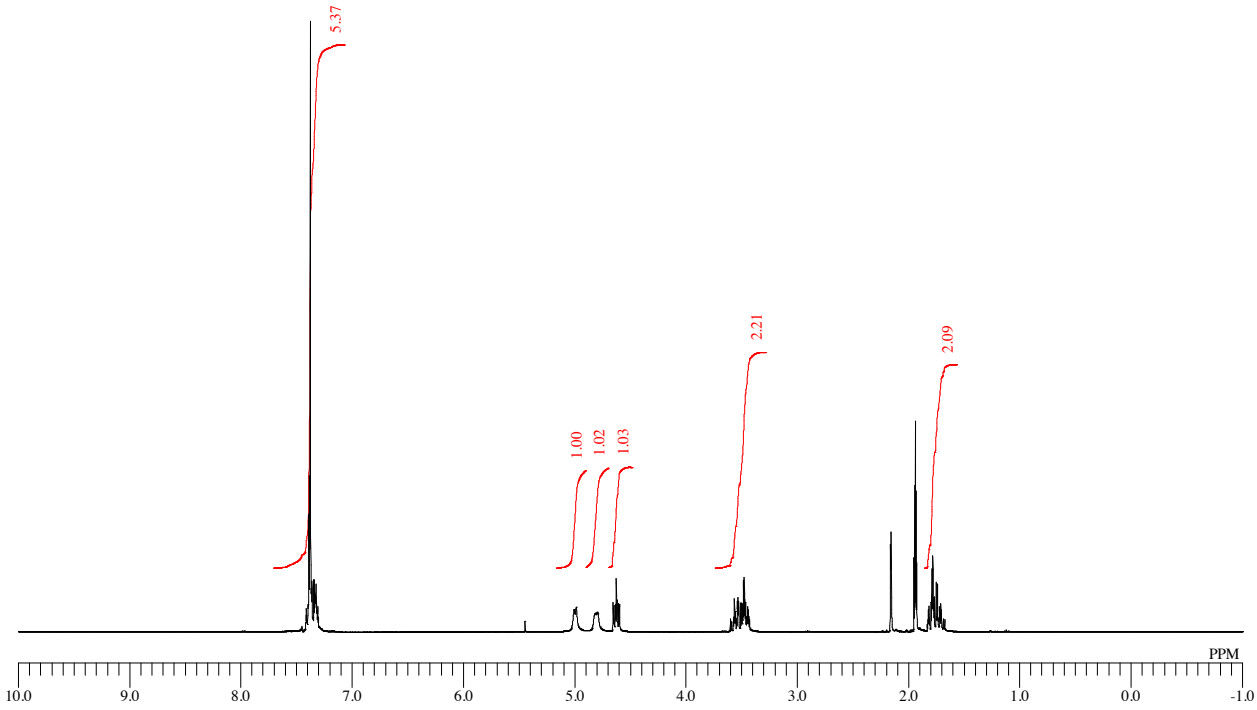
^{13}C NMR: (100 MHz, CD_3CN)



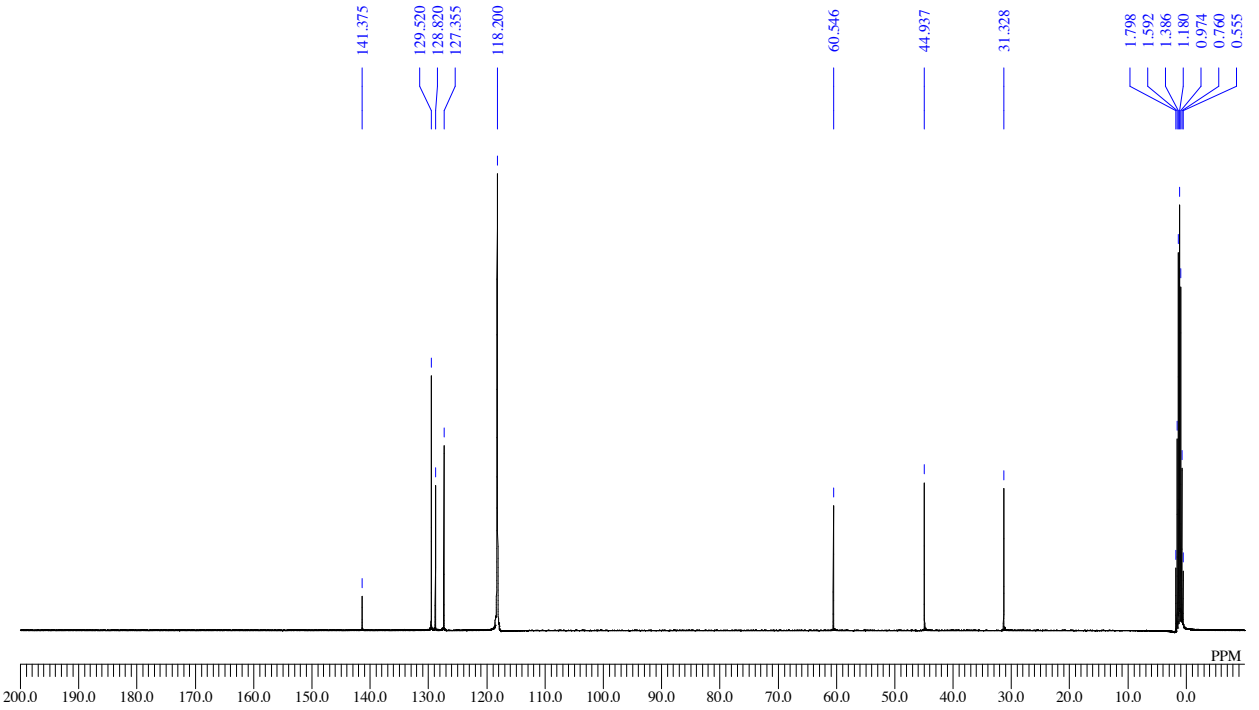


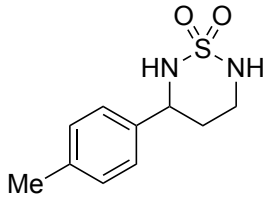
11a

^{1}H NMR: (400 MHz, CD_3CN)



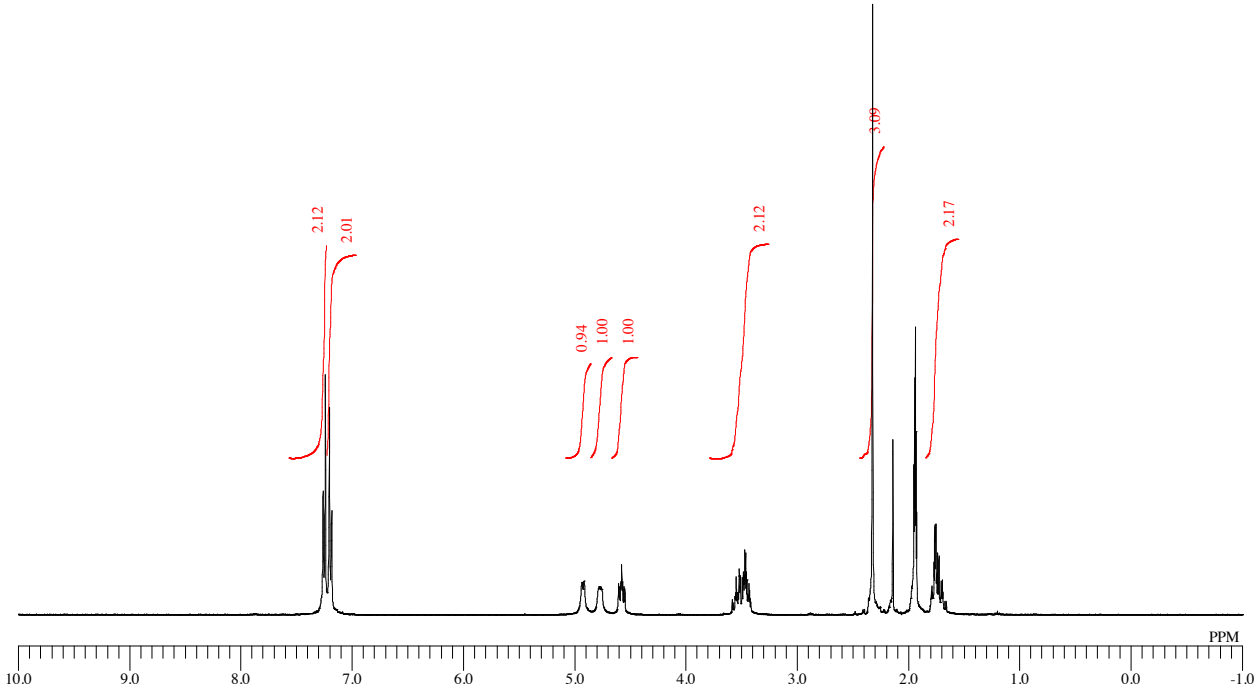
^{13}C NMR: (100 MHz, CD_3CN)



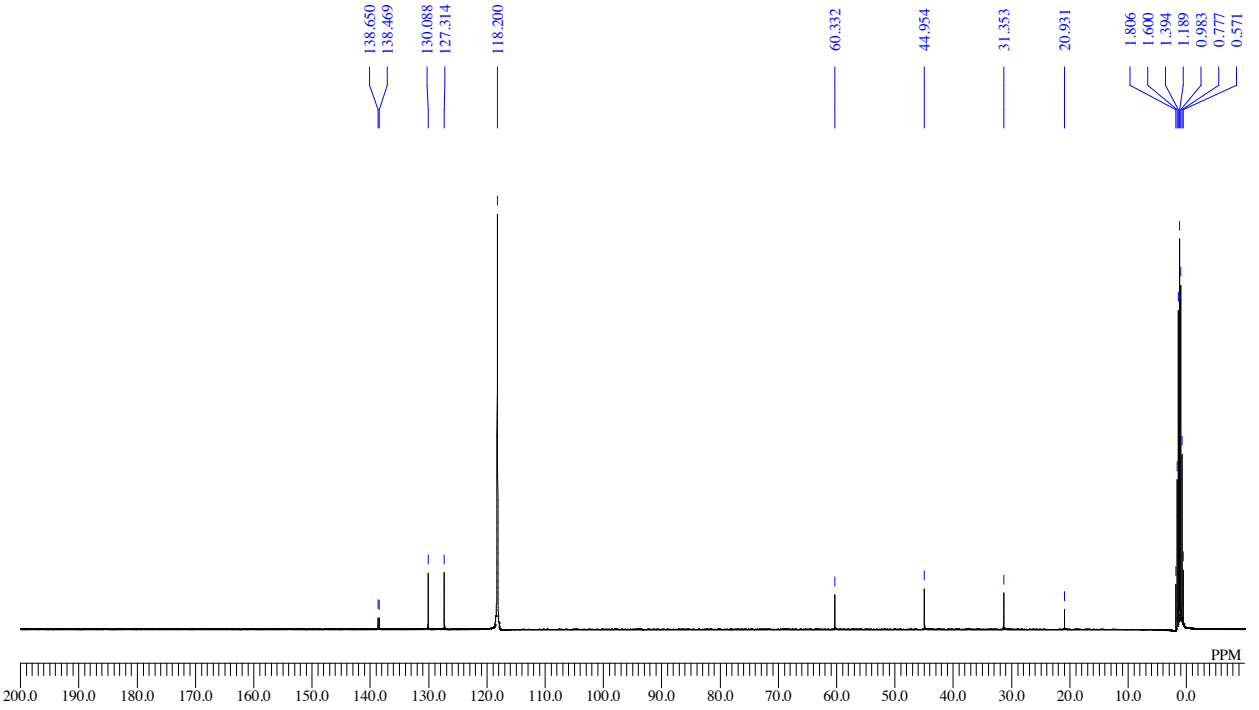


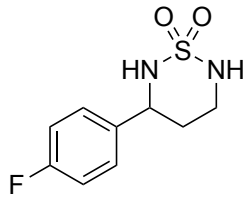
11b

^{1}H NMR: (400 MHz, CD_3CN)



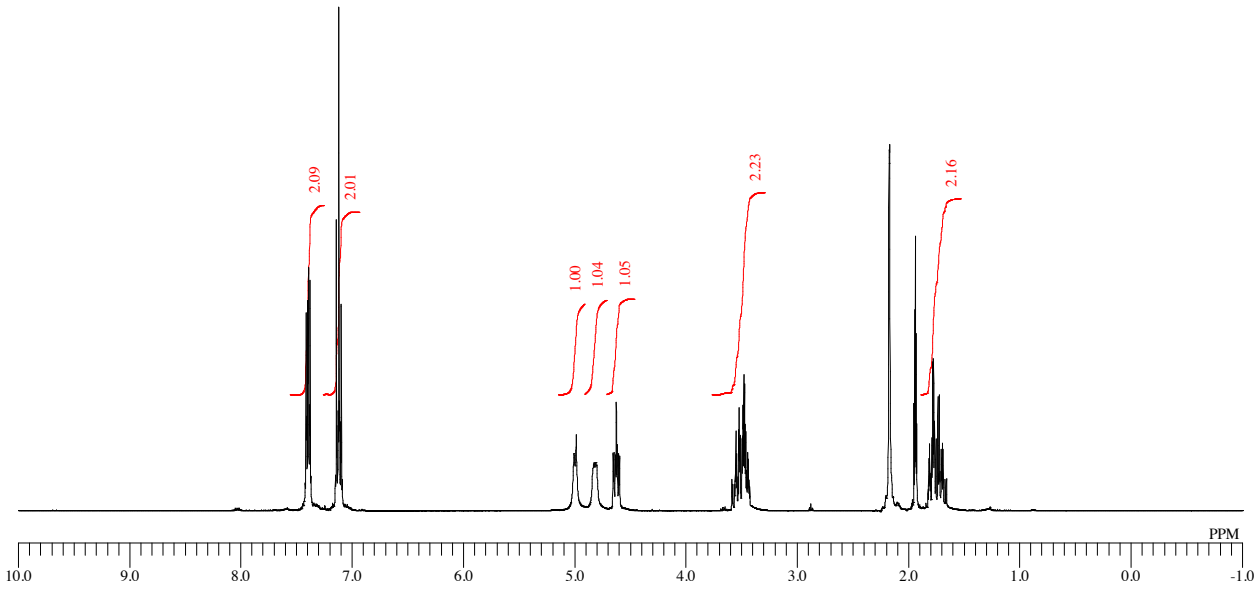
^{13}C NMR: (100 MHz, CD_3CN)



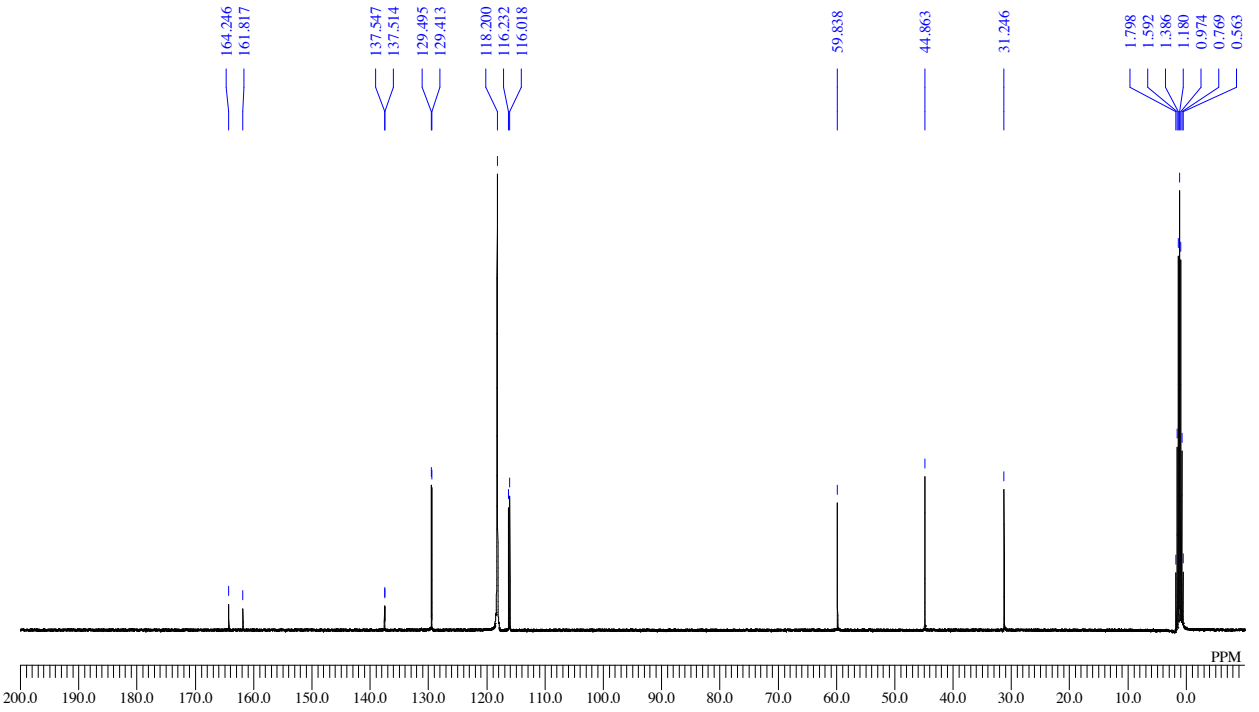


11c

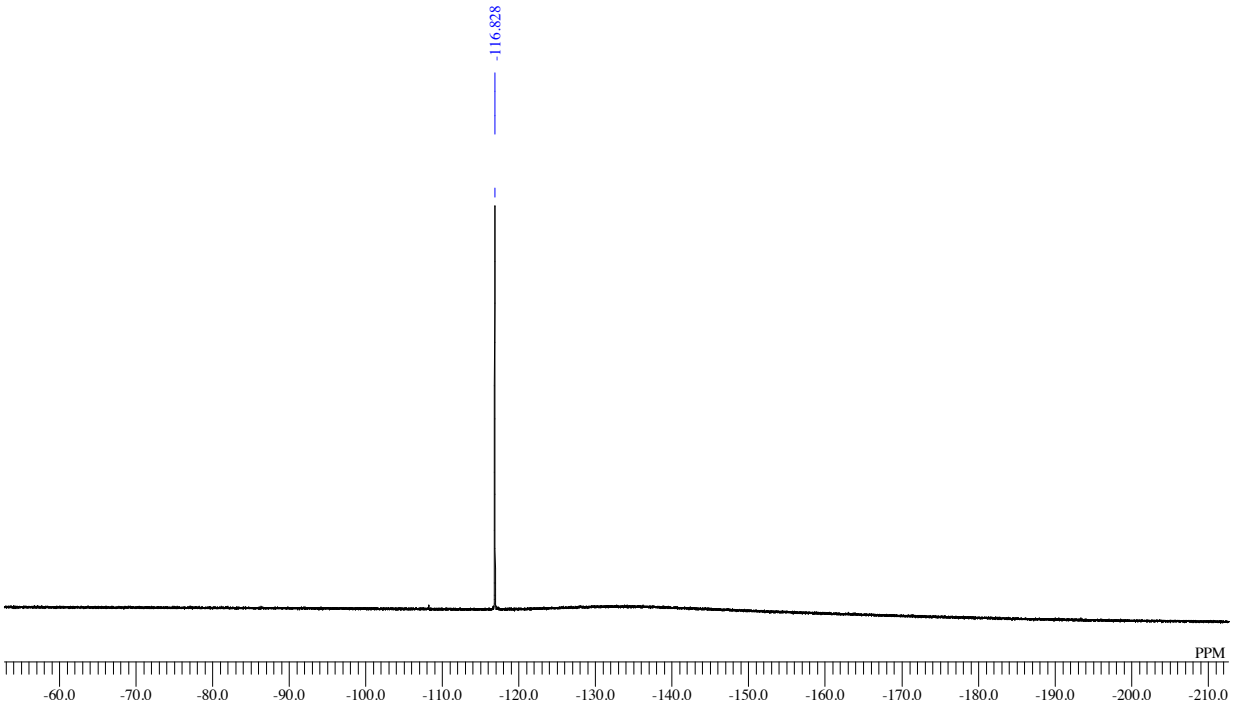
^{1}H NMR: (400 MHz, CD_3CN)

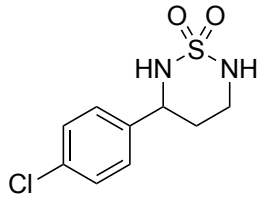


^{13}C NMR: (100 MHz, CD_3CN)



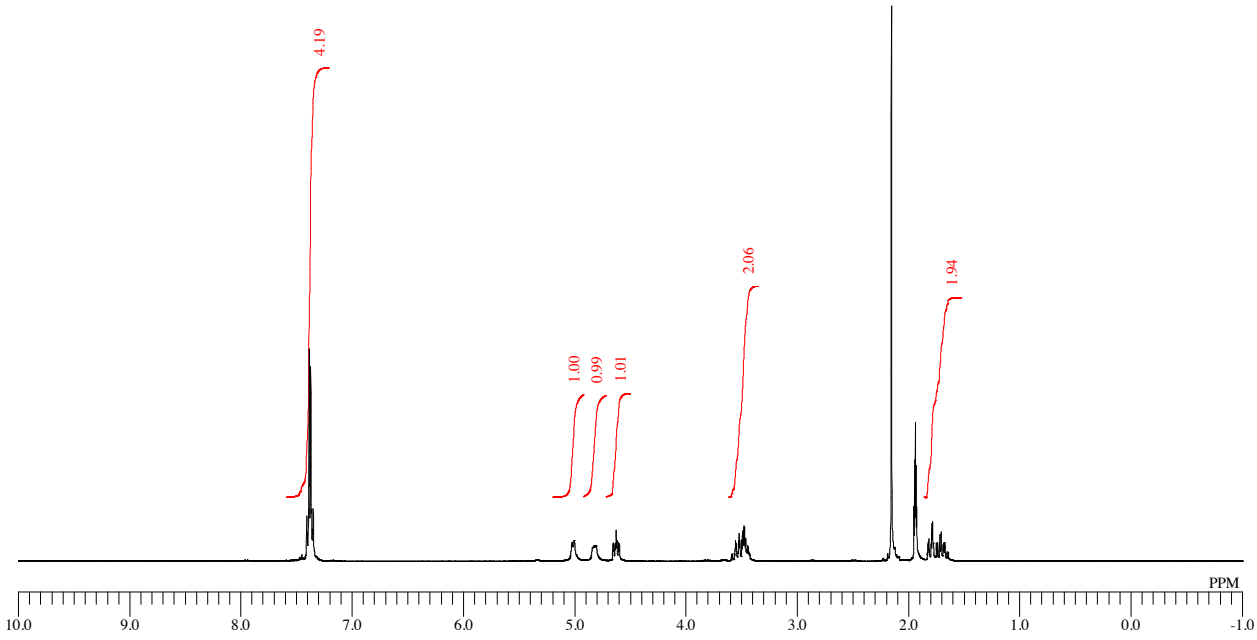
^{19}F NMR: (377 MHz, CD_3CN)



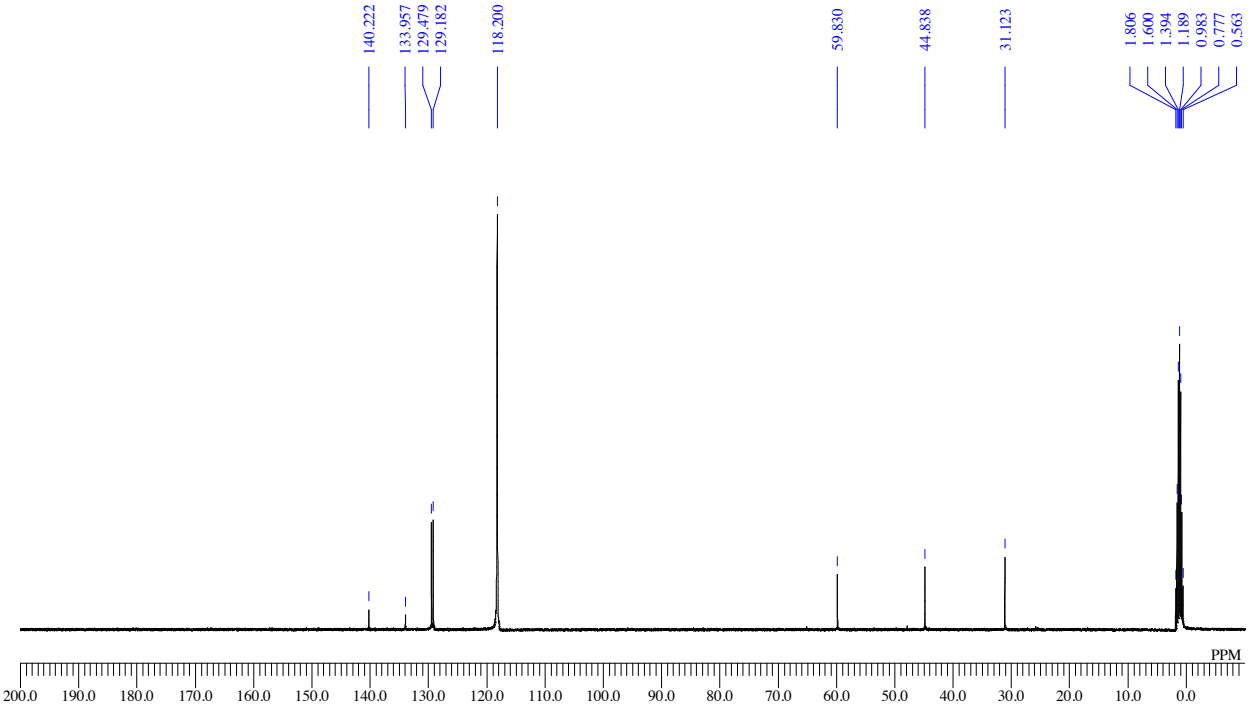


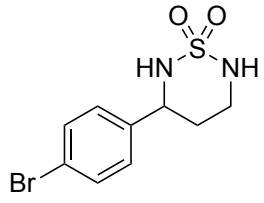
11d

^{1}H NMR: (400 MHz, CD_3CN)



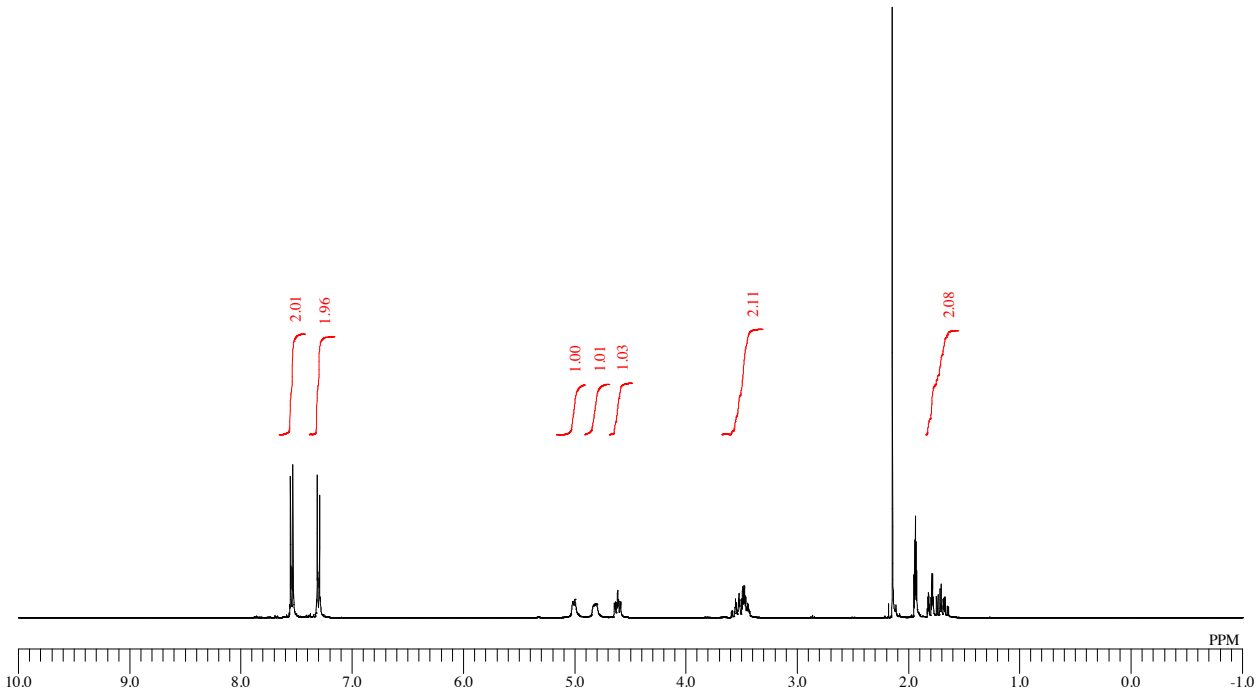
^{13}C NMR: (100 MHz, CD_3CN)



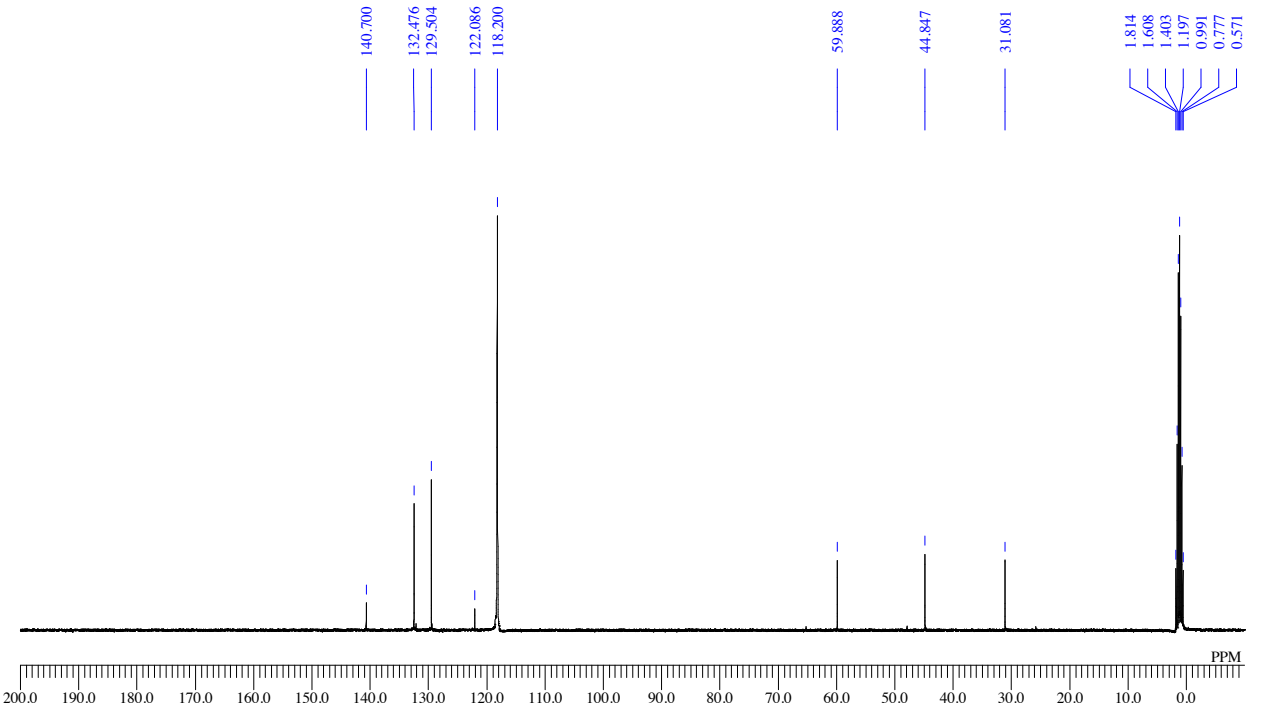


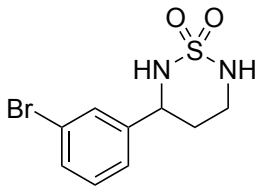
11e

^{1}H NMR: (400 MHz, CD_3CN)



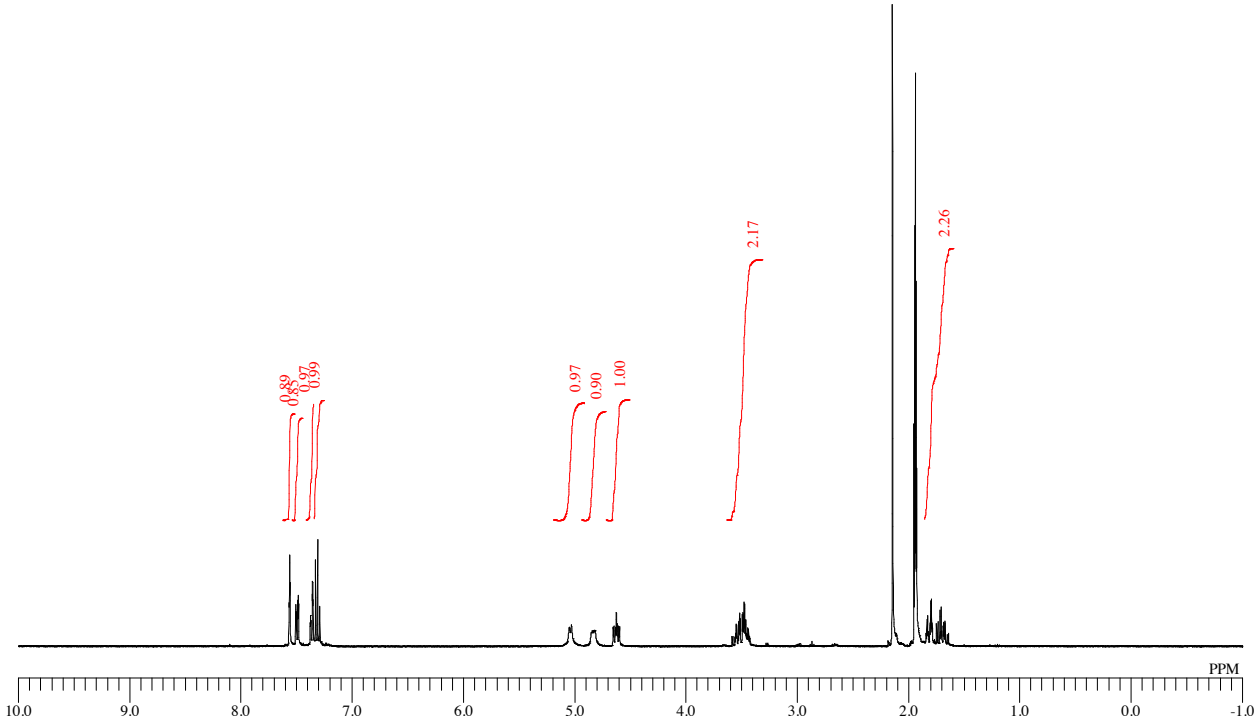
^{13}C NMR: (100 MHz, CD_3CN)



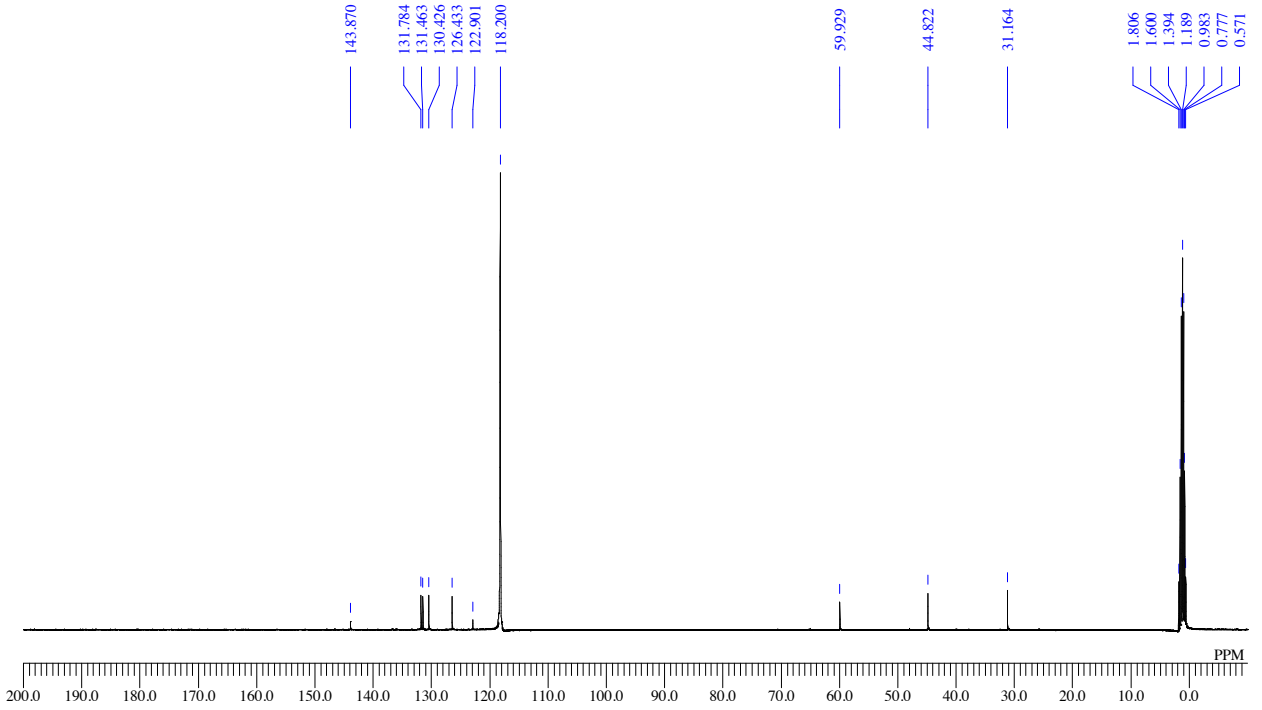


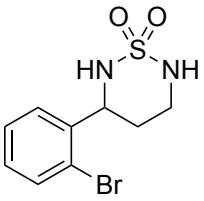
11f

^{1}H NMR: (400 MHz, CD_3CN)



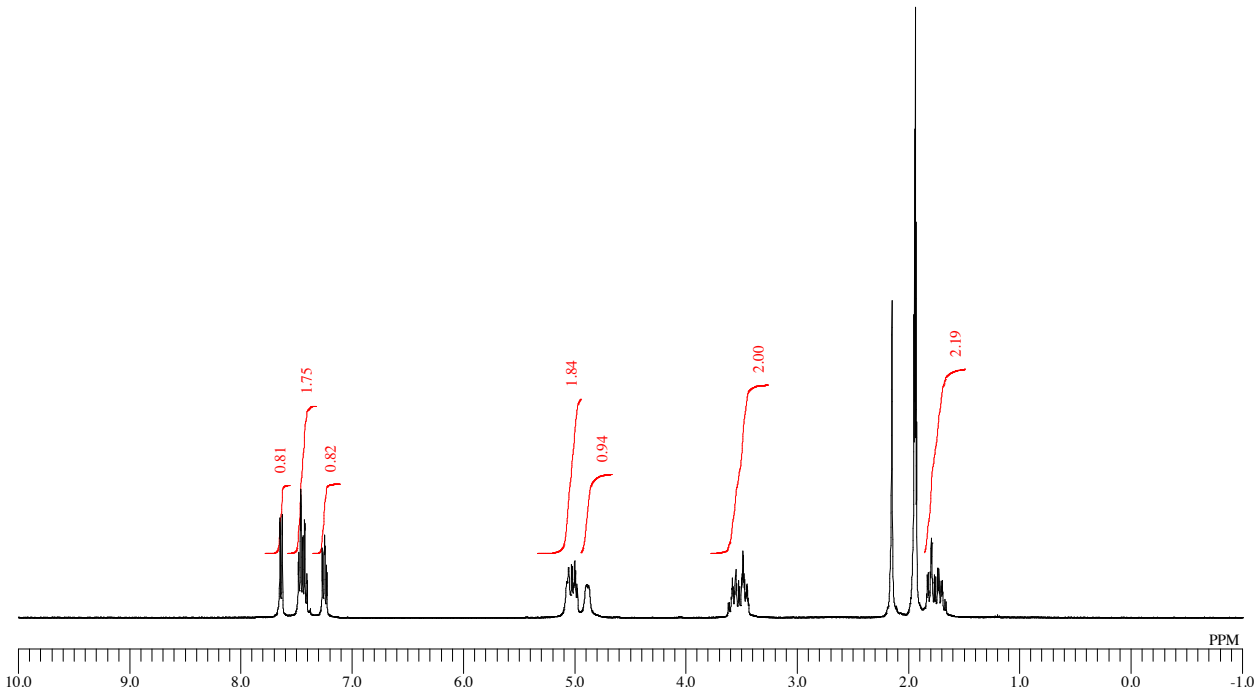
^{13}C NMR: (100 MHz, CD_3CN)



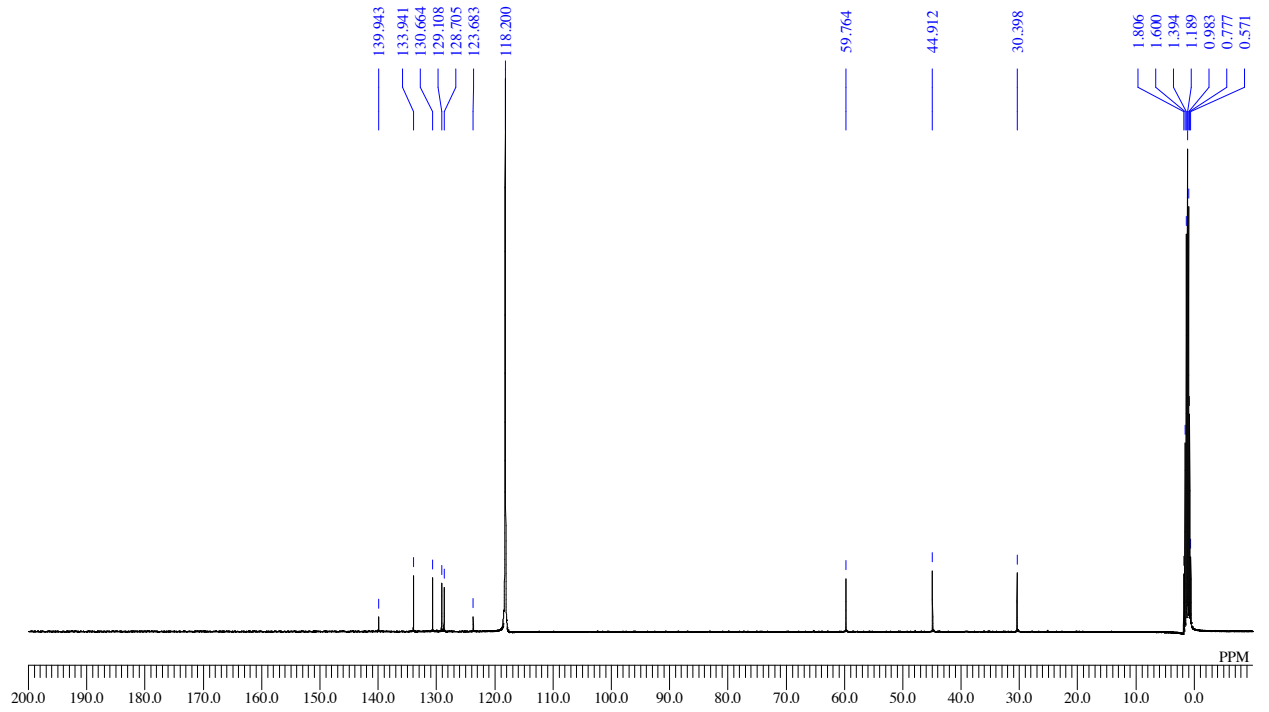


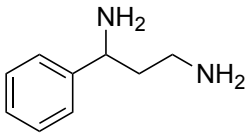
11g

^{1}H NMR: (400 MHz, CD_3CN)



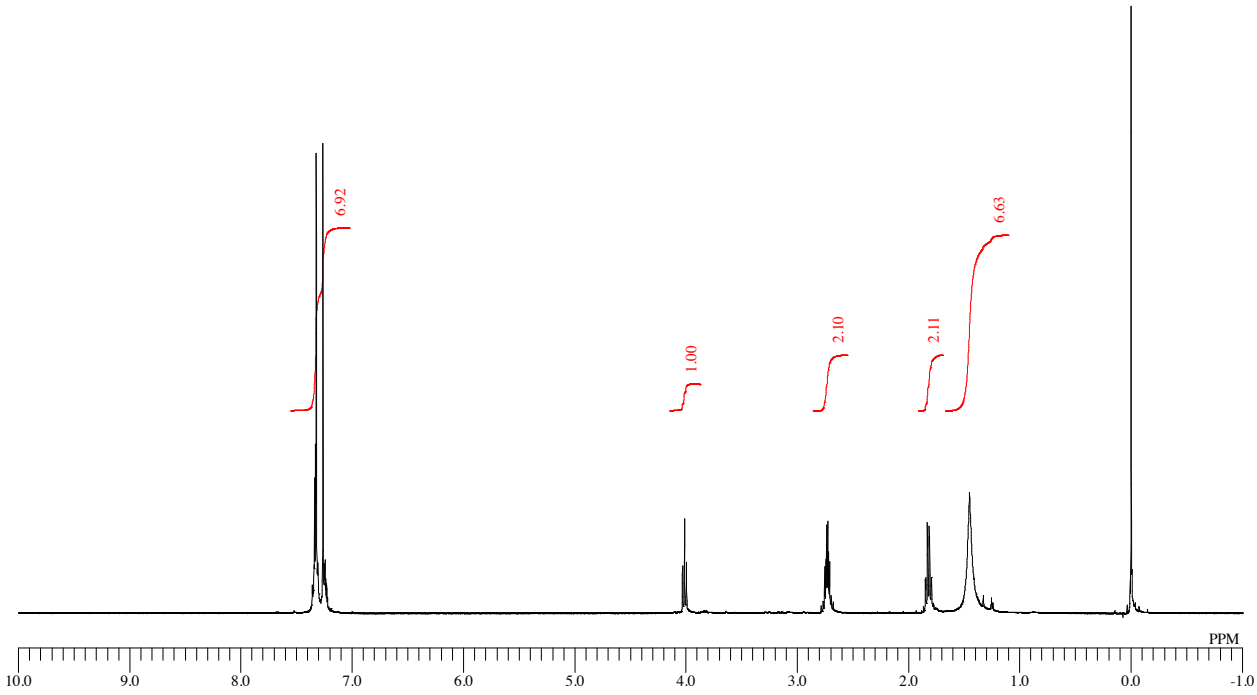
^{13}C NMR: (100 MHz, CD_3CN)



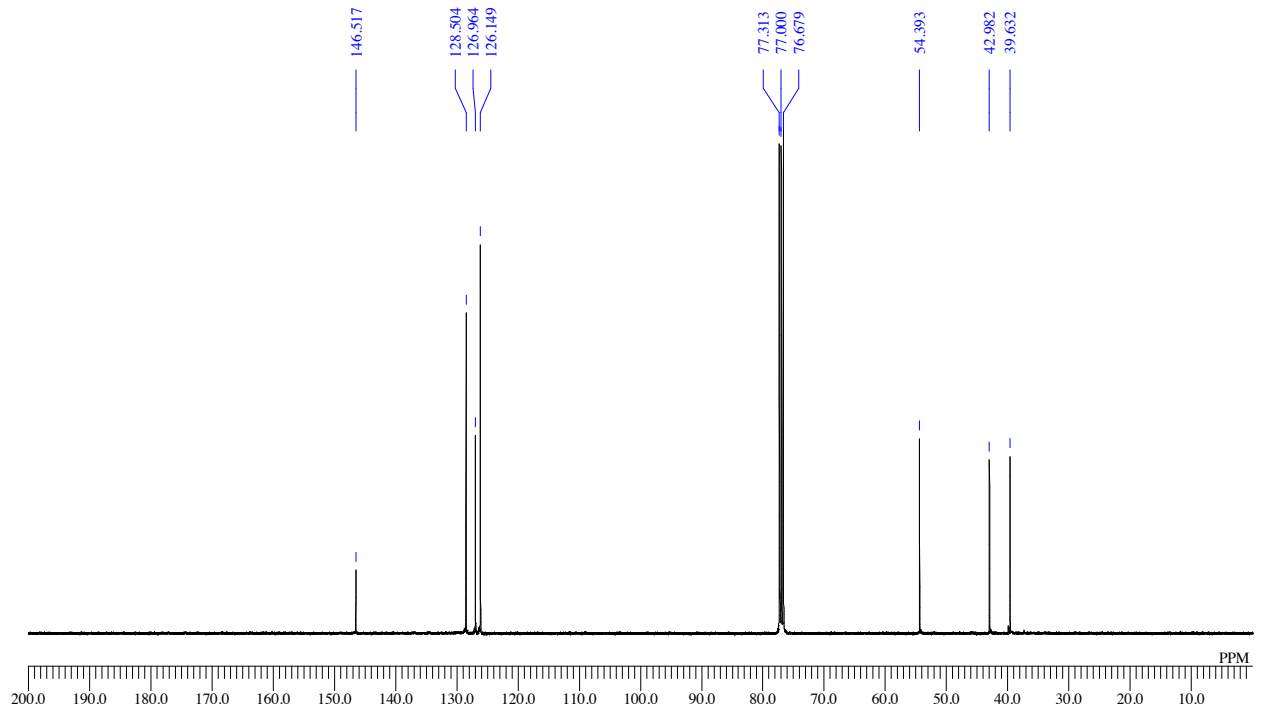


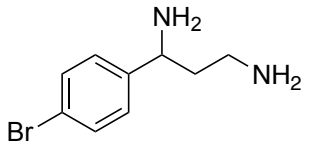
12a

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



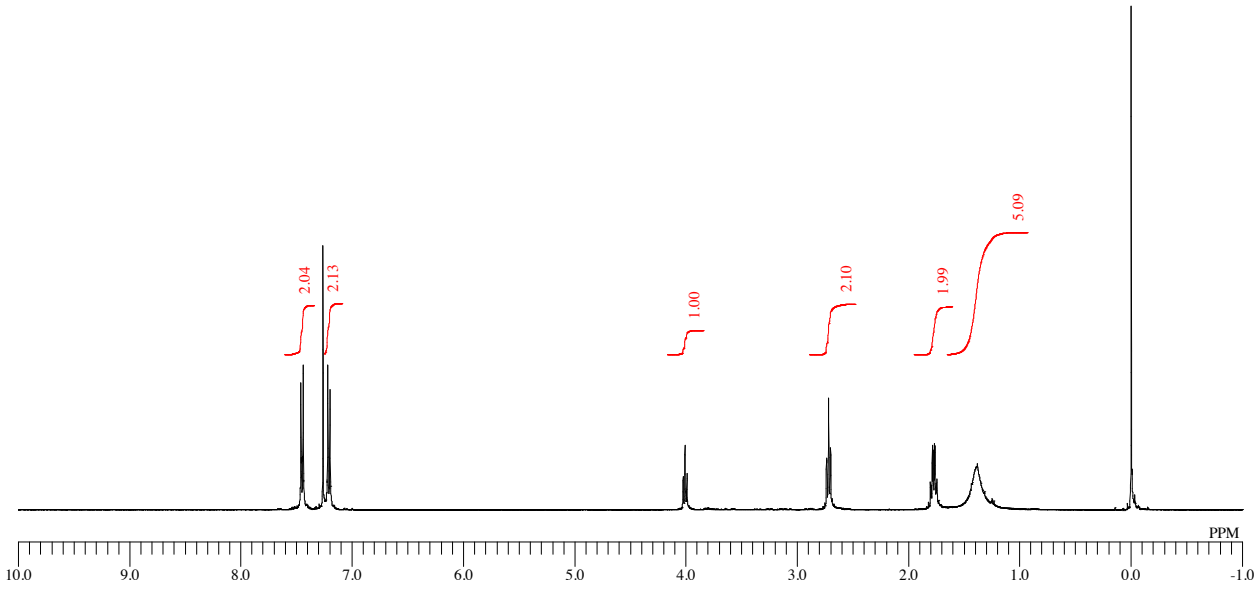
^{13}C NMR: (100 MHz, $CDCl_3$)





12e

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



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