Electronic Supplementary Information

A novel methodology for the synthesis of condensed selenium heterocycles based on the annulation and annulation − methoxylation reactions of selenium dihalides

Maxim V. Musalov, Vladimir A. Yakimov, Vladimir A. Potapov,* Svetlana V. Amosova, Tatyana N. Borodina and Sergey V. Zinchenko

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Division of The Russian Academy of Sciences, 1 Favorsky Str., Irkutsk 664033, Russian Federation, E-mail: v.a.potapov@mail.ru

Table of Contents

Experimental

General

X-ray diffraction experiments were carried out with a Bruker D8 Venture Photon 100 CMOS diffractometer with Mo-K_α radiation (λ = 0.71073 Å). ^{1}H (400.1 MHz), ^{13}C (100.6 MHz) and ^{77}Se (76.3 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer in 5-10% solution in $CDCl_3$ referenced to TMS (^{1}H and ^{13}C NMR, internal) and Me_2Se (^{77}Se NMR, external) or to the residual chloroform peaks 7.26 ppm (^{1}H) and 77.16 (^{13}C). All coupling constants (*J* values) were reported in Hertz (Hz). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet. Elemental analysis was performed on a Thermo Scientific Flash 2000 Elemental Analyzer.

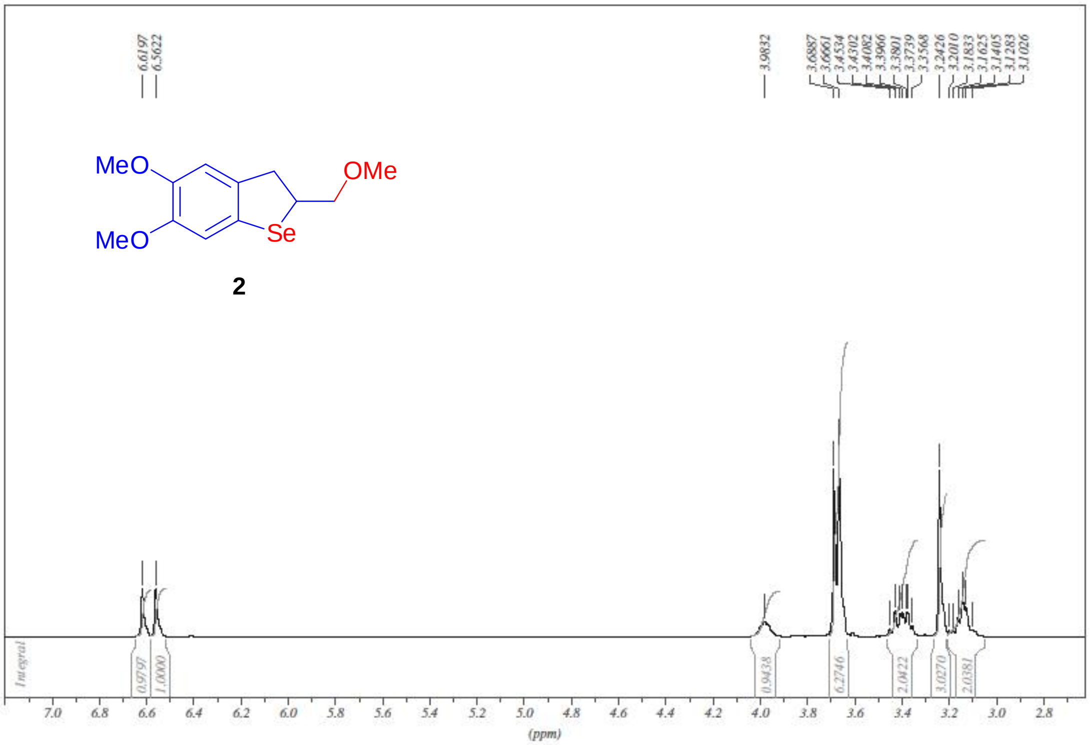
Products of the methyleugenol halogenation (1a,b)

2,3-Dichloro- and 2,3-dibromopropylbenzenes **1a**,**b** were isolated by column chromatography (silica gel, eluent: hexane → chloroform/hexane 1 : 10) from the reaction of selenium dihalides with methyleugenol in chloroform under the conditions described for the reaction of the selenium dichloride with allyl phenyl ether [1].

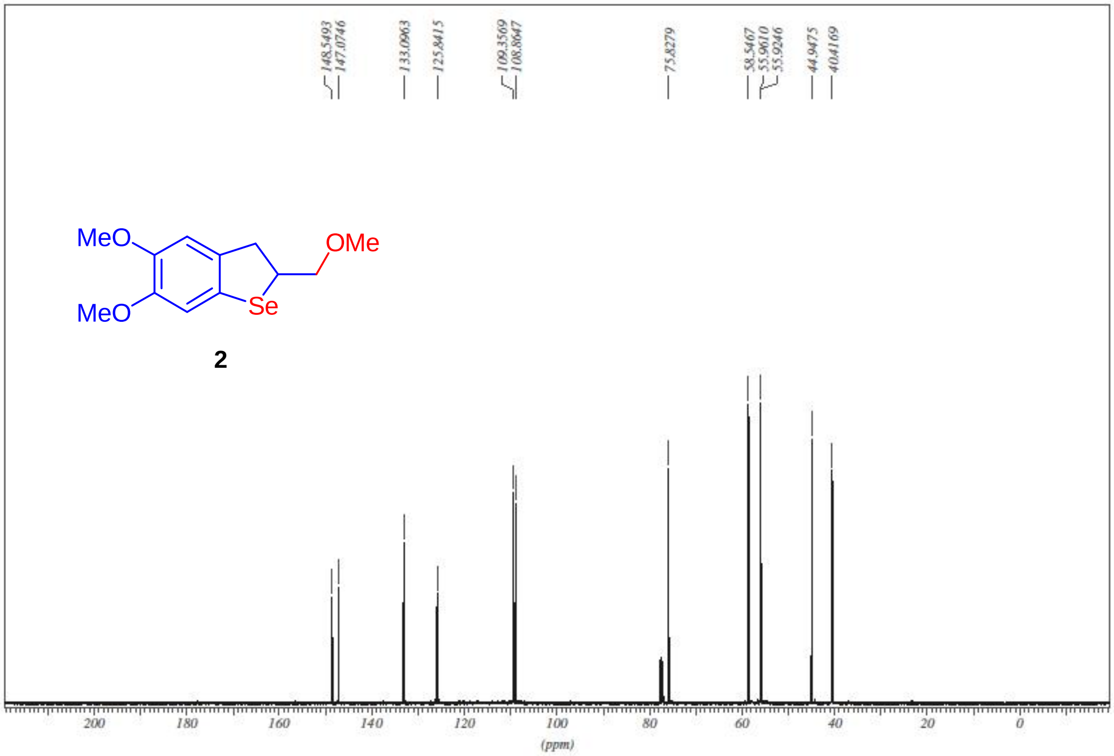
2,3-Dichloropropylbenzene **1a**, 60% yield, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78-2.85 (m, 1H, $ArCH_2$), 2.90-2.98 (m, 1H, $ArCH_2$), 3.36-3.45 (m, 1H, $ClCH_2$), 3.69-3.77 (m, 1H, $ClCH_2$), 3.77 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 4.07-4.14 (m, 1H, ClCH), 6.63-6.78 (m, 3H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.88 ($ArCH_2$), 46.38 ($ClCH_2$), 55.97 (CH_3O), 56.26 (CH_3O), 58.79 (ClCH), 111.32 (HCAr), 112.78 (HCAr), 121.58 (HCAr), 130.68 (H_2CCAr), 148.06 (MeOCAr), 148.94 (MeOCAr). Found: C 53.03; H 5.66; Cl 28.46. Calc. for $C_{11}H_{14}Cl_2O_2$: C 52.74; H 5.47; Cl 28.16.

2,3-Dibromopropylbenzene **1b**, 51% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95-3.04 (m, 1H, $ArCH_2$), 3.18-3.27 (m, 1H, $ArCH_2$), 3.45-3.54 (m, 1H, $BrCH_2$), 3.69-3.76 (m, 1H, $BrCH_2$), 3.75 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 4.20-4.28 (m, 1H, BrCH), 6.60-6.78 (m, 3H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.87 ($BrCH_2$), 41.21 ($Ar\underline{C}H_2$), 52.44 (BrCH), 55.61 (CH_3O), 55.71 (CH_3O), 111.02 (HC_{Ar}), 112.66 (HC_{Ar}), 121.47 (HC_{Ar}), 131.77 ($H_2C\underline{C}_{Ar}$), 147.98 ($MeO\underline{C}_{Ar}$), 148.68 ($MeO\underline{C}_{Ar}$). Found: C 38.81; H 3.99; Br 46.98. Calc. for $C_{11}H_{14}Cl_2O_2$: C 39.08; H 4.17; Br 47.28.

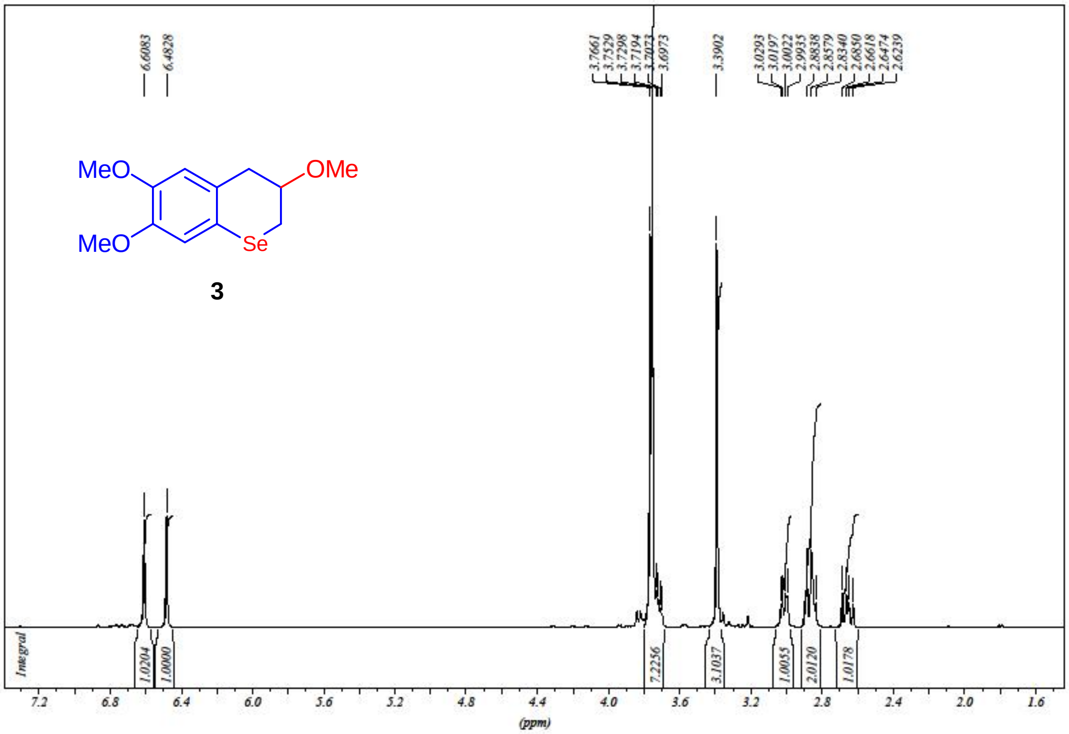
Examples of ^{1}H and ^{13}C NMR spectra of the obtained compounds



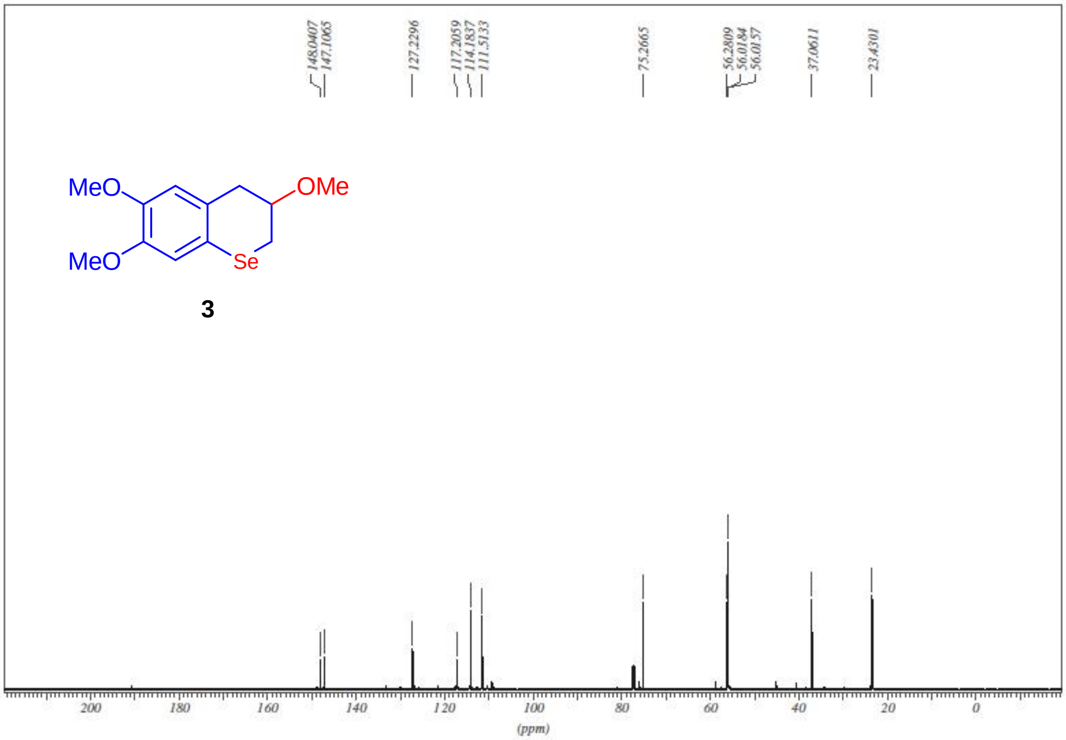
^{1}H NMR spectrum of compound **2**



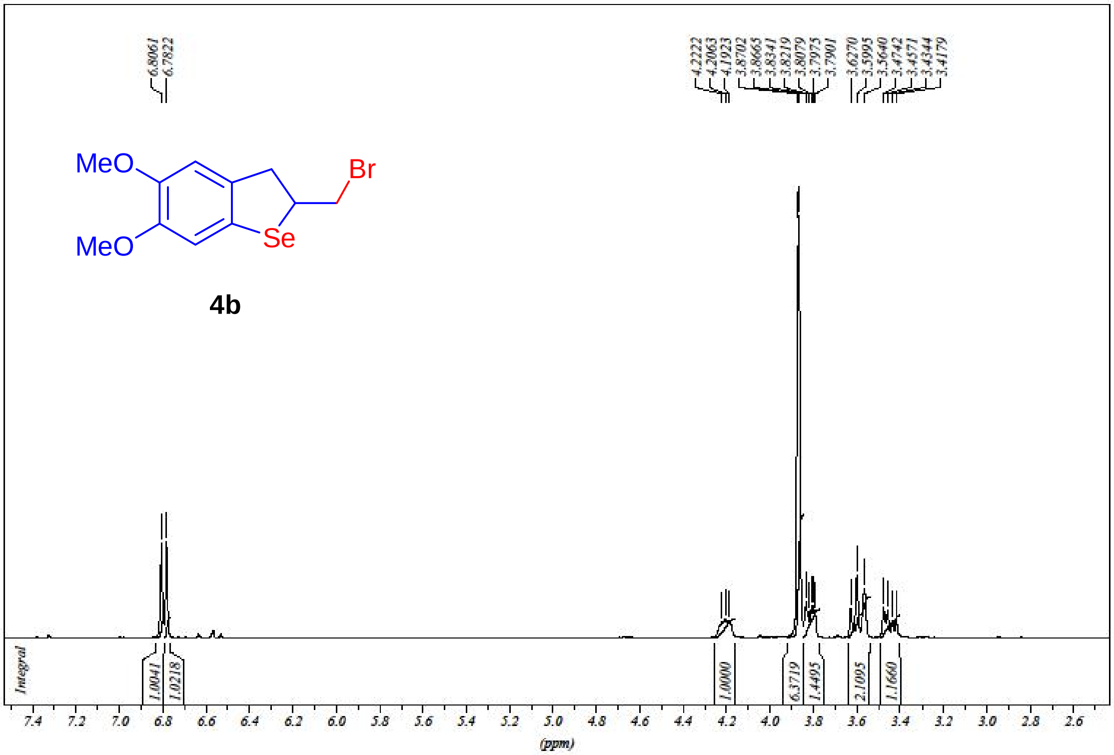
^{13}C NMR spectrum of compound **2**



^{1}H NMR spectrum of compound **3**

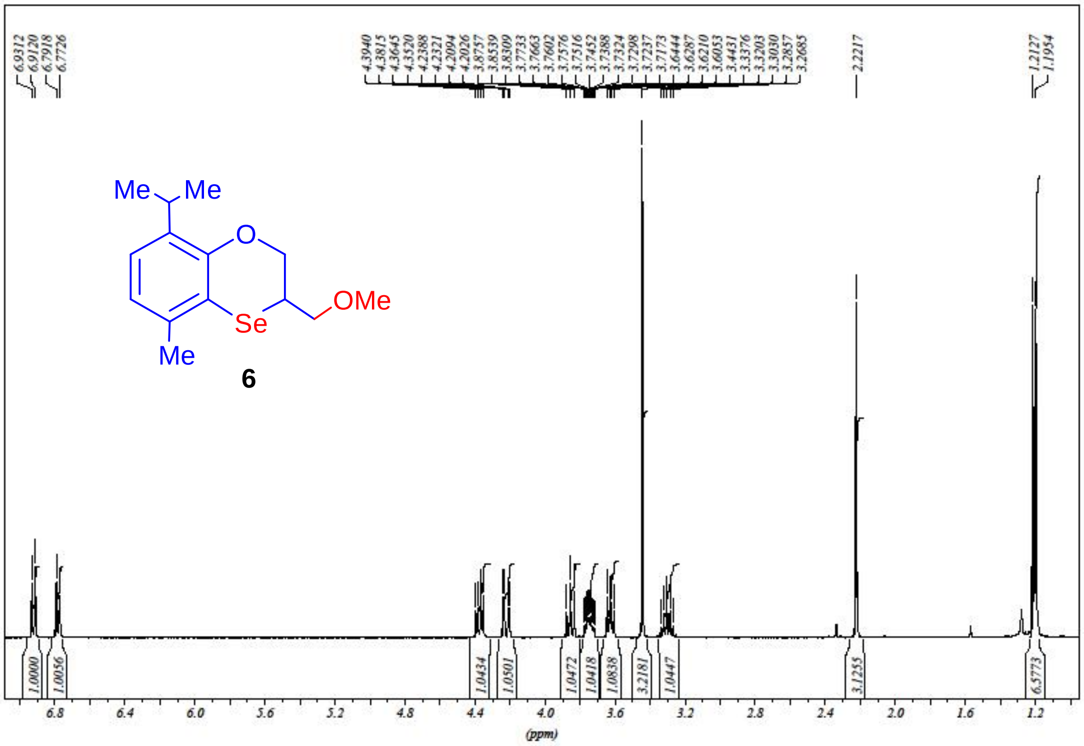


^{13}C NMR spectrum of compound **3**



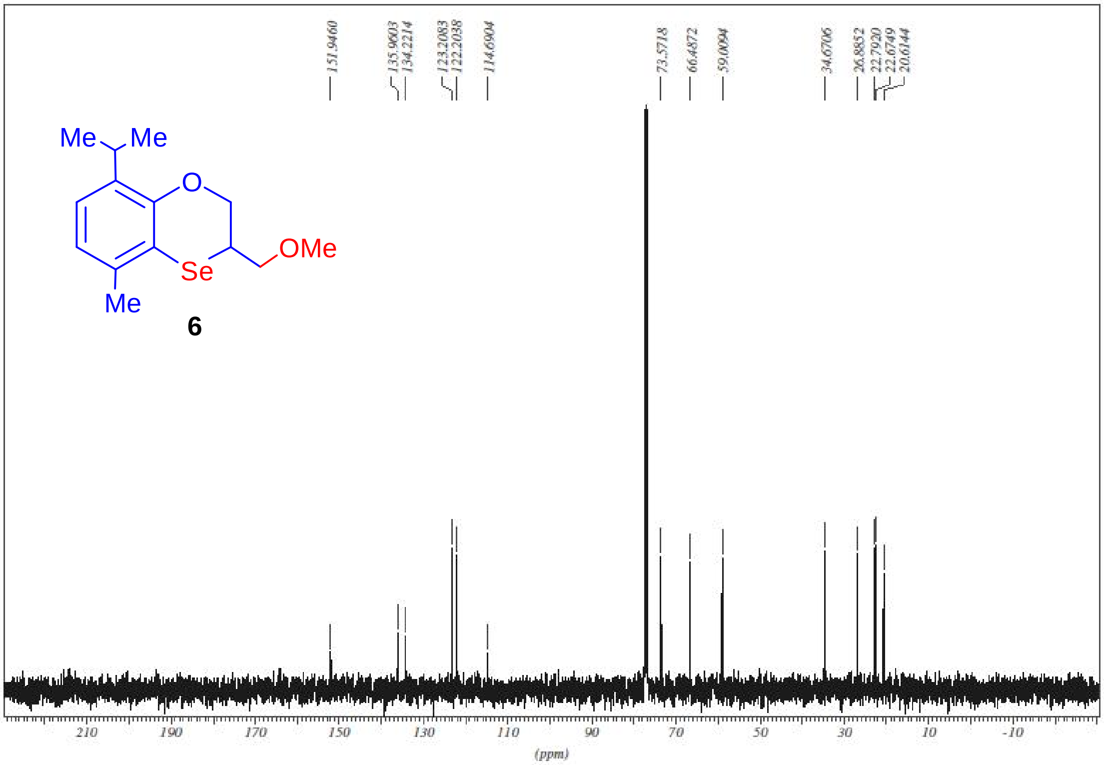
4b

^{1}H NMR spectrum of compound **4b**

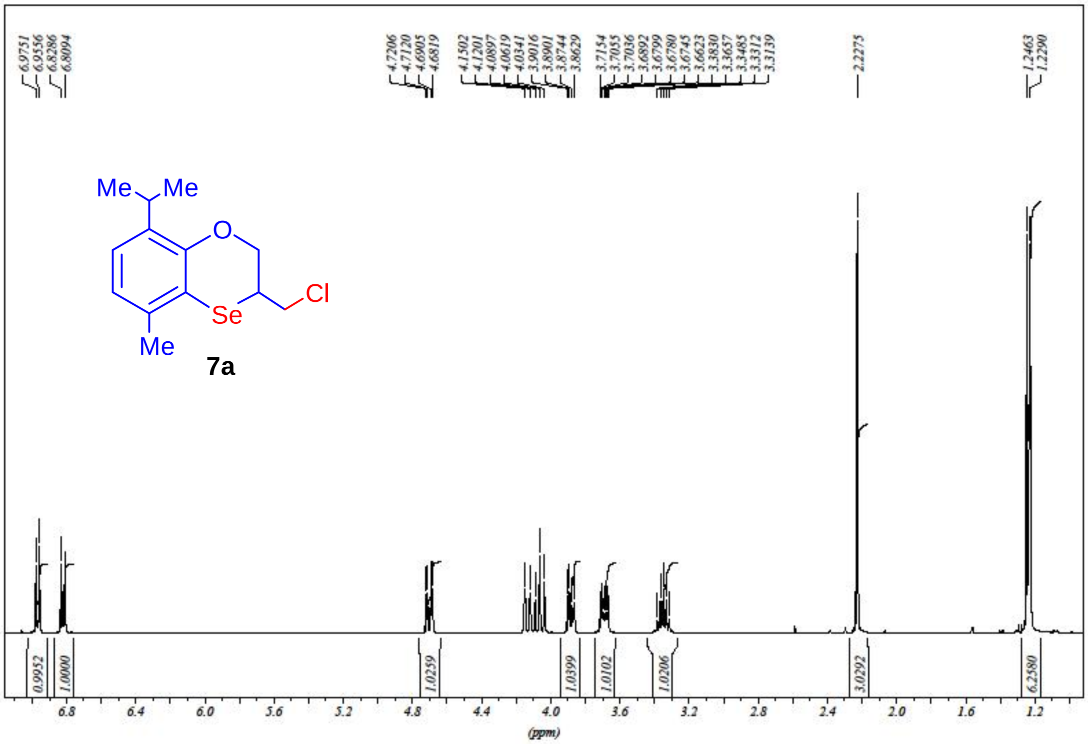


6

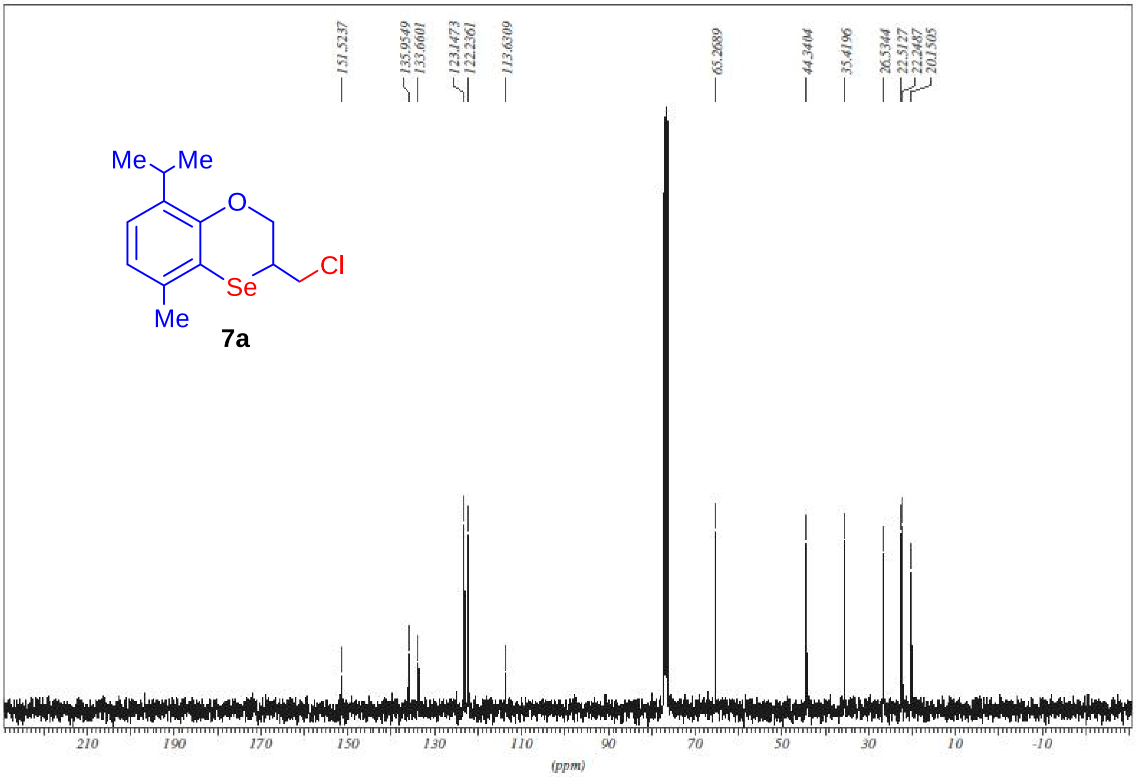
^{1}H NMR spectrum of compound **6**



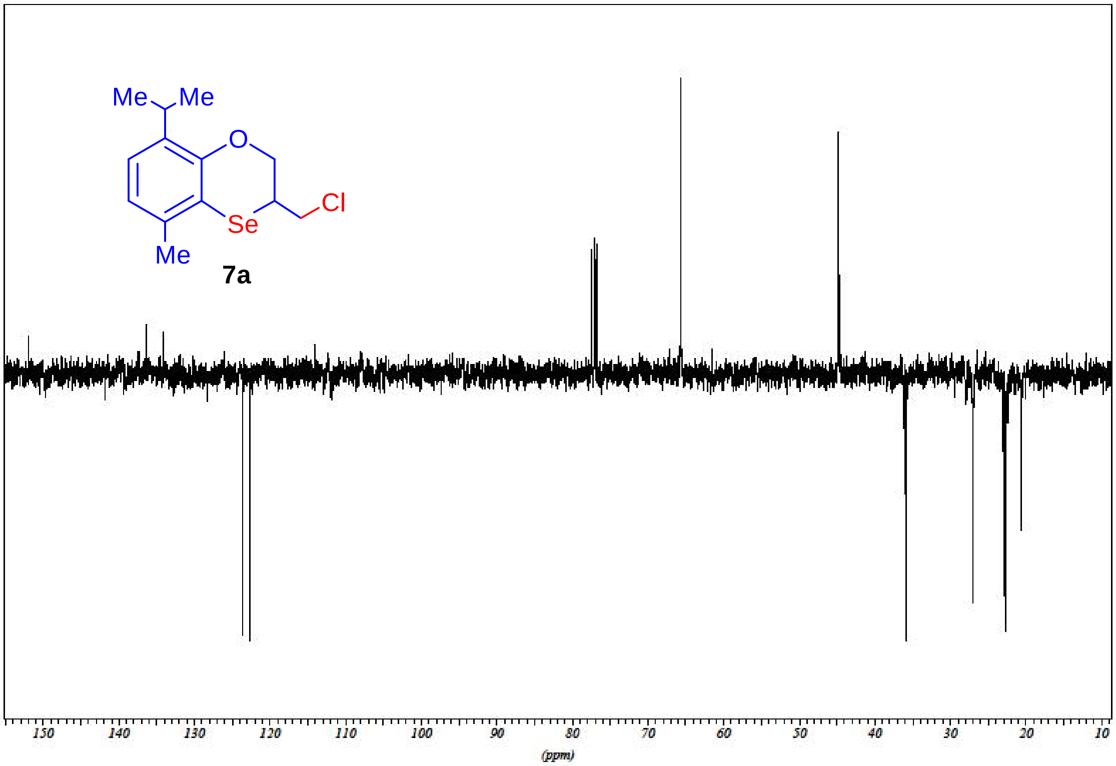
^{13}C NMR spectrum of compound **6**



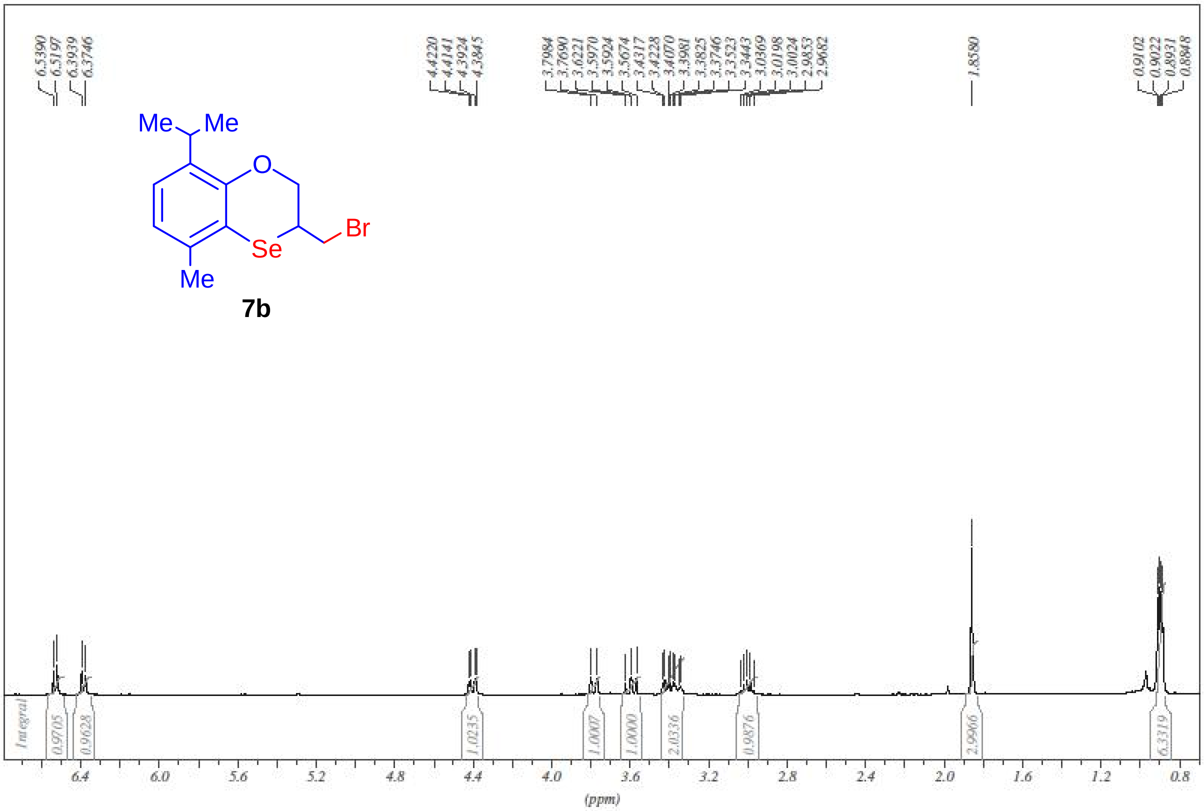
^{1}H NMR spectrum of compound **7a**



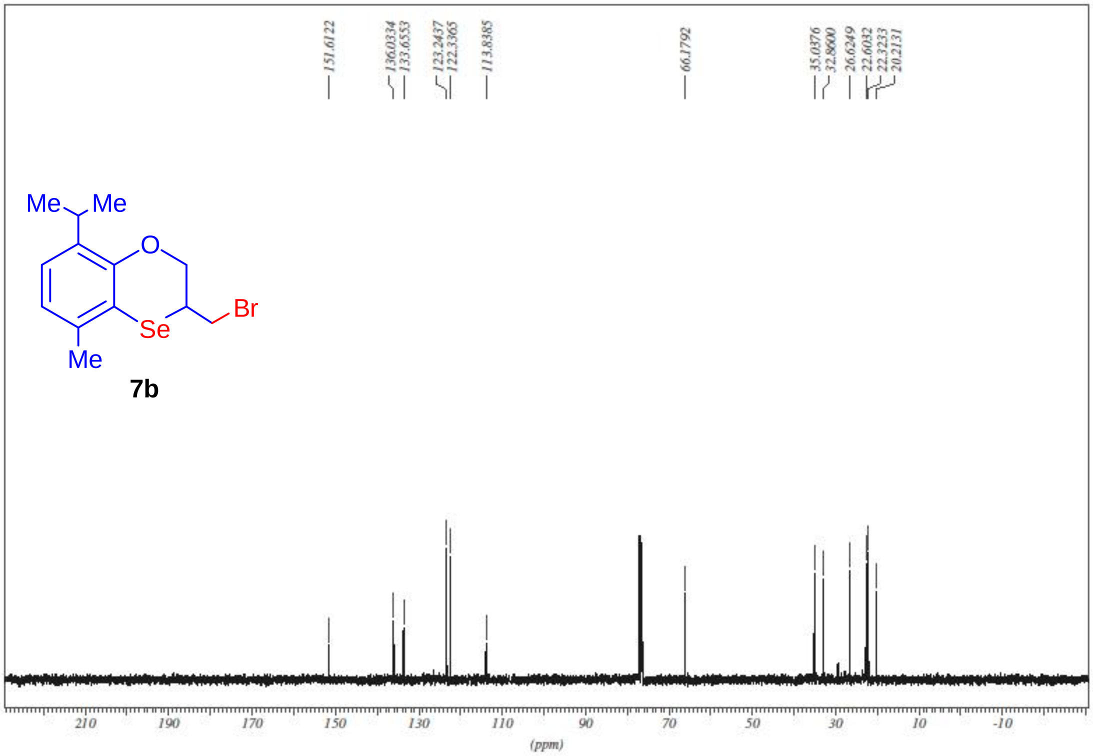
^{13}C NMR spectrum of compound **7a**



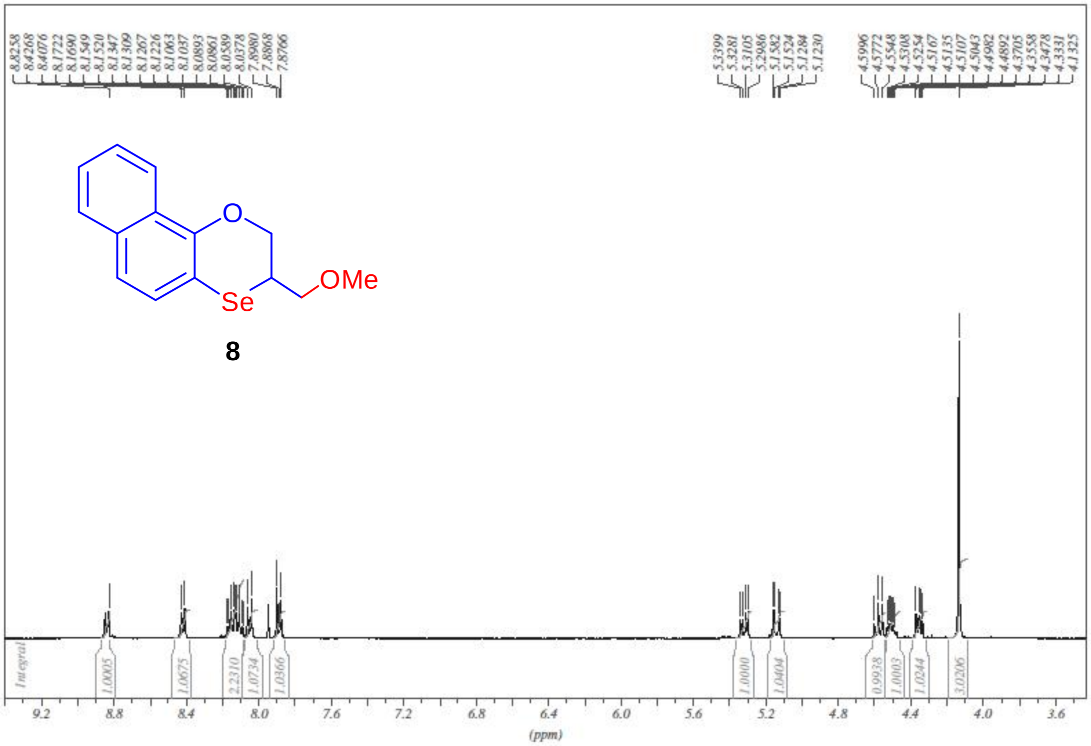
^{13}C NMR *J*-modulation spectrum of compound **7a**



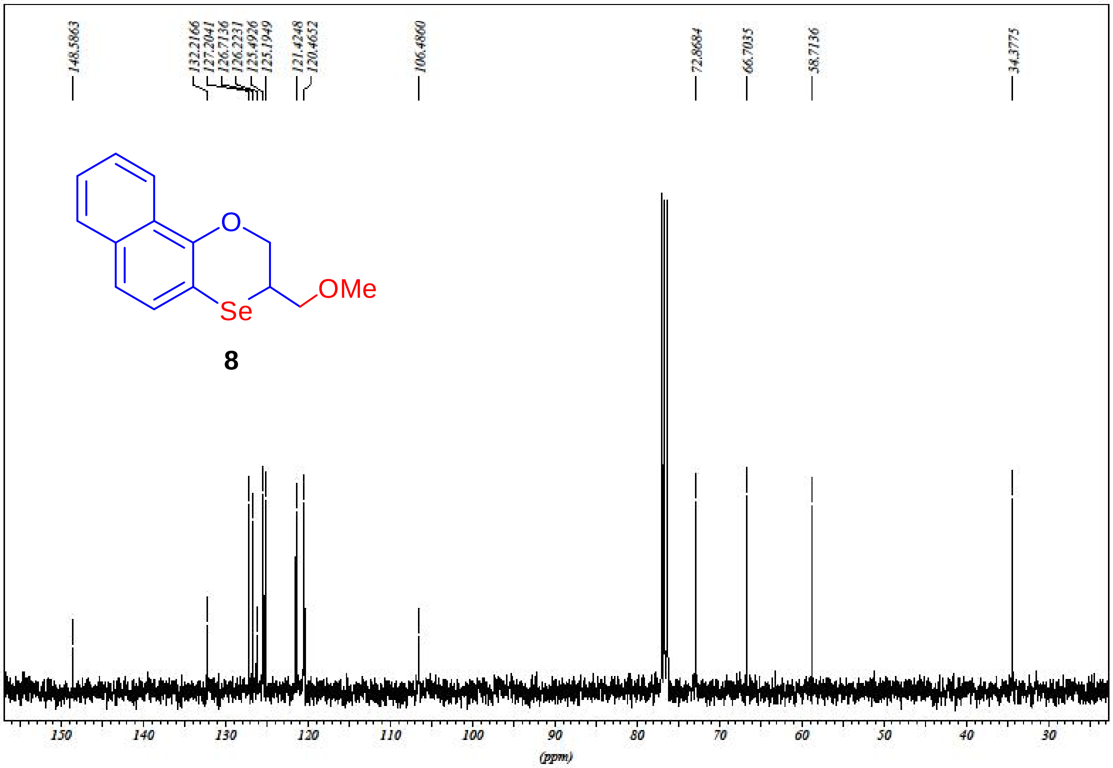
^{1}H NMR spectrum of compound **7b**



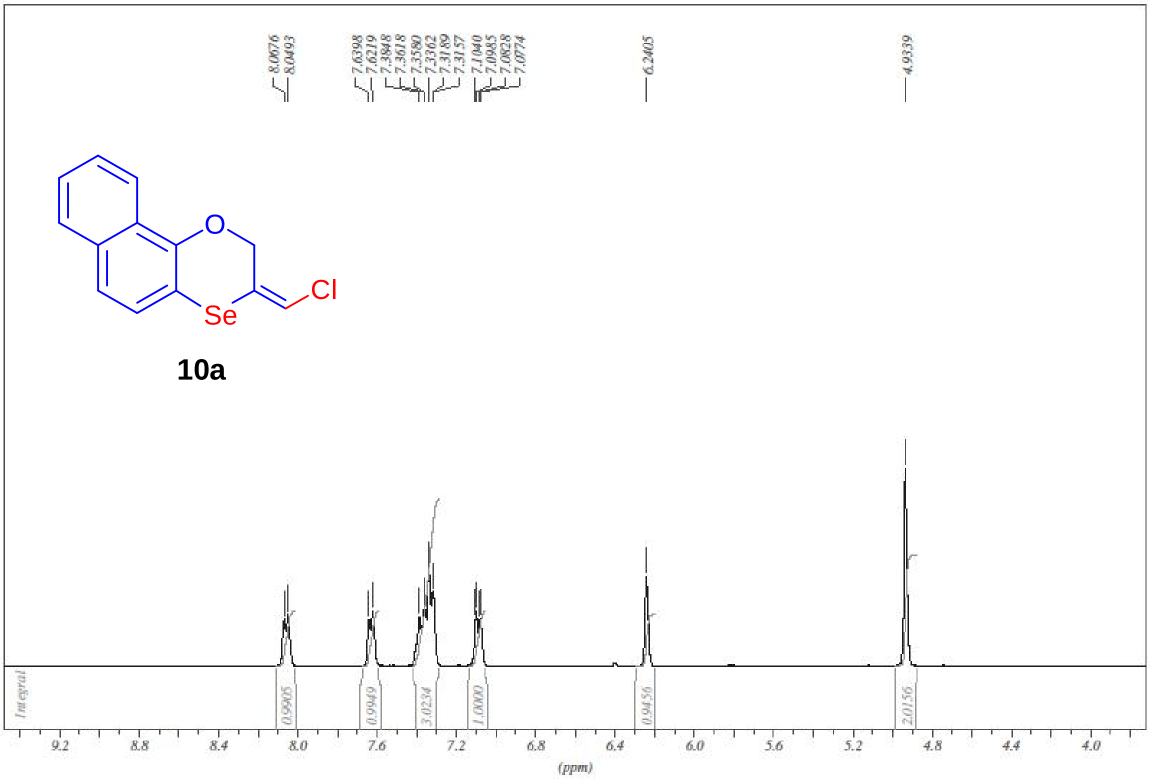
^{13}C NMR spectrum of compound **7b**



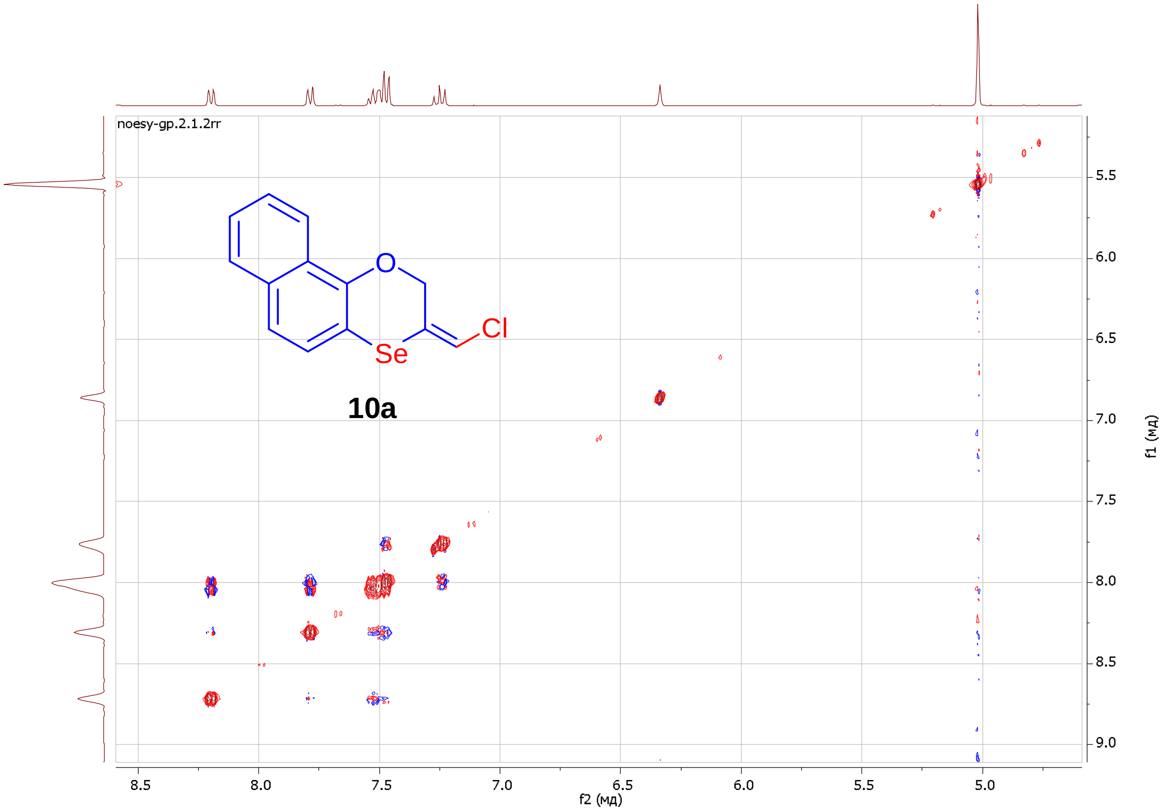
^{1}H NMR spectrum of compound **8**



^{13}C NMR spectrum of compound **8**



^{1}H NMR spectrum of compound **10a**



NMR NOESY spectrum of compound **10a** (*E*-configuration)

X-ray data of compounds 2 and 4a

Data were collected on a BRUKER D8 VENTURE PHOTON 100 CMOS diffractometer with MoK$_{\alpha}$ radiation (λ = 0.71073 Å) using the φ and ω scans technique. The structures were solved and refined by direct methods using the SHELX [2]. Data were corrected for absorption effects using the multi-scan method (SADABS). All non-hydrogen atoms were refined anisotropically using SHELX [2]. The coordinates of the hydrogen atoms were calculated from geometrical positions.

Crystal data and experimental details are given in Table 1.

Table 1 contains CCDC reference number of 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

Table 1. X-ray crystallographic data for compounds 2 and 4b

Compound	**2**	**4b**
CCDC number	1893458	1893457
Empirical formula	$C_{12}H_{16}O_3Se$	$C_{11}H_{13}O_2SeBr$
Formula mass [g/mol]	286.54	336.08
Temperature [K]	100(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	Cc
a [Å]	12.3669(6)	9.4516(4)
b [Å]	6.1164(3)	17.5281(6)
c [Å]	15.6194(7)	8.3971(3)
α [°]	90	90
β [°]	91.018(2)	118.8310(10)
γ [°]	90	90
V [Å^3]	1181.28(10)	1218.70(8)
Z	4	4

$D_{\mathrm{calcd.}}$ [g·cm^{-3}]	1.611	1.832
μ [mm^{-1}]	3.168	6.338
θ rande [°]	2.61–30.08	2.32–30.10
Reflections collected	40146	20079
Independent reflections	3278 [R_{int} = 0.0539]	3144 [R_{int} = 0.0377]
R_1, wR_2 [$I > 2\sigma(I)$]	0.0297, 0.0723	0.0316, 0.0791
R_1, wR_2 (all data)	0.0321, 0.0734	0.0516, 0.0986
Completeness [%]	99.9	99.8
Crystal size [mm]	0.67×0.67×0.47	0.25×0.20×0.07
Goodness of fit	1.080	1.159

References

[1] V. A. Potapov, M. V. Musalov and S. V. Amosova, *Tetrahedron Lett.*, 2011, **52**, 4606.

[2] G. M. Sheldrick, *Acta Crystallogr.*, 2008, **D64**, 112.