Carbon-Carbon Bond Formation via the Electrophilic Addition of Carbocations to Allenes

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I. Materials. CH₂Cl₂ was distilled from P₂O₅ before use. Arylpropa-1,2-dienes were prepared from corresponding dibromocyclopropanes with ethylmagnesium bromide according to the known procedure. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. All ¹H NMR experiments were measured with tetramethylsilane (0 ppm) in CDCl₃ or the signal of residual chloroform (7.26 ppm) as the internal reference and ¹³C NMR experiments were measured in relative to the signal of residual chloroform (77.0 ppm) in CDCl₃.

II. Reaction of Arylpropa-1,2-dienes 1 with 1,3-Diarylprop-2-en-1-ols 2 in the Presence of ZnX₂ for the Synthesis of Allylic Halides 3.

(1) (Z)-3-Phenyl-(E)-2-(1,3-diphenylallyl)allyl iodide (3a).

Typical procedure I. Under nitrogen atmosphere, anhydrous ZnI₂ (64 mg, 0.2 mmol) was added to a Schlenk tube. A solution of 1a (23 mg, 0.2 mmol) and 2a (43 mg, 0.2 mmol) in 2 mL of CH₂Cl₂ was then added at 0 °C. The reaction mixture was stirred at 0 °C and the reaction was monitored by TLC. When the reaction was complete, the mixture was eluted with 10 mL of CH₂Cl₂ and filtered through a short column of silica gel (eluent: CH₂Cl₂ 15 mL × 3). The organic phase was concentrated under reduced pressure and purified by chromatography on silica gel (eluent: petroleum ether) to afford 3a (52 mg, 60%) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.17 (m, 15H, Ar-H), 6.61-6.52 (m, 2H, CH=), 6.36 (d, J = 16.0 Hz, 1H, CH=), 4.78 (d, J = 7.6 Hz, 1H, PhCH), 4.22 (d, J = 9.2 Hz, 1H, one proton of CH₂I), 3.91 (d, J = 8.8 Hz, 1H, one proton of CH₂I); ¹³C NMR (100 MHz, CDCl₃) δ 141.3, 141.1, 137.0, 132.1, 130.9, 130.2, 128.7, 128.5, 128.2, 127.5, 127.1, 127.0, 126.3, 53.2, 8.3; IR (neat) ν (cm⁻¹) 3025, 1598, 1492, 1448, 1152, 1074, 1029; MS (EI, 70ev) m/z (%) 436 (M⁺), 408 (M⁺-Cl), 380 (M⁺-2Cl), 352 (M⁺-3Cl), 324 (M⁺-4Cl), 296 (M⁺-5Cl), 268 (M⁺-6Cl), 240 (M⁺-7Cl), 212 (M⁺-8Cl), 184 (M⁺-9Cl), 156 (M⁺-10Cl), 128 (M⁺-11Cl), 100 (M⁺-12Cl), 72 (M⁺-13Cl).
The following compounds were prepared according to this procedure.

(2) (Z)-3-Phenyl-(E)-2-(1,3-diphenallyl)allyl bromide (3b).

![Chemical Structure](image)

The reaction of anhydrous ZnBr$_2$ (90 mg, 0.4 mmol), 1a (47 mg, 0.4 mmol), and 2a (84 mg, 0.4 mmol) in CH$_2$Cl$_2$ (4 mL) afforded 3b (62 mg, 40%) as an oil (eluent: petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44-7.16 (m, 15H, Ar-H), 6.61-6.53 (m, 2H, CH=), 6.37 (d, $J$ = 16.0 Hz, 1H, CH=), 4.73 (d, $J$ = 7.2 Hz, 1H, PhCH), 4.25 (d, $J$ = 9.6 Hz, 1H, one proton of CH$_2$Br), 3.95 (d, $J$ = 9.2 Hz, 1H, one proton of CH$_2$Br); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.0, 140.3, 137.1, 136.6, 132.1, 130.8, 128.8, 128.7, 128.53, 128.49, 128.45, 127.5, 127.3, 127.0, 126.3, 52.6, 32.7; IR (neat) $\nu$ (cm$^{-1}$) 3058, 3025, 2920, 1647, 1599, 1493, 1450, 1209, 1075, 1028; MS (EI, 70ev) m/z (%) 390 (M$^+$(81Br), 1.8), 388 (M$^+$(79Br), 1.8), 115 (100); HRMS (EI) calcd for C$_{24}$H$_{21}$I (M$^+$): 436.0688; found: 436.0682.

(3) (Z)-3-Phenyl-(E)-2-(1,3-diphenallyl)allyl chloride (3c).

![Chemical Structure](image)

The reaction of anhydrous ZnCl$_2$ (68 mg, 0.49 mmol), 1a (57 mg, 0.49 mmol), and 2a (102.5 mg, 0.49 mmol) in CH$_2$Cl$_2$ (5 mL) afforded 3c (60 mg, 36%) as an oil (eluent: petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45-7.18 (m, 15H, Ar-H), 6.62-6.51 (m, 2H, CH=), 6.37 (d, $J$ = 15.6 Hz, 1H, CH=), 4.69 (d, $J$ = 7.2 Hz, 1H, PhCH), 4.30 (d, $J$ = 10.8 Hz, 1H, one proton of CH$_2$Cl), 3.99 (d, $J$ = 10.8 Hz, 1H, one proton of CH$_2$Cl); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.9, 140.1, 137.1, 136.4, 132.4,
The reaction of anhydrous ZnI$_2$ (128 mg, 0.4 mmol), 1b (52 mg, 0.4 mmol), and 2a (84 mg, 0.4 mmol) in CH$_2$Cl$_2$ (4 mL) afforded 3d (96 mg, 53%) as an oil (eluent: petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46-7.07 (m, 14H, Ar-H), 6.62-6.46 (m, 2H, CH=), 6.34 (d, $J$ = 16.0 Hz, 1H, CH=), 4.75 (d, $J$ = 7.2 Hz, 1H, PhCH), 4.22 (d, $J$ = 9.2 Hz, 1H, one proton of CH$_2$I), 2.32 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.1, 140.5, 137.0, 136.9, 134.0, 131.9, 130.9, 130.2, 129.2, 128.70, 128.67, 128.5, 128.2, 127.4, 126.9, 126.3, 53.2, 21.2, 8.8; IR (neat) ν (cm$^{-1}$) 3022, 2919, 1901, 1600, 1510, 1446, 1306, 1263, 1152, 1113, 1074, 1025; MS (EI, 70ev) m/z (%) 450 (M$^+$, 0.17), 323 (M$^+$-I, 100); HRMS (EI) calcd for C$_{25}$H$_{23}$I (M$^+$): 450.0845; found: 450.0848.

(5) (Z)-3-(p-Tolyl)-(E)-2-(1,3-diphenallyl)allyl chloride (3e).

The reaction of anhydrous ZnCl$_2$ (56 mg, 0.4 mmol), 1b (52 mg, 0.4 mmol), and 2a (84 mg, 0.4 mmol) in CH$_2$Cl$_2$ (4 mL) afforded 3e (47 mg, 33%) as an oil (eluent: petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42-7.00 (m, 14H, Ar-H), 6.61-6.52 (m, 2H, CH=), 6.35 (d, $J$ = 16.0 Hz, 1H, CH=), 4.68 (d, $J$ = 7.6 Hz, 1H, PhCH), 4.31
(d, J = 10.8 Hz, 1H, one proton of CH₂Cl), 4.00 (d, J = 10.8 Hz, 1H, one proton of CH₂Cl), 2.34 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 141.1, 139.4, 137.2, 137.1, 133.5, 132.4, 132.0, 131.0, 129.2, 128.8, 128.7, 128.5, 127.4, 126.9, 126.3, 52.4, 43.5, 21.2; IR (neat) ν (cm⁻¹) 3027, 2921, 1694, 1602, 1493, 1450, 1260, 1181, 1025; MS (EI, 70ev) m/z (%) 360 (M⁺(³⁷Cl), 4.0), 358 (M⁺(³⁵Cl), 12.1), 115 (100); HRMS (EI) calcd for C₂₅H₂₃³⁵Cl (M⁺): 358.1488; found: 358.1475.

(6) **(Z)-3-(p-Chlorophenyl)-(E)-2-(1,3-diphenylallyl)allyl iodide (3f).**

The reaction of anhydrous ZnI₂ (98 mg, 0.3 mmol), 1c (46 mg, 0.3 mmol), and 2a (64 mg, 0.3 mmol) in CH₂Cl₂ (3 mL) afforded 3f (72 mg, 50%) as an oil (eluent: petroleum ether): ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.17 (m, 14H, Ar-H), 6.55 (dd, J = 15.4, 7.4 Hz, 1H, CH=), 6.48 (s, 1H, CH=), 6.36 (d, J = 16.0 Hz, 1H, CH=), 4.76 (d, J = 7.2 Hz, 1H, PhCH), 4.15 (d, J = 8.8 Hz, 1H, one proton of CH₂Cl), 3.86 (d, J = 9.2 Hz, 1H, one proton of CH₂Cl); ¹³C NMR (100 MHz, CDCl₃) δ 142.1, 140.8, 136.9, 135.4, 132.8, 132.2, 130.5, 129.5, 128.81, 128.76, 128.73, 128.66, 128.5, 127.5, 127.1, 126.3, 53.1, 7.6; IR (neat) ν (cm⁻¹) 3058, 3026, 1636, 1596, 1490, 1449, 1152, 1092, 1013; MS (EI, 70ev) m/z (%) 345 (M⁺(³⁷Cl)-I, 29.6), 343 (M⁺(³⁵Cl)-I, 71.8), 115 (100); HRMS (EI) calcd for C₂₄H₂₀³⁵ClI (M⁺): 470.0298; found: 470.0295.

(7) **(Z)-3-Phenyl-(E)-2-(1,3-di(p-chlorophenyl)allyl)allyl iodide (3g).**

The reaction of anhydrous ZnI₂ (128 mg, 0.4 mmol), 1a (46 mg, 0.4 mmol), and 2b (113 mg, 0.4 mmol) in CH₂Cl₂ (4 mL) afforded 3g (106 mg, 53%) as an oil (eluent: petroleum ether): ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.16 (m, 13H, Ar-H), 6.55-6.42
(m, 2H, CH=), 6.26 (d, J = 16.4 Hz, 1H, CH=), 4.73 (d, J = 6.8 Hz, 1H, PhCH), 4.18 (d, J = 9.2 Hz, 1H, one proton of CH2I), 3.87 (d, J = 8.8 Hz, 1H, one proton of CH2I); 

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.6, 139.2, 136.6, 135.2, 133.1, 132.8, 131.1, 130.9, 130.4, 130.0, 128.9, 128.65, 128.56, 128.1, 127.5, 127.2, 52.4, 8.0; IR (neat) \(\nu\) (cm\(^{-1}\)) 3025, 2960, 2870, 1898, 1645, 1595, 1488, 1446, 1405, 1223, 1152, 1090, 1013; MS (EI, 70ev) \(m/z\) (%) 381 (M\(^+\)(\(^{37,37}\)Cl)-I, 4.45), 379 (M\(^+\)(\(^{35,37}\)Cl)-I, 24.39), 377 (M\(^+\)(\(^{35,35}\)Cl)-I, 35.80), 115 (100); HRMS (EI) calcd for C\(_{24}\)H\(_{19}\)\(^{35,35}\)Cl\(_2\)I (M\(^+\)): 503.9909; found: 503.9910.

III. Reaction of Allenes 1 with 1,3-Diarylprop-2-en-1-ols 2 in the Presence of ZnCl\(_2\) for the Synthesis of Indene Derivatives 4.

(1) (E)-2-(1,3-Diphenylallyl)-3-phenyl-1H-indene (4a).

Typical procedure II. Under nitrogen atmosphere, anhydrous ZnCl\(_2\) (30 mg, 0.2 mmol) was added to a Schlenk tube. A solution of 1d (39 mg, 0.2 mmol) and 2a (43 mg, 0.2 mmol) in 2 mL of CH\(_2\)Cl\(_2\) was then added. The reaction mixture was stirred at room temperature and the reaction was monitored by TLC. When the reaction was complete, the mixture was diluted with 15 mL of CH\(_2\)Cl\(_2\) and filtered through a short column of silica gel (eluent: CH\(_2\)Cl\(_2\) 15 mL \(\times\) 3). The organic phase was concentrated under reduced pressure and purified by chromatography on silica gel (eluent: petroleum ether) to afford 4a (69 mg, 89%) as an oil: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.52-7.14 (m, 19H, Ar-H), 6.65 (dd, J = 15.8, 7.0 Hz, 1H, CH=), 6.43 (d, J = 15.6 Hz, 1H, CH=), 4.96 (d, J = 6.8 Hz, 1H, PhCH), 3.61 (d, J = 22.4 Hz, 1H, one proton of CH\(_2\)), 3.28 (d, J = 22.4 Hz, 1H, one proton of CH\(_2\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.9, 144.6, 143.4, 142.9, 140.7, 137.2, 135.1, 131.6, 129.0, 128.6, 128.53, 128.47, 128.1, 127.5, 127.4, 126.4, 126.3, 126.3, 124.6, 123.7, 120.1, 47.4, 38.0; IR
(neat) ν (cm⁻¹) 3023, 2921, 2852, 1599, 1491, 1451, 1389, 1153, 1027; MS (EI, 70ev) m/z (%) 384 (M⁺, 46.8), 293 (100); HRMS (EI) calcd for C₃₀H₂₄ (M⁺): 384.1878; found: 384.1874.

The following compounds were prepared according to this procedure.

(2) \((E)-2-(1,3\text{-Diphenylallyl})-6\text{-methyl}-3\text{-p-tolyl-}1\text{H-indene} (4b)\).

![Reaction scheme for 4b]

The reaction of anhydrous ZnCl₂ (30 mg, 0.2 mmol), 1e (46 mg, 0.2 mmol), and 2a (45 mg, 0.2 mmol) in CH₂Cl₂ (2 mL) afforded 4b (66 mg, 77%) as an oil (eluent: petroleum ether): \(^1\)H NMR (400 MHz, CDCl₃) δ 7.41-6.98 (m, 17H, Ar-H), 6.64 (dd, \(J = 16.0, 6.8\) Hz, 1H, CH=), 6.43 (d, \(J = 15.2\) Hz, 1H, CH=), 4.95 (d, \(J = 6.4\) Hz, 1H, PhCH), 3.55 (d, \(J = 22.8\) Hz, 1H, one proton of CH₂), 3.22 (d, \(J = 22.8\) Hz, 1H, one proton of CH₂), 2.42 (s, 3H, CH₃), 2.37 (s, 3H, CH₃); \(^13\)C NMR (100 MHz, CDCl₃) δ 143.6, 143.4, 143.2, 140.4, 137.3, 137.0, 134.2, 132.2, 131.8, 131.5, 129.3, 128.9, 128.5, 128.4, 128.1, 127.3, 126.9, 126.3, 126.2, 124.6, 119.8, 47.3, 37.8, 21.4, 21.3; IR (neat) ν (cm⁻¹) 3024, 2920, 1599, 1492, 1448, 1392, 1180, 1028; MS (EI, 70ev) m/z (%) 412 (M⁺, 44.1), 193 (100); HRMS (EI) calcd for C₃₂H₂₈ (M⁺): 412.2191; found: 412.2193.

(3) \((E)-6\text{-Chloro-3-(4-chlorophenyl)-2-(1,3-diphenylallyl)-}1\text{H-indene} (4c)\).

![Reaction scheme for 4c]

The reaction of anhydrous ZnCl₂ (28 mg, 0.2 mmol), 1f (52 mg, 0.2 mmol), and 2a (42 mg, 0.2 mmol) in CH₂Cl₂ (2 mL) afforded 4c (73 mg, 81%) as an oil (eluent: petroleum ether): \(^1\)H NMR (400 MHz, CDCl₃) δ 7.52-7.00 (m, 17H, Ar-H), 6.60 (dd,
$J = 15.6, 6.8$ Hz, 1H, CH=), $6.39$ (d, $J = 16.0$ Hz, 1H, CH=), $4.87$ (d, $J = 6.4$ Hz, 1H, PhCH), $3.58$ (d, $J = 23.2$ Hz, 1H, one proton of CH$_2$), $3.27$ (d, $J = 23.2$ Hz, 1H, one proton of CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.7, 144.4, 144.0, 142.9, 138.8, 136.9, 133.6, 133.0, 131.8, 131.0, 130.8, 130.3, 129.0, 128.62, 128.58, 127.9, 127.6, 126.7, 126.5, 126.3, 124.1, 120.6, 47.5, 38.1; IR (neat) $\nu$ (cm$^{-1}$) 3027, 2923, 1701, 1593, 1490, 1453, 1394, 1265, 1153, 1091, 1014; MS (EI, 70ev) m/z (%) 456 ($M^+$ ($^{37}$Cl), 2.0), 454 ($M^+$ ($^{35}$,$^{37}$Cl), 13.0), 452 ($M^+$ ($^{35}$,$^{35}$Cl), 18.0), 115 (100); HRMS (EI): m/z calcd for C$_{30}$H$_{22}$^{35}$,$^{37}$Cl$_2$ ($M^+$): 452.1099; found: 452.1097.

The reaction of anhydrous ZnCl$_2$ (30 mg, 0.2 mmol), 1f (53 mg, 0.2 mmol), and 2a (43 mg, 0.2 mmol) in CH$_2$Cl$_2$ (2 mL) was carried out under reflux temperature, and afforded 4c (78 mg, 85%) as an oil (eluent: petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48-7.00 (m, 17H, Ar-H), 6.59 (dd, $J = 15.4$, 7.0 Hz, 1H, CH=), 6.38 (d, $J = 16.0$ Hz, 1H, CH=), 4.87 (d, $J = 7.2$ Hz, 1H, PhCH), 3.57 (d, $J = 23.4$ Hz, 1H, one proton of CH$_2$), 3.26 (d, $J = 23.4$ Hz, 1H, one proton of CH$_2$).

(4) ($E$)-3-(4-Chlorophenyl)-2-(1,3-diphenylallyl)-6-methyl-1H-indene (4d).

The reaction of anhydrous ZnCl$_2$ (30 mg, 0.2 mmol), 1g (47 mg, 0.2 mmol), and 2a (43 mg, 0.2 mmol) in CH$_2$Cl$_2$ (2 mL) afforded 4d (76 mg, 90%) as an oil (eluent: petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46-7.00 (m, 17H, Ar-H), 6.62 (dd, $J = 16.0$, 6.8 Hz, 1H, CH=), 6.40 (d, $J = 15.6$ Hz, 1H, CH=), 4.88 (d, $J = 6.4$ Hz, 1H, PhCH), 3.56 (d, $J = 23.0$ Hz, 1H, one proton of CH$_2$), 3.24 (d, $J = 23.0$ Hz, 1H, one
proton of CH₂), 2.36 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 144.1, 143.2, 143.0, 142.9, 139.2, 137.1, 134.5, 133.7, 133.3, 131.6, 131.4, 130.3, 128.8, 128.50, 128.47, 128.0, 127.4, 127.0, 126.4, 126.2, 124.7, 119.5, 47.4, 38.0, 21.3; IR (neat) ν (cm⁻¹) 3025, 1701, 1598, 1489, 1448, 1395, 1265, 1177, 1090, 1030, 1015; MS (EI, 70 ev) m/z (%) 434 (M⁺(³⁷Cl), 10.0), 432 (M⁺(³⁵Cl), 30.0), 115 (100); HRMS (EI) calcd for C₃₁H₂₅³⁵Cl (M⁺): 432.1645; found: 432.1642.

(5) (E)-3-(4-Bromophenyl)-2-(1,3-diphenylallyl)-6-methyl-1H-indene (4e).

The reaction of anhydrous ZnCl₂ (29 mg, 0.2 mmol), 1h (55 mg, 0.2 mmol), and 2a (42 mg, 0.2 mmol) in CH₂Cl₂ (2 mL) afforded 4e (79 mg, 86%) as an oil (eluent: petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 8.4 Hz, 2H, Ar-H), 7.40-7.16 (m, 13H, Ar-H), 7.10-7.03 (m, 2H, Ar-H), 6.61 (dd, J = 16.0, 6.8 Hz, 1H, CH=), 6.40 (d, J = 15.2 Hz, 1H, CH=), 4.87 (d, J = 6.8 Hz, 1H, PhCH), 3.55 (d, J = 22.8 Hz, 1H, one proton of CH₂), 3.23 (d, J = 22.8 Hz, 1H, one proton of CH₂), 2.36 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 143.2, 143.1, 142.8, 139.3, 137.1, 134.6, 134.2, 131.8, 131.6, 131.4, 130.7, 128.6, 128.5, 128.0, 127.4, 127.0, 126.5, 126.2, 124.7, 121.5, 119.5, 47.4, 38.0, 21.4; IR (neat) ν (cm⁻¹) 3058, 3025, 2918, 1598, 1486, 1449, 1392, 1264, 1178, 1071, 1011; MS (EI, 70 ev) m/z (%) 478 (M⁺(⁸¹Br), 19.54), 476 (M⁺(⁷⁹Br), 18.99), 115 (100); HRMS (EI) calcd for C₃₁H₂₅⁷⁹Br: 476.1140; found: 476.1142.

(6) (E)-2-(1,3-Diphenylallyl)-3-ethyl-1H-indene (4f).

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The reaction of anhydrous ZnCl$_2$ (30 mg, 0.2 mmol), 1i (29 mg, 0.2 mmol), and 2a (43 mg, 0.2 mmol) in CH$_2$Cl$_2$ (2 mL) afforded 4f (41 mg, 61%) as an oil (eluent: petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43-7.07 (m, 14H, Ar-H), 6.44 (d, $J = 16.0$ Hz, 1H, CH=), 4.98 (d, $J = 6.8$ Hz, 1H, PhCH), 3.40 (d, $J = 22.4$ Hz, 1H, one proton of CH$_2$), 3.11 (d, $J = 22.4$ Hz, 1H, one proton of CH$_2$), 2.68 (q, $J = 7.2$ Hz, 2H, CH$_2$), 1.21 (t, $J = 7.4$ Hz, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.8, 143.4, 143.2, 142.0, 140.5, 137.3, 131.4, 131.2, 128.53, 128.46, 128.1, 127.3, 126.4, 126.2, 126.1, 124.1, 123.5, 118.9, 47.2, 38.2, 18.7, 13.6; IR (neat) $\nu$ (cm$^{-1}$) 3025, 2967, 1699, 1600, 1493, 1452, 1394, 1286, 1073, 1025; MS (EI, 70ev) m/z (%) 336 (M$^+$, 31.8), 115 (100); HRMS (EI) calcd for C$_{26}$H$_{24}$ (M$^+$): 336.1878; found: 336.1877.

(7) (E)-2-(1,3-Bis(4-chlorophenyl)allyl)-3-phenyl-1H-indene (4g).

The reaction of anhydrous ZnCl$_2$ (30 mg, 0.2 mmol), 1d (38 mg, 0.2 mmol), and 2b (56 mg, 0.2 mmol) in CH$_2$Cl$_2$ (2 mL) afforded 4g (80 mg, 89%) as an oil (eluent: petroleum ether): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51-7.34 (m, 6H, Ar-H), 7.31-7.09 (m, 11H, Ar-H), 6.54 (dd, $J = 15.8$, 7.0 Hz, 1H, CH=), 6.35 (d, $J = 16.4$ Hz, 1H, CH=), 4.91 (d, $J = 6.4$ Hz, 1H, ArCH), 3.56 (d, $J = 23.2$ Hz, 1H, one proton of CH$_2$), 3.26 (d, $J = 23.2$ Hz, 1H, one proton of CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.7, 143.6, 142.7, 141.6, 141.1, 135.5, 134.8, 133.1, 132.3, 131.6, 130.7, 129.3, 128.9, 128.7, 128.6, 127.6, 127.5, 126.4, 124.8, 123.7, 120.2, 46.8, 38.0; IR (neat) $\nu$ (cm$^{-1}$) 3024, 2921, 1898, 1695, 1595, 1488, 1461, 1400, 1265, 1177, 1091, 1013; MS (EI, 70ev) m/z (%) 456 (M$^+$,$^{37,37}$Cl), 4.0), 454 (M$^+$,$^{35,37}$Cl), 23.0), 452 (M$^+$,$^{35,35}$Cl), 34.0), 191 (100); HRMS (EI) calcd for C$_{30}$H$_{22}$,$^{35,35}$Cl$_2$ (M$^+$): 452.1099; found: 452.1102.

(8) (E)-2-(1,3-Bis(4-methoxyphenyl)allyl)-3-phenyl-1H-indene (4h).
The reaction of anhydrous ZnCl₂ (31 mg, 0.2 mmol), 1d (39 mg, 0.2 mmol), and 2c (55 mg, 0.2 mmol) in CH₂Cl₂ (2 mL) afforded 4h (58 mg, 64%) as an oil (eluent: petroleum ether/ethyl acetate = 50/1): ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.11 (m, 13H, Ar-H), 6.83 (t, J = 8.8 Hz, 4H, Ar-H), 6.47 (dd, J = 16.4, 6.8 Hz, 1H, CH=), 6.35 (d, J = 16.0 Hz, 1H, CH=), 4.88 (d, J = 6.8 Hz, 1H, PhCH), 3.79 (s, 3H, OCH₃), 3.77 (s, 3H, OCH₃), 3.59 (d, J = 23.2 Hz, 1H, one proton of CH₂), 3.28 (d, J = 23.2 Hz, 1H, one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 158.1, 146.0, 145.3, 142.9, 140.2, 135.7, 135.2, 130.7, 130.1, 129.8, 129.1, 129.0, 128.6, 127.41, 127.36, 126.2, 124.5, 123.7, 120.0, 114.0, 113.8, 55.30, 55.26, 46.5, 38.0; IR (neat) ν (cm⁻¹) 3029, 2953, 2834, 1607, 1509, 1461, 1391, 1298, 1248, 1176, 1034; MS (EI, 70ev) m/z (%) 444 (M⁺, 56.0), 121 (100); HRMS (EI): m/z calcd for C₃₂H₂₈O₂: 444.2089; found: 444.2078.

(9) (E)-2-(1-(4-Methoxyphenyl)-3-(4-nitrophenyl)allyl)-6-methyl-3-p-tolyl-1H-indene (4i).

The reaction of anhydrous ZnCl₂ (29 mg, 0.2 mmol), 1e (45 mg, 0.2 mmol), and 2d (59 mg, 0.2 mmol) in CH₂Cl₂ (2 mL) afforded 4i (69 mg, 69%) as an oil (eluent: petroleum ether/ethyl acetate = 50/1): ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 8.4 Hz, 2H, Ar-H), 7.50-7.00 (m, 11H, Ar-H), 6.90-6.72 (m, 3H, Ar-H + CH=), 6.44 (d, J = 16.4 Hz, 1H, CH=), 4.93 (d, J = 6.4 Hz, 1H, ArCH), 3.77 (s, 3H, OCH₃), 3.52 (d, J = 23.2 Hz, 1H, one proton of CH₂), 3.27 (d, J = 22.8 Hz, 1H, one proton of CH₂), 2.42 (s, 3H, CH₃), 2.37 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 146.7, 143.8,
143.3, 143.0, 142.4, 140.8, 137.4, 137.2, 134.8, 134.5, 132.1, 129.3, 129.2, 129.0, 
128.8, 127.0, 126.7, 124.6, 124.0, 119.9, 114.0, 55.3, 46.9, 37.9, 21.4, 21.3; IR (neat) 
ν (cm⁻¹) 2922, 1643, 1597, 1512, 1459, 1340, 1248, 1178, 1109, 1036; MS (EI, 70ev) 
m/z (%) 487 (M⁺, 34.6), 57 (100); HRMS (EI) calcd for C₃₃H₂₉NO₃ (M⁺): 487.2147; 
found: 487.2151.

The reaction of anhydrous ZnCl₂ (28 mg, 0.2 mmol), 1e (46 mg, 0.2 mmol), and 2e 
(58 mg, 0.2 mmol) in CH₂Cl₂ (2 mL) afforded 4i (70 mg, 71%) as an oil (eluent: 
petroleum ether/ethyl acetate = 50/1): ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 8.4 
Hz, 2H, Ar-H), 7.46-7.00 (m, 11H, Ar-H), 6.88-6.74 (m, 3H, Ar-H + CH=), 6.43 (d, J 
= 16.4 Hz, 1H, CH=), 4.93 (d, J = 6.4 Hz, 1H, ArCH), 3.77 (s, 3H, OCH₃), 3.51 (d, J 
= 22.8 Hz, 1H, one proton of CH₂), 2.62 (d, J = 22.8 Hz, 1H, one proton of CH₂), 2.41 
(s, 3H, CH₃), 2.37 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 146.7, 143.8, 
143.3, 143.0, 142.4, 140.8, 137.4, 137.2, 134.8, 134.5, 132.1, 129.3, 129.2, 129.0, 
128.8, 127.0, 126.7, 124.6, 123.9, 119.9, 114.0, 55.2, 46.9, 37.9, 21.4, 21.3; IR (neat) 
ν (cm⁻¹) 2922, 1643, 1596, 1510, 1462, 1341, 1302, 1249, 1177, 1109, 1035; MS (EI, 
70ev) m/z (%) 487 (M⁺, 5.45), 135 (100); HRMS (EI) calcd for C₃₃H₂₉NO₃ (M⁺): 
487.2147; found: 487.2142.

IV. Reaction of Allenes 1 with Diarylmethanols 5 for the Synthesis of Indene 
Derivatives 6.

(1) 2-Benzydryl-6-methyl-3-p-tolyl-1H-indene (6a).
Typical procedure III. Under nitrogen atmosphere, anhydrous ZnCl₂ (56 mg, 0.4 mmol) was added to a Schlenk tube. A solution of 1e (44 mg, 0.2 mmol) and 5a (73 mg, 0.4 mmol) in 2 mL of CH₂Cl₂ was then added. The reaction mixture was stirred at room temperature and the reaction was monitored by TLC. When the reaction was complete, the mixture was diluted with 15 mL of CH₂Cl₂ and filtered through a short column of silica gel (eluent: CH₂Cl₂ 15 mL × 3). The organic phase was concentrated under reduced pressure and purified by chromatography on silica gel (eluent: petroleum ether) to afford 6a (68 mg, 88%) as an oil: \(^1\)H NMR (400 MHz, CDCl₃) δ 7.30-7.00 (m, 17H, Ar-H), 5.46 (s, 1H, Ph₂CH), 3.37 (s, 2H, CH₂), 2.38 (s, 3H, CH₃), 2.35 (s, 3H, CH₃); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 144.1, 143.5, 143.4, 143.3, 141.0, 137.0, 134.3, 132.2, 129.2, 129.1, 128.8, 128.2, 126.9, 126.2, 124.5, 119.9, 50.1, 38.6, 21.4, 21.3; IR (neat) ν (cm⁻¹) 3024, 2918, 1599, 1491, 1448, 1394, 1345, 1265, 1181, 1131, 1075, 1030; MS (EI, 70ev) m/z (%) 386 (M⁺, 53.2), 167 (100); HRMS (EI) calcd for C₃₀H₂₆: 386.2035; found: 386.2043.

The following compounds were prepared according to this procedure.

(2) 2-(Bis(4-methoxyphenyl)methyl)-6-methyl-3-p-tolyl-1H-indene (6b).

The reaction of anhydrous ZnCl₂ (57 mg, 0.4 mmol), 1e (46 mg, 0.2 mmol), and 5b (99 mg, 0.4 mmol) in CH₂Cl₂ (2 mL) afforded 6b (76 mg, 82%) as an oil (eluent: petroleum ether/ethyl acetate = 50/1): \(^1\)H NMR (400 MHz, CDCl₃) δ 7.29-7.17 (m,
5H, Ar-H), 7.14-7.01 (m, 6H, Ar-H), 6.80 (d, J = 8.4 Hz, 4H, Ar-H), 5.34 (s, 1H, Ar₂CH), 3.78 (s, 6H, OCH₃), 3.35 (s, 2H, CH₂), 2.40 (s, 3H, CH₃), 2.36 (s, 3H, CH₃);
¹³C NMR (100 MHz, CDCl₃) δ 157.9, 144.3, 143.3, 140.3, 136.5, 134.2, 132.3, 129.9, 129.7, 129.2, 128.8, 126.8, 124.5, 119.8, 113.8, 113.6, 55.2, 48.4, 38.6, 21.33, 21.28;
IR (neat) ν (cm⁻¹) 2924, 2834, 1609, 1582, 1508, 1460, 1300, 1246, 1176, 1109, 1035;
MS (EI, 70ev) m/z (%) 446 (M⁺, 47.3), 227 (100); HRMS (EI) calcd for C₃₂H₃₀O₂ (M⁺): 446.2246; found: 446.2245.

A large scale reaction for the synthesis of 6b.

Under nitrogen atmosphere, anhydrous ZnCl₂ (1.363 g, 10 mmol) was added to a Schlenk tube. A solution of 1e (1.100 g, 5 mmol) and 5b (2.441 g, 10 mmol) in 50 mL of CH₂Cl₂ was then added. The reaction mixture was stirred at room temperature and the reaction was monitored by TLC. When the reaction was complete, the mixture was diluted with 40 mL of CH₂Cl₂ and filtered through a short column of silica gel (eluent: CH₂Cl₂ 30 mL × 3). The organic phase was concentrated under reduced pressure and purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford 6b (1.873 g, 84%) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.17 (m, 5H, Ar-H), 7.14-6.98 (m, 6H, Ar-H), 6.84-6.74 (m, 4H, Ar-H), 5.36 (s, 1H, Ar₂CH), 3.76 (s, 6H, OCH₃), 3.35 (s, 2H, CH₂), 2.39 (s, 3H, CH₃), 2.35 (s, 3H, CH₃).

(3) 2-(Bis(4-chlorophenyl)methyl)-6-methyl-3-p-tolyl-1H-indene (6c).
The reaction of anhydrous ZnCl\(_2\) (52 mg, 0.4 mmol), 1e (43 mg, 0.2 mmol), and 5c (101 mg, 0.4 mmol) in CH\(_2\)Cl\(_2\) (2 mL) afforded 6c (85 mg, 96\%) as an oil (eluent: petroleum ether): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28-7.17 (m, 9H, Ar-H), 7.14-7.00 (m, 6H, Ar-H), 5.38 (s, 1H, Ar\(_2\)CH), 3.30 (s, 2H, CH\(_2\)), 2.40 (s, 3H, CH\(_3\)), 2.37 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.1, 143.0, 142.1, 142.0, 141.7, 137.3, 134.7, 132.3, 131.9, 130.3, 129.4, 128.7, 128.5, 127.1, 124.6, 120.1, 48.9, 38.5, 21.4, 21.3; IR (neat) \(\nu\) (cm\(^{-1}\)) 3023, 2920, 1902, 1632, 1488, 1452, 1400, 1348, 1266, 1180, 1091, 1041; MS (EI, 70ev) \(m/z\) (%) 458 (M\(^+\)(37Cl), 0.5), 456 (M\(^+\)(35, 37Cl), 3.1), 454 (M\(^+\)(35, 35Cl), 4.4), 219 (100); HRMS (EI) calcd for C\(_{30}\)H\(_{24}\)\(_{35, 35}\)Cl\(_2\) (M\(^+\)): 454.1255; found: 454.1251.

\(4\) 2-((4-Chlorophenyl)(phenyl)methyl)-6-methyl-3-p-tolyl-1\(H\)-indene (6d).

The reaction of anhydrous ZnCl\(_2\) (56 mg, 0.4 mmol), 1e (44 mg, 0.2 mmol), and 5d (89 mg, 0.4 mmol) in CH\(_2\)Cl\(_2\) (2 mL) afforded 6d (73 mg, 87\%) as an oil (eluent: petroleum ether): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30-7.16 (m, 10H, Ar-H), 7.16-7.00 (m, 6H, Ar-H), 5.41 (s, 1H, PhCH), 3.33 (s, 2H, CH\(_2\)), 2.39 (s, 3H, CH\(_3\)), 2.36 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.6, 143.2, 143.1, 142.7, 142.6, 141.3, 137.1, 134.4, 132.03, 132.02, 130.4, 129.3, 129.0, 128.7, 128.4, 127.0, 126.4, 124.6, 120.0, 49.5, 38.6, 21.4, 21.3; IR (neat) \(\nu\) (cm\(^{-1}\)) 3025, 2918, 1903, 1657, 1601, 1488, 1449, 1400, 1347, 1267, 1181, 1091, 1015; MS (EI, 70ev) \(m/z\) (%) 422 (M\(^+\)(37Cl), 4.4), 420
(M\(^{+}(^{35}\text{Cl})\), 13.2), 219 (100); HRMS (EI) calcd for C\(_{30}\text{H}_{25}\text{^{35}\text{Cl}}\) (M\(^{+}\)): 420.1645; found: 420.1650.

(5) 3-(4-Chlorophenyl)-2-((4-chlorophenyl)(phenyl)methyl)-6-methyl-1\(H\)-indene (6e).

The reaction of anhydrous ZnCl\(_2\) (56 mg, 0.4 mmol), 1g (46 mg, 0.2 mmol), and 5d (87 mg, 0.4 mmol) in CH\(_2\)Cl\(_2\) (2 mL) afforded 6e (75 mg, 89%) as an oil (eluent: petroleum ether): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 (d, \(J = 8.0\) Hz, 2H, Ar-H), 7.29-7.18 (m, 8H, Ar-H), 7.13-7.02 (m, 6H, Ar-H), 5.35 (s, 1H, PhCH), 3.35 (s, 2H, CH\(_2\)), 2.36 (s, 3H, CH\(_3\)); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.7, 143.3, 143.1, 142.7, 142.3, 140.2, 134.8, 133.5, 133.4, 132.2, 130.3, 130.2, 128.90, 128.88, 128.5, 127.1, 126.6, 124.7, 119.8, 49.6, 38.8, 21.4; IR (neat) ν (cm\(^{-1}\)) 3025, 2918, 1649, 1488, 1451, 1396, 1178, 1091, 1014; MS (EI, 70ev) \(m/z\) (%) 442 (M\(^{+}(^{35},^{37}\text{Cl})\), 2.0), 440 (M\(^{+}(^{35}\text{Cl})\), 3.0), 69 (100); HRMS (EI) calcd for C\(_{29}\text{H}_{22}\text{^{35},^{37}\text{Cl}}\) (M\(^{+}\)): 440.1099; found: 440.1093.

(6) 2-Benzhydryl-3-(4-bromophenyl)-6-methyl-1\(H\)-indene (6f).

The reaction of anhydrous ZnCl\(_2\) (56 mg, 0.4 mmol), 1h (58 mg, 0.2 mmol), and 5a (74 mg, 0.4 mmol) in CH\(_2\)Cl\(_2\) (2 mL) afforded 6f (73 mg, 79%) as an oil (eluent: petroleum ether): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53 (d, \(J = 8.0\) Hz, 2H, Ar-H),

S16
7.30-7.16 (m, 9H, Ar-H), 7.16-7.00 (m, 6H, Ar-H), 5.39 (s, 1H, PhCH), 3.38 (s, 2H, CH₂), 2.36 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 144.4, 143.7, 143.2, 142.7, 139.9, 134.6, 134.2, 131.8, 130.6, 129.0, 128.3, 127.0, 126.4, 124.6, 121.5, 119.6, 50.1, 38.9, 21.4; IR (neat) ν (cm⁻¹) 3025, 1598, 1486, 1448, 1392, 1264, 1179, 1072, 1031, 1010; MS (EI, 70ev) m/z (%) 452 (M⁺(⁸¹Br), 7.66), 450 (M⁺(⁷⁹Br), 7.46), 167 (100); HRMS (EI) calcd for C₂₉H₂₃⁷⁹Br (M⁺): 450.0983; found: 450.0978.

(7) 2-Benzhydryl-3-ethyl-1H-indene (6g).

The reaction of anhydrous ZnCl₂ (56 mg, 0.4 mmol), 1i (28 mg, 0.2 mmol), and 5a (74 mg, 0.4 mmol) in CH₂Cl₂ (2 mL) afforded 6g (46 mg, 76%) as an oil (eluent: petroleum ether): ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.05 (m, 14H, Ar-H), 5.54 (s, 1H, Ph₂CH), 3.20 (s, 2H, CH₂), 2.62 (q, J = 7.8 Hz, 2H, CH₂), 1.13 (t, J = 7.8 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 145.7, 143.8, 143.3, 142.3, 141.1, 129.1, 128.3, 126.2, 126.1, 124.1, 123.5, 118.9, 49.8, 39.3, 18.8, 13.4; IR (neat) ν (cm⁻¹) 3025, 2918, 1658, 1600, 1509, 1488, 1449, 1400, 1347, 1266, 1181, 1131, 1091, 1015; MS (EI, 70ev) m/z (%) 310 (M⁺, 17.0), 167 (100); HRMS (EI) calcd for C₂₄H₂₂ (M⁺): 310.1722; found: 310.1721.

V. Reference:
\textit{MB-4c}-1

\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{OH} \\
\text{N}_{2} \text{ rt} & \quad \text{ZnCl}_{2} (1.0 \text{ equiv}) \\
\text{CH}_{2}Cl_{2} & \\
\text{5 h 50 mm} & \\
\end{align*}

\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \\
\text{Ph} & \\
\end{align*}