# Supporting Information

## SYNTHESIS OF 3-ETHENYLINDOLES VIA INTRAMOLECULAR CYCLIZATION OF ARYL RADICAL WITH ALLENE GENERATED BY SAMARIUM(II) DIIODIDE

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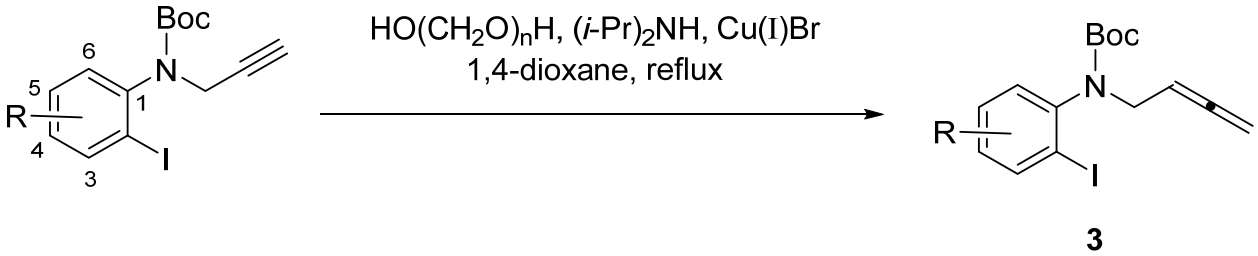
All reactions were performed using dried glasswares under an atmosphere of argon. All chemicals were purchased at the highest commercial grade and used without further purification. Melting points were measured with a Yanaco MP micro-melting apparatus and uncorrected. NMR spectra were measured on Varian INOVA 400NB ($^1$H: 400 MHz, $^{13}$C: 100 MHz) spectrometers with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm. IR spectra were taken with Shimadu FTIR-8400 spectrophotometers. A JEOL JMS-GC mate spectrometer for low-resolution and high-resolution electron ionizations MS (LR-EIMS and HR-EIMS) and A JEOL JMS-SX 102A QQ spectrometer for low-resolution and high-resolution fast atom bombardment MS (LR-FABMS and HR-FABMS) were used. Silica gel 60N (60-230 mesh, Kanto Chemical Co., Inc.) for column chromatography and silica gel 60 $F_{254}$ pre-coated glass plates (0.25 mm-thickness, Merck) for analytical thin-layer chromatography (TLC) were used.




**3**

**General procedure for synthesis of *N*-(2,3-butadien-1-yl)-2-iodoanilines.**

***N*-(2,3-butadien-1-yl)-*N*-(*tert*-butoxycarbonyl)-2-iodoaniline (3a)**[1]

CuBr (402 mg, 2.80 mmol), paraformaldehyde (420 mg, 14.0 mmol) and ($i$-Pr)$_2$NH (1.6 mL, 11.2 mmol) were added to a solution of *N*-(2-iodophenyl)-*N*-*tert*-butoxycarbonyl-2-propynylamine[2] (2.00 g, 5.60 mmol) in 1,4-dioxane (21 mL) at room temperature and the mixture was refluxed with stirring for 2 h. The mixture was filtered through Celite® and the filtrate was concentrated under reduced pressure to leave a residue, which was purified by column chromatography over silica gel with *n*-hexane-EtOAc (19:1) to give **3a** (1.20 g, 58%).

Colorless prisms; mp 57-58 ºC (*n*-hexane); IR (KBr) $cm^{-1}$; 1697, 1956, 3008; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.35 and 1.54 (each s, 6H and 3H), 3.65-3.80 (m, 1H), 4.41-4.57 (m, 1H), 4.64-4.79 (m, 2H), 5.28 (quint, $J$ = 6.8 Hz, 1H), 6.99 (t, $J$ = 7.6 Hz, 1H), 7.20 (d, $J$ = 7.6 Hz, 1H), 7.33 (t, $J$ = 7.6 Hz, 1H), 7.86 (d, $J$ = 7.6 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ major: 28.2 (3C), 48.2, 76.0, 80.3, 86.7, 100.6, 128.6, 128.7, 130.0, 139.3, 144.2, 153.7, 209.3. minor: 28.4 (3C), 49.3, 76.3, 80.8, 87.2, 100.5, 129.0, 129.1, 130.3, 139.6, 144.6, 153.9, 209.4; LR-FAB MS *m/z* (%) 372 ($MH^+$, 100); HR-FAB MS *m/z* calcd for $C_{15}H_{19}INO_2$ ($MH^+$): 372.0461; found: 372.0466.

**_N_-(2,3-Butadien-1-yl)-_N_-(*tert*-butoxycarbonyl)-2-iodo-4-methoxyaniline (3b)**

Allene **3b** was synthesized with a similar manner to **3a**. Yellowish oil (405 mg, 56%); IR ($CHCl_3$) $cm^{-1}$; 1693, 1956, 3005; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.36 and 1.53 (each s, 6.3H and 2.7H), 3.60-3.74 (m, 1H), 3.78 and 3.80 (each s, 0.9H and 2.1H), 4.39-4.54 (m, 1H), 4.63-4.78 (m, 2H), 5.26 (quint, $J$ = 6.8 Hz, 1H), 6.85 (dd, $J$ = 8.4, 2.4 Hz, 1H), 7.07 and 7.17 (each d, $J$ = 8.4 Hz, 0.67H and 0.33H), 7.36 (d, $J$ = 2.4 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ major: 28.2 (3C), 48.3, 55.6, 75.9, 80.2, 86.8, 100.7, 114.4, 123.9, 129.9, 137.2, 154.1, 158.4, 209.3. minor: 28.4 (3C), 49.5, 55.6, 76.2, 80.7, 87.2, 100.7, 114.8, 124.3, 130.3, 137.6, 154.2, 158.8, 209.0; LR-EIMS *m/z* (%) 401 ($M^+$, 4.9), 346 (14), 345 (100), 300 (11), 275 (35), 262 (39), 218 (36), 174 (24), 57 (70); HR-EIMS calcd for $C_{16}H_{20}INO_3$ ($M^+$): 401.0488; found: 401.0494.

**_N_-(2,3-Butadien-1-yl)-_N_-(*tert*-butoxycarbonyl)-2-iodo 4-methylaniline (3c)**

Allene **3c** was synthesized with a similar manner to **3a**. Pale yellow oil (742 mg, 72%); IR ($CHCl_3$) $cm^{-1}$; 1693, 1956, 3005; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.36 and 1.53 (each s, 6.3H and 2.7H), 2.31 (s, 3H), 3.63-3.76 (m, 1H), 4.39-4.53 (m, 1H), 4.64-4.78 (m, 2H), 5.27 (quint, $J$ = 6.8 Hz, 1H), 7.02-7.17 (m, 2H), 7.67-7.71 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ major: 20.5, 28.2 (3C), 48.3, 76.0, 80.2, 86.8, 100.3, 129.3, 129.5, 138.7, 139.6, 141.6, 153.9, 209.3. minor: 20.5, 28.4 (3C), 49.3, 76.2, 80.6, 87.2, 100.3,

129.75, 129.83, 139.2, 139.9, 142.0, 154.0, 209.1; LR-EIMS *m/z* (%) 385 ($M^+$, 0.4), 330 (14), 329 (100), 259 (11), 246 (32), 202 (33), 158 (58), 57 (71); HR-EIMS calcd for $C_{16}H_{20}INO_2$ ($M^+$): 385.0539; found: 385.0533.

**_N_-(2,3-Butadien-1-yl)-_N_-(*tert*-butoxycarbonyl)-2-iodo 4-methoxycarbonylaniline (3d)**

Allene **3d** was synthesized with a similar manner to **3a**. Colorless oil (270 mg, 65%); IR ($CHCl_3$) $cm^{-1}$; 1699, 1720, 1956; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.35 and 1.55 (each s, 7H and 2H), 3.70-3.84 (m, 1H), 3.93(s, 3H), 4.40-4.55 (m, 1H), 4.64-4.77 (m, 2H), 5.27 (quin, $J$ = 6.8 Hz, 1H), 7.26 (d, $J$ = 8.0 Hz, 1H), 8.00 (d, $J$ = 8.0 Hz, 1H), 8.53 (s, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ major: 28.2 (3C), 48.1, 52.5, 76.2, 80.9, 86.5, 100.4, 129.7, 123.0, 130.2, 140.6, 148.3, 153.1, 165.2, 209.4. minor: 28.4 (3C), 49.2, 52.5, 76.5, 81.3, 86.9, 100.2, 129.7, 123.0, 130.2, 140.9, 148.3, 153.1, 165.2, 209.4; LR-FAB MS *m/z* (%) 430 ($MH^+$, 100); HR-FAB MS *m/z* calcd for $C_{17}H_{21}INO_4$ ($MH^+$): 430.0515; found: 430.0512.

**_N_-(2,3-Butadien-1-yl)-_N_-(*tert*-butoxycarbonyl)-4-chloro-2-iodoaniline (3e)**

Allene **3e** was synthesized with a similar manner to **3a**. Yellowish oil (463 mg, 58%); IR ($CHCl_3$) $cm^{-1}$; 1699, 1956; $^1H$ NHR (400 MHz, $CDCl_3$) $\delta$ 1.36 and 1.53 (each s, 6.3H and 2.7H), 3.62-3.76 (m, 1H), 4.38-4.54 (m, 1H), 4.63-4.80 (m, 2H), 5.25 (quint, $J$ = 6.4 Hz, 1H), 7.11 and 7.20 (each d, $J$ = 8.0 Hz, 0.7H and 0.3H), 7.31 (dd, $J$ = 8.0, 2.0 Hz, 1H), 7.85 (d, $J$ = 2.0 Hz, 1H); $^{13}C$ NMR (100 MHz) $\delta$ major: 28.2 (3C), 48.1, 76.2, 80.7, 86.5, 100.9, 128.9, 130.4, 133.3, 138.6, 143.0, 153.4, 209.4. minor: 28.4 (3C), 49.2, 76.4, 81.1, 87.0, 100.9, 129.2, 130.8, 133.7, 138.9, 143.3, 153.7, 209.1; LR-EIMS *m/z* (%) 405 ($M^+$, 0.3), 351 (33), 350 (13), 349 (100), 307 (12), 306 (12), 305 (37), 304 (25), 270 (30), 266 (25), 222 (12), 180 (11), 178 (34), 143 (15), 57 (34), 56 (53); HR-EIMS calcd for $C_{15}H_{17}ClINO_2$ ($M^+$): 404.9993; found: 404.9984.

**_N_-(2,3-Butadien-1-yl)-_N_-(*tert*-butoxycarbonyl)-2-iodo-6-methoxyaniline (3f)**

Allene **3f** was synthesized with a similar manner to **3a**. Colorless prisms (550 mg, 53%); mp 80-81 ºC (*n*-hexane); IR (KBr) $cm^{-1}$: 1701, 1950, 2978; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.34 and 1.54 (each s, 7H and 2H), 3.795 and 3.801 (each s, 2.6H and 0.4H), 3.95-4.03 and 4.07-4.25 (each m, 0.3H and 1.7H), 4.52-4.68 (m, 2H), 5.29-5.39 (m, 1H), 6.865 and 6.888 (each dd, $J$ = 8.0, 1.2 Hz, 0.85H and 0.15H), 6.950 and 6.956 (each t, $J$ = 8.0 Hz, 0.85H and 0.15H), 7.424 and 7.440 (each dd, $J$ = 8.0, 1.2 Hz, 0.85H and 0.15H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ major: 28.2 (3C), 47.5, 55.8, 75.0, 79.8, 86.8, 102.3, 111.5, 129.4, 130.6, 133.3, 154.2, 156.3, 209.2. minor: 28.5 (3C), 49.2, 56.0, 75.1, 80.5, 87.5, 102.5, 112.0, 129.7, 130.9, 133.7, 153.7, 156.7, 208.9; LR-EIMS *m/z* (%) 401 ($M^+$, 1.7), 346 (14), 345 (100), 275 (32), 262 (26), 234 (16), 174 (10), 57 (29); HR-EIMS calcd for $C_{16}H_{20}INO_3$ ($M^+$): 401.0488; found: 401.0479.

**_N_-(2,3-Butadien-1-yl)-_N_-(*tert*-butoxycarbonyl)-2-iodo-5-methoxyaniline (3g)**

Allene **3g** was synthesized with a similar manner to **3a**. Colorless oil (664 mg, 64%); IR ($CHCl_3$) $cm^{-1}$; 1697, 1956, 3005; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.37 and 1.54 (each s, 6.3H and 2.7H), 3.65-3.82 (m, 1H), 3.79 (s, 3H), 4.39-4.53 (m, 1H), 4.67-4.79 (m, 2H), 5.29 (quint, $J$ = 6.8 Hz, 1H), 6.61 (dd, $J$ = 8.8, 2.8 Hz, 1H), 6.79 and 6.87 (d and brs, $J$ = 2.8 Hz, 0.7H and 0.3H), 7.70 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ major: 28.2 (3C), 48.2, 55.5, 76.1, 80.4, 86.8, 89.0, 114.7, 116.0, 139.2, 145.1, 153.6, 160.2, 209.3. minor: 28.4 (3C), 49.3, 55.5, 76.3, 80.8, 87.3, 88.8, 115.3, 116.2, 139.5, 145.4, 153.6, 160.5, 209.3; LR-EIMS *m/z* (%) 401 ($M^+$, 0.7), 345 (22), 262 (18), 219 (13), 218 (100), 174 (47), 57 (63); HR-EIMS calcd for $C_{16}H_{20}INO_3$ ($M^+$): 401.0488; found: 401.0483.

**_N_-(2,3-Butadien-1-yl)-_N_-(*tert*-butoxycarbonyl)-2-iodo-3-methoxyaniline (3h)**

Allene **3h** was synthesized with a similar manner to **3a**. Yellowish oil (614 mg, 59%); IR ($CHCl_3$) $cm^{-1}$; 1693, 1956, 3009; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.34 and 1.54 (each s, 6.3H and 2.7H), 3.63-3.76 (m, 1H), 3.88 and 3.91 (each s, 1H and 2H), 4.43-4.59 (m, 1H), 4.63-4.79 (m, 2H), 5.28 (quint, $J$ = 2.4 Hz, 1H), 6.74 (d, $J$ = 8.0 Hz, 1H), 6.84 and 6.94 (each d, $J$ = 7.6 Hz, 0.7H and 0.3H), 7.24-7.33 (m, 1H); $^{13}C$

NMR (100 MHz, $CDCl_3$) $\delta$ major: 28.2 (3C), 48.1, 56.6, 75.9, 80.2, 86.8, 92.8, 109.4, 122.5, 129.0, 145.8, 153.8, 159.2, 209.3. minor : 28.5 (3C), 49.2, 56.6, 76.2, 80.7, 87.2, 92.8, 109.9, 122.7, 129.6, 146.1, 153.9, 159.6, 209.3; LR-FAB MS *m/z* (%) 402 ($MH^+$, 100); HR-FAB MS *m/z* calcd for $C_{16}H_{21}INO_3$ ($MH^+$): 402.0566; found: 402.0563.

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