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Stereoselective alkyne semihydrogenations with an air-stable copper(I) catalyst†

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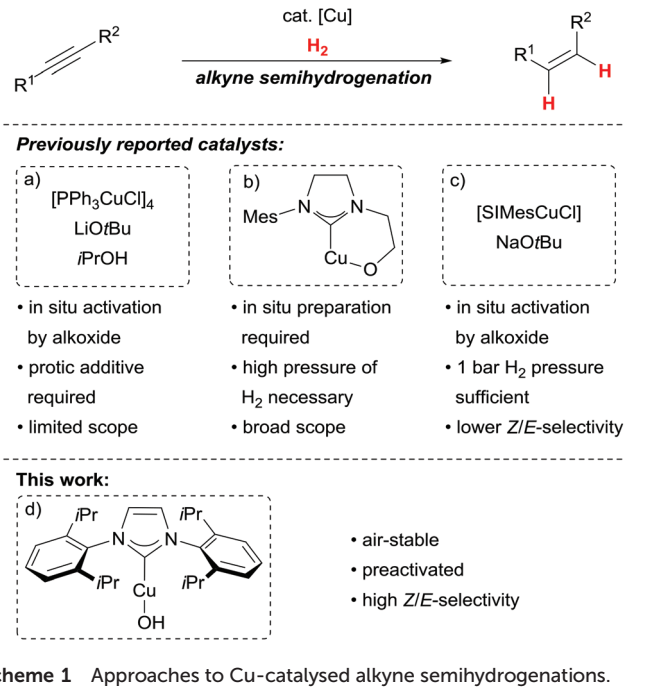
An air-stable and preactivated copper(I) hydroxide/N-heteroyclic carbene (NHC) complex for alkyne semihydrogenations is reported. Next to an enhanced practicability of the process, the resulting alkenes are obtained with high *Z*-selectivities and no overreduction to the corresponding alkanes.

Introduction

Catalytic stereoselective alkyne semihydrogenations are powerful and atom-economic synthetic alternatives to olefination reactions.[1,2] The resulting alkenes are valuable building blocks especially for diastereoselective follow-up reactions.[3] For *Z*-selective alkyne semihydrogenations, the Lindlar catalyst[4] has become the first choice, however, it suffers from *E*/*Z*-isomerisation processes and overreduction to the corresponding alkanes.[2] While the latter leads to loss of the desired functionality, the former can be problematic with foresight to tedious separations and consecutive diastereoselective transformations.

Hydrogenations catalysed by readily available first row transition metals are desirable from an economic point of view.[5] Among them, homogeneous catalysts based on copper(I) have recently emerged as viable alternatives for *Z*-selective alkyne semihydrogenations.[6–10] Key reactivity for these catalytic processes is the reported stereoselective insertion of alkynes into copper(I) hydride bonds.[11–13] While most of the disclosed catalysts allow for good to excellent *Z*-stereoselectivity in alkyne semihydrogenations, all studied copper(I) complexes need to be prepared *in situ* as the active catalysts are unstable. This feat can be ascribed to the formation of a Cu–O-bond, which allows for H_2 activation[14] but at the same time renders the corresponding complexes sensitive to air and moisture. The need for preactivation hampers the practicability of the overall processes, as can be seen from the studied catalysts so far: a triphenylphosphine/copper(I) complex can be used under an H_2 amosphere (5 bar) at elevated temperatures in combination with iso-propanol to transform alkynes into the corresponding *Z*-alkenes (Scheme 1a).[6] This catalyst has to be activated with an alkoxide at elevated temperatures (100 °C) and is limited to mainly unfunctionalised substrates.[15]

We have introduced a highly stereoselective alkyne semihydrogenation based upon copper(I)/N-heterocylic carbene (NHC) complexes bearing an alkoxide tether (Scheme 1b).[7] This system requires high H_2 pressure (100 bar) and the catalyst needs to be generated *in situ* from sensitive mesitylcopper(I). More recently, an NHC/copper(I) complex has been reported which allows for alkyne semihydrogenations at 1 bar H_2. The catalyst has to be generated *in situ* from a copper(I) chloride/NHC precursor with sodium *tert*-butanolate and shows somewhat reduced *Z*/*E*-selectivity (Scheme 1c).[8]



Scheme 1 Approaches to Cu-catalysed alkyne semihydrogenations.

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Herein, we report on the identification of a preactivated and air-stable NHC/copper(I) hydroxide complex, [IPrCuOH],[16] for highly *Z*-selective alkyne semihydrogenations. The stability of the precatalyst allows for a more practical effectuation of the semihydrogenation without jeopardizing the stereoselectivity.[17]

Results and discussion

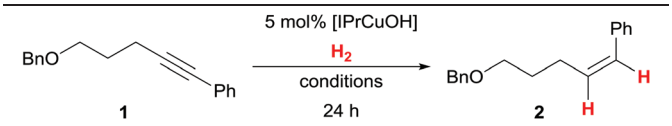
Optimisation of the alkyne semihydrogenation

The alkyne semihydrogenation has been optimised using pentynol-derived internal alkyne **1** (Table 1): generally, *E*/*Z*-isomerisation processes and/or overreduction remained negligible. Under previously optimised reaction conditions (40 °C, 100 bar H_2)[7] as well as with slightly reduced H_2 pressure of 80 bar, [IPrCuOH] shows complete conversion of the internal alkyne to the corresponding *Z*-styrene derivative **2** (Table 1, entries 1 and 2). Alkene **2** could be isolated with 93% yield. Lowering the pressure to 50 bar H_2 led to incomplete conversion of **1** in THF (Table 1, entry 3). At these limiting conditions (40 °C, 50 bar H_2), the alkyne semihydrogenation in DMF or toluene gave little turnover (25% and 26% respectively, Table 1, entries 4 and 5). During the investigation of the substrate scope (see below), we found that generally higher turnovers were obtained at higher H_2 pressure. Additionally, for some compounds, more forcing conditions (100 bar H_2, 60 °C) were required for full conversion (as in Table 1, entry 6). When lowering the H_2 pressure to 1 bar (balloon) an alkyne semihydrogenation could not be observed (Table 1, entry 7). The sterically more demanding copper(I) hydroxide complex [IPr*CuOH][17b] displayed lower activity under forcing conditions (Table 1, entry 8).[18]

Substrate scope

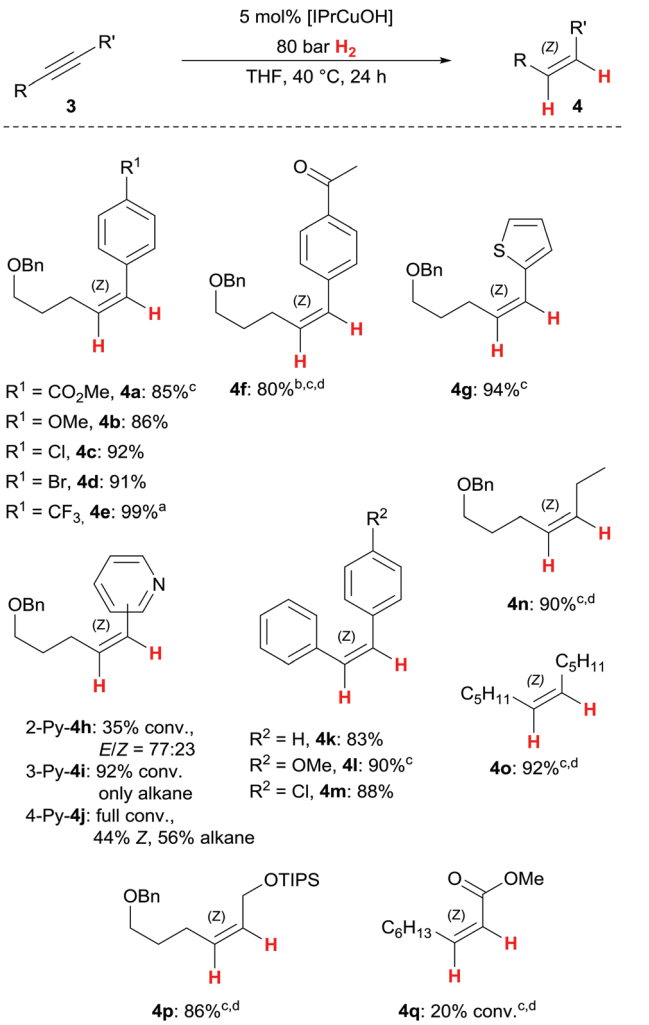
With optimised reaction conditions in hand, we set out to investigate the substrate scope of the *Z*-selective alkyne semihydrogenation with [IPrCuOH] and found generally broad applicability, while *Z*-stereoselectivity remained high (Scheme 2). A variety of electron-rich and electron-poor aryl/alkyl-substituted alkynes **3a–3e** based upon the pentynol-framework gave the corresponding *Z*-alkenes **4a–4e** in high yields. Unlike our previously reported copper(I)/NHC complex (Scheme 1b),[7] [IPrCuOH] does not fully tolerate ketone functional groups, which is showcased by partial overreduction of **4f** to the benzylic alcohol (ratio ketone/benzylic alcohol = 88 : 12). We hypothesise that the presence of an intermediate alcohol(ate) disturbs the overall chemoselectivity, as in this case overreduction to the alkane was substantial (15%). This effect of additional alcohol(ate)s mirrors those of our previous study.[7] In contrast, the tolerance of heterocycles differs from our earlier results: thiophene **4g**, which was unreactive with the tethered catalyst,[7] can now be obtained in good yield

Table 1 Optimisation of alkyne semihydrogenation with IPrCuOH[a,b]



Entry	Conditions	Conversion[c]
1	THF, 40 °C, 100 bar H_2	Full
2	THF, 40 °C, 80 bar H_2	Full (93%[d])
3	THF, 40 °C, 50 bar H_2	87%
4	DMF, 40 °C, 50 bar H_2	25%
5	Toluene, 40 °C, 50 bar H_2	26%
6	THF, 60 °C, 100 bar H_2	Full
7	THF, 60 °C, 1 bar H_2	n.d.
8	[IPr*CuOH] instead of [IPrCuOH], 60 °C, 100 bar H_2	67%

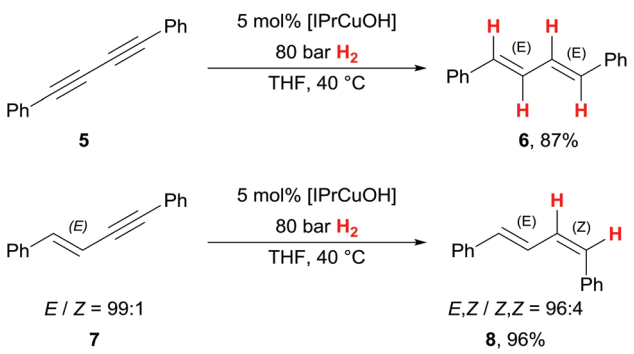
[a] Reactions were carried out on 0.13 mmol scale. [b] In all cases, the *E*/*Z*/alkane ratio was >99 : 1 : 1. [c] Determined by ^{1}H NMR and GC analysis. [d] Isolated yield, 0.26 mmol scale.



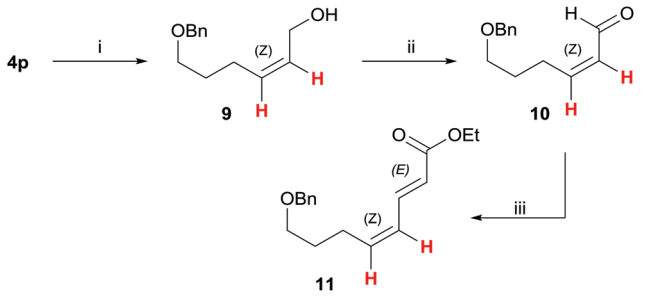
Scheme 2 Cu-catalyzed alkyne semihydrogenation with [IPrCuOH], substrate scope. If not noted otherwise, the ratio *Z*/*E*/alkane is >99 : 1 : 1. [a] Contains 5% alkane. [b] Ketone/benzylic alcohol ratio 88 : 12, contains 15% alkane. Reaction was run for 48 h. [c] 100 bar H_2 employed. [d] Reaction at 60 °C.

(94%): pyridine isomers **3h–3j**, viable substrates with our earlier catalyst,[7] give varying results in terms of overreduction and/or *E*/*Z* isomerisation. This displays a vulnerability of the copper(I) catalyst to strongly coordinating substrates. The present protocol is applicable to diaryl- and dialkylalkynes alike: tolane (**3k**) and its derivatives prove to be suitable precursors for *Z*-stilbenes **4k–4m** under the semihydrogenation conditions. Notably, methoxy-substituted tolane **3l** required a somewhat higher H_2 pressure (100 bar). In a similar vein, dialkylalkynes **3n** and **3o** require slightly more forcing conditions (100 bar H_2, 60 °C) to allow full conversion to the desired *Z*-alkenes **4n** and **4o**. The protected allylic alcohol **4p** is available from the corresponding propargylic silyl ether in high yield and excellent stereoselectivity using elevated temperature and H_2 pressure. This example marks one of the strong points of our catalytic process, as *Z*-allylic alcohols are important building blocks for diastereoselective follow-up reactions (see below for a synthetic elaboration of **4p**). Finally, methyl-2-nonynoate (**3q**) shows excellent selectivity towards the corresponding *Z*-acrylate in our semihydrogenation protocol, albeit with low conversion (20%). Further investigations are needed to identify superior catalysts for this challenging, yet synthetically valuable semihydrogenation of propiolates.

When investigating diyne **5**, selectively only the *E*,*E*-diene **6** was isolated with high yield (87%) with our catalyst (Scheme 3). This is of note, as this class of compounds has been reported to get reduced to a *Z*-monoalkene by an earlier copper(I) hydrogenation catalyst[6] in alkyne semihydrogenation. To investigate the possible origin of this unexpected *E*-selectivity, we prepared *E*-enyne **7**, a potential reaction intermediate in a stepwise diyne semihydrogenation from **5** towards **6**. From this experiment, we isolated 96% of the *E*,*Z*-diene **8**, representing only minor loss of stereochemical integrity of the primarily installed *E*-alkene. With this result, it seems reasonable to conclude that diynes such as **5** do not react step-wise as isolated triple bonds. A potential alkenylcopper(I) intermediate could equilibrate to a butatrienylcopper(I) intermediate[19] (not shown), which accounts for the formation of the thermodynamically more preferred *E*,*E*-diene **6** from diyne **5**.



Scheme 3 Cu-catalysed semihydrogenation of a diyne and an enyne.



Scheme 4 Derivatisation of allyl silyl ether **4p**. Reaction conditions: (i) 1.1 equiv. TBAF, THF, rt, 3 h, 83%; (ii) 1.4 equiv. DMP, CH_2Cl_2, rt, 3 h, 88%; (iii) 1.5 equiv. triethyl phosphonoacetate, 1.5 equiv. NaH, THF, 0 °C to rt, 22 h, 86%, *Z*,*E*/*Z*,*Z* = >20 : 1.

Follow-up chemistry of (*Z*)-allylic alcohols

Finally, to demonstrate the usefulness of the present highly *Z*-selective alkyne semihydrogenation, we further elaborated silyl ether **4p** (Scheme 4): after silyl ether deprotection with TBAF to the allylic alcohol **9** (83%), subsequent oxidation with the Dess–Martin periodinane[20] gave *Z*-acrolein-derivative **10** (88%). A subsequent Horner–Wadsworth–Emmons reaction was carried out to yield *E*,*Z*-sorbic acid derivative **11** in 86% yield. This approach underlines that a stereoselective alkyne semihydrogenation with [IPrCuOH] can serve as key step to generate alkene geometries with high selectivity.

Conclusions

In summary, we have developed a highly *Z*-stereoselective alkyne semihydrogenation protocol, relying on an air-stable and preactivated NHC/copper(I) hydroxide complex, [IPrCuOH]. The practicability of this catalyst circumvents previous shortcomings of other copper(I) complexes as it does not require preactivation. A variety of products are accessible *via* this protocol in high yields and excellent *Z*-selectivities. The findings presented here could make a contribution towards widely applicable catalysis with easily accessible first-row transition metals.

Experimental

All reactions were carried out in flame-dried glassware under a nitrogen atmosphere using standard Schlenk techniques. NMR spectra were recorded on AvanceII 400 MHz or AvanceIII 500 MHz or 700 MHz instruments (Bruker). Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard according to literature values.[21] Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz), integration. All hydrogenation reactions were carried out in glass vials (50 × 14 mm, Schütt), equipped with a magnetic stir

bar, a rubber septum pinched with a needle (0.90 × 50 mm, Braun) in autoclaves Berghof BR-100 or BR-300 equipped with heating blocks. For preparation and characterisation of the starting materials, see the ESI.†

General procedure alkyne semihydrogenation

The reaction vessel was placed in a N_2-purged autoclave under a counterflow of N_2. The autoclave was purged with N_2 (3 × 10 bar) and H_2 (3 × 20 bar) before the appropriate H_2 pressure was applied (pressure is given as initial pressure before heating). The heating block was pre-heated before the autoclave was placed inside. After the reported reaction time the autoclave was allowed to cool to rt and H_2 was released. The autoclave was purged with N_2 (3 × 10 bar) before the reaction vessel was taken out. The reaction mixture was filtered through a small plug of silica (1 mL *tert*-butyl methyl ether as eluent), and all volatiles were removed under reduced pressure. Reactions were subsequently analysed either by GC and/or NMR. The crude mixture was then subjected to purification as indicated with the appropriate substrates.

(*Z*)-(5-(Benzyloxy)pent-1-en-1-yl)benzene (2)

Prepared from **1** (64 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5.0 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (80 bar) at 40 °C for 19 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 50 : 1 as eluent afforded **2** (60 mg, 0.24 mmol, 93%) as a colorless oil. R_f = 0.65 (cyclohexane/*tert*-butyl methyl ether 10 : 1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.76–1.84 (m, 2H), 2.48 (m_c, 2H), 3.53 (t, J = 6.5 Hz, 2H), 4.50 (s, 2H), 5.69 (dt, J = 11.7 Hz, J = 7.4 Hz, 1H), 6.46 (m_c, 1H), 7.22–7.26 (m, 1H), 7.28–7.36 (m, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.4, 30.1, 69.9, 73.0, 126.6, 127.6, 127.7, 128.3, 128.5, 128.9, 129.5, 132.4, 137.8, 138.7 ppm; HRMS (APCI) calcd for $C_{18}H_{21}O^+$ [$(M + H)^+$]: Calculated 253.1587, found: 253.1582. The data is in accordance with literature.[7]

Methyl (*Z*)-4-(5-(benzyloxy)pent-1-en-1-yl)benzoate (4a)

Prepared from **3a** (79 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (100 bar) at 40 °C for 24 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 25 : 1 as eluent afforded **4a** (67 mg, 0.22 mmol, 85%) as a colorless oil. R_f = 0.33 (cyclohexane/*tert*-butyl methyl ether 9 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.79 (m_c, 2H), 2.46 (m_c, 2H), 3.51 (t, J = 6.4 Hz, 2H), 3.92 (s, 3H), 4.48 (s, 2H), 5.78 (dt, J = 11.7 Hz, J = 7.4 Hz, 1H), 6.46 (d, J = 11.7 Hz, 1H), 7.26–7.36 (m, 7H), 7.99 (m_c, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.6, 30.0, 52.1, 69.7, 73.1, 127.6, 127.7, 128.2, 128.5, 128.7, 128.8, 129.6, 134.6, 138.6, 142.4, 167.1 ppm; HRMS (APCI) for $C_{20}H_{23}O_3^+$ [$(M + H)^+$]: Calculated 311.1642, found 311.1642. The data is in accordance with literature.[7]

(*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-methoxybenzene (4b)

Prepared from **3b** (72 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (80 bar) at 40 °C for 19 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 50 : 1 as eluent afforded **4b** (62 mg, 0.22 mmol, 86%) as a colorless oil. R_f = 0.41 (cyclohexane/*tert*-butyl methyl ether 10 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.79 (m_c, 2H), 2.45 (m_c, 2H), 3.52 (t, J = 6.4 Hz, 2H), 3.81 (s, 3H), 4.49 (s, 2H), 5.58 (dt, J = 11.7 Hz, J = 7.3 Hz, 1H), 6.38 (m_c, 1H), 6.86 (m_c, 2H), 7.24 (m_c, 2H), 7.27–7.36 (m, 5H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.4, 30.2, 55.4, 69.9, 73.0, 113.7, 127.6, 127.7, 128.5, 128.9, 130.1, 130.5, 130.8, 138.8, 158.4 ppm; HRMS (EI) calcd for $C_{19}H_{22}O_2^+$ [$(M)^+$]: 282.1614, found: 282.1610. The data is in accordance with literature.[7]

(*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-chlorobenzene (4c)

Prepared from **3c** (71 mg, 0.25 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (80 bar) at 40 °C for 19 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 50 : 1 as eluent afforded **4c** (66 mg, 0.23 mmol, 92%) as a colorless oil. R_f = 0.59 (cyclohexane/*tert*-butyl methyl ether 10 : 1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.78 (m_c, 2H), 2.42 (m_c, 2H), 3.51 (t, J = 6.4 Hz, 2H), 4.48 (s, 2H), 5.69 (dt, J = 11.7 Hz, J = 7.4 Hz, 1H), 6.39 (d, J = 11.7 Hz, 1H), 7.22 (m, 2H), 7.27–7.30 (m, 5H), 7.33–7.36 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.4, 30.0, 69.7, 73.1, 127.6, 127.7, 128.3, 128.4, 128.5, 130.2, 132.4, 133.1, 136.2, 138.6 ppm; HRMS (EI) calcd for $C_{18}H_{19}ClO^+$ [$(M)^+$]: 286.1119, found: 286.1133; IR (ATR) ν = 2854 (m), 1490 (s), 1453 (m), 1362 (m), 1091 (s), 1013 (m), 840 (s), 734 (s), 696 (s) cm^{-1}.

(*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-bromobenzene (4d)

Prepared from **3d** (83 mg, 0.25 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (80 bar) at 40 °C for 19 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 50 : 1 as eluent afforded **4d** (77 mg, 0.23 mmol, 91%) as a colorless oil. R_f = 0.69 (cyclohexane/*tert*-butyl methyl ether 10 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.77 (m_c, 2H), 2.41 (m_c, 2H), 3.50 (t, J = 6.4 Hz, 2H), 4.47 (s, 2H), 5.69 (dt, J = 11.7 Hz, J = 7.4 Hz, 1H), 6.36 (m_c, 1H), 7.15 (m_c, 2H), 7.27–7.30 (m, 3H), 7.33–7.36 (m, 2H), 7.43 (m_c, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.4, 30.0, 69.7, 73.1, 120.5, 127.6, 127.7, 128.4, 128.5, 130.5, 131.4, 133.2, 136.6, 138.6 ppm; HRMS (APCI) calcd for $C_{18}H_{20}BrO^+$ [$(M + H)^+$]: 331.0692, found: 331.0689; IR (ATR) ν = 2930 (m), 2856 (m), 1486 (s), 1453 (m), 1102 (s), 1071 (s), 1028 (m), 1009 (s), 837 (s), 734 (s), 696 (s) cm^{-1}.

(*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-(trifluoromethyl)benzene (4e)

Prepared from **3e** (82 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (3.0 mg, 6.4 μmol, 2.5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (80 bar) at 40 °C for 19 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 50 : 1 as eluent afforded **4e** (87 mg, 0.26 mmol, 99%) as a colorless oil, containing 5% of the corresponding alkane. R_f = 0.32 (cyclohexane/*tert*-butyl methyl ether 30 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.79 (m_c, 2H), 2.44 (m_c, 2H), 3.51 (t, J = 6.3 Hz, 2H), 4.48 (s, 2H), 5.79 (dt, J = 11.7 Hz, J = 7.4 Hz, 1H), 6.46 (d, J = 11.7 Hz, 1H), 7.27–7.35 (m, 5H), 7.38 (m_c, 2H), 7.56 (m_c, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.5, 30.0, 69.7, 73.1, 124.4 (q, J = 272 Hz), 125.2 (q, J = 3.7 Hz), 127.7, 127.8, 128.3, 128.5, 129.1, 134.6, 138.6, 141.3 ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ = −62.4 ppm; HRMS (EI) calcd for $C_{12}H_{12}F_3O^+$ [(M − Bn)$^+$]: 229.0835, found: 229.0839; IR (ATR) ν = 2861 (w), 1616 (m), 1454 (m), 1323 (s), 1162 (s), 1112 (s), 1066 (s), 1016 (s), 852 (m), 744 (m), 697 (m) cm^{-1}.

(*Z*)-1-(4-(5-(Benzyloxy)pent-1-en-1-yl)phenyl)ethan-1-one (4f)

Prepared from **3f** (74 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (100 bar) at 60 °C for 48 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 30 : 1 as eluent afforded **4f** (59 mg, 0.20 mmol, 80%) as a colorless oil, containing 15% of the corresponding alkane. R_f = 0.39 (cyclohexane/*tert*-butyl methyl ether 4 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.79 (m_c, 2H), 2.46 (m_c, 2H), 2.58 (s, 3H), 3.51 (t, J = 6.3 Hz, 2H), 4.47 (s, 2H), 5.79 (dt, J = 11.7 Hz, J = 7.4 Hz, 1H), 6.46 (d, J = 11.7 Hz, 1H), 7.25–7.38 (m, 5H), 7.37 (m_c, 2H), 7.90 (m_c, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.6, 26.7, 30.0, 69.7, 73.1, 127.6, 127.7, 128.4, 128.5, 128.7, 129.0, 134.8, 135.3, 138.6, 142.6, 197.8 ppm; HRMS (EI) calcd for $C_{20}H_{22}O_2^+$ [(M)$^+$]: 294.1614, found: 294.1621. The data is in accordance with literature.[7]

(*Z*)-2-(5-(Benzyloxy)pent-1-en-1-yl)thiophene (4g)

Prepared from **3g** (69 mg, 0.27 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (100 bar) at 40 °C for 19 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 60 : 1 as eluent afforded **4g** (63 mg, 0.24 mmol, 94%) as a colorless oil. R_f = 0.68 (cyclohexane/*tert*-butyl methyl ether 10 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.85 (m_c, 2H), 2.53 (m_c, 2H), 3.56 (t, J = 6.5 Hz, 2H), 4.52 (s, 2H), 5.59 (dt, J = 11.5 Hz, J = 7.3 Hz, 1H), 6.55 (m_c, 1H), 6.99–7.02 (m, 2H), 7.25 (m, 1H), 7.27 (m_c, 1H), 7.34 (m_c, 4H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.1, 29.7, 70.0, 73.1, 122.3, 125.1, 126.9, 127.3, 127.6, 127.8, 128.5, 130.5, 138.8, 140.8 ppm; HRMS (APCI) calcd for $C_{16}H_{19}OS^+$ [(M + H)$^+$]: 259.1151, found: 259.1146; IR (ATR) ν = 2854 (w), 1452 (m), 1362 (m), 1102 (s), 1048 (m), 1027 (m), 851 (m), 826 (m), 734 (s), 693 (s) cm^{-1}.

(*Z*)-1,2-Diphenylethene (4k)

Prepared from **3k** (46 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (80 bar) at 40 °C for 19 h. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **4k** (38 mg, 0.21 mmol, 83%) as a colorless oil. R_f = 0.58 (cyclohexane); ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 6.63 (s, 2H), 7.18–7.27 (m, 10H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 127.5, 128.6, 129.2, 130.6, 137.8 ppm; HRMS (EI) calcd for $C_{14}H_{12}^+$ [(M)$^+$]: 180.0934, found: 180.0933. The data is in accordance with literature.[7]

(*Z*)-1-Methoxy-4-styrylbenzene (4l)

Prepared from **3l** (53 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (100 bar) at 40 °C for 24 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 100 : 1 as eluent afforded **4l** (48 mg, 0.23 mmol, 90%) as a colorless oil. R_f = 0.64 (cyclohexane/*tert*-butyl methyl ether 10 : 1); ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.77 (s, 3H), 6.54 (m_c, 2H), 6.75 (m_c, 2H), 7.17–7.27 (m, 7H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 55.5, 113.9, 127.3, 128.6, 129.1, 129.2, 130.1, 130.2, 130.5, 138.1, 159.2 ppm; HRMS (APCI) calcd for $C_{15}H_{15}O^+$ [(M + H)$^+$]: 211.1117, found: 211.1124. The data is in accordance with literature.[22]

(*Z*)-1-Chloro-4-styrylbenzene (4m)

Prepared from **3m** (54 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (80 bar) at 40 °C for 24 h. Purification by flash column chromatography on silica gel using pentane as eluent afforded **4m** (48 mg, 0.22 mmol, 88%) as a colorless oil. R_f = 0.67 (pentane); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.54 (d, J = 12.2 Hz, 1H), 6.64 (d, J = 12.2 Hz, 1H), 7.17–7.20 (m_c, 4H), 7.22–7.27 (m, 5H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 127.5, 128.5, 128.6, 128.9, 129.1, 130.4, 131.1, 132.9, 135.8, 137.0 ppm; HRMS (APCI) calcd for $C_{14}H_{11}^+$ [(M − Cl$^-$)$^+$]: 179.0855, found: 179.0857. The data is in accordance with literature.[22]

(*Z*)-((Hept-4-en-1-yloxy)methyl)benzene (4n)

Prepared from **3n** (52 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5.0 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (100 bar) at 60 °C for 24 h. Purification *via* flash column chromatography on silica using cyclohexane/*tert*-butyl methyl ether 100 : 1 as eluent afforded **4n** (47 mg, 0.23 mmol, 90%) as a colorless oil. R_f = 0.79 (cyclohexane/*tert*-butyl methyl ether 10 : 1); ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.5 Hz, 3H), 1.68 (m_c, 2H), 2.05 (m_c, 2H), 2.14 (m_c, 2H), 3.49 (t, J = 6.5 Hz, 2H), 4.51 (s, 2H), 5.33 (dtt, J = 10.8 Hz, J = 7.2 Hz,

J = 1.3 Hz, 1H), 5.39 (dtt, J = 10.8 Hz, J = 7.2 Hz, J = 1.3 Hz, 1H), 7.27–7.31 (m, 1H), 7.33–7.36 (m, 4H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$): δ = 14.5, 20.6, 23.9, 29.9, 70.0, 73.1, 127.6, 127.8, 128.5, 128.5, 132.4, 138.8 ppm; HRMS (APCI) for $C_{14}H_{21}O^+$ [$(M + H)^+$]: Calculated 205.1587, found 205.1585. The data is in accordance with literature.[7]

(*Z*)-Dodec-6-ene (4o)

Prepared from **3o** (52 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (100 bar) at 60 °C for 24 h. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **4o** (48 mg, 0.24 mmol, 92%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.0 Hz, 6H), 1.28–1.36 (m, 12H), 1.99–2.04 (m, 4H), 5.36 (m_c, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2, 22.7, 27.3, 29.6, 31.7, 130.1 ppm; HRMS (EI) calcd for [$(M)^+$]: 168.1873, found: 168.1874. The data is in accordance with literature.[7]

(*Z*)-((6-(Benzyloxy)hex-2-en-1-yl)oxy)triisopropylsilane (4p)

Prepared from **3p** (92 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (100 bar) at 60 °C for 24 h. Purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether 50 : 1 as eluent afforded **4p** (80 mg, 0.22 mmol, 86%) as a colorless oil. R_f = 0.68 (cyclohexane/*tert*-butyl methyl ether 10 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04–1.14 (m, 21H), 1.69 (m_c, 2H), 2.15 (m_c, 2H), 3.48 (t, J = 6.5 Hz, 2H), 4.31 (d, J = 6.0 Hz, 2H), 4.50 (s, 2H), 5.42 (dtt, J = 11.0 Hz, J = 7.4 Hz, J = 1.6 Hz, 1H), 5.58 (dtt, J = 11.0 Hz, J = 5.9 Hz, J = 1.5 Hz, 1H), 7.26–7.31 (m, 1H), 7.33–7.36 (m, 4H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 12.2, 18.2, 24.4, 29.7, 59.8, 69.8, 73.0, 127.6, 127.7, 128.5, 129.7, 130.7, 138.8 ppm; ^{29}Si DEPT (99 MHz, J = 20 Hz, $CDCl_3$): δ = 13.8 ppm; HRMS (EI) calcd for $C_{19}H_{31}O_2Si^+$ [$(M - C_3H_7)^+$]: 319.2088, found: 319.2095; IR (ATR) ν = 2941 (m), 2864 (s), 1454 (m), 1362 (m), 1091 (s), 1068 (s), 881 (s), 804 (m), 732 (s), 676 (s), 657 (s) cm^{-1}.

(1*E*,3*E*)-1,4-Diphenylbuta-1,3-diene (6)

Prepared from **5** (53 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (80 bar) at 40 °C for 19 h. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **6** (46 mg, 0.22 mmol, 87%) as a white crystalline solid. R_f = 0.35 (cyclohexane); ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 6.71 (m_c, 2H), 7.00 (m_c, 2H), 7.23–7.26 (m, 2H), 7.35 (m_c, 4H), 7.46–7.47 (m, 4H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 126.8, 128.0, 129.1, 129.6, 133.2, 137.8 ppm; HRMS (EI) calcd for $C_{16}H_{14}^+$ [$(M)^+$]: 206.1090, found: 206.1093. The data is in accordance with literature.[22]

(1*Z*,3*E*)-1,4-Diphenylbuta-1,3-diene (8)

Prepared from **7** (52 mg, 0.26 mmol, 1.0 equiv.) and [IPrCuOH] (6.0 mg, 13 μmol, 5.0 mol%) according to the general procedure. The reaction mixture was stirred under H_2 atmosphere (80 bar) at 40 °C for 19 h. Purification by filtration through a plug of silica (3 cm) using cyclohexane as eluent afforded **8** (51 mg, 0.25 mmol, 96%) as a colorless oil. *E*,*Z*/*Z*,*Z* = 96 : 4 as judged by ^{1}H NMR. R_f = 0.41 (cyclohexane); ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 6.45 (m, 1H), 6.55 (d, J = 11.5 Hz, 1H), 6.75 (d, J = 15.6 Hz, 1H), 7.23–7.43 (m, 11H) ppm. Spectrum contains <5% alkane-containing products, which were not further characterised; ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 125.6, 127.0, 127.5, 128.1, 128.8, 129.0, 129.5, 130.6, 130.7, 135.3, 137.8, 138.1 ppm; HRMS (EI) calcd for $C_{16}H_{14}^+$ [$(M)^+$]: 206.1090, found: 206.1091. The data is in accordance with literature.[22]

(*Z*)-6-(Benzyloxy)hex-2-en-1-ol (9)

In a flame-dried Schlenk tube (15 mL) equipped with a magnetic stirring bar **4p** (0.70 g, 1.9 mmol, 1.0 equiv.) was dissolved in THF (4 mL). To this mixture, TBAF (1.0 M in THF, 2.1 mL, 2.1 mmol, 1.1 equiv.) was added dropwise. After 3 h the reaction was quenched by addition of H_2O (10 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 × 10 mL) and the combined organic layers were dried over Na_2SO_4. All volatiles were removed under reduced pressure to give the crude product. Purification *via* flash column chromatography on silica using cyclohexane/*tert*-butyl methyl ether 3 : 1 as eluent afforded **9** (0.33 g, 1.6 mmol, 83%) as a colorless oil. R_f = 0.35 (cyclohexane/*tert*-butyl methyl ether 1 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.64 (br s, 1H), 1.70 (m_c, 2H), 2.21 (m_c, 2H), 3.49 (t, J = 6.3 Hz, 2H), 4.17 (d, J = 6.9 Hz, 2H), 4.50 (s, 2H), 5.50–5.56 (m, 1H), 5.63–5.68 (m, 1H), 7.27–7.31 (m, 1H), 7.32–7.37 (m, 4H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.0, 29.4, 58.5, 69.3, 73.0, 127.6, 127.7, 128.5, 129.4, 132.3, 138.5 ppm; HRMS (ESI) calcd for $C_{13}H_{19}O_2^+$ [$(M + H)^+$]: 207.1380, found: 207.1383; IR (ATR) ν = 3354 (m), 2859 (m), 1453 (m), 1363 (m), 1098 (s), 1028 (s), 734 (s), 696 (s), 612 (m) cm^{-1}.

(*Z*)-6-(Benzyloxy)hex-2-enal (10)

In a flame dried Schlenk tube (15 mL) equipped with a magnetic stirring bar **9** (0.10 g, 0.49 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (0.15 M, 3.2 mL) and DMP (0.29 g, 0.68 mmol, 1.4 equiv.) was added. The mixture was stirred at rt for 3 h. The reaction mixture was filtered and concentrated under reduced pressure. Purification *via* flash column chromatography on silica using cyclohexane/*tert*-butyl methyl ether 4 : 1 as eluent afforded **10** (87 mg, 0.43 mmol, 88%) as a colorless oil. R_f = 0.41 (cyclohexane/*tert*-butyl methyl ether 3 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.82 (m_c, 2H), 2.73 (m_c, 2H), 3.52 (t, J = 6.1 Hz, 2H), 4.49 (s, 2H), 5.97 (ddt, J = 11.2 Hz, J = 8.1 Hz, J = 1.5 Hz, 1H), 6.62 (dt, J = 11.2 Hz, J = 8.2 Hz, 1H), 7.27–7.37 (m, 5H), 10.08 (d, J = 8.1 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.9, 29.3, 68.9, 73.2, 127.8, 128.6,

130.7, 138.3, 152.5, 191.1 ppm; HRMS (EI) calcd for $C_{13}H_{16}O_2^+$ [$(M)^+$]: 204.1145, found: 204.1144; IR (ATR) ν = 2858 (m), 1676 (s), 1452 (m), 1363 (m), 1099 (s), 1027 (m), 736 (s), 697 (s), 608 (m) cm^{-1}.

Ethyl (2*E*,4*Z*)-8-(benzyloxy)octa-2,4-dienoate (11)

To a cooled (0 °C) suspension of NaH (60 wt% in mineral oil, 44 mg, 1.1 mmol, 1.5 equiv.) in THF (0.15 M, 5 mL) was added triethyl phosphonoacetate (0.24 g, 1.1 mmol, 1.5 equiv.) dropwise. The resulting mixture is stirred at 0 °C for 30 min. Compound **10** (0.15 mg, 0.72 mmol, 1.0 equiv.) was added to this mixture. After completion of the addition the resulting mixture was warmed to rt and stirred for 22 h. The reaction was quenched by addition of sat. aq. NH_4Cl (4 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 × 5 mL) and the combined organic layers were washed with brine (15 mL) and dried over Na_2SO_4. All volatiles were removed under reduced pressure. Purification *via* flash column chromatography on silica using cyclohexane/*tert*-butyl methyl ether 20 : 1 as eluent afforded **11** (0.17 g, 0.62 mmol, 86%) as a colorless oil. R_f = 0.56 (cyclohexane/*tert*-butyl methyl ether 4 : 1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, J = 7.1 Hz, 3H), 1.74 (m_c, 2H), 2.42 (m_c, 2H), 3.49 (t, J = 6.4 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 4.50 (s, 2H), 5.85 (dt, J = 11.2 Hz, J = 7.9 Hz, 1H), 5.88 (d, J = 15.3 Hz, 1H), 6.14 (m_c, 1H), 7.27–7.30 (m, 1H), 7.33–7.36 (m, 4H), 7.62 (ddd, J = 15.2 Hz, J = 11.2 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4, 25.1, 29.5, 60.4, 69.5, 73.2, 121.7, 127.1, 127.7, 127.8, 128.5, 138.6, 139.4, 140.7, 167.3 ppm; HRMS (EI) calcd for $C_{17}H_{22}O_3^+$ [$(M)^+$]: 274.1564, found: 274.1571; IR (ATR) ν = 2856 (m), 1709 (s), 1634 (s), 1605 (m), 1304 (m), 1266 (s), 1166 (s), 1098 (s), 961 (s), 995 (m), 872 (m), 735 (s), 696 (s) cm^{-1}.

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