Journal of Organometallic Chemistry 694 (2009) 571–575

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Gold(I)-catalyzed hydroarylation of allenes with indoles

Kristina L. Toups, Gordon T. Liu, Ross A. Widenhoefer *

Department of Chemistry, French Family Science Center, Duke University, 124 Science Drive, Durham, NC 27708-0346, United States

ARTICLE INFO

Article history:
Received 11 September 2008
Received in revised form 24 November 2008
Accepted 25 November 2008
Available online 7 December 2008

Keywords:
Intermolecular hydroarylation
Gold(I)-catalysis
Allene
Indole

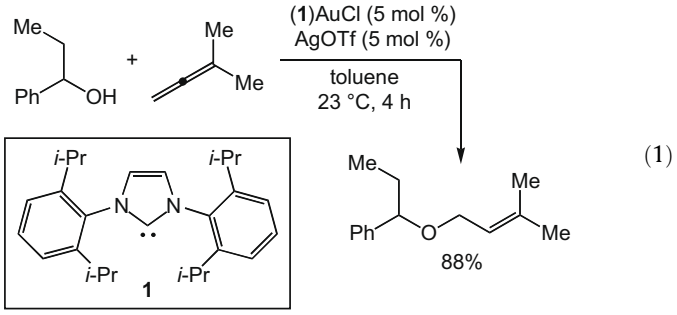
ABSTRACT

Reaction of a monosubstituted, 1,3-disubstituted, or tetrasubstituted allene with various indoles catalyzed by a 1:1 mixture of a gold(I) *N*-heterocyclic carbene complex and AgOTf at room temperature leads to hydroarylation with formation of 3-allyl-indoles in modest to good yield.

1. Introduction

The transition metal-catalyzed addition of the C–H bond of an arene across a C–C multiple bond is an attractive, atom-economical approach to the synthesis of functionalized arenes [1]. Although most of the effort in this area has been directed toward the hydroarylation of alkenes [2] and alkynes [3], cationic gold(I) complexes have been identified recently as effective catalysts for the intramolecular hydroarylation of allenes with electron-rich arenes [4,5], including the enantioselective intramolecular hydroarylation of allenes with indoles [6]. Lacking, however, are examples of the intermolecular hydroarylation of electronically unactivated allenes with arenes [7]. Only recently has Gagné disclosed the intermolecular hydroarylation of allenes catalyzed by a cationic gold(I) phosphite complex that was restricted to di- and trimethoxybenzenes [8].

We have recently reported that the gold(I) *N*-heterocyclic carbene complex (**1**)AuCl [**1** = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidine] is an effective pre-catalyst for the intermolecular hydrofunctionalization of allenes with oxygen [9] and nitrogen [10] nucleophiles (Eq. (1)). We have also demonstrated the effective intramolecular hydroarylation of indoles catalyzed by cationic gold(I) phosphine complexes [5]. On the basis of these precedents, we considered that (**1**)AuCl might also function as an effective pre-catalyst for the intermolecular hydroarylation of allenes with indoles. Indeed, here we report that mixtures of (**1**)AuCl and AgOTf catalyze the intermolecular hydroarylation of allenes with various indoles to form 3-allylic indoles resulting from attack of the indole C3 carbon atom at the allenyl sp^2 carbon atom(s).



(1)

2. Results and discussion

The conditions optimized for the catalytic intermolecular hydroalkoxylation and hydroamination of allenes proved effective for the intermolecular hydroarylation without further optimization [9,10]. Typically 1.5 equiv. of allene relative to indole were employed in these gold(I)-catalyzed hydroarylation reactions to offset any loss of allene under reaction conditions, although a number of reactions proceeded to completion with only 1.05 equiv. of allene. As an example of gold(I)-catalyzed hydroarylation, reaction of 1,2-dimethylindole with dimethyl 2,3-butadienylmalonate (**2**; 1.05 equiv.) catalyzed by a 1:1 mixture of (**1**)AuCl and AgOTf (5 mol%) at room temperature for 48 h led to isolation of (*E*)-3-allylic indole **3** in 82% yield as a single regio- and stereoisomer (Table 1, entry 1).

1,3-Disubstituted allenes **4**–**7** also underwent gold(I)-catalyzed hydroarylation to form the corresponding (*E*)-3-allylic indoles **8**–**11** in 48–89% yield with excellent diastereoselectivity (Table 1,

* Corresponding author. Tel.: +1 919 660 1533; fax: +1 919 660 1605.
E-mail address: ross.widenhoefer@duke.edu (R.A. Widenhoefer).

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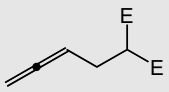
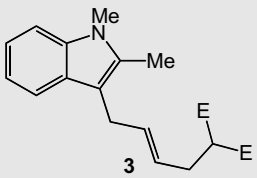
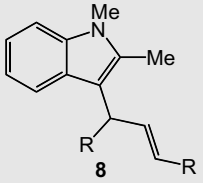
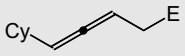
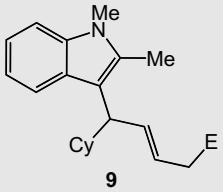
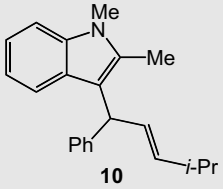
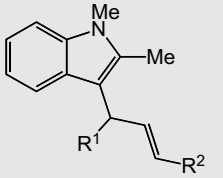
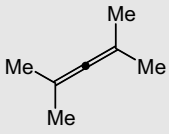
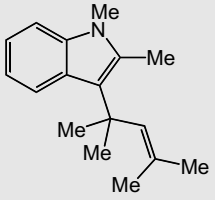
doi:10.1016/j.jorganchem.2008.11.058

Table 1
Intermolecular hydroarylation of allenes with 1,2-dimethylindole catalyzed by a 1:1 mixture of (**1**)AuCl and AgOTf in 1,4-dioxane at room temperature.

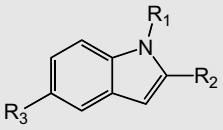
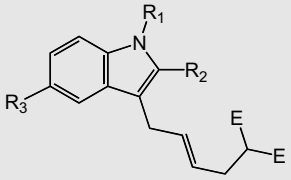
Entry	Allene	Allylic indole (s)	Allene equivalent	Time (h)	Yield (%)[a]
1	 **2** (E = CO_2Me)	 **3**	1.05	48	82
2	 **4** (R = *n*-pentyl)	 **8**	2.0	24	64
3	 **5** (E = CO_2Et)	 **9**	1.5	48	48
4	 **6**	 **10**	1.5	2	82
5	 **7**	 **11a** (R^1 = Ph, R^2 = Me) **11b** (R^1 = Me, R^2 = Ph)	1.5	2	89(~1:1.2)[b]
6	 **12**	 **13**	1.5	48	56

[a] Isolated yields for materials of >95% purity.
[b] Ratio determined by ^{1}H NMR analysis.

entries 2–5). In the case of differentially disubstituted allenes, the regioselectivity of hydroarylation was affected by both the electronic and steric nature of the allenyl substituents. As examples, hydroarylation of ethyl 5-cyclohexyl-3,4-pentadienoate (**5**) formed **9** with exclusive attack of indole at the more electron-rich cyclohexyl-bound allenyl carbon atom (Table 1, entry 3), whereas hydroarylation of 4-methyl-1-phenyl-1,2-pentadiene (**6**) formed **10** with exclusive attack of indole at the less sterically encumbered phenyl-bound allenyl carbon atom (Table 1, entry 4). In comparison, 1-phenyl-1,2-butadiene (**7**) underwent hydroarylation to form a 1:1.2 mixture of regioisomeric 3-allylic indoles **11a** and **11b** in good yield (Table 1, entry 5). Although 1,1-disubstituted and trisubstituted allenes failed to undergo efficient gold(I)-catalyzed hydroarylation, the tetrasubsituted allene 2,4-dimethyl-2,3-pentadiene (**12**) underwent gold(I)-catalyzed hydroarylation with 1,2-dimethylindole to form the 3-(1,1,3-trimethyl-2-butenyl) indole derivative **13** in 56% yield (Table 1, entry 6).

1,2-Dimethylindole was initially targeted as a nucleophile for the hydroarylation of allenes owing to the enhanced nucleophilicity of *N*-alkylindoles relative to *N*-unsubstituted indoles and because substitution at the indole C2 carbon precludes the formation of multiple addition products [2]. Nevertheless, indoles that lacked substitution at the N1 and/or C2 position or that possessed an electron-withdrawing group at the C5 position underwent efficient gold(I)-catalyzed hydroarylation, albeit at higher catalyst loading (Table 2). For example, treatment of 1-methylin-

Table 2
Intermolecular hydroarylation of substituted indoles with dimethyl 2,3-butadienylmalonate (**2**; 1.05 equiv.) catalyzed by a 1:1 mixture of (**1**)AuCl (10 mol%) and AgOTf (10 mol%) in 1,4-dioxane at room temperature for 48 h.

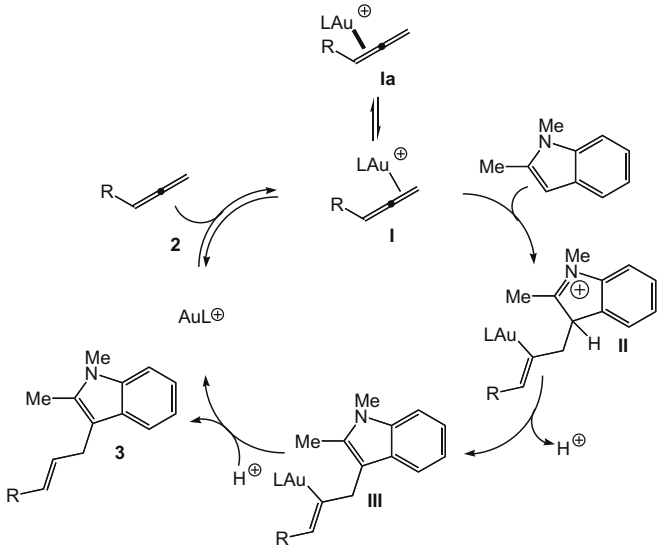
Entry	Indole	Allylic indole[a]	Yield(%)[b]
			
1[c]	R^1 = Me, R^2 = R^3 = H	**14**	61
2	R^1 = H, R^2 = Me, R^3 = H	**15**	67
3	R^1 = R^2 = H, R^3 = Me	**16**	53
4	R^1 = R^2 = Me, R^3 = Cl	**17**	77

[a] E = CO_2Me.
[b] Isolated yields for materials of >95% purity.
[c] Reaction time = 24 h.

dole with allene **2** (1.05 equiv.) catalyzed by a 1:1 mixture of (**1**)AuCl and AgOTf (10 mol%) at room temperature for 24 h led to isolation of (*E*)-3-allylic indole **14** in 61% yield as a single regio- and stereoisomer (Table 2, entry 1). Similarly, gold(I)-catalyzed reaction of allene **2** with 2-methylindole, 5-methylindole, or 5-chloro-1,2-dimethylindole at room temperature for 48 h led to isolation of (*E*)-3-allylic indoles **15**–**17** in 53–77% yield as single isomers (Table 2, entries 2–4).

The mechanism of gold(I)-catalyzed allene hydroarylation likely mirrors that of the related hydroalkoxylation and hydroamination processes [9,10]. Halide abstraction from (**1**)AuCl with AgOTf generates the active catalyst (**1**)AuOTf [11] that presumably undergoes displacement of the triflate ligand with allene to generate an equilibrating mixture of gold π-allene complexes **I** and **Ia** (Scheme 1). Outer-sphere attack of the indole on the gold allene complex **I** in which gold is positioned cis to the proximal alkyl group would form iminium ion **II**. Deprotonation of **II** followed by protonolysis of the Au–C bond of neutral gold vinyl species **III** would release the alkylated indole and regenerate the cationic gold NHC complex.

Despite the apparent similarity of the mechanisms, gold(I)-catalyzed allene hydroarylation displayed lower regioselectivity than did allene hydroalkoxylation or hydroamination. In particular, both



Scheme 1.

the hydroalkoxylation and hydroamination of 1-phenyl-1,2-propadiene (**7**) led to exclusive attack of the nucleophile at the more electron-rich methyl-bound allene terminus [9,10] as compared to the nonselective hydroarylation of **7**. We have previously invoked nucleophile-dependent kinetic trapping of equilibrating gold(I) π-allene complexes such as **I** and **Ia** under Curtin–Hammett conditions to account for the dependence of the nucleophile on the regioselectivity of gold(I)-catalyzed allene hydrofunctionalization [9], although, the origins of this nucleophile-dependent selectivity have not been fully delineated.

3. Conclusions

In summary, we have developed a gold(I)-catalyzed protocol for the hydroarylation of monosubstituted, 1,3-disubstituted, and tetrasubstituted allenes with indoles at room temperature. We continue to work toward the elucidation of the mechanisms of gold(I)-catalyzed hydrofunctionalization and toward the development of more effective allene hydroarylation processes.

4. Experimental

4.1. General methods

Reactions were performed under a nitrogen atmosphere employing standard Schlenk and drybox techniques unless specified otherwise. NMR spectra were obtained on Varian spectrometers operating at 400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR in $CDCl_3$ at 25 °C unless noted otherwise. IR spectra were obtained on a Nicolet Avatar 360-FT IR spectrometer. Gas chromatography was performed on a Hewlett-Pakard 5890 gas chromatograph equipped with a 15 m or 25 m polydimethylsiloxane capillary column and FID detector. Column chromatography was performed employing 230–400 mesh silica gel (Silicycle). Catalytic reactions were performed in sealed glass tubes under an atmosphere of dry nitrogen unless noted otherwise. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (EMD Chemicals Inc.). Room temperature is 23 °C.

All solvents were purchased from Aldrich or Acros in anhydrous form and used as received. All reagents, 2,4-dimethyl-2,3-pentadiene (**12**), 1-methylindole, 2-methylindole, and 5-methylindole were purchased from major suppliers and used as received. Dimethyl 2,3-butadienylmalonate (**2**) [10], 6,7-tridecadiene (**4**) [12], ethyl 5-cyclohexyl-3,4-pentadienoate (**5**) [13], 4-methyl-1-phenyl-1,2-pentadiene (**6**) [14], and 1-phenyl-1,2-butadiene (**7**) [10] were prepared employing published procedures.

4.2. Hydroarylation products

4.2.1. (E)-Dimethyl 2-(4-(1,2-dimethyl-1H-indol-3-yl)but-2-enyl)malonate (**3**)

A mixture of (**1**)AuCl (9.3 mg, 0.015 mmol) and AgOTf (3.9 mg, 0.015 mmol) was treated with a solution of 1,2-dimethylindole (24 mg, 0.31 mmol), **2** (58 mg, 0.31 mmol), and *n*-hexadecane (25 μL, 0.08 mmol) in 1,4-dioxane (0.6 mL) and the resulting suspension was stirred at room temperature for 48 h. Column chromatography of the reaction mixture (hexanes–EtOAc = 4:1) gave **3** (79 mg, 82%) as a pale yellow oil. TLC (hexanes–EtOAc = 5:1): R_f = 0.21. ^{1}H NMR: δ 7.49 (d, J = 7.6 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.18 (t, J = 7.1 Hz, 1H), 7.09 (t, J = 7.1 Hz, 1H), 5.72 (td, J = 6.9, 15.0 Hz, 1H), 5.46 (td, J = 7.4, 15.0 Hz, 1H), 3.70 (s, 6H), 3.68 (s, 3H), 3.44 (d, J = 7.6 Hz, 2H), 3.43 (t, J = 7.6 Hz, 1H), 2.61 (t, J = 7.6 Hz, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR: δ 169.6, 136.7, 133.2, 133.0, 127.8, 125.1, 120.7, 118.8, 118.3, 108.8, 108.6, 52.6, 52.1, 32.0, 29.6, 27.8, 10.3. IR (neat, cm^{-1}): 2952, 1749, 1733, 1615, 1435, 1231, 740. HRMS calcd. (found) for $C_{19}H_{23}O_4N$ (M^+): 329.1627 (329.1626).

The *E*-configuration of the C=C bond of **3** and of hydroarylation products **8**–**11** was established by the large ($J_{HH} \approx 15$ Hz) coupling constant of the olefinic hydrogen atoms.

4.2.2. (E)-1,2-Dimethyl-3-(7-tridecen-6-yl)-1H-indole (**8**)

TLC (hexanes–EtOAc = 20:1): R_f = 0.62. ^{1}H NMR: δ 7.60 (d, J = 8.0 Hz, 1H), 7.23 (dd, J = 0.8, 8.0 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 5.79 (dd, J = 6.8, 15.2 Hz, 1H), 5.44 (td, J = 5.6, 15.2 Hz, 1H), 3.64 (s, 3H), 3.46 (q, J = 7.2 Hz, 1H), 2.35 (s, 3H), 1.97 (q, J = 6.8 Hz, 2H), 1.83 (q, J = 8.0 Hz, 2H), 1.36–1.16 (m, 12H), 0.89–0.81 (m, 6H). ^{13}C{^{1}H} NMR: δ 133.8, 132.5, 129.4, 126.8, 120.3, 119.8, 118.4, 114.0, 108.7, 40.4, 35.4, 32.8, 32.1, 31.7, 29.7, 29.5, 28.0, 22.9, 22.8, 14.3, 10.8. IR (neat, cm^{-1}): 2924, 2854, 1469, 1407, 965, 735. HRMS calcd. (found) for $C_{23}H_{35}N$ (M^+): 325.2770 (325.2765).

4.2.3. (E)-Ethyl 5-cyclohexyl-5-(1,2-dimethyl-1H-idol-3-yl)pent-3-enoate (**9**)

TLC (hexanes–EtOAc = 5:1): R_f = 0.38. ^{1}H NMR: δ 7.58 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 6.01 (dd, J = 8.4, 15.2 Hz, 1H), 5.53 (td, J = 7.3, 14.8 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.62 (s, 3H), 3.18 (t, J = 9.4 Hz, 1H), 3.04–2.93 (m, 2H), 2.33 (s, 3H), 2.04–0.67 (m, 11H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR: δ 172.2, 136.8, 136.2, 132.7, 126.4, 121.5, 120.2, 119.4, 118.3, 112.5, 108.6, 60.4, 47.7, 41.0, 38.1, 32.4, 21.5, 29.7, 29.5, 26.6, 26.4, 14.2, 10.7. IR (neat, cm^{-1}): 2918, 2848, 1730, 1471, 1445, 1368, 1300, 1161, 1126, 1098, 964, 739. HRMS calcd. (found) for $C_{23}H_{31}O_2N$ (M^+): 353.2355 (353.2362).

4.2.4. (E)-1,2-Dimethyl-3-(4-methyl-1-phenylpent-2-enyl)-1H-indole (**10**)

TLC (hexanes–CH_2Cl_2 = 9:1): R_f = 0.36. ^{1}H NMR: δ 7.34 (d, J = 8.0 Hz, 1H), 7.28–7.08 (m, 7H), 6.94 (t, J = 7.2 Hz, 1H), 5.98 (dd, J = 6.8, 15.2 Hz, 1H), 5.45 (dd, J = 6.8, 15.2 Hz, 1H), 4.92 (d, J = 7.6 Hz, 1H), 3.61 (s, 3H), 2.37–2.27 (m, 1H), 2.30 (s, 3H), 1.00 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (125.7 MHz): δ 144.6, 138.6, 136.8, 133.2, 128.9, 128.2, 128.1, 127.1, 125.8, 120.4, 119.6, 118.7, 113.0, 108.6, 45.0, 31.1, 29.8, 29.6, 22.7, 10.8. IR (neat, cm^{-1}): 2955, 1600, 1492, 1470, 1367, 971, 736, 699. HRMS calcd. (found) for $C_{22}H_{25}N$ (M^+): 303.1987 (303.1987).

4.2.5. Compounds **11a** and **11b** (1:1.2 mixture of regioisomers)

TLC (hexanes–CH_2Cl_2 = 9:1): R_f = 0.36. ^{1}H NMR (**11a**): δ *7.65–6.94* (m, 9H), 6.09 (qdd, J = 1.2, 7.4, 15.2 Hz, 1H), 5.51 (dqd, J = 1.2, 7.4, 15.2 Hz, 1H), 4.95 (d, J = 7.2 Hz, 1H), 3.67 (s, 3H), 2.34 (s, 3H), 1.74–1.72 (m, 3H). ^{1}H NMR (**11b**): δ *7.65–6.94* (m, 9H), 6.62 (dd, J = 5.6, 16.0 Hz, 1H), 6.45 (dd, J = 1.6, 16.0 Hz, 1H), 3.99–3.91 (m, 1H), 3.67 (s, 3H), 2.40 (s, 3H), 1.59 (d, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz; **11a** + **11b**): δ 144.4, 138.0, 136.8, 135.4, 133.0, 132.2, 128.5, 128.1, 127.7, 126.9, 126.8, 126.5, 126.1, 126.0, 125.8, 120.4, 119.5, 119.3, 119.3, 118.7, 118.6, 114.1, 112.9, 108.7, 60.4, 45.2, 45.1, 22.9, 29.4, 21.1, 20.5, 18.0, 14.2, 10.6. IR (neat, cm^{-1}): 3024, 2927, 1612, 1470, 1367, 966, 736, 696. HRMS calcd. (found) for $C_{20}H_{21}N$ (M^+): 275.1674 (275.1673).

4.2.6. 3-(2,4-Dimethylpent-3-en-2-yl)-1,2-dimethyl-1H-indole (**13**)

TLC (hexanes–EtOAc = 5:1): R_f = 0.48. ^{1}H NMR: δ 7.81 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 5.62–5.60 (m, 1H), 3.61 (s, 3H), 2.40 (s, 3H), 1.66 (d, J = 1.6 Hz, 3H), 1.58 (s, 6H), 1.17 (d, J = 1.2 Hz, 3H). ^{13}C{^{1}H} NMR: δ 136.6, 136.3, 131.9, 131.0, 121.1, 119.6, 118.0, 108.4, 36.9, 31.9, 29.7, 29.3, 26.7, 18.2, 12.4. IR (neat, cm^{-1}): 2924, 1465, 1367, 1071, 735, 669, 650. HRMS calcd. (found) for $C_{17}H_{23}N$ (M^+): 241.1831 (241.1831).

4.2.7. (E)-dimethyl 2-(4-(1-methyl-1H-indol-3-yl)but-2-enyl)malonate (**14**)

TLC (hexanes–EtOAc = 4:1): R_f = 0.28. ^{1}H NMR: δ 7.53 (d, J = 8.0 Hz, 1H), 7.29–7.16 (m, 2H), 7.08 (t, J = 7.2 Hz, 1H), 6.79 (s, 1H), 5.78 (td, J = 7.0, 15.2 Hz, 1H), 5.53 (td, J = 7.4, 15.2 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 6H), 3.44 (t, J = 7.4 Hz, 1H), 3.43 (d, J = 7.2 Hz, 2H), 2.63 (t, J = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR: δ 169.7, 137.4, 132.8, 127.9, 126.6, 126.1, 121.7, 119.3, 118.9, 113.3, 109.3, 52.7, 52.1, 32.8, 32.0, 28.7. IR (neat, cm^{-1}): 2953, 1733, 1435, 1231, 1152, 971, 740. HRMS calcd. (found) for $C_{18}H_{21}NO_4$ (M^+): 315.1471 (315.4173).

4.2.8. (E)-dimethyl 2-(4-(2-methyl-1H-indol-3-yl)but-2-enyl)malonate (**15**)

TLC (hexanes–EtOAc = 7:3): R_f = 0.30. ^{1}H NMR: δ 7.85 (s, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.25 (dd, J = 1.0, 7.8 Hz, 1H), 7.12 (dt, J = 1.2, 7.0 Hz, 1H), 7.07 (dt, J = 1.0, 6.7 Hz, 1H), 5.71 (dtd, J = 1.2, 6.2, 15.2 Hz, 1H), 5.45 (td, J = 7.3, 15.2 Hz, 1H), 3.67 (s, 6H), 3.42 (t, J = 7.6 Hz, 1H), 3.40 (d, J = 7.2 Hz, 2H), 2.61 (t, J = 7.1 Hz, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR: δ 169.7, 135.4, 132.9, 131.4, 128.8, 125.3, 121.1, 119.3, 118.4, 110.4, 109.6, 52.6, 52.2, 32.0, 27.6, 11.7. IR (neat, cm^{-1}): 3399, 2953, 2360, 1731, 1435, 1232, 1154, 970, 742. HRMS calcd. (found) for $C_{18}H_{21}NO_4$ (M^+): 315.1471 (315.1473).

4.2.9. (E)-dimethyl 2-(4-(5-methyl-1H-indol-3-yl)but-2-enyl)malonate (**16**)

TLC (hexanes–EtOAc = 4:1): R_f = 0.19. ^{1}H NMR: δ 7.95 (s, 1H), 7.38 (s, 1H), 7.28 (t, J = 8.2 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.94 (d, J = 2.0 Hz, 1H), 5.84 (td, J = 7.1, 15.2 Hz, 1H), 5.58 (td, J = 7.4, 15.2 Hz, 1H), 3.74 (s, 6H), 3.50 (t, J = 7.8 Hz, 1H), 3.47 (d, J = 6.4 Hz, 2H), 2.69 (t, J = 7.2 Hz, 2H), 2.51 (s, 3H). ^{13}C{^{1}H} NMR: δ 169.7, 135.0, 132.8, 128.6, 127.8, 126.1, 123.8, 122.0, 118.9, 114.4, 111.0, 52.7, 52.2, 32.1, 28.8, 21.7. IR (neat, cm^{-1}): 3409, 2953, 2358, 1731, 1434, 1228, 1153, 971, 794. HRMS calcd. (found) for $C_{18}H_{21}NO_4$ (M^+): 315.1471 (315.1473).

4.2.10. (E)-dimethyl 2-(4-(5-chloro-1,2-dimethyl-1H-indol-3-yl)but-2-enyl)malonate (**17**)

TLC (hexanes–EtOAc = 7:3): R_f = 0.29. ^{1}H NMR: δ 7.39 (d, J = 1.8 Hz, 1H), 7.13 (dd, J = 0.8, 8.8 Hz, 1H), 7.07 (dd, J = 1.6, 9.0 Hz, 1H), 5.64 (ttd, J = 1.2, 6.0, 15.2 Hz, 1H), 5.39 (ttd, J = 1.6, 7.2, 15.2 Hz, 1H), 3.66 (s, 6H), 3.62 (s, 3H), 3.39 (t, J = 7.6 Hz, 1H), 3.35 (d, J = 5.6 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR: δ 169.6, 135.2, 134.8, 132.6, 128.9, 125.5, 124.6,

120.8, 117.7, 109.7, 108.7, 52.6, 52.1, 32.0, 29.9, 27.7, 10.4. IR (neat, cm^{-1}): 2952, 1734, 1476, 1435, 1231, 1152, 792. HRMS calcd. (found) for $C_{19}H_{22}NO_4Cl$ (M^+): 363.1237 (363.1238).

4.3. Control experiments

Control experiments established that both (**1**)AuCl and AgOTf were required for effective hydroarylation catalysis and ruled out the presence of acid-, silver-, or ligand-catalyzed pathways for allene hydroarylation. Treatment of a mixture of 1,2-dimethylindole (29 mg, 0.20 mmol) and **6** (48 mg, 0.37 mmol) with 1) (**1**)AuCl (6.2 mg, 0.010 mmol), 2) **1** (3.9 mg, 0.010 mmol) and AgOTf (2.6 mg, 0.010 mmol), or 3) **1** (3.9 mg, 0.010 mmol) and triflic acid (1.5 mg, 0.010 mmol) in each case resulted in no consumption of 1,2-dimethylindole after 2 h at room temperature.

Acknowledgements

The authors thank the NSF (CHE-0555425), NIH (GM-080422), and Johnson&Johnson for support of this research. KLT was supported in part though a Pharmacological Sciences Training Program fellowship. We thank Prof. Michael Gagné (UNC–Chapel Hill) for disclosing his results regarding the gold(I)-catalyzed hydroarylation of allenes prior to publication.

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