Electronic Supplementary Material (ESI) for New Journal of Chemistry.

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New methodology of nucleophilic substitution at three different centers of seleniranium intermediate in reactions of 2-bromomethyl-1,3-thiaselenole with mercapto benzazoles

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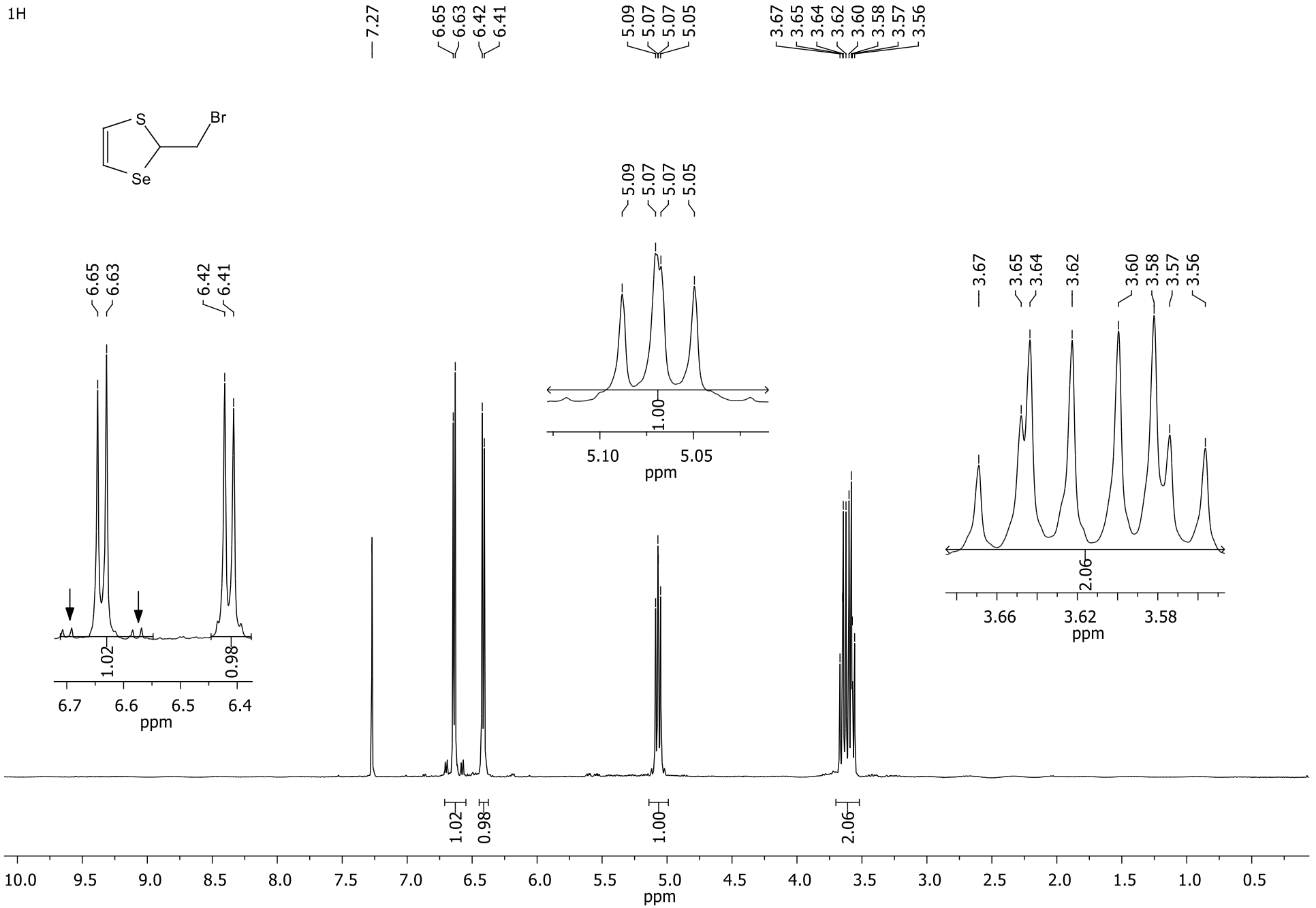
NMR Spectra of all the synthesised compounds

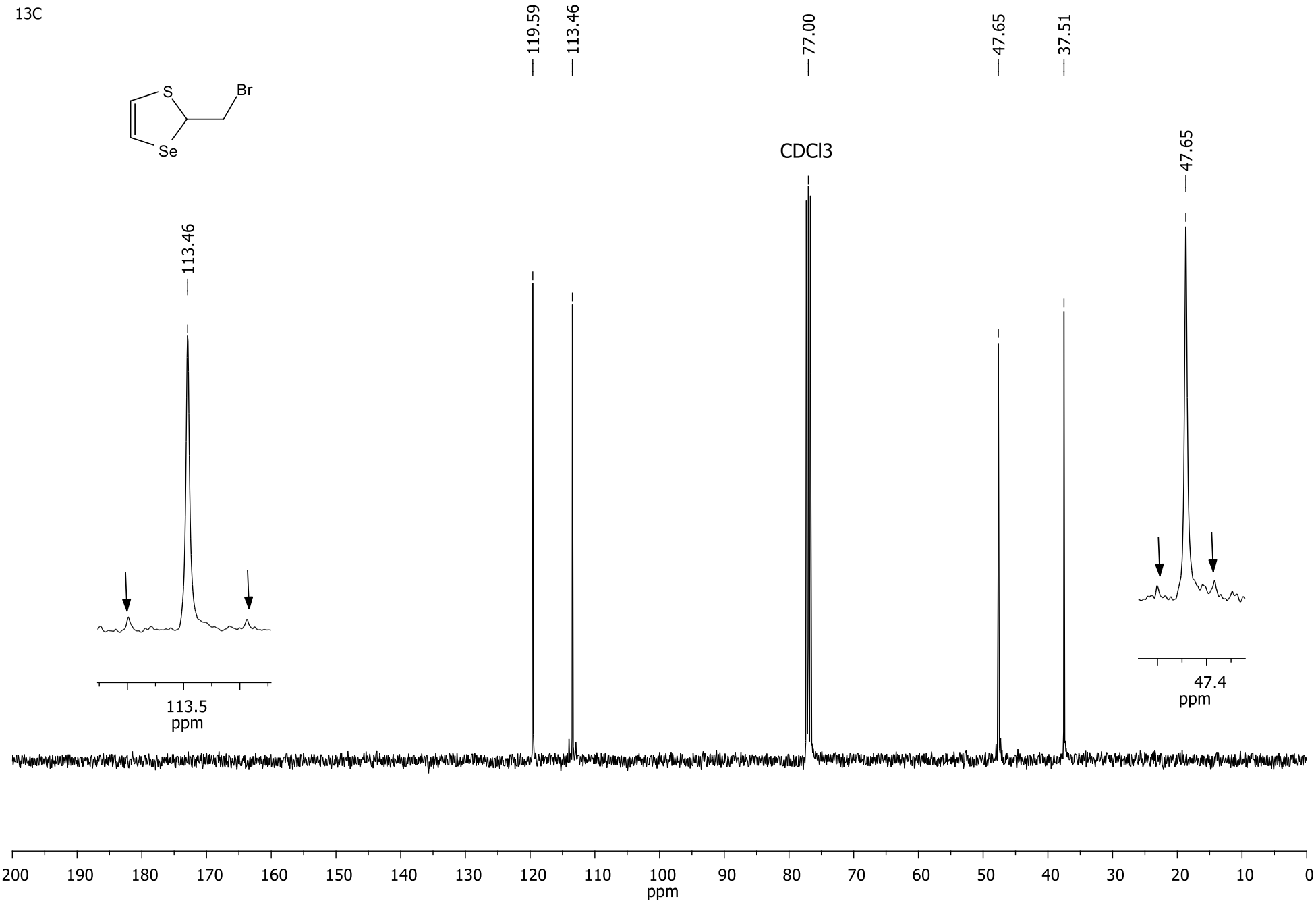
Starting 2-bromomethyl-1,3-thiaselenole (**1**) was prepared from $SeBr_2$ and divinyl sulfide according to the previously described procedure. [S. V. Amosova, I. A. Novokshonova, M. V. Penzik, A. S. Filippov, A. I. Albanov and V. A. Potapov, Tetrahedron Lett., 2017, 58, 4381.]

2-Bromomethyl-1,3-thiaselenole (1). Modified procedure for the synthesis 2-bromomethyl-1,3-thiaselenole **1**. A solution of bromine (5.85 g, 36.63 mmol) in CCl_4 (30 mL) was added dropwise to powdered selenium (2.89 g, 36.63 mmol, carefully ground) in CCl_4 (70 mL) over 15-20 min under an Ar atmosphere and the mixture stirred for 2 h. The formed solution of $SeBr_2$ in CCl_4 (100 mL) and divinyl sulfide (3.15 g, 36.63 mmol) in CCl_4 (10 mL) were simultaneously added dropwise over 1 h to a flask containing CCl_4 (15-20 mL) so that the molar ratio of both reagents in the mixture was 1:1. The reaction mixture was stirred for 3 h, then a solution of pyridine (3.47 g, 43.92 mmol) in CCl_4 (10 mL) was added over 10-15 min, and the mixture stirred overnight. The reaction mixture was filtered, and the solution stirred for 24 h and filtered again. Most of the solvent was removed by rotary evaporation. The residue (25-30 mL) was allowed to stand for 1 h and filtered. The solvent and the remaining pyridine were removed from the filtrate *in vacuo* to give high purity thiaselenole **1** (6.35 g, brown oil) in 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.64 (d, 1H, $^3J_{H,H}$ = 6.3 Hz, $^2J_{Se,H}$ = 49.3 Hz, $^3J_{Se,H}$ = 21.0 Hz, SeCH=HCS), 6.42 (d, 1H, $^3J_{H,H}$ = 6.3 Hz, SeCH=HCS), 5.07 (dd, 1H, $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,H}$ = 8.2 Hz, $^2J_{Se,H}$ = 24.0 Hz, SCHSe), 3.64 (dd, 1H, $^2J_{H,H}$ = 10.0 Hz, $^3J_{H,H}$ = 8.2 Hz, CH_2Br), 3.57 (dd, 1H, $^2J_{H,H}$ = 10.0 Hz, $^3J_{H,H}$ = 7.3 Hz, CH_2Br); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.59 (SeCH=HCS), 113.46 ($^1J_{Se,C}$ = 106.6 Hz, SeCH=HCS), 47.65 ($^1J_{Se,C}$ = 71.3 Hz, SCHSe), 37.51 (CH_2Br); ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 521.57; MS (EI): m/z (%) = 244 (21, M+), 151 (74), 84 (99), 58 (87), 49 (100); Anal. Calcd for C_4H_5BrSSe: C, 19.69; H, 2.07; Br, 32.75; S, 13.14; Se, 32.36. Found: C, 19.43; H, 2.18; Br, 32.64; S, 13.44; Se, 32.21.



^{1}H NMR spectrum of 2-bromomethyl-1,3-thiaselenole (1)



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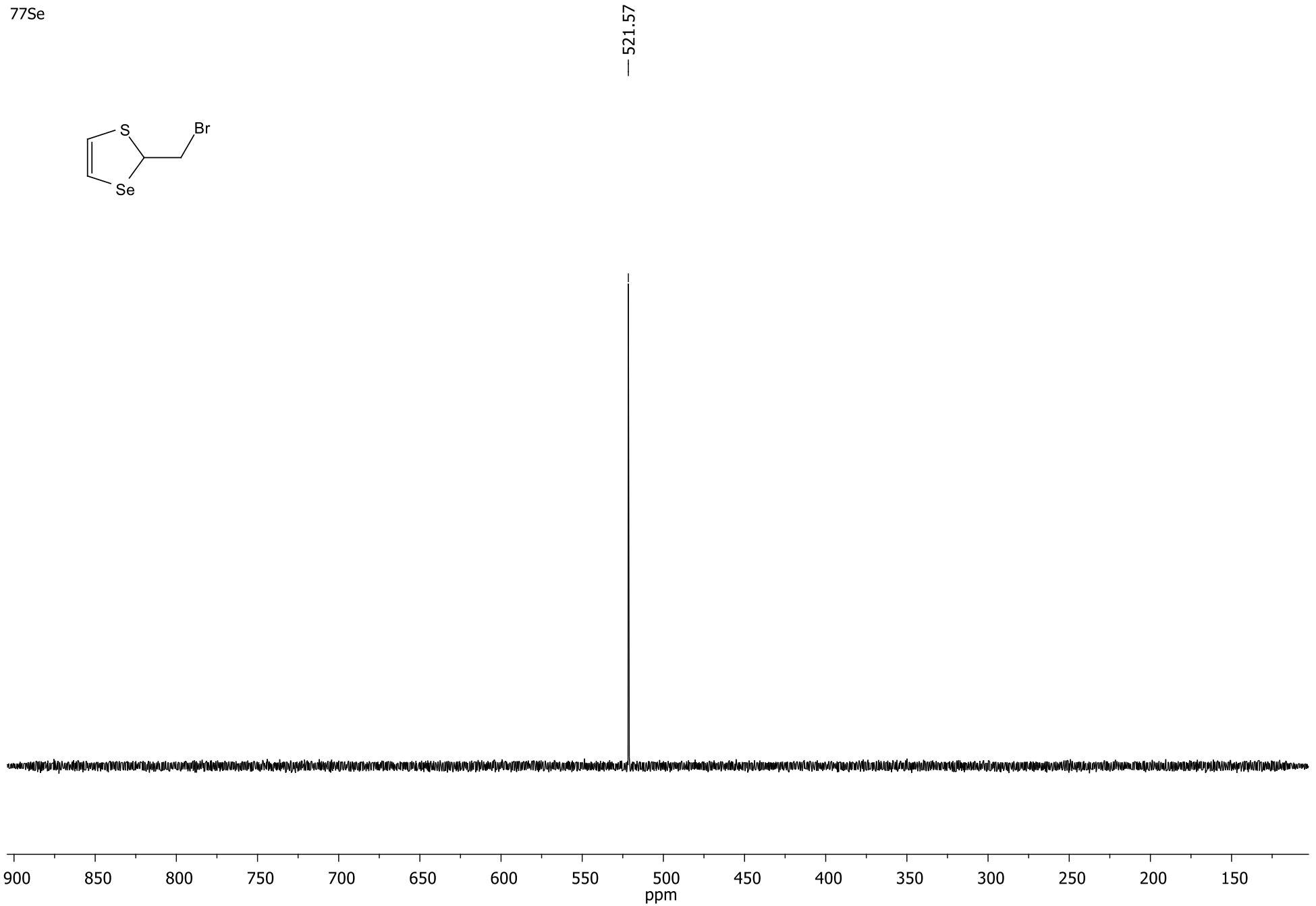

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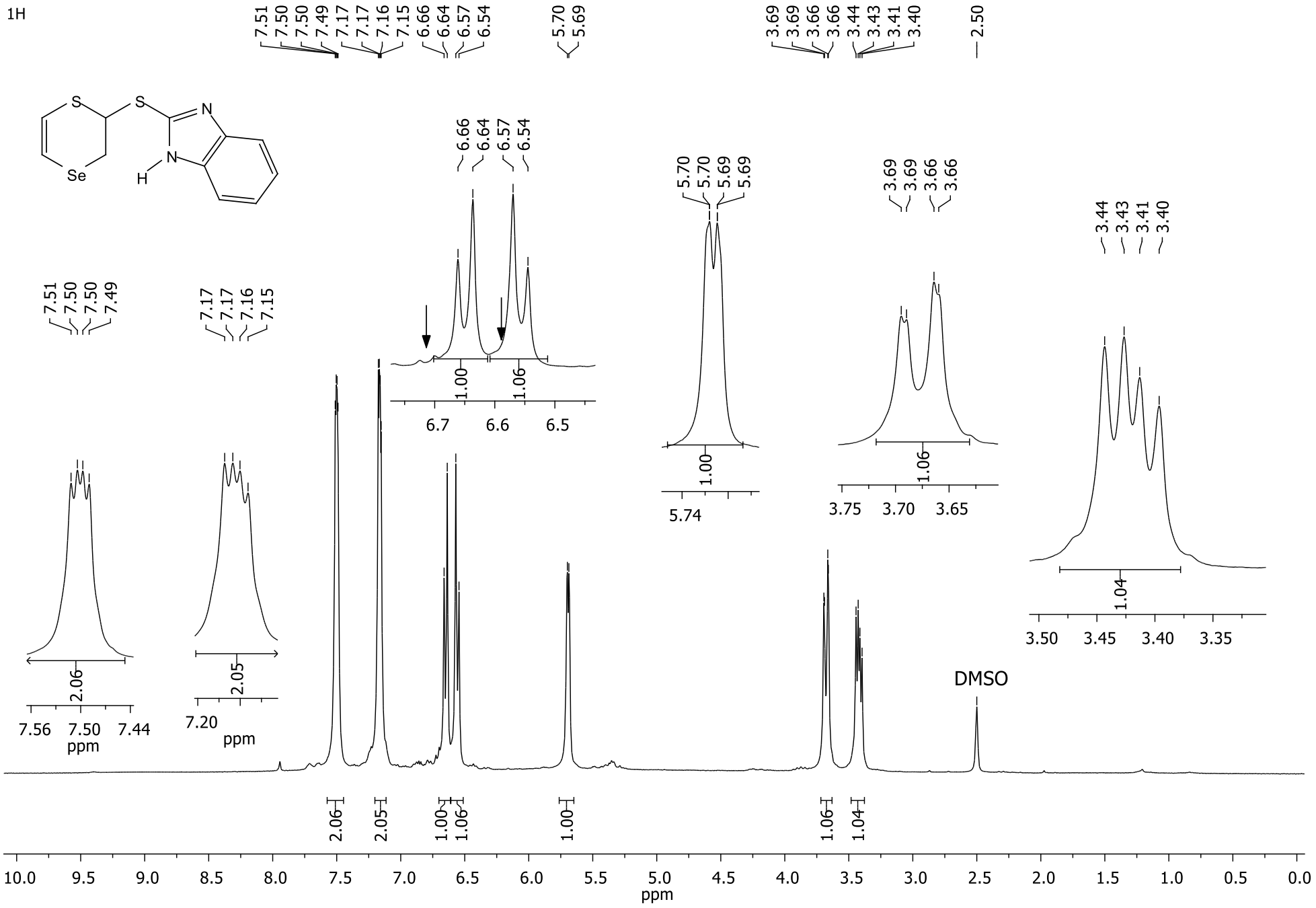
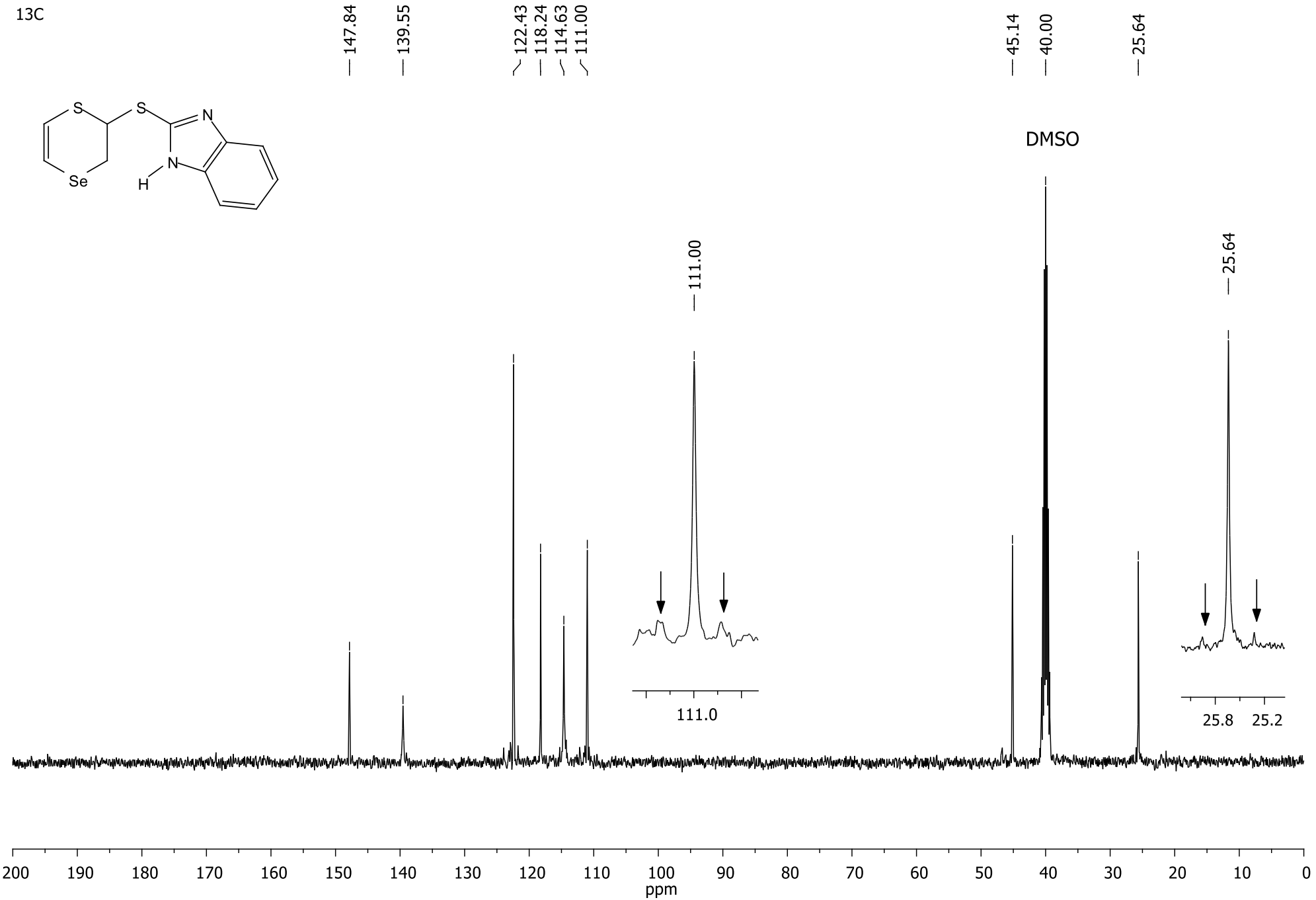


[1]H NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1*H*-1,3-benzimidazole (3a)



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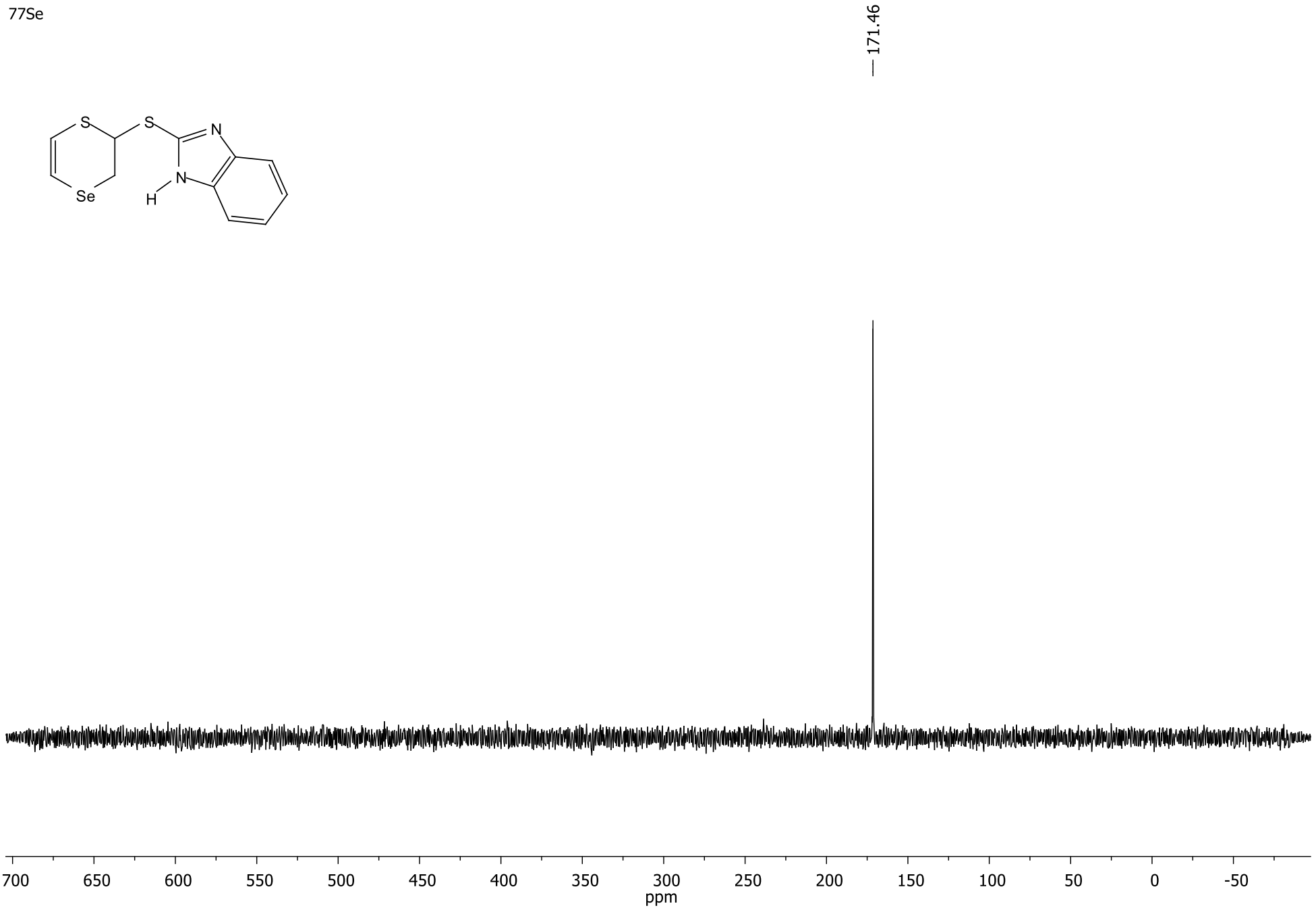

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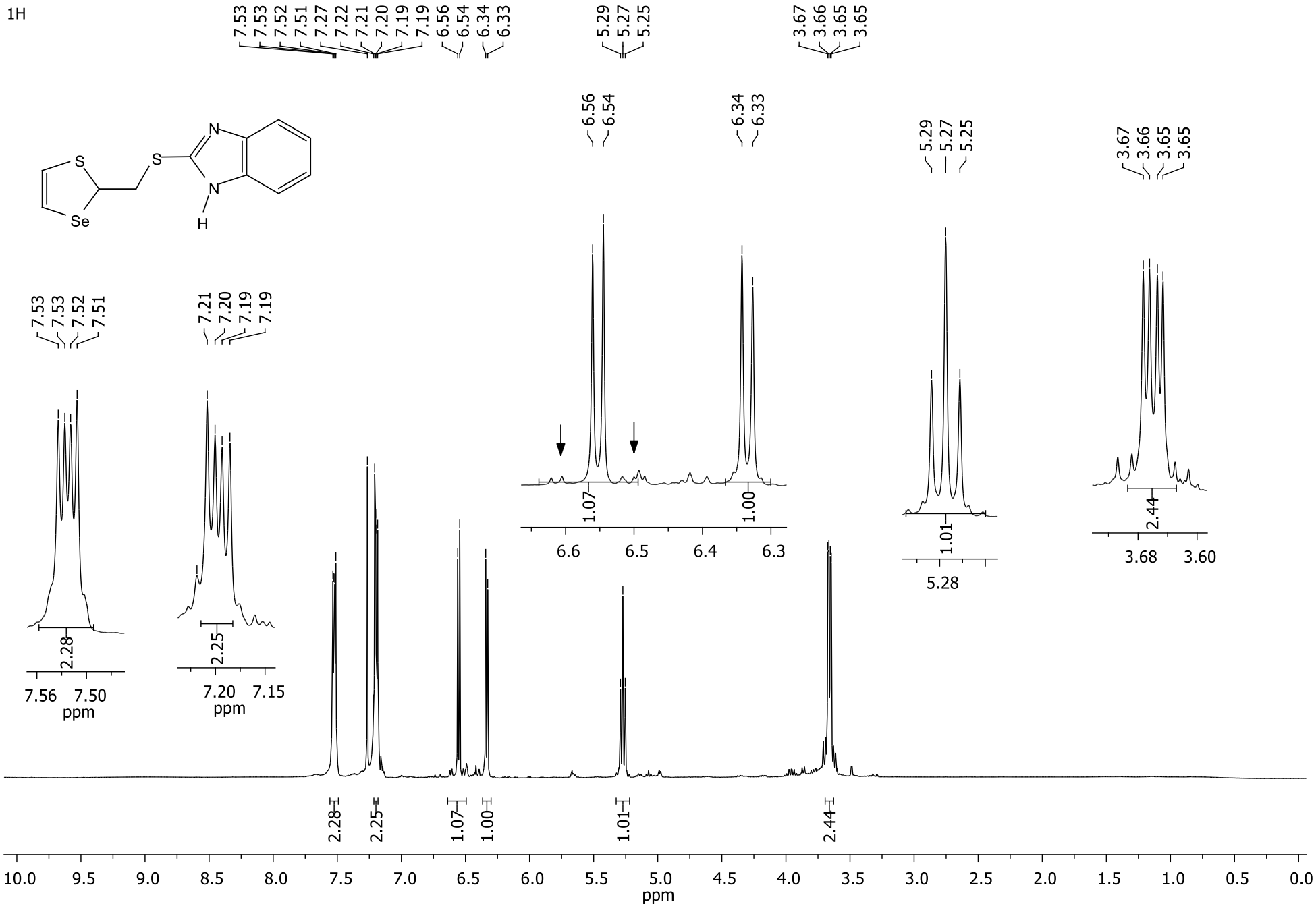
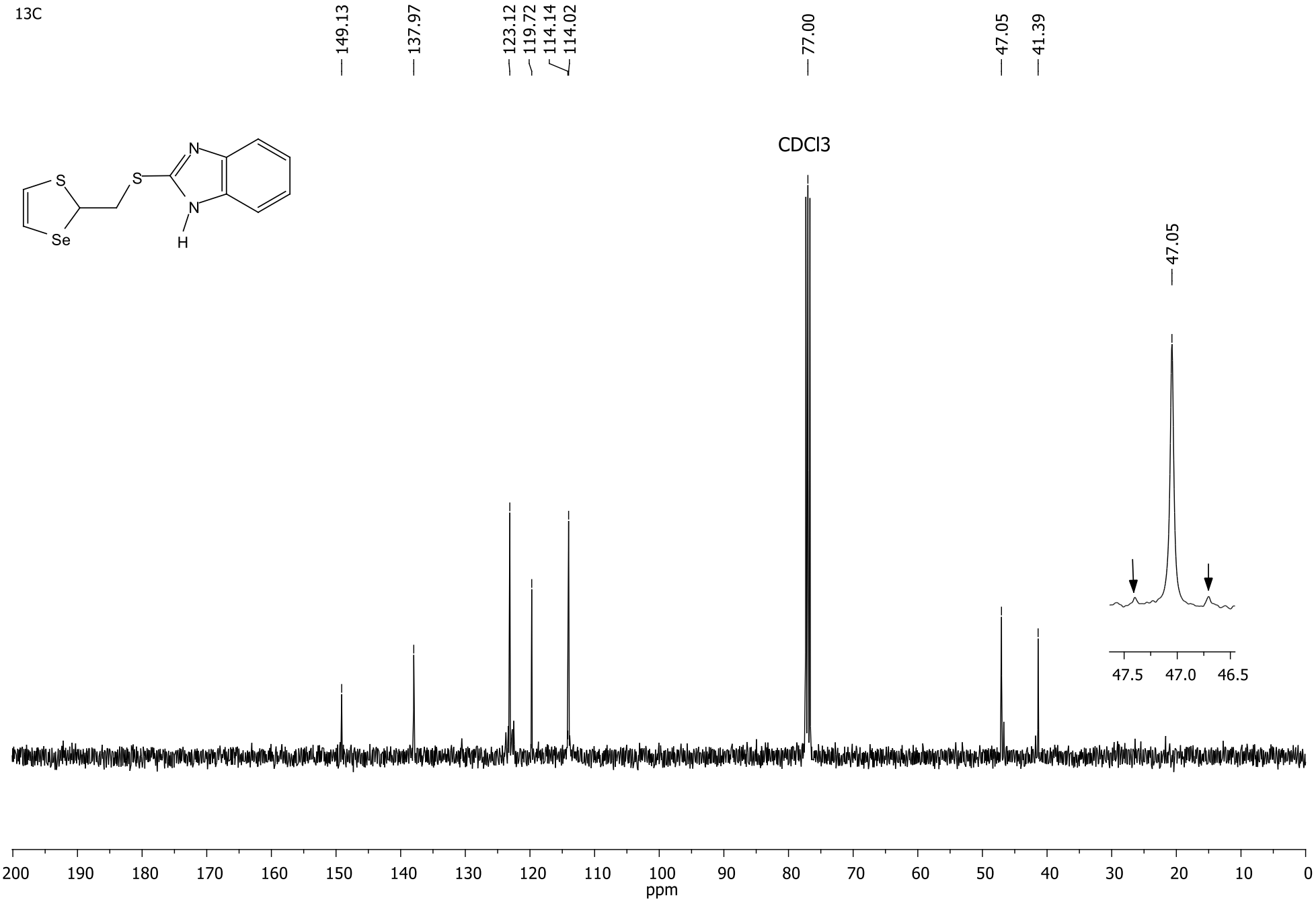


^{1}H NMR spectrum of 2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1*H*-1,3-benzimidazole (4a)



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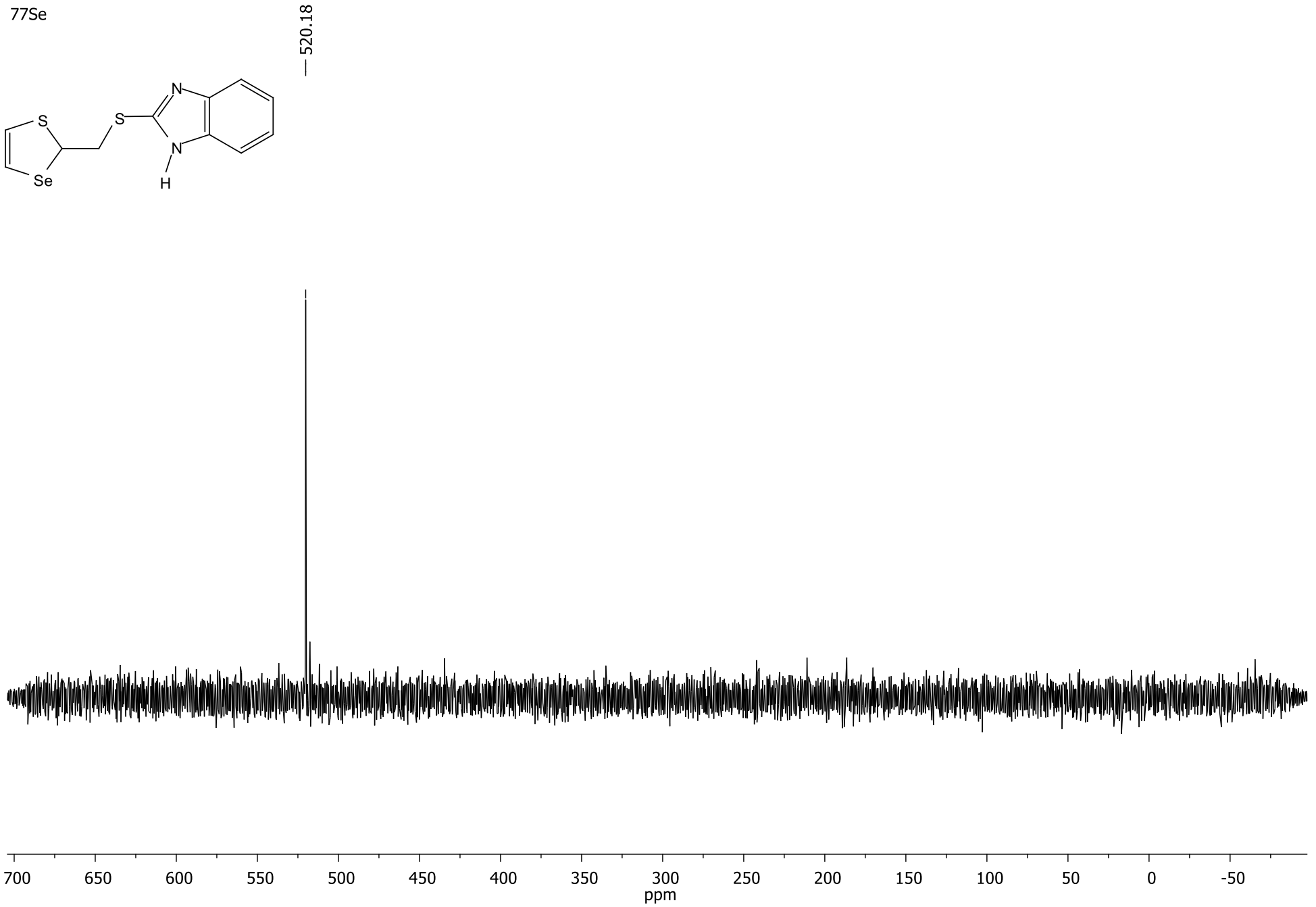

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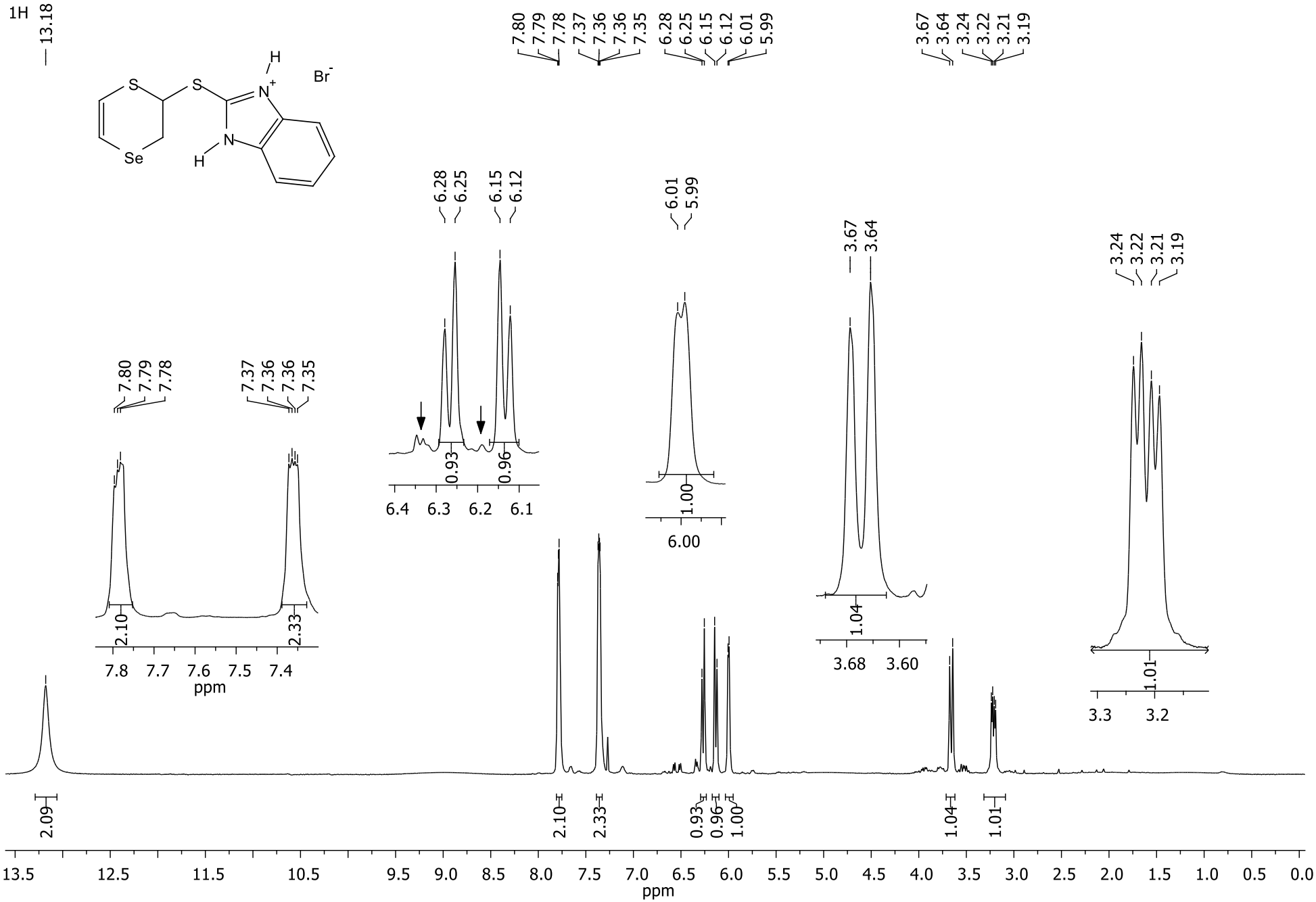
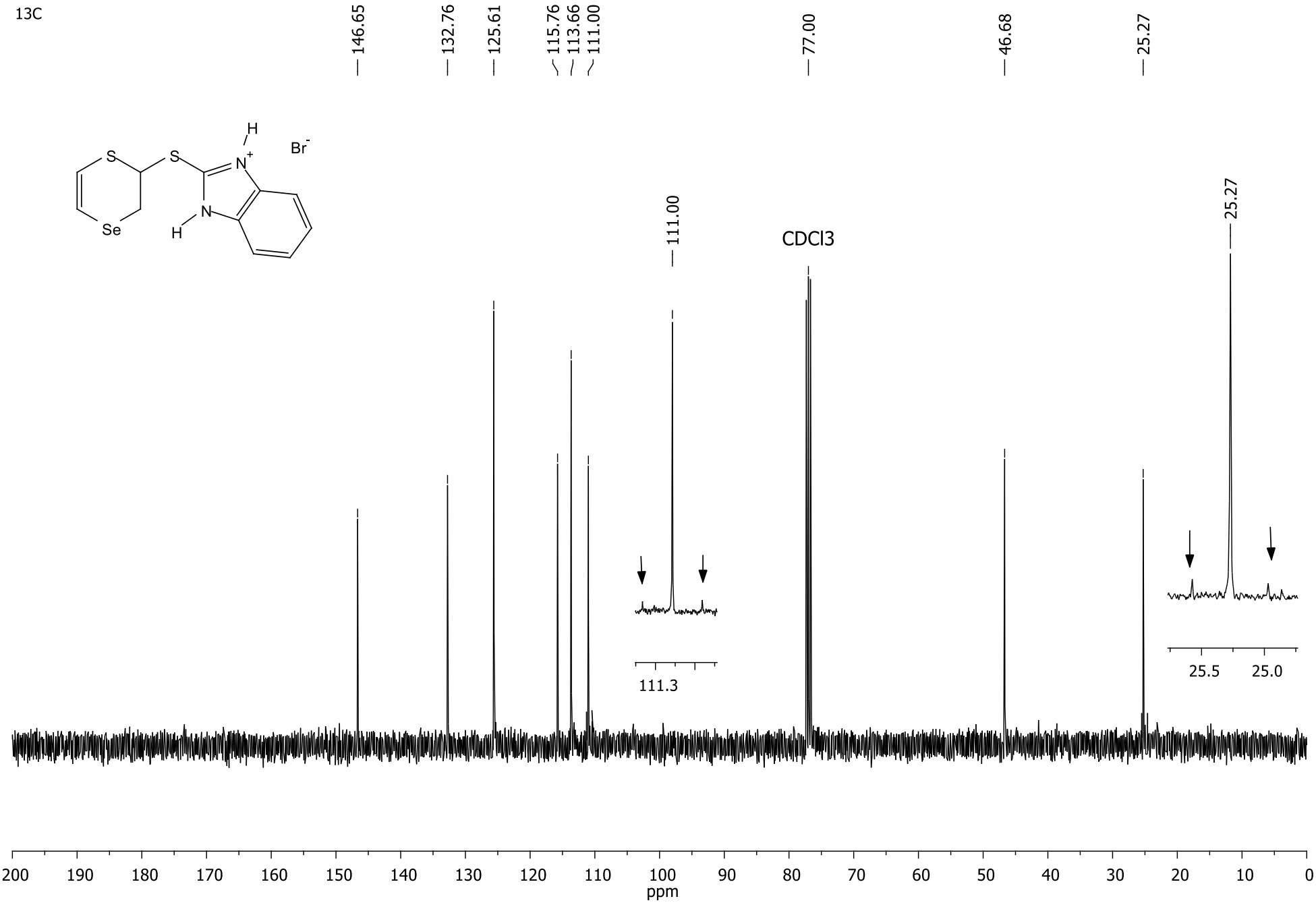


[1]H NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-3*H*-1,3-benzimidazol-1-ium bromide (5a)



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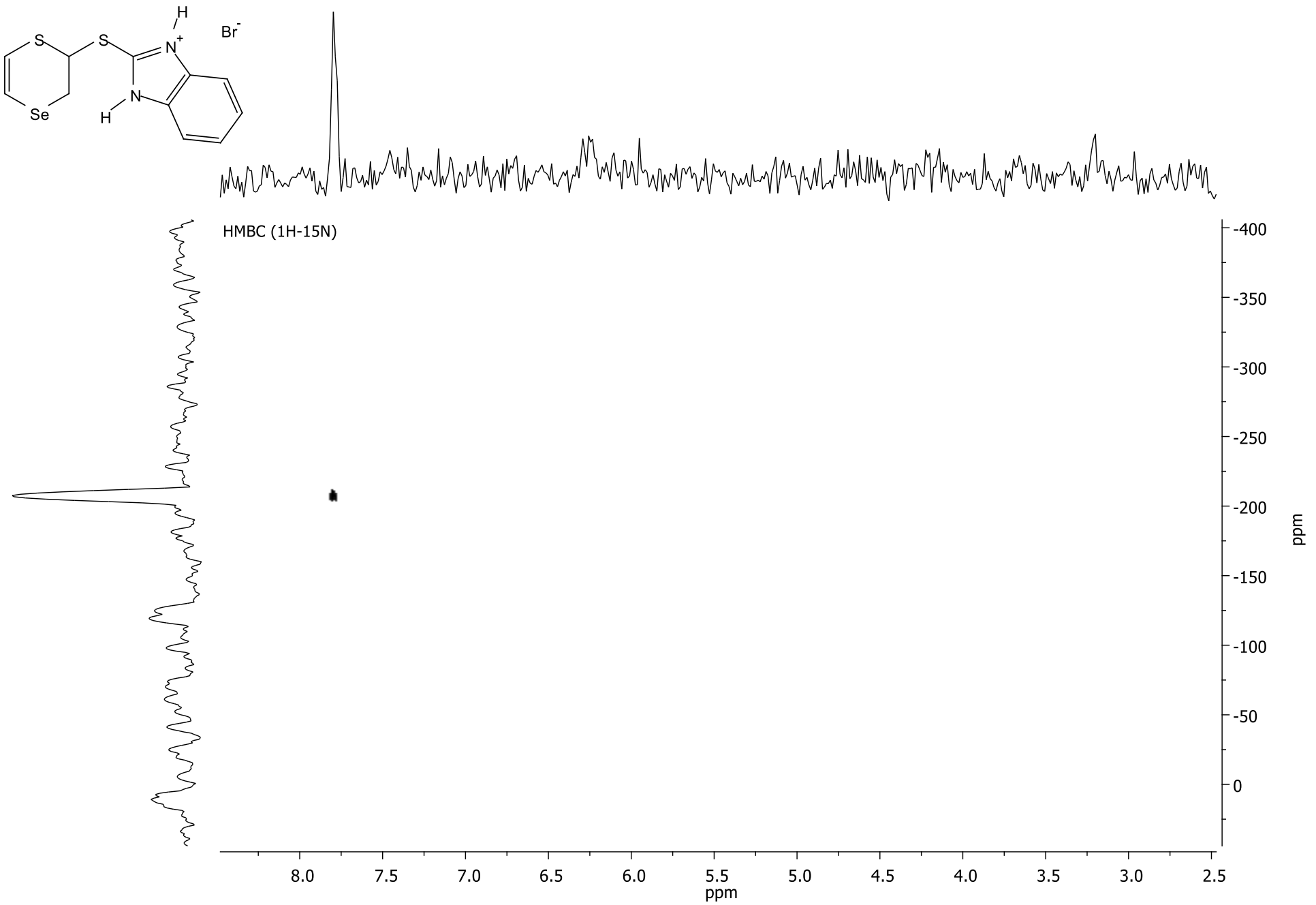
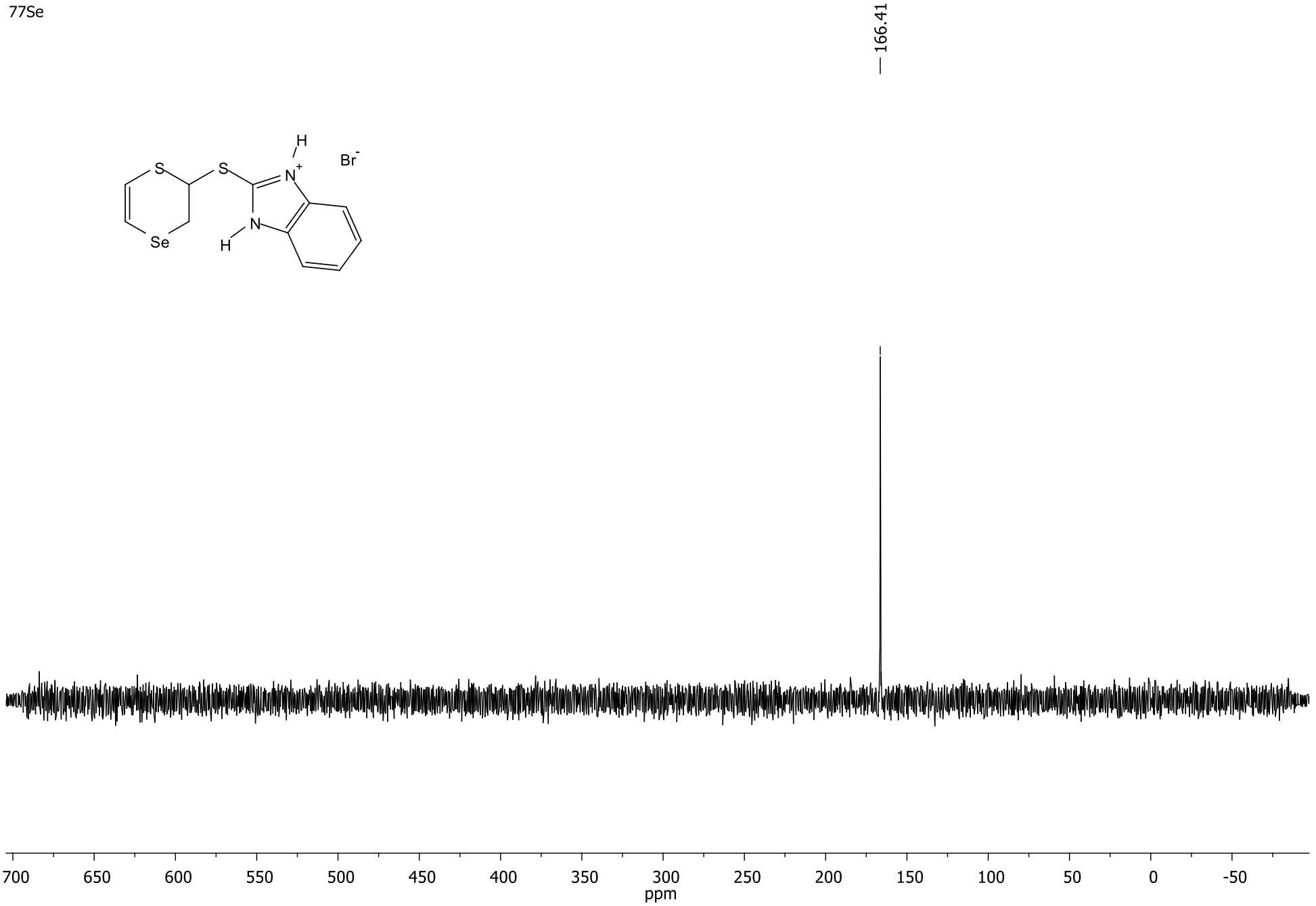
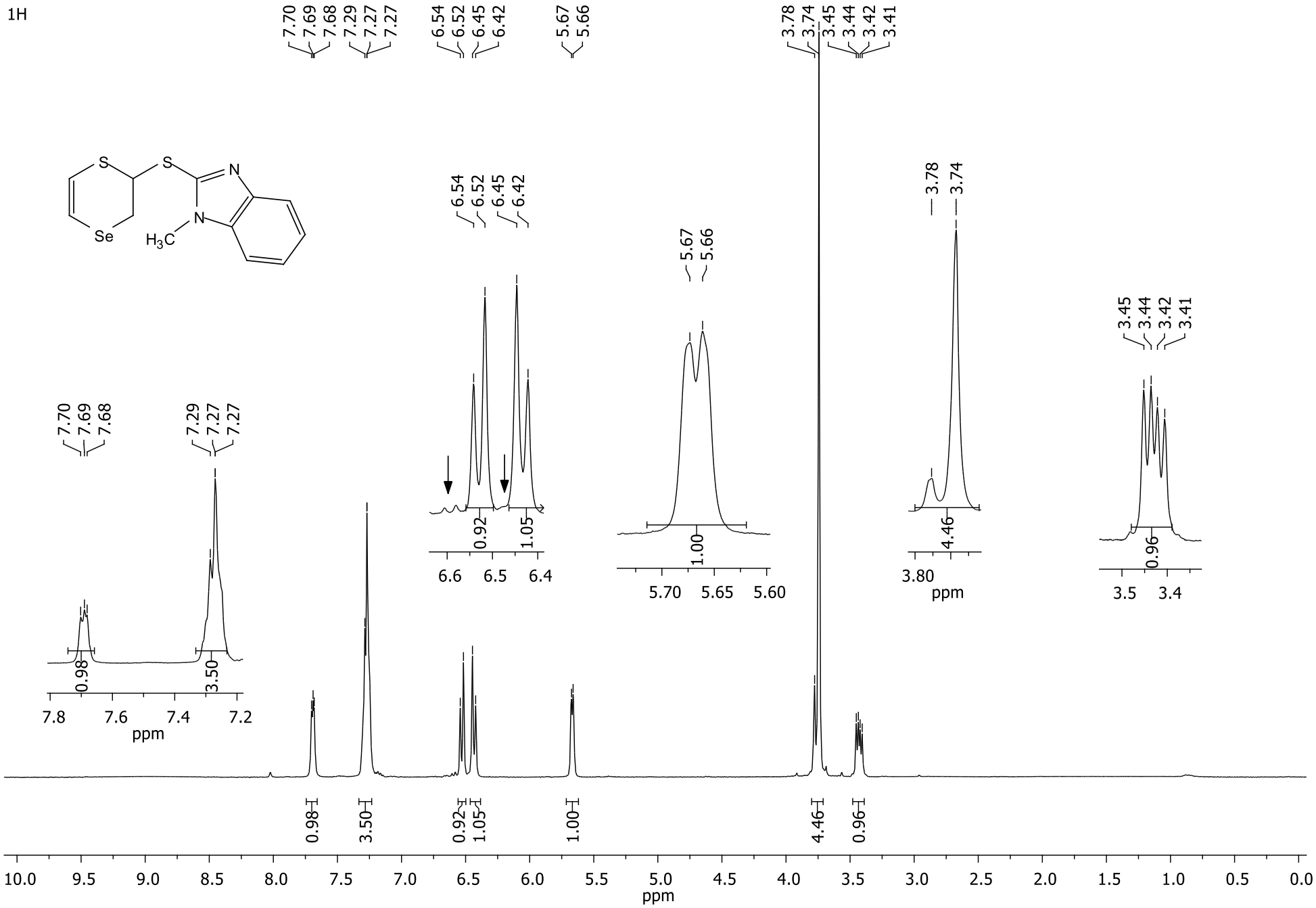


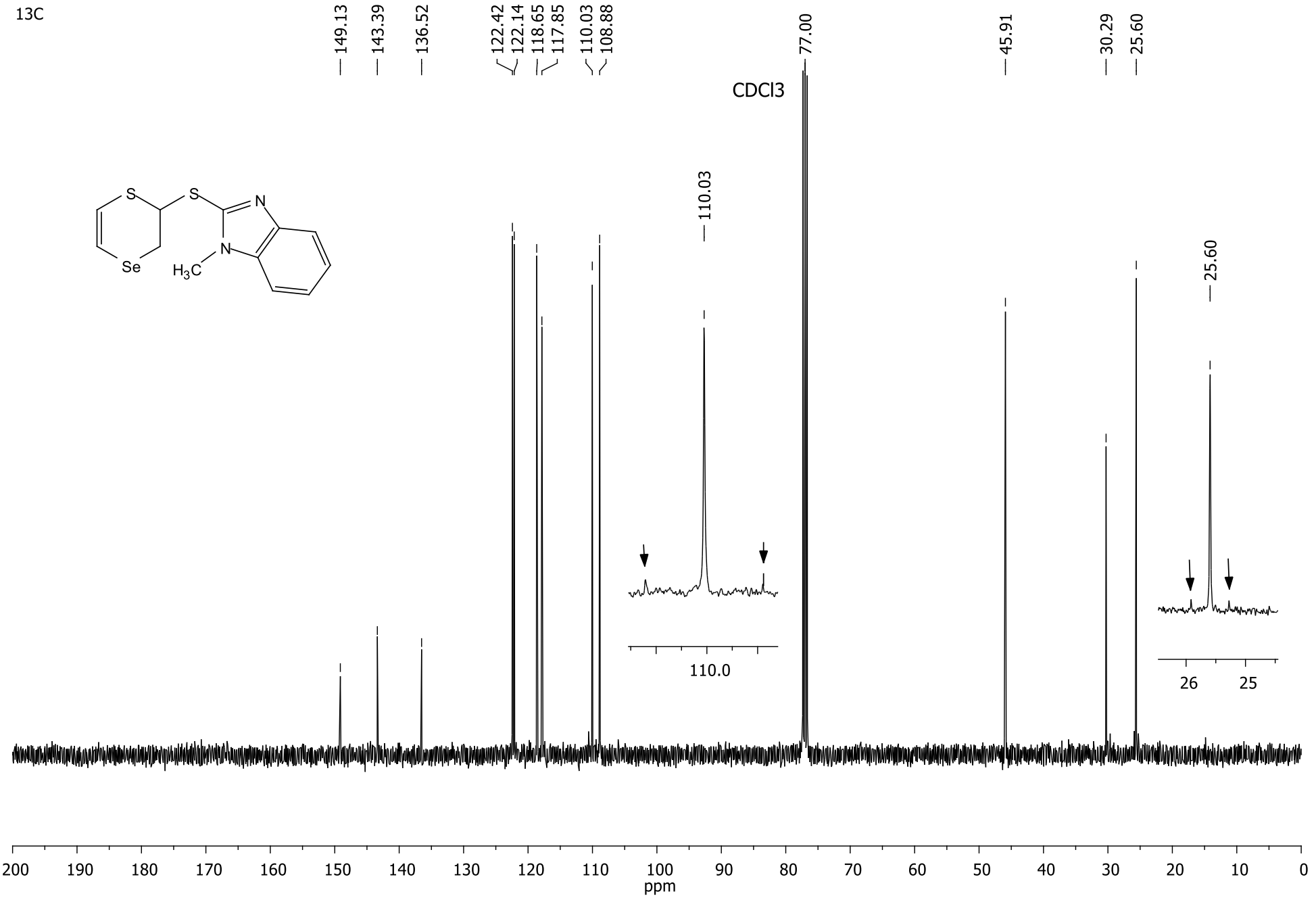
HMBC (^{1}H-^{15}N) NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-3*H*-1,3-benzimidazol-1-ium bromide (5a)



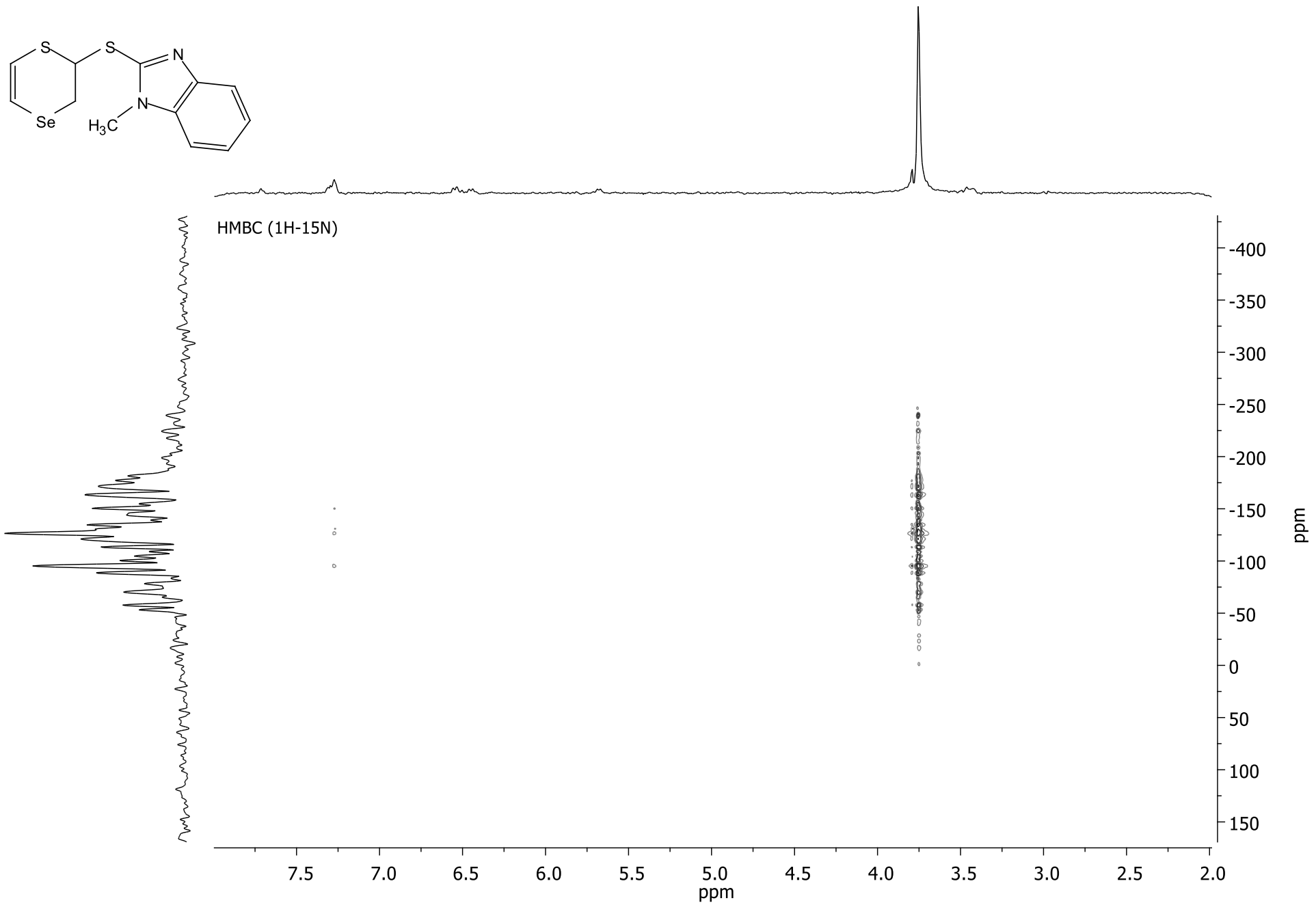
^{77}Se NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-3*H*-1,3-benzimidazol-1-ium bromide (5a)



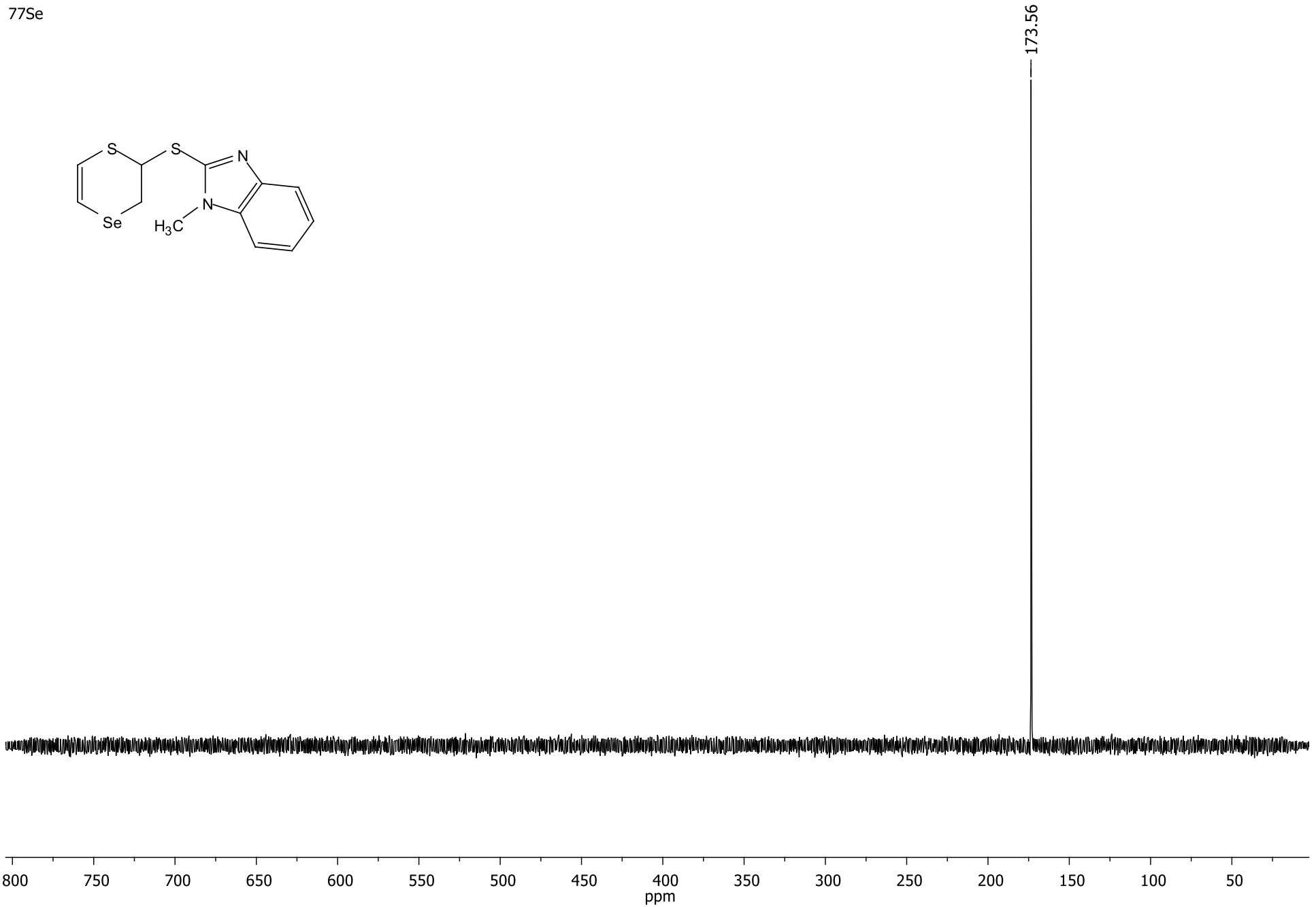
^{1}H NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1-methyl-1*H*-1,3-benzimidazole (3b)



^{13}C NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1-methyl-1*H*-1,3-benzimidazole (3b)



HMBC (^{1}H-^{15}N) NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1-methyl-1*H*-1,3-benzimidazole (3b)



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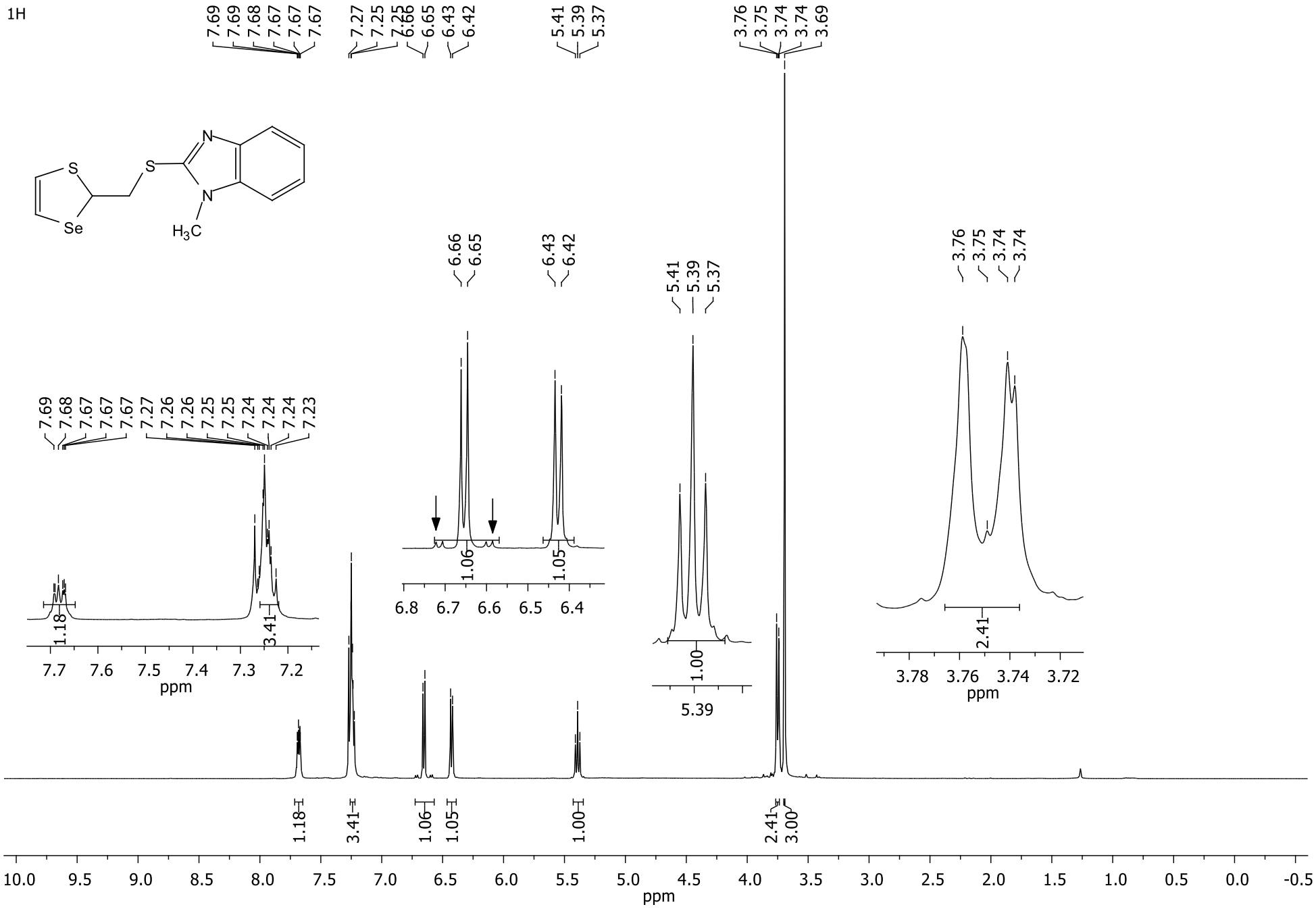
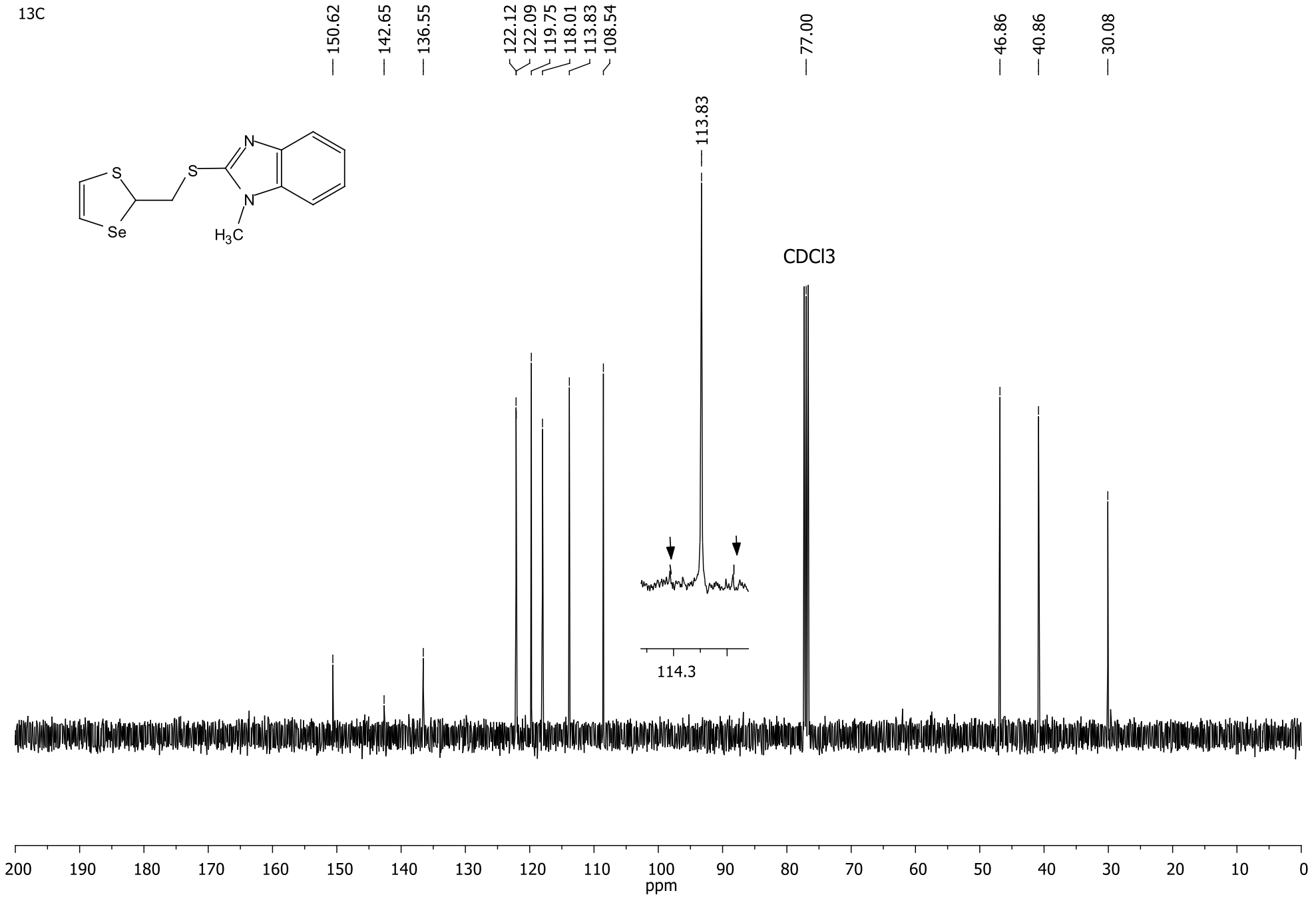
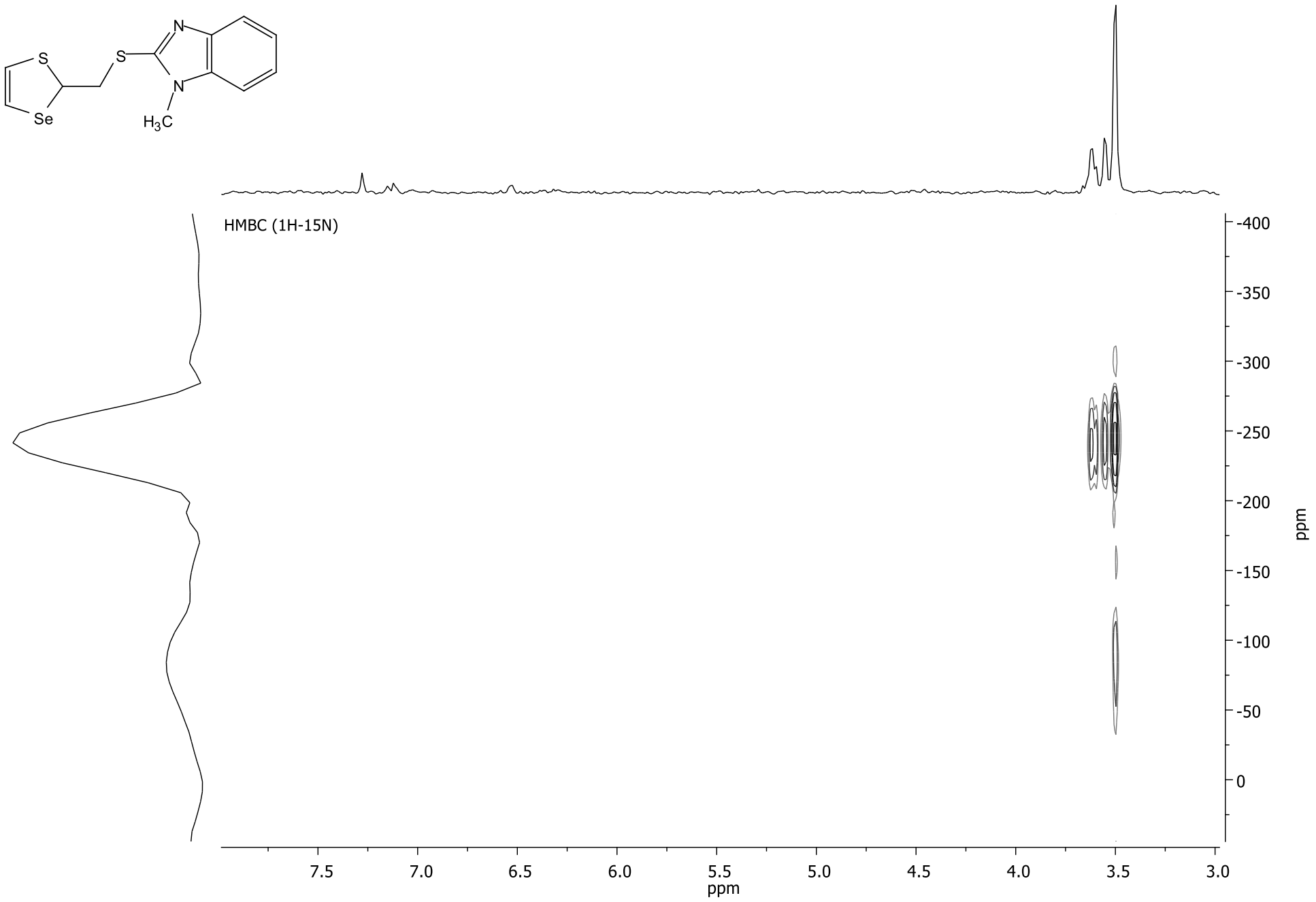


[1]H NMR spectrum of 1-methyl-2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1*H*-1,3-benzimidazole (4b)



^{13}C NMR spectrum of 1-methyl-2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1*H*-1,3-benzimidazole (4b)



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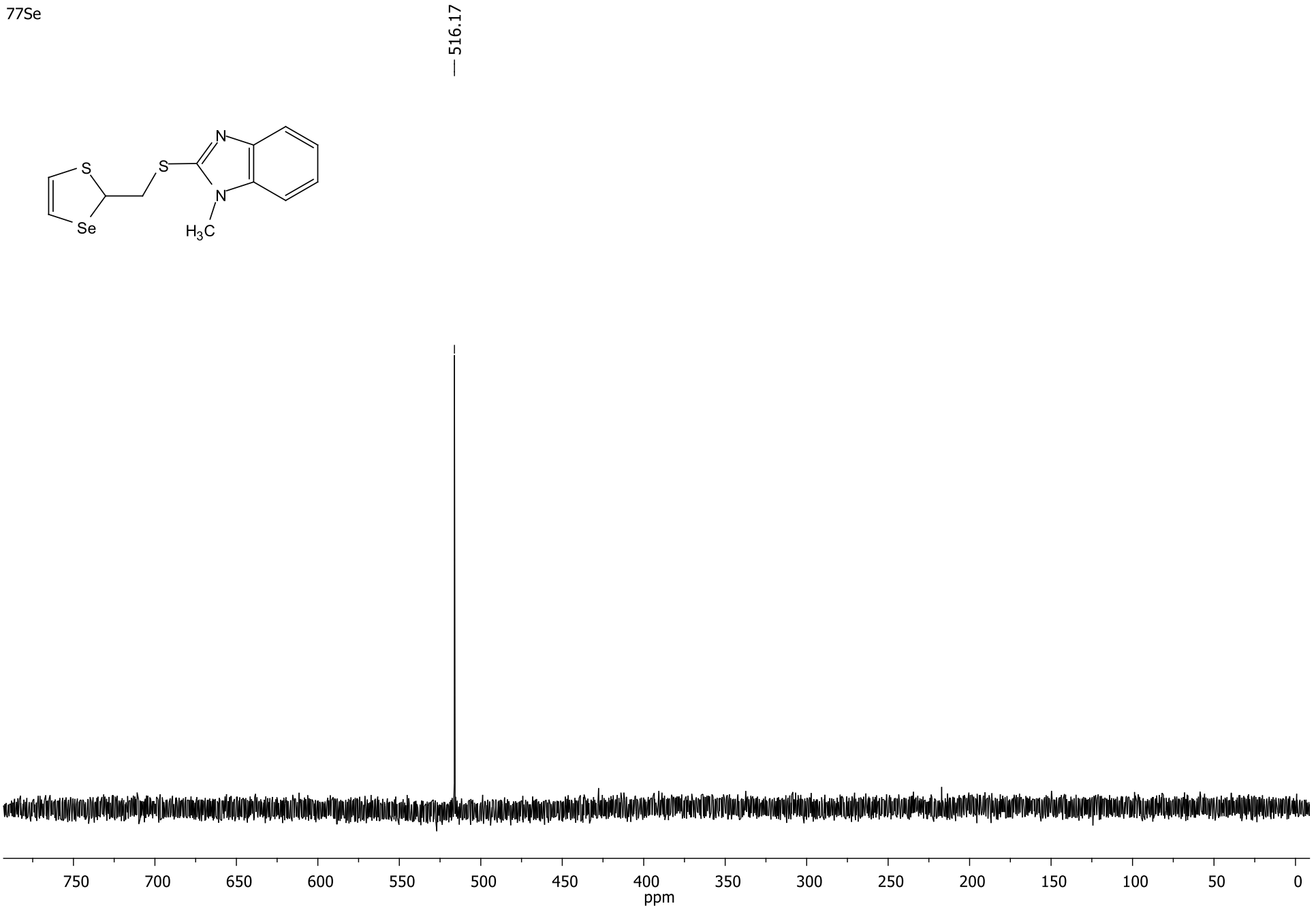
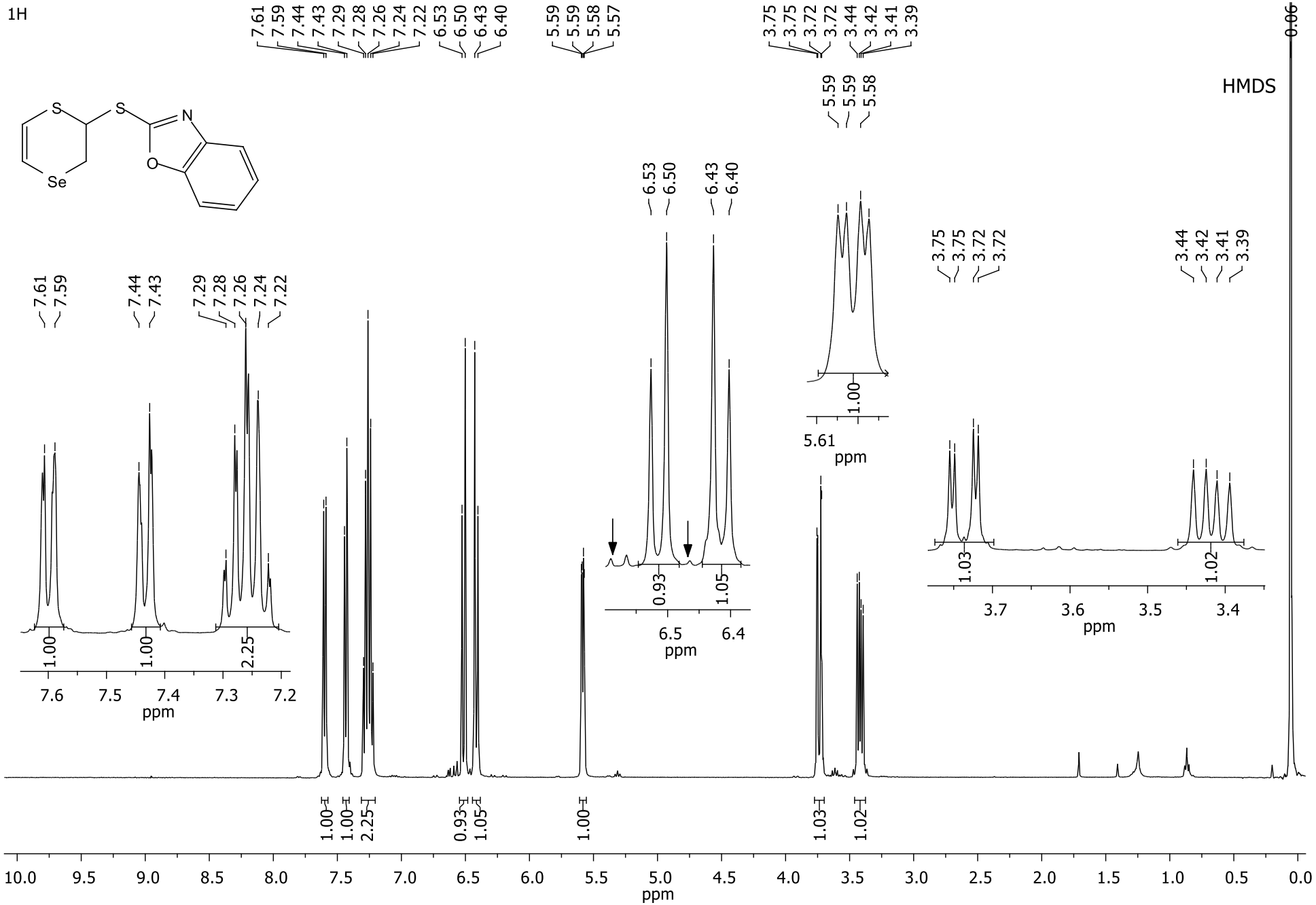
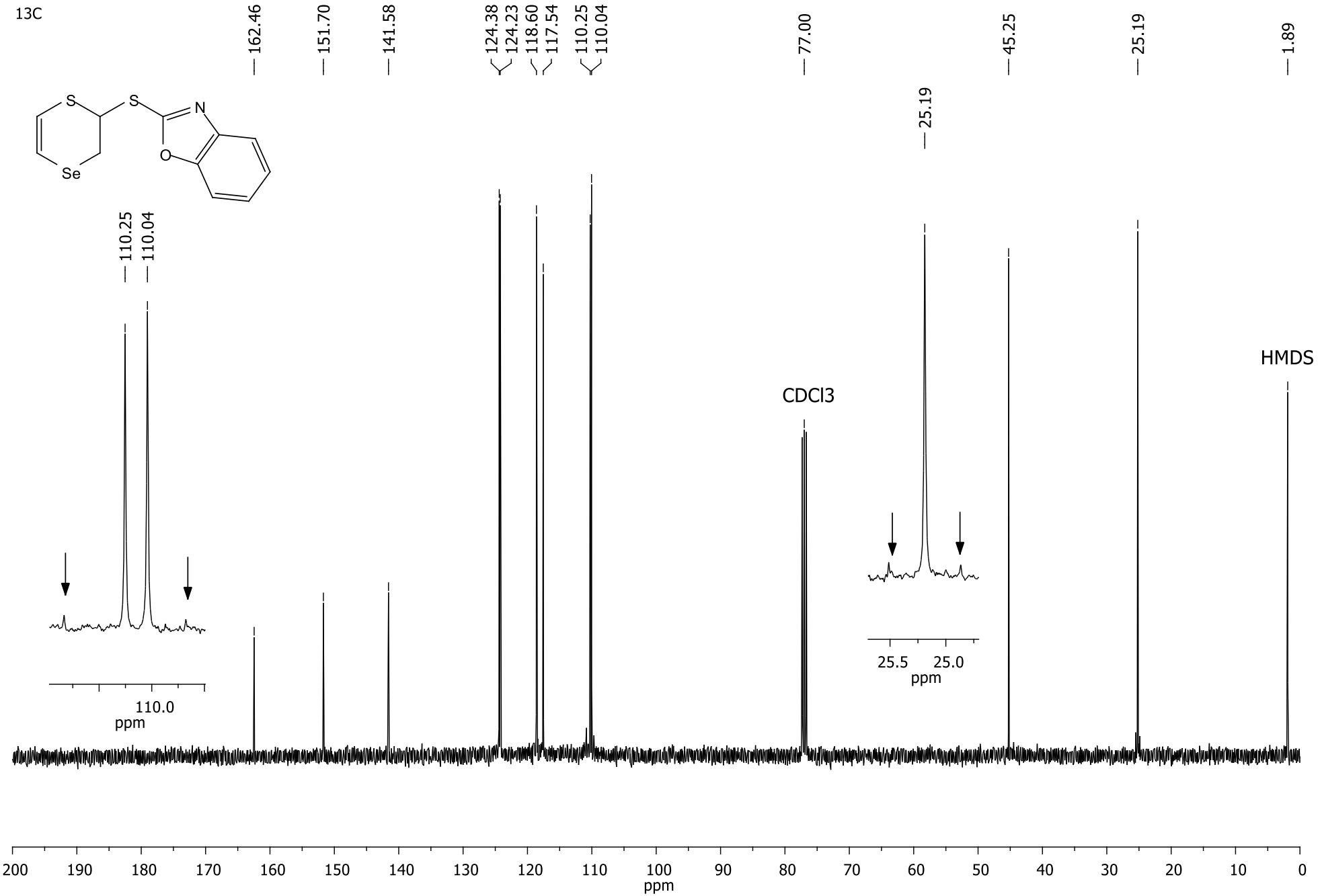


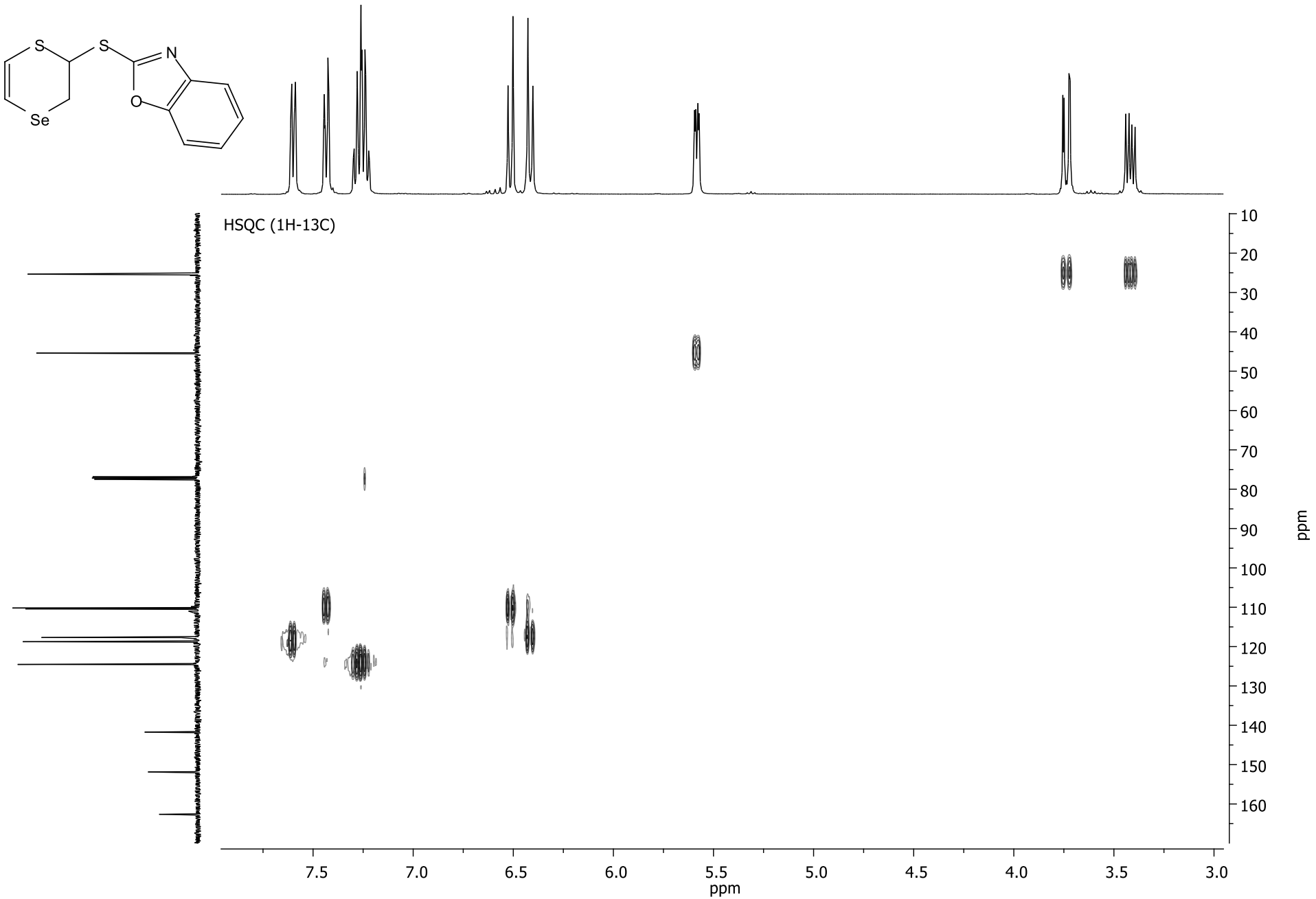
^{77}Se NMR spectrum of 1-methyl-2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1*H*-1,3-benzimidazole (4b)



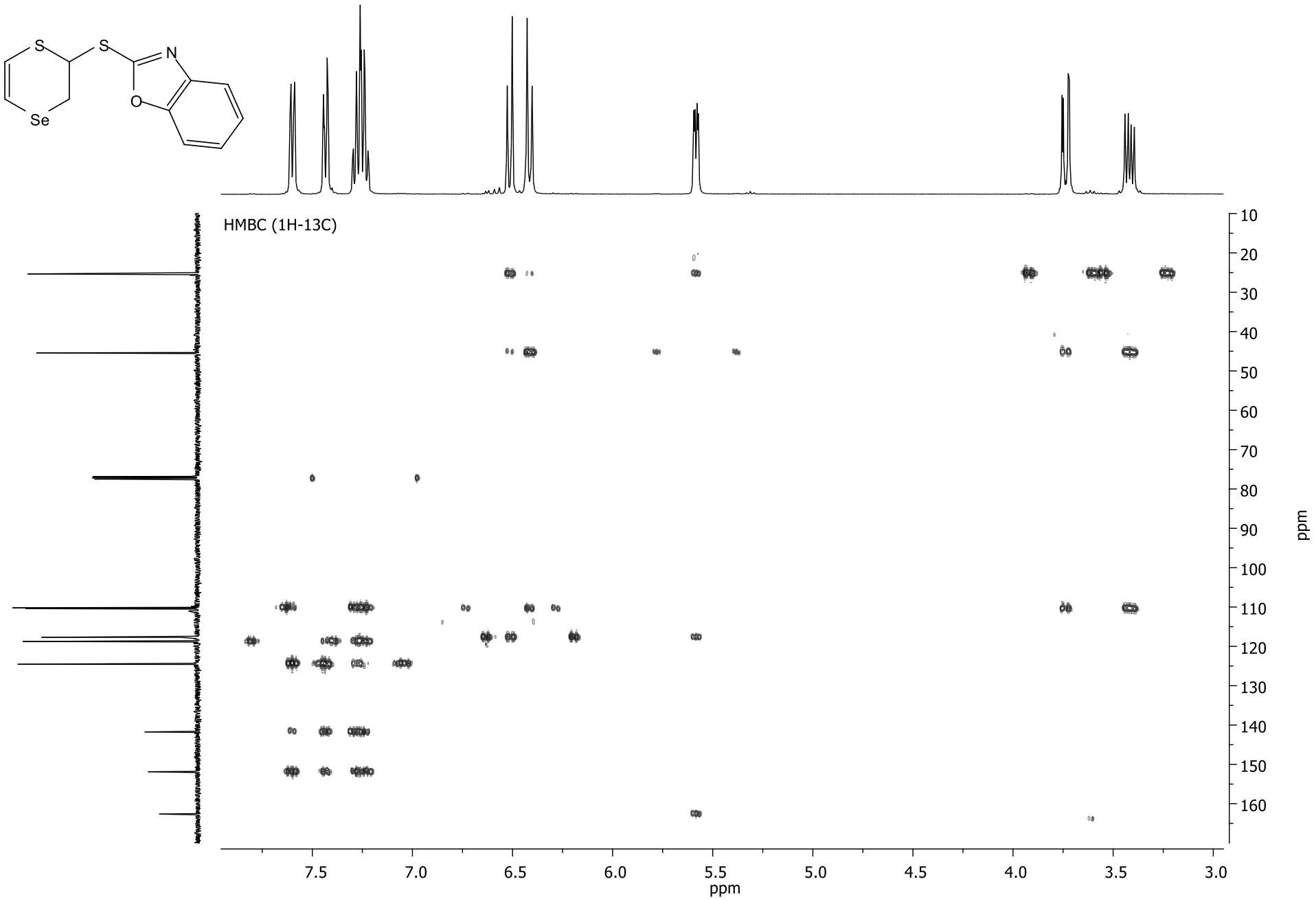
[1]H NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1,3-benzoxazole (3c)



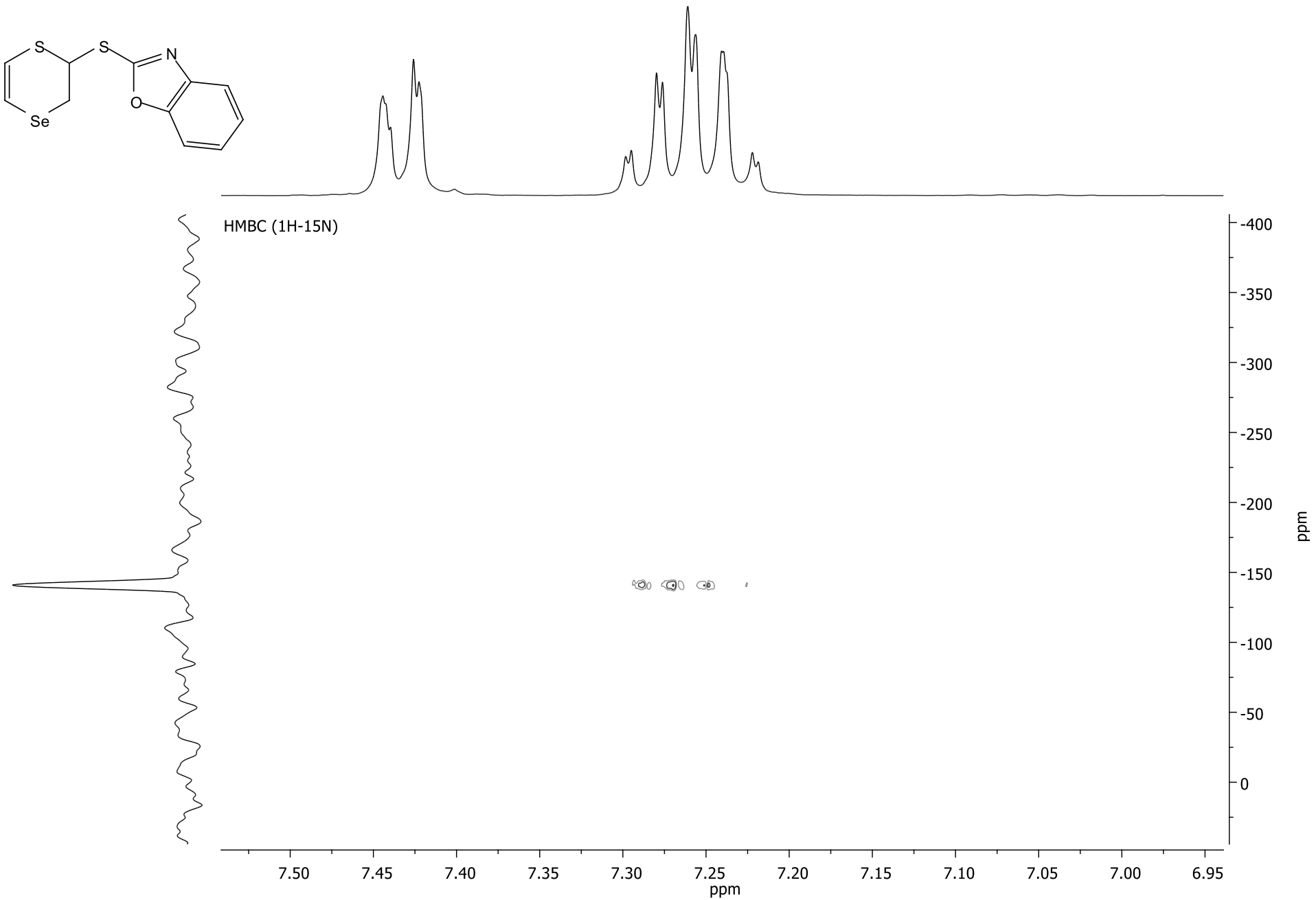
^{13}C NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1,3-benzoxazole (3c)



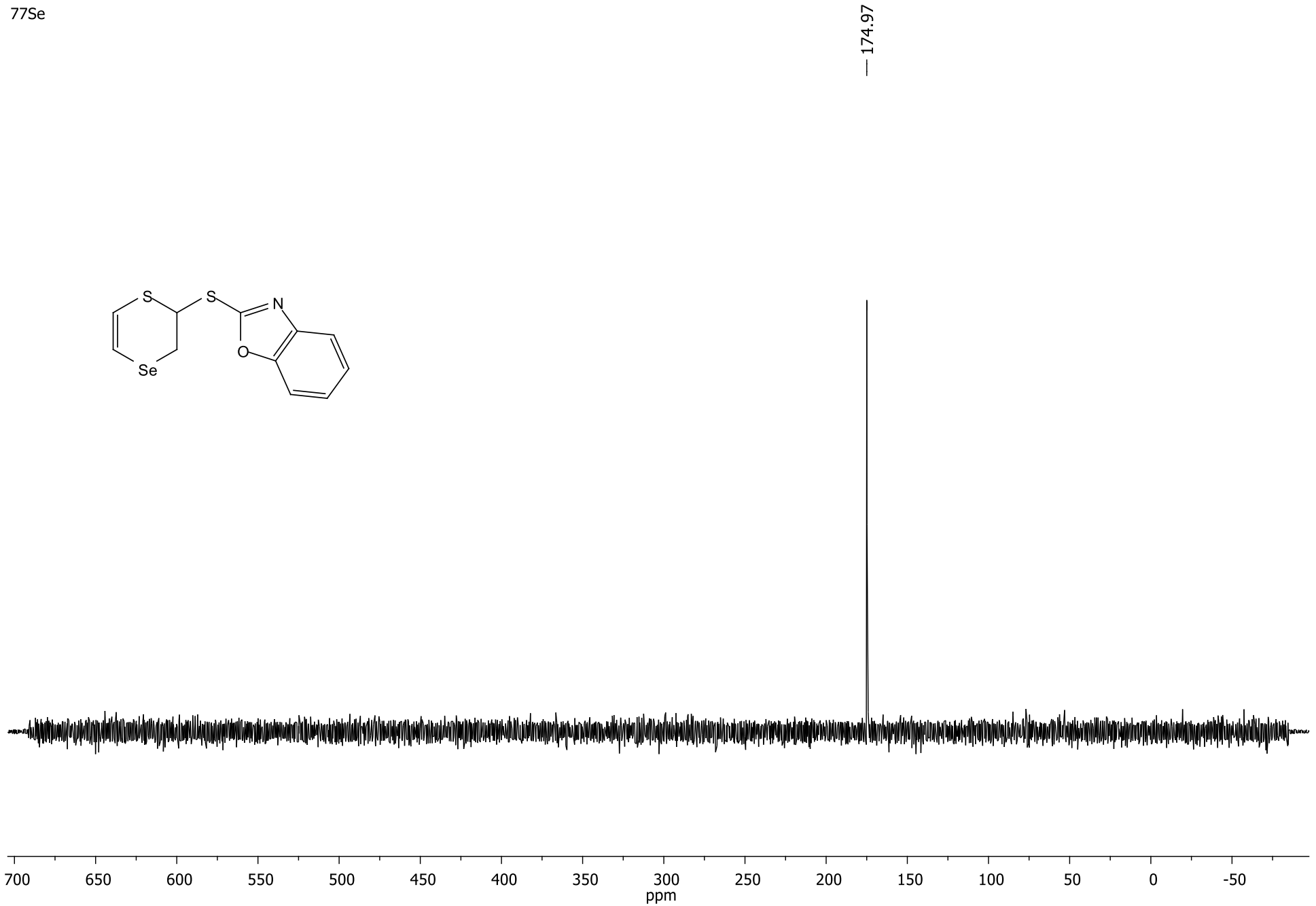
HSQC (^{1}H-^{13}C) NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1,3-benzoxazole (3c)



HMBC (^{1}H-^{13}C) NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1,3-benzoxazole (3c)



HMBC (^{1}H-^{15}N) NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1,3-benzoxazole (3c)



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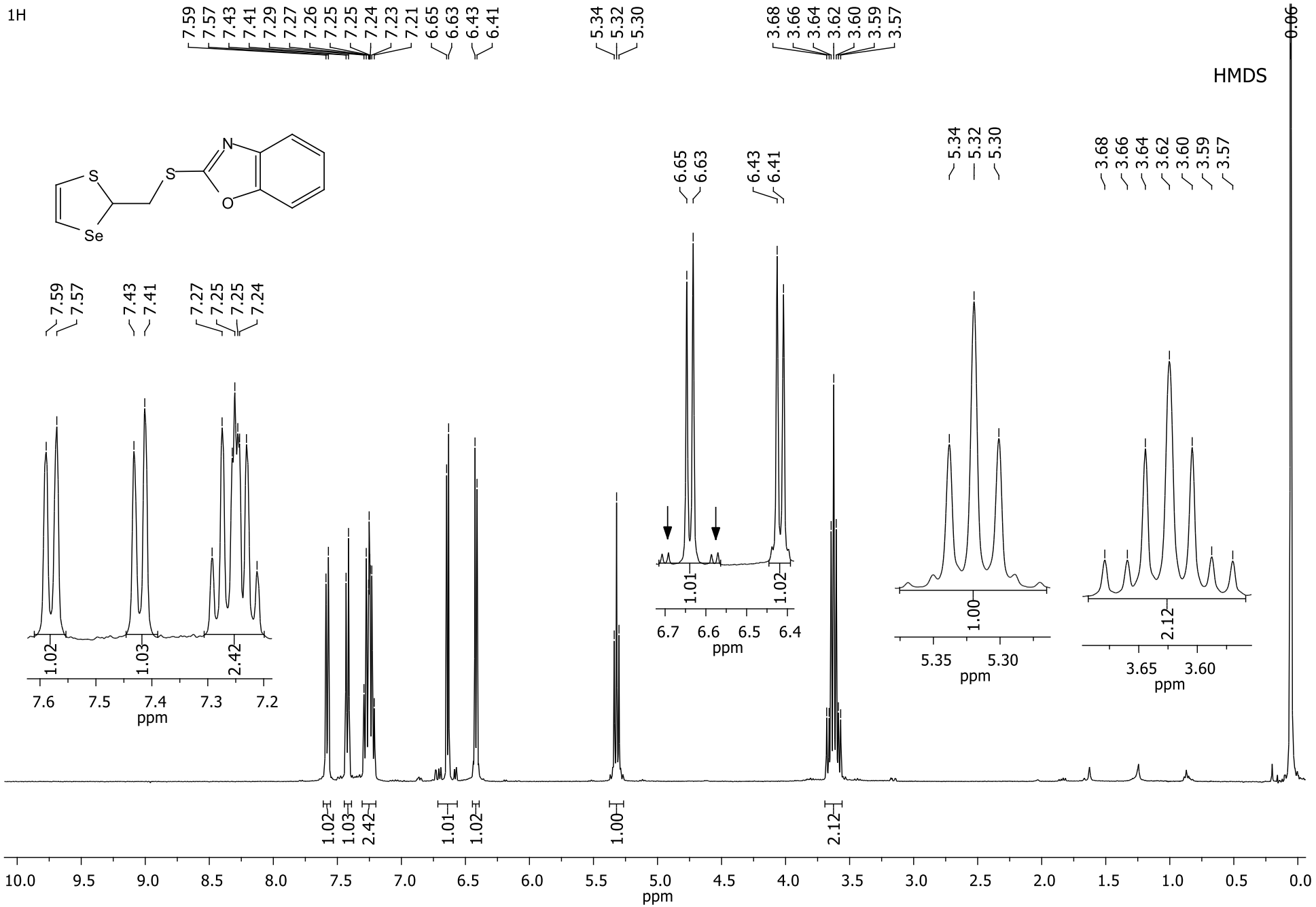
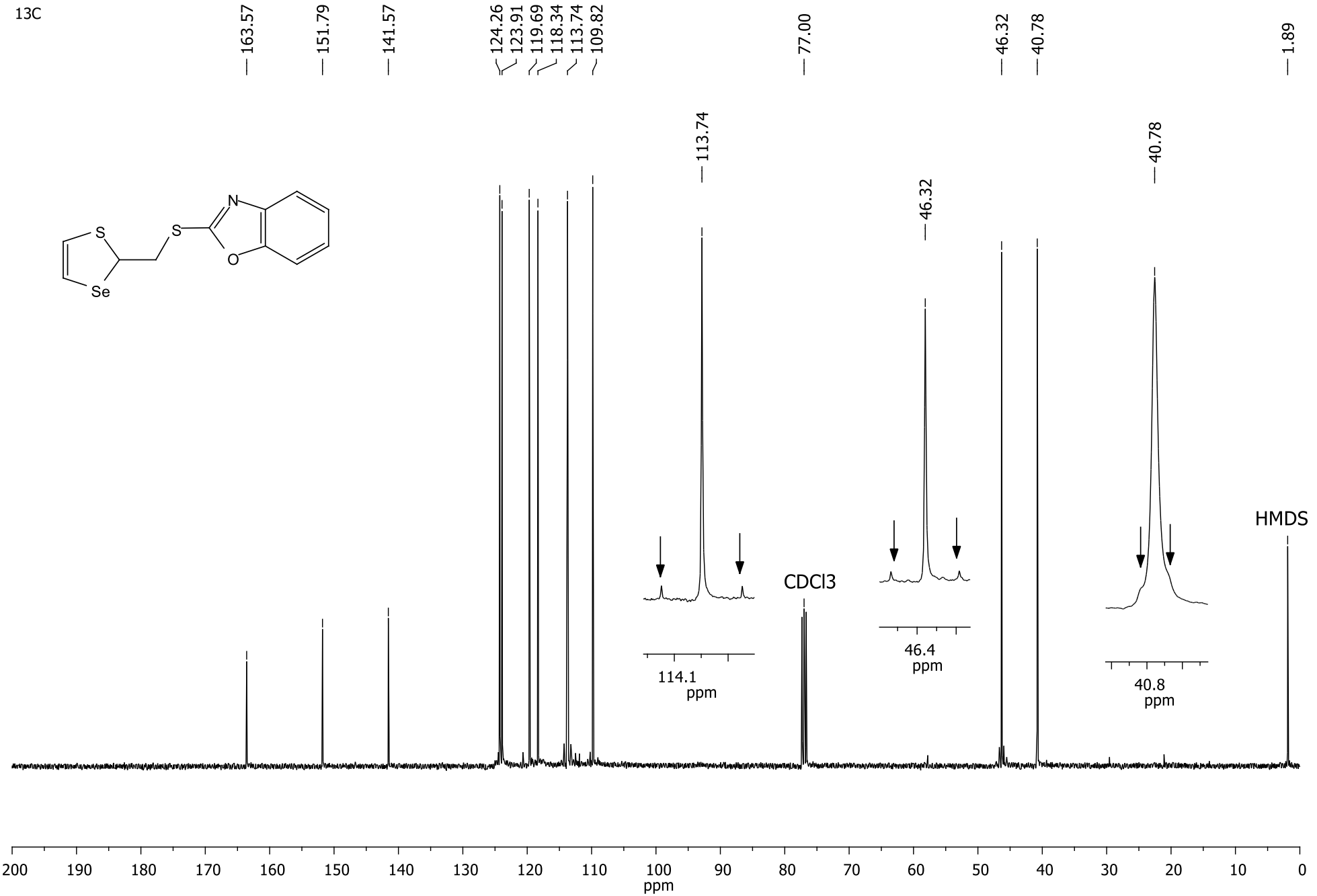


[1]H NMR spectrum of 2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1,3-benzoxazole (4c)



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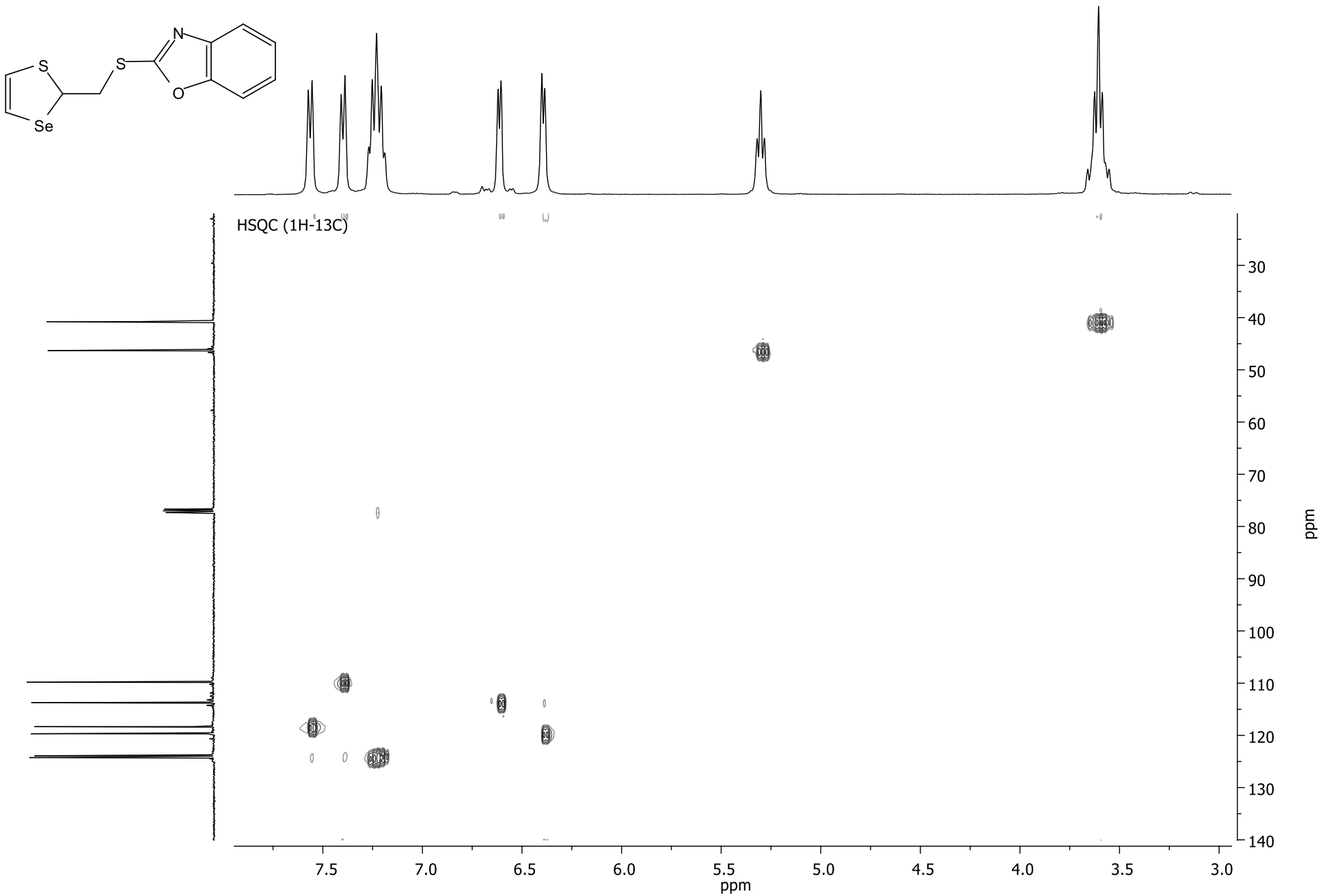
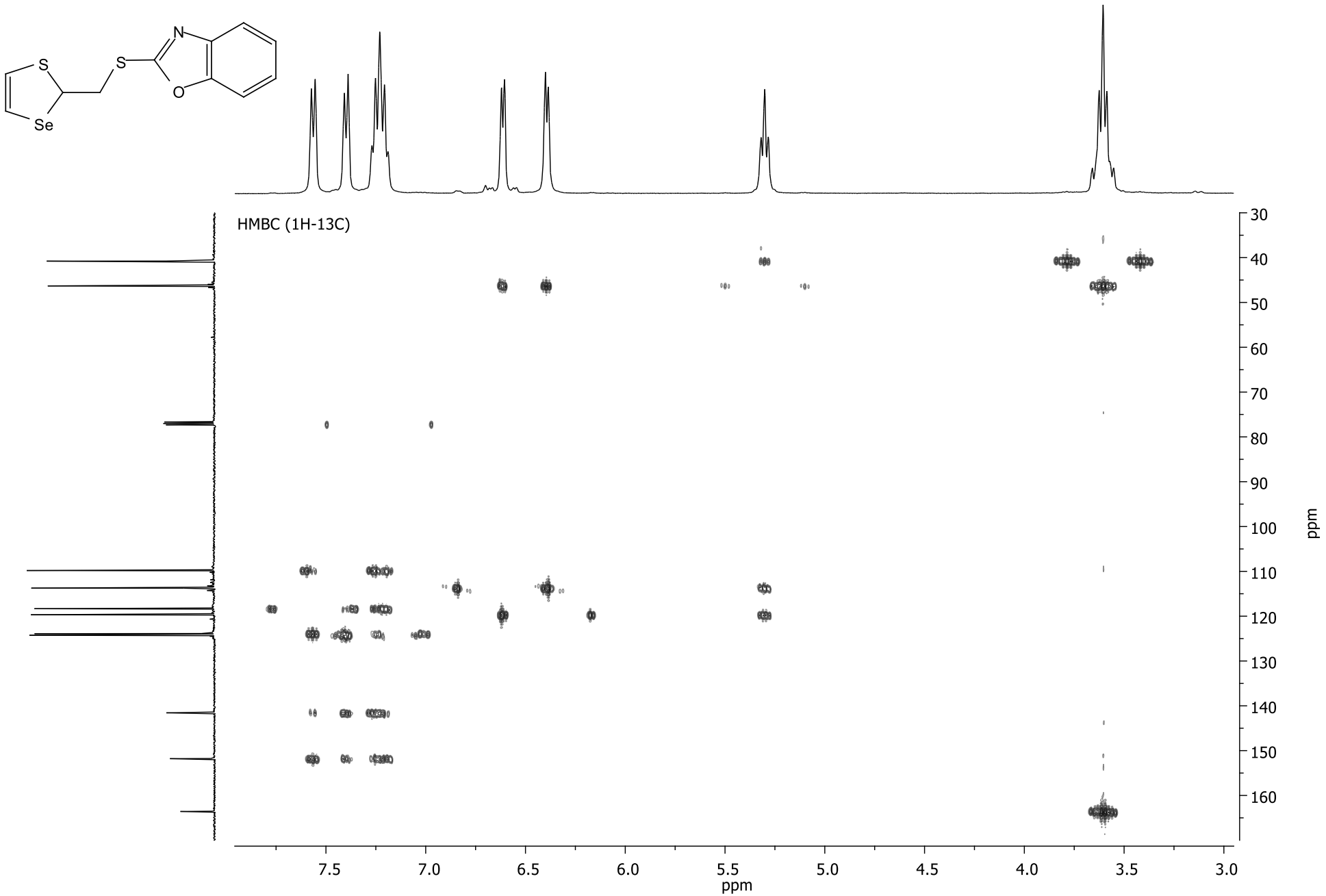


HSQC (^{1}H-^{13}C) NMR spectrum of 2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1,3-benzoxazole (4c)



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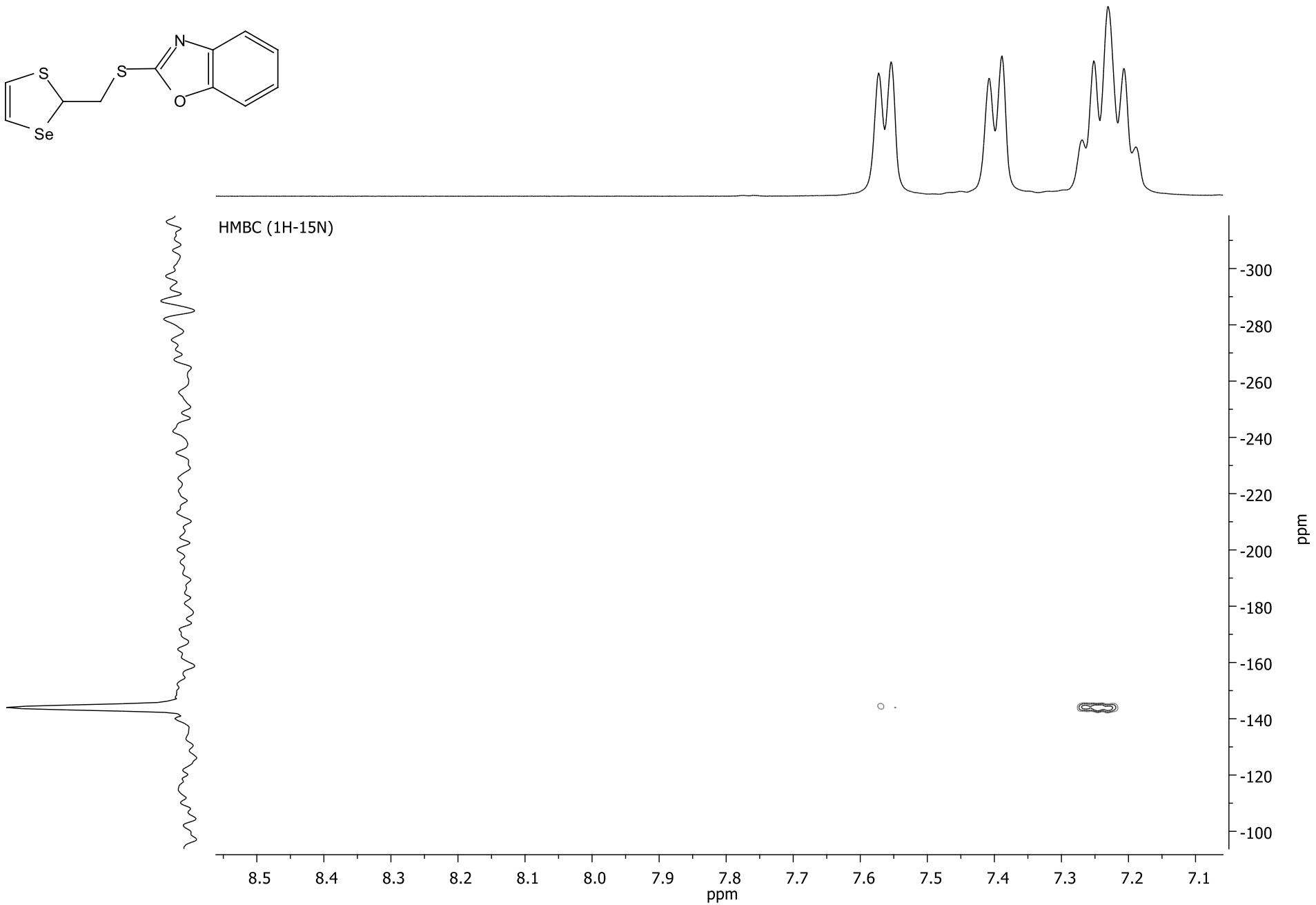
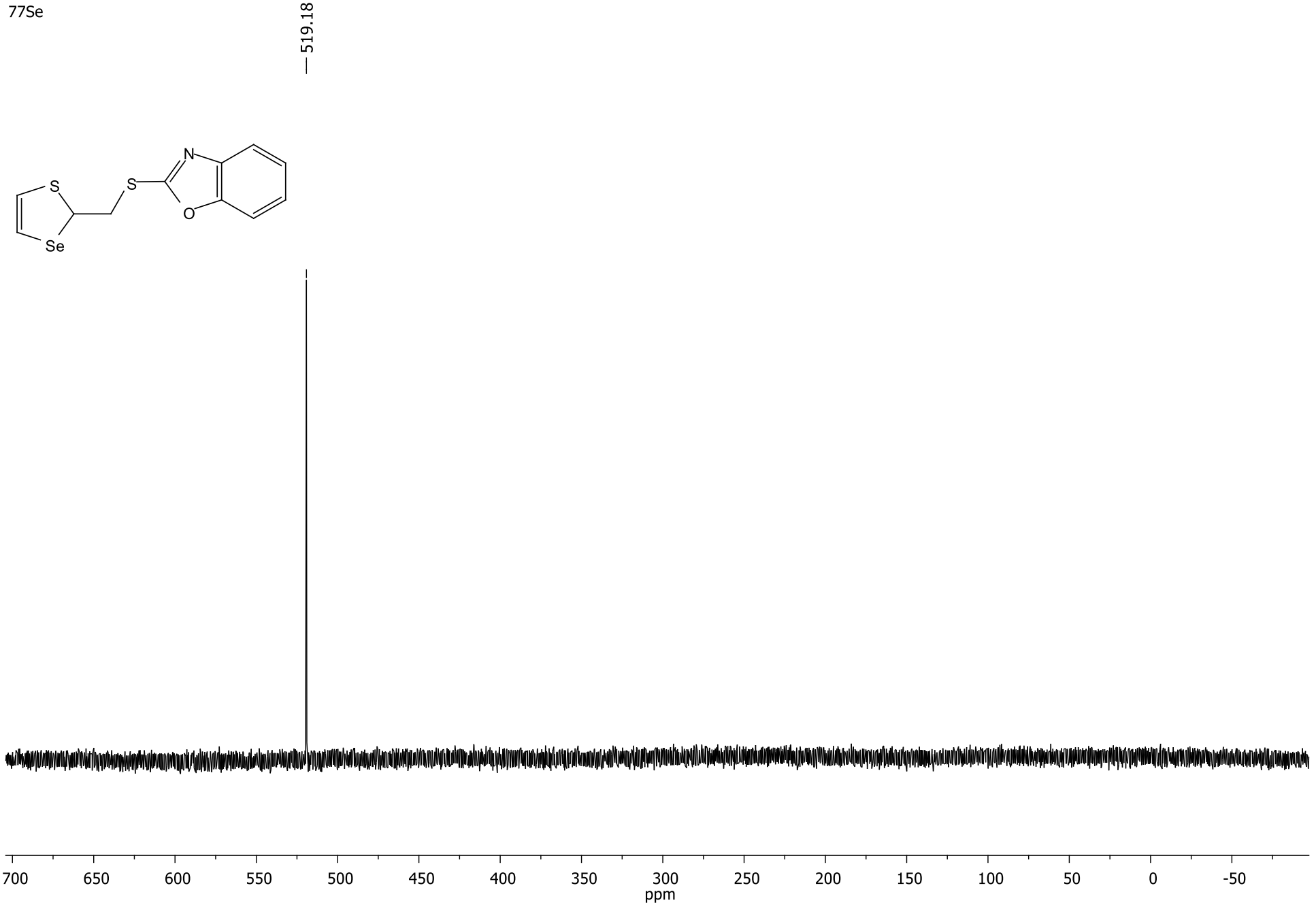


HMBC (^{1}H-^{15}N) NMR spectrum of 2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1,3-benzoxazole (4c)



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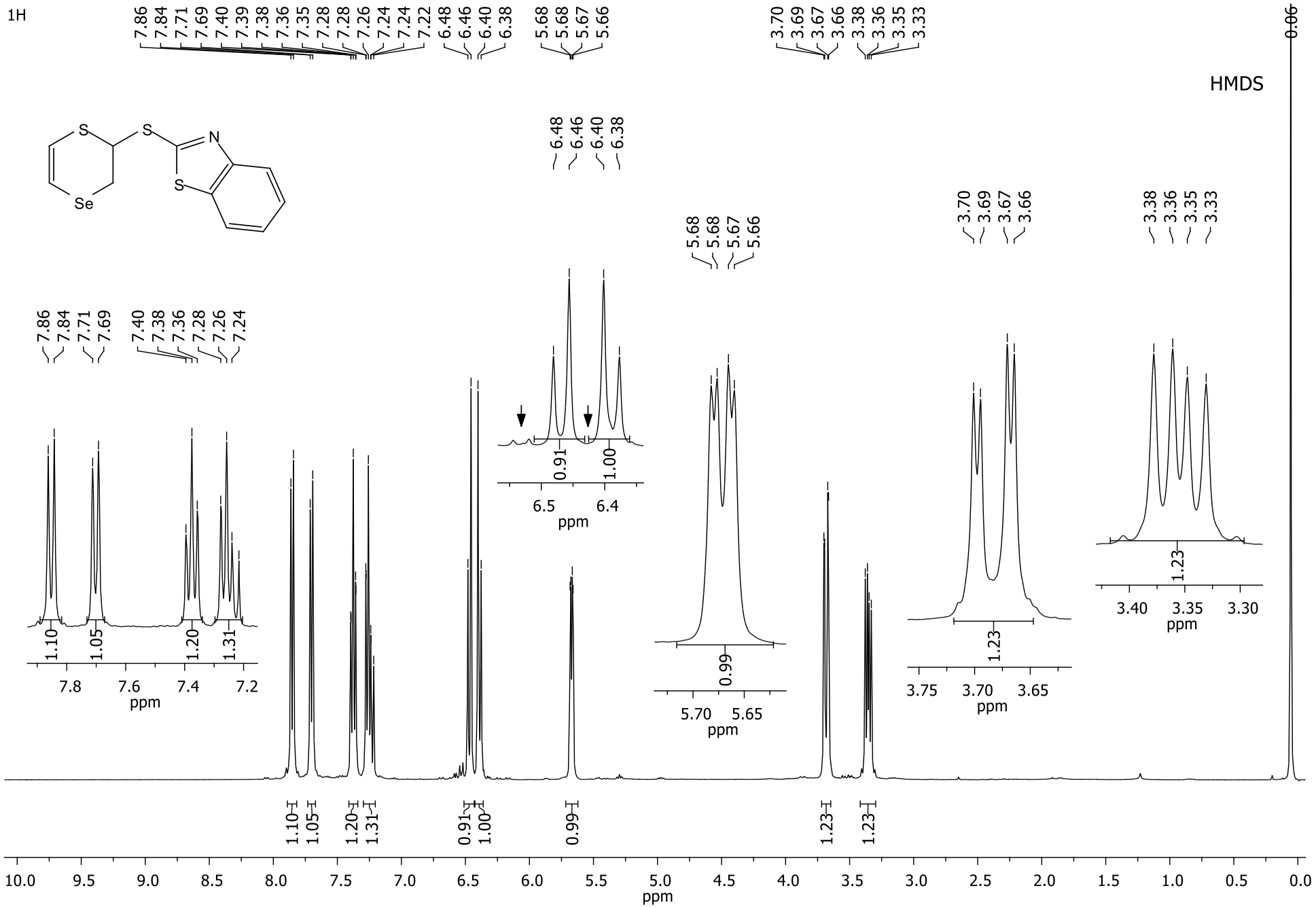
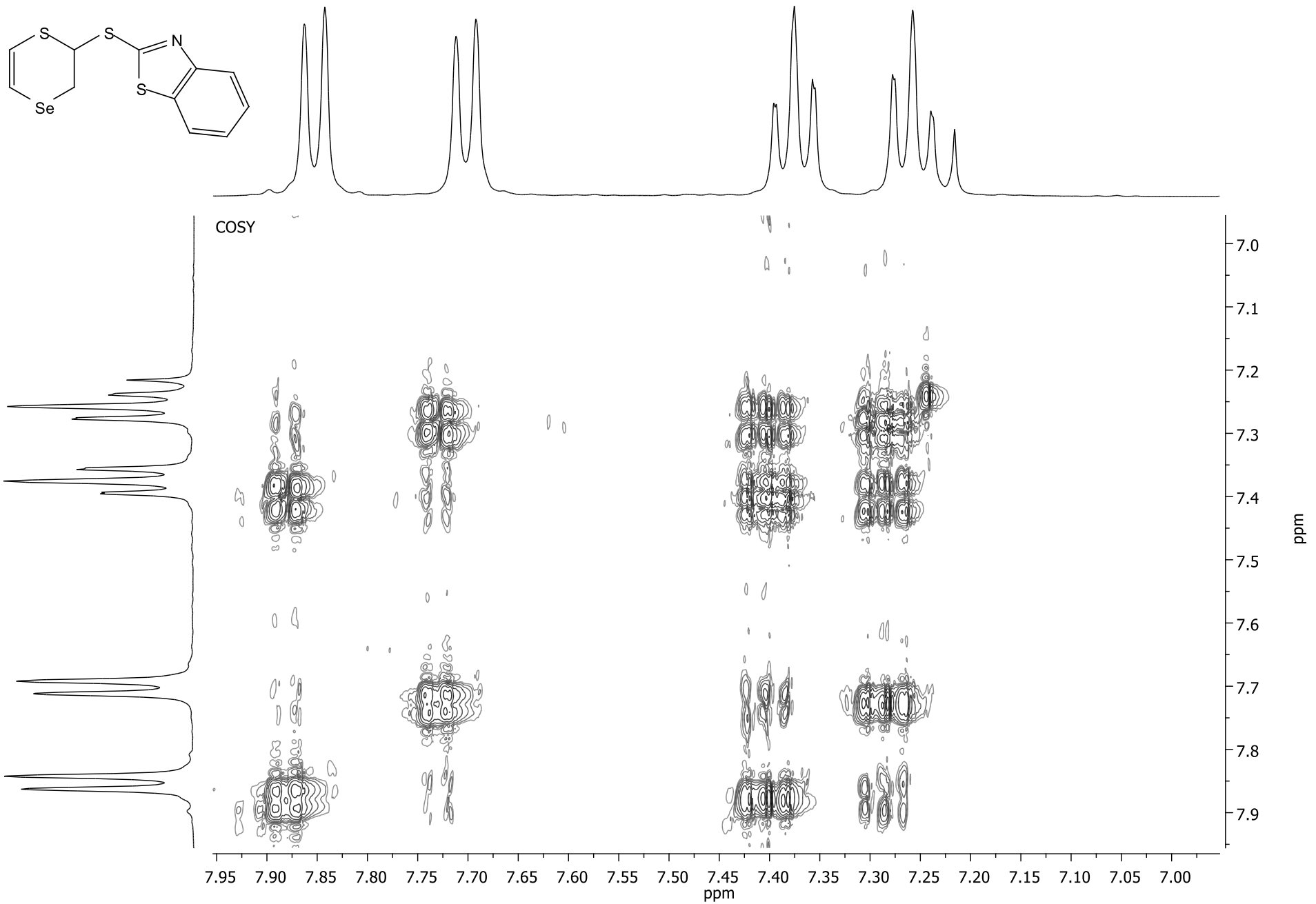
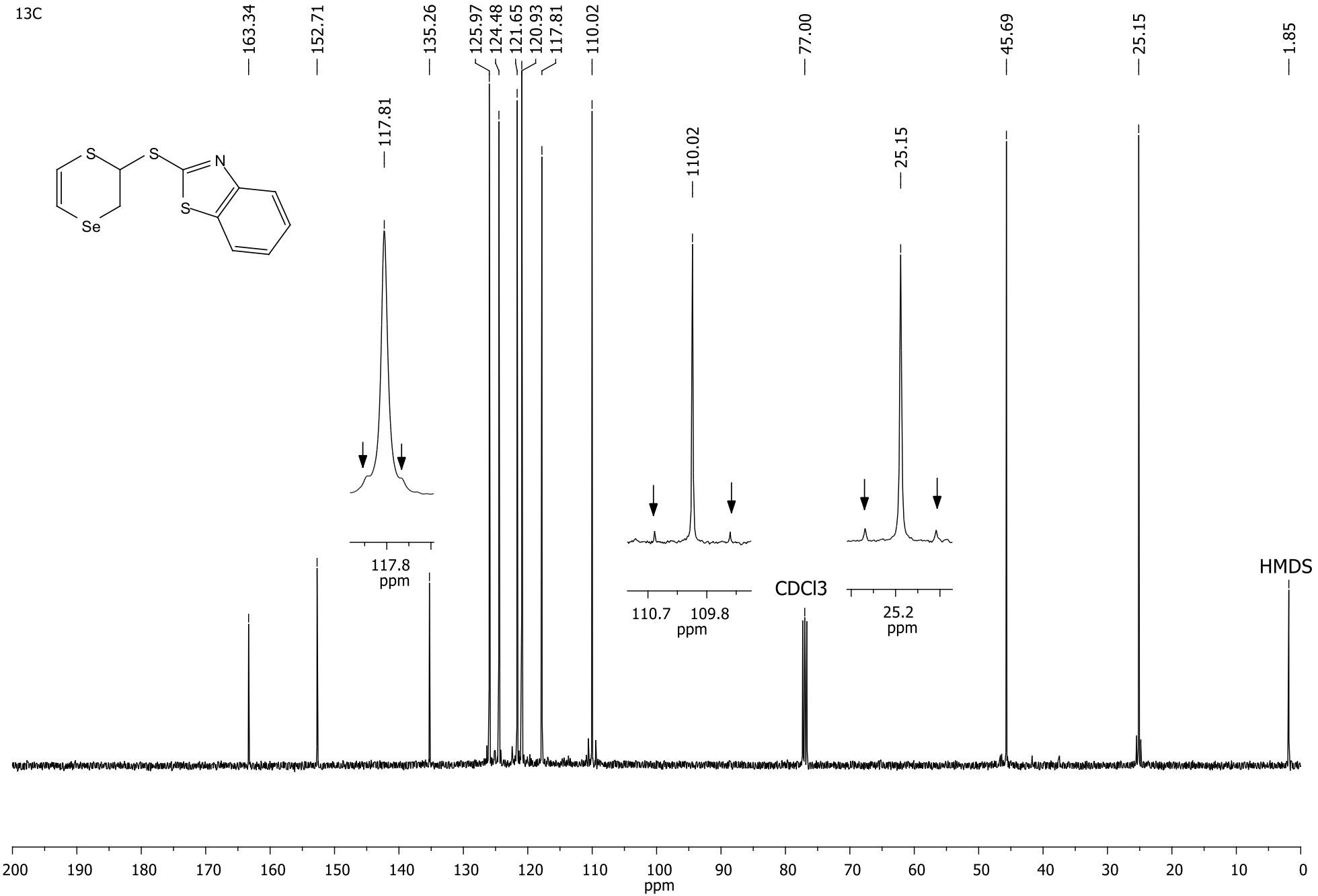


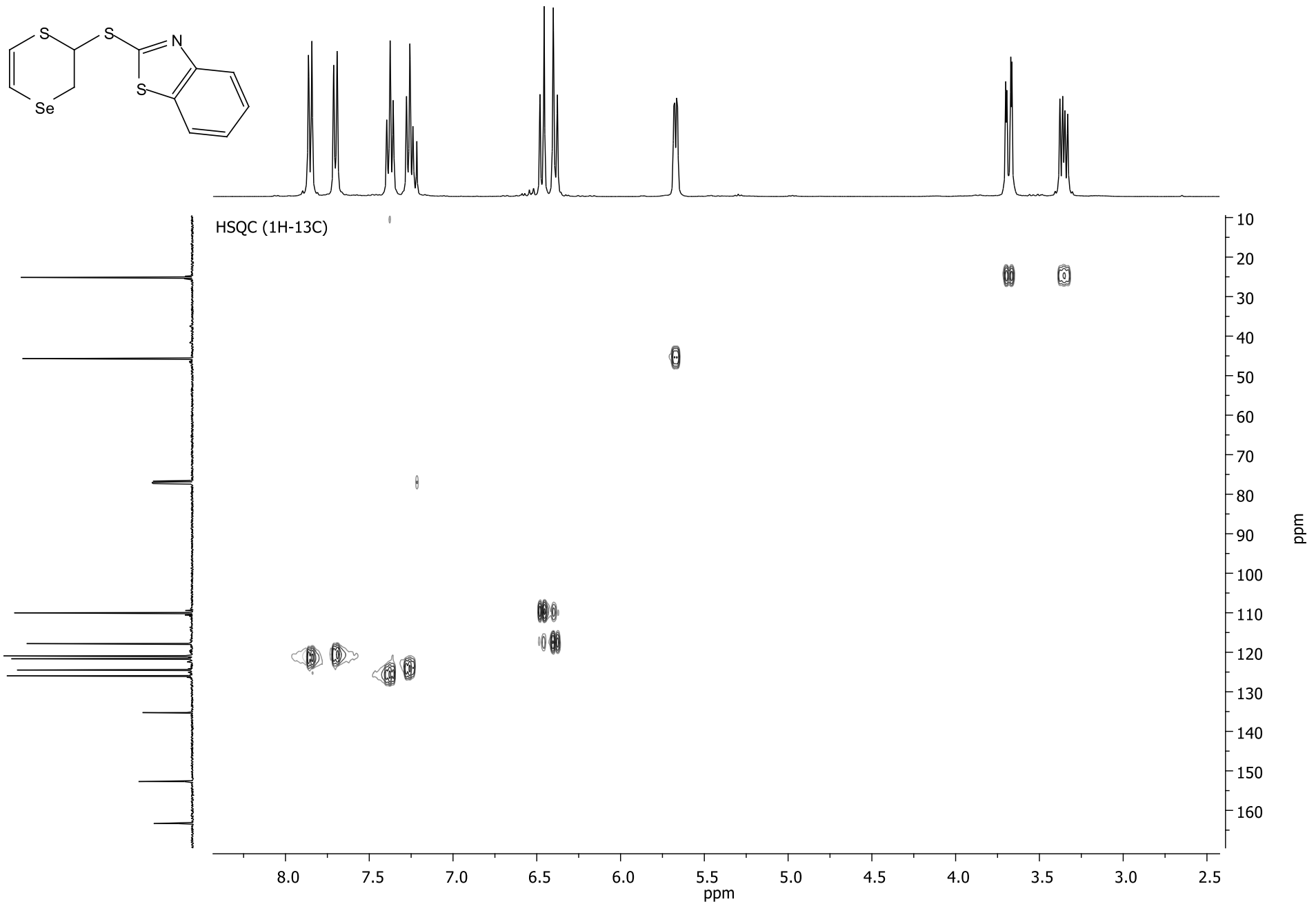
^{1}H NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1,3-benzothiazole (3d)



COSY NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1,3-benzothiazole (3d)



^{13}C NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1,3-benzothiazole (3d)



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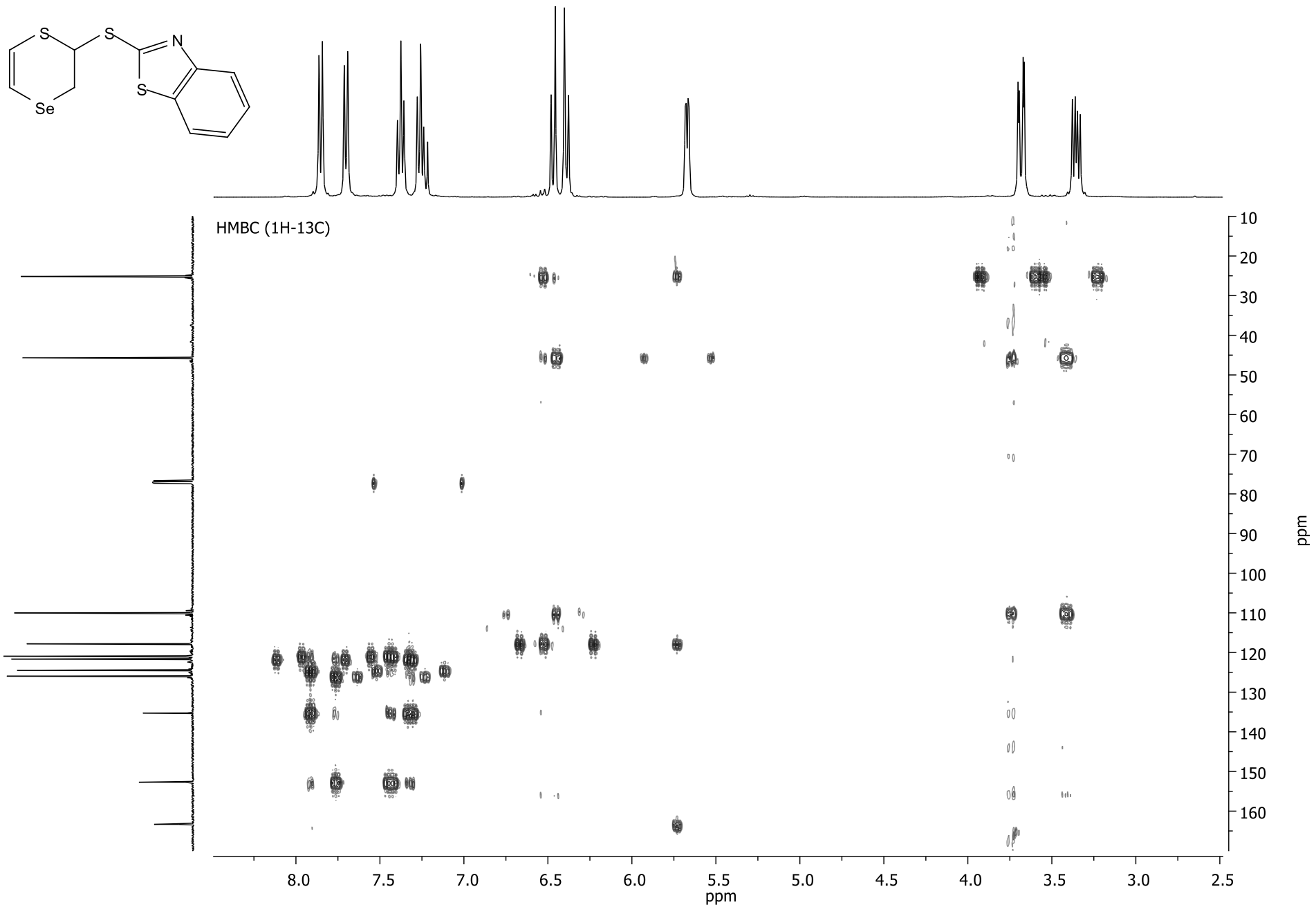

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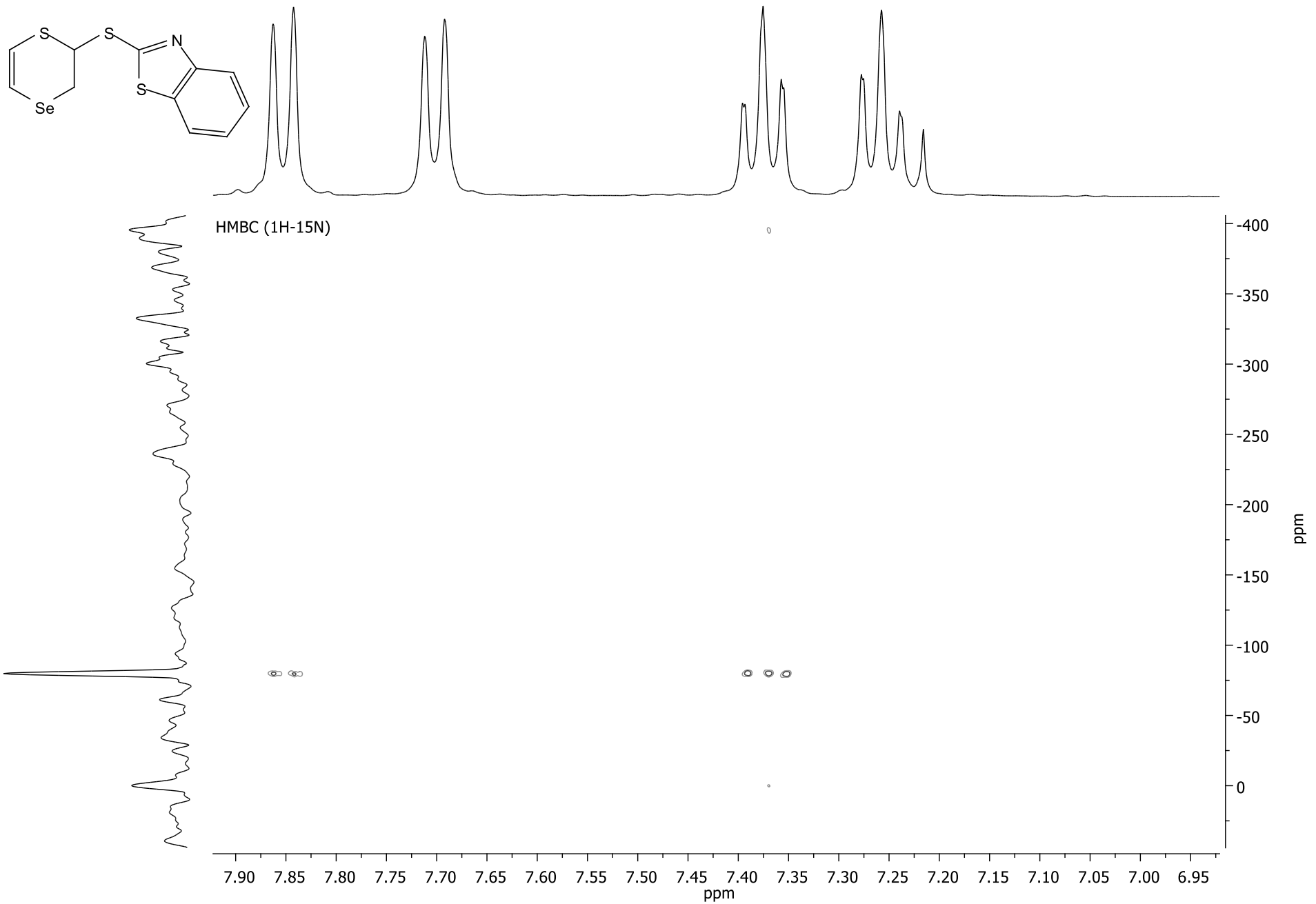

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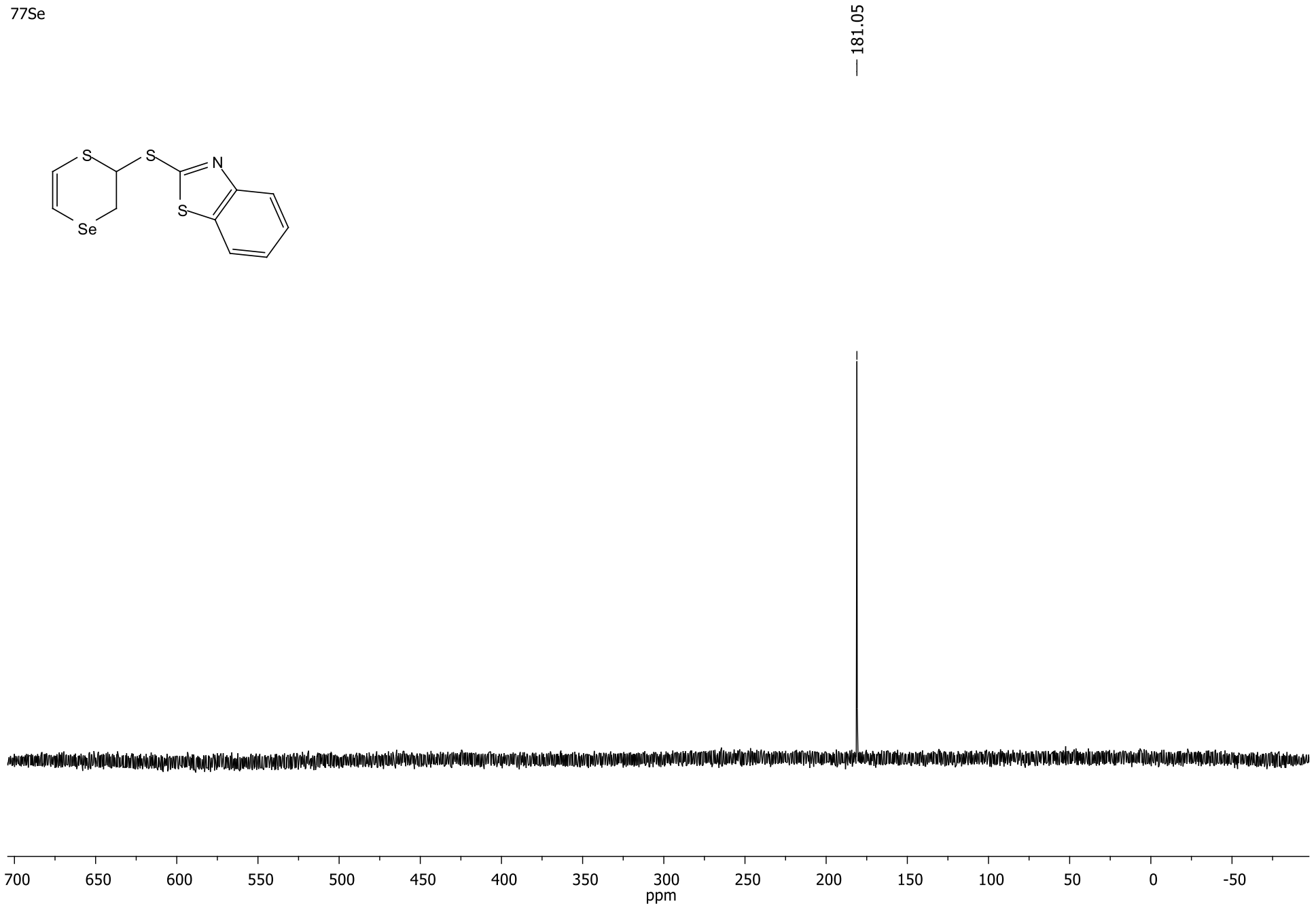
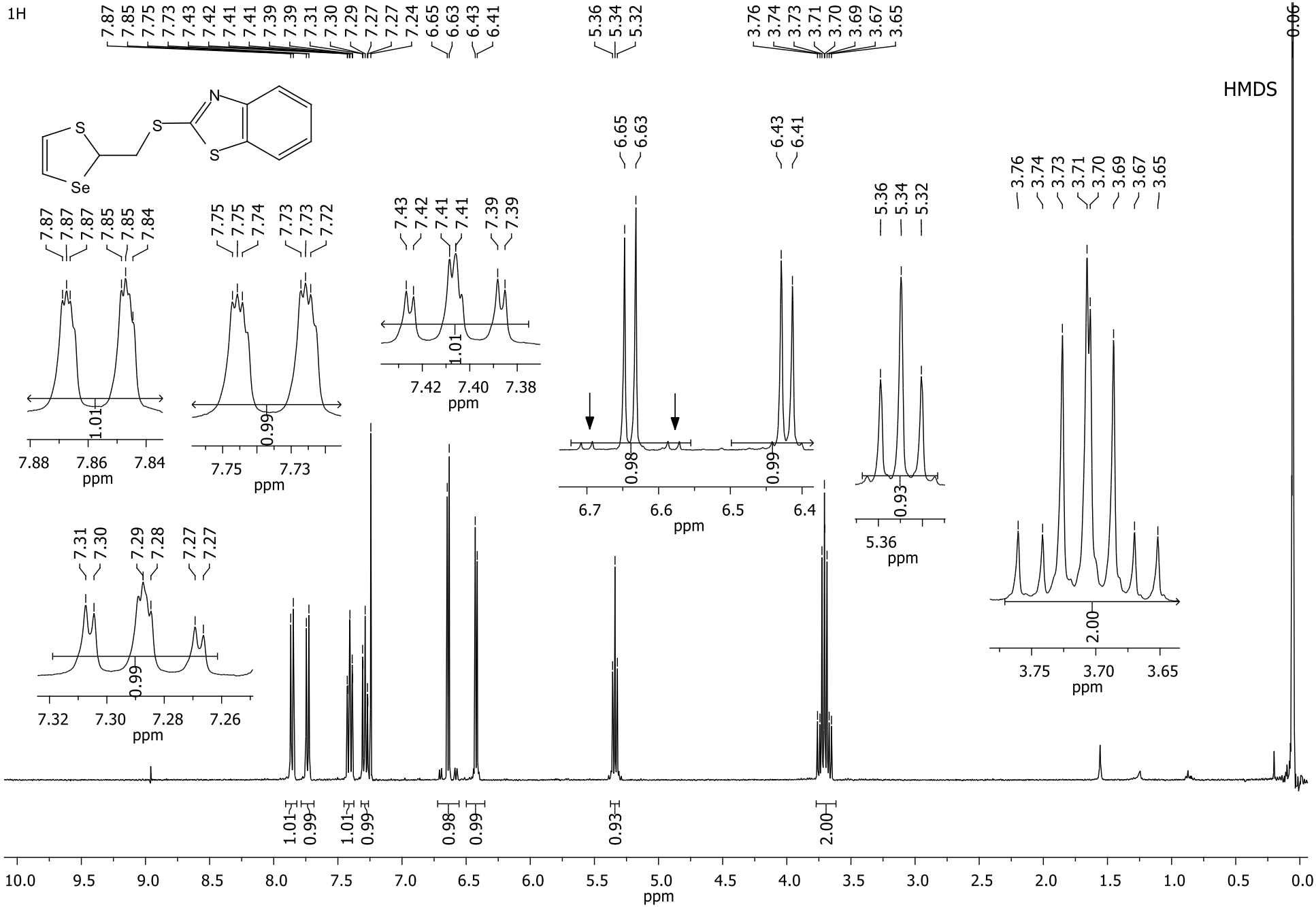
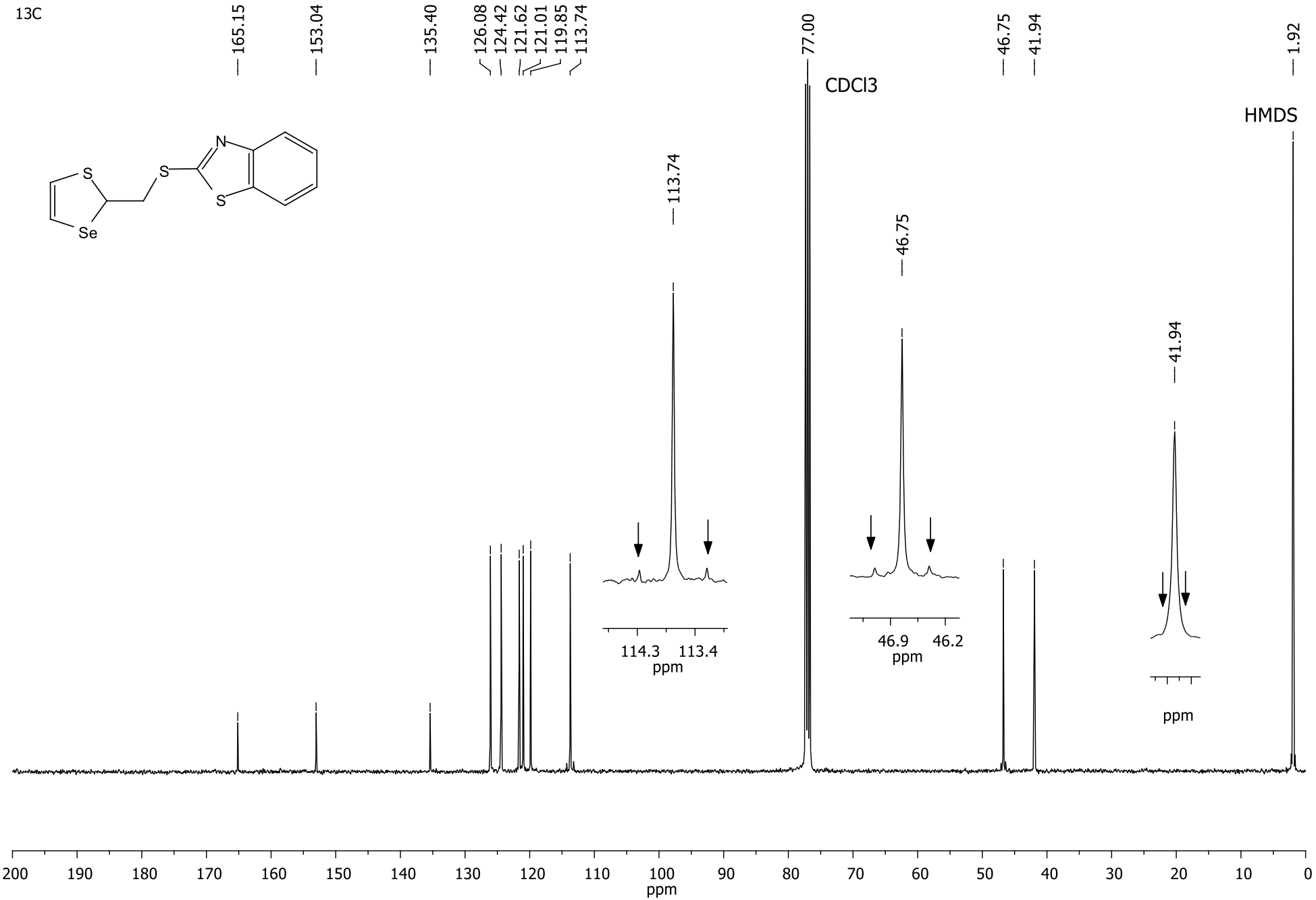


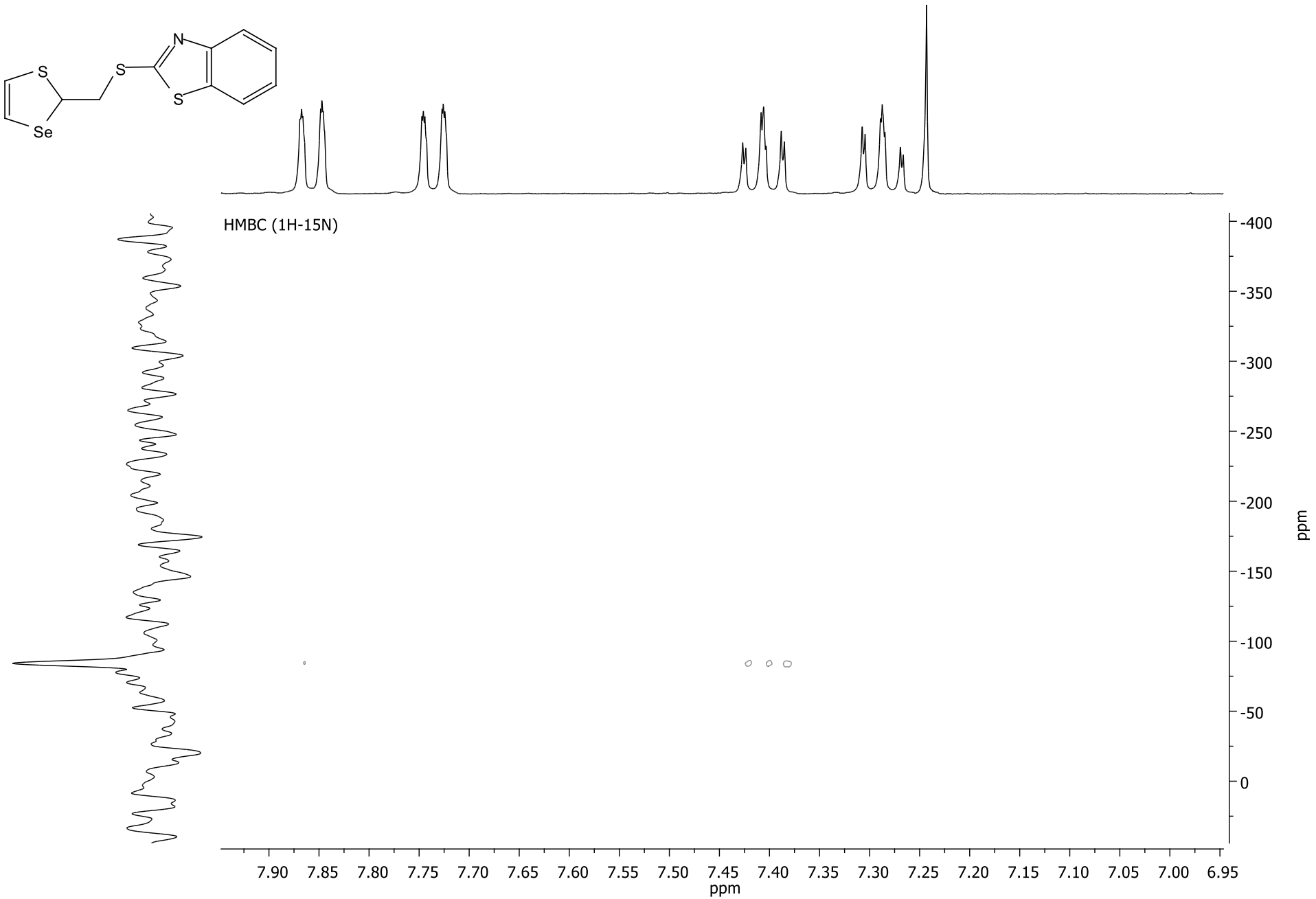
^{77}Se NMR spectrum of 2-(2,3-dihydro-1,4-thiaselenin-2-ylsulfanyl)-1,3-benzothiazole (3d)



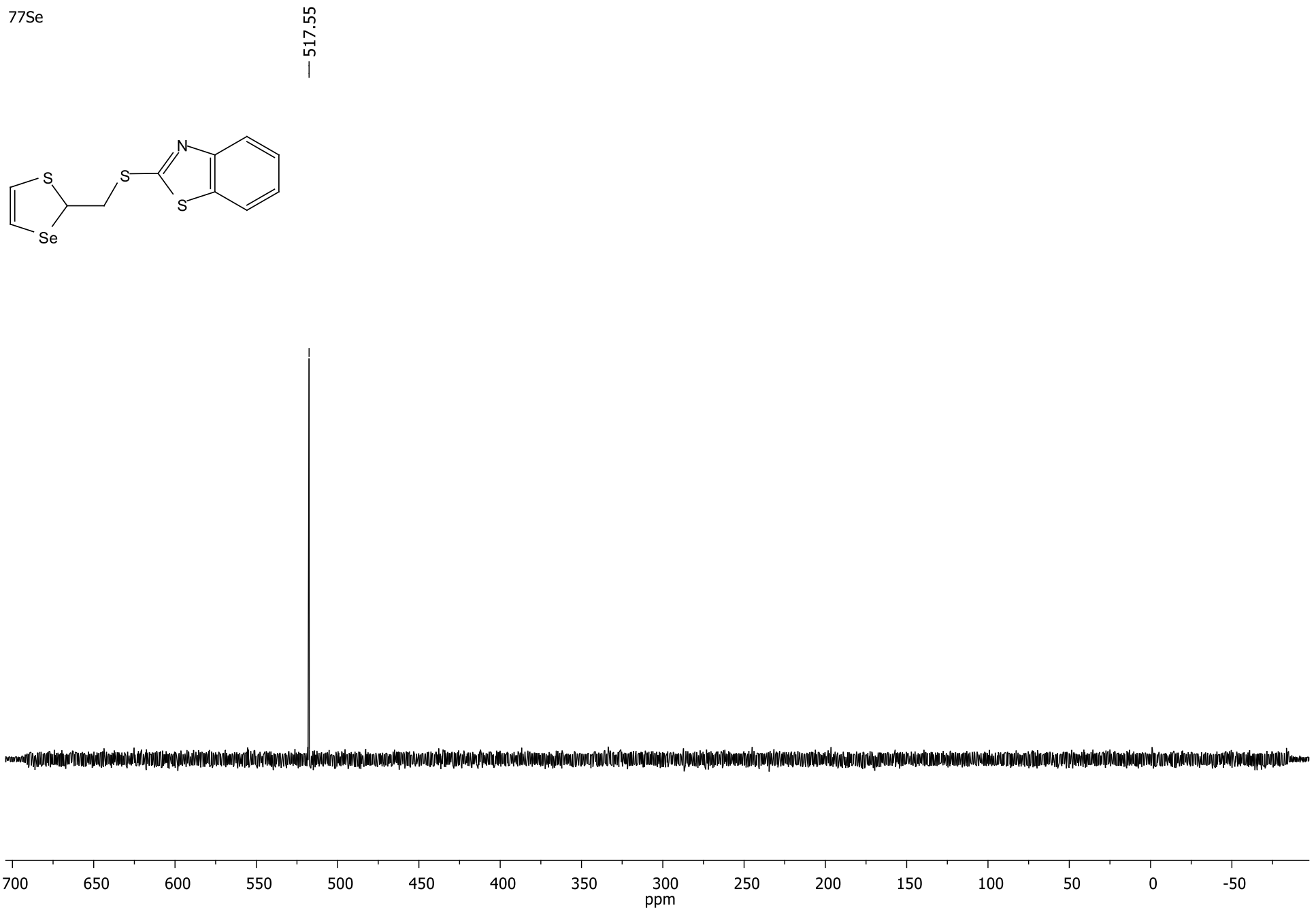
^{1}H NMR spectrum of 2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1,3-benzothiazole (4d)



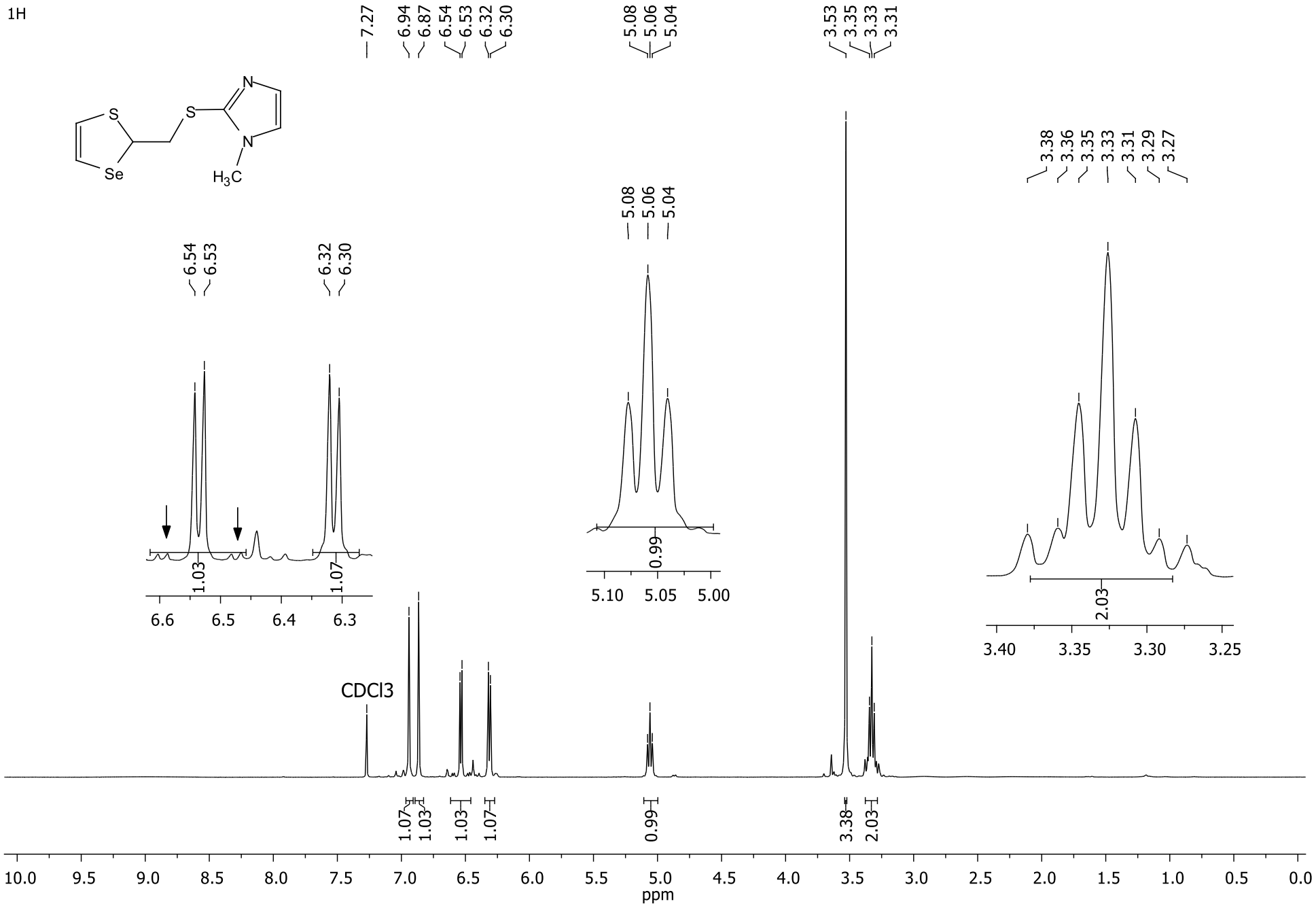
^{13}C NMR spectrum of 2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1,3-benzothiazole (4d)



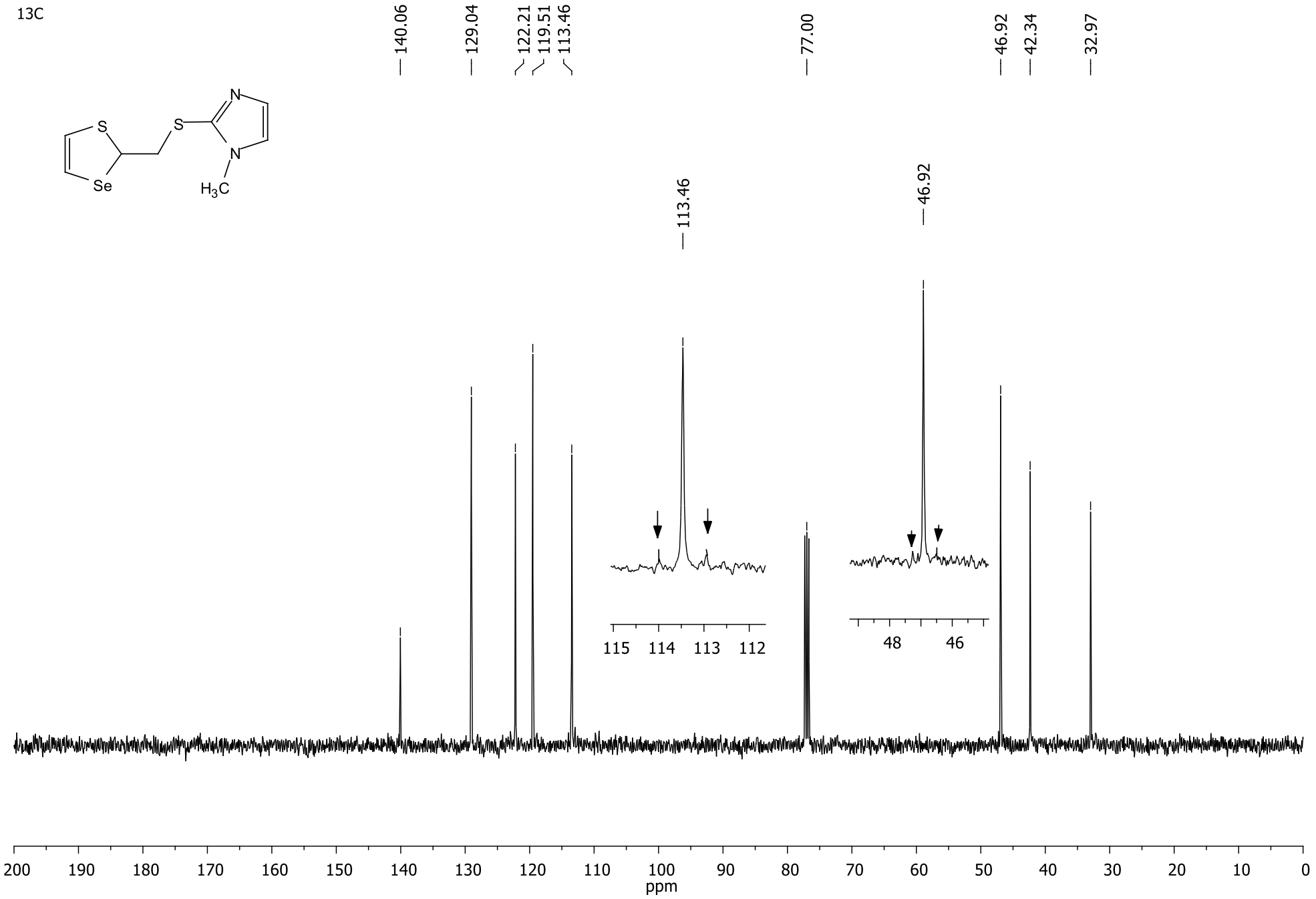
HMBC (^{1}H-^{15}N) NMR spectrum of 2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1,3-benzothiazole (4d)



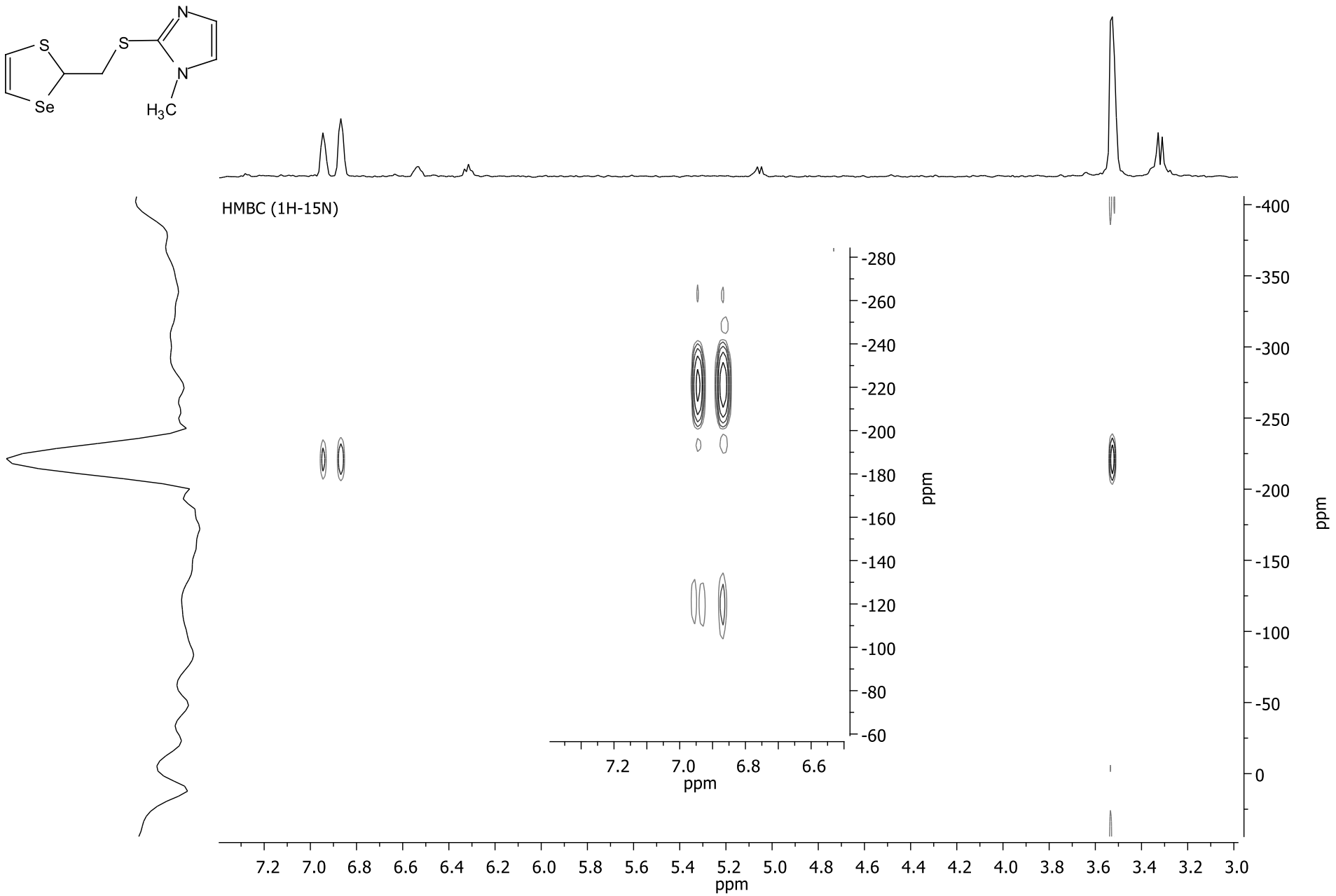
^{77}Se NMR spectrum of 2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1,3-benzothiazole (4d)



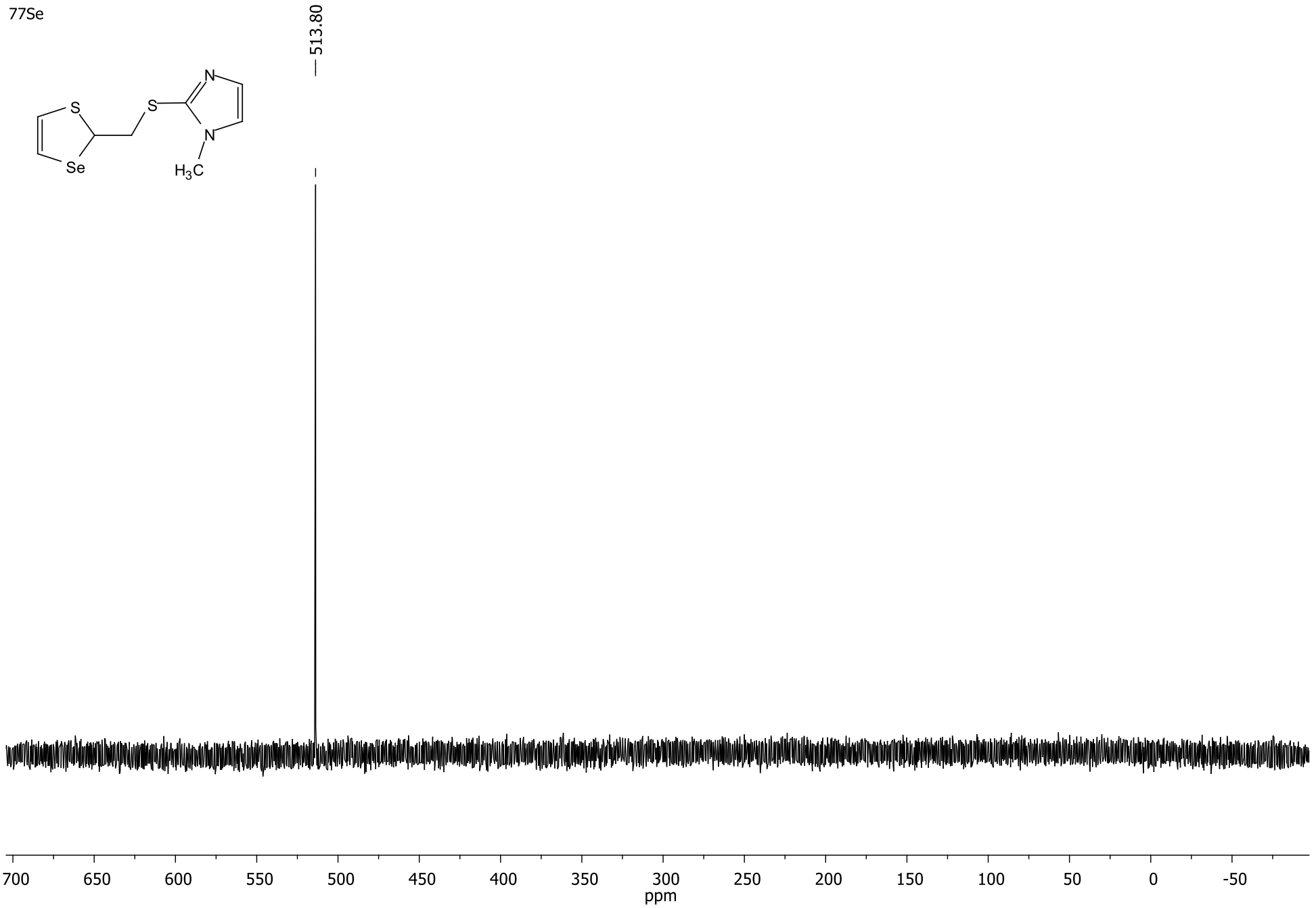
^{1}H NMR spectrum of 1-methyl-2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1*H*-imidazole (4e)



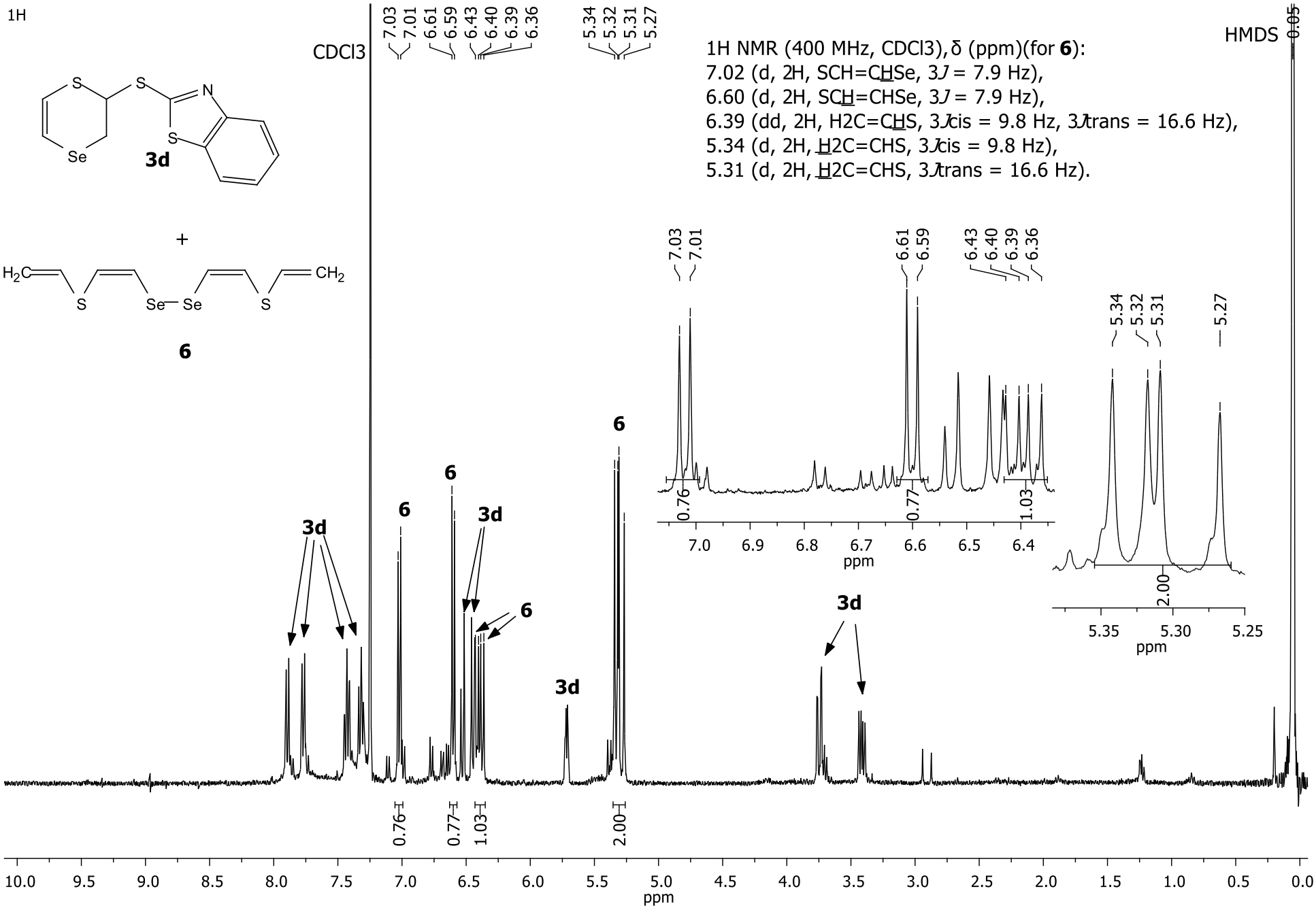
^{13}C NMR spectrum of 1-methyl-2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1*H*-imidazole (4e)



HMBC (^{1}H-^{15}N) NMR spectrum of 1-methyl-2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1*H*-imidazole (4e)



^{77}Se NMR spectrum of 1-methyl-2-[(1,3-thiaselenol-2-ylmethyl)sulfanyl]-1*H*-imidazole (4e)



[1]H NMR spectrum of 1,2-bis[(*Z*)-2-(vinylsulfanyl)ethenyl]diselane (6) mixed with 3d