SN1 reactions of propargylic alcohols, and we similarly reported that the basicity of the chosen nucleophile. Every system has to be optimized to avoid competitive Meyer−Schuster and Rupe rearrangements. They are also very easy to separate from the desired organic products. 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 use of aqueous HBF₄. These catalysts are compatible with technical solvents and presence of air, and they are also applicable to C-, O-, and S-nucleophiles.

**RESULTS AND DISCUSSION**

Surprisingly, phosphorus-containing acids have not been explored in these substitution reactions despite their range of pHₐₓ⁻¹ 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. 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)₃P(O)₃R 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; when water was added, all phosphate was converted into phosphonic acid (83%) and triphenylphosphate (17%).

With three promising candidates in hand, phosphinic acid, diethyl phosphate 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. Of note, while phosphate B was recovered at the end of these reactions, phosphate A completely hydrolyzed into a previously reported anilinium phosphate salt, which was catalytically...
Table 1. Screening of Phosphorus-Based Acid Catalysts

| entry | catalyst | 1a (%) | 3aa (%) | 4aa (%) |
|-------|----------|--------|---------|---------|
| 1     | (HO)P(O)H₂ | 10     | <5      | >95     | <5      |
|       |          | 10<sup>a</sup> | <5<sup>′</sup> | 79<sup>′</sup> | 13<sup>′</sup> |
| 2     | (HO)P(O)H  | 10     | <95     |      | <5      |
| 3     | (HO)P(O)    | 10     | 95      |      | <5      |
| 4     | (HO)P(O)(OPh)₂ | 10 | <5       | 72     | <5      |
| 5     | (HO)P(OPh)₂ | 10     | <5      | 72     | <5      |
| 6     | (HO)₂P(O)H  | 10     | <5      | 90     | 5       |
| 7     | (HO)P(OEt)₂ | 10     | <5      | 90     | 5       |
| 8     | (HO)P(OEt)₃ | 10     | 51      | 62     | <5      |
| 9     | (HO)P(OEt)₃ | 10     | 5       | 70     | 26      |
| 10    | (HO)P(OEt)₃ | 10     | <5      | 94     | <5      |
| 11    | (HO)P(OEt)₃ | 10     | 5       | 9       | <5      |
| 12    | (HO)P(OEt)₃ | 10     | 1        | 47     | 43      |
| 13    | (HO)P(OEt)₃ | 10     | 5       | 69     | 11      |

<sup>a</sup>Reaction conditions: 1a (0.5 mmol) and 2a (2 equiv) in technical cumene (0.5 mL). ¹<sup>1</sup>H NMR yields/recoveries are the average of two independent experiments and were determined with respect to 1,3,5-trimethoxybenzene as internal standard. ¹<sup>1</sup>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

| entry | solvent  | 1a (%) | 3aa (%) | 4aa (%) |
|-------|----------|--------|---------|---------|
| 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 |

<sup>a</sup>Reaction conditions: 1a (0.5 mmol) and 2a (1.5 equiv) in technical cumene (0.5 mL). ¹<sup>1</sup>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 either 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 arylation 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 Bronsted 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) or p-nitrobenzenesulfonic acid (together with decomposition).<sup>18</sup>

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-cyanoalnine, 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 benzydryl alcohol as the starting material.

Finally, to further showcase the potential of catalysts A and B, we reacted three typical O-, C-, and N-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 Bronsted acids for nucleophilic substitution reactions of propargylic alcohols with N-nucleophiles of increasing basicity. Allylic alcohols as well as O-, C-, and N-nucleophiles were also suitable substrates under the reported conditions,
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. 2,4-Acetamidobenzaldehyde (1a), 2,4-dinitrobenzaldehyde (1b), 2,4-dinitroaniline (1c), 2-phenylacetylene (1d), 2-propyn-1-ol (1e), 2-propyn-1-ol 4-methyl (1f), 4-toluidine (1g) 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. Basic silica gel was prepared by submerging silica gel into petroleum ether containing 2% v/v NEt₃ 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. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on Bruker AVANCE 400 spectrometer (¹H: 400 MHz, ¹³C: 101 MHz, ¹⁹F: 377 MHz) at 23 °C. The chemical shifts, δ, are given in ppm relatively to tetramethylsilane (0.00 ppm), CDCl₃ (77.0 ppm), benzo trifluoride (−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 (1.0 equiv) and (HO)P(OEt)₂ 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 NEt₃).

### Table 3. N-Nucleophile Scope

| Entry | Aniline | Conditions | 1a (%)b | 3aX (%)b | 4aX (%)b |
|-------|---------|------------|---------|----------|----------|
| 1     | H₂N–CN–NO₂  | 2b         | 1 mol % A, 18 h | <5 | >95 (84) | <5 |
| 2     | H₂N–CN–N=C–CN  | 2c        | 1 mol % A, 18 h | <5 | >95 (88) | <5 |
| 3     | H₂N–CN–F    | 2d        | 1 mol % A, 24 h | 14 | 69 (56)  | 11 |
| 4     | H₂N–CN–Me   | 2e        | 10 mol % A, 18 h | <5 | >95 (88) | <5 |
| 5     | H₂N–CN–Me   | 2f        | 10 mol % A, 18 h | <5 | 85 (77)  | 10 |
| 6     | H₂N–CN–Me   | 2a        | 10 mol % A, 18 h | <5 | >95 (90) | <5 |
| 7     | H₂N–CN–O-Me | 2g        | 10 mol % A, 24 h | 14 | 75 (57)  | 6  |
| 8     | H₂N–CN–O-Me | 2h        | 1 mol % A, 18 h | 10 | 90 (70)  | -- |
| 9     | H₂N–CN–O-Me | 2i        | 5 mol % A, 18 h | <5 | 65 (47)  | 21 |
| 10    | H₂N–CN–O-Me | 2j        | 2.5 mol % A, 18 h | 15 | 69       | 16 |
| 11    | H₂N–CN–O-Me | 2k        | 5 mol % A, 24 h | <5 | >95 (90) | -- |

The reaction conditions: 1a (2 mmol) and 2X (1.5 equiv) in technical toluene (2 mL). H NMR yields/recoveries are the average of two independent experiments and were determined with respect to 1,3,5-trimethoxybenzene as internal standard. Isolated yields are provided in brackets. ⁹⁰ °C.
Table 4. Propargylic Alcohols Scope with (HO)P(OEt)2 A

| Entry | Propargylic alcohol | A (mol %) | 1X (%) | 3X (%) |
|-------|---------------------|-----------|--------|--------|
| 1     | MeO                  | 1b        | 1      | 6      | 87     |
| 2     | MeO                  | 1c        | 10     | 7      | 82     |
| 3     | nBu                 | 1d        | 0.5    | <5     | 80     |
| 4     | nBu                 | 1e        | 5      | <5     | 73     |
| 5     | Cl                   | 1f        | 10     | <5     | 62     |

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

Scheme 1. Reactions with an Allylic Alcohol

**Scheme 2. Synthesis of 3gn**

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

Table 5. Further Nucleophile Scope

| Entry | H-Nuc | Conditions | A or B | 1a (%) | 3aX (%) |
|-------|-------|------------|--------|--------|---------|
| 1     | Ph     | Toluene, 18 h | 2X     | 5 mol % A, 90 °C | <5 | 95 |
|       |       | Ar = 4-MeOC6H4 |       | 1 mol % B, RT | <5 | >95 (73) |
| 2     | Ph     | Toluene, 18 h | 2X     | 5 mol % A, 90 °C | <5 | >95 |
|       |       | Ar = 4-MeOC6H4 |       | 1 mol % B, 40 °C | <5 | >95 (93) |
| 3     | Ph     | Toluene, 18 h | 2X     | 5 mol % A, 90 °C | <5 | >95 |
|       |       | Ar = 4-MeOC6H4 |       | 1 mol % B, 40 °C | <5 | >95 (83) |

"Reaction conditions: 1g (2 mmol) and 2X (1.5 equiv) in technical toluene (2 mL)." 1H NMR yields/recoveries are the average of two independent experiments and were determined with respect to 1,3,5-trimethoxybenzene as internal standard. *Isolated yields are provided in brackets.
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). 13C{1H} NMR (101 MHz, CDCl3): δ 159.2, 157.4 (d, JCEF = 237 Hz), 143.1, 132.3, 128.4, 115.4 (d, JCEF = 22 Hz), 155.2 (d, JCH = 7 Hz), 113.9, 85.6, 79.3, 55.2, 50.3, 30.7, 21.8, 18.4, 13.5. 19F NMR (CDCl3, 376 MHz): δ −126.9 (s); IR: νmax 3390 (NH), 2250 (C=C); HRMS (ESI) m/z: [M + H]+ Calcd for C21H26NO2 294.1858; found 294.1857.

N-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]methylenebenzotriazoline (3af). Following the general procedure from 1a (0.436 g, 2 mmol) and benzaldehyde (0.182 g, 1.5 mmol) with (HO)P(O)(OPh)2 (2.5 μL, 10 mol %) in technical toluene (4 mL), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 9:1 gradient) as a white solid (0.287 g, 90%). Mp = 95–97 °C. Rf = 0.32 (petroleum ether/EtOAc, 4:1); 1H NMR (CDCl3, 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, 1H), 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); 13C{1H} NMR (101 MHz, CDCl3): δ 159.2, 157.7, 146.7, 132.8, 129.0, 128.5, 113.9, 85.3, 79.4, 55.3, 49.6, 30.7, 21.8, 18.4, 13.5; IR: νmax 3391 (NH), 2115 (C=C); HRMS (ESI) m/z: [M + H]+ Calcd for C21H24NO2 294.1858; found 294.1854.

4-Methoxy-N-[1-(4-methoxyphenyl)hept-2-yn-1-yl]maleimide (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 (2.5 μL, 10 mol %) in technical toluene (4 mL), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 9:1 gradient) as a white solid (0.464 g, 70%). Mp = 57–59 °C. Rf = 0.43 (petroleum ether/EtOAc, 4:1); 1H NMR (CDCl3, 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); 13C{1H} NMR (101 MHz, CDCl3): 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, 50.7, 30.8, 21.8, 18.4, 13.5; IR: νmax 3365 (NH), 2234 (C=C); HRMS (ESI) m/z: [M + H]+ Calcd for C21H24NO2 294.1856; found 294.1854.

N-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]benzothioamide (3aj). Following the general procedure from 1a (0.436 g, 2 mmol) and thiobenzamide (0.411 g, 3 mmol) with (HO)P(O)(OPh)2 (2.5 μL, 10 mol %) in technical toluene (4 mL), the title compound was isolated by column chromatography (petroleum ether/EtOAc, 9:1 gradient) as a white solid (0.287 g, 90%). Mp = 95–97 °C. Rf = 0.32 (petroleum ether/EtOAc, 4:1); 1H NMR (CDCl3, 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, 1H), 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); 13C{1H} NMR (101 MHz, CDCl3): δ 159.2, 152.7, 141.0, 132.8, 128.3, 115.7, 114.6, 113.9, 85.4, 79.7, 55.7, 55.3, 50.7, 50.7, 30.8, 21.8, 18.4, 13.5; IR: νmax 3365 (NH), 2234 (C=C); HRMS (ESI) m/z: [M + H]+ Calcd for C21H24NO2 294.1856; found 294.1854.

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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; Rf = 0.25 (petroleum ether/EtOAc, 4:1); 1H NMR (CDCl3, 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); 13C{1H} NMR (101 MHz, CDCl3) 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 is in agreement with the literature.6

4-[(1-Mesitylthethyl)-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(O)(Et)2 A (2.0 μL, 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%). Rf → 120.0, 114.3, 113.4, 100.4, 81.7, 73.6, 55.3, 48.6. The spectroscopic data for this compound is in agreement with the literature.

(E)-N-(1,3-Diphenylallyl)benzamide (3gj). Following the general procedure from (E)-1,3-diphenylprop-2-en-1-ol (0.210 g, 1.5 mmol) and benzamide (0.418 g, 1.5 mmol) with (HO)P(O)(OPh)2 B (2.5 mg, 1 mol %) at 40 °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], Rf = 0.72 (petroleum ether/EtOAc, 4:1); 1H NMR (CDCl3, 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); 13C{1H} NMR (101 MHz, CDCl3) 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, 126.5, 55.2. The spectroscopic data for this compound is in agreement with the literature.21

3-[1-(4-Methoxyphenyl)hept-2-yn-1-yl]H-indole (3al). Following the general procedure from 1a (0.436 g, 2 mmol) and indole (0.351 g, 3 mmol) with (HO)P(O)(O)Ph2 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; Rf = 0.43 (silica gel, petroleum ether/EtOAc, 4:1); 1H NMR (CDCl3, 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 = 2.0 Hz, 2H), 5.17–1.49 (m, 2H), 1.47–1.38 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); 13C{1H} NMR (101 MHz, CDCl3) δ: 158.2, 138.7, 134.2, 128.7, 126.0, 122.0, 119.7, 113.9, 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 agreement with the literature.22

1-[1-(Benzoyloxy)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)(O)Ph2 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%). Rf = 0.50 (petroleum ether/EtOAc, 4:1); 1H NMR (CDCl3, 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); 13C{1H} NMR (101 MHz, CDCl3) 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 agreement 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)(O)Ph2 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%). Rf = 0.69 (petroleum ether/EtOAc, 4:1); 1H NMR (CDCl3, 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 =...
(E)-Benzy1[(3-diphenylallyl)sulfane (3gn). Following the general procedure from (E)-1,3-diphenylprop-2-en-1-ol (0.210 g, 1.0 mmol) with (HO)3P(OEt)2 (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 = 62−13.6 °C. IR: νmax (C≡C): 2191 (C≡C); HRMS (ESI) m/z: [M + H]+ Calcd for C36H35OS: 525.1626; found 525.1634.

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**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 13C 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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