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Author(s):
Boehm, Philip; Kehl, Niklas; Morandi, Bill

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Shuttle Catalysis

Rhodium-Catalyzed Anti-Markovnikov Transfer Hydroiodination of Terminal Alkynes**

*Philip Boehm, Niklas Kehl, and Bill Morandi**

Abstract: A rhodium-catalyzed anti-Markovnikov hydroiodination of aromatic and aliphatic terminal alkynes is reported. Depending on the choice of ligand and substrate, either (*E*)- or (*Z*)-configured alkenyl iodides are obtained in high to exclusive isomeric purity. The reaction exhibits a broad substrate scope and high functional group tolerance, employing easily accessible or commercially available aliphatic iodides as HI surrogates through a shuttle process. The synthesized vinyl iodides were applied in several C–C and C–heteroatom bond-forming reactions with full retention of the stereoselectivity. The developed method could be used to significantly shorten the total synthesis of a marine *cis*-fatty acid. Additionally, initial deuterium-labeling experiments and stoichiometric reactions shed some light on the potential reaction mechanism.

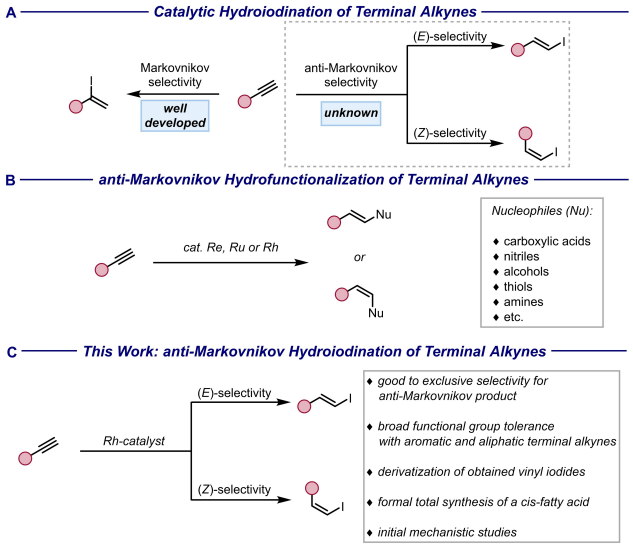

Figure 1. Context of this work.

Introduction

Vinyl iodides are of tremendous importance as functional handles for, e.g., cross-coupling reactions,[1] halogen-metal exchange reactions,[2] or radical cascade reactions.[3] Additionally, vinyl iodides are present in natural products and bioactive molecules,[4] and radiolabeled vinyl iodides have been used for the in vivo imaging of serotonin transporters.[5] As such, methods towards their selective generation are in high demand.

The hydroiodination of alkynes represents the most commonly used strategy to access vinyl iodides.[6,7] However, these methods only provide the branched (Markovnikov) vinyl iodide products (Figure 1A, left).[8] In contrast, there is only a limited number of methods for the installation of linear (anti-Markovnikov) vinyl iodides. For instance, for the highly selective synthesis of (*E*)-vinyl iodides, the classical approach is a two-step sequence of *syn*-hydrometallation, e.g., hydrozirconation with Schwartz reagent (Cp_2ZrHCl; Cp = cyclopentadienyl) of alkynes, and subsequent iodination.[9] An alternative prominent example which affords predominantly anti-Markovnikov (*E*)-vinyl iodides is the Takai olefination of aldehydes with iodoform and chromium(II).[10] However, those protocols require the use of (super)stoichiometric and often dangerous to handle metal precursors, generating stoichiometric amounts of metal waste. Additionally, the substrate scope of these methods is usually quite limited. One notable exception is an elegant study by Lalic and co-workers.[11] They reported the copper-catalyzed anti-Markovnikov selective hydrobromination of terminal alkynes. Still, the reaction is limited to the synthesis of (*E*)-vinyl bromides, the catalytic synthesis of (*E*)-vinyl iodides remains elusive (Figure 1A, right).

Due to their intrinsic higher thermodynamic instability compared to linear (*E*)-configured vinyl iodides, the linear (*Z*)-configured vinyl iodides are even more challenging to access from alkynes. The classical approach to (*Z*)-vinyl iodides is the Stork-Zhao olefination of aldehydes.[12,13] In contrast, there are only isolated reports on the (*Z*)-selective anti-Markovnikov hydroiodination of alkynes by Heck,[14] Stille,[15] and Oshima.[16] Still, these usually require multistep protocols,[14–16] and stoichiometric metal precursors,[16] thus significantly prolonging synthetic sequences and generating stoichiometric amounts of metal waste. To the best of our knowledge, the direct catalytic anti-Markovnikov

[*] P. Boehm, N. Kehl, Prof. Dr. B. Morandi
Laboratorium für Organische Chemie, ETH Zürich
Vladimir-Prelog-Weg 3, HCI, 8093 Zürich (Switzerland)
E-mail: bill.morandi@org.chem.ethz.ch

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selective synthesis of (*Z*)-vinyl iodides from alkynes remained elusive so far (Figure 1A, right).

Following pioneering studies by Dixneuf,[17] the rhenium-, rhodium-, or ruthenium-catalyzed anti-Markovnikov hydrofunctionalization of terminal alkynes has emerged as a growing field over the last decades.[18] Numerous nucleophiles have successfully been employed in various anti-Markovnikov hydrofunctionalizations, including carboxylic acids,[19] alcohols,[20] thiols,[21] amines,[22] or cyanides[23] amongst others (Figure 1B).[18] However, the use of such a strategy to selectively generate vinyl halide products is hitherto undisclosed.

Herein, we report a straightforward rhodium-catalyzed synthesis of linear vinyl iodides from terminal aryl- or alkylalkynes. Depending on the substrate and the ligand, either the (*E*)- or the (*Z*)-alkenyl iodide could be obtained. For the (*E*)-alkenyl iodides, good to exclusive selectivity for the linear over the branched product is observed, while (*Z*)-alkenyl iodides are obtained as the single isomer in all cases.

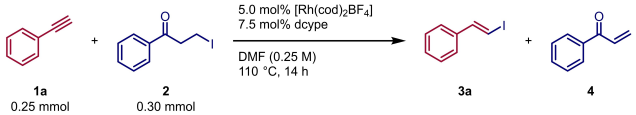
Results and Discussion

Hydroiodination of Aromatic Alkynes

In the context of our ongoing studies on shuttle catalysis and transfer halogenation,[24] we became interested in developing an anti-Markovnikov transfer hydrohalogenation of alkynes. Initial attempts using different hydrogen iodide (HI) surrogates, e.g., $Et_3N{\cdot}HI$,[25] under rhodium catalysis proved unfruitful (Table 1, entry 8). We then found that donor **2** provided the corresponding linear (*E*)-alkenyl iodide **3a** from phenylacetylene (**1a**) using 5.0 mol% $[Rh(cod)_2BF_4]$ (cod = 1,5-cyclooctadiene) and 7.5 mol% 1,2-bis(dicyclohexylphosphino)ethane (dcype) as catalyst system in *N*,*N*-dimethylformamide (DMF) in 97% yield with 18:1 selectivity for the linear over the branched product after 14 hours at 110 °C (entry 1; see Supporting Information for full optimization details). An analogous donor molecule compared to **2** was already used in a previous iridium-catalyzed Markovnikov-selective hydrohalogenation developed within our group.[24b] Other ligands, such as tris[3,5-bis(trifluoromethyl)phenyl]phosphine (3,5-CF_3-PPh_3) or *trans*-1,2-bis(diphenylphosphino)ethylene (*trans*-1,2-dppe), were moderately successful in the reaction (entries 2 and 3). Additionally tested rhodium precursors, e.g., [Rh(cod)(Tp)] (Tp = tris(1-pyrazolyl)borohydride), which was an effective catalyst in previously reported anti-Markovnikov hydrofunctionalization reactions,[22b,23] showed reduced yield and regioselectivity in the hydroiodination (entry 4). Lowering the catalyst loading to 2.5 mol% rhodium resulted in significantly reduced yield and regioselectivity. Similarly, reducing the amount of dcype ligand had a slightly detrimental effect (entries 5 and 6). Using commercially available *tert*-butyl iodide instead of **3a** gave incomplete conversion of the starting material, a reduced yield of 81%, and the linear:branched (l:b) ratio dropped to 15:1 (entry 7). The polar, aprotic solvent *N*,*N*-dimethylformamide (DMF) was necessary for the reaction to reach high conversion and selectivity; using toluene instead drastically diminished the yield and the l:b ratio (entry 9). Temperatures lower than 110 °C reduced the conversion (entry 10), while higher temperatures led to significant decomposition of the starting materials. Other transition metal catalysts, including a ruthenium catalyst which was previously reported to catalyze anti-Markovnikov hydrofunctionalizations showed little to no conversion to the desired product (entry 11, see Supporting Information for details).[26]

The rhodium-catalyzed anti-Markovnikov hydroiodination of terminal alkynes showed a broad functional group tolerance (Table 2). Electron-neutral (**1a**, **1g**–**1i**), electron-rich (**1c** and **1d**) aryl acetylenes and aryl acetylenes with extended π-systems (**1e** and **1f**) were smoothly converted to the corresponding alkenyl iodides in fair to excellent yields (60–97%) and with high selectivity for the linear product (84:16 up to >99:1). The rhodium-catalyzed anti-Markovnikov hydroiodination exhibited reproducible yields, even when conducting the reaction on a bigger scale (5 mmol). Moderate steric bulk in proximity to the terminal alkyne was well-tolerated, and substrate **3b** with a methyl group in *ortho*-position to the acetylene moiety was obtained in 83% yield with 92:8 selectivity for the anti-Markovnikov product. Product **3j** with a methoxy group in *meta*-position was obtained in 90% yield and 94:6 selectivity for the linear product. Substrate **1k** with a boronic ester functional group was well-tolerated under our reaction conditions. Furthermore, several (poly)halogenated substrates were cleanly converted to the corresponding vinyl iodides **3l**–**3q** in good to nearly quantitative yields (70–98%) and with almost exclusive regioselectivity for the linear product (94:6–99:1). Trifluoromethyl chalcogens (–OCF_3 and –SCF_3) were well-tolerated, and the corresponding vinyl iodides **3r** and **3s** were isolated in 88% (l:b 88:12) and 83% yield (l:b 99:1), respectively. Substrates with electron-withdrawing groups performed well in the rhodium-catalyzed anti-Markovnikov hydroiodination. Vinyl iodide products with an acetoxy

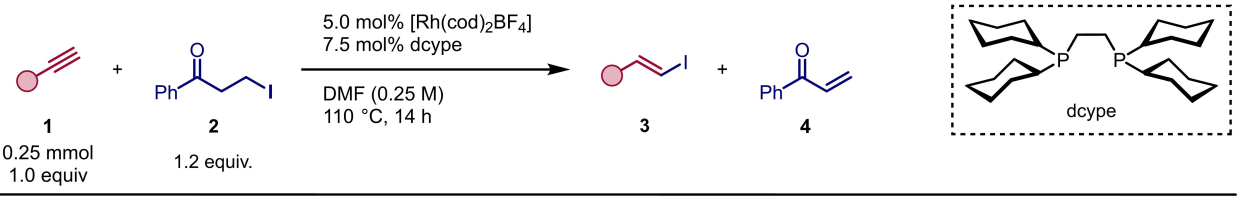
Table 1: Selected optimization data for the hydroiodination.[a]

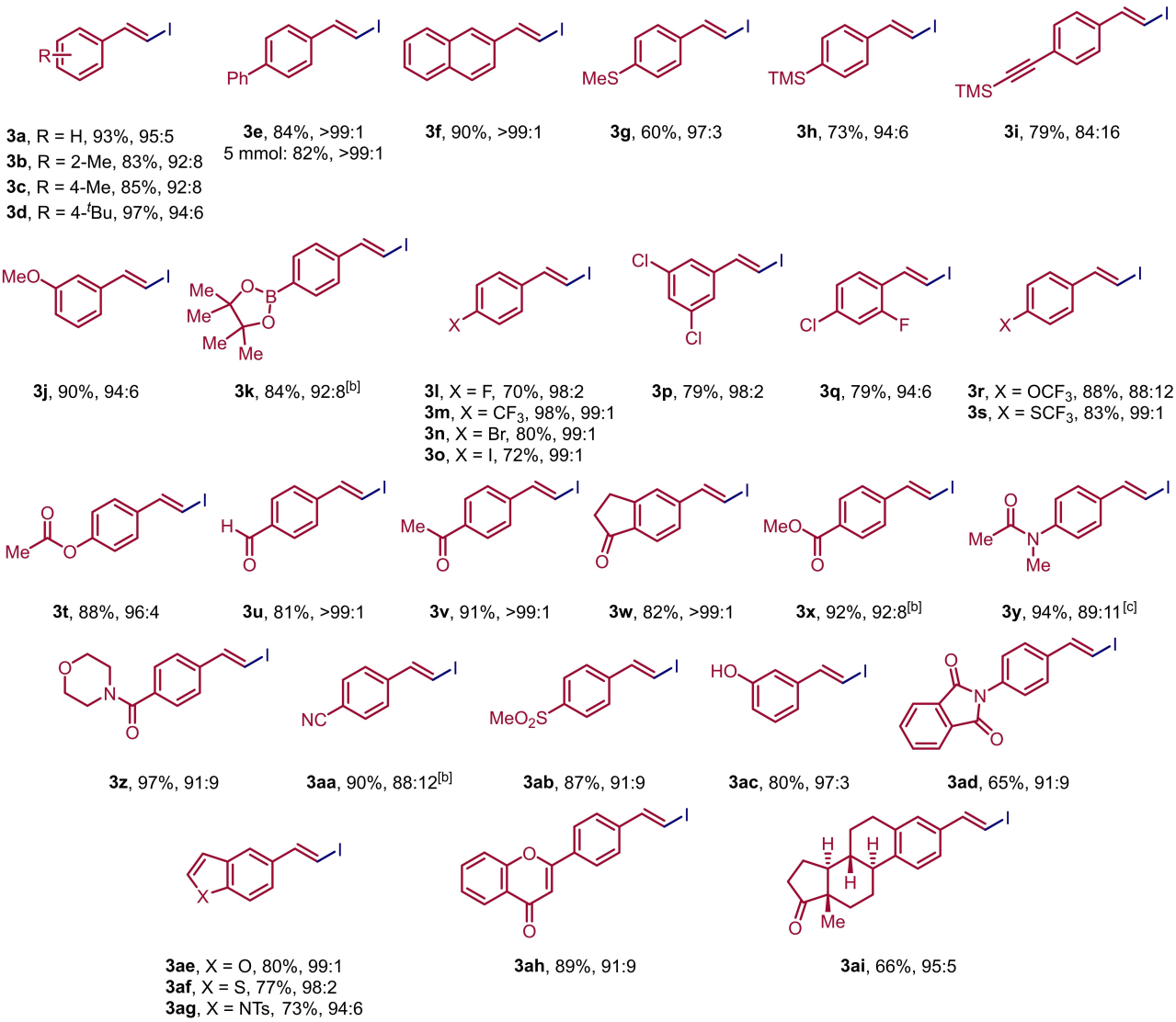


Entry	Deviations from above	**3a** [%][a]	a-M : M[a]
1	none	**97**	**18:1**
2	3,5-CF_3-PPh_3 instead of dcype	49	12:1
3	*trans*-1,2-dppe instead of dcype	22	0.8:1
4	[Rh(cod)(Tp)] instead of $[Rh(cod)_2BF_4]$	51	9:1
5	2.5 mol% $[Rh(cod)_2BF_4]$, 2.5 mol% dcype	29	2:1
6	5.0 mol% $[Rh(cod)_2BF_4]$, 5.0 mol% dcype	88	16:1
7	*tert*-butyl iodide instead of **2**	81	15:1
8	$NEt_3{\cdot}HI$ instead of **2**	n.d.	–
9	toluene instead of DMF	18	2:1
10	100 °C instead of 110 °C	61	15:1
11	*Ru*, *Ir*, *Pd* or *Ni* instead of $[Rh(cod)_2BF_4]$	<5	–

[a] Product yield and anti-Markovnikov:Markovnikov ratio were determined by GC analysis with *n*-decane as internal standard.

Table 2: Scope with respect to aromatic terminal alkynes.[a]





[a] Yields given for isolated single isomers or for isomeric mixtures with the linear:branched regioselectivity ratio noted above. [b] 4-iodobutan-2-one (1.2 equiv) instead of **2**. [c] Isolated with 5% of the corresponding styrene. For details, see Supporting Information.

group (**3t**), carbonyl groups (**3v** and **3w**), an ester (**3x**), an acetamide (**3y**), a morpholine-amide (**3z**), a nitrile moiety (**3aa**), and a methyl sulfone (**3ab**) were obtained in very good to almost quantitative yields (80–98% yield) and good to exclusive selectivity for the anti-Markovnikov product (88:12 to >99:1). An aldehyde group, potentially prone to rhodium-catalyzed oxidative addition,[27] was left untouched and the corresponding alkenyl iodide **3u** was isolated in 81% yield as the exclusive linear regioisomer. Substrate **1ac** with a free alcohol group was also tolerated, affording the corresponding vinyl iodide **3ac** in almost quantitative yield (97%) with 91:9 selectivity for the linear product. Protected amines (**3ad**) and several heterocycles (benzofuran **3ae**, benzothiophene **3af**, and tosyl-protected indole **3ag**) were compatible with the hydroiodination reaction (73–97% yield, 91:9–99:1 regioselectivity). More complex flavone **1ah** and estrone derivative **1ai** were reacted to give vinyl iodides **3ah** and **3ai** in 89% (l:b 91:9) and 66% yield (l:b 95:5), respectively.

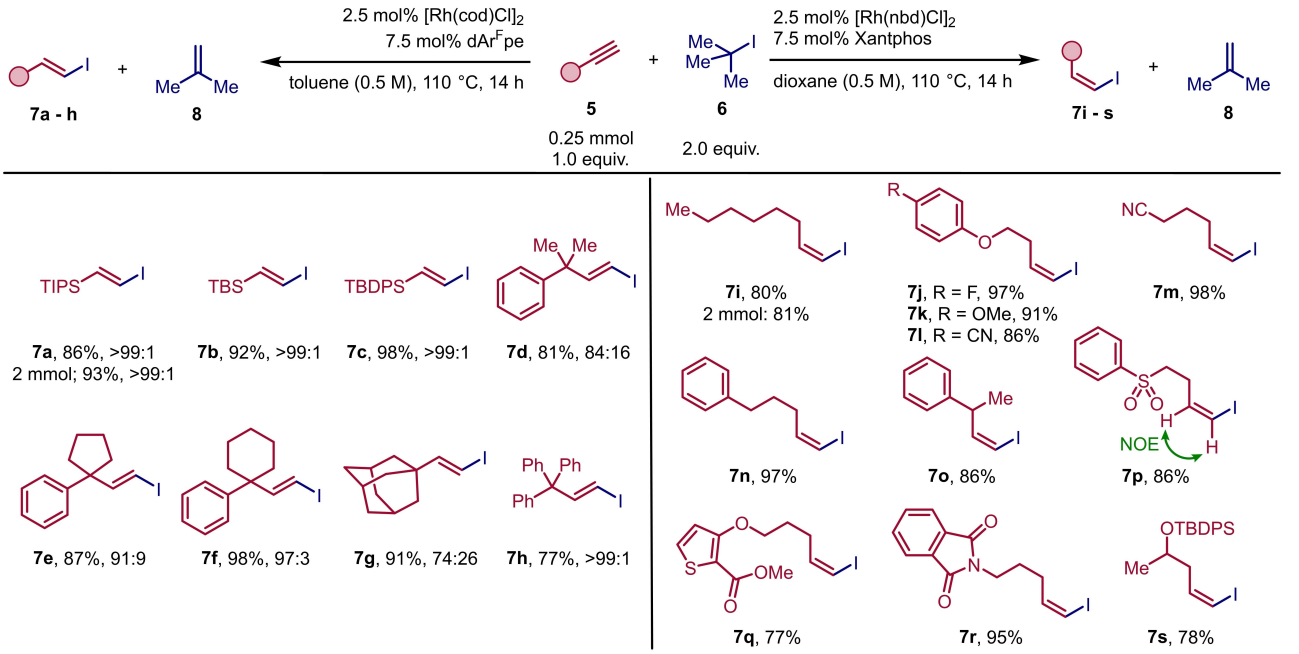
Hydroiodination of Aliphatic Alkynes

We next turned our attention towards the rhodium-catalyzed anti-Markovnikov hydroiodination of aliphatic acetylenes. Unfortunately, the conditions for the hydroiodination of aryl acetylenes afforded no product in the attempted hydroiodination of alkyl acetylenes, but a slight alteration of the reaction conditions to a catalyst system comprised of 2.5 mol% $[Rh(cod)Cl]_2$ and 7.5 mol% 1,2-bis[bis(pentafluorophenyl)phosphino]ethane (dArFpe) with 2.0 equivalents of commercially available *tert*-butyl iodide **6** in toluene (0.5 M) at 110 °C converted tri-*isopropyl* silyl (TIPS) protected acetylene **5a** to the desired vinyl iodide **7a** in good yield (86 %) with exclusive regioselectivity for the linear product (see Supporting Information for optimization details). Similar to the hydroiodination of aryl acetylenes, the hydroiodination of alkyl acetylenes proved to be scalable, and **7a** was isolated in a slightly higher yield (93 %) on a 2 mmol scale (Table 3). Other silyl-substituted acetylenes were efficiently converted to the (*E*)-alkenyl halides **7b** and **7c** in good to excellent yield (86 and 92 %, respectively) with exclusive selectivity for the anti-Markovnikov product. Alkyl substituents were also well tolerated under the reaction conditions. In accordance with previously reported anti-Markovnikov hydrofunctionalizations,[23] it has to be noted that proximal steric bulk is necessary to achieve high selectivity for the anti-Markovnikov product. When substrates without steric bulk are used, an almost 1:1 mixture of Markovnikov and anti-Markovnikov product is obtained (see Supporting Information for unsuccessful substrates). Alkenyl iodide substrates with two methyl groups (**7d**), a cyclopentyl group (**7e**), or a cyclohexyl group (**7f**) in proximity to the acetylene moiety were isolated using the rhodium-catalyzed hydroiodination in good to almost quantitative yields (81–98 %) and with good to almost exclusive regioselectivity (84:16–97:3). Adamantyl-substituted alkenyl iodide **7g** was isolated in 91 % yield with slightly reduced regioselectivity (l:b 74:26), while trityl vinyl iodide **7h** was obtained in 77 % yield as the single regioisomer.

As previously mentioned, (*Z*)-vinyl iodides are notoriously difficult to access,[14–16] therefore, an operationally simple method for the synthesis of (*Z*)-vinyl iodides from terminal alkynes in a one-step procedure using only commercially available starting materials would be of particular interest.

During the optimization of the rhodium-catalyzed anti-Markovnikov hydroiodination of aliphatic acetylenes, it was observed that the use of Xantphos as ligand led to the linear alkenyl iodide with exclusive (*Z*)-configuration of the double bond. After some slight re-optimization of the reaction conditions, we could access the (*Z*)-vinyl iodides in high yields (see Supporting Information for details). Several alkyl-substituted alkynes were efficiently converted to their corresponding (*Z*)-vinyl iodides. Vinyl iodide **7i** derived from 1-octyne was isolated in 80 % yield as single regio- and stereoisomer as determined by NMR spectroscopy, even when conducting the reaction on a bigger scale (2 mmol). Substrates **7j**, **7k**, and **7l** with a fluoro substituent, a methoxy group, and a cyano group on the distal arene, respectively, were obtained in good to almost quantitative yields (86–97 %). Alkyl cyanide **7m** was well tolerated (98 % yield). Simple hydrocarbon substrates **7n** and **7o** were isolated as single isomers in 97 % and 86 % yield, respec-

Table 3: Scope with respect to aliphatic terminal alkynes.[a]



[a] Yields given for isolated single isomers or for isomeric mixtures with the linear:branched regioselectivity ratio noted above. For details, see Supporting Information.

tively. A phenyl sulfone did not have a detrimental influence on the hydroiodination, and substrate **7p** was obtained in 86 % yield as a single isomer. The correct stereochemistry of the double bond of substrate **7p** was further confirmed by NOESY NMR analysis. Substrates bearing a thiophene heterocycle or a masked amine were cleanly converted to their corresponding (*Z*)-vinyl iodides **7q** and **7r** in 77 % and 95 % yield, respectively. Additionally, vinyl iodide **7s** from a TBDPS-protected homopropargylic alcohol was obtained in 78 % yield, showcasing the potential of this method for the synthesis of polyketides.[28,29] In all cases, the products were isolated as the exclusive anti-Markovnikov (*Z*)-isomer. No Markovnikov, or (*E*)-isomer was observed for any substrate. The reason for this complete switch in stereoselectivity is unknown at this point and the topic of ongoing investigations in our laboratories. Unlike in the case of the (*E*)-selective anti-Markovnikov hydroiodination of aliphatic acetylenes, in the (*Z*)-selective hydroiodination, steric bulk in proximity to the alkyne was not tolerated (see Supporting Information for unsuccessful substrates). Furthermore, attempts to extend this (*Z*)-selective hydroiodination to aryl acetylenes were unfruitful.

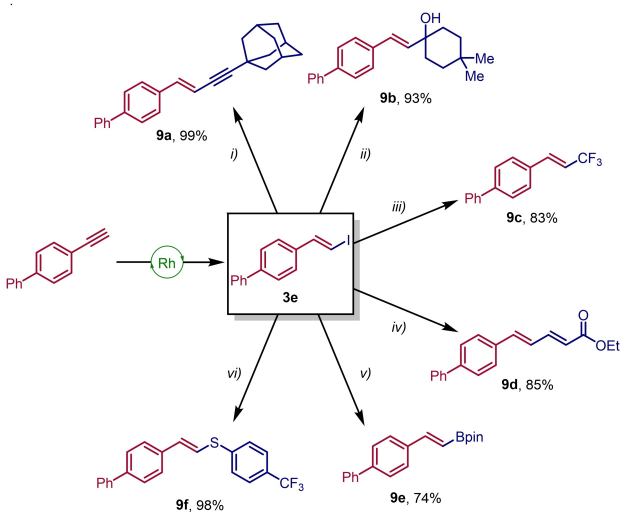
Summarizing the scope exploration for the (*E*)-selective anti-Markovnikov hydroiodination of aromatic and aliphatic acetylenes, and the (*Z*)-selective anti-Markovnikov hydroiodination of aliphatic acetylenes, the reactions exhibit a broad functional group tolerance and high selectivities for the desired regio- and stereoisomer. We therefore believe that this reaction has several advantages over current state-of-the-art methods for the synthesis of (*E*)- and (*Z*)-selective anti-Markovnikov vinyl iodides, such as improved substrate scope compared to classical *syn*-hydrometalation approaches, or better selectivity for the (*E*)- or (*Z*)-isomer compared to, e.g., the Takai, or the Stork-Zhao olefination.

Applications of Vinyl Iodides

Vinyl iodides are versatile intermediates in organic synthesis and can be engaged in a great variety of different C–C and C-heteroatom bond forming reactions.[1] To highlight the synthetic utility of the products formed with our hydroiodination methodology, we utilized a representative vinyl iodide in several reactions for further downstream functionalization, yielding formal hydrofunctionalization products which are often times difficult to access using standard methods (Scheme 1).

Using alkenyl iodide **3e**, which was prepared on a larger scale using our developed reaction (see Table 2), a Sonogashira alkynylation with adamantyl-alkyne **5r** proceeded to enyne **9a** in almost quantitative yield (99 %). Similarly, a copper-mediated trifluoromethylation developed by Bräse[30] afforded the product of formal anti-Markovnikov hydrotrifluoromethylation, **9c**, in 83 % yield. Correspondingly, a Mizoroki-Heck reaction of **3e** with ethyl acrylate gave diene **9d** in 85 % yield.

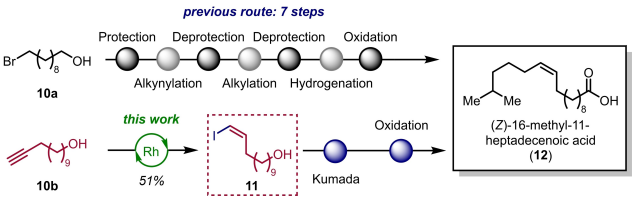
Alkenyl iodides are also prominently used for metal-halogen exchange reactions.[2] We could further show the utility of our products in a Grignard reaction and a



Scheme 1. Conditions for the derivatization of alkenyl iodide **3e**: (i) $[Pd(PPh_3)_2Cl_2]$ (3 mol%), CuI (10 mol%), 1-ethynyladamantane (**5r**) (1.2 equiv), DIPA (3.0 equiv), THF, 0 °C to r.t., 14 h; (ii) *i*PrMgCl·LiCl (1.2 equiv), THF, −15 °C, 30 min, then cyclohexanone (1.1 equiv), −15 °C to r.t., 14 h; (iii) CuI (1.7 equiv), KF (1.5 equiv), $TMSCF_3$ (1.2 equiv), DMPU, 80 °C, 16 h; (iv) $Pd(OAc)_2$ (5 mol%), NEt_3 (2.5 equiv), ethyl acrylate (5.0 equiv), DMF, 100 °C, 14 h; (v) *n*-BuLi (2.3 equiv), THF, -78 °C, then 2-*iso*-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.6 equiv), -78 °C to r.t., 2.5 h; (vi) NiI_2 (1.25 mol%), $P(OiPr)_3$ (5 mol%), DIPEA (2.5 equiv), 4-(trifluoromethyl)benzenethiol (1.15 equiv), DMF, 120 °C, 12 h.

lithiation/borylation sequence. Substrate **3e** readily forms the corresponding Grignard reagent with *i*PrMgCl·LiCl, which can then be converted to tertiary alcohol **9b** in 93 % yield. When treating **3e** with *n*BuLi, lithium-halogen exchange occurred and after further reaction with *iso*-propoxyboronic acid pinacol ester, vinyl boronate **9e** could be isolated in 74 % yield. To conclude the product diversification, a nickel-catalyzed C–S coupling of vinyl iodide **3e** with a thiol, according to a report by Lautens, was conducted.[31] Product **9f** could be isolated in 98 % yield. In all cases, the products were obtained without any deterioration of the (*E*)/(*Z*)-ratio.

To further showcase the synthetic utility of our presented rhodium-catalyzed anti-Markovnikov hydroiodination, we have used our method in the concise total synthesis of a *cis*-fatty acid (Scheme 2). The fatty acid which was shown to have antileishmanial activity was previously synthesized in 7 steps from commercially available starting materials.[32] Those steps included several protection and



Scheme 2. Improved total synthesis of **12**.

deprotection manipulations rendering the reported synthetic sequence inefficient.

We started our synthesis from commercially available alkyne **10b** by reacting it under our standard conditions for the (*Z*)-selective hydroiodination. The desired (*Z*)-vinyl iodide **11** could be isolated in 51 % yield as a single isomer. After Kumada coupling of the vinyl iodide with an alkyl Grignard reagent, followed by oxidation of the pendent alcohol to the carboxylic acid, we obtained isomerically pure *cis*-fatty acid **12** (see Supporting Information for details on the synthesis). By using our hydroiodination reaction, we could reduce the step count to 3 from commercially available starting materials without using any protecting groups. This concise synthesis demonstrates the synthetic potential of our transformation to rapidly access widely occurring unsaturated fatty acids with full control over the stereochemistry of the double bonds. We also believe that the hydroiodination could be a complementary approach to the well-established alkene metathesis in total synthesis.[33]

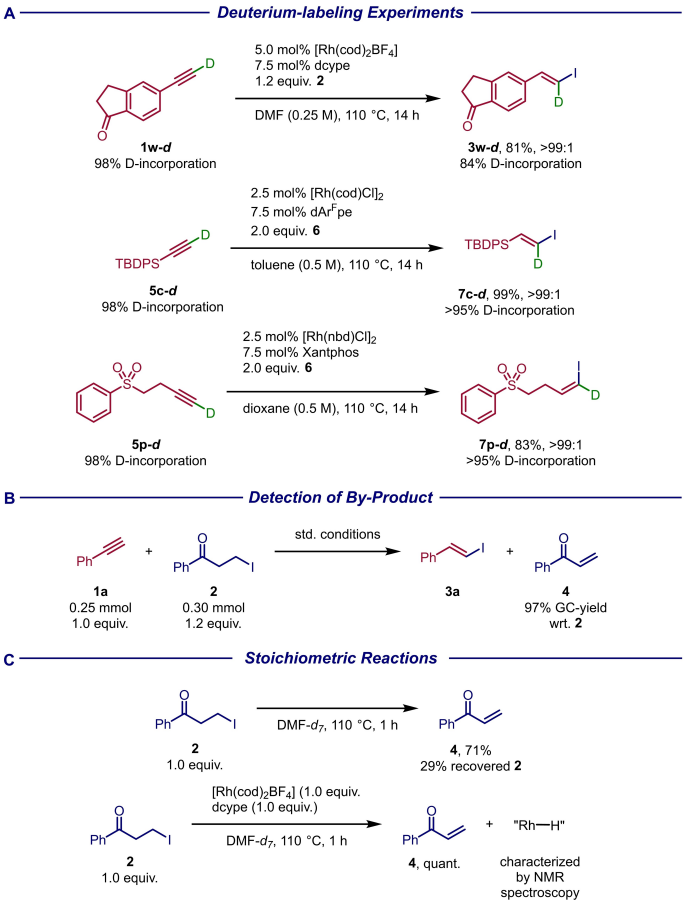
Preliminary Mechanistic Experiments

To gain initial mechanistic insights into the rhodium-catalyzed anti-Markovnikov hydroiodination of terminal alkynes, several preliminary mechanistic experiments were conducted (Scheme 3). First, deuterated substrates, **1w-*d***, **5c-*d***, and **5p-*d***, were synthesized and subjected to the reaction conditions (Scheme 3A). The product **3w-*d*** was isolated exclusively as the linear (*E*)-isomer in 81 % yield. The deuterium is located at the *ipso*-carbon with 84 % deuterium incorporation. Similarly, the deuterium label in the two products **7c-*d*** and **7p-*d*** was exclusively observed at the *ipso*-carbon.

We were additionally able to detect the by-product of hydrogen iodide donor **2**, phenyl vinyl ketone **4**, in 97 % GC-yield with respect to the 1.2 equiv of donor **2** initially used (Scheme 3B).

We then conducted several stoichiometric experiments (Scheme 3C). When heating donor **2** in DMF-d_7 at the reaction temperature, 110 °C, for one hour, significant hydrogen iodide elimination was observable, and phenyl vinyl ketone **4** was formed in 71 % yield (with 29 % of **2** remaining). When heating **2** in DMF-d_7 with equimolar [Rh(cod)$_2$BF$_4$] and dcype, complete consumption of **2** was observable within one hour. Concomitantly, the formation of a rhodium hydride species was detected. The rhodium-hydride was stable over a prolonged period of time and could be characterized by ^{1}H and ^{31}P NMR spectroscopy, as well as ^{31}P–^{1}H HMBC and ^{103}Rh–^{1}H HSQC measurements.

Studies for further elucidation of the reaction mechanism are necessary, but we propose that donor **2** undergoes heat-induced hydrogen iodide elimination, which is accelerated by the rhodium catalyst. Subsequent oxidative addition of the rhodium into the H–I bond generates a rhodium(III) hydride. The alkyne undergoes migratory insertion into the Rh–H bond; the regioselectivity might be dictated by sterics. Subsequent C–I bond forming reductive elimination affords the product and closes the catalytic cycle. The observed



Scheme 3. Mechanistic experiments.

deuterium retention in the deuterium-labeling experiments speaks against a 1,2-hydride shift, which, in contrast, was recently observed in related, anti-Markovnikov hydrofunctionalization reactions proposed to involve a rhodium-vinylidene pathway.[18,23,34] While this pathway can be confidently excluded for our hydroiodination reaction, the actual operating mechanism, including the factors governing the origins of the anti-Markovnikov selectivity and the (*E*)/(*Z*)-selectivity, remain unclear and will be the focus of further studies.

Conclusion

In conclusion, we have reported an efficient rhodium-catalyzed anti-Markovnikov hydroiodination of terminal alkynes. The reaction proceeds with readily accessible or commercially available hydrogen iodide donor molecules and shows a broad substrate scope in both aryl and alkyl alkynes with high yields. The reaction exhibits a good selectivity for the anti-Markovnikov over the Markovnikov product. Depending on the choice of ligand and substrate, we could control the stereoselectivity of the formed double bond in the case of aliphatic alkenyl iodide products. We could use the synthesized alkenyl iodides for a variety of downstream cross-coupling and metal-halogen exchange

reactions. Additionally, the developed hydroiodination reaction could be used to streamline the synthesis of a *cis*-fatty acid. We believe that the newly developed method will have broad impact in the organic community in simplifying the access to vinyl iodides and alkenes with desired regio- and stereochemistry. Further studies concerning the release of iodide from the donor molecules **2** or **6** and the observed anti-Markovnikov selectivity and the (*E*)/(*Z*)-selectivity are ongoing in our laboratories.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Anti-Markovnikov Selectivity · Hydrofunctionalization · Rhodium · Shuttle Catalysis · Vinyl Iodides

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