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Supporting Information

Efficient Tandem Process for the Catalytic Deprotection of *N*-Allyl Amides and Lactams in Aqueous Media: A Novel Application of the Bis(allyl)-Ruthenium(IV) Catalysts [Ru(η³:η²:η³-$C_{12}H_{18}$)Cl_2] and [{Ru(η³:η³-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$]

Victorio Cadierno,* José Gimeno,* Noel Nebra

Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Facultad de Química, Universidad de Oviedo, Julián Clavería 8, E-33006 Oviedo, Spain

PREPARATION OF THE STARTING MATERIALS

General methods: Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H), or 75.4 MHz (^{13}C) or a Bruker AC-400 instrument at 400.1 MHz (^{1}H), or 100.6 MHz (^{13}C). Chemical shifts are referred to the residual peak of the deuterated solvent used ($CDCl_3$). DEPT experiments have been carried out for all the compounds reported. GC/MS measurements were performed on a Agilent 6890N equipment coupled to a 5973 mass detector (70eV electron impact ionization) using a HP-1MS column. High-resolution mass spectra were recorded on a Finnigan-Mat 95 spectrometer. Flash chromatography was performed using Merck silica gel 60 (230-400 mesh). Compounds 3a,[1] 3c,[2] 3d,[2] 3e,[1] 3g,[3] 3i,[4] 3j,[5] 4a,[6] 4d,[7] 4f,[8] 4g,[9] 5a,[10] 5g,[2] 5h,[11] 5j,[12] 5k,[13] 5l,[14] 6a,[15] 6b,[16] 6c,[15] 6f,[17] and 7[18] were prepared by following the methods reported in the literature.

Synthesis of *N*-allyl amides 3b,f,h,k: To a solution of the appropriate acid chloride (5 mmol) in 50 mL of toluene was added allylamine (0.750 mL, 10 mmol) at 0ºC. The reaction mixture was allowed to stir for 12 h at room temperature, and then filtered to remove the solid precipitate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography on silica gel using a 25% ethyl acetate/hexanes mixture as eluent. Spectroscopic data are as follows:

***N*-Allyl-2-fluorobenzamide (3b): Pale-yellow oil; yield: 0.833 g (93%); IR (Nujol): *n* = 1646 (s, C=O), 3346 (s, N-H) cm^{-1}; ^{1}H NMR ($CDCl_3$): *d* = 4.07 (m, 2H, NCH_2), 5.12-5.26 (m, 2H, $=CH_2$), 5.90 (m, 1H, =CH), 6.84 (br, 1H, NH), 7.07, 7.23, 7.42 and 8.04 (m, 1H each, C_6H_4F); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): *d* = 41.9 (s, NCH_2), 115.6 (d, *J* = 24.9 Hz, CH of C_6H_4F), 116.0 (s, $=CH_2$), 120.6 (d, *J* = 11.7 Hz, C of C_6H_4F), 124.4 (d, *J* = 2.9 Hz, CH of C_6H_4F), 131.6 (s, =CH), 132.8 (d, *J* = 8.8 Hz, CH of C_6H_4F), 133.5 (s, CH of C_6H_4F), 160.2 (d, *J* = 247.3 Hz, C of C_6H_4F), 162.8 (s, C=O); MS (EI 70eV): *m/z* (%) = 179 (10) [M^+], 165 (20) [M^+-CH_2], 123 (100) [M^+-$NHCH_2CH=CH_2$], 95 (20) [M^+-$CONHCH_2CH=CH_2$], 75 (10) [M^+-F- $CONHCH_2CH=CH_2$]; HR-MS: *m/z* = 179.07420, calcd. for $C_{10}H_{10}FNO$: 179.07409.**

***N*-Allyl-3-methoxybenzamide (3f): Colourless oil; yield: 0.841 g (88%); IR (Nujol): *n* = 1641 (s, C=O), 3313 (s, N-H) cm^{-1}; ^{1}H NMR ($CDCl_3$): *d* = 3.79 (s, 3H, OCH_3), 4.05 (m, 2H, NCH_2), 5.12-5.24 (m, 2H, $=CH_2$), 5.88 (m, 1H, =CH), 6.56 (br, 1H, NH), 6.99 (m, 1H, C_6H_4OMe), 7.26-7.36 (m, 3H, C_6H_4OMe); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): *d* = 42.1 (s, NCH_2), 55.0 (s, OCH_3), 112.0, 117.3, 118.4 and 129.1 (s, CH of C_6H_4OMe), 116.2 (s, $=CH_2$), 133.8 (s, =CH), 135.6 and 159.4 (s, C of C_6H_4OMe), 166.9 (s, C=O); MS (EI 70eV): *m/z* (%) = 191 (20) [M^+], 176 (5) [M^+-Me], 135 (100) [M^+-$NHCH_2CH=CH_2$], 107 (25) [M^+-$CONHCH_2CH=CH_2$], 92 (10) [M^+-Me-$CONHCH_2CH=CH_2$]; HR-MS: *m/z* = 191.09347, calcd. for $C_{11}H_{13}O_2N$: 191.09408.**

***N*-Allyl-hexanamide (3h): Colourless oil; yield: 0.698 g (90%); IR (Nujol): *n* = 1644 (s, C=O), 3289 (s, N-H) cm^{-1}; ^{1}H NMR ($CDCl_3$): *d* = 0.88 (t, *J* = 6.5 Hz, 3H, CH_3), 1.30 (m, 4H, CH_2), 1.64 (m, 2H, CH_2), 2.18 (t, *J* = 7.7 Hz, 2H, CH_2CO), 3.87 (m, 2H, NCH_2), 5.12 (m, 2H, $=CH_2$),**

5.77 (m, 2H, =CH and NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 13.8 (s, CH_3), 22.3, 25.4, 31.4 and 36.7 (s, CH_2), 41.8 (s, NCH_2), 116.1 (s, $=CH_2$), 134.3 (s, =CH), 173.0 (s, C=O); MS (EI 70eV): *m/z* (%) = 155 (2) [M^+], 140 (2) [M^+-Me], 126 (10) [M^+-Et], 112 (10) [M^+-*n*Pr], 99 (100) [M^+-$NHCH_2CH=CH_2$], 84 (30) [M^+-*n*Pent], 71 (10) [M^+-$CONHCH_2CH=CH_2$], 57 (70) [M^+-*n*Pent-$CH=CH_2$]; HR-MS: *m/z* = 155.13016, calcd. for $C_9H_{17}NO$: 155.13046.

***N*-Allyl-cyclopentanepropanamide (3k): Colourless oil; yield: 0.761 g (84%); IR (Nujol): *n* = 1645 (s, C=O), 3286 (s, N-H) cm^{-1}; ^1H NMR ($CDCl_3$): *d* = 1.05 (m, 2H, CH_2), 1.45-1.71 (m, 9H, CH_2 and CH), 2.17 (t, *J* = 7.8 Hz, 2H, CH_2CO), 3.81 (m, 2H, NCH_2), 5.08 (m, 2H, $=CH_2$), 5.79 (m, 1H, =CH), 6.02 (br, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 24.7, 31.6, 32.1 and 35.6 (s, CH_2), 39.4 (s, CH), 41.5 (s, NCH_2), 115.7 (s, $=CH_2$), 134.0 (s, =CH), 172.9 (s, C=O); MS (EI 70eV): *m/z* (%) = 181 (2) [M^+], 125 (5) [M^+-$NHCH_2CH=CH_2$], 112 (40) [M^+-C_5H_9], 99 (100) [M^+-$CH_2C_5H_9$], 84 (20) [M^+-$CH_2CH_2C_5H_9$], 57 (40) [M^+-$COCH_2CH_2C_5H_9$]; HR-MS: *m/z* = 181.14639, calcd. for $C_{11}H_{19}NO$: 181.14666.**

Synthesis of *N*-allyl amides 4b,c,e,h: To a solution of the appropriate *NH*-amide (5 mmol) and allyl bromide (0.606 mL, 7 mmol) in 50 mL of acetonitrile was added NaOH (0.280 g, 7 mmol) at room temperature. The reaction mixture was allowed to stir for 20 h, and then filtered to remove the solid precipitate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography on silica gel using a 25% ethyl acetate/hexanes mixture as eluent. Spectroscopic data are as follows:

***N*-Allyl-*N*-methyl-hexanamide (4b): Colourless oil; yield: 0.803 g (95%); IR (Nujol): ν = 1661 (s, C=O) cm^{-1}; MS (EI 70eV): *m/z* (%) = 169 (5) [M^+], 154 (10) [M^+-Me], 140 (15) [M^+-Et], 126 (60) [M^+-*n*Pr], 112 (50) [M^+-*n*Bu], 98 (100) [M^+-*n*Pent], 70 (100) [M^+-CO-*n*Pent]; HR-MS: *m/z* = 169.14666, calcd. for $C_{10}H_{19}NO$: 169.14681; Two rotamers are observed in solution.[19] *NMR data for the major rotamer:* ^{1}H NMR ($CDCl_3$): δ = 0.74 (br, 3H, CH_3), 1.17 (m, 4H, CH_2), 1.49 (m, 2H, CH_2), 2.15 (m, 2H, CH_2CO), 2.80 (s, 3H, NCH_3), 3.77 (br, 2H, NCH_2), 4.99 (m, 2H, $=CH_2$), 5.63 (m, 1H, =CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.7 (s, CH_3), 22.3, 24.6, 31.4 and 33.3 (s, CH_2), 34.5 (s, NCH_3), 51.9 (s, NCH_2), 116.7 (s, $=CH_2$), 132.5 (s, =CH), 172.7 (s, C=O); *NMR data for the minor rotamer:* ^{1}H NMR ($CDCl_3$): δ = 0.74 (br, 3H, CH_3), 1.17 (m, 4H, CH_2), 1.49 (m, 2H, CH_2), 2.15 (m, 2H, CH_2CO), 2.76 (s, 3H, NCH_3), 3.84 (br, 2H, NCH_2), 4.99 (m, 2H, $=CH_2$), 5.63 (m, 1H, =CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.7 (s, CH_3), 22.3, 24.9, 31.4 and 32.6 (s, CH_2), 34.5 (s, NCH_3), 49.7 (s, NCH_2), 116.2 (s, $=CH_2$), 133.0 (s, =CH), 173.2 (s, C=O).**

***N*-Allyl-*N*-methyl-cyclopentanepropanamide (4c): Colourless oil; yield: 0.791 g (81%); IR (Nujol): ν = 1651 (s, C=O) cm^{-1}; MS (EI 70eV): *m/z* (%) = 195 (2) [M^+], 180 (2) [M^+-Me], 126 (70) [M^+-C_5H_9], 113 (70) [M^+-$CH_2C_5H_9$], 98 (100) [M^+-$CH_2CH_2C_5H_9$], 70 (60) [M^+-$COCH_2CH_2C_5H_9$], 55 (50) [M^+-Me-$COCH_2CH_2C_5H_9$]; HR-MS: *m/z* = 195.16231, calcd. for $C_{12}H_{21}NO$: 195.16263; Two rotamers are observed in solution.[19] *NMR data for the major rotamer:* ^{1}H NMR ($CDCl_3$): δ = 1.05 (m, 2H, CH_2), 1.46-1.72 (m, 9H, CH_2 and CH), 2.27 (m, 2H, CH_2CO), 2.90 (s, 3H, NCH_3), 3.86 (m, 2H, NCH_2), 5.09 (m, 2H, $=CH_2$), 5.70 (m, 1H, =CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.0, 31.5, 32.1 and 32.4 (s, CH_2), 33.5 (s, NCH_3), 39.7 (s, CH), 49.8 (s, NCH_2), 116.4 (s, $=CH_2$), 132.6 (s, =CH), 173.1 (s, C=O); *NMR data for the minor rotamer:* ^{1}H NMR ($CDCl_3$): δ =**

1.05 (m, 2H, CH_2), 1.46-1.72 (m, 9H, CH_2 and CH), 2.27 (m, 2H, CH_2CO), 2.86 (s, 3H, NCH_3), 3.94 (m, 2H, NCH_2), 5.09 (m, 2H, $=CH_2$), 5.70 (m, 1H, =CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 25.0, 31.2, 32.4 and 32.7 (s, CH_2), 34.7 (s, NCH_3), 39.7 (s, CH), 52.1 (s, NCH_2), 116.9 (s, $=CH_2$), 132.9 (s, =CH), 173.6 (s, C=O).

***N*-Allyl-*N*-methyl-2-methoxybenzamide (4e): Colourless oil; yield: 0.903 g (88%); IR (Nujol): *n* = 1651 (s, C=O) cm^{-1}; MS (EI 70eV): *m/z* (%) = 205 (10) [M^+], 174 (10) [M^+-OMe], 135 (100) [M^+-$NMeCH_2CH=CH_2$], 70 (15) [M^+-COC_6H_4OMe]; HR-MS: *m/z* = 205.11021, calcd. for $C_{12}H_{15}O_2N$: 205.10973; Two rotamers are observed in solution.[19] *NMR data for the major rotamer:* ^1H NMR ($CDCl_3$): *d* = 3.00 (s, 3H, NCH_3), 3.66 (br, 2H, NCH_2), 3.76 (s, 3H, OCH_3), 5.05-5.26 (m, 2H, $=CH_2$), 5.62 (m, 1H, =CH), 6.84-6.96 and 7.14-7.31 (m, 2H each, C_6H_4OMe); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 35.6 (s, NCH_3), 53.5 (s, NCH_2), 55.4 (s, OCH_3), 110.8, 120.6, 127.5 and 130.2 (s, CH of C_6H_4OMe), 117.5 (s, $=CH_2$), 125.9 and 155.1 (s, C of C_6H_4OMe), 133.2 (s, =CH), 169.5 (s, C=O); *NMR data for the minor rotamer:* ^1H NMR ($CDCl_3$): *d* = 2.73 (s, 3H, NCH_3), 3.78 (s, 3H, OCH_3), 4.13 (br, 2H, NCH_2), 5.05-5.26 (m, 2H, $=CH_2$), 5.79 (m, 1H, =CH), 6.84-6.96 and 7.14-7.31 (m, 2H each, C_6H_4OMe); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 32.1 (s, NCH_3), 49.2 (s, NCH_2), 55.4 (s, OCH_3), 110.8, 120.8, 127.7 and 130.2 (s, CH of C_6H_4OMe), 116.8 (s, $=CH_2$), 126.2 and 155.1 (s, C of C_6H_4OMe), 132.5 (s, =CH), 169.1 (s, C=O).**

2-[Allyl(2-fluorobenzoyl)amino]-benzoic acid ethyl ester (4h): Yellow oil; yield: 1.293 g (79%); IR (Nujol): *n* = 1652 and 1721 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$): *d* = 1.36 (t, *J* = 7.2 Hz, 3H, CH_3), 3.90 (m, 2H, NCH_2), 4.32 (q, *J* = 7.2 Hz, 2H, OCH_2), 5.13 (m, 2H, $=CH_2$), 5.97 (m,

1H, =CH), 6.70-7.73 (m, 8H, C_6H_4F and $C_6H_4CO_2Et$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 13.8 (s, CH_3), 52.4 (s, NCH_2), 61.1 (s, OCH_2), 117.9 (s, $=CH_2$), 115.6 (d, *J* = 21.6 Hz, CH of C_6H_4F), 123.3 (d, *J* = 2.4 Hz, CH of C_6H_4F), 124.6 (d, *J* = 17.5 Hz, C of C_6H_4F), 127.6, 130.4, 131.0 and 132.2 (s, CH of $C_6H_4CO_2Et$), 128.4 (d, *J* = 2.9 Hz, CH of C_6H_4F), 129.8 and 141.1 (s, C of $C_6H_4CO_2Et$), 130.6 (d, *J* = 8.1 Hz, CH of C_6H_4F), 132.5 (s, =CH), 157.5 (d, *J* = 248.4 Hz, C of C_6H_4F), 165.0 and 165.5 (s, C=O); MS (EI 70eV): *m/z* (%) = 327 (2) [M^+], 282 (10) [M^+-Et], 254 (10) [M^+-CO_2Et], 204 (100) [M^+-COC_6H_4F], 158 (100) [M^+-CO_2Et-C_6H_4F], 123 (90) [M^+-$N(CH_2CH=CH_2)C_6H_4CO_2Et$], 95 (30) [$M^+$-$CON(CH_2CH=CH_2)C_6H_4CO_2Et$]; HR-MS: *m/z* = 327.12617, calcd. for $C_{19}H_{18}O_3FN$: 327.12652.

Synthesis of *N*,*N*-diallyl amides 5b,c,d,e,f,i: To a solution of the appropriate acid chloride (5 mmol) in 50 mL of toluene was added diallylamine (1.234 mL, 10 mmol) at 0ºC. The reaction mixture was allowed to stir for 12 h at room temperature, and then filtered to remove the solid precipitate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography on silica gel using a 25% ethyl acetate/hexanes mixture as eluent. Spectroscopic data are as follows:

***N*,*N*-Diallyl-2-fluorobenzamide (5b): Pale-yellow oil; yield: 0.932 g (85%); IR (Nujol): *n* = 1655 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$): *d* = 3.72 and 4.12 (br, 2H each, NCH_2), 5.03-5.22 (m, 4H, $=CH_2$), 5.61 and 5.80 (m, 1H each, =CH), 7.09 and 7.30 (m, 2H each, C_6H_4F); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 46.1 and 50.3 (s, NCH_2), 115.4 (d, *J* = 21.2 Hz, CH of C_6H_4F), 117.1 and 117.7 (s, $=CH_2$), 124.1 and 128.1 (s, CH of C_6H_4F),**

124.3 (br, C of C_6H_4F), 130.6 (d, *J* = 8.0 Hz, CH of C_6H_4F), 131.9 and 132.5 (s, =CH), 157.7 (d, *J* = 247.4 Hz, C of C_6H_4F), 166.3 (s, C=O); MS (EI 70eV): *m/z* (%) = 219 (5) [M^+], 178 (15) [M^+-$CH_2CH=CH_2$], 123 (100) [M^+-$N(CH_2CH=CH_2)_2$], 95 (25) [M^+-$CON(CH_2CH=CH_2)_2$], 75 (5) [M^+-F-$CON(CH_2CH=CH_2)_2$]; HR-MS: *m/z* = 218.09742 (M^+-H), calcd. for $C_{13}H_{13}FNO$: 218.09756.

***N*,*N*-Diallyl-3-fluorobenzamide (5c): Pale-yellow oil; yield: 0.953 g (87%); IR (Nujol): *n* = 1652 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$): *d* = 3.79 and 4.09 (br, 2H each, NCH_2), 5.20 (m, 4H, $=CH_2$), 5.69 and 5.80 (br, 1H each, =CH), 7.04-7.20 (m, 3H, C_6H_4F), 7.33 (m, 1H, C_6H_4F); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 46.9 and 50.5 (s, NCH_2), 113.8 (d, *J* = 22.7 Hz, CH of C_6H_4F), 116.6 (d, *J* = 20.9 Hz, CH of C_6H_4F), 117.7 (s, $=CH_2$), 122.1 (s, CH of C_6H_4F), 130.1 (d, *J* = 7.6 Hz, CH of C_6H_4F), 132.4 and 132.8 (s, =CH), 138.0 (d, *J* = 1.3 Hz, C of C_6H_4F), 162.3 (d, *J* = 247.5 Hz, C of C_6H_4F), 170.2 (s, C=O); MS (EI 70eV): *m/z* (%) = 219 (10) [M^+], 178 (15) [M^+-$CH_2CH=CH_2$], 123 (100) [M^+-$N(CH_2CH=CH_2)_2$], 95 (30) [M^+-$CON(CH_2CH=CH_2)_2$], 75 (5) [M^+-F-$CON(CH_2CH=CH_2)_2$]; HR-MS: *m/z* = 218.09755 (M^+-H), calcd. for $C_{13}H_{13}FNO$: 218.09756.**

***N*,*N*-Diallyl-4-fluorobenzamide (5d): Pale-yellow oil; yield: 1.019 g (93%); IR (Nujol): *n* = 1639 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$): *d* = 3.82 and 4.09 (br, 2H each, NCH_2), 5.19 (m, 4H, $=CH_2$), 5.79 (br, 2H, =CH), 7.05 and 7.43 (m, 2H each, C_6H_4F); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 47.1 and 50.6 (s, NCH_2), 115.3 (d, *J* = 21.5 Hz, CH of C_6H_4F), 117.6 (s, $=CH_2$), 128.8 (d, *J* = 8.1 Hz, CH of C_6H_4F), 132.1 (s, C of C_6H_4F), 132.6 and 132.9 (s, =CH), 163.3 (d, *J* = 249.2 Hz, C of C_6H_4F), 170.7 (s, C=O); MS (EI 70eV): *m/z* (%) = 219 (5) [M^+], 178 (10) [M^+-$CH_2CH=CH_2$], 123 (100) [M^+-$N(CH_2CH=CH_2)_2$], 95 (25) [M^+-$CON(CH_2CH=CH_2)_2$], 75 (5)**

[M^+-F-CON($CH_2CH=CH_2$)$_2$]; HR-MS: *m/z* = 218.09731 (M^+-H), calcd. for $C_{13}H_{13}FNO$: 218.09756.

***N*,*N*-Diallyl-2-methoxybenzamide (5e): Colourless oil; yield: 1.016 g (88%); IR (Nujol): *n* = 1649 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): *d* = 3.68 and 4.13 (m, 2H each, NCH_2), 3.80 (s, 3H, OCH_3), 5.02-5.28 (m, 4H, $=CH_2$), 5.61 and 5.83 (m, 1H each, =CH), 6.87-6.96 (m, 2H, C_6H_4OMe), 7.18-7.34 (m, 2H, C_6H_4OMe); ^{13}C{^{1}H} NMR ($CDCl_3$): *d* = 45.9 and 50.5 (s, NCH_2), 55.4 (s, OCH_3), 110.8, 120.7, 127.5 and 130.2 (s, CH of C_6H_4OMe), 116.7 and 117.5 (s, $=CH_2$), 126.0 and 155.0 (s, C of C_6H_4OMe), 132.6 and 133.4 (s, =CH), 169.2 (s, C=O); MS (EI 70eV): *m/z* (%) = 231 (5) [M^+], 190 (10) [M^+-$CH_2CH=CH_2$], 135 (100) [M^+-N($CH_2CH=CH_2$)$_2$], 92 (10) [M^+-Me-CON($CH_2CH=CH_2$)$_2$], 77 (20) [M^+-OMe-CON($CH_2CH=CH_2$)$_2$]; HR-MS: *m/z* = 230.11765 (M^+-H), calcd. for $C_{14}H_{16}O_2N$: 230.11755.**

***N*,*N*-Diallyl-3-methoxybenzamide (5f): Colourless oil; yield: 0.958 g (83%); IR (Nujol): *n* = 1643 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): *d* = 3.77 (s, 3H, OCH_3), 3.80 and 4.09 (m, 2H each, NCH_2), 5.13-5.22 (m, 4H, $=CH_2$), 5.71-5.83 (m, 2H =CH), 6.94 (m, 3H, C_6H_4OMe), 7.25 (m, 1H, C_6H_4OMe); ^{13}C{^{1}H} NMR ($CDCl_3$): *d* = 46.8 and 50.6 (s, NCH_2), 55.2 (s, OCH_3), 111.7, 115.5, 118.5 and 129.4 (s, CH of C_6H_4OMe), 117.5 (s, $=CH_2$), 132.6 and 133.2 (s, =CH), 137.4 and 159.4 (s, C of C_6H_4OMe), 171.4 (s, C=O); MS (EI 70eV): *m/z* (%) = 231 (10) [M^+], 190 (10) [M^+-$CH_2CH=CH_2$], 135 (100) [M^+-N($CH_2CH=CH_2$)$_2$], 107 (20) [M^+-CON($CH_2CH=CH_2$)$_2$], 92 (10) [M^+-Me-CON($CH_2CH=CH_2$)$_2$], 77 (10) [M^+-OMe-CON($CH_2CH=CH_2$)$_2$]; HR-MS: *m/z* = 230.11725 (M^+-H), calcd. for $C_{14}H_{16}O_2N$: 230.11755.**

***N,N*-Diallyl-hexanamide (5i): Colourless oil; yield: 0.887 g (91%); IR (Nujol): n = 1656 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): d = 0.87 (t, J = 6.3 Hz, 3H, CH_3), 1.29 (m, 4H, CH_2), 1.62 (m, 2H, CH_2), 2.28 (t, J = 7.1 Hz, 2H, CH_2CO), 3.85 (d, J = 2.8 Hz, 2H, NCH_2), 3.96 (d, J = 5.7 Hz, 2H, NCH_2), 5.06-5.19 (m, 4H, $=CH_2$), 5.69-8.20 (m, 2H, =CH); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): d = 13.9 (s, CH_3), 22.4, 24.9, 31.5 and 32.9 (s, CH_2), 47.7 and 49.0 (s, NCH_2), 116.4 and 116.9 (s, $=CH_2$), 132.9 and 133.4 (s, =CH), 173.1 (s, C=O); MS (EI 70eV): *m/z* (%) = 195 (5) [M^+], 180 (5) [M^+-Me], 166 (10) [M^+-Et], 152 (40) [M^+-*n*Pr], 139 (40) [M^+-*n*Bu], 124 (30) [M^+-*n*Pent], 96 (20) [M^+-*n*PentCO], 82 (40) [M^+-*n*PentCO-$CH_2CH=CH_2$], 70 (40) [M^+-$CON(CH_2CH=CH_2)_2$]; HR-MS: *m/z* = 195.16183, calcd. for $C_{12}H_{21}NO$: 195.16176.**

Synthesis of *N*-allyl lactams 6d-e: To a solution of the appropriate *NH*-lactam (5 mmol) and allyl bromide (0.606 mL, 7 mmol) in 50 mL of acetonitrile was added NaOH (0.280 g, 7 mmol) at room temperature. The reaction mixture was allowed to stir for 20 h, and then filtered to remove the solid precipitate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography on silica gel using a 25% ethyl acetate/hexanes mixture as eluent. Spectroscopic data are as follows:

***N*-Allyl-2-azocanone (6d): Colourless oil; yield: 0.753 g (90%); IR (Nujol): n = 1642 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): d = 1.36-1.76 (m, 8H, CH_2), 2.44 (m, 2H, CH_2CO), 3.38 (m, 2H, NCH_2), 3.89 (d, J = 6.0 Hz, 2H, NCH_2), 5.04-5.11 (m, 2H, $=CH_2$), 5.73 (m, 1H, =CH); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): d = 24.2, 26.1, 28.6, 28.8 and 33.6 (s, CH_2), 46.0 and 47.3 (s, NCH_2), 117.0 (s, $=CH_2$), 133.5 (s, =CH), 174.6 (s, C=O); MS (EI**

70eV): *m/z* (%) = 168 (2) [M^+], 153 (5) [M^+-CH_2], 140 (5) [M^+-$CH{=}CH_2$], 126 (5) [M^+-$CH_2CH{=}CH_2$], 112 (30) [M^+-$NCH_2CH{=}CH_2$], 99 (100) [M^+-$CH_2NCH_2CH{=}CH_2$], 84 (30) [M^+-$CH_2CH_2NCH_2CH{=}CH_2$], 57 (80) [M^+-$CH_2CH_2CH_2CH_2NCH_2CH{=}CH_2$]; HR-MS: *m/z* = 167.13064, calcd. for $C_{10}H_{17}NO$: 167.13046.

***N*-Allyl-caprylolactam (6e):** Colourless oil; yield: 0.788 g (87%); IR (Nujol): *n* = 1639 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$): *d* = 1.45-1.82 (m, 10H, CH_2), 2.49 (m, 2H, CH_2CO), 3.44 (m, 2H, NCH_2), 3.95 (d, *J* = 5.9 Hz, 2H, NCH_2), 5.14 (m, 2H, $=CH_2$), 5.76 (m, 1H, =CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): *d* = 22.0, 24.7, 25.5, 26.5, 28.3 and 34.6 (s, CH_2), 47.2 and 47.4 (s, NCH_2), 117.2 (s, $=CH_2$), 133.4 (s, =CH), 175.0 (s, C=O); MS (EI 70eV): *m/z* (%) = 181 (2) [M^+], 167 (5) [M^+-CH_2], 152 (20) [M^+-$2CH_2$], 138 (20) [M^+-$3CH_2$], 124 (10) [M^+-$4CH_2$], 112 (15) [M^+-$5CH_2$], 96 (10) [M^+-$6CH_2$], 84 (10) [M^+-$7CH_2$], 70 (100) [M^+-$8CH_2$], 55 (20) [M^+-$7CH_2$-$CH{=}CH_2$]; HR-MS: *m/z* = 181.14577, calcd. for $C_{11}H_{19}NO$: 181.14611.

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