Supporting Information
for

**Sulfinyl-Mediated Stereoselective Overman
Rearrangements and Diels-Alder Cycloadditions**

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NMR data for (E)- and (Z)-hydroxy vinyl sulfoxides

¹H NMR (CDCl₃, 400 MHz) 2e ^{13}C NMR (CDCl_3 , 100 MHz) 2e

¹H NMR (CDCl₃, 400 MHz) 3e

¹³C NMR (CDCl₃, 100 MHz) 3e

¹H NMR (CDCl₃, 400 MHz) 2j

¹³C NMR (CDCl₃, 100 MHz) 2j

^1H NMR (CDCl_3 , 400 MHz) 3j

^{13}C NMR (CDCl_3 , 100 MHz) 3j

¹H NMR (CDCl₃, 400 MHz) 2k

¹³C NMR (CDCl₃, 100 MHz) 2k

^1H ^1H COSY (CDCl_3 , 400 MHz) 2k

^1H ^{13}C HSQC (CDCl_3 , 100 MHz) 2k

^1H NMR (CDCl_3 , 400 MHz) 3k

^{13}C NMR (CDCl_3 , 100 MHz) 3k

^1H ^1H COSY (CDCl_3 , 400 MHz) 3k

^1H ^{13}C HSQC (CDCl_3 , 100 MHz) 3k

¹H NMR (CDCl₃, 300 MHz) 8d

¹³C NMR (CDCl₃, 75 MHz) 8d

^1H NMR (CDCl_3 , 400 MHz) 8i

^{13}C NMR (CDCl_3 , 100 MHz) 8i

^1H NMR (CDCl_3 , 500 MHz) 8j

^{13}C NMR (CDCl_3 , 125 MHz) 8j

¹H NMR (CDCl₃, 500 MHz) 8k

¹³C NMR (CDCl₃, 125 MHz) 8k

¹H NMR (CDCl₃, 400 MHz) 9d

¹³C NMR (CDCl₃, 100 MHz) 9d

¹H NMR (CDCl₃, 400 MHz) 10d

¹³C NMR (CDCl₃, 100 MHz) 10d

^1H NMR (CDCl_3 , 400 MHz) 9i

^{13}C NMR (CDCl_3 , 100 MHz) 9i

^1H NMR (CDCl_3 , 400 MHz) 10i

^{13}C NMR (CDCl_3 , 100 MHz) 10i

^1H NMR (CDCl_3 , 400 MHz) 9j

^{13}C NMR (CDCl_3 , 100 MHz) 9j

^1H NMR (CDCl_3 , 400 MHz) 10j

^{13}C NMR (CDCl_3 , 100 MHz) 10j

¹H NMR (CDCl₃, 300 MHz) 9k

¹³C NMR (CDCl₃, 100 MHz) 9k

¹H NMR (CDCl₃, 300 MHz) 10k

¹³C NMR (CDCl₃, 100 MHz) 10k

¹H NMR (CDCl₃, 400 MHz) 4e Cc1ccc(cc1)S(=O)(=O)[C@H](CCOC(=N)C(C)(C)C)C=C[C@@H](COSSi(C)(C)C(C)(C)C)c1ccccc1

TBDPSO

¹H NMR (CDCl₃, 400 MHz) 5e+5e'

¹³C NMR (CDCl₃, 100 MHz) 5e+5e'

¹H NMR (CDCl₃, 400 MHz) 11a

¹³C NMR (CDCl₃, 100 MHz) 11a

^1H ^1H COSY (CDCl_3 , 400 MHz) 11a

^1H ^{13}C HSQC (CDCl_3 , 400 MHz) 11a

¹H NMR (CDCl₃, 400 MHz) 12a+12a'

¹³C NMR (CDCl₃, 100 MHz) 12a+12a'

^1H ^1H COSY (CDCl_3 , 400 MHz) 12a+12a'

^1H ^{13}C HSQC (CDCl_3 , 400 MHz) 12a+12a'

^1H NMR (CDCl_3 , 400 MHz) 11c

^{13}C NMR (CDCl_3 , 100 MHz) 11c

^1H NMR (CDCl_3 , 400 MHz) 12c+12c'

^{13}C NMR (CDCl_3 , 100 MHz) 12c+12c'

¹H NMR (CDCl₃, 400 MHz) 11d

¹³C NMR (CDCl₃, 100 MHz) 11d

¹H NMR (CDCl₃, 400 MHz) 12d+12d'

¹³C NMR (CDCl₃, 100 MHz) 12d+12d'

NMR data for sulfinyl trichloroacetamides and derivatives

¹H NMR (CDCl₃, 400 MHz) 13e:14e

¹³C NMR (CDCl₃, 100 MHz) 13e:14e

¹H NMR (CDCl₃, 500 MHz) 15e:16e

¹³C NMR (CDCl₃, 125 MHz) 15e:16e

^1H NMR (CDCl_3 , 400 MHz) 14c

^{13}C NMR (CDCl_3 , 100 MHz) 14c

^1H NMR (CDCl_3 , 400 MHz) 15c:16c

54 : 46

^{13}C NMR (CDCl_3 , 100 MHz) 15c:16c

54 : 46

¹H NMR (CDCl₃, 400 MHz) 13d:14d, 5:95

¹³C NMR (CDCl₃, 100 MHz) 13d:14d, 5:95

^1H NMR (CDCl_3 , 500 MHz) 25 + 26

^{13}C NMR (CDCl_3 , 125 MHz) 25 + 26

^1H ^1H COSY (CDCl_3 , 400 MHz) 25 + 26

^1H ^{13}C HSQC (CDCl_3 , 400 MHz) 25 + 26

^1H NMR (CDCl_3 , 400 MHz) 21j

^{13}C NMR (CDCl_3 , 100 MHz) 21j

^1H ^{13}C HSQC (CDCl_3 , 400 MHz) 21j

^1H NMR (CDCl_3 , 400 MHz) 22j

^{13}C NMR (CDCl_3 , 100 MHz) 22j

^1H ^{13}C HSQC (CDCl_3 , 400 MHz) 22j

¹H NMR (CDCl₃, 400 MHz) 21k

¹³C NMR (CDCl₃, 100 MHz) 21k

^1H ^1H COSY (CDCl_3 , 400 MHz) 21k

^1H ^{13}C HSQC (CDCl_3 , 400 MHz) 21k

¹H NMR (CDCl₃, 400 MHz) 22k

¹³C NMR (CDCl₃, 100 MHz) 22k

^1H ^1H COSY (CDCl_3 , 400 MHz) 22k

^1H ^{13}C HSQC (CDCl_3 , 400 MHz) 22k

¹H NMR (CDCl₃, 400 MHz) 23i

¹³C NMR (CDCl₃, 100 MHz) 23i

¹H NMR (CDCl₃, 400 MHz) 24i

¹³C NMR (CDCl₃, 100 MHz) 24i

CC(C=C(C(=O)NCCl)(C)C)C(=O)Sc1ccc(C)cc1 CC(C=C(C(=O)NCCl)(C)C)S(=O)(c1ccccc1)C2=CC=CC=C2

¹H NMR (CDCl₃, 400 MHz) 24j

¹³C NMR (CDCl₃, 100 MHz) 24j

¹H NMR (CDCl₃, 500 MHz) 23k

¹³C NMR (CDCl₃, 125 MHz) 23k

¹H NMR (CDCl₃, 500 MHz) 24k

^{13}C NMR (CDCl_3 , 125 MHz) 24k

^1H ^1H COSY (CDCl_3 , 500 MHz) 24k

^1H ^{13}C HSQC (CDCl_3 , 400 MHz) 24k

^1H NMR (CDCl_3 , 400 MHz) 27

^{13}C NMR (CDCl_3 , 100 MHz) 27

^1H ^1H COSY (CDCl₃, 400 MHz) 27

¹H NMR (CDCl₃, 400 MHz) 28

¹³C NMR (CDCl₃, 100 MHz) 28

^1H ^1H COSY (CDCl₃, 400 MHz) 28

^1H ^{13}C HSQC (CDCl₃, 400 MHz) 28

¹H NMR (CDCl₃, 500 MHz) 29

¹³C NMR (CDCl₃, 125 MHz) 29

^1H ^1H COSY (CDCl_3 , 500 MHz) 29

^1H ^{13}C HSQC (CDCl_3 , 500 MHz) 29

Diels Alder adducts: from *Z,E*-dienes

^1H NMR (CDCl_3 , 400 MHz) 30i

^{13}C NMR (CDCl_3 , 100 MHz) 30i

$^1\text{H } ^{13}\text{C HSQC (CDCl}_3, 400 \text{ MHz) 30i}$

¹H NMR (CDCl₃, 400 MHz) 31i

¹³C NMR (CDCl₃, 100 MHz) 31i

^1H NMR (CDCl_3 , 400 MHz) 30j

^{13}C NMR (CDCl_3 , 100 MHz) 30j

CC1=C(C(=O)NCCl)C(=C(C=C1)S(=O)(=O)c2ccc(C)cc2)C(=O)N3C(=O)c4ccccc4C3=O

¹H NMR (CDCl₃, 500 MHz) 30k

^{13}C NMR (CDCl_3 , 125 MHz) 30k

^1H ^1H COSY (CDCl_3 , 500 MHz) 30k

^1H ^{13}C HSQC (CDCl_3 , 500 MHz) 30k

Chemical structure of the compound is shown above the spectrum. The structure is a complex bicyclic molecule with a sulfonamide group (SO_2NH_2) and a phenyl group (Ph). The spectrum shows peaks corresponding to the structure, with integration values provided for several peaks.

Integration values (from left to right): 0.97, 21.36, 2.33, 2.11, 1.11, 1.15, 1.10, 1.17, 1.18, 3.42.

Chemical structure of the compound is shown above the spectrum. The structure is a complex polycyclic molecule featuring a central carbon atom bonded to a phenyl group (Ph), a sulfonyl group (SO₂Ph), a carbonyl group (C=O), and a nitrogen atom (N). The nitrogen atom is part of a five-membered ring containing a carbonyl group (C=O) and a phenyl group (Ph). The molecule also contains a chlorine atom (Cl) and a trifluoroacetyl group (CF₃CO).

^1H ^1H COSY (CDCl_3 , 500 MHz) 31k

^1H ^{13}C HSQC (CDCl_3 , 500 MHz) 31k

Diels-Alder adducts: from *E,E*-dienes

^1H NMR (CDCl_3 , 400 MHz) 35h

^{13}C NMR (CDCl_3 , 100 MHz) 35h

^1H ^1H COSY (CDCl_3 , 400 MHz) 35h

^1H ^{13}C HSQC (CDCl_3 , 400 MHz) 35h

¹H NMR (CDCl₃, 300 MHz) 36h

¹³C NMR (CDCl₃, 125 MHz) 36h

^1H ^1H COSY (CDCl_3 , 300 MHz) 36h

^1H ^{13}C HSQC (CDCl_3 , 300 MHz) 36h

Chemical structure of compound 10 is shown in the inset. The structure is a complex polycyclic molecule featuring a trichloroacetamido group (Cl_3COCHN), a p-toluenesulfonyl group ($\text{SO}_2\text{p-Tol}$), and a phenyl group (Ph).

^1H NMR spectrum (CDCl₃) of compound 10. The x-axis represents chemical shift in ppm (t1), ranging from 0.0 to 10.0. The spectrum shows several peaks with corresponding integration values:

- Peak at ~1.0 ppm: Integration 1.07
- Peak at ~2.1 ppm: Integration 13.59
- Peak at ~2.3 ppm: Integration 0.92
- Peak at ~2.5 ppm: Integration 2.08
- Peak at ~2.7 ppm: Integration 0.95
- Peak at ~2.9 ppm: Integration 0.93
- Peak at ~3.1 ppm: Integration 3.00
- Peak at ~3.3 ppm: Integration 3.19

¹H ¹³C HSQC (CDCl₃, 300 MHz) 35j

^1H NMR (CDCl_3 , 500 MHz) 36j

^{13}C NMR (CDCl_3 , 125 MHz) 36j

^1H NMR (CDCl_3 , 300 MHz) 37

^{13}C NMR (CDCl_3 , 100 MHz) 37

^1H ^1H COSY (CDCl_3 , 300 MHz) 37

^1H ^{13}C HSQC (CDCl_3 , 100 MHz) 37

^1H NMR (CDCl_3 , 300 MHz) 38

^{13}C NMR (CDCl_3 , 125 MHz) 38

^1H ^1H COSY (CDCl₃, 300 MHz) 38

^1H ^{13}C HSQC (CDCl₃, 500 MHz) 38

¹H NMR (CDCl₃, 500 MHz) 39

¹³C NMR (CDCl₃, 125 MHz) 39

^1H ^1H COSY (CDCl_3 , 500 MHz) 39

^1H ^{13}C HSQC (CDCl_3 , 500 MHz) 39

^1H ^{13}C HMBC (CDCl_3 , 500 MHz) 39