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Syntheses of vinylindoles via a Brønsted acid catalyzed highly regio- and stereoselective *cis*-hydroarylation of ynamides☆

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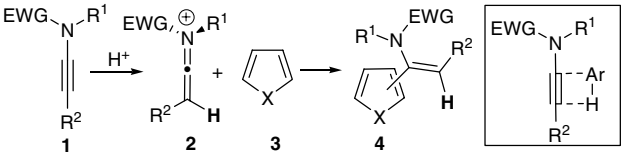
Abstract—A highly regio- and stereoselective Brønsted acid-catalyzed coupling of ynamides and indoles is described. This process is the equivalent of hydroarylation of ynamides and leads to the efficient syntheses of vinylindoles. Diels–Alder reaction between the vinylindoles and DMAD afforded carbazole derivatives in good yields.

Indoles are of paramount importance, because they are ubiquitous structural motifs in natural molecules and pharmaceuticals.[1] As a result, expeditious and selective functionalizations of this ring system are of great interest to both synthetic organic chemists and medicinal chemists.[1,2] Vinylindoles are viable key building blocks that are frequently employed in the syntheses of alkaloids and biologically important heterocycles.[3] The existing methods for the synthesis of vinylindoles, however, have serious limitations which are characterized by the necessity to introduce electron-withdrawing protecting groups and/or reactive functional groups, such as halogen, acyl groups, phosphoranes, or amines on to the heterocycles prior to the vinylation.[1b,4a] Thus, developing a general method for direct vinylation of unfunctionalized indoles holds great synthetic potential.[4]

Recently, ynamides have emerged as a class of highly versatile reagents and have been employed for the construction of an array of structurally diverse carbocycles, heterocycles, and organic building blocks.[5–7] Early this year, we reported a Brønsted acid-catalyzed intramolecular ynamide-arene cyclization by taking advantage of in situ generated active ketene iminium intermediates, and its application to the total synthesis of β-carboline indole alkaloids.[7a] Based on the nucleophilic property



Scheme 1. Synthetic design.

of heteroarenes, the possibility of intermolecular trapping of the in situ generated ketene iminium intermediates **2** with heteroarenes **3** was envisioned, and is outlined in Scheme 1. Herein, we report a Brønsted acid-catalyzed highly regio- and stereoselective *cis*-hydroarylation of ynamides, which provides a method for the direct construction of vinyl indoles.

In order to establish the feasibility of this methodology, readily available ynamide **5** and indole were employed as the model substrates for the initial screening. The reactions were conducted employing ynamide **5** and indole in a 1:1.4 ratio under various potential catalytic systems (Table 1).

The initial efforts were focused on alkynophilic transition metal π-acids, such as $PtCl_2$ and $PtCl_4$, which proved to be inefficient.[6b] In these cases, very complex reaction mixtures were obtained, in which only trace amounts of the desired products were observed by ^1H NMR analysis. A series of Brønsted acids were then examined, leading to the identification of Tf_2NH as the most active catalyst. At room temperature, with 5% loading of Tf_2NH, the desired vinylindole **6** was separated in 84%

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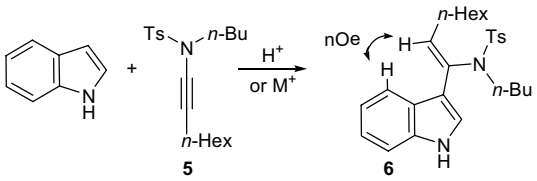
Table 1. Catalysts screening



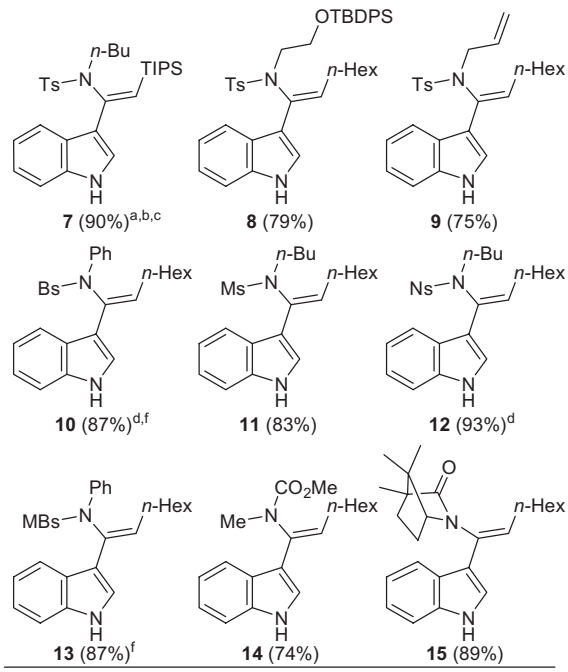
Entry	M^+ [mol%]	Solvent	Temp	Yield[a]
1	$PtCl_2$ [10%]	Toluene	80 °C	ND
2	$PtCl_4$ [10%]	Toluene	80 °C	ND
3	PNBSA [10%][b]	Toluene	80 °C	ND
4	Tf_2NH [5%]	CH_2Cl_2	rt	84%[c]
5	Tf_2NH [10%]	CH_2Cl_2	−35 °C	81%[d]

[a] Isolated yields.
[b] PNBSA = *p*-nitrobenzenesulfonic acid.
[c] *Z*/*E* = 6:1 by ^1H NMR.
[d] *Z*/*E* > 30:1 by ^1H NMR.

yield (Table 1, entry 4).[7a,8] This hydroarylation is highly regioselective furnishing exclusively the expected C-3 vinylation product **6**.[1b,2] This reaction, however, is moderately stereoselective when conducted at room temperature favoring the formation of *Z*-enamide as the major isomer with a *Z*/*E* ratio of 6:1. This stereoselectivity can be explained by the rationale that indole prefers to approach the ketene iminium inter- mediate **2** from the less hindered side in order to avoid steric interaction with R^2 group (Scheme 1), which is consistent with our previous observations.[7a]. To our delight, formation of the *E*-isomer was almost completely suppressed when the reaction was conducted at −35 °C with a relatively higher loading of the catalyst (Table 1, entry 5).[9] The fact that Tf_2NH is a better catalyst for this transformation is somewhat unexpected, since PNBSA gave superior results in the intramolecular version of this transformation described in my earlier work.[7a]

This new methodology has some distinct advantages over the existing methods: (1) There is no need to introduce protecting group on the indole nitrogen, (2) the hydroarylation employs unfunctionalized indole, which circumvents the need to introduce other functional groups, (3) the reaction is catalyzed by a Brønsted acid instead of a transition metal, and (4) more importantly, an enamide motif, which is otherwise difficult to introduce, is conveniently generated and can be employed for various transformations.[10,11]

The generality of this hydroarylation protocol was first tested by the reactions using indole and various ynamides, as shown in Scheme 2. Relatively acid-sensitive functional groups, such as silyl, silyl ether, and allyl, survived the reaction conditions affording the desired vinylindoles in good yields (**7**–**9**). A series of electronically different sulfonyl-substituted ynamides (such as Bs, Ns, Ms, and MBs) were also successfully employed in this transformation with comparable efficiency (**10**–**13**). For vinylindoles **10** and **12**, however, the reactions were observed to be slower, and resulted in a relatively larger amount of the *E*-isomers. This can be explained by the fact that lone pair electrons on the ynamide nitrogen were

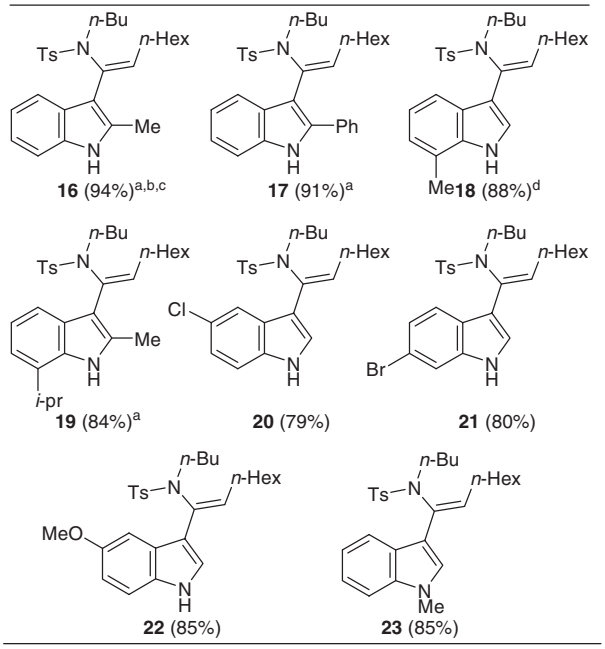


a) All reactions were conducted at -35 °C, using ynamides and indole at the ratio of 1/1.4 with 10 mol% Tf_2NH in CH_2Cl_2 (0.1M).
b) Isolated yields for all entries.
c) *Z*/*E* >25:1 by ^1H NMR unless othewise indicated.
d) *Z*/*E* = 10:1 by ^1H NMR.
e) *Z*/*E* = 13:1 by ^1H NMR.
f) Bs = Benzenesulfonyl, PMBs = *P*-methoxybenzenesulfonyl.

Scheme 2. Coupling of indole with different ynamides.

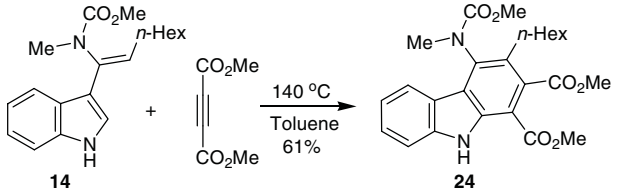
more delocalized due to the electron-withdrawing effect of the phenyl and nitro substituents.[7a] Thus, relatively higher energy was required to generate the ketene iminium intermediates from the protonation of these two ynamide precursors. In addition to sulfonyl-substituted ynamides, carbamate-derived ynamide was also a viable substrate giving the desired vinylindole **14** in 74% yield. The anticipated vinylindole **15** was isolated in 89% yield when an aza-camphor-derived ynamide was tested.

The scope of this method toward various substituted indole derivatives was then studied using ynamide **5** as the model substrate, as summarized in Scheme 3. A series of indoles with electronically neutral alkyl and aryl substitutions, including 2-methylindole, 2-phenylindole, 7-methylindole, and 2-methyl-7-isopropylindole, were first investigated. The hydroarylation processes were proved to be very efficient in these cases giving the desired vinyl- indoles in good to excellent yields (**16**–**19**). It was also observed that sterically demanding C-2 substituted indoles are less reactive for the vinylation process (**16**, **17**, and **19**), thus requiring a much higher temperature (25 °C) for the reactions to proceed at a reasonable speed. Intriguingly, though conducted at room temperature, the *Z*-enamides were the exclusive isomers produced in these reactions. This can be attributed to the increased steric interaction between the C-2 substituents and the approaching ketene iminium intermediates. This transformation can also tolerate a variety of functional groups, such as chloro, bromo, and methoxy (**20**–**22**). Finally, an *N*-protected indole was also



a) Reactions were conducted at rt.
b) Isolated yields for all entries.
c) *Z*/*E* > 25:1 by ^{1}H NMR.
d) Reactions were conducted at -35 °C unless othewise indicated.

Scheme 3. Coupling of substituted indole with ynamide **5**.



Scheme 4. Diels–Alder reaction of vinylindole **14**.

tested, leading to the efficient synthesis of *N*-methyl vinylindole **23** in comparable yields.

The most attractive feature of this methodology is that the products can be considered synthetic equivalents to masked dienamides, which are excellent substrates for [4+2] cycloaddition reactions.[12,13] At elevated temperatures, the Diels–Alder reaction of vinylindole **14** with DMAD was quite efficient, affording the oxidized cycloadduct carbazole **24** in 61% yield, as shown in Scheme 4.[14]

In conclusion, a Brønsted acid-catalyzed hydroarylation of ynamides was developed, leading to the efficient construction of biologically and synthetically useful vinylindoles with high regio- and stereochemical control. Diels–Alder reactivity of the vinylindole derivative was probed and found to be efficient. Further applications of the methodology to the synthesis of alkaloids are currently underway in this laboratory.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.07.098.

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9. Representative procedure: Synthesis of vinylindole **6**: A solution of ynamide **5** (168.0 mg, 0.5 mmol) and indole (82.0 mg, 0.7 mmol) in 5 mL of dry methylene chloride was cooled to −35 °C. To this stirring mixture, a solution of Tf_2NH (14.0 mg, 0.05 mmol) in 0.35 mL of CH_2Cl_2 was added slowly, leading to a bright yellow solution which became darker as the reaction proceeded. The reaction was kept at −35 °C for 1 h with the reaction process monitored by TLC analysis. Upon completion, the reaction mixture was warmed up to room temperature, and the stir was continued for another 30 min. Several drops of triethylamine were then added to the reaction mixture to neutralize the acid, resulting in a colorless solution. The solution was concentrated in vacuo, and the residue was purified by silica gel column flash chromatography [gradient eluent: 10–25% EtOAc in hexane] to give vinylindole **6** (183.0 mg, 81%) as a white solid. $R_f = 0.30$ (20% EtOAc in Hexane); mp 140–142 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.47 (br s, 1H), 7.82 (d, 1H, $J = 8.0$ Hz), 7.77 (d, 2H, $J = 8.0$ Hz), 7.39 (d, 1H, $J = 8.0$ Hz), 7.33 (d, 2H, $J = 8.0$ Hz), 7.22 (t, 1H, $J = 8.0$ Hz), 7.19 (t, 1H, $J = 8.0$ Hz), 6.86 (d, 1H, $J = 2.5$ Hz), 6.16 (t, 1H, $J = 7.5$ Hz), 3.50–3.38 (m, 2H), 2.48 (s, 3H), 2.32–2.05 (m, 2H), 1.59–1.42 (m, 4H), 1.42–1.21 (m, 8H), 0.96 (t, 3H, $J = 7.0$ Hz), 0.86 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 143.9, 138.9, 137.2, 132.7, 130.7, 130.1, 128.0, 126.1, 124.7, 122.8, 120.8, 120.4, 115.5, 112.0, 49.5, 32.3, 31.6, 30.1, 29.9, 29.7, 23.2, 21.8, 20.6, 14.4, 14.0; IR (film) cm^{-1} 3385 (m), 2958 (s), 2927 (s), 1459 (w), 1338 (m), 1159 (s), 1089 (m); mass spectrum (ESI): *m/e* (% relative intensity) 475.4 (100) $(M+Na)^+$, 453.4 (16) $(M+H)^+$, 365.2 (27), 337.2 (23), 285.2 (15); *m/e* calcd for $C_{27}H_{36}N_2O_2SNa$ 475.2390, found 475.2398.

   Characterization of selected new compounds: Vinylindole **7** (58 mg, 90% yield): $R_f = 0.33$ (20% EtOAc in hexane); mp 160–162 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.17 (br s, 1H), 7.96–7.90 (m, 1H), 7.44 (d, 2H, $J = 8.1$ Hz), 7.44–7.33 (m, 1H), 7.25–7.18 (m, 4H), 6.13 (s, 1H), 6.08 (d, 1H, $J = 2.7$ Hz), 3.61 (t, 2 H, $J = 7.8$ Hz), 2.45 (s, 3H), 1.76–1.46 (m, 5H), 1.29 (d, 18H, $J = 7.5$ Hz), 0.89 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 167.0, 161.4, 159.8, 152.9, 151.4, 150.6, 146.6, 146.1, 144.3, 143.6,140.5, 135.0, 73.9, 54.4, 45.0, 44.0, 43.1, 37.3, 36.0; IR (film) cm^{-1} 3378 (m), 2942 (s), 2866 (s), 1596 (m), 1344 (m), 1156 (s), 773 (s); mass spectrum (ESI): *m/e* (% relative intensity) 547.3 (100) $(M+Na)^+$, 525.3 (23) $(M+H)^+$; *m/e* calcd for $C_{30}H_{44}N_2O_2SSiNa$ 547.2785, found 547.2784.

   Vinylindole **16** (22 mg, 94% yield): $R_f = 0.35$ (20% EtOAc in hexane); mp 89–90 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.16 (br s, 1H), 7.67 (d, 1H, $J = 7.8$ Hz), 7.65 (d, 2H, $J = 8.1$ Hz), 7.33 (d, 1H, $J = 7.8$ Hz), 7.22 (d, 2H, $J = 8.1$ Hz), 7.13 (dt, 1H, $J = 0.9$, 7.2 Hz), 7.05 (dt, 1H, $J = 0.9$, 7.2 Hz), 5.69 (t, 1H, $J = 7.2$ Hz), 3.36 (t, 2H, $J = 7.8$ Hz), 2.48 (s, 3H), 2.41 (s, 3H), 2.19 (q, 2H, $J = 7.2$ Hz), 1.71–1.58 (m, 2H), 1.56–1.20 (m, 10H), 0.96 (t, 3H, $J = 6.9$ Hz), 0.90 (t, 3H, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 143.5, 138.6, 136.0, 135.4, 135.1, 130.0, 129.7, 128.6, 127.7, 121.7, 120.2, 119.8, 111.9, 110.7, 49.7, 32.2, 31.4, 30.0, 29.9, 29.8, 23.2, 21.7, 20.7, 14.4, 14.1, 13.2; IR (thin film) cm^{-1} 3385 (m), 2958 (s), 2928 (s), 1460 (m), 1334 (m), 1152 (s); mass spectrum (ESI): *m/e* (% relative intensity) 489.4 (100) $(M+Na)^+$, 467.4 (20) $(M+H)^+$; HRMS (ESI) calcd for $C_{28}H_{39}N_2O_2S$ 467.2727, found 467.2726.
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14. Synthesis of Carbazole **24**: A solution of vinylindole **14** (15.0 mg, 0.048 mmol) and DMAD (14.0 mg, 0.10 mmol) in toluene (0.5 mL) was heated at 140 °C in a sealed tube. The reactions were monitored by TLC analysis. Upon completion, the solution was cooled to room temperature. Evaporation of the solvent under reduced pressure afforded a residue which was purified by silica gel flash chromatograph to afford carbazole **24** as a light yellow solid (13.2 mg, 61 % yield). $R_f = 0.56$ (33% EtOAc in hexane); 186–187 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (br s, 1H), 7.87 (d, 1H, $J = 8.1$ Hz), 7.60–7.50 (m, 2H), 7.36–7.30 (m, 1H), 4.06 (s, 3H), 4.02 (s, 3H), 3.58 (s, 3H), 3.40 (s, 3H), 2.78–2.58 (m, 2H), 1.64–1.26 (m, 8H), 0.94 (t, 3H, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 166.4, 156.6, 140.4, 139.9, 139.5, 134.5, 129.1, 127.6, 122.7, 122.0, 121.2, 120.5, 111.4, 108.6, 53.3, 52.9, 52.7, 36.5, 31.7, 31.3, 30.2, 29.2, 22.7, 14.3; IR (film) cm^{-1} 3346 (w), 2953 (m), 1996 (s), 1210 (m); mass spectrum (ESI): *m/e* (% relative intensity) 477.2 (100) $(M+Na)^+$; *m/e* calcd for $C_{25}H_{30}N_2O_6Na$ 477.1996, found 477.1994.