Supporting Information

Homo-coupling of terminal alkynes using a simple, cheap

Ni(dppe)Cl₂/Ag₂O catalyst system

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General remarks

All reactions were carried out under nitrogen atmosphere with oven-dried glassware. All commercially available reagents were used as received without further purification. With the exception of phenylacetylene and trimethylsilylacetylene, the aromatic terminal alkynes¹ and aliphatic terminal alkynes² were prepared according to the published procedures. Column chromatography was performed on silica gel (200–300 mesh). All yields were referred to isolated yields (average of two runs) of compounds estimated to be >95% pure as determined by ¹H NMR. The known compounds were partly characterized by melting points (for solid samples), MS, ¹H and ¹³C NMR, and compared to authentic samples or the literature data. New compounds were characterized by ¹H NMR, ¹³C NMR and HRMS. Melting points were measured with a X-4 micro melting point apparatus and are uncorrected.

General procedure for the homocoupling of terminal alkynes

An oven-dried 25-mL three-necked flask was charged with Ni(dppe)Cl₂ (0.05 mmol) and Ag₂O (1.0 mmol). Then the terminal alkyne (1 mmol) (if solid) was added. The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. The terminal alkyne (if liquid), DCE (5 mL) were added via a syringe at this time. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was then filtered through a silica-gel pad that was washed with ethyl acetate. The combined organic phases were evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give the desired products.

Characterization data of the products

1,4-Diphenylbuta-1,3-diyne (Table 2, entry 1). White solid: mp 84–85 °C (lit.³ mp 85–86 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.53 (d, *J* = 6.8 Hz, 4H), 7.40–7.31 (m, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 132.5, 129.3, 128.5, 121.8, 81.7, 74.1; MS (EI, *m/z*, rel.%): 203 ([M+1]⁺, 15%), 202 (M⁺, 100%), 200 ([M-2]⁺, 15%). CAS Number: 886-66-8.

1,4-Bis(3-methylphenyl)buta-1,3-diyne (Table 2, entry 2). White solid: mp 67–68 °C (lit.⁴ mp 68–70 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.34 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 2.34 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 138.2, 133.0, 130.2, 129.7, 128.4, 121.7, 81.7, 73.8, 21.2; MS (EI, *m/z*, rel.%): 231 ([M+1]⁺, 10%), 230 (M⁺, 100%), 229 ([M-1]⁺, 10%). CAS Number: 53903-61-0.

1,4-Bis(4-methylphenyl)buta-1,3-diyne (Table 2, entry 3). White solid: mp 135–136 °C (lit.⁴ mp 137–138 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.41 (d, *J* = 7.6 Hz, 4H), 7.14 (d, *J* = 7.6 Hz, 4H), 2.36 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 139.6, 132.5, 129.3, 118.9, 81.6, 73.5, 21.7; MS (EI, *m/z*, rel.%): 231 ([M+1]⁺, 10%), 230 (M⁺, 100%), 229 ([M-1]⁺, 15%). CAS Number: 22666-07-5.

1,4-Bis(3-aminophenyl)buta-1,3-diyne (Table 2, entry 4). Grey green solid: mp 123–124 °C (lit.⁵ mp 124–125 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.11 (t, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.82 (s, 2H), 6.68 (dd, *J* = 8.2, 1.8 Hz, 2H), 3.69 (s, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ 146.4, 129.5, 123.0, 122.6, 118.5, 116.3, 81.7, 73.5; MS (EI, *m/z*, rel.%): 233 ([M+1]⁺, 10%), 232 (M⁺, 100%). CAS Number: 31661-59-3.

1,4-Bis(N-phenylacetamide)buta-1,3-diyne (Table 2, entry 5). Blue solid: mp 249–250 °C. ¹H NMR (DMSO-d₆, 400 MHz): δ 10.10 (s, 2H), 7.87 (s, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 2.05 (s, 6H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 169.0, 139.7, 129.6, 127.2, 122.3, 120.8, 120.7, 81.9, 73.3, 24.1; MS (EI, *m/z*, rel.%): 316 (M⁺, 10%), 274 ([M-42]⁺, 20%), 232 ([M-84]⁺, 100%). CAS Number: 31665-68-6.

1,4-Bis(3-*t*-butylphenylcarbamate)buta-1,3-diyne (Table 2, entry 6). White solid: mp 231–233 °C. ¹H NMR (DMSO-d₆, 400 MHz): δ 9.53 (s, 2H), 7.67 (s, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 1.46 (s, 18H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 152.8, 140.1, 129.6, 126.2, 121.3, 120.7, 119.9, 82.0, 79.7, 73.2, 28.2; MS (MALDI): *m/z* 455 ([M+Na]⁺), 471 ([M+K]⁺). CAS Number: 288619-97-6.

1,4-Bis(2-fluorophenyl)buta-1,3-diyne (Table 2, entry 7). White solid: mp 138–139 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.52 (t, *J* = 7.2 Hz, 2H), 7.40–7.32 (m, 2H), 7.16–7.07 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ 163.8 (d, *J* = 252.1 Hz), 134.4, 131.2 (d, *J* = 7.9 Hz), 124.2 (d, *J* = 3.3 Hz), 115.8 (d, *J* = 20.5 Hz), 110.5 (d, *J* = 15.5 Hz), 78.5, 76.0; MS (EI, *m/z*, rel.%): 239 ([M+1]⁺, 15%), 238 (M⁺, 100%), 236 ([M-2]⁺, 15%). CAS Number: 332919-95-6.

1,4-Bis[*p*-(1-hydroxyethyl)phenyl]buta-1,3-diyne (Table 2, entry 8). Pale yellow solid: mp 161–162 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.51 (d, *J* = 8.4 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 4.96–4.87 (m, 2H), 1.79 (d, *J* = 3.6 Hz, 2H), 1.49 (d, *J* = 6.4 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 147.1, 132.8, 125.6, 120.9, 81.5, 73.9, 70.1, 25.3;

HRMS: calcd. for C₂₀H₁₈O₂: 290.1307 [M⁺]; found: 290.1312.

1,4-Bis[*p*-(1-acetyloxyethyl)phenyl]buta-1,3-diyne (Table 2, entry 9). White solid: mp 127–129 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.50 (d, *J* = 8.0 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 5.86 (q, *J* = 6.6 Hz, 2H), 2.08 (s, 6H), 1.52 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.1, 143.0, 132.7, 126.2, 121.2, 81.4, 74.1, 71.8, 22.1, 21.3; HRMS: calcd. for C₂₄H₂₂O₄: 374.1518 [M⁺]; found: 374.1523.

1,4-Bis(*p*-carbomethoxyphenyl)buta-1,3-diyne (Table 2, entry 10). White solid: mp 189–190 °C (lit.⁶ mp 190–191 °C). ¹H NMR (CDCl₃, 400 MHz): δ 8.02 (d, *J* = 8.4 Hz, 4H), 7.59 (d, *J* = 8.4 Hz, 4H), 3.93 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 166.3, 132.5, 130.6, 129.6, 126.2, 81.9, 76.3, 52.4; MS (EI, *m/z*, rel.%): 318 (M⁺, 90%), 287 ([M-31]⁺, 100%), 259 ([M-59]⁺, 30%), 200 ([M-118]⁺, 30%). CAS Number: 120617-78-9.

1,4-Bis(*p*-benzoylphenyl)buta-1,3-diyne (Table 2, entry 11). White solid: mp 184–185 °C (lit.⁷ mp 185 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.79 (d, *J* = 6.8 Hz, 8H), 7.67–7.59 (m, 6H), 7.50 (t, *J* = 7.6 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ 195.8, 137.9, 137.2, 132.8, 132.5, 130.2, 130.1, 128.5, 125.7, 82.0, 76.5; MS (EI, *m/z*, rel.%): 410 (M⁺, 100%), 333 ([M-77]⁺, 90%), 105 ([M-40]⁺, 40%). CAS Number: 1086430-12-7.

1,4-Bis(*p*-acetylphenyl)buta-1,3-diyne (Table 2, entry 12). Blue solid: mp 176–178 °C (lit.⁷ mp 176 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.94 (d, *J* = 8.4 Hz, 4H), 7.62 (d, *J* = 8.4 Hz, 4H), 2.61 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 197.1, 137.1, 132.7, 128.3, 126.2, 82.0, 76.6, 26.7; MS (EI, *m/z*, rel.%): 286 (M⁺, 40%), 271 ([M-15]⁺,

100%), 228 ($[M-58]^+$, 20%). CAS Number: 217451-41-7.

1,4-Bis(trimethylsilyl)buta-1,3-diyne (Table 2, entry 13). White solid: mp 110–112 °C (lit.⁸ mp 110–113 °C). ^1H NMR (CDCl_3 , 400 MHz): δ 0.18 (s, 18H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 88.1, 86.1, -0.3; MS (EI, m/z , rel.%): 194 (M^+ , 10%), 179 ($[M-15]^+$, 100%). CAS Number: 4526-07-2.

1,6-Diphenoxy-2,4-hexadiyne (Table 2, entry 14). White solid: mp 77–78 °C (lit.⁴ mp 77–79 °C). ^1H NMR (CDCl_3 , 400 MHz): δ 7.30 (t, $J = 7.8$ Hz, 4H), 7.00 (t, $J = 7.2$ Hz, 2H), 6.94 (d, $J = 8.0$ Hz, 4H), 4.75 (s, 4H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 157.5, 129.6, 121.9, 115.0, 74.7, 71.1, 56.3; MS (EI, m/z , rel.%): 262 (M^+ , 5%), 168 ($[M-94]^+$, 100%), 115 ($[M-147]^+$, 60%). CAS Number: 30980-37-1.

1,6-Bis(naphthalen-2-yloxy)hexa-2,4-diyne (Table 2, entry 15). White solid: mp 138–140 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.80–7.72 (m, 6H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.4$ Hz, 2H), 7.20 (s, 2H), 7.15 (d, $J = 8.8$ Hz, 2H), 4.86 (s, 4H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 155.4, 134.3, 129.7, 129.5, 127.8, 127.1, 126.6, 124.2, 118.7, 107.6, 74.7, 71.3, 56.3; MS (EI, m/z , rel.%): 362 (M^+ , 5%), 218 ($[M-144]^+$, 40%), 144 ($[M-218]^+$, 100%). CAS Number: 104109-20-8.

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^1H NMR and ^{13}C NMR spectra of the products**1,4-Diphenylbuta-1,3-diyne (Table 2, entry 1)**

1,4-Bis(3-methylphenyl)buta-1,3-diyne (Table 2, entry 2)

1,4-Bis(4-methylphenyl)buta-1,3-diyne (Table 2, entry 3)

1,4-Bis(3-aminophenyl)buta-1,3-diyne (Table 2, entry 4)

1,4-Bis(N-phenylacetamide)buta-1,3-diyne (Table 2, entry 5)

1,4-Bis(3-tert-butyl phenylcarbamate)buta-1,3-diyne (Table 2, entry 6)

1,4-Bis(2-fluorophenyl)buta-1,3-diyne (Table 2, entry 7)

1,4-Bis[*p*-(1-hydroxyethyl)phenyl]buta-1,3-diyne (Table 2, entry 8)

1,4-Bis[*p*-(1-acetyloxyethyl)phenyl]buta-1,3-diyne (Table 2, entry 9)

1,4-Bis(*p*-carbomethoxyphenyl)buta-1,3-diyne (Table 2, entry 10)

1,4-Bis(p-benzoylphenyl)buta-1,3-diyne (Table 2, entry 11)

1,4-Bis(p-acetylphenyl)buta-1,3-diyne (Table 2, entry 12)

1,4-Bis(trimethylsilyl)-1,3-butadiyne (Table 2, entry 13)

1,6-Diphenoxy-2,4-hexadiyne (Table 2, entry 14)

1,6-Bis(naphthalen-2-yloxy)hexa-2,4-diyne (Table 2, entry 15)