

“One-Step” Alkynylation of Adamantyl Iodide with Silver-(I) Acetylides

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^1H and ^{13}C n.m.r spectra were recorded on a Bruker DRX500 (500.13MHz; 125.77MHz) in deuteriochloroform (CDCl_3). Coupling constants are given in Hz and chemical shifts are expressed as δ values in ppm. High and low resolution EI mass spectral data were obtained on a KRATOS MS 25 RFA. Microanalyses were performed by the University of Queensland Microanalytical Service. Column chromatography was undertaken on silica gel (Flash Silica gel 230–400 mesh), with distilled solvents. *N*-Methyl morpholine was distilled from calcium hydride under an argon atmosphere and stored over predried sodium hydroxide pellets. Melting points were determined on a Fischer Johns Melting Point apparatus and are uncorrected. Acetylenes were purchased from the Aldrich Chem. Co. Silver(I) acetylides were stored in the fridge in the absence of light and generally lasted for many months.

Representative procedure: Silver(I) phenylacetylide (159 mg, 0.76 mmol) was added to a solution of 1-iodoadamantane (100 mg, 0.38 mmol) in anhydrous *N*-methyl morpholine (3 mL) and the suspension heated at reflux under argon in the dark. After 16–24 h the solvent was removed under high vacuum; the residue diluted with dichloromethane (~ 3 mL) and passed through celite. The filtrate was then washed with a solution (0.1 M) of sodium azide (20 mL), dried (Na_2SO_4) and evaporated. Column chromatography [petroleum spirit (40–60°C)] of the crude on silica gel gave 1-(phenylethynyl)adamantane as a white solid (60 mg, 67%), which was recrystallized from petroleum spirit (colourless needles), m.p. 82–84°C. ^1H NMR δ 1.70–1.74 (m, 6H), 1.93–1.96 (m, 6H), 1.96–2.03 (m, 3H), 7.22–7.29 (m, 3H), 7.36–7.40 (m, 2H). ^{13}C NMR δ 28.0, 30.0, 36.4, 42.9, 79.3, 98.4, 124.1, 127.3, 128.1, 131.6. Mass spectrum m/z (EI) 236 (M^+ , 100%), 193 (10), 179 (60), 167 (7), 165 (11), 149 (9), 143 (8), 141 (7), 131 (8), 119 (5), 97 (7). *Anal.* Calcd. for $\text{C}_{18}\text{H}_{20}$: C, 91.47; H, 8.53. Found: C, 91.41; H, 8.61.

[(4-Methylphenyl)ethynyl]adamantane. Colourless crystals 28% yield m.p. 89°C. ^1H NMR δ 1.68–1.70 (m, 6H), 1.93–1.94 (m, 6H), 1.95–1.98 (m, 3H), 2.30 (s, 3H), 7.05 (d, 2H, $J=8.0$), 7.25 (d, 2H, $J=8.0$). ^{13}C NMR δ 21.4, 28.1, 30.0, 36.4, 42.9, 79.3, 97.6, 121.0, 128.8, 131.5, 137.2. Mass spectrum m/z (EI) 251 (12), 250 (M^+ , 55%), 194 (5), 193 (22), 178 (6), 156 (6), 115 (5), 91 (6). Calcd. for $\text{C}_{19}\text{H}_{22}$: 250.17215 Found: 250.1718. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{22}$: C, 91.14; H, 8.86. Found: C, 91.38; H, 9.11.

[(4-*n*-Pentylphenyl)ethynyl]adamantane. Colourless crystals 57% yield m.p. 71-76°C. ¹H NMR δ 0.86 (3H, t, J=7.2), 1.24-1.38 (4H, m), 1.52-1.60 (2H, m, J=7.5), 1.69-1.70 (6H, m), 1.93-1.94 (6H, m) 1.96-1.97 (3H, m), 2.55 (2H, t, J=7.6), 7.05 (2H, d, J=8.4), 7.27 (2H, d, J=8.3). ¹³C NMR δ 14.0, 22.5, 28.0, 30.0, 31.0, 31.4, 35.7, 36.4, 42.9, 79.3, 97.6, 121.2, 128.2, 131.5, 142.3. Mass spectrum m/z (EI) 308 (5), 301 (39), 306 (M⁺, 100%), 250 (19), 249 (74), 193 (6), 179 (8), 178 (7), 165 (6), 155 (7), 153 (6), 141 (5), 128 (5), 115 (7), 91 (9), 79 (9), 43 (17), 41 (10). Calcd. for C₂₃H₃₀: 306.23475 Found: 306.2345. *Anal.* Calcd. for C₂₃H₃₀: C, 90.13; H, 9.87. Found: C, 90.06; H, 10.12.

[(2-Chlorophenyl)ethynyl]adamantane. Colourless crystals 62% yield m.p. 63-64°C. ¹H NMR δ 1.71 (6H, bs), 1.98 (9H, bs), 7.13-7.16 (2H, m) 7.33-7.35 (1H, m), 7.39-7.40 (1H, m). ¹³C NMR δ 28.0, 30.4, 36.4, 42.7, 76.3, 104.0, 123.9, 126.2, 128.3, 129.0, 133.1, 135.8. Mass spectrum m/z (EI) 272 (39), 271 (23), 270 (M⁺, 100%), 227 (13), 215 (13), 213 (38), 179 (12), 178 (26), 165 (17), 115 (11), 94 (14), 93 (16), 91 (23), 86 (27), 84 (29), 80 (20), 79 (24), 77 (20), 55 (16), 51 (21), 49 (58), 44 (11), 41 (27), 40 (16), 39 (14). Calcd. for C₁₈H₁₉Cl: 270.1175 Found: 270.1180. *Anal.* Calcd. for C₁₈H₁₉Cl: C, 79.84; H, 7.07. Found: C, 79.82; H, 7.12.

[(4-Methoxyphenyl)ethynyl]adamantane. Colourless crystals 51% yield m.p. 112-114 °C. ¹H NMR δ 1.68-1.70 (6H, m), 1.92-1.93 (6H, m), 1.95-1.97 (3H, m), 3.77 (3H, s), 6.77 (2H, d, J=6.8), 7.27 (2H, d, J=6.8). ¹³C NMR δ 28.0, 30.0, 36.4, 43.0, 55.2, 79.0, 96.8, 113.7, 116.2, 132.9, 158.9. Mass spectrum m/z (EI) 267 (42), 266 (M⁺, 100%), 223 (8), 210 (14), 209 (61), 194 (7), 172 (10), 165 (9), 145 (6), 133 (6), 121 (7), 115 (6), 91 (9), 79 (6), 77 (6), 41 (8), 39 (5). Calcd. for C₁₉H₂₂O: 266.1671 Found: 266.1673. *Anal.* Calcd. for C₁₉H₂₂O: C, 85.67; H, 8.32. Found: C, 85.74; H, 8.53.

1-Adamantyl-2-dimethylamino-5-ethynylbenzene. Pale yellow crystals 20% yield m.p. 71°C. ¹H NMR δ 1.73-1.74 (6H, m), 2.03-2.05 (3H, m), 2.12-2.14 (6H, m) 2.56 (6H, s), 2.99 (1H, s), 7.26 (1H, d, J=8.1), 7.31 (1H, dd, J=8.1, 2.0), 7.42 (1H, d, J=2.0). ¹³C NMR δ 29.2, 37.0, 37.5, 41.3, 47.2, 76.0, 84.3, 119.1, 125.4, 130.4, 131.2, 147.6, 156.5. Mass spectrum m/z (EI) 249 (7), 240 (6), 169 (8), 168 (40), 158 (7), 156 (6), 155 (7), 144 (7), 135 (5), 115 (6), 91 (6), 79 (6), 77 (6), 41 (9). Calcd. for C₂₀H₂₅N: 279.1987 Found: 279.1989. *Anal.* Calcd. for C₂₀H₂₅N: C, 85.97; H, 9.02; N, 5.01. Found: C, 85.96; H, 9.14; N, 4.80.

[(4-Ethynylphenyl)ethynyl]adamantane. Pale yellow oil 40% yield. ¹H NMR δ 1.69-1.70 (6H, m), 1.92-1.94 (6H, m), 1.96-1.98 (3H, m), 3.10 (1H, s), 7.31 (2H, d, J=8.5), 7.36 (2H, d, J=8.5). ¹³C NMR δ 27.9, 30.1, 36.3, 42.7, 78.3, 79.0, 83.5, 100.6, 120.8, 124.7, 131.5, 131.8. Mass spectrum m/z (EI) 261 (22), 260 (M⁺ 100%), 204 (16), 203 (47), 202 (48), 189 (14), 166 (16), 165 (13), 151 (10), 139 (15), 115 (13), 91 (15).

1-Adamantyl-1-hexyne. Colourless oil 29% yield. ^1H NMR δ 0.88 (3H, t, $J=7.2$), 1.34-1.45 (4H, m), 1.64-1.65 (6H, m), 1.80-1.81 (6H, m), 1.91 (3H, m), 2.14 (2H, t, $J=7.1$). ^{13}C NMR δ 13.6, 18.4, 21.8, 28.1, 29.4, 31.4, 36.4, 43.4, 78.8, 89.0. Mass spectrum m/z (EI) 217 (8), 216 (M^+ , 49%), 201 (38), 188 (6), 176 (6), 175 (26), 174 (10), 161 (5), 160 (26), 149 (6), 145 (10), 136 (10), 135 (100), 133 (7), 132 (5), 131 (15), 129 (5), 121 (10), 119 (10), 118 (7), 117 (25), 115 (8), 107 (7), 106 (7), 105 (13), 95 (8), 94 (10), 93 (18), 92 (9), 91 (35), 85 (5), 81 (17), 80 (13), 79 (27), 77 (14), 69 (6), 67 (11), 65 (6), 57 (10), 55 (14), 53 (7), 43 (9), 41 (24), 39 (11). Calcd. for $\text{C}_{16}\text{H}_{24}$: 216.1878 Found: 216.1875.

1-Adamantyl-3,3-dimethyl-1-butyne. Colourless oil 42% yield. ^1H NMR δ 1.15 (9H, s), 1.63-1.65 (6H, m), 1.77-1.79 (6H, m), 1.88-1.90 (3H, m). ^{13}C NMR δ 27.1, 28.2, 29.2, 31.6, 36.5, 43.5, 87.2, 87.5. Mass spectrum m/z (EI) 217 (6), 216 (M^+ , 28%), 202 (17), 201 (100), 173 (7), 160 (5), 159 (22), 145 (24), 143 (74), 121 (19), 119 (18), 117 (23), 115 (16), 109 (7), 108 (8), 107 (23), 106 (7), 105 (33), 103 (7), 95 (15), 94 (10), 93 (35), 92 (11), 91 (66), 81 (20), 80 (10), 79 (57), 63 (6), 57 (14), 55 (25), 53 (23), 52 (5), 51 (12). Calcd. for $\text{C}_{16}\text{H}_{24}$: 216.1878 Found: 216.1878.

1-Adamantyl-2-(cyclohex-1-enyl)ethyne. Pale yellow oil 25% yield. ^1H NMR δ 1.50-1.62 (4H, m), 1.65-1.67 (6H, m), 1.83-1.85 (6H, m), 1.91-1.93 (3H, m), 2.02-2.08 (4H, m), 5.97-5.99 (1H, m). ^{13}C NMR δ 21.6, 22.4, 25.6, 28.1, 29.8, 29.8, 36.4, 43.1, 80.9, 95.7, 120.9, 133.2. Mass spectrum m/z (EI) 241 (8), 240 (M^+ , 38%), 212 (8), 183 (7), 141 (5), 135 (24), 129 (7), 128 (5), 115 (6), 105 (7), 93 (6), 91 (12), 79 (10), 77 (8), 67 (5), 55(6), 41 (10), 38 (7), 36 (24). Calcd. for $\text{C}_{18}\text{H}_{24}$: 240.1878 Found: 240.1879.

1-Adamantyl-2-(triisopropylsilyl)ethyne. Opaque oil 25% yield. ^1H NMR δ 0.96-1.04 (3H, m), 1.02 (18H, d, $J=7.0$), 1.65-1.66 (6H, m), 1.85-1.86 (6H, m), 1.89-1.93 (3H, m). ^{13}C NMR (C_6D_6) δ 11.7, 19.1, 28.4, 30.8, 36.7, 43.5, 78.0, 118.8. Mass spectrum m/z (EI) 316 (M^+ , 1), 274 (9), 273 (38), 203 (11), 74 (23). Calcd. for $\text{C}_{21}\text{H}_{36}\text{Si}$: 316.2586 Found: 316.2583.