Supporting Information

Palladium-catalyzed Sonogashira Reactions of Aryl Amines with Alkynes via *in situ*-Formation of Arenediazonium Salts

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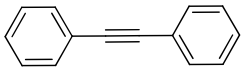
General comments: All reactions were carried out under argon atmosphere. DMSO was distilled from sodium ketyl or CaH and stored in ©Aldrich Sure/Stor flasks under argon. $Pd(OAc)_2$, anilines, alkynes, AcOH, *tert*-BuONO and all the ligands were purchased from Aldrich and used as received. Column chromatography was performed using Merck Silicagel 60 (0.043-0.06 mm). NMR data were recorded on a Bruker ARX 300 and Bruker ARX 400 spectrometers. ^{13}C and ^{1}H NMR spectra were referenced to signals of deutero solvents and residual protiated solvents, respectively. Gas chromatography analysis was performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thickness) using argon as carrier gas. Gas chromatography-mass analysis was carried out on an Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.25 mm i.d., 0.25 µm film thickness) using helium carrier gas.

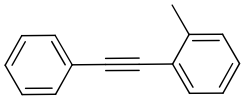
General procedure for the Sonogashira reaction: A 10 mL Schlenk flask, charged with $Pd(OAc)_2$ (2 mol%), TFP (6 mol%), a stirring bar and septum, was evacuated and backfilled with argon (the cycle was performed three times) and then charged under a positive pressure of argon with DMSO (2 ml), aniline (1.3 mmol), AcOH (1.3 mmol), *tert*-BuONO (1.3 mmol) and phenyl acetylene (1 mmol) at room temperature. Then, the Schlenk was transferred to an oil bath and heated at 32°C for 16 hours. The cooled mixture was partitioned between ethyl acetate and saturated NH_4Cl, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to provide the desired product.

1,2-Diphenylethyne



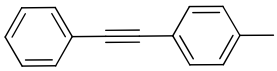
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.67 (m, 4H), 7.38-7.48 (m, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 131.6, 128.3, 128.2, 123.2, 89.4.
GC-MS (EI, 70eV): m/z(%) = 178 (M^+, 100), 152 (10), 89 (5), 76 (5).

1-Methyl-2-(phenylethynyl)benzene



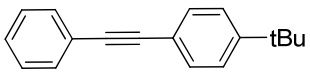
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25-7.60 (m, 9H), 2.61 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 140.4, 132.1, 131.7, 129.7, 128.6, 128.5, 128.4, 125.8, 123.8, 123.2, 93.6, 88.6, 20.9.
GC-MS (EI, 70eV): m/z(%) = 192 (M^+, 100), 191 (98), 165 (20), 115 (10).

1-Methyl-4-(phenylethynyl)benzene



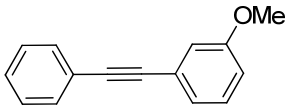
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.53 (m, 2H), 7.41-7.44 (m, 2H), 7.32-7.38 (m, 3H), 7.14-7.17 (m, 2H), 2.36 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 138.3, 131.5, 131.4, 129.1, 128.3, 128.1, 123.4, 120.1, 89.5, 88.6, 21.5.
GC-MS (EI, 70eV): m/z(%) = 192 (M^+, 100), 165 (10).

1-*tert*-Butyl-4-(phenylethynyl)benzene



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.53 (m, 5 H), 7.31-7.38 (m, 4 H), 1.33 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 151.6, 131.8, 131.6, 128.5, 128.3, 125.4, 123.8, 120.5, 89.8, 88.7, 35.0, 31.4.
GC-MS (EI, 70eV): m/z(%) = 234 (M^+, 40), 219 (100), 202 (10), 191 (10), 178 (10).

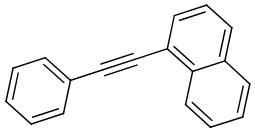
1-Methoxy-3-(phenylethynyl)benzene



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64-7.71 (m, 2H), 7.41-7.48 (m, 3H), 7.36 (t, 1H, *J* = 7.9Hz), 7.25-7.25 (m, 1H), 7.19-7.23 (m, 1H), 6.98-7.03 (m, 1H), 3.89 (s, 3H).

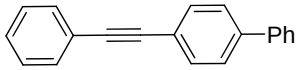
^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 131.5, 129.3, 128.3, 128.2, 124.2, 124.1, 123.1, 116.3, 114.8, 89.3, 89.2, 55.1.
GC-MS (EI, 70eV): m/z(%) = 208 (M^+, 100), 178 (25), 165 (25), 139 (10).

1-(Phenylethynyl)naphthalene



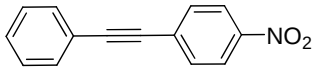
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43-8.46 (m, 1H), 7.75-7.89 (m, 3H), 7.24-7.65 (m, 8H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 133.2, 133.1, 131.6, 130.3, 128.42, 128.45, 128.3, 128.2, 126.7, 126.4, 126.2, 125.3, 123.3, 120.8, 94.3, 87.5.
GC-MS (EI, 70eV): m/z(%) = 228 (M^+, 100), 202 (10).

4-(Phenylethynyl)biphenyl



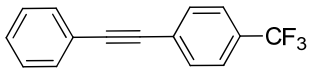
^{1}H NMR (300 MHz, $CDCl_3$): δ7.52-7.64 (m, 8 H), 7.44-7.49 (m, 2 H), 7.36-7.41 (m, 4 H).
^{13}C NMR (75 MHz, $CDCl_3$): δ140.9, 140.4, 132.1, 131.6, 128.9, 128.4, 128.2, 127.7, 127.0, 123.1, 122.1, 90.0, 89.4.
GC-MS (EI, 70eV): m/z(%) = 254 (M^+, 100).

1-Nitro-4-(phenylethynyl)benzene



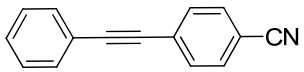
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, 2H, *J*= 8.9Hz), 7.59 (d, 2H, *J*= 8.9Hz), 7.47-7.55 (m, 2H), 7.30-7.39 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 146.9, 132.2, 131.8, 130.2, 129.2, 128.5, 123.6, 122.0, 94.6, 87.5.
GC-MS (EI, 70eV): m/z(%) = 223 (M^+, 100), 193 (75), 176 (70), 166 (30), 151 (25), 88 (10).

1-(Phenylethynyl)-4-trifluoromethylbenzene



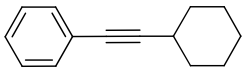
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61-7.64 (m, 4 H), 7.55-7.59 (m, 2 H), 7.36-7.39 (m, 3 H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 131.9, 131.8, 129.9 (*J*=32.4Hz), 128.9, 128.5, 127.1 (*J*= 1.4Hz), 125.2 (*J*= 3.9Hz), 123.9 (*J*= 270.1Hz), 122.6, 91.8, 87.9
GC-MS (EI, 70eV): m/z(%) = 246 (M^+, 100), 227 (10), 176 (10), 98 (10).

4-(Phenylethynyl)benzonitrile



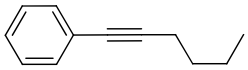
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.67 (m, 6H), 7.38-7.42 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 133.1, 132.1, 131.9, 129.2, 128.6, 128.3, 122.3, 118.6, 111.5, 93.9, 87.8.
GC-MS (EI, 70eV): m/z(%) = 203 (M^+, 100), 176 (10).

(Cyclohexylethynyl)benzene



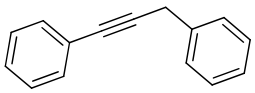
^{1}H NMR (300 MHz, $CDCl_3$): δ7.30-7.36 (m, 2H), 7.16-7.24 (m, 3H), 2.47-2.56 (m, 1H), 1.23-1.82 (m, 10H)
^{13}C NMR (75 MHz, $CDCl_3$): δ131.5, 128.1, 127.3, 124.1, 94.5, 80.5, 32.8, 29.8, 26.1, 25.0.
GC-MS (EI, 70eV): m/z(%) = 184 (M^+, 60), 169 (10), 155 (60), 141 (100), 128 (60), 115 (55), 102 (20), 91 (15), 77 (10), 63 (5), 51 (5).

Hex-1-ynylbenzene



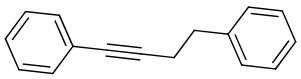
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.60 (m, 2H), 7.35-7.44 (m, 3H), 2.55 (t, 2H, *J*=7.0Hz), 1.69-1.79 (m, 2H), 1.58-1.68 (m, 2H), 1.11 (t, 3H, *J*=7.2Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 131.4, 128.1, 127.3, 124.1, 90.2, 80.6, 30.9, 22.1, 19.1, 13.5.
GC-MS (EI, 70eV): m/z(%) = 158 (M^+, 40), 143 (60), 129 (70), 115 (100), 102 (15), 89 (10), 63 (10).

Prop-1-yne-1,3-diyldibenzene



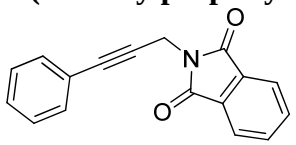
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.47 (m, 4H), 7.24-7.35 (m, 6H), 3.80 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 136.7, 131.5, 128.4, 128.3, 127.9, 127.8, 126.7, 123.6, 87.7, 82.6, 25.5.
GC-MS (EI, 70eV): m/z(%) = 192 (M^+, 100), 191 (99), 162 (20), 115 (10), 95 (10).

But-1-yne-1,4-diyldibenzene



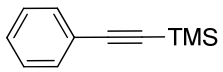
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.37 (m, 2H), 7.23-7.34 (m, 8H), 2.92 (t, 2H, *J* = 7.6 Hz), 2.68 (t, 2H, *J* = 7.6 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 140.8, 131.5, 128.5, 128.5, 128.3, 127.6, 126.3, 123.6, 89.5, 81.5, 35.4, 21.8.
GC-MS (EI, 70eV): m/z(%) = 206 (M^+, 80), 205 (40), 191 (20), 115 (70), 91 (100), 65 (10).

2-(3-Phenylprop-2-ynyl)isoindoline-1,3-dione



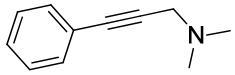
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76-7.82 (m, 2H), 7.60-7.67 (m, 2H), 7.29-7.35 (m, 2H), 7.13-7.22 (m, 3H), 4.59 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 167.1, 134.1, 131.9, 131.8, 128.4, 128.1, 123.4, 122.2, 82.9, 82.6, 27.8.
GC-MS (EI, 70eV): m/z(%) = 261 (M^+, 100), 232 (80), 204 (60), 178 (20), 165 (15), 104 (20), 76 (25).

Trimethyl(phenylethynyl)silane



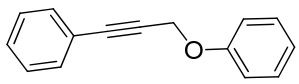
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.43 (m, 2H), 7.17-7.23 (m, 3H), 0.2 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 131.9, 128.5, 128.2, 123.2, 105.2, 94.0, 0.
GC-MS (EI, 70eV): m/z(%) = 174 (M^+, 20), 159 (100).

***N*,*N*-Dimethyl-3-phenylprop-2-yn-1-amine**



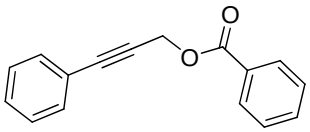
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 6H), 3.62 (s, 2H), 7.09-7.55 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 131.5, 129.2, 129.1, 129.0, 85.9, 83.6, 59.5, 45.2.
GC-MS (EI, 70eV): m/z(%) = 159 (M^+, 50), 158 (50), 132 (10), 118 (15), 91 (100), 82 (80), 68 (40).

(3-Phenoxyprop-1-ynyl)benzene



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15-7.50 (m, 10H), 4.75 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 157.8, 131.8, 129.6, 129.3, 128.7, 128.4, 121.5, 115.1, 87.2, 84.1, 56.6.
GC-MS (EI, 70eV): m/z(%) = 208 (M^+, 20), 115 (100), 89 (10), 65 (10).

3-Phenylprop-2-ynyl benzoate



^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08-8.12 (m, 2H), 7.54-7.60 (m, 1H), 7.43-7.48 (m, 4H), 7.30-7.33 (m, 3H), 5.16 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ165.9, 133.2, 131.9, 129.8, 129.6, 128.7, 128.4, 128.3, 122.2, 53.3.

GC-MS (EI, 70eV): m/z(%) = 236 (M^+, 100), 208 (30), 191 (10).