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

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An air-stable and preactivated copper(I) hydroxide/N-heterocyclic 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 catalyst4 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 H2 activation14 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 H2 atmosphere (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 ºC) and is limited to mainly unfunctionalised substrates.15

We have introduced a highly stereoselective alkyne semihydrogenation based upon copper(I)/N-heterocyclic carbene (NHC) complexes bearing an alkoxide tether (Scheme 1b).7 This system requires high H2 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 H2. 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.
Herein, we report on the identification of a preactivated and air-stable NHC/copper(i) hydroxide complex, [IPrCuOH], for highly Z-selective alkyne semihydrogenations. The stability of the precatalyst allows for a more practical effectuation of the semihydrogenation without jeopardizing the stereoselectivity.

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 H2) as well as with slightly reduced H2 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 H2 led to incomplete conversion of 1 in THF (Table 1, entry 3). At these limiting conditions (40 °C, 50 bar H2), 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 H2 pressure. Additionally, for some compounds, more forcing conditions (100 bar H2, 60 °C) were required for full conversion (as in Table 1, entry 6). When lowering the 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] displayed lower activity under forcing conditions (Table 1, entry 8).

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), [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. In contrast, the tolerance of heterocycles differs from our earlier results: thiophene 4g, which was unreactive with the tethered catalyst, can now be obtained in good yield.

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

| Entry | Conditions | Conversion |
|-------|------------|------------|
| 1     | THF, 40 °C, 100 bar H2 | Full |
| 2     | THF, 40 °C, 80 bar H2 | Full (93%)c |
| 3     | THF, 40 °C, 50 bar H2 | 87% |
| 4     | DMF, 40 °C, 50 bar H2 | 25% |
| 5     | Toluene, 40 °C, 50 bar H2 | 26% |
| 6     | THF, 60 °C, 100 bar H2 | Full |
| 7     | THF, 60 °C, 1 bar H2 | n.d. |
| 8     | [IPr*CuOH] instead of [IPrCuOH], 60 °C, 100 bar H2 | 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 1H NMR and GC analysis.

Scheme 2 Cu-catalyzed alkyne semihydrogenation with [IPrCuOH], substrate scope. If not noted otherwise, the ratio Z/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 H2 employed. d Reaction at 60 °C.
(94%): pyridine isomers 3h–3j, viable substrates with our earlier catalyst, 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-nonenoylacetate (3q) shows excellent selectivity towards the corresponding $Z$-acylate 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 $E,Z$-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 in alkyn 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 allenylcopper(i) intermediate could equilibrate to a butatrienylcopper(i) intermediate (not shown), which accounts for the formation of the thermodynamically more preferred $E,E$-diene 6 from diyne 5.

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 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. Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, mc = centrosymmetric multiplet), coupling constants (Hz), integration. All hydrogenation reactions were carried out in glass vials (50 × 14 mm, Schütt), equipped with a magnetic stir...
General procedure alkyne semihydrogenation

The reaction vessel was placed in a N₂-purged autoclave under a counterflow of N₂. The autoclave was purged with N₂ (3 × 10 bar) and H₂ (3 × 20 bar) before the appropriate H₂ 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 H₂ was released. The autoclave was purged with N₂ (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)-1-(5-(Benzylxoy)pent-1-ene-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 H₂ 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. Rf = 0.41 (cyclohexane/tert-butyl methyl ether 10:1); 1H NMR (500 MHz, CDCl₃): δ = 1.79 (mc, 2H), 2.45 (mc, 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 (mc, 1H), 6.86 (mc, 2H), 7.24 (mc, 2H), 7.27–3.76 (mc, 5H) ppm; 13C NMR (126 MHz, CDCl₃): 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) calc'd for C₁₉H₂₂O₂⁺ [M⁺]: 282.1614, found: 282.1610. The data is in accordance with literature.⁷

(Z)-1-(5-(Benzylxoy)pent-1-ene-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 H₂ 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. Rf = 0.59 (cyclohexane/tert-butyl methyl ether 10:1); 1H NMR (500 MHz, CDCl₃): δ = 1.78 (mc, 2H), 2.42 (mc, 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 (mc, 1H), 7.22 (mc, 2H), 7.27–3.70 (mc, 5H), 7.33-3.76 (mc, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 23.4, 30.0, 69.7, 73.1, 127.6, 127.7, 128.3, 128.4, 128.5, 130.2, 132.4, 133.1, 133.6, 138.6 ppm; HRMS (EI) calc'd for C₁₉H₁₄ClO⁺ [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-(Benzylxoy)pent-1-ene-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 H₂ 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. Rf = 0.69 (cyclohexane/tert-butyl methyl ether 10:1); 1H NMR (500 MHz, CDCl₃): δ = 1.77 (mc, 2H), 2.41 (mc, 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 (mc, 1H), 7.15 (mc, 2H), 7.27–3.70 (mc, 3H), 7.33–3.76 (mc, 2H), 7.43 (mc, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃): 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) calc'd for C₁₉H₁₄BrO⁺ [M⁺]: 331.0684, found: 331.0689; IR (ATR) ν = 2930 (m), 2856 (m), 1486 (s), 1453 (m), 1102 (s), 1071 (s), 1028 (m), 1089 (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 H₂ 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. Rₘ = 0.32 (cyclohexane/tert-butyl methyl ether 30:1); ¹H NMR (500 MHz, CDCl₃): δ = 1.79 (m, 2H), 2.44 (m, 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, 2H), 7.56 (m, 2H) ppm; ₁³C NMR (126 MHz, CDCl₃): 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 ppm; HRMS (EI) calcd for C₁₆H₁₉OS⁺ [(M + H)⁺]: 259.1151, found: 259.1146; IR (ATR) ν = 2854 (w), 1452 (m), 1362 (m), 1279 (m), 1239 (s), 1189 (s), 1108 (s), 1089 (m), 1048 (m), 1027 (m), 831 (m), 826 (m), 734 (s), 693 (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 H₂ 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. Rₘ = 0.58 (cyclohexane); ¹H NMR (500 MHz, CDCl₃): δ = 6.63 (s, 2H), 7.18-7.27 (m, 10H) ppm; ₁³C NMR (126 MHz, CDCl₃): δ = 127.5, 128.6, 129.2, 130.6, 137.8 ppm; HRMS (EI) calcd for C₁₅H₁₄O⁺ [(M⁺)]: 211.1117, found: 211.1124. The data is in accordance with literature.²²

(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 H₂ 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. Rₘ = 0.64 (cyclohexane/tert-butyl methyl ether 10:1); ¹H NMR (500 MHz, CDCl₃): δ = 3.77 (s, 3H), 6.54 (m, 2H), 6.75 (m, 2H), 7.17-7.27 (m, 7H) ppm; ₁³C NMR (126 MHz, CDCl₃): 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 (EI) calcd for C₁₃H₁₀O⁺ [(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 H₂ 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. Rₘ = 0.67 (pentane); ¹H NMR (500 MHz, CDCl₃): δ = 6.54 (d, J = 12.2 Hz, 1H), 6.64 (d, J = 12.2 Hz, 1H), 7.17-7.20 (m, 4H), 7.22-7.27 (m, 5H) ppm; ₁³C NMR (126 MHz, CDCl₃): 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 C₁₄H₁₁O⁺ [(M + Cl)⁺]: 179.0855, found: 179.0857. The data is in accordance with literature.²²

(Z)-1-(Hept-4-1-xylo)methylbenzene (4n)

Prepared from 3n (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 H₂ atmosphere (100 bar) at 60 °C for 24 h. Purification via flash column chromatography on silica gel using cyclohexane/tert-butyl methyl ether 100:1 as eluent afforded 4n (47 mg, 0.23 mmol, 90%) as a colorless oil. Rₘ = 0.79 (cyclohexane/tert-butyl methyl ether 10:1); ¹H NMR (700 MHz, CDCl₃): δ = 0.96 (t, J = 7.5 Hz, 3H), 1.68 (m, 2H), 2.26 (m, 2H), 3.49 (t, J = 6.5 Hz, 2H), 4.51 (s, 2H), 5.53 (dt, J = 10.8 Hz, J = 7.2 Hz,
Prepared from 5 (53 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 H₂ atmosphere (80 bar) at 40 °C for 19 h. Purification by filtration through a plug of silica (3 cm) using cyclohexane as eluent afforded 6 (46 mg, 0.22 mmol, 87%) as a white crystalline solid. ¹H NMR (500 MHz, CDCl₃): δ = 6.71 (m, 2H), 7.00 (mε, 2H), 7.23–7.26 (m, 2H), 7.35 (mε, 4H), 7.46–7.47 (m, 4H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 126.8, 128.0, 129.1, 133.2, 137.8 ppm; HRMS (EI) calcd for C₁₆H₁₄O₂⁺ ([M⁺]+): 206.1090, found: 206.1091. The data is in accordance with literature.²²

(1Z,3E)-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 H₂ 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 ¹H NMR. Rᵣ = 0.41 (cyclohexane); ¹H NMR (500 MHz, CDCl₃): 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; ¹³C NMR (126 MHz, CDCl₃): 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 C₁₆H₁₄⁺ ([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, 19 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 H₂O (10 mL). The aqueous phase was extracted with tert-butyl methyl ether (2 × 10 mL) and the combined organic layers were dried over Na₂SO₄. 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. Rᵣ = 0.35 (cyclohexane/tert-butyl methyl ether 1:1); ¹H NMR (500 MHz, CDCl₃): δ = 1.64 (br s, 1H), 1.70 (mε, 2H), 2.21 (mε, 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), 6.53–6.58 (m, 1H), 7.27–7.31 (m, 1H), 7.32–7.37 (m, 4H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 24.0, 29.4, 58.5, 69.3, 73.0, 127.6, 127.7, 128.5, 130.7, 133.9, 138.5 ppm; HRMS (ESI) calcd for C₁₅H₁₂O₂⁺ ([M⁺]+): 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-en-1-ol (9)

In a flame dried Schlenk tube (15 mL) equipped with a magnetic stirring bar 4p (0.70 g, 19 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (0.15 M, 3.2 mL) and DMP (0.29 g, 6.68 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. Rᵣ = 0.41 (cyclohexane/tert-butyl methyl ether 3:1); ¹H NMR (500 MHz, CDCl₃): δ = 1.82 (mε, 2H), 2.73 (mε, 4H), 3.52 (d, J = 6.1 Hz, 2H), 4.49 (s, 2H), 5.79 (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; ¹³C NMR (126 MHz, CDCl₃): δ = 24.9, 29.3, 68.9, 73.2, 127.8, 128.6,
130.7, 138.3, 152.5, 191.1 ppm; HRMS (EI) calc. for C_{13}H_{16}O_{2}^+ ([M]^+): 204.1145, found: 204.1144; IR (ATR) ν = 2858 (m), 1767 (s), 1452 (m), 1363 (m), 1099 (s), 1027 (m), 736 (s), 697 (s), 608 (m) cm⁻¹.

Ethyl (2E,4Z)-8-(benzylxoy)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. NH₄Cl (4 mL). The mixture was warmed to rt and stirred for 22 h. The reaction was quenched by addition of sat. aq. NH₄Cl (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 Na₂SO₄. All volatiles were removed under reduced pressure. Purification via flash 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.

1H NMR (500 MHz, CDCl₃): δ = 1.29 (t, J = 7.1 Hz, 3H), 1.74 (mc, 2H), 2.42 (mc, 2H), 3.49 (t, J = 7.1 Hz, 2H), 4.50 (s, 2H), 5.85 (dt, J = 11.2 Hz, 3H, 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; 13C NMR (126 MHz, CDCl₃): δ = 14.4, 25.1, 29.5, 60.4, 69.5, 73.2, 121.7, 127.1, 127.7, 128.7, 128.8, 136.8, 139.6, 140.7, 167.3 ppm; HRMS (EI) calc. for C_{13}H_{18}O_{2}^+ ([M]^+): 215.1564, found: 215.1751; 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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