Supporting Information

Efficient Synthesis of N-Butadiene Substituted Oxindole Derivatives

Table of Contents

1. General Methods.

2. General Procedure for Oxindole Derived Alkenylation Compounds and Characterization Data.

3. NMR Spectra of Oxindole Derived Alkenylation Compounds and Structure Determination.

4. Mechanism Study.
1. General Methods
NMR data were obtained for $^1$H at 400 MHz or 600 MHz, and for $^{13}$C at 100 MHz or 151 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl$_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether. N-substituted oxindoles were prepared according to the literature procedures.

2. General Procedure for Synthesis of Oxindoles and Oxindole Derived Alkenylation Compounds and Characterization Data

a. General Procedure for Synthesis of 1a$^{1,2}$:

Step 1: Iron chips (2.98 g, 53.2 mmol) were added in one portion to commercial 2-nitrophenylacetic acid (3.62 g, 20 mmol) in of glacial acetic acid (45 mL). The resulting mixture was heated to 100 °C for 4 h, then concentrated to dryness, sonicated in AcOEt and filtered to remove the insolubles. The filtrate was washed twice with 1 N HCl, H$_2$O, brine, dried over anhydrous sodium sulfate and concentrated, affording compound 2 (2.49 g, 95% yield).

Step 2: To a suspension of 2-oxindole (655.8 mg, 5.00 mmol), CuI (95 mg, 0.50 mmol) and K$_2$CO$_3$ (1.5 g, 11.0 mmol) in CH$_3$CN (15.0 mL), 2-bromo-1-propene (0.53 mL, 6.0 mmol) and MeNHCH$_2$CH$_2$NHMe (0.10 mL, 1.0 mmol) were added under nitrogen atmosphere. The reaction mixture was then stirred and reflux overnight. The reaction mixture was allowed to cool to room temperature, 1 M HCl was added, and the solution was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give compound 3 as a light red solid (605.5 mg, 70% yield).

Step 3: To a solution of 3 (412 mg, 2.3 mmol) in THF (7 ml) was added 60% sodium hydride (368 mg, 9.2 mmol). Methyl iodide (0.5 mL, 8.05 mmol) was added at 0 °C. The reaction mixture was then stirred at rt for 18 h and poured onto saturated aqueous NH$_4$Cl. The solution was extracted with DCM. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give compound 1a as a colorless oil (439.2 mg, 95% yield).

References:


b. Synthesis Oxindole Derived Alkenylation Compounds:
3,3-dimethyl-1-(prop-1-en-2-yl)indolin-2-one 1a (10.1 mg, 0.05 mmol), methyl acrylate 2a (13.6 μL, 3.0 equiv.), [Cp*Rh(MeCN)₃(SbF₆)₂] (2.1 mg, 5 mol %), Cu(acac)₂ (26.2 mg, 2 equiv.) and HOAc (6 μL, 2 equiv.) were stirred in DCE (0.5 mL) at 130 °C for 12 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:20) to give the product 3a as a yellow oil (13.5 mg, 95%).

c. Synthesis of Oxindole Derived Alkenylation Compound Derivative 4:
methyl (2E,4Z)-5-(3,3-dimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate 3a (14.25 mg, 0.05 mmol), NaOH (3.6 mg, 3 equiv.) were stirred in MeOH at room temperature for 12 h. After completion, the reaction mixture was acidified with 1N hydrochloric acid and extracted with ethyl acetate flash chromatography eluting with ethyl acetate and petroleum ether (1:5) to give the product 4 as a white solid (18.5 mg, 78%).

d. Synthesis of Oxindole Derived Alkenylation Compound Derivative 5:
To a solution of the product 3a (28.5 mg, 0.1 mmol) in anhydrous THF (1 mL) at -78°C was added DIBAL-H (1.0 M in heptane, 0.3 mL, 0.3 mmol) carefully over 5 min. The resulting solution was stirred at -78 °C for 2 h and quenched with saturated aqueous NH₄Cl (0.1 mL). The layer was separated and extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. Concentration in vacuo and purification by column chromatography afforded the alcohol 5 (16.7 mg, 65%) as a light yellow oil.

3,3-dimethyl-1-(prop-1-en-2-yl)indolin-2-one (1a). 18 h, colorless oil, 95% yield; ¹H NMR (400 MHz, CDCl₃): δ = 7.23-7.19 (m, 2H), 7.05 (td, J₁ = 7.6 Hz, J₂ = 1.2 Hz, 1H), 6.93 (dd, J₁ = 8.0 Hz, J₂ = 1.2 Hz, 1H), 5.37 (d, J = 1.2 Hz, 1H), 5.14 (d, J = 0.8 Hz, 1H), 2.10 (s, 3H), 1.40 (s, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): 180.3, 141.7, 138.1, 135.9, 127.5, 122.5, 122.5, 114.3, 109.4, 44.1, 24.6, 19.7 ppm. ESI HRMS: calcd. for C₁₃H₁₅NO⁺Na 224.1051, found 224.1049.

methyl (2E,4Z)-5-(3,3-dimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate (3a). 12 h, white solid: mp 82-84 °C, 95% yield; ¹H NMR (400 MHz, CDCl₃): δ = 7.23 (dd, J₁ = 6.0 Hz, J₂ = 1.2 Hz, 1H), 7.19 (dd, J₁ = 8.0 Hz, J₂ = 1.2 Hz, 1H), 7.08 (dd, J₁ = 7.6 Hz, J₂ = 0.8 Hz, 1H), 7.02 (dd, J₁ = 15.6 Hz, J₂ = 11.2 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.41 (d, J = 11.2 Hz, 1H), 5.93 (d, J = 15.6 Hz, 1H), 3. 65 (s, 3H), 2.14 (s, 3H), 1.48 (s, 3H), 1.43 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 180.2, 166.9, 141.3, 138.1, 138.0, 135.8, 127.8, 126.9, 123.0, 122.7, 122.1, 109.3, 51.5, 44.5, 25.1, 24.3, 20.4 ppm. ESI HRMS: calcd. for C₁₇H₁₉NO₃⁺Na 308.1263, found 308.1267.

methyl (2E,4Z)-5-(4-bromo-3,3-dimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate (3b). 12 h, white solid: mp 106-108 °C, 85% yield; ¹H NMR (400 MHz, CDCl₃): δ = 7.20 (dd, J₁ = 8.4 Hz, J₂ = 0.8 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.96 (dd, J₁ = 15.6 Hz, J₂ = 11.6 Hz, 1H), 6.61 (dd, J₁ = 8 Hz, J₂ = 0.8 Hz, 1H), 6.42 (d, J = 11.6 Hz, 1H), 5.94 (d, J = 15.6 Hz, 1H), 3. 67 (s, 3H), 2.13 (s, 3H), 1.63
(s, 3H), 1.58 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 179.5, 166.8, 143.2, 137.5, 133.2, 129.3, 127.4, 127.3, 122.7, 119.1, 108.2, 51.6, 46.6, 21.9, 21.4, 20.4 ppm. ESI HRMS: calcd. for C$_{17}$H$_{18}$BrNO$_3$+Na 386.0368, found 386.0367.

methyl (2$^E$,4$^Z$)-5-(5-chloro-3,3-dimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate (3c). 12 h, white solid: mp 96-98 °C, 80% yield; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.23 (s, 1H), 7.19 (d, $J$ = 8.4 Hz, 1H), 6.97 (t, $J$ = 12.6 Hz, 1H), 6.60 (d, $J$ = 8.4 Hz, 1H), 6.42 (d, $J$ = 10.8 Hz, 1H), 5.95 (d, $J$ = 15.6 Hz, 1H), 3.67 (s, 3H), 2.13 (s, 3H), 1.48 (s, 3H), 1.42 (s, 3H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 179.6, 166.8, 139.7, 137.6, 137.3, 128.4, 127.8, 127.0, 123.3, 122.5, 110.2, 51.6, 44.7, 24.9, 24.2, 20.3 ppm. ESI HRMS: calcd. for C$_{17}$H$_{18}$ClNO$_3$+Na 342.0873, found 342.0878.

methyl (2$^E$,4$^Z$)-5-(5-bromo-3,3-dimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate (3d). 12 h, white solid: mp 136-138 °C, 80% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.36 (d, $J$ = 2 Hz, 1H), 7.33 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.0 Hz, 1H), 6.96 (dd, $J_1$ = 11.6 Hz, 1H), 5.94 (d, $J$ = 15.6 Hz, 1H), 3.68 (s, 3H), 2.14 (s, 3H), 1.49 (s, 3H), 1.43 (s, 3H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 179.4, 166.8, 140.3, 137.8, 137.6, 137.2, 130.8, 127.0, 126.2, 122.6, 110.7, 100.0, 51.6, 44.7, 24.9, 24.2, 20.3 ppm. ESI HRMS: calcd. for C$_{17}$H$_{18}$BrNO$_3$+Na 386.0368, found 386.0368.

methyl (2$^E$,4$^Z$)-5-(5-fluoro-3,3-dimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate (3e). 12 h, colorless oil, 80% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.02-6.95 (m, 2H), 7.90 (dd, $J_1$ = 8.8 Hz, $J_2$ = 2.4 Hz, 1H), 6.61-6.58 (m, 1H), 6.41 (d, $J$ = 11.2 Hz, 1H), 5.94 (d, $J$ = 15.6 Hz, 1H), 3.67 (s, 3H), 2.13 (s, 3H), 1.48 (s, 3H), 1.42 (s, 3H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 179.9, 166.9, 160.8, 158.4, 137.9, 137.8, 137.4, 137.1, 137.1, 127.0, 122.3, 114.3, 114.0, 111.0, 110.7, 109.9, 109.9, 51.6, 44.9, 44.9, 24.9, 24.3, 20.4 ppm. ESI HRMS: calcd. for C$_{17}$H$_{18}$FNO$_3$+Na 326.1168, found 326.1165.

methyl (2$^E$,4$^Z$)-5-(3,3,5-trimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate (3f). 12 h, yellow oil, 96% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.06-6.99 (m, 3H), 6.57 (d, $J$ = 8.0 Hz, 1H), 6.39 (d, $J$ = 11.2 Hz, 1H), 5.92 (d, $J$ = 15.6 Hz, 1H), 3.66 (s, 3H), 2.35 (s, 3H), 2.13 (s, 3H), 1.47 (s, 3H), 1.41 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 180.27, 167.00, 138.98, 138.34, 138.21, 135.84, 132.65, 128.14, 126.73, 123.58, 122.00, 109.11, 51.56, 44.55, 25.15, 24.41, 21.09, 20.45 ppm. ESI HRMS: calcd. for C$_{18}$H$_{21}$NO$_3$+Na 322.1419, found 322.1415.

methyl (2$^E$,4$^Z$)-5-(6-chloro-3,3-dimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate (3g). 12 h, white solid: mp 88-90 °C, 70% yield; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.16 (d, $J$ = 8.0 Hz, 1H), 7.07 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1H), 6.98 (dd, $J_1$ = 15.6 Hz, $J_2$ = 11.6 Hz, 1H), 6.67 (d, $J$ = 1.6 Hz, 1H), 6.44 (d, $J$ = 11.2 Hz, 1H), 6.97 (d, $J$ = 15.2 Hz, 1H), 3.68 (s, 3H), 2.13 (s, 3H), 1.47 (s,
methyl (2E,4Z)-5-(3,3-diethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate (3h). 12 h, yellow oil, 72% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.23$-$7.16$ (m, 2H), 7.12-$7.04$ (m, 2H), 6.66 (d, $J = 7.6$ Hz, 1H), 6.42 (d, $J = 11.2$ Hz, 1H), 5.92 (d, $J = 15.6$ Hz, 1H), 3.63 (s, 3H), 2.13 (s, 3H), 2.04-$1.97$ (m, 2H), 1.87-$1.82$ (m, 2H), 0.74 (t, $J = 7.2$ Hz, 3H), 0.59 (t, $J = 7.6$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 179.0, 166.9, 143.1, 138.5, 138.4, 129.8, 125.9, 125.8, 121.5, 121.0, 117.6, 108.3, 50.5, 26.3, 19.6, 19.1, 18.9 ppm. ESI HRMS: calcd. for C$_{19}$H$_{23}$NO$_3$+Na 336.1576, found 336.1576.

methyl (2E,4Z)-5-(2'-oxospiro[cyclopropane-1,3'-indolin]-1'-yl)hexa-2,4-dienoate (3i). 17 h, white solid: mp 116-118 °C, 90% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.20$ (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.10 (dd, $J_1 = 15.2$ Hz, $J_2 = 11.2$ Hz, 1H), 6.50 (td, $J_1 = 7.6$ Hz, $J_2 = 0.8$ Hz, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.42 (d, $J = 11.6$ Hz, 1H), 5.95 (d, $J = 15.2$ Hz, 1H), 3.67 (s, 3H), 2.18 (s, 3H), 1.88-$1.75$ (m, 2H), 1.64-$1.54$ (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 174.9, 166.0, 141.1, 137.4, 137.3, 129.8, 125.9, 125.8, 121.5, 121.0, 117.6, 108.3, 50.5, 26.3, 19.6, 19.1, 18.9 ppm. ESI HRMS: calcd. for C$_{17}$H$_{17}$NO$_3$+Na 342.1105, found 342.1105.

methyl (2E,4Z)-5-(2-oxoindolin-1-yl)hexa-2,4-dienoate (3l). 12 h, yellow solid: mp 111-113 °C, 75% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.31$-$7.21$ (m, 2H), 7.10-$7.04$ (m, 2H), 6.65 (d, $J = 7.6$ Hz, 1H), 6.43 (d, $J = 11.6$ Hz, 1H), 5.96 (d, $J = 15.2$ Hz, 1H), 3.70-$3.66$ (m, 5H), 2.15 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 173.8, 166.9, 143.9, 138.0, 137.9, 128.1, 127.2, 124.8, 124.6, 122.9, 122.5, 109.3, 51.6, 36.0, 20.4 ppm. ESI HRMS: calcd. for C$_{15}$H$_{15}$NO$_3$+Na 280.0953, found 280.0953.

ethyl (2E,4Z)-5-(2-oxoindolin-1-yl)hexa-2,4-dienoate (3m). 12 h, yellow oil, 75% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.29$-$7.20$ (m, 2H), 7.09-$7.03$ (m, 2H), 6.65 (d, $J = 7.6$ Hz, 1H), 6.43 (d, $J = 11.6$ Hz, 1H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.73-$3.59$ (m, 2H), 2.15 (s, 3H), 1.22 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 173.9, 166.5, 143.9, 138.0, 137.9, 128.1, 127.2, 124.8, 124.6, 122.9, 122.5, 109.4, 60.4, 36.0, 20.4, 14.2 ppm. ESI HRMS: calcd. for C$_{16}$H$_{17}$NO$_3$+Na 294.1106, found 294.1106.

butyl (2E,4Z)-5-(2-oxoindolin-1-yl)hexa-2,4-dienoate (3n). 12 h, yellow solid: mp 35-37 °C, 61% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.29$-$7.20$ (m, 2H), 7.09-$7.02$ (m, 2H), 6.64 (d, $J = 7.6$ Hz, 1H), 6.41 (d, $J = 11.6$ Hz, 1H), 5.94 (d, $J = 15.2$ Hz, 1H), 4.09-4.05 (m, 2H), 3.72-$3.58$ (m, 2H), 2.15 (s, 3H), 1.60-$1.53$ (m, 2H), 1.36-$1.25$ (m, 2H), 0.88 (t, $J = 7.6$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 173.9, 166.5, 143.9, 138.0, 137.9, 128.1, 127.2, 124.8, 124.6, 122.9, 122.5, 109.4, 60.4, 36.0, 20.4, 14.2 ppm. ESI HRMS: calcd. for C$_{16}$H$_{17}$NO$_3$+Na 294.1106, found 294.1106.
tert-butyl (2E,4Z)-5-(2-oxoindolin-1-yl)hexa-2,4-dienoate (3o). 12 h, yellow solid: mp 86-88 °C, 75% yield; 1H NMR (400 MHz, CDCl3): δ = 7.30-7.22 (m, 2H), 7.00 (dd, J1 = 15.6 Hz, J2 = 11.6 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 6.41 (d, J = 11.6 Hz, 1H), 5.90 (d, J = 15.6 Hz, 1H), 3.73-3.59 (m, 2H), 2.15 (s, 3H), 1.43 (s, 9H) ppm; 13C NMR (100 MHz, CDCl3): δ = 173.9, 166.6, 143.9, 137.8, 137.8, 128.0, 127.1, 124.7, 124.6, 122.9, 109.4, 64.3, 36.0, 30.6, 20.4, 19.1, 13.6 ppm. ESI HRMS: calcd. for C18H21NO3+Na 322.1419, found 322.1414.

benzyl (2E,4Z)-5-(2-oxoindolin-1-yl)hexa-2,4-dienoate (3p). 12 h, yellow oil, 66% yield; 1H NMR (400 MHz, CDCl3): δ = 7.32-7.25 (m, 6H), 7.22 (dd, J1 = 8.0 Hz, J2 = 1.2 Hz, 1H), 7.12 (dd, J1 = 15.6 Hz, J2 = 11.6 Hz, 1H), 7.06 (dd, J1 = 7.6 Hz, J2 = 1.2 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 6.41 (d, J = 11.6 Hz, 1H), 5.99 (d, J = 15.6 Hz, 1H), 5.15-5.08 (m, 2H), 3.66-3.63 (m, 2H), 2.15 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ = 173.9, 166.3, 143.9, 138.4, 138.2, 135.9, 128.5, 128.1, 128.1, 128.0, 127.0, 124.8, 124.6, 122.9, 122.4, 109.4, 66.2, 36.0, 20.4 ppm. ESI HRMS: calcd. for C21H19NO3+Na 356.1263, found 356.1261.

phenyl (2E,4Z)-5-(3,3-dimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoate (3q). 17 h, white solid: mp 115-117 °C, 62% yield; 1H NMR (400 MHz, CDCl3): δ = 7.33 (t, J = 8.0 Hz, 2H), 7.25-7.16 (m, 4H), 7.10-7.03 (m, 3H), 6.71 (d, J = 7.6 Hz, 1H), 6.50 (d, J = 11.2 Hz, 1H), 6.12 (d, J = 15.2 Hz, 1H), 2.19 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ = 180.2, 164.9, 150.6, 141.2, 139.7, 139.1, 135.7, 129.3, 127.9, 126.7, 125.7, 123.1, 122.8, 121.5, 109.3, 44.5, 25.2, 24.3, 20.6 ppm. ESI HRMS: calcd. for C22H21NO3+Na 370.1419, found 370.1419.

methyl (2E,4Z)-5-(3,3-dimethyl-2-oxoindolin-1-yl)-5-phenylpenta-2,4-dienoate (3r). 12 h, yellow solid: mp 175-177 °C, 63% yield; 1H NMR (400 MHz, CDCl3): δ = 7.41-7.39 (m, 2H), 7.35-7.32 (m, 3H), 7.31-7.28 (m, 1H), 7.20 (dd, J1 = 15.2 Hz, J2 = 11.6 Hz, 1H), 7.11-7.05 (m, 2H), 7.01 (d, J = 11.6 Hz, 1H), 6.47-6.42 (m, 1H), 6.14 (d, J = 15.2 Hz, 1H), 3.69 (s, 3H), 1.58 (s, 3H), 1.56 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ = 180.4, 166.8, 141.9, 138.4, 138.4, 135.3, 134.4, 129.8, 129.0, 127.8, 126.1, 125.2, 123.9, 123.2, 122.7, 110.3, 51.6, 44.7, 25.2, 24.8 ppm. ESI HRMS: calcd. for C22H21NO3+Na 370.1419, found 370.1416.

(2E,4Z)-5-(3,3-dimethyl-2-oxoindolin-1-yl)hexa-2,4-dienoic acid (4). 12 h, white solid: mp 178-180 °C, 78% yield; 1H NMR (600 MHz, CDCl3): δ = 7.24 (d, J = 7.2 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.10-7.04 (m, 2H), 6.67 (d, J = 7.8 Hz, 1H), 6.42 (d, J = 11.4 Hz, 1H), 5.90 (d, J = 15.0 Hz, 1H), 2.15 (s, 3H),
1.46 (s, 3H), 1.42 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 180.30, 170.71, 141.23, 139.95, 139.12, 135.76, 127.91, 126.68, 123.15, 122.80, 121.50, 109.35, 44.53, 25.14, 24.36, 20.56 ppm. ESI HRMS: calcd. for C$_{16}$H$_{17}$NO$_3$+Na 294.1106, found 294.1108.

1-((2$E$,4$Z$)-6-hydroxyhexa-2,4-dien-2-yl)-3,3-dimethylindolin-2-one (5). 2 h, colorless oil, 65% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.25-7.18 (m, 2H), 7.07 (td, $J_1 = 7.6$ Hz, $J_2 = 0.8$ Hz, 1H), 6.70 (d, $J = 7.6$ Hz, 1H), 6.30 (dd, $J_1 = 9.6$ Hz, $J_2 = 1.2$ Hz, 1H), 6.00-5.88 (m, 2H), 4.08 (d, $J = 4.8$ Hz, 2H), 2.05 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 180.36, 141.50, 135.86, 134.04, 130.08, 128.46, 127.79, 125.08, 122.74, 122.62, 109.47, 63.19, 44.39, 25.02, 24.37, 19.89 ppm. ESI HRMS: calcd. for C$_{16}$H$_{19}$NO$_2$+Na 280.1313, found 280.1307.
3. NMR Spectra of Oxindole Derived Alkenylation Compounds and Structure Determination
irradiation of HA at 2.15 ppm

noe of Hb at 6.42 ppm

noe of He at 6.68 ppm

noe of Hc at 6.68 ppm

noe of Ha at 6.42 ppm

irradiation of Ha at 2.15 ppm
C-H HMOC

C-H HMOC
Irradiation of Ha at 7.01 ppm

NOE of Hb at 7.19 ppm

NOE of Hd at 7.39 ppm

Irradiation of Hb at 7.01 ppm

NOE of Hc at 6.15 ppm

NOE of Hf at 7.19 ppm

3r
irradiation of Hb at 7.20 ppm

noe of Hα and Hε at 7.08 ppm

noe of Hα at 7.02 ppm

irradiation of Hε at 7.19 ppm

noe of Hε at 6.13 ppm

noe of Hα at 7.01 ppm
4. Mechanism Study

Deuterium-labeling experiments were carried out to study the mechanism of this coupling reaction. 1a was stirred in the absence of methyl acrylate at 130 °C for 2 h under standard conditions with AcOD/DCE, the deuterium rate was obtained from 1H NMR.
To investigate the mechanism of this reaction, deuterium experiments and a kinetic isotope effect (KIE) study were conducted. A deuterium kinetic isotope effect (KIE) was determined to be 1.4, thus indicating that C-H bond cleavage might not be involved in the rate-determining step (substrate [D]-1a with only 70% deuterium incorporation probably led to incorrect KIE value, and the conclusion is likely to be inaccurate).

<table>
<thead>
<tr>
<th>Time/h</th>
<th>Yield/% (3a)</th>
<th>Yield/% (3a')</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.4</td>
<td>11.2</td>
</tr>
<tr>
<td>2</td>
<td>40.4</td>
<td>19.6</td>
</tr>
<tr>
<td>3</td>
<td>58.9</td>
<td>30.8</td>
</tr>
<tr>
<td>4</td>
<td>70.8</td>
<td>44.2</td>
</tr>
<tr>
<td>5</td>
<td>86.9</td>
<td>56.8</td>
</tr>
</tbody>
</table>
Yield and time relation of product 3a and 3a’

\[ y = 15.94x + 8.06 \quad R^2 = 0.9946 \]

\[ y = 11.58x - 2.22 \quad R^2 = 0.993 \]

yield 3a

yield 3a’