Supplementary Material

Multi-purpose thiocyanate-containing protic ionic liquids in chemodivergent transformations of imidazolidin-2-(thi)one-based diols

Valery P. Ermolaev,‡[a] Nina K. Ratmanova,‡*[b] Vladimir V. Baranov,[c] Irina I. Levina,[d] Victor N. Khrustalev,[b,c] Olga A. Ivanova,[e] Angelina N. Kravchenko,[c] Igor V. Trushkov,[c] Ivan A. Andreev*[b]

[a] *Higher Chemical College of the Russian Academy of Sciences, D. I. Mendeleev Russian University of Chemical Technology, Miusskaya Ploshchad' 9, 125047 Moscow, Russian Federation*

[b] *Science Faculty, Patrice Lumumba Peoples' Friendship University of Russia (RUDN University), Miklukho-Maklaya st. 6, 117198 Moscow, Russian Federation; ratmanova_nk@pfur.ru; andreev_ia@pfur.ru*

[c] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky pr. 47, 119991 Moscow, Russian Federation*

[d] *N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Kosygina st. 4, 119334 Moscow, Russian Federation*

[e] *Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie gory 1-3, 119991 Moscow, Russian Federation*

‡ *These authors contributed equally to this work*

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General information

NMR spectra were recorded on Bruker Avance 500 instrument at room temperature (r.t.) unless otherwise stated with an operating frequency of 500 and 126 MHz, respectively; the chemical shifts δ were measured in ppm with respect to solvent (DMSO-d_6: ^{1}H, δ = 2.50 ppm; ^{13}C δ = 39.52 ppm).[S1] ^{19}F NMR spectra were recorded at 470 MHz with *ca*. 1 equiv of internal reference compounds: trifluorotoluene for **2h,i** or fluorobenzene for HMpzOTf (δ = –60.94 or –112.83 ppm, respectively, in DMSO-d_6).[S2] Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet; br., broad. Coupling constants (*J*) are given in Hz. To achieve a good resolution of ^{1}H NMR spectra for products **2** and **3**, the samples were employed in less than 10 mg amounts. Infrared spectra were recorded on Infralum FT-801 and Infralum FT-08 with ATR (Attenuated Total Reflectance) module. High resolution and accurate mass measurements were carried out using a Bruker microTOF-Q™ ESI-TOF (Electro Spray Ionization / Time of Flight) and Thermo Scientific™ LTQ Orbitrap mass spectrometers using nanoelectrospray ionization (nano-ESI). Elemental analyses were performed with Fisons EA-1108 CHNS elemental analyzer instrument. Melting points (m.p.s) were determined using the Stuart® SMP3 melting point apparatus.

Analytical thin-layer chromatography (TLC) was carried out on Macherey-Nagel silica gel plates ($60F_{254}$, supported on aluminum); the visualization was performed by UV lamp (254 nm).

All reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Thiocyanate-containing protic ionic liquids (PILs, HMimNCS and $Et_3N{\cdot}HNCS$) were synthesized according to known procedures.[S3] Starting 4,5-dihydroxy-4,5-diarylimidazolidine-2-(thi)ones **1** were prepared according to the literature procedures and were fully characterized earlier: **1a-c**,[S4] **1d-e,g-l**,[S5] **1f**.[S6]

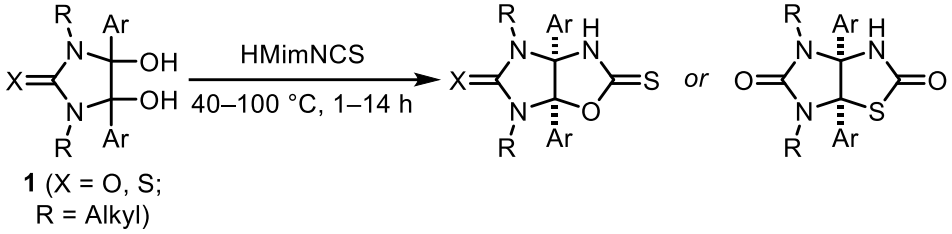
The single-crystal X-ray diffraction data for **2c**, **3a** and **3j** were collected on a four-circle XtaLAB Rigaku Synergy-S diffractometer equipped with a HyPix-6000HE area-detector (*T* = 100 K, λ(Cu*K*α)-radiation, graphite monochromator, shutterless ω-scan mode). The data were integrated and corrected for absorption by the *CrysAlisPro* program.[S7] The single-crystal X-ray diffraction data for HMpzOTf were collected on a three-circle Bruker D8 QUEST diffractometer equipped with a PHOTON-III area-detector (*T* = 100 K, λ(Mo*K*α)-radiation, graphite monochromator, φ and ω scan mode) and corrected for absorption using the SADABS program.[S8] The data were indexed and integrated using the SAINT program.[S9] For details, see the full crystallographic data (CIFs).

The structures were solved by intrinsic phasing modification of direct methods[S10] and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. One of the two solvate dimethylsulfoxide molecules in **2c** was disordered over two sites with the occupancies of 0.8581(9):0.1419(9). The hydrogen atoms of the *NH*-groups in **2c** and **3a** were objectively localized in the difference-Fourier maps and refined isotropically. The hydrogen atom of the

NH-group in HMpzOTf was placed in calculated position and refined within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.2U_{eq}(N)]. The hydrogen atom of the *NH*-group in HMpzOTf was objectively localized in the difference-Fourier maps and refined isotropically with fixed displacement parameters [U_{iso}(H) = 1.2U_{eq}(N)]. The other hydrogen atoms in all compounds were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and 1.2U_{eq}(C) for the other groups]. All calculations were carried out using the SHELXTL[S11] and OLEX[S12] programs.

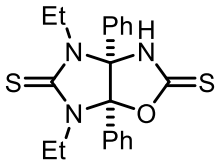
Crystallographic data for all investigated compounds were deposited into the Cambridge Crystallographic Data Centre, CCDC 2444500 (**2c**), CCDC 2444501 (**3a**), CCDC 2444502 (**3j**) and CCDC 2444503 (HMPzOTf). These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and FIZ Karlsruhe http://www.ccdc.cam.ac.uk/structures.

General procedure for synthesis of (thi)oxoimidazo[4,5-*d*]oxazolethiones 2 and imidazo[4,5-*d*]thiazoldiones 3 (GP)



The **GP** is in accordance with our previous work.[1] A 4 mL vial was charged with starting 4,5-dihydroxy-4,5-diarylimidazolidine-2-(thi)one **1**. Thiocyanate-based PIL (HMimNCS, *ca*. 8.5 equiv, corresponding to *ca*. 1 M final concentration of starting material in PIL) preliminary melted with a heat-gun was added. The vial was tightly sealed, placed into the preheated oil bath (typically 70 °C), and vigorously stirred for 1 h unless stated otherwise. The vial was removed from the bath and allowed to cool to ambient temperature. Distilled water (*ca.* 3 mL) was added to the reaction mixture, and it was rubbed with a spatula. The precipitated product was filtered, washed with distilled water (4 × 5 mL),[2] and dried on air. To remove traces of water and residual PIL, the product was dried under reduced pressure on a rotary evaporator at 80 °C for several hours. The purity of obtained compounds **2** and **3** was additionally proved by an elemental analysis.

(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithione (2a) was synthesized according to the **GP** from **1a** (100 mg, 0.292 mmol) and HMimNCS (0.292 mL).[3] Product **2a** was obtained as an off-white solid (94 mg, 84%); m.p. = 199–201 °C (lit. = 243–245 °C (dec.),[S4] MeOH). Spectral data are well consistent with the published ones.[S4]



^{1}H NMR (500 MHz, DMSO-d_6):[4] δ = 1.13 (t, ^3J = 7.1 Hz, 3H, CH_3), 1.22 (t, ^3J = 7.0 Hz, 3H, CH_3), 3.08–3.21 (m, 2H, CH_2), 3.89 (dq, ^2J = 14.0 Hz, ^3J = 7.1 Hz, 1H, CH_2), 3.92 (dq, ^2J = 14.2 Hz, ^3J = 7.0 Hz, 1H, CH_2), 6.73–6.98 (m, 4H, CH, Ph), 7.07–7.35 (m, 6H, CH, Ph), 11.94 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6, 50 °C): δ = 13.1 (CH_3), 13.3 (CH_3), 39.7 (CH_2), 39.8 (CH_2), 90.4 (C-bridge), 108.3 (C-bridge), 126.7 (2 × CH, Ph), 126.8 (2 × CH, Ph), 128.2 (2 × CH, Ph), 128.3 (2 × CH, Ph), 129.4 (CH, Ph), 129.5 (CH, Ph), 130.9 (C, Ph), 131.4 (C, Ph), 182.3 (EtN-C=S), 187.3 (NH-C=S).

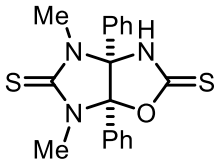
1) For graphical representation of experiment, see ref. S13.
2) The distilled water washings after each run, containing an SCN-PIL, may be combined and subjected to the regeneration procedure (see ref. S2).
3) The TLC control of reaction progress was impossible due to the identical R_f values for **1a** and **2a** in petroleum ether – EtOAc mixtures.
4) The multiplets at 3.89 and 3.92 ppm are the overlapping doublets of quartets from different CH_2-groups.

IR (KBr): ṽ = 3141 (br. m, NH), 2980 (w), 2936 (w), 1520 (s), 1447 (s), 1399 (s), 1352 (m), 1320 (w), 1277 (m), 1243 (w), 1199 (s), 1174 (m), 1082 (w), 1045 (m), 1008 (w), 927 (w), 856 (m), 802 (m), 759 (m), 702 (m) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{20}H_{22}N_3OS_2$ $[M+H]^+$, 384.1199; found, 384.1187.

Elemental analysis calcd (%) for $C_{20}H_{21}N_3OS_2$: C 62.63, H 5.52, N 10.96; found: C 62.73, H 5.46, N 10.91.

(3a*SR*,6a*SR*)-4,6-Dimethyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithione (2b) was synthesized according to the **GP** from **1b** (100 mg, 0.318 mmol) and HMimNCS (0.318 mL). Product **2b** was obtained as an off-white solid (96 mg, 85%); m.p. = 193–195 °C (lit. = 223–225 °C (dec.),[S4] MeOH). Spectral data are well consistent with the published ones.[S4]



^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.005 (s, 3H, CH_3), 3.014 (s, 3H, CH_3), 6.83–6.99 (m, 4H, CH, Ph), 7.13–7.25 (m, 6H, CH, Ph), 12.07 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 31.2 (CH_3), 31.6 (CH_3), 90.1 (C-bridge), 107.7 (C-bridge), 126.7 (2 × CH, Ph), 126.8 (2 × CH, Ph), 128.5 (2 × CH, Ph), 128.7 (2 × CH, Ph), 129.6 (CH, Ph), 129.8 (CH, Ph), 131.06 (C, Ph), 131.12 (C, Ph), 183.4 (MeN-C=S), 187.3 (NH-C=S).

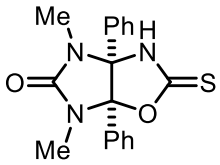
IR (KBr): ṽ = 3064 (br. m, NH), 2974 (w), 2932 (w), 1509 (vs), 1495 (vs), 1446 (s), 1376 (s), 1325 (m), 1249 (w), 1180 (s), 1071 (w), 1017 (m), 998 (w), 970 (w), 928 (w), 861 (w), 758 (m), 701 (s) cm^{-1}.

Elemental analysis calcd (%) for $C_{18}H_{17}N_3OS_2$: C 60.82, H 4.82, N 11.82; found: C 60.81, H 4.86, N 12.02.

The gram-scale experiment (1.000 g, 3.181 mmol of **1b**; 3.181 mL of HMimNCS) was carried out under identical conditions in a 15 mL vial. After addition of distilled water (*ca*. 7 mL) the obtained suspension was poured into a beaker with 80 mL of distilled water to maximize slurrying of the product. The precipitate was filtered, washed thoroughly with warm distilled water (*ca*. 50 °C, 20× 10 mL) to remove excessive PIL, and dried on air. To remove traces of water and residual PIL, the compound was dried under reduced pressure on a rotary evaporator at 80 °C for 7.5 hours. Product **2b** was obtained as an off-white solid (1.078 g, 95%).

Elemental analysis calcd (%) for $C_{18}H_{17}N_3OS_2$: C 60.82, H 4.82, N 11.82; found: C 60.63, H 4.67, N 11.84.

(3a*SR*,6a*SR*)-4,6-Dimethyl-3a,6a-diphenyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2c) was synthesized according to the **GP** (2.5 h) from **1c** (100 mg, 0.335 mmol) and HMimNCS (0.335 mL). Product **2c** was obtained as a white solid (98 mg, 86%); m.p. = 205–206 °C (lit. = 227–230 °C,[S4] MeOH). Spectral data are well consistent with the published ones.[S4]



^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.71 (s, 6H, 2 × CH_3), 6.93–7.00 (m, 4H, CH, Ph), 7.14–7.21 (m, 6H, CH, Ph), 11.78 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 26.5 (CH_3), 27.0 (CH_3), 86.3 (C-bridge), 105.7 (C-bridge), 126.8 (2 × CH, Ph), 127.0 (2 × CH, Ph), 128.3 (2 × CH, Ph), 128.4 (2 × CH, Ph), 129.1 (CH, Ph), 129.4 (CH, Ph), 131.6 (C, Ph), 132.0 (C, Ph), 157.4 (C=O), 187.8 (C=S).

IR (KBr): ṽ = 3112 (br. s, NH), 2936 (m), 1699 (vs, C=O), 1495 (s), 1447 (s), 1419 (m), 1395 (s), 1337 (m), 1310 (m), 1278 (w), 1232 (w), 1190 (s), 1178 (s), 1156 (m), 1134 (w), 1076 (w), 1055 (w), 1039 (m), 1024 (m), 950 (w), 915 (m), 874 (m), 848 (s), 758 (m), 696 (s) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{18}H_{18}N_3O_2S$ $[M+H]^+$, 340.1114; found, 340.1106.

Elemental analysis calcd (%) for $C_{18}H_{17}N_3O_2S$: C 63.70, H 5.05, N 12.38; found: C 63.61, H 5.02, N 12.27.

Transparent small needle-like prism crystals of **2c** precipitated from DMSO-d_6 in NMR tube. The structure of **2c** is shown in Fig. S1.

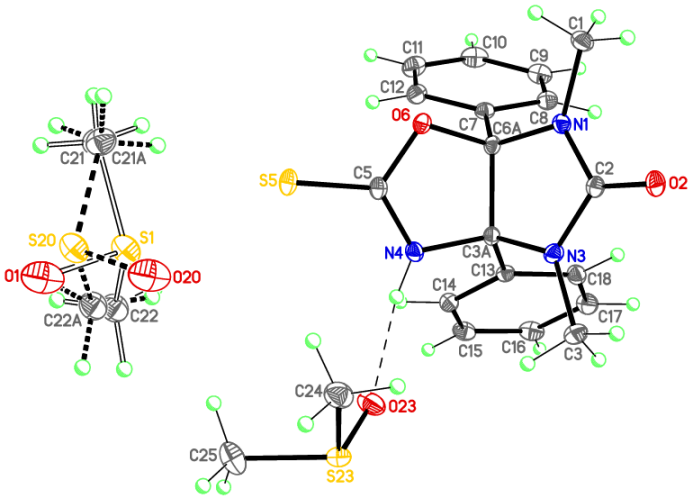
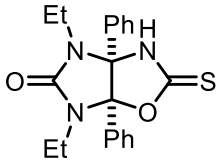


Figure S1. Crystal structure of **2c**·DMSO-d_6; thermal ellipsoids are shown at a 50% probability level (CCDC 2444500).

(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2d) was synthesized according to the **GP** from **1d** (100 mg, 0.306 mmol) and HMimNCS (0.306 mL). Product **2d** was obtained as a white solid (98 mg, 87%); m.p. = 218–220 °C.



^{1}H NMR (500 MHz, DMSO-d_6):[1] δ = 1.07 (t, ^3J = 7.2 Hz, 3H, CH_3), 1.13 (t, ^3J = 7.1 Hz, 3H, CH_3), 2.947 (dq, ^2J = 14.3 Hz, ^3J = 7.1 Hz, 1H, CH_2), 2.955 (dq, ^2J = 14.4 Hz, ^3J = 7.2 Hz, 1H, CH_2), 3.389 (dq, ^2J = 14.4 Hz, ^3J = 7.2 Hz, 1H, CH_2), 3.392 (dq, ^2J = 14.3 Hz, ^3J = 7.1 Hz, 1H, CH_2), 6.82–7.02 (br. s, 4H, CH, Ph), 7.08–7.25 (m, 6H, CH, Ph), 11.66 (s, 1H, NH).

1) The multiplets at 2.947/2.955 and 3.389/3.392 ppm are pairwise overlapping doublets of quartets from different CH_2-groups.

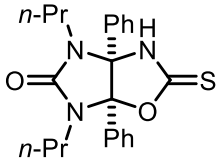
^{13}C NMR (126 MHz, DMSO-d_6): δ = 14.2 (2 × CH_3), 36.2 (CH_2), 36.3 (CH_2), 86.7 (C-bridge), 106.8 (C-bridge), 127.0 (2 × CH, Ph), 127.1 (2 × CH, Ph), 128.22 (2 × CH, Ph), 128.24 (2 × CH, Ph), 129.2 (CH, Ph), 129.4 (CH, Ph), 131.9 (C, Ph), 132.7 (C, Ph), 157.3 (C=O), 187.9 (C=S).

IR (KBr): ṽ = 3149 (br. m, NH), 2979 (w), 2939 (w), 1694 (vs, C=O), 1497 (s), 1449 (s), 1415 (s), 1379 (w), 1355 (m), 1333 (w), 1248 (w), 1218 (w), 1199 (m), 1173 (s), 1095 (w), 1064 (m), 1027 (w), 908 (m), 878 (m), 845 (m), 759 (m), 697 (m) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{20}H_{22}N_3O_2S$ $[M+H]^+$, 368.1427; found, 368.1422.

Elemental analysis calcd (%) for $C_{20}H_{21}N_3O_2S$: C 65.37, H 5.76, N 11.44; found: C 65.41, H 5.77, N 11.42.

(3a*SR*,6a*SR*)-3a,6a-Diphenyl-4,6-dipropyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2e) was synthesized according to the **GP** from **1e** (100 mg, 0.282 mmol) and HMimNCS (0.282 mL). Product **2e** was obtained as an off-white solid (106 mg, 95%); m.p. = 147–149 °C.



^{1}H NMR (500 MHz, DMSO-d_6):[1] δ = 0.78 (t, ^3J = 7.4 Hz, 3H, CH_3), 0.82 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.49 (qt, ^3J = 7.4 Hz, ^3J = 7.3 Hz, 2H, CH_2), 1.60 (qt, ^3J = 7.4 Hz, ^3J = 7.0 Hz, 2H, CH_2), 2.78 (dt, ^2J = 14.3 Hz, ^3J = 7.3 Hz, 1H, CH_2), 2.82 (dt, ^2J = 14.4 Hz, ^3J = 7.0 Hz, 1H, CH_2), 3.36 (dt, ^2J = 14.3 Hz, ^3J = 7.3 Hz, 1H, CH_2), 3.37 (dt, ^2J = 14.4 Hz, ^3J = 7.0 Hz, 1H, CH_2), 6.92 (br. s, 4H, CH, Ph), 7.06–7.25 (m, 6H, CH, Ph), 11.55 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 11.06 (CH_3), 11.10 (CH_3), 21.6 (CH_2), 21.8 (CH_2), 43.0 (CH_2), 43.1 (CH_2), 86.7 (C-bridge), 106.6 (C-bridge), 127.0 (2 × CH, Ph), 127.1 (2 × CH, Ph), 128.2 (2 × CH, Ph), 128.3 (2 × CH, Ph), 129.2 (CH, Ph), 129.4 (CH, Ph), 131.7 (C, Ph), 132.5 (C, Ph), 157.5 (C=O), 188.0 (C=S).

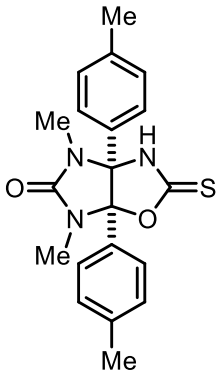
IR (neat): ṽ = 3155 (br. m, NH), 2964 (m), 2934 (w), 2874 (w), 2353 (m), 2324 (m), 1695 (vs, C=O), 1487 (s), 1447 (s), 1411 (s), 1376 (m), 1342 (w), 1241 (w), 1208 (m), 1171 (vs), 1070 (s), 1031 (w), 1003 (w), 954 (w), 915 (m), 887 (m), 850 (s), 750 (s), 692 (s) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{22}H_{26}N_3O_2S$ $[M+H]^+$, 396.1740; found, 396.1734.

Elemental analysis calcd (%) for $C_{22}H_{25}N_3O_2S$: C 66.81, H 6.37, N 10.62; found: C 66.80, H 6.46, N 10.67.

1) The multiplets at 2.78/2.82 and 3.36/3.37 ppm are pairwise overlapping doublets of triplets from different CH_2-groups.

(3a*SR*,6a*SR*)-4,6-Dimethyl-2-thioxo-3a,6a-di-*p*-tolylhexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2f) was synthesized according to the **GP** from **1f** (100 mg, 0.306 mmol) and HMimNCS (0.306 mL). Product **2f** was obtained as an off-white solid (102 mg, 90%); m.p. = 198–200 °C.



^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.15 (br. s, 6H, 2 × CH_3), 2.67 (s, 3H, CH_3N), 2.68 (s, 3H, CH_3N), 6.81–6.89 (m, 4H, CH, Ar), 6.96–7.05 (m, 4H, CH, Ar), 11.71 (s, 1H, NH).

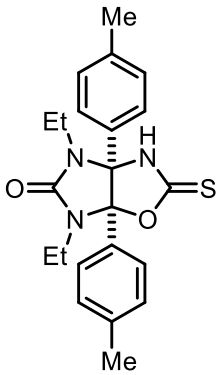
^{13}C NMR (126 MHz, DMSO-d_6): δ = 20.45 (CH_3), 20.51 (CH_3), 26.4 (CH_3N), 27.0 (CH_3N), 86.2 (C-bridge), 105.8 (C-bridge), 126.8 (2 × CH, Ar), 126.9 (2 × CH, Ar), 128.8 (C, Ar), 128.9 (2 × CH, Ar), 129.0 (2 × CH, Ar), 129.1 (C, Ar), 138.5 (C, Ar), 138.8 (C, Ar), 157.4 (C=O), 187.8 (C=S).

IR (neat): ṽ = 3147 (br. m, NH), 2924 (w), 1687 (vs, C=O), 1615 (w), 1476 (s), 1447 (s), 1413 (m), 1389 (s), 1329 (w), 1307 (w), 1283 (w), 1239 (w), 1172 (vs), 1078 (w), 1057 (w), 1034 (m), 1014 (w), 955 (m), 892 (s), 872 (m), 819 (m), 757 (m), 713 (m) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{20}H_{21}N_3NaO_2S$ $[M+Na]^+$, 390.1247; found, 390.1243.

Elemental analysis calcd (%) for $C_{20}H_{21}N_3O_2S$: C 65.37, H 5.76, N 11.44; found: C 65.35, H 5.78, N 11.51.

(3a*SR*,6a*SR*)-4,6-Diethyl-2-thioxo-3a,6a-di-*p*-tolylhexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2g) was synthesized according to the **GP** from **1g** (100 mg, 0.282 mmol) and HMimNCS (0.282 mL). Product **2g** was obtained as an off-white solid (109 mg, 97%); m.p. = 125–127 °C.



^{1}H NMR (500 MHz, DMSO-d_6):[1] δ = 1.05 (t, ^3J = 7.2 Hz, 3H, C$\underline{H_3}$CH$_2$), 1.11 (t, ^3J = 7.2 Hz, 3H, C$\underline{H_3}$CH$_2$), 2.16 (s, 6H, 2 × CH_3), 2.91 (dq, ^2J = 14.5 Hz, ^3J = 7.2 Hz, 1H, CH_2), 2.92 (dq, ^2J = 14.5 Hz, ^3J = 7.2 Hz, 1H, CH_2), 3.34 (dq, ^2J = 14.5 Hz, ^3J = 7.2 Hz, 2H, CH_2), 6.77–6.89 (m, 4H, Ar), 6.95–7.04 (m, 4H, Ar), 11.57 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 14.3 (2 × $\underline{C}H_3CH_2$), 20.49 (CH_3), 20.54 (CH_3), 36.1 (CH_2N), 36.3 (CH_2N), 86.6 (C-bridge), 106.9 (C-bridge), 126.9 (2 × CH, Ar), 127.1 (2 × CH, Ar), 128.80 (2 × CH, Ar), 128.84 (2 × CH, Ar), 129.0 (C, Ar), 129.7 (C, Ar), 138.6 (C, Ar), 138.8 (C, Ar), 157.3 (C=O), 187.9 (C=S).

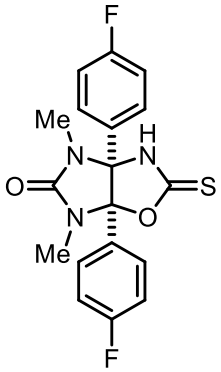
IR (neat): ṽ = 3140 (br. m, NH), 2977 (m), 2933 (m), 1693 (vs, C=O), 1616 (w), 1492 (s), 1450 (s), 1409 (s), 1350 (m), 1247 (m), 1218 (w), 1195 (w), 1170 (vs), 1088 (w), 1061 (s), 1018 (w), 970 (w), 951 (w), 909 (m), 856 (s), 798 (m), 760 (w), 733 (w), 712 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{22}H_{26}N_3O_2S$ $[M+H]^+$, 396.1740; found, 396.1741.

1) The multiplets at 2.91, 2.92 and 3.34 ppm are the overlapping doublets of quartets from different CH_2-groups.

Elemental analysis calcd (%) for $C_{22}H_{25}N_3O_2S$: C 66.81, H 6.37, N 10.62; found: C 66.82, H 6.42, N 10.70.

(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Fluorophenyl)-4,6-dimethyl-2-thioxohexahydro-5*H*-imidazo [4,5-*d*]oxazol-5-one (2h) was synthesized according to the **GP** (4 h) from **1h** (100 mg, 0.299 mmol) and HMimNCS (0.299 mL). Product **2h** was obtained as an off-white solid (93 mg, 83%); m.p. = 196–198 °C.



^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.707 (s, 3H, CH_3), 2.709 (s, 3H, CH_3), 6.96–7.11 (m, 8H, CH, Ar), 11.86 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 26.4 (CH_3), 27.0 (CH_3), 86.0 (C-bridge), 105.3 (C-bridge), 115.4 (d, $^2J_{CF}$ = 22 Hz, 2 × CH, Ar), 115.6 (d, $^2J_{CF}$ = 22 Hz, 2 × CH, Ar), 128.0 (d, $^4J_{CF}$ = 3 Hz, C, Ar), 128.3 (d, $^4J_{CF}$ = 3 Hz, C, Ar), 129.4 (d, $^3J_{CF}$ = 9 Hz, 2 × CH, Ar), 129.5 (d, $^3J_{CF}$ = 9 Hz, 2 × CH, Ar), 157.2 (C=O), 162.3 (d, $^1J_{CF}$ = 248 Hz, C, Ar), 162.4 (d, $^1J_{CF}$ = 248 Hz, C, Ar), 187.6 (C=S).

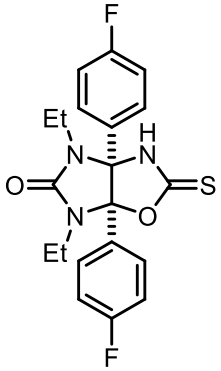
^{19}F NMR (470 MHz, DMSO-d_6): δ = –112.1 (ArF), –111.6 (ArF).

IR (neat): ṽ = 3126 (br. m, NH), 2944 (w), 1724 (vs, C=O), 1604 (m), 1504 (vs), 1447 (s), 1414 (m), 1389 (s), 1335 (m), 1234 (s), 1185 (vs), 1158 (s), 1056 (m), 1032 (s), 1010 (m), 944 (m), 866 (s), 828 (s), 751 (m), 718 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{18}H_{15}F_2N_3NaO_2S$ $[M+Na]^+$, 398.0745; found, 398.0751.

Elemental analysis calcd (%) for $C_{18}H_{15}F_2N_3O_2S$: C 57.59, H 4.03, N 11.19; found: C 57.62, H 4.15, N 11.20.

(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-fluorophenyl)-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2i) was synthesized according to the **GP** from **1i** (100 mg, 0.276 mmol) and HMimNCS (0.276 mL). Product **2i** was obtained as a yellow solid (96 mg, 86%); m.p. = 178–180 °C.



^{1}H NMR (500 MHz, DMSO-d_6):[1] δ = 1.07 (t, ^3J = 7.1 Hz, 3H, CH_3), 1.12 (t, ^3J = 7.0 Hz, 3H, CH_3), 2.95 (dq, ^2J = 14.1 Hz, ^3J = 7.0 Hz, 2H, CH_2), 3.38 (dq, ^2J = 14.1 Hz, ^3J = 7.0 Hz, 1H, CH_2), 3.39 (dq, ^2J = 14.1 Hz, ^3J = 7.1 Hz, 1H, CH_2), 6.79–7.20 (m, 8H, CH, Ar), 11.72 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 14.2 (2 × CH_3), 36.2 (CH_2), 36.3 (CH_2), 86.3 (C-bridge), 106.2 (C-bridge), 115.3 (d, $^2J_{CF}$ = 22 Hz, 2 × CH, Ar), 115.4 (d, $^2J_{CF}$ = 22 Hz, 2 × CH, Ar), 128.2 (d, $^4J_{CF}$ = 3 Hz, C, Ar), 129.0 (d, $^4J_{CF}$ = 3 Hz, C, Ar), 129.5 (d, $^3J_{CF}$ = 9 Hz, 2 × CH, Ar), 129.6 (d, $^3J_{CF}$ = 9 Hz, 2 × CH, Ar), 157.0 (C=O), 162.3 (d, $^1J_{CF}$ = 248 Hz, C, Ar), 162.4 (d, $^1J_{CF}$ = 248 Hz, C, Ar), 187.6 (C=S).

^{19}F NMR (470 MHz, DMSO-d_6): δ = –112.1 (ArF), –111.6 (ArF).

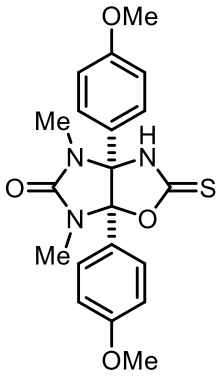
1) The multiplets at 2.95, 3.38 and 3.39 ppm are the overlapping doublets of quartets from different CH_2-groups.

IR (neat): ṽ = 3158 (br. m, NH), 2985 (w), 2943 (w), 1691 (vs, C=O), 1604 (m), 1504 (s), 1462 (s), 1409 (s), 1358 (m), 1237 (s), 1176 (s), 1158 (s), 1088 (m), 1062 (s), 1011 (w), 969 (w), 945 (w), 908 (m), 862 (s), 814 (s), 757 (m), 734 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{20}H_{20}F_2N_3O_2S$ $[M+H]^+$, 404.1239; found, 404.1235.

Elemental analysis calcd (%) for $C_{20}H_{19}F_2N_3O_2S$: C 59.54, H 4.75, N 10.42; found: C 59.50, H 4.72, N 10.40.

(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyl-2-thioxohexahydro-5*H*-imidazo [4,5-*d*]oxazol-5-one (2j) was synthesized according to the **GP** (40 °C, 2 h; then 45 °C,[1] 12 h) from **1j** (100 mg, 0.279 mmol) and HMimNCS (0.279 mL). Product **2j** was obtained as an off-white solid (98 mg, 88%), contains admixtures of thermodynamic product **3j** (~ 7%) and traces of a minor isomer of starting material; m.p. = 128–130 °C.



^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.676 (s, 3H, CH_3), 2.680 (s, 3H, CH_3), 3.646 (s, 3H, CH_3O), 3.648 (s, 3H, CH_3O), 6.72–6.79 (m, 4H, CH, Ar), 6.83–6.93 (m, 4H, CH, Ar), 11.68 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 26.4 (CH_3), 27.0 (CH_3), 55.13 (CH_3O), 55.14 (CH_3O), 86.1 (C-bridge), 106.0 (C-bridge), 113.81 (2 × CH, Ar), 113.84 (2 × CH, Ar), 123.6 (C, Ar), 123.8 (C, Ar), 128.3 (2 × CH, Ar), 128.4 (2 × CH, Ar), 157.4 (C=O), 159.6 (C, Ar), 159.8 (C, Ar), 187.7 (C=S).

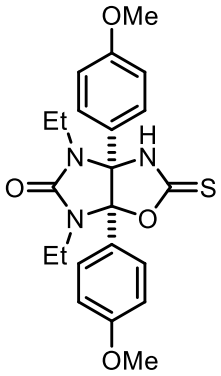
IR (KBr): ṽ = 3155 (br. m, NH), 2957 (w), 2838 (w), 1730 (s, C=O), 1703 (s, C=O), 1611 (m), 1584 (w), 1513 (vs), 1464 (m), 1417 (w), 1389 (m), 1306 (m), 1257 (s), 1173 (vs), 1035 (m), 956 (w), 941 (w), 911 (w), 865 (w), 832 (m), 758 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{20}H_{22}N_3O_4S$ $[M+H]^+$, 400.1326; found, 400.1314.

Elemental analysis calcd (%) for $C_{20}H_{21}N_3O_4S$: C 60.14, H 5.30, N 10.52; found: C 59.77, H 5.29, N 10.75.

1) The oil bath temperature was slightly increased with the thickening of the reaction mixture.

(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-methoxyphenyl)-2-thioxohexahydro-5*H*-imidazo[4,5-*d*] oxazol-5-one (2k) was synthesized according to the **GP** (50 °C, 8 h) from **1k** (100 mg, 0.259 mmol) and HMimNCS (0.259 mL). Product **2k** was obtained as an off-white solid (94 mg, 85%); m.p. = 167–169 °C.



^{1}H NMR (500 MHz, DMSO-d$_6$, 50 °C):[1] δ = 1.07 (t, ^3J = 7.1 Hz, 3H, CH$_3$), 1.13 (t, ^3J = 7.1 Hz, 3H, CH$_3$), 2.95 (dq, ^2J = 14.2 Hz, ^3J = 7.1 Hz, 2H, CH$_2$), 3.36 (dq, ^2J = 14.2 Hz, ^3J = 7.1 Hz, 2H, CH$_2$), 3.66 (br. s, 6H, 2 × CH$_3$O), 6.70–6.78 (m, 4H, CH, Ar), 6.81–6.90 (m, 4H, CH, Ar), 11.43 (s, 1H, NH).

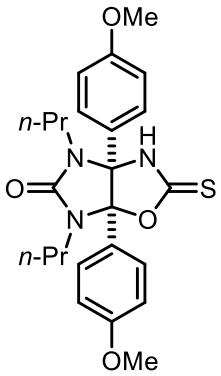
^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 14.3 (2 × CH$_3$), 36.0 (CH$_2$), 36.2 (CH$_2$), 55.1 (CH$_3$O), 55.2 (CH$_3$O), 86.5 (C-bridge), 107.0 (C-bridge), 113.7 (4 × CH, Ar), 123.7 (C, Ar), 124.4 (C, Ar), 128.4 (2 × CH, Ar), 128.5 (2 × CH, Ar), 157.3 (C=O), 159.7 (C, Ar), 159.8 (C, Ar), 187.8 (C=S).

IR (KBr): ṽ = 3126 (br. m, NH), 2973 (m), 2937 (m), 2837 (w), 1693 (vs, C=O), 1613 (s), 1582 (w), 1513 (vs), 1500 (vs), 1462 (s), 1443 (m), 1416 (s), 1379 (w), 1355 (m), 1336 (w), 1306 (s), 1261 (s), 1169 (s), 1066 (m), 1030 (m), 916 (w), 875 (m), 854 (s), 820 (m), 767 (w), 738 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for C$_{22}$H$_{26}$N$_3$O$_4$S [M+H]$^+$, 428.1639; found, 428.1648.

Elemental analysis calcd (%) for C$_{22}$H$_{25}$N$_3$O$_4$S: C 61.81, H 5.89, N 9.83; found: C 61.67, H 5.80, N 9.76.

(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dipropyl-2-thioxohexahydro-5*H*-imidazo [4,5-*d*]oxazol-5-one (2l) was synthesized according to the **GP** from **1l** (100 mg, 0.241 mmol) and HMimNCS (0.241 mL). Product **2l** was obtained as an off-white solid (97 mg, 88%); m.p. = 163–165 °C.



^{1}H NMR (500 MHz, DMSO-d$_6$):[2] δ = 0.76 (t, ^3J = 7.4 Hz, 3H, CH$_3$), 0.80 (t, ^3J = 7.4 Hz, 3H, CH$_3$), 1.47 (qt, ^3J = 7.4 Hz, ^3J = 7.2 Hz, 2H, CH$_2$), 1.57 (qt, ^3J = 7.4 Hz, ^3J = 7.1 Hz, 2H, CH$_2$), 2.74 (dt, ^2J = 14.6 Hz, ^3J = 7.2 Hz, 1H, CH$_2$), 2.79 (dt, ^2J = 13.9 Hz, ^3J = 7.1 Hz, 1H, CH$_2$), 3.27–3.37 (m, 2H, CH$_2$), 3.65 (br. s, 6H, 2 × CH$_3$O), 6.69–6.79 (m, 4H, CH, Ar), 6.79–6.88 (m, 4H, CH, Ar), 11.47 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d$_6$): δ = 11.06 (CH$_3$), 11.11 (CH$_3$), 21.6 (CH$_2$), 21.9 (CH$_2$), 42.9 (CH$_2$), 43.0 (CH$_2$), 55.1 (CH$_3$O), 55.2 (CH$_3$O), 86.5 (C-bridge), 106.8 (C-bridge), 113.65 (2 × CH, Ar), 113.72 (2 × CH, Ar), 123.5 (C, Ar), 124.2 (C, Ar), 128.4 (2 × CH, Ar), 128.5 (2 × CH, Ar), 157.5 (C=O), 159.69 (C, Ar), 159.74 (C, Ar), 187.9 (C=S).

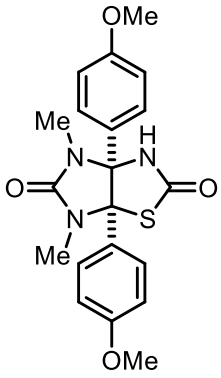
1) The multiplets at 2.95 and 3.36 ppm are the overlapping doublets of quartets from different CH$_2$-groups.
2) The multiplets at 2.74/2.79 and 3.27–3.37 ppm are the overlapping (and unresolved in the second case) doublets of triplets from different CH$_2$-groups.

IR (KBr): ṽ = 3161 (br. m, NH), 2969 (m), 2933 (m), 2838 (w), 1691 (vs, C=O), 1613 (m), 1583 (w), 1514 (s), 1493 (s), 1460 (s), 1413 (s), 1370 (m), 1304 (s), 1262 (s), 1207 (m), 1167 (s), 1096 (w), 1076 (m), 1031 (m), 915 (w), 884 (m), 856 (m), 831 (m), 763 (w), 735 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{24}H_{30}N_3O_4S$ $[M+H]^+$, 456.1952; found, 456.1956.

Elemental analysis calcd (%) for $C_{24}H_{29}N_3O_4S$: C 63.28, H 6.42, N 9.22; found: C 63.20, H 6.35, N 9.25.

(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3j) was synthesized according to the **GP** (100 °C) from **1j** (100 mg, 0.279 mmol) and HMimNCS (0.279 mL). Product **3j** was obtained as an off-white solid (84 mg, 76%); m.p. = 196–198 °C.



^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.66 (s, 3H, C$\underline{H_3}$N-C_{bridge}-NH), 2.69 (s, 3H, C$\underline{H_3}$N-C_{bridge}-S), 3.642 (s, 3H, CH_3O), 3.643 (s, 3H, CH_3O), 6.65–6.72 (m, 4H, CH, Ar), 6.72–6.81 (m, 2H, CH, Ar), 6.94–7.05 (m, 2H, CH, Ar), 9.70 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 26.6 (CH_3), 29.5 (CH_3), 55.2 (2 × CH_3O), 86.0 (S-C_{bridge}), 89.4 (HN-C_{bridge}), 113.4 (2 × CH, Ar), 113.5 (2 × CH, Ar), 124.7 (C, Ar), 126.3 (C, Ar), 128.5 (2 × CH, Ar), 129.5 (2 × CH, Ar), 158.2 (MeN-$\underline{C}$=O), 159.2 (C, Ar), 159.5 (C, Ar), 170.2 (NH-$\underline{C}$=O).

IR (KBr): ṽ = 3248 (br. m, NH), 3013 (w), 2965 (w), 2935 (w), 2839 (w), 2047 (w), 1720 (s, C=O), 1698 (vs, C=O), 1609 (m), 1583 (w), 1512 (s), 1482 (m), 1440 (m), 1393 (m), 1297 (m), 1258 (s), 1216 (m), 1176 (s), 1123 (w), 1031 (s), 922 (w), 868 (w), 846 (s), 803 (w), 783 (w), 751 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{20}H_{22}N_3O_4S$ $[M+H]^+$, 400.1326; found, 400.1325.

Elemental analysis calcd (%) for $C_{20}H_{21}N_3O_4S$: C 60.14, H 5.30, N 10.52; found: C 60.26, H 5.38, N 10.52.

Transparent irregular-shaped prism crystals of **3j** were achieved by dissolution of the compound in refluxing isopropanol, followed by complete evaporation of the solvent and resuspension of the residue in the same volume of isopropanol. The structure of **3j** is shown in Fig. S2.

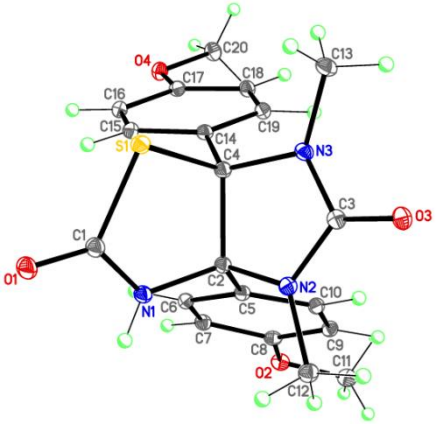
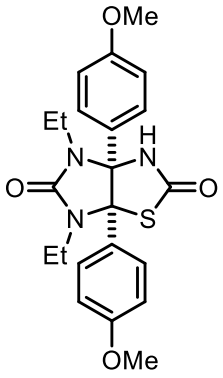


Figure S2. Crystal structure of **3j**; thermal ellipsoids are shown at a 50% probability level (CCDC 2444502).

Performing the reaction in $Et_3N{\cdot}HNCS$ (0.279 mL) under similar conditions (**1j**, 100 mg, 0.279 mmol, **GP**, 100 °C, 6 h) afforded **3j** in better yield (92 mg, 83%).

(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-methoxyphenyl)tetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3k) was synthesized according to the **GP** (100 °C) from **1k** (100 mg, 0.259 mmol) and HMimNCS (0.259 mL). Product **3k** was obtained as an off-white solid (97 mg, 87%); m.p. = 192–193 °C.



^{1}H NMR (500 MHz, DMSO-d_6):[1] δ = 1.11 (t, ^3J = 7.2 Hz, 3H, CH_3), 1.13 (t, ^3J = 7.2 Hz, 3H, CH_3), 2.87 (dq, ^2J = 14.2 Hz, ^3J = 7.2 Hz, 1H, CH_2), 2.95–3.07 (m, 2H, CH_2), 3.43 (dq, ^2J = 14.2 Hz, ^3J = 7.2 Hz, 1H, CH_2), 3.649 (s, 3H, CH_3O), 3.653 (s, 3H, CH_3O), 6.60–6.80 (m, 6H, CH, Ar), 6.94–7.09 (m, 2H, CH, Ar), 9.53 (s, 1H, NH).

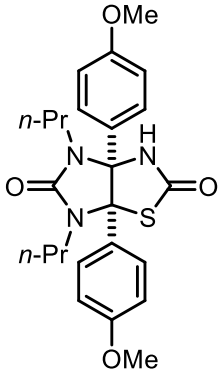
^{13}C NMR (126 MHz, DMSO-d_6): δ = 13.7 (CH_3), 14.8 (CH_3), 35.8 (CH_2), 38.7 (CH_2), 55.1 (2 × CH_3O), 86.7 (C-bridge), 89.9 (C-bridge), 113.3 (2 × CH, Ar), 113.4 (2 × CH, Ar), 125.5 (C, Ar), 126.7 (C, Ar), 128.5 (2 × CH, Ar), 129.7 (2 × CH, Ar), 158.4 (EtN-<u>C</u>=O), 159.3 (C, Ar), 159.5 (C, Ar), 170.8 (NH-<u>C</u>=O).

IR (KBr): ṽ = 3187 (br. m, NH), 3109 (br. m, NH), 2934 (w), 2838 (w), 1708 (vs, C=O), 1690 (vs, C=O), 1610 (m), 1583 (w), 1513 (s), 1463 (s), 1414 (m), 1379 (w), 1356 (w), 1307 (m), 1260 (s), 1204 (w), 1178 (s), 1056 (w), 1034 (m), 939 (w), 850 (s), 809 (w), 788 (w), 717 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{22}H_{26}N_3O_4S$ $[M+H]^+$, 428.1639; found, 428.1625.

Elemental analysis calcd (%) for $C_{22}H_{25}N_3O_4S$: C 61.81, H 5.89, N 9.83; found: C 61.71, H 5.76, N 9.77.

(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dipropyltetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3l) was synthesized according to the **GP** (100 °C, 8 h) from **1l** (100 mg, 0.241 mmol) and HMimNCS (0.241 mL). Product **3l** was obtained as an off-white solid (93 mg, 85%); m.p. = 199–201 °C.



^{1}H NMR (500 MHz, DMSO-d_6):[2] δ = 0.76 (t, ^3J = 7.4 Hz, 3H, CH_3), 0.84 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.44–1.53 (m, 1H, CH_2), 1.53–1.64 (m, 3H, CH_2), 2.70 (dt, ^2J = 14.4 Hz, ^3J = 7.4 Hz, 1H, CH_2), 2.84–2.94 (m, 2H, CH_2), 3.39 (dt, ^2J = 14.4 Hz, ^3J = 7.4 Hz, 1H, CH_2), 3.649 (s, 3H, CH_3O), 3.653 (s, 3H, CH_3O), 6.52–6.78 (m, 6H, CH, Ar), 6.93–7.06 (m, 2H, CH, Ar), 9.49 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 11.2 (CH_3), 11.4 (CH_3), 21.2 (CH_2), 22.3 (CH_2), 42.9 (CH_2), 45.7 (CH_2), 55.16 (CH_3O), 55.19 (CH_3O), 86.8 (C-bridge),

1) The multiplets at 1.11 and 1.13 ppm are the overlapping triplets from CH_3-groups; the multiplets at 2.95–3.07 ppm are the overlapping and unresolved doublets of quartets from different CH_2-groups.
2) The multiplets at 2.84–2.94 ppm are the overlapping and unresolved doublets of triplets from different CH_2-groups.

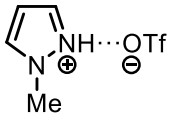
89.9 (C-bridge), 113.2 (2 × CH, Ar), 113.5 (2 × CH, Ar), 125.4 (C, Ar), 126.6 (C, Ar), 128.5 (2 × CH, Ar), 129.8 (2 × CH, Ar), 158.7 (*n*-PrN-C=O), 159.3 (C, Ar), 159.6 (C, Ar), 170.9 (NH-C=O).

IR (KBr): $\tilde{\nu}$ = 3211 (br. m, NH), 3122 (br. w, NH), 2966 (m), 2933 (w), 2873 (w), 2838 (w), 1706 (vs, C=O), 1690 (vs, C=O), 1610 (m), 1582 (w), 1512 (s), 1456 (s), 1412 (m), 1372 (m), 1306 (m), 1260 (s), 1181 (s), 1068 (w), 1032 (m), 883 (w), 844 (m), 810 (w), 790 (w), 752 (w), 716 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{24}H_{30}N_3O_4S$ $[M+H]^+$, 456.1952; found, 456.1941.

Elemental analysis calcd (%) for $C_{24}H_{29}N_3O_4S$: C 63.28, H 6.42, N 9.22; found: C 63.40, H 6.42, N 9.14.

Synthesis of 1-methylpyrazolium trifluoromethanesulfonate (HMpzOTf)



The synthesis of HMpzOTf was achieved according to a slightly modified procedure developed by us previously to obtain $Et_3N{\cdot}TfOH$.[S14] Et_2O (16 mL) was added dropwise under vigorous stirring and external ice-salt bath cooling to neat trifluoromethanesulfonic acid (TfOH, 4.26 mL, 48.1 mmol).[1] 1-Methylpyrazole[2] (4.00 mL, 48.1 mmol, 1 equiv) was added dropwise to the resulting transparent solution under the same conditions, leading to turbidity. Upon complete addition of Mpz, a yellow bottom layer of biphasic mixture solidified spontaneously into a moon-white solid, ceasing the stirring entirely. The upper ethereal layer was decanted off; the residue was crushed with a teflon(-coated) spatula[3] and stirred with additional Et_2O (2 × 16 mL, 15÷20 min each) followed by decantation of pink-colored liquid. The resulting solid was dried on a rotary evaporator (80 °C, 3 mbar, 4 h) to afford HMpzOTf as a mobile oily liquid (11.07 g, 99%; $d_{exp.} \approx 1.44 \div 1.49$, 50 °C → r.t.). Being cooled to r.t., PIL becomes supersaturated. Spontaneous solidification (Fig. S3) accompanied by a heat evolution occurred upon mechanical impact (shaking, touching with a spatula or a pipette tip during NMR preparation) providing HMpzOTf as a moon white hygroscopic solid, which was stored in a desiccator; m.p. = 48–49 °C.

^{1}H NMR (500 MHz, DMSO-d_6, *ca*. 1 M): δ = 3.92 (s, 3H, Me), 6.45 (dd, ^3J = 2.3 Hz, ^3J = 2.3 Hz, 1H, Pz), 7.84 (d, ^3J = 2.3 Hz, 1H, Pz), 7.95 (d, ^3J = 2.3 Hz, 1H, Pz), 13.41 (br. s, 1H, NH^+).

^{13}C NMR (126 MHz, DMSO-d_6, *ca*. 1 M): δ = 38.3 (Me), 106.6 (CH, Pz), 120.95 (q, $^1J_{CF}$ = 323 Hz, CF_3), 133.5 (CH, Pz), 136.9 (CH, Pz).

^{19}F NMR (470 MHz, DMSO-d_6): δ = –77.5 (CF_3).

1) **CAUTION!** Et_2O addition was accompanied by severe fuming and strong exotherm. Thus, a fuming hood and protective wear are required. Transferring of neat viscous PIL into other flask may be very troublesome; a pre-weighed 50 mL one-neck round-bottom reaction flask was used for the synthesis.

2) 1-Methylpyrazole was distilled (b.p. = 125–126 °C) to achieve a colorless liquid and stored in a fridge prior to use.

3) **Caution!** HMpzOTf is hygroscopic and obtains a coloration upon handling with an ordinary spatula. Thus, all operations with this reagent should be performed as fast as possible with minimum exposure both to air and steel weighing instruments.

IR (KBr):[1] ṽ = 3527 (br. m, NH), 3136 (br. w, NH), 2726 (w), 1639 (w), 1584 (w), 1515 (w), 1441 (m), 1413 (m), 1277 (br. vs, SO_3), 1247 (br. vs, CF_3), 1167 (vs, CF_3), 1106 (m), 1030 (vs, SO_3), 987 (w), 909 (w), 785 (m), 639 (vs), 576 (w) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_4H_7N_2^+$ $[HMpz]^+$, 83.0604; found, 83.0600; calcd for $CF_3O_3S^-$ $[TfO]^-$, 148.9526; found, 148.9520.

Elemental analysis calcd (%) for $C_5H_7F_3N_2O_3S$: C 25.87, H 3.04, N 12.07; found: C 25.87, H 3.17, N 12.06.

Colorless long needle-like prism crystals of HMpzOTf were achieved upon mechanical impact with a spatula on a melted PIL cooled to *ca.* 30 °C according to our previous procedure.[S2] Separated crystals were quickly drawn out with a spatula from the amorphous crystallizing mass before the complete solidification occurred; the resulting crystals had a similar m.p. = 47.5–48.5 °C (the structure and the appearance of crystals are shown in Fig. S3).

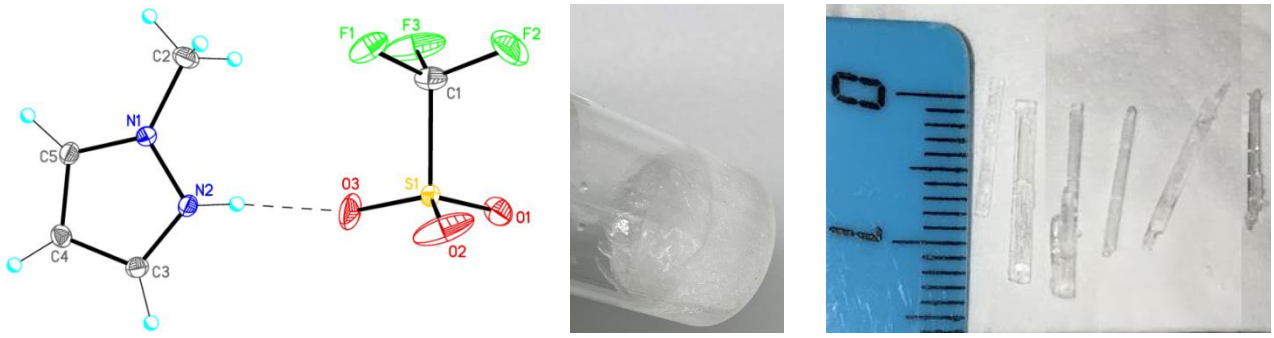
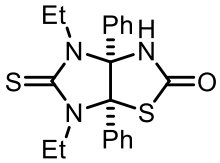


Figure S3. Crystal structure of HMpzOTf; thermal ellipsoids are shown at a 50% probability level (CCDC 2444503).

Procedure for the rearrangement of 2a to 3a

(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyl-5-thioxohexahydro-2*H*-imidazo[4,5-*d*]thiazol-2-one (3a) was synthesized according to the **GP** (100 °C, 6 h) from **2a** (100 mg, 0.261 mmol) and HMpzOTf (0.261 mL, *ca*. 6.2 equiv, corresponding to *ca*. 1 M final concentration of starting material in PIL). Product **3a** was obtained as an off-white solid (75 mg, 75%); m.p. = 228–230 °C (dec.).



^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.14 (t, ^3J = 7.1 Hz, 3H, CH_3), 1.24 (t, ^3J = 6.9 Hz, 3H, CH_3), 3.07 (dq, ^2J = 14.0 Hz, ^3J = 6.9 Hz, 1H, CH_2), 3.26 (dq, ^2J = 14.0 Hz, ^3J = 6.9 Hz, 1H, CH_2), 3.69 (dq, ^2J = 14.2 Hz, ^3J = 7.1 Hz, 1H, CH_2), 3.98 (dq, ^2J = 14.2 Hz, ^3J = 7.1 Hz, 1H, CH_2), 6.59–6.77 (m, 2H, CH, Ar), 6.93–7.27 (m, 8H, CH, Ar), 9.93 (s, 1H, NH).

1) The assignements of trifluoromethanesulfonate anion were made according to the ref. S15.

^{13}C NMR (126 MHz, DMSO-d_6): δ = 12.9 (CH_3), 13.7 (CH_3), 39.8 (CH_2), 41.6 (CH_2), 90.9 (C-bridge), 91.4 (C-bridge), 127.0 (2 × CH, Ar), 128.1 (2 × CH, Ar), 128.3 (2 × CH, Ar), 128.5 (2 × CH, Ar), 129.0 (C, Ar), 129.2 (C, Ar), 132.7 (C, Ar), 133.6 (C, Ar), 170.4 (C=O), 182.3 (C=S).

IR (KBr): ṽ = 3214 (br. m, NH), 3065 (w), 2977 (w), 2934 (w), 1696 (vs, C=O), 1469 (s), 1444 (m), 1394 (s), 1352 (s), 1316 (m), 1271 (s), 1237 (m), 1211 (w), 1180 (w), 1122 (m), 1086 (w), 1011 (m), 923 (w), 879 (w), 815 (m), 777 (m), 717 (w), 694 (m) cm^{-1}.

HRMS (ESI-TOF): *m/z* calcd for $C_{20}H_{21}N_3NaOS_2$ $[M+Na]^+$, 406.1018; found, 406.1023.

Elemental analysis calcd (%) for $C_{20}H_{21}N_3OS_2$: C 62.63, H 5.52, N 10.96; found: C 62.43, H 5.30, N 10.81.

Transparent small irregular-shaped prism crystals of **3a** (accompanied by colorless flakes and platelets) were grown by slow evaporation of the compound's solution in aq. ethanol. The structure of **3a** is shown in Fig. S4.

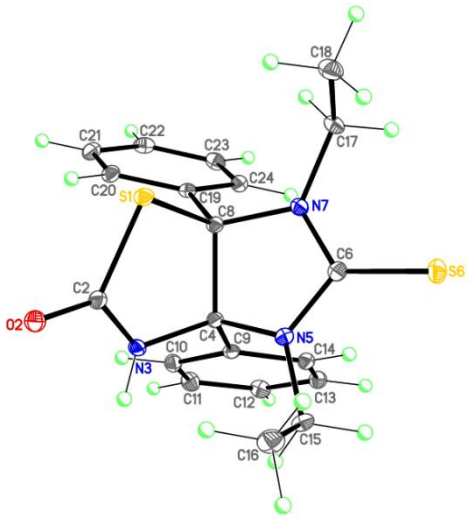


Figure S4. Crystal structure of **3a**; thermal ellipsoids are shown at a 50% probability level (CCDC 2444501).

The gram-scale experiment (1.000 g, 2.607 mmol of **2a**; 5.214 mL of HMpzOTf, *ca*. 12.4 equiv, corresponding to *ca*. 0.5 M final concentration of starting material in PIL) was carried out under similar conditions in a 15 mL vial. After addition of distilled water (*ca*. 7 mL) the obtained suspension was poured into a beaker with 80 mL of distilled water to maximize slurrying of the product. The resulting precipitate was filtered, washed with distilled water (10 × 10 mL) to remove excessive PIL, and dried on air. To remove traces of water and residual PIL, the compound was dried under reduced pressure on a rotary evaporator at 80 °C for 6 hours. Product **3a** was obtained as an off-white solid (0.968 g, 97%).

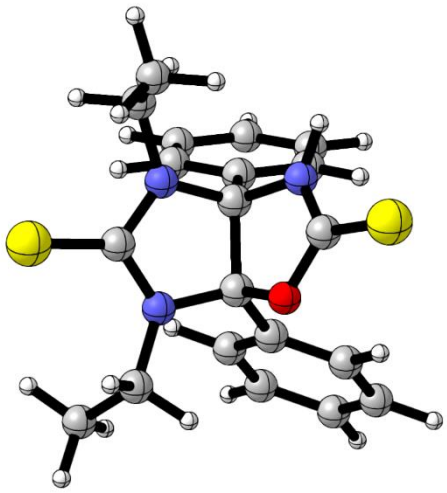
Elemental analysis calcd (%) for $C_{20}H_{21}N_3OS_2$: C 62.63, H 5.52, N 10.96; found: C 62.59, H 5.51, N 10.97.

DFT studies

Calculations were performed using the density functional theory in the Gaussian 16 software package.[S16] All geometry optimizations and frequency calculations were carried out at PBE0[S17]-D3[S18]/Def2-TZVPP[S19] level of theory. The optimizations were conducted with tight convergence criteria and an ultrafine integration grid. All optimized geometries were characterized to be a minimum with no imaginary frequencies or a transition state with a single imaginary frequency. For transition states, the imaginary frequency was followed in both directions (starting materials and product) to ensure that the correct transition state was found. Energies mentioned in the paper refer to the difference of the Gibbs free energies. Three-dimensional structures were generated using CYLview20 build 0001.[S20]

Cartesian coordinates and energetic parameters

2a



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E_0^{298} = – 1809.269697 a.u.

G^{298} = – 1809.323178 a.u.

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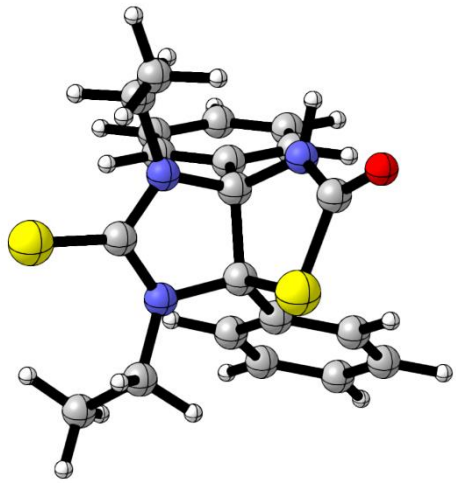
3a



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E_0^{298} = – 1809.283006 a.u.

G^{298} = – 1809.335749 a.u.

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C	2.5646000	3.1873250	-1.3511920
H	3.3254570	3.7965730	-1.8238790
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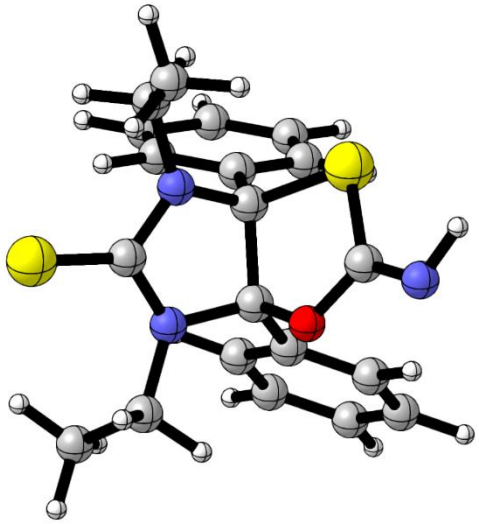
Intermediate G



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E_0^{298} = – 1809.251262 a.u.

G^{298} = – 1809.304096 a.u.

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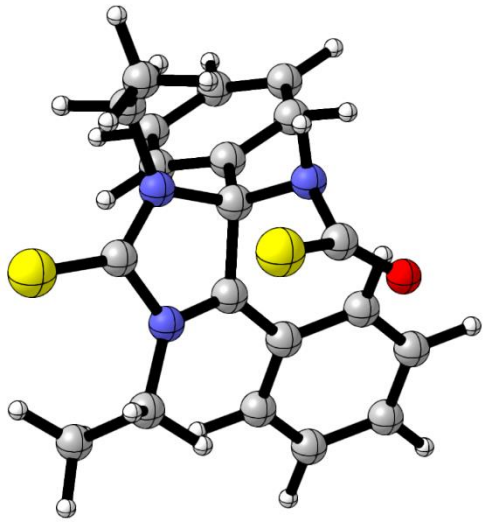
_C–O_ bond fission in 2a



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E_0^{298} = – 1809.192146 a.u.

G^{298} = – 1809.245742 a.u.

Imaginary Frequency = – 80.86 cm^{-1}

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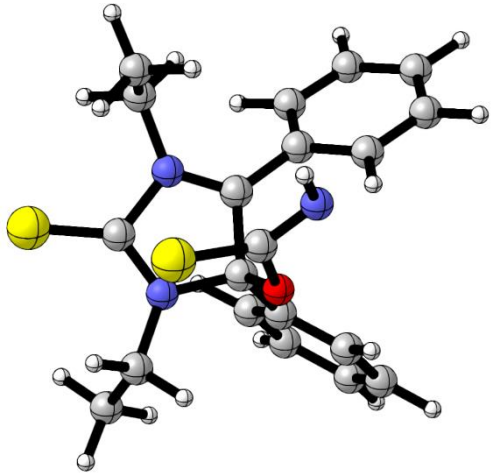
N	0.2034790	0.6356220	-1.8449810
H	0.8020320	1.3709220	-2.2027600
C	0.2065770	0.7015370	-0.4123570
C	1.9045970	-0.2445090	0.8788270
C	-0.2297330	-0.6377040	0.1756010
C	0.6178680	-0.6856570	-2.4767740
C	-0.6959120	1.8170610	0.1207410
C	-0.6896940	2.1124070	1.4813080
H	-0.0227860	1.5777720	2.1493310
C	-1.5203210	3.0978560	1.9870880
H	-1.5088210	3.3199830	3.0472420
C	-2.3594380	3.8030690	1.1346260
H	-3.0062310	4.5778990	1.5280510
C	-2.3642070	3.5129210	-0.2205970

H	-3.0144530	4.0613690	-0.8913750
C	-1.5407530	2.5166910	-0.7272840
H	-1.5455310	2.2699060	-1.7808270
C	-1.5667020	-1.1696330	0.0488470
C	-2.3549000	-0.7954770	-1.0495480
H	-1.9225140	-0.1855290	-1.8287280
C	-3.6471830	-1.2704630	-1.1658850
H	-4.2344660	-0.9987430	-2.0335540
C	-4.1860050	-2.0898730	-0.1858970
H	-5.2024840	-2.4530320	-0.2803820
C	-3.4271140	-2.4384240	0.9247920
H	-3.8517250	-3.0574690	1.7049080
C	-2.1279540	-1.9895910	1.0401380
H	-1.5679440	-2.2396410	1.9275340
C	2.3529330	2.0181630	0.0612580
H	2.7525830	2.2487650	1.0525200
H	1.6718970	2.8270980	-0.2116770
C	3.4859090	1.8907160	-0.9395350
H	4.0270500	2.8384110	-0.9750240
H	3.1252780	1.6379460	-1.9350350
H	4.1743060	1.1018800	-0.6420070
C	0.9058580	-2.5058990	1.3565240
H	1.8942520	-2.8266860	1.0249150
H	0.1618280	-3.1105050	0.8417480
C	0.8014140	-2.6125240	2.8659600
H	0.8613160	-3.6647590	3.1471670
H	-0.1365480	-2.2109460	3.2520600
H	1.6229320	-2.0798750	3.3405590

_C–N_ bond fission in 2a



ZPE = 0.377941 a.u.

E_0^{298} = –1809.183089 a.u.

G^{298} = –1809.236603 a.u.

Imaginary Frequency = – 43.06 cm^{-1}

0 1

S	-3.2444390	-0.1332110	-1.8714520
S	-2.6976930	0.6942220	2.0731280
O	-0.2272640	-0.3358230	1.8153400
N	-0.8969820	0.9583500	-1.0458830
N	-1.3779180	-1.0186060	-0.1561220

N	-0.2593590	1.6814580	2.7775990
H	-0.8393290	2.4301490	3.1419120
C	0.1430780	0.6873050	-0.3236480
C	-1.8784240	-0.1182990	-0.9865320
C	-0.1283240	-0.5910160	0.4699710
C	-1.0229410	0.7962040	2.2637610
C	1.4119640	1.3867720	-0.3333730
C	1.9967510	1.6965020	-1.5679100
H	1.4848070	1.4468670	-2.4894820
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H	4.9219000	2.9803450	-0.4696810
C	3.3608450	2.2192410	0.7900550
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C	1.7949860	-2.0158340	1.2777900
H	1.6212940	-1.6250820	2.2708960
C	2.8189870	-2.9207480	1.0333610
H	3.4498890	-3.2466470	1.8513830
C	3.0376210	-3.4033280	-0.2475150
H	3.8401230	-4.1067330	-0.4340350
C	2.2243080	-2.9840550	-1.2920460
H	2.3876210	-3.3589750	-2.2950500
C	1.1954780	-2.0903320	-1.0492410
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C	-2.1103040	-2.1781800	0.3206760
H	-3.1346620	-1.8476970	0.4955060
H	-1.6865630	-2.4222230	1.2947690
C	-2.0517450	-3.3559760	-0.6327880
H	-2.6613160	-4.1693180	-0.2359710
H	-1.0323210	-3.7225060	-0.7551880
H	-2.4504170	-3.0813380	-1.6099380

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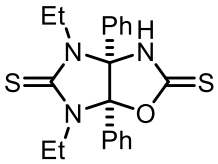
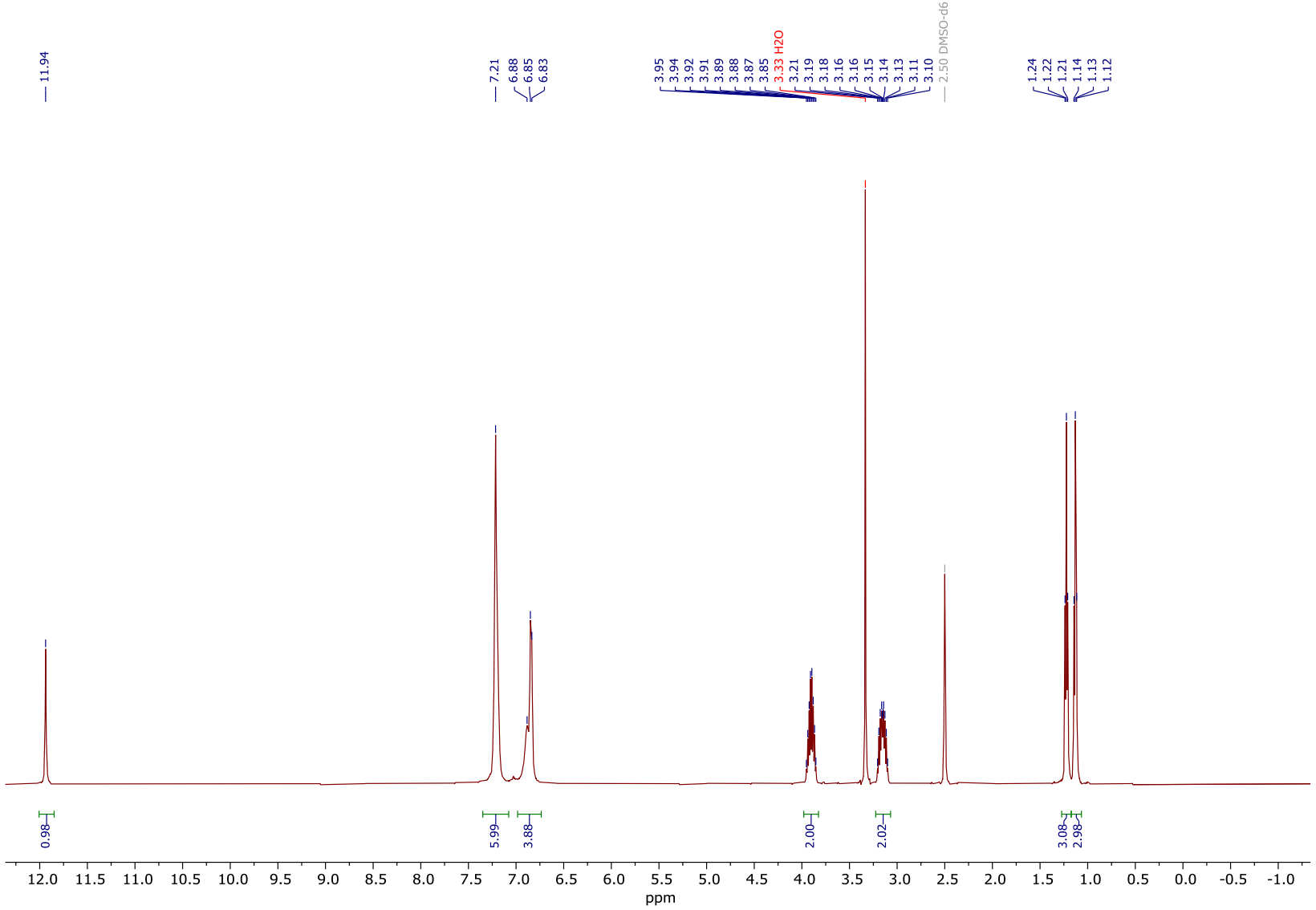
Copies of NMR spectra

Kinetic control products (2)

(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithione (2a)

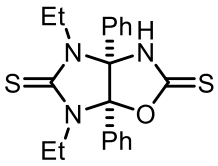
^{1}H NMR (500 MHz, DMSO-d$_6$)

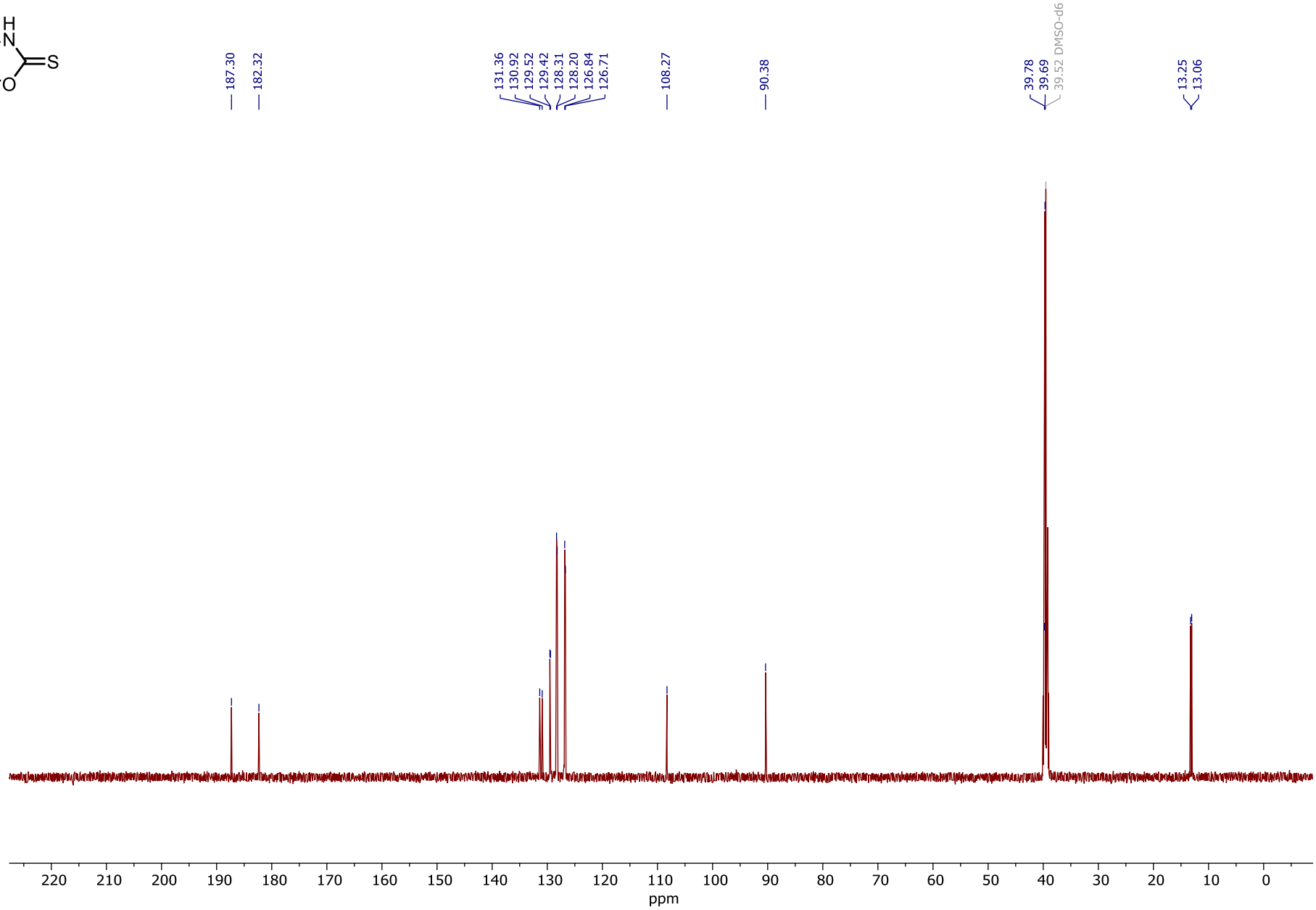




(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithione (2a)

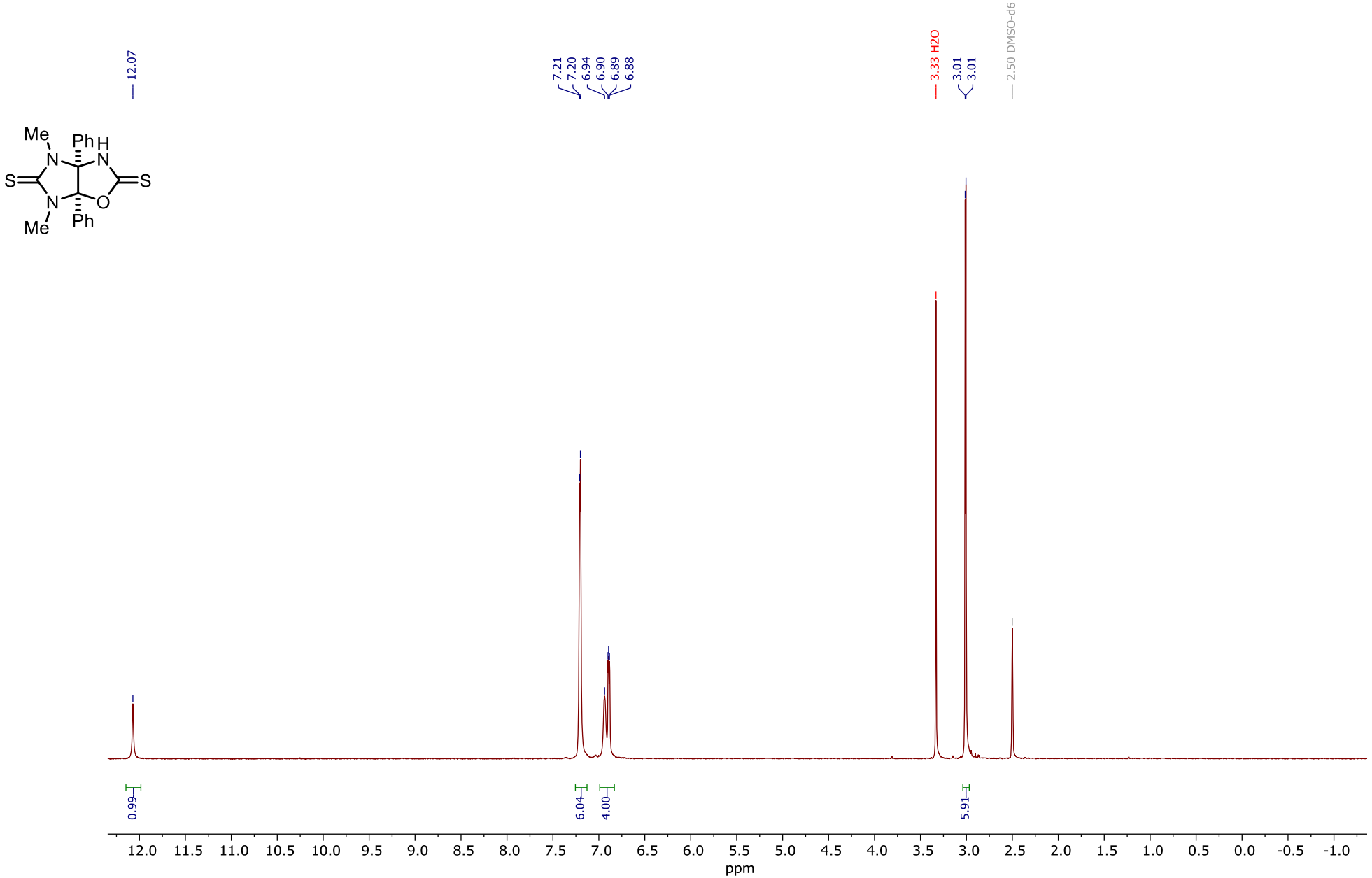
^{13}C NMR (126 MHz, DMSO-d$_6$, 50 °C)





(3a*SR*,6a*SR*)-4,6-Dimethyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithione (2b)

^{1}H NMR (500 MHz, DMSO-d$_6$)



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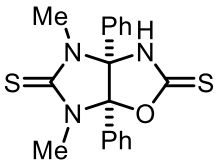
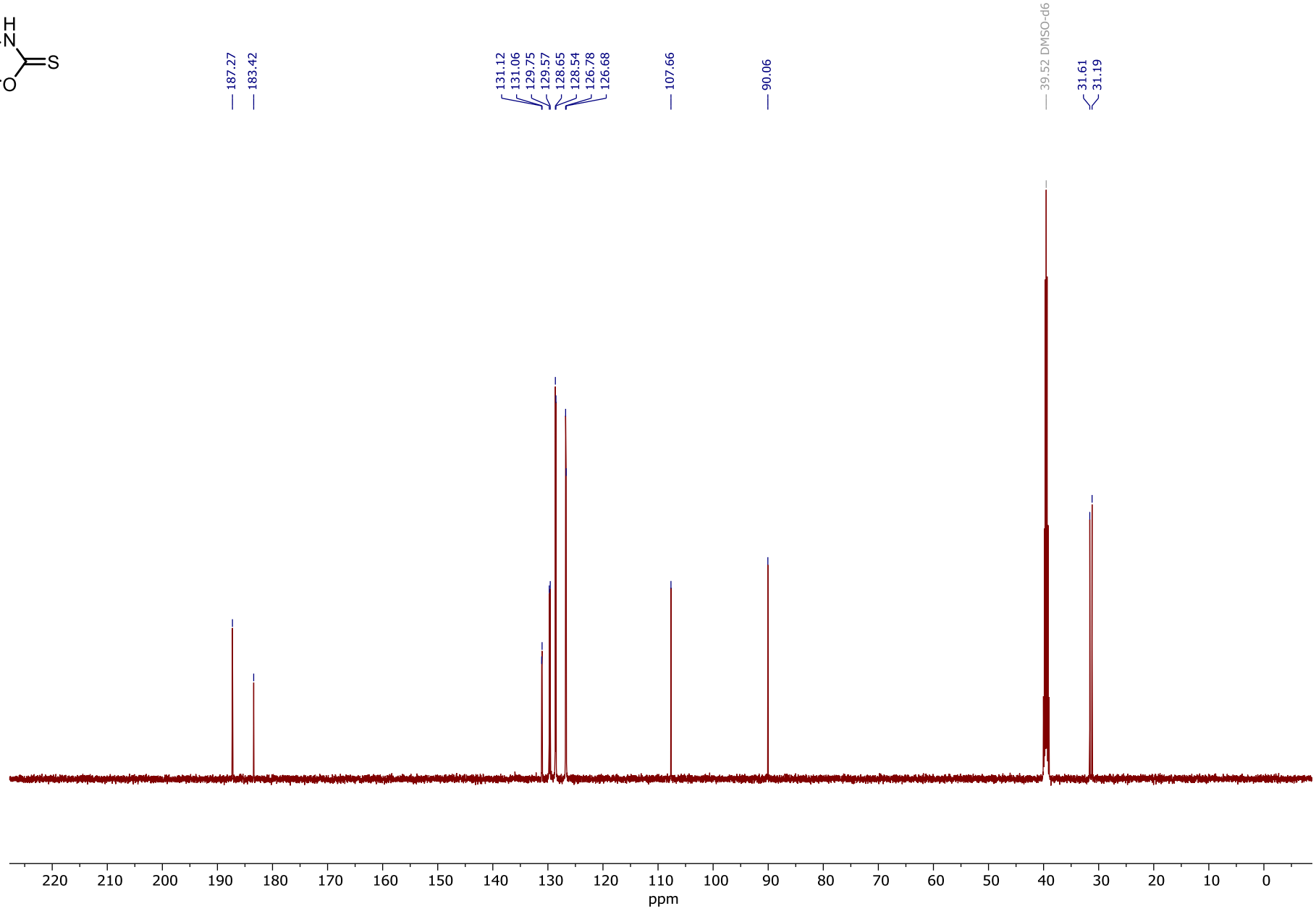
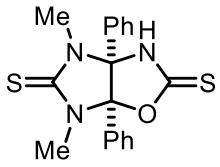
^{13}C NMR (126 MHz, DMSO-d$_6$)

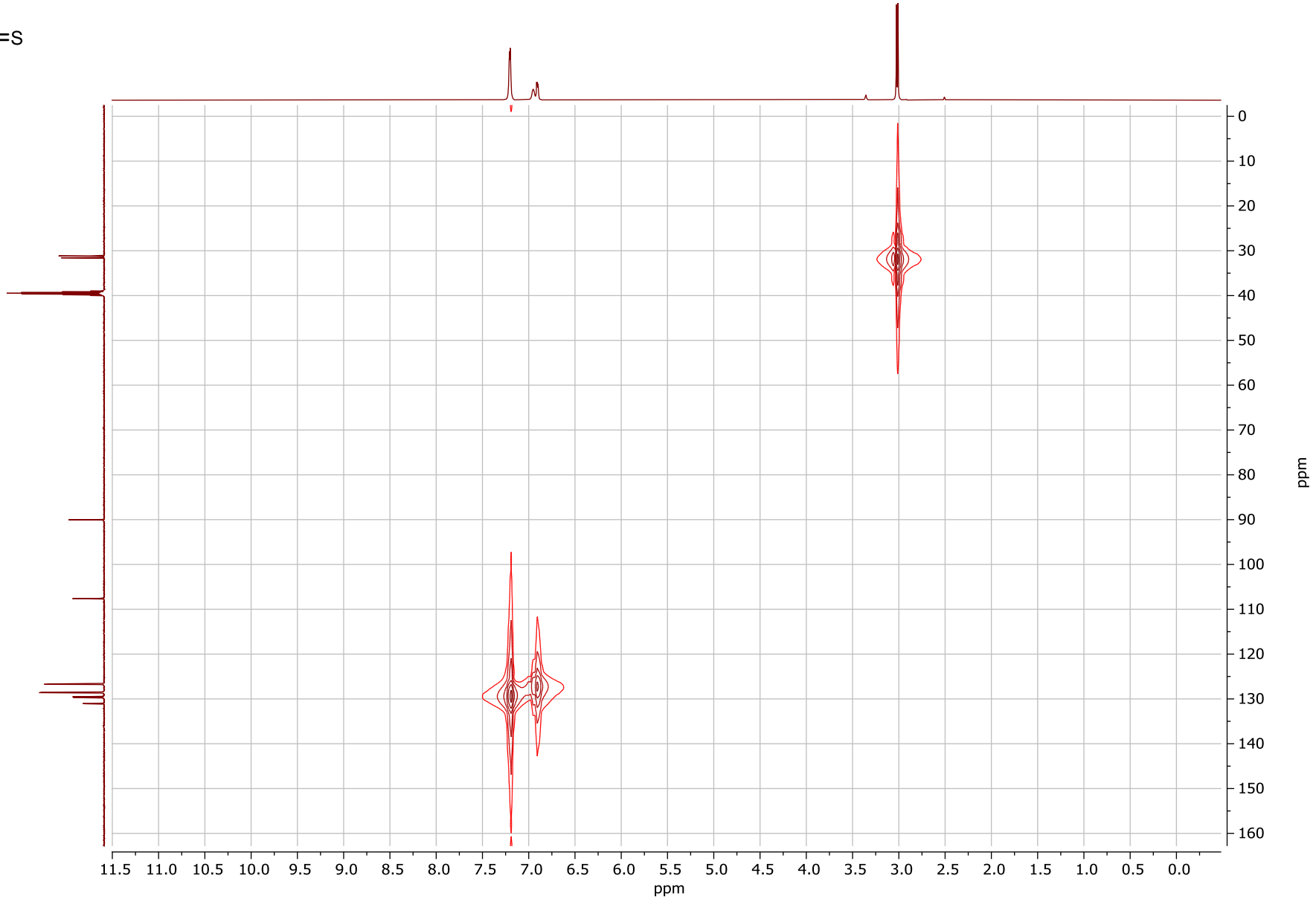




(3a*SR*,6a*SR*)-4,6-Dimethyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithione (2b)

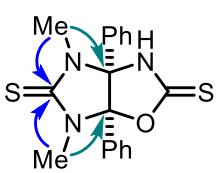
^{1}H–^{13}C HSQC (DMSO-d_6)

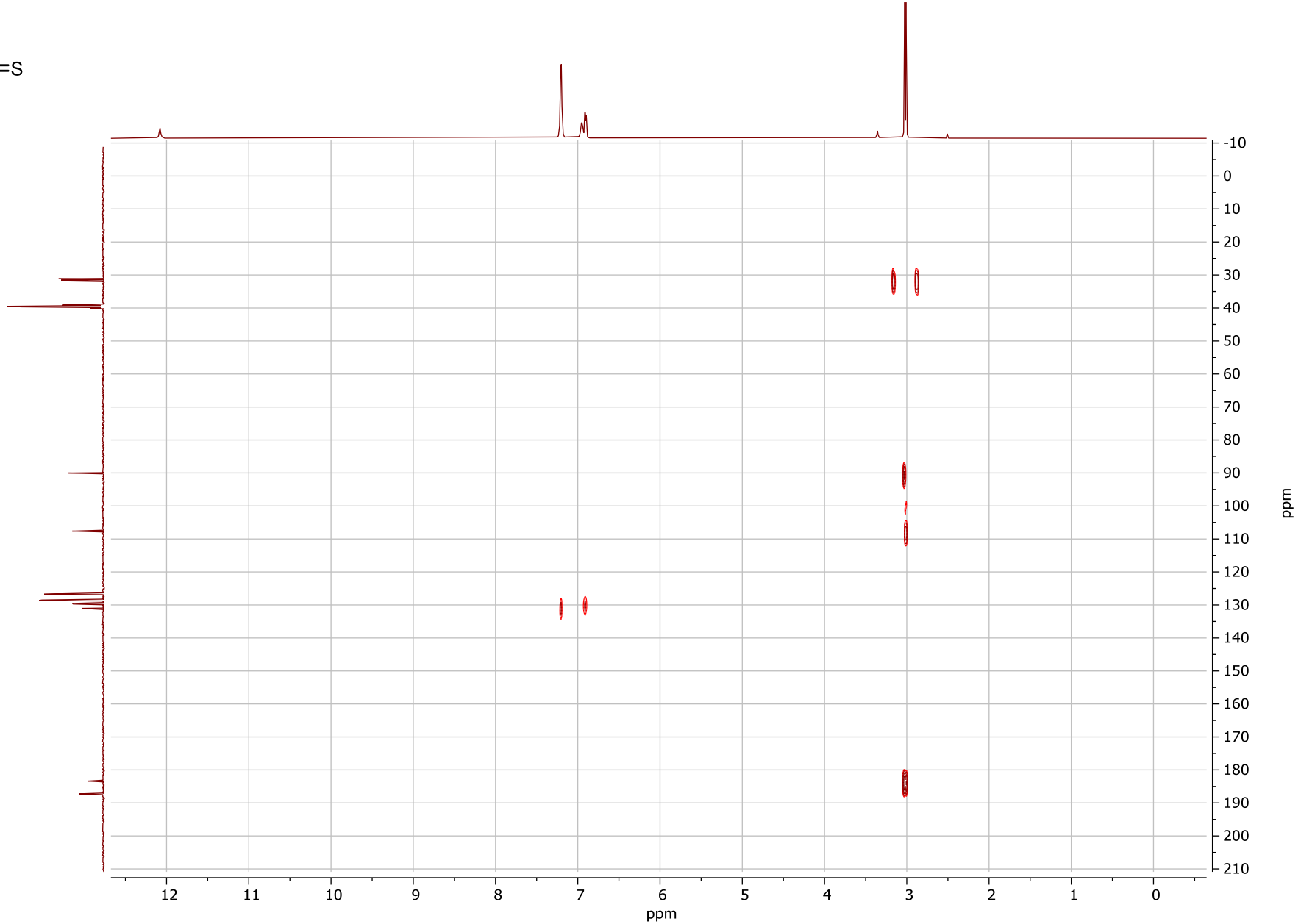




(3a*SR*,6a*SR*)-4,6-Dimethyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithione (2b)

^{1}H–^{13}C HMBC (DMSO-d_6)





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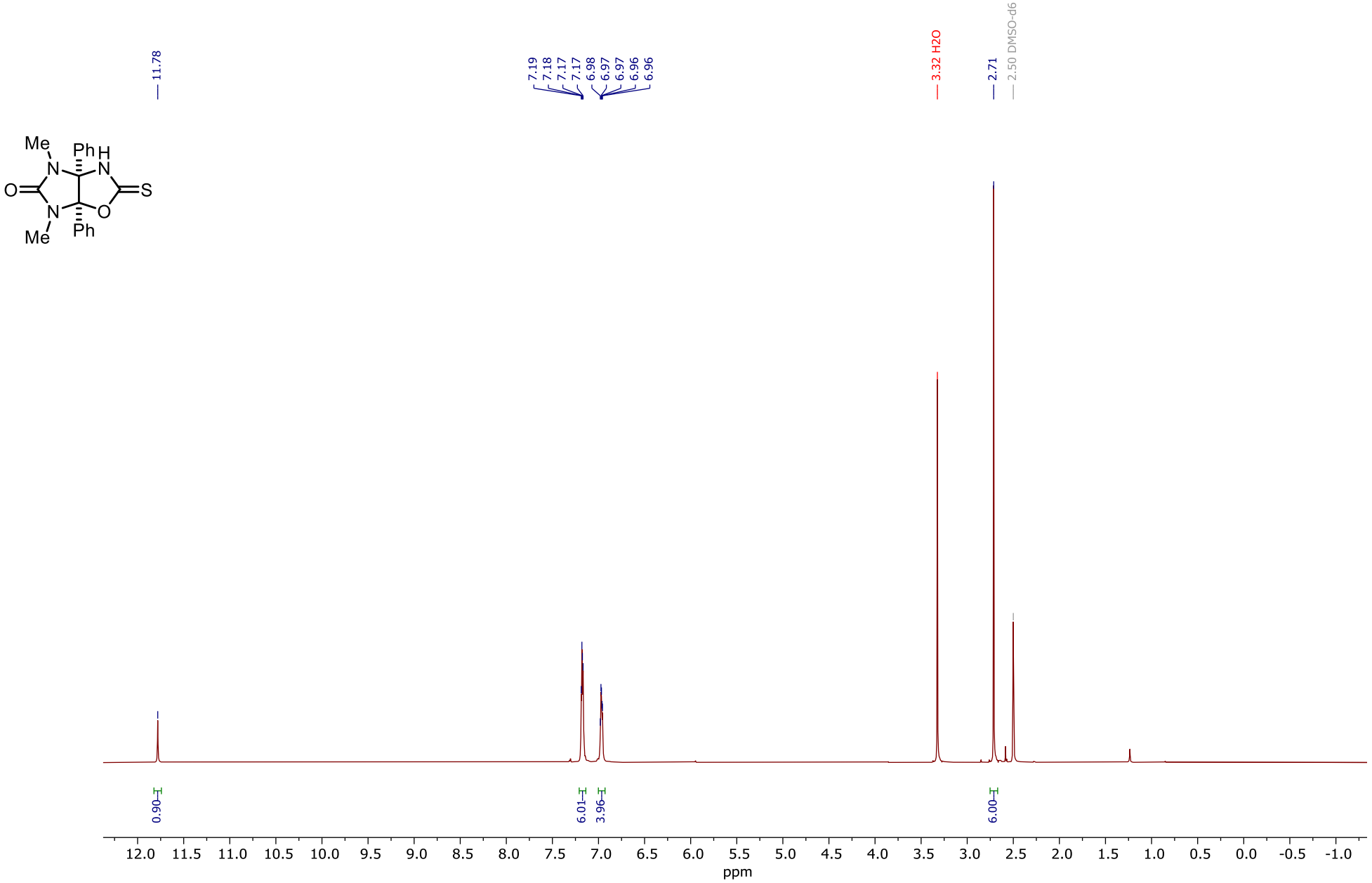
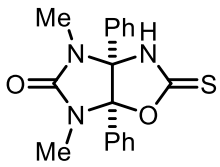
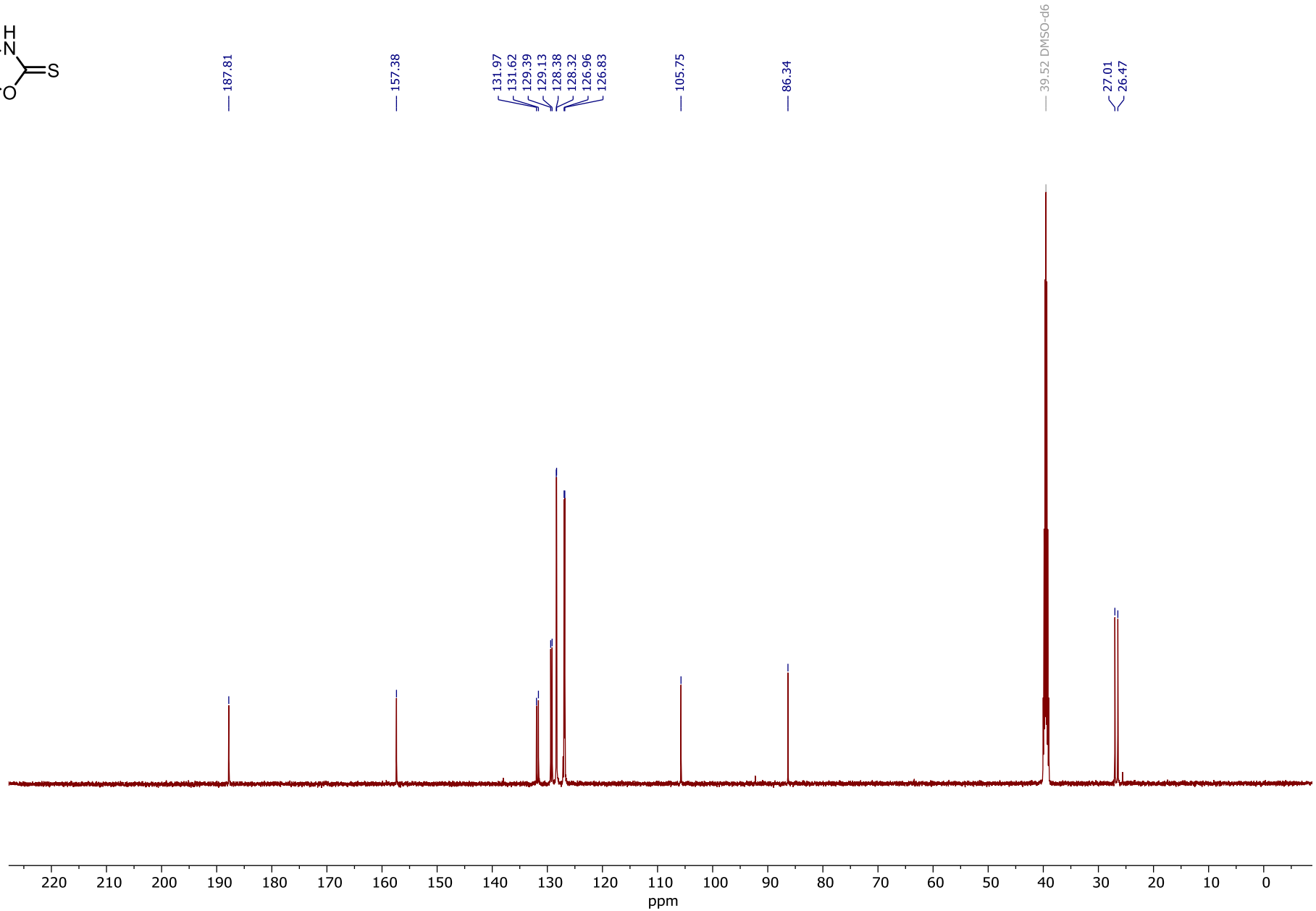
^{1}H NMR (500 MHz, DMSO-d$_6$)



(3a*SR*,6a*SR*)-4,6-Dimethyl-3a,6a-diphenyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2c)

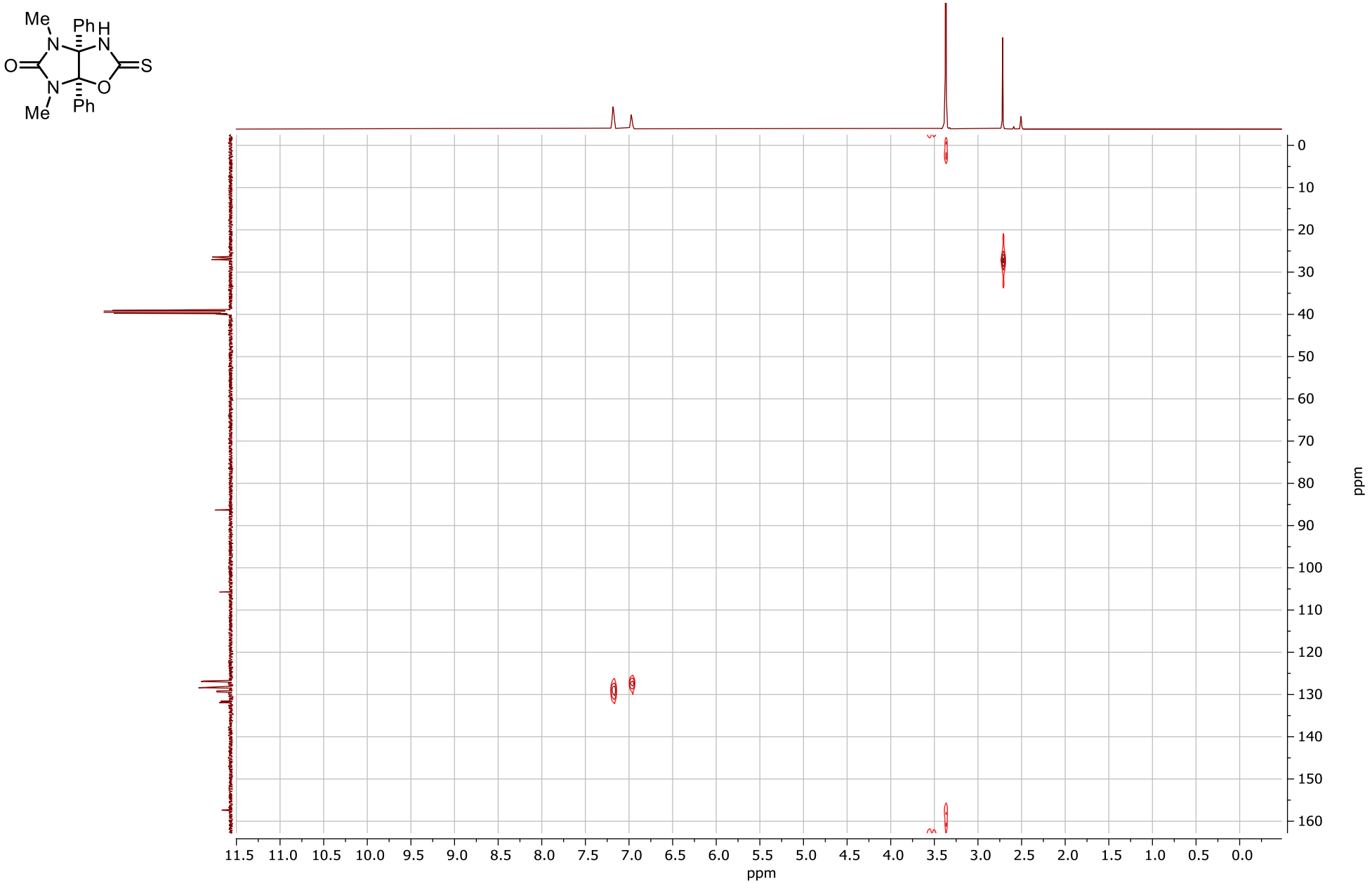
^{13}C NMR (126 MHz, DMSO-d$_6$)





(3a*SR*,6a*SR*)-4,6-Dimethyl-3a,6a-diphenyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2c)

^{1}H–^{13}C HSQC (DMSO-d_6)



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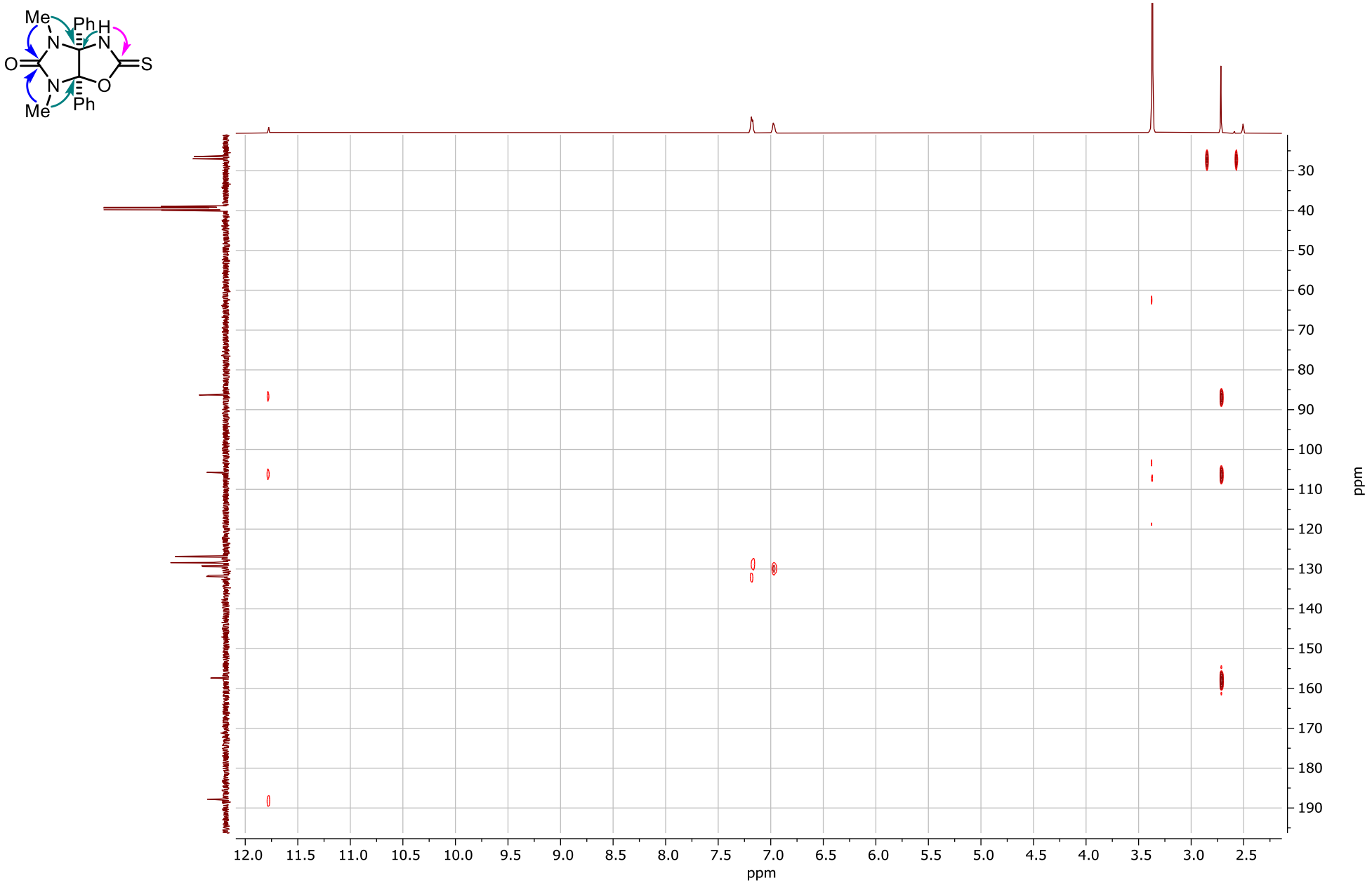
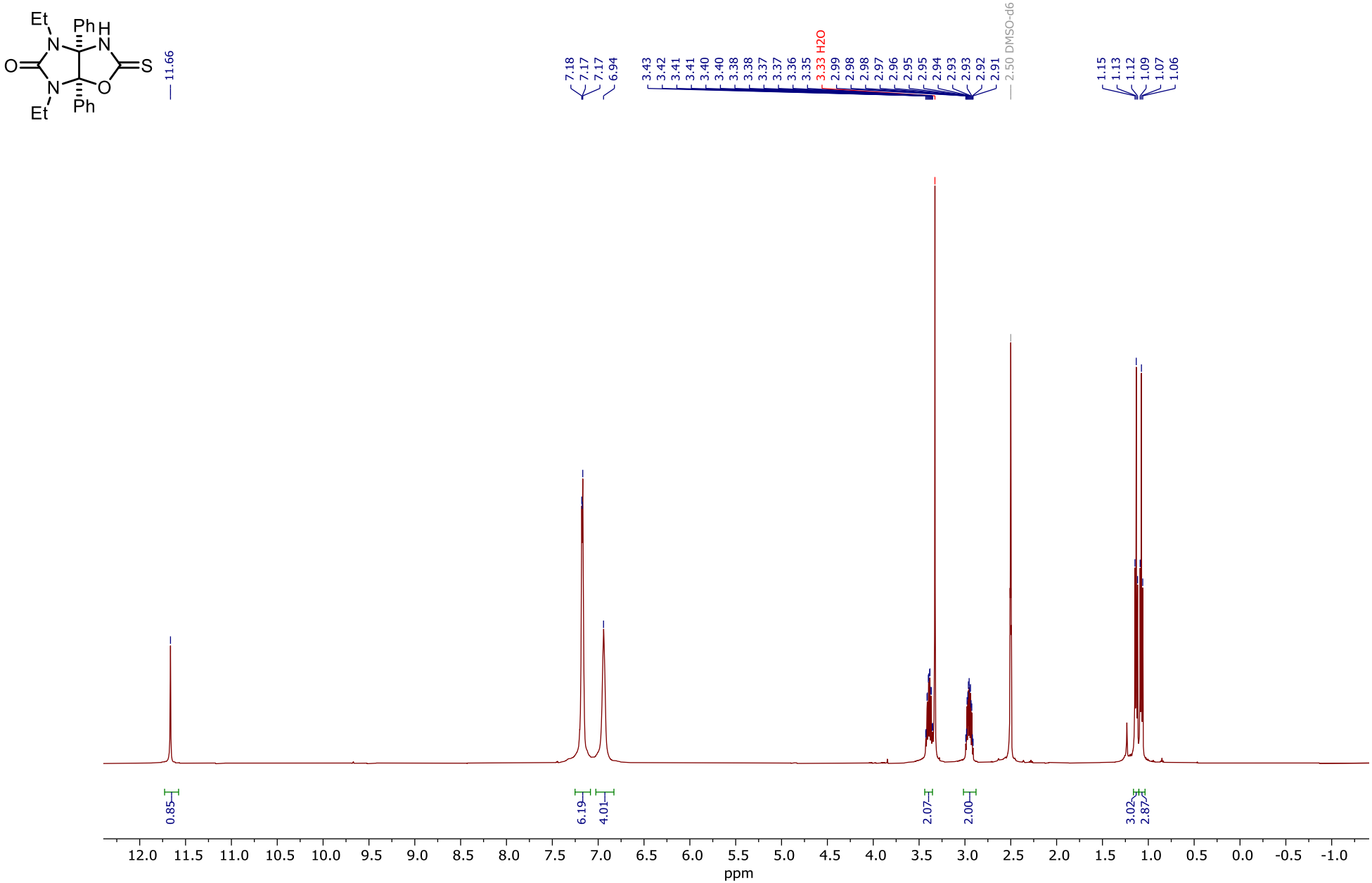
^{1}H–^{13}C HMBC (DMSO-d_6)



(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2d)

^{1}H NMR (500 MHz, DMSO-d$_6$)



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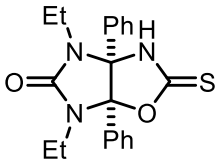
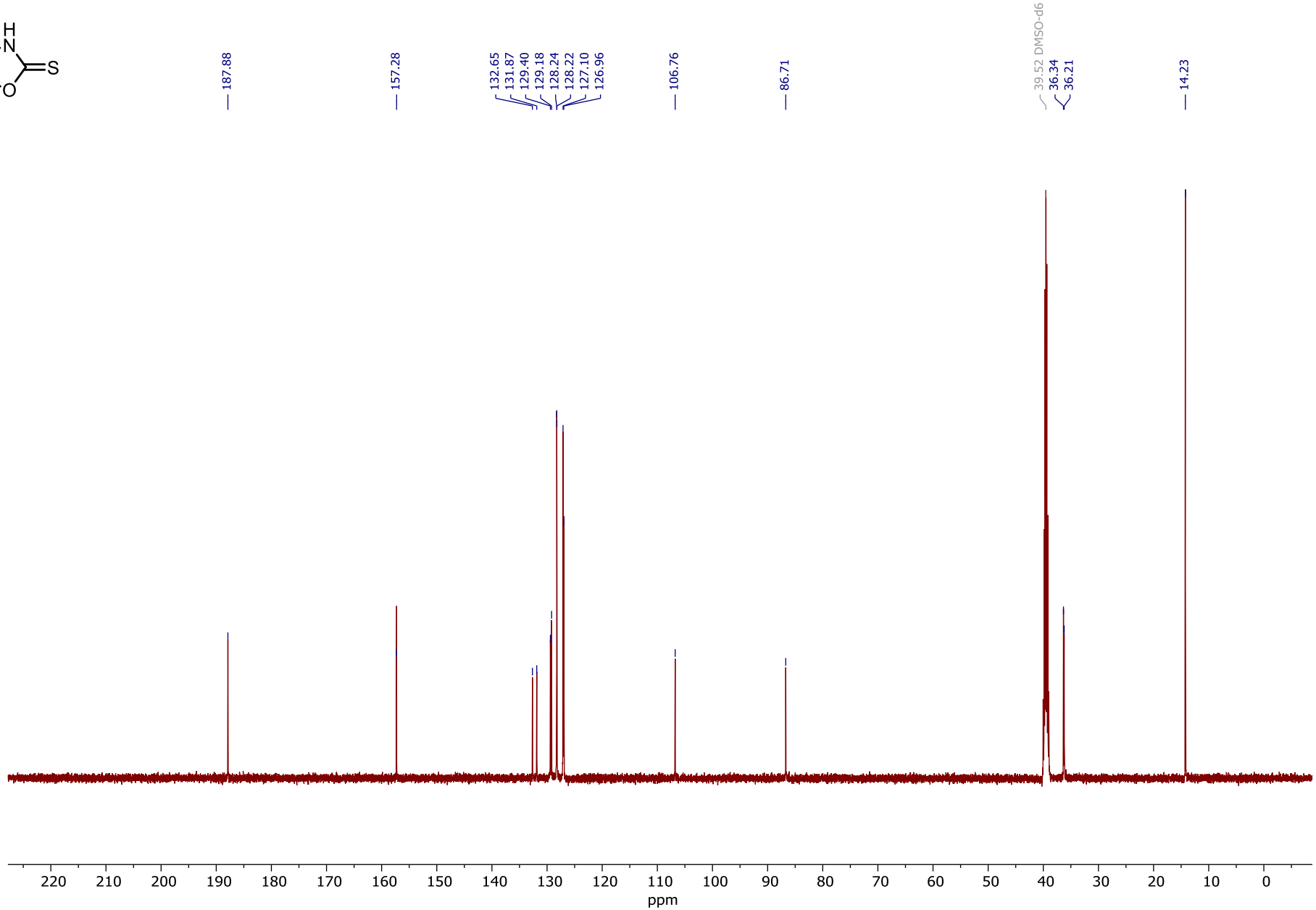
^{13}C NMR (126 MHz, DMSO-d$_6$)





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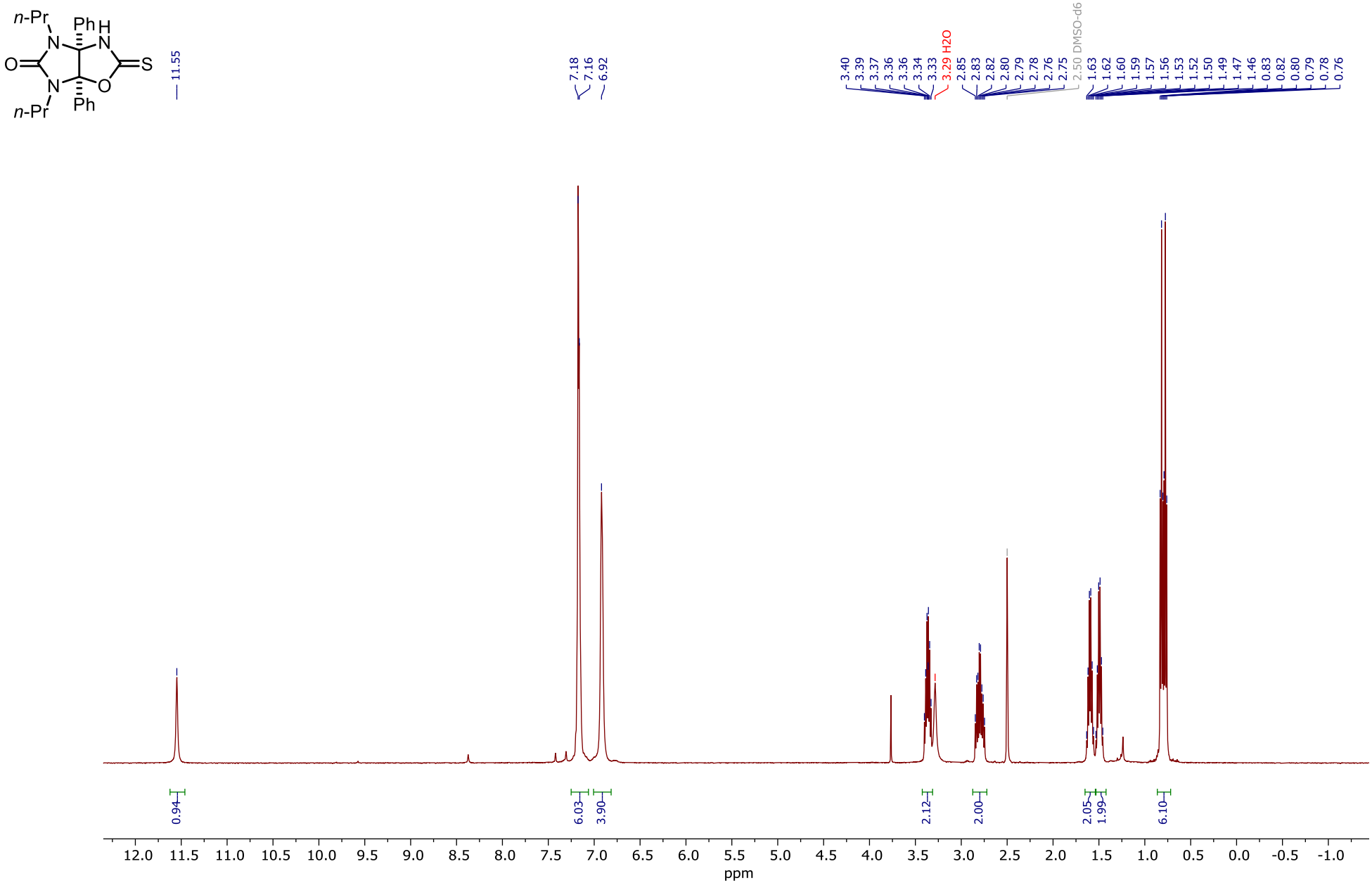
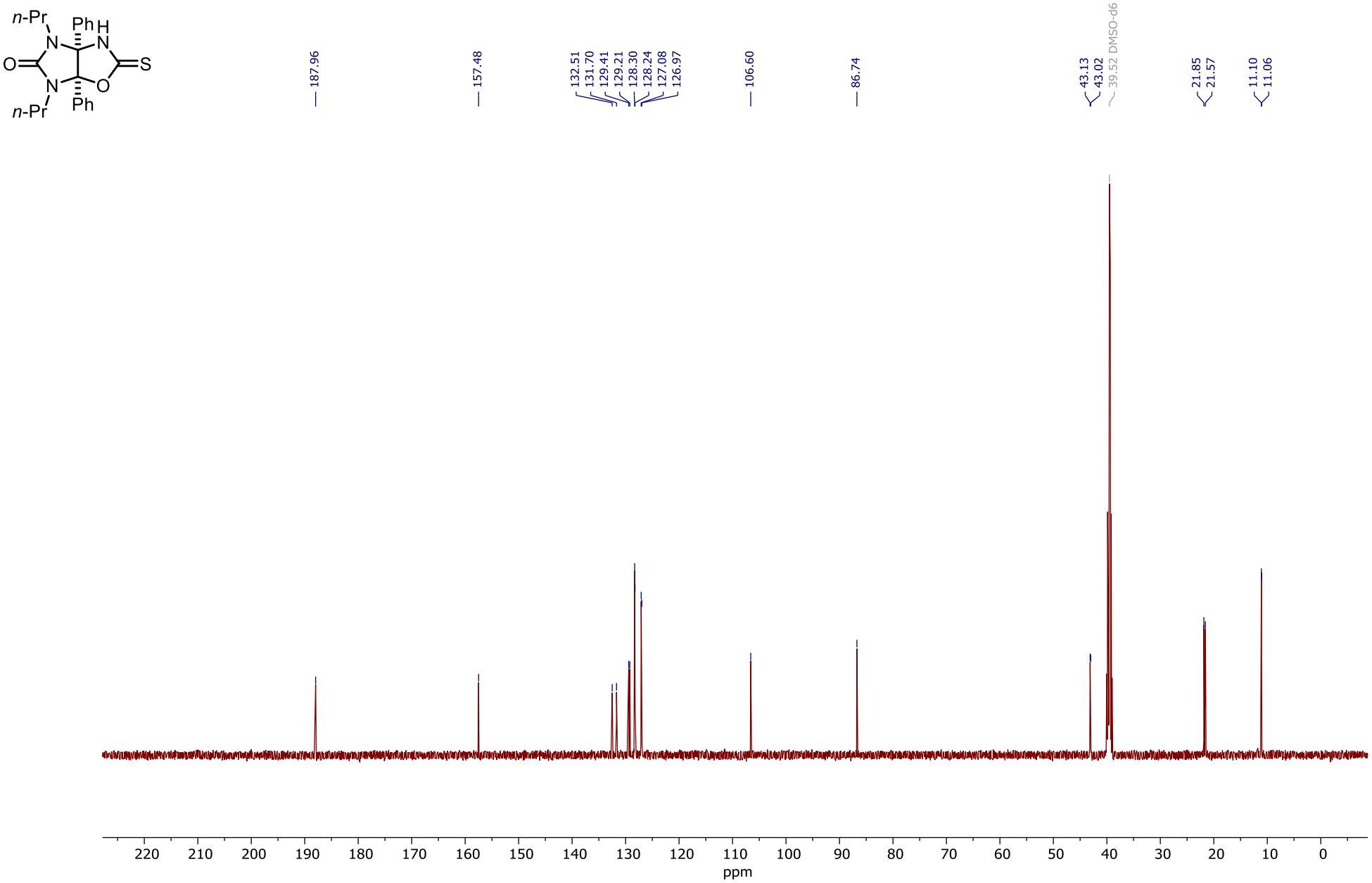
^{1}H NMR (500 MHz, DMSO-d$_6$)



(3a*SR*,6a*SR*)-3a,6a-Diphenyl-4,6-dipropyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2e)

^{13}C NMR (126 MHz, DMSO-d$_6$)



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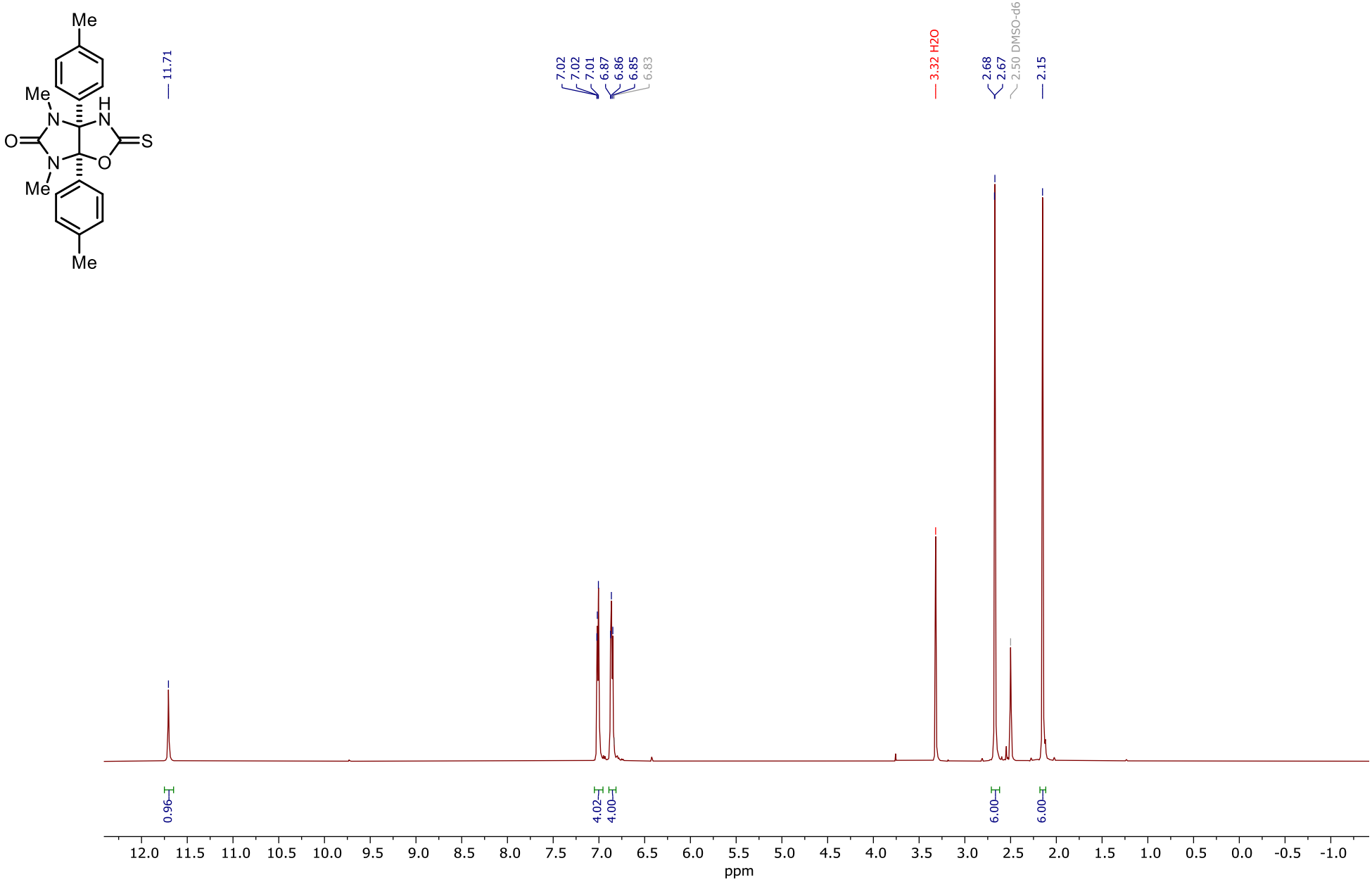
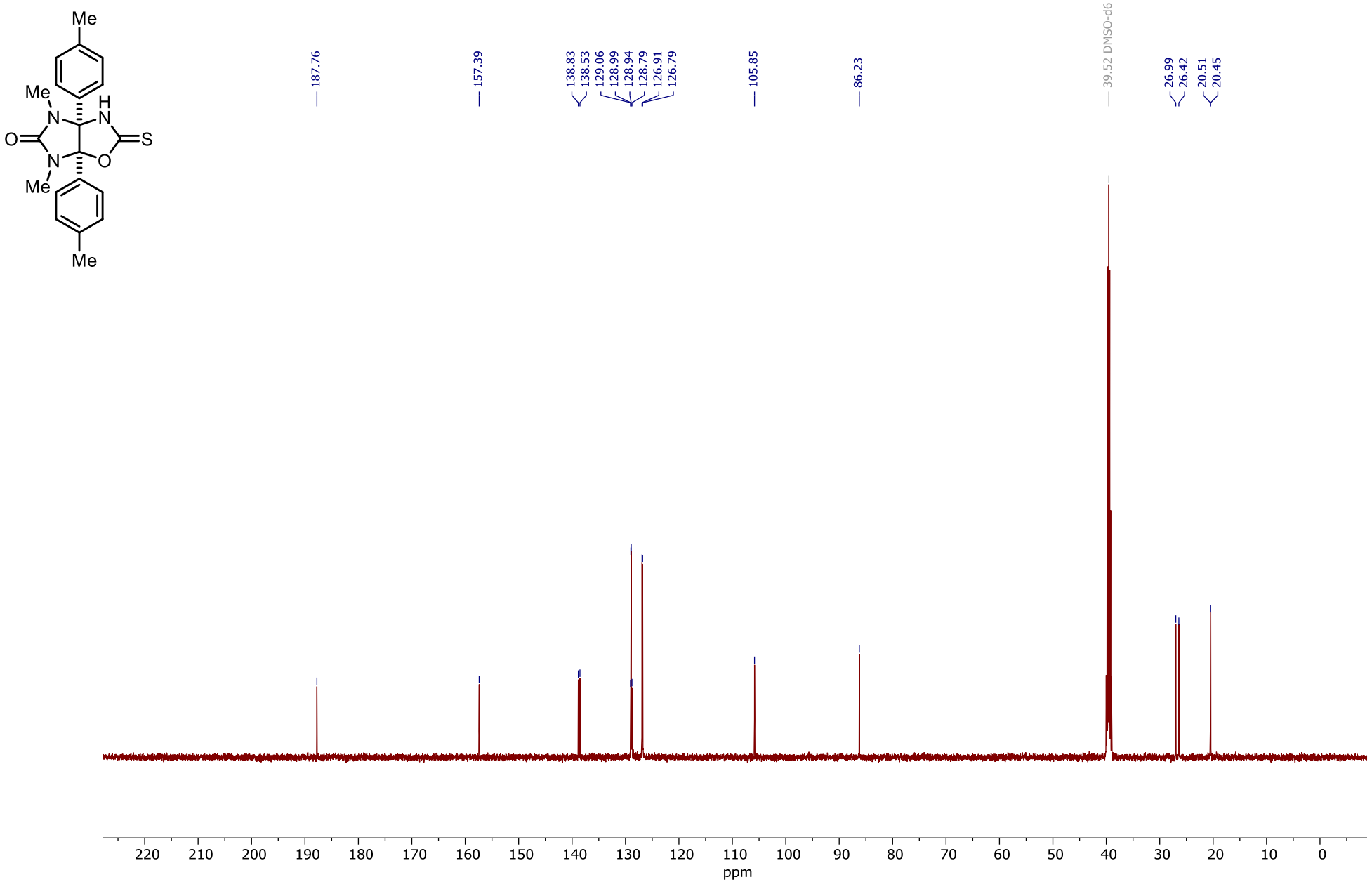
^{1}H NMR (500 MHz, DMSO-d$_6$)



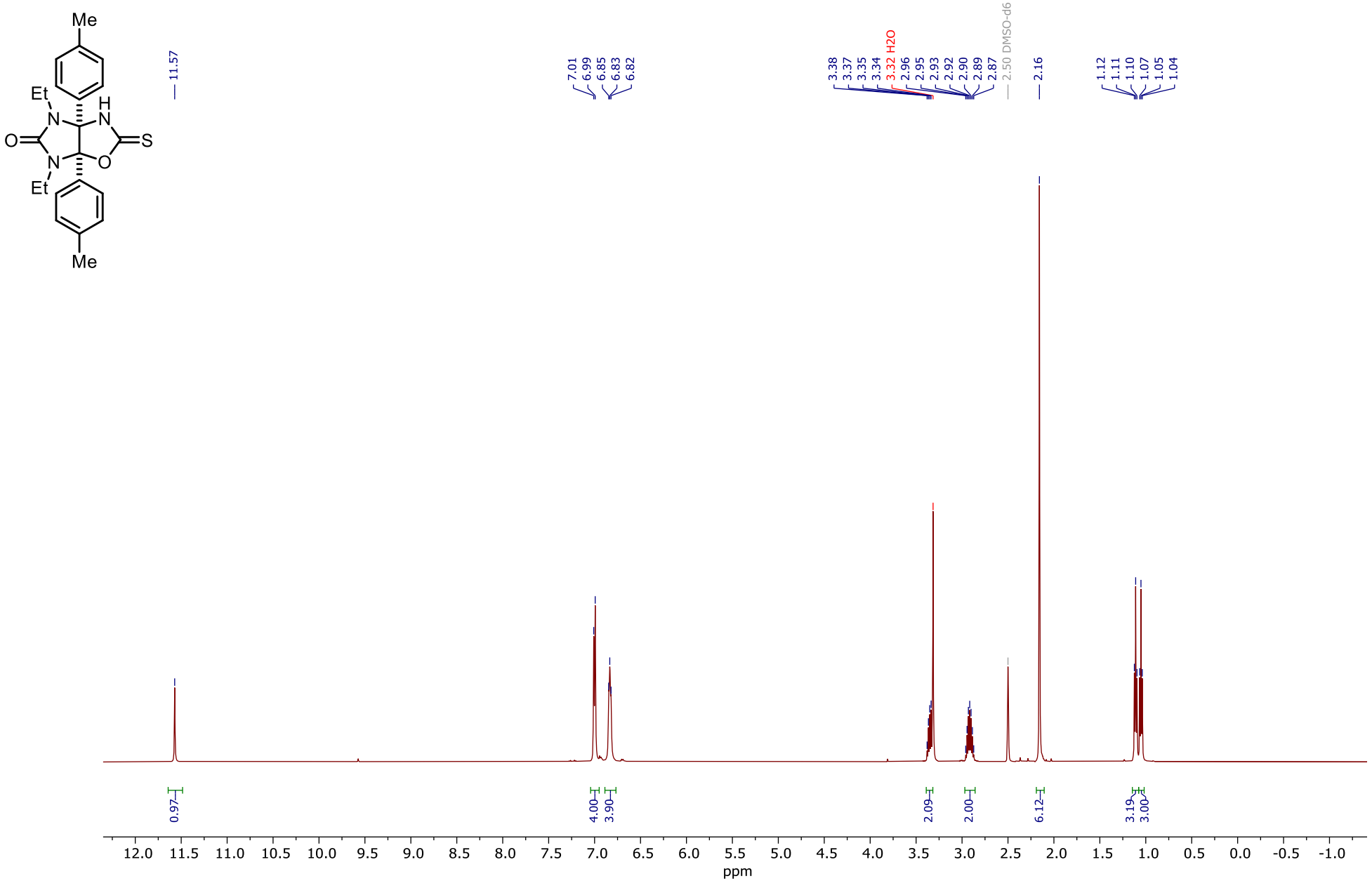
(3a*SR*,6a*SR*)-4,6-Dimethyl-2-thioxo-3a,6a-di-*p*-tolylhexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2f)

^{13}C NMR (126 MHz, DMSO-d$_6$)



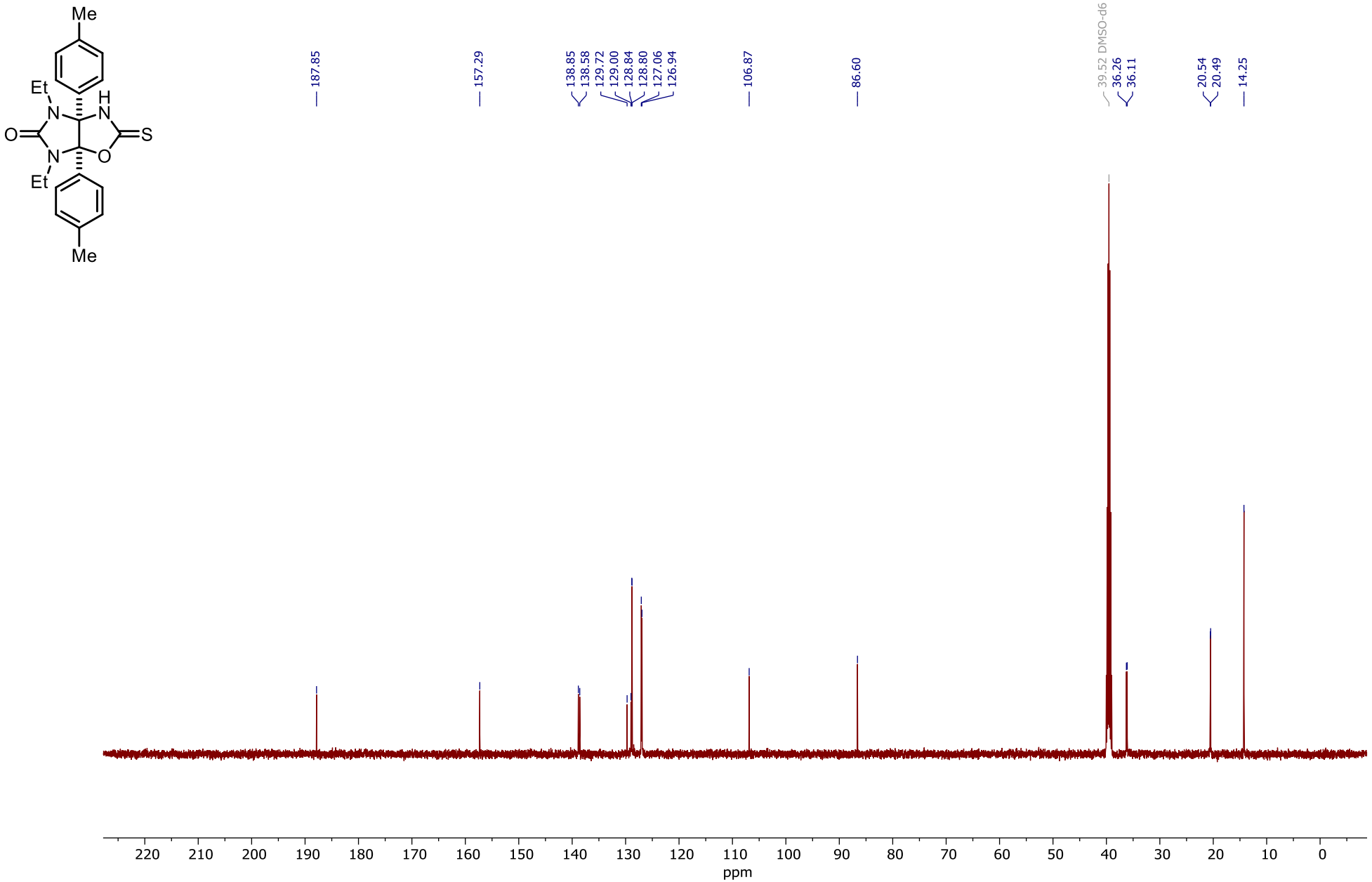
(3a*SR*,6a*SR*)-4,6-Diethyl-2-thioxo-3a,6a-di-*p*-tolylhexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2g)

^{1}H NMR (500 MHz, DMSO-d$_6$)



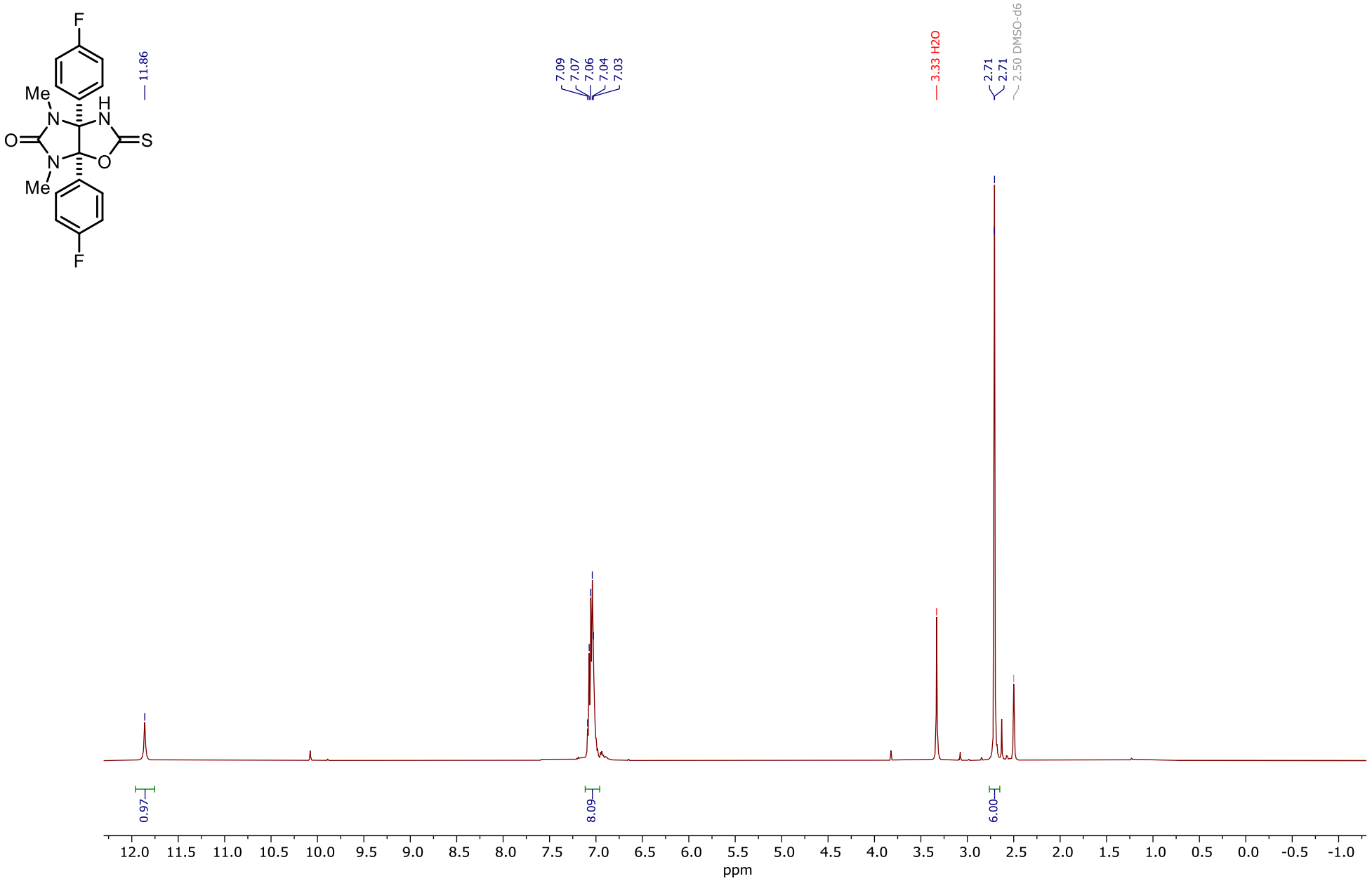
(3a*SR*,6a*SR*)-4,6-Diethyl-2-thioxo-3a,6a-di-*p*-tolylhexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2g)

^{13}C NMR (126 MHz, DMSO-d$_6$)



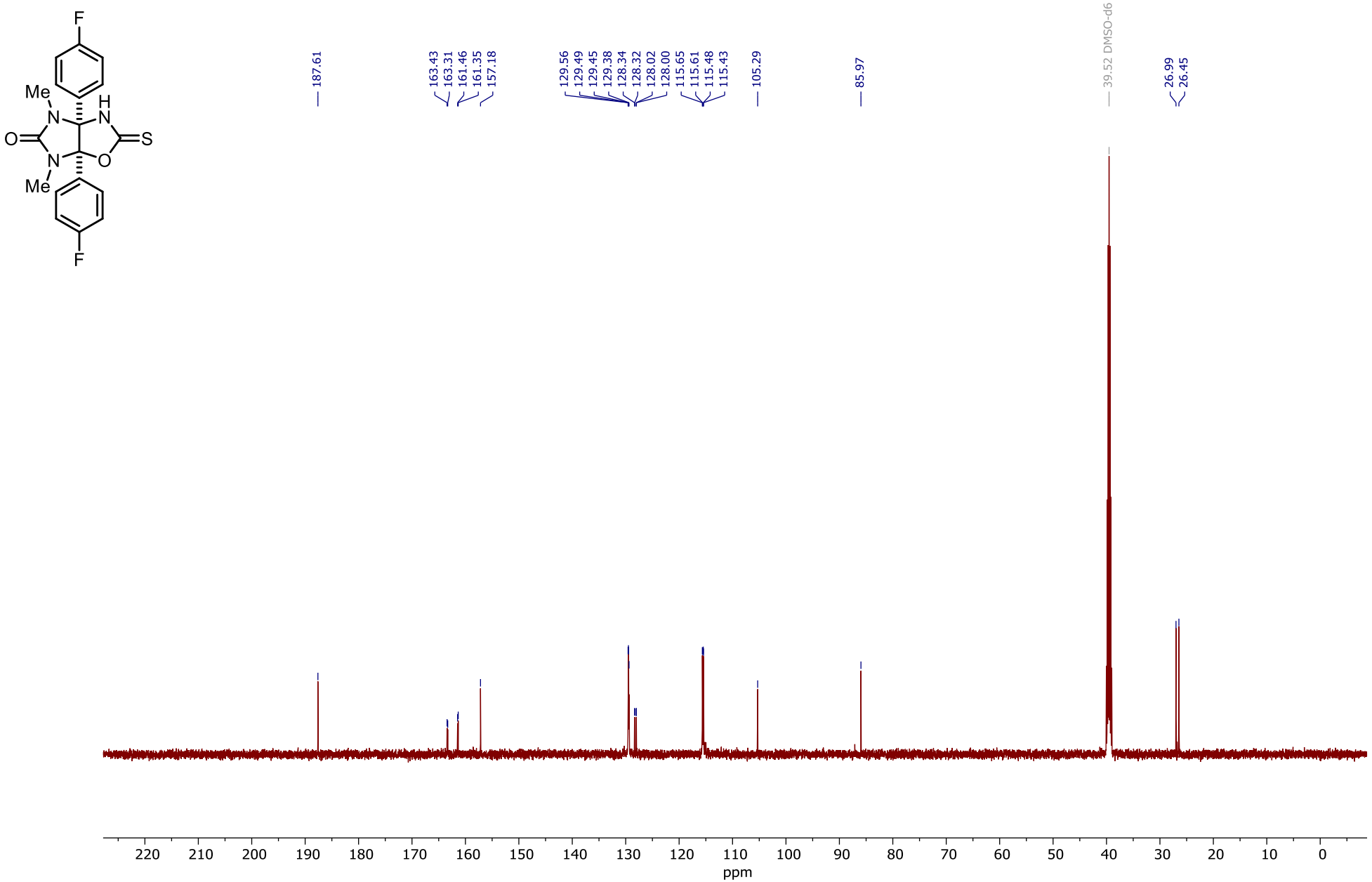
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Fluorophenyl)-4,6-dimethyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2h)

^{1}H NMR (500 MHz, DMSO-d$_6$)



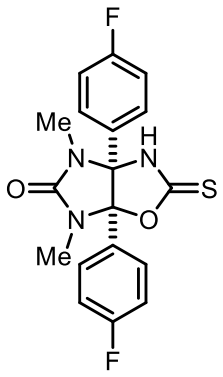
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Fluorophenyl)-4,6-dimethyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2h)

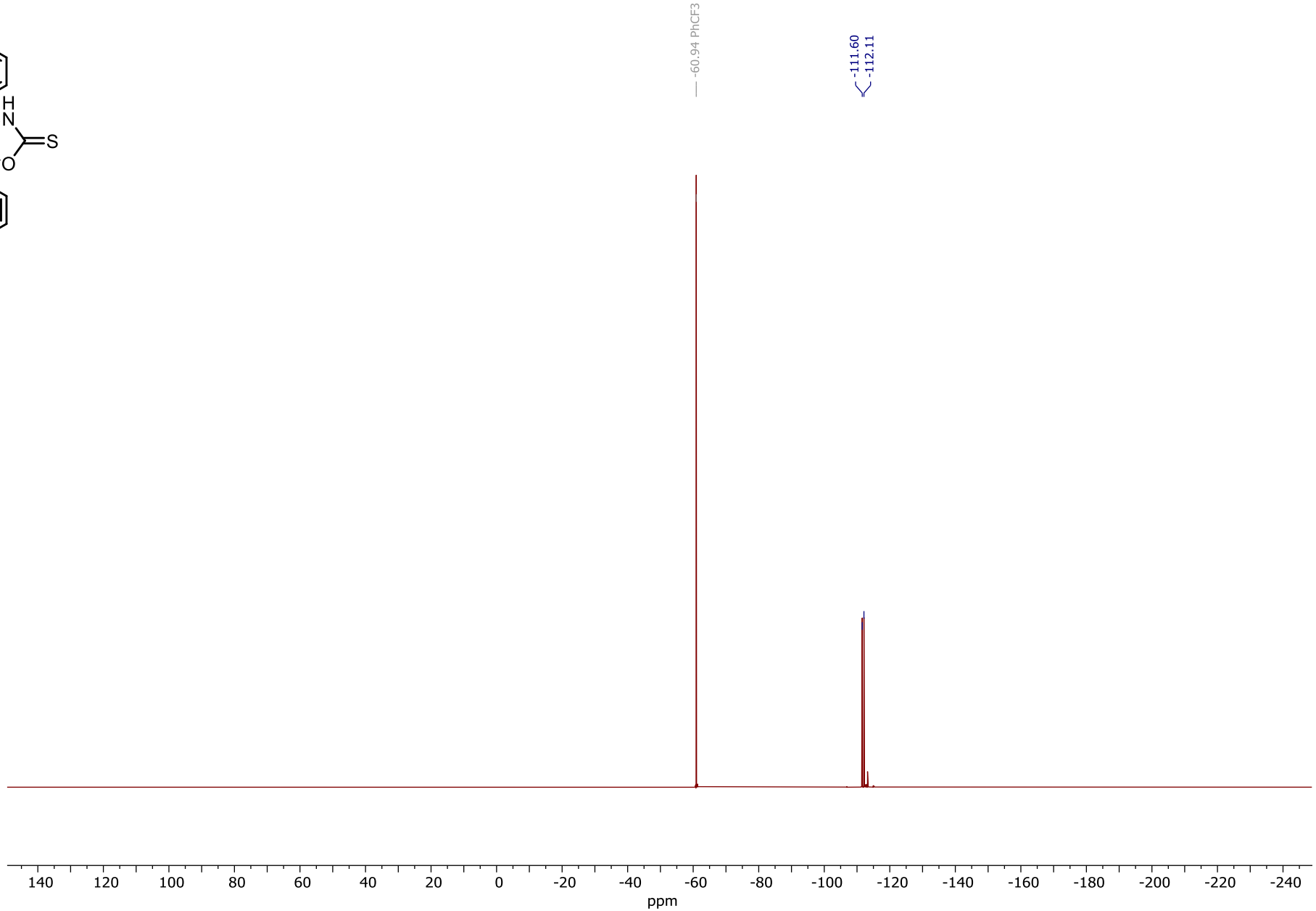
^{13}C NMR (126 MHz, DMSO-d$_6$)



(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Fluorophenyl)-4,6-dimethyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2h)

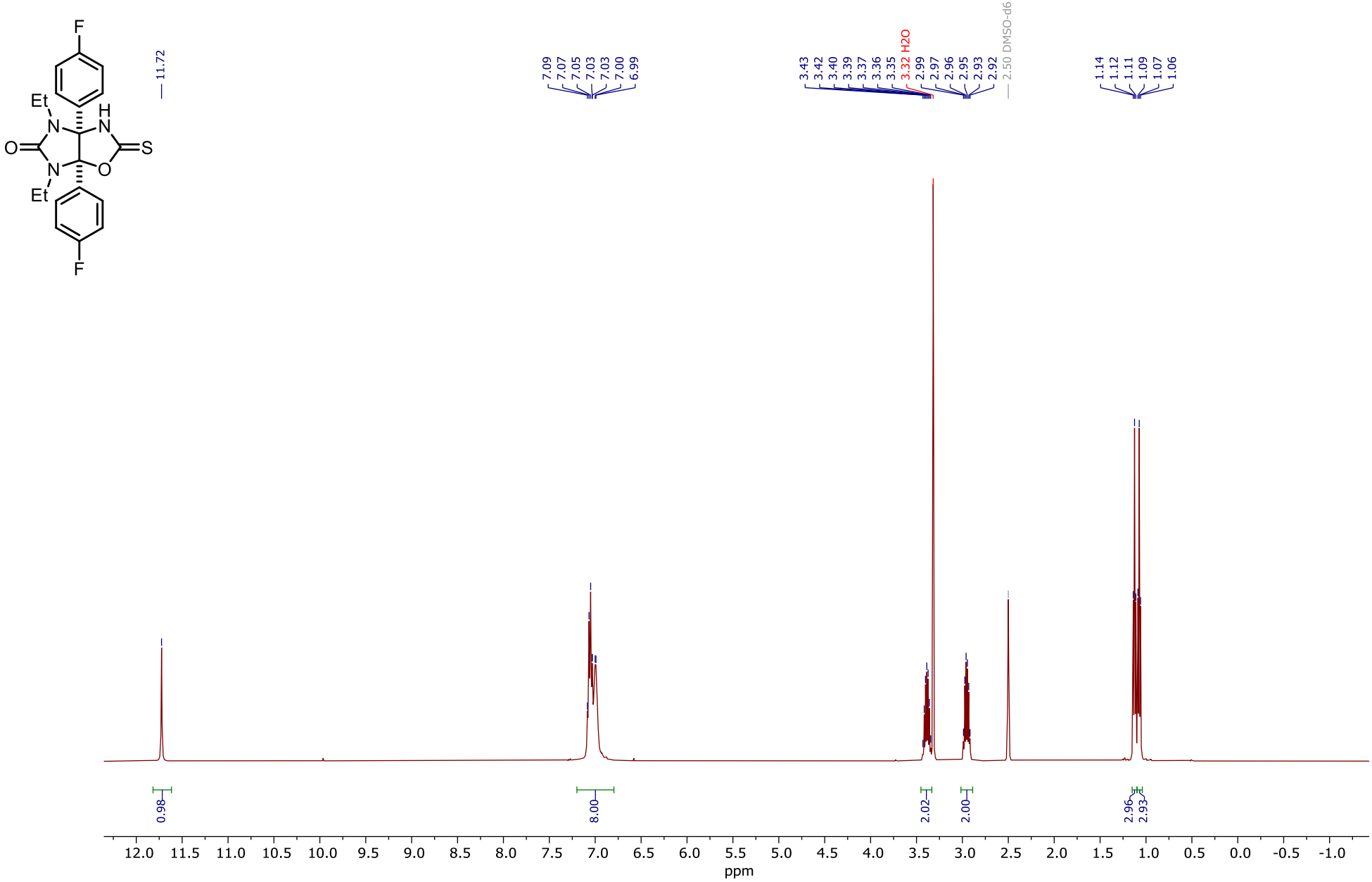
^{19}F NMR (470 MHz, DMSO-d_6)





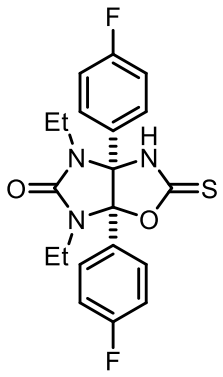
(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-fluorophenyl)-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2i)

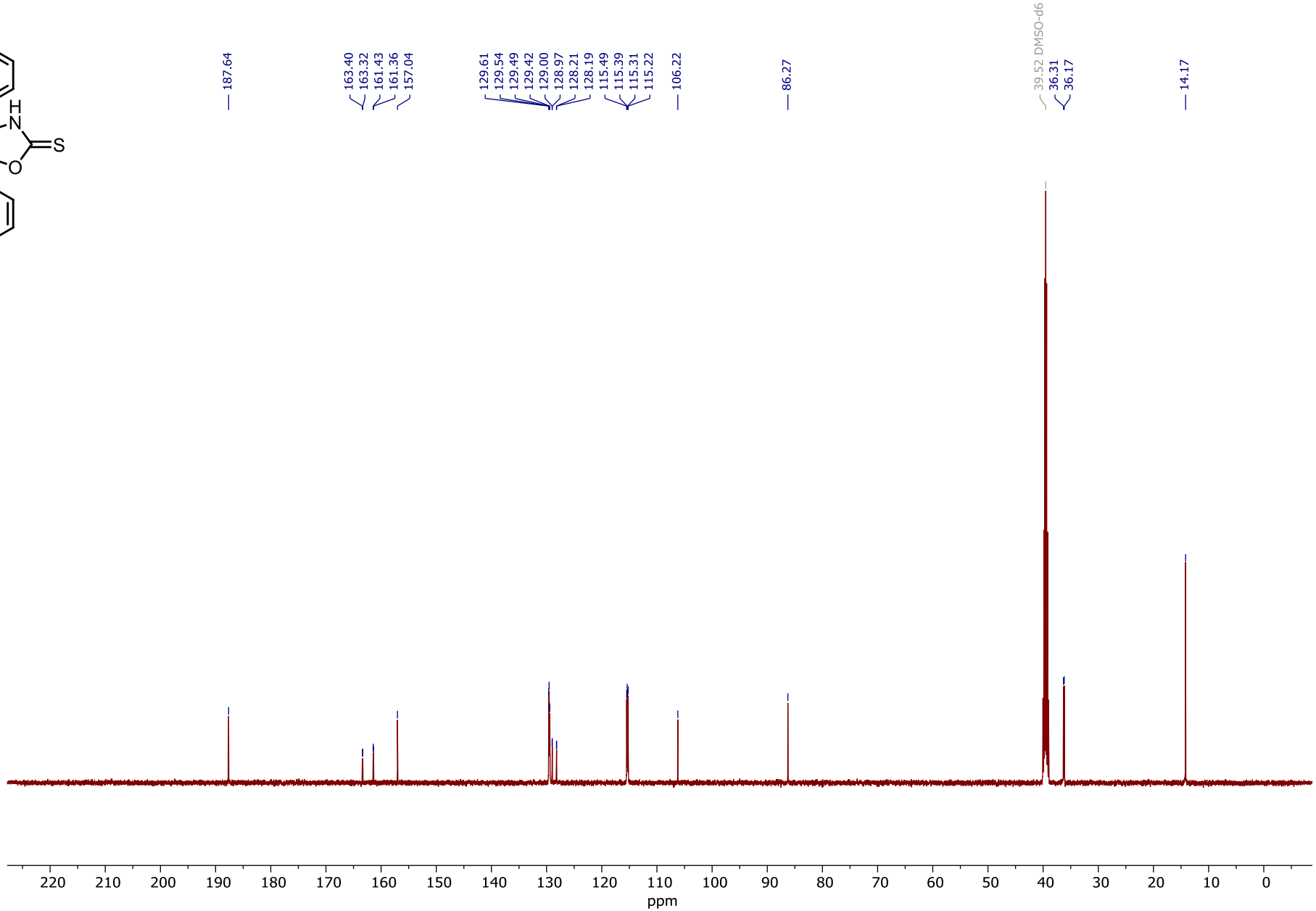
^{1}H NMR (500 MHz, DMSO-d$_6$)



(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-fluorophenyl)-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2i)

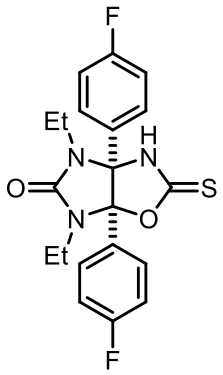
^{13}C NMR (126 MHz, DMSO-d$_6$)

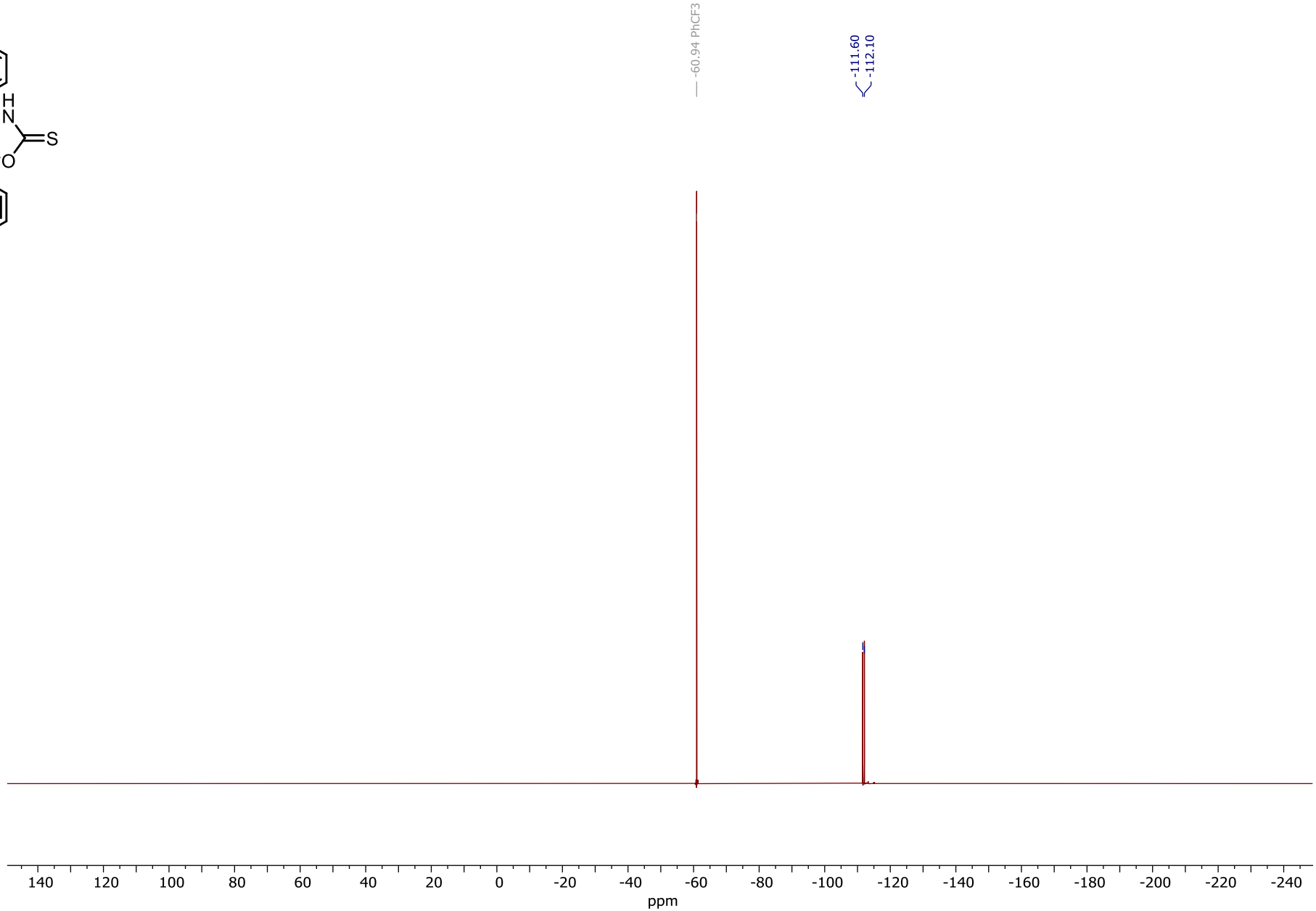




(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-fluorophenyl)-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2i)

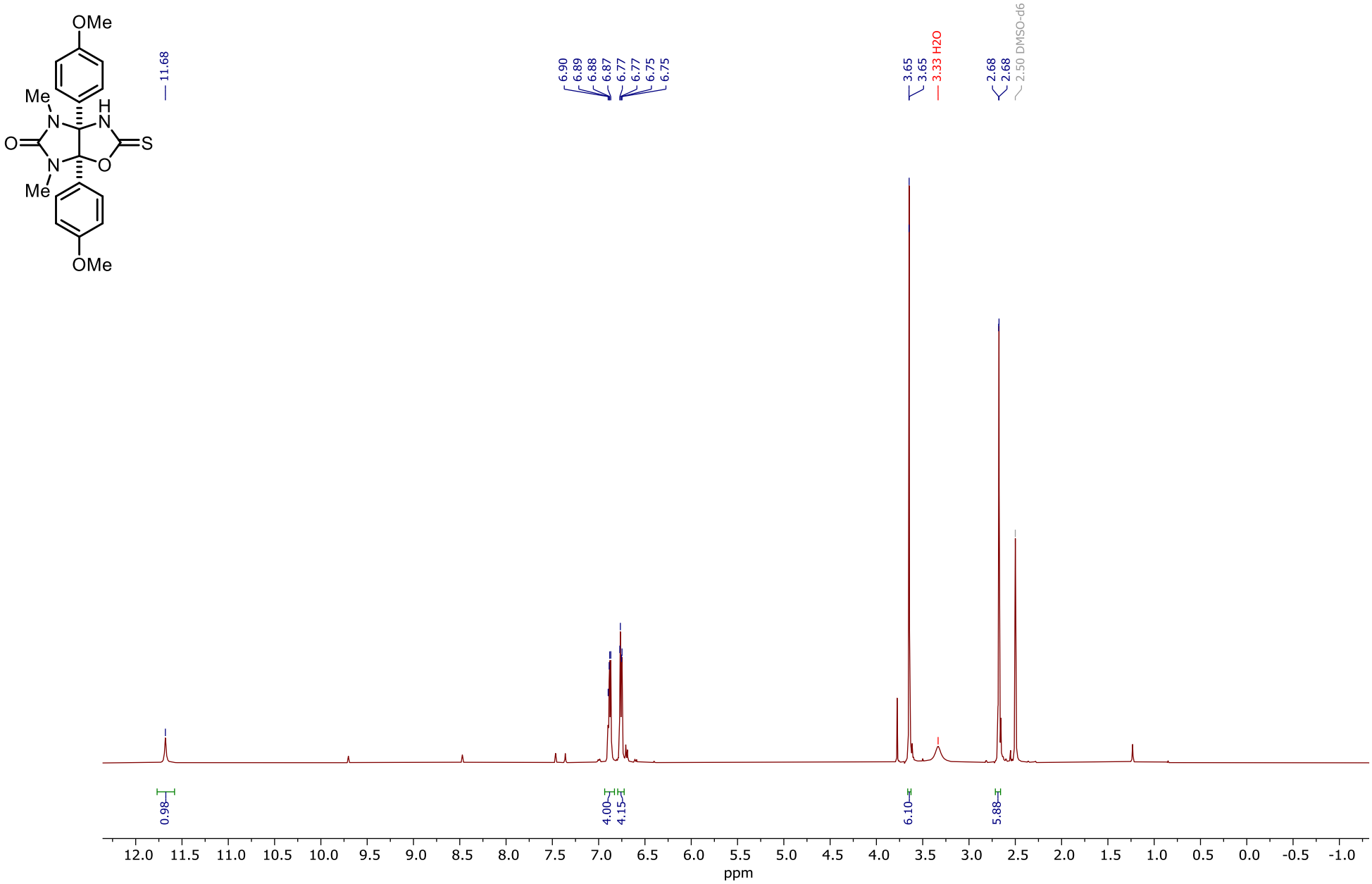
^{19}F NMR (470 MHz, DMSO-d_6)





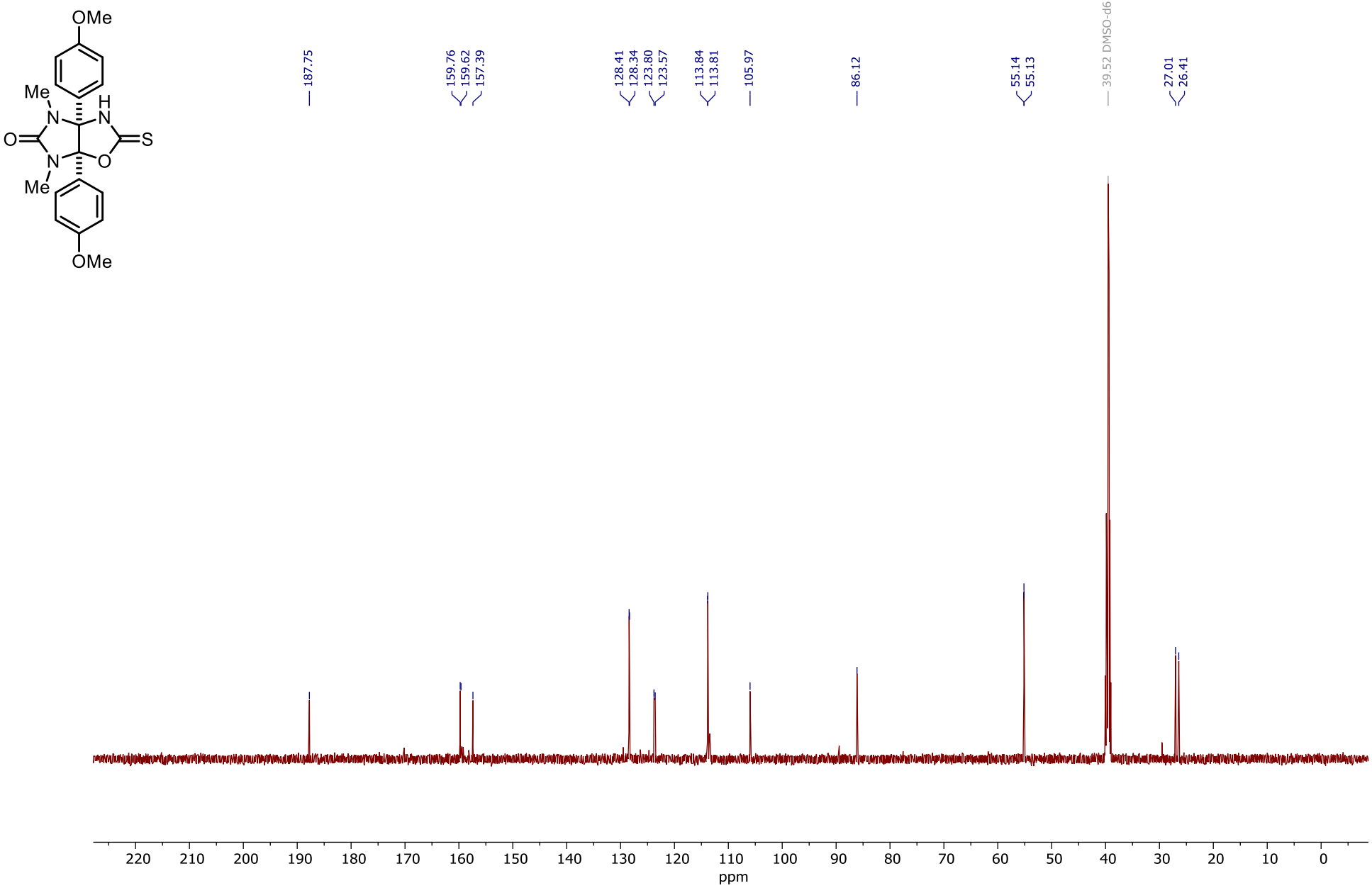
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2j)

^{1}H NMR (500 MHz, DMSO-d$_6$)



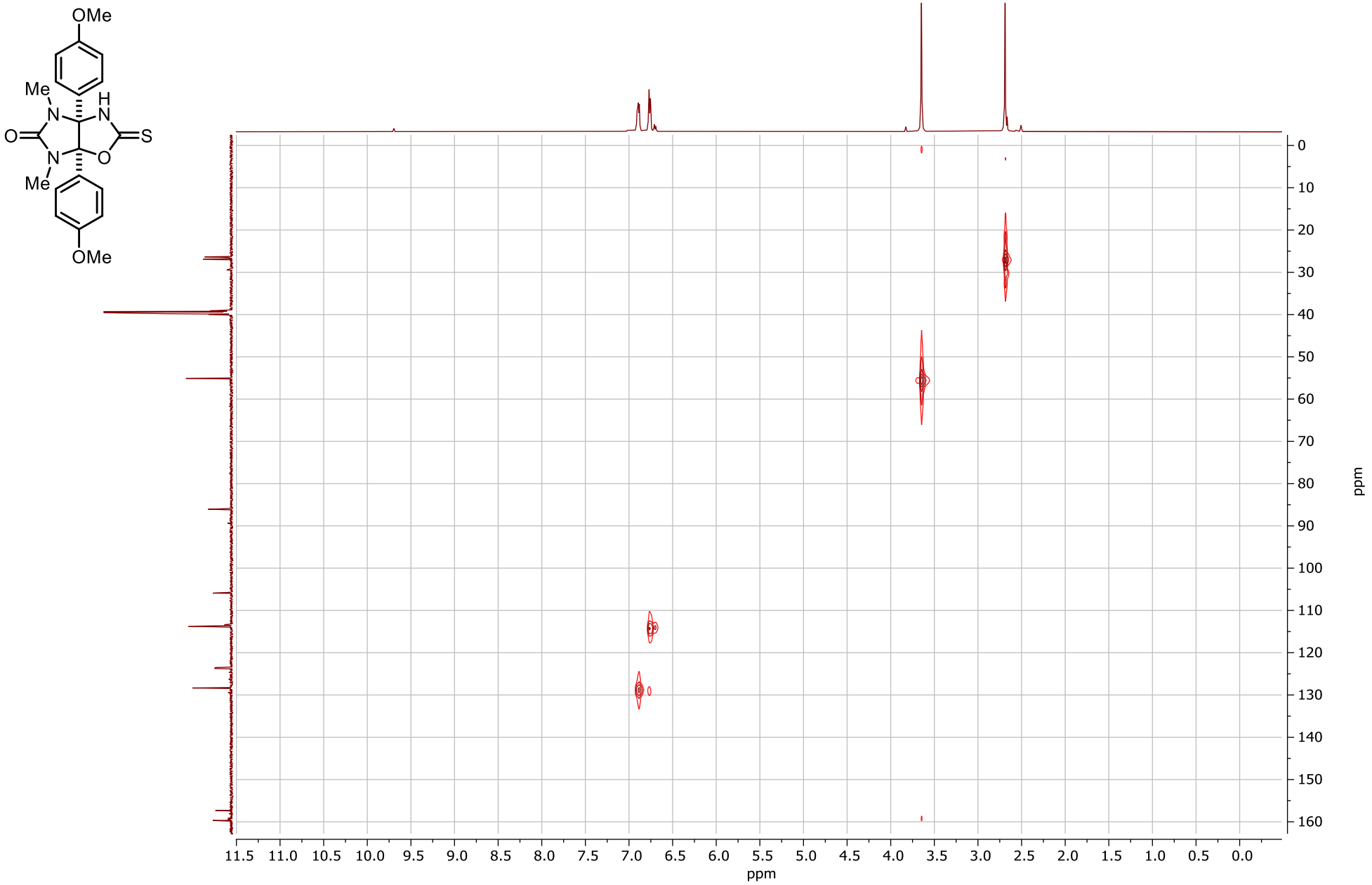
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2j)

^{13}C NMR (126 MHz, DMSO-d$_6$)



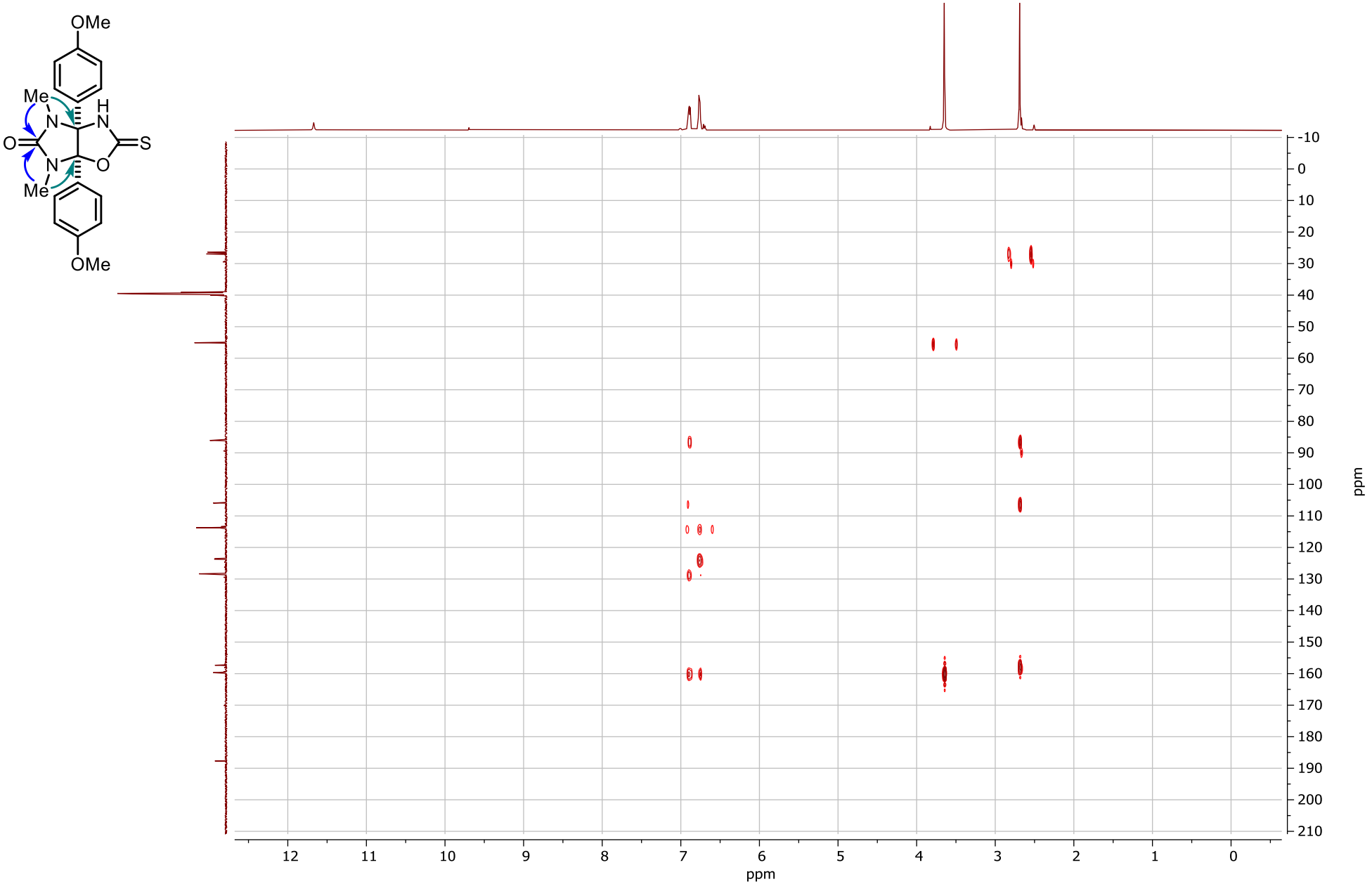
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2j)

^{1}H–^{13}C HSQC (DMSO-d_6)



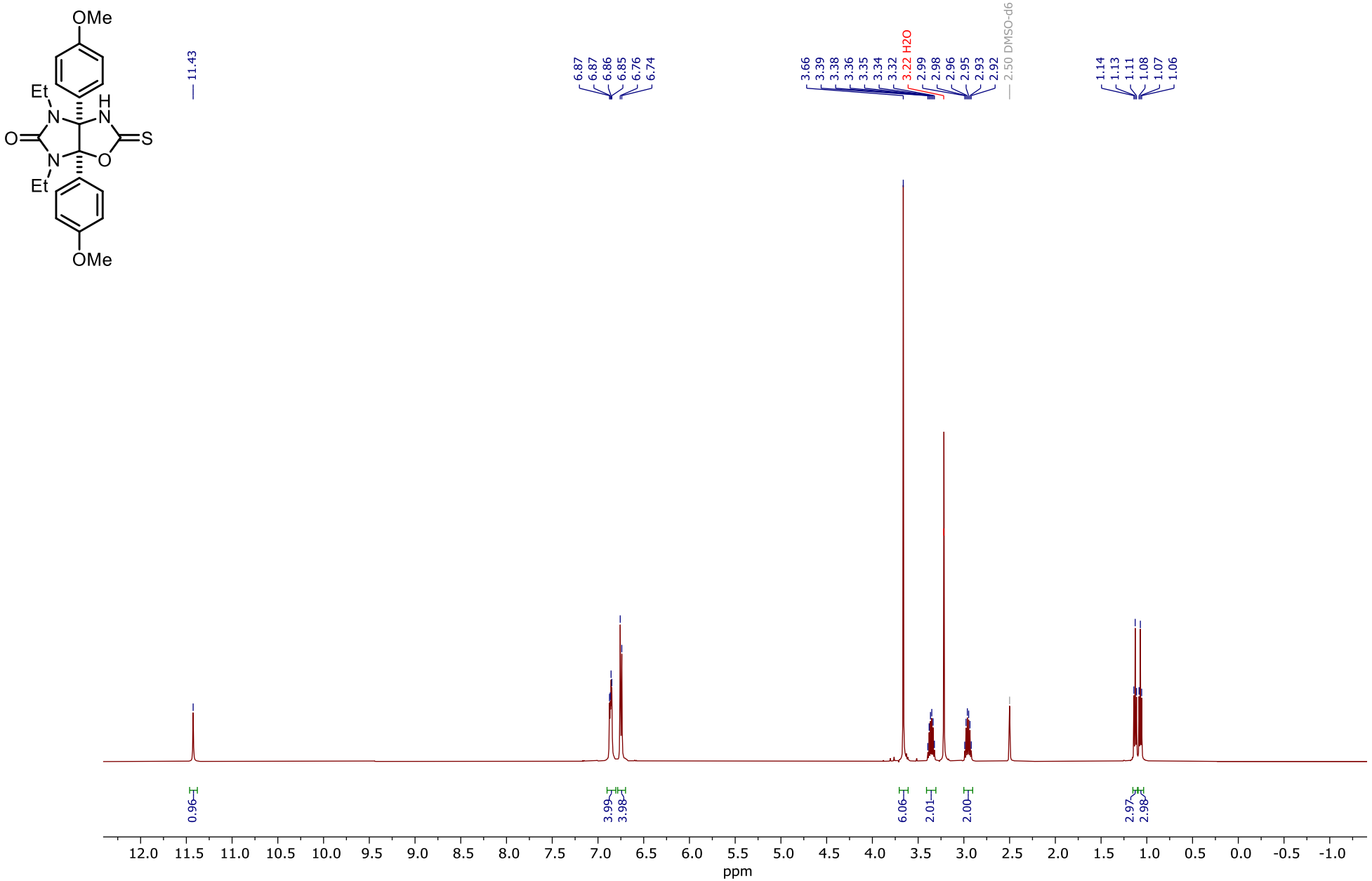
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2j)

^{1}H–^{13}C HMBC (DMSO-d_6)



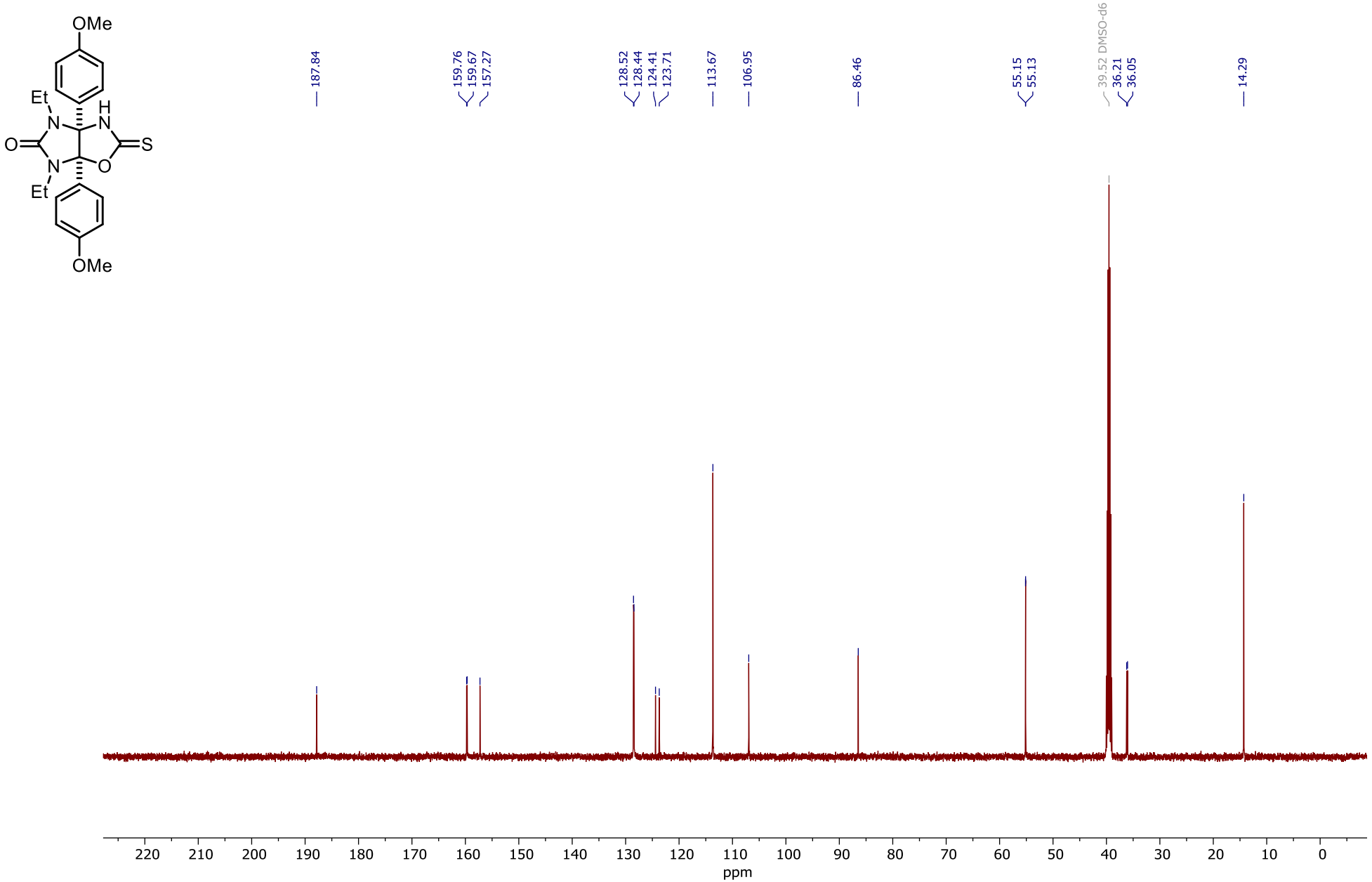
(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-methoxyphenyl)-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2k)

^{1}H NMR (500 MHz, DMSO-d$_6$, 50 °C)



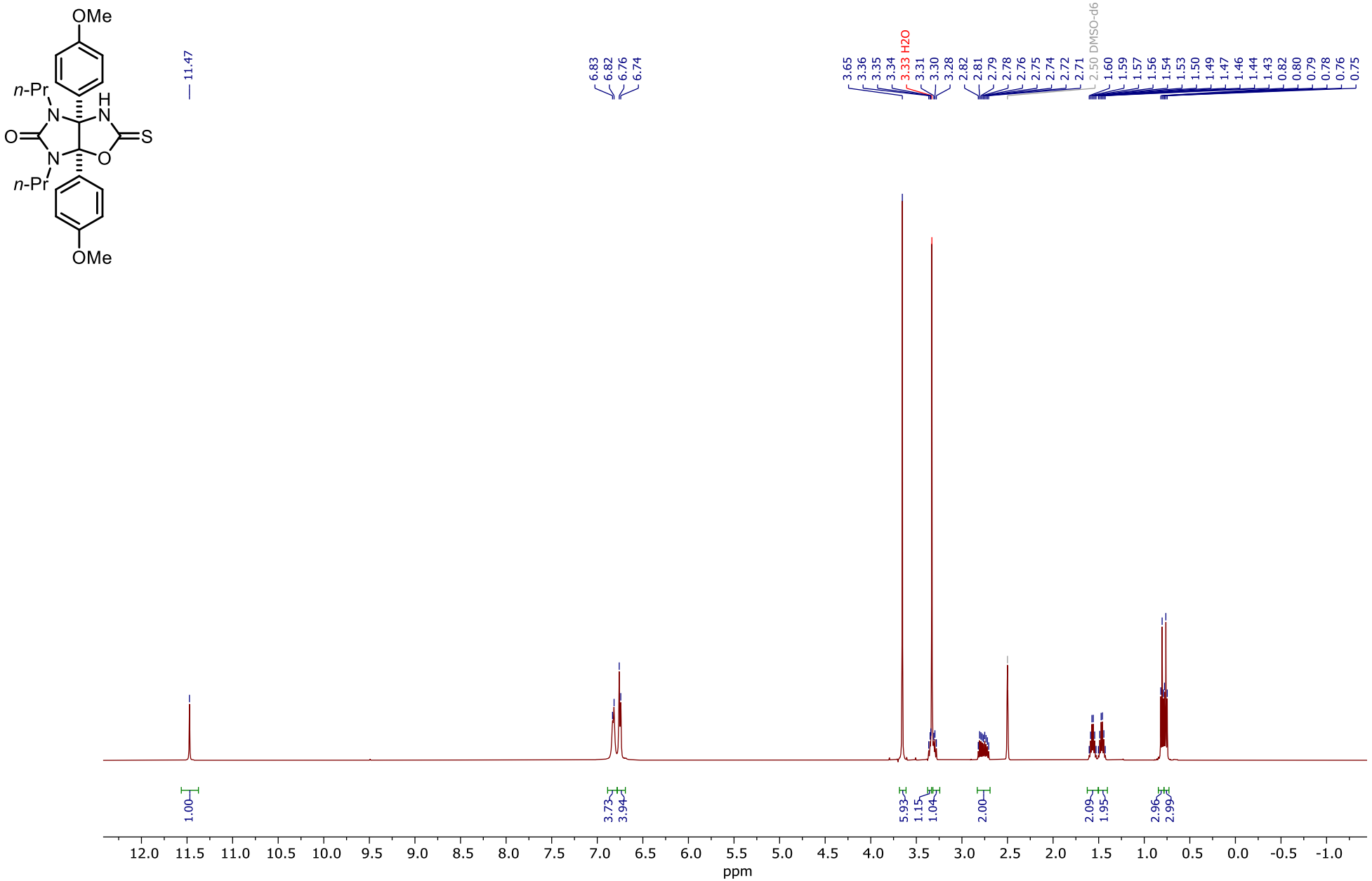
(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-methoxyphenyl)-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2k)

^{13}C NMR (126 MHz, DMSO-d$_6$)



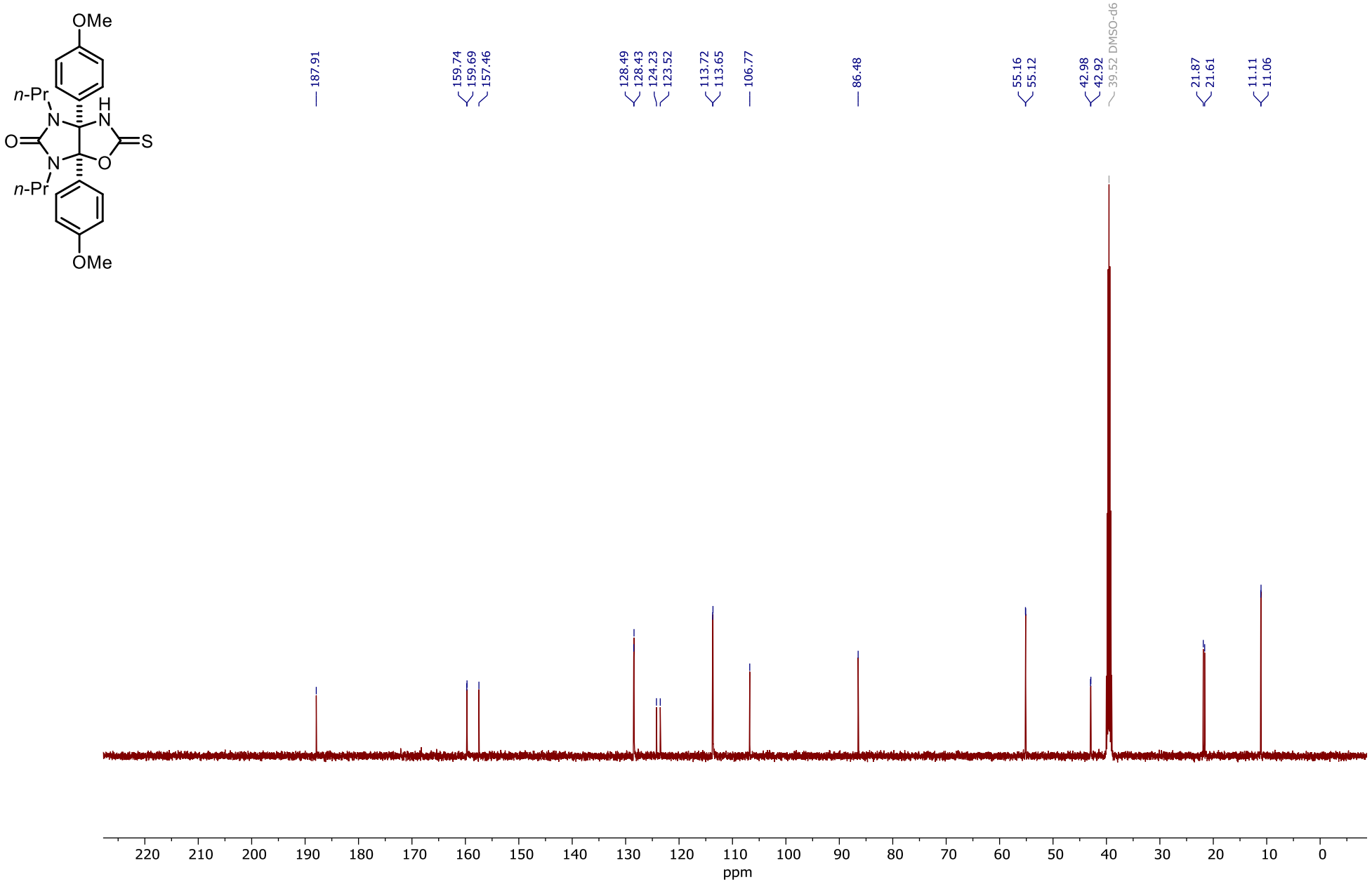
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dipropyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2l)

^{1}H NMR (500 MHz, DMSO-d$_6$)



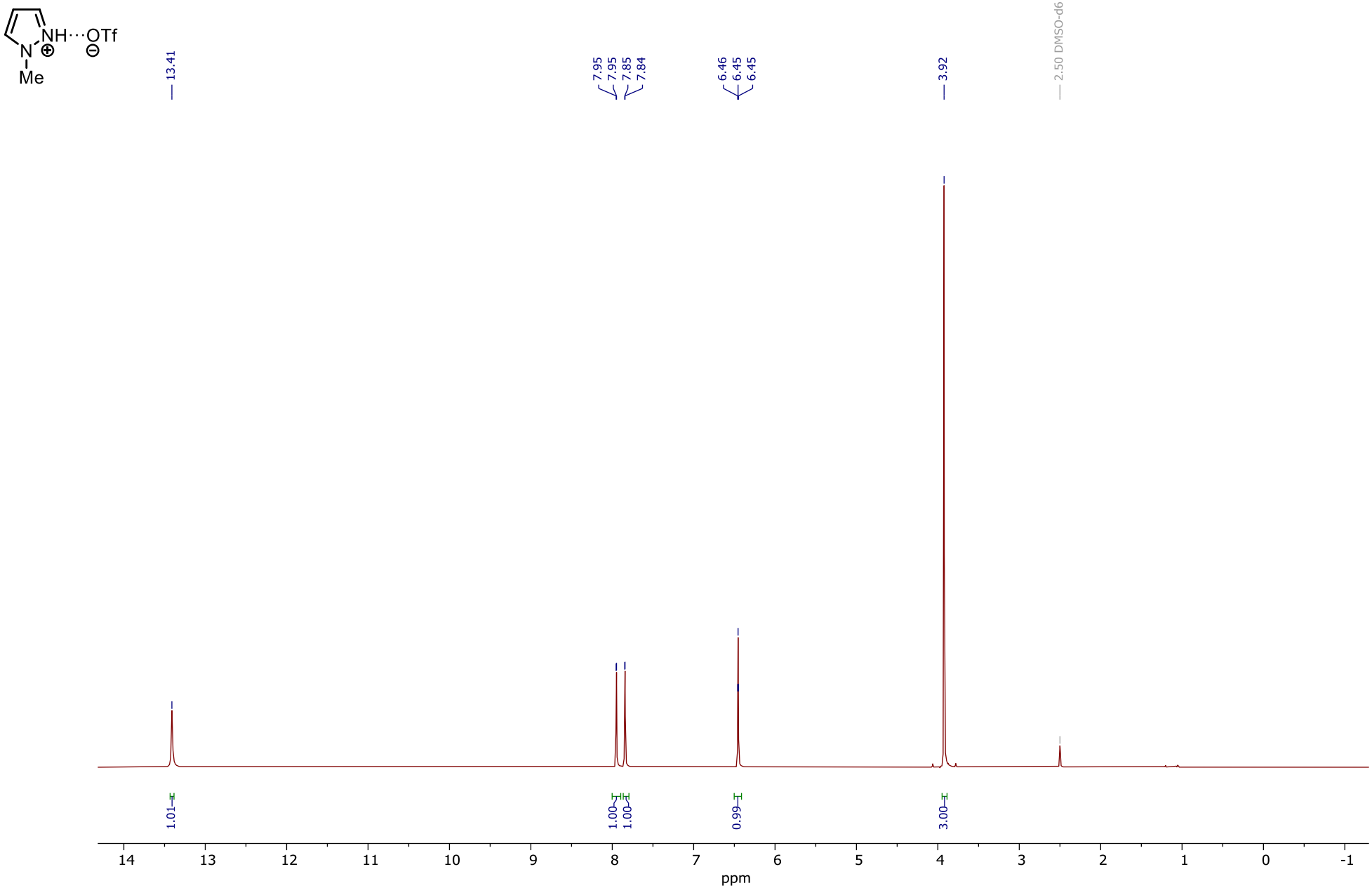
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dipropyl-2-thioxohexahydro-5*H*-imidazo[4,5-*d*]oxazol-5-one (2l)

^{13}C NMR (126 MHz, DMSO-d$_6$)



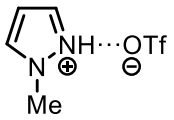
1-Methylpyrazolium trifluoromethanesulfonate (HMpzOTf)

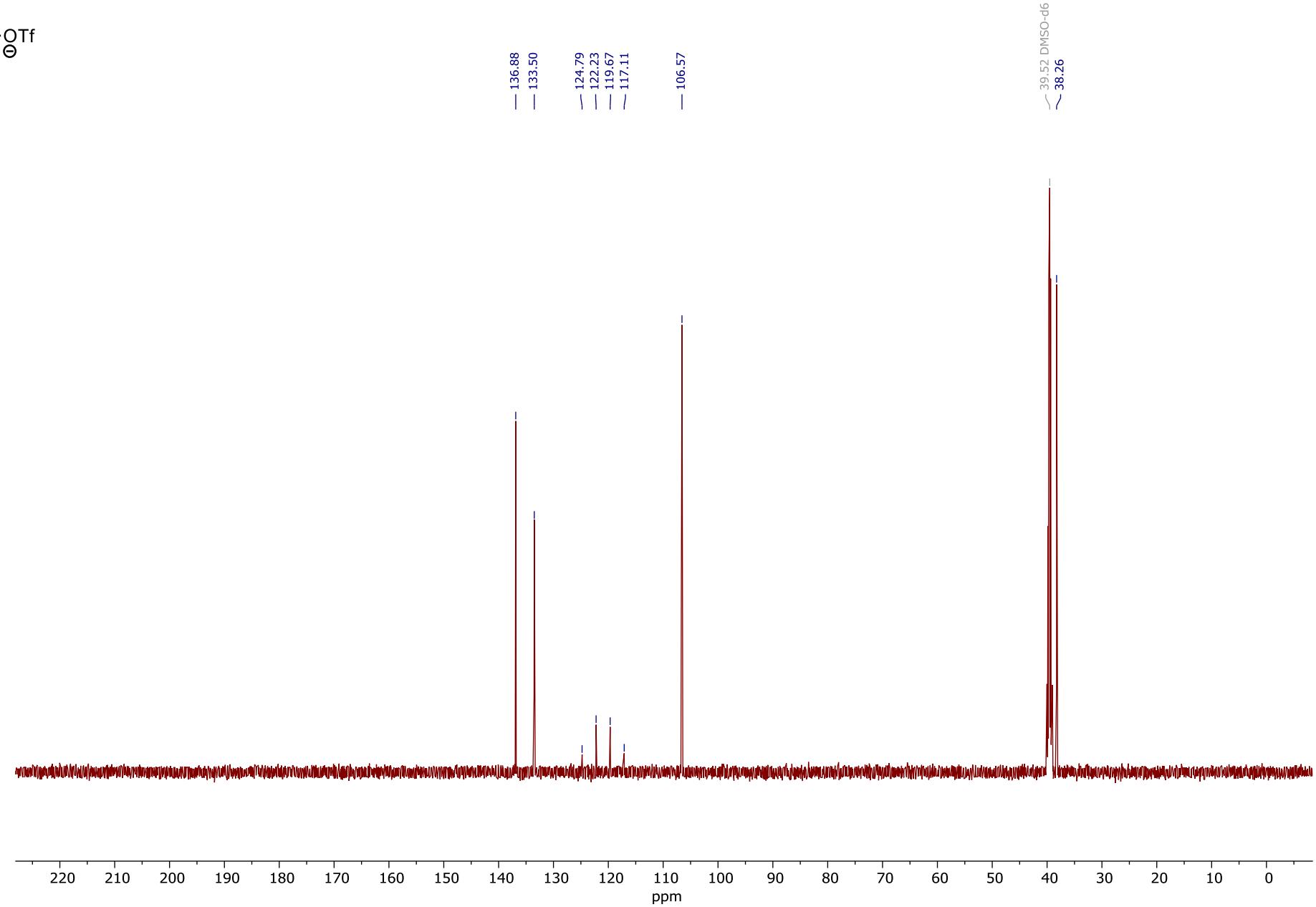
^{1}H NMR (500 MHz, DMSO-d_6)



1-Methylpyrazolium trifluoromethanesulfonate (HMpzOTf)

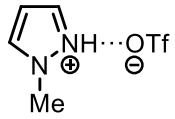
^{13}C NMR (126 MHz, DMSO-d$_6$)

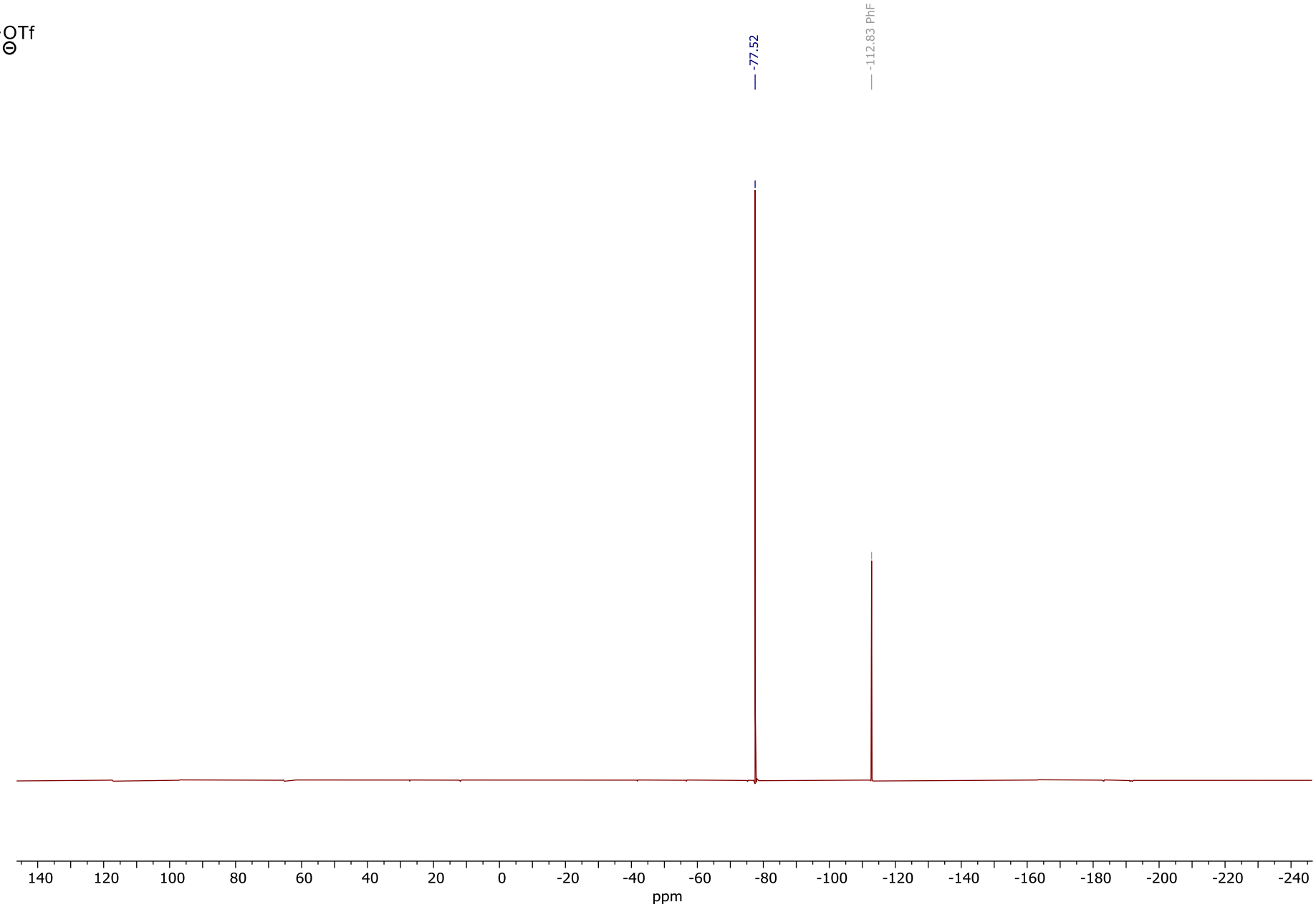




1-Methylpyrazolium trifluoromethanesulfonate (HMpzOTf)

^{19}F NMR (470 MHz, DMSO-d_6)

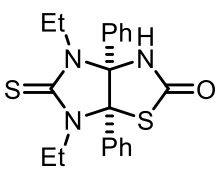


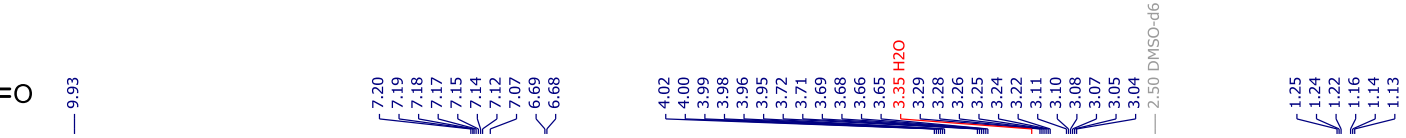


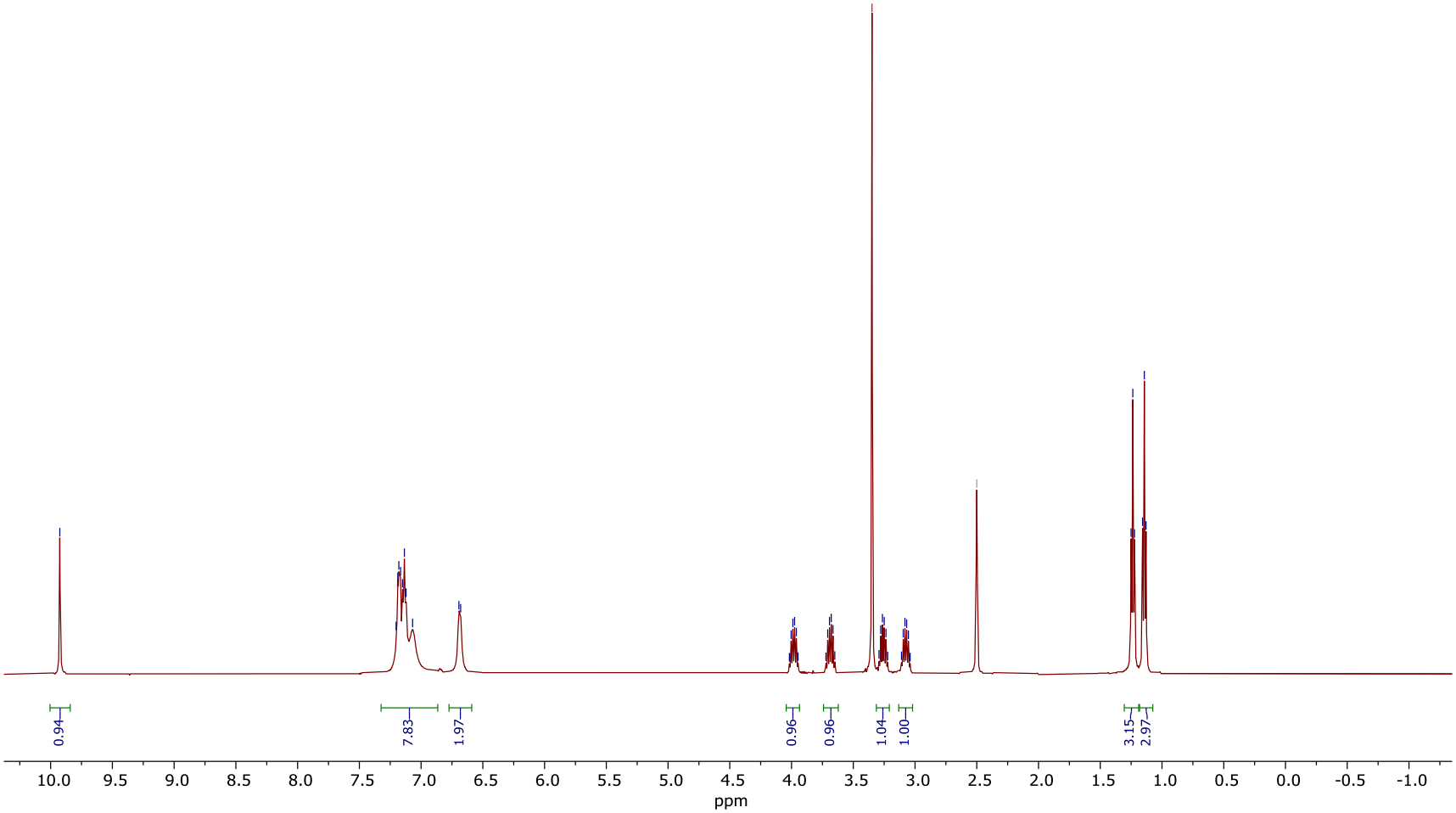
Thermodynamic control products (3)

(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyl-5-thioxohexahydro-2*H*-imidazo[4,5-*d*]thiazol-2-one (3a)

^{1}H NMR (500 MHz, DMSO-d$_6$)

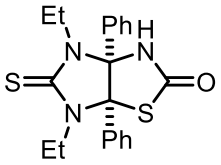


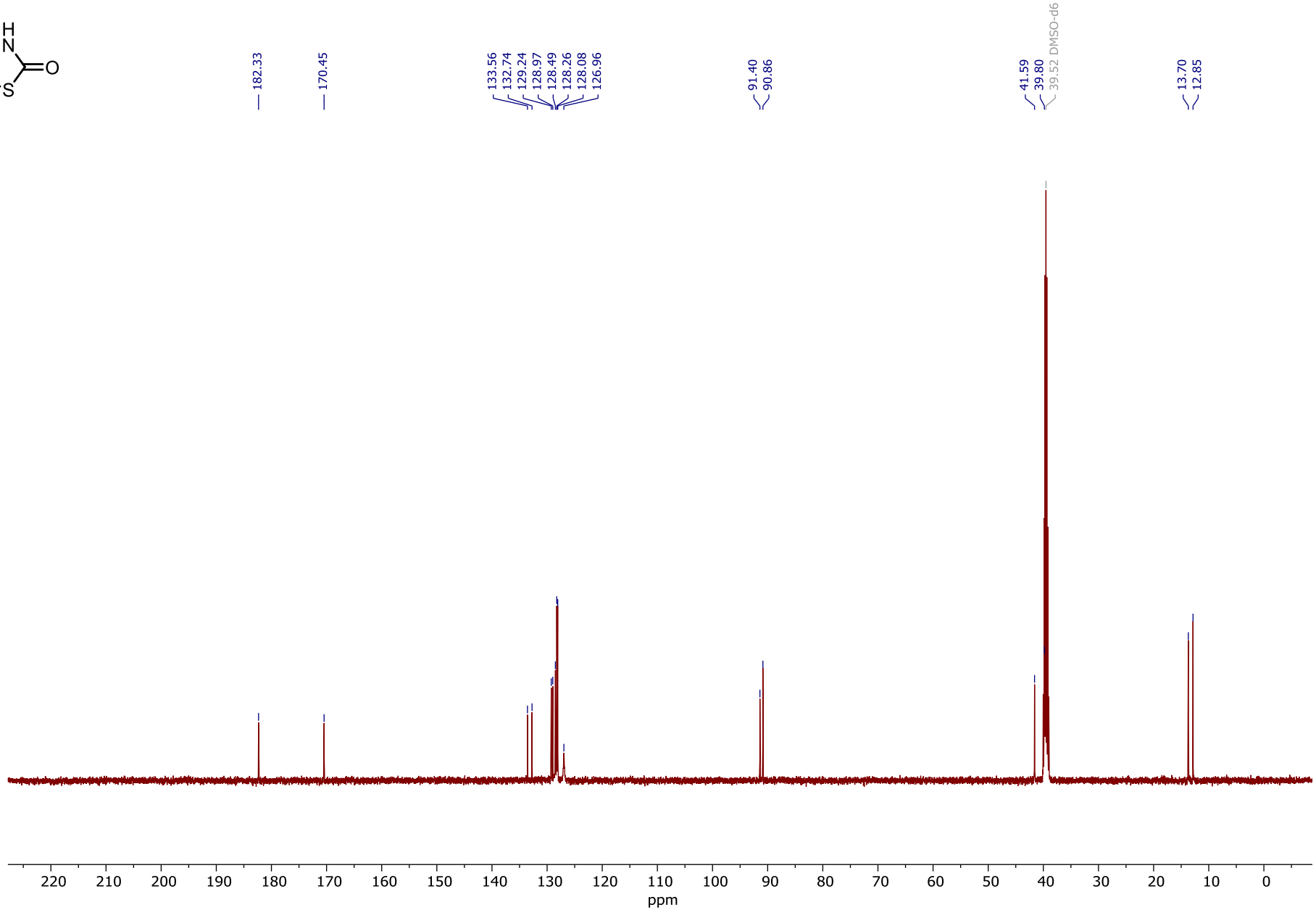




(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyl-5-thioxohexahydro-2*H*-imidazo[4,5-*d*]thiazol-2-one (3a)

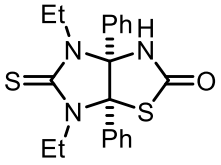
^{13}C NMR (126 MHz, DMSO-d$_6$)

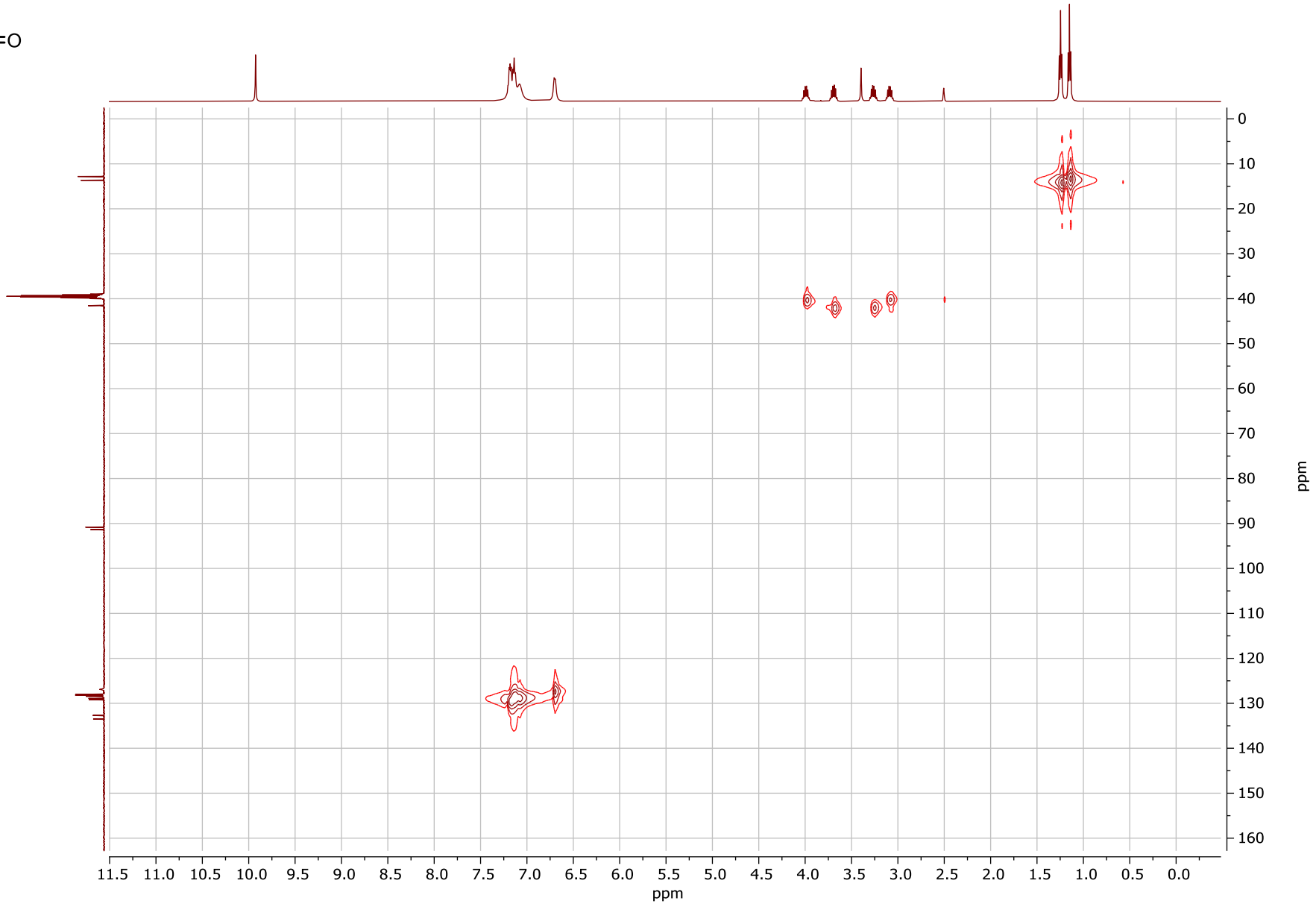




(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyl-5-thioxohexahydro-2*H*-imidazo[4,5-*d*]thiazol-2-one (3a)

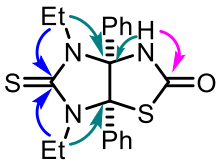
^{1}H–^{13}C HSQC (DMSO-d_6)

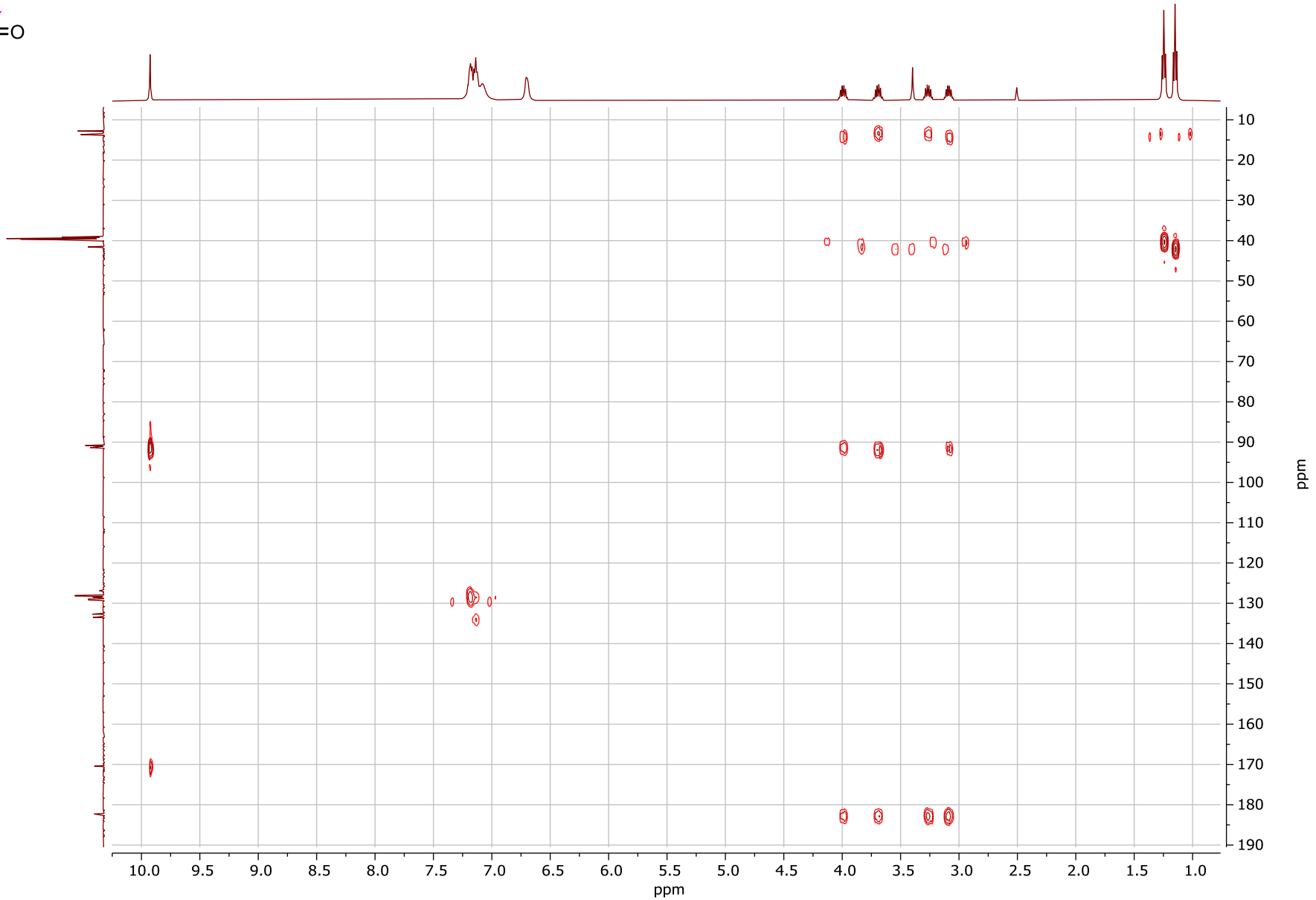




(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-diphenyl-5-thioxohexahydro-2*H*-imidazo[4,5-*d*]thiazol-2-one (3a)

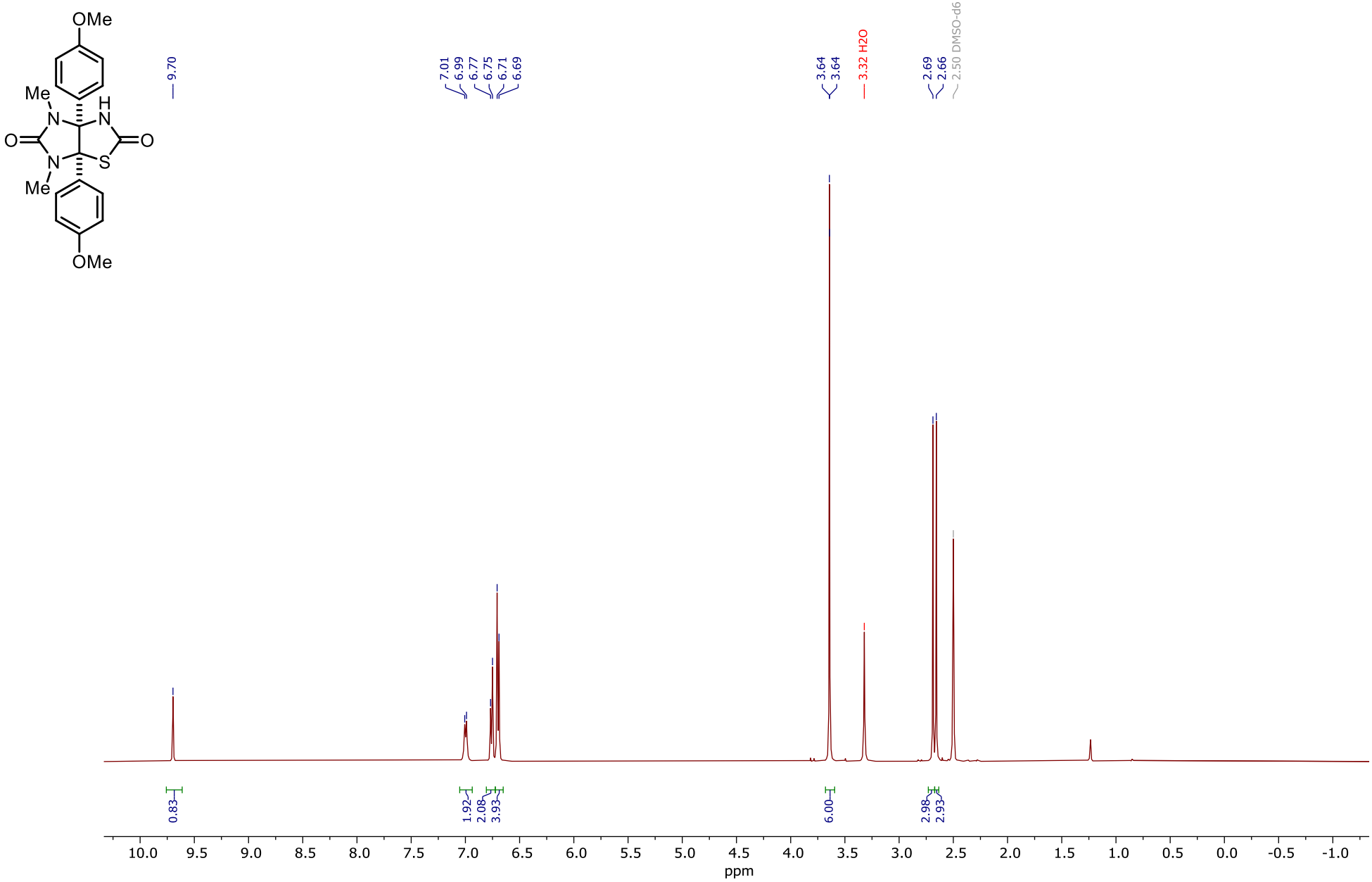
^{1}H–^{13}C HMBC (DMSO-d_6)





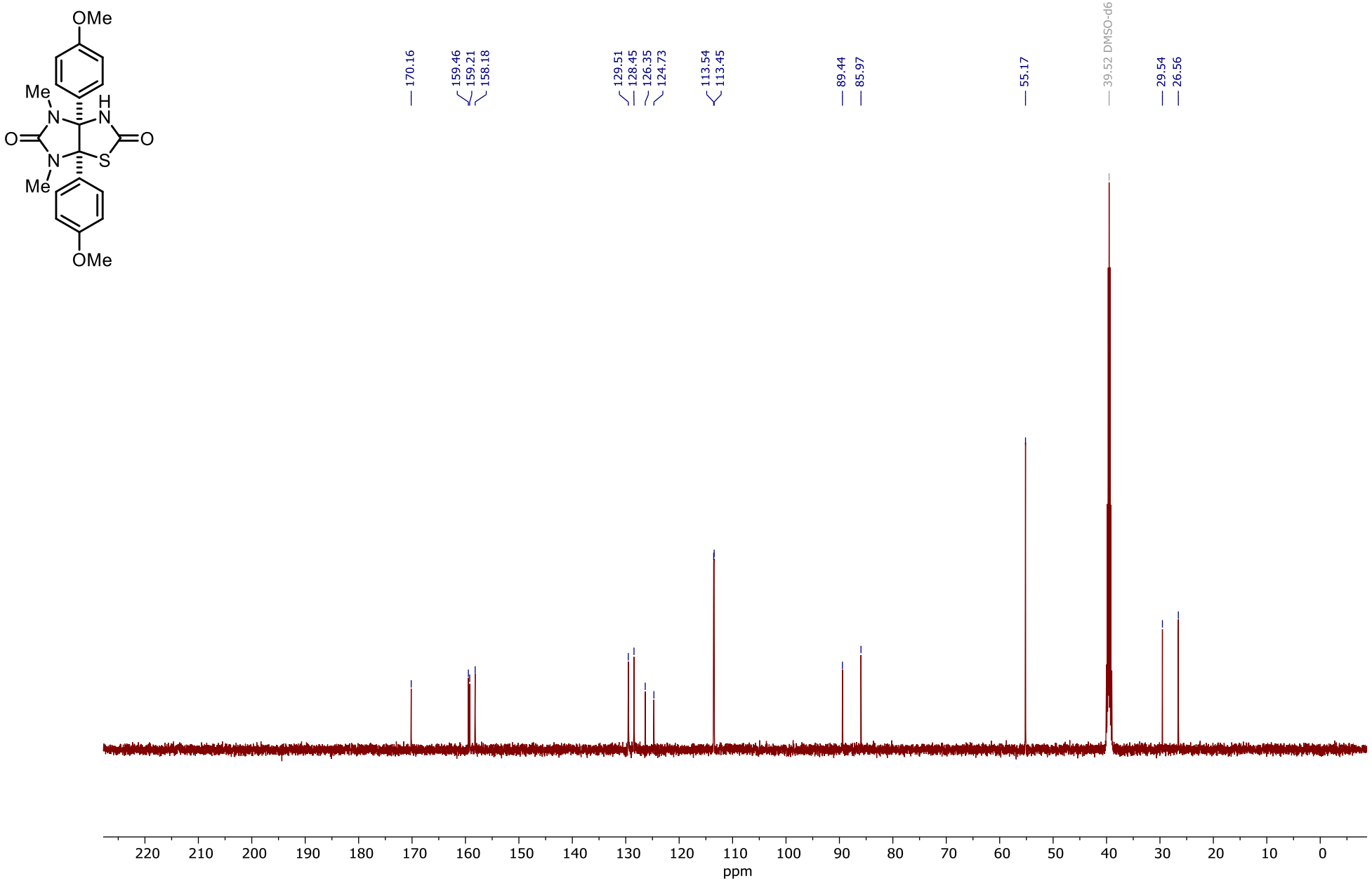
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3j)

^{1}H NMR (500 MHz, DMSO-d$_6$)



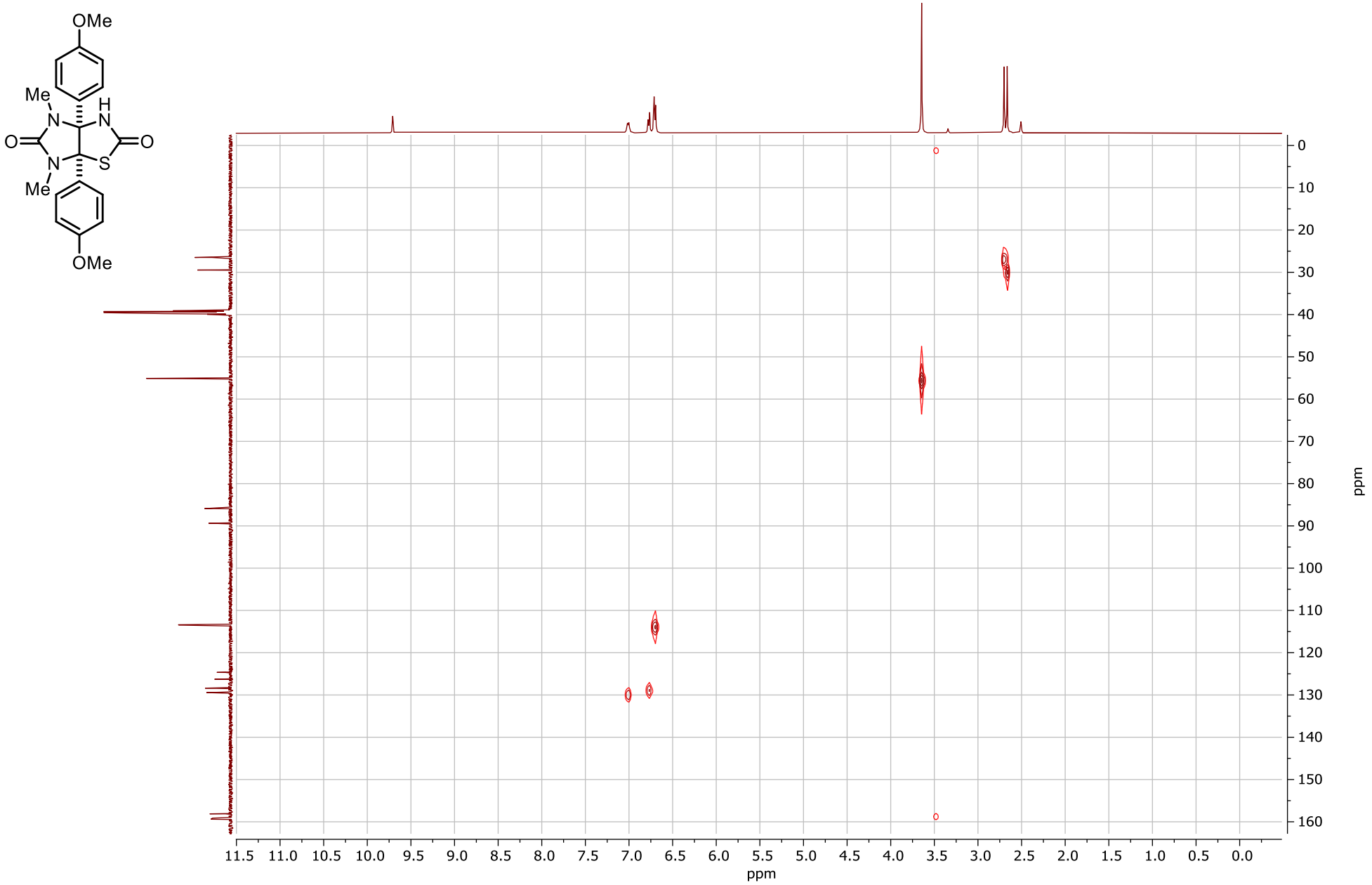
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3j)

^{13}C NMR (126 MHz, DMSO-d$_6$)



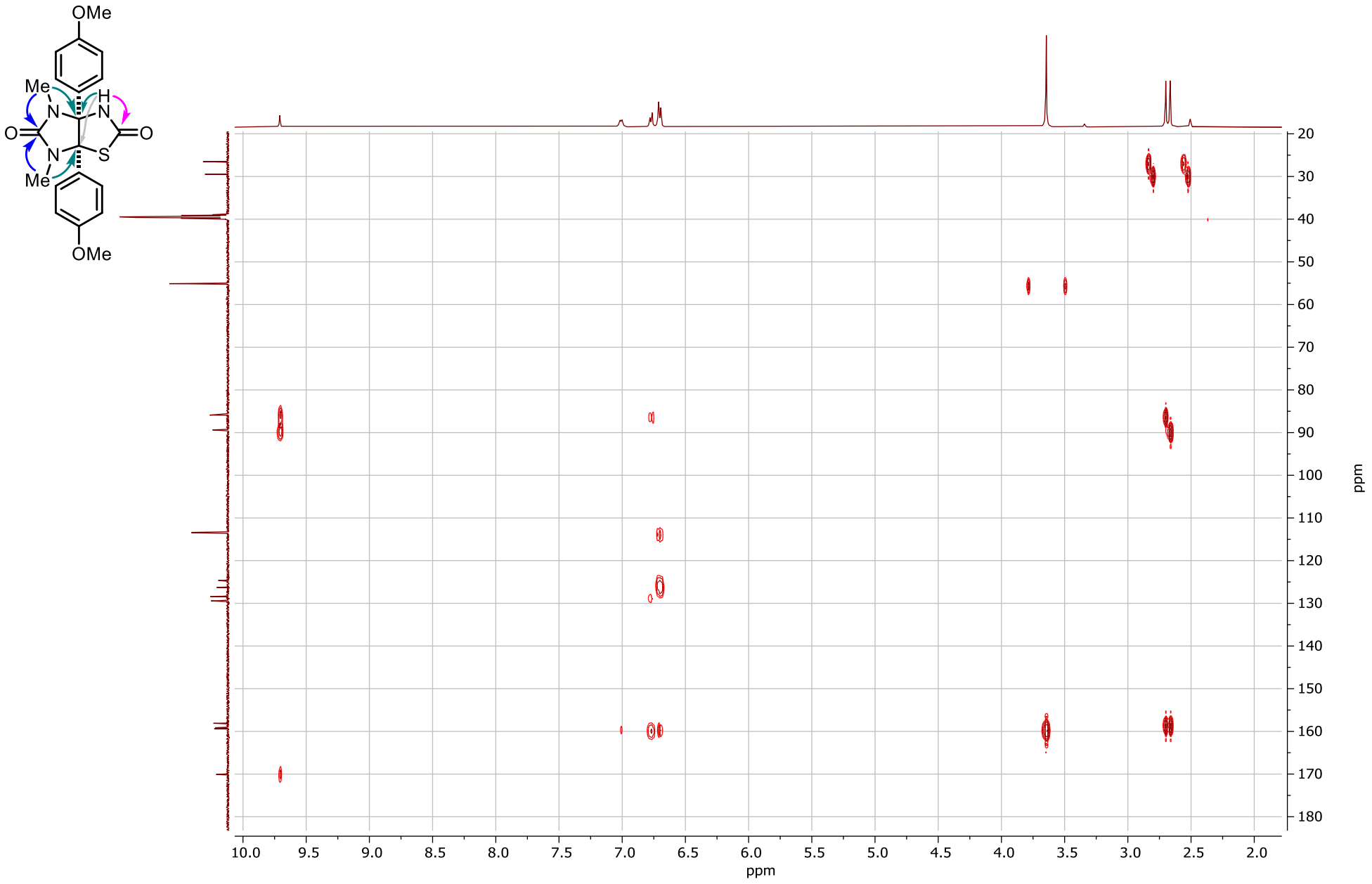
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3j)

^{1}H–^{13}C HSQC (DMSO-d_6)



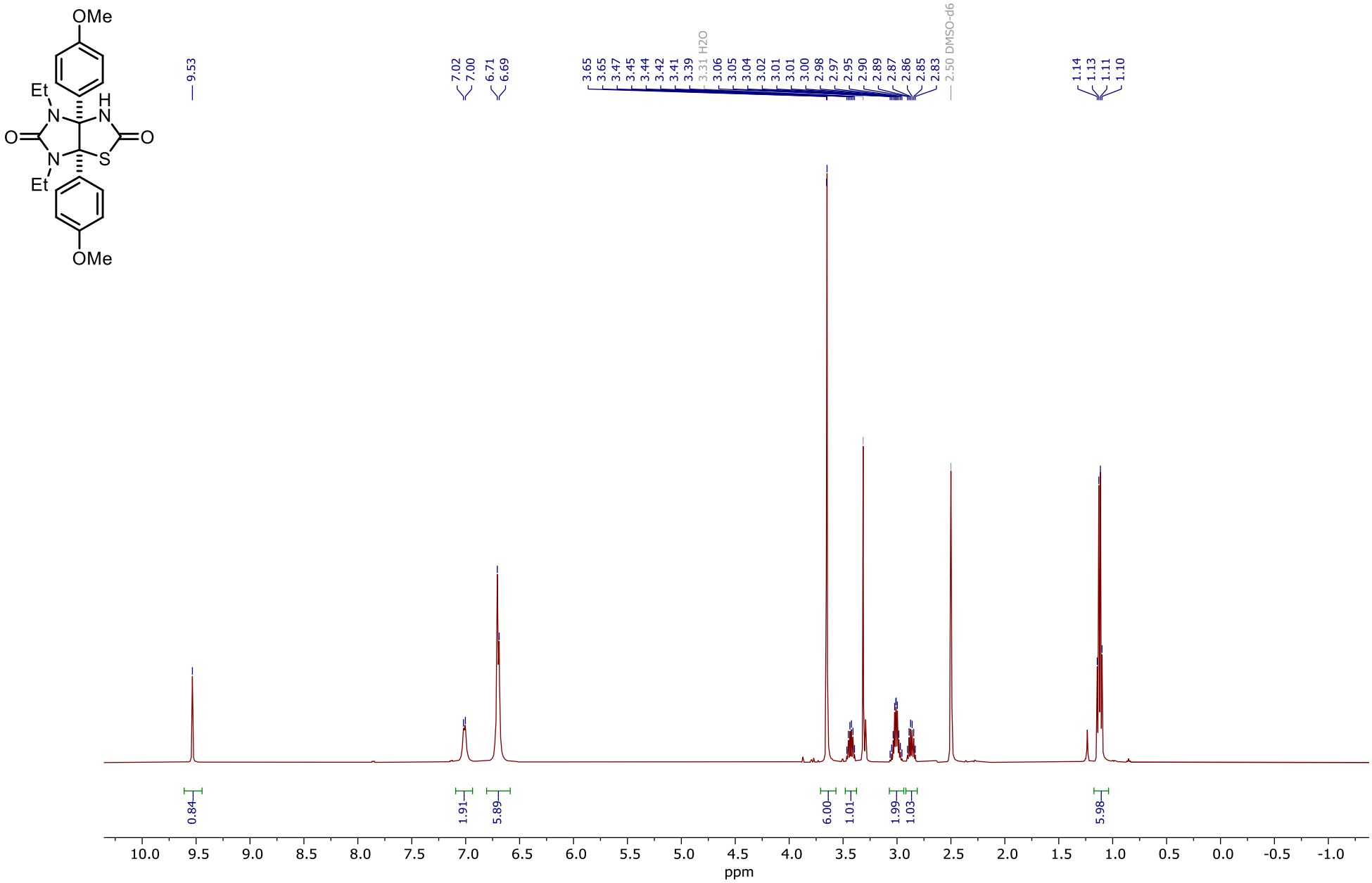
(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dimethyltetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3j)

^{1}H–^{13}C HMBC (DMSO-d_6)



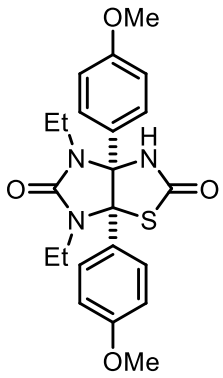
(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-methoxyphenyl)tetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3k)

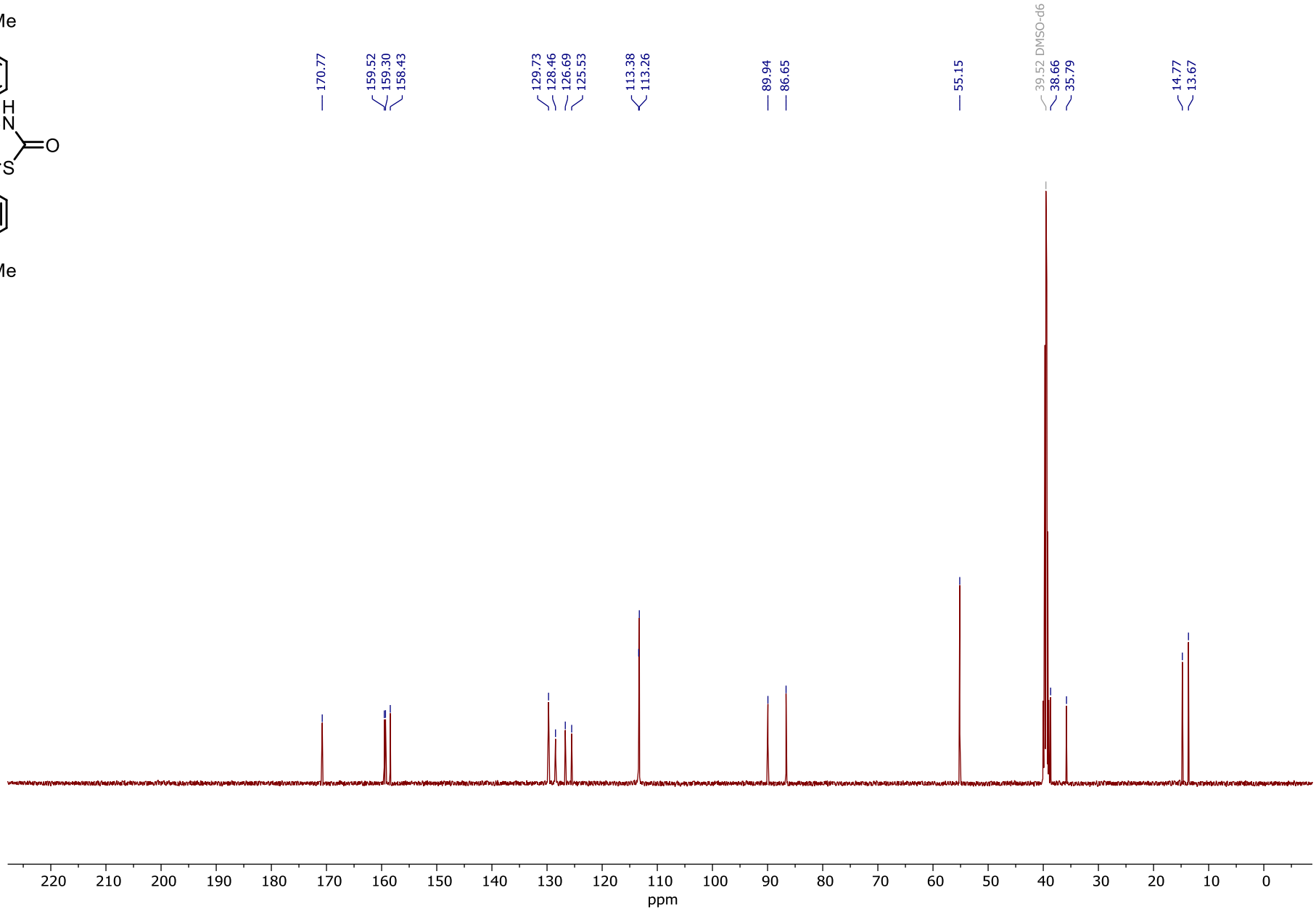
^{1}H NMR (500 MHz, DMSO-d$_6$)



(3a*SR*,6a*SR*)-4,6-Diethyl-3a,6a-*bis*(4-methoxyphenyl)tetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3k)

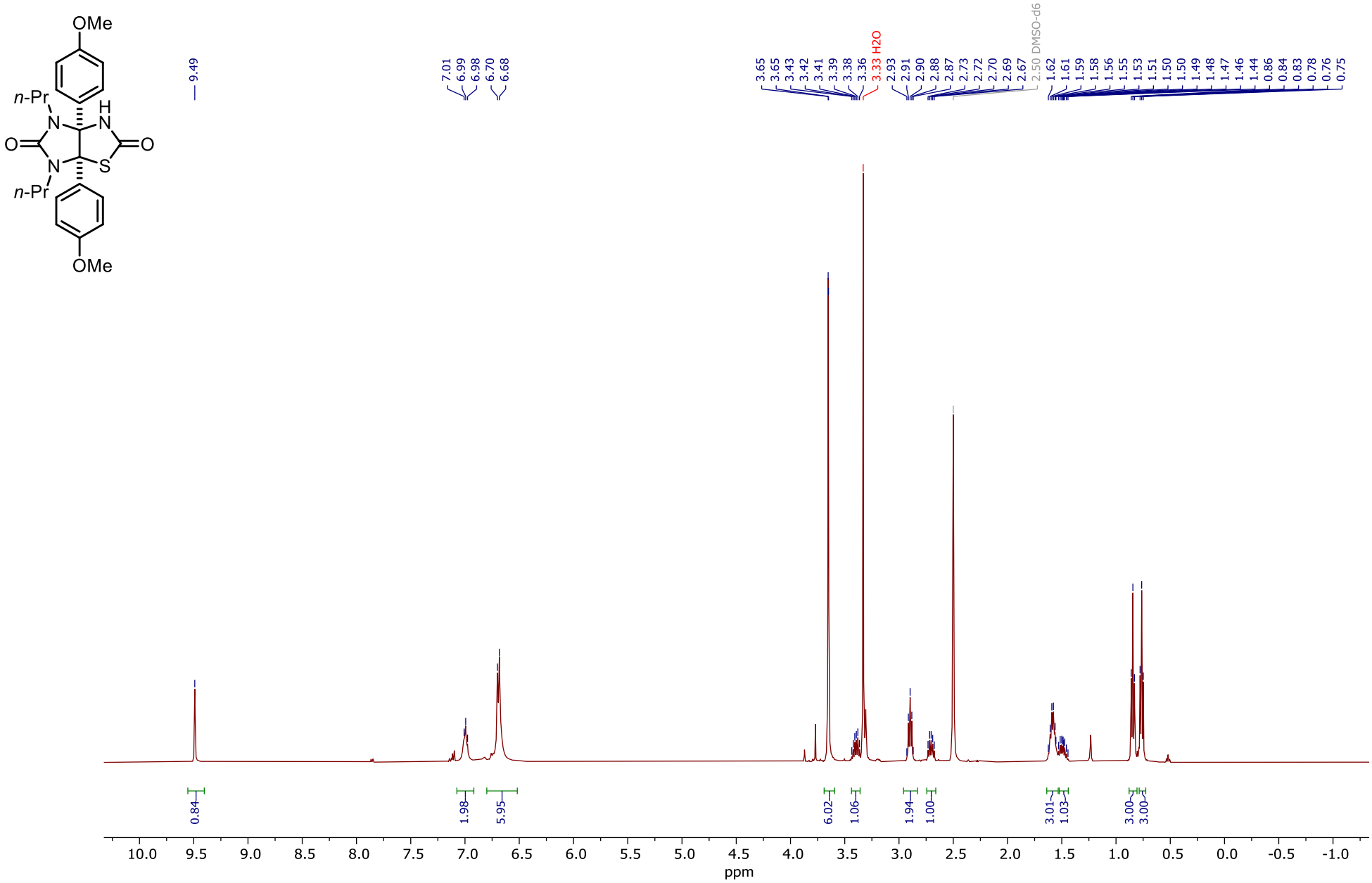
^{13}C NMR (126 MHz, DMSO-d$_6$)





(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dipropyltetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3l)

^{1}H NMR (500 MHz, DMSO-d$_6$)



(3a*SR*,6a*SR*)-3a,6a-*bis*(4-Methoxyphenyl)-4,6-dipropyltetrahydro-2*H*-imidazo[4,5-*d*]thiazole-2,5(3*H*)-dione (3l)

^{13}C NMR (126 MHz, DMSO-d$_6$)