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## Highly Regio- and Stereoselective Asymmetric Bromoazidation of Chiral $\alpha$ . $\beta$ -Unsaturated Carboxylic Acid Derivatives: Scope and Limitations

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### Received August 1, 2006



Lewis acid catalyzed asymmetric bromoazidation of chiral  $\alpha,\beta$ -unsaturated carboxylic acid derivatives was performed using *N*-bromosuccinimide (NBS) and trimethylsilyl azide (TMSN<sub>3</sub>) as the bromine and azide sources. Among the Lewis acids, Yb(OTf)<sub>3</sub> was found to be the best catalyst. Regio- and *anti*-selectivity of 100% and moderate to good diastereoselectivity (up to 89:11) with good yields were obtained when Oppolzer's bornane sultam chiral auxilairy was used. Diastereoselectivity of >95:05 was observed when (2*S*,*SS*)-2,5-diphenylpyrrolidine was used as the chiral auxiliary.

1,2-Haloazidation of alkenes is an important oxidative reaction in organic chemistry. These vicinal haloazides are versatile chemical intermediates for the synthesis of numerous functionalized compounds such as vinyl azides,<sup>1</sup> amines,<sup>2</sup> heterocycles,<sup>3</sup> and particularly aziridines.<sup>4</sup> The study of catalytic highly regioand stereoselective haloazidation of alkenes, especially  $\alpha$ , $\beta$ unsaturated carbonyl compounds, still remains a challenging task to organic chemists.

In the literature, 1,2-haloazides are usually prepared by addition of Br<sub>2</sub>/NaN<sub>3</sub>,<sup>5</sup> NBS/NaN<sub>3</sub>,<sup>4</sup> I<sub>2</sub>/AgN<sub>3</sub>,<sup>6</sup> and ICl/NaN<sub>3</sub><sup>7</sup> onto alkenes. Although no problems have been reported, bromine azide and iodine azide are potentially explosive. There are also a few methods for the haloazidation of alkenes using NBS/TMSN<sub>3</sub>/Nafion-H resin (cat.),<sup>8</sup> PhI(OAc)<sub>2</sub>/Et<sub>4</sub>NX/TMSN<sub>3</sub>,<sup>9</sup> CAN/NaI/NaN<sub>3</sub>,<sup>10</sup> IPy<sub>2</sub>BF<sub>4</sub>/TMSN<sub>3</sub>,<sup>11</sup> and Oxone/wet-Al<sub>2</sub>O<sub>3</sub>/KI/

 $NaN_3^{12}$  mostly under noncatalytic conditions. The above methods except  $IPy_2BF_4/TMSN_3^{11}$  have not been utilized for the haloazidation of  $\alpha,\beta$ -unsaturated carbonyl compounds.

 $\alpha,\beta$ -Unsaturated carbonyl compounds represent a synthetically useful class of substrate for various alkene oxidative reactions. In particular, haloazidation of  $\alpha,\beta$ -unsaturated carbonyl compounds would provide the functionalized azidohalogenated compounds, which can be transformed to various useful organic compounds by replacing the halogen atom with a series of nucleophiles, where the azido functionality would serve as a protected amino group. However, little attention has been paid to haloazidation of  $\alpha,\beta$ -unsaturated carbonyl compounds. Asymmetric haloazidation reaction has also not been explored. Herein, we report a Lewis acid catalyzed asymmetric bromoazidation of chiral  $\alpha,\beta$ -unsaturated carboxylic acid derivatives using N-bromosuccinimide (NBS) and trimethylsilyl azide (TMSN<sub>3</sub>) as the bromine and azide sources, in which 100% regioselectivity and high diastereoselectivity (>95:5) of the anti- $\alpha$ -bromo- $\beta$ azido carbonyl compounds are demonstrated with good yields.

A current interest in our laboratory is to develop asymmetric 1,2-halofunctionalization of alkenes, especially  $\alpha$ , $\beta$ -unsaturated carbonyl compounds.13 A reliable possibility for exerting stereochemical control in the stereogenic centers is the use of the chiral auxiliary methodology. Recently we have found that Lewis acid activates NBS to facilitate the formation of bromonium ion intermediate from alkenes.<sup>13a</sup> Accordingly, we anticipated that a suitable Lewis acid might catalyze the bromoazidation of chiral  $\alpha,\beta$ -unsaturated carboxylic acid derivatives containing a suitable chiral auxiliary with NBS and TMSN<sub>3</sub>. Initially, asymmetric bromoazidation was investigated on cinnamic acid derivatives containing two well-known chiral auxiliaries such as Evans oxazolidinone14 and Oppolzer's sultam.<sup>15</sup> N-Cinnamoyl-2-oxazolidinone 1a was selected as a model substrate for the screening of the Lewis acids as catalysts for bromoazidation with NBS and TMSN<sub>3</sub> (Table 1). The metal halides and acetates, such as CuCl<sub>2</sub>, Co(OAc)<sub>2</sub>, Cu(OAc)<sub>2</sub>, Mn-(OAc)<sub>2</sub>, and Ni(OAC)<sub>2</sub>, showed poor to moderate catalytic effect for the bromoazidation of 1a (entries 2–6). The metal triflates Zn(OTf)<sub>2</sub>, La(OTf)<sub>3</sub>, Y(OTf)<sub>3</sub>, Sm(OTf)<sub>3</sub>, and Yb(OTf)<sub>3</sub> as

(12) Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. *Tetrahedron Lett.* **2002**, *43*, 1201–1203.

Hassner, A.; Fowler, F. W. J. Org. Chem. 1968, 33, 2686–2691.
 Wasserman, H. H.; Brunner, R. K.; Buynak, J. D.; Carter, C. G.;
 Oku, T.; Robinson, R. P. J. Am. Chem. Soc. 1985, 107, 519–521.

<sup>(3)</sup> For the synthesis of tetrazoles via Hassner-Ritter reaction: (a) Ranganathan, S.; Ranganathan, D.; Mehrotra, A. K. *Tetrahedron Lett.* **1973**, *14*, 2265–2268. (b) Moorthy, S. N.; Devaprabakara, D. *Tetrahedron Lett.* **1975**, *16*, 257–260.

<sup>(4) (</sup>a) Van Ende, D.; Krief, A. Angew. Chem., Int. Ed. Engl. 1974, 13, 279–280. (b) Denis, J. N.; Krief, A. Tetrahedron 1979, 35, 2901–2903.

<sup>(5) (</sup>a) Hassner, A.; Boerwinkle, F. J. Am. Chem. Soc. 1968, 90, 216–218.
(b) Boerwinkle, F.; Hassner, A. Tetrahedron Lett. 1968, 3921–3924.
(c) Hassner, A.; Boerwinkle, F. Tetrahedron Lett. 1969, 3309–3312.

<sup>(6)</sup> Hantzsch, A.; Schümann, M. Ber. Dtsch. Chem. Ges. 1900, 33, 522.
(7) (a) Hassner, A.; Levy, L. A. J. Am. Chem. Soc. 1965, 87, 4203–4204. (b) Fowler, F. W.; Hassner, A.; Levy, L. A. J. Am. Chem. Soc. 1967, 89, 2077–2082.

<sup>(8)</sup> Olah, G. O.; Wang, Q.; Li, X.-Y.; Prakash, G. K. S. Synlett **1990**, 487–489.

<sup>(9)</sup> Kirschning, A.; Hashem, Md. A.; Monenschein, H.; Rose, L.; Schöning, K.-U. J. Org. Chem. 1999, 64, 6522-6526.

<sup>(10)</sup> Nair, V.; George, T. G.; Sheeba, V.; Augustine, A.; Balagopal, L.; Nair, L. G. *Synlett* **2000**, 1597–1598.

<sup>(11)</sup> Barluenga, J.; Alvarez-Perez, M.; Fananas, F. J.; Gonzales, J. M. Adv. Synth. Catal. 2001, 343, 335–337.

<sup>(13) (</sup>a) Hajra, S.; Bhowmick, M.; Karmakar, A. *Tetrahedron Lett.* **2005**, *46*, 3073–3077. (b) (b) Hajra, S.; Karmakar, A.; Bhowmick, M. *Tetrahedron* **2005**, *61*, 2279–2286. (c) Hajra, S.; Karmakar, A.; and Bhowmick, M. *Tetrahedron: Asymmetry* **2006**, *17*, 210–222.

<sup>(14) (</sup>a) Evans, D. A. Aldrichimica Acta **1982**, 15, 23. (b) Evans, D. A.; Shaw, J. T. Actual. Chim. **2003**, 35.

<sup>(15)</sup> Vandewalle, M.; Van, der Eycken, J.; Oppolzer, W.; Vullioud, C. *Tetrahedron* **1986**, *42*, 4035–4043.

O N Ar	ML <sub>n</sub> (10 mol%), NBS (1.2 equiv) TMSN <sub>3</sub> (1.5 equiv) ➤	
6-0	CH <sub>2</sub> Cl <sub>2</sub> , 25 °C	
<b>1</b> 1a: Ar = C <sub>6</sub> H <sub>5</sub>		
<b>1b</b> : Ar = 4-MeC	C <sub>6</sub> H₄	

TABLE 1. Screening of Lewis Acids as Catalysts for the Bromoazidation of 1 with NBS and  $\rm TMSN_3$ 

		N N O	N₃ Ĕr A	r + <	$\sim 0$ $\frac{N_3}{\overline{z}}$ Ar +	N N	O Br O Br
		2		3		anti-4/4'	
entry	sub- strate	MLn	<i>T</i> (h)	conv <sup>a</sup> (%)	ratio <sup>a</sup> (2+3):(4+4')	dr of (2:3) <sup><i>a</i></sup>	yield <sup>a</sup> (%)
1	1a	none	24	<5	ND	ND	
2	1a	CuCl <sub>2</sub>	24	60	71:29	57:43	70
3	1a	Cu(OAc) <sub>2</sub>	24	75	88:12	55:45	47
4	1a	$Co(OAc)_2$	24	66	72:28	57:43	54
5	1a	Mn(OAc) <sub>2</sub>	12	100	77:23	57:43	62
6	1a	Ni(OAc) <sub>2</sub>	10	100	87:13	57:43	65
7	1a	$Mg(OTf)_2$	24	16	85:15	53:47	44
8	1a	Cu(OTf) <sub>2</sub>	24	78	87:13	53:47	33
9	1a	Zn(OTf) <sub>2</sub>	5.5	100	>95:5	56:44	77
10	1a	La(OTf)3	12	100	>95:5	57:43	59
11	1a	Y(OTf) <sub>3</sub>	3.5	100	>95:5	57:43	53
12	1a	Sm(OTf)3	6	100	>95:5	55:45	52
13	1a	Yb(OTf) <sub>3</sub>	4	100	>95:5	59:41	90 (87)
14	1b	Yb(OTf) <sub>3</sub>	2	100	>95:5	55:45	97 (93)

<sup>*a*</sup> Determined by <sup>1</sup>H NMR spectrum analysis of the crude reaction mixture with succinic anhydride as an internal standard. Yields in the parentheses refer to the isolated yields. ND: not determined.

catalysts showed good results (entries 9–13). Among these, Yb-(OTf)<sub>3</sub> was found to be the best catalyst. It should be noted that in the absence of Lewis acid the substrate **1a** did not undergo the bromoazidation reaction (entry 1). When **1a** was treated with TMSN<sub>3</sub> (1.5 equiv) and NBS (1.2 equiv) in CH<sub>2</sub>-Cl<sub>2</sub> in the presence of the Yb(OTf)<sub>3</sub> catalyst (10 mol %) and MS 4Å at room temperature (25 °C), within 4 h it gave the desired bromoazides **2a** and **3a** in good yield (entry 13). Without MS 4Å, 10–15% of halohydroxylated product<sup>13a</sup> was observed. The electron-rich cinnamoyl substrate **1b** also underwent the clean bromoazidation under the same reaction conditions. However, the diastereoselectivities of the above bromoazidation reactions were rather low.

Yb(OTf)<sub>3</sub>-catalyzed bromoazidation of (2R)-N-cinnamoylbornanesultam 5a did not occur at room temperature (Table 2; entry 1), but at 45 °C it provided the clean bromoazides 6a and 7a with moderate diastereoselectivity in good yield (entry 2). This Yb(OTf)<sub>3</sub>-catalyzed bromoazidation reaction was further studied with other cinnamoyl substrates. Electron-rich cinnamoyl substrates 5b and 5c smoothly underwent the bromoazidation reaction at room temperature and afforded the bromoazides with good diastereoselectivity and yields (entries 3 and 5). Substrates 5b and 5c also responded to the bromoazidation reaction even at lower temperature such as -20 °C; however, diastereoselectivity went down (entries 4 and 6). The ortho-substituted electron-deficient cinnamoyl substrates 5d and 5e did not undergo the bromoazidation reaction even at 45 °C. However, substrates 5f and 5g containing the same electron-withdrawing groups at the para position underwent the bromoazidation reaction at 45 °C and provided a nonseparable mixture of

## TABLE 2. Yb(OTf)<sub>3</sub>-Catalyzed Bromoazidation of (2R)-N-Enoylbornanesultams 5



<sup>*a*</sup> Determined by HPLC. NR: no reaction. <sup>*b*</sup> Combined isolated yields of **6** and **7** after column chromatography. NR: no reaction. <sup>*c*</sup> Combined isolated yield of **6f** and **7f** along with 17% of undesired compounds. <sup>*d*</sup> Combined isolated yield of **6g** and **7g** along with 24% of undesired compounds.

diastereomers<sup>16</sup> (entries 9 and 10). The bromoazidation of **5f** and **5g** required an excess of reagents (0.15 equiv of Yb(OTf)<sub>3</sub>, 1.8 equiv of NBS, and 2.0 equiv of TMSN<sub>3</sub>) and longer reaction time for 100% of conversion. Steric effect along with electronic effect might be responsible for substrates **5d** and **5e** not undergoing the bromoazidation reaction. Stereochemistry of the bromoazides **6** and **7** were assigned by analogy with our earlier work.<sup>13a</sup>

It was found that oxazolidinone chiral auxiliary provided poor diastereoselectivity (Table 1) and sultam showed moderate to good diastereoselectivity (Table 2) for the Yb(OTf)<sub>3</sub>-catalyzed bromoazidation of **1** and **5**, respectively. We further investigated the bromoazidation reaction of  $\alpha,\beta$ -unsaturated carboxylic acid derivatives possessing *C*<sub>2</sub>-symmetry with 2,5-diphenylpyrrolidine<sup>17</sup> as a chiral auxiliary. When cinnamide **8a** was treated with Yb(OTf)<sub>3</sub> (0.10 equiv), TMSN<sub>3</sub> (1.5 equiv), and NBS (1.2 equiv) in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C, it provided *anti*- $\alpha$ -bromo- $\beta$ -azido carbonyl compound **9a** with high diastereoselectivity (dr >95: 05) and in good yield (Table 3; entry 1). However, bromoazidation of **8a** at room temperature or at 0 °C showed poor diastereoselectivity of 50:50 and 62:38, respectively.

This bromoazidation reaction was further studied using other cinnamoyl substrates containing electron-donating and -withdrawing substituents on the aromatic ring as well as alkenoyl substrates. It was found that the  $\beta$ -(2-naphthyl)-enoyl substrate **8b** smoothly underwent bromoazidation (entry 2) with high diastereoselectivity (94:06) at -20 °C. The more electron-rich cinnamoyl substrate **8c** also efficiently underwent bromoazidation reaction with slightly lower diastereoselectivity (85: 15; entry 3). The electron-deficient cinnamoyl substrates **8d** and

<sup>(16)</sup> In addition, a minor amount (17–24%) of nonseparable undesired compounds was obtained.

<sup>(17)</sup> Aldous, D. J.; Dutton, W. M.; Steel, P. G. *Tetrahedron: Asymmetry* **2000**, *11*, 2455–2462.

TABLE 3. Yb(OTf)<sub>3</sub>-Catalyzed Bromoazidation of 8



<sup>*a*</sup> Determined from the <sup>1</sup>H NMR spectrum of the crude reaction mixture. NR: no reaction. <sup>*b*</sup> Isolated yields of pure **9** after column chromatography. NR: no reaction. <sup>*c*</sup> Combined isolated yield of **9f** diastereomers along with 15% of undesired compounds. <sup>*d*</sup> Determined by HPLC. <sup>*e*</sup> Combined isolated yield of **9g** diastereomers along with 24% of undesired compounds.

#### SCHEME 1



8e, similar to 5f and 5g, did not undergo any bromoazidation reaction under the same reaction conditions, even with the use of excess reagents at room temperature (25  $^{\circ}\mathrm{C})$  and at 45  $^{\circ}\mathrm{C}$ gave mixture of uncharacterized products. However, the substrates 8f and 8g containing the same electron-withdrawing groups at the *para* position yielded the bromoazides<sup>18</sup> **9f** and 9g at 35 °C (entries 6 and 7). It is to be noted that bromoazidation of substrates 8f and 8g also required, similar to substrates 5f and 5g, an excess of reagents (0.15 equiv of Yb(OTf)<sub>3</sub>, 1.8 equiv of NBS, and 2.0 equiv of TMSN<sub>3</sub>) and longer reaction time for 100% of conversion. The crotonyl substrate 8h underwent bromoazidation reaction at -20 °C and yielded the anti- $\alpha$ -bromo- $\beta$ -azido carbonyl compound **9h** with >95:05 diastereoselectivity and 100% regioselectivity (entry 8). However, alkenoyl substrate 8i showed the reactivity only at room temperature (25 °C) and provided the bromoazide compound 9i with high diastereoselectivity and moderate yield (entry 9). The stereochemistry of 9 was confirmed from the single-crystal X-ray analysis of major compound 9c (see Supporting Information).

Removal of the chiral auxiliary of the bromoazides would provide enantiomerically pure *anti*- $\alpha$ -bromo- $\beta$ -azido carboxylic acids. As example, an aqueous THF (10:1) solution of compound **6b** was treated with LiOH (1.5 equiv) and 30% of H<sub>2</sub>O<sub>2</sub> (10 equiv) at -4 °C. Within 6 h, it produced the *anti*- $\alpha$ -bromo- $\beta$ -azido carboxylic acid **10b** in 61% yield along with a minor amount (25%) of parent cinnamic acid **11b** (Scheme 1), which might have been produced by retro-bromoazidation reaction under the alkaline condition. Sultam chiral auxiliary was recovered in 88% yield, and its optical purity was the same as that of the parent sultam.

In summary, we have developed a Lewis acid catalyzed asymmetric bromoazidation reaction of chiral  $\alpha,\beta$ -unsaturated carbonyl compounds with NBS and TMSN3 as the bromine and azide sources. The metal halides and acetates showed poor to moderate catalytic effect for the bromoazidation reaction, but metal triflates were found to be good catalysts. Among the metal triflates, Yb(OTf)<sub>3</sub> was found to be the best catalyst. Regioand anti-selectivity of 100% and moderate to good diastereoselectivity (up to 89:11) with good yields were observed when bornanesultam was used as the chiral auxiliary. Use of the (2S,5S)-2,5-diphenylpyrolidine as a chiral auxiliary provided very high diastereoselectivity (>95:05) depending upon the reaction conditions. Alkenoyl, cinnamoyl, and electron-rich cinnamoyl substrates smoothly underwent the Yb(OTf)3catalyzed bromoazidation reactions with NBS and TMSN<sub>3</sub>. The cinnamoyl substrates possessing electron-withdrawing substituents at the para position also responded to the reaction at higher temperature, but the cinnamoyl substrates containing electronwithdrawing substituents at the ortho position did not. This methodology offers an efficient method for the synthesis of chiral anti- $\alpha$ -bromo- $\beta$ -azido carboxylic acid derivatives using commercially available NBS and TMSN3 as the bromine and azide sources.

#### **Experimental Section**

General Procedure for the Bromoazidation of Compounds 1, 5, and 8. To a well-stirred suspended solution of substrate 1, 5, or 8 (0.50 mmol) and MS 4Å (0.100 g) in dry CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL; for the substrates 8, 20% of THF was used when the reaction was performed at -20 °C) was added Yb(OTf)<sub>3</sub> (0.031 g, 0.05 mmol) under argon atmosphere. The temperature of the reaction mixture was maintaied as specified in Tables 1, 2, and 3. TMSN<sub>3</sub> (0.1 mL, 0.75 mmol) and NBS (0.107 g, 0.60 mmol) were successively added. Reaction was monitored by TLC, quenched with saturated NaHCO<sub>3</sub>, and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic layers were washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. Flash column chromatography of the crude mixture using petroleum ether—EtOAc as an eluent gave pure  $\alpha$ -bromo- $\beta$ -azido carbonyl compounds 2/3, 6, and 9. Minor isomers 7 and of 9 could not be isolated in pure form.

*anti*-(2*R*,2*′R*,3*′R*)-*N*-[3′-Azido-2′-bromo-3′-(4-methoxyphenyl)propionyl]-bornanesultam (6b). White solid, mp 144–146 °C;  $[\alpha]^{25}_{D} = -116.57$  (*c* 0.29, CHCl<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 500, 532, 547, 668, 831, 1026, 1116, 1136, 1177, 1215, 1255, 1294, 1314,-1329, 1384,1459, 1515, 1613, 1693 (CO), 2104 (N<sub>3</sub>), 2342, 2361, 2961. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  0.99 (s, 3H), 1.17 (s, 3H), 1.20–1.55 (m, 3H), 1.85–2.05 (m, 2H), 2.10–2.25 (m, 2H), 3.55 (s, 2H), 3.82 (s, 3H), 4.04 (m, 1H), 4.90–5.10 (m, 2H), 6 94 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  19.8, 20.6, 26.4, 32.7, 37.5, 44.5, 45.2, 47.9, 48.8, 52.9, 55.2, 65.0, 65.9, 114.2 (2C), 127.1, 129.4 (2C), 160.3, 166.3. Anal. Calcd for C<sub>20</sub>H<sub>25</sub>BrN<sub>4</sub>O<sub>4</sub>S: C, 48.29; H, 5.07; N, 11.26. Found: C, 48.67; H, 5.06; N, 11.06. Diastereomeric ratio was determined by HPLC [ZORBAX Eclipse XBD-C18 column, acetonitrile/water (80/20 v/v), 1 mL/min, 250 nm].

*anti*-(2'*R*,3'*R*,2*S*,5*S*)-1-[3'-Azido-2'-bromo-3'-phenyl-propionyl]-2,5-diphenyl-pyrrolidine (9a). White solid, mp 167–169 °C;  $[\alpha]^{25}_{D}$ = -248.30 (*c* 0.94, CHCl<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 466, 536, 570, 604, 612, 668, 702, 755, 767, 802, 900, 1002, 1028, 1077, 1168, 1205, 1308, 1359, 1418, 1452, 1493, 1583, 1660 (CO), 2111 (N<sub>3</sub>), 2342, 2361, 2961, 3028, 3057. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  1.60– 2.05 (m, 2H), 2.35–2.75 (m, 2H), 4.12 (d, *J* = 10.5 Hz, 1H), 4.94 (d, *J* = 10.5 Hz, 1H), 5.36 (d, *J* = 7.7 Hz, 1H), 5.60 (d, *J* = 7.7 Hz, 1H), 6.75–6.90 (m, 2H), 7.00–7.65 (m, 13H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  30.6, 32.9, 45.5, 62.4 (2C), 66.2, 125.1 (2C),

<sup>(18)</sup> In addition, a minor amount (15-24%) of nonseparable undesired compounds was obtained.

## JOC Note

125.6 (2C), 126.9, 127.8 (2C), 128.0, 128.4 (2C), 128.5 (2C), 128.8, 129.2 (2C), 136.1, 142.1, 142.9, 166.0. Anal. Calcd for  $C_{25}H_{23}$ -BrN\_4O: C, 63.16; H, 4.88; N, 11.79. Found: C, 63.46; H, 5.25; N, 11.47.

Acknowledgment. We wish to thank DST, New Delhi for providing financial support (project no. SR/S1/OC-13/2004) and for providing XRD facility to the Department of Chemistry, IIT Guwahati under FIST programme (sanction no. SR/FST/ CSII-007/2003) for extending support for single XRD data. M.B. and D.S. would like to thank IIT, Kharagpur and CSIR, New Delhi, respectively, for their fellowships.

**Supporting Information Available:** General experimental details, characterization data of other bromoazides 2/3, 6, 9 and 10b; <sup>1</sup>H, <sup>13</sup>C, and DEPT-135 NMR spectra of bromoazides 6, 9, and 10b; HPLC traces of crude reaction mixture; ORTEP diagram and file for the single-crystal X-ray analysis of compound 9c in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061593K