Supporting Information

Synthesis of Primary Propargylic Alcohols from Terminal

Alkyne Using Rongalite as the C1 Unit

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1. General.

All substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ¹H spectra were recorded in CDCl₃ on 400/600 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quadruple), coupling constants (Hz) and integration. ¹³C spectra were recorded in CDCl₃ on 100/150 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. The X-ray crystal structure determinations of 3q were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

safety note

The combination of DMSO and strong base may cause safety problems when thinking about a larger scale synthesis. While no problems were observed in this study, care should be shown when handling DMSO and strong base in large scale synthesis.

2. General procedure for the synthesis of 3 (3a as an example).

A mixture of **1a** ethynylbenzene (0.5 mmol), **2** (0.6 mmol) and *t*-BuOK (0.5 mmol) in DMSO (1.0 mL) was stirred at rt for 5 min in a pressure vessel, and then moved to 100 °C oil bath for 2.0 h. The resulting mixture was dropped into 25 mL H₂O and extracted with EtOAc 3 times (3 ×25 mL). The organic extract was dried with anhydrous Na₂SO₄, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 8/1) to afford the product **3a** as light yellow oil (54.6 mg, 83%).

3. Evidence in support of the mechanism

(1) The reaction of 1a and 2 was also performed in DMSO-*d6* to and none of the deuterated product 3a was generated (H>99%). (see below).



(2) We systematically screened the reaction temperature for the reaction of phenylacetylene and paraformaldehyde, the results indicate that as the temperature increased, the yield gradually decreased, when the temperature reaches 80° C, the corresponding product **3a** cannot be generated. Perhaps the high temperature caused the reaction to become complex.



4. Crystallographic data of 3q.



3-(4-chlorophenyl)prop-2-yn-1-ol (CCDC: 2190850)



Figure S1. X-ray crystal structure of 3q.

Bond precision:	C-C = 0.0035 A	Wavelength=0.71073			
Cell:	a=15.423(3) alpha=90	b=4.9337(9) beta=110.313(2)	c=11.308(2) gamma=90		
Temperature:	273 К		-		
	Calculated	Reported			
Volume	806.9(3)	806.9(2)			
Space group	P 21/c	P 21/c			
Hall group	: -P 2ybc	-P 2ybc			
Moiety formula	C9 H7 C1 O	?			
Sum formula	C9 H7 Cl O	С9 Н7 СІ О			
Mr	166.60	166.60			
Dx,g cm-3	1.371	1.371			
Z	4	4			
Mu (mm-1)	0.406	0.406			
F000	344.0	344.0			
F000′	344.73				
h,k,lmax	23,7,16	22,7,16			
Nref	2829	2632			
Tmin,Tmax	0.915,0.930	0.864,0.86	4		
Tmin'	0.915				
Correction method= # Reported T Limits: Tmin=0.864 Tmax=0.864 AbsCorr = MULTI-SCAN					
Data completenes	ss= 0.930	Theta(max) = 32.035			
R(reflections) = 0.0625(2363) wR2(reflections) = 0.2021(2632)					
S = 1.059 Npar= 125					

 Table S1. Crystal data and structure refinement for compound 3q (CCDC: 2190850)

5. Characterization data for target compound.



3a, 83%

3-phenylprop-2-yn-1-ol (3a):

Yield: 83%; light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.44–7.43 (m, 2H), 7.33–7.28 (m, 3H), 4.50 (s, 2H), 2.17 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 131.6, 128.4, 128.3, 122.5, 87.2, 85.6, 51.5. The data are in agreement with those previously reported in the literature.^{1a}



3-(m-tolyl)prop-2-yn-1-ol (3b):

Yield: 76%; orange oil;¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 9.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 4.46 (s, 2H), 2.30 (s, 3H), 2.26 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.7, 132.0, 129.1, 128.5, 128.0, 122.1, 86.8, 85.7, 51.6, 21.3. The data are in agreement with those previously reported in the literature.^{2a}



3-(2,4-dimethylphenyl)prop-2-yn-1-ol (3c):

Yield: 74%; light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.29 (d, *J* = 4.2 Hz, 1H), 6.99 (s, 1H), 6.92 (s, 1H), 4.51 (s, 2H), 2.38 (s, 3H), 2.29 (s, 3H), 2.22 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 140.0, 138.5, 131.9, 130.2, 126.3, 119.2, 90.3, 84.6, 51.6, 21.3, 20.5. The data are in agreement with those previously reported in the literature. ^{1b}



3-(p-tolyl)prop-2-yn-1-ol (3d):

Yield: 80%; orange oil; ¹H NMR (600 MHz, CDCl₃) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.48 (s, 2H), 2.33 (s, 3H), 2.30 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 138.6, 131.5, 129.0, 119.4, 86.5, 85.7, 51.5, 21.4. The data are in agreement with those previously reported in the literature.^{1b}



3-(4-ethylphenyl)prop-2-yn-1-ol (3e):

Yield: 77%; orange oil; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.46 (s, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.03 (s, 1H), 1.21 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.7, 131.5, 127.7, 119.5, 86.5, 85.8, 51.7, 28.9, 15.4; HRMS (ESI) *m*/*z* calcd for C₁₁H₁₂O⁺ (M)⁺ 160.0883, found 160.0881.



3f, 70%

3-(4-propylphenyl)prop-2-yn-1-ol (3f):

Yield: 70%; light yellow oil;¹H NMR (400 MHz, CDCl₃) δ 7.33–7.31 (m, 2H), 7.09 (d, *J* = 7.2 Hz, 2H), 4.47 (d, *J* = 4.0 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.89 (s, 1H), 1.62 (dd, *J* = 14.8, 7.6 Hz, 2H), 0.92 (dd, *J* = 8.0, 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 131.4, 128.3, 119.5, 86.4, 85.8, 51.7, 38.0, 24.5, 13.9; HRMS (ESI) *m/z* calcd for C₁₂H₁₄O⁺ (M)⁺ 174.1039, found 174.1038.



3-(4-butylphenyl)prop-2-yn-1-ol (3g):

Yield: 67%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.50 (s, 2H), 2.66–2.57 (m, 2H), 2.36 (s, 1H), 1.60 (dt, *J* = 12.8, 7.6 Hz, 2H), 1.38 (dt, *J* = 14.8, 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.3, 131.4, 128.2, 119.4, 86.5, 85.7, 51.6, 35.6, 33.4, 22.4, 14.1; HRMS (ESI) m/z calcd for C₁₃H₁₇O⁺ (M+H)⁺ 189.1274, found 189.1279.



3-(4-pentylphenyl)prop-2-yn-1-ol (3h):

Yield: 69%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 4.49 (s, 2H), 2.63–2.53 (m, 2H), 2.00 (d, *J* = 18.4 Hz, 1H), 1.60 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.31 (d, *J* = 3.2 Hz, 4H), 0.88 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.6, 131.6, 128.4, 120.0, 86.5, 85.8, 51.6, 35.8, 31.4, 30.9, 22.5, 14.0; HRMS (ESI) m/z calcd for C₁₄H₁₉O⁺ (M+H)⁺ 203.1430, found 203.1431.



3-(4-methoxyphenyl)prop-2-yn-1-ol (3i):

Yield: 72%; light yellow solid; mp: 67.3—68.5°C; ¹H NMR (600 MHz, CDCl₃) δ 7.36 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 4.47 (d, *J* = 4.2 Hz, 2H), 3.79 (d, *J* = 5.4 Hz, 3H), 2.49 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 159.5, 133.1, 114.5, 113.8, 85.9, 85.4, 55.2, 51.5. The data are in agreement with those previously reported in the literature.^{1a}



3-(4-ethoxyphenyl)prop-2-yn-1-ol (3j):

Yield: 74%; light yellow solid; mp: 72.9—74.5°C; ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.32 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.49 (d, *J* = 6.0 Hz, 2H), 4.03 (q, *J* = 6.8 Hz, 2H), 2.00 (s, 1H), 1.43 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 158.8, 133.0, 114.2(3), 114.2, 85.7, 85.6, 63.5, 51.7, 14.9; HRMS (ESI) m/z calcd for C₁₁H₁₃O₂⁺ (M+H)⁺ 177.0910, found 177.0909.



3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol (3k):

Yield: 68%; light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.54 (dd, J = 22.8, 7.8 Hz, 4H), 4.52 (s, 2H), 2.14 (s, 1H); ¹³C NMR (150 MHz, CDCl3) δ 131.9, 130.1, 126.3, 125.2 (d, J = 2.5 Hz, ³ J_{CF}), 103.9, 89.6, 84.3, 51.5. The data are in agreement with those previously reported in the literature.^{1a}

3-(2-fluorophenyl)prop-2-yn-1-ol (3l):

Yield: 73%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, J = 10.4, 4.8 Hz, 1H), 7.33–7.27 (m, 1H), 7.08 (dt, J = 17.2, 5.2 Hz, 2H), 4.54 (s, 2H), 2.35 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 133.6, 130.3, 123.9, 115.4 (d, J = 20.5 Hz, ² J_{CF}), 111.0 (d, J = 15.5 Hz, ³ J_{CF}), 92.4, 78.9, 51.5. The data are in agreement with those previously reported in the literature.^{1b}



3-(3-fluorophenyl)prop-2-yn-1-ol (3m):

Yield: 70%; light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.30–7.27 (m, 1H), 7.22 (d, J = 7.8 Hz, 1H), 7.13 (d, J = 9.0 Hz, 1H), 7.04 (s, 1H), 4.50 (d, J = 5.4 Hz, 2H), 1.79 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 129.9, 127.5, 118.5 (d, J = 15.2 Hz, ³ J_{CF}), 115.9 (d, J = 14.0 Hz, ³ J_{CF}), 88.1, 84.5, 51.5. The data are in agreement with those previously reported in the literature.^{2a}



3-(3-chlorophenyl)prop-2-yn-1-ol (3n):

Yield: 81%; light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.41 (s, 1H), 7.29 (s, 2H), 7.23 (d, J = 6.6 Hz, 1H), 4.49 (s, 2H), 2.26 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 134.0, 131.5, 129.7, 129.5, 128.7, 124.2, 88.4, 84.2, 51.4. The data are in agreement with those previously reported in the literature.^{2b}



3-(3-bromophenyl)prop-2-yn-1-ol (3o):

Yield: 82%; light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.56 (s, 1H), 7.43 (d, J = 6.0 Hz, 1H), 7.33 (s, 1H), 7.15 (d, J = 7.2 Hz, 1H), 4.48 (s, 2H), 2.55 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 134.3, 131.6, 130.1, 129.7, 124.4, 122.0, 88.5, 84.0, 51.3. The data are in agreement with those previously reported in the literature.^{2b}



3-(4-fluorophenyl)prop-2-yn-1-ol (3p):

Yield: 80%; light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.43–7.37 (m, 2H), 6.99 (dd, J = 8.4, 7.8 Hz, 2H), 4.48 (s, 2H), 2.18 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 162.5 (d, J = 165.6 Hz, ¹ J_{CF}), 133.5 (d, J = 5.5 Hz, ³ J_{CF}), 118.5, 115.6 (d, J = 14.6 Hz, ³ J_{CF}), 86.9, 84.6, 51.5. The data are in agreement with those previously reported in the literature.^{2a}



3-(4-chlorophenyl)prop-2-yn-1-ol (3q):

Yield: 75%; yellow solid; mp: 77.1–78.6°C; ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.30 (m, 2H), 7.27–7.22 (m, 2H), 4.47 (s, 2H), 2.19 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ = 134.3, 132.7, 128.5, 120.8, 88.1, 84.5, 51.5. The data are in agreement with those previously reported in the literature.^{1a}



3-(4-bromophenyl)prop-2-yn-1-ol (3r):

Yield: 76%; pale orange solid; mp: 79.5–81.2°C; ¹H NMR (600 MHz, CDCl₃) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.48 (d, *J* = 5.4 Hz, 2H), 1.75 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 133.1, 131.6, 122.8, 121.4, 88.3, 84.7, 51.6. The data are in agreement with those previously reported in the literature.^{1b}

3s, 66%

3-(thiophen-2-yl)prop-2-yn-1-ol (3s):

Yield: 66%; brown oil; ¹H NMR (400 MHz, CDCl3) δ 7.30–7.14 (m, 2H), 6.96 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.49 (d, *J* = 7.2 Hz, 2H), 2.25 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 132.3, 127.4, 126.9, 122.3, 91.1, 78.9, 51.6. The data are in agreement with those previously reported in the literature.^{1b}



3-(thiophen-3-yl)prop-2-yn-1-ol (3t):

Yield: 69%; brown oil; ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 2.0 Hz, 1H), 7.26 (dd, *J* = 4.8, 3.2 Hz, 1H), 7.16–7.08 (m, 1H), 4.48 (s, 2H), 1.99 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 129.8, 129.1, 125.4, 121.5, 86.8, 80.8, 51.6. The data are in agreement with those previously reported in the literature.^{2a}



3-(4-(4-propylcyclohexyl)phenyl)prop-2-yn-1-ol (3u):

Yield: 78%; pale orange solid; mp: 131.2–132.7°C; ¹H NMR (600 MHz, CDCl₃) δ 7.36 (s, 2H), 7.15 (s, 2H), 4.48 (s, 2H), 2.45 (s, 1H), 1.87–1.86 (m, 5H), 1.42 (d, J =

11.4 Hz, 2H), 1.35 (s, 2H), 1.29 (s, 1H), 1.21 (s, 2H), 1.04 (d, J = 10.8 Hz, 2H), 0.90 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 148.5, 131.6, 126.8, 119.7, 86.4, 85.9, 51.6, 44.5, 39.6, 36.9, 34.1, 33.4, 20.0, 14.3; HRMS (ESI) m/z calcd for C₁₈H₂₅O⁺ (M+H)⁺ 257.1900, found 257.1897.



methyl 4-(3-hydroxyprop-1-yn-1-yl)benzoate (3v)

Yield: 53%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 4.45 (s, 2H), 3.85 (s, 3H), 1.78 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 131.6, 129.8, 129.5, 127.2, 90.2, 84.9, 52.2, 51.6; The data are in agreement with those previously reported in the literature.^{2c}



3,3'-(1,4-phenylene)bis(prop-2-yn-1-ol) (3w)

Yield: 36%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (s, 4H), 4.43 (s, 4H), 1.75 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 131.6, 122.7, 89.0, 85.2, 51.6; The data are in agreement with those previously reported in the literature.^{2d}

3x, 61%

4-phenoxybut-2-yn-1-ol (3x)

Yield: 61%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.23 (t, *J* = 8.4 Hz, 2H), 6.94–6.88 (m, 3H), 4.66 (s, 2H), 4.23 (s, 2H), 1.62 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.6, 129.5, 121.5, 114.8, 85.5, 80.7, 55.9, 51.1; The data are in agreement with those previously reported in the literature.^{2e}



3-(4-(methylthio)phenyl)prop-2-yn-1-ol (3y):

Yield: 77%; Light yellow solid; mp: 56.9–59.0°C; ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.49 (s, 2H), 2.48 (s, 3H), 1.96 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 139.6, 131.9, 125.7, 118.7, 85.4, 51.7, 15.2. The data are in agreement with those previously reported in the literature.⁴

3-phenylpropiolaldehyde (4):

Yield: 89%; colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 9.42 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 176.8, 133.3, 131.3, 128.7, 119.4, 95.1, 88.4.³



6. Copies of ¹H NMR, ¹³C NMR

































30 170

f1 (ppm) Ċ











f1 (ppm)
























7. References.

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