

BiCl₃-Catalyzed Propargylic Substitution Reaction of Propargylic Alcohols with Carbon-, Oxygen-, Sulfur- and Nitrogen-centered Nucleophiles

Supplementary Information

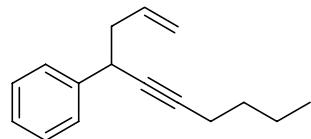
Zhuang-ping Zhan,* Wen-zhen Yang, Rui-feng Yang, Jing-liang Yu,
Jun-ping Li and Hui-juan Liu

Department of Chemistry and The Key Laboratory for Chemical Biology of Fujian Province, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, P. R. China. Fax: +86-592-2185780.

General All reagents were obtained commercially and used without further purification. Acetonitrile was distilled over Phosphorus pentoxide. Melting points are uncorrected. NMR spectra were recorded in CDCl₃ (¹H at 400 MHz and ¹³C at 100 MHz). Column chromatography was performed on silica gel (300-400 mesh).

General procedure for Nucleophilic Substitution of Propargylic Alcohols catalyzed by 10mol% BiCl₃: To a 5-mL flask, 1.0 mmol propargylic alcohol, 3.0 mmol nucleophile, 2 mL CH₃CN and 0.1 mmol BiCl₃ were successively added, the reaction mixture was stirred at 35°C or at 60°C, and monitored periodically by TLC. Upon completion, the solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by silica gel column chromatography (EtOAc/hexane) to afford the substitution products described below.

1-(dec-1-en-5-yn-4-yl)benzene (3aa)¹:

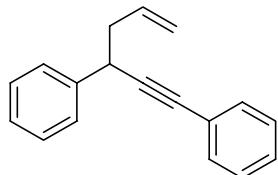


Yield 91%. A pale yellow oil. A pale yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 0.91 (t, 3H, *J* = 7.2 Hz), 1.37-1.55 (m, 4H), 2.23 (td, 2H, *J* = 7.2 and 2.4 Hz), 2.45 (dd, apparent t, 2H, *J* = 7.2 and 7.2 Hz), 3.65 (tt, 1H, *J* = 7.2 and 2.4 Hz), 4.98-5.06 (m, 2H), 5.82 (ddt, 1H, *J* = 17.2, 10.4 and 7.2 Hz), 7.16-7.23 (m, 1H), 7.26-7.36 (m, 4H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 14.1, 18.9, 22.3, 31.5, 38.3, 43.3, 81.0, 83.7, 116.3, 126.2, 127.1, 127.9, 135.4, 141.6 ppm; IR (film): 3062, 3029, 2204, 1644, 1599, 1581,

1494 cm⁻¹.

Data are in accordance with previously reported results.¹

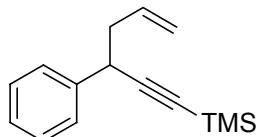
4,6-diphenylhex-1-en-5-yne (3ba)²:



Yield 89%. A pale yellow oil. **¹H NMR** (CDCl₃, 400 MHz): δ 2.61 (dd, apparent t, 2H, *J* = 7.2 and 7.2 Hz), 3.93 (t, 1H, *J* = 7.2 Hz), 5.06-5.16 (m, 2H), 5.93 (ddt, 1H, *J* = 17.1, 10.2 and 7.2 Hz), 7.23-7.51 (m, 10H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 38.8, 43.0, 83.7, 90.8, 116.8, 123.3, 126.4, 127.2, 127.4, 127.8, 128.1, 131.2, 135.0, 140.8 ppm; **IR** (film): 3062, 3029, 2199, 1641, 1598, 1490 cm⁻¹.

Data are in accordance with previously reported results.²

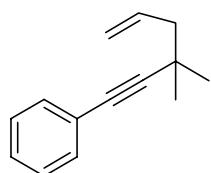
trimethyl(3-phenylhex-5-en-1-ynyl)silane (3ca)¹:



Yield 78%. A colorless oil. **¹H NMR** (CDCl₃, 400 MHz): δ 0.23 (s, 9H), 2.52 (dd, apparent t, 2H, *J* = 7.2 and 7.2 Hz), 3.74 (t, 1H, *J* = 7.2 Hz), 5.04-5.11 (m, 2H), 5.87 (ddt, 1H, *J* = 17.0, 10.2 and 7.2 Hz), 7.20-7.41 (m, 5H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 0.7, 39.2, 43.1, 87.6, 107.4, 116.7, 126.3, 127.1, 128.0, 134.8, 140.5 ppm; **IR** (film): 3064, 3029, 2174, 1641, 1602, 1494 cm⁻¹.

Data are in accordance with previously reported results.¹

1-(3,3-dimethylhex-5-en-1-ynyl)benzene (3da)¹:

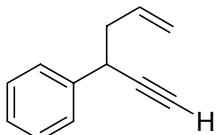


Yield 70%. A pale yellow oil. **¹H NMR** (CDCl₃, 400 MHz): δ 1.28 (s, 6H), 2.26 (d, 2H, *J* = 7.2 Hz) 5.10 (d, 1H, *J* = 16.8 Hz), 5.11 (d, 1H, *J* = 10.0 Hz), 6.01 (ddt, 1H, *J* = 16.4,

10.8 and 7.2 Hz), 7.24-7.29 (m, 3H), 7.36-7.40 (m, 2H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 28.9, 31.5, 47.8, 80.7, 96.9, 117.4, 124.1, 127.5, 128.3, 131.6, 135.3 ppm; **IR** (film): 3078, 3061, 2229, 1641, 1598, 1488, 1443 cm⁻¹.

Data are in accordance with previously reported results.¹

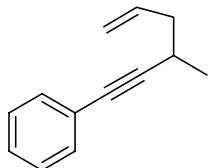
1-(hex-5-en-1-yn-3-yl)benzene (3ea)²:



Yield 61%. A colorless oil. **¹H NMR** (CDCl₃, 400 MHz): δ 2.30 (d, 1H, *J* = 2.4 Hz), 2.52 (dd, apparent t, 2H, *J* = 7.1 and 7.1 Hz), 3.71 (td, 1H, *J* = 7.1 and 2.4 Hz), 5.06 (d, 1H, *J* = 9.3 Hz), 5.08 (d, 1H, *J* = 18.0 Hz), 5.85 (ddt, 1H, *J* = 17.1, 10.2 and 7.0 Hz), 7.20-7.40 (m, 5H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 37.7, 42.4, 71.4, 85.4, 117.2, 126.9, 127.5, 128.5, 135.2, 140.8 ppm; **IR** (film): 3311, 3087, 3023, 2116, 1635, 1599, 1497 cm⁻¹.

Data are in accordance with previously reported results.²

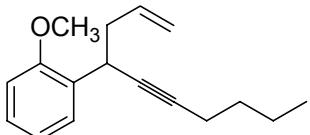
1-(3-methylhex-5-en-1-ynyl)benzene (3fa)¹:



Yield 10%. A pale yellow oil. **¹H NMR** (CDCl₃, 400 MHz): δ 1.26 (d, 3H, *J* = 7.0 Hz), 2.22-2.38 (m, 2H), 2.67-2.78 (m, 1H), 5.06-5.16 (m, 2H), 5.95 (ddt, 1H, *J* = 16.4, 10.8 and 7.2 Hz), 7.23-7.30 (m, 3H), 7.38-7.41 (m, 2H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 20.5, 26.5, 41.1, 81.1, 94.0, 116.7, 123.9, 127.5, 128.1, 131.6, 136.0 ppm; **IR** (film): 3080, 3060, 2230, 1641, 1599, 1489, 1445 cm⁻¹.

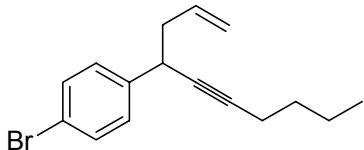
Data are in accordance with previously reported results.¹

1-(dec-1-en-5-yn-4-yl)-2-methoxybenzene (3ga):



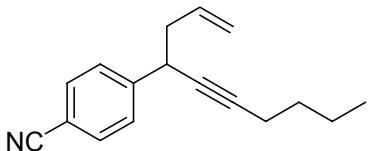
Yield 86%. A pale yellow oil. **¹H NMR** (CDCl₃, 400 MHz): δ 0.92 (t, 3H, *J* = 7.2 Hz), 1.38-1.55 (m, 4H), 2.23 (td, 2H, *J* = 6.9 and 2.1 Hz), 2.27-2.51 (m, 2H), 3.81(s, 3H), 4.13 (tt, 1H, *J* = 6.5 and 2.1 Hz), 5.01 (d, 1H, *J* = 9.6 Hz), 5.02 (d, 1H, *J* = 18.0 Hz), 5.89 (ddt, 1H, *J* = 17.0, 10.2 and 7.0 Hz), 6.83 (d, 1H, *J* = 8.2 Hz), 6.95 (apparent t, 1H, *J* = 7.5 Hz), 7.20 (apparent t, 1H, *J* = 8.2 Hz), 7.53 (apparent d, 1H, *J* = 7.6 Hz) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 13.6, 18.5, 21.9, 31.1, 31.2, 41.0, 55.2, 81.3, 83.0, 110.2, 116.1, 120.4, 127.6, 128.6, 130.4, 136.3, 156.1 ppm; **IR** (film): 3073, 3004, 1634, 1602, 1494, 1240 cm⁻¹; **Anal** calcd for C₁₇H₂₂O: C, 84.25; H, 9.15. Found: C, 84.51; H, 9.01.

1-bromo-4-(dec-1-en-5-yn-4-yl)benzene (3ha):



Yield 87%. A pale yellow oil. **¹H NMR** (CDCl₃, 400 MHz): δ 0.91 (t, 3H, *J* = 7.2 Hz), 1.37-1.54 (m, 4H), 2.23 (td, 2H, *J* = 7.0 and 2.2 Hz), 2.43 (t, 2H, *J* = 7.0 Hz), 3.63 (tt, 1H, *J* = 7.0 and 2.2 Hz), 4.98-5.04 (m, 2H), 5.75-5.86 (m, 1H), 7.23 (apparent d, 2H, *J* = 8.4 Hz), 7.43 (apparent d, 2H, *J* = 8.4 Hz) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 13.7, 18.5, 22.0, 31.2, 37.6, 42.9, 80.6, 84.2, 117.1, 120.4, 129.3, 131.4, 135.3, 141.2 ppm; **IR** (film): 3077, 2217, 1641, 1590, 1489 cm⁻¹; **Anal** calcd for C₁₆H₁₉Br: C, 65.99; H, 6.58. Found: C, 65.76; H, 6.65.

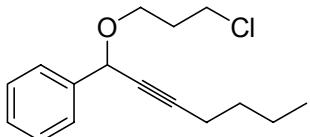
4-(dec-1-en-5-yn-4-yl)benzonitrile (3ia):



Yield 17%. A pale yellow oil. **¹H NMR** (CDCl₃, 400 MHz): δ 0.92 (t, 3H, *J* = 7.2 Hz), 1.37-1.59 (m, 4H), 2.24 (td, 2H, *J* = 7.2 and 2.4 Hz), 2.46 (dd, apparent t, 2H, *J* = 7.0 and 7.0 Hz), 3.73 (tt, 1H, *J* = 6.8 and 2.0 Hz), 4.98-5.07 (m, 2H), 5.79 (ddt, 1H, *J* = 17.2, 10.4 and 7.2 Hz), 7.46 (apparent d, 2H, *J* = 8.2 Hz), 7.61 (apparent d, 2H, *J* = 8.2 Hz) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 13.5, 18.3, 21.8, 30.9, 37.9, 42.5, 79.4, 84.8, 110.4, 117.4, 118.8, 128.3, 132.0, 134.6, 147.4 ppm; **IR** (film): 3073, 2230, 1693, 1607,

1502, 1462 cm⁻¹; **Anal** calcd for C₁₇H₁₉N: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.55; H, 8.55; N, 5.45.

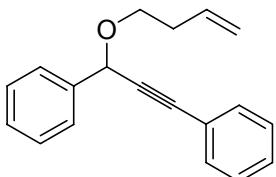
1-(1-(3-chloropropoxy)hept-2-ynyl)benzene (3ab)³:



Yield 89%. A colorless oil. **¹H NMR** (CDCl₃, 400 MHz): δ 0.92 (t, 3H, *J* = 7.2 Hz), 1.38-1.48 (m, 2H) 1.49-1.58 (m, 2H), 2.06 (quintet, 2H, *J* = 6.1 Hz), 2.29 (td, 2H, *J* = 7.0 and 2.0 Hz), 3.61 (dt, 1H, *J* = 9.5 and 5.8 Hz), 3.65 (t, 2H, *J* = 6.5 Hz), 3.78 (dt, 1H, *J* = 9.5 and 5.8 Hz), 5.16 (t, 1H, *J* = 2.0 Hz), 7.28-7.39 (m, 3H), 7.48-7.52 (m, 2H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 13.5, 18.5, 21.9, 30.6, 32.7, 42.0, 64.4, 71.9, 77.7, 88.6, 127.3, 128.1, 128.3, 139.2 ppm; **IR** (film): 3069, 3031, 2228, 1602, 1579, 1501, 1112 cm⁻¹.

Data are in accordance with previously reported results.³

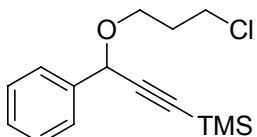
3-(but-3-enyloxy)-1,3-diphenylprop-1-yne (3bb)³:



Yield 83%. A yellow oil. **¹H NMR** (CDCl₃, 400 MHz): δ 2.39-2.46 (m, 2H), 3.63 (dt, 1H, *J* = 9.2 and 6.8 Hz), 3.78 (dt, 1H, *J* = 9.2 and 6.8 Hz), 5.02-5.15 (m, 2H), 5.42 (s, 1H), 5.86 (ddt, 1H, *J* = 17.2, 10.4 and 6.8 Hz), 7.28-7.41 (m, 6H), 7.45-7.50 (m, 2H), 7.56-7.60 (m, 2H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 34.1, 67.6, 72.0, 87.1, 87.5, 116.4, 122.6, 127.4, 128.2, 128.3, 128.4, 131.8, 135.1, 138.8 ppm; **IR** (film): 3064, 3032, 1601, 1490, 1451 cm⁻¹.

Data are in accordance with previously reported results.³

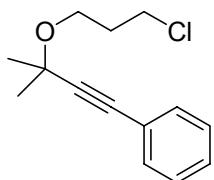
(3-(3-chloropropoxy)-3-phenylprop-1-ynyl)trimethylsilane (3cb)³:



Yield 85%. A colorless oil. **1H NMR** (CDCl_3 , 400 MHz): δ 0.21 (s, 9H), 2.06 (quintet, 2H, $J = 6.4$ Hz), 3.61-3.68 (m, 3H), 3.81 (dt, 1H, $J = 9.6$ and 6.0 Hz), 5.17 (s, 1H), 7.30-7.40 (m, 3H), 7.48-7.52 (m, 2H) ppm; **13C NMR** (CDCl_3 , 100 MHz): δ -0.17, 32.7, 41.9, 64.5, 72.1, 92.7, 102.8, 127.4, 128.3, 128.4, 138.2 ppm; **IR** (film): 3064, 3031, 2171, 1603, 1494, 1452, 1250, 1071, 843 cm^{-1} .

Data are in accordance with previously reported results.³

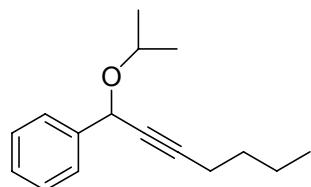
1-(3-(3-chloropropoxy)-3-methylbut-1-ynyl)benzene (3db)³:



Yield 65%. A colorless oil. **1H NMR** (CDCl_3 , 400 MHz): δ 1.54 (s, 6H), 2.05 (quintet, 2H, $J = 6.4$ Hz), 3.68 (t, 2H, $J = 6.4$ Hz), 3.77 (t, 2H, $J = 6.0$ Hz), 7.28-7.32 (m, 3H), 7.40-7.45 (m, 2H) ppm; **13C NMR** (CDCl_3 , 100 MHz): δ 28.7, 33.2, 42.1, 60.4, 70.5, 84.0, 91.3, 122.8, 128.1, 128.2, 131.6 ppm; **IR** (film): 3081, 3057, 2233, 1598, 1489, 1443, 1154, 1069, 756 cm^{-1} .

Data are in accordance with previously reported results.³

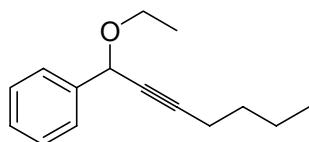
1-(1-isopropoxyhept-2-ynyl)benzene (3ac)⁴:



Yield 66%. A pale yellow oil. **1H NMR** (CDCl_3 , 400 MHz): δ 0.90 (t, 3H, $J = 7.2$ Hz), 1.19 (d, 3H, $J = 6.0$ Hz), 1.23 (d, 3H, $J = 6.0$ Hz), 1.35-1.46 (m, 2H), 1.47-1.56 (m, 2H), 2.26 (td, 2H, $J = 7.2$ and 2.0 Hz), 3.95 (septet, 1H, $J = 6.0$ Hz), 5.17 (t, 1H, $J = 2.0$ Hz), 7.25-7.37 (m, 3H), 7.47-7.52 (m, 2H) ppm; **13C NMR** (CDCl_3 , 100 MHz): δ 13.6, 18.5, 21.7, 21.9, 22.7, 30.7, 69.0, 69.2, 78.8, 87.4, 127.3, 127.9, 128.3, 140.2 ppm; **IR** (film): 3064, 3032, 1603, 1493, 1452 cm^{-1} .

Data are in accordance with previously reported results.⁴

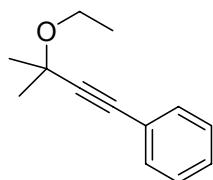
1-(1-ethoxyhept-2-ynyl)benzene (3ad)⁴:



Yield 84%. A colorless oil. **¹H NMR** (CDCl₃, 400 MHz): δ 0.91 (t, 3H, *J* = 7.2 Hz), 1.23 (t, 3H, *J* = 7.0 Hz), 1.37-1.58 (m, 4H), 2.28 (td, 2H, *J* = 7.2 and 2.0 Hz), 3.52 (dq, 1H, *J* = 9.2 and 6.8 Hz), 3.69 (dq, 1H, *J* = 9.2 and 6.8 Hz), 5.14 (t, 1H, *J* = 2.0 Hz), 7.25-7.52 (m, 5H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 13.6, 15.2, 18.6, 22.0, 30.8, 63.6, 71.7, 78.2, 88.1, 127.4, 128.1, 128.4, 139.6 ppm; **IR** (film): 3062, 3023, 2925, 2856, 2229, 1599, 1486, 1065 cm⁻¹.

Data are in accordance with previously reported results.⁴

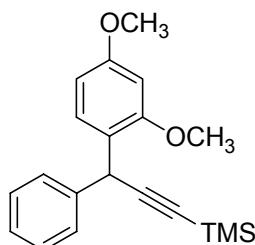
1-(3-ethoxy-3-methylbut-1-ynyl)benzene (3dc)⁵:



Yield 75%. A colorless oil. **¹H NMR** (CDCl₃, 400 MHz): δ 1.24 (t, 3H, *J* = 7.1 Hz), 1.55 (s, 6H), 3.69 (q, 2H, *J* = 7.1 Hz), 7.28-7.45 (m, 5H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 15.8, 28.9, 59.5, 70.3, 83.7, 91.7, 122.9, 128.1, 128.2, 131.6 ppm; **IR** (film): 3085, 3054, 2980, 2930, 2871, 2225, 1595, 1494, 1167 cm⁻¹.

Data are in accordance with previously reported results.⁵

(3-(2,4-dimethoxyphenyl)-3-phenylprop-1-ynyl)trimethylsilane (3cc)⁶:

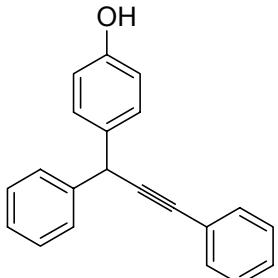


Yield 75%. A colorless solid. (m.p. 82-84°C). **¹H NMR** (CDCl₃, 400 MHz): δ 0.19 (s, 9H), 3.77 (s, 3H), 3.78 (s, 3H), 5.40 (s, 1H), 6.41 (d, 1H, *J* = 2.4 Hz), 6.48 (dd, 1H, *J* = 8.4 and 2.4 Hz), 7.13-7.19 (m, 1H), 7.22-7.28 (m, 2H), 7.35-7.40 (m, 2H), 7.42 (d, 1H, *J* = 8.4 Hz) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 0.19, 36.5, 55.4, 55.5, 87.4, 98.6,

104.5, 107.8, 122.7, 126.4, 127.7, 128.2, 129.4, 141.9, 157.0, 159.9 ppm; **IR** (film): 3027, 2998, 2169, 1612, 1588, 1503, 1452, 1249, 1036 cm^{-1} .

Data are in accordance with previously reported results.⁶

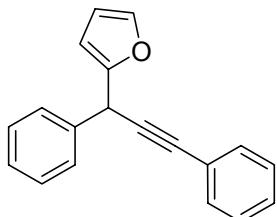
4-(1,3-diphenylprop-2-ynyl)phenol (3bc)⁷:



Yield 93%. A yellow solid (m.p. 82-86°C). **¹H NMR** (CDCl_3 , 400 MHz): δ 4.91 (brs, 1H), 5.14 (s, 1H), 6.76 (apparent d, 2H, J = 8.5 Hz), 7.20-7.34 (m, 8H), 7.39-7.49 (m, 4H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 42.8, 84.7, 90.4, 115.4, 123.4, 126.8, 127.7, 127.9, 128.2, 128.6, 129.1, 131.6, 134.0, 141.9, 154.2 ppm; **IR** (film): 3353, 3058, 3027, 2921, 2848, 2216, 1618, 1602, 1509, 1490 cm^{-1} .

Data are in accordance with previously reported results.⁷

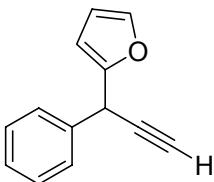
2-(1,3-diphenylprop-2-ynyl)furan (3bd)⁷:



Yield 85%. A yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 5.26 (s, 1H), 6.28 (apparent d, 1H, J = 3.0 Hz), 6.30-6.33 (m, 1H), 7.23-7.39 (m, 7H), 7.45-7.51 (m, 4H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 37.8, 83.9, 87.4, 106.6, 110.3, 123.1, 127.3, 127.8, 128.1, 128.2, 128.6, 131.7, 138.8, 142.2, 153.7 ppm; **IR** (film): 3117, 3061, 3030, 1598, 1501, 1491, 1453, 1071 cm^{-1} .

Data are in accordance with previously reported results.⁷

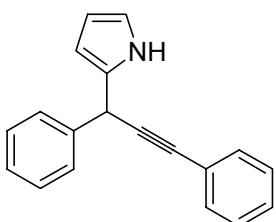
2-(1-phenylprop-2-ynyl)furan (3eb)⁸:



Yield 50%. A pale yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 2.44 (d, 1H, $J = 2.5$ Hz), 5.06 (d, 1H, $J = 2.5$ Hz), 6.21-6.24 (m, 1H), 6.29-6.32 (m, 1H), 7.24-7.44 (m, 6H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 37.0, 72.0, 81.9, 106.7, 110.3, 127.5, 127.7, 128.6, 138.2, 142.3, 153.1 ppm; **IR** (film): 3293, 3063, 3030, 2122, 1599, 1503, 1453 cm^{-1} .

Data are in accordance with previously reported results.⁸

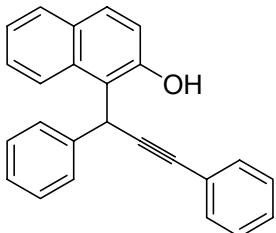
2-(1,3-diphenylprop-2-ynyl)-1H-pyrrole (3be)⁹:



Yield 60%. A brown solid. (m.p. 68-71°C). **¹H NMR** (CDCl_3 , 400 MHz): δ 5.28 (s, 1H), 6.02-6.06 (m, 1H), 6.15 (dd, 1H, $J = 6.0$ and 2.8 Hz), 6.68-6.71 (m, 1H), 7.23-7.37 (m, 6H), 7.42-7.49 (m, 4H), 8.16 (brs, 1H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 37.3, 84.2, 88.6, 106.6, 108.7, 117.4, 123.2, 127.3, 127.8, 128.2, 128.3, 128.8, 130.6, 131.8, 140.2 ppm; **IR** (film): 3431, 1597, 1489, 1452 cm^{-1} .

Data are in accordance with previously reported results.⁹

1-(1,3-diphenylprop-2-ynyl)naphthalen-2-ol (3bf)⁷:

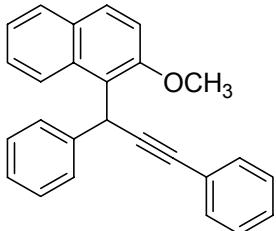


Yield 94%. A pale yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 6.27 (s, 1H), 6.38 (s, 1H), 7.16 (d, 1H, $J = 8.9$ Hz), 7.20-7.50 (m, 12H), 7.75 (d, 1H, $J = 8.9$ Hz), 7.80 (d, 1H, $J = 8.0$ Hz), 8.03 (d, 1H, $J = 8.6$ Hz) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 33.7, 86.0, 88.3, 117.6, 119.1, 122.5, 123.0, 123.3, 126.8, 127.0, 127.2, 128.3, 128.5, 128.7, 128.8, 129.6, 129.8, 131.8, 132.3, 139.5, 152.3 ppm; **IR** (film): 3420, 3054, 3027, 2918, 2848,

2217, 1631, 1595, 1520, 1490 cm⁻¹.

Data are in accordance with previously reported results.⁷

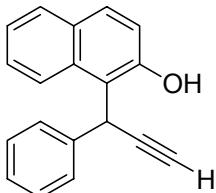
1-(1,3-diphenylprop-2-ynyl)-2-methoxynaphthalene (3bg)⁹:



Yield 90%. A white solid. (m.p. 110-111°C) **¹H NMR** (CDCl₃, 400 MHz): δ 3.88 (s, 3H), 6.52 (s, 1H), 7.10-7.29 (m, 9H), 7.39-7.43 (m, 2H), 7.48-7.51 (m, 2H), 7.71 (apparent d, 1H, *J* = 8.8 Hz), 7.75 (d, 1H, *J* = 8.8 Hz), 8.15 (apparent d, 1H, *J* = 8.7 Hz) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 32.9, 57.1, 84.3, 90.7, 113.6, 122.1, 123.6, 124.1, 125.7, 126.2, 126.4, 127.3, 128.1, 128.4, 128.5, 128.6, 129.9, 130.2, 131.9, 132.2, 141.1, 154.3 ppm; **IR** (film): 3054, 3023, 2995, 2853, 2162, 1634, 1596, 1523, 1490, 1235 cm⁻¹.

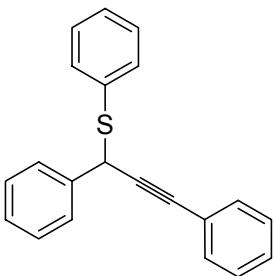
Data are in accordance with previously reported results.⁹

1-(1-phenylprop-2-ynyl)naphthalen-2-ol (3ec):



Yield 62%. A colorless oil. **¹H NMR** (CDCl₃, 400 MHz): δ 2.60 (d, 1H, *J* = 3.9 Hz), 6.08 (s, 1H), 6.14 (d, 1H, *J* = 3.9 Hz), 7.13 (d, 1H, *J* = 8.8 Hz), 7.18-7.45 (m, 7H), 7.74 (d, 1H, *J* = 8.8 Hz), 7.78 (d, 1H, *J* = 8.0 Hz), 7.94 (d, 1H, *J* = 8.6 Hz) ppm; **¹³C NMR** (CDCl₃, 100 MHz): δ 32.9, 73.9, 83.4, 117.3, 119.1, 123.1, 123.4, 126.9, 127.1, 128.7, 128.9, 129.7, 130.0, 132.3, 138.9, 152.1 ppm; **IR** (film): 3455, 3284, 3058, 3027, 2926, 2840, 2112, 1630, 1599, 1520, 1490 cm⁻¹; **Anal** calcd for C₁₉H₁₄O: C, 88.34; H, 5.46. Found: C, 88.51; H, 5.40.

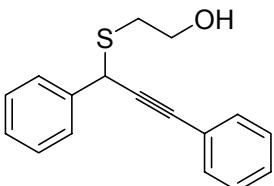
Phenyl 1,3-diphenyl-2-propynyl sulfide (3bh)¹⁰:



Yield 90%. A pale yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 5.22 (s, 1H), 7.26-7.35 (m, 9H), 7.37-7.40 (m, 2H), 7.43-7.49 (m, 4H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 44.2, 86.8, 87.3, 122.8, 127.8, 128.0, 128.2, 128.3, 128.36, 128.41, 128.6, 131.6, 133.3, 134.4, 138.0 ppm; **IR** (film): 3054, 3023, 2930, 2202, 1598, 1583, 1490 cm^{-1} .

Data are in accordance with previously reported results.¹⁰

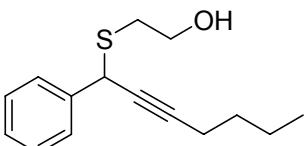
2-Hydroxyethyl 1,3-diphenyl-2-propynyl sulfide (3bi)¹⁰:



Yield 89%. A pale yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 2.06 (brs, 1H), 2.86 (dt, 1H, J = 13.9 and 6.0 Hz), 3.00 (dt, 1H, J = 13.9 and 6.0 Hz), 3.75-3.82 (m, 2H), 5.05 (s, 1H), 7.27-7.40 (m, 6H), 7.47-7.51 (m, 2H), 7.55-7.60 (m, 2H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 34.7, 39.1, 60.8, 86.1, 87.0, 122.5, 127.8(2), 128.2, 128.3, 128.5, 131.6, 138.0 ppm; **IR** (film): 3389, 3050, 3038, 2914, 2875, 2209, 1598, 1490 cm^{-1} .

Data are in accordance with previously reported results.¹⁰

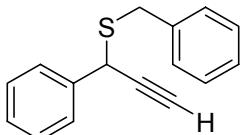
2-(1-phenylhept-2-ynylthio)ethanol (3ae):



Yield 90%. A pale yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 0.92 (t, 3H, J = 7.5 Hz), 1.37-1.48 (m, 2H), 1.49-1.59 (m, 2H), 2.22 (brs, 1H), 2.30 (td, 2H, J = 7.2 and 2.0 Hz), 2.76 (dt, 1H, J = 14.0 and 6.0 Hz), 2.90 (dt, 1H, J = 14.0 and 6.0 Hz), 3.67-3.75 (m, 2H), 4.81 (t, 1H, J = 2.0 Hz), 7.23-7.36 (m, 3H), 7.47 -7.52 (m, 2H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 13.6, 18.6, 22.0, 30.9, 34.9, 38.9, 60.8, 76.8, 87.1, 127.8, 127.9,

128.6, 138.9 ppm; **IR** (film): 3405, 3061, 3028, 2871, 1598, 1493, 1453 cm^{-1} ; **Anal**
 calcd for $\text{C}_{15}\text{H}_{20}\text{OS}$: C, 72.53; H, 8.12; S, 12.91. Found: C, 72.84; H, 8.31; S, 12.61.

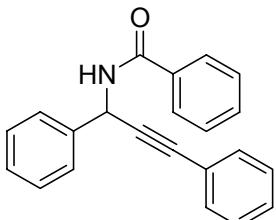
Phenylmethyl 1-phenyl-2-propynyl sulfide (3ed)¹⁰:



Yield 55%. A pale yellow oil. **$^1\text{H NMR}$** (CDCl_3 , 400 MHz): δ 2.65 (d, 1H, $J = 2.4$ Hz), 3.77 (d, 1H, $J = 13.3$ Hz), 3.99 (d, 1H, $J = 13.3$ Hz), 4.54 (d, 1H, $J = 2.4$ Hz), 7.23-7.37 (m, 8H), 7.43-7.47 (m, 2H) ppm; **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz): δ 36.4, 37.9, 74.1, 81.7, 127.1, 127.8, 127.9, 128.49, 128.52, 129.0, 137.1, 137.4 ppm; **IR** (film): 3284, 3058, 3023, 2921, 2848, 2112, 1598, 1485 cm^{-1} .

Data are in accordance with previously reported results.¹⁰

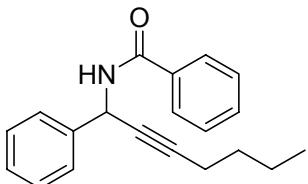
N-(1,3-diphenylprop-2-ynyl)benzamide (3bj)¹¹:



Yield 75%. A white solid. (m.p. 167-168 °C). **$^1\text{H NMR}$** (CDCl_3 , 400 MHz): δ 6.48 (d, 1H, $J = 8.4$ Hz), 6.74 (d, 1H, $J = 8.4$ Hz), 7.30-7.51 (m, 11H), 7.63-7.67 (m, 2H), 7.80-7.84 (m, 2H) ppm; **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz): δ 45.6, 85.1, 86.9, 122.4, 127.1, 127.2, 128.2, 128.3, 128.6, 128.8, 131.8, 133.8, 139.0, 166.2 ppm; **IR** (film): 3288, 3030, 2228, 1634, 1594, 1504, 1445, 1326 cm^{-1} .

Data are in accordance with previously reported results.¹¹

N-(1-phenylhept-2-ynyl)benzamide (3af)¹¹:

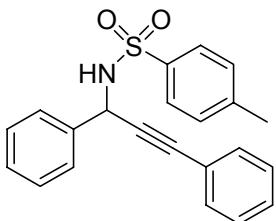


Yield 60%. A white solid. (m.p. 133-135 °C). **$^1\text{H NMR}$** (CDCl_3 , 400 MHz): δ 0.91 (t, 3H, $J = 7.2$ Hz), 1.37-1.47 (m, 2H), 1.48-1.57 (m, 2H), 2.25 (td, 2H, $J = 7.2$ and 2.4

Hz), 6.21 (d, 1H, $J = 8.4$ Hz), 6.74 (brs, 1H), 7.23-7.40 (m, 5H), 7.43-7.48 (m, 1H), 7.54-7.59 (m, 2H), 7.75-7.79 (m, 2H) ppm; ^{13}C NMR (CDCl₃, 100 MHz): δ 13.6, 18.5, 22.0, 30.7, 45.3, 77.8, 85.8, 127.1, 127.2, 127.9, 128.5, 128.6, 131.7, 134.0, 139.8, 166.2 ppm; IR (film): 3296, 3030, 1638, 1602, 1489, 1454, 1322 cm⁻¹.

Data are in accordance with previously reported results.¹¹

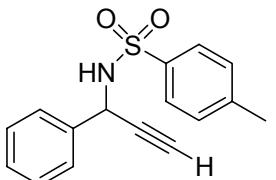
1,3-diphenyl-N-tosylprop-2-yn-1-amine (3bk)¹¹:



Yield 80%. A white solid. (m.p. 186-188 °C). ^1H NMR (CDCl₃, 400 MHz): δ 2.32 (s, 3H), 4.90 (brs, 1H), 5.56 (d, 1H, $J = 9.2$ Hz), 7.10-7.14 (m, 2H), 7.22-7.38 (m, 8H), 7.56 (apparent d, 2H, $J = 7.2$ Hz), 7.82 (apparent d, 2H, $J = 8.4$ Hz) ppm; ^{13}C NMR (CDCl₃, 100 MHz): δ 21.5, 49.8, 85.4, 86.7, 122.0, 127.4, 127.6, 128.1, 128.5, 128.6, 128.8, 129.6, 131.6, 137.4, 143.6 ppm; IR (film): 3267, 3062, 2221, 1597, 1490, 1450, 1331, 1156 cm⁻¹.

Data are in accordance with previously reported results.¹¹

1-phenyl-N-tosylprop-2-yn-1-amine (3ee)¹²:



Yield 46%. A white solid. (m.p. 131-132 °C). ^1H NMR (CDCl₃, 400 MHz): δ 2.31 (d, 1H, $J = 2.0$ Hz), 2.42 (s, 3H), 5.09 (d, 1H, $J = 8.8$ Hz), 5.31 (dd, 1H, $J = 8.8$ and 2.4 Hz), 7.25-7.33 (m, 5H), 7.42-7.47 (m, 2H), 7.76 (apparent d, 2H, $J = 8.4$ Hz) ppm; ^{13}C NMR (CDCl₃, 100 MHz): δ 21.6, 49.0, 74.8, 80.4, 127.2, 127.5, 128.5, 128.7, 129.5, 137.0, 137.3, 143.6 ppm; IR (film): 3279, 3032, 2121, 1598, 1494, 1452, 1329, 1160 cm⁻¹.

Data are in accordance with previously reported results.¹²

References:

- ¹ M. R. Luzung and F. D. toste, *J. Am. Chem. Soc.* 2003, **125**, 15760.
- ² T. Schwier, M. Rubin and V. Gevorgyan, *Org. Lett.* 2004, **6**, 1999.
- ³ B. Sherry, A. T. Radosevich and F. D. Toste, *J. Am. Chem. Soc.* 2003, **125**, 6076.
- ⁴ R. Mahrwald and S. Quint, *Tetrahedron*. 2000, **56**, 7463.
- ⁵ K-O. Henseling, *Chem. Ber.* 1977, **110**, 1027.
- ⁶ M. Georgy, V. Boucard, J-M. Campagne, *J. Am. Chem. Soc.* 2005, **127**, 14180.
- ⁷ J. J. Kennedy-Smith, L. A. Young and F. D. Tostle, *Org. Lett.* 2004, **6**, 1325.
- ⁸ Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai and S. Uemura, *J. Am. Chem. Soc.* 2002, **124**, 11846.
- ⁹ Y. Nishibayashi, Y. Inada, M. Yoshikawa, M. Hidai and S. Uemura, *Angew. Chem. Int. Ed.* 2003, **42**, 1495.
- ¹⁰ Y. Inada, Y. Nishibayashi, M. Hidai and S. Uemura, *J. Am. Chem. Soc.* 2002, **124**, 15172.
- ¹¹ R. Mahrwal and Quint, S. *Tetrahedron Lett.* 2001, **42**, 1655.
- ¹² Y. Nishibayashi, M. D. Milton, Y. Inada, M. Yoshikawa, I. Wakiji, M. Hidai and S. Uemura, *Chem. Eur. J.* 2005, **11**, 1433.