

DNA-supported palladium nanoparticles as a reusable catalyst for the copper-and ligand-free Sonogashira reaction

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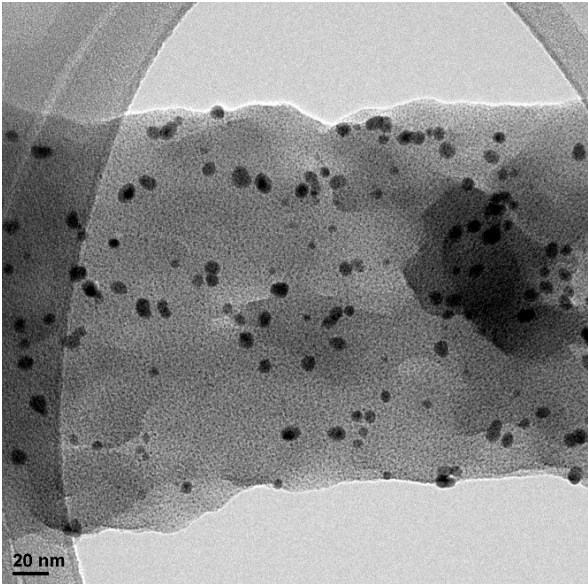
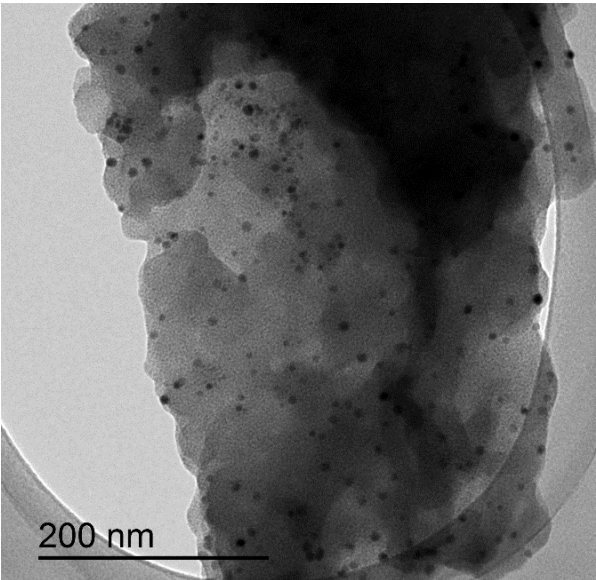
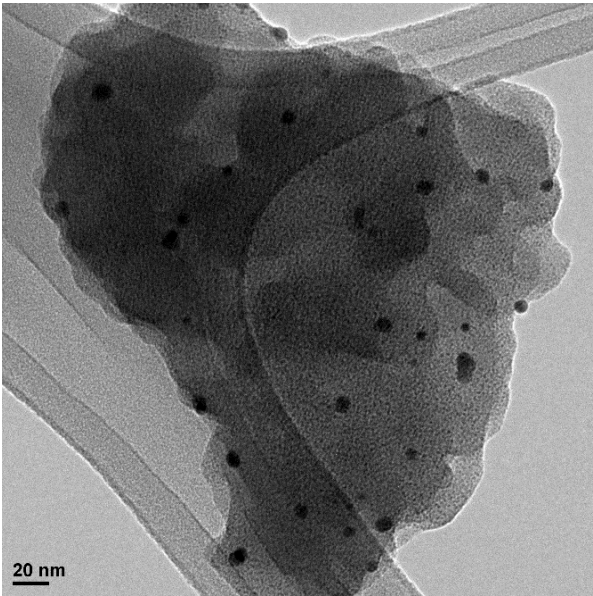
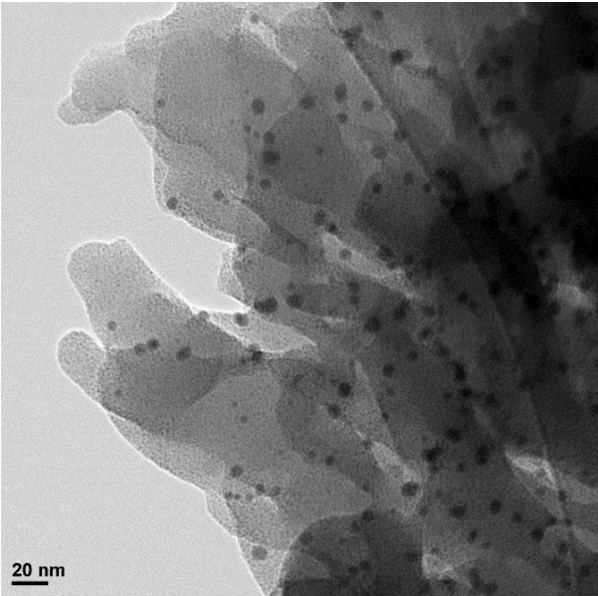
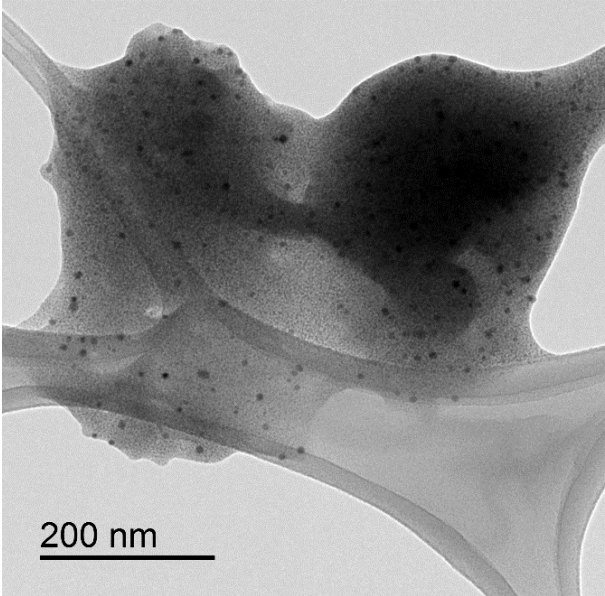
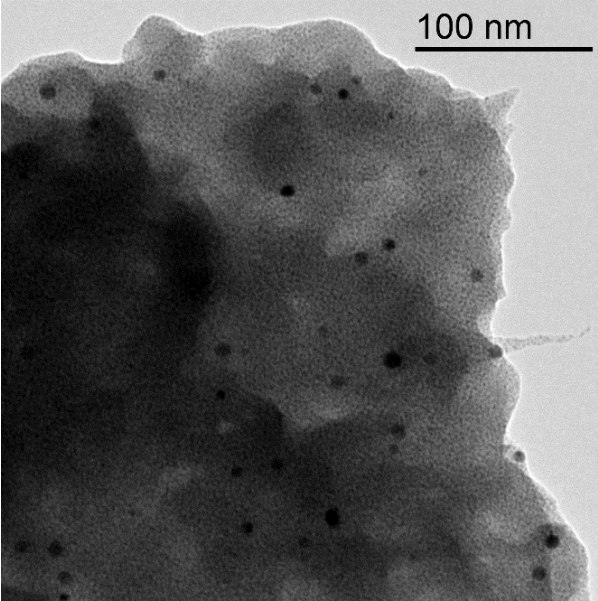
General

All reagents and solvents were commercially available of the best grade (Aldrich, Acros, Alfa Aesar) and were used without further purification. Melting points were measured with a Fisher Johns apparatus and are uncorrected. UV-Vis spectra were obtained on a Thermo Scientific GENESYS 10S spectrophotometer. Infrared analysis was performed with a Jasco 4100LE (Pike MIRacle ATR) spectrophotometer; wavenumbers (ν) are given in cm^{-1} . NMR spectra were recorded on a Bruker Avance 300 (300 MHz for ^1H NMR; 75 MHz for ^{13}C NMR) using CDCl_3 as solvent and TMS as the reference; chemical shifts are given in (δ) parts per million and coupling constants (J) in hertz. Low resolution mass spectra were obtained in the electron impact mode (EI) at 70 eV on an Agilent 5973 spectrometer; fragment ions in m/z with relative intensities (%) in parentheses. HRMS analyses were carried out on Finnigan MAT95S spectrometer. The purity of volatile compounds and the chromatographic analyses (GLC) were determined with an Agilent 6890N instrument equipped with a flame ionization detector and an HP-5MS 30 m capillary column (0.32 mm diameter, 0.25 μm film thickness), using nitrogen (2 mL/min) as carrier gas, $T_{\text{injector}} = 270$ $^{\circ}\text{C}$, $T_{\text{column}} = 60$ $^{\circ}\text{C}$ (3 min) and 60–270 $^{\circ}\text{C}$ (15 $^{\circ}\text{C}/\text{min}$); retention times (t_r) are given in min. Analytical thin layer chromatography was carried out on aluminium sheets with silica gel 60 F₂₅₄ (Merck). Column chromatography and preparative chromatography were performed using silica gel 60 of 40–60 microns and P/UV254, respectively (hexane or hexane/EtOAc as eluent).

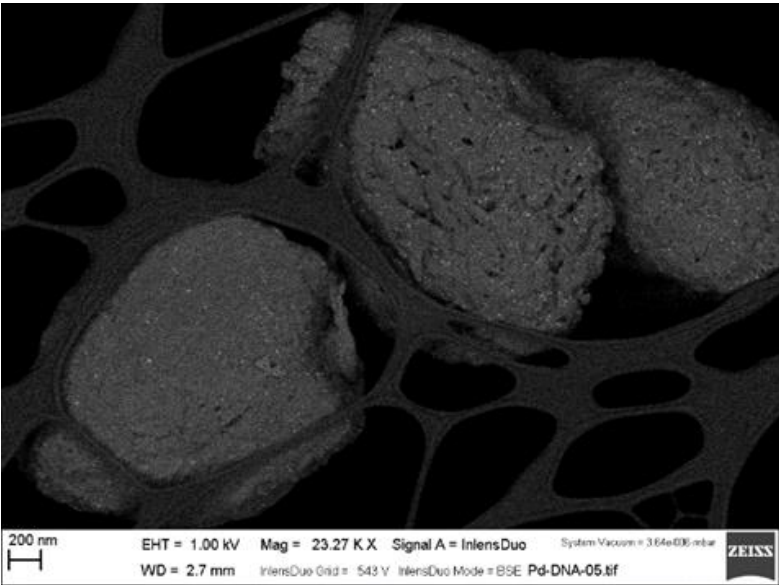
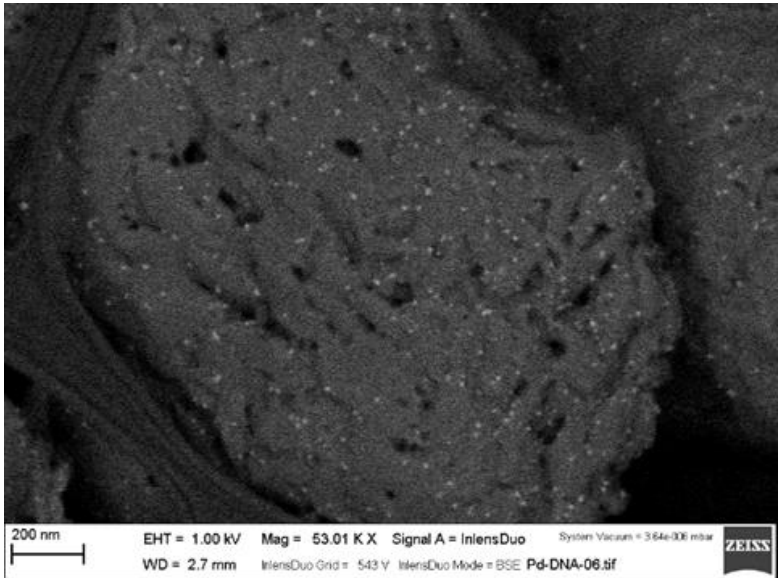
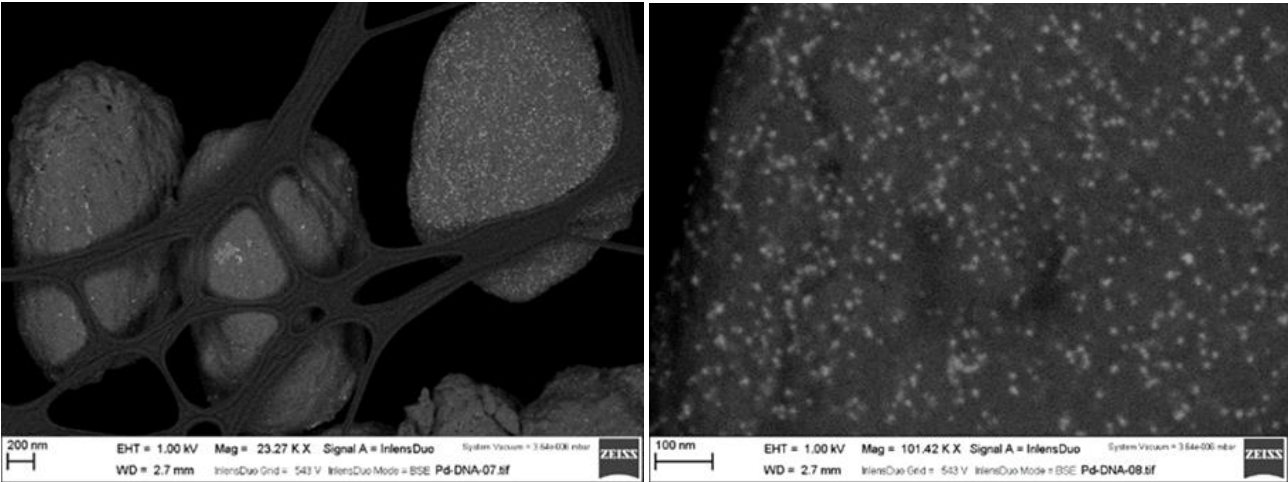
TEM analyses were carried out with a JEOLJEM-2010 apparatus equipped with a Gatan acquisition camera. The size distribution of the palladium nanoparticles was determined by measuring the particle diameter with Image J 1.49b software on the images from TEM. ICP-MS were performed on an Agilent 7700x instrument equipped with HMI (high matrix introduction) and He mode ORS as standard. SEM analyses were carried out on a HITACHI S-3000N apparatus; the equipment consists of a secondary electron detector scintillator-photomultiplier type and a semiconductor retro-dispersed electron detector. EDX is associated with SEM and/or TEM with an X-ray detector 3001 XFlash-type Bruker for microanalysis. The XPS spectra were obtained with a VG-Microtech-Multilab 3000 spectrometer equipped with a semiesferic electron analyser of 9 channeltrons (with pass energy of 2–200 eV) and a radiation source of X-ray with anodes of Mg and Al.

Typical procedure for the preparation of PdNPs/DNA. A 0.5 M solution of Li_2PdCl_4 was prepared by stirring PdCl_2 (1.0 equiv.) and LiCl (2.0 equiv.) in dry MeOH under argon for 24 h at rt. An aliquot of the this solution (0.15 mL) and NaOAc (0.05 g) were added to 0.10 g of salmon-sperm DNA at rt under argon; extra amount of dry methanol (up to 1.0 mL) can be added to facilitate stirring, which was continued for 2–3 days. The mixture was diluted with H_2O (2 mL); the precipitate was filtered and washed with H_2O (3×2 mL) to produce a grey solid that was dried at rt.

Transmission electron microscopy (TEM) images of PdNPs/DNA



Scanning Electron Microscopy (SEM) images of PdNPs/DNA



Typical procedure for the Sonogashira reaction catalysed by PdNPs/DNA

All reactions were performed using tubes in a multi-reactor system under air. Cs_2CO_3 (1.4 mmol, 456 mg) was slowly added to a solution of iodobenzene (**1a**, 1.0 mmol, 0.11 mL) and phenylacetylene (**2a**, 1.0 mmol, 0.10 mL) in MeOH (2 mL), followed by the addition of PdNPs/DNA (8 mg, 0.5 mol%) and additional MeOH (2 mL). The reaction mixture was subjected to constant stirring at 65 °C for 24 h, time after which it became cloudy yellowish as a result of the catalyst being converted into a slurry. The solvent was evaporated under vacuum, followed by the addition of EtOAc (3×5 mL) and washing with water (3×5 mL). The organic phase was dried with anhydrous Mg_2SO_4 , filtered through Celite and the filtrate was evaporated under reduced pressure. The resulting brown amber reaction crude was purified by column chromatography (hexane) to give pale yellow crystals of 1,2-diphenylethyne (**3aa**) in 85% yield.

Leaching study and hot filtration test

Palladium leaching was studied after the first run of a standard reaction (24 h) of **1a** and **2a**: the resulting solution was filtered through celite and a 10 μL aliquot of the filtrate was diluted with 5 mL H_2O and analysed by ICP-MS. The palladium content of this solution was determined to be 0.01 wt% of the original amount.

A standard reaction was interrupted after 2 h and subjected to hot filtration through celite and silica gel. A filtrate aliquot was analysed by GLC showing 33% conversion into **3aa**. The rest of the filtrate was further warmed (24 h) at the same temperature (65 °C), time after which the conversion into **3aa** decreased to 11% as a result of some by-product formation.

Reutilisation of PdNPs/DNA catalyst

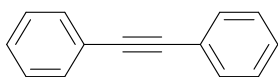
The resulting suspension from a standard Sonogashira reaction was subjected to centrifugation in order to precipitate the PdNPs/DNA catalyst, which was washed with distilled water and ethyl acetate, to remove the remnants of the starting materials and, finally, dried in air. The catalyst was used in subsequent reactions under the same standard conditions.

Comparison of PdNPs/DNA with commercial Pd catalysts

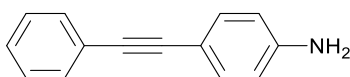
The catalytic activity of PdNPs/DNA was compared with that of commercial PdCl_2 , $\text{Pd}(\text{OAc})_2$, $\text{PdCl}_2(\text{PPh}_3)_2$ and $\text{Pd}(10 \text{ wt\%})/\text{C}$ following the typical procedure for the Sonogashira reaction at a 0.5 mmol scale (see Table 4).

Characterisation of compounds 3

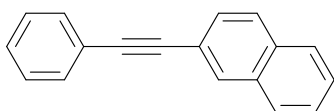
All compounds **3**, except **3ga** (new), were characterised by comparison of their physical and spectroscopic data with those of authentic commercial samples and/or with those described in the literature:



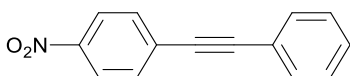
1,2-Diphenylethyne (3aa):¹ White crystals; 0.151 g (85% yield); m.p. 55 °C [lit.,^{1c} 56 °C]; t_r 13.13 min; R_f 0.53 (hexane). IR (neat): ν = 3062, 3031, 1598, 1492, 1442 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.58–7.55 (m, 4H), 7.40–7.36 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ = 131.6, 128.4, 123.3, 89.4. GC-MS (EI): m/z (%) = 178 (100) [M^+], 179 (15), 177 (10), 176 (19), 89 (4), 76 (5).



4-(Phenylethynyl)aniline (3ab):² Brown crystals; 0.150 g (78% yield); m.p. 125–127 °C [lit.,² 126–128 °C]; t_r 15.9 min; R_f 0.52 (hexane/EtOAc, 9:3). IR (neat): ν = 3476, 3380, 3198, 3037, 2920, 2848, 2211, 1615, 1590, 1513 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.48 (d, J = 8.1 Hz, 2H), 7.35–7.27 (m, 5H), 6.61 (d, J = 8.7 Hz, 2H), 3.81 (br s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ = 146.7, 133.0, 131.4, 128.3, 127.7, 123.9, 114.8, 112.6, 90.1, 87.3. GC-MS (EI): m/z (%) = 193 (100) [M^+] 165 (13), 139 (2), 96 (5).

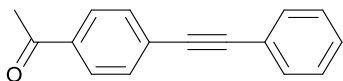


2-(Phenylethynyl)naphthalene (3ba):³ Amber oil; 0.185 g (81% yield); t_r 16.95 min; R_f 0.47 (hexane). IR (neat) ν 3056, 1933, 1884, 1805, 1569, 1488 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 8.48 (d, J = 8.7 Hz, 1H), 7.89 (t, J = 7.7 Hz, 2H), 7.80 (dd, J = 7.2, 1.1 Hz, 1H), 7.70–7.43 (m, 7H), 7.41 (d, J = 1.4, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ = 133.3, 133.2, 131.7, 130.4, 128.8, 128.5, 128.4, 128.3, 126.8, 126.5, 126.3, 125.3, 123.5, 121.0, 94.4, 87.6. GC-MS (EI): m/z (%) = 228 (100) [M^+] 230 (19), 227 (18), 226 (40), 200 (5), 114 (6), 113 (7).

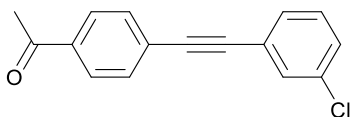


1-Nitro-4-(phenylethynyl)benzene (3ca):² Yellow crystals; 0.144 g (69% yield); m.p. 118 °C [lit.,² 118 °C]; t_r 16.10 min; R_f 0.53 (hexane/EtOAc, 9:1). IR (neat) ν = 3104, 2917, 2848, 2213, 1590, 1508, 1493 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 8.24 (d, J = 9.0 Hz, 2H), 7.69 (d, J = 9.0 Hz,

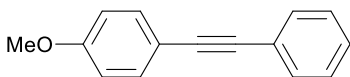
2H), 7.60–7.57 (m, 2H), 7.43–7.40 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ = 147.0, 132.3, 131.9, 130.3, 130.0, 128.6, 123.6, 122.1, 94.7, 87.6. GC-MS (EI): m/z (%) = 223 (100) [M^+], 194 (11), 177 (17), 176 (60), 165 (25), 151 (20), 149 (14).



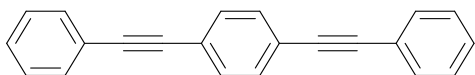
1-[4-(Phenylethynyl)phenyl]ethan-1-one (3da):⁴ Orange crystals, 0.182 g (83% yield); m.p. 87 °C [lit.,⁴ 89–91 °C]; t_r 16.0 min; R_f 0.30 (hexane/EtOAc, 9:1). IR (neat): ν = 3005, 2923, 2854, 2216, 1677, 1601, 1260 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.93 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.57–7.53 (m, 2H), 7.38–7.35 (m, 3H), 2.60 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ = 197.3, 136.2, 131.7, 128.8, 128.5, 128.3, 128.2, 122.6, 92.7, 88.6, 26.6. GC-MS (EI): m/z (%) = 220 (67) [M^+], 221 (11), 206 (16), 205 (100), 177 (17), 176 (46), 151 (15), 150 (9), 88 (10).



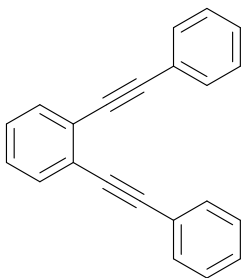
1-[4-[(3-Chlorophenyl)ethynyl]phenyl]ethan-1-one (3dc):⁵ White crystals; 0.176 g (70% yield); m.p. 88 °C; t_r 17.19 min; R_f 0.25 (hexane/EtOAc, 9:1). IR (neat) ν = 3060, 2922, 2852, 2218, 1676, 1598, 1258 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.95 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 7.54 (t, J = 1.5 Hz, 1H), 7.43 (dt, J = 7.1, 1.5 Hz, 1H), 7.37–7.30 (m, 2H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 197.3, 136.5, 134.3, 131.8, 131.6, 129.8, 129.7, 129.1, 128.3, 127.6, 124.4, 91.1, 89.7, 26.7; GC-MS (EI): m/z (%) = 257 (3) [$\text{M}^+ + 1$, Cl^{37}], 256 (19) [M^+ , Cl^{37}], 255 (9) [$\text{M}^+ + 1$, Cl^{35}], 254 (53) [$\text{M}^+ + 1$, Cl^{35}], 241 (32), 240 (15), 239 (100), 177 (8), 176 (51), 175 (9), 150 (8), 119 (6), 88 (7).



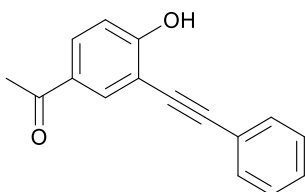
1-(4-Methoxyphenyl)-2-phenylacetylene (3ea):⁶ Pale yellow solid; 0.166 g (80% yield); m.p. 50–52 °C [lit.,⁶ 51–53 °C]; t_r 12.53 min; R_f 0.63 (hexane/EtOAc, 8:2). IR (neat) 3050, 2219, 1508, 1245, 1029, 753 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ = 7.46–7.50 (m, 4H), 7.31–7.34 (m, 3H), 6.88 (d, J = 8.2 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ = 55.3, 88.1, 89.4, 114.0, 115.4, 123.6, 127.9, 128.3, 131.4, 133.0, 159.6. GC-MS (EI): m/z (%) = 209 (17) [$\text{M}^+ + 1$], 208 (100) [M^+], 193 (50), 165 (34), 164 (13), 163 (9), 139 (8).



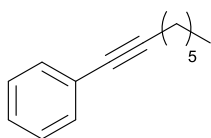
1,4-Bis(phenylethynyl)benzene (3ga):⁷ White solid; 0.144 g (52% yield); m.p. 176–178 °C [lit.,^{6b} 178–180 °C]; t_r 21.63 min, R_f 0.25 (hexane). IR (neat): ν = 3046, 1805, 1736, 1647, 1594, 1513 cm^{-1} . ¹H NMR (300 MHz, CDCl_3): δ = 7.53–7.49 (m, 8H), 7.36–7.31 (m, 6H); ¹³C NMR (75 MHz, CDCl_3): δ = 131.4, 131.3, 128.3, 128.2, 122.9, 122.8, 91.0, 88.9; GC-MS (EI): m/z (%) = $[\text{M}^+]$ (100) 178, 276 (16), 139 (9).



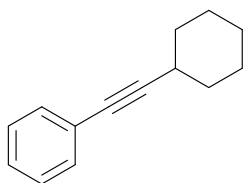
1,2-Bis(phenylethynyl)benzene (3ha):⁸ Orange crystals; 0.128 g (51% yield); m.p. 50 °C [lit.,^{7c} 51–52 °C]; t_r 19.8 min; R_f 0.56 (hexane). IR (neat): ν = 3058, 1953, 1884, 1596, 1493, 1441 cm^{-1} . ¹H NMR (300 MHz, CDCl_3): δ = 7.59–7.55 (m, 6H), 7.36–7.29 (m, 8H). ¹³C NMR (75 MHz, CDCl_3): δ = 131.8, 131.7, 128.4, 128.3, 128.0, 125.9, 123.3, 93.6, 88.4; GC-MS (EI): m/z (%) = 278 (100) $[\text{M}^+]$, 277 (24), 276 (64), 274 (14), 138 (13), 137 (7).



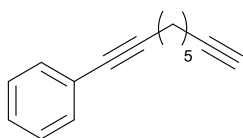
1-[4-Hydroxy-3-(phenylethynyl)phenyl]ethan-1-one (3ia): Yellow crystals; 0.127 g (54% yield); m.p. 175 °C; t_r 17.95 min; R_f 0.42 (hexane/EtOAc, 8:2). IR (neat): ν = 3115, 3082, 3060, 3036, 2995, 2917, 2858, 1671, 1605 cm^{-1} . ¹H NMR (300 MHz, CDCl_3) δ = 8.22 (s, 1H), 7.95 (dd, J = 8.6, 1.8 Hz, 1H), 7.87 (dd, J = 7.0, 1.6 Hz, 2H), 7.55 (d, J = 8.6 Hz, 1H), 7.49–7.37 (m, 3H), 7.07 (s, 1H), 2.67 (s, 3H). ¹³C NMR (75 MHz, CDCl_3): δ 197.63, 157.6, 157.4, 132.9, 129.8, 129.4, 129.1, 128.9, 125.1, 125.0, 122.1, 111.1, 101.6, 26.8. GC-MS (EI): m/z (%) = 236 (64) $[\text{M}^+]$, 221 (100), 193 (37), 165 (20), 164 (9), 139 (14), 110 (8), 82 (7). HRMS (EI): m/z calcd. for $\text{C}_{16}\text{H}_{12}\text{O}$ 236.0837, found 236.0845.



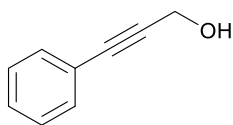
Oct-1-yn-1-ylbenzene (3ad):⁹ Yellow oil; 0.135 g (73% yield); t_r 12.05 min; R_f 0.76 (hexane). IR (neat): $\nu = 3084, 3066, 3035, 3025, 2955, 2929, 2857, 1597, 1488 \text{ cm}^{-1}$. ^1H NMR (300 MHz, CDCl_3): $\delta = 7.41\text{--}7.38$ (m, 2H), 7.29–7.25 (m, 3H), 2.40 (t, $J = 7.0 \text{ Hz}$, 2H), 1.65–1.54 (m, 2H), 1.50–1.40 (m, 2H), 1.34–1.29 (m, 4H), 0.90 (t, $J = 7.0 \text{ Hz}$, 3H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 131.5, 128.2, 127.4, 124.1, 90.5, 80.6, 31.4, 28.8, 28.7, 22.6, 19.4, 14.1$; GC-MS (EI): m/z (%) = 186 (36) [M^+], 157 (16), 144 (24), 143 (64), 142 (8), 130 (23), 129 (58), 128 (51), 127 (12), 115 (100), 102 (20), 91 (25), 89 (10).



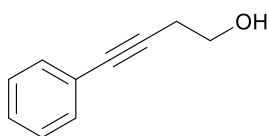
(Cyclohexylethynyl)benzene (3ae):¹⁰ Yellow oil; 0.122 g (68% yield); t_r 12.48 min; R_f 0.62 (hexane). IR (neat): $\nu = 3056, 2953, 2923, 2853, 1953, 1598, 1491, 1444 \text{ cm}^{-1}$. ^1H NMR (300 MHz, CDCl_3): $\delta = 7.43\text{--}7.40$ (m, 2H), 7.31–7.27 (m, 3H), 2.65–2.56 (m, 1H), 1.95–1.87 (m, 1H), 1.83–1.73 (m, 2H), 1.62–1.50 (m, 4H), 1.44–1.33 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 131.2, 127.8, 127.0, 123.8, 94.1, 80.1, 32.4, 29.3, 25.6, 24.6$. GC-MS (EI): m/z (%) = 184 (65) [M^+], 169 (15), 156 (32), 155 (63), 154 (9), 153 (12), 143 (15), 142 (41), 141 (100), 130 (30), 129 (29), 128 (55), 127 (16), 115 (45), 102 (24), 91 (16), 77 (10).



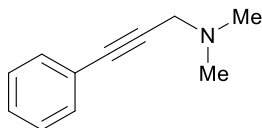
Nona-1,8-diyn-1-ylbenzene (3af):¹¹ Colourless oil; 0.101 g (51% yield); t_r 13.07 min; R_f 0.50 (hexane). IR (neat): $\nu = 3299, 2938, 2859, 1597, 1488 \text{ cm}^{-1}$. ^1H NMR (300 MHz, CDCl_3): $\delta = 7.41\text{--}7.37$ (m, 2H), 7.29–7.24 (m, 3H), 2.42 (d, $J = 6.8 \text{ Hz}$, 2H), 2.25–2.20 (m, 2H), 1.95 (t, $J = 2.7 \text{ Hz}$, 1H), 1.69–1.54 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 131.5, 128.1, 127.5, 123.4, 90.0, 84.4, 80.7, 68.3, 28.2, 27.9, 19.3, 18.3$. GC-MS (EI): m/z (%) = 195 (12) [M^+], 168 (42), 167 (100), 165 (20), 155 (27), 154 (14), 153 (34), 141 (18), 129 (23), 128 (42), 127 (11), 117 (18), 116 (13), 115 (96), 102 (12), 91 (23), 89 (13), 77 (11).



3-Phenylprop-2-yn-1-ol (3ag):^{1b} Yellow oil; 0.112 g (86% yield); t_r 9.98 min; R_f 0.47 (hexane/EtOAc, 8:2). IR (neat): ν = 3323, 2908, 2858, 1586, 1488 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.46–7.42 (m, 2H), 7.33–7.30 (m, 3H), 4.50 (d, J = 6.1 Hz, 2H), 1.81 (br s, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ = 131.6, 128.5, 128.3, 122.5, 87.2, 85.7, 51.6; GC-MS (EI): m/z (%) = 131 (100) [M^+], 115 (22), 104 (23), 103 (49), 102 (23), 78 (24), 77 (33), 63 (11).



4-Phenylbut-3-yn-1-ol (3ah):¹² Light yellow oil; 0.122 g (84% yield); t_r 10.68 min; R_f 0.30 (hexane/EtOAc, 8:2). IR (neat): ν = 3439, 3055, 2929, 2854, 1972, 1597, 1489, 1445 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.43–7.38 (m, 2H), 7.31–7.28 (m, 3H), 3.82 (q, J = 6.2 Hz, 2H), 2.69 (t, J = 6.2 Hz, 2H), 1.88 (t, J = 6.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ = 131.5, 128.1, 127.7, 123.1, 86.2, 82.2, 60.9, 23.6. GC-MS (EI): m/z (%) = 146 (39) [M^+], 116 (35), 115 (100), 89 (9).



***N,N*-Dimethyl-3-phenylprop-2-yn-1-amine (3ai):**¹⁰ Amber oil; 0.112 g (71% yield); t_r 10.33 min; R_f 0.2 (hexane/EtOAc, 8:2). IR (neat) ν = 3065, 2971, 2939, 2821, 2773 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.46–7.42 (m, 2H), 7.31–7.28 (m, 3H), 3.47 (s, 2H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ = 131.5, 128.0, 127.8, 123.0, 85.0, 84.4, 48.4, 44.0. GC-MS (EI): m/z (%) = 158 (95) [M^+], 143 (11), 116 (17), 115 (100), 89 (12), 82 (32).

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NMR spectra of compounds 3

