Supplementary Material

Efficient and Stereoselective Syntheses of Isomerically Pure 4-Aminotetrahydro-2*H*-thiopyran 1-Oxide Derivatives

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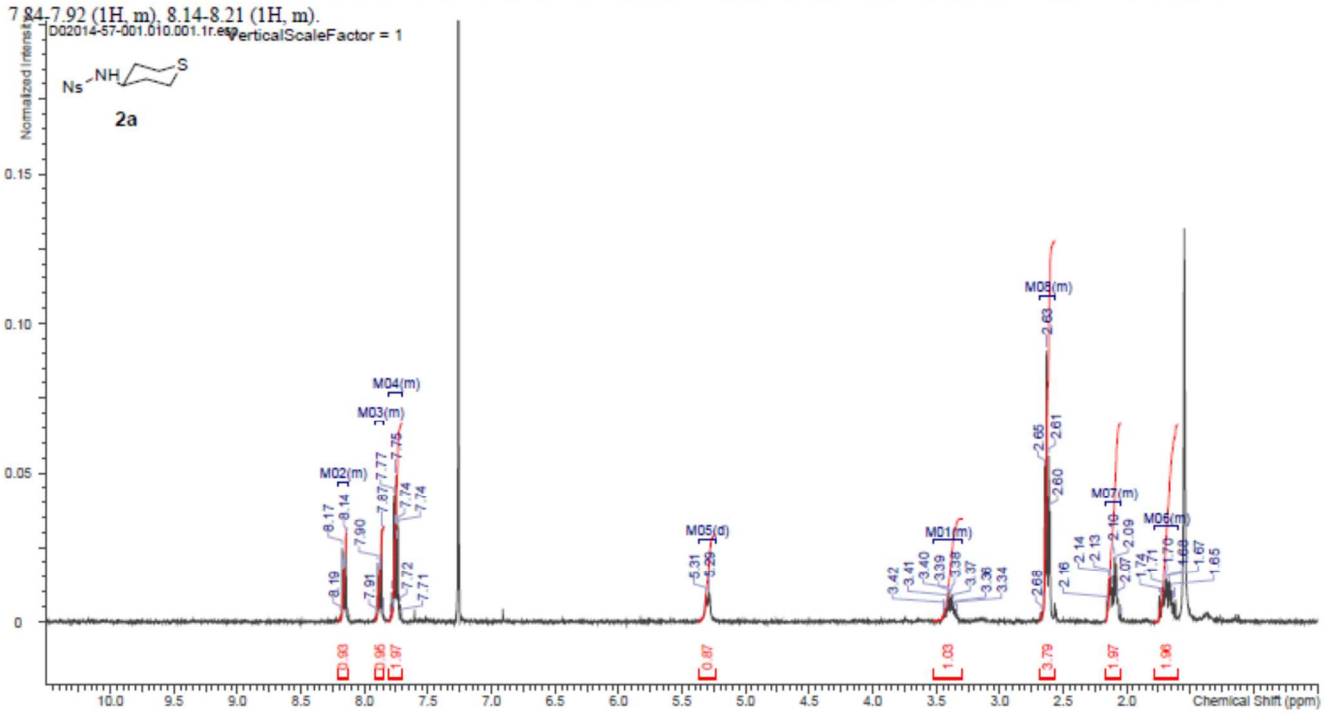
^{1}H NMR Spectral Data

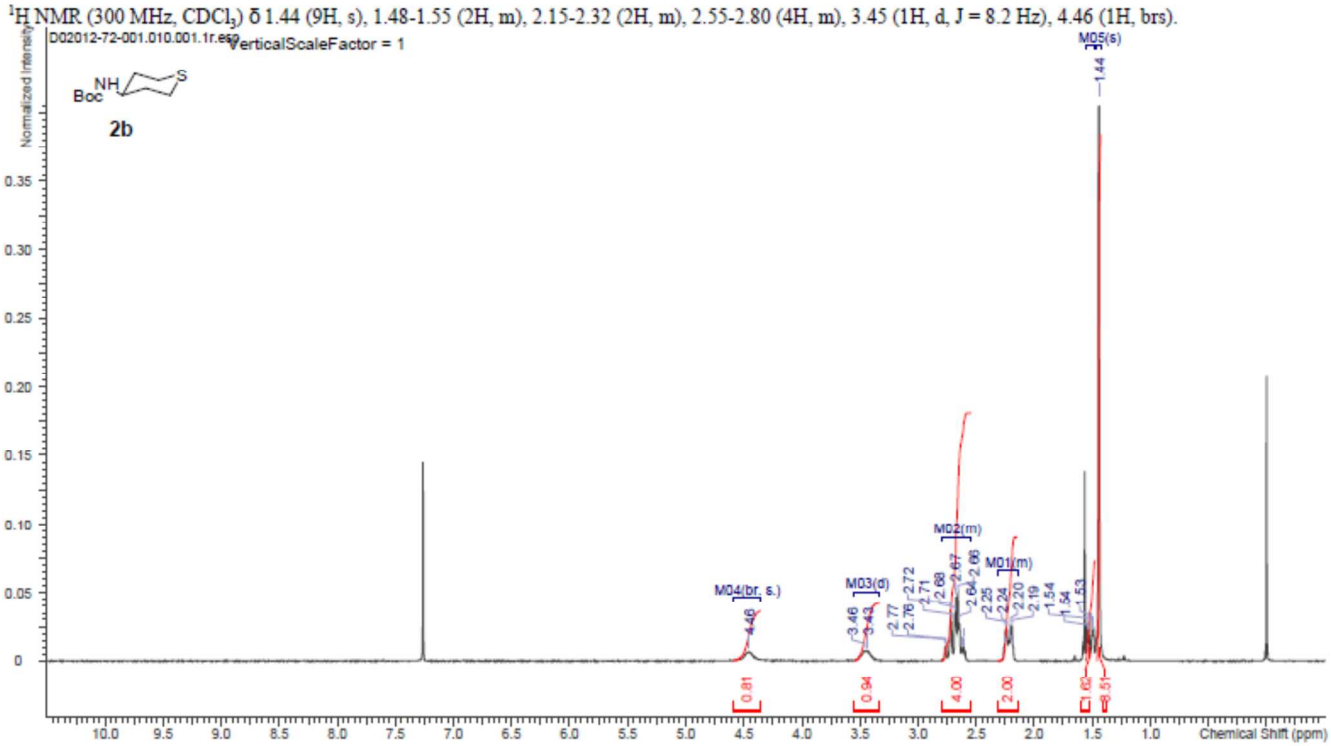
^{1}H NMR spectrum of Ns-**2a**

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60-1.79 (2H, m), 2.05-2.16 (2H, m), 2.57-2.68 (4H, m), 3.30-3.52 (1H, m), 5.30 (1H, d, J = 7.8 Hz), 7.70-7.81 (2H, m), 7.84-7.92 (1H, m), 8.14-8.21 (1H, m).



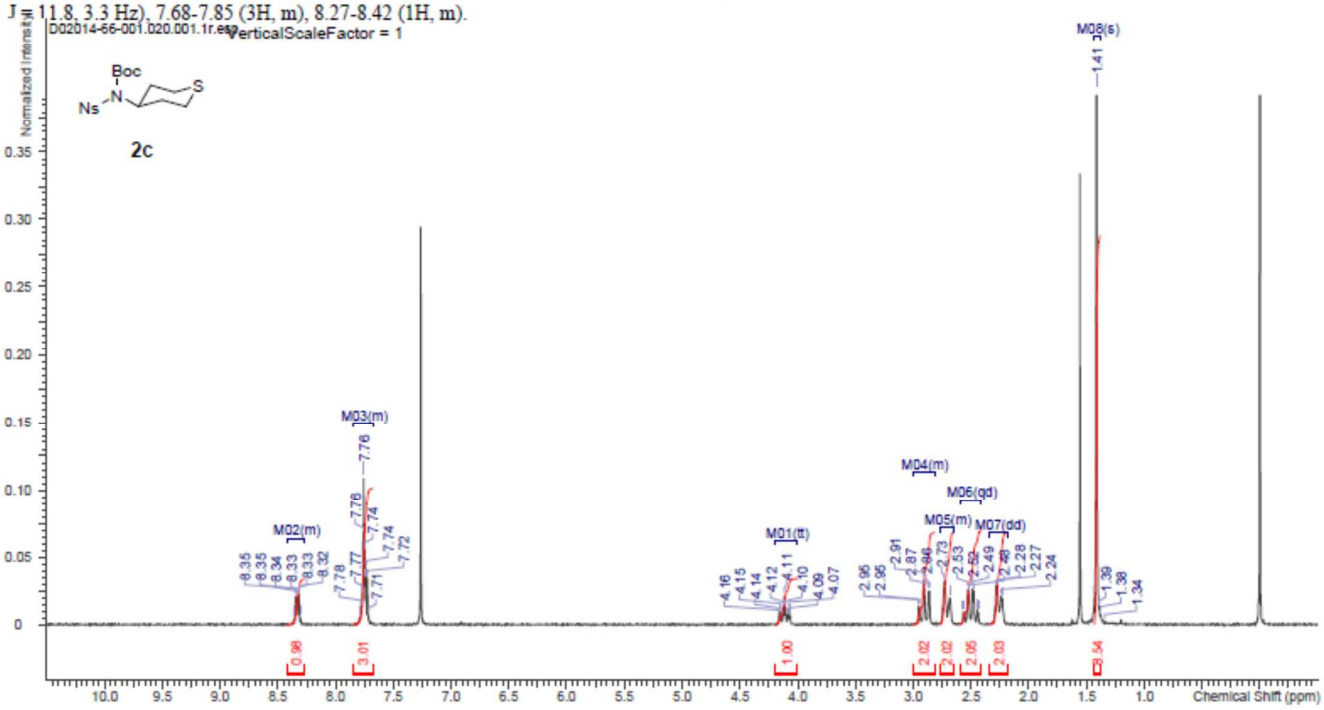
^{1}H NMR spectrum of Boc-**2b**

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (9H, s), 1.48-1.55 (2H, m), 2.15-2.32 (2H, m), 2.55-2.80 (4H, m), 3.45 (1H, d, J = 8.2 Hz), 4.46 (1H, brs).



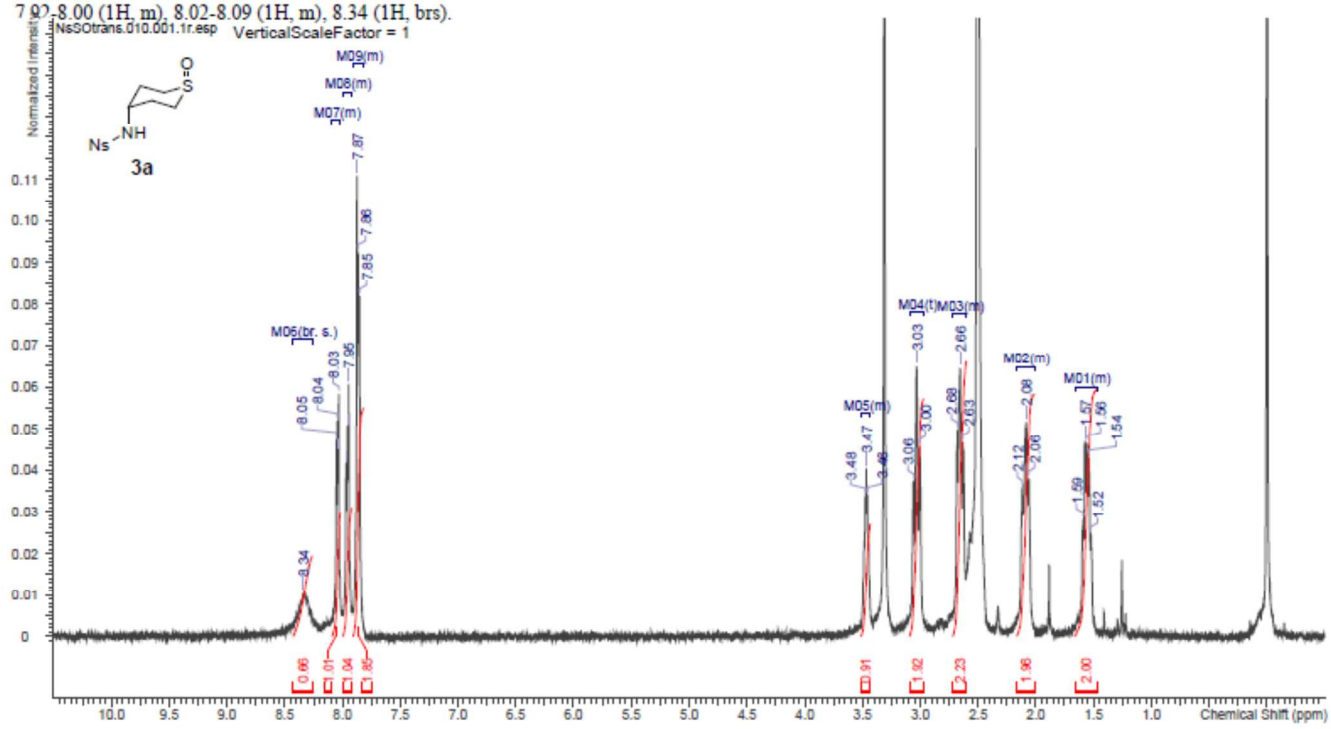
^{1}H NMR spectrum of Ns,Boc-**2c**

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (9H, s), 2.26 (2H, dd, J = 12.7, 3.0 Hz), 2.50 (2H, qd, J = 12.3, 3.3 Hz), 2.65-2.77 (2H, m), 2.81-3.00 (2H, m), 4.11 (1H, tt, J = 11.8, 3.3 Hz), 7.68-7.85 (3H, m), 8.27-8.42 (1H, m).



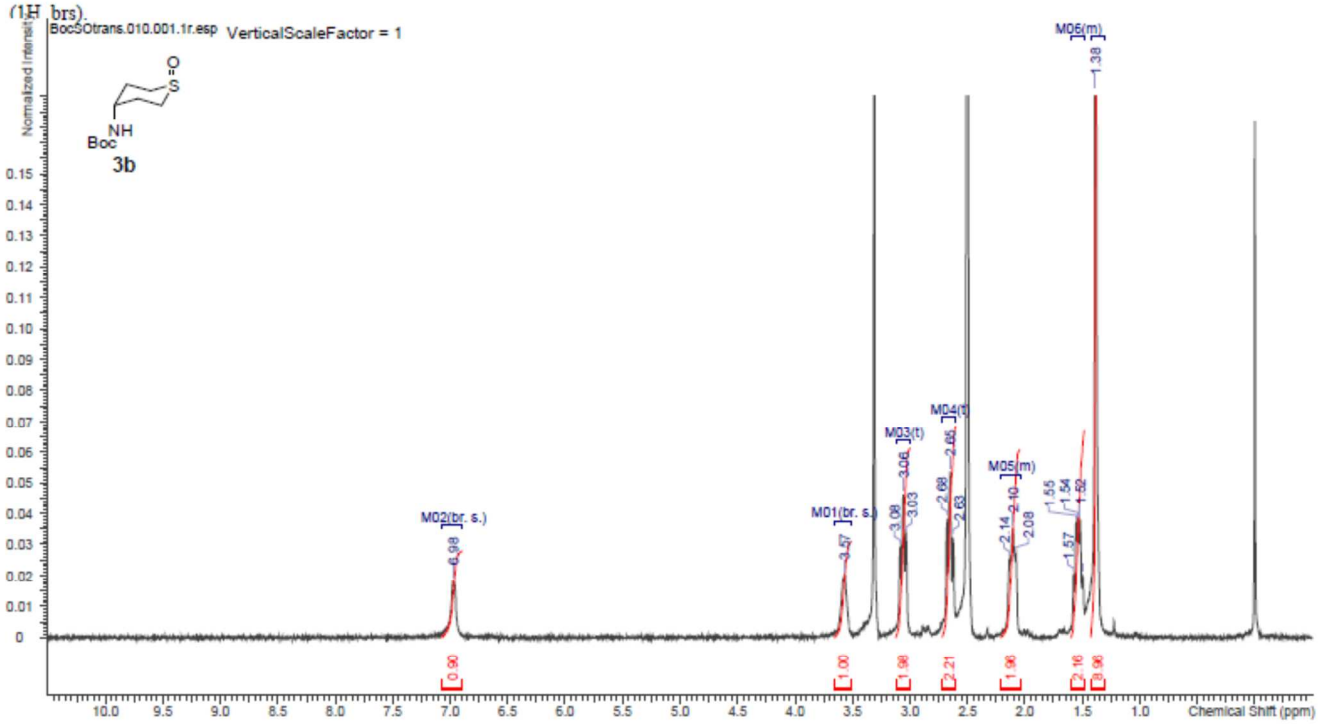
^{1}H NMR spectrum of *trans*-Ns-**3a**

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.47-1.66 (2H, m), 2.01-2.16 (2H, m), 2.60-2.72 (2H, m), 3.03 (2H, t, J = 10.9 Hz), 3.43-3.51 (1H, m), 7.82-7.91 (2H, m), 7.92-8.00 (1H, m), 8.02-8.09 (1H, m), 8.34 (1H, brs).



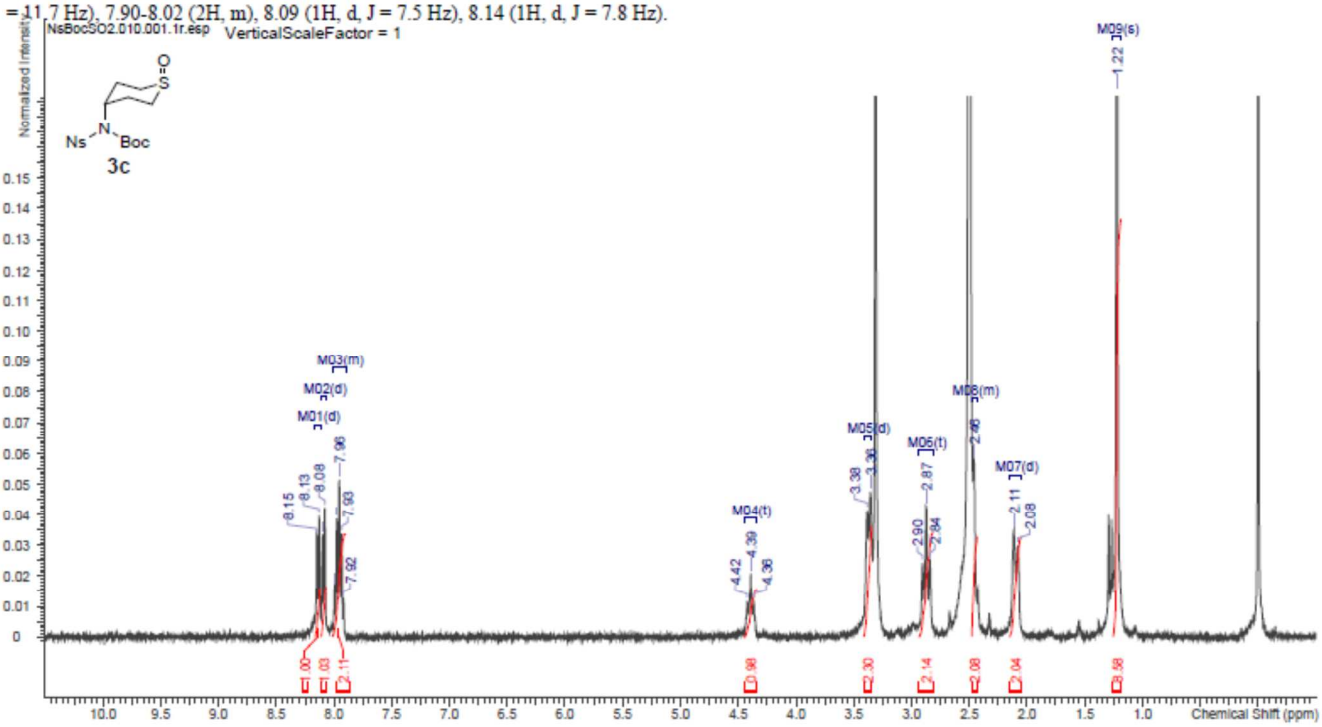
^{1}H NMR spectrum of *trans*-Boc-**3b**

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.38 (9H, s), 1.48-1.60 (2H, m), 2.04-2.21 (2H, m), 2.65 (2H, t, J = 9.9 Hz), 3.06 (2H, t, J = 10.6 Hz), 3.57 (1H, brs), 6.98 (1H, brs).



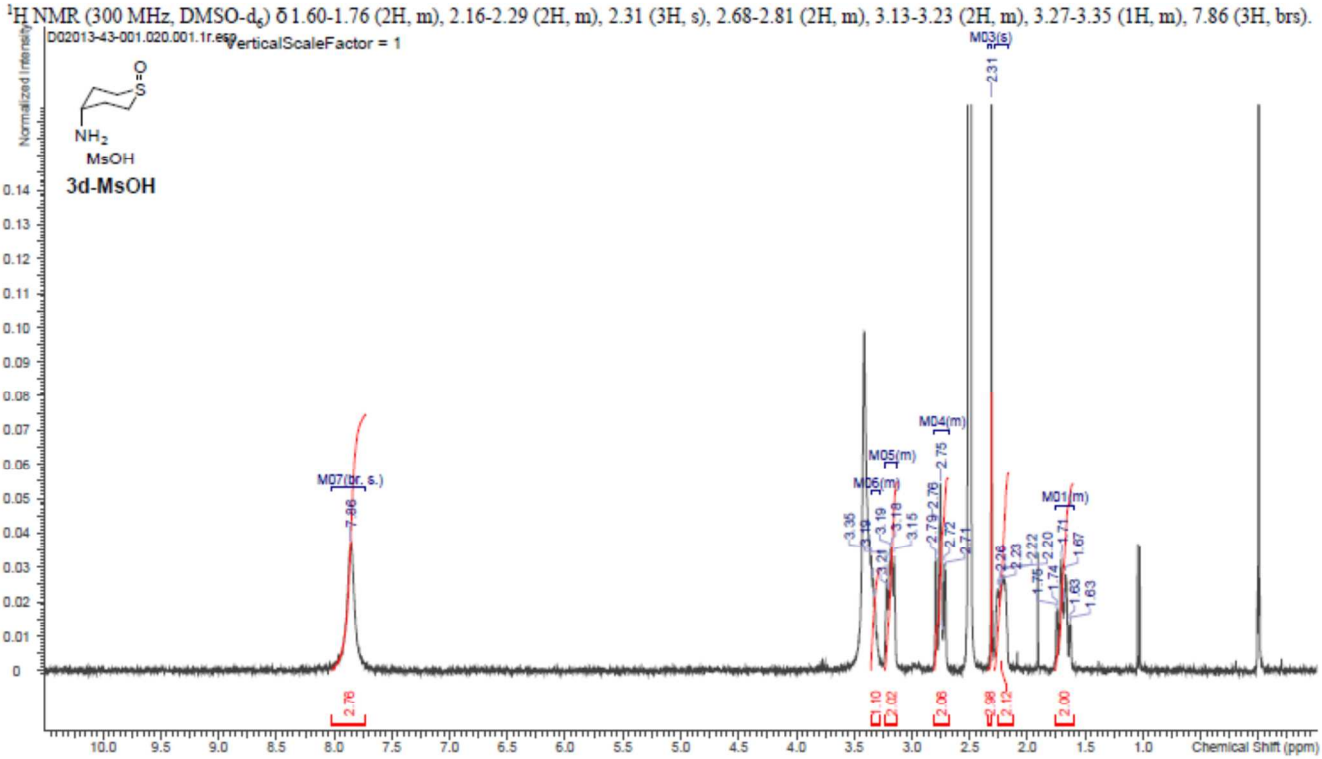
^{1}H NMR spectrum of *trans*-Ns,Boc-**3c**

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.22 (9H, s), 2.10 (2H, d, J = 13.2 Hz), 2.43-2.48 (2H, m), 2.87 (2H, t, J = 12.4 Hz), 3.37 (2H, d, J = 10.7 Hz), 4.39 (1H, t, J = 11.7 Hz), 7.90-8.02 (2H, m), 8.09 (1H, d, J = 7.5 Hz), 8.14 (1H, d, J = 7.8 Hz).



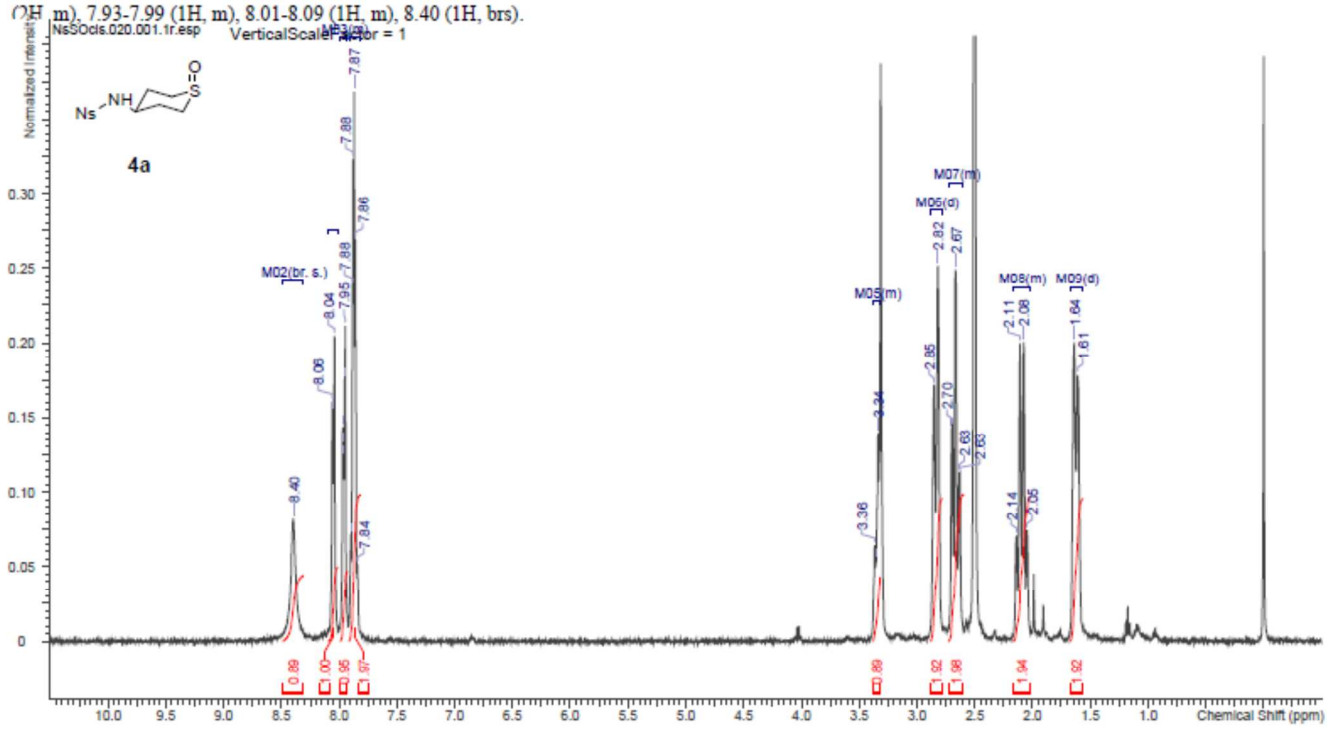
^{1}H NMR spectrum of *trans*-**3d-MsOH**

^{1}H NMR (300 MHz, DMSO-d_6) δ 1.60-1.76 (2H, m), 2.16-2.29 (2H, m), 2.31 (3H, s), 2.68-2.81 (2H, m), 3.13-3.23 (2H, m), 3.27-3.35 (1H, m), 7.86 (3H, brs).



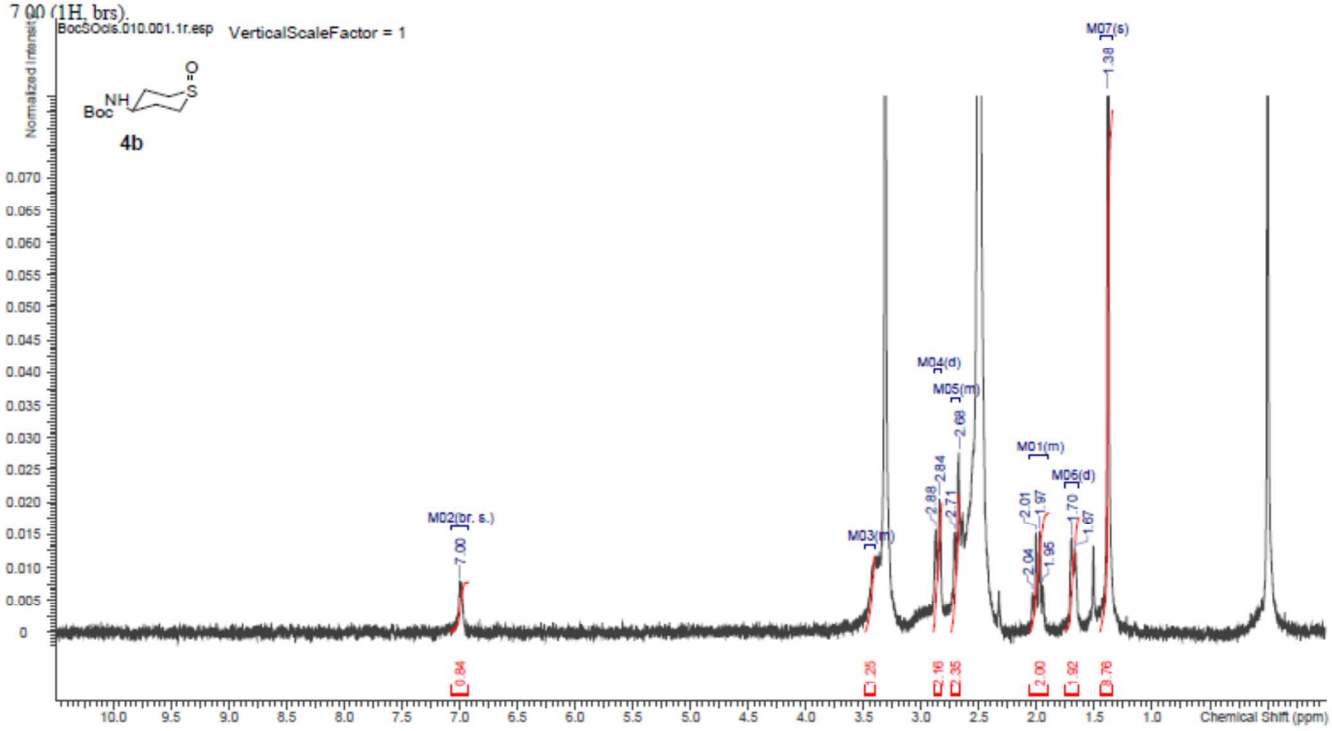
^{1}H NMR spectrum of *cis*-Ns-**4a**

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.62 (2H, d, J = 11.4 Hz), 2.02-2.17 (2H, m), 2.60-2.73 (2H, m), 2.84 (2H, d, J = 13.2 Hz), 3.32-3.38 (1H, m), 7.82-7.91 (2H, m), 7.93-7.99 (1H, m), 8.01-8.09 (1H, m), 8.40 (1H, brs).



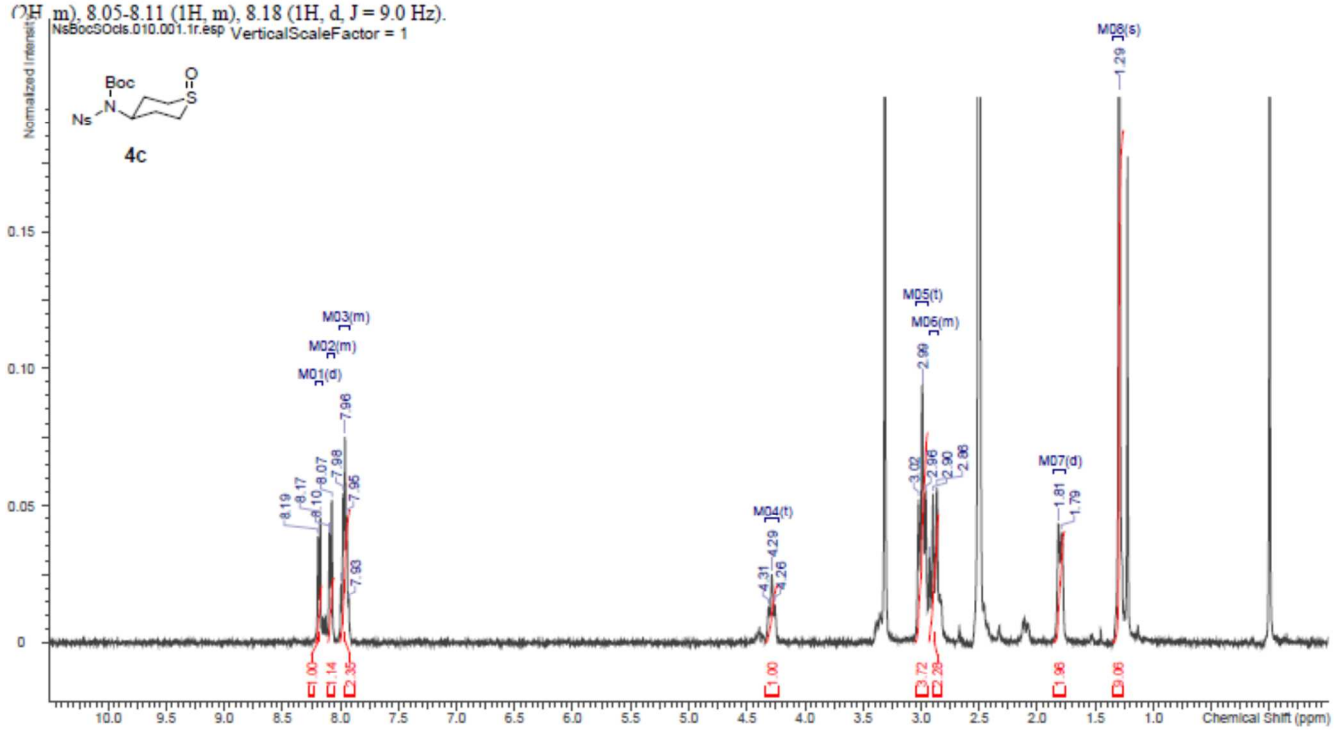
^{1}H NMR spectrum of *cis*-Boc-**4b**

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.38 (9H, s), 1.68 (2H, d, J = 11.0 Hz), 1.90-2.06 (2H, m), 2.67-2.74 (2H, m), 2.86 (2H, d, J = 13.1 Hz), 3.40-3.48 (1H, m), 7.00 (1H, brs).

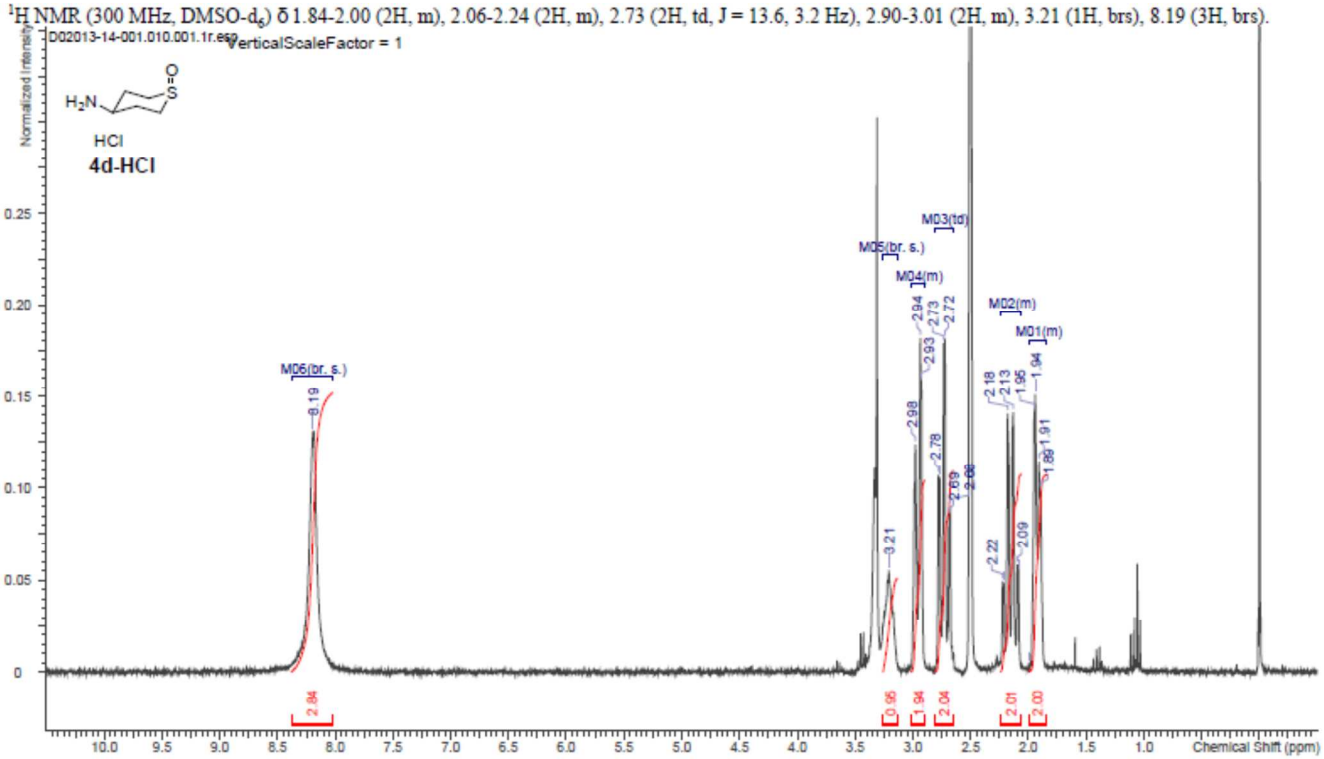


^{1}H NMR spectrum of *cis*-Ns,Boc-**4c**

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.29 (9H, s), 1.80 (2H, d, J = 10.0 Hz), 2.85-2.93 (2H, m), 2.99 (4H, t, J = 11.8 Hz), 4.29 (1H, t, J = 11.4 Hz), 7.92-8.01 (2H, m), 8.05-8.11 (1H, m), 8.18 (1H, d, J = 9.0 Hz).

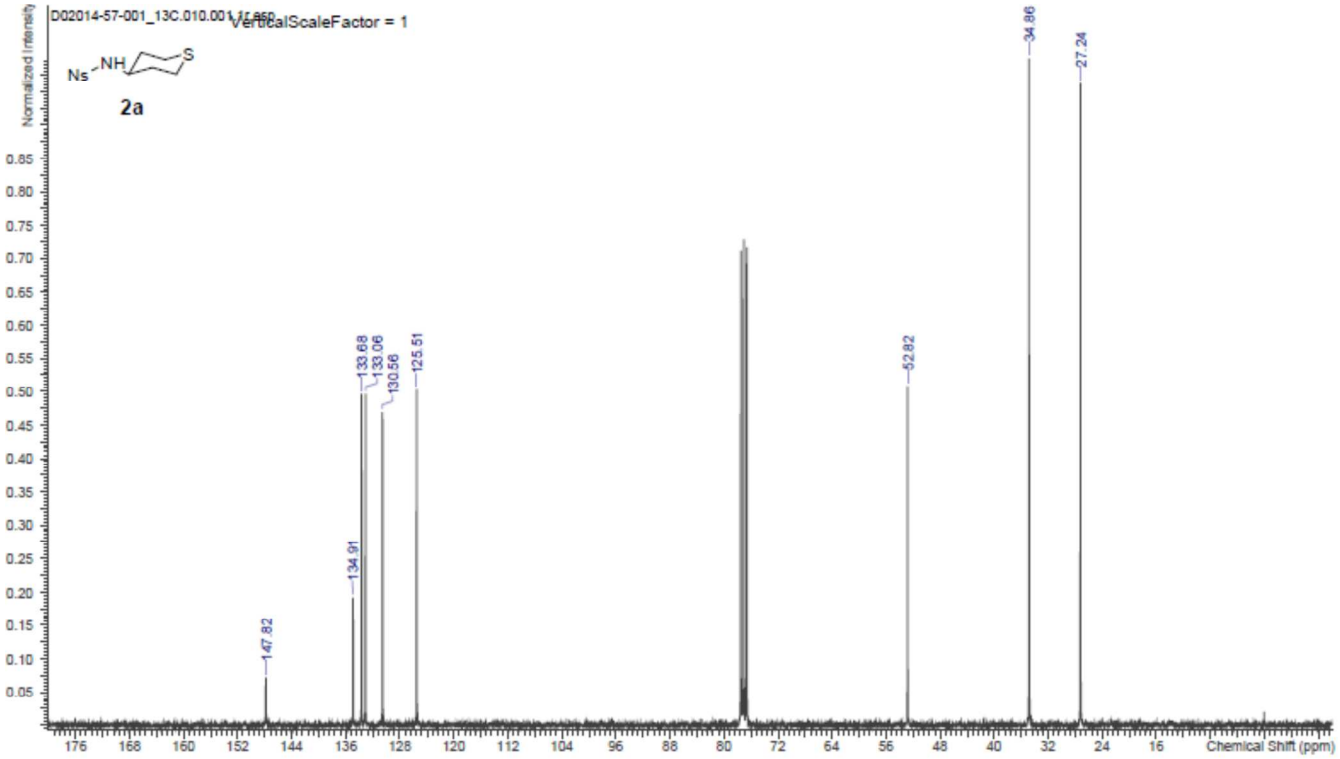


^{1}H NMR spectrum of *cis*-**4d-HCl**

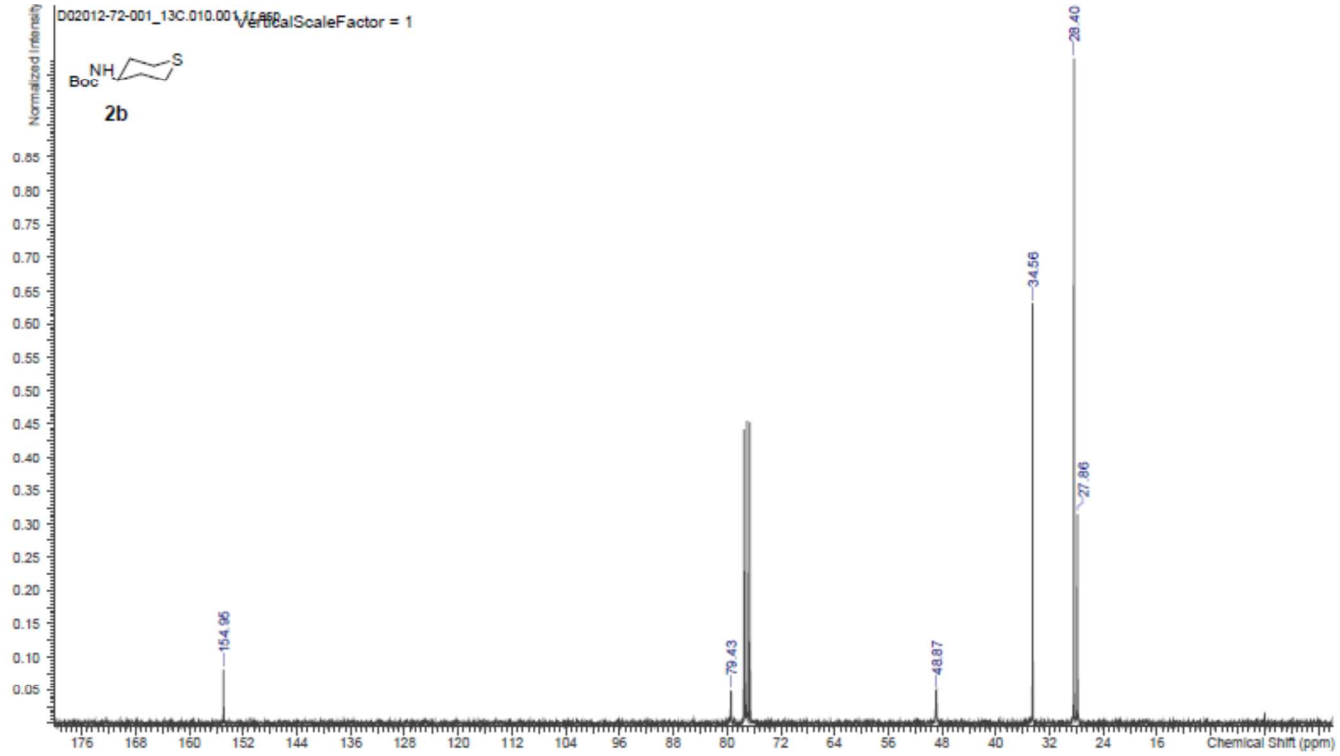


^{13}C NMR Spectral Data

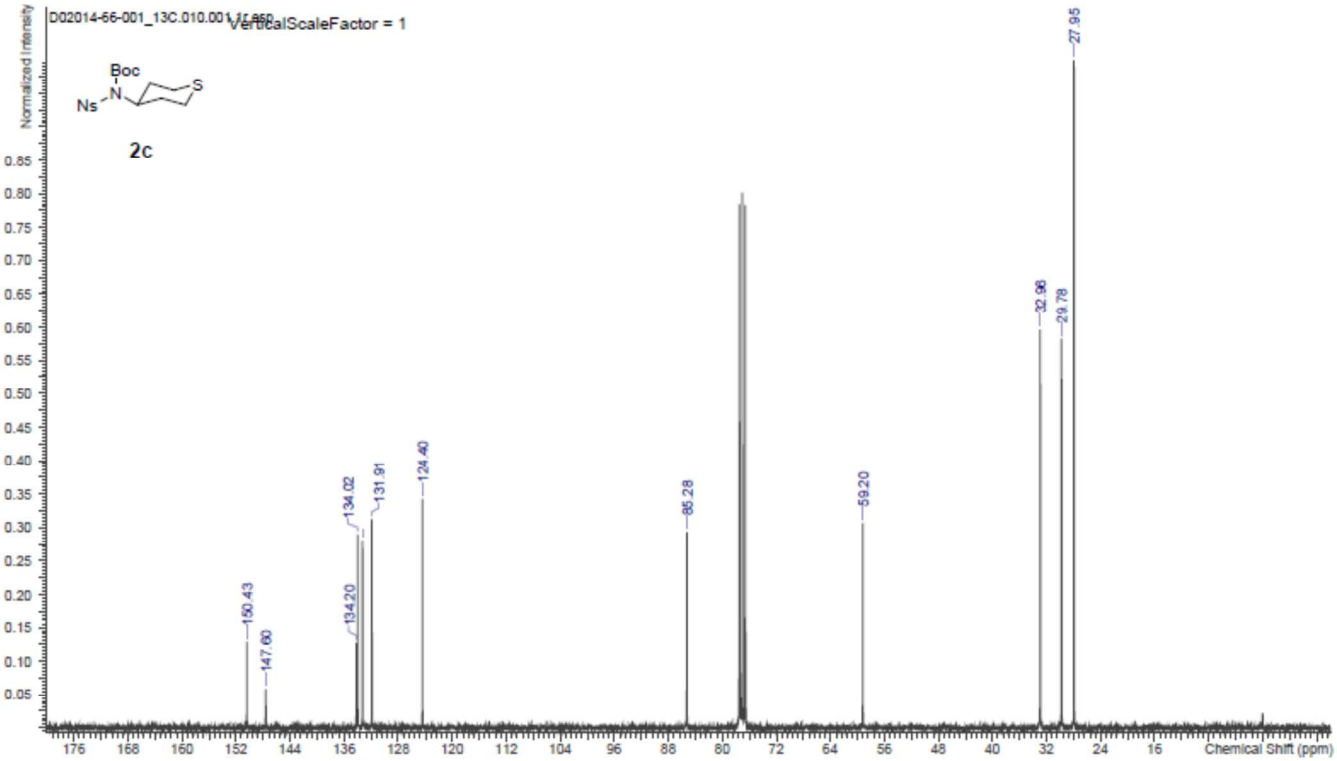
^{13}C NMR spectrum of Ns-**2a**



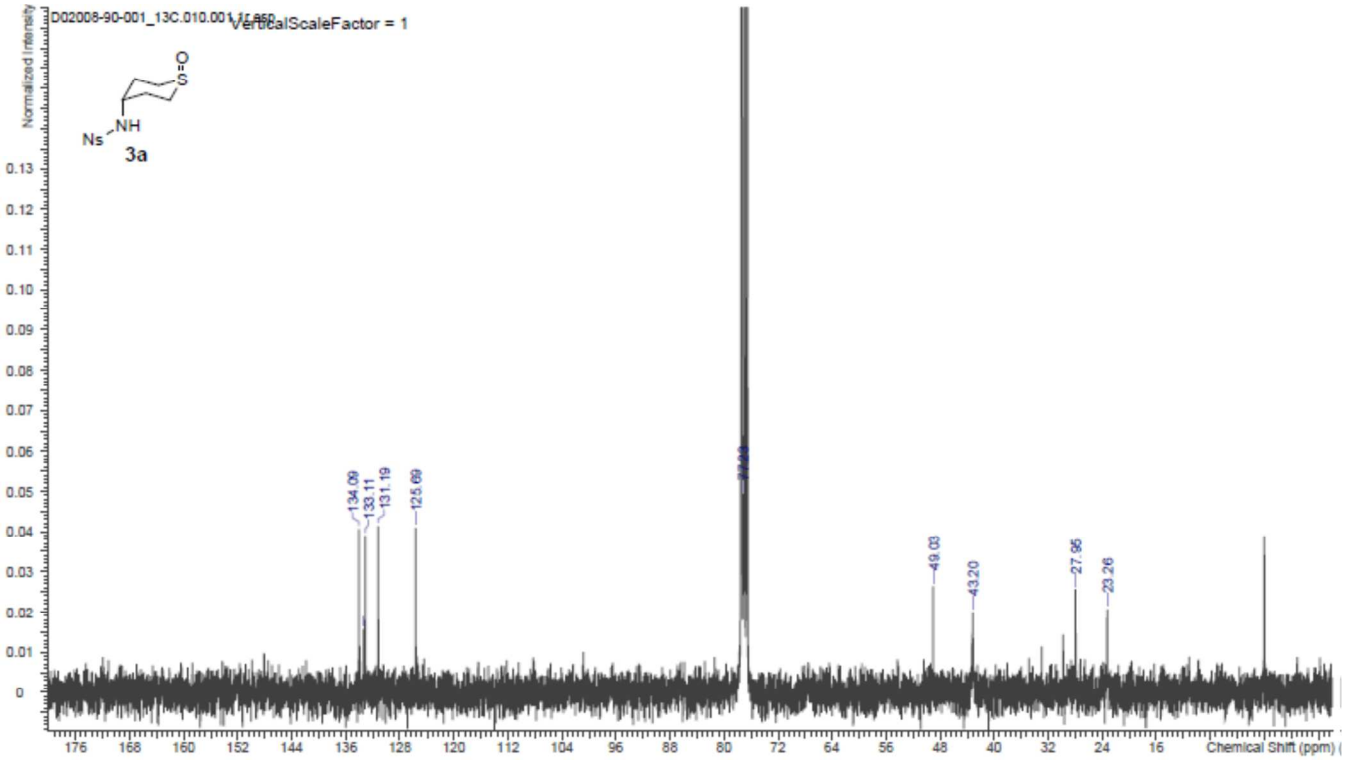
^{13}C NMR spectrum of Boc-**2b**



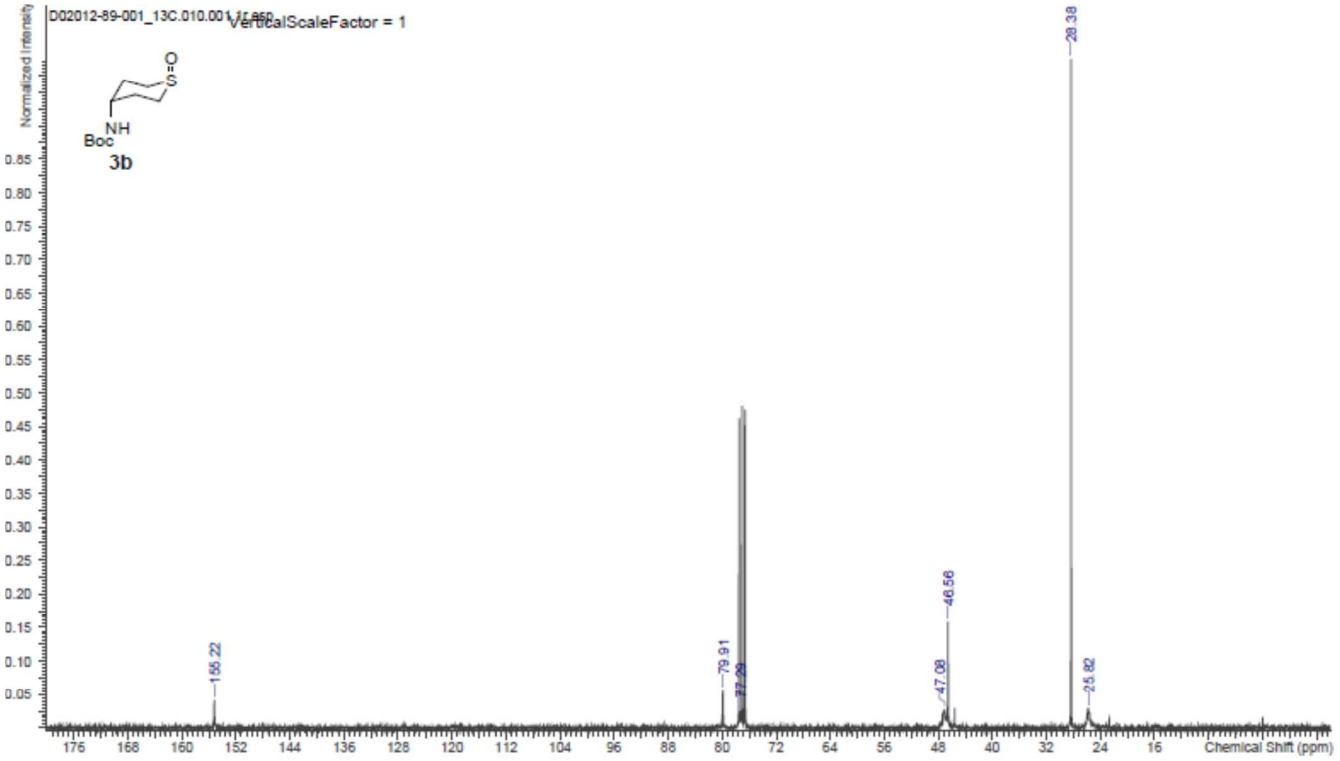
^{13}C NMR spectrum of Ns,Boc-**2c**



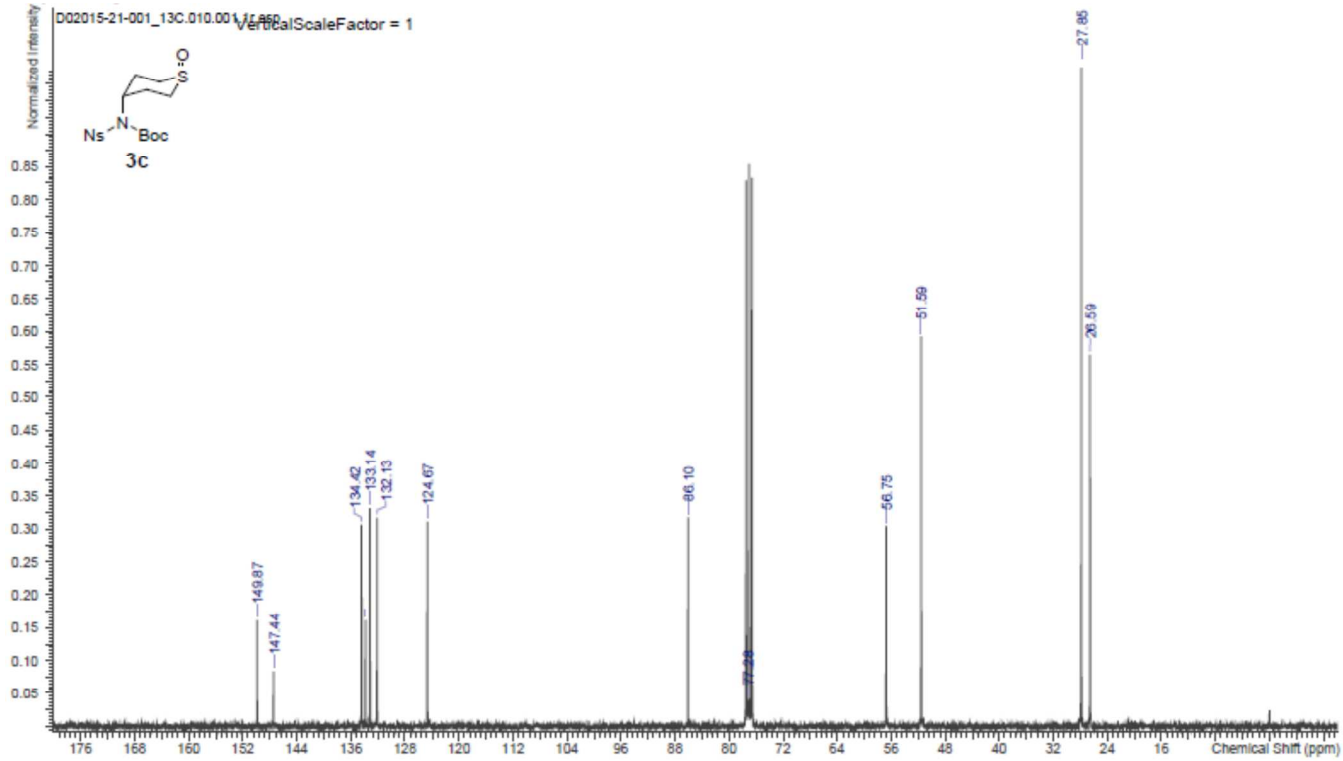
^{13}C NMR spectrum of *trans*-Ns-**3a**



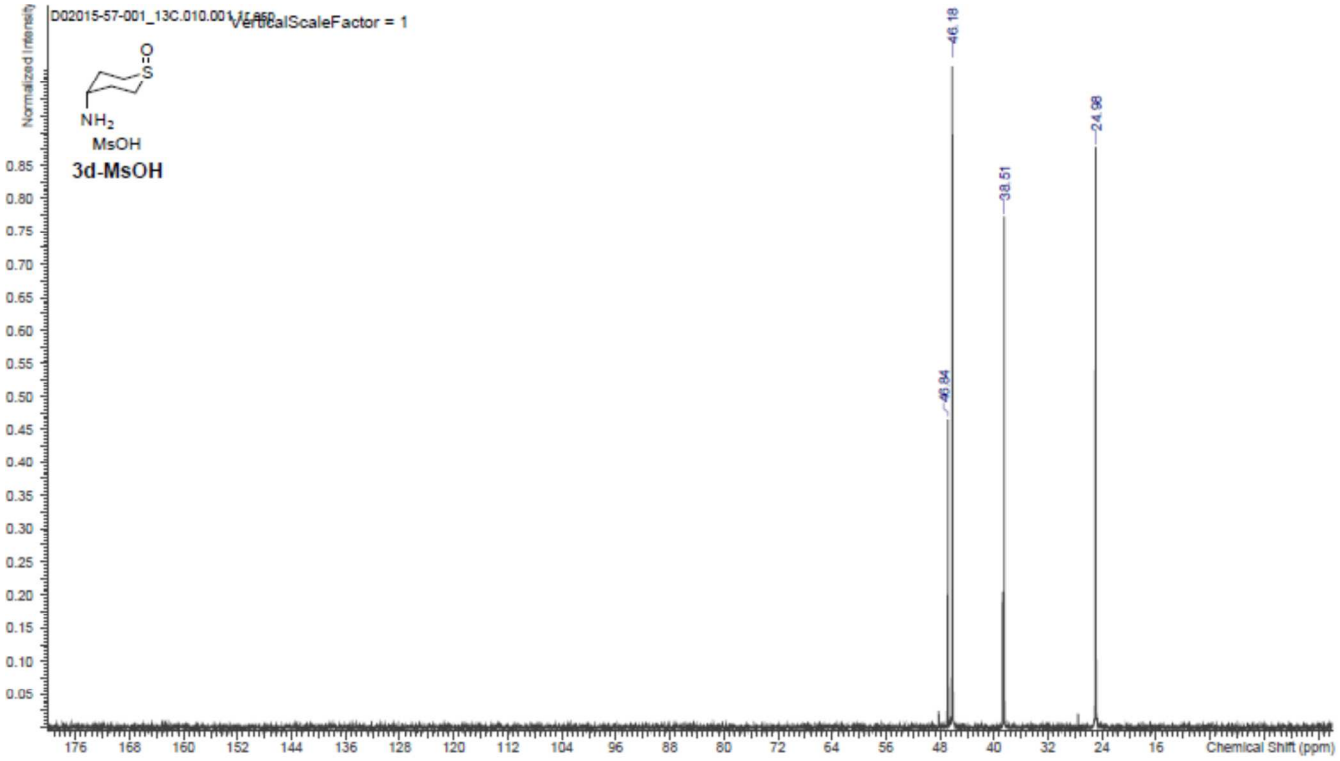
^{13}C NMR spectrum of *trans*-boc-**3b**



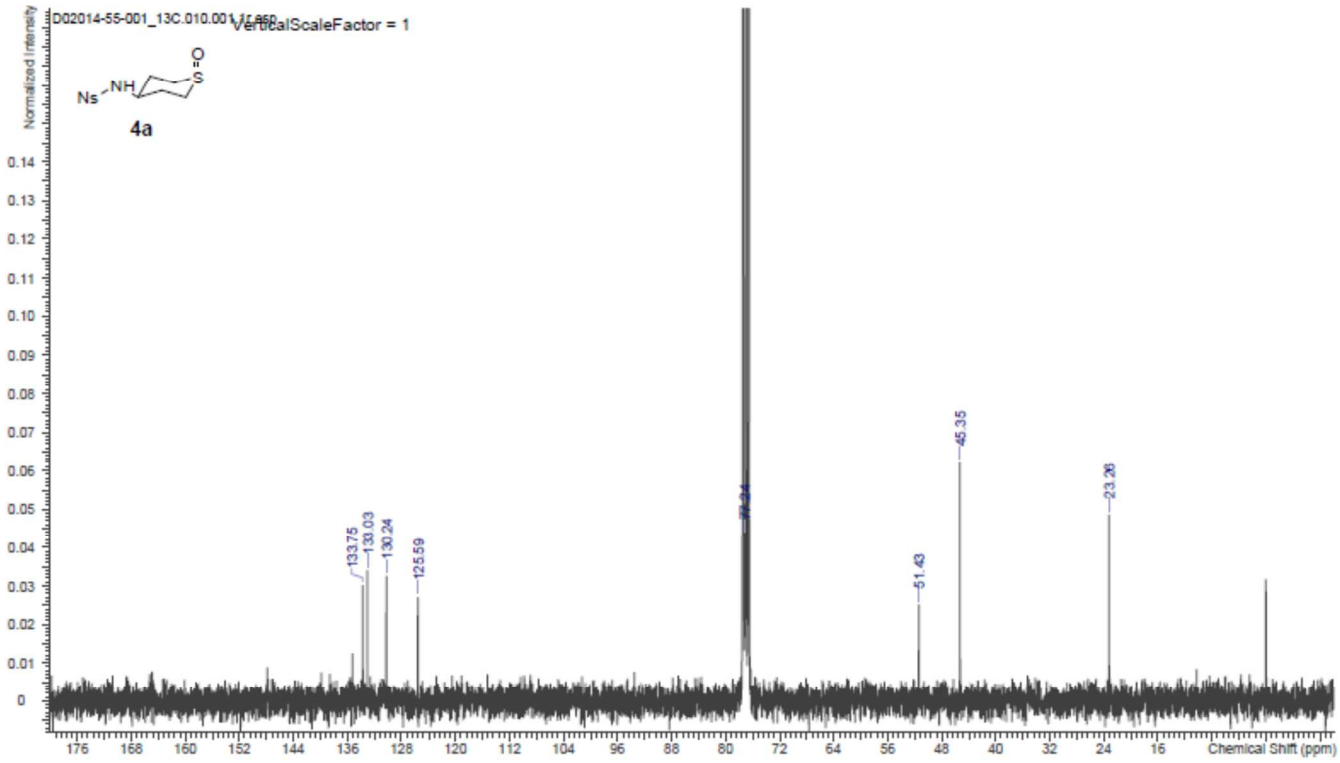
^{13}C NMR spectrum of *trans*-Ns,Boc-**3c**



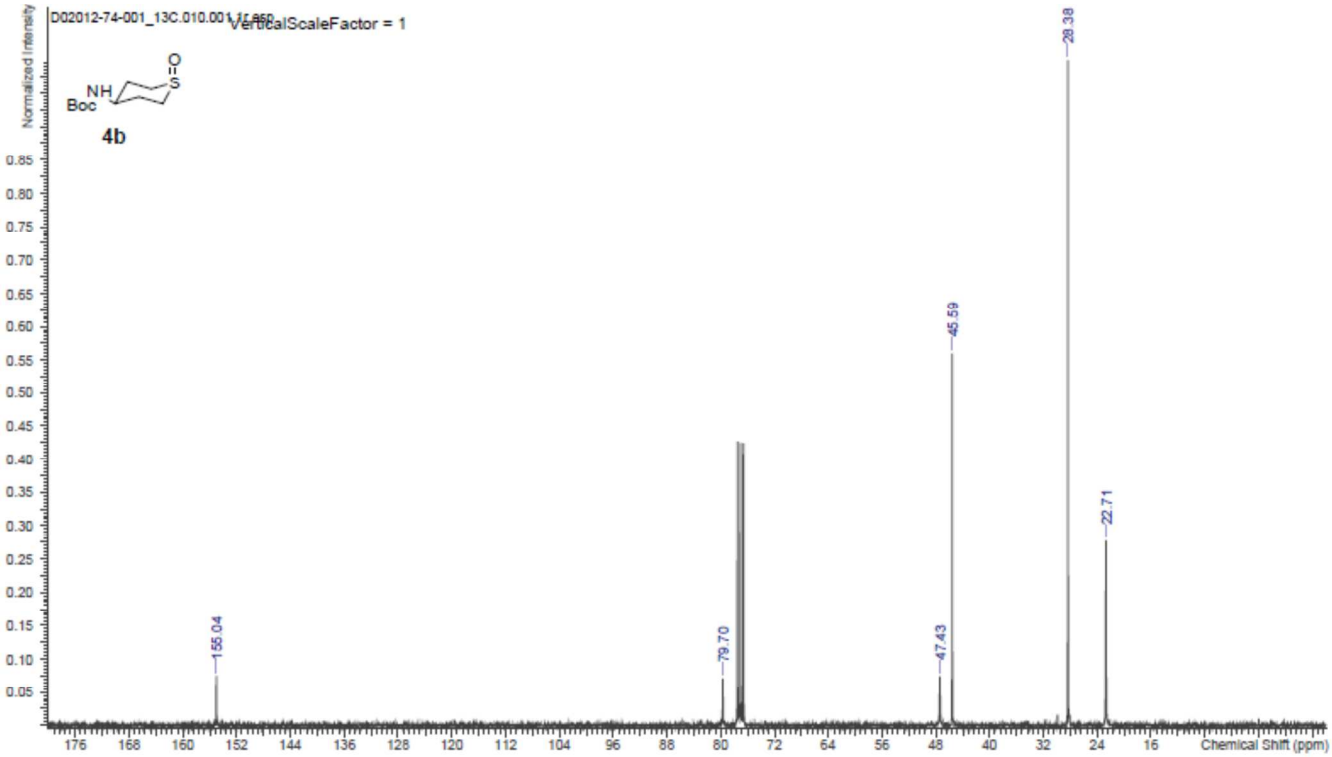
^{13}C NMR spectrum of *trans*-**3d-MsOH**



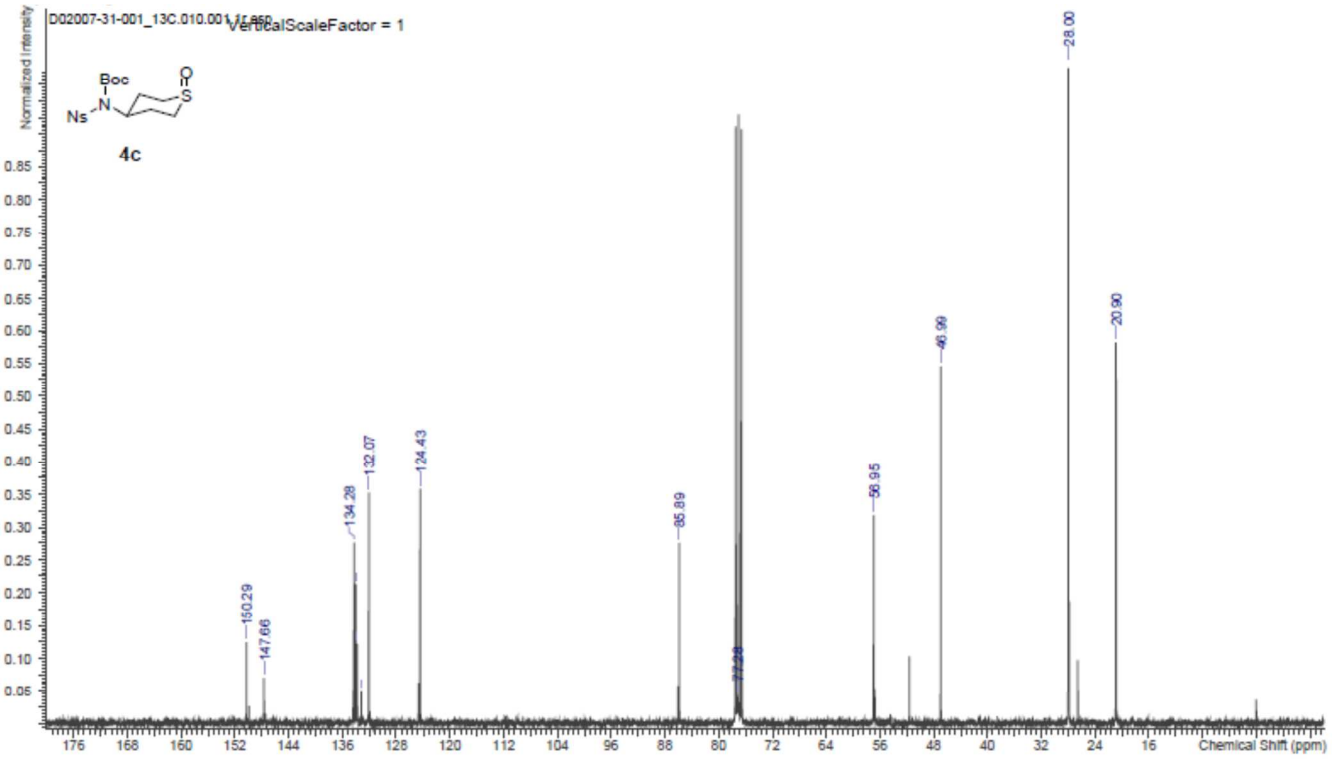
^{13}C NMR spectrum of *cis*-Ns-**4a**



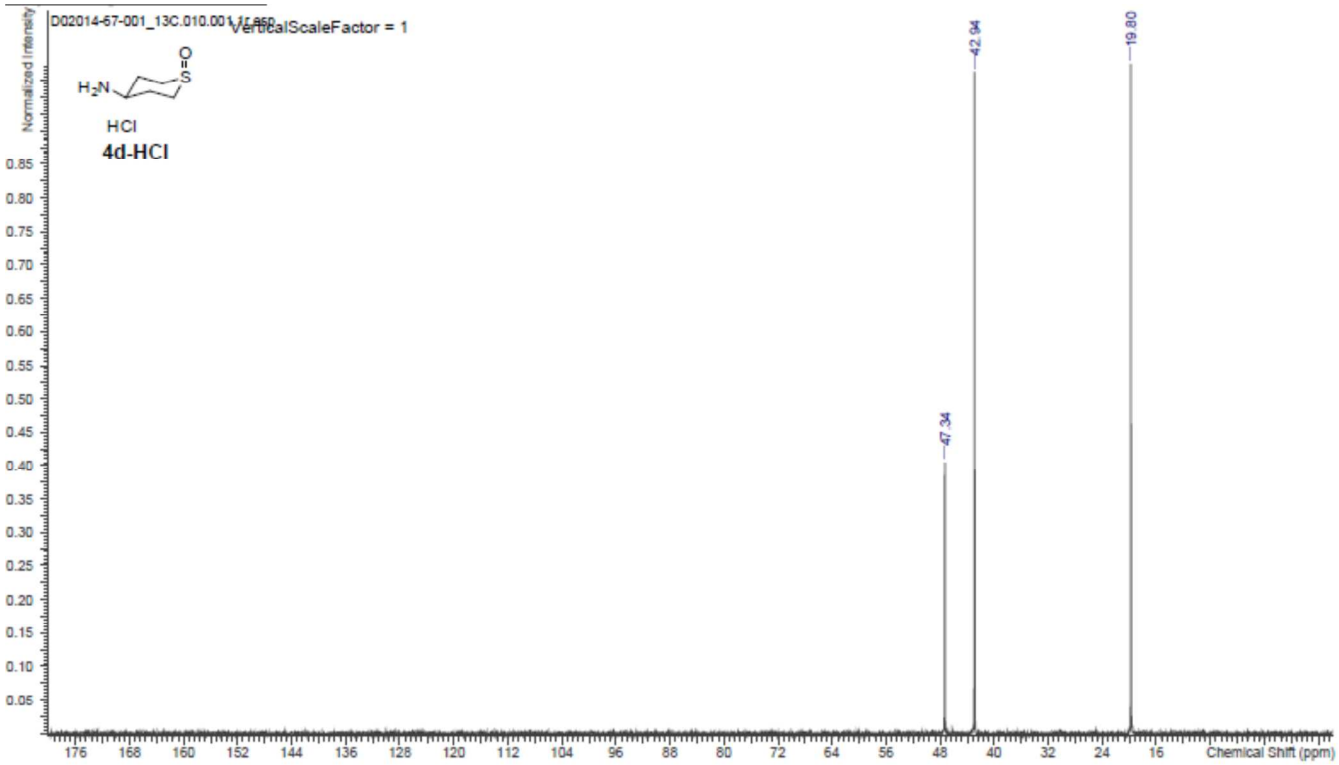
^{13}C NMR spectrum of *cis*-Boc-**4b**



^{13}C NMR spectrum of *cis*-Ns,Boc-**4c**

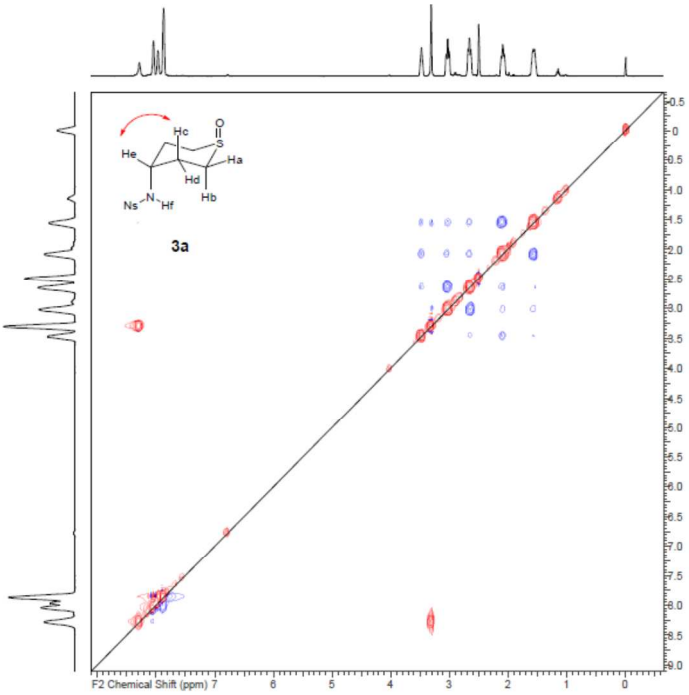


^{13}C NMR spectrum of *cis*-**4d-HCl**

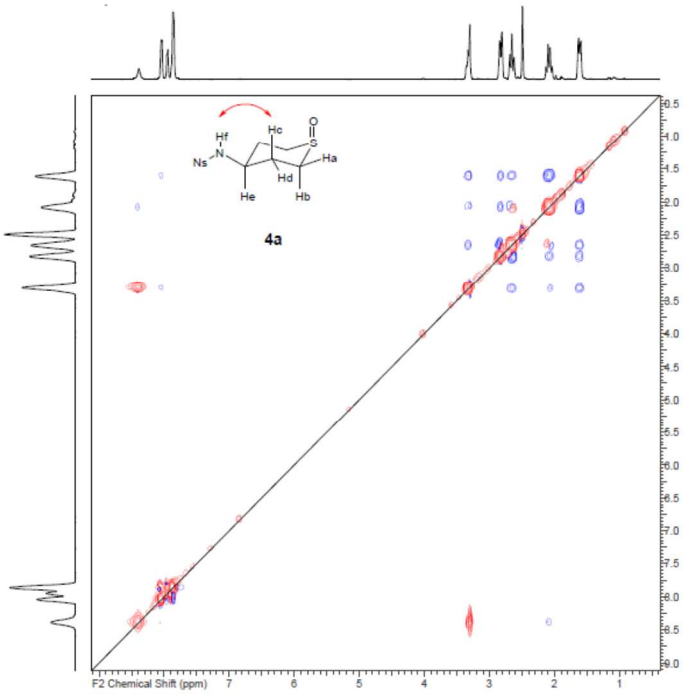


2D-NMR Spectral Data

2D-NMR spectrum of *trans*-Ns-**3a**



2D-NMR spectrum of *cis*-Ns-**4a**



X-ray structure analysis for *trans*-Ns-3a and *cis*-Ns-4a

Crystal data for trans-Ns-3a: $C_{11}H_{14}N_2O_5S_2$, *MW* = 318.36; crystal size, 0.60 x 0.40 x 0.40 mm; colorless, prism; monoclinic, space group $P2_1/c$, a = 11.106(7) Å, b = 11.070(7) Å, c = 11.153(8) Å, $\alpha = \gamma = 90°$, β = 101.85(4)°, V = 1342.0(15) Å^3, Z = 4, Dx = 1.576 g/cm^3, T = 100 K, μ = 3.817 mm^{-1}, λ = 1.54187 Å, R_1 = 0.117, wR_2 = 0.335.

Crystal data for cis-Ns-4a: $C_{11}H_{14}N_2O_5S_2$, *MW* = 318.36; crystal size, 0.70 x 0.25 x 0.20 mm; colorless, prism; orthorhombic, space group *P*bca, a = 9.411(3) Å, b = 14.986(4) Å, c = 19.855(6) Å, $\alpha = \beta = \gamma = 90°$, V = 2800.1(15) Å^3, Z = 8, Dx = 1.510 g/cm^3, T = 100 K, μ = 3.659 mm^{-1}, λ = 1.54187 Å, R_1 = 0.033, wR_2 = 0.101.

All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Cu-Kα radiation. The structure was solved by direct methods with SIR92[15] (*trans*-Ns-3a) or SHELXS-97 [16] (*cis*-Ns-4a) and was refined using full-matrix least-squares on F^2 with SHELXL-97.[16] All non-H atoms were refined with anisotropic displacement parameters. CCDC 1538028 for *trans*-Ns-3a and CCDC 1538029 for *cis*-Ns-4a contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ***http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx?***.

References

15. Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G., and Camalli, M. J. Appl. Cryst. 1994, 27, 435-436.

16. Sheldrick, G.M. Acta Cryst. A 2008, 64, 112–122.