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Phosphinito palladium(II) complexes as catalysts for the synthesis of 1,3-enynes, aromatic alkynes and ynones

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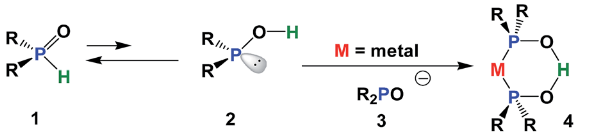
An air-stable phosphinito palladium(II) complex (Ph1-Phoxide) has been found to be an efficient catalyst in the formation of C–C bonds. The coupling of terminal alkynes formed *gem*-1,3-enynes as the only reaction products. Aromatic alkynes can be synthesized from the coupling of terminal alkynes and haloaromatic compounds (Sonogashira coupling). The phosphinito palladium(II) complex also catalyses the coupling between acyl chlorides and terminal alkynes (Sonogashira coupling), furnishing ynones in excellent yields.

1. Introduction

Secondary phosphine oxides (SPOs)[1] are a class of pre-ligands[2] that are valued for their stability in air and in moisture.[3] Because of the tautomeric equilibrium between the pentavalent phosphorus oxide **1** and the trivalent phosphinous acid **2** (Scheme 1),[4] SPOs form hydrogen bond-stabilized bidentate ligands.[2,5] The shift of this equilibrium in favour of either species, and therefore the formation of transition metal complex **4**, depends on metal coordination,[6] the solvents used in the process[7] and the phosphine substituents.[8] The formation of **4** can be rationalized as the coordination of phosphinous acid **2** and phosphinito ligand **3**, which in turn, have their origin in two SPOs. A strong symmetric hydrogen bridge is formed in the presence of a metal, leading to the formation of mononuclear metal complex **4** (Scheme 1).



Scheme 1 Tautomerization of SPOs and chelate formation.

Many phosphinito transition metal complexes have been synthesized,[2] including complexes of palladium,[9] platinum,[10] molybdenum,[5e] nickel,[5b] gold,[3c] rhodium[5d,6e] and ruthenium.[11] Applications of SPO Pd complexes in catalysis include Negishi cross-coupling (POPd1, POPd5 and POPd7),[12] conjugate addition of arylsiloxanes[13] to α,β-unsaturated carbonyl compounds (POPd1),[14] Suzuki–Miyaura (POPd1, POP7 and Ph1-Phoxide)[15] and Stille and Hiyama-type coupling (POPd1)[16] (Fig. 1).

SPO Pd complex **8** exhibits high catalytic activity in Heck-type reactions as well as high stability towards moisture and air.[17]

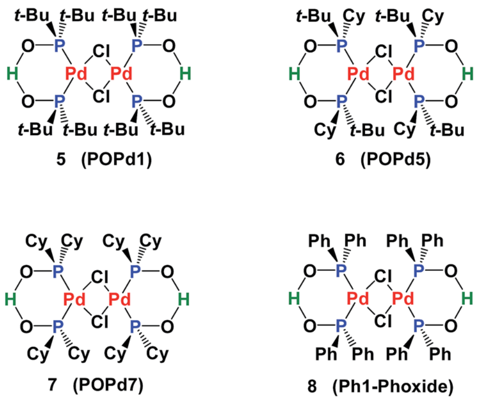
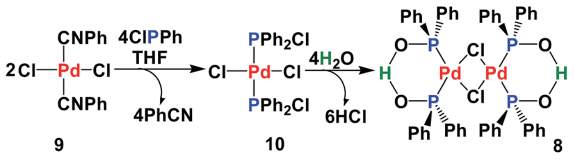


Fig. 1 Structures of SPO Pd complexes.



Scheme 2 Synthesis of the SPO Pd complex Ph1-Phoxide.

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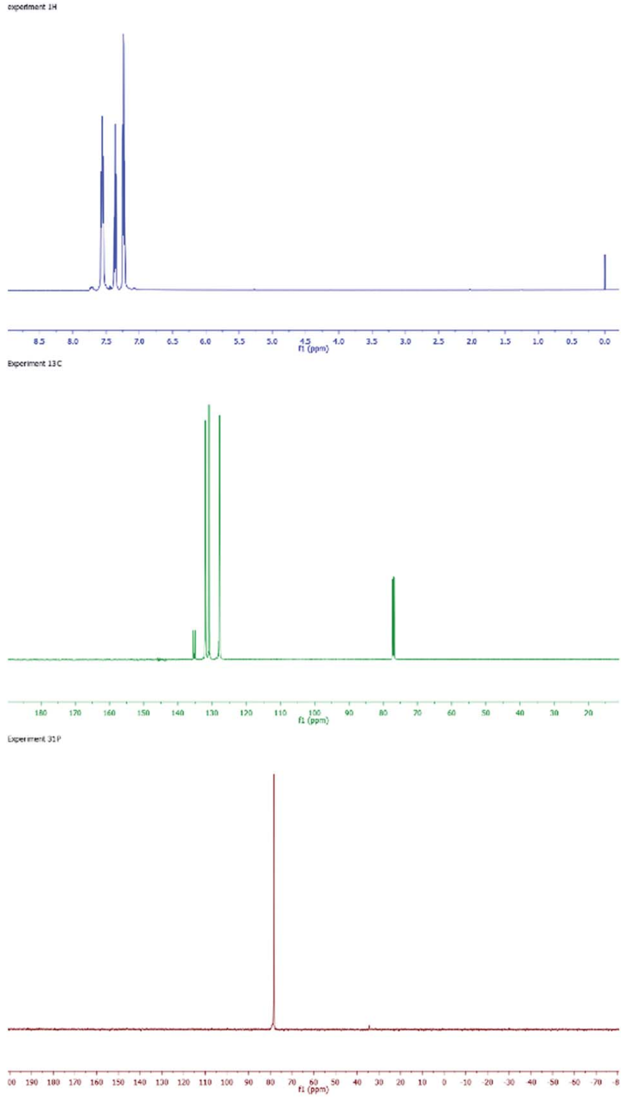


Fig. 2 NMR spectra of complex **8**: ^{1}H (blue), ^{13}C (green) and ^{31}P (red).

The SPOs Pd complex **8** was first synthesized by Dixon[18] in 1971 and then later synthesized and crystallized by many groups.[19] From a structural view point, **8** can be considered as a dimer of complex **4**. However, our synthesis of **8** was achieved by hydrolysis of the palladium chlorodiphenylphosphine complex **10** (Scheme 2). Fig. 2 shows the NMR spectra (^{1}H, ^{13}C and ^{31}P) of complex **8**, which is a homogeneous yellow solid.

Driven by our interest in the catalytic properties of SPO Pd complex **8** in organic reactions and its application in the synthesis of natural products,[17] we report herein the results obtained in the application of complex **8** as a catalyst for the synthesis of 1,3-enynes, aromatic-alkynes and ynones (Sonogashira coupling). Additionally, we report the utility of complex **8** in the synthesis of anemarchalconyn, a natural product isolated from the rhizomes of *Anemarrhena asphodeloides*. To the best of our knowledge, the use of the Pd SPO complex **8** in these reactions has not been reported previously.

2. Results and discussion

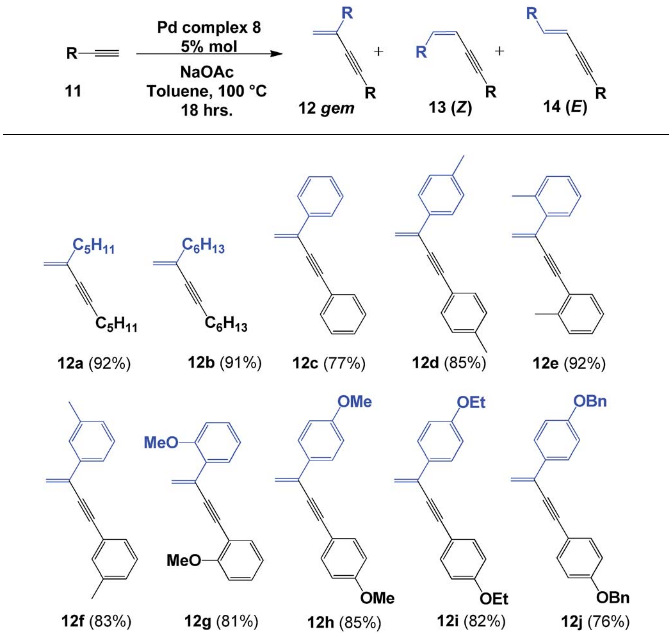
2.1. Synthesis of 1,3-enynes

Initially, we were interested in evaluating the ligation properties of the secondary phosphine oxides in complex **8**, with the thought that the sterically demanding groups in that complex influence the selectivity of the reaction. The first reaction examined was the coupling of two alkynes to obtain 1,3-enynes.[20,21] As shown in Table 1, the dimerization reaction of alkynes in the presence of 5 mol% complex **8**, NaOAc and toluene as the solvent at 100 °C affords 1,3-enynes **12a–12j** in good to excellent yield. In all cases, the use of a microwave reactor allowed for a significant reduction in reaction time, from 18 h to 30 minutes, without affecting yield.

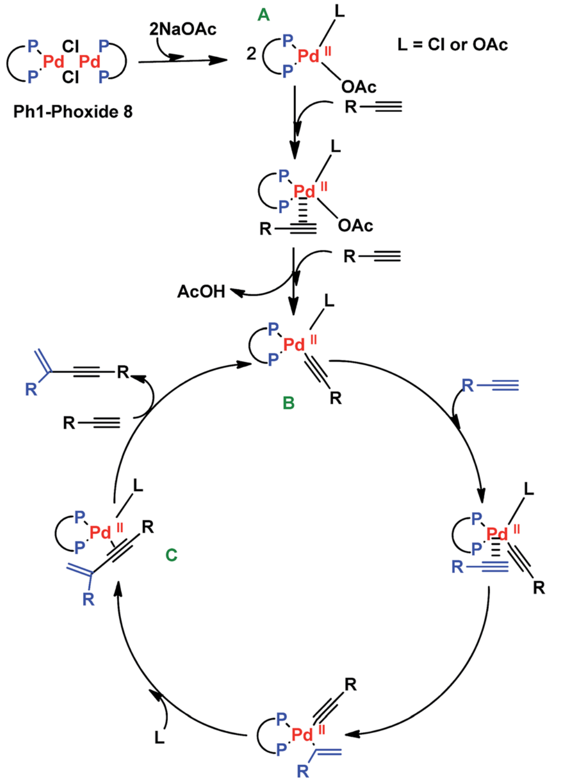
This alkyne dimerization reaction can result in three different isomers, *gem*, (*Z*) and (*E*), depending on the reaction conditions and/or the catalyst. In this case, only the *gem* isomer was formed, which suggests that the presence of the sterically bulky group on the SPO has an effect on the regioselectivity of the reaction. The same reaction in the presence of Pd(OAc)$_2$ and PPh$_3$ gives a mixture of the three isomers.

The proposed mechanism for the enyne formation is shown in Scheme 3. The first step involves the rupture of the Ph1-Phoxide **8** by sodium acetate to form the catalytic precursor **A**. This precursor promotes ligand exchange with the alkyne substrates **B** and C–C coupling between them, generating species **C**. The enyne is obtained by insertion of another alkyne substrate molecule, regenerating the proposed catalytic species **B** (Scheme 3).[20]

Table 1 Synthesis of 1,3-enynes[a,b]

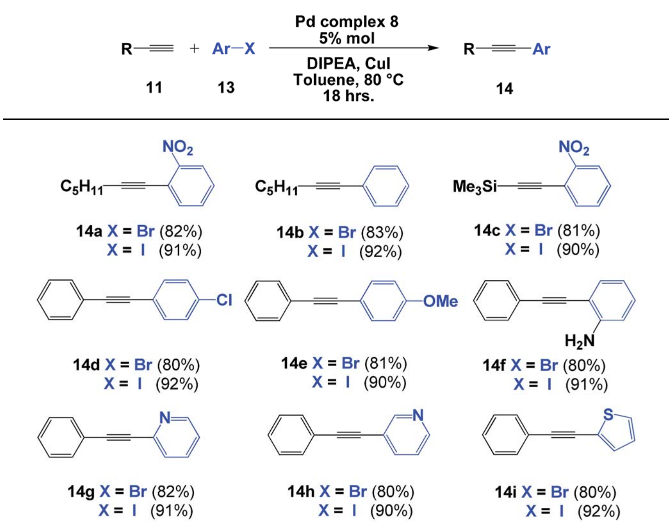


[a] Reagents: alkyne **11** (1 mmol), Pd complex **8** (5% mmol), NaOAc (2 mmol), toluene (25 mL). [b] Yield of isolated product after chromatographic purification.



Scheme 3 Proposed mechanism for 1,3-enynes formation.

Table 2 Synthesis of phenyl-alkynes[a,b]



14a X = Br (82%) X = I (91%)
14b X = Br (83%) X = I (92%)
14c X = Br (81%) X = I (90%)
14d X = Br (80%) X = I (92%)
14e X = Br (81%) X = I (90%)
14f X = Br (80%) X = I (91%)
14g X = Br (82%) X = I (91%)
14h X = Br (80%) X = I (90%)
14i X = Br (80%) X = I (92%)

[a] Reagents: alkyne **11** (1 mmol), aryl halide **13** (1 mmol), Pd complex **8** (5% mmol), CuI (5% mmol), DIPEA (2 mmol), toluene (25 mL). [b] Yield of isolated product after chromatographic purification.

2.2. Synthesis of aromatic-alkynes

Following these results, we extended the use of SPO Pd complex **8** towards the coupling of terminal alkynes to aromatic rings (Sonogashira coupling).[22,23] Iodobenzene derivatives were tested first, as they are often used as model substrates for a class of reactions. The phenyl-alkynes **14a–14f** were isolated in excellent yields (90%, Table 2). The yield decreased to 80% when substituted bromobenzenes were used. No product was observed with chlorobenzene derivatives. When the reactions were carried out in the absence of CuI, only alkyne dimers were isolated. Again, the use of a microwave reactor allowed for a significant reduction in reaction time, from 18 h to 20 minutes, without affecting yield.

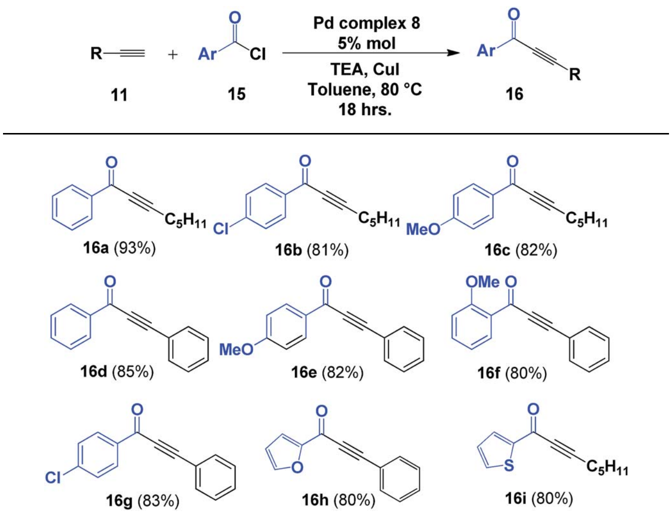
The reaction also works with halogenated heterocycles. For example, 2- and 3-halopyridines were alkynylated under the same reaction conditions; both products were obtained in excellent yield. Notably, alkynylation of the 3-position of pyridine is known to be a difficult reaction, but this reaction proceeds smoothly in the presence of complex **8** (90% for iodo- and 80% for bromo-substituted aryls). The reaction also tolerates halothiophenes, providing the alkyne-aryl adduct in excellent yield (Table 2).

2.3. Synthesis of ynones

SPO complex **8** was also applied in the synthesis of α,β-acetylenic carbonyl compounds (ynones), using highly reactive acyl chlorides as substrates. Ynones are often employed as key intermediates in natural product synthesis.[24,25] In this case, the ynones were obtained in excellent yield when the reaction was performed in the presence of triethylamine in toluene at 100 °C; the scope of the reaction was then examined using these optimum reaction conditions. Ynones **16a–16i** were obtained in high yield (Table 3). When the reactions were carried out with microwave heating, similar yields were obtained in 1 h.

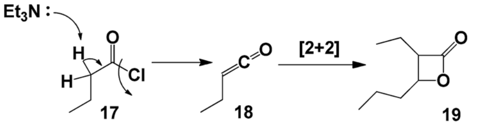
It is noteworthy that when the reaction was carried out with an alkyl acyl chloride (butyryl chloride **17**), the only product observed was the β-lactone **19**. This product could be explained

Table 3 Synthesis of ynones[a,b]

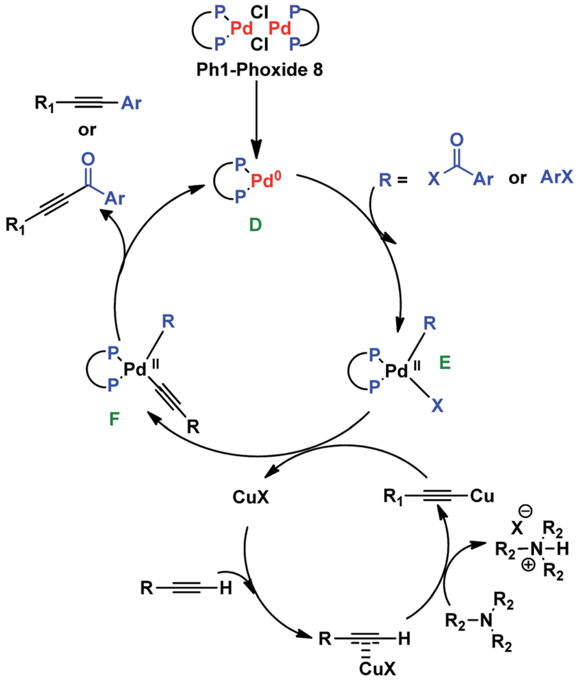


16a (93%)
16b (81%)
16c (82%)
16d (85%)
16e (82%)
16f (80%)
16g (83%)
16h (80%)
16i (80%)

[a] Reagents: alkyne **11** (1 mmol), acyl chloride **15** (1 mmol), Pd complex **8** (5% mmol), CuI (5% mmol), TEA (2 mmol), toluene (25 mL). [b] Yield of isolated product after chromatographic purification.



Scheme 4 Reaction of alkyl acyl chloride in presence of TEA.



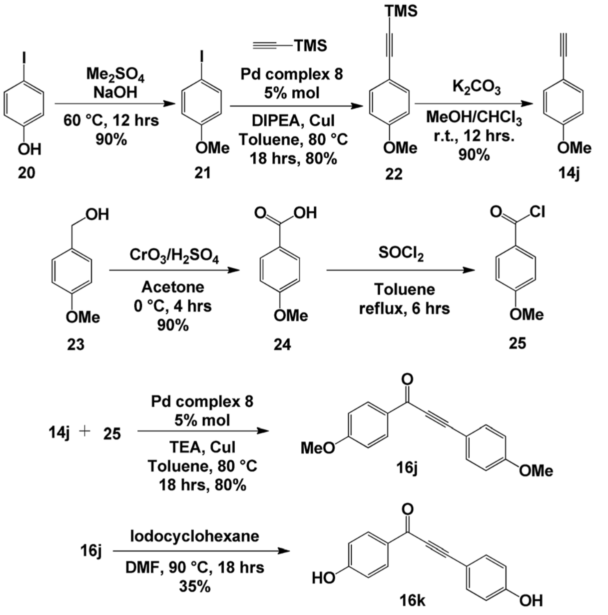
Scheme 5 Proposed mechanism for aromatic-alkynes and ynones formation.

as a result of [2 + 2] cycloaddition of ketene **18**, which was formed from alkyl acyl chloride **17** in presence of triethylamine (Scheme 4).[26]

The mechanism involved in both ynones and phenyl-alkynes synthesis is proposed as follows: the formation of the catalytic species **D** is performed *in situ* by rupture of the dimeric complex **8**. Then species **E** is formed by oxidative addition of an acyl chloride or an aryl halide. A trasmetallation reaction between the complex **E** and the copper acetylide generates species **F**. Finally, the products are formed by reductive elimination, which regenerates the palladium catalyst (Scheme 5).[22]

2.4. Synthesis of anemarchalconyn

With optimized conditions for ynone formation and aryl alkynylation, we decided to apply our methodology to synthesis of a natural product that would utilize SPO complex **8** in two separate steps. Anemarchalconyn (**16k**, Scheme 6) was isolated from the rhizomes of *Anemarrhena asphodeloides* and has inhibitory effects on the adipogenic differentiation of preadipocyte 3T3-L1 cells, with an IC50 value of 5.3 μM.[27] The synthesis began with the methylation of 4-iodophenol **20**, followed by the addition of ethynyltrimethylsilane to 4-iodoanisole **21** in the presence of palladium complex **8**, generating intermediate **22** in 80% yield. The silyl group was removed using basic conditions to give alkyne **14j** in 90% yield. Oxidation of *p*-anisyl alcohol **23**, followed by activation of carbonyl group, afforded acyl chloride **25**. The key step in the synthesis was the coupling between alkyne **14j** and acyl chloride **25** catalysed by the palladium complex **8**, giving ynone **16j** in 80% yield. Finally, removal of the methyl ether protecting group furnished anemarchalconyn (**16k**) in 35% yield (Scheme 1). The ^1H and ^{13}C NMR spectroscopic data matched those reported for the natural product.[27]



Scheme 6 Synthesis of anemarchalconyn.

3. Conclusions

In conclusion, we have demonstrated that an air-stable palladium(II) phosphinito complex **8** (Ph1-Phoxide), was able to catalyse the regioselective dimerization of alkynes to obtain *gem*-1,3-enynes, the coupling of haloaromatics and acyl chlorides and the formation of ynones from alkynes and acyl chlorides. Furthermore, the methodology was applied to the synthesis of anemarchalconyn, an aromatic ynone isolated from the rhizomes of *Anemarrhena asphodeloides*.

4. Experimental section

4.1. General methods

All reactions were conducted under a dried argon stream. The reagents were purchased from Aldrich Chemical Co, St. Louis Missouri, United States, and used without further purification unless stated otherwise. Yields refer to the chromatographically and spectroscopically (^1H and ^{13}C) homogeneous materials, unless otherwise stated. All glassware was flame-dried before use. The reactions were monitored by TLC carried out on 0.25 mm E. Merck silica gel plates. The developed TLC plates were visualised under a short-wave UV lamp or by heating after they were dipped in $Ce(SO_4)_2$. Flash column chromatography (FCC) was performed using silica gel (230–400) and employed a solvent polarity correlated with the TLC mobility. NMR experiments were conducted on a Varian 300 MHz instrument in $CDCl_3$ (99.9% D) as the solvent; the chemical shifts (δ) were referenced to $CDCl_3$ (7.26 ppm ^1H, 77.00 ppm ^{13}C) or Me_4Si (0.00 ppm). The chemical shifts are reported with respect to the solvent peak in parts per million (ppm). Microwave irradiation experiments were performed on a Monowave 450-Anton Paar, using standard sealed microwave glass vials.

4.2. General procedures

4.2.1. Synthesis of complex Ph1-Phoxide 8. A solution of Ph_2PCl (0.75 mL 4.04 mmol) in anhydrous THF (5 mL) was added dropwise whilst stirring to a solution of $PdCl_2(C_6H_5CN)_2$ (0.76 g, 2 mmol) **9** in anhydrous THF (10 mL) placed in a Schlenk flask at room temperature. When the complete formation of the dichlorophosphane complex **10** was confirmed by ^{31}P NMR spectroscopy (δ = 87 ppm), 0.5 mL of H_2O was added to the reaction mixture, which was stirred at room temperature during 48 h. After that time, the solvent was removed under reduced pressure to give the complex **8** as a yellow crystalline powder (92% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.7–7.2 (m, 40H); ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = 78.6.

4.2.2. General procedure for the synthesis of *gem*-1,3-enynes. A solution of alkyne **11** (1 mmol), NaOAc (2 mmol) and catalyst **8** (5% mmol) in anhydrous toluene (25 mL) was heated for 18 h at 100 °C in a silicon oil bath, using a condenser system. Then, the mixture was cooled to room temperature, diluted with EtOAc (25 mL), washed with brine (3 × 25 mL), dried over magnesium sulphate, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using hexane–EtOAc.

4.2.3. General procedure for the synthesis of aromatic-alkynes. A solution of aryl halide **13** (1 mmol), DIPEA (2 mmol), CuI (5% mmol) and catalyst **8** (5% mmol) in anhydrous toluene (15 mL) was placed in a round bottom flask and evacuated/backfilled with N_2 three times. Then, an N_2-purged solution of alkyne **11** (1 mmol) in anhydrous toluene (10 mL) was added. The reaction mixture was stirred and heated at 80 °C for 18 h under N_2 atmosphere. After that time, the reaction mixture was allowed to cool to room temperature, diluted with EtOAc (25 mL), washed successively with 10% citric acid solution (2 × 20 mL), 10% $NaHCO_3$ solution (2 × 20 mL) and brine (3 × 20 mL), dried over magnesium sulphate, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using hexane–EtOAc.

4.2.4. General procedure for the synthesis of ynones. A solution of acyl chloride **15** (1 mmol), TEA (2 mmol), CuI (5% mmol) and catalyst **8** (5% mmol) in anhydrous toluene (15 mL) was placed in a round bottom flask and evacuated/backfilled with N_2 three times. Then, an N_2-purged solution of alkyne **11** (1 mmol) in anhydrous toluene (10 mL) was added. The reaction mixture was stirred and heated at 80 °C for 18 h under N_2 atmosphere. After that time, the reaction mixture was allowed to cool to room temperature, before being quenched with saturated aqueous ammonium chloride solution (15 mL). The mixture was extracted with ethyl acetate (2 × 15 mL). The combined organic layers were washed successively with 10% citric acid solution (2 × 20 mL), 10% $NaHCO_3$ solution (2 × 20 mL) and brine (3 × 20 mL), dried over magnesium sulphate, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using hexane–EtOAc.

4.3. Characterization data

4.3.1. 12a[28] (92% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 5.20 (d, J = 1.8 Hz, 1H), 5.12 (d, J = 1.8 Hz, 1H), 2.29 (t, J = 6.9 Hz, 2H), 2.21 (t, J = 7.2 Hz, 2H), 1.59–1.48 (m, 4H), 1.36–1.29 (m, 8H), 0.90 (t, J = 7.2 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.4, 119.3, 90.1, 81, 37.5, 31.1, 31, 28.5, 27.8, 22.5, 22.2, 19.3, 14. Anal. calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.40; H, 12.50.

4.3.2. 12b[28] (91% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 5.20 (d, J = 1.8 Hz, 1H), 5.12 (d, J = 1.8 Hz, 1H), 2.29 (t, J = 6.9 Hz, 2H), 2.21 (t, J = 7.2 Hz, 2H), 1.59–1.48 (m, 4H), 1.36–1.29 (m, 12H), 0.90 (t, J = 7.2 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.4, 119.3, 90.1, 81, 37.5, 31.1, 31, 29.1, 28.8, 28.1, 27.7, 22.5, 22.3, 19.3, 14. Anal. calcd for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found: C, 87.16; H, 12.79.

4.3.3. 12c[29] (77% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.75–7.70 (m, 2H), 7.56–7.53 (m, 2H), 7.42–7.32 (m, 6H), 6.01 (d, J = 1.0 Hz, 1H), 5.79 (d, J = 1.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 137.3, 131.7, 130.6, 128.4, 128.3, 126.1, 123.1, 120.6, 90.8, 88.6. Anal. calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.01; H, 5.88.

4.3.4. 12d[30] (85% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 5.91 (d, J = 1.0 Hz, 1H), 5.68 (d, J = 0.9 Hz, 1H), 2.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.4, 138.1, 134.5, 131.5, 130.5, 129.1, 129, 125.9, 120, 119.4, 90.7, 88, 21.4, 21. Anal. calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.01; H, 6.90.

4.3.5. 12e[30] (92% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.39 (dd, J = 7.6, 2.0 Hz, 1H), 7.33 (dd, J = 7.6, 2.0 Hz, 1H), 7.23–7.17 (m, 5H), 7.13–7.09 (m, 1H), 5.86 (d, J = 2.0 Hz, 1H), 5.53 (d, J = 2.0 Hz, 1H), 2.49 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.1, 135.5, 132, 131.8, 130.4, 129.4, 128.8, 128.3, 127.9, 125.9, 125.5, 125, 123, 93.3, 89.6, 20.7, 20.3. Anal. calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.02; H, 6.91.

4.3.6. 12f[30] (83% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.52–7.51 (m, 2H), 7.35–7.32 (m, 2H), 7.28–7.21 (m, 2H), 7.15–7.13 (m, 2H), 5.95 (d, J = 1.0 Hz, 1H), 5.73 (d, J = 1.0 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138, 137.9, 137.3, 132.2, 130.7, 129.3, 129.1, 128.7, 128.3, 128.2, 126.8, 123.3, 123, 120.4, 90.8, 88.4, 21.5, 21.2. Anal. calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.03; H, 6.92.

4.3.7. 12g[30] (81% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.29–7.25 (m, 2H), 6.99–6.85 (m, 4H), 6.09 (brs, 1H), 5.95 (brs, 1H), 3.88 (s, 6H); ^{13}C

NMR (75 MHz, $CDCl_3$): δ 160, 157.2, 133.4, 130.5, 129.5, 129, 128, 127.1, 125.4, 120.5, 120.4, 112.7, 111.4, 110.7, 94.1, 85.2, 55.8, 55.6. Anal. calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.76; H, 6.08.

4.3.8. 12h[30] (85% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.83 (d, J = 0.7 Hz, 1H), 5.61 (d, J = 0.7 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.7, 159.6, 133.1, 130.1, 127.3, 118.1, 115.3, 114, 113.7, 90.5, 87.5, 55.3, 55.2. Anal. calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.75; H, 6.07.

4.3.9. 12i[30] (82% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 5.82 (brs, 1H), 5.60 (brs, 1H), 4.07–4.01 (m, 4H), 1.41 (t, J = 6.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 159, 133.1, 130.1, 129.9, 127.3, 117.9, 115.1, 114.5, 114.2, 90.6, 87.5, 63.5, 63.4, 14.8, 14.7 Anal. calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.14; H, 6.86.

4.3.10. 12j[30] (76% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.46–7.32 (m, 12H), 6.96 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 5.83 (brs, 1H), 5.61 (brs, 1H), 5.08 (brs, 2H), 5.07 (brs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 158, 136.9, 136.6, 133.1, 130.3, 130, 128.6, 128.6, 128.1, 128, 127.5, 127.4, 127.3, 118.2, 115.5, 114.9, 114.6, 90.5, 87.6, 70, 70; Anal. calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.46; H, 5.77.

4.3.11. 14a[31] (82% for bromo- and 91% for iodo-substituted aryls). ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (dd, J = 8.3, 1.2 Hz, 1H), 7.51 (dd, J = 7.8, 1.6 Hz, 1H), 7.46 (ddd, J = 7.8, 7.7, 1.2 Hz, 1H), 7.33 (ddd, J = 8.3, 7.7, 1.6 Hz, 1H), 2.42 (t, J = 7.2 Hz, 2H), 1.63–1.56 (m, 2H), 1.45–1.28 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150, 134.6, 132.3, 127.7, 124.2, 119.3, 99.2, 75.9, 30.9, 27.9, 22.1, 19.7, 13.9. Anal. calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.82; H, 6.91; N, 6.39.

4.3.12. 14b[32] (83% for bromo- and 92% for iodo-substituted aryls). ^1H NMR (300 MHz, $CDCl_3$): δ 7.43–7.41 (m, 2H), 7.30–7.29 (m, 3H), 2.43 (t, J = 7.2 Hz, 2H), 1.67–1.60 (m, 2H), 1.48–1.37 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 133.1, 129.8, 129.1, 125.6, 92.1, 82.1, 32.7, 30.1, 23.9, 21, 15.7; anal. calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.61; H, 9.32.

4.3.13. 14c[33] (81% for bromo- and 90% for iodo-substituted aryls). ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (dd, J = 8.2, 1.4 Hz, 1H), 7.64 (dd, J = 7.8, 1.4 Hz, 1H), 7.54 (ddd, J = 7.8, 7.8, 1.4 Hz, 1H), 7.46–7.41 (m, 1H), 0.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 150.3, 135.2, 132.7, 128.9, 124.5, 118.5, 103.8, 99.4, −0.3; anal. calcd for $C_{11}H_{13}NO_2Si$: C, 60.24; H, 5.97; N, 6.39. Found: C, 60.21; H, 5.95; N, 6.37.

4.3.14. 14d[32] (80% for bromo- and 92% for iodo-substituted aryls). ^1H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.36–7.32 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.9, 134.5, 133.3, 130.3, 130.1, 130, 124.6, 123.4, 91.9, 89.9; anal. calcd for $C_{14}H_9Cl$: C, 79.06; H, 4.27. Found: C, 79.02; H, 4.23.

4.3.15. 14e[32] (81% for bromo- and 90% for iodo-substituted aryls). ^1H NMR (300 MHz, $CDCl_3$): δ 7.52–7.50 (m, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.36–7.32 (m, 3H), 6.88 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.2, 134.7, 133.1, 130, 129.6, 125.2, 117, 115.6, 91, 89.7, 56.9; anal. calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.48; H, 5.77.

4.3.16. 14f[34] (80% for bromo- and 91% for iodo-substituted aryls). ^1H NMR (300 MHz, $CDCl_3$): δ 7.59–7.55 (m, 2H), 7.43–7.37 (m, 4H), 7.21–7.15 (m, 1H), 6.79–6.75 (m, 2H), 4.29 (brs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.1, 132.6, 131.9, 130.2, 128.8, 128.6, 123.7, 118.5, 114.8, 108.4, 95.1, 86.3; anal. calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.99; H, 5.72; N, 7.23.

4.3.17. 14g[35] (83% for bromo- and 91% for iodo-substituted aryls). ^1H NMR (300 MHz, $CDCl_3$): δ 8.59 (brd, J = 4.1 Hz, 1H); 7.64 (ddd, J = 7.7, 7.7, 1.8 Hz, 1H), 7.60–7.54 (m, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.37–7.30 (m, 3H), 7.23–7.17 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.7, 143.1, 135.9, 131.7, 128.7, 128.1, 126.9, 122.5, 122, 89, 88.4. Anal. calcd for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.08; H, 5.03; N, 7.80.

4.3.18. 14h[36] (80% for bromo- and 90% for iodo-substituted aryls). ^1H NMR (300 MHz, $CDCl_3$): δ 8.77 (brs, 1H), 8.55 (dd, J = 6.4, 1.4 Hz, 1H), 7.80 (td, J = 8.0, 2.4 Hz, 1H), 7.56–7.54 (m, 2H), 7.38–7.36 (m, 3H), 7.30–7.26 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1, 148.4, 138.3, 131.6, 128.7, 128.3, 122.9, 122.4, 120.3, 92.5, 85.8, anal. calcd for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.09; H, 5.04; N, 7.80.

4.3.19. 14i[37] (80% for bromo- and 92% for iodo-substituted aryls). ^1H NMR (300 MHz, $CDCl_3$): δ 7.52–7.50 (m, 2H), 7.35–7.32 (m, 3H), 7.29–7.28 (m, 2H), 7.01 (dd, J = 5.0, 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.3, 131.8, 128.8, 128.7, 127.6, 127.5, 123.7, 123.3, 93.4, 83. Anal. calcd for $C_{12}H_8S$: C, 78.22; H, 4.38; S, 17.40. Found: C, 78.20; H, 4.35; S, 17.38.

4.3.20. 16a[38] (93% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, J = 8.25 Hz, 2H), 7.59 (td, J = 7.6, 1.1 Hz, 1H), 7.4 (m, 2H), 2.49 (t, J = 7.1 Hz, 2H), 1.68 (m, 2H), 1.34–1.48 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.2, 136.9, 133.8, 129.5, 128.4, 96.8, 79.6, 31, 27.4, 22, 19.1, 13.8. Anal. calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.94; H, 8.02.

4.3.21. 16b[39] (81% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.08 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 2.50 (t, J = 7.1 Hz, 2H), 1.68 (m, 2H), 1.34–1.47 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177, 140.5, 135.5, 131, 128.9, 97.6, 79.5, 31.2, 27.6, 22.2, 19.3, 14. Anal. calcd for $C_{14}H_{15}ClO$: C, 71.4; H, 6.44. Found: C, 71.3; H, 6.42.

4.3.22. 16c[39] (82% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 2.48 (t, J = 7.1 Hz, 2H), 1.67 (m, 2H), 1.34–1.47 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177, 164.4, 132, 130.4, 113.8, 95.1, 79.7, 55.6, 31.2, 27.6, 22.2, 19.2, 14. Anal. calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.21; H, 7.87.

4.3.23. 16d[38] (85% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (dd, J = 8.0, 1.6 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.48–7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.2, 137, 134.4, 133.3, 131.1, 129.8, 129, 128.9, 120.2, 93.4, 87.2. Anal. calcd for $C_{15}H_{10}O$: C, 87.36; H, 4.84. Found: C, 87.35; H, 4.83.

4.3.24. 16e[38] (82% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.32–7.28 (m, 3H), 6.87 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.6, 164.5, 132.9, 131.9, 130.6, 130.2, 128.6, 120.2, 113.8, 92.3, 86.9, 55.5. Anal. calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.32; H, 5.11.

4.3.25. 16f[38] (80% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.07 (ddd, J = 7.8, 1.8, 0.3 Hz, 1H), 7.65–7.61 (m, 2H), 7.57–7.51 (m, 1H), 7.48–7.36 (m, 3H), 7.08–7.00 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.7, 159.8, 134.9, 132.9, 132.5, 130.4, 128.5, 126.7, 120.6, 120.2, 112.1, 91.5, 89.1, 55.9. Anal. calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.31; H, 5.09.

4.3.26. 16g[38] (83% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.51–7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.4, 140.6, 135.3, 132.9, 130.8, 130.7, 128.8, 128.6, 119.8, 93.5, 86.5. Anal. calcd for $C_{15}H_9ClO$: C, 74.85; H, 3.77. Found: C, 74.86; H, 3.78.

4.3.27. 16h[40] (80% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.71–7.64 (m, 3H), 7.48–7.39 (m, 4H), 6.62 (dd, J = 3.8, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 164.7, 153.2, 147.9, 132.9, 130.8, 128.6, 120.8, 119.9, 112.6, 91.8, 86.2. Anal. calcd for $C_{13}H_8O_2$: C, 79.58; H, 4.11. Found: C, 79.55; H, 4.8.

4.3.28. 16i[39] (80% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.88 (dd, J = 3.8, 1.0 Hz, 1H), 7.67 (dd, J = 4.9, 1.0 Hz, 1H), 7.14 (t, J = 3.9 Hz, 1H), 2.46 (t, J = 7.1 Hz, 2H), 1.66 (m, 2H), 1.46–1.33 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.2, 145.2, 135, 128.3, 95.6, 79.4, 31.2, 27.5, 22.2, 19.2, 14. Anal. calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S, 15.54. Found: C, 69.83; H, 6.81; S, 15.52.

4.4. Synthesis of anemarchalconyn

4.4.1. 1-Iodo-4-methoxybenzene 21. *p*-Iodophenol **20** (1 g, 4.5 mmol) and NaOH (800 mg, 20 mmol) were mixed and ground in a mortar to have a fine powder. Then, the mixture was placed in a three-necked round-bottomed flask (100 mL) fitted with an efficient stirrer, separatory funnel and reflux condenser. The mixture was cooled at 0 °C. There was then added through the separatory funnel, with stirring, dimethyl sulfate (252 mg, 4.5 mmol). This addition at 0 °C requires one hour. The mixture was then heated for 18 h at 60 °C. After that time, the reaction mixture was allowed to cool to room temperature, before being quenched with H_2O (25 mL). The mixture was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed successively with 10% citric acid solution (2 × 20 mL) and brine (3 × 20 mL), dried over magnesium sulphate, filtered and concentrated under reduced pressure. A with solid was obtained after the recrystallization of the residue with hexane–EtOAc (947 mg, 90% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.7, 138.4, 116.6, 82.9, 55.5. Anal. calcd for C_7H_7IO: C, 35.92; H, 3.01. Found: C, 35.91; H, 3.00.

4.4.2. ((4-Methoxyphenyl)ethynyl)trimethylsilane 22. A solution of 1-iodo-4-methoxybenzene **21** (850 mg, 3.63 mmol), DIPEA (480 mg, 3.72 mmol), CuI (34 mg, 0.18 mmol, 5% mmol) and catalyst **8** (196 mg, 0.18 mmol, 5% mmol) in anhydrous toluene (20 mL) was placed in a round bottom flask and evacuated/backfilled with N_2 three times. Then, an N_2-purged solution of ethynyltrimethylsilane (365 mg, 3.72 mmol) in anhydrous toluene (10 mL) was added. The reaction mixture was stirred and heated at 80 °C for 18 h under N_2 atmosphere. After that time, the reaction mixture was allowed to cool to room temperature, diluted with EtOAc (25 mL), washed successively with 10% citric acid solution (2 × 20 mL), 10% $NaHCO_3$ solution (2 × 20 mL) and brine (3 × 20 mL), dried over magnesium sulphate, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using hexane–EtOAc, to give 592 mg of **22** (80% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.41 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.7, 133.4, 115.2, 113.7, 105.1, 92.4, 55.2, 0.06. Anal. calcd for $C_{12}H_{16}OSi$: C, 70.53; H, 7.89. Found: C, 70.51; H, 7.87.

4.4.3. 1-Ethynyl-4-methoxybenzene 14j. K_2CO_3 (45 mg, 0.33 mmol) and the mixture MeOH–$CHCl_3$ (10 mL, 1 : 1) were added to ((4-methoxyphenyl)ethynyl)trimethylsilane **22** (200 mg, 0.98 mmol) in a 50 mL recovery flask. The suspension was stirred at room temperature for 18 h. After that time, the reaction mixture was diluted with EtOAc (25 mL), washed successively with 10% citric acid solution (2 × 20 mL) and brine (3 × 20 mL), dried over magnesium sulphate, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using hexane–EtOAc, to give 116 mg of **14j** (90% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H), 3.02 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 159.9, 133.5, 114.2, 113.9, 93.9, 83.6, 55.3. Anal. calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.76; H, 6.08.

4.4.4. 4-Methoxybenzoic acid 24. A solution of (4-methoxyphenyl)methanol **23** (600 mg, 4.41 mmol) in 10 mL of acetone was added to a 100 mL three-necked flask fitted with a long-stem dropping funnel and a thermometer. The agitated solution was cooled in a water bath to about 20°. The Jones reagent (CrO_3/H_2SO_4) was added from the dropping funnel. The rate of addition was adjusted so that the temperature of the reaction mixture does not rise above 25°. After the complete conversion of starting material, monitored by thin layer chromatographic, the reaction mixture was allowed to cool to room temperature, before being quenched with isopropanol (10 mL). Then, the reaction mixture was filtrated to eliminate chromium salts. The resulting residue was purified by flash column chromatography on silica gel using hexane–EtOAc, to give 603 mg of **24** (90% yield). ^1H NMR (300 MHz, DMSO-d_6): δ 7.90 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 169.3, 165.8, 131.3, 122.5, 114.2, 55.8. Anal. calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 63.13; H, 5.28.

4.4.5. 4-Methoxybenzoyl chloride 25. To stirred solution of carboxylic acid **24** (200 mg, 1.36 mmol) in toluene (10 mL), $SOCl_2$ (810 mg, 6.8 mmol) was added at room temperature. Then, the reaction mixture was stirred and heated at reflux temperature for 6 h under N_2 atmosphere. After that time, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting residue was used in next reaction without further purification.

4.4.6. 1,3-Bis(4-methoxyphenyl)prop-2-yn-1one 16j. A solution of acyl chloride **25** (150 mg, 0.87 mmol), CuI (8 mg, 0.043 mmol, 5% mmol) and catalyst **8** (47 mg, 0.043 mmol, 5% mmol) in anhydrous TEA (15 mL) was placed in a round bottom flask and evacuated/backfilled with N_2 three times. Then, an N_2-purged solution of alkyne **14j** (92 mg, 0.7 mmol) in anhydrous TEA (10 mL) was added. The reaction mixture was stirred and heated at 80 °C for 18 h under N_2 atmosphere. After that time, the reaction mixture was allowed to cool to room temperature, before being quenched with saturated aqueous ammonium chloride solution (15 mL). The mixture was extracted with ethyl acetate (2 × 15 mL). The combined organic layers were washed successively with 10% citric acid solution (2 × 20 mL), 10% $NaHCO_3$ solution (2 × 20 mL) and brine (3 × 20 mL), dried over magnesium sulphate, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using hexane–EtOAc. To give 149 mg of **16j** (80% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, $J = 8.7$ Hz, 2H), 7.63 (d, $J = 8.7$ Hz, 2H), 6.99 (d, $J = 8.7$ Hz, 2H), 6.93 (d, $J = 8.7$ Hz, 2H), 3.90 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.7, 164.3, 161.6, 134.9, 131.9, 130.5, 114.4, 113.8, 112.2, 93.4, 86.8, 55.6, 55.4. Anal. calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.66; H, 5.28.

4.4.7. Anemarchalconyn 16k.[27] A solution of **16j** (145 mg, 0.54 mmol) in 5 mL of DMF was placed in a round bottom. Then, iodocyclohexane (1.3 mL, 10.0 mmol) was added.[41] The reaction system was equipped with reflux condenser under argon. The reaction mixture was stirred and heated at 90 °C for 18 h under N_2 atmosphere. After that time, the reaction mixture was allowed to cool to room temperature, before being quenched with saturated aqueous ammonium chloride solution (10 mL). The mixture was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed successively with 10% $NaHCO_3$ solution (2 × 10 mL) and brine (2 × 10 mL), dried over magnesium sulphate, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using hexane–EtOAc. To give 45 mg of anemarchalconyn **16k** (35% yield). ^{1}H NMR (300 MHz, CD_3OD): δ 8.07 (d, $J = 8.7$ Hz, 2H), 7.55 (d, $J = 8.7$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (75 MHz, CD_3OD): δ 178.5, 165.2, 161.8, 136.3, 133.2, 130.3, 117.1, 116.6, 111.5, 95.7, 87.2. Anal. calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.58; H, 4.20.

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