Gold(I)-catalysed synthesis of cyclic sulfamidates by intramolecular allene hydroamination

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Experimental

^{1}H NMR spectra were recorded on Bruker AV 300, DPX 400 and AV 400 spectrometers at 300 and 400 MHz respectively and referenced to residual solvent. ^{13}C NMR spectrum were recorded using the same spectrometers at 75 and 100 MHz respectively. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (TMS) or to residual solvent peaks ($CDCl_3$ at δ_H 7.26). *J* values are given in Hz and s, d, dd, t, q and m abbreviations correspond to singlet, doublet, doublet of doublet, triplet, quartet and multiplet. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat or as a chloroform solution to a diamond/ZnSe plate.

Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 precoated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic $KMnO_4$. Anhydrous dichloromethane (DCM) and anhydrous dichloroethane (DCE) was distilled from CaH_2.

Allenic alcohols were prepared either by Johnson-Claisen rearrangements of the corresponding propargyl alcohols[1] or alternatively by Crabbé homologation of homopropargyl alcohols.[2] Sulfamate formation was conducted according to standard procedures.[3]

General procedure for catalyst screen (Table 1)

Under an inert atmosphere (nitrogen), 1-cyclohexylpenta-3,4-dien-1-yl sulfamate was dissolved in dry dichloromethane (0.3 M). Catalyst (5 mol%) and silver salt (5 mol%) were

added. When starting material was consumed, as determined by TLC, the reaction mixture was filtered through a plug of silica with diethyl ether, and concentrated *in vacuo*. Purification by column chromatography (2:1 hexane/dichloromethane to 1:2 hexane/dichloromethane) afforded the title compound as separable diastereoisomers.

Chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold(I)[4] and chloro[tris(2,4-di-*tert*-butylphenyl)phosphite]gold[5] and [bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold(I) (2:1) toluene adduct were purchased from Sigma-Aldrich.

1. S. Ma and W. Gao, *J. Org. Chem.*, 2002, **67**, 6104.

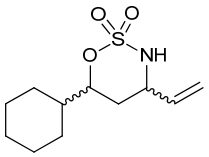
2. B. M. Trost, A. B. Pinkerton and M. Seidel, *J. Am. Chem. Soc.*, 2001, **123**, 12466.

3. C. G. Espino, P. M. When, J. Chow and J. Du Bois, *J. Am. Chem. Soc.*, 2001, **123**, 6935.

4. N. Marion, R. S. Ramón and S. P. Nolan, *J. Am. Chem. Soc.*, 2009, **131**, 448.

5. C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer and A. M. Echavarren, *J. Org. Chem.*, 2008, **73**, 7721.

6-cyclohexyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (2)

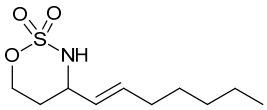


Under an inert atmosphere (nitrogen), 1-cyclohexylpenta-3,4-dien-1-yl sulfamate (60 mg, 0.24 mmol) was dissolved in dry dichloromethane (0.7 mL) and PPh_3AuNTf_2 (8.0 mg, 10.2 μmol) was added. The reaction mixture was stirred for 5 days, then filtered through a plug of silica with diethyl ether and concentrated *in vacuo*. Purification by column chromatography (2:1 hexane/dichloromethane to 1:2 hexane/dichloromethane) afforded the title compound as separable diastereoisomers (60 mg, 0.24 mmol, 99%, *cis*/*trans* = 1.2:1).

cis-**2**: white solid; R_f 0.31 (2:1 dichloromethane/hexane); m.p. 91°C; δ_H (400 MHz, $CDCl_3$) 5.81 (ddd, *J* = 17.3, 10.6, 5.1 Hz, 1H), 5.38 - 5.18 (m, 2H), 4.56 (ddd, *J* = 11.9, 6.4, 2.0 Hz, 1H), 4.31 - 4.17 (m, 1H), 3.98 (d, *J* = 10.3 Hz, 1H), 1.98 - 1.43 (m, 8H), 1.36 - 0.96 (m, 5H); δ_C (101 MHz, $CDCl_3$) 135.3 (CH), 117.3 (CH_2), 88.3 (CH), 56.4 (CH), 42.2 (CH), 32.5 (CH_2), 28.3 (CH_2), 28.0 (CH_2), 26.3 (CH_2), 25.9 (CH_2), 25.7 (CH_2); ν_{max}/cm^{-1} 3276, 2927, 2852, 1650, 1436, 1347, 1175; m/z (ESI^+) 263 ($M + NH_4^+$, 100%), 246 (15%); HRMS (ESI^+) found 263.1428, $C_{11}H_{23}O_3N_2S$ $(M + NH_4)^+$ requires 263.1424.

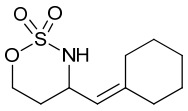
trans-**2**: colourless oil; R_f 0.15 (2:1 dichloromethane/hexane) δ_H (400 MHz, $CDCl_3$) 6.18 (ddd, *J* = 17.4, 10.7, 5.5 Hz, 1H), 5.28 (ddd, J = 10.7, 1.9, 0.7 Hz, 1H), 5.25 (ddd, *J* = 17.4, 1.8, 0.7 Hz, 1H), 4.67 – 4.56 (m, 1H), 4.48 (d, *J* = 6.6 Hz, 1H), 4.29 - 4.13 (m, 1H), 2.08 – 1.91 (m, 1H), 1.99 - 1.92 (m, 1H), 1.88 (ddd, *J* = 14.5, 3.9, 2.9 Hz, 1H), 1.83 - 1.61 (m, 5H), 1.34 - 0.96 (m, 5H); δ_C (101 MHz, $CDCl_3$) 136.0 (CH), 117.2 (CH_2), 86.3 (CH), 55.3 (CH), 41.7 (CH), 30.4 (CH_2), 28.4 (CH_2), 28.2 (CH_2), 26.3 (CH_2), 25.8 (CH_2), 25.6 (CH_2); ν_{max}/cm^{-1} 3277, 2927, 2854, 1645, 1408, 1361, 1175, 870; m/z (ESI^+) 263 ($M + NH_4^+$, 100%), 246 (15%), 149 (15%); HRMS (ESI^+) found 263.1428, $C_{11}H_{23}O_3N_2S$ $(M + NH_4)^+$ requires 263.1424.

(*E*)-4-(hept-1-en-1-yl)-1,2,3-oxathiazinane 2,2-dioxide (4)



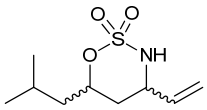
Under an inert atmosphere (nitrogen), deca-3,4-dien-1-yl sulfamate (45 mg, 0.19 mmol) was dissolved in dry dichloromethane (0.7 mL) and PPh_3AuNTf_2 (8.3 mg, 10.6 µmol) was added. The reaction mixture was stirred for 24h, then filtered through a plug of silica with diethyl ether and concentrated *in vacuo*, affording the title compound as a colourless oil (42 mg, 0.18 mmol, 94%). R_f 0.49 (7:3 petroleum ether/ethyl acetate); δ_H (300 MHz, $CDCl_3$) 5.81 - 5.68 (m, 1H), 5.44 - 5.33 (m, 1H), 4.73 (td, J = 11.9, 3.1 Hz, 1H), 4.58 - 4.48 (m, 1H), 4.32 - 4.16 (m, 2H), 2.09 - 1.96 (m, 2H), 1.95 - 1.72 (m, 2H), 1.42 - 1.16 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H); δ_C (75.5 MHz, $CDCl_3$) 134.9 (CH), 126.8 (CH), 71.8 (CH_2), 56.9 (CH), 32.3 (CH_2), 31.4 (CH_2), 29.9 (CH_2), 28.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); ν_{max}/cm^{-1} 3245, 2926, 1433, 1346, 1190, 1170; m/z (ESI^+) 251 ($M + NH_4^+$, 100%), 216 (6%), 156 (6%); HRMS (ESI^+) found 251.1428, $C_{10}H_{23}O_3N_2S$ $(M + NH_4)^+$ requires 251.1424.

4-(cyclohexylidenemethyl)-1,2,3-oxathiazinane 2,2-dioxide (6)



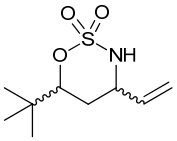
Under an inert atmosphere (nitrogen), 4-cyclohexylidenebut-3-en-1-yl sulfamate (50 mg, 0.22 mmol) was dissolved in dry dichloromethane (0.7 mL). PPh_3AuCl (5.4 mg, 10.8 µmol) and AgOTf (2.8 mg, 10.8 µmol) were added. The reaction mixture was stirred for 24 h, then filtered through a plug of silica using diethyl ether as eluent and concentrated *in vacuo*, affording the title compound as a colourless oil (33 mg, 0.14 mmol, 66%). R_f 0.51 (1:1 petroleum ether/ethyl acetate); δ_H (400 MHz, $CDCl_3$) 5.56 - 5.42 (m, 1H), 4.78 - 4.66 (m, 1H), 4.59 - 4.49 (m, 1H), 4.05 - 3.71 (m, 2H), 2.17 (d, J = 6.7 Hz, 2H), 2.06 - 1.50 (m, 9H); δ_C (101 MHz, $CDCl_3$) 132.1 (C_{quat}), 126.5 (CH), 72.2 (CH_2), 53.8 (CH), 44.2 (CH_2), 30.2 (CH_2), 28.5 (CH_2), 25.4 (CH_2), 22.8 (CH_2), 22.2 (CH_2); ν_{max}/cm^{-1} 3246, 2922, 1421, 1347, 1187; m/z (ESI^+) 440 ($M + NH_4^+$, 100%), 232 (43%), 199 (20%), 149 (27%); HRMS (ESI^+) found 249.1271, $C_{10}H_{21}O_3N_2S$ $(M + NH_4)^+$ requires 249.1267.

6-isobutyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (8)



Under an inert atmosphere (nitrogen), 2-methylocta-6,7-dien-4-yl sulfamate (52 mg, 0.24 mmol) was dissolved in dry dichloroethane (0.7 mL) and PPh_3AuNTf_2 (10.0 mg, 12.7 µmol) was added. The reaction mixture was stirred at 40°C for 5 days, then filtered through a plug of silica with diethyl ether and concentrated *in vacuo*. Purification by column chromatography (4:1 petroleum ether/ethyl acetate) afforded the title compound as an inseparable mixture of diastereoisomers, colourless oil (49 mg, 0.18 mmol, 94%, *cis*/*trans* 1.8:1). R_f 0.52 (4:1 petroleum ether/ethyl acetate); δ_H (300 MHz, $CDCl_3$) *cis*-isomer: 5.81 (ddd, J = 17.3, 10.6, 5.0 Hz, 1H), 5.37 - 5.22 (m, 2H), 4.90 - 4.79 (m, 2H), 3.90 (d, *J* = 10.2 Hz, 1H), 1.96 - 1.80 (m, 2H), 1.80-1.66 (m, 1H), 1.60 - 1.45 (2H), 1.00 - 0.87 (m, 6H) *trans*-isomer: 6.18 (ddd, *J* = 17.3, 10.7, 5.5 Hz, 1H), 5.37 - 5.22 (m, 2H), 5.00 - 4.91 (m, 2H), 4.44 (d, *J* = 7.1 Hz, 1H), 1.96 - 1.80 (m, 2H), 1.80 - 1.66 (m, 1H), 1.44 - 1.32 (m, 2H), 1.00 - 0.87 (m, 6H); δ_C (75 MHz, $CDCl_3$) *cis*-isomer: 135.1 (CH), 117.4 (CH_2), 82.7 (CH), 56.3 (CH), 44.3 (CH_2), 35.6 (CH), 23.8 (CH_2), 23.0 (CH_3), 22.0 (CH_3) *trans*-isomer: 135.9 (CH), 117.4 (CH_2), 81.1 (CH), 55.2 (CH), 43.6 (CH_2), 33.5 (CH), 24.1 (CH_2), 23.0 (CH_3), 21.9 (CH_3); ν_{max}/cm^{-1} 3245, 2960, 2874, 1650, 1413, 1356, 1185; m/z (ESI^+) 237 ($M+NH_4^+$, 100%), HRMS (ESI^+) found 237.1270, $C_9H_{21}O_3N_2S$ $(M + NH_4)^+$ requires 237.1267.

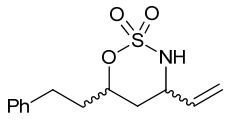
6-(*tert*-butyl)-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (10)



Under an inert atmosphere (nitrogen), 2,2-dimethylhepta-5,6-dien-3-yl sulfamate (57 mg, 0.24 mmol) was dissolved in dry dichloroethane (0.7 mL) and PPh_3AuNTf_2 (10.0 mg, 12.7 µmol) was added. The reaction mixture was stirred at 40°C for 4 days, then filtered through a plug of silica with diethyl ether and concentrated *in vacuo.* Purification by column chromatography (petroleum ether to 2:1 petroleum ether/ethyl acetate) afforded the title compound as an inseparable mixture of diastereoisomers, colourless oil (53 mg, 0.22 mmol, 93%, *cis*/*trans* 2:1). R_f 0.44 (4:1 petrol ether/ethyl acetate); δ_H (300 MHz, $CDCl_3$) *cis*-isomer:

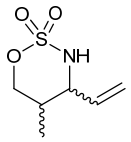
5.82 (ddd, *J* = 17.3, 10.6, 5.0 Hz, 1H), 5.42 - 5.15 (m, 2H), 4.58 - 4.39 (m, 1H), 4.28 - 4.15 (m, 2H), 1.95 – 1.82 (m, 1H), 1.65 – 1.46 (1H, m), 0.98 (s, 9H) *trans*-isomer: 6.20 (ddd, *J* = 17.4, 10.7, 5.4 Hz, 1H), 5.42 - 5.15 (m, 2H), 4.58 – 4.39 (m, 1H), 4.30 - 4.01 (m, 2H), 2.10 - 1.97 (m, 1H), 1.95 – 1.82 (m, 1H), 0.98 (s, 9H); δ_C (75 MHz, $CDCl_3$) *cis*-isomer 135.2 (CH), 117.3 (CH_2), 91.3 (CH), 56.3 (CH), 34.5 (CH_2), 29.9 (C_{quat}), 25.4 (CH_3) *trans*-isomer 135.9 (CH), 117.1 (CH_2), 88.5 (CH), 55.2 (CH), 34.4 (C_{quat}), 27.8 (CH_2), 25.2 (CH_3); ν_{max}/cm^{-1} 3252, 2962, 2877, 1650, 1413, 1346, 1183; m/z (ESI^+) 237 ($M + NH_4^+$, 100%) HRMS (ESI^+) found 237.1269, $C_9H_{21}O_3N_2S$ $(M + NH_4)^+$ requires 237.1267.

6-phenethyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (12)



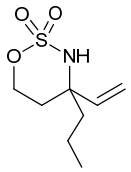
Under an inert atmosphere (nitrogen), 1-phenylhepta-5,6-dien-3-yl sulfamate (50 mg, 0.19 mmol) was dissolved in dry dichloromethane (0.7 mL) and PPh_3AuNTf_2 (7.3 mg, 9.3 μmol) was added. The reaction mixture was stirred at room temperature for 5 days then filtered through a plug of silica with diethyl ether and concentrated *in vacuo*. Purification by column chromatography (6:1 pentane/ethyl acetate to 4:1 pentane/ethyl acetate) afforded the title compound as an inseparable mixture of diastereoisomers, colourless oil (48 mg, 0.18 mmol, 95%, *cis*/*trans* 1.8:1). δ_H (400 MHz, $CDCl_3$) *cis*-isomer: 7.42 - 7.19 (m, 5H), 5.85 (ddd, *J* = 17.3, 10.6, 5.0 Hz, 1H), 5.41 - 5.25 (m, 2H), 4.86 - 4.76 (m, 1H), 4.37 - 4.24 (m, 1H), 4.04 (d, *J* = 10.4 Hz, 1H), 3.00 - 2.71 (m, 2H), 2.22 - 2.04 (m, 1H), 2.03 - 1.86 (m, 2H), 1.63 (dt, *J* = 14.3, 11.9 Hz, 1H) *trans*-isomer: 7.42 – 7.19 (m, 5H), 6.16 (ddd, *J* = 17.2, 10.7, 5.5 Hz, 1H), 5.41 - 5.25 (m, 2H), 4.91 (m, 1H), 4.54 (d, *J* = 6.8 Hz, 1H), 4.37 - 4.24 (m, 1H), 3.00 - 2.71 (m, 2H), 2.36 (dtd, *J* = 14.4, 9.2, 5.3 Hz, 1H), 2.03 - 1.86 (m, 3H); δ_C (75 MHz, $CDCl_3$) *cis*-isomer: 140.4 (C_{quat}), 135.0 (CH), 128.8 (CH), 128.6 (CH), 126.5 (CH), 117.5 (CH_2), 83.1 (CH), 56.3 (CH), 37.1 (CH_2), 35.2 (CH_2), 30.7 (CH_2) *trans*-isomer: 140.5 (C_{quat}), 135.6 (CH), 128.7 (CH), 128.6 (CH), 126.4 (CH), 117.5 (CH_2), 81.9 (CH), 55.0 (CH), 36.5 (CH_2), 33.1 (CH_2), 31.1 (CH_2); ν_{max}/cm^{-1} 3262, 3028, 2931, 1603, 1497, 1416, 1360, 1183; m/z (ESI^+) 285 ($M + NH_4^+$, 100%), 214 (60%); HRMS (ESI^+) found 285.1272, $C_{13}H_{21}O_3N_2S$ $(M + NH_4)^+$ requires 285.1267.

5-methyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (14)



Under an inert atmosphere (nitrogen), 2-methylpenta-3,4-dien-1-yl sulfamate (50 mg, 0.28 mmol) was dissolved in dry dichloromethane (0.7 mL) and PPh_3AuNTf_2 (13 mg, 16.5 µmol) was added. The reaction mixture was stirred for 3 days at room temperature and flushed through a plug of silica with diethyl ether and concentrated *in vacuo*. Purification by column chromatography (dichloromethane to 1% methanol in dichloromethane) afforded the title compound as a colourless oil (36 mg, 0.23 mmol, 75%, major/minor 3:1); δ_H (400 MHz, $CDCl_3$) major-isomer: 5.81 - 5.66 (m, 1H), 5.42 - 5.23 (m, 2H), 4.84 (dd, J = 11.1, 2.5 Hz, 1H), 4.58 - 4.42 (m, 2H), 4.33 (dd, J = 11.5, 1.9 Hz, 1H), 2.00 - 1.79 (m, 1H), 1.08 (d, J = 7.2 Hz, 3H) minor-isomer: 5.81 – 5.66 (m, 1H), 5.42 – 5.23 (m, 2H), 4.42 – 4.35 (m, 2H), 3.87 (dd, J = 17.6, 9.8 Hz, 1H), 2.00-1.79 (m, 1H), 0.89 (d, J = 6.8 Hz, 3H); δ_C (101 MHz, $CDCl_3$) major-isomer: 133.9 (CH), 117.0 (CH_2), 77.7 (CH_2), 59.8 (CH), 30.8 (CH), 9.7 (CH_3) minor-isomer: 133.7 (CH), 120.1 (CH_2), 76.4 (CH_2), 63.4 (CH), 33.3 (CH), 12.0 (CH_3); ν_{max}/cm^{-1} 3266, 2977, 1647, 1423, 1358, 1185, 919; m/z (ESI^+) 195 ($M + NH_4^+$, 100%), 187 (10%); HRMS (ESI^+) found 195.0794, $C_6H_{15}O_3N_2S$ $(M + NH_4)^+$ requires 195.0798.

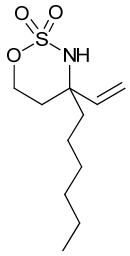
4-propyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (16)



Under an inert atmosphere (nitrogen), 3-vinylidenehexyl sulfamate (54 mg, 0.26 mmol) was dissolved in dry dichloromethane (0.7 mL) and PPh_3AuNTf_2 (10.0 mg, 11.4 µmol) was added. The reaction mixture was stirred for 18 h, then filtered through a plug of silica with diethyl ether and concentrated *in vacuo* affording the title compound as a colourless oil (50 mg, 0.24 mmol, 92%). R_f 0.41 (dichloromethane); δ_H (400 MHz, $CDCl_3$) 5.97 - 5.85 (m, 1H), 5.30 (d, J = 11.1 Hz, 1H), 5.12 (d, J = 17.7 Hz, 1H), 4.73 - 4.64 (m, 1H), 4.60 (ddd, J = 11.8, 5.6, 4.0 Hz, 1H), 4.28 (s, 1H), 2.04 - 1.96 (m, 1H), 1.91 - 1.81 (m, 1H), 1.81 - 1.71 (m, 1H), 1.56 - 1.35 (m, 2H), 1.34 - 1.20 (m, 1H), 0.91 (t, J = 7.2 Hz, 3H); δ_C (101 MHz, $CDCl_3$) 139.9 (CH), 115.1 (CH_2), 69.2 (CH_2), 63.0 (C_{quat}), 43.2 (CH_2), 32.2 (CH_2), 16.2 (CH_2), 14.2 (CH_3);

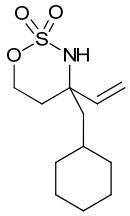
ν_{max}/cm^{-1} 3263, 2963, 2876, 1641, 1407, 1354; m/z (ESI^+) 223 ($M + NH_4^+$, 100%), 185 (5%); HRMS (ESI^+) found 223.1113, $C_8H_{19}O_3N_2S$ $(M + NH_4)^+$ requires 223.1111.

4-hexyl-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (18)



Under an inert atmosphere (nitrogen), 3-vinylidenenonyl sulfamate (50 mg, 0.2 mmol) was dissolved in dry dichloromethane (0.7 mL) and PPh_3AuNTf_2 (7.8 mg, 10.0 μmol) was added. The reaction mixture was stirred at room temperature for 48 hours. The reaction mixture was filtered through a plug of silica with diethyl ether and concentrated *in vacuo*. Purification by column chromatography (gradient elution: 1:1 petrol ether/dichloromethane to dichloromethane) gave the desired material as a yellow oil (35 mg, 0.14 mmol, 70%). δ_H (300 MHz, $CDCl_3$) 5.91 (dd, J = 17.5, 10.8 Hz, 1H), 5.30 (d, J = 11.1 Hz, 1H), 5.12 (d, J = 17.7 Hz, 1H), 4.77 - 4.48 (m, 2H), 4.16 (s, 1H), 2.01 (m, 1H), 1.92 - 1.70 (m, 2H), 1.60 - 1.51 (m, 1H), 1.44 - 1.14 (m, 8H), 0.88 (dd, J = 9.3, 4.2 Hz, 3H); δ_C (75 MHz, $CDCl_3$) 140.0 (CH), 115.2 (CH_2), 69.2 (CH_2), 63.0 (C_{quat}), 41.1 (CH_2), 32.3 (CH_2), 31.7 (CH_2), 29.4 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 14.2 (CH_3); ν_{max}/cm^{-1} 3264, 2956, 2931, 2859, 1642, 1407, 1356, 1186, 777; m/z (ESI^+) 270 ($M + Na^+$, 100%); HRMS (ESI^+) found 270.1138, $C_{11}H_{21}O_3NNaS$ $(M + Na)^+$ requires 270.1134.

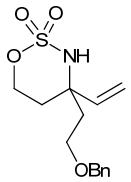
4-(cyclohexylmethyl)-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (20)



Under an inert atmosphere (nitrogen), 3-(cyclohexylmethyl)penta-3,4-dien-1-yl sulfamate (100 mg, 0.38 mmol) was dissolved in dry dichloroethane (1.4 mL) and PPh_3AuNTf_2 (17.2

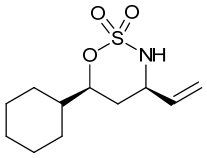
mg, 22 μmol) was added. The reaction mixture was stirred at 40°C for 4 days. The room temperature reaction mixture was filtered through a plug of silica with diethyl ether and concentrated *in vacuo*. Purification by column chromatography (2:1 petroleum ether/diethyl ether) gave the desired material as a colourless oil (37 mg, 0.14 mmol, 37%). δ_H (300 MHz, $CDCl_3$) 6.00 (dd, J = 17.8, 11.1 Hz, 1H), 5.31 (d, J = 11.1 Hz, 1H), 5.15 (d, J = 17.8 Hz, 1H), 4.77 – 4.64 (ddd, J = 11.8, 9.4, 3.2, 1H), 4.56 (ddd, J = 11.8, 5.0, 4.1 Hz, 1H), 4.12 (s, 1H), 2.06 – 1.83 (m, 2H), 1.72 – 1.37 (m, 6H), 1.31 – 1.04 (m, 4H), 1.04 – 0.82 (m, 3H); δ_C (101 MHz, $CDCl_3$) 140.2 (CH), 115.0 (CH_2), 69.1 (CH_2), 63.4 (C_{quat}), 49.4 (CH_2), 35.3 (CH_2), 35.0 (CH_2), 33.3 (CH_2), 33.0 (CH), 26.4 (CH_2), 26.4 (CH_2), 26.1 (CH_2); ν_{max}/cm^{-1} 3381, 2921, 2850, 1557, 1449, 1348, 1176, 926; m/z (ESI^+) 282 ($M + Na^+$, 100%), 278 (40%), 163 (30%); HRMS (ESI^+) found 260.1319, $C_{12}H_{22}O_3NS$ $(M + H)^+$ requires 260.1315.

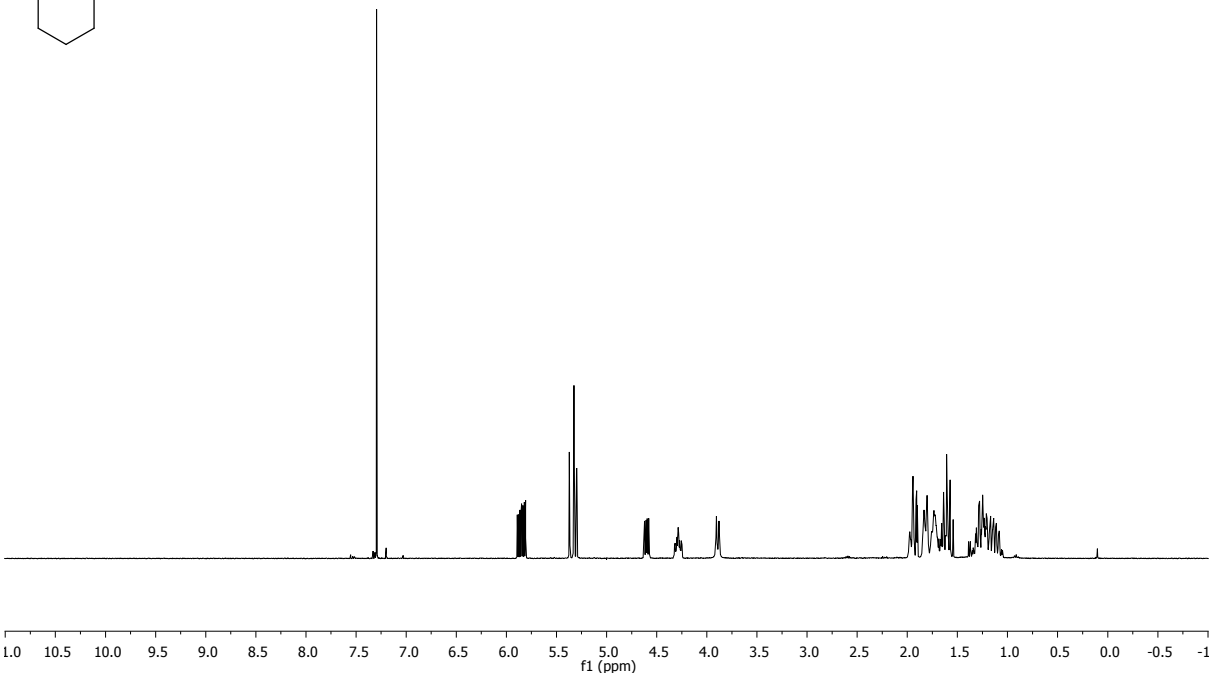
4-(2-(benzyloxy)ethyl)-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide (22)



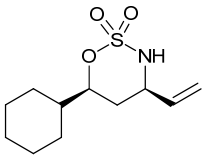
Under an inert atmosphere (nitrogen), 3-(2-benzyloxy)ethyl)penta-3,4-dien-1-yl (50 mg, 0.17 mmol) was dissolved in dry dichloromethane (0.7 mL) and PPh_3AuNTf_2 (6.6 mg, 8.4 μmol) was added. The reaction mixture was stirred at room temperature for 5 days. The room temperature reaction mixture was filtered through a plug of silica with diethyl ether and concentrated *in vacuo*. Purification by column chromatography (9:1 dichloromethane/ ethyl acetate) gave the desired material as a colourless oil (45 mg, 0.15 mmol, 90%). δ_H (300 MHz, $CDCl_3$) 7.47 – 7.26 (m, 5H), 6.00 (ddd, J = 17.7, 11.0, 0.6 Hz, 1H), 5.78 (s, 1H), 5.34-5.12 (m, 2H), 4.72 (td, J = 11.4, 2.4 Hz, 1H), 4.60-4.41 (m, 3H), 3.73 – 3.53 (m, 2H), 2.15 – 1.94 (m, 2H), 1.89 – 1.74 (m, 2H); δ_C (75 MHz, $CDCl_3$) 140.3 (CH), 137.1 (C_{quat}), 128.7 (CH), 128.1 (CH), 128.0 (CH), 115.4 (CH_2), 73.5 (C_{quat}), 68.8 (CH_2), 65.6 (CH_2), 62.4 (CH_2), 40.1 (CH_2), 30.6 (CH_2); ν_{max}/cm^{-1} 3247, 2874, 1703, 1496, 1455, 1407, 1358, 1187, 778; m/z (ESI^+) 315 ($M + NH_4^+$, 90%), 298 $(M + H)^+$, 100%), 149 (25%); HRMS (ESI^+) found 298.1115, $C_{14}H_{20}O_4NS$ $(M + H)^+$ requires 298.1108.

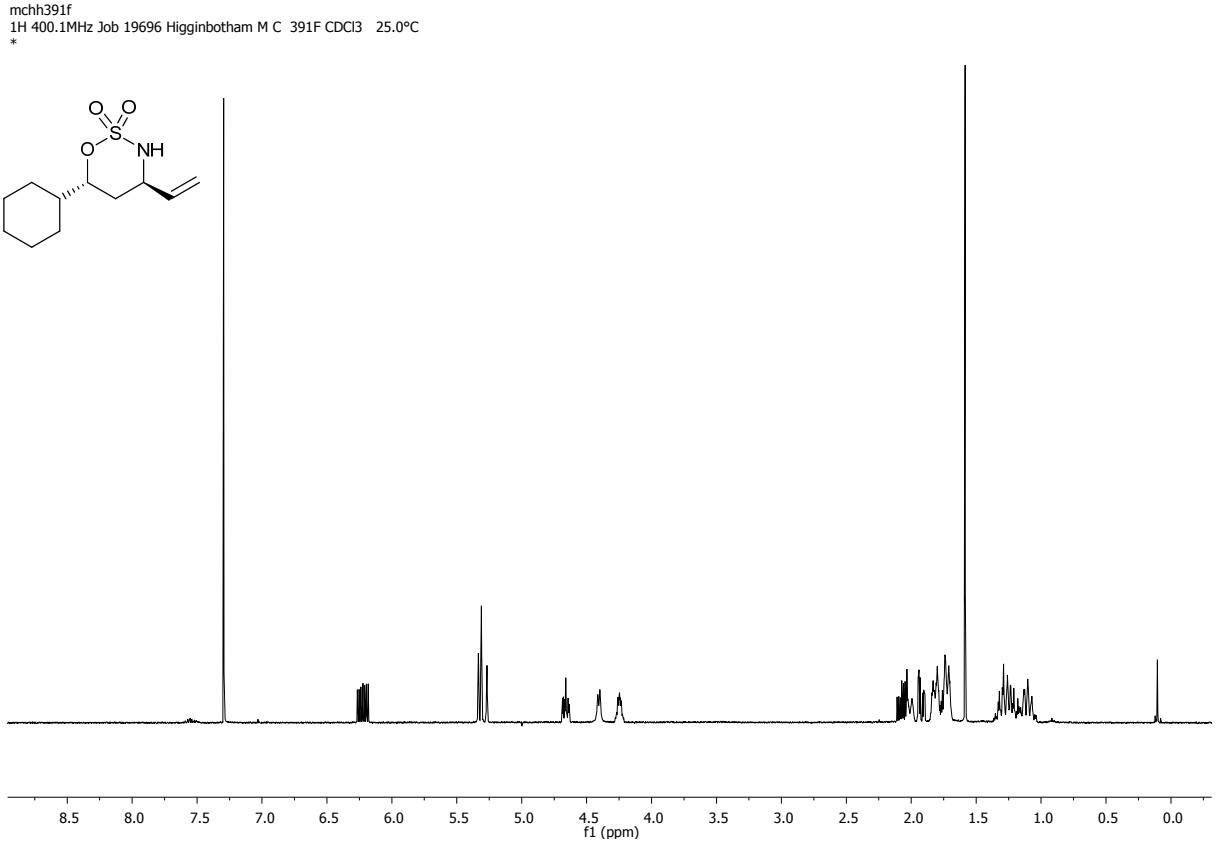
mchh379dc
1H 400.1MHz Job 19668 Higginbotham M C 379DC CDCl3 25.0°C
*

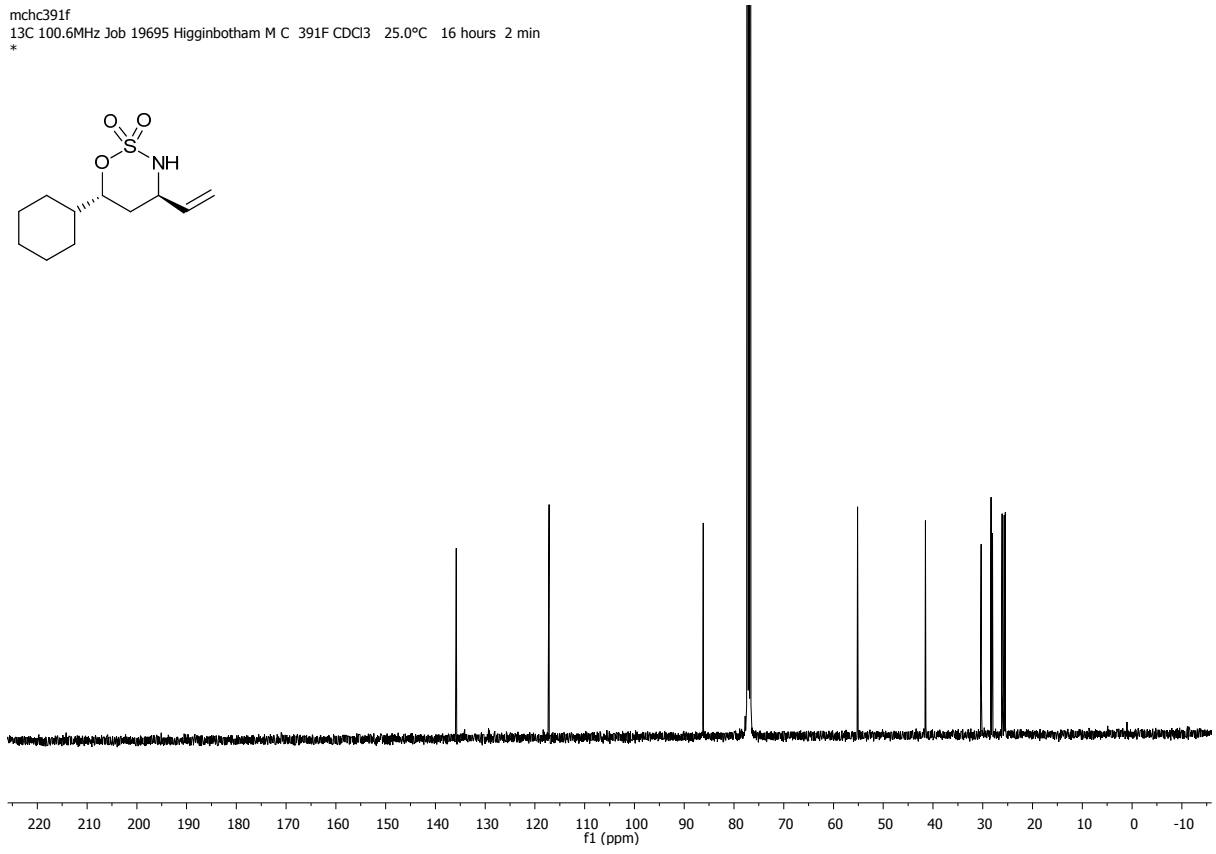




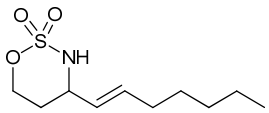
mchc379dc
13C 100.6MHz Job 19669 Higginbotham M C 379DC CDCl3 25.0°C 6 hours 19 min
*



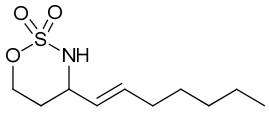


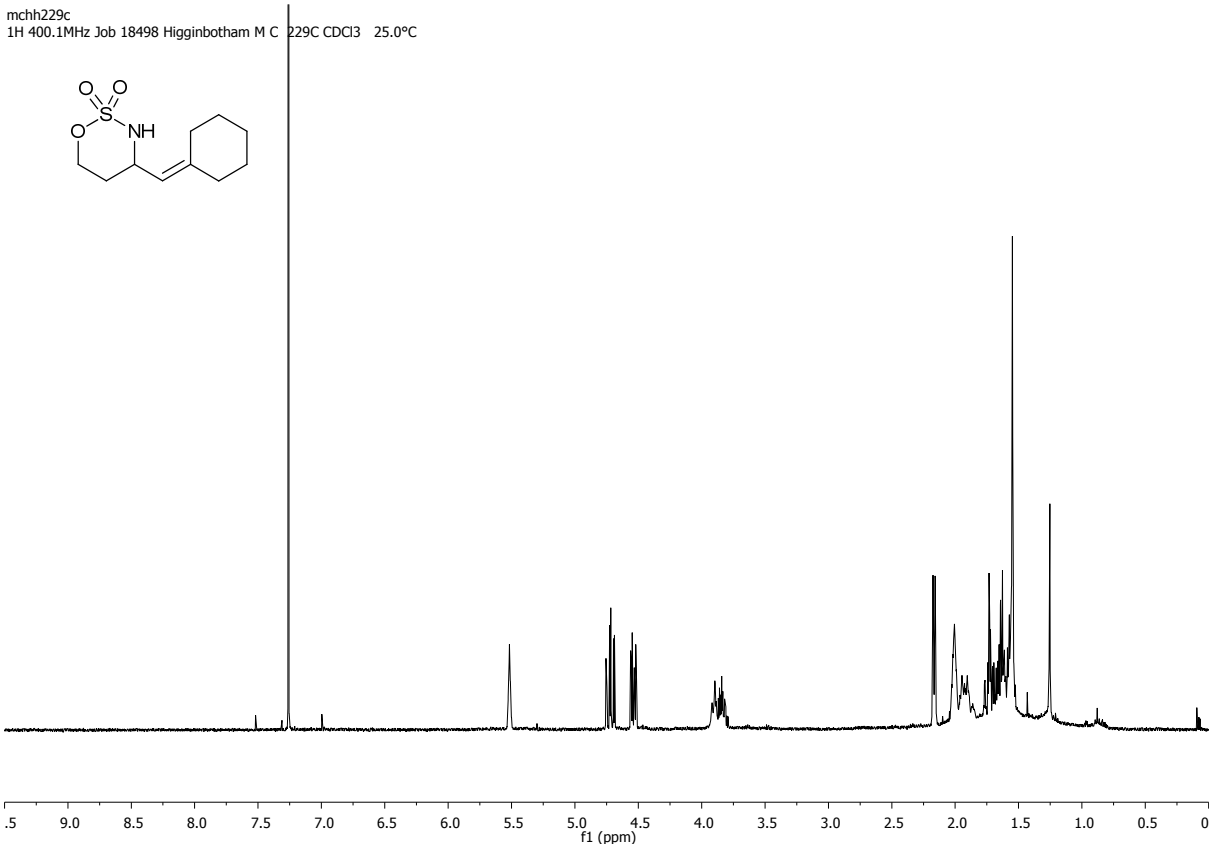


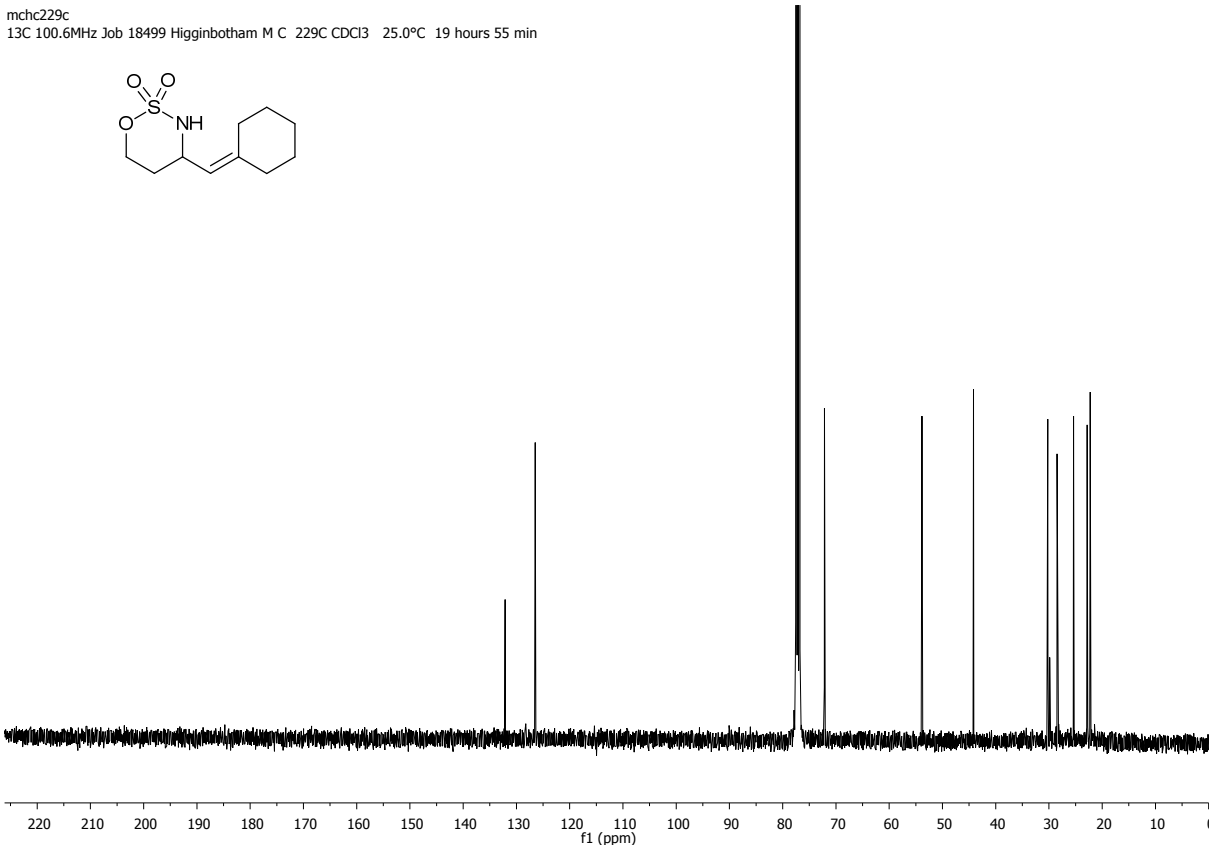
mchh201a
1H 300.1MHz Job 1617 Higginbotham M C 201A CDCl3 25.0'C
crude



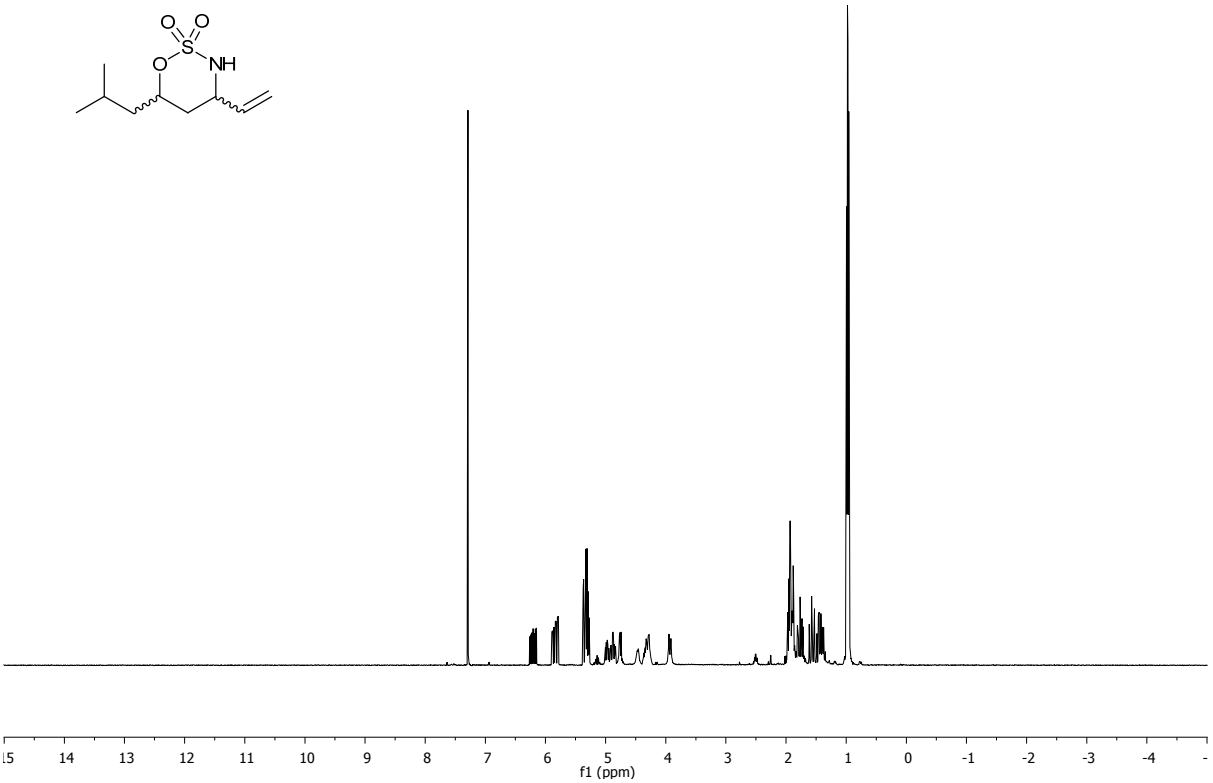
mchc201c
13C 75.5MHz Job 7285 Higginbotham M C 201C CDCl3 25.0°C 3 hours 1 min
*



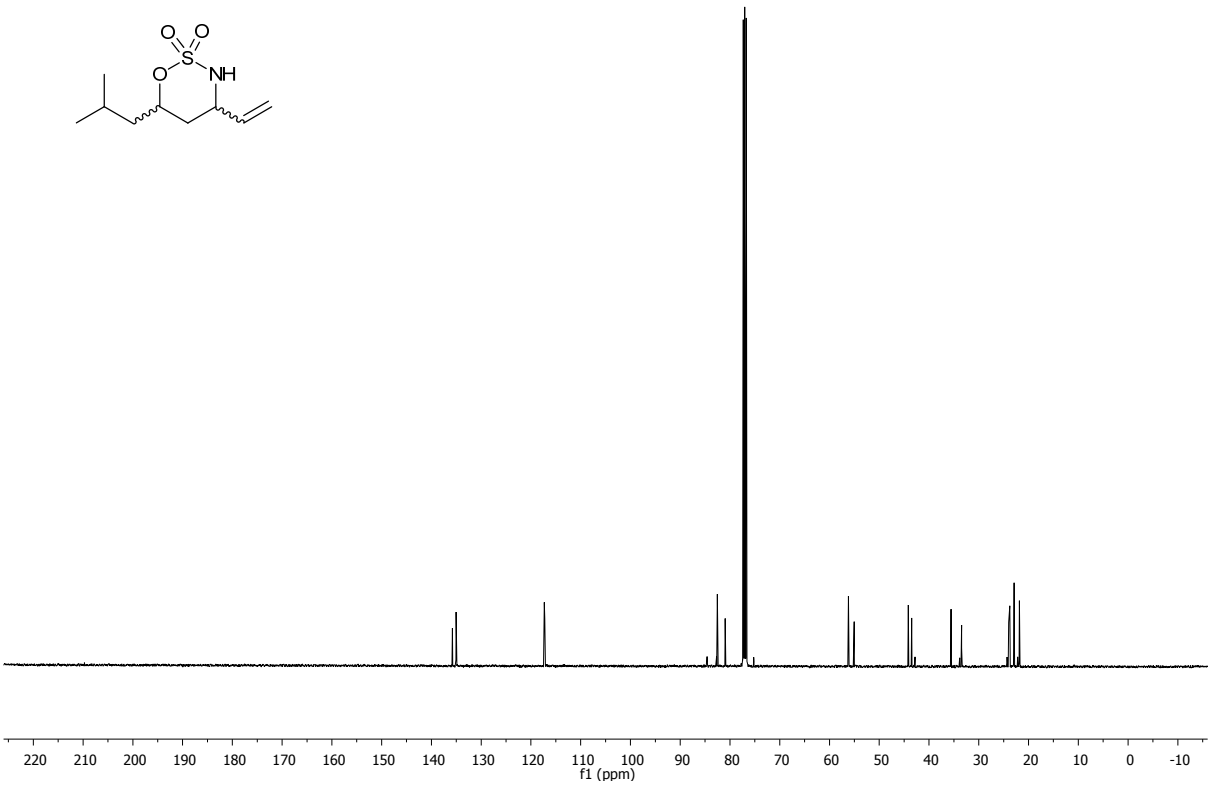




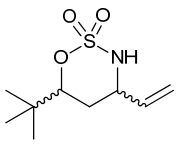
mchh265g
1H 300.1MHz Job 14736 Higginbotham M C 265G CDCl3 20.6°C
*



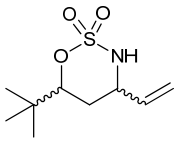
mchc265i
13C 100.6MHz Job 19601 Higginbotham M C 265I CDCl3 25.0°C 10 hours 41 min
*



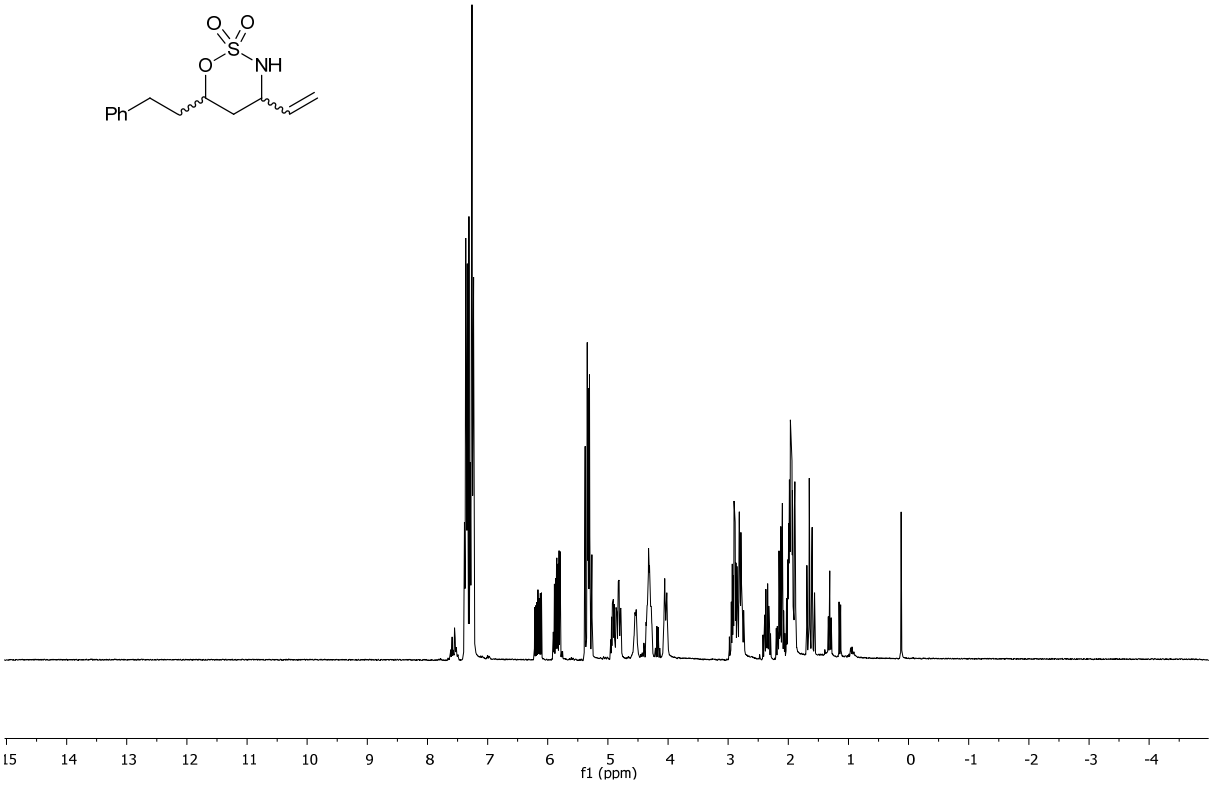
mchh266f
1H 300.1MHz Job 14729 Higginbotham M C 266F CDCl3 19.9°C
*



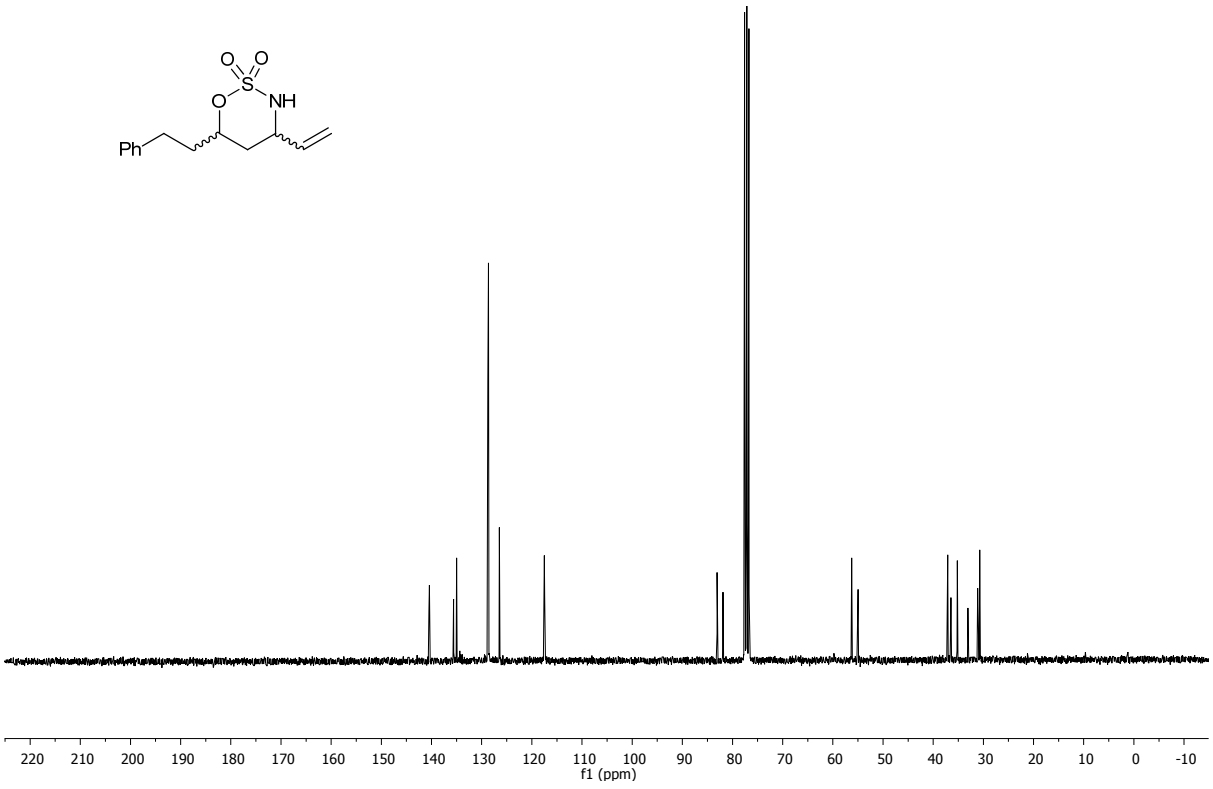
mchc266f
13C 75.5MHz Job 14793 Higginbotham M C 266F CDCl3 21.0°C 0 hour 18 min
*



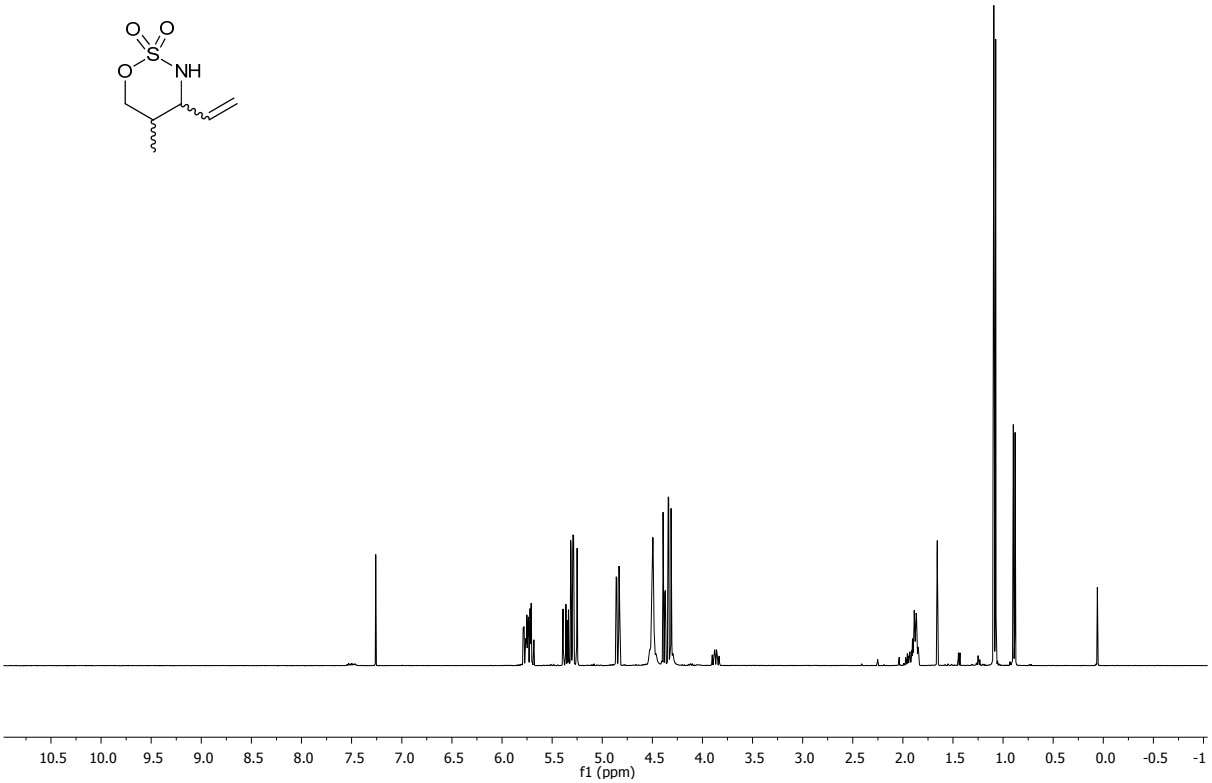
mchh358h
1H 300.1MHz Job 14516 Higginbotham M C 358H CDCl3 21.2°C
*



mchc358h
13C 75.5MHz Job 14576 Higginbotham M C 358H CDCl3 22.1°C 3 hours 1 min
*



mchh296b
1H 400.1MHz Job 19360 Higginbotham M C 296B CDCl3 25.0°C
*



mchc296b
13C 100.6MHz Job 19362 Higginbotham M C 296B CDCl3 25.0°C 2 hours 40 min
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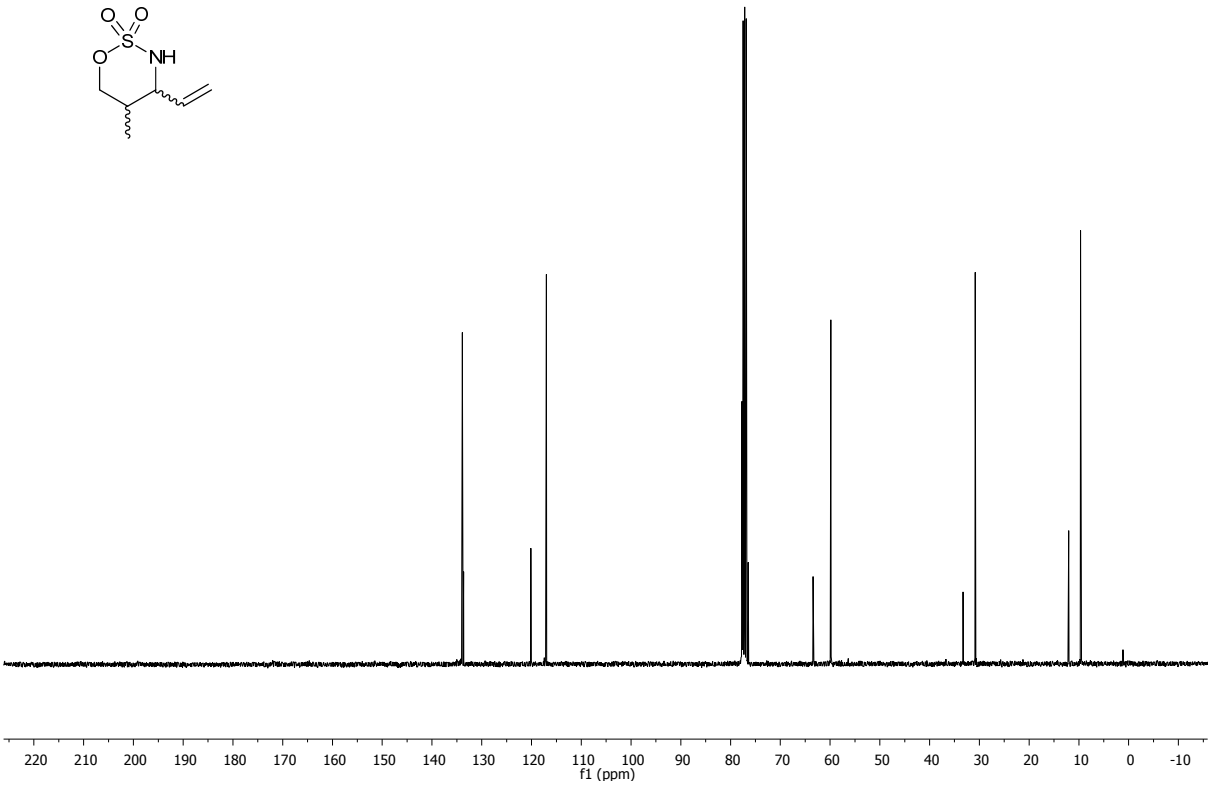
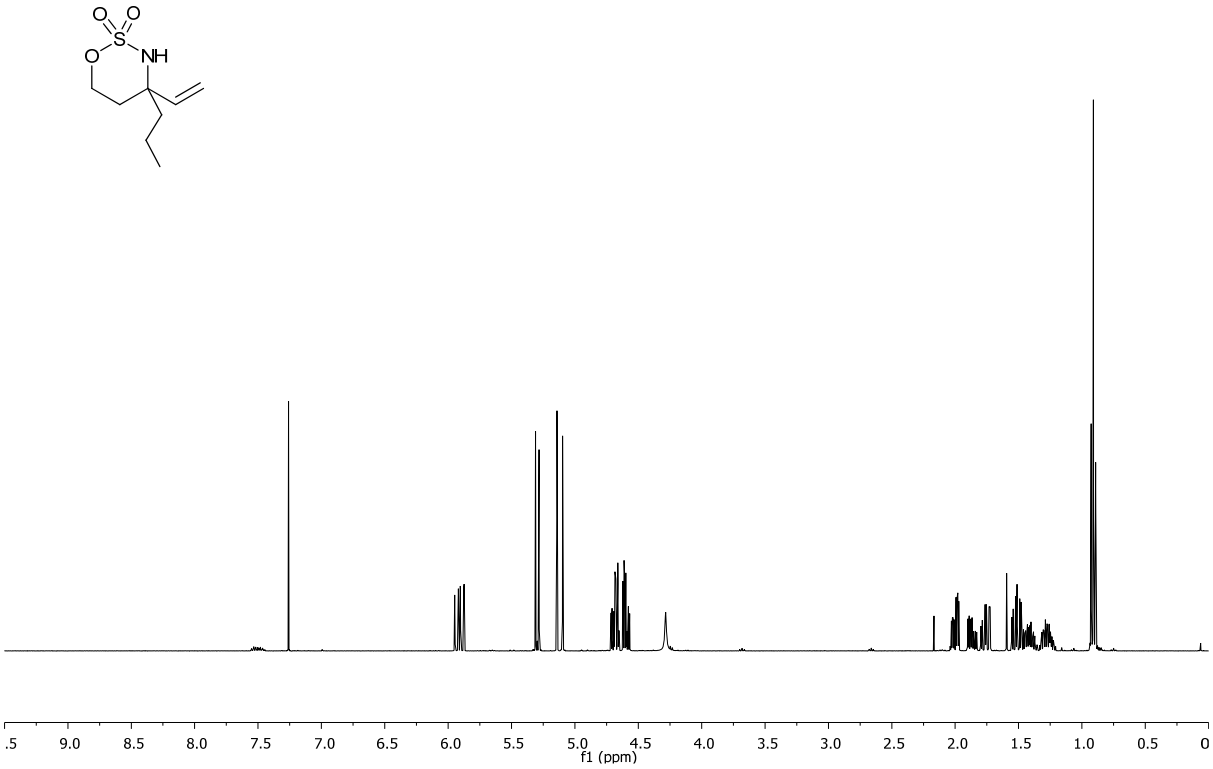
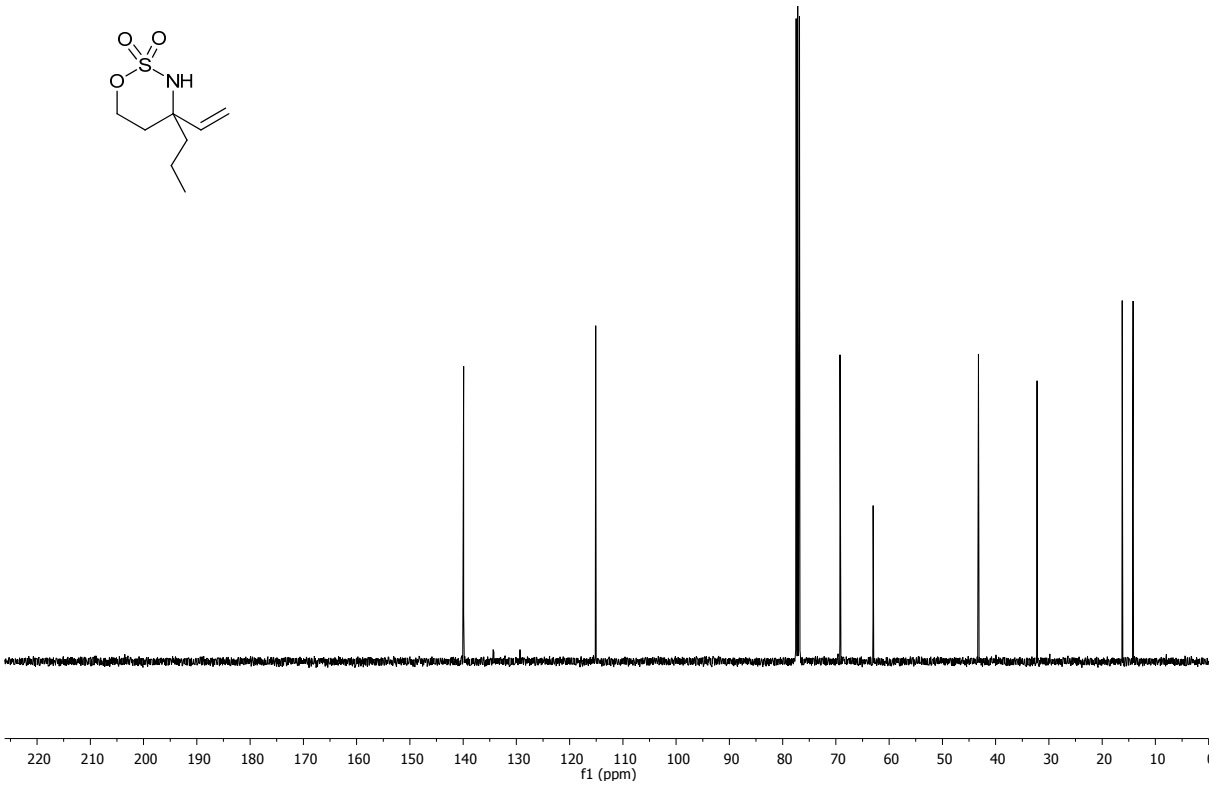


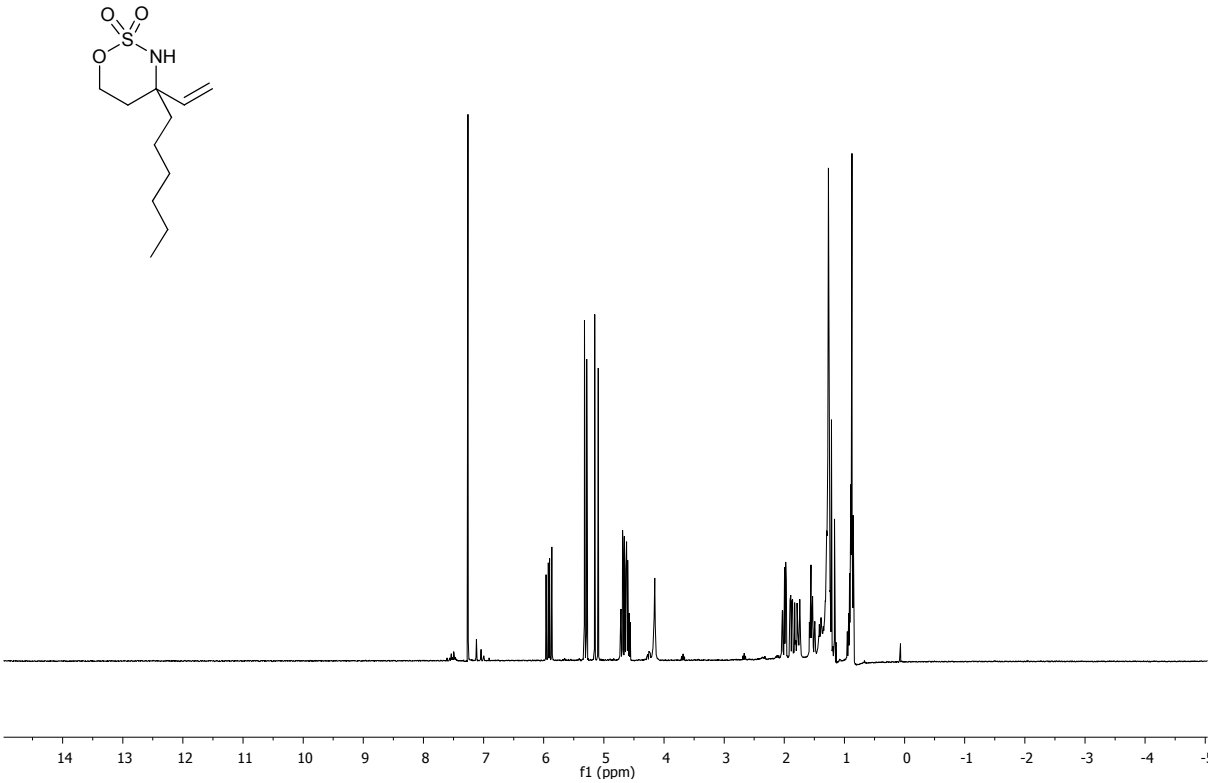
mchh220c
1H 400.1MHz Job 18467 Higginbotham M C 220C CDCl3 25.0'C



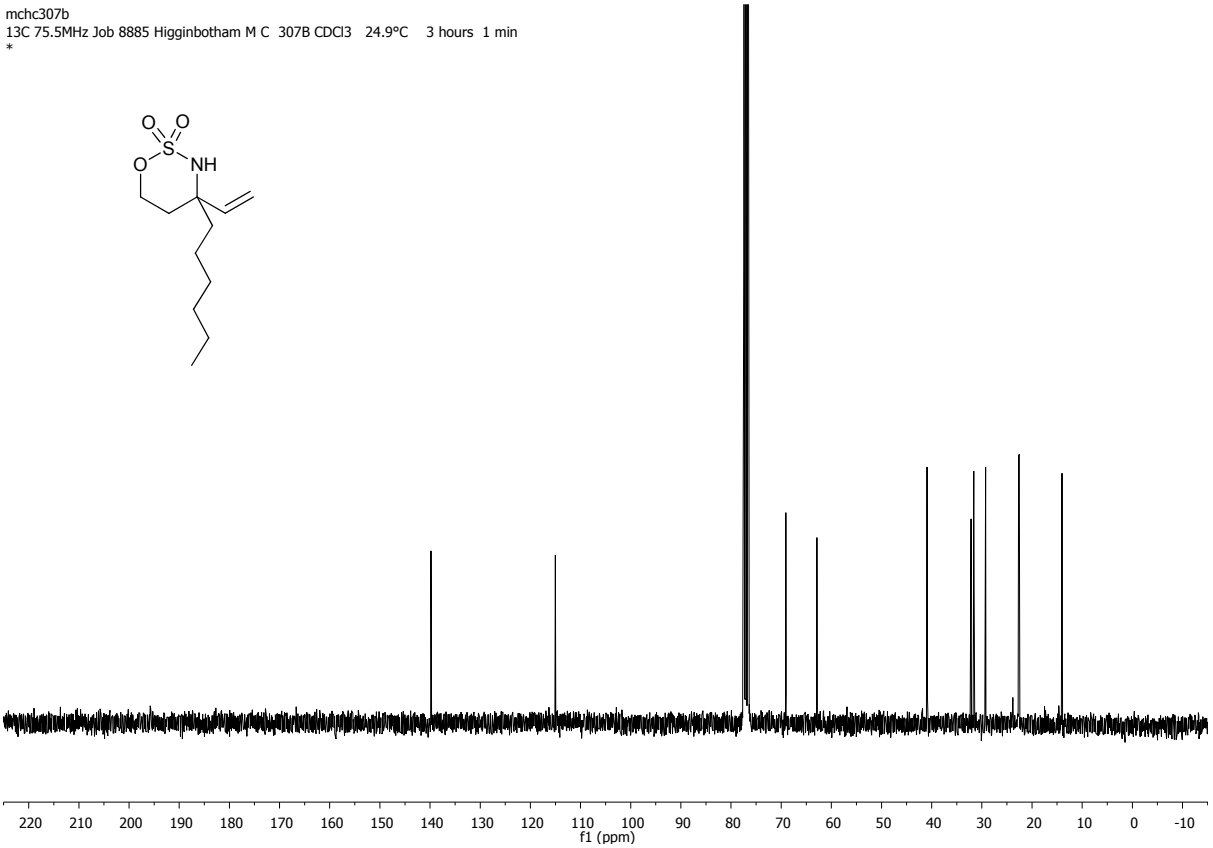
mchc220c
13C 100.6MHz Job 18468 Higginbotham M C 220C CDCl3 25.0'C 0 hour 58 min

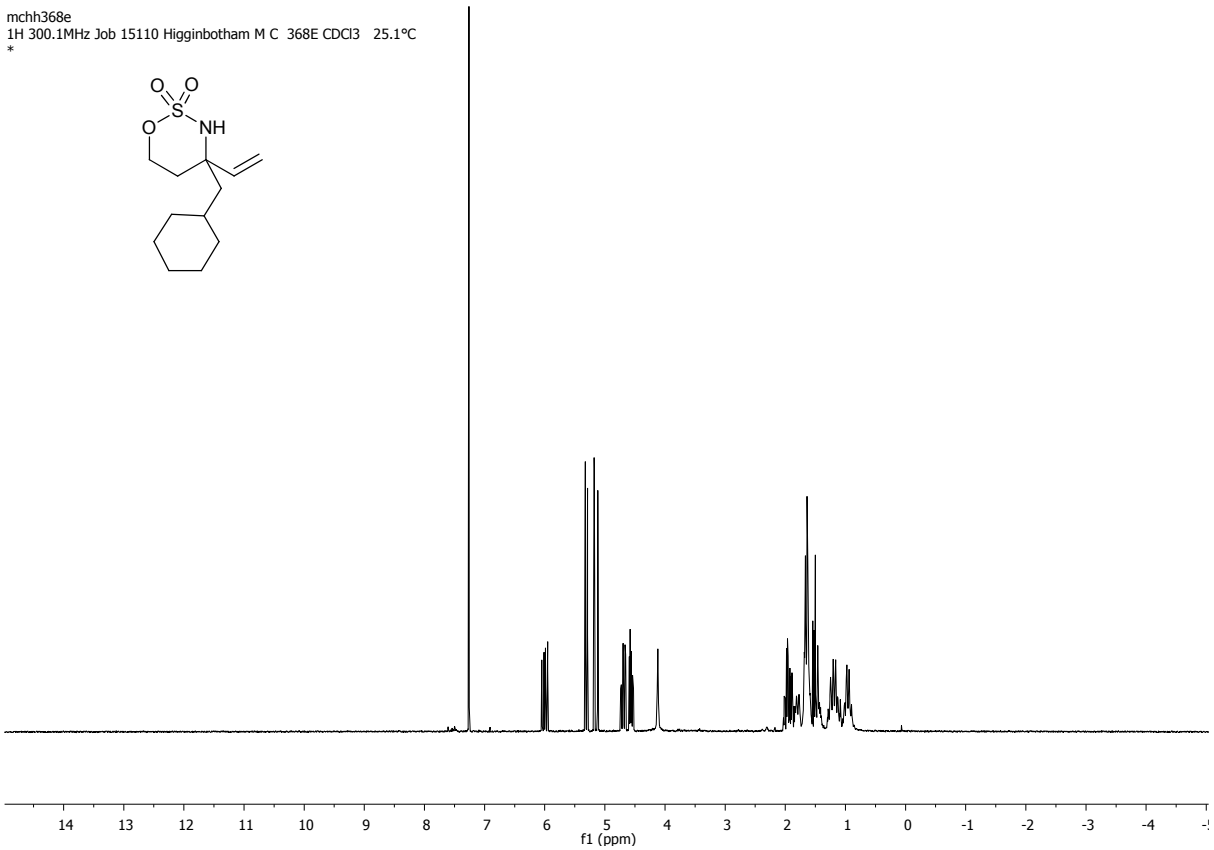


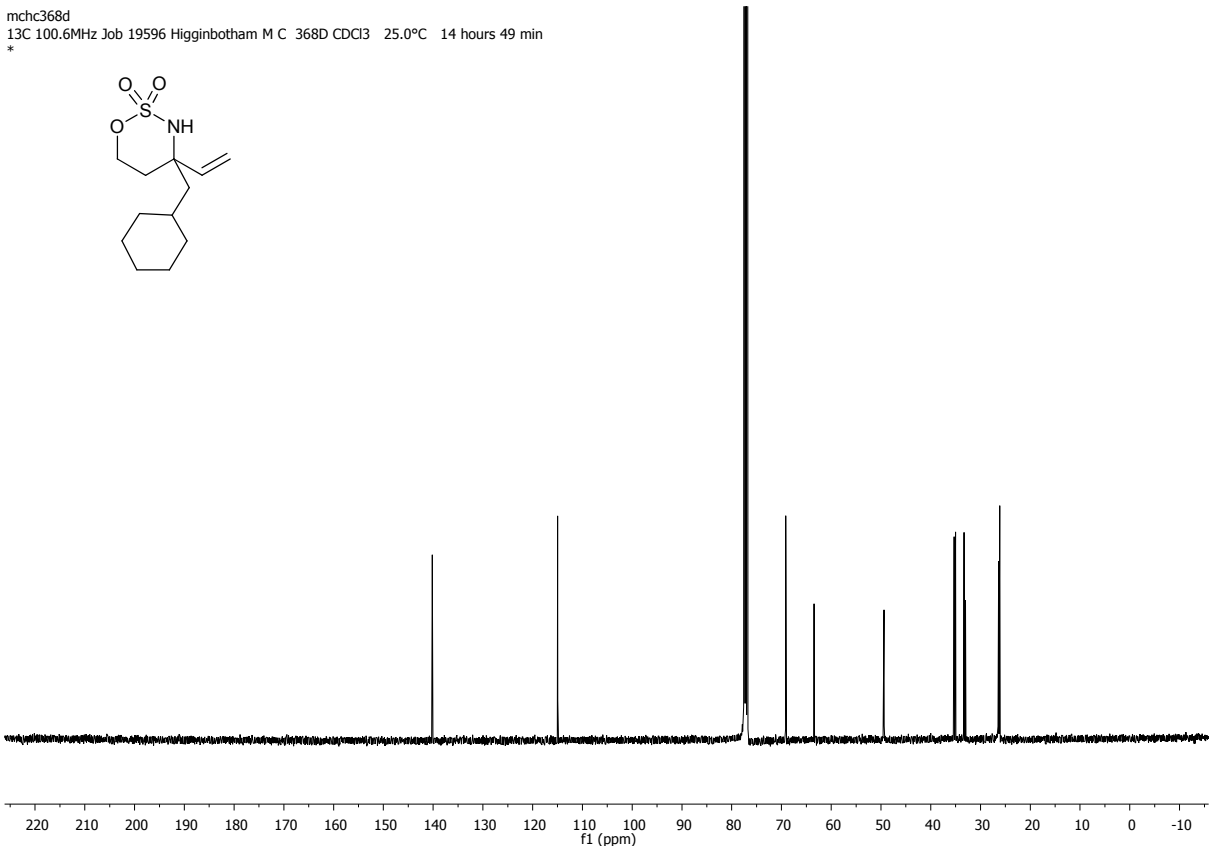
mchh307b
1H 300.1MHz Job 8862 Higginbotham M C 307B CDCl3 24.9°C
35mg



mchc307b
13C 75.5MHz Job 8885 Higginbotham M C 307B CDCl3 24.9°C 3 hours 1 min
*




mchh368e
1H 300.1MHz Job 15110 Higginbotham M C 368E CDCl3 25.1°C
*
O
O
S
O
NH
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


mchc368d
13C 100.6MHz Job 19596 Higginbotham M C 368D CDCl3 25.0°C 14 hours 49 min
*
O
O
S
O
NH
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

mchh390b
1H 300.1MHz Job 16497 Higginbotham M C 390B CDCl3 21.8°C
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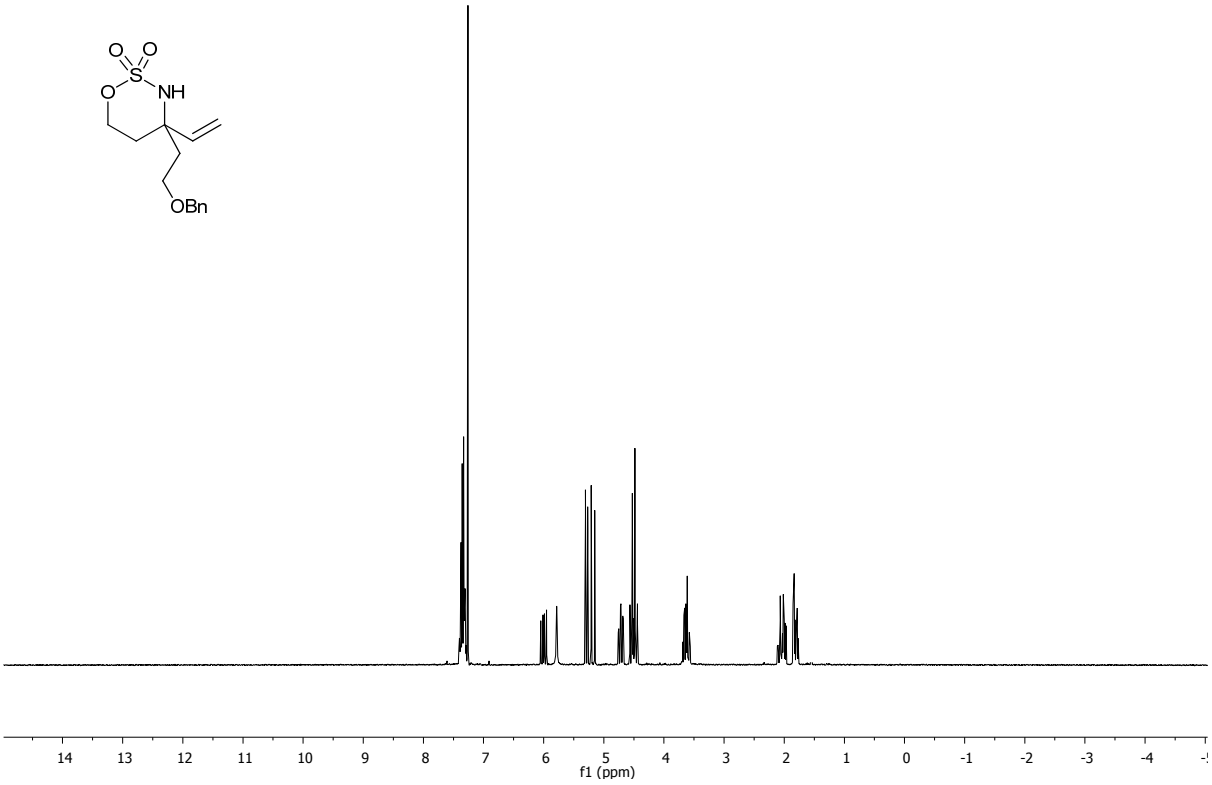

mchc390b
13C 75.5MHz Job 16667 Higginbotham M C 390B CDCl3 22.0°C 3 hours 1 min
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