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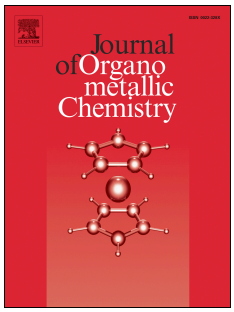

Palladium-catalyzed, ligand-free S_N2' substitution reactions of organoaluminum with propargyl acetates for the synthesis of multi-substituted allenes

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Graphical Abstract

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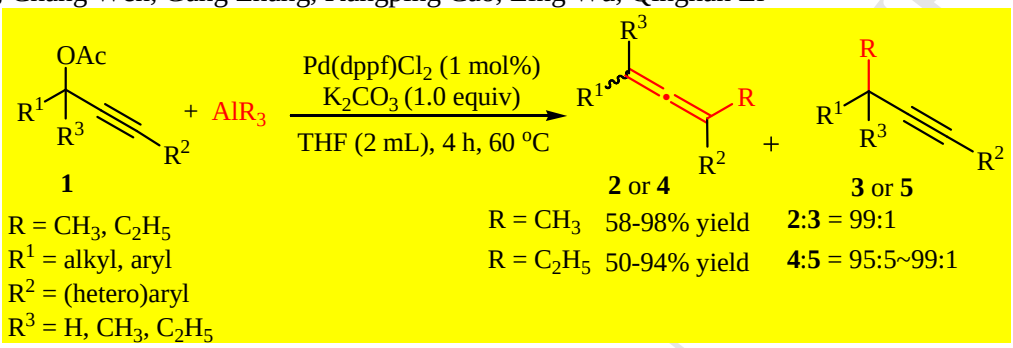

1

R = CH_3, C_2H_5
R^1 = alkyl, aryl
R^2 = (hetero)aryl
R^3 = H, CH_3, C_2H_5

2 or **4**

R = CH_3 58-98% yield
R = C_2H_5 50-94% yield

3 or **5**

2:**3** = 99:1
4:**5** = 95:5~99:1

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Palladium-catalyzed, ligand-free S_N2' substitution reactions of organoaluminum with propargyl acetates for the synthesis of multi-substituted allenes

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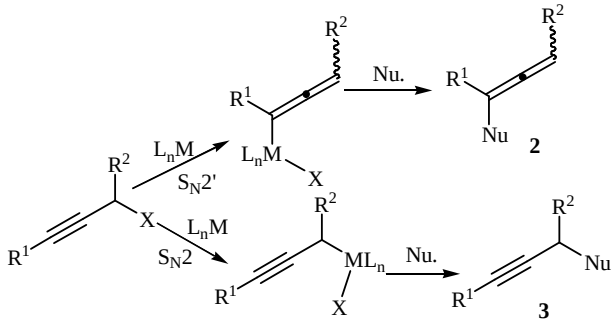
ABSTRACT

We describe a convenient method for the synthesis of multi-substituted allenes from S_N2' substitution reactions organoaluminum with propargyl acetates: The S_N2' substitution reaction of organoaluminum (0.4 mmol) with propargyl acetates (0.5 mmol) mediated by $PdCl_2$(dppf) (1 mol%) at 60 °C in THF without ligand could produce multi-substituted allenes in moderate to good yields(up to 98%) and high selectivities (up to 99%). Their structures have been determined by HRMS and $^1H(^{13}C)$NMR data.

1. Introduction

Allenes are very useful building blocks and functional groups that are widely applied for many transformations in organic synthesis[1-9]. Allene moieties have also been found in natural products [10-11], pharmaceuticals[10-11], and molecular materials [12]. Because of these, the synthesis of allenes has inspired ample interest of organic and medical chemistry. Developing efficient reactions for the synthesis of allenes from simple and readily available organic compounds is very important[13-36]. Until now numerous synthetic methodologies have been developed to access allenes[37-47]. Among these methods hitherto developed, the metal-catalyzed S_N2'-type displacement of propargyl alcohol derivatives with organometal species is one of the most generally useful ones (Scheme 1) [43-46]. However, this type of reactions has been less explored due to a complication of two competitive pathways. A key success of this reaction relies mainly on suitable catalytic systems and/or appropriate organometallic reagents that can selectively produce either compound **2** or **3**. Therefore, the development of rapid and more efficient procedures for the synthesis of allenes still remains a challenge.

Our previous studies show that organoaluminium reagents are highly efficient nucleophiles for cross-coupling reactions with aromatic halides[48-50] or benzylic halides[51], and the investigations have demonstrated that palladium is a good catalytic metal[52-53]. To continue our effort to develop coupling reactions using reactive organometallic reagents[33-34, 54-58], we herein report a palladium(II)-catalyzed, ligand free S_N2'-substitution reactions of propargyl acetates with organoaluminum reagent at 60 °C in short reaction time with good yields for tri- and tetra-substituted allenes. The process was simple and easily performed, and it provides an efficient method for the synthesis of multi-substituted allene derivatives. Notably, in our procedure palladium is used as the single catalyst and ligands free.



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

2. Results and Discussion

Our initial studies used 1,3-diphenylprop-2-ynyl acetate (**1a**) [33,59] and trimethylaluminum($AlMe_3$) as model substrates. According to our previous studied results, in preliminary study, treatment of propargyl acetate (**1a**) with $AlMe_3$ use various palladium salt as catalyst and K_2CO_3 (1.0 equiv.) as base without ligand in THF at 60 °C for 6 h. The results showed that $Pd(OAc)_2$, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ and $PdCl_2$(dppf) were all effective in catalyzing the S_N2' substitution reaction of $AlMe_3$ with propargyl acetate (**1a**) (Table 1, entries 1-4). However, the catalytic system

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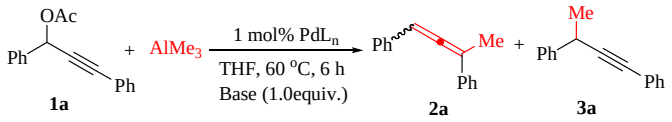
of $PdCl_2(dppf)/K_2CO_3$ showed the highest capability of conversion (100%) among metals/ K_2CO_3 combinations (Table 1, entry 6). While using K_3PO_4 as base, the $PdCl_2(dppf)$-catalyzed the S_N2' substitution reaction of propargyl acetate (**1a**) with $AlMe_3$ produced the product 1-methyl-1,3-diphenyl-allene (**2a**)[13] and 1,3-diphenylbutyne (**3a**) only in 45% conversion (Table 1, entry 7). When treatment of propargyl acetate (**1a**) with $AlMe_3$ in THF at 60 °C in the absence of K_2CO_3 to afford both 1-methyl-1,3-diphenyl-allene (**2a**) and 1,3-diphenylbutyne (**3a**) with only a 81% conversion and a ratio of 28: 72 in favor of the alkyne **3a** (Table 1, entry 8). Compared with the results of Entry 6, it can be seen that potassium carbonate plays an important role in the reaction, which may be the result of the formation of aluminum carbonate adducts.

Table 1 Effect of the palladium source, the loading of Me_3Al and the base on the S_N2' substitution reaction.[a]



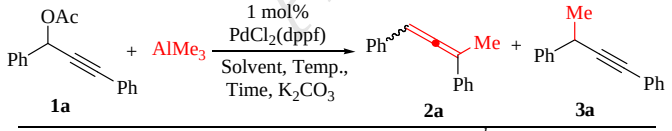
1a **2a** **3a**

Entry	PdLn	Base	Conv. (%)[b]	**2a**/**3a**(%)[c]
1	$PdCl_2$	K_2CO_3	5	99/1
2	$Pd(acac)_2$	K_2CO_3	11	99/1
3	$Pd(PPh_3)_2Cl_2$	K_2CO_3	35	99/1
4	$Pd(OAc)_2$	K_2CO_3	21	99/1
5	$Pd(PPh_3)_4$	K_2CO_3	53	99/1
6	$PdCl_2(dppf)$	K_2CO_3	100	99/1
7	$PdCl_2(dppf)$	K_3PO_4	45	99/1
8	$PdCl_2(dppf)$	-	81	28/72
9[d]	$PdCl_2(dppf)$	K_2CO_3	100	64/36
10[e]	$PdCl_2(dppf)$	K_2CO_3	100	99/1
11[f]	$PdCl_2(dppf)$	K_2CO_3	100	99/1
12[g]	$PdCl_2(dppf)$	K_2CO_3	40	99/1

[a] **1a**/$AlMe_3$/PdL_n = 0.5/0.5/0.005mmol. [b] Conversion of **2a+3a** was determined by ^{1}H NMR spectra. [c] The ratio of **2a**/**3a** was determined by ^{1}HNMR. [d] **1a** /$AlMe_3$/PdL_n = 0.5/0.3/0.005mmol. [e] **1a**/$AlMe_3$/PdL_n = 0.5/0.4/0.005mmol. [f] **1a**/$AlMe_3$/PdL_n = 0.5/0.6/0.005mmol. [g] **1a**/$AlMe_3$/$PdCl_2(dppf)/K_2CO_3$ = 0.5/ 0.4/0.005/0.5 mmol, R.T.

Subsequently, the effect of the amount of $AlMe_3$ was also investigated. When the $AlMe_3$ loading was decreased from 0.5 mmol to 0.4 mmol or increased from 0.5 mmol to 0.6 mmol, the reaction conversation and selectivity remained unchanged (Table 1, entries 10 and 11). While the $AlMe_3$ loading was decreased from 0.5 mmol to 0.3 mmol, the reaction selectivity decreased from 99:1 to 64:36 (Table 1, entry 9). Furthermore, when the reaction temperature was decreased from 60 °C to room temperature, the conversion of the product **2a** and **3a** was decreased from 100% to 40% (Table 1, entries 10 and 12).

Table 2 Effect of the solvent, the reaction time and the reaction temperature on S_N2' substitution reaction.[a]



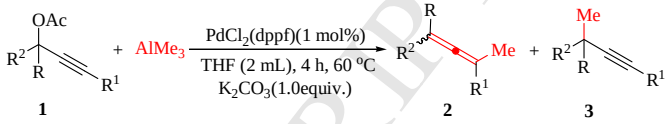
1a **2a** **3a**

Entry	Solvent	Time (h)	Conv.(%)[b]	**2a**/**3a**(%)[c]
1	Toluene	6	71	99/1
2	n-Hexane	6	55	99/1
3	THF	3	95[d]	99/1
4	THF	4	100(97)[d]	99/1
5	THF	5	100(97)[d]	99/1

[a] **1a** /$AlMe_3$/ $PdCl_2(dppf)/K_2CO_3$ = 0.5/0.4/0.005/0.5 mmol, 60 °C. [b] Conversion of **2a+3a** was determined by ^{1}H NMR spectra. [c] The ratio of **2a**/**3a** was determined by ^{1}HNMR. [d] Isolated yield.

To further study the reactivity and selectivity, the reaction of **1a** with $AlMe_3$ under others conditions were investigated. Firstly, various solvents were screened under the model reaction conditions, and the results are summarized in Table 2 (entries 1-2). A brief examination of the influence of solvent on the conversion of the product **2a** and **3a** revealed that THF was the solvent of choice. In toluene or hexane, the conversion was less efficient (Table 2, entries 1-2). Further studies indicated that the reaction time influenced the conversion of the product **2a** and **3a**. It was found that the most favorable reaction time is 4 h (Table 2, entry 4). Extensive screening showed that the optimized the S_N2' substitution reaction conditions were 1 mol % $Pd(PPh_3)_2Cl_2$, 1.0 mmol K_2CO_3, 0.4 mmol $AlMe_3$, 0.5 mmol propargyl acetate in THF at 60 °C for 4 h.

Table 3. $PdCl_2(dppf)$-catalyzed the S_N2' substitution reaction of propargyl acetates with $AlMe_3$.[a]



1 **2** **3**

Entry	**1**	R	R^1	R^2	Prod.	**2**:**3**[b]	**2**Yield(%)[c]
1	**1a**	H	Ph	Ph	**2a**	99/1	97
2	**1b**	H	Ph	2-MePh	**2b**	99/1	85
3	**1c**	H	Ph	3-MePh	**2c**	99/1	97
4	**1d**	H	Ph	4-MePh	**2d**	99/1	98
5	**1e**	H	Ph	2-MeOPh	**2e**	99/1	97
6	**1f**	H	Ph	2-ClPh	**2f**	99/1	95
7	**1g**	H	Ph	4-BrPh	**2g**	99/1	66
8	**1h**	H	Ph	1- naphthyl	**2h**	99/1	87
9	**1i**	H	Ph	2- naphthyl	**2i**	99/1	80
10	**1j**	Me	Ph	Me	**2j**	99/1	89
11	**1k**	Me	2-FPh	Me	**2k**	99/1	91
12	**1l**	Me	3-BrPh	Me	**2l**	99/1	73
13	**1m**	Me	2-thienyl	Me	**2m**	99/1	66
14	**1n**	Me	Ph	Et	**2n**	99/1	95
15	**1o**	Me	2-FPh	Et	**2o**	99/1	91
16	**1p**	Me	3-FPh	Et	**2p**	99/1	97
17	**1q**	Me	4-FPh	Et	**2q**	99/1	80
18	**1r**	Me	3-ClPh	Et	**2r**	99/1	89
19	**1s**	Me	3-BrPh	Et	**2s**	99/1	63(66)[d]
20	**1t**	Me	4-MePh	Et	**2t**	99/1	92
21	**1u**	Me	2-thienyl	Et	**2u**	99/1	70
22	**1v**	Me	Ph	Ph	**2v**	99/1	58
23	**1w**	Me	Ph	4-ClPh	**2w**	99/1	84
24	**1x**	Me	Ph	4-FPh	**2x**	99/1	74

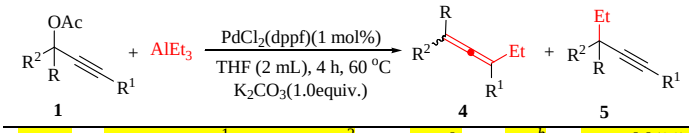
[a] **1**/$AlMe_3$/$PdCl_2(dppf)/PPh_3$/ K_2CO_3 = 0.5/0.4/0.005/0.5 mmol, 4h, 60 °C. [b] The ratio of **2**/**3** was determined by ^{1}HNMR. [c] Isolated yield, two runs. [d] 5h.

With the optimized conditions in hand, the scope of this reaction was studied by using various propargyl acetates, and results are presented in Table 3 (entries 1-24). The corresponding products tri- and tetra-substituted allenes (i.e., **2a**–**2x**) were obtained in good yields with high selectivities. Reactions of aromatic propargyl acetates with either electron-donating or electron-withdrawing groups on the aromatic ring furnished tri- and tetra-substituted allenes (i.e., **2b**–**2g**, **2k-2l**, **2o-2t** and **2w**, **2x**) in good isolated yields from 66% to 98% (Table 3, entries 2-7, 11,12, 15-20, 23 and 24). Aromatic propargyl acetates containing 1-naphthyl and 2-naphthyl substituents also produced the tri-substituted allene products (i.e., **2h** and **2i**) with 99% selectivity in yields of 80% and 87% (Table 3, entries 8 and 9). The S_N2' substitution reactions of $AlMe_3$ with heteroaromatic propargyl acetates containing thienyl group was also explored, and after 4 h, tetra-substituted allenes **2m** and **2u** were formed with 99% selectivity in yields of 66% and 70%, respectively (Table 3, entries 13 and 21). More importantly, the tetra-substituted allenes bearing biaryl group **2v-2x** resulting from propargyl acetates **1w-1x** were obtained in 99% selectivity with isolated yields of 58-84% (Table 3, entries 22-24).

To broaden the reaction scope, we subsequently examined the S_N2' substitution reactions of $AlEt_3$. Results showed that the

reactions of the secondary propargyl acetates **1(b, c, d, y, z)** or the tertiary propargyl acetates **1(m, t, o, r, aa)** underwent the coupling reactions smoothly to give the tri- or tetra-substituted allenes (i.e., **4b**, **4c, 4d, 4y, 4z, 4aa, 4m, 4t, 4o, 4r**) with high selectivity (up to 99:1) and good isolated yields (50-94%, Table 4, entries 1-10). Under the same conditions, aliphatic propargyl acetates bearing TMS group **1z** reacted with $AlEt_3$ to provide the tri-substituted allenes **4z** with good isolated yields (83%) and high selectivity (99%) (Table 4, entry 5). In addition, the tetra-substituted allenes bearing a thienyl group **4m** resulting from propargyl acetate **1m** was obtained with isolated yield of 50% and 99% selectivity (Table 4, entry 7).

Table 4. $PdCl_2$(dppf) -catalyzed the S_N2' substitution reaction of propargyl acetates with $AlEt_3$.[a]



1 4 5

Entry	1	R	R^1	R^2	Prod.	4:5[b]	4 Yield(%)[c]
1	**1b**	H	Ph	2-MePh	**4b**	98/2	86
2	**1c**	H	Ph	3-MePh	**4c**	95/5	83
3	**1d**	H	Ph	4-MePh	**4d**	95/5	81
4	**1y**	H	Ph	3-BrPh	**4y**	98/2	79
5	**1z**	H	TMS	4-ClPh	**4z**	99/1	83
6	**1aa**	Me	4-MePh	Me	**4aa**	98/2	79
7	**1m**	Me	2-thienyl	Me	**4m**	99/1	50
8	**1t**	Me	4-MePh	Et	**4t**	98/2	83
9	**1o**	Me	2-FPh	Et	**4o**	99/1	74
10	**1r**	Me	3-ClPh	Et	**4r**	99/1	94

[a] **1**/$AlMe_3$/$PdCl_2$(dppf)/PPh_3/ K_2CO_3 = 0.5/0.4/0.005/0.5 mmol, 4h, 60 °C. [b] The ratio of **4**/**5** was determined by ^{1}HNMR. [c] Isolated yield, two runs.

3. Conclusion

In conclusion, a palladium-catalyzed cross-coupling reaction of substituted propargyl acetates with trimethylaluminum reagents is reported. The S_N2' substitution reactions of aromatic propargyl acetates with trimethylaluminum or triethylaluminum afford tri- and tetra-substituted allenes in good to excellent yields with high selectivities. The S_N2' substitution reactions of aromatic propargyl acetates containing 1/2-naphthyl substituents producing the tri-substituted allenes products of **2h** and **2i** in 87% and 80% yields with 99% selectivity. The S_N2' substitution reactions of 2-methyl-4-arylbut-3-yn-2-yl acetate with trimethylaluminum or triethylaluminum can smoothly to give the tetra-substituted allenes product of **2(j-x)** and **4(aa, m, t, o, r)** in excellent yields (up to 97%) with high selectivities (up to 99%). This methodology provides useful procedure for the synthesis of tri- and tetra-substituted allenes. Further studies on the application of this catalyst to other organoaluminum reagents are currently under way.

4. Experimental Section:

4.1. Materials and instruments

^{1}H 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). All reactions were carried out under nitrogen atmosphere. Chemical reagents and solvents were purchased from Damas-beta and Aldrich, and were used without further purification with the exception of these reagents: THF, Et_2O, Hexane and Toluene were distilled from Sodium under Nitrogen. Compounds of propargyl acetates **1a-1z** and **1aa** were prepared according to literature procedures[33,59]. Purification of the reaction products was carried out by flash chromatography.

4.2 General Procedures for the Synthesis of Propargyl Acetates 1(a-i)

To a solution of the alkyne (16.5 mmol) in anhydrous THF (25ml) at -78ºC under nitrogen atmosphere was added n-BuLi 1.6 M (16.5 mmol). The reaction was stirred at this temperature for 20 minutes then at room temperature for 1h. After cooling to -78 °C, the aldehyde (15.0 mmol) was added and the reaction was stirred at room temperature for 1h. After addition of acetate anhydrous (30.0 mmol) at 0°C, the reaction mixture was warmed to room temperature and stirred for 2h before quenched with a saturated aqueous NH_4Cl solution . The mixture was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and evaporated to give the crude products. The crude product was subjected to flash column chromatography on silica gel (hexane or ethyl acetate and hexane) to afford the corresponding propargylic acetate **1(a-i)**.

1,3-Diphenylprop-2-ynyl acetate (**1a**) [59]: Yield:1.06g (85 %),Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 2H), 7.48-7.46 (m, 2 H), 7.42- 7.34 (m, 3 H), 7.32-7.27 (m, 3 H), 6.70 (s, 1H), 2.11 (s, 3H) ppm. ^{13}C 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.

3-Phenyl-1-*o*-tolylprop-2-ynyl acetate (**1b**) [33]: Yield:1.66 g, 84%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69-7.65 (m, 1H), 7.50-7.46 (m, 2H), 7.35-7.28 (m, 5H), 7.24-7.18 (m, 1H), 6.77 (s, 1H), 2.46 (s, 3H), 2.15 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.8, 136.4, 135.3, 131.9, 130.7, 128.9, 128.7, 128.3, 128.1, 126.4, 122.3, 86.9, 85.5, 64.2, 21.0, 19.2 ppm.

3-Phenyl-1-*m*-tolylprop-2-ynyl acetate (**1c**) [33]: Yield:1.68 g, 85%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.45 (m, 2H), 7.44-7.38 (m, 2H), 7.35-7.29 (m, 4H), 7.18 (d, J = 7.6 Hz, 1H), 6.67 (s, 1H), 2.38 (s, 3H), 2.14 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.9, 138.6, 137.1, 131.9, 129.9, 128.8, 128.6, 128.5, 128.2, 124.9, 122.2, 86.8, 85.7, 66.1, 21.5, 21.2 ppm.

3-Phenyl-1-*p*-tolylprop-2-ynyl acetate (**1d**) [33]: Yield:1.53 g, 78%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.44 (m, 4H), 7.37-7.28 (m, 3H), 7.24-7.20 (m, 2H), 6.67 (s, 1H), 2.39 (s, 3H), 2.14 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 138.9, 134.3, 131.9, 129.3, 128.8, 128.2, 127.8, 122.1, 86.9, 85.7, 65.9, 21.2, 21.0 ppm.

1-(2-Methoxyphenyl)-3-phenylprop-2-ynyl acetate (**1e**) [33]: Yield: 1.74 g, 83%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (dd, J_1 = 1.6, J_2 = 7.6 Hz, 1H), 7.51-7.43 (m, 2H), 7.39-7.33 (m, 1H), 7.32-7.27 (m, 3H), 7.05 (s, 1H), 7.04-7.01 (m, 1H), 6.92 (dd, J = 1.2, 8.4 Hz, 1H), 3.83 (s, 3H), 2.13 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.8, 156.8, 131.9, 130.4, 129.1, 128.6, 128.2, 125.2, 122.5, 120.6, 110.8, 86.5, 85.7, 61.0, 55.6, 21.1 ppm.

1-(2-Chlorophenyl)-3-phenylprop-2-ynyl acetate (**1f**) [33]: Yield: 1.81 g, 85%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86-7.83 (m, 1H), 7.51-7.44 (m, 2H), 7.43-7.39 (m, 1H), 7.38-7.29 (m, 5H), 6.96 (s, 1H), 2.15 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 134.6, 133.5, 132.1, 130.3, 129.8, 129.5, 128.8, 128.3, 127.2, 122.1, 87.5, 84.6, 63.3, 21.0 ppm.

1-(4-Bromophenyl)-3-phenylprop-2-ynyl acetate (**1g**) [58]: Yield: 2.06 g, 84%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56-7.50 (m, 2H), 7.49-7.44 (m, 2H), 7.42-7.38(m, 2H), 7.36-7.33 (m, 3H), 6.67 (s, 1H), 2.14 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.5, 143.4, 131.9, 131.8, 128.5, 128.3, 128.2, 122.8, 119.8, 90.3, 84.1, 72.6, 22.1 ppm.

1-(Naphthalen-1-yl)-3-phenylprop-2-ynyl Acetate (1h)[33]: Yield: 1.185g (75 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (d, J = 8.4 Hz, 1H), 7.88 (d, J= 7.2 Hz, 1H) 7.82(t, J = 7.0 Hz, 2H), 7.54 (t , J = 7.6 Hz, 1H), 7.48- 7.41 (m, 4 H), 7.33 (s, 1H), 7.22 (t, J = 3.0Hz, 3H), 2.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 134.1, 132.5, 132.0, 130.7, 130.1, 128.9(d, J = 5.7Hz), 128.4,126.7(d, J = 3.1Hz), 126.1, 125.3, 123.9, 122.2, 87.7, 85.8, 64.7, 21.2.ppm.

1-(Naphthalen-2-yl)-3-phenylprop-2-ynyl Acetate(1i) [33]: Yield: 1.343g (85 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (s, 1H), 7.86-7.79 (m, 3 H), 7.69 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.50-7.45 (m, 4 H), 7.28(t, J = 2.6 Hz, 3H), 6.88(s, 1H), 2.11(s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.8, 134.5, 133.5, 133.1, 132.0, 128.9, 128.7, 128.3, 128.3 (d, J = 1.8Hz), 127.7, 127.2, 126.7, 126.5, 125.2, 122.1, 87.4, 85.7, 66.3, 21.2 ppm.

*4.3 General procedures for the synthesis of propargyl acetates **1(j-x)***

n-BuLi (9.5 mL, 15.2mmol, 1.6M in hexane) was added to anhydrous THF (30 mL) under an argon atmosphere and the flask was cooled to –78°C. Then, alkyne (12.2mmol) was added dropwise and stirred for 30 minutes at –78°C. Subsequently, acetone (0.92 g, 1.16 mL, 15.85mmol) was added dropwise. The reaction mixture was stirred for 2 h at room temperature. Then, acetate anhydrous (1.68 g, 1.56 mL, 16.5mmol) was added dropwise at 0 °C. The mixture was stirred overnight at room temperature and. After 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 acetate **1(j-x)**.

2-Methyl-4-phenylbut-3-yn-2-yl acetate (**1j**) [57]: Yield: 0.654g (60 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.41 (m, 2H), 7.24-7.28 (m, 3H), 2.02 (s, 3H), 1.74 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.1, 131.7, 128.2, 128.1, 122.6, 90.1, 83.9, 72.3, 28.9, 21.8 ppm.

2-Methyl-4-(2-fluorophenyl)but -3-yn-2-yl Acetate (1k) [58]: Yield: 0.791g (67 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.44-7.40 (m, 1H), 7.30-7.24 (m, 1H), 7.08-7.01 (m, 2H), 2.05 (s, 3H), 1.76 (s, 6H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 162.8 (d, J = 250.0 Hz), 133.8 (d, J = 1.1 Hz), 130.2 (d, J = 7.9Hz), 123.8 (d, J = 3.8 Hz), 115.4 (d, J = 20.8 Hz), 111.3 (d, J = 15.5 Hz), 95.5 (d, J = 3.3Hz), 72.4, 29.0, 22.0ppm.

2-Methyl-4-(3-bromophenyl)but-3-yn-2-yl Acetate (1l) [58]: Yield: 0.743g (50 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.59 (s, 1H), 7.44-7.29 (m, 3H), 7.17-7.14 (m, 1H), 2.06 (d, J = 1.6Hz, 3H), 1.75 (d, J = 2.0Hz, 6H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 134.6, 131.5, 130.4, 129.7, 128.2, 124.7, 122.0, 91.6, 82.5, 72.2, 29.0, 22.0 ppm.

2-Methyl-4-(2-thienyl)but-3-yn-2-yl Acetate (1m) [58]: Yield: 0.907g (81 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21-7.19 (m, 1H), 7.18-7.17 (m, 1H), 6.92-6.90 (m, 1H), 2.00 (t, J = 2.2Hz, 3H), 1.71 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 132.4, 127.3, 126.9, 122.5, 94.0, 77.4, 72.4, 29.0, 22.0 ppm.

3-Methyl-1-phenylpent -1-yn-3-yl Acetate (1n) [58]: Yield: 0.684g (59 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (t, J = 3.6 Hz, 2H), 7.29-7.25 (m, 3H), 2.11-2.04 (m, 4H), 1.96-1.87 (m, 1H), 1.74 (s, 3H), 1.08 (t, J = 7.4 Hz, 3H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 131.9, 128.3, 128.2, 122.8, 89.3, 85.1, 76.2, 34.7, 26.1, 22.0, 8.8 ppm.

3-Methyl-1-(2-fluorophenyl)pent-1-yn-3-yl Acetate (1o) [58]: Yield: 0.838g (67 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.41 (m, 1H), 7.30-7.24 (m, 1H), 7.08-7.01 (m, 2H), 2.12-2.07 (m, 1H), 2.05 (s, 3H), 1.97-1.88 (m, 1H), 1.75 (s, 3H), 1.10 (t, J = 3.8 Hz, 3H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 163.0 (d, J = 250.2 Hz), 133.8 (d, J = 1.3 Hz), 130.1 (d, J = 7.9 Hz), 123. 9 (d, J = 3.8 Hz), 115.5 (d, J = 20.7Hz), 111.5 (d, J = 15.6Hz), 94.6 (d, J = 3.4Hz), 78.6, 76.2, 34.7, 26.1, 22.0, 8.7ppm.

3-Methyl-1-(3-fluorophenyl)pent-1-yn-3-yl Acetate (1p) [58]: Yield: 0.588g (47 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27-7.20 (m, 2H), 7.15-7.11 (m, 1H), 7.02-6.97 (m, 1H), 2.10-2.01 (m, 4H), 1.96-1.87 (m, 1H), 1.73 (s, 3H), 1.07 (t, J = 3.0 Hz,3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 163.6 (d, J = 244.8 Hz), 129.8 (d, J = 8.6 Hz), 127.8 (d, J = 3.0 Hz), 124.7 (d, J = 9.4 Hz) 118.7 (d, J = 22.6 Hz), 115.7 (d, J = 21.0 Hz), 90.35, 83.9 (d, J = 3.4 Hz), 76.0, 34.6, 26.0, 21.9, 8.7 ppm.

3-Methyl-1-(4-fluorophenyl)pent-1-yn-3-yl Acetate (1q) [58]: Yield: 0.400g (32 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (q, J = 3.2 Hz, 2H), 6.94 (t, J = 8.0Hz, 2H), 2.06-1.97 (m, 4H), 1.92-1.83 (m, 1H), 1.69 (s, 3H), 1.04 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 162.6 (d, J = 247.9 Hz), 133.8 (d, J = 8.3Hz), 118.9 (d, J = 3.4 Hz), 115.5 (d, J = 21.9Hz), 89.1, 84.1, 76.1, 34.6, 26.1, 22.0, 8.7 ppm..

3-Methyl-1-(3-chlorophenyl)pent-1-yn-3-yl Acetate (1r) [58]: Yield: 0.746g (56 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.39 (m, 1H), 7.33-7.26 (m, 1H), 7.24-7.22 (m, 1H), 7.20-7.15 (m, 1H), 2.06-1.97 (m, 4H), 1.92-1.83 (m, 1H), 1.70 (s, 3H), 1.04 (t, J = 7.4Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 133.9, 131.6, 129.9, 129.4, 128.5, 124.4, 90.5, 83.6, 75.8, 34.5, 25.9, 21.9, 8.6 ppm.

3-Methyl-1-(3-bromophenyl)pent-1-yn-3-yl Acetate (1s) [58]: Yield: 0.715g (46 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (t, J = 1.8 Hz, 1H), 7.45-7.41 (m, 1H), 7.29-7.26 (m, 1H), 7.15 (t, J = 7.8 Hz, 1H), 2.11-2.00 (m, 4H), 1.97-1.86 (m, 1H), 1.73 (d, J = 6.8 Hz, 3H), 1.10-1.05 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.5, 134.7, 131.8(d, J = 39.8Hz), 130.1(d, J = 76.2 Hz), 128.3 (d, J = 12.6 Hz), 124.9, 122.5 (d, J= 77.9 Hz), 90.1 (d, J = 136.7 Hz), 84.4(d, J = 147.6 Hz), 76.2(d, J = 33.0 Hz), 34.7(d, J = 7.1 Hz), 26.1 (d, J = 12.5 Hz), 22.1(d, J = 6.8 Hz), 8.8(d, J = 4.1 Hz) ppm.

3-Methyl-1-(4-methylphenyl)pent-1-yn-3-yl Acetate (1t) [58]: Yield: 0.812g (66 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H), 2.09-2.00 (m, 4H),1.94-1.85 (m, 1H), 1.72 (s, 3H), 1.06 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.5, 138.4, 131.8, 129.0, 119.8, 88.7, 85.2, 76.4, 34.7, 26.2, 22.1, 21.5, 8.8 ppm.

3-methyl-1-(thiophen-2-yl)pent-1-yn-3-yl acetate (1u) Yield: 0.952g (80 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24-7.20 (m, 2H), 6.96- 6.94 (m, 1H), 2.08-2.03 (m, 4H), 1.96-1.89 (m, 1H), 1.73 (s, 3H), 1.07 (t, J = 7.2 Hz,3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 132.4, 127.3, 126.9, 93.2, 78.4, 76.2, 34.6, 26.0, 22.0, 8.8 ppm. HRMS(ESI):m/z calcd for $C_{12}H_{15}O_2S^+$ $(M + H)^+$ 223.07145, found 223.07132.

2,4-Diphenylbut-3-yn-2-yl Acetate (1v) [58]: Yield: 0.770g (77 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, J = 7.6 Hz, 2 H), 7.52-7.50 (m, 2 H), 7.36 (t, J = 7.6 Hz, 2H), 7.30-7.27 (m, 4H), 2.06 (s, 3H), 1.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 142.8, 132.0, 128.6, 128.4, 128.3, 127.9, 125.0, 122.5, 88.6, 87.2, 76.1, 32.2, 21.9 ppm.

4-(4-Chlorophenyl)-2-phenylbut-3-yn-2-yl Acetate (1w) [58]: Yield: 1.101 g (70 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59-7.55 (m, 2H), 7.52-7.49 (m, 2H), 7.34-7.29 (m, 5H), 2.07 (s, 3H), 1.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 141.5, 133.7, 132.0, 128.8, 128.6, 128.4, 126.6, 122.3, 88.1, 87.5, 75.6, 32.1, 21.8 ppm

4-(4-Fluorophenyl)-2-phenylbut-3-yn-2-yl Acetate (1x) [58]: Yield: 0.715 g (48 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64-7.60 (m, 2H), 7.52-7.50 (m, 2H), 7.33-7.30 (m, 3H), 7.06-7.02 (m, 2H), 2.07 (s, 3H), 1.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.7, 162.4 (d, J = 245.1 Hz), 138.7, 132.0, 128.8, 128.4, 127.1 (d, J = 8.2 Hz), 122.4, 115.3 (d, J = 20.5 Hz), 88.3, 87.5, 75.7, 32.2, 21.9 ppm.

1-(3-bromophenyl)-3-phenylprop-2-ynyl acetate (**1y**): 2.18 g, 83%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (s, 1H), 7.52-7.46 (m, 4H), 7.31-7.23(m, 4H), 6.65 (s, 1H), 2.12 (s, 3H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 139.4, 132.1, 131.9, 130.8, 130.3, 129.0, 128.4, 126.4, 122.7, 121.8, 87.5, 85.0, 65.2, 21.1ppm.

1-(4-Chlorophenyl)-3-(trimethylsilyl)prop-2-ynyl acetate (**1z**) [58]: 1.56 g, 74%, yellow oil. ^{1}H 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 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.

2-Methyl-4-(4-methylphenyl)but-3-yn-2-yl acetate (**1aa**) [58]: 2.19 g, 83%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H), 2.01 (s, 3H), 1.72 (s, 6H) ppm. ^{13}CNMR (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.

4.4 General Procedures for the Coupling Reaction of Propargyl acetates with Trimethylaluminum or Triethylaluminum

Under a dry nitrogen atmosphere, a mixture of $PdCl_2$(dppf) (0.0037 g, 0.005 mmol), and K_2CO_3 (0.0691 g, 0.50 mmol) in a reaction vessel was added an trimethylaluminum or triethylaluminum (0.4 mmol) in 2 mL THF followed by an addition of propargyl acetate (0.50 mmol). The resulted solution was stirred at 60 ^{o}C for 4 h. After completion the reaction, the mixture was diluted with 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 *in 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**.

1,3-Diphenylbuta-1,2-diene (**2a**) [33]: Yield: 0.100g (97 %), Yellow oil. ^{1}H NMR (400 MHz, CDCl3) δ: 7.48–7.44 (m, 2 H), 7.36–7.28 (m, 6 H), 7.25–7.20 (m, 2 H), 6.48 (q, J = 2.8 Hz, 1 H), 2.23 (d, J = 2.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.9, 136.4, 134.6, 128.8, 128.6, 127.2(d, J = 1.4Hz),127.0, 126.0, 104.7, 96.7, 16.9 ppm.

1-(2-Methylphenyl)-3-pethylbuta-1,2-diene (**2b**) [33]: Yield: 0.095 g, 85%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, J = 7.6 Hz, 2H), 7.36-7.31 (m, 3H), 7.25-7.20 (m, 1H), 7.17-7.11 (m, 3H), 6.66 (q, J = 3.2 Hz, 1H), 2.40 (s, 3H), 2.23 (d, J = 3.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.5, 136.6, 135.3, 132.7, 130.8, 128.5, 127.5, 126.95, 126.91, 126.2, 125.8, 103.5, 94.1, 20.1, 16.9 ppm.

1-(3-Methylphenyl)-3-phenylbuta-1,2-diene (**2c**) [33]: Yield: 0.106 g, 97 %, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.23 (dd, J = 8.4, 16.4 Hz, 2H), 7.21-7.12 (m, 2H), 7.02 (d, J = 7.2 Hz, 1H), 6.45 (q, J = 2.8 Hz, 1H), 2.33 (s, 3H), 2.23 (d, J = 2.8 Hz, 3H) ppm. ^{13}C 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**) [33]: Yield: 0.107g, 98%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.43 (m, 2H), 7.34-7.31 (m, 2H), 7.25-7.20 (m, 3H), 7.13 (d, J = 8.0 Hz, 2H), 6.46 (q, J = 2.8 Hz, 1H), 2.33 (s, 3H), 2.22 (d, J = 2.8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 206.5, 136.6, 136.5, 131.6, 129.5, 128.3, 126.9, 126.8, 125.7, 104.5, 96.4, 21.2, 16.9 ppm.

1-(2-Methoxyphenyl)-3-phenylbuta-1,2-diene (**2e**) [33]: Yield: 0.114 g, 97%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.44 (m, 2H), 7.38-7.31 (m, 3H), 7.25-7.18 (m, 2H), 6.91-6.86 (m, 3H), 3.86 (s, 3H), 2.22 (d, J = 3.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.3, 156.1, 136.5, 128.4, 128.1, 127.8, 126.8, 125.7, 122.8, 120.7, 111.1, 103.8, 90.5, 55.6, 16.8 ppm.

1-(2-Chlorophneyl)-3-phenylbuta-1,2-diene (**2f**) [33]: Yield: 0.116 g, 96%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.40 (m, 3H), 7.37-7.33 (m, 3H), 7.25-7.22 (m, 1H), 7.18-7.12 (m, 2H), 6.91 (q, J = 2.8 Hz, 1H), 2.23 (d, J = 2.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.8, 135.8, 132.2, 129.8, 128.5, 128.4, 128.1, 127.2, 126.8, 125.7, 104.8, 93.1, 16.7 ppm.

1-(4-bromophneyl)-3-phenylbuta-1,2-diene (**2h**) [58]: Yield: 0.094g, 66%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.43 (m, 2H), 7.35-7.32 (m, 2H), 7.31-7.21 (m, 5H), 6.44 (q, J = 2.7 Hz, 1H), 2.23 (d, J = 2.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.9, 136.1, 133.1, 132.6, 128.8, 128.5, 128.2, 127.1, 125.8, 105.1, 95.7, 16.8 ppm.

1-(Naphthylen-1-yl)-3-phenylbuta-1,2-diene (2h) [58]: Yield: 0.111g (87 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26(d, J = 7.6Hz,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), 7.39 (t, J = 7.6 Hz, 1H), 7.33-7.30 (t, J = 7.4 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 2.0 Hz, 1H), 2.26 (d, J = 2.4 Hz,1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.3, 136.5, 134.1, 131.1, 130.8, 128.8, 128.6, 127.8, 127.1, 126.3, 126.0, 125.8, 125.8, 125.7, 123.8, 103.5, 93.5, 17.0 ppm.

1-(Naphthylen-2-yl)-3-phenylbuta-1,2-diene (2i) [57]: Yield: 0.102g (80 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76, -7.69(m, 4H), 7.48 (d, J = 8.0 Hz, 3H), 7.44-7.37 (m, 2H), 7.32(t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.63 (d, J = 2.0 Hz, 1H), 2.25 (d, J = 2.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.5, 136.4, 133.9, 132.8, 132.2, 128.6, 128.4, 127.84, 127.82, 127.2, 126.4, 126.0, 125.79, 125.76, 124.9, 104.9, 97.1,17.0 ppm.

1-(4-methylpenta-2,3-dien-2-yl)benzene (2j) [58]: Yield: 0.070g (89 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37(d, J = 8.0 Hz, 2H), 7.30(t, J = 6.0Hz, 2H), 7.16 (t, J = 8.0Hz, 1H), 2.05(s, 3H), 1.79(s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.1, 138.9, 128.3, 126.2, 125.8, 98.2, 97.0, 20.6, 17.4 ppm.

1-Fluoro-2-(4-methylpenta-2,3-dien-2-yl)benzene (2k) [58]: Yield: 0.080g (91 %), Yellow oil. ^{1}H NMR (400 MHz. $CDC1_3$) δ: 7.17-7.13 (m ,1H), 7.02-6.99 (d, J = 4 Hz, 1H), 6.96-6.85 (m ,2H), 1.97 (q, J_1 = J_2 = 4 Hz , 3H), 1.66 (t, J = 3.2 Hz, 6H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.7 (d, J = 1.5 Hz), 160.2 (d, J = 247.5 Hz), 129.4 (d, J = 3.8 Hz), 127.9 (d, J = 8.2 Hz), 127.4 (d, J = 11.7 Hz), 123.8 (d, J = 3.6 Hz), 116.0 (d, J = 22.7 Hz), 95.1 (d, J = 1.5 Hz), 93.8, 20.6, 19.4 (d, J = 2.8 Hz) ppm.

1-Bromo-3-(4-methylpenta-2,3-dien-2-yl)benzene (2l) [58]: Yield: 0.070g (73 %), Yellow oil. ^{1}H NMR (400 MHz. $CDC1_3$) δ: 7.44-7.41 (m, 1H),7.35 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.29-7.27 (m, 1H), 7.18-7.11 (m, 1H), 2.05 (s, 3H), 1.75 (d, J = 4 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.1, 138.8, 137.8, 128.3, 127.0, 125.8, 123.0, 98.2, 96.8, 21.7, 20.6, 17.5 ppm.

2-(4-methylpenta-2,3-dien-2-yl)thiophene (2m) [58]: Yield: 0.054g (66 %), Yellow oil. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.11 (d, J = 5.2 Hz, 1H), 6.95-6.93 (m, 1H), 6.84 (t, J = 3.6 Hz, 1H), 2.04 (d, J = 0.8 Hz, 3H), 1.78 (d, J = 0.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.1, 145.1, 127.5, 124.0, 122.4, 98.0, 94.4, 77.5, 77.2, 76.8, 20.6, 18.3 ppm.

1-(4-methylhexa-2,3-dien-2-yl)benzene (2n) [58]: Yield: 0.082g (95 %), Yellow oil. ^{1}H NMR (400 MHz. $CDC1_3$) δ: 7.38 (d, J = 8 Hz, 2H), 7.30 (t, J = 8 Hz, 2H), 7.16 (t, J = 6 Hz,1H), 2.11-

2.04(m , 5H) , 1.78 (s, 3H), 1.05-1.01 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.3, 138.9, 129.1, 128.3, 126.1, 125.7, 103.4, 100.1, 27.6, 19.0, 17.5, 12.5 ppm.

1-Fluoro-2-(4-methylhexa-2,3-dien-2-yl)benzene (2o) [58]: Yield: 0.086g (91 %), Yellow oil. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.20- 7.15 (m ,1H), 7.03- 7.00 (m ,1H), 6.97- 6.85 (m ,2H), 1.98 (t, J = 2.4Hz ,3H), 1.94-1.91 (m ,2H), 1.66 (d, J = 3.6 Hz ,3H), 0.97- 0.92 (m ,3H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.9 (d, J = 2.0 Hz), 160.4 (d, J = 247.6Hz), 129.6 (d, J = 3.9Hz), 127.8 (d, J =8.2 Hz), 127.5 (d, J = 13.7 Hz), 123.8 (d, J = 3.6 Hz), 116.1 (d, J = 22.7 Hz), 101.4 (d, J = 1.3 Hz), 95.7, 27.3 ,19.6 (d, J = 2.8 Hz) 19.0, 12.3ppm.

1-Fluoro-3-(3-methylhexa-2,3-dien-2-yl)benzene (2p) [58]: Yield: 0.092g (97 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25-7.21 (m, 1H), 7.14 (d, J = 8Hz, 1H), 7.09-7.05 (m, 1H), 6.87-6.83 (m, 1H), 2.11-2.04 (m, 5H), 1.79 (s, 3H), 1.02 (t, J = 8Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.6, 163.3 (d, J = 242.5Hz), 141.7 (d, J = 7.4Hz), 129.6 (d, J =8.3Hz), 121.2(d, J = 2.6Hz), 112.7 (dd, J_1 = 21.4, J_2 = 38.2 Hz), 104.0, 99.6 (d, J = 2.5Hz), 27.5, 18.9, 17.4, 12.4 ppm.

1-Fluoro-4-(4-methylhexa-2,3-dien-2-yl)benzene (2q) [58]: Yield: 0.076g (80 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34- 7.30 (m, 2H), 6.98 (t, J = 8.0 Hz ,2H), 2.04 (s, 5H), 1.78 (s, 3H), 1.04-1.00 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.0, 161.6 (d, J = 241.2Hz), 127.0 (d, J = 7.8Hz), 115.1, 114.9, 103.6, 99.3, 27.6, 9.0, 17.7, 12.4 ppm.

1-Chloro-3-(4-methylhexa-2,3-dien-2-yl)benzene (2r) [58]: Yield: 0.092g (89 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (s, 1H), 7.26- 7.19 (m, 2H), 7.14- 7.12 (m, 1H), 2.11-2.04 (m, 5H), 1.79 (s, 3H), 1.02 (t, J = 8.0 Hz ,3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.6, 141.1, 134.3, 129.4, 126.1, 125.7, 123.7, 104.1, 99.4, 27.5, 18.9, 17.5, 12.4 ppm.

1-Bromo-3-(3-methylhexa-2,3-dien-2-yl)benzene (2s) [58]: Yield: 0.079g (63 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40-7.27 (m, 1H), 7.21-7.19 (m, 2H), 6.99-6.98 (m, 1H), 2.34 (s, 1H), 2.07-2.05 (m, 4H), 1.78 (s, 3H), 1.05-1.01 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.3, 138.9, 137.8, 128.3, 127.0, 126.4, 125.6, 122.8, 103.2, 100.1, 27.6, 19.0, 17.6, 12.5 ppm.

1-Methyl-4-(4-methylpenta-2,3-dien-2-yl)benzene (2t) [58]: Yield: 0.085g (92 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, J = 8.4 Hz, 2H), 7.10(d, J = 8.0 Hz, 2H), 2.32 (s, 3H), 2.09-2.03 (m, 5H), 1.77 (s, 3H), 1.02 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.0, 136.0, 135.8, 129.0, 125.6, 103.2, 100.0, 27.7, 21.2, 19.0, 17.6, 12.5 ppm.

2-(4-methylhexa-2,3-dien-2-yl)thiophene (2u) Yield: 0.062g (70 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (d, J = 4.8 Hz, 1H), 6.94 (t, J = 4.2 Hz, 1H), 6.84 (d, J = 2.8 Hz, 1H), 2.08-2.03 (m, 5H), 1.77 (m, 3H), 1.04 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.3, 145.2, 127.4, 123.8, 122.2, 104.4, 96.5, 27.8, 19.0, 18.3, 12.4 ppm. HRMS(ESI):m/z calcd for $C_{11}H_{15}S^+$ $(M + H)^+$ 178.08162, found 178.08138.

2,4-Diphenylpenta-2,3-diene (2v) [58]: Yield: 0.064g (58 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.42 (m, 4H), 7.33-7.29 (m, 4H), 7.22-7.20 (m, 2H), 2.20 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.0, 137.4, 128.6, 126.9, 125.9, 102.5, 16.9 ppm.

2-phenyl-4-(4-chlorophenyl)penta-2,3-diene (2w) [58]: Yield: 0.107g (84 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42-7.39 (m, 2H), 7.35-7.27 (m, 6H), 7.25-7.19 (m, 2H), 2.19 (s, 3H), 2.17 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.0, 137.0, 135.9, 132.6, 128.6 (d, J = 2.8 Hz), 127.2, 127.0, 125.9, 102.9, 101.8, 16.9, 16.9 ppm.

2-phenyl-4-(4-fluorophenyl)penta-2,3-diene (2x) [58]: Yield: 0.088g (74 %), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.41 (m, 2H), 7.38-7.35 (m, 2H), 7.34-7.30 (m, 2H), 7.23-7.19 (m, 1H), 7.02-6.97 (m, 2H), 2.19 (s, 3H), 2.18 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.6 (d, J = 2.1 Hz), 205.63, 162.0 (d, J = 244.3 Hz), 137.2, 133.3 (d, J = 3.2 Hz), 128.6, 127.4 (d, J = 7.9 Hz), 127.0, 125.9, 115.4 (d, J = 21.4Hz), 102.7, 101.7, 17.2, 17.0 ppm.

1-methyl-2-(3-phenylpenta-1,2-dien-1-yl)benzene (4b):Yield: 0.1014g (87%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.38 (m, 3H), 7.30-7.27 (m, 2H), 7.19-7.08 (m, 4H), 6.74-6.73 (m, 1H), 2.57-2.53 (m, 2H), 2.38 (s, 3H), 1.21-1.17 (m, 3H) ppm ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.5, 136.5, 135.8, 132.6, 130.7, 128.8, 127.3, 127.00, 126.7, 126.3, 126.1, 110.6, 96.9, 23.6, 20.1, 12.7 ppm. HRMS (ESI) m/z calcd for $C_{18}H_{19}^+$ $(M+H)^+$ 235.14813, found 235.14836.

1-methyl-3-(3-phenylpenta-1,2-dien-1-yl)benzene (4c): Yield: 0.0972g (83%), yellow oil..^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71-7.68 (m, 2H), 7.55-7.51 (m, 2H), 7.45-7.38 (m, 4H), 7.25 (m, 1H), 6.78-6.76 (m, 1H), 2.85-2.79 (m, 2H), 2.55 (d, J = 4.0 Hz ,3H), 1.47-1.42 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.4, 138.4, 136.4, 134.7, 128.7, 128.6, 128.0, 127.5, 127.1, 126.2, 124.0, 111.6, 98.8, 23.3, 21.5, 12.7 ppm. HRMS (ESI) m/z calcd for $C_{18}H_{19}^+$ $(M+H)^+$ 235.14813, found 235.14827.

1-methyl-4-(3-phenylpenta-1,2-dien-1-yl)benzene (4d): Yield: 0.095g (81 %), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 7.6 Hz ,2H), 7.49 (t, J = 7.6Hz ,2H), 7.44-7.36 (m, 3H), 7.30(d, J = 8.0 Hz ,2H), 6.74 (t, J = 3.2Hz ,1H), 2.78-2.74 (m, 2H), 2.51 (s, 3H), 1.38 (t, J = 7.2Hz ,3H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.0, 136.8, 136.2, 131.9, 129.5, 128.5, 127.0, 126.9, 126.1, 121.4, 98.4, 23.9, 21.5, 12.8 ppm.

2-(5-methylhexa-3,4-dien-3-yl)thiophene (4m): Yield: 0.044g (50%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15(d, J = 4.8 Hz, 1H), 7.00-6.96(m, 1H), 6.92-6.90(m, 1H), 2.43(q, J = 7.2 Hz, 2H), 1.85(s, 6H), 1.16(t, J = 7.2 Hz ,3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.5, 144.5, 127.4, 123.6, 122.0, 101.3, 100.1, 24.6, 20.6, 20.5, 12.6ppm. HRMS (ESI) m/z calcd for $C_{11}H_{15}S^+$ $(M+H)^+$ 179.08890, found 179.08853.

1-methyl-4-(5-methylhepta-3,4-dien-3-yl)benzene (4t): Yield: 0.083g (83%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 2.39 (q, J = 7.2 Hz, 2H), 2.30 (s, 3H), 2.13-2.01(m, 2H), 1.78 (s, 3H), 1.09 (t, J = 7.6 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.4, 135.7, 129.3, 129.0, 126.5, 125.8, 107.2, 105.3, 94.4, 27.7, 23.4, 21.1, 19.2, 12.9, 12.6ppm. HRMS (ESI) m/z calcd for $C_{15}H_{21}^+$$(M+H)^+$ 201.16378, found 201.16356.

1-fluoro-2-(5-methylhepta-3,4-dien-3-yl)benzene (4o): Yield: 0.075g (74%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.25 (m, 1H), 7.17-7.09 (m, 1H), 7.07-6.96(m, 2H), 2.40 (q, J = 7.2 Hz, 2H), 2.09-1.98 (m, 2H), 1.79 (m, 3H), 1.07-1.03 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.8, 160.3 (d, J = 246.7 Hz), 129.7 (d, J = 4.1 Hz) 127.8 (d, J = 8.0 Hz), 123.8 (d, J = 3.5 Hz), 115.1(d, J = 22.8 Hz), 105.6, 103.1 (d, J = 72.4 Hz), 86.9 (d, J = 6.5 Hz), 27.5, 25.6, 19.2, 12.9, 12.4ppm. HRMS (ESI) m/z calcd for $C_{14}H_{18}F^+$$(M+H)^+$ 205.13871, found 205.13860.

1-chloro-3-(5-methylhepta-3,4-dien-3-yl)benzene (4r): Yield: 0.103g (94%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (t, J = 2.0 Hz, 1H), 7.26-7.17 (m, 2H), 7.13-7.10 (m, 1H), 2.37 (q, J = 7.2 Hz, 2H), 2.15-2.03 (m, 2H), 1.80 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H), 1.03 (t, J = 7.6 Hz, 3H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.0, 140.9, 134.4, 129.5, 126.1 (d, J = 15.7 Hz), 124.0, 106.6, 106.3, 93.7, 27.6, 23.3, 19.0, 12.7, 12.5ppm. HRMS (ESI) m/z calcd for $C_{14}H_{18}Cl^+$ $(M+H)^+$ 221.10915, found 221.10960.

1-bromo-3-(3-phenylpenta-1,2-dienyl)benzene (4y): Yield: 0.117g (79%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-

7.42 (m, 3H), 7.34-7.30 (m, 3H), 7.25-7.21 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.49 (t, *J* = 3.2 Hz, 1H), 2.65-2.52 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 206.7, 137.3, 135.9, 130.3, 130.0, 129.6, 128.7, 127.4, 126.2, 125.4, 123.1, 112.4, 97.7, 23.3, 12.7ppm. HRMS (ESI) m/z calcd for $C_{17}H_{16}Br^+$ $(M+H)^+$ 299.04299, found 299.04373.

1-(1-(4-chlorophenyl)penta-1,2-dien-3-yl)trimethylsilane (**4z**): Yield: 0.103g (83%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.26-7.16 (m, 4H), 6.15-6.12 (m, 1H), 2.20-2.01(m, 2H), 1.11 (s, 9H), 1.00 (t, *J* = 7.2 Hz, 3H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 201.5, 135.2, 131.8, 128.8, 127.7, 127.4, 120.6, 107.4, 96.4, 34.6, 30.4, 29.6, 20.6, 12.8ppm. HRMS (ESI) m/z calcd for $C_{14}H_{20}ClSi^+(M+H)^+$ 251.10173, found 251.10179.

1-methyl-4-(5-methylhexa-3,4-dien-3-yl)benzene (4aa): Yield: 0.073g (79%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.27-7.24 (m, 2H), 7.10-7.08 (m, 2H), 2.40-2.34 (m, 2H), 2.30 (d, *J* = 2.0 Hz, 3H), 1.79 (d, *J* = 2.4 Hz, 6H), 1.11-1.07 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 201.3, 135.8, 135.7, 129.0, 125.9, 105.2, 98.9, 23.4, 21.1, 20.7, 12.8ppm. HRMS (ESI) m/z calcd for $C_{14}H_{19}^+$ $(M+H)^+$ 187.14813, found 187.14801.

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Highlights

Palladium-catalyzed, ligand-free S_N2' substitution reactions of organoaluminum with propargyl acetates for the synthesis of multi-substituted allenes

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1. 1 mol% $Pd(dppf)Cl_2$ complexes showed high activity in S_N2' substitution reactions of organoaluminum with propargyl acetates.
2. The multi-substituted allenes derivatives were obtained in good to excellent yields (50-98 %) with high selectivities (up to 99%).
3. Both aromatic and heteroaromatic propargyl acetates are tolerated in the reactions.
4. This catalyst system provided one of the most convenient approaches to the construction of multi-substituted allenes.

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