

Efficient Generation of Indeno[1,2-*c*]chromenes via Pd-Catalyzed Reaction of 2-Alkynylhalobenzenes with 2-Alkynylphenols

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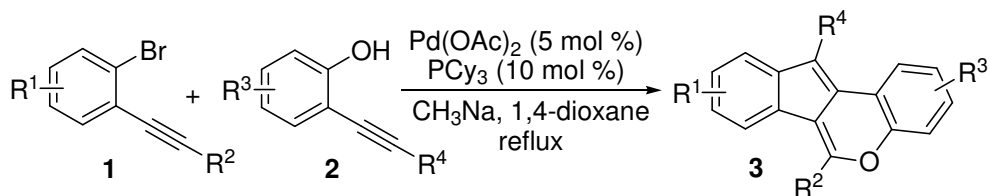
Supporting Information

1. General experimental methods (S2).
2. General experimental procedure and characterization data (S2-S9).
3. ¹H and ¹³C NMR spectra of compound **3** (S10-S47).

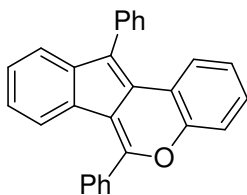
General experimental methods:

All reactions were performed in reaction tubes under air atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35°C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

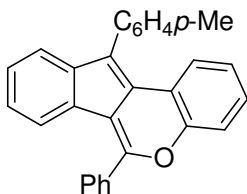
General experimental procedure for the synthesis of indeno[1,2-c]chromenes via a Pd-catalyzed reaction of 2-alkynylbromobenzene with 2-alkynylphenol.



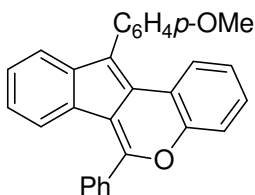
2-Alkynylhalobenzene (0.40 mmol) was added to a mixture of Pd(OAc)₂ (5 mol %), tricyclohexylphosphine (10 mol %), CH₃ONa (0.80 mmol), and 2-alkynylphenol (0.60 mmol) in 1,4-dioxane (3.0 mL). The mixture was stirred under reflux. After completion of the reaction as indicated by TLC, the mixture was cooled and diluted by EtOAc (10 mL), washed with saturated brine (2 × 10 mL), and dried by anhydrous Na₂SO₄. Evaporation of the solvent followed by purification on silica gel provided the product 3.



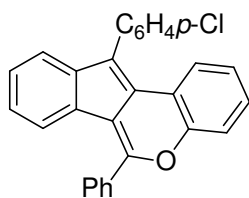
6,11-Diphenylindeno[1,2-c]chromene (**3a**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.90-7.87 (m, 2H), 7.69 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.62-7.44 (m, 10H), 7.38-7.29 (m, 3H), 7.11-7.04 (m, 2H). ^{13}C NMR (100 MHz) δ 152.6, 150.1, 144.4, 136.6, 133.8, 130.5, 130.0, 129.7, 129.5, 128.9, 128.8, 127.7, 127.4, 126.7, 126.5, 124.9, 124.3, 123.8, 122.8, 121.5, 120.1, 119.3, 117.7, 117.3. HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{18}\text{O}$ $[\text{M}+\text{H}]^+$ requires 371.1436, found 371.1424.



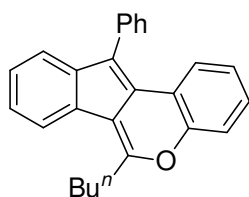
6-Phenyl-11-(*p*-tolyl)indeno[1,2-c]chromene (**3b**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.89-7.87 (m, 2H), 7.75-7.73 (m, 1H), 7.63-7.60 (m, 3H), 7.50-7.43 (m, 4H), 7.39-7.35 (m, 3H), 7.33-7.29 (m, 2H), 7.10-7.05 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz) δ 152.4, 150.1, 144.5, 137.1, 133.9, 133.5, 130.5, 129.8, 129.6, 129.5, 128.8, 127.6, 126.65, 126.60, 124.9, 124.2, 123.6, 122.7, 121.4, 120.2, 119.4, 117.6, 117.3, 21.5. HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{20}\text{O}$ $[\text{M}+\text{H}]^+$ requires 385.1592, found 385.1599.



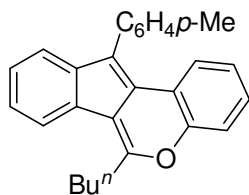
11-(4-Methoxyphenyl)-6-phenylindeno[1,2-c]chromene (**3c**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.90-7.88 (m, 2H), 7.73 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.64-7.62 (m, 3H), 7.52-7.49 (m, 3H), 7.46-7.44 (m, 1H), 7.39-7.31 (m, 3H), 7.12-7.07 (m, 4H), 3.95 (s, 3H). ^{13}C NMR (100 MHz) δ 158.9, 134.2, 131.1, 130.5, 129.5, 128.7, 127.6, 126.7, 124.8, 124.2, 122.7, 121.4, 119.3, 117.7, 114.3, 55.3. HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{H}]^+$ requires 401.1542, found 401.1530.



11-(4-Chlorophenyl)-6-phenylindeno[1,2-c]chromene (**3d**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.88-7.86 (m, 2H), 7.66 (dd, $J = 8.4, 1.2\text{ Hz}$, 1H), 7.62-7.60 (m, 3H), 7.54-7.49 (m, 5H), 7.46-7.44 (m, 1H), 7.35-7.32 (m, 3H), 7.11-7.08 (m, 2H). ^{13}C NMR (100 MHz) δ 152.9, 150.1, 143.9, 135.1, 133.7, 133.2, 131.4, 130.6, 129.7, 129.5, 129.2, 128.8, 127.9, 126.8, 125.0, 124.7, 124.4, 124.1, 122.9, 121.5, 119.8, 119.0, 117.8, 117.2. HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{17}\text{ClO}$ $[\text{M}+\text{H}]^+$ requires 405.1046, found 405.1045.

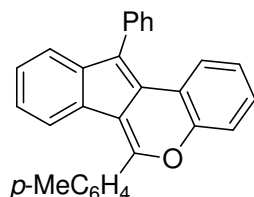


6-Butyl-11-phenylindeno[1,2-c]chromene (**3e**). Yellow solid, ^1H NMR (400 MHz, CDCl_3): δ 7.96 (d, $J = 7.6\text{ Hz}$, 1H), 7.64 (d, $J = 8.0\text{ Hz}$, 1H), 7.55-7.51 (m, 4H), 7.47-7.27 (m, 6H), 7.05-7.00 (m, 1H), 3.23 (t, $J = 7.6\text{ Hz}$, 2H), 1.99-1.91 (m, 2H), 1.61-1.55 (m, 2H), 1.02 (t, $J = 7.6\text{ Hz}$, 3H). ^{13}C NMR (100 MHz) δ 157.2, 149.9, 144.1, 136.8, 130.1, 129.8, 128.8, 127.4, 127.3, 125.9, 125.2, 124.9, 124.1, 123.4, 122.9, 121.5, 120.2, 119.5, 117.4, 116.2, 32.4, 29.6, 22.7, 13.9. HRMS (ESI) calculated for $\text{C}_{26}\text{H}_{22}\text{O}$ $[\text{M}+\text{H}]^+$ requires 351.1749, found 351.1746.

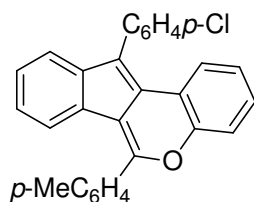


6-Butyl-11-(p-tolyl)indeno[1,2-c]chromene (**3f**). Yellow solid, ^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, $J = 7.2\text{ Hz}$, 1H), 7.69 (dd, $J = 8.0, 0.9\text{ Hz}$, 1H), 7.44-7.32 (m, 8H), 7.29-7.25 (m, 1H), 7.04-7.01 (m, 1H), 3.21 (t, $J = 7.6\text{ Hz}$, 2H), 2.47 (s, 3H), 1.97-1.90 (m, 2H), 1.59-1.53 (m, 2H), 1.01 (t, $J = 7.2\text{ Hz}$, 3H). ^{13}C NMR (100 MHz) δ 157.0, 149.9,

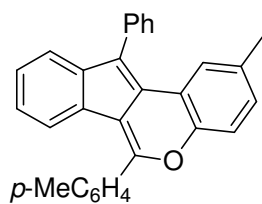
144.2, 136.8, 133.7, 129.9, 129.8, 129.5, 127.3, 125.9, 125.2, 124.9, 124.0, 123.2, 122.8, 121.5, 120.3, 119.6, 117.4, 116.3, 32.3, 29.6, 22.7, 21.4, 14.0. HRMS (ESI) calculated for $C_{27}H_{24}O$ $[M+H]^+$ requires 365.1905, found 365.1890.



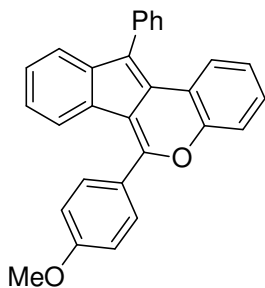
11-Phenyl-6-(p-tolyl)indeno[1,2-c]chromene (**3g**). Red solid, 1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 2H), 7.68 (dd, J = 8.0, 1.2 Hz, 1H), 7.60-7.53 (m, 5H), 7.48-7.40 (m, 4H), 7.37-7.28 (m, 3H), 7.11-7.03 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz) δ 152.9, 150.1, 144.3, 140.8, 136.7, 130.9, 130.0, 129.8, 129.45, 129.43, 128.9, 127.6, 127.4, 126.6, 126.3, 124.8, 124.2, 123.8, 122.7, 121.5, 120.1, 119.3, 117.7, 117.0, 21.7. HRMS (ESI) calculated for $C_{29}H_{20}O$ $[M+H]^+$ requires 385.1592, found 385.1579.



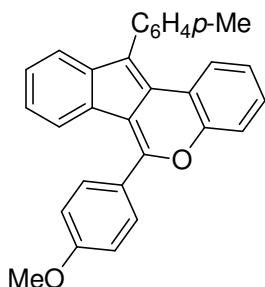
11-(4-Chlorophenyl)-6-(p-tolyl)indeno[1,2-c]chromene (**3h**). Red solid, 1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2H), 7.66 (dd, J = 8.0, 1.2 Hz, 1H), 7.58-7.56 (m, 1H), 7.56-7.52 (m, 4H), 7.47-7.41 (m, 3H), 7.36-7.32 (m, 3H), 7.12-7.10 (m, 2H), 2.52 (s, 3H). ^{13}C NMR (100 MHz) δ 153.2, 150.2, 143.9, 140.9, 135.2, 134.2, 133.2, 131.5, 130.8, 129.8, 129.5, 129.4, 129.2, 127.9, 126.6, 124.7, 124.3, 122.8, 121.6, 119.8, 119.0, 117.8, 117.0, 21.7. HRMS (ESI) calculated for $C_{29}H_{19}ClO$ $[M+H]^+$ requires 419.1203, found 419.1178.



2-Methyl-11-phenyl-6-(*p*-tolyl)indeno[1,2-*c*]chromene (**3i**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, J = 8.0 Hz, 2H), 7.60-7.52 (m, 5H), 7.47-7.44(m, 2H), 7.41-7.37(m, 3H), 7.34-7.29 (m, 2H), 7.11-7.07 (m, 2H), 2.50 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz) δ 153.0, 148.3, 144.2, 140.7, 136.7, 133.6, 131.0, 130.0, 129.8, 129.4, 128.73, 128.67, 127.4, 126.4, 125.9, 124.8, 124.0, 122.5, 121.4, 119.7, 119.2, 117.4, 116.9, 21.6, 21.2. HRMS (ESI) calculated for $\text{C}_{30}\text{H}_{22}\text{O}$ $[\text{M}+\text{H}]^+$ requires 399.1749, found 399.1760.

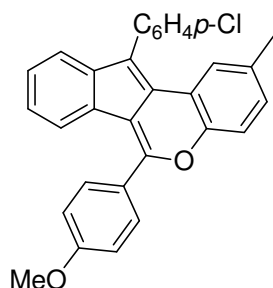


6-(4-Methoxyphenyl)-11-phenylindeno[1,2-*c*]chromene (**3j**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.0Hz, 1H), 7.63-7.53 (m, 5H), 7.48-7.42 (m, 2H), 7.38-7.28 (m, 3H), 7.13-7.10 (m, 3H), 7.07-7.03 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz) δ 161.3, 152.7, 150.1, 144.2, 136.7, 131.1, 130.0, 129.9, 128.9, 127.6, 127.4, 126.5, 126.0, 124.8, 124.1, 123.9, 122.6, 121.4, 120.1, 119.3, 117.6, 116.8, 114.1, 113.5, 55.4. HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{H}]^+$ requires 401.1542, found 401.1525.

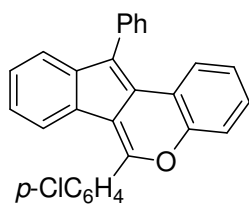


6-(4-Methoxyphenyl)-11-(*p*-tolyl)indeno[1,2-*c*]chromene (**3k**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.83-7.81 (m, 2H), 7.73 (dd, J = 8.0, 1.2Hz, 1H), 7.60 (d, J = 7.6Hz, 1H), 7.47-7.45 (m, 2H), 7.43-7.26 (m, 6H), 7.11-7.03 (m, 4H), 3.90 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz) δ 161.2, 152.6, 150.1, 144.3, 136.9, 133.6, 131.1, 129.8, 129.6, 127.5, 126.5, 126.2, 126.1, 124.8, 124.1, 123.8, 122.6, 121.4, 120.2, 119.3, 117.6, 116.9, 114.1,

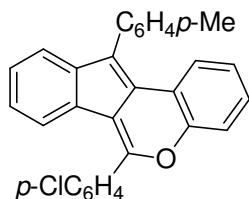
55.4, 21.4. HRMS (ESI) calculated for $C_{30}H_{22}O_2$ $[M+H]^+$ requires 415.1698, found 415.1694.



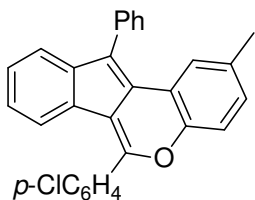
11-(4-Chlorophenyl)-6-(4-methoxyphenyl)-2-methylindeno[1,2-c]chromene (**3l**). Red solid, 1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.4 Hz, 2H), 7.61-7.59 (m, 1H), 7.53 (m, 4H), 7.47 (s, 1H), 7.37-7.32 (m, 3H), 7.16-7.10 (m, 4H), 3.95 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz) δ 161.3, 153.1, 148.3, 143.8, 135.3, 133.8, 133.1, 131.5, 131.1, 129.8, 128.9, 126.5, 126.0, 124.5, 124.4, 124.2, 122.7, 121.4, 119.5, 118.9, 117.5, 116.6, 114.1, 55.5, 21.3. HRMS (ESI) calculated for $C_{30}H_{21}ClO_2$ $[M+H]^+$ requires 449.1308, found 449.1326.



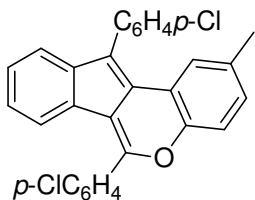
6-(4-Chlorophenyl)-11-phenylindeno[1,2-c]chromene (**3m**). Red solid, 1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.4 Hz, 2H), 7.67 (dd, J = 8.0, 1.2 Hz, 1H), 7.60-7.56 (m, 6H), 7.52-7.42 (m, 3H), 7.37-7.30 (m, 3H), 7.14-7.05 (m, 2H). ^{13}C NMR (100 MHz) δ 151.2, 150.0, 144.5, 136.7, 136.5, 132.2, 130.9, 129.9, 129.5, 129.1, 128.9, 127.8, 127.5, 126.92, 126.86, 124.9, 124.4, 123.7, 122.9, 121.3, 119.9, 119.5, 117.6. HRMS (ESI) calculated for $C_{28}H_{17}ClO$ $[M+H]^+$ requires 405.1046, found 405.1024.



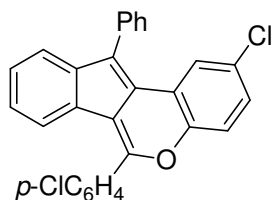
6-(4-Chlorophenyl)-11-(*p*-tolyl)indeno[1,2-*c*]chromene (**3n**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, J = 8.4 Hz, 2H), 7.72 (dd, J = 8.0, 1.2 Hz, 1H), 7.60-7.58 (m, 2H), 7.51-7.41 (m, 4H), 7.37-7.29 (m, 5H), 7.13-7.06 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz) δ 151, 150.0, 144.6, 137.2, 136.6, 134.2, 133.3, 132.2, 131.0, 129.7, 129.6, 129.1, 128.8, 127.7, 126.9, 124.9, 124.3, 123.5, 122.9, 121.3, 120.1, 119.5, 117.6, 21.5. HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{19}\text{ClO}$ $[\text{M}+\text{H}]^+$ requires 419.1203, found 419.1191.



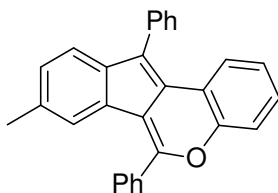
6-(4-Chlorophenyl)-2-methyl-11-phenylindeno[1,2-*c*]chromene (**3o**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, J = 8.0 Hz, 2H), 7.60-7.56 (m, 6H), 7.51-7.45 (m, 3H), 7.39-7.32 (m, 3H), 7.14-7.09 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz) δ 151.2, 148.2, 144.4, 136.5, 133.9, 132.3, 130.9, 129.9, 129.54, 129.51, 129.1, 128.8, 127.5, 126.8, 126.5, 124.8, 123.8, 122.8, 121.3, 119.6, 119.4, 117.3, 21.2. HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{19}\text{ClO}$ $[\text{M}+\text{H}]^+$ requires 419.1203, found 419.1178.



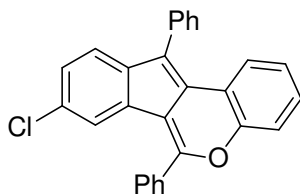
6,11-Bis(4-chlorophenyl)-2-methylindeno[1,2-*c*]chromene (**3p**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.83-7.81 (m, 2H), 7.61-7.59 (m, 2H), 7.55-7.46 (m, 6H), 7.36-7.33 (m, 3H), 7.18-7.10 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz) δ 151.5, 148.2, 144.1, 136.6, 135.0, 134.1, 133.3, 132.2, 131.4, 130.9, 129.4, 129.13, 129.09, 129.07, 126.9, 124.9, 124.6, 124.1, 122.9, 121.4, 119.4, 119.1, 117.5, 21.3. HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{18}\text{Cl}_2\text{O}$ $[\text{M}+\text{H}]^+$ requires 453.0813, found 453.0780.



2-Chloro-6-(4-chlorophenyl)-11-phenylindeno[1,2-c]chromene (**3q**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.83 (m, 2H), 7.62-7.51 (m, 9H), 7.38-7.36 (3H), 7.28-7.27 (m, 1H), 7.17-7.13 (m, 1H). ^{13}C NMR (100 MHz) δ 148.4, 136.8, 135.6, 134.3, 131.9, 130.9, 129.7, 129.5, 129.2, 129.1, 127.9, 127.7, 127.1, 124.2, 123.4, 121.4, 121.3, 119.8, 118.9. HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{16}\text{Cl}_2\text{O}$ $[\text{M}+\text{H}]^+$ requires 439.0656, found 439.0635.



8-Methyl-6,11-diphenylindeno[1,2-c]chromene (**3r**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.89-7.87 (m, 2H), 7.67-7.53 (m, 8H), 7.47-7.41 (m, 2H), 7.31-7.21 (m, 3H), 7.16-7.14 (m, 1H), 7.06-7.02 (m, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz) δ 152.3, 150.0, 142.1, 136.8, 133.9, 132.4, 130.5, 130.1, 129.9, 129.6, 128.8, 128.7, 127.8, 127.5, 127.4, 126.5, 124.7, 124.2, 123.0, 121.9, 120.2, 119.1, 117.6, 117.3, 21.8. HRMS (ESI) calculated for $\text{C}_{29}\text{H}_{20}\text{O}$ $[\text{M}+\text{H}]^+$ requires 385.1592, found 385.1590.



8-Chloro-6,11-diphenylindeno[1,2-c]chromene (**3s**). Red solid, ^1H NMR (400 MHz, CDCl_3): δ 7.89-7.87 (m, 2H), 7.67-7.66 (m, 4H), 7.59-7.56 (m, 4H), 7.51-7.45 (m, 3H), 7.36-7.32 (m, 1H), 7.30-7.25 (m, 2H), 7.10-7.07 (m, 1H). ^{13}C NMR (100 MHz) δ 153.7, 150.1, 142.6, 136.2, 134.3, 133.3, 130.9, 129.9, 129.4, 128.98, 128.95, 128.5, 127.9, 127.6, 126.7, 125.8, 124.8, 124.5, 124.2, 121.4, 120.1, 119.9, 117.7, 116.5. HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{17}\text{ClO}$ $[\text{M}+\text{H}]^+$ requires 405.1046, found 405.1033.

