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

Supplementary Information for

Mild and Selective Silicon-mediated Access to Enantioenriched 1,2-Mercaptoamines and β-Amino arylchalcogenides

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1. General experimental

All reactions were carried out in an oven-dried glassware under inert atmosphere (N_2). Solvents were dried using a solvent purification system (Pure-Solv™). All commercial materials were purchased from various commercial sources and used as received, without further purification. *N*-Ts,[1] *N*-Boc,[2] *N*-H[3] aziridines and silyl chalcogenides[4] were prepared according to literature reported procedures.

Flash column chromatography purifications were performed with Silica gel 60 (230-400 mesh). Thin layer chromatography was performed with TLC plates Silica gel 60 F_{254}, which was visualised under UV light, or by staining with an ethanolic acid solution of *p*-anisaldehyde followed by heating. High resolution mass spectra (HRMS) were recorded by Electrospray Ionization (ESI). GC-MS was performed on a Varian CP 3800/Saturn 2200 instrument.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using Mercury 400, Bruker 400 Ultrashield, and Varian Gemini 200 spectrometers operating at 400 MHz and 200 MHz (for ^{1}H), 100 MHz and 50 MHz (for ^{13}C). ^{77}Se NMR spectra were recorded using Bruker 400 Ultrashield and Varian Gemini 200 spectrometers, operating at 76 MHz and 38 MHz, respectively. ^{125}Te NMR spectra were recorded in $CDCl_3$ at 126 MHz with a Bruker Ultrashield 400 Plus instrument. NMR signals were referenced to nondeuterated residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C). Diphenyl diselenide $(PhSe)_2$ was used as an external reference for ^{77}Se NMR ($\delta = 461$ ppm). $(PhTe)_2$ was used as an external reference for ^{125}Te ($\delta = 420$ ppm). Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (J) are given in Hertz (Hz), rounded to the nearest 0.1 Hz. ^{1}H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, ap d = apparent doublet, m = multiplet, dd = doublet of doublet, bs = broad singlet, bd = broad doublet, ecc.), coupling constant (J) or line separation (ls), and assignment. Where reported, NMR assignments are made according to spin systems, using, where appropriate, APT and 2D NMR experiments (COSY, HSQC) to assist the assignment.

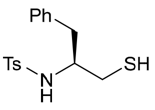
Naming of Compounds. Compound names are those generated by ChemBioDraw 15.0 software (PerkinElmer), following IUPAC nomenclature.

2. Synthesis and Characterization of new compounds

2.1. Synthesis of *N*-Tosyl β-aminothiols (3a-e)

General Procedure. A solution of *N*-Tosyl aziridine **1** (0.5 mmol, 1.0 eq.) and bis(trimethylsilyl)sulfide (HMDST, **2**) (0.6 mmol, 1.2 eq.) in dry THF (2 mL) was cooled under inert atmosphere at 0°C, and treated with TBAF (0.12 mL of 1M THF solution, 0.12 mmol). The reaction was stirred for 10 min and then citric acid (50% *aq* solution) was added. Afterwards, the mixture was diluted with diethyl ether, washed with water, and dried over Na_2SO_4. The solvent was evaporated under vacuum affording compounds **3a-e** pure enough to be used without further purification.

(*S*)-*N*-(1-Mercapto-3-phenylpropan-2-yl)-4-methylbenzenesulfonamide (3a)



3a

Following the general procedure, (*S*)-2-benzyl-1-tosylaziridine **1a** (32 mg, 0.11 mmol) and bis(trimethylsilyl)sulfide (24 mg, 0.132 mmol) gave *N*-Tosyl β-aminothiol **3a** (92%, 33 mg) as a yellowish oil.

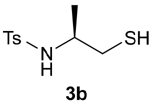
H NMR (200 MHz, $CDCl_3$): δ = 1.29 (1H, ap t, *J* = 8.8 Hz, S**H)**, 2.42 (3H, s),2.54 (1H, ddd, *J* = 4.0, 8.5, 14.0 Hz, C$\mathbf{H_a}$$H_b$SH), 2.59-2.68 (1H, m, C$H_a$$\mathbf{H_b}$SH), 2.70-2.85 (2H, m), 3.53-3.75 (1H, m), 4.71 (1H, d, *J* = 8.0 Hz, N**H**), 6.98-7.03 (2H, m), 7.17-7.24 (5H, m), 7.61 (2H, ap d, ls = 8.4 Hz) ppm.

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.5 (CH_3), 28.7 (CH_2), 38.9 (CH_2), 55.5 (CH), 126.8 (CH), 128.7 (CH), 129.1 (CH), 129.2 (CH), 129.6 (CH), 136.4 (C), 137.2 (C), 143.4 (C) ppm.

MS (EI) *m/z* (%): 274 [$M^{+\cdot}$-CH_2SH, (27)], 230 [$M^{+\cdot}$-Bn, (40)], 155 (39), 91 [Bn^+, (100)], 74 (33), 65 (24).

HRMS (ESI) calc. $C_{16}H_{19}NNaO_2S_2$ $[M+Na]^+$ 344.0755, found 344.0762.

(*S*)-*N*-(1-Mercaptopropan-2-yl)-4-methylbenzenesulfonamide (3b)



3b

Following the general procedure, (*S*)-2-methyl-1-tosylaziridine **1b** (106 mg, 0.50 mmol) and bis(trimethylsilyl)sulfide (107 mg, 0.60 mmol) gave *N*-Tosyl β-aminothiol **3b** (87%, 107 mg) as a yellowish oil.

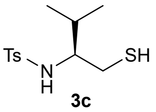
^{1}H NMR (200 MHz, $CDCl_3$): *δ* (ppm) = 1.10 (3H, d, *J* = 6.6 Hz), 1.24 (1H, dd, *J* = 7.0, 8.4 Hz, S**H**), 2.43 (3H, s), 2.52-2.59 (2H, m), 3.42-3.61 (1H, m), 5.10 (1H, bs), 7.31 (2H, ap d, ls = 8.2 Hz), 7.77 (2H, ap d, ls = 8.2 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): *δ* (ppm) = 16.6 (CH_3), 21.5 (CH_3), 34.6 (CH_2), 35.7 (CH), 127.7 (CH), 129.6 (CH), 135.2 (C), 144.3 (C).

MS (EI) *m/z* (%): 198 [$M^{+\cdot}$-CH_2SH, (67)], 155 (65), 91 [Bn^+, (100)], 65 (22).

HRMS (ESI) calc. $C_{10}H_{15}NNaO_2S_2$ $[M+Na]^+$ 268.0442, found 268.0439.

(*S*)-*N*-(1-Mercapto-3-methylbutan-2-yl)-4-methylbenzenesulfonamide (3c)



3c

Following the general procedure, (*S*)-2-isopropyl-1-tosylaziridine **1c** (120 mg, 0.50 mmol) and bis(trimethylsilyl)sulfide (107 mg, 0.60 mmol) gave *N*-Tosyl β-aminothiol **3c** (90%, 123 mg) as a yellowish oil. $[\alpha]_{\mathrm{D}}^{22} = -16.3^\circ$ (c = 1.8; CHCl$_3$).

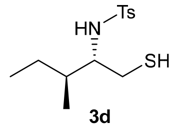
^{1}**H NMR** (200 MHz, CDCl$_3$): δ (ppm) = 0.78 (3H, d, J = 6.6 Hz, (C**H**$_3$)$_2$CH), 0.80 (3H, d, J = 7.0 Hz, (C**H**$_3$)$_2$CH), 1.15 (1H, dd, J = 8.0, 9.4 Hz, S**H**), 1.79-1.93 (1H, m, C**H**(CH$_3$)$_2$), 2.42 (3H, s), 2.50 (1H, dd, J = 5.6, 9.4 Hz, C**H**$_{\mathbf{a}}$H$_b$SH), 2.61 (1H, dd, J = 5.6, 8.0 Hz, CH$_a$**H**$_{\mathbf{b}}$SH), 3.04-3.15 (1H, m, C**H**NH), 4.94 (1H, bd, J = 8.8 Hz, N**H**), 7.29 (2H, ap d, ls = 8.0 Hz), 7.76 (2H, ap d, ls = 8.0 Hz).

^{13}**C NMR** (50 MHz, CDCl$_3$): δ (ppm) = 18.1 (CH$_3$), 18.9 (CH$_3$), 21.5 (CH$_3$), 27.2 (CH$_2$), 29.5 (CH), 60.0 (CH), 127.0 (CH), 129.6 (CH), 137.9 (C), 143.4 (C).

MS (EI) *m/z* (%): 226 [M$^{+\cdot}$-CH$_2$SH,(69)], 155 (58), 91 [Bn$^+$, (100)], 65 (22).

HRMS (ESI) calc. $C_{12}H_{20}NO_2S_2$ [M+H]$^+$ 274.0935, found 274.0921.

N-((2*S*,3*S*)-1-Mercapto-3-methylpentan-2-yl)-4-methylbenzenesulfonamide (3d)



3d

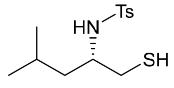
Following the general procedure, (*S*)-2-isobutyl-1-tosylaziridine **1e** (51 mg, 0.20 mmol) and bis(trimethylsilyl)sulfide (43 mg, 0.24 mmol) gave *N*-Tosyl β-aminothiol **3e** (91%, 52 mg). $[\alpha]_{\mathrm{D}}^{22} = -13.6^\circ$ (c = 1.3; CHCl$_3$).

^{1}**H NMR** (200 MHz, CDCl$_3$): δ (ppm) = 0.75-0.83 (6H, m), 1.13 (1H, dd, J = 7.9, 9.3 Hz, S**H**), 0.90-1.10 (1H, m), 1.37-1.66 (2H, m), 2.42 (3H, s), 2.45-2.67 (2H, m), 3.12-3.24 (1H, m), 4.94 (1H, d, J = 8.8 Hz), 7.30 (2H, ap d, ls = 8.4 Hz), 7.76 (2H, ap d, ls = 8.4 Hz).

^{13}**C NMR** (50 MHz, CDCl$_3$): δ (ppm) = 11.2 (CH$_3$), 14.9 (CH$_3$), 21.5 (CH$_3$), 24.7 (CH$_2$), 26.7 (CH$_2$), 36.3 (CH), 58.6 (CH), 127.0 (CH), 129.7 (CH), 137.8 (C), 143.4 (C).

HRMS (ESI) calc. $C_{13}H_{21}NNaO_2S_2$ [M+Na]$^+$ 310.0911, found 310.0919.

(*S*)-*N*-(1-Mercapto-4-methylpentan-2-yl)-4-methylbenzenesulfonamide (3e)



3e

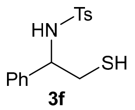
Following the general procedure, (*S*)-2-((*S*)-sec-butyl)-1-tosylaziridine **1d** (25 mg, 0.10 mmol) and bis(trimethylsilyl)sulfide (21 mg, 0.12 mmol) gave *N*-Tosyl β-aminothiol **3d** (84%, 24 mg). $[\alpha]_{\mathrm{D}}^{22} = -14.1^\circ$ (c = 0.8; CHCl$_3$).

^{1}**H NMR** (200 MHz, CDCl$_3$): δ (ppm) = 0.70 (3H, d, J = 6.4 Hz), 0.81 (3H, d, J = 6.4 Hz), 1.18 (1H, ap t, J = 8.8 Hz, S**H**), 1.20-1.30 (2H, m), 1.44-1.52 (1H, m), 2.42 (3H, s), 2.53 (2H, dd, J = 4.2, 9.0 CH$_2$S), 3.43-3.49 (1H, m), 4.92 (1H, d, J = 8.4 Hz), 7.29 (2H, ap d, ls = 8.4 Hz), 7.76 (2H, ap d, ls = 8.4 Hz).

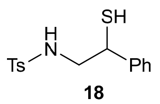
^{13}**C NMR** (50 MHz, CDCl$_3$): δ (ppm) = 21.3, 21.5, 21.7, 23.3, 27.9, 43.3, 56.6, 127.4, 129.2, 137.8, 142.9.

HRMS (ESI) calc. $C_{13}H_{21}NNaO_2S_2$ [M+Na]$^+$ 310.0911, found 310.0925.

N-(2-Mercapto-1-phenylethyl)-4-methylbenzenesulfonamide (3f) and *N*-(2-mercapto-2-phenylethyl)-4-methylbenzenesulfonamide (18)



3f



18

Following the general procedure, 2-phenyl-1-tosylaziridine (27 mg, 0.10 mmol) and bis(trimethylsilyl)sulfide (21 mg, 0.12 mmol) gave the mixture of regioisomer **3f** and **18** in a 75:25 ratio.

^{1}**H NMR** (300 MHz, $CDCl_3$): *δ* (ppm) = *major regioisomer* (**3f**) 1.13 (1H, ap t, *J* = 8.8 Hz, S**H**), 2.37 (3H, s), 2.75-2.96 (2H, m, CH_2S), 4.38-4.46 (1H, m), 5.45 (1H, bs), 6.90-7.38 (7H, m), 7.61 (2H, ap d, ls = 8.8 Hz); *minor regioisomer* (**18**) 1.97 (1H, d, *J* =6.8 Hz, S**H**), 2.44 (3H, s), 3.29-3.48 (2H, m, CH_2N), 3.94-4.06 (1H, m), 5.45 (1H, bs), 6.90-7.38 (7H, m), 7.61 (2H, ap d, ls = 8.8 Hz).

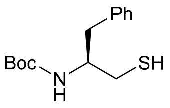
^{13}**C NMR** (50 MHz, $CDCl_3$): *δ* (ppm) = 21.5, 31.6 (CH_2S, *major regioisomer*), 43.8 (CHS, *minor regioisomer*), 50.6 (CH_2N, *major regioisomer*), 58.7 (CHN, *major regioisomer*), 126.5, 126.7, 127.0, 127.1, 127.9, 128.0, 128.5, 128.6, 129.0, 129.4, 129.5, 129.8, 137.2, 138.4, 143.8.

MS (ESI, positive) 308.4 $[M+H]^+$

2.2. Synthesis of *N*-Boc β-aminothiols (6a-c)

General procedure. A solution of aziridine **5** (0.5 mmol, 1.0 eq.) and bis(trimethylsilyl)sulfide (HMDST, **2**) (0.6 mmol, 1.2 eq.) in dry THF (3 mL) was treated with TBAF (0.6 mL of 1M THF solution, 1.2 mmol). The reaction was stirred at room temperature for 1 h and then citric acid (50% *aq* solution) was added. Afterwards, the mixture was diluted with diethyl ether, washed with water, and dried over Na_2SO_4. The solvent was evaporated under vacuum affording the desired *N*-Boc β-aminothiols **6** pure enough to be used without further purification.

(*S*)-*tert*-Butyl (1-mercapto-3-phenylpropan-2-yl)carbamate (6a)



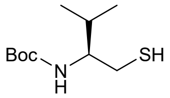
6a

Following the general procedure, *tert*-butyl (*S*)-2-benzylaziridine-1-carboxylate **5a** (70 mg, 0.3 mmol) and bis(trimethylsilyl)sulfide (64 mg, 0.36 mmol) gave the *N*-Boc β-aminothiol **6a** (93%, 75 mg) as a yellowish oil. All recorded spectroscopic data matched those previously reported in the literature.[5] $[\alpha]_{\mathrm{D}}^{22} = -21.6^\circ$ (*c* = 0.9; $CHCl_3$).

^{1}**H NMR** (200 MHz, $CDCl_3$): *δ* (ppm) = 1.29 (1H, ap t, *J* = 8.8 Hz, S**H)**, 1.42 (9H, s), 2.51-2.77 (2H, m), 2.86 (2H, bd, *J* = 7.2 Hz),3.87-4.08 (1H, m), 4.76 (1H, d, *J* = 8.0 Hz, N**H**), 7.17-7.37 (5H, m).

^{13}**C NMR** (50 MHz, $CDCl_3$): *δ* (ppm) = 28.4 (CH_3), 37.0 (CH_2), 38.8 (CH_2), 52.6 (CH), 79.5 (C), 126.5 (CH), 128.4 (CH), 129.4 (CH), 137.4 (C), 155.1 (C).

(*S*)-*tert*-Butyl (1-mercapto-3-methylbutan-2-yl)carbamate (6b)



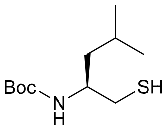
6b

Following the general procedure, *tert*-butyl (*S*)-2-isopropylaziridine-1-carboxylate (46 mg, 0.25 mmol) and bis(trimethylsilyl)sulfide (53 mg, 0.30 mmol) gave the *N*-Boc β-aminothiol **6b** (87%, 48 mg) as a yellowish oil. All recorded spectroscopic data matched those previously reported in the literature.[6] $[\alpha]_{\mathrm{D}}^{22} = -6.2^\circ$ (*c* = 1; $CHCl_3$).

^{1}**H NMR** (200 MHz, $CDCl_3$): *δ* (ppm) = 0.91 (6H, ap t, *J* = 7.0 Hz, (C**H**$_3$)$_2$CH), 1.29 (1H, dd, *J* = 7.9, 10.8 Hz, S**H**), 1.44 (9H, s), 1.76-1.92 (1H, m, C**H**(CH_3)$_2$), 2.65 (2H, bd, *J* = 6.2, C**H$_2$**SH), 3.42-3.61 (1H, m, C**H**NH), 4.60 (1H, bd, *J* = 9.0 Hz, N**H**).

^{13}C NMR (50 MHz, CDCl$_3$): δ (ppm) = 19.4 (CH$_3$), 19.5 (CH$_3$), 28.4 (CH$_3$), 31.2 (CH), 35.9 (CH$_2$), 54.9 (CH), 79.1 (C), 155.8 (CO).

***tert*-Butyl (S)-(1-mercapto-4-methylpentan-2-yl)carbamate (6c)**



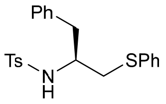
6c

Following the general procedure, *tert*-butyl (S)-2-isobutylaziridine-1-carboxylate (50 mg, 0.25 mmol) and bis(trimethylsilyl)sulfide (53 mg, 0.30 mmol) gave the *N*-Boc β-aminothiol **6c** (76%, 44 mg) as a yellowish oil. All recorded spectroscopic data matched those previously reported in the literature. $[\alpha]_D^{22} = -4.4°$ (c = 1; CHCl$_3$).

2.3. Synthesis of β-phenylchalcogenoamines by NRORs of aziridines with phenylchalcogeno silanes

General procedure. A solution of aziridine (**1**, *N*-Ts aziridine; **5**, *N*-Boc aziridine or **10**, *N*-H aziridine) (0.5 mmol, 1.0 eq.) and phenylchalcogeno silane (**7a**, PhSSiMe$_3$; **7b**, PhSeSiMe$_3$; **7c**, PhTeSiMe$_3$) (0.6 mmol, 1.2 eq.) in dry THF (3 mL) was treated with TBAF (0.24 mL of 1M THF solution, 0.24 mmol). The reaction was stirred at room temperature for 5-6 h, until complete consumption of starting material was observed by TLC. Afterwards, NH$_4$Cl (sat. *aq* solution) was added, the mixture was diluted with diethyl ether, washed with water, and dried over Na$_2$SO$_4$. The solvent was evaporated under vacuum and the crude material was purified by flash column chromatography to afford β-phenylchalcogenoamines **8**, **9** or **11**.

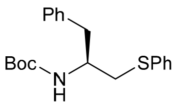
(*S*)-4-Methyl-*N*-(1-phenyl-3-(phenylthio)propan-2-yl)benzenesulfonamide (8a)



8a

Following the general procedure, (*S*)-2-benzyl-1-tosylaziridine **1a** (43 mg, 0.15 mmol) and (Phenylthio)trimethylsilane **7a** (34 μL, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 4:1), *N*-Tosyl β-aminophenylsulfide **8a** (89%, 53 mg) as a white solid. Recorded spectroscopic data matched those previously reported in the literature.[7]

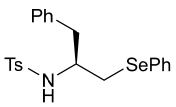
***tert*-Butyl (*S*)-(1-phenyl-3-(phenylthio)propan-2-yl)carbamate (9a)**



9a

Following the general procedure, *tert*-butyl (*S*)-2-benzylaziridine-1-carboxylate **5a** (35 mg, 0.15 mmol) and (Phenylthio)trimethylsilane **7a** (34 μL, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 8:1), *N*-Boc β-aminophenylsulfide **9a** (76%, 39 mg) as a white solid. Recorded spectroscopic data matched those previously reported in the literature.[8] $[\alpha]_D^{21} = +23.1°$ (c = 1; CH$_2$Cl$_2$).

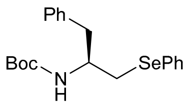
(*S*)-4-Methyl-*N*-(1-phenyl-3-(phenylselanyl)propan-2-yl)benzenesulfonamide (8b)



8b

Following the general procedure, (*S*)-2-benzyl-1-tosylaziridine **1a** (29 mg, 0.10 mmol) and (Phenylseleno)trimethylsilane **7b** (27 mg, 0.12 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 5:1), *N*-Tosyl β-aminophenylselenide **8b** (92%, 37 mg) as a pale yellowish solid. Recorded spectroscopic data matched those previously reported in the literature.[9] $[\alpha]_{\mathrm{D}}^{22} = -51.4°$ (c = 1.2; CH_2Cl_2).

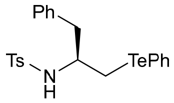
tert-Butyl (S)-(1-phenyl-3-(phenylselanyl)propan-2-yl)carbamate (9b)



9b

Following the general procedure, *tert*-butyl (*S*)-2-benzylaziridine-1-carboxylate **5a** (23 mg, 0.10 mmol) and (Phenylseleno)trimethylsilane **7b** (27 mg, 0.12 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 9:1), *N*-Boc β-aminophenylselenide **9b** (79%, 31 mg). Recorded spectroscopic data matched those previously reported in the literature.[9] $[\alpha]_{\mathrm{D}}^{21} = +15.1°$ (c = 1.5; CH_2Cl_2).

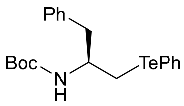
(S)-4-methyl-N-(1-phenyl-3-(phenyltellanyl)propan-2-yl)benzenesulfonamide (8c)



8c

Following the general procedure, (*S*)-2-benzyl-1-tosylaziridine **1a** (29 mg, 0.10 mmol) and (Phenyltelluro)trimethylsilane **7c** (34 mg, 0.12 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 5:1), *N*-Tosyl β-aminophenyltelluride **8c** (84%, 42 mg). Recorded spectroscopic data matched those previously reported in the literature.[10] $[\alpha]_{\mathrm{D}}^{20} = -24.8°$ (c = 0.6; CH_2Cl_2).

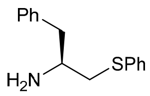
tert-Butyl (S)-(1-phenyl-3-(phenyltellanyl)propan-2-yl)carbamate (9c)



9c

Following the general procedure, *tert*-butyl (*S*)-2-benzylaziridine-1-carboxylate **5a** (35 mg, 0.15 mmol) and (Phenyltelluro)trimethylsilane **7c** (50 mg, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 9:1), *N*-Boc β-aminophenyltelluride **9c** (73%, 48 mg) as a white solid. Recorded spectroscopic data matched those previously reported in the literature.[11] $[\alpha]_{\mathrm{D}}^{21} = -15.5°$ (c = 0.7; CH_2Cl_2).

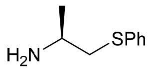
(S)-1-Phenyl-3-(phenylthio)propan-2-amine (11aa)



11aa

Following the general procedure, (*S*)-2-benzylaziridine **10a** (13 mg, 0.10 mmol) and (Phenylthio)trimethylsilane **7a** (23 μL, 0.12 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminophenylsulfide **11aa** (63%, 15 mg) as a yellowish oil. Recorded spectroscopic data matched those previously reported in the literature.[12] $[\alpha]_{\mathrm{D}}^{21} = +44.7°$ (c = 0.8; $CHCl_3$).

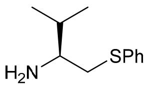
(S)-1-(Phenylthio)propan-2-amine (11ab)



11ab

Following the general procedure, (*S*)-2-methylaziridine **10b** (9 mg, 0.15 mmol) and (Phenylthio)trimethylsilane **7a** (34 μL, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminophenylsulfide **11ab** (56%, 14 mg) as a yellowish oil. Recorded spectroscopic data matched those previously reported in the literature.[12] $[\alpha]_{\mathrm{D}}^{21} = +49.8°$ (c = 1.3; $CHCl_3$).

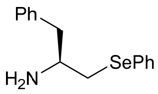
(*S*)-3-Methyl-1-(phenylthio)butan-2-amine (11ac)



11ac

Following the general procedure, (*S*)-2-isopropylaziridine **10c** (13 mg, 0.15 mmol) and (Phenylthio)trimethylsilane **7a** (34 µL, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminophenylsulfide **11ac** (64%, 19 mg) as a yellowish oil. Recorded spectroscopic data matched those previously reported in the literature.[12] $[\alpha]_D^{21} = -21.2°$ ($c = 0.2$; $CHCl_3$).

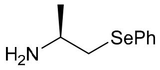
(*S*)-1-Phenyl-3-(phenylselanyl)propan-2-amine (11ba)



11ba

Following the general procedure, (*S*)-2-benzylaziridine **10a** (20 mg, 0.15 mmol) and (Phenylseleno)trimethylsilane **7b** (41 mg, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminophenylselenide **11ba** (65%, 28 mg) as a yellowish oil. Recorded spectroscopic data matched those previously reported in the literature.[13]

(*S*)-1-(Phenylselanyl)propan-2-amine (11bb)



11bb

Following the general procedure, (*S*)-2-methylaziridine **10b** (9 mg, 0.15 mmol) and (Phenylseleno)trimethylsilane **7b** (41 mg, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminophenylselenide **11bb** (55%, 18 mg) as a yellowish oil.

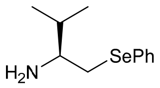
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.19 (3H, dd, J = 6.3, 12.4 Hz), 2.45 (2H, bs, NH_2), 2.84 (1H, dd, J = 7.7, 12.2 Hz, $C\mathbf{H_a}H_bSe$), 3.05 (1H, dd, J = 4.8, 12.2 Hz, $CH_a\mathbf{H_b}Se$), 3.08-3.16 (1H, m, $C\mathbf{H}NH_2$), 2.24-2.30 (3H, m), 7.52-7.56 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 23.1, 38.7, 46.7, 127.0, 129.1, 130.0, 132.8.

^{77}Se NMR(76 MHz, $CDCl_3$): δ (ppm) 254.1.

MS (ESI, positive): 238 $[M+Na]^+$.

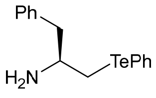
(*S*)-3-Methyl-1-(phenylselanyl)butan-2-amine (11bc)



11bc

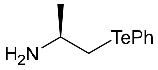
Following the general procedure, (*S*)-2-isopropylaziridine **10c** (9 mg, 0.10 mmol) and (Phenylseleno)trimethylsilane **7b** (28 mg, 0.12 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminophenylsulfide **11bc** (62%, 15 mg) as an oil. Recorded spectroscopic data matched those previously reported in the literature.[14] $[\alpha]_D^{22} = +64.2°$ ($c = 0.7$; $CHCl_3$).

(*S*)-1-Phenyl-3-(phenyltellanyl)propan-2-amine (11ca)


11ca

Following the general procedure, (*S*)-2-benzylaziridine **10a** (20 mg, 0.15 mmol) and (Phenyltelluro)trimethylsilane **7c** (50 mg, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminophenyltelluride **11ca** (63%, 32 mg) as a yellowish oil.[15] $[\alpha]_D^{21} = -55.6^\circ$ (*c* = 0.8; $CHCl_3$).

(*S*)-1-(Phenyltellanyl)propan-2-amine (11cb)


11cb

Following the general procedure, (*S*)-2-methylaziridine **10b** (9 mg, 0.15 mmol) and (Phenyltelluro)trimethylsilane **7c** (50 mg, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminophenyltelluride **11cb** (58%, 23 mg) as a yellowish oil. $[\alpha]_D^{22} = +28.4^\circ$ (*c* = 1.4; $CHCl_3$).

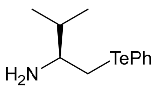
^{1}HNMR (400 MHz, $CDCl_3$): *δ* (ppm) 1.23 (3H, d, *J* = 6.2 Hz), 2.31 (2H, bs, NH_2), 2.95 (1H, dd, *J* = 7.0, 11.8 Hz, $C\mathbf{H_a}H_bTe$), 3.11 (1H, dd, *J* = 5.2, 11.8 Hz, $CH_a\mathbf{H_b}Te$), 3.14-3.21 (1H, m, C**H**NH_2), 7.2-7.24 (2H, m), 7.28-7.32 (1H, m), 7.75-7.78 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 21.7, 24.3, 47.8, 111.6, 127.7, 129.2, 138.4.

^{125}Te NMR (126 MHz, $CDCl_3$): *δ* (ppm) 390.5.

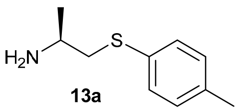
MS (ESI, positive): 288 $[M+Na]^+$.

(*S*)-3-Methyl-1-(phenyltellanyl)butan-2-amine (11cc)


11cc

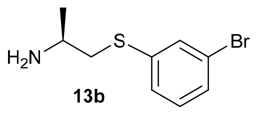
Following the general procedure, (*S*)-2-isopropylaziridine **10c** (13 mg, 0.15 mmol) and (Phenyltelluro)trimethylsilane **7c** (50 mg, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminophenylsulfide **11bc** (67%, 29 mg) as an oil. Recorded spectroscopic data matched those previously reported in the literature.[16]

(*S*)-1-(*p*-Tolylthio)propan-2-amine (13a)


13a

Following the general procedure, (*S*)-2-methylaziridine **10b** (9 mg, 0.15 mmol) and trimethyl(p-tolylthio)silane **12a** (35 mg, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminosulfide **13a** (58%, 15 mg) as a yellowish oil. Recorded spectroscopic data matched those previously reported in the literature.[17]

1-((3-Bromophenyl)thio)propan-2-amine (13b)


13b

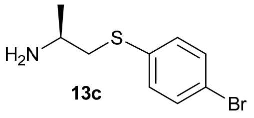
Following the general procedure, 2-methylaziridine **10b** (14 mg, 0.24 mmol) and ((3-bromophenyl)thio)trimethylsilane **12b** (75 mg, 0.29 mmol) gave, after purification by flash column chromatography (petroleum ether:EtOAc 1:2), 1-((3-bromophenyl)thio)propan-2-amine **3c** (29 mg, 58%).

^{1}**HMR** (400 MHz, $CDCl_3$): δ (ppm) 1.18 (3H, d, J = 6.3 Hz), 1.86 (2H, bs, NH_2), 2.78 (1H, dd, J = 7.9, 13.0 Hz, CH_aH_bS), 3.02 (1H, dd, J = 4.7, 13.0, CH_aH_bS), 3.06-3.14 (1H, m, $CHNH_2$), 7.13 (1H, t, J = 7.9 Hz), 7.25- 7.31 (2H, m), 7.48 (1H, apt, J = 1.8 Hz).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ (ppm) 22.8, 43.6, 46.0, 122.7, 127.5, 128.9, 130.1, 131.4, 138.7.

MS (ESI, positive): 246.6 $[M+H]^+$.

1-((4-Bromophenyl)thio)propan-2-amine (13c)



13c

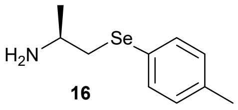
Following the general procedure, 2-methylaziridine **10b** (14 mg, 0.24 mmol) and ((4-bromophenyl)thio)trimethylsilane **12c** (75 mg, 0.29 mmol) gave, after purification by flash column chromatography (petroleum ether:EtOAc 1:2), 1-((4-bromophenyl)thio)propan-2-amine **13c** (33 mg, 61%).

^{1} **H NMR** (400 MHz, $CDCl_3$): δ (ppm) 1.13 (3H, d, J = 6.3 Hz), 1.78 (2H, bs, NH_2), 2.72 (1H, dd, J = 8.0, 13.1, CH_aH_bS), 2.96 (1H, dd, J = 4.6, 13.1, CH_aH_bS), 2.99-3.08 (1H, m, $CHNH_2$), 7.18 (2H, apd, J = 8.5 Hz), 7.35 (2H, apd, J = 8.5 Hz).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ (ppm) 22.8, 43.9, 45.9, 119.8, 130.89, 131.84, 135.7.

MS (ESI, positive): 246.3 $[M+H]^+$.

(*S*)-1-(*p*-Tolylselanyl)propan-2-amine (16)



16

Following the general procedure, (*S*)-2-methylaziridine **10b** (9 mg, 0.15 mmol) and trimethyl(*p*-tolylselanyl)silane **14** (41 mg, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminoselenide **16** (55%, 18 mg) as a yellowish oil.

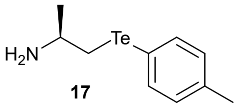
^{1}**H NMR** (400 MHz, $CDCl_3$): δ (ppm) 1.18 (3H, d, J = 6.3 Hz), 2.31 (3H, s), 2.48 (2H, bs, NH_2), 2.79 (1H, dd, J = 7.9, 12.3 Hz, $C\mathbf{H_a}H_bSe$), 2.99 (1H, dd, J = 4.8, 12.4 Hz, $CH_a\mathbf{H_b}Se$), 3.04-3.12 (1H, m, $C\mathbf{H}NH_2$), 7.07 (2H, ap d, J = 8.0 Hz), 7.42 (2H, ap d, J = 8.0 Hz).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ (ppm) 21.1, 23.0, 38.8, 46.7, 125.9, 133.4, 137.2.

^{77}**Se NMR** (76 MHz, $CDCl_3$): δ (ppm) 246.7.

MS (ESI, positive): 252.0 $[M+Na]^+$.

(*S*)-1-(*p*-Tolyltellanyl)propan-2-amine (17)



17

Following the general procedure, (*S*)-2-methylaziridine **10b** (9 mg, 0.15 mmol) and trimethyl(*p*-tolyltellanyl)silane **15** (53 mg, 0.18 mmol) gave, after flash column chromatography (petroleum ether/EtOAc 1:2), β-aminotelluride **17** (69%, 29 mg) as a yellowish oil.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ (ppm) 1.19 (3H, d, J = 6.2 Hz), 2.15 (2H, bs, NH_2), 2.33 (3H, s), 2.87 (1H, dd, J = 7.1, 11.0 Hz, $C\mathbf{H_a}H_bTe$), 3.04 (1H, dd, J = 5.1, 11.9 Hz, $CH_a\mathbf{H_b}Te$), 3.08-3.15 (1H, m, $C\mathbf{H}NH_2$), 7.01

(2H, ap d, *J* = 7.9 Hz), 7.64 (2H, ap d, *J* = 7.09 Hz).

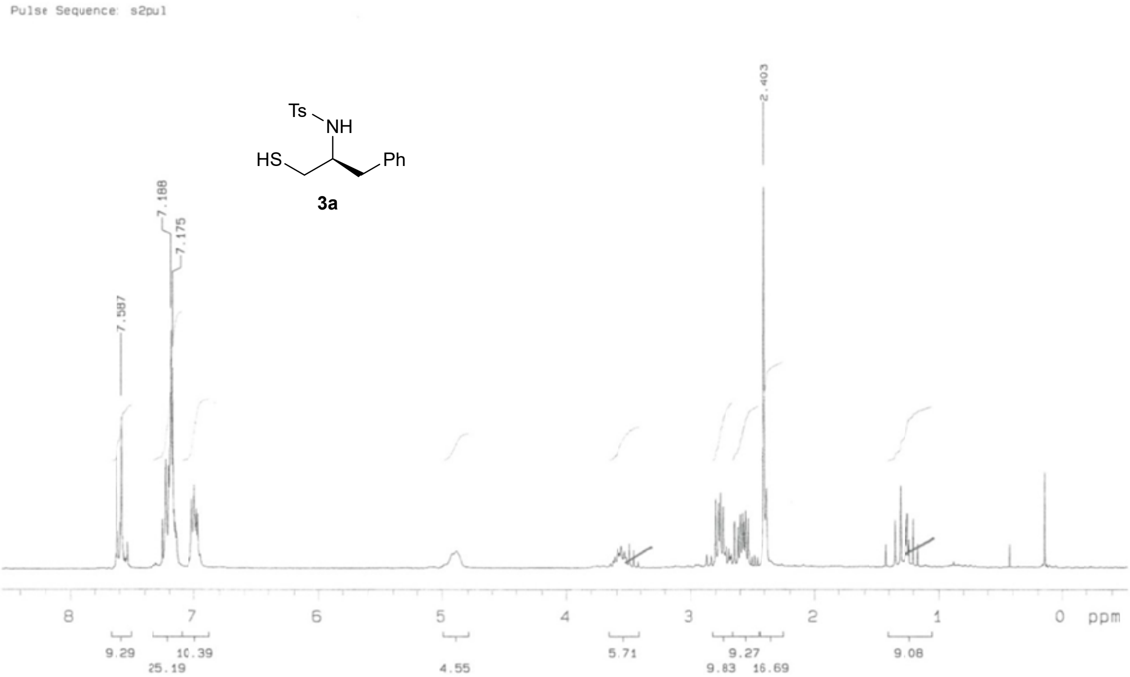
^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 21.2, 22.0, 24.4, 47.7, 107.3, 130.2, 137.7, 138.8.

^{125}Te (126 MHz, $CDCl_3$): δ (ppm) 377.1

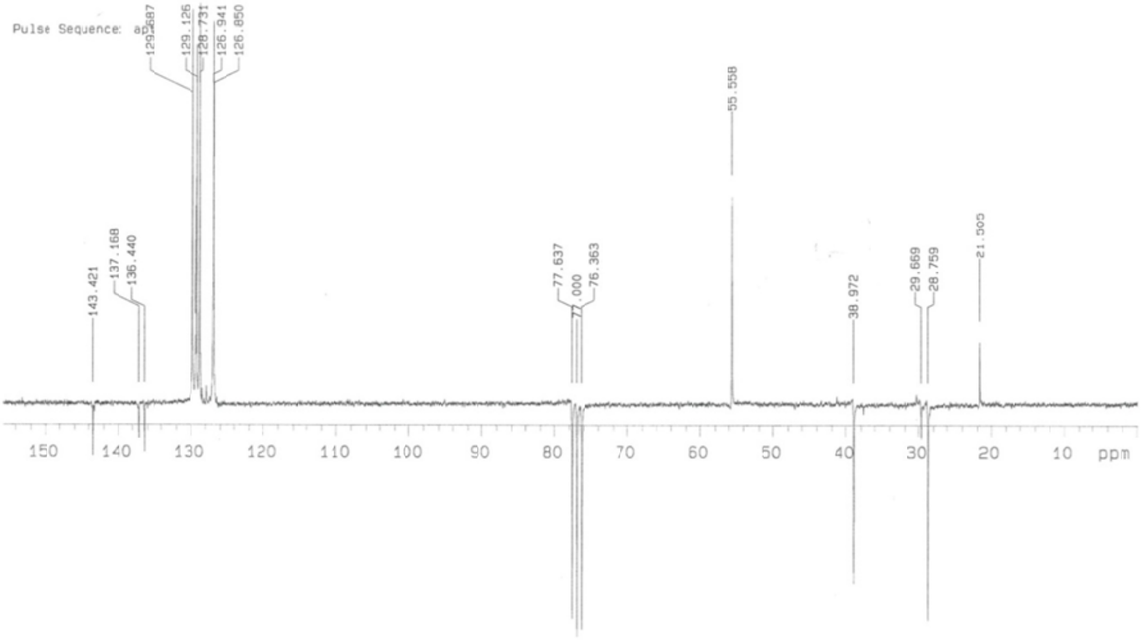
MS (ESI, positive): 302.1 $[M\text{+Na}]^+$.

3. Copy of NMR spectra of new compounds

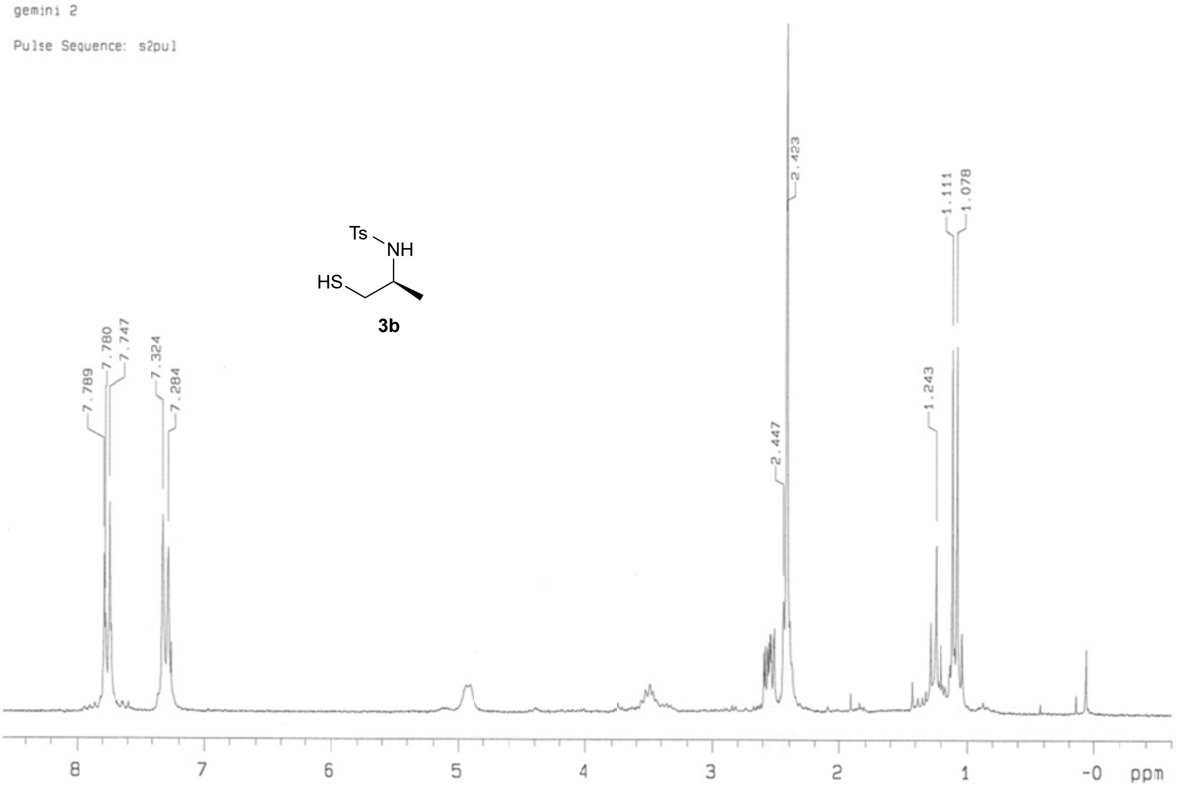
^{1}H NMR spectrum of compound **3a** (200 MHz, CDCl$_3$)



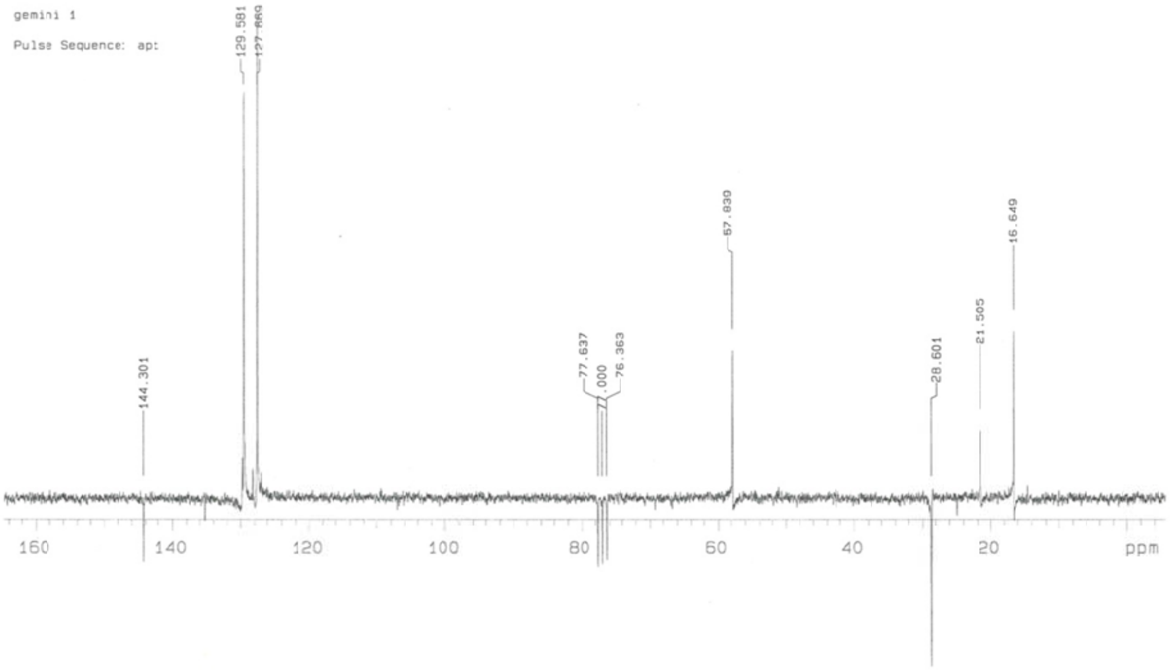
^{13}C NMR spectrum of compound **3a** (50 MHz, CDCl$_3$)



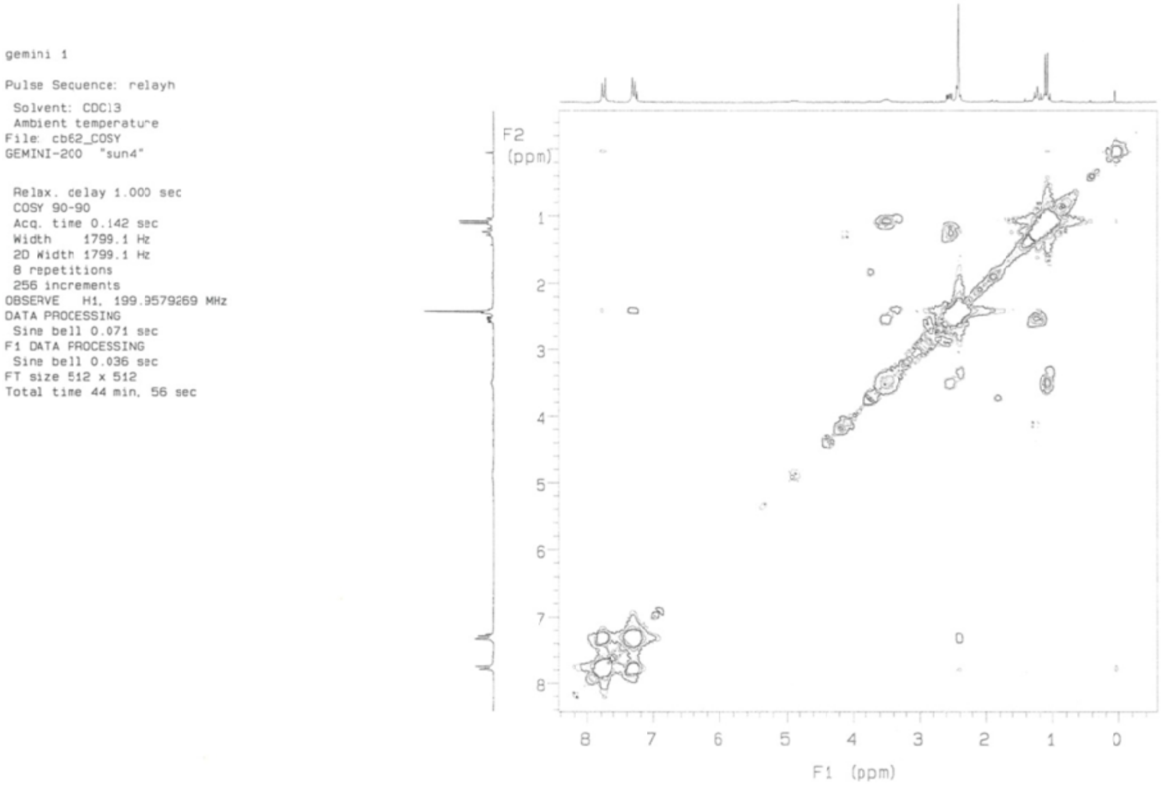
^{1}H NMR spectrum of compound **3b** (200 MHz, $CDCl_3$)



^{13}C NMR (APT) spectrum of compound **3b** (50 MHz, $CDCl_3$)



^{1}H-^{1}H COSY spectrum of compound **3b** (200 MHz, $CDCl_3$)



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gemini 1

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 Acq. time 0.142 sec
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 2D Width 1799.1 Hz
 8 repetitions
 256 increments
OBSERVE   H1, 199.9579269 MHz
DATA PROCESSING
 Sine bell 0.071 sec
F1 DATA PROCESSING
 Sine bell 0.036 sec
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Total time 44 min, 56 sec
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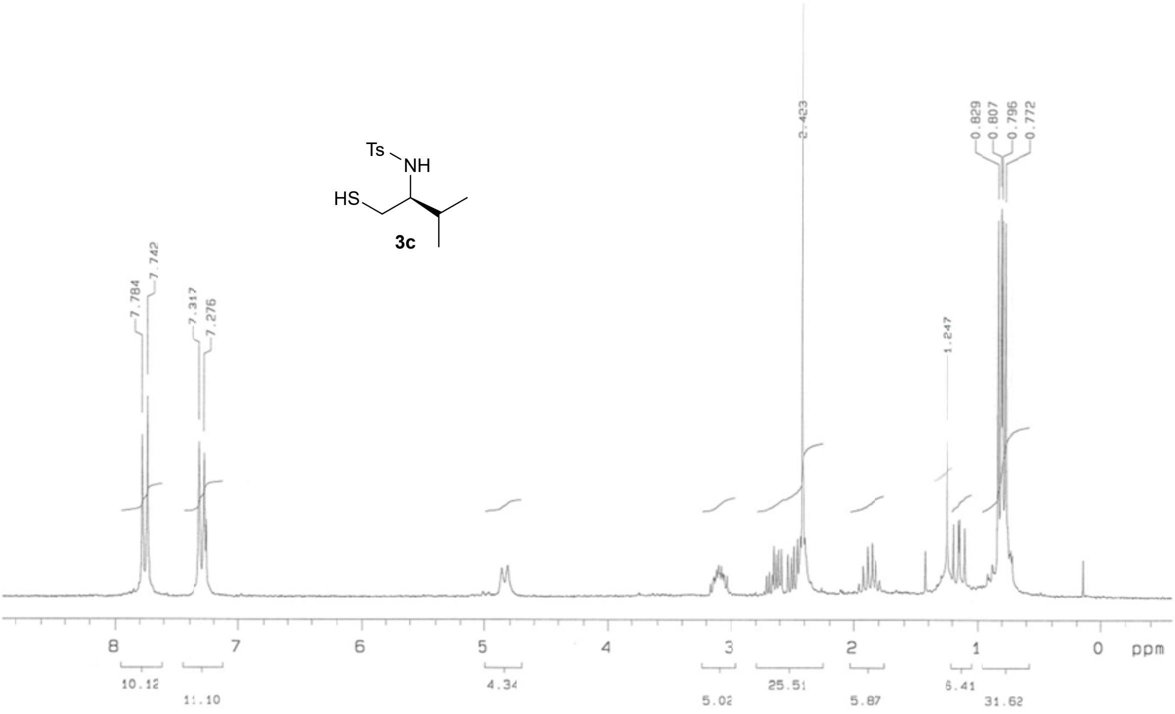
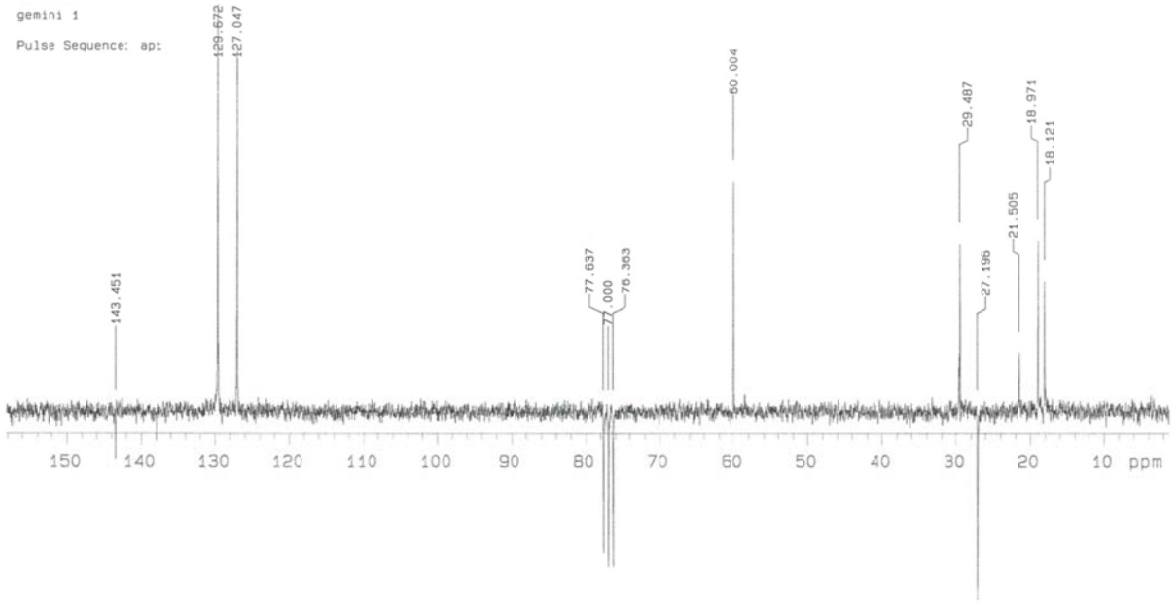
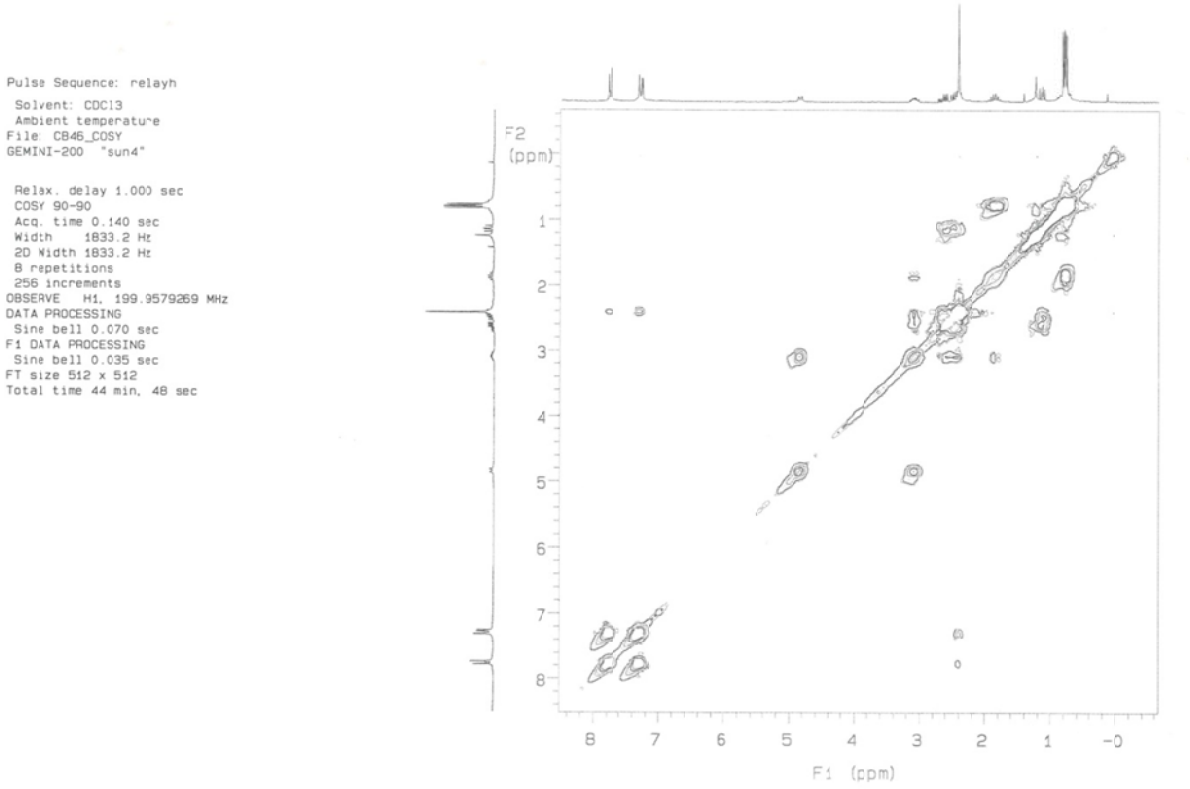
^{1}H NMR spectrum of compound **3c** (200 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **3c** (50 MHz, $CDCl_3$)



^{1}H-^{1}H COSY spectrum of compound **3c** (200 MHz, $CDCl_3$)



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 Ambient temperature
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 Acq. time 0.140 sec
 Width     1833.2 Hz
 2D Width 1833.2 Hz
 8 repetitions
 256 increments
OBSERVE   H1, 199.9579269 MHz
DATA PROCESSING
 Sine bell 0.070 sec
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 Sine bell 0.035 sec
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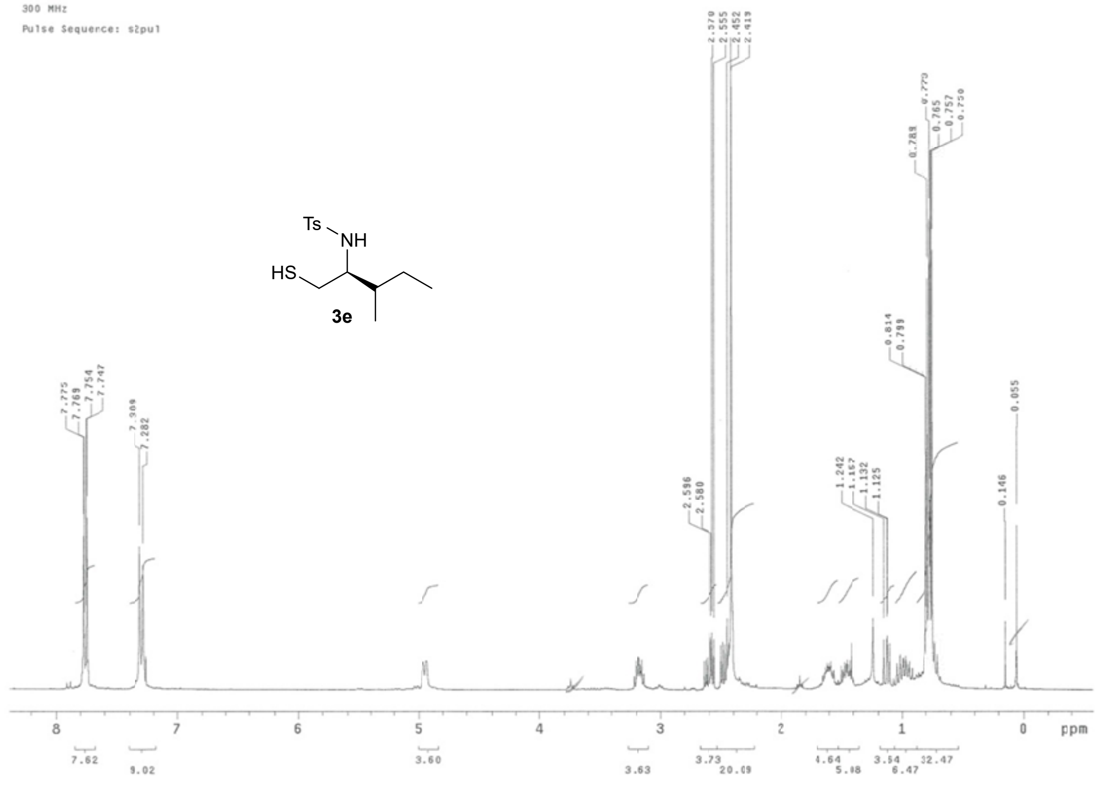
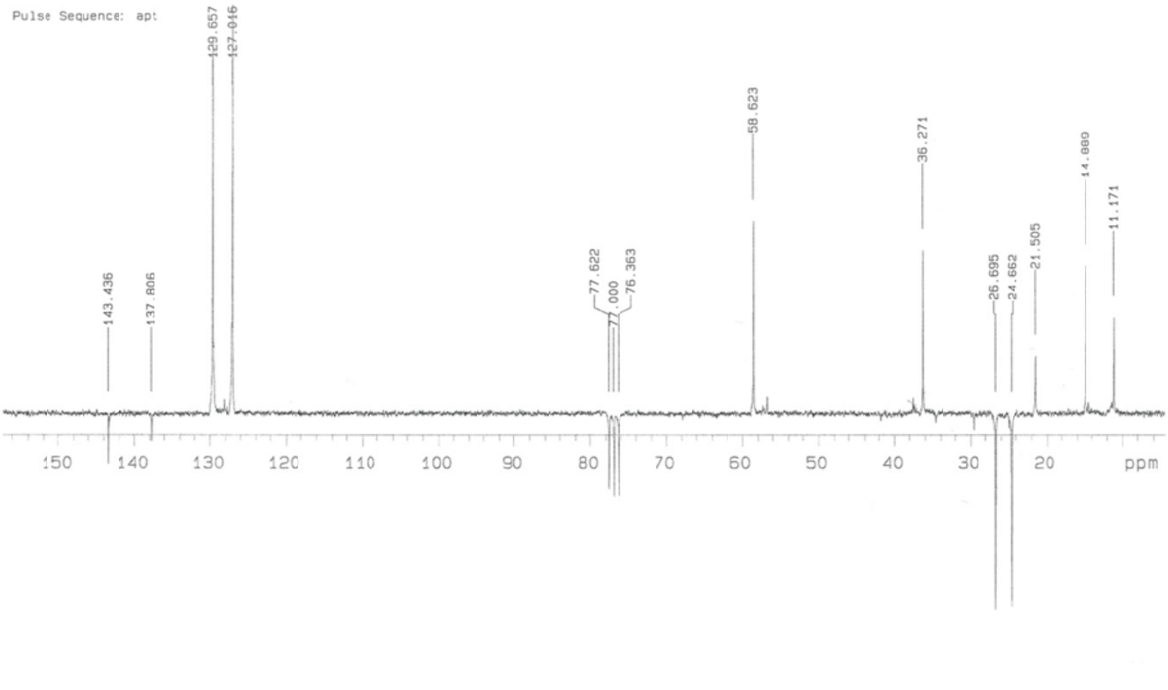
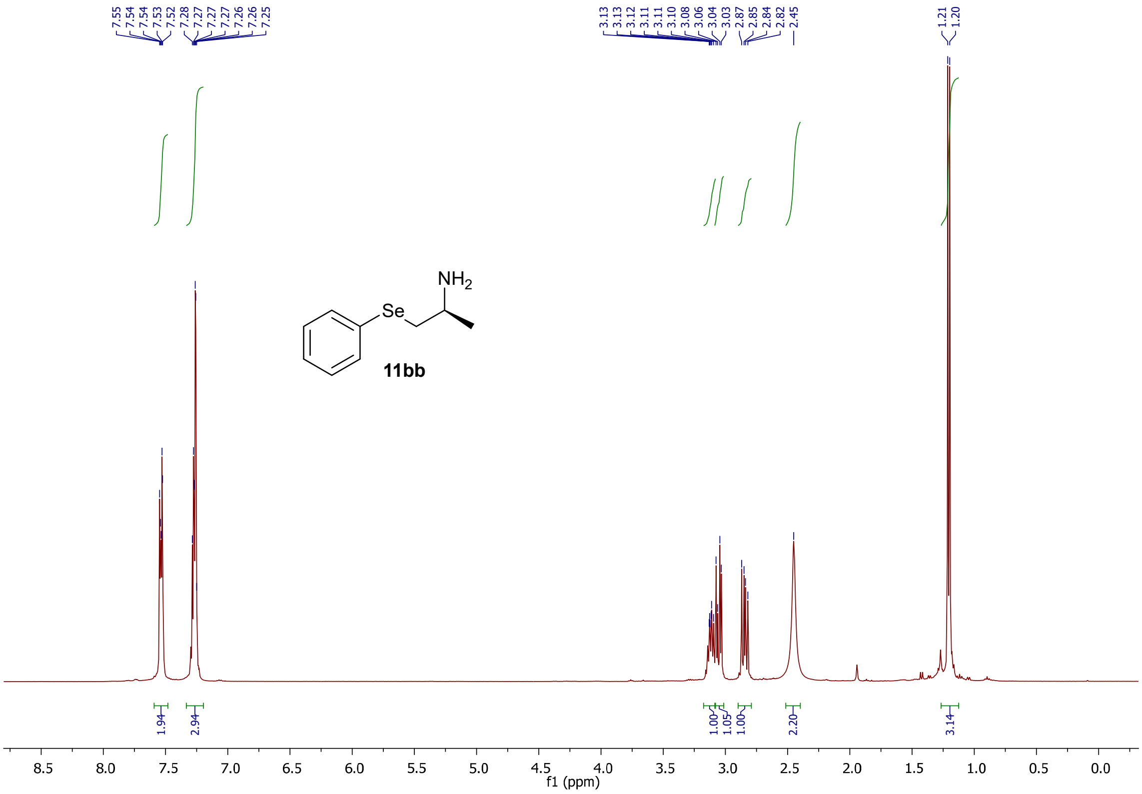
^{1}H NMR spectrum of compound **3d** (300 MHz, $CDCl_3$)



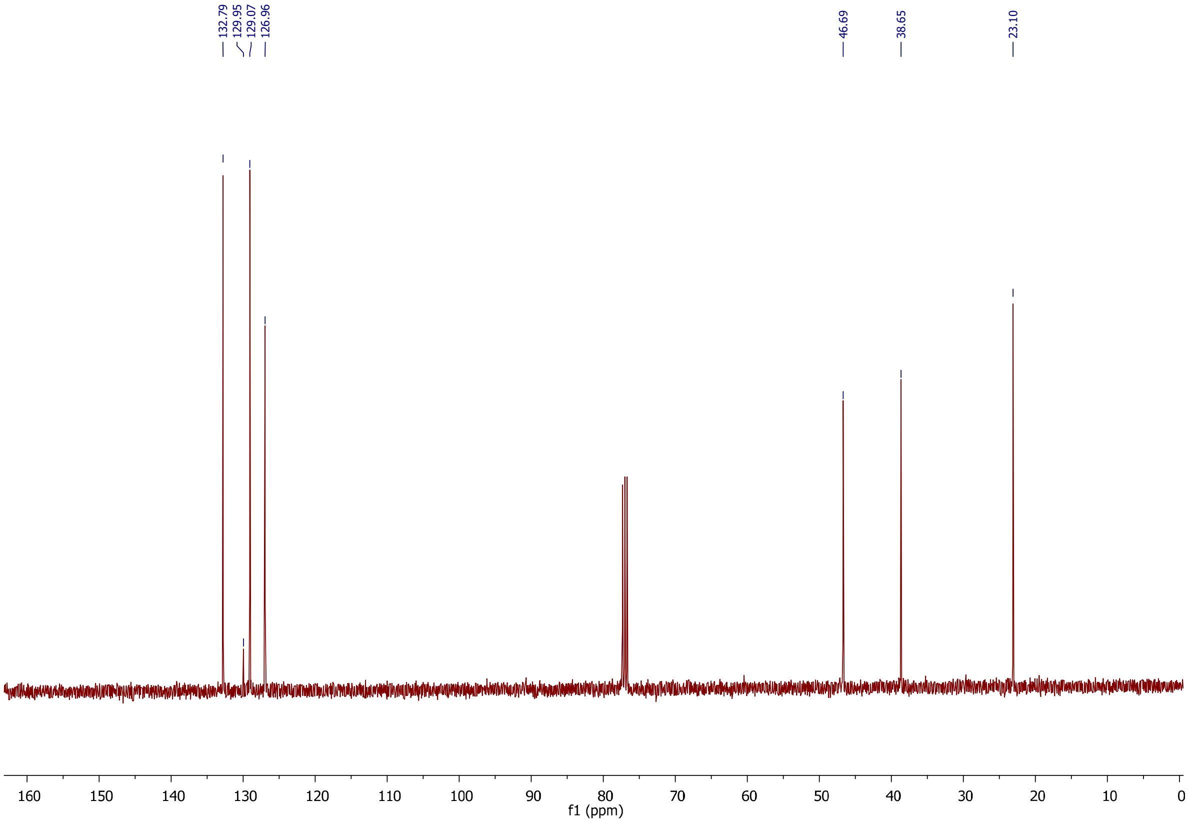
^{13}C NMR spectrum of compound **3d** (50 MHz, $CDCl_3$)



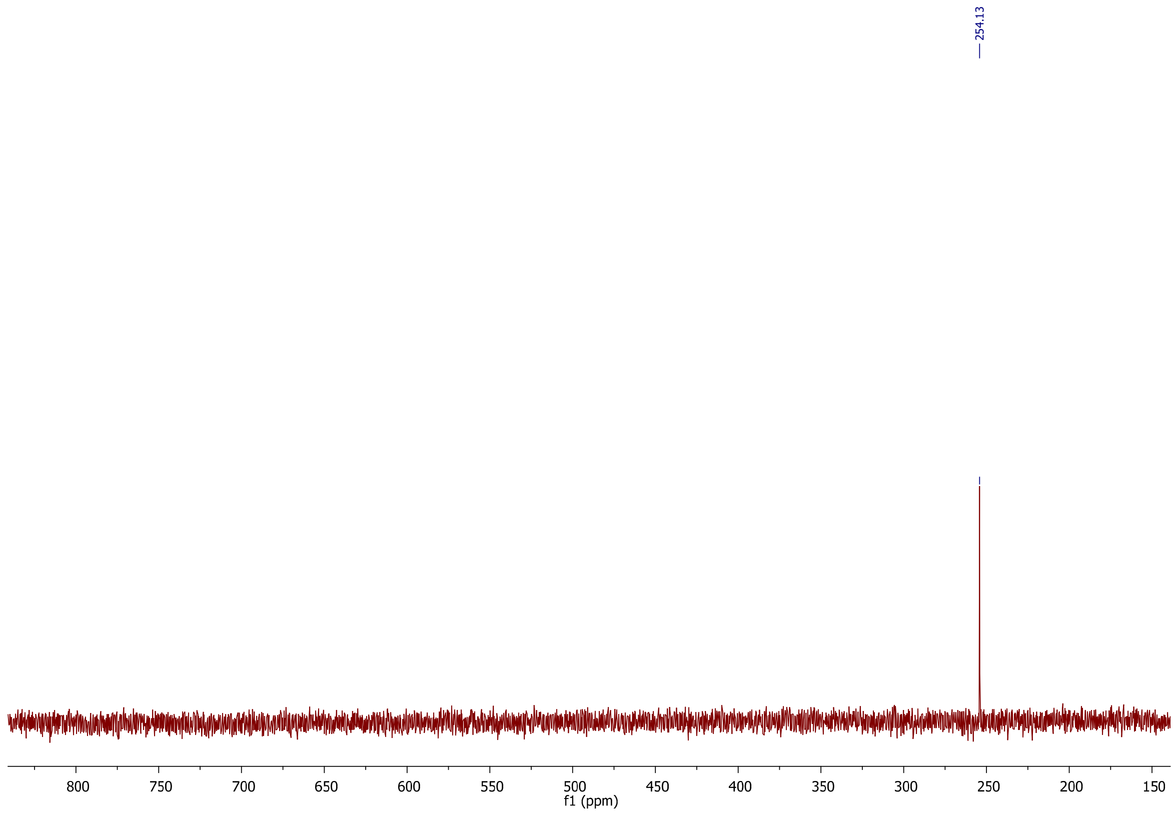
^{1}H NMR spectrum of compound **11bb** (400 MHz, CDCl$_3$)



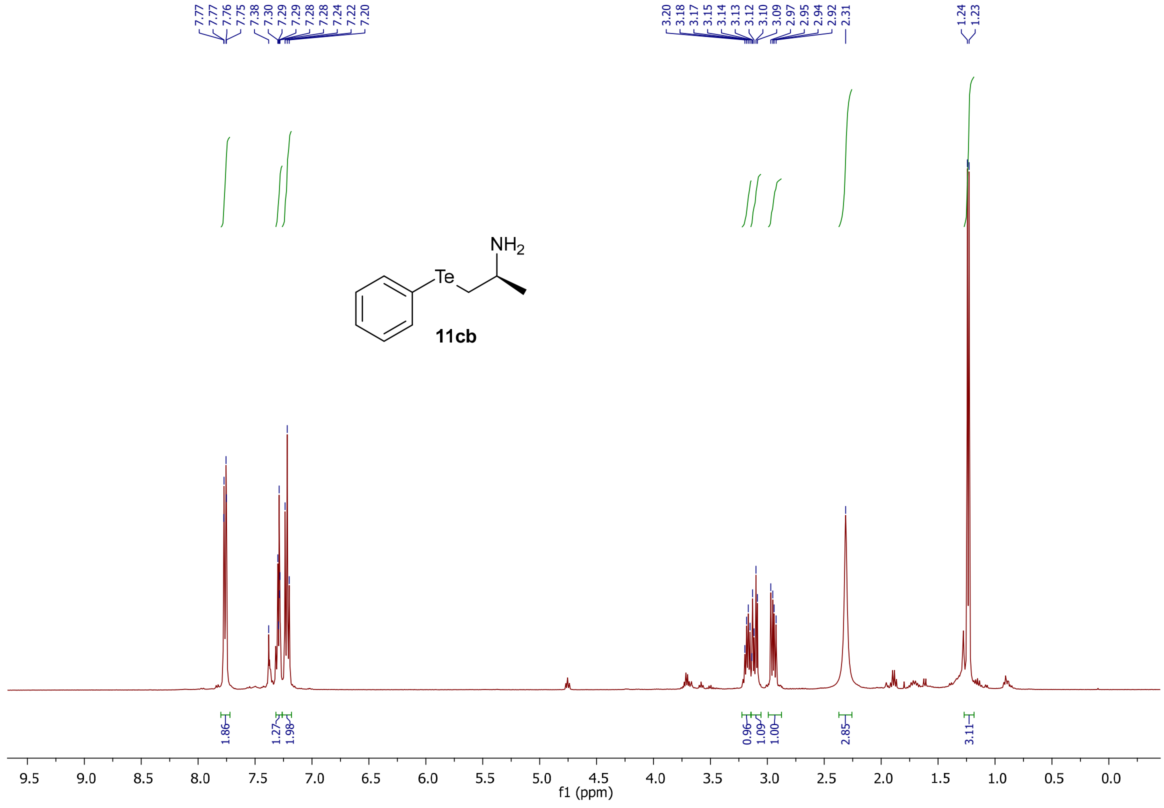
^{13}C NMR spectrum of compound **11bb** (100 MHz, CDCl$_3$)



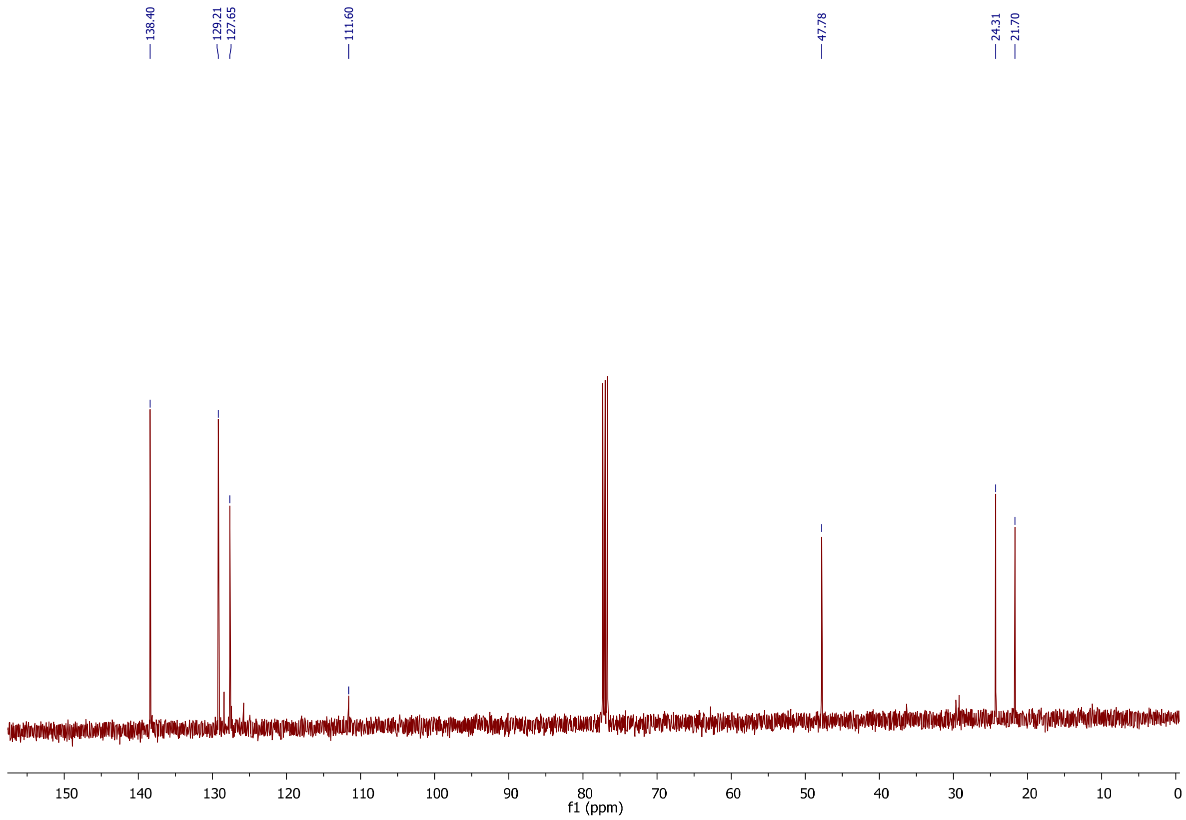
^{77}Se NMR spectrum of compound **11bb** (76 MHz, CDCl$_3$)



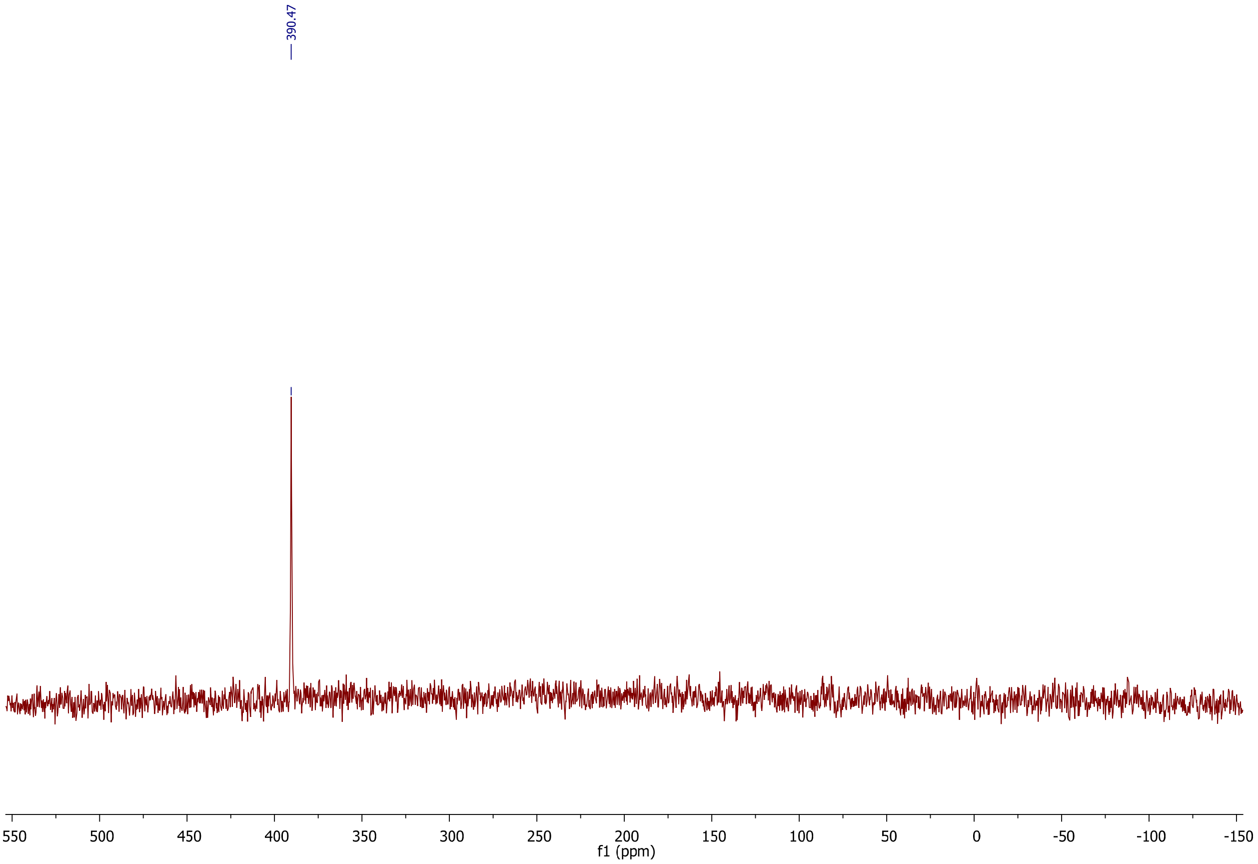
^{1}H NMR spectrum of compound **11cb** (400 MHz, CDCl$_3$)



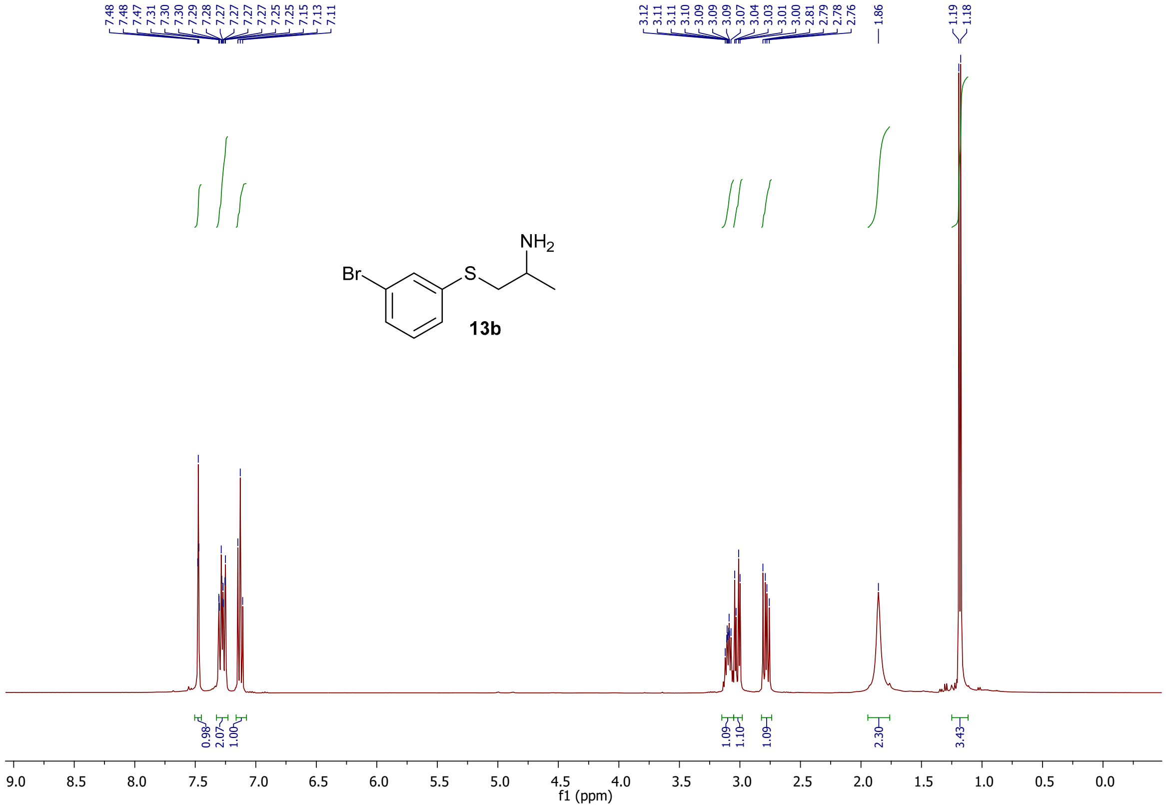
^{13}C NMR spectrum of compound **11cb** (100 MHz, CDCl$_3$)



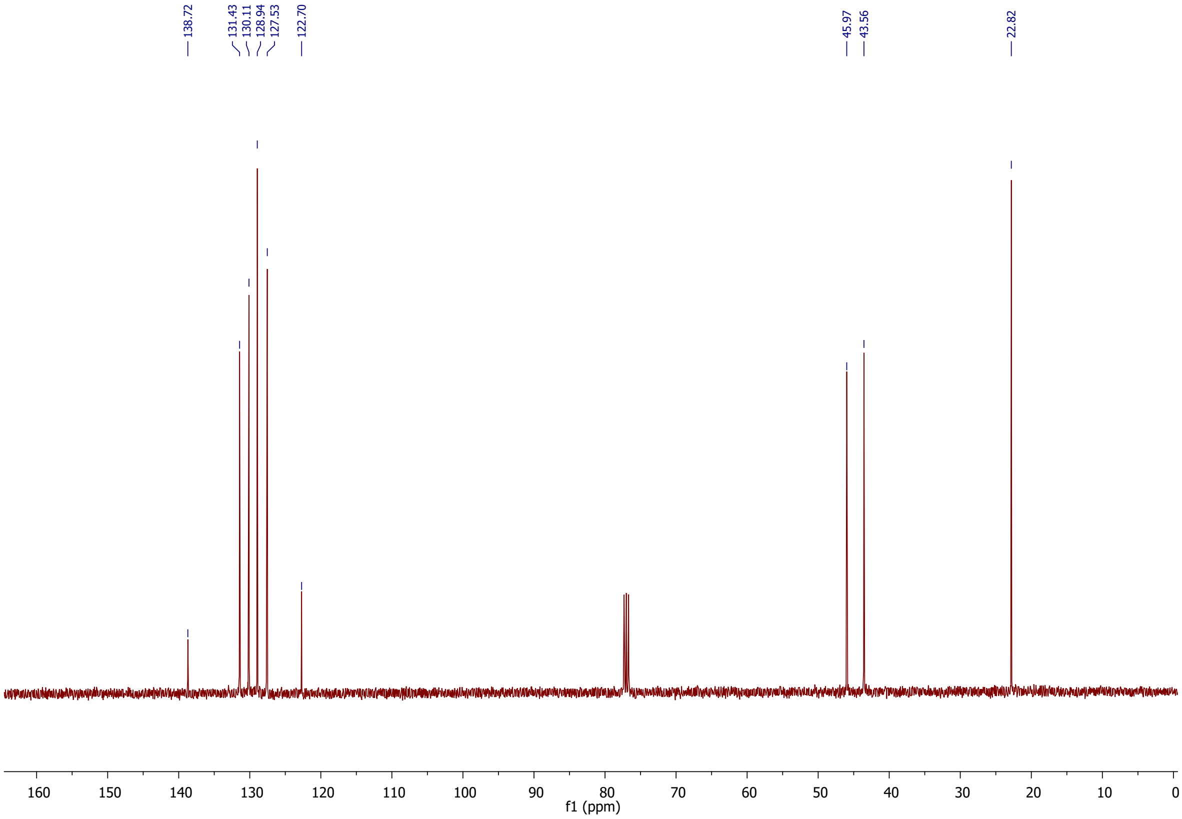
^{125}Te NMR spectrum of compound **11cb** (126 MHz, CDCl$_3$)



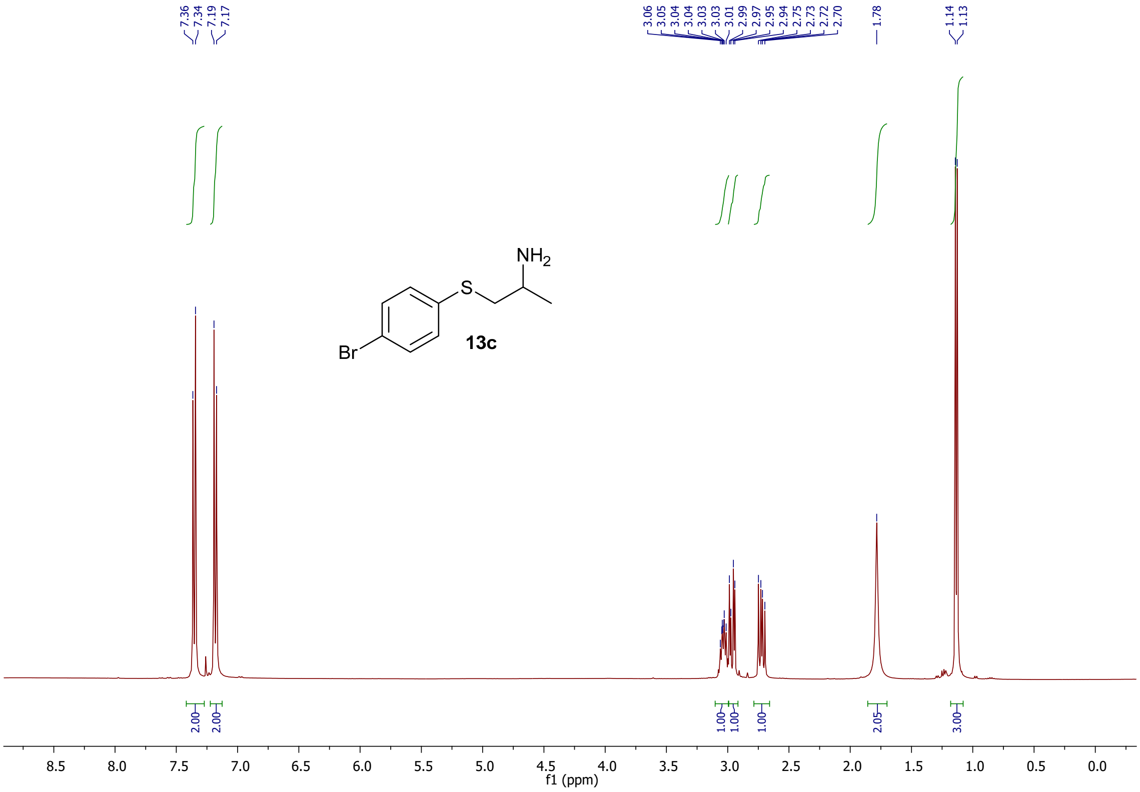
^{1}H NMR of compound **13b** (400 MHz, $CDCl_3$)



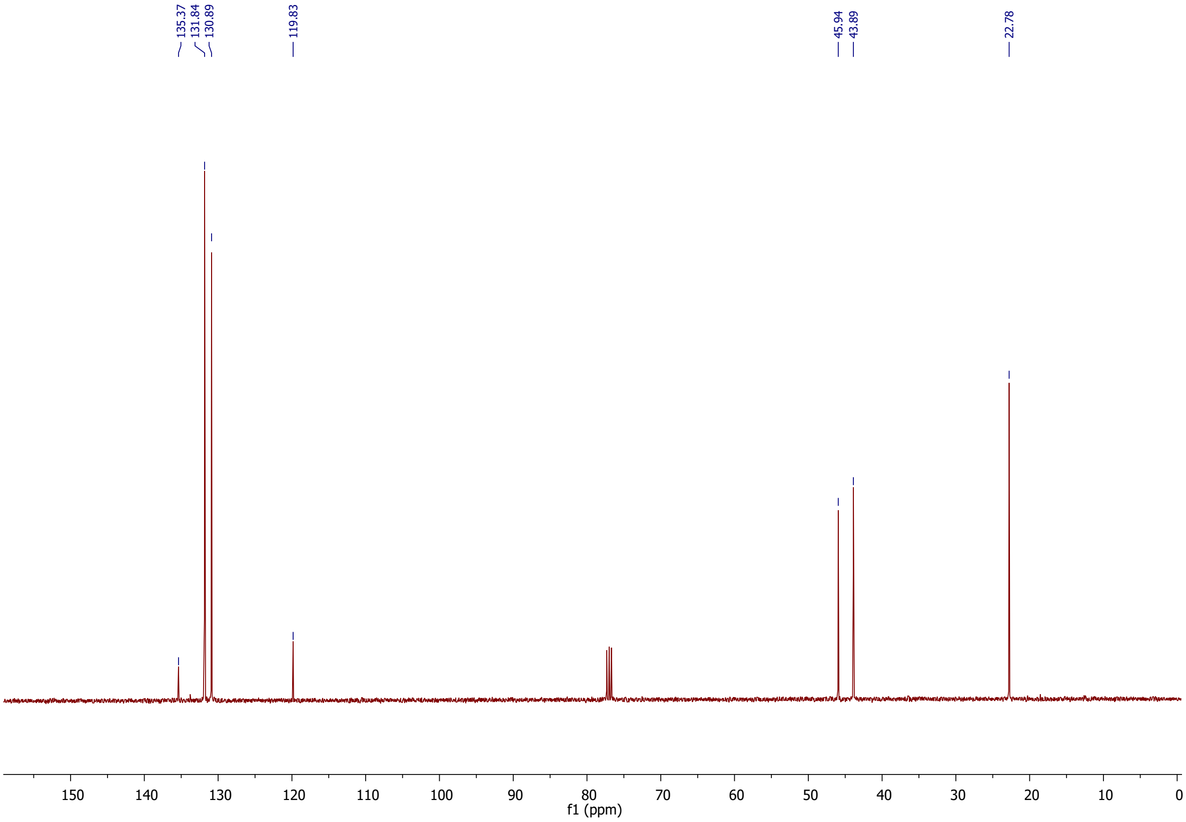
^{13}C NMR of compound **13b** (100 MHz, $CDCl_3$)



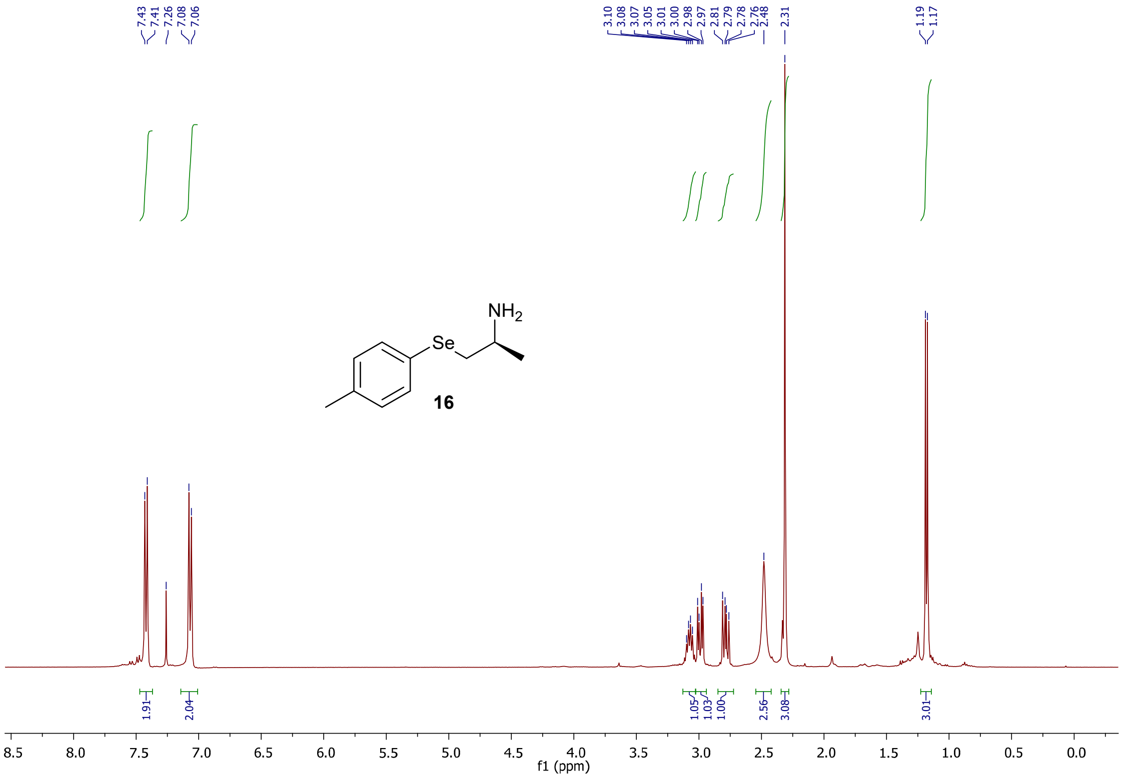
^{1}H NMR of compound **13c** (400 MHz, $CDCl_3$)



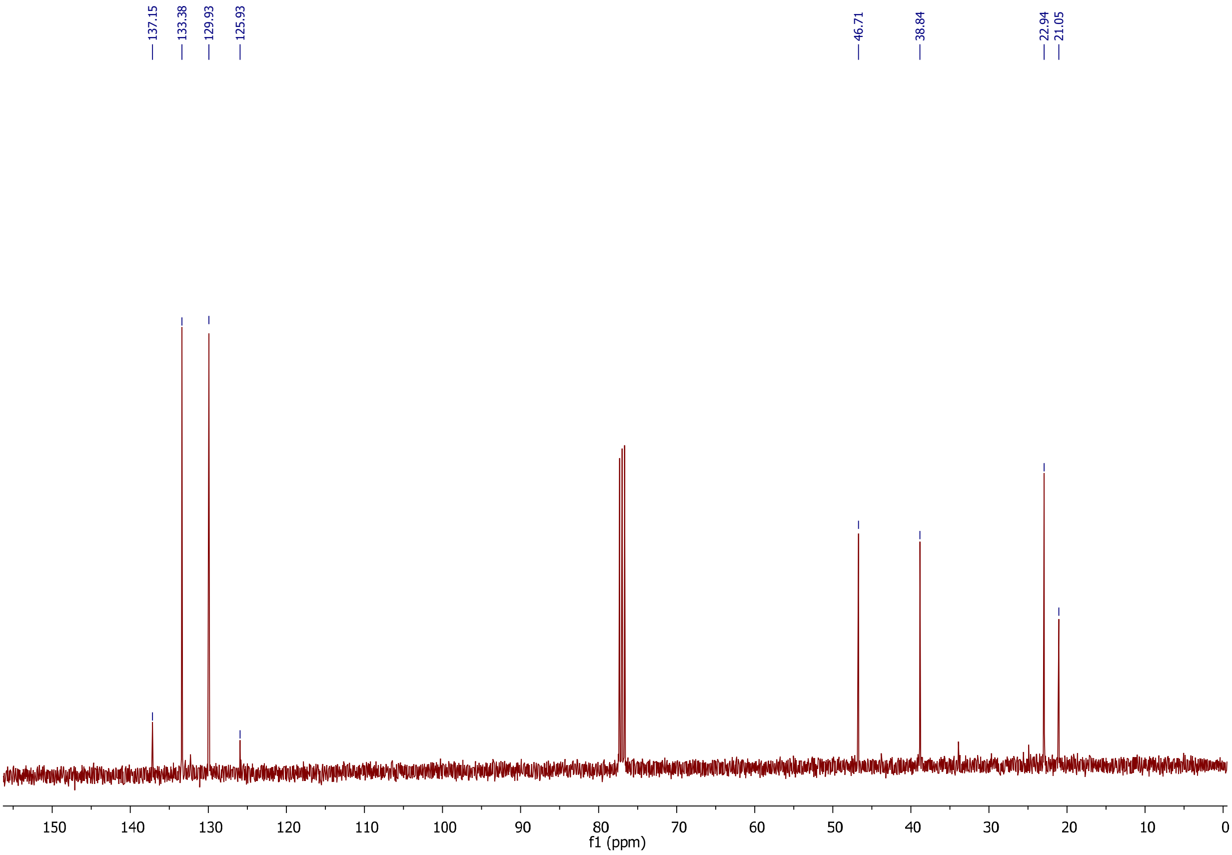
^{13}C NMR of compound **13c** (100 MHz, $CDCl_3$)



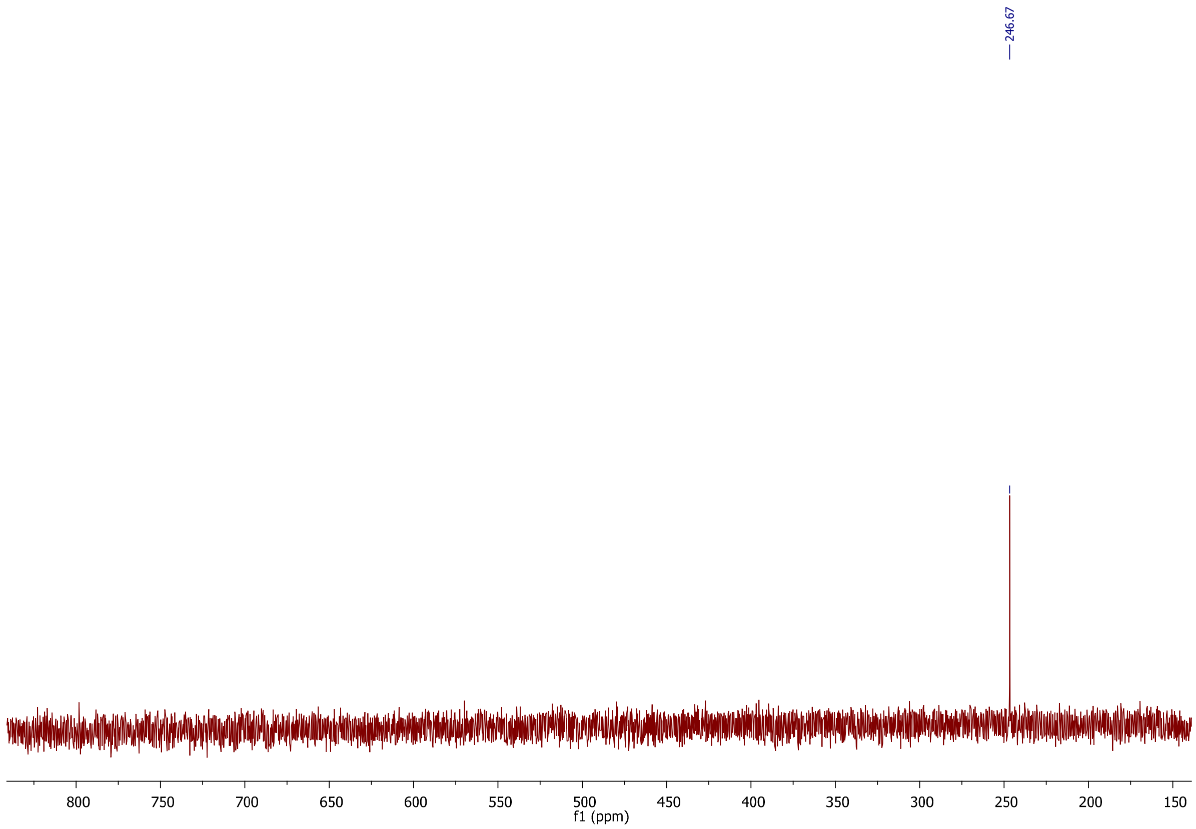
^{1}H NMR spectrum of compound **16** (400 MHz, CDCl$_3$)



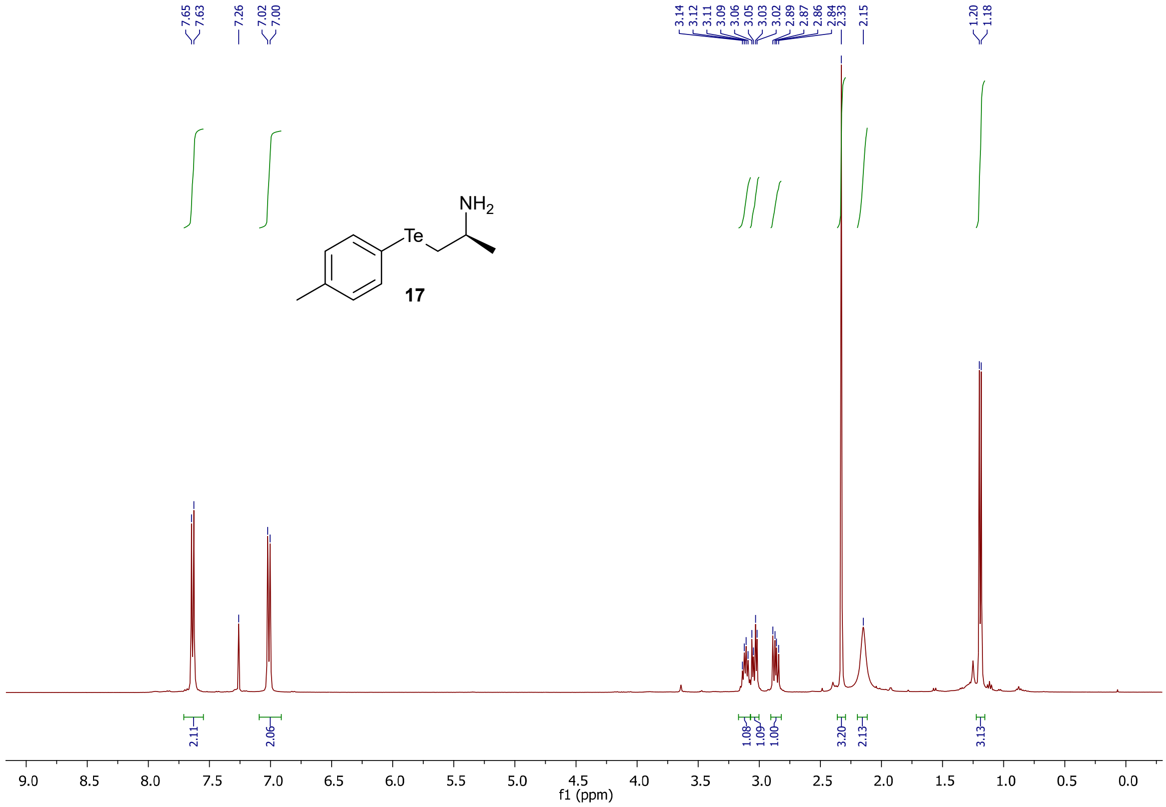
^{13}C NMR spectrum of compound **16** (100 MHz, CDCl$_3$)



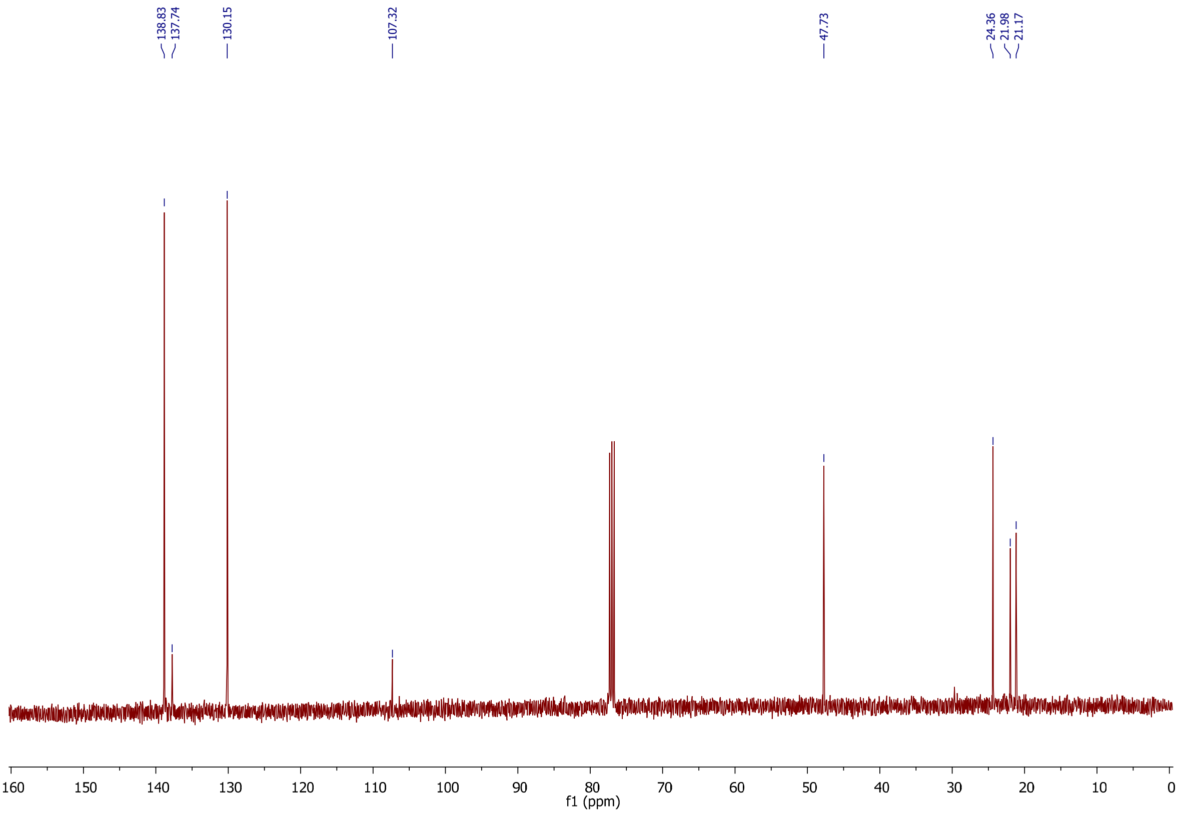
^{77}Se NMR spectrum of compound **16** (76 MHz, $CDCl_3$)



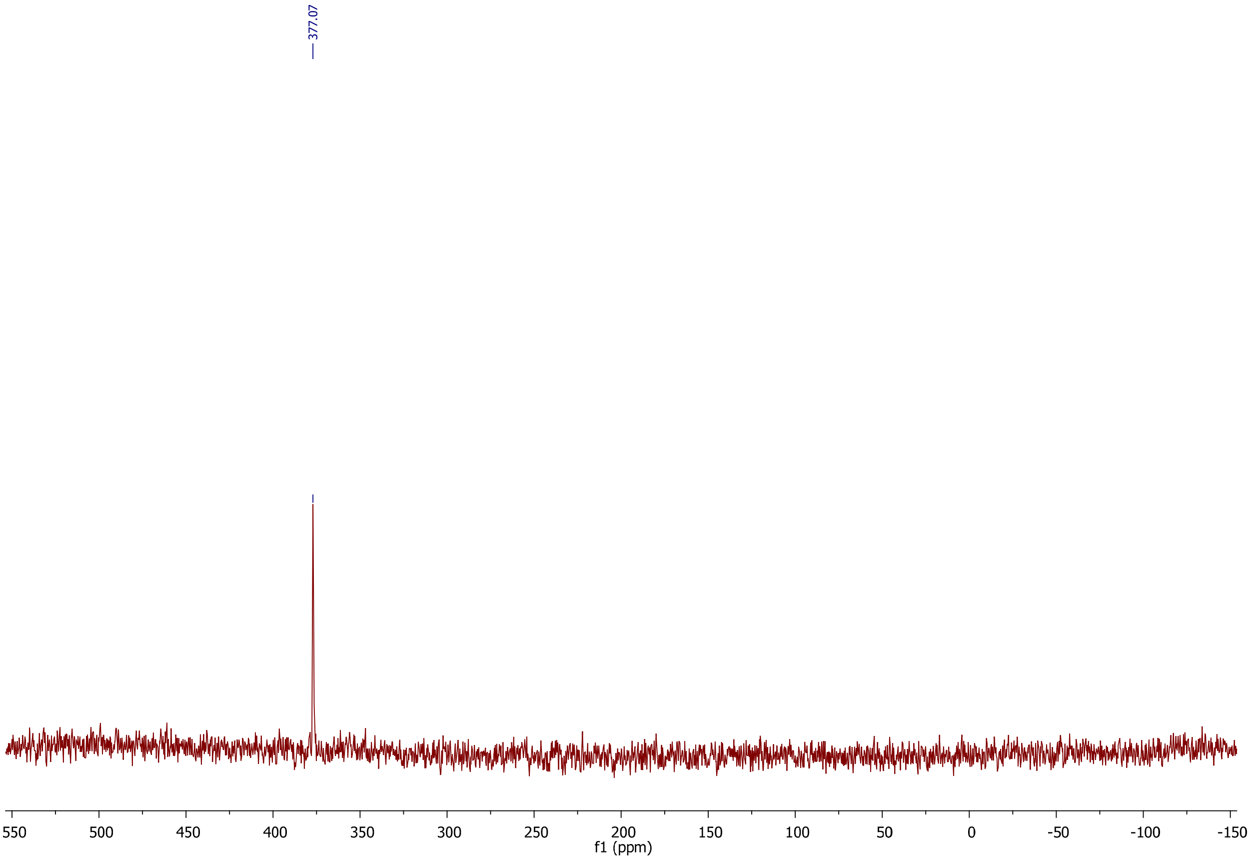
^{1}H NMR spectrum of compound **17** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **17** (100 MHz, $CDCl_3$)



^{125}Te NMR spectrum of compound **17** (126 MHz, $CDCl_3$)



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