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Taming Brønsted Acid Reactivity: Nucleophilic Substitutions of Propargylic Alcohols with N-Nucleophiles Mediated by Phosphorus-Based Brønsted Acid Catalysts

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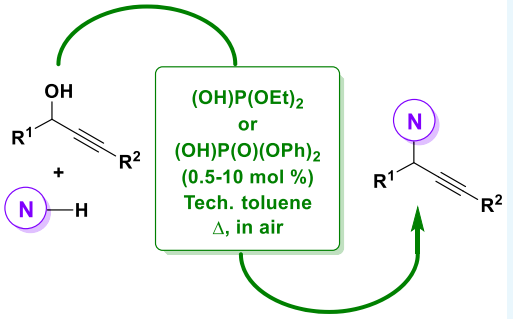
Supporting Information

ABSTRACT: The activity of diethyl phosphite and diphenyl phosphate in propargylation reactions with N-nucleophiles of varying basicity is presented. A careful choice of the reaction conditions minimized undesired rearrangements and arylation processes, typical side reactions with Brønsted acid catalysis. These systems are compatible with technical solvents and presence of air, and they are also applicable to C-, O-, and S-nucleophiles.



INTRODUCTION

Significant effort has been placed in the development of efficient direct nucleophilic substitution of alcohols, particularly allylic ones, even before it was identified by the ACS Green Chemistry Institute Pharmaceutical Roundtable as a priority area in the preparation of pharmaceutical intermediates.[1] The transformation of propargylic alcohols is of particular interest because of their synthetic versatility, and, accordingly, a range of transition-metal and acid catalysts have been reported for this purpose.[2] Brønsted acids are especially promising in terms of cost, oxygen, and moisture stability, and they are also very easy to separate from the desired organic products.[3]

Sulfonic acids[4] and phosphomolybdic acid on silica[5] have been used with a wide range of C-, N-, and O-nucleophiles in S_N1 reactions of propargylic alcohols, and we similarly reported the use of aqueous HBF_4.[6] These catalysts are compatible with air and reagent-grade solvents, but they are obviously limited by the basicity of the chosen nucleophile. Every system has to be optimized to avoid competitive Meyer−Schuster and Rupe rearrangements.[7−9] Furthermore, Friedel−Crafts reactions are notoriously competitive for electron-rich aromatic nucleophiles, such as anilines. Accordingly, only anilines with electron-withdrawing groups are suitable substrates with the reported systems[10] as even catalysts of modest acidity can mediate these arylations.[11]

RESULTS AND DISCUSSION

Surprisingly, phosphorus-containing acids have not been explored in these substitution reactions despite their range of pK_a[12] and versatile reactivity. Hence, we started by screening a selection of phosphorus-based acids in hot cumene with alcohol **1a** and 4-methylaniline **2a** as the model substrates in air (Table 1). Complete conversion into propargylic amine **3aa** was observed with phosphinic acid, but phosphonic and phosphoric acids led to no or very low conversions (Table 1, entries 1−3).

Diphenyl phosphate led to high conversions to **3aa**, with only 1 mol % acid loading to minimize decomposition (Table 1, entry 4), and so did diphenyl and diethyl phosphites (Table 1, entries 5−6), even if their tautomeric equilibria are expected to be displaced toward their phosphonate form.[13] Triphenyl and triethyl phosphites were both acceptable catalysts for the model reaction (Table 1, entries 7 and 8), as they generate in situ the corresponding $(HO)P(OR)_2$ derivatives. Indeed, when triphenylphosphite was heated at 110 °C for 24 h in technical solvent, 11% of hydrolyzed diphenylphosphite was formed together with 2% of oxidized triphenylphosphate;[14] when water was added, all phosphite was converted into phosphonic acid (83%) and triphenylphosphate (17%).

With three promising candidates in hand, phosphinic acid, diethyl phosphite **A**, and diphenyl phosphate **B**, we then reduced the amount of nucleophile to 1.5 equiv, which only decreased the conversions with phosphinic acid (Table 1, entry 1), while lower temperatures significantly reduced the conversion into **3aa** with all catalysts. We chose catalyst **A** over **B** since it is more than 30 times cheaper.[15] Of note, while phosphate **B** was recovered at the end of these reactions, phosphite **A** completely hydrolyzed[16] into a previously reported anilinium phosphate salt,[17] which was catalytically

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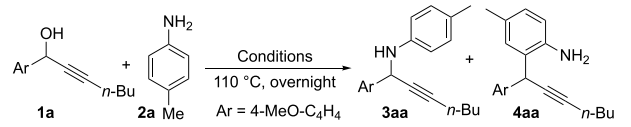
Table 1. Screening of Phosphorus-Based Acid Catalysts[a]



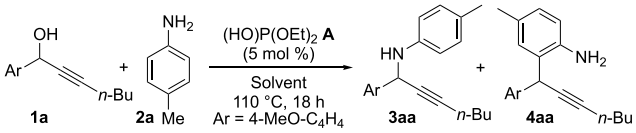
entry	catalyst	(mol %)	1a (%)[b]	3aa (%)[b]	4aa (%)[b]
1	$(HO)P(O)H_2$	10	<5	>95	<5
		10[c]	<5[c]	79[c]	13[c]
		5	<5	>95	<5
2	$(HO)_2P(O)H$	10	<95	<5	<5
3	$(HO)_3P(O)$	10	<95	<5	<5
4	$(HO)P(O)(OPh)_2$ **B**	10	<5	72	<5
		5	<5	72	<5
		1	14	83	<5
5	$(HO)P(OPh)_2$	10	<5	90	5
		5	31	62	<5
		1	70	26	<5
6	$(HO)P(OEt)_2$ **A**	10	<5	94	<5
		5	9	84	<5
		1	47	43	<5
7	$P(OPh)_3$	10	5	69	11
8	$P(OEt)_3$	10	<5	67	11

[a]Reaction conditions: **1a** (0.5 mmol) and **2a** (2 equiv) in technical cumene (0.5 mL). [b]^{1}H NMR yields/recoveries are the average of two independent experiments and were determined with respect to 1,3,5-trimethoxybenzene as internal standard. [c]1.5 equiv of **2a**.

inactive, as expected from the reactions with phosphonic acid (Table 1, entry 2).

Different solvents were then tested with phosphite **A** (Table 2). Identical results were obtained with cumene or toluene,

Table 2. Solvent Screening with $(HO)P(OEt)_2$ A[a]



entry	solvent	1a (%)[b]	3aa (%)[b]	4aa (%)[b]
1	cumene	9	84	<5
2	toluene	9	85	<5
3	dioxane	14	77	<5
4	2-Me-THF	18	74	<5
5	benzonitrile	<5	46	7
6	iPrOH	>95	no reaction	no reaction

[a]Reaction conditions: **1a** (0.5 mmol) and **2a** (1.5 equiv) in technical solvent (0.5 mL). [b]^{1}H NMR yields/recoveries are the average of two independent experiments and were determined with respect to 1,3,5-trimethoxybenzene as internal standard.

while ether solvents led to relatively lower conversions (Table 2, entries 1−4). Only 46% conversion into **3aa** was obtained in benzonitrile, while no reaction was observed in isopropanol (Table 2, entries 5 and 6). No chlorinated solvents were screened due to their significant environmental and health hazards.

When varying the nucleophiles, the conditions often had to be adapted, either because they reacted under milder conditions or to minimize the decomposition and/or formation of undesired byproducts. Unsurprisingly, anilines bearing electron-withdrawing groups readily reacted with only 1 mol % **A** (Table 3, entries 1 and 2), and higher loading led to the formation of an enone derived from of a Meyer−Schuster rearrangement.

The conditions originally optimized with *p*-toluidine led to the preferential formation of Friedel−Crafts products with *o*-toluidine, but **3ad** was the major product when lower catalyst loadings and longer reaction times were employed (Table 3, entry 3). Lower reaction temperatures also minimized the formation of arylated byproducts but at the expense of the overall conversion.

The reaction with *p*-anisidine suffered from incomplete conversions of the starting alcohol **1a**, but higher acid loadings or reaction temperatures only led to similar conversions into **3ag** and increased decomposition. Instead, longer reaction times helped to increase the reaction conversions and **3ag** was formed in 65, 75, and 87% NMR yield after 18, 24, and 48 h, respectively (Table 3, entry 7).

Secondary anilines were also screened with lower acid loadings to either prevent the formation of an undesired enone (**2h**, Table 3, entry 8) or a Friedel−Craft arylation product (**2i**, Table 3, entry 9). The reaction of **1a** and benzyl amine only led to traces of the substitution product. We then tested Brønsted acids previously reported for propargylation reactions with primary amines, but again only traces of the desired product were obtained with either phosphomolybdic acid on silica (together with unreacted starting materials)[5a] or *p*-nitrobenzenesulfonic acid (together with decomposition).[18]

Excellent results were obtained with either benzamide or thiobenzamide (Table 3, entries 10 and 11). Meyer−Schuster rearrangement was competitive in the reactions with benzamide **2j**, which was minimized by lowering the reaction temperature, or alternatively, using phosphate catalyst **B**, which selectively formed amide **3aj**. In contrast, the reaction with thiobenzamide was completely selective with diethylphosphite **A**, even when higher acid loadings were used.

Different alcohols were successfully reacted with *p*-cyanoaniline, starting with those with different acetylenic substituents (Table 4, entries 1 and 2). A lower acid loading was used with mesityl-substituted alcohol **1d** to minimize an undesired Meyer−Schuster rearrangement product (Table 4, entry 3). We also observed that electron-rich aromatics were not required for the substitution reaction to proceed (Table 4, entries 4 and 5), although no reaction was observed without an aromatic group at the propargylic position.

Interestingly, an allylic alcohol was also a good substrate for our catalytic systems (Scheme 1), although we only obtained very low conversions (<20%) with *p*-anisyl alcohol or benzhydryl alcohol as the starting material.

Finally, to further showcase the potential of catalysts **A** and **B**, we reacted three typical O-, C-, and S-nucleophiles with propargylic alcohol **1a** (Table 5). Excellent results were obtained under relatively mild conditions with indole, benzyl alcohol, and benzyl mercaptan, particularly, with acid **B**. Allylic alcohol **1g** also reacted readily with a S-nucleophile (Scheme 2).

CONCLUSIONS

We have developed two catalytic systems based on the readily available Brønsted acids for nucleophilic substitution reactions of propargylic alcohols with N-nucleophiles of increasing basicity. Allylic alcohols as well as O-, S-, and C-nucleophiles were also suitable substrates under the reported conditions,

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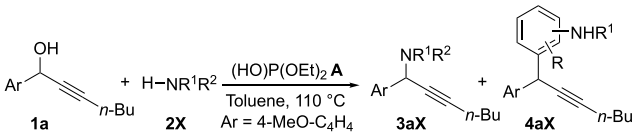
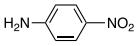
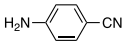
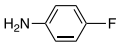
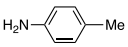
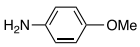
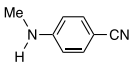
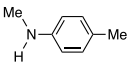
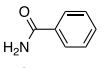
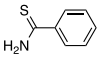
Table 3. N-Nucleophile Scope[a]



Entry	Aniline		Conditions	1a (%)[b]	3aX (%)[b,c]	4aX (%)[b]
1		**2b**	1 mol % **A**, 18 h	<5	>95 (84)	<5
2		**2c**	1 mol % **A**, 18 h	<5	>95 (88)	<5
3		**2d**	1 mol % **A**, 24 h	14	69 (56)	11
4		**2e**	10 mol % **A**, 18 h	<5	>95 (88)	<5
5		**2f**	10 mol % **A**, 18 h	<5	85 (77)	10
6		**2a**	10 mol % **A**, 18 h	<5	>95 (90)	<5
7		**2g**	10 mol % **A**, 24 h	14	75 (57)	6
8		**2h**	1 mol % **A**, 18 h	10	90 (70)	--
9		**2i**	5 mol % **A**, 18 h 2.5 mol % **A**, 18 h	<5 15	65 (47) 69	21 16
10[d]		**2j**	10 mol % **A**, 24 h 5 mol % **B**, 24 h	<5 <5	91 (78) >95 (90)	--
11		**2k**	1 mol % **A**, 18 h	<5	>95 (90)	--

[a]Reaction conditions: **1a** (2 mmol) and **2X** (1.5 equiv) in technical toluene (2 mL). [b]^{1}H NMR yields/recoveries are the average of two independent experiments and were determined with respect to 1,3,5-trimethoxybenzene as internal standard. [c]Isolated yields are provided in brackets. [d]90 °C.

and all reactions were carried out in technical solvents and in the presence of air.

EXPERIMENTAL SECTION

General Remarks. All reactions were carried out in air using technical solvents without any particular precautions to exclude moisture or oxygen. Commercially available reagents were used as received. $(HO)P(OEt)_2$ **A** and $(HO)P(O)(OPh)_2$ **B** were purchased from Sigma-Aldrich with 98 and 99% purities, respectively. Propargylic alcohols **1a**,[6] **1b**,[6] **1c**,[6] **1d**,[6] **1e**,[19] and **1f**[16] were prepared according to the literature procedures. Column chromatography and thin-layer chromatography were performed on silica gel (Kieselgel 60), using UV light and a phosphomolybdic acid dip to visualize the products. Basified silica was prepared by submerging silica gel into petroleum ether containing 2% v/v NEt_3 overnight. Melting point ranges were determined on an Electrothermal Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded in reciprocal centimetres (cm^{-1}) using a Fourier transform-infrared attenuated total reflection spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AVANCE 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 377 MHz) at 23 °C. The chemical shifts, δ, are given in ppm relatively to tetramethylsilane (0.00 ppm), $CDCl_3$ (77.0 ppm), benzotrifluoride (−63.72 ppm), or solvent residual peak. The multiplicity is given in br, s, d, t, and m for broad, singlet, doublet, triplet, and multiplet, respectively. High-resolution mass spectra were recorded on either a Micromass Autospec Premier, Micromass LCT Premier or a VG Platform II spectrometer using ESI techniques at the Mass Spectroscopy Service of Imperial College London.

General Procedure. The chosen nucleophile (1.5 equiv) was added to a solution of propargylic alcohol **1** (1.0 equiv) and $(HO)P(OEt)_2$ **A** or $(HO)P(O)(OPh)_2$ **B** in technical toluene (1 M). The reaction mixture was stirred at 110 °C on a heating block for 18 h before being cooled to room temperature and concentrated under reduced pressure. The residue was then purified by column chromatography (basified silica gel, eluent was basified with 2% v/v NEt_3).

*N-[1-(4-Methylaniline)hept-2-yn-1-yl]-4-methoxybenzene (**3aa**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and 4-toluidine (0.321 g, 3 mmol) with $(HO)P(OEt)_2$ **A** (26.0 μL, 10 mol %), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 97:3) as a yellow oil (0.549 g, 90%). R_f = 0.67 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.64 (d, J = 8.0 Hz, 2H), 5.15 (br s, 1H), 3.86 (br s, 1H), 3.80 (s, 3H), 2.24 (s, 3H), 2.21 (td, J = 7.0; 2.0 Hz, 2H), 1.51−1.43 (m, 2H), 1.41−1.31 (m, 2H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 159.1, 144.5, 132.7, 129.5, 128.3, 127.4, 114.2, 113.9, 85.2, 79.6, 55.2, 49.9, 30.7, 21.8, 20.4, 18.4, 13.5; IR: ν_{max} 3397 (NH), 2226 (C≡C); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{26}NO$ 308.2009; found 308.1987.

*N-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]-4-nitroaniline (**3ab**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and 4-nitroaniline (0.414 g, 3 mmol) with $(HO)P(OEt)_2$ **A** (2.5 μL, 1 mol %), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 9:1) as a

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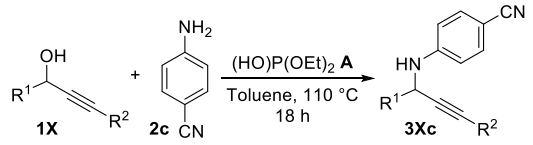
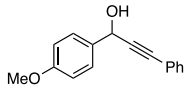
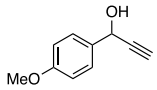
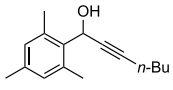
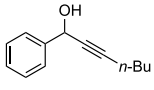
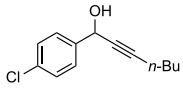
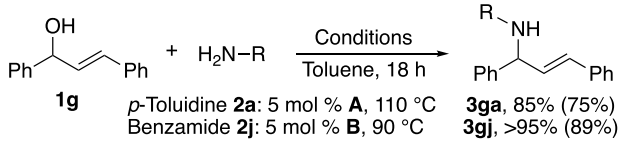
Table 4. Propargylic Alcohols Scope with (HO)P(OEt)$_2$ A[a]



Entry	Propargylic alcohol		A (mol %)	1X (%)[b]	3Xc (%)[b,c]
1		**1b**	1	6	87 (87)
2		**1c**	10	7	82 (70)
3[d]		**1d**	0.5	<5	80 (85)
4		**1e**	5	<5	73 (57)
5		**1f**	10	<5	62 (52)

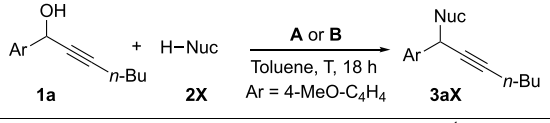
[a]Reaction conditions: **1a** (2 mmol) and **2X** (1.5 equiv) in technical toluene (2 mL). [b]^{1}H NMR yields/recoveries are the average of two independent experiments and were determined with respect to 1,3,5-trimethoxybenzene as internal standard. [c]Isolated yields are provided in brackets. [d]12% of the corresponding enone was also formed in this reaction according to the ^{1}H NMR.

Scheme 1. Reactions with an Allylic Alcohol[a,b,c]



[a]Reaction conditions: **1g** (2 mmol) and **2X** (1.5 equiv) in technical toluene (2 mL). [b]^{1}H NMR yields/recoveries are the average of two independent experiments and were determined with respect to 1,3,5-trimethoxybenzene as internal standard. [c]Isolated yields are provided in brackets.

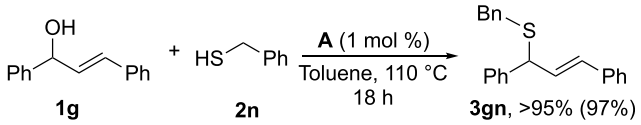
Table 5. Further Nucleophile Scope[a]



Entry	H-Nuc		Conditions	1a (%)[b]	3aX (%)[b,c]
1		**2l**	5 mol % **A**, 90 °C	<5	95
			1 mol % **B**, RT	<5	>95 (73)
2		**2m**	5 mol % **A**, 90 °C	<5	>95
			1 mol % **B**, 40 °C	<5	>95 (93)
3		**2n**	5 mol % **A**, 90 °C	<5	>95
			1 mol % **B**, 40 °C	<5	>95 (83)

[a]Reaction conditions: **1g** (2 mmol) and **2X** (1.5 equiv) in technical toluene (2 mL). [b]^{1}H NMR yields/recoveries are the average of two independent experiments and were determined with respect to 1,3,5-trimethoxybenzene as internal standard. [c]Isolated yields are provided in brackets.

Scheme 2. Synthesis of 3gn[a,b,c]



[a]Reaction conditions: **1g** (2 mmol) and **2n** (1.5 equiv) in technical toluene (2 mL). [b]^{1}H NMR yield is the average of two independent experiments and was determined with respect to 1,3,5-trimethoxybenzene as internal standard. [c]Isolated yield is provided in brackets.

yellow solid (0.570 g, 84%). Mp = 113−115 °C; R_f = 0.33 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (d, J = 9.0 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 9.0 Hz, 2H), 5.29 (d, J = 6.5 Hz, 1H), 4.78 (d, J = 6.5 Hz, 1H), 3.82 (s, 3H), 2.23 (td, J = 7.0; 2.0 Hz, 2H), 1.52−1.45 (m, 2H), 1.42−1.33 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 159.6, 151.5, 138.7, 130.7, 128.4, 126.0, 114.2, 112.2, 86.5, 77.6, 55.3, 49.3, 30.8, 22.1, 18.5, 13.7; IR: ν_{max} 3401 (NH), 2227 (C≡C) 1905 (N=O); HRMS (ESI) m/z: [M − H]$^-$ Calcd for $C_{20}H_{21}N_2O_3$ 337.1552; found 337.1564.

*4-[(1-(4-Methoxyphenyl)hept-2-yn-1-yl)amino]-benzonitrile (**3ac**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and 4-cyanoaniline (0.354 g, 3 mmol) with (HO)P(OEt)$_2$ **A** (2.5 μL, 1 mol %), the title compound was isolated by column chromatography (petroleum ether → petroleum ether/EtOAc, 4:1 gradient) as a bright yellow oil (0.559 g, 88%). R_f = 0.33 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H) 6.67 (d, J = 9.0 Hz, 2H), 5.23 (d, J = 6.5 Hz, 1H), 4.49 (d, J = 6.5 Hz, 1H), 3.82 (s, 3H), 2.23 (td, J = 7.0; 2.0 Hz, 2H), 1.52−1.44 (m, 2H), 1.41−1.32 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 159.5, 149.6, 133.4, 131.0, 128.3, 120.2, 114.1, 113.3, 99.8, 86.2, 78.0, 55.3, 48.9, 30.6, 21.8, 18.3, 13.5; IR: ν_{max} 3355 (NH), 2213 (C≡N), 2159 (C≡C); HRMS (ESI) m/z: [M − H]$^-$ Calcd for $C_{21}H_{23}N_2O$ 319.1810; found 319.1809.

*N-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]-2-methylaniline (**3ad**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and 2-methylaniline (0.319 mL, 3 mmol) with (HO)P(OEt)$_2$ **A** (2.5 μL, 1 mol %) for 24 h, the title compound was isolated by column chromatography (petroleum ether) as an orange oil (0.343 g, 56%). R_f = 0.74 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, J = 8.5 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 7.0 Hz, 1H), 6.91 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.0 Hz, 1H), 6.71 (t, J = 7.5 Hz, 1H), 5.22 (d, J = 6.0 Hz, 1H), 3.84 (s, 1H), 3.82 (s, 3H), 2.22 (td, J = 5.0; 2.0 Hz, 2H), 2.13 (s, 3H), 1.52−1.45 (m, 2H), 1.42−1.33 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 159.2, 144.8, 132.7, 130.0, 128.3, 126.8, 122.5, 117.8, 113.9, 111.6, 85.3, 79.6, 55.2, 49.5, 30.7, 21.9, 18.5, 17.6, 13.5; IR: ν_{max} 3407 (NH), 2227 (C≡C); HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{21}H_{26}NO$ 308.2014; found 308.2020.

*4-Fluoro-N-[1-(4-methoxyphenyl)hept-2-yn-1-yl]aniline (**3ae**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and 4-fluoroaniline (0.378 mL, 3 mmol) with (HO)P(OEt)$_2$ **A** (26.0 μL, 10 mol %), the title compound was isolated by column (petroleum ether/EtOAc, 95:5) as an orange oil (0.548 g, 88%). R_f = 0.53 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 8.5 Hz, 2H),

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6.91−6.86 (m, 4H), 6.67 (d, J = 9.0 Hz, 1H), 6.65 (d, J = 9.0 Hz, 1H), 5.12 (s, 1H), 3.94 (s, 1H), 3.81 (s, 3H), 2.21 (t, J = 7.0 Hz, 2H), 1.50−1.43 (m, 2H), 1.40−1.31 (m, 2H), 0.87 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 159.2, 157.4 (d, $^1J_{FC}$ = 237 Hz), 143.1, 132.3, 128.4, 115.4 (d, $^2J_{FC}$ = 22 Hz), 155.2 (d, $^3J_{FC}$ = 7 Hz), 113.9, 85.6, 79.3, 55.2, 50.3, 30.7, 21.8, 18.4, 13.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −126.9 (s); IR: ν_{max} 3390 (NH), 2250 (C≡C); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}NOF$ 312.1764; found 312.1779.

*N-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]aniline (**3af**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and aniline (0.274 mL, 3 mmol) with $(HO)P(OEt)_2$ **A** (26.0 μL, 10 mol %) in technical toluene (4 mL), the title compound was isolated by column (petroleum ether/EtOAc, 95:5) as an orange oil (0.451 g, 77%). R_f = 0.60 (petroleum ether/EtOAc, 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, J = 8.5 Hz, 2H), 7.18 (t, J = 7.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.75 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 8.5 Hz, 2H), 5.19 (s, 1H), 3.98 (br s, 1H), 3.81 (s, 3H), 2.21 (td, J = 7.0; 2.0 Hz, 2H), 1.51−1.44 (m, 2H), 1.41−1.32 (m, 2H), 0.87 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 159.2, 146.7, 132.6, 129.0, 128.3, 118.2, 114.0, 113.9, 85.3, 79.4, 55.3, 49.6, 30.7, 21.8, 18.4, 13.5; IR: ν_{max} 3391 (NH), 2115 (C≡C); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}NO$ 294.1858; found 294.1854.

*4-Methoxy-N-[1-(4-methoxyphenyl)hept-2-yn-1-yl]aniline (**3ag**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and 4-methoxyaniline (0.370 g, 3 mmol) with $(HO)P(OEt)_2$ **A** (26.0 μL, 10 mol %) for 24 h, the title compound was isolated by column chromatography (petroleum ether) as a yellow oil (0.366 g, 57%). R_f = 0.43 (petroleum ether/EtOAc, 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 6.69 (d, J = 9.0 Hz, 2H), 5.11 (s, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.70 (br s, 1H), 2.20 (td, J = 7.0; 2.0 Hz, 2H), 1.50−1.43 (m, 2H), 1.40−1.31 (m, 2H), 0.87 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 159.1, 152.7, 141.0, 132.8, 128.3, 115.7, 114.6, 113.9, 85.4, 79.7, 55.7, 55.3, 50.7, 30.8, 21.8, 18.4, 13.5; IR: ν_{max} 3365 (NH), 2234 (C≡C); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{26}NO_2$ 324.1964; found 324.1961.

*4-[(1-(4-Methoxyphenyl)hept-2-yn-1-yl)amino]-benzonitrile (**3ah**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and 4-cyano-*N*-methylaniline (0.396 g, 3 mmol) with $(HO)P(OEt)_2$ **A** (2.5 μL, 1 mol %), the title compound was isolated by column chromatography (petroleum ether) as a white solid (0.464 g, 70%). Mp = 57−59 °C; R_f = 0.43 (petroleum ether/EtOAc, 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 8.87 (d, J = 9.0 Hz, 2H), 5.80 (s, 1H), 3.81 (s, 3H), 2.78 (s, 3H), 2.29 (td, J = 7.0; 2.0 Hz, 2H), 1.57−1.50 (m, 2H), 1.46−1.37 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 159.2, 152.2, 133.4, 129.6, 128.4, 120.3, 113.8, 113.0, 98.9, 87.4, 75.6, 55.2, 54.3, 33.5, 30.7, 21.9, 18.4, 13.5; IR: ν_{max} 2211 (C≡N), 2160 (C≡C); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}N_2O$ 333.1967; found 333.1969.

*N-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]-N-4-dimethylaniline (**3ai**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and *N*-methyl-4-toluidine (0.380 mL, 3 mmol) with $(HO)P(OEt)_2$ **A** (13.0 μL, 5 mol %), the title compound was isolated by column chromatography (petroleum ether → petroleum ether/EtOAc, 9:1 gradient) as a yellow oil (0.302 g, 47%). R_f = 0.81 (petroleum ether/EtOAc, 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 5.63 (s, 1H), 3.80 (s, 3H), 2.61 (s, 3H), 2.28 (s, 3H), 2.26 (td, J = 7.0; 2.0 Hz, 2H), 1.58−1.48 (m, 2H), 1.46−1.37 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 158.9, 148.3, 131.2, 129.5, 128.8, 127.8, 115.8, 113.4, 87.1, 78.3, 56.5, 55.2, 33.4, 31.0, 21.9, 20.3, 18.4, 13.5; IR: ν_{max} 2102 (C≡C); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{28}NO$ 322.2171; found 322.2185.

*N-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]benzamide (**3aj**).* Following the general procedure from **1a** (0.218 g, 1 mmol) and benzamide (0.182 g, 1.5 mmol) with $(HO)P(O)(OPh)_2$ **B** (12.5 mg, 5 mol %) at 90 °C, the title compound was isolated by column chromatography (petroleum ether → petroleum ether/EtOAc, 9:1 gradient) as a white solid (0.287 g, 90%). Mp = 95−97 °C. R_f = 0.32 (petroleum ether/EtOAc, 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 8.5 Hz, 2H), 7.51−7.39 (m, 5H), 6.88 (d, J = 8.5 Hz, 2H), 6.52 (d, J = 8.5 Hz, 1H), 6.15 (d, J = 8.5, 1H), 3.80 (s, 3H), 2.27 (td, J = 7.0; 2.0 Hz, 2H), 1.58−1.50 (m, 2H), 1.47−1.38 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 165.9, 159.2, 134.0, 131.8, 131.6, 128.5, 128.3, 127.0, 113.9, 85.6, 78.0, 55.3, 44.8, 30.7, 22.0, 18.4, 13.5; IR: ν_{max} 3291 (NH), 2227 (C≡C), 1895 (C═O); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}NO_2$ 322.1807; found 322.1791.

*N-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]benzothioamide (**3ak**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and thiobenzamide (0.411 g, 3 mmol) with $(HO)P(O)(OPh)_2$ **B** (2.5 μL, 1 mol %), the title compound was isolated by column chromatography (petroleum ether → petroleum ether/EtOAc, 98:2 gradient) as a brown oil (0.606 g, 90%). R_f = 0.71 (petroleum ether/EtOAc, 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 8.0 Hz, 2H), 7.41−7.35 (m, 3H) 7.19 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 4.05 (s, 2H), 3.77 (s, 3H), 2.76 (t, J = 7.5 Hz, 2H), 1.63−1.55 (m, 2H), 1.42−1.33 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 163.8, 157.9, 151.5, 134.1, 134.0, 131.9, 129.4, 129.3, 128.7, 126.1, 113.7, 55.2, 34.3, 34.0, 26.2, 22.2, 13.8; IR: ν_{max} 3063 (NH), 2224 (C≡C); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}NOS$ 338.1579; found 388.1568.

*4-[(1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-yl)amino]-benzonitrile (**3bc**).* Following the general procedure from **1b** (0.715 g, 3 mmol) and 4-cyanoaniline (0.532 g, 4.5 mmol) with $(HO)P(OEt)_2$ **A** (4.0 μL, 1 mol %) at 90 °C, the title compound was isolated by column chromatography (toluene) as a pale yellow solid (0.890 g, 88%). Mp = 92−94 °C. R_f = 0.26 (petroleum ether/EtOAc, 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 9.0 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H), 7.41 (dd, J = 8.0; 2.0 Hz, 2H), 7.33−7.30 (m, 3H), 6.95 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 9.0 Hz, 2H), 5.48 (d, J = 6.5 Hz, 1H), 4.59 (d, J = 6.5 Hz, 1H), 3.83 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 159.7, 149.5, 133.5, 131.7, 130.4, 128.6, 128.5, 128.3, 122.3, 120.1, 114.3, 113.4, 100.2, 87.0, 85.5, 55.3, 49.4; IR: ν_{max} 3330 (NH), 2214 (C≡N), 2050 (C≡C); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}N_2O$ 339.1497; found 339.1502.

*4-[(1-(4-Methoxyphenyl)prop-2-yn-1-yl)amino]-benzonitrile (**3cc**).* Following the general procedure from **1c** (0.486 g, 3 mmol) and 4-cyanoaniline (0.532 g, 4.5 mmol) with $(HO)P(OEt)_2$ **A** (4.0 μL, 10 mol %), the crude product was washed with cold petroleum ether/Et_2O (4:1, 100 mL)

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and then purified by column chromatography (toluene) to isolate the title compound as a pale brown solid (0.551 g, 70%). Mp = 150−153 °C; R_f = 0.25 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 6.70 (d, J = 9.0 Hz, 2H), 5.27 (dd, J = 6.5; 2.0 Hz, 1H), 4.49 (d, J = 6.5 Hz, 1H), 3.83 (s, 3H), 2.52 (d, J = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 159.8, 149.3, 133.5, 129.7, 128.4, 120.0, 114.3, 113.4, 100.4, 81.7, 73.6, 55.3, 48.6. The spectroscopic data for this compound are in accordance with the literature.[6]

*4-[(1-Mesitylhept-2-yn-1-yl)amino]benzonitrile (**3dc**).* Following the general procedure from **1d** (0.691 g, 3 mmol) and 4-cyanoaniline (0.532 g, 4.5 mmol) with (HO)P(OEt)$_2$ **A** (2.0 μL, 0.5 mol %), the title compound was isolated by column chromatography (petroleum ether → petroleum ether/EtOAc, 95:5 gradient) as a yellow oil (0.839 g, 85%). R_f = 0.63 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (d, J = 9.0 Hz, 2H), 6.88 (s, 2H), 6.65 (d, J = 9.0 Hz, 2H), 5.53 (dt, J = 4.5; 2.0 Hz, 1H), 4.42 (d, J = 4.5 Hz, 1H), 2.48 (s, 6H), 2.27 (s, 3H), 2.18 (td, J = 7.0; 2.0 Hz, 2H), 1.50−1.42 (m, 2H), 1.39−1.31 (m, 2H), 0.87 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 149.8, 137.7, 136.1, 133.5, 132.3, 130.3, 120.3, 112.7, 99.4, 85.5, 77.5, 45.1, 30.5, 21.9, 20.8, 20.5, 18.4, 13.5; IR: ν_{max} 3337 (NH), 2211 (C≡N), 2161 (C≡C); HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{23}H_{27}N_2$ 331.2174; found 331.2180.

*4-[(1-Phenylhept-2-yn-1-yl)amino]benzonitrile (**3ec**).* Following the general procedure from **1e** (0.376 g, 2 mmol) and 4-cyanoaniline (0.354 g, 3 mmol) with (HO)P(OEt)$_2$ **A** (13.0 μL, 5 mol %), the title compound was isolated by column (petroleum ether → petroleum ether/EtOAc, 9:1 gradient) as a yellow oil (0.329 g, 57%). R_f = 0.48 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 9.0 Hz, 2H), 7.44−7.32 (m, 5H), 6.67 (d, J = 9.0 Hz, 2H), 5.28 (d, J = 6.5 Hz, 1H), 4.58 (d, J = 6.5 Hz, 1H), 2.22 (td, J = 7.0; 2.0 Hz, 2H), 1.52−1.45 (m, 2H), 1.41−1.32 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 149.6, 138.9, 133.4, 128.8, 128.2, 127.0, 120.2, 113.3, 99.8, 86.5, 77.7, 49.4, 30.5, 21.8, 18.3, 13.5; IR: ν_{max} 3349 (NH), 2212 (C≡N), 2107 (C≡C); HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{21}N_2$ 289.1705; found 289.1712.

*4-[(1-(4-Chlorophenyl)hept-2-yn-1-yl)amino]benzonitrile (**3fc**).* Following the general procedure from **1f** (0.668 g, 3 mmol) and 4-cyanoaniline (0.532 g, 4.5 mmol) with (HO)P(OEt)$_2$ **A** (39.0 μL, 10 mol %), the title compound was isolated by column chromatography (toluene) as a yellow oil (0.502 g, 52%). R_f = 0.50 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 6.65 (d, J = 8.5 Hz, 2H), 5.26 (d, J = 6.5 Hz, 1H), 4.56 (d, J = 6.5 Hz, 2H), 2.22 (td, J = 7.0; 2.0 Hz, 2H), 1.50−1.44 (m, 2H), 1.40−1.31 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ: 150.8, 139.2, 134.0, 134.0, 129.5, 129.3, 120.6, 114.0, 99.6, 86.7, 78.5, 48.7, 31.1, 22.2, 18.4, 13.5; IR: ν_{max} 3567 (NH), 2209 (C≡N), 2114 (C≡C); HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{20}N_2Cl$ 323.1315; found 323.1304.

*(E)-N-(1,3-Diphenylallyl)-4-methylaniline (**3ga**).* Following the general procedure from (*E*)-1,3-diphenylprop-2-en-1-ol (0.420 g, 2 mmol) and 4-toluidine (0.320 g, 3 mmol) with (HO)P(OEt)$_2$ **A** (13.0 μL, 5 mol %), the title compound was isolated by column chromatography (petroleum ether → petroleum ether/EtOAc, 9:1 gradient) as a yellow oil (0.446 g, 75%). R_f = 0.69 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43−7.20 (m, 10H), 6.95 (d, J = 8.5 Hz, 2H), 6.62 (d, J = 16.0 Hz, 1H), 6.55 (d, J = 8.5 Hz, 2H), 6.39 (dd, J = 16.0; 6.0 Hz, 1H), 5.04 (d, J = 6.0 Hz, 1H), 3.99 (br s, 1H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 144.9, 142.2, 136.6, 131.0, 130.9, 129.6, 128.7, 128.5, 127.6, 127.4, 127.1, 126.8, 126.4, 113.7, 60.9, 20.3. The spectroscopic data for this compound are in accordance with the literature.[20]

*(E)-N-(1,3-Diphenylallyl)benzamide (**3gj**).* Following the general procedure from (*E*)-1,3-diphenylprop-2-en-1-ol (0.210 g, 1 mmol) and benzamide (0.181 g, 1.5 mmol) with (HO)P(OPh)$_2$ **B** (12.5 mg, 5 mol %) at 90 °C, the crude product was washed with cold EtOAc (50 mL) to isolate the title compound as a white solid (0.278 g, 89%). Mp = 153−155 °C [lit. 163−164 °C]; R_f = 0.72 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, J = 7.0 Hz, 2H), 7.53−7.22 (m, 13H), 6.62 (d, J = 16.0 Hz, 1H), 6.53 (br s, 1H), 6.45 (dd, J = 16.0; 6.0 Hz, 1H), 6.03 (t, J = 7.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 166.4, 140.8, 136.3, 134.3, 131.7, 131.6, 128.8, 128.7, 128.6, 128.5, 127.8, 127.7, 127.2, 127.0, 126.5, 55.2. The spectroscopic data for this compound are in accordance with the literature.[21]

*3-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]-1H-indole (**3al**).* Following the general procedure from **1a** (0.436 g, 2 mmol) and indole (0.351 g, 3 mmol) with (HO)P(O)(OPh)$_2$ **B** (2.5 mg, 1 mol %) at 40 °C, the crude product was washed with cold petroleum ether (100 mL) to yield the title compound as a pale brown solid (0.461 g, 73%). Mp = 67−69 °C; R_f = 0.43 (silica gel, petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (br s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.05 (s, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 8.5 Hz, 2H), 5.17 (s, 1H), 3.77 (s, 3H), 2.25 (td, J = 7.0; 2.0 Hz, 2H), 1.57−1.49 (m, 2H), 1.47−1.38 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 158.2, 138.7, 134.2, 128.7, 126.0, 122.3, 122.0, 119.7, 119.3, 118.0, 113.7, 111.0, 83.1, 80.0, 55.2, 34.1, 31.1, 22.0, 18.6, 13.6. The spectroscopic data for this compound are in accordance with the literature.[22]

*1-[1-(Benzyloxy)hept-2-yn-1-yl]-4-methoxybenzene (**3am**).* Following the general procedure from **1a** (0.218 g, 1 mmol) and benzyl alcohol (0.155 mL, 1.5 mmol) with (HO)P(O)(OPh)$_2$ **B** (2.5 mg, 1 mol %) at 40 °C, the title compound was isolated by column chromatography (silica gel, petroleum ether → petroleum ether/EtOAc, 9:1 gradient) as a yellow oil (0.286 g, 93%). R_f = 0.50 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 8.5 Hz, 2H), 7.38−7.31 (m, 5H), 6.89 (d, J = 8.5 Hz, 2H), 5.16 (t, J = 2.0 Hz, 1H), 4.67−4.59 (m, 2H), 3.80 (s, 3H), 2.31 (td, J = 7.0; 2.0 Hz, 2H), 1.59−1.52 (m, 2H), 1.49−1.40 (m, 2H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 159.5, 138.1, 131.5, 128.8, 128.2, 128.0, 127.5, 113.7, 88.4, 77.9, 70.3, 69.4, 55.2, 30.77, 21.9, 18.5, 13.5. The spectroscopic data for this compound are in accordance with the literature.[23]

*Benzyl[1-(4-methoxyphenyl)hept-2-yn-1-yl]sulfane (**3an**).* Following the general procedure from **1a** (0.327 g, 1.5 mmol) and benzyl mercaptan (0.264 mL, 2.25 mmol) with (HO)P(O)(OPh)$_2$ **B** (3.8 mg, 1 mol %) at 40 °C, the title compound was isolated by column chromatography (silica gel, petroleum ether/EtOAc, 95:5) as a yellow oil (0.406 g, 83%). R_f = 0.69 (petroleum ether/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37−7.22 (m, 7H), 6.84 (d, J = 8.5 Hz, 2H), 4.54 (t, J = 2.0 Hz, 1H), 3.95 (d, J = 13.5 Hz, 1H), 3.79 (s, 3H), 3.72 (d, J =

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13.5 Hz, 1H), 2.33 (td, J = 7.0; 2.0 Hz, 2H), 1.61−1.53 (m, 2H), 1.51−1.42 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 158.9, 137.9, 130.5, 129.0, 128.9, 128.4, 126.9, 113.7, 86.7, 77.9, 55.2, 38.1, 36.4, 30.9, 22.0, 18.6, 13.6; IR: ν_{max} 2219 (C≡C); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}OS$ 325.1626; found 325.1634.

*(E)-Benzyl(1,3-diphenylallyl)sulfane (**3gn**).* Following the general procedure from (*E*)-1,3-diphenylprop-2-en-1-ol (0.210 g, 1 mmol) and benzyl mercaptan (0.176 mL, 1.5 mmol) with $(HO)P(OEt)_2$ **A** (1.0 μL, 1 mol %), the title compound was isolated by column chromatography (silica gel, petroleum ether) as a white solid (0.306 g, 97%). Mp = 62−64 °C [lit. 63−64 °C]; R_f = 0.40 (petroleum ether/EtOAc, 4:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.39−7.23 (m, 15H), 6.41 (d, J = 7.0 Hz, 2H), 4.46 (d, J = 6.5 Hz, 1H), 3.72−3.63 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 140.2, 138.1, 136.5, 131.3, 129.3, 129.0, 128.6, 128.5, 128.4, 127.9, 127.6, 127.4, 126.9, 126.4, 51.5, 36.0. The spectroscopic data for this compound are in accordance with the literature.[24]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01427.

^1H and ^{13}C NMR of all of the reported compounds; FAIR data for NMR spectra are also available; see ref 25 (PDF)

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Notes

The authors declare no competing financial interest.

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