CuI-catalysed synthesis of (*E*)-arylvinyl aryl ethers

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(*E*)-Arylvinyl aryl ethers have been synthesised from (*E*)-arylvinyl bromide and phenols in 1,4-dioxan in high yield catalysed by CuI/*N*,*N*-dimethylglycine in the presence of Cs_2CO_3.

Keywords: aryl vinyl ether, synthesis, Ullmann-ether reaction, (*E*)-arylvinyl bromide, phenol, CuI, *N*,*N*-dimethylglycine, stereoselectivity

Aryl vinyl ethers are intermediates in a variety of reactions including cycloaddition, cyclopropanation, and metathesis processes, as well as in the synthesis of polymers. In addition, aryl vinyl ethers have found applications in the construction of natural products and compounds which exhibit interesting biological activities.[1] Over the past decade, attention has been devoted to the development of copper-catalysed Ullmann-ether coupling reactions for the synthesis of aryl ethers.[2–10] However, only a few methods have appeared for the copper-catalysed synthesis of vinyl ethers of synthetic, polymeric, or biological importance.[11–14] The most efficient methods for the synthesis of aryl vinyl ethers are based upon Hg-[15,16] and Pd-mediated [17,18] coupling reactions of phenols with different vinyl sources. These suffer from either the toxicity of mercury or the high cost of Pd, as well as the latter's air sensitivity, potentially limiting their use for many industrial applications. Reports of the Cu-catalysed vinylation of phenols have appeared recently.[19–26] Ma and co-workers reported α- and β-amino acids can accelerate Ullmann-type aryl amination whilst the coupling reactions of phenols with aryl halides can be carried out at relatively low temperatures.[27–31] We now report a Ullmann-type of reaction between (*E*)-arylvinyl bromides and phenols using Ma's CuI-*N*,*N*-dimethylglycine catalytic system.[29] This affords (*E*)-arylvinyl aryl ethers efficiently (Scheme 1).

Results and discussion

The Ullmann-ether reaction of (*E*)-arylvinyl bromides (**1**) and phenols (**2**) was carried out at 100 °C for 24 h under N_2 atmosphere (Scheme 1). (*E*)-1-(2-bromovinyl)-4-methylbenzene and *p*-cresol were initially chosen as the model substrates using catalytic amount of CuI and *N*,*N*-dimethylglycine and 5 mL of 1,4-dioxan as the solvent. The expected 4-methylphenyl-*E*-(4-methyl)-styryl ether **3a** was obtained in 94% yield (Table 1, entry 1). Using the same conditions, we have examined the substrate scope of this reaction. Our experiments indicate that a range of (*E*)-arylvinyl bromides underwent the cross-coupling process to produce the corresponding arylvinyl aryl ethers in good to excellent yields (Scheme 1, Table 1). Electron-donating and electron-withdrawing group on the aromatic ring of the (*E*)-arylvinyl bromides or phenols had virtually no effect on the outcome of the reaction. For example, compounds with substituents such as Me, Bu-*t*, OMe, F and Cl on the aromatic ring could be smoothly transformed to the corresponding arylvinyl aryl ethers in high yields under these reaction conditions. The results are listed in Table 1 (entries 2–7). The reaction was found to be equally efficient for phenols bearing Me on the *o*-position of the aromatic ring, affording the products in good yields (Table 1, entries 3 and 4). The stereochemical assignment of the configuration of the products was made on the basis of ^{1}H NMR spectroscopy. This showed that the stereoselectivity was good, as determined by the coupling constant of the "=C–H" (J = 12.4 Hz).

Table 1 Synthesis of arylvinyl aryl ethers[a]

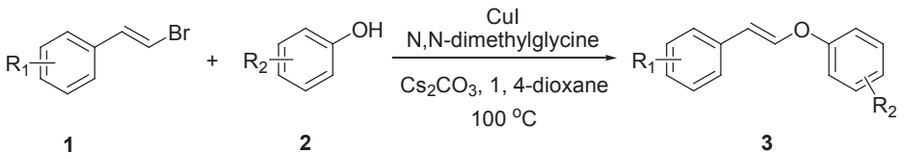
Entry	R^1	R^2	Product **3**	Yields of **3**/%[b]
1	4-Me	4-Me	**3a**	94
2	4-Me	4-Bu-*t*	**3b**	91
3	4-Me	2-Me	**3c**	89
4	4-Me	2,4-Me_2	**3d**	90
5	4-Me	4-MeO	**3e**	94
6	4-F	4-Me	**3f**	91
7	4-Cl	4-Me	**3g**	92

[a]Reaction conditions: (*E*)-arylvinyl bromide (1 mmol), phenol (1.2 mmol), Cs_2CO_3 (2.2 mmol), CuI (0.1 mmol), *N*,*N*-dimethylglycine (0.3 mmol), 1,4-dioxane (4 mL), 100 °C, 24 h.

[b]Isolated yields based on arylvinyl bromide.

Conclusion

In summary, (*E*)-arylvinyl aryl ethers can be synthesised by an Ullmann-ether reaction between (*E*)-arylvinyl bromides and phenols in the presence of a catalytic amount of CuI and *N*,*N*-dimethylglycine using 1,4-dioxan as the solvent. The stereoselectivity was good, as determined by the coupling constant of the "=C–H" (J = 12.4 Hz) in the ^{1}H NMR spectra.



1 **2** **3**

Scheme 1

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Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker DPX-400 spectrometer with $SiMe_4$ as an internal standard. High resolution mass spectra were determined using a Finnigan-NAT GC/MS/DS 8430 spectrometer. All reactions were monitored by TLC with HuanghaiGF$_{254}$ silica gel coated plates. Column chromatography was carried out using 300–400 mesh silica gel at medium pressure.

Synthesis of (E)-arylvinyl aryl ethers **3***; general procedure*

A stirred solution of (*E*)-arylvinyl bromide **1** (1 mmol) and phenol **2** (1.2 mmol) in 1,4-dioxane (4 mL) was treated with Cs_2CO_3 (2.2 mmol), CuI (0.1 mmol), *N*,*N*-dimethylglycine (0.3 mmol) under a nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 24 h. After the completion of the reaction, monitored by TLC, the reaction system was cooled to room temperature, diluted with EtOAc (20 mL) and filtered. The filtrate was washed with saturated brine (20 mL) and water (20 mL), dried over Na_2SO_4, and concentrated. The residue was chromatographed to afford the corresponding (*E*)-arylvinyl aryl ethers **3**.

4-Methylphenyl-E-*(4-methyl)-styryl ether (***3a***, Table 1, entry 1):* Yield 94%; light yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (6H, s), 6.28 (1H, d, *J*=12.4 Hz), 6.95 (2H, d, *J*=8.4 Hz), 7.08–7.20 (7H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 21.1, 113.0, 116.8, 125.5, 129.3, 130.1, 132.3, 132.6, 136.2, 143.3, 155.1. HRMS calcd for $C_{16}H_{16}O$ *m/z* 224.1201; found *m/z* 224.1207.

4-tert-*Butylphenyl*-E-*(4-methyl)-styryl ether (***3b***, Table 1, entry 2):* Yield 91%; light yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (9H, s), 2.33 (3H, s), 6.32 (1H, d, *J*=12.4 Hz), 7.01 (2H, d, *J*=8.8 Hz), 7.11–7.22 (5H, m), 7.31 (2H, d, *J*=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 31.5, 34.3, 113.1, 116.4, 125.5, 126.5, 129.4, 132.3, 136.2, 143.2, 146.0, 155.0. HRMS calcd for $C_{19}H_{22}O$ *m/z* 266.1671; found *m/z* 266.1666.

2-Methylphenyl-E-*(4-methyl)-styryl ether (***3c***, Table 1, entry 3):* Yield 89%; light yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (3H, s), 2.37 (3H, s), 6.28 (1H, d, *J*=12.4 Hz), 7.02–7.25 (9H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1, 21.1, 112.6, 116.4, 123.3, 125.5, 127.0, 128.18, 129.4, 131.2, 132.4, 136.2, 143.6, 155.3. HRMS calcd for $C_{16}H_{16}O$ *m/z* 224.1201; found *m/z* 224.1204.

2,4-Dimethylphenyl-E-*(4-methyl)-styryl ether (***3d***, Table 1, entry 4):* Yield 90%; light yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (3H, s), 2.32 (3H, s), 2.34 (3H, s), 6.20 (1H, d, *J*=12.4 Hz), 6.89–7.21 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0, 20.6, 21.1, 111.8, 116.7, 125.4, 127.4, 128.0, 129.4, 131.9, 132.5, 132.9, 136.0, 144.3, 153.1. HRMS calcd for $C_{17}H_{18}O$ *m/z* 238.1358; found *m/z* 238.1360.

4-Methoxylphenyl-E-*(4-methyl)-styryl ether (***3e***, Table 1, entry 5):* Yield 94%; light yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (3H, s), 3.79 (3H, s), 6.23 (1H, d, *J*=12.4 Hz), 6.88 (2H, d, *J*=8.8 Hz), 6.99 (2H, d, *J*=8.8 Hz), 7.05–7.11 (3H, m), 7.18 (2H, d, *J*=8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 21.1, 113.0, 116.8, 125.5, 129.3, 130.1, 132.3, 132.6, 136.2, 143.3, 155.1. HRMS calcd for $C_{16}H_{16}O_2$ *m/z* 240.1150; found *m/z* 240.1154.

4-Methylphenyl-E-*(4-fluro)-styryl ether (***3f***, Table 1, entry 6):* Yield 91%; light yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (3H, s), 6.25 (1H, d, *J*=12.4 Hz), 6.93–7.24 (9H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 115.0, 116.9, 126.9, 127.0, 130.1, 130.2, 130.2, 132.8, 143.8, 155.0. HRMS calcd for $C_{15}H_{13}FO_2$ *m/z* 244.0900; found *m/z* 244.0906.

4-Methylphenyl-E-*(4-chloro)-styryl ether (***3g***, Table 1, entry 7):* Yield 92%. Yellow vicious liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (3H, s), 6.21 (1H, d, *J*=12.4 Hz), 6.92 (2H, d, *J*=8.4 Hz), 7.09–7.24 (9H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 116.4, 117.0, 126.7, 128.8, 130.2, 131.9, 133.0, 133.9, 144.6, 154.9. HRMS calcd for $C_{15}H_{13}ClO_2$. *m/z* 260.0604; found *m/z* 260.0601.

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References

1 M.S. Kabir, M. Lorenz, O.A. Namjoshi and J.M. Cook, *Org. Lett.*, 2010, **12**, 464.
2 F. Monnier and M. Taillefer, *Angew. Chem., Int. Ed.*, 2009, **48**, 6954.
3 I.P. Beletskaya and A.V. Cheprakov, *Coord. Chem. Rev.*, 2004, **248**, 2337.
4 R. Fraln and D. Kikeji, *Synthesis*, 2006, 2271.
5 J.P. Corbet and G. Mignani, *Chem. Rev.*, 2006, **106**, 2651.
6 M. Kienle, S.R. Dubakka, K. Brade and P. Knochel, *Eur. J. Org. Chem.*, 2007, 4166.
7 M. Carril, R. SanMartin and E. Dominguez, *Chem. Soc. Rev.*, 2008, **37**, 639.
8 A. Shafir, P.A. Lichtor and S.L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 3490.
9 R.A. Altman and S.L. Buchwald, *Org. Lett.*, 2007, **9**, 643.
10 H. Harada, R.K. Thalji, R.G. Bergman and J.A. Ellman, *J. Org. Chem.*, 2008, **73**, 6772.
11 M. Taillefer, A. Ouali, B. Renard and J.F. Spindler, *Chem. Eur. J.*, 2006, **12**, 5301.
12 W.L. Bao, Y.Y. Liu and X. Lv, *Synthesis*, 2008, **12**, 1911.
13 A. Ouali, R. Laurent, A.M. Caminade, J.P. Majoral and M. Taillefer, *J. Am. Chem. Soc.*, 2006, **128**, 15990.
14 H. Kaddouri, V. Vicente, A. Ouali, F. Ouazzani and M. Taillefer, *Angew. Chem., Int. Ed.*, 2009, **48**, 333.
15 V.N. Kizhnyae, F.A. Pokatilov, N.A. Tsypina, G.V. Ratovskii, L.I. Vereshchagin and A.I. Smirnov, *Russ. J. Org. Chem.*, 2002, **38**, 1056.
16 Y.L. Chen, K.G. Hedberg and K.J. Guarino, *Tetrahedron Lett.*, 1989, **30**, 1067.
17 A.Y. Lebedev, V.V. Izmer, D.N. Kazyul'kin, I.P. Beletskaya and A.Z. Voskoboynikov, *Org. Lett.*, 2002, **4**, 623.
18 M.C. Willis, D. Taylor and A.T. Gillmore, *Chem. Commun.*, 2003, 2222.
19 P.Y.S. Lam, G. Vincent, D. Bonne, C.G. Clark. and S. Deudon, *Tetrahedron Lett.*, 2003, **44**, 4927.
20 P.Y.S. Lam., G. Vincent, C.G. Clark, S. Deudon and P.K. Jadhav, *Tetrahedron Lett.*, 2001, **42**, 3415.
21 M. Blouin and R. Frenette, *J. Org. Chem.,* 2001, **66**, 9043.
22 Z. Wan, C.D. Jones, T.M. Koenig, Y.J. Pu and D. Mitchell, *Tetrahedron Lett.*, 2003, **44**, 8257.
23 D. Ma, Q. Cai and X. Xie, *Synlett*, 2005, **11**, 1767.
24 G. Shen, X. Lv, W. Qian and W. Bao, *Tetrahedron Lett.*, 2008, **49**, 4556.
25 Z. Wang, W. Bao and Y. Jiang, *Chem. Commun.*, 2005, 2849.
26 J. Mao, Q. Hua, J. Guo, D. Shi and S. Ji, *Synlett*, 2008, **13**, 2011.
27 D.W. Ma, Y.D. Zhang, J.C. Yao, S.H. Wu and F.G. Tao, *J. Am. Chem. Soc.*, 1998, **120**, 12459.
28 H. Zhang, Q. Cai and D.W. Ma, *J. Org. Chem.*, 2005, **70**, 5164.
29 D.W. Ma and Q. Cai, *Org. Lett.*, 2003, **5**, 3799.
30 W. Zhu and D.W. Ma, *J. Org. Chem.*, 2005, **70**, 2696.
31 X.A. Xie, Y. Chen and D.W. Ma, *J. Am. Chem. Soc.*, 2006, **128**, 16050.

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