Supporting Information

Sulfur Dioxide Mediated One-Pot, Three and Four-Component Syntheses of Polyfunctional Sulfonamides and Sulfonic Esters. Study of the Stereoselectivity of the Ene-Reaction of Sulfur Dioxide.

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Material and Methods:

All solvents were distilled prior to use: THF and Et_2O from Na and benzophenone; DMF, CH_2Cl_2, and toluene from P_2O_5. Solvent after reactions and extractions were evaporated in a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC): columns of silica gel (0.040-0.63 μm, silica gel *60*,240-400 mesh). Thin layer chromatography (TLC) for reaction monitoring; detection by UV light. *Pancaldi* reagent ($(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O), or $KMnO_4$. M.p.: uncorrected; IR Spectra : spectrometer; υ in cm^{-1}. ^{1}H-NMR Spectra: 400 MHz spectrometer; δ(H) in ppm rel.to internal Me_4Si (= 0.00 ppm) or to the solvent's residual ^{1}H-signal ($CH\text{-}Cl_3$, δ(H) 7.27; C_6HD_5, δ(H) 7.16; CHD_2COCD_3, δ(H) 1.95; CD_2HCN, δ(H) 2.50; CHD_2SOCD_3, δ(H) 2.50, CH_2OD, δ(H) 3.31) as internal reference, all ^{1}H-signal assignments were confirmed by double irradiation experiments or by 2D COSY-DQF or COSY-45 spectra. ^{13}C-NMR Spectra: same instruments as above (101.61MHz); δ(C) in ppm rel. to internal Me_4Si (= 0.00 ppm) or to solvents ^{13}C-signal ($CDCl_3$, C_6D_6, δ(C) 128.4; $(CD_3)_2CO$, δ(C) 29.8; CD_3CN, δ(C) 1.3; $(CD_3)_2SO$, δ(C) 39.5, CD_3OD, δ(C) 49.2) as internal reference; coupling constants J in Hz (±0.5 Hz). Ms, chemical ionization (NH_3) mode m/z amu [% relative base peak(100%)]

General Procedure 1 (Table 1, entries 1-4) for the three-component syntheses of sulfonamides.

(*t*-Bu)$Me_2SiOSO_2CF_3$ (37 mg, 0.14 mmol, 0.05 equiv) in anh. CH_2Cl_2 (2 mL) was degassed by freeze-thaw cycles on the vacuum line. SO_2 (1.2 mL, 27.4 mmol, 10 equiv), dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CH_2Cl_2 solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 30 min at this temperature the enoxysilane **2a** (2.74 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred at during 2 h at -78 °C. Then the excess of SO_2 and the solvent were evaporated under reduced pressure (10^{-1} Torr) to dryness (ca. 1h), while temperature slowly reached 20 °C. Halogenating agent (Br_2, 0.15 mL, 3.01 mmol, 1.1 equiv) was added at -20 °C. After 1 h at this temperature, the mixture was transferred to a solution of the amine (3.29 mmol, 1.2 equiv) in 2 mL CH_2Cl_2 in presence of Et_3N (0.45 mL, 3.29 mmol, 1.2 equiv) under Ar atmosphere. The mixture was finally stirred at this temperature for 2 h, and poured into ice-water (20 mL) and extracted with CH_2Cl_2 (15 mL, 3 times). The combined organic extracts were washed with brine (20

mL), dried (Na_2SO_4) and the solvent eliminated under reduced pressure under reflux. Purification by FC.

General Procedure 2. (Table 1, entries 5-9 and 11-14) for the three component syntheses of sulfonamides.

(*t*-Bu)$Me_2SiOSO_2CF_3$ (37 mg, 0.14 mmol, 0.05 equiv) in anh. CH_3CN (2 mL) was degassed by freeze-thaw cycles on the vacuum line. SO_2 (1.8 mL, 41.1 mmol, 15 equiv) dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CH_3CN solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 30 min at this temperature the enoxysilanes **2b**, **2c** or **2e** (2.74 mmol, 1 equiv) in CH_3CN (2 mL) were added slowly. The mixture was stirred at -78°C during 5-7 h. Then, the excess of SO_2 and the solvent were evaporated under reduced pressure (10^{-1} Torr) to dryness (ca. 1h), while temperature slowly reached 20 °C. Halogenating agent (Br_2, 0.15 mL, 3.01 mmol, 1.1 equiv) was added at -20 °C. After 1h at this temperature, the mixture was transferred into a solution of the amines (3.29 mmol, 1.2 equiv) in 3 mL pyridine or in 2 mL CH_2Cl_2 in presence of Et_3N (0.45 mL, 3.29 mmol, 1.2 equiv) under Ar atmosphere. The mixture was finally stirred at this temperature for 2 h, and poured into ice-water (20 mL) and extracted with CH_2Cl_2 (15 mL, 3 times). When pyridine was used 20 mL of ether were added and the mixture was washed with a saturated aqueous solution of $CuSO_4$ (30 mL, 3 times). Combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and the solvent eliminated under reduced pressure under reflux. Purification by FC.

General Procedure 3 (Table 1, entry 10) for sulfonamides preparation.

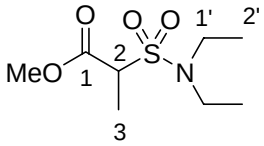
(*t*-Bu)$Me_2SiOSO_2CF_3$ (37 mg, 0.14 mmol, 0.05 equiv) in anh. CH_3CN (2 mL) was degassed by freeze-thaw cycles on the vacuum line. SO_2 (1.8 mL, 41.1 mmol, 15 equiv), dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CH_3CN solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 30 min at this temperature the enoxysilane **2d** (2.74 mmol, 1 equiv) in CH_3CN (2 mL) was added slowly. The mixture was stirred at -78°C 3 h. Then the excess of SO_2 and the solvent were evaporated under reduced pressure (10^{-1} Torr) to dryness (ca. 1h), while temperature slowly reached 20 °C. Halogenating agent (only NCS, 402 mg, 3.01 mmol, 1.1 equiv) was added at -20 °C. After 1 h at this temperature, the mixture

was transferred to a solution of the Et_2NH (240 mg, 3.29 mmol, 1.2 equiv) in 3 mL pyridine under Ar atmosphere. The mixture was finally stirred at this temperature for 2 h, and poured into a mixture of ice-water (10 mL) and ether (20 mL) and then washed with a saturated aqueous solution of $CuSO_4$ (30 mL, 3 times). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and the solvent eliminated under reduced pressure under reflux. Purification by FC.

General Procedure 4 (Table 1, entries 15-17) for the three component syntheses of sulfonic esters.

(*t*-Bu)$Me_2SiOSO_2CF_3$ (0.14 mmol, 0.05 equiv) in anh. CH_3CN (2 mL) was degassed by freeze-thaw cycles on the vacuum line. SO_2 (1.8 mL, 41.1 mmol, 15 equiv), dried through a column packed with phosphorus pentoxide and aluminum oxide, was transferred on the vacuum line to the CH_3CN solution frozen at -196 °C. The mixture was allowed to melt and to warm to -40 °C. After 30 min. at this temperature the methallylsilane **23** (2.74 mmol, 1 equiv) in CH_3CN (2 mL) were added slowly. The mixture was stirred at -40 °C during 5 h. After cooling to -78 °C, the excess of SO_2 and the solvent were evaporated under reduced pressure (10^{-1} Torr) to dryness (ca. 1h). Halogenating agent (NCS, 3.01 mmol, 1.1 equiv) was added at -20 °C. After 1h at this temperature, the mixture was transferred into a solution of alcohol in excess, in the presence of Et_3N (0.45 mL, 3.29 mmol, 1.2 equiv) under Ar atmosphere. The mixture was finally stirred at this temperature for 1 h, and poured into ice-water (20 mL) and extracted with CH_2Cl_2 (15 mL, 3 times). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and the solvent eliminated under reduced pressure under reflux. The residue was purified by FC.

(±)-Methyl-2-[(diethylamino)sulfonyl]propanoate (5).



5 was prepared as described above in the **general procedure 1** from enoxysilane **2a** and Et_2NH. FC (4:1 light petroleum ether/EtOAc, R_f 0.25): 398 mg (65%), colorless oil.

IR (film): ν 2980, 1750, 1455, 1385, 1340, 1205, 1140, 1020, 945 cm^{-1}. UV (CH_3CN): λ_{max} = 197 nm (ε = 2600). ^1H NMR (400 MHz, $CDCl_3$): δ 3.96 (q, 1H, ^3J = 7.1, H-C(2)), 3.79 (s, 3H, OCH_3), 3.32 (m, 4H, CH_2N), 1.61 (d, 3H, ^3J = 7.1, H-C(3)), 1.22 (t, 6H, ^3J = 7.1, Me-C(2')).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 167.7 (s, C(1)), 62.4 (d, ^1J(C,H) = 140, C(2)), 53.0 (q, ^1J(C,H) = 148, OMe), 42.6 (t, ^1J(C,H) = 139, C(1')), 14.7 (q, ^1J(C,H) = 127, C(2')), 12.9 (q, ^1J(C,H) = 132, C(3)). CI-MS (NH_3): m/z 241 (4, $[M+18]^+$), 224 (100, $[M+1]^+$). Anal. Calcd for $C_8H_{17}NO_4S$ (223.29): C, 43.03, H, 7.67, N, 6.27. Found: C, 43.01, H, 7.65, N, 6.34.

(±)-Methyl-2-[(benzylamino)sulfonyl]propanoate (6).

6 was prepared as described above in the **general procedure 1** from enoxysilane **2a and** $BnNH_2$. FC (4:1 light petroleum ether/EtOAc, R_f 0.18): 430 mg (61%), yellow oil.

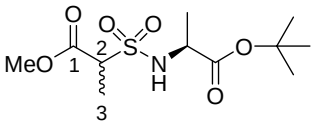
IR (film): ν 3305, 2955, 1740, 1335, 1205, 1130, 1065, 860, 700 cm^{-1}. UV (CH_3CN): λ_{max} = 269 nm (ε = 2700). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.3-7.2 (m, 5H, Ph), 5.08 (t, 1H, ^3J = 6.1, H-N), 4.36 (d, 2H, ^3J(CH_2(Bn), NH)= 6.1, CH_2(Bn)), 3.94 (q, 1H, ^3J = 7.1, H-C(2)), 3.77 (s, 3H, OMe), 1.63 (d, 3H, ^3J = 7.1, H_3C(3)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 167.9 (s, C(1)), 136.8 (s, C(Ar)), 128.9 (d, ^1J(C,H) = 161, C(Ar)), 128.2 (d, ^1J(C,H) = 166, C(Ar)), 128.0 (d, ^1J(C,H) = 162, C(Ar)), 62.2 (d, ^1J(C,H) = 140, C(2)), 53.2 (q, ^1J(C,H) = 148, OMe), 47.9 (t, ^1J(C,H) = 140, C(1')), 12.7 (q, ^1J(C,H) = 132, C(3)). CI-MS (NH_3): m/z 275 (16, $[M+18]^+$), 258 (8, $[M+1]^+$), 106 (100, $[M-151]^+$). Anal. Calcd for $C_{12}H_{17}NO_4S$ (257.30): C, 51.35, H, 5.88, N, 5.44. Found: C, 51.05, H, 5.83, N, 5.24.

(±)-Methyl-2-{[benzyl(methyl)amino]sulfonyl)}propanoate (7).

7 was prepared as described above in the **general procedure 1** from enoxysilane **2a and** BnMeNH. FC (4:1 light petroleum ether/EtOAc, R_f 0.26): 520 mg (70%), yellowish solid, mp 44-45°C.

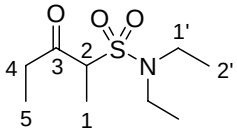
IR (KBr): ν 2955, 1745, 1455, 1438, 1340, 1201, 1150, 1140, 995, 940, 735 cm^{-1}. UV (CH_3CN): λ_{max} = 212 nm (ε = 4780), 200 nm (ε = 3800). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.3-7.2 (m, 5H, Ph), 4.34 (d, 1H, ^2J = 14.4, CH_2(Bn)), 4.25 (d, 1H, ^2J = 14.4, CH_2(Bn)), 4.02 (q, 1H, ^3J = 7.1, H-C(2)), 3.74 (s, 3H, OMe), 2.73 (s, 3H, NMe), 1.59 (d, 3H, ^3J = 7.1, H_3C(3)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 167.4 (s, C(1)), 135.7 (s, C(Ar)), 128.6 (d, ^1J(C,H) = 156, C(Ar)), 128.2 (d, ^1J(C,H) = 159, C(Ar)), 127.9 (d, ^1J(C,H) = 159, C(Ar)), 61.7 (d, ^1J(C,H) = 140, C(2)), 54.4 (t, ^1J(C,H) = 139, CH_2(Bn)), 52.9 (q, ^1J(C,H) = 148, OMe), 34.7 (q, ^1J(C,H) = 140, NMe), 12.8 (q, ^1J(C,H) = 129, C(3)). CI-MS (NH_3): m/z 289 (27, $[M+18]^+$), 272 (42, $[M+1]^+$), 120 (100, $[M-151]^+$), 91 (70, $[M-180]^+$). Anal. Calcd for $C_{12}H_{17}NO_4S$ (271.33): C, 53.12, H, 6.32, N, 5.16. Found: C, 53.11, H, 6.39, N, 5.14.

***Tert*-butyl(2*S*,1'*R*)-and(2*S*,1'*S*)-*N*-[1'-(methoxycarbonyl)ethanesulfonyl]*L*-alaninate (8)**



8 was prepared as described above in the **general procedure 1** from enoxysilane **2a** using *L*-alanine *tert*-butyl ester hydrochloride, and Et_3N (2.4 equiv.). FC (4:1 light petroleum ether/EtOAc, R_f 0.26): 445 mg (55%) 4:1 mixture of two diastereoisomers, light yellow oil.
IR (film): ν 3300, 2980, 2955, 1750, 1735, 1560, 1445, 1435, 1370, 1340, 1255, 1205, 1140, 1070, 980, 845 cm^{-1}. UV (CH_3CN): λ_{max} = 268 nm (ε = 2400), 197nm (ε = 4100). Data of major diastereoisomer (80%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37 (d, 1H, ^3J = 8.3, H-N), 4.08 (dq, 1H, ^3J = 8.3, 7.3, H-C(2)), 4.05 (q, 1H, ^3J = 7.3, H-C(1')), 3.78 (s, 3H, OMe), 1.63 (d, 3H, ^3J = 7.3, H_3C(2')), 1.47 (s, 9H, *t*-Bu), 1.43 (d, 3H, ^3J = 7.3, H_3C(3)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.8 (s, CO_2Me), 167.9 (s, C(1), 82.7 (s, $C_{quat.}$(*t*-Bu)), 63.1 (d, ^1J(C,H) = 140, C(2)), 62.5 (d, ^1J(C,H) = 140, C(1')), 53.1 (q, ^1J(C,H) = 140, OMe), 27.9 (q, ^1J(C,H) = 148, $C_{quat.}$(*t*-Bu)), 20.5 (q, ^1J(C,H) = 130, C(2')), 12.7 (q, ^1J(C,H) = 132, C(3)). Data of minor diastereoisomer (20%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.27 (d, 1H, ^3J = 8.5, H-N), 4.11 (dq, 1H, ^3J = 8.5, 7.3, H-C(2)), 3.99 (q, 1H, ^3J = 7.3, H-C(1')), 3.79 (s, 3H, OMe), 1.62 (d, 3H, ^3J = 7.3, H_3C(2')), 1.47 (s, 9H, *t*-Bu), 1.42 (d, 3H, ^3J = 7.3, H_3C(3)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.7 (s, CO_2Me), 167.7 (s, C(1)), 82.6 (s, $C_{quat.}$(*t*-Bu)), 63.1 (d, ^1J(C,H) = 140, C(2)), 62.5 (d, ^1J(C,H) = 140, C(1')), 53.0 (q, ^1J(C,H) = 140, OMe), 27.9 (q, ^1J(C,H) = 148, $C_{quat.}$(*t*-Bu)), 20.3 (q, ^1J(C,H) = 130, C(2')), 13.0 (q, ^1J(C,H) = 132, C(3)). CI-MS (NH_3): m/z 313 (100, $[M+18]^+$), 296 (3, $[M+1]^+$). Anal. Calcd for $C_{11}H_{21}NO_6S$ (295.35): C, 44.73, H, 7.17, N, 4.74. Found: C, 44.51, H, 7.15, N, 4.69.

***N,N*-Diethyl-3-oxopentane-2-sulfonamide (9).**



9 was prepared as described above in the **general procedure 2** from enoxysilane **2b** and Et_2NH. FC (4:1 light petroleum ether/EtOAc, R_f 0.32): 534 mg (88%), colorless oil.
IR (film): ν 2980, 1740, 1320, 1120, 840, 795 cm^{-1}. UV (CH_3CN): λ_{max} = 197 nm (ε = 2660), 216 nm ((ε = 2200). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07 (q, 1H, ^3J = 7.1, H-C(2)), 3.30 (q, 4H, ^3J = 7.1, H_2C(1')), 2.91 (dq, 1H, ^2J = 14.8, ^3J = 6.5, H-C(4)), 2.68 (dq, 1H, ^2J = 14.8, ^3J = 6.5, H-C(4)), 1.53 (d, 3H, ^3J = 7.1, H-C(1)), 1.24 (t, 6H, ^3J = 7.1, H_3C (2')), 1.11 (t, 3H, ^3J = 6.5, H_3C(5)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 203.5 (s, C(3)), 68.1 (d, ^1J(C,H) = 164, C(2)),

42.3 (t, ^1J(C,H) = 169, C(1')), 35.5 (t, ^1J(C,H) = 166, C(4)), 14.5 (q, ^1J(C,H) = 176, C(2')), 12.2 (q, ^1J(C,H) = 161, C(1)), 7.5 (q, ^1J(C,H) = 158, C(5)). CI-MS (NH_3): m/z 239 (52, $[M+18]^+$), 222 (70, $[M+1]^+$), 72 (100, $C_4H_{10}N^+$). Anal. Calcd for $C_9H_{19}NO_3S$ (221.31): C, 48.84, H, 8.58. Found: C, 48.98, H, 8.54.

***N,N*-Diethyl-2-oxo-2-phenylethanesulfonamide (10)**

10 was prepared as described above in the **general procedure 2** from enoxysilane **2c** and Et_2NH. FC (4:1 light petroleum ether/EtOAc, R_f 0.33), 470 mg (67%), yellow oil.

IR (film): ν 2975, 2940, 1680, 1598, 1450, 1337, 1275, 1205, 1145, 1020, 1005, 940, 755 cm^{-1}. UV (CH_3CN): λ_{max} = 248 nm (ε = 6500), 208 nm (ε = 5100). ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, 2H, ^3J = 8.2, ^4J = 1.2, H_{ortho}-C(Ph)), 7.64 (tt, 1H, ^3J = 7.3, ^4J = 1.2, H_{para}-C(Ph)), 7.52 (td, 2H, ^3J = 8.2, ^4J = 1.2, H_{meta}-C(Ph)), 4.57 (s, 2H, H-C(1)), 3.30 (q, 4H, ^3J = 7.1, H_2C(1')), 1.21 (t, 6H, ^3J = 7.1, H_3C (2')). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 189.2 (s, C(2)), 135.8 (s, C(Ph)), 134.2 (d, ^1J(C,H) = 161, HC(Ph)), 129.4 (d, ^1J(C,H) = 161, HC(Ph)), 129.2 (d, ^1J(C,H) = 163, HC(Ph)), 59.1 (t, ^1J(C,H) = 137, C(1)), 42.9 (t, ^1J(C,H) = 139, C(1')), 14.7 (q, ^1J(C,H) = 128, C(2')). CI-MS (NH_3): m/z 273 (5, $[M+18]^+$), 256 (98, $[M+1]^+$), 105 (71, $[M-150]^+$). Anal. Calcd for $C_{12}H_{17}NO_3S$ (255.33): C, 56.45, H, 6.71, N, 5.49. Found: C, 56.51, H, 6.55, N, 5.21.

***N*-benzyl-2-oxo-2-phenylethanesulfonamide (11).[1]**

11 was prepared as described above in the **general procedure 2** from enoxysilane **2c** and $BnNH_2$. FC (4:1 light petroleum ether/EtOAc, R_f = 0.20): 72%, light yellow crystals. Same spectral data as those reported for this compound.

***N*-Benzyl,*N*-methyl-2-oxo-2-phenylethanesulfonamide (12).**

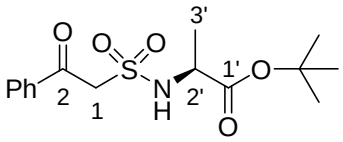
12 was prepared as described above in **general procedure 2** from enoxysilane **2c** and BnMeNH. FC (4:1 light petroleum ether/EtOAc, R_f 0.30): 600 mg (72%), yellow oil.

IR (film): ν 3055, 2945, 1680, 1600, 1450, 1340, 1275, 1155, 995, 775 cm^{-1}. UV (CH_3CN): λ_{max} = 263 nm (ε = 6800), 252 nm (ε = 7600). ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, 2H, ^3J = 8.0, ^4J = 1.8, H_{ortho}-C(Ph)), 7.58 (tt, 1H, ^3J = 7.3, ^4J = 1.8, H_{para}-C(Ph)), 7.46 (td, 2H, ^3J = 8.0, ^4J = 1.8, H_{meta}-C(Ph)), 7.29-7.18 (m, 5H, H-Ph(Bn)), 4.56 (s, 2H, H-C(1)), 4.27 (s, 2H, CH_2(Bn)), 2.75 (s, 3H, H_3C-N). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 189.7 (s, C(2)), 135.9 (s,

[1] Vega, J.A. ; Alajarin, R. ; Vaquero, J. ; Alvarez-Builla, J. *Tetrahedron* **1998**, *54*, 3589.

C(Ar)), 135.7 (s, C(Ar)), 134.6 (d, ^1J(C,H) = 161, HC(Ph)), 129.6 (d, ^1J(C,H) = 161, HC(Ph)), 129.1 (d, ^1J(C,H) = 163, HC(Ph)), 128.5 (m, C(Ph)), 57.7 (t, ^1J(C,H) = 138, C(1)), 54.5 (t, ^1J(C,H) = 139, CH_2(Bn)), 34.7 (q, ^1J(C,H) = 140, CH_3-N). CI-MS (NH_3): m/z 320 (2, $[M+18]^+$), 304 (53, $[M+1]^+$), 120 (100, $[M-183]^+$). Anal. Calcd for $C_{16}H_{17}NO_3S$ (303.38): C, 63.35, H, 5.65, N, 4.62. Found: C, 63.57, H, 5.82, N, 4.45.

***Tert*-butyl*N*-[2-oxo-2-phenyl ethane-1-sulfonyl]*L*-alaninate (<u>13</u>)**



<u>13</u> was prepared as described above in the **general procedure 2** from enoxysilane **<u>2c</u>**, *L*-alanine *tert*-butyl ester hydrochloride and Et_3N (2.4 equiv.). FC (4:1 light petroleum ether/EtOAc, R_f 0.21): 511 mg (57%), yellow oil.

IR (film): ν 3290, 2980, 2935, 1730, 1685, 1600, 1450, 1370, 1345, 1280, 1240, 1160, 1135, 980, 750 cm^{-1}. UV (CH_3CN): λ_{max} = 249 nm (ε = 7650), 208 nm (ε = 5700). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, 2H, ^3J = 8.2, ^4J = 1.2, H_{ortho}-C(Ph)), 7.63 (tt, 1H, ^3J = 7.4, ^4J = 1.2, H_{para}-C(Ph)), 7.50 (td, 2H, ^3J = 8.2, ^4J = 1.2, H_{meta}-C(Ph)), 5.58 (d, 1H, ^3J = 8.5, H-N), 4.74 (d, 1H, ^2J = 15.6, H-C(1)), 4.72 (d, 1H, ^2J = 15.6, H-C(1)), 4.20 (qd, 1H, ^3J = 8.5, ^3J = 7.1, H-C(2')), 1.44 (d, 3H, ^3J = 7.1, H_3C(3'), 1.43 (s, 9H, *t*-Bu). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 187.7 (s, C(1)), 171.6 (s, COO), 135.5 (s, C(Ph)), 134.4 (d, ^1J(C,H) = 163, HC(Ph)), 128.8 (d, ^1J(C,H) = 163, HC(Ph)), 128.7 (d, ^1J(C,H) = 160, HC(Ph)), 82.5 (s, Cquat(*t*-Bu)), 59.6 (t, ^1J(C,H) = 136, C(1)), 52.9 (d, ^1J(C,H) = 144, C(2')), 27.8 (q, ^1J(C,H) = 127, Me(*t*-Bu)), 19.7 (q, ^1J(C,H) = 131, H_3C(3'). CI-MS (NH_3): m/z 345 (14, $[M+18]^+$), 328 (1, $[M+1]^+$), 272 (100, $[M-55]^+$), 105 (94, $[M-222]^+$). Anal. Calcd for $C_{15}H_{21}NO_5S$ (327.40): C, 55.03, H, 6.47, Found: C, 55.20, H, 6.36.

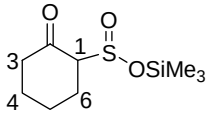
***N*,*N*-Diethyl-2-oxocyclohexanesulfonamide (<u>14</u>).**

<u>14</u> was prepared as described above in the **general procedure 3** from enoxysilane **<u>2d</u>** and Et_2NH. Purification by FC (85:15 light petroleum ether/EtOAc, R_f 0.3): 67%, colorless solid, mp 62-63°C.

IR (KBr): ν 2942, 1713, 1464, 1454, 1329, 1204, 1144, 1020, 941, 712 cm^{-1}. UV (CH_3CN): λ_{max} = 196 (ε = 5326). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (*br*.t, 1H, ^3J = 4.8, H-C(1)), 3.35-3.47 (m, 4H, H_2C(1')), 2.90 (dddd, 1H, ^2J = 14.1, ^3J = 6.9, 5.8, 4.8 H_a-C(6)), 2.62 (m, 1H, H-

C(3)), 2.45 (dt, 1H, ^2J = 14.1, ^3J = 4.6, H_{eq}-C(*6*)), 2.05-2.20 (m, 3H, H-C(3), H-C(4), H-C(5)), 1.72 (m, 2H, H-C(4), H-C(5)), 1.21 (t, 3H, ^3J = 7.8, $H_3C(2')$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 204.8 (s, CO), 69.9 (d, ^1J(C,H) = 137, C(1)), 42.4 (t, ^1J(C,H) = 141, C(1')), 40.9 (t, ^1J(C,H) = 138, C(6)), 28.9 (t, ^1J(C,H) = 140, C(2)), 26.5 (t, ^1J(C,H) = 152, C(4)), 21.1 (t, ^1J(C,H) = 147.1, C(5)), 14.5 (q, ^1J(C,H) = 139, C(2')). CI-MS (NH_3): m/z 234 (100, $[M+18]^+$), 251 (11, $[M+1]^+$). Anal. Calcd for $C_{10}H_{19}NO_3S$ (233.33): C, 51.48, H, 8.21. Found: C, 51,46, H, 8.29.

(±)-Trimethylsilyl-2-oxocyclohexane sulfinate (<u>3d</u>).



(*t*-Bu)$Me_2SiOSO_2CF_3$ (3.7 µl, 0.05equiv) in anh. CD_3CN (0.4 mL) was degassed in an NMR tube by freeze-thaw cycles on the vacuum line. SO_2 (0.05 mL, 1.11 mmol, 15 equiv), dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CD_3CN solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 30 min at this temperature the enoxysilane 1-trimethylsilyloxycyclohexene **<u>2d</u>** (16 mg, 0.07 mmol, 1 equiv) was added quickly under Ar. The mixture was monitored by ^{1}H NMR at -40 °C during 1 h, after which time formation of sulfinate **<u>3d</u>** was complete. Only one single diastereoisomer was observed (*see Figure S1*).
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 (dd, 1H, ^3J = 11.7, ^3J = 8.2, H-C(1)), 2.44 (dt, 1H, ^2J = 10.7, ^3J = 5.3, H-C(3)), 2.32 (dt, 1H, ^2J = 10.7, ^3J = 5.3, H-C(3)), 2.28 (ddd, 2H, ^2J = 11.9, ^3J = 5.9, ^3J = 3.3, H-C(6)), 1.98 (m, 2H, H-C(4)), 1.83 (sx, 1H, ^3J = 5.9, H-C(5)), 1.72 (dtt, 1H, ^2J = 9.8, ^3J = 3.9, ^3J = 3.8, H-C(5)), 0.3-0.11(m, TBS and TMS group).^{13}C NMR (100 MHz, CD_3CN, 203K): δ 213.3 (s, C(2)); 80.0 (d, ^1J(H,C) = 132, C(1)); 47.2 (t, ^1J(H,C) = 130, C(3)); 31.7 (t, ^1J(H,C) = 134, C(6)); 28.5 (t, ^1J(H,C) = 128, C(5)); 28.0 (t, ^1J(H,C) = 126, C(4)); 5.0 (q, ^1J(H,C) = 132, C(Si)).

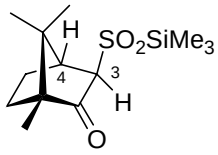
<u>The same experiment was performed **without** Lewis acid.</u>

Enoxysilane **<u>2d</u>** (16 mg, 0.07 mmol, 1 equiv) in anh. CD_3CN (0.1 mL) was degassed in an NMR tube by freeze-thaw cycles on the vacuum line. SO_2 (0.3 mL) dried by passing through column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CD_3CN solution frozen at -196 °C. The mixture was allowed to melt and to warm quickly to -78 °C. The mixture was monitored by ^{1}H NMR at -40 °C during 36 h, after which time no more change was observed.

After 2 h at -40 °C, 75% of starting material was converted into a mixture of two diastereoisomers in a proportion of 6:4. After 36 h at room temperature, reaction was complete and the ratio of two diastereoisomers was 5:4. No more change was observed (*see Figure S2 and S3*).

Data of the major diastereoisomer: ^{13}C NMR (100 MHz, CD_3CN, 233K): δ 207.2 (s, C(2)); 76.7 (d, ^{1}J(H,C) = 138, C(1)); 42.4 (t, ^{1}J(H,C) = 130, C(3)); 27.1 (t, ^{1}J(H,C) = 134, C(6)); 26.3 (t, ^{1}J(H,C) = 127, C(5)); 25.9 (t, ^{1}J(H,C) = 126, C(4)); 4.8 (q, ^{1}J(H,C) = 122, C(Si)). Data of the minor diastereoisomer *:*^{13}C NMR (100 MHz, CD_3CN, 233K): δ 211.8 (s, C(2)); 77.7 (d, ^{1}J(H,C) = 136, C(1)); 41.7 (d, ^{1}J(H,C) = 134, C(3)); 25.9(d, ^{1}J(H,C) = 131, C(6)); 23.6 (t, ^{1}J(H,C) = 126, C(5)); 22.80 (t, ^{1}J(H,C) = 130, C(4)); 3.8 (q, ^{1}J(H,C) = 128, C(Si)).

(1*R*,3*R*,4*S*)-Trimethylsilyl-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane-3-*exo*-sulfinate (3e).



(*t*-Bu)$Me_2SiOSO_2CF_3$ (3.7 µl , 0.05equiv) in anh. CD_3CN (0.4 mL) was degassed in an NMR tube by freeze-thaw cycles on the vacuum line. SO_2 (0.03 mL, 0.6 mmol, 15 equiv), dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CD_3CN solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 30 min at this temperature the camphor-derived-enoxysilane **2e** (9 mg, 0.04 mmol, 1 equiv) was added quickly under Ar. The mixture was monitored by ^{1}H NMR at -78 °C. After 20 min the formation of sulfinate **3e** was complete. A mixture of two diastereoisomers in proportion of 95:5 was observed. By rising temperature to 25°C the reaction mixture became black and all the material was decomposed.

The same experiment was also performed **without** Lewis acid.

2d (9 mg, 0.04 mmol, 1 equiv) in anh. CD_3CN (0.1 mL) was degassed in an NMR tube by freeze-thaw cycles on the vacuum line. SO_2 (0.4 mL) dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CD_3CN solution frozen at -196 °C. The mixture was allowed to melt and to warm quickly to -78 °C. The mixture was monitored by ^{1}H NMR at -40 °C during 12 h, after which time no more change was observed.

After 2 h at -40 °C, starting material was fully converted into a mixture of two diastereoisomers in a proportion of 95:5. After 6 h at -40 °C the ratio of those two diastereoisomers was 75:25. After 12 h at -40 °C the ratio was 1:1 and then more change was observed.

Data of the major diastereoisomer: ^{1}H NMR (400 MHz, CD_3CN, 203K): δ 3.36 (s, 1H, H-C(3)); 2.51 (d, 1H, ^{3}J = 4.1, H-C(4)); 2.22 (tdd, 1H, ^{2}J = 12.9, ^{3}J = 4.1, ^{3}J = 4.9, H-C(5)); 1.87 (td, 1H, ^{2}J = 12.9, ^{3}J = 7.2, H-C(5)); 1.59 (q, 2H, ^{2}J = 12.9 ^{3}J = 9.59, H-C(6)); 1.07 (s, 3H, Me-C(7)); 0.99 (s, 3H, Me-C(7)); 0.98 (s, 3H, Me-C(1)). ^{13}C NMR (100 MHz, CD_3CN, 203K): δ 214.4 (s, C(2)); 83.9 (d, ^{1}J(H,C) = 152, C(3)); 62.0 (s, C(1)); 49.2 (s, C(7)); 48.7 (d, ^{1}J(H,C) = 150, C(4)); 30.3 (t, ^{1}J(H,C) = 136, C(6)); 28.2 (t, ^{1}J(H,C) = 134, C(5)); 24.0 (q, ^{1}J(H,C) = 130, C(7)); 21.8 (q, ^{1}J(H,C) = 126, C(7)); 12.4 (q, ^{1}J(H,C) = 126, C(1)); 3.7 (q, ^{1}J(H,C) = 128, C(Si)). Data of the minor diastereoisomer: ^{13}C NMR (100 MHz, CD_3CN, 243K): δ 213.7 (s, C(2)); 80.0 (d, ^{1}J(H,C) = 152, C(3)); 60.3 (s, C(1)); 48.7 (s, C(7)); 46.0 (d, ^{1}J(H,C) = 150, C(4)); 29.8 (t, ^{1}J(H,C) = 136, C(6)); 25.1 (t, ^{1}J(H,C) = 134, C(5)); 22.5 (q, ^{1}J(H,C) = 130, C(7)); 20.8 (q, ^{1}J(H,C) = 126, C(7)); 12.2 (q, ^{1}J(H,C) = 126, C(1)); 3.0 (q, ^{1}J(H,C) = 128, C(Si)).

(±)-Trimethylsilyl 2-oxopropane-1-sulfinate (3g).

The enoxysilane **9** (10 mg, 0.08 mmol, 1 equiv) in anh. CD_3CN (0.1 mL) was degassed in an NMR tube by freeze-thaw cycles on the vacuum line. SO_2 (0.4 mL) dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CD_3CN solution frozen at -196 °C. The mixture was allowed to melt and to warm quickly to room temperature. The mixture was monitored by ^{1}H NMR during 1 h at 27 °C, after which time reaction was complete.

^{1}H NMR (400 MHz, CD_3CN, 300K): δ 3.98 (*br*.s, 2H, H-C(3)); 2.24 (s, 3H, H-C(1)); 0.35 (s, 9H, Me_3Si)). ^{13}C NMR (100 MHz, CD_3CN, 300K): δ 203.7 (s, C(1)); 70.9 (t, ^{1}J(H,C) = 139, C(3)); 31.5 (q, ^{1}J(H,C) = 129, C(1)); 1.27 (m, C(Si)).

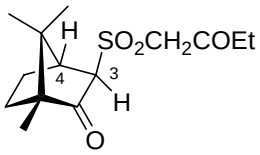
(±)-Trimethylsilyl 3,3-dimethyl-2-oxobutane-1-sulfinate (3f).

The enoxysilane **2f** (10 mg, 0.06mmol, 1 equiv) in anh. CD_3CN (0.1 mL) was degassed in an NMR tube by freeze-thaw cycles on the vacuum line. SO_2 (0.4 mL) dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CD_3CN solution frozen at -196 °C. The mixture was allowed to melt and

to warm quickly to -78 °C. The mixture was monitored by ^{1}H NMR from -60 °C to -10 °C during 8 h, after which time no more change was observed.

^{1}H NMR (400 MHz, CD_3CN, 283K): δ 3.96 (*br*.s, 2H, H-C(4)); 1.13 (s, 3H, H-C(1)); 0.28 (s, 9H, H-C(Si)). ^{13}C NMR (100 MHz, CD_3CN, 283K): δ 220.0 (s, C(3)); 72.1 (t, ^1J(H,C) = 150, C(4)); 49.9 (s, C(2)), 30.3 (q, ^1J(H,C) = 128, C(1)); 5.6 (q, ^1J(H,C) = 127, C(Si)).

(1*R*,3*R*,4*S*)-3-[(2-Ethoxyprop-2-enyl)sulfonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (<u>28</u>).

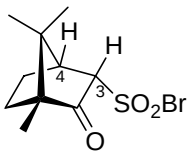


(*t*-Bu)$Me_2SiOSO_2CF_3$ (37 mg, 0.14 mmol, 0.05equiv) in anh. CH_3CN (2 mL) was degassed by freeze-thaw cycles on the vacuum line. SO_2 (1.8 mL, 41.1 mmol, 15 equiv), dried by passing through a column packed with phosphorus pentoxide and aluminium oxide, was transferred on the vacuum line to the CH_3CN solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 30 min at this temperature enoxysilane **<u>2e</u>** (615 mg, 2.74 mmol, 1 equiv) in CH_3CN (2 mL) was added slowly. After stirring the mixture 3h at -78 °C, the excess of SO_2 and the solvent were slowly evaporated under reduced pressure (10^{-1} Torr) to dryness (ca. 1h) at 20°C. A 1 M solution of Bu_4NF in THF (2.74 mL, 2.74 mmol, 1 equiv) and 1-bromobut-2-one (6.85 mmol, 2.5 equiv) were added under Ar. The mixture was stirred at this temperature for 1 h, then at -40 °C for 1 h, and gradually allowed to reach 20 °C in about 10 h. After the addition of H_2O (20 mL), and neutralization with $NaHCO_3$, the moisture was extracted with CH_2Cl_2 (15 mL, 3 times). The combined organic extracts were washed with brine (20 mL), dried ($MgSO_4$) and the solvent eliminated under reduced pressure under reflux. FC (85:15 light petroleum ether/EtOAc, R_f 0.3): 685 mg (92%), white solid, mp 76-78 °C.

IR (KBr): ν 3479, 2974, 2877, 1744, 1451, 1397, 1322, 1256, 1144, 1038, 990 cm^{-1}. UV (CH_3CN): λ_{max} = 223 (ε =5234). *^{1}H NMR (400 MHz, $CDCl_3$)*: δ 4.62 (d, AB, 1H, ^2J = 14.6, Ha-C(1')), 4.51 (d, AB, 1H, ^3J(H_3-H_4) = 1.5, H-C(3)), 4.18 (d, 1H, ^2J = 14.6, Hb-C(1')), 2.8 (dq, 1H, ^2J = 10.9, ^3J($H_{1''}$-$H_{2''}$) = 7.8, Ha-C(1'')), 2.7 (td, 1H, ^3J(H_4-H_5) = 6.2, ^3J(H_4-H_3) = 1.5, H-C(4)), 2.65 (dq, 1H, ^2J = 10.9, ^3J($H_{1''}$-$H_{2''}$) = 7.8, Hb-C(1'')), 2.3 (dddd, 1H, ^2J = 12.8, ^3J(H_5-H_4) = 5.1, ^3J(H_5-H_6) = 4.5, Ha-C(5)), 1.97 (m, 1H, Hb-C(5)), 1.8 (ddd, 2H, ^2J = 12.7,

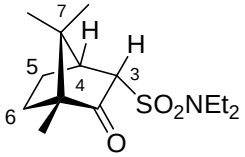
^{3}J(H$_6$-H$_{5a}$) = 4.5, ^{3}J(H$_6$-H$_{5b}$) = 2.3, H-C(6)), 1.13 (t, 3H, ^{3}J(H$_{2''}$-H$_{1''}$) = 7.8, H-C(2'')), 1.06 (s, 3H, *Me*-C(7)), 0.99 (s, 3H, *Me*-C(7)), 0.94 (s, 3H, *Me*-C(1)). *^{13}C NMR (100.6 MHz, CDCl$_3$)*: δ 207.7 (s, CO), 200.4 (s, CO), 68.6 (d ^{1}J (C,H) = 148, C(3)), 59.5 (t, ^{1}J (C,H) = 137, C(1')) , 46.1 (s, C(1)), 42.7 (s, C(7)), 40.5 (t, ^{1}J (C,H) = 136, C(1'')), 38.3 (d, ^{1}J (C,H) = 129, C(4)), 29.9 (t, ^{1}J (C,H) = 145, C(6)), 23.1 (t, ^{1}J (C,H) = 129, C(5)), 19.6 (q, ^{1}J (C,H) = 135, C(2'')), 18.1 (q, ^{1}J (C,H) = 138, *Me*-C(7)), 9.5 (q, ^{1}J (C,H) = 142, *Me*-C(7)), 9.4 (q, ^{1}J (C,H) = 140, *Me*-C(1)). CI-MS (NH_3): m/z 290 (100, $[M+18]^+$, 273 (46, $[M+1]^+$).

(1*R*,3*S*,4*S*)-Trimethylsilyl-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane-3-*endo*-sulfonylbromide (<u>27</u>).



1*H NMR (400 MHz, CD$_3$CN, 203K)*: δ 3.36 (d, 1H, ^{3}J(H$_{exo}$-H$_4$) = 4.1, H$_{exo}$-C(3)), 2.51 (dd, ^{3}J(H$_4$-H$_{5a}$) = 4.1, ^{3}J(H$_4$-H$_{exo}$) = 4.1, H-C(4)), 2.22 (dtd, 1H, ^{2}J = 12.9, ^{3}J(H$_{5a}$-H$_6$) = 4.9, ^{3}J(H$_{5a}$-H$_4$) = 4.1 H$_a$-C(5)), 1.87 (td, 1H, ^{2}J = 12.9, ^{3}J(H$_{5b}$-H$_6$) = 7.2, H$_b$-C(5)), 1.59 (q, 2H, ^{3}J(H$_6$-H$_5$) = 9.6, H-C(6)), 1.07 (s, 3H, Me-C(7)), 0.99 (s, 3H, Me-C(7)), 0.98 (s, 3H, Me-C(1)). *^{13}C NMR (100.6 MHz, CDCl$_3$)*: δ 211.4 (s, CO), 79.2 (d, ^{1}J(C,H) = 152, C(3)), 58.5 (s, C(1)), 46.4 (s, C(7)), 45.3 (d, ^{1}J(C,H) = 150, C(4)), 28.2 (t, ^{1}J(C,H) = 136, C(6)), 26.5 (t, ^{1}J(C,H) = 134, C(5)), 20.2 (q, ^{1}J(C,H) = 130, *Me*-C(7)), 18.2 (q, ^{1}J(C,H) = 126, *Me*-C(7)), 8.7 (q, ^{1}J(C,H) = 126, *Me*-C(1)).

(1*R*,3*S*,4*S*)-*N*,*N*-Diethyl-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane-3-*endo*-sulfonamide (<u>15</u>).

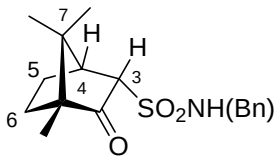


<u>**15**</u> was prepared as described above in the **general procedure 2** from enoxysilane <u>**2e**</u> and Et_2NH. FC (4:1 light petroleum ether/EtOAc, R_f = 0.5), 543 mg (69%), colorless solid, mp = 70-71°C.

IR (KBr): ν 2965, 1740, 1445, 1325, 1135, 1015, 940, 685 cm^{-1}. UV (CH_3CN): λ_{max} = 194 nm (ε = 3036). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (dd, 1H, ^{3}J = 4.3, ^{4}J = 1.8, H$_{exo}$-C(3)), 3.48 (dq, 1H, ^{2}J = 14.5, ^{3}J = 7.1, CH_2N), 3.27 (dq, 1H, ^{2}J = 14.5, ^{3}J = 7.1, CH_2N), 2.51 (t, 1H, ^{3}J =

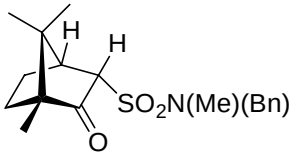
4.3, H-C(4)), 2.31 (m, 1H, H_a-C(5)), 1.86 (m, 1H, H_b-C(5)), 1.71 (m, 2H, H-C(6)), 1.21 (t, 3H, ^3J = 7.1, CH_3(Et)), 1.04 (s, 3H, CH_3-C(7)), 0.95 (s, 3H, CH_3-C(7)), 0.87 (s, 3H, CH_3-C(1)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 208.5 (s, CO), 70.5 (d, ^1J(C,H) = 136, C(3)), 59.3 (s, C(1)), 47.5 (d, ^1J(C,H) = 148, C(4)), 45.6 (s, C(7)), 42.1 (t, ^1J(C,H) = 139, CH_2N), 29.7 (t, ^1J(C,H) = 134, C(6)), 21.8 (t, ^1J(C,H) = 137, C(5)), 19.7 (q, ^1J(C,H) = 125, Me-C(7)), 18.6 (q, ^1J(C,H) = 126, Me-C(7)), 14.8 (q, ^1J(C,H) = 127, C(2')), 9.7 (q, ^1J(C,H) = 127, Me-C(1)). CI-MS (NH_3): m/z 305 (16, $[M+18]^+$), 288 (100, $[M+1]^+$), 124 (17, $[M-163]^+$). Anal. Calcd for $C_{14}H_{25}NO_3S$ (287.42): C, 58.51, H, 8.77, N, 4.87. Found: C, 58.35, H, 8.87, N, 4.78. (*see Figure S5*)

(1*R*,3*S*,4*S*)-*N*-Benzyl-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane-3-*endo*-sulfonamide (16).



16 was prepared as described above in the **general procedure 2** from enoxysilane **2e** and $BnNH_2$. FC (4:1 light petroleum ether/EtOAc, R_f 0.41), (60%), yellow solid, mp 113-114°C. IR (KBr): ν 3445, 3310, 2965, 2940, 1740, 1330, 1320, 1155, 1040, 700, 610 cm^{-1}. UV (CH_3CN): λ_{max} = 190 (ε = 8070). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.27 (m, 5H, Ph(Bn)), 5.18 (t, ^3J = 6.1, HN), 4.42 (dd, 1H, ^2J = 14.5, ^3J = 6.1, H_2C(Bn)), 4.33 (dd, 1H, ^2J = 14.5, ^3J = 6.1, H_2C(Bn)), 3.61 (dd, 1H, ^3J = 4.3, ^4J = 1.8, H_{exo}-C(3)), 2.51 (t, 1H, ^3J = 4.3, H-C(4)), 2.30 (m, 1H, H_a-C(5)), 1.85 (m, 1H, H_b-C(5)), 1.71 (m, 2H, H-C(6)), 1.00 (s, 3H, H_3C(7)), 0.93 (s, 3H, H_3C(7)), 0.66 (s, 3H, H_3C(1)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 208.5 (s, CO), 136.2 (s, C_{quat}(Ph)), 129.0 (d, ^1J(C,H) = 153, HC(Ph)), 128.3 (d, ^1J(C,H) = 160, HC(Ph)), 128.2 (d, ^1J(C,H) = 160, HC(Ph)), 69.7 (d, ^1J(C,H) = 135, C(3)), 59.4 (s, C(1)), 47.6 (d, ^1J(C,H) = 148, C(4)), 46.6 (t, ^1J(C,H)= 140, H_2C(Bn)), 45.9 (s, C(7)), 30.2 (t, ^1J(C,H) = 134, C(6)), 21.6 (t, ^1J(C,H) = 137, C(5)), 19.5 (q, ^1J(C,H) = 125, C(7)), 18.5 (q, ^1J(C,H) = 126, C(7)), 9.6 (q, ^1J(C,H) = 127, Me-C(1)). EI-MS: m/z = 321 (2, [M+1]), 106 (100, [M-215]). Anal. Calcd for $C_{17}H_{23}NO_3S$ (321.43): C, 63.52, H, 7.21, N, 4.36. Found: C, 63.57, H, 7.34, N, 4.23.

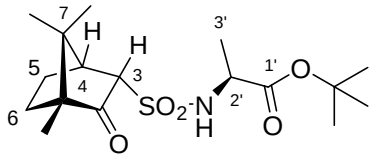
(1*R*,3*S*,4*S*)-*N*-Benzyl-*N*,1,7,7-tetramethyl-2-oxobicyclo[2.2.1]heptane-3-*endo*-sulfonamide (<u>17</u>).



<u>17</u> was prepared as described above in the **general procedure 2** from enoxysilane **<u>2e</u>**. Purification by FC (9:1 light petroleum ether/EtOAc, R_f 0.3), 521 mg (75%), colorless solid, mp 92-93 °C.

IR (KBr): ν = 2970, 2930, 1745, 1335, 1150, 990, 938, 765, 735 cm^{-1}. UV (CH_3CN): λ_{max} = 211 nm (ε = 5400). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.27 (m, 5H, Ph), 4.61(d, 1H, ^2J = 14.7, H_2C(Bn)), 4.31 (d, 1H, ^2J = 14.7, H_2C(Bn)), 3.82 (dd, 1H, ^3J = 4.1, ^4J = 1.8, H_{exo}-C(3)), 2.87 (s, 3H, CH_3-N) 2.55 (t, 1H, ^3J = 4.1, H-C(4)), 2.36 (td, 1H, ^2J = 13.2, ^3J = 8.2, H_a-C(5)) 1.93 (m, 1H, H_b-C(5)), 1.76 (m, 2H, H-C(6)), 1.05 (s, 3H, H_3C(7)), 0.96 (s, 3H, H_3C(7)), 0.85 (s, 3H, H_3C(1)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 208.5 (s, CO), 136.2 (s, $C_{quat.}$(Ph)), 128.8 (d, ^1J(C,H) = 153, C(Ph)), 128.4 (d, ^1J(C,H) = 160, C(Ph)), 127.9 (d, ^1J(C,H) = 160,C(Ph)), 69.3. (d, ^1J(C,H) = 135, C(3)), 59.4 (s, C(1)), 54.3 (t, ^1J(C,H) = 140, H_2C(Bn)), 47.3 (d, ^1J(C,H) = 148, C(4)), 45.9 (s, C(7)), 34.6 (q, ^1J(C,H) = 140, MeN), 29.7 (t, ^1J(C,H) = 134, C(6)), 22.0 (t, ^1J(C,H) = 137, C(5)), 19.7 (q, ^1J(C,H) = 125, C(7)), 18.7 (q, ^1J(C,H) = 126, C(7)), 9.8 (q, ^1J(C,H) = 127, Me-C(1)). CI-MS (NH_3): m/z 353 (59, $[M+18]^+$), 336 (53, $[M+1]^+$), 170 (100, $[M-165]^+$), 153 (52, $[M-182]^+$). Anal. Calcd for $C_{18}H_{25}NO_3S$ (335.46): C, 64.45, H, 7.51, N, 4.18. Found: C, 64.41, H, 7.55, N, 4.14. (*see Figure S6 and S7*)

***Tert*-butyl *N*-{[((1*R*,3S,4*S*)1,7,7-trimethyl-2-oxobicyclo[2.2.1]hept-3-*endo*-yl)}sulfonyl] *L*-alaninate (<u>18</u>).**



<u>18</u> was prepared as described above in the **general procedure 2** from enoxysilane **<u>2e</u>** and *L*-alanine *tert*-butyl ester hydrochloride using Et_3N (2.4 equiv.). FC (4:1 light petroleum ether/EtOAc, R_f 0.49) 572 mg (58%), light yellow oil.

IR (film): ν 3290, 2970, 2935, 1745, 1340, 1160, 1135, 735, 605 cm^{-1}. UV (CH_3CN): λ_{max} =

195 nm (ε = 4400). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44 (d, 1H, ^3J = 8.8, HN), 4.1 (m, 2H, H-C(3), H-C(2')), 2.56 (t, 1H, ^3J = 4.1, H-C(4)), 2.25 (m, 1H, H_a-C(5)), 1.85 (m, 1H, H_b-C(5)), 1.71 (m, 2H, H-C(6)), 1.46 (d, 3H, ^3J = 7.1, H_3C(3')), 1.45 (s, 9H, *t*-Bu), 1.0 (s, 3H, H_3C(7)), 0.96 (s, 3H, H_3C(7)), 0.87 (s, 3H, H_3C(1)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 208.8 (s, CO), 171.9 (s, COO), 82.6 (s, C_{quat}-*t*Bu), 70.7 (d, ^1J(C,H) = 135, C(3)), 59.4 (s, C(1)), 52.9 (d, ^1J(C,H) = 144, C(2')), 46.8 (d, ^1J(C,H) = 149, C(4)), 45.9 (s, C(7)), 30.3 (t, ^1J(C,H) = 134, C(6)), 27.9 (q, ^1J(C,H) = 127, *t*-Bu), 21.5 (t, ^1J(C,H) = 137, C(5)), 20.1 (q, ^1J(C,H) = 135, H_3C(3')), 19.7 (q, ^1J(C,H) = 125, H_3C(7)), 18.5 (q, ^1J(C,H) = 126, H_3C(7)), 9.7 (q, ^1J(C,H) = 127, H_3C(1)). CI-MS (NH_3): m/z 377 (14, $[M+18]^+$), 360 (1, $[M+1]^+$), 304 (100, $[M-55]^+$), 258 (55, $[M-101]^+$). Anal. Calcd for $C_{17}H_{29}NO_5S$ (359.48): C, 56.8, H, 8.13, N, 3.9. Found: C, 55.32, H, 8.02, N, 3.64.

***N, N*-Diethyl-2-methylprop-2-ene-1-sulfonamide (24).**

24 was prepared as described above in the **general procedure 4** from **23** and Et_2NH**.** FC (5:1 light petroleum ether/EtOAc, R_f 0.47), (78%), colorless oil.

IR (film): ν 2976, 2936, 1644, 1458, 1382, 1350, 1329, 1201, 1143, 1126, 1019, 936, 790, 711cm^{-1}. UV (CH_3CN): λ_{max} = 210 nm (ε = 1364). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.13 (*br*.s, 1H, H-C(3)), 5.02 (*br*s,1H, H-C(3)), 3.62 (s, 2H, H-C(1)), 3.29 (q, 4H, ^3J = 7.1, H-C(1')), 2.0 (s, 3H, Me-C(2)), 1.21 (t, 6H, ^3J = 7.1, H-C(2')). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 134.9 (s, C(2)), 119.6 (t, ^1J(C,H) = 157, C(3)), 60.3 (t, ^1J(C,H) = 138, C(1)), 42.5 (t, ^1J(C,H) = 139, C(1')), 22.8 (q, ^1J(C,H) = 128, Me-C(2)), 14.9 (q, ^1J(C,H) = 127, C(2')). CI-MS (NH_3): m/z 209 (14, $[M+18]^+$), 192 (74, $[M+1]^+$), 176 (12, $[M-15]^+$), 136 (14, $[M-55]^+$), 127 (47, $[M-64]^+$), 112 (100, $[M-79]^+$), 86 (42, $[M-105]^+$). Anal. Calcd for $C_8H_{17}NO_2S$ (191.29): C, 50.53, H, 8.96, N, 7.32. Found: C, 50.28, H, 8.85, N, 7.40.

***N*-Benzyl-2-methylprop-2-ene-1-sulfonamide (25).**

25 was prepared as described above in the **general procedure 4** from **23** and $BnNH_2$**.** FC (4:1 light petroleum ether/EtOAc, R_f = 0.32), (75%), colorless solid, mp : 68-69°C.

IR (film): ν 3236, 3032, 2976, 2928, 1647, 1492, 1453, 1400, 1310, 1134, 10612, 902, 875, 734, 695cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.31 (m, 5H, H-Ph (Bn)), 5.16 (*br*.s, 1H, H-C(3)), 4.97 (*br*.s,1H, H-C(3)), 4.56 (t, 1H, ^3J = 6.1, H-N), 4.32 (d, 2H, ^3J = 6.1, H_2C(Bn)), 3.68 (s, 2H, H-C(1)), 1.96 (s, 3H, Me-C(2)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.9 (s, Cquat(Ph)), 134.9 (s, C(2)), 129.1 (d, ^1J(C,H) = 160, HC(Ph)), 128.3 (d, ^1J(C,H) = 161,

HC(Ph)), 128.1 (d, ^1J(C,H) = 161, HC(Ph)), 119.9 (t, ^1J(C,H) = 160, C(3)), 61.1 (t, ^1J(C,H) = 140, C(1)), 47.9 (t, ^1J(C,H) = 139, C(CH_2N)), 22.8(q, ^1J(C,H) = 131, Me-C(2)). CI-MS (NH_3): m/z 243 (20, $[M+18]^+$), 226 (74, $[M+1]^+$), 160 (35, $[M-65]^+$), 145 (25, $[M-80]^+$), 120 (13, $[M-105]^+$), 106 (100, $[M-119]^+$), 91 (50, $[M-105]^+$). Anal. Calcd for $C_{11}H_{15}NO_2S$ (225.31): C, 58.64, H, 6.71, N, 6.22. Found: C, 58.77, H, 6.72, N, 6.19.

Methyl 2-oxo-2-phenylethane-1-sulfonate (19)[2].

19 was prepared as described above in the **general procedure 5** from enoxysilane **2c** and MeOH. FC (4:1 light petroleum ether/EtOAc, R_f 0.25), 68%, colorless crystal. Same characteristics as those reported in literature.

Ethyl 2-oxo-2-phenylethanesulfonate (20)[2].

20 was prepared as described above in the **general procedure 5** from enoxysilane **2c** and EtOH. FC (4:1 light petroleum ether/EtOAc, R_f 0.25), 65%, colorless crystal.

Isopropyl 2-oxo-2-phenylethanesulfonate (21):

21 was prepared as described above in the **general procedure 5** from enoxysilane **2c** and isopropanol. FC (9:1 light petroleum ether/EtOAc, R_f 0.18), (30%), light yellow solid

IR (KBr): ν 2990, 1685, 1600, 1450, 1360, 1275, 1175, 1095, 915 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, 2H, ^3J = 8.2, ^4J = 1.3, H_{ortho}-C(Ph)), 7.67 (tt, 1H, ^3J = 7.4, ^4J = 1.3, H_{para}-C(Ph)), 7.53 (td, 2H, ^3J = 8.2, ^4J = 1.3, H_{meta}-C(Ph)), 5.05 (q, 1H, ^3J = 6.1, H-C(isopropyl)), 4.69 (s, 2H, H-C(1)), 1.42 (d, 6H, ^3J = 6.1, Me_2C(isopropyl)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 187.7 (s, CO), 135.7 (s, C_{quat}(Ph)), 134.9 (d, ^1J(C,H) = 162, HC(Ph)), 129.2 (d, ^1J(C,H) = 163, HC(Ph)), 129.0 (d, ^1J(C,H) = 162, HC(Ph)), 79.6 (d, ^1J(C,H) = 151, Me_2C(isopropyl)), 58.2 (t, ^1J(C,H) = 138, C(1)), 23.1 (q, ^1J(C,H) = 128, Me(isopropyl)). CI-MS (NH_3): m/z 260 (1, $[M+18]^+$), 243 (1, $[M+1]^+$), 105 (100, $[M-137]^+$). Anal. Calcd for $C_{11}H_{14}O_4S$ (242.29): C, 54.53, H, 5.82. Found: C, 54.48, H, 5.89.

Phenyl 2-oxo-2-phenylethane-1-sulfonate (22).

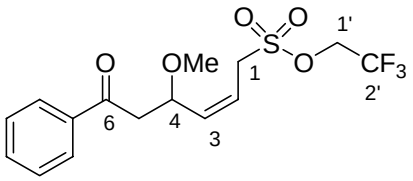
22 was prepared as described above in the **general procedure 5** from enoxysilane **2c** and phenol. FC (9:1 light petroleum ether/EtOAc, R_f 0.19), 265 mg (35%), colorless solid.

IR (KBr): ν 3065, 2970, 1685, 1595, 1585, 1490, 1450, 1380, 1275, 1190, 1140, 870, 785,

[2] Efimova, T.P. ; Lipina, E. S. ; Berkova, G. A. ; Pozdnyakov, v. p. *Zh. Org. Khim.,* **1996**, *32*, 1424.

6890 cm^{-1}. UV (CH_3CN): λ_{max} = 249 nm (ε = 9400), 211 nm (ε = 7800). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, 2H, ^3J = 8.2, ^4J = 1.3, H_{ortho}-C(Ph)), 7.67 (tt, 1H, ^3J = 7.4, ^4J = 1.3, H_{para}-C(Ph)), 7.54 (td, 2H, ^3J = 8.2, ^4J = 1.3, H_{meta}-C(Ph)), 7.4 (m, 5H, Ph(phenoxy)), 4.81 (s, 2H, H-C(1)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 186.6 (s, CO), 149.4 (s, C_{quat}(Ar)), 135.4 (s, C(Ph)), 134.8 (d, ^1J(C,H) = 163, HC(Ph)), 132.8 (d, ^1J(C,H) = 163, C(Ar)), 130.2 (d, ^1J(C,H) = 165, C(Ar)), 129.4 (d, ^1J(C,H) = 164, HC(Ph), 129.1 (d, ^1J(C,H) = 163, HC(Ph), 127.8 (d, ^1J(C,H) = 168, C(Ar)), 56.3(t, ^1J(C,H) = 139, C(1)). CI-MS (NH_3): m/z 294 (6, $[M+18]^+$), 277 (2, $[M+1]^+$), 121 (88, $[M-156]^+$), 105 (100, $[M-172]^+$).

(±)-2',2',2'-Trifluoroethyl (2*Z*)-4-methoxy-6-oxo-6-phenyl hex-2-ene-1-sulfonate (<u>45b</u>).

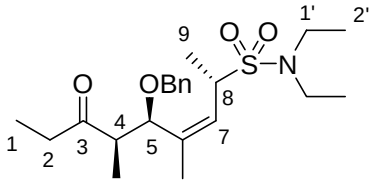


(*t*-Bu)$Me_2SiOSO_2CF_3$ (0.94 mmol, 0.1 equiv) in anh. CH_2Cl_2 (10 mL) was degassed by freeze-thaw cycles on the vacuum line. SO_2 (122 mmol, 13 equiv), dried by passing through a column packed with phosphorus pentoxide and aluminum oxide, was transferred on the vacuum line to the CH_2Cl_2 solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 30 min at this temperature a solution of (*E*)-1-methoxy-1,3-butadiene **<u>35</u>** (4.7 mmol, 0.5 equiv) and 1-phenyl-1-trimethylsiloxyethylene **<u>2c</u>** (9.4 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL) were added dropwise under vigorous stirring and Ar atmosphere. The mixture was stirred at -78 °C for 5 h. After cooling to -78 °C, the excess of SO_2 and the solvent were evaporated under reduced pressure (10^{-1} Torr) to dryness (ca. 1h) while temperature slowly reached 20 °C. Halogenating agent (only NCS 12.2 mmol, 1.3 equiv, dissolving in CH_2Cl_2) was added at -20 °C. After 2.5 h at this temperature, the trifluoroethanol (56.4 mmol, 6equiv) and pyridine (56.4 mmol, 6 equiv) was added at a time to the reaction mixture under Ar. The mixture was finally stirred at this temperature for 2 h, and poured into a CH_2Cl_2 (200 mL) and then washed with a saturated aqueous solution of $CuSO_4$ (250 mL, 3 times). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and the solvent eliminated under reduced pressure under reflux. The residue was purified by FC (4:1 light petroleum ether/EtOAc, R_f 0.25) afforded (70%) of a brownish oil.

IR (film): 2984, 2936, 2827, 1684, 1598, 1581, 1450, 1373, 1285, 1177, 1104, 1041, 962, 755, 733, 690. UV (CH_3CN): 283 (1750), 260 (1850), 242 (5400), 201 (8700). ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, 2H, ^3J = 8.0, ^4J = 1.3, H_{ortho}-C(Ph)), 7.59 (tt, 1H, ^3J = 8.0, ^4J = 1.3,

H_{para}-C(Ph)), 7.47 (td, 2H, ^3J = 8.0, ^4J = 1.3, H_{meta}-C(Ph)), 5.85 (ddt, 1H, ^3J = 11.4, ^3J = 8.9, ^4J = 1.2, H-C(3)), 5.75 (dt, 1H, ^3J = 11.4, ^3J = 6.8, H-C(2)), 4.65 (dq, 1H, ^3J = 8.9, ^3J = 6.8, H-C(4)), 4.56 (q, 2H, ^3J = 8.0, H-C(1')), 4.44 (ddd, 1H, ^2J = 14.8, ^3J = 8.3, ^4J = 1.2, H-C(1)), 4.16 (ddd, 1H, ^2J = 14.8, ^3J = 6.8, ^4J = 1.2, H-C(1)), 3.42 (dd, 1H, ^2J = 17.0, ^3J = 6.2, H-C(5)), 3.33 (s, 3H, OMe), 3.16 (dd, 1H, ^3J = 17.0, 6.8, H-C(5)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 197.2 (s, C(6)), 139.3 (d, ^1J(C,H) = 158, C(3)), 136.7 (s, C(Ph)), 133.5 (d, ^1J(C,H) = 161, HC(Ph)), 128.7 (d, ^1J(C,H) = 162, HC(Ph)), 128.1 (d, ^1J(C,H) = 160, HC(Ph)), 123.6 (q, ^1J(C,F) = 278, C(2')), 117.8 (d, ^1J(C,H) = 166, C(2)), 73.2 (d, ^1J(C,H) = 145, C(4)), 64.2 (dq, ^2J(C,F) = 155, C(1')), 56.8 (q, ^1J(C,H) = 142, OMe), 50.4 (t, ^1J(C,H) = 140, C(1)), 43.9 (t, ^1J(C,H) = 126, C(5)). CI-MS (NH_3): m/z 367 (13, $[M+H]^+$), 247 (3), 203 (16), 173 (8), 105 (100), 78 (14). Anal. Calcd for $C_{15}H17F_3O_5S$ (366.36): C 49.18, H 4.68. Found: C 49.18, H 4.64.

(±)-(4*RS*,5*RS*,7*Z*,8*RS*)-5-(Benzyloxy)-*N*,*N*-diethyl-4,6-dimethyl-3-oxonon-7-ene-8-sulfonamide (<u>46a</u>).

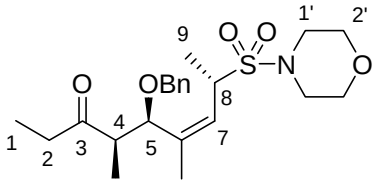


$NHTf_2$ (0.5 M in CH_2Cl_2, 0.59 mL, 0.29 mmol, 0.3 equiv) in anh. CH_2Cl_2 (2 mL) was degassed by freeze-thaw cycles on the vacuum line. SO_2 (0.8 mL, 19.4 mmol, 20 equiv), dried by passing through a column packed with phosphorus pentoxide and aluminum oxide, was transferred on the vacuum line to the CH_2Cl_2 solution frozen at -196 °C. The mixture was allowed to melt and to warm to -78 °C. After 30 min at this temperature a solution of diene **<u>36</u>** (181mg, 0.96 mmol, 1 equiv) and the enoxysilane **<u>2b</u>** (200 mg, 1.26 mmol, 1.3 equiv) in CH_2Cl_2 (0.5 mL) were added dropwise under vigorous stirring and Ar atmosphere. The mixture was stirred at -78 °C for 12 h. At this temperature, the excess of SO_2 and the solvent were evaporated under reduced pressure (10^{-1} Torr) to dryness (ca. 1h) while temperature slowly reached 20 °C. Halogenating agent (only NCS, 402 mg, 3.01 mmol, 1.1 equiv) was added at -20 °C. After 1h at this temperature, the dark mixture was transferred into a solution of the Et_2NH (240 mg, 3.29 mmol, 1.2 equiv) in 3 mL pyridine under Ar. The mixture was finally stirred at this temperature for 2 h, and poured into a mixture of ice-water (10 mL) and Et_2O (20 mL) and then washed with a aqueous saturated solution of $CuSO_4$ (30 mL, 3 times). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and the

solvent eliminated under reduced pressure under reflux. Purification by FC (4:1 light petroleum ether/EtOAc, R_f = 0.31), 910 mg (81%), yellowish oil.

IR (film): ν 2974, 2875, 1713, 1455, 1332, 1140, 1010, 937, 737 cm^{-1}. UV (CH_3CN): λ_{max} = 216 (ε = 5338). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.28 (m, 5H, Ph(Bn)), 5.57 (d, 1H, $^3J(H_8\text{-}H_7)$ = 9.2, H-C(7)), 4.48 (d, AB, 1H, ^2J = 12.0, CH_2(Bn)), 4.34 (d, 1H, $^3J(H_5\text{-}H_4)$ = 8.0, H-C(5)), 4.24 (d, AB, 1H, ^2J = 12.0, CH_2(Bn)), 4.02 (qd, 1H, $^3J(H_8\text{-}H_7)$ = 9.2, $^3J(H_8\text{-}H_9)$ = 6.8, H-C(8)), 3.31 (m, 4H, H-C(1')), 2.98 (dq, 1H, $^3J(H_4\text{-}H_5)$ = $^3J(H_4\text{-}Me_4)$ = 7.7, H-C(4)), 2.53 (dq, 1H, ^2J = 18.8, $^3J(H_2\text{-}H_1)$ = 7.1, Ha-C(2)), 2.41 (dq, 1H, ^2J = 18.8, $^3J(H_2\text{-}H_1)$ = 7.1, Hb-C(2)), 1.79 (s, 3H, *Me*-C(6)), 1.32 (d, 3H, $^3J(H_9\text{-}H_8)$ = 6.8, H-C(9)), 1.19 (t, 6H, ^3J = 7.7, CH_3-CH_2N), 1.03 (t, 3H, $^3J(H_1\text{-}H_2)$ = 7.1, H-C(1)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 213.2 (s, CO), 140.1 (s, C(6)), 130.6-125 (C(ar)), 122.7 (d, ^1J(C,H) = 153, C(7)), 70.1 (t, ^1J(C,H) = 147, CH_2(Bn)), 56.9 (d, ^1J(C,H) = 139, C(8)), 49.3 (d, ^1J(C,H) = 140, C(5)), 43.5 (d, ^1J(C,H) = 143, C(4)), 42.0 (t, ^1J(C,H) = 146, C(1')), 36.4 (t, ^1J(C,H) = 128, C(2)), 19.1 (q, ^1J(C,H) = 152, *Me*-C(6)), 16.7 (q, ^1J(C,H) = 145, *Me*-C(9)), 14.3 (q, ^1J(C,H) = 144, CH_3-CH_2N)), 13.9 (q, ^1J(C,H) = 139, *Me*-C(4)), 7.4 (q, ^1J(C,H) = 130, C(1)). CI-MS (NH_3): m/z =427 (100, $[M+18]^+$), 410 (20, $[M+1]^+$). Anal. Calcd for $C_{22}H_{35}NO_4S$ (409.23): C, 64.51, H, 8.61, N, 3.42. Found: C, 64.70, H, 8.55, N, 3.36.

(±)-Morpholine (4*RS*, 5*RS*, 7*Z*, 8*SR*)-5-(Benzyloxy)-4,6-dimethyl-3-oxooct-7-ene-8-sulfonamide (<u>46b</u>).

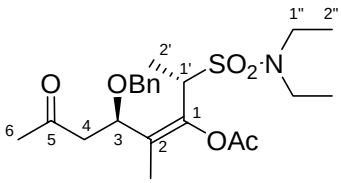


Sulfonamide **<u>46b</u>** was prepared as described above for **<u>46a</u>** from the same starting diene **<u>36</u>** and enoxysilane **<u>2b</u>**. The intermediate sulfonyl chloride was reacted with *N*-morpholine (289 mg, 3.29 mmol). FC (7:3 light petroleum ether/EtOAc, R_f 0.32), 703 mg (63%), colorless oil.

IR (film): ν 2973, 2937, 1713, 1497, 1455, 1337, 1261, 1149, 1115, 1071, 1028, 956, 743, 699 cm^{-1}. UV (CH_3CN): λ_{max} = 218 (ε =4178). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.35 (m, 5H, Ph(Bn)), 5.59 (d, 1H, $^3J(H_7\text{-}H_8)$ = 10.6, H-C(7)), 4.48 (d, AB, 1H, ^2J = 11.5 CH_2(Bn)), 4.39 (d, 1H, $^3J(H_5\text{-}H_4)$ = 7.7, H-C(5)), 4.24 (d, AB, 1H, ^2J = 11.5, CH_2(Bn)), 4.04 (dq, 1H, $^3J(H_8\text{-}H_7)$ = 10.6, $^3J(H_8\text{-}H_9)$ = 6.7, H-C(8)), 3.74 (t, 2H, $^3J(H_{2'a}\text{-}H_{1'})$ = 4.5, H_a-C(2')), 3.72 (t, 2H, $^3J(H_{2'b}\text{-}H_{1'})$ = 4.2, H_b-C(2')), 3.38 (t, 2H, $^3J(H_{1'a}\text{-}H_{2'})$ = 4.2, H_a-C(1')), 3.34 (t, 2H, $^3J(H_{1'b}\text{-}H_{2'})$ = 4.2, H-C(1'b)), 2.96 (qd, 1H, $^3J(H_4\text{-}H_5)$ = $^3J(H_4\text{-}Me_4)$ = 7.7, H-C(4)), 2.64 (qd,

1H, ^2J = 16.6, $^3J(H_{2a}\text{-}H_1)$ = 6.7, H_a-C(2)), 2.54 (qd, 1H, ^2J = 16.6, $^3J(H_{2b}\text{-}H_1)$ = 6.7, H_b-C(2)), 1.80 (s, 3H, CH_3-C(6)), 1.39 (d, 3H, $^3J(H_9\text{-}H_8)$ = 6.7, H-C(9)), 1.27 (t, 3H, $^3J(H_1\text{-}H_2)$ = 6.7, H-C(1)), 1.03 (d, 3H, $^3J(H_4\text{-}Me_4)$ = 7.7, *Me*-C(4)). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 214.5 (s, CO), 140.1 (s, C(6)), 130.6-125 (C(ar)), 122.7 (d, ^1J(C,H) = 153, C(7)), 70.6 (t, ^1J(C,H) = 152, CH_2(Bn)), 67.5 (t, ^1J(C,H) = 161, C(2')), 56.8 (d, ^1J(C,H) = 132, C(8)), 48.3 (d, ^1J(C,H) = 143, C(5)), 43.9 (d, ^1J(C,H) = 139, C(4)), 38.2 (t, ^1J(C,H) = 139, C(1')), 37.7 (t, ^1J(C,H) = 148, C(2)), 18.9 (q, ^1J(C,H) = 139, C(6)), 17.4 (q, ^1J(C,H) = 142, C(9)), 13.8 (q, ^1J(C,H) = 155, *Me*-C(4)), 7.9 (q, ^1J(C,H) = 134, C(1)). CI-MS (NH_3) : m/z =425 (100, $[M+18]^+$), 408 (12, $[M+1]^+$). Anal. Calcd for $C_{22}H_{33}NO_4S$ (407.63): C, 62.38, H, 7.85, N, 3.31. Found: C, 62.26, 7.76, N, 3.22.

(±)-(1*E*,3*RS*)-3-(Benzyloxy)-1-{(1'*RS*)-1'-[(diethylamino)sulfonyl]ethyl}-2-methyl-5-oxohex-1-enyl acetate (<u>47a</u>)



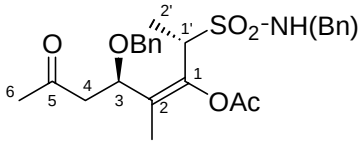
The 0.5 M solution of Tf_2NH (0.61ml, 0.30 mmol, 0.2 eq.) in CH_2Cl_2 was diluted with CH_2Cl_2 (3.5 ml). SO_2 (2.5 ml) was condensed at –196 °C. The mixture was stirred at –78 °C for 15 min, when the solution of **<u>37</u>** (0.42 g, 1.5 mmol, 1 eq.) and isopropenyloxy trimethylsilane **<u>38</u>** (0.5 ml, 3.0 mmol, 2 eq.) in CH_2Cl_2 (1 ml) was added slowly dropwise at –95 °C. The reaction mixture was stirred for 14 h at –80 °C. Reaction mixture was degassed at –78 °C (0.01 mbar) for 2 h, followed by evaporation at 20 °C to dryness.

The oily residue was dissolved in MeCN (2 ml) and NCS (0.23 g, 1.68 mmol, 1.1 eq.) was added at –40 °C and stirring was continued for 0.5 h. Then the mixture was cannulated into a solution of Et_2NH (0.17 ml, 1.68 mmol, 1.1 eq.) in pyridine (3 ml) at –20 °C. The mixture was allowed to reach 20 °C and partitioned between CH_2Cl_2 and HCl (2 M). The aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with aqueous. $NaHCO_3$, brine (10 ml), dried over Na_2SO_4 and evaporated. The residue was purified by FC (light petroleum ether/ EtOAc 1:1 : 0.22 g (30%) of **<u>47a</u>**, colorless oil.

IR (film): ν 2978, 2938, 2876, 1760, 1716, 1670, 1626, 1595, 1455, 1370, 1353, 1327, 1201, 1166, 1142, 1129, 1070, 1045, 1018, 938, 917 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (m, 5H, Ph), 4.70 (dd, 1H, *J*=9.3, 1.8 Hz, H(3)), 4.60 (d, 1H, *J*=12.3, O<u>C</u>H_2Ph), 4.28 (d, 1H, *J*=12.3, O<u>C</u>H_2Ph), 3.70 (q, 1H, *J*=6.8, H(1')), 3.25 (dq, 2H, *J*=14.5, 7.1, Ha(1")), 3.08 (dq, 2H,

J=14.5, 7.1, Hb(1")), 2.87 (dd, 1H, *J*=9.3, 16.3, Ha(4)), 2.76 (dd, 1H, *J*=1.8, 16.3, Hb(4)), 2.23 (s, 3H, OAc), 2.16 (s, 3H, H(5)), 1.60 (s, 3H, Me(2)), 1.27 (d, 3H, *J*=6.8, H(2')), 1.07 (t, 3H, *J*=7.1, H(2")). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 205.9 (s, C(5)), 168.4 (s, $\underline{C}OCH_3$), 138.8 (s, C(1)), 137.7 (s, Ar), 128.3 (d, ^1J(C,H)=154, Ar), 128.2 (d, ^1J(C,H)=157, Ar), 127.8 (d, ^1J(C,H)=155, Ar), 127.6 (s, C(2)), 70.9 (d, ^1J(C,H)=145, C(3)), 69.5 (t, ^1J(C,H)=144, $\underline{C}H_2Ph$), 57.9 (d, ^1J(C,H)=141, C(1')), 46.9 (t, ^1J(C,H)=129, C(4)), 41.9 (t, ^1J(C,H)=138, C(1")), 30.5 (q, ^1J(C,H)=125, C(6)), 20.4 (q, ^1J(C,H)=128, $CO\underline{C}H_3$), 14.4 (q, ^1J(C,H)=134, Me(3)), 11.3 (q, ^1J(C,H)=128, C(2')). CI-MS (NH_3) : m/z 457 ([M+18], 15), 290(3), 243(3), 224(8), 214(9), 169(14), 155(48), 153(14), 141(8), 139(15), 137(30), 136(30), 125(19), 113(43), 111(27), 108(11), 105(15), 92(11), 91(100), 82(8), 74(98), 73(15), 72(97). Anal. Calcd for $C_{22}H_{33}NO_6S$ (439.24): C 60.11, H 7.57. Found: C 59.96, H 7.66.

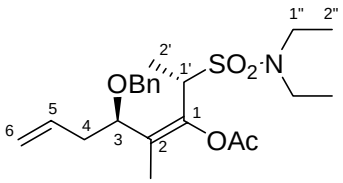
(±)-(1*E*, 3*RS*)-1-{(1'*RS*)-1'-[(Benzylamino)sulfonyl]ethyl}-3-(benzyloxy)-2-methyl-5-oxohex-1-enyl acetate (<u>47b</u>)



Same procedure as for the preparation of **<u>47a</u>**, using $BnNH_2$ instead of Et_2NH. Yield: 30% of **<u>47b</u>**.

IR (film): ν 3274, 3066, 3034, 2929, 1754, 1718, 1670, 1496, 1455, 1417, 1371, 1326, 1204, 1150, 1067, 1046, 1028 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.29 (m, 10H, Ar), 4.77 (dd, 1H, *J*=9.3 2.2, H(3)), 4.68 (*b*.t, 1H, *J*=5.6, NH), 4.50 (d, 1H, *J*=11.5, $O\underline{C}H_2Ph$), 4.28 (d, 1H, *J*=11.5, $O\underline{C}H_2Ph$), 4.22 (d, 2H, *J*=5.6, $NH\underline{C}H_2Ph$), 4.07 (q, 1H, *J*=6.7, H(1')), 2.92 (dd, 1H, *J*=9.3, 16.3, Ha(4)), 2.60 (*b*.d, 1H, *J*=16.3, Hb(4)), 2.33 (s, 3H, OAc), 2.16 (s, 3H, H(6)), 1.62 (s, 3H, Me(2)), 1.45 (d, 3H, *J*=6.7, H(2')). Rotamer in NH region (1:9): 4.41 (t, 1H, *J*=5.76, NH), 4.21 (d, 2H, *J*=5.76, $NH\underline{C}H_2Ph$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 205.9 (s, C(5)), 168.8 (s, $\underline{C}OCH_3$), 138.8 (s, C(1)), 137.6 (s, Ar), 131.0 (s, Ar), 128.9 (d, ^1J(C,H)=161, Ar),128.5 (d, ^1J(C,H)=160, Ar), 128.2 (s, C(2)), 128.1 (d, ^1J(C,H)=160, Ar), 128.0 (d, ^1J(C,H)=160, Ar), 127.8 (d, ^1J(C,H)=157, Ar), 72.0 (d, ^1J(C,H)=141, C(3)), 70.2 (t, ^1J(C,H)=140, $O\underline{C}H_2Ph$), 58.0 (d, ^1J(C,H)=136, C(1')), 47.4 (t, ^1J(C,H)=130, $NH\underline{C}H_2Ph$), 47.2 (t, ^1J(C,H)=127, C(4)), 30.8 (q, ^1J(C,H)=127, C(6)), 20.6 (q, ^1J(C,H)=130, $CO\underline{C}H_3$), 12.6 (q, ^1J(C,H)=130, Me(2)), 11.4 (q, ^1J(C,H)=129, C(2')).Anal. Calcd for $C_{25}H_{31}NO_6S$ (473.58): C, 63.40, H, 6.60. Found: C, 63.24, H, 6.51.

(±)-(1*E*, 3*RS*)-3-(Benzyloxy)-1-{(1'*RS*)-1'-[(diethylamino)sulfonyl]ethyl}-2-methylhexa-1,5-dienyl acetate (<u>48 a</u>):

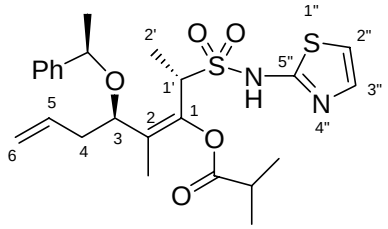


Same procedure as for the preparation of **<u>47a</u>**, using diene **<u>37</u>**, allyltrimethylsilane (**<u>40</u>**) and Et_2NH. FC (light petroleum ether/ EtOAc 1:1): 25% of **48a**, colorless oil.

IR (film): ν 3066, 2978, 2937, 1761, 1671, 1642, 1497, 1454, 1370, 1351, 1329, 1199, 1165, 1143, 1130, 1091, 1072, 1046, 1018 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.24 (m, 5H, Ar), 5.82 (dddd, 1H, *J*=17.3, 10.2, 8.0, 6.8, H(5)), 5.14 (dq, 1H, *J*=17.3, 1.5, Ha(6)), 5.09 (dm, 1H, *J*=10.2, Hb(6)), 4.58 (d, 1H, *J*=12.3, O<u>C</u>H_2Ph), 4.50 (d, 1H, *J*=12.3, O<u>C</u>H_2Ph), 4.27 (dd, 1H, *J*=8.0 6.5, H(3)), 4.21 (q, 1H, *J*=7.0, H(1')), 3.37 (dq, 2H, *J*=14.8, 7.0, Ha(1")), 3.22 (dq, 2H, *J*=14.8, 7.0, Hb(1")), 2.54 (ddd, 1H, *J*=14.8, 8.0, 6.5, Ha(4)), 2.34 (ddd, 1H, *J*=14.5, 8.0, 6.8, Hb(4)), 2.24 (s, 3H, Ac), 1.62 (s, 3H, Me(2)), 1.36 (d, 3H, *J*=7.0 Hz, H(2')), 1.18 (t, 6H, *J*=7.0, H(2")). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 168.1 (s, <u>C</u>OCH_3), 139.0 (s, C1), 138.6 (s, Ar), 134.1 (d, ^1J(C,H)=160, C(5)),130.9 (s, C2), 128.3 (d, ^1J(C,H)=160, Ar), 127.6 (d, ^1J(C,H)=157, Ar), 127.4 (d, ^1J(C,H)=161, Ar), 117.9 (t, ^1J(C,H)=154, C(6)) 77.8 (d, ^1J(C,H)=141, C(3)), 70.5 (t, ^1J(C,H)=142, O<u>C</u>H_2Ph), 58.4 (d, ^1J(C,H)=137, C(1')), 42.1 (t, ^1J(C,H)=136, C(1")), 38.6 (t, ^1J(C,H)=129, C(4)), 20.6 (q, ^1J(C,H)=130, CO<u>C</u>H_3),14.6 (q, ^1J(C,H)=127, C(2")), 13.2 (q, ^1J(C,H)=132, Me(2)), 11.5 (q, ^1J(C,H)=129, C(2')).

CI-MS (NH_3) : m/z 441 ([M+18], 10), 340(5), 245(3), 192(4), 153(7), 137(5), 120(8), 105(7), 92(11), 91(100), 77(5), 74(18), 72(15) Anal. Calcd for $C_{22}H_{33}NO_5S$ (423.21): C, 62.38, H 7.85. Found: C, 62.38, H, 7.81.

(±)-(1*E*, 3*RS*)-2-Methyl-3-{[(1*SR*)-1-phenylethyl]oxy}-1-{(1*SR*)-1-[(1,3 thiazol-2-ylamino)sulfonyl]ethyl}hexa-1,5-dien-1-yl 2-methylpropanoate (<u>48b</u>):



Same procedure as for the preparation of **48a**, using diene **37**, allyltrimethylsilane (**40**) and 2-aminothiazole. FC (CH_2Cl_2/ Et_2O 3:2). 20% of **48b**, colorless oil.

IR (film): ν 3147, 3106, 2978, 2928, 2812, 1752, 1668, 1641, 1572, 1538, 1451, 1418, 1330, 1301, 1224, 1116, 915 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.18 (m, 5H, Ar), 6.95 (d, 1H, *J*=4.5, H(3")), 6.44 (d, 1H, *J*=4.5, H(2")), 5.97-5.84 (m, 1H, H(5)), 5.14 (d, 1H, *J*=17.3, Ha(6)), 5.08 (d, 1H, *J*=10.2, Hb(6)), 4.42 (q, 1H, *J*=6.4, O<u>CH</u>(Me)Ph), 3.98 (dd, 1H, *J*=8.3, 3.8, H(3)), 3.58 (q, 1H, *J*=7.0, H(1')), 2.65 (sp, 1H, *J*=7.0, OC(O)<u>CH</u>$(CH_3)_2$), 2.50-2.41 (m, 2H, H(4)), 1.51 (s, 3H, Me(2)), 1.38 (d, 3H, *J*=6.4, OCH(<u>Me</u>)Ph), 1.29 (d, 3H, *J*=7.0, H(2')), 1.22, 1.21 (2d, 6H, *J*=7.0, OCOCH(<u>CH_3</u>)$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 174.6 (s, C(1")), 171.0 (s, <u>CO</u>$CH(CH_3)_2$), 143.6 (s, C(1)), 137.9 (s, Ph), 135.4 (d, ^1J(C,H)=153, C(5)), 128.4 (d, ^1J(C,H)=160, Ph), 127.7 (d, ^1J(C,H)=161, Ph), 126.5 (d, ^1J(C,H)=158, Ph), 124.0 (d, ^1J(C,H)=195, C(3")), 117.7 (s, C(2)), 116.8 (t, ^1J(C,H)=157, C(6)), 108.0 (d, ^1J(C,H)=196, C(2")), 73.9 (d, ^1J(C,H)=144, O<u>CH</u>(Me)Ph), 73.5 (d, ^1J(C,H)=143, C(3)), 57.8 (d, ^1J(C,H)=137, C(1')), 37.5 (t, ^1J(C,H)=125, C(4)), 34.1 (d, ^1J(C,H)=130, OCO<u>CH</u>$(CH_3)_2$), 25.0 (q, ^1J(C,H)=131, OCH(<u>Me</u>)Ph), 19.1, 19.0 (2q, ^1J(C,H)=128, OCOCH(<u>CH_3</u>)$_2$), 12.4 (q, ^1J(C,H)=131, C(2')), 11.0 (q, ^1J(C,H)=128, Me(2)). CI-MS (NH_3) : m/z 492 ([M+1], 73), 492([M], 1), 451(3), 429(4), 389(2), 376(9), 359(12), 331(7), 301(31), 259(5), 246(10), 205(5), 171/5), 138(7), 105(18), 101(100), 100(11). HRMS Calcd for $C_{24}H_{32}N_2O_5S_2$ + Na 515.1650. Found: 515.1659.

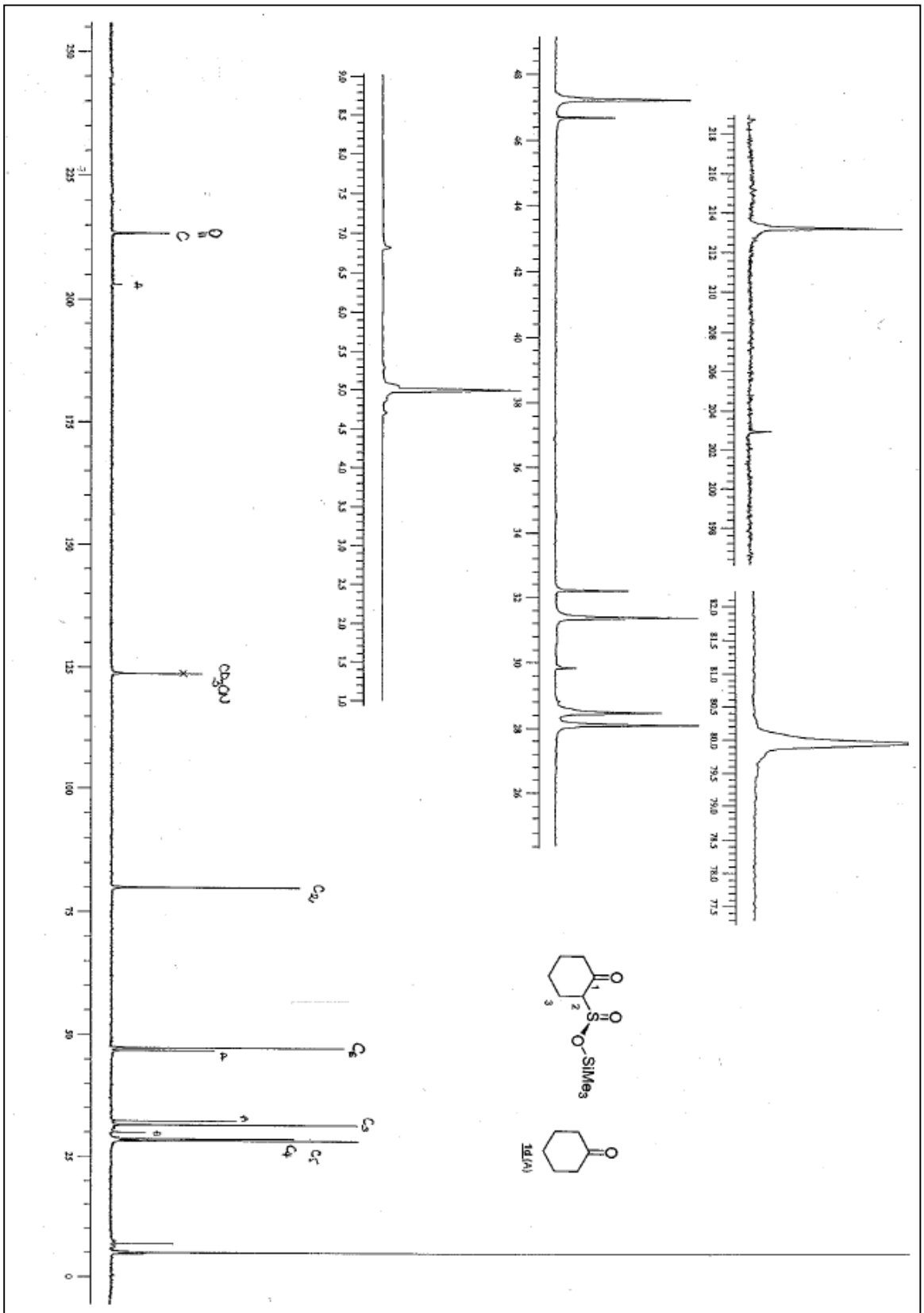

SiMe3
14d (A)

Figure S1: ^{13}C NMR (proton noise decoupled) spectrum of **3d** and **1d** (ca. 15%). Mixture obtained by reaction of **2d** +SO_2/ (*t*Bu)Me_2SiOTf, shows as a single diastereoisomer for **3d**.

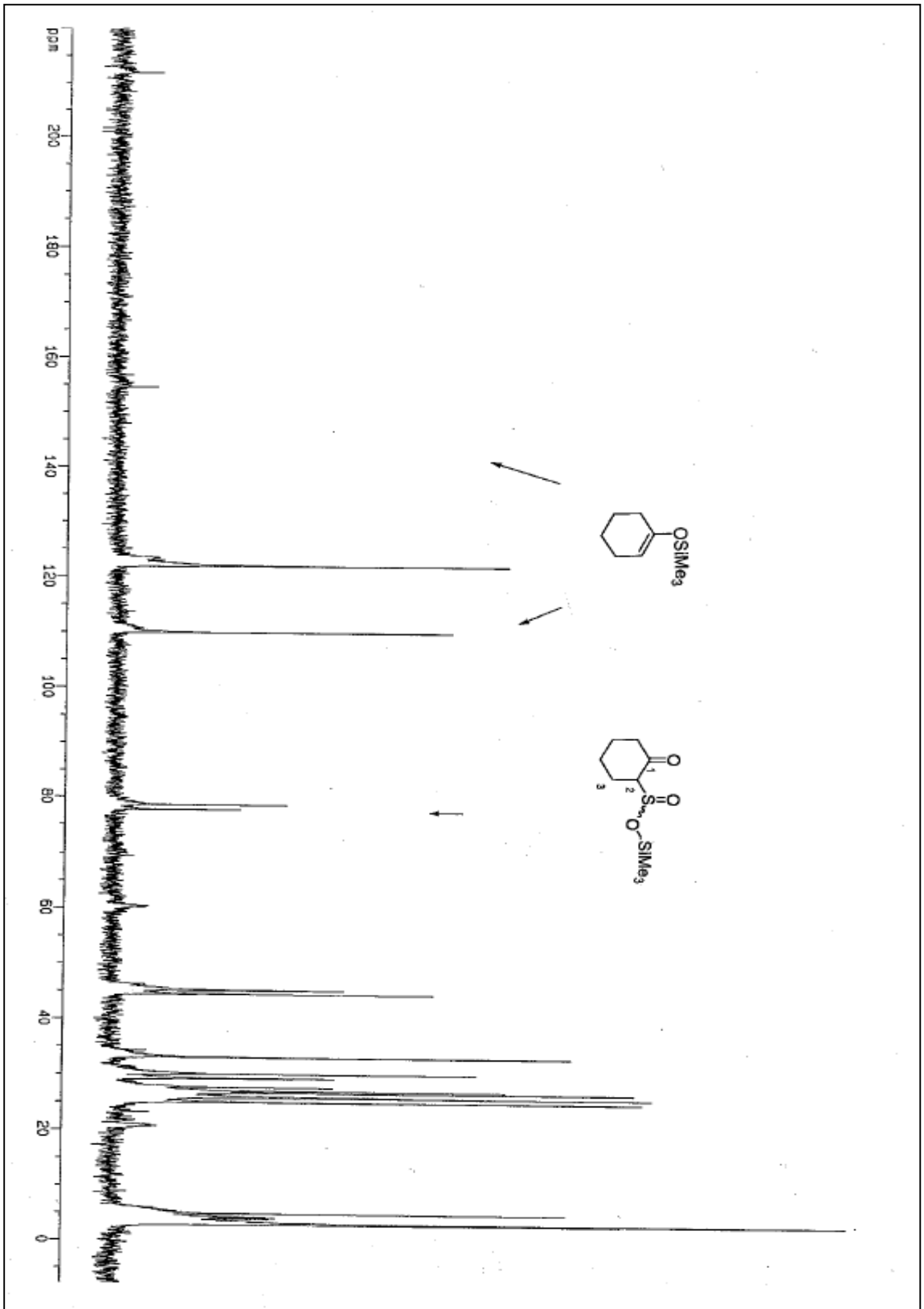


Figure S2: ^{13}C NMR (proton noise decoupled) spectrum of **3d** and **2d** (30%) obtained by reaction of **2d** +SO_2in CD_3CN, no Lewis acid. A 6:4 mixture of two diastereoisomers for **3d** is formed.

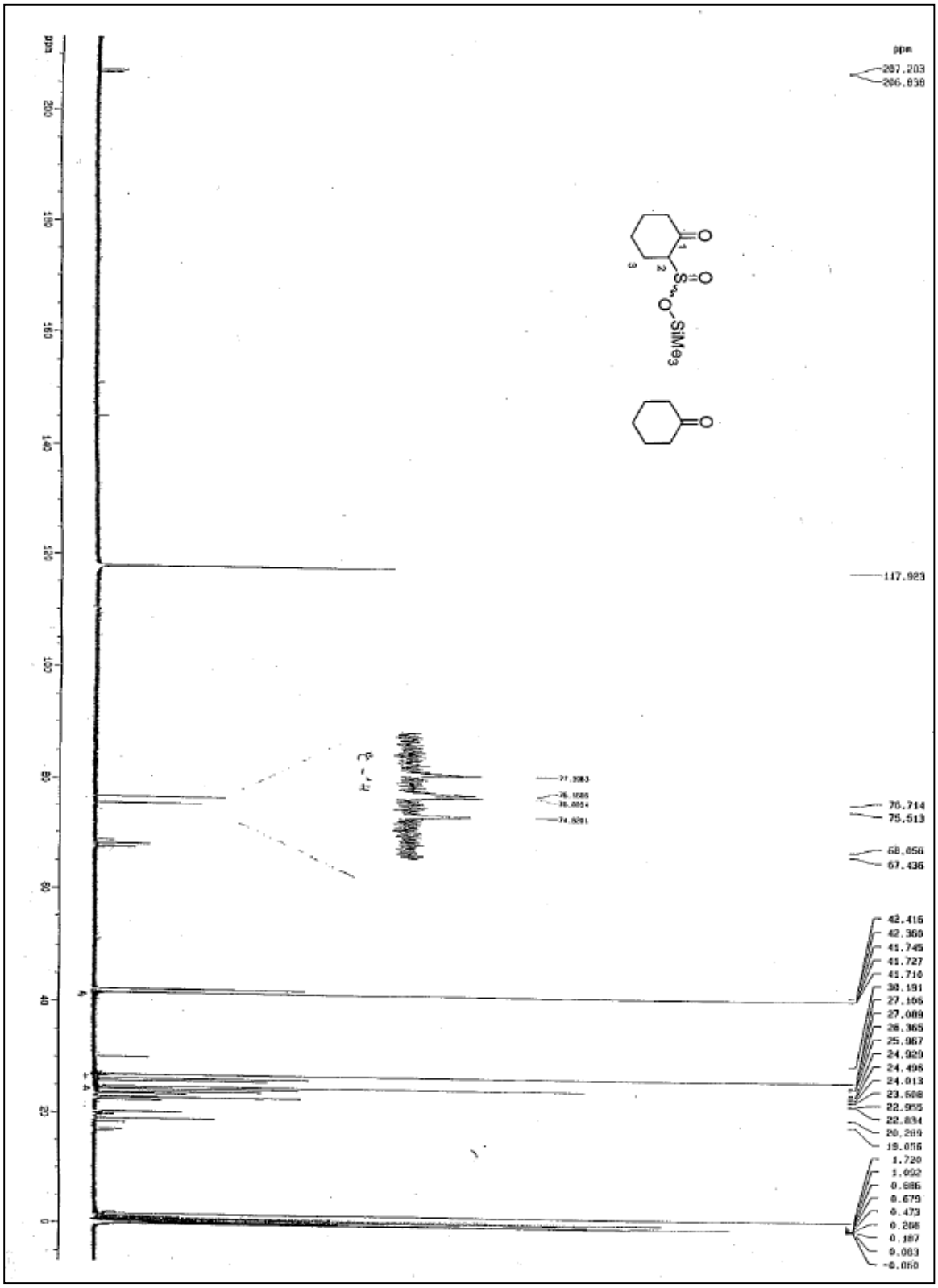


Figure S3: ^{13}C NMR (proton noise decoupled) spectrum of **3d** and **1d** (<5%) obtained by reaction of **2d** +SO_2 in CD_3CN, no Lewis acid. A 5:4 mixture of two diastereoisomer **3d** is obtained after 36 h at 300 K.

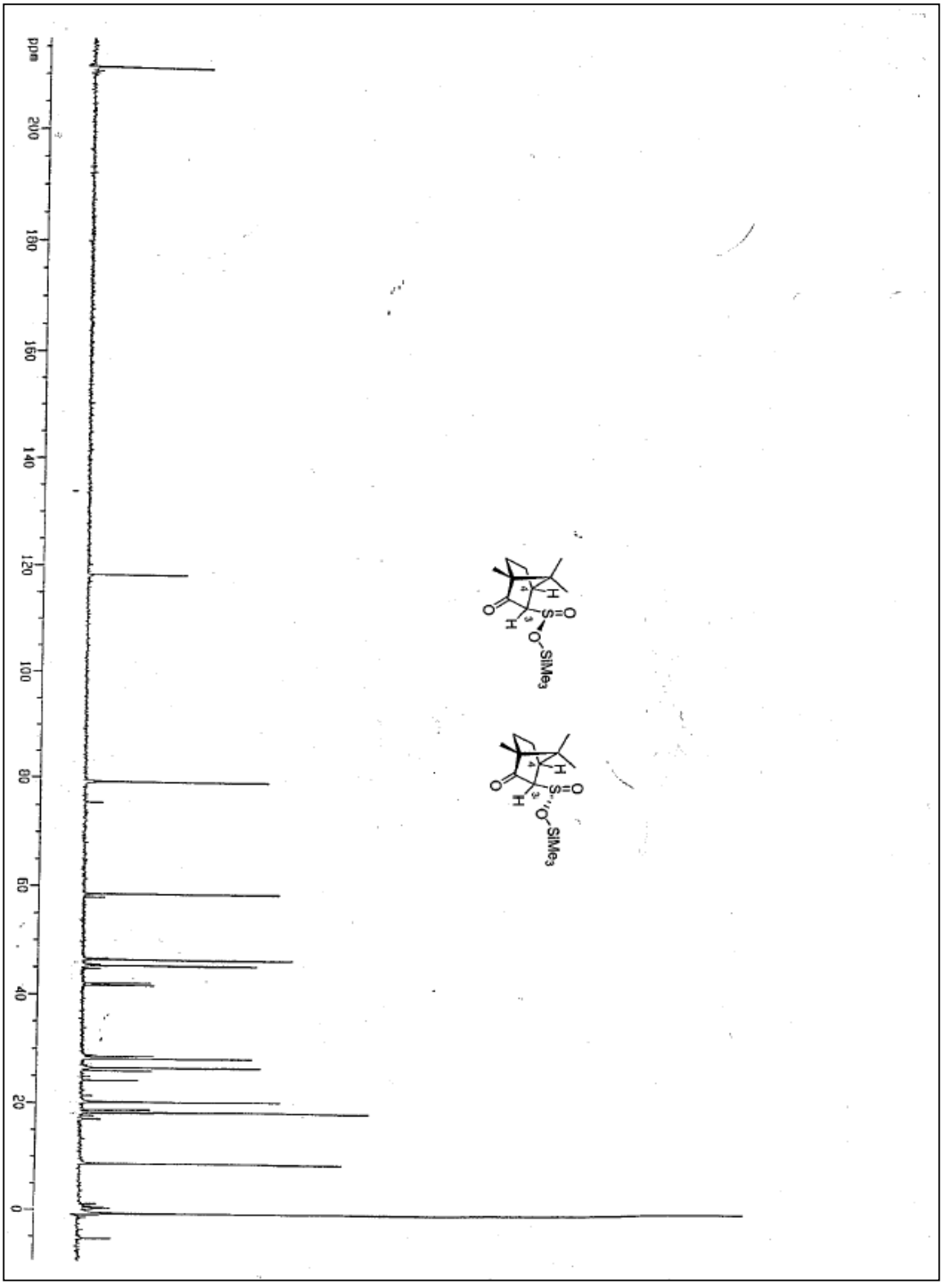


Figure S4: ^{13}C NMR (proton noise decoupled) spectrum of **3e** in presence of TBSOTf obtained by reaction of **2e** +SO_2 in CD_3CN at -78°C, 20 min. It shows one major diastereoisomer.

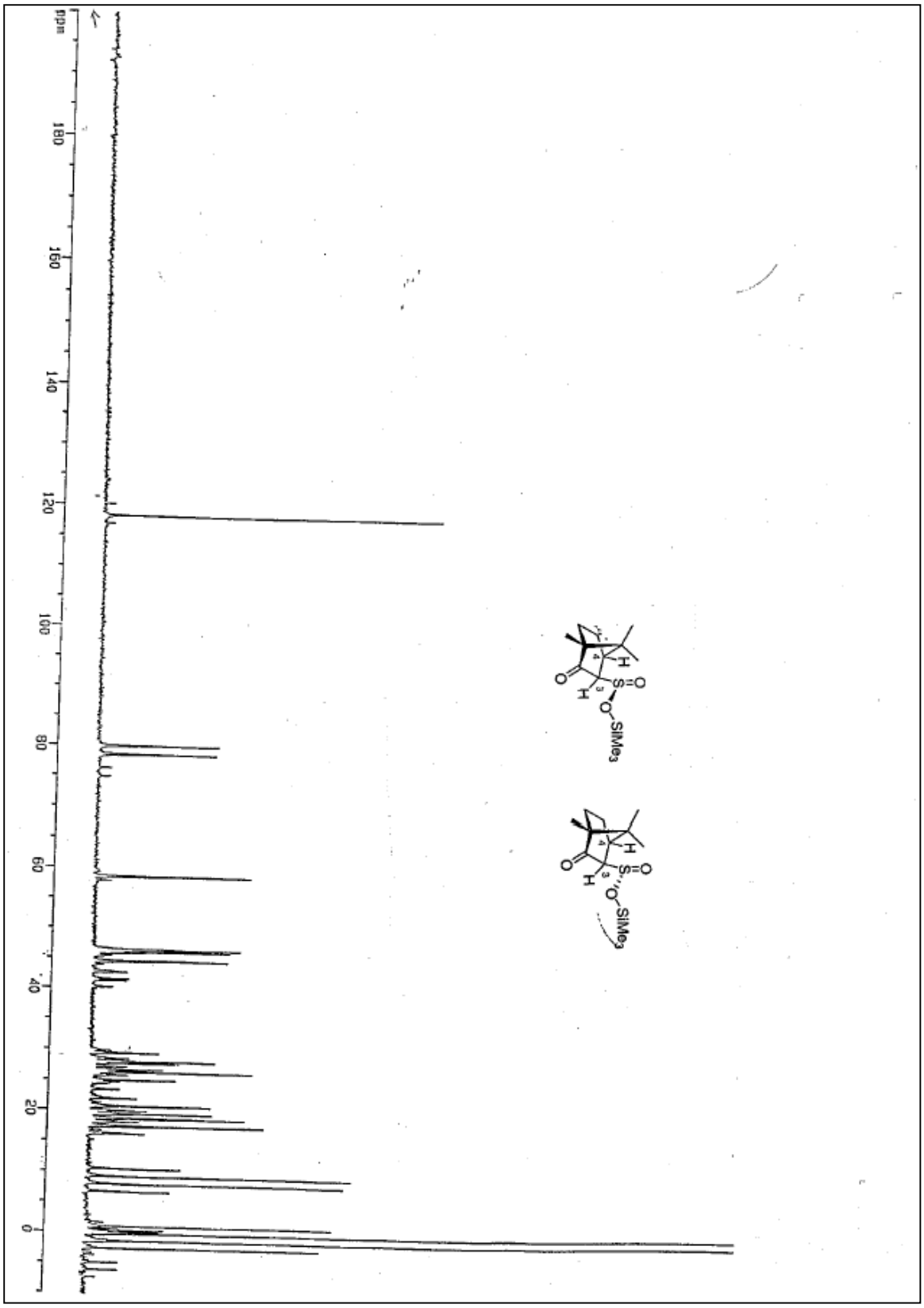


Figure S5: ^{13}C NMR (with ^{1}H coupling) spectrum of **3e** before equilibration of the diastereoisomers (-78°C, 40 min.).

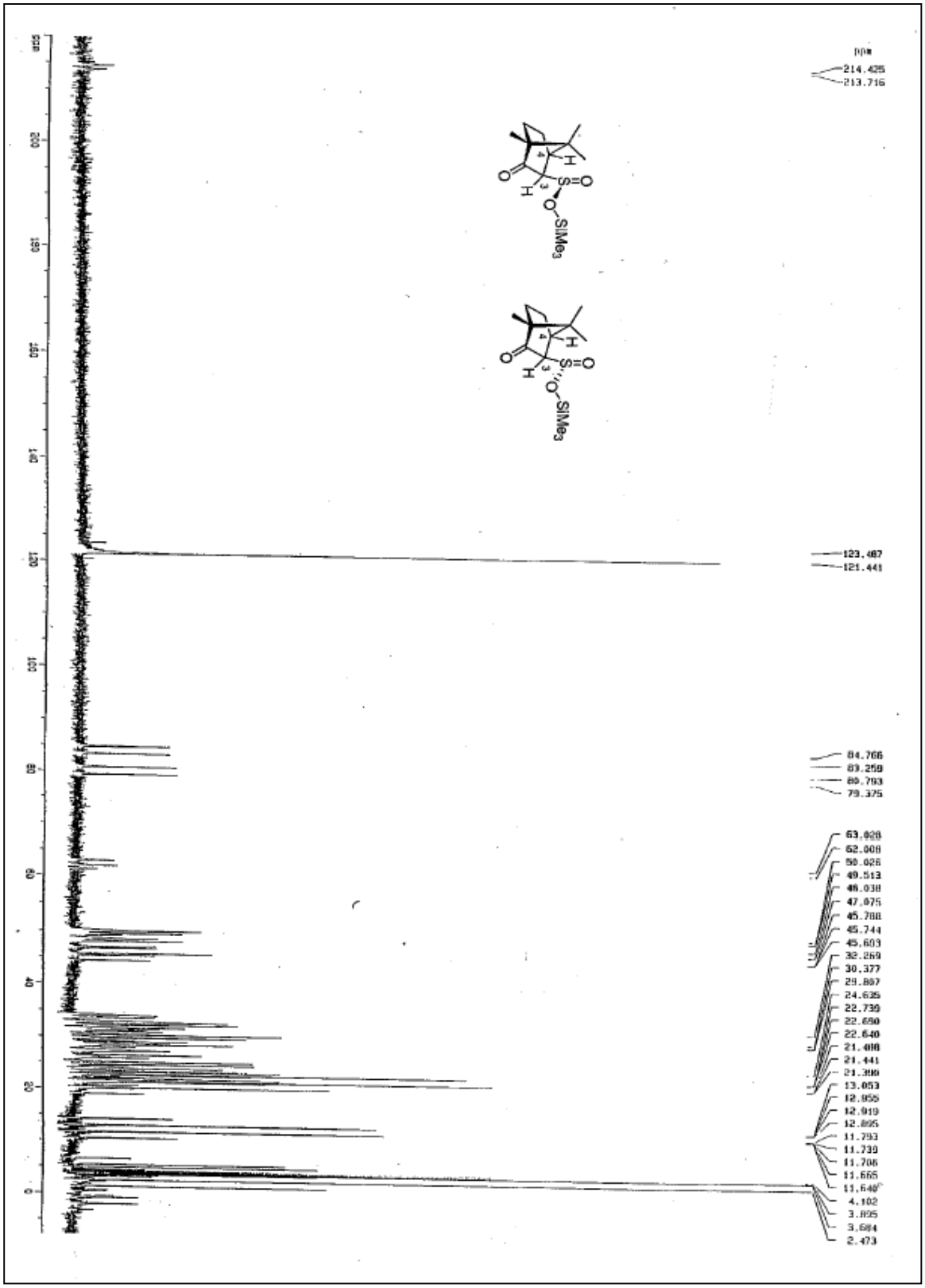


Figure S6: ^{13}C NMR spectrum (with ^{1}H coupling) of **3e** in absence of Lewis acid, after equilibration for 12 h. at -40°C in CD_3CN. A 1:1 mixture of two diastereoisomeric sulfinates **3e** is obtained.

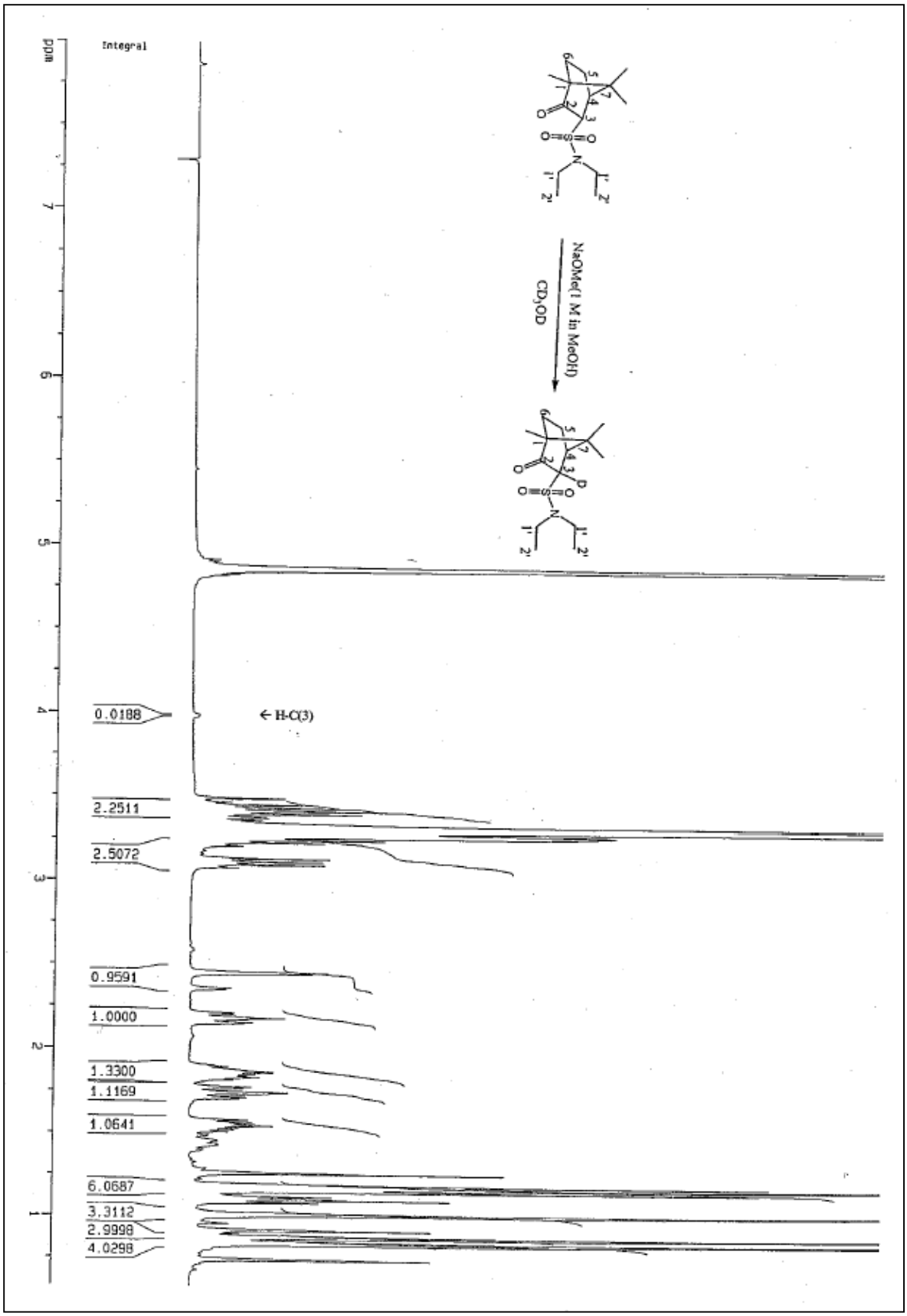


Figure S7. ^{1}H NMR spectrum of **15**/**D-15** in CD_3OH / CD_3OD.

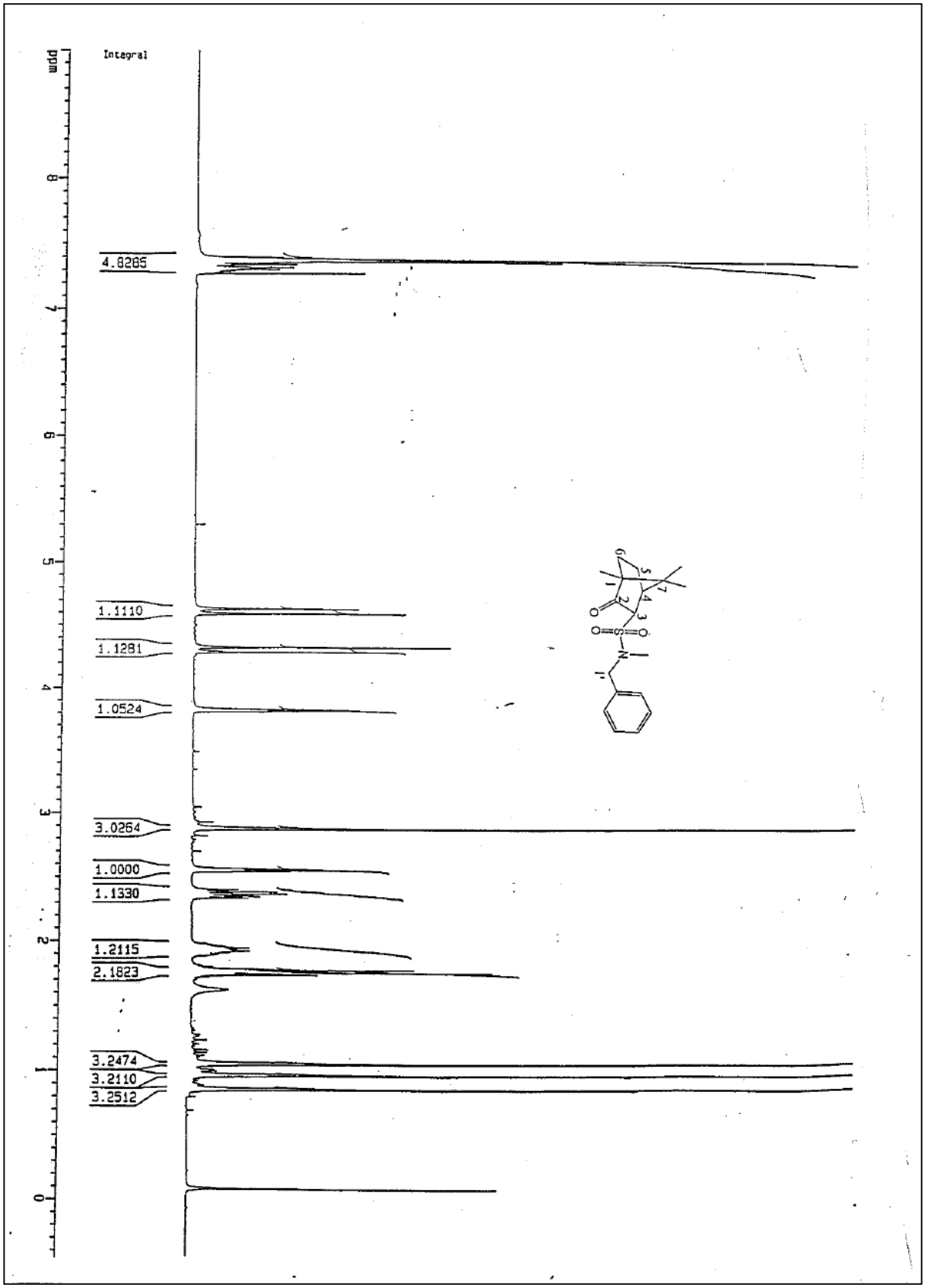


Figure S8. ^{1}H NMR spectrum of **16** in $CDCl_3$.

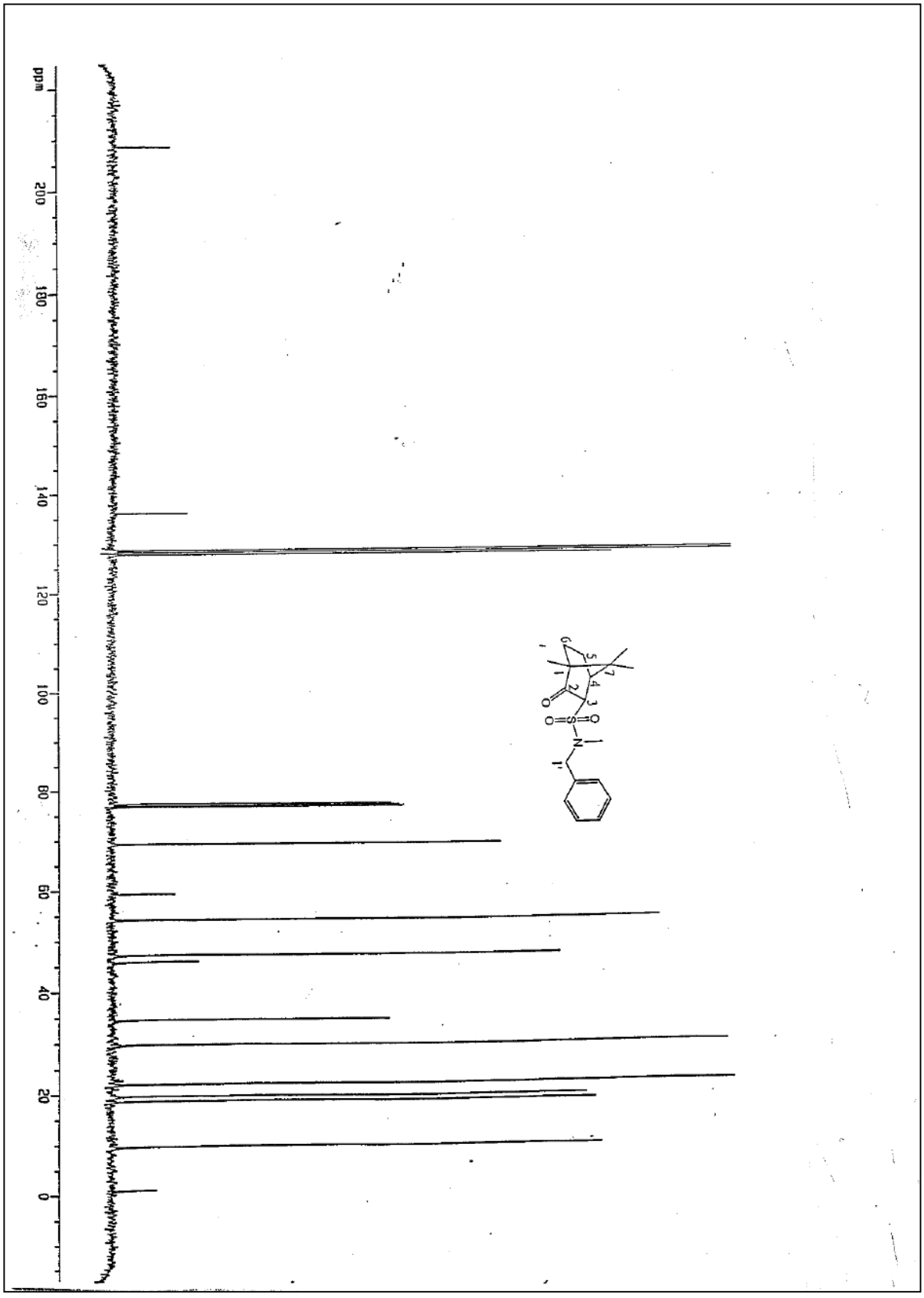


Figure S9. ^{13}C NMR spectrum of **16** in $CDCl_3$.