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ARTICLE TYPE

Nickel-Catalyzed Substitution Reactions of Propargyl Halides with Organotitanium Reagents

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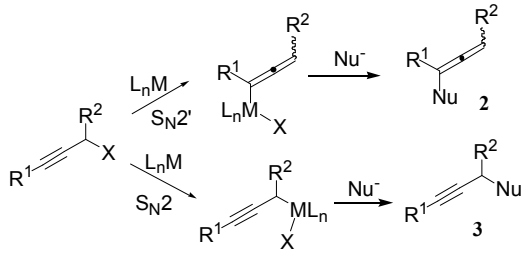
A simple and mild catalytic coupling reaction of propargyl halides with organotitanium reagents is reported. The reaction of propargyl bromide with organo-titanium reagents mediated by $NiCl_2$ (2 mol%) and PCy_3 (4 mol%) in CH_2Cl_2 affording coupling product allenes in good to excellent yields (up to 95%) at room temperature. However, $NiCl_2(PPh_3)_2$ becomes the best catalyst for substituted propargyl halides to yield allenes or alkynes preferentially. On the basis of the experimental results, a possible catalytic cycle has been proposed.

Introduction

Allenes and alkynes are important structural scaffolds found in many natural and pharmaceutical products,[1] and in addition, they serve as building blocks for many organic transformations.[2] Owing to the importance of allenes and alkynes framework, their synthesis and applications have attracted considerable attentions over the past decades.[3] Synthetic protocols for substituted allenes include elimination of allylic compounds,[4] isomerization of alkynes,[5] a reaction of aldehyde and terminal alkynes,[6] and a few cases of metal-catalyzed reactions of propargylic compounds.[7,8] For the synthesis of alkynes, numerous new synthetic methodologies have been developed in recent years. Among the methods hitherto developed, Sonogashira coupling reactions which are conducted in general at elevated temperatures have been a central focus in recent years.[9] In addition, metal-catalyzed coupling reactions of electrophiles with alkynylmetallic reagents provide an alternative route for the synthesis of alkyne compounds.[10] For metal-catalyzed reactions, the coupling reaction of propargyl derivatives with organometallic nucleophiles is especially interesting since the reaction may proceed via either an S_N2' process for a formation of an allene **2** or an S_N2 process to furnish an alkyne **3** (**Scheme 1**).[2b] However, this type of reactions has been less explored due to a complication of two competitive pathways. A key success of this reaction relies mainly on suitable catalytic systems and/or appropriate organometallic reagents that can selectively produce either compound **2** or **3**.

Organotitanium reagents, which can be easily prepared from the corresponding halide, is a highly efficient nucleophiles for cross-coupling reactions with aromatic halides[11] or benzylic halides.[12] To the best of our knowledge, there is no report on direct coupling of propargylic halide with organotitanium reagents for the synthesis of allenes or alkynes. Recent investigations have demonstrated that the nickel is a good catalyst for many cross-coupling reactions.[13]



Scheme 1 S_N2' and S_N2 Processes of Metal-catalyzed Coupling Reactions of Propargyl Derivatives with Organometallic Nucleophiles

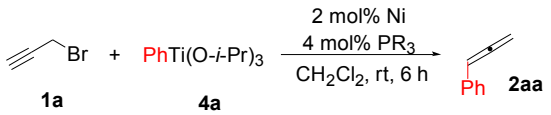
To continue our effort to develop efficient coupling reactions using reactive organometallic reagents,[11d,14] we herein report a novel nickel(II)-catalyzed substitution reactions of propargyl halides with organotitanium reagents at ambient temperature in short time with good yields for the synthesis of allenes or alkynes.

Results and Discussion

Initially, the reaction of propargyl bromide HC≡CCH$_2$Br (**1a**) with PhTi(O-*i*-Pr)$_3$ (**4a**) was selected as the substrates for the catalyst screening study (eq. 1). The primary metal screening was performed with PCy_3, and the results are listed in Table **1**. When 2 mol% $NiCl_2(PPh_3)_2$ was used as the catalyst, the reaction proceeded via the S_N2' process smoothly to afford the corresponding product phenylallene **2aa** with 73% conversion in CH_2Cl_2 at room temperature over 6 h (Table 1, entry 1). To our delight, when 4 mol% PCy_3 was used, the reaction conversion was significantly elevated to 97% (Table 1, entry 2). Subsequently, we surveyed other nickel(II) complex with PCy_3 and found that the $NiCl_2$ (2 mol%)/PCy_3 (4 mol%) complex exhibited the best activity (Table 1, entry 5). Since the outcome of each coupling reaction depends on the relative steric hindrance and electronic property of the ligand, further optimization of the reaction conditions was then aimed at exploring the efficacy of $NiCl_2$ with other phosphine ligands (Table 1, entries 6-9). It was found that the $NiCl_2/PPh_3$, $NiCl_2/P(p\text{-tolyl})_3$, $NiCl_2/P(o\text{-tolyl})_3$, and $NiCl_2$/dppm complex were also effective for the reaction. But the catalytic system of $NiCl_2$ (2 mol%)/PCy_3 (4 mol%) complex have the highest capability of conversion (>99%) among $NiCl_2$/Phosphine (Table 1, entry 5). When $Pd(OAc)_2$ was used as

a metal source, a lower 68% conversion of **2aa** was obtained (Table 1, entry 10). Under the above reaction conditions, phenyl boronic acid and phenyl potassium fluoborate were also examined as a nucleophile source. However, without or with 2 equiv. Cs_2CO_3, $PhB(OH)_2$ was inert for the coupling reaction (Table 1, entries 11 and 12). When $PhBF_3K$ was used as a nucleophile source, 13% conversion of **2aa** was obtained with $NiCl_2/PCy_3$ and 55% conversion of **2aa** was obtained with $Pd(OAc)_2/PCy_3$(Table 1, entries 13 and 14). Therefore, the optimal reaction conditions were as follows: 2 mol% $NiCl_2$ and 4 mol% PCy_3 conducting in CH_2Cl_2 at room temperature over 6 h (Table 1, entry 5).

Table 1. Optimizations of coupling reactions of propargyl bromide (**1a**) and $PhTi(O\text{-}i\text{-}Pr)_3$ (**4a**)[a]



1a 1.0 mmol **4a** 1.5 mmol (1)

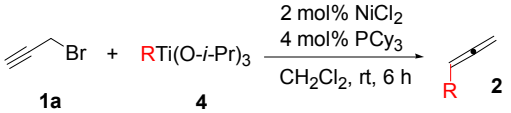
Entry	[Ni]	PR_3	Nucleophile	Conv.[b] (%)
1	$NiCl_2(PPh_3)_2$	-	**4a**	73
2	$NiCl_2(PPh_3)_2$	PCy_3	**4a**	97
3	$Ni(acac)_2$	PCy_3	**4a**	97
4	$NiBr_2$	PCy_3	**4a**	97
5	$NiCl_2$	PCy_3	**4a**	>99
6	$NiCl_2$	PPh_3	**4a**	92
7	$NiCl_2$	P(*p*-tolyl)$_3$	**4a**	96
8	$NiCl_2$	P(*o*-tolyl)$_3$	**4a**	94
9	$NiCl_2$	dppm[c]	**4a**	96
10	$Pd(OAc)_2$	PCy_3	**4a**	68
11[d]	$NiCl_2$	PCy_3	$PhB(OH)_2$	-
12[e]	$NiCl_2$	PCy_3	$PhB(OH)_2$	6
13	$NiCl_2$	PCy_3	$PhBF_3K$	13
14	$Pd(OAc)_2$	PCy_3	$PhBF_3K$	55

[a] **1a/4a**/M/L = 1.00/1.50/0.020/0.040 mmol; CH_2Cl_2, 2 mL. [b] Conversion of **2aa** is based on ^1H NMR spectra. [c] dppm (1,1-bis(diphenylphosphino)methane) = 2 mol%. [d] 1.50 mmol $PhB(OH)_2$. [e] 1.50 mmol $PhB(OH)_2$ and 3.00 mmol of Cs_2CO_3.

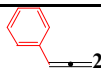
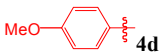
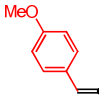
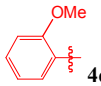
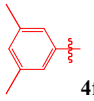
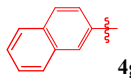
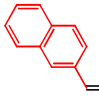
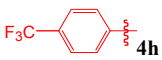
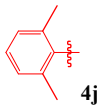
With the optimized conditions in hand, the scope of catalytic substitution reaction with organotitanium reagents of $RTi(O\text{-}i\text{-}Pr)_3$ was then explored (eq. 2), and results are presented in Table 2 (entries 1-11). Reactions of aryltitanium reagents bearing electron-donating substituents on the aromatic ring furnished mono-substituted allenes **2ab-2ag** in good to excellent isolated yields from 87 to 95% (Table 2, entries 2-7). The catalytic system also works well for aryl nucleophile bearing an electron-withdrawing trifluoromethyl substituent, furnishing **2ah** in a 94% yields (Table 2, entry 8). In contrast, reactions employing aliphatic cyclohexyl nucleophile required a higher catalyst loading of 6 mol% and a longer reaction time of 12 h to afford the allene **2ai** in a yield of 92% (Table 2, entry 9). Unfortunately, we use other alkyltitanium reagents, such as $^nBuTi(O\text{-}i\text{-}Pr)_3$ and $^sBuTi(O\text{-}i\text{-}Pr)_3$, without success. This may be due to the boiling point of the corresponding allene products is too low and can not be separated.

It is worth noting that a reaction of **1a** with $(2,6\text{-}Me_2C_6H_3)Ti(O\text{-}i\text{-}Pr)_3$ (**4j**) containing a sterically hindered $2,6\text{-}Me_2C_6H_3$ nucleophile produced a mixture of two compounds of **2aj** and **2aj'** (Table 2, entry 10). The total conversion is >99% with a ratio of 38:62 in favor of **2aj'**. The desired allene **2aj** is a minor product in a 20% yield. The structure of **2aj'** that is in a 61% yield was confirmed by the ^1H NMR spectrum and high-resolution mass spectrum. Compound **2aj'** is formed from two molecules of **1a** and one $2,6\text{-}Me_2C_6H_3$ nucleophile.

Table 2. Monosubstituted allenes from coupling reactions of propargyl bromide **1a** with $RTi(O\text{-}i\text{-}Pr)_3$[a]



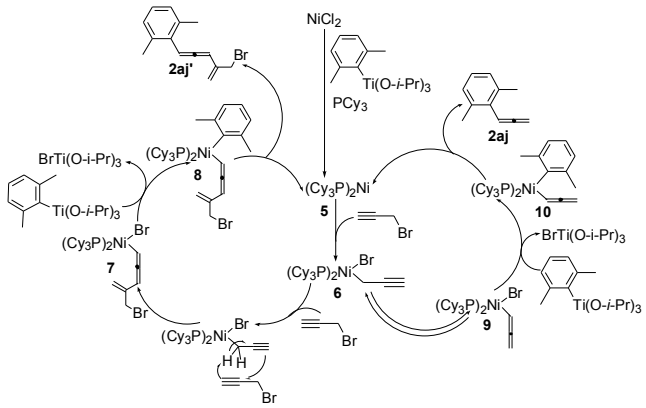
1a 1.0 mmol **4** 1.5 mmol (2)

Entry	**4** (R)	Product **2**	Yield[b] (%)
1	 **4a**	 **2aa**	87%
2	 **4b**	 **2ab**	91%
3	 **4c**	 **2ac**	92%
4	 **4d**	 **2ad**	91%
5	 **4e**	 **2ae**	93%
6	 **4f**	 **2af**	95%
7	 **4g**	 **2ag**	90%
8	 **4h**	 **2ah**	94%
9[c]	 **4i**	 **2ai**	91%
10[d]	 **4j**	 **2aj**  **2aj'**	20% 61%

[a] **1/4**/$NiCl_2/PCy_3$ = 1.00/1.50/0.020/0.040 mmol; CH_2Cl_2, 2 mL; room temperature. [b] Isolated yield are in parenthesis. [c] $NiCl_2/PCy_3$ = 0.060 /0.120 mmol (6 mol%), 12 h. [d] >99% conversion, **2aj**: **2aj'**=38: 62.

A likely catalytic cycle for the formation of **2aj'** is proposed as shown in Scheme **2**. The first reaction involves replacements of both chloride ions in $NiCl_2$ with two $2,6\text{-}Me_2C_6H_3$ groups followed by reductive elimination of two $2,6\text{-}Me_2C_6H_3$ groups

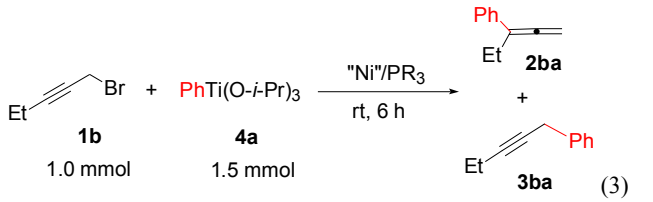
and coordination of PCy_3 to furnish a Ni(0) active species of $Ni(PCy_3)_2$ (**5**). Oxidative addition of propargyl bromide (**1a**) to **5** affords a Ni(II) species of $(Cy_3P)_2Ni(CH_2C{\equiv}CH)Br$ (**6**). Complex **6** could also be isomerize to **9**. However, $(2,6\text{-}Me_2C_6H_3)Ti(O\text{-}i\text{-}Pr)_3$ (**4j**) containing a sterically hindered $2,6\text{-}Me_2C_6H_3$ groups, its steric hindrance slow down the transmetallation reaction, allowing the reaction of **6** with another molecule of propargyl bromide. Then, α-H of propargyl group of **6** is attacked by one molecule of **1a** to affords an intermediate **7**. Transmetallation of **7** with $(2,6\text{-}Me_2C_6H_3)Ti(O\text{-}i\text{-}Pr)_3$ gives a Ni(II) intermediate **8**, which undergoes a reductive elimination process to produce the coupling product **2aj'** and to regenerate the active species **5** for the next cycle of reaction. While, transmetallation of **9** with $(2,6\text{-}Me_2C_6H_3)Ti(O\text{-}i\text{-}Pr)_3$ gives a Ni(II) intermediate **10**, which undergoes a reductive elimination process to produce the coupling product **2aj** and to regenerate the active species **5** for the next cycle of reaction.



Scheme 2. The proposed catalytic cycle for the formation of **2aj'** and **2aj.**

Encouraged by the above good performance of the current catalyst system, we subsequently investigated coupling reactions of substituted propargyl bromide (eq. 3). However, a reaction of 1-bromo-2-pentyne (**1b**) with $PhTi(O\text{-}i\text{-}Pr)_3$ employing the catalyst of 2 mol% $NiCl_2$ and 4 mol% PCy_3 yielded both S_N2' and S_N2 products of 1-phenyl-1-ethyl-allene (**2ba**) and 1-phenyl-2-pentyne (**3ba**) with only a 50% conversion (Table 3, entry 1). The product ratio is about 3:1 in favor of the allene **2ba**. Therefore, the reaction conditions were re-tuned. We initially optimized the reaction of 1-bromo-2-pentyne (**1b**) with $PhTi(O\text{-}i\text{-}Pr)_3$ in CH_2Cl_2 at room temperature catalyzed by $NiCl_2$ (4 mol%)/PCy_3 (8 mol%) complex. The reaction proceeded smoothly to afford the product **2ba** and **3ba** with a 77% conversion and a ratio of 82:18 in favor of **2ba**. Then, the effect of solvents was investigated (Table 3, entries 2-4). The results indicated that solvents played an important role in adjusting the conversion and product ratio of the reaction. THF was found to be the most suitable solvent for the reaction, affording the product **2ba** and **3ba** with 90% conversion and a ratio of 86:14 in favor of **2ba** (Table 3, entry 4). To further improve the converation and the product ratio of the reaction, various phosphine ligands were investigated (Table 3, entries 5-7). The results showed that PPh_3 could produce **2ba** and **3ba** with product ratio of 94:6, but in 82% conversion (Table 3, entry 5). Pleasingly, the $NiCl_2(PPh_3)_2$ complex was significantly improved the converation and the product ratio of the reaction. The coupling product **2ba** and **3ba** was obtained in a 95% conversion and the best selectivity (**2ba**:**3ba** = 95:5, Table 3, entry 8). Thus, the optimized catalytic system was 4 mol% $NiCl_2(PPh_3)_2$, 1.0 mmol substituted propargyl bromide, 1.5 mmol $RTi(O\text{-}i\text{-}Pr)_3$ in THF at room temperature (eq. 3, Table 3, entry 8).

Table 3. Optimization of reactions of 1-bromo-2-pentyne (**1b**) and $PhTi(O\text{-}i\text{-}Pr)_3$ (**4a**)[a]



(3)

Entry	[Ni] (4 mol%)	Ligand (8mol%)	Solvent	Conv. (%)[b]	**2ba:3ba**
1[c]	$NiCl_2$	PCy_3	CH_2Cl_2	50	75:25
2	$NiCl_2$	PCy_3	CH_2Cl_2	77	82:18
3	$NiCl_2$	PCy_3	Et_2O	88	81:19
4	$NiCl_2$	PCy_3	THF	90	86:14
5	$NiCl_2$	PPh_3	THF	82	94:6
6	$NiCl_2$	PPh_2Me	THF	50	80:20
7	$NiCl_2$	$P(o\text{-tolyl})_3$	THF	80	83:17
8	$NiCl_2(PPh_3)_2$	-	THF	95	95:5

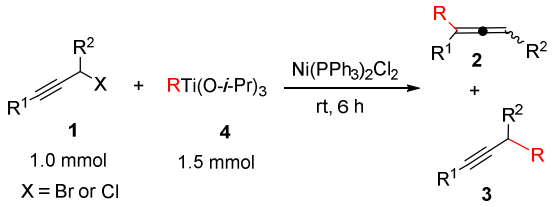
[a] **1b**/**4a**/"Ni"/L = 1.00/1.50/0.040/0.080 mmol; solvent, 2 mL, 6h. [b] Conversions were based on ^1H NMR spectra. [c] 2 mol% $NiCl_2$, 4 mol % PCy_3.

Under the optimized reaction conditions, the reaction scope was further explored on substrates propargyl bromides of **1b**, **1c**, **1d** and propargyl chlorides of **1e**, **1f** using a catalytic system of $NiCl_2(PPh_3)_2$ (eq. 4), and results are summarized in Table **4**. Coupling reactions of **1b** with aryltitanium reagents of **4a**, **4c**, **4f** or **4j** afforded 1,1-disubstituted allenes **2ba**, **2bc**, **2bf** and **2bj** in >90% selectivity with moderate to good isolated yields (68-84%; Table 4, entries 1-4). Coupling reactions of 1-bromo-2-butyne (**1c**) with phenyl or 2-methylphenyl also gave predominantly allene products of **2ca** and **2cc** with excellent selectivity (>90%) and good isolated yields (Table 4, entries 5 and 6). The catalytic system also applies to the secondary propargyl bromide of 3-bromo-1-butyne (**1d**), furnishing 1,3-disubstituted products of 1-methyl-3-phenylallene (**2da**) and 1-methyl-3-(2-methylphenyl)-allene (**2dc**) in >90% selectivity with isolated yields of 81 and 64%, respectively (Table 4, entries 7 and 8).

In contrast, the coupling reaction of 1-chloro-2-octyne (**1e**) with phenyl favoured a formation of an alkyne product **3ea** in 69% selectivity (Table 4, entry 9) over a reaction time of 6 h. It was further found that the alkynes **3ea**, **3ec** and **3ef** became predominant products when the reaction time was extended to 12 h (Table 4, entries 10-12). Furthermore, in order to explain the experimental results, corresponding bromine derivate of **1e** submit to reaction, it was also found that the alkyne product **3ga** (that is product **3ea**) was predominant product when 1-bromo-2-octyne (**1g**) coupled with phenyl nucleophile (Table 4, entry 16). So, the reverse selectivity for the coupling reactions of **1e** and **1g** attributes to an effect of the long-chain *n*-pentyl substituent at the *sp* carbon. The same, coupling reactions of 1-phenyl-3-

chloropropyne (**1f**) with aryl also favoured a formation of alkyne products of **3fa** and **3fc** in >90% selectivity with yields of 90 and 70% (Table 4, entries 14 and 15). However, the allene **2ej** remained as the major product when **1e** coupled with the hindered 2,6-dimethylphenyl nucleophile (Table 4, entry 13). This result may attributes to an effect of the different stability of intermediate which from oxidative addition of propargyl halides to $(R'_3P)_2Ni$ and the steric hindrance of the aryltitanium reagents. $(R'_3P)_2Ni$(alkynyl)Cl which from oxidative addition of propargyl chlorides to $(R'_3P)_2Ni$ is more stable than the isomerization of $(R'_3P)_2Ni$(allenyl)Cl. In the equilibrium mixture of intermediate $(R'_3P)_2Ni$(alkynyl)Cl accounted for the major. So, transmetallation of $(R'_3P)_2Ni$(alkynyl)Cl with aryltitanium reagents gives intermediate $(R'_3P)_2Ni$(alkynyl)Ar, which undergoes a reductive elimination process to produce the coupling product alkynes **3ea**, **3ec**, **3ef**, **3fa** and **3fc**. When **1e** coupled with the 2,6-dimethylphenyl nucleophile, which steric hindrance slow down the transmetallation reaction, allowing the intermediate $(R'_3P)_2Ni$(alkynyl)Ar isomerize to $(R'_3P)_2Ni$(allenyl)Cl with smaller steric hindrance. Then, transmetallation of $(R'_3P)_2Ni$(allenyl)Cl with aryltitanium reagents gives a Ni(II) intermediate $(R'_3P)_2Ni$(allenyl)Ar, which undergoes a reductive elimination process to produce the allene **2ej** (see Scheme **3**).

Table 4. Coupling reactions of substituted propargyl bromides or chlorides with ArTi(O-*i*-Pr)[a]



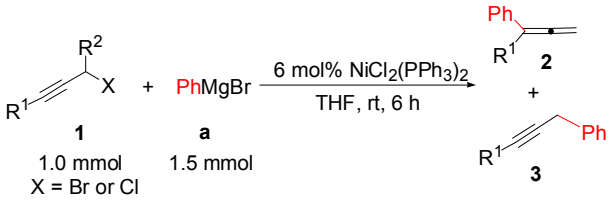
1 1.0 mmol, X = Br or Cl; **4** 1.5 mmol (3)

Entry	1 X	R^1	R^2	4 R	2:3 (conv., %)[b]	Product (yield, %)[c]
1	Br	Et	H (**1b**)	**4a**	**2ba**:**3ba** = 95:5 (95)[d]	**2ba** (84)
2	Br	Et	H (**1b**)	**4c**	**2bc**:**3bc** = 97:3 (86)	**2bc** (82)
3	Br	Et	H (**1b**)	**4f**	**2bf**:**3bf** = 93:7 (78)	**2bf** (68)
4	Br	Et	H (**1b**)	**4j**	**2bj**:**3bj** = 96:4 (74)	**2bj** (71)
5	Br	Me	H (**1c**)	**4a**	**2ca**:**3ca** = 92:8 (87)[d]	**2ca** (77)
6	Br	Me	H (**1c**)	**4c**	**2cc**:**3cc** = 95:5 (95)[d]	**2cc** (88)
7	Br	H	Me (**1d**)	**4a**	**2da**:**3da** = 95:5 (90)	**2da** (81)
8	Br	H	Me (**1d**)	**4c**	**2dc**:**3dc** = 95:5 (72)	**2dc** (64)
9	Cl	^{n}Pent	H (**1e**)	**4a**	**2ea**:**3ea** = 31:69 (87)	**2ea** (22) **3ea** (55)
10	Cl	^{n}Pent	H (**1e**)	**4a**	**2ea**:**3ea** = 1:99 (>99)[e]	**3ea** (90)
11	Cl	^{n}Pent	H (**1e**)	**4c**	**2ec**:**3ec** = 1: 99 (99)[e]	**3ec** (95)
12	Cl	^{n}Pent	H (**1e**)	**4f**	**2ef**:**3ef** = 10:90 (99)[e]	**3ef** (81)
13	Cl	^{n}Pent	H (**1e**)	**4j**	**2ej**:**3ej** = 86:14 (99)[e]	**2ej** (75)
14	Cl	Ph	H (**1f**)	**4a**	**2fa**:**3fa** = 3:97 (97)	**3fa** (90)
15	Cl	Ph	H (**1f**)	**4c**	**2fc**:**3fc** = 9:91 (87)	**3fc** (70)
16	Br	^{n}Pent	H (**g**)	**4a**	**2ga**:**3ga** = 1:99 (>99)[e]	**3ga** (91)

[a] Propargyl halide/Ti reagent/Ni = 1.0/1.5/0.06 mmol, THF, 2 mL; room temperature, 6h. [b] Conversion represented in parenthesis is based on ^{1}H NMR spectra. [c] Isolated yield is in parenthesis. [d] Propargyl halide/Ti reagent/Ni = 1.0/1.5/0.04 mmol. [e] 12h.

Substitution reactions of **1b**, **1e**, or **1f** with phenyl Grignard reagent catalyzed by 6 mol% of $NiCl_2(PPh_3)_2$ were examined for a purpose of comparison (eq. 4). Results showed that a roughly 1:1 ratio of **2**:**3** was obtained no matter what the R^1 is an alkyl or an aryl group. This study demonstrates an advantage of organotitanium compounds as nucleophile sources over Grignard reagents in terms of product selectivity.

Table 5. Coupling reactions of substituted propargyl bromides or chlorides with Grignard reagent [a]



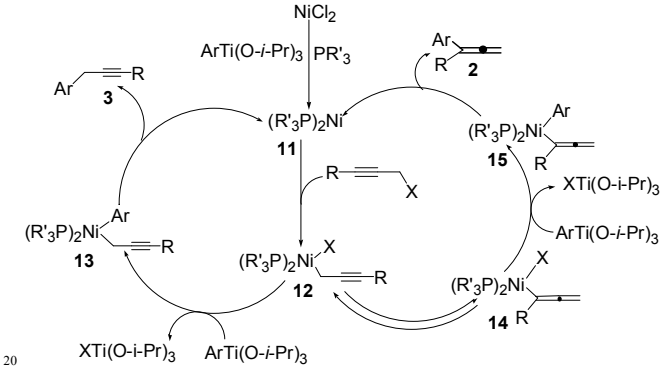
1 1.0 mmol, X = Br or Cl; **a** 1.5 mmol (4)

Entry	1 (X	R^1	R^2)	Conv. (%)[b]	2ba:3ba
1	**1b** (Br	Et	H)	97	54:46
2[c]	**1e** (Cl	^{n}Pent.	H)	>99	51:49

3	**1f**	(Cl	Ph	H)	>99	47:53

[a] Propargyl halide/PhMgBr/$NiCl_2(PPh_3)_2$ = 1.0/1.5/0.06 mmol, 2 mL THF, room temperature, 6h. [b] Conversion is based on ^1H NMR spectra. [c] 12h.

A proposed possible reaction process for the coupling reaction, based on the above results and on previous mechanistic studies on the coupling reaction of propargyl derivatives with organometallic nucleophiles, is shown in Scheme **3**. The first reaction involves replacements of both chloride ions in $NiCl_2$ with two aryl groups followed by reductive elimination of two aryl groups and coordination of PR'$_3$ to furnish a Ni(0) active species of Ni(PR'$_3$)$_2$ (**11**). Then, oxidative addition of propargyl halides to complex **11** affords a Ni(II) species of (R'$_3$P)$_2$Ni(CH$_2$C≡CH-R)X (**12**). Complex **12** could be isomerize to the corresponding complex **14**. Transmetalation of aryltitanium with **12** or **14** gives aryl(propargyl)nickel(II) intermediate **13** or aryl(allenyl)nickel(II) intermediate **15** and XTi(O-*i*-Pr)$_3$. Finally complex **13** or **15** undergoes reductive elimination affords the desired product of an alkyne **3** or an allene **2** and regenerates the active Ni(0) species for the next catalytic cycle.



Scheme 3. The proposed catalytic cycle for the formation of **2** and **3.**

Conclusions

A nickel-catalyzed coupling reaction of propargyl bromides or substituted propargyl bromides or chlorides with organotitanium reagents is reported. Coupling reactions of aryl or alkyl nucleophiles with the simple propargyl bromide **1a** afford monosubstituted allenes in high yields. Depending on the type of substituents on the substituted propargyl bromides or chlorides, 1,1-disubstituted allenes, 1,3-disubstituted allenes, or substituted alkynes are obtained in high to excellent selectivity. Profound steric effects of bulk aryl nucleophiles or of propargyl chloride with a long chain *n*-pentyl substituent are observed. The most steric bulky 2,6-Me$_2$C$_6$H$_3$ nucleophile couples with propargyl bromide **1a**, producing a major product of **2aj'** which is derived from one 2,6-Me$_2$C$_6$H$_3$ and two molecules of **1a**. Coupling reactions of **1e** favoured alkyne products of **3ef** with conversions of up to >99%. However, the coupling reaction of **1e** with 2,6-Me$_2$C$_6$H$_3$ nucleophile shifts the selectivity back to the allene product of **2ej** with the ratio of **2ej**:**3ej** to be 86:14. For coupling reactions of 3-phenyl propargyl chloride, the alkynes were obtained as the predominant products. This methodology provides useful procedure for the synthesis of allenes and alkynes. Further studies on the reaction mechanism and the application of this catalyst to other coupling reactions are currently under way.

Experimental Section

General Procedures: ^1H and ^{13}C NMR spectra were obtained with a Varian Mercury-400 (^1H, 400 MHz; ^{13}C, 100 MHz) spectrometer, and chemical shifts were measured relative to tetramethylsilane (0.00 ppm) as an internal reference. Mass spectroscopy were performed using a Finnigan MAT 95 XL ThermoQuest Mass Spectrometer. Elemental analyses were performed using a Heraeus CHN-O-RAPID instrument. All syntheses and manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Solvents were dried by refluxing for at least 24 h over P_2O_5 (dichloromethane) or sodium/benzophenone (THF, diethylether, n-hexane or toluene) and were freshly distilled prior to use. Nickel compounds, phosphines, and propargyl halides were obtained commercially and used directly for coupling reactions. Organotitanium compounds of RTi(O-*i*-Pr)$_3$ (R = Ph (**4a**),[11d] 4-MeC$_6$H$_4$ (**4b**),[11d] 2-MeC$_6$H$_4$ (**4c**),[11d] 4-MeOC$_6$H$_4$ (**4d**),[12a] 3,5-Me$_2$C$_6$H$_3$ (**4f**),[11d] 2-Naphthyl (**4g**),[12a] 4-CF$_3$C$_6$H$_4$ (**4h**),[11d] or *c*-C$_6$H$_{11}$ (**4i**)[11e]) were prepared according to literature procedures. Purification of reaction products was carried out by flash chromatography.

General procedures for the synthesis of Organotitanium Reagents(4a-j)

To a three-necked round bottom flask containing magnesium turning (2.43 g, 0.100 mol) in 100 mL of THF and equipped with an addition funnel, a septum and a condenser, aryl bromide (0.100 mol) in 50 mL THF was slowly added over a period of 1 h under a dry nitrogen atmosphere. The reaction mixture was stirred for another 2 h to give a Grignard solution. The above solution was transferred via a cannula to a solution of Ti(O-*i*-Pr)$_4$ (22.4 mL, 0.0750 mol) and $TiCl_4$ (2.80 mL, 0.0250 mol) in 50 mL THF cooling at 0 °C. The resulted solution was allowed to warm to room temperature and reacted for 3 h. The solvent was removed under reduced pressures to give a solid. The residue was extracted with hexane (3 × 100 mL), and the combined extract was concentrated and cooled at 4 or -18 °C to furnish a crystalline material of ArTi(O-*i*-Pr)$_3$.

(2-MeOC$_6$H$_4$)Ti(O-*i*-Pr)$_3$ (**4e**): pale yellow crystals, 19.8 g (59.6%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 6.8 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.75 (s, br, 3H), 3.80 (s, 3H), 1.28 (d, *J* = 6.0 Hz, 18H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.1, 162.7, 135.2, 127.6, 119.4, 107.9, 77.3, 54.4, 25.7 ppm. Anal. calcd. for $C_{16}H_{28}O_4Ti$: C, 57.84; H, 8.49%. Found: C, 57.69; H, 8.37%.

(2,6-Me$_2$C$_6$H$_3$)Ti(O-*i*-Pr)$_3$ (**4j**): yellow crystals, 19.6 g (59.3%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.03 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 2H), 4.69 (sept, *J* = 6.0 Hz, 3H), 2.65 (s, 6H), 1.35 (d, *J* = 6.0 Hz, 18 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 184.1, 142.3, 128.1, 125.4, 77.9, 26.7, 26.1 ppm. Anal. calcd. for $C_{17}H_{30}O_3Ti$: C, 61.82; H, 9.16 %. Found: C, 61.20; H, 8.88 %.

General Procedures for the Coupling Reaction of Propargyl Bromide with Organotitanium Reagents

Under a dry nitrogen atmosphere, a mixture of $NiCl_2$ (0.0026 g, 0.020 mmol) and tricyclohexylphosphine (0.0112 g, 0.0400 mmol) in a reaction vessel was added an organotitanium compound (1.5 mmol) in 2 mL CH_2Cl_2 followed by an addition of propargyl bromide (**1a**, 0.107 mL, 1.00 mmol). The resulted solution was stirred at room temperature for 6 h to furnish an orange-yellow solution which was quenched with 2 mL of de-ionized water. The solution was extracted with CH_2Cl_2 (3 × 30 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated. The coupling products were purified by column chromatography.

Phenyl-1,2-propadiene (**2aa**)[3e]. colorless liquid, 0.101 g (87.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.28 (m, 4H), 7.23-7.17 (m, 1H), 6.17 (t, *J* = 6.8 Hz, 1H), 5.15 (d, *J* = 6.8 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.8, 133.9, 128.6, 126.9, 126.7, 93.93, 78.7 ppm.

1-(4-Methylphenyl)-1,2-propadiene (**2ab**)[5]. colorless liquid, 0.118 g (91.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.13 (t, *J* = 6.8 Hz, 1H), 5.11 (t, *J* = 6.8 Hz, 2H), 2.32 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.6, 136.6, 130.9, 129.3, 126.6, 93.7, 78.6, 21.1 ppm.

1-(2-Methylphenyl)-1,2-propadiene (**2ac**)[3f]. colorless liquid, 0.120 g (92.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.18-7.08 (m, 3H), 6.34 (t, *J* = 6.8 Hz, 1H), 5.11 (d, *J* = 6.8 Hz, 2H), 2.35 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 210.4, 134.9, 132.1, 130.4, 127.2, 126.8, 126.1, 91.1, 77.9, 19.8 ppm.

1-(4-Methoxyphenyl)-1,2-propadiene (**2ad**)[3f]. colorless liquid, 0.133 g (91.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.13 (t, *J* = 6.8 Hz, 1H), 5.13 (d, *J* = 6.8 Hz, 2H), 3.80 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.3, 158.7, 127.7, 126.1, 114.1, 93.3, 78.7, 55.3 ppm.

1-(2-Methoxyphenyl)-1,2-propadiene (**2ae**)[3e]. colorless liquid, 0.136 g (93.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.57 (t, *J* = 6.8 Hz, 1H), 5.10 (d, *J* = 6.8 Hz, 2H), 3.83 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 210.2, 155.9, 127.9, 127.7, 122.3, 120.8, 110.9, 87.8, 78.0, 55.5 ppm.

1-(3,5-Dimethylphenyl)-1,2-propadiene (**2af**). colorless liquid, 0.137 g (95.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 2H), 6.84 (s, 1H), 6.10 (t, *J* = 6.8 Hz, 1H), 5.12 (d, *J* = 6.8 Hz, 2H), 2.29 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.7, 138.1, 133.6, 128.7, 124.5, 93.9, 78.6, 21.2 ppm. HRMS (EI) m/z cacld. for $C_{11}H_{12}$: 144.0939. Found: 144.0930.

1-(2-Naphthyl)-1,2-propadiene (**2ag**)[3g]. white solid, 0.150 g (90.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.75 (m, 3H), 7.66 (s, 1H), 7.53-7.39 (m, 3H), 6.34 (t, *J* = 6.8 Hz, 1H), 5.22 (d, *J* = 6.8 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 210.3, 133.7, 132.6, 131.4, 128.2, 127.7, 127.6, 126.2, 125.6, 125.4, 124.6, 94.3, 79.0 ppm.

1-(4-trifluoromethylphenyl)-1,2-propadiene (**2ah**). colorless liquid, 0.173 g (94.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.19 (t, *J* = 6.8 Hz, 1H), 5.21 (d, *J* = 6.8 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 210.4, 137.9, 128.8 (q, *J* = 32.0 Hz), 126.8, 125.5 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270 Hz), 93.2, 79.3 ppm. HRMS (EI) m/z cacld. for $C_{10}H_7F_3$: 184.0500. Found: 184.0491.

1-cyclohexyl-1,2-propadiene (**2ai**)[3h]. yellow liquid, 0.112 g (91.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13-5.06 (m, 1H), 4.72-4.66 (m, 2H), 2.04-1.92 (m, 1H), 1.80-1.68 (m, 4H), 1.67-1.59 (m, 1H), 1.34-1.04 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 207.4, 96.1, 75.4, 36.6, 33.0, 26.1, 26.0 ppm.

1-(2,6-Dimethylphenyl)-1,2-propadiene (**2aj**). colorless liquid, 0.029 g (20.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06-7.00 (m, 3H), 6.24 (t, *J* = 7.2 Hz, 1H), 4.91 (d, *J* = 7.2 Hz, 2H), 2.36 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 210.3, 136.5, 131.2, 128.1, 126.7, 89.5, 75.8, 21.1 ppm. HRMS (EI) m/z cacld. for $C_{11}H_{12}$:144.0939. Found: 144.0945.

1-(2,6-Dimethylphenyl)-4-(bromomethyl)-1,2,4-pentatriene (**2aj'**). colorless liquid, 0.081 g (61.0% based on 2 molecules of the substrate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.08 (m, 1H), 7.05-7.00 (m, 2H), 6.61 (s, 1H), 5.54 (t, *J* = 6.8 Hz, 1H), 5.09-5.06 (m, 2H), 4.23 (s, 2H), 2.19 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 210.4, 136.3, 134.7, 132.8, 130.7, 127.4, 127.3, 89.7, 78.9, 33.3, 20.1 ppm. HRMS (EI) m/z cacld. for $C_{14}H_{15}Br$: 262.0357. Found: 262.0351.

General Procedures for the Coupling Reaction of Substituted Propargyl Halides with Organotitanium Reagents

Under a dry nitrogen atmosphere, $NiCl_2(PPh_3)_2$ (0.026 or 0.039 g, 0.0400 or 0.0600 mmol), was added an organotitanium compound (1.5 mmol) in 2 mL THF followed by an addition of substituted propargyl bromide or chloride (1.00 mmol). The resulted solution was stirred at room temperature for a given period. The solution was quenched with 2 mL of de-ionized water and extracted with CH_2Cl_2 (3 × 30 mL). The organic phase was washed with brine (3 × 30 mL), dried over anhydrous $MgSO_4$ and concentrated. The coupling products were purified by column chromatography.

3-Phenyl-1,2-pentadiene (**2ba**)[3i]. colorless liquid, 0.121 g (84.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 5.10 (t, *J* = 4.0 Hz, 2H), 2.43 (qt, *J* = 4.0, 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 208.3, 136.5, 128.3, 126.5, 125.9, 106.7, 78.8, 22.3, 12.4 ppm.

3-(2-Methylphenyl)-1,2-pentadiene (**2bc**)[3i]. colorless liquid, 0.130 g (82.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.14 (m, 4H), 4.81 (t, *J* = 3.6 Hz, 2H), 2.33 (s, 3H), 2.31 (qt, *J* = 3.6, 7.2 Hz, 2H), 1.07 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 206.4, 137.5, 136.0, 130.4, 127.9, 126.8, 125.8, 105.4, 75.7, 26.5, 20.1, 12.3 ppm.

3-(3,5-Dimethylphenyl)-1,2-pentadiene (**2bf**). colorless liquid, 0.117 g (68.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (s, 2H), 6.85 (s, 1H), 5.08 (t, *J* = 3.6 Hz, 2H), 2.41 (qt, *J* = 3.6, 7.6 Hz, 2H), 2.31 (s, 6H), 1.14 (t, *J* = 7.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 208.4, 137.7, 136.4, 128.3, 123.8, 106.7, 78.4, 22.5, 21.3, 12.5 ppm. HRMS (EI) m/z cacld. for $C_{13}H_{16}$: 172.1252. Found: 172.1245.

3-(2,6-Dimethylphenyl)-1,2-pentadiene (**2bj**). colorless liquid, 0.122 g (71.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.09-7.00 (m, 3H), 4.75 (t, *J* = 4.0 Hz, 2H), 2.29 (s, 6H), 2.13 (qt, *J* = 4.0, 7.6 Hz, 2H), 1.10 (t, *J* = 7.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 205.3, 137.5, 135.9, 127.5, 126.8, 104.2, 75.2, 25.5, 19.9, 12.0 ppm. HRMS (EI) m/z cacld. for $C_{13}H_{16}$: 172.1252 . Found: 172.1254.

3-Phenyl-1,2-butadiene (**2ca**)[3j]. colorless liquid, 0.100 g (77.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.38 (m, 2H), 7.36-7.28 (m, 2H), 7.23-7.17 (m, 1H), 5.02 (q, *J* = 3.2 Hz, 2H), 2.10 (t, *J* = 3.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.0, 136.7, 128.3, 126.5, 125.6, 99.8, 76.9, 16.6 ppm.

3-(2-Methylphenyl)-1,2-butadiene (**2cc**)[3k]. colorless liquid, 0.127 g (88.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.12 (m, 4H), 4.75 (q, *J* = 3.2 Hz, 2H), 2.36 (s, 3H), 2.04 (t, *J* = 3.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 207.6, 137.7, 135.8, 130.5, 127.5, 126.9, 125.8, 98.8, 74.2, 20.4, 20.3 ppm.

1-Phenyl-1,2-butadiene (**2da**)[3l]. colorless liquid, 0.105 g (81.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.27 (m, 4H), 7.19-7.15 (m, 1H), 6.09 (dq, *J* = 3.2, 7.2 Hz, 1H), 5.53 (dq, *J* = 7.2, 7.2

Hz, 1H), 1.78 (dd, J = 3.2, 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 206.0, 135.0, 128.5, 126.6, 93.9, 89.6, 14.1 ppm.

1-(2-Methylphenyl)-1,2-butadiene (**2dc**). colorless liquid, 0.092 g (64.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35, (d, J = 7.6 Hz, 1H), 7.17-7.05 (m, 3H), 6.27 (dq, J = 3.2, 7.2 Hz, 1H), 5.48 (dq, J = 7.2, 7.2 Hz, 1H), 2.35 (s, 3H), 1.78 (dd, J = 3.2, 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 206.7, 134.8, 133.1, 130.4, 127.2, 126.5, 126.0, 91.3, 88.6, 19.8, 14.2 ppm. HRMS (EI) m/z cacld. for $C_{11}H_{12}$: 144.0939. Found: 144.0947.

3-Phenyl-1,2-octadiene (**2ea**). colorless liquid, 0.041 g (22.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 5.06 (t, J = 3.2 Hz, 2H), 2.44-2.37 (m, 2H), 1.60-1.51 (m, 2H), 1.42-1.30 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 208.6, 136.5, 128.3, 126.5, 125.9, 105.0, 78.0, 31.7, 29.4, 27.5, 22.5, 14.1 ppm. HRMS (EI) m/z cacld. for $C_{14}H_{18}$: 186.1409. Found: 186.1410.

Phenyl-2-octyne (**3ea**)[3m]. colorless liquid, 0.168 g (90.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.28 (m, 4H), 7.25-7.19 (m, 1H), 3.63-3.57 (m, 2H), 2.26-2.19 (m, 2H), 1.58-1.49 (m, 2H), 1.43-1.28 (m, 4H), 0.91(t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.6, 128.4, 127.8, 126.3, 82.7, 77.5, 31.1, 28.7, 25.1, 22.2, 18.8, 14.0 ppm.

1-(2-Methylphenyl)-2-octyne (**3ec**)[3m]. colorless liquid, 0.190 g (95.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 1H), 7.22-7.12 (m, 3H), 3.49 (s, 2H), 2.31 (s, 3H), 2.24-2.18 (m, 2H), 1.57-1.48 (m, 2H), 1.42-1.27 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.9, 135.8, 129.9, 128.1, 126.6, 126.1, 82.9, 77.1, 31.1, 28.7, 23.3, 22.2, 19.2, 18.8, 14.0 ppm.

1-(3,5-Dimethylphenyl)-2-octyne (**3ef**). colorless liquid, 0.174 g (81.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.96 (s, 2H), 6.86 (s, 1H), 3.50 (s, 2H), 2.30 (s, 6H), 2.24-2.18 (m, 2H), 1.58-1.48 (m, 2H), 1.44-1.28 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.9, 137.5, 128.0, 125.6, 82.4, 77.7, 31.1, 28.7, 24.9, 22.2, 21.2, 18.8, 14.0 ppm. HRMS (EI) m/z cacld. for $C_{16}H_{22}$: 214.1722. Found: 214.1720.

3-(2,6-Dimethyl)-1,2-octadiene (**2ej**). colorless liquid, 0.161 g (75.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.08-7.00 (m, 3H), 4.72 (t, J = 3.6 Hz , 2H), 2.30 (s, 6H) , 2.13-2.06 (m, 2H), 1.53-1.48 (m, 2H), 1.38-1.30 (m, 4H) , 0.90 (t, J = 6.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 205.3, 137.5, 135.8, 127.5, 126.8, 102.9, 74.8, 32.5, 31.7, 27.2, 22.6, 19.9, 14.1 ppm. HRMS (EI) m/z cacld. for $C_{16}H_{22}$: 214.1722. Found: 214.1727.

1-(2,6-Dimethyl)-2-octyne (**3ej**). colorless liquid, 0.010 g (4.6%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.06-6.97 (m, 3H), 3.44 (t, J = 2.4 Hz, 2H), 2.39 (s, 6H), 2.09 (tt, J = 2.4, 6.8 Hz, 2H), 1.49-1.40 (m, 2H), 1.35-1.24 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.2, 135.0, 128.0, 126.4, 80.2, 76.9, 31.1, 28.7, 22.2, 19.9, 19.3, 18.8, 14.0 ppm. HRMS (EI) m/z cacld. for $C_{16}H_{22}$: 214.1722. Found: 214.1717.

1,3-Diphenylpropyne (**3fa**)[3m]. colorless liquid, 0.173 g (90.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.40 (m, 4H), 7.37-7.32 (t, J = 7.2 Hz, 2 H), 7.31-7.24 (m, 4H), 3.84 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.7, 131.6, 128.5, 128.2, 127.9, 127.8, 126.6, 123.6, 87.5, 82.6, 25.7 ppm.

Phenyl-3-(2-methylphenyl)propyne (**3fc**)[3n]. colorless liquid, 0.145 g (70.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 6.4 Hz, 1H), 7.46-7.40 (m, 2H), 7.31-7.26 (m, 3H), 7.23-7.16 (m, 3H), 3.74 (s, 2H), 2.37 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.0, 135.0, 131.6, 130.1, 128.3, 128.2, 127.7, 126.9, 126.2, 123.7, 87.2, 82.7, 23.9, 19.3 ppm.

Phenyl-2-octyne (**3ga**)[3m]. colorless liquid, 0.169 g (91.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 4H), 7.25-7.22 (m, 1H), 3.59-3.58 (m, 2H), 2.24-2.20 (m, 2H), 1.55-1.52 (m, 2H), 1.41-1.32 (m, 4H), 0.91(t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.6, 128.4, 127.6, 126.3, 82.7, 77.5, 31.1, 28.7, 25.1, 22.2, 18.8, 14.0 ppm.

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Notes and references

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