Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Generation of Alkoxysulfonyl Radicals from Chlorosulfates and their Intramolecular Capture with Alkynes to get Sultones

Lara Cala, Olaya García-Pedrero, Rubén Rubio-Presa, Francisco J. Fañanás, and Félix Rodríguez

Contents

1. General Information

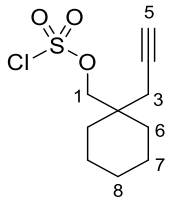
^{1}H NMR spectra were recorded on a Bruker AMX-400 (400 MHz), Bruker AV-300 (300 MHz), Bruker DPX-300 (300 MHz) or Bruker AV-600 (600 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CDCl_3$: δ= 7.26 ppm; CD_3CN: δ= 1.94 ppm). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, dd: double doublet, ddd: double doublet of doublets, dtd: double triplet of doublets, td: triplet of doublets, t: triplet, q: quartet, m: multiplet, app: apparent), coupling constants (J in Hz), integration and assignment. ^{13}C NMR spectra were recorded on a Bruker AMX-400 (100 MHz), Bruker AV-300 (75 MHz), Bruker DPX-300 (75 MHz) or Bruker AV-600 (150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ = 77.2 ppm; C_6D_6 = 128.1 ppm; CD_3CN: δ = 118.3 ppm). Two-dimensional NMR experiments (COSY, HSQC, HMBC and NOESY) were recorded on a Bruker AV-300 (300 MHz) or a Bruker AV-600 (600 MHz). High-resolution mass spectrometry was carried out on a Finnigan-Mat 95 spectrometer. Solvents were dried with a PureSolv® column system before use.

2. Experimental Procedures and Characterization Data

2.1 Synthesis of Starting Chlorosulfate Derivatives 1 or 3

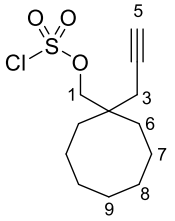
Chlorosulfate derivatives **1** were synthesized according to the method we have previously described.[1] Most of these chlorosulfates were rapidly used without purification. However, some of them were characterized.

[1-(Prop-2-yn-1-yl)cyclohexyl]methyl chlorosulfate (1a)



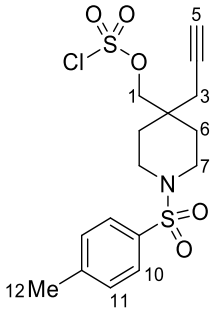
Colorless oil. R_f = 0.4 (silica gel, hexanes:EtOAc 1:50). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.47 (s, 2H, H_1), 2.35 (d, *J* = 2.7 Hz, 2H, H_3), 2.08 (t, *J* = 2.7 Hz, 1H, H_5), 1.61 – 1.39 (m, 10H, $H_{6\text{-}8}$). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 80.6, 79.6, 71.6, 36.8, 31.4, 25.5, 24.8, 21.0. **HRMS** (ESI+) $C_{10}H_{15}ClO_3S$ $[M+Na]^+$ calcd. 273.0323, found 273.0321.

[1-(Prop-2-yn-1-yl)cyclooctyl]methyl chlorosulfate (1b)



Colorless oil. R_f = 0.4 (silica gel, hexanes:EtOAc 1:50). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.38 (s, 2H, H_1), 2.27 (d, *J* = 2.7 Hz, 2H, H_3), 2.06 (t, *J* = 2.7 Hz, 1H, H_5), 1.66 – 1.51 (m, 14H, $H_{6\text{-}9}$). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 79.9, 79.6, 71.3, 39.8, 30.9, 29.1, 28.3, 25.9, 25.3, 22.2. **HRMS** (ESI+) $C_{12}H_{19}ClO_3S$ $[M+Na]^+$ calcd. 301.0636, found 301.0628.

[4-(Prop-2-yn-1-yl)-1-tosylpiperidin-4-yl]methyl chlorosulfate (1d)



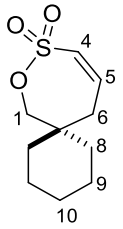
[1] L. Cala, I. Rivilla, F. P. Cossío, F. J. Fañanás, F. Rodríguez, *Chem. Eur. J.* **2019**, *25*, 13083-13087.

Colorless oil. R_f = 0.4 (silica gel, hexanes:EtOAc 1:50). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 2H, H_{10}), 7.39 – 7.25 (m, 2H, H_{11}), 4.33 (s, 2H, H_1), 3.31 – 3.13 (m, 2H, H_{7a}), 2.88 – 2.69 (m, 2H, H_{7b}), 2.43 (s, 3H, H_{12}), 2.23 (d, *J* = 2.5 Hz, 2H, H_3), 2.08 (d, *J* = 2.5 Hz, 1H, H_5), 1.77 – 1.54 (m, 4H, H_6). **^{13}C NMR** (75 MHz, C_6D_6) δ 144.3, 133.3, 130.3, 127.9, 79.6, 78.6, 73.1, 66.2, 41.7, 35.5, 30.5, 23.5, 21.9, 15.6.

2.2 Synthesis of Sultone Derivatives 2 or 4

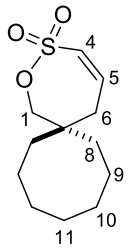
A 0.1 M solution of the corresponding chlorosulfate **1** (or **3**) in acetonitrile was placed in a carousel tube with a magnetic stirring bar. Triethylborane (10 mol%, 1M in hexanes) and tris(trimethylsilyl)silane (1.1 equivalent) were added. The reaction mixture was bubbled with air for 10 seconds and then stirred for 15 minutes. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the corresponding pure compound **2** (or **4**).

8-Oxa-9-thiaspiro[5.6]dodec-10-ene 9,9-dioxide (2a)



Colorless oil. R_f = 0.24 (silica gel, hexanes:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.58 (d, *J* = 11.1 Hz, 1H, H_4), 6.44 (dt, *J* = 11.1, 7.2 Hz, 1H, H_5), 4.30 (s, 2H, H_1), 2.54 (d, *J* = 7.2 Hz, 2H, H_6), 1.57-1.35 (m, 10H, $H_{8\text{-}10}$). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.9, 131.2, 78.8, 37.1, 35.9, 33.3, 25.7, 21.3. **HRMS** (ESI+) $C_{10}H_{16}O_3S$ $[M+Na]^+$ calcd. 239.0712, found 239.0715.

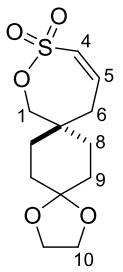
2-Oxa-3-thiaspiro[6.7]tetradec-4-ene 3,3-dioxide (2b)



Colorless oil. R_f = 0.26 (silica gel, hexanes:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.56 (dd, *J* = 11.0, 0.7 Hz, 1H, H_4), 6.41 (dt, *J* = 11.0, 7.2 Hz, 1H, H_5), 4.19 (s, 2H, H_1), 2.47 (dd, *J* = 7.2, 0.7 Hz,

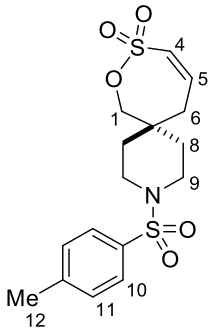
2H, H_6), 1.67 – 1.34 (m, 14H, $H_{8\text{-}H11}$). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.0, 131.2, 78.1, 40.3, 36.4, 30.5, 28.3, 28.0, 25.4, 22.5. **HRMS** (ESI+) $C_{12}H_{20}O_3S$ $[M+Na]^+$ calcd. 267.1025, found 267.1027.

1,4,10-Trioxa-11-thiadispiro[4.2.6^8.2^5]hexadec-12-ene 11,11-dioxide (2c)



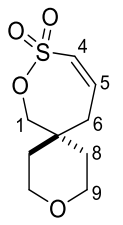
Colorless oil. R_f = 0.35 (silica gel, hexanes:EtOAc 3:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.63 (d, *J* = 11.0 Hz, 1H, H_4), 6.44 (dt, *J* = 11.0, 7.3 Hz, 1H, H_5), 4.34 (s, 2H, H_1), 3.96 (s, 4H, H_{10}), 2.60 (d, *J* = 7.3 Hz, 2H, H_6), 1.64 (s, 8H, H_8 and H_9). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.5, 131.8, 107.9, 78.3, 64.3, 36.1, 35.1, 30.5, 30.3. **HRMS** (ESI+) $C_{12}H_{18}O_5S$ $[M+Na]^+$ calcd. 297.0767, found 297.0770.

3-Tosyl-8-oxa-9-thia-3-azaspiro[5.6]dodec-10-ene 9,9-dioxide (2d)



White solid. R_f = 0.11 (silica gel, hexanes:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H, H_{10}), 7.34 (d, *J* = 8.2 Hz, 2H, H_{11}), 6.58 (d, *J* = 11.1 Hz, 1H, H_4), 6.35 (dt, *J* = 11.1, 7.2 Hz, 1H, H_5), 4.19 (s, 2H, H_1), 3.10 (ddd, *J* = 11.9, 6.8, 4.3 Hz, 2H, H_{9a}), 2.92 (ddd, *J* = 11.9, 7.9, 4.0 Hz, 2H, H_{9b}), 2.46 (d, *J* = 7.2, 2H, H_6), 2.44 (s, 3H, H_{12}), 1.77 – 1.52 (m, 4H, H_8). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 137.5, 132.7, 132.1, 129.8, 127.6, 76.8, 41.6, 35.5, 34.9, 31.9, 21.5. **HRMS** (ESI+) $C_{16}H_{21}NO_5S$ $[M+Na]^+$ calcd. 394.0753, found 394.0750.

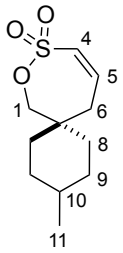
3,8-Dioxa-9-thiaspiro[5.6]dodec-10-ene 9,9-dioxide (2e)



Colorless oil. R_f = 0.22 (silica gel, hexanes:EtOAc 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.64 (dt, *J* = 11.0, 0.8 Hz, 1H, H_4), 6.44 (dt, *J* = 11.0, 7.2 Hz, 1H, H_5), 4.39 (s, 2H, H_1), 3.74 – 3.62 (m, 4H, H_9),

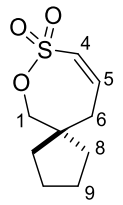
2.66 (d, *J* = 7.2 Hz, 2H, H_6), 1.75 – 1.48 (m, 4H, H_8). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.9, 132.2, 77.9, 64.5, 63.1, 35.8, 34.9, 34.8, 33.0. **HRMS** (ESI+) $C_9H_{14}O_4S$ $[M+Na]^+$ calcd. 241.0505, found 241.0510.

3-methyl-8-oxa-9-thiaspiro[5.6]dodec-10-ene 9,9-dioxide (2f)



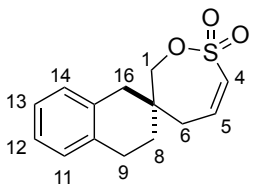
Colorless oil. R_f = 0.30 (silica gel, *n*-hexane:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.52 (d, *J* = 11.1 Hz, 1H, H_4), 6.40 (dt, *J* = 11.1, 7.1 Hz, 1H, H_5), 4.38 (s, 2H, H_1), 2.40 (d, *J* = 7.1 Hz, 2H, H_6), 1.75 (dt, *J* = 13.5, 4.4 Hz, 2H, H_{8a}), 1.64 – 1.53 (m, 2H, H_{8b}), 1.42 – 1.28 (m, 1H, H_{10}), 1.21 (td, *J* = 13.5, 3.9 Hz, 2H, H_{9a}), 0.99 (ddd, *J* = 14.2, 11.2, 3.2 Hz, 2H, H_{9b}), 0.90 (d, *J* = 6.5 Hz, 3H, H_{11}). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.8, 130.6, 75.4, 40.2, 37.1, 34.1, 32.2, 30.4, 22.2. **HRMS** (APCI) $C_{11}H_{19}O_3S$ $[M+H]^+$ calcd. 231.1049, found 231.1053.

7-Oxa-8-thiaspiro[4.6]undec-9-ene 8,8-dioxide (2g)



Colorless oil. R_f = 0.23 (silica gel, *n*-hexane:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.61 (d, *J* = 11.1 Hz, 1H, H_4), 6.45 (dt, *J* = 11.1, 6.9 Hz, 1H, H_5), 4.29 (s, 2H, H_1), 2.61 (d, *J* = 6.9 Hz, 2H, H_6), 1.77 – 1.53 (m, 8H, H_{8-9}). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.9, 132.1, 78.8, 45.3, 38.0, 35.7, 24.6. **HRMS** (APCI) $C_9H_{14}O_3S$ $[M+H]^+$ calcd. 203.0736, found 203.0745.

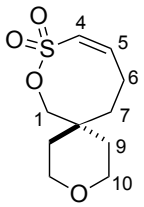
3,4-dihydro-1*H*,5'*H*,7'*H*-spiro[naphthalene-2,6'-[1,2]oxathiepine] 2',2'-dioxide (2h)



White solid. R_f = 0.15 (silica gel, *n*-hexane:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 4H, H_{11-14}), 6.67 (dd, *J* = 11.0, 1.2 Hz, 1H, H_4), 6.46 (ddd, *J* = 11.0, 7.6, 6.8 Hz, 1H, H_5), 4.43 (d, *J* = 12.2 Hz, 1H, H_{1a}), 4.30 (d, *J* = 12.2 Hz, 1H, H_{1b}), 2.87 – 2.78 (m, 2H, H_9), 2.76 – 2.50 (m, 4H, H_6 and H_{16}), 1.94 – 1.73 (m, 2H, H_8). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.4, 134.7, 132.9, 132.1,

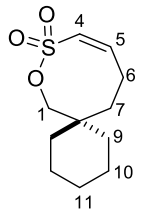
129.6, 128.9, 126.5, 126.3, 78.2, 37.3, 36.5, 35.5, 29.8, 25.2. **HRMS** (APCI) $C_{14}H_{17}O_3S$ $[M+H]^+$ calcd. 265.0893, found 265.0898.

(*Z*)-3,8-dioxa-9-thiaspiro[5.7]tridec-10-ene 9,9-dioxide (2i)



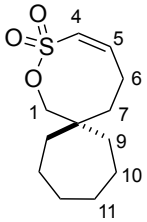
White solid. R_f = 0.17 (silica gel, *n*-hexane:EtOAc 2:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.48 (dt, *J* = 11.1, 9.3 Hz, 1H, H_5), 6.16 (d, *J* = 11.1, 1H, H_4), 4.27 (s, 2H, H_1), 3.73 – 3.60 (m, 4H, H_{10}), 2.57 (bt, *J* = 9.3 Hz, 2H, H_6), 1.72 – 1.59 (m, 4H, H_9), 1.55 – 1.44 (m, 2H, H_7). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.4, 124.0, 75.4, 63.0, 35.7, 34.5, 33.2, 21.1. **HRMS** (APCI) $C_{10}H_{17}O_4S$ $[M+H]^+$ calcd. 233.0842, found 233.0849.

(*Z*)-8-Oxa-9-thiaspiro[5.7]tridec-10-ene 9,9-dioxide (2j)



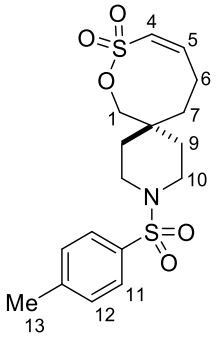
Colorless oil. R_f = 0.26 (silica gel, hexanes:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.47 (dt, *J* = 11.2, 9.2 Hz, 1H, H_5), 6.15 (dt, *J* = 11.2, 0.8 Hz, 1H, H_4), 4.23 (s, 2H, H_1), 2.57 (bt, *J* = 9.2 Hz, 2H, H_6), 1.80 – 1.10 (m, 12H, H_7 and $H_{9\text{-}11}$). **^{13}C NMR** (75 MHz, C_6D_6) δ 143.9, 124.1, 77.8, 36.7, 35.9, 33.4, 26.4, 21.7, 21.3. **HRMS** (ESI+) $C_{11}H_{18}O_3S$ $[M+Na]^+$ calcd. 253.0869, found 253.0851

(*Z*)-9-oxa-10-thiaspiro[6.7]tetradec-11-ene 10,10-dioxide (2k)



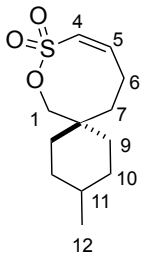
Colorless oil. R_f = 0.42 (silica gel, *n*-hexane:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.46 (dt, *J* = 11.2, 9.1 Hz, 1H, H_5), 6.14 (d, *J* = 11.2, 1H, H_4), 4.11 (s, 2H, H_1), 2.52 (bt, *J* = 9.1 Hz, 2H, H_6), 1.56 – 1.39 (m, 14H, H_7 and $H_{9\text{-}11}$). **^{13}C NMR** (75 MHz, C_6D_6) δ 143.9, 124.1, 77.9, 37.0, 36.2, 35.7, 31.0, 22.6, 22.0. **HRMS** (APCI) $C_{12}H_{21}O_3S$ $[M+H]^+$ calcd. 245.1206, found 245.1216.

(*Z*)-3-Tosyl-8-oxa-9-thia-3-azaspiro[5.7]tridec-10-ene 9,9-dioxide (2l)



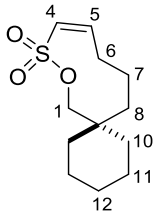
White solid. R_f = 0.18 (silica gel, *n*-hexane:EtOAc 1:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H, H_{11}), 7.35 (d, *J* = 8.0 Hz, 2H, H_{12}), 6.43 (dt, *J* = 11.2, 9.2 Hz, 1H, H_5), 6.12 (d, *J* = 11.2 Hz, 1H, H_4), 4.06 (s, 2H, H_1), 3.23 (dt, *J* = 11.4, 4.8 Hz, 2H, H_{10a}), 2.76 (ddd, *J* = 12.6, 9.5, 3.4 Hz, 2H, H_{10b}), 2.51 (bt, *J* = 9.2 Hz, 2H, H_6), 2.46 (s, 3H, H_{13}), 1.78 – 1.49 (m, 6H, H_7 and H_9). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.1, 143.2, 132.7, 130.0, 127.8, 124.0, 73.8, 41.5, 35.9, 34.6, 32.1, 21.7, 21.2. **HRMS** (APCI) $C_{17}H_{23}NO_5S_2$ $[M+H]^+$ calcd. 386.1090, found 386.1096.

(*Z*)-3-methyl-8-oxa-9-thiaspiro[5.7]tridec-10-ene 9,9-dioxide (2m)



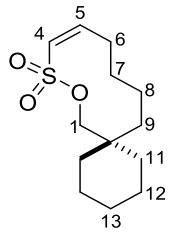
White solid. R_f = 0.20 (silica gel, *n*-hexane:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.47 (dt, *J* = 11.2, 9.4 Hz, 1H, H_5), 6.12 (d, *J* = 11.2 Hz, 1H, H_4), 4.29 (s, 2H, H_1), 2.55 (bt, *J* = 9.4 Hz, 2H, H_6), 1.92 – 1.73 (m, 2H, H_7), 1.60 – 1.50 (m, 2H, H_{9a}), 1.47– 1.40 (m, 2H, H_{9b}), 1.39 – 1.31 (m, 1H, H_{11}), 1.20 – 1.01 (m, 4H, H_{10}), 0.91 (d, *J* = 6.5 Hz, 3H, H_{12}). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.8, 123.6, 73.6, 39.7, 36.0, 33.5, 32.5, 29.9, 22.2, 21.5. **HRMS** (APCI) $C_{12}H_{21}O_3S$ $[M+H]^+$ calcd. 245.1206, found 245.1217.

(*Z*)-8-Oxa-9-thiaspiro[5.8]tetradec-10-ene 9,9-dioxide (2n)



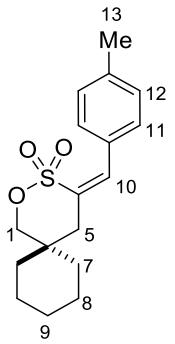
Colorless oil. R_f = 0.31 (silica gel, hexanes:EtOAc 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.49 (d, *J* = 10.6 Hz, 1H, H_4), 6.31 (dt, *J* = 10.6, 9.3 Hz, 1H, H_5), 4.14 (s, 2H, H_1), 2.66 (dt, *J* = 9.3, 6.9 Hz, 2H, H_6), 1.76 – 1.64 (m, 2H, H_7), 1.56 – 1.29 (m, 12H, H_8 and $H_{10\text{-}12}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 129.2, 78.9, 36.9, 33.0, 29.7, 28.2, 25.9, 21.2, 21.0. **HRMS** (ESI+) $C_{12}H_{20}O_3S$ $[M+Na]^+$ calcd. 267.1025, found 267.1018.

(*Z*)-8-Oxa-9-thiaspiro[5.9]pentadec-10-ene 9,9-dioxide (2o)



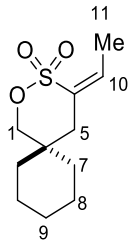
Colorless oil. R_f = 0.35 (silica gel, hexanes:EtOAc 5:1). **^{1}H NMR** (401 MHz, $CDCl_3$, 50 ºC) δ 6.38 (d, *J* = 10.8 Hz, 1H, H_4), 6.24 (dt, *J* = 10.8, 8.7 Hz, 1H, H_5), 3.93 (s, 2H, H_1), 2.67 (bs, 2H, H_6), 1.65 – 1.54 (m, 2H, H_7), 1.54 – 1.16 (m, 14H, H_8, H_9 and $H_{11\text{-}13}$). **^{13}C NMR** (101 MHz, CDCl3, 50 ºC) δ 148.7, 127.8, 74.7, 36.8, 33.1, 30.4, 26.5, 26.0, 26.0, 21.2, 17.8. **HRM**S (ESI+) $C_{13}H_{22}O_3S$ $[M+Na]^+$ calcd. 281.1182, found 281.1186.

(*Z*)-4-(4-Methylbenzylidene)-2-oxa-3-thiaspiro[5.5]undecane 3,3-dioxide (4a)



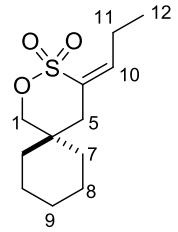
Colorless oil. R_f = 0.26 (silica gel, hexanes:EtOAc 4:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (appd, *J* = 8.1 Hz, 2H, H_{11}), 7.18 (appd, *J* = 8.0 Hz, 2H, H_{12}), 6.85 (s, 1H, H_{10}), 4.32 (s, 2H, H_1), 2.76 (s, 2H, H_5), 2.37 (s, 3H, H_{13}), 1.68 – 1.41 (m, 10H, $H_{7\text{-}9}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 136.6, 132.0, 130.0, 129.6, 128.5, 79.2, 44.8, 36.0, 32.1, 25.9, 21.3, 21.2. **HRMS** (ESI+) $C_{17}H_{22}O_3S$ $[M+Na]^+$ calcd. 307.1362, found 307.1361.

(*Z*)-4-Ethylidene-2-oxa-3-thiaspiro[5.5]undecane 3,3-dioxide (4b)



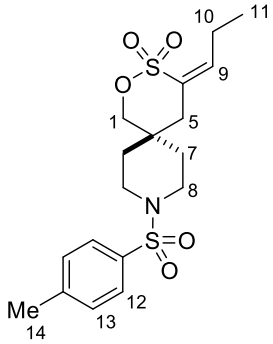
Colorless oil. R_f = 0.21 (silica gel, hexanes:EtOAc 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.94 (qt, *J* = 7.4, 1.3 Hz, 1H, H_{10}), 4.27 (s, 2H, H_1), 2.58 (bs, 2H, H_5), 2.11 (dt, *J* = 7.4, 1.2 Hz, 3H, H_{11}), 1.49 – 1.38 (m, 10H, $H_{7\text{-}9}$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.1, 132.4, 79.7, 43.9, 35.8, 31.9, 25.9, 21.1, 14.1. **HRMS** (ESI+) $C_{11}H_{18}O_3S$ $[M+Na]^+$ calcd. 253.0869, found 253.0877.

(*Z*)-4-Propylidene-2-oxa-3-thiaspiro[5.5]undecane 3,3-dioxide (4c)



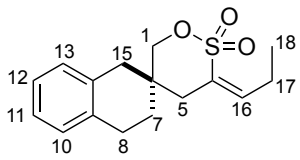
Colorless oil. R_f = 0.38 (silica gel, *n*-hexane:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.81 (t, *J* = 7.7 Hz, 1H, H_{10}), 4.25 (s, 2H, H_1), 2.59 (p, *J* = 7.6 Hz, 2H, H_{11}), 2.56 (bs, 2H, H_5), 1.50 – 1.34 (m, 10H, $H_{7\text{-}9}$), 1.05 (t, *J* = 7.5 Hz, 3H, H_{12}). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.2, 131.1, 79.8, 44.2, 36.0, 32.1, 26.1, 21.5, 21.4, 13.8. **HRMS** (APCI) $C_{12}H_{20}O_3S$ $[M+H]^+$ calcd. 245.1206, found 245.1207.

(*Z*)-4-Propylidene-9-tosyl-2-oxa-3-thia-9-azaspiro[5.5]undecane 3,3-dioxide (4d)



White solid. R_f = 0.25 (silica gel, *n*-hexane:EtOAc 2:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H, H_{12}), 7.35 (d, *J* = 8.1 Hz, 2H, H_{13}), 5.80 (t, *J* = 7.7 Hz, 1H, H_9), 4.17 (s, 2H, H_1), 3.11 (ddd, *J* = 11.5, 6.5, 4.5 Hz, 2H, H_{8a}), 2.91 (ddd, *J* = 12.1, 8.0, 3.9 Hz, 2H, H_{8b}), 2.58 (p, *J* = 7.6 Hz, 2H, H_{10}), 2.50 (bs, 2H, H_5), 2.45 (s, 3H, H_{14}), 1.73 – 1.59 (m, 4H, H_7), 1.04 (t, *J* = 7.5 Hz, 3H, H_{11}). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.1, 142.4, 133.2, 130.1, 130.0, 127.8, 77.4, 43.8, 41.7, 34.2, 30.9, 21.7, 21.6, 13.8. **HRMS** (APCI) $C_{18}H_{25}NO_5S_2$ $[M+H]^+$ calcd. 400.1247, found 400.1256.

(*Z*)-3'-propylidene-3,4-dihydro-1H-spiro[naphthalene-2,5'-[1,2]oxathiane] 2',2'-dioxide (4e)

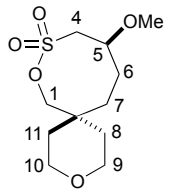


White solid. R_f = 0.28 (silica gel, *n*-hexane:EtOAc 5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.19 – 7.09 (m, 4H, $H_{10\text{-}13}$), 5.81 (t, *J* = 7.8, 1H, H_{16}), 4.30 (d, *J* = 1.9 Hz, 2H, H_1), 2.83 (t, *J* = 6.8 Hz, 2H, H_8), 2.7 (s, 2H, H_{15}), 2.65 – 2.59 (m, 4H, H_5 and H_{17}), 1.77 (td, 2H, H_7), 1.07 (t, 3H, H_{18}). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.8, 134.8, 133.2, 130.8, 129.7, 129.1, 126.6, 126.4, 79.2, 43.57, 36.2, 35.6, 28.7, 25.1, 21.6, 13.8. **HRMS** (APCI) $C_{16}H_{21}O_3S$ $[M+H]^+$ calcd. 293.1206, found 293.1207.

2.3 Synthesis of Sultone Derivative 9

Sodium methoxide (0.3 mL of a 1 M solution in methanol; 2 equiv) was added to a solution of **2i** (35 mg, 0.15 mmol) in THF (0.5 mL). The mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the corresponding pure compound **9**.

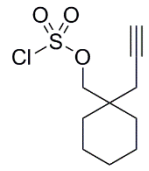
11-Methoxy-3,8-dioxa-9-thiaspiro[5.7]tridecane 9,9-dioxide (9)

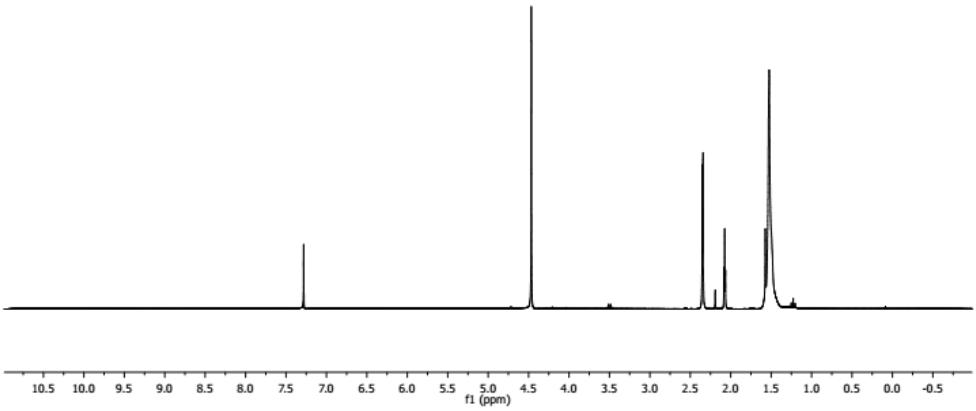


Colorless oil. R_f = 0.30 (silica gel, *n*-hexane:EtOAc 5:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.29 (d, *J* = 12.2 Hz, 1H, H_1), 4.17 (d, *J* = 12.2 Hz, 1H, $H_{1'}$), 3.81 – 3.75 (m, 4H, H_5), 3.73 – 3.61 (m, 4H, $H_{9,10}$), 3.52 (dd, *J* = 15.2, 3.3 Hz, 1H, H_4), 3.45 (dd, *J* = 15.2, 9.4 Hz, 1H, $H_{4'}$), 3.36 (s, 3H, CH_3O), 2.13 – 2.05 (m, 1H, H_6), 1.88 – 1.81 (m, 1H, $H_{6'}$), 1.78 – 1.67 (m, 2H, H_7), 1.60 – 1.45 (m, 4H, $H_{8,11}$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 77.4, 75.9, 63.8, 56.6, 51.6, 34.7, 34.2, 32.3, 30.6, 25.7. **HRMS** (APCI) $C_{11}H_{21}O_5S$ $[M+H]^+$ calcd. 265.1104, found 265.1112.

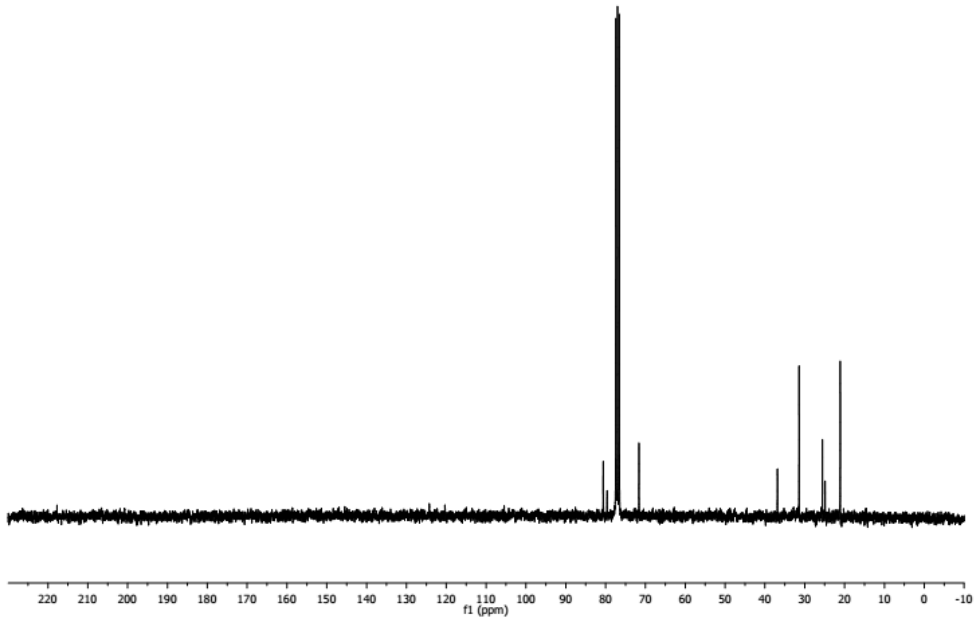
3. NMR Spectra

[1-(Prop-2-yn-1-yl)cyclohexyl]methyl chlorosulfate (1a)



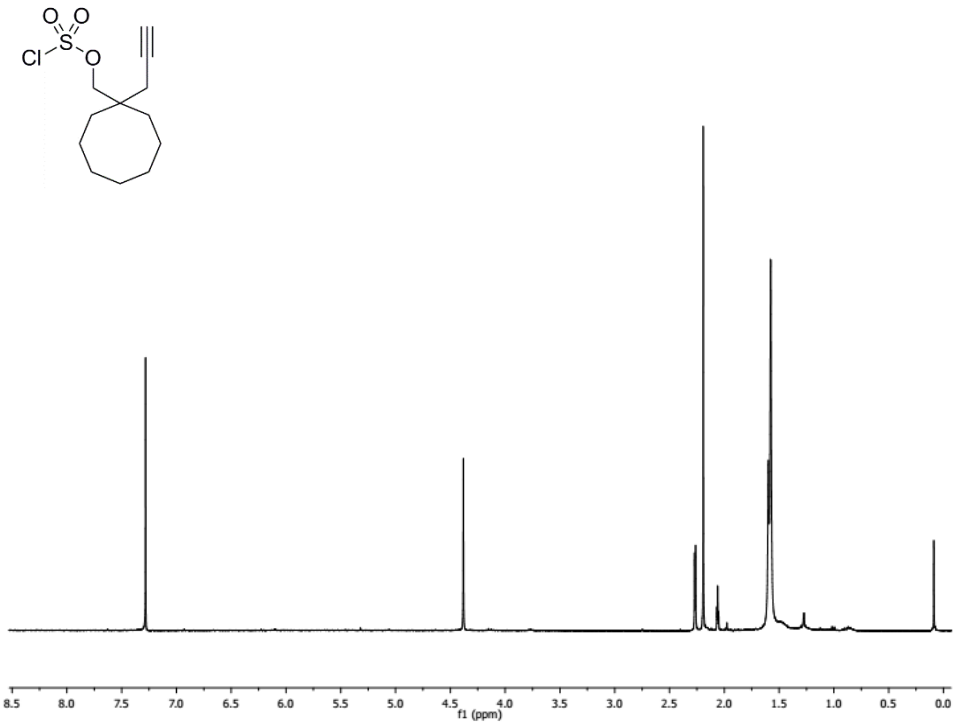


^{1}H NMR

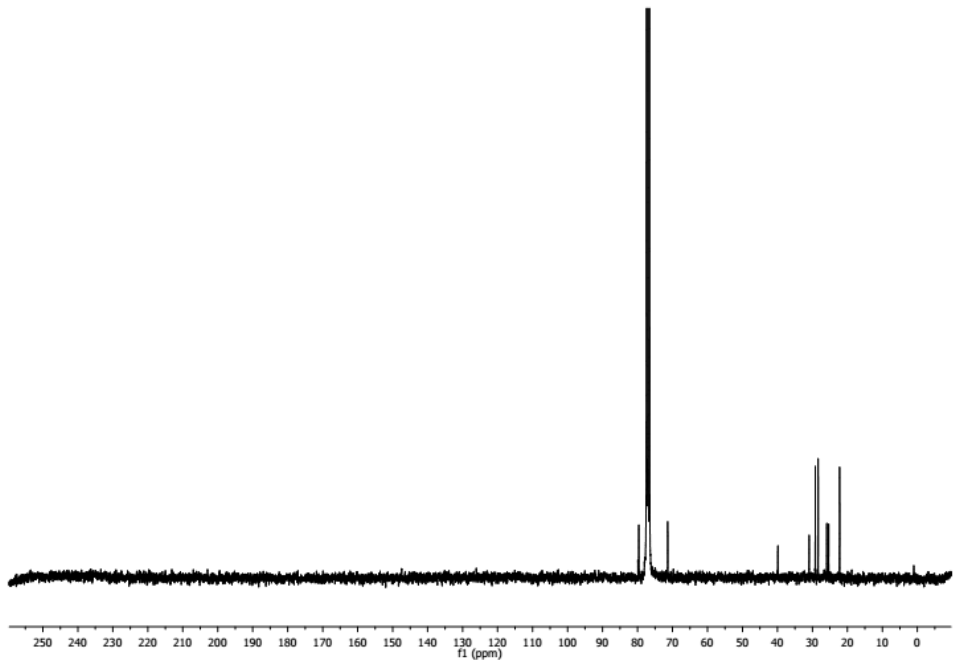


^{13}C NMR

[1-(Prop-2-yn-1-yl)cyclooctyl]methyl chlorosulfate (1b)

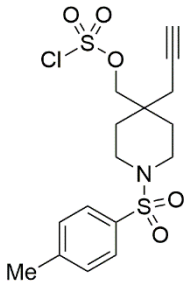


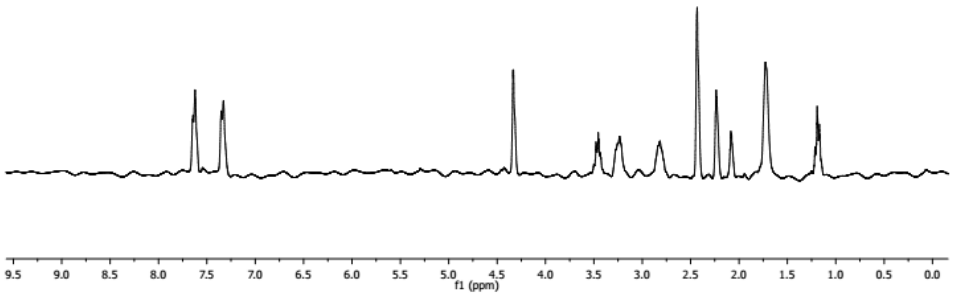
^{1}H NMR



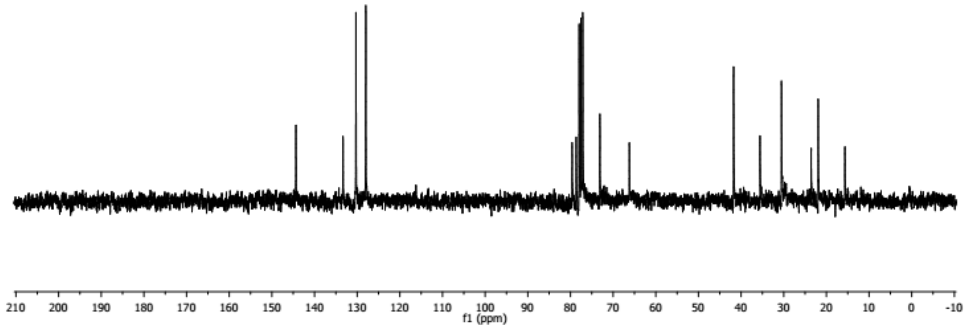
^{13}C NMR

[4-(Prop-2-yn-1-yl)-1-tosylpiperidin-4-yl]methyl chlorosulfate (1d)



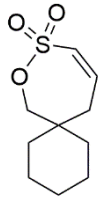


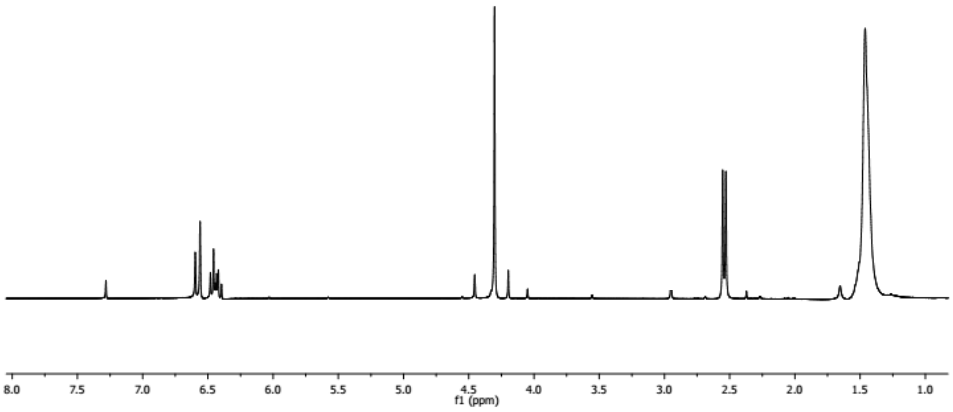
^{1}H NMR



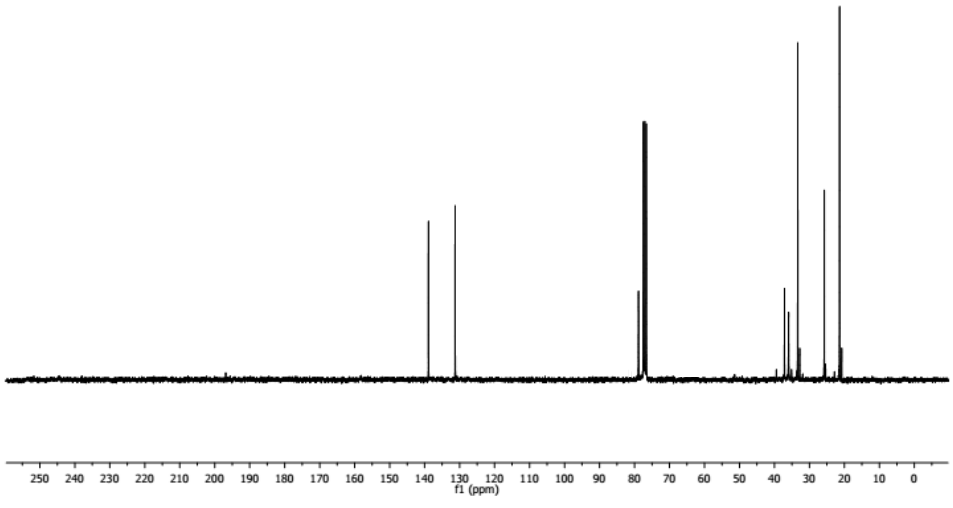
^{13}C NMR

8-Oxa-9-thiaspiro[5.6]dodec-10-ene 9,9-dioxide (2a)



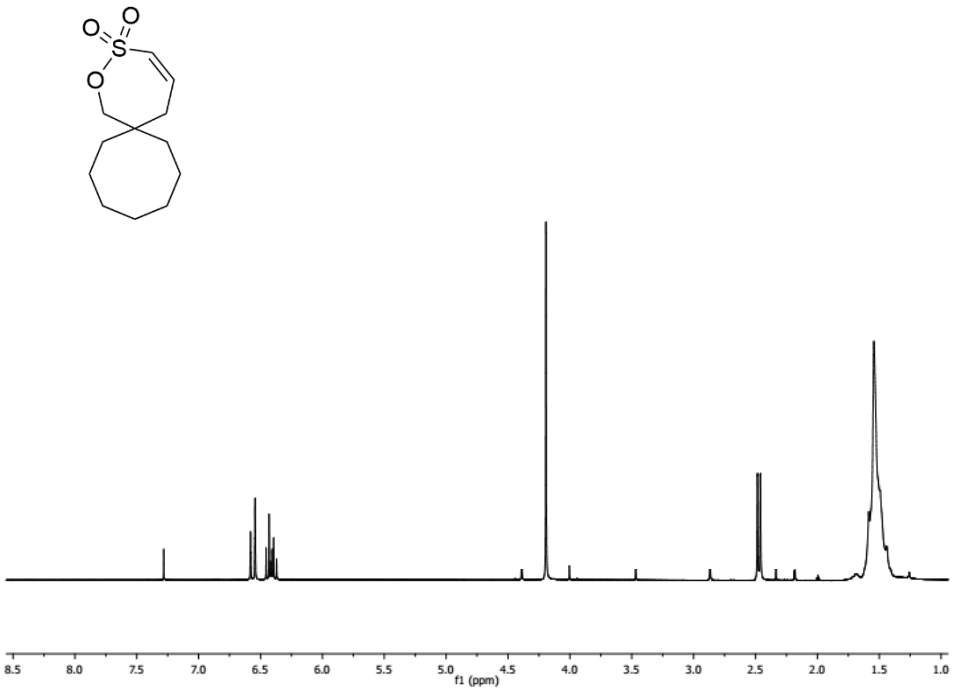


^{1}H NMR

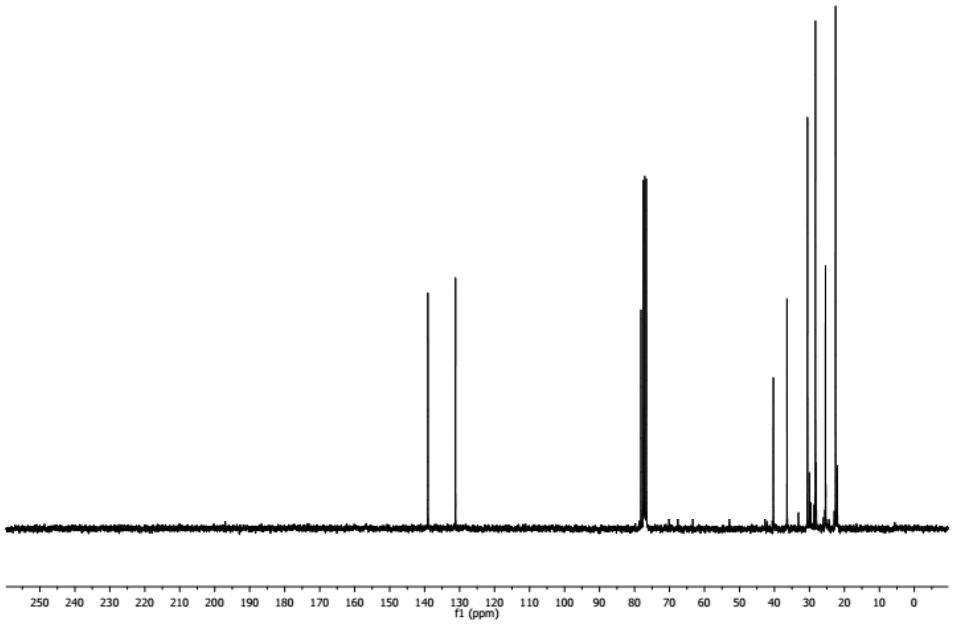


^{13}C NMR

2-Oxa-3-thiaspiro[6.7]tetradec-4-ene 3,3-dioxide (2b)

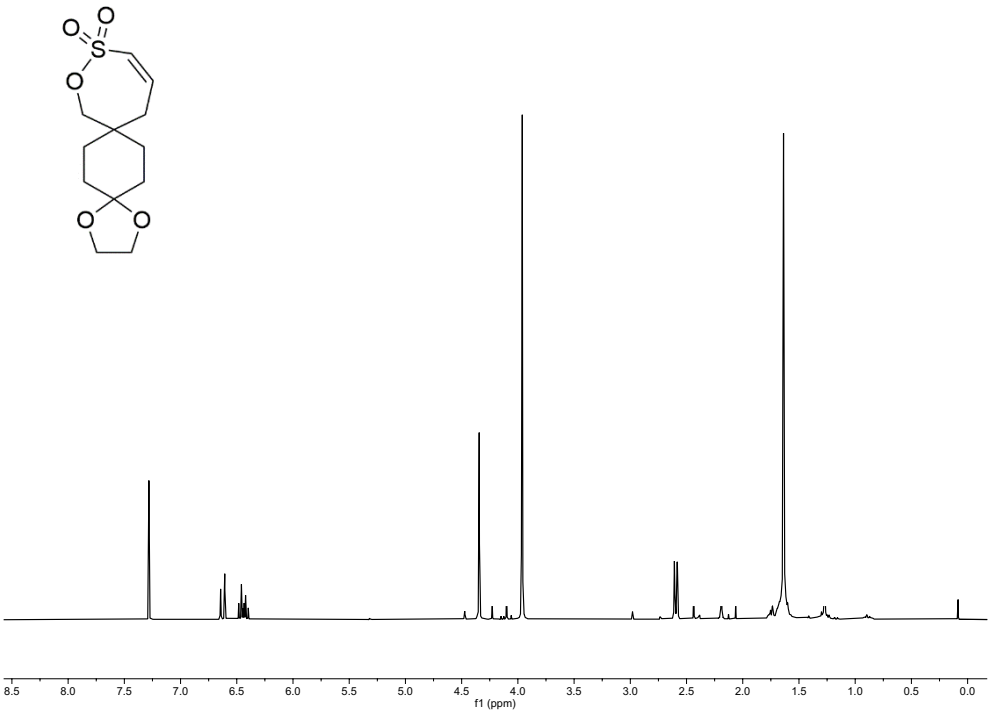


^{1}H NMR

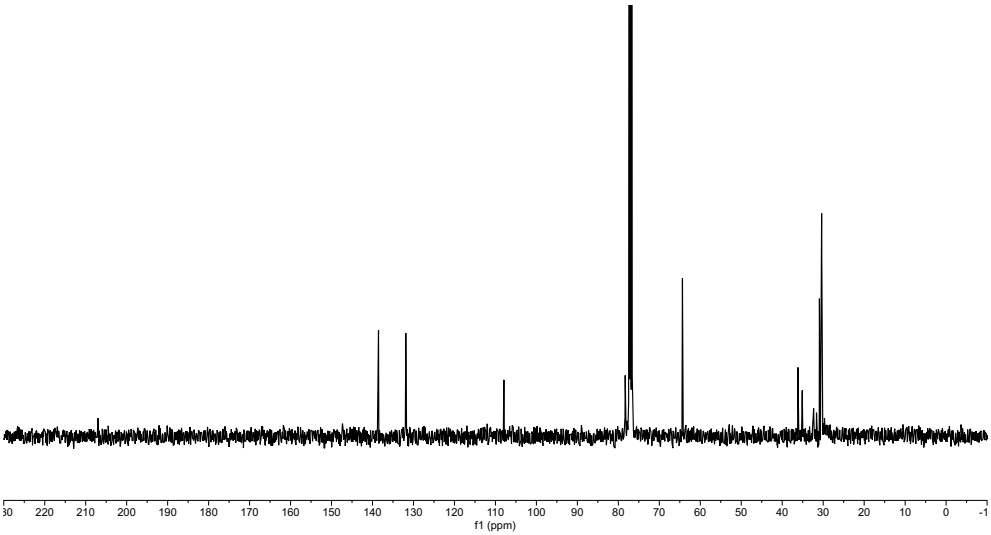


^{13}C NMR

1,4,10-Trioxa-11-thiadispiro[4.2.6^{8}.2^{5}]hexadec-12-ene 11,11-dioxide (2c)

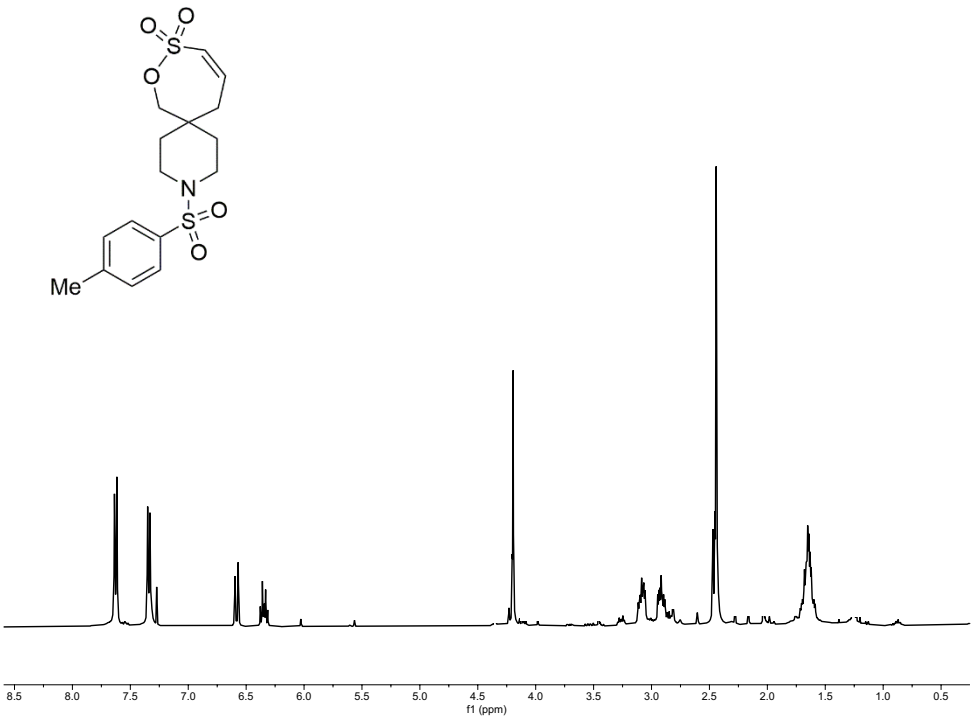


^{1}H NMR

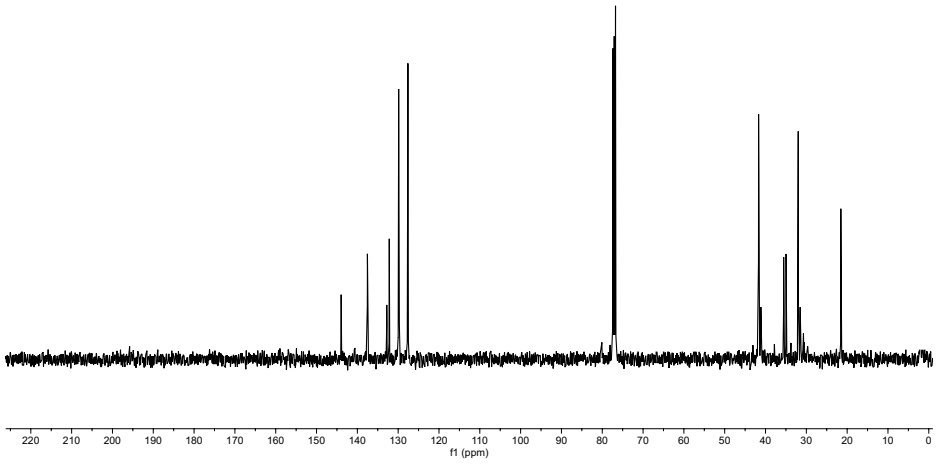


^{13}C NMR

3-Tosyl-8-oxa-9-thia-3-azaspiro[5.6]dodec-10-ene 9,9-dioxide (2d)

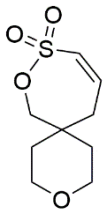


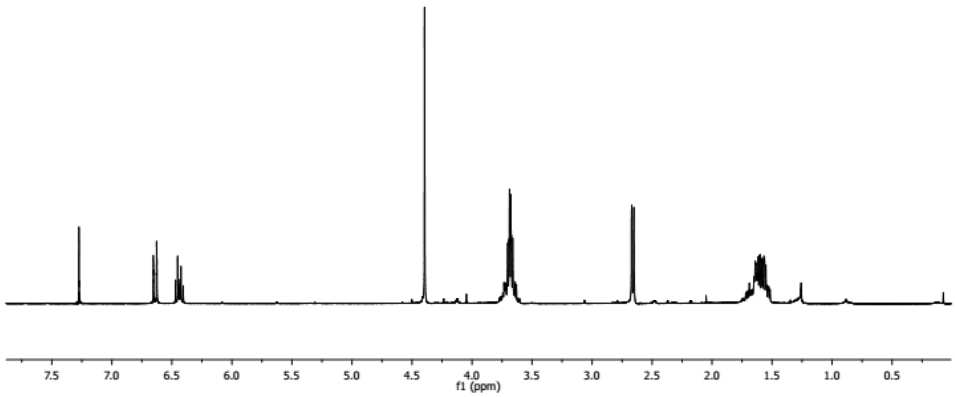
^{1}H NMR



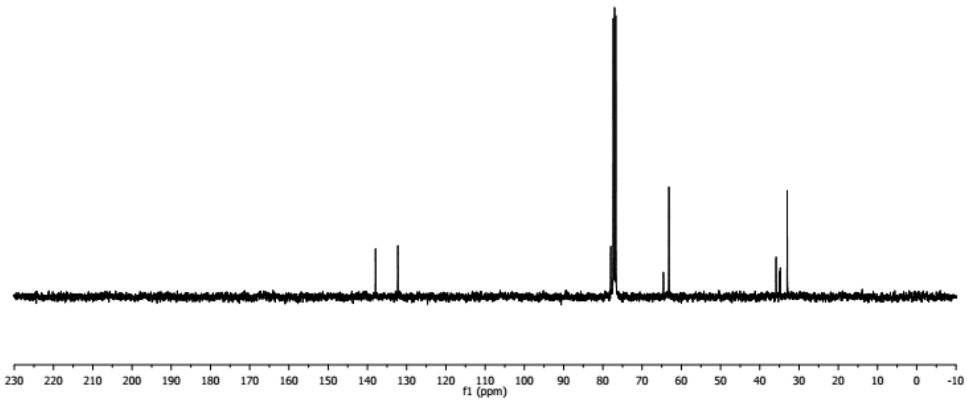
^{13}C NMR

3,8-Dioxa-9-thiaspiro[5.6]dodec-10-ene 9,9-dioxide (2e)



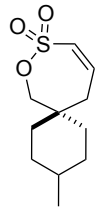


^{1}H NMR

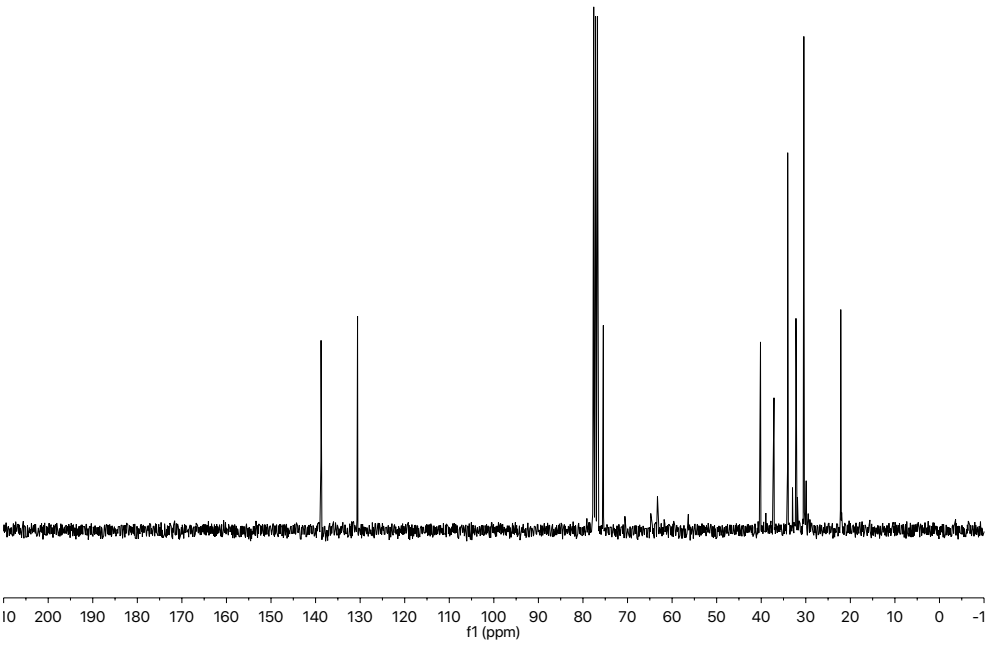


^{13}C NMR

3-Methyl-8-oxa-9-thiaspiro[5.6]dodec-10-ene 9,9-dioxide (2f)

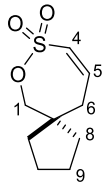


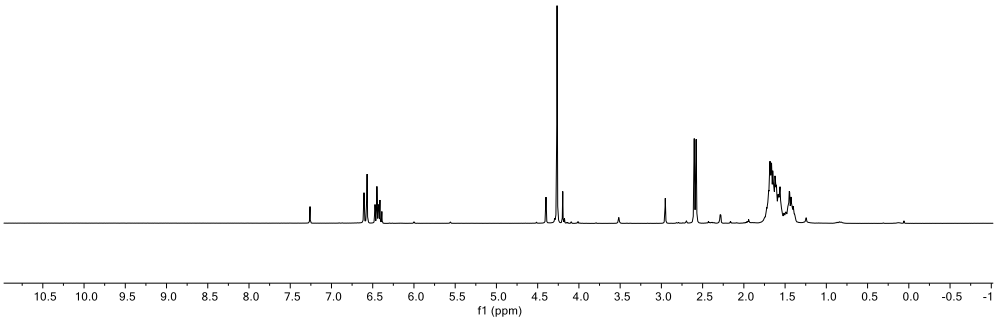
^{1}H NMR



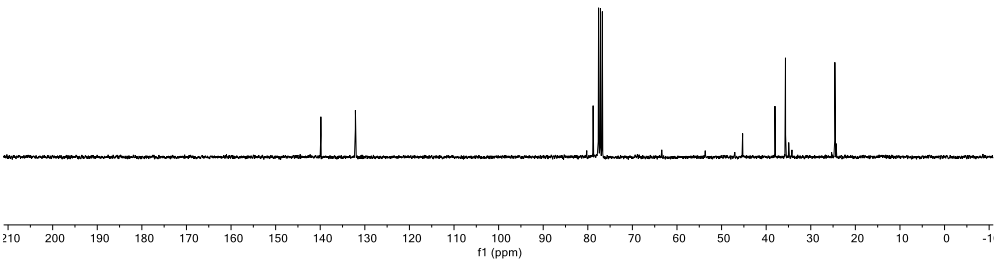
^{13}C NMR

7-Oxa-8-thiaspiro[4.6]undec-9-ene 8,8-dioxide (2g)



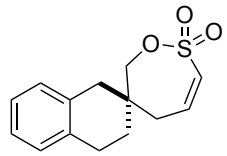


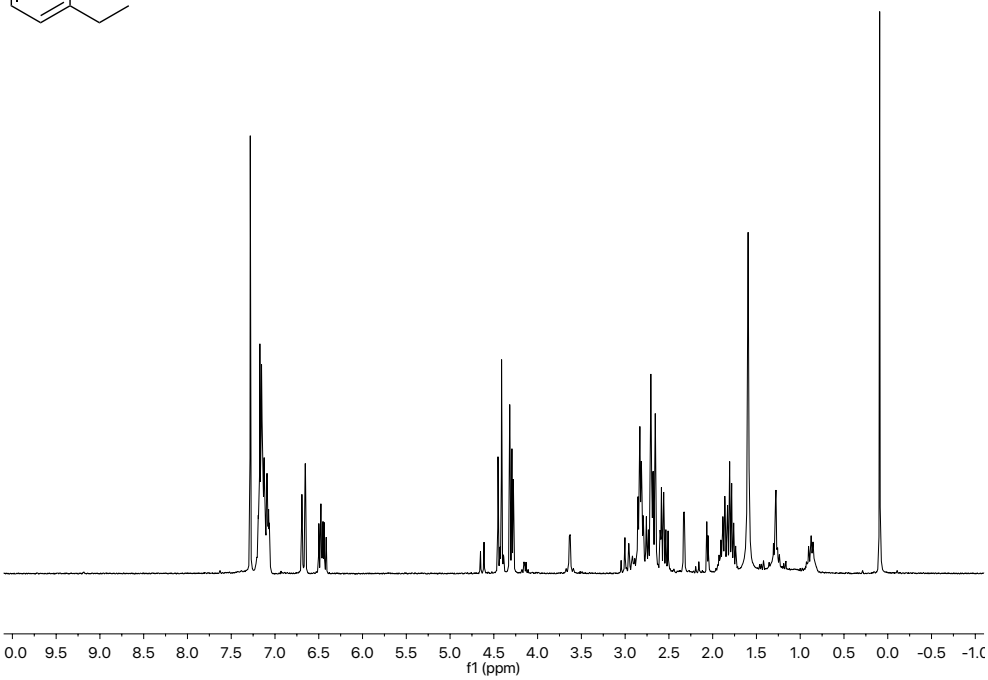
^{1}H NMR



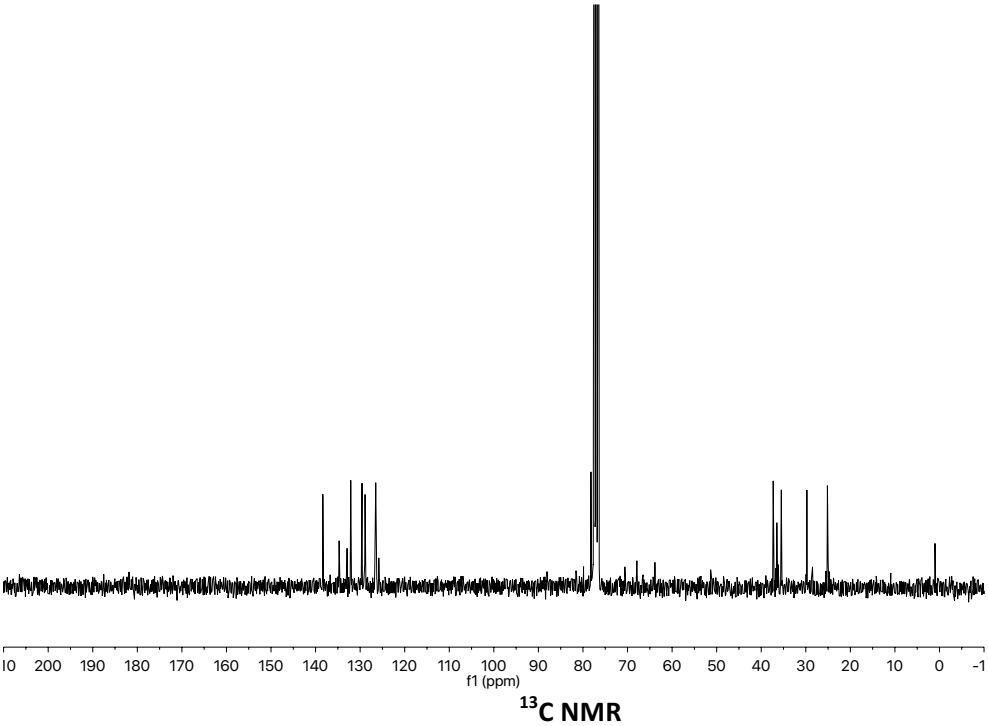
^{13}C NMR

3,4-Dihydro-1H,5'H,7'H-spiro[naphthalene-2,6'-[1,2]oxathiepine] 2',2'-dioxide (2h)



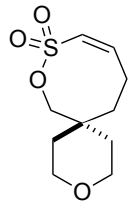


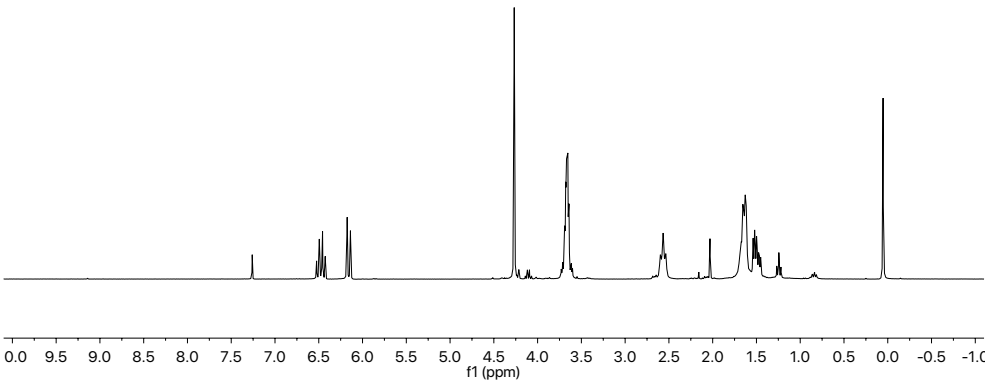
^{1}H NMR



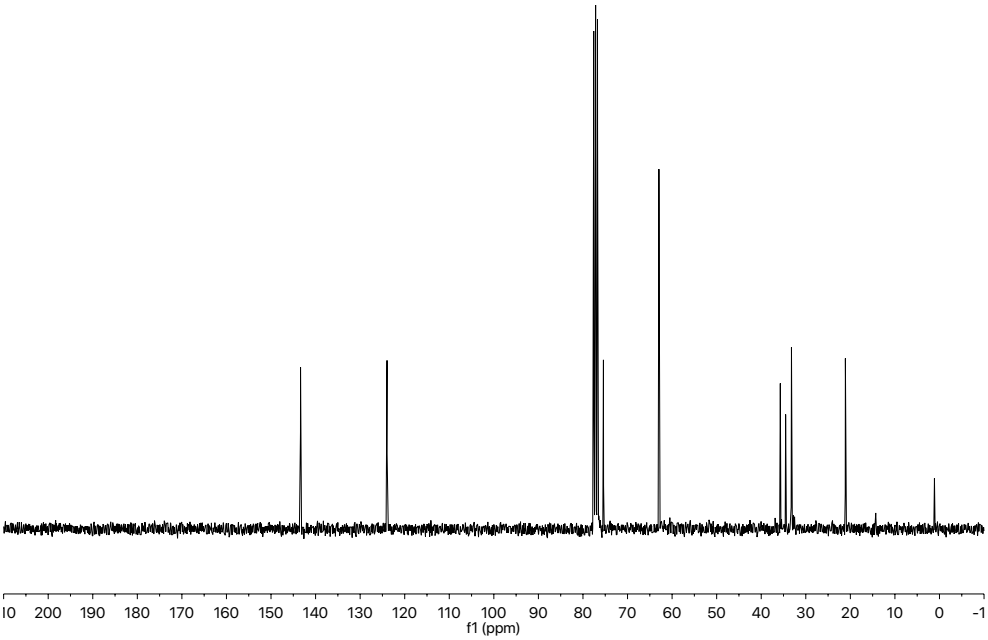
^{13}C NMR

(*Z*)-3,8-Dioxa-9-thiaspiro[5.7]tridec-10-ene 9,9-dioxide (2i)



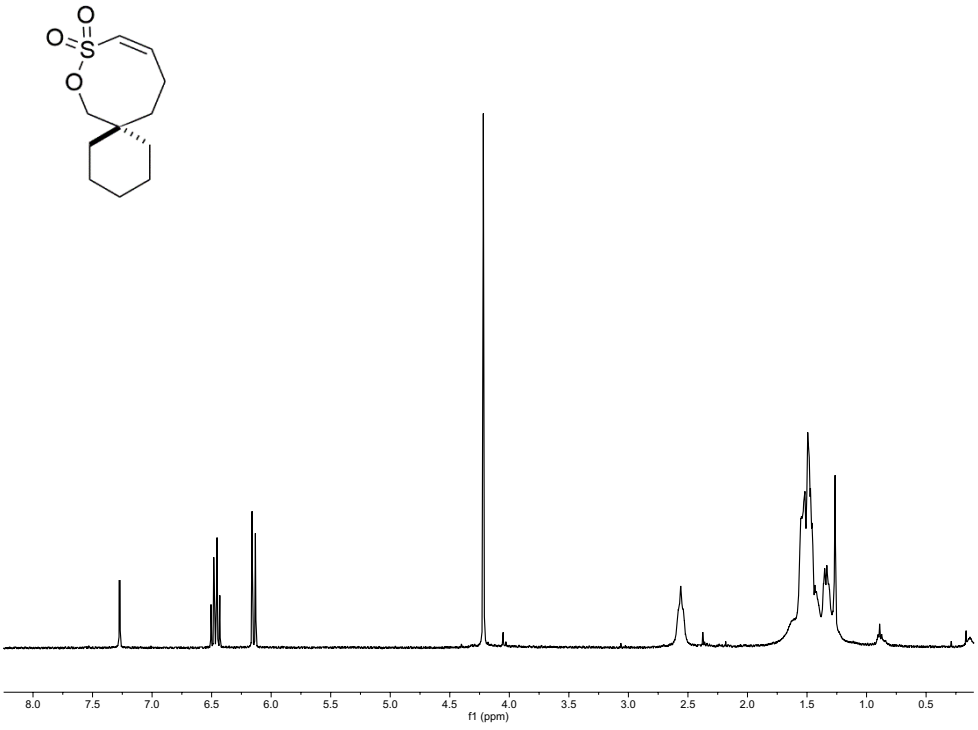


^{1}H NMR

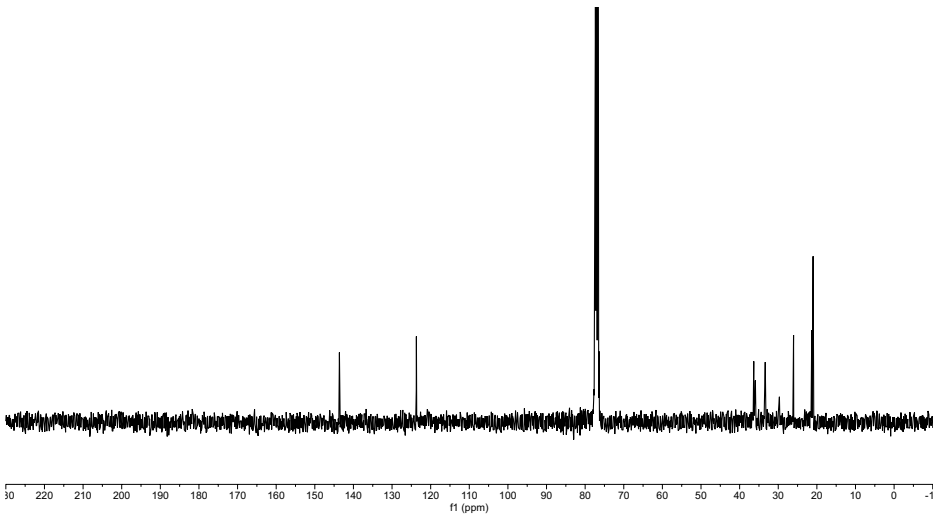


^{13}C NMR

(*Z*)-8-Oxa-9-thiaspiro[5.7]tridec-10-ene 9,9-dioxide (2j)

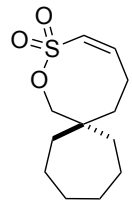


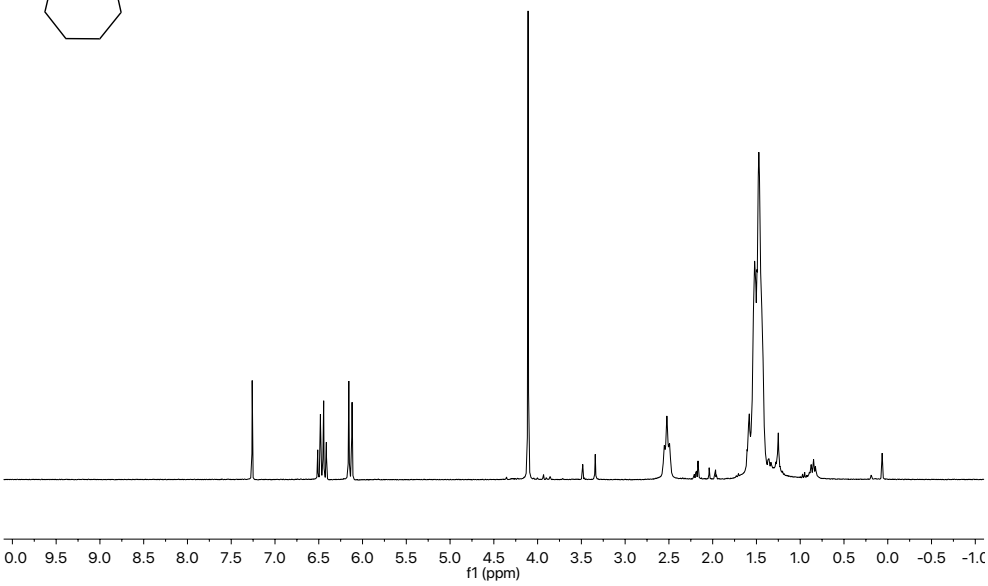
^{1}H NMR



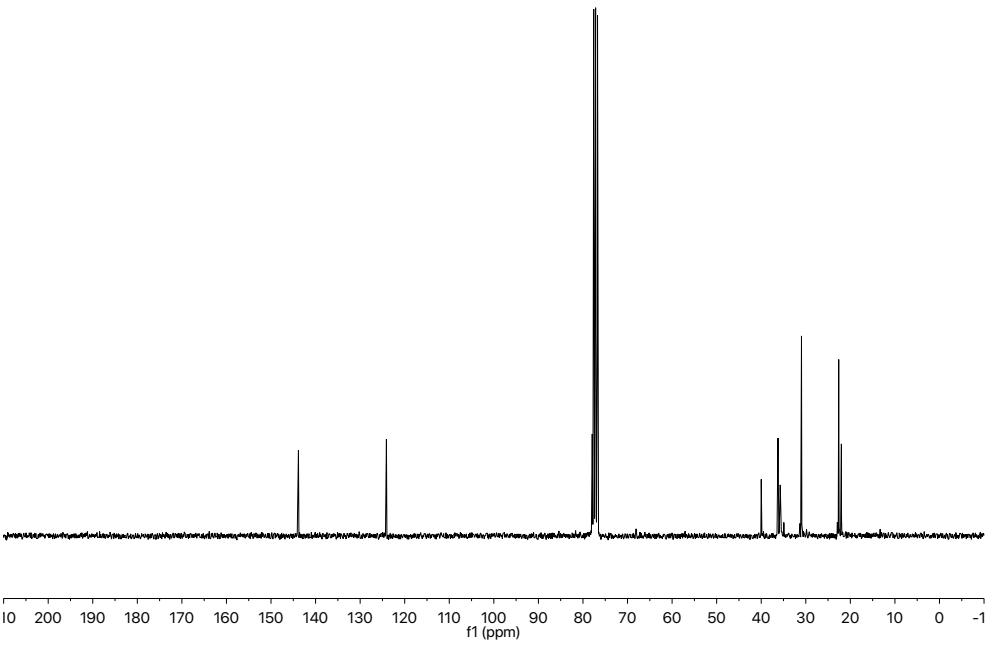
^{13}C NMR

(*Z*)-9-oxa-10-thiaspiro[6.7]tetradec-11-ene 10,10-dioxide (2k)



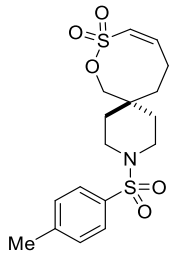


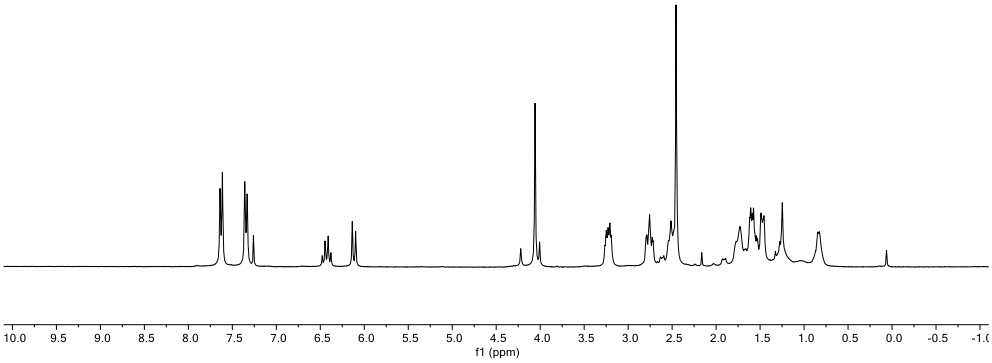
^{1}H NMR



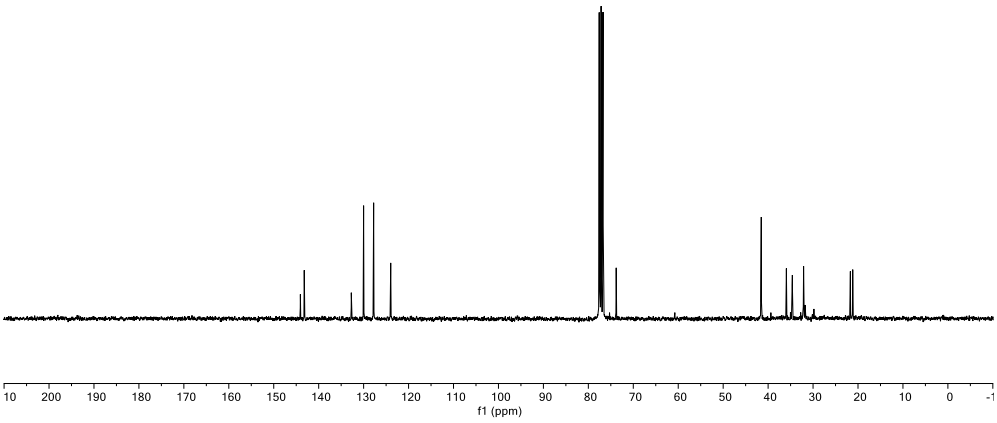
^{13}C NMR

(*Z*)-3-Tosyl-8-oxa-9-thia-3-azaspiro[5.7]tridec-10-ene 9,9-dioxide (2l)



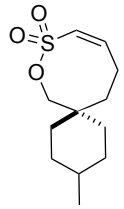


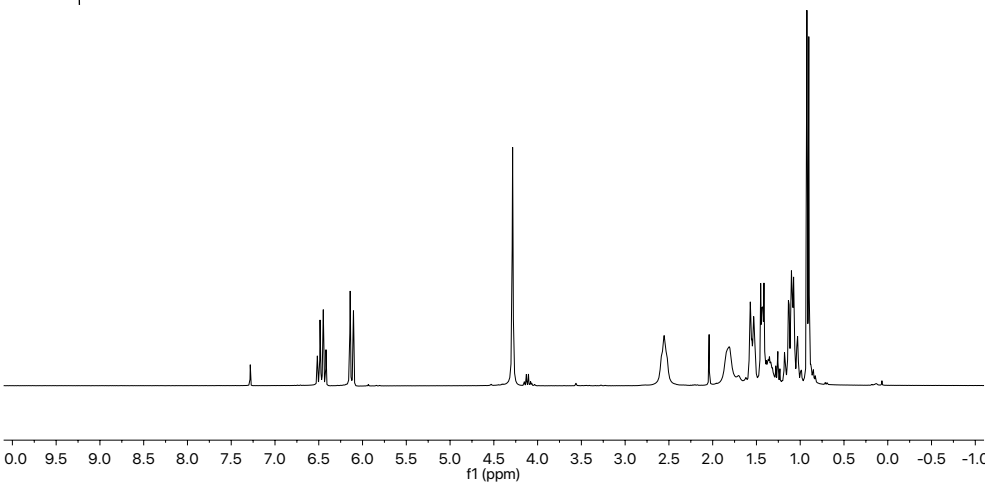
^{1}H NMR



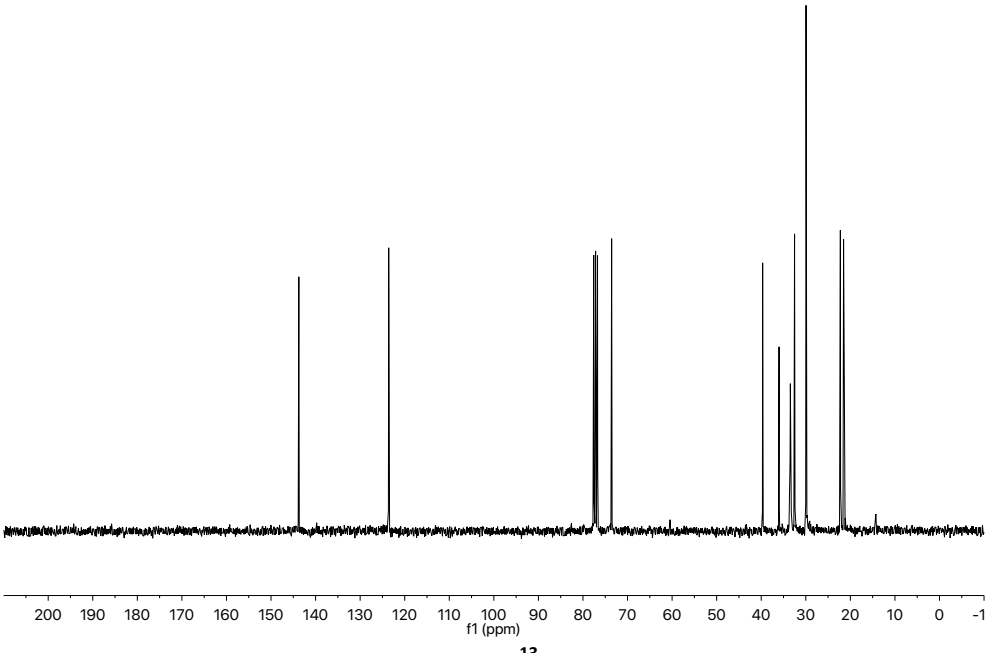
^{13}C NMR

(*Z*)-3-Methyl-8-oxa-9-thiaspiro[5.7]tridec-10-ene 9,9-dioxide (2m)



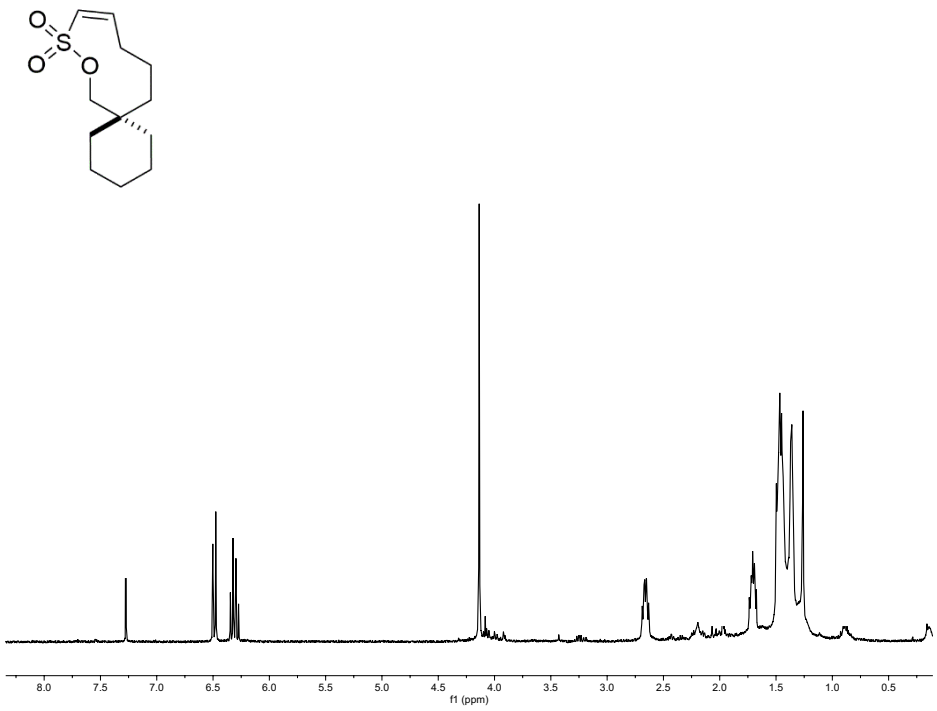


^{1}H NMR

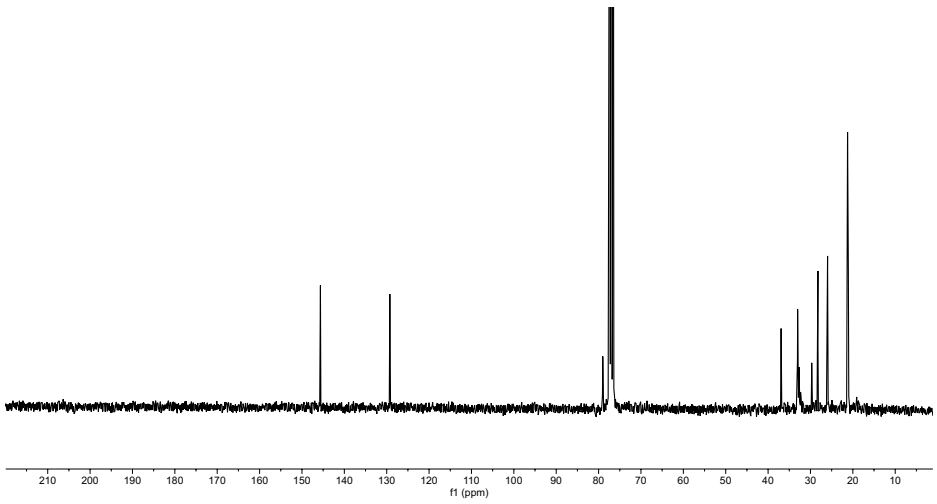


^{13}C NMR

(*Z*)-8-Oxa-9-thiaspiro[5.8]tetradec-10-ene 9,9-dioxide (2n)

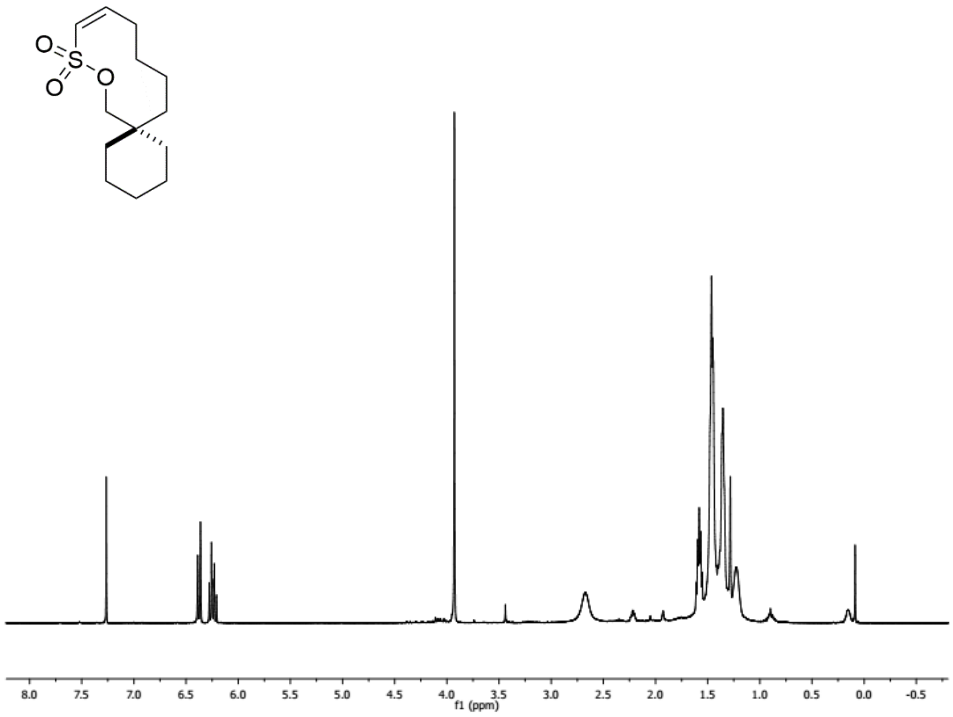


^{1}H NMR

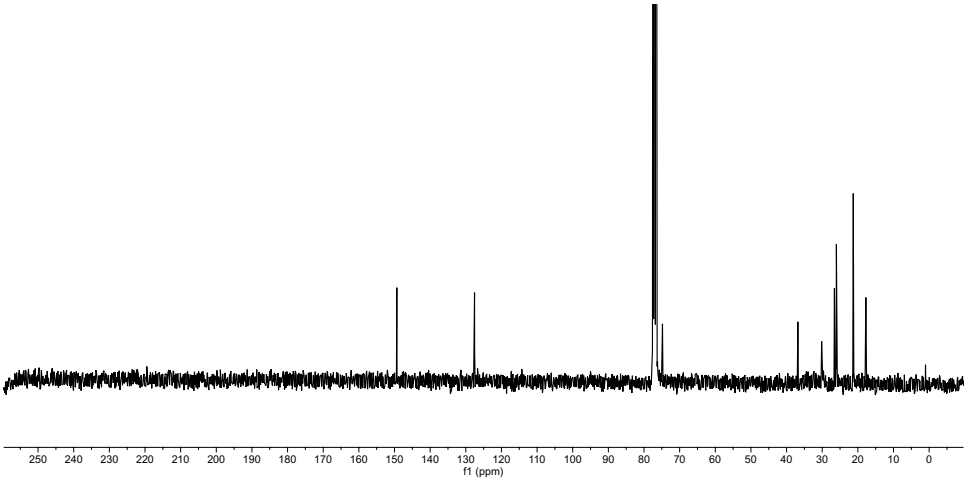


^{13}C NMR

(*Z*)-8-Oxa-9-thiaspiro[5.9]pentadec-10-ene 9,9-dioxide (2o)

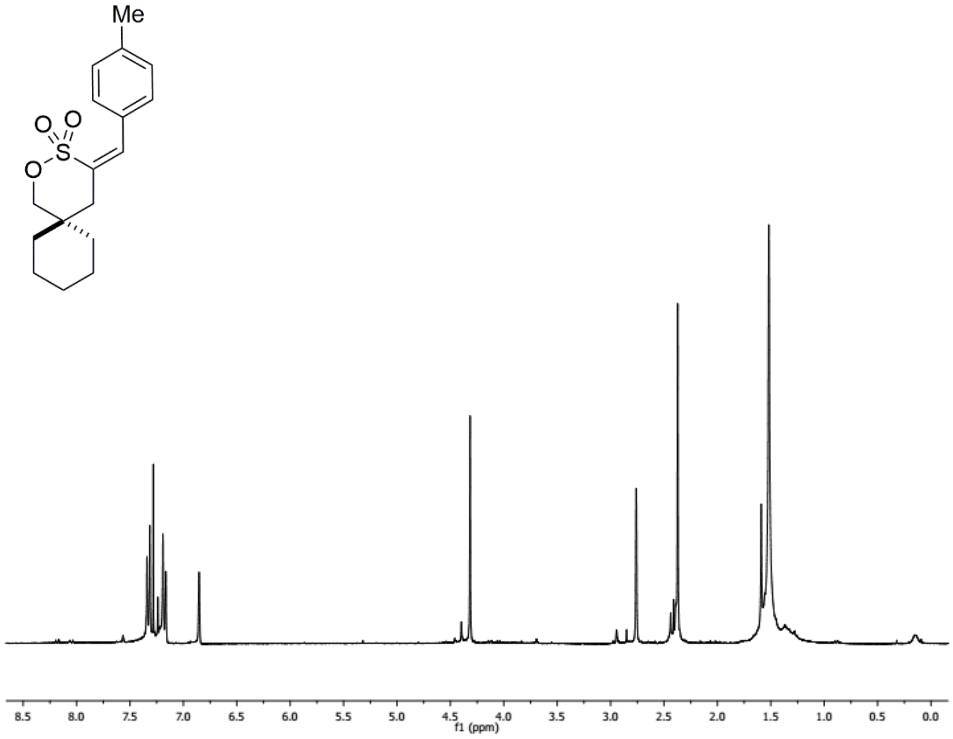


^{1}H NMR

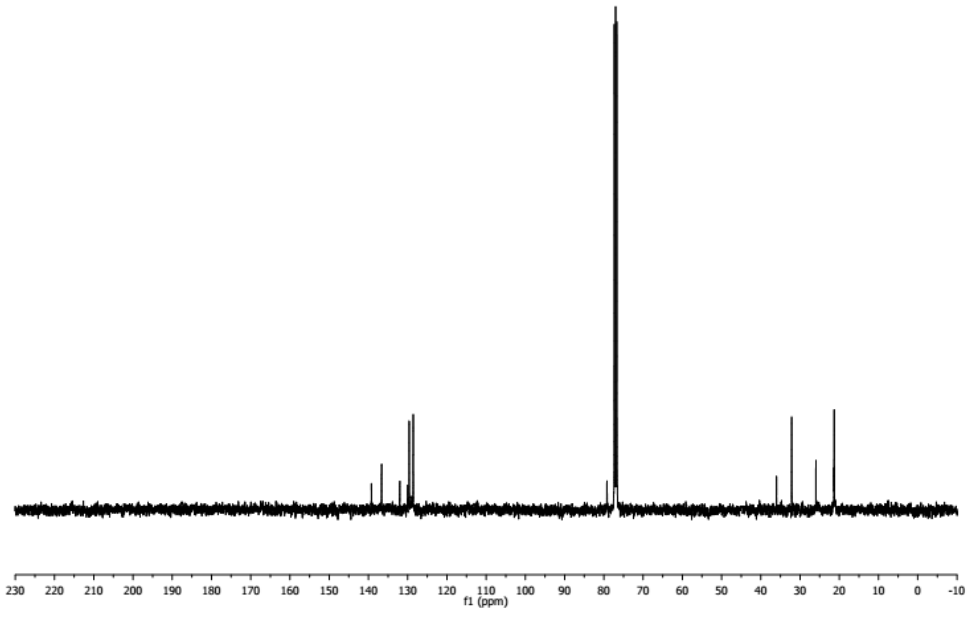


^{13}C NMR

(*Z*)-4-(4-Methylbenzylidene)-2-oxa-3-thiaspiro[5.5]undecane 3,3-dioxide (4a)

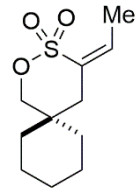


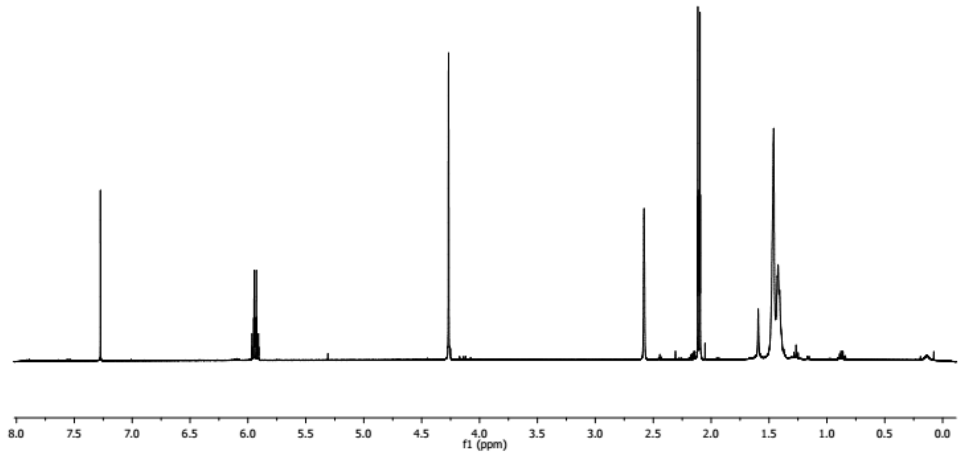
^{1}H NMR



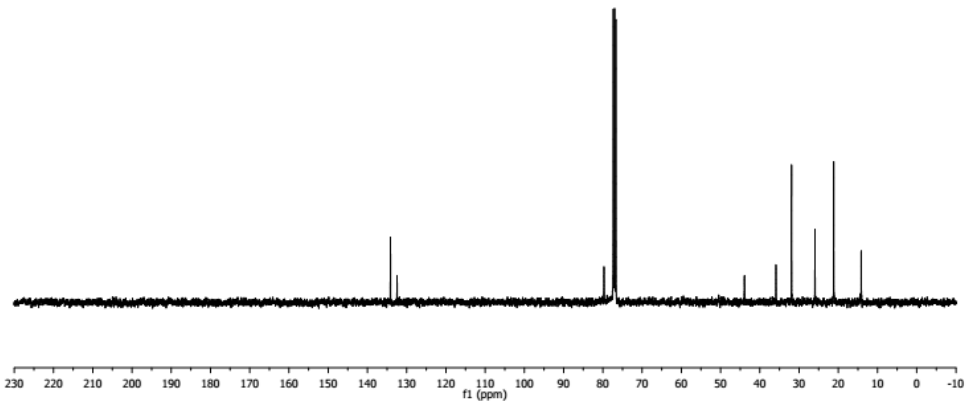
^{13}C NMR

(*Z*)-4-Ethylidene-2-oxa-3-thiaspiro[5.5]undecane 3,3-dioxide (4b)

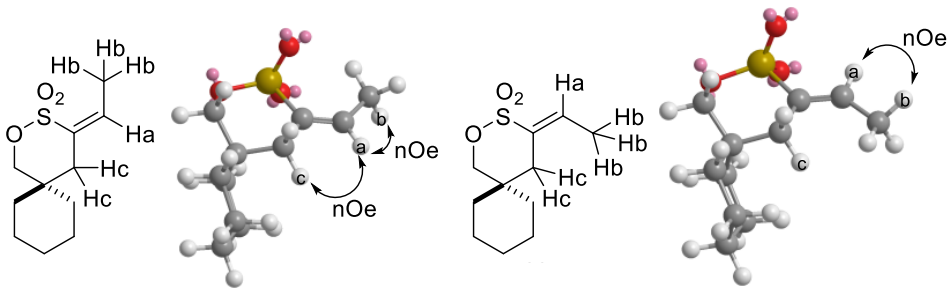




^{1}H NMR



^{13}C NMR



Ha: 5.95 ppm (qt, *J* = 7.4, 1.1 Hz)
Hc: 2.59 ppm (dt, *J* = 7.4, 1.1 Hz)
Hb: 2.11 ppm (apps)

Ha: 6.71 ppm (qt, *J* = 7.0, 1.2 Hz)
Hb: 1.85 (apps)

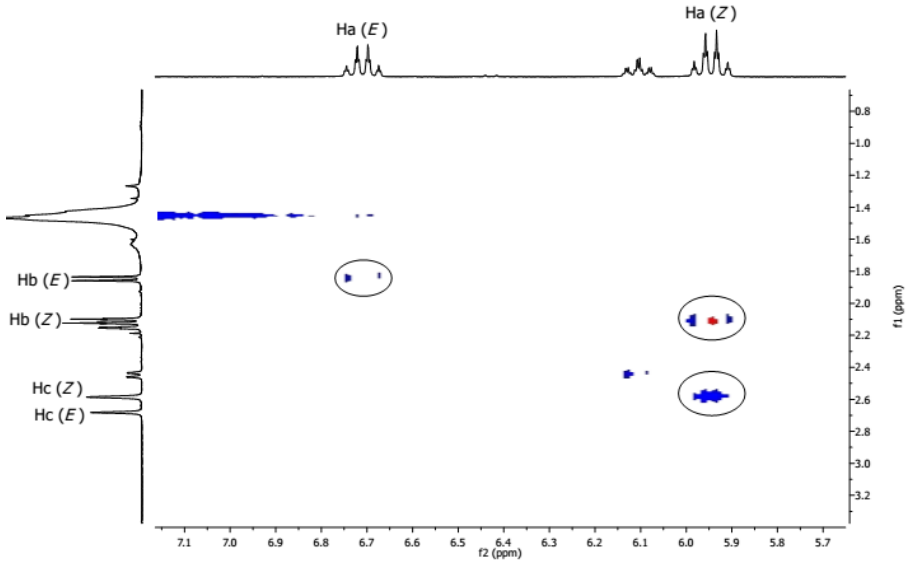
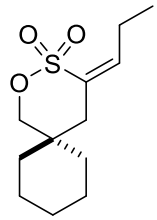
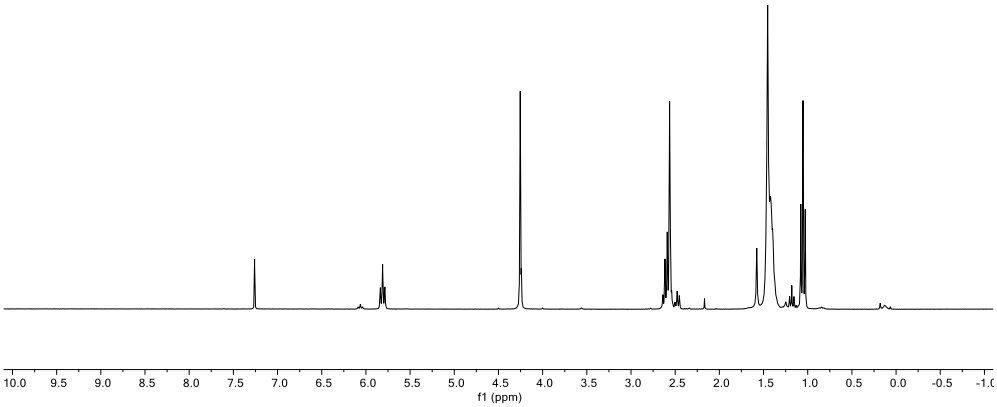


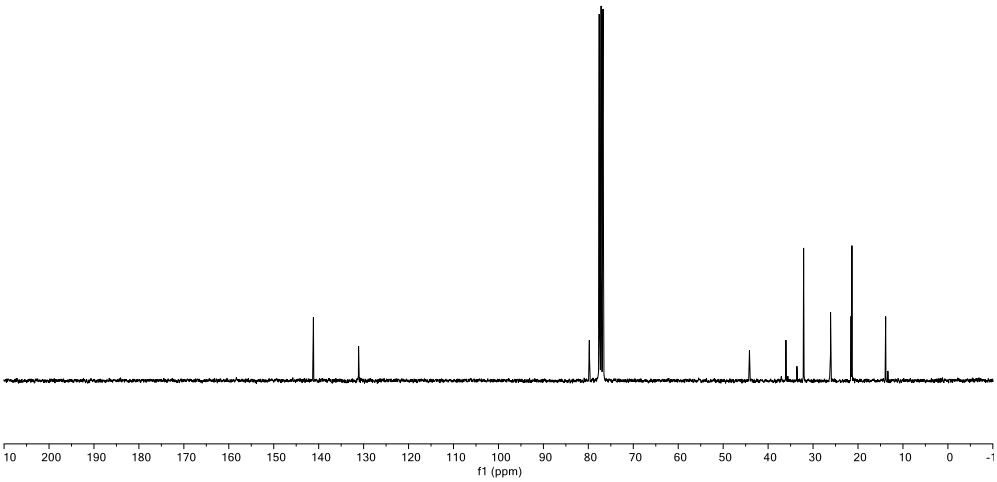
Figure. Determination of the relative configuration of **4b** through ^{1}H NMR and NOESY experiments. These experiments were performed on a fraction of the chromatographic column where the very minor *E*-isomer was obtained along with the major *Z*-isomer.

(*Z*)-4-Propylidene-2-oxa-3-thiaspiro[5.5]undecane 3,3-dioxide (4c)



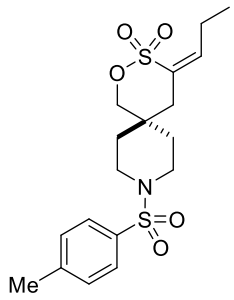


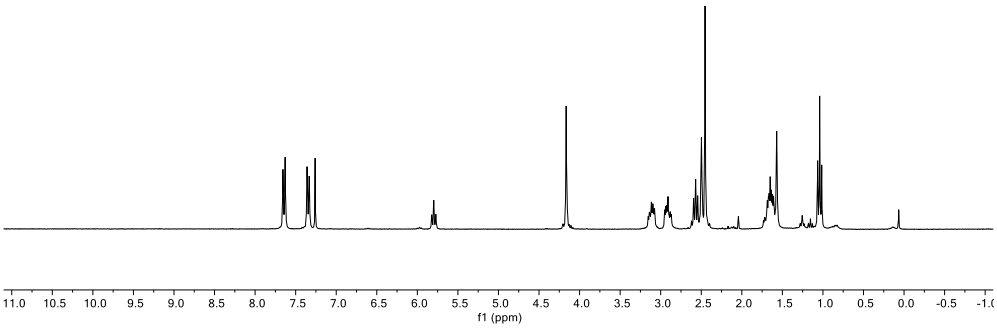
^{1}H NMR



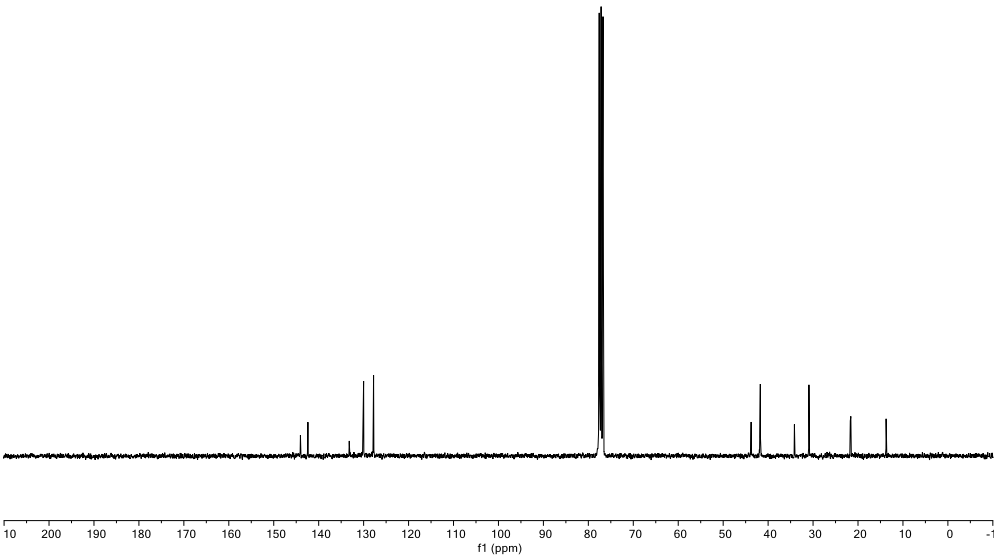
^{13}C NMR

(*Z*)-4-Propylidene-9-tosyl-2-oxa-3-thia-9-azaspiro[5.5]undecane 3,3-dioxide (4d)



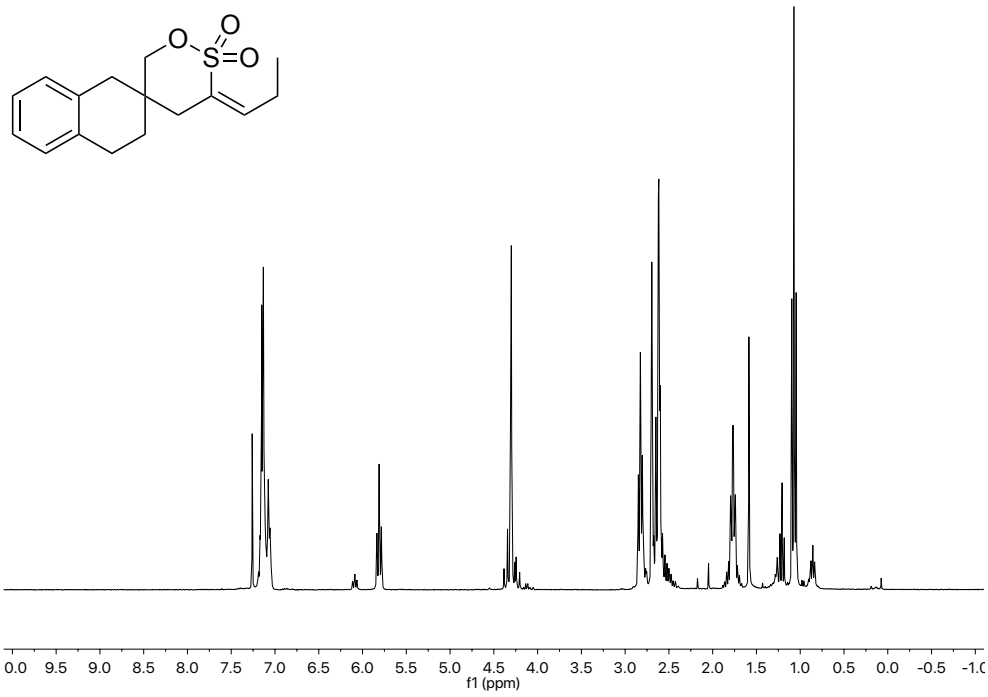


^{1}H NMR

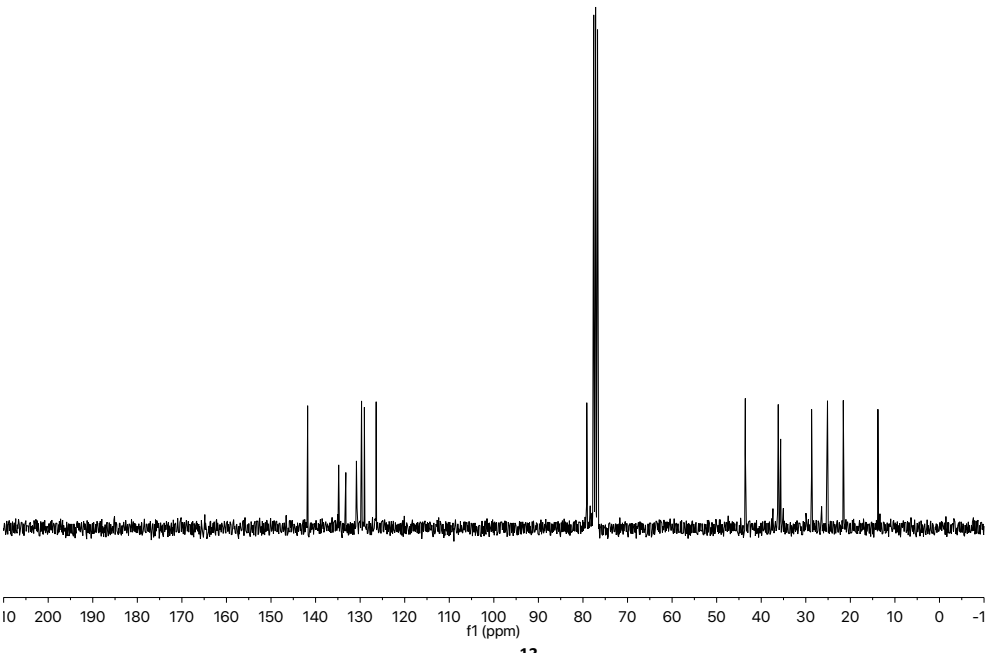


^{13}C NMR

(*Z*)-3'-Propylidene-3,4-dihydro-1*H*-spiro[naphthalene-2,5'-[1,2]oxathiane] 2',2'-dioxide (4e)

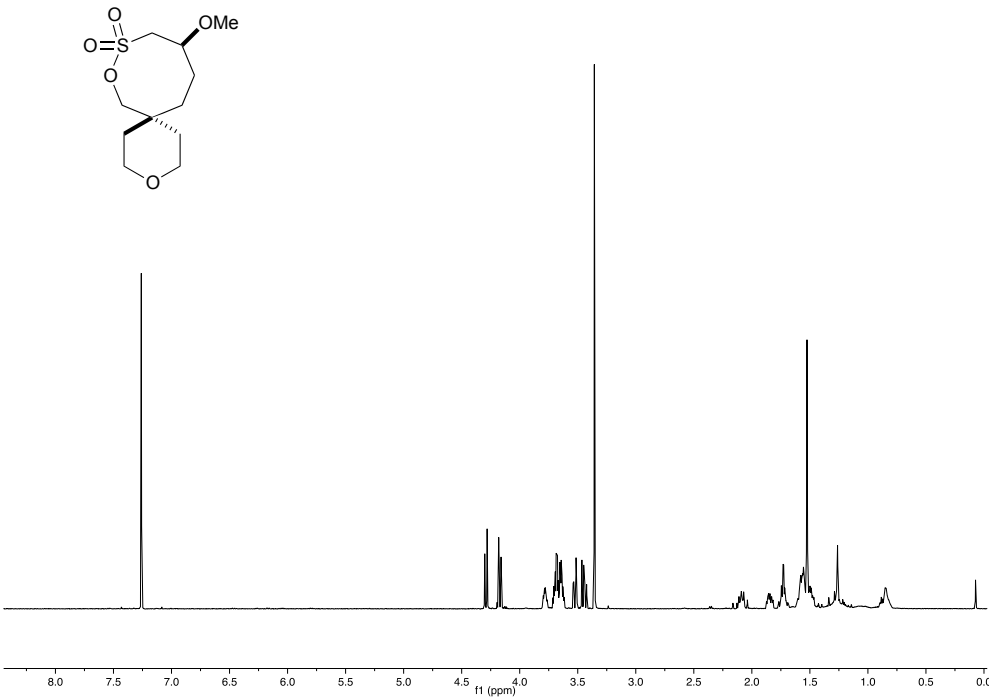


^{1}H NMR

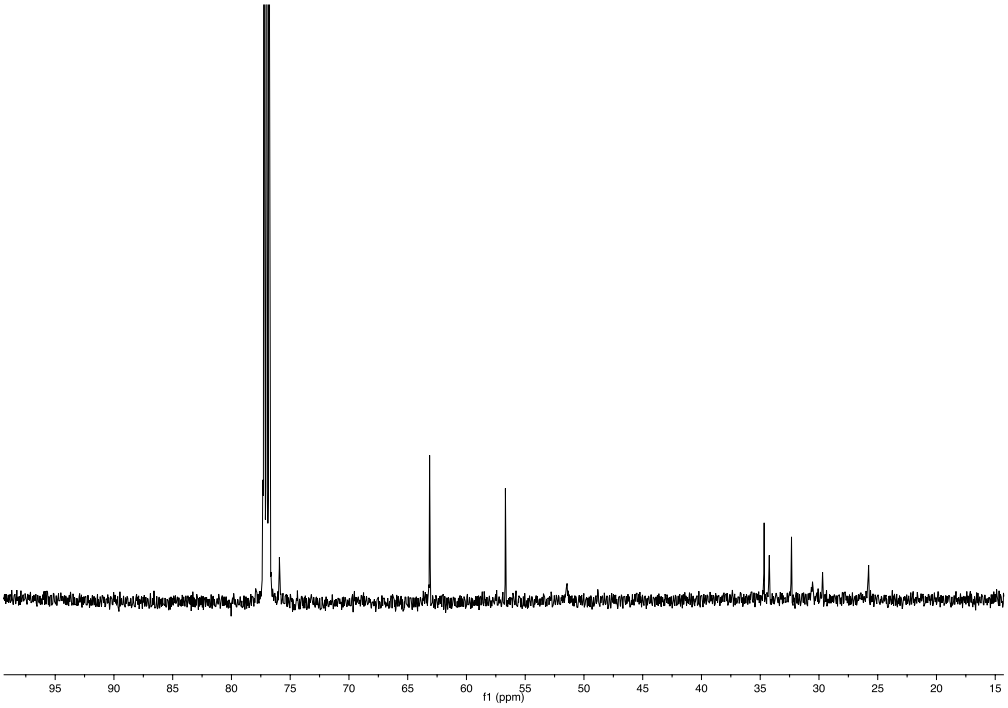


^{13}C NMR

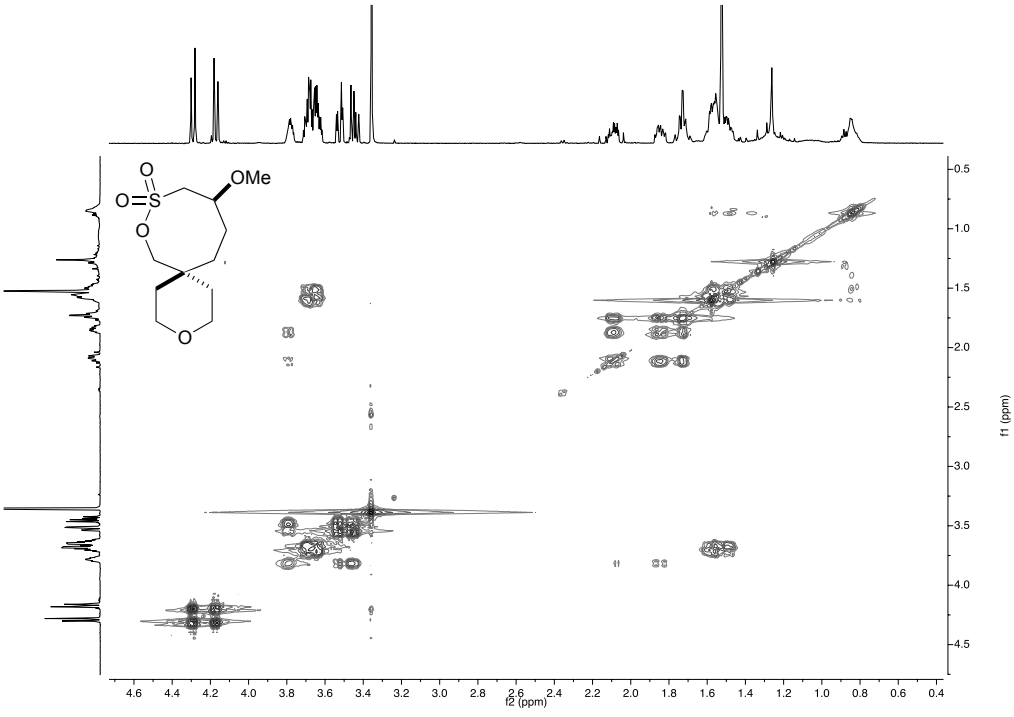
11-Methoxy-3,8-dioxa-9-thiaspiro[5.7]tridecane 9,9-dioxide (9)



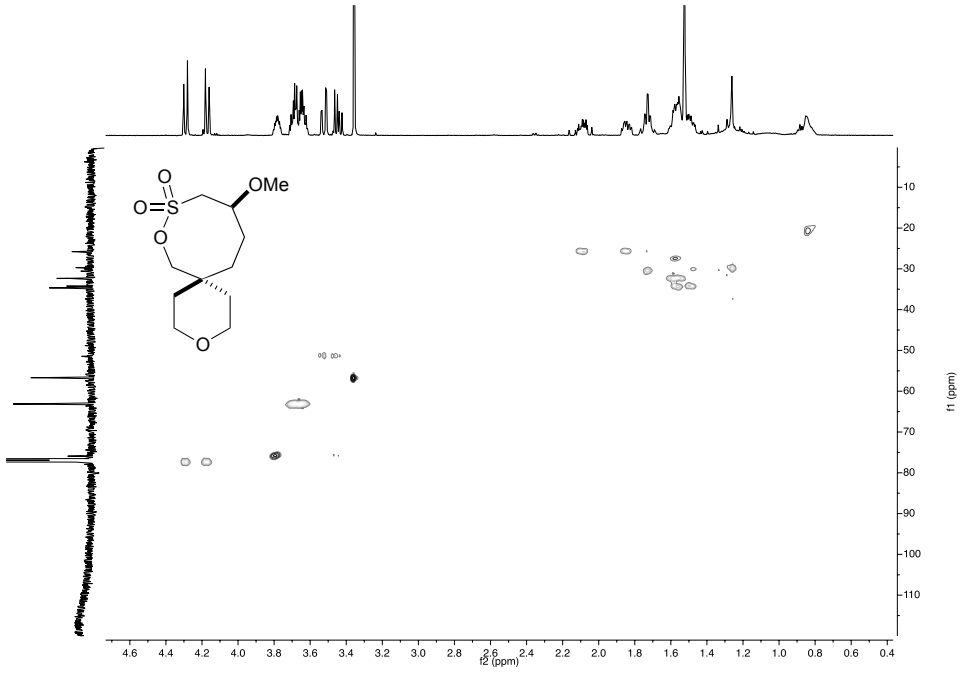
^{1}H NMR



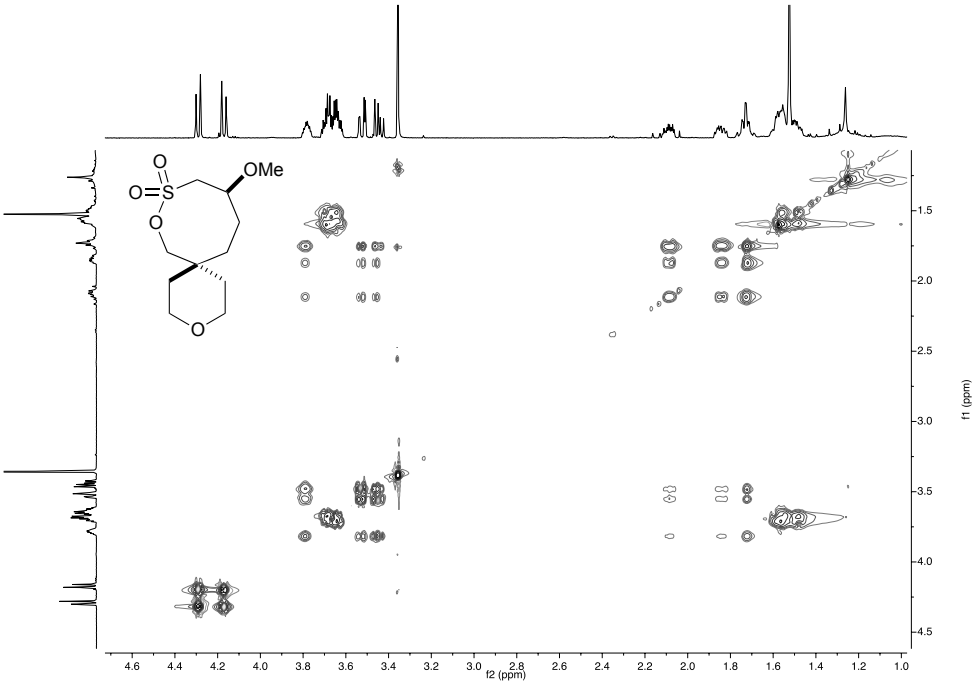
^{13}C NMR



COSY



HSQC



TOCSY

4. X-Ray

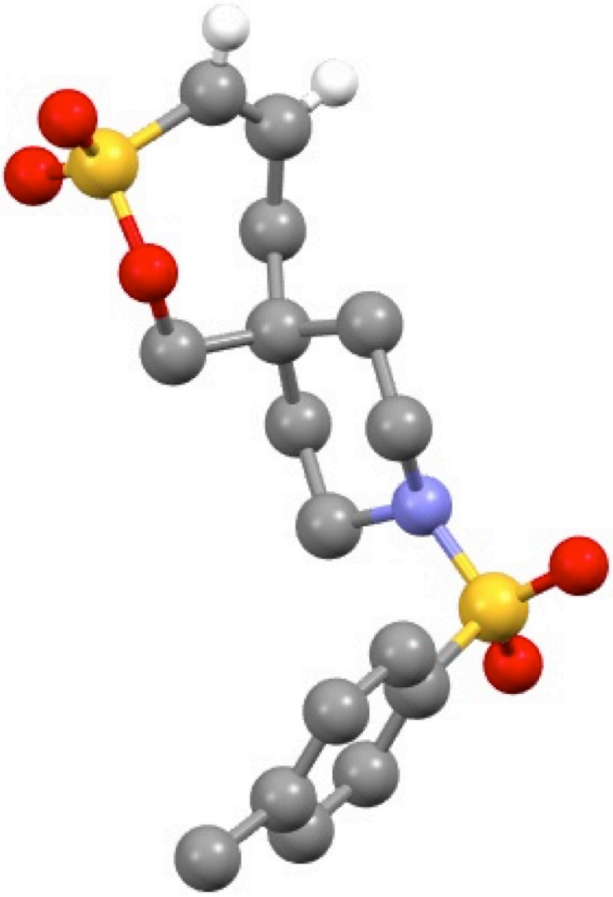


Figure. Representation of 3-methyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*c*][1,2]oxathiine 1,1-dioxide (**2d**)