[4+1] Cycloaddition of N-Heterocyclic Carbenes with Vinyl Isocyanates

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Supporting Information

General procedure for the reaction of N-heterocyclic carbenes with vinyl isocyanates: a solution of acyl azide (1 equiv.) and carbene precursor (2 equiv.) in xylene (ca. 0.05M) was heated at 80 °C for 2 h and then refluxed for 16 h. The resulting solution was directly chromatographed on silica gel (hexane, then EtOAc / hexane).

3-[Phenyl-(2-phenylamino-ethyl)-amino]-1,4,5,6-tetrahydro-indol-2-one (3) Yield 66%, mp (EtOAc / Hexane) 150-151 °C; IR (neat) $\bar{\nu}$ 3322, 3025, 2925, 1678 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.54 (bs, 1H), 7.23 (t, J = 7.6 Hz, 2H), 7.13 (t, J = 7.6 Hz, 2H), 6.86 (d, J = 7.2 Hz, 3H), 6.64 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 8.8 Hz, 2H), 5.66 (t, J = 4.4 Hz, 1H), 5.19 (bs, 1H), 4.04 (t, J = 5.6 Hz, 2H), 3.39 (t, J = 5.6 Hz, 2H), 2.26 (q, J = 6.0 Hz, 2H), 2.06 (t, J = 6.4 Hz, 2H), 1.67 (quintet, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 148.6, 145.5, 135.5, 131.8, 131.8, 129.4, 129.3, 120.1, 117.3, 117.0, 112.8, 111.3, 48.7, 42.0, 24.3, 23.7, 23.3; MS (EI) m/e (rel. intensity) 345 (M^+ , 1), 256 (1), 240 (18), 225 (1), 106 (100); HRMS calcd for $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}$ (M^+) 345.1841, found 345.1840; Anal. calcd for $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}$: C, 76.48; H, 6.72; N, 12.17. Found: C, 76.62; H, 6.76; N, 12.01.

5,5-(Ethylenedioxy)-3-[phenyl-(2-phenylamino-ethyl)-amino]-1,4,5,6-tetrahydro-indol-2-one (11) Yield 57%; IR (neat) $\bar{\nu}$ 3330, 2926, 2888, 1682 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.13 (bs, 1H), 7.24 (t, J = 7.6 Hz, 2H), 7.12 (t, J = 7.6 Hz, 2H), 6.88-6.93 (m, 3H), 6.63 (t, J = 7.6 Hz, 1H), 6.57 (d, J = 7.2 Hz, 2H), 5.47 (t, J = 4.8 Hz, 1H), 5.10 (bs, 1H), 4.09 (t, J = 6.0 Hz, 2H), 3.88-3.92 (m, 2H), 3.79-3.83 (m, 2H), 3.36 (t, J = 5.6 Hz, 2H), 2.51 (d, J = 4.8 Hz, 2H), 2.22 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 148.6, 145.0, 135.1, 134.1, 129.4, 129.3, 127.1, 121.2, 118.8, 117.0, 112.8, 109.3, 105.9, 64.9, 48.5, 42.1, 35.0, 34.2; MS (EI) m/e (rel. intensity) 403 (M^+ , 16), 373 (5), 328 (4), 310 (4), 298 (91), 284 (11), 240 (11), 225 (19); HRMS calcd for $\text{C}_{24}\text{H}_{25}\text{N}_3\text{O}_3$ (M^+) 403.1896, found 403.1899.

3-[Phenyl-(2-phenylamino-ethyl)-amino]-4,5,6,7-tetrahydro-1H-cyclohepta[b]pyrrol-2-one (12) Yield 55%, mp (EtOAc / Hexane) 165-166 °C; IR (neat) $\bar{\nu}$ 3310, 3053, 2925, 1678 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.43 (bs, 1H), 7.21 (t, J = 8.0 Hz, 2H), 7.11-7.15 (m, 2H), 6.77-6.83 (m, 3H), 6.60-6.67 (m, 3H), 5.70 (t, J = 5.2 Hz, 1H), 5.30 (bs, 1H), 4.00 (t, J = 6.0 Hz, 2H), 3.41 (t, J = 6.0 Hz, 2H), 2.45 (q, J = 5.6 Hz, 2H), 2.24 (t, J = 6.0 Hz, 2H), 1.76 (quintet, J = 5.6 Hz, 2H), 1.62 (quintet, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 148.4, 145.8, 138.5, 136.1, 135.8, 129.4, 129.4, 119.5, 118.5, 117.2, 116.0, 113.0, 49.0, 42.1, 29.9, 29.3, 27.9, 25.0; MS (EI) m/e (rel. intensity) 359 (M^+ , 19), 266 (6), 254 (83), 240 (6), 225 (4), 212 (15); HRMS calcd for $\text{C}_{23}\text{H}_{25}\text{N}_3\text{O}$ (M^+) 359.1993, found 359.1998.

3-[Phenyl-(2-phenylamino-ethyl)-amino]-1,4,5,6,7,8-hexahydro-cycloocta[b]pyrrol-2-one

(13) Yield 52%, mp (EtOAc / Hexane) 160-161 °C; IR (neat) $\bar{\nu}$ 3320, 3050, 2928, 1682 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.67 (bs, 1H), 7.17-7.21 (m, 2H), 7.12 (t, J = 7.6 Hz, 2H), 6.77-6.81 (m, 3H), 6.65 (t, J = 7.6 Hz, 1H), 6.61 (d, J = 7.2 Hz, 2H), 5.62 (t, J = 8.8 Hz, 1H), 5.14 (bs, 1H), 3.92 (t, J = 6.0 Hz, 2H), 3.41 (t, J = 6.0 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 2.48 (q, J = 8.0 Hz, 2H), 1.38-1.58 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 148.3, 147.1, 140.7, 139.6, 137.6, 129.4, 119.2, 117.3, 115.1, 113.9, 113.1, 49.9, 42.0, 26.1, 25.1, 24.7, 24.6, 21.9; MS (EI) m/e (rel. intensity) 373 (M^+ , 34), 359 (2), 280 (10), 268 (100), 254 (15), 240 (13), 226 (3), 212 (5); HRMS calcd for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}$ (M^+) 373.2154, found 373.2151.

3,3-Spiro(1,3-diphenyl-imidazolidino)-1,3-dihydro-benzo[f]indol-2-one (14)

Yield 51%; IR (neat) $\bar{\nu}$ 3237, 3058, 2931, 1724 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.38 (bs, 1H), 7.68-7.73 (m, 3H), 7.46 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.11 (s, 1H), 7.02 (t, J = 8.0 Hz, 4H), 6.73 (t, J = 7.6 Hz, 2H), 6.57 (d, J = 8.0 Hz, 4H), 4.09-4.15 (m, 2H), 3.92-3.98 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.7, 144.2, 138.7, 135.1, 130.9, 129.3, 129.2, 127.6, 127.5, 126.1, 124.8, 120.6, 116.6, 107.0, 81.7, 47.1; MS (EI) m/e (rel. intensity) 391 (M^+ , 2), 363 (100), 363 (35), 347 (12), 286 (2), 257 (6), 244 (19), 230 (4); HRMS calcd for $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}$ (M^+) 391.1685, found 391.1679.

3-[Phenyl-(2-phenylamino-cyclohexyl)-amino]-1,4,5,6-tetrahydro-indol-2-one (15)

Yield 65%; IR (neat) $\bar{\nu}$ 3331, 3051, 2931, 1682 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.13-7.17 (m, 2H), 7.10 (bs, 1H), 7.02-7.06 (m, 2H), 6.91-6.96 (m, 3H), 6.54 (t, J = 7.2 Hz, 1H), 6.42 (d, J = 8.0 Hz, 2H), 5.43 (t, J = 4.8 Hz, 1H), 4.80 (bs, 1H), 4.30 (dt, J = 11.2, 3.2 Hz, 1H), 3.28 (dt, J = 10.0, 3.2 Hz, 1H), 2.29-2.32 (m, 1H), 2.15 (q, J = 5.6 Hz, 3H), 1.91-1.98 (m, 1H), 1.68-1.81 (m, 4H), 1.34-1.56 (m, 3H), 1.13-1.29 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 147.8, 144.6, 135.4, 132.6, 129.2, 128.9, 123.8, 122.6, 116.1, 112.7, 108.5, 62.1, 54.2, 33.6, 32.8, 26.2, 25.0, 24.1, 23.2, 23.0; MS (EI) m/e (rel. intensity) 399 (M^+ , 38), 364 (10), 363 (35), 347 (4), 306 (16), 278 (2), 265 (9), 239 (35), 226 (27), 174 (100); HRMS calcd for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}$ (M^+) 399.2311, found 399.2314.

1,3-Bis-(3,4-dihydro-naphthalen-2-yl)-6,9-diphenyl-1,3,6,9-tetraaza-spiro[4.4]nonane-2,4-dione (16)

Yield 71%; IR (neat) $\bar{\nu}$ 2937, 2864, 1783, 1726 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, J = 8.0 Hz, 4H), 7.07-7.15 (m, 5H), 6.99-7.04 (m, 4H), 6.92-6.96 (m, 5H), 6.90 (s, 1H), 6.32 (s, 1H), 3.95-3.98 (m, 2H), 3.76-3.80 (m, 2H), 2.88 (t, J = 8.4 Hz, 2H), 2.44 (t, J = 8.0 Hz, 2H), 2.28 (t, J = 9.2 Hz, 2H), 2.17 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.3, 152.4, 142.8, 134.7, 134.6, 134.4, 133.3, 132.7, 129.7, 129.5, 128.2, 127.5, 127.4, 127.4, 127.2, 126.8, 126.7, 126.6, 126.3, 122.4, 121.1, 117.5, 92.6, 46.4, 28.4, 28.2, 25.8, 25.4; MS (ESI) m/e (rel. intensity) 587[($\text{M}+\text{Na}$) $^+$, 14], 416 (100), 379 (18), 348 (11), 245 (22), 223 (8); HRMS calcd for $\text{C}_{37}\text{H}_{32}\text{N}_4\text{O}_2\text{Na}^+[(\text{M}+\text{Na})^+]$ 587.2417, found 587.2379.

1-Hydroxy-1-[phenyl-(2-phenylamino-ethyl)-amino]-1,3,4,5-tetrahydro-benzo[e]indol-2-one (17)

Yield 27%; IR (neat) $\bar{\nu}$ 3423, 3310, 3060, 1675 cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2) δ 8.37 (bs, 1H), 7.36-7.49 (m, 4H), 7.18-7.34 (m, 5H), 7.07-7.14 (m, 1H), 6.97-7.04 (m, 3H), 6.82 (s, 1H), 5.77 (bs, 1H), 4.03 (t, J = 6.4 Hz, 2H), 3.91 (t, J = 6.4 Hz, 2H), 2.79 (t, J = 8.0 Hz, 2H), 2.23 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.6, 153.8, 141.6, 141.5, 136.6, 135.5, 132.7, 130.5, 129.8, 128.3, 128.2, 127.0, 126.8, 126.7, 125.6, 125.2, 123.9, 119.7, 107.9, 47.4, 44.2, 28.2, 28.0; MS (EI) m/e (rel. intensity) 411 (M^+ , 0.3), 359 (0.5), 240 (11), 212 (1), 119 (39), 106 (100); HRMS calcd for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_2$ (M^+) 411.1947, found 411.1946.

1,3-Di-cyclopent-1-enyl-6,9-diphenyl-1,3,6,9-tetraaza-spiro[4.4]nonane-2,4-dione (18)

Yield 70%, mp (EtOAc / Hexane) 185-187 °C; IR (neat) $\bar{\nu}$ 2937, 2853, 1782, 1730 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.28 (m, 4H), 6.97 (t, J = 7.2 Hz, 2H), 6.82 (d, J = 8.4 Hz, 4H), 5.89 (s, 1H), 5.76 (t, J = 2.0 Hz, 1H), 3.93 (dt, J = 13.2, 8.8 Hz, 2H), 3.71 (dt, J = 13.2, 8.4 Hz, 2H), 2.37-2.43 (m, 4H), 2.25 (t, J = 7.6 Hz, 4H), 1.89 (quintet, J = 7.6 Hz, 2H), 1.68 (quintet, J = 7.2 Hz, 2H); ^{13}C

NMR (100 MHz, CDCl₃) δ 169.3, 152.2, 142.8, 135.3, 131.7, 129.6, 126.1, 122.2, 119.6, 117.3, 92.0, 46.2, 31.7, 31.6, 30.7, 30.5, 22.0, 21.8; MS (EI) *m/e* (rel. intensity) 440 (M⁺, 100), 411 (11), 384 (6), 331 (31), 303 (27), 292 (77), 250 (44), 222 (60); HRMS calcd for C₂₇H₂₈N₄O₂ (M⁺) 440.2212, found 440.2210; Anal. calcd for C₂₇H₂₈N₄O₂: C, 73.60; H, 6.41; N, 12.72. Found: C, 73.42; H, 6.45; N, 12.55.

3-Hydroxy-3-[phenyl-(2-phenylamino-ethyl)-amino]-1,3-dihydro-indol-2-one (20) Yield 14%; IR (neat) δ 3422, 3323, 3057, 1673 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂) δ 8.38 (bs, 1H), 7.37-7.50 (m, 5H), 7.18-7.32 (m, 8H), 6.99-7.03 (m, 1H), 6.35 (bs, 1H), 4.04 (t, *J* = 6.8 Hz, 2H), 3.95 (t, *J* = 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 154.2, 141.7, 141.5, 139.2, 130.4, 129.8, 128.9, 128.4, 128.2, 126.8, 125.6, 123.8, 123.1, 119.7, 106.3, 47.5, 44.3; MS (EI) *m/e* (rel. intensity) 359 (M⁺, 2), 240 (11), 212 (3), 119 (52), 106 (100); HRMS calcd for C₂₂H₂₁N₃O₂ (M⁺) 359.1634, found 359.1626.

1-Hydroxy-1-[phenyl-(2-phenylamino-ethyl)-amino]-1,3-dihydro-benzo[*e*]indol-2-one (22) Yield 32%; IR (neat) δ 3421, 3316, 3056, 1674 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂) δ 8.39 (bs, 1H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.20-7.50 (m, 12H), 6.45 (bs, 1H), 4.10-4.13 (m, 2H), 4.01-4.04 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 162.9, 154.5, 141.6, 141.3, 136.3, 134.2, 130.7, 130.0, 128.7, 128.5, 128.4, 127.7, 127.6, 127.1, 126.5, 124.7, 123.9, 120.3, 115.7, 104.2, 47.7, 44.6; MS (EI) *m/e* (rel. intensity) 409 (M⁺, 1), 391 (24), 348(2), 302 (6), 287 (9), 240 (10), 223 (6), 215 (5), 202 (3); HRMS calcd for C₂₆H₂₃N₃O₂ (M⁺) 409.1790, found 409.1784.