A Facile and Expedient Route to Allyl and Propargyl Amines Using *N*-(α-Benzotriazolylalkyl)amines as Stabilized Iminium Salts

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Abstract: *N*-(α-Benzotriazolylalkyl)amines **1a**–**g** serve as stabilized iminium salts for the preparation of allylamines **3a**–**i** in 82–94% yield in two steps starting from benzotriazole, an amine, an aldehyde, and the corresponding vinyl Grignard. Propargylamines **7a**–**e** were also prepared in good yields following the same approach using propargyl Grignard reagents.

Key words: allylamines, propargylamines, benzotriazole, grignard reaction, iminium salts

Syntheses of allylamines are of considerable interest.[1] Allylamine functionality is present in several natural products[2] and allylamines are also valuable starting materials for the synthesis of interesting amino acids[3] and carbohydrates.[4] Primary allylamines are used in the preparation of important enamine synthons.[5] 1-Aminoallyl anions, easily available by the deprotonation of allylamines or the tautomeric enamines, are effective as aldehyde or ketone homoenolate synthons.[5c,6] Allylamines are optimal reagents for allylation through boronic acid coupling.[7] They are also important in medicinal therapeutics.[1b,c]

Important synthetic methods for allylamines can be classified as:[8] (i) modification of compounds already containing the C–C–C–N skeleton, e.g., reduction of α,β-unsaturated imines and oximes, rearrangements of aziridines, dehydration of vicinal amino alcohols, and hydroboration[9] or reduction of propargylamines;[10] (ii) formation of allylic C–N bond by a nucleophilic allylic substitution or direct allylic amination of alkenes;[1a] (iii) formation of the C=C bond by Wittig type reactions;[11] (iv) introduction of the C=C group by reaction of alkenyl cuprates or stannates with Mannich equivalents,[12] or by modified Bruylants[13] reaction using vinyl Grignards.[6b] A recent report describes the utility of silver tetrafluoborate as a catalyst in the Bruylants reaction of α-amino nitriles with vinyl Grignard reagents giving increased yields of allylamines.[14]

We have previously applied benzotriazole methodology advantageously to allylamine synthesis using 1-allylbenzotriazoles in reactions of class (ii).[15] We now show that benzotriazole methodology can also be successfully applied to vinylation type reactions of class (iv).

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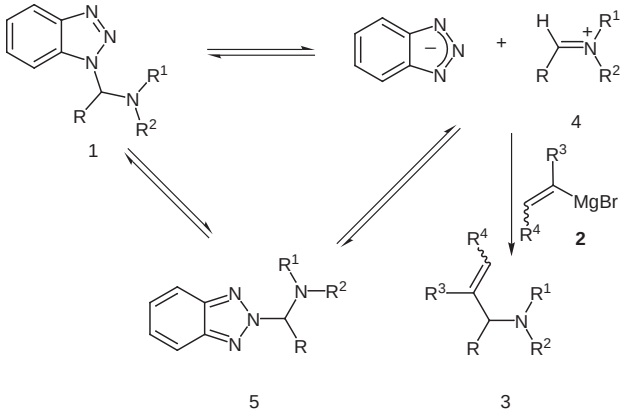
The synthetic utility of benzotriazole and its derivatives is well documented.[16] *N*-(α-Benzotriazolylalkyl)amines are highly versatile synthetic intermediates used extensively in organic synthesis and are conveniently prepared from benzotriazole, an amine, and an aldehyde[17] in one-pot reactions. The methine carbon in these intermediates exhibits a high degree of nucleophilicity, making them extremely flexible intermediates. The high degree of nucleophilicity of *N*-(α-aminoalkyl)benzotriazoles is expressed in the existence of two isomers **1** and **5** in solution in a mobile equilibrium via the intermediate formation of an iminium salt **4** (Scheme 1).[17a] Recent studies from our group have successfully applied this concept to the synthesis of functionalized amines and amides,[18] secondary and tertiary amines,[19] *N*,*N*-disubstituted hydroxylamines,[19] and enamines.[20] Thus, these benzotriazole stabilized 'iminium salts' together with vinylic organometallics as nucleophiles should offer an easy access to allylamines in two steps starting from an aldehyde, an amine, and benzotraizole.

N-(α-Benzotriazolylalkyl)amines **1a**–**g** were prepared by known methods (see experimental section). When **1a** was treated with vinyl magnesium bromide (1.0 M solution in THF), in toluene at 50 °C for 2 hours, the expected allylamine **3a** was isolated in 92% yield. The extent of the reaction was followed on TLC after aliquot work up. The byproduct benzotriazole was removed by aqueous base wash (2 N NaOH). This methodology was shown to be quite general allowing the preparation of allylamines **3b**–**i** in 82–94% yields. Structures of all new compounds are supported by ^{1}H and ^{13}C NMR spectra and elemental analysis or HRMS. Other vinylic Grignard reagents such as isopropenyl and 1-propenyl magnesium bromide also yielded the expected allylamines in excellent yields (Table 1). The proton NMR spectrum of the crude allylamine **3c** derived from 1-propenyl magnesium bromide shows that **3c** exists as a mixture of *E* and *Z* isomers in the ratio 86:14. This was further confirmed by GCMS analysis. Styryl magnesium bromide was prepared from an isomeric mixture of styryl bromides by magnesium insertion and was used to prepare allylamine **3i** as a mixture of *E* and *Z* isomers with the *E* isomer predominating in 72% yield. Allylamine **3h** was previously reported twice from reactions of class (ii)[21] in yields of 60% and 53%. The benzotriazolyl substituted amine **1f** when treated with isopropenyl magnesium bromide in toluene at 50 °C for 30 minutes gave **3h** in 92% isolated yield. This enhanced reactivity of **1f** is explained by the greater stability caused

by the *N*-methyl group on the corresponding iminium ion which increases the dissociation (Scheme 1).



	R	NR^1R^2
1a	Ph	$N(CH_2Ph)_2$
1b	Ph	morpholenyl
1c	2-naphthyl	morpholenyl
1d	4-pyridyl	piperidinyl
1e	*p*-$CH_3C_6H_4$	morpholenyl
1f	H	$N(CH_3)Ph$
1g	isopropyl	piperidinyl

Scheme 1

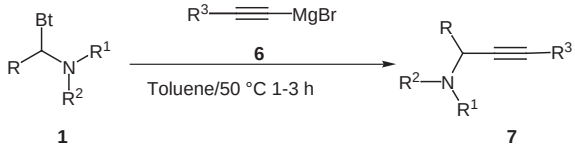
Table 1 Allylamines **3** Prepared

3	R	NR^1R^2	R^3	R^4	Yield (%)[a]
a	Ph	$N(CH_2Ph)_2$	H	H	93
b	Ph	$N(CH_2Ph)_2$	CH_3	H	86
c	Ph	$N(CH_2Ph)_2$	H	CH_3	86
d	Ph	morpholenyl	H	H	82
e	2-naphthyl	morpholenyl	H	H	90
f	4-pyridyl	piperidinyl	CH_3	H	92
g	*p*-$CH_3C_6H_4$	morpholenyl	H	H	91
h	H	$N(CH_3)Ph$	CH_3	H	92
i	isopropyl	piperidinyl	H	Ph	94

[a] All yields refer to pure isolated product.

On treatment of **1a** with propynylmagnesium bromide under the above conditions, propargylamine **7a** was isolated in 90% yield (Scheme 2). Other propargylamines **7b**–**e** were also synthesized following this approach and the results are summarized in Table 2. Propargylamines are important precursors of allylamines as they can be converted to the latter by reduction[10] or hydroboration.[9]

Compared to the conventional methods for the preparation of allyl or propargyl-amines, the present method possesses distinct advantages as (i) the starting *N*-(α-benzotriazolylalkyl)amines **1** are available in 82–94% yields in one-pot reactions, (ii) starting materials **1** can be used for further transformations without any purification and (iii) the Grignard addition requires no catalyst. In Bruylants type reactions[6b,14], the required α-amino nitriles are usually prepared by the reaction of the corresponding amine hydrochlorides with the carbonyl components in the presence of KCN, and good yields of allylamines need an added catalyst.[14] Thus the present method offers a convenient procedure for the preparation of allylamines in excellent yields.



	R	R^3	NR^1R^2
7a	Ph	CH_3	$N(CH_2Ph)_2$
7b	Ph	CH_3	morpholenyl
7c	2-naphthyl	CH_3	morpholenyl
7d	*p*-$CH_3C_6H_4$	Ph	morpholenyl
7e	isopropyl	Ph	piperidinyl

Bt =

Scheme 2

Table 2 α-Propargylamines **7**

7	R	R^1R^2N	R^3	Yield[a] (%)
a	Ph	$N(CH_2Ph)_2$	CH_3	90
b	Ph	morpholenyl	CH_3	88
c	2-naphthyl	morpholenyl	CH_3	83
d	*p*-$CH_3C_6H_4$	morpholenyl	Ph	87
e	isopropyl	piperidinyl	Ph	90

[a] All yields refer to pure isolated product.

In conclusion, we have presented a preparatively useful method for the synthesis of allylamines in overall two steps and in excellent yields starting from easily accessible materials. Since α-benzotriazolylalkylamines of various structural types are readily available and since there are a wide variety of Grignard reagents, this should frequently be the method of choice for the preparation of allylamines.

Melting points were determined using a Bristoline hot-stage microscope and are uncorrected. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Gemini 300 MHz NMR spectrometer in chloroform-*d* solution. GC/GCMS was performed on a HP 5890 series. Column chromatography was performed on silica gel. Elemental analyses were performed on a Carlo Erba-1106 instrument. Except for styryl magnesium bromide, all the Grignard reagents (as solution in THF) were procured from Aldrich. Styryl magnesium bromide was prepared from styryl bromide following standard procedure. Toluene was distilled from sodium metal prior to use. All the reactions were performed under a nitrogen atmosphere and in flame dried glassware.

The following benzotriazole derivatives were prepared according to the literature procedures: 1*H*-1,2,3-benzotriazol-1-yl-*N*,*N*-dibenzyl-phenylmethaneamine[17e](**1a**), [1-phenyl(-1-morpholino)-methyl]-1*H*-1,2,3-benzotriazole[17b](**1b**), [1-piperidino-1-(4-pyridinyl)-methyl]-1*H*-1,2,3-benzotriazole[17f] (**1d**), 1-[(4-methylphenyl)(morpholino) methyl]-1*H*-1,2,3-benzotriazole[17b] (**1e**), 1-[*N*-methyl-*N*-phenylmethyl]-1*H*-1,2,3-benzotriazole[17c](**1f**), 1-(2-methyl-1-piperidinopropyl)-1*H*-1,2,3-benzotriazole[17c](**1g**).

Allylamines 3a–i; General Procedure

To a solution of the appropriate benzotriazolylalkyl/aryl amine (10 mmol) in toluene (50 mL), was added the proper vinylic Grignard reagent (0.5 M solution in THF, 1.5 equiv) over a period of 10 min at r.t. The mixture was heated and stirred at 50 °C for 0.5–2 h. The reaction mixture was cooled to r.t., was poured into a saturated solution of NH_4Cl (200 mL) containing crushed ice, and extracted with Et_2O. The combined etheral layers was washed successively with 2 N NaOH, water and brine, and dried over anhyd Na_2SO_4. The solution was concentrated in vacuo and the crude product was further purified by column chromatography on silica gel (230–400 mesh) using hexane–EtOAc as the eluent.

***N*,*N*-Dibenzyl-*N*-(1-phenyl-2-propenyl)amine (3a)**

Obtained as a colorless liquid (2 h) (93%).

^{1}H NMR: δ = 3.52 (d, *J* = 13.8 Hz, 2 H), 3.67 (d, *J* = 13.8 Hz, 2 H), 4.27 (d, *J* = 8.7 Hz, 1 H), 5.20 (d, *J* = 17.4 Hz, 1 H), 5.45 (d, *J* = 10.2 Hz, 1 H), 6.02–6.20 (m, 1 H), 7.18–7.51 (m, 15 H).

^{13}C NMR: δ = 53.4, 64.9, 119.2, 126.6, 126.7, 127.9, 128.0, 128.4, 135.0, 139.7, 141.2. HRMS–FAB: *m/z* $[M+H]^+$ calcd for $C_{23}H_{24}N$, 314.1908; found, 314.1935.

***N*,*N*-Dibenzyl-2-methyl-1-phenyl-2-propen-1-ylamine (3b)**

Obtained as a colorless liquid (2 h) (86%).

^{1}H NMR: δ = 3.39 (s, 3 H), 3.45 (d, *J* = 14.3 Hz, 2 H), 3.77 (d, *J* = 14.3 Hz, 2 H), 4.26 (s, 1 H), 4.97 (s, 1 H), 5.12 (s, 1 H), 7.22–7.38 (m, 15 H).

^{13}C NMR: δ = 20.1, 53.2, 70.0, 114.2, 126.7, 127.0, 128.0, 128.1, 128.7, 129.2, 138.8, 139.2, 145.4.

HRMS –FAB: *m/z* $[M+H]^+$ calcd for $C_{24}H_{26}N$, 328.2065; found, 328.2065.

***N*,*N*-Dibenzyl-1-phenyl-2-buten-1-ylamine (3c)**

Obtained as white crystals (from hexane) (2 h) (86%, *E*/*Z*, 86:14).

Mp 84.0–84.5 °C.

^{1}H NMR (*E*): δ = 1.52 (dd, *J* = 6.7, 1.8 Hz, 3 H), 3.5 (d, *J* = 13.8 Hz, 2 H), 3.79 (d, *J* = 13.8 Hz, 2 H), 5.82–5.89 (m, 1 H), 5.95–6.04 (m, 1 H), 7.23–7.62 (m, 15 H).

^{13}C NMR: δ = 13.4, 53.7, 58.3, 126.6, 128.0, 128.1, 128.6, 128.8, 140.1, 142.3.

Anal. Calcd for $C_{24}H_{25}N$: C, 88.03; H, 7.69; N, 4.28. Found: C, 87.57; H, 8.16; N, 4.26

4-(1-Phenyl-2-propenyl)morpholine[22] (3d)

Obtained as a colorless liquid (1.5 h) (82%).

^{1}H NMR: δ = 2.29–2.35 (m, 4 H), 3.60 (d, *J* = 9.4 Hz, 1 H), 3.66–3.69 (m, 4 H), 5.09 (d, *J* = 9.4 Hz, 1 H), 5.22 (d, *J* = 17.2 Hz, 1 H), 5.81–5.98 (m, 1 H), 7.21–7.32 (m, 5 H).

^{13}C NMR: δ = 51.8, 66.9, 75.3, 116.4, 127.0, 127.7, 128.4, 139.5, 141.3

4-[1-(2-Naphthyl)-2-propenyl]morpholine (3e)

Obtained as a pale yellow liquid (1 h) (90%).

^{1}H NMR: δ = 2.30–2.41 (m, 2 H), 2.50–2.60 (m, 2 H), 3.64–3.75 (m, 4 H), 3.79 (d, *J* = 8.7 Hz, 1 H), 5.14 (dd, *J* = 10.0, 1.5 Hz, 1 H), 5.29 (ddd, *J* = 17.1, 1.8, 0.6 Hz, 1 H), 6.00 (ddd, *J* = 17.1, 10.0, 8.7 Hz, 1 H), 7.40–7.50 (m, 2 H), 7.53 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.74–7.76 (m, 1 H), 7.77–7.84 (m, 3 H).

^{13}C NMR: δ = 52.0, 67.1, 75.6, 116.9, 125.7, 125.8, 126.0, 126.7, 127.6, 127.7, 128.3, 132.8, 133.4, 139.1, 139.5.

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.59; H, 7.56; N, 5.53. Found: C, 80.24; H, 8.12; N, 5.75.

4-[2-Methyl-1-(4-pyridinyl)-2-propenyl]piperidine (3f)

Obtained as a colorless liquid (1 h) (92%).

^{1}H NMR: δ = 1.42–1.60 (m, 8 H), 2.26 (br t, *J* = 3.5 Hz, 4 H), 3.62 (s, 1 H), 4.77–4.80 (m, 1 H), 5.12–5.14 (m, 1 H), 7.28–7.30 (m, 2 H), 8.49–8.52 (m, 2 H).

^{13}C NMR: δ = 17.1, 24.5, 26.0, 52.7, 77.8, 114.1, 123.2, 145.2, 149.4, 150.8.

HRMS–FAB: *m/z* $[M+H]^+$ calcd for $C_{14}H_{21}N_2$, 217.1704; found, 216.1749.

4-[1-(4-Methylphenyl)-2-propenyl]morpholine (3g)

Obtained as a pale yellow liquid (1 h) (91%).

^{1}H NMR: δ = 2.21–2.28 (m, 5 H), 2.38–2.44 (m, 2 H), 3.50 (d, *J* = 8.7 Hz, 1 H), 3.59–3.64 (m, 4 H), 5.00 (dd, *J* = 10.2, 1.5 Hz, 1 H), 5.13 (dd, *J* = 16.8, 1.5 Hz, 1 H), 5.82 (ddd, *J* = 17.1, 10.2, 8.7 Hz, 1 H), 7.03–7.07 (m, 2 H), 7.12–7.17 (m, 2 H).

^{13}C NMR: δ = 21.0, 51.9, 67.0, 75.1, 116.3, 127.7, 129.2, 136.8, 138.5, 139.8.

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.15; H, 9.20; N, 6.69.

***N*-Methyl-*N*-(2-methyl-2-propenyl)aniline (3h)[20]**

Obtained as a colorless liquid (30 min) (92%).

^{1}H NMR: δ = 1.70–1.71 (m, 3 H), 2.93 (s, 3 H), 3.78 (br s, 2 H), 4.78–4.84 (m, 2 H), 6.65–6.69 (m, 3 H), 7.17–7.23 (m, 2 H).

^{13}C NMR: δ = 19.9, 38.0, 58.7, 110.6, 111.8, 116.0, 128.9, 141.3

1-[(*E*)-1-Isopropyl-3-phenyl-2-propenyl]piperidine (3i)

Obtained as a yellow liquid (1 h) (94%).

^{1}H NMR: δ = 0.86 (d, *J* = 6.6 Hz, 3 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 1.36–1.42 (m, 2 H), 1.53–1.57 (m, 4 H), 1.88–1.99 (m, 1 H), 2.30–2.60 (m, 5 H), 6.11 (dd, *J* = 15.9, 9.6 Hz, 1 H), 6.36 (d, *J* = 16.2 Hz, 1 H), 7.18–7.39 (m, 5 H).

^{13}C NMR: δ = 19.3, 20.4, 25.0, 26.5, 28.7, 51.0, 74.8, 126.2, 127.1, 128.5, 129.1, 132.8, 137.3.

Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.52; H, 10.90; N, 5.90.

Preparation of Propargylamines 7a–e; General Procedure

To a solution of the appropriate benzotriazolylalkyl/aryl amine (10 mmol) in toluene (50 mL), was added the proper alkynyl Grignard reagent (0.5 M solution in THF, 1.5 equiv) over a period of 10 min at r.t. The mixture was heated and stirred at 50 °C for 1–3 h, poured into a saturated solution of NH_4Cl (200 mL) containing crushed ice, and extracted with Et_2O. The combined etheral layers was washed successively with 2 N NaOH, water and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was further purified by column chromatography over silica gel (230–400 mesh) using hexane–EtOAc as an eluent.

***N*,*N*-Dibenzyl-1-phenyl-2-butyn-1-ylamine (7a)**

Obtained as a colorless liquid (1 h) (90%).

^{1}H NMR: δ = 2.06 (d, *J* = 1.5 Hz, 3 H), 3.43 (d, *J* = 13.5 Hz, 2 H), 3.68 (d, *J* = 13.5 Hz, 2 H), 4.65 (bs, 1 H), 7.16–7.42 (m, 13 H), 7.66 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR: δ = 3.7, 54.4, 55.5, 74.0, 83.8, 126.9, 127.2, 127.9, 128.2, 128.2, 128.8, 139.7.

Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30. Found: C, 88.40; H, 7.60; N, 4.33.

4-(1-Phenyl-2-butynyl)morpholine (7b)
Obtained as a colorless liquid (3 h) (88%).

^{1}H NMR: δ = 1.95 (d, *J* = 2.1 Hz, 3 H), 2.48−2.58 (m, 4 H), 3.66−3.76 (m, 4 H), 4.47−4.48 (br d, 1 H), 7.21−7.40 (m, 3 H), 7.50−7.60 (m, 2 H).

^{13}C NMR: δ = 3.34, 49.6, 61.5, 66.9, 74.6, 83.5, 127.3, 127.8, 128.3, 138.2.

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.37; H, 8.35; N, 6.53.

4-[1-(2-Naphthyl)-2-butynyl]morpholine (7c)
Obtained as a pale yellow liquid (30 min) (83%).

^{1}H NMR: δ = 2.02 (d, *J* = 2.4 Hz, 3 H), 2.54−2.66 (m, 4 H), 3.66−3.78 (m, 4 H), 4.64−4.65 (br d, 1 H), 7.45−7.52 (m, 2 H), 7.70 (dd, *J* = 8.4, 1.8 Hz, 1 H), 7.82−7.89 (m, 3 H), 8.02 (bs, 1 H).

^{13}C NMR: δ = 3.6, 49.8, 61.7, 66.9, 74.6, 84.0, 125.8, 125.8, 126.4, 127.2, 127.4, 127.7, 127.9, 132.8, 132.9, 135.7.

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.06; H, 7.37; N, 5.27.

4-[1-(4-Methylphenyl)-3-phenyl-2-propynyl]morpholine (7d)
Obtained as a colorless liquid (2 h) (87%).

^{1}H NMR: δ = 2.35 (s, 3 H), 2.61−2.65 (m, 4 H), 3.72−3.73 (m, 4 H), 4.74 (s, 1 H), 7.17(br d, *J* = 8.4 Hz, 2 H), 7.30−7.33 (m, 3 H), 7.50−7.52 (m, 4 H).

^{13}C NMR: δ = 21.1, 9.8, 61.7, 65.8, 67.1, 85.2, 88.2, 122.9, 128.1, 128.2, 128.4, 128.5, 128.8, 131.7, 134.7, 137.4.

Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.29; H, 7.50; N, 4.81.

4-(1-Isopropyl-3-phenyl-2-propynyl)piperidine (7e)
Obtained as a colorless liquid (2 h) (90%).

^{1}H NMR: δ = 1.01 (d, *J* = 6.6 Hz, 3 H), 1.097 (d, *J* = 6.6 Hz, 3 H), 1.43−1.64 (m, 6 H), 1.87−1.95 (m, 1 H), 2.40−2.42 (m, 2 H), 2.61−2.65 (m, 2 H), 2.98 (d, *J* = 9.9 Hz, 1 H), 7.25−7.7.30 (m, 3 H), 7.42−7.46 (m, 2 H).

^{13}C NMR: δ = 19.8, 20.6, 24.7, 26.2, 30.4, 50.8, 65.6, 85.9, 87.9, 123.8, 127.6, 128.2, 131.7.

HRMS–FAB): *m/z* $[M+H]^+$ calcd for $C_{17}H_{24}N$, 242.1908; found, 242.1895.

[1-(4-Morpholino)-1-(2-naphthyl)]methyl-1*H*-1,2,3-benzotriazole (1c)
Benzotriazole (5g, 42 mmol) was taken together with morpholine (3.66 mL, 42 mmol) in absolute EtOH (50 mL). The mixture was stirred for 10 min at r.t. followed by the addition of 2-naphthaldehyde (6.5 g, 42 mmol). The reaction mixture was stirred at r.t. for an additional 15 h and then it was concentrated under reduced pressure to yield the benzotriazolylarylamine **1c** in quantitative yield. The product was sufficiently pure for the subsequent reaction with Grignard reagent.

^{1}H NMR: δ = 2.66−2.69 (m, 4 H), 3.78−3.81 (m, 4 H), 6.84 (s, 1 H), 7.36−7.58 (m, 6 H), 7.73−7.97 (m, 5 H).

^{13}C NMR: δ = 50.1, 66.8, 83.1, 111.5, 120.0, 124.0, 124.7, 126.5, 126.7, 127.4, 127.6, 128.2, 128.7, 132.3, 133.0, 133.3, 146.1.

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