One-Carbon Homologation of Aldehydes to *N*-(α-Haloacyl)benzotriazoles

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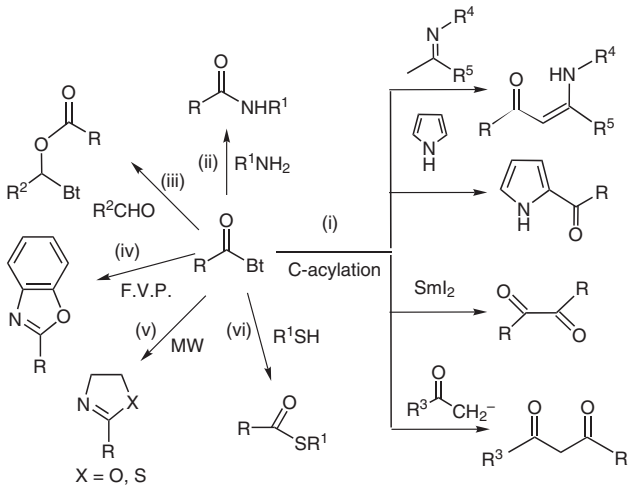
Abstract: One-carbon homologated *N*-(α-haloacyl)benzotriazoles have been synthesized from the corresponding aromatic and aliphatic aldehydes. Vinylbenzotriazoles, prepared by the reaction of aldehydes with the one-carbon synthon $BtCH_2P^+Ph_3Cl^-$, were subsequently treated with Br_2/Et_3N to give 1-bromovinylbenzotriazoles. These were then treated with NBS/NIS in $CH_3CN–H_2O$ to furnish one-carbon homologated *N*-(α-haloacyl)benzotriazoles in 53–77% yields. We have also demonstrated the utility of these new reagents in organic synthesis.

Key words: *N*-acylbenzotriazole, homologation, aldehyde, acylation, *N*-halosuccinimide

N-Acylbenzotriazoles[1a] are important synthetic reagents whose numerous applications in organic synthesis include: (i) C-acylation reagents for the synthesis of 1,3-,[1b] and 1,2-diketones,[1c–d] enaminones,[1e] 1-substituted-2-azinyl-1-ethanones,[1f] and for the regiospecific acylation of heterocycles;[1g–h] (ii) N-acylation reagents for the preparation of amides,[2a–c] peptides,[2d] and *N*-acylsulfonamides;[2e] (iii) O-acylation reagents in their additions to aldehydes to give esters;[3] (iv) in the preparation of benzoxazoles by flash vacuum pyrolysis;[4] (v) in the syntheses of oxazolines and thiazolines under microwave irradiation[5] and (vi) as S-acylation reagents in the synthesis of thiol esters[6] (Scheme 1).

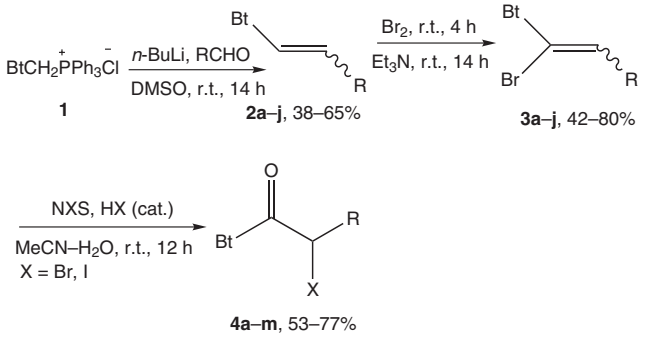


Scheme 1

Unlike acid chlorides, *N*-acylbenzotriazoles are stable, crystalline compounds that can be stored at room temperature without decomposition. Use of *N*-acylbenzotriazoles avoids racemization,[2b,2d] assures regiospecificity,[1g–h] and the resulting products are generally obtained in high yields. They are also the reagents of choice when the corresponding acid chlorides are unstable or difficult to isolate, for example RCOCl, with R = 4-diethylaminophenyl, 2-pyridyl, 2-indolyl or 2-pyrrolyl. We recently reported a mild, one-pot procedure for efficient conversion of carboxylic acids into the corresponding *N*-acylbenzotriazoles[7] which has several advantages over previous methods.[2a,8]

α-Haloacyl halides are important reagents from which a wide variety of compounds may be obtained by replacing both the halogens on the α-carbon and on the acyl function.[9] Following the widespread utility of *N*-acylbenzotriazoles in organic synthesis, we now introduce *N*-(α-haloacyl)benzotriazoles as convenient alternatives to α-haloacyl halides. Analogous to acyl halides, α-haloacyl halides are unstable and difficult to handle, and their preparation involves vigorous conditions and extended reaction times.[10–11] The present method for the synthesis of *N*-(α-haloacyl)benzotriazoles from aldehydes involves one carbon homologation using $BtCH_2P^+Ph_3Cl^-$ (**1**).

Reaction of **1** with *n*-BuLi and aryl, alkyl or heterocyclic aldehydes (RCHO; R = Ph, *p*-tolyl, 2-thienyl etc.) gave vinylbenzotriazoles **2a–j** in 38–65% yields, following a previously reported general procedure (Scheme 2, Table 1).[12] Treatment of **2a–j** with bromine followed by Et_3N gave the corresponding 1-(1-bromovinyl)benzotriazoles **3a–j** in 42–80% yields (Scheme 2, Table 1). The vinylbenzotriazoles **2a–j** and 1-(1-bromovinyl)benzotriazoles **3a–j** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis.



Scheme 2 Synthesis of *N*-(α-haloacyl)benzotriazoles. For R, see Table 1.

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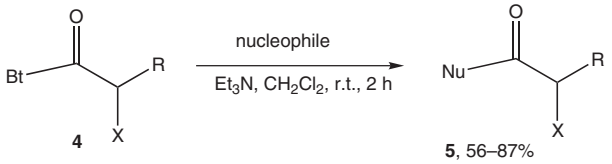
Table 1 Preparation of 2-Substituted Vinylbenzotriazoles **2a–j,** 1-Bromovinylbenzotriazoles **3a–j** and *N*-(α-Haloacyl)benzotriazoles **4a–m**

Entry	R	Yield (%)[a]	Yield (%)[a]	Yield (%)[a]	
				X = Br	X = I
1	Ph	**2a** (64)	**3a** (80)	**4a** (75)	–
2	*p*-Me C_6H_4	**2b** (65)	**3b** (61)	**4b** (73)	–
3	*o*-Me C_6H_4	**2c** (47)	**3c** (63)	**4c** (71)	–
4	Et	**2d** (54)	**3d** (52)	**4d** (67)	–
5	*i*-Pr	**2e** (64)	**3e** (49)	**4e** (53)	–
6	$(CH_3)_2CHCH_2$	**2f** (53)	**3f** (52)	**4f** (70)	–
7	*n*-Pr	**2g** (59)	**3g** (53)	**4g** (58)	**4k** (69)
8	*n*-Heptyl	**2h** (38)	**3h** (54)	**4h** (61)	**4l** (53)
9	$C_6H_5CH_2CH_2$	**2i** (41)	**3i** (42)	**4i** (77)	**4m** (64)
10	Thienyl	**2j** (53)	**3j** (52)	–	–

[a] Isolated product yield.

Reaction of 1-(1-bromovinyl)benzotriazoles **3a–i** with *N*-bromosuccinimide (NBS) in the presence of a catalytic amount of HBr in a mixture of acetonitrile and water, furnished *N*-(α-bromoacyl)benzotriazoles **4a–i** in 53–77% yields (Scheme 2, Table 1). However, compound **3j**, which was prepared from a heterocyclic aldehyde (2-thiophenecarboxaldehyde), did not give the corresponding *N*-(α-bromoacyl)benzotriazole. Reaction of **3g–i** with *N*-iodosuccinimide (NIS) in the presence of a catalytic amount of HI furnished *N*-(α-iodoacyl)benzotriazoles **4k–m** in good yields (Scheme 2, Table 1). *N*-(α-Haloacyl)benzotriazoles **4a–i** and **4k–m** are novel compounds and were fully characterized by ^1H and ^{13}C NMR spectroscopy and by elemental analysis.

In the applications of *N*-(α-haloacyl)benzotriazoles, treatment of several *N*-(α-haloacyl)benzotriazoles with various amines and alcohols gave *N*-(α-halo)amides and ester **5a–h** in 56–87% yields (Scheme 3, Table 2). Compounds **5b** and **5d–h** are novel and were fully characterized by ^1H and ^{13}C NMR spectroscopy and by elemental analysis.



Scheme 3

In conclusion, we have developed a new methodology for one-carbon homologation of both aliphatic and aromatic aldehydes to *N*-(α-haloacyl)benzotriazoles using the one-carbon synthon $BtCH_2P^+Ph_3Cl^-$. These *N*-(α-haloacyl)benzotriazoles are excellent acylating reagents.

Table 2 Preparation of *N*-(α-Halo)amides and Ester **5a–h**

Entry	4	Nucleophile	Yield (%)
1	**4a**	$C_6H_5CH_2NH_2$	**5a** (87)
2	**4f**	$C_6H_5CH_2NH_2$	**5b** (75)
3	**4f**	$C_6H_5(CH_2)_2NH_2$	**5c** (69)
4	**4f**	*p*-Me-$C_6H_4(CH_2)_2NH_2$	**5d** (63)
5	**4k**	*p*-Me-$C_6H_4(CH_2)_2NH_2$	**5e** (56)
6	**4l**	*p*-Me-$C_6H_4(CH_2)_2NH_2$	**5f** (76)
7	**4f**	$C_6H_5CH(CH_3)NH_2$	**5g** (61)
8	**4k**	$C_6H_5CH_2OH$	**5h** (82)

Melting points are uncorrected. Solvents were dried according to standard procedures. Aldehydes and benzotriazole were purchased and used without further purification. Column chromatography was carried out using silica gel 200–425 mesh. All of the reactions with air-sensitive compounds were carried out under N_2 atmosphere. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Gemini 300 NMR spectrometer in $CDCl_3$ (with TMS for ^1H and $CDCl_3$ for ^{13}C as the internal reference). Chemical shifts for minor isomers are given in parenthesis.

Preparation of Vinylbenzotriazoles 2a–j; General Procedure

To a solution of [(benzotriazol-1-yl)methyl]triphenyl phosphonium chloride (21.7 g, 50 mmol) in DMSO, *n*-BuLi (1.6 M, 31 mL, 50 mmol) was added under nitrogen at 25 °C. After 1 h, aldehyde (60 mmol) was added dropwise and the reaction was continued for 12 h. The reaction mixture was then poured into H_2O (100 mL) and extracted with $CHCl_3$ (2 × 150 mL). The organic layer was washed with brine (2 × 50 mL) and dried over $MgSO_4$. Evaporation of the solvent gave a residue that was purified by column chromatography (hexanes–EtOAc, 10:1) to give vinylbenzotriazoles **2a–j**.

1-[(*E*)-2-Phenyl-1-ethenyl]-1*H*-1,2,3-benzotriazole (2a)
Yield: 64%; white microcrystals; mp 112–114 °C (Lit.[13] 115–116 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.61 (m, 8 H), 7.77 (d, *J* = 8.4 Hz, 1 H), 7.94 (dd, *J* = 12.9, 1.1 Hz, 1 H), 8.12 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 110.3, 120.7, 121.3, 122.0, 124.9, 126.8, 128.5, 128.7, 129.3, 131.7, 134.6, 146.6.

1-[2-(4-Methylphenyl)-1-ethenyl]-1*H*-1,2,3-benzotriazole (2b)
Yield: 65%; white microcrystals; mp 147–150 °C (Lit.[13] 148–151 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.39–7.45 (m, 4 H), 7.56 (t, *J* = 7.8 Hz, 1 H), 7.75 (d, *J* = 8.4 Hz, 1 H), 7.88 (d, *J* = 14.7 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 110.0, 120.3, 120.9, 121.1, 124.5, 126.4, 128.1, 129.6, 131.4, 131.4, 138.5, 146.2.

1-[2-(2-Methylphenyl)-1-ethenyl]-1*H*-1,2,3-benzotriazole (2c)
Yield: 53%; white microcrystals; mp 101–102 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.48 (s, 3 H), 7.26–7.29 (m, 3 H), 7.42–7.47 (m, 1 H), 7.57–7.62 (m, 2 H), 7.67–7.83 (m, 3 H), 8.12 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.9, 109.9, 119.2, 120.3, 122.3, 124.5, 125.3, 126.4, 128.2, 128.4, 130.6, 131.4, 133.3, 136.3, 146.2.

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.50; H, 5.64; N, 18.13.

1-(1-Butenyl)-1*H*-1,2,3-benzotriazole (2d)[14]
Yield: 54%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 7.5 Hz, 3 H), 2.30–2.40 (m, 2 H), 6.55 (dt, *J* = 14.0, 6.9 Hz, 1 H), 7.29 (d, *J* = 14.2 Hz, 1 H), 7.35–7.41 (m, 1 H), 7.48–7.54 (m, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 8.06 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 23.6, 110.3, 120.3, 122.5, 124.4, 125.3, 128.0, 131.6, 146.3.

1-(3-Methyl-1-butenyl)-1*H*-1,2,3-benzotriazole (2e)[14]
Yield: 64%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 6.7, 6 H), 2.59–2.66 (m, 1 H), 6.50 (dd, *J* = 14.4, 7.2 Hz, 1 H), 7.27 (d, *J* = 14.4 Hz, 1 H), 7.35–7.40 (m, 1 H), 7.48–7.53 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 1 H), 8.06 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2, 29.4, 110.0, 120.0, 121.0, 124.1, 127.7, 130.1, 131.3, 146.0.

1-[(*EZ*)-4-Methyl-1-pentenyl]-1*H*-1,2,3-benzotriazole (2f)
Yield: 51%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (0.91) (d, *J* = 6.6 Hz, 6 H), 1.73–1.90 (m, 1 H), 2.19–2.24 (2.31–2.36) (m, 2 H), 6.45–6.55 (5.84–5.92) (m, 1 H), 7.28 (7.04) (d, *J* = 14.1 Hz, 1 H), 7.37–7.42 (m, 1 H), 7.49–7.55 (7.65–7.67) (m, 2 H), 8.06–8.09 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2, 28.3 (30.8), 39.2 (36.3), 110.0 (109.6), 120.1 (119.8), 122.2 (120.6), 123.4, 124.2 (124.0), 127.8 (127.6), 128.7, 131.3, 146.0 (145.1).

Anal. Calcd for $C_{12}H_{15}N_3$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.30; H, 7.54; N, 21.08.

1-(1-Pentenyl)-1*H*-1,2,3-benzotriazole (2g)[12]
Yield: 59%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.2 Hz, 3 H), 1.52–1.64 (m, 2 H), 2.28 (dq, *J* = 7.5 Hz, 1.5 Hz, 2 H), 6.49 (dt, *J* = 14.4, 7.2 Hz, 1 H), 7.25–7.39 (m, 2 H), 7.46 (m, 1 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4, 22.2, 32.0, 109.9, 119.8, 122.7, 123.1, 124.1, 127.7, 131.2, 145.9.

1-(1-Nonenyl)-1*H*-1,2,3-benzotriazole (2h)
Yield: 38%; colorless microcrystals; mp 43–44 °C (Lit.[13] 15 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 6.9 Hz, 3 H), 1.25–1.69 (m, 10 H), 2.35 (qd, *J* = 7.5 Hz, 1.2 Hz, 2 H), 6.54 (dt, *J* = 14.1, 7.2 Hz, 1 H), 7.30–7.44 (m, 2 H), 7.52–7.58 (m, 1 H), 7.68 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.9, 29.0, 29.1, 30.1, 31.7, 110.0, 120.1, 122.7, 123.7, 124.2, 127.8, 131.3, 146.0.

Anal. Calcd for $C_{15}H_{21}N_3$: C, 74.04; H, 8.70; N, 17.27. Found: C, 73.76; H, 8.61; N, 17.27.

1-(4-Phenyl-1-butenyl)-1*H*-1,2,3-benzotriazole (2i)
Yield: 41%; colorless microcrystals; mp 127–128 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.61–2.68 (m, 2 H), 2.89 (t, *J* = 7.5 Hz, 2 H), 6.47–6.57 (m, 1 H), 7.16–7.40 (m, 7 H), 7.47–7.58 (m, 2 H), 8.06 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.3, 35.1, 109.5, 119.9, 120.5, 124.2, 126.0, 127.7, 128.3, 128.4, 132.7, 140.9, 145.0.

Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.34; H, 6.04; N, 16.65.

1-[2-(2-Thienyl)ethenyl]-1*H*-1,2,3-benzotriazole (2j)
Yield: 53%; white microcrystals; mp 90–92 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03–7.06 (m, 1 H), 7.17 (d, *J* = 3.3 Hz, 1 H), 7.27 (d, *J* = 4.8 Hz, 1 H), 7.39–7.44 (m, 1 H), 7.53–7.62 (m, 2 H), 7.68–7.79 (m, 2 H), 8.10 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.7, 114.5, 120.1, 120.3, 124.5, 125.1, 127.4, 127.7, 128.1, 131.1, 138.1, 145.9.

Anal. Calcd for $C_{12}H_9N_3S$: C, 63.41; H, 3.99; N, 18.49. Found: C, 63.64; H, 3.94; N, 18.28.

Preparation of 1-(1-Bromovinyl)benzotriazoles 3a–j; General Procedure
To a solution of vinylbenzotriazole **2** (11 mmol) in CH_2Cl_2 (20 mL) was added Br_2 (1.84 g, 11.5 mmol) in CH_2Cl_2 (5 mL) at 0 °C and the mixture was stirred at r.t. for 4 h. Et_3N (6 mL) was added at 0 °C and the mixture was stirred at r.t. for 14 h. The reaction mixture was filtered and the filtrate was washed with HCl (1 N, 10 mL), brine (10 mL) and dried over $MgSO_4$. Evaporation of the solvent gave a crude product that was purified by flash column chromatography (hexanes–EtOAc, 19:1).

1-(1-Bromo-2-phenyl-1-ethenyl)-1*H*-1,2,3-benzotriazole (3a)
Yield: 80%; white microcrystals; mp 78–80 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 7.5 Hz, 2 H), 7.18–7.08 (m, 3 H), 7.51–7.41 (m, 4 H), 8.13 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 108.8, 110.4, 120.4, 124.9, 128.0, 128.7, 128.9, 129.3, 131.8, 132.6, 136.1, 145.6.

Anal. Calcd for $C_{14}H_{10}BrN_3$: C, 56.02; H, 3.36; N, 14.00. Found: C, 55.98; H, 3.20; N, 13.84.

1-[1-Bromo-2-(4-methylphenyl)-1-ethenyl]-1*H*-1,2,3-benzotriazole (3b)
Yield: 61%; white needles; mp 158–160 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 6.61 (d, *J* = 8.1 Hz, 2 H), 6.89 (d, *J* = 8.1 Hz, 2 H), 7.37 (s, 1 H), 7.54–7.42 (m, 3 H), 8.13 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 107.6, 110.5, 120.3, 124.9, 128.8, 129.5, 129.8, 131.8, 136.2, 139.6, 145.6.

Anal. Calcd for $C_{15}H_{12}BrN_3$: C, 57.34; H, 3.85; N, 13.37. Found: C, 57.61; H, 3.70; N, 13.41.

1-[1-Bromo-2-(2-methylphenyl)-1-ethenyl]-1*H*-1,2,3-benzotriazole (3c)
Yield: 75%; pale yellow microcrystals; mp 81–82 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 6.48 (d, *J* = 7.8 Hz, 1 H), 6.70 (t, *J* = 7.5 Hz, 1 H), 7.01 (t, *J* = 7.5 Hz, 1 H), 7.09 (d, *J* = 7.8 Hz, 1 H), 7.32–7.36 (m, 2 H), 7.42–7.46 (m, 1 H), 7.51 (s, 1 H), 8.03 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.0, 109.7, 110.1, 120.2, 124.6, 126.0, 127.2, 128.6, 128.9, 130.2, 131.9, 134.3, 136.1, 145.3.

Anal. Calcd for $C_{15}H_{12}BrN_3$: C, 57.34; H, 3.85; N, 13.37. Found: C, 57.18; H, 3.75; N, 13.25.

1-(1-Bromo-1-butenyl)-1*H*-1,2,3-benzotriazole (3d)
Yield: 52%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, *J* = 7.4 Hz, 3 H), 2.00–1.90 (m, 2 H), 6.52 (t, *J* = 7.7 Hz, 1 H), 7.48–7.42 (m, 1 H), 7.56–7.64 (m, 2 H), 8.11 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5, 23.5, 107.4, 110.7, 120.5, 124.9, 128.9, 132.7, 140.8, 145.6.

Anal. Calcd for $C_{10}H_{10}BrN_3$: C, 47.64; H, 3.40; N, 16.67. Found: C, 47.63; H, 3.87; N, 16.54.

1-(1-Bromo-3-methyl-1-butenyl)-1*H*-1,2,3-benzotriazole (3e)
Yield: 49%; brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 6.6 Hz, 6 H), 2.14–2.22 (m, 1 H), 6.37 (d, *J* = 10.3 Hz, 1 H), 7.42–7.49 (m, 1 H), 7.57–7.66 (m, 2 H), 8.11 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2, 29.9, 106.0, 110.3, 120.2, 124.7, 128.6, 132.5, 145.3, 146.0.

Anal. Calcd for $C_{11}H_{12}BrN_3$: C, 49.64; H, 4.54; N, 15.79. Found: C, 49.29; H, 4.49; N, 15.79.

1-[(*EZ*)-1-Bromo-4-methyl-1-pentenyl]-1*H*-1,2,3-benzotriazole (3f)
Yield: 56%; brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (1.05) (d, *J* = 6.6 Hz, 6 H), 1.68–1.75 (1.90–1.99) (m, 1 H, *i*-Pr CH), 1.84 (2.37) (t, *J* = 7.5 Hz, 2 H, CH_2), 6.48–6.56 (m, 1 H), 7.42–7.48 (m, 1 H), 7.56–7.70 (m, 2 H), 8.08–8.13 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1 (22.4), 27.9 (27.9), 38.3 (39.5), 107.7, 110.5 (110.7), 120.3, 124.7 (124.6), 128.6 (128.4), 132.5, 134.1, 138.5, 145.4.

Anal. Calcd for $C_{12}H_{14}BrN_3$: C, 51.44; H, 5.04; N, 15.00. Found: C, 51.33; H, 4.95; N, 15.37.

1-[(*EZ*)-1-Bromo-1-pentenyl]-1*H*-1,2,3-benzotriazole (3g)
Yield: 53%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (0.84) (t, *J* = 7.5 Hz, 3 H), 1.58–1.70 (1.38–1.57) (m, 2 H), 2.45 (1.91) (q, *J* = 7.5 Hz, 2 H), 6.46–6.55 (m, 1 H), 7.40–7.48 (m, 1 H), 7.54–7.61 (m, 1 H), 7.68–7.70 (m, 1 H), 8.07–8.12 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (13.4), 21.3 (21.7), 32.5 (31.5), 110.7, 120.2, 123.0, 124.6 (124.7), 128.3 (128.6), 135.0, 139.2, 145.5.

Anal. Calcd for $C_{11}H_{12}BrN_3$: C, 49.64; H, 4.54; N, 15.79. Found: C, 49.29; H, 4.42; N, 15.98.

1[(*EZ*)-1-Bromo-1-nonenyl]-1*H*-1,2,3-benzotriazole (3h)
Yield: 54%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (0.90) (t, *J* = 6.6 Hz, 3 H), 1.12–1.25 (m, 7 H), 1.30–1.46 (m, 3 H), 1.93 (2.47) (q, *J* = 7.5 Hz, 2 H), 6.52 (t, *J* = 7.8 Hz, 1 H), 7.43–7.47 (m, 1 H), 7.54–7.70 (m, 2 H), 8.08–8.14 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (14.0), 22.5 (22.6), 28.4 (27.9), 28.7 (29.0), 28.8 (29.1), 29.6 (30.6), 31.5 (31.7), 107.3, 110.4 (110.7), 120.2, 124.6 (124.7), 128.5 (128.3), 132.4 (135.2), 139.4, 145.3

Anal. Calcd for $C_{15}H_{20}BrN_3$: C, 55.91; H, 6.26; N, 13.04. Found: C, 55.82; H, 6.31; N, 13.10.

1-(1-Bromo-4-phenyl-1-butenyl)-1*H*-1,2,3-benzotriazole (3i)
Yield: 42%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23–2.30 (m, 2 H), 2.72, (q, *J* = 7.5 Hz, 2 H), 6.50 (t, *J* = 7.8 Hz, 1 H), 7.02–7.04 (m, 2 H), 7.14–7.22 (m, 3 H), 7.38–7.43 (m, 2 H), 7.49–7.54 (m, 1 H), 8.08 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.3, 34.5, 108.1, 110.4, 120.0, 124.6, 126.2, 128.2, 128.4, 128.5, 132.2, 137.8, 139.8, 145.2.

Anal. Calcd for $C_{16}H_{14}BrN_3$: C, 58.55; H, 4.30; N, 12.80. Found: C, 58.76; H, 4.13; N, 12.61.

1-[1-Bromo-2-(2-thienyl)ethenyl]-1*H*-1,2,3-benzotriazole (3j)
Yield: 52%; white needles; mp 135–136 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93 (d, *J* = 3.6 Hz, 1 H), 7.01 (d, *J* = 3.9 Hz, 1 H), 7.42–7.47 (m, 1 H), 7.49–7.61 (m, 2 H), 7.67–7.71 (m, 2 H), 8.10 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.8, 112.1, 114.0, 120.5, 120.8, 124.8, 127.8, 128.4, 130.8, 131.3, 139.9, 146.2.

Anal. Calcd for $C_{12}H_8BrN_3S$: C, 47.07; H, 2.63; N, 13.72. Found: C, 47.28; H, 2.50; N, 13.43.

Preparation of *N*-(α-Haloacyl)benzotriazoles 4a–m; General Procedure
To a solution of 1-(1-bromovinyl)benzotriazole **3** (2 mmol) in MeCN–H_2O (8:1), NBS (0.35 g, 3 mmol) or NIS (0.88 g, 4 mmol) was added in one portion. A catalytic amount of conc. HBr (48%, 2 μL) or conc. HI (51%, 2 μL) was then added and the mixture was stirred at r.t. for 12. The reaction mixture was then diluted with Et_2O (30 mL) and treated dropwise with aqueous sodium thiosulfate until the yellow color had disappeared. The mixture was then washed with aq $NaHCO_3$ (10 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated in vacuo. The crude product was purified by flash chromatography on silica gel (hexanes–EtOAc, 95:5).

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-bromo-2-phenyl-1-ethanone (4a)
Yield: 75%; white microcrystals; mp 118–121 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06 (s, 1 H), 7.43–7.36 (m, 3 H), 7.55–7.50 (m, 1 H), 7.77–7.65 (m, 3 H), 8.11–8.14 (m, 1 H), 8.27–8.30 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.4, 114.7, 120.7, 127.0, 129.3, 129.6, 130.0, 131.2, 131.4, 134.6, 146.6, 166.3.

Anal. Calcd for $C_{14}H_{10}BrN_3O$: C, 53.19; H, 3.19; N, 13.29. Found: C, 52.92; H, 3.07; N, 13.17.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-bromo-2-(4-methylphenyl)-1-ethanone (4b)
Yield: 73%; white microcrystals; mp 142–144 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 7.05 (s, 1 H), 7.20 (d, *J* = 8.1 Hz, 2 H), 7.56–7.51 (m, 1 H), 7.71–7.63 (m, 3 H), 8.13 (d, *J* = 8.2 Hz, 1 H), 8.30 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 45.3, 114.5, 120.5, 126.7, 129.2, 129.8, 130.9, 131.2, 131.4, 139.9, 146.4, 166.1.

Anal. Calcd for $C_{15}H_{12}BrN_3O$: C, 54.56; H, 3.66; N, 12.73. Found: C, 54.50; H, 3.55; N, 12.47.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-bromo-2-(2-methylphenyl)-1-ethanone (4c)
Yield: 71%; pale yellow microcrystals; mp 120–121 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.62 (s, 3 H), 7.23–7.28 (m, 4 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.67–7.72 (m, 2 H), 8.10 (d, *J* = 8.4 Hz, 1 H), 8.32 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.4, 43.6, 114.4, 120.4, 126.7, 127.0, 128.8, 129.6, 130.9, 131.1, 133.2, 136.5, 146.2, 166.0.

Anal. Calcd for $C_{15}H_{12}BrN_3O$: C, 54.56; H, 3.66; N, 12.73. Found: C, 54.55; H, 3.51; N, 12.78.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-bromo-1-butanone (4d)
Yield: 67%; white microcrystals; mp 59–63 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.2 Hz, 3 H), 2.44–2.24 (m, 2 H), 5.79 (t, *J* = 7.5 Hz, 1 H), 7.55 (t, *J* = 7.8 Hz, 1 H), 7.71 (t, *J* = 7.5 Hz, 1 H), 8.16 (d, *J* = 8.1 Hz, 1 H), 8.30 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.9, 27.4, 45.4, 114.4, 120.4, 126.6, 130.8, 131.0, 146.4, 167.9.

Anal. Calcd for $C_{10}H_{10}BrN_3O$: C, 44.80; H, 3.76; N, 15.67. Found: C, 44.02; H, 3.58; N, 14.41.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-bromo-3-methyl-1-butanone (4e)
Yield: 53%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 6.6 Hz, 3 H), 1.28 (d, *J* = 6.6 Hz, 3 H), 2.54–2.64 (m, 1 H), 5.71 (d, *J* = 8.1 Hz, 1 H), 7.53–7.58 (m, 1 H), 7.68–7.73 (m, 1 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 8.32 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1, 20.2, 31.9, 51.9, 114.5, 120.4, 126.7, 130.8, 131.1, 146.4, 167.8.

Anal. Calcd for $C_{11}H_{12}BrN_3O$: C, 46.83; H, 4.29; N, 14.89. Found: C, 46.66; H, 4.71; N, 14.70.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-bromo-4-methyl-1-pentanone (4f)
Yield: 70%; pale yellow microcrystals; mp 59–60 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (dd, *J* = 6.6, 2.1 Hz, 6 H), 1.84–1.98 (m, 1 H), 2.20 (t, *J* = 7.2 Hz, 2 H), 5.94 (t, *J* = 7.5 Hz, 1 H), 7.55 (t, *J* = 7.5 Hz, 1 H), 7.71 (t, *J* = 8.1 Hz, 1 H), 8.16 (d, *J* = 8.1 Hz, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 22.5, 26.4, 42.3, 42.4, 114.4, 120.4, 126.6, 130.8, 131.1, 146.4, 168.1.

Anal. Calcd for $C_{12}H_{14}BrN_3O$: C, 48.67; H, 4.76; N, 14.19. Found: C, 48.81; H, 4.68; N, 13.78.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-bromo-1-pentanone (4g)
Yield: 58%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.2 Hz, 3 H), 1.49–1.72 (m, 2 H), 2.20–2.40 (m, 2 H), 5.86 (t, *J* = 7.5 Hz, 1 H), 7.53–7.59 (m, 1 H), 7.68–7.74 (m, 1 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4, 20.6, 35.8, 43.5, 100.2, 114.5, 120.5, 126.7, 130.9, 146.4, 168.1.

Anal. Calcd for $C_{11}H_{12}BrN_3O$: C, 46.83; H, 4.29; N, 14.89. Found: C, 46.67; H, 4.72; N, 14.70.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-bromo-1-nonanone (4h)
Yield: 61%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.28–1.62 (m, 10 H), 2.20–2.40 (m, 2 H), 5.85 (t, *J* = 7.5 Hz, 1 H), 7.51–7.56 (m, 1 H), 7.67–7.72 (m, 1 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.5, 27.2, 28.8, 28.9, 31.6, 33.9, 43.7, 114.4, 120.4, 126.6, 130.8, 131.1, 146.4, 168.0.

Anal. Calcd for $C_{15}H_{20}BrN_3O$: C, 53.26; H, 5.96; N, 12.42. Found: C, 52.78; H, 6.00; N, 11.54.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-bromo-4-phenyl-1-butanone (4i)
Yield: 77%; yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.53–2.73 (m, 2 H), 2.79–3.01 (m, 2 H), 5.79 (t, *J* = 7.2 Hz, 1 H), 7.15–7.29 (m, 5 H), 7.52 (t, *J* = 7.2 Hz, 1 H), 7.67 (t, *J* = 7.2 Hz, 1 H), 8.13 (d, *J* = 8.4 Hz, 1 H), 8.25 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.3, 35.4, 43.2, 114.5, 120.5, 126.6, 126.7, 128.5, 128.7, 130.9, 131.1, 139.6, 146.4, 167.8.

Anal. Calcd for $C_{16}H_{14}BrN_3O$: C, 55.83; H, 4.10; N, 12.21. Found: C, 56.07; H, 3.96; N, 11.97.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-iodo-1-pentanone (4k)
Yield: 69%; brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.5 Hz, 3 H), 1.43–1.68 (m, 2 H), 2.25 (q, *J* = 7.5 Hz, 2 H), 5.99 (t, *J* = 7.5 Hz, 1 H), 7.52–7.58 (m, 1 H), 7.68–7.73 (m, 1 H), 8.14 (d, *J* = 8.4 Hz, 1 H), 8.27 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2, 19.2, 22.6, 36.8, 114.4, 120.3, 126.4, 130.6, 131.1, 146.4, 169.6.

Anal. Calcd for $C_{11}H_{12}IN_3O$: C, 40.14; H, 3.67; N, 12.77. Found: C, 40.53; H, 3.52; N, 12.56.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-iodo-1-nonanone (4l)
Yield: 53%; brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.28–1.60 (m, 10 H), 2.23–2.31 (m, 2 H), 5.97 (t, *J* = 7.5 Hz, 1 H), 7.51–7.56 (m, 1 H), 7.67–7.72 (m, 1 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 8.28 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 19.5, 22.5, 28.7, 28.9, 29.3, 31.6, 35.0, 114.5, 120.3, 126.5, 130.7, 131.1, 146.5, 169.7.

Anal. Calcd for $C_{15}H_{20}IN_3O$: C, 46.77; H, 5.23; N, 10.91. Found: C, 46.96; H, 5.23; N, 10.69.

1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-iodo-4-phenyl-1-butanone (4m)
Yield: 64%; brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.58 (q, *J* = 7.5 Hz, 2 H), 2.72–2.95 (m, 2 H), 5.91 (t, *J* = 7.5 Hz, 1 H), 7.15–7.29 (m, 5 H), 7.48–7.53 (m, 1 H), 7.64–7.69 (m, 1 H), 8.12 (d, *J* = 8.1 Hz, 1 H), 8.24 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7, 35.2, 36.6. 114.4, 120.3, 126.5, 128.4, 128.6, 130.6, 131.1, 139.4, 146.4, 169.4.

HRMS calcd for $C_{16}H_{14}IN_3O$ $[M + H]^+$: 392.0260; found: 392.0208.

Preparation of *N*-(α-Haloacyl)amides and Esters 5a–h; General Procedure

To a solution of *N*-(α-haloacyl)benzotriazole **4** (0.1 g, 0.33 mmol) and Et_3N (0.03 g, 0.66 mmol) in CH_2Cl_2 (5 mL) was added a soln of nucleophile (1 equiv) in CH_2Cl_2 (5 mL) at 0 °C and the mixture was stirred at r.t. for 4 h. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with H_2O (5 mL), brine (5 mL) and dried over $MeSO_4$. Filtration and evaporation of the solvent gave the crude product which was purified by flash column chromatography (EtOAc–hexanes, 4:6).

***N*-Benzyl-2-bromo-2-phenylacetamide (5a)**

Yield: 87%; colorless microcrystals; mp 90–91 °C (Lit.[16] 95–96 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.47 (d, *J* = 5.4 Hz, 2 H), 5.47 (s, 1 H), 7.08 (br s, 1 H), 7.25–7.46 (m, 10 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.3, 51.2, 127.6, 127.7, 128.3, 128.7, 128.9, 129.1, 137.2, 137.3, 167.1.

***N*-Benzyl-2-bromo-4-methylpentanamide (5b)**

Yield: 75%; colorless microcrystals; mp 66–67 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.0 Hz, 3 H), 0.96 (d, *J* = 6.3 Hz, 3 H), 1.77–1.98 (m, 3 H), 4.35 (dd, *J* = 9.0, 5.4 Hz, 1 H), 4.44 (d, *J* = 5.7 Hz, 2 H), 6.77 (br s, 1 H), 7.26–7.36 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 22.7, 26.3, 44.0, 44.5, 50.3, 127.6, 127.7, 128.8, 137.5, 169.0.

Anal. Calcd for $C_{13}H_{18}BrNO$: C, 54.94; H, 6.38; N, 4.93. Found: C, 55.24; H, 6.67; N, 4.81.

***N*-Phenethyl-2-bromo-4-methylpentanamide (5c)**

Yield: 69%; white microcrystals; mp 73–75 °C (Lit.[17] 76 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 5.7 Hz, 3 H), 0.94 (d, *J* = 6.0 Hz, 3 H), 1.74–1.92 (m, 3 H), 2.84 (t, *J* = 6.3 Hz, 2 H), 3.53 (q, *J* = 6.3 Hz, 2 H), 4.26 (dd, *J* = 8.7, 5.1 Hz, 1 H), 6.40 (br s, 1 H), 7.19–7.32 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 22.6, 26.3, 35.4, 41.1, 44.6, 50.3, 126.6, 128.6, 128.8, 138.4, 169.0.

***N*-(4-Methylphenethyl)-2-bromo-4-methylpentanamide (5d)**

Yield: 63%; white microcrystals; mp 89–90 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 6.3 Hz, 3 H), 0.94 (d, *J* = 6.3 Hz, 3 H), 1.77–1.94 (m, 3 H), 2.32 (s, 3 H), 2.79 (t, *J* = 6.9 Hz, 2 H), 3.51 (q, *J* = 6.6 Hz, 2 H), 4.26 (dd, *J* = 9.3, 5.4 Hz, 1 H), 6.37 (br s, 1 H), 7.08–7.14 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 22.6, 26.3, 34.9, 41.3, 44.6, 50.4, 128.7, 129.3, 135.3, 136.1, 169.0.

Anal. Calcd for $C_{15}H_{22}BrNO$: C, 57.70; H, 7.10; N, 4.49. Found: C, 58.07; H, 7.29; N, 4.67.

***N*-(4-Methylphenethyl)-2-iodopentanamide (5e)**

Yield: 56%; white microcrystals; mp 80–81 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.5 Hz, 3 H), 1.26–1.45 (m, 2 H), 1.92 (q, *J* = 7.5 Hz, 2 H), 2.33 (s, 3 H), 2.79 (t, *J* = 6.9 Hz, 2 H), 3.47–3.56 (m, 2 H), 4.19 (t, *J* = 7.2 Hz, 1 H), 5.95 (br s, 1 H), 7.09–7.15 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1, 21.0, 22.6, 26.7, 34.9, 38.8, 41.2, 128.7, 129.3, 135.4, 136.1, 170.1.

Anal. Calcd for $C_{14}H_{20}INO$: C, 48.71; H, 5.89; N, 4.06. Found: C, 49.08; H, 5.94; N, 3.85.

***N*-(4-Methylphenethyl)-2-iodononanamide (5f)**

Yield: 76%; white microcrystals; mp 84–85 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.0 Hz, 3 H), 1.26 (br s, 10 H), 1.93–1.95 (m, 2 H), 2.33 (s, 3 H), 2.79 (t, *J* = 6.6 Hz, 2 H), 3.47–3.56 (m, 2 H), 4.17 (t, *J* = 7.2 Hz, 1 H), 5.95 (br s, 1 H), 7.11 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 21.0, 22.6, 27.1, 28.7, 29.0, 29.4, 31.7, 34.9, 36.9, 41.2, 128.7, 129.3, 135.4, 136.1, 170.1.

Anal. Calcd for $C_{18}H_{28}INO$: C, 53.87; H, 7.03; N, 3.49. Found: C, 54.06; H, 6.96; N, 3.47.

***N*-(1-Phenylethyl)-2-bromo-4-methylpentanamide (5g)**

Yield: 61%; white microcrystals; mp 78–79 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89–0.97 (m, 6 H), 1.50 (dd, *J* = 6.9, 2.4 Hz, 3 H), 1.79–1.97 (m, 3 H), 4.28–4.36 (m, 1 H), 5.08 (quin, *J* = 7.2 Hz, 1 H), 6.62 (br s, 1 H), 7.24–7.38 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 21.6, 21.7, 22.7, 26.4, 44.5, 49.4, 49.5, 50.5, 126.0, 126.1, 127.5, 127.6, 128.8, 142.6, 168.2.

Anal. Calcd for $C_{14}H_{20}BrNO$: C, 56.38; H, 6.76; N, 4.70. Found: C, 56.25; H, 6.81; N, 4.51.

Benzyl 2-Iodopentanoate (5h)

Yield: 82%; colorless gel.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.5 Hz, 3 H), 1.25–1.48 (m, 2 H), 1.97 (q, *J* = 7.5 Hz, 2 H), 4.35 (t, *J* = 7.5 Hz, 1 H), 5.17 (s, 2 H), 7.33–7.37 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1, 20.8, 22.6, 37.9, 67.4, 128.2, 128.4, 128.6, 135.2, 171.3.

Anal. Calcd for $C_{12}H_{15}IO_2$: C, 45.30; H, 4.75; N, 0.0. Found: C, 44.95; H, 4.63; N, 0.37.

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