Eur. J. Org. Chem. **2007** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2007 · ISSN 1434–193X

SUPPORTING INFORMATION

Title: Diastereoselective Cyclisation of *N*-Alkenylideneamines into 3,4-Dihydro-2*H*-pyrrol-1-ium Halides
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Ref. No.: O200601081

General Procedure for the Synthesis of *N*-(alkenylidene)-alkyl-amines 9 from amino acid methyl ester hydrochlorides: The appropriate amino acid methyl ester hydrochloride (10.0 mmol) was dissolved in CH_2Cl_2 (10 mL) and treated with 10.5 mmol (1.48 ml, 1.05 eq) triethylamine. After 1 h at room temperature 1.35 g (12.0 mmol, 1.20 eq) 2,2-dimethyl-pent-4-enal and 2 g $MgSO_4$ were added and the mixture was stirred overnight. The suspension was filtered, the organic solvents were removed and Et_2O was added again. The suspension was filtered, and the solid was washed with Et_2O. After removing the Et_2O a colourless oil was obtained and used without further purification.

(2*S*,3*S*)-Methyl-2-(2,2-dimethyl-pent-4-enylideneamino)-3-methyl-pentanoate 9b: Starting material *L*-isoleucine methyl ester hydrochloride (242 mg, 1.33 mmol). Yield: 251 mg (79%). Colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.78 (t, 3H, CH_2-C*H*$_3$, *J* = 7.4 Hz); 0.80 (d, 3H, CH-C*H*$_3$, *J* = 8.4 Hz); 0.99 (s, 3H, C*H*$_3$); 1.00 (s, 3H, C*H*$_3$); 1.29-1.45 (m, 2H, C*H*$_2$-CH_3); 1.94-2.03 (m, 1H, C*H*-CH_3); 2.11 (d, 2H, C*H*$_2$-CH=, *J* = 7.5 Hz); 3.42 (d, 1H, C*H*-COO, *J* = 7.6 Hz); 3.64 (s, 3H, COOC*H*$_3$); 4.92-4.97 (m, 2H, =C*H*$_2$); 5.62-5.75 (m, 1H, =C*H*); 7.43 (s, 1H, C*H*=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 10.8 (CH_2-*C*H$_3$); 15.6 (CH-*C*H$_3$); 24.6 (2C$_q$-*C*H$_3$); 24.8 (*C*H$_2$-CH_3); 37.3 (*C*H-CH_3); 39.4 (*C*(CH_3)$_2$); 44.6 (*C*H$_2$-CH=); 51.7 (COO*C*H$_3$); 79.1 (*C*H-COOCH_3); 117.4 (=*C*H$_2$); 134.5 (=*C*H); 172.6 (*C*OO); 174.0 (*C*H=N) ppm.

(2*S*)-Methyl-2-(2,2-Dimethyl-pent-4-enylideneamino)-3-methyl-butanoate 9c: Starting material *L*-valine methyl ester hydrochloride (1.17 g, 6.98 mmol). Yield: 1.41 g (90%). Colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.78 (d, 3H, CH-C*H*$_3$, *J* = 6.8 Hz); 0.82 (d, 3H, CH-C*H*$_3$, *J* = 6.8 Hz); 1.00 (s, 3H, C*H*$_3$); 1.01 (s, 3H, C*H*$_3$); 2.12 (d, 2H, C*H*$_2$-CH=, *J* = 7.4 Hz); 2.15-2.22 (m, 1H, C*H*(CH_3)$_2$); 3.32 (d, 1H, C*H*-COO, *J* = 7.4 Hz); 3.65 (s, 3H, COOC*H*$_3$); 4.92-4.98 (m, 2H, =C*H*$_2$); 5.65-5.74 (m, 1H, =C*H*); 7.43 (s, 1H, C*H*=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 18.5 (CH-*C*H$_3$); 19.5 (CH-*C*H$_3$); 24.6 (2C$_q$-*C*H$_3$); 31.1 (*C*H-(CH_3)$_2$); 39.4 (*C*(CH_3)$_2$); 44.6 (*C*H$_2$-CH=); 51.8 (COO*C*H$_3$); 80.2 (*C*H-COOCH_3); 117.5 (=*C*H$_2$); 134.5 (=*C*H); 172.6 (*C*OO); 174.1 (*C*H=N) ppm.

General Procedure for the Synthesis of *N*-(alkenylidene)-alkyl-amines 9 using amines: The appropriate amine (10.0 mmol) was dissolved in CH_2Cl_2 (10 mL). 2,2-dimethyl-pent-4-enal (1.35 g, 12.0 mmol) and 2 g $MgSO_4$ were added and the mixture was stirred overnight at

room temperature. After filtration and removing the organic solvent a colourless oil was obtained and used without further purification.

[(*1S,2R*)-2-(*tert*-Butyl-dimethyl-silanyloxy)-1-methyl-2-phenyl-ethyl]-(2,2-dimethyl-pent-4-enyliden)-amin 9d: Starting material 2-(*tert*-butyl-dimethyl-silanyloxy)-1-methyl-2-phenyl-ethylamine (80 mg, 0.30 mmol). Yield: 92 mg (87%). Colourless oil. $[\alpha]_D^{20}$ = -31.2 ° (c = 1.05, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = -0.24 (s, 3H, Si-CH_3); 0.02 (s, 3H, Si-CH_3); 0.73 (s, 3H, C_q-CH_3); 0.80 (s, 3H, C_q-CH_3); 0.82 (s, 9H, C(CH_3)$_3$); 1.25 (d, 3H, CH-CH_3, *J* = 6.3 Hz); 1.86-1.90 (m, 2H, CH_2-CH=); 3.10-1.18 (m, 1H, C*H*-CH_3); 4.55 (d, 1H, C*H*-O, *J* = 7.6 Hz); 4.82-4.91 (m, 2H, =CH_2); 5.32-5.48 (m, 1H, =C*H*); 7.02 (s, 1H, C*H*=N); 7.12-7.21 (m, 5H, CH_{ar}) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = -4.9 (Si-*C*H_3); -4.6 (Si-*C*H_3); 18.2 (*C*(CH_3)$_3$); 19.5 (CH-*C*H_3); 24.2 (C_q-*C*H_3); 24.3 (C_q-*C*H_3); 25.8 (3C, C(*C*H_3)$_3$); 38.5 (*C*(CH_3)$_2$); 44.4 (*C*H_2-CH=); 73.9 (*C*H-CH_3); 78.9 (*C*H-O); 116.9 (=*C*H_2); 126.9 (*C*H_{ar}); 127.4 (2*C*H_{ar}); 127.5 (2*C*H_{ar}); 134.8 (=*C*H); 143.4 (*C*$_{ar}$); 170.7 (*C*H=N) ppm. $C_{22}H_{37}NOSi$ (359.621): calcd. C 73.48, H 10.37, N 3.89; found: C 73.27, H 10.71, N 3.81.

(*S*)-1-Methoxy-3-methyl-*N*-(2,2-dimethyl-pent-4-enylidene)butan-2-amine 9e: Starting material 1-methoxy-3-methylbutan-2-amine (588 mg, 5.02 mmol). Yield: 807mg (76%). Colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.83 (d, 3H, CH-CH_3, *J* = 6.8 Hz); 0.86 (d, 3H, CH-CH_3, *J* = 6.8 Hz); 1.04 (s, 6H, 2CH_3); 1.76-1.87 (m, 1H, C*H*(CH_3)$_2$); 2.16 (d, 2H, CH_2-CH=, *J* = 7.4 Hz); 2.76-2.82 (m, 1H, C*H*-CH_2O); 3.30 (s, 3H, OCH_3); 3.35 (dd, 1H, C*H*H-O, *J* = 7.8 Hz, *J* = 9.7 Hz); 3.54 (dd, 1H, CHH_2-O, *J* = 4.0 Hz, *J* = 9.7 Hz); 4.99-5.04 (m, 2H, =CH_2); 5.71-5.85 (m, 1H, =C*H*); 7.44 (s, 1H, C*H*=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 18.6 (CH-*C*H_3); 19.9 (CH-*C*H_3); 24.7 (C_q-*C*H_3); 25.0 (C_q-*C*H_3); 29.8 (*C*H-(CH_3)$_2$); 39.0 (*C*(CH_3)$_2$); 44.8 (*C*H_2-CH=); 58.8 (O*C*H_3); 74.8 (*C*H_2-O); 76.3 (*C*H-CH_2O); 117.0 (=*C*H_2); 135.0 (=*C*H); 171.1 (*C*H=N) ppm. $C_{13}H_{25}NO$ (EI): calcd. 211.1936; found: 211.19364.

(*R*)-*N*-(2,2-Dimethylpent-4-enylidene)-1-phenylethanamine 9f: Starting material *R*-1-phenylethanamine (2.92 g, 24.1 mmol). Yield: 5.18 g (quant.). Colourless oil. $[\alpha]_D^{20}$ = +42.6 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.98 (s, 3H, CH_3); 0.99 (s, 3H, CH_3); 1.37 (d, 3H, CH_3-CH, *J* = 6.7 Hz); 2.11 (d, 2H, CH_2-CH=, *J* = 7.4 Hz); 4.20 (q, 1H, C*H*-CH_3 *J* = 6.7 Hz); 4.90-4.95 (m, 2H, =CH_2); 5.64-5.73 (m, 1H, =C*H*); 7.12-7.28 (m, 5H, CH_{ar}); 7.52 (s, 1H, C*H*=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.6 (*C*H_3); 24.8 (*C*H_3);

25.0 (CH$_3$); 38.9 (C(CH$_3$)$_2$); 44.7(CH$_2$); 69.2 (CH-CH$_3$); 117.3 (=CH$_2$); 126.5 (3CH$_{ar}$); 128.3 (2CH$_{ar}$); 134.8 (=CH); 145.5 (C_{ar}); 169.6 (CH=N) ppm. $C_{15}H_{21}N$ (EI): calcd. 215.16740; found: 215.16735. $C_{15}H_{21}N$ (215.167): calcd. C 83.67, H 9.83, N 6.50; found: C 83.91, H 9.69, N 6.45.

***rac*-*N*-(2,2-Dimethylpent-4-enylidene)-1-(naphthalen-1-yl)ethanamine 9g:** Starting material *rac*-1-(naphthalen-1-yl)-ethanamine (181 mg, 1.06 mmol). Yield: 232 mg (82%). Yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.98 (s, 3H, CH_3); 0.99 (s, 3H, CH_3); 1.51 (d, 3H, CH_3-CH, J = 6.8 Hz); 2.10 (d, 2H, CH_2-CH=, J = 7.5 Hz); 4.88-4.92 (m, 2H, =CH_2); 5.00 (q, 1H, CH-CH$_3$ J = 6.6 Hz); 5.59-5.73 (m, 1H, =CH); 7.35-7.42 (m, 3H, CH_{ar}); 7.57 (s, 1H, CH=N); 7.65 (d, 2H, 2CH_{ar}, J = 7.5 Hz); 7.75-7.79 (m, 1H, CH_{ar}); 8.07 (d, 1H, CH_{ar}, J = 7.5 Hz) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.5 (CH$_3$); 24.6 (CH$_3$); 24.8 (CH$_3$); 39.0 (C(CH$_3$)$_2$); 44.7(CH$_2$); 65.2 (CH-CH$_3$); 117.3 (=CH$_2$); 123.7 (CH$_{ar}$); 123.8 (CH$_{ar}$); 125.2 (CH$_{ar}$); 125.6 (CH$_{ar}$); 125.7 (CH$_{ar}$); 127.1 (CH$_{ar}$); 128.9 (CH$_{ar}$); 130.6 (C_{ar}); 133.9 (C_{ar}); 134.8 (=CH); 141.4 (C_{ar}); 169.6 (CH=N) ppm. $C_{19}H_{23}N$ (EI): calcd. 265.18305; found: 265.18309.

(*R*)-*N*-(2,2-Dimethyl-pent-4-enylidene)-1-phenyl-2-(phenylthio)ethanamine 9h: Starting material (*R*)-1-phenyl-2-(phenylthio)ethanamine (0.15 g, 0.65 mmol). Yield: 0.20 g (95%). Colourless oil. $[\alpha]_D^{20}$ = -42.1 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.97 (s, 3H, CH_3); 0.98 (s, 3H, CH_3); 2.10 (d, 2H, CH_2-CH=, J = 7.5 Hz); 3.19 (dd, 1H, S-CH'H, J = 9.4 Hz, J = 13.2 Hz); 3.29 (dd, 1H, S-CH'H, CH$_2$, J = 4.1 Hz, J = 13.6 Hz); 4.11 (dd, 1H, CHH-CH, J = 4.1 Hz, J = 9.4 Hz); 4.90-4.95 (m, 2H, =CH_2); 5.65-5.79 (m, 1H, =CH); 7.06-7.33 (m, 10H, CH_{ar}); 7.47 (s, 1H, CH=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.6 (CH$_3$); 24.7 (CH$_3$); 39.3 (C(CH$_3$)$_2$); 42.0 (S-CH$_2$); 44.6 (CH$_2$-CH=); 73.4 (CH); 117.3 (=CH$_2$); 125.8 (CH$_{ar}$); 126.8 (2CH$_{ar}$); 127.2 (CH$_{ar}$); 128.5 (2CH$_{ar}$); 128.9 (2CH$_{ar}$); 129.0 (2CH$_{ar}$); 134.9 (=CH); 136.6 (C_{ar}); 143.3 (C_{ar}); 172.0 (CH=N) ppm.

(*1R*)-*N*-(2,2-dimethylpent-4-enylidene)-1-phenyl-2-(phenylsulfinyl)ethanamine 9i: Starting material (*R*)-1-phenyl-2-(phenylsulfinyl)ethanamine (38 mg, 0.15 mmol). Yield: 33 mg (65%). Colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.00 (s, 3H, CH_3); 1.01 (s, 3H, CH_3); 2.13 (d, 2H, CH_2-CH=, J = 7.5 Hz); 3.22 (dd, 1H, S-CH'H, J = 7.9 Hz, J = 12.8 Hz); 3.31 (dd, 1H, S-CH'H, CH$_2$, J = 6.4 Hz, J = 12.8 Hz); 4.58 (dd, 1H, CHH-CH, J = 6.4 Hz, J = 7.5 Hz); 4.94-5.10 (m, 2H, =CH_2); 5.62-5.76 (m, 1H, =CH); 7.26-7.52 (m, 10H, CH_{ar}); 7.60

(s, 1H, C*H*=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.6 (2*C*H_3); 39.4 (*C*$(CH_3)_2$); 44.5 (*C*H_2-CH=); 66.6 (S-*C*H_2); 69.0 (*C*H); 117.6 (=*C*H_2); 124.3 (2*C*H_{ar}); 127.4 (2*C*H_{ar}); 127.8 (*C*H_{ar}); 128.8 (2*C*H_{ar}); 129.4 (2*C*H_{ar}); 131.2 (*C*H_{ar}); 134.6 (=*C*H); 141.7 (*C*$_{ar}$); 144.1 (*C*$_{ar}$); 172.7 (*C*H=N) ppm.

(*R*)-Methyl-2-(2,2-dimethyl-pent-4-enylideneamino)-2-phenylacetate 9j: Starting material (*R*)-methyl-2-amino-2-phenylacetate hydrochloride (1.09 g, 5.40 mmol). Yield: 1.40 g (quant.). Colourless oil. $[\alpha]_D^{20}$ = -14.0 ° (c = 3.08, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.02 (s, 6H, 2C*H*$_3$); 2.13 (d, 2H, C*H*$_2$-CH=, *J* = 7.4 Hz); 3.62 (s, 3H, COOC*H*$_3$); 4.89-4.94 (m, 3H, =C*H*$_2$, C*H*-COOCH$_3$); 5.58-5.74 (m, 1H, =C*H*); 7.18-7.36 (m, 5H, C*H*$_{ar}$); 7.54 (s, 1H, C*H*=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.4 (*C*H_3); 24.5 (*C*H_3); 39.6 (*C*$(CH_3)_2$); 44.5(*C*H_2); 52.4 (COO*C*H_3); 76.1 (*C*H-COO); 117.5 (=*C*H_2); 127.6 (2*C*H_{ar}); 127.8 (*C*H_{ar}); 128.5 (2*C*H_{ar}); 134.5 (=*C*H); 138.2 (*C*$_{ar}$); 171.6 (*C*OO); 174.5 (*C*H=N) ppm. $C_{16}H_{21}NO_2^+$ (EI): calcd. 259.1572; found: 259.1574.

(*S*)-Methyl-2-(2,2-dimethyl-pent-4-enylideneamino)-2-phenylacetate 9j(*S*): Starting material (*S*)-methyl-2-amino-2-phenylacetate hydrochloride (1.08 g, 5.36 mmol). Yield: 1.39 g (quant.). Colourless oil. $[\alpha]_D^{20}$ =+15.3 ° (c = 3.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 6H, 2C*H*$_3$); 2.21 (d, 2H, C*H*$_2$-CH=, *J* = 7.5 Hz); 3.70 (s, 3H, COOC*H*$_3$); 4.97-5.02 (m, 3H, =C*H*$_2$, C*H*-COOCH$_3$); 5.66-5.82 (m, 1H, =C*H*); 7.26-7.44 (m, 5H, C*H*$_{ar}$); 7.62 (s, 1H, C*H*=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.6 (*C*H_3); 24.7 (*C*H_3); 39.7 (*C*$(CH_3)_2$); 44.6(*C*H_2); 52.5 (COO*C*H_3); 76.1 (*C*H-COO); 117.7 (=*C*H_2); 127.8 (2*C*H_{ar}); 128.0 (*C*H_{ar}); 128.6 (2*C*H_{ar}); 134.6 (=*C*H); 138.3 (*C*$_{ar}$); 171.8 (*C*OO); 174.7 (*C*H=N) ppm. $C_{16}H_{22}NO_2^+$ (ESI+): calcd. 260.1645; found: 260.1642.

(*2S*)-2-Bromomethyl-1-((*1S*)-1-methoxycarbonyl-2-methyl-propyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Bromide and (*2R*)-2-Bromomethyl-1-((*1S*)-1-methoxycarbonyl-2-methyl-propyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Bromide 10c: Starting material **9c** (0.20 g, 0.89 mmol). Diastereomers were not separated. Yield: 0.34 g (0.89 mmol, quant.). d. r. = 46:54. Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.09, 1.10 (s, 3H, C*H*$_3$); 1.12, 1.14 (s, 3H, C*H*$_3$); 1.18, 1.46 (d, 3H, CH–C*H*$_3$, *J* = 6.6 Hz, *J* = 6.5 Hz); 1.55, 1.61 (d, 3H, CH–C*H*$_3$, *J* = 8.9 Hz, *J* = 9.0 Hz); 2.04–2.23 (m, 1H, C*H*–CH$_3$); 2.48–2.59 (m, 2H, C*H*$_2$–C$(CH_3)_2$); 3.32–3.70 (m, 2H, C*H*$_2$–Br); 3.80, 4.44 (d, 1H, C*H*–COO, *J* = 9.5 Hz, *J* = 11.2 Hz); 3.85, 3.90 (s, 3H, COOC*H*$_3$); 5.24–5.33, 5.53–5.61 (m, 1H, C*H*–N); 9.08, 9.13 (s, 1H,

C*H*=N^+) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 18.8, 19.0 (CH–*C*H_3); 19.1, 19.2 (CH–*C*H_3); 24.8, 24.9 (C_q–*C*H_3); 25.6, 26.8 (C_q–*C*H_3); 30.8, 35.0 (*C*H–CH_3); 32.0, 33.1 (*C*H_2–Br); 38.0, 38.5 (*C*H_2–C(CH_3)$_2$); 49.1, 49.3 (*C*(CH_3)$_2$); 54.4, 54.9 (COO*C*H_3); 68.1, 69.6 (*C*H–N); 73.1, 75.1 (*C*H–COO); 166.4, 167.4 (*C*OO); 189.6, 190.7 (*C*H=N^+) ppm. HRMS (ESI$^+$ in MeCN): calcd. for $C_{13}H_{23}NBrO_2^+$: 304.0907; found: 304.0907.

(*2S*)-2-Bromomethyl-1-[(*1S,2R*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-methyl-2-phenyl-ethyl]-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Bromide and (*2R*)-2-Bromomethyl-1-[(*1S,2R*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-methyl-2-phenyl-ethyl]-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Bromide 10d: Starting material **9d** (69 mg, 0.19 mmol). Diastereomers were not separated. Yield: 95 mg (0.18 mmol, 96%). d. r. = 50:50. White foam. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = –0.03, 0.01 (s, 3H, Si–C*H*$_3$); 0.34, 0.45 (s, 3H, Si–C*H*$_3$); 1.11, 1.18 (s, 9H, C(C*H*$_3$)$_3$); 1.63, 1.73 (s, 3H, C*H*$_3$); 1.75, 1.76 (s, 3H, C*H*$_3$); 1.94, 2.09 (d, 3H, CH–C*H*$_3$, *J* = 6.8 Hz, *J* = 6.8 Hz); 2.11–2.75 (m, 2H, C*H*$_2$–C(CH_3)$_2$); 3.80–4.18 (m, 2H, C*H*$_2$–Br); 4.15–4.57 (m, 1H, C*H*–CH_3); 4.43–4.57, 6.40–6.45 (m, 1H, C*H*–N); 5.69, 5.87 (d, 1H, C*H*–O, *J* = 6.5 Hz); 7.57–7.81 (m, 5H, C*H*$_{ar}$); 9.39, 10.52 (s, 1H, C*H*=N^+) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = –4.4, –4.3 (2C, Si–*C*H_3); 16.0, 17.9 (CH–*C*H_3); 18.0 (*C*(CH_3)$_3$); 25.3, 25.5 (C_q–*C*H_3); 25.8, 26.4 (C_q–*C*H_3); 25.9 (3C, C(*C*H_3)$_3$); 31.7, 32.5 (*C*H_2–Br); 38.4, 38.9 (*C*H_2–C(CH_3)$_2$); 48.1, 48.2 (*C*(CH_3)$_2$); 63.9, 64.2 (*C*H–CH_3); 72.5, 73.6 (*C*H–N); 74.7, 75.7 (*C*H–O); 126.8, 127.2 (2*C*H_{ar}); 128.8, 129.0 (*C*H_{ar}); 129.1, 129.6 (2*C*H_{ar}); 139.0, 139.6 (*C*$_{ar}$); 187.6, 189.7 (*C*H=N^+) ppm. $C_{22}H_{37}NBrOSi^+$ (EI): calcd. 438.1828; found: 438.1827.

(*2S*)-2-Bromomethyl-4,4-dimethyl-1-((*1R*)-1-phenyl-ethyl)-3,4-dihydro-2*H*-pyrrolium Bromide and (*2R*)-2-Bromomethyl-4,4-dimethyl-1-((*1R*)-1-phenyl-ethyl)-3,4-dihydro-2*H*-pyrrolium Bromide 10f: Starting material **9f** (105 mg, 0.488 mmol). Diastereomers were not separated. Yield: 183 mg (0.488 mmol, quant.). d. r. = 45:55. White foam. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.42, 1.46 (s, 3H, C*H*$_3$); 1.53, 1.61 (s, 3H, C*H*$_3$); 2.02, 2.04 (d, 3H, CH–C*H*$_3$, *J* = 7.4 Hz, *J* = 7.1 Hz); 1.79–2.55 (m, 2H, C*H*$_2$–C(CH_3)$_2$)); 3.64–3.80 (m, 1H, CH*H*–Br); 3.93–4.08 (m, 1H, C*H*H–Br); 5.13, 5.46 (q, 1H, C*H*–Ph, *J* = 6.9 Hz, *J* = 6.6 Hz); 4.48–4.59, 5.90–6.01 (m, 1H, C*H*–N); 7.22–7.60 (m, 5H, C*H*$_{ar}$); 9.07, 10.46 (s, 1H, C*H*=N^+) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 21.5, 21.8 (CH–*C*H_3); 24.6, 25.3 (C_q–*C*H_3); 26.0, 26.5 (C_q–*C*H_3); 31.6, 33.3 (*C*H_2–Br); 39.0, 39.6 (*C*H_2– C(CH_3)$_2$); 47.9, 48.0 (*C*(CH_3)$_2$); 62.5, 63.0 (*C*H–Ph); 69.1, 72.3 (*C*H–N); 126.8, 128.1 (2*C*H_{ar}); 129.8, 130.1 (2*C*H_{ar}); 130.1, 130.2

(CH$_{ar}$); 134.7, 135.0 (C_{ar}); 186.1, 187.4 (CH=N$^+$) ppm. $C_{15}H_{21}NBr^+$ (EI): calcd. 294.0857; found: 294.0857. $C_{15}H_{21}Br_2N$ (375.142): calcd. C 48.02, H 5.64, Br 42.60, N 3.73; found: C 47.84, H 5.91, Br 42.43, N 3.82.

***rac*-4,4-Dimethyl-1-(1-naphthalen-1-yl-ethyl)-2-((phenylselanyl)methyl)pyrrolidine 14c:** Starting material **9g** (100 mg, 0.377 mmol). Diastereomers were not separated. Yield: 129 mg (0.305 mmol, 81%). d. r. = 48:52. Colourless oil. R_f = 0.48 and 0.50 (hexane/ EtOAc, 9:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.98, 1.00 (s, 3H, C$_q$–CH_3); 1.03, 1.10 (s, 3H, C$_q$–CH_3); 1.42, 1.46 (d, 3H, CH–CH_3, J = 6.4 Hz); 1.54, 1.66 (dd, 1H, CH–CH'H–C$_q$, J = 6.8 Hz, J = 13.2 Hz); 1.84–1.93 (m, 1H, CH–CH'H–C$_q$); 2.40, 2.69 (d, 1H, N–CH'H, J = 8.3 Hz); 2.52, 2.74 (d, 1H, N–CH'H, J = 8.3 Hz); 2.92–3.30 (m, 3H, CH_2Se, CH–CH$_2$Se); 4.11, 4.51 (q, 1H, CH–CH$_3$, J = 6.8 Hz); 7.10–7.86 (m, 12H, CH_{ar}) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 17.0, 22.0 (CH–CH$_3$); 28.4, 28.7 (C$_q$–CH$_3$); 28.6, 29.7 (C$_q$–CH$_3$); 33.3, 35.7 (CH$_2$Se); 35.6, 37.0 (C(CH$_3$)$_2$); 46.8, 46.9 (CH–CH$_2$); 57.0, 61.8 (CH); 62.7 (CH); 63.9, 66.7 (N–CH$_2$); 124.5, 124.6 (CH$_{ar}$); 125.3, 125.4 (CH$_{ar}$); 125.4, 125.5 (CH$_{ar}$); 126.5, 126.9 (CH$_{ar}$); 127.2, 127.4 (CH$_{ar}$); 127.5, 127.6 (CH$_{ar}$); 128.4, 128.6 (2CH$_{ar}$); 128.7, 129.0 (CH$_{ar}$); 129.3, 129.5 (CH$_{ar}$); 128.8, 129.2 (C_{ar}); 131.6, 131.8 (C_{ar}Se); 133.3, 133.7 (2CH$_{ar}$); 134.2 (C_{ar}); 141.3, 141.5 (CH–C_{ar}) ppm. HRMS (EI): calcd. for $C_{25}H_{29}NSe$: 423.14652; found: 423.14655.

(*2R*)-4,4-Dimethyl-1-((*1R*)-1-phenyl-2-(phenylthio)ethyl)-2-((phenylselanyl)methyl) pyrrolidine and (*2S*)-4,4-Dimethyl-1-((*1R*)-1-phenyl-2-(phenylthio)ethyl)-2-((phenyl-selanyl)methyl)pyrrolidine 14d: Starting material **9h** (0.10 g, 0.31 mmol). Diastereomers were not separated. Yield: 67 mg (0.14 mmol, 45%). d. r. = 41:59. Colourless oil. R_f = 0.40 and 0.42 (hexane/ EtOAc, 9:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.67, 0.92 (s, 3H, C$_q$–CH_3); 0.99, 1.05 (s, 3H, C$_q$–CH_3); 1.41–1.75 (m, 2H, CH–CH_2–C$_q$); 2.14, 2.37 (d, 1H, N–CH'H, J = 8.2 Hz); 2.56, 2.63 (d, 1H, N–CH'H, J = 8.2 Hz); 2.69–3.11 (m, 3H, CH_2Se, CH–CH$_2$Se); 3.27, 3.31 (dd, 1H, S–CH'H, J = 4.4 Hz, J = 11.8 Hz); 3.17, 3.43 (dd, 1H, S–CH'H, J = 8.0 Hz, J = 12.3 Hz); 3.89, 3.60 (t, 1H, CH–Ph, J = 7.7 Hz); 7.05–7.26 (m, 15H, CH_{ar}) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 27.9, 28.6 (C$_q$–CH$_3$); 29.1, 29.3 (C$_q$–CH$_3$); 33.4, 33.6 (CH$_2$Se); 35.3, 36.0 (C(CH$_3$)$_2$); 35.7, 37.6 (S–CH$_2$); 45.6, 46.1 (CH–CH$_2$); 59.1, 60.8 (CH–Ph); 60.9, 63.1 (CH); 59.9, 63.3 (N–CH$_2$); 125.6, 126.1 (CH$_{ar}$); 126.5, 126.7 (CH$_{ar}$); 127.7, 128.0 (2CH$_{ar}$); 128.2, 128.5 (CH$_{ar}$); 128.7, 128.8 (2CH$_{ar}$); 128.9, 129.0 (2CH$_{ar}$); 128.9, 129.2 (2CH$_{ar}$); 129.4, 129.5 (2CH$_{ar}$); 130.7, 130.9 (C_{ar}Se); 132.4, 133.1 (2CH$_{ar}$); 136.4, 137.3

(C_{ar}S); 141.1 (CH–C_{ar}) ppm. HRMS (ESI^+): calcd. for $C_{27}H_{32}NSSe$: 482.1415; found: 482.1419.

(*2R*)-4,4-Dimethyl-1-((*1R*)-1-phenyl-2-(phenylsulfinyl)ethyl)-2-((phenylselanyl)methyl) pyrrolidine and (*2S*)-4,4-Dimethyl-1-((*1R*)-1-phenyl-2-(phenylsulfinyl)ethyl)-2-((phenyl-selanyl)methyl)pyrrolidine 14e : Starting material **9i** (33 mg, 0.097 mmol). Diastereomers were separated. d. r. = 33:67. Minor isomer: Yield: 12 mg (0.024 mmol, 25%). Colourless oil. R_f = 0.65 (hexane/ EtOAc, 1:1). $[\alpha]_D^{20}$ = +76.4 ° (c = 1.10, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3H, C_q–C*H*$_3$); 1.11 (s, 3H, C_q–C*H*$_3$); 1.47 (dd, 1H, CH–CH'*H*–C_q, *J* = 6.4 Hz, *J* = 12.8 Hz); 1.65 (dd, 1H, CH–CH'*H*–C_q, *J* = 8.3 Hz, *J* = 12.8 Hz); 2.26 (d, 1H, N–CH'*H*, *J* = 8.3 Hz); 2.77 (d, 1H, N–C*H*'H, *J* = 8.3 Hz); 2.78–2.88 (m, 2H, CH*H*Se, C*H*–CH_2Se); 3.11–3.18 (m, 2H, C*H*HSe, S–C*H*'H); 3.57 (dd, 1H, S–CH'*H*, *J* = 8.7 Hz, *J* = 13.1 Hz); 4.08 (dd, 1H, C*H*–Ph, *J* = 7.4 Hz, *J* = 8.4 Hz); 6.93–6.96 (m, 2H, C*H*$_{ar}$); 7.24–7.28 (m, 6H, C*H*$_{ar}$) ; 7.44–7.52 (m, 5H, C*H*$_{ar}$) ; 7.68–7.71 (m, 2H, C*H*$_{ar}$) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 28.0 (C_q–*C*H$_3$); 29.5 (C_q–*C*H$_3$); 33.1 (*C*H_2Se); 35.7 (*C*(CH_3)$_2$); 46.0 (CH–*C*H_2); 57.4 (*C*H–Ph); 59.2 (*C*H); 60.2 (N–*C*H_2); 62.5 (S–*C*H_2); 124.8 (2*C*H$_{ar}$); 127.1 (*C*H$_{ar}$); 128.1 (*C*H$_{ar}$); 128.4 (2*C*H$_{ar}$); 129.0 (2*C*H$_{ar}$); 129.2 (2*C*H$_{ar}$); 129.4 (2*C*H$_{ar}$); 130.4 (C_{ar}Se); 131.4 (*C*H$_{ar}$); 133.4 (2*C*H$_{ar}$); 134.6 (CH–C_{ar}); 144.4 (SC_{ar}) ppm. $C_{27}H_{31}NOSSe$ (496.566): calcd. C 65.31, H 6.29, N 2.82.; found: C 65.25, H 6.07, N 2.74. Major isomer: Yield: 24 mg (0.048 mmol, 50%). Colourless oil. R_f = 0.54 (hexane/ EtOAc, 1:1). $[\alpha]_D^{20}$ = –46.0 ° (c = 1.20, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.96 (s, 3H, C_q–C*H*$_3$); 1.06 (s, 3H, C_q–C*H*$_3$); 1.62 (dd, 1H, CH–CH'*H*–C_q, *J* = 5.7 Hz, *J* = 12.8 Hz); 1.79 (dd, 1H, CH–CH'*H*–C_q, *J* = 8.6 Hz, *J* = 12.8 Hz); 2.35 (d, 1H, N–CH'*H*, *J* = 8.6 Hz); 2.61 (d, 1H, N–C*H*'H, *J* = 8.7 Hz); 2.84–2.88 (m, 2H, CH_2Se); 3.10–3.13 (m, 2H, C*H*–CH_2Se, S–C*H*'H); 3.24 (dd, 1H, S–CH'*H*, *J* = 3.7 Hz, *J* = 12.7 Hz); 4.30 (dd, 1H, C*H*–Ph, *J* = 3.8 Hz, *J* = 10.6 Hz); 7.20–7.58 (m, 15H, C*H*$_{ar}$) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 28.7 (C_q–*C*H$_3$); 29.2 (C_q–*C*H$_3$); 33.5 (*C*H_2Se); 36.0 (*C*(CH_3)$_2$); 46.0 (CH–*C*H_2); 59.8 (*C*H–Ph); 61.1 (*C*H); 61.2 (S–*C*H_2); 64.1 (N–*C*H_2); 124.0 (2*C*H$_{ar}$); 126.7 (*C*H$_{ar}$); 128.1 (*C*H$_{ar}$); 128.7 (2*C*H$_{ar}$); 128.8 (2*C*H$_{ar}$); 129.1 (2*C*H$_{ar}$); 129.4 (2*C*H$_{ar}$); 130.6 (C_{ar}Se); 131.2 (*C*H$_{ar}$); 132.6 (2*C*H$_{ar}$); 139.9 (CH–C_{ar}); 144.8 (SC_{ar}) ppm. HRMS (ESI^+): calcd. for $C_{27}H_{32}NOSSe$: 498.1364; found: 498.1364.

(*R*)-Methyl-2-(2,2-dimethyl-hex-5-enylideneamino)-2-phenylacetate 15a: Starting material (*R*)-methyl-2-amino-2-phenylacetate hydrochloride (0.61 g, 3.0 mmol) and 2,2-dimethylhex-5-enal (0.40 g, 3.1 mmol). Yield: 0.75 g (91%). Colourless oil. $[\alpha]_D^{20}$ = -15.4 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 3H, C*H*$_3$); 1.11 (s, 3H, C*H*$_3$); 1.49-1.57 (m, 2H, C*H*$_2$-C$_q$); 1.93-2.01 (m, 2H, C*H*$_2$-CH=); 3.70 (s, 3H, COOC*H*$_3$); 4.87-4.99 (m, 3H, =C*H*$_2$ und C*H*-COO); 5.70-5.83 (m, 1H, =C*H*); 7.26-7.45 (m, 5H, C*H*$_{ar}$); 7.58 (s, 1H, C*H*=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.6 (*C*H$_3$); 24.8 (*C*H$_3$); 28.9(=CH-*C*H$_2$); 39.6 (C$_q$-*C*H$_2$); 39.7 (*C*(CH$_3$)$_2$); 52.5 (COO*C*H$_3$); 76.3 (*C*H-COO); 114.3 (=*C*H$_2$); 127.8 (2*C*H$_{ar}$); 128.0 (*C*H$_{ar}$); 128.6 (2*C*H$_{ar}$); 138.4 (*C*$_{ar}$); 139.1 (=*C*H); 171.8 (*C*OO); 174.8 (*C*H=N) ppm. $C_{17}H_{23}NO_2$ (273.370): calcd. C 74.69, H 8.48, N 5.12; found: C 74.56, H 8.54, N 5.15.

(*R*)-Methyl-2-(2,2,4-trimethyl-pent-4-enylideneamino)-2-phenylacetate 15b: Starting material (*R*)-methyl-2-amino-2-phenylacetate hydrochloride (0.76 g, 3.8 mmol) and 2,2,4-trimethylpent-4-enal (0.50 g, 4.0 mmol). Yield: 0.89 g (86%). Yellowish oil. $[\alpha]_D^{22}$ = -12.4 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 3H, C*H*$_3$); 1.13 (s, 3H, C*H*$_3$); 1.58 (s, 3H, C*H*$_3$); 2.19 (s, 2H, C*H*$_2$); 3.70 (s, 3H, CH-COOC*H*$_3$); 4.62 (s, 1H, =C*H*H); 4.76 (s, 1H, =C*H*H); 4.98 (s, 1H, C*H*-COOCH$_3$); 7.26-7.44 (m, 5H, C*H*$_{ar}$); 7.66 (s, 1H, C*H*=N) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.5 (*C*H$_3$); 25.2 (*C*H$_3$); 25.3 (*C*H$_3$); 40.0 (*C*(CH$_3$)$_2$); 48.6 (*C*H$_2$); 52.4 (COO*C*H$_3$); 76.3 (*C*H-COOCH$_3$); 114.6 (=*C*H$_2$); 128.0 (2*C*H$_{ar}$); 128.6 (2*C*H$_{ar}$); 128.9 (*C*H$_{ar}$); 138.1 (*C*$_{ar}$); 142.6 (=*C*); 175.1 (*C*H=N); 171.7 (*C*OOCH$_3$) ppm. $C_{17}H_{24}O_2N$ (ESI+): calcd. 274.1802; found: 274.1802.

***N*-(2,2-Dimethyl-1-phenylpent-4-enylidene)-1-phenylethanamine 15d:** 2,2-dimethyl-1-phenylpent-4-en-1-one (500 mg, 2.66 mmol), tetraisopropylorthotitanate (11.1 ml, 37.2 mmol) and *R*-1-phenylethanamine were dissolved in dry THF (5 mL) under argon in a flame-dried flask and stirred for 7 d at room temperature. A 0.5 N solution of NaOH was added. The aqueous layer was separated and washed with Et_2O (3 x 10 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under vacuum. The remaining yellow oil was purified by column chromatography (40 g silica gel, 2.3 cm column diameter, cyclohexane / EtOAc mixture). Yield: 404 mg (58%). Colourless liquid. $[\alpha]_D^{22}$ = +122.8 ° (c = 1.00,

CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 3H, CH_3); 1.11 (s, 3H, CH_3); 1.28 (d, 3H, CH-CH_3, *J* = 6.4 Hz); 2.36 (dd, 2H, CH_2, *J* = 1.5 Hz, *J* = 7.2 Hz); 4.10 (q, 1H, C*H*-CH_3, *J* = 6.5 Hz); 4.99-5.06 (m, 2H, =CH_2); 5.82-5.95 (m, 1H, =C*H*); 6.79 (d, 1H, CH_{ar}, *J* = 6.4 Hz); 7.05 (d, 1H, CH_{ar}, *J* = 7.2 Hz); 7.16-7.41 (m, 8H, CH_{ar}) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 25.3 (*C*H_3); 26.5 (2*C*H_3); 42.9 (*C*$(CH_3)_2$); 45.1 (*C*H_2); 60.8 (*C*H-CH_3); 117.0 (=*C*H_2); 126.4 (2*C*H_{ar}); 126.7 (2*C*H_{ar}); 126.9 (*C*H_{ar}); 127.5 (2*C*H_{ar}); 128.0 (*C*H_{ar}); 128.2 (2*C*H_{ar}); 136.2 (=*C*H); 137.7 (C_q-C_{ar}); 146.6 (CH-C_{ar}); 174.8 (*C*=N) ppm. $C_{21}H_{25}N$ (291.430): calcd. C 86.55, H 8.65, N 4.81; found: C 86.34, H 8.73, N 4.84.

General Procedure for the Synthesis of *N*-(alkenylidene)-alkyl-amines 18 from 4,5-Didesoxy-2,3-O-isopropylidene-D-erythro-4-pentenose: 4,5-didesoxy-2,3-*O*-isopropylidene-D-*erythro*-4-pentenose (72%ig) (0.50 g, 2.3 mmol) and the amine (2.2 mmol, 0.95 eq) were dissolved in dry CH_2Cl_2 (10 mL). After adding 3 g $MgSO_4$ the mixture was stirred for 2 h at room temperature. The suspension was filtered, and the solid was washed with CH_2Cl_2. After removing the solvent a colourless oil was obtained and used without further purification.

***N*-(*4S*,*5R*)-Benzyl-((2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)methylene)amine 18a:** Starting material benzylamin (0.24 ml, 2.2 mmol) and 4,5-didesoxy-2,3-*O*-isopropylidene-D-*erythro*-4-pentenose (72%ig) (0.50 g, 2.3 mmol). Yield: 0.54 g (quant.). Colourless oil.$[\alpha]_D^{20}$ = +9.3 ° (c = 1.00, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.41 (s, 3H, CH_3); 1.57 (s, 3H, CH_3); 4.60 (d, 2H, C*HH*', *J* = 2.3 Hz); 4.70 (dd, 1H, C*H*, *J* = 6.4 Hz; *J* = 6.8 Hz); 4.79 (dd, 1H, C*H*, *J* = 6.8 Hz, *J* = 7.2 Hz); 5.23-5.40 (m, 2H, =CH_2); 5.69-5.80 (m, 1H, =C*H*); 7.30-7.34 (m, 5H, CH_{ar}); 7.62 (d, 1H, C*H*=N, *J* = 6.4 Hz) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 25.4 (*C*H_3); 27.8 (*C*H_3); 64.8 (*C*H_2); 79.5 (*C*H); 79.8 (*C*H); 110.1 (*C*$(CH_3)_2$); 118.7 (=*C*H_2); 127.2 (*C*H_{ar}); 128.2 (2*C*H_{ar}); 128.6 (2*C*H_{ar}); 133.0 (=*C*H); 138.4 (C_{ar}); 163.1 (*C*H=N) ppm. $C_{15}H_{19}O_2N$(EI): calcd. 245.1416; found: 245.1418.

(*R*)-*N*-((*4S*,*5R*)-2,2-Dimethyl-5-vinyl-[1,3]dioxolan-4-yl)methylene)-1-phenylethanamine 18b: Starting material *R*-1-phenyl-ethylamin (0.27 g, 2.2 mmol) and 4,5-didesoxy-2,3-*O*-isopropylidene-D-*erythro*-4-pentenose (72%ig) (0.50 g, 2.3 mmol). Yield: 0.57 g (quant.). Colourless oil. $[\alpha]_D^{20}$ = +65.5 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.39 (s, 3H, C_q-CH_3); 1.50 (d, 3H, CH-CH_3, *J* = 6.8 Hz); 1.54 (s, 3H, C_q-CH_3); 4.34 (q, 1H, C*H*-CH_3, *J* = 6.7 Hz); 4.69 (dd, 1H, C*H*-O, *J* = 6.5 Hz, *J* = 6.8 Hz); 4.76 (dd, 1H, C*H*-O, *J* = 6.7 Hz,

J = 6.9 Hz); 5.04 (d, 1H, =C*H*H, *J* = 10.3 Hz); 5.24 (d, 1H, =C*H*H, *J* = 17.1 Hz); 5.50-5.61 (ddd, 1H, =C*H*, *J* = 6.6 Hz, *J* = 10.4 Hz, *J* = 17.1 Hz); 7.17-7.32 (m, 5H, CH_{ar}); 7.56 (d, 1H, C*H*=N, *J* = 6.4 Hz) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 23.7 (CH-*C*H_3); 25.4 (C_q-*C*H_3); 27.8 (C_q-*C*H_3); 69.3 (*C*H-*C*H_3); 79.7 (2*C*H-O); 110.2 (*C*$(CH_3)_2$); 118.5 (=*C*H_2); 126.7 (*C*H_{ar}); 127.1 (2*C*H_{ar}); 128.5 (2*C*H_{ar}); 133.0 (=*C*H); 144.1 (*C*$_{ar}$); 161.2 (*C*H=N) ppm. $C_{16}H_{21}O_2N$(EI): calcd. 259.15723; found: 259.15722.

(*S*)-*N*-((*4S*,*5R*)-2,2-Dimethyl-5-vinyl-[1,3]dioxolan-4-yl)methylene)-1-phenylethanamine18c: Starting material *S*-1-phenyl-ethylamin (0.27 g, 2.2 mmol) and 4,5-didesoxy-2,3-*O*-isopropylidene-D-*erythro*-4-pentenose (72%ig) (0.50 g, 2.3 mmol). Yield: 0.57 g (quant.). Colourless oil. $[\alpha]_D^{20}$ = -53.1 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.40 (s, 3H, C_q-C*H*$_3$); 1.47 (d, 3H, CH-C*H*$_3$, *J* = 6.6 Hz); 1.56 (s, 3H, C_q-C*H*$_3$); 4.36 (q, 1H, C*H*-C*H*$_3$, *J* = 6.7 Hz); 4.70 (dd, 1H, N=CH-C*H*-O, *J* = 6.6 Hz, *J* = 6.8 Hz); 4.82 (dd, 1H, C=CH-C*H*-O, *J* = 6.9 Hz, *J* = 6.9 Hz); 5.04 (d, 1H, =CH*H*, *J* = 10.1 Hz); 5.24 (d, 1H, =C*H*H, *J* = 17.1 Hz); 5.77 (ddd, 1H, =C*H*, *J* = 6.8 Hz, *J* = 10.4 Hz, *J* = 17.1 Hz); 7.21-7.34 (m, 5H, CH_{ar}); 7.59 (d, 1H, C*H*=N, *J* = 6.4 Hz) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.5 (CH-*C*H_3); 25.4 (C_q-*C*H_3); 27.8 (C_q-*C*H_3); 69.6 (*C*H-*C*H_3); 79.6 (*C*H-O); 79.7 (*C*H-O); 110.2 (*C*$(CH_3)_2$); 118.5 (=*C*H_2); 125.8 (*C*H_{ar}); 126.7 (2*C*H_{ar}); 128.5 (2*C*H_{ar}); 133.2 (=*C*H); 144.0 (*C*$_{ar}$); 161.1 (*C*H=N) ppm. $C_{16}H_{21}O_2N$ (EI): calcd. 259.15723; found: 259.15725.

(*S*)-Methyl-2-[((*4S*,*5R*)-2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)methyleneamino]-2-phenylacetate 18d: Starting material (*S*)-methyl-2-amino-2-phenylacetate hydrochloride (88 mg, 0.44 mmol) and 4,5-didesoxy-2,3-*O*-isopropylidene-D-*erythro*-4-pentenose (72%ig) (0.10 g, 0.46 mmol). Yield: 136 mg (quant.). Colourless oil. $[\alpha]_D^{20}$ = +73.5 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.40 (s, 3H, C*H*$_3$); 1.55 (s, 3H, C*H*$_3$); 5.03 (s, 3H, COOC*H*$_3$); 4.79 (m, 2H, 2C*H*-O); 4.95-4.99 (m, 1H, =C*H*H); 5.03 (s, 1H, C*H*-COO); 5.19-5.25 (m, 1H, =C*H*H); 5.42-5.53 (m, 1H, =C*H*); 7.30-7.37 (m, 5H, CH_{ar}); 7.55 (d, 1H, C*H*=N, *J* = 5.8 Hz) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 25.3 (*C*H_3); 27.7 (*C*H_3); 52.6 (COO*C*H_3); 75.9 (*C*H-COO); 79.5 (*C*H); 79.7 (*C*H); 110.4 (*C*$(CH_3)_2$); 118.6 (=*C*H_2); 127.8 (2*C*H_{ar}); 128.8 (*C*H_{ar}); 128.9 (2*C*H_{ar}); 132.5 (=*C*H); 137.3 (*C*$_{ar}$); 166.2 (*C*H=N); 171.1 (*C*OOCH$_3$) ppm. $C_{17}H_{21}O_4N$ (EI): calcd. 303.14706; found: 303.14705.

(*3aR*,*4R*,*6aS*)-4-((2,4,6-Triisopropyl-phenylselanyl)methyl)-5-benzyl-tetrahydro-2,2-dimethyl-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole and (*3aR*,*4S*,*6aS*)-4-((2,4,6-Triisopropyl-

phenylselanyl)methyl)-5-benzyl-tetrahydro-2,2-dimethyl-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole 20c: Starting material **18a (**0.746 g, 3.04 mmol) and 2,4,6-triisopropylphenyl-selenenyl bromide (3.84 mmol). Diastereomers were not separated. Yield: 0.53 g (1.00 mmol, 33%). d. r. = 62:38. Colourless oil. R_f = 0.73 (hexane/ EtOAc 7:3). HRMS (ESI^+ in MeOH): calcd. for $C_{30}H_{44}SeO_2N^+$: 530.2532; found: 530.2525. Major isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.16 (d, 12H, CH(CH_3)$_2$, *J* = 7.1 Hz); 1.19 (d, 6H, CH(CH_3)$_2$, *J* = 7.0 Hz); 1.26 (s, 3H, CH_3); 1.45 (s, 3H, CH_3); 1.95 (dd, 1H, C*H*H, *J* = 4.6 Hz, *J* = 11.4 Hz); 2.31–2.38 (m, 1H, C*H*N); 2.88–3.05 (m, 5H, CH*H*, CH*H*–Ph, CH_2Se, C*H*(CH$_3$)$_2$); 3.81–3.96 (m, 3H, C*H*H–Ph, 2C*H*(CH$_3$)$_2$); 4.48 (dd, 1H, CH–C*H*–O, *J* = 4.5 Hz, *J* = 6.4 Hz); 4.65 (dd, 1H, CH$_2$C*H*–O, *J* = 4.6 Hz, *J* = 6.4 Hz); 6.95 (s, 2H, CH_{ar}); 7.04–7.23 (m, 5H, CH_{ar}) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.8 (2*C*H$_3$); 24.9 (4*C*H$_3$); 25.8 (*C*H$_3$); 26.5 (*C*H$_3$); 27.4 (*C*H$_2$Se); 34.3 (*C*H(CH$_3$)$_2$); 34.4 (2*C*H(CH$_3$)$_2$); 56.7 (*C*H$_2$Ph); 59.3 (*C*H$_2$N); 67.8 (*C*HN); 77.7 (*C*HCH$_2$); 81.2 (*C*HCH); 111.5 (*C*(CH$_3$)$_2$); 121.8 (2*C*H$_{ar}$); 127.0 (*C*H$_{ar}$); 128.0 (*C*$_{ar}$Se); 128.3 (2*C*H$_{ar}$); 128.8 (2*C*H$_{ar}$); 138.0 (*C*$_{ar}$); 149.6 (*C*$_{ar}$); 153.1 (2*C*$_{ar}$); ppm. Minor isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.15 (d, 12H, CH(CH_3)$_2$, *J* = 6.9 Hz); 1.18 (d, 6H, CH(CH_3)$_2$, *J* = 6.8 Hz); 1.24 (s, 3H, CH_3); 1.44 (s, 3H, CH_3); 2.41 (dd, 1H, C*H*H, *J* = 3.8 Hz, *J* = 12.0 Hz); 2.66–2.84 (m, 5H); 3.36 (d, 1H, CH*H*–Ph, *J* = 12.9 Hz); 3.81–3.96 (m, 3H, C*H*H–Ph, 2C*H*(CH$_3$)$_2$); 4.55–4.58 (m, 2H, C*H*–O); 6.93 (s, 2H, CH_{ar}); 7.04–7.23 (m, 5H, CH_{ar}) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 24.1 (4*C*H$_3$); 24.8 (2*C*H$_3$); 25.3 (*C*H$_3$); 27.4 (*C*H$_3$); 31.1 (*C*H$_2$Se); 34.3 (*C*H(CH$_3$)$_2$); 34.5 (2*C*H(CH$_3$)$_2$); 57.1 (*C*H$_2$Ph); 58.2 (*C*H$_2$N); 68.2 (*C*HN); 78.2 (*C*HCH$_2$); 84.5 (*C*HCH); 112.9 (*C*(CH$_3$)$_2$); 121.8 (2*C*H$_{ar}$); 127.0 (*C*H$_{ar}$); 127.6 (*C*$_{ar}$Se); 128.4 (2*C*H$_{ar}$); 128.9 (2*C*H$_{ar}$); 138.6 (*C*$_{ar}$); 149.6 (*C*$_{ar}$); 153.1 (2*C*$_{ar}$); ppm.

(*3aR*,*4R*,*6aS*)-Tetrahydro-2,2-dimethyl-5-((*S*)-1-phenylethyl)-4-((phenylselanyl)methyl)-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole 20e(*R)* and (*3aR*,*4S*,*6aS*)- Tetrahydro-2,2-dimethyl-5-((*S*)-1-phenylethyl)-4-((phenylselanyl)methyl)-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole 20e(*S*): Starting material **18c** (0.52 g, 2.0 mmol) and phenylselenyl bromide (0.65 g, 2.7 mmol). Diastereomers were separated. d. r. = 40:60. Major isomer **20e(*R*):** Yield: 0.26 g (0.62 mmol, 31%). Colourless oil. R_f = 0.28 (cyclohexane/ EtOAc, 9:1). $[\alpha]_D^{23}$ = +73.2 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.21 (d, 3H, CH–CH_3, *J* = 6.8 Hz); 1.33 (s, 3H, CH_3); 1.54 (s, 3H, CH_3); 2.32 (dd, 1H, C*H*H, *J* = 4.5 Hz, *J* = 10.9 Hz); 2.67 (dt, 1H, C*H*N, *J* = 4.2 Hz, *J* = 10.4 Hz); 2.82 (dd, 1H, CH*H*Se, *J* = 3.6 Hz, *J* = 11.9 Hz); 2.93 (dd, 1H, C*H*HSe, *J* = 3.9 Hz, *J* = 10.7 Hz); 2.98 (d, 1H, CH*H*, *J* = 10.7 Hz); 3.99 (q, 1H, C*H*–Ph, *J* = 7.2 Hz); 4.44 (dd, 1H, CH$_2$C*H*–O, *J* = 4.5 Hz, *J* = 6.4 Hz); 4.62 (dd, 1H, CH–C*H*–O, *J*

= 4.9 Hz, *J* = 6.4 Hz); 7.20–7.43 (m, 10H, C*H*$_{ar}$) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 15.4 (CH–*C*H$_3$); 25.9 (C$_q$–*C*H$_3$); 26.0 (*C*H$_2$Se); 26.5 (C$_q$–*C*H$_3$); 54.2 (*C*H$_2$N); 57.3 (*C*H–Ph); 66.4 (*C*HN); 77.1 (*C*HCH$_2$); 81.3 (*C*HCH); 111.4 (*C*(CH$_3$)$_2$); 126.7 (*C*H$_{ar}$); 126.9 (*C*H$_{ar}$); 127.3 (2*C*H$_{ar}$); 128.3 (2*C*H$_{ar}$); 129.1 (2*C*H$_{ar}$); 131.2 (*C*$_{ar}$Se); 132.3 (2*C*H$_{ar}$); 145.2 (*C*$_{ar}$) ppm. $C_{22}H_{27}O_2NSe$ (416.415): calcd. C 63.45, H 6.54, N 3.36; found C 63.40, H 6.24, N 3.28. Miner isomer **20e(*S*):** Yield: 0.18 g (0.44 mmol, 22%). Colourless oil. R_f = 0.17 (cyclohexane/ EtOAc, 9:1). $[\alpha]_D^{23}$ = –47.1 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.30 (s, 3H, C*H*$_3$); 1.35 (d, 3H, CH–C*H*$_3$, *J* = 6.8 Hz); 1.50 (s, 3H, C*H*$_3$); 2.84 (dd, 1H, CH*H*Se, *J* = 9.8 Hz, *J* = 12.1 Hz); 2.97 (d, 2H, C*H*$_2$, *J* = 7.9 Hz); 3.06 (dd, 1H, CH*H*Se, *J* = 3.4 Hz, *J* = 12.4 Hz); 3.22 (dd, 1H, C*H*N, *J* = 2.3 Hz, *J* = 9.8 Hz); 3.87 (q, 1H, C*H*–Ph, *J* = 6.6 Hz); 4.62 (dd, 1H, CH–C*H*–O, *J* = 1.1 Hz, *J* = 6.4 Hz); 4.67 (dd, 1H, CH$_2$C*H*–O, *J* = 2.6 Hz, *J* = 4.5 Hz); 7.11–7.29 (m, 10H, C*H*$_{ar}$) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 23.1 (CH–*C*H$_3$); 25.5 (C$_q$–*C*H$_3$); 26.4 (*C*H$_2$Se); 27.1 (C$_q$–*C*H$_3$); 54.3 (*C*H$_2$N); 58.4 (*C*H–Ph); 64.3 (*C*HN); 78.8 (*C*HCH$_2$); 84.6 (*C*HCH); 111.9 (*C*(CH$_3$)$_2$); 126.6 (*C*H$_{ar}$); 127.2 (*C*H$_{ar}$); 127.5 (2*C*H$_{ar}$); 128.5 (2*C*H$_{ar}$); 129.2 (2*C*H$_{ar}$); 131.9 (2*C*H$_{ar}$); 130.4 (*C*$_{ar}$Se); 143.2 (*C*$_{ar}$) ppm. HRMS (EI): calcd. for $C_{22}H_{28}O_2NSe$: 418.1280; found 418.1276.

(*3aR*,*4R*,*6aS*)-Tetrahydro-2,2-dimethyl-5-((*S*)-1-phenylethyl)-4-((phenylselanyl)methyl)-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole 20e(*R)* and (*3aR*,*4S*,*6aS*)- Tetrahydro-2,2-dimethyl-5-((*S*)-1-phenylethyl)-4-((phenylselanyl)methyl)-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole 20e(*S*): Starting material **18c** (0.52 g, 2.0 mmol) and phenylselenyl bromide (0.65 g, 2.7 mmol). Diastereomers were separated. d. r. = 40:60. Major isomer **20e(*R*):** Yield: 0.26 g (0.62 mmol, 31%). Colourless oil. R_f = 0.28 (cyclohexane/ EtOAc, 9:1). $[\alpha]_D^{23}$ = +73.2 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.21 (d, 3H, CH–C*H*$_3$, *J* = 6.8 Hz); 1.33 (s, 3H, C*H*$_3$); 1.54 (s, 3H, C*H*$_3$); 2.32 (dd, 1H, C*H*H, *J* = 4.5 Hz, *J* = 10.9 Hz); 2.67 (dt, 1H, C*H*N, *J* = 4.2 Hz, *J* = 10.4 Hz); 2.82 (dd, 1H, CH*H*Se, *J* = 3.6 Hz, *J* = 11.9 Hz); 2.93 (dd, 1H, C*H*HSe, *J* = 3.9 Hz, *J* = 10.7 Hz); 2.98 (d, 1H, CH*H*, *J* = 10.7 Hz); 3.99 (q, 1H, C*H*–Ph, *J* = 7.2 Hz); 4.44 (dd, 1H, CH$_2$C*H*–O, *J* = 4.5 Hz, *J* = 6.4 Hz); 4.62 (dd, 1H, CH–C*H*–O, *J* = 4.9 Hz, *J* = 6.4 Hz); 7.20–7.43 (m, 10H, C*H*$_{ar}$) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 15.4 (CH–*C*H$_3$); 25.9 (C$_q$–*C*H$_3$); 26.0 (*C*H$_2$Se); 26.5 (C$_q$–*C*H$_3$); 54.2 (*C*H$_2$N); 57.3 (*C*H–Ph); 66.4 (*C*HN); 77.1 (*C*HCH$_2$); 81.3 (*C*HCH); 111.4 (*C*(CH$_3$)$_2$); 126.7 (*C*H$_{ar}$); 126.9 (*C*H$_{ar}$); 127.3 (2*C*H$_{ar}$); 128.3 (2*C*H$_{ar}$); 129.1 (2*C*H$_{ar}$); 131.2 (*C*$_{ar}$Se); 132.3 (2*C*H$_{ar}$); 145.2 (*C*$_{ar}$) ppm. $C_{22}H_{27}O_2NSe$ (416.415): calcd. C 63.45, H 6.54, N 3.36; found C 63.40, H 6.24, N 3.28. Miner isomer **20e(*S*):** Yield: 0.18 g (0.44 mmol, 22%). Colourless oil. R_f = 0.17

(cyclohexane/ EtOAc, 9:1). $[\alpha]_D^{23}$ = –47.1 ° (c = 1.00, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.30 (s, 3H, C*H*$_3$); 1.35 (d, 3H, CH–C*H*$_3$, *J* = 6.8 Hz); 1.50 (s, 3H, C*H*$_3$); 2.84 (dd, 1H, CH*H*Se, *J* = 9.8 Hz, *J* = 12.1 Hz); 2.97 (d, 2H, C*H*$_2$, *J* = 7.9 Hz); 3.06 (dd, 1H, CH*H*Se, *J* = 3.4 Hz, *J* = 12.4 Hz); 3.22 (dd, 1H, C*H*N, *J* = 2.3 Hz, *J* = 9.8 Hz); 3.87 (q, 1H, C*H*–Ph, *J* = 6.6 Hz); 4.62 (dd, 1H, CH–C*H*–O, *J* = 1.1 Hz, *J* = 6.4 Hz); 4.67 (dd, 1H, CH_2C*H*–O, *J* = 2.6 Hz, *J* = 4.5 Hz); 7.11–7.29 (m, 10H, C*H*$_{ar}$) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 23.1 (CH–*C*H$_3$); 25.5 (C_q–*C*H$_3$); 26.4 (*C*H$_2$Se); 27.1 (C_q–*C*H$_3$); 54.3 (*C*H$_2$N); 58.4 (*C*H–Ph); 64.3 (*C*HN); 78.8 (*C*HCH$_2$); 84.6 (*C*HCH); 111.9 (*C*(CH$_3$)$_2$); 126.6 (*C*H$_{ar}$); 127.2 (*C*H$_{ar}$); 127.5 (2*C*H$_{ar}$); 128.5 (2*C*H$_{ar}$); 129.2 (2*C*H$_{ar}$); 131.9 (2*C*H$_{ar}$); 130.4 (*C*$_{ar}$Se); 143.2 (*C*$_{ar}$) ppm. HRMS (EI): calcd. for $C_{22}H_{28}O_2NSe$: 418.1280; found 418.1276.

(*1R*, *3S*, *4R*)-3-((*2R*)-*N*-Benzyl-4,4-dimethylpyrrolidin-2-ylselanylmethyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one and (*1R*, *3S*, *4R*)-3-((*2S*)-*N*-Benzyl-4,4-dimethyl-pyrrolidin-2-ylselanylmethyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one 21a: Starting material **9a (**0.11 g, 0.55 mmol). Diastereomers were not separated. Yield: 47 mg (0.11 mmol, 33%). d. r. = 59:41. Colourless oil. R_f = 0.47 (hexane/ Et_2O, 5:1). ^{1}H-NMR (300 MHz, $CDCl_3$): $C_{24}H_{35}NOSe$ (432.501): calcd. C 66.65, H 8.16, N 3.24; found: C 66.90, H 8.40, N 3.07. Major isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 3H, C*H*$_3$); 0.92 (s, 3H, C*H*$_3$); 0.98 (s, 3H, C*H*$_3$); 1.02 (s, 3H, C*H*$_3$); 1.09 (s, 3H, C*H*$_3$); 1.41–1.52 (m, 1H, CH*H*); 1.58–1.72 (m, 2H, C*H*$_2$); 1.76–1.87 (m, 3H, C*H*H, C*H*$_2$); 1.99 (d, 1H, CH*H*–N, *J* = 9.1 Hz); 2.14–2.19 (m, 1H, C*H*); 2.63 (d, 1H, C*H*H–N, *J* = 9.1 Hz); 2.80–3.11 (m, 3H, C*H*$_2$–Se, C*H*); 3.17 (d, 1H, CH*H*–Ph, *J* = 12.4 Hz); 3.65 (d, 1H, C*H*–Se, *J* = 5.0 Hz); 4.08 (d, 1H, CH*H*–Ph, *J* = 13.2 Hz); 7.18–7.35 (m, 5H, C*H*$_{ar}$) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 9.8 (*C*H$_3$); 19.7 (*C*H$_3$); 19.8 (*C*H$_3$); 23.5 (*C*H$_2$); 29.0 (*C*H$_3$); 29.9 (*C*H$_2$Se); 30.1 (*C*H$_3$); 30.5 (*C*H$_2$); 35.8 (*C*(CH$_3$)$_2$); 46.4 (CH–*C*H$_2$–C_q); 46.5 (*C*H–Se); 47.0 (C_q–CO); 48.5 (*C*H–CHSe); 58.1 (*C*H$_2$–Ph); 58.2 (C_q–CO); 63.5 (*C*H–N); 68.2 (N–*C*H$_2$–C_q); 126.8 (*C*H$_{ar}$); 128.3 (2*C*H$_{ar}$); 128.7 (2*C*H$_{ar}$); 139.8 (CH–*C*$_{ar}$); 218.3 (C=O) ppm. Minor isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 3H, C*H*$_3$); 0.92 (s, 3H, C*H*$_3$); 0.99 (s, 3H, C*H*$_3$); 1.00 (s, 3H, C*H*$_3$); 1.09 (s, 3H, C*H*$_3$); 1.41–1.52 (m, 1H, CH*H*); 1.58–1.72 (m, 2H, C*H*$_2$); 1.76–1.87 (m, 3H, C*H*H, C*H*$_2$); 1.99 (d, 1H, CH*H*–N, *J* = 9.1 Hz); 2.14–2.19 (m, 1H, C*H*); 2.64 (d, 1H, C*H*H–N, *J* = 9.0 Hz); 2.80–3.11 (m, 3H, C*H*$_2$–Se, C*H*); 3.16 (d, 1H, CH*H*–Ph, *J* = 11.4 Hz); 3.65 (d, 1H, C*H*–Se, *J* = 5.0 Hz); 4.06 (d, 1H, CH*H*–Ph, *J* = 13.2 Hz); 7.18–7.35 (m, 5H, C*H*$_{ar}$) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 9.8 (*C*H$_3$); 19.7 (*C*H$_3$); 19.8 (*C*H$_3$); 23.4 (*C*H$_2$); 29.0 (*C*H$_3$); 29.7 (*C*H$_2$Se); 30.1 (*C*H$_3$); 30.6 (*C*H$_2$); 35.8 (*C*(CH$_3$)$_2$); 46.1 (*C*H–Se); 46.2 (CH–*C*H$_2$–C_q); 47.0 (C_q–CO); 48.4 (*C*H–CHSe);

58.2 (C_q–CO); 58.3 (CH$_2$–Ph); 63.8 (CH–N); 68.3 (N–CH$_2$–C_q); 126.8 (CH$_{ar}$); 128.2 (2CH$_{ar}$); 128.8 (2CH$_{ar}$); 140.0 (CH–C_{ar}); 218.7 (C=O) ppm.

(*S*)-Methyl 2-((*2R*)-4,4-Dimethyl-2-((*1R*, *2S*, *4R*)-4,7,7-trimethyl-3-oxo-bicyclo[2.2.1]hept-2-yl-selanylmethyl)pyrrolidin-1-yl)-2-phenylacetate and *(S)*-Methyl 2-((*2S*)-4,4-Dimethyl-2-((*1R*, *2S*, *4R*)-4,7,7-trimethyl-3-oxo-bicyclo[2.2.1]hept-2-yl-selanylmethyl)pyrrolidin-1-yl)-2-phenylacetate 21d: Starting material **9j(*S*)** (425 mg, 1.64 mmol). Diastereomers were not separated. Yield: 191 mg (0.39 mmol, 40%). d. r. = 22:78. White solid. R_f = 0.22 (hexane/ EtOAc 9:1). M. p. 59–62°C. HRMS ((ESI$^+$): calcd. for $C_{26}H_{38}O_3NSe^+$: 492.2011; found 492.2011. $C_{26}H_{37}O_3NSe$ (490.537): calcd. C 63.66, H 7.60, N 2.86; found: C 64.02, H 7.65, N 2.75. Major isomer**:** ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.75 (s, 3H, CH_3); 0.82 (s, 3H, CH_3); 0.84 (s, 3H, CH_3); 0.94 (s, 3H, CH_3); 1.03 (s, 3H, CH_3); 1.39–1.64 (m, 2H, CH_2); 1.68–1.74 (m, 4H, 2CH_2); 2.02–2.05 (m, 1H, CHH–N); 2.17–2.24 (m, 1H, CHH–N); 2.76–2.83 (m, 2H, SeCH$_2$–CH–N, CH–CHSe); 2.86–2.89 (m, 1H, CHH–Se); 2.98–3.19 (m, 1H, CHH–Se); 3.47–3.50 (m, 1H, CH–Se); 3.60 (s, 3H, COOCH_3); 4.52 (s, 1H, CH–COO); 7.22–7.28 (m, 5H, CH_{ar}) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 9.7 (CH$_3$); 19.6 (2CH$_3$); 23.3 (CH$_2$); 26.9 (CH$_2$Se); 28.2 (CH$_3$); 29.0 (CH$_3$); 30.4 (CH$_2$); 36.2 (C(CH$_3$)$_2$); 45.8 (CH–CH$_2$–C_q); 46.4 (C_q–CO); 46.8 (CH–Se); 48.2 (CH–CHSe); 51.9 (COOCH$_3$); 60.8 (CH–Ph); 58.2 (C_q–CO); 63.8 (N–CH$_2$–C_q); 67.8 (CH–N); 128.2 (CH$_{ar}$); 128.4 (2CH$_{ar}$); 129.4 (2CH$_{ar}$); 135.1 (CH–C_{ar}); 172.5 (COO); 218.3 (C=O) ppm. Minor isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3H, CH_3); 0.82 (s, 3H, CH_3); 0.84 (s, 3H, CH_3); 0.94 (s, 3H, CH_3); 1.04 (s, 3H, CH_3); 1.39–1.64 (m, 2H, CH_2); 1.68–1.74 (m, 4H, 2CH_2); 2.02–2.05 (m, 1H, CHH–N); 2.17–2.24 (m, 1H, CHH–N); 2.76–2.83 (m, 2H, SeCH$_2$–CH–N, CH–CHSe); 2.90–2.94 (m, 1H, CHH–Se); 2.98–3.19 (m, 1H, CHH–Se); 3.49–3.52 (m, 1H, CH–Se); 3.61 (s, 3H, COOCH_3); 4.70 (s, 1H, CH–COO); 7.22–7.28 (m, 5H, CH_{ar}) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 9.7 (CH$_3$); 19.6 (2CH$_3$); 23.4 (CH$_2$); 28.3 (CH$_3$); 29.1 (CH$_3$); 29.4 (CH$_2$Se); 30.3 (CH$_2$); 36.0 (C(CH$_3$)$_2$); 46.1 (CH–CH$_2$–C_q); 46.5 (C_q–CO); 46.8 (CH–Se); 48.4 (CH–CHSe); 52.1 (COOCH$_3$); 60.5 (CH–Ph); 58.0 (C_q–CO); 63.5 (N–CH$_2$–C_q); 67.4 (CH–N); 128.2 (CH$_{ar}$); 128.3 (2CH$_{ar}$); 129.4 (2CH$_{ar}$); 135.2 (CH–C_{ar}); 172.4 (COO); 218.1 (C=O) ppm.