Tetrahedron 64 (2008) 11325–11327

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A smooth access to benzotriazoles via azide-benzyne cycloaddition

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ARTICLE INFO

Article history:
Received 9 July 2008
Received in revised form 26 August 2008
Accepted 27 August 2008
Available online 4 October 2008

Keywords:
Benzotriazole
Cycloaddition
Benzyne
Azide
Cesium fluoride

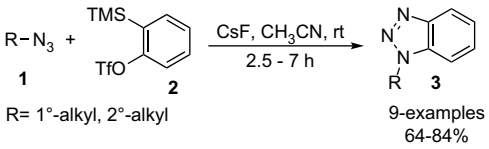
ABSTRACT

A facile synthesis of 1-alkyl benzotriazoles is achieved through fluoride triggered azide-benzyne cycloaddition. Various alkyl azides were treated with 2-(trimethylsilyl) phenyl triflate in the presence of CsF in acetonitrile to afford the corresponding substituted benzotriazoles in good yield.

1. Introduction

Benzotriazoles are important structural motifs of a variety of biologically active compounds for antitumor, antifungal, anti-inflammatory and antidepressant activities, although could not be found in nature.[1] In particular, 1-alkyl benzotriazoles show exceptional binding affinities to a range of proteins.[2] Further, benzotriazoles have great significance in synthetic organic chemistry as valuable intermediates, protecting groups etc.[3] In light of this importance, a facile and efficient method for the synthesis of benzotriazoles is an attractive objective.

The commonly used method for the preparation of benzotriazoles involves the diazotation reaction of *ortho*-phenylenediamines.[4] The alternative method, cycloaddition of azides with arynes, to benzotriazoles is little explored[5] with limited examples having inconvenience in generating the arynes.[6] In the recent times, benzyne was generated simply from 2-(trimethylsilyl)phenyl trifluoromethanesulfonate under mild conditions and used in various cycloaddition reactions.[7] This prompted us to study the practicability of obtaining benzotriazoles from 2-(trimethylsilyl)phenyl triflate, which was not reported previously. In continuation of our work on cycloadditions, [8] herein we report the efficient synthesis of 1-alkyl benzotriazoles via cycloaddition of azide and benzyne under mild reaction conditions (Scheme 1). Larock et al. have parallely explored the similar strategy for the synthesis of benzotriazoles.[9] This reaction is an analogous to the Huisgen 1,3-dipolar cycloaddition of azides and alkynes, which received a significant applications after the development of copper(I)-catalyzed cycloaddition (click reaction).[10,11]



Scheme 1. Synthesis of 1-alkyl benzotriazoles.

2. Results and discussions

Accordingly, the treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2**) with benzyl azide (**1a**) and cesium fluoride in acetonitrile at room temperature afforded the corresponding benzotriazole in 82% yield (entry 1). With this success, a variety of alkyl azides were studied to investigate the scope of the cycloaddition reaction (Table 1). The results revealed that the reactions of structurally different primary alkyl azides **1b** to **1e** were successfully participated in the cycloaddition reaction with **2**, under the described reaction conditions to provide the corresponding 1-alkyl benzotriazoles **3b** to **3e** in good yield (entries 2–5). Similarly, the reactions of various interesting secondary azide substrates **1f** to **1i** (derived from glucose di-acetonide, AZT and others) with **2** were proceeded smoothly to afford the furanolinked triazoles having structural resemblance to nucleosides **3h**, **3i** and others **3f**, **3g** (entries 6–9). Notably, several functionalities/protecting groups

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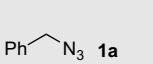
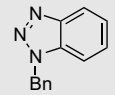
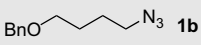
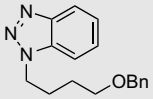
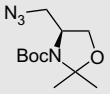
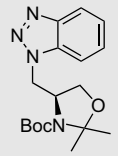
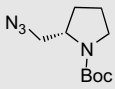
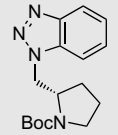
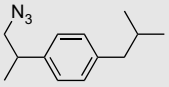
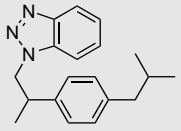
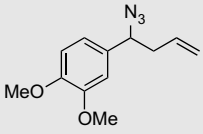
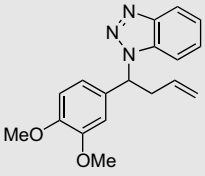
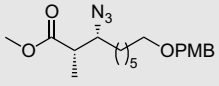
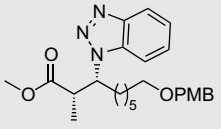
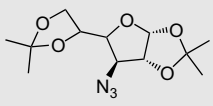
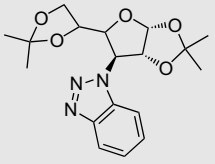
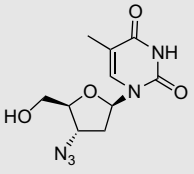
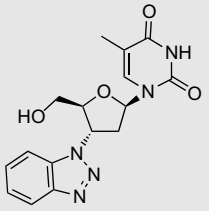
doi:10.1016/j.tet.2008.08.115

Table 1
Cycloaddition of alkyl azides with **2** to 1-alkyl benzotriazoles[a]

Entry	Azide	Time (h)	Product	Yield (%)[b]
1	 **1a**	3	 **3a**	82 (62)[c]
2	 **1b**	2.5	 **3b**	84 (65)[c]
3	 **1c**	2.5	 **3c**	66
4	 **1d**	2.5	 **3d**	69
5	 **1e**	3	 **3e**	74
6	 **1f**	4	 **3f**	73
7	 **1g**	3	 **3g**	74
8	 **1h**	5	 **3h**	82
9	 **1i**	7	 **3i**	64

[a] Reaction conditions: CsF, CH_3CN, rt.
[b] Isolated yields.
[c] Yield from TBAF mediated reaction.

such as ester, ether, amide, *tert*-butylcarbamate, benzyl, *p*-methoxybenzyl, and acetonide were found to be stable under the present reaction conditions. Finally, the reaction of **2** with **1a** and **1b** was tested in the presence of tetrabutylammonium fluoride (TBAF), a metal-free fluorinating agent, and found to be efficient to afford the benzotriazoles **3a** (62%) and **3b** (65%), respectively, however with lower yields.

3. Conclusion

In conclusion, we have successfully developed an extremely facile, new and efficient method for the synthesis of 1-alkyl benzotriazoles by the cycloaddition of 2-(trimethylsilyl) phenyl trifluoromethanesulfonate with alkyl azide in the presence of CsF at room temperature.

4. Experimental

4.1. General

All the solvents and reagents were purified by standard techniques. Crude products were purified by column chromatography on silica gel of 60–120 mesh. IR spectra were recorded on Perkin–Elmer 683, Nicolet Nexus 670 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, DMSO-d_6 solvent on a Varian Gemini 200 and Bruker AV-300 NMR spectrometer. Chemical shifts were reported in parts per million (ppm) with respect to internal TMS. Coupling constants (J) are quoted in hertz (Hz). Optical rotations were measured on Perkin Elmer-343 digital polarimeter using a 1 mL cell with a 1 dm path length, the concentration c is given in g/100 mL. Mass spectra were obtained on Finnegan MAT1020B, micromass VG 70–70H or agilent technologies LC/MSD treapSL spectrometer operating at 70 eV using direct inlet system.

4.2. General experimental procedure (for 3a to 3i)

To a stirred solution of 2-(trimethylsilyl) phenyl trifluoromethanesulfonate **2** (1.0 mmol) in acetonitrile (15 mL), alkyl azide (1.0 mmol), and CsF (2.0 mmol) were added. The reaction mixture was stirred for the given time (see Table 1) at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with ethyl acetate (10 mL) and washed with brine solution (1×15 mL). The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The crude compound was purified by column chromatography (hexanes and ethyl acetate) to afford the corresponding 1-alkyl benzotriazole.

*4.2.1. 1-Benzyl-1H-benzo[d][1,2,3]triazole (**3a**)*

White solid; yield: 29 mg (82%); R_f (hexanes/EtOAc, 9:1)=0.2; mp=113–115 °C; IR (KBr): ν 3426, 2924, 1449, 1224, 746, 718 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.07 (d, J=7.8 Hz, 1H, Ar*H*), 7.44–7.23 (m, 8H, Ar*H*), 5.86 (s, 2H, Ar-C*H*$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.5, 134.9, 129.4 (2C), 129.2, 128.6, 127.8 (2C), 127.6, 124.1, 120.3, 109.9, 52.5; ESI (MS): 209 (M+H)$^+$; HRMS (ESI) calcd for $C_{13}H_{11}N_3Na$: 232.0845 [M+Na]$^+$, found: 232.0849 [M+Na]$^+$.

*4.2.2. 1-(4-(Benzyloxy) butyl)-1H-benzo[d][1,2,3]triazole (**3b**)*

Viscous liquid; yield: 40 mg (84%); R_f (hexanes/EtOAc, 9:1)=0.15; IR (KBr): ν 2926, 2856,1452, 1100, 743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, J=8.3 Hz, 1H, Ar*H*), 7.51–7.23 (m, 8H, Ar*H*), 4.69 (t, J=6.7 Hz, 2H, BtC*H*$_2$), 4.47 (s, 2H, ArC*H*$_2$), 3.52 (t, J=6.0 Hz, 2H, ArCH$_2$OC*H*$_2$), 2.18 (qt, J=7.5 Hz, 2H, BtCH$_2$C*H*$_2$), 1.68 (qt, J=6.7 Hz, 2H, OCH$_2$C*H*$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 138.2, 132.9, 128.3 (2C), 127.6 (3C), 127.1, 123.7, 119.9, 109.3, 73.0, 69.3, 47.9, 26.8, 26.7; ESI (MS): 282 (M+H)$^+$; HRMS (ESI) calcd for $C_{17}H_{20}N_3O$: 282.1600 [M+H]$^+$, found: 282.1607 [M+H]$^+$.

*4.2.3. (S)-tert-Butyl 4-((1H-benzo[d][1,2,3]triazol-1-yl)methyl)-2,2-dimethyloxazolidine-3-carboxylate (**3c**)*

Viscous liquid; yield: 36 mg (66%); R_f (hexanes/EtOAc, 7:3)=0.6; $[\alpha]_D$ +10.8 (c 0.75, $CHCl_3$); IR (KBr): ν 2925, 2855, 761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15–8.03 (m, 1H, Ar*H*), 7.81 (d, J=8.3 Hz, 1H, Ar*H*), 7.66–7.34 (m, 2H, Ar*H*), 4.97–4.74 (m, 2H, BtC*H*$_2$), 4.47–4.32 (m, 1H, NC*H*), 4.24–3.87 (m, 2H, OC*H*$_2$), 1.55 (s, 9H, (C*H*$_3$)$_3$C),

1.48 (s, 3H, CH_3), 1.46 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1, 145.8, 127.5, 124.0, 119.8 (2C), 109.9, 93.9, 80.9, 65.0, 56.7, 48.4, 27.2 (3C), 26.9, 24.0; ESI (MS): 333 $(M+H)^+$; HRMS (ESI) calcd for $C_{17}H_{25}N_4O_3$: 333.1921 $[M+H]^+$, found: 333.1906 $[M+H]^+$.

*4.2.4. (S)-tert-Butyl 2-((1H-benzo[d][1,2,3]triazol-1-yl)methyl)pyrrolidine-1-carboxylate (**3d**)*

Yellow viscous liquid; yield: 35 mg (69%); R_f (hexanes/EtOAc, 7:3)=0.3; $[\alpha]_D$ −8.8 (*c* 1, $CHCl_3$); IR (KBr): ν 2924, 2854, 1690, 1393, 1168, 748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12–8.02 (m, 1H, Ar*H*), 7.76 (d, *J*=8.3 Hz, 1H, Ar*H*), 7.57–7.33 (m, 2H, Ar*H*), 4.96–4.63 (m, 2H, BtCH_2), 4.38–4.25 (m, 1H, NC*H*), 3.47–2.98 (m, 2H, NCH_2), 2.14–1.56 (m, 4H, CHCH_2CH_2), 1.53 (s, 9H, (CH_3)$_3$C); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 144.8, 132.6, 126.3 (2C), 122.9, 118.6, 78.8, 55.6, 48.7, 45.8, 28.6, 27.7 (3C), 13.1; ESI (MS): 303 $(M+H)^+$; HRMS (ESI) calcd for $C_{16}H_{23}N_4O_2$: 303.1815 $[M+H]^+$, found: 303.1829 $[M+H]^+$.

*4.2.5. 1-(2-(4-Isobutylphenyl)propyl)-1H-benzo[d][1,2,3]-triazole (**3e**)*

White solid; yield: 36 mg (74%); R_f (hexanes/EtOAc, 9:1)=0.1; mp=63–65 °C; IR (KBr): ν 3448, 2924, 1634, 1457, 761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, *J*=7.5 Hz, 1H, Ar*H*), 7.36–6.98 (m, 7H, Ar*H*), 4.86–4.63 (m, 2H, BtCH_2), 3.53–3.49 (m, 1H, ArC*H*), 2.42 (d, *J*=6.7 Hz, 2H, ArCH_2), 1.89–1.74 (m, 1H, (CH_3)$_2$C*H*), 1.36 (d, *J*=6.7 Hz, 3H, ArCHCH_3), 0.88 (s, 3H, CH_3), 0.86 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.5, 140.5, 139.8, 133.2, 129.4 (2C), 126.9, 126.7 (2C), 123.5, 119.7, 109.3, 55.5, 44.9, 40.3, 30.1, 22.3 (2C), 18.4; ESI(MS): 294 $(M+H)^+$; HRMS (ESI) calcd for $C_{19}H_{24}N_3$: 294.1964 $[M+H]^+$, found: 294.1978 $[M+H]^+$.

*4.2.6. 1-(1-(3,4-Dimethoxyphenyl)but-3-enyl)-1H-benzo[d][1,2,3]triazole (**3f**)*

Viscous liquid; yield: 38 mg (73%); R_f (hexanes/EtOAc, 7:3)=0.15; IR (KBr): ν 2924, 1514, 1261, 748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, *J*=7.5 Hz, 1H, Ar*H*), 7.60–7.40 (m, 3H, Ar*H*), 7.14–6.89 (m, 3H, Ar*H*), 6.00–5.76 (m, 2H, C*H*=C*H*), 5.36–5.08 (m, 2H, BtC*H*, CH=C*H*), 3.98 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.78–3.58 (m, 1H, BtCHCH_xH$_Y$), 3.41–3.28 (m, 1H, BtCHCH$_x$$H_Y$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.3, 149.0, 146.1, 133.3, 132.7, 131.1, 127.0, 123.8, 119.9, 119.3, 118.6, 110.9, 109.8 (2C), 63.3, 55.9, 55.8, 39.1; ESI (MS): 310 $(M+H)^+$; HRMS (ESI) calcd for $C_{18}H_{20}N_3O_2$: 310.1550 $[M+H]^+$, found: 310.1555 $[M+H]^+$.

*4.2.7. (2S,3R)-Methyl 3-(1H-benzo[d][1,2,3]triazol-1-yl)-9-(4-methoxybenzyloxy)-2-methylnonanoate (**3g**)*

Viscous liquid; yield: 35 mg (69%); R_f (hexanes/EtOAc, 7:3)=0.3; $[\alpha]_D$ −4.4 (*c* 1, $CHCl_3$); IR (KBr): ν 2925, 2854, 1735, 758 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J*=8.3 Hz, 1H, Ar*H*), 7.60–7.36 (m, 3H, Ar*H*), 7.31–7.20 (m, 2H, Ar*H*), 6.88 (d, *J*=8.3 Hz, 2H, Ar*H*), 4.93 (dt, *J*=3.7 Hz, 1H, BtC*H*), 4.38 (s, 2H, OCH_2), 3.81 (s, 3H, OCH_3), 3.74 (s, 3H, COOCH_3), 3.39–3.30 (m, 3H, Ar-CH$_2$-OCH_2, C*H*COOCH$_3$), 2.43–2.29 (m, 1H, BtCHCH_xH$_Y$), 1.97–1.84 (m, 1H, BtCHCH_xH$_Y$), 1.53–1.43 (m, 2H, OCH$_2$CH_2), 1.31–1.04 (m, 6H, OCH$_2$CH$_2$CH_2CH_2CH_2), 0.89 (d, *J*=6.7 Hz, 3H, CH_3CHCOOCH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.8, 159.3, 145.8, 134.1, 130.8, 129.3 (2C), 127.6, 124.1, 120.3, 113.9 (2C), 109.5, 72.6, 70.1, 61.9, 55.4, 52.3, 45.3, 33.5, 29.6, 28.3, 26.2, 26.0, 14.8; ESI (MS): 440 $(M+H)^+$; HRMS (ESI) calcd for $C_{25}H_{33}N_3O_4Na$: 462.2363 $[M+H]^+$, found: 462.2367$[M+H]^+$.

*4.2.8. 1-((3Ar,6S,6aR)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-tetrahydrofuro[2,3-d][1,3]dioxol-6-yl)-1H-benzo[d][1,2,3]triazole (**3h**)*

$[\alpha]_D$ +53.1 (*c* 1, $CHCl_3$); white solid; yield: 49 mg (82%); R_f (hexanes/EtOAc, 9:1)=0.15; mp=125–127 °C; IR (KBr): ν 3424, 2926, 1062, 747 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.05 (d, *J*=8.0 Hz, 1H, Ar*H*), 7.64–7.22 (m, 3H, Ar*H*), 6.37 (d, *J*=3.6 Hz, 1H, BtCHCHC*H*OO), 5.20 (dd, *J*=3.6 Hz, 2H, BtC*H*, BtCHCHC*H*O), 4.41 (dd, *J*=3.6 Hz, 1H, BtCHC*H*CHOO), 3.86 (d, *J*=5.1 Hz, 2H, BtCHC*H*CHO, BtCHCHCHCH_xH$_Y$), 3.02–2.85 (m, 1H, BtCHCHCHCH$_x$$H_Y$), 1.63 (s, 3H, C$H_3$), 1.42 (s, 3H, C$H_3$), 1.40 (s, 3H, C$H_3$), 0.90 (s, 3H, C$H_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.5, 133.9, 127.3, 124.3, 119.9, 112.7, 110.8, 109.6, 106.8, 84.6, 81.1, 72.3, 67.8, 63.8, 27.1, 27.0, 26.4, 24.9; ESI (MS): 362 $(M+H)^+$; HRMS (ESI) calcd for $C_{18}H_{24}N_3O_5$: 362.1710 $[M+H]^+$, found: 362.1722 $[M+H]^+$.

*4.2.9. 1-((2R,4S,5S)-4-(1H-Benzo[d][1,2,3]triazol-1-yl)-5-(hydroxymethyl)-tetrahydrofuran-2-yl)-5-methyl pyrimidine-2,4(1H,3H)-dione (**3i**)*

$[\alpha]_D$ +2.8 (*c* 0.75, MeOH); white solid; yield: 37 mg (64%); R_f (hexanes/EtOAc, 4:6)=0.1; mp=205–207 °C; IR (KBr): ν 3436, 2924, 1643, 760 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ 9.37 (s, 1H, N*H*), 8.07 (d, *J*=7.9 Hz, 1H, Ar*H*), 7.78–7.23 (m, 4H, Ar*H*, C*H*=C), 6.36 (t, *J*=6.3 Hz, 1H, BtCHCH$_2$C*H*), 5.83–5.67 (m, 1H, BtC*H*), 4.59–4.48 (m, 1H, BtCHC*H*), 4.10–3.95 (m, 1H, CH_xH$_Y$OH), 3.77–3.64 (m, 1H, CH$_x$$H_Y$OH), 2.35–2.22 (m, 1H, BtCHCH_xH$_Y$), 2.06–1.99 (m, 1H, BtCHCH$_x$$H_Y$), 1.95 (s, 3H, CH=CC$H_3$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 160.5, 137.8, 128.0, 124.6, 120.2, 114.1, 111.2, 109.8, 109.2 (2C), 88.8, 85.1, 61.7, 56.9, 32.0, 14.2; ESI (MS): 344 $(M+H)^+$; HRMS (ESI) calcd for $C_{16}H_{18}N_5O_4$: 344.1353 $[M+H]^+$, found: 344.1358 $[M+H]^+$.

Acknowledgements

M.S. and C.L.R. thank the CSIR, New Delhi for financial assistance.

References and notes

1. (a) Katarzyna, K.; Najda, A.; Justyna, Z.; Chomicz, L.; Piekarczyk, J.; Myjak, P.; Bretner, M. *Bioorg. Med. Chem.* **2004**, *12*, 2617–2624; (b) Al-Soud, Y. A.; Al-Masoudi, N. A.; Ferwanah, A. S. *Bioorg. Med. Chem.* **2003**, *11*, 1701–1708; (c) Caliendo, G.; Greco, G.; Grieco, P.; Novelino, E.; Perissutti, E.; Santagada, V.; Barbarulo, D.; Esposito, E.; De Blasi, A. *Eur. J. Med. Chem.* **1996**, *31*, 207–213.
2. Rewcastle, G. W.; Palmer, B. D.; Bridges, A. J.; Showalter, H. D. H.; Sun, L.; Nelson, J.; McMichael, A.; Kraker, A. J.; Fry, D. W.; Denny, W. A. *J. Med. Chem.* **1996**, *39*, 918–928.
3. (a) Katritzky, A. R.; Manju, K.; Singh, S. K.; Meher, N. K. *Tetrahedron* **2005**, *61*, 2555–2581; (b) Katritzky, A. R.; Rogovoy, B. V. *Chem.—Eur. J.* **2003**, *9*, 4586–4593; (c) Katritzky, A. R.; Lan, X. F.; Yang, J. Z.; Denisko, O. V. *Chem. Rev.* **1998**, *98*, 409–548; (d) Katritzky, A. R.; Pleynet, D. P. M.; Yang, B. *J. Org. Chem.* **1997**, *62*, 4155–4158; (e) Hagan, D. J.; Gimenez-Arnau, E.; Schwalbe, C. H.; Stevens, M. F. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2739–2746; (f) Miller, R. B.; Stowell, J. G. *J. Org. Chem.* **1983**, *48*, 886–888.
4. (a) Chan, M. S.; Hunter, W. E. U.S. Patent 4,299,965, 1981; (b) Muir, J. C.; Pattenden, G.; Ye, T. *Tetrahedron Lett.* **1998**, *39*, 2861–2864.
5. (a) Kitamura, T.; Fukatsu, N.; Fujiwara, Y. *J. Org. Chem.* **1998**, *63*, 8579–8581; (b) Mitchell, G.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 403–412; (c) Reynolds, G. A. *J. Org. Chem.* **1964**, *29*, 3733–3734.
6. The starting materials used for the generation of benzyne were either explosive or commercially not available.
7. (a) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211–1214; (b) Jin, T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 3323–3325; (c) Liu, Z.; Shi, F.; Martinez, P. D. G.; Raminelli, C.; Larock, R. C. *J. Org. Chem.* **2008**, *73*, 219–226; (d) Huang, X.-C.; Liu, Y.-L.; Liang, Y.; Pi, S.-F.; Wang, F.; Li, J.-H. *Org. Lett.* **2008**, *10*, 1525–1528 and references cited therein.
8. (a) Chandrasekhar, S.; Basu, D.; Rambabu, Ch. *Tetrahedron Lett.* **2006**, *47*, 3059–3063; (b) Chandrasekhar, S.; Rao, Ch. L.; Nagesh, Ch.; Reddy, Ch. R.; Sridhar, B. *Tetrahedron Lett.* **2007**, *48*, 5869–5872.
9. Shi, F.; Waldo, J. P.; Chen, Y.; Larock, R. C. *Org. Lett.* **2008**, *10*, 2409–2412.
10. Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, NY, 1984.
11. (a) Tomoe, C. M.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057–3064; (b) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599; (c) Lutz, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 2–5; (d) Gil, M. V.; Arevalo, M. J.; Lopez, O. *Synthesis* **2007**, 1589–1620.