

Support-controlled Chemoselective Olefin-Imine Addition Photocatalyzed by Cadmium Sulfide on a Zinc Sulfide Carrier.

Marc Gärtner,^a Joachim Ballmann,^a Cornelia Damm,^b Frank W. Heinemann,^a and Horst Kisch^{*a}

^a Universität Erlangen-Nürnberg, Institut für Anorganische Chemie, Egerlandstr. 1, D-91058 Erlangen (Germany)

^b Universität Erlangen-Nürnberg, Institut für Werkstoffwissenschaften, Martensstr. 7, D-91058 Erlangen (Germany)

α -(Benzoylimido)- α -phenyl-acetonitrile (3a)

^1H NMR (270 MHz, CDCl_3) δ = 7.4-7.8 (m, 6H, m-H Ar, p-H Ar, m-H Ar-CO, p-H Ar-CO), 8.0 (d, 2H, $^3J_{\text{HH}}$ = 7.3 Hz, o-H Ar-CO), 8.2 (d, 2H, $^3J_{\text{HH}}$ = 7.3 Hz, o-H Ar); ^{13}C NMR (67 MHz, CDCl_3) δ = 109.9 (s, CN), 128.8, 129.0, 129.3, 129.9 (s, o-C Ar, m-C Ar, o-C Ar-CO, m-C Ar-CO), 131.1, 131.8 (s, ipso-C Ar-CO, ipso-C Ar), 134.4, 134.6 (s, p-C Ar-CO, p-C Ar), 141.5 (s, Ar-C-CN), 177.9 (s, CO); MS (FD) m/z : 234 [M^+], 137; IR (KBr): $\tilde{\nu}$ = 2228 ($\text{C}\equiv\text{N}$), 1674 ($\text{C}=\text{O}$), 1613 ($\text{C}=\text{N}$); elemental analysis calcd (%): C 76.91, H 4.30, N 11.96; found: C 76.11, H 4.05, N 11.58.

α -(Benzoylimido)- α -(p-fluorophenyl)-acetonitrile (3b)

^1H NMR (270 MHz, CDCl_3) δ = 7.2-7.4 (m, 2H, m-H Ar), 7.5-7.6 (m, 2H, m-H Ar-CO), 7.6-7.8 (m, 1H, p-H Ar-CO), 8.0-8.1 (m, 2H, o-H Ar-CO), 8.2-8.3 (m, 2H, o-H Ar); ^{13}C NMR (67 MHz, CDCl_3) δ = 109.8 (s, CN), 116.8 (d, $^2J_{\text{CF}}$ = 22.5 Hz, m-C Ar), 128.2 (d, $^4J_{\text{CF}}$ = 3.1 Hz, ipso-C Ar), 128.8 (s, m-C Ar-CO), 129.9 (s, o-C Ar-CO), 131.1 (s, ipso-C Ar-CO), 131.6 (d, $^3J_{\text{CF}}$ = 9.7 Hz, o-C Ar), 134.5 (s, p-C Ar-CO), 140.3 (d, $^5J_{\text{CF}}$ = 0.9 Hz, Ar-C-CN), 167.0 (d, $^1J_{\text{CF}}$ = 327.5 Hz, p-C Ar), 177.8 (s, CO); ^{19}F NMR (376 MHz, CDCl_3) δ = (-109.4)-(-109.2) (m, 1F); MS (FD) m/z : 252 [M^+], 105; IR (KBr): $\tilde{\nu}$ = 2223 ($\text{C}\equiv\text{N}$), 1685 ($\text{C}=\text{O}$), 1578 ($\text{C}=\text{N}$).

α -(Benzoylimido)- α -(p-chlorophenyl)-acetonitrile (3c)

^1H NMR (270 MHz, CDCl_3) δ = 7.5-7.7 (m, 4H, m-H Ar, m-H Ar-CO), 7.7-7.8 (m, 1H, p-H Ar-CO), 8.0-8.1 (m, 2H, o-H Ar-CO), 8.1-8.2 (m, 2H, o-H Ar); ^{13}C NMR (67 MHz, CDCl_3) δ = 109.7 (s, CN), 128.9, 129.8, 129.9, 130.2 (s, o-C Ar, m-C Ar, o-C Ar-CO, m-C Ar-CO), 130.3 (s, ipso-C Ar), 131.0 (s, ipso-C Ar-CO), 134.5 (s, p-C Ar-CO), 140.5 (s, p-C Ar), 141.4 (s, Ar-C-CN), 177.7 (s, CO); MS (FD) m/z : 268 [M^+], 105; IR (KBr): $\tilde{\nu}$ = 2232 ($\text{C}\equiv\text{N}$), 1678 ($\text{C}=\text{O}$), 1611 ($\text{C}=\text{N}$); elemental analysis calcd (%): C 67.05, H 3.38, N 10.43; found: C 66.47, H 2.74, N 10.17.

α -(Benzoylimido)- α -(p-bromophenyl)-acetonitrile (3d)

^1H NMR (270 MHz, CDCl_3) δ = 7.5-7.6 (m, 2H, Ar-H), 7.6-7.8 (m, 3H, Ar-H), 8.0-8.1 (m, 4H, Ar-H); ^{13}C NMR (67 MHz, CDCl_3) δ = 109.7 (s, CN), 128.8 (s, m-C Ar-CO), 129.9 (s, o-C Ar-CO), 130.1 (s, p-C Ar), 130.2 (s, o-C Ar), 130.7 (s, ipso-C Ar), 131.0 (s, ipso-C

Ar-CO), 132.7 (s, m-C Ar), 134.5 (s, p-C Ar-CO), 140.7 (s, Ar-C-CN), 177.7 (s, CO); MS (FD) m/z: 313 [M^+], 105; IR (KBr): $\tilde{\nu}$ = 2231 (C \equiv N), 1677 (C=O), 1606 (C=N); elemental analysis calcd (%): C 57.53, H 2.90, N 8.95; found: C 56.80, H 2.30, N 8.73.

α -(Benzoylimido)- α -tolyl-acetonitrile (3e)

^1H NMR (270 MHz, CDCl_3): δ = 2.4 (s, 3H, Me), 7.2-7.3 (m, 2H, Ar-H), 7.3-7.4 (m, 2H, Ar-H), 7.4-7.5 (m, 1H, Ar-H), 7.8-8.1 (m, 4H, Ar-H); ^{13}C NMR (67 MHz, CDCl_3): δ = 21.9 (s, Me), 128.8, 129.1 (s, o-C Ar, m-C Ar), 129.3 (s, ipso-C Ar), 129.9, 130.1 (s, o-C Ar-CO, m-C Ar-CO), 131.4 (s, ipso-C Ar-CO), 134.5 (s, p-C Ar-CO), 141.4 (s, Ar-C-CN), 146.2 (s, p-C Ar), 178.4 (s, CO); MS (EI) m/z: 248 [M^+], 225, 149, 105, 77, 57; IR (KBr): $\tilde{\nu}$ = 2224 (C \equiv N), 1674 (C=O), 1600 (C=N); elemental analysis calcd (%): C 77.40, H 4.87, N 11.28; found: C 76.74, H 4.62, N 11.06.

α -(Benzoylimido)- α -(p-methoxyphenyl)-acetonitrile (3f)

^1H NMR (270 MHz, CDCl_3) δ = 4.0 (s, 3H, MeO), 7.1 (d, 2H, $^3J_{\text{HH}} = 8.9$ Hz, m-H Ar), 7.5 (dd, 2H, $^3J_{\text{HH}} = 7.8$ Hz, $^3J_{\text{HH}} = 7.5$ Hz, m-H Ar-CO), 7.7 (t, 1H, $^3J_{\text{HH}} = 7.3$ Hz, p-H Ar-CO), 8.1 (d, 2H, $^3J_{\text{HH}} = 7.3$ Hz, o-H Ar-CO), 8.2 (d, 2H, $^3J_{\text{HH}} = 8.9$ Hz, o-H Ar); ^{13}C NMR (67 MHz, CDCl_3) δ = 55.8 (s, MeO), 110.2 (s, CN), 114.8 (s, m-C Ar), 124.8 (s, ipso-C Ar), 128.7, 129.9, 131.4 (s, o-C Ar, o-C Ar-CO, m-C Ar-CO), 132.0 (s, ipso-C Ar-CO), 134.2 (s, p-C Ar-CO), 140.7 (s, Ar-C-CN), 164.9 (s, p-C Ar), 178.0 (s, CO); MS (FD) m/z: 264 [M^+], 254; IR (KBr): $\tilde{\nu}$ = 2221 (C \equiv N), 1670 (C=O), 1577 (C=N); elemental analysis calcd (%): C 72.72, H 4.58, N 10.60; found: C 73.14, H 4.64, N 10.44.

α -(Benzoylamino)- α -(cyclopent-2-enyl)- α -phenyl-acetonitrile (4a)

^1H NMR (270 MHz, CDCl_3) δ = 1.8-2.8 (m, 4H, CH_2CH_2), 3.6 (m, 1H, CH-C-N), 5.5 (m, 0.5H, N-C-C-C=CH a), 5.7 (m, 0.5H, N-C-C-C=CH b), 6.1 (m, 0.5H, N-C-C-HC=C b) 6.2 (m, 0.5H, N-C-C-HC=C a), 6.6 (s, 0.5H, NH b), 6.7 (s, 0.5H, NH a), 7.4-7.7 (m, 8H, m-H Ar, p-H Ar, m-H Ar-CO, p-H Ar-CO), 7.8-7.9 (m, 2H, o-H Ar-CO); ^{13}C NMR (67 MHz, CDCl_3) δ = 24.8 26.1 (s, $\text{CH}_2\text{-C=C}$), 32.4 (s, $\text{CH}_2\text{-CH}$), 57.7-57.8 (s, CH-C-N), 60.4-60.8 (s, Ar-C-CN), 118.8-118.9 (s, CN), 125.0-125.1 (s, o-C Ar-CO), 129.9 (s, CH=C-C-C-N), 126.9-127.0 (s, o-C Ar), 128.0 (s, CH-C-C-N), 128.3-128.4 (s, p-C Ar), 128.6, 128.7, 128.8 (s, m-C Ar m-C Ar-CO), 132.3, 133.0 (s, p-C Ar-CO), 136.9-137.2 (s, ipso-C Ar-CO), 137.2 138.1 (s, ipso-C Ar), 165.7-166.1 (s, CO); MS (FD) m/z: 302 [M^+], 465, 452,

302, 235, 229, 179, 158, 145, 67; IR (KBr): $\tilde{\nu}$ = 3195 (N-H), 3060-2848 (CH₂) 1644 (C=O), 1601 1580 (C=C); elemental analysis calcd (%): C 79.44, H 6.00, N 9.26; found: C 79.17, H 7.74, N 9.30.

α -(Benzoylamino)- α -(cyclopent-2-enyl)- α -(p-fluoro-phenyl)-acetonitrile (4b)

¹H NMR (270 MHz, CDCl₃) δ = 1.8-2.6 (m, 4H, CH₂CH₂), 3.5 (m, 1H, CH-C-N), 5.4-5.7 (m, 1H, N-C-C-C=CH), 6.1-6.3 (m, 1H, N-C-C-HC=C), 6.6-6.7 (s, 1H, NH), 7.0-7.2 (m, 2H, m-H Ar), 7.4-7.7 (m, 5H, o-H Ar m-H Ar-CO, p-H Ar-CO), 7.7-7.9 (m, 2H, o-H Ar-CO); ¹³C NMR (67 MHz, CDCl₃) δ = 24.8-26.1 (s, CH₂-C-C-N), 32.4 (s, CH₂-C=C), 57.7-57.8 (s, CH-C-N), 60.0-60.4 (s, Ar-C-CN), 115.5 (d, ²J_{CF} = 6.4 Hz, m-C Ar), 115.9 (d, ²J_{CF} = 6.4 Hz, m-C Ar), 118.6-118.7 (s, CN), 126.6 (s, CH=C-C-C-N), 126.9 (d, ³J_{CF} = 6.9 Hz, o-C Ar), 127.0 (d, ³J_{CF} = 6.9 Hz, o-C Ar), 127.0-127.1 (s, o-C Ar-CO), 127.7 (s, CH-C-C-N), 128.8-128.9 (s, m-C Ar-CO), 132.4-132.8 (s, p-C Ar-CO), 132.7 (d, ⁴J_{CF} = 9.7 Hz, ipso-C Ar), 132.9 (d, ⁴J_{CF} = 9.7 Hz, ipso-C Ar), 137.5-138.4 (s, ipso-C Ar-CO), 160.1 (d, ¹J_{CF} = 99.7 Hz, p-C Ar), 165.0 (d, ¹J_{CF} = 99.7 Hz, p-C Ar), 164.2-166.1 (s, CO); ¹⁹F NMR (376 MHz, CDCl₃) δ = (-111.0)-(-110.9) (m, 0.64F), (-110.9)-(-110.7) (m, 0.36F); MS (FD) m/z: 320 [M⁺], 304, 253, 67; IR (KBr): $\tilde{\nu}$ = 3292 (N-H), 3049-2850 (CH₂) 1644 (C=O), 1602 1579 (C=C); elemental analysis calcd (%): C 74.98, H 5.35, N 8.74; found: C 72.72, H 5.23, N 8.42.

α -(Benzoylamino)- α -(cyclopent-2-enyl)- α -(p-chloro-phenyl)-acetonitrile (4c)

¹H NMR (270 MHz, CDCl₃) δ = 1.8-2.7 (m, 4H, CH₂CH₂), 3.5 (m, 1H, CH-C-N), 5.5 5.6 (m, 1H, N-C-C-C=CH), 6.2 (m, 1H, N-C-C-HC=C), 6.7 (s, 1H, NH), 7.3-7.7 (m, 7H, o-H Ar, m-H Ar, m-H Ar-CO, p-H Ar-CO), 7.7-7.9 (m, 2H, o-H Ar-CO); ¹³C NMR (67 MHz, CDCl₃) δ = 24.8 26.0 (s, CH₂-C-C-N), 32.4 (s, CH₂-C=C), 57.6-57.7 (s, CH-C-N), 60.2-60.5 (s, Ar-C-CN), 118.4-118.5 (s, CN), 126.5, 126.6, 127.0, 127.1 (s, m-C Ar, o-C Ar-CO), 127.6 (s, CH=C-C-C-N), 128.7, 128.8, 128.9 (s, o-C Ar, m-C Ar-CO), 132.5 (s, CH-C-C-N), 132.6-132.7 (s, p-C Ar), 134.3-134.4 (s, p-C Ar-CO), 135.7-135.9 (s, ipso-C Ar-CO), 137.6-138.4 (s, ipso-C Ar), 165.7-166.2 (s, CO); MS (FD) m/z: 337 [M⁺], 270, 67; IR (KBr): $\tilde{\nu}$ = 3278 (N-H), 3056-2854 (CH₂), 1646 (C=O), 1602 1581 (C=C); elemental analysis calcd (%): C 71.32, H 5.09, N 8.32; found: C 71.53, H 4.65, N 8.39.

α -(Benzoylamino)- α -(cyclopent-2-enyl)- α -(p-bromo-phenyl)-acetonitrile (4d)

^1H NMR (270 MHz, CDCl_3) δ = 1.8-2.6 (m, 4H, CH_2CH_2), 3.5 (m, 1H, CH-C-N), 5.5 (m, 0.5H, N-C-C-C=CH a), 5.6 (m, 0.5H, N-C-C-C=CH b), 6.1-6.2 (m, 1H, N-C-C-HC=C), 6.6 (s, 0.5H, NH b), 6.7 (s, 0.5H, NH a), 7.3-7.7 (m, 7H, o-H Ar, m-H Ar, m-H Ar-CO, p-H Ar-CO), 7.7-7.9 (m, 2H, o-H Ar-CO); ^{13}C NMR (67 MHz, CDCl_3) δ = 24.8-26.0 (s, $\text{CH}_2\text{-C-C-N}$), 32.4 (s, $\text{CH}_2\text{-C=C}$), 57.5 (s, CH-C-N), 60.3-60.5 (s, Ar-C-CN), 118.4-118.5 (s, CN), 122.4-122.5 (s, p-C Ar), 126.5-127.6 (s, CH=C-C-C-N), 126.8-126.9 (s, o-C Ar-CO), 127.0-127.1 (s, m-C Ar-CO), 128.8-128.9 (s, o-C Ar), 131.8-131.9 (s, m-C Ar), 132.5 (s, CH-C-C-N), 132.6-132.7 (s, p-C Ar-CO), 136.2-136.5 (s, ipso-C Ar-CO), 137.6-138.5 (s, p-C Ar), 165.7-166.1 (s, CO); MS (FD) m/z: 381 [M^+], 136, 39; IR (KBr): $\tilde{\nu}$ = 3271 (N-H), 3057-2854 (CH_2) 1646 (C=O), 1602-1580 (C=C); elemental analysis calcd (%): C 63.00, H 4.49, N 7.35; found: C 63.46, H 4.26, N 7.39.

α -(Benzoylamino)- α -(cyclopent-2-enyl)- α -tolyl-acetonitrile (4e)

^1H NMR (270 MHz, CDCl_3) δ = 1.8-2.7 (m, 7H, Me, CH_2CH_2), 3.5 (m, 1H, CH-C-N), 5.5-5.6 (m, 1H, N-C-C-HC=C), 6.0-6.2 (m, 1H, N-C-C-C=CH), 6.7-6.8 (s, 1H, NH), 7.1-7.2 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, o-H Ar), 7.3-7.6 (m, 5H, m-H Ar, m-H Ar-CO, p-H Ar-CO), 7.7-7.8 (d, 2H, $^3J_{\text{HH}} = 6.8$ Hz, o-H Ar-CO); ^{13}C NMR (67 MHz, CDCl_3) δ = 21.0 (s, Me), 24.7-24.9 (s, $\text{CH}_2\text{-C-C-N}$), 32.3 (s, $\text{CH}_2\text{-C=C}$), 57.5-57.6 (s, CH-C-N), 60.4 (s, Ar-C-CN), 118.9 (s, CN), 125.0, 125.1, 127.0, 127.2 (s, o-C Ar, o-C Ar-CO), 128.1 (s, CH=C-C-C-N), 128.7, 128.8, 129.3, 129.4 (s, m-C Ar, m-C Ar-CO), 132.2-132.3 (s, p-C Ar-CO), 133.1 (s, CH-C-C-N), 134.1-134.4 (s, ipso-C Ar-CO), 137.0-137.9 (s, p-C Ar), 138.1-138.2 (s, ipso-C Ar), 166.2 (s, CO); MS (EI) m/z: 317 [M^+], 290, 251, 149, 105, 77; IR (KBr): $\tilde{\nu}$ = 3290 (N-H), 3047-2848 (CH_2) 1653 (C=O), 1601-1579 (C=C); elemental analysis calcd (%): C 79.72, H 6.37, N 8.85; found: C 78.83, H 6.67, N 8.96.

α -(Benzoylamino)- α -(cyclopent-2-enyl)- α -(p-methoxyphenyl)-acetonitrile (4f)

^1H NMR (270 MHz, CDCl_3) δ = 1.8-2.6 (m, 4H, CH_2CH_2), 3.6 (m, 1H, CH-C-N), 3.8 (s, 3H, MeO), 5.6 (m, 1H, N-C-C-C=CH), 6.0-6.3 (m, 1H, N-C-C-HC=C), 6.7 (s, 1H, NH), 6.8-7.0 (m, 2H, m-H Ar), 7.4-7.7 (m, 5H, o-H Ar, m-H Ar-CO, p-H Ar-CO), 7.7-7.9 (m, 2H, o-H Ar-CO); ^{13}C NMR (67 MHz, CDCl_3) δ = 24.9-26.0 (s, $\text{CH}_2\text{-C-C-N}$), 32.4 (s, $\text{CH}_2\text{-C=C}$), 55.3 (s, MeO), 57.6-57.8 (s, CH-C-N), 60.1-60.6 (s, Ar-C-CN), 114.0-114.1 (s, m-C Ar), 118.8-119.0 (s, CN), 126.3, 126.4, 126.9, 127.1 (s, o-C Ar-CO, m-C Ar-CO), 128.0 (s, CH=C-C-C-N), 128.6-128.7 (s, o-C Ar), 129.0-129.2 (s, ipso-C Ar), 132.1-

132.2 (s, CH-C-C-N), 133.0-133.1 (s, p-C Ar-CO), 137.0-137.9 (s, ipso-C Ar-CO), 159.3-159.4 (s, p-C Ar), 165.7-166.1 (s, CO); MS (FD) m/z: 332 [M⁺], 266, 238, 212; IR (KBr): $\tilde{\nu}$ = 3259 (N-H), 3049-2845 (CH₂) 1640 (C=O), 1611-1580 (C=C); elemental analysis calcd (%): C 75.88, H 6.06, N 8.43; found: C 75.50, H 6.35, N 8.42.

α -(Benzoylamino)- α -(cyclohex-2-enyl)- α -phenyl-acetonitril (5a)

¹H NMR (270 MHz, CDCl₃) δ = 1.1-2.1 (m, 6H, CH₂-CH₂-CH₂), 2.8-3.1 (m, 1H, CH-C-N), 5.7-5.9 (m, 1H, N-C-C-HC=C), 6.0-6.2 (m, 1H, N-C-C-C=CH), 6.4-6.7 (s, 1H, NH), 7.2-7.6 (m, 7H, m-H Ar, p-H Ar, m-H Ar-CO, p-H Ar-CO), 7.7-7.8 (m, 2H, o-H Ar-CO), ¹³C NMR (67 MHz, CDCl₃) δ = 21.3 (s, CH₂-C-C-N), 24.2 (s, CH₂-C-C=C), 24.9 (s, CH₂-C=C), 46.4 (s, CH-C-N), 60.8 (s, Ar-C-CN), 119.1 (s, CN), 124.4 (s, CH=C-C-C-N), 125.5-127.1 (s, o-C Ar-CO, m-C Ar-CO), 128.4 (s, p-C Ar), 128.6-128.8 (s, o-C Ar, m-C Ar), 132.4 (s, p-C Ar-CO), 133.0 (s, ipso-C Ar-CO), 134.2 (s, CH-C-C-N), 136.0 (s, ipso-C Ar), 166.3 (s, CO); MS (EI) m/z: 317 [M⁺], 280, 237, 167, 149, 105, 77; IR (KBr): $\tilde{\nu}$ = 3300 (N-H), 3060-2925 (CH₂) 1645 (C=O), 1601-1578 (C=C); Elemental analysis calcd (%): C 79.72, H 6.37, N 8.85; found: C 79.58, H 6.69, N 8.87.

α -(Benzoylamino)- α -(cyclohex-2-enyl)- α -(p-fluoro-phenyl)-acetonitrile (5b)

¹H NMR (270 MHz, CDCl₃) δ = 1.1-2.2 (m, 6H, CH₂-CH₂-CH₂), 2.7-3.0 (m, 1H, CH-C-N), 5.4-5.9 (m, 1H, N-C-C-HC=C), 6.0-6.2 (m, 1H, N-C-C-C=CH), 6.5-6.6 (s, 1H, NH), 6.9-7.1 (m, 2H, m-H Ar), 7.3-7.7 (m, 5H, o-H Ar, m-H Ar-CO, p-H Ar-CO), 7.7-7.8 (d, 2H, ³J_{HH} = 7.1 Hz, o-H Ar-CO), ¹³C NMR (67 MHz, CDCl₃) δ = 21.7 (s, CH₂-C-C-N), 24.6-25.3 (s, CH₂-C-C=C), 25.4-26.0 (s, CH₂-C=C), 46.9-47.0 (s, CH-C-N), 60.8 (s, Ar-C-CN), 116.0-116.3 (d, ³J_{CF} = 7.6Hz, m-C Ar), 118.4-119.4 (s, CN), 122.6-124.6 (s, CH=C-C-C-N), 127.4, 127.5, 127.7, 127.8 (s, o-C Ar-CO, m-C Ar-CO), 129.3 (s, o-C Ar), 132.3 (s, CH-C-C-N), 132.9 (s, p-C Ar-CO), 133.3 (s, ipso-C Ar-CO), 135.0-135.4 (s, ipso-C Ar), 163.0 (d, ¹J_{CF} = 335Hz, p-C Ar), 166.3-166.7 (s, CO); ¹⁹F NMR (376 MHz, CDCl₃) δ = (-113.5)-(-113.4) (m, 1F); MS (EI) m/z: 335 [M⁺], 308, 255, 237, 149, 105, 83, 57, 43; IR (KBr): $\tilde{\nu}$ = 3280 (N-H), 3033-2833 (CH₂) 1645 (C=O), 1602-1579 (C=C); Elemental analysis calcd (%): C 75.43, H 5.73, N 8.38; found: C 74.51, H 5.88, N 8.22.

α -(Benzoylamino)- α -(cyclohex-2-enyl)- α -(p-chloro-phenyl)-acetonitrile (5c)

¹H NMR (270 MHz, CDCl₃) δ = 1.1-2.3 (m, 6H, CH₂-CH₂-CH₂), 2.8-3.1 (m, 1H, CH-C-N), 5.4-5.9 (m, 1H, N-C-C-HC=C), 6.1-6.4 (m, 1H, N-C-C-C=CH), 6.6-6.7 (s, 1H, NH), 7.2-

7.7 (m, 7H, o-H Ar, m-H Ar, m-H Ar-CO, p-H Ar-CO), 7.7-7.9 (m, 2H, o-H Ar-CO); ^{13}C NMR (67 MHz, CDCl_3) δ = 21.8 (s, $\text{CH}_2\text{-C-C-N}$), 25.4-26.0 (s, $\text{CH}_2\text{-C-C=C}$), 30.1 (s, $\text{CH}_2\text{-C=C}$), 46.8 (s, CH-C-N), 60.9 (s, Ar-C-CN), 118.3 (s, CN), 122.5 (s, CH=C-C-C-N), 127.3-127.5 (s, m-C Ar, o-C Ar-CO), 127.6 (s, CH-C-C-N), 129.3-129.4 (s, o-C Ar, m-C Ar-CO), 133.0 (s, p-C Ar-CO), 133.2 (s, p-C Ar), 134.9-135.1 (s, ipso-C Ar-CO), 135.6-135.9 (s, ipso-C Ar), 166.3 (s, CO); MS (EI) m/z : 351 [M^+], 324, 271, 230, 149, 105, 77, 57, 43; IR (KBr): $\tilde{\nu}$ = 3370 (N-H), 3057-2865 (CH_2) 1646 (C=O), 1600-1578 (C=C); Elemental analysis calcd (%): C 71.89, H 5.46, N 7.98; found: C 71.21, H 5.26, N 8.03.

α -(Benzoylamino)- α -(cyclohex-2-enyl)- α -(p-bromo-phenyl)-acetonitrile (5d)

^1H NMR (270 MHz, CDCl_3) δ = 1.1-2.3 (m, 6H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 2.8-3.2 (m, 1H, CH-C-N), 5.4-6.0 (m, 1H, N-C-C-HC=C), 6.1-6.3 (m, 1H, N-C-C-C=CH), 6.6-6.7 (s, 1H, NH), 7.2-7.7 (m, 7H, o-H Ar, m-H Ar, m-H Ar-CO, p-H Ar-CO), 7.8-8.0 (m, 2H, o-H Ar-CO); ^{13}C NMR (67 MHz, CDCl_3) δ = 21.8 (s, $\text{CH}_2\text{-C-C-N}$), 25.3-25.4 (s, $\text{CH}_2\text{-C-C=C}$), 26.0 (s, $\text{CH}_2\text{-C=C}$), 46.8 (s, CH-C-N), 60.9-70.0 (s, Ar-C-CN), 118.3 (s, CN), 122.4 (s, p-C Ar), 127.4 (s, o-C Ar-CO), 127.5 (s, CH=C-C-C-N), 127.6 (s, m-C Ar-CO), 129.3 (s, o-C Ar), 132.4 (s, m-C Ar), 133.0 (s, p-C Ar-CO), 133.1 (s, CH-C-C-N), 135.6 (s, ipso-C Ar-CO), 136.4 (s, ipso-C Ar), 166.3 (s, CO); MS (EI) m/z : 395 [M^+], 370, 315, 265, 237, 149, 105, 83, 57, 42; IR (KBr): $\tilde{\nu}$ = 3318 (N-H), 3034-2865 (CH_2) 1640 (C=O), 1599-1578 (C=C); Elemental analysis calcd (%): C 63.81, H 4.84, N 7.09; found: C 63.00, H 4.67, N 7.08.

α -(Benzoylamino)- α -(cyclohex-2-enyl)- α -tolyl-acetonitrile (5e)

^1H NMR (270 MHz, CDCl_3) δ = 1.1-2.1 (m, 6H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 2.3 (s, 3H, Me), 2.8-3.1 (m, 1H, CH-C-N), 5.5 (m, 0.5H, N-C-C-HC=C a), 5.7 (m, 0.5H, N-C-C-HC=C b), 6.1 (m, 1H, N-C-C-C=CH), 6.7 (s, 1H, NH b), 6.8 (s, 1H, NH a), 7.1-7.3 (m, 2H, o-H Ar), 7.3-7.6 (m, 5H, m-H Ar, m-H Ar-CO, p-H Ar-CO), 7.7 (d, 2H, $^3J_{\text{HH}} = 7.4$ Hz, o-H Ar-CO); ^{13}C NMR (67 MHz, CDCl_3) δ = 21.0-21.4 (s, $\text{CH}_2\text{-C-C-N}$), 24.3 (s, $\text{CH}_2\text{-C-C=C}$), 24.8-24.9 (s, Me), 25.5 (s, $\text{CH}_2\text{-C=C}$), 46.2-46.3 (s, CH-C-N), 60.8 (s, Ar-C-CN), 118.3-119.1 (s, CN), 122.7-124.4 (s, CH=C-C-C-N), 125.3, 125.4, 127.0, 127.1 (s, o-C Ar, o-C Ar-CO), 128.7, 128.9, 129.3, 129.4 (s, m-C Ar, m-C Ar-CO), 132.2-132.3 (s, p-C Ar-CO), 133.0-133.1 (s, ipso-C Ar-CO), 133.9 (s, CH-C-C-N), 134.4 (s, p-C Ar), 138.2 (s, ipso-C Ar), 166.0-166.3 (s, CO); MS (EI) m/z : 331 [M^+], 304, 251, 210, 167, 105, 77; IR (KBr): $\tilde{\nu}$ =

3294 (N-H), 3030-2856 (CH₂) 1654 (C=O), 1602-1580 (C=C); Elemental analysis calcd (%): C 79.97, H 6.71, N 8.48; found: C 79.03, H 6.99, N 8.71.

α -(Benzoylamino)- α -(cyclohex-2-enyl)- α -(p-methoxyphenyl)-acetonitrile (5f)

¹H NMR (270 MHz, CDCl₃) δ = 1.1-2.1 (m, 6H, CH₂-CH₂-CH₂), 2.7-3.1 (m, 1H, CH-C-N), 3.7 (s, 3H, MeO), 5.5-5.7 (m, 1H, N-C-C-HC=C), 6.0-6.1 (m, 1H, N-C-C-C=CH), 6.5-6.6 (s, 1H, NH), 6.9 (d, 2H, ³J_{HH} = 8.6 Hz, o-H Ar), 7.3-7.7 (m, 5H, m-H Ar, m-H Ar-CO, p-H Ar-CO), 7.7 (d, 2H, ³J_{HH} = 7.1 Hz, o-H Ar-CO); ¹³C NMR (67 MHz, CDCl₃) δ = 21.3-21.4 (s, CH₂-C-C-N), 24.3-24.9 (s, CH₂-C-C=C), 25.0-25.5 (s, CH₂-C=C), 46.3-46.6 (s, CH-C-N), 55.3 (s, MeO), 60.4-60.5 (s, Ar-C-CN), 114.0-114.1 (s, m-C Ar), 118.4-119.2 (s, CN), 122.6-124.4 (s, CH=C-C-C-N), 126.7-126.8 (s, o-C Ar-CO), 126.8-127.0 (s, m-C Ar-CO), 128.7-128.8 (s, o-C Ar), 132.3 (s, p-C Ar-CO), 133.1-133.2 (s, ipso-C Ar), 134.0 (s, ipso-C Ar-CO), 134.6 (s, CH-C-C-N), 159.5 (s, p-C Ar), 165.9-166.2 (s, CO); MS (EI) m/z: 347 [M⁺], 320, 266, 226, 215, 105, 77; IR (KBr): $\tilde{\nu}$ = 3294 (N-H), 3030-2856 (CH₂) 1654 (C=O), 1602-1580 (C=C).