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$SnCl_4$-PROMOTED ETHENYLATION REACTION OF HYDROXYLATED HETEROARENES

Kensuke Akamatsu, Ryo Amemiya, and Masahiko Yamaguchi*

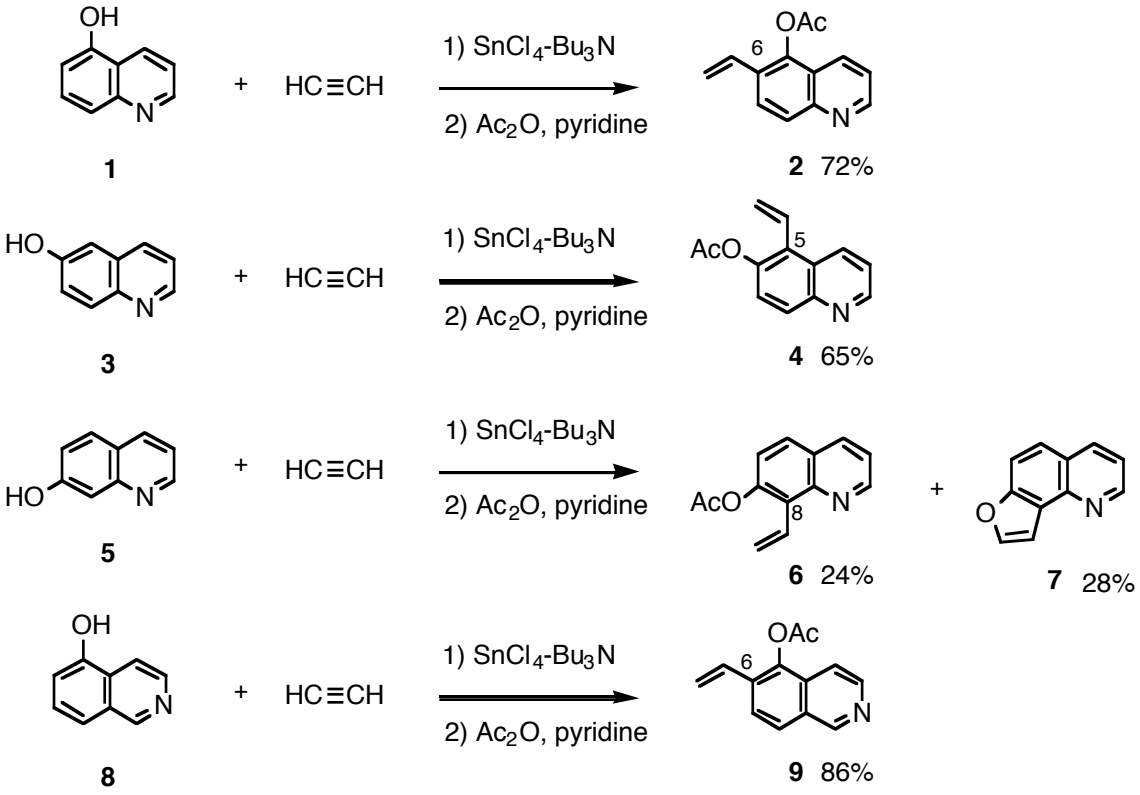
Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University, Aoba, Sendai 980-8578

Abstract – Reaction of hydroxylated heteroarenes and acetylene in the presence of $SnCl_4$ and Bu_3N (or Et_3N) gives the corresponding ethenylated arenes. The reaction takes place at the neighboring position of the hydroxy group, and is applicable to quinolines, an isoquinoline, pyridines, and *N*-trifluoromethanesulfonylated indoles provided that the optimized conditions for the ethenylation and workup are employed.

Ethenylated heteroarenes are important intermediates for the preparation of biologically active substances and materials. Although a number of methods were developed for their synthesis, they in general employed ethenylation reactions of halogenated heteroarenes.[1,2] The direct substitution of the heteroaromatic hydogen with a vinyl group apparently is the most straightforward. Such transformation, however, is not facile. An exception is *N*-ethenylation of pyrroles or carbazoles with acetylene under basic conditions.[3] We previously developed *ortho*-ethenylation reaction of phenols with acetylene in the presence of $SnCl_4$ and Bu_3N.[4] Mechanistically the reaction proceeded *via* carbometalation of phenoxytin and ethynyltin followed by protodestannylation of the resulted organotin intermediate. Described here is the application of the method to hydroxylated nitrogen heteroarenes. It turned out that hydroxylated quinolines, an isoquinoline, pyridines, and *N*-protected indoles could be ethenylated at the neighboring position of the hydroxy group provided that suitable conditions for the ethenylation and workup were employed depending on the heteroarene.

Acetylene was introduced to a mixture of $SnCl_4$ (5 eq.) and Bu_3N (5 eq.) in chlorobenzene at –40 °C to generate ethynyltin, to which 5-hydroxyquinoline (**1**), $SnCl_4$ (2 eq.), and Bu_3N (2 eq.) were added. The mixture was heated at 60 °C for 3 h with continuous introduction of acetylene. Then, 3.2 M NaOH and THF were added, and the mixture was heated at reflux for 1 h for the protodestannylation. After usual aqueous workup and acetylation, 5-acetoxy-6-ethenylquinoline (**2**) was obtained in 72% yield (Scheme 1).

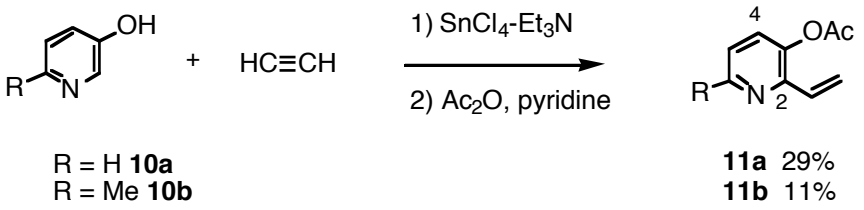
The conditions of the protodestannylation under alkaline conditions turned out to be critical to obtain the product in a high yield, and prolonged treatment considerably decomposed the product. The reaction of 6-hydroxyquinoline (**3**) gave 5-ethenylated product (**4**) in 65% yield, and 7-hydroxyquinoline (**5**) gave 8-ethenylated product (**6**) in 24% yield. Both reactions took place exclusively at the α-position of the azanaphthalene nuclei, and the other isomer could not be detected, which is analogous to the ethenylation of 2-naphthol.[4] It is also noted that larger amounts of $SnCl_4$-Bu_3N reagents are required in the reactions of **1**, **3**, and **5** compared to naphthols.[4] It may be ascribed to the deactivation of intermediate by the nitrogen atoms of the substrates. The low yield of **6** is due to the formation of a cyclized product (**7**) during the reaction. 8-Hydroxyquinoline and 4-hydroxyquinoline, however, did not give the ethenylated products, and were recovered unchanged. The unreactiveness of the former compound may be due to the deactivation of the stannyloxy intermediate by the chelate formation of the 1-nitrogen. The behavior of the latter compound is similar to that of 4-hydroxypyridine (*vide infra*). Ethenylation of 5-hydroxyisoquinoline (**8**) required a higher temperature compared to **1**, and the reaction at 100 °C for 0.5 h gave 5-acetoxy-6-ethenylisoquinoline (**9**) in 86% yield after the alkaline workup and acetylation.



Scheme 1.

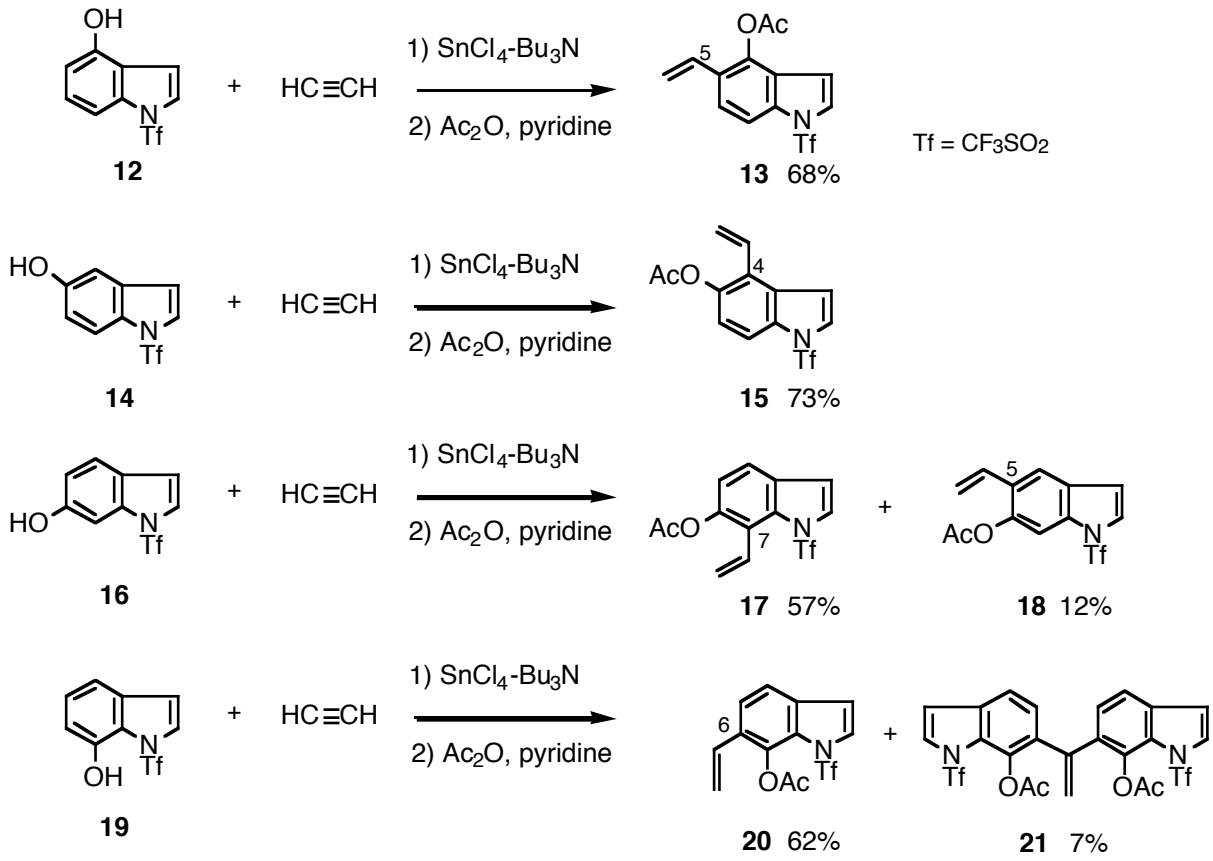
3-Hydroxypyridines could also be reacted with acetylene in the presence of $SnCl_4$ and Et_3N (Scheme 2). Use of Et_3N gave slightly better results than Bu_3N in these cases. Ethenylation of 3-hydroxypyridine (**10a**) at 130 °C for 0.5 h followed by workup with 1.6 M Na_2CO_3 and ethanol at reflux for 4 h gave 2-

ethenylated pyridine (**11a**)[5] in 29% yield. The workup with 3.2 M NaOH lowered the yield. The reaction took place at the 2-position selectively, and no product reacted at the 4-position was detected. 3-Hydroxy-6-methylpyridine (**10b**) was also converted to 2-ethenylated product (**11b**). Considerable amounts of the starting materials were recovered, and prolonged reaction time did not improve the yields. 2-Hydroxypyridine and 4-hydroxypyridine did not give the ethenylation products.



Scheme 2.

Since the parent hydroxyindoles could not be ethenylated under the conditions, 1-nitrogen atoms were protected with trifluoromethanesulfonyl group. The treatment of 4-hydroxy-1-(trifluoromethanesulfonyl)indole (**12**) with acetylene in the presence of $SnCl_4$ and Bu_3N at 60 °C for 1 h followed by workup with 1.6 M K_2CO_3 at 40 °C for 0.5 h gave 4-acetoxy-5-ethenyl-1-(trifluoromethanesulfonyl)indole (**13**) in 68% yield after acetylation (Scheme 3). Alkaline workup with



Scheme 3.

3.2 M NaOH caused considerable decomposition. The reaction of 5-hydroxyindole (**14**) gave 4-ethenylated **15**, and 6-hydroxyindole (**16**) gave 7-isomer (**17**) as the major product accompanied by the 5-isomer (**18**). The C-C bond formation of the indoles occurred at the α-position as was hydroxyquinolines. In contrast to the inertness of 8-hydroxyquinoline, 7-hydroxyindole (**19**) gave the 6-ethenylated **20** in 62% yield in the presence of large excess $SnCl_4$ (52 eq.) and Bu_3N (52 eq.), which was accompanied by a bisindole (**21**) in 7% yields. Under the standard conditions, **20** and **21** were obtained in 41 and 38% yields, respectively, which may be due to the formation of the less amount of ethynyltin intermediate. Thus, the present synthesis provides a series of ethenylated indoles at the 4-, 5-, 6-, or 7-position.

To summarize, hydroxylated heteroarenes could be ethenylated at the neighboring position of the hydroxy group with acetylene in the presence of $SnCl_4$ and an amine.

EXPERIMENTAL

5-Hydroxyquinoline (**1**), 6-hydroxyquinoline (**3**), 5-hydroxyisoquinoline (**8**), 3-hydroxypyridine (**10a**), and 4-hydroxyindole were purchased from Wako Pure Chemical Industries, Ltd. 7-Hydroxyquinoline (**5**) was purchased from Acros Organics. 5-Hydroxyindole was purchased from Tokyo Kasei Kogyo Co., Ltd. 3-Hydroxy-6-methylpyridine (**10b**) was purchased from Lancaster. 6-Hydroxyindole[6] and 7-hydroxyindole[7] were synthesized according to the literatures. The trifluoromethanesulfonated indoles (**12**, **14**, **16**, and **19**) were synthesized from the hydroxyindoles by i) *t*-butyldimethylsilylation, ii) trifluoromethanesulfonylation,[8] and iii) desilylation. $SnCl_4$, Bu_3N, and PhCl were distilled from CaH_2. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Mercury. Melting points were determined with Yanagimoto micro melting point apparatus without correction. IR spectra were measured on a JASCO FT/IR-400 spectrophotmeter. Low- and high-resolution MS spectra were recorded on a JEOL JMS-DX-303 or a JMS-AX-500 spectrometer. Elemental analyses were conducted with a Yanaco CHN CORDER MT-5.

5-Acetoxy-6-ethenylquinoline (2). Under an argon atmosphere, acetylene was introduced to chlorobenzene (5 mL) at -40 °C for 10 min. Then, $SnCl_4$ (0.59 mL, 5 mmol) and Bu_3N (1.19 mL, 5 mmol) were added. The mixture was warmed to rt, to which 5-hydroxyquinoline (**1**) (145 mg, 1 mmol), $SnCl_4$ (0.23 mL, 2 mmol), and Bu_3N (0.48 ml, 2 mmol) were added. The mixture was stirred at 60 °C for 3 h with continuous introduction of acetylene. Then, THF (10 mL) and 3.2 M NaOH (50 mL) were added, and the mixture was heated at reflux for 1 h. After neutralized with 4 M hydrochloric acid, the organic materials were extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to about 150 mL. Et_3N (4.2 mL, 30 mmol), acetic anhydride (1.4 mL, 15 mmol), and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine were added, and the mixture was stirred at rt for 9 h,

when sat. $NaHCO_3$ was added. The organic materials were extracted with ethyl acetate, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (hexane / ethyl acetate = 10) giving **2** (154 mg, 72%). Pale yellow solid. mp 102.0-102.5 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.50 (3H, s), 5.49 (1H, d, *J* = 11.6 Hz), 5.93 (1H, d, *J* = 17.6 Hz), 6.87 (1H, dd, *J* = 17.6, 11.6 Hz), 7.41 (1H, dd, *J* = 8.0, 4.0 Hz), 7.93 (1H, d, *J* = 9.6 Hz), 7.99 (1H, d, *J* = 9.6 Hz), 8.07 (1H, d, *J* = 8.0 Hz), 8.88 (1H, dd, *J* = 4.0, 1.6 Hz). ^{13}C-NMR (100 MHz) δ 20.7, 117.7, 121.6, 122.5, 126.3, 126.8, 127.6, 129.4, 129.9, 142.5, 148.4, 150.3, 168.7. IR (KBr) 1755, 1567, 1371, 1198, 1144, 926, 870, 839, 813, 780 cm^{-1}. MS (EI) m/z 213 (M^+, 17%), 171 (100%), 170 (78%), 43 (11%). HRMS calcd for $C_{13}H_{11}NO_2$: 213.0790. Found: 213.0776. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.29; H, 5.30; N, 6.57.

6-Acetoxy-5-ethenylquinoline (4). Pale yellow solid. mp 63.5-64.0 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.34 (3H, s), 5.62 (1H, dd, *J* = 17.6, 1.6 Hz), 5.77 (1H, dd, *J* = 12.0, 1.6 Hz), 6.90 (1H, dd, *J* = 17.6, 12.0 Hz), 7.41 (1H, dd, *J* = 8.0, 3.6 Hz), 7.42 (1H, d, *J* = 8.8 Hz), 8.05 (1H, d, *J* = 8.8 Hz), 8.45 (1H, d, *J* = 8.8 Hz), 8.81 (1H, dd, *J* = 3.6, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2, 121.2, 122.7, 125.0, 127.1, 127.2, 128.7, 130.0, 133.0, 145.2, 146.5, 149.7, 169.1. IR (KBr) 1759, 1499, 1372, 1194, 1027, 946, 884, 821 cm^{-1}. MS (EI) m/z 213 (M^+, 11%), 171 (100%), 170 (27%), 43 (11%). HRMS calcd for $C_{13}H_{11}NO_2$: 213.0790. Found: 213.0770. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.02; H, 5.30; N, 6.50.

7-Acetoxy-8-ethenylquinoline (6). Pale yellow solid. mp 58.5-59.0 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.37 (3H, s), 5.75 (1H, dd, *J* = 11.6, 2.4 Hz), 6.01 (1H, dd, *J* = 17.6, 2.4 Hz), 7.28 (1H, d, *J* = 8.8 Hz), 7.40 (1H, dd, *J* = 8.0, 4.4 Hz), 7.45 (1H, dd, *J* = 17.6, 11.6 Hz), 7.73 (1H, d, *J* = 8.8 Hz), 8.13 (1H, dd, *J* = 8.0, 1,6 Hz), 8.94 (1H, dd, *J* = 4.4, 1.6 Hz). ^{13}C-NMR (100 MHz, CD_3OD) δ 21.2, 121.3, 122.0, 124.3, 127.9, 128.2, 128.9, 129.9, 137.8, 147.6, 149.9, 151.0, 170.5. IR (KBr) 3027, 1761, 1498, 1369, 1200, 1172, 1012 cm^{-1}. MS (EI) m/z 213 (M^+, 23%), 171 (32%), 170 (100%), 43 (6%). HRMS calcd for $C_{13}H_{11}NO_2$: 213.0790. Found: 213.0790. **Furo[2,3-*h*]quinoline (7).** Yellow solid. mp 132.0-133.0 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43 (1H, dd, *J* = 8.0, 4.4 Hz), 7.55 (1H, d, *J* = 1.6 Hz), 7.67 (1H, d, *J* = 8.8 Hz),7.73 (1H, d, *J* = 8.8 Hz), 7.80 (1H, d, *J* = 1.6 Hz), 8.25 (1H, dd, *J* = 8.0, 1.6 Hz), 8.96 (1H, dd, *J* = 4.4, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 106.0, 113.3, 119.8, 124.1, 124.2, 125.0, 136.5, 143.4, 144.6, 149.6, 154.7. IR (KBr) 1615, 1509, 1368, 1304, 1262, 1237, 1158, 1134, 1056, 827, 802 cm^{-1}. MS (EI) m/z 169 (M^+, 100%), 141(82%), 140 (47%), 114 (40%), 84 (34%). HRMS calcd for $C_{11}H_7NO$: 169.0528. Found: 169.0519.

5-Acetoxy-6-ethenylisoquinoline (9). Under an argon atmosphere, acetylene was introduced to chlorobenzene (5 mL) at -40 °C for 10 min. Then, $SnCl_4$ (0.59 mL, 5 mmol) and Bu_3N (1.19 mL, 5 mmol) were added. The mixture was warmed to rt, to which 5-hydroxyisoquinoline (**8)** (145 mg, 1 mmol),

$SnCl_4$ (0.23 mL, 2 mmol), and Bu_3N (0.48 ml, 2 mmol) were added. The mixture was stirred at 100 °C for 0.5 h with continuous introduction of acetylene. Then, THF (10 mL) and 3.2 M NaOH (50 mL) were added, and the mixture was heated at reflux for 1 h. After neutralized with 4 M hydrochloric acid, the organic materials were extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to about 150 mL. Et_3N (4.2 mL, 30 mmol), acetic anhydride (1.4 mL, 15 mmol), and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine were added, and the mixture was stirred at rt for 9 h, when sat. $NaHCO_3$ was added. The organic materials were extracted with ethyl acetate, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (hexane / ethyl acetate = 10) giving **9** (185 mg, 86%). Pale yellow solid. mp 74.0-74.5 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.50 (3H, s), 5.54 (1H, d, *J* = 10.8 Hz), 5.95 (1H, d, *J* = 17.6 Hz), 6.89 (1H, dd, *J* = 17.6, 10.8 Hz), 7.52 (1H, d, *J* = 5.6 Hz), 7.79 (1H, d, *J* = 8.0 Hz) , 7.83 (1H, d, *J* = 8.0 Hz), 8.54 (1H, d, *J* = 5.6 Hz), 9.21 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.7, 114.3, 118.9, 124.4, 125.5, 128.6, 129.5, 130.1, 130.4, 142.2, 143.9, 151.9, 168.5. IR (KBr) 1761, 1623, 1428, 1362, 1197, 1165, 832 cm^{-1}. MS (EI) m/z 213 (M^+, 11%), 171 (100%), 170 (37%), 43 (14%). HRMS calcd for $C_{13}H_{11}NO_2$: 213.0790. Found: 213.0746. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.00; H, 5.33; N, 6.48.

3-Acetoxy-2-ethenylpyridine (11a).[5] Under an argon atmosphere, acetylene was introduced to chlorobenzene (5 mL) at -40 °C for 10 min. Then, $SnCl_4$ (0.59 mL, 5 mmol) and Et_3N (0.70 mL, 5 mmol) were added. The mixture was warmed to rt, to which 3-hydroxypyridine (**9a)** (95 mg, 1 mmol), $SnCl_4$ (0.23 mL, 2 mmol), and Et_3N (0.28 mL, 2 mmol) were added. The mixture was stirred at 130 °C for 0.5 h with continuous introduction of acetylene. Then, EtOH (10 mL) and 1.6 M Na_2CO_3 (50 mL) were added, and the mixture was heated at reflux for 4 h. After neutralized with 4 M hydrochloric acid, the organic materials were extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to about 150 mL. Et_3N (4.2 mL, 30 mmol), acetic anhydride (1.4 mL, 15 mmol), and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine were added, and the mixture was stirred at rt for 9 h, when sat. $NaHCO_3$ was added. The organic materials were extracted with ethyl acetate, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (hexane / ethyl acetate = 10) giving **11a** (40 mg, 29%) and recovered 3-acetoxypyridine (55 mg, 40%). Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.37 (3H, s), 5.54 (1H, dd, *J* = 12.8, 2.0 Hz), 6.42 (1H, dd, *J* = 17.6, 2.0 Hz), 6.88 (1H, dd, *J* = 17.6, 12.8 Hz), 7.22 (1H, dd, *J* = 8.0, 4.0 Hz), 7.42 (1H, dd, *J* = 8.0, 2.8 Hz), 8.50 (1H, dd, *J* = 4.0, 2.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.1, 120.3, 123.0, 129.3, 130.4, 144.1, 146.7, 147.4, 168.6. IR (neat) 2984, 1733, 1306, 1253, 1195, 1152, 1036, 932 cm^{-1}. MS (EI) *m/z* 163 (M^+, 51%), 121 (93%), 120 (100%), 43 (27%). HRMS calcd for $C_9H_9NO_2$: 163.0633. Found: 163.0585.

3-Acetoxy-6-methyl-2-ethenylpyridine (11b). Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.34

(3H, s), 2.55 (3H, s), 5.50 (1H, dd, *J* = 11.2 , 2.4Hz), 6.41 (1H, dd, *J* = 16.8, 2.4 Hz), 6.84 (1H, dd, *J* = 16.8, 11.2 Hz), 7.05 (1H, d, *J* = 8.0 Hz), 7.27 (1H, d, *J* = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.0, 24.3, 120.0, 122.7, 129.6, 130.4, 142.1, 146.3, 155.6, 168.8. IR (neat) 2963, 2929, 1766, 1458, 1371, 1200, 1099, 924, 895 cm^{-1}. MS (EI) *m/z* 177 (M^+, 17%), 135 (67%), 134 (100%), 43 (17%). HRMS calcd for $C_{10}H_{11}NO_2$: 177.0790. Found: 177.0762.

4-Acetoxy-1-trifluoromethanesulfonyl-5-ethenylindole (13). Under an argon atmosphere, acetylene was introduced to chlorobenzene (5 mL) at -40 °C for 10 min. Then, $SnCl_4$ (0.59 mL, 5 mmol) and Bu_3N (1.19 mL, 5 mmol) were added. The mixture was warmed to rt, to which 4-hydroxy-1-(trifluoromethanesulfonyl)indole (**12)** (265 mg, 1 mmol), $SnCl_4$ (0.23 mL, 2 mmol), and Bu_3N (0.48 ml, 2 mmol) were added. The mixture was stirred at 60 °C for 1 h with continuous introduction of acetylene. Then, THF (10 mL) and 1.6 M K_2CO_3 (50 mL) were added, and the mixture was stirred at 40 °C for 0.5 h. After acidified with 4 M hydrochloric acid, the organic materials were extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to about 150 mL. Et_3N (4.2 mL, 30 mmol), acetic anhydride (1.4 mL, 15 mmol), and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine were added, and the mixture was stirred at rt for 9 h, when sat. $NaHCO_3$ was added. The organic materials were extracted with ethyl acetate, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (hexane / ethyl acetate = 10) giving **13** (225 mg, 68%). Pale yellow solid. mp 85.5-86.0 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.44 (3H, s), 5.39 (1H, d, *J* = 11.2 Hz), 5.79 (1H, d, *J* = 17.6 Hz), 6.66 (1H, d, *J* = 3.6 Hz), 6.81 (1H, dd, *J* = 17.6, 11.2 Hz), 7.33 (1H, d, *J* = 3.6 Hz), 7.60 (1H, d, *J* = 8.8 Hz), 7.75 (1H, d, *J* = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.8, 108.3, 111.7, 116.8, 119.3(q, *J* = 320.6 Hz), 124.0, 124.8, 126.5, 126.6, 129.4, 135.6, 140.6, 168.3. IR (KBr) 1778, 1416, 1234, 1209, 1174, 1152, 1106, 656, 629 cm^{-1}. MS (EI) m/z 333 (M^+, 20%), 291 (100%), 158 (83%), 43 (20%). HRMS calcd for $C_{13}H_{10}NO_4F_3S$: 333.0283. Found: 333.0278. Anal. Calcd for $C_{13}H_{10}NO_4F_3S$: C, 46.85; H, 3.02; N, 4.20; S, 9.62. Found: C, 46.89; H, 3.19; N, 4.17; S, 9.91.

5-Acetoxy-1-trifluoromethanesulfonyl-4-ethenylindole (15). Pale yellow solid. mp 66.5-67.0 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.35 (3H, s), 5.64 (1H, dd, *J* = 11.2, 1.2 Hz), 5.80 (1H, dd, *J* = 18.4, 1.2 Hz), 6.82 (1H, dd, *J* = 18.4, 11.2 Hz), 7.03 (1H, d, *J* = 3.6 Hz), 7.09 (1H, d, *J* = 8.8 Hz), 7.42 (1H, d, *J* = 3.6 Hz), 7.80(1H, d, *J* = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.1, 110.5, 113.2, 119.3(q, *J* = 319.8 Hz), 120.4, 121.0, 124.2, 127.2, 128.9, 129.8, 133.2, 144.9, 169.1. IR (KBr) 1768, 1406, 1239, 1198, 1143, 1105, 737, 640 cm^{-1}. MS (EI) m/z 333 (M^+, 25%), 291 (100%), 158 (57%), 43 (16%). HRMS calcd for $C_{13}H_{10}NO_4F_3S$: 333.0283. Found: 333.0268.

6-Acetoxy-1-trifluoromethanesulfonyl-7-ethenylindole (17). The alkaline treatment was conducted for 15 min, which gave higher yields of the product than the reaction for 30 min. Pale yellow solid. mp 72.0-73.0 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.23 (3H, s), 5.62 (1H, dd, *J* = 18.4, 1.2 Hz),

5.56 (1H, dd, *J* = 11.6, 1.2 Hz), 6.80 (1H, d, *J* = 3.6 Hz), 6.84 (1H, dd, *J* = 18.4, 11.6 Hz), 7.12 (1H, d, *J* = 8.0 Hz), 7.46 (1H, d, *J* = 3.6 Hz), 7.52 (1H, d, *J* = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2, 111.4, 119.2 (q, *J* = 321.5 Hz), 120.4, 120.6, 121.0, 121.2, 129.4, 129.8, 130.4, 133.8, 146.6, 169.4. IR (KBr) 1778, 1416, 1234, 1209, 1174, 1152, 1106, 656, 629 cm^{-1}. MS (EI) m/z 333 (M^+, 20%), 291 (100%), 158 (83%), 43 (20%). HRMS calcd for $C_{13}H_{10}NO_4F_3S$: 333.0283. Found: 333.0278. **6-Acetoxy-1-trifluoromethanesulfonyl-5-vinylindole (18).** Yellow solid. mp 68.5-69.0 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.37 (3H, s), 5.38 (1H, d, *J* = 10.8 Hz), 5.79 (1H, d, *J* = 17.6 Hz), 6.77 (1H, d, *J* = 3.6 Hz), 6.81 (1H, dd, *J* = 17.6, 10.8 Hz), 7.30 (1H, s), 7.38 (1H, d, *J* = 3.6 Hz), 8.06 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.0, 108.2, 111.4, 116.8, 119.1, 119.3 (q, *J* = 320.6 Hz),127.1, 128.4, 128.7, 130.1, 134.5, 146.3, 169.1. IR (KBr) 1766, 1415, 1233, 1198, 1172, 1146, 1128, 1092, 914, 630 cm^{-1}. MS (EI) m/z 333 (M^+, 26%), 291 (80%), 158 (100%), 43 (17%). HRMS calcd for $C_{13}H_{10}NO_4F_3S$: 333.0283. Found: 333.0265.

7-Acetoxy-1-trifluoromethanesulfonyl-6-ethenylindole (20). A large excess of $SnCl_4$ (5.9 mL, 50 mmol) and Bu_3N (1.9 mL, 50 mmol) were used at the initial acetylene introduction. Pale yellow solid. mp 82.5-83.0 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.39 (3H, s), 5.39 (1H, d, *J* = 10.8 Hz), 5.80 (1H, dd, *J* = 17.6 Hz), 6.72 (1H, dd, *J* = 17.6, 10.8 Hz), 6.79 (1H, d, *J* = 4.4 Hz), 7.43 (1H, d, *J* = 4.4 Hz), 7.46 (1H, d, *J* = 8.8 Hz), 7.59 (1H, d, *J* = 8.8 Hz). ^{13}C-NMR (100 MHz) δ 21.1, 111.0, 117.2, 119.3(q, *J* = 321.3 Hz), 119.5, 123.5, 127.6, 129.3, 129.4, 130.0, 133.8, 134.9, 168.8. IR (KBr) 1775, 1416, 1275, 1233, 1214, 1180, 1144, 1119, 1088, 1023, 655, 617 cm^{-1}. MS (EI) *m/z* 333 (M^+, 24%), 291 (100%), 158 (32%), 43 (15%). HRMS calcd for $C_{13}H_{10}NO_4F_3S$: 333.0274. Found: 333.0268. Anal. Calcd for $C_{13}H_{10}NO_4F_3S$: C, 46.85; H, 3.02; N, 4.20; S, 9.62. Found: C, 47.00; H, 3.14; N, 4.17; S, 9.92. **1,1-Bis(7-acetoxy-1-trifluoromethanesulfonylindol-6-yl)ethene (21).** Yellow solid. mp 184.0-185.0 °C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.89 (6H, s), 5.74 (2H, s), 6.80 (2H, d, *J* = 3.6 Hz), 7.40 (2H, d, *J* = 8.0 Hz), 7.46 (2H, d, *J* = 8.0 Hz), 7.46 (2H, d, *J* = 3.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.9, 110.8, 119.3 (q, *J* = 321.0 Hz), 119.3, 122.5, 127.5, 127.9, 129.7, 133.0, 133.9, 135.2, 141.6, 168.5. IR (KBr) 3445, 1779, 1413, 1232, 1180, 1142, 1092, 631 cm^{-1}. MS (EI) *m/z* 638 (M^+, 41%), 596 (44%), 554 (100%), 537 (32%), 421 (83%), 288 (69%), 259 (44%), 43 (28%). HRMS calcd for $C_{24}H_{16}N_2O_8F_6S_2$: 638.0252. Found: 638.0236.

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