Supporting Information
for DOI: 10.1055/s-0036-1588302
© Georg Thieme Verlag KG Stuttgart · New York 2016
Organopromoted Direct Synthesis of 1,1-Diphenyl-3-arylidanes via [3+2] Cycloaddition of Triphenylcarbenium Tetrafluoroborate with Styrenes

Nakin Surapanich,*a Patcharin Chaisuwanb

*a Department of Chemistry, Faculty of Science and Technology, Rajabhat Rajanagarindra University, 422 Marupong Road, Tombon Na Muang, Amphoe Muang, Chachoengsao 24000, Thailand.

b School of Chemistry, Suranaree University of Technology, 111 University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand.

nakin_s@hotmail.com

Supporting Information

List of Contents

(A) General Methods S2

(B) General Procedure for the Synthesis of 1,1-Diphenyl-3-arylidanes S2

(C) Analytical data for the products S2 — S5

(D) ¹H and ¹³C NMR Spectra S7 — S18
General Methods

The $^1$H and $^{13}$C NMR spectras were recorded on either Bruker DPX-300 (300 MHz) spectrometer or Bruker Advance-500 (500 MHz) in CDCl$_3$. $^1$H NMR chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard. $^{13}$C NMR chemical shifts are reported in ppm with residual non-deuterated solvent peak as an internal standard. NMR data are reported as follow: $^1$H NMR chemical shifts, measured in parts per million (ppm) down field from tetramethylsilane (TMS) signal ($\delta$), proton count, multiplicity, observed coupling constant ($J$) in Hertz (Hz). The IR spectra were recorded a Perkin Elmer EX FI-IR system spectrometer. The high resolution mass spectra were recorded using a Bruker Micro TOF spectrometer at Faculty of science, Mahidol University.

Column chromatography was performed using Merck silica gel 60 (Art. 7734). Preparatory layer chromatography (PLC) was performed using Merck silica gel 60 F$_{254}$ (Art. 7747). Analytical TLC was performed with Merck TLC aluminium sheet silica gel 60 F$_{254}$ (Art. 5554) with 0.2 mm thickness. All chemicals were purchased from Sigma-Aldrich, and Acros Organics and were used without prior purification.

General Procedure for the Synthesis of 1,1-Diphenyl-3-arylinidanes

A round bottom flask equipped with a magnetic stir-bar was charged with styrene (1.0 mmol), benzophene (0.3 mmol), triethylamine (1.0 mmol) and toluene (2.5 mL). After stirring for 1.0 min, triphenylcarbenium tetrafluoroborate (1.5 mmol) was added and the resulting mixture was allowed to react at 80 °C for 48 h. After the end of the reaction, the mixture was filtered through a plug of Celite and eluted with hexanes/EtOAc (8:2). The filtrate was concentrated in vacuo and purified by column chromatography on silica gel.

Analytical data for the products

1,1,3-Triphenylindane (6a): a white solid, mp 111.5–112.5 °C. IR (KBr, cm$^{-1}$): $\nu_{\text{max}}$ 3080, 3061, and 3025 (aromatic), 2966, 2928, and 2862 (CH of aliphatic), 1596, and 1491 (aromatic), 1470, 1454, and 1444 (CH of aliphatic). $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta = 7.35$–$7.16$ (m, 17 H), $6.92$ (d, $J = 6.8$ Hz, 1 H), $6.92$ (d, $J = 6.8$ Hz, 1 H), $4.20$ (dd, $J = 6.4$, 11.1 Hz, 1 H), $3.20$ (dd, $J = 6.4$, 12.6 Hz, 1 H), $2.90$ (dd, 11.1, 12.6 Hz, 1 H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$
1,1-Diphenyl-3-(4-bromophenyl)indane (6b): a white solid, mp 117.5–119.0 °C. IR (KBr, cm⁻¹): ν max 3058, 3022, 2972, 2943, 2876, 1595, 1489, 1443, 1404, 1071, 1012, 820, 755, 700.

1H NMR (300 MHz, CDCl₃): δ = 7.44 (d, 8.3 Hz, 2 H), 7.28–7.09 (m, 15 H), 6.89 (d, J = 6.9 Hz, 1 H), 4.16 (dd, J = 6.3, 11.0 Hz, 1 H), 3.20 (dd, J = 6.4, 12.6 Hz, 1 H), 2.86 (dd, 11.0, 12.6 Hz, 1 H). 13C NMR (75 MHz, CDCl₃): δ = 149.39, 147.73, 146.00, 145.60, 142.91, 131.62, 130.30, 128.54, 128.44, 128.01, 127.29, 126.93, 126.33, 126.15, 126.12, 124.86, 120.38, 60.81, 54.05, 48.45. HRMS (ESI-TOF) m/z [(M + Na)+] calcd for C₂₇H₂₂Na: 369.1619; found: 369.1531.

1,1-Diphenyl-3-(4-chlorophenyl)indane (6c): a white solid, mp 108.0–109.8 °C. IR (KBr, cm⁻¹): ν max 3058, 3021, 2968, 2869, 1596, 1491, 1443, 1408, 1088, 1013, 826, 755, 699.

1H NMR (500 MHz, CDCl₃): δ = 7.36–7.21 (m, 16 H), 7.15 (d, J = 6.9 Hz, 1 H), 6.94 (d, J = 7.3 Hz, 1 H), 4.21 (dd, J = 6.3, 11.0 Hz, 1 H), 3.24 (dd, J = 6.3, 12.8 Hz, 1 H), 2.90 (dd, 11.1, 12.6 Hz, 1 H). 13C NMR (125 MHz, CDCl₃): δ = 149.37, 147.75, 146.00, 145.59, 142.37, 132.30, 129.91, 128.66, 128.54, 128.45, 128.04, 128.01, 127.28, 126.91, 126.33, 126.14, 126.11, 124.85, 60.79, 54.09, 48.37. HRMS (ESI-TOF) m/z [(M + Na)+] calcd for C₂₇H₂₁ClNa: 403.1229; found: 403.1210.

1,1-Diphenyl-3-(3-chlorophenyl)indane (6d): a white solid, mp 90.0–92.1 °C. IR (KBr, cm⁻¹): ν max 3059, 3020, 2967, 2935, 2867, 1593, 1570, 1489, 1473, 1442, 1428, 1078, 758, 701.

1H NMR (500 MHz, CDCl₃): δ = 7.31–7.10 (m, 17 H), 6.93 (d, J = 7.4 Hz, 1 H), 4.17 (dd, J = 6.3, 11.0 Hz, 1 H), 3.21 (dd, J = 6.3, 12.6 Hz, 1 H), 2.87 (dd, 11.0, 12.6 Hz, 1 H). 13C NMR (125 MHz, CDCl₃): δ = 149.41, 147.71, 146.00, 145.78, 145.56, 134.35, 129.77, 128.62, 128.53, 128.47, 128.05, 128.02, 127.33, 126.97, 126.82, 126.34, 126.16, 126.14, 124.90, 60.82, 53.97, 48.73. HRMS (ESI-TOF) m/z [(M + Na)+] calcd for C₂₇H₂₁ClNa: 403.1229; found: 403.1233.

1,1-Diphenyl-3-(2-chlorophenyl)indane (6e): a white solid, mp 103.2–104.7 °C. IR (KBr, cm⁻¹): ν max 3057, 3017, 2974, 2974, 2875, 1596, 1491, 1472, 1439, 1035, 749, 699.

1H NMR (300 MHz, CDCl₃): δ = 7.40 (m, 1 H), 7.35–7.13 (m, 16 H), 7.0 (d, J = 7.0 Hz, 1 H), 4.85 (dd,
\[ J = 6.7, 10.2 \text{ Hz}, 1 \text{ H}), 3.36 (\text{dd, } J = 6.7, 12.8 \text{ Hz}, 1 \text{ H}), 2.86 (\text{broad t, } J = 11.3 \text{ Hz}, 1 \text{ H}). \] 
\[^{13}\text{C NMR (75 MHz, CDCl}_3\]): \( \delta = 149.68, 148.25, 145.80, 144.92, 141.46, 134.50, 129.48, 128.43, 128.32, 128.01, 127.95, 127.68, 127.18, 127.02, 126.88, 126.27, 126.03, 125.05, 60.83, 52.35, 45.71. \] 
HRMS (ESI-TOF) \( m/z \) [(M + Na\(^{+}\)] calcd for C\(_{27}\)H\(_{21}\)ClNa: 403.1229; found: 403.1244.

**1,1-Diphenyl-3-(4-fluorophenyl)indane (6f):** a white solid, mp 124.0‒125.7 °C. IR (KBr, cm\(^{-1}\)): \( \nu_{\text{max}} 3064, 3032, 3018, 2974, 2944, 2877, 1599, 1508, 1492, 1470, 1443, 1223, 1156, 759, 699. \) \(^1\text{H NMR (500 MHz, CDCl}_3\]): \( \delta = 7.31‒7.17 (\text{m, } 14 \text{ H}), 7.11 (\text{d, } J = 7.0 \text{ Hz}, 1 \text{ H}), 7.01 (\text{m, } 2 \text{ H}), 6.90 (\text{d, } J = 6.9 \text{ Hz}, 1 \text{ H}), 4.18 (\text{dd, } J = 6.4, 11.0 \text{ Hz}, 1 \text{ H}), 3.21 (\text{dd, } J = 6.3, 12.6 \text{ Hz}, 1 \text{ H}). \) 
\[^{13}\text{C NMR (125 MHz, CDCl}_3\]): \( \delta = 161.70 (\text{d, } J_{\text{CF}} = 247.0 \text{ Hz}), 149.34, 147.87, 146.42, 145.71, 139.52 (\text{d, } J_{\text{CF}} = 3.2 \text{ Hz}), 129.94 (\text{d, } J_{\text{CF}} = 8.0 \text{ Hz}), 128.57, 128.47, 128.04, 128.00, 127.26, 126.84, 126.31, 126.12, 126.10, 124.88, 115.31 (\text{d, } J_{\text{CF}} = 21 \text{ Hz}), 60.78, 54.23, 48.25. \] 
HRMS (ESI-TOF) \( m/z \) [(M + Na\(^{+}\)] calcd for C\(_{27}\)H\(_{21}\)FNa: 387.1525; found: 387.1545.

**3-(3,3-Diphenylindan-1-yl)benzaldehyde (6g):** a pale pink solid, mp 169.0‒170.6 °C. IR (KBr, cm\(^{-1}\)): \( \nu_{\text{max}} 3049, 3019, 2978, 2944, 2883, 2840, 2810, 2746, 1694, 1580, 1492, 1444, 1152, 759, 696. \) \(^1\text{H NMR (500 MHz, CDCl}_3\]): \( \delta = 10.03 (\text{s, } 1 \text{ H}), 7.81 (\text{m, } 2 \text{ H}), 7.56 (\text{m, } 2 \text{ H}), 7.36‒7.23 (\text{m, } 12 \text{ H}), 7.18 (\text{d, } J = 7.4 \text{ Hz}, 1 \text{ H}) 6.93 (\text{d, } J = 7.2 \text{ Hz}, 1 \text{ H}), 4.34 (\text{dd, } J = 6.3, 11.0 \text{ Hz}, 1 \text{ H}), 2.95 (\text{dd, } J = 6.3, 12.6 \text{ Hz}, 1 \text{ H}). \) 
\[^{13}\text{C NMR (125 MHz, CDCl}_3\]): \( \delta = 192.33, 149.53, 147.61, 145.71, 145.52, 145.12, 136.83, 134.78, 129.66, 129.26, 128.53, 128.49, 128.26, 128.09, 128.05, 127.41, 127.08, 126.40, 126.25, 126.21, 124.80, 60.89, 54.06, 48.78. \] 
HRMS (ESI-TOF) \( m/z \) [(M + Na\(^{+}\)] calcd for C\(_{28}\)H\(_{22}\)ONa: 397.1568; found: 397.1570.

**1,1-Diphenyl-3-(3-nitrophenyl)indane (6h):** a white solid, mp 135.8‒136.8 °C. IR (KBr, cm\(^{-1}\)): \( \nu_{\text{max}} 3061, 3033, 2973, 2941, 2872, 1596, 1530, 1491, 1442, 1342, 1087, 701. \) \(^1\text{H NMR (500 MHz, CDCl}_3\]): \( \delta = 8.16 (\text{m, } 2 \text{ H}), 7.63 (\text{d, } J = 7.9 \text{ Hz}, 1 \text{ H}), 7.53 (\text{t, } J = 7.7 \text{ Hz}, 1 \text{ H}), 7.36‒7.22 (\text{m, } 12 \text{ H}), 7.18 (\text{d, } J = 7.3 \text{ Hz}, 1 \text{ H}), 6.94 (\text{d, } J = 7.5 \text{ Hz}, 1 \text{ H}), 4.37 (\text{dd, } J = 6.4, 10.8 \text{ Hz}, 1 \text{ H}), 3.31 (\text{dd, } J = 6.4, 12.7 \text{ Hz}, 1 \text{ H}), 2.94 (\text{dd, } J = 11.0, 12.5 \text{ Hz}, 1 \text{ H}). \) 
\[^{13}\text{C NMR (125 MHz, CDCl}_3\]): \( \delta = 149.56, 148.56, 147.32, 146.12, 145.32, 145.03, 134.78, 129.46, 128.50, 128.46, 128.14, 128.10, 127.56, 127.34, 126.49, 126.37, 126.30, 124.69, 123.46, 121.82, 60.90, 54.04, 48.74. \] 
HRMS (ESI-TOF) \( m/z \) [(M + Na\(^{+}\)] calcd for C\(_{27}\)H\(_{21}\)NO\(_2\)Na: 414.1470; found: 414.1464.
1,1-Diphenyl-3-\((p\)-tolyl\)indane (6i): a white solid, mp 127.0–127.8 °C. IR (KBr, cm\(^{-1}\)): \(\nu_{\text{max}}\) 3057, 3017, 2923, 2854, 1597, 1513, 1492, 1455, 1377, 755, 700. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.35–7.05\) (m, 17 H), 6.92 (d, \(J = 6.7\) Hz, 1 H), 4.16 (dd, \(J = 6.5, 11.0\) Hz, 1 H), 3.19 (dd. \(J = 6.4, 12.5\) Hz, 1 H), 2.86 (dd, \(J = 11.2, 12.0\) Hz, 1 H), 2.35 (s, 3 H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 149.35, 148.08, 146.82, 145.84, 140.78, 136.14, 129.22, 128.60, 128.50, 128.45, 127.99, 127.95, 127.13, 126.62, 126.02, 125.98, 124.98, 60.77, 54.14, 48.55, 21.06. HRMS (ESI-TOF) \(m/z\) \([(M + Na)^+]\) calcd for C\(_{28}\)H\(_{24}\)Na: 383.1776; found: 383.1748.

4-(3,3-Diphenylindan-1-yl)phenyl acetate (6j): a white solid, mp 123.9–125.5 °C. IR (KBr, cm\(^{-1}\)): \(\nu_{\text{max}}\) 3054, 3034, 2985, 2934, 2873, 1758, 1596, 1507, 1491, 1443, 1369, 1216, 1198, 760, 699. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.35–6.94\) (m, 18 H), 4.20 (dd, \(J = 6.4, 11.0\) Hz, 1 H), 3.20 (dd. \(J = 6.4, 12.6\) Hz, 1 H), 2.89 (dd, \(J = 11.1, 12.6\) Hz, 1 H), 2.29 (s, 3 H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 169.56, 149.37, 149.32, 147.85, 146.30, 145.73, 141.43, 129.47, 128.75, 128.46, 128.02, 127.98, 127.23, 126.81, 126.28, 126.09, 126.05, 125.03, 121.54, 60.78, 54.23, 48.41, 21.14. HRMS (ESI-TOF) \(m/z\) \([(M + Na)^+]\) calcd for C\(_{29}\)H\(_{24}\)O\(_2\)Na: 427.1674; found: 427.1675.

1,1-Diphenyl-3-(4-(chloromethyl)phenyl)indane (6l): a white solid, mp 116.2–117.5 °C. IR (KBr, cm\(^{-1}\)): \(\nu_{\text{max}}\) 3081, 3058, 3021, 2972, 2942, 2875, 1596, 1491, 1443, 1089, 1015, 825, 755, 700. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.36–7.10\) (m, 17 H), 6.93 (d, \(J = 7.4\) Hz, 1 H), 4.60 (s, 2 H), 4.20 (dd, \(J = 6.4, 11.0\) Hz, 1 H), 3.20 (dd, \(J = 6.4, 12.6\) Hz, 1 H), 2.90 (dd, \(J = 11.2, 12.6\) Hz, 1 H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 149.45, 147.89, 146.28, 145.76, 144.36, 135.81, 130.26, 129.58, 128.97, 128.85, 128.59, 128.49, 128.05, 128.01, 127.28, 127.62, 127.26, 126.85, 126.80, 126.47, 126.32, 126.13, 125.00, 60.87, 54.12, 48.73, 46.15. HRMS (ESI-TOF) \(m/z\) \([(M + Na)^+]\) calcd for C\(_{28}\)H\(_{23}\)ClNa: 417.1386; found: 417.1274.

1-Methyl-1,3,3-triphenylindane (6m): a white solid, mp 144.2–145.0 °C. IR (KBr, cm\(^{-1}\)): \(\nu_{\text{max}}\) 3082, 3056, 3026, 2969, 2951, 2868, 1594, 1488, 1444, 1373, 1028, 765, 750, 700. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.35–6.98\) (m, 19 H), 3.39 (d, \(J = 13.5\) Hz, 1 H), 3.09 (d, \(J = 13.5\) Hz, 1 H), 1.52 (s, 3 H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 150.51, 149.31, 148.83, 148.49, 147.46, 128.75, 128.65, 127.92, 127.83, 127.56, 127.41, 127.33, 126.86, 126.78, 125.96, 125.63, 125.56, 125.00, 61.34, 60.91, 51.16, 28.81. HRMS (ESI-TOF) \(m/z\) \([(M + Na)^+]\) calcd for C\(_{28}\)H\(_{24}\)Na: 383.1776; found: 383.1774.
$^1$H and $^{13}$C NMR spectra
$^1$H NMR Spectrum of 6a (300 MHz, CDCl$_3$)

$^{13}$C NMR and DEPT-135 Spectra of 6a (75 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 6b (300 MHz, CDCl₃)

$^{13}$C NMR and DEPT-135 Spectra of 6b (75 MHz, CDCl₃)
$^1$H NMR Spectrum of 6c (500 MHz, CDCl$_3$)

$^{13}$C NMR and DEPT-135 Spectra of 6c (125 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 6d (500 MHz, CDCl$_3$)

$^{13}$C NMR and DEPT-135 Spectra of 6d (125 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 6e (300 MHz, CDCl$_3$)

$^{13}$C NMR and DEPT-135 Spectra of 6e (75 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 6f (500 MHz, CDCl$_3$)

$^{13}$C NMR and DEPT-135 Spectra of 6f (125 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 6g (500 MHz, CDCl$_3$)

$^{13}$C NMR and DEPT-135 Spectra of 6g (125 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 6h (500 MHz, CDCl$_3$)

$^{13}$C NMR and DEPT-135 Spectra of 6h (125 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 6j (300 MHz, CDCl$_3$)

$^{13}$C NMR and DEPT-135 Spectra of 6j (75 MHz, CDCl$_3$)
$^{1}H$ NMR Spectrum of 6l (500 MHz, CDCl$_3$)

$^{13}C$ NMR and DEPT-135 Spectra of 6l (125 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 6m (300 MHz, CDCl$_3$)

$^{13}$C NMR and DEPT-135 Spectra of 6m (75 MHz, CDCl$_3$)