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Ruthenium-Catalyzed *E*-Selective Alkyne Semi-Hydrogenation with Alcohols as Hydrogen Donors

Andreas Ekebergh, Romain Begon and Nina Kann*

Chemistry and Biochemistry, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden

semi-hydrogenation, ruthenium, alkyne, E-alkene, alcohol, hydrogen borrowing, amine alkylation

ABSTRACT: Selective direct ruthenium-catalyzed semi-hydrogenation of diaryl alkynes to the corresponding *E*-alkenes has been achieved using alcohols as the hydrogen source. The method employs a simple ruthenium catalyst, does not require external ligands and affords the desired products in >99% NMR yield in most cases (up to 93% isolated yield). Best results were obtained using benzyl alcohol as the hydrogen donor, although biorenewable alcohols such as furfuryl alcohol could also be applied. In addition, tandem semi-hydrogenation – alkylation reactions were demonstrated, with potential applications in the synthesis of resveratrol derivatives.

Introduction

The alkene motif is present in a variety of important molecules, including natural products, pharmaceuticals and fragrances (Figure 1).[1] Stereoselective installation of this functionality therefore remains central to organic synthesis. Semi-hydrogenation of alkynes is a natural synthetic transformation to obtain alkenes. However, *E*-selective alkyne semi-hydrogenations have historically been more difficult to achieve than *Z*-selective. The former transformation has typically been limited to alkynes bearing alcohols, amines or ketones in the propargylic position, generally requiring stoichiometric reagents,[2] or proceeding via two-step methods such as *trans*-hydrosilylation followed by protodesilylation.[3]

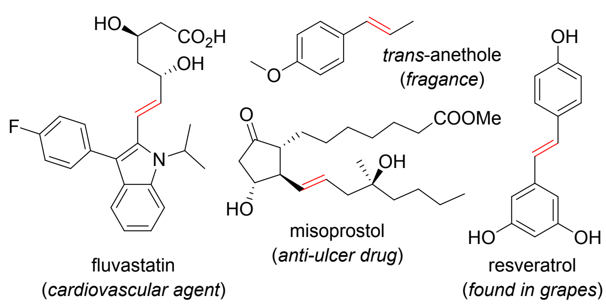
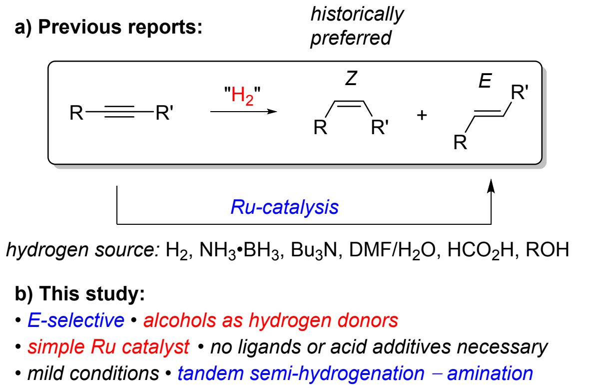


Figure 1. Selected *E*-alkenes.

Lately, hydrogenation based on homogeneous transition metal catalysis has begun to offer a remedy to these limitations.[2] For example iron,[4] cobalt,[5] nickel,[6] palladium,[7] manganese,[8] and iridium[9] have been used to obtain alkenes from alkynes with *E*-selectivity. In particular, an iridium-catalyzed method for alkyne semi-hydrogenation recently reported by Yang et al. deserves highlighting,[9a] as it allows the selective formation of either the *E*- or the *Z*-alkene isomer simply by adding a bulkier ligand (COD) to the reaction system in the latter case. In addition, an inexpensive and sustainable alcohol (ethanol) is used as the hydrogen source.

A few accounts of direct ruthenium-based *E*-selective semi-hydrogenations of alkynes have also been published in the last decade (Scheme 1).[10] Several of the reported ruthenium systems require elevated temperatures (145-180 °C),[10c, 10h] or stoichiometric or excess amounts of organic acids (1-50 equivalents).[10c, 10k] Despite displaying good substrate scope in the presence of other reductive-sensitive functional groups, these harsh reaction conditions could limit the utility of these methods. Milder methods for semi-hydrogenations based on ruthenium have recently been described.[10d, 10j] Fürstner and co-workers used high pressures of dihydrogen (10 bar) with silver triflate as additive at ambient temperatures,[10d] or propargylic alcohols as substrates at lower pressures (1 bar),[10l] while Lindhardt recently published a method proceeding at 45 °C with dihydrogen generated *in situ* in a closed two-chamber system.[10j] Djukic et al. have shown that μ-chlorido, μ-hy droxobridged ruthenacycles can effect the hydrogenation of triple bonds using isopropanol as the hydrogen donor at 90 °C,[10b] while Gelman has reported an elegant semi-hydrogenation of alkynes involving ligand-metal cooperation as the mode of action, using a ruthenium catalyst and a mixture of formic acid and sodium formate as the hydrogen source.[10i]

Scheme 1. Ruthenium-catalyzed methods for alkyne semi-hydrogenation to *E*-alkenes.



By adding D_2O, this procedure could also be applied towards deuterium labelling.

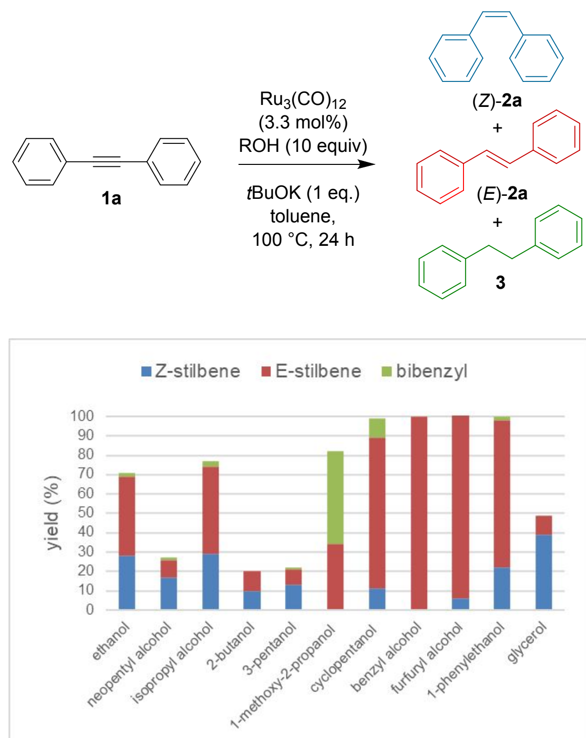
While conducting a ruthenium catalyzed 'borrowing hydrogen' reaction involving alcohols and amines in the presence of an alkyne functionality,[11] we noticed that small amounts of the corresponding alkene were formed. We envisioned that a transfer hydrogenation between the alcohol and the alkyne competed with the borrowing hydrogen reaction to a minor extent. Indeed, in 1981, Shvo and co-workers presented a ruthenium catalyzed oxidative ester formation from alcohols using diphenylacetylene as a hydrogen acceptor.[10a] Despite recent reports on alkyne semi-hydrogenations, the scope of ruthenium catalyzed transfer hydrogenation between alcohols and alkynes has, to the best of our knowledge, not been investigated in detail.[10b] We herein present a relatively mild semi-hydrogenation of alkynes which can be performed without the necessity of external ligands or stoichiometric amounts of organic/inorganic acids or bases. The procedure performs well with diaryl acetylenes and is experimentally facile, using only commercially available reagents and without the need for any special equipment.

Results and Discussion

For the initial investigation of the transfer hydrogenation between alcohols and alkynes, diphenylacetylene (**1a**) was used as a model substrate (Scheme 2). A selection of different alcohols were screened for efficiency, *E*/*Z*-selectivity and their ability to avoid over-reduction. The reaction was performed in the presence of a simple ruthenium catalyst, $Ru_3(CO)_{12}$, and initially with stoichiometric amounts of *t*BuOK as base, using toluene as the solvent and heating the reactions in a heating block. Experiments were analyzed by ^{1}H NMR using 2,5-dimethylfuran as internal standard.[12] Of the screened hydrogen donors, benzylic alcohols (benzyl and furfuryl alcohol, 1-phenylethanol) stood out both in terms of selectivity and efficiency. In particular, benzyl alcohol produced *E*-stilbene ((*E*)-**2a**) with 100% selectivity over *Z*-stilbene ((*Z*)-**2a**) whilst only generating ~ 2% bibenzyl (**3**) via over-reduction. A number of other alcohols also displayed good compatibility with the reaction. Cyclopentanol generated the semi-hydrogenation product in good yields, with only minor overreduction, while longer non-cyclic secondary aliphatic alcohols (2-butanol, 3-pentanol) reacted sluggishly. Isopropyl alcohol and ethanol both showed a good conversion to alkene, while the more hindered neopentyl alcohol and glycerol reacted slowly. Interestingly, the reactivity of isopropyl alcohol could be greatly enhanced by introducing a methoxy group in the 1-position, generating a substantial amount of bibenzyl. Control experiments were also performed. Excluding base from the reaction significantly lowered the efficiency, affording 13% of (*Z*)-**2a** and no other products. The alcohol and catalyst, as expected, proved to be essential to the reaction, with no products formed in their absence.

While benzyl alcohol outperformed the other hydrogen donors, the generation of reactive benzaldehyde *in situ* could under some circumstances be problematic due to its potential reactivity with nucleophiles. Isopropyl alcohol, on the other hand, forms acetone, which is less prone to adduct formation with nucleophiles. Additionally, compared to benzyl alcohol and benzaldehyde, both isopropyl alcohol and acetone can be easily removed through evaporation, thus expediting the purification of the product. Further optimization was thus performed using isopropyl alcohol as the hydrogen donor, aiming to improving the *E*/*Z*-selectivity and yield.

Scheme 2. Screening of alcohols as hydrogen donors for Ru-catalyzed alkyne hydrogenation.[a]



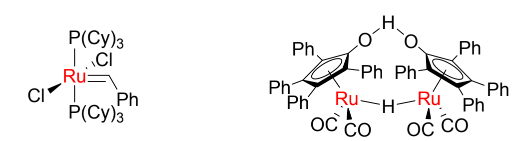
[a]NMR yield (2,5-dimethylfuran as internal standard). Reactions were heated in a heating block.

In addition to $Ru_3(CO)_{12}$, nine other commercially available ruthenium catalysts were screened using isopropyl alcohol as the hydrogen donor (Table 1). The reactivity of the catalysts varied from very low when using $RuCl_3$ (entry 2), Cp*RuCl(COD) (entry 5) or the Shvo catalyst (entry 9 and Figure 2), to being higher but unselective for the semi-hydrogenation product when $RuCl_2(PPh_3)_3$ was employed (entry 7). The Grubbs 1st generation catalyst (Figure 2) gave the fully reduced bibenzyl product **3** with nearly complete selectivity in a good yield (entry 4). However, our interest lay in the selective semi-hydrogenation to form the (*E*)-**2a**. In this context, catalyst $RuCl_2(DMSO)_4$ displayed good properties, with a combined yield of 91% and 6:1 in terms of the *E/Z* selectivity (entry 3). $RuCl(CO)H(PPh_3)_3$ also performed well, affording only (*E*)-**2a** in a good yield, albeit with some concomitant over-reduction to **3** (entry 6). Viable catalysts for the *E*-selective semi-hydrogenation of diphenylacetylene, using isopropyl alcohol as the hydrogen donor, were thus found to be $Ru_3(CO)_{12}$, $RuCl_2(DMSO)_4$ and $RuCl(CO)H(PPh_3)_3$. $RuCl_2(DMSO)_4$ was selected for further studies when using isopropyl alcohol as the hydrogen donor.

Table 1. Catalyst screening in the Ru-catalyzed reduction of phenylacetylene (**1a**).[a]

entry	catalyst	yield[b] **2** (%)	*E:Z* 2	yield[b] **3** (%)
1	$[Ru(p\text{-cymene})Cl_2]_2$	30	1:1	3
2	$RuCl_3$	4	3:1	0
3	$RuCl_2(DMSO)_4$	91	6:1	10
4[c]	Grubbs catalyst	3	1:0	75
5	Cp*RuCl(COD)	4	3:1	o
6	$RuCl(CO)H(PPh_3)_3$	69	1:0	13
7	$RuCl_2(PPh_3)_3$	28	1:0	39
8	$Cp^*RuCl(PPh_3)_3$	18	8:1	o
9[c]	Shvo catalyst	8	7:1	o
10	$Ru_3(CO)_{12}$	74	1.5:1	3

[a]Reaction and conditions as in Scheme 2, but with different catalysts. Isopropyl alcohol was used as the hydrogen donor. Catalyst amount corresponds to 10 mol% Ru. [b]NMR yield (2,5-dimethylfuran as internal standard). [c]See Figure 2.



Grubbs 1st generation catalyst   Shvo catalyst

Figure 2. Structures of the Grubbs 1st generation and Shvo catalysts.

With two catalyst systems in hand, i.e. $Ru_3(CO)_{12}$/benzyl alcohol and $RuCl_2(DMSO)_4$/*i*PrOH, further studies concerning the loading of catalyst, base and hydrogen donor were performed (Table 2). For $Ru_3(CO)_{12}$/benzyl alcohol, using a catalyst amount corresponding to 2 mol% Ru and reducing the amount of base to 0.2 equivalents did not affect the yield (entries 1 and 4), while lowering the amount of alcohol (entry 5) or temperature (entry 6) had a negative effect on the yield as well as the *E/Z* selectivity. Interestingly, reducing the amount of catalyst while maintaining the base at 1 equivalent decreased the yield of the alkene (entry 2). Hence, the activity of the catalyst is related to the relative amount of base. The same behavior was observed when using 5 mol% catalyst (entry 3). $RuCl_2(DMSO)_4$/*i*PrOH was also evaluated, but displayed a much slower reaction rate. Reducing the amount of catalyst, base and alcohol dramatically reduced the yield within the investigated time frame of 24 h (entries 7-10).

Table 2. Optimization of reaction conditions using phenylacetylene (**1a**).[a]

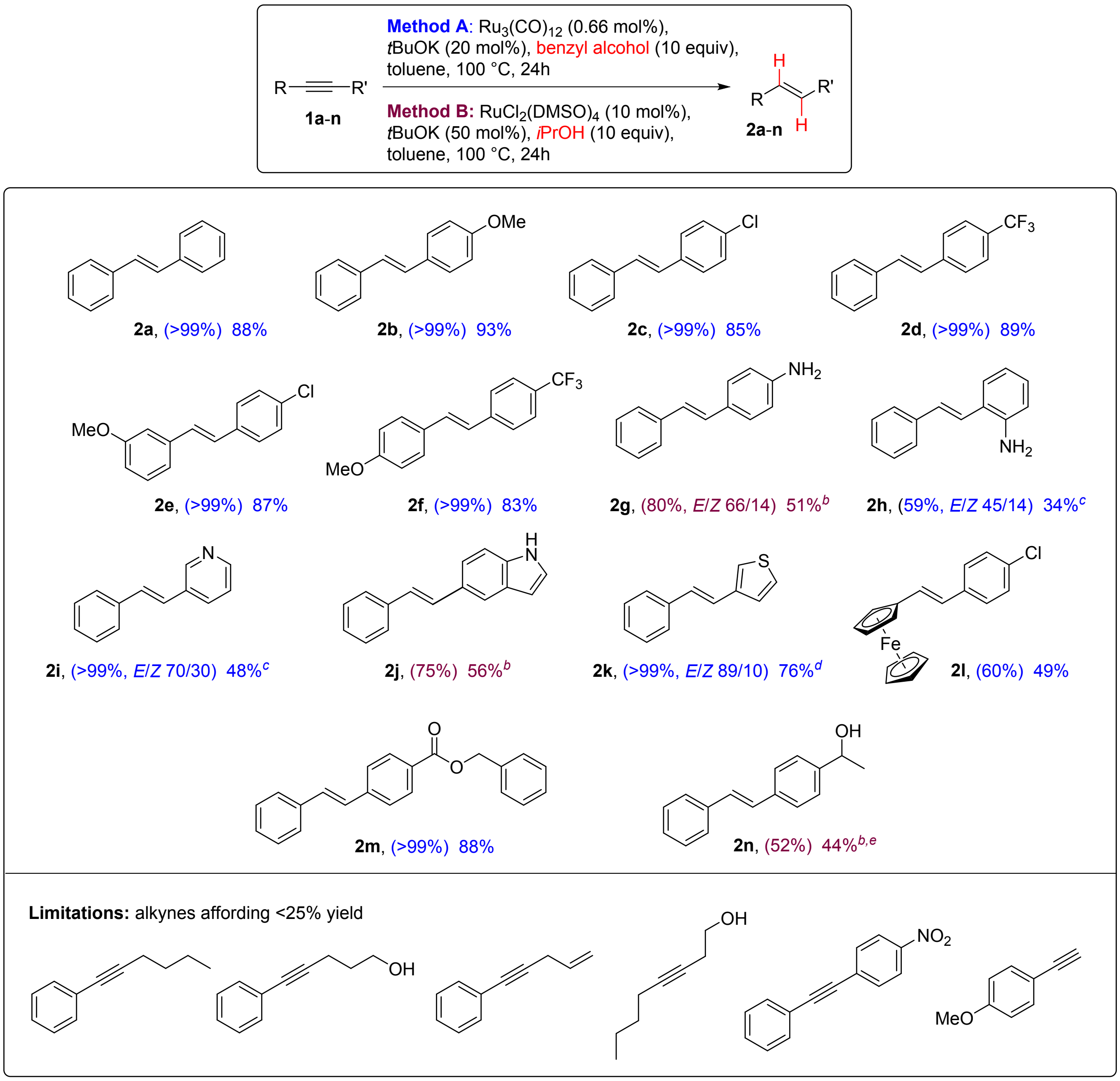
entry	catalyst (mol% Ru)	*t*BuOK (equiv)	yield[b] **2** (%)	*E:Z* **2**
1[c]	$Ru_3(CO)_{12}$ (10)	1	>99	1:0
2[c]	$Ru_3(CO)_{12}$ (2)	1	93	1:0[d]
3[c]	$Ru_3(CO)_{12}$ (5)	1	89	1:0
4[c]	$Ru_3(CO)_{12}$ (2)	0.2	>99	1:0
5[c,e]	$Ru_3(CO)_{12}$ (2)	0.2	17	1:2.4
6[c,f]	$Ru_3(CO)_{12}$ (2)	0.2	79	2.3:1
7[g]	$RuCl_2(DMSO)_4$ (10)	1	91	6:1
8[g]	$RuCl_2(DMSO)_4$ (2)	1	19	1:1
9[g]	$RuCl_2(DMSO)_4$ (2)	0.2	19	1:1
10[e,g]	$RuCl_2(DMSO)_4$ (2)	0.2	5	4:1

[a]Reactions performed at 100 °C (heating block) with 10 equivalents hydrogen donor for 24 h unless otherwise indicated. Only trace bibenzyl (**3**) formed unless otherwise indicated. [b]NMR yield (2,5-dimethylfuran as internal standard). [c]Benzyl alcohol as hydrogen donor. [d]4% bibenzyl (**3**) formed. [e]2 equivalents hydrogen donor. [f]Reaction performed at 80 °C. [g]Isopropyl alcohol as hydrogen donor.

The optimized conditions for $Ru_3(CO)_{12}$/benzyl alcohol (Method A) were then applied to a series of alkynes (**1a-n**, Scheme 3) to investigate the scope. Diaryl acetylenes with varying electronic properties were well tolerated and formed their corresponding hydrogenated *E*-isomers selectively, with close to quantitative conversion (as determined by ^{1}H NMR) and high isolated yields (compounds **2a-f**). Electron rich compounds such as **1c** reacted slightly slower and longer reaction times were needed to achieve full conversion. Primary amines and pyridines (**1g-i**) proved to be more challenging substrates. The hydrogenation of the *p*-amino derivative proceeded sluggishly under the standard conditions. Increasing the catalytic loading fourfold gave a satisfactory hydrogenation yield, accompanied, however, by the formation of substantial amounts of another compound (Scheme 4). Interestingly, further analysis showed that this compound resulted from a hydrogen borrowing process[13] between benzaldehyde, formed *in situ* from the benzyl alcohol hydrogen donor and the primary amine, to form an intermediate imine that could be reduced to the corresponding amine **4** (Scheme 4) using a second equivalent of hydrogen. The fact that a concomitant semi-hydrogenation – amine alkylation process is feasible is not surprising, as $Ru_3(CO)_{12}$ has been employed for the direct amination of alcohols via hydrogen borrowing under similar conditions.[14] This tandem process could potentially be applied towards the synthesis of resveratrol derivatives such as **5**, reported as a promising lead compound for the treatment of Alzheimer's disease.[15] Switching to different reaction conditions, utilizing *i*PrOH as hydrogen donor with $RuCl_2(DMSO)_4$ as the catalyst

(Method B), suppressed the competing hydrogen borrowing reaction, allowing isolation of alkene **2g** in a moderate yield. The more sterically challenging *ortho*-amine could be reduced using Method A, but required a higher catalytic loading to proceed (compound **2h**). In this case, the hydrogen borrowing product was not observed, most likely owing to the more hindered position of the amino group in the substrate. Similarly to the other nitrogen-containing compounds, 3-(phenylethynyl)pyridine also required a higher catalytic loading and also a longer reaction time, but afforded **2i** in a high NMR yield. The lack of reactivity is most likely due to deactivation of the catalyst through coordination by the nitrogen. This could also explain the lack of reports on the ruthenium-catalyzed semi-hydrogenation of aniline-containing compounds. The protons ortho to the nitrogen displayed broad signals in ^{1}H NMR after completion of the reaction, indicating coordination. The stability of this

Scheme 3. Scope of the semi-hydrogenation reaction.[a]

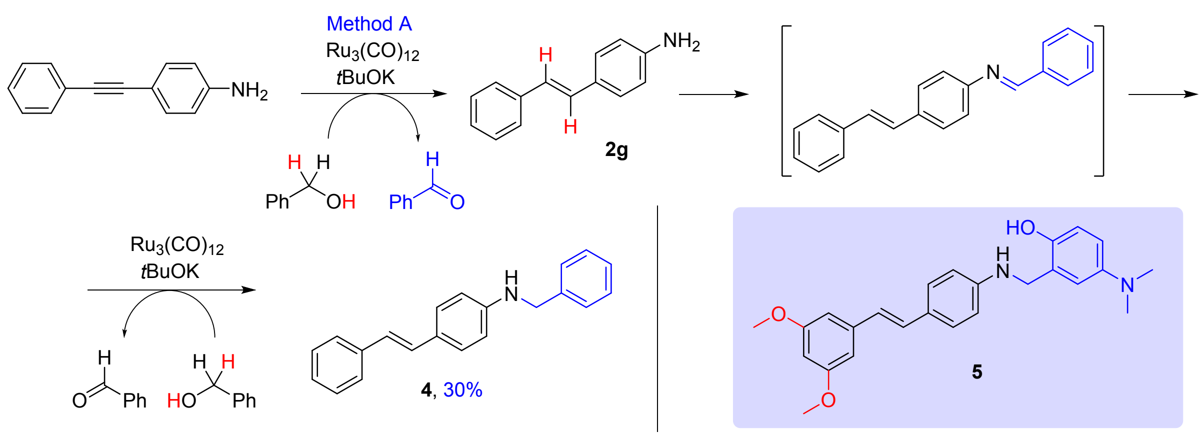


[a]Prepared using method A unless otherwise stated; reactions were heated in a heating block. See SI for deviations in terms of reaction time. Yields in parentheses refer to NMR yields of *E*-alkene (for **2g-i** and **2k** a mixture of *E* and *Z* alkenes). Isolated yields refer to *E* alkene only. [b]Prepared using Method B. See SI for deviations in terms of reaction time. Product **2n** is a result of semihydrogenation with concomitant reduction of the carbonyl group. [c]3.33 mol% $Ru_3(CO)_{12}$ used. [d]Product contains 3% of the (*Z*)-isomer.[e]20 mol% $RuCl_2(DMSO)_4$ used.

interaction was further validated as it was maintained even after column chromatography on silica. The ruthenium could be removed by chromatography on amine-functionalized silica, supplying pure semi-hydrogenation product with some loss in yield due to the more elaborate purification required. Other heterocyclic alkyne substrates were more successful, with indole- and thiophene-derivatives **2j** and **2k** formed in 56% and 76% yields, respectively. A ferrocenyl-substituted

E-alkene (**2l**) could be obtained in moderate yield, while appending an ester substituent to diphenyl acetylene was unproblematic (**2m**), although transesterification occurs if the corresponding methyl ester is used as precursor instead. Exchanging the ester for a ketone gave interesting results. Method A afforded the benzylated ketone **6** (Fig. 3), instead of the expected semi-hydrogenation product. This product is most likely also the result of a hydrogen borrowing-type mechanism (as for **4**), but in this case involving carbon-carbon bond formation instead of amine alkylation. Method B instead effected concomitant alkyne semi-hydrogenation and transfer hydrogenation of the ketone, producing alcohol **2n** in a moderate yield. In terms of limitations of the reaction, alkyl/aryl substituted alkynes as well as dialkylacetylenes were unsuccessful, showing both low reactivity as well as the formation of byproducts. Analysis of the crude products by ^{1}H NMR showed that while some alkene was formed in the reaction, double bond isomerization had also occurred,

Scheme 4. Tandem alkyne semi-hydrogenation and direct amine alkylation.



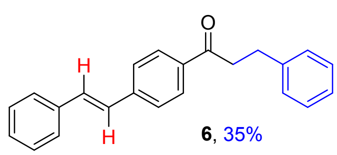


Figure 3. Product of tandem alkyne semi-hydrogenation and ketone alkylation (Method A).

resulting in a mixture of products. In addition, while a *p*-CF_3 substituent on diphenylacetylene was well tolerated (**2d**), the corresponding *p*-NO_2 compound afforded a complex mixture, where some concomitant reduction of the nitro group had taken place. Terminal alkynes such as 1-ethynyl-4-methoxybenzene afforded a complex mixture, with only trace amounts of products.

The reaction could be monitored over time using ^{1}H NMR, which revealed an initial hydrogenation to form the *Z*-isomer that underwent an isomerization process to the *E*-isomer (Figure 4). This observation is in line with previous reports.[10c, 10k, 16]

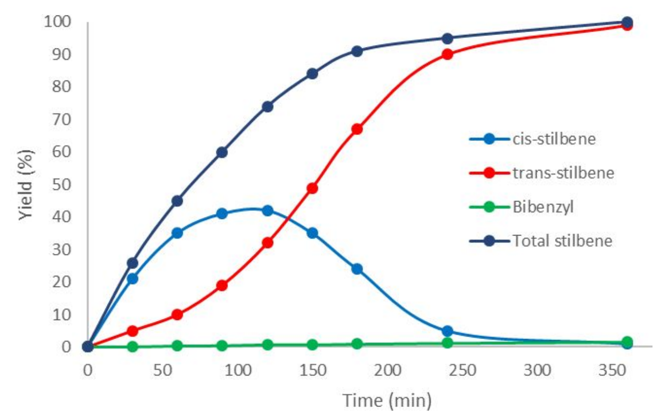
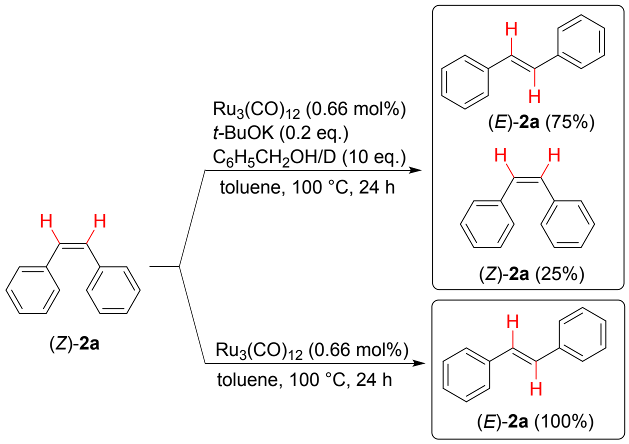


Figure 4. Compound distribution over time.

The isomerization was further investigated by subjecting *cis*-stilbene to the standard reaction conditions in the presence of deuterated benzyl alcohol (Bn-OD). *Z*-Stilbene ((*Z*)-**2a**) was isomerized into *E*-stilbene ((*E*)-**2a**) under these conditions, but without incorporation of deuterium (Scheme 5). This observation differs from the recent study by Lindhardt and co-workers,[10j] in which they found that isomerization of (*Z*)-**2a** in presence of a ruthenium catalyst and D_2 results in incorporation of deuterium at the alkenylic positions. We further found that the isomerization to (*E*)-**2a** occurred in the presence of the catalyst alone. These results indicate that the isomerization process does not proceed *via* a hydrogenation/rotation/β-hydride elimination route. No isomerization was observed when omitting the catalyst while including the other reactants. Both benzaldehyde and benzyl benzoate were observed as side products after the transfer-hydrogenation reaction. Benzyl benzoate is likely formed *via* a second reaction between benzaldehyde and benzyl alcohol with subsequent oxidation, as previously reported by Shvo.[10a]

Scheme 5. Investigation of the isomerization process.



Conclusion

In conclusion, a methodology for the selective semi-hydrogenation of diaryl alkynes to *E*-alkenes was developed, involving the use of a simple Ru-catalyst, a low catalyst loading, ligand-free conditions and alcohols as the source of hydrogen. While benzyl alcohol gave the most favourable *E*-selectivity and conversion, renewable alcohols such as furfuryl alcohol could also be applied as hydrogen donors with good results. A tandem semi-hydrogenation − amine alkylation reaction, the latter via hydrogen borrowing, was also demonstrated, using 4-(phenylethynyl)aniline (**1g**) as the substrate. Reaction monitoring indicates that the high *E*-selectivity in the semi-hydrogenation is due to isomerization of initially formed *Z*-alkene by the catalyst, rather than a result of the semi-hydrogenation process itself.

Experimental Section

General Remarks. All reactions were carried out under argon atmosphere with dry solvents in oven dried glassware, unless otherwise noted. Toluene, triethylamine (Et_3N), ethanol (EtOH), ethyl acetate (EtOAc) and petroleum ether were bought from commercial vendors. Toluene was purchased in anhydrous form and used without further purification. Et_3N was dried over molecular sieves (3Å). EtOH, EtOAc and petroleum ether were used as received. Reagents as well as alkynes **1a** and **1c** were purchased from commercial vendors and used as received, unless otherwise stated. For the Sonogashira reaction, oxygen free Et_3N was obtained by bubbling argon through the solvent for 15 min. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm 2 E. Merck silica gel plates (60F-254) using UV light as visualizing agent. Flash chromatography was performed on a Biotage Isolera One using Biotage KP-Sil columns (packed with 50µm irregular silica) using 254 nm and 280 nm UV-light for monitoring. NMR spectra were recorded on samples in deuterated chloroform ($CDCl_3$) or DMSO (DMSO-d_6) on an Agilent 400 MHz (101 MHz for ^{13}C) instrument. Residual undeuterated chloroform (^1H: δ = 7.26 ppm, ^{13}C: δ = 77.2 ppm) or DMSO (^1H: δ = 2.50 ppm, ^{13}C: δ = 39.5 ppm) were used as internal reference. The following abbreviations, or a combination thereof, were used to characterize the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Melting points (mp) were recorded on a Mettler FP 90/82 melting point apparatus and are uncorrected. IR spectra were recorded with a PerkinElmer Spectrum ONE FT-IR spectrometer using KBr pellet sample preparation. High-resolution mass determinations were obtained with an Agilent QTOF 6520 with Infinity UHPLC and electrospray ionization.

General procedure for the preparation of internal alkynes 1b and 1d-n *via* Sonogashira reaction. Arylhalide, bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) and copper(I) iodide (CuI) (see each compound for amounts) were transferred to a dry 20 mL Biotage microwave reaction vial equipped with a cross-shaped magnetic stirring bar. The vial was sealed using a cap with septum, evacuated of air and refilled with argon (3 cycles). The alkyne and dry deoxygenated Et_3N were thereafter transferred to the vial. The obtained mixture was further deoxygenated by bubbling argon through for 5 min while stirring. The argon inlet was removed and the reaction was heated in a Radleys HeatOn™ block to 80 °C for indicated amount of time. The reaction was cooled to room temperature and concentrated under reduced pressure. The crude product was taken up in approximately 5 ml CH_2Cl_2 and the slurry was transferred to a 3g Biotage KP-Sil samplet. After allowing the samplet to dry it was transferred to a 25 g column and purified by flash chromatography.

*1-Methoxy-4-(phenylethynyl)benzene (**1b**).*[17] The reaction was performed according to the general procedure using 4-iodoanisole (1.17 g, 5.0 mmol), $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), CuI (28 mg, 0.15 mmol), phenylacetylene (0.81 ml, 7.4 mmol) and Et_3N (13 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 95:5 (10 column volumes) -> 95:5 (10 column volumes). Product **1b** was obtained as a light orange crystalline solid (991 mg, 95%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.47 (XX' signal of AA'XX' spin system, 2H), 7.37 – 7.30 (m, 3H), 6.88 (AA' signal of AA'XX' spin system, 2H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.7, 133.2, 131.6, 128.4, 128.1, 123.7, 115.5, 114.1, 89.5, 88.2, 55.5.

*1-(Phenylethynyl)-4-(trifluoromethyl)benzene (**1d**).*[18] The reaction was performed according to the general procedure using 1-iodo-4-(trifluoromethyl)benzene (554 mg, 2.0 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol), CuI (7.6 mg, 0.04 mmol), phenylacetylene (0.26 ml, 2.4 mmol) and Et_3N (6 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (5 column volumes) ->85:15 (15 column volumes). Product **1d** was obtained as a white crystalline solid (512 mg, >99%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 4H), 7.58 – 7.52 (m, 2H), 7.41 – 7.35 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 132.0, 131.9, 130.0 (q, J = 32.7 Hz), 129.0, 128.6, 127.3 (q, J = 1.5 Hz), 125.4 (q, J = 3.8 Hz), 124.1 (q, J = 272.2 Hz), 122.7, 91.9, 88.1.

*1-((4-Chlorophenyl)ethynyl)-3-methoxybenzene (**1e**).*[19] The reaction was performed according to the general procedure using 4-bromochlorobenzene (957 mg, 5 mmol), $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), CuI (28 mg, 0.15 mmol), 3-ethynylanisole (0.94 ml, 7.4 mmol) and Et_3N (16 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (15 column volumes). Product **1e** was obtained as a white crystalline solid (573 mg, 47%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (XX' signal of AA'XX' spin system, 2H), 7.33 (AA' signal of AA'XX' spin system, 2H), 7.29 – 7.24 (m, 1H), 7.12 (ddd, J = 7.6, 1.5, 1.0 Hz, 1H), 7.05 (ddd, J = 2.7, 1.4, 0.4 Hz, 1H), 6.91 (ddd, J = 8.3, 2.6, 1.0 Hz, 1H), 3.83 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.5, 134.5, 133.0, 129.6, 128.8, 124.3, 124.0, 121.8, 116.5, 115.3, 90.4, 88.2, 55.5.

*1-Methoxy-4-((4-(trifluoromethyl)phenyl)ethynyl)-benzene (**1f**).*[20] The reaction was performed according to the general procedure using 1-iodo-4-(trifluoromethyl)benzene (272 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol), 4-ethynylanisole (0.13 ml, 1.02 mmol) and Et_3N (3 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 95:5 (20 column volumes) -> 95:5 (10 column volumes). Product **1f** was obtained as a white crystalline solid (264 mg, 96%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 4H), 7.49 (XX' signal of AA'XX' spin system, 2H), 6.90 (AA' signal of AA'XX' spin system, 2H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.2, 133.4, 131.7, 129.7 (q, J = 32.6 Hz), 127.6 (q, J = 1.5 Hz), 125.4 (q, J = 3.8 Hz), 124.2 (q, J = 272.1 Hz), 114.8, 114.2, 92.1, 87.0, 55.4.

*4-(Phenylethynyl)aniline (**1g**).*[21] The reaction was performed according to the general procedure using 4-iodoaniline (1.1 g, 5 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), phenylacetylene (0.66 ml, 6 mmol) and Et_3N (15 ml). Flash chromatography gradient: Petroleum ether/EtOAc 98:2 -> 93:7 (10 column volumes) -> 93:7 (10 column volumes) -> 4:1 (10 column volumes). Product **1g** was obtained as an orange crystalline solid (822 mg, 85%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.39 – 7.28 (m, 5H), 6.65 (AA' signal of AA'XX' spin system, 2H), 3.82 (br s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.8, 133.1, 131.5, 128.4, 127.8, 124.0, 114.9, 112.8, 90.2, 87.5.

*2-(Phenylethynyl)aniline (**1h**).*[22] The reaction was performed according to the general procedure using 2-iodoaniline (1.1 g, 5 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), phenylacetylene (0.66 ml, 6 mmol) and Et_3N (15 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (5 column volumes) -> 85:15 (15 column volumes). Product **1h** was obtained as a yellow crystalline solid (769 mg, 80%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.40 – 7.32 (m, 4H), 7.14 (ddd, J = 8.1, 7.4, 1.6 Hz, 1H), 6.75 – 6.70 (m, 2H), 4.28 (br s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.9, 132.2, 131.6, 129.8, 128.5, 128.3, 123.4, 118.1, 114.4, 108.0, 94.8, 86.0.

*3-(Phenylethynyl)pyridine (**1i**).*[23] The reaction was performed according to the general procedure using 3-bromopyridine (0.48 ml, 5 mmol), $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), CuI (28 mg, 0.15 mmol), phenylacetylene (0.81 ml, 7.4 mmol) and Et_3N (16 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 9:1 (10 column volumes) -> 9:1 (15 column volumes). Product **1i** was obtained as a light brown crystalline solid (546 mg, 61%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, J = 2.2, 0.9 Hz, 1H), 8.55 (dd, J = 4.9, 1.7 Hz, 1H), 7.81 (ddd, J = 7.9, 2.2, 1.7 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.40 – 7.35 (m, 3H), 7.29 (ddd, J = 7.9, 4.9, 0.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.4, 148.7, 138.6, 131.8, 129.0, 128.6, 123.2, 122.7, 120.6, 92.8, 86.1.

*5-(Phenylethynyl)-1H-indole (**1j**).*[24] The reaction was performed according to the general procedure using 5-iodoindole (1.22 g, 5 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), phenylacetylene (0.6 g, 6 mmol) and Et_3N (15 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (10 column volumes) -> 9:1 (20 column volumes) -> 9:1 (20 column volumes). Product **1j** was obtained as a light yellow crystalline solid (882 mg, 81%): ^1H NMR (400 MHz, DMSO-d_6) δ 11.35 (br s, 1H), 7.80 (dt, J = 1.5, 0.7 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.47 – 7.35 (m, 5H), 7.27 (dd, J = 8.4, 1.6 Hz, 1H), 6.48 (ddd, J = 2.9, 1.9, 0.9 Hz, 1H); $^{13}C\{^1H\}$ (101 MHz, DMSO-d_6) δ 135.7, 131.1, 128.7, 128.1, 127.6, 126.7, 124.3, 123.9, 123.2, 112.3, 111.9, 101.4, 91.6, 86.6.

*3-(Phenylethynyl)thiophene (**1k**).*[25] The reaction was performed according to the general procedure using 3-bromothiophene (815 mg, 5 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), phenylacetylene (0.6 g, 6 mmol) and Et_3N (15 ml). Flash chromatography: Petroleum ether (10 column volumes). Product **1k** was obtained as a clear oil that crystallized in matter of days (788 mg, 86%). The compound turns orange upon air exposure: ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 3H), 7.39 – 7.32 (m, 3H), 7.31 (dd, J = 5.0, 3.0 Hz, 1H), 7.21 (dd, J = 5.0, 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 131.7, 130.0, 128.7, 128.5, 128.4, 125.5, 123.3, 122.4, 89.0, 84.6.

*(4-Chlorophenylethynyl)ferrocene (**1l**).*[26] The reaction was performed according to the general procedure using 4-bromochlorobenzene (0.618 ml, 3.2 mmol), $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), CuI (28 mg, 0.15 mmol), ethynylferrocene (1.0 g, 4.8 mmol) and Et_3N (16 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 98:2 (10 column volumes) -> 98:2 (10 column volumes). Product **1l** was obtained as a red crystalline solid (634 mg, 61%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (XX' signal of AA'XX' spin system, 2H), 7.30 (AA' signal of AA'XX' spin system, 2H), 4.51 – 4.49 (m, 2H), 4.26 – 4.24(m, 7H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 133.7, 132.7, 128.7, 122.6, 89.6, 84.8, 71.6, 70.2, 69.2, 65.1.

*Benzyl 4-(phenylethynyl)benzoate (**1m**).* This compound was prepared in two steps via the corresponding methyl ester. *Step 1 – Sonogashira reaction:* Methyl 4-(phenylethynyl)benzoate[27] was first prepared according to the general procedure using methyl 4-iodoacetophenone (1.23 g, 5 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), phenylacetylene (0.61 g, 6 mmol) and Et_3N (15 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (10 column volumes) -> 95:5 (10 column volumes) -> 9:1 (5 column volumes) -> 9:1 (15 column volumes). Product was obtained as a light yellow crystalline solid (689 mg, 58%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (XX' signal of AA'XX' spin system, 2H), 7.59 (AA' signal of AA'XX' spin system, 2H), 7.57 – 7.52 (m, 2H), 7.40 – 7.34 (m, 3H), 3.93 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.7, 131.9, 131.6, 129.64, 129.59, 128.9, 128.6, 128.1, 122.8, 92.5, 88.8, 52.4. *Step 2 – transesterification:* A dry 5 ml reaction vial containing methyl 4-(phenylethynyl)benzoate (71 mg, 0.3 mmol), *t*BuOK (17 mg, 0.15 mmol), benzyl alcohol (0.31 ml, 3 mmol) and toluene (0.7 ml) was heated in a Radleys HeatOn™ block to 100 °C for 24 h under an atmosphere of argon. The reaction was cooled to room temperature and the toluene was evaporated under a stream of N_2. The resulting mixture was taken up in ~0.5 ml DCM and transferred to a 1g Biotage KP-Sil samplet. After allowing the samplet to dry it was transferred to a 10 g column and purified through flash chromatography. Gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (5 column volumes) -> 9:1 (25 column volumes). Product **1m** was obtained as a white crystalline solid: mp = 103 – 105°C; ν_{max}/cm^{-1} 3031 (C-H), 2958 (C-H), 2213 (C≡C), 1709 (C=O), 1604 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (XX' signal of AA'XX' spin system, 2H), 7.59 (AA' signal of AA'XX' spin system, 2H), 7.57 – 7.53 (m, 2H), 7.49 – 7.45 (m, 2H), 7.44 – 7.34 (m, 6H), 5.38 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.0, 136.0, 131.9, 131.6, 129.8, 129.6, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 122.8, 92.6, 88.8, 67.0; HRMS (ESI+ QTOF) calculated for $C_{22}H_{17}O_2$ [M + H]+ 313.1223, found 313.1221.

*1-(4-(Phenylethynyl)phenyl)ethan-1-one (**1n**)*.[28] The reaction was performed according to the general procedure using methyl 4-iodobenzoate (1.3 g, 5 mmol), $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), CuI (28 mg, 0.15 mmol), phenylacetylene (0.81 g, 7.4 mmol) and Et_3N (16 ml). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (5 column volumes) -> 99:1 (3 column volumes) -> 9:1 (11 column volumes). Product **1n** was obtained as an off-white crystalline solid (337 mg, 31%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (XX' signal of AA'XX' spin system, 2H), 7.61 (AA' signal of AA'XX' spin system, 2H), 7.58 – 7.52 (m, 2H), 7.41 – 7.34 (m, 3H), 2.60 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.4, 136.3, 131.8, 131.8, 128.9, 128.6, 128.4, 128.3, 122.7, 92.8, 88.7, 26.7.

Semi-hydrogenation of internal alkynes, Method A: To an oven-dried 5 ml Biotage microwave reaction vial equipped with a magnetic stirring bar was transferred alkyne, $Ru_3(CO)_{12}$ and *t*BuOK (see each compound for amounts). The vial was sealed with a Biotage cap and connected to a Schlenk-line. The atmosphere was evacuated and the vial was refilled with argon (3 cycles). Dry toluene and benzyl alcohol were subsequently transferred (no special precautions were taken to exclude air from these components). The Schlenk-connection was removed and the sealed system was heated in a Radleys HeatOn™ block to 100 °C. After being stirred at that temperature for an indicated period of time, the reaction was allowed to cool to room temperature and toluene was removed under a stream of N_2. The reported NMR-yields were obtained using 2,5-dimethylfuran as internal standard.[29] Everything was taken up in ~2 ml $CDCl_3$ and a ^{1}H-NMR was recorded (no of transients: 2, relaxation delay: 60s). The spectrum was phase corrected and baseline corrected before being integrated. The amount of product was calculated as previously described using the 2,5-dimethylfuran H_{Ar} peak at δ 5.87 ppm and appropriate product peaks. As an example, the hydrogenation of phenylacetylene with cyclopentanol as hydrogen donor can be found in the SI (Fig. S1). The $CDCl_3$ was after analysis evaporated and the crude mixture was taken up in ~1-3 ml DCM and transferred to either a 1 g or 3 g Biotage KP-Sil samplet. After drying the samplet was transferred to a 10 g or a 25 g column and purified through flash chromatography.

Method B: As for Method A but using $RuCl_2(DMSO)_4$ (10 mol%) as the catalyst, *i*PrOH (10 equivalents) as the hydrogen donor, and 50 mol% *t*BuOK as the base.

*(E)-Stilbene ((E)-**2a**)*.[30] The reaction was performed according to Method A using diphenylacetylene (107 mg, 0.60 mmol), $Ru_3(CO)_{12}$ (2.6 mg, 0.004 mmol), *t*BuOK (14 mg, 0.12 mmol), benzyl alcohol (0.62 ml, 6.0 mmol) and toluene (1.4 ml) with a reaction time of 24 h. NMR-yield (*E/Z* %): 100/0. Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (10 column volumes). Product (*E*)-**2a** was obtained as a white crystalline solid (95 mg, 88 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 4H), 7.42 – 7.35 (m, 6H), 7.31 – 7.25 (m, 1H), 7.12 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.5, 128.8 (2 signals overlap), 127.8, 126.6.

*(E)-1-Methoxy-4-styrylbenzene (**2b**)*.[6] The reaction was performed according to Method A using 1-methoxy-4-(phenylethynyl)benzene (187 mg, 0.90 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol), *t*BuOK (20 mg, 0.18 mmol), benzyl alcohol (0.93 ml, 9.0 mmol) and toluene (2.1 ml) with a reaction time of 44 h. NMR-yield (*E/Z* %): 100/0. Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 95:5 (20 column volumes) -> 95:5 (10 column volumes). Product **2b** was obtained as an off white crystalline solid which was contaminated with 11 % benzyl benzoate (198 mg total, 177 mg only considering product, 93%). An analytically pure sample could be obtained through recrystallization from EtOH: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.47 (XX' signal of AA'XX' spin system, 2H), 7.36 (dd, J = 8.4, 6.9 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.09 (d, J = 16.3 Hz, 1H), 6.99 (d, J = 16.3 Hz, 1H), 6.92 (AA' signal of AA'XX' spin system, 2H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 137.8, 130.3, 128.8, 128.3, 127.9, 127.3, 126.7, 126.4, 114.3, 55.5.

*(E)-1-Chloro-4-styrylbenzene (**2c**)*.[10j] The reaction was performed according to Method A using 1-chloro-4-(phenylethynyl)benzene (128 mg, 0.60 mmol), $Ru_3(CO)_{12}$ (2.6 mg, 0.004 mmol), *t*BuOK (14 mg, 0.12 mmol), benzyl alcohol (0.62 ml, 6.0 mmol) and toluene (1.4 ml) with a reaction time of 42 h. NMR-yield (*E/Z* %): 100/0. Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 95:5 (10 column volumes) -> 95:5 (10 column volumes). Product **2c** was obtained as a white crystalline solid (109 mg, 85 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.45 (XX' signal of AA'XX' spin system, 2H), 7.42 – 7.36 (m, 2H), 7.34 (AA' signal of AA'XX' spin system, 2H), 7.32 – 7.27 (m, 1H), 7.10 (d, J = 16.4, 1H), 7.05 (d, J = 16.4, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 136.0, 133.3, 129.4, 129.0, 128.9, 128.0, 127.8, 127.5, 126.7.

*(E)-1-Styryl-4-(trifluoromethyl)benzene (**2d**)*.[31] The reaction was performed according to Method A using 1-(2-phenylethynyl)-4-(trifluoromethyl)benzene (195 mg, 0.79 mmol), $Ru_3(CO)_{12}$ (3.4 mg, 0.005 mmol), *t*BuOK (18 mg, 0.16 mmol), benzyl alcohol (0.82 ml, 7.9 mmol) and toluene (1.8 ml) with a reaction time of 24 h. NMR-yield (*E/Z* %): ~100/0 (product peaks overlap with benzyl alcohol, rendering exact measurement difficult). Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (5 column volumes) -> 99:1 (5 column volumes). Product **2d** was obtained as a white crystalline solid (175 mg, 89 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 4H), 7.58 – 7.54 (m, 2H), 7.44 – 7.39 (m, 2H), 7.37 – 7.31 (m, 1H), 7.22 (d, J = 16.3 Hz, 1H), 7.13 (d, J = 16.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.8 (q, J = 1.5 Hz), 136.6, 131.2, 129.2 (q, J = 32.4 Hz), 128.8, 128.3, 127.1 (q, J = 0.8 Hz), 126.8, 126.6, 125.6 (q, J = 3.8 Hz), 124.3 (q, J = 272 Hz).

*(E)-1-(4-Chlorostyryl)-3-methoxybenzene (**2e**)*.[32] The reaction was performed according to Method A using 1-chloro-4-[2-(3-methoxyphenyl)ethynyl]benzene (218 mg, 0.9 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol), *t*BuOK (20 mg, 0.18 mmol), benzyl alcohol (0.93 ml, 9.0 mmol) and toluene (2.1 ml) with a reaction time of 24 h. NMR-yield (*E/Z* %): 100/0. Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 97:3 (20 column volumes) -> 97:3 (10 column volumes). Product **2e** was obtained as a white crystalline solid (191 mg, 87%): mp = 71°C; ν_{max}/cm^{-1} 3006

(C-H), 2835 (C-H), 1605 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (XX' signal of AA'XX' spin system, 2H), 7.34 – 7.31 (AA' signal of AA'XX' spin system, 2H), 7.31 – 7.26 (m, 1H), 7.10 (ddd, J = 7.7, 1.6, 0.9 Hz, 1H), 7.05 (s, 2H), 7.04 (dd, J = 2.5, 1.5 Hz, 1H), 6.84 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 3.85 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.0, 138.6, 135.9, 133.4, 129.8, 129.3, 129.0, 127.8, 127.8, 119.4, 113.6, 111.9, 55.4; HRMS (ESI+ QTOF) calculated for $C_{15}H_{14}ClO$ [M + H]+ 245.0728, found 245.0730.

(E)-1-Methoxy-4-(4-(trifluoromethyl)styryl)benzene ***(2f)***.[10j] The reaction was performed according to Method A using 1-methoxy-4-((4-(trifluoromethyl)phenyl)ethynyl)-benzene (83 mg, 0.3 mmol), $Ru_3(CO)_{12}$ (1.3 mg, 0.002 mmol), *t*BuOK (7 mg, 0.06 mmol), benzyl alcohol (0.31 ml, 3.0 mmol) and toluene (0.69 ml) with a reaction time of 42 h. NMR-yield (*E/Z* %): 100/0. Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (10 column volumes) -> 95:5 (10 column volumes). Product **2f** was obtained as a white crystalline solid contaminated with a small amount of benzyl benzoate (69 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 4H), 7.48 (XX' signal of AA'XX' spin system, 2H), 7.15 (d, J = 16.3 Hz, 1H), 6.98 (d, J = 16.3 Hz, 1H), 6.93 (AA' signal of AA'XX' spin system, 2H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.9, 141.1, 130.7, 129.4, 128.8 (q, J = 32.4 Hz), 128.1, 126.3, 125.6 (q, J = 3.9 Hz), 124.9, 124.3 (q, J = 271 Hz), 114.2, 55.3.

(E)-4-Styrylaniline ***(2g)***.[33] The reaction was performed according to Method B using 4-(phenylethynyl)aniline (58 mg, 0.3 mmol), $RuCl_2(DMSO)_4$ (14.5 mg, 0.03 mmol), *t*BuOK (17 mg, 0.15 mmol), 2-propanol (0.23 ml, 3.0 mmol) and toluene (0.77 ml) with a reaction time of 24 h. NMR-yield (*E/Z* %): 65/14. Flash chromatography gradient: Petroleum ether/EtOAc 95:5 -> 85:15 (30 column volumes). Product **2g** was obtained as a light yellow crystalline solid (30 mg, 51%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.39 – 7.29 (m, 4H), 7.25 – 7.18 (m, 1H), 7.03 (d, J = 16.3 Hz, 1H), 6.93 (d, J = 16.3 Hz, 1H), 6.67 (AA' signal of AA'XX' spin system, 2H), 3.75 (br s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.3, 138.1, 128.8, 128.7, 128.2, 127.9, 127.0, 126.2, 125.2, 115.3.

(E)-2-Styrylaniline ***(2h)***.[34] The reaction was performed according to Method A using 2-(2-phenylethynyl)aniline (174 mg, 0.90 mmol), $Ru_3(CO)_{12}$ (19 mg, 0.03 mmol), *t*BuOK (20 mg, 0.18 mmol), benzyl alcohol (0.93 ml, 9.0 mmol) and toluene (2.1 ml) with a reaction time of 28 h. NMR-yield (*E/Z* %): 45/14. Flash chromatography gradient: Petroleum ether/EtOAc 98:2 -> 9:1 (30 column volumes). Product **2h** was obtained as a white crystalline solid that rapidly turned brown upon air exposure (60 mg, 34%). A sample was obtained for analytical purposes through recrystallization from EtOH: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.44 (dd, J = 7.7, 1.5 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.33 – 7.27 (m, 1H), 7.20 (d, J = 16.1 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.02 (d, J = 16.1 Hz, 1H), 6.89 – 6.82 (m, 1H), 6.74 (dd, J = 8.0, 1.2 Hz, 1H), 3.82 (br s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.1, 137.7, 130.4, 128.80, 128.78, 127.7, 127.4, 126.5, 124.4, 123.9, 119.7, 116.4.

(E)-3-Styrylpyridine ***(2i)***.[35] The reaction was performed according to general procedure 2 using 3-(2-phenylethynyl)pyridine (54 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (6.3 mg, 0.01 mmol), *t*BuOK (6.7 mg, 0.06 mmol), benzyl alcohol (0.31 ml, 3.0 mmol) and toluene (0.69 ml) with a reaction time of 70 h. NMR-yield (*E/Z* %): 70/30. The crude product was transferred to an amino-functionalized 1 g samplet instead of the unfunctionalized samplet described in general procedure 2. Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 85:15 (15 column volumes) -> 85:15 (10 column volumes). Product **2i** was obtained as a light yellow crystalline solid (26 mg, 48%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 2.3 Hz, 1H), 8.49 (dd, J = 4.8, 1.6 Hz, 1H), 7.83 (dddd, J = 8.0, 2.2, 1.6, 0.6 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.41 – 7.35 (m, 2H), 7.33 – 7.26 (m, 2H), 7.17 (d, J = 16.4 Hz, 1H), 7.07 (d, J = 16.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.6, 136.7, 133.1, 132.8, 130.9, 128.9, 128.3, 126.8, 125.0, 123.7.

(E)-5-Styryl-1H-indole ***(2j)***.[36] The reaction was performed according to Method B using 5-(phenylethynyl)-1*H*-indole (131 mg, 0.6 mmol), $RuCl_2(DMSO)_4$ (29 mg, 0.06 mmol), *t*BuOK (34 mg, 0.3 mmol), 2-propanol (0.46 ml, 6.0 mmol) and toluene (1.54 ml) with a reaction time of 72 h. NMR-yield: 75%. Flash chromatography gradient: Petroleum ether/EtOAc 96:4 -> 92:8 (10 column volumes) -> 92:8 (8 column volumes). Product **2j** was obtained as an off white crystalline solid (74 mg, 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (br s, 1H), 7.77 (dt, J = 1.6, 0.8 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.46 (dd, J = 8.5, 1.7 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.25 (d, J = 16.3 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.21 (dd, J = 3.3, 2.3 Hz, 1H), 7.09 (d, J = 16.3 Hz, 1H), 6.57 (ddd, J = 3.1, 2.0, 1.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.1, 135.7, 130.2, 129.6, 128.8, 128.3, 127.1, 126.3, 126.2, 124.9, 120.8, 119.6, 111.4, 103.1.

(E)-3-Styrylthiophene ***(2k)***.[37] The reaction was performed according to Method A using 3-(phenylethynyl)thiophene (166 mg, 0.90 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol), *t*BuOK (20 mg, 0.18 mmol), benzyl alcohol (0.93 ml, 9.0 mmol) and toluene (2.1 ml) with a reaction time of 48 h. NMR-yield (*E/Z* %): 89/10. Flash chromatography: Petroleum ether (10 column volumes). Product **2k** was obtained as a white crystalline solid which was contaminated with 3% (*Z*)-3-styrylthiophene (127 mg, 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.41 – 7.31 (m, 4H), 7.30 – 7.25 (m, 2H), 7.15 (d, J = 16.3 Hz, 1H), 6.98 (d, J = 16.3 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.2, 137.5, 128.79, 128.78, 127.6, 126.4, 126.3, 125.0, 123.0, 122.5.

(E)-(4-Chlorophenyl)ferrocenylethene ***(2l)***. The reaction was performed according to Method A using 1-chloro-4-(ferroceneethynyl)benzene (192 mg, 0.60 mmol), $Ru_3(CO)_{12}$ (2.6 mg, 0.004 mmol), *t*BuOK (14 mg, 0.12 mmol), benzyl alcohol (0.62 ml, 6.0 mmol) and toluene (1.4 ml) with a reaction time of 24 h. NMR-yield (*E/Z* %): 60/n.d. Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (10 column volumes) -> 97:3 (10 column volumes). Product **2l** was obtained as a red crystalline solid (95 mg, 49%): mp = 154 – 158°C; ν_{max}/cm^{-1} 3083 (C-H), 2956 (C-H), 2924 (C-H), 2854 (C-H), 1632 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (XX' signal of AA'XX' spin system, 2H), 7.29 (AA' signal of AA'XX' spin system, 2H), 6.85 (d, J = 16.1 Hz, 1H), 6.64 (d, J = 16.1 Hz, 1H), 4.47 – 4.45 (t, J = 1.9 Hz, 2H), 4.29 (t, J = 1.8 Hz, 2H), 4.14 (s, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.5, 132.3, 128.9, 127.9, 127.0, 124.8, 83.0, 69.7, 69.3, 67.1; HRMS (ESI+ QTOF) calculated for $C_{18}H_{16}ClFe$ [M + H]+ 323.0284, found 323.0268.

Benzyl (E)-4-styrylbenzoate ***(2m)***. The reaction was performed according to Method A using benzyl 4-

(phenylethynyl)benzoate (84 mg, 0.27 mmol), $Ru_3(CO)_{12}$ (1.2 mg, 0.0018 mmol), *t*BuOK (6.1 mg, 0.054 mmol), benzyl alcohol (0.28 ml, 0.27 mmol) and toluene (0.65 ml) with a reaction time of 24 h. NMR-yield (*E/Z* %): 100/0. Flash chromatography gradient: Petroleum ether/EtOAc 1:0 -> 1:0 (5 column volumes) -> 9:1 (20 column volumes). Product **2m** was obtained as a white crystalline solid (60 mg, 71%): mp = 123 – 129°C; ν_{max}/cm^{-1} 3027 (C-H), 2952 (C-H), 2892 (C-H), 1708 (C=O), 1603 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.60 – 7.52 (m, 4H), 7.50 – 7.45 (m, 2H), 7.44 – 7.34 (m, 5H), 7.33 – 7.28 (m, 1H), 7.22 (d, *J* = 16.3 Hz, 1H), 7.13 (d, *J* = 16.4 Hz, 1H), 5.38 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.3, 142.1, 136.8, 136.2, 131.4, 130.3, 129.0, 128.9, 128.7, 128.4, 128.4, 128.3, 127.7, 126.9, 126.5, 66.8; HRMS (ESI+ QTOF) calculated for $C_{22}H_{19}O_2$ [M + H]+ 315.1380, found 315.1378.

*(E)-1-(4-Styrylphenyl)ethan-1-ol (**2n**).* The reaction was performed according to Method B using 1-(4-(phenylethynyl)phenyl)ethan-1-one (66 mg, 0.3 mmol), $RuCl_2(DMSO)_4$ (29 mg, 0.006 mmol), *t*BuOK (17 mg, 0.15 mmol), 2-propanol (0.23 ml, 3.0 mmol) and toluene (0.77 ml) with a reaction time of 70 h. NMR-yield (*E/Z* %): 52/0. Flash chromatography gradient: Petroleum ether/EtOAc 100:0 -> 85:15 (20 column volumes) -> 85:15 (10 column volumes). Product **2n** was obtained as a white crystalline solid (29 mg, 44%): mp = 118 – 120°C; ν_{max}/cm^{-1} 3307 (O-H), 3024 (C-H), 2973 (C-H); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 4H), 7.41 – 7.33 (m, 4H), 7.29 – 7.24 (m, 1H), 7.11 (s, 2H), 4.92 (qd, *J* = 6.4, 2.9 Hz, 1H), 1.81 (d, *J* = 2.5 Hz, 1H), 1.52 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.3, 137.4, 136.8, 128.8, 128.8, 128.4, 127.8, 126.8, 126.6, 125.9, 70.4, 25.3; HRMS (ESI+ QTOF) calculated for $C_{16}H_{15}$ [M+H-[H_2O]]+ 207.1168, found 207.1178.

Tandem semi-hydrogenation/hydrogen borrowing.

*(E)-N-Benzyl-4-styrylaniline (**4**).*[38] The reaction was performed according to Method A using 4-(phenylethynyl)aniline (39 mg, 0.2 mmol), $Ru_3(CO)_{12}$ (4.2 mg, 0.007 mmol), *t*BuOK (4.5 mg, 0.04 mmol), benzyl alcohol (0.21 ml, 2.0 mmol) and toluene (0.46 ml) with a reaction time of 24 h. NMR-yield (4-[(*E*)-styryl]aniline/ *N*-benzyl-4-[(*E*)-styryl]aniline %): 23/51. Flash chromatography gradient: Petroleum ether/EtOAc 98:2 -> 9:1 (30 column volumes). Product **4** was obtained as an off-white crystalline solid (17 mg, 30%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.41 – 7.28 (m, 9H), 7.24 – 7.19 (tt, *J* = 1.3, 7.3 Hz, 1H), 7.04 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 16.3 Hz, 1H), 6.65 (AA' signal of AA'XX' spin system, 2H), 4.38 (s, 2H), 4.20 (br s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.9, 139.3, 138.2, 128.9, 128.8, 128.7, 127.9, 127.6, 127.5, 127.2, 126.9, 126.2, 124.7, 113.1, 48.3.

*(E)-3-phenyl-1-(4-styrylphenyl)propan-1-one (**6**).* The reaction was performed according to Method A using 1-(4-(phenylethynyl)phenyl)ethan-1-one (66 mg, 0.3 mmol), $Ru_3(CO)_{12}$ (1.3 mg, 0.002 mmol), *t*BuOK (6.7 mg, 0.06 mmol), benzyl alcohol (0.31 ml, 3.0 mmol) and toluene (0.69 ml) with a reaction time of 24 h. NMR-yield: 45%. Flash chromatography gradient: Petroleum ether/EtOAc 100:0 -> 100:0 (5 column volumes) -> 80:20 (25 column volumes). A mixture of product **6** and benzyl alcohol was obtained after chromatography. The mixture was recrystallized from boiling EtOAc, yielding pure **6** as white crystals. The mother liquid was recrystallized again yielding another batch of pure **6** (33 mg, 35%): mp = 150 – 155°C; ν_{max}/cm^{-1} 3026 (C-H), 2927 (C-H), 1681 (C=O), 1602 (C=C); ^{1}H NMR (400 MHz,) δ 7.96 (XX' signal of AA'XX' spin system, 2H), 7.58 (AA' signal of AA'XX' spin system, 2H), 7.56 – 7.52 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 7.23 (d, *J* = 16.4 Hz, 1H). 7.13 (d, *J* = 16.3 Hz, 1H), 3.35 – 3.28 (m, 2H), 3.09 (dd, J = 8.5, 6.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.7, 142.1, 141.5, 136.8, 135.8, 131.6, 128.9, 128.7, 128.7, 128.6, 128.4, 127.6, 126.9, 126.7, 126.3, 40.6, 30.4; HRMS (ESI+ QTOF) calculated for $C_{23}H_{21}O$ [M + H]+ 313.1592, found 313.1592.

ASSOCIATED CONTENT

^{1}H and $^{13}C\{^1H\}$ NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*kann@chalmers.se

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Ru3(CO)12 (0.66 mol%)
ROH, tBuOK
toluene, 100 °C, 24h
R1
R2
H
√ E-selective
√ Alcohol hydrogen donor
√ Simple Ru-catalyst
√ No added ligand
√ Tandem hydrogen borrowing possible
>99% NMR yield for most examples
Up to 93% isolated yield