Advancing selectivity control with highly reactive organometallic reagents

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Chapter 3

NHC-Cu(I)-Catalyzed α-Selective Allylic Alkylation With Organolithium Reagents

A Cu-catalyzed allylic alkylation procedure with organolithium reagents is described which follows an unusual regioselectivity resulting in the formation of the α-alkylated product. The effect of the ligand is shown to be the key factor in imparting selectivity. The methodology is complementary to previously developed γ-selective Cu-catalyzed allylic alkylation procedures with organolithium compounds.

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1 Introduction

Selectivity is considered one of the most challenging aspects in the field of catalytic reactions.[1] The development of catalytic systems is not limited to the enhancement of the reaction rate, more often it is aimed at gaining total control over the selectivity. When more than one product can arise from a reaction, it is valuable to obtain selectively one of them. A more ideal and complex goal in modern catalysis is to potentially be able to generate every possible product of a reaction in a selective way, switching the selectivity from one to another depending on synthetic requirements by mean of small changes in the reaction conditions or catalytic system.

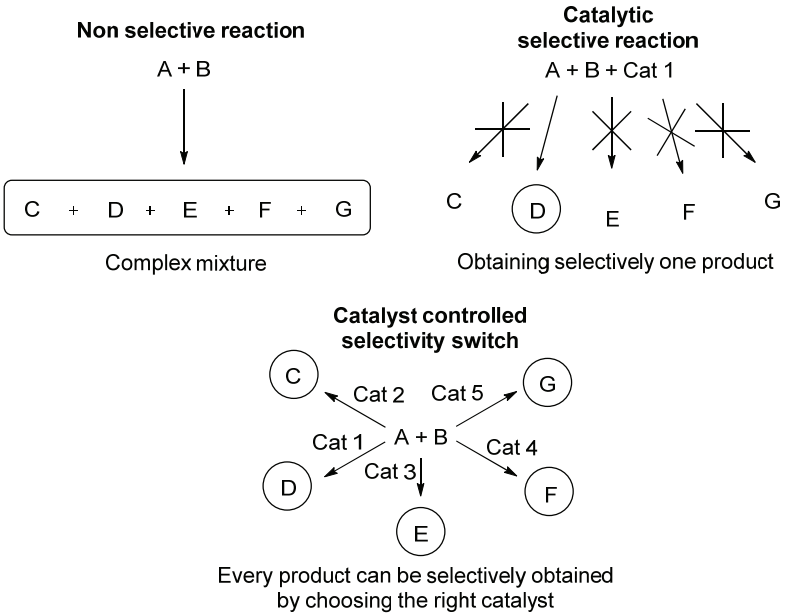
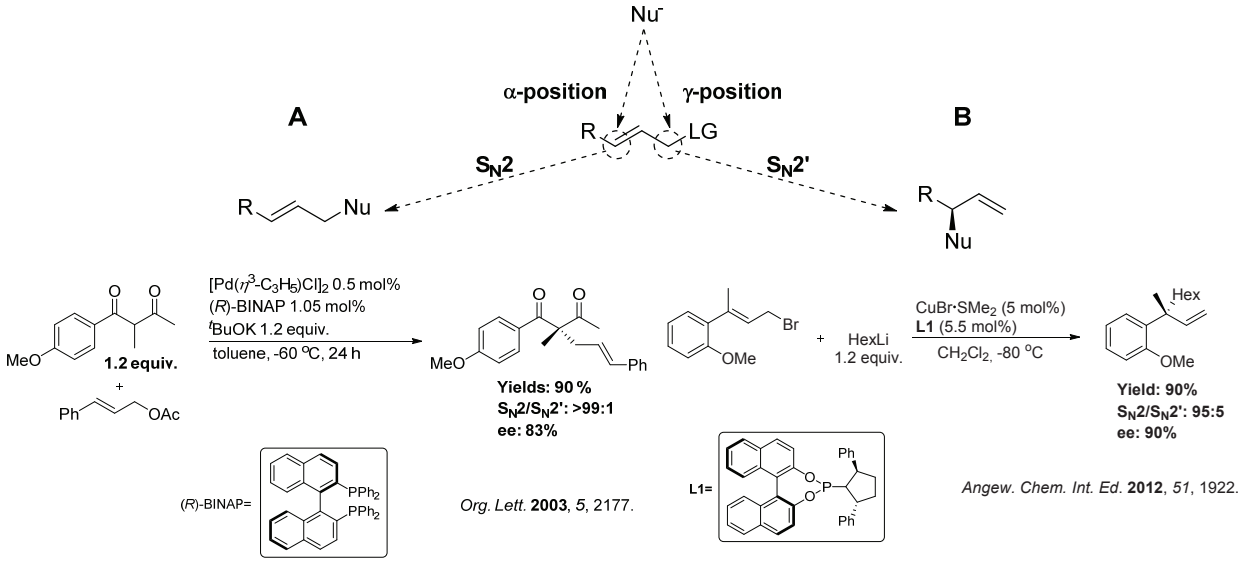


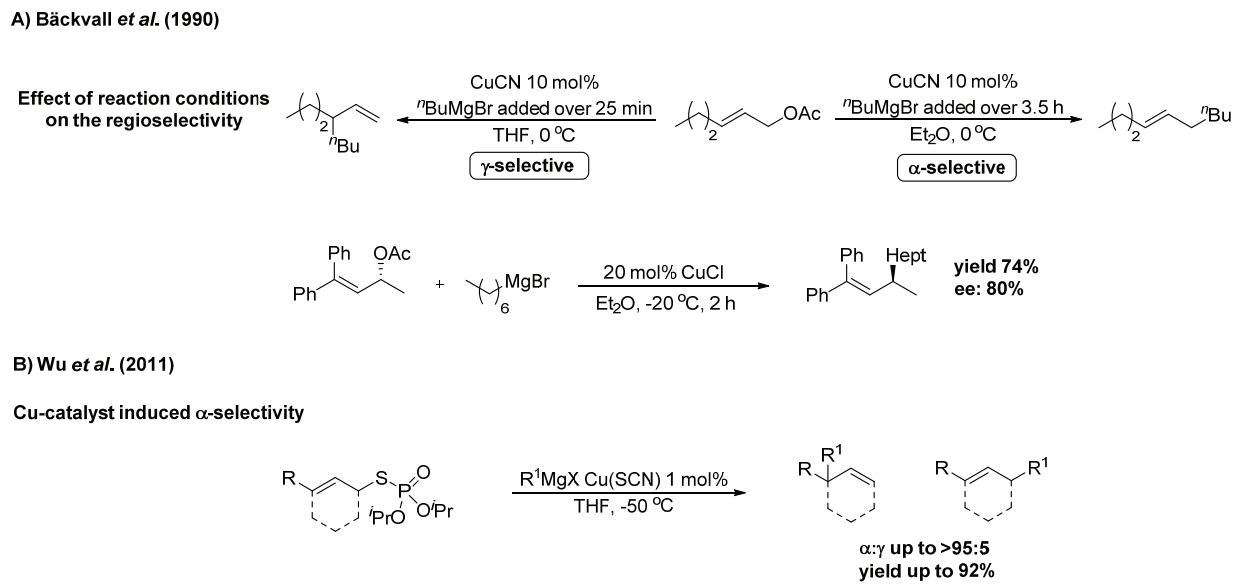
Figure 1. Selectivity control using catalysts.

Allylic substitution reactions of unsymmetrically substituted allylic compounds are good examples of systems requiring control of the regioselectivity as they are featured by the presence of two reactive sites located at the α and the γ position with respect to the leaving group (Scheme 1).[2] This duality is fundamental as the attack of a nucleophile on one or the other position results in the formation of different products. Transition metal catalysis has proven very effective in controlling a selective pathway of the reaction. The different features of the various transition metals are reflected in the different performance of each metal in terms of selectivity and scope. In the C-C bond forming reactions, while Pd (α-selective, Scheme 1, A) and Ir (γ-selective) have been proven proficient in promoting allylic alkylations with soft nucleophiles, Ni in turns catalyzes the reactions of hard nucleophiles following regioselective pathways strongly influenced by the nature of the substrate.[2,3] Cu is well-established in the field of γ-selective reactions (Scheme 1, B) involving the use of hard organometallic reagents. For this purpose Cu has been thoroughly investigated showing high versatility, and asymmetric versions of this reaction have been developed, covering a wide range of allylic systems and organometallic reagents.[4]



Scheme 1. Regioselectivity in allylic alkylations.

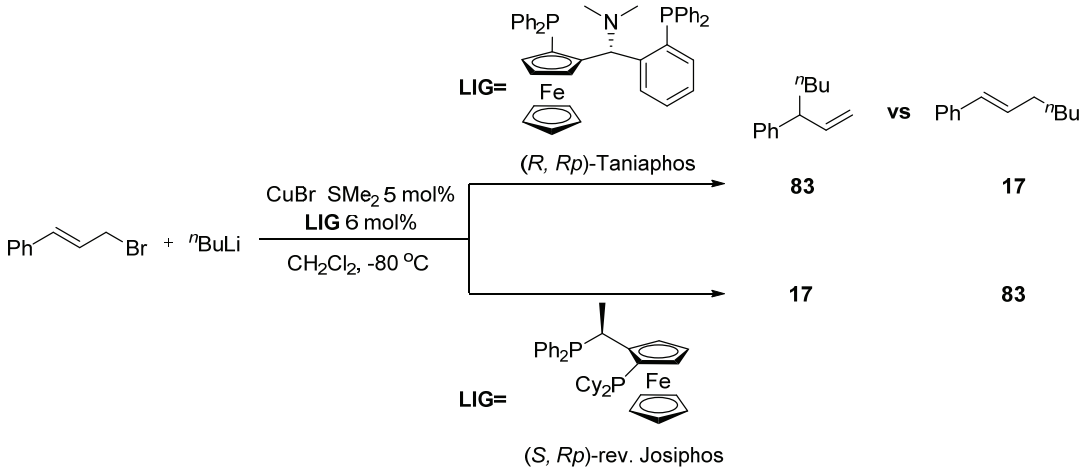
Despite of the spectacular results obtained with the *γ*-allylic substitutions, the use of Cu to catalyze *α*-allylic substitutions has been rarely reported.[5-7] In early reports it was highlighted how the change in reaction conditions (solvent, Cu salt, temperature) can influence the regioselectivity giving rise, in specific cases, to the formation of the α-substituted product.[5] Remarkably most of these examples were observed as exceptions and were not part of studies dedicated to the development of a Cu catalyzed α-allylic alkylation (AA) protocol. In 1990 Bäckvall rationalized the effects of the various parameters in a study dedicated to the regiocontrol in allylic systems and later on applied the principles to the synthesis of α-methyl substituted carboxylic acids.[6] Recently Wu and coworkers specifically developed an α-selective Cu catalyzed allylic alkylation with Grignard reagents with phosphorothioate esters in wich total regiocontrol could be achieved by a careful choice of the copper salt and of the leaving group (Scheme 2, Equation B).[7]



Scheme 2. Previous example of α-selective copper catalyzed allylic alkylations.

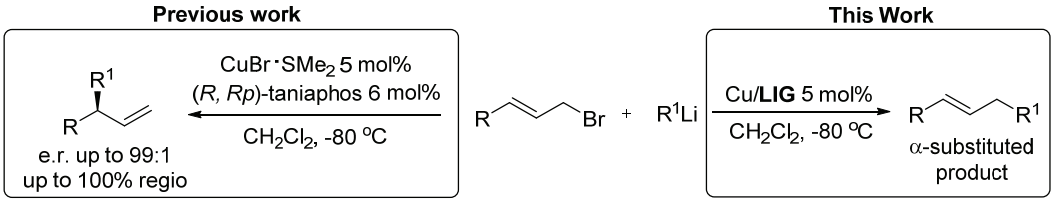
2 Goal

While these examples are mainly focused on the use of Grignard reagents, we were interested in the development of a Cu-catalyzed α-selective-allylic alkylation with organolithium reagents.[8] Organolithium reagents represent a highly valuable class of compounds in organic chemistry due to their low cost, synthetic versatility and ease of preparation.[9] Thus the use of these compounds for catalytic processes is an attractive alternative to other organometallic reagents. However, the use of these reagents in catalysis has been hampered by their extremely reactive nature. Recently, we described the first general γ-selective Cu catalyzed asymmetric allylic alkylation (AAA) with organolithium reagents proceeding without side reactions and with excellent level of chemo- regio- and enantioselectivity.[8a] During our investigations, we highlighted how the ligand plays a crucial role in determining the regioselectivity of the reaction (Scheme 3).



Scheme 3. Influence of the ligand on the regioselectivity of the Cu-catalyzed allylic alkylation with organolithium compounds.

Inspired by these finding we envisioned not only the development of a new Cu catalyzed α-allylic alkylation procedure with organolithium reagents, but also that the regioselectivity could be dictated simply by the choice of the ligand. This would enable full control on the selectivity of the reaction which would allow switching from the γ-substituted product to the α-substituted one without changing the reaction conditions, but with just an operationally simple change in ligand (Scheme 4).



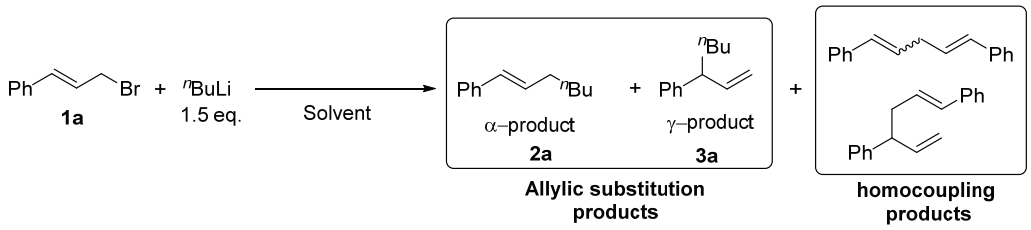
Nat. Chem. **2011**, *3*, 377.

Scheme 4. Aim of the project.

3 Results and discussion

Before further investigating the effect of the ligand on the regioselectivity, we tested if the *α*-allylic alkylation of allylbromides with organolithium compounds could be carried out via a simple uncatalyzed S_N2 displacement of the halide. Remarkably the non-catalyzed S_N2 substitution of cinnamyl-bromide **1a** by ^{n}BuLi is affected by the formation of high levels of homocoupling of the substrate (probably due to lithium-halogen exchange) and by low regioselectivity (Table 1, entry 1-3). The use of solvents others than dichloromethane (DCM), even at low temperatures, still resulted in low regioselectivity and relevant amounts of homocoupling products (Entry 4-8). It is clearly necessary then, in order to achieve a neat S_N2 substitution of the allyl-halide, to develop a catalytic system capable to direct the regiochemistry of the substitution and suppress the eventual side reactions originating from the high intrinsic reactivity of organolithium reagents.

Table1. Blank reactions of cinnamyl bromide 1a with ^{n}BuLi.

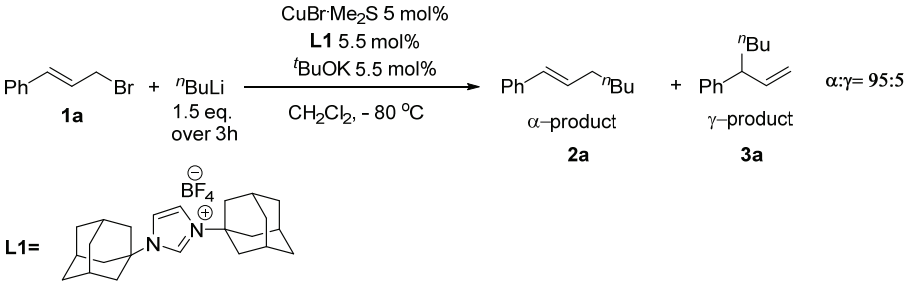


Entry	solvent	addition time	temperature	conversion (%)[a]	2a:3a:homocoupling[a,b]
1	DCM	3h	-80 °C	83	48:16:36
2	DCM	3h	r.t.	Full	47:19:34
3	DCM	direct	r.t.	Full	48:21:31
4	toluene	3h	-80 °C	50	58:15:27
5	toluene	direct	r.t.	Full	52:24:24
6	toluene	3h	r.t.	Full	50:24:26
7	THF	3h	-80 °C	Full	20:6:74
8	MTBE	3h	-80 °C	Full	52:18:30

Conditions: reactions were performed on 0.3 mmol scale. When slow addition was applied ^{n}BuLi was diluted to a 0.45 M solution with hexane. [a]Determined by NMR. [b]Determined by GC.

After proving that the reaction without catalyst is plagued by multiple drawbacks, we focused our attention on the identification of a suitable catalytic system to induce *α*-selectivity to the reaction. We were especially attracted by the possibility of testing NHC-carbene ligands.[10] As previously reported by our group, allylbromides could undergo efficient *γ*-AAA with organolithium reagents by using Cu in combination with the biphosphine ligandTaniaPhos or electron-poor phosphorus ligands like phosporamidites.[11] Although NHC-carbenes ligands have been already introduced in the field of allylic alkylation with Grignard reagents to generate enantioenriched *γ*-substituted products,[12-15] we anticipated that the strong σ-donating ligands of NHC-carbenes[10] could affect the outcome of this reaction. To estimate the sole effect of the ligand on the regioselectivity, we did not vary the conditions used for the *γ*-AAA with organolithium reagent and allyl-bromides ($CuBr{\cdot}SMe_2$, DCM, -80 °C) exchanging only Taniaphos ligand with the commercially available NHC carbene salt **L1**. The free carbene

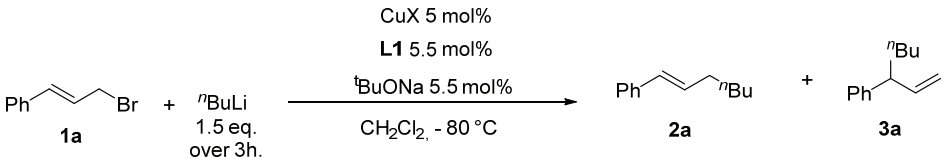
was generated by treating the corresponding salt with ^{t}BuONa. To our delight the reaction showed a completely inverted selectivity (see Scheme 2) with the linear product almost totally dominant in the crude mixture (α:γ 95:5). Moreover, no side products were identified arising from reduction or halogen-lithium exchange of the substrate.



Scheme 5. Preliminary results using carbene ligands.

This result showed NHC carbenes as a very attractive class of ligands for the α-selective AA. Nevertheless we set out to study the influence of the other reaction parameters. First of all different copper sources were screened. CuBr·SMe_2 afforded the best results in comparison with CuTC (widely applied instead in combination with Grignard reagents for the γ-selective AAA, Table 2, entry 2) and also with CuSCN[7] (previously proven efficient in α-selective AA, Table 2,entry 4).

Table 2. Screening of copper salts.

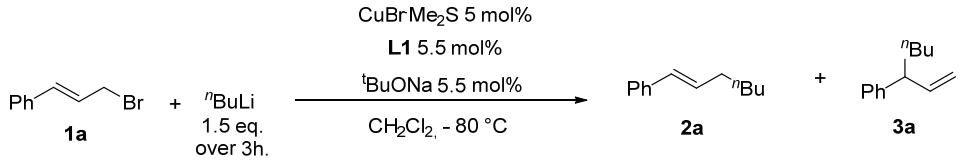


Entry	CuX	conversion (%)[a]	2a:3a: homo-coupling product (%)[a,b]
1	CuBr·Me_2S	Full conv.	95:5:-
2	CuTC	55	83:9:8
3	CuCl	96	72:10:18
4	CuSCN	Full conv.	92:8:-

Conditions: reactions were performed on 0.3 mmol scale. ^{n}BuLi was diluted to a 0.45 M solution with hexane and added over 3 h. [a]Determined by NMR. [b]Determined by GC.

The next step was to identify whether this reaction was really dependent on the presence of both the ligand and the copper, or if only one of this element was sufficient to catalyze the α-selective AA. When copper alone was used as catalyst, the reaction proceeded with lower regio- and chemoselectivity (10% homocoupling was detected, Table 3, entry 2). The use of the NHC ligand alone resulted in no catalytic activity (Table 3, entry 3), as the outcome of the reaction was comparable with the blank reaction (Table 3, entry 4).

Table 3. Influence of both copper salt and carbene ligand in the *α*-selective allylic alkylation.

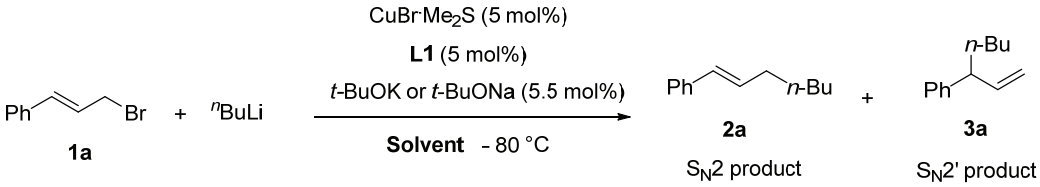


Entry	Solvent	Copper	Ligand	2a:3a (%)[a,b]	Conversion (%)[b]	Homo-coupling product (% in final mixture)[a]
1	DCM	Yes	Yes	95 : 5	Full conv.	Not detected
2	DCM	Yes	No	81 : 19	Full conv.	10
3	DCM	No	Yes	73 : 27	80	33
4	DCM	No	No	75 : 25	83	36

Conditions: reactions were performed on 0.3 mmol scale. ^{n}BuLi was diluted to a 0.45 M solution with hexane and added over 3 h. [a]Determined by NMR. [b]Determined by GC.

With the clear evidence in hand that the *α*-selective AA with organolithium and allylbromide is enabled by the presence of a specific catalytic system, we examined the effect of the solvent. Toluene turned out to be a viable alternative to DCM (Table 4, entry 2). This is particularly relevant in case of a scale up of the reaction, as DCM is a chlorinated solvent that in presence of organolithium can potentially generate reactive carbene species,[16] while toluene is a non-toxic solvent. Nevertheless the selectivity was slightly better in DCM, so we proceeded in our studies with this solvent. As expected, due to their capability to disaggregate the cluster of organolithium compounds, ethereal solvents enhanced the reactivity of the organolithium reagent promoting the formation of homocoupled products (Table 4, entries 3 and 4).

Table 4. Solvent effect on the catalytic reaction.

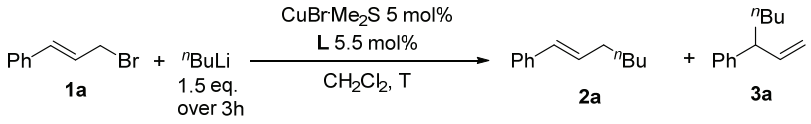


Entry	Solvent	conversion (%)[a]	2a:3a: homo-coupling product (%)[a,b]
1	DCM	Full	95 : 5 : -
2	Toluene	Full	94 : 4 : 2
3	THF	Full	20 : 6 : 74
4	MTBE	Full	52 : 18: 30

Conditions: reactions were performed on 0.3 mmol scale. ^{n}BuLi was diluted to a 0.45 M solution with hexane and added over 3 h. [a]Determined by NMR. [b]Determined by GC.

Finally also the influence of the temperature and the speed of the addition were studied. Increasing the temperature of the reaction lowered the selectivity and gave rise to homocoupling products (Table 5, entries 1 and 2). Lowering the temperature further than -80 °C didn't improve the selectivity (Table 5, entry 4).

Table 5. Temperature effect on the catalytic reaction.

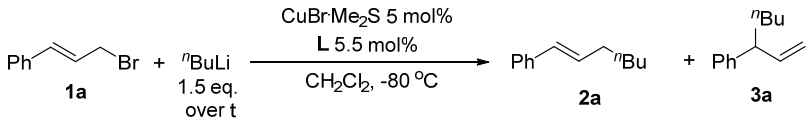


Entry	T (°C)	2a:3a: homo-coupling product (%)[a,b]
1	- 50	76:19:5
2	- 74	88:10:2
3	- 80	95:5:-
4	- 82	94:5:1

Conditions: reactions were performed on 0.3 mmol scale. ^{n}BuLi was diluted to a 0.45 M solution with hexane and added over 3 h. Full conversion was observed in all cases. [a]Determined by NMR. [b]Determined by GC.

Not surprisingly, shortening the addition time of the lithium reagent negatively affected the regioselectivity and gave rise to considerable amount of homocoupling product, probably due to the accumulation an excess of organolithium species in the reaction mixture (Table 6, entries 1 and 2).

Table 6. Effect of the adition time on the catalytic reaction.

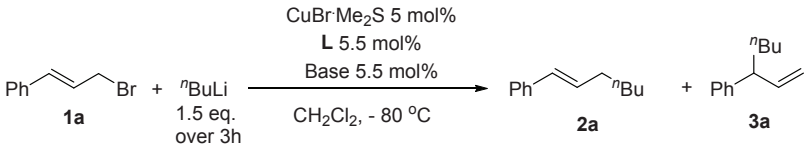


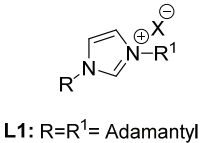
Entry	t	2a:3a: homo-coupling product (%)[a,b]
1	90 s	66:10:24
2	1 h	84:6:10
3	3h	95:5:-

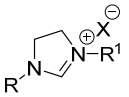
Conditions: reactions were performed on a 0.3 mmol scale. ^{n}BuLi was diluted to a 0.45 M solution with hexane and added over the specified time t. [a]Determined by NMR. [b]Determined by GC.

The fine-tuning of the reaction led us to identify the optimal conditions comprising the use of $CuBr{\cdot}SMe_2$ in combination with a carbene ligand in DCM at -80 °C. Different commercially available carbenes bearing an imidazolinium as well as an imidazolium core and different substituents at the nitrogen, were proven to be competent ligands giving high regioselectivity for the *α*-position with exception of ligand **L9** (Table 7, entries 1-6). Remarkably we could simplify our system avoiding the use of ^{t}BuONa. The organolithium reagent itself can deprotonate the carbene salts liberating the free carbene that consequently forms the complex with copper. Accordingly to our results, this deprotonation takes place more rapidly than all the other possible reactions between the organolithium reagent, the substrate and the copper. This means that the flask can be charged with copper, carbene salt and substrate. Than the slow addition of the organolithium reagent can be started. The first few drops of organolithium reagents will selectively deprotonate the carbene salts triggering the copper complex formation. The rest of the organolithium will react normally in the catalyzed AA.

Table 7. NHC ligands screening for the *α*-selective Cu-catalyzed allylic alkylation.

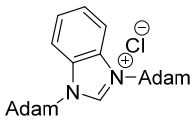




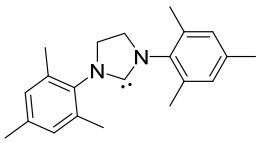


L1: R=R^1= Adamantyl X= BF_4^-
L2: R=R^1= Cy X= BF_4^-
L3: R=R^1= Mes X= Cl^-
L4: R=R^1= 2,6-(^{i}Pr)$_2$C$_6$H$_3$ X= Cl^-
L5: R=R^1= 2-(^{i}Pr)C$_6$H$_4$ X= Cl^-

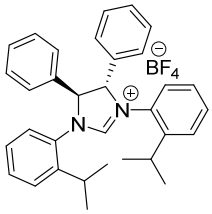
L6: R=R^1= Mes X= Cl^-
L7: R=R^1= 2-(^{i}Pr)C$_6$H$_4$ X= BF_4^-
L8: R= Mes R^1= 2,6-(^{i}Pr)$_2$C$_6$H$_4$ X= Cl^-
L9: R=R^1= 2,6-(^{i}Pr)$_2$C$_6$H$_4$ X= Cl^-



L10



L11



L12

Entry[a]	Ligand	Base	2a:3a[b]
1	**L1**	^{t}BuONa 5.5 mol%	95 : 5
2	**L2**	^{t}BuONa 5.5 mol%	97 : 3
3	**L3**	^{t}BuONa 5.5 mol%	92 : 8
4	**L6**	^{t}BuONa 5.5 mol%	95 : 5
5	**L9**	^{t}BuONa 5.5 mol%	70 : 30
6	**L10**	^{t}BuONa 5.5 mol%	91 : 9
7	**L1**	-	95 : 5
8	**L2**	-	98 : 2
9	**L3**	-	92 : 8
10	**L4**	-	85 : 15
11	**L5**	-	95 : 5
12	**L6**	-	95 : 5
13	**L7**	-	94 : 6
14	**L8**	-	73 : 27
15	**L9**	-	70 : 30
16	**L11**	-	93 : 7
17	**L12**	-	98 : 2
18	**PPh_3 5 mol%**	-	23 : 77
19	**PPh3 10 mol%**	-	21 : 79

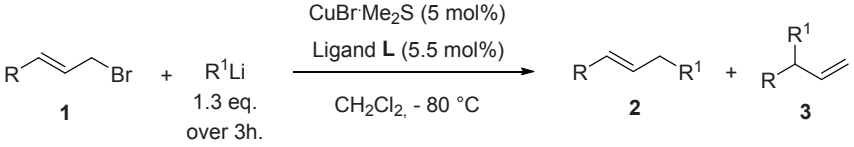
[a] Reaction conditions: 0.3 mmol of **1a**, 0.0165 mmol of NHC salt and 0.015 mmol of CuBr·SMe_2 in 2 ml of dry CH_2Cl_2 cooled at -80˚C. ^{n}BuLi (0.45 mmol, 1.6 M in hexane) diluted with hexane (final conc. 0.45 M) added via syringe pump over 3 h. [b] Determined by GC and ^{1}H-NMR analysis.

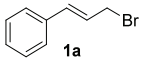
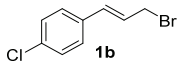
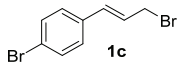
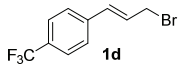
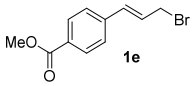
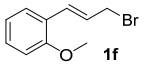
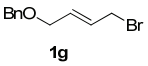
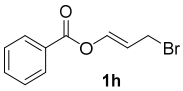
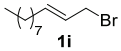
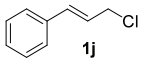
Among the commercially available ligands that were screened carbene **L1**, **L2** and **L6** emerged for their total selectivity toward the formation of the *α*-substituted product (Table 7, entries 7, 8 and 12). All the carbenes screened were featured by high *α*-selectivity. Lower selectivity was

observed in the case of NHC ligands bearing *N*-aryl substituents with two hindered substituents on the *ortho*-positions (**L8** and **L9**, Table 7 entries 14 and 15). Also the chiral carbene **L12** led to excellent levels of selectivity (Table 7, entry 17).

Having established the optimized conditions, we set out to explore the scope of this Cu-catalyzed α-selective AA (Table 8). We chose the readily available ligand **L2** as it showed excellent selectivity during the ligand screening. This α-selective AA protocol proved to be very efficient for a variety of organolithium reagents. Both long and short alkyllithium reagents were suitable reagents for the cross-coupling with cinnamyl bromide **1a** (Table 8, entries 1-5). ^{sec}BuLi could also be used providing high regioselectivity (Table 8, entry 6).[17] Substrates bearing different electron withdrawing groups also proceeded with total regioselectivity giving rise in all cases to the corresponding linear products **2** in very good yields (Table 8, entries 7-10). Importantly, no traces of side products coming from halogen\lithium exchange were observed when aromatic halides were used (Table 8, entries 7 and 8). The chemoselectivity of this system was further tested by using the ester containing substrate **1e**. It should be emphasized that no 1,2-addition to the ester took place and only linear product **2j** was obtained when ligand **L7** was used, thus showing the great activityand high chemoselectivity of the catalytic system (Table 8, entry 10). The same ligand was the optimal one for the catalytic cross-coupling of ^{n}BuLi with electron rich *o*-OMe-substituted cinnamyl bromide **1f** (Table 8, entry 11) and functionalized allyl bromides **1g** and **1h** (Table 8, entries 12 and 13). In the latter cases a slight decrease in the regioselectivity was observed but complete chemoselectivity remained. The alkylation of alkyl-substituted allyl bromide **1i** proceeded with lower selectivity but it still led to preferential α-substitution when ligand **L12** was used (Table 8, entry 14). Finally, the α-selective AA of the less reactive allyl chlorides was explored. As illustrated by the reaction between cinnamyl chloride **1j** and ^{n}BuLi (Table 8, entry 15), these allylic compounds are also suitable substrates for this catalytic transformation and afford the corresponding linear product with excellent selectivity.

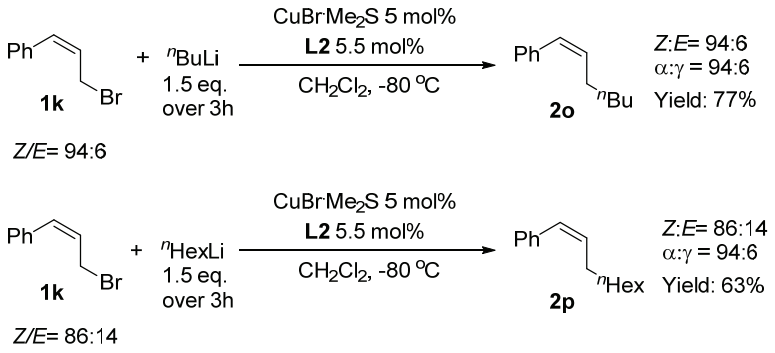
Table 8. Scope of the *α*-selective Cu-catalyzed allylic alkylation with alkyllithium reagents.



Entry[a]	1	R^1	L	2:3[b]	2	Yield (%)[c]
1	 **1a**	^{n}Bu	**L2**	98:2	**2a**	78
2	**1a**	Et	**L2**	96:4	**2b**	60
3	**1a**	^{i}Bu	**L2**	97:3	**2c**	76
4	**1a**	^{n}Hex	**L2**	98:2	**2d**	70
5	**1a**	Me	**L2**	91:9	**2e**	99[f]
6	**1a**	^{sec}Bu	**L12**	90:10	**2f**	50[d]
7	 **1b**	^{n}Bu	**L2**	98:2	**2g**	86
8	 **1c**	^{n}Bu	**L2**	98:2	**2h**	86
9	 **1d**	^{n}Bu	**L2**	98:2	**2i**	75
10[e]	 **1e**	^{n}Bu	**L7**	99:1	**2j**	72
11	 **1f**	^{n}Bu	**L7**	98:2	**2k**	83
12	 **1g**	^{n}Bu	**L7**	85:15	**2l**	90
13[e]	 **1h**	^{n}Bu	**L7**	90:10	**2m**	72
14	 **1i**	^{n}Bu	**L12**	75:25	**2n**	95
15	 **1j**	^{n}Bu	**L12**	94:6	**2a**	85

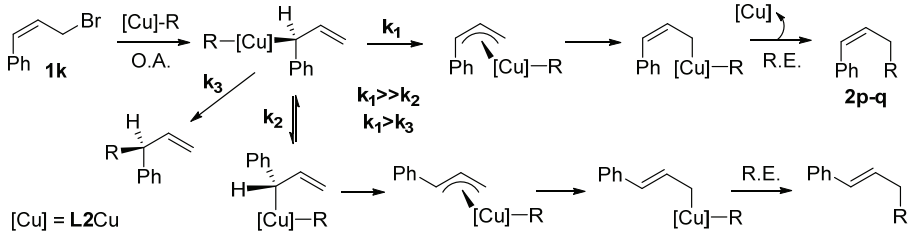
[a]0.3 mmol of substrate, 0.0165 mmol of L and 0.015 mmol of CuBr·SMe_2 in 2 mL of dry CH_2Cl_2. R^1Li (0.4 mmol) diluted with hexane (final conc. 0.45 M) added via syringe pump over 3 h. [b] Determined by ^{1}H-NMR [c] Determined by GC analysis. [c] Yield of isolated product. [d] The product was obtained as a racemate. [e] 1.0 equiv of ^{n}BuLi used. [f] Conversion.

With a thoroughly established scope in hand we finally decided to test the *Z*-cinnamyl-bromide **1k** in order to investigate the possible isomerization of the double bond in the allylic system during the reaction (see Scheme 6).



Scheme 6. Regioselectivity in allylic alkylations.

Interestingly, isomerization of cis-double bonds has been observed in previous examples of copper-mediated *α*-selective allylic alkylation of cinnamyl substrates (Scheme 6).[18] The double bond isomerization[19,20] was proposed to arise from an initial S_N2'-selective formation of a σ-allyl complex and a subsequent double bond rotation which competes with product formation. Assuming the formation of a S_N2' *σ*-allyl complex in our catalytic system, the complete absence of isomerization might suggest a very fast rearrangement to a *π*-allyl intermediate ($k_1>>k_2$), probably promoted by the electron rich character of the NHC ligand. This rearrangement would be also faster than reductive elimination, thus precluding the formation of the S_N2'product ($k_1>k_3$). Further isomerization and reductive elimination would give rise to the linear product (Scheme 7). An alternative pathway would be the direct formation of a [*σ*+*π*] Cu(III) complex[21] with retention of the geometrical information and subsequent reductive elimination (see Scheme 7).

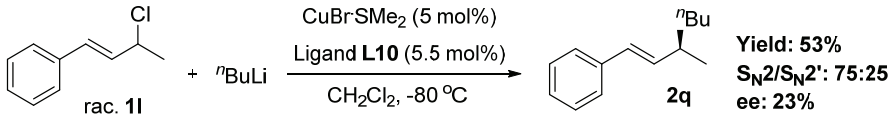


Scheme 7. Proposed mechanism for the *α*-selectivity and the retention of the olefin geometry.

4 Conclusions and future perspectives

The results described in this chapter represent a significant advance in the field of Cu-catalyzed AA. The use of NHC ligand in combination with organolithium reagents afforded an example of fully *α*-selective Cu-catalyzed allylic alkylation. This protocol is perfectly complementary with our previously reported *γ*-selective Cu-catalyzed AAA. In combination, these two methodologies represent a rare example in which the selectivity of the reaction can be completely switched just by a simple ligand change leaving the rest of the conditions untouched. This protocol showed also high chemoselectivity when sensible groups like esters and aromatic halides were present in the substrate. Moreover the reaction proceeds with retention of the geometry of the olefinic double bond in the substrate.

A future development of this methodology could be the enantioselective S_N2 substitution of secondary allyl-halides. In this direction preliminary examination has been conducted leading to promising results (Scheme 8).



Scheme 8. Preliminary results with racemic secondary allylic chlorides.

Nevertheless the instability of secondary allylhalides still represent an obstacle for a general study and extension of this methodology to secondary allylic systems. It would be of great value to extend the nature of the allylic substrates that could undergo Cu-catalyzed AA procedures with organolithium in order to access also more stable secondary substrates to exploit in an *α*-selective Cu-catalyzed asymmetric allylic alkylation.

5 Experimental section

General Methods

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV light (254 nm) and/or phosphomolybdic acid or potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies 19091s-433, Palo Alto, CA). Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI) or a LTQ Orbitrap XL (APCI; ESI). ^{1}H NMR and ^{13}C NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) or a Varian VXR200 (200 and 50 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H, δ = 77.36 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration (nH). All reactions were carried out under a nitrogen atmosphere using oven dried glassware or using standard Schlenk techniques. CH_2Cl_2 was dried and distilled over calcium hydride; toluene was dried and distilled over sodium; ^{n}hexane was dried over molecular sieves. Cinnamyl bromide (**1a**), cinnamyl chloride (**1j**), Na^{t}OBu and all copper-salts (CuCl, CuSCN, CuTC (Copper(I)-thiophene-2-carboxylate) and CuBr·SMe_2) were purchased from Sigma-Aldrich and used without further purification. Allyl bromides **1b-h** were prepared following literature procedures (**1b**[22], **1c**[23], **1d**[22], **1e**[22], **1f**[24], **1g**[25], **1h**[26], **1k**[24], **1i**[27], **1l**[28]). Organolithium reagents were purchased from Sigma-Aldrich (MeLi (1.6 M in diethyl ether), EtLi (0.5 M in benzene/cyclohexane 9:1), ^{n}HexLi (2.3 M in ^{n}hexane), ^{sec}BuLi (1.4 M in cyclohexane), PhLi (1.8 M in dibutyl ether) or from Acros (^{n}BuLi (1.6 M in ^{n}hexane), ^{iso}BuLi (1.6 M in ^{n}heptane). All ligands were purchased from Sigma-Aldrich except ligands **L4**,[29] **L5**,[30] **L7**[29] and **L9**[31] that were prepared as reported in the literature.

Procedure 1: Cu-NHC catalyzed allylic alkylation of allylic halides with organolithium reagents preforming the catalyst by addition of NaO^{t}Bu or KO^{t}Bu

A flame-dried Schlenk tube equipped with septum and stirring bar under nitrogen atmosphere is charged with copper salt (0.015 mmol, 5 mol%), NHC ligand salt (0.0165 mmol, 5.5 mol%) (the copper and ligand salts used in each experiment are reported in the optimization and scope tables) and solid base (NaO^{t}Bu or KO^{t}Bu as reported) (0.0165 mmol, 5.5 mol%). The tube is evacuated and backfilled with nitrogen three times, then dry CH_2Cl_2 (1 mL) is added and the

solution is stirred under nitrogen at r.t. for 1 h. The solution was cooled down (at the reported temperature) and stirred over 10 min. The allylic halide (0.3 mmol) was dissolved in dry CH_2Cl_2 (1 mL), injected in the mixture under stirring and stirred over 10 min. In a separate flame-dried Schlenk tube, the organolithium reagent (reported equivalents) was diluted to a combined volume of 1 mL with dry hexane (dry toluene was employed in the case of MeLi due to gelation) under nitrogen and slowly injected dropwise in the reaction mixture (over the reported time) using a syringe pump. The flow of inert gas was turned off during the addition to prevent the drops of organolithium reagent from drying on the tip of the needle. Once the addition was complete, the mixture is stirred for 2 h. The reaction was quenched with NH_4Cl sat. (2 mL), the mixture was warmed up to r.t., diluted with CH_2Cl_2 (5 mL) and the layers are separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were dried over Na_2SO_4, filtered and the solvent was evaporated *in vacuo*. Purification was performed by column chromatography on silica gel using different mixtures of pentane:Et_2O as eluent. Note: Gas chromatography analysis was carried out to determine the S_N2:S_N2':homocoupling ratio on a sample obtained after work up, which had been passed through a short plug of silica gel to remove transition metal residues.

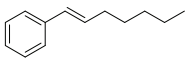
Procedure 2: Cu-NHC catalyzed allylic alkylation of allylic halides with organolithium reagents preforming the catalyst by addition of ^{n}BuLi

A flame-dried Schlenk tube equipped with septum and stirring bar under nitrogen atmosphere was charged with $CuBr{\cdot}SMe_2$ (0.015 mmol, 5 mol%) and NHC ligand salt (0.0165 mmol, 5.5 mol%). The tube was evacuated and backfilled with nitrogen three times, then dry CH_2Cl_2 (1 mL) was added and the solution was stirred under nitrogen at r.t. for 1 h. The solution was cooled down to -80 °C, then 2 drops of ^{n}BuLi (0.0165 mmol, 5.5 mol%, 1.6 M) were injected in the mixture and stirred over 15 min. The addition of allylic halide and organolithium reagent, work up of the reaction and analysis were performed in as described in procedure 1.

Procedure 3: Cu-NHC catalyzed allylic alkylation of allylic halides with organolithium reagents without preformation of the catalyst

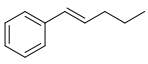
A flame-dried Schlenk tube equipped with septum and stirring bar under nitrogen atmosphere was charged with $CuBr{\cdot}SMe_2$ (0.015 mmol, 5 mol%) and NHC ligand salt (0.0165 mmol, 5.5 mol%) (the ligand salt used in each experiment are reported in the optimization and scope tables). The tube was evacuated and backfilled with nitrogen three times, then dry CH_2Cl_2 (1 mL) was added and the solution was stirred under nitrogen at r.t. for 1 h. The solution was cooled down to -80 °C and stirred over 10 min. The addition of allylic halide and organolithium reagent, work up of the reaction and analysis were performed as previously described in procedure 1.

Characterization of products 2

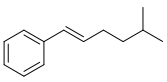


(*E*)-Hept-1-enylbenzene (2a): Synthesized according to Procedure 3. Colorless oil obtained as a 98:2 mixture of **2a** and **3a** after column chromatography (SiO_2, pentane), [78% yield] from **1a** as starting material and ^{n}BuLi. A 94:6 mixture of **2a** and **3a** was obtained after column chromatography (SiO_2, pentane), [85% yield] from **1j** as starting material and ^{n}BuLi. The physical data were identical in all respects to those previously reported.[32] **2a** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.36 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.9, 7.1 Hz 1H), 2.21 (q, *J* = 7.1 Hz, 2H), 1.54-1.44 (m,

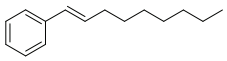
2H), 1.40-1.31 (m, 4H), 0.89 (t, *J* = 5.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 137.9, 131.2, 129.7, 128.4, 126.7, 125.9, 33.0, 31.4, 29.1, 22.6, 14.1.



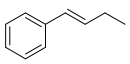
(*E*)-Pent-1-enylbenzene (2b): Synthesized according to Procedure 3 from **1a** as starting material and EtLi. Colorless oil obtained as a 96:4 mixture of **2b** and **3b** after column chromatography (SiO_2, pentane), [60% yield]. The physical data were identical in all respects to those previously reported.[33] **2b:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.35 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 6.7 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.28–6.18 (m, 1H), 2.20 (q, *J* = 7.1 Hz, 2H), 1.56–1.45 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 137.9, 131.0, 129.9, 128.4, 126.7, 125.9, 35.1, 22.5, 13.7.



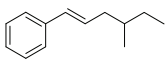
(*E*)-(5-Methyl)-hex-1-enylbenzene (2c): Synthesized according to Procedure 3 from **1a** as starting material and ^{i}BuLi. Colorless oil obtained as a 97:3 mixture of **2c** and **3c** after column chromatography (SiO_2, pentane), [76% yield]. The physical data were identical in all respects to those previously reported.[33] **2c:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.35 (d, *J* = 7.3, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 7.1 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.6, 6.8 Hz, 1H), 2.25 (dt, *J* = 7.8, 7.2 Hz, 2H), 1.62 (sept, *J* = 6.6 Hz, 1H), 1.36 (q, *J* = 7.3 Hz, 2H), 0.93 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 138.0, 131.3, 129.5, 128.4, 126.7, 125.8, 38.5, 30.9, 27.5, 22.5.



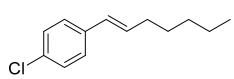
(*E*)-Non-1-enylbenzene (2d): Synthesized according to Procedure 3 from **1a** as starting material and ^{n}HexLi. Colorless oil obtained as a 98:2 mixture of **2d** and **3d** after column chromatography (SiO_2, pentane), [70% yield]. The physical data were identical in all respects to those previously reported.[34] **2d:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.21 (dt, *J* = 6.8, 1.1 Hz, 2H), 1.47 (quint, *J* = 6.8 Hz, 2H), 1.40-1.20 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 137.9, 131.2, 129.6, 128.4, 126.7, 125.9, 33.0, 31.8, 29.4, 29.2, 22.6, 14.1.



(*E*)-But-1-enylbenzene (2e): Synthesized according to Procedure 3 from **1a** as starting material and MeLi. Colorless oil obtained as a 91:9 mixture of **2e** and **3e** [yield not determined]. The product was not purified due to the high volatility and R_f similar to toluene, used for diluting the MeLi. Analysis was performed by comparing the physical data with precedent literature.[35] **2e:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.40-7.19 (m, 5H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.0 Hz, 1H), 2.30 (dq, *J* = 7.3, 5.8 Hz, 2H), 1.17 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 137.9, 132.6, 128.7, 128.4, 126.7, 125.8, 26.05, 13.6.

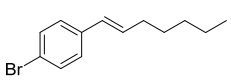


(*E*)-(2-Methyl)-hex-1-enylbenzene (2f): Synthesized according to Procedure 3 from **1a** as starting material and ^{sec}BuLi. Colorless oil obtained as a 90:10 mixture of **2f** and **3f** after column chromatography (SiO_2, pentane) [50% yield]. The physical data were identical in all respects to those previously reported.[8b] **2f:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8,7.2 Hz, 1H), 2.22 (ddd, *J* = 13.8, 6.4, 1.1 Hz, 1H), 2.05 (ddd, *J* = 13.8, 7.4, 3.7 Hz, 1H), 1.57–1.47 (m, 1H), 1.46–1.36 (m, 1H), 1.27–1.14 (m, 1H), 0.92 (t, *J* = 6.7 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 138.3, 131.1, 130.2, 128.8, 127.1 126.3, 40.5, 35.3, 29.5, 19.5, 11.9.

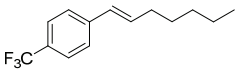


(*E*)-4-(Hept-1-enyl)-1-chlorobenzene (2g): Synthesized according to Procedure 3 from **1b** as starting material and ^{n}BuLi. Colorless oil obtained as a 98:2 mixture of **2g** and **3g** after column chromatography (SiO_2,

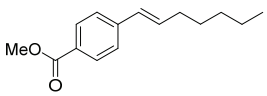
pentane), [86% yield]. The physical data were identical in all respects to those previously reported.[36] **2g:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.30–7.22 (m, 4H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.7, 6.7 Hz, 1H), 2.20 (dt, *J* = 7.8, 6.7 Hz, 2H), 1.47 (quint, *J* = 7.2 Hz, 2H), 1.40–1.28 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 136.4, 132.2, 132.0, 128.5, 128.5, 127.1, 33.0, 31.4, 29.0, 22.5, 14.0.



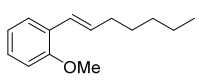
(*E*)-4-(Hept-1-enyl)-1-bromobenzene (2h): Synthesized according to Procedure 3 from **1c** as starting material and ^{n}BuLi. Colorless oil obtained as a 98:2 mixture of **2h** and **3h** after column chromatography (SiO_2, pentane), [86% yield]. The physical data were identical in all respects to those previously reported.[37] **2h:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.31 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.9, 6.6 Hz, 1H), 2.19 (dt, *J* = 7.2, 6.7 Hz, 2H), 1.47 (quint, *J* = 7.3 Hz, 2H), 1.39–1.27 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 136.9, 132.1, 131.5, 128.5, 127.4, 120.31, 33.0, 31.4, 28.9, 22.5, 14.0.



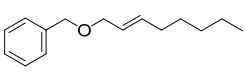
(*E*)-4-(Hept-1-enyl)-1-trifluoromethylbenzene (2i): Synthesized according to Procedure 3 from **1d** as starting material and ^{n}BuLi. Colorless oil obtained as a 98:2 mixture of **2i** and **3i** after column chromatography (SiO_2, pentane), [75% yield]. The physical data were identical in all respects to those previously reported.[8b] **2i:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.8, 6.1 Hz, 1H), 2.24 (dt, *J* = 7.1, 6.9 Hz, 2H), 1.49 (quint, *J* = 7.2 Hz, 2H), 1.40–1.29 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 141.4, 134.1, 128.5, 126.0. 125.6, 125.4, 123.0, 33.0, 31.4, 28.8, 22.5, 14.0.



(*E*)-Methyl-4-(hept-1-enyl)benzoate (2j): Synthesized according to Procedure 3 from **1e** as starting material and ^{n}BuLi. Colorless oil obtained as a 99:1 mixture of **2j** and **3j** after column chromatography (SiO_2, pentane/Et_2O), [72% yield]. The physical data were identical in all respects to those previously reported.[38] **2j:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.96 (dt, *J* = 8.4, 1.8 Hz, 2H), 7.38 (d, *J* = 8.4, 1.8 Hz, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.35 (d, *J* = 15.9, 6.10 Hz, 1H), 3.90 (s, 3H), 2.23 (dt, *J* = 7.2, 5.7 Hz, 2H), 1.48 (quint, *J* = 7.1 Hz, 2H), 1.39–1.28 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 167.0, 142.5, 134.2, 129.8, 129.0, 128.2, 125.7, 51.9, 33.1, 31.4, 28.8, 22.5, 14.0.

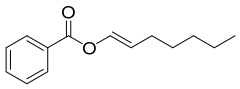


(*E*)-2-(Hept-1-enyl)-1-methoxybenzene (2k): Synthesized according to Procedure 3 from **1f** as starting material and ^{n}BuLi. Colorless oil obtained as a 96:4 mixture of **2k** and **3k** after column chromatography (SiO_2, pentane/Et_2O= 98:2), [83% yield]. The physical data were identical in all respects to those previously reported.[39] **2k:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.42 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.18 (dt, *J* = 6.4, 1.6 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.9, 6.9 Hz, 1H), 3.85 (s, 3H), 2.23 (dt, *J* = 7.0, 6.6 Hz, 2H), 1.48 (quint, *J* = 7.2 Hz, 2H), 1.39–1.29 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 156.2, 132.0, 127.7, 127.0, 126.3, 124.1, 120.6, 110.8, 55.4, 33.4, 31.5, 29.2, 22.6, 14.1.

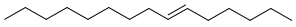


(*E*)-(Oct-2-enyloxy)methylbenzene (2l): Synthesized according to Procedure 3 from **1g** as starting material and ^{n}BuLi. Colorless oil obtained as a 85:15 mixture of **2l** and **3l** after column chromatography (SiO_2, pentane/Et_2O= 98:2), [90% yield]. The spectra were compared with precedent literature.[40] **2l:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.38–7.32 (m, 4H), 7.31–7.26 (m, 1H), 5.78–5.66 (m, 1H), 5.66–5.55 (m, 1H), 4.51 (s, 2H), 3.98 (dt, *J* = 6.1, 0.8 Hz, 2H), 2.06 (dt, *J* = 7.1, 6.8 Hz, 2H), 1.45–1.20 (m, 6H), 0.90 (t, *J* = 6.6

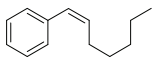
Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 135.1, 128.3, 127.8, 127.5, 127.4, 126.1, 71.8, 71.0, 32.3, 31.4, 28.7, 22.5, 14.0.



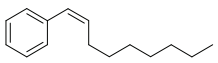
(*E*)-Hept-1-enylbenzoate (2m): Synthesized according to Procedure 3 from **1h** as starting material and ^{n}BuLi. Colorless oil obtained as pure **2m** from a 90:10 mixture of **2m** and **3m** after column chromatography (SiO_2, pentane/Et_2O= 80:1), [72% yield]. The physical data were identical in all respects to those previously reported.[41] **2m:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 (dt, *J* = 12.4, 1.4 Hz, 1H), 5.61 (dt, *J* = 12.4, 7.5 Hz, 1H), 2.07 (dq, *J* = 7.4, 6.3 Hz, 2H), 1.43 (quint, *J* = 7.1 Hz, 2H), 1.38–1.28 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 163.9, 135.5, 133.3, 129.8, 129.3, 128.4, 115.7, 31.2, 29.2, 27.3, 22.4.



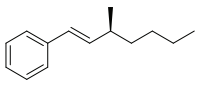
(*E*)-6-Pentadecene (2n): Synthesized according to Procedure 3 from **1i** as starting material and ^{n}BuLi. Colorless oil obtained as a 75:25 mixture of **2n** and **3n** after column chromatography (SiO_2, pentane), [95% yield]. The physical data were identical in all respects to those previously reported.[42] **2n:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 5.41–5.36 (m, 2H), 2.05–1.86 (m, 4H), 1.43–1.16 (m, 18H), 0.97–0.79 (m, 6H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 130.7, 33.0, 32.9, 32.3, 31.8, 30.0, 29.9, 29.7, 29.7, 29.5, 23.1, 22.9, 14.5, 14.4. One ^{13}C signal is missing or overlapping (C=C double bond).



(*Z*)-Hept-1-enylbenzene (2o): Synthesized according to Procedure 3 from **1k** (*Z*:*E* ratio = 94:6) as starting material and ^{n}BuLi. Colorless oil obtained as a 94:6 mixture of **2o** (*Z*:*E* ratio = 94:6) and **3o** after column chromatography (SiO_2, pentane), [77% yield]. The physical data were identical in all respects to those previously reported.[36] **(*Z*)-2o:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.38-7.28 (m, 4H), 7.25-7.23 (m, 1H), 6.43 (d, *J* = 11.7 Hz, 1H), 5.69 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.35 (qt, *J* = 7.3, 1.7 Hz, 2H), 1.48 (quint, *J* = 7.3 Hz, 2H), 1.39-1.28 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 133.4, 128.8, 128.5, 128.2, 126.8, 126.5, 31.7, 29.8, 28.7, 22.6, 14.1.



(*Z*)-Non-1-enylbenzene (2p): Synthesized according to Procedure 3 from **1k** (*Z*:*E* ratio = 86:14) as starting material and ^{n}HexLi. Colorless oil obtained as a 93:7 mixture of **2p** (*Z*:*E* ratio = 86:14) and **3p** after column chromatography (SiO_2, pentane), [63% yield]. The physical data were identical in all respects to those previously reported.[43] **(*Z*)-2p:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.41–7.31 (m, 4H), 7.23 (t, *J* = 6.9 Hz, 1H), 6.45 (d, *J* = 11.6 Hz, 1H), 5.72 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.38 (qd, *J* = 7.5, 1.7 Hz, 2H), 1.47 (quint, *J* = 7.3 Hz, 2H), 1.39-1.24 (m, 8H), 0.93 (dd, *J* = 8.2, 4.5 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$, 25 °C) δ 138.2, 133.6, 129.1, 129.0, 128.4, 126.7, 32.2, 30.3, 29.7, 29.5, 29.0, 23.0, 14.4.



(*E*)- (3-Methyl)-hept-1-enylbenzene (2q): Synthesized according to Procedure 3 from **1l** as starting material and ^{n}BuLi. Colorless oil obtained as a 75:25 mixture of **2q** and **3q** after column chromatography (SiO_2, pentane), [53% yield, 23% ee]. The physical data were identical in all respects to those previously reported.[28] ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.38-7.34 (m, 2 H), 7.34 - 7.25 (m, 2 H), 7.23 - 7.16 (m, 1 H), 6.34 (d, *J* = 15.9 Hz, 1 H), 6.11 (dd, *J* = 15.9, 8.0 Hz, 1 H), 2.29 (m, 1 H), 1.43 - 1.26 (m, 6 H), 1.08 (d, *J* = 6.8 Hz, 3 H), 0.90 (t, *J* = 6.9 Hz, 3 H). ^{13}C-NMR (100.59 MHz, $CDCl_3$, 25 °C): δ = 138.2, 137.3, 128.7, 128.1, 126.9, 126.2, 37.5, 37.1, 29.9, 23.1, 20.9, 14.3. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OB-H column, n-heptane, 45 min, 0.5 ml/min, 40 °C, 248 nm, retention times (min.): 10.925 (minor) and 11.386 (major).

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