Supporting Information

Palladium-Catalyzed Carbonylative Sonogashira Coupling between Aryl Triazenes and Alkynes

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1. General Considerations:

NMR spectra were recorded on 300 MHz spectrometer at 295 K in $CDCl_3$ or DMSO. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H-NMR) and 77.00 ppm (^{13}C-NMR); references for d_6-DMSO were 2.50 ppm (^{1}H-NMR) and 40.00 ppm (^{13}C-NMR). High-resolution mass spectrometry (HRMS) was performed using an ESI-TOF/MS. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh.

2. General Preparation of the Aryl Triazenes

Aryl amine (10 mmol) was added to 3.3 mL of 37% HCl (aq.) in 5 mL H_2O at 0 ˚C, then sodium nitrite (1.03 g, 15 mmol) in 3 mL of H_2O was added drop-wise. After stirring for 10 min., the mixture was slowly transferred to a solution of secondary amine (25 mmol) and K_2CO_3 (11 g, 80 mmol) in 30 mL of ice water and MeCN (v/v=2:1). After stirring at room temperature for another 30 min., the misture was extracted with ethyl acetate (20 mL × 3). The combined organic phase was dried over Na_2SO_4 and the product was obtained by column chromatography using pentane (PE) and ethyl acetate (EA) as the eluent. The preparation and NMR spectra of **1a-h, 1j, 1n, 1p** and **1q** data were reported in our previous communication.[1]

3,3-Diethyl-1-(naphthalen-1-yl)triaz-1-ene (1i).[2] Red oil, purified by column chromatography (PE/EA=40), 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 – 8.56 (m, 1H), 7.89 – 7.76 (m, 1H), 7.73 – 7.57 (m, 1H), 7.54 – 7.34 (m, 4H), 3.10 – 2.94 (m, 2H), 1.36 (t, J = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 134.3, 127.8, 127.6, 126.0, 125.8, 125.7, 125.1, 124.9, 124.8, 123.7, 111.5, 42.2, 11.2.

(3-(pyrrolidin-1-yldiazenyl)phenyl)methanol (1k). Colorless thick oil, purified by column chromatography (PE/EA=3), 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (t, J = 1.8 Hz, 1H), 7.39 – 7.23 (m, 2H), 7.10 (dt, J = 7.1, 1.7 Hz, 1H), 4.60 (s, 2H), 3.92 – 3.54 (m, 4H), 3.74 (s, 1H), 2.06 – 1.85 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 141.6, 128.5, 123.4, 119.1,

118.4, 64.4, 48.1, 23.4. EI-MS m/z (rel intensity): 205 ([M]$^+$, 27), 135 (59), 107 (98), 89 (100), 77 (59). HRMS (ESI) Calc. for $C_{11}H_{16}N_3O$ $(M+H)^+$: 206.12879; found: 206.12868.

1-((4-Methoxyphenyl)diazenyl)pyrrolidine (1l).[3] Light yellow solid, purified by column chromatography (PE/EA=40), 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 3.83 – 3.75 (m, 4H), 2.05 – 2.00 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 145.2, 129.2, 121.1, 113.9, 55.3, 48.4, 23.7.

2-Methyl-5-(pyrrolidin-1-yldiazenyl)benzonitrile (1m). Light yellow solid, mp 80 – 82 °C; purified by column chromatography (PE/EA=5), 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.3 Hz, 1H), 7.48 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 4.02 – 3.46 (m, 4H), 2.47 (s, 3H), 2.00 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 137.6, 130.5, 124.8, 124.7, 123.6, 118.3, 112.6, 51.0, 46.3, 23.6, 19.7. EI-MS m/z (rel intensity): 214 ([M]$^+$, 40), 144 (48), 116 (100), 89 (43). HRMS (ESI) Calc. for $C_{12}H_{15}N_4$ $(M+H)^+$: 215.12912; found: 215.12916.

1-((3,4,5-trimethoxyphenyl)diazenyl)piperidine (1o). Light yellow solid, mp 86 – 88 °C; purified by column chromatography (PE/EA=5), 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (s, 2H), 3.87 (s, 6H), 3.82 (s, 3H), 3.78 – 3.71 (m, 4H), 1.75 – 1.63 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 146.8, 136.0, 97.5, 60.9, 55.9, 48.1, 25.2, 24.3. EI-MS m/z (rel intensity): 279 ([M]$^+$, 40), 167 (100), 152 (25), 137 (17). HRMS (ESI) Calc. for $C_{14}H_{22}N_3O_3$ $(M+H)^+$: 280.16557; found: 280.16570.

3. Typical procedure for carbonylative Sonogashira reactions

To each Wheaton vial (10 mL volume) equipped with a septum, a small cannula, and a stirring bar was added $Pd(OAc)_2$ (4.04 mg, 18 μmol), P(*o*-Tol)$_3$ (10.92 mg, 36 μmol), aryl triazene (0.6 mmol) and alkyne (0.9 mmol). Then vials were purged with argon before THF (4 mL) was injected by syringe. After that, $MeSO_3H$ (47 μL, 0.72 mmol) was added to each vial through a Hamilton syringe. The vials were then placed on an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments in air. After flushing the autoclave three times with CO, a pressure of 20 bar was set and the reaction was stirred for 20 h at 70 °C. After the cooling to room temperature, the pressure was released carefully. The solvent was removed under reduced pressure and the crude products were purified by column chromatography on silica gel (pentane/ethyl acetate).

4. Analytical data of the products.

3-Phenyl-1-(p-tolyl)prop-2-yn-1-one (3aa).[4] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 90) as white solid in 73% yield (96.5 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.63 (m, 2H), 7.52 – 7.37 (m, 3H), 7.34 – 7.27 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 145.2, 134.5, 133.0, 132.9, 130.6, 129.6, 129.6, 129.3, 128.6, 120.2, 92.5, 86.9, 21.8.

1,3-Diphenylprop-2-yn-1-one (3ja).[4] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 90) as white solid in 70% yield (86.6 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 – 8.15 (m, 2H), 7.70 – 7.54 (m, 3H), 7.54 – 7.33 (m, 5H). ^{13}C NMR (75 MHz, None) δ 177.7, 136.6, 133.9, 132.9, 130.6, 129.3, 128.5, 128.4, 119.8, 92.9, 86.7.

3-Phenyl-1-(o-tolyl)prop-2-yn-1-one (3ga).[5] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 60) as yellow oil in 47% yield (62.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.41 – 7.24 (m, 5H), 7.22 – 7.15 (m, 1H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 140.4, 135.7, 133.1, 132.9, 132.1, 130.5, 128.6, 125.8, 120.3, 91.8, 88.3, 21.9.

1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-one (3ba).[6] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 50) as white solid in 70% yield (106.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.09 (m, 2H), 7.70 – 7.62 (m, 2H), 7.52 – 7.36 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 140.6, 135.2, 133.0, 130.9, 130.7, 128.9, 128.6, 119.7, 93.5, 86.5.

3-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (3ca).[6] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 80) as white solid in 77% yield (126.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.73 – 7.65 (m, 2H), 7.55 – 7.46 (m, 1H), 7.48 – 7.39 (m, 2H). δ ^{13}C NMR (101 MHz,

$CDCl_3$) δ 176.6, 139.3, 135.1 (q, J_{F-C} = 32.6 Hz), 133.2, 131.2, 129.7, 125.6 (q, J_{F-C}= 3.8 Hz),128.7, 119.6, 94.4, 86.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7.

4-(3-Phenylpropioloyl)benzonitrile (3da).[7] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 20) as white solid in 84% yield (116.5 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.56 – 7.46 (m, 1H), 7.48 – 7.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 139.5, 133.1, 132.8, 132.4, 131.3, 129.7, 128.7, 120.7, 119.3, 117.8, 117.0, 95.0, 86.3.

Methyl 4-(3-phenylpropioloyl)benzoate (3ea).[5] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 10) as white solid in 75% yield (118.9 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 2H), 8.11 (d, *J* = 8.6 Hz, 2H), 7.68 – 7.60 (m, 2H), 7.48 – 7.41 (m, 1H), 7.42 – 7.33 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 165.8, 139.7, 134.5, 133.0, 130.9, 129.6, 129.2, 128.6, 119.6, 94.0, 86.6, 52.3.

1-Phenyl-3-(m-tolyl)prop-2-yn-1-one (3jb).[8] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 80) as white solid in 73% yield (96.5 mg); ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 – 8.12 (m, 2H), 7.59 – 7.50 (m, 1H), 7.49 – 7.37 (m, 4H), 7.25 – 7.16 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 138.4, 136.8, 134.0, 133.4, 131.7, 130.1, 129.5, 128.5, 128.5, 128.5, 119.8, 93.4, 86.6, 21.1.

3-(4-Ethylphenyl)-1-phenylprop-2-yn-1-one (3jc).[9] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 80) as yellow solid in 69% yield (97.0 mg); ^1H NMR (300 MHz, $CDCl_3$) δ 8.32 – 8.24 (m, 2H), 7.71 – 7.63 (m, 3H), 7.61 – 7.51 (m, 2H), 7.33 – 7.26 (m, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 147.7, 136.9, 133.9, 133.1, 129.4, 128.5, 128.2, 117.1, 93.8, 86.7, 28.9, 15.1.

3-(4-Hexylphenyl)-1-phenylprop-2-yn-1-one (3jf). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 60) as yellow oil in 71% yield (123.7 mg); ^1H NMR (300 MHz, $CDCl_3$) δ 8.28 – 8.18 (m, 2H), 7.67 – 7.53 (m, 3H), 7.57 – 7.44 (m, 2H), 7.29 – 7.18 (m, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.69 – 1.54 (m, 2H), 1.41 – 1.22 (m, 6H), 0.96 – 0.81 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 146.4, 136.9, 133.9, 133.0, 129.4, 128.7, 128.5, 117.1, 93.8, 86.7, 36.0, 31.5, 30.9, 28.8, 22.5, 14.0. EI-MS m/z (rel intensity): 290 ($[M]^+$, 87), 262 (21), 219 (53), 213 (40), 191 (100). HRMS (ESI) Calc. for $C_{21}H_{22}ONa$ $(M+Na)^+$: 313.15629; found: 313.15658.

3-(Naphthalen-1-yl)-1-phenylprop-2-yn-1-one (3jj).[10] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 80) as yellow solid in 87% yield (133.8 mg); ^1H NMR (300 MHz, $CDCl_3$) δ 8.48 – 8.40 (m, 1H), 8.38 – 8.29 (m, 2H), 8.02 – 7.86 (m, 3H), 7.73 – 7.45 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 137.0, 134.0, 133.5, 133.1, 133.0, 131.4, 129.5, 128.6, 128.5, 127.7, 126.9, 125.7, 125.1, 117.6, 91.6, 91.4.

Ferrocenylethynyl phenyl ketone (3jl).[11] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 40) as red solid in 49% yield (92.4 mg); ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 – 8.14 (m, 2H), 7.68 – 7.56 (m, 1H), 7.58 – 7.46 (m, 2H), 4.73 – 4.65 (m, 2H), 4.47 – 4.39 (m, 2H), 4.29 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 137.1, 133.7, 129.3, 128.5, 96.6, 85.5, 73.1, 70.8, 70.8, 70.5, 70.4, 60.2.

1-(4-Methoxyphenyl)-3-(4-propylphenyl)prop-2-yn-1-one (3ld). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 40) as white solid in 71% yield (120.3 mg), mp 66 – 67 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 2.62 (t, *J* = 7.6Hz, 2H), 1.75 – 1.56 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 164.4, 146.0, 133.0, 132.0, 130.4, 128.9, 117.5, 113.9, 93.1, 86.8, 55.6, 38.1, 24.3, 13.8. EI-MS m/z (rel intensity): 278 ($[M]^+$, 75), 263 (100), 235 (55), 171 (40), 128 (36). HRMS (ESI) Calc. for $C_{19}H_{19}O_2$ $(M+H)^+$: 279.13796; found: 279.13816.

3-(4-Butylphenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-yn-1-one (3oe). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 10) as white solid in 52% yield (110.1 mg); mp 50 – 53 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.49 (s, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 3.94 (s, 9H), 2.63 (d, *J* = 7.8 Hz, 2H), 1.67 – 1.51 (m, 2H), 1.43 – 1.24 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 152.9, 146.4, 143.3, 132.9, 132.1, 128.8, 117.0, 106.7, 106.7, 106.6, 93.5, 86.5, 60.88, 60.83, 56.11, 56.05, 35.6, 33.1, 22.1, 13.8. EI-MS m/z (rel intensity): 352 ($[M]^+$, 100), 309 (27), 281 (15), 185 (14). HRMS (ESI) Calc. for $C_{22}H_{24}O_4Na$ $(M+Na)^+$: 375.15668; found: 375.15672.

3-(4-Butylphenyl)-1-(naphthalen-1-yl)prop-2-yn-1-one (3ie). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 100) as yellow solid in 57% yield (106.9 mg), mp 144 – 146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.15 (d, *J* = 8.8Hz, 1H), 8.54 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.76 (m, 1H), 7.64 – 7.41 (m, 5H), 7.19 – 7.08 (m, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.67 – 1.57 (m, 2H), 1.36 – 1.17 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.8, 146.2, 134.9, 134.3, 133.8, 133.1, 133.0, 130.7, 128.8, 128.8, 128.5, 126.7, 126.0, 124.4, 117.3, 92.4, 88.3, 35.7, 33.2, 22.3, 13.9. EI-MS m/z (rel intensity): 312 ([M]$^+$, 72), 184 (12), 269 (40), 241 (100), 127 (19). HRMS (ESI) Calc. for $C_{23}H_{20}ONa$ (M+Na)$^+$: 335.14064; found: 335.14086.

3-(4-Butylphenyl)-1-(4-iodophenyl)prop-2-yn-1-one (3ne). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 100) as yellow solid in 56% yield (130.4 mg), mp 55 – 57 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.82 (m, 4H), 7.63 – 7.55 (m, 2H), 7.26 – 7.19 (m, 2H), 2.71 – 2.59 (m, 2H), 1.67 – 1.54 (m, 2H), 1.43 – 1.29 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 146.7, 137.9, 136.3, 133.2, 130.7, 128.8, 116.9, 102.4, 94.5, 86.4, 35.8, 33.2, 22.3, 13.9. EI-MS m/z (rel intensity): 388 ([M]$^+$, 100), 360 (19), 345 (41), 317 (83), 189 (53), 142 (23), 114(19). HRMS (ESI) Calc. for $C_{19}H_{18}IO$ (M+H)$^+$: 389.03968; found: 389.03972.

3-(2-Bromophenyl)-1-(4-chlorophenyl)prop-2-yn-1-one (3bg).[12] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 65) as white solid in 52% yield (99.7 mg); ^{1}H NMR (300 MHz, THF) δ 8.28 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.76 (m, 2H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.48 (m, 2H). ^{13}C NMR (75 MHz, THF) δ 176.6, 141.4, 136.7, 136.5, 134.1, 132.1, 130.4, 129.3, 127.4, 122.9, 91.6, 90.7.

1-(4-Bromophenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (3qh). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 100) as bwown solid in 71% yield (150.4 mg), mp 133 – 134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 2H), 7.80 – 7.72 (m, 2H), 7.71 – 7.60 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 135.2, 133.1, 133.1, 132.1, 132.0, 130.8, 129.9, 125.6, 125.57 (q, $J_{F\text{-}C}$ = 3.8 Hz). 90.9, 87.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7. EI-MS m/z (rel intensity): 352 ([M]$^+$, 29), 354 ([M]$^+$, 28), 324 (63), 326(62), 197 (100), 176 (16). HRMS (ESI) Calc. for $C_{16}H_9BrF_3O$ (M+H)$^+$: 352.97834 (^{79}Br) and 374.96028 (^{81}Br); found: 352.97806 and 374.96016.

3-(4-Acetylphenyl)-1-(2-bromophenyl)prop-2-yn-1-one (3hi).[13] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 20) as white solid in 42% yield (82.5 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 – 7.89 (m, 3H), 7.77 – 7.59 (m, 3H), 7.51 – 7.36 (m, 2H), 2.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 177.2, 138.1, 137.1, 135.0, 133.6, 133.1, 132.8, 132.8, 132.7, 128.3, 127.4, 121.3, 92.1, 89.6, 26.7.

3-(4-Acetylphenyl)-1-(3-(hydroxymethyl)phenyl)prop-2-yn-1-one (3ki). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 2) as brown oil in 50% yield (82.7 mg); ^{1}H NMR (300 MHz, *d*^{8}-THF) δ 8.11 – 8.03 (m, 2H), 7.87 – 7.80 (m, 2H), 7.70 – 7.63 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.26 (m, 2H), 3.17 (s, 2H), 2.59 (s, 3H). ^{13}C NMR (75 MHz, *d*^{8}-THF) δ 196.7, 177.5, 137.9, 133.9, 133.1, 130.3, 129.5, 129.3, 128.8, 127.7, 125.6, 91.2, 89.4, 64.2, 26.7. HRMS (ESI) Calc. for $C_{18}H_{15}O_3$ (M+H)$^+$: 279.10157; found: 279.10177.

1-(3-Phenoxyphenyl)-3-(thiophen-3-yl)prop-2-yn-1-one (3pk). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 60) as brown oil in 65% yield (119.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 1H), 7.82 – 7.75 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.33 (m, 3H), 7.32 – 7.21 (m, 2H), 7.23 – 7.14 (m, 1H), 7.11 – 7.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 158.0, 156.3, 138.5, 134.1, 130.3, 130.0, 129.9, 126.2, 124.1, 124.0, 119.6, 119.2, 118.6, 88.7, 87.1. EI-MS m/z (rel intensity): 304 ([M]$^+$, 87), 276 (30), 147 (15), 135 (100). HRMS (ESI) Calc. for $C_{19}H_{13}O_2S$ (M+H)$^+$: 305.06308; found: 305.06327.

1,4-Diphenylbut-2-yn-1-one (3jm).[14] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 90) as brown oil solid in 62% yield (82.2 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 – 8.12 (m, 2H), 7.66 – 7.56 (m, 1H), 7.52 – 7.45 (m, 2H), 7.45 – 7.27 (m, 5H), 3.93 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.95, 136.72, 134.35, 133.96, 129.51, 128.78, 128.48, 127.95, 127.15, 93.36, 81.06, 25.47.

Methyl 4-(3-(triisopropylsilyl)propioloyl)benzoate (3en). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 60) as grey solid in 59% yield (101.8 mg), mp 44 – 45 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.6 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 3.93 (s, 3H), 1.21 – 1.08 (m, 21H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6,

166.0, 139.7, 134.5, 129.7, 129.3, 102.7, 99.4, 52.4, 18.5, 11.0. EI-MS m/z (rel intensity): 344 ([M]$^+$, 3), 301 (100), 273 (30), 2455 (59), 163(25). HRMS (ESI) Calc. for $C_{20}H_{29}O_3Si$ (M+H)$^+$: 345.18805; found: 345.18786.

5-(Hept-2-ynoyl)-2-methylbenzonitrile (3mo). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 25) as brown oil in 41% yield (55.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 1.8 Hz, 1H), 8.23 – 8.13 (m, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 2.63 (s, 3H), 2.51 (t, *J* = 7.1 Hz, 2H), 1.73 – 1.58 (m, 2H), 1.56 – 1.42 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 147.7, 135.2, 133.9, 132.7, 130.6, 117.1, 113.3, 98.3, 79.0, 29.7, 22.0, 20.8, 18.9, 13.4. EI-MS m/z (rel intensity): 225 ([M]$^+$, 11), 210 (17), 183 (100), 154 (30), 144 (98), 109 (35). HRMS (ESI) Calc. for $C_{15}H_{15}NONa$ (M+Na)$^+$: 248.10459; found: 248.10463.

4-(4-Phenoxybut-2-ynoyl)benzonitrile (3dp). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 25) as white solid in 55% yield (86.2 mg), mp 90 – 91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.44 – 7.30 (m, 2H), 7.14 – 6.98 (m, 3H), 5.01 (s, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 157.0, 138.8, 132.4, 129.8, 129.7, 122.3, 117.7, 117.3, 115.2, 90.6, 84.0, 55.7. EI-MS m/z (rel intensity): 261 ([M]$^+$, 100), 232 (9), 184 (94), 130 (52), 102 (57), 77 (62), 51(50). HRMS (ESI) Calc. for $C_{17}H_{11}NO_2Na$ (M+Na)$^+$: 284.06820; found: 284.06798.

4-Hydroxy-1-phenylbut-2-yn-1-one (3kq).[15] Prepared according to the GP and purified by column chromatography (PE:EA ratio of 3) as colorless oil in 31% yield (30.1 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 – 8.08 (m, 2H), 7.67 – 7.56 (m, 1H), 7.55 – 7.43 (m, 2H), 4.57 (s, 2H), 2.51 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8, 136.2, 134.5, 129.7, 128.7, 92.3, 83.3, 51.0.

1-(4-Chlorophenyl)-5-hydroxypent-2-yn-1-one (3br). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 4) as yellow oil in 33% yield (41.6 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 3.90 (t, *J* = 6.2 Hz, 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 2.63 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 140.7, 134.9, 130.9, 128.9, 94.1, 80.3, 60.2, 23.5. EI-MS m/z (rel intensity): 208 ([M]$^+$, 5), 180 (64), 178 (100), 149 (35), 139 (47), 115 (62), 75 (45), 31 (79). HRMS (ESI) Calc. for $C_{11}H_{10}ClO_2$ (M+H)$^+$: 209.03638; found: 209.03624.

4-(3-(1-Hydroxycyclohexyl)propioloyl)benzonitrile (3ds). Prepared according to the GP and purified by column chromatography (PE:EA ratio of 5) as brown oil in 37% yield (56.8 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 2.47 (s, 1H), 2.21 – 2.01 (m, 5H), 2.01 – 1.68 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 139.2, 132.5, 132.4, 129.8, 127.5, 117.8, 117.2, 99.8, 80.4, 74.3, 42.3, 37.3, 25.6, 23.6. HRMS (ESI) Calc. for $C_{16}H_{16}NO_2$ (M+H)$^+$: 254.11756; found: 254.11738.

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6. NMR copies of the products.