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Supporting Information

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Ruthenium-catalyzed anti-Markovnikov addition of amides to alkynes: An efficient synthesis of enamides**

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Synthesis of 1-(*(E)*-hex-1-enyl)2-pyrolidinon-2-one (4a):
An oven-dried flask was charged with bis-(2-methallyl)-cycloocta-1,5-diene-ruthenium(II) (6.4 mg, 0.02 mmol) and DMAP (4.99 mg, 0.04 mmol) and was flushed with argon. Subsequently, tri-*n*-butylphosphine (15 µL, 0.06 mmol), 2-pyrrolidinone **(2a)** (85.1 mg, 1 mmol)1-hexyne (**1a**) (229 µL, 2.0 mmol), and dry toluene (3.0 mL) were added via syringe. The resulting green solution was stirred for 15 h at 100 °C and was then poured into aqueous $NaHCO_3$ solution (30 mL). The resulting mixture was extracted repeatedly with 20 mL portions of ethyl acetate, the combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered, and the volatiles were removed in vacuo. The residue was purified by column chromatography (SiO_2, ethyl acetate / hexanes 3:1) yielding **4a** (158.9 mg, 95 % yield, 97 % isomeric purity) as a colorless oil.
^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.86 (d, ^3J = 14.7 Hz, 1H), 4.92 (dt, ^3J = 14.7 Hz, 7.2 Hz, 1H), 3.48 (t, ^3J = 7.2 Hz, 2H), 2.46 (t, ^3J = 8.1 Hz, 2H), 2.01-2.14 (m, 4H), 1.24-1.39 (m, 4H), 0.88 (t, ^3J = 7.2 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 172.2, 123.6, 112.5, 45.3, 32.3, 31.3, 29.7, 22.1, 17.4, 13.9 ppm;

MS (EI, 70 eV): m/z (%) = 167 (20), 124 (100, [M]+), 86 (23), 69 (12), 41 (21); HRMS (EI) calc. for $C_{10}H_{17}NO$: 167.131014 u, found: 167.130871 u.

Synthesis of 1-(*(E)*-4-phenylbut-1-enyl)2-pyrolidin-2-one (4b): Compound **4b** was synthesized following the above procedure from 2-pyrolidinone (**2a**) (77 µL, 1.0 mmol) and 1-(but-3-ynyl)benzene (**1b**) (281 µL, 2.0 mmol) yielding a 30:1 mixture of **4b** and **5b** as a white solid (197.5 mg, 97 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.16-7.25 (m, 2H), 7.07-7.14 (m, 3H), 6.85 (d, ^{3}J = 14.7 Hz, 1H), 4.88 (dt, ^{3}J = 14.7 Hz, 7.2 Hz, 1H), 3.39 (t, ^{3}J = 7.2 Hz, 2H), 2.63 (t, ^{3}J = 8.3 Hz, 2H), 2.28-2.42 (m, 4H), 1.93-2.05 (m, 2H) ppm;
13C-NMR (75.5 MHz, $CDCl_3$): 171.8, 140.6, 127.4, 127.3, 124.9, 123.2, 110.3, 44.2, 35.7, 31.0, 30.3, 16.4 ppm; MS (EI, 70 eV): m/z (%) = 215 (7), 124 (100, $[M]^+$), 96 (7), 69 (8), 41 (13), HRMS (EI) calc. for $C_{14}H_{17}NO$: 215.131014 u, found: 215.13050 u.

Synthesis of 1-(*(E)*-dodeca-1,11-dienyl)2-pyrolidin-2-one (4c): Compound **4c** was synthesized following the above procedure from 2-pyrolidinone (**2a**)(77 µL, 1.0 mmol) and dodec-1-en-11-yne (**1c**) (463 µL, 2.0 mmol) yielding a 30:1 mixture of **4c** and **5c** as a pale yellow oil (241.1 mg, 99 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.79 (d, ^{3}J = 14.4 Hz, 1H), 5.72 (dd, ^{3}J = 17.1 Hz, 10.2 Hz, 1H), 4.76-4.95 (m, 3H), 3.41 (t, ^{3}J = 7.1 Hz, 2H), 2.38 (t, ^{3}J = 8.2 Hz, 2H), 1.93-2.04 (m, 6H), 1.20-1.33 (m, 12H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 172.2, 138.7, 123.2, 113.7, 112.0, 44.9, 33.4, 30.9, 29.7, 29.6, 29.0, 28.6, 28.5, 17.0 ppm; MS (EI, 70 eV): m/z (%) = 249 (11), 166 (4), 124 (100, $[M]^+$), 98 (13), 86 (70), 69 (12), 41 (21); HRMS (EI) calc. for $C_{16}H_{27}NO$: 249.209264 u, found: 249.209310 u.

Synthesis of 1-(*(E)*-5-chloropent-1-enyl)2-pyrolidinon-2-one (4d):

Compound **4d** was synthesized following the above procedure from 2-pyrolidinone (**2a**) (77 µL, 1.0 mmol) and 1-(*(E)*-5-chloropent-1-enyl (**1d)** (212 µL, 2.0 mmol) yielding a 30:1 mixture of **4d** and **5d** as a colorless oil (148.2 mg, 81 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.85 (d, ^{3}J = 14.3 Hz, 1H), 4.83 (dt, ^{3}J = 14.3 Hz, 7.2 Hz, 1H), 3.40-3.52 (m, 4H), 2.41 (t, ^{3}J = 8.1 Hz, 2H), 2.12-2.22 (m, 2H), 1.97-2.10 (m, 2H), 1.75-1.84(m, 2H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 171.9, 123.8, 109.0, 44.3, 43.2, 31.8, 30.3, 26.3 , 16.5 ppm; MS (EI, 70 eV): m/z (%) = 187 (21), 124 (100, $[M]^+$), 96 (11), 69 (15), 41 (24); HRMS (EI) calc. for $C_9H_{14}ClNO$: 187.076392 u, found: 187.076305 u.

Synthesis of *(E)*-methyl 3-(2-oxopyrrolidin-1-yl)acrylate (4e) [CAS: 145294-78-6]:

Compound **4e** was synthesized following the above procedure from 2-pyrolidinone (**2a**) (77 µL, 1.0 mmol) and methyl propiolate (**1e)**(178 µL, 2.0 mmol) yielding a 30:1 mixture of **4e** and **5e** as a white solid (167 mg, 99 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 8.09 (d, ^{3}J = 13.9 Hz, 1H), 5.91 (d, ^{3}J = 13.9 Hz, 1H), 3.72 (s, 3H), 3.54 (t, ^{3}J = 6.8 Hz, 2H), 2.53 (t, ^{3}J = 8.1 Hz, 2H), 2.10-2.21 (m, 2H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 174.6, 168.0, 137.9, 100.7 , 51.8, 45.3, 31.3, 17.8 ppm; MS (EI, 70 eV): m/z (%) = 169 (76), 138 (85), 110 (100. $[M]^+$), 82 (84), 70 (27), 55 (17), 41 (36); HRMS (EI) calc. for $C_8H_{11}NO_3$: 169.073894 u, found: 169.073984 u.

Synthesis of 1-(*(E)*-3-methoxyprop-1-enyl)pyrrolidin-2-one (4f):

Compound **4f** was synthesized following the above procedure from 2-pyrolidinone (**2a**) (77 µL, 1.0 mmol) and 3-methoxyprop-1-yne (**1f**) (169 µL, 2.0 mmol) yielding a 8:1 mixture of **4f** and **5f** as a colorless oil (145.1 mg, 93 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$):

7.04 (d, ^3J = 14.3Hz, 1H), 4.97 (dt, ^3J = 14.3 Hz,7.0 Hz, 1H), 3.89 (d, ^3J = 7.2, 2H), 3.48 (t, ^3J = 7.2 Hz, 2H), 3.25 (s, 3H), 2.42 (t, 3J = 8.3 Hz, 2H), 2.01-2.11 (m, 2H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 172.5, 126.4, 106.2, 70.4, 56.5, 44.2, 30.2, 16.5 ppm; MS (EI, 70 eV): m/z (%) = 155 (86), 140 (31), 124 (100, $[M]^+$), 112 (29), 96 (19), 56 (17), 41 (63); HRMS (EI) calc. for $C_8H_{13}NO_2$: 155.094629 u, found: 155.094590 u.

Synthesis of 1-(*(E)*-3-methylbuta-1,3-dienyl)pyrrolidin-2-one (4g)[CAS: 112682-83-4]:

Compound **4g** was synthesized following the above procedure from 2-pyrolidinone (**2a**) (77 µL, 1.0 mmol) and 2-methylbut-1-en-3-yne (**1g**) (190 µL, 2.0 mmol) yielding a 24:1 mixture of **4g** and **5g** as a white solid (141.0 mg, 98 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.05 (d, ^3J = 14.7 Hz, 1H), 5.70 (d, ^3J = 14.7 Hz, 1H), 4.88(s, 1H), 4.84 (s, 1H), 3.55(t, ^3J = 7.2 Hz, 2H), 2.49 (t, ^3J = 8.1 Hz, 2H), 2.03-2.17 (m, 2H), 1.87 (s, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.3, 140.6, 123.6, 115.0, 114.4, 45.2, 31.2, 18.8 , 17.4 ppm; MS (EI, 70 eV): m/z (%) = 151 (100, $[M]^+$), 136 (51), 123 (20), 67 (62), 41 (60); HRMS (EI) calc. for $C_9H_{13}NO$: 151.099714 u, found: 151.099835 u.

Synthesis of 1-(*(E)*-2-styryl)pyrrolidin-2-one (4h) [CAS: 6908-67-4]:

Compound **4h** was synthesized following the above procedure from 2-pyrolidinone (**2a**) (77 µL, 1.0 mmol) and 1-ethynylbenzene (**1h**) (220 µL, 2.0 mmol) yielding a 30:1 mixture of **4h** and **5h** as a white solid (180.0 mg, 99 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.51 (d, ^3J = 15.1 Hz, 1H), 7.14-7.26 (m, 4H), 7.02-7.09 (m, 1H), 5.75 (d, ^3J = 15.1 Hz, 1H), 3.48 (t, ^3J = 7.2 Hz, 2H), 2.39 (t, ^3J = 8.1 Hz, 2H), 1.92-2.05 (m, 2H) ppm;^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.6, 133.6, 128.9, 126.7, 125.8, 123.8, 111.9, 45.4, 31.5, 17.6 ppm; MS (EI, 70 eV): m/z (%) = 187 (100, $[M]^+$), 159

(6), 132 (96), 77 (16), 51 (7); HRMS (EI) calc. for $C_{12}H_{13}NO$: 187.099714 u, found: 187.099632 u.

Synthesis of 1-(*(E)*-3,3-dimethylbut-1-enyl)pyrrolidin-2-one (4i):

Compound **4i** was synthesized following the above procedure from 2-pyrolidinone (**2a**) (77 µL, 1.0 mmol) and 3,3-dimethylbut-1-yne (**1i**) (246 µL, 2.0 mmol) yielding a 30:1 mixture of **4i** and **5i** as a white solid (165.0 mg, 99 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.83 (d, ^{3}J = 14.7Hz, 1H), 4.98 (d, ^{3}J = 14.7 Hz, 1H), 3.47 (t, ^{3}J = 7.2 Hz, 2H), 2.47 (t, 3J = 8.1 Hz, 2H), 2.01-2.12 (m, 2H), 1.05 (s, 9H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.0, 124.0, 120.3, 45.3, 32.0, 31.4, 30.2 , 17.4 ppm; MS (EI, 70 eV): m/z (%) = 167 (19), 152 (100, $[M]^+$), 134 (4), 69 (7), 41 (18); HRMS (ESI_{pos}) calc. for $C_{10}H_{17}NO{\cdot}Na$: 190.120788 [M^+] u, found: 190.120335 u.

Synthesis of 1-(*(E)*-2-(trimethylsilyl)vinyl)pyrrolidin-2-one (4j):

Compound (**4j**) was synthesized following the above procedure from 2-pyrolidinone (**2a**) (77 µL, 1.0 mmol) and ethynyltrimethylsilane (**1j**) (277 µL, 2.0 mmol) yielding a 3:1 mixture of **4j** and **5j** as a colorless oil (120.1 mg, 69 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): (d, ^{3}J = 17.3 Hz, 1H), 4.72(d, ^{3}J = 17.3 Hz, 1H), 3.50(t, ^{3}J = 7.2 Hz, 2H), 2.47 (t, ^{3}J = 8.3 Hz, 2H), 2.04-2.10 (m, 2H), 0.06 (s, 9H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 173.0, 133.6, 106.2, 44.6, 31.7, 17.3, -0.8 ppm; MS (EI, 70 eV): m/z (%) = 183 (14), 168 (100, $[M]^+$), 142 (30), 73 (6), 59 (8); HRMS (EI) calc. for $C_9H_{11}NOSi$: 183.107942 u, found: 183.107889 u.

Synthesis of 1-(*(E)*-hex-1-enyl)azetidin-2-one (4k):

Compound **4k** was synthesized following the above procedure from azetidin-2-one (**2b**) (71.1 mg, 1.0 mmol) and 1-hexyne (229 µL,

2.0 mmol) (**1a**) yielding a 2:1 mixture of **4k** and **5k** as a pale yellow oil (104.1 mg, 70 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.32 (d, ^{3}J = 14.7 Hz, 1H), 4.95 (dt, ^{3}J = 14.7 Hz, 7.2 Hz, 1H), 3.32 (t, ^{3}J = 6.0 Hz, 2H), 1.93-2.02 (m, 2H), 1.30-1.36 (m, 4H), 0.85-0.90 (t, ^{3}J = 7.2 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 163.5, 121.6, 111.8, 38.0, 35.8, 31.8, 29.0, 22.0, 13.8 ppm.; MS (EI, 70 eV): m/z (%) = 153 (33), 124 (4), 110 (81), 82 (21), 68 (100, $[M]^+$), 55 (18), 41 (36); HRMS (EI) calc. For $C_9H_{15}NO$: 153.115364 u, found: 153.115538 u.

Synthesis of 1-(*(E)*-hex-1-enyl)piperidin-2-one (4l):

Compound **4l** was synthesized following the above procedure from piperidin-2-one (**2c**) (99.1 mg, 1.0 mmol) and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding a 30:1 mixture of **4l** and **5l** as a pale yellow oil (170.1 mg, 94 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.46 (d, ^{3}J = 13.9 Hz, 1H), 4.98 (dt, ^{3}J = 13.9 Hz, 7.0 Hz, 1H), 3.32 (t, ^{3}J = 6.0 Hz, 2H), 2.41 (t, ^{3}J = 6.6 Hz 2H), 1.97-2.09 (m, 2H), 1.71-1.86 (m, 4H), 1.21-1.35 (m, 4H), 0.83 (t, ^{3}J = 7.2 Hz, 3H) ppm;^{13}C-NMR (75.5 MHz, $CDCl_3$): 167.1, 125.7, 110.5, 44.2, 31.9, 31.5, 29.1, 21.7, 21.1, 19.7, 12.9 ppm; MS (EI, 70 eV): m/z (%) = 181 (32), 152 (16), 138 (100, $[M]^+$), 124 (38), 110 (19), 100 (25), 82 (15), 55 (27), 41 (18); HRMS (EI) calc. for $C_{11}H_{19}NO$: 181.146664 u, found: 181.146654 u.

Synthesis of 1-(*(E)*-hex-1-enyl)azonan-2-one (4m):

Compound **4m** was synthesized following the above procedure from azonan-2-one (**2d**) (141.2 mg, 1.0 mmol) and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding a 30:1 mixture of **4m** and **5m** as a pale yellow oil (186.0 mg, 86 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.20 (d, ^{3}J = 14.7 Hz, 1H), 5.00 (dt, ^{3}J = 14.7 Hz, 7.0 Hz, 1H), 3.72 (t, ^{3}J = 5.7 Hz, 2H), 2.54-2.64 (m, 2H,), 2.02-2.14 (m, 2H), 1.78-1.89 (m, 2H), 1.63-1.75 (m, 2H), 1.40-1.60 (m, 3H), 1.24-1.39 (m, 4H), 0.88 (t, ^{3}J = 7.0 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 174.0, 125.6, 112.8, 45.9, 35.7, 32.9, 30.6, 28.7, 26.1, 25.8, 25.6, 22.7, 22.5, 14.3 ppm; MS (EI, 70 eV):

m/z (%) = 223 (28), 180 (100, $[M]^+$), 166 (50), 112 (29), 55 (31), 41 (27); HRMS (EI) calc. for $C_{14}H_{25}NO$: 223.193614 u, found: 223.193523 u.

Synthesis of *N*-(*(E)*-hex-1-enyl)-*N*-methylformamide (4n):

Compound **4n** was synthesized following the above procedure from *N*-methylformamide (**2e**) (59.1 mg, 1.0 mmol)and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding a 30:1 mixture of **4n** and **5n** as a pale yellow oil (110.2 mg, 83 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): δ8.24 (s, 1H, H-8), 6.42 (d, ^3J = 13.9 Hz, 2H), 5.05 (dt, ^3J = 13.9 Hz, 7,2 Hz, 1H), 2.98 (s, 3H), 2.04-2.09 (m, 2H), 1.30-1.35 (m, 4H), 0.87 (t, ^3J = 7.2 Hz, 3H,) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 162.0, 128.1, 111.6, 32.2, 29.7, 27.5, 22.1, 13.9 ppm; MS (EI, 70 eV): m/z (%) = 141 (25), 98 (100, $[M]^+$), 70 (51), 60 (16), 42 (26); HRMS (EI) calc. for $C_8H_{15}NO$: 141.115364 u, found: 141.115488 u.

Synthesis of *N*-(*(E)*-hex-1-enyl)-N-methylacetamide (4o):

Compound **4o** was synthesized following the above procedure from *N*-methylacetamide (**2f**) (73.1 mg, 1.0 mmol) and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding a 3:1 mixture of **4o** and **5o** as a pale yellow oil (126.1 mg, 84 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.57 (d, ^3J = 13.9 1H), 4.99 (dt, ^3J = 13.9 Hz, 7.1 Hz, 1H), 3.04 (s, 3H), 2.18 (s, 3H), 2.04-2.10 (m, 2H), 1.33-1.39 (m, 4H), 0.90 (t, ^3J = 6.6 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 168.9, 128.7, 112.3, 32.4, 30.1, 29.6, 22.1, 22.0, 13.9 ppm; MS (EI, 70 eV): m/z (%) = 155 (17), 112 (18), 98 (13), 70 (100, $[M]^+$), 43 (18); HRMS (EI) calc. for $C_9H_{17}NO$: 155.131014 u, found: 155.130913 u.

Synthesis of 1-(*(Z)*-hex-1-enyl)pyrrolidine-2,5-dione (4p):

Compound **4p** was synthesized following the above procedure from pyrrolidine-2,5-dione (**2g**) (99.1 mg, 1.0 mmol)and 1-hexyne

(229 µL, 2.0 mmol) (**1a**) yielding 1:2 mixture of **4p** and **5p** as a white solid (22.0 mg, 12 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 5.86 (d, ^{3}J = 8.7 Hz, 1H), 5.68-5.76 (m, 1H), 2.77 (s, 4H), 1.87-1.98 (m, 2H), 1.25-1.40 (m, 4H), 0.86 (t, ^{3}J = 7.2 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 175.6, 133.8, 116.6, 30.7, 28.4 , 27.8, 22.3, 13.8 ppm; MS (EI, 70 eV): m/z (%) = 181 (27), 138 (75), 100 (100, $[M]^+$), 82 (98), 67 (28), 56 (70), 41(22); HRMS (EI) calc. for $C_{10}H_{15}NO_2$: 181.110279 u, found: 181.110517 u.

Synthesis of *N*-(4-acetylphenyl)-*N*-(*(E)*-hex-1-enyl)acetamide (4q):

Compound **4q** was synthesized following the above procedure from *N*-(4-acetylphenyl)acetamide (**2h**) (177.2 mg, 1.0 mmol)and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding 30:1 mixture of **4q** and **5q** as a white solid (84 mg, 33 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.98-8.04 (m, 2H), 7.20-7.32 (m, 3H), 4.35 (dt, ^{3}J = 14.2 Hz, 7.0 Hz, 1H), 2.95 (s, 3H), 1.88-.97 (m, 2H), 1.83 (s, 3H, H-8), 1.33-1.21 (m, 4H), 0.78 (t, ^{3}J = 7.2 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.9, 166.8, 143.5, 135.9, 129.0, 128.2, 127.2, 114.8, 30.9, 28.7, 25.7, 22.2, 21.1, 12.8 ppm; MS (EI, 70 eV): m/z (%) = 259 (30), 217 (18), 202 (13), 174 (100, $[M]^+$), 130 (17), 77 (5), 43 (51); HRMS (EI) calc. for $C_{16}H_{21}NO_2$: 259.157229 u, found: 259.157132 u.

Synthesis of *N*-(4-ethoxyphenyl)-*N*-(*(E)*-hex-1-enyl)acetamide (4r):

Compound **4r** was synthesized following the above procedure from *N*-(4-ethoxyphenyl)acetamide (**2i**) (179.2 mg, 1.0 mmol) and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding 30:1 mixture of **4r** and **5r** as a white solid (245.3 mg, 94 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.38 (d, ^{3}J = 14.3 Hz, 1H), 6.96-7.02 (m, 2H), 6.86-6.92 (m, 2H), 4.34 (dt, ^{3}J = 14.3 Hz, 7,2 Hz, 1H), 4.0 (q, ^{3}J = 6.8 Hz, 2H), 1.90 (m, 2H), 1.77 (s, 3H), 1.38 (t,

^{3}J = 6.8 Hz, 3H), 1.12-1.23 (m, 4H), 0.77 (t, ^{3}J = 6.4 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$):168.5, 158.6, 132.5, 129.6, 128.2, 115.3, 114.3, 63.5, 31.9, 29.5, 23.0, 21.9, 14.6, 13.7 ppm; MS (EI, 70 eV): m/z (%) = 261 (51), 219 (25), 176 (100, $[M]^+$), 148 (12), 108 (5), 65 (7), 43 (18); HRMS (EI) calc. for $C_{16}H_{23}NO_2$: 261.172879 u, found: 261.172931u.

Synthesis of *N*-(*(E)*-hex-1-enyl)-N-isopropylacrylamide (4s):
Compound **4s** was synthesized following the above procedure from *N*-isopropylacrylamide (**2j**) (113.2 mg, 1.0 mmol) and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding 30:1 mixture of **4s** and **5s** as a colorless oil (74.0 mg, 38 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.54 (dd, $^{3}J_{trans}$ = 17.0, $^{3}J_{cis}$ = 10.2 1H), 6.26 (dd, $^{3}J_{trans}$ = 13.9 Hz, $^{2}J_{gem}$ = 2.3 Hz, 1H), 5.92 (d, ^{3}J = 13.6 Hz, 1H), 5.53 (dd, $^{3}J_{cis}$ = 10.4 Hz, $^{2}J_{gem}$ = 2.3 Hz 1H), 5.43 (dt, ^{3}J = 13.6 Hz, 7.1 Hz, 1H), 4.69-4.83 (m, 1H), 2.05-2.15 (m, 2H), 1.27-1.43 (m, 4H), 1.10 (d, ^{3}J = 7.2 Hz, 6H), 0.90 (t, ^{3}J = 7.2 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 164.2, 133.6, 129.1, 125.3, 122.9, 44.5, 30.3, 28.8, 21.2, 19.0 , 12.8 ppm; MS (EI, 70 eV): m/z (%) = 195 (23), 180 (12), 152 (32), 138 (82), 110 (22), 98 (83), 55 (100, $[M]^+$); HRMS (EI) calc. for $C_{12}H_{21}NO$: 195.162314 u, found: 195.162119 u.

Synthesis of 1,4-di(*(E)*-hex-1-enyl)piperazine-2,5-dione (4t):
Compound **4t** was synthesized following the above procedure from piperazine-2,5-dione (**2k**) (114.1 mg, 1.0 mmol) and 1-hexyne (458 µL, 4.0 mmol) (**1a**) yielding 30:1 mixture of **4t** and **5t** as a white solid (275.2 mg, 99 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.18 (d, ^{3}J = 14.6, 2H), 5.10 (dt, ^{3}J = 14.6 Hz, 7.2 Hz, 2H), 4.14 (s, 4H), 2.05-2.13 (m, 4H), 1.26-1.41 (m, 8H), 0.88 (t, ^{3}J = 6.8 Hz, 6H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 160.1, 123.7, 114.8, 47.4, 31.9, 29.7, 22.0, 13.8 ppm; MS (EI, 70 eV): m/z (%) = 278 (93), 235 (92), 207 (87), 112 (35), 68 (100, $[M]^+$),

41 (61); HRMS (EI) calc. for $C_{16}H_{26}N_2O_2$: 278.199427 u, found: 278.199679 u.

Synthesis of (4*S*,5*R*)-1-(*(E)*-hex-1-enyl)-3,4-dimethyl-5-phenylimidazolidin-2-one (4u):

Compound **4u** was synthesized following the above procedure from (4*R*,5*S*)-1,5-dimethyl-4-phenylimidazolidin-2-one (**2l**) (190.3 mg, 1.0 mmol) and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding 23:1 mixture of **4u** and **5u** as a white solid (262.1 mg, 99 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.26-7.33 (m, 3H), 7.05-7.11 (m, 2H), 6.70 (d, ^3J = 14.7 Hz 1H), 4.78 (d, ^3J = 8.7 Hz 1H), 4.26 (dt, ^3J = 14.7 Hz, 7.2 Hz, 1H), 3.81 (dq, ^3J = 8.7 Hz, 6.6 Hz, 1H), 2.76 (s, 3H), 1.79-1.88 (m, 2H), 1.03-1.15 (m, 4H), 0.74 (t, ^3J = 6.8 Hz, 3H), 0.73 (d, ^3J = 6.6 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 158.0, 135.7, 128.3, 127.9, 127.5, 123.2, 109.1, 60.6, 55.7, 32.4, 29.7, 28.8, 21.7, 15.2, 13.8 ppm; MS (EI, 70 eV): m/z (%) = 272 (27), 229 (100, $[M]^+$), 190 (8), 172 (7), 117 (12), 104 (7), 91 (11); HRMS (EI) calc. for $C_{17}H_{24}N_2O$: 272.188862 u, found: 272.188802 u.

Synthesis of (*S*)-methyl-1-(*(E)*-hex-1-enyl)-5-oxopyrrolidine-2-carboxylate (4v):

Compound **4v** was synthesized following the above procedure from (*S*)-methyl 5-oxopyrrolidine-2-carboxylate (**2m**) (143.1 mg, 1.0 mmol) and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding 6:1 mixture of **4v** and **5v** as a pale yellow oil (210.3 mg, 96 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.74 (d, ^3J = 14.7 Hz, 1H;), 4.77 (dt, ^3J = 14.7 Hz, 7.2 Hz, 1H), 4.32 (m, 1H), 3.69 (s, 3H), 2.26-2.62 ((br)m, 4H), 1.93-2.07 ((br)m, 2H), 1.19-1.27 (m, 4H), 0.08 (t, ^3J = 7.2 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 171.8, 171.1, 121.8, 111.9, 57.5, 51.6, 31.0, 28.8, 28.7, 21.9, 29.7, 28.8, 21.7, 15.2, 13.8 ppm; MS (EI, 70 eV): m/z (%) = 225 (28), 182 (81), 166 (100, $[M]^+$), 154 (16), 144 (18), 84 (24),

41 (22); HRMS (EI) calc. for $C_{12}H_{19}NO_3$: 225.136494 u, found: 225.136698 u.

Synthesis of (*S*)-3-((*E*)-hex-1-enyl)-4-isopropyloxazolidin-2-one (4w):

Compound **4w** was synthesized following the above procedure from (*S*)-4-isopropyloxazolidin-2-one (**2n**) (129.2 mg, 1.0 mmol) and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding 30:1 mixture of **4w** and **5w** as a white solid (198.9 mg, 97 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.42 (d, ^3J = 14.3 Hz, 1H), 4.91 (dt, ^3J = 14.3 Hz, 7.2 Hz, 1H), 4.11-4.23 (m, 2H), 3.95 (dt, ^3J = 8.7 Hz, 3.4 Hz 1H), 2.25-2.42 (m, 1H), 1.96-2.03 (m, 2H), 1.21-1.34 (m, 4H), 0.86 (d, ^3J = 7.2 Hz, 3H), 0.84 (t, ^3J = 7.2 Hz, 3H), 0.77 (d, 3J = ~7 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 154.7, 121.6, 111.3, 61.9, 57.5, 31.2, 28.8, 25.1, 21.1, 16.9, 12.9, 12.8 ppm; MS (EI, 70 eV): m/z (%) = 211 (18), 168 (100, $[M]^+$), 86 (15), 55 (17), 41 (23), HRMS (EI) calc. for $C_{12}H_{21}NO_2$: 211.157229 u, found: 211.157331 u.

Synthesis of (4*R*,5*S*)-3-((*E*)-hex-1-enyl)-5-methyl-4-phenyloxazolidin-2-one (4x):

Compound **4x** was synthesized following the above procedure from aus (4R,5S)-5-methyl-4-phenyloxazolidin-2-one (**2o**) (177.2 mg, 1.0 mmol) and 1-hexyne (229 µL, 2.0 mmol) (**1a**) yielding 24:1 mixture of **4x** and **5x** as a white solid (211.1 mg, 84 %);^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.24-7.37 (m, 5H), 6.49 (d, ^3J = 14.6 Hz, 1H), 5.60 (d, ^3J = 7.5 Hz, 1H), 4.87 (dt, ^3J = 14.6 Hz, 7.2 Hz, 1H), 4.26 (dt, ^3J = 13.9 Hz, 6.4 Hz, 1H), 1.97-2.01 (m, 2H), 1.20-1.35 (m, 4H), 0.83 (t, ^3J = 7.2 Hz, 3H), 0.76 (d, ^3J = 6.4 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 154.9, 134.7, 129.0, 128.9, 126.3, 122.9, 112.7, 79.4, 54.8, 32.6, 30.1, 22.5, 14.3, 13.5 ppm; MS (EI, 70 eV): m/z (%) = 259 (29), 216 (10), 172 (43), 118 (100, $[M]^+$), 91 (22), 55 (21), 41 (18);

HRMS (EI) calc. for $C_{16}H_{21}NO_2$: 259.157229 u, found: 259.157094 u.

Synthesis of 1-(*(Z)*-hex-1-enyl)2-pyrolidinon-2-one (5a):
An oven-dried flask was charged with bis-(2-methallyl)-cycloocta-1,5-diene-ruthenium(II) (6.4 mg, 0.02 mmol), DMAP (4.99 mg, 0.04 mmol), bis(dicyclohexylphosphino)methane (12.3 mg, 0.03 mmol) and was flushed with argon. Subsequently, 1-hexyne (**1a**) (229 µL, 2.0 mmol), 2-pyrolidinone **(2a)** (85.1 mg, 1 mmol), toluene (3.0 mL) and deoxygenated water (144 µL, 8 mmol) were added via syringe. The resulting green solution was stirred for 15 h at 100 °C and was then poured into aqueous $NaHCO_3$ solution (30 mL) and the resulting mixture was extracted repeatedly with 20 mL portions of ethyl acetate. The combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered, and the volatiles were removed in vacuo. The residue was purified by column chromatography (SiO_2, ethyl acetate / hexanes 3:1) yielding a 5:1 mixture of **5a** and **4a** (166.1 mg, 99 %) as a colorless oil.
^{1}H-NMR (300.1 MHz, $CDCl_3$): 6.30 (d, ^3J = 9.7 Hz, 1H), 3.69 (dt, ^3J = 9.7 Hz, 7.5 Hz, 1H), 3.69 (t, ^3J = 7.2 Hz, 2H), 2.34 (t, ^3J = 8.3 Hz, 2H), 1.99-2.14 (m, 4H), 1.21-1.36 (m, 4H), 0.84 (t, ^3J = 7.2 Hz, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 174.9, 122.6, 117.3, 49.0, 32.8, 30.7, 27.3, 22.6, 19.0, 14.3 ppm; MS (EI, 70 eV): m/z (%) = 167 (20), 124 (100, $[M]^+$), 86 (25), 69 (16), 41 (27); HRMS (ESI_{pos}) calc. for $C_{10}H_{17}NO{\cdot}Na$: 190.120783 [M^+] u, found: 190.12105u.

Synthesis of 1-(*(Z)*-4-phenylbut-1-enyl)2-pyrolidin-2-one (5b):
Compound **5b** was synthesized following the above procedure from 2-pyrolidinone (**2a**) (77 µL, 1.0 mmol) and 1-(but-3-ynyl)benzene (**1b**) (281 µL, 2.0 mmol) yielding a 8:1 mixture of **5b** and **4b** as a white solid (198.0 mg, 92 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.20-7.25 (m, 2H), 7.10-7.17 (m, 3H), 6.33 (d,

^{3}J = 9.8 Hz, 1H), 4.84 (dt, ^{3}J = 9.4 Hz, 7.5 Hz, 1H), 3.56 (t, ^{3}J = 7.2 Hz, 2H), 2.5 (t, ^{3}J = 8.3 Hz, 2H), 2.4-2.5 (m, 2H), 2.32 (t, ^{3}J = 8.3 Hz, 2H), 1.90-2.01 (m, 2H) ppm;^{13}C-NMR (75.5 MHz, $CDCl_3$): 174.4, 141.3, 128.4, 128.2, 125.9, 122.7, 115.4, 48.4, 36.2, 30.1, 29.1, 18.4 ppm; MS (EI, 70 eV): m/z (%) = 215 (18), 142 (36), 124 (100, $[M]^+$), 111 (22), 86 (27), 41 (20); HRMS (ESI_{pos}) calc. for $C_{10}H_{17}NO{\cdot}Na$: 238.120783 [M^+] u, found: 238.12107 u.