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Article

Cu(I)-catalyzed cascade reaction of *N*-tosylhydrazones with 3-butyn-1-ol: A new synthesis of tetrahydrofurans

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ABSTRACT

The Cu(I)-catalyzed cascade coupling/cyclization reaction of *N*-tosylhydrazones with 3-butyn-1-ol has been explored. This new strategy represents a simple platform for the synthesis of tetrahydrofurans in moderate to good yields.

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1. Introduction

N-Tosylhydrazones are useful synthetic intermediates that have been employed in organic chemistry for almost 60 years. Compounds belonging to this particular class are air and moisture stable and can be readily prepared by the condensation of aldehydes or ketones with commercially available tosylhydrazine. In particular, *N*-tosylhydrazones have been proven to be useful substrates for the *in situ* generation of non-stabilized diazo compounds through the Bamford–Stevens reaction [1]. The diazo compounds generated in this way have been studied extensively in terms of their application to catalytic carbene transfer reactions [2]. More recently, *N*-tosylhydrazones have been established as versatile substrates in transition-metal-catalyzed cross-coupling reactions [3–7]. In this context, we previously reported the Cu(I)-catalyzed

cross-coupling of terminal alkynes and *N*-tosylhydrazones as an efficient strategy for the formation of *tri*-substituted allenes (Scheme 1(A)) [8]. We subsequently modified and simplified this methodology, resulting in the development of several efficient methods for the construction of 1,3-disubstituted allenes [9] and *tetra*-substituted allenes [10] by the Cu-catalyzed cross-coupling reactions of terminal alkynes and *N*-tosylhydrazones. The work represents further extensions of our previous studies on Cu(I)-catalyzed allene synthesis from terminal alkynes and *N*-tosylhydrazones.

The Cu-carbene species involved in this type of reaction are formed from the *in situ*-generated diazo substrate, which undergoes a migratory insertion reaction, followed by a protonation or nucleophilic substitution step to give the allene product. Since allenes are reactive structures that can undergo a wide range of transformations [11–19], we envisaged that it could be

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Scheme 1. Synthesis and tandem transformation of allenes through the Cu(I)-catalyzed cross-coupling of *N*-tosylhydrazones with terminal alkynes.

possible to intercept these intermediates in a cascade transformation sequence, thereby providing facile access to increasingly complex structures. In this context, we have shown that the allene intermediates generated by the Cu(I)-catalyzed cross-coupling of *N*-tosylhydrazones with terminal alkynes undergo 6π -electron cycloaddition and isomerization reactions to afford phenanthrenes [20,21]. We have also demonstrated that the introduction of a suitable intramolecular nucleophile (i.e., an $-OH$ or $-NH_2$ group) to the substrate allows for the initial allene product to undergo a cyclization to afford a benzofuran or indole (Scheme 1(B)) [22]. As part of our ongoing interest in the development of new reactions for organic synthesis, we report herein the Cu(I)-catalyzed cascade reaction of *N*-tosylhydrazones with 3-buten-1-ol (Scheme 1(C)). Notably, this reaction provides facile access to tetrahydrofuran derivatives, which are an important compounds class with numerous applications across various areas of research [23–25].

2. Experimental

2.1. General

All of the reactions were performed under nitrogen in 10-mL microwave tubes. Dioxane was dried over Na metal before being used. Column chromatography was performed over 200–300 mesh silica gel (Qingdao, China). 1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker ARX 400 spectrometer. Chemical shifts (δ) are reported

in parts per million (ppm) relative to the chemical shift of tetramethylsilane (TMS), which was used as an internal reference. Infrared (IR) spectra were recorded on Nicolet iS10 and the peaks reported in wavenumbers (cm^{-1}). HRMS analysis was conducted on Bruker APEX IV FTMS using a FT-ICR mass analyzer. The *N*-tosylhydrazones evaluated in the current study were prepared using a literature procedure [2]. Unless otherwise noted, materials obtained from commercial suppliers were used as supplied without further purification.

2.2. General procedure for the Cu(I)-catalyzed reaction of *N*-tosylhydrazones **1a–g** with 3-buten-1-ol

3-Butyn-1-ol (**2**, 42 mg, 0.6 mmol) was added to a mixture of CuI (3.8 mg, 0.02 mmol), bathophenanthroline (6.64 mg, 0.02 mmol), tetrabutylammonium bromide (TBAB) (19.3 mg, 0.06 mmol), LiO^tBu (48 mg, 0.6 mmol) and *N*-tosylhydrazone (**1a**, 70 mg, 0.2 mmol) in 1,4-dioxane (1 mL) under nitrogen, and the resulting mixture was stirred at 110 °C for 4 h. Upon completion of the reaction, as determined by TLC, the reaction was cooled to room temperature and treated with TsOH (68.8 mg, 0.4 mmol), and the resulting mixture was stirred for 2 h at 80 °C. The reaction was then cooled to ambient temperature and evaporated to dryness to give a crude mixture, which was purified by column chromatography over silica gel to afford pure **3a** as a white solid (35 mg, 75%).

2-(Diphenylmethylene)tetrahydrofuran (3a). White solid (35 mg, 75%); mp = 101–103 °C; R_f = 0.55 (1:100, EtOAc/petroleum ether); 1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.26–7.19 (m, 5H), 7.11 (t, J = 7.3 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 142.1, 139.9, 130.5, 128.9, 128.2, 127.7, 126.0, 125.3, 110.6, 71.3, 30.2, 24.9; IR (film): 3030, 2289, 1641, 1599, 1497, 1203, 1175, 1037, 910, 701, 656 cm^{-1} ; EI-MS (m/z , relative intensity): 236 (M^+ , 90), 217 (3), 207 (5), 180 (40), 165 (100), 152 (10), 115 (12), 83 (5); HRMS (EI) calcd. for $C_{17}H_{17}O$ [$M+H$] $^+$: 237.1271; found: 237.1274.

2-(Di-*p*-tolylmethylene)tetrahydrofuran (3b). Waxy liquid, (32 mg, 60%); R_f = 0.55 (1:100, EtOAc/petroleum ether); 1H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.1 Hz, 2H), 7.12–7.04 (m, 6H), 4.22 (t, J = 6.7 Hz, 2H), 2.60 (t, J = 7.5 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H), 2.02–1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 139.2, 137.3, 135.4, 134.7, 130.2, 128.9, 128.8, 128.4, 110.3, 71.1, 30.0, 24.9, 21.1, 21.0; IR (film): 2974, 2918, 1712, 1642, 1609, 1510, 1408, 1172, 1034, 819, 665 cm^{-1} ; EI-MS (m/z , relative intensity): 264 (M^+ , 100), 249 (3), 235 (5), 221 (8), 208 (40), 193 (60), 178 (38), 165 (10), 152 (5), 139 (3), 129 (8), 115 (5), 89 (5); HRMS (EI) calcd. for $C_{19}H_{21}O$ [$M+H$] $^+$: 265.1587; found: 265.1583.

2-(Di(thiophen-3-yl)methylene)tetrahydrofuran (3c). Light brown liquid (31 mg, 63%); R_f = 0.50 (1:100, EtOAc/petroleum ether); 1H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 3.0, 4.9 Hz, 1H), 7.24 (dd, J = 1.2, 5.0 Hz, 1H), 7.20–7.17 (m, 2H), 7.08 (dd, J = 1.2, 2.9 Hz, 1H), 6.97 (dd, J = 1.1, 4.9 Hz, 1H), 4.32 (t, J = 6.8 Hz, 2H), 2.62 (t, J = 7.5 Hz, 2H), 2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 141.5, 140.1, 129.7, 128.4, 124.7, 123.7, 123.0, 120.6,

101.6, 71.7, 30.0, 24.7; IR (film): 2960, 2924, 1650, 1461, 1377, 1260, 1167, 1082, 1035, 795 cm^{-1} ; EI-MS (m/z , relative intensity): 248 (M^+ , 100), 237 (5), 219 (5), 207 (12), 192 (70), 177 (40), 147 (15), 134 (8), 89 (5); HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{13}\text{OS}_2$ [$M+H$] $^+$: 249.0402; found: 249.0399.

2-(Bis(4-fluorophenyl)methylene)tetrahydrofuran (3d). White solid (38 mg, 70%); mp = 87–89 °C; R_f = 0.38 (1:60, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.33 (dd, J = 5.7, 7.8 Hz, 2H), 7.13 (dd, J = 5.6, 7.6 Hz, 2H), 7.01 (t, J = 8.2 Hz, 2H), 6.93 (t, J = 8.3 Hz, 2H), 4.27 (t, J = 6.7 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H), 2.02 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.2 (d, J = 75.3 Hz), 159.8 (d, J = 75.0 Hz), 155.2, 137.8 (d, J = 3.4 Hz), 135.8 (d, J = 3.2 Hz), 131.9 (d, J = 7.9 Hz), 130.3 (d, J = 7.5 Hz), 115.2 (d, J = 21.2 Hz), 114.5 (d, J = 21.1 Hz), 108.6, 71.5, 30.1, 24.9; IR (film): 2969, 2901, 1642, 1603, 1507, 1223, 1033, 836, 800, 652 cm^{-1} ; EI-MS (m/z , relative intensity): 272 (M^+ , 95), 243 (3), 216 (50), 201 (100), 183 (8), 133 (4), 120 (3), 101 (8); HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{15}\text{F}_2\text{O}$ [$M+H$] $^+$: 273.1086; found: 273.1082.

2-(Bis(4-chlorophenyl)methylene)tetrahydrofuran (3e). White waxy solid (40 mg, 66%); R_f = 0.43 (1:100, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.28 (m, 4H), 7.20 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 4.28 (t, J = 6.8 Hz, 2H), 2.58 (t, J = 7.5 Hz, 2H), 2.06–1.99 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 140.1, 138.0, 131.8, 130.1, 128.6, 127.9, 108.5, 71.6, 29.7, 24.8; IR (film): 2924, 1642, 1691, 1176, 1091, 1033, 907, 731 cm^{-1} ; EI-MS (m/z , relative intensity): 304 (M^+ , 100), 248 (50), 234 (15), 213 (25), 199 (60), 178 (40), 163 (28), 149 (5), 137 (5), 125 (10), 99 (8); HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{O}$ [$M+H$] $^+$: 305.0495; found: 305.0490.

2-(Bis(4-(trifluoromethyl)phenyl)methylene)tetrahydrofuran (3f). Colorless liquid (46 mg, 62%); R_f = 0.45 (1:100, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.53–7.33 (m, 8H), 4.32 (t, J = 6.7 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 2.05 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.6, 142.1, 140.3, 133.9, 132.0, 129.0, 128.2, 127.1 (q, J = 3.6 Hz), 125.6 (d, J = 3.8 Hz), 123.3 (d, J = 3.7 Hz), 122.1 (d, J = 3.7 Hz), 108.4, 72.0, 30.5, 24.7; IR (film): 2951, 1643, 1331, 1280, 1260, 1166, 1123, 1074 cm^{-1} ; EI-MS (m/z , relative intensity): 372 (M^+ , 100), 353 (10), 330 (5), 316 (8), 302 (10), 282 (5), 247 (6), 233 (60), 183 (8); HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{15}\text{F}_6\text{O}$ [$M+H$] $^+$: 373.1022; found: 373.1017.

2-(Bis(4-methoxyphenyl)methylene)tetrahydrofuran (3g). Light yellow liquid (35 mg, 58%); R_f = 0.40 (1:30, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 6.83 (dd, J = 8.7, 23.0 Hz, 4H), 4.24 (t, J = 6.7 Hz, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 2.59 (t, J = 7.5 Hz, 2H), 2.60–1.96 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.8, 157.1, 144.5, 142.0, 136.5, 131.4, 130.2, 130.0, 129.3, 127.6, 124.6, 113.6, 113.2, 71.1, 55.2, 29.9, 25.0, 21.6, 21.4; IR (film): 2925, 2853, 1608, 1509, 1246, 1173, 1033, 653 cm^{-1} ; EI-MS (m/z , relative intensity): 296 (M^+ , 100), 281 (10), 267 (10), 253 (12), 240 (75), 225 (40), 207 (45), 165 (15), 113 (20); HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{21}\text{O}_3$ [$M+H$] $^+$: 297.1485; found: 297.1490.

2-(Di-*m*-tolylmethylene)tetrahydrofuran (3h). White oil

(25.8 mg, 50%); R_f = 0.55 (1:100, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.23–7.16 (m, 2H), 7.18–7.12 (m, 2H), 7.04–6.99 (m, 3H), 6.94–6.93 (d, J = 6.9 Hz, 2H), 4.24 (t, J = 6.7 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 2.31 (s, 3H), 2.28 (s, 3H), 1.99 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 142.1, 140.0, 137.7, 129.7, 128.0, 127.6, 127.5, 126.7, 126.3, 110.7, 71.3, 30.2, 25.0, 21.6, 21.5; IR (film): 3030, 2970, 2316, 1642, 1599, 1484, 1246, 1164, 1040, 784, 704 cm^{-1} ; EI-MS (m/z , relative intensity): 264 (M^+ , 100), 231 (5), 221 (10), 208 (50), 193 (60), 178 (50), 165 (10), 152 (5), 129 (5), 115 (3); HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{21}\text{O}$ [$M+H$] $^+$: 265.1587; found: 265.1585.

2-(Bis(3-methoxyphenyl)methylene)tetrahydrofuran (3i). White oil (34.8 mg, 59%); R_f = 0.40 (1:40, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.22 (t, J = 7.9 Hz, 2H), 7.16 (t, J = 7.9 Hz, 2H), 7.05–7.04 (m, 1H), 6.95 (d, J = 7.9 Hz, 1H), 6.75–6.79 (m, 3H), 6.88 (dd, J = 2.0, 7.9 Hz, 1H), 4.27 (t, J = 6.7 Hz, 2H), 3.77 (s, 3H), 3.74 (m, 3H), 2.61 (t, J = 7.5 Hz, 2H), 2.00 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 159.2, 155.7, 143.4, 141.2, 129.2, 128.6, 123.1, 116.1, 114.9, 111.6, 110.6, 110.3, 71.5, 55.2, 55.1, 30.4, 24.8; IR (film): 2920, 2845, 1643, 1600, 1490, 1283, 1222, 1032, 876, 779 cm^{-1} ; EI-MS (m/z , relative intensity): 296 (M^+ , 100), 281 (3), 253 (3), 240 (30), 225 (20), 209 (20), 195 (10), 181 (5), 165 (5), 152 (5), 139 (5); HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{21}\text{O}_3$ [$M+H$] $^+$: 297.1485; found: 297.1484.

2-(Bis(3-fluorophenyl)methylene)tetrahydrofuran (3j). White oil (34.3 mg, 63%); R_f = 0.50 (1:100, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.26 (m, 1H), 7.20–7.15 (m, 2H), 7.08–7.06 (m, 1H), 6.97–6.88 (m, 3H), 6.84–6.79 (m, 1H), 4.30 (t, J = 6.8 Hz, 2H), 2.60 (t, J = 7.5 Hz, 2H), 2.03 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.9 (d, J_F = 245.9 Hz), 161.7 (d, J_F = 243.4 Hz), 155.8, 142.7 (d, J_F = 7.8 Hz), 140.5 (d, J_F = 8.2 Hz), 128.7 (d, J_F = 8.6 Hz), 127.9 (d, J_F = 8.6 Hz), 125.2 (d, J_F = 2.7 Hz), 123.3 (d, J_F = 2.7 Hz), 116.3 (d, J_F = 20.6 Hz), 114.5 (d, J_F = 22.5 Hz), 112.3 (d, J_F = 20.9 Hz), 111.1 (d, J_F = 21.4 Hz), 107.8, 70.8, 29.5, 23.7; IR (film): 2978, 2344, 1640, 1609, 1580, 1486, 1439, 1183, 1165, 1039, 780, 744 cm^{-1} ; EI-MS (m/z , relative intensity): 272 (M^+ , 100), 253 (3), 230 (10), 216 (30), 201 (80), 183 (10), 170 (3), 133 (5), 115 (5), 101 (8); HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{15}\text{F}_2\text{O}$ [$M+H$] $^+$: 273.1085; found: 273.1085.

2-(Bis(2-fluorophenyl)methylene)tetrahydrofuran (3k). White oil (30.7 mg, 56%); R_f = 0.50 (1:100, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.28 (m, 1H), 7.20–7.16 (m, 3H), 7.14–6.97 (m, 4H), 4.21 (t, J = 6.7 Hz, 2H), 2.62 (t, J = 7.5 Hz, 2H), 2.05 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.4 (d, J_F = 246.1 Hz), 160.1 (d, J_F = 247.4 Hz), 157.8, 132.3 (d, J_F = 3.5 Hz), 132.0 (d, J_F = 3.9 Hz), 128.5 (d, J_F = 15.6 Hz), 128.1 (d, J_F = 8.2 Hz), 127.9 (d, J_F = 8.3 Hz), 127.3 (d, J_F = 15.4 Hz), 123.8 (d, J_F = 3.4 Hz), 123.6 (d, J_F = 3.3 Hz), 115.7 (d, J_F = 23.0 Hz), 115.6 (d, J_F = 22.5 Hz), 97.9, 71.9, 28.9, 24.9; IR (film): 3058, 2848, 1662, 1645, 1576, 1490, 1225, 1179, 991, 758 cm^{-1} ; EI-MS (m/z , relative intensity): 272 (M^+ , 100), 253 (1), 243 (3), 240 (20), 216 (40), 201 (90), 183 (20), 170 (2), 133 (5), 101 (5); HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{15}\text{F}_2\text{O}$ [$M+H$] $^+$: 273.1085; found: 273.1083.

2.3. General procedure for the Cu(I)-catalyzed reaction of *N*-tosylhydrazones 4a–c with 3-butyne-1-ol

3-Butyn-1-ol (**2**, 42 mg, 0.6 mmol) was added to a mixture of CuI (3.8 mg, 0.02 mmol), bathophenanthroline (6.64 mg, 0.02 mmol), TBAB (19.3 mg, 0.06 mmol), LiO^tBu (48 mg, 0.6 mmol) and *N*-tosylhydrazone (**4a**, 85.3 mg, 0.2 mmol) in 1,4-dioxane (1 mL) under nitrogen, and the resulting mixture was stirred at 110 °C for 4 h. Upon completion of the reaction, as determined by TLC analysis, the mixture was cooled to room temperature and treated with TsOH (68.8 mg, 0.4 mmol), and the resulting mixture was stirred at 80 °C for 2 h. The mixture was then cooled to ambient temperature and evaporated under vacuum to give a crude residue, which was purified by column chromatography over silica gel to afford pure **5a** as white solid (42 mg, 67%).

(*E*)-2-([1,1'-Biphenyl]-4-yl(phenyl)methylene)tetrahydrofuran (**5a**). White solid (42 mg, 67%); mp = 141–142 °C; R_f = 0.45 (1:200, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.45–7.41 (m, 4H), 7.27–7.25 (m, 4H), 7.13 (t, J = 7.3 Hz, 1H), 4.27 (t, J = 6.7 Hz, 2H), 2.70 (t, J = 7.5 Hz, 2H), 2.04 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.6, 141.9, 141.2, 139.1, 137.8, 130.6, 129.2, 128.6, 128.3, 126.9, 126.4, 126.1, 110.2, 71.5, 30.3, 24.8; IR (film): 3051, 2927, 1631, 1596, 1489, 1442, 1260, 1171, 1033, 765, 692 cm^{-1} ; EI-MS (m/z , relative intensity): 312 (M^+ , 100), 256 (40), 241 (38), 165 (20), 121 (25); HRMS (EI) calcd. for $\text{C}_{23}\text{H}_{21}\text{O}$ [$\text{M}+\text{H}$] $^+$ 313.1587; found: 313.1588.

(*E*)-2-((3,4-Dimethylphenyl)(phenyl)methylene)tetrahydrofuran (**5b**). White solid (38 mg, 72%); mp = 90–91 °C; R_f = 0.46 (1:200, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, J = 7.6 Hz, 2H), 7.24 (dd, J = 6.3, 9.0 Hz, 2H), 7.12–7.07 (m, 2H), 6.96–6.93 (m, 2H), 4.25 (t, J = 6.7 Hz, 2H), 2.62 (t, J = 7.5 Hz, 2H), 2.26 (s, 3H), 2.22 (s, 3H), 2.03–1.96 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 140.2, 139.5, 136.2, 134.2, 131.6, 129.4, 128.9, 127.9, 127.7, 125.1, 110.4, 110.2, 71.3, 30.2, 24.9, 19.8, 19.4; IR (film): 3018, 2920, 1641, 1503, 1443, 1171, 1039, 819, 701, cm^{-1} ; EI-MS (m/z , relative intensity): 264 (M^+ , 100), 249 (6), 221 (10), 207 (60), 193 (45), 178 (40), 165 (12), 96 (20); HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{21}\text{O}$ [$\text{M}+\text{H}$] $^+$ 265.1587; found: 265.1589.

(*E*)-2-((4-Chlorophenyl)(phenyl)methylene)tetrahydrofuran (**5c**). White solid (37 mg, 68%); mp = 107–108 °C; R_f = 0.43 (1:100, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, J = 7.4 Hz, 2H), 7.29–7.23 (m, 4H), 7.12 (d, J = 8.4 Hz, 3H), 4.26 (t, J = 6.7 Hz, 2H), 2.60 (t, J = 7.5 Hz, 2H), 2.02 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 139.6, 138.6, 130.8, 127.9, 127.4, 126.8, 124.5, 108.6, 70.4, 29.2, 23.9; IR (film): 2960, 2887, 1642, 1596, 1490, 1259, 1089, 1031, 1015, 920, 767 cm^{-1} ; EI-MS (m/z , relative intensity): 270 (M^+ , 100), 214 (35), 200 (15), 179 (50), 165 (80), 139 (5), 115 (5), 82 (6); HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{16}\text{ClO}$ [$\text{M}+\text{H}$] $^+$ 271.0884; found: 271.0886.

2.4. General procedure for the Cu(I)-catalyzed reaction of *N*-tosylhydrazones **7a–c** and 3-butyne-1-ol

3-Butyn-1-ol (**2**, 63 mg, 0.9 mmol) was added to a mixture of CuI (5.7 mg, 0.03 mmol), bathophenanthroline (9.96 mg, 0.03 mmol), TBAB (28.98 mg, 0.09 mmol), Li^tOBu (72 mg, 0.9 mmol) and *N*-tosylhydrazone (**7a**, 68.4 mg, 0.3 mmol) in 1,4-dioxane

(1 mL) under nitrogen, and the resulting mixture was stirred at 110 °C for 4 h. Upon completion of the reaction, as determined by TLC analysis, the mixture was cooled to room temperature and treated with TsOH (103.2 mg, 0.6 mmol) before being heated at 70 °C for 2 h. The mixture was then cooled to room temperature and evaporated under vacuum to give a crude mixture, which was purified by column chromatography over silica gel to afford pure **8a** as a colorless liquid (43 mg, 63%).

(*E*)-2-(4-(Trifluoromethyl)benzylidene)tetrahydrofuran (**8a**). Colorless liquid (43 mg, 63%); R_f = 0.42 (1:50, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 10.0 Hz, 2H), 5.93 (s, 1H), 4.16 (t, J = 6.8 Hz, 2H), 2.84 (t, J = 7.4 Hz, 2H), 2.17–2.10 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.3, 141.6, 129.8, 125.2 (q, J = 3.8 Hz, CF_3), 98.3, 69.8, 28.7, 25.1; IR (film) 2931, 1653, 1371, 1180, 1123, 1084 cm^{-1} ; EI-MS (m/z , relative intensity): 228 (M^+ , 95), 209 (20), 186 (100), 158 (85), 138 (18), 89 (15); HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{12}\text{F}_3\text{O}$ [$\text{M}+\text{H}$] $^+$ 229.0835; found: 229.0837.

(*E*)-4-((Dihydrofuran-2(3H)-ylidene)methyl)benzonitrile (**8b**). Colorless liquid (39 mg, 70%); R_f = 0.35 (1:30, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 5.90 (s, 1H), 4.18 (t, J = 6.9 Hz, 2H), 2.85 (dt, J = 1.9, 7.6 Hz, 2H), 2.15 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.7, 142.9, 132.1, 126.9, 119.5, 107.1, 98.6, 70.0, 29.0, 25.1; IR (film): 2924, 2854, 2219, 1708, 1661, 1602, 1392, 1173, 1028, 984, 845, 734 cm^{-1} ; EI-MS (m/z , relative intensity): 185 (M^+ , 90), 177 (2), 143 (100), 129 (15), 115 (75), 102 (5), 88 (10); HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{12}\text{NO}$ [$\text{M}+\text{H}$] $^+$ 186.0913; found: 186.0916.

(*E*)-2-(2-Chloro-4-(trifluoromethyl)benzylidene)tetrahydrofuran (**8c**). Colorless liquid (46 mg, 58%); R_f = 0.40 (1:40, EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 1.4 Hz, 1H), 7.44 (d, J = 8.3 Hz, 1H), 7.28 (dd, J = 1.8, 8.4 Hz, 1H), 6.13 (s, 1H), 4.20 (t, J = 6.8 Hz, 2H), 2.79 (dt, J = 1.9, 7.5 Hz, 2H), 2.13 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.2, 136.8, 129.8, 124.5 (q, J = 3.9 Hz), 122.3 (dd, J = 3.8, 7.6 Hz), 95.1, 70.2, 28.4, 25.1; IR (film): 2923, 2854, 1660, 1605, 1417, 1328, 1168, 1129, 1083 cm^{-1} ; EI-MS (m/z , relative intensity): 262 (M^+ , 80), 243 (20), 220 (100), 192 (60), 157 (40), 138 (18), 87 (13); HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{11}\text{ClF}_3\text{O}$ [$\text{M}+\text{H}$] $^+$ 263.0448; found: 263.0445.

3. Results and discussion

The symmetrical *N*-tosylhydrazone **1a**, which was derived from benzophenone and 3-butyne-1-ol (**2**), was selected as a model substrate for this reaction with copper(I) iodide as the catalyst. Under similar reaction conditions to those previously reported by our group for the Cu(I)-catalyzed cross-coupling of *N*-tosylhydrazones with alkynes [9,10,21,22], the reaction afforded an isomeric mixture of the tetrahydrofuran product **3a** and dihydrofuran **3a'** (Table 1, entry 1). The structures of **3a** and **3a'** were established based on their NMR and MS data. The structure of **3a** was further confirmed by X-ray crystallography (Fig. 1) [26]. In this experiment, we also observed a very small amount of the corresponding allene, the structure of which was confirmed by ^1H and ^{13}C NMR spectroscopy. A series of screen-

Table 1
Optimization of the reaction conditions.

Entry	Cu(I)/L (10 mol%)	Solvent	[O] or acid	T/°C	Yield ^a
1	CuI	Dioxane	—	90	3a+3a' , 45%
2	CuI/phen	Dioxane	—	90	3a+3a' , 57%
3	CuI/phen	Toluene	—	90	3a+3a' , 30%
4	CuI/phen	DCE	—	90	3a+3a' , 25%
5	Cu(MeCN) ₄ PF ₆ /phen	Dioxane	—	90	3a+3a' , 38%
6	Cu(OAc) ₂ /phen	Dioxane	—	90	3a+3a' , 10%
7	Cu(OEt) ₂ /phen	Dioxane	—	90	3a+3a' , 8%
8	CuCl/phen	Dioxane	—	90	3a+3a' , 35%
9	CuI/phen	Dioxane	—	110	3a+3a' , 64%
10	CuI/phen	Dioxane	BQ	110	Decomposed
11	CuI/phen	Dioxane	DDQ	110	Decomposed
12	CuI/phen	Dioxane	TsOH	90	3a , 59%
13	CuI/phen	Dioxane	TsOH	110	3a , 68%
14	CuI/phen	Dioxane	TFA	110	3a , 66%
15	CuI/bathophen	Dioxane	TsOH	110	3a , 75%

Reaction conditions: For step 1, **1a** (0.2 mmol), **2** (3.0 equiv.), Cu(I) (10 mol%), phen or bathophen (10 mol%), TBAB (30 mol%) and base (3.0 equiv.) in dioxane (1 mL) at 90–110 °C for 4 h. For step 2, [O] or TsOH (2.0 equiv.) at 70–80 °C for 2 h.

^a Isolated yield after column chromatography.

Fig. 1. X-ray structure of **3a**. Thermal ellipsoids shown at 30% probability.

ing experiments were performed to determine the optimum solvent for this transformation, and the results revealed that the polar aprotic solvent dioxane gave the best results (Table 1, entries 3 and 4). We also tested various bases, including K₂CO₃, Cs₂CO₃, NaOH, KOH, NaH, LiO^tBu and NaOCH₃, as well as several phase transfer catalysts (PTCs), including tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC) and tetrabutylammonium iodide (TBAI). The results of these experiments revealed that the use of a combination of LiO^tBu and

TBAB gave the highest yield of the desired product.

Following on from these preliminary results, we proceeded to screen several other important parameters with the aim of further improving the yield and the chemoselectivity of this reaction. We initially evaluated a series of different Cu catalysts using phenanthroline as a ligand (Table 1, entries 5–9). The results revealed that the use of the CuI catalyst in combination with phenanthroline resulted in improved performance (Table 1, entries 2 and 9). However, the nature of the catalyst did not appear to have an adverse impact on the ratio of **3a** and **3a'**. We therefore decided to convert the isomeric mixture generated from the Cu(I)-catalyzed coupling reaction into a single product using either an oxidation or an acid-promoted rearrangement. However, in the presence of an oxidant such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 1,4-benzoquinone (BQ) or PhI(OAc)₂, the isomeric mixture decomposed to form a complex mixture (Table 1, entries 10 and 11). Pleasingly, the treatment of the completed Cu(I)-catalyzed reaction mixture with 2 equiv. of TsOH or trifluoroacetic acid (TFA) for 2 h at 80 °C afforded **3a** as a single product in moderate yield (Table 1, entries 12–14). Based on these results, we screened several other reaction parameters, including the reaction temperature, reaction time and molar ratio of the substrates. Finally, we concluded that the optimum conditions for this transformation were as follows: 1:3 (mol/mol) ratio of *N*-tosylhydrazone **1a** and 3-butyn-1-ol (**2**), 10 mol% CuI, 10 mol% bathophenanthroline, 30 mol% TBAB and 3.0 equiv. of LiO^tBu at 110 °C (Table 1, entry 15).

With the optimum reaction conditions in hand, we proceeded to investigate the scope and generality of this reaction by screening a variety of *N*-tosylhydrazones (**1a–k**), which were derived from the corresponding symmetrical diaryl-methanones, with 3-butyn-1-ol (**2**). As shown in Scheme 2,

Scheme 2. Evaluation of the substrate scope of *N*-tosylhydrazones derived from symmetrical diaryl-methanones. Reaction conditions: *N*-tosylhydrazone **1a–k** (0.2 mmol), 3-butyn-1-ol (**2**, 3.0 equiv.), CuI (10 mol%), bathophenanthroline (L) (10 mol%), TBAB (30 mol%) and LiO^tBu (3.0 equiv.) in dioxane (1 mL) at 110 °C for 4 h. TsOH (2.0 equiv.) was then added, and the resulting mixture was heated at 80 °C for 2 h. Isolated yield by column chromatography.

Scheme 3. Reactions of *N*-tosylhydrazones derived from unsymmetrical diarylmethanone. The reactions were conducted under the same conditions as those described above in Scheme 2. The yields refer to the isomeric mixtures prior to being purified by column chromatography.

these reactions afforded the corresponding 2-(diarylmethylene)tetrahydrofurans **3a–k** in moderate to good yields. Notably, *N*-tosylhydrazones bearing an electron-rich or electron-deficient substituent on the *para*, *meta* or *ortho* positions of their aromatic rings were found to be good substrates for this transformation. The *N*-tosylhydrazone derived from di-3-thienyl ketone (**1c**) also reacted smoothly to give the corresponding product **3c** in 63% yield.

Encouraged by the successful tandem cyclization of the symmetrical *N*-tosylhydrazones with 3-alkynol, we proceeded to extend this strategy to a series of unsymmetrical *N*-tosylhydrazones, which were derived from the corresponding unsymmetrical ketones. As shown in Scheme 3, *N*-tosylhydrazones **4a–c** reacted with 3-alkynol (**2**) to give the corresponding 2-(diarylmethylene)tetrahydrofurans **5a–c** with good stereoselectivity. The outcome of the reaction was found to be largely unaffected by the structure of the unsymmetrical *N*-tosylhydrazone substrate or the nature of the substituents on the aromatic ring. All of these reactions gave the *E* isomer as the major product, with only trace amounts of the corresponding *Z* isomers **6a–c** being detected by crude ^1H NMR and GC-MS analysis. Pleasingly, the minor *Z* isomers were separated or isomerized to the corresponding *E* isomers during column chromatographic purification over silica gel.

Finally, we investigated the reaction of several unsymmetrical *N*-tosylhydrazones **7a–c**, which were derived from the corresponding aromatic aldehydes, with 3-alkynol (**2**) under the optimized reaction conditions. As demonstrated in Scheme

Scheme 4. Reaction of *N*-tosylhydrazones derived from aromatic aldehydes. The reactions were conducted under the same conditions as those described above in Scheme 2. The yields refer to the isomeric mixtures prior to their purification by column chromatography.

Scheme 5. Proposed reaction mechanism of Cu(I)-catalyzed cascade reaction of *N*-tosylhydrazones with 3-butyn-1-ol.

4, the substituent at the *para* position of the aromatic ring of the *N*-tosylhydrazones had no discernible impact on the reaction. The presence of an electron-withdrawing group was therefore tolerated under these conditions, affording the corresponding 2-(diarylmethylene)tetrahydrofurans in moderate yields. Similarly, the *E* isomers **8a–c** were determined to be the major products, with only small amounts of the corresponding *Z* isomers **9a–c** being detected by ^1H NMR and GC-MS analysis of the crude products in each case. Once again, the minor isomers were readily separated or isomerized to the corresponding *E* isomer by column chromatography over silica gel.

Based on the results described above we proposed a plausible mechanism to account for this Cu(I)-catalyzed tandem cyclization, which is shown in Scheme 5. The initial reaction of 3-butyn-1-ol with the Cu(I) catalyst would give the Cu(I) acetylide **A**, which would react with the *in situ* generated diazo intermediate **B** to generate the Cu(I)-carbene species **C**. The alkynyl migratory insertion of Cu(I)-carbene **C** to the carbenic carbon would give intermediate **D**, which would be protonated to give allene **E**. Finally, allene **E** would undergo a cyclization reaction via an intramolecular nucleophilic addition reaction to afford the final product **3a**, with the concomitant regeneration of the Cu(I) catalyst.

4. Conclusions

We have investigated a Cu(I)-catalyzed tandem cyclization reaction of *N*-tosylhydrazones with 3-butyn-1-ol. This reaction represents a straightforward approach for the synthesis of 2-(diarylmethylene)tetrahydrofurans and proceeds via the formation of a carbene intermediate, followed by sequential cyclization and isomerization steps. These results further demonstrate the generality of this approach for the formation of allenes via the Cu(I)-catalyzed reaction of *N*-tosylhydrazones with terminal alkynes [27].

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Graphical Abstract

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Cu(I)-catalyzed cascade reaction of *N*-tosylhydrazones with 3-butyne-1-ol: A new synthesis of tetrahydrofurans

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A simple and efficient method has been developed for the synthesis of tetrahydrofurans. This method is based on the Cu(I)-catalyzed cascade coupling/cyclization reaction of *N*-tosylhydrazones with 3-butyne-1-ol, and involves a Cu(I) carbene migratory insertion as one of its key steps.

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一价铜催化的*N*-对甲基苯磺酰肼与3-丁炔-1-醇的串联反应：一种四氢呋喃类化合物的新合成方法

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摘要: 最近几年来, 利用稳定的重氮类化合物和*N*-对甲基苯磺酰肼类化合物作为金属卡宾前体, 在过渡金属催化下通过形成金属卡宾的偶联反应引起了人们广泛的兴趣。金属卡宾前体与有机金属物种反应, 可以生成金属卡宾中间体, 并发生金属上基团的转移插入过程, 得到新的有机金属物种, 从而实现丰富的偶联反应。这类经由金属卡宾转移插入过程的交叉偶联反应为构建C–C键, C–N键以及许多环状化合物和不饱和有机分子结构提供了可靠而强有力的工具。本课题组一直致力于研究该类经由金属卡宾中间体的催化转化和偶联反应, 报道了在铜催化下, 对甲基苯磺酰肼以及重氮类化合物可以与端炔反应, 通过所形成的炔基铜卡宾中间体的转移插入过程, 可高效得到联烯类化合物。该类反应条件相对温和, 并且有很好的底物普适性。不仅各种多取代的联烯类化合物, 而且苯并呋喃, 菲以及呋喃等结构都可由这类铜催化的肼和炔烃的偶联反应来得到。在这些反应中, 通过炔基铜卡宾中间体上炔基的转移插入过程, 在形成了C(Sp³)-Cu键以后, 通过铜的1,3-迁移过程, 可以得到联烯结构, 随后发生分子内杂原子的亲核进攻或者6π电子环化过程来实现苯并呋喃, 菲等杂环类结构的构建。

另一方面, 该类反应进一步拓展和研究, 可望得到其他有价值的有机分子骨架。环状的醚类结构, 如四氢呋喃结构, 也

是有机化合物中常见的结构类型, 我们希望从目前已经发展成熟的卡宾前体与炔烃生成联烯的偶联反应出发, 通过分子内的串联过程来高效地构建取代的环状醚类结构. 我们设想, 在炔烃上引入氧原子作为亲核试剂, 在形成联烯化合物以后, 通过分子内氧原子对联烯基的亲核进攻, 来实现串联的分子内关环反应, 从而构建环状醚类结构. 本文以CuI为催化剂, 3-丁炔-1-醇为炔烃偶联组分, 采用二芳基对甲苯磺酰脲作为金属卡宾前体, 实现了取代四氢呋喃的合成. 在对甲苯磺酰脲与3-丁炔-1-醇类化合物发生偶联反应生成二芳基联烯基化合物以后, 采用一锅法实现分子内的关环反应, 从而生成亚烯基取代的四氢呋喃化合物.

该串联反应不仅具有原料易得和操作较为简便等优点, 而且底物普适性和官能团耐受性都较好, 多种取代的二芳基脲类化合物都能以较好的收率得到目标产物, 从而为四氢呋喃类化合物的合成提供了一种新的方法. 该反应进一步展示了经由金属卡宾中间体的交叉偶联反应的普遍性, 将在有机化学和有机合成领域具有广泛的研究和应用价值.

关键词: 铜催化; 联烯; 四氢呋喃; 交叉偶联反应; 端炔

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