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

Synthesis of new chiral N-heterocyclic diselenides and their application in alkoxyselenylation reaction

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Supporting Information

Spectral Data

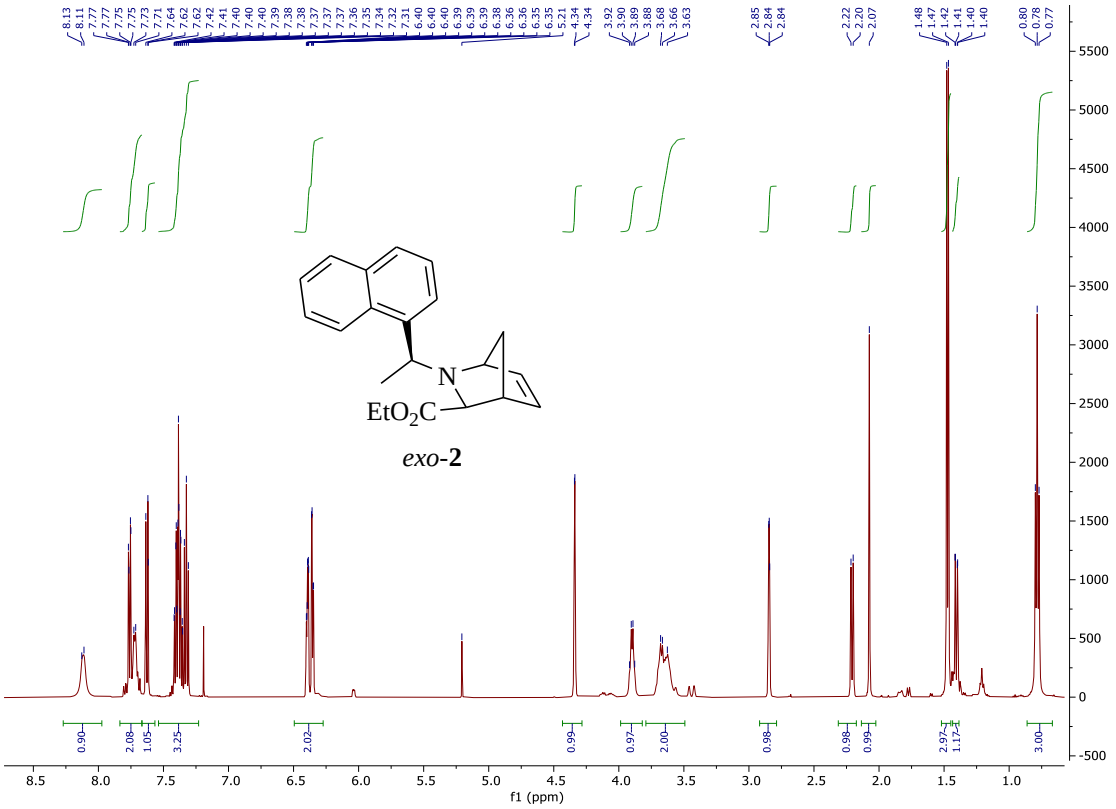


Figure S1. ^{1}H NMR spectrum of *exo*-(1*S*,3*S*,4*R*)-ethyl-2-((*R*)-1-(naphthalen-1-yl)ethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate **2** (400 MHz, chloroform-*d*).

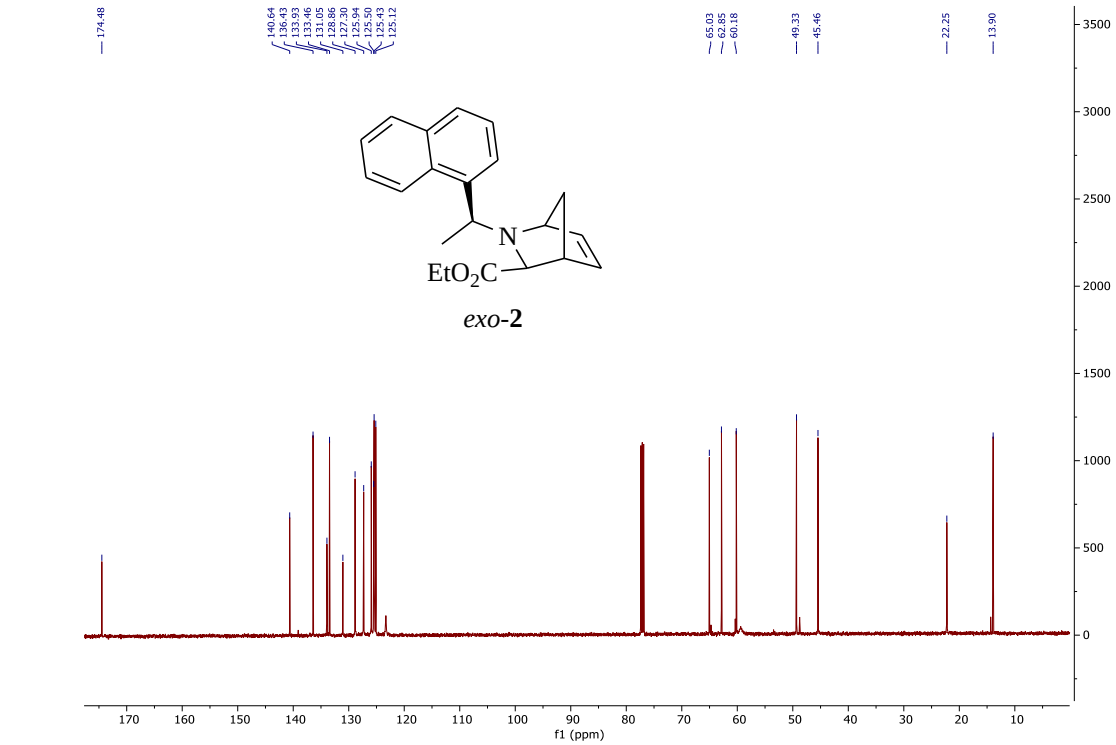


Figure S2. ^{13}C NMR spectrum of *exo*-(1*S*,3*S*,4*R*)-ethyl-2-((*R*)-1-(naphthalen-1-yl)ethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate **2** (100 MHz, chloroform-*d*).

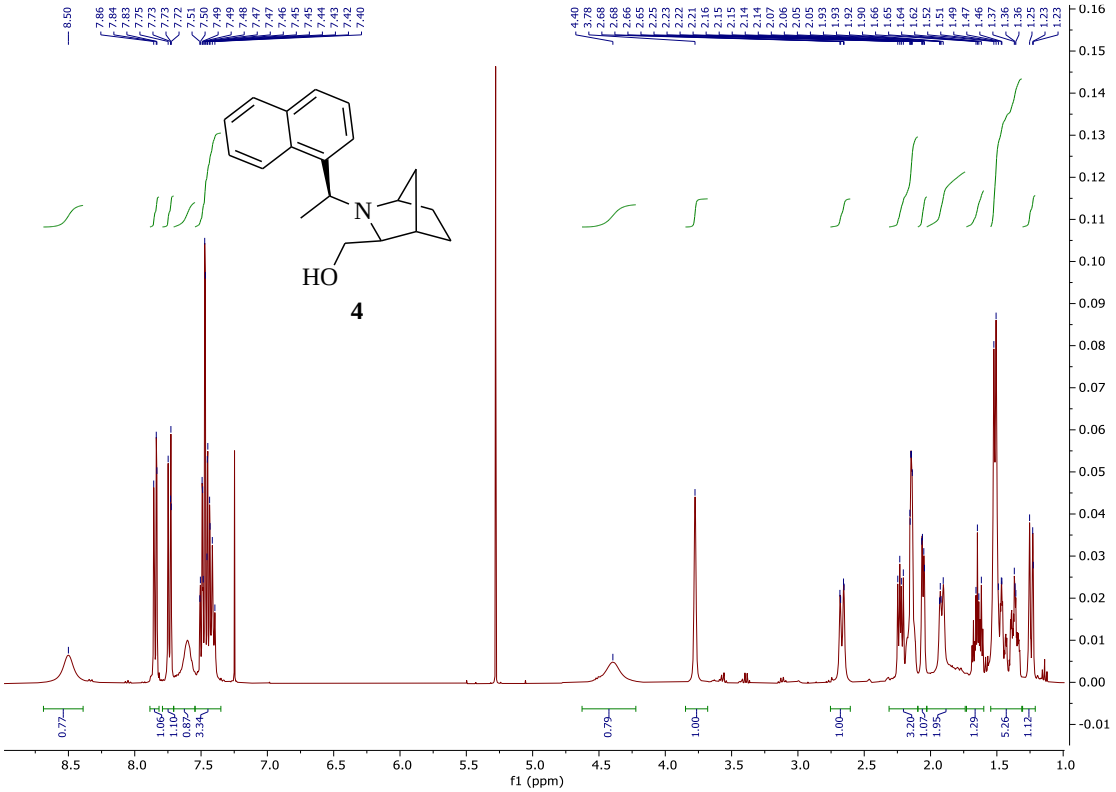


Figure S3. ^{1}H NMR spectrum of ((1*R*,3*S*,4*S*)-2-((*R*)-1-(naphthalen-1-yl)ethyl)-2-azabicyclo[2.2.1] heptan-3-yl)methanol **4** (400 MHz, chloroform-*d*).

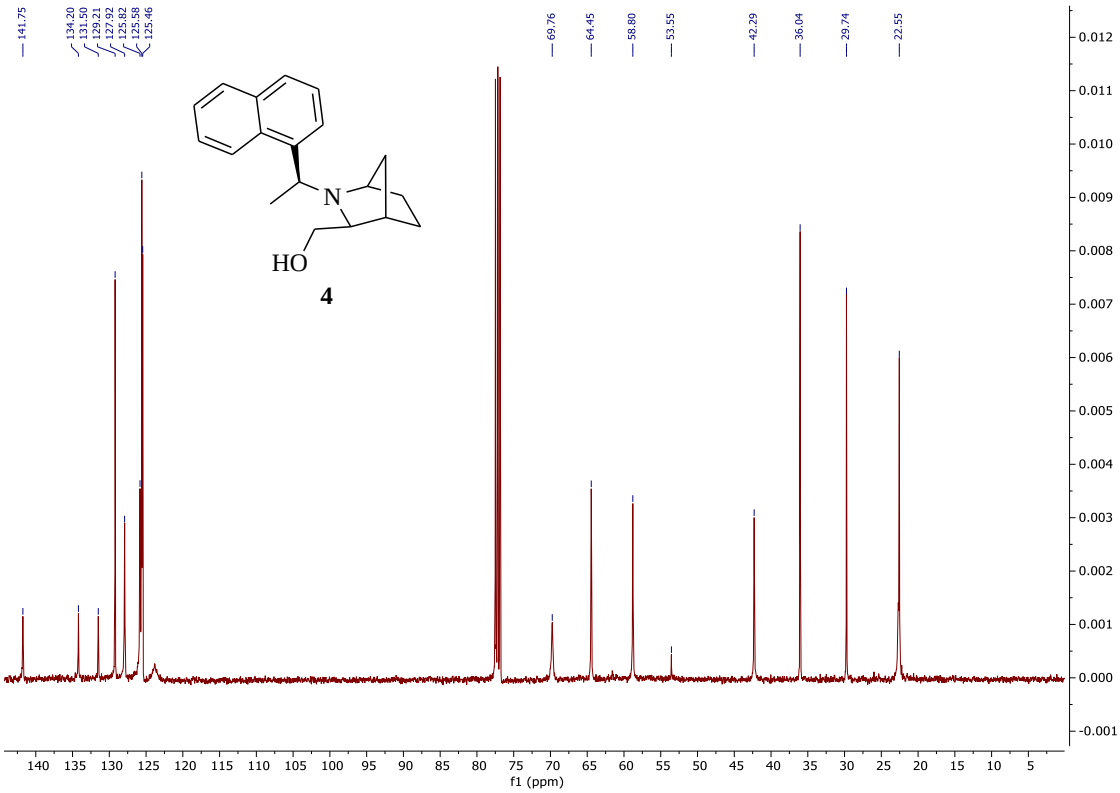


Figure S4. ^{13}C NMR spectrum of ((1*R*,3*S*,4*S*)-2-((*R*)-1-(naphthalen-1-yl)ethyl)-2-azabicyclo[2.2.1] heptan-3-yl)methanol **4** (100 MHz, chloroform-*d*).

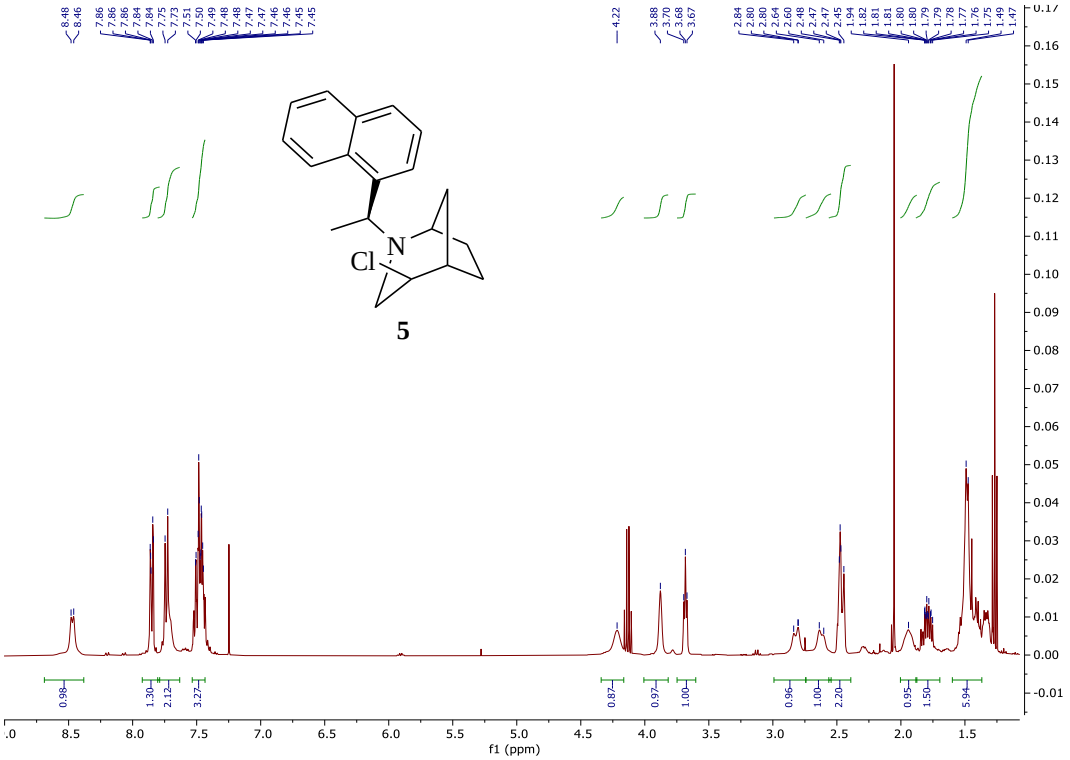


Figure S5. [1]H NMR spectrum of (1*R*,4*R*,5*S*)-4-chloro-2-((*R*)-1-(naphthalen-1-yl)ethyl)-2-azabicyclo[3.2.1]octane **5** (400 MHz, chloroform-*d*).

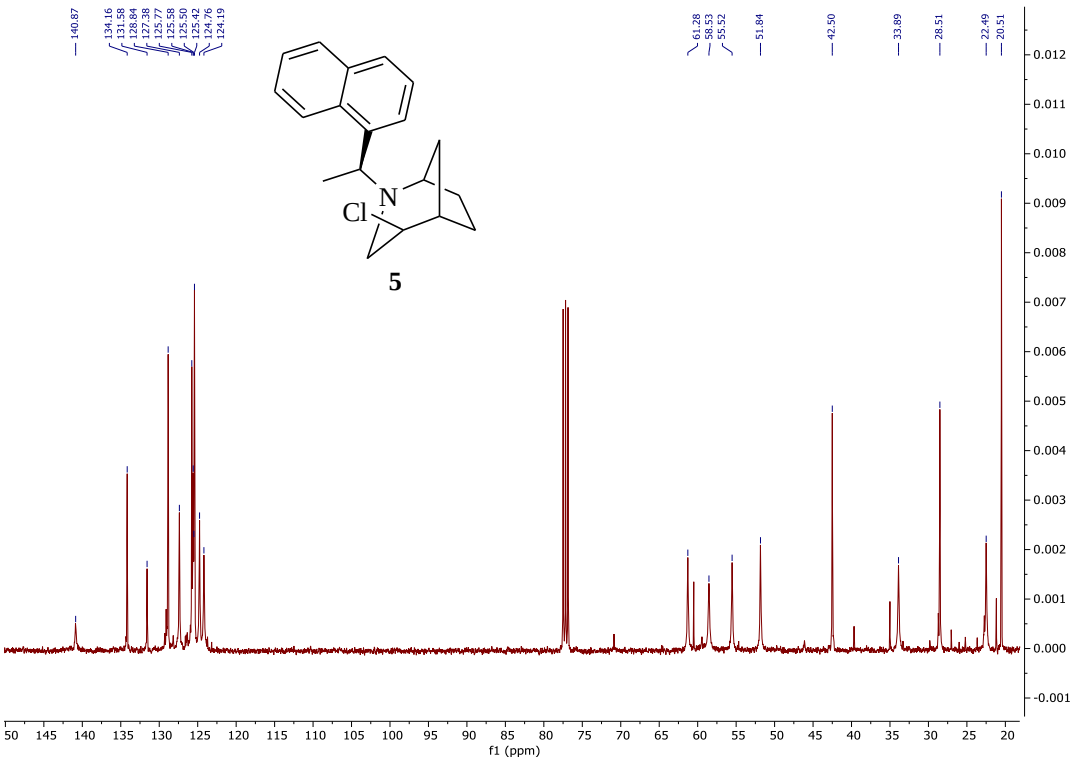


Figure S6. [13]C NMR spectrum of (1*R*,4*R*,5*S*)-4-chloro-2-((*R*)-1-(naphthalen-1-yl)ethyl)-2-azabicyclo[3.2.1]octane **5** (100 MHz, chloroform-*d*).

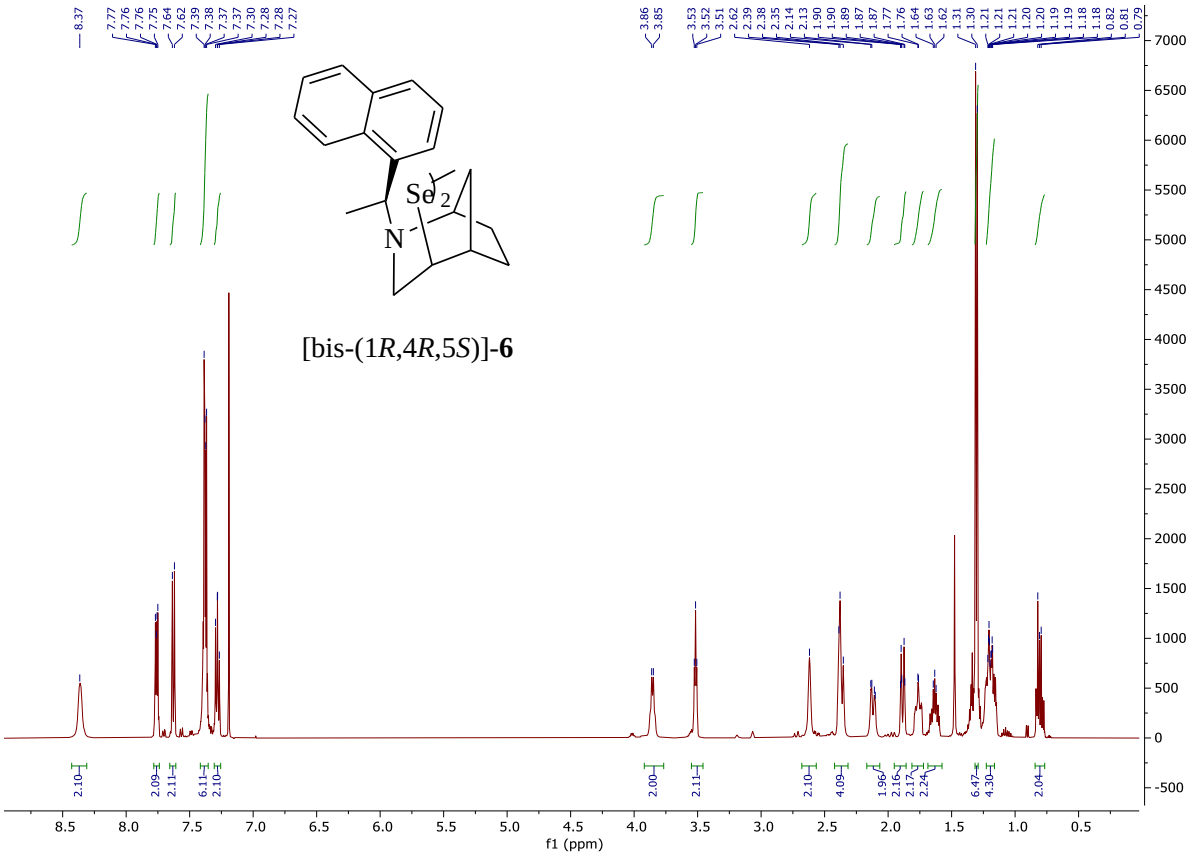


Figure S7. ^{1}H NMR spectrum of bis{(1*R*,4*R*,5*S*)-2-[(*R*)-1-(2-naphtyl)ethyl]-2-azabicyclo[3.2.1]octan-4-yl} diselenide **6** (400 MHz, chloroform-*d*).

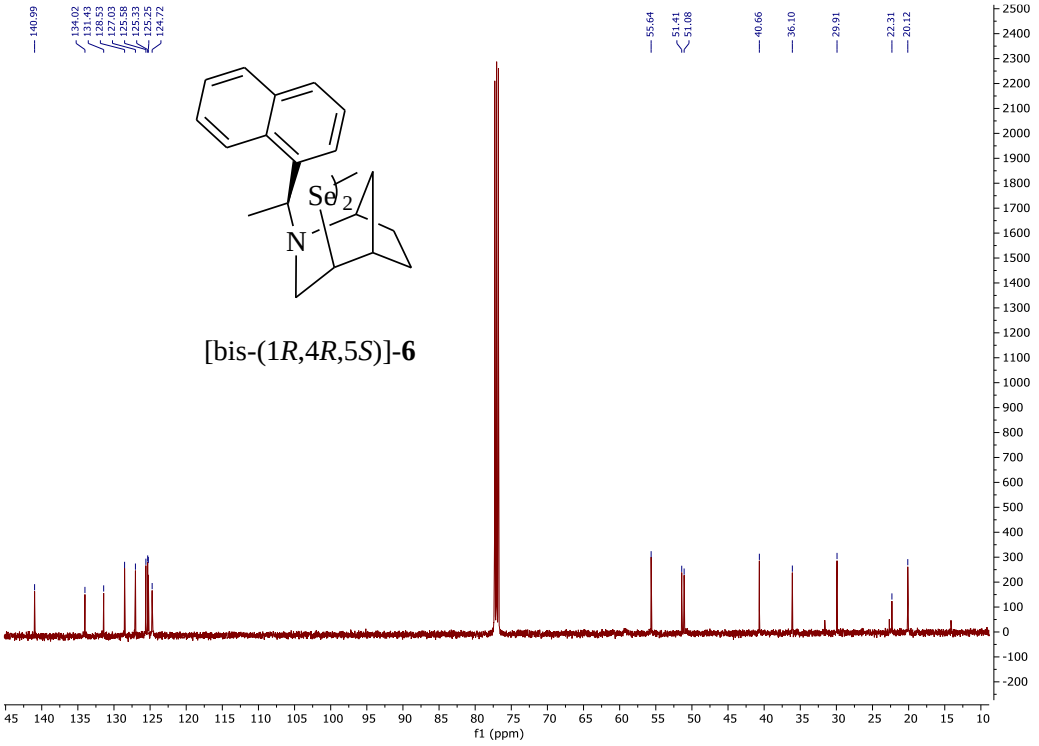


Figure S8. ^{13}C NMR spectrum of bis{(1*R*,4*R*,5*S*)-2-[(*R*)-1-(2-naphtyl)ethyl]-2-azabicyclo[3.2.1]octan-4-yl} diselenide **6** (100 MHz, chloroform-*d*).

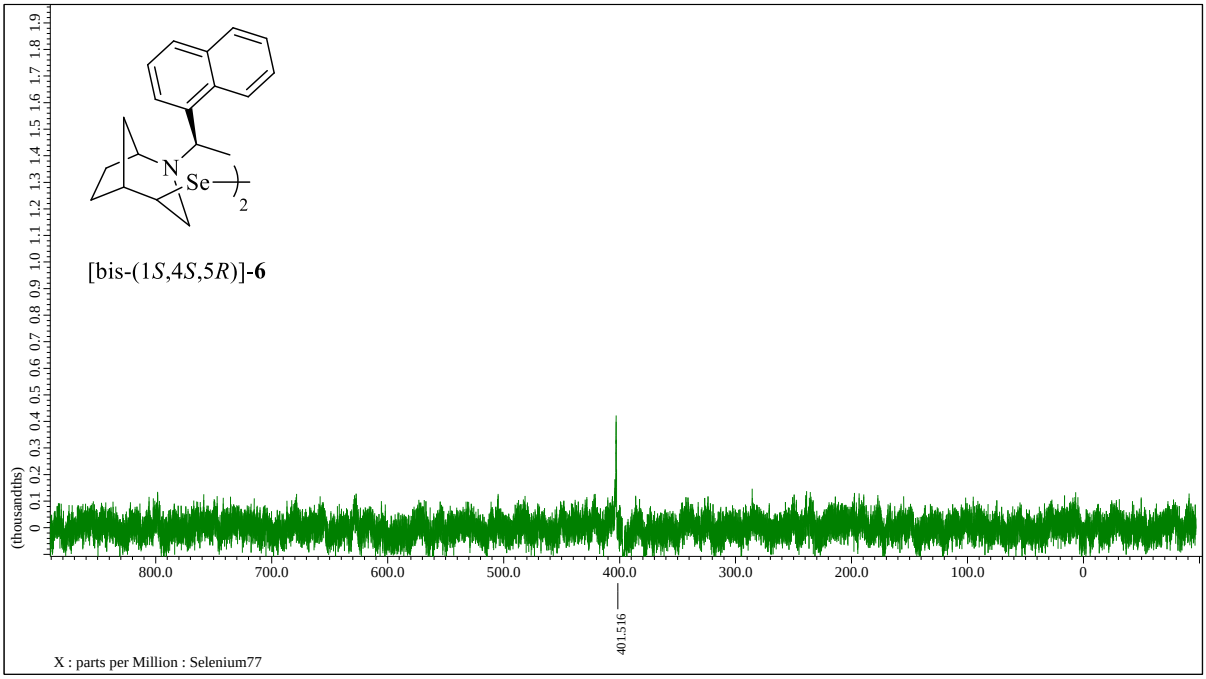


Figure S9. ^{77}Se NMR spectrum of bis{(1*S*,4*S*,5*R*)-2-[(*R*)-1-(2-naphtyl)ethyl]-2-azabicyclo[3.2.1]octan-4-yl} diselenide **6** (50 MHz, chloroform-*d*).

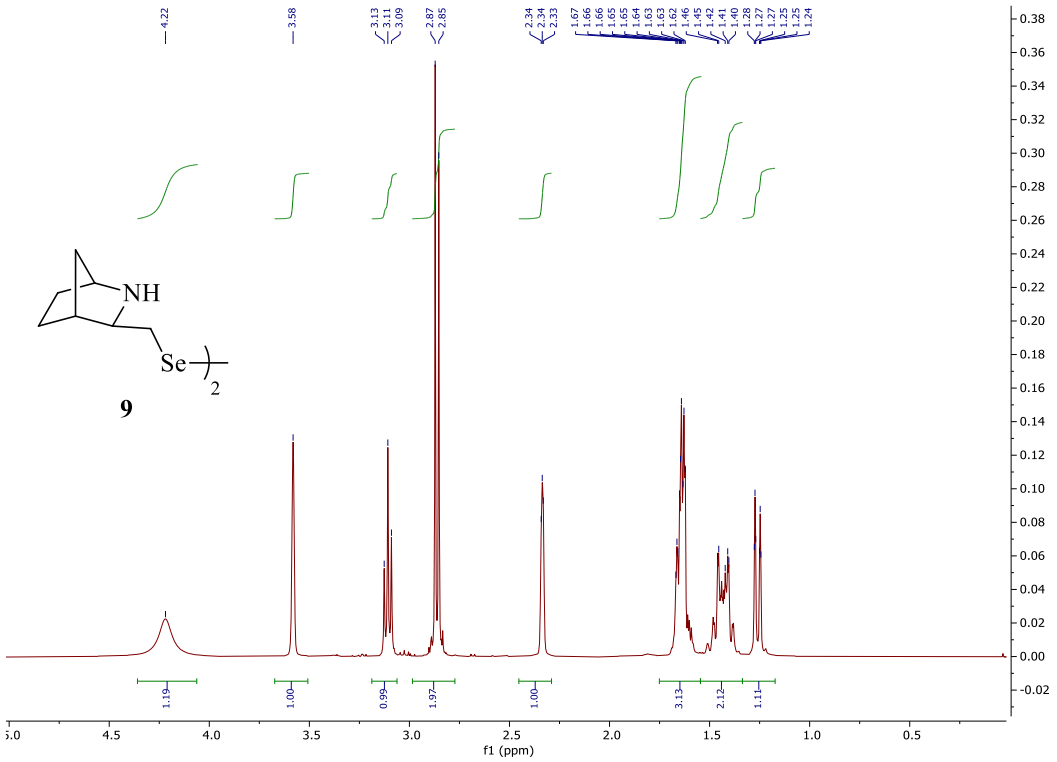


Figure S10. ^{1}H NMR spectrum of bis[((1*S*,3*R*,4*R*)-2-azabicyclo[2.2.1]heptan-3-yl)methyl] diselenide **9** (400 MHz, chloroform-*d*).

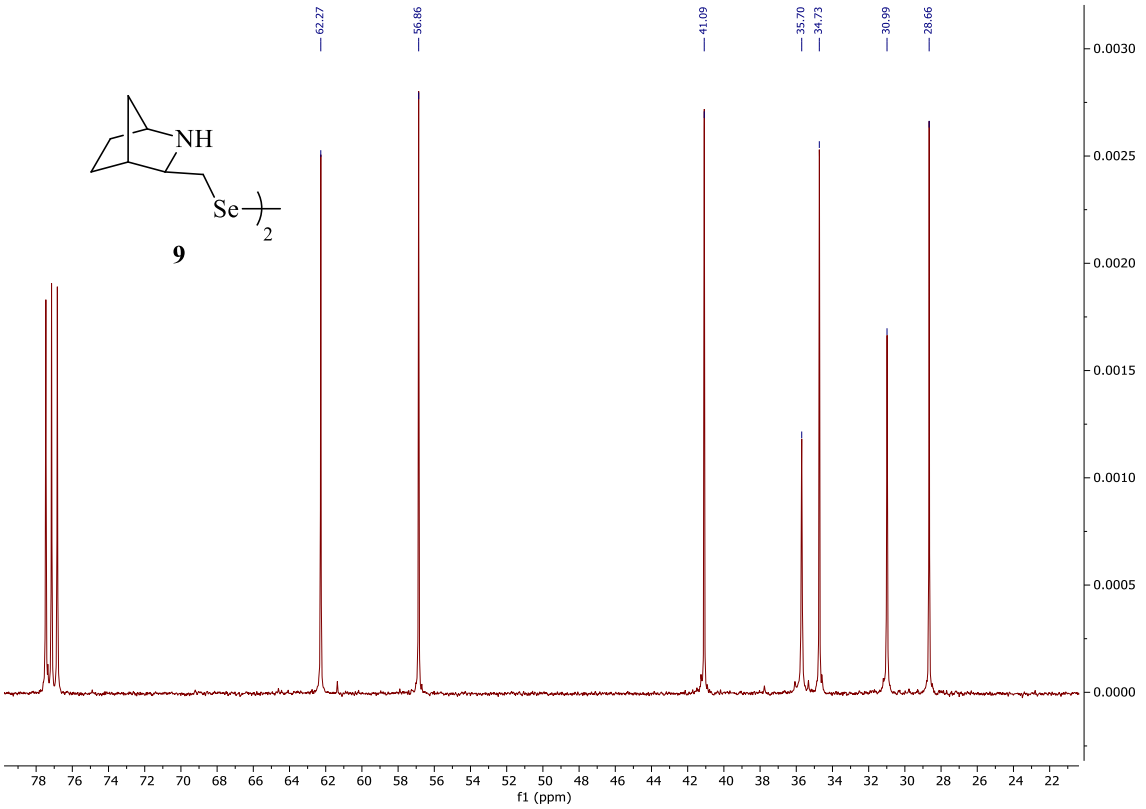


Figure S11. ^{13}C NMR spectrum of bis[((1*S*,3*R*,4*R*)-2-azabicyclo[2.2.1]heptan-3-yl)methyl] diselenide **9** (100 MHz, chloroform-*d*).

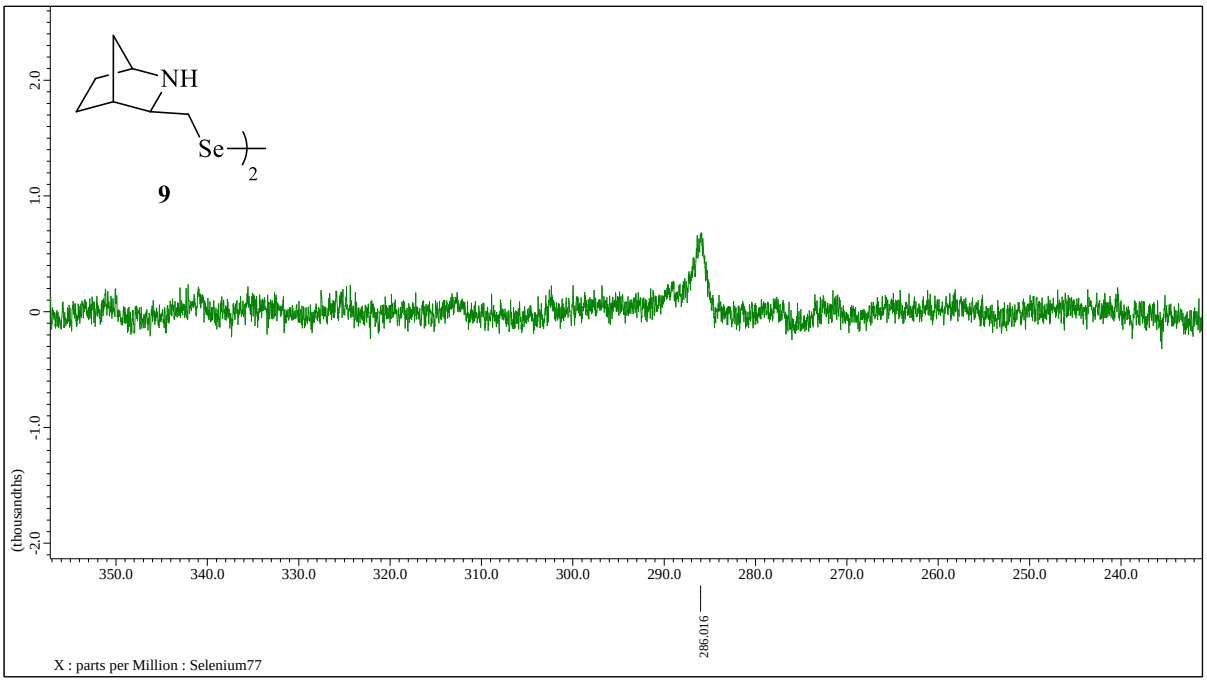


Figure S12. ^{77}Se NMR spectrum of bis[((1*S*,3*R*,4*R*)-2-azabicyclo[2.2.1]heptan-3-yl)methyl] diselenide **9** (50 MHz, chloroform-*d*).

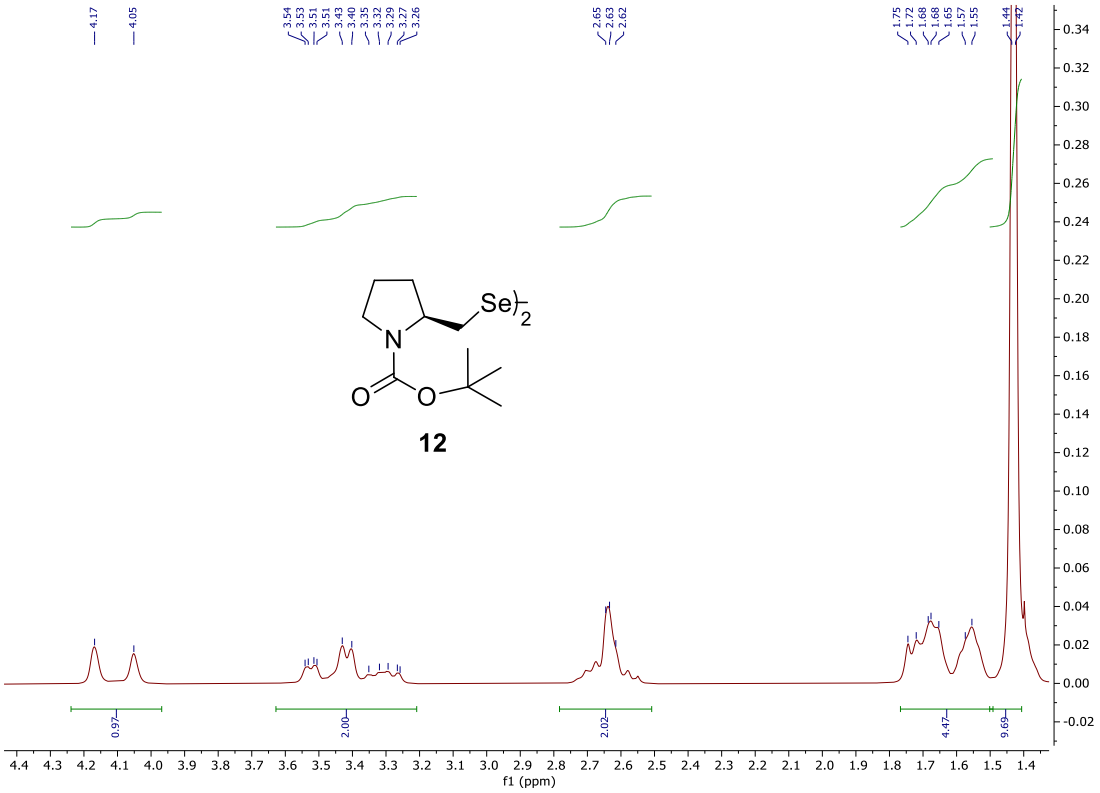


Figure S13. [1]H NMR spectrum of (2*S*, 2*'S*)bis(*N*-*tert*-butyloxycarbonyl-2-pirrolidine)methyl diselenide **12** (400 MHz, chloroform-*d*).

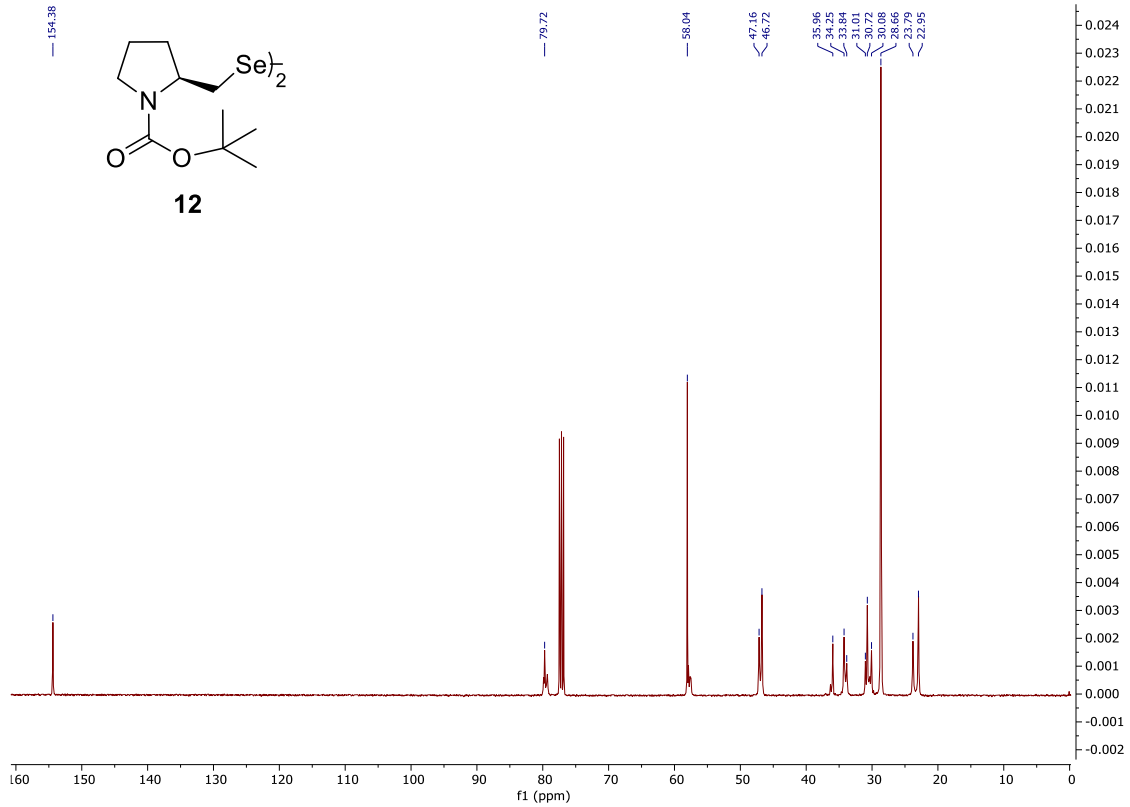


Figure S14. [13]C NMR spectrum of (2*S*, 2*'S*)bis(*N*-*tert*-butyloxycarbonyl-2-pirrolidine)methyl diselenide **12** (100 MHz, chloroform-*d*).

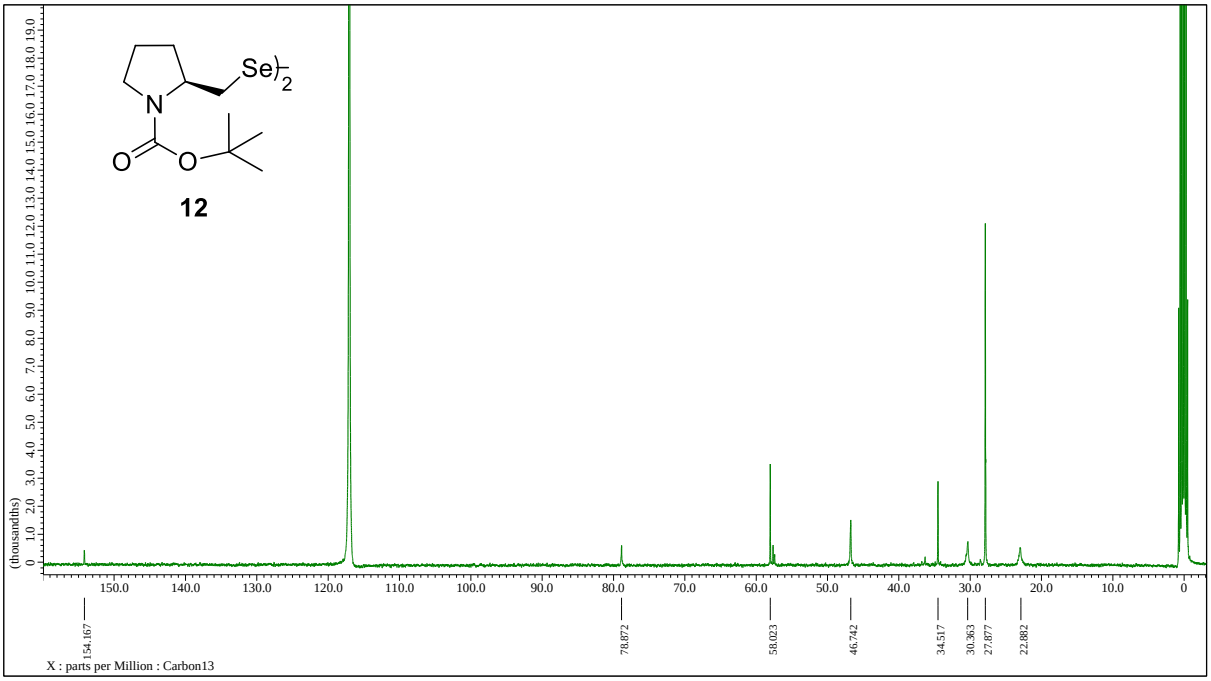


Figure S15. ^{13}C NMR spectrum of (2*S*, 2*'S*)bis(*N*-*tert*-butyloxycarbonyl-2-pirrolidine)methyl diselenide **12** (100 MHz, acetonitryle-d_3).

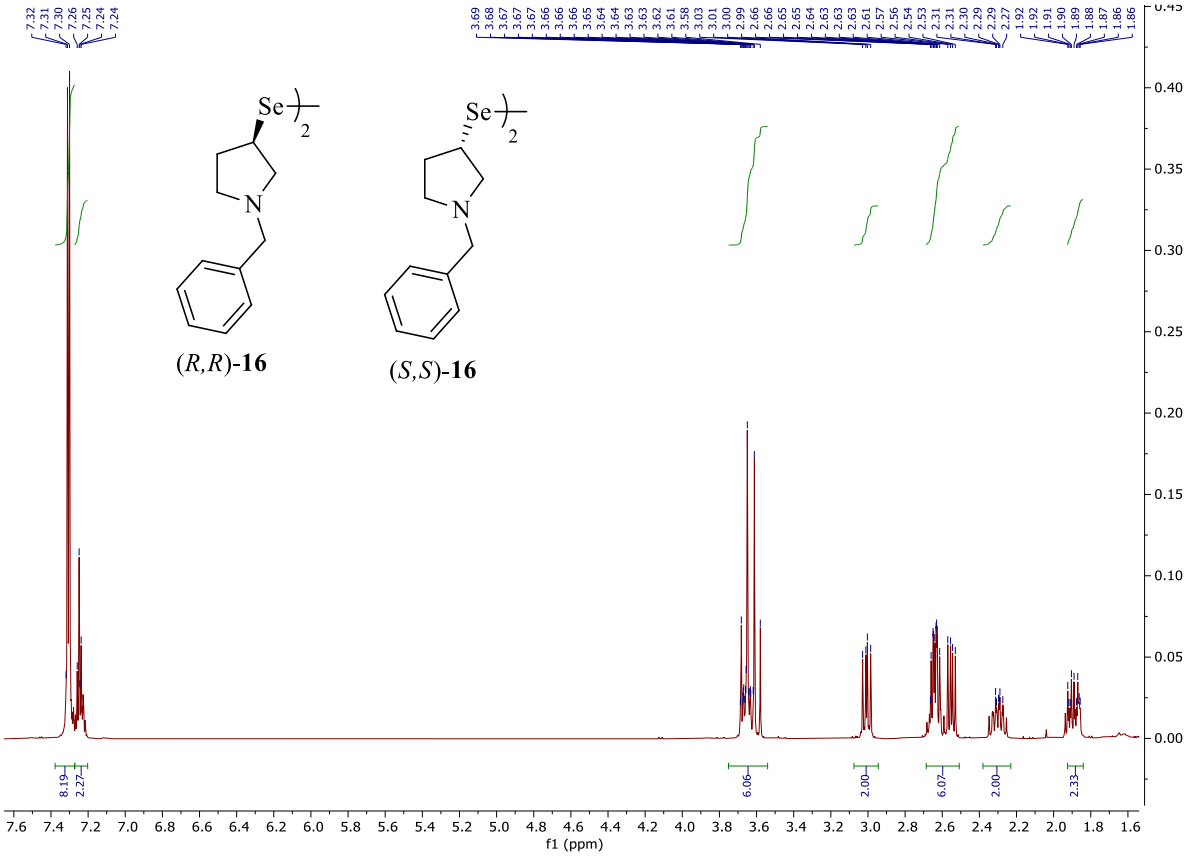


Figure S16. ^{1}H NMR spectrum of (*R*, *R*)-bis(N-benzylpyrrolidin-3-yl)diselenide (*R*, *R*)-**16** and (*S*, *S*)-**16** (400 MHz, chloroform-*d*).

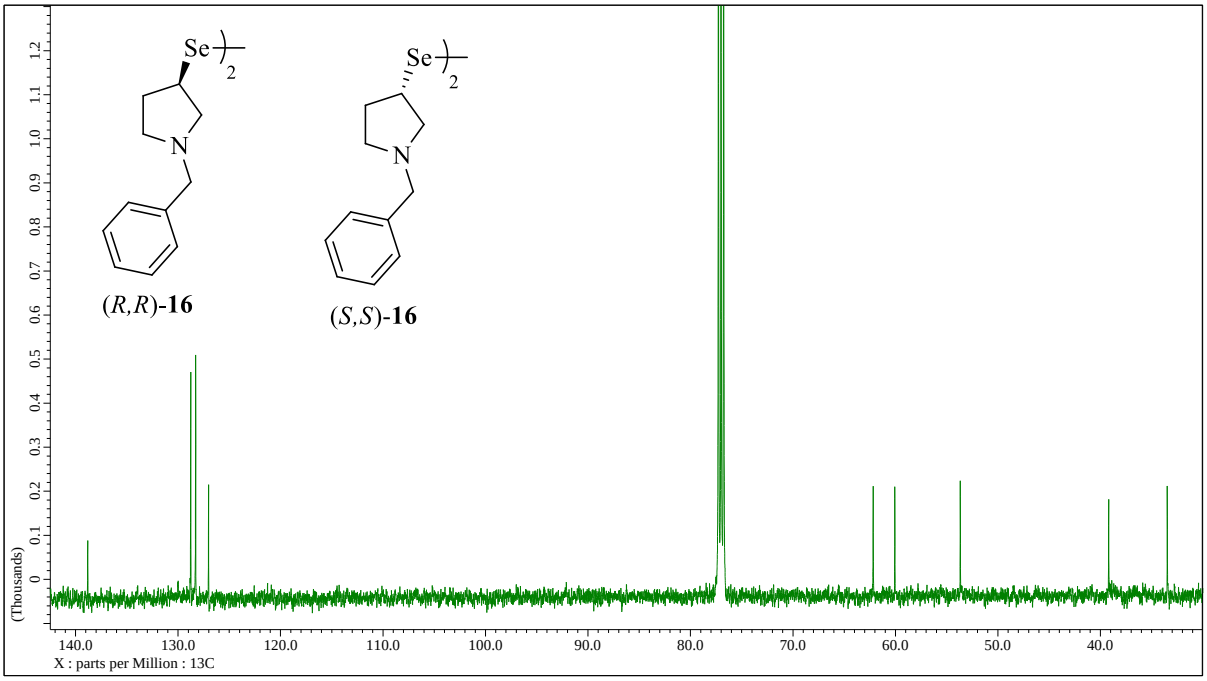


Figure S17. ^{13}C NMR spectrum of (*R*, *R*)-bis(N-benzylpyrrolidin-3-yl)diselenide (*R*, *R*)-**16** and (*S*, *S*)-**16** (100 MHz, chloroform-*d*).

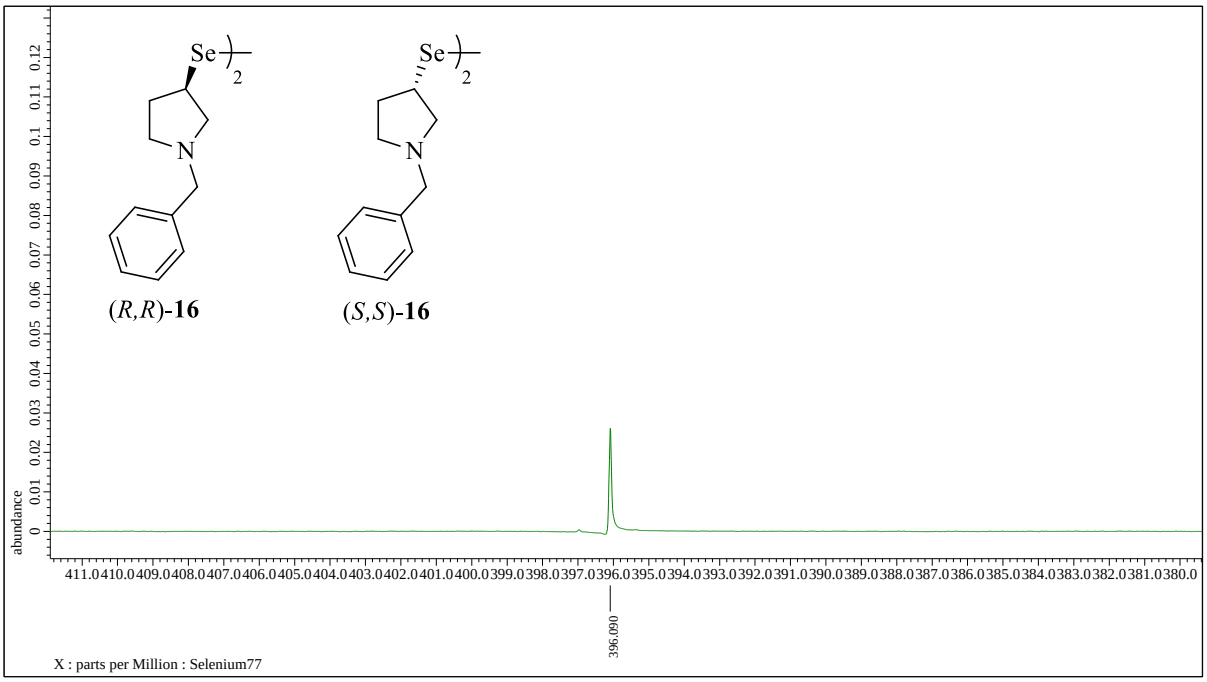
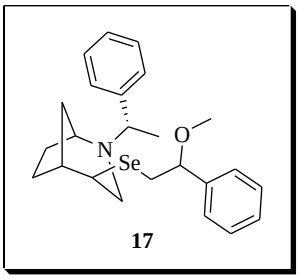


Figure S18. ^{77}Se NMR spectrum of (*R*, *R*)-bis(N-benzylpyrrolidin-3-yl)diselenide (*R*, *R*)-**16** and (*S*, *S*)-**16** (50 MHz, chloroform-*d*).

The asymmetric alkoxyselenylation of alkenes

(1*S*,4*S*,5*R*)-4-((2-methoxy-2-phenylethyl)selenyl)-2-((*S*)-1-phenylethyl)-2-azabicyclo [3.2.1]octane (17)



17

Yellow oil. Yield 0.05 g (72%). *De* = 26%. ^{1}H NMR ($CDCl_3$, 600 MHz) (major diastereoisomer) δ 1.27-1.33 (m, 6H), 1.67-1.76 (m, 2H), 2.09-2.16 (m, 1H), 2.35-2.50 (m, 2H), 2.55-2.69 (m, 3H), 2.83-2.91 (m, 1H), 3.10 (s, 3H, OCH_3), 3.32-3.37 (m, 1H), 3.55-3.58 (m, 1H), 4.17-4.21 (m, 1H), 7.17-7.43 (m, 10H) ppm, (minor diastereoisomer) δ 3.19 (s, 3H, OCH_3) ppm. HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $(C_{24}H_{31}NOSe)^+$ 430.1650, found 430.1653.

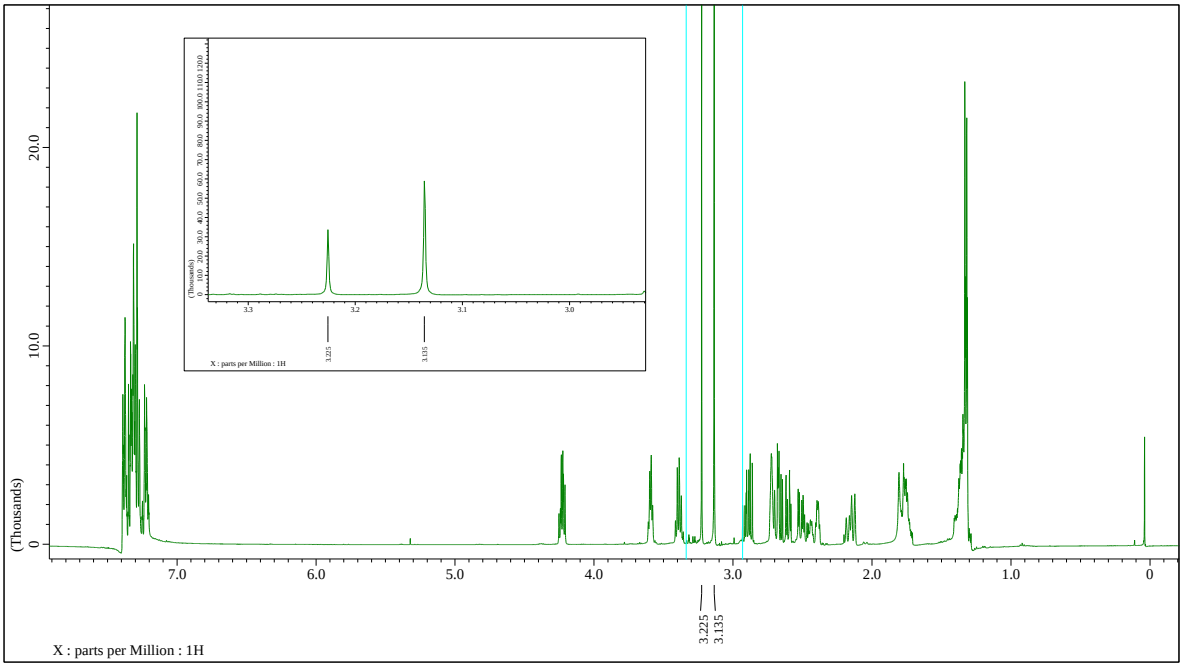


Figure S19. ^{1}H NMR spectrum of (1*S*,4*S*,5*R*)-4-((2-methoxy-2-phenylethyl)selenyl)-2-((*S*)-1-phenylethyl)-2-azabicyclo [3.2.1]octane **17** after purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C.

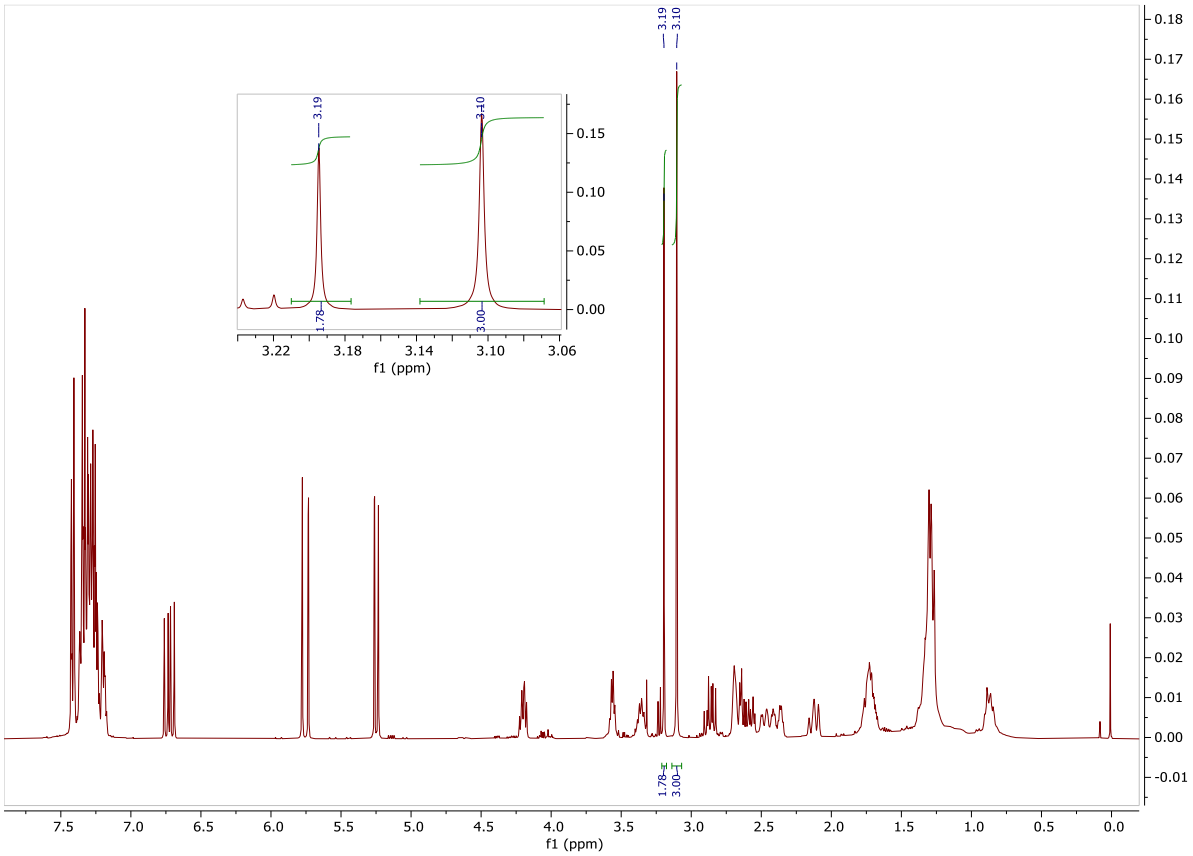
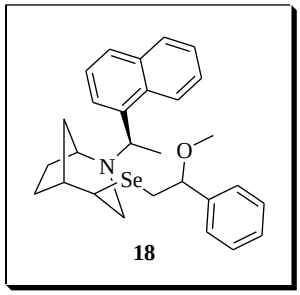


Figure S20. ^{1}H NMR spectrum of (1*S*,4*S*,5*R*)-4-((2-methoxy-2-phenylethyl)selenyl)-2-((*S*)-1-phenylethyl)-2-azabicyclo [3.2.1]octane **17** before purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C.

(1*S*,4*S*,5*R*)-4-((2-methoxy-2-phenylethyl)selenyl)-2-((*R*)-1-(1-naphthyl)ethyl)-2-azabicyclo [3.2.1] octane (18)



18

Yellow oil. Yield 0.06 g (91%). *De* = 22%. ^{1}H NMR ($CDCl_3$, 600 MHz) (major diastereoisomer) δ 1.20-1.29 (m, 3H), 1.36-1.38 (m, 4H), 1.55 (s, 1H), 1.62-1.68 (m, 1H), 1.79-1.85 (m, 1H), 2.08-2.15 (m, 1H), 2.37-2.40 (m, 1H), 2.44-2.58 (m, 2H), 2.60-2.76 (m, 3H), 2.96 (s, 1H), 3.09 (s, 1H), 3.16 (s, 3H, OCH_3), 3.60 (q, 1H, J = 6,6 Hz), 4.01-4.08 (m, 2H), 4.19-4.24 (m, 1H), 7.12-7.29 (m, 3H), 7.36-7.43 (m, 2H), 7.63-7.67 (m, 1H), 7.76-7.77 (m, 1H) ppm, (minor diastereoisomer) δ 3.17 (s, 3H, OCH_3) ppm. HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $(C_{28}H_{33}NOSe)^+$ 480.1808, found 480,1798.

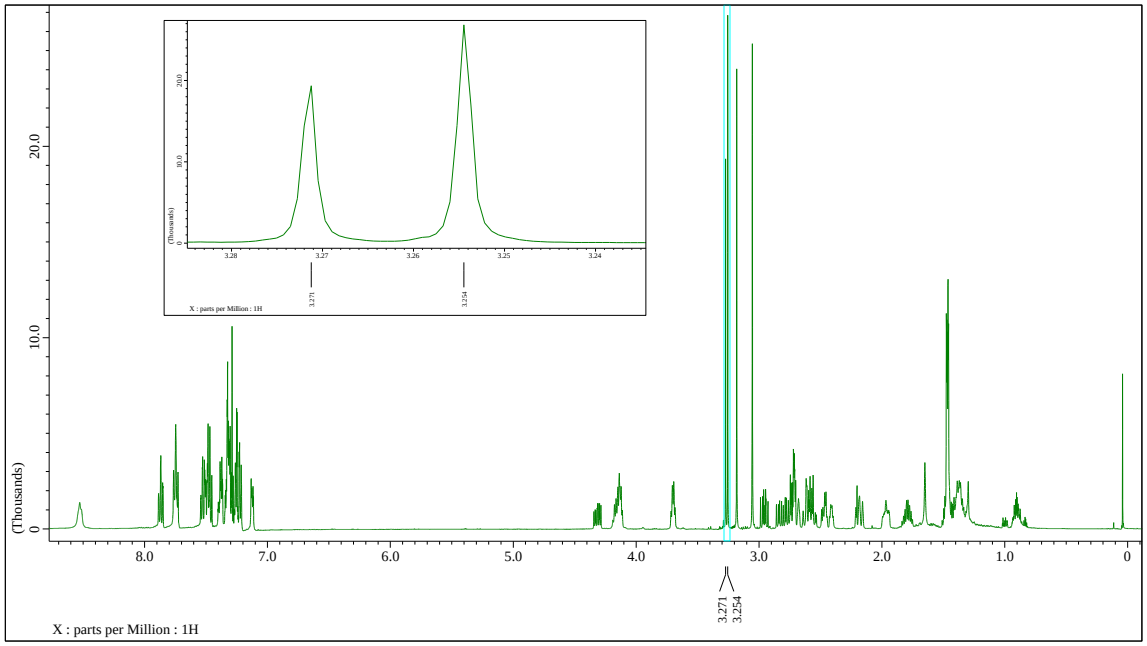


Figure S21. ^{1}H NMR spectrum of (1*S*,4*S*,5*R*)-4-((2-methoxy-2-phenylethyl)selenyl)-2-((*R*)-1-(1-naphthyl)ethyl)-2-azabicyclo [3.2.1] octane **18** after purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C.

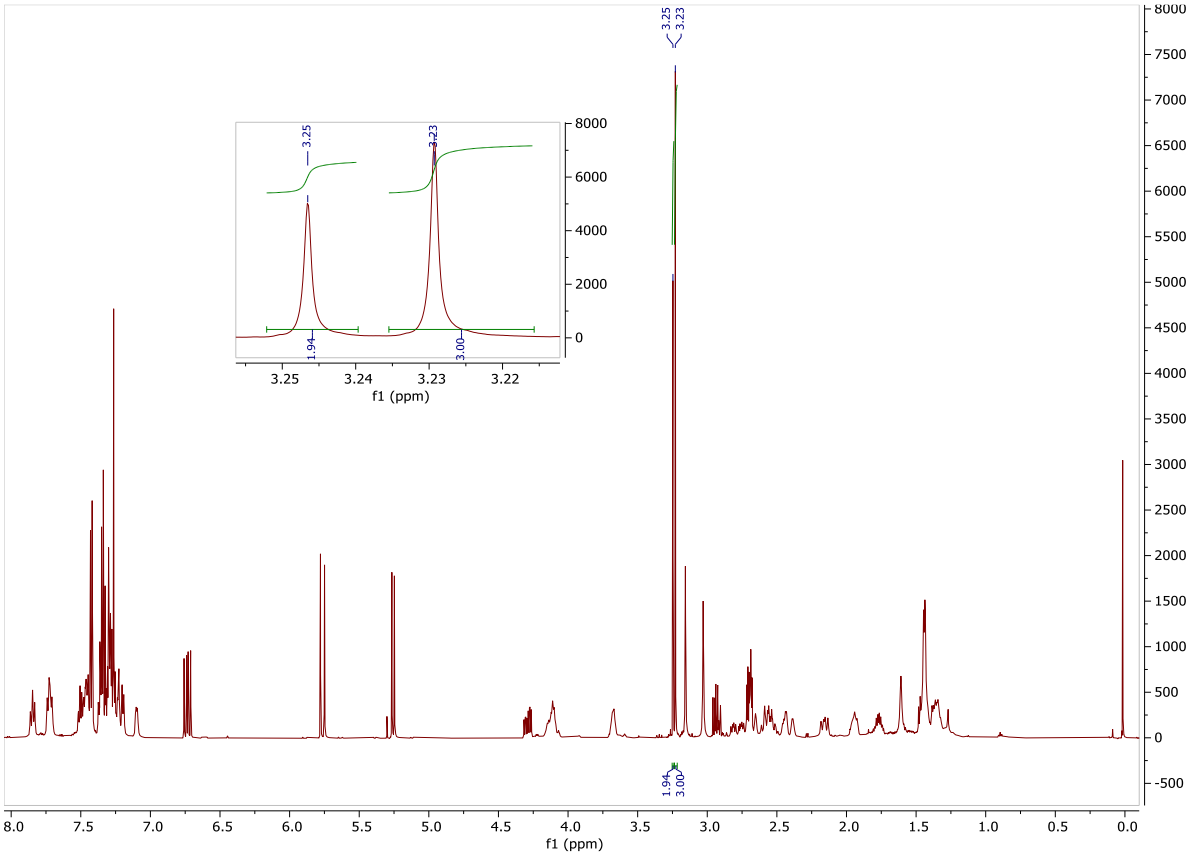
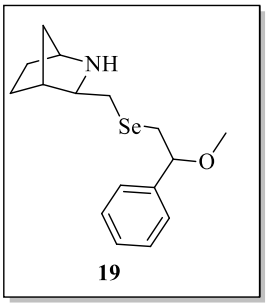


Figure S22. ^{1}H NMR spectrum of (1*S*,4*S*,5*R*)-4-((2-methoxy-2-phenylethyl)selenyl)-2-((*R*)-1-(1-naphthyl)ethyl)-2-azabicyclo [3.2.1] octane **18** before purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C.

(1*S*,3*R*,4*R*)-3-(((2-methoxy-2-phenylethyl)selenyl)methyl)-2-azabicyclo[2.2.1]heptane (19)



19

Yellow oil. Yield 0.009 g (11%). *De* < 95%. ^{1}H NMR ($CDCl_3$, 600 MHz) (major diastereoisomer) δ 1.17 (s, 1H), 1.47-1.47 (m, 1H), 1.76-1.81 (m, 1H), 2.25 (t, 1H, *J* = 7,2 Hz), 2.64-2.70 (m, 2H), 2.87-2.94 (m, 2H), 3.21 (s, 3H, OCH_3), 3.44-3.53 (m, 2H), 3.99-4.08 (m, 2H), 4.23-4.30 (m, 2H), 4.36-4.40 (m, 1H), 7.17-7.31 (m, 5H) ppm, (minor diastereoisomer) δ 3.22 (s, 3H, OCH_3) ppm. HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $(C_{16}H_{23}NOSe)^+$ 325.1066, found 325.0832

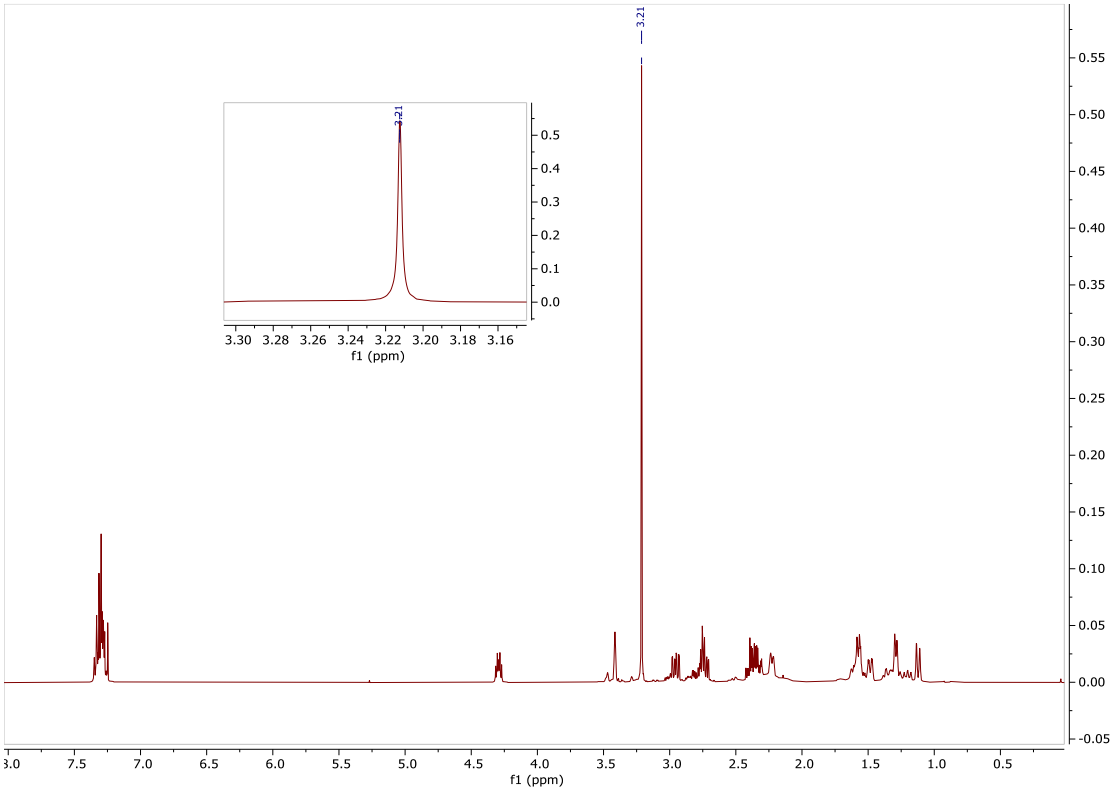


Figure S23. ^{1}H NMR spectrum of (1*S*,3*R*,4*R*)-3-(((2-methoxy-2-phenylethyl)selenyl)methyl)-2-azabicyclo[2.2.1]heptane **19** after purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C (5 eq of styrene).

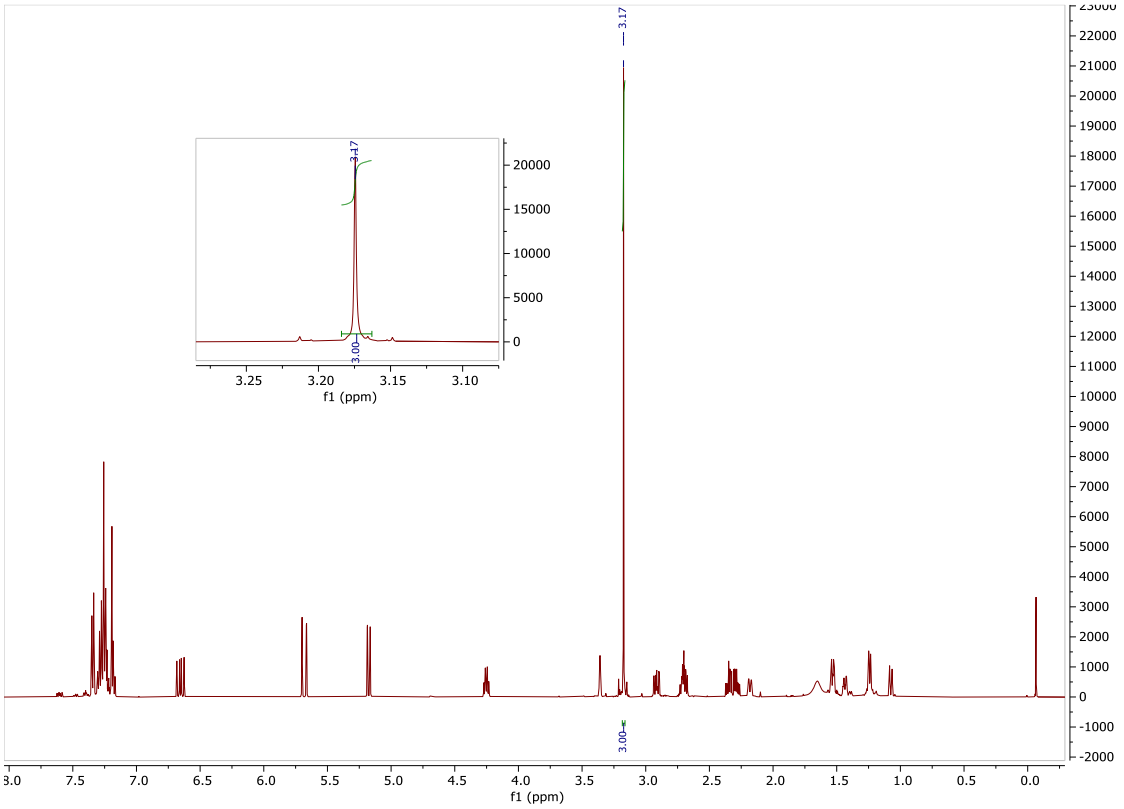


Figure S24. ^{1}H NMR spectrum of (1*S*,3*R*,4*R*)-3-(((2-methoxy-2-phenylethyl)selenyl)methyl)-2-azabicyclo[2.2.1]heptane **19** before purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C (5 eq of styrene).

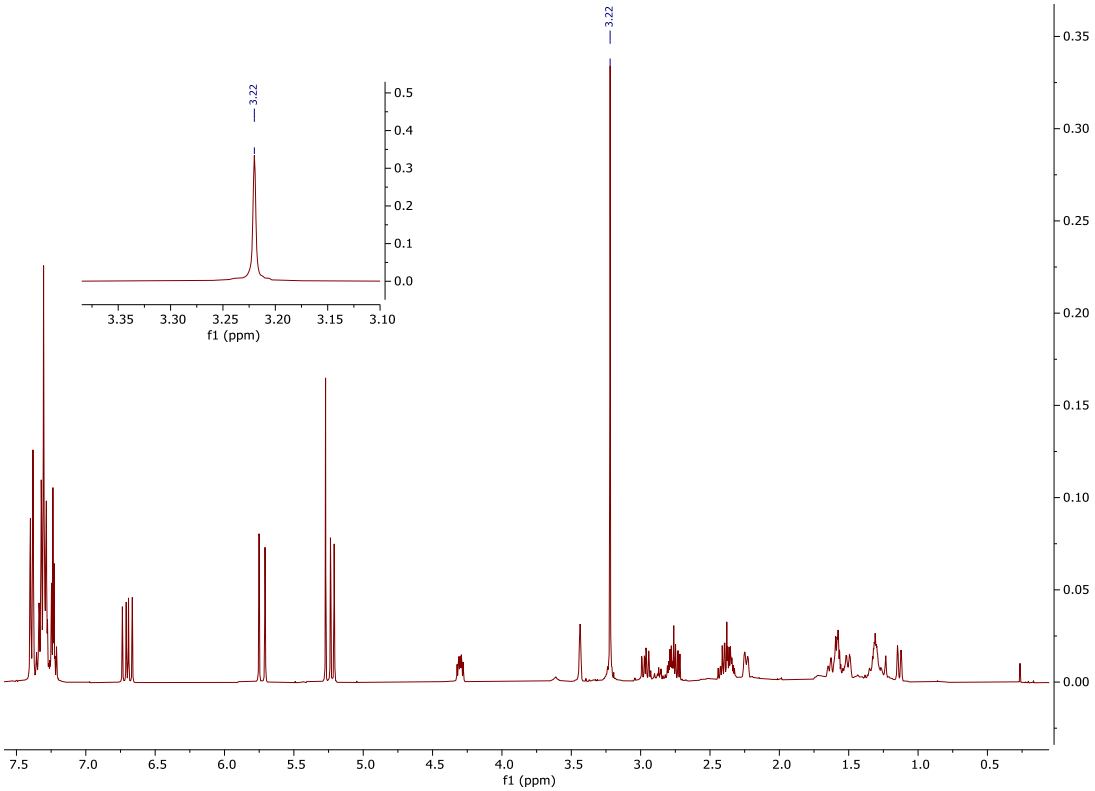


Figure S25. ^{1}H NMR spectrum of (1*S*,3*R*,4*R*)-3-(((2-methoxy-2-phenylethyl)selenyl)methyl)-2-azabicyclo[2.2.1]heptane **19** after purification (400 MHz, chloroform-*d*). Reaction performed in rt (5 eq of styrene).

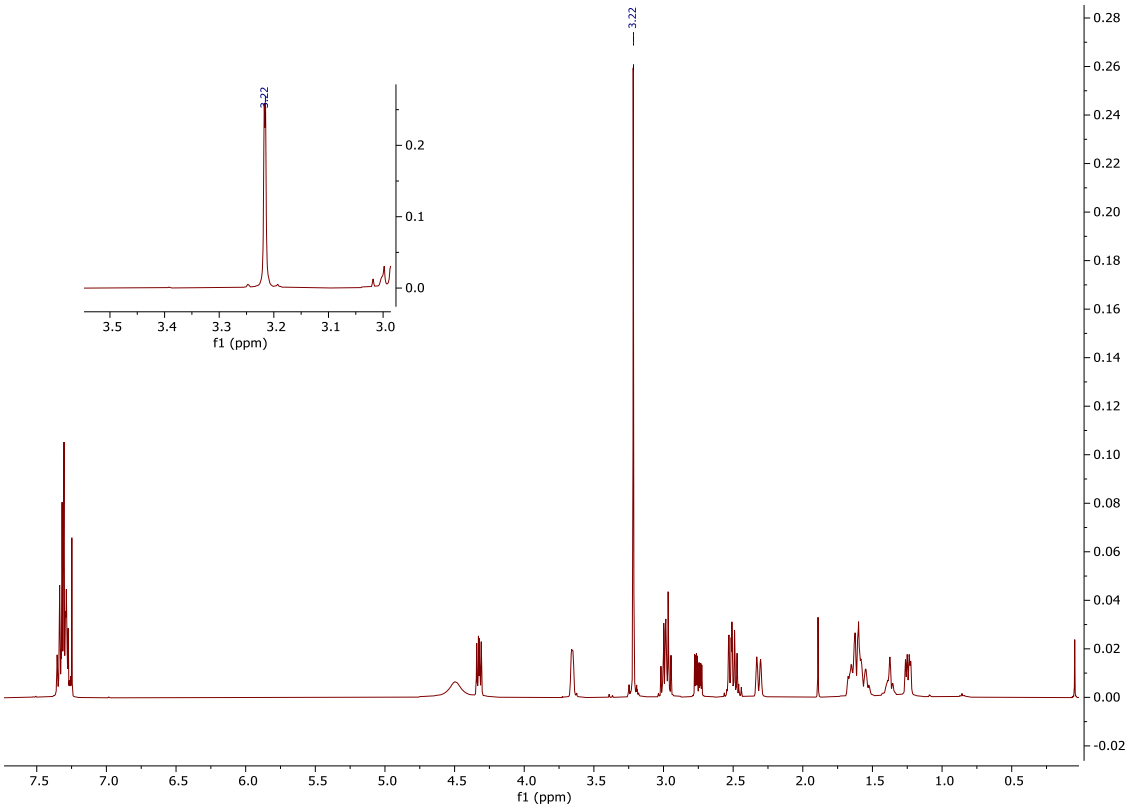
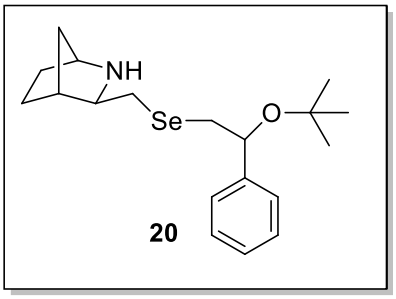


Figure S26. ^{1}H NMR spectrum of (1*S*,3*R*,4*R*)-3-(((2-methoxy-2-phenylethyl)selenyl)methyl)-2-azabicyclo[2.2.1]heptane **19** after purification (400 MHz, chloroform-*d*). Reaction performed in rt (1 eq of styrene).

(1S,3R,4R)-3-(((2-(tert-butoxy)-2-phenylethyl)selanyl)methyl)-2-azabicyclo[2.2.1] heptane 20



Yellow oil. Yield 0.061 g (66%). *De* ~90%. ^{1}H NMR ($CDCl_3$, 400 MHz) (major diastereoisomer) δ = 1.11 (s, 9H, O-*tert*-Bu), 1.43-1.69 (m, 5H), 1.92-2.06 (m, 2H), 2.44-2.48 (m, 1H), 2.74-2.92 (m, 3H), 3.34 (q, 1H, *J* = 8.0 MHz), 4.13 (s, 1H), 4.68-4.72 (m, 1H), 7.20-7.36 (m, 5H, Ar-H) ppm, (minor diastereoisomer) δ = 1.12 (s, 3H, O-*tert*-Bu). HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $(C_{19}H_{29}NOSe)^+$ 368.1494, found 368.1493.

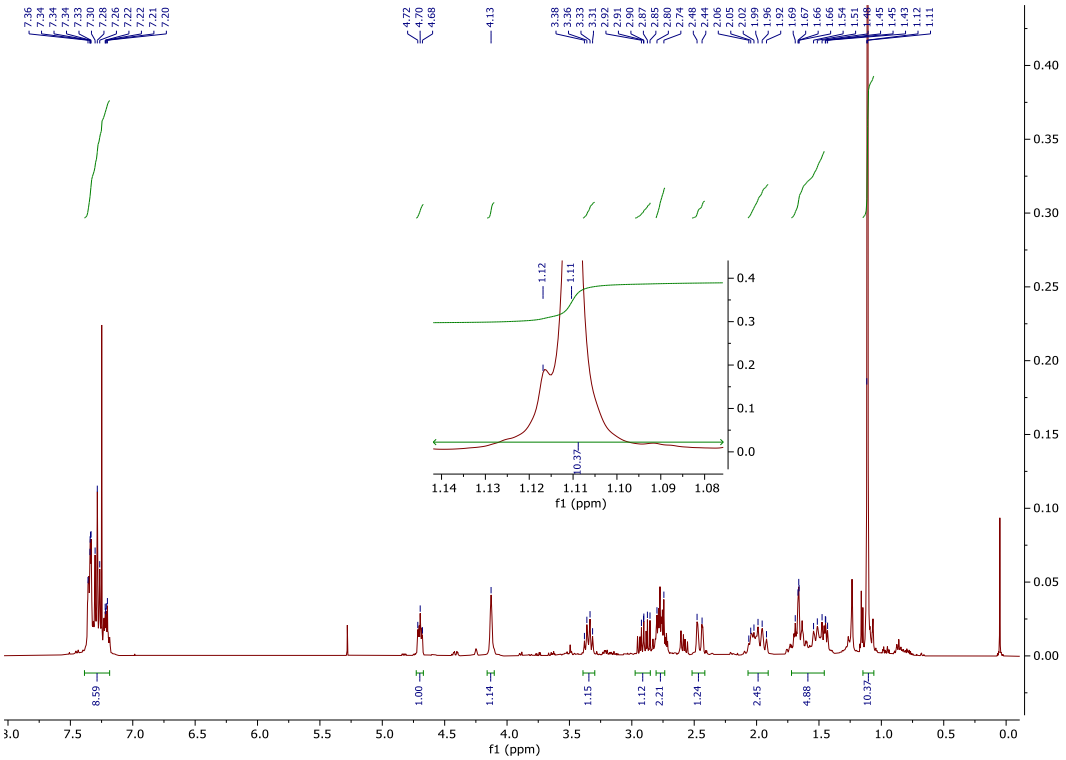


Figure S27. ^{1}H NMR spectrum of (1S,3R,4R)-3-(((2-(tert-butoxy)-2-phenylethyl)selanyl)methyl)-2-azabicyclo[2.2.1] heptane after purification (400 MHz, chloroform-*d*). Reaction performed at rt.

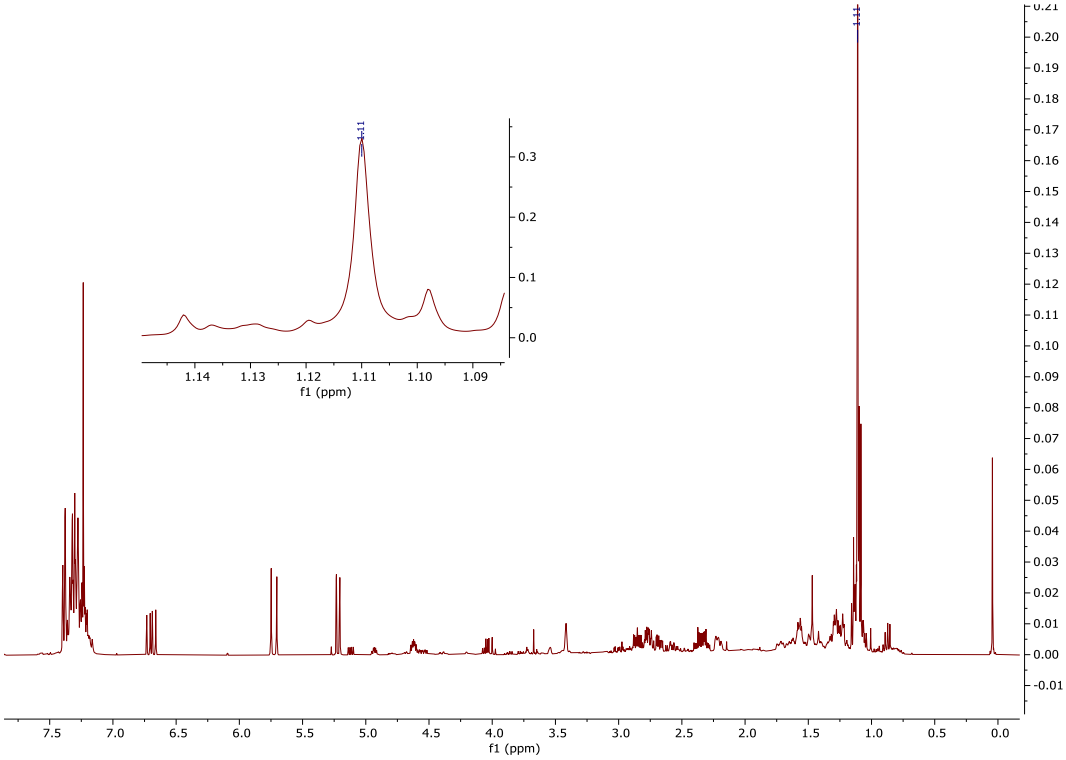
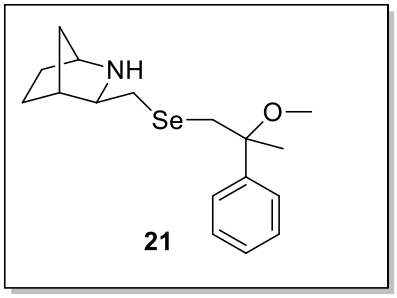


Figure S28. ^{1}H NMR spectrum of (1S,3R,4R)-3-(((2-(tert-butoxy)-2-phenylethyl)selanyl)methyl)-2-azabicyclo[2.2.1] heptane before purification (400 MHz, chloroform-*d*). Reaction performed at rt.

(1S,3R,4R)-3-(((2-methoxy-2-phenylpropyl)selanyl)methyl)-2-azabicyclo[2.2.1]heptane (21)



Yellow oil. Yield 0.044 g (52%). *De* ~ 23%. HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $(C_{17}H_{25}NOSe)^+$ 338.3500, found 338.1287.

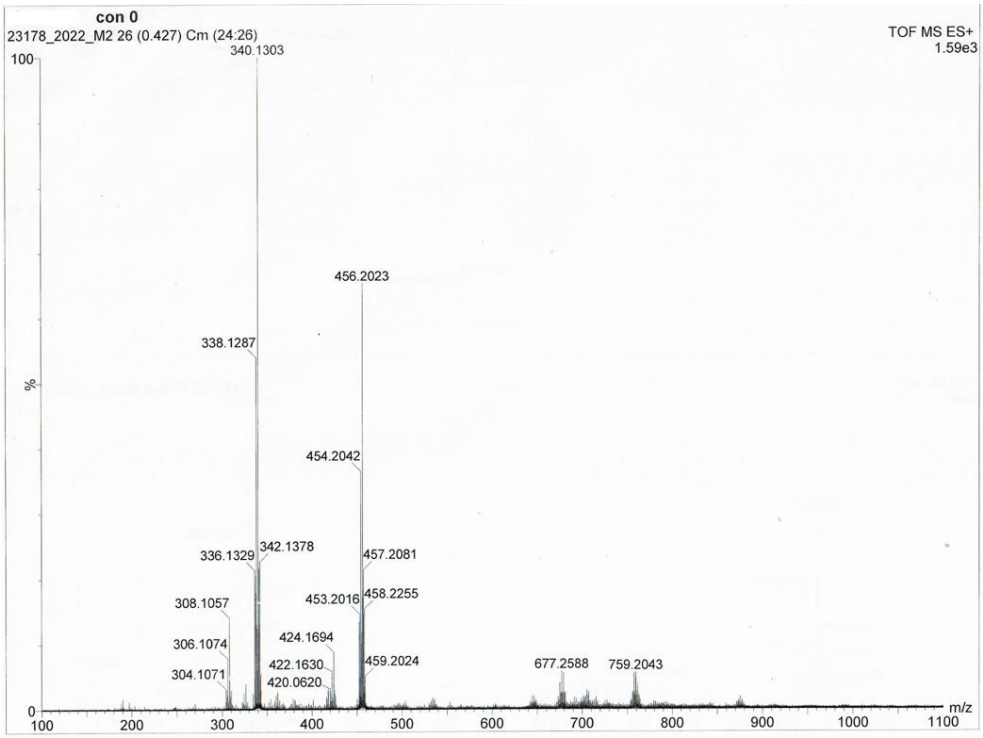


Figure S29. MS spectrum of (1*S*,3*R*,4*R*)-3-(((2-methoxy-2-phenylpropyl)selanyl)methyl)-2-azabicyclo[2.2.1]heptane **21**.

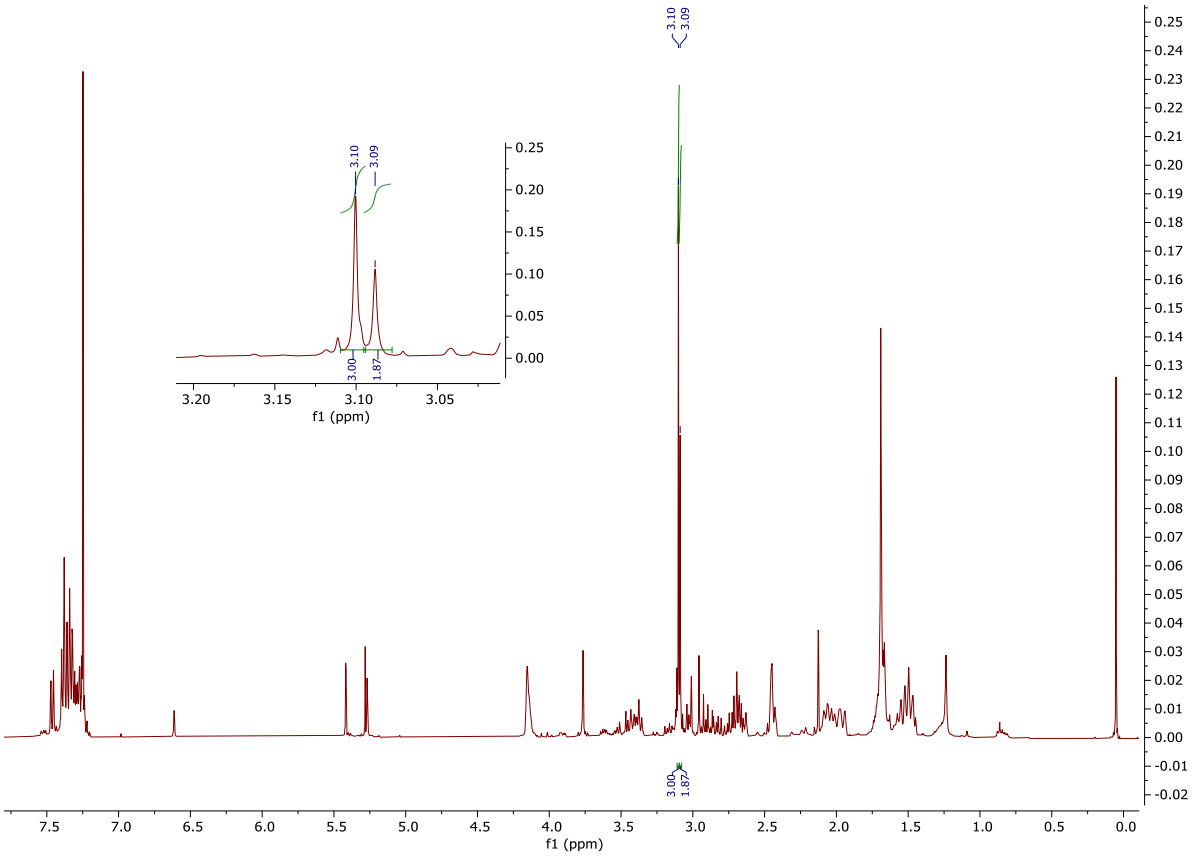
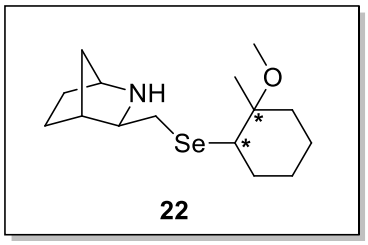


Figure S30. ^{1}H NMR spectrum of (1*S*,3*R*,4*R*)-3-(((2-methoxy-2-phenylpropyl)selanyl)methyl)-2-azabicyclo[2.2.1]heptane **21** (400 MHz, chloroform-*d*). Reaction performed at rt.

(1*S*,3*R*,4*R*)-3-(((2-methoxy-2-methylcyclohexyl)selanyl)methyl)-2-azabicyclo[2.2.1] heptane (22)



22

Yellow oil. Only trace amount of product was observed. *De* not determined. HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $(C_{15}H_{27}NOSe)^+$ 316.3400, found 316.1381.

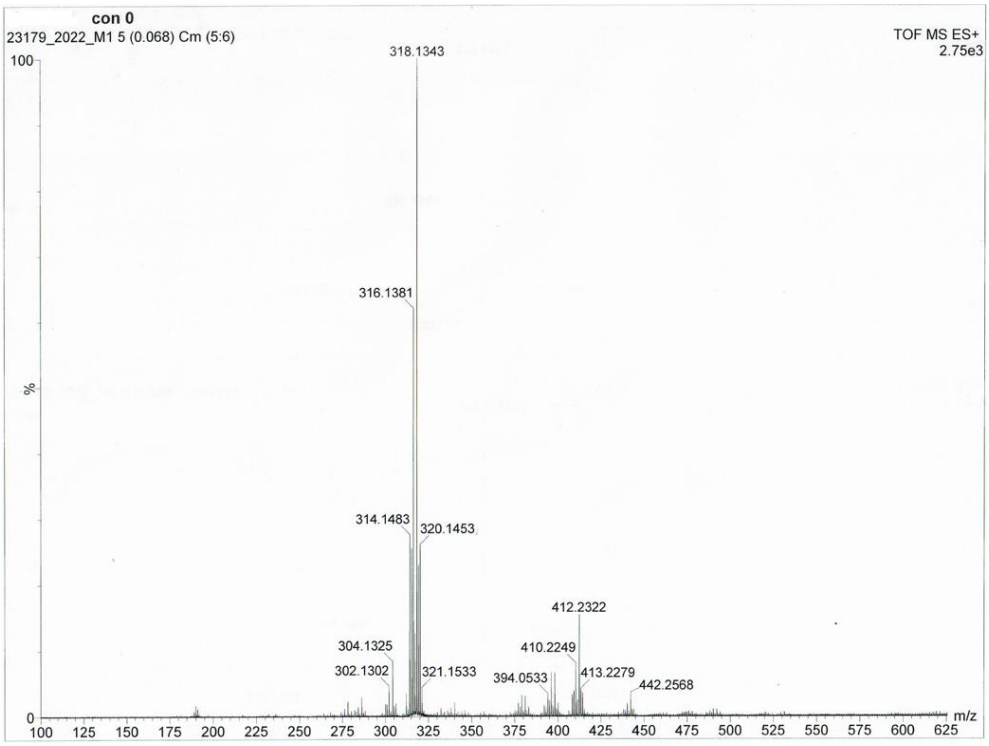
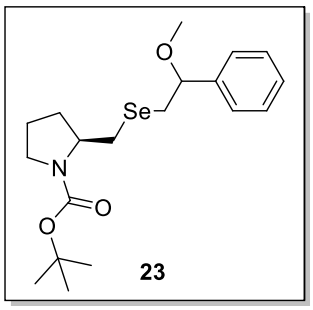


Figure S31. MS spectrum of (1*S*,3*R*,4*R*)-3-(((2-methoxy-2-methylcyclohexyl)selanyl)methyl)-2-azabicyclo[2.2.1] heptane **22**

(2*S*)-1-*tert*-buthoxycarbonyl-2-(((2-methoxy-2-phenylethyl)selenyl)methyl)pyrrolidine (23)



Yellow oil. Yield 0.07 g (97%). *De* < 30%. ^{1}H NMR ($CDCl_3$, 600 MHz) (major diastereoisomer) δ = 1.36 (s, 9H), 1.72-1.87 (m, 4H), 1.88-1.91 (m, 1H), 2.38-2.60 (m, 1H), 2.72-2.81 (m, 1H), 2.87-2.96 (m, 1H), 3.21 (s, 3H, OCH_3), 3.21-3.31 (m, 2H), 3.76-3.88 (m, 1H), 4,26 (br s, 1H), 7.19-7.27 (m, 5H) ppm, (minor diastereoisomer) δ = 3.20 (s, 3H, OCH_3) ppm. HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $(C_{19}H_{29}NO_3Se)^+$ 422.1211, found 422.1219.

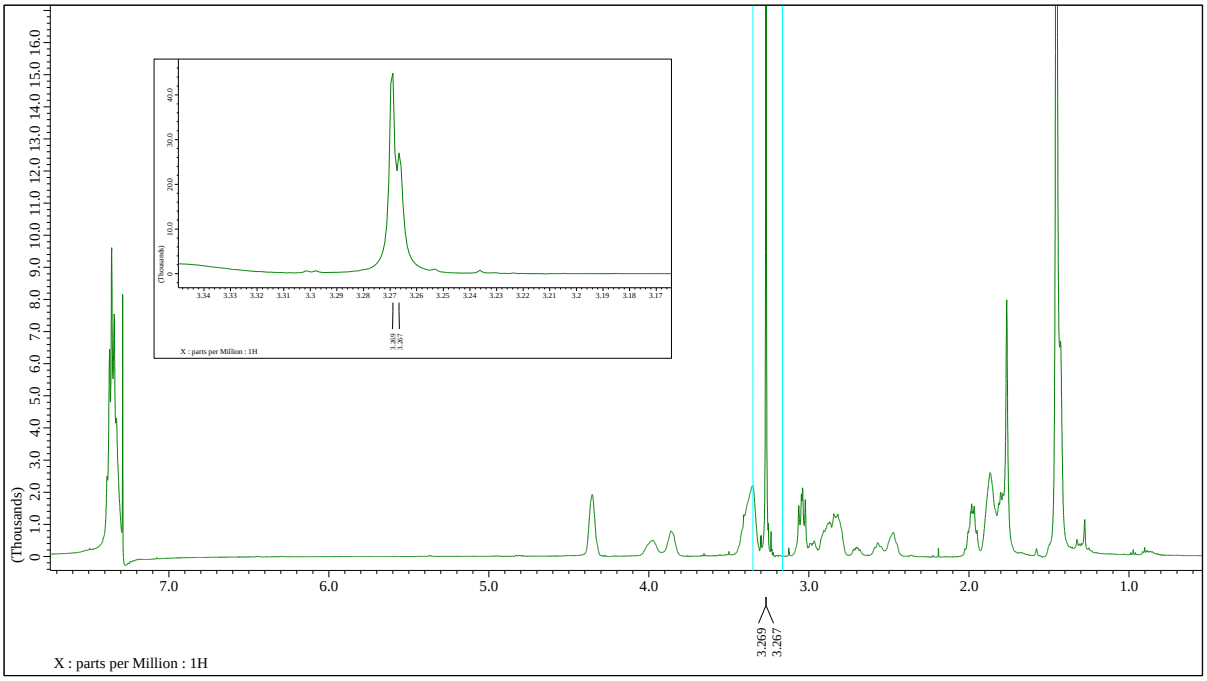


Figure S32. ^{1}H NMR spectrum of (2*S*)-1-*tert*-buthoxycarbonyl-2-(((2-methoxy-2-phenylethyl)selenyl)methyl)pyrrolidine **23** after purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C.

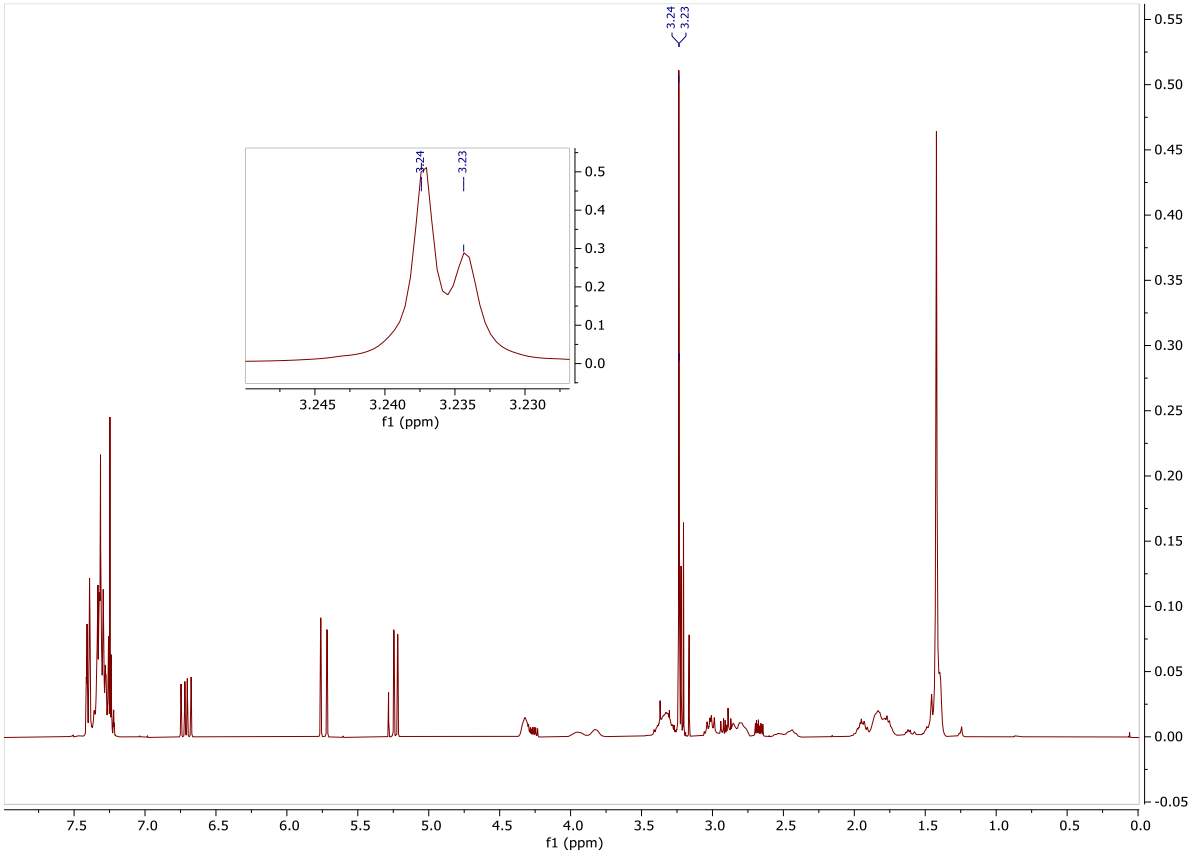
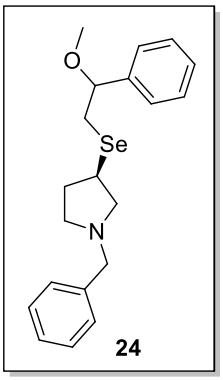


Figure S33. ^{1}H NMR spectrum of (2*S*)-1-*tert*-buthoxycarbonyl-2-(((2-methoxy-2-phenylethyl)selenyl)methyl)pyrrolidine **23** before purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C.

(3*R*)-1-benzyl-3-((2-methoxy-2-phenylethyl)selenyl) pyrrolidine (24)



Yellow oil. Yield 0.05g (75%). *De* = 8%. ^{1}H NMR ($CDCl_3$, 600 MHz) (minor diastereoisomer) δ 1.73-1.76 (m, 1H), 2.23-2.34 (m, 1H), 2.36-2.38 (m, 1H), 2.45-2.47 (m, 1H), 2.59-2.61 (m, 1H), 2.71-2.74 (m, 1H), 2.91-2.98 (m, 2H), 3,17 (s, 3H, OCH_3), 3.25-3.31 (m, 1H), 3.51-3.58 (m, 2H), 4.24-4.27 (m, 1H), 7.17-7.19 (m, 1H), 7.21-7.24 (m, 6H), 7.27-7.30 (m, 3H) ppm, (minor diastereoisomer) δ 3.16 (s, 3H, OCH_3) ppm. HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $(C_{20}H_{25}NOSe)^+$ 376.1180, found 376.1181

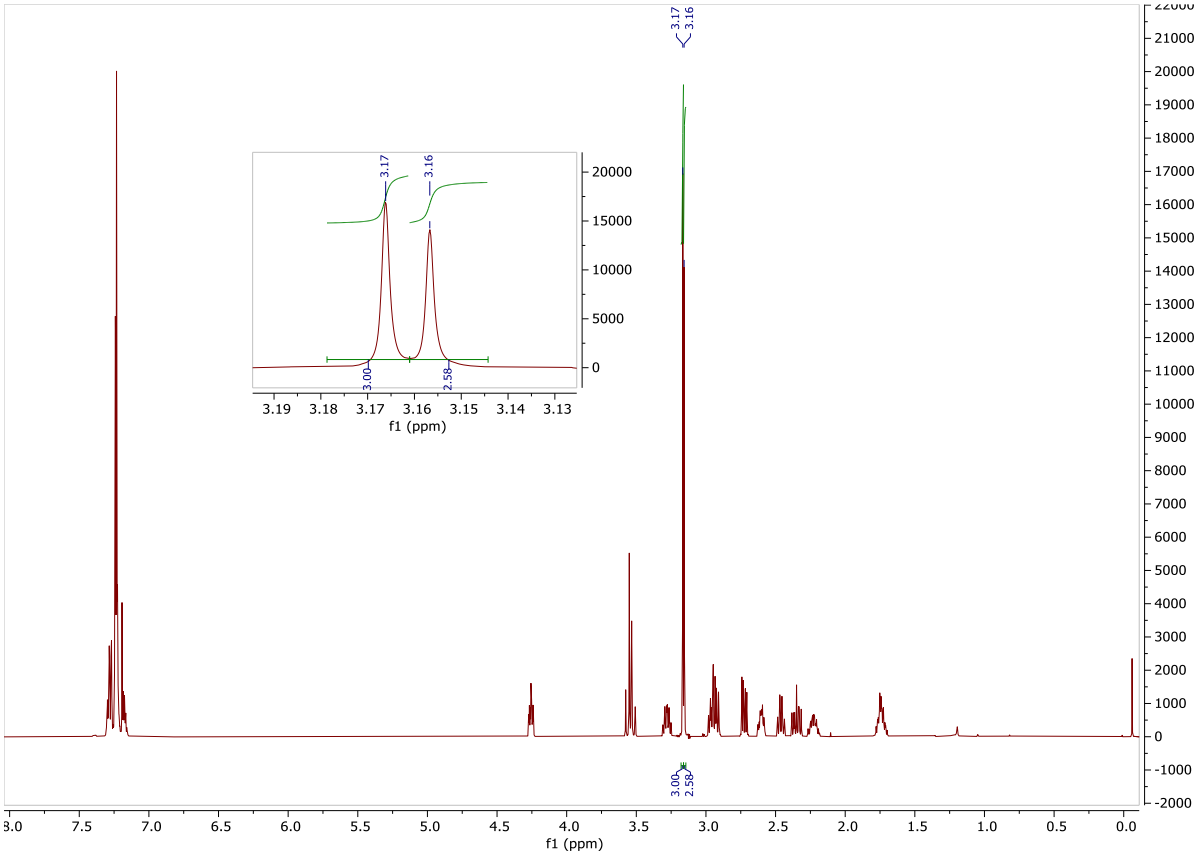
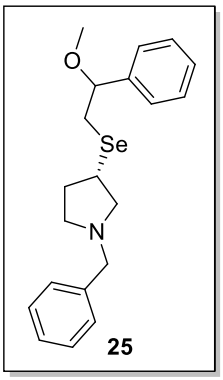


Figure S34. ^{1}H NMR spectrum of (3*R*)-1-benzyl-3-((2-methoxy-2-phenylethyl)selenyl) pyrrolidine **24** after purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C.

(3*S*)-1-benzyl-3-((2-methoxy-2-phenylethyl)selenyl) pyrrolidine (25)



Yellow oil. Yield 0.05 g (69%). *De* < 5%. ^{1}H NMR ($CDCl_3$, 600 MHz) (major diastereoisomer) δ 1.23-1.32 (m, 1H), 1.98-2.07 (m, 1H), 2.27-2.47 (m, 1H), 2.54-2.80 (m, 3H), 2.95-3.12 (m, 2H), 3.22 (s, 3H, OCH_3), 3.57-3.71 (m, 3H), 4.29-4.33 (m, 1H), 7.22-7.36 (m, 10H) ppm, (minor diastereoisomer) δ 3.21 (s, 3H, OCH_3) ppm. HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $(C_{20}H_{25}NOSe)^+$ 376.1180, found 376.1181.

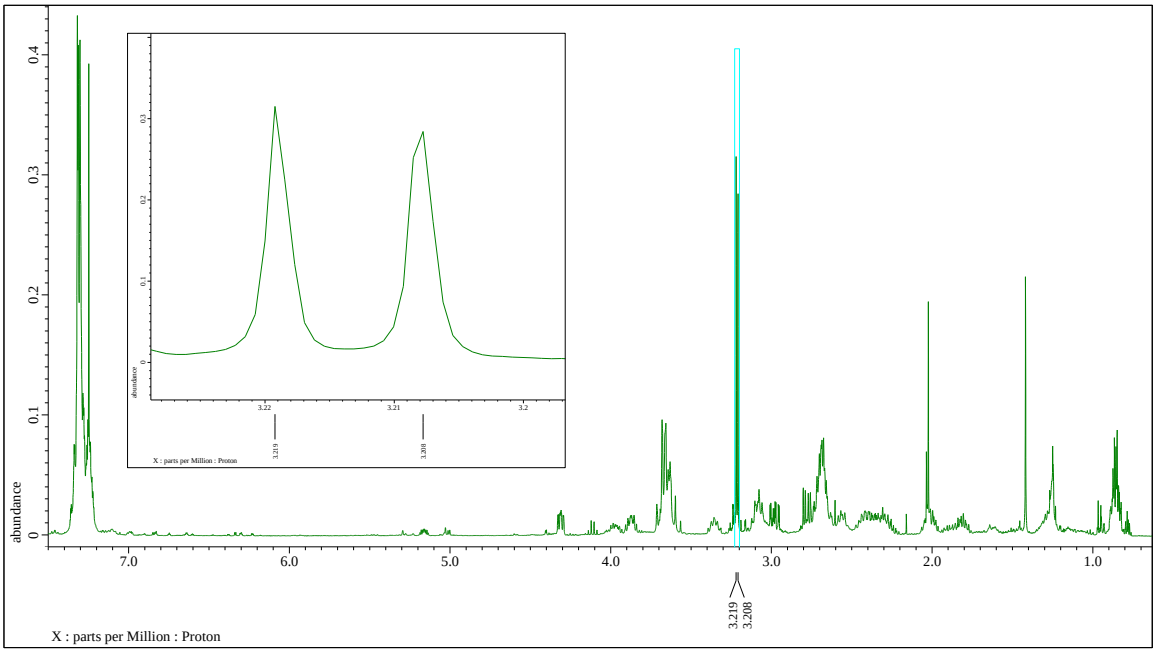


Figure S35. ^{1}H NMR spectrum of (3*S*)-1-benzyl-3-((2-methoxy-2-phenylethyl)selenyl) pyrrolidine **25** after purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C.

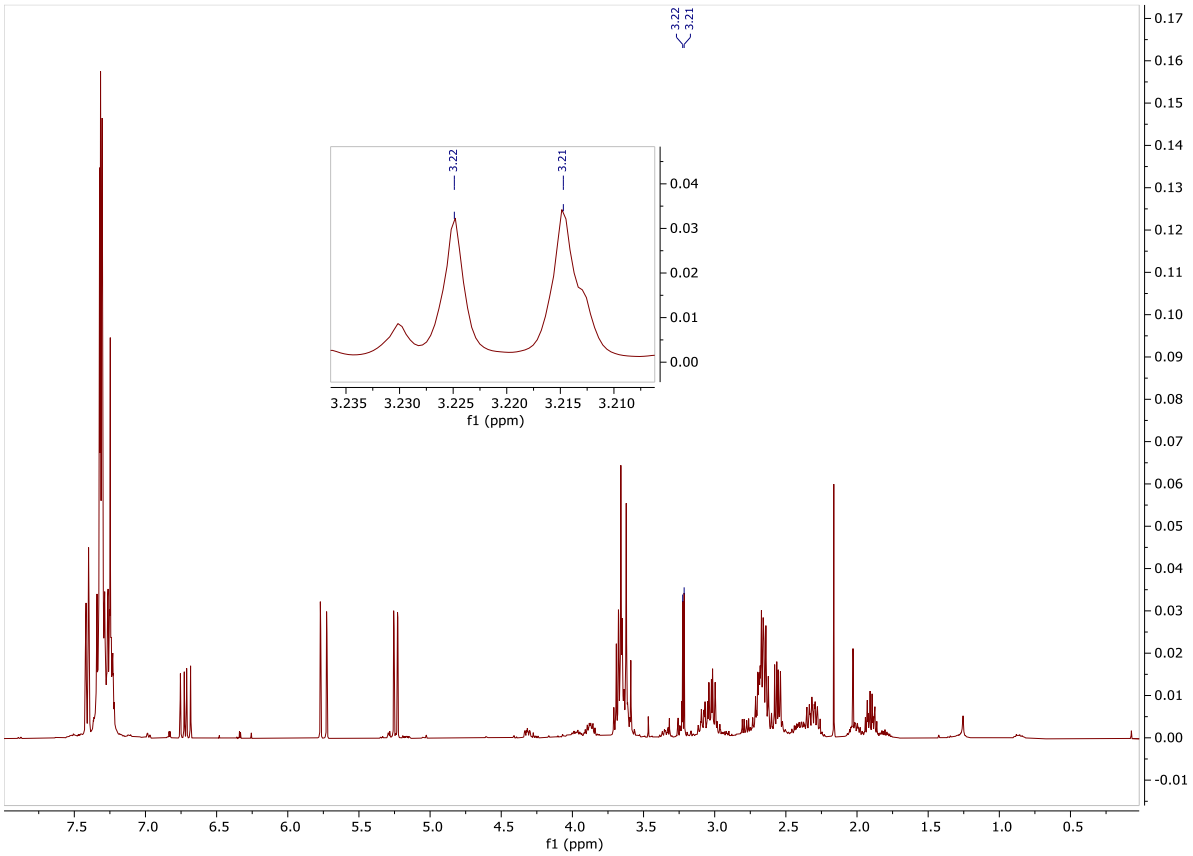


Figure S36. ^{1}H NMR spectrum of (3*S*)-1-benzyl-3-((2-methoxy-2-phenylethyl)selenyl) pyrrolidine **25** before purification (400 MHz, chloroform-*d*). Reaction performed in -20 ^{0}C.