Eur. J. Org. Chem. **2008** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2008 · ISSN 1434–193X

SUPPORTING INFORMATION

Title: Ruthenium-Catalyzed Allenyl Carbamate Formation from Propargyl Alcohols and Isocyanates
Author(s): Edgar Haak*
Ref. No.: O200701067

Experimental Details

All reactions were carried out in a dry atmosphere under argon using standard Schlenck techniques. The chemicals used were dried and purified according to common procedures. Products were identified by spectroscopic analysis (^{1}H NMR, ^{13}C NMR, IR, MS, HRMS).

Preparation and characterization data of ligands:

Ligands **1cL**, **2aL**–**2cL**, **2eL**, **3aL**, **3eL**–**3gL** and **4aL**–**4cL** have previously been published in *Eur. J. Org. Chem.* **2007**, 2815–2824.

144 mg 4-hydroxy-5-methyl-4-cyclopentene-1,3-dione monohydrate (1 mmol) and 125 μL N,N'-dimethyl ethylenediamine (85 %, 1 mmol) were dissolved in 5 mL of methanol and refluxed for 2 h under argon. Evaporation of the solvent and chromatography on silica furnished 176 mg (99 %) **2dL** ($C_{10}H_{14}N_2O_1$) as dark red foam.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (s, 3 H), 2.91 (s, 3 H), 3.14 (s, 3 H), 3.20–3.24 (m, 2 H), 3.28–3.31 (m, 2 H), 4.19 (s, 1 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 7.4 (CH_3), 39.2 (CH_3), 40.1 (CH_3), 48.6 (CH_2), 50.3 (CH_2), 82.0 (CH), 94.8 (C), 146.7 (C), 158.6 (C), 198.3 (C) ppm. IR: ν = 2916 (w), 2855 (m), 1583 (s), 1448 (m), 1412 (m), 1374 (w), 1349 (s), 1254 (s), 1118 (w), 1080 (s), 1046 (m), 966 (w), 921 (w), 837 (w), 811 (w), 755 (m), 721 (w), 689 (w), 666 (w), 642 (m) cm^{-1}. MS (EI): *m/z* (%): 178 [M^+] (80), 163 (100), 135 (21). HRMS: [M^+] calcd.: 178.11061, found: 178.11027.
175 mg **2dL** (0.98 mmol) were dissolved in 2 mL of pyridine. After addition of a catalytic amount of DMAP and 1.5 eq. benzoyl chloride (for **3bL**) or 1.5 eq. acetyl chloride (for **3cL**) the reaction mixture was stirred at 100°C under argon for 2 h. Aqueous workup and chromatography on silica furnished **3bL** and **3cL**.
3bL ($C_{17}H_{18}N_2O_2$) 226 mg (82 %) dark red foam: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.83 (s, 3 H), 3.10 (s, 3 H), 3.21 (tr, J = 6.0 Hz, 2 H), 3.22 (s, 3 H), 3.52 (tr, J = 6.0 Hz, 2 H), 7.30 (tr, J = 7.1

Hz, 2 H), 7.37 (tr, J = 7.3 Hz, 1 H), 7.64 (d, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 8.0 (CH_3), 40.5 (CH_3), 44.4 (CH_3), 48.7 (CH_2), 50.7 (CH_2), 98.2 (C), 101.3 (C), 127.2 (CH), 129.7 (CH), 130.9 (CH), 141.1 (C), 146.6 (C), 165.9 (C), 187.3 (C), 192.7 (C) ppm. IR: ν = 3053 (w), 2962 (w), 2925 (w), 2861 (w), 1648 (w), 1599 (s), 1582 (s), 1555 (s), 1496 (w), 1436 (s), 1400 (s), 1354 (m), 1327 (m), 1282 (w), 1255 (m), 1235 (w), 1169 (w), 1114 (w), 1072 (m), 1017 (m), 937 (m), 863 (m), 834 (w), 801 (s), 775 (m), 756 (m), 733 (w), 705 (s), 651 (s) cm^{-1}. MS (EI): *m/z* (%): 282 [M$^+$] (40), 267 (78), 161 (23), 105 (100), 77 (38). HRMS: [M$^+$] calcd.: 282.13683, found: 282.13659.

3cL ($C_{12}H_{16}N_2O_2$) 183 mg (85 %) dark red foam: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3 H), 2.46 (s, 3 H), 3.17 (s, 3 H), 3.26 (tr, J = 6.0 Hz, 2 H), 3.37 (s, 3 H), 3.56 (tr, J = 6.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 7.9 (CH_3), 28.9 (CH_3), 40.3 (CH_3), 45.1 (CH_3), 48.4 (CH_2), 50.6 (CH_2), 98.8 (C), 102.2 (C), 147.0 (C), 165.5 (C), 189.6 (C), 194.1 (C) ppm. IR: ν = 2959 (w), 2914 (m), 2863 (w), 1604 (s), 1563 (s), 1434 (s), 1398 (s), 1374 (s), 1342 (s), 1280 (m), 1254 (m), 1196 (w), 1145 (w), 1112 (w), 1077 (w), 1057 (w), 1014 (m), 959 (m), 938 (m), 870 (m), 836 (m), 761 (m), 750 (m), 735 (m) cm^{-1}. MS (EI): *m/z* (%): 220 [M$^+$] (59), 205 (100), 177 (12), 149 (11). HRMS: [M$^+$] calcd.: 220.12118, found: 220.12109.

144 mg 4-hydroxy-5-methyl-4-cyclopentene-1,3-dione monohydrate (1 mmol) and 148 mg N,N'-bis(2-hydroxyethyl)-ethylenediamine (1 mmol) were dissolved in 5 mL of methanol and refluxed for 2 h under argon. The solvent was evaporated and the crude product was dissolved in 2 mL of pyridine. After addition of a catalytic amount of DMAP and 1.5 eq. acetyl chloride the reaction mixture was stirred at 100°C under argon for 2 h. Aqueous workup and chromatography on silica furnished **3dL**.

3dL ($C_{18}H_{24}N_2O_6$) 295 mg (81 %) red foam: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.89 (s, 3 H), 2.05 (s, 3 H), 2.06 (s, 3 H), 2.45 (s, 3H), 3.46 (tr, J = 5.4 Hz, 2 H), 3.70 (tr, J = 5.5 Hz, 2 H), 3.74 (tr, J = 5.4 Hz, 2 H), 4.29 (tr, J = 5.4 Hz, 2H), 4.32 (s br, 4 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 7.9 (CH_3), 20.4 (CH_3), 20.5 (CH_3), 29.3 (CH_3), 46.5 (CH_2), 50.1 (CH_2), 50.6 (CH_2), 55.0 (CH_2), 61.1 (CH_2), 61.2 (CH_2), 98.9 (C), 99.5 (C), 146.0 (C), 163.6 (C), 170.1 (c), 170.2 (C), 189.6 (C), 193.7 (C) ppm. IR: ν = 2956 (w), 2869 (w), 1737 (s), 1640 (w), 1603 (s), 1553 (s), 1426 (m), 1353 (m), 1228 (s), 1169 (w), 1047 (m), 959 (w), 761 (w), 604 (w) cm^{-1}. MS (EI): *m/z* (%): 364 [M$^+$] (60), 307 (22), 305 (31), 278 (23), 261 (21), 236 (68), 218 (24), 205 (20), 87 (100). HRMS: [M$^+$] calcd.: 364.16344, found: 364.16351.

Preparation and characterization data of ruthenium-complexes:

Complexes **1a**–**1c**, **2a**–**2c**, **2e**, **3a**, **3e**–**3g** and **4a**–**4c** have previously been published in *Eur. J. Org. Chem.* **2007**, 2815–2824.

General procedure of complex synthesis: 150 mg Triruthenium-dodecacarbonyl ($C_{12}O_{12}Ru_3$, 0.23 mmol) and 0.7 mmol of the corresponding ligand were dissolved in 5 mL of toluene and refluxed for 4–12 h (TLC control). The solvent was evaporated and chromatography on silica furnished the complexes **2d**, **3b**, **3c** and **3d**.

2d ($C_{13}H_{14}N_2O_4Ru_1$) 225 mg (88 %) yellow powder: ^{1}H NMR (400 MHz, CD_3OD): δ = 2.06 (s, 3 H), 2.57 (s, 3 H), 2.61–2.72 (m, 2 H), 2.76 (s, 3 H), 3.39–3.47 (m, 2 H), 4.42 (s, 1 H) ppm. ^{13}C NMR (100 MHz, DEPT, CD_3OD): δ = 11.0 (CH_3), 39.5 (CH_3), 42.7 (CH_3), 47.3 (CH), 49.4 (CH_2), 52.3 (CH_2), 66.5 (C), 114.2 (C), 121.5 (C), 168.9 (C), 197.3 (CO) ppm. IR: ν = 3063 (w), 2260 (w), 2922 (w), 2867 (w), 2807 (w), 2043 (s), 1972 (s), 1946 (s), 1611 (s), 1555 (s), 1517 (s) 1457 (w), 1416 (m), 1364 (s), 1308 (m), 1257 (m), 1085 (w), 949 (w), 837 (w), 721 (m), 698 (m), 667 (m) cm^{-1}. MS (EI): *m/z* (%): 364 [M^+] (3), 339, 338, 337, 336, 335, 334, 333, 330 [1:4:1:8:4:5:3:1, Distribution of (M^+ - CO)-Isotopes] (12), 252 (20), 178 (80), 163 (100), 135 (28).

3b ($C_{20}H_{18}N_2O_5Ru_1$) 236 mg (72 %) yellow powder: ^{1}H NMR (400 MHz, CD_3OD): δ = 2.01 (s, 3 H), 2.09 (s, 3 H), 2.50 (ddd, J = 12.0, 7.7, 3.5 Hz, 1 H), 2.73 (ddd, J = 12.5, 5.5, 3.5 Hz, 1 H), 2.80 (s, 3 H), 3.28 (ddd, J = 12.1, 5.4, 3.4 Hz, 1 H), 3.46 (ddd, J = 12.5, 7.7, 3.4 Hz, 1H), 7.44 (tr, J = 7.8 Hz, 2 H), 7.55 (tr, J = 7.3 Hz, 1 H), 7.88 (d, J = 7.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 11.1 (CH_3), 42.4 (CH_3), 42.9 (CH_3), 51.1 (CH_2), 51.4 (CH_2), 62.3 (C), 73.9 (C), 113.4 (C), 119.7 (C), 130.1 (CH), 130.7 (CH), 135.1 (CH), 137.7 (C), 169.2 (C), 194.0 (C), 196.7 (CO) ppm. IR: ν = 2960 (w), 2922 (w), 2866 (w), 2810 (w), 2052 (s), 1964 (s), 1626 (s), 1546 (m), 1448 (m), 1412 (m), 1359 (m), 1323 (m), 1256 (w), 1215 (w), 1116 (w), 1077 (m), 1024 (w), 953 (w), 921 (m), 864 (w), 839 (w), 802 (w), 782 (w), 740 (m), 726 (m), 689 (m) cm^{-1}. MS (EI): *m/z* (%): 468 [M^+] (1), 443, 442, 441, 440, 439, 438, 437, 434 [1:4:1:8:4:3:3:1, Distribution of (M^+ - CO)-Isotopes] (10), 412 (15), 384 (21), 282 (30), 161 (45), 105 (100).

3c ($C_{15}H_{16}N_2O_5Ru_1$) 213 mg (75 %) yellow powder: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 2.59 (s, 3 H), 2.63 (s, 3 H), 2.66–2.77 (m, 2 H), 2.86 (s, 3 H), 3.28–3.33 (m, 1H), 3.37–3.43 (m, 1 H) ppm. ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 11.5 (CH_3), 31.5 (CH_3), 41.5 (CH_3), 47.2 (CH_3), 48.7 (CH_2), 50.6 (CH_2), 63.0 (C), 77.2 (C), 107.8 (C), 124.9 (C), 170.3 (C), 195.0 (C), 201.0 (CO) ppm. IR: ν = 2924 (w), 2868 (w), 2806 (w), 2057 (m), 2020 (s), 1967 (s), 1932 (s), 1711 (w), 1671 (w), 1566 (s), 1443 (m), 1409 (s), 1349 (m), 1320 (m), 1263 (m), 1185 (w),

1077 (w), 1044 (w), 957 (w), 927 (w), 726 (m), 694 (m) cm^{-1}. MS (EI): *m/z* (%): 406 [M^+] (2), 381, 380, 379, 378, 377, 376, 375, 372 [1:4:1:8:5:3:3:1, Distribution of (M^+ - CO)-Isotopes] (10), 222 (30), 205 (18), 179 (100).

3d ($C_{21}H_{24}N_2O_9Ru_1$) 303 mg (79 %) orange powder: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 2.07 (s, 3 H), 2.12 (s, 3 H), 2.63 (s, 3 H), 2.89–3.01 (m, 2 H), 3.26–3.50 (m, 4 H), 3.62–3.76 (m, 2 H), 4.10–4.41 (m, 4 H) ppm. ^{13}C NMR (50 MHz, DEPT, $CDCl_3$): δ = 11.0 (CH_3), 20.5 (CH_3), 20.7 (CH_3), 31.1 (CH_3), 46.2 (CH_2), 47.7 (CH_2), 51.4 (CH_2), 55.9 (CH_2), 60.6 (CH_2), 62.0 (CH_2), 62.3 (C), 62.5 (C), 107.8 (C), 122.1 (C), 170.2 (C), 170.4 (C), 171.0 (C), 194.4 (C), 200.5 (CO) ppm. IR: ν = 2924 (w), 2854 (w), 2054 (s), 1975 (s), 1929 (s), 1736 (s), 1560 (m), 1511 (m), 1476 (w), 1450 (m),1407 (w), 1359 (m), 1267 (w), 1223 (s), 1049 (m), 958 (w), 685 (m), 599 (m) cm^{-1}. MS (ESI, TBME): *m/z* (%): 574 [M^+ + Na + H] (100), 554, 553, 552, 551, 550, 549, 548, 545 [1:4:1:7:4:3:3:1, Distribution of (M^+ + H)-Isotopes] (75), 523 [M^+ - CO + H] (24), 495 [M^+ - 2 CO + H] (15), 467 [M^+ - 2 CO + H] (42), 365 [M^+ - $Ru(CO)_3$ + H] (80).

Preparation and characterization data of iron-complexes:

General procedure of complex synthesis: 364 mg diiron-nonacarbonyl ($C_9O_9Fe_2$, 1.0 mmol) and 0.7 mmol of the corresponding ligand were dissolved in 5 mL of toluene and stirred at 60°C for 1 h (TLC control). The solvent was evaporated and chromatography on silica furnished the complexes **2b-Fe** and **3d-Fe**.

2b-Fe ($C_{24}H_{20}N_2O_4Fe_1$) 255 mg (80 %) yellow powder: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 6 H), 2.87 (ddd, J = 16.6, 7.0, 3.5 Hz, 2 H), 3.40 (ddd, J = 15.6, 6.5, 4.2 Hz, 2 H), 7.32–7.40 (m, 6 H), 7.51–7.55 (m, 4 H) ppm. ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 41.3 (CH_3), 49.9 (CH_2), 70.9 (C), 114.5 (C), 127.8 (CH), 128.2 (CH), 131.8 (C), 132.2 (CH), 165.5 (C), 210.1 (CO) ppm. IR: ν = 3054 (w), 2959 (w), 2919 (w), 2869 (w), 2028 (s), 1953 (s), 1625 (s), 1519 (m), 1495 (m), 1442 (m), 1412 (m), 1360 (m), 1265 (m), 1198 (w), 1116 (m), 1072 (w), 1052 (m), 1029 (w), 1005 (w), 948 (m), 915 (m), 847 (m), 751 (m), 727 (s), 695 (s), 653 (m), 607 (s), 586 (s) cm^{-1}. MS (EI): *m/z* (%): 456 [M^+] (15), 428 [M^+ - CO] (28), 400 [M^+ - 2 CO] (10), 372 [M^+ - 3 CO] (40), 316 [M^+ - $Fe(CO)_3$] (100), 273 (40). HRMS: [M^+ - CO] calcd.: 428.08233, found: 428.08174, [M^+ - 2 CO] calcd.: 400.08742, found: 400.08672.

3d-Fe ($C_{21}H_{24}N_2O_9Fe_1$) 273 mg (77 %) orange powder: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 2.07 (s, 3 H), 2.08 (s, 3 H), 2.67 (s, 3 H), 2.96–3.02 (m, 1 H), 3.14–3.23 (m, 3 H), 3.54–3.63 (m, 3 H), 3.84–3.90 (m, 1 H), 4.14–4.17 (m, 1 H), 4.26–4.36 (m, 3 H) ppm. ^{13}C NMR (100

MHz, DEPT, $CDCl_3$): δ = 11.0 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 31.6 (CH_3), 46.8 (CH_2), 48.0 (CH_2), 50.3 (CH_2), 53.2 (CH_2), 61.0 (CH_2), 62.2 (CH_2), 64.4 (C), 64.6 (C), 109.6 (C), 116.5 (C), 164.9 (C), 170.5 (C), 170.7 (C), 201.1 (C), 208.5 (CO) ppm. IR: ν = 2960 (w), 2931 (w), 2041 (s), 1959 (s), 1737 (s), 1667 (w), 1626 (m), 1534 (m), 1437 (w), 1387 (m), 1357 (m), 1331 (w), 1225 (s), 1039 (s), 958 (w), 718 (m), 645 (w), 606 (m), 578 (s), 552 (s) cm^{-1}. MS (EI): *m/z* (%): 504 [M^+] (18), 476 [M^+ - CO] (8), 448 [M^+ - 2 CO] (30), 420 [M^+ - 3 CO] (29), 392 (20), 377 (17), 364 [M^+ - $Fe(CO)_3$] (20), 306 (23), 87 (100). HRMS: [M^+] calcd.: 504.08312, found: 504.08316.

Preparation and characterization data of allenyl carbamates:

General catalytic procedure for allenyl carbamate formation: 3 mol-% of catalyst **2**–**4** were dissolved in 0.5 mL of toluene and 3 mol-% of $BF_3{\cdot}Et_2O$ diluted in toluene, 1 mmol of the propargyl alcohol and 1 mmol of the isocyanate were subsequently added. The mixture was stirred at 100 °C for 3 hours (**9m** 8 hours) or at r. t. for 3 days under argon. Evaporation of the solvent and chromatography on silica furnished the allenyl carbamates **9**.

9a ($C_{12}H_{13}N_1O_2$) 102 mg (50 %) yellow crystals: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (d, J = 2.0 Hz, 6 H), 6.79 (br, NH), 7.08 (tr, J = 7.3 Hz, 1 H), 7.23 (sept, J = 2.0 Hz), 7.31 (tr, J = 7.4 Hz, 2 H), 7.38 (d, J = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 22.0 (CH_3), 108.8 (CH), 112.1 (C), 120.6 (CH), 124.5 (CH), 129.1 (CH), 137.2 (C), 153.4 (C), 189.6 (C). IR: ν = 3307 (m), 3137 (w), 3062 (m), 2974 (m), 2925 (m), 2858 (w), 1981 (w), 1710 (s), 1599 (s), 1524 (s), 1501 (s), 1442 (s), 1313 (m), 1206 (s), 1153 (m), 1132 (m), 1071 (s), 1028 (m), 993 (m), 899 (w), 752 (s), 691 (s) cm^{-1}. MS (EI): *m/z* (%): 203 [M^+] (22), 119 (64), 91 (41), 84 (100), 83 (43). HRMS: [M^+] calcd.: 203.09463, found: 203.09451.

9b ($C_{13}H_{15}N_1O_2$) 94 mg (43 %) yellow crystals: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.82 (d, J = 2.0 Hz, 6 H), 4.39 (d, J = 6.1 Hz, 2 H), 7.20 (sept, J = 2.0 Hz, 1 H), 7.27–7.35 (m, 5 H). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 22.0 (CH_3), 45.1 (CH_2), 109.2 (CH), 111.7 (C), 127.5 (CH), 127.6 (CH), 128.7 (CH), 138.0 (C), 154.3 (C), 189.4 (C). IR: ν = 3330 (m), 3064 (w), 3032 (w), 2984 (w), 2927 (m), 2856 (w), 1985 (w), 1708 (s), 1519 (s), 1456 (m), 1365 (m), 1258 (s), 1233 (s), 1201 (m), 1133 (s), 1081 (m), 1043 (s), 987 (m), 934 (m), 794 (w), 737 (m), 699 (s), 610 (m) cm^{-1}. MS (EI): *m/z* (%): 217 [M^+] (17), 133 (20), 105 (18), 91 (100), 84 (55), 83 (18). HRMS: [M^+] calcd.: 217.11028, found: 217.11042.

9c ($C_{12}H_{19}N_1O_2$) 94 mg (45 %) yellow crystals: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12–1.41 (m, 4 H), 1.58–1.76 (m, 4 H), 1.82 (d, J = 2.1 Hz, 6 H), 1.91–1.96 (m, 2 H), 3.49–3.53 (m, 1 H), 4.73 (br, NH), 7.18 (sept, J = 2.0 Hz, 1 H). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 22.0 (CH_3), 24.6 (CH_2), 25.4 (CH_2), 33.2 (CH_2), 49.9 (CH), 109.0 (CH), 111.4 (C), 153.2 (C), 189.5 (C). IR: ν =

3320 (m), 3063 (w), 2930 (s), 2855 (m), 1980 (w), 1706 (s), 1660 (m), 1526 (s), 1450 (m), 1315 (m), 1274 (m), 1251 (m), 1224 (s), 1137 (s), 1058 (s), 965 (m), 931 (w), 891 (m), 767 (m), 732 (m) cm^{-1}. MS (EI): *m/z* (%): 209 [M^+] (18), 84 (100), 83 (56). HRMS: [M^+] calcd.: 209.14158, found: 209.14156.

9d ($C_9H_{13}N_1O_2$) 72 mg (43 %) yellow crystals: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.83 (d, J = 2.1, 6 H), 3.84 (trtr, J = 5.8, 1.5 Hz, 2 H), 4.93 (br, NH), 5.14 (dq, J = 10.3, 1.4 Hz, 1 H), 5.22 (dq, J = 17.2, 1.4 Hz, 1 H), 5.85 (ddtr, J = 17.2, 10.3, 5.5 Hz, 1 H), 7.18 (sept, J = 2.0 Hz, 1 H). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 22.0 (CH_3), 43.5 (CH_2), 109.1 (CH), 111.7 (C), 116.3 (CH_2), 134.1 (CH), 154.2 (C), 189.4 (C). IR: ν = 3331 (m), 3067 (w), 2985 (m), 2917 (m), 2862 (w), 1982 (w), 1709 (s), 1520 (s), 1461 (m), 1364 (w), 1230 (s), 1134 (s), 1074 (s), 1041 (s), 986 (s), 923 (s), 792 (m), 768 (m) cm^{-1}. MS (EI): *m/z* (%): 167 [M^+] (16), 97 (15), 84 (100), 83 (43). HRMS: [M^+] calcd.: 167.09463, found: 167.09482.

9e ($C_{13}H_{15}N_1O_2$) 140 mg (65 %) yellow crystals: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (tr, J = 7.4 Hz, 3 H),1.83 (d, J = 2.0 Hz, 3 H), 2.01–2.12 (m, 2 H), 6.95 (br, NH), 7.06 (tr, J = 7.4 Hz, 1 H), 7.29 (tr, J = 7.4 Hz, 2 H), 7.33 (sext, J = 2.1 Hz, 1 H), 7.38 (d, J = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 11.8 (CH_3), 20.5 (CH_3), 28.3 (CH_2), 110.8 (CH), 118.2 (C), 120.6 (CH), 123.7 (CH), 129.0 (CH), 137.3 (C), 151.2 (C), 188.6 (C). IR: ν = 3309 (m), 3137 (w), 3062 (w), 2968 (m), 2934 (m), 2877 (w), 1972 (w), 1711 (s), 1599 (s), 1535 (s), 1501 (m), 1441 (s), 1403 (m), 1313 (m), 1205 (s), 1181 (m), 1156 (m), 1111 (m), 1085 (s), 1047 (s), 1027 (s), 993 (m), 899 (w), 847 (m), 750 (s), 691 (s) cm^{-1}. MS (EI): *m/z* (%): 217 [M^+] (38), 119 (100), 98 (48), 93 (41), 91 (41), 83 (82). HRMS: [M^+] calcd.: 217.11028, found: 217.11017.

9f ($C_{14}H_{17}N_1O_2$) 170 mg (74 %) yellow crystals: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (tr, J = 7.4 Hz, 3 H), 1.81 (d, J = 2.0 Hz, 3 H), 1.98–2.15 (m, 2 H), 4.37 (d, J = 6.0 Hz, 2 H), 5.10 (br, NH), 7.25–7.32 (m, 5 H), 7.34 (sext, J = 1.9 Hz, 1 H). ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 11.8 (CH_3), 20.5 (CH_3), 28.3 (CH_2), 45.0 (CH_2), 111.2 (CH), 117.8 (C), 127.4 (CH), 127.5 (CH), 128.6 (CH), 138.0 (C), 154.3 (C), 188.4 (C). IR: ν = 3296 (m), 3068 (m), 3029 (w), 2965 (m), 2933 (w), 2900 (w), 2843 (w), 1974 (m), 1720 (m), 1688 (s), 1547 (s), 1493 (w), 1452 (m), 1406 (w), 1362 (w), 1266 (s), 1243 (s), 1206 (m), 1132 (s), 1082 (w), 1068 (w), 999 (s), 943 (w), 910 (m), 816 (m), 770 (m), 752 (m), 695 (s), 673 (s), 610 (m) cm^{-1}. MS (EI): *m/z* (%): 231 [M^+] (32), 98 (55), 91 (100), 83 (96). HRMS: [M^+] calcd.: 231.12593, found: 231.12571.

9g ($C_{13}H_{21}N_1O_2$) 108 mg (48 %) yellow crystals: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (tr, J = 7.3 Hz, 3 H), 1.11–1.43 (m, 4 H), 1.59–1.77 (m, 4 H), 1.82 (d, J = 2.0 Hz, 3 H), 1.90–1.96 (m, 2 H), 2.01–2.14 (m, 2 H), 3.46–3.57 (m, 1 H), 4.74 (br, NH), 7.28 (sext, J = 2.1 Hz, 1 H). ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 11.9 (CH_3), 20.6 (CH_3), 24.6 (CH_2), 25.4 (CH_2), 28.3 (CH_2),

33.2 (CH_2), 49.9 (CH), 111.1 (CH), 117.7 (C), 153.3 (C), 188.3 (C). IR: ν = 3302 (m), 3061 (w), 2930 (m), 2854 (m), 1969 (w), 1696 (s), 1542 (s), 1449 (m), 1371 (w), 1312 (m), 1275 (m), 1250 (m), 1228 (s), 1144 (m), 1074 (m), 1043 (s), 994 (m), 968 (m), 893 (m), 805 (m), 765 (m), 664 (s) cm^{-1}. MS (EI): *m/z* (%): 223 [M^+] (19), 98 (33), 97 (28), 83 (100). HRMS: [M^+] calcd.: 223.15723, found: 223.15722.

9h ($C_{10}H_{15}N_1O_2$) 125 mg (69 %) yellow crystals: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (tr, J = 7.4 Hz, 3 H), 1.83 (d, J = 2.0 Hz, 3 H), 2.01–2.14 (m, 2 H), 3.84 (trtr, J = 5.8, 1.5 Hz, 2 H), 4.97 (br, NH), 5.14 (dq, J = 10.3, 1.4 Hz, 1 H), 5.22 (dq, J = 17.2, 1.4 Hz, 1 H), 5.85 (ddtr, J = 17.2, 10.3, 5.5 Hz, 1 H), 7.29 (sext, J = 2.1 Hz, 1 H). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 11.9 (CH_3), 20.6 (CH_3), 28.3 (CH_2), 43.4 (CH_2), 111.2 (CH), 116.3 (CH_2), 117.9 (C), 134.1 (CH), 154.1 (C), 188.4 (C). IR: ν = 3313 (m), 3061 (m), 2969 (m), 2932 (m), 2901 (m), 2876 (w), 1974 (m), 1704 (s), 1543 (s), 1454 (m), 1260 (s), 1237 (s), 1135 (s), 1084 (m), 1004 (s), 919 (m), 806 (m), 766 (m), 615 (s) cm^{-1}. MS (EI): *m/z* (%): 181 [M^+] (23), 98 (44), 83 (100). HRMS: [M^+] calcd.: 181.11028, found: 181.11015.

9i ($C_{15}H_{17}N_1O_2$) 150 mg (62 %) yellow crystals: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56–1.66 (m, 6 H), 2.22–2.28 (m, 4 H), 6.81 (br, NH), 7.08 (tr, J = 7.3 Hz, 1 H), 7.24 (br, 1 H), 7.31 (tr, J = 7.5 Hz, 2 H), 7.39 (d, J = 7.9 Hz, 2 H).^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 25.8 (CH_2), 27.2 (CH_2), 32.7 (CH_2), 108.5 (CH), 118.8 (C), 119.2 (CH), 123.8 (CH), 129.1 (CH), 137.3 (C), 151.2 (C), 186.2 (C). IR: ν = 3315 (m), 3135 (w), 3064 (w), 2926 (m), 2855 (m), 1968 (w),1728 (m), 1706 (s), 1598 (m), 1537 (s), 1499 (m), 1442 (m), 1414 (m), 1315 (m), 1218 (s), 1118 (w), 1094 (m), 1044 (s), 1022 (m), 996 (m), 849 (w), 752 (s), 716 (m) cm^{-1}. MS (EI): *m/z* (%): 243 [M^+] (36), 124 (100), 119 (88), 109 (63), 95 (58), 93 (45), 91 (79), 81 (79). HRMS: [M^+] calcd.: 243.12593, found: 243.12586.

9j ($C_{16}H_{19}N_1O_2$) 175 mg (68 %) yellow crystals: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51–1.71 (m, 6 H), 2.19–2.23 (m, 4 H), 4.38 (d, J = 6.0 Hz, 2 H), 5.21 (br, NH), 7.20 (br, 1 H), 7.26–7.35 (m, 5 H). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 25.8 (CH_2), 27.2 (CH_2), 32.8 (CH_2), 45.1 (CH_2), 108.8 (CH), 118.7 (C), 127.4 (CH), 127.5 (CH), 128.6 (CH), 138.0 (C), 154.3 (C), 186.0 (C). IR: ν = 3304 (m), 3057 (w), 3033 (w), 2924 (m), 2852 (m), 1970 (w), 1699 (s), 1530 (s), 1435 (m), 1414 (m), 1367 (m), 1269 (m), 1230 (s), 1189 (m), 1135 (s), 1085 (w), 1043 (s), 998 (s), 971 (m), 894 (w), 851 (w), 804 (m), 768 (m), 750 (s), 696 (s), 645 (s) cm^{-1}. MS (EI): *m/z* (%): 257 [M^+] (20), 124 (65), 91 (100). HRMS: [M^+] calcd.: 257.14158, found: 257.14149.

9k ($C_{15}H_{23}N_1O_2$) 146 mg (59 %) yellow crystals: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09–1.39 (m, 4 H), 1.55–1.73 (m, 10 H), 1.91–1.96 (m, 2 H), 2.19–2.23 (m, 4 H), 3.46–3.57 (m, 1 H), 4.77 (br, NH), 7.18 (br, 1 H). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 24.6 (CH_2), 25.4 (CH_2), 25.8

(CH_2), 27.2 (CH_2), 32.8 (CH_2), 33.2 (CH_2), 49.8 (CH), 108.7 (CH), 118.4 (C), 153.3 (C), 185.9 (C). IR: ν = 3320 (m), 3054 (w), 2929 (s), 2854 (m), 1971 (w), 1698 (s), 1538 (s), 1447 (m), 1418 (w), 1313 (m), 1279 (m), 1249 (m), 1227 (s), 1189 (m), 1143 (m), 1089 (m), 1043 (s), 994 (m), 967 (m), 892 (m), 849 (m), 805 (m), 766 (m), 651 (s) cm^{-1}. MS (EI): *m/z* (%): 249 [M^+] (31), 124 (100), 109 (69), 95 (72). HRMS: [M^+] calcd.: 249.17288, found: 249.17290.

9l ($C_{12}H_{17}N_1O_2$) 147 mg (71 %) yellow crystals: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52–1.68 (m, 6 H), 2.19–2.23 (m, 4 H), 3.84 (trtr, J = 5.6, 1.6 Hz, 2 H), 5.03 (br, NH), 5.14 (dq, J = 10.3, 1.4 Hz, 1 H), 5.22 (dq, J = 17.2, 1.4 Hz, 1 H), 5.85 (ddtr, J = 17.2, 10.3, 5.5 Hz, 1 H), 7.18 (br, 1 H). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ = 25.8 (CH_2), 27.2 (CH_2), 32.8 (CH_2), 43.4 (CH_2), 108.8 (CH), 116.2 (CH_2), 118.6 (C), 134.1 (CH), 154.1 (C), 186.0 (C). IR: ν = 3336 (m), 3062 (w), 2941 (m), 2925 (m), 2856 (m), 1971 (w), 1702 (s), 1541 (s), 1436 (m), 1418 (m), 1281 (s), 1233 (s), 1189 (s), 1139 (s), 1093 (m), 1012 (s), 913 (s), 851 (m), 809 (s), 765 (m), 600 (s) cm^{-1}. MS (EI): *m/z* (%): 207 [M^+] (38), 124 (100), 109 (68), 95 (75). HRMS: [M^+] calcd.: 207.12593, found: 207.12591.

9m ($C_{11}H_{11}N_1O_2$) 95 mg (50 %) yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.77 (dd, J = 7.1, 2.3 Hz, 3 H), 5.81 (qd, J = 7.1, 5.7 Hz, 1 H), 6.99–7.09 (m, 3 H), 7.26 (tr, J = 7.4 Hz, 2 H), 7.38 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 16.5 (CH_3), 101.9 (CH), 111.5 (CH), 119.5 (CH), 124.3 (CH), 129.5 (CH), 137.8 (C), 151.7 (C), 194.9 (C). IR: ν = 3298 (m), 3138 (w), 3063 (w), 2990 (w), 2940 (w), 1980 (w), 1705 (s), 1599 (m), 1528 (s), 1501 (s), 1443 (s), 1314 (m), 1211 (s), 1158 (w), 1115 (m), 1090 (s), 1048 (s), 1027 (s), 905 (w), 857 (w), 750 (s), 734 (s) 690 (s) cm^{-1}. MS (EI): *m/z* (%): 189 [M^+] (100), 119 (33), 93 (58), 70 (31). HRMS: [M^+] calcd.: 189.07898, found: 189.07869.