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$P(PhCH_2NCH_2CH_2)_3N$: An Efficient Lewis Base Catalyst for the Synthesis of Propargylic Alcohols and Morita−Baylis−Hillman Adducts via Aldehyde Alkynylation

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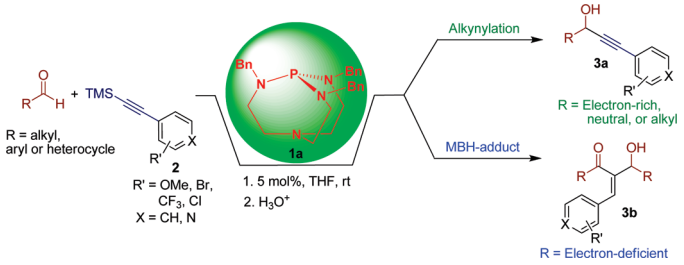

Proazaphosphatrane $P(PhCH_2NCH_2CH_2)_3N$ (**1a**) is an efficient catalyst for the addition of aryl trimethylsilyl alkynes to a variety of aromatic, aliphatic, and heterocyclic aldehydes in THF at room temperature. The reaction conditions are mild and employ a low catalyst loading (ca. 5 mol %). Only propargylic alcohols were isolated in good to excellent isolated yields when electron-rich, electron-neutral, heterocyclic, and aliphatic aldehydes were employed, whereas β-branched Morita−Baylis−Hillman (MBH) type adducts were isolated with electron-deficient aromatic aldehydes after conventional acid hydrolysis of the TMS ether products. Alkynes containing heterocyclic and aromatic groups bearing electron-withdrawing or -donating substituents underwent clean addition to cyclohexanecarboxaldehyde and to electron-rich aromatic aldehydes to give propargylic alcohols in excellent isolated yields. β-Branched Morita−Baylis−Hillman (MBH) type adducts were isolated when electron-deficient aromatic aldehydes were employed. Reaction pathways to both types of products are proposed.

Introduction

Propargylic alcohols are useful in the synthesis of complex multifunctional natural products, such as (−)-reveromycin B, aspinolide B, (±)-blastmycinone, (−)-methylenolactocin, (+)-sterpurene, and (−)-chlorothricolide, via carbon−carbon bond forming reactions.[1−3] Several methods have been described in the literature over the decades for the synthesis of propargylic alcohols,[4−7] and the most common technique for their synthesis is via the use of metal bases (e.g., *n*-BuLi) to generate the acetylide ion.[4−6] Heavy metals have also been

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used in the preparation of propargylic alcohols.[5,6] For example, Carreira et al. have worked extensively on stereoselective alkynylations of aldehydes, mainly with Zn metal-based catalytic systems.[5] In addition, Ag-, In-, and Ru-based catalyst systems for terminal alkyne addition have also been reported.[6]

In recent years, several reports on the Lewis base activation of a variety of organosilyl reagents associated with the synthesis of important organic intermediates have appeared.[8] Pertinent to the present work on activation of silyl-terminated alkynes to generate the corresponding acetylide nucleophiles are past examinations of this process.[7] In 1976, Kuwajima et al. first reported the use of tetrabutylammonium fluoride (3−5 mol %) for the reaction between 1-trimethylsilyl-2-phenylacetylene with aldehydes and ketones, providing products in yields ranging from 5% to 87%.[7a,7b] Shioiri et al. reported the use of a quaternary ammonium fluoride salt derived from cinchonine (10 mol %) at −20 °C to facilitate the reaction of 1-trimethylsilyl-2-phenylacetylene with aldehydes, and Morita−Baylis−Hillman (MBH) type adducts were isolated in 23−92% yields. Among the eleven aldehydes screened, alkynylation product was obtained in the case of benzaldehyde and *o*-phthalaldehyde in minor quantities, whereas alkynylation was observed as a major product with *p*-anisaldehyde and 3,4-dimethoxybenzaldehyde.[7c] The use of 10 mol % of KOEt in THF as solvent at 0 °C was reported by Sheidt et al. to provide good yields of alkynylated product when triethoxysilylacetylenes were used as reagents with aldehydes, ketones, and imines.[7d] In 2006, Mukaiyama et al. reported that 10 mol % of $[Bu_4N][OPh]$ at −78 °C in THF as solvent gave 39−100% isolated alkynylated product yields with aldehydes and four ketone substrates.[7e] Matsukawa et al. reported the synthesis of propargylic alcohols using tris-(2,4,6-trimethoxyphenyl)phosphine (10 mol %) as a catalyst for reaction between 1-trimethylsilyl-2-phenylacetylene and various aldehydes in DMF as solvent at 100−120 °C providing products in 74−96% isolated yield.[7f] Tetrabutylammonium triphenyldifluorosilicate (10 mol %) was reported to promote the reaction between 1-trimethylsilyl-2-phenylacetylene and benzaldehyde, giving the alkynylated product in 81% yield.[7g] However, the generality of this process remains to be established.[7g] The use of tetraphenylphosphonium hydrogen difluoride (3−8 mol %) to catalyze the reaction of 1-trimethylsilyl-2-phenylacetylene with one aldehyde and three ketones in DMF solvent at 50 °C provided moderate product yields (46−64%).[7h] Corey et al. utilized a 1:1 mixture of CsF and CsOH for silyl activation of 1-trimethylsilyl-2-phenylacetylene in the alkynylation of two aldehydes, which gave good product yields (85 and 90%), although 1.6 equiv of fluoride ion was required.[7i]

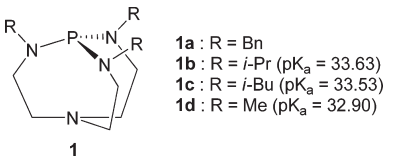
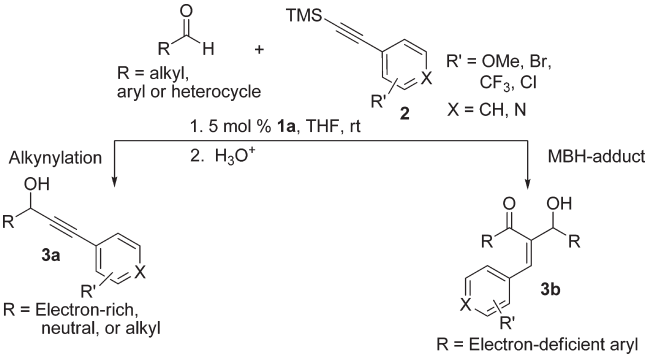


FIGURE 1. Proazaphosphatranes.

SCHEME 1. 1a-Catalyzed Alkynylation and MBH Reactions



Discovered for the first time in our laboratories, proazaphosphatranes of the type shown in Figure 1 are strongly basic, with pK_a values of 32−34 in CH_3CN for their P-protonated $N_{basal} \rightarrow P$ transannulated conjugated acids.[9] If such transannulation occurs during a catalytic cycle, the nucleophilicity of the phosphorus center would be enhanced. The catalytic activation of silicon centers by the phosphorus of proazaphosphatranes has been invoked, for example, for silylation of alcohols with silyl chloride,[10a,10b] for the synthesis of cyanohydrins by the addition of trimethylsilyl nitrile to carbonyl compounds,[10c,10d] for desilylation of TBDMS ethers,[10e] for nucleophilic aromatic substitution of aryl fluorides with aryl silylethers,[10f,10g] for allylation of aromatic aldehydes,[10h] and for the reduction of aldehydes and ketones with poly(methylhydrosiloxane).[10i]

Results and Discussion

In the present work, we report the use of proazaphosphatrane **1a** as an efficient catalyst for the synthesis of

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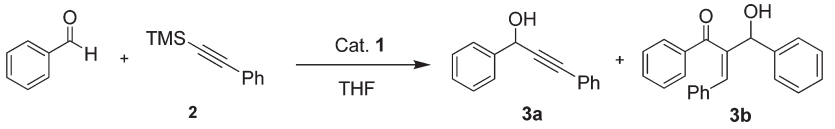
TABLE 1. Survey of Proazaphosphatranes as Catalysts for the Synthesis of Propargylic Alcohols[a]



entry	catalyst	mol (%)	**2** (equiv)	temp (°C)	yield of **3a** (%)[b]	yield of **3b** (%)[b]
1	**1a**	5	1.5	25	79	6
2	**1a**	3	1.5	25	20	-
3	**1a**	5	2.0	25	82 (27−100)[c−i]	2
4	**1a**	5	2.0	0	81	2
5	**1b**	5	2.0	25	72	10[j]
6	**1c**	5	2.0	25	42	-
7	**1d**	5	2.0	25	69	-
8	none	-	2.0	25	n.r.[k]	n.r.[k]

[a]Reaction conditions: aldehyde (2.0 mmol), THF (2 mL), 24 h, followed by 1 N HCl (3 mL). [b]Isolated yield after silica gel column chromatography. [c]76% yield with 3 mol % of $^{n}Bu_4NF$ (ref 7a). [d]76% yield with 5 mol % of $^{n}Bu_4NF$ (ref 7b). [e]27% yield with 10 mol % of the quaternary ammonium fluoride salt derived from cinchonine (ref 7c). [f]100% yield with 10 mol % of $NBu_4(OPh)$ (ref 7e). [g]95% yield with 10 mol % of tris(2,4,6-trimethoxyphenyl)phosphine (ref 7f). [h]81% yield with 10 mol % of $^{n}Bu_4N(Ph_3SiF_2)$ (ref 7g). [i]64% yield with 3 mol % of $Ph_4P(HF_2)$ (ref 7h). [j]Determined by ^1H NMR spectroscopic integration. [k]No reaction.

propargylic alcohols using electron-rich, electron-neutral, heterocyclic, and aliphatic aldehydes with trimethylsilylacetylenes, whereas β-branched Morita−Baylis−Hillman (MBH) type adducts are obtained as the sole products in the case of electron-deficient aromatic aldehydes (Scheme 1).

We first screened the reaction between benzaldehyde and 1-trimethylsilyl-2-phenylacetylene (**2**) (as shown in the reaction scheme in Table 1) using **1a** as a catalyst. With 5 mol % catalyst and 1.5 equiv of alkyne **2** in THF solvent, complete conversion to a mixture of **3a** and **3b** was observed by ^1H NMR spectroscopy. Silica gel column chromatography allowed **3a** to be isolated in 79% yield and the MBH-type adduct **3b** in 6% yield (Table 1, entry 1). We then attempted to minimize formation of the MBH product **3b** by lowering the catalyst **1a** loading to 3 mol % (Table 1, entry 2). Unfortunately, the corresponding alkynylation product **3a** was isolated in only 20% yield and only starting aldehyde was recovered from the remainder of the reaction mixture. Gratifyingly, increasing the trimethylsilyl alkyne to 2 equiv (Table 1, entry 3) increased the yield of the alkynylation product **3a** to 82% with only a 2% yield of the MBH side product **3b**. Lowering the temperature to 0 °C had no significant effect on the ratio of the two products (Table 1, entry 4). We then screened proazaphosphatranes **1b**−**d** in the reaction in Table 1 using the best catalytic conditions reported in this table (entry 3) and the results are recorded in Table 1, entries 5−7. From these results, it is seen that **1a** functioned best for making **3a** under the conditions in entry 3 of Table 1. No reaction was observed under our conditions in the absence of catalyst (Table 1, entry 8).

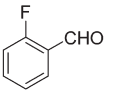
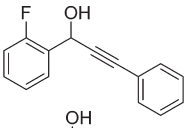
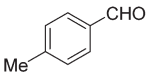
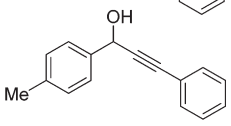
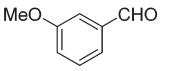
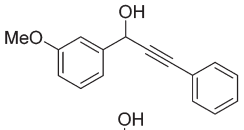
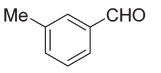
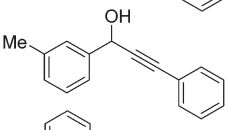
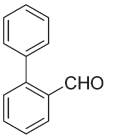
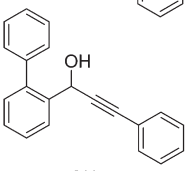
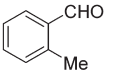
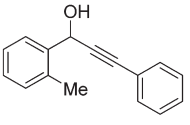
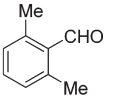
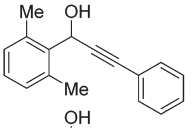
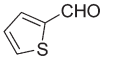
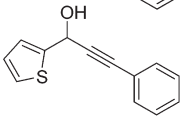
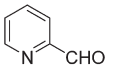
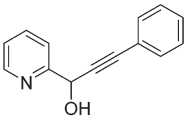
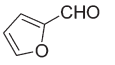
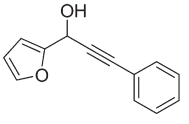
To examine the scope of this methodology a wide variety of aldehydes consisting of electron-rich, electron-poor, heterocyclic, and aliphatic examples were screened under the optimized conditions in Table 1, entry 3, and the results are summarized in Tables 2 and 3. Electron-deficient *o*-fluorobenzaldehyde reacted efficiently with alkyne **2** to yield the desired alkynylation product in an excellent isolated yield (Table 2, entry 1). Aldehydes with electron-donating substituents, such as *p*-tolualdehyde (Table 2, entry 2), *m*-methoxybenzaldehyde (Table 2, entry 3), and *m*-tolualdehyde (Table 2, entry 4), resulted in very good isolated yields of alkynylation products, except in the case of *m*-tolualdehyde, wherein 6% of the MBH adduct was isolated. Pleasingly, excellent isolated yields with no observable MBH side product were obtained when sterically hindered aldehydes, such as *o*-phenylbenzaldehyde (Table 2, entry 5), *o*-tolualdehyde (Table 2, entry 6), and 2,6-dimethylbenzaldehyde (Table 2, entry 7), were employed under our conditions. The versatility of our protocol was extended to the heterocyclic aldehyde, thiophene-2-carboxaldehyde, providing a 91% yield of alkynylation product (Table 2, entry 8). Unfortunately, pyridine- and furan-2-carboxaldehyde gave complicated mixtures, the reason for which is not presently clear (Table 2, entries 9 and 10, respectively).

After screening aromatic aldehydes, we tested several aliphatic examples (Table 3). All the substrates in this table selectively gave propargylic alcohols, and MBH-type adduct formation was not observed. We conjecture that this is because the intermediate **E** (shown in Scheme 2) required for MBH-type adduct formation cannot be stabilized by aliphatic aldehydes (vide infra). Cyclohexanecarboxaldehyde (Table 3, entry 1), isobutyraldehyde (Table 3, entry 2) and heptaldehyde (Table 3, entry 3) led to generally excellent isolated yields of alkynylated product (96%, 94%, and 84%, respectively). Interestingly, catalyst **1a** was efficient in producing a high yield of alkynylation product with a long-chain unsaturated aliphatic aldehyde (Table 3, entry 4).

We next screened several electron-poor aldehydes and observed that β-branched MBH-type adducts formed exclusively under our conditions (Table 4). This may be attributed to the formation of the stabilized intermediate **E** shown in Scheme 2 (vide infra). Acid-sensitive electron-deficient methyl 4-formylbenzoate selectively gave the MBH adduct in good isolated yield (Table 4, entry 1). Electron-poor halogen-containing 3-iodobenzaldehyde (Table 4, entry 2) and 4-bromobenzaldehyde (Table 4, entry 4) also stereoselectively afforded the MBH-type adducts in good isolated yields and electron-deficient 4-(trifluoromethyl)benzaldehyde yielded the MBH adduct in excellent isolated yield (Table 4, entry 3).

We then screened alkynes with various electron-withdrawing, electron-donating, and heterocyclic functionalities. Gratifyingly they all tolerated our reaction conditions well,

TABLE 2. Reactions of Electron-Rich Aromatic and Heterocyclic Aldehydes with 1-Trimethylsilyl-2-phenylacetylene (2), Using Proazaphosphatrane 1a as the Catalyst[a]

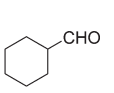
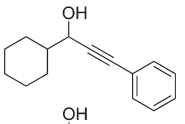
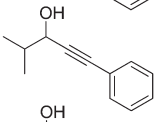
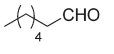
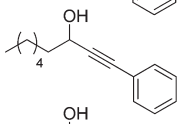
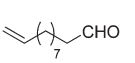
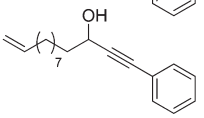
entry	aldehyde	product	yield (%)[b]	lit. yield (%)
1			95	–
2			82	100[c]
3			91	–
4			83	–
5			91	–
6			97	99[c]
7			96	–
8			91	87[c]
9[d]			–	–
10[d]			–	–

[a]Reaction conditions: aldehyde (2.0 mmol), **2** (4.0 mmol), **1a** (5 mol %), THF (2 mL), rt, 24 h, followed by 1 N HCl (3 mL). [b]Isolated yield after column chromatography. [c]10 mol % of $NBu_4(OPh)$ (ref 7e). [d]A complex mixture was observed that we were unable to separate.

giving good to excellent isolated yields of alkynylation products (Table 5). We also examined substituents on the alkyne phenyl group. With an electron-donating methoxy group, an excellent isolated product yield of 92% was realized (Table 5, entry 1). An electron-deficient trifluoromethyl group at the para position (Table 5, entry 2) led to a good isolated yield of the desired product and halogens (both bromo and chloro at ortho and meta positions, respectively) resulting in good isolated product yields (Table 5, entries 4 and 5). Heterocyclic functionalities (such as pyridyl or thiophenyl) on the alkynes also underwent complete conversion, giving good to excellent isolated yields of the desired pro duct under our reaction conditions (Table 5, entries 3 and 6). The use of terminally silylated aliphatic alkynes, such as hex-1-ynyltrimethylsilane (Table 5, entry 7), produced no observable product with the reaction conditions reported in Table 5, footnote a.

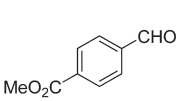
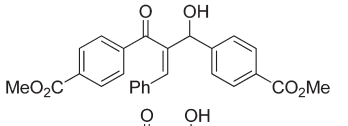
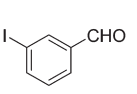
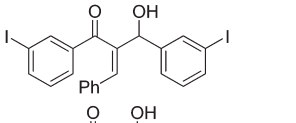
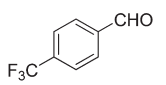
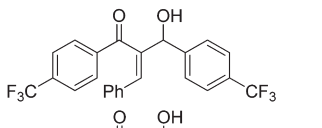
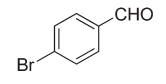
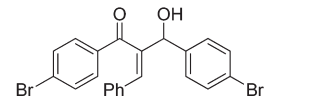
Electron-rich aromatic aldehydes were also evaluated in the presence of a variety of aromatic-substituted alkynes (Table 6). Bulky 2,6-dimethylbenzaldehyde reacted with the electron-rich alkyne in entry 1 of Table 6 giving a quantitative conversion to the alkynylated product in excellent isolated yield (92%). A terminal silylated aromatic alkyne substituted with a bromine at the ortho or a chloro group at the meta position afforded the desired products with 2-biphenylcarboxaldehyde and *o*-tolualdehyde (Table 6, entries 2−4) in

TABLE 3. Reactions of Aliphatic Aldehydes with 1-Trimethylsilyl-2-phenylacetylene (2), Using Proazaphosphatrane 1a as the Catalyst[a]

entry	aldehyde	product	yield (%)[b]	lit. yield (%)
1			96	79[c],85[d],88[e]
2			94	–
3			84	–
4			79	–

[a]Reaction conditions: aldehyde (2.0 mmol), **2** (4.0 mmol), **1a** (5 mol %), THF (2 mL), rt, 24 h, followed by 1 N HCl (3 mL). [b]Isolated yield after column chromatography. [c]With 10 mol % of $NBu_4(OPh)$ (ref 7e). [d]With 3.2 equiv of a 1:1 mixture of CsOH/CsF (ref 7i). [e]88% yield with 10 mol % of tris(2,4,6-trimethoxyphenyl)phosphine (ref 7f).

TABLE 4. Reactions of Electron-Deficient Aldehydes with 1-Trimethylsilyl-2-phenylacetylene (2), Using 1a as the Catalyst[a]

entry	aldehyde	product	yield (%)[b]
1			85
2			78
3			93
4			79

[a]Reaction conditions: aldehyde (2.0 mmol), **2** (4.0 mmol), **1a** (5 mol %), THF (2 mL), rt, 24 h, followed by 1 N HCl (3 mL). [b]Isolated yield after column chromatography.

good to moderate isolated yields. *o*-Tolualdehyde in the presence of an electron-deficient or electron-rich alkyne (having a *p*-trifluoromethyl group or a *p*-methoxy group on the terminal phenylacetylene) gave good isolated yields of the alkynylated product (Table 6, entries 5 and 6, respectively). Heterocyclic alkynes, such as thiophenyl and pyridyl, also underwent complete conversion to give modest to good isolated yields of the desired product with *o*-tolualdehyde under our reaction conditions (Table 6, entries 7 and 8, respectively).

In accord with the results shown in Table 4, we obtained MBH-type adducts stereoselectively as the cis-isomer (as determined by 2D NOESY NMR, Table 4, entry 2) when the reaction was carried out between electron-deficient aldehydes and substituted terminally silylated alkynes (Table 7). Here the product yields ranged from modest (65%) to moderate (74%).

A rationale for the selectivity in the formation of the two different types of products we observed can be given by using a combination of mechanisms for the two reactions[11] (Scheme 2). After activation of the silyl group of **2** by proazaphosphatrane **1a** to form the activated pentacoordinated silicon species **A**, **A** dissociates to form the cationic intermediate **B** and the acetylide counteranion. To obtain some insight into this pathway, we carried out ^{29}Si NMR experiments at −40 °C in which we combined 1-trimethylsilyl-2-phenylacetylene (δ ^{29}Si NMR, −18.5 ppm in THF) with proazaphosphatrane **1a** in equimolar ratio in THF. A new ^{29}Si peak appeared at δ 7.17 ppm, which was attributed to the tetracoordinate silicon species **B** from which the acetylide anion had been displaced. This chemical shift accords with the previously reported value for a 1:1 mixture of TMSCN and **1d** in C_6D_6 (δ ^{29}Si 7.5 ppm) in which CN^- had presumably been displaced.[10c] If the anion had not been displaced in both cases, an upfield rather than a downfield shift from the parent TMSCN molecule would have been observed since the silicon would have become 5-coordinate.[10c]

(11) Yoshizawa, K.; Shioiri, T. *Tetrahedron Lett.* **2006**, *47*, 757–761.

SCHEME 2. Proposed Mechanism for the Alkynylation and MBH Reactions

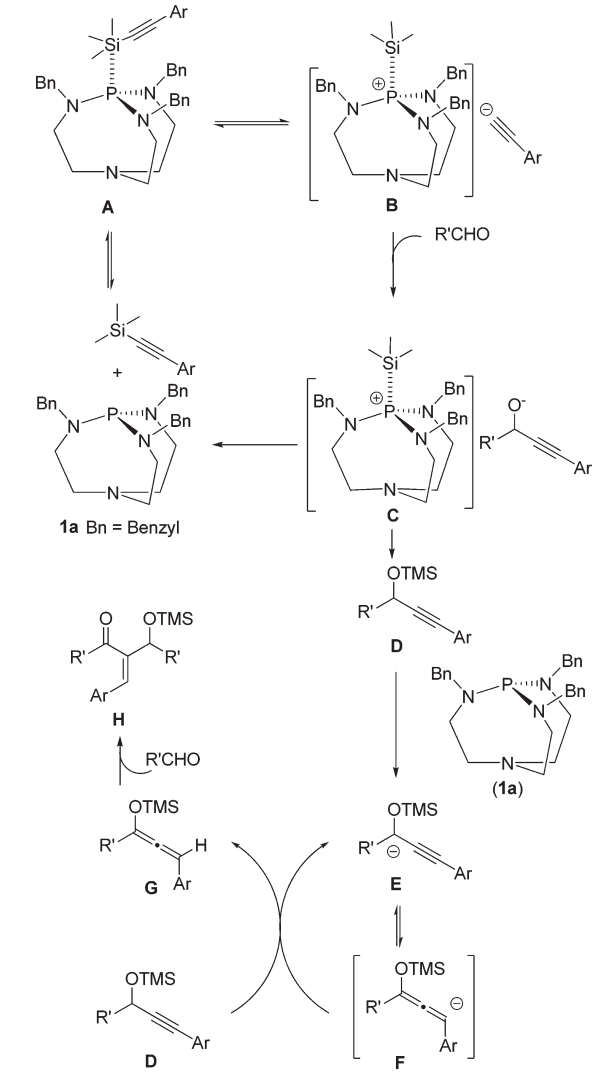
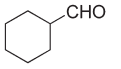
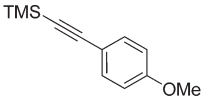
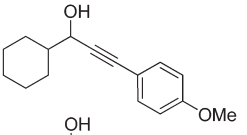
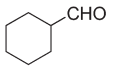
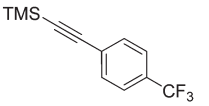
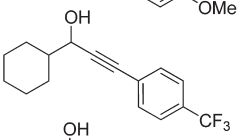
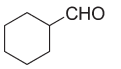
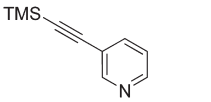
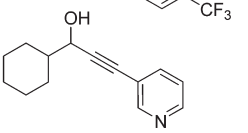
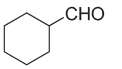
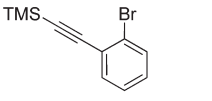
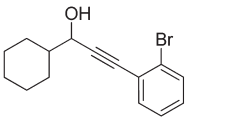
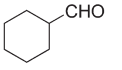
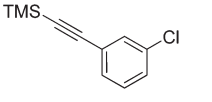
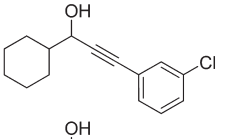
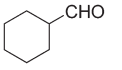
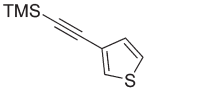
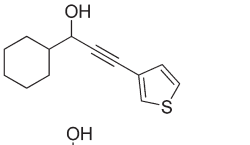
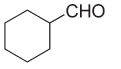
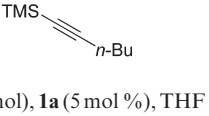
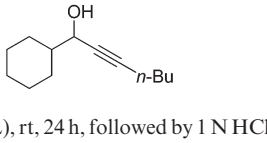


TABLE 5. Reactions of Cyclohexanecaboxaldehyde with Substituted 1-Trimethylsilylacetylenes, Using 1a as the Catalyst[a]

entry	aldehyde	alkyne	product	yield (%)[b]
1				92
2				84
3				88
4				86
5				84
6				91
7				nr[c]

[a]Reaction conditions: aldehyde (2.0 mmol), **2** (4.0 mmol), **1a** (5 mol %), THF (2 mL), rt, 24 h, followed by 1 N HCl (3 mL). [b]Isolated yield after column chromatography. [c]No reaction.

We used similar reasoning to account for the formation of both α- and γ-addition products in the reaction of crotyltrimethylsilane with aldehydes in the presence of **1b**.[10h] The acetylide ion in Scheme 2 then nucleophilically attacks the aldehyde to give the ionic intermediate **C**. Transfer of the silyl group to the alkoxide regenerates catalyst **1a** and the alkynylated product **D** is formed concomitantly. In the case of electron-deficient aldehydes, **D** can undergo a deprotonation step to form intermediate **E**, followed by rearrangement of **E** to give the allenic anion **F**. Anion **F** could abstract a proton from **D** to generate **E** and give allene **G**, which has been previously isolated as a crude product and which, after addition of an aldehyde, produced **H**, which in turn was converted to the MBH-type adduct upon acid hydrolysis.[11]

Conclusion

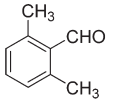
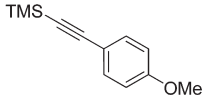
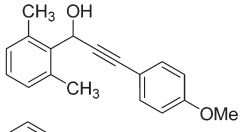
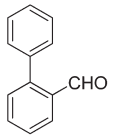
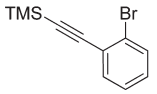
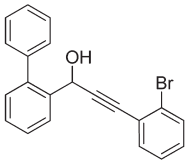
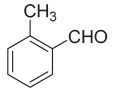
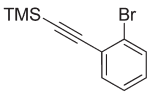
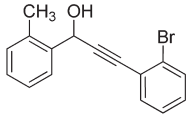
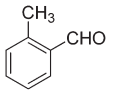
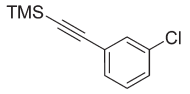
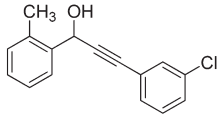
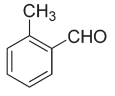
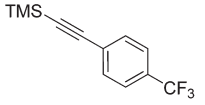
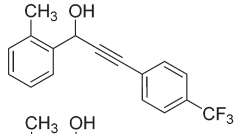
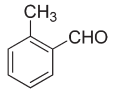
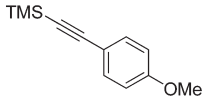
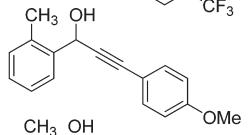
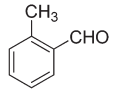
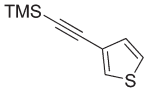
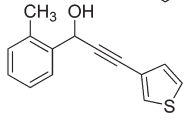
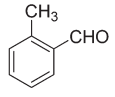
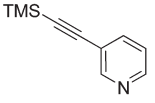
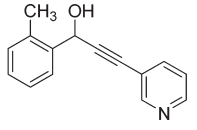
We have found that the nonionic Lewis basic proazaphosphatrane **1a** is an efficient catalyst for addition of 1-aryl-2-(trimethylsilyl)acetylenes to aldehydes at room temperature. The selectivity of this reaction for the synthesis of propargylic alcohols is facilitated by electron-rich, electron-neutral, heterocyclic, and aliphatic aldehydes, whereas MBH-type adducts are isolated when electron-deficient aldehydes are employed, regardless of the substituents on the propargylic alcohol and despite the use of excess alkyne. Attempts to maximize yields of MBH-type adducts by using a ratio of 0.5 equiv of alkyne to aldehyde and by increasing the catalyst loading to 10 mol % resulted in a 1:1 ratio of alkynylation to MBH product. We believe our protocol will find many applications in organic syntheses, including the synthesis of a variety of useful polyfunctional aromatics. The use of low metal-free catalyst loading (ca. 5 mol %), the high isolated product yields, the broad scope, and room temperature reaction conditions are attractive features of this protocol.

Experimental Section

General Procedure for Alkynylation and MBH Reactions. A flat-bottomed screw-capped vial was charged with proazaphosphatrane catalyst **1a** (44.4 mg, 0.1 mmol, 5 mol %) in a nitrogen-filled glovebox. To the vial was added, at room temperature, 2.0 mL of anhydrous THF, followed by the addition of aldehyde (2.0 mmol). The resulting solution was stirred at room temperature for 15 min and then aryl(trimethylsilyl)acetylene (4.0 mmol) was added over a period of 2 min. Progress of the reaction was monitored by TLC. The reaction mixture was stirred for 24 h and quenched with 3 mL of an aq solution of HCl (1 N). The mixture was stirred for an additional 1 h and then neutralized with saturated aq $NaHCO_3$ solution. The crude product was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic extracts were dried over anhydrous $MgSO_4$ (ca. 2.0 g). The crude product was purified by column chromatography with 30% EtOAc/hexane as eluent.

1-(2,6-Dimethylphenyl)-3-phenylprop-2-yn-1-ol (Table 2, entry 7). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was

TABLE 6. Reactions of Electron-Rich Aromatic Aldehydes with Variously Substituted 1-Trimethylsilylacetylenes, Using 1a as Catalyst[a]

entry	aldehyde	alkyne	product	yield (%)[b]
1				92
2				81
3				78
4				72
5				83
6				86
7				67
8				88

[a]Reaction conditions: aldehyde (2.0 mmol), **2** (4.0 mmol), **1a** (5 mol %), THF (2 mL), rt, 24 h, followed by 1 N HCl (3 mL). [b]Isolated yield after column chromatography.

afforded as a colorless oil in 96% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49−7.46 (m, 2H), 7.34−7.33 (m, 3H), 7.16−7.15 (m, 1H), 7.09−7.08 (m, 2H), 6.16 (s, 1H), 2.62 (s, 6H), 2.52 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 136.9, 136.6, 131.9, 129.5, 128.7, 128.5, 128.4, 123.0, 88.9, 86.1, 61.1, 20.8 ppm; HRMS *m*/*z* calcd for $C_{17}H_{16}O$ 236.12011, found 236.12053.

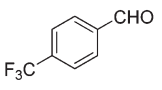
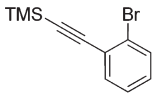
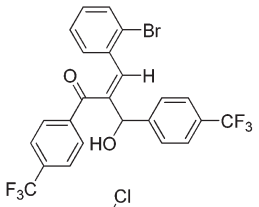
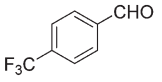
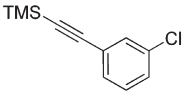
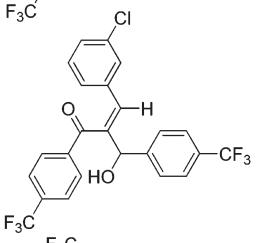
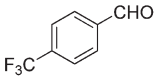
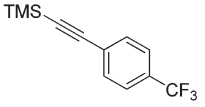
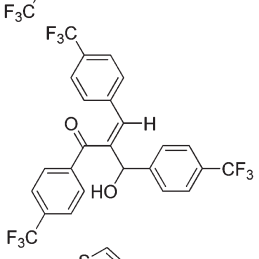
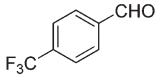
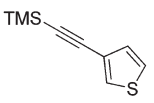
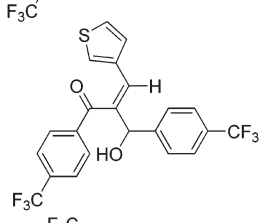
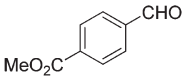
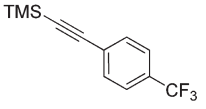
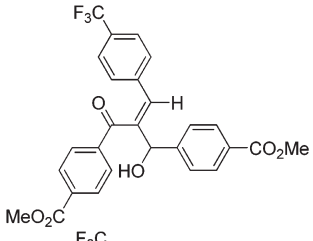
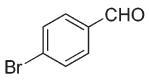
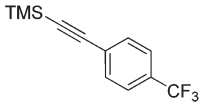
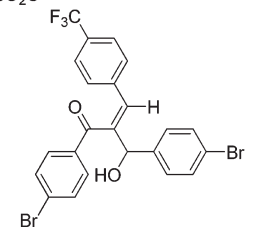
1-Phenyltridec-12-en-1-yn-3-ol (Table 3, entry 4). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 79% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44−7.42 (m, 2H), 7.31−7.30 (m, 3H), 5.86−5.76 (m, 1H), 5.01−4.91 (m, 2H), 4.59 (q, 1H, J = 4.0 Hz), 2.03 (q, 2H, J = 8.0 Hz), 1.85 (d, 1H, J = 4.0 Hz), 1.81−1.77 (m, 2H), 1.52−1.30 (m, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 139.4, 131.9, 128.6, 128.5, 122.9, 114.3, 90.4, 85.1, 63.3, 38.1, 34.1, 29.7, 29.6, 29.5, 29.4, 29.2, 25.5 ppm; HRMS *m*/*z* calcd for $C_{19}H_{26}O$ 270.19835, found 270.19875.

(*Z*)-2-(Hydroxy(4-(methoxycabonyl)phenyl)methyl)-3-phenyl-1-(4-(methoxycarbonyl)phenyl)prop-2-en-1-one (Table 4, entry 1). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 85% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, 2H, J = 8.0 Hz), 7.76 (d, 2H, J = 8.0 Hz), 7.61 (d, 2H, J = 8.0 Hz), 7.50 (d, 2H, J = 8.0 Hz), 7.07 (s, 1H), 7.03 (s, 4H), 5.81 (s, 1H), 3.94 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 199.8, 166.9, 166.3 146.2, 141.1, 139.5, 134.7, 133.9, 133.9, 130.1, 129.9, 129.6, 129.3, 129.2, 128.9, 128.5, 126.6, 76.6, 52.6, 52.4 ppm; HRMS *m*/*z* calcd for $C_{26}H_{22}O_2$ 430.14164, found 430.14262.

(*Z*)-2-(Hydroxy(3-iodophenyl)methyl)-1-(3-iodophenyl)-3-phenylprop-2-en-1-one (Table 4, entry 2). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 78% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (s, 1H), 7.78 (s, 1H), 7.60 (d, 1H, J = 8.0 Hz), 7.56−7.51 (m, 2H), 7.35 (d, 1H, J = 8.0 Hz), 7.08−7.00 (m, 7H), 6.86 (t, 1H, J = 8.0 Hz), 5.64 (s, 1H), 3.40 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 198.8, 143.3, 142.1, 140.9, 138.4, 137.8, 137.3, 135.6, 134.7, 133.6, 130.5, 130.1, 129.2, 128.8, 128.8, 128.5, 126.0, 94.8, 94.2, 76.1 ppm; HRMS *m*/*z* calcd for $C_{22}H_{16}I_2O_2$ 565.92398, found 565.92536.

(*Z*)-2-(Hydroxy(4-(trifluoromethyl)phenyl)methyl)-3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (Table 4, entry 3). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 93% isolated yield. ^{1}H NMR (CD_3CN, 400 MHz)

TABLE 7. Reactions of Electron-Deficient Aldehydes with Substituted 1-Trimethylsilylacetylenes, Using 1a as Catalyst[a]

entry	aldehyde	alkyne	product	yield (%)[b]
1				68
2				74
3				72
4				68
5				73
6				65

[a]Reaction conditions: aldehyde (2.0 mmol), **2** (4.0 mmol), **1a** (5 mol %), THF (2 mL), rt, 24 h, followed by 1 N HCl (3 mL). [b]Isolated yield after column chromatography.

δ 7.83 (d, 2H, J = 8.0 Hz), 7.64 (s, 4H), 7.55 (d, 3H, J = 8.0 Hz), 7.18 (s, 1H), 7.13 (s, 4H), 5.79 (s, 1H), 4.26 (d, 1H, 4.0 Hz) ppm; ^{13}C NMR (CD_3CN, 100.6 MHz) δ 198.4, 146.6, 142.4, 139.7, 135.2, 133.4 (q, J = 32.0 Hz), 131.8, 131.7 (q, J = 32.0 Hz), 129.9, 129.0, 128.5, 127.6, 125.4 (q, J = 4.0 Hz), 125.3 (q, J = 4.0 Hz), 124.5 (q, J = 273.0 Hz), 123.9 (q, J = 270.0 Hz), 75.2 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4, −64.1 ppm; HRMS m/z calcd for $C_{24}H_{16}F_6O_2$ 450.10545, found 450.10641.

(*Z*)-1-(4-Bromophenyl)-2-((4-bromophenyl)(hydroxy)methyl)-3-phenylprop-2-en-1-one (Table 4, entry 4). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 79% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48−7.42 (m, 4H), 7.31−7.26 (m, 4H), 7.08−7.06 (m, 5H), 6.97 (s, 1H), 5.67 (s, 1H), 3.28 (d, 1H, J = 4.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 199.4, 141.1, 140.1, 134.9, 134.7, 133.2, 131.9, 131.8, 131.0, 129.2, 128.9, 128.8, 128.5, 128.4, 122.2, 76.4 ppm; HRMS m/z calcd for $C_{22}H_{16}Br_2O_2$ 469.95170, found 469.95310.

1-Cyclohexyl-3-(4-methoxyphenyl)prop-2-yn-1-ol (Table 5, entry 1). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 92% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, 1H, J = 8.0 Hz), 7.25−7.24 (m, 1H), 6.90−6.83 (m, 2H), 4.42 (d, 1H, J = 4.0 Hz), 3.85 (s, 3H), 2.47 (br s, 1H), 1.94−1.66 (m, 6H), 1.24−1.17 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 160.2, 133.8, 129.9, 120.6,

112.2, 110.8, 93.8, 82.0, 67.9, 56.0, 44.5, 28.9, 28.4, 26.7, 26.2 ppm; HRMS m/z calcd for $C_{16}H_{20}O_2$ 244.14632, found 244.14668.

1-Cyclohexyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol (Table 5, entry 2). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 84% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55−7.49 (m, 4H), 4.38 (d, 1H, J = 4.0 Hz), 2.37 (br s, 1H), 1.93−1.66 (m, 6H), 1.28−1.11 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 132.1, 130.2 (q, J = 30.2 Hz), 126.8, 125.4, 125.4, 125.3, 124.0 (q, J = 271.6 Hz), 92.0, 84.5, 67.8, 44.4, 28.9, 28.4, 26.6, 26.1 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.3 ppm; HRMS m/z calcd for $C_{16}H_{17}F_3O$ 282.12314, found 282.12345.

1-Cyclohexyl-3-(pyridin-3-yl)prop-2-yn-1-ol (Table 5, entry 3). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 88% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.73 (s, 1H), 8.49 (d, 1H, J = 4.0 Hz), 7.71 (d, 1H, J = 8.0 Hz), 7.26−7.22 (m, 1H), 4.37 (d, 1H, J = 4.0 Hz), 4.01 (br s, 1H), 1.91−1.66 (m, 6H), 1.28−1.11 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 152.2, 148.4, 139.1, 123.3, 120.5, 115.5, 94.0, 82.0, 67.5, 44.5, 28.9, 28.6, 26.6, 26.2, 26.1 ppm; HRMS m/z calcd for $C_{14}H_{17}NO$ 215.13101, found 215.13147.

3-(2-Bromophenyl)-1-cyclohexylprop-2-yn-1-ol (Table 5, entry 4). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 86% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, 1H, J = 8.0 Hz), 7.45 (d, 1H, J = 4.0 Hz), 7.23 (t, 1H, J = 8.0 Hz), 7.16 (t, 1H, J = 8.0 Hz), 4.44 (s, 1H), 2.30 (d, 1H, J = 4.0 Hz), 1.94−1.69 (m, 6H), 1.27−1.18 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 133.7, 132.6, 129.7, 127.2, 125.8, 125.1, 94.3, 84.3, 67.9, 44.5, 28.9, 28.3, 26.7, 26.2, 26.1 ppm; HRMS m/z calcd for $C_{15}H_{17}BrO$ 292.04627, found 292.04691.

3-(3-Chlorophenyl)-1-cyclohexylprop-2-yn-1-ol (Table 5, entry 5). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 84% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (s, 1H), 7.29−7.20 (m, 3H), 4.37 (s, 1H), 2.10 (s, 1H), 1.92−1.68 (m, 6H), 1.29−1.10 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 134.3, 131.7, 130.0, 129.7, 128.8, 124.7, 90.8, 84.5, 67.8, 44.5, 28.9, 28.5, 26.6, 26.1, 26.1 ppm; HRMS m/z calcd for $C_{15}H_{17}ClO$ 248.09679, found 248.09739.

1-Cyclohexyl-3-(thiophen-3-yl)prop-2-yn-1-ol (Table 5, entry 6). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 91% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24−7.19 (m, 2H), 6.97−6.94 (m, 1H), 4.38 (d, 1H, J = 8.0 Hz), 2.31 (s, 1H), 1.92−1.63 (m, 6H), 1.30−1.08 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 132.3, 127.1, 122.9, 93.5, 79.1, 68.0, 44.4, 28.9, 28.5, 26.6, 26.1 ppm; HRMS m/z calcd for $C_{13}H_{16}OS$ 220.09218, found 220.09246.

1-(2,6-Dimethylphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (Table 6, entry 1). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 92% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, 1H, J = 8.0 Hz), 7.28 (t, 1H, J = 8.0 Hz), 7.12−7.04 (m, 3H), 6.91−6.39 (m, 2H), 6.19 (s, 1H), 3.83 (s, 3H), 2.69 (s, 1H), 2.62 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 160.4, 137.1, 136.7, 133.8, 130.2, 129.4, 128.3, 120.6, 112.2, 110.9, 93.1, 82.4, 61.2, 55.9, 20.7 ppm; HRMS m/z calcd for $C_{18}H_{18}O_2$ 266.13067, found 266.13699.

1-(Biphenyl-2-yl)-3-(2-bromophenyl)prop-2-yn-1-ol (Table 6, entry 2). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 81% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, 1H, J = 8.0 Hz), 7.59 (d, 1H, J = 8.0 Hz), 7.51−7.40 (m, 8H), 7.34−7.17 (m, 3H), 5.74 (s, 1H), 2.47 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 141.2, 140.4, 138.2, 133.8, 132.6, 130.4, 129.9, 129.8, 128.5, 128.1, 127.7, 127.2, 125.9, 124.9, 94.5, 85.3, 62.5 ppm; HRMS m/z calcd for $C_{21}H_{15}BrO$ 362.03062, found 362.03139.

3-(2-Bromophenyl)-1-*o*-tolylprop-2-yn-1-ol (Table 6, entry 3). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow solid in 78% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84−7.81 (m, 1H), 7.59−7.48 (m, 2H), 7.28−7.16 (m, 5H), 5.88 (d, 1H, J = 4.0 Hz), 2.53 (s, 3H), 2.46 (d, 1H, J = 4.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 138.3, 136.3, 133.8, 132.6, 131.0, 129.9, 128.8, 127.2, 127.0, 126.5, 125.9, 124.9, 93.4, 85.3, 63.3, 19.3 ppm; HRMS m/z calcd for $C_{16}H_{13}BrO$ 300.01497, found 300.01572.

3-(3-Chlorophenyl)-1-*o*-tolylprop-2-yn-1-ol (Table 6, entry 4). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 72% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (t, 1H, J = 4.0 Hz), 7.45 (s, 1H), 7.34−7.20 (m, 6H), 5.82 (s, 1H), 2.49 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 138.3, 136.2, 134.4, 131.8, 131.1, 130.1, 129.8, 129.1, 128.8, 126.8, 126.5, 124.4, 90.1, 85.3, 63.1, 19.3 ppm; HRMS m/z calcd for $C_{16}H_{13}ClO$ 256.06549, found 256.06600.

1-*o*-Tolyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol (Table 6, entry 5). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a colorless oil in 83% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (t, 1H, J = 4.0 Hz), 7.59−7.54 (m, 4H), 7.29−7.21 (m, 3H), 5.84 (d, 1H, J = 4.0 Hz), 2.52 (d, 1H, J = 8.0 Hz), 2.50 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 138.2, 136.2, 132.4, 131.6, 130.5 (q, J = 33 Hz), 128.9, 126.8, 126.6, 125.5, 125.4, 121.3 (q, J = 270 Hz), 91.3, 85.3, 63.1, 19.2 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.26 ppm; HRMS m/z calcd for $C_{17}H_{13}F_3O$ 290.0906, found 290.0918.

3-(4-Methoxyphenyl)-1-*o*-tolylprop-2-yn-1-ol (Table 6, entry 6). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 86% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82−7.80 (m, 1H), 7.43 (d, 1H, J = 8.0 Hz), 7.32−7.21 (m, 4H), 6.92−6.85 (m, 2H), 5.87 (d, 1H, J = 4.0 Hz), 3.85 (s, 3H), 3.70 (d, 1H, J = 4.0 Hz), 2.51 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 160.4, 138.7, 136.4, 133.8, 130.9, 130.2, 128.5, 127.1, 126.4, 120.6, 110.9, 93.0, 83.1, 63.3, 56.0, 19.2 ppm; HRMS m/z calcd for $C_{17}H_{16}O_2$ 252.1148, found 252.1150.

3-(Thiophen-3-yl)-1-*o*-tolylprop-2-yn-1-ol (Table 6, entry 7). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 67% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (t, 1H, J = 4.0 Hz), 7.28−7.20 (m, 5H), 7.98 (t, 1H, J = 4.0 Hz), 5.85 (d, 1H, J = 8.0 Hz), 2.49 (s, 3H), 2.22 (d, 1H, J = 8.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 138.3, 136.2, 132.6, 131.1, 128.8, 127.6, 127.2, 126.8, 126.5, 122.6, 92.5, 80.1, 63.4, 19.3 ppm; HRMS m/z calcd for $C_{14}H_{12}OS$ 228.0605, found 228.0609.

3-(Pyridin-3-yl)-1-*o*-tolylprop-2-yn-1-ol (Table 6, entry 8). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow solid in 88% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.73 (s, 1H), 8.42 (d, 1H, J = 8.0 Hz), 7.71−7.69 (m, 2H), 7.26−7.20 (m, 4H), 5.84 (s, 1H), 5.35 (br s, 1H), 2.48 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 152.1, 148.4, 139.2, 138.7, 136.0, 130.9, 128.5, 126.7, 126.4, 123.4, 120.4, 93.7, 82.4, 62.5, 19.3 ppm; HRMS m/z calcd for $C_{15}H_{13}NO$ 223.0992, found 223.0997.

(*Z*)-3-(2-Bromophenyl)-2-(hydroxy(4-(trifluoromethyl)phenyl)-methyl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (Table 7, entry 1). The general reaction procedure described in the paper

was followed for the synthesis and purification; the product was afforded as a colorless oil in 68% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63−7.59 (m, 6H), 7.38−7.25 (m, 4H), 6.91 (br s, 3H), 5.89 (s, 1H), 3.33 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 198.3, 144.9, 142.3, 139.4, 135.5, 134.6, 134.2, 131.2, 130.6 (q, J = 32.0 Hz), 130.3, 129.3, 127.4, 127.0, 126.8 (q, J=270.0 Hz), 126.2 (q, J=272.0 Hz), 125.9, 124.8, 123.5, 76.5 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.0, −63.8 ppm; HRMS m/z calcd for $C_{24}H_{15}BrF_6O_2$ 528.01595, found 528.01759.

(*Z*)-3-(3-Chlorophenyl)-2-(hydroxy(4-(trifluoromethyl)phenyl)-methyl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (Table 7, entry 2). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a white solid in 74% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66−7.40 (m, 8H), 7.01−6.89 (m, 5H), 5.80 (s, 1H), 3.22 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 198.7, 144.5, 142.4, 138.7, 136.1, 134.8 (q, J=25.0 Hz), 134.4, 132.0, 130.7 (q, J = 32.0 Hz), 129.7, 129.4, 129.0, 128.8, 126.9, 126.8 (q, J = 290 Hz), 126.6 (q, J = 320 Hz), 125.7, 125. 4, 75.8 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.1, −63.8 ppm; HRMS m/z calcd for $C_{24}H_{15}ClF_6O_2$ 484.0644, found 484.0665.

(*Z*)-2-(Hydroxy(4-(trifluoromethyl)phenyl)methyl)-1,3-bis(4-(trifluoromethyl)phenyl)prop-2-en-1-one (Table 7, entry 3). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 72% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, 2H, J = 8.0 Hz), 7.60−7.53 (m, 4H), 7.41 (d, 2H, J = 8.0 Hz), 7.33 (d, 2H, J=8.0 Hz), 7.16 (d, 2H, J=8.0 Hz), 7.04 (s, 1H), 5.84 (d, 1H, J=4.0 Hz), 3.18 (d, 1H, J=4.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 198.5, 144.5, 143.6, 138.9, 138.1, 134.9 (q, J=32.0 Hz), 131.7, 130.7 (q, J=32.0 Hz), 130.7 (q, J= 32.0 Hz), 129.6, 129.3, 127.1, 125.8, 125.4, 125.3, 124.1 (q, J = 271.0 Hz), 123.8 (q, J=271.0 Hz), 123.4 (q, J=271.0 Hz), 75.9 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.1, −63.5, −63.9 ppm; HRMS m/z calcd for $C_{25}H_{15}F_9O_2$ 518.09283, found 518.09409.

(*Z*)-2-(Hydroxy(4-(trifluoromethyl)phenyl)methyl)-3-(thiophen-3-yl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (Table 7, entry 4). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a green oil in 68% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, 2H, J = 8.0 Hz), 7.58−7.53 (m, 6H), 7.15 (d, 1H, J=8.0 Hz), 7.00 (s, 1H), 6.84−6.79 (m, 2H), 5.75 (d, 1H, J = 4.0 Hz), 3.06 (d, 1H, J = 4.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 198.5, 144.7, 139.3, 138.9, 137.1, 134.9 (q, J = 33.0 Hz), 130.8 (q, J = 33.0 Hz), 130.4, 129.8, 128.6, 128.1, 127.0, 125.7, 125.3, 124.1 (q, J = 270.0 Hz), 123.6 (q, J = 271.0 Hz), 76.2 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.7, −65.4 ppm; HRMS m/z calcd for $C_{22}H_{14}F_6O_2S$ 456.06186, found 456.06315.

(*Z*)-1-(4-(Methoxycarbonyl)phenyl)-2-((4-(methoxycarbonyl)-phenyl)(hydroxy)methyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (Table 7, entry 5). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 73% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, 2H, J = 8.0 Hz), 7.80 (d, 2H, J = 8.0 Hz), 7.63 (d, 2H, J = 8.0 Hz), 7.50 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J=8.0 Hz), 7.15 (d, 2H, J=8.0 Hz), 7.03 (s, 1H), 5.84 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.35 (d, 1H, J = 4.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 198.9, 166.8, 166.1, 145.6, 143.8, 139.1, 134.4, 130.9, 130.3, 130.1 (q, J = 33.0 Hz), 129.8, 129.2, 126.7, 125.5, 124.4, 123.8 (q, J=263.0 Hz), 76.2, 55.6, 52.4 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.3 ppm; HRMS m/z calcd for $C_{27}H_{21}F_3O_6$ 498.12902, found 498.13023.

(*Z*)-1-(4-Bromophenyl)-2-((4-bromophenyl)(hydroxy)methyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (Table 7, entry 6). The general reaction procedure described in the paper was followed for the synthesis and purification; the product was afforded as a yellow oil in 65% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49−7.44 (m, 4H), 7.34−7.26 (m, 6H), 7.16 (d, 2H, J=8.0 Hz), 6.94 (s, 1H), 5.69 (d, 1H, J=4.0 Hz), 3.08 (d, 1H, J= 4.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 198.5, 143.8, 139.6, 138.3, 134.7, 132.2, 132.1, 132.0, 130.9, 130.4, 129.3, 128.5, 125.5, 123.9 (q, J = 267 Hz), 122.5, 76.0 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.2 ppm; HRMS m/z calcd for $C_{23}H_{15}Br_2F_3O_2$ 537.9358, found 537.9391.

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Supporting Information Available: Complete experimental details, references to the known compounds, complete characterization of unknown compounds, copies of ^{1}H and ^{13}C NMR spectra for all alkynylation, MBH products, and HRMS reports for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.