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Nickel-catalyzed substitution reactions of propargyl halides with organotitanium reagents†

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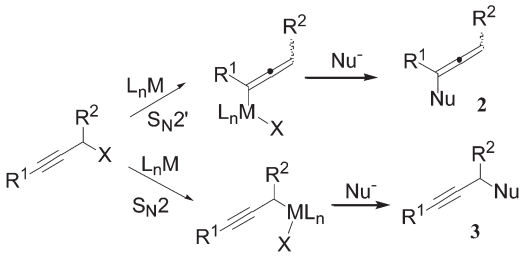
A simple and mild catalytic coupling reaction of propargyl halides with organotitanium reagents is reported. The reaction of propargyl bromide with organo-titanium reagents mediated by $NiCl_2$ (2 mol%) and PCy_3 (4 mol%) in CH_2Cl_2 afforded coupling product allenes in good to excellent yields (up to 95%) at room temperature. However, $NiCl_2(PPh_3)_2$ was 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 the framework of allenes and alkynes, their synthesis and applications have attracted considerable attention 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 the formation of an allene **2**, or an S_N2 process to give an alkyne **3** (Scheme 1).[2b] However, this type of reaction has been less often explored due to the complication of two competitive pathways. The success of this reaction relies mainly on suitable catalytic systems and/or appropriate organometallic reagents that can selectively produce either compound **2** or **3**.



Scheme 1 S_N2' and S_N2 processes of the metal-catalyzed coupling reactions of propargyl derivatives with organometallic nucleophiles.

Organotitanium reagents, which can be easily prepared from the corresponding halides, are 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 the direct coupling of propargylic halide with organotitanium reagents for the synthesis of allenes or alkynes. Recent investigations have demonstrated that nickel is a good catalyst for many cross-coupling reactions.[13]

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

Results and discussion

Initially, the reaction of propargyl bromide $HC{\equiv}CCH_2Br$ (**1a**) with $PhTi(O\text{-}i\text{-}Pr)_3$ (**4a**) was selected as the basis for the catalyst screening study (eqn (1)). The primary metal screening was

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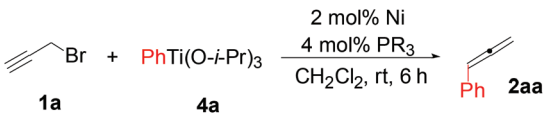
performed with PCy_3, and the results are listed in Table 1. When 2 mol% $NiCl_2(PPh_3)_2$ was used as the catalyst, the reaction smoothly proceeded *via* the S_N2' process to give the corresponding product phenylallene **2aa**, with 73% conversion in CH_2Cl_2 at room temperature over 6 h (Table 1, entry 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) complexes 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 properties 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 complexes were also effective for the reaction, but the catalytic system of $NiCl_2$ (2 mol%)/PCy_3 (4 mol%) had the highest conversion capability (>99%) among the $NiCl_2$/phosphine complexes (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, with or without 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, a 13% conversion of **2aa** was obtained with $NiCl_2/PCy_3$ and a 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, conducted in CH_2Cl_2 at room temperature over 6 h (Table 1, entry 5).

With the optimized conditions in hand, the scope of the catalytic substitution reaction with organotitanium reagents of $RTi(O\text{-}i\text{-}Pr)_3$ was then explored (eqn (2)), and the results are presented in Table 2 (entries 1–11). The reactions of aryltitanium reagents bearing electron-donating substituents on the aromatic ring gave mono-substituted allenes **2ab–2ag** in good

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

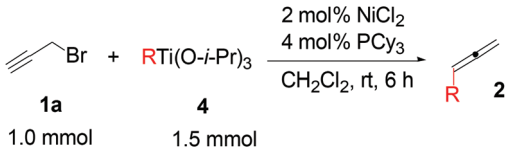


(1)

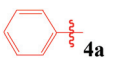
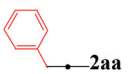
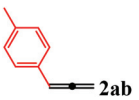
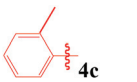
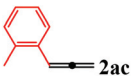
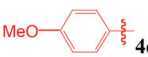
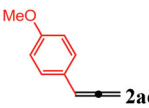
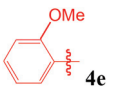
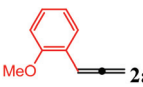
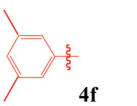
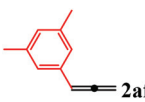
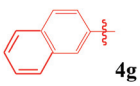
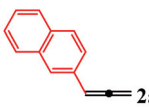
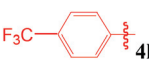
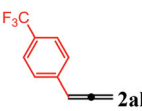
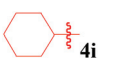
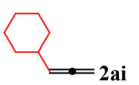
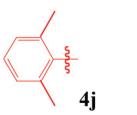
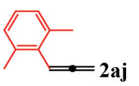
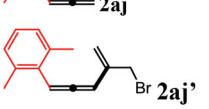
Entry	[Ni]	PR_3	Nucleophile	Conv.[b] (%)
1	$NiCl_2(PPh_3)_2$	—	**4a**	73
2	$NiCl_2(PPh_3)_2$	PCy_3	**4a**	97
3	$Ni(acac)_2$	PCy_3	**4a**	97
4	$NiBr_2$	PCy_3	**4a**	97
5	$NiCl_2$	PCy_3	**4a**	>99
6	$NiCl_2$	PPh_3	**4a**	92
7	$NiCl_2$	$P(p\text{-tolyl})_3$	**4a**	96
8	$NiCl_2$	$P(o\text{-tolyl})_3$	**4a**	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.

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



(2)

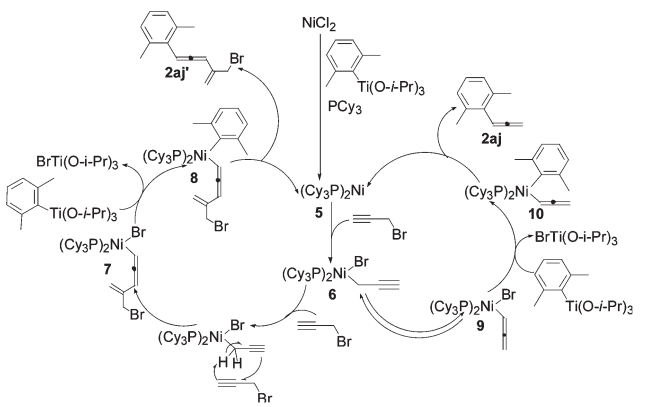
Entry	4 (R)	Product 2	Yield[b] (%)
1			87%
2			91%
3			92%
4			91%
5			93%
6			95%
7			90%
8			94%
9[c]			91%
10[d]			20%
			61%

[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. [c] $NiCl_2/PCy_3$ = 0.060/0.120 mmol (6 mol%), 12 h. [d] >99% conversion, **2aj** : **2aj'** = 38 : 62.

to excellent isolated yields from 87 to 95% (Table 2, entries 2–7). The catalytic system also works well for an aryl nucleophile bearing an electron-withdrawing trifluoromethyl substituent, giving **2ah** in a 94% yield (Table 2, entry 8). In contrast, reactions employing an aliphatic cyclohexyl nucleophile required a higher catalyst loading of 6 mol% and a longer reaction time of 12 h to give the allene **2ai** in a yield of 92% (Table 2, entry 9). Unfortunately, we used other alkyltitanium reagents, such as ^{n}BuTi(O-i-Pr)$_3$ and ^{s}BuTi(O-i-Pr)$_3$, without success. This may be due to the fact that the boiling point of the corresponding allene products is too low and they cannot be separated.

It is worth noting that a reaction of **1a** with (2,6-$Me_2C_6H_3$)-Ti(O-i-Pr)$_3$ (**4j**) containing a sterically hindered 2,6-$Me_2C_6H_3$ nucleophile produced a mixture of the two compounds **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 ^{1}H NMR and high-resolution mass spectra. Compound **2aj′** is formed from two molecules of **1a** and one 2,6-$Me_2C_6H_3$ nucleophile.

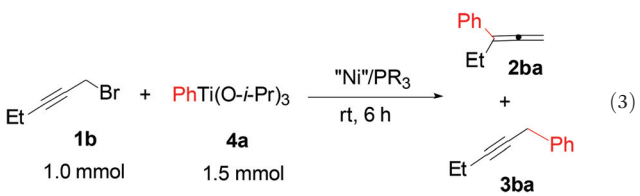
A likely catalytic cycle for the formation of **2aj′** is proposed as shown in Scheme 2. The first reaction involves the replacement of both chloride ions in $NiCl_2$ with two 2,6-$Me_2C_6H_3$ groups, followed by reductive elimination of two 2,6-$Me_2C_6H_3$ groups and coordination of PCy_3 to give a Ni(0) active species Ni(PCy_3)$_2$ (**5**). Oxidative addition of propargyl bromide (**1a**) to **5** gives a Ni(II) species (Cy_3P)$_2$Ni($CH_2C{\equiv}CH$)Br (**6**). Complex **6** could also be isomerized to **9**. However, (2,6-$Me_2C_6H_3$)Ti(O-i-Pr)$_3$ (**4j**) contains sterically hindered 2,6-$Me_2C_6H_3$ groups, and its steric hindrance slows down the transmetallation reaction, allowing the reaction of **6** with another molecule of propargyl bromide. Then, the α-H of the propargyl group of **6** is attacked by one molecule of **1a** to give an intermediate **7**. Transmetallation of **7** with (2,6-$Me_2C_6H_3$)Ti(O-i-Pr)$_3$ gives a Ni(II) intermediate **8**, which undergoes a reductive elimination process to produce the coupling product **2aj′** and regenerate the active species **5** for the next cycle of the reaction. Meanwhile, transmetallation of **9** with (2,6-$Me_2C_6H_3$)Ti(O-i-Pr)$_3$ gives a Ni(II) intermediate **10**, which undergoes a reductive elimination process to produce the coupling product **2aj** and regenerate the active species **5** for the next cycle of the reaction.



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

Encouraged by the good performance of the current catalyst system shown above, we subsequently investigated coupling reactions of substituted propargyl bromide (eqn (3)). However, the reaction of 1-bromo-2-pentyne (**1b**) with PhTi(O-i-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 retuned. We initially optimized the reaction of 1-bromo-2-pentyne (**1b**) with PhTi(O-i-Pr)$_3$ in CH_2Cl_2 at room temperature, catalyzed by the $NiCl_2$ (4 mol%)/PCy_3 (8 mol%) complex. The reaction proceeded smoothly to give the products **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 products **2ba** and **3ba** with 90% conversion and a ratio of 86 : 14 in favor of **2ba** (Table 3, entry 4). To further improve the conversion and 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 significantly improved the conversion and product ratio of the reaction. The coupling products **2ba** and **3ba** were 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

Table 3 Optimization of the reaction of 1-bromo-2-pentyne (**1b**) and PhTi(O-i-Pr)$_3$ (**4a**)[a]



(3)

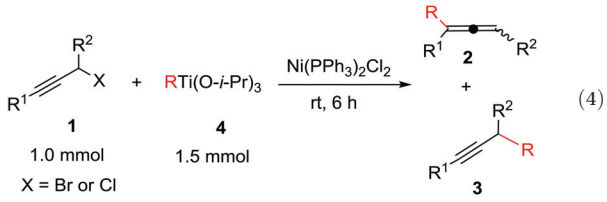
Entry	[Ni] (4 mol%)	Ligand (8 mol%)	Solvent	Conv.[b] (%)	**2ba** : **3ba**
1[c]	$NiCl_2$	PCy_3	CH_2Cl_2	50	75 : 25
2	$NiCl_2$	PCy_3	CH_2Cl_2	77	82 : 18
3	$NiCl_2$	PCy_3	Et_2O	88	81 : 19
4	$NiCl_2$	PCy_3	THF	90	86 : 14
5	$NiCl_2$	PPh_3	THF	82	94 : 6
6	$NiCl_2$	PPh_2Me	THF	50	80 : 20
7	$NiCl_2$	P(*o*-tolyl)$_3$	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, 6 h. [b] Conversions were based on ^{1}H NMR spectra. [c] 2 mol% $NiCl_2$, 4 mol% PCy_3.

bromide, and 1.5 mmol $RTi(O\text{-}i\text{-}Pr)_3$ in THF at room temperature (eqn (3), Table 3, entry 8).

Under the optimized reaction conditions, the reaction scope was further explored with the propargyl bromides **1b**, **1c**, **1d** and propargyl chlorides **1e**, **1f** using a catalytic system of $NiCl_2(PPh_3)_2$ (eqn (4)), and results are summarized in Table 4. Coupling reactions of **1b** with the aryltitanium reagents **4a**, **4c**, **4f** or **4j** gave 1,1-disubstituted allenes **2ba**, **2bc**, **2bf** and **2bj** in >90% selectivity with moderate to good isolated yields

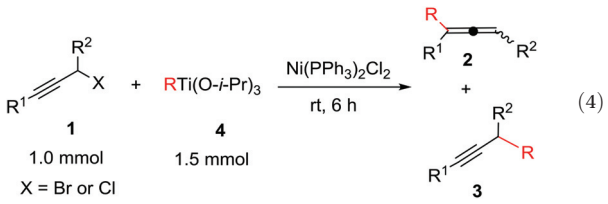
Table 4 Coupling reactions of substituted propargyl bromides or chlorides with ArTi(O-i-Pr)[a]



(4)

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)

Table 4 *(Contd.)*



(4)

Entry	1 X R^1 R^2	4 R	2 : 3 (conv., %)[b]	Product (yield, %)[c]
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 (1g)	**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, 6 h. [b] Conversion represented in parenthesis is based on ^{1}H NMR spectra. [c] Isolated yield is given in parentheses. [d] Propargyl halide/Ti reagent/Ni = 1.0/1.5/0.04 mmol. [e] 12 h.

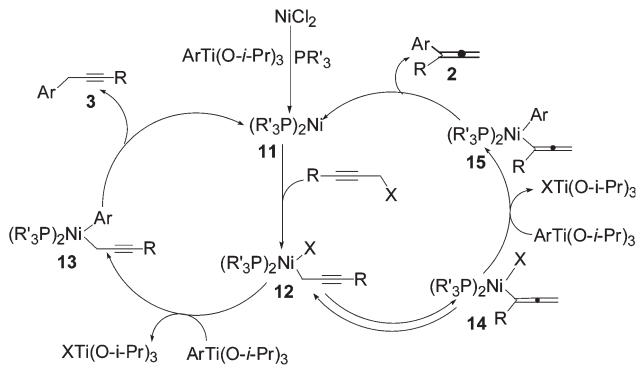
(68–84%; Table 4, entries 1–4). Coupling reactions of 1-bromo-2-butyne (**1c**) with phenyl or 2-methylphenyl also gave predominantly allene products **2ca** and **2cc** with excellent selectivity (>90%) and good isolated yields (Table 4, entries 5 and 6). The catalytic system also applies to the secondary propargyl bromide 3-bromo-1-butyne (**1d**), giving 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 the 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, the corresponding bromine derivate **1e** was submitted to the reaction, and it was also found that the alkyne product **3ga** (that is, product **3ea**) was the predominant product when 1-bromo-2-octyne (**1g**) coupled with the

phenyl nucleophile (Table 4, entry 16). So, the reverse selectivity for the coupling reactions of **1e** and **1g** is attributed to an effect of the long-chain *n*-pentyl substituent at the sp carbon. Similarly, coupling reactions of 1-phenyl-3-chloropropyne (**1f**) with aryl also favoured the formation of alkyne products **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 be attributed to an effect of the different stability of the intermediate from oxidative addition of propargyl halides to $(R'_3P)_2Ni$, and the steric hindrance of the aryltitanium reagents. $(R'_3P)_2Ni$(alkynyl)Cl from oxidative addition of propargyl chlorides to $(R'_3P)_2Ni$ is more stable than from the isomerization of $(R'_3P)_2Ni$(allenyl)Cl. In the equilibrium mixture of compounds of $(R'_3P)_2Ni$(allenyl)Cl and $(R'_3P)_2Ni$(alkynyl)Cl, 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** couples with the 2,6-dimethylphenyl nucleophile, steric hindrance slows down the transmetallation reaction, allowing the intermediate $(R'_3P)_2Ni$(alkynyl)Ar to 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).

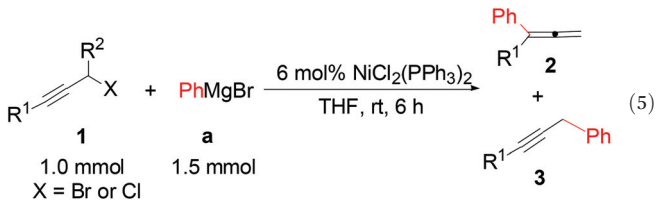
Substitution reactions of **1b**, **1e**, or **1f** with a phenyl Grignard reagent catalyzed by 6 mol% of $NiCl_2(PPh_3)_2$ were examined for the purpose of comparison (eqn (5)). Results showed that a rough 1 : 1 ratio of **2** : **3** was obtained no matter whether the R^1 was an alkyl or an aryl group. This study demonstrates an advantage of organotitanium compounds as nucleophile sources over Grignard reagents in terms of product selectivity (Table 5).

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 the replacement of both chloride ions in



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

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



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, 6 h. [b] Conversion is based on ^{1}H NMR spectra. [c] 12 h.

$NiCl_2$ with two aryl groups followed by reductive elimination of two aryl groups and coordination of PR'_3 to give a Ni(0) active species of $Ni(PR'_3)_2$ (**11**). Then, oxidative addition of propargyl halides to complex **11** gives a Ni(II) species of $(R'_3P)_2Ni$-$(CH_2C{\equiv}CH\text{-}R)X$ (**12**). Complex **12** could be isomerized 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 $XTi(O\text{-}i\text{-}Pr)_3$. Finally complex **13** or **15** undergoes reductive elimination giving the desired product of an alkyne **3** or an allene **2**, and regenerates the active Ni(0) species for the next catalytic cycle.

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** give 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 sterically bulky 2,6-$Me_2C_6H_3$ nucleophile couples with propargyl bromide **1a**, producing a major product **2aj′** which is derived from one 2,6-$Me_2C_6H_3$ and two molecules of **1a**. Coupling reactions of **1e** favoured alkyne products **3ef** with conversions of up to >99%. However, the coupling reaction of **1e** with the 2,6-$Me_2C_6H_3$ nucleophile shifts the selectivity back to the allene product **2ej**, with the ratio of **2ej** : **3ej** equal to 86 : 14. For coupling reactions of 3-phenyl propargyl chloride, the alkynes were obtained as the predominant products. This methodology provides a 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

^{1}H and ^{13}C NMR spectra were obtained with a Varian Mercury-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer, and chemical shifts were measured relative to tetramethylsilane (0.00 ppm) as an internal reference. Mass spectroscopy was 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$_4$ (**4 h**),[11d] or *c*-C$_6$H$_{11}$ (**4i**)[11e]) were prepared according to literature procedures. Purification of the 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 turnings (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 to 0 °C. The resultant solution was allowed to warm to room temperature and reacted for 3 h. The solvent was removed under reduced pressure 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 give a crystalline material ArTi(O-i-Pr)$_3$.

(2-MeOC$_6$H$_4$)Ti(O-i-Pr)$_3$ (4e). Pale yellow crystals, 19.8 g (59.6%). ^{1}H 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{^{1}H} 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$_4$Ti: 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%). ^{1}H 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{^{1}H} 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$_3$Ti: 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, to 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$_2$Cl$_2$ followed by an addition of propargyl bromide (**1a**, 0.107 mL, 1.00 mmol). The resultant solution was stirred at room temperature for 6 h to give an orange–yellow solution which was quenched with 2 mL of de-ionized water. The solution was extracted with CH$_2$Cl$_2$ (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{^{1}H} 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{^{1}H} 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{^{1}H} 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{^{1}H} 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{^{1}H} 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{^{1}H} 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 calcd 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{^{1}H} 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{^{1}H} 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 calcd 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{^{1}H} 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{^{1}H} 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 calcd 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{^{1}H} 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 calcd 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, to $NiCl_2(PPh_3)_2$ (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 resultant 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{^{1}H} 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{^{1}H} 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{^{1}H} 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 calcd 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, $CDCl_3$): δ 7.09–7.00 (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{^{1}H} 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 calcd 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{^{1}H} 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{^{1}H} 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{^{1}H} 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%). ^{1}H 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{^{1}H} 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 calcd for $C_{11}H_{12}$: 144.0939. Found: 144.0947.

3-Phenyl-1,2-octadiene (2ea). Colorless liquid, 0.041 g (22.0%). ^{1}H 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{^{1}H} 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 calcd for $C_{14}H_{18}$: 186.1409. Found: 186.1410.

Phenyl-2-octyne (3ea).[3m] Colorless liquid, 0.168 g (90.0%). ^{1}H 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{^{1}H} 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%). ^{1}H 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{^{1}H} 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%). ^{1}H 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 calcd 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 calcd 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 calcd 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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