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Selective Propargylation of Carbonyl Compounds and Imines with Barium Reagents

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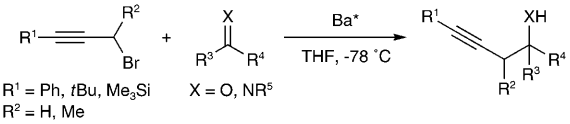
Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: A Barbier-type regioselective propargylation of aldehydes and ketones with (3-bromobut-1-ynyl)trimethylsilane has been achieved using reactive barium as a low-valent metal in THF. Especially in the case of ketones, the corresponding homopropargylic alcohols form almost exclusively. In the reaction of α,β-unsaturated carbonyl compounds, only 1,2-adducts have been observed. This method is also applicable to propargylation of imines, and the corresponding homopropargylic amines are obtained regiospecifically in good yields with diastereomeric ratios of up to 87:13.

Keywords: aldehydes · barium · imines · ketones · propargylation

Introduction

Propargylation of electrophiles is a useful method to introduce a carbon–carbon triple bond into organic compounds.[1] One problem of this reaction, which employs a propargylic or allenylic metal reagent, is to control its regioselectivity. Organomagnesium and organozinc reagents prepared from γ-alkylated propargyl bromides are known to add to aldehydes selectively at the γ-position to give allenylic alcohols.[2] On the other hand, there are not many satisfactory methods for the selective synthesis of homopropargylic alcohols.[1d,3] We have previously shown that reactive barium promotes a Barbier-type reaction of a Me_3Si-substituted propargyl bromide with aldehydes and ketones, which provides homopropargylic alcohols exclusively.[4] We report here, further studies about the regioselective propargylation by using carbonyl compounds and imines as electrophiles (Scheme 1).



Scheme 1. Barbier-type reaction of propargylic bromides with carbonyl compounds and imines promoted by reactive barium.

Results and Discussion

First, according to the standard experimental procedure,[4] a mixture of 3-bromo-1-phenyl-1-butyne (**1a**) and benzaldehyde (**2a**) was exposed to reactive Rieke barium,[5,6] which was generated from barium iodide and lithium biphenylide,[7] and a 3:1 mixture of homopropargylic alcohol **3a** and allenylic alcohol **4a** was obtained in 48% combined yield (Table 1, entry 1). The use of (3-bromo-1-butynyl)trimethylsilane (**1c**) resulted in a better yield with a similar α/γ selectivity (Table 1, entry 3), though the reaction of a bulky *tert*-butyl group-substituted α-methylated propargylic bromide **1b** was not regioselective (Table 1, entry 2).

Then, we examined the barium-promoted regioselective propargylation of various aldehydes **2b**–**2k** and ketones **2l**–**2s** with the Me_3Si-substituted α-methylated propargylic bromide **1c**, and the results are summarized in Table 2. As a consequence, not only aromatic aldehydes **2b**–**2i** but α,β-unsaturated aldehyde **2j** and aliphatic aldehyde **2k** were also allowed to react with the barium reagent to give the corresponding homopropargylic alcohols **3d**–**3m** selectively in

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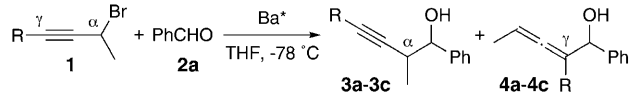
Table 1. Reactive barium-promoted Barbier-type reaction of various α-methylated propargylic bromides **1** with benzaldehyde (**2a**).



Entry	R	Yield [%][a]	Products	α/γ[b]	d.r. of **3**[b]
1	Ph (**1a**)	48	**3a+4a**	3:1	54:46
2	*t*Bu (**1b**)	57	**3b+4b**	1:1	62:38[c]
3	Me_3Si (**1c**)	92	**3c+4c**	3:1	58:42[c]

[a] Yield of isolated product. [b] Determined by ^{1}H NMR analysis. [c] *Erythro/threo* ratio assigned by the reported data.[12,3i]

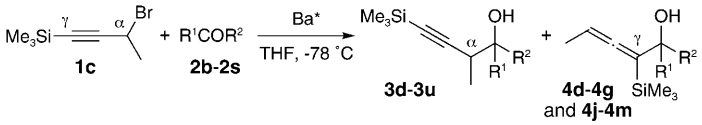
satisfactory yields (Table 2, entries 1–10). In the case of 2- or 4-hydroxybenzaldehyde (**2f** or **2g**), no allenylic alcohol was observed at all (Table 2, entries 5 and 6). As for ketones **2l**–**2s**, only propargylation took place (Table 2, entries 11–18). 2-Cyclohexenone (**2s**), which is a good Michael acceptor, shows an exclusive 1,2-selectivity (Table 2, entry 18). Heteroaromatic carbonyl compounds **2h**, **2i**, **2q**, and **2r** also underwent the selective propargylation under the standard reaction conditions. Noteworthy is the fact that the desired product of readily enolizable **2s** was obtained in good yield (Table 2, entry 18), which indicates that an in situ generated barium reagent is not so basic. Concerning stereoselectivity of the homopropargylic alcohols **3**, a mixture of diastereomers with moderate ratios of up to 70:30 was obtained in each case (Tables 1 and 2).

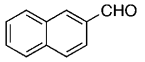
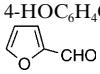
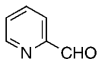
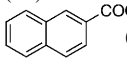
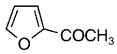
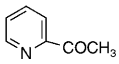
Next, we attempted the reactive barium-promoted Barbier-type propargylation of imines.[8] Table 3 summarizes the results of the reaction of various γ-substituted propargyl bromides **5** with aromatic aldimine **6a**. The size of the R group in **5** affects the α/γ ratio of the product and in fact, when 3-bromo-1-phenyl-1-propyne (**5a**) was used as a propargylating agent, a 2:1 mixture of the corresponding homopropargylic amine **7a** and allenylic amine **8a** was obtained in moderate yield (Table 3, entry 1). In contrast, the introduction of a bulkier *t*Bu group to the γ-position of **5** remarkably improved the regioselectivity and the homopropargylic amine **7b** was formed nearly exclusively in 44% yield (Table 3, entry 2). Finally, we have found that Me_3Si-substituted propargyl bromide **5c** gave the best results in terms of both regioselectivity and isolated yield (Table 3, entry 3).

Abstract in Japanese:

我々はTHF中で活性バリウムを低原子価金属として用いることにより、(3-ブロモ-1-ブチニル)トリメチルシランによるアルデヒド類やケトン類のBarbier型位置選択的プロパルギル化反応を達成した。特にケトンの場合に、対応するホモプロパルギル型アルコールがほぼ特異的に生成する。α,β-不飽和カルボニル化合物の反応では、1,2-付加体のみが見られた。本手法は、イミン類のプロパルギル化反応にも適用でき、対応するホモプロパルギル型アミンが位置特異的かつ最高87:13のジアステレオマー比で収率良く得られる。

Table 2. Regioselective propargylation of various aldehydes **2b**–**2k** and ketones **2l**–**2s** with a Me_3Si-substituted α-methylated propargylic barium reagent.



Entry	R^1COR^2	Yield [%][a]	Products	α/γ[b]	d.r. of **3**[b]
1		78	**3d+4d**	4:1	55:45
2		96	**3e+4e**	5:1	63:37[c]
3		70	**3f+4f**	10:1	70:30
4		82	**3g+4g**	10:1	61:39
5	2-HOC_6H_4CHO (**2f**)	73	**3h**	>99:1	53:47
6	4-HOC_6H_4CHO (**2g**)	73	**3i**	>99:1	58:42
7	 (**2h**)	83	**3j+4j**	3:2	51:49
8	 (**2i**)	50	**3k+4k**	20:1	60:40
9	(*E*)-PhCH=CHCHO (**2j**)	47	**3l+4l**	20:1	58:42
10	*t*BuCHO (**2k**)	84	**3m+4m**	4:1	31:69[c]
11	$PhCOCH_3$ (**2l**)	99	**3n**	>99:1	65.35
12	4-$MeC_6H_4COCH_3$ (**2m**)	99	**3o**	>99:1	53:47
13	4-$MeOC_6H_4COCH_3$ (**2n**)	67	**3p**	>99:1	66:34
14	 (**2o**)	66	**3q**	>99:1	69:31
15	 (**2p**)	74	**3r**	>99:1	57:43
16	 (**2q**)	95	**3s**	>99:1	58:42
17	 (**2r**)	70	**3t**	>99:1	51:49
18	 (**2s**)	87	**3u**	>99:1	68:32

[a] Yield of isolated product. [b] Determined by ^{1}H NMR analysis. [c] *Erythro/threo* ratio assigned by the reported data.[3i]

We thus verified the practicability of the present propargylation, and *N*-phenylbenzaldimine derivatives possessing different substituents have been applied (Table 4). As a consequence, not only an electron-donating group-substituted benzaldimine (**6a**) shown in Table 3, but an electron-withdrawing group-substituted benzaldimine, such as **6c**, was also propargylated regiospecifically, though the chemical yield was not satisfactory (Table 4, entry 2). It is interesting to note that the existence of a phenolic OH group on the aromatic ring did not affect the reaction course (Table 4, entry 3). Benzaldimines **6e** and **6f**, which were derived from electron-donating group-substituted anilines, were also efficiently transformed into the targeted homopropargylic amines **7g** and **7h**, respectively, by this method (Table 4, entries 4 and 5).

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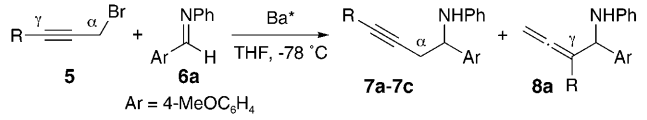
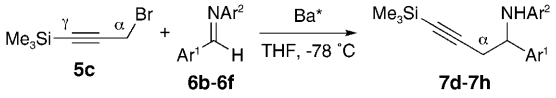
Table 3. Reactive barium-promoted Barbier-type reaction of various propargylic bromides with imine **6a**.



Entry	R	Yield [%][a]	Products	α/γ[b]
1	Ph (**5a**)	56	**7a+8a**	2:1
2	*t*Bu (**5b**)	44	**7b**	>99:1
3	Me_3Si (**5c**)	74	**7c**	>99:1

[a] Yield of isolated product. [b] Determined by ^{1}H NMR analysis.

Table 4. Regioselective propargylation of various imines **6b–6f** with a trimethylsilylated propargylic barium reagent.

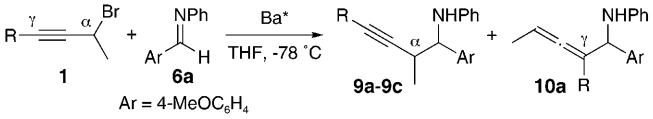


Entry	Ar^1	Ar^2		Yield [%][a]	Product	α/γ[b]
1	Ph	Ph	**6b**	47	**7d**	>99:1
2	4-$CF_3C_6H_4$	Ph	**6c**	35	**7e**	>99:1
3	2-HOC_6H_4	Ph	**6d**	55	**7f**	>99:1
4	Ph	2-$MeOC_6H_4$	**6e**	73	**7g**	>99:1
5	Ph	4-$MeOC_6H_4$	**6f**	67	**7h**	>99:1

[a] Yield of isolated product. [b] Determined by ^{1}H NMR analysis.

The scope of the barium-promoted Barbier-type reaction of aldimines has been further extended to γ-substituted α-methylated propargylic bromides **1** (Table 5). Under the optimized reaction conditions, aromatic aldimine **6a** was treated with in situ generated barium reagent from 3-bromo-1-phenyl-1-butyne (**1a**) and as a result, a 9:1 mixture of homopropargylic amine **9a** and allenylic amine **10a** was obtained in 66% combined yield (Table 5, entry 1). However, a marked tendency to α-selectivity was observed again when the propargylic bromide **1** bearing a bulkier γ-substituent was used as the propargylating agent. For example, the predominant formation of homopropargylic amines **9** has been accomplished employing **1b** and **1c** as precursors of propargylic barium reagents (Table 5, entries 2 and 3). As for diastereoselectivity of the present propargylation of imines, modest diastereomeric ratios were observed for the major regioisomers **9a** and **9c** (Table 5, entries 1 and 3).

Table 5. Reactive barium-promoted Barbier-type reaction of various α-methylated propargylic bromides **1** with imine **6a**.

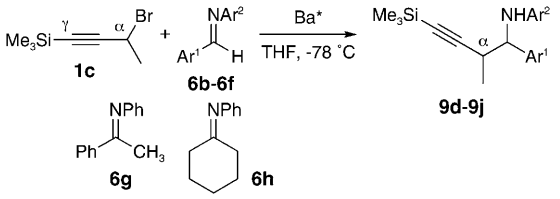


Entry	R	Yield [%][a]	Products	α/γ[b]	d.r. of **9**[b]
1	Ph (**1a**)	66	**9a+10a**	9:1	70:30
2	*t*Bu (**1b**)	64	**9b**	>99:1	50:50
3	Me_3Si (**1c**)	68	**9c**	>99:1	60:40

[a] Yield of isolated product. [b] Determined by ^{1}H NMR analysis.

On the basis of the previously mentioned results, we carried out a survey of the applicability of aromatic aldimines in the reaction with the Me_3Si-substituted α-methylated propargylic bromide **1c**, and some examples are shown in Table 6. In addition to *N*-phenylbenzaldimine (**6b**), its electron-rich and electron-poor derivatives **6c–6f** were tested as substrates and as a result, the desired homopropargylic amines **9** were obtained with almost perfect regioselectivity in every case (Table 6). Even in the presence of a hydroxy group at the *o*-position, the imine **6d** still underwent propargylation exclusively and no allenylic amine was formed at all (Table 6, entry 3). Use of CF_3-substituted benzaldimine **6c** resulted in the highest diastereomeric ratio of 87:13 (Table 6, entry 2). We further tested ketimines **6g** and **6h** as electrophiles in the present propargylation reaction and found that exclusive α-selectivity was still observed for the imines, though the isolated yields of the products **9i** and **9j** (Table 6, entries 6 and 7) were relatively low compared with those of aldimine-derived products **9d–9h** arising from the lower reactivity of the ketimines and resulting dimerization of propargylic bromide **1c**. In the case of propargylation of ketimine **6g**, a 81:19 mixture of diastereomers was obtained (Table 6, entry 6).

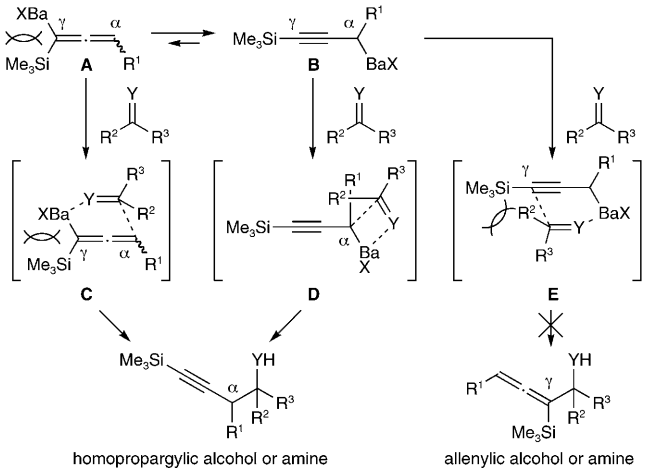
Table 6. Regioselective propargylation of various imines **6b–6h** with a Me_3Si-substituted α-methylated propargylic barium reagent.



Entry	Ar^1	Ar^2		Yield [%][a]	Product	α/γ[b]	d.r. of **9**[b]
1	Ph	Ph	**6b**	66	**9d**	>99:1	50:50
2	4-$CF_3C_6H_4$	Ph	**6c**	61	**9e**	>99:1	87:13
3	2-HOC_6H_4	Ph	**6d**	72	**9f**	>99:1	50:50
4	Ph	2-$MeOC_6H_4$	**6e**	54	**9g**	>99:1	60:40
5	Ph	4-$MeOC_6H_4$	**6f**	>99	**9h**	>99:1	74:26
6	–	–	**6g**	33	**9i**	>99:1	81:19
7	–	–	**6h**	55	**9j**	>99:1	–

[a] Yield of isolated product. [b] Determined by ^{1}H NMR analysis.

Scheme 2 shows a possible reaction mechanism, which gives homopropargylic alcohols or amines and allenylic alcohols or amines. Two pathways are considered for the former propargylated products (α-adducts). A barium reagent generated from (3-bromo-1-propynyl)trimethylsilane or (3-bromo-1-butynyl)trimethylsilane, and reactive barium is anticipated to exist at equilibrium between the allenic isomer **A** and the acetylenic isomer **B**.[1a,b] The homopropargylic alcohol or amine is thus transformable from both isomers **A** and **B** in their reaction with a carbonyl compound or an



Scheme 2. Plausible reaction pathways to homopropargylic alcohols/amines and allenylic alcohols/amines (R^1 = H, Me; Y = O, NR^4).

imine through the transition state structure **C** or **D**, however, the transition state **D** is more reasonable with regard to its lesser steric repulsion.[9] The four-membered cyclic transition-state assembly is also suggested by the mechanism of α-selective allylation of carbonyl compounds with allylic barium reagents.[5b,c] In contrast, the corresponding allenylic alcohol or amine (γ-adduct) is possible to be formed by an S_E2'-type reaction of **B** with the carbonyl compound or imine via the six-membered cyclic transition state **E**, which is, however, less stabilized by a steric bulkiness of the Me_3Si group of **B**.

Conclusions

In summary, we have achieved a novel Barbier-type reaction of α-methylated or α-unsubstituted trimethylsilylpropargyl bromide with carbonyl compounds or imines by employing reactive barium as a promoter. This method is synthetically useful in terms of regioselectivity and affords various (trimethylsilyl)homopropargylic alcohols and amines in satisfactory yields. Moreover, the Me_3Si group can be further converted to other functional groups.[10] Further studies on related reactions promoted by barium reagents are now in progress.

Experimental Section

General Information

Column chromatography was conducted with 70–230 mesh silica gel. Infrared (IR) spectra were recorded on an FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a 400-MHz or 500-MHz spectrometer. Chemical shifts of ^{1}H NMR spectra were reported relative to tetramethylsilane ($\delta = 0$) or chloroform ($\delta = 7.26$). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a 100-MHz spectrometer. Chemical shifts of ^{13}C NMR spectra were reported relative to $CDCl_3$ ($\delta = 77.0$). Mass spectra were recorded on a JEOL JMS-AX500 mass spectrometer using fast-atom-bombardment (FAB) ionization. All experiments were carried out in a two-necked flask under an atmosphere of standard grade argon gas (oxygen < 10 ppm).

Generation of Reactive Barium (Ba)*

An oven-dried Schlenk flask (20 mL) equipped with a teflon-coated magnetic stirring bar was flushed with argon. Freshly cut lithium (15.2 mg, 2.2 mmol) and biphenyl (339 mg, 2.2 mmol) were put into an apparatus and covered with dry THF (3 mL), and the mixture was stirred for 1.5 h at room temperature (lithium was completely consumed). Anhydrous BaI_2 (470 mg, 1.1 mmol) was placed in a separate oven-dried, two-necked flask (30 mL) also equipped with a teflon-coated magnetic stirring bar under argon atmosphere; this was covered with dry THF (5 mL), and stirred for 20 min at room temperature. To the solution of BaI_2 in THF was added at room temperature a solution of the lithium biphenylide in THF under an argon stream. The reaction mixture was stirred for 30 min at room temperature, and the resulting dark brown suspension of reactive barium thus prepared, was ready to use.

Synthesis of Homopropargylic Alcohols

A solution of propargylic bromide (0.5 mmol) and carbonyl compound (0.5 mmol) in dry THF (4 mL) was added dropwise to the resulting dark brown suspension of reactive barium (1.1 mmol) in THF (8 mL) at −78 °C. After the reaction was completed (monitored by TLC), the reaction mixture was treated with a saturated aqueous solution of NH_4Cl (10 mL) at −78 °C, and the aqueous layer was extracted with ether (10 mL). The combined organic extracts were washed with a solution of sodium thiosulfate (15 mL, 1 N), dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. The residual crude product was purified by column chromatography on silica gel to give a mixture of homopropargylic alcohol and allenylic alcohol. The α/γ ratio was determined by ^{1}H NMR analysis.

2-Methyl-1,4-diphenylbut-3-yn-1-ol (**3a**, a 54:46 mixture of diastereomers, Table 1, entry 1):[11] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.18$ (d, 1.4 H, J = 7.0 Hz), 1.22 (d, 1.6 H, J = 7.0 Hz), 2.30 (br s, 0.54 H), 2.62 (br s, 0.46 H), 3.02 (m, 0.54 H), 3.08 (m, 0.46 H), 4.60 (d, 0.46 H, J = 7.0 Hz), 4.80 (d, 0.54 H, J = 5.5 Hz), 7.18–7.49 ppm (m, 10 H).

2,5,5-Trimethyl-1-phenylhex-3-yn-1-ol (**3b**, a 62:38 mixture of *erythro* and *threo* isomers, Table 1, entry 2):[12] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.04$ (s, 3.6 H), 1.06 (s, 5.4 H), 1.60 (d, 1.2 H, J = 6.8 Hz), 1.71 (d, 1.8 H, J = 7.0 Hz), 2.72 (m, 0.6 H), 2.81 (m, 0.4 H), 4.40 (d, 0.4 H, J = 7.2 Hz), 4.64 (d, 0.6 H, J = 5.6 Hz), 7.24–7.39 ppm (m, 5 H).

2-Methyl-4-(trimethylsilyl)-1-phenylbut-3-yn-1-ol (**3c**, a 58:42 mixture of *erythro* and *threo* isomers, Table 1, entry 3):[3i,11a–d,13] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.18$ (s, 5.2 H), 0.23 (s, 3.8 H), 1.12 (d, 1.3 H, J = 7.1 Hz), 1.15 (d, 1.7 H, J = 7.0 Hz), 2.84 (m, 0.58 H), 2.91 (m, 0.42 H), 4.52 (d, 0.42 H, J = 7.3 Hz), 4.75 (d, 0.58 H, J = 5.5 Hz), 5.19–5.22 (m, 1 H), 7.31–7.43 ppm (m, 5 H).

2-Methyl-4-(trimethylsilyl)-1-*p*-tolylbut-3-yn-1-ol (**3d**, a 55:45 mixture of diastereomers, Table 2, entry 1): IR (neat): $\tilde{\nu}$ = 3417, 2960, 2166, 1608 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.18$ (s, 5 H), 0.23 (s, 4 H), 1.11 (d, 1.7 H, J = 7.0 Hz), 1.14 (d, 1.7 H, J = 7.0 Hz), 2.40 (s, 3 H), 2.45 (br s, 1 H), 2,83 (m, 0.44 H), 2.90 (m, 0.56 H), 4.49 (d, 0.44 H, J = 7.2 Hz), 4.73 (d, 0.56 H, J = 5.6 Hz), 7.19–7.21 (m, 2 H), 7.28–7.32 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.06$ (3 C), 15.6, 17.2, 21.1, 35.3, 36.5, 76.0, 77.2, 87.3, 87.9, 107.8, 108.3, 126.4, 126.6, 128.6, 128.7, 128.9, 137.2, 137.6, 138.2 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{15}H_{21}OSi$: 245.1362 [M−H]; found: 245.1364.

1-(4-Methoxyphenyl)-2-methyl-4-(trimethylsilyl)but-3-yn-1-ol (**3e**, a 63:37 mixture of *erythro* and *threo* isomers, Table 2, entry 2):[3j] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.13$ (s, 5.7 H), 0.18 (s, 3.3 H), 1.04 (d, 1.1 H, J = 7.0 Hz), 1.09 (d, 1.9 H, J = 7.0 Hz), 2.76 (m, 0.37 H), 2.84 (m, 0.63 H), 3.81 (s, 3 H), 4.42 (m, 0.37 H), 4.67 (m, 0.63 H), 5.08–5.21 (m, 1 H), 6.85–6.89 (m, 2 H) 7.29–7.31 ppm (m, 2 H).

2-Methyl-4-(trimethylsilyl)-1-(naphthalen-1-yl)but-3-yn-1-ol (**3f**, a 70:30 mixture of diastereomers, Table 2, entry 3): IR (neat): $\tilde{\nu}$ = 3437, 2960, 2164, 1597 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.10$ (s, 2.7 H), 0.18 (s, 6.3 H), 1.08 (d, 2.1 H, J = 7.0 Hz), 1.19 (d, 0.9 H, J = 7.1 Hz), 2.41 (br s,

0.7H), 2.79 (br s, 0.3H), 3.07–3.17 (m, 1H), 5.25 (d, 0.3H, J=6.1 Hz), 5.63 (d, 0.7H, J=4.7 Hz), 7.46–7.53 (m, 3H) 7.60–8.13 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.09 (3C), 14.9, 18.2, 34.1, 36.0, 72.3, 74.1, 77.2, 87.2, 88.5, 107.2, 108.8, 123.0, 123.3, 124.1, 124.4, 125.1, 125.2, 125.4 (2C), 125.9, 126.0 (2C), 128.0 (2C), 128.4, 128.9 (3C), 130.4, 133.6, 136.6 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{18}H_{22}OSi$: 282.1441 [M]; found: 282.1534.

2-Methyl-4-(trimethylsilyl)-1-(naphthalen-2-yl)but-3-yn-1-ol (**3g**, a 61:39 mixture of diastereomers, Table 2, entry 4): IR (neat): $\tilde{\nu}$=3408, 2960, 2164, 1603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.12 (s, 5.5H), 0.19 (s, 3.5H), 1.10 (d, 1.2H, J=7.0 Hz), 1.12 (d, 1.8H, J=7.0 Hz), 2.46 (br s, 0.61H), 2.77 (br s, 0.39H), 2.89 (m, 0.39H), 2.96 (m, 0.61H), 4.64 (d, 0.39H, J=7.2 Hz), 4.88 (d, 0.61H, J=5.3 Hz), 7.43–7.50 (m, 3H) 7.80–7.82 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.07 (3C), 15.6, 17.2, 35.4, 36.4, 76.2, 77.2, 87.6, 88.2, 107.5, 108.1, 124.4, 124.6 (2C), 125.0, 125.4, 125.8, 125.9 (2C), 126.0, 126.1, 127.6 (3C), 128.0 (3C), 133.0 (2C), 133.2, 138.7 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{18}H_{22}OSi$: 282.1441 [M]; found: 282.1532.

2-[1-Hydroxy-2-methyl-4-(trimethylsilyl)but-3-ynyl]phenol (**3h**, a 53:47 mixture of diastereomers, Table 2, entry 5): IR (neat): $\tilde{\nu}$=3344, 2960, 2164, 1589 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.14 (s, 4.8H), 0.19 (s, 4.2H), 1.06 (d, 1.4H, J=7.0 Hz), 1.19 (d, 1.6H, J=7.0 Hz), 2.92 (m, 0.53H), 2.97 (m, 0.47H), 3.19 (br s, 0.47H), 3.41 (br s, 0.53H), 4.54 (d, 0.47H, J=8.5 Hz), 4.93 (d, 0.53H, J=5.2 Hz), 6.81–6.88 (m, 2H), 6.96–6.99 (m, 1H), 7.14–7.19 (m, 1H), 7.85 (br s, 0.47H), 8.10 ppm (br s, 0.53H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.02 (3C), 14.8, 17.1, 34.6, 35.3, 78.2, 79.0, 87.9, 88.7, 107.2, 107.7, 117.2, 117.4, 119.4, 119.5, 123.6, 123.7, 128.0, 128.9, 129.1, 129.4, 155.4, 155.8 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{14}H_{19}O_2Si$: 247.1155 [M−H]; found: 247.1138.

4-[1-Hydroxy-2-methyl-4-(trimethylsilyl)but-3-ynyl]phenol (**3i**, a 58:42 mixture of diastereomers, Table 2, entry 6): IR (neat): $\tilde{\nu}$=3354, 2962, 2164, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.12 (s, 5.2H), 0.17 (s, 3.8H), 1.02 (d, 1.3H, J=6.8 Hz), 1.08 (d, 1.7H, J=6.8 Hz), 2.31 (br s, 0.58H), 2.70 (br s, 0.42H), 2.76 (m, 0.42H), 2.84 (m, 0.58H), 4.40 (dd, 0.42H, J=2.4, 7.7 Hz), 4.62 (dd, 0.58H, J=1.9, 5.3 Hz), 5.60 (br s, 1H), 6.74–6.77 (m, 2H) 7.22–7.34 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.03 (1.7C), 0.98 (1.3C), 15.9, 17.1, 35.3, 36.3, 76.0, 77.2, 87.5, 88.1, 107.8, 108.2, 114.8, 115.2, 127.9, 128.0, 132.5, 133.1, 155.3, 155.6 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{14}H_{19}O_2Si$: 247.1155 [M−H]; found: 247.1180.

1-(Furan-2-yl)-2-methyl-4-(trimethylsilyl)but-3-yn-1-ol (**3j**, a 51:49 mixture of diastereomers, Table 2, entry 7): IR (neat): $\tilde{\nu}$=3427, 2960, 2168 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.13 (s, 4.5H), 0.16 (s, 4.5H), 1.14 (d, 1.5H, J=7.0 Hz), 1.18 (d, 1.5H, J=7.2 Hz), 2.24 (d, 0.5H, J=6.0 Hz), 2.34 (d, 0.5H, J=6.5 Hz), 3.03 (m, 1H), 4.50 (m, 0.5H), 4.67 (m, 0.5H), 6.24–6.35 (m, 2H), 7.37–7.38 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.13 (3C), 16.1, 17.2, 33.4, 33.9, 70.7, 70.9, 87.2, 88.2, 106.9 (2C), 107.1, 107.3, 107.5, 110.1, 141.7, 142.1, 153.9, 154.3 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{12}H_{17}O_2Si$: 221.0998 [M−H]; found: 221.0923.

2-Methyl-4-(trimethylsilyl)-1-(pyridin-2-yl)but-3-yn-1-ol (**3k**, a 60:40 mixture of diastereomers, Table 2, entry 8): IR (neat): ν=3197, 2960, 2166, 1595 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.11 (s, 3.6H), 0.12 (s, 5.4H), 1.12 (d, 1.2H, J=7.3 Hz), 1.24 (d, 1.8H, J=7.0 Hz), 2,75 (m, 0.6H), 3.05 (m, 0.4H), 4.23 (br s, 0.6H), 4.50 (br s, 0.4H), 4.62 (d, 0.6H, J=6.7 Hz), 4.77 (d, 0.4H, J=4.3 Hz), 7.21–7.24 (m, 1H), 7.40–7.47 (m, 1H), 7.65–7.70 (m, 1H), 8.54–8.55 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.28 (3C), 15.9, 16.4, 34.8, 35.3, 74.6, 75.6, 87.0, 87.5, 107.6, 108.5, 121.4, 122.1, 122.6, 122.7, 135.9, 136.1, 147.8, 148.1, 159.1, 159.5 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{13}H_{20}ONSi$: 234.1315 [M+H]; found: 234.1338.

(*E*)-4-Methyl-6-(trimethylsilyl)-1-phenylhex-1-en-5-yn-3-ol (**3l**, a 58:42 mixture of diastereomers, Table 2, entry 9): IR (neat): $\tilde{\nu}$=3404, 2960, 2166, 1601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.20 (s, 9H), 1.19 (d, 1.3H, J=7.1 Hz), 1.22 (d, 1.7H, J=7.0 Hz), 2.60 (br s, 1H), 2.69 (m, 0.58H), 2.79 (m, 0.42H), 4.12 (m, 0.58H), 4.22 (m, 0.42H), 6.22 (dd, 0.58H, J=6.6, 15.9 Hz), 6.30 (dd, 0.42H, J=6.6, 15.9 Hz), 6.64 (d, 1H, J=16.1 Hz), 7.23–7.40 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.10 (3C), 16.2, 16.9, 34.3, 34.8, 75.0, 75.4, 87.4, 87.9, 107.2, 107.7, 126.5 (2C), 127.7, 128.6 (3 C), 128.7, 129.2, 132.0, 132.1, 136.5, 136.6 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{16}H_{21}OSi$: 257.1362 [M−H]; found: 257.1297.

2,2,4-Trimethyl-6-(trimethylsilyl)hex-5-yn-3-ol (**3m**, a 31:69 mixture of *erythro* and *threo* isomers, Table 2, entry 10):[3i] ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.14 (s, 2.8H), 0.15 (s, 6.2H), 0.96 (s, 2.07H), 1.00 (s, 0.93H), 1.24 (d, 0.93H, J=6.8 Hz), 1.29 (d, 2.07H, J=7.0 Hz), 2.70 (m, 0.31H), 2.82 (m, 0.69H), 2.97 (dd, 0.69H, J=1.4, 10.6 Hz), 3.38 ppm (t, 0.31H, J=7.0 Hz).

3-Methyl-5-(trimethylsilyl)-2-phenylpent-4-yn-2-ol (**3n**, a 65:35 mixture of diastereomers, Table 2, entry 11): IR (neat): $\tilde{\nu}$=3464, 2960, 2166, 1603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.12 (s, 3.3H), 0.18 (s, 5.7H), 0.93 (d, 1.9H, J=7.0 Hz), 1.06 (d, 1.1H, J=7.0 Hz), 1.62 (s, 1.1H), 1.68 (s, 1.9H), 2.22 (br s, 0.65H), 2.41 (br s, 0.35H), 2,83–2.92 (m, 1H), 7.21–7.49 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.2 (3C), 15.6, 15.7, 24.9, 29.5, 39.7, 40.5, 74.8, 75.3, 87.8, 87.9, 108.1, 108.2, 125.0, 125.5, 126.5, 126.9, 127.7, 127.9, 144.7, 145.3 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{15}H_{21}OSi$: 245.1362 [M−H]; found: 245.0913.

3-Methyl-5-(trimethylsilyl)-2-*p*-tolylpent-4-yn-2-ol (**3o**, a 53:47 mixture of diastereomers, Table 2, entry 12): IR (neat): $\tilde{\nu}$=3467, 2960, 2166, 1606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.13 (s, 4.8H), 0.17 (s, 4.2H), 0.93 (d, 1.6H, J=7.0 Hz), 1.03 (d, 1.4H, J=7.2 Hz), 1.61 (s, 1.4H), 1.66 (s, 1.6H), 2.20 (br s, 0.47H), 2.33 (s, 3H), 2.40 (br s, 0.53H), 2,81–2.89 (m, 1H), 7.11–7.15 (m, 2H), 7.24–7.37 (m, 1.47H), 7.83–7.87 ppm (m, 0.53H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.06 (3C), 15.7, 15.8, 20.9 (2C), 25.0, 29.5, 39.8, 40.6, 74.8, 75.3, 87.7, 87.8, 108.4, 108.5, 125.0, 125.6, 128.4, 128.6, 136.1, 136.5, 141.9, 142.3 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{16}H_{25}OSi$: 261.1676 [M+H]; found: 261.1298.

2-(4-Methoxyphenyl)-3-methyl-5-(trimethylsilyl)pent-4-yn-2-ol (**3p**, a 66:34 mixture of diastereomers, Table 2, entry 13): IR (neat): $\tilde{\nu}$=3494, 2958, 2164, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.14 (s, 3.1H), 0.17 (s, 5.9H), 0.94 (d, 2.0H, J=7.0 Hz), 1.03 (d, 1.0H, J=7.0 Hz), 1.61 (s, 1.0H), 1.66 (s, 2.0H), 2.20 (br s, 1H), 2,82 (m, 0.66H), 2.86 (m, 0.34H), 3.80 (s, 3H), 6.84–6.88 (m, 2H), 7.31–7.41 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.08 (3C), 15.7, 15.9, 24.9, 29.4, 39.9, 40.7, 55.2, 74.7, 75.2, 87.7, 87.8, 108.4 (2C), 113.1, 113.3, 126.3, 126.9, 137.1, 137.4, 158.2, 158.5 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{16}H_{23}O_2Si$: 275.1468 [M−H]; found: 275.1483.

3-Methyl-5-(trimethylsilyl)-2-(naphthalen-2-yl)pent-4-yn-2-ol (**3q**, a 69:31 mixture of diastereomers, Table 2, entry 14): IR (neat): $\tilde{\nu}$=3467, 2962, 2164, 1601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.11 (s, 2.8H), 0.19 (s, 6.2H), 0.95 (d, 2.1H, J=7.1 Hz), 1.08 (d, 0.9H, J=7.1 Hz), 1.73 (s, 0.9H), 1.76 (s, 2.1H), 2.34 (br s, 0.69H), 2.52 (br s, 0.31H), 2.99 (m, 1H), 7.44–7.49 (m, 2.69H), 7.62–7.65 (m, 0.31H), 7.79–7.85 (m, 3H), 7.93–7.95 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.10 (3C), 15.7, 15.8, 25.1, 29.7, 39.6, 40.5, 75.1, 75.6, 88.1, 108.1, 108.2, 123.4, 124.0, 124.1, 124.5, 125.7, 125.8, 125.9, 126.0, 127.4 (2C), 127.5, 127.6, 128.2 (2C), 132.2, 132.4, 132.9, 133.1, 142.2, 142.8 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{19}H_{23}OSi$: 295.1519 [M−H]; found: 295.1345.

3-Methyl-5-(trimethylsilyl)-2-(naphthalen-1-yl)pent-4-yn-2-ol (**3r**, a 57:43 mixture of diastereomers, Table 2, entry 15): IR (neat): $\tilde{\nu}$=3550, 2960, 2164, 1599 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.17 (s, 9H), 0.94 (d, 1.7H, J=7.0 Hz), 0.98 (d, 1.3H, J=7.0 Hz), 1.84 (s, 1.7H), 1.96 (s, 1.3H), 2.46 (br s, 0.43H), 2.80 (br s, 0.57H), 3.63 (m, 0.43H), 3.71 (m, 0.57H), 7.35–7.53 (m, 3.57H) 7.74–7.87 (m, 2.43H), 8.37 (m, 0.43H), 8.86 ppm (m, 0.57H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.14 (3C), 15.8, 16.9, 24.6, 28.7, 37.9, 38.3, 75.5, 78.5, 87.8, 88.2, 108.2, 108.5, 124.4, 124.9, 125.0, 125.2 (2C), 125.3, 125.5 (3C), 127.2, 128.5, 129.1 (2C), 129.5, 130.1, 130.9, 134.7, 134.8, 139.3, 140.0 ppm; HRMS (FAB$^+$): m/z (%) calcd for $C_{19}H_{23}OSi$: 295.1519 [M−H]; found: 295.1355.

2-(Furan-2-yl)-3-methyl-5-(trimethylsilyl)pent-4-yn-2-ol (**3s**, a 58:42 mixture of diastereomers, Table 2, entry 16): IR (neat): $\tilde{\nu}$=3454, 2960, 2168 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.14 (s, 5.2H), 0.15 (s, 3.8H), 1.05 (d, 1.3H, J=7.0 Hz), 1.09 (d, 1.7H, J=7.0 Hz), 1.58 (s, 1.3H), 1.62 (s, 1.7H), 2.45 (br s, 1H), 2.95 (q, 0.58H, J=7.0 Hz), 3.13 (q, 0.42H, J=7.2 Hz), 6.27–6.33 (m, 2H), 7.34–7.36 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.03 (3C), 15.6, 16.0, 22.3, 25.0, 38.3, 38.4, 72.8, 73.1, 87.7,

87.9, 105.6, 105.8, 106.3, 107.4, 107.5, 110.0, 141.3, 141.7, 157.0, 157.4 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{13}H_{21}O_2Si$: 237.1311 [$M+H$]; found: 237.0962.

3-Methyl-5-(trimethylsilyl)-2-(pyridin-2-yl)pent-4-yn-2-ol (**3t**, a 51:49 mixture of diastereomers, Table 2, entry 17): IR (neat): $\tilde{\nu}=3381$, 2960, 2168, 1593 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.12$ (s, 4.5H), 0.15 (s, 4.5H), 0.98 (d, 1.5H, $J=7.1$ Hz), 1.07 (d, 1.5H, $J=7.1$ Hz), 1.65 (s, 1,5H), 1.67 (s, 1,5H), 2.81 (q, 0.5H, $J=6.9$ Hz), 2.94 (q, 0.5H, $J=7.0$ Hz), 4.84 (br s, 0.5H), 5.62 (br s, 0.5H), 7.20–7.23 (m, 1H), 7.47–7.49 (m, 0.5H), 7.66–7.70 (m, 1.5H), 8.50–8.52 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=0.05$ (3C), 15.1, 15.4, 24.9, 26.9, 39.2, 39.3, 74.6, 74.9, 86.8, 108.7, 109.5, 120.3, 120.6, 122.0, 122.1, 136.3 (2C), 146.7, 147.4, 162.0, 163.4 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{14}H_{20}ONSi$: 246.1315 [M−H]; found: 246.1330.

1-[4-(Trimethylsilyl)but-3-yn-2-yl]cyclohex-2-enol (**3u**, a 68:32 mixture of diastereomers, Table 2, entry 18): IR (neat): $\tilde{\nu}=3427$, 2954, 2166 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.15$ (s, 6.1H), 0.16 (s, 2.9H), 1.15 (d, 0.96H, $J=7.2$ Hz), 1.17 (d, 2.04H, $J=7.0$ Hz), 1.68–1.97 (m, 6H), 2.04 (br s, 0.68H), 2.09 (br s, 0.32H), 2.58–2.67 (m, 1H), 5.69 (d, 0.32H, $J=10.4$ Hz), 5.72 (d, 0.68H, $J=10.4$ Hz), 5.89–5.95 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=0.10$ (3C), 15.2, 15.4, 18.6, 18.9, 25.2, 25.3, 31.7, 33.0, 38.3, 38.6, 70.7, 87.3, 108.3, 129.6, 130.4, 131.5, 131.8 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{13}H_{21}OSi$: 221.1362 [M−H]; found: 221.1486.

Synthesis of Homopropargylic Amines

A solution of propargylic bromide (1.0 mmol) and imine (0.5 mmol) in dry THF (4 mL) was added dropwise to the resulting dark brown suspension of reactive barium (1.1 mmol) in THF (8 mL) at −78 °C. After the reaction was completed (monitored by TLC), the reaction mixture was treated with a saturated aqueous solution of NH_4Cl (10 mL) at −78 °C, and the aqueous layer was extracted with ether (10 mL). The combined organic extracts were washed with a solution of sodium thiosulfate (15 mL, 1 N), dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. The residual crude product was purified by column chromatography on silica gel to give a mixture of homopropargylic amine and allenylic amine. The α/γ ratio was determined by ^{1}H NMR analysis.

N-(1-(4-Methoxyphenyl)-4-phenylbut-3-ynyl)benzenamine (**7a**, Table 3, entry 1): IR (neat): $\tilde{\nu}=3406$, 3053, 3026, 1600 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.81$–2.96 (m, 2H), 3.77 (s, 3H), 4.53–4.58 (m, 1H), 5.03–5.13 (m, 1H), 6.40–7.40 ppm (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=29.2$, 55.2, 56.3, 85.9, 113.4, 113.7, 113.9, 114.0, 117.7, 127.5, 128.2, 128.5, 129.1, 131.6, 134.4, 147.2, 158.9 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{23}H_{22}ON$: 328.1703 [$M+H$]; found: 328.1707.

N-(1-(4-Methoxyphenyl)-5,5-dimethylhex-3-ynyl)benzenamine (**7b**, Table 3, entry 2): IR (neat): $\tilde{\nu}=3288$, 2941, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.19$ (s, 9H), 2.52 (dd, 1H, $J=7.0$, 16.5 Hz), 2.65 (dd, 1H, $J=5.3$, 16.6 Hz), 3.76 (s, 3H), 4.38 (m, 1H), 4.44 (br s, 1H), 6.50–6.53 (m, 2H), 6.63–6.67 (m, 1H), 6.82–6.86 (m, 2H), 7.06–7.10 (m, 2H), 7.28–7.31 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=27.4$, 28.8, 31.2, 55.2, 56.4, 74.3, 92.3, 113.7, 113.8, 117.5, 127.4, 129.0, 134.8, 147.5, 158.7 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{22}H_{28}ON$: 322.2172 [$M+H$]; found: 322.2164.

N-(1-(4-Methoxyphenyl)-4-(trimethylsilyl)but-3-ynyl)benzenamine (**7c**, Table 3, entry 3): IR (neat): $\tilde{\nu}=3402$, 2956, 2173, 1603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.15$ (s, 9H), 2.63 (dd, 1H, $J=7.0$, 16.9 Hz), 2.73 (dd, 1H, $J=5.2$ Hz, 16.9 Hz), 3.79 (s, 3H), 4.42 (s, 1H), 4.44 (m, 1H), 6.50–6.52 (m, 2H), 6.61–6.69 (m, 1H), 6.84–6.87 (m, 2H), 7.08–7.11 (m, 2H), 7.28–7.34 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=0.0$ (3C), 29.9, 55.2, 56.1, 88.2, 102.9, 113.8, 113.9, 117.7, 127.4, 129.1, 134.4, 147.3, 158.8 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{20}H_{26}ONSi$: 324.1785 [$M+H$]; found: 324.1777.

N-(4-(Trimethylsilyl)-1-phenylbut-3-ynyl)benzenamine (**7d**, Table 4, entry 1): IR (neat): $\tilde{\nu}=3410$, 2958, 2173, 1601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.17$ (s, 9H), 2.65 (dd, 1H, $J=7.2$, 17.0 Hz), 2.76 (dd, 1H, $J=5.2$, 17.0 Hz), 4.28 (dd, 1H, $J=5.2$, 7.2 Hz), 4.48 (br s, 1H), 6.48–6.70 (m, 3H), 7.03–7.41 ppm (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=0.0$ (3C), 29.8, 56.7, 88.4, 102.7, 113.2, 113.8, 117.1, 117.8, 126.4, 127.4, 128.6, 129.1 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{19}H_{24}NSi$: 294.1679 [$M+H$]; found: 294.1672.

N-(1-(4-(Trifluoromethyl)phenyl)-4-(trimethylsilyl)but-3-ynyl)benzenamine (**7e**, Table 4, entry 2): IR (neat): $\tilde{\nu}=3406$, 2960, 2175, 1603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.17$ (s, 9H), 2.66 (dd, 1H, $J=7.0$, 17.2 Hz), 2.79 (dd, 1H, $J=5.6$ Hz, 16.9 Hz), 4.48 (d, 1H, $J=4.4$ Hz), 4.55 (dd, 1H, $J=5.5$, 11.6 Hz), 6.50–6.52 (m, 2H), 6.61–6.69 (m, 1H), 7.08–7.11 (m, 2H), 7.50–7.55 (m, 2H), 7.58–7.64 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=-0.1$ (3C), 25.7, 29.6, 56.3, 89.2, 101.8, 113.8, 118.2, 125.6 (2C), 126.9, 129.3, 146.6, 146.8 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{20}H_{23}NF_3Si$: 362.1553 [$M+H$]; found: 362.1570.

N-(1-(2-Hydroxyphenyl)-4-(trimethylsilyl)but-3-ynyl)benzenamine (**7f**, Table 4, entry 3): IR (neat): $\tilde{\nu}=3238$, 2958, 2175, 1603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.15$ (s, 9H), 2.59 (dd, 1H, $J=4.1$, 16.7 Hz), 2.67 (dd, 1H, $J=9.5$, 16.7 Hz), 3.74 (m, 1H), 3.92 (m, 1H), 4.70–4.74 (m, 1H), 6.81–6.90 (m, 2H), 7.18–7.41 ppm (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=0.0$ (3C), 23.7, 44.3, 63.8, 92.0, 103.5, 116.7, 119.5, 123.6, 124.5, 125.8, 129.4, 130.3, 146.9, 156.5 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{19}H_{22}ONSi$: 308.1472 [$M+H$]; found: 308.1453.

2-Methoxy-*N*-(4-(trimethylsilyl)-1-phenylbut-3-ynyl)benzenamine (**7g**, Table 4, entry 4): IR (neat): $\tilde{\nu}=3417$, 2958, 2175, 1601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.15$ (s, 9H), 2.70 (dd, 1H, $J=7.0$, 16.9 Hz), 2.79 (dd, 1H, $J=5.8$, 16.9 Hz), 3.89 (s, 3H), 4.49 (s, 1H), 5.15 (s, 1H), 6.28–6.32 (m, 1H), 6.61–6.69 (m, 2H), 6.79–6.82 (m, 1H), 7.28–7.41 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=0.0$ (3C), 29.9, 55.5, 56.6, 88.3, 102.9, 109.4, 111.5, 116.9, 121.1, 126.5, 127.4, 128.6, 137.2, 142.6, 147.1 ppm; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{20}H_{26}ONSi$: 324.1785 [$M+H$]; found: 324.1777.

4-Methoxy-*N*-(4-(trimethylsilyl)-1-phenylbut-3-ynyl)benzenamine (**7h**, Table 4, entry 5):[14] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.16$ (s, 9H), 2.69 (dd, 1H, $J=8.0$, 16.9 Hz), 2.75 (dd, 1H, $J=5.5$, 16.9 Hz), 3.76 (s, 3H), 4.00 (s, 1H), 4.75 (dd, 1H, $J=5.6$, 8.0 Hz), 6.82–6.84 (m, 2H), 7.08–7.11 (m, 2H), 7.24–7.34 (m, 3H), 7.43–7.45 ppm (m, 2H).

N-(1-(4-Methoxyphenyl)-2-methyl-4-phenylbut-3-ynyl)benzenamine (**9a**, a 70:30 mixture of diastereomers, Table 5, entry 1): IR (neat): $\tilde{\nu}=3408$, 3055, 2933, 2835, 2247, 1601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.17$ (d, 2.1H, $J=7.1$ Hz), 1.34 (d, 0.9H, $J=7.1$ Hz), 3.03 (m, 0.3H), 3.23 (m, 0.7H), 3.76 (s, 3H), 4.29 (d, 0.3H, $J=5.3$ Hz), 4.39 (d, 0.7H, $J=4.7$ Hz), 6.53–7.40 ppm (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=17.5$, 19.0, 33.5, 35.3, 55.1, 60.5, 61.4, 83.8, 90.2, 90.5, 113.4, 113.5, 113.6, 113.7, 117.3, 117.4, 127.9 (2C), 128.0, 128.2 (3C), 128.7, 129.0 (4C), 131.5, 131.6, 131.8, 147.1, 147.5, 158.7 ppm, 158.8; HRMS (FAB$^+$): *m/z* (%) calcd for $C_{24}H_{24}ON$: 342.1859 [$M+H$]; found: 342.1868.

N-(1-(4-Methoxyphenyl)-2,5,5-trimethylhex-3-ynyl)benzenamine (**9b**, a 50:50 mixture of diastereomers, Table 5, entry 2): IR (neat): $\tilde{\nu}=3406$, 2966, 1603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.01$ (d, 1.5H, $J=7.2$ Hz), 1.20 (d, 1.5H, $J=7.0$ Hz), 1.21 (s, 9H), 2.72 (m, 0.5H), 2.96 (m, 0.5H), 3.77 (s, 3H), 4.10 (d, 0.5H, $J=5.6$ Hz), 4.24 (d, 0.5H, $J=4.6$ Hz), 4.52 (br s, 0.5H), 4.64 (br s, 0.5H), 6.50–6.52 (m, 2H), 6.61–6.65 (m, 1H), 6.80–6.84 (m, 2H), 7.04–7.09 (m, 2H), 7.26–7.30 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=17.9$, 19.3, 27.4, 31.2, 32.7, 34.7, 55.1, 60.5, 61.7, 78.9, 79.1, 92.5, 92.7, 113.2, 113.5, 113.6 (2C), 117.1, 117.2, 128.0, 128.8, 129.0 (2C), 132.1, 134.6, 147.3, 147.8, 158.7 ppm (2C); HRMS (FAB$^+$): *m/z* (%) calcd for $C_{22}H_{28}ON$: 322.2172 [$M+H$]; found: 322.2164.

N-(1-(4-Methoxyphenyl)-2-methyl-4-(trimethylsilyl)but-3-ynyl)benzenamine (**9c**, a 60:40 mixture of diastereomers, Table 5, entry 3): IR (neat): $\tilde{\nu}=3402$, 2958, 2164, 1603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.18$ (s, 9H), 1.09 (d, 1.2H, $J=7.0$ Hz), 1.26 (d, 1.8H, $J=7.0$ Hz), 2.78–2.86 (m, 0.4H), 3.02–3.09 (m, 0.6H), 3.79 (s, 3H), 4.18 (d, 0.6H, $J=7.0$ Hz), 4.32 (d, 0.4H, $J=7.0$ Hz), 6.50–6.52 (m, 2H), 6.61–6.69 (m, 1H), 6.83–6.88 (m, 2H), 7.06–7.12 (m, 2H), 7.28–7.34 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=0.1$ (3C), 18.8, 22.2, 33.7, 35.7, 55.2, 60.2, 61.3, 88.1, 88.3, 107.4, 107.7, 113.3, 113.5, 113.7 (2C), 117.3, 117.4, 128.0, 128.8, 129.0 (2C), 131.8, 134.1, 147.2, 147.6, 158.8 ppm (2C); HRMS (FAB$^+$): *m/z* (%) calcd for $C_{21}H_{26}ONSi$: 336.1785 [M−H]; found: 336.1763.

N-(2-Methyl-4-(trimethylsilyl)-1-phenylbut-3-ynyl)benzenamine (**9d**, a 50:50 mixture of diastereomers, Table 6, entry 1):[15] ^{1}H NMR (400 MHz,

$CDCl_3$): $\delta = 0.19$ (s, 9H), 1.07 (d, 1.5H, $J = 7.2$ Hz), 1.25 (d, 1.5H, $J = 7.0$ Hz), 2.83 (m, 0.5H), 3.04 (m, 0.5H), 4.20 (d, 0.5H, $J = 4.7$ Hz), 4.33 (d, 0.5H, $J = 4.5$ Hz), 4.52 (br s, 1H), 6.53–6.55 (m, 2H), 6.65 (m, 1H), 7.08–7.12 (m, 2H), 7.20–7.38 ppm (m, 5H).

N-(1-(4-(Trifluoromethyl)phenyl)-2-methyl-4-(trimethylsilyl)but-3-ynyl)-benzenamine (**9e**, a 87:13 mixture of diastereomers, Table 6, entry 2): IR (neat): $\tilde{\nu} = 3408$, 2962, 2166, 1603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.16 (s, 9H), 1.09 (d, 2.6H, $J = 7.2$ Hz), 1.30 (d, 0.4H, $J = 7.0$ Hz), 2.85 (m, 0.13H), 3.07 (m, 0.87H), 4.30 (d, 0.13H, $J = 4.9$ Hz), 4.39 (d, 0.87H, $J =$ 5.1 Hz), 6.40–6.52 (m, 2H), 6.60–6.68 (m, 1H), 7.08–7.11 (m, 2H), 7.48–7.60 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.0$ (3C), 17.5, 33.7, 60.7, 88.9, 106.7, 113.6 (2C), 117.9, 125.6, 128.2, 129.2 (2C), 144.2, 146.7 ppm; HRMS (FAB^+): *m/z* (%) calcd for $C_{21}H_{25}NF_3Si$: 376.1710 [$M+H$]; found: 376.1731.

N-(1-(2-Hydroxyphenyl)-2-methyl-4-(trimethylsilyl)but-3-ynyl)benzenamine (**9f**, a 50:50 mixture of diastereomers, Table 6, entry 3): IR (neat): $\tilde{\nu} = 3325$, 2958, 2162, 1603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 4.5H), 0.20 (s, 4.5H), 1.13 (d, 1.5H, $J = 7.0$ Hz), 1.23 (d, 1.5H, $J =$ 7.2 Hz), 3.01 (m, 1H), 3.98 (d, 0.5H, $J = 9.7$ Hz), 4.43 (d, 0.5H, $J =$ 4.4 Hz), 4.90 (br s, 1H), 6.74–6.91 (m, 6H), 7.07–7.21 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.0$ (3C), 15.2, 18.0, 32.3, 35.2, 64.2, 65.9, 88.7, 89.1, 107.3 (2C), 116.5 (2C), 116.9, 117.0, 117.3, 119.5, 119.8, 121.4, 123.3, 123.9, 128.1, 128.8, 129.1, 129.2, 129.3, 129.9, 147.0, 147.4, 156.4, 157.5 ppm; MS HRMS (FAB^+): *m/z* (%) calcd for $C_{20}H_{26}ONSi$: 324.1785 [$M+H$]; found: 324.1787.

2-Methoxy-*N*-(2-methyl-4-(trimethylsilyl)-1-phenylbut-3-ynyl)benzenamine (**9g**, a 60:40 mixture of diastereomers, Table 6, entry 4): IR (neat): $\tilde{\nu} = 3745$, 2958, 2166, 1603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.17$ (s, 9H), 1.10 (d, 1.8H, $J = 7.1$ Hz), 1.29 (d, 1.2H, $J = 7.1$ Hz), 2.87 (m, 0.4H), 3.10 (m, 0.6H), 3.89 (s, 1.8H), 3.91 (s, 1.2H), 4.24 (m, 0.4H), 4.35 (m, 0.6H), 5.26 (br s, 0.6H), 5.36 (br s, 0.4H), 6.28–6.35 (m, 1H), 6.56–6.61 (m, 1H), 6.62–6.69 (m, 1H), 6.73–6.78 (m, 1H), 7.22–7.37 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.0$ (3C), 17.5, 19.0, 33.8, 35.7, 55.5, 60.6, 61.6, 87.9, 88.2, 107.3, 107.8, 109.3, 109.4, 110.9, 111.3, 116.3, 116.5, 121.0, 121.1, 127.0, 127.2, 127.3, 127.8 (2C), 127.9, 128.3, 137.0, 137.4, 140.0, 142.3, 147.0 ppm; HRMS (FAB^+): *m/z* (%) calcd for $C_{21}H_{28}ONSi$: 338.1941 [$M+H$]; found: 338.1949.

4-Methoxy-*N*-(2-methyl-4-(trimethylsilyl)-1-phenylbut-3-ynyl)benzenamine (**9h**, a 74:26 mixture of diastereomers, Table 6, entry 5): IR (neat): $\tilde{\nu} = 3381$, 2958, 2164, 1603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.19$ (s, 2.3H), 0.20 (s, 6.7H), 1.10 (d, 0.8H, $J = 7.2$ Hz), 1.26 (d, 2.2H, $J =$ 7.0 Hz), 2.84 (m, 0.74H), 3.07 (m, 0.26H), 3.70 (s, 3H), 4.15 (d, 0.74H, $J = 5.8$ Hz), 4.31 (m, 0.26H), 6.49–6.53 (m, 2H), 6.69–6.71 (m, 2H), 7.23–7.41 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0$ (3C), 17.1, 18.6, 33.7, 35.5, 55.6, 61.7, 62.8, 88.0, 88.1, 107.5, 107.7, 114.0, 114.6, 114.7 (2C), 115.0, 127.1, 127.2, 127.7, 127.9, 128.2, 140.0, 141.3, 141.8, 142.2, 151.9, 152.0 ppm; HRMS (FAB^+): *m/z* (%) calcd for $C_{21}H_{26}ONSi$: 336.1785 [$M-H$]; found: 336.1799.

N-(3-methyl-5-(trimethylsilyl)-2-phenylpent-4-yn-2-yl)benzenamine (**9i**, a 81:19 mixture of diastereomers, Table 6, entry 6): IR (neat): $\nu = 3372$, 2983, 2958, 2166, 1604 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.19$ (s, 7.3H), 0.22 (s, 1.7H), 0.91 (d, 0.6H, $J = 7.0$ Hz), 0.96 (d, 2.4H, $J =$ 7.0 Hz), 1.69 (s, 0.6H), 1.82 (s, 2.4H), 2.75 (q, 0.81H, $J = 7.0$ Hz), 2.79 (q, 0.19H, $J = 7.0$ Hz), 4.46 (br s, 1H), 6.25–6.41 (m, 2H), 6.59–6.67 (m, 1H), 6.94–7.05 (m, 2H), 7.22–7.36 (m, 3H), 7.44–7.53 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.1$ (3C), 15.2, 16.1, 16.8, 23.8, 41.6, 41.7, 60.4, 60.7, 88.5, 88.6, 107.9, 108.1, 115.6, 115.9, 117.3, 117.5, 126.7, 126.9, 127.0, 127.3, 128.0, 128.5, 128.6, 128.7, 143.0, 144.1, 146.2, 146.3 ppm; HRMS (FAB^+): *m/z* (%) calcd for $C_{21}H_{28}NSi$: 322.1992 [$M+H$]; found: 322.1997.

N-(1-(4-(trimethylsilyl)but-3-yn-2-yl)cyclohexyl)benzenamine (**9j**, Table 6, entry 7): IR (neat): $\tilde{\nu} = 3423$, 2943, 2856, 2161, 1599 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.20$ (s, 9H), 1.12 (d, 3H, $J = 7.0$ Hz), 1.20–1.29 (m, 1H), 1.48–1.83 (m, 8H), 2.11–2.17 (m, 1H), 3.06 (q, 1H, $J = 7.0$ Hz), 3.43 (br s, 1H), 6.72–6.77 (m, 3H), 7.12–7.17 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.2$ (3C), 14.8, 21.6, 26.0, 32.2, 32.5, 34.8, 58.3, 86.4, 110.2, 117.0 (2C), 118.0, 129.0 (2C), 146.3 ppm; HRMS (FAB^+): *m/z* (%) calcd for $C_{19}H_{30}NSi$: 300.2149 [$M+H$]; found: 300.2139.

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