Supporting Information (Experimental Section: 13 pages)

Direct Amination of Olefins through Sequential Triazolinedione (TAD) Ene Reaction and Carbanion-Assisted Cleavage of the N-N Urazole Bond

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General Aspects: ^{1}H- and ^{13}C-NMR spectra were measured on a Bruker AC 200 (^{1}H: 200 MHz, ^{13}C: 50 MHz) or Bruker AC 250 (^{1}H: 250 MHz, ^{13}C: 63 MHz) with $CHCl_3$ (δ = 7.26 ppm) for ^{1}H and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C as internal standard. IR spectra were recorded on a FT-IR Perkin-Elmer 1600 Infrared Ratio-Recording spectrophotometer. Melting points were taken on a Büchi B-545 apparatus and are not corrected.
TLC analysis was conducted on precoated silicia-gel aluminum sheets 60 F_{254} (40×80 mm) from Merck (Darmstadt, Germany). Spots were visualized by irradiation under an UV lamp or with the phosphomolybdic acid test spray. Silica gel (32-63 μm, Woelm) was used for flash chromatography.

Materials: Solvents and commercially available chemicals were purified by standard procedures. THF was freshly distilled over sodium/acetophenone. 4-Methyl-1,2,4-

triazoline-3,5-dione (MTAD) was prepared by oxidation with *t*-butyl hypochlorite from 4-methylurazole and was freshly sublimed before use.[14]

General Procedure for the MTAD Ene Reaction with Olefins 1a-f: The corresponding olefin **1** (10.0 mmol) was dissolved in CH_2Cl_2 (50 mL) and MTAD (1.13 g, 10.0 mmol) was slowly added at 0 °C for 5 min. The reaction mixture was stirred at 20 °C for 16 h. After removal of the solvent (20 °C/ 30 torr), the crude product **2** was used in the next step without further purification.

1-(2-Cyclopenten-1-yl)-4-methyl-1,2,4-triazolidine-3,5-dione[3b] (2a): ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.72-1.84 (m, 1 H), 2.14-2.60 (m, 3 H), 3.05 (s, 3 H), 5.23-5.31 (m, 1 H), 5.66 (dm, J = 5.8 Hz, 1 H), 6.14 (dm, J = 5.7 Hz, 1 H), 8.60 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 25.1 (q), 26.7 (t), 31.5 (t), 62.5 (d), 127.0 (d), 138.3 (d), 153.7 (s), 155.4 (s).

1-(2-Cyclohexen-1-yl)-4-methyl-1,2,4-triazolidine-3,5-dione[3b] (2b): ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.55-2.04 (m, 6 H), 3.02 (s, 3 H), 4.69 (m, 1 H), 5.49 (dm, J = 9.9 Hz, 1 H), 5.97 (dm, J = 9.9 Hz, 1 H), 9.22 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 20.3 (t), 24.2 (t), 25.0 (q), 26.0 (t), 52.4 (d), 124.4 (d), 133.7 (d), 153.6 (s), 155.2 (s).

1-(2-Cyclohepten-1-yl)-4-methyl-1,2,4-triazolidine-3,5-dione[3c] (2c): ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.26-2.25 (m, 8 H), 3.04 (s, 3 H), 4.78 (m, 1 H), 5.55 (dt, J = 11.5 Hz, J = 2.5 Hz, 1 H), 5.88 (dm, J = 11.6 Hz, 1 H), 9.36 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 25.1 (q), 26.1 (t), 27.5 (t), 28.3 (t), 31.6 (t), 57.7 (d), 130.5 (d), 133.6 (d), 153.7 (s), 155.6 (s).

4-Methyl-1-(1,1,2-trimethyl-2-propenyl)-1,2,4-triazolidine-3,5-dione[15] (2d): ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.47 (s, 6 H), 1.72 (m, 3 H), 2.94 (s, 3 H), 3.62 (br s, 1 H), 4.87-4.88 (m, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 18.7 (q), 24.4 (2×q), 24.6 (q), 64.2 (s), 112.0 (t), 146.8 (s), 153.8 (s), 154.7 (s).

Ene Reaction of the Olefin 1e with MTAD: The crude product consisted of a 54:46 mixture of ***threo/erythro*-2e** which was used in the next step without any further purification.[7c]

4-Methyl-1-[(1*R)-1-[(1*R**)-1-methoxyethyl]-2-methyl-2-propenyl]-1,2,4-triazolidine-3,5-dione (*threo*-2e):** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.16 (d, J = 6.2 Hz, 3 H), 1.69 (s, 3 H), 3.03 (s, 3 H), 3.29 (s, 3 H), 3.75 (dq, J = 6.2 Hz, J = 6.0 Hz, 1 H), 4.37 (d, J = 5.9 Hz, 1 H), 4.93 (s, 1 H), 5.02 (s, 1 H), 8.18 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 16.0 (q), 21.1 (q), 25.0 (q), 56.2 (q), 63.2 (d), 75.3 (d), 115.2 (t), 139.9 (s), 153.9 (s), 154.2 (s).

4-Methyl-1-[(1*R)-1-[(1*S**)-1-methoxyethyl]-2-methyl-2-propenyl]-1,2,4-triazolidine-3,5-dione (*erythro*-2e):** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.15 (d, J = 6.3 Hz, 3 H), 1.74 (s, 3 H), 3.01 (s, 3 H), 3.30 (s, 3 H), 3.83 (dq, J = 6.2 Hz, J = 4.3 Hz, 1 H), 4.47 (d, J = 4.2 Hz, 1 H), 5.03 (s, 1 H), 5.06 (s, 1 H), 8.62 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 15.4 (q), 21.7 (q), 25.0 (q), 56.2 (q), 63.4 (d), 77.3 (d), 117.4 (t), 138.9 (s), 152.9 (s), 154.2 (s).

For both diastereomers: IR (KBr) 3460-3300 (NH) cm^{-1}, 1760 (C=O), 1710 (C=O), 1700 (C=O); Anal. Found: C, 52.67; H, 7.35; N, 18.66%. Calcd for $C_{10}H_{17}N_3O_3$ (227.3): C, 52.85; H, 7.54; N, 18.49%.

Ene Reaction of the Olefin 1f with MTAD: The crude product consisted of a 87:13 mixture of ***threo/erythro*-2f'** which was recrystallized from 1:3 CH_2Cl_2/Et_2O at –20 °C (d.r. 95:5).[7c]

1-[(1*R)-1-[(1*R**)-1-Hydroxyethyl]-2-methyl-2-propenyl]-4-methyl-1,2,4-triazolidine-3,5-dione (*threo*-2f'):** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.20 (d, *J* = 6.0 Hz, 3 H), 1.68 (s, 3 H), 2.60 (br s, 1 H), 3.00 (s, 3 H), 4.21-4.33 (m, 2 H), 4.97 (s, 1 H), 5.00 (s, 1 H), 8.08 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 21.1 (q), 21.4 (q), 25.6 (q), 66.3 (d), 66.6 (d), 116.4 (t), 140.4 (s), 154.5 (s), 155.1 (s).

1-[(1*R)-1-[(1*S**)-1-Hydroxyethyl]-2-methyl-2-propenyl]-4-methyl-1,2,4-triazolidine-3,5-dione (*erythro*-2f'):** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.14 (d, *J* = 6.3 Hz, 3 H), 1.75 (s, 3 H), 2.60 (br s, 1 H), 3.00 (s, 3 H), 4.21-4.33 (m, 2 H), 5.06 (s, 1 H), 5.08 (s, 1 H), 8.08 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 20.6 (q), 22.0 (q), 26.0 (q), 65.2 (d), 67.6 (d), 117.7 (t), 140.0 (s), 153.5 (s), 154.7 (s).

For both diastereomers: IR (KBr) 3500-3080 (NH) cm^{-1}, 1760 (C=O), 1720 (C=O); Anal. Found: C, 50.54; H, 7.36; N, 19.47%. Calcd for $C_9H_{15}N_3O_3$ (213.2): C, 50.69; H, 7.09; N, 19.71%.

Reaction of *threo*-2f' with 3,4-Dihydro-2*H*-pyran[13]: A solution of ***threo*-2f'** (2.50 g, 10.7 mmol), 3,4-dihydro-2*H*-pyran (2.96 g, 35.2 mmol), and *p*-TsOH (17 mg, 0.1 mmol) in CH_2Cl_2 (75 mL) was stirred at 20 °C for 18 h. After removal of the solvent (20 °C/ 30 torr) the crude product was purified by silica-gel chromatography, eluted first with 2:1 Et_2O/petroleum ether and then with Et_2O to give the ***threo*-2f** urazole in 67% yield.

4-Methyl-1-[(1*R)-1-[(1*R**)-1-[(tetrahydro-2*H*-pyran-2-yl)oxy]ethyl]-2-methyl-2-propenyl]-1,2,4-triazolidine-3,5-dione (*threo*-2f, d.r. > 95:5):** Colorless prisms (1:1 CH_2Cl_2/Et_2O at –20 °C), mp = 105.0-106.0 °C; IR (KBr) 3190 (NH) cm^{-1}, 1765 (C=O), 1700 (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.16 (d, *J* = 6.1 Hz, 3 H), 1.40-1.82 (m, 9 H), 3.02 (s, 3 H), 3.42-3.53 (m, 1 H), 4.03 (dm, *J* = 10.7 Hz, 1 H), 4.13 (dq, *J* = 9.2 Hz, *J* = 6.1 Hz, 1 H), 4.32 (d, *J* = 8.9 Hz, 1 H), 4.49-4.53 (m, 1 H), 4.96 (qn, *J* = 1.5 Hz, 1 H), 5.08 (m, 1 H), 8.48 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 17.2 (q), 20.4 (q), 21.4 (t), 24.8 (t), 24.9 (q), 31.4 (t), 65.0 (d), 65.7 (t), 70.1 (d), 99.1 (d), 116.7 (t), 139.4 (s), 153.7 (s), 155.3 (s); Anal. Found: C, 56.72; H, 7.62; N, 13.82%. Calcd for $C_{14}H_{23}N_3O_4$ (297.4): C, 56.55; H, 7.80; N, 14.13%.

General Procedure for the Alkylation of the Allylic Urazoles 2a-f: The corresponding allylic urazole **2** (7.5 mmol) was dissolved in freshly distilled THF (40 mL) under an argon-gas atmosphere and NaH (0.30 g, 7.5 mmol) was slowly added. The resulting suspension was stirred at 65 °C for 3 h. After cooling, the α-bromoacetophenone (1.49 g, 7.5 mmol) was added and the reaction mixture stirred at 65 °C for 18 h. The solvent was removed (40 °C/ 30 torr) and the crude product **3** was purified by silica-gel chromatography, eluted first with a 1:1 and subsequently with a 3:1 Et_2O/petroleum ether mixture to give the corresponding pure alkylated allylic urazole **3**.

1-(2-Cyclopenten-1-yl)-4-methyl-2-(2-oxo-2-phenylethyl)-1,2,4-triazolidine-3,5-dione (3a): Colorless prisms (1:4 CH_2Cl_2/Et_2O at –20 °C), 78% yield, mp = 91.0-92.0 °C; IR (KBr) 1772 (C=O) cm^{-1}, 1715 (C=O), 1690 (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.73-1.87 (m, 1 H), 2.09-2.24 (m, 1 H), 2.26-2.59 (m, 2 H), 3.13 (s, 3 H), 4.94 (s, 2 H), 5.28-5.38 (m, 1 H), 5.57 (dm, *J* = 5.5 Hz, 1 H), 5.98 (dm, *J* = 5.8 Hz, 1 H), 7.42-7.49 (m, 2 H), 7.55-7.62 (m, 1 H), 7.79-7.84 (m, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 25.1 (t), 25.6 (q), 31.4 (t), 53.1

(t), 64.4 (d), 127.7 (2×d), 128.8 (2×d), 129.0 (d), 134.0 (d), 134.2 (s), 136.7 (d), 155.8 (s), 157.3 (s), 191.8 (s); Anal. Found: C, 64.24; H, 5.82; N, 14.14%. Calcd for $C_{16}H_{17}N_3O_3$ (299.3): C, 64.20; H, 5.73; N, 14.04%.

1-(2-Cyclohexen-1-yl)-4-methyl-2-(2-oxo-2-phenylethyl)-1,2,4-triazolidine-3,5-dione (3b): Colorless prisms (1:1:1 CH_2Cl_2/ Et_2O/ *n*-pentane at –20 °C), 81% yield, mp = 90.0-100.0 °C; IR (KBr) 1775 (C=O) cm^{-1}, 1717 (C=O), 1692 (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.57-2.03 (m, 6 H), 3.17 (s, 3 H), 4.81 (m, 1 H), 4.99 (d, *J* = 18.0 Hz, 1 H), 5.08 (d, *J* = 18.3 Hz, 1 H), 5.48 (dm, *J* = 10.1 Hz, 1 H), 5.86 (dm, *J* = 10.0 Hz, 1 H), 7.48 (t, *J* = 7.3 Hz, 2 H), 7.62 (tm, *J* = 7.5 Hz, 1 H), 7.86 (dm, *J* = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 21.0 (t), 24.3 (t), 25.7 (q), 25.9 (t), 52.9 (t), 54.5 (d), 126.8 (d), 127.9 (2×d), 129.0 (2×d), 132.5 (d), 134.1 (d), 134.4 (s), 155.6 (s), 157.1 (s), 191.8 (s); Anal. Found: C, 65.26; H, 6.08; N, 13.12%. Calcd for $C_{17}H_{19}N_3O_3$ (313.4): C, 65.16; H, 6.11; N, 13.41%.

1-(2-Cyclohepten-1-yl)-4-methyl-2-(2-oxo-2-phenylethyl)-1,2,4-triazolidine-3,5-dione (3c): Colorless prisms (Et_2O at –20 °C), 70% yield, mp = 101.6-102.4 °C; IR (KBr) 1770 (C=O) cm^{-1}, 1726 (C=O), 1709 (C=O), 1688 (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.28-2.28 (m, 8 H), 3.13 (s, 3 H), 4.68-4.78 (m, 1 H), 5.00 (s, 2 H), 5.51 (dm, *J* = 11.6 Hz, 1 H), 5.70-5.80 (m, 1 H), 7.47 (tm, *J* = 7.5 Hz, 2 H), 7.60 (tm, *J* = 7.3 Hz, 1 H), 7.87 (dm, *J* = 7.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 25.6 (q), 26.3 (t), 27.1 (t), 28.3 (t), 32.1 (t), 52.3 (t), 58.9 (d), 127.8 (2×d), 128.9 (2×d), 131.4 (d), 132.8 (d), 134.09 (d), 134.13 (s), 155.1 (s), 156.7 (s), 191.6 (s); Anal. Found: C, 65.90; H, 6.44; N, 12.64%. Calcd for $C_{18}H_{21}N_3O_3$ (327.4): C, 66.04; H, 6.47; N, 12.84%.

4-Methyl-2-(2-oxo-2-phenylethyl)-1-(1,1,2-trimethyl-2-propenyl)-1,2,4-triazolidine-3,5-dione (3d): Colorless prisms (2:1 Et_2O/*n*-pentane at –20 °C), 60% yield, mp =

78.0-79.0 °C; IR (KBr) 1776 (C=O) cm^{-1}, 1713 (C=O), 1694 (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.55 (s, 6 H), 1.68-1.69 (m, 3 H), 3.13 (s, 3 H), 4.88 (m, 1 H), 5.00 (m, 1 H), 5.05 (s, 2 H), 7.45-7.51 (m, 2 H), 7.62 (tm, *J* = 7.3 Hz, 1 H), 7.82-7.86 (m, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 19.1 (q), 25.1 (2×q), 25.7 (q), 55.0 (t), 66.9 (s), 111.9 (t), 127.7 (2×d), 129.0 (2×d), 134.0 (d), 134.4 (s), 149.1 (s), 157.4 (s), 158.8 (s), 192.6 (s); Anal. Found: C, 64.65; H, 6.65; N, 13.22%. Calcd for $C_{17}H_{21}N_3O_3$ (315.4): C, 64.75; H, 6.71; N, 13.32%.

4-Methyl-1-[(1*R)-1-[(1*R**)-1-methoxyethyl]-2-methyl-2-propenyl]-2-(2-oxo-2-phenylethyl)-1,2,4-triazolidine-3,5-dione and 4-Methyl-1-[(1*R**)-1-[(1*S**)-1-methoxyethyl]-2-methyl-2-propenyl]-2-(2-oxo-2-phenylethyl)-1,2,4-triazolidine-3,5-dione (3e, d.r. 52:48):** Colorless prisms (2:1 Et_2O/*n*-pentane at –20 °C), 44% yield, mp = 52.0-53.0 °C; IR (KBr) 1773 (C=O) cm^{-1}, 1712 (C=O), 1693 (C=O); ^1H NMR ($CDCl_3$, 250 MHz) for the mixture of diastereomers: δ 1.11 (d, *J* = 6.1 Hz, 3 H), 1.15 (d, *J* = 6.1 Hz, 3 H), 1.62 (s, 6 H), 2.94 (s, 3 H), 3.02 (s, 3 H), 3.16 (s, 3 H), 3.18 (s, 3 H), 3.78 (qn, *J* = 6.4 Hz, 1 H), 3.81 (qn, *J* = 6.0 Hz, 1 H), 4.23 (d, *J* = 6.4 Hz, 1 H), 4.37 (d, *J* = 5.2 Hz, 1 H), 4.98-5.21 (m, 8 H), 7.41-7.62 (m, 6 H), 7.80-7.88 (m, 4 H); ^{13}C NMR ($CDCl_3$, 63 MHz) for the mixture of diastereomers: δ 15.7 (q), 15.9 (q), 21.8 (2×q), 25.7 (q), 25.8 (q), 52.5 (t), 53.2 (t), 55.6 (q), 56.4 (q), 65.8 (2×d), 74.8 (d), 76.7 (d), 115.4 (t), 116.8 (t), 127.6 (2×d), 127.7 (2×d), 128.7 (2×d), 128.9 (2×d), 133.6 (d), 134.0 (d), 134.2 (s), 134.6 (s), 139.2 (s), 141.0 (s), 154.9 (s), 156.2 (s), 156.7 (s), 157.0 (s), 191.9 (s), 192.2 (s); Anal. Found: C, 62.50; H, 6.80; N, 12.04%. Calcd for $C_{18}H_{23}N_3O_4$ (345.4): C, 62.59; H, 6.71; N, 12.17%.

4-Methyl-2-(2-oxo-2-phenylethyl)-1-[(1*R)-1-[(1*R**)-1-[(tetrahydro-2*H*-pyran-2-yl)oxy]ethyl]-2-methyl-2-propenyl]-1,2,4-triazolidine-3,5-dione (*threo*-3f, d.r. > 95:5):** Colorless prisms (1:3 CH_2Cl_2/Et_2O at –20 °C), 78% yield, mp = 140.0-140.4 °C; IR (KBr)

1767 (C=O) cm^{-1}, 1690 (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.11-1.55 (m, 9 H), 1.65 (s, 3 H), 3.19 (s, 3 H), 3.37–3.47 (m, 1 H), 3.78-3.86 (m, 1 H), 4.46-4.51 (m, 2 H), 4.58 (dd, *J* = 6.1 Hz, *J* = 2.5 Hz, 1 H), 5.02 (s, 1 H), 5.10 (d, *J* = 18.3 Hz, 1 H), 5.22 (d, *J* = 18.3 Hz, 1 H), 5.28 (s, 1 H), 7.45 (tm, *J* = 7.5 Hz, 2 H), 7.59 (tm, *J* = 7.3 Hz, 1 H), 7.82-7.85 (m, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 16.6 (q), 20.3 (t), 22.2 (q), 25.1 (t), 25.8 (q), 30.9 (t), 53.3 (t), 64.0 (t), 65.8 (d), 68.3 (d), 95.5 (d), 115.8 (t), 127.8 (2×d), 128.8 (2×d), 133.8 (d), 134.5 (s), 141.2 (s), 156.7 (s), 157.2 (s), 192.5 (s); Anal. Found: C, 63.37; H, 6.96; N, 10.02%. Calcd for $C_{22}H_{29}N_3O_5$ (415.5): C, 63.60; H, 7.04; N, 10.11%.

General Procedure for the Synthesis of the Ureas 4: The corresponding urazole **3** (1.5 mmol) was dissolved in MeOH (8 mL) and 3 *N* aqueous KOH (3 mL) was added. The resulting solution was stirred at 80 °C for 18 h. After cooling, the reaction mixture was extracted with CH_2Cl_2 (5×5 mL) and the organic extracts dried over $MgSO_4$. After removal of the solvent (40 °C/ 30 torr) the crude product **4** was purified by silica-gel chromatography eluted first with Et_2O and subsequently with a 3:1 Et_2O/acetone mixture to give the corresponding pure allylic urea **4**.

***N*-(2-Cyclopenten-1-yl)-*N'*-methylurea (4a):** Colorless prisms (1:4 CH_2Cl_2/Et_2O at –20 °C), 58% yield, mp = 123.0-124.0 °C; IR (KBr) 3340 (NH) cm^{-1}, 1623 (C=O); ^1H NMR ($CDCl_3$, 250 MHz): δ 1.41-1.51 (m, 1 H), 2.15-2.42 (m, 3 H), 2.69 (d, *J* = 4.9 Hz, 3 H), 4.72 (m, 1 H), 5.40 (d, *J* = 8.2 Hz, 1 H), 5.55 (q, *J* = 4.0 Hz, 1 H), 5.64 (dq, *J* = 5.5 Hz, *J* = 2.0 Hz, 1 H), 5.83 (dq, *J* = 5.6 Hz, *J* = 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 26.8 (q), 31.0 (t), 31.9 (t), 56.3 (d), 132.1 (d), 133.5 (d), 159.3 (s); Anal. Found: C, 59.93; H, 8.90; N, 19.64%. Calcd for $C_7H_{12}N_2O$ (140.2): C, 59.98; H, 8.63; N, 19.98%.

***N*-(2-Cyclohexen-1-yl)-*N'*-methylurea[16] (4b):** 72% yield, ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.41-1.95 (m, 6 H), 2.70 (d, J = 4.7 Hz, 3 H), 4.20 (m, 1 H), 5.30 (d, J = 8.1 Hz, 1 H), 5.47 (m, 1 H), 5.56 (dm, J = 10.1 Hz, 1 H), 5.76 (dm, J = 10.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 19.3 (t), 24.4 (t), 26.3 (q), 29.8 (t), 44.9 (d), 129.1 (d), 130.0 (d), 159.8 (s).

***N*-(2-Cyclohepten-1-yl)-*N'*-methylurea (4c):** Colorless prisms (1:4 CH_2Cl_2/Et_2O at –20 °C), 68% yield, mp = 143.8-144.2 °C; IR (KBr) 3357 (NH) cm^{-1}, 3302 (NH), 1624 (C=O); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.23-2.19 (m, 8 H), 2.72 (d, J = 4.9 Hz, 3 H), 4.32 (m, 1 H), 5.40 (q, J = 4.0 Hz, 1 H), 5.46 (d, J = 7.9 Hz, 1 H), 5.56 (dm, J = 12.5 Hz, 1 H), 5.68-5.78 (m, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 26.6 (t), 26.7 (q), 28.0 (t), 28.5 (t), 34.7 (t), 51.2 (d), 131.0 (d), 136.6 (d), 159.2 (s); Anal. Found: C, 64.46; H, 9.36; N, 16.62%. Calcd for $C_9H_{16}N_2O$ (168.2): C, 64.25; H, 9.59; N, 16.65%.

***N*-Methyl-*N'*-(1,1,2-trimethyl-2-propenyl)urea (4d):** Colorless prisms (1:4 CH_2Cl_2/Et_2O at –20 °C), 62% yield, mp = 118.0-119.0 °C; IR (KBr) 3378 (NH) cm^{-1}, 3324 (NH), 1642 (C=O); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.33 (s, 6 H), 1.72 (s, 3 H), 2.66 (d, J = 4.7 Hz, 3 H), 4.84 (s, 1 H), 4.92 (s, 1 H), 5.07 (br s, 1 H), 5.17 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 18.8 (q), 26.5 (q), 27.7 (2×q), 55.0 (s), 110.5 (t), 150.7 (s), 158.6 (s); Anal. Found: C, 61.72; H, 9.98; N, 17.66%. Calcd for $C_8H_{16}N_2O$ (156.2): C, 61.51; H, 10.32; N, 17.93%.

***N*-Methyl-*N'*-[(1*R**)-1-[(1*R**)-1-methoxyethyl]-2-methyl-2-propenyl]urea and *N*-Methyl-*N'*-[(1*R**)-1-[(1*S**)-1-methoxyethyl]-2-methyl-2-propenyl]urea (4e, d.r. 52:48):** Colorless prisms (1:4 CH_2Cl_2/Et_2O at –20 °C), 64% yield, mp = 84.4-86.5 °C; IR (KBr) 3345 (NH) cm^{-1}, 1633 (C=O); ^{1}H NMR ($CDCl_3$, 250 MHz) for the diastereomeric mixture: δ 1.03 (d, J = 6.4 Hz, 3 H), 1.10 (d, J = 6.3 Hz, 3 H), 1.68 (s, 3 H), 1.71 (s, 3 H), 2.69 (m, 6 H), 3.25 (s, 3 H), 3.27 (s, 3 H), 3.38-3.53 (m, 2 H), 3.98 (dd, J = 7.8 Hz, J = 3.6 Hz, 1 H), 4.19 (dd,

J = 8.3 Hz, *J* = 4.6 Hz, 1 H), 4.85-4.88 (m, 4 H), 5.47-5.62 (m, 4 H); ^{13}C NMR ($CDCl_3$, 63 MHz) for the diastereomeric mixture: δ 14.8 (q), 16.2 (q), 19.8 (q), 19.9 (q), 26.7 (q), 26.8 (q), 56.4 (q), 56.5 (q), 58.3 (d), 59.7 (d), 76.9 (d), 77.6 (d), 111.9 (t), 113.0 (t), 143.5 (s), 144.7 (s), 159.1 (s), 159.4 (s); Anal. Found: C, 57.88; H, 9.53; N, 14.90%. Calcd for $C_9H_{18}N_2O_2$ (186.3): C, 58.04; H, 9.74; N, 15.04%.

***N*-Methyl-*N'*-[(1*R**)-1-[(1*R**)-1-[(tetrahydro-2*H*-pyran-2-yl)oxy]ethyl]-2-methyl-2-propenyl]urea (*threo*-4f, d.r. > 95:5):** Colorless needles (1:4 CH_2Cl_2/Et_2O at –20 °C), 70% yield, mp = 143.1-143.9 °C; IR (KBr) 3346 (NH) cm^{-1}, 1628 (C=O); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.11 (d, *J* = 6.1 Hz, 3 H), 1.45-1.76 (m, 9 H), 2.74 (d, *J* = 4.6 Hz, 3 H), 3.39-3.48 (m, 1 H), 3.82-3.93 (m, 3 H), 4.57-4.59 (m, 1 H), 4.72 (q, *J* = 4.6 Hz, 1 H), 4.91 (t, *J* = 1.5 Hz, 1 H), 4.98 (s, 1 H), 5.38 (d, *J* = 5.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 16.9 (q), 19.1 (q), 19.9 (t), 25.2 (t), 27.0 (q), 31.0 (t), 61.3 (d), 63.1 (t), 71.6 (d), 96.3 (d), 113.0 (t), 144.7 (s), 159.2 (s); Anal. Found: C, 60.65; H, 9.57; N, 10.81%. Calcd for $C_{13}H_{24}N_2O_3$ (256.4): C, 60.91; H, 9.44; N, 10.93%.

General Procedure for the Synthesis of the Amines 5: The corresponding urazole **3** (1.5 mmol) was dissolved in MeOH (2 mL) and 50% KOH (2 mL) was added. The solution was placed into a sealed tube under an argon-gas atmosphere and was heated at 80 °C for 18 h. The temperature was increased to 155 °C and the solution stirred at this temperature for 6 h. After cooling, the reaction mixture was extracted with Et_2O (5×5 mL) and the organic extracts dried over $MgSO_4$. After removal of the solvent (20 °C/ 450 torr), the amine **5** was purified by Kugelrohr distillation.

For urazoles **3a**, **3d** and **3e** solid KOH (10 equiv.) instead of a 50% aqu. solution and ethylene glycol instead of MeOH as solvent were used. The corresponding allylic amines **5a**, **5d** and **5e** were isolated by distillation directly from the reaction mixture.

2-Cyclopenten-1-amine[17] (5a): 45% yield (Kugelrohr distillation from the reaction mixture at 100 °C/ 615 torr). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.28-1.43 (m, 1 H), 2.11-2.46 (m, 3 H), 3.83-3.94 (m, 1 H), 5.65 (dm, J = 7.1 Hz, 1 H), 5.75 (dm, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 30.9 (t), 33.4 (t), 57.5 (d), 132.9 (d), 135.1 (d).

2-Cyclohexen-1-amine[17] (5b): 67% yield (Kugelrohr distillation at 135 °C/ 615 torr). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.19-1.98 (m, 6 H), 3.20-3.29 (m, 1 H), 5.56 (dm, J = 10.0 Hz, 1 H), 5.62-5.71 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 19.9 (t), 24.7 (t), 32.2 (t), 46.8 (d), 129.2 (d), 131.7 (d).

2-Cyclohepten-1-amine[18] (5c): 68% yield (Kugelrohr distillation at 100 °C/ 110 torr). IR (neat) 3460 (NH) cm^{-1}, 3354 (NH), 1651 (C=C); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.16-2.21 (m, 8 H), 3.56 (d, J = 9.0 Hz, 1 H), 5.54 (dm, J = 11.4 Hz, 1 H), 5.72 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 26.3 (t), 28.2 (t), 28.4 (t), 37.5 (t), 52.2 (d), 130.7 (d), 137.4 (d); MS (70 eV) m/z = 111 (M^+, 10), 94 (16), 82 (100), 79 (19), 56 (34). Exacts mass for $C_7H_{13}N$, calcd: 111.1048; found: 111.1050.

2,3-Dimethyl-2-buten-1-amine (5d): 40% yield (Kugelrohr distillation from the reaction mixture at 130 °C/ 550 torr). IR (neat) 3445 (NH) cm^{-1}, 1652 (C=C); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.23 (s, 6 H), 1.65 (br s, 2 H), 1.79 (m, 3 H), 4.71 (qn, J = 1.4 Hz, 1 H), 4.89 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 18.9 (q), 29.4 (2xq), 52.9 (s), 108.1 (t), 153.8 (s); MS (70 eV) m/z = 84 (M^+-15, 94), 58 (100), 57 (18), 42 (23), 41 (25), 30 (17).

(*R, *R**)-4-Methyl-2-methoxy-4-penten-3-amine and (*R**, *S**)-4-Methyl-2-methoxy-4-penten-3-amine (5e, d.r. 52:48):** 45% yield (Kugelrohr distillation from the reaction mixture at 130 °C/ 550 torr). IR (neat) 3377 (NH) cm^{-1}, 3308 (NH), 1649 (C=C); ^{1}H NMR

($CDCl_3$, 200 MHz) for the diastereomeric mixture: δ 1.04 (d, *J* = 6.1 Hz, 3 H), 1.06 (d, *J* = 5.8 Hz, 3 H), 1.73 (s, 6 H), 3.22-3.51 (m, 10 H), 4.85 (m, 1 H), 4.88 (m, 1 H), 4.93 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) for the diastereomeric mixture: δ 12.8 (q), 15.2 (q), 17.7 (q), 19.8 (q), 56.4 (q), 56.8 (q), 59.1 (d), 63.1 (d), 78.1 (d), 79.1 (d), 111.9 (t), 114.0 (t), 145.9 (s), 146.0 (s).

(*R, *R**)-4-Methyl-2-[(tetrahydro-2*H*-pyran-2-yl)oxy]-4-penten-3-amine (*threo*-5f, d.r. > 95:5):** 41% (silica-gel chromatography eluted first with a 1:1 Et_2O/ petroleum ether and subsequently with a 3:1 Et_2O/MeOH mixture). IR (neat) 3387 (NH) cm^{-1}, 3319 (NH), 1649 (C=C); ^1H NMR ($CDCl_3$, 200 MHz): δ 1.03 (d, *J* = 6.1 Hz, 3 H), 1.49-1.88 (m, 9 H), 3.23 (d, *J* = 7.9 Hz, 1 H), 3.42-3.53 (m, 1 H), 3.71 (dq, *J* = 8.0 Hz, *J* = 6.2 Hz, 1 H), 3.87-3.98 (m, 1 H), 4.64-4.67 (m, 1 H), 4.82 (qn, *J* = 1.6 Hz, 1 H), 4.91 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 15.8 (q), 17.7 (q), 19.7 (t), 24.9 (t), 30.9 (t), 63.0 (d and t), 73.5 (d), 96.0 (d), 113.6 (t), 146.3 (s); MS (70 eV) m/z = 155 (M^+- 44, 2), 85 (32), 84 (29), 70 (100), 55 (31), 43 (37), 41 (35).

(*R, *R**)-6-Benzoyl-1-(2-cyclohexen-1-yl)-dihydro-3,5-dimethyl-1,3,5-triazine-2,4(1*H*, 3*H*)-dione and (*R**, *S**)-6-Benzoyl-1-(2-cyclohexen-1-yl)-dihydro-3,5-dimethyl-1,3,5-triazine-2,4(1*H*, 3*H*)-dione (6b, d.r. 52:48):** The urazole **3b** (1.00 g, 3.2 mmol) was dissolved in freshly distilled THF (25 mL) under an argon-gas atmosphere and NaH (0.13 g, 3.2 mmol) was added. The suspension was stirred for 30 min at 20 °C. After addition of Me_2SO_4 (0.44 g, 3.5 mmol), the reaction mixture was stirred at the same temperature for 12 h. The solvent was removed (30 °C/ 30 torr) and the crude product purified by silica-gel chromatography, eluted first with a 3:1 Et_2O/petroleum ether mixture and subsequently with Et_2O to give **6b** in 80% yield as a 52:48 mixture of diastereomers. An analytical sample was obtained by recrystallization from Et_2O at –20 °C; colorless

prisms, mp = 106.0-107.0 °C; IR (KBr) 1712 (C=O) cm^{-1}, 1675 (C=O); ^1H NMR ($CDCl_3$, 250 MHz) for the diastereomeric mixture: δ 1.07-1.19 (m, 1 H), 1.43-2.09 (m, 11 H), 2.93 (s, 3 H), 2.94 (s, 3 H), 3.13 (s, 3 H), 3.14 (s, 3 H), 4.95-5.03 (m, 2 H), 5.29 (dm, *J* = 10.3 Hz, 1 H), 5.54 (dm, *J* = 10.4 Hz, 1 H), 5.58 (s, 1 H), 5.59 (s, 1 H), 5.91 (dm, *J* = 10.1 Hz, 1 H), 6.13 (dm, *J* = 10.0 Hz, 1 H), 7.46-7.55 (m, 4 H), 7.59-7.68 (m, 2 H), 7.76-7.86 (m, 4 H); ^{13}C NMR ($CDCl_3$, 63 MHz) for the diastereomeric mixture: δ 20.0 (t), 20.9 (t), 24.4 (t), 24.7 (t), 28.0 (t), 28.5 (t), 28.6 (2×q), 34.2 (q), 34.5 (q), 50.4 (d), 51.1 (d), 66.1 (d), 67.4 (d), 125.0 (d), 126.5 (d), 128.4 (4×d), 129.0 (2×d), 129.2 (2×d), 134.0 (d), 134.2 (d), 134.5 (d), 134.6 (d), 135.0 (s), 135.2 (s), 152.75 (s), 152.83 (s), 153.25 (s), 153.33 (s), 192.8 (s), 193.0 (s); Anal. Found: C, 66.50; H, 6.32; N, 12.78%. Calcd for $C_{18}H_{21}N_3O_3$ (327.4): C, 66.04; H, 6.47; N, 12.84%.

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