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Iron-Catalyzed Synthesis of β-Chlorovinyl and α,β-Alkynyl Ketones from Terminal and Silylated Alkynes with Acid Chlorides

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Abstract: A simple efficient method for the iron-(III)-catalyzed synthesis of substituted β-chlorovinyl ketones and α,β-alkynyl ketones from terminal and silyl-substituted alkynes with acid chlorides, respectively, is described. This method features easily available starting materials, a cheap and non-toxic catalyst, simple manipulation and mild reaction conditions. Evidence shows that the catalytic addition of the acid chloride to a terminal alkyne to give (*Z*)-β-chlorovinyl ketones favours a concerted pathway *via* a four-membered ring transition state between the two alkyne carbons and the carbon-chloride bond of the acid chloride.

Keywords: acid chlorides; alkynes; α,β-alkynyl ketones; β-chlorovinyl ketones; iron

Introduction

β-Chloroalkenyl ketones are valuable and versatile synthetic intermediates for the synthesis of various novel heterocyclic compounds.[1] Traditional approaches to these compounds involved Friedel–Crafts addition of acid chlorides to alkynes in the presence of stoichiometric amounts of Lewis acids.[2] Recently, metal-catalyzed addition of acid chlorides to alkynes has become a prevailing method for the synthesis of substituted β-chloroalkenyl ketones. In this context, Tanaka et el. reported a series of rhodium-catalyzed addition reactions of chloroformate esters,[3a] perfluorinated acid chlorides,[3b] ethyl chloroglyoxylate,[3c] chloroacetyl chlorides,[3d] and α-keto acid chlorides[3e] to terminal alkynes. Recently, Tsuji and co-workers described an IrCl(cod)(IPr)-catalyzed addition of aromatic acid chlorides to terminal alkynes to form β-chloro-α,β-unsaturated ketones.[4] These rhodium- and iridium-catalyzed β-chloroacylations of alkynes are generally considered to proceed *via* oxidative addition of acyl chloride to metal complexes followed by addition to the alkyne. Another type of β-chloroacylation of alkynes is the Lewis acid-catalyzed addition of acyl chloride to alkyne. Apart from the earlier Lewis acid-catalyzed addition pathway,[2] in 2006, Zhou and co-workers reported a $GaCl_3$-catalyzed synthesis of β-chloroalkenyl ketones from terminal alkynes and acid chlorides.[5] However this reaction proceeds with lower stereoselectivity. Recently, Wang et al. showed an $FeBr_2$-catalyzed synthesis of β-chloroalkenyl ketones by the addition of acid chlorides to terminal alkynes at high temperature (110 °C).[6a] Later, Sarvari and Mardanesh demonstrated a ZnO-catalyzed formation of β-chloroalkenyl ketones under solvent-free conditions.[6b] The methods described above for synthesizing β-chloroalkenyl ketones generally required a long reaction time, an expensive catalyst or relatively harsh reaction conditions. In addition, several research groups have reported facile decarbonylative additions of acid chlorides to terminal alkynes[7a] and alkenes.[7b] Our continued interest in metal-catalyzed addition reactions[8a–e] and the coupling of acid chlorides[8f–h] prompted us to explore the possibility of using low-cost and non-toxic iron complexes as catalysts for the addition reactions. Herein, we wish to report a convenient $FeCl_3$-catalyzed regio- and stereoselective synthesis of substituted β-chloroalkenyl ketones from acid chlorides and terminal alkynes under mild reaction conditions.

Results and Discussion

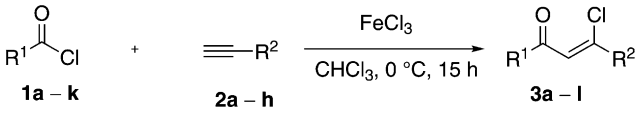
Treatment of 4-methoxybenzoyl chloride (**1a**) with phenylacetylene (**2a**) in the presence of 10 mol% $FeCl_3$ in $CHCl_3$ at 0 °C for 15 h gave the substituted β-chloroalkenyl ketone **3a** in 90% isolated yield with excellent regio- and stereoselectivity ($Z/E > 99/1$) (Table 1, entry 1). Product **3a** was thoroughly characterized by its ^1H NMR, ^{13}C NMR and mass spectroscopic data.

To evaluate the effect of the catalyst on the β-chloroalkenyl ketone formation reaction, various iron salts were used for the reaction of **1a** with **2a** in $CHCl_3$. Among those iron salts used, $FeCl_3$ gave the best results and afforded **3a** in 90% yield. Other iron salts including $FeCl_3 \cdot 6H_2O$, $Fe(acac)_3$, $Fe(ClO_4)_3$, $FeSO_4 \cdot 7H_2O$, $FeBr_2$, $FeCl_2$, and $Fe(OAc)_2$, are less effective giving **3a** in 23, 36, 17, 12, 15, 20 and 8% yields, respectively. The solvent employed is also vital to the catalytic reaction. The best solvent is $CHCl_3$ in which **3a** was obtained in 90% yield. 1,2-Dichloroethane is also effective giving **3a** in 53% yield. Other solvents including dichloromethane, toluene, CH_3CN, THF and benzene are less effective for the catalytic reaction (see the Supporting Information for details). It is important to mention that control experiments showed that in the absence of an iron salt, no desired product **3a** was obtained.

Under similar reaction conditions, various substituted acid chlorides (**1b–k**) reacted smoothly with phenylacetylene (**2a**) to give the corresponding β-chloroalkenyl ketones. Benzoyl chloride **1b** underwent the chloroacylation reaction effectively with **2a**, affording β-chloroalkenyl ketone derivative **3b** in 81% yield (Table 1, entry 2). Notably, all *ortho-*, *meta-,* and *para*-methylbenzoyl chlorides **1c**, **1d** and **1e** could be smoothly transformed in to desired products **3c**, **3d** and **3e** in 68, 74 and 84% yields, respectively (entries 3–5). In a similar manner, 2-fluoro-, 4-fluoro- and 4-bromobenzoyl chlorides **1f**, **1g** and **1h** gave chlorovinyl ketone derivatives **3f**, **3g** and **3h** in 74, 68 and 81% yields, respectively (entries 6–8). The scope of the catalytic reaction can further be extended to a heterocyclic acid chloride. Thus, thiophene-2-carbonyl chloride (**1i**) reacted with **2a** to give **3i** in 83% yield (entry 9). Aliphatic acid chlorides also worked well for this reaction. Thus, pentanoyl chloride (**1j**) and isobutyryl chloride (**1k**) reacted nicely with **2a** to give **3j** and **3k** in 79 and 85% yields, respectively (entries 10 and 11).

The present iron-catalyzed chloroacylation reaction can also apply to various terminal alkynes **2b–h**. Thus, the reactions of 2-methyl-, 3-methyl-, 4-methyl- and 4-chlorophenylacetylene **2b–e** with **1b** gave β-chloroalkenyl ketones **3l–o** in 70, 76, 71 and 83% yields, respectively (Table 1, entries 12–15). In a similar manner, 1-pentyne (**2f**) and 1-decyne (**2g**) reacted

Table 1. Results of the reaction of acid chlorides with terminal alkynes.[a]



1a – k **2a – h** **3a – l**

1a: R^1 = 4-MeO-C_6H_4 **2a**: R^2 = Ph
1b: R^1 = Ph **2b**: R^2 = 2-Me-C_6H_4
1c: R^1 = 2-Me-C_6H_4 **2c**: R^2 = 3-Me-C_6H_4
1d: R^1 = 3-Me-C_6H_4 **2d**: R^2 = 4-Me-C_6H_4
1e: R^1 = 4-Me-C_6H_4 **2e**: R^2 = 4-Cl-C_6H_4
1f: R^1 = 2-F-C_6H_4 **2f**: $R^2 = (CH_2)_3$-CH_3
1g: R^1 = 4-F-C_6H_4 **2g**: $R^2 = (CH_2)_7$-CH_3
1h: R^1 = 4-Br-C_6H_4
1i: R^1 = 2-thienyl **2h**:
1j: $R^1 = (CH_2)_3$-CH_3
1k: $R^1 = CH(CH_3)_2$

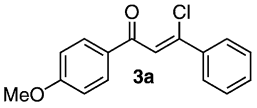
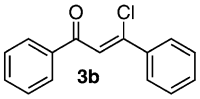
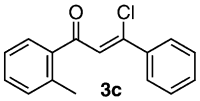
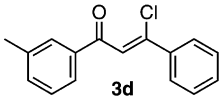
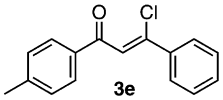
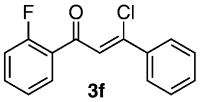
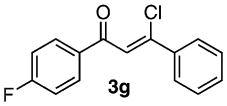
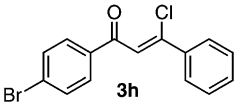
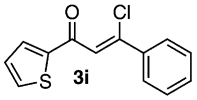
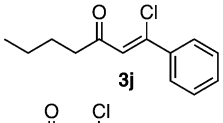
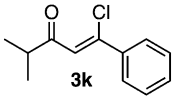
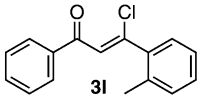
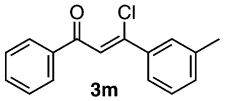
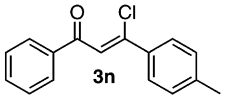
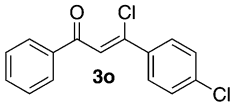
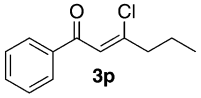
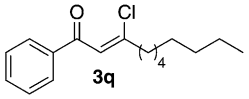
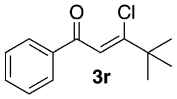
Entry	1	2	Product 3	Yield [%][b] (Z/E)[c]
1	**1a**	**2a**	 **3a**	90 (> 99/1)
2	**1b**	**2a**	 **3b**	81 (98/2)
3	**1c**	**2a**	 **3c**	68 (98/2)
4	**1d**	**2a**	 **3d**	74 (98/2)
5	**1e**	**2a**	 **3e**	84 (99/1)
6	**1f**	**2a**	 **3f**	74 (99/1)
7	**1g**	**2a**	 **3g**	68 (99/1)
8	**1h**	**2a**	 **3h**	81 (99/1)
9	**1i**	**2a**	 **3i**	83 (99/1)
10	**1j**	**2a**	 **3j**	79 (97/3)
11	**1k**	**2a**	 **3k**	85 (98/2)

Table 1. (Continued)

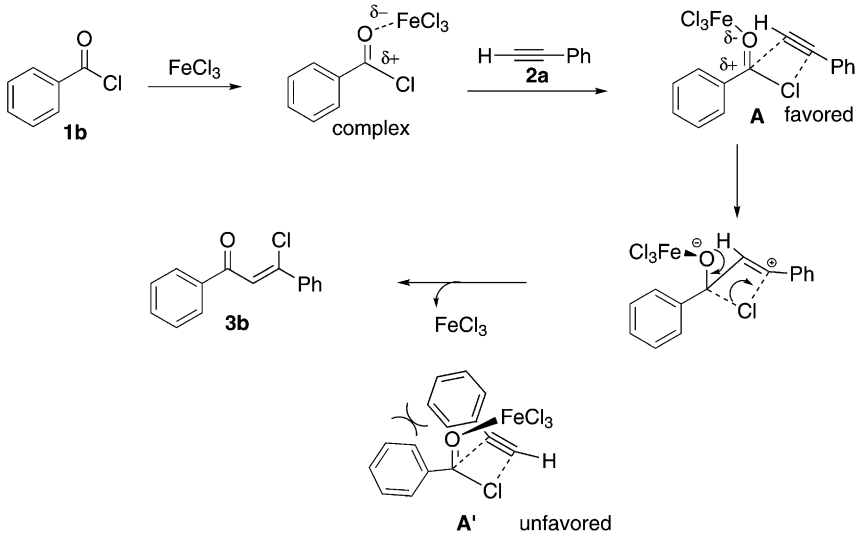
Entry	1	2	Product 3	Yield [%][b] (*Z*/*E*)[c]
12	**1b**	**2b**	 **3l**	70 (97/3)
13	**1b**	**2c**	 **3m**	76 (99/1)
14	**1b**	**2d**	 **3n**	71 (99/1)
15	**1b**	**2e**	 **3o**	83 (99/1)
16	**1b**	**2f**	 **3p**	82 (99/1)
17	**1b**	**2g**	 **3q**	76 (97/3)
18	**1b**	**2h**	 **3r**	76 (99/1)

[a] Unless otherwise mentioned, all reactions were carried out with acid chloride **1** (1.0 mmol), alkyne **2** (1.5 mmol), $FeCl_3$ (10 mol%) and $CHCl_3$ (2.0 mL) at 0 °C for 15 h under N_2.
[b] Isolated yields.
[c] Determined by ^1H NMR spectroscopy.

with **1b** to afford products **3p** and **3q** in 82 and 76% yields, respectively (entries 16 and 17). Sterically more demanded *tert*-butylacetylene (**2h**) also reacted well with **1b** to provide the expected β-chloroalkenyl ketone derivative **3r** in 76% yield (entry 18).

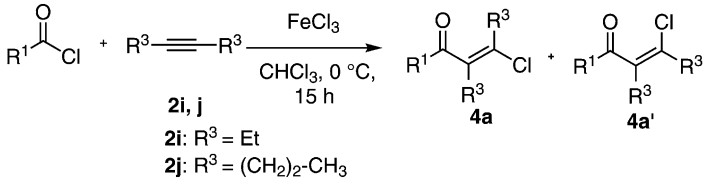
The catalytic chloroacylation reaction was successfully extended to internal alkynes with various acid chlorides (Scheme 1). Thus, treatment of hex-3-yne with 4-methoxybenzoyl chloride (**1a**) gave the corresponding β-chloroalkenyl ketone **4a** in 89% yield with excellent regio- and stereoselectivity. In contrast to the observed stereochemistry of the chloroacylation of terminal alkynes, the acyl and the chloro groups in product **4a** are *trans* to each other with an *E*/*Z* ratio >99/1. Other acid chlorides **1b**, **1g**, **1h** and **1i** also reacted efficiently with hex-3-yne to give the corresponding addition products **4b–e** in good to excellent yields, but with lower stereoselectivity (Scheme 1). The major species in these reactions are also *E* isomers. In a similar manner, symmetrically substituted octa-4-yne reacted smoothly with acid chlorides **1a**, **lb**, **1g**, **1h** and **1i** under similar reaction conditions to provide chloroacylation products **3s–w** in good to excellent yields with similar *E*/*Z* ratios as those of products **4f–j**. It is noteworthy that diphenylacetylene does not react with acid chloride **1a** to give the expected chloroacylation product. The reaction is likely prohibited by the large steric repulsion arising from the two phenyl, acyl and chloro groups during the formation of the expected product.

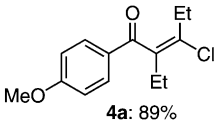
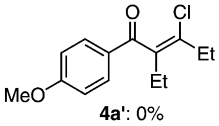
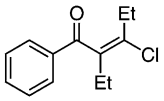
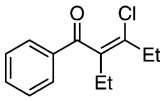
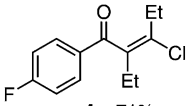
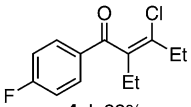
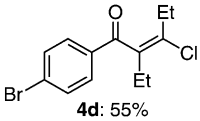
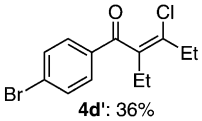
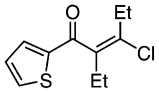
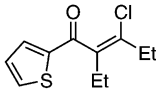
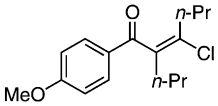
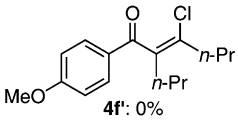
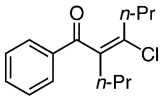
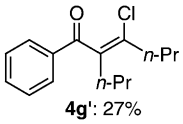
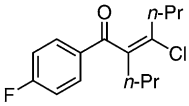
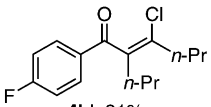
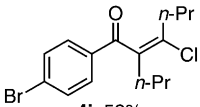
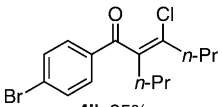
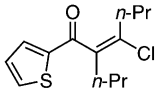
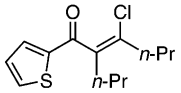
The reaction of acyl chlorides with alkynylsilanes catalyzed by $FeCl_3$ was also investigated. Surprisingly, the reaction of acid chloride (**1a**) with 1-phenyl-2-(trimethylsilyl)acetylene (**2k**) under reaction conditions similar to those shown in Table 1 gave **3a** in 24% yield along with α,β-alkynyl ketone **5a** in 67% (Table 2, entry 1). To improve the yield of **5a**, various solvents were tried (see the Supporting Information for details). The use of CH_3NO_2 gave **5a** in 78% yield along with **3a** in 9% yield. Finally when temperature



Scheme 1. Proposed mechanism for the addition of acid chlorides to terminal alkynes.

Table 2. Chloroacylation of various acid chlorides with 3-hexyne and 4-octyne.



Entry	1	2	Product **4**: yield [%][b]	Product **4′**: yield [%][b]
1	**1a**	**2i**	 **4a**: 89%	 **4a'**: 0%
2	**1b**	**2i**	 **4b**: 64%	 **4b'**: 28%
3	**1g**	**2i**	 **4c**: 71%	 **4c'**: 23%
4	**1h**	**2i**	 **4d**: 55%	 **4d'**: 36%
5	**1i**	**2i**	 **4e**: 71%	 **4e'**: 18%
6	**1a**	**2j**	 **4f**: 83%	 **4f'**: 0%
7	**1b**	**2j**	 **4g**: 64%	 **4g'**: 27%
8	**1g**	**2j**	 **4h**: 57%	 **4h'**: 31%
9	**1h**	**2j**	 **4i**: 52%	 **4i'**: 35%
10	**1i**	**2j**	 **4j**: 72%	 **4j'**: 18%

[a] Unless otherwise mentioned, all reactions were carried out with acid chloride **1** (1.0 mmol), alkyne **2** (1.5 mmol), $FeCl_3$ (10 mol%) and $CHCl_3$ (2.0 mL) at 0 °C for 15 h under N_2.
[b] Isolated yields.

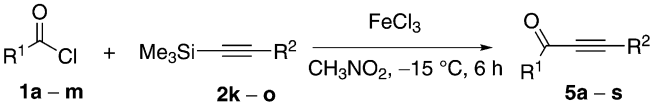
was reduced to −15 °C from 0 °C the reaction gave **5a** exclusively in 89% yield as determined by an NMR integration method (Table 2, entry 8) or 80% isolated yield. It is interesting to note that alkynyl ketones are contained in several biologically active molecules[9a] and play a crucial role as key intermediates in the synthesis of natural products[9b–e] and heterocyclic compounds.[9f–o] Various methods for the synthesis of

alkynyl ketones were reported including an equimolar $AlCl_3$-mediated reaction of alkynylsilanes with acid chlorides in CS_2,[10] alkynones have been typically synthesised by transition metal-catalyzed cross-coupling reactions of acid chlorides and terminal alkynes.[11] Alternatively, the cross-couplings of acid chlorides with the corresponding organometallic reagents and carbonylative coupling reactions have attracted much attention.[12] To the best of our knowledge, there is no known example using low-cost transition metal complexes as catalyst for the coupling of acid chlorides with alkynylsilanes under very mild conditions.

To probe the generality of the formation of alkynyl ketone, we investigated the reaction of different acid chlorides with alkynylsilanes. The conditions for the synthesis of **5a** using $FeCl_3$ (10 mol%) in CH_3NO_2 at −15 °C for 6 h were chosen as the standard conditions for these catalytic reactions. As revealed in Table 3, the variety of acid chlorides reacted smoothly with 1-phenyl-2-(trimethylsilyl)acetylene (**2k**) to give the corresponding α,β-alkynyl ketones. Thus, benzoyl **1b**, *ortho*-, *meta*-, *para*-methylbenzoyl chlorides **1c**, **1d** and **1e** underwent reaction with **2k** to afford the corresponding products **5b**, **5c**, **5d** and **5e** in 84, 72, 79 and 81% yields, respectively (Table 3, entries 2–5). 2-Fluoro-, 4-fluoro-, 4-bromo-, and 4-chlorobenzoyl chlorides **1f**, **1g**, **1h** and **1l** provided **5f**, **5g**, **5h** and **5i** on reaction with **2k** in 77, 81,79 and 76% yields, respectively (entries 6–9). Under similar reaction condition, *ortho*-, *meta*-, *para*-tolyl(trimethylsilyl)acetylenes **2l**, **2m** and **2n** reacted with **1b** to to produce **5j**, **5k** and **5l** in 66, 71 and 78% yields, respectively (entries 10–12). Similarly, thiophene-2-carbonyl chloride (**1i**) gave **5n** in 78% yield (entry 14). Aliphatic acid chloride **1j** is also compatible with the present reaction (entry 15) affording product **5o** in 63% yield. The present catalytic reaction was also successfully extended to aliphatic alkynes **2p** and **q**. Thus, 1-(trimethylsilyl)-2-*tert*-butylacetylene **2p** reacted well with **1b** and **1g** to give conjugated ynones **5p** and **5q** in 93 and 76% yields, respectively (entries 16 and 17). In a similar manner, the reaction of 1-(trimethylsilyl)propyne (**2q**) with **1b** gave **5r** in 46% yield (entry 18). In addition, sterically bulkier 1-naphthoyl chloride **1m** also reacted smoothly with **2k** to give the conjugated ynone **5s** in good yield (entry 19).

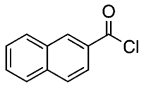
The observed different stereochemistry for the addition of acid chloride to terminal and internal alkynes is intriguing. The major products from the Friedel–Crafts addition of acid chlorides to alkyne which requires equimolar amounts of acid chloride-$AlCl_3$ complex, have the chlorine and the carbonyl groups configured in a *trans* relationship. As well, the $GaCl_3$-catalyzed reaction also proceeded with lower stereoselectivity.[2,5,13] Although the true mechanism is not yet known, we propose the following schemes to account for this $FeCl_3$-catalyzed chloroacylation chemis-

Table 3. Results on the formation of conjugated ynones.[a]



1a: R^1 = 4-MeOC$_6$H$_4$
1b: R^1 = Ph
1c: R^1 = 2-Me-C$_6$H$_4$
1d: R^1 = 3-Me-C$_6$H$_4$
1e: R^1 = 4-Me-C$_6$H$_4$
1f: R^1 = 2-F-C$_6$H$_4$
1g: R^1 = 4-F-C$_6$H$_4$
1h: R^1 = 4-Br-C$_6$H$_4$
1i: R^1 = 2-thienyl
1j: R^1 = $(CH_2)_3CH_3$
1l: R^1 = 4-Cl-C$_6$H$_4$

2k: R^2 = Ph
2l: R^2 = 2-Me-C$_6$H$_4$
2m: R^2 = 3-Me-C$_6$H$_4$
2n: R^2 = 4-Me-C$_6$H$_4$
2o: R^2 = 4-Cl-C$_6$H$_4$
2p: R^2 = C(CH$_3$)$_3$
2q: R^2 = CH$_3$

1m: 

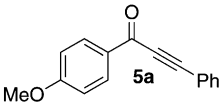
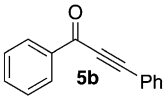
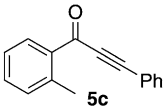
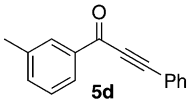
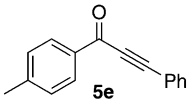
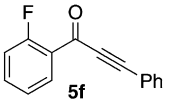
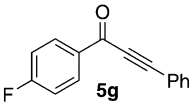
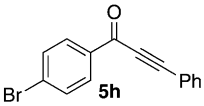
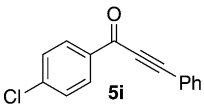
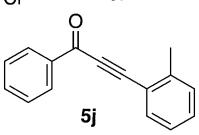
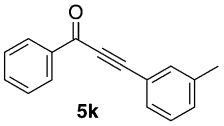
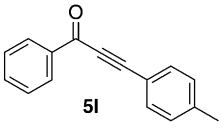
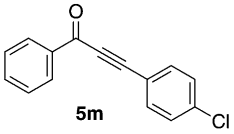
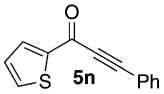
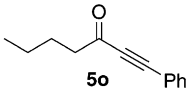
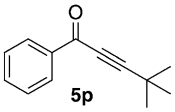
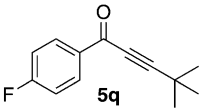
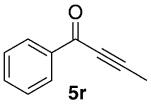
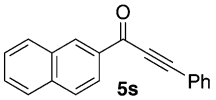
Entry	1	2	Product 5	Yield [%][b]
1	**1a**	**2k**	 **5a**	80
2	**1b**	**2k**	 **5b**	84
3	**1c**	**2k**	 **5c**	72
4	**1d**	**2k**	 **5d**	79
5	**1e**	**2k**	 **5e**	81
6	**1f**	**2k**	 **5f**	77
7	**1g**	**2k**	 **5g**	81
8	**1h**	**2k**	 **5h**	79
9	**1l**	**2k**	 **5i**	76
10	**1b**	**2l**	 **5j**	66

Table 3. (Continued)

Entry	1	2	Product 5	Yield [%][b]
11	**1b**	**2m**	 **5k**	71
12	**1b**	**2n**	 **5l**	78
13	**1b**	**2o**	 **5m**	80
14	**1i**	**2k**	 **5n**	78
15	**1j**	**2k**	 **5o**	63
16	**1b**	**2p**	 **5p**	93
17	**1g**	**2p**	 **5q**	76
18	**1b**	**2q**	 **5r**	46
19	**1m**	**2k**	 **5s**	74

[a] Unless otherwise mentioned, all reactions were carried out with acid chloride **1** (1.0 mmol), alkyne **2** (1.25 mmol), $FeCl_3$ (10 mol%) and CH_3NO_2 (2.0 mL) at −15 °C for 6 h under N_2.

[b] Isolated yields.

try, based on our observed results. In the catalytic reaction, $FeCl_3$ likely acts as a Lewis acid interacting with the carbonyl group in the acid chloride as shown in Scheme 1 and Scheme 2. For the addition of acyl chloride to terminal alkyne (Scheme 1), the reaction probably proceeds *via* a four-membered ring transition state **A** between the alkyne carbons and carbon-chloride bond as suggested in Scheme 1. This pathway explains the observed regiochemistry with the carbonyl and chloro group of acid chloride adding to the terminal carbon and internal carbon of alkyne in the final product **3**. In addition, it also rationalizes the origin of the *Z* stereochemistry of the final product. The other arrangement **A′** (see Table 2) is unfavourable due to the strong steric effect between the aromatic substituents of the two substrates.

For the reaction of the acid chloride with an internal alkyne, the formation of a four-membered ring transition state like **A** or **A′** is less likely due the steric repulsion between the substituents on the two substrates. The reaction probably proceeds *via* the addition of internal alkyne to the acid chloride-$FeCl_3$ complex followed by chloride elimination to give a alkenyl cation **C** (Scheme 2).[14a] Attack of cation **C** by $FeCl_4^-$ at the cationic carbon leads to the formation of both *E*- and *Z*-products.[14b–e] It is noteworthy that the alkenyl cation is expected to have a linear structure based on theoretical calculations performed by us. Moreover, this mechanism also accounts for the formation of α,β-alkynyl ketones **5**.

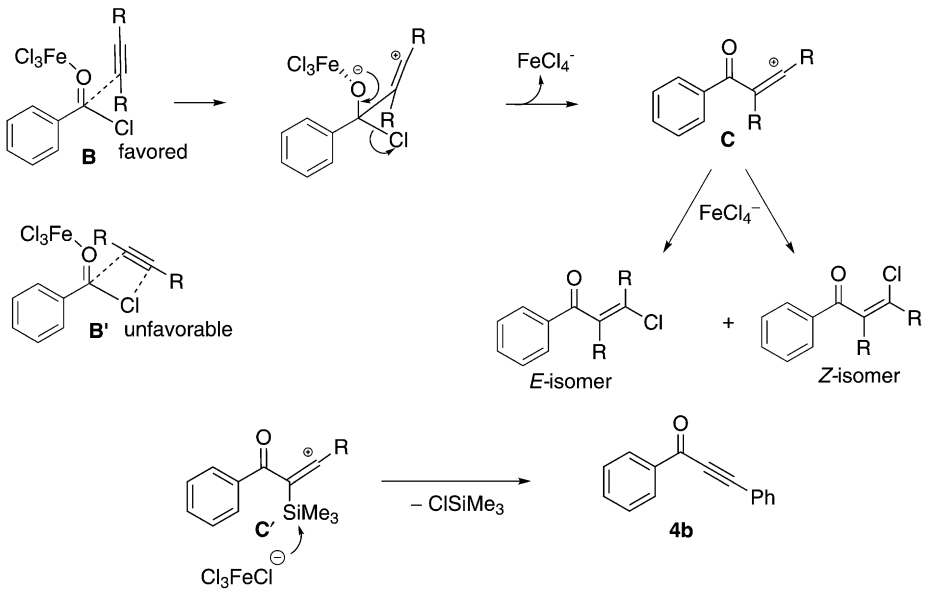
For the $FeCl_3$-catalyzed reaction of acid chlorides with alkynylsilanes, the formation of alkenyl cation **C′** is also expected. Additional stabilization of this cation by the trimethylsilyl group likely occurs that leads to the attack of trimethylsilyl group by $FeCl_4^-$ anion to form a carbon-carbon triple bond.[14f]

We proposed that $FeCl_3$ first interacts with acid chloride at the keto group instead of the chloro group to initiate the catalytic reaction based on the literature reports.[15] To further verify the mechanism, three reactions of phenylacetylene **2a** with benzoyl bromide in the presence of 10, 20 and 50% of $FeCl_3$ under the standard reaction conditions (Table 1) were carried out. In all these reactions, β-bromoalkenyl ketone was isolated as the only product in 76, 63 and 47% yields, respectively (see Scheme 3 for detailed conditions). There is no chloroacylation product **3b** observed. The results do not support a classical acylium ion, generated by removing the chloride anion from the acid chloride by $FeCl_3$, as the intermediate. Instead, the results favour a concerted pathway for the breaking of acylhalide bond *via* a 4-membered ring intermediate **A**.

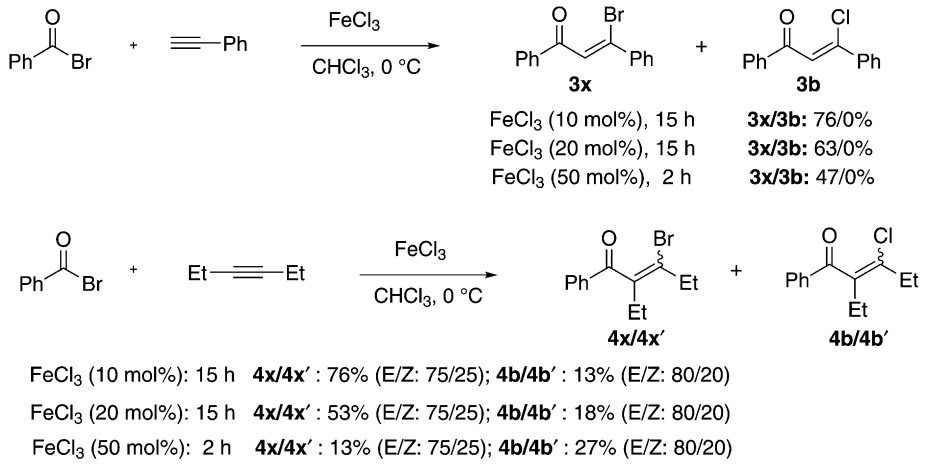
In contrast, the reaction of benzoyl bromide with hex-3-yne in the presence of 10, 20 and 50% of $FeCl_3$ under the standard reaction conditions afforded a mixture of β-bromo- and β-chloroalkenyl ketones as shown in Scheme 3. These results clearly show that the chloride in $FeCl_3$ is incorporated in the final product and support the proposed step-wise mechanism in Scheme 2. It is important to mention that $FeBr_3$ does not catalyze the reaction of acid chloride with alkynes to give the corresponding addition product under the standard reaction conditions.

Conclusions

In summary, we have successfully developed a very mild and convenient iron-catalyzed addition of acid chlorides to terminal alkynes to give the corresponding β-chloroalkenyl ketones in very good yields with



Scheme 2. Proposed mechanism for the addition of acid chlorides to internal alkynes.



Scheme 3. $FeCl_3$-catalyzed addition of acid bromides to alkynes.

excellent regio- and stereoselectivity. Experiments using acid bromides and terminal alkynes as the substrates in the presence of $FeCl_3$ reveal that the addition of acid bromide to terminal alkyne favours a concerted pathway for the breaking of the acyl-halide bond *via* a 4-membered ring intermediate A. The present iron-catalyzed addition reaction is successfully extended to alkynylsilanes to give alkynyl ketones. Further extension of the reaction to the intramolecular version and the detailed mechanistic investigations are in progress.

Experimental Section

General Procedure for the Iron-Catalyzed Synthesis of β-Chloroalkenyl Ketone Derivatives from Acid Chlorides with Alkynes (Table 1 and Table 2)

A sealed tube (15 mL) fitted with a septum containing $FeCl_3$ (01.00 mmol) was evacuated and purged with nitrogen gas three times. $CHCl_3$ (2.0 mL), acid chloride (1.00 mmol) and alkyne (1.5 mmol) were added to the system and the reaction mixture was stirred at 0 °C for 15 h under N_2. The mixture was filtered through a short Celite pad and washed with dichloromethane several times. The filtrate was concentrated by vacuum and separated on a silica gel column using hexane/EtOAc as eluent to give the corresponding pure β-chloroalkenyl ketones.

(*Z*)-3-Chloro-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (3a): Pale yellow solid; mp 87–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.97$ (d, $J = 8.8$ Hz, 2H), 7.72 (t, $J = 7.2$ Hz, 2H), 7.43–7.40 (m, 3H), 7.26 (s, 1H), 6.94 (d, $J = 8.8$ Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 188.7 (*C*O), 163 (C), 141.8 (C), 137.3 (C), 131.1 (2*C*H), 130.5 (C), 130.3 (*C*H), 128.6 (2*C*H), 127.0 (2*C*H), 121.9 (*C*H), 113.9 (2*C*H), 55.4 (CH_3); HR-MS (EI$^+$): $m/z =$ 272.0598, calcd. for $C_{16}H_{13}ClO_2$: 272.0604; IR (KBr): $\nu =$ 2839, 1658, 1600, 1509, 1259, 1167, 1023 cm^{-1}.

(*Z*)-3-Chloro-1,3-diphenylprop-2-en-1-one (3b): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (d, $J =$ 7.2 Hz, 2H), 7.74 (dd, $J = 2.0$ Hz, $J = 8.0$ Hz, 2H), 7.57 (t, $J =$ 7.6 Hz, 1H), 7.49–7.41 (m, 5H), 7.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 189.8$ (*C*O), 143.2 (C), 137.7 (C), 137.3 (*C*H), 133.3 (C), 130.5 (*C*H), 128.6 (6*C*H), 127.1 (2*C*H), 121.4 (*C*H); HR-MS (EI$^+$): $m/z = 242.0505$, calcd. for $C_{15}H_{11}ClO$: 242.0498; IR (KBr): $\nu = 1664$, 1597, 1575, 1447, 1207, 1017 cm^{-1}.

(*Z*)-3-Chloro-3-phenyl-1-*o*-tolylprop-2-en-1-one (3c): Colourless oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.75–7.72 (m, 2H), 7.65 (d, $J = 10.8$ Hz, 1H), 7.46–7.38 (m, 4H), 7.28 (d, $J = 8.8$ Hz, 2H), 7.17 (s, 1H), 2.58 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.2$ (*C*O), 142.9 (C), 138.4 (C), 137.2 (C), 131.8 (*C*H), 131.5 (*C*H), 130.5 (*C*H), 129.2 (*C*H), 128.6 (2*C*H), 127.1 (2*C*H), 125.7 (*C*H), 124.0 (*C*H), 20.8 (CH_3); HR-MS (EI$^+$): $m/z = 256.0655$, calcd. for $C_{16}H_{13}ClO$: 256.0655; IR (KBr): $\nu = 3062$, 2923, 1666, 1573, 1488, 1450, 817 cm^{-1}.

(*Z*)-3-chloro-3-phenyl-1-*m*-tolylprop-2-en-1-one (3d): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.81$ (s, 1H), 7.80–7.75 (m, 3H), 7.46–7.44 (m, 3H), 7.39–7.37 (m, 2H), 7.34 (s, 1H), 2.44 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 190.0 (*C*O), 143.0 (C), 138.5 (C), 137.7 (C), 137.3 (C), 134.1 (*C*H), 131.0 (*C*H), 129.0 (*C*H), 128.6 (2*C*H), 128.5 (*C*H), 127.0 (2*C*H), 125.9 (*C*H), 121.7 (*C*H), 21.3 (CH_3); HR-MS (EI$^+$): $m/z = 256.0651$, calcd. for $C_{16}H_{13}ClO$: 256.0655; IR (KBr): $\nu = 3054$, 2923, 1666, 1589, 1249, 1164, 1033 cm^{-1}.

(*Z*)-3-Chloro-3-phenyl-1-*p*-tolylprop-2-en-1-one (3e): Colourless oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.91$ (d, $J = 8.4$ Hz, 2H), 7.77–7.74 (m, 2H), 7.56–7.43 (m, 3H), 7.32 (s, 1H), 7.29 (d, $J = 8.4$ Hz, 2H), 2.42 (s, 3H);); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 189.5$ (*C*O), 144.2 (C), 142.5 (C), 137.3 (C), 135.1 (C), 130.3 (CH), 129.5 (2CH), 129.3 (2CH), 128.8 (2CH), 127.0 (2CH), 121.7 (C), 21.6 (CH_3); HR-MS (EI$^+$): $m/z = 256.0655$, calcd. for $C_{16}H_{13}ClO$: 256.0655; IR (KBr): $\nu = 3054$, 2923, 1658, 1604, 1241, 1033, 825 cm^{-1}.

(*Z*)-3-Chloro-1-(2-fluorophenyl)-3-phenylprop-2-en-1-one (3f): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.87$ (td, $J = 2.0$ Hz, $J = 7.6$ Hz, 1H), 7.74 (dd, $J = 1.2$ Hz, $J =$ 6.8 Hz, 2H), 7.54–7.48 (m, 1H), 7.45–7.37 (m, 4H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.15–7.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 186.5$ (d, $J_{C,F} = 2.9$ Hz, CO), 161.2 (d, $J_{C,F} =$ 251.9 Hz, C), 144.1 (C), 137.4 (2C), 134.4 (d, $J_{C,F} = 9.6$ Hz, CH), 131.0 (CH), 130.7 (CH), 128.7 (2CH), 127.1 (2CH), 124.6 (CH), 123.5 (d, $J_{C,F} = 6.6$ Hz, CH), 116.5 (d, $J_{C,F} =$ 22.7 Hz, CH); HR-MS (EI$^+$): $m/z = 260.0408$, calcd. for $C_{15}H_{10}ClFO$: 260.0404; IR (KBr): $\nu = 1665$, 1610, 1479, 1452, 1271, 1020 cm^{-1}.

(*Z*)-3-Chloro-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (3g): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (dd, $J = 5.2$ Hz, $J = 8.8$ Hz, 2H), 7.73 (dd, $J = 2.0$ Hz, $J =$ 7.2 Hz, 2H), 7.44–7.42 (m, 3H), 7.28 (s, 1H), 7.14 (t, $J =$ 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 188.4$ (CO), 165.8 (d, $J_{C,F} = 253.3$ Hz, C), 143.4 (C), 137.1 (C), 134.0 (d, $J_{C,F} = 3.0$ Hz, C), 131.3 (CH), 131.2 (CH), 130.6 (CH), 128.6 (2CH), 127.1 (2CH), 121.2 (CH), 115.9 (CH), 115.7 (CH); HR-MS (EI$^+$): $m/z = 260.0408$, calcd. for $C_{15}H_{10}ClFO$: 260.0404; IR (KBr): $\nu = 1665$, 1610, 1479, 1452, 1271, 1020 cm^{-1}.

(*Z*)-1-(4-Bromophenyl)-3-chloro-3-phenylprop-2-en-1-one (3h): Pale yellow solid; mp 78–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.83$ (d, $J = 8.4$ Hz, 2H), 7.73 (dd, $J = 1.2$ Hz, $J =$ 7.2 Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.44–7.42 (m, 3H), 7.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 188.7$ (*C*O), 143.9 (C), 137.0 (C), 136.4 (2C), 132.0 (2CH), 130.7 (*C*H), 130.1 (2*C*H), 128.4 (C), 127.1 (2*C*H), 120.8 (*C*H); HR-MS (EI$^+$): $m/z = 319.9602$, calcd. for $C_{15}H_{10}BrClO$: 319.9604, IR (KBr): $\nu = 1664$, 1658, 1509, 1267, 1167, 1016 cm^{-1}.

(*Z*)-3-Chloro-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one (3i): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.75–7.72 (m, 3H), 7.65 (d, $J = 4.8$ Hz, 1H), 7.46–7.39 (m, 3H), 7.32 (s, 1H), 7.12 (t, $J = 4.4$ Hz 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 180.9$ (*C*O), 145.5 (C), 144.3 (C), 137 (C), 134.2 (*C*H), 132.0 (*C*H), 130.6 (*C*H), 128.6 (2*C*H), 128.2 (*C*H), 127.2 (2 *C*H), 120.3 (*C*H); HR-MS (EI$^+$): $m/z = 248.0068$, calcd. for $C_{13}H_9ClOS$: 248.0063; IR (KBr): $\nu = 3100$, 2341, 1643, 1586, 1574, 1412, 1245, 1061 cm^{-1}.

(*Z*)-1-Chloro-1-phenylhept-1-en-3-one (3j): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.65$ (d, $J = 6.8$ Hz, 2H), 7.40–7.37 (m, 3H), 6.77 (s, 1H), 2.67 (t, $J = 7.2$ Hz, 2H), 1.68–1.60 (m, 2H), 1.38–1.32 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.9$ (*C*O), 142.2 (C), 137.4 (C), 130.5 (*C*H), 128.5 (2*C*H), 127.2 (2*C*H), 123. 8 (*C*H), 44.1 (CH_2), 26.0 (CH_2), 22.2 (CH_2), 13.8 (CH_3); HR-MS (EI$^+$): $m/z = 222.0817$, calcd. for $C_{13}H_{15}ClO$: 222.0811; IR (KBr): $\nu = 2976$, 2862, 2203, 1668, 1060 cm^{-1}.

(*Z*)-1-Chloro-4-methyl-1-phenylpent-1-en-3-one (3k): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.63$ (d, $J =$ 7.2 Hz, 2H), 7.36–7.35 (m, 3H), 6.83 (s, 1H), 2.81 (m, 1H), 1.13 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 201.8 (*C*O), 142.6 (C), 137.3 (C), 130.3 (*C*H), 128.4 (2*C*H) 127.0 (2*C*H), 122.1 (*C*H), 41.6 (*C*H), 17.8 (2 CH_3); HR-MS (EI$^+$): $m/z = 208.0655$, calcd. for $C_{12}H_{13}ClO$: 208.0655; IR (KBr): $\nu = 2969$, 2869, 2203, 1668, 1070 cm^{-1}.

(*Z*)-3-Chloro-1-phenyl-3-*o*-tolylprop-2-en-1-one (3l): Colourless oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (d, $J = 7.2$ Hz, 2H), 7.61–7.55 (m, 3H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.35–7.25 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 190.1$ (*C*O), 144 (C), 138.7 (C), 138.0 (C), 137.5 (C), 133.5 (*C*H), 131.5 (*C*H), 128.9 (4*C*H), 128.8 (*C*H), 128.0 (*C*H), 124.6 (*C*H), 121.5 (*C*H), 21.6 (CH_3); HR-MS (EI$^+$): $m/z = 256.0655$, calcd. for $C_{16}H_{13}ClO$: 256.0655; IR (KBr): $\nu =$ 2923 1664, 1597, 1575, 1447, 1207, 1017 cm^{-1}.

(*Z*)-3-Chloro-1-phenyl-3-*m*-tolylprop-2-en-1-one (3m): Colourless oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.89$ (d, $J = 8.4$ Hz, 2H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.46–7.40 (m, 3H), 7.28–7.17 (m, 4H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 187.7$ (*C*O), 149.0 (C), 137.3 (C), 137.2 (C), 135.3 (C), 133.1 (*C*H), 130.1 (*C*H), 129.3 (*C*H), 128.5 (2*C*H), 128.3 (2*C*H), 127.8 (*C*H), 125.9 (*C*H), 122.6 (*C*H), 19.3 (CH_3); HR-MS (EI$^+$): $m/z = 256.0655$, calcd. for $C_{16}H_{13}ClO$: 256.0655; IR (KBr): $\nu = 2923$ 1662, 1591, 1545, 1443, 1205, 1017 cm^{-1}.

(*Z*)-3-Chloro-1-phenyl-3-*p*-tolylprop-2-en-1-one (3n): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (d, $J = 7.2$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.47 (t, $J = 8.0$ Hz, 2H), 7.33 (s, 1H), 7.23 (d, $J = 7.6$ Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 189.8 (*C*O), 143.7 (C), 141.0 (C), 137.9 (C), 134.5 (C), 133.1 (C), 129.3 (2*C*H), 128.6 (4*C*H), 127.1 (2*C*H), 120.4 (*C*H), 21.3 (CH_3); HR-MS (EI$^+$): $m/z = 256.0651$, calcd. for $C_{16}H_{13}ClO$: 256.0655; IR (KBr): $\nu = 2837$, 1658, 1608, 1509, 1267, 1167, 1023 cm^{-1}.

(*Z*)-3-Chloro-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (3o): Pale yellow solid; mp 55–57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.97$ (dd, $J = 2.0$ Hz, $J = 6.8$ Hz, 2H), 7.67 (dd, $J = 2.0$ Hz, $J = 6.8$ Hz, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.48 (td, $J = 1.2$ Hz, $J = 7.2$ Hz, 2H), 7.39 (dd, $J = 2.4$ Hz, $J = 6.8$ Hz, 2H), 7.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 189.6$ (*C*O), 141.8 (C), 137.4 (C), 136.6 (C), 135.5 (C), 133.4 (*C*H), 128.9 (2*C*H), 128.7 (2*C*H), 128.6 (2*C*H), 128.4 (2*C*H), 121.8 (*C*H); HR-MS (EI$^+$): $m/z = 276.0113$, calcd. for $C_{15}H_{10}Cl_2O$: 276.0109; IR (KBr): $\nu = 2357$, 1665, 1596, 1487, 1448, 1095, 1012 cm^{-1}.

(*Z*)-3-Chloro-1-phenylhex-2-en-1-one (3p): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.89$ (d, $J = 7.2$ Hz, 2H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.11 (s, 1H), 2.94 (t, $J = 7.2$ Hz, 2H), 1.75–1.65 (m, 2H), 0.96 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 188.5$ (*C*O), 157.3 (C), 138.1 (C), 132.9 (*C*H), 128.6 (2*C*H), 128.2 (2*C*H), 123.5 (*C*H), 38.1 (CH_2), 21.1 (CH_2), 13.2 (CH_3); HR-MS (EI$^+$): $m/z = 208.0656$, calcd. for $C_{12}H_{13}ClO$: 208.0655; IR (KBr): $\nu = 2359$, 2341, 1692, 1563, 1447 cm^{-1}.

(*Z*)-3-Chloro-1-phenylundec-2-en-1-one (3q): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.89$ (d, $J = 7.2$ Hz, 2H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.09 (s, 1H), 2.95 (t, $J = 7.2$ Hz, 2H), 1.70–1.62 (m, 2H), 1.35–1.24 (m, 10H), 0.85 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 188.5$ (*C*O), 157.7 (C), 138.1 (C), 132.9 (*C*H), 128.6 (2*C*H), 128.2 (2*C*H), 123.2 (*C*H), 36.4 (CH_2), 31.7 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.8 (CH_2), 27.7 (CH_2), 22.6 (CH_2), 14.0 (CH_3); HR-MS (EI$^+$): $m/z = 278.1435$, calcd. for $C_{17}H_{23}ClO$: 278.1437; IR (KBr): $\nu = 2926$, 2856, 1694, 1598, 1448, 1221 cm^{-1}.

(*Z*)-3-Chloro-4,4-dimethyl-1-phenylpent-2-en-1-one (3r): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.90$ (d, $J = 7.6$ Hz, 2H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 6.69 (s, 1H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 191.5 (*C*O), 154.6 (C), 137.3 (C), 133.2 (*C*H), 128.7 (2*C*H), 128.5 (2*C*H), 119.4 (*C*H), 39.8 (C), 28.6 (3*C*H$_3$); HR-MS (EI$^+$): $m/z = 222.0804$, calcd. for $C_{13}H_{15}ClO$: 222.0811; IR (KBr): $\nu = 2969$, 1671, 1598, 1448, 1220, 1015 cm^{-1}.

(*E*)-3-Chloro-2-ethyl-1-(4-methoxyphenyl)pent-2-en-1-one (4a): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.85$ (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 3.85 (s, 3H), 2.48 (q, $J = 7.6$ Hz, 2H), 2.17 (q, $J = 7.6$ Hz, 2H), 1.02–097 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.0$ (*C*O), 164.1 (C), 137.4 (C), 136.4 (C), 131.8 (2*C*H), 131.8 (C), 129.4 (2 *C*H), 55.4 (CH_3), 30.6 (CH_2), 25.8 (CH_2), 12.3 (CH_3), 11.8 (CH_3); HR-MS (EI$^+$): $m/z = 252.0913$, calcd. for $C_{14}H_{17}ClO_2$: 252.0917; IR (KBr): $\nu = 2970$, 2935, 1598, 1250, 1159 cm^{-1}.

(*E*)-3-Chloro-2-ethyl-1-phenylpent-2-en-1-one (4b): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.88$ (d, $J = 7.2$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 2.50 (q, $J = 7.6$ Hz, 2H), 2.17 (q, $J = 7.2$ Hz, 2H), 1.23–0.98 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.4$ (*C*O), 137.4 (C), 137.3 (C), 136.4 (C), 133.7 (*C*H), 129.3 (2*C*H), 128.7 (2*C*H), 30.6 (CH_2), 25.7 (CH_2), 12.3 (CH_3), 11.8 (CH_3); HR-MS (EI$^+$): $m/z = 222.0812$, calcd. for $C_{13}H_{15}ClO$: 222.0811; IR (KBr): $\nu = 2974$, 2937, 1732, 1669, 1449, 1286, 1244, 1168 cm^{-1}.

(*Z*)-3-Chloro-2-ethyl-1-phenylpent-2-en-1-one (4b′): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.90$ (dd, $J = 1.0$ Hz, $J = 7.6$ Hz, 2H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 2.51 (q, $J = 7.2$ Hz, 2H), 2.39 (q, $J = 7.6$ Hz, 2H), 1.21 (t, $J = 7.6$ Hz, 3H), 1.02 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.1$ (*C*O), 136.9 (C), 135.7 (C), 133.4 (*C*H), 129.4 (2*C*H), 128.6 (2*C*H), 28.2 (CH_2), 24.7 (CH_2), 13.1 (CH_3), 12.5 (CH_3); HR-MS (EI$^+$): $m/z = 222.0812$, calcd. for $C_{13}H_{15}ClO$: 222.0811; IR (KBr): $\delta = 2973$, 2939, 1731, 1667, 1450, 1289, 1241, 1169 cm^{-1}.

General Procedure for the Iron-Catalyzed Synthesis of α,β-Alkynyl Ketone Derivatives from Acid Chlorides with Alkynylsilanes

A sealed tube (15 mL) fitted with a septum containing $FeCl_3$ (0.100 mmol) was evacuated and purged with nitrogen gas three times. CH_3NO_2 (2.0 mL), acid chloride (1.00 mmol) and alkynylsilenes (1.5 mmol) were added to the system and the reaction mixture was stirred at −15 °C for 6 h under N_2. The mixture was filtered through a short Celite pad and washed with dichloromethane several times. The filtrate was concentrated by vacuum and separated on a silica gel column using hexane/EtOAc as eluent to give the corresponding pure α,β-alkynyl ketones.

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (5a): Pale yellow solid; mp 91–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.17 (d, $J = 9.2$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 176.6$ (CO), 164.4 (C), 132.9 (2CH), 131.9 (2CH), 130.5 (CH), 130.2 (C), 128.6 (2CH), 120.3 (C), 113.8 (2CH), 92.2 (C), 86.8 (C), 55.5 (CH_3); HR-MS (EI$^+$): $m/z = 236.0832$, calcd. for $C_{16}H_{12}O_2$: 236.0837; IR (KBr): $\nu = 2198$, 1628, 1600, 1507, 1307, 1260, 1160, 1031 cm^{-1}.

1,3-Diphenylprop-2-yn-1-one (5b): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.20$ (d, $J = 7.2$ Hz, 2H), 7.52 (d, $J =$ 6.8 Hz, 2H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.43 (t, $J = 7.2$ Hz, 1H), 7.37 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 177.7$ (CO), 136.6 (C), 133.9 (CH), 132.8 (2CH), 130.6 (CH), 129.3 (2CH), 128.5 (2CH), 128.4 (2CH), 119.8 (C), 92.9 (C), 86.7 (C); HR-MS (EI$^+$): $m/z =$ 206.0728, calcd. for $C_{15}H_{10}O$: 206.0732; IR (KBr): $\nu = 2198$, 1628, 1600, 1507, 1307, 1260, 1160, 1031 cm^{-1}.

3-Phenyl-1-*o*-tolylprop-2-yn-1-one (5c): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.31$ (dd, $J = 0.8$ Hz, $J =$ 7.2 Hz, 1H), 7.65 (dd, $J = 1.2$ Hz, $J = 8.0$ Hz, 2H), 7.48–7.34 (m, 5H), 7.26 (d, $J = 8.8$ Hz, 1H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 179.7$ (*C*O), 140.4 (C), 135.7 (C), 133.1 (*C*H), 132.8 (3*C*H), 132.1 (*C*H), 130.5 (*C*H), 128.6 (2*C*H), 125.8 (*C*H), 120.3 (C), 91.7 (C), 88.3 (C), 21.8 (CH_3); HR-MS (EI$^+$): $m/z = 220.0885$, calcd. for $C_{16}H_{12}O$: 220.0888; IR (KBr): $\nu = 2962$,2923, 2198, 1643, 1280, 1203,1010, 802, 609 cm^{-1}.

3-Phenyl-1-*m*-tolylprop-2-yn-1-one (5d): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.02$ (d, $J = 7.6$ Hz, 1H), 7.99 (S, 1H), 7.66 (dd, $J = 1.2$ Hz, $J = 6.4$ Hz, 2H), 7.46–7.38 (m, 5H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 178.1 (*C*O), 138.4 (C), 136.8 (C), 134.9 (CH), 132.9 (2CH), 130.6 (CH), 129.7 (CH), 128.6 (2CH), 128.4 (CH), 127.0 (CH), 120.1 (C), 92.8 (C), 86.9 (C), 21.2 (CH_3); HR-MS (EI^+): $m/z = 220.0887$, calcd. for $C_{16}H_{12}O$: 220.0888; IR (KBr): $\nu = 3062$, 2923, 2206, 1643, 1295, 1164, 817 cm^{-1}.

3-Phenyl-1-*p*-tolylprop-2-yn-1-one (5e): Pale yellow solid; mp 87–88; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.11$ (d, $J =$ 8.4 Hz, 2H), 7.67 (d, $J = 6.8$ Hz, 2H), 7.48 (t, $J = 8.4$ Hz, 1H), 7.46–7.39 (m, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 177.6$ (*C*O), 145.2 (C), 134.5 (C), 132.9 (2CH), 130.6 (CH), 129.6 (2CH), 129.3 (2CH), 128.6 (2CH), 120.2 (C), 92.5 (C), 86.9 (C), 21.7 (CH_3); HR-MS (EI^+): $m/z = 220.0881$, calcd. for $C_{16}H_{12}O$: 220.0888; IR (KBr): $\nu = 3054$, 2923, 2198, 1635, 1604, 1288, 1172, 825 cm^{-1}.

1-(2-Fluorophenyl)-3-phenylprop-2-yn-1-one (5f): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.12$–8.02 (m, 1H), 7.65 (d, $J = 7.2$ Hz, 2H), 7.60–7.55 (m, 1H), 7.47 (d, $J =$ 7.6 Hz, 1H), 7.46–7.38 (m, 2H), 7.28 (td, $J = 2.8$ Hz, $J =$ 6.8 Hz, 1H), 7.19 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 174.1$ (*C*O), 162.0 (d, $J_{C,F} = 259.9$ Hz, C), 135.5 (d, $J_{C,F} = 9.1$ Hz, *C*H), 133.1 (2*C*H), 131.7 (*C*H), 130.8 (*C*H), 128.6 (2*C*H), 124.1 (d, $J_{C,F} = 3.7$ Hz, *C*H), 120.0 (C), 117.0 (d, $J_{C,F} = 21.2$ Hz, *C*H), 92.9 (C), 88.4 (C); HR-MS (EI^+): $m/z = 224.0635$, calcd. for $C_{15}H_9FO$: 224.0637; IR (KBr): $\nu =$ 3062, 2198, 1643, 1481, 1450, 1311, 1010, 833 cm^{-1}.

1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-one (5g): Pale yellow solid; mp 61–63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.18 (dd, $J = 2.0$ Hz, $J = 6.8$ Hz, 2H), 7.62 (dd, $J = 1.2$ Hz, $J =$ 6.8 Hz, 2H), 7.42 (t, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 8.4$ Hz, 2H), 7.14 (t, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 176.0 (CO), 166.2 (d, $J_{C,F} = 254.7$ Hz, C), 133.1 (C), 132.8 (2CH), 132.0 (CH), 131.9 (CH), 130.7 (CH), 128.5 (2 CH), 119.6 (C), 115.7 (CH), 115.5 (CH), 93.1 (C), 86.4 (C); HR-MS (EI^+): $m/z = 224.0639$, calcd. for $C_{15}H_9FO$ 224.0637; IR (KBr): $\nu = 2205$, 1635, 1225, 1146 cm^{-1}.

1-(4-Bromophenyl)-3-phenylprop-2-yn-1-one (5h): White solid; mp 109–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.05$ (d, $J = 8.4$ Hz, 2H), 7.67–7.63 (m, 4H), 7.47 (t, $J = 7.2$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 176.8$ (CO), 135.6 (C), 133.0 (2 CH), 131.9 (2CH), 130.9 (3CH), 129.5 (C), 128.7 (2CH), 93.6 (C), 86.5 (C); HR-MS (EI^+): $m/z = 283.9835$, calcd. for $C_{15}H_9BrO$: 283.9837; IR (KBr): $\nu = 2198$, 1733, 1717, 1652, 1558, 1206, 1066, 1005 cm^{-1}.

1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-one (5i): Colourless solid; mp 104–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.13 (d, $J = 2.0$ Hz, $J = 6.8$ Hz, 2H), 7.66 (dd, $J = 1.2$ Hz, $J =$ 8.0 Hz, 2H), 7.48–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 176.6$ (*C*O), 140.6 (C), 135.2 (C), 133.0 (2*C*H), 130.9 (*C*H), 130.8 (2*C*H), 128.9 (2*C*H), 128.7 (2*C*H), 119.8 (C), 93.6 (C), 86.5 (C); HR-MS (EI^+): $m/z = 240.0340$, calcd. for $C_{15}H_9ClO$: 240.0342; IR (KBr): $\nu = 2198$, 1643, 1581, 1280, 840 cm^{-1}.

1-Phenyl-3-*o*-tolylprop-2-yn-1-one (5j): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.22$ (d, $J = 8.0$ Hz, 2H), 7.63–7.58 (m, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.34 (t, $J =$ 7.6 Hz, 1H), 7.25–7.18 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 178.1$ (*C*O), 142.3 (C), 137.2 (C), 134.3 (*C*H), 133.9 (*C*H), 131.1 (*C*H), 130.1 (*C*H), 129.7 (2*C*H), 128.9 (2*C*H), 126.2 (*C*H), 120.1 (C), 92.4 (C), 91.0 (C), 21.1 (CH_3); HR-MS (EI^+): $m/z = 220.0881$, calcd. for $C_{16}H_{12}O$: 220.0888, found ; IR (KBr): $\nu = 3062$, 2923, 2190, 1643, 1450, 1288, 1010, 833 cm^{-1}.

1-Phenyl-3-*m*-tolylprop-2-yn-1-one (5k): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.22$ (dd, $J = 1.6$ Hz, $J =$ 8.4 Hz, 2H), 7.60 td, $J = 3.2$ Hz, $J = 13.6$ Hz, 1H), 7.52–7.46 (m, 4H), 7.29 (d, $J = 7.6$ Hz, 1H), 7.27 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 178.2$ (*C*O), 138.7 (C), 137.1 (C), 134.3 (*C*H), 133.7 (*C*H), 132.0 (*C*H), 130.4 (*C*H), 129.7 (2*C*H), 128.8 (3*C*H), 120.1 (C), 93.7 (C), 86.9 (C), 21.4 (CH_3); HR-MS (EI^+): $m/z = 220.0884$, calcd. for $C_{16}H_{12}O$ 220.0888; IR (KBr): $\nu = 3062$, 2923, 2198, 1643, 1581, 1234, 1164, 902 cm^{-1}.

1-Phenyl-3-*p*-tolylprop-2-yn-1-one (5l): Pale yellow solid; mp 70–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.19$ (d, $J =$ 7.2 Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.53 (d, $J = 7.6$ Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.16 (d, $J = 7.6$ Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 178.2$ (*C*O), 141.8 (C), 137.1 (C), 134.2 (*C*H), 133.3 (2*C*H), 129.7 (2*C*H) 128.8 (4*C*H) 117.1 (C), 94.1 (C), 87.0 (C), 21.9 (*C*H$_3$); HR-MS (EI^+): $m/z = 220.0887$, calcd. for $C_{16}H_{12}O$ 220.0888; IR (KBr): $\nu = 3059$, 2923, 2195, 1643, 1581, 1234, 1164, 902 cm^{-1}.

3-(4-Chlorophenyl)-1-phenylprop-2-yn-1-one (5m): Pale yellow solid; mp 106–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.20$ (d, $J = 7.6$ Hz, 2H), 7.65–7.60 (m, 3H), 7.52 (t, $J =$ 7.2 Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 177.8$ (*C*O), 137.1 (C), 136.7 (C), 134.2 (3*C*H), 129.5 (2*C*H), 129.1 (2*C*H), 128.6 (2*C*H), 118.5 (C), 91.5 (C), 87.5 (C); HR-MS (EI^+): $m/z = 240.0539$, calcd. for $C_{15}H_9ClO$: 240.0342; IR (KBr): $\nu = 2923$, 2198, 1635, 1295, 1017 cm^{-1}.

3-Phenyl-1-(thiophen-2-yl)prop-2-yn-1-one (5n): Pale yellow solid; mp 53–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.98 (d, $J = 3.6$ Hz, 1H), 7.73 (d, $J = 4.8$ Hz, 1H), 7.63 (d, $J =$ 8.4 Hz, 2H), 7.46 (t, $J = 6.8$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 2H), 7.16 (t, $J = 4.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 169.7 (CO), 144.8 (C), 135.2 (CH), 135.0 (CH),132.9 (2CH), 130.8 (CH), 128.6 (2CH), 128.2 (CH), 119.8 (C), 91.6 (C), 86.4 (C); HR-MS (EI^+): $m/z = 212.0291$, calcd. for $C_{13}H_8OS$: 212.0296; IR (KBr): $\nu = 2199$, 1617, 1513, 1409, 1358, 1229. 1212, 1052 cm^{-1}.

1-Phenylhept-1-yn-3-one (5o): Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (dd, $J = 2.0$ Hz, $J = 6.0$ Hz, 2H), 7.42 (td, $J = 2.0$ Hz, $J = 7.2$ Hz, 1H), 7.35 (td, $J = 1.6$ Hz, $J =$ 7.2 Hz, 2H), 2.64 (t, $J = 7.2$ Hz, 2H), 1.69–1.67 (m, 2H), 1.40–1.35 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 188.1$ (CO), 132.8 (2CH), 130.5 (CH), 128.5 (2CH), 119.9 (C), 90.4 (C), 87.7 (C), 45.1 (CH_2), 26.1 (CH_2), 22.0 (CH_2), 13.7 (CH_3); HR-MS (EI^+): $m/z = 186.1044$, calcd. for $C_{13}H_{14}O$: 186.1045; IR (KBr): $\nu =$ 2959, 2873, 2203, 1671, 1070 cm^{-1}.

4,4-Dimethyl-1-phenylpent-2-yn-1-one (5p): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.09$ (d, $J = 8.0$ Hz, 2H), 7.56 (td, $J = 1.2$ Hz, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 177.9$ (CO), 136.7 (C), 133.5 (CH), 129.1 (2CH), 128.2 (2CH), 103.5 (C), 77.8 (C), 29.8 (3CH_3), 27.7 (C); HR-MS (EI^+):

m/z = 186.1037, calcd. for $C_{13}H_{14}O$: 186.1045; IR (KBr): ν = 2958, 2217, 1652, 1598, 1504, 1284, 1229, 1151 cm^{-1}.

4,4-Dimethyl-1-phenylpent-2-yn-1-one (5q): Colourless oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.0 Hz, 2H), 7.56 (td, *J* = 1.2 Hz, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9 (CO), 136.7 (C), 133.5 (CH), 129.1 (2CH), 128.2 (2CH), 103.5 (C), 77.8 (C), 29.8 ($3CH_3$), 27.7 (C); HR-MS (EI^+): *m/z* = 186.1037, calcd. for $C_{13}H_{14}O$: 186.1045; IR (KBr): ν = 2958, 2217, 1652, 1598, 1504, 1284, 1229, 1151 cm^{-1}.

1-Phenylbut-2-yn-1-one (5r): Colourless oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.1 (CO), 136.7 (C), 133.8 (CH), 129.4 (2CH), 128.4 (2CH), 92.4 (C), 78.9 (C), 4.2 (CH_3); HR-MS (EI^+): *m/z* = 144.0572, calcd. for $C_{10}H_8O$: 144.0575; IR (KBr): ν = 2972, 2211, 1652, 1598, 1504, 1151 cm^{-1}.

1-(Naphthalen-2-yl)-3-phenylprop-2-yn-1-one (5s): Pale yellow solid; mp 94–95 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.90 (t, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9 (CO), 136.1 (C), 134.4 (C), 133.0 (2CH), 132.6 (CH). 132.4 (C), 130.7 (CH), 129.8 (CH), 129.0 (CH), 128.7 (2CH), 128.5 (CH), 127.9 (CH), 126.9 (CH), 123.9 (CH), 120.2 (C), 93.0 (C), 87.0 (C); HR-MS (EI^+): *m/z* = 256.0879, calcd. for $C_{19}H_{12}O$: 256.0888; IR (KBr): ν = 2200, 1635, 1623, 1300, 1181, 1123 cm^{-1}.

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