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Synthesis of multi-substituted allenes from organoalane reagents and propargyl esters by using a nickel catalyst†

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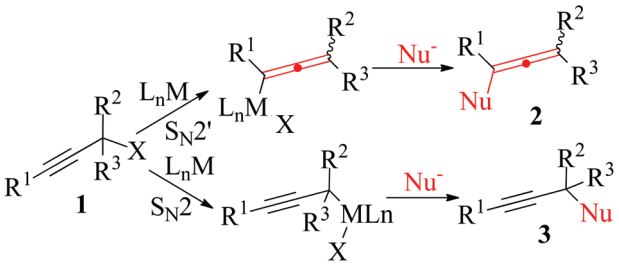
A highly efficient and simple route for the synthesis of multi-substituted allenes has been developed by a nickel catalyzed S_N2' substitution reaction of propargyl esters with organic aluminium reagents under mild conditions, which gave the corresponding multi-substituted allenes in good to excellent yields (up to 92%) and high selectivities (up to 99%) at 60 °C for 6 h in THF. Aryls bearing electron-donating or electron-withdrawing groups in propargyl esters gave products in good yields. In addition, the multi-substituted allenes bearing a thienyl or a pyridyl group were obtained in 95–97% selectivities with isolated yields of 72–83%. Furthermore, the S_N2' substitution reaction worked efficiently with propargyl carbonate compounds as well. On the basis of the experimental results, a possible catalytic cycle has been proposed.

Introduction

Allenes 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] Thus, their synthesis and applications have attracted considerable attention over the past few decades. The development of some simple and efficient methods for the synthesis of multi-substituted allenes from simple and easily available organic compounds is very important. To date, numerous effective synthetic methodologies for the synthesis of allenes have been reported.[3,4] Synthetic protocols for substituted allenes include elimination of allylic compounds,[5] isomerization of alkynes,[6] a reaction of aldehyde and terminal alkynes,[7] and a few cases of metal-catalyzed reactions of propargylic compounds.[8,9] Among them, the metal-catalyzed S_N2'-type substitution reaction of propargylic derivatives with organometallic reagents is one of the most generally useful reactions (Scheme 1).[2b] However, this type of reaction has been less explored due to the 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**.

In continuation of our effort to develop efficient coupling reactions using reactive organometallic reagents to synthesise tri- and tetra-substituted allenes,[10] we herein report a $Ni(PhP_3)_2Cl_2$ (4 mol%)/PPh_3 (8 mol%)/K_2CO_3 (2.0 equiv.) catalyzed S_N2' substitution reaction of propargyl acetates with organoaluminum reagents at 60 °C in short reaction time with good yields. This process is simple and easy to perform, and it provides an efficient method for the synthesis of multi-substituted allene derivatives.



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

Results and discussion

To optimize the reaction conditions, the effects of nickel source, phosphine ligand, solvent, reaction time, the amount of organoaluminum reagent, and the molar ratio of metal to ligand on the S_N2' substitution reaction were investigated using propargyl acetate (**1a**) (Tables 1 and 2). In a preliminary study, with the use of only $NiCl_2$ as the catalyst, the S_N2' substitution reaction of propargyl acetate (**1a**) with trimethylaluminum ($AlMe_3$) afforded 1-methyl-1,3-diphenyl-allene (**2a**)

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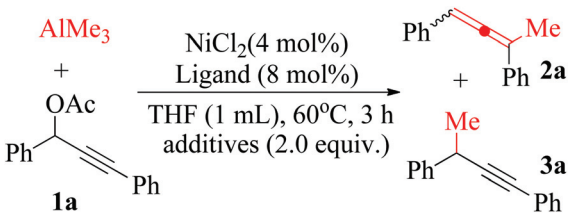
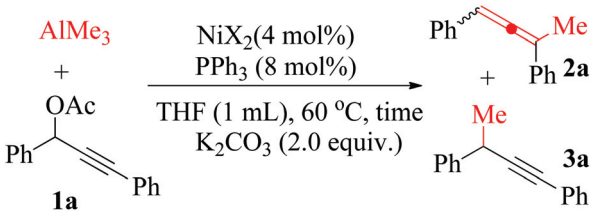
Table 1 Effect of the ligand and solvent on the cross-coupling of propargyl acetate (**1a**) with $AlMe_3$ [a]



Entry	Ligand	Additives	Solvent	**2a** : **3a**[b] (%)	**2a** yield[c] (%)
1[d]	—	—	THF	75 : 25	15
2[d]	PPh_3	—	THF	88 : 12	20
3[d]	PPh_3	K_2CO_3	THF	90 : 10	45
4	PPh_3	K_3PO_4	THF	50 : 50	15
5	PPh_3	K_2CO_3	THF	90 : 10	68
6	PCy_3	K_2CO_3	THF	90 : 10	50
7	dppe	K_2CO_3	THF	50 : 50	20
8	P(2-furyl)$_3$	K_2CO_3	THF	90 : 10	65
9	PPh_3	K_2CO_3	Hexane	50 : 50	20
10	PPh_3	K_2CO_3	Et_2O	1 : 99	30
11	PPh_3	K_2CO_3	Toluene	50 : 50	10

[a] **1a**/$AlMe_3$/$NiCl_2$/ligand = 0.5/0.6/0.02/0.04 mmol. [b] The ratio of **2a**/**3a** was determined by ^{1}H NMR. [c] Isolated yield of **2a**. [d] RT.

Table 2 Effect of the metal and the loading of $AlMe_3$ on the cross-coupling of propargyl acetates (**1a**) with $AlMe_3$ [a]



Entry	NiX_2	$AlMe_3$ (mmol)	Time (h)	**2a** : **3a**[b] (%)	**2a** yield[c] (%)
1	$NiBr_2$	0.6	3	89 : 11	25
2	$Ni(OAc)_2$	0.6	3	50 : 50	10
3	$Ni(acac)_2$	0.6	3	50 : 50	10
4	$Ni(PPh_3)_2Cl_2$	0.6	3	99 : 1	70
5	$Ni(PPh_3)_2Cl_2$	0.7	3	99 : 1	30
6	$Ni(PPh_3)_2Cl_2$	0.3	3	99 : 1	75
7	$Ni(PPh_3)_2Cl_2$	0.3	6	99 : 1	86
8[d]	$Ni(PPh_3)_2Cl_2$	0.3	6	99 : 1	38
9[e]	$Ni(PPh_3)_2Cl_2$	0.3	6	99 : 1	60
10[f]	$Ni(PPh_3)_2Cl_2$	0.3	6	99 : 1	50
11[g]	$Ni(PPh_3)_2Cl_2$	0.3	6	99 : 1	30

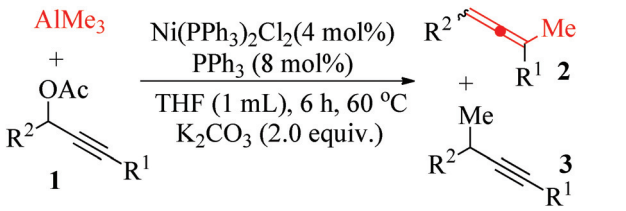
[a] **1a**/$AlMe_3$/NiX_2/PPh_3 = 0.5/0.6/0.02/0.04 mmol. [b] The ratio of **2a**/**3a** was determined by ^{1}H NMR. [c] Isolated yield of **2a**. [d] **1a**/$AlMe_3$/$Ni(PPh_3)_2Cl_2$/PPh_3 = 0.5/0.3/0.01/0.02 mmol. [e] **1a**/$AlMe_3$/$Ni(PPh_3)_2Cl_2$/PPh_3 = 0.5/0.3/0.025/0.05 mmol. [f] **1a**/$AlMe_3$/$Ni(PPh_3)_2Cl_2$/PPh_3 = 0.5/0.6/0.02/0.02 mmol. [g] **1a**/$AlMe_3$/$Ni(PPh_3)_2Cl_2$/PPh_3 = 0.5/0.6/0.02/0.06 mmol.

with 15% yield and a ratio of 75 : 25 in favor of the allene **2a** (Table 1, entry 1). When 8 mol% PPh_3 was used as the ligand, the $NiCl_2$-catalyzed S_N2' substitution reaction of propargyl acetate (**1a**) with $AlMe_3$ produced the product **2a** with 20% yield (Table 1, entry 2). The product ratio was about 88 : 12 in favor of the allene **2a**. To our delight, when 2.0 equiv. of K_2CO_3 were used as the additive, the $NiCl_2$/PPh_3 catalyzed S_N2' substitution reaction of propargyl acetate (**1a**) with $AlMe_3$ produced the product **2a** with 45% yield and a ratio of 90 : 10 in favor of allene **2a** (Table 1, entry 3), while the S_N2' substitution reaction of propargyl acetate (**1a**) with $AlMe_3$ produced the product **2a** with 68% yield and a ratio of 90 : 10 in favor of the allene **2a** at 60 °C (Table 1, entry 5). Other phosphine ligands were further examined (Table 1, entries 6–8). It was found that the PPh_3 ligand was the best effective one for studying reactivity and selectivity (Table 1, entry 5). Other phosphine ligands did not provide satisfactory results. The solvents were then screened under the model reaction conditions, and the results are summarized in Table 1 (entries 9–11). Solvents such as toluene, diethyl ether and hexane were unsuitable for this reaction since they gave lower yields and selectivity.

To further study the reactivity and product selectivity, other parameters of the reaction conditions were optimized (eqn (2), Table 2). Other nickel sources with PPh_3 were subsequently surveyed. Although $NiBr_2$, $Ni(OAc)_2$ and $Ni(acac)_2$ can effectively catalyze the S_N2' substitution reactions, the product selectivity and yield of **2a** were low (Table 2, entries 1–3). Gratifyingly, excellent selectivity (**2a** : **3a** > 99%) and good yield of **2a** (70%) were obtained using $Ni(PPh_3)_2Cl_2$ (Table 2, entry 4). The effect of the amount of $AlMe_3$ was also investigated. When the $AlMe_3$ loading was decreased from 0.6 mmol to 0.3 mmol, the yield of **2a** increased from 70% to 75% (Table 2, entries 4 and 6). However, when the $AlMe_3$ loading was increased from 0.6 mmol to 0.7 mmol, the yield of **2a** decreased from 70% to 30% (Table 2, entries 4 and 5). Also, excellent selectivity (**2a** : **3a** > 99%) and good yield of **2a** (86%) were obtained when the reaction time was extended to 6 h (Table 2, entry 7). On increasing or decreasing the amount of $Ni(PPh_3)_2Cl_2$, **2a** was obtained in low yield (Table 2, entries 8 and 9). When the ratio of $Ni(PPh_3)_2Cl_2$ and PPh_3 was altered to 1 : 1 or 1 : 3, low yield of **2a** is obtained (Table 2, entries 10 and 11). Therefore, the optimal S_N2' substitution reaction conditions were 4 mol% $Ni(PPh_3)_2Cl_2$, 8 mol% PPh_3, 1.0 mmol K_2CO_3, 0.3 mmol $AlMe_3$, and 0.5 mmol propargyl acetate in THF (1 mL) at 60 °C for 6 h.

Under the optimized reaction conditions, the scope of catalytic S_N2' substitution reactions of propargyl acetates with $AlMe_3$ was then explored (eqn (3)), and the results are presented in Table 3. In all the cases, high yield and excellent selectivity were obtained for all evaluated substrates (Table 3, **2a–2q**). The S_N2' substitution reactions of secondary propargyl acetates **1(a–q)** with $AlMe_3$ gave tri-substituted allenes **2(a–q)** in >97% selectivity with excellent isolated yields (71–91%, Table 3, entries 1–17). Reactions of aromatic propargyl acetate reagents bearing electron-donating substituents (Table 3, entries 2–5) or electron-withdrawing substituents (Table 3, entries 6–9) on the aromatic ring furnished tri-substituted allenes **2(b–i)** in good to excellent isolated yields from 81 to 91% and high selectivity (>99%) (Table 3, entries 2–9). Furthermore, the propargyl acetate bearing a bulky 1-naphthyl

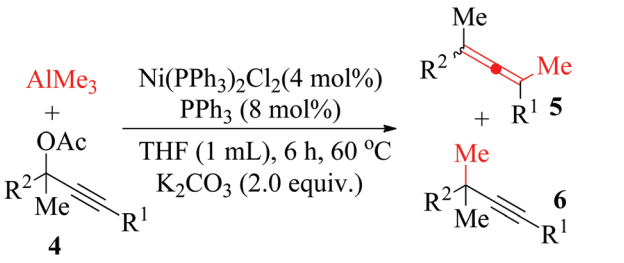
Table 3 Tri-substituted allenes from the S_N2' substitution reactions of propargyl acetates (**1**) with $AlMe_3$ [a]



Entry	1	R^1	R^2	2 : 3 [b] (%)	2 yield [c] (%)
1	**1a**	Ph	Ph	99 : 1	85 (**2a**)
2	**1b**	Ph	*o*-MePh	99 : 1	83 (**2b**)
3	**1c**	Ph	*m*-MePh	99 : 1	83 (**2c**)
4	**1d**	Ph	*p*-MePh	99 : 1	83 (**2d**)
5	**1e**	Ph	*o*-MeOPh	99 : 1	81 (**2e**)
6	**1f**	Ph	*o*-ClPh	99 : 1	87 (**2f**)
7	**1g**	Ph	*p*-ClPh	99 : 1	91 (**2g**)
8	**1h**	Ph	*p*-BrPh	99 : 1	88 (**2h**)
9	**1i**	Ph	*p*-CF_3Ph	99 : 1	87 (**2i**)
10	**1j**	Ph	1-Naphthyl	99 : 1	80 (**2j**)
11	**1k**	Ph	*n*-Pentyl	97 : 3	81 (**2k**)
12	**1l**	Ph	Benzyl	99 : 1	87 (**2l**)
13	**1m**	Ph	3-Pyridyl	95 : 5	72 (**2m**)
14	**1n**	Me_3Si	Ph	99 : 1	84 (**2n**)
15	**1o**	Me_3Si	*p*-MePh	98 : 2	82 (**2o**)
16	**1p**	Me_3Si	*p*-ClPh	98 : 2	86 (**2p**)
17	**1q**	Me_3Si	2-Naphthyl	98 : 2	71 (**2q**)
18	**1r**	Pentyl	TMS	—	0 (**2r**)

[a] **1**/$AlMe_3$/$Ni(PPh_3)_2Cl_2$/PPh_3 = 0.5/0.3/0.02/0.04 mmol. [b] The ratio of **2**/**3** was determined by ^{1}H NMR. [c] Isolated yield of **2**, two runs.

Table 4 Tetra-substituted allenes from the S_N2' substitution reactions of propargyl acetates (**4**) with $AlMe_3$ [a]



Entry	4	R^1	R^2	5 : 6 [b] (%)	5 yield [c] (%)
1	**4a**	Ph	Me	99 : 1	84 (**5a**)
2	**4b**	*p*-MePh	Me	98 : 2	88 (**5b**)
3	**4c**	*m*-ClPh	Me	99 : 1	91 (**5c**)
4	**4d**	*o*-FPh	Me	99 : 1	92 (**5d**)
5	**4e**	*m*-FPh	Me	99 : 1	92 (**5e**)
6	**4f**	*p*-FPh	Me	99 : 1	92 (**5f**)
7	**4g**	*m*-BrPh	Me	99 : 1	86 (**5g**)
8	**4h**	*p*-BrPh	Me	99 : 1	91 (**5h**)
9	**4i**	2-Thienyl	Me	97 : 3	83 (**5i**)
10	**4j**	Ph	Et	99 : 1	83 (**5j**)
11	**4k**	*o*-FPh	Et	99 : 1	90 (**5k**)
12	**4l**	*m*-FPh	Et	99 : 1	90 (**5l**)
13	**4m**	*p*-FPh	Et	99 : 1	92 (**5m**)
14	**4n**	*m*-ClPh	Et	99 : 1	88 (**5n**)
15	**4o**	*m*-BrPh	Et	99 : 1	87 (**5o**)
16	**4p**	*p*-MePh	Et	98 : 2	84 (**5p**)
17	**4q**	Ph	4-FPh	98 : 2	83 (**5q**)
18	**4r**	Ph	4-ClPh	97 : 3	85 (**5r**)

[a] **4**/$AlMe_3$/$Ni(PPh_3)_2Cl_2$/PPh_3 = 0.5/0.3/0.02/0.04 mmol. [b] The ratio of **5**/**6** was determined by ^{1}H NMR. [c] Isolated yield of **5**, two runs.

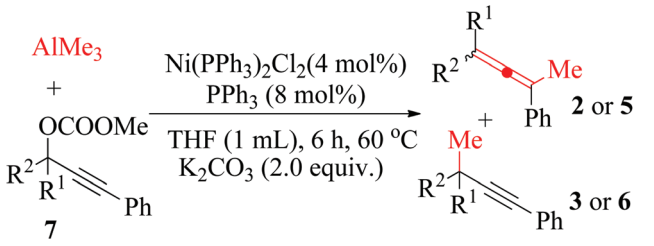
group also produced the tri-substituted allene **2j** with 99% selectivity in an isolated yield of 80% (Table 3, entry 10). The propargyl acetates bearing the *n*-pentyl and benzyl groups were also explored, and after 6 h, **2k** and **2l** were formed with 97–99% selectivity in isolated yields of 81–87% (Table 3, entries 11 and 12). For aromatic propargyl acetates containing the pyridyl group, the catalytic system was still effective enough to furnish **2m** in a 72% yield with 95% selectivity (Table 3, entry 13). Under the same conditions, aliphatic propargyl acetates bearing the TMS group **1(n–q)** also reacted with $AlMe_3$ to provide the tri-substituted allenes **2(n–q)** with good isolated yields (71–86%) and high selectivity (up to 99%) (Table 3, entries 14–17). However, the S_N2' substitution reactions of 1-(trimethylsilyl)oct-1-yn-3-yl acetate (**1r**) with $AlMe_3$ couldn't produce the trimethyl(nona-2,3-dien-2-yl)silane (**2r**).

The S_N2' substitution reactions of the tertiary propargyl acetates **4(a–r)** with $AlMe_3$ gave tetra-substituted allenes **5(a–r)** with >97% selectivity and excellent isolated yields (83–92%, Table 4, entries 1–18). The results indicate that the aromatic propargyl acetates with electron-donating groups (**4b**, **4p**) or electron-withdrawing groups (**4c–4h**, **4k–4o**) on the aromatic rings underwent the S_N2' substitution reactions smoothly to give the tetra-substituted allenes (*i.e.*, **5b**, **5p**, **5c–5h**, **5k–5o**) with high selectivity (up to 99%) and good to excellent isolated yields (83–92%, Table 4, entries 2, 16, 3–8 and 11–15). In addition, the tetra-substituted allene bearing a thienyl group **5i** resulting from propargyl acetate **4i** was obtained in an isolated yield of 83% with 97% selectivity (Table 4, entry 9). More importantly, the tetra-substituted allenes bearing the biaryl groups **5q–5r** resulting from propargyl acetates **4q–4r** were obtained with 97–98% selectivity in isolated yields of 83–85% (Table 4, entries 17 and 18).

For comparison, coupling reactions of other propargyl esters **7(a, b)** with $AlMe_3$ catalyzed by the same catalytic system were conducted (eqn (5)). The results showed that the propargyl carbonate underwent the coupling reactions smoothly to give the tri- and tetra-substituted allenes (*i.e.*, **2a**, **5a**) with high selectivity (up to 98 : 2) and good isolated yields (81–83%, Table 5, entries 1 and 2). This study demonstrates that the synthesis method of allenes for different propargyl esters has good tolerance.

In order to further explore the reaction mechanism, control experiments were carried out (eqn (6); for details see the ESI†). Under the above conditions, 4 mol% $Ni(PPh_3)_2Cl_2$ and 4 mol% $AlMe_3$ were added to the reaction system with 1,3-diphenylprop-2-ynyl acetate as the substrate (eqn (6)). After 2 hours, the reaction mixture was analyzed by infrared spectroscopy, and it was found that the characteristic peak of the allylene structure appeared at around 1967 cm^{-1}. At the same time, the reaction mixture was analyzed by ^{1}H NMR, and it was found that the characteristic peak of allylene appeared at 6.46 ppm. However,

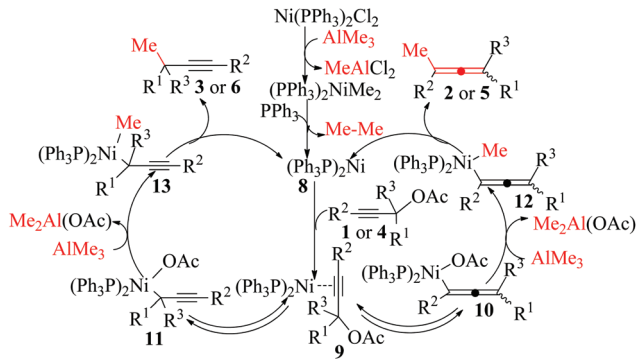
Table 5 $Ni(PPh_3)_2Cl_2/Ph_3P$-catalyzed S_N2' substitution reactions of propargyl carbonates (7) with $AlMe_3$ [a]



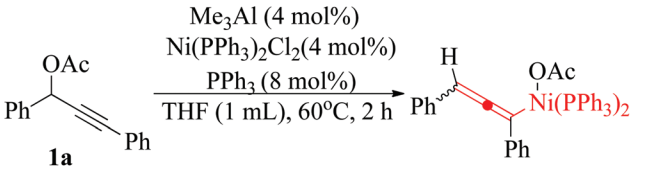
Entry	7	R^1	R^2	2 : 3/5 : 6 [b] (%)	2 or 5 yield [c] (%)
1	**7a**	Ph	H	97 : 3	81 (**2a**)
2	**7b**	Me	Me	98 : 2	83 (**5a**)

[a] 7/$AlMe_3$/$Ni(PPh_3)_2Cl_2$/PPh_3 = 0.5/0.3/0.02/0.04 mmol. [b] The ratio of **2 : 3/5 : 6** was determined by ^1H NMR. [c] Isolated yield of **2** or **5**, two runs.

the same results were not obtained when only 4 mol% $Ni(PPh_3)_2Cl_2$ was used to react with 1,3-diphenylprop-2-ynyl acetate. The results show that the transmetalation and reduction of $Ni(PPh_3)_2Cl_2$ with $AlMe_3$ gives Ni(0) active species of $Ni(PPh_3)_2$, and then Ni(0) activates the tri-bond of propargyl acetates to form a π-complex and then isomerizes to form the metallene structure. Thus, a proposed possible reaction mechanism for the coupling reaction, based on known nickel chemistry and the above results on the coupling reaction of propargyl acetates with organometallic nucleophiles, is shown in Scheme 2. The first reaction involves replacements of both chloride ions in $Ni(PPh_3)_2Cl_2$ with two alkyl groups of AlR_3 followed by the reductive elimination of two alkyl groups and coordination of PR_3 to furnish a Ni(0) active species of $Ni(PPh_3)_2$ (**8**). Then, the Ni(0) is attacked by the triple bond of propargyl acetates to form a π-complex (**9**), which is then converted to the corresponding complex **10** or complex **11**. Complex **11** could isomerize to complex **10**. Complex **10** is more stable than complex **11**, so complex **10** is major. Transmetalation of **10** or **11** with AlR_3 gives an alkyl(allenyl) nickel(II) intermediate **12** or alkyl(propargyl)nickel(II) intermediate **13** and $R_2Al(OAc)$. Finally, complex **12** or **13** undergoes reductive elimination to afford the desired product of an allene **2/5** or an alkyne **3/6** and regenerates the active Ni(0) species for the next catalytic cycle.



Scheme 2 The proposed catalytic cycle for the formation of **2** or **5** and **3** or **6**.



(6)

Conclusions

A nickel-catalyzed S_N2' substitution reaction of substituted propargyl acetates or carbonate with organoaluminum reagents is reported. The S_N2' substitution reactions of aromatic propargyl acetates and aliphatic propargyl acetates with organoaluminum reagents afford tri- and tetra-substituted allenes in good to excellent yields (up to 92%) with high selectivity (up to 99%). The S_N2' substitution reactions of propargyl acetates bearing the *n*-pentyl group and TMS group produce the tri-substituted allenes in 71–86% yields with 98–99% selectivities. The S_N2' substitution reactions of aromatic propargyl acetate containing the pyridyl group also produce the allene product **2m** in a 72% yield with selectivity of up to 95%. The S_N2' substitution reactions of 2-methyl-4-arylbut-3-yn-2-yl acetate with $AlMe_3$ can smoothly give the tetra-substituted allenes in excellent yields (up to 92%) with high selectivity (up to 99%). The S_N2' substitution reactions of 2-methyl-4-thienyl but-3-yn-2-yl acetate (**4i**) with $AlMe_3$ can smoothly give the tetra-substituted allene product **5i** in 83% yield with 97% selectivity. More importantly, the tetra-substituted allenes bearing the biaryl group were obtained with 97–98% selectivities in isolated yields of 83–85%. Furthermore, the S_N2' substitution reactions worked efficiently with propargyl carbonate as well. The methodology provides a useful procedure for the synthesis of tri- and tetra-substituted allenes. Further studies on the application of this catalyst to other organoaluminum reagents and propargyl ester are currently underway.

Experimental section

General procedures

^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer. The chemical shifts are reported relative to TMS. Analytical thin-layer chromatography (TLC) was performed on silica 60F-254 plates. Flash column chromatography was carried out on silica gel (200–400 mesh). HRMS were recorded on a Bruker Micro TOF spectrometer equipped with an ESI ion source, FT-IR169 infrared spectrometer (the solid is pressed by KBr and the liquid by liquid membrane). All reactions were carried out under a nitrogen atmosphere. Chemical reagents and solvents were purchased from Adamas-

beta and Aldrich, and were used without further purification with the exception of the following reagents: THF, ether and toluene were distilled from sodium under nitrogen. Compounds of propargyl carbonate **7(a, c)** were synthesized as reported in the literature.[12] Purification of reaction products was carried out by flash chromatography. Trimethylaluminum ($AlMe_3$): flammable, reacts explosively in water, need nitrogen protection, with the bottle being sealed with a sealing film to avoid light and cold storage.

General procedures for the synthesis of propargyl acetates 1(a–q)

n-BuLi (5.16 mL, 8.25 mmol, 1.6 M in hexane) was added to a solution of alkyne (8.25 mmol) in anhydrous THF (15 ml) at −78 °C under a nitrogen atmosphere. The reaction mixture was stirred for 20 minutes at −78 °C, and then for 1 h at room temperature. Aldehyde (7.5 mmol) was added at −78 °C, and the mixture was stirred for 1 h at room temperature. After addition of acetate anhydrous (1.53 g, 1.42 mL, 15.0 mmol) at 0 °C, the reaction mixture was warmed to room temperature and stirred for 2 h. Then, a saturated aqueous NH_4Cl solution was added. The mixture was extracted with ethyl acetate (3 × 15 mL). The combined ethyl acetate layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was chromatographed on silica gel (hexane or ethyl acetate and hexane) to afford the desired propargyl acetates **1(a–q)**.

1,3-Diphenylprop-2-ynyl acetate (1a).[4h] Eluent: PE/EA = 10/1, 1.53 g, 82%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.58 (m, 2H), 7.48–7.46 (m, 2H), 7.42–7.35 (m, 3H), 7.32–7.27 (m, 3H), 6.70 (s, 1H), 2.11 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.9, 137.3, 132.0, 129.1, 128.9, 128.8, 128.4, 127.9, 122.2, 87.2, 85.7, 66.2, 21.2 ppm. IR (KBr) ν: 3075, 2947, 2238, 1762, 1604, 1497, 1456, 1376 cm^{-1}.

3-Phenyl-1-*o*-tolylprop-2-ynyl acetate (1b).[4h] Eluent: PE/EA = 10/1, 1.68 g, 85%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69–7.67 (m, 1H), 7.46–7.44 (m, 2H), 7.31–7.24 (m, 5H), 7.21–7.18 (m, 1H), 6.80 (s, 1H), 2.46 (s, 3H), 2.12 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.8, 136.4, 135.2, 132.0, 130.9, 129.0, 128.8, 128.3, 128.2, 126.4, 122.2, 86.9, 85.55, 64.4, 21.1, 19.2 ppm.

3-Phenyl-1-*m*-tolylprop-2-ynyl acetate (1c).[4h] Eluent: PE/EA = 10/1, 1.66 g, 84%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.46 (m, 2H), 7.41–7.39 (m, 2H), 7.31–7.28 (m, 4H), 7.18–7.16 (d, J = 7.2 Hz, 1H), 6.67 (s, 1H), 2.37 (s, 3H), 2.11 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.9, 138.5, 137.2, 132.0, 129.8, 128.9, 128.7, 128.5, 128.4, 125.0, 122.3, 87.0, 85.84, 66.2, 21.5, 21.2 ppm.

3-Phenyl-1-*p*-tolylprop-2-ynyl acetate (1d).[4h] Eluent: PE/EA = 10/1, 1.50 g, 76%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.45 (m, 4H), 7.30–7.26 (m, 3H), 7.20–7.18 (d, J = 8.0 Hz, 2H), 6.67 (s, 1H), 2.34 (s, 3H), 2.08 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.9, 138.9, 134.4, 131.9, 129.4, 128.8, 128.3, 127.9, 122.2, 86.9, 85.9, 66.0, 21.3, 21.2 ppm.

1-(2-Methoxyphenyl)-3-phenylprop-2-ynyl acetate (1e).[4h] Eluent: PE/EA = 10/1, 1.76 g, 84%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, J = 1.6, 7.6 Hz, 1H), 7.49–7.46 (m, 2H), 7.39–7.33 (m, 1H), 7.37–7.27 (m, 3H), 7.03–7.00 (m, 2H), 6.92 (dd, J = 1.2, 8.4 Hz, 1H), 3.85 (s, 3H), 2.11 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.8, 156.9, 132.1, 130.5, 129.1, 128.7, 128.3, 125.4, 122.5, 120.8, 111.0, 86.5, 85.9, 61.1, 55.8, 21.2 ppm.

1-(2-Chlorophenyl)-3-phenylprop-2-ynyl acetate (1f).[4h] Eluent: PE/EA = 10/1, 1.79 g, 84%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.83 (m, 1H), 7.47–7.45 (m, 2H), 7.40–7.37 (m, 1H), 7.34–7.25 (m, 5H), 6.99 (s, 1H), 2.11 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.4, 134.6, 133.4, 131.9, 130.3, 129.8, 129.5, 128.9, 128.3, 127.2, 122.0, 87.4, 84.7, 63.3, 20.8 ppm.

1-(4-Chlorophenyl)-3-phenylprop-2-ynyl acetate (1g).[4h] Eluent: PE/EA = 10/1, 1.69 g, 79%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.52 (m, 2H), 7.47–7.45 (m, 2H), 7.37–7.35 (m, 2H), 7.31–7.29 (m, 3H), 6.66 (s, 1H), 2.11 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.7, 135.8, 134.9, 131.9, 129.3, 129.0, 128.9, 128.4, 121.9, 87.4, 85.2, 65.4, 21.1 ppm.

1-(4-Bromophenyl)-3-phenylprop-2-ynyl acetate (1h).[4h] Eluent: PE/EA = 10/1, 2.04 g, 83%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2H), 7.47–7.45 (m, 4H), 7.34–7.27 (m, 3H), 6.64 (s, 1H), 2.11 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.7, 143.4, 132.0, 131.9, 129.6, 129.0, 128.4, 123.2, 121.9, 87.4, 85.1, 65.47, 22.1 ppm.

3-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-ynyl acetate (1i).[4h] Eluent: PE/EA = 10/1, 1.81 g, 90%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (dd, J = 8.0, 22.4 Hz, 4H), 7.48 (d, J = 6.8 Hz 2H), 7.36–7.29 (m, 3H), 6.74 (s, 1H), 2.14 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.7, 141.1, 132.0, 131.1, 129.2, 128.5, 128.2, 125.8 (q, J = 3.8 Hz), 121.8, 87.8, 84.9, 65.4, 21.1 ppm.

1-(Naphthalen-1-yl)-3-phenylprop-2-ynyl acetate (1j).[4h] Eluent: PE/EA = 10/1, 1.85 g, 82%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J = 8.4 Hz, 1H), 7.88–7.80 (m, 3H), 7.56–7.41 (m, 5H), 7.33–7.22 (m, 4H), 2.08 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 170.0, 134.1, 132.5, 132.0, 130.7, 130.1, 128.9, 128.8, 128.3, 126.8, 126.7, 126.1, 125.3, 123.9, 122.3, 87.7, 85.8, 64.6, 21.2 ppm.

1-Phenyloct-1-yn-3-yl acetate (1k).[4h] Eluent: PE/EA = 10/1, 1.47 g, 85%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.40 (m, 2H), 7.25–7.24 (m, 3H), 5.59 (t, J = 6.8 Hz, 1H), 2.04 (s, 3H), 1.84–1.78 (m, 2H), 1.49–1.46 (m, 2H), 1.32–1.30 (m, 4H), 0.89 (t, J = 5.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.5, 131.6, 128.3, 128.0, 122.2, 86.5, 84.9, 64.2, 34.7, 31.1, 24.6, 22.3, 20.7, 13.8 ppm.

1,4-Diphenylbut-3-yn-2-yl acetate (1l).[4h] Eluent: PE/EA = 10/1, 1.18 g, 65%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.37 (m, 2H), 7.31–7.23 (m, 8H), 5.78 (t, J = 6.8 Hz, 1H), 3.15 (d, J = 6.4 Hz, 2H), 2.05 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.9, 136.0, 131.8, 129.8, 128.7, 128.4, 128.3, 127.0, 122.2, 86.2, 86.1, 65.1, 41.3, 21.0 ppm.

3-Phenyl-1-(pyridin-3-yl)prop-2-ynyl acetate (1m).[4h] Eluent: PE/EA = 1/1, 1.16 g, 62%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (s, 1H), 8.67–8.65 (m, 1H), 7.98–7.95 (m, 1H), 7.53–7.51 (m, 2H), 7.37–7.34 (m, 4H), 6.77 (s, 1H), 2.17 (s, 3H)

ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.6, 150.1, 149.3, 135.4, 133.0, 131.9, 129.1, 128.4, 123.5, 121.6, 87.8, 84.5, 64.0, 21.0 ppm.

1-Phenyl-3-(trimethylsilyl)prop-2-ynyl acetate (1n).[4h] Eluent: PE/EA = 10/1, 1.47 g, 80%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 2H), 7.40–7.33 (m, 3H), 6.49 (s, 1H), 2.08 (s, 3H), 0.20 (m, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.6, 136.9, 128.9, 128.5, 127.8, 101.2, 92.5, 65.9, 21.1, −0.3 ppm.

1-*p*-Tolyl-3-(trimethylsilyl)prop-2-ynyl acetate (1o).[4h] Eluent: PE/EA = 10/1, 1.56 g, 80%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.47 (s, 1H), 2.38 (s, 3H), 2.03 (s, 3H), 0.20 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.4, 138.6, 134.1, 129.2, 127.8, 101.6, 91.1, 65.6, 21.1, 21.1, −0.3 ppm.

1-(4-Chlorophenyl)-3-(trimethylsilyl)prop-2-ynyl acetate (1p).[4h] Eluent: PE/EA = 10/1, 1.56 g, 74%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.45 (s, 1H), 2.06 (s, 3H), 1.24 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.6, 135.4, 134.5, 129.2, 128.7, 96.5, 74.9, 65.1, 30.7, 27.5, 21.1, −0.4 ppm.

1-(Naphthalen-2-yl)-3-(trimethylsilyl)prop-2-ynyl acetate (1q).[4h] Eluent: PE/EA = 10/1, 1.78 g, 80%, white solid; mp = 55–57 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.13 (s, 1H), 6.88–6.95 (m, 3H), 6.79 (d, J = 8.4 Hz, 1H), 6.57–6.54 (m, 2H), 5.86 (s, 1H), 1.16 (s, 3H), 0.45 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.5, 135.1, 133.2, 132.9, 128.4, 128.1, 127.5, 127.0, 126.4, 126.2, 125.1, 96.3, 75.4, 65.9, 30.7, 27.4, 21.0, −0.3 ppm.

1-(Trimethylsilyl)oct-1-yn-3-yl acetate (1r). Eluent: PE/EA = 10/1, 0.99 g, 55%, colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.36 (t, J = 1.6 Hz, 1H), 2.06 (s, 3H), 1.68–1.73 (m, 2H), 1.39–1.43 (m, 2H), 1.28–1.31 (m, 2H), 0.88 (t, J = 1.7 Hz, 3H), 0.55 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 170.0, 102.9, 90.3, 64.5, 34.9, 31.3, 24.7, 22.6, 21.2, 14.0, −0.07 ppm. HRMS (ESI) m/z calcd for $C_{13}H_{25}O_2Si^+$ $(M + H)^+$ 241.16183, found 241.16157.

General procedures for the synthesis of propargyl acetates 4(a–r)

n-BuLi (9.5 mL, 15.2 mmol, 1.6 M in hexane) was added to anhydrous THF (30 mL) under an argon atmosphere and the flask was cooled to −78 °C. Then, alkyne (12.2 mmol) was added dropwise and stirred for 30 minutes at −78 °C. Subsequently, acetone (0.92 g, 1.16 mL, 15.85 mmol) was added dropwise. The reaction mixture was stirred for 2 h at room temperature. Then, acetate anhydrous (1.68 g, 1.56 mL, 16.5 mmol) was added dropwise at 0 °C. The mixture was stirred overnight at room temperature. After reaction completion, sat. aq. NH_4Cl (15 mL) was added and the mixture was extracted with diethyl ether (3 × 15 mL), washed with sat. $NaHCO_3$ (10 mL), H_2O (10 mL) and dried over Na_2SO_4. The crude product was chromatographed on silica gel (ethyl acetate/hexane) to afford the corresponding propargyl acetates **4(a–r)**.

2-Methyl-4-phenylbut-3-yn-2-yl acetate (4a).[10d] Eluent: PE/EA = 10/1, 2.09 g, 85%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.38 (m, 2H), 7.25–7.22 (m, 3H), 2.02 (s, 3H), 1.73 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.2, 131.8, 128.3, 128.1, 122.6, 90.3, 83.9, 72.3, 28.8, 21.9 ppm.

2-Methyl-4-(4-methylphenyl)but-3-yn-2-yl acetate (4b).[10d] Eluent: PE/EA = 10/1, 2.19 g, 83%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, J = 8 Hz, 2H), 7.07 (d, J = 8 Hz, 2H), 2.30 (s, 3H), 2.01 (s, 3H), 1.72 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.5, 138.4, 131.8, 129.1, 119.7, 89.6, 84.2, 72.6, 29.2, 22.0, 21.5 ppm.

2-Methyl-4-(3-chlorophenyl)but-3-yn-2-yl acetate (4c).[10d] Eluent: PE/EA = 10/1, 2.48 g, 86%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 1H), 7.31–7.21 (m, 3H), 2.05 (s, 3H), 1.74 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.6, 134.2, 131.9, 130.2, 129.6, 128.8, 124.6, 91.8, 82.9, 72.5, 29.2, 22.1 ppm.

2-Methyl-4-(2-fluorophenyl)but-3-yn-2-yl acetate (4d). Eluent: PE/EA = 10/1, 2.25 g, 86%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 1H), 7.28–7.25 (m, 1H), 7.08–7.01 (m, 2H), 2.06 (s, 3H), 1.76 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.5, 162.3 (d, J = 250.2 Hz), 133.8 (d, J = 2.0 Hz), 130.2 (d, J = 7.9 Hz), 123.8 (d, J = 4.8 Hz), 115.5 (d, J = 20.1 Hz), 111.3 (d, J = 15.5 Hz), 95.5 (d, J = 3 Hz), 77.6, 72.5, 29.1, 22.0 ppm. HRMS (ESI) m/z calcd for $C_{13}H_{14}FO_2^+$ $(M + H)^+$ 221.09723, found 221.09702.

2-Methyl-4-(3-fluorophenyl)but-3-yn-2-yl acetate (4e).[10d] Eluent: PE/EA = 10/1, 2.26 g, 84%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.21 (m, 2H), 7.18–7.12 (m, 1H), 7.01–6.97 (m, 1H), 2.03 (s, 3H), 1.75 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.3, 163.5, 161.1, 129.8 (d, J = 9 Hz), 127.6 (d, J = 3 Hz), 124.6 (d, J = 9 Hz), 118.5 (d, J = 22 Hz), 115.6 (d, J = 21 Hz), 91.3, 82.8, 72.1, 28.9, 21.9 ppm.

2-Methyl-4-(4-fluorophenyl)but-3-yn-2-yl acetate (4f).[10d] Eluent: PE/EA = 10/1, 2.31 g, 86%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.38 (m, 2H), 7.01–6.96 (m, 2H), 2.05 (s, 3H), 1.74 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.5, 162.5 (d, J = 247.9 Hz), 133.8 (d, J = 8.4 Hz), 118.8 (d, J = 3.5 Hz), 115.5 (d, J = 22 Hz), 90.1, 83.0, 72.5, 29.1, 22.0 ppm.

2-Methyl-4-(3-bromophenyl)but-3-yn-2-yl acetate (4g). Eluent: PE/EA = 10/1, 2.74 g, 80%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.41 (d, J = 2.6 Hz, 1H), 7.33 (d, J = 2 Hz, 1H), 7.15–7.11 (m, 1H), 2.03 (s, 3H), 1.74 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.2, 134.6, 131.5, 130.5, 129.7, 128.2, 124.7, 122.1, 91.6, 82.5, 72.2, 29.1, 22.0 ppm. HRMS (ESI) m/z calcd for $C_{13}H_{14}BrO_2^+$ $(M + H)^+$ 281.01717, found 281.01813.

2-Methyl-4-(4-bromophenyl)but-3-yn-2-yl acetate (4h).[10d] Eluent: PE/EA = 10/1, 2.92 g, 85%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 8 Hz, 2H), 7.22 (d, J = 8 Hz, 2H), 2.03 (s, 3H), 1.72 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.6, 131.9, 128.5, 128.3, 122.7, 90.3, 84.1, 72.6, 29.3, 22.2 ppm.

2-Methyl-4-(2-thienyl)but-3-yn-2-yl acetate (4i).[10d] Eluent: PE/EA = 10/1, 2.06 g, 81%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.17 (m, 2H), 6.92–6.91 (m, 1H), 2.01 (s, 3H), 1.72 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.4, 132.4, 127.2, 125.9, 122.5, 94.1, 77.5, 72.4, 28.9, 22.1 ppm.

3-Methyl-1-phenylpent-1-yn-3-yl acetate (4j).[10d] Eluent: PE/EA = 10/1, 2.16 g, 82%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.42 (m, 2H), 7.29–7.27 (m, 3H), 2.33 (s, 3H), 1.92 (q, J = 3.6 Hz, 2H), 1.73 (s, 3H), 1.06 (t, J = 3.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.5, 131.9, 128.3, 128.2, 122.8, 89.4, 85.1, 76.2, 34.5, 26.1, 22.1, 8.8 ppm.

3-Methyl-1-(2-fluorophenyl)pent-1-yn-3-yl acetate (4k). Eluent: PE/EA = 10/1, 2.32 g, 82%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.41 (m, 1H), 7.31–7.24 (m, 1H), 7.08–7.01 (m, 2H), 2.10–2.02 (m, 1H), 2.04 (s, 3H), 1.97–1.91 (m, 1H), 1.75 (s, 3H), 1.09 (t, J = 2 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.5, 162.5 (d, J = 250.2 Hz), 133.8 (d, J = 2.0 Hz), 130.1 (d, J = 7.9 Hz), 123.8 (d, J = 3.7 Hz), 115.5 (d, J = 20.8 Hz), 111.4 (d, J = 15.6 Hz), 94.5 (d, J = 3.4 Hz), 78.6, 76.2, 34.6, 26.1, 22.0, 8.7 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{16}FO_2^+$ $(M + H)^+$ 235.11288, found 235.11340.

3-Methyl-1-(3-fluorophenyl)pent-1-yn-3-yl acetate (4l).[10d] Eluent: PE/EA = 10/1, 2.46 g, 86%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.15 (m, 2H), 7.14–7.13 (m, 1H), 7.12–6.96 (m, 1H), 2.05 (s, 3H), 1.92 (q, J = 3.6 Hz, 2H), 1.73 (s, 3H), 1.07 (t, J = 3.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 162.2 (d, J = 244.8 Hz), 129.8 (d, J = 8.6 Hz), 127.8 (d, J = 12 Hz), 124.6 (d, J = 9.4 Hz), 118.7 (d, J = 22.6 Hz), 115.6 (d, J = 21 Hz), 90.5, 83.9, 76.1, 34.6, 26.1, 22.0, 8.7 ppm.

3-Methyl-1-(4-fluorophenyl)pent-1-yn-3-yl acetate (4m). Eluent: PE/EA = 10/1, 2.29 g, 80%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.39 (m, 2H), 6.99–6.95 (m, 2H), 2.07–2.02 (m, 1H), 2.03 (s, 3H), 1.94–1.90 (m, 1H), 1.73 (s, 3H), 1.07 (t, J = 3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 162.5 (d, J = 247.9 Hz), 133.8 (d, J = 8.3 Hz), 118.8 (d, J = 3.4 Hz), 115.4 (d, J = 21 Hz), 89.1, 84.0, 76.1, 34.6, 26.1, 22.0, 8.7 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{16}FO_2^+$ $(M + H)^+$ 235.11288, found 235.11250.

3-Methyl-1-(3-chlorophenyl)pent-1-yn-3-yl acetate (4n). Eluent: PE/EA = 10/1, 2.45 g, 80%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.39 (d, J = 4 Hz, 1H), 7.33–7.15 (m, 3H), 2.04 (s, 3H), 2.02–1.99 (m, 1H), 1.88 (q, J = 3.6 Hz, 2H), 1.72 (s, 3H), 1.05 (t, J = 1.8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 133.9, 131.5, 129.9, 129.5, 128.5, 124.5, 90.5, 83.6, 75.8, 34.5, 26.0, 21.9, 8.7 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{16}ClO_2^+$ $(M + H)^+$ 251.08333, found 251.08340.

3-Methyl-1-(3-bromophenyl)pent-1-yn-3-yl acetate (4o). Eluent: PE/EA = 10/1, 2.91 g, 81%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.42 (m, 1H), 7.36–7.19 (m, 3H), 2.07 (s, 3H), 2.04–2.01 (m, 1H), 1.95–1.88 (m, 2H), 1.73 (s, 3H), 1.08 (t, J = 1.8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 134.2, 131.7, 130.1, 129.5, 128.6, 124.5, 90.6, 83.6, 76.1, 34.6, 26.1, 22.0, 8.8 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{16}BrO_2^+$ $(M + H)^+$ 295.03282, found 295.03207.

3-Methyl-1-(4-methylphenyl)pent-1-yn-3-yl acetate (4p). Eluent: PE/EA = 10/1, 2.11 g, 75%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 2 Hz, 2H), 7.12 (d, J = 2 Hz, 2H), 2.36 (s, 3H), 2.12–2.05 (m, 1H), 2.05 (s, 3H), 1.99–1.91 (m, 1H), 1.76 (s, 3H), 1.10 (t, J = 1.8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 168.4, 137.4, 130.8, 128.1, 118.8, 87.6, 84.2, 75.5, 33.6, 25.2, 21.1, 20.4, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{19}O_2^+$ $(M + H)^+$ 231.13796, found 231.13725.

4-(4-Fluorophenyl)-2-phenylbut-3-yn-2-yl acetate (4q). Eluent: PE/EA = 10/1, 2.15 g, 76%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.59 (m, 2H), 7.53–7.51 (m, 2H), 7.33–7.30 (m, 3H), 7.06–7.03 (m, 2H), 2.06 (s, 3H), 1.96 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 168.7, 162.3 (d, J = 245.1 Hz), 138.7, 132.1, 128.8, 128.5, 127.2 (d, J = 8.2 Hz), 122.5, 115.3 (d, J = 20.5 Hz), 88.3, 87.5, 75.6, 32.2, 21.8 ppm. HRMS (ESI) m/z calcd for $C_{18}H_{16}FO_2^+$ $(M + H)^+$ 283.11288, found 283.11273.

4-(4-Chlorophenyl)-2-phenylbut-3-yn-2-yl acetate (4r). Eluent: PE/EA = 10/1, 2.21 g, 74%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.55 (m, 2H), 7.52–7.48 (m, 2H), 7.35–7.31 (m, 5H), 2.06 (s, 3H), 1.95 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 168.6, 141.5, 133.6, 132.1, 128.8, 128.6, 128.4, 126.5, 122.3, 88.1, 87.5, 75.6, 32.1, 21.9 ppm. HRMS (ESI) m/z calcd for $C_{18}H_{16}ClO_2^+$ $(M + H)^+$ 299.08333, found 299.08298.

General procedures for the S_N2' substitution reaction of propargyl esters with organoaluminum

Under a dry nitrogen atmosphere, to a mixture of $Ni(PPh_3)_2Cl_2$ (0.0131 g, 0.02 mmol), PPh_3 (0.0104 g, 0.04 mmol) and K_2CO_3 (0.138 g, 1.0 mmol) in a reaction vessel was added organoaluminum (0.3 mmol) in 1 mL THF followed by an addition of propargyl ester (0.50 mmol). The resulting solution was stirred at 60 °C for 6 h. After completion of the reaction, the mixture was diluted with a saturated ammonium chloride solution (5 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was subjected to flash column chromatography on silica gel (hexane or ethyl acetate and hexane) to afford the corresponding allene products **2** or **5**.

1,3-Diphenylbuta-1,2-diene (2a).[4h] Eluent: PE, 0.088 g, 85%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.32 (m, 2H), 7.21–7.13 (m, 6H), 7.09–7.03 (m, 2H), 6.34 (q, J = 2.4 Hz, 1H), 2.08 (d, J = 3.2 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 206.8, 136.4, 134.6, 128.7, 128.5, 127.11, 127.09, 126.9, 125.9, 104.6, 96.7, 16.9 ppm.

1-(2-Methylphenyl)-3-phenylbuta-1,2-diene (2b).[4h] Eluent: PE, 0.091 g, 83%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 7.6 Hz, 2H), 7.38–7.30 (m, 3H), 7.23–7.19 (m, 1H), 7.17–7.10 (m, 3H), 6.66 (q, J = 3.2 Hz, 1H), 2.40 (s, 3H), 2.23 (d, J = 2.8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 207.5, 136.5, 135.2, 132.6, 130.6, 128.4, 127.5, 126.91, 126.86, 126.1, 125.8, 103.4, 94.1, 20.0, 16.9 ppm.

1-(3-Methylphenyl)-3-phenylbuta-1,2-diene (2c).[4h] Eluent: PE, 0.091 g, 83%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.25–7.14 (m, 4H), 7.03 (d, J = 7.2 Hz, 1H), 6.46 (q, J = 2.8 Hz, 1H), 2.33 (s, 3H), 2.23 (d, J = 2.0 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 206.8, 138.2, 136.4, 134.4, 128.6, 128.4, 127.9, 127.5, 127.1, 125.8, 124.1, 104.3, 96.6, 21.5, 16.8 ppm.

1-(4-Methylphenyl)-3-phenylbuta-1,2-diene (2d).[4h] Eluent: PE, 0.091 g, 83%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.23–7.20 (m,

3H), 7.10 (d, J = 7.6 Hz, 2H), 6.44 (q, J = 2.8 Hz, 1H), 2.32 (s, 3H), 2.21 (d, J = 2.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 206.5, 136.8, 136.5, 131.4, 129.4, 128.4, 126.9, 126.8, 125.7, 104.3, 96.4, 21.2, 16.8 ppm.

1-(2-Methoxyphenyl)-3-phenylbuta-1,2-diene (2e).[4h] Eluent: PE/EA = 10/1, 0.095 g, 81%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 7.16–7.09 (m, 2H), 6.90 (d, J = 2.4 Hz, 1H), 6.84 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 3.73 (s, 3H), 2.17 (d, J = 2.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 207.1, 156.0, 136.5, 131.5, 128.3, 128.1, 128.0, 127.7, 126.7, 125.7, 122.7, 120.7, 110.9, 103.6, 90.5, 55.4, 16.7 ppm. IR (KBr) ν: 2947, 2849, 1942, 1600, 1498, 1388 cm^{-1}.

1-(2-Chlorophenyl)-3-phenylbuta-1,2-diene (2f).[4h] Eluent: PE, 0.105 g, 87%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.40 (m, 3H), 7.34–7.28 (m, 3H), 7.22–7.19 (m, 1H), 7.14–7.05 (m, 2H), 6.91 (q, J = 2.8 Hz, 1H), 2.21 (d, J = 2.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 207.8, 135.9, 132.2, 129.9, 128.5, 128.4, 128.0, 127.2, 126.8, 125.8, 104.8, 93.1, 16.7 ppm.

1-(4-Chlorophenyl)-3-phenylbuta-1,2-diene (2g).[4h] Eluent: PE, 0.110 g, 91%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.24–7.18 (m, 5H), 6.39 (q, J = 2.4 Hz, 1H), 2.19 (d, J = 3.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 207.0, 136.1, 133.2, 132.7, 128.9, 128.6, 128.1, 127.3, 125.9, 105.1, 95.8, 16.8 ppm.

1-(4-Bromophenyl)-3-phenylbuta-1,2-diene (2h).[10d] Eluent: PE, 0.125 g, 88%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.39 (m, 4H), 7.34–7.30 (m, 2H), 7.22–7.16 (m, 3H), 6.40 (q, J = 2.8 Hz, 1H), 2.21 (d, J = 2.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 207.1, 136.0, 133.7, 131.9, 128.6, 128.5, 128.3, 127.3, 125.9, 120.7, 105.2, 95.7, 16.8 ppm.

1-(4-Trifluoromethylphenyl)-3-phenylbuta-1,2-diene (2i).[4h] Eluent: PE, 0.119 g, 87%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.45 (q, 2.8 Hz, 1H), 2.21 (d, J = 2.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 207.9, 138.7, 135.8, 128.7, 127.5, 127.1, 126.0, 125.7 (q, J = 3.3 Hz), 123.1, 105.4, 95.9, 16.7 ppm. IR (KBr) ν: 2949, 2867, 1943, 1761, 1624, 1496, 1386 cm^{-1}.

1-(Naphthalen-1-yl)-3-phenylbuta-1,2-diene (2j).[4h] Eluent: PE, 0.103 g, 80%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, J = 6.8 Hz, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.51–7.44 (m, 4H), 7.38 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 7.21 (q, J = 2.0 Hz, 1H), 2.26 (d, J = 2.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 208.1, 136.4, 134.0, 130.9, 130.6, 128.7, 128.5, 127.6, 127.0, 126.1, 125.8, 125.7, 125.62, 125.60, 123.6, 103.4, 93.3, 16.9 ppm. IR (KBr) ν: 2994, 2837, 1939, 1635, 1446, 1379 cm^{-1}.

2-Phenyl-nona-2,3-diene (2k).[4h] Eluent: PE, 0.075 g, 83%, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (m, 2H), 7.30–7.26 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 5.46–5.41 (m, 1H), 2.11–2.07 (m, 5H), 1.49–1.42 (m, 2H), 1.34–1.27 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 204.2, 137.8, 128.3, 126.3, 125.7, 100.3, 93.2, 31.5, 29.06, 29.02, 22.6, 17.3, 14.2 ppm. IR (KBr) ν: 2969, 2871, 1956, 1605, 1498, 1458, 1379 cm^{-1}.

1,4-Diphenylpenta-2,3-diene (2l).[4h] Eluent: PE/EA = 20/1, yellow oil, 0.192 g, 87%. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.19 (m, 10H), 5.59 (s, 1H), 3.44 (m, 2H), 2.09 (m, 3H) ppm. 7.43–7.38 (m, 2H), 7.36–7.27 (m, 6H), 7.25–7.16 (m, 2H), 5.63–5.56 (m, 1H), 3.45 (d, J = 7.2 Hz, 2H), 2.11 (d, J = 2.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 204.8, 140.5, 137.4, 128.6, 128.5 (d, J = 6.7 Hz), 126.6, 126.3, 128, 100.9, 92.6, 35.9, 17.2 ppm. IR (KBr) ν: 3037, 2937, 2868, 1943, 1603, 1497, 1452, 1380 cm^{-1}.

3-(3-Phenylbuta-1,2-dienyl)pyridine (2m).[4h] Eluent: PE/EA = 2/1, yellow oil, 0.149 g, 72%. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, J = 1.6 Hz, 1H), 8.42 (d, J = 4.8 Hz, 1H), 7.58 (dd, J = 1.6, 8.0 Hz, 1H), 7.43 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.24–7.16 (m, 2H), 6.43 (q, J = 2.4 Hz, 1H), 2.22 (d, J = 2.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 207.2, 148.4, 148.1, 135.7, 133.6, 130.5, 128.5, 127.4, 125.9, 123.6, 105.4, 93.3, 16.7 ppm.

Phenyl-3-trimethylsilylbuta-1,2-diene (2n).[4h] Eluent: PE, 0.085 g, 84%, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.20 (m, 4H), 7.13–7.10 (m, 1H), 5.81 (q, J = 2.8 Hz, 1H), 1.81 (d, J = 2.8 Hz, 3H), 0.15 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 205.7, 136.1, 128.5, 125.9, 125.8, 95.4, 88.5, 15.1, −1.7 ppm.

1-(4-Methylphenyl)-3-trimethylsilylbuta-1,2-diene (2o).[4h] Eluent: PE, 0.089 g, 82%, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 8.23 (q, J = 2.8 Hz, 1H), 2.50 (s, 3H), 2.00 (d, J = 2.8 Hz, 3H), 1.33 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.6, 135.9, 133.40, 129.34, 126.4, 112.4, 94.1, 34.3, 29.3, 21.2, 14.8, −1.7 ppm.

1-(4-Chlorophenyl)-3-trimethylsilylbuta-1,2-diene (2p).[4h] Eluent: PE, 0.102 g, 86%, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.25 (d, J = 8.4 Hz, 2H), 6.19 (d, J = 8.4 Hz, 2H), 5.04 (q, J = 2.8 Hz, 1H), 0.83 (d, J = 2.8 Hz, 3H), 0.16 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 202.0, 134.9, 131.9, 128.7, 127.6, 113.1, 93.5, 34.3, 29.5, 14.7, −1.6 ppm.

3-(Naphthalen-2-yl)-3-trimethylsilylbuta-1,2-diene (2q).[4h] Eluent: PE, 0.089 g, 71%, white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.72–6.77 (m, 3H), 6.60 (s, 1H), 6.47–6.36 (m, 3H), 5.23 (q, J = 2.8 Hz, 1H), 0.85 (d, J = 2.8 Hz, 3H), 0.16 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 202.5, 134.0, 133.9, 132.5, 128.2, 127.8, 127.7, 126.2, 125.4, 125.0, 124.6, 113.0, 94.6, 34.4, 29.3, 14.9, −1.7 ppm. IR (KBr) ν: 2989, 2837, 1953, 1635, 1468, 1370 cm^{-1}.

1,3-Diphenylpenta-1,2-diene (2r).[11] Eluent: PE/EA = 100/1; 0.081 g, 73%, colorless oil. ^1H NMR (400 MHz, $CDCl_3$):δ = 7.47–7.41 (m, 2H), 7.36–7.25 (m, 6H), 7.24–7.14 (m, 2H), 6.56 (t, J = 3.2 Hz, 1H, CH═), 2.67–2.48 (m, 2H), 1.19 (t, J = 7.6 Hz, 206.2, 136.2, 134.7, 128.7, 128.4, 126.99, δH, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 126.96, 126.7, 126.0, 111.6, 98.6, 23.1, 12.5 ppm.

1-(4-Methylpenta-2,3-dien-2-yl)benzene (5a).[10d] Eluent: PE, 0.067 g, 84%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ =

7.76–7.71 (m, 3H), 7.55 (s, 1H), 7.42–7.35 (m, 3H), 6.01 (q, J = 2.7 Hz, 1H), 1.85 (d, J = 2.7 Hz, 3H), 0.17 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 202.1, 138.7, 128.1, 126.1, 125.8, 98.2, 96.9, 20.4, 17.4 ppm. IR (KBr) ν: 2992, 2867, 1963, 1634, 1557, 1510, 1467, 1381 cm^{-1}.

1-Methyl-4-(4-methylpenta-2,3-dien-2-yl)benzene (5b).[10d] Eluent: PE, 0.076 g, 88%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.31 (m, 2H), 7.18–7.13 (m, 2H), 2.38 (s, 3H), 2.09 (s, 3H), 1.83 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.8, 135.9, 135.8, 129.1, 125.7, 98.2, 96.8, 21.2, 20.5, 17.5 ppm. IR (KBr) ν: 2993, 2873, 1962, 1654, 1577, 1510, 1450, 1374 cm^{-1}.

1-Chloro-3-(4-methylpenta-2,3-dien-2-yl)benzene (5c).[10d] Eluent: PE, 0.088 g, 91%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1H), 7.22–7.16 (m, 2H), 7.15–7.11 (m, 1H), 2.02 (s, 3H), 1.80 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 202.3, 141.1, 134.3, 129.5, 126.1, 125.9, 123.9, 97.7, 97.5, 20.4, 17.2 ppm.

1-Fluoro-2-(4-methylpenta-2,3-dien-2-yl)benzene (5d). Eluent: PE, 0.081 g, 92%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.12 (m, 1H), 7.03–6.99 (m, 1H), 6.88–6.82 (m, 2H), 1.94 (s, 3H), 1.64 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 203.7 (d, J = 1.5 Hz), 160.5 (d, J = 247.5 Hz), 129.4 (d, J = 3.8 Hz), 127.9 (d, J = 8.2 Hz), 127.5 (d, J = 11.6 Hz), 123.9 (q, J = 3.6 Hz), 116.2 (d, J = 22.7 Hz), 95.1 (d, J = 1.5 Hz), 93.8, 20.5, 19.5 ppm. HRMS (ESI) m/z calcd for $C_{12}H_{14}F^+$ $(M + H)^+$ 177.10741, found 177.10725.

1-Fluoro-3-(4-methylpenta-2,3-dien-2-yl)benzene (5e).[10d] Eluent: PE, 0.084 g, 92%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.21 (m, 1H), 7.14–7.11 (d, J = 8.1 Hz, 1H), 7.06–7.02 (d, J = 12.0 Hz, 1H), 6.88–6.83 (m, 1H), 2.03 (s, 3H), 1.79 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.7, 164.5, 162.1, 141.7 (d, J = 7.4 Hz), 129.6 (d, J = 8.3 Hz), 121.5 (d, J = 2.6 Hz), 112.7 (q, J = 38.6 Hz), 104.2, 99.7, 22.5, 18.9 ppm.

1-Fluoro-4-(4-methylpenta-2,3-dien-2-yl)benzene (5f).[10d] Eluent: PE, 0.084 g, 92%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.28 (m, 2H), 6.99–6.96 (m, 2H), 2.03 (s, 3H), 1.79 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.8 (d, J = 2 Hz), 162.8, 160.2, 134.8 (d, J = 3.1 Hz), 127.2 (d, J = 7.8 Hz), 115.1 (d, J = 21.3 Hz), 97.3, 97.2, 20.6, 17.5 ppm. IR (KBr) ν: 2996, 2874, 1962, 1607, 1498, 1451, 1376, 1234 cm^{-1}.

1-Bromo-3-(4-methylpenta-2,3-dien-2-yl)benzene (5g). Eluent: PE, 0.101 g, 86%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.36 (m, 1H), 7.31–7.29 (m, 1H), 7.21–7.17 (m, 1H), 6.99–6.97 (m, 1H), 2.04 (s, 3H), 1.78 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 202.4, 141.0, 134.3, 129.5, 129.4, 125.9, 123.9, 97.7, 97.4, 20.5, 17.3 ppm. HRMS (ESI) m/z calcd for $C_{12}H_{14}Br^+$ $(M + H)^+$ 237.02734, found 237.02737.

1-Bromo-4-(4-methylpenta-2,3-dien-2-yl)benzene (5h).[10d] Eluent: PE, 0.108 g, 91%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 2H), 7.31–7.27 (m, 2H), 2.06 (s, 3H), 1.75 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 202.1, 138.9, 128.2, 125.8, 122.8, 98.2, 97.1, 20.6, 17.6 ppm.

2-(4-Methylpenta-2,3-dien-2-yl)thiophene (5i).[10d] Eluent: PE, 0.068 g, 83%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.13–7.11 (m, 1H), 6.96–6.93 (m, 1H), 6.86–6.83 (m, 1H), 2.05 (s, 3H), 1.79 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.1, 145.1, 127.5, 124.1, 122.4, 98.1, 94.5, 20.6, 18.3 ppm. IR (KBr) ν: 2942, 1950, 1531, 1447, 1374 cm^{-1}.

1-(4-Methylhexa-2,3-dien-2-yl)benzene (5j).[10d] Eluent: PE, 0.071 g, 83%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.37 (m, 2H), 7.30–7.28 (m, 2H), 7.17–7.15 (m, 1H), 2.06 (s, 6H), 1.78 (s, 2H), 1.05–1.01 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.3, 139.0, 128.3, 126.2, 125.7, 103.4, 100.1, 27.6, 18.8, 17.6, 12.5 ppm.

1-Fluoro-2-(4-methylhexa-2,3-dien-2-yl)benzene (5k). Eluent: PE, 0.086 g, 90%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.27 (m, 1H), 7.15–7.11 (m, 1H), 7.08–6.96 (m, 2H), 2.08 (s, 3H), 2.04–2.01 (m, 2H), 1.76 (s, 3H), 1.06–1.02 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 202.9 (d, J = 1.7 Hz), 160.5 (d, J = 247.6 Hz), 129.3 (d, J = 4.0 Hz), 127.8 (d, J = 8.2 Hz), 127.5 (d, J = 11.7 Hz), 123.8 (d, J = 3.6 Hz), 116.2 (d, J = 22.7 Hz), 101.5 (d, J = 1.3 Hz), 95.8, 27.5, 19.6, 19.1, 12.3 ppm. HRMS (ESI) m/z calcd for $C_{13}H_{16}F^+$ $(M + H)^+$ 191.12306, found 191.12286.

1-Fluoro-3-(3-methylhexa-2,3-dien-2-yl)benzene (5l).[10d] Eluent: PE, 0.086 g, 90%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.21 (m, 1H), 7.15 (d, J = 8 Hz, 1H), 7.08–7.04 (m, 1H), 6.86–6.81 (m, 1H), 2.11–2.05 (m, 2H), 2.03 (s, 3H), 1.78 (s, 3H), 1.03 (t, J = 4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.6, 164.5, 162.1, 141.7 (d, J = 7.2 Hz), 129.6 (d, J = 8.2 Hz), 121.3 (d, J = 2.6 Hz), 112.6 (q, J = 38.6 Hz), 104.1, 99.6 (d, J = 2.5 Hz), 27.6, 18.9, 17.5, 12.4 ppm.

1-Fluoro-4-(4-methylhexa-2,3-dien-2-yl)benzene (5m).[10d] Eluent: PE, 0.087 g, 92%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.31 (m, 2H), 7.01–6.96 (m, 2H), 2.12–2.07 (m, 2H), 2.06 (s, 3H), 1.79 (s, 3H), 1.03 (t, J = 3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.1, 161.6 (d, J = 243.5 Hz), 127.1 (d, J = 7.8 Hz), 115.2, 115.0, 103.7, 99.4, 27.6, 19.2, 17.8, 12.6 ppm.

1-Chloro-3-(4-methylhexa-2,3-dien-2-yl)benzene (5n).[10d] Eluent: PE, 0.091 g, 88%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1H), 7.24–7.19 (m, 2H), 7.15–7.11 (m, 1H), 2.11–2.06 (m, 2H), 2.03 (s, 3H), 1.79 (s, 3H), 1.03 (t, J = 3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.5, 141.1, 134.3, 129.5, 126.1, 125.6, 123.8, 104.1, 99.5, 27.5, 18.9, 17.5, 12.4 ppm.

1-Bromo-3-(4-methylhexa-2,3-dien-2-yl)benzene (5o). Eluent: PE, 0.109 g, 87%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.39 (m, 1H), 7.35–7.30 (m, 1H), 7.24–7.20 (m, 1H), 7.18–7.02 (m, 1H), 2.11–2.08 (m, 2H), 2.07 (s, 3H), 1.81 (s, 3H), 1.06 (t, J = 4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.3, 142.8, 139.5, 128.3, 128.2, 125.7, 123.1, 103.2, 100.2, 27.6, 19.1, 17.5, 12.4 ppm. HRMS (ESI) m/z calcd for $C_{13}H_{16}Br^+$ $(M + H)^+$ 251.04299, found 251.04298.

1-Methyl-4-(4-methylpenta-2,3-dien-2-yl)benzene (5p). Eluent: PE, 0.078 g, 84%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 2 Hz, 2H), 7.11 (d, J = 2 Hz, 2H), 2.32 (s, 3H), 2.06 (s, 3H), 2.07–2.02 (m, 2H), 1.78 (s, 3H), 1.03 (t, J = 1.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 201.1, 135.9, 135.8, 129.0, 125.6, 103.2, 100.1, 27.7, 21.3, 18.9, 17.6,

12.5 ppm. HRMS (ESI) *m*/*z* calcd for $C_{14}H_{19}^+$ $(M + H)^+$ 187.14813, found 187.14836.

1-Fluoro-4-(3-phenylbuta-1,2-dienyl)benzene (5q). Eluent: PE, 0.099 g, 83%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 1H), 7.40–7.38 (m, 1H), 7.38–7.36 (m, 2H), 7.34–7.29 (m, 2H), 7.23–7.18 (m, 1H), 7.02–6.96 (m, 2H), 2.18 (s, 3H), 2.16 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 205.6 (d, J = 2.1 Hz), 162.1 (d, J = 244.3 Hz), 137.2, 133.3 (d, J = 3.2 Hz), 128.6, 127.5 (d, J = 7.9 Hz), 127.1, 125.9, 115.5 (d, J = 21.4 Hz), 102.6, 101.7, 17.1, 17.0 ppm. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{16}F^+$ $(M + H)^+$ 239.12306, found 239.12309.

1-Chloro-4-(3-phenylbuta-1,2-dienyl)benzene (5r). Eluent: PE, 0.108 g, 85%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2H), 7.36–7.34 (m, 3H), 7.33–7.30 (m, 1H), 7.29–7.27 (m, 1H), 7.24–7.21 (m, 1H), 2.21 (s, 3H), 2.18 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 205.9, 137.1, 135.8, 132.6, 128.63, 128.61, 127.2, 127.1, 126.0, 103.0, 101.8, 16.9, 16.8 ppm. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{16}Cl^+$ $(M + H)^+$ 255.09350, found 255.09341.

Conflicts of interest

There are no conflicts to declare.

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