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Hg(OTf)$_2$-Catalyzed Direct Vinylation of Tryptamines and Versatile Applications for Tandem Reactions†

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Graphical Abstract

We have developed a unique catalytic protocol for direct gem-vinylation of tryptamine derivatives employing Hg(OTf)$_2$ as the optimum catalyst. The intermolecular vinylations with a series of aromatic acetylenes proceeded under ambient temperature at the C2 positions of indoles with high functional group tolerance. Based on the mechanistic insights, we further developed the tandem reactions successfully constructing a quaternary center.

Introduction

The indole ring system is ubiquitous in natural products and has been exploited as a privileged motif for the development of pharmaceuticals and biologically active agents. During the course of our synthesis on naturally occurring alkaloids and their analogues, we sought to develop a catalytic protocol that allows gem-selective vinylation of tryptamine derivatives with intentions to minimize the number of steps and amount of waste. Metal-catalyzed cross-couplings are one of the most reliable means to install alkenyl groups onto aromatic rings with exquisite control in regio-selectivity and olefin geometry. However, it requires premodifications of both coupling partners (Scheme 1a). The direct C-H functionalization of aromatic systems without the need for premodifications emerged as a direct and atom-economical alternative to cross-couplings and the Mizoroki-Heck reaction. For example, the Fujiwara-Moritani reaction offers direct oxidative functionalization of arenes, yielding trans-substituted product as the major olefin isomer (Scheme 1b). With regards to catalytic direct vinylation of an indole system, two types of approaches have been exploited to date. The first approach involves an oxidative addition, which usually takes place at the electron-rich C3 position of indoles and thereby yields a C3-vinylated product. In most cases, catalytic functionalization of C-H at the C2 position poses a difficult problem and often requires a directing group at the N1 or C3 positions, entailing high temperature conditions (Scheme 1c). The
other approach employs a metal activator of alkynes, generating electrophilic metal complexes and subsequent hydroarylation reactions. In 2007, Echavarren and coworkers reported the direct C2 vinylation of 3-substituted indoles using a cationic gold (I)-catalyst. This conversion offers a rare example of the gem-selective C-H alkenylation at the indole C2 position (Scheme 1d), while related manipulations at the pyrrole C2 position have been explored a bit more due to the distinct regio-selectivities between indole and pyrrole systems as a nucleophile. To our knowledge, catalytic and chemo-selective protocols for the gem-2-vinylation of 3-substituted indole derivatives remain very limited, despite the importance on indole alkaloid synthesis. Herein, we report a Hg(OTf)₂-catalyzed direct coupling reaction of indoles and aryl acetylenes yielding 2-vinylated tryptamine derivatives under mild conditions. Several applications for the tandem reactions are also described.

**Results and discussion**

Employing tryptamine derivative 1 protected with a nosyl group and phenyl acetylene 2a as the substrates, we screened catalytic conditions effecting the direct vinylation at the indole C2 position (Table 1). We first applied Echavarren’s conditions exploiting a cationic gold (I) complex. The coupling of 1 and 2a gave the desired product 3a having a gem-substituted vinyl group in 38% yield (entry 1). A further reaction of the product 3a gave the dimeric product 4 in a comparable yield (37%). In order to achieve highly chemoselective intermolecular alkenylations without affecting the labile products bearing the vinyl group conjugated to an indole system, we found that Hg(OTf)₂, also known as Nishizawa reagent, was the optimum catalyst for the sensitive transformation. As shown in entry 2, treatment of 1 and 2a (1.5 equiv.) in dichloromethane with Hg(OTf)₂ (5 mol%) at room temperature for 3 h afforded the desired vinylated product 3a in 82% yield. Reducing the amount of catalyst to 1 mol% (entry 3) resulted in longer reaction time (24 h), giving a slightly lower yield (74%). Other mercury (II) salts, including Hg(OOCF₃)₂ and Hg(OAc)₂, were not capable of performing the catalytic conversions (entry 4). Single application of trifluoromethanesulfonic acid as the Brønsted acid mediator resulted in no conversion (entry 5).

**Table 1**

We then investigated the scope of intermolecular vinylations, employing a series of aromatic terminal alkynes (Figure 1). The presence of electron withdrawing substituents on the aromatic ring
gave the corresponding products 3b-3d in good yields. Alkynes 2e and 2f, conjugated with either coumarine or indole moieties, also afforded the functionalized tryptamine derivatives 3e and 3f. Conversion of the aromatic acetylene 2g, bearing an electron donating methoxy substituent, also proceeded efficiently to give 3g in 83% yield. In addition, this protocol was shown to be a successful application for direct vinylation of L-tryptophan derivative (5 → 6). On the whole, the intermolecular vinylation of tryptamine derivatives with various aromatic terminal alkynes occurs regioselectively at the indole C2 position under ambient temperature.

**Figure 1.**

To gain mechanistic insights, we performed a conversion employing an internal acetylene 7 (Scheme 2). Hg(OTf)$_2$-catalyzed alkenylation with 7 also proceeded to afford 8 despite diminished reactivity and lower yield (66%). This implies a plausible reaction mechanism, shown in Scheme 3, initiated by the formation of π–complex A, and thereby activating the aromatic acetylene. Friedel-Crafts type C-C bond formation (intermediate A → B) would occur regioselectively at the indole C2 position due to the presence of alkyl substituent at the C3 position. Regeneration of the indole system could form an intermediate C. In situ generation of triflic acid would allow subsequent protonation at the terminal olefinic position (intermediate C → D), giving product 3a and the regenerated catalyst. To verify the hypothesis, we then conducted the reaction with deuterated terminal acetylene 2a-D (Scheme 2). In fact, the deuterium was incorporated on the vinylated product 3a-D at both terminal olefinic positions at almost the same ratios (~25%). This is consistent with the proposed mechanism involving protonation and subsequent elimination of the mercury catalyst (C → D → 3a) aside from the lower deuterium incorporation in 3a-D. The substantial loss of deuterium (almost 50%) might be attributed to proton exchange between product 3a and the cationic species E by a catalytic amount of triflic acid (Scheme 3).

**Scheme 2.**

**Scheme 3.**

Taking the mechanistic insights into account, we then envisioned tandem reactions by making use of the electrophilic nature of the vinylated product 3a, presumably being in equilibrium with the cationic species E. As shown in Scheme 4, the stirred mixture of 1 and 2a in the presence of Hg(OTf)$_2$ was subjected to sequential treatment of N-methylindole 9 at 45 ºC. The expected tandem
coupling reactions gave a 66% yield of the bis-indole compound 10 with successful construction of a quaternary carbon center. Likewise, we also attempted the sequential reaction with the internal acetylene 11 bearing a hydroxyl group. Intermolecular alkenylation and subsequent intramolecular C-O bond formation produced 12 in 65% yield, allowing direct formation of the tetrahydrofuran ring attached to an indole system.\(^\text{17}\)

[Scheme 4.]

Throughout our investigations so far, we found the unique conversion employing aromatic acetylene 2i with a \(N,N\)-dimethylaniline group as a notable exception (Scheme 5). Treatment of 1 and 2i with \(\text{Hg(OTf)}_2\) (10 mol%) produced not only the expected 3i (42%), but also significant amounts of 13 (18%) and 14 (24%). The unexpected products 13 and 14 are composed of the pyrrolidinoindoline skeleton,\(^\text{18}\) bearing one or two units of \(N,N\)-dimethyl-4-vinyl-aniline groups. The formation of 14 suggests a mechanistic rationale involving the C3 vinylation incorporating a quaternary carbon and subsequent cyclization between the resulting iminium species and sulphone amide, followed by a second vinylation at the N1 position. Despite a lower yield of the C2 vinylated product 3i, the unique reactivity of the aromatic acetylene 2i, capable of divergent C2/C3 \(\text{gem}\) -vinylations, prompted us to perform the conversion with tryptamine derivatives 15 bearing a methyl substituent at the indole C2 position. As expected, the intermolecular coupling of 15 with 2i proceeded regioselectively at C3 with complete conversion of 15. In addition to the expected mono-vinylated product 16, bis-vinylated product 17, containing two \(N,N\)-dimethyl-4-vinyl-aniline groups, was also formed. Since treatment of 16 and 2i under identical conditions effected vinylation at the N1 position to form 17, we assume intermolecular sequential alkenylations through C3 vinylation, followed by an ene-type reaction of 16 with an activated species of 2i giving 17. It is likely that the treatment of 2i and \(\text{Hg(OTf)}_2\) could generate an allenyl mercury intermediate F expected to exert anomalous reactivity with increased ionic and electrophilic properties compared to that of 2a.

[Scheme 5.]

In summary, we have developed a \(\text{Hg(OTf)}_2\)-catalyzed protocol allowing direct and intermolecular alkenylation of tryptamines with aromatic acetylenes at room temperature. Derivatives of tryptamine and tryptophan were efficiently alkenylated at the C2 position in a highly chemoselective and regiocontrolled manner. A variety of functionalities and substituents on aryl
group attached to acetylenes were well tolerated except for the dimethyl amino substituent. Based on the mechanistic insights, we further realized a three-component coupling as well as a sequential cyclization demonstrating the versatile applicability of this protocol in the development of tandem reactions for assembling elaborated indole derivatives.
Experimental section

NMR spectra were recorded on JEOL JNM-ECX 400 (1H/400 MHz, 13C/100 MHz) spectrometers. Chemical Shifts are reported in δ (ppm) using chloroform, acetonitrile and dimethyl sulfoxide as an internal standard of δ 7.26, 1.94, 2.50 and 77.16, 118.26, 39.52 for 1H and 13C-NMR, respectively. The medium pressure liquid chromatography (MPLC) purifications were performed on a YAMAZEN YFLC-AI-580. Analytical ultra performance liquid chromatography (UPLC) was carried out on WATERS ACQUITY™ UPLC® H-Class system with ACQUITY UPLC® BEH C18 1.7 μm 2.1×50 mm column and PDA detector (210-400 nm). Sample was dissolved in MeCN and UPLC fractionation conditions consisted of a linear gradient from 50% H2O/50% MeCN to 5% H2O/95% MeCN in 3 min at a flow rate of 0.5 mL/min, held at MeCN 100% for 0.50 min at a flow rate of 0.5 mL/min, then a convex gradient back to 80% H2O/20% MeCN in 0.5 min at a flow rate of 0.5 mL/min, then held at 80% H2O/20% MeCN for 0.5 min at a flow rate of 0.5 mL/min. Total run time for each injection was 4.5 min. Compound was detected by 252 nm UV absorption and characterized by photo diode array. Analytical high performance liquid chromatography (HPLC) was carried out on GILSON 321pump equipped with a GILSON UV/VIS-151 detector, GILSON FC203B fraction collector and Inertsil® SIL-100A 10×250 mm column. Where necessary, solvents were distilled from appropriate drying agents prior to use. Flash column chromatography was performed using Kanto Silica Gel 60N.

General procedure for vinylation of tryptamine and tryptophane derivatives: 2-nitro-N-(2-(2-(1-phenylvinyl)-1H-indol-3-yl)ethyl)benzenesulfonamide (3a).

To a solution of tryptamine derivative 1 (128 mg, 0.371 mmol) and aryl acetylene 2a (60 μl, 0.542 mmol) in dichloromethane (3.6 ml) was added Hg(OTf)2 (9.02 mg, 0.0181 mmol). After stirring for 3 h at room temperature, the mixture was added saturated NaHCO3 (aq.) and extracted with EtOAc. The organic extracts were washed with saturated NaHCO3 (aq.), water and brine, dried over Na2SO4, and concentrated. The residue was purified by silica-gel column chromatography to afford 3a (136 mg, 0.304 mmol, 82%) as a pale yellow amorphous. 1H-NMR (400 MHz, CDCl3) δ 2.85 (2H, t, J = 7.3 Hz), 3.30 (2H, td, J = 7.3, 5.7 Hz), 5.24 (1H, t, J = 5.7 Hz), 5.51 (1H, s), 5.68 (1H, s), 7.00 (1H, ddd, J = 7.9, 7.0, 0.9 Hz), 7.16 (1H, ddd, J = 8.2, 7.0, 0.9 Hz), 7.25 (1H, d, J = 7.9 Hz), 7.30-7.34 (5H, m), 7.37 (1H, d, J = 7.9 Hz), 7.59-7.65 (2H, m), 7.69 (1H, dd, J = 5.9, 3.6 Hz), 7.96 (1H, br-s), 7.98 (1H, dd, J = 5.9, 3.4 Hz); 13C-NMR (100 MHz, CDCl3) δ 25.00, 43.96, 110.08, 111.08, 117.31, 118.58, 119.92, 122.77, 125.53, 127.74, 128.20, 128.62, 128.70, 131.02, 132.74, 133.43, 133.47, 135.38, 135.44, 139.77, 141.04, 147.67; UPLC analysis: t = 1.49 min (λ max 300 nm); HR-MS (ESI) calcd. for C24H21N3O3SNa [M+Na]+ 470.1150, found 470.1161. According
to this procedure, deuterium labeling experiment was performed using deuterated 2a-D.

\[ \text{N-(2-(2-(1-(2-bromophenyl)vinyl)-1H-indol-3-yl)ethyl)-2-nitrobenzenesulfonamide (3b).} \]

According to general procedure, tryptamine derivative 1 (70.8 mg, 0.205 mmol) was treated with corresponding aryl acetylene and \( \text{Hg(OTf)}_2 \) for 4.5 h to afford 3b (90.6 mg, 0.172 mmol, 84%) as a pale yellow amorphous. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) 2.70 (2H, t, \( J = 7.5 \) Hz), 3.20 (2H, td, \( J = 7.5, 5.9 \) Hz), 5.14 (1H, t, \( J = 5.9 \) Hz), 5.42 (1H, s), 5.74 (1H, s), 7.00 (1H, t, \( J = 7.5 \) Hz), 7.15 (1H, t, \( J = 7.5 \) Hz), 7.22-7.28 (2H, m), 7.34-7.43 (3H, m), 7.54 (1H, d, \( J = 7.7 \) Hz), 7.64 (1H, d, \( J = 3.2 \) Hz), 7.66 (1H, d, \( J = 3.4 \) Hz), 7.74 (1H, dd, \( J = 5.9, 3.2 \) Hz), 7.88 (1H, br-s), 8.02 (1H, dd, \( J = 5.9, 3.4 \) Hz); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \( \delta \) 24.97, 43.86, 110.12, 111.05, 118.60, 118.72, 120.02, 123.10, 123.21, 125.50, 127.91, 128.76, 129.97, 131.11, 131.56, 132.76, 133.33, 133.44, 133.64, 133.98, 135.61, 141.12, 141.19, 147.84; UPLC analysis: \( t = 1.76 \) min (\( \lambda_{\text{max}} \) 304 nm); HR-MS (ESI) calcd. for C\(_{24}\)H\(_{20}\)N\(_3\)O\(_4\)Br\(_2\)Na \([M+Na]^+\) 548.0256, found 548.0264.

\[ \text{N-(2-(2-(1-(4-fluorophenyl)vinyl)-1H-indol-3-yl)ethyl)-2-nitrobenzenesulfonamide (3c).} \]

According to general procedure, tryptamine derivative 1 (107 mg, 0.309 mmol) was treated with corresponding aryl acetylene and \( \text{Hg(OTf)}_2 \) for 2 h to afford 3c (121 mg, 0.259 mmol, 84%) as a pale yellow amorphous. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) 2.84 (2H, t, \( J = 7.3 \) Hz), 3.29 (2H, td, \( J = 7.3, 5.7 \) Hz), 5.24 (1H, t, \( J = 5.7 \) Hz), 5.50 (1H, s), 5.64 (1H, s), 7.00 (1H, m), 7.01 (2H, d, \( J = 8.8 \) Hz), 7.16 (1H, ddd, \( J = 8.2, 7.0, 0.7 \) Hz), 7.26-7.33 (3H, m), 7.37 (1H, d, \( J = 8.2 \) Hz), 7.61-7.66 (2H, m), 7.69 (1H, ddd, \( J = 5.9, 3.6 \) Hz), 7.95-8.00 (2H, m); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \( \delta \) 24.96, 43.91, 110.12, 111.12, 115.60 (d, \( J = 21.9 \) Hz), 117.24, 118.59, 119.99, 122.88, 125.55, 128.13, 129.43 (d, \( J = 7.6 \) Hz), 130.97, 132.73, 133.35, 133.47, 135.19, 135.48, 135.87 (d, \( J = 2.9 \) Hz), 140.02, 147.63, 162.96 (d, \( J = 248.9 \) Hz); UPLC analysis: \( t = 1.72 \) min (\( \lambda_{\text{max}} \) 301 nm); HR-MS (ESI) calcd. for C\(_{24}\)H\(_{20}\)N\(_3\)O\(_4\)FSNa \([M+Na]^+\) 488.1056, found 488.1082.

\[ \text{N-(2-(2-(1-(3,5-bis(trifluoromethyl)phenyl)vinyl)-1H-indol-3-yl)ethyl)-2-nitrobenzenesulfonamide (3d).} \]

According to general procedure, tryptamine derivative 1 (789 mg, 2.28 mmol) was treated with corresponding aryl acetylene and \( \text{Hg(OTf)}_2 \) for 3.5 h to afford 3d (1.14 g, 1.95 mmol, 86%) as a pale yellow amorphous. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) 2.82 (2H, t, \( J = 7.0 \) Hz), 3.30 (2H, td, \( J = 7.0, 5.9 \) Hz), 5.23 (1H, t, \( J = 5.9 \) Hz), 5.76 (1H, s), 5.84 (1H, s), 7.04 (1H, ddd, \( J = 8.2, 7.0, 0.9 \) Hz), 7.21 (1H, ddd, \( J = 8.2, 7.0, 0.9 \) Hz), 7.32 (1H, ddd, \( J = 8.2, 0.9 \) Hz), 7.41 (1H, dd, \( J = 8.2, 0.9 \) Hz), 7.61-7.67 (2H, m), 7.67-7.71 (1H, m), 7.80 (2H, br-s), 7.87 (1H, br-s), 7.95 (1H, br-s), 7.98-8.02 (1H, m); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \( \delta \) 25.34, 43.81, 111.13, 111.39, 118.97, 120.42, 120.50,
122.36 (q, \( J = 3.8 \) Hz), 123.27 (q, \( J = 273.7 \) Hz), 123.55, 125.59, 127.71, 128.10, 131.02, 132.29 (q, \( J = 33.4 \) Hz), 132.78, 133.50, 133.55, 133.60, 135.91, 142.04, 147.78; UPLC analysis: \( t = 2.18 \) min (\( \lambda_{\text{max}} = 285 \) nm); HR-MS (ESI) calcd. for \( \text{C}_{26}\text{H}_{19}\text{N}_{3}\text{O}_{4}\text{F}_{6}\text{SNa} \ [\text{M+Na}]^{+} \ 606.0898 \), found 606.0905.

2-nitro-\( N\)-(2-(2-(1-(2-oxo-2\( H\)-chromen-3-yl)vinyl)-1\( H\)-indol-3-yl)ethyl)benzenesulfonamide (3e). According to general procedure, tryptamine derivative 1 (71.3 mg, 0.206 mmol) was treated with corresponding aryl acetylene and Hg(OTf)\(_2\) for 11 h to afford 3e (89.7 mg, 0.174 mmol, 84%) as a pale yellow amorphous. \( ^{1}H\)-NMR (400 MHz, DMSO-d\(_6\)) \( \delta \) 2.88-2.96 (2H, m), 3.08-3.16 (2H, m), 5.67 (1H, d, \( J = 0.9 \) Hz), 5.92 (1H, d, \( J = 0.9 \) Hz), 7.00 (1H, ddd, \( J = 7.9, 7.0, 0.9 \) Hz), 7.08 (1H, ddd, \( J = 8.2, 7.0, 0.9 \) Hz), 7.26 (1H, d, \( J = 8.2 \) Hz), 7.64 (1H, ddd, \( J = 8.4, 7.3, 1.6 \) Hz), 7.74 (1H, ddd, \( J = 7.5, 1.6 \) Hz), 7.78 (1H, ddd, \( J = 7.5, 1.6 \) Hz), 7.81 (1H, td, \( J = 7.6, 1.6 \) Hz), 7.91 (2H, m), 7.94 (1H, s), 8.19 (1H, s), 10.9 (1H, s); \( ^{13}C\)-NMR (100 MHz, DMSO-d\(_6\)) \( \delta \) 25.59, 43.26, 109.04, 111.23, 115.92, 118.82, 119.24, 120.79, 121.78, 124.43, 124.56, 126.88, 127.97, 128.80, 129.31, 131.98, 132.59, 132.96, 133.87, 133.93, 135.28, 135.56, 141.83, 147.62, 153.21, 159.06; UPLC analysis: \( t = 1.50 \) min (\( \lambda_{\text{max}} = 297 \) nm); HR-MS (ESI) calcd. for \( \text{C}_{27}\text{H}_{21}\text{N}_{3}\text{O}_{6}\text{SNa} \ [\text{M+Na}]^{+} \ 538.1049 \), found 538.1043.

2-nitro-\( N\)-(2-(2-(1-(1-tosyl-1\( H\)-indol-5-yl)vinyl)-1\( H\)-indol-3-yl)ethyl)benzenesulfonamide (3f).

According to general procedure, tryptamine derivative 1 (70.5 mg, 0.204 mmol) was treated with corresponding aryl acetylene and Hg(OTf)\(_2\) for 4 h to afford 3f (104 mg, 0.162 mmol, 79%) as a pale yellow amorphous. \( ^{1}H\)-NMR (400 MHz, CDCl\(_3\)) \( \delta \) 2.36 (3H, s), 2.84 (2H, t, \( J = 7.3 \) Hz), 3.29 (2H, td, \( J = 7.3, 5.7 \) Hz), 5.21 (1H, t, \( J = 5.7 \) Hz), 5.49 (1H, d, \( J = 0.9 \) Hz), 5.67 (1H, d, \( J = 0.9 \) Hz), 6.60 (1H, ddd, \( J = 3.6, 0.7 \) Hz), 6.99 (1H, ddd, \( J = 7.9, 7.3, 0.9 \) Hz), 7.16 (1H, ddd, \( J = 8.2, 7.3, 0.9 \) Hz), 7.23-7.27 (3H, m), 7.30 (1H, dd, \( J = 8.6, 1.8 \) Hz), 7.36 (1H, d, \( J = 7.9 \) Hz), 7.45 (1H, d, \( J = 1.8 \) Hz), 7.55-7.62 (3H, m), 7.64-7.67 (1H, m), 7.79 (2H, d, \( J = 8.4 \) Hz), 7.89 (1H, br-s), 7.90-7.95 (2H, m); \( ^{13}C\)-NMR (100 MHz, CDCl\(_3\)) \( \delta \) 21.69, 24.99, 43.92, 49.32, 109.25, 110.03, 111.12, 113.55, 117.16, 118.53, 119.88, 120.74, 122.71, 124.31, 125.45, 126.93, 127.17, 128.09, 130.12, 130.84, 131.01, 132.69, 133.34, 133.42, 134.76, 135.14, 135.41, 135.60, 140.79, 145.35, 147.56; UPLC analysis: \( t = 2.23 \) min (\( \lambda_{\text{max}} = 297 \) nm); HR-MS (ESI) calcd. for \( \text{C}_{33}\text{H}_{21}\text{N}_{3}\text{O}_{6}\text{S}_{2}\text{Na} \ [\text{M+Na}]^{+} \ 663.1348 \), found 663.1368.

\( \text{N}\)-(2-(2-(1-(4-methoxyphenyl)vinyl)-1\( H\)-indol-3-yl)ethyl)-2-nitrobenzenesulfonamide (3g).

According to general procedure, tryptamine derivative 1 (108 mg, 0.312 mmol) was treated with corresponding aryl acetylene and Hg(OTf)\(_2\) for 1.7 h to afford 3g (123 mg, 0.258 mmol, 83%) as a
pale yellow amorphous. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 2.85 (2H, t, $J = 7.3$ Hz), 3.30 (2H, td, $J = 7.3, 5.7$ Hz), 3.83 (3H, s), 5.22 (1H, br-t, $J = 5.7$ Hz), 5.40 (1H, s), 5.59 (1H, s), 6.86 (2H, d, $J = 8.6$ Hz), 6.99 (1H, ddd, $J = 7.9, 7.3, 0.7$ Hz), 7.15 (1H, ddd, $J = 8.2, 7.3, 0.9$ Hz), 7.25 (2H, d, $J = 8.6$ Hz), 7.26 (1H, d, $J = 7.9$ Hz), 7.36 (1H, d, $J = 8.2$ Hz), 7.63 (2H, dd, $J = 5.9, 3.4$ Hz), 7.69 (1H, dd, $J = 6.1, 3.4$ Hz), 7.95 (1H, br-s), 7.99 (1H, dd, $J = 5.9, 3.4$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 24.98, 43.97, 55.48, 109.94, 111.06, 114.02, 115.74, 118.57, 119.91, 122.71, 125.60, 128.26, 128.96, 131.06, 132.23, 132.72, 133.40, 133.53, 135.42, 135.71, 140.51, 147.71, 160.01; UPLC analysis: $t$ = 1.64 min ($\lambda_{\text{max}}$ 266, 295 nm); HR-MS (ESI) calcd. for C$_{26}$H$_{23}$N$_3$O$_6$SNa [M+Na]$^+$ 528.1205, found 528.1222.

(S)-methyl 2-(2-nitrophenylsulfonamido)-3-(2-(1-phenylvinyl)-1H-indol-3-yl)propanoate (6).

According to general procedure, tryptamine derivative 1 (124 mg, 0.307 mmol) was treated with corresponding aryl acetylene and Hg(OTf)$_2$ for 3.5 h to afford 6 (129 mg, 0.256 mmol, 83%) as a pale yellow amorphous. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.02 (1H, dd, $J = 14.5, 8.2$ Hz), 3.12 (1H, dd, $J = 14.5, 5.9$ Hz), 3.39 (3H, s), 4.39 (1H, td, $J = 8.2, 5.9$ Hz), 5.57 (1H, s), 5.73 (1H, s), 5.89 (1H, d, $J = 8.2$ Hz), 7.00 (1H, ddd, $J = 7.9, 7.0, 0.9$ Hz), 7.14 (1H, ddd, $J = 7.9, 7.0, 0.9$ Hz), 7.22 (1H, d, $J = 7.9$ Hz), 7.36 (5H, br-s), 7.40 (1H, d, $J = 7.9$ Hz), 7.53 (1H, td, $J = 7.5, 1.8$ Hz), 7.56 (1H, td, $J = 7.5, 1.8$ Hz), 7.68 (1H, dd, $J = 7.5, 1.8$ Hz), 7.80 (1H, dd, $J = 7.5, 1.8$ Hz), 7.99 (1H, br-s); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 28.52, 52.49, 57.20, 107.89, 111.06, 117.69, 118.67, 120.14, 122.84, 125.54, 127.85, 128.27, 128.75, 130.27, 132.72, 133.34, 133.87, 135.33, 136.15, 139.52, 141.09, 147.10, 171.38; UPLC analysis: $t$ = 1.59 min ($\lambda_{\text{max}}$ 301 nm); HR-MS (ESI) calcd. for C$_{26}$H$_{23}$N$_3$O$_6$SNa [M+Na]$^+$ 528.1205, found 528.1222.

(Z)-2-nitro-N-(2-(2-(1-phenylprop-1-en-1-yl)-1H-indol-3-yl)ethyl)benzenesulfonamide (8).

According to general procedure, tryptamine derivative 1 (106 mg, 0.307 mmol) was treated with internal acetylene 7 and Hg(OTf)$_2$ for 28 h to afford 8 (93.1 mg, 0.202 mmol, 66% yield, 13:1 mixture of cis:trans isomers), as a pale yellow amorphous. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 1.80 (3H, d, $J = 7.0$ Hz), 2.82 (2H, t, $J = 7.5$ Hz), 3.28 (2H, td, $J = 7.5, 6.1$ Hz), 5.25 (1H, t, $J = 6.1$ Hz), 6.41 (1H, q, $J = 7.0$ Hz), 7.06 (1H, ddd, $J = 8.2, 7.0, 0.9$ Hz), 7.15-7.27 (6H, m), 7.31 (1H, d, $J = 8.2$ Hz), 7.45 (1H, d, $J = 7.9$ Hz), 7.60 (1H, td, $J = 7.7, 1.4$ Hz), 7.66 (1H, td, $J = 7.7, 1.4$ Hz), 7.74 (1H, dd, $J = 7.7, 1.4$ Hz), 7.88 (1H, br-s), 7.99 (1H, dd, $J = 7.7, 1.6$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 16.35, 25.45, 43.78, 110.18, 111.13, 118.44, 119.73, 122.23, 125.48, 126.62, 127.56, 127.84, 128.60, 129.31, 131.16, 132.73, 133.19, 133.45, 133.46, 133.57, 135.96, 140.61, 147.93; UPLC analysis: $t$ = 1.77 min ($\lambda_{\text{max}}$ 284 nm); HR-MS (ESI) calcd. for C$_{25}$H$_{23}$N$_3$O$_4$SNa [M+Na]$^+$ 484.1307 found 484.1316.
**Compound (10).**

To a solution of tryptamine derivative 1 (70.6 mg, 0.204 mmol) and phenyl acetylene (29 μl, 0.260 mmol) in 1,2-dichloroethane (3.0 ml) was added to Hg(OTf)₂ (5.00 mg, 0.0100 mmol). After stirring for 5.5 h at room temperature, N-methyl indole 9 (62 μl, 0.496 mmol) was then added to the reaction mixture and stirred at room temperature for 12 h and at 45 °C for 10.5 h. The mixture was cooled to room temperature and added saturated NaHCO₃ (aq.) and extracted with EtOAc. The organic extracts were washed with saturated NaHCO₃ (aq.), water and brine, dried over Na₂SO₄, and concentrated. The residue was purified by silica-gel column chromatography to afford 10 (77.9 mg, 0.135 mmol, 66%) as a pale yellow amorphous. "H-NMR (400 MHz, CDCl₃) δ 2.36 (3H, s), 2.74 (1H, dd, J = 9.7, 0.9 Hz), 2.76 (1H, d, J = 8.6 Hz), 2.92-3.02 (2H, m), 3.72 (3H, s), 5.07 (1H, br-t, J = 5.9 Hz), 6.40 (1H, s), 6.95 (1H, ddd, J = 7.9, 7.0, 0.9 Hz), 7.02 (1H, ddd, J = 7.9, 7.0, 1.1 Hz), 7.10 (1H, ddd, J = 8.2, 7.0, 1.1 Hz), 7.17 (1H, d, J = 8.2 Hz), 7.19-7.30 (7H, m), 7.34 (1H, d, J = 8.2 Hz), 7.40 (1H, d, J = 7.9 Hz), 7.60 (1H, td, J = 7.7, 1.4 Hz), 7.66 (1H, td, J = 7.7, 1.6 Hz), 7.76 (1H, dd, J = 7.7, 1.4 Hz), 7.94 (1H, dd, J = 7.7, 1.6 Hz), 7.97 (1H, br-s); "C-NMR (100 MHz, CDCl₃) δ 26.06, 29.03, 32.90, 43.41, 44.97, 107.03, 109.75, 111.04, 118.03, 119.34, 119.55, 121.32, 121.48, 121.58, 121.87, 125.46, 126.29, 126.79, 127.76, 128.35, 128.51, 129.33, 131.15, 132.76, 133.39, 133.68, 133.85, 137.96, 141.56, 146.87, 147.86; UPLC analysis: t = 2.21 min (λ_max 284 nm); HR-MS (ESI) calcd. for C₃₃H₃₀N₄O₄SNa [M+Na]+ 601.1885, found 601.1883.

**Compound (12).**

To a solution of tryptamine derivative 1 (70.8 mg, 0.205 mmol) and 11 (61.2 mg, 0.300 mmol) in 1,2-dichloroethane (3.0 ml) was added Hg(OTf)₂ (5.00 mg, 0.0100 mmol). After stirring at room temperature for 14 h, the mixture was treated with additional 11 (50.0 mg, 0.245 mmol) and stirred for 5 h. The mixture was then added saturated NaHCO₃ (aq.) and extracted with EtOAc. The organic extracts were washed with saturated NaHCO₃ (aq.), water and brine, dried over Na₂SO₄, and concentrated. The residue was purified by silica-gel column chromatography to afford 12 (73.5 mg, 0.134 mmol, 65%) as a pale yellow amorphous. "H-NMR (400 MHz, CDCl₃) δ 2.01 (1H, m), 2.15 (1H, m), 2.68 (2H, dd, J = 7.7, 6.6 Hz), 2.89 (2H, td, J = 7.0, 2.9 Hz), 3.15 (1H, m), 3.25 (1H, m), 3.90 (3H, s), 4.14 (1H, td, J = 8.2, 5.2 Hz), 4.23 (1H, q, J = 7.7 Hz), 5.95 (1H, t, J = 5.0 Hz), 6.91 (1H, t, J = 7.7 Hz), 7.09 (1H, t, J = 7.7 Hz), 7.23 (1H, d, J = 7.7 Hz), 7.27 (1H, d, J = 7.7 Hz), 7.48 (2H, d, J = 8.4 Hz), 7.53 (2H, m), 7.58 (1H, m), 7.93 (1H, m), 7.96 (2H, d, J = 8.4 Hz), 8.33 (1H, br-s); "C-NMR (100 MHz, CDCl₃) δ 24.41, 25.87, 38.53, 43.38, 52.28, 68.45, 85.02, 107.11, 111.16, 118.23, 119.81, 122.14, 125.29, 125.79, 128.63, 129.43, 129.87, 131.12, 132.42, 133.03, 133.30, 134.41, 138.94, 147.49, 149.71, 166.84; UPLC analysis: t = 1.59 min (λ_max 283 nm);
HR-MS (ESI) calcd. for C_{28}H_{27}N_{3}O_{7}SNa [M+Na]^{+} 572.1467, found 572.1474.

\[ N-(2-(2-(1-(4-(dimethylamino)phenyl)vinyl)-1H-indol-3-yl)ethyl)-2-nitrobenzenesulfonamide (3i) \]

To a solution of tryptamine derivative 1 (86.4 mg, 0.250 mmol) and aryl acetylene 2i (109 mg, 0.751 mmol) in dichloromethane (3.5 ml) was added Hg(OTf)_{2} (12.5 mg, 0.0251 mmol). After stirring at room temperature for 24 h, the mixture was added saturated NaHCO_{3} (aq.) and extracted with EtOAc. The organic extracts were washed with saturated NaHCO_{3} (aq.), water and brine, dried over Na_{2}SO_{4}, and concentrated. The residue was purified by silica-gel column chromatography to afford 3i (51.0 mg, 0.104 mmol, 42%), 13 (21.8 mg, 0.0444 mmol, 18%) and 14 (38.1 mg, 0.0599 mmol, 24%).

3i: \( ^{1}H\)-NMR (400 MHz, CDCl_{3}) \( \delta \) 2.89 (2H, t, \( J = 7.3 \) Hz), 2.99 (6H, s), 3.33 (2H, td, \( J = 7.3, 5.9 \) Hz), 5.24 (1H, t, \( J = 5.9 \) Hz), 5.29 (1H, d, \( J = 1.1 \) Hz), 5.55 (1H, d, \( J = 1.1 \) Hz), 6.66 (2H, d, \( J = 8.8 \) Hz), 6.98 (1H, ddd, \( J = 7.9, 7.0, 0.9 \) Hz), 7.14 (1H, ddd, \( J = 8.2, 7.0, 1.1 \) Hz), 7.19 (2H, d, \( J = 8.8 \) Hz), 7.25 (1H, d, \( J = 8.2 \) Hz), 7.35 (1H, d, \( J = 7.9 \) Hz), 7.59-7.65 (2H, m), 7.68 (1H, m), 7.94 (1H, s); \( ^{13}C\)-NMR (100 MHz, CDCl_{3}) \( \delta \) 25.00, 40.55, 44.05, 109.71, 111.00, 112.15, 113.95, 118.50, 119.79, 122.48, 125.54, 127.40, 128.31, 128.58, 131.07, 132.70, 133.34, 133.69, 135.34, 136.24, 140.64, 147.72, 150.74; UPLC analysis: \( t = 1.88 \) min (\( \lambda_{\text{max}} 300 \) nm); HR-MS (ESI) calcd. for C_{26}H_{27}N_{4}O_{4}S [M+H]^{+} 491.1753, found 491.1760.

13: \( ^{1}H\)-NMR (400 MHz, CDCl_{3}) \( \delta \) 2.27 (1H, ddd, \( J = 12.0, 5.4, 1.1 \) Hz), 2.57 (1H, ddd, \( J = 12.0, 11.1, 7.5 \) Hz), 2.92 (6H, s), 3.21 (1H, ddd, \( J = 11.1, 10.0, 5.4 \) Hz), 3.67 (1H, ddd, \( J = 10.0, 7.5, 1.6 \) Hz), 4.77 (1H, br-s), 5.04 (1H, d, \( J = 0.9 \) Hz), 5.13 (1H, s), 5.58 (1H, d, \( J = 1.6 \) Hz), 6.52 (2H, d, \( J = 8.8 \) Hz), 6.59 (1H, d, \( J = 7.7 \) Hz), 6.80 (2H, d, \( J = 8.8 \) Hz), 6.80 (1H, td, \( J = 7.5, 1.1 \) Hz), 7.07 (1H, d, \( J = 7.5 \) Hz), 7.12 (1H, td, \( J = 7.7, 1.1 \) Hz), 7.58 (1H, td, \( J = 7.7, 1.6 \) Hz), 7.61 (1H, dd, \( J = 7.9, 1.6 \) Hz), 7.67 (1H, td, \( J = 7.7, 1.4 \) Hz), 7.86 (1H, dd, \( J = 7.9, 1.4 \) Hz); \( ^{13}C\)-NMR (100 MHz, CDCl_{3}) \( \delta \) 37.18, 40.60, 47.95, 63.96, 82.53, 109.62, 111.91, 114.95, 119.66, 124.29, 129.03, 129.24, 130.46, 131.03, 131.78, 133.29, 133.48, 148.35, 149.31, 149.81, 150.70; UPLC analysis: \( t = 2.13 \) min (\( \lambda_{\text{max}} 243 \) nm); HR-MS (ESI) calcd. for C_{26}H_{27}N_{4}O_{4}S [M+H]^{+} 491.1753, found 491.1760.

14: \( ^{1}H\)-NMR (400 MHz, CD_{3}CN) \( \delta \) 2.29-2.34 (2H, m), 2.91 (6H, s), 2.93 (6H, s), 3.24 (1H, m), 4.00 (1H, m), 4.73 (1H, s), 5.00 (1H, d, \( J = 1.1 \) Hz), 5.07 (1H, s), 5.22 (1H, d, \( J = 1.1 \) Hz), 5.81 (1H, s), 6.37 (1H, d, \( J = 7.7 \) Hz), 6.42 (2H, d, \( J = 9.1 \) Hz), 6.61 (2H, d, \( J = 9.1 \) Hz), 6.64 (2H, d, \( J = 9.1 \) Hz), 6.66 (2H, d, \( J = 9.1 \) Hz), 6.78 (1H, td, \( J = 7.5, 0.9 \) Hz), 7.06 (1H, ddd, \( J = 7.9, 7.5, 1.4 \) Hz), 7.19 (1H, dd, \( J = 7.5, 0.9 \) Hz), 7.57 (1H, ddd, \( J = 7.9, 6.8, 1.8 \) Hz), 7.64-7.72 (3H, m); \( ^{13}C\)-NMR (100 MHz, CD_{3}CN) \( \delta \) 40.20, 40.50, 40.63, 49.22, 64.16, 86.93, 105.83, 108.82, 112.65, 112.83, 114.51, 119.65, 124.95, 125.03, 125.11, 128.20, 129.66, 129.69, 130.62, 131.42, 132.35, 133.01,
UPLC analysis: \( t = 3.11 \text{ min (} \lambda_{\text{max}} \text{ 294 nm)} \); HR-MS (ESI) calcd. for \( \text{C}_{36}\text{H}_{38}\text{N}_{5}\text{O}_{4}\text{S} \ [\text{M+H}]^+ 636.2645 \), found 636.2639.

**Compounds (16 and 17).**

A solution of tryptamine derivative 15 (73.0 mg, 0.203 mmol) and aryl acetylene 2i (35.0 mg, 0.241 mmol) in dichloromethane (3.0 ml) was added to Hg(OTf)$_2$ (10.0 mg, 0.0201 mmol) and stirred for 17.5 h at room temperature. Additional aryl acetylene 2i (29.0 mg, 0.200 mmol) was added and stirred again for 5.5 h. The mixture was added sat NaHCO$_3$ aq. and extracted with EtOAc. The organic extracts were washed with sat NaHCO$_3$ aq., water and brine, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica-gel column chromatography to afford 16 (48.8 mg, 0.0967 mmol, 48%) and 17 (49.4 mg, 0.0761 mmol, 37%).

**16:** $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 2.13 (3H, s), 2.14-2.22 (1H, m), 2.40-2.49 (1H, m), 2.49-2.61 (2H, m), 2.82 (6H, s), 5.15 (1H, t, $J = 5.7$ Hz), 5.36 (1H, s), 5.49 (1H, s), 6.35 (2H, d, $J = 8.8$ Hz), 6.46 (2H, d, $J = 8.8$ Hz), 7.22 (1H, td, $J = 6.8$, 0.9 Hz), 7.25 (1H, d, $J = 1.8$ Hz), 7.33 (1H, ddd, $J = 7.7$, 6.8, 1.8 Hz), 7.44 (1H, d, $J = 7.7$ Hz), 7.62-7.71 (2H, m), 7.80 (1H, m), 7.85 (1H, m); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 16.77, 35.24, 39.19, 40.38, 65.69, 111.68, 115.65, 120.25, 122.75, 125.47, 126.06, 127.65, 128.42, 128.60, 131.04, 132.89, 133.33, 133.66, 141.53, 147.84, 147.93, 149.97, 155.62, 184.79; UPLC analysis: $t = 1.47$ min ($\lambda_{\text{max}}$ 269 nm); HR-MS (ESI) calcd. for \( \text{C}_{27}\text{H}_{28}\text{N}_{4}\text{O}_{4}\text{SNa} \ [\text{M+Na}]^+ 527.1729 \), found 527.1732.

**17:** $^1$H-NMR (400 MHz, CD$_3$CN) $\delta$ 2.13 (1H, td, $J = 12.0$, 5.0 Hz), 2.44 (1H, td, $J = 12.0$, 5.0 Hz), 2.53 (1H, m), 2.85 (6H, s), 2.88 (6H, s), 3.07 (1H, m), 3.77 (1H, d, $J = 1.4$ Hz), 3.89 (1H, d, $J = 1.4$ Hz), 4.83 (1H, s), 5.00 (1H, d, $J = 0.9$ Hz), 5.34 (1H, d, $J = 0.9$ Hz), 5.60 (1H, s), 5.83 (1H, br-t, $J = 5.7$ Hz), 6.19 (1H, d, $J = 7.5$ Hz), 6.41 (2H, d, $J = 9.1$ Hz), 6.44 (2H, d, $J = 9.1$ Hz), 6.61 (2H, d, $J = 9.1$ Hz), 6.72 (2H, br-d, $J = 9.1$ Hz), 6.80 (1H, td, $J = 7.5$, 1.1 Hz), 7.01 (1H, td, $J = 7.5$, 1.1 Hz), 7.08 (1H, dd, $J = 7.5$, 1.1 Hz), 7.72 (1H, td, $J = 7.7$, 1.6 Hz), 7.76 (1H, td, $J = 7.7$, 1.6 Hz), 7.83 (1H, dd, $J = 7.7$, 1.6 Hz), 7.85 (1H, dd, $J = 7.7$, 1.6 Hz); $^{13}$C-NMR (100 MHz, CD$_3$CN) $\delta$ 40.46, 40.57, 40.91, 41.31, 56.93, 80.17, 108.13, 109.86, 112.00, 112.68, 113.48, 120.15, 123.47, 124.46, 125.97, 127.81, 129.33, 130.85, 131.50, 132.15, 133.58, 133.67, 135.04, 143.93, 148.76, 148.84, 150.54, 151.76, 153.46, 155.92; UPLC analysis: $t = 2.86$ min ($\lambda_{\text{max}}$ 279, 301 nm); HR-MS (ESI) calcd. for \( \text{C}_{35}\text{H}_{40}\text{N}_{4}\text{O}_{4}\text{S} \ [\text{M+H}]^+ 650.2801 \), found 650.2785.

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Figure and Scheme Legends:

**Table 1.** Screening of catalyst for coupling of 1 with 2a.

**Figure 1.** Intermolecular *gem*-alkenylation of either tryptamine or tryptophan derivative (1, 5) with aromatic acetylene 2.

**Scheme 1.** Synthesis of branched olefins.
**Scheme 2.**
**Scheme 3.** Proposed mechanism.
**Scheme 4.**
**Scheme 5.**
References and Notes

The dimer 4 was obtained as 5:1 mixture of diastereomers. Although 4 was not fully characterized, NMR spectra of 4 were consistent with the data reported in ref. 8a.


The stereogenic center in 5 was almost completely retained through the vinylation, see supporting information.

In place of the CH$_2$CH$_2$NHNs substituent at indole C3 position, substrates bearing CH$_2$CH$_2$NBoc or CH$_2$CH$_2$-phthalimide group were also applicable for the gem-vinylation without substantial decrease of the yields. The intermolecular alkenylation of 1 with aliphatic acetylenes were not successful.

\[
\begin{align*}
\text{NHNs} & \quad \text{Ar} \quad 2 \\
\text{Hg(O Tf)_2} & \quad (5 \text{ mol%}) \\
\text{CH}_2\text{Cl}_2, \text{ r.t.} \\
\text{NHNs} & \quad \text{Ar}
\end{align*}
\]

3b 86%
3c 84%
3d 86%
3e 84%
3f 79%
3g 83%

\[
\begin{align*}
\text{NHNs} & \quad \text{Ph} \quad 2a \\
\text{Hg(O Tf)_2} & \quad (5 \text{ mol%}) \\
\text{CH}_2\text{Cl}_2, \text{ r.t.} \\
\text{NHNs} & \quad \text{CO}_2\text{Me}
\end{align*}
\]

6: 83%
<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time</th>
<th>Yield: (3a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{AuCl(PPh}_3\text{)} + \text{AgSbF}_6]) (7 mol%)</td>
<td>8 h</td>
<td>38% (^a)</td>
</tr>
<tr>
<td>2</td>
<td>(\text{Hg(OTf)}_2) (5 mol%)</td>
<td>3 h</td>
<td>82%</td>
</tr>
<tr>
<td>3</td>
<td>(\text{Hg(OTf)}_2) (1 mol%)</td>
<td>24 h</td>
<td>74% (^b)</td>
</tr>
<tr>
<td>4</td>
<td>(\text{Hg(OCOCF}_3\text{)}_2) (10 mol%)</td>
<td>18 h</td>
<td>9%</td>
</tr>
<tr>
<td>5</td>
<td>(\text{TfOH}) (10 mol%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) \(4\) (37\%): dimer of \(3a\), \(^b\) Recovery of \(1\) (17\%)
a) cross-couplings

\[ \text{Y} \text{R} \xrightarrow{\text{Ar-X}} \text{Y} \text{R} \xrightarrow{\text{Ar-\(X\)}} \text{Y} \text{R} \]

\text{trans} \quad \text{cis} \quad \text{gem}

\text{X, Y: metal or halogen etc.}

b) Mizoroki-Heck / Fujiwara-Moritani reactions

\[ \text{Ar-\(X\)} \xrightarrow{\text{cat. Pd}} \text{Ar-\(R\)} \quad \text{Ar-\(R\)} \]

\text{X = halogen or hydrogen} \quad \text{major} \quad \text{minor}

c) Alkenylation of indole C2 position

\[ \text{Z: directing group} \]

d) Direct alkenylation of 3-substituted indoles

\[ \text{this study} \quad \text{gem-selective} \]
\[
\begin{align*}
\text{1} & \quad \text{NHNS} & \quad \text{Ph} & \quad \text{Me} & \quad \text{Hg(OTf)}_2 \quad (5 \text{ mol\%}) & \quad \text{CH}_2\text{Cl}_2 & \quad \text{r.t.,} \ 3 \text{ h} \\
\Rightarrow & & & & & & 8 \ 66\% \\
\text{(cis/trans = 13/1)} \\
\text{1} & \quad \text{NHNS} & \quad \text{Ph} & \quad \text{D} & \quad \text{Hg(OTf)}_2 \quad (5 \text{ mol\%}) & \quad \text{CH}_2\text{Cl}_2 & \quad \text{r.t.,} \ 3 \text{ h} \\
& & & & & & 3a-D \quad \text{D} \quad \text{cis-D:} \ 24\% \quad \text{trans-D:} \ 23\%
\end{align*}
\]
Hg(OTf)$_2$ (5 mol%) \( \rightarrow \) Hg(OTf)$_2$ (5 mol%)

$\text{Ph} - \text{CH}_2\text{CH} = \text{CH} - \text{Ph}$

$\text{NHNs}$

$\text{CH}_2\text{Cl}_2$, r.t.

45 $^\circ$C

66%

$\text{NHNs}$

$\text{Me}$

$\text{N}$

$\text{Me}$

$\text{Ph}$

$\text{N}$

$\text{Me}$

$\text{NHNs}$

$\text{CO}_2\text{Me}$

$\text{MeO}_2\text{C}$
\[
\begin{align*}
\text{NHNs} & \quad \text{NHNs} \\
1 & \quad + \quad \text{Me-N-Me} \\
& \quad \text{Me-N-Me} \\
\text{2i (3.0 eq.)} & \quad \text{Me-N-Me} \\
& \quad \text{Me-N-Me} \\
3i (42\%) & \quad \text{Me-N-Me} \\
& \quad \text{Me-N-Me} \\
13 (18\%) & \quad \text{Me-N-Me} \\
& \quad \text{Me-N-Me} \\
14 (24\%) & \quad \text{Me-N-Me} \\
& \quad \text{Me-N-Me} \\
\end{align*}
\]

\[
\begin{align*}
\text{NHNs} & \quad \text{NHNs} \\
15 & \quad + \quad \text{2i (2.2 eq.)} \\
& \quad \text{Me-N-Me} \\
\text{Me-N-Me} & \quad \text{Me-N-Me} \\
16 (48\%) & \quad \text{Me-N-Me} \\
& \quad \text{Me-N-Me} \\
17 (37\%) & \quad \text{Me-N-Me} \\
& \quad \text{Me-N-Me} \\
\end{align*}
\]
\[
\text{NHNs} \quad + \quad \text{FG} \quad \rightarrow \quad \text{Hg(OTf)}_2 \quad (5 \text{ mol}\%)
\]

\[
\text{CH}_2\text{Cl}_2 \quad \text{gem-vinylation}
\]