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Highly Efficient Synthesis of Multi-Substituted Allenes from Propargyl Acetates and Organoaluminum Reagents Mediated by Palladium

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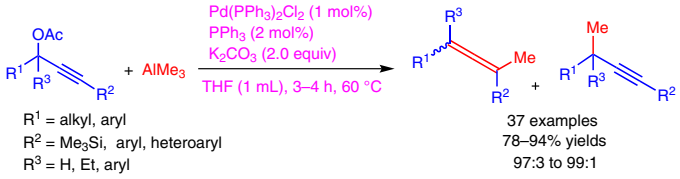

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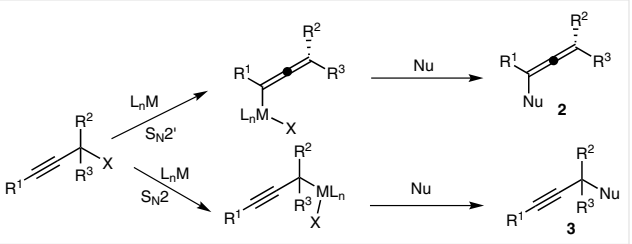
Abstract A simple and mild catalytic S_N2' substitution reaction of propargyl acetates with organoaluminum reagents is reported. The S_N2' substitution reaction of propargyl acetates with organoaluminum reagents mediated by $Pd(PhP_3)_2Cl_2$ (1 mol%)/PPh_3 (2 mol%)/K_2CO_3 in tetrahydrofuran at 60 °C for 3–4 hours afforded the corresponding multi-substituted allenes in good yields (up to 94%) with high selectivities (up to 99%). The process was simple and easily performed, which offers an efficient method to synthesize the multi-substituted allene derivatives.

Key words allenes, palladium, propargyl acetates, organoaluminum reagent, S_N2' substitution reaction

Multi-substituted allenes are very important intermediates and functional groups that are widely applied in organic synthesis.[1,2] Allene moieties have also been found in a large number of medicinal and natural products[3] and photoelectric materials.[4] Therefore, the synthesis of allenes has attracted great interest in organic and medicinal chemistry. Developing some simple and effective methods for the synthesis of multi-substituted allenes from simple and easily available organic compounds is very important. Until now numerous effective methodologies for the synthesis allenes have been reported.[5,6] The synthetic method of substituted allenes include isomerization of alkynes,[7] elimination of allylic derivatives,[8] coupling reactions of terminal alkynes and aldehydes,[9] and metal-catalyzed S_N2'-type substitution reactions of propargylic derivatives.[10,11] Among them, the metal-catalyzed S_N2'-type substitution reactions of propargylic derivatives with organometallic reagents is one of the most generally useful ones (Scheme 1). However, there are two competing possible reaction pathways; the successful application of S_N2'-type substitution reaction depends on the choice of catalyst and/or organometallic species to selectively produce either the allene product **2** or the alkyne product **3**. Therefore, the development of rapid and more efficient method for the synthesis of allenes is still a challenge.



Scheme 1 Metal-catalyzed S_N2' and S_N2 substitution reaction of propargylic derivatives with organometallic species

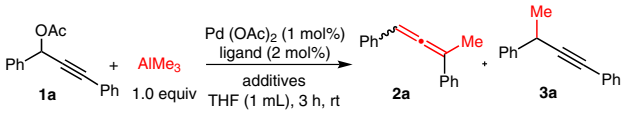
Our previous studies show that the catalytic system of 1 mol% $Pd(OAc)_2$/2 mol% (*o*-tolyl)$_3$P worked efficiently for the cross-coupling of propargyl acetates with organoaluminum reagents, producing the trisubstituted allenes in good to excellent yields of up to 94% in tetrahydrofuran.[6f] However, the reaction of trimethylaluminum ($AlMe_3$) with 2-methyl-4-phenylbut-3-yn-2-yl acetate, employing the catalyst of 1 mol% $Pd(OAc)_2$/2 mol% (*o*-tolyl)$_3$P, yielded tetrasubstituted allene 1,1,3-trimethyl-3-phenylallene in only 80% yield and with low selectivity (90:10). To continue our effort to develop cross-coupling reactions using reactive organometallic reagents,[6h,i,12] we herein report a highly efficient coupling reactions of propargyl acetates with organoaluminum species for the synthesis of tri- and tetrasubstituted allene derivatives using a $Pd(PhP_3)_2Cl_2$ (1 mol%)/PPh_3(2 mol%)/K_2CO_3 (2 equiv) as catalyst. Excellent yields (up to 94%) and high selectivities (up to 99%) were obtained for a wide range of substrates at 60 °C for 3–4 hours in THF.

To optimize the reaction conditions, effects of phosphine ligand, palladium source, reaction time, solvent, 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** (Table 1 and Table 2). We initially investigated the S_N2' substitution reaction of propargyl acetates (**1a** with trimethylaluminum without mental and ligand in THF for 3 hours at ambient temperature. The reaction proceeded to afford both allene **2a** and alkyne **3a** with only a 10% conversion and a ratio of 1:99 in favor of the alkyne **3a** (Table 1, entry 1). When only $Pd(OAc)_2$ was used as the catalyst, the S_N2' substitution reaction of propargyl acetate **1a** with trimethylaluminum afforded both allene **2a** and alkyne **3a** with only a 12% conversion and the ratio of products remained unchanged (entry 2). When 2 mol% PPh_3 was used as ligand, the $Pd(OAc)_2$ catalyzed the S_N2' substitution reaction of propargyl acetate **1a** with trimethylaluminum to give the products **2a** and **3a** in 16% conversion (entry 3). The product ratio is about 57:43 in favor of the allene **2a**. The other phosphine ligands were then examined (entries 4, 5). It was found that the PPh_3 ligand was best effective for reactivity and selectivity (entry 3). Other phosphine ligands did not provide satisfactory results. To our delight, when 2.0 equivalents of K_2CO_3 was used as additive, the $Pd(OAc)_2/PPh_3$-catalyzed the S_N2' substitution reaction of propargyl acetate **1a** with trimethylaluminum gave the products **2a** and **3a** in a ratio of 60:40 in favor of the allene **2a** with 96% conversion (entry 6). However, the S_N2' substitution reaction of trimethylaluminum with propargyl acetate **1a** produced the product **2a** and **3a** in a ratio of 95:5 in favor of the allene **2a** with 98% conversion at 60 °C over 3 hours (entry 7).

Subsequently, the effect of the amount of trimethylaluminum was investigated. The result revealed that the reaction selectivity increased from 95:5 to 98:2 when the trimethylaluminum loading was increased from 0.5 mmol to 0.6 mmol (Table 1, entries 7 and 8). While using K_3PO_4 as additive, the product conversion decreased from 98% to 58% (entry 9). However, when the ratio of $Pd(OAc)_2$ and PPh_3 was altered to 1:4, the product conversion and the reaction selectivity remained unchanged (entries 8 and 10).

To improve the reactivity and selectivity, the S_N2' substitution reaction of **1a** with trimethylaluminum under other conditions was investigated. First, various solvents were tested in the presence of $Pd(OAc)_2$ and PPh_3 (Table 2, entries 1, 2). Toluene and hexane reduced the selectivity greatly, and the ratios of product were only 72:28 and 53:47, respectively. In contrast, excellent conversion (98%) and good selectivity (**2a**/**3a** = 98:2) could be obtained in THF as solvent (Table 1, entry 8). Subsequently, other palladium sources with PPh_3 were surveyed. Although $PdCl_2$ and $Pd(acac)_2$ can effectively catalyze the S_N2' substitution reaction, the product selectivity and conversion were low (Table 2, entries 3, 4). Pleasingly, excellent conversion (>99%) and high selectivity (**2a**/**3a** >99%) were obtained using $Pd(PPh_3)_2Cl_2$ (Table 2, entry 5). The product selectivity and conversion decreased when only $Pd(PPh_3)_2Cl_2$ was used as the catalyst (entry 6). Therefore, the optimal S_N2' substitution reaction conditions were 1 mol% $Pd(PPh_3)_2Cl_2$, 2 mol% PPh_3, 1.0 mmol K_2CO_3, 0.6 mmol trimethylaluminum, and 0.5 mmol propargyl acetate in THF (1 mL) at 60 °C for 3 hours.

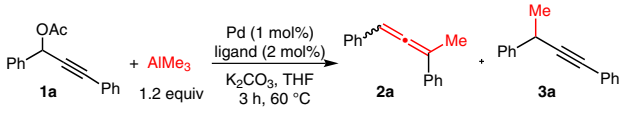
Table 1 Effect of the Ligands, the Loading of $AlMe_3$, and the Additives on the S_N2' Substitution Reaction[a]



Entry	Ligand (2 mol%)	Additive (2.0 equiv)	Conv. (%)[b]	**2a**/**3a** (%)[c]
1	–	–	10	1:99
2[d]	–	–	12	1:99
3	PPh_3	–	16	57:43
4	PCy_3	–	10	45:55
5	dppe	–	12	1:99
6	PPh_3	K_2CO_3	96	60:40
7[e]	PPh_3	K_2CO_3	98	95:5
8[f]	PPh_3	K_2CO_3	98	98:2
9[f]	PPh_3	K_3PO_4	58	99:1
10[g]	PPh_3	K_2CO_3	98	98:2

[a] Ratio of **1a**/$AlMe_3$/$Pd(OAc)_2$/ligand = 0.5:0.5:0.005:0.01 mmol.
[b] Conversion of **2a** + **3a** was determined by ^1H NMR spectra.
[c] The ratio of **2a**/**3a** was determined by ^1H NMR analysis.
[d] Only $Pd(OAc)_2$ was used.
[e] Reaction carried out at 60 °C.
[f] $AlMe_3$ = 0.6 mmol, 60 °C.
[g] Ratio of **1a**/$AlMe_3$/$Pd(OAc)_2$/ligand = 0.5:0.6:0.005:0.02 mmol, 60 °C.

Table 2 Effect of the Palladium Source and Solvent on the S_N2' Substitution Reaction[a]

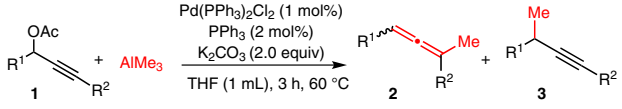


Entry	Pd salt	Solvent	Conv. (%)[b]	**2a**/**3a** (%)[c]
1	$Pd(OAc)_2$	hexane	92	72:28
2	$Pd(OAc)_2$	toluene	99	53:47
3	$PdCl_2$	THF	80	91:9
4	$Pd(acac)_2$	THF	97	95:5
5	$Pd(PPh_3)_2Cl_2$	THF	>99	>99:1
6[d]	$Pd(PPh_3)_2Cl_2$	THF	94	93:7

[a] Ratio of **1a**/$AlMe_3$/Pd(II)/PPh_3 = 0.5:0.6:0.005:0.01 mmol.
[b] Conversion of **2a** + **3a** was determined by ^1H NMR spectra.
[c] The ratio of **2a**/**3a** was determined by ^1H NMR analysis.
[d] Only 1 mol% $Pd(PPh_3)_2Cl_2$ was used.

With the optimized conditions in hand, the scope of the catalytic the S_N2' substitution reaction of different propargyl acetates with trimethylaluminum was then explored, 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**–**p**). Aromatic propargyl acetates with both electron-donating groups (Table 3, entries 2–5) and electron-withdrawing groups (entries 6–9) on the aromatic ring furnished the trisubstituted allenes in 80–88% yield with 99% selectivity (entries 2–9). Furthermore, the propargyl acetates bearing a bulky 1-naphthyl or 2-naphthyl group also gave the trisubstituted allene products with 99% selectivity in yields of 80 and 78% (entries 10 and 11). The S_N2' substitution reactions of trimethylaluminum with propargyl acetates bearing *n*-pentyl group was also explored, and after 3 hours, **2l** was formed with 99% selectivity in 83% yield (entry 12). Under the same conditions, aliphatic propargyl acetates, such as propargyl acetates **1m**–**p**, also reacted with trimethylaluminum to provide the trisubstituted allenes (i.e., **2m**–**p**) in good isolated yields and high selectivity (entries 13–16).

Table 3 $Pd(PPh_3)_2Cl_2/Ph_3P$-Catalyzed S_N2' Substitution Reaction of Propargyl Acetates **1** with $AlMe_3$[a]

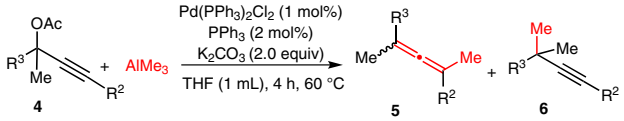


Entry	**1** R^1, R^2	Product	**2**/**3** (%)[b]	**2** Yield (%)[c]
1	**1a** Ph, Ph	**2a**	99:1	85
2	**1b** 2-MeC_6H_4, Ph	**2b**	99:1	81
3	**1c** 3-MeC_6H_4, Ph	**2c**	99:1	87
4	**1d** 4-MeC_6H_4, Ph	**2d**	99:1	83
5	**1e** 2-$MeOC_6H_4$, Ph	**2e**	99:1	79
6	**1f** 2-ClC_6H_3, Ph	**2f**	99:1	88
7	**1g** 4-ClC_6H_4, Ph	**2g**	99:1	87
8	**1h** 4-BrC_6H_4, Ph	**2h**	99:1	88
9	**1i** 4-$F_3CC_6H_4$, Ph	**2i**	99:1	83
10	**1j** 1-naphthyl, Ph	**2j**	99:1	80
11	**1k** 2-naphthyl, Ph	**2k**	99:1	78
12	**1l** *n*-pentyl, Ph	**2l**	99:1	83
13	**1m** Ph, Me_3Si	**2m**	99:1	88
14	**1n** 4-MeC_6H_4, Me_3Si	**2n**	99:1	81
15	**1o** 4-ClC_6H_4, Me_3Si	**2o**	99:1	87
16	**1p** 2-naphthyl, Me_3Si	**2p**	99:1	79

[a] Ratio of **1**/$AlMe_3$/$Pd(PPh_3)_2Cl_2$/PPh_3 = 0.5:0.6:0.005.0.01 mmol, 3 h.
[b] The ratio of **2**/**3** was determined by ^1H NMR analysis.
[c] Isolated yield, two runs.

Encouraged by the good performance of the current catalyst system shown above, the S_N2' substitution reactions of 2-methyl-4-phenylbut-3-yn-2-yl acetate (**4a**) with $AlMe_3$ was subsequently investigated. The reaction of propargyl acetate **4a** with $AlMe_3$, employing the catalyst of 1 mol% $Pd(PPh_3)_2Cl_2$ and 2 mol% PPh_3, yielded the S_N2' product 1,1,3-trimethyl-3-phenylallene (**5a**) in 80% yield and good selectivity (**5a**/**6a** = 95:5) (Table 4, entry 1). Pleasingly, when the reaction time was extended to 4 hours, the reaction proceeded smoothly to give the products **5a** and **6a** in a ratio of 97:3 in favor of **5a** and the product **5a** in 85% yield (entry 2). Thus, the optimized catalytic system was 1 mol% Pd $(PPh_3)_2Cl_2$, 2 mol% PPh_3, 1.0 mmol K_2CO_3, 0.5 mmol substituted propargyl acetate, and 0.6 mmol trimethylaluminum in THF (1 mL) at 60 °C for 4 hours.

Table 4 $Pd(PPh_3)_2Cl_2/Ph_3P$-Catalyzed S_N2' Substitution Reaction of Propargyl Acetates **4** with $AlMe_3$[a]



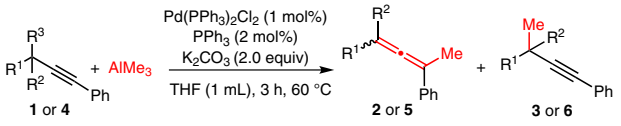
Entry	**4** R^2, R^3	Product	Ratio of **5**/**6** (%)[b]	**5** Yield (%)[c]
1[d]	**4a** Ph, Me	**5a**	95:5	80
2	**4a** Ph, Me	**5a**	97:3	85
3	**4b** 4-MeC_6H_4, Me	**5b**	98:2	89
4	**4c** 3-ClC_6H_4, Me	**5c**	99:1	94
5	**4d** 3-FC_6H_4, Me	**5d**	99:1	94
6	**4e** 2-FC_6H_4, Me	**5e**	99:1	90
7	**4f** 3-BrC_6H_4, Me	**5f**	99:1	86
8	**4g** 4-BrC_6H_4, Me	**5g**	99:1	93
9	**4h** 4-FC_6H_4, Me	**5h**	99:1	94
10	**4i** 2-thienyl, Me	**5i**	99:1	88
11	**4j** Ph, Et	**5j**	99:1	83
12	**4k** 3-FC_6H_4, Et	**5k**	99:1	86
13	**4l** 3-ClC_6H_4, Et	**5l**	99:1	92
14	**4m** 4-FC_6H_4, Et	**5m**	99:1	93
15	**4n** 2-FC_6H_4, Et	**5n**	99:1	90
16	**4o** 3-BrC_6H_4, Et	**5o**	99:1	87
17	**4p** 4-MeC_6H_4, Et	**5p**	97:3	84
18	**4q** Ph, Ph	**5q**	96:4	75
19	**4r** Ph, 4-FC_6H_4	**5r**	97:3	80
20	**4s** Ph, 4-ClC_6H_4	**5s**	97:3	81

[a] Ratio of **4**/$AlMe_3$/$Pd(PPh_3)_2Cl_2$/PPh_3 = 0.5:0.6:0.005:0.01 mmol, 4 h.
[b] The ratio of **5**/**6** was determined by ^1H NMR analysis.
[c] Isolated yield, two runs.
[d] Reaction time: 3 h.

Under the optimized reaction conditions, the reaction scope was further explored with the substituted propargyl acetates **4a–s** and $AlMe_3$, and the results are summarized in Table 4. The S_N2' substitution reactions of propargyl acetates **4a–s** with $AlMe_3$ gave tetrasubstituted allenes **5a–s** with >95% selectivity in excellent isolated yields (78–94%, Table 4, entries 2–20). The results indicate that the reactions of aromatic propargyl acetates with both electron-donating groups **4b**, **4p** and electron-withdrawing groups **4c–h**,**k–o**) on the aromatic rings underwent the S_N2' substitution reactions smoothly to give the tetrasubstituted allenes (i.e., **5c–h**,**k–o**) with high selectivity (up to 99:1) and in good to excellent isolated yields (86–94%, Table 4, entries 4–9, 12–16). In addition, the tetrasubstituted allene bearing a thienyl group **5i** resulting from propargyl acetate **4i** was obtained in 88% yield and 99% selectivity (entry 10). More importantly, the tetrasubstituted allene bearing biaryl group **5q–s** resulting from propargyl acetate **4q–s** were obtained in 78–81% yield and 96–97% selectivity (entries 18–20).

For comparison, coupling reactions of other propargyl ester **1q–s** and **4t**,**u** with trimethylaluminum catalyzed by the optimum catalytic system were conducted. Results showed that the reactions of propargyl carbonate or sulfonic acid ester underwent the S_N2' substitution reactions smoothly to give the tri- and tetrasubstituted allenes (i.e., **2a** or **5a**) with high selectivity (up to 99:1) and in good isolated yields (78–82%, Table 5, entries 1–4).

Table 5 $Pd(PPh_3)_2Cl_2/Ph_3P$-Catalyzed S_N2' Substitution Reaction of Other Types of Propargyl Ester **1** or **4**) with Organoaluminum Reagent[a]



Entry	**1** or **4** R^1, R^2, R^3	Product	**2**/**3** or **5**/**6** (%)[b]	**2** or **5** Yield (%)[c]
1[d]	**1q** Ph, H, OCO_2Me	**3a**	98: 2	78
2	**1r** Ph, H, OMs	**3a**	99: 1	82
3	**4t** Me, Me, OCO_2Me	**5a**	98: 2	81
4	**4u** Me, Me, OMs	**5a**	97: 3	80

[a] Ratio of **4**/$AlMe_3$/$Pd(PPh_3)_2Cl_2$/PPh_3 = 0.5:0.6:0.005:0.01 mmol, 4 h.
[b] The ratio of **2**/**3** or **5**/**6** was determined by ^1H NMR analysis.
[c] Isolated yield, two runs.
[d] Reaction time: 3 h.

In conclusion, we have developed a highly selective S_N2' substitution reaction of propargyl acetates with organoaluminum reagents catalyzed by palladium. The S_N2' substitution reactions of propargyl acetates with organoaluminum afforded tri- and tetrasubstituted allenes in excellent yields with high selectivities. Coupling reactions of propargyl acetates bearing *n*-pentyl group produced the trisubstituted allene product of **2l** in 83% yield with 99% selectivity. Coupling reactions of 4-aryl-2-methylbut-3-yn-2-yl acetates **4** with trimethylaluminum gave smoothly the tetrasubstituted allenes **5** in excellent yields (up to 94%) with high selectivities (up to 99%). This methodology provides a useful procedure for the synthesis of tri- and tetrasubstituted allenes. Further studies on the application of this catalyst to other organoaluminum reagents are currently under way.

^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer. The chemical shifts are reported relative to TMS. Analytical 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. All reactions were carried out under N_2 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, hexane, and toluene, which were distilled from Na under N_2. Propargyl acetates **1a–p**[6h,13] and **4a–s**[14] were prepared according to literature procedures. Purification of reaction products was carried out by flash chromatography.

All known compounds have been clearly identified by comparing their ^1H NMR data with the corresponding literature data, and new products have been characterized with spectroscopic analysis (see Supporting Information).

Propargyl Acetates 1a–p; General Procedure

n-BuLi (5.16 mL, 8.25 mmol, 1.6 M in hexane) was added to a solution of the respective alkyne (8.25 mmol) in anhyd THF (15 mL) at –78 °C under N_2 atmosphere. The reaction mixture was stirred for 20 min at –78 °C, then for 1 h at r.t. The corresponding aldehyde (7.5 mmol) was added at –78 °C, and the mixture was stirred for 1 h at r.t. After the addition of Ac_2O (1.53 g, 1.42 mL, 15.0 mmol) at 0 °C, the reaction mixture was warmed to r.t. and stirred for 2 h. Then, sat. aq NH_4Cl was added and the mixture was extracted with EtOAc (3 × 15 mL). The combined EtOAc layers were washed with brine (20 mL), dried (Na_2SO_4), and concentrated under vacuum. The crude product was chromatographed on silica gel (hexane or EtOAc and hexane) to afford the desired propargyl acetate **1a–p**.

1,3-Diphenylprop-2-ynyl Acetate (1a)[6h]

Yield: 1.57 g (84%); yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.57 (m, 2 H), 7.49–7.45 (m, 2 H), 7.43–7.36 (m, 3 H), 7.35–7.28 (m, 3 H), 6.71 (s, 1 H), 2.15 (s, 3 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.7, 137.1, 131.8, 128.9, 128.7, 128.6, 128.2, 127.7, 122.0, 87.0, 85.5, 66.0, 21.0.

3-Phenyl-1-(*o*-tolyl)prop-2-ynyl Acetate (1b)[6h]

Yield: 1.74 g (88%); yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.65 (m, 1 H), 7.49–7.45 (m, 2 H), 7.34–7.27 (m, 5 H), 7.23–7.18 (m, 1 H), 6.78 (s, 1 H), 2.46 (s, 3 H), 2.15 (s, 3 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.8, 136.3, 135.2, 131.9, 130.8, 128.9, 128.7, 128.3, 128.1, 126.3, 122.2, 86.9, 85.4, 64.2, 21.0, 19.1

3-Phenyl-1-(*m*-tolyl)prop-2-ynyl Acetate (1c)[6h]

Yield: 1.64 g (83%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.46 (m, 2 H), 7.43–7.39 (m, 2 H), 7.35–7.28 (m, 4 H), 7.19 (d, *J* = 7.6 Hz, 1 H), 6.67 (s, 1 H), 2.38 (s, 3 H), 2.14 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.9, 138.5, 137.1, 131.9, 129.8, 128.8, 128.6, 128.5, 128.3, 124.9, 122.2, 86.9, 85.7, 66.1, 21.4, 21.2.

3-Phenyl-1-(*p*-tolyl)prop-2-ynyl Acetate (1d)[6h]

Yield: 1.46 g (74%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.43 (m, 4 H), 7.37–7.29 (m, 3 H), 7.25–7.21 (m, 2 H), 6.67 (s, 1 H), 2.38 (s, 3 H), 2.13 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.9, 138.9, 134.2, 131.8, 129.3, 128.7, 128.2, 127.8, 122.1, 86.8, 85.7, 65.9, 21.2, 21.1.

1-(2-Methoxyphenyl)-3-phenylprop-2-ynyl Acetate (1e)[6h]

Yield: 1.76 g (84%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 1.6, 7.6 Hz, 1 H), 7.51–7.44 (m, 2 H), 7.39–7.32 (m, 1 H), 7.31–7.27 (m, 3 H), 7.05 (s, 1 H), 7.04–7.01 (m, 1 H), 6.91 (dd, *J* = 1.2, 8.4 Hz, 1 H), 3.84 (s, 3 H), 2.12 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.8, 156.7, 131.9, 130.4, 129.0, 128.6, 128.2, 125.2, 122.4, 120.6, 110.8, 86.4, 85.7, 60.9, 55.6, 21.1.

1-(2-Chlorophenyl)-3-phenylprop-2-ynyl Acetate (1f)[6h]

Yield: 1.77 g (83%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.84 (m, 1 H), 7.51–7.45 (m, 2 H), 7.44–7.39 (m, 1 H), 7.38–7.29 (m, 5 H), 6.97 (s, 1 H), 2.15 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.5, 134.6, 133.5, 132.0, 130.3, 129.7, 129.54, 128.8, 128.3, 127.2, 122.0, 87.4, 84.6, 63.3, 20.9.

1-(4-Chlorophenyl)-3-phenylprop-2-ynyl Acetate (1g)[6h]

Yield: 1.73 g (81%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.50 (m, 2 H), 7.48–7.44 (m, 2 H), 7.41–7.35 (m, 2 H), 7.34–7.28 (m, 3 H), 6.67 (s, 1 H), 2.14 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.7, 135.7, 134.9, 131.8, 129.2, 128.9, 128.8, 128.3, 121.8, 87.3, 85.0, 65.3, 21.1.

1-(4-Bromophenyl)-3-phenylprop-2-ynyl Acetate (1h)

Yield: 2.09 g (85%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.51 (m, 2 H), 7.49–7.45 (m, 2 H), 7.41–7.38 (m, 2 H), 7.36–7.32 (m, 3 H), 6.67 (s, 1 H), 2.14 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 143.4, 131.9, 131.8, 128.4, 128.3, 128.2, 122.7, 119.8, 90.3, 84.0, 72.5, 22.1.

3-Phenyl-1-[4-(trifluoromethyl)phenyl]prop-2-ynyl Acetate (1i)[6h]

Yield: 1.79 g (89%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.8, 20.0 Hz, 4 H), 7.51–7.44 (m, 2 H), 7.38–7.29 (m, 3 H), 6.74 (s, 1 H), 2.14 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.5, 141.1, 131.8, 131.1 (q, *J* = 32.5 Hz), 129.1, 128.2, 128.1, 125.6 (q, *J* = 3.9 Hz), 123.9 (q, *J* = 271 Hz), 121.8, 87.6, 84.8, 65.4, 20.3.

1-(Naphthalen-1-yl)-3-phenylprop-2-ynyl Acetate (1j)[6h]

Yield: 1.80 g (80%); yellow solid; mp 56–58 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.0 Hz, 1 H), 7.91–7.88 (m, 3 H), 7.63–7.45 (m, 5 H), 7.35–7.28 (m, 4 H), 2.14 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.9, 134.0, 132.4, 131.9, 130.6, 130.0, 128.9, 128.8, 128.3, 126.69, 126.66, 126.0, 125.2, 123.8, 122.2, 87.6, 85.7, 64.6, 21.1.

1-(Naphthalen-2-yl)-3-phenylprop-2-ynyl Acetate (1k)[6h]

Yield: 1.80 g (80%); yellow solid; mp 65–67 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1 H), 7.91–7.81 (m, 3 H), 7.71 (dd, *J* = 1.6, 8.4 Hz, 1 H), 7.54–7.46 (m, 4 H), 7.35–7.29 (m, 3 H), 6.88 (s, 1 H), 2.14 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.9, 134.5, 133.3, 133.1, 131.9, 128.9, 128.6, 128.3, 128.2, 127.8, 127.2, 126.7, 126.4, 125.1, 122.1, 87.4, 85.6, 66.4, 21.2.

1-Phenyloct-1-yn-3-yl Acetate (1l)[6h]

Yield: 1.47 g (85%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.42 (m, 2 H), 7.35–7.28 (m, 3 H), 5.61 (t, *J* = 6.8 Hz, 1 H), 2.12 (s, 3 H), 1.89–1.83 (m, 2 H), 1.55–1.47 (m, 2 H), 1.38–1.32 (m, 4 H), 0.95–0.89 (m, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.2, 131.8, 128.5, 128.3, 122.3, 86.7, 85.2, 64.6, 34.9, 31.4, 24.7, 22.5, 21.2, 14.0.

1-Phenyl-3-(trimethylsilyl)prop-2-ynyl Acetate (1m)[6h]

Yield: 1.51 g (82%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.51 (m, 2 H), 7.42–7.32 (m, 3 H), 6.48 (s, 1 H), 2.11 (s, 3 H), 0.21 (m, 9 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.7, 136.9, 128.9, 128.7, 127.8, 101.3, 92.5, 65.8, 21.2, –0.3.

1-(*p*-Tolyl)-3-(trimethylsilyl)prop-2-ynyl Acetate (1n)[6h]

Yield: 1.56 g (80%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.0 Hz, 2 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 6.44 (s, 1 H), 2.35 (s, 3 H), 2.09 (s, 3 H), 0.19 (s, 9 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.7, 138.9, 134.1, 129.4, 127.8, 101.4, 92.2, 65.7, 21.2, 21.1, –0.3.

1-(4-Chlorophenyl)-3-(trimethylsilyl)prop-2-ynyl Acetate (1o)[6h]

Yield: 1.52 g (72%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 6.45 (s, 1 H), 2.11 (s, 3 H), 0.21 (s, 9 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.6, 135.7, 134.8, 129.3, 128.8, 100.8, 92.8, 65.2, 21.2, –0.3.

1-(Naphthalen-2-yl)-3-(trimethylsilyl)prop-2-ynyl Acetate (1p)[6h]

Yield: 1.82 g (82%); white solid; mp 54–56 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 1 H), 7.88–7.81 (m, 3 H), 7.63–7.60 (m, 1 H), 7.51–7.45 (m, 2 H), 6.66 (s, 1 H), 2.12 (s, 3 H), 0.21 (s, 9 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.8, 134.3, 133.4, 132.9, 128.5, 128.3, 127.6, 127.3, 126.6, 126.4, 125.2, 101.3, 92.7, 66.1, 21.1, –0.3.

Propargyl Acetates 4a–s; General Procedure

n-BuLi (9.5 mL, 15.2 mmol, 1.6 M in hexane) was added to anhyd THF (30 mL) under an argon atmosphere and the flask was cooled to –78 °C. Then, the respective alkyne (12.2 mmol) was added dropwise and the mixture was stirred for 30 min at –78 °C. Subsequently, acetone (0.92 g, 1.16 mL, 15.85 mmol) or other corresponding ketone

(15.85 mmol) was added dropwise. The reaction mixture was stirred for 2 h at r.t. Then, Ac_2O (1.68 g, 1.56 mL, 16.5 mmol) was added dropwise at 0 °C. The mixture was stirred overnight at r.t. After completion of the reaction, sat. aq NH_4Cl (15 mL) was added and the mixture was extracted with Et_2O (3 × 15 mL). The combined Et_2O layers were washed with sat. aq $NaHCO_3$ (10 mL) and H_2O (10 mL), and dried (Na_2SO_4). The crude product was chromatographed on silica gel (EtOAc/hexane) to afford the corresponding propargyl acetate **4a–s**.

2-Methyl-4-phenylbut-3-yn-2-yl Acetate (4a)

Yield: 2.07 g (84%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.39 (m, 2 H), 7.25–7.23 (m, 3 H), 2.01 (s, 3 H), 1.73 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.1, 131.7, 128.3, 128.1, 122.6, 90.2, 83.9, 72.3, 28.9, 21.9.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{15}O_2^+$ (M + H)$^+$: 203.10666; found: 203.10670.

2-Methyl-4-(4-methylphenyl)but-3-yn-2-yl Acetate (4b)

Yield: 2.24 g (85%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8 Hz, 2 H), 7.07 (d, *J* = 8 Hz, 2 H), 2.31 (s, 3 H), 2.02 (s, 3 H), 1.73 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 138.4, 131.8, 129.0, 119.7, 89.6, 84.15, 72.6, 29.2, 22.1, 21.5.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{17}O_2^+$ (M + H)$^+$: 217.11503; found: 217.11492.

2-Methyl-4-(3-chlorophenyl)but-3-yn-2-yl Acetate (4c)

Yield: 2.45 g (85%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 1 H), 7.31–7.20 (m, 3 H), 2.04 (s, 3 H), 1.74 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.5, 134.2. 131.9, 130.1, 129.6, 128.8, 124.6, 91.7, 82.9, 72.4, 29.2, 22.2.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}ClO_2^+$ (M + H)$^+$: 237.06768; found: 237.06754.

2-Methyl-4-(3-fluorophenyl)but-3-yn-2-yl Acetate (4d)

Yield: 2.31 g (86%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.20 (m, 2 H), 7.18–7.13 (m, 1 H), 7.01–6.98 (m, 1 H), 2.03 (s, 3 H), 1.74 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.2, 163.5, 161.0, 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), 91.2, 82.8, 72.1, 28.9, 21.8.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}FO_2^+$ (M + H)$^+$: 221.09723; found: 221.09747.

2-Methyl-4-(2-fluorophenyl)but-3-yn-2-yl Acetate (4e)

Yield: 2.20 g (82%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 1 H), 7.28–7.24 (m, 1 H), 7.08–7.01 (m, 2 H), 2.05 (s, 3 H), 1.77 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 162.2 (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), 115.4 (d, *J* = 20.1 Hz), 111.3 (d, *J* = 15.5 Hz), 95.5 (d, *J* = 3 Hz), 77.6, 72.4, 29.0, 22.0.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}FO_2^+$ (M + H)$^+$: 221.09723; found: 221.09702.

2-Methyl-4-(3-bromophenyl)but-3-yn-2-yl Acetate (4f)

Yield: 2.71 g (79%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1 H), 7.41 (d, *J* = 2.6 Hz, 1 H), 7.33 (d, *J* = 2 Hz, 1 H), 7.15–7.12 (m, 1 H), 2.03 (s, 3 H), 1.73 (s, 6 H).

^{13}C{^{1}H} 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.

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 (4g)

Yield: 2.85 g (83%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8 Hz, 2 H), 7.22 (d, *J* = 8 Hz, 2 H), 2.01 (s, 3 H), 1.71 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.5, 131.9, 128.4, 128.3, 122.8, 90.3, 84.1, 72.6, 29.2, 22.2.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}BrO_2^+$ (M + H)$^+$: 281.01717; found: 281.01694.

2-Methyl-4-(4-fluorophenyl)but-3-yn-2-yl Acetate (4h)

Yield: 2.36 g (88%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 2 H), 7.00–6.96 (m, 2 H), 2.04 (s, 3 H), 1.74 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 162.5 (d, *J* = 247.9 Hz), 133.8 (d, *J* = 8.4Hz), 118.8 (d, *J* = 3.5 Hz), 115.5 (d, *J* = 22 Hz), 90.0, 83.0, 72.4, 29.1, 22.1.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}FO_2^+$ (M + H)$^+$: 221.09723; found: 221.09711.

2-Methyl-4-(2-thienyl)but-3-yn-2-yl Acetate (4i)

Yield: 2.11 g (83%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.17 (m, 2 H), 6.92–6.90 (m, 1 H), 2.00 (s, 3 H), 1.71 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.3, 132.4, 127.3, 125.9, 122.5, 94.0, 77.5, 72.4, 28.9, 22.0.

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{13}SO_2^+$ (M + H)$^+$: 209.06308; found: 209.06319.

3-Methyl-1-phenylpent-1-yn-3-yl Acetate (4j)

Yield: 2.11 g (80%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.42 (m, 2 H), 7.28–7.27 (m, 3 H), 2.34 (s, 3 H), 1.92 (q, *J* = 3.6 Hz, 2 H), 1.74 (s, 3 H), 1.07 (t, *J* = 3.6 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 131.9, 128.3, 128.2, 122.8, 89.3, 85.1, 76.2, 34.6, 26.1, 22.0, 8.8.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{15}O_2^+$ (M + H)$^+$: 217.12231; found: 217.12178.

3-Methyl-1-(3-fluorophenyl)pent-1-yn-3-yl Acetate (4k)

Yield: 2.49 g (87%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.15 (m, 2 H), 7.14–7.14 (m, 1 H), 7.12–6.97 (m, 1 H), 2.05 (s, 3 H), 1.92 (q, *J* = 3.6 Hz, 2 H), 1.73 (s, 3 H), 1.07 (t, *J* = 3.6 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 162.3 (d, *J* = 244.8 Hz), 129.8 (d, *J* = 8.6 Hz), 127.8 (d, *J* = 12 Hz), 124.7 (d, *J* = 9.4 Hz), 118.7 (d, *J* = 22.6 Hz), 115.7 (d, *J* = 21 Hz), 90.4, 83.9, 76.0, 34.6, 26.0, 21.9, 8.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}FO_2^+$ (M + H)$^+$: 235.11288; found: 235.11235.

3-Methyl-1-(3-chlorophenyl)pent-1-yn-3-yl Acetate (4l)

Yield: 2.39 g (78%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.39 (d, *J* = 4 Hz, 1 H), 7.32–7.16 (m, 3 H), 2.04 (s, 3 H), 2.02–1.99 (m, 1 H), 1.89 (q, *J* = 3.6 Hz, 2 H), 1.70 (s, 3 H), 1.05 (t, *J* = 1.8 Hz, 3 H).

^{13}C{^{1}H} 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.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}ClO_2^+$ (M + H)$^+$: 251.08333; found: 251.08340.

3-Methyl-1-(4-fluorophenyl)pent-1-yn-3-yl Acetate (4m)

Yield: 2.29 g (80%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.39 (m, 2 H), 6.99–6.95 (m, 2 H), 2.07–2.02 (m, 1 H), 2.03 (s, 3 H), 1.94–1.90 (m, 1 H), 1.73 (s, 3 H), 1.07 (t, *J* = 3 Hz, 3 H).

^{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), 89.0, 84.0, 76.1, 34.6, 26.1, 22.0, 8.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}FO_2^+$ (M + H)$^+$: 235.11288; found: 235.11250.

3-Methyl-1-(2-fluorophenyl)pent-1-yn-3-yl Acetate (4n)

Yield: 2.29 g (81%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 1 H), 7.30–7.24 (m, 1 H), 7.08–7.01 (m, 2 H), 2.10–2.03 (m, 1 H), 2.05 (s, 3 H), 1.97–1.90 (m, 1 H), 1.75 (s, 3 H), 1.10 (t, *J* = 2 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 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), 115.4 (d, *J* = 20.8 Hz), 111.4 (d, *J* = 15.6 Hz), 94.6 (d, *J* = 3.4 Hz), 78.6, 76.2, 34.6, 26.0, 22.0, 8.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}FO_2^+$ (M + H)$^+$: 235.11288; found: 235.11340.

3-Methyl-1-(3-bromophenyl)pent-1-yn-3-yl Acetate (4o)

Yield: 2.84 g (79%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.42 (m, 1 H), 7.36–7.18 (m, 3 H), 2.07 (s, 3 H), 2.04–2.00 (m, 1 H), 1.94–1.88 (m, 2 H), 1.73 (s, 3 H), 1.07 (t, *J* = 1.8 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.4, 134.1, 131.7, 130.0, 129.5, 128.6, 124.5, 90.6, 83.7, 76.0, 34.6, 26.0, 22.0, 8.8.

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)

Yield: 2.16 g (77%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 2 Hz, 2 H), 7.11 (d, *J* = 2 Hz, 2 H), 2.36 (s, 3 H), 2.12–2.06 (m, 1 H), 2.05 (s, 3 H), 1.99–1.92 (m, 1 H), 1.76 (s, 3 H), 1.11 (t, *J* = 1.8 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 168.5, 137.4, 130.8, 128.0, 118.8, 87.7, 84.2, 75.4, 33.7, 25.2, 21.1, 20.5, 7.8.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{19}O_2^+$ (M + H)$^+$: 231.13796; found: 231.13725.

2,4-Diphenylbut-3-yn-2-yl Acetate (4q)

Yield: 2.32 g (72%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.63 (m, 2 H), 7.52–7.50 (m, 2 H), 7.38–7.34 (m, 2 H), 7.31–7.28 (m, 4 H), 2.07 (s, 3 H), 1.97 (s, 3 H).

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{17}O_2^+$ (M + H)$^+$: 265.12231; found: 265.12219.

4-(4-Fluorophenyl)-2-phenylbut-3-yn-2-yl Acetate (4r)

Yield: 2.12 g (75%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.60 (m, 2 H), 7.52–7.50 (m, 2 H), 7.33–7.31 (m, 3 H), 7.06–7.02 (m, 2 H), 2.07 (s, 3 H), 1.96 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 168.7, 162.3 (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.

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 (4s)

Yield: 2.15 g (72%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.55 (m, 2 H), 7.52–7.49 (m, 2 H), 7.34–7.30 (m, 5 H), 2.07 (s, 3 H), 1.94 (s, 3 H).

^{13}C{^{1}H} 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.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{16}ClO_2^+$ (M + H)$^+$: 299.08333; found: 299.08298.

S_N2' Substitution Reaction of Propargyl Acetates with Trimethylaluminum; General Procedure

Under a dry argon atmosphere, a mixture of $Pd(PPh_3)_2Cl_2$ (0.0035 g, 0.005 mmol), PPh_3 (0.0026 g, 0.0100 mmol), and K_2CO_3 (0.138 g, 1.0 mmol) were stirred in THF (2 mL). Then, $AlMe_3$ (0.6 mmol) and propargyl acetate (0.50 mmol) were added, respectively. The mixture was stirred for 3–4 h at 60 °C. After completion of the reaction, sat. aq NH_4Cl (5 mL) was added and extracted with EtOAc (3 × 15 mL). The combined EtOAc layers was dried (Na_2SO_4), filtered, and evaporated under vacuum. The crude product was chromatographed on silica gel (hexane or EtOAc and hexane) to afford the corresponding allene product **2** or **5**.

1,3-Diphenylbuta-1,2-diene (2a)[6h]

Yield: 0.088 g (85%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.43 (m, 2 H), 7.35–7.30 (m, 6 H), 7.24–7.16 (m, 2 H), 6.47 (q, *J* = 2.8 Hz, 1 H), 2.22 (d, *J* = 2.8 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 206.8, 136.3, 134.5, 128.7, 128.5, 127.03, 127.02, 126.9, 125.8, 104.5, 96.6, 16.8.

1-(2-Methylphenyl)-3-phenylbuta-1,2-diene (2b)[6h]

Yield: 0.089 g (81%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.6 Hz, 2 H), 7.37–7.31 (m, 3 H), 7.25–7.21 (m, 1 H), 7.17–7.11 (m, 3 H), 6.67 (q, *J* = 3.2 Hz, 1 H), 2.40 (s, 3 H), 2.23 (d, *J* = 3.2 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 207.4, 136.6, 135.3, 132.7, 130.7, 128.4, 127.5, 126.95, 126.90, 126.2, 125.8, 103.5, 94.1, 20.0, 16.9.

1-(3-Methylphenyl)-3-phenylbuta-1,2-diene (2c)[6h]

Yield: 0.095 g (87%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.0 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 2 H), 7.23 (dd, *J* = 8.4, 16.4 Hz, 2 H), 7.20–7.12 (m, 2 H), 7.02 (d, *J* = 7.2 Hz, 1 H), 6.44 (q, *J* = 2.8 Hz, 1 H), 2.32 (s, 3 H), 2.23 (d, *J* = 2.8 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 206.8, 138.3, 136.4, 134.4, 128.6, 128.4, 127.9, 127.5, 127.0, 125.8, 124.1, 104.3, 96.6, 21.4, 16.8.

1-(4-Methylphenyl)-3-phenylbuta-1,2-diene (2d)[6h]

Yield: 0.091 g (83%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.44 (m, 2 H), 7.34–7.30 (m, 2 H), 7.25–7.21 (m, 3 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 6.46 (q, *J* = 2.8 Hz, 1 H), 2.33 (s, 3 H), 2.21 (d, *J* = 2.8 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 206.5, 136.7, 136.5, 131.6, 129.5, 128.4, 126.9, 126.8, 125.8, 104.4, 96.4, 21.2, 16.8.

1-(2-Methoxyphenyl)-3-phenylbuta-1,2-diene (2e)[6h]

Yield: 0.093 g (79%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.45 (m, 2 H), 7.38–7.30 (m, 3 H), 7.24–7.18 (m, 2 H), 6.90–6.86 (m, 3 H), 3.86 (s, 3 H), 2.22 (d, *J* = 3.3 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 207.2, 156.1, 136.6, 128.4, 128.1, 127.8, 126.8, 125.7, 122.8, 120.7, 111.0, 103.7, 90.5, 55.6, 16.8.

1-(2-Chlorophenyl)-3-phenylbuta-1,2-diene (2f)[6h]

Yield: 0.106 g (88%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.41 (m, 3 H), 7.37–7.32 (m, 3 H), 7.26–7.22 (m, 1 H), 7.18–7.11 (m, 2 H), 6.91 (q, *J* = 2.8 Hz, 1 H), 2.23 (d, *J* = 2.6 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 207.8, 135.9, 132.2, 129.8, 128.5, 128.4, 128.0, 127.2, 126.8, 125.8, 104.8, 93.0, 16.6.

1-(4-Chlorophenyl)-3-phenylbuta-1,2-diene (2g)[6h]

Yield: 0.105 g (87%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.43 (m, 2 H), 7.35–7.32 (m, 2 H), 7.30–7.22 (m, 5 H), 6.44 (q, *J* = 2.6 Hz, 1 H), 2.22 (d, *J* = 2.6 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 206.9, 136.0, 133.1, 132.6, 128.8, 128.5, 128.0, 127.2, 125.8, 105.0, 95.7, 16.7.

1-(4-Bromophenyl)-3-phenylbuta-1,2-diene (2h)

Yield: 0.125 g (88%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.43 (m, 2 H), 7.35–7.32 (m, 2 H), 7.30–7.22 (m, 5 H), 6.44 (q, *J* = 2.7 Hz, 1 H), 2.24 (d, *J* = 2.6 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 206.9, 136.0, 133.1, 132.6, 128.8, 128.5, 128.0, 127.2, 125.8, 105.0, 95.7, 16.7.

1-(4-Trifluoromethylphenyl)-3-phenylbuta-1,2-diene (2i)[6h]

Yield: 0.114 g (83%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.52 (m, 2 H), 7.45–7.39 (m, 4 H), 7.36–7.32 (m, 2 H), 7.25–7.21 (m, 1 H), 6.51 (q, *J* = 3.3 Hz, 1 H), 2.24 (d, *J* = 3.4 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 207.8, 138.5, 135.7, 128.9 (q, *J* = 32.5 Hz), 128.6, 127.4, 127.0, 125.9, 125.6 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 270 Hz), 105.3, 95.8, 16.6.

1-(Naphthylen-1-yl)-3-phenylbuta-1,2-diene (2j)[6h]

Yield: 0.103 g (80%); yellow solid; mp 39–41 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.8 Hz, 1 H), 7.78–7.86 (m, 1 H), 7.74 (d, *J* = 8.2 Hz, 1 H), 7.56 (d, *J* = 6.6 Hz, 1 H), 7.51–7.43 (m, 4 H), 7.42 (t, *J* = 7.8 Hz, 1 H), 7.36 (t, *J* = 7.8 Hz, 2 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 7.21 (q, *J* = 3.0 Hz, 1 H), 2.27 (d, *J* = 2.6 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 208.2, 136.4, 134.0, 130.9, 130.6, 128.7, 128.5, 127.6, 127.0, 126.2, 125.9, 125.73, 125.68, 125.6, 122.7, 103.4, 93.4, 16.9.

1-(Naphthylen-2-yl)-3-phenylbuta-1,2-diene (2k)[6h]

Yield: 0.10 g (78%); yellow solid; mp 40–42 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.70 (m, 4 H), 7.52–7.50 (m, 3 H), 7.48–7.42 (m, 2 H), 7.36–7.32 (m, 2 H), 7.25–7.22 (m, 1 H), 6.66 (q, *J* = 2.6 Hz, 1 H), 2.27 (d, *J* = 2.6 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 207.4, 136.3, 133.7, 132.7, 132.0, 128.5, 128.3, 127.69, 127.68, 127.1, 126.2, 125.9, 125.63, 125.62, 124.8, 104.7, 96.9, 16.8.

2-Phenylnona-2,3-diene (2l)[6h]

Yield: 0.077 g (83%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2 H), 7.33–7.25 (m, 2 H), 7.19–7.16 (m, 1 H), 5.46–5.41 (m, 1 H), 2.13–2.10 (m, 2 H), 2.08 (d, *J* = 2.6 Hz, 3 H), 1.54–1.43 (m, 2 H), 1.37–1.28 (m, 4 H), 0.89 (t, *J* = 7.4 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 204.1, 137.8, 128.2, 126.2, 125.6, 100.2, 93.1, 31.4, 28.93, 28.88, 22.5, 17.2, 14.1.

Phenyl-3-trimethylsilylbuta-1,2-diene (2m)[6h]

Yield: 0.089 g (88%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.20 (m, 4 H), 7.14–7.10 (m, 1 H), 5.82 (q, *J* = 2.7 Hz, 1 H), 1.80 (d, *J* = 2.6 Hz, 3 H), 0.15 (s, 9 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 205.6, 136.1, 128.5, 125.9, 125.7, 95.5, 88.3, 15.1, –1.7.

1-(4-Methylphenyl)-3-trimethylsilylbuta-1,2-diene (2n)[6h]

Yield: 0.088 g (81%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12–7.07 (m, 4 H), 5.80 (q, *J* = 3.0 Hz, 1 H), 2.32 (s, 3 H), 1.81 (d, *J* = 3.3 Hz, 3 H), 0.14 (s, 9 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 205.6, 135.4, 133.0, 129.2, 125.8, 95.4, 88.1, 21.1, 15.2, –1.7.

1-(4-Chlorophenyl)-3-trimethylsilylbuta-1,2-diene (2o)[6h]

Yield: 0.103 g (87%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.20 (m, 2 H), 7.14–7.11 (m, 2 H), 5.77 (q, *J* = 3.0 Hz, 1 H), 1.82 (d, *J* = 2.7 Hz, 3 H), 0.13 (s, 9 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 205.4, 134.7, 131.1, 128.6, 127.0, 96.0, 87.5, 15.0, –1.8.

3-(Naphthalen-2-yl)-3-trimethylsilylbuta-1,2-diene (2p)[6h]

Yield. 0.099 g (79%); white solid; mp 41–43 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.72 (m, 3 H), 7.57 (s, 1 H), 7.45–7.35 (m, 3 H), 6.00 (q, *J* = 2.7 Hz, 1 H), 1.85 (d, *J* = 2.7 Hz, 3 H), 0.18 (s, 9 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 206.1, 133.8, 133.7, 132.1, 128.0, 127.6, 127.4, 126.0, 125.0, 124.4, 124.0, 95.7, 88.8, 15.2, –1.7.

1-(4-Methylpenta-2,3-dien-2-yl)benzene (1,1,3-Trimethyl-3-phenylallene, 5a)

Yield: 0.068 g (85%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.71 (m, 3 H), 7.56 (s, 1 H), 7.42–7.36 (m, 3 H), 6.00 (q, *J* = 2.7 Hz, 1 H), 1.85 (d, *J* = 2.7 Hz, 3 H), 0.17 (s, 9 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 202.1, 138.7, 128.2, 126.1, 125.8, 98.1, 96.9, 20.5, 17.4.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{15}^+$ (M + H)$^+$: 159.11683; found: 159.11682.

1-Methyl-4-(4-methylpenta-2,3-dien-2-yl)benzene (5b)

Yield: 0.077 g (89%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 2 H), 7.18–7.14 (m, 2 H), 2.38 (s, 3 H), 2.09 (s, 3 H), 1.84 (s, 6 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 201.8, 135.9, 135.8, 129.0, 125.7, 98.0, 96.8, 21.2, 20.6, 17.5.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{17}^+$ (M + H)$^+$: 173.12520; found: 173.12508.

1-Chloro-3-(4-methylpenta-2,3-dien-2-yl)benzene (5c)

Yield: 0.091 g (94%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 1 H), 7.22–7.17 (m, 2 H), 7.14–7.11 (m, 1 H), 2.02 (s, 3 H), 1.79 (s, 6 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 202.3, 141.0, 134.3, 129.4, 126.1, 125.9, 123.9, 97.7, 97.4, 20.4, 17.3.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{14}Cl^+$ (M + H)$^+$: 193.07785; found: 193.07784.

1-Fluoro-3-(4-methylpenta-2,3-dien-2-yl)benzene (5d)

Yield: 0.086 g (94%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.22 (m, 1 H), 7.14–7.12 (d, *J* = 8.1 Hz, 1 H), 7.06–7.03 (d, *J* = 12.0 Hz, 1 H), 6.88–6.83 (m, 1 H), 2.03 (s, 3 H), 1.79 (s, 6 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 201.7, 164.5, 162.1, 141.8 (d, *J* = 7.4 Hz), 129.6 (d, *J* = 8.3 Hz), 121.3 (d, *J* = 2.6 Hz), 112.7 (q, *J* = 38.6 Hz), 104.1, 99.7, 22.6, 18.9.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{14}F^+$ (M + H)$^+$: 177.10741; found: 177.10742.

1-Fluoro-2-(4-methylpenta-2,3-dien-2-yl)benzene (5e)

Yield: 0.079 g (90%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.11 (m, 1 H), 7.02–6.99 (m, 1 H), 6.88–6.83 (m, 2 H), 1.94 (s, 3 H), 1.63 (s, 6 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 203.7 (d, *J* = 1.5 Hz), 160.4 (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), 116.1 (d, *J* = 22.7 Hz), 95.1 (d, *J* = 1.5 Hz), 93.8, 20.6, 19.5.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{14}F^+$ (M + H)$^+$: 177.10741; found: 177.10725.

1-Bromo-3-(4-methylpenta-2,3-dien-2-yl)benzene (5f)

Yield: 0.101 g (86%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 2 H), 7.29–7.26 (m, 2 H), 2.05 (s, 3 H), 1.84 (s, 6 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 202.1, 138.8, 137.8, 128.3, 127.0, 125.8, 123.0, 98.2, 96.8, 20.5, 17.4.

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 (5g)

Yield: 0.11 g (93%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 2 H), 7.29–7.26 (m, 2 H), 2.05 (s, 3 H), 1.75 (s, 6 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 202.1, 138.9, 128.3, 125.8, 122.8, 98.2, 97.0, 20.6, 17.4.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{14}Br^+$ (M + H)$^+$: 237.02734; found: 237.02730.

1-Fluoro-4-(4-methylpenta-2,3-dien-2-yl)benzene (5h)

Yield: 0.086 g (94%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.29 (m, 2 H), 6.99–6.95 (m, 2 H), 2.02 (s, 3 H), 1.78 (s, 6 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 201.8 (d, *J* = 2 Hz), 162.8, 160.3, 134.7 (d, *J* = 3.1 Hz), 127.2 (d, *J* = 7.8 Hz), 115.0 (d, *J* = 21.3 Hz), 97.3, 97.2, 20.5, 17.5.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{14}F^+$ (M + H)$^+$: 177.10741; found: 177.10733.

2-(4-Methylpenta-2,3-dien-2-yl)thiophene (5i)

Yield: 0.072 g (88%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12–7.10 (m, 1 H), 6.95–6.93 (m, 1 H), 2.04 (s, 3 H), 1.78 (s, 6 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 201.1, 145.1, 127.5, 124.0 122.4, 98.0, 99.4, 20.6, 178.3.

HRMS (ESI): *m*/*z* calcd for $C_{10}H_{13}S^+$ (M + H)$^+$: 165.07325; found: 165.07307.

1-(4-Methylhexa-2,3-dien-2-yl)benzene (5j)

Yield: 0.071 g (83%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.39 (m, 2 H), 7.33–7.28 (m, 2 H), 7.19–7.18 (m, 1 H), 2.07 (s, 6 H), 1.81 (s, 2 H), 1.07–1.03 (m, 3 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 201.1, 138.8, 128.1, 126.0, 125.5, 103.2, 99.9, 27.4, 18.8, 17.4, 12.3.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{17}^+$ (M + H)$^+$: 173.13248; found: 173.13249.

1-Fluoro-3-(3-methylhexa-2,3-dien-2-yl)benzene (5k)

Yield: 0.082 g (86%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.20 (m, 1 H), 7.14 (d, *J* = 8 Hz, 1 H), 7.08–7.05 (m, 1 H), 6.87–6.82 (m, 1 H), 2.11–2.05 (m, 2 H), 2.03 (s, 3 H), 1.79 (s, 3 H), 1.03 (t, *J* = 4 Hz, 3 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 201.6, 164.5, 162.0, 141.7 (d, *J* = 7.2 Hz), 129.6 (d, *J* = 8.2 Hz), 121.2 (d, *J* = 2.6 Hz), 112.6 (q, *J* = 38.6 Hz), 104.0, 99.6 (d, *J* = 2.5 Hz), 27.6, 18.9, 17.4, 12.4.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}F^+$ (M + H)$^+$: 191.12306; found: 191.12244.

1-Chloro-3-(4-methylhexa-2,3-dien-2-yl)benzene (5l)

Yield: 0.095 g (92%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 1 H), 7.23–7.19 (m, 2 H), 7.14–7.12 (m, 1 H), 2.10–2.06 (m, 2 H), 2.04 (s, 3 H), 1.79 (s, 3 H), 1.03 (t, *J* = 3 Hz, 3 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 201.6, 141.1, 134.3, 129.4, 126.1, 125.7, 123.8, 104.1, 99.4, 27.5, 18.9, 17.4, 12.4.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}Cl^+$ (M + H)$^+$: 207.09350; found: 207.09361.

1-Fluoro-4-(4-methylhexa-2,3-dien-2-yl)benzene (5m)

Yield: 0.088 g (93%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.31 (m, 2 H), 7.00–6.95 (m, 2 H), 2.12–2.08 (m, 2 H), 2.05 (s, 3 H), 1.78 (s, 3 H), 1.03 (t, *J* = 3 Hz, 3 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 201.0, 161.6 (d, *J* = 243.5 Hz), 127.1 (d, *J* = 7.8 Hz), 115.2, 115.0, 103.7, 99.4, 27.6, 19.1, 17.8, 12.5.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}F^+$ (M + H)$^+$: 191.12306; found: 191.12381.

1-Fluoro-2-(4-methylhexa-2,3-dien-2-yl)benzene (5n)

Yield: 0.086 g (90%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.27 (m, 1 H), 7.15–7.12 (m, 1 H), 7.08–6.97 (m, 2 H), 2.11 (s, 3 H), 2.06–2.01 (m, 2 H), 1.77 (s, 3 H), 1.06 (t, *J* = 4 Hz, 3 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 202.9 (d, *J* = 1.7 Hz), 160.4 (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), 116.1 (d, *J* = 22.7 Hz), 101.4 (d, *J* = 1.3 Hz), 95.8, 27.5, 19.6, 19.0, 12.3.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}F^+$ (M + H)$^+$: 191.12306; found: 191.12286.

1-Bromo-3-(4-methylhexa-2,3-dien-2-yl)benzene (5o)

Yield: 0.109 g (87%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.40 (m, 1 H), 7.34–7.30 (m, 1 H), 7.24–7.21(m, 1 H), 7.18–7.01 (m, 1 H), 2.11–2.09 (m, 2 H), 2.08 (s, 3 H), 1.81 (s, 3 H), 1.06 (t, *J* = 4 Hz, 3 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 201.3, 142.8, 139.4, 128.3, 128.2, 125.7, 123.0, 103.2, 100.2, 27.6, 19.0, 17.6, 12.4.

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)

Yield: 0.078 g (84%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 2 Hz, 2 H), 7.10 (d, *J* = 2 Hz, 2 H), 2.32 (s, 3 H), 2.05 (s, 3 H), 2.07–2.03 (m, 2 H), 1.77 (s, 3 H), 1.03 (t, *J* = 1.8 Hz, 3 H).

^{13}C {^{1}H} 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.

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

2,4-Diphenylpenta-2,3-diene (5q)

Yield: 0.083 g (75%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.42 (m, 4 H), 7.33–7.29 (m, 4 H), 7.21–7.18 (m, 2 H), 2.19 (s, 6 H).

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{17}^+$ (M + H)$^+$: 221.13248; found: 221.13303.

2-Phenyl-4-(4-fluorophenyl)penta-2,3-diene (5r)

Yield: 0.095 g (80%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.41 (m, 1 H), 7.40–7.39 (m, 1 H), 7.38–7.35 (m, 2 H), 7.33–7.29 (m, 2 H), 7.23–7.18 (m, 1 H), 7.01–6.96 (m, 2 H), 2.19 (s, 3 H), 2.17 (s, 3 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 205.6 (d, *J* = 2.1 Hz), 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* = 21.4 Hz), 102.7, 101.7, 17.1, 17.0.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{16}F^+$ (M + H)$^+$: 239.12306; found: 239.12309.

2-Phenyl-4-(4-chlorophenyl)penta-2,3-diene (5s)

Yield: 0.103 g (81%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2 H), 7.35–7.33 (m, 3 H), 7.32–7.30 (m, 1 H), 7.29–7.27 (m, 1 H), 7.24–7.21 (m, 1 H), 2.20 (s, 3 H), 2.18 (s, 3 H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 205.9, 137.0, 135.9, 132.6, 128.64, 128.61, 127.2, 127.0, 126.0, 103.0, 101.8, 16.94, 16.89.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{16}Cl^+$ (M + H)$^+$: 255.09350; found: 255.09341.

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