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Pd-catalyzed decarboxylative allylic coupling of acetates of Baylis–Hillman alcohols with propiolic acids: a highly regio- and stereoselective synthesis of 1,5-diarylpent-1-en-4-yne derivatives†

Satyanarayana Tummanapalli,* Parthasarathy Muthuraman, Dhanunjaya Naidu Vangapandu, Gnanakalai Shanmugavel, Sanjeeva Kambampati and Kee Wei Lee

Pd-catalyzed decarboxylative allylic coupling of acetates of Baylis–Hillman alcohols with alkynyl carboxylic acids leading to the formation of an important class of 1,5-diarylpent-1-en-4-ynes in a highly regio- and stereoselective manner has been developed. Decarboxylative coupling happened *via* an exclusively S_N2' pathway. Acetates of the Baylis–Hillman alcohols derived from alkyl acrylates, ethyl vinyl ketone and phenyl vinyl sulfone provided exclusively (*E*)-1,5-diarylpent-1-en-4-ynes while the acetates of the Baylis–Hillman alcohols derived from acrylonitrile provided exclusively (*Z*)-1,5-diarylpent-1-en-4-ynes.

Due to the many advantages over traditional oxidative coupling reactions,[1,2] decarboxylative cross coupling reactions have become an important tool for the construction of carbon–carbon bonds in modern synthetic organic chemistry. Decarboxylative cross coupling reactions employ more stable and inexpensive carboxylic acids as key reaction partners while traditional coupling reactions have typically involved expensive and usually air-sensitive organometallic species as their reaction partners.[1,2] Recently alkynyl carboxylic acids have been inducted into decarboxylative coupling partners by providing aryl alkyne derivatives.[3] In 2008, Lee *et al.* reported first decarboxylative coupling of alkynyl carboxylic acids with aryl halides.[3a] Later Li *et al.* expanded the scope of substrates to benzyl chlorides, bromides, and acetate in this coupling by providing desired benzyl alkynes.[3e] Tunge and co-workers independently reported the first intramolecular Pd-catalyzed decarboxylative allylic rearrangement of allyl alkynoates in 2005.[4] The Baylis–Hillman reaction is another important atom-economical carbon–carbon bond forming reaction providing densely functionalized molecules. Applications of Baylis–Hillman adducts in many organic transformations have been well documented.[5] In continuation of our interest in the decarboxylative coupling and studies in the application of Baylis–Hillman adducts in various synthetic organic transformations[6] we herein report Pd-catalyzed decarboxylative S_N2' allylic coupling of acetates of the Baylis–Hillman alcohols with the alkynyl carboxylic acids leading to the formation of important class of 1,5-diarylpent-1-en-4-ynes in a highly regio- and stereoselective manner. To the best our knowledge there is no study reported on the Pd-catalyzed decarboxylative allylic coupling of alkynyl carboxylic with acetates of Baylis–Hillman adducts.[7,8] Furthermore, S_N2' Pd-catalyzed decarboxylative addition of alkynyl carboxylic on allylic acetate has also not been described.[9] In addition, 1,5-diarylpent-1-en-4-yne is an important structural moiety present in the extracts of some medicinal plants.[10] Rooperol (**1a**), hypoxoside (**1b**) and many other 1,5-diarylpent-4-yne-1,2-diol derivatives found in plant extracts which were reported to exhibit medicinal properties such as anticancer, anti-inflammatory, antibacterial, and antioxidant activity (Fig. 1).[10]

Being interested in the decarboxylative coupling and the development of new synthetic methodologies particularly using Baylis–Hillman adducts, we studied the Pd-catalyzed decarboxylative allylic coupling of acetates of the Baylis–Hillman alcohols with the alkynyl carboxylic acids. Accordingly, we subjected allyl acetate **2a**[11] and phenyl propiolic acid **3a** to decarboxylative coupling conditions using of a catalyst combination of 5 mol% of $Pd(OAc)_2$ and 10 mol% of *S*-Phos at

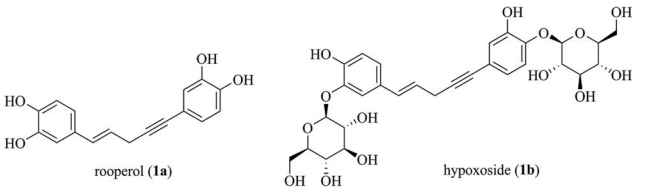

Fig. 1 Structures of rooperol (**1a**) and hypoxoside (**1b**).

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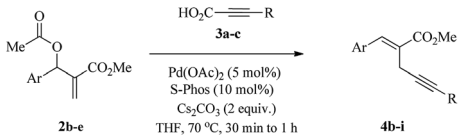
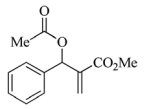
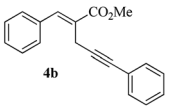
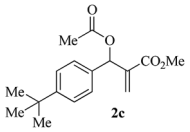
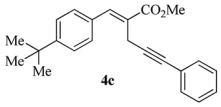
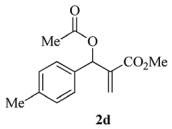
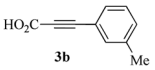
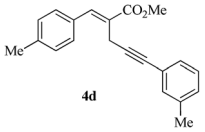
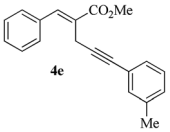
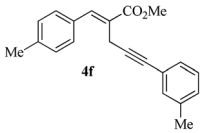
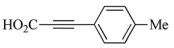
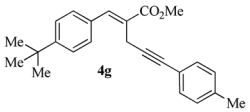
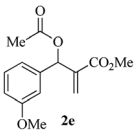
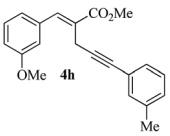
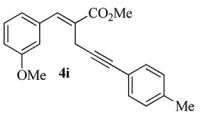
† Electronic supplementary information (ESI) available: Experimental procedures, ^{1}H NMR, 2D NOESY, ^{13}C NMR and MS data of all the products. See DOI: 10.1039/c5ra06168g

Table 1 Regio- and stereo-selective Pd-catalyzed allylic decarboxylative coupling of methyl acrylate derived acetates **2b–e** leading to the formation of (*E*)-1,5-diarylpent-1-en-4-ynes **4a–i**



Entry	Acetate[a]	Propiolic acid	Product(s)[b]	Yield[c] (%)
1	 **2b**	 **3a**	 **4b**	86
2	 **2c**	**3a**	 **4c**	81
3	 **2d**	 **3b**	 **4d**	86
4	**2b**	**3b**	 **4e**	82
5	**2d**	**3b**	 **4f**	79
6	**2c**	 **3c**	 **4g**	85
7	 **2e**	**3a**	 **4h**	78
8	**2e**	**3c**	 **4i**	83

[a] Acetates of Baylis–Hillman alcohol **2b–e** were prepared by following the typical procedure described in ref. 11. [b] Reactions were carried out following the typical procedure described in ref. 12. [c] Isolated yields after chromatographic purification on silica gel.

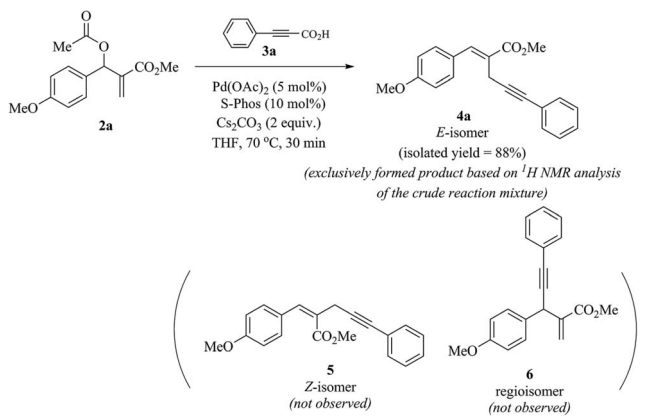
70 °C. Work-up and silica gel column chromatography provided (*E*)-methyl-2-(4-methylbenzylidene)-5-phenylpent-4-ynoate (**4a**) as the exclusive isolated product in 88% yield.[12,13] Proton NMR analysis of the crude reaction mixture did not indicate the presence of other regioisomer **6** or the corresponding *Z*-isomer **5**. Formation of exclusively *E*-isomer **4a** suggests that decarboxylative coupling between allyl acetate **2a** and phenyl propiolic acid **3a** happened in a highly regio- and stereoselective manner *via* exclusively S_N2' allylic pathway.

The *E*-stereochemistry was assigned based on the literature precedence of *E*/*Z*-stereochemical assignments of 3-aryl-(2-substituted)-prop-2-enoates.[14] The *E*-stereochemistry of **4a** was further ascertained by 2D NOESY. A strong NOE cross peak between the CH_2 (allylic methylene proton) and Ar-H_{ortho} (*ortho* proton of the benzene ring) was observed, while there was

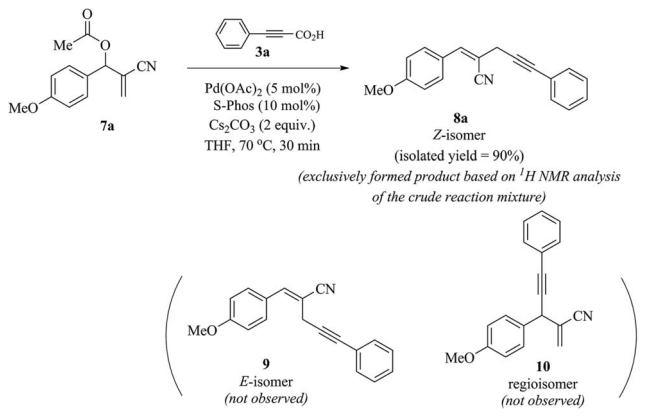
no (or a weak) NOE correlation between the CH_2 (allylic methylene) and CH (olefinic proton of the double bond). To provide the generality of the palladium-catalyzed allylic decarboxylative coupling, other acetates **2b–e** were treated with propiolic acids **3a–c** in the presence of 5 mol% of $Pd(OAc)_2$ and 10 mol% of *S*-Phos following the standard reaction procedure.[12] The crude products, obtained after usual work-up, were purified by silica gel chromatography to furnish pure (*E*)-1,5-diarylpent-1-en-4-yne derivatives **4b–i** in high yields (Table 1).

Encouraged by these results, we extended our studies to the acetates of Baylis–Hillman adducts derived from acrylonitrile. Accordingly, we subjected acetate **7a** (derived from Baylis–Hillman alcohol of benzaldehyde and acrylonitrile)[15] to decarboxylative coupling with phenyl propiolic acid **3a** using a catalyst combination of 5 mol% of $Pd(OAc)_2$ and 10 mol% of *S*-Phos following the standard reaction procedure.[16] Work-up and silica gel column chromatography provided exclusively (*Z*)-2-(4-methoxybenzylidene)-5-phenylpent-4-ynenitrile (**8a**) in 90% yield.[16] (Scheme 2). Proton NMR analysis of the crude reaction mixture did not indicate the presence of other regioisomer **10** or the corresponding *E*-isomer **9**. Again, formation of exclusively *Z*-isomer **8a** clearly suggests that, in acrylonitrile derived acetate **7a** case too, decarboxylative coupling happened regioselectively *via* exclusively S_N2' pathway. However, in contrast to the methyl acrylate derived acetates (**2a–e**, Scheme 1 and Table 1), in this case (acrylonitrile derived acetate **7a**), the isolated product **8a** was formed with a shift in the stereoselectively, *i.e.*, from *E* to *Z* (Scheme 2). The *Z*-stereochemistry in the case of **8a** was ascertained by 2D NOESY experiments where a strong NOE cross peak was observed between the CH_2 (allylic methylene proton) and CH (olefinic proton of the double bond), while there was no (or a weak) NOE correlation between the CH_2 (allylic methylene proton) and Ar-H_{ortho} (*ortho* proton of the benzene ring). To expand the substrate scope, we treated other acrylonitrile derived acetates **7a–f**[12] to stereoselective S_N2' allylic decarboxylative coupling with aryl propiolic acids **3a–c** (Table 2). Upon standard work-up and silica gel chromatographic purification, pure (*Z*)-1,5-diarylpent-1-en-4-yne derivatives **8b–k** were isolated in high yields with exclusively *Z*-stereochemistry (Table 2).[16]

Being fascinated by reversal in the stereochemistry when EWG (electron withdrawing group) was changed from methyl ester to cyano group and to understand the effect of other EWG on the stereochemical outcome in this Pd-catalyzed allylic decarboxylative coupling, we further extended our studies to the acetates of Baylis–Hillman adducts derived from other EWG (ketone, sulfone, other esters *etc.*). Accordingly, we subjected acetate **11** derived from Baylis–Hillman alcohol of benzaldehyde and ethyl vinyl ketone[11] to decarboxylative coupling with aryl propiolic acids **3a** and **3c** using standard reaction procedure.[16] Work-up and silica gel column chromatography provided corresponding products **14** and **15** exclusively with (*E*)-stereoselectivity (Table 3). Proton NMR analysis of the crude reaction mixture did not indicate the presence of *Z*-isomer. Similarly, acetate **12** derived from Baylis–Hillman alcohol of 4-methylbenzaldehyde and ethyl acrylate[11] provided corresponding products **16** and **17** exclusively with (*E*)-stereoselectivity (Table 3). Again, proton NMR analysis of the crude reaction mixture did not indicate the presence of *Z*-isomer. Finally, we extended our studies to Baylis–Hillman acetates **13a–b** derived from phenyl vinyl sulfone[11] to decarboxylative coupling with aryl propiolic acids **3a** and **3c** using standard reaction procedure.[12] Work-up and silica gel column chromatography provided corresponding products **18** and **19** exclusively with (*E*)-stereoselectivity (Table 3). Formation of exclusively *E*-isomers **14–19** clearly suggests that the decarboxylative coupling happened regioselectively *via* exclusively S_N2' pathway in the case of electron withdrawing groups (EWG) such as ethyl vinyl ketone (**11**), ethyl acrylate (**12**) and phenyl vinyl sulfone (**13**). However, unlike the cyano group (Scheme 2, Table 2), the electron withdrawing group, ethyl vinyl ketone (**11**) and phenyl vinyl sulfone (**13**) and ethyl acrylate (**12**) provided similar *E*-stereoselectivity like the methyl acrylate (Scheme 1, Table 1).

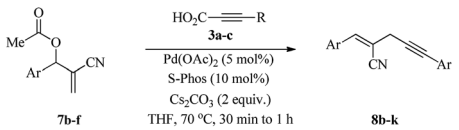


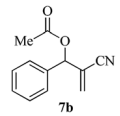
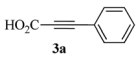
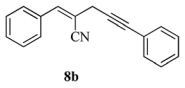
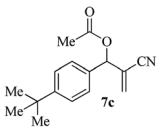
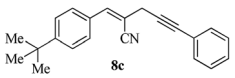
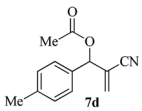
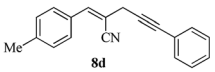
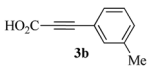
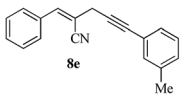
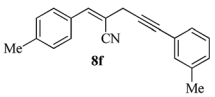
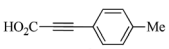
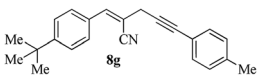
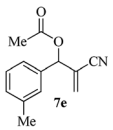
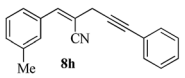
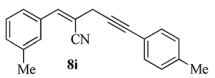
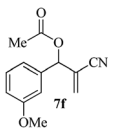
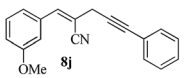
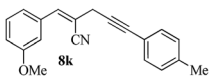
Scheme 1 Regio- and stereo-selective Pd-catalyzed allylic decarboxylative coupling of methyl acrylate derived acetate **2a** leading to the formation of exclusively *E*-isomer **4a**.[12]



Scheme 2 Regio- and stereo-selective Pd-catalyzed allylic decarboxylative coupling of acrylonitrile derived acetate **7a** leading to the formation of exclusively *Z*-isomer **8a**.[16]

Table 2 Regio- and stereo-selective Pd-catalyzed allylic decarboxylative coupling of acrylonitrile derived acetates **7a–f** leading to the formation of (*Z*)-1,5-diarylpent-1-en-4-ynes **8a–k**



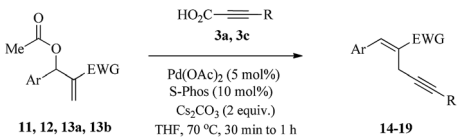
Entry	Acetate[a]	Propiolic acid	Product(s)[b]	Yield[c] (%)
1	 **7b**	 **3a**	 **8b**	79
2	 **7c**	**3a**	 **8c**	83
3	 **7d**	**3a**	 **8d**	87
4	**7b**	 **3b**	 **8e**	80
5	**7d**	**3b**	 **8f**	82
6	**7c**	 **3c**	 **8g**	81
7	 **7e**	**3a**	 **8h**	78
8	**7e**	**3c**	 **8i**	80
9	 **7f**	**3a**	 **8j**	82
10	**7f**	**3c**	 **8k**	84

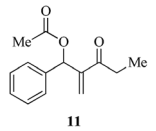
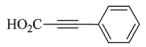
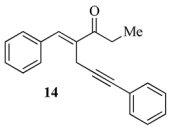
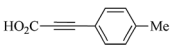
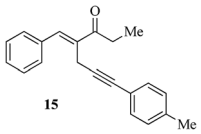
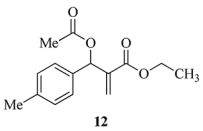
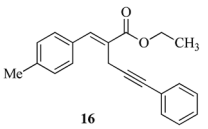
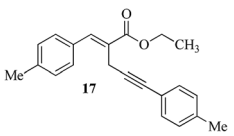
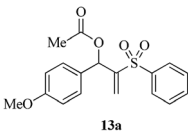
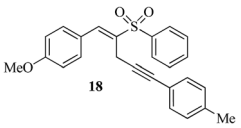
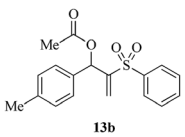
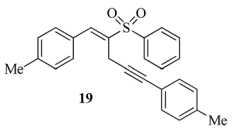
[a] Acetates of Baylis–Hillman alcohol **7a–f** were prepared by following the typical procedure described in ref. 15. [b] Reactions were carried out following the typical procedure described in ref. 16. [c] Isolated yields after chromatographic purification on silica gel.

Transition state models and plausible explanation of the stereochemical switch between the acetates derived from methyl acrylate and acrylonitrile

The stereochemical reversal from an ester group to a cyano group is consistent with earlier reports on other synthetic transformations using the Baylis–Hillman adducts.[6d,7,18] and with formation of similar products using other strategies. The *E*-selectivity in the case of aryl propiolates of Baylis–Hillman alcohols derived from methyl acrylate can possibly be explained using transition state models **TS-1a** and **TS-1b** (Scheme 3, Path-I). Ester, ethyl ketone and phenyl sulfone groups are relatively bulkier and exert more steric effect on aryl group in **TS-1a** than the methylene group on aryl group in

Table 3 Regio- and stereoselective Pd-catalyzed allylic decarboxylative coupling of Baylis–Hillman acetates derived from other EWG; ethyl vinyl ketone (**11**), ethyl acrylate (**12**) and phenyl vinyl sulfone (**13a**, **13b**)



Entry	Acetate[a]	Propiolic acid	Product(s)[b]	Yield[c] (%)
1	 **11**	 **3a**	 **14**	78
2	**11**	 **3c**	 **15**	80
3	 **12**	**3a**	 **16**	83
4	**12**	**3c**	 **17**	85
5	 **13a**	**3c**	 **18**	79
6	 **13b**	**3c**	 **19**	85

[a] Acetates of Baylis–Hillman alcohol **11**, **12**, **13a** and **13b** were prepared by following the typical procedure described in ref. 11. [b] Reactions were carried out following the typical procedure described in ref. 12. [c] Isolated yields after chromatographic purification on silica gel.

TS-1b. Therefore, product will form *via* more favoured transition state **TS-1b** leading to the formation of *E*-isomer. Similarly, The *Z*-selectivity in the case of aryl propiolates of Baylis–Hillman alcohols derived from acrylonitrile can be explained by transition state models **TS-2a** and **TS-2b** (Scheme 3, Path-II). Being a small linear group, CN group will have relatively lower steric effect on aryl group in **TS-2a** when compared to the methylene group on aryl group in **TS-2b**. Therefore, in this case (aryl propiolates of Baylis–Hillman alcohols derived from acrylonitrile) product will form *via* more favoured transition state **TS-2a** leading to the formation of *Z*-isomer.

Conclusions

In conclusion, we have developed a highly regio- and stereoselective palladium-catalyzed S_N2' allylic decarboxylative coupling between acetates of the Baylis–Hillman alcohols and aryl propiolic acids leading to the formation of important classes of 1,5-diarylpent-1-en-4-ynes with exclusively *E*- or *Z*-selectivity. Acetates of the Baylis–Hillman alcohols derived from alkyl acrylates, ethyl vinyl ketone and phenyl vinyl sulfone provide exclusively (*E*)-1,5-diarylpent-1-en-4-ynes and the acetates obtained from acrylonitrile provide exclusively (*Z*)-1,5-diarylpent-1-en-4-ynes.

Acknowledgements

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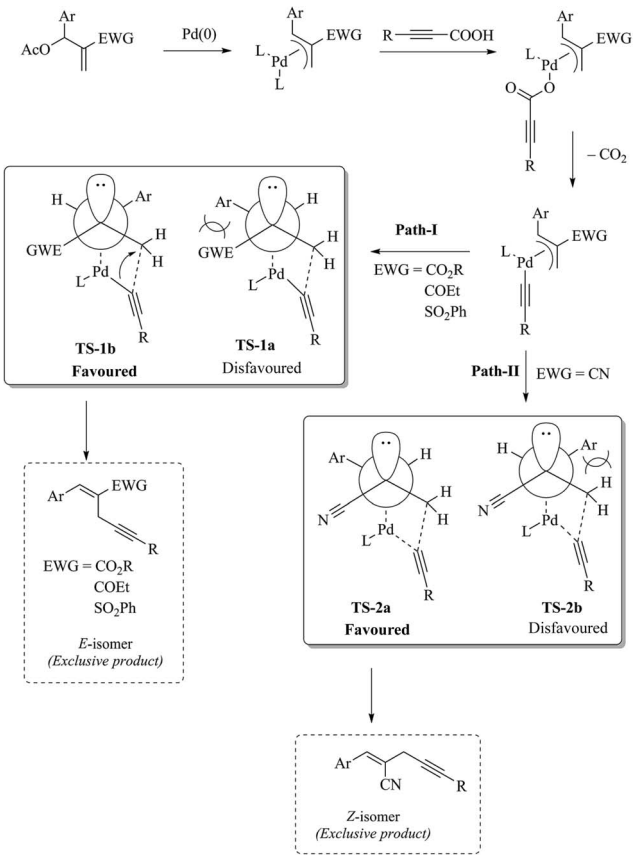

Scheme 3 Plausible mechanism and transition state models leading *E*-selectivity in the case of acetates derived from alkyl acrylates (**2a–e**, **12**) ethyl vinyl ketone (**11**) and phenyl vinyl sulfone and (**13a–b**) and *Z*-selectivity in the case of acrylonitrile derived acetates **7a–f**.

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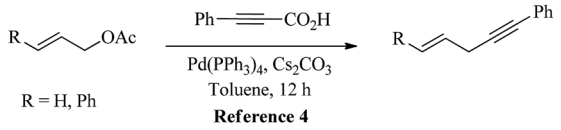
7 Very recently our work on a Palladium-catalyzed tandem intramolecular decarboxylative coupling *via* the allylic rearrangement of aryl propiolates derived from the Baylis–Hillman adducts leading to the formation important class of 1,5-diarylpent-1-en-4-ynes highly regio- and stereoselective manner has acceptedT. Satyanarayana, V. Dhanunjaya Naidu, M. Parthasarathy and N. Shashidhar, *Tetrahedron Lett.*, 2015, **56**, 2008–2013.

8 During their original study of intramolecular Pd-catalyzed decarboxylative allylic rearrangement of allyl alkynoates, Tunge and co-workers also reported two isolated examples of Pd-catalyzed decarboxylative allylic S_N2 type substitution between two allyl acetates and phenyl propiolic acid.[4] In their case, no any coupling involving S_N2'-type Pd-catalyzed decarboxylative allylic substitution was observed.



Reference 4

9 Pd-catalyzed allylic substitution involving the attack of various nucleophiles on an allylic Pd intermediate, providing S_N2 or S_N2' substitution products, has been investigated with great intensity.[17]

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11 Typical procedure for the synthesis of methyl-2-(acetoxy(4-methoxyphenyl)methyl)acrylate (**2a**): To a solution of methyl-2-(hydroxy(4-methoxyphenyl)methyl)acrylate (0.45 mmol) and pyridine (0.90 mmol) in dichloromethane (5 mL), was added acetyl chloride (0.54 mmol) at 0 °C. Reaction mixture was allowed to slowly warm to room temperature while stirring was continued. Upon reaction completion as judged by TLC, the resulting mixture was diluted with dichloromethane (10 mL), washed with 2 N HCl solution (5 mL), satd $NaHCO_3$ solution (5 mL) and dried over Na_2SO_4. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica (EtOAc–hexanes) to afford methyl-2-(acetoxy(4-methoxyphenyl)methyl)acrylate **2a** (0.42 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H), 3.68 (s, 3H), 3.77 (s, 3H), 5.86–5.87 (m, 1H), 6.37 (s, 1H), 6.63 (s, 1H), 6.86 (d, J = 8.79 Hz, 2H), 7.28 (d, J = 8.67 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 51.9, 55.2, 72.8, 113.8, 125.1, 129.1, 129.8, 139.7, 159.6, 165.4, 169.4; ESI-MS calc. for $C_{14}H_{17}O_5$ $[M + H]^+$ = 265; found: m/z 265.

12 Typical procedure for the synthesis of (*E*)-methyl-2-(4-methoxybenzylidene)-5-phenylpent-4-ynoate (**4a**): To a stirred solution of methyl-2-(acetoxy(4-methoxyphenyl)-methyl)acrylate **2a** (0.42 mmol) in dry THF (15 mL), were added $Pd(OAc)_2$ (0.021 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (0.042 mmol), Cs_2CO_3 (0.84 mmol) and 3-phenylpropiolic acid (0.50 mmol). The mixture was heated to 70 °C for 30 min. Upon reaction completion as judged by TLC, the resulting mixture was diluted with ethyl acetate (10 mL), washed with water (5 mL), brine (5 mL) and dried over Na_2SO_4. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica (EtOAc–hexanes) to afford (*E*)-methyl-2-(4-methoxybenzylidene)-5-phenylpent-4-ynoate **4a** (0.36 mmol, 85%). ^{1}H NMR (400 MHz, CDCl3): δ 3.62 (s, 2H), 3.85 (s, 3H), 3.86 (s, 3H), 6.97 (d, J = 8.83 Hz, 2H), 7.26–7.28 (m, 3H), 7.39–7.42 (m, 2H), 7.58 (d, J = 8.71 Hz, 2H), 7.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7, 52.2, 55.3, 80.8, 87.2, 114.1, 123.6, 125.4, 127.5, 127.7, 128.1, 131.7, 131.7, 140.5, 160.3, 168.0; ESI-MS calc. for $C_{19}H_{19}O_3$ $[M + H]^+$: 307; found: m/z 307.

13 Similar compounds were synthesized using the organometallic species involving different synthetic strategies such as the addition of (a) alkynyl Grignard on acetates of the Baylis–Hillman alcohols[19a] (b) alkynyl cuprate[19b] and alkynyl indium[19c] species on bromides derived from the Baylis–Hillman alcohols.

14 In 3-aryl-(2-substituted)-prop-2-enoates, the β-vinylic proton *cis* to the ester group of the *E*-isomers appear at $\delta \sim 7.7$ ppm while the δ-vinylic proton *trans* to the ester group of the *Z*-isomers appear at $\delta \sim 6.8$ ppm.[7,18]

15 Typical procedure for the synthesis of 2-cyano-1-(4-methoxyphenyl)allyl acetate (**7a**): To a stirred solution of 2-(hydroxy(4-methoxyphenyl)methyl)acrylonitrile (0.52 mmol), pyridine (1.04 mmol) in dichloromethane (5 mL), acetyl

chloride (0.63 mmol) was added at 0 °C. Reaction mixture was allowed to slowly warm to room temperature while stirring was continued. Upon reaction completion as judged by TLC, the resulting mixture was diluted with dichloromethane (10 mL), washed with 2 N HCl solution (5 mL), satd. $NaHCO_3$ solution (5 mL) and dried over Na_2SO_4. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica (EtOAc–hexanes) to afford 2-cyano-1-(4-methoxyphenyl)allyl acetate **7a** (0.69 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H), 3.81 (s, 3H), 5.97 (d, J = 1.39 Hz, 1H), 6.05 (d, J = 1.07 Hz, 1H), 6.28 (s, 1H), 6.90–6.93 (d, J = 8.78 Hz, 2H), 7.32 (d, J = 8.53 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 55.3, 74.0, 114.3, 116.3, 123.3, 127.7, 128.5, 131.5, 160.2, 169.2; ESI-MS calc. for $C_{13}H_{14}NO_3$ $[M + H]^+$ = 232; found: m/z 232.

16 Typical procedure for the synthesis of (*Z*)-2-(4-methoxybenzylidene)-5-phenylpent-4-ynenitrile (**8a**): To a stirred solution of 2-cyano-1-(4-methoxyphenyl)allyl acetate **7a** (0.43 mmol) in dry THF (15 mL), were added $Pd(OAc)_2$ (0.021 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (0.042 mmol), Cs_2CO_3 (0.86 mmol) and 3-phenylpropiolic acid (0.50 mmol). The mixture was heated to 70 °C for 30 min. Upon reaction completion as judged by TLC, the resulting mixture was diluted with ethyl acetate (10 mL), washed with water (5 mL), brine (5 mL) and dried over Na_2SO_4. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica (EtOAc–hexanes) to afford (*Z*)-2-(4-methoxybenzylidene)-5-phenylpent-4-ynenitrile (**8a**) (0.38 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.56 (d, J = 3.0, Hz, 2H), 3.85 (s, 3H), 6.92–6.95 (m, 2H), 7.31–7.34 (m, 3H), 7.45–7.49 (m, 2H), 7.74–7.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 55.4, 83.2, 85.5, 103.1, 114.2, 118.7, 122.8, 126.0, 128.3, 128.4, 130.6, 131.7, 143.8, 161.2; ESI-MS calc. for $C_{19}H_{16}NO$ $[M + H]^+$: 274; found: m/z 274.

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