SUPPORTING INFORMATION

Gold-Catalyzed Reactions of 2-Alkynyl-phenylamines with α,β -Enones.

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General considerations: ^1H -NMR (200 MHz) and ^{13}C -NMR (50.3 MHz) spectra (CDCl_3 , unless otherwise stated; TMS as internal standard) were recorded. EI (70eV) mass spectra were recorded. IR spectra were recorded. Only the most significant IR absorptions are given. Unless otherwise stated, all starting materials, catalysts, and solvents were commercially available and were used as purchased. Reaction products were purified by flash chromatography on silica gel by elution with *n*-hexane/EtOAc mixtures. The atomic point charges of **1a** and **1l** were evaluated by means of chemical calculations according to the following procedures. The ground state geometries were optimized at the Hartree Fock level of theory (HF) using the 6-311G(d) basis set. These geometries were then refined within Density Functional Theory (DFT) using the hybrid Becke-Lee-Yang-Parr (B3LYP) functional.¹ Several conformers were taken into account using the same 6-311G(d) basis set. The atomic charges were finally optimized, on the basis of the Kohn-Sham density matrix from the B3LYP calculations, using the Breneman fitting scheme with the constrain of reproducing both molecular dipole and quadrupole moments.² From a careful inspection it turned out that the charges appeared as basically insensitive to the conformational changes, e.g. mutual rotation of the two phenyl rings or rotation of the $-\text{NH}_2$ group. The calculations were carried out with the Gamess suite programs.³

2-Naphthalen-2-ylethynyl-phenylamine (1b). ^1H NMR (200 MHz, CDCl_3): δ 4.97 (bs, 2H), 6.59-6.67 (m, 1H), 6.76-6.80 (m, 1H), 7.07-7.15 (m, 1H), 7.30-7.46 (m, 1H), 7.49-7.51 (m, 3H), 7.76-7.84 (m, 3H), 8.05 (s, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 86.9, 94.7, 106.9, 114.3, 116.9, 120.7, 126.7, 127.7, 127.8, 128.1, 128.3, 129.9, 130.9, 131.9, 132.6, 133.0, 149.0. IR (neat): 3480, 3390, 780, 660 cm^{-1} . MS (EI) m/z : 244 $[(\text{M}+1)^+, 100]$. Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{N}$: C, 88.86; H, 5.39; N, 5.76. Found C, 88.82; H, 5.41; N, 5.71.

4-Methyl-2-phenylethynyl-phenylamine (1c). ^1H NMR (200 MHz, CDCl_3): δ 2.21 (s, 3H), 4.34 (bs, 2H), 6.65 (d, $J = 2.9$, 1H), 6.91 (s, 1H), 7.21-7.33 (m, 4H), 7.48-7.51 (m, 2H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 20.2, 86.1, 94.4, 109.2, 115.7, 123.3, 128.1, 128.3, 128.4, 129.0, 129.1, 132.6,

145.4. IR (KBr): 3500, 3400, 2200, 1625, 1600, 700, 660 cm^{-1} . MS (EI) m/z : 207 (M^+ , 100). Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{N}$: C, 86.92; H, 6.32; N, 6.76. Found C, 86.91 ; H, 6.33; N, 6.72.

1-(2-Amino-3-chloro-5-nitro-phenyl)-3-methyl-pent-1-yn-3ol (1j). ^1H NMR (200 MHz, CDCl_3): δ 1.12 (t, J = 7.3, 3H), 1.61 (s, 3H), 1.82 (q, J = 7.3, 2H), 5.36 (bs, 2H), 8.07 (d, J = 2.5, 1H), 8.13 (d, J = 2.5, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 9.1, 29.2, 36.4, 69.1, 77.1, 100.8, 107.2, 117.4, 125.4, 126.7, 137.4, 149.6. IR (KBr): 3500, 3350, 1610, 1510, 1315, 630, 610 cm^{-1} . MS (EI) m/z : 269 [$(\text{M}+1)^+$, 85], 268 (M^+ , 89), 251 (100), 250 (95), 180(70). Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{ClN}_2\text{O}_3$: C, 53.64; H, 4.88; N, 10.43. Found C, 53.63 ; H, 4.85; N, 10.45.

2-(3-Ethoxy-3-methyl-pent-1-ynyl)-phenylamine (1k). ^1H NMR (200 MHz, CDCl_3): δ 1.06 (t, J = 7.4, 3H), 1.24 (t, J = 7.0, 3H), 1.53 (s, 3H), 1.84 (q, J = 7.3, 2H), 3.65 (q, J = 7.0, 2H), 5.29 (bs, 2H), 8.12 (d, J = 2.5, 1H), 8.16 (d, J = 2.9, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 8.8, 15.8, 25.8, 29.7, 34.3, 59.5, 74.0, 78.5, 99.5, 107.6, 117.5, 125.4, 126.8, 137.7, 149.5. IR (KBr): 3500, 3450, 1600, 1530, 1320, 740, 730 cm^{-1} . MS (EI) m/z : 297 [$(\text{M}+1)^+$, 4], 267 (100). Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{ClN}_2\text{O}_3$: C, 67.79; H, 7.58; N, 5.27. Found C, 67.71; H, 7.56; N, 5.19.

2-Naphthalen-2-yl-1H-indole (2b). ^1H NMR (200 MHz, CDCl_3): δ 6.93 (s, 1H), 7.24-8.02 (m, 11H), 8.49 (s, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 100.6, 110.9, 120.3, 120.7, 122.5, 123.0, 123.7, 126.1, 126.6, 127.8, 128.1, 128.3, 128.7, 129.6, 132.8, 133.5, 137.0, 137.8. IR (neat): 3440 cm^{-1} . MS (EI) m/z : 244 [$(\text{M}+1)^+$, 100]. Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{N}$: C, 88.86; H, 5.39; N, 5.76. Found C, 88.79; H, 5.31; N, 5.79.

1,3-Diphenyl-3-(2-phenyl-1H-indol-3-yl)-propan-1-one (4c). ^1H NMR (200 MHz, CDCl_3): δ 3.80-3.95 (m, 2H), 5.25-5.40 (m, 1H), 7.00-7.75 (m, 18H), 8.05 (bs, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 36.8, 44.5, 111.1, 119.7, 120.6, 122.0, 125.9, 127.6, 128.0, 128.1, 128.40, 128.42, 128.44, 128.7, 128.8, 132.8, 136.9, 144.5, 198.7. IR (neat): 3380, 1660, 1600, 745, 660 cm^{-1} . MS (ESI) m/z : 401 (M^+ , 34), 282 (100), 204 (19), 105 (14), 77 (16). Anal. Calcd. for $\text{C}_{29}\text{H}_{23}\text{NO}$: C, 86.75; H, 5.77; N, 3.49. Found C, 86.74; H, 5.75; N, 3.46.

4-(2-Naphthalen-2-yl-1H-indol-3-yl)-butan-2-one (4e). ^1H NMR (200 MHz, CDCl_3): δ 2.05 (s, 3H), 2.74-2.82 (m, 2H), 3.19-3.27 (m, 2H), 7.13-7.92 (m, 11H), 8.30 (bs, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 19.3, 29.8, 44.6, 111.6, 112.1, 119.1, 119.5, 122.4, 126.3, 126.5, 126.8, 127.0, 128.0, 128.4, 128.7, 129.3, 131.2, 132.9, 133.9, 134.7, 137.0, 208.2. IR (neat): 3400, 1730, 750 cm^{-1} . MS (ESI) m/z : 313 (M^+ , 55), 257 (100). Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{NO}$: C, 84.31; H, 6.11; N, 4.47. Found C, 84.28; H, 6.09; N, 4.51.

4-(2-Naphthalen-2-yl-1H-indol-3-yl)-cycloheptanone (4f). ^1H NMR (200 MHz, CDCl_3): δ 0.87-2.74 (m, 9H), 3.40-3.46 (m, 2H), 7.11-7.90 (m, 11H), 8.32 (bs, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 24.4, 29.6, 34.5, 37.8, 43.8, 50.5, 111.2, 119.4, 120.4, 122.1, 126.4, 126.6, 127.7, 128.1, 128.5, 133.3, 214.2. IR (neat): 3340, 1680, 760 cm^{-1} . MS (ESI) m/z : 353 (M^+ , 100), 295 (37), 269 (69). Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{NO}$: C, 84.95; H, 6.56; N, 3.96. Found C, 84.88; H, 6.39; N, 3.99.

4-(5-Methyl-2-phenyl-1H-indol-3-yl)-butan-2-one (4g). ^1H NMR (200 MHz, CDCl_3): δ 2.05 (s, 3H), 2.44 (s, 3H), 2.66-2.74 (m, 2H), 3.08-3.16 (m, 2H), 6.96-7.47 (m, 8H), 8.14 (bs, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 18.7, 21.5, 29.6, 44.5, 110.6, 111.0, 116.1, 116.4, 123.6, 127.5, 127.8, 128.8, 132.8, 133.1, 134.2, 134.5, 209.0. IR (KBr): 3400, 1710, 1600, 760, 690 cm^{-1} . MS (ESI) m/z : 277 (M^+ , 100), 221 (69). Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}$: C, 82.28; H, 6.90; N, 5.05. Found C, 82.26; H, 6.86; N, 5.04.

4-[2-(4-chloro-phenyl)-1H-indol-3-yl]-butan-2-one (4h). ^1H NMR (200 MHz, CDCl_3): δ 2.06 (s, 3H), 2.71-2.79 (m, 2H), 3.08-3.16 (m, 2H), 7.11-7.57 (m, 8H), 8.19 (bs, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): δ 18.7, 29.9, 44.3, 111.0, 112.0, 118.9, 119.6, 122.6, 128.6, 129.0, 131.4, 133.2, 133.6, 135.9, 208.6. IR (neat): 3400, 1710, 730 cm^{-1} . MS (ESI) m/z : 297 (M^+ , 61), 240 (100), 205 (33). Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{ClNO}$: C, 72.60; H, 5.42; N, 4.70. Found C, 72.56; H, 5.41; N, 4.66.

4-[5,7-Dichloro-2-(3,4-dihydronaphthalen-1-yl)-1H-indol-3-yl]-butan-2-one (4i). ^1H NMR (200 MHz, CDCl_3): δ 2.06 (s, 3H), 2.45-2.53 (m, 2H), 2.64-2.72 (m, 2H), 2.85-2.95 (m, 4H), 6.27 (t, J = 4.6 Hz, 1H), 6.81-6.84 (m, 1H), 7.10-7.21 (m, 4H), 7.45 (d, J = 1.5 Hz, 1H), 8.16 (bs, 1H). ^{13}C

NMR (50, 3 MHz, CDCl₃): δ 18.8, 23.0, 27.2, 29.7, 44.2, 113.7, 116.7, 117.0, 121.4, 124.8, 125.1, 126.7, 127.8, 127.9, 129.9, 130.3, 131.2, 132.3, 133.6, 135.6, 136.1, 208.1. IR (neat): 3445, 1710, 720 cm⁻¹. MS (ESI) m/z : 386 [(M+2)⁺, 13], 385 [(M+1)⁺, 46], 384 (M⁺, 23), 383 [(M-1)⁺, 73], 329 (19), 328 (46), 327 (74), 326 (96), 325 (100). Anal. Calcd. for C₂₂H₁₉Cl₂NO: C, 68.76; H, 4.98; N, 3.64. Found C, 68.70; H, 4.93; N, 3.66.

4-(2-Ethynyl-phenylamino)-butan-2-one (8a). ¹H NMR (200 MHz, CDCl₃): δ 2.11 (s, 3H), 2.66-2.73 (m, 2H), 3.39-3.45 (m, 3H), 4.86 (bs, 1H), 6.59 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H). ¹³C NMR (50, 3 MHz, CDCl₃): δ 30.2, 37.7, 44.5, 80.5, 83.1, 106.5, 109.3, 116.3, 130.3, 132.7, 148.9, 207.4. IR (neat): 3400, 3280, 2080, 1715, 735 cm⁻¹. MS (ESI) m/z : 188 [(M+1)⁺, 48], 187 (M⁺, 100), 130 (23). Anal. Calcd. for C₁₂H₁₃NO: C, 76.98; H, 7.00; N, 7.48. Found C, 76.93; H, 7.03; N, 7.46.

4-(2-Phenylethynyl-phenylamino)-butan-2-one (8b). ¹H NMR (200 MHz, CDCl₃): δ 2.16 (s, 3H), 2.76 (t, J = 6.3 Hz, 2H), 3.49 (t, J = 6.3 Hz, 2H), 6.59-6.68 (m, 2H), 7.15-7.20 (m, 1H), 7.32-7.37 (m, 4H), 7.52-7.57 (m, 2H). ¹³C NMR (50, 3 MHz, CDCl₃): δ 30.3, 37.9, 42.7, 85.7, 95.2, 107.9, 109.4, 116.5, 123.2, 128.1, 128.3, 129.9, 131.4, 132.2, 148.3, 207.6. IR (neat): 3400, 2200, 1720, 680 cm⁻¹. MS (ESI) m/z : 263 (M⁺, 100), 206 (52). Anal. Calcd. for C₁₈H₁₇NO: C, 82.10; H, 6.51; N, 5.32. Found C, 82.05; H, 6.48; N, 5.34.

4-(2-Naphthalen-2-yl-indol-1-yl)-butan-2-one (9a). ¹H NMR (200 MHz, CDCl₃): δ 1.95 (s, 3H), 2.65-2.72 (m, 2H), 4.49-4.56 (m, 2H), 6.63 (s, 1H), 6.63-7.93 (m, 11H). ¹³C NMR (50, 3 MHz, CDCl₃): δ 30.1, 38.6, 43.0, 103.4, 109.8, 120.2, 120.7, 121.9, 126.5, 126.6, 126.8, 127.7, 128.1, 128.2, 128.3, 128.5, 130.1, 132.8, 133.2, 137.3, 140.9, 206.3. IR (neat): 1710, 760 cm⁻¹. MS (ESI) m/z : 314 [(M+1)⁺, 100], 257 (59). Anal. Calcd. for C₂₂H₁₉NO: C, 84.31; H, 6.11; N, 4.47. Found C, 84.27; H, 6.14; N, 4.45.

4-Indol-1-yl-butan-2-one (9b). ¹H NMR (200 MHz, CDCl₃): δ 2.15 (s, 3H), 2.95 (t, J = 6.6 Hz, 2H), 4.42 (t, J = 6.6 Hz, 2H), 6.47 (d, J = 4.6 Hz, 1H), 7.07-7.35 (m, 4H), 7.62 (d, J = 7.6 Hz, 1H).

¹³C NMR (50, 3 MHz, CDCl₃): δ 30.3, 40.5, 43.3, 101.4, 109.0, 119.4, 121.0, 121.5, 128.1, 132.8, 135.0, 206.2. IR (neat): 1725, 725 cm⁻¹. MS (ESI) *m/z*: 188 [(M+1)⁺, 71), 187 (M⁺, 100), 145 (76) 130 (73). Anal. Calcd. for C₁₂H₁₃NO: C, 76.98; H, 7.00; N, 7.48. Found C, 76.97; H, 7.04; N, 7.45.

4-(2-Phenyl-indol-1-yl)-butan-2-one (9c). ¹H NMR (200 MHz, CDCl₃): δ 1.98 (s, 3H), 2.69 (t, J = 7.6 Hz, 2H), 4.45 (t, J = 7.6 Hz, 2H), 6.52 (s, 1H), 7.13-7.44 (m, 8H), 7.62 (d, J = 7.7 Hz, 1H). ¹³C NMR (50, 3 MHz, CDCl₃): δ 30.1, 38.5, 43.1, 102.8, 109.7, 120.1, 120.7, 121.8, 128.1, 128.4, 128.6, 129.2, 132.7, 137.1, 141.0, 206.2. IR (neat): 1715, 690 cm⁻¹. MS (ESI) *m/z*: 263 (M⁺, 100), 207 (87). Anal. Calcd. for C₁₈H₁₇NO: C, 82.10; H, 6.51; N, 5.32. Found C, 82.09; H, 6.50; N, 5.33.

4-[3-(3-Oxo-butyl)-indol-1-yl]-butan-2-one (10a). ¹H NMR (200 MHz, CDCl₃): δ 2.06 (s, 3H), 2.12 (s, 3H), 2.76-3.02 (m, 6H), 4.30 (t, J = 6.6 Hz, 2H), 6.88 (s, 1H), 7.07-7.29 (m, 3H), 7.54 (d, J = 7.5 Hz, 1H). ¹³C NMR (50, 3 MHz, CDCl₃): δ 19.1, 29.9, 30.53, 40.2, 43.3, 44.0, 109.1, 113.9, 118.8, 121.6, 125.5, 127.7, 135.8, 206.4, 208.7. IR (neat): 1720, 725 cm⁻¹. MS (ESI) *m/z*: 257 (M⁺, 81), 200 (100). Anal. Calcd. for C₁₆H₁₉NO₂: C, 74.68; H, 7.44; N, 5.44. Found C, 74.69; H, 7.47; N, 5.39.

4-[3-(3-Oxo-butyl)-2-phenyl-indol-1-yl]-butan-2-one (10b). ¹H NMR (200 MHz, CDCl₃): δ 1.94 (s, 3H), 2.00 (s, 3H), 2.58-2.66 (m, 4H), 2.89-2.97 (m, 2H), 4.27 (t, J = 7.4 Hz, 2H), 7.13-7.60 (m, 9H), 7.72. ¹³C NMR (50, 3 MHz, CDCl₃): δ 18.8, 29.7, 30.0, 38.3, 43.2, 44.7, 109.6, 112.6, 118.9, 119.5, 121.9, 128.4, 128.7, 130.4, 131.6, 135.9, 206.3, 206.5. IR (neat): 1720, 730, 690 cm⁻¹. MS (ESI) *m/z*: 333 (M⁺, 60), 276 (100), 218 (61). Anal. Calcd. for C₂₂H₂₃NO₂: C, 79.25; H, 6.95; N, 4.20. Found C, 79.28; H, 6.91; N, 4.19.

4-[1-(3-Oxo-butyl)-2-phenyl-1H-indol-3-yl]-octan-2-one (10c). ¹H NMR (200 MHz, CDCl₃): δ 0.74 (t, J = 6.5 Hz, 3H), 1.06-1.20 (m, 4H), 1.50-1.65 (m, 1H), 1.91 (s, 3H), 1.96 (s, 3H), 2.58-2.66 (m, 4H), 2.67-2.82 (m, 1H), 3.05-3.20 (m, 1H), 4.18-4.25 (m, 2H), 7.11-7.48 (m, 8H), 7.72 (d, J = 7.5 Hz, 1H). ¹³C NMR (50, 3 MHz, CDCl₃): δ 13.9, 22.5, 30.1, 33.0, 35.1, 38.3, 43.3, 49.8, 109.7, 115.6, 119.2, 120.1, 121.6, 128.5, 130.4, 130.8, 131.9, 136.3, 137.6, 206.4, 208.5. IR (neat):

1720, 730, 680 cm^{-1} . MS (ESI) m/z : 389 (M^+ , 30), 332 (100). Anal. Calcd. for $\text{C}_{26}\text{H}_{31}\text{NO}_2$: C, 80.17; H, 8.02; N, 3.60. Found C, 80.16; H, 8.03; N, 3.63.

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