

Lewis acid-catalyzed formation of indene derivatives via tandem reactions of aryacetylenes with the cations generated from 2-silylmethyl cyclopropyl carbinols

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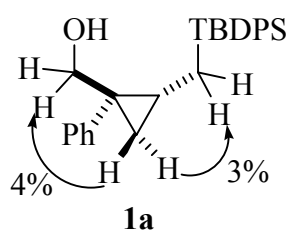
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General. Reaction flasks were flame-dried. ¹H, ¹³C, COSY and nOe spectra were recorded on JEOL JNM-LA400 FTNMR instrument using solutions in CDCl₃. The ¹H and ¹³C spectra were referred, respectively, to TMS used as an internal standard and the central line for CDCl₃. IR spectra were taken neat using NaCl plates on a BRUKER-VERTEX 70 FTIR Spectrometer. Elemental (C and H) analyses were performed on a ThermoQuest EA 1110 elemental analyzer. All the reactions were carried out using freshly distilled dry solvents and under dry nitrogen. Column chromatography was performed over silica gel, 100-200 mesh, from Acme Chemicals using mixtures of hexanes and EtOAc as the eluent. The separation of products was achieved by radial chromatography using plates coated with silica gel PF₂₅₄ (E-Merck). Solvents were removed under reduced pressure on a rotary evaporator. The organic extracts were dried with anhydrous Na₂SO₄.

Procedure (I): General procedure for SnCl₄-induced tandem reaction of silylmethyl-substituted cyclopropylcarbinol with aryacetylenes. A solution of cyclopropylcarbinol (0.5 mmol) and an aryacetylene (2.5 mmol) in CH₂Cl₂ (8 mL) was cooled to – 50 °C in a round bottom flask and mixed with a solution of SnCl₄ in CH₂Cl₂ (1 mL, 1.0 M, 1.0 mmol) dropwise over 15 min using a motor-driven syringe. The reaction was allowed to warm gradually to 0 °C over 3 hours when it was quenched with saturated aqueous NaHCO₃ (10 mL) and stirred vigorously for 10 min. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL). The combined organic solution was washed with brine, dried, filtered, and concentrated. The crude material was purified by chromatography.

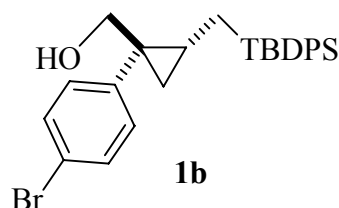
Procedure (II): Typical procedure for the SnCl₄-induced tandem reaction of silylmethyl substituted cyclopropyl carbinol **1a with 1-phenyl-2-trimethylsilylacetylene.** A solution of cyclopropyl carbinol **1a** (0.5 mmol), 1-phenyl-2-trimethylsilylacetylene (2.5 mmol) in CH₂Cl₂ (8 mL) was cooled to -50 °C in a round bottom flask and mixed with 1.0 M solution of SnCl₄ in CH₂Cl₂ (1 mL, 1.0 mmol) dropwise using a motor-driven syringe over 30 min. The reaction was allowed to warm gradually to -30 °C and stirred for 3 hours at this temperature before quenching with saturated aqueous NaHCO₃ (10 mL) and further vigorous stirring for 10 min. The layers were separated and the aqueous solution was extracted with CH₂Cl₂ (2 × 10 mL). The combined organic solution was washed with brine, dried over Na₂SO₄, filtered, and concentrated. The crude material was purified by chromatography.

Procedure (III): General Procedure for the oxidative cleavage of carbon-SiPh₂Bu^t bond under modified conditions. To an ice-cooled solution of KH (164 mg, 3.4 mmol) in DMF (5 mL) was added cumene hydroperoxide (260 μL, 80% solution, 1.7 mmol) drop-wise over 5 min. After the solution was warmed to 40 °C, a solution of the substrate (0.34 mmol) in DMF (5 mL) was added drop-wise over 5 min, followed by the addition of *n*-Bu₄NF (2.04 mmol, 2.1 mL of 1M solution in THF). After stirring the reaction mixture for 60 h at 40 °C, saturated aqueous Na₂SO₃ (20 mL) was added and the mixture was stirred vigorously for 30 min. The solution was extracted with Et₂O (5 × 30 mL). The combined organic solution was washed with brine (20 mL), dried, and concentrated *in vacuo*. The crude material was purified by radial chromatography.

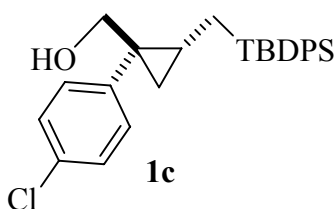


¹H NMR (400 MHz, CDCl₃): δ 7.57-7.55 (4H, dd, *J* = 7.8, 1.2 Hz), 7.4-7.17 (11H, m), 3.67-3.64 (1H, d, *J* = 11.2 Hz), 3.15-3.12 (1H, d, *J* = 11.2 Hz), 1.29-1.25 (1H, dd, *J* = 15.4, 3.4 Hz), 1.01-0.93 (1H, m), 0.95 (9H, s), 0.75-0.72 (1H, dd, *J* = 11.0, 4.9 Hz), 0.51-0.48 (1H, t, *J* = 4.9 Hz), 0.33-0.26 (1H, dd, *J* = 15.4, 5.1 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 139.4, 136.1, 136.0, 135.0, 130.6, 129.1, 129.0, 128.3, 127.5, 127.4, 126.6, 72.0, 34.4, 27.8, 18.2, 18.0,

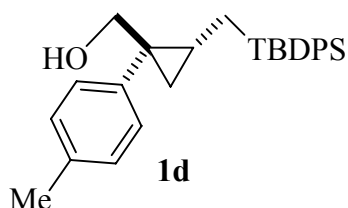
14.2, 11.3. FTIR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3377, 3070, 2932, 2860, 1494, 1468, 1446, 1266, 1106, 1017, 822, 737, 703. Anal Calcd for $\text{C}_{27}\text{H}_{32}\text{OSi}$: C, 80.95; H, 8.05. Found: C, 80.80; H, 7.90.



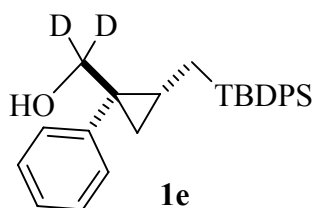
^1H NMR (400 MHz, CDCl_3): δ 7.61–7.59 (4H, m), 7.46–7.37 (8H, m), 7.08–7.01 (2H, m), 3.63–3.60 (1H, d, $J = 11.2$ Hz), 3.19–3.17 (1H, d, $J = 11.2$ Hz), 1.51 (1H, bs), 1.29–1.24 (1H, m), 1.00 (9H, s), 0.79–0.75 (1H, dd, $J = 7.8, 5.1$ Hz), 0.51–0.48 (1H, t, $J = 5.1$ Hz), 0.40–0.33 (1H, dd, $J = 14.9, 9.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 139.4, 138.6, 136.0, 136.01, 134.7, 132.4, 131.4, 129.1, 129.0, 127.6, 127.5, 120.6, 71.7, 33.8, 27.7, 18.2, 18.0, 14.2, 11.2. FTIR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3350, 3068, 2958, 2928, 2856, 1488, 1470, 1444, 1105, 1010, 820, 732, 700. Anal Calcd for $\text{C}_{27}\text{H}_{31}\text{BrOSi}$: C, 67.63; H, 6.52. Found: C, 67.50; H, 6.55.



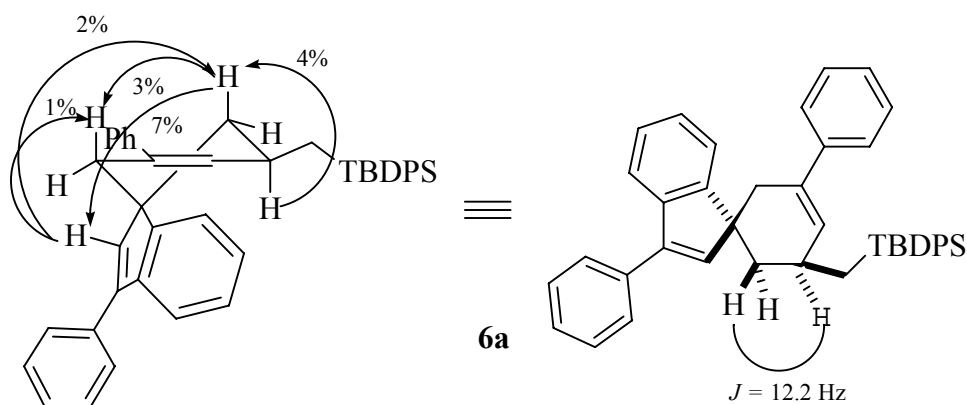
^1H NMR (400 MHz, CDCl_3): δ 7.58–7.55 (4H, m), 7.42–7.26 (8H, m), 7.14–7.09 (2H, m), 3.61–3.58 (1H, d, $J = 11.2$ Hz), 3.18–3.15 (1H, d, $J = 11.2$ Hz), 1.29–1.20 (2H, m), 0.97 (9H, s), 0.76–0.73 (1H, dd, $J = 8.5, 5.1$ Hz), 0.48–0.45 (1H, t, $J = 9.8$ Hz), 0.37–0.31 (1H, dd, $J = 15.3, 9.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 138.1, 136.1, 136.0, 134.8, 132.4, 132.0, 129.1, 129.05, 128.4, 127.6, 127.5, 71.7, 33.8, 27.8, 18.3, 18.1, 18.0, 11.3. FTIR (CD_2Cl_2): $\nu_{\max}/\text{cm}^{-1}$ 3360 (broad), 3069, 2930, 2858, 1492, 1467, 1426, 1265, 1104, 1015, 823, 738, 703. Anal Calcd for $\text{C}_{27}\text{H}_{31}\text{ClOSi}$: C, 74.54; H, 7.18. Found: C, 74.30; H, 7.20.



^1H NMR (400 MHz, CDCl_3): δ 7.59-7.56 (4H, m), 7.39-7.31 (6H, m), 7.14-7.07 (4H, m), 3.68-3.64 (1H, d, $J = 11.0$ Hz), 3.16-3.13 (1H, d, $J = 11.0$ Hz), 2.34 (3H, s), 1.32-1.27 (2H, m), 0.97 (9H, s), 0.75-0.71 (1H, dd, $J = 9.7, 5.1$ Hz), 0.49-0.47 (1H, t, $J = 5.1$ Hz), 0.38-0.32 (1H, dd, $J = 15.4, 9.7$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 136.2, 136.1, 136.05, 135.0, 130.5, 129.1, 129.0, 128.95, 127.5, 127.4, 72.0, 33.9, 27.8, 21.1, 18.3, 18.0, 17.9, 11.3. FTIR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3360, 3069, 2930, 2858, 1492, 1426, 1265, 1015, 823, 738, 703. Anal Calcd for $\text{C}_{28}\text{H}_{34}\text{OSi}$: C, 81.10; H, 8.26. Found: C, 81.20; H, 8.30.

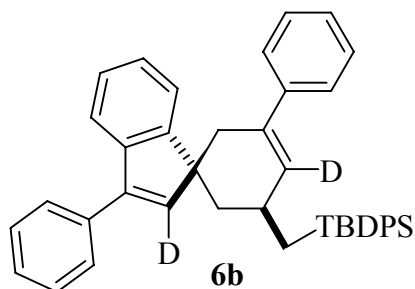


^1H NMR (400 MHz, CDCl_3): δ 7.56 (4H, bs), 7.36-7.15 (11 H, m), 1.43-1.40 (1H, m), 1.28-1.25 (1H, m), 0.95 (9H, s), 0.73-0.69 (1H, m), 0.50-0.46 (1H, q, $J = 9.3, 5.1$ Hz), 0.36-0.28 (1H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 139.5, 136.0, 134.9, 130.5, 128.9, 128.1, 127.4, 127.3, 126.4, 70.8 (quin), 34.0, 27.7, 26.8, 18.0, 17.9, 17.7, 14.1, 11.2. FTIR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3374, 3069, 2995, 2959, 2856, 1427, 1105, 731, 701. $\text{C}_{27}\text{H}_{30}\text{D}_2\text{OSi}$: C, 80.54; H, 8.51. Found: C, 80.40; H, 8.50.

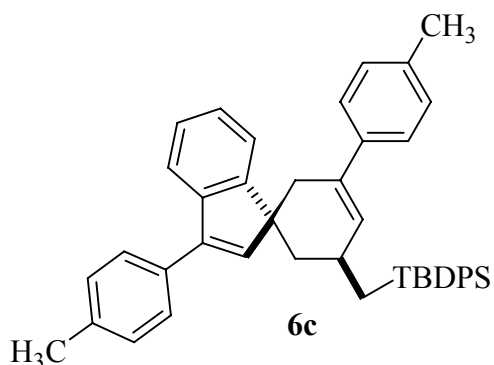


^1H NMR (400 MHz, CDCl_3): δ 7.54-7.50 (4H, m), 7.42-7.28 (6H, m), 7.25-7.10 (4H, m), 7.07-6.99 (4H, m), 6.95-6.90 (2H, m), 6.83-6.81 (2H, m), 6.64-6.62 (2H, m), 6.19 (1H, s), 5.57 (1H, bs), 2.60-2.55 (1H, d, $J = 17.4$ Hz), 2.47-2.17 (1H, m), 1.99-1.95 (1H, dd, $J = 12.2, 4.4$ Hz), 1.69 (1H, m), 1.50-1.44 (1H, t, $J = 11.4$ Hz), 1.27-1.22 (1H, dd, $J = 14.9, 6.6$ Hz), 1.17-1.12 (1H, dd, $J = 14.9, 7.8$ Hz), 0.93 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 144.5,

141.0, 140.3, 138.3, 136.1, 136.05, 134.8, 132.6, 131.6, 129.0, 128.96, 128.6, 128.1, 128.06, 127.7, 127.6, 127.5, 126.7, 126.5, 125.5, 124.7, 46.5, 44.0, 36.4, 29.6, 27.8, 18.2, 16.8. FTIR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3054, 3026, 2929, 2856, 1598, 1493, 1427, 1266, 1105, 1028, 738, 700. Anal Calcd for $\text{C}_{43}\text{H}_{42}\text{Si}$: C, 88.00; H, 7.21. Found: C, 88.20; H, 7.25.

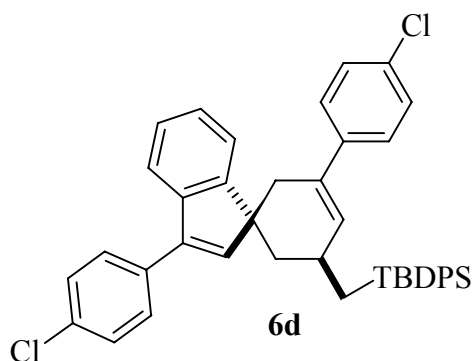


^1H NMR (400 MHz, CDCl_3): δ 7.54-7.50 (4H, m), 7.41-7.28 (6H, m), 7.25-7.10 (4H, m), 7.07-6.99 (4H, m), 6.95-6.90 (2H, m), 6.83-6.81 (2H, m), 6.64-6.62 (2H, m), 2.60-2.55 (1H, d, $J = 17.3$ Hz), 2.47-2.17 (1H, dd, $J = 17.3, 3.9$ Hz), 1.98-1.95 (1H, m), 1.70 (1H, m), 1.50-1.44 (1H, dd, $J = 11.2$ Hz), 1.27-1.21 (1H, dd, $J = 14.9, 6.6$ Hz), 1.17-1.11 (1H, dd, $J = 14.9, 7.8$ Hz), 0.93 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 144.4, 140.9, 138.3, 136.1, 134.9, 134.7, 132.5, 131.5, 129.0, 128.7, 128.1, 127.7, 127.6, 126.7, 126.6, 125.5, 124.7, 46.4, 43.9, 36.3, 29.5, 27.8, 18.2, 16.8. Anal Calcd for $\text{C}_{43}\text{H}_{40}\text{D}_2\text{Si}$: C, 87.70; H, 7.53. Found: C, 87.60; H, 7.50.

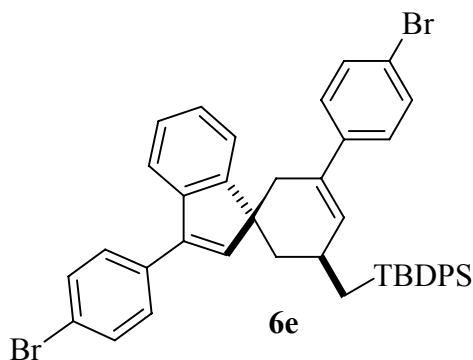


^1H NMR (400 MHz, CDCl_3): δ 7.54-7.50 (4H, m), 7.43-7.23 (6H, m), 7.03-7.01 (2H, m), 6.96-6.85 (6H, m), 6.72-6.70 (2H, m), 6.64-6.62 (2H, m), 6.16 (1H, s), 5.55 (1H, bs), 2.56-2.52 (1H, d, $J = 17.3$ Hz), 2.42-2.36 (1H, dt, $J = 17.3, 2.7$ Hz), 2.31 (3H, s), 2.24 (3H, s), 1.95-1.92 (1H, d, $J = 12.2$ Hz), 1.69 (1H, m), 1.48-1.45 (1H, t, $J = 12.2$ Hz), 1.26-1.21 (1H, m), 1.16-1.10 (1H, dd, $J = 15.1, 7.6$ Hz), 0.93 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 144.7,

140.2, 138.1, 138.0, 136.4, 136.1, 136.05, 135.6, 134.9, 134.8, 132.4, 131.7, 130.7, 129.0, 128.9, 128.8, 128.5, 128.3, 127.6, 127.5, 126.5, 125.4, 124.6, 46.5, 43.9, 36.3, 29.6, 27.8, 21.2, 21.0, 18.2, 16.9. FTIR (neat): $\nu_{\max}/\text{cm}^{-1}$ 2926, 2856, 1598, 1423, 1104, 1020, 814, 698. Anal Calcd for $\text{C}_{45}\text{H}_{46}\text{Si}$: C, 87.89; H, 7.54. Found: C, 87.90; H, 7.60.

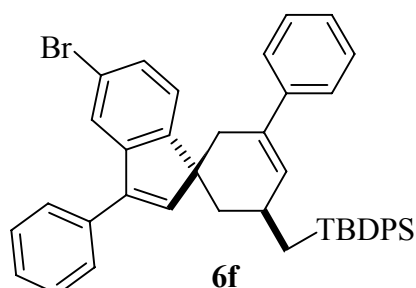


^1H NMR (400 MHz, CDCl_3): δ 7.60-7.51 (4H, m), 7.41-7.28 (6H, m), 7.21-7.12 (2H, m), 7.0-6.88 (6H, m), 6.69-6.67 (2H, m), 6.59-6.57 (2H, m), 6.20 (1H, s), 5.54 (1H, broad s), 2.53-2.48 (1H, d, $J = 17.1$ Hz), 2.44-2.38 (1H, dt, $J = 17.1, 2.4$ Hz), 2.02-1.98 (1H, dd, $J = 12.2, 4.4$ Hz), 1.71 (1H, m), 1.51-1.48 (1H, t, $J = 12.2$ Hz), 1.27-1.22 (1H, dd, $J = 15.1, 6.8$ Hz), 1.20-1.14 (1H, dd, $J = 15.1, 7.8$ Hz), 0.94 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 143.9, 140.9, 139.4, 136.5, 136.1, 136.0, 134.8, 134.6, 132.5, 132.1, 131.4, 130.5, 129.9, 129.1, 129.0, 128.3, 127.8, 127.7, 127.6, 127.55, 126.5, 126.0, 125.7, 46.3, 43.9, 36.4, 29.7, 27.7, 18.2, 16.7. FTIR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3068, 2928, 2856, 1592, 1491, 1427, 1263, 1098, 1014, 820, 738, 701. Anal Calcd for $\text{C}_{43}\text{H}_{40}\text{Cl}_2\text{Si}$: C, 78.76; H, 6.15. Found: C, 78.60; H, 6.10.

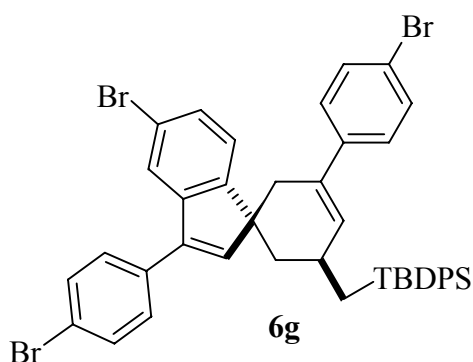


^1H NMR (400 MHz, CDCl_3): δ 7.60-7.51 (4H, m), 7.48-7.28 (10H, m), 7.14-7.12 (2H, m), 6.98-6.83 (3H, m), 6.62-6.57 (3H, m), 6.19 (1H, s), 5.55 (1H, bs), 2.52-2.48 (1H, d, $J = 17.1$ Hz), 2.42-2.38 (1H, d, $J = 17.1$ Hz), 2.02-1.98 (1H, dd, $J = 12.2, 4.4$ Hz), 1.73-1.71 (1H, m),

1.45-1.42 (1H, m), 1.18-1.14 (2H, m), 0.94 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 143.9, 140.8, 139.8, 136.5, 136.1, 136.0, 134.8, 134.5, 132.2, 131.6, 131.5, 131.2, 130.8, 130.2, 129.2, 129.1, 129.0, 127.7, 127.6, 127.55, 126.5, 126.3, 125.7, 46.2, 43.9, 36.4, 29.7, 27.7, 18.2, 16.7. Anal Calcd for $\text{C}_{43}\text{H}_{40}\text{Br}_2\text{Si}$: C, 69.35; H, 5.41. Found: C, 69.40, H, 5.40.

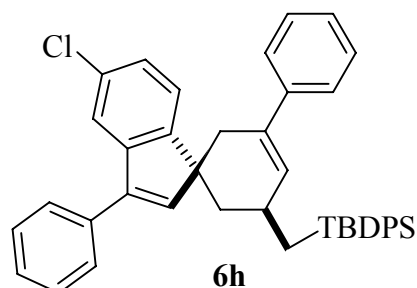


^1H NMR (400 MHz, CDCl_3): δ 7.56-7.51 (3H, m), 7.41-7.03 (15H, m), 6.94-6.92 (2H, d, $J = 8.6$ Hz), 6.78-6.76 (1H, d, $J = 7.1$ Hz), 6.41-6.39 (2H, d, $J = 8.6$ Hz), 6.13 (1H, s), 5.62 (1H, s), 2.57-2.46 (2H, m), 1.92-1.87 (1H, dd, $J = 12.9, 4.8$ Hz), 1.59 (1H, bs), 1.49-1.43 (1H, m), 1.28-1.23 (1H, dd, $J = 15.1, 6.4$ Hz), 1.17-1.11 (1H, dd, $J = 15.1, 8.3$ Hz), 0.94 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 143.2, 140.8, 139.7, 138.0, 136.1, 136.0, 134.5, 134.5, 134.5, 132.4, 132.3, 131.7, 130.5, 129.1, 129.05, 128.4, 128.2, 128.1, 127.7, 127.6, 127.5, 126.9, 124.7, 119.3, 46.2, 43.8, 36.4, 29.6, 27.7, 18.2, 16.5. Anal Calcd for $\text{C}_{43}\text{H}_{41}\text{BrSi}$: C, 77.57; H, 6.21. Found: C, 77.50; H, 6.14.

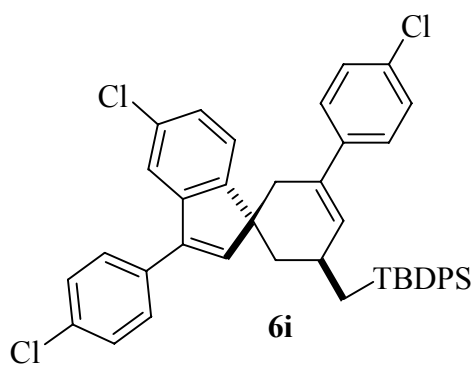


^1H NMR (400 MHz, CDCl_3): δ 7.57-6.86 (17H, m), 6.62-6.59 (2H, m), 6.37-6.35 (2H, d, $J = 8.6$ Hz), 6.13 (1H, s), 5.60 (1H, s), 2.44 (2H, bs), 1.94-1.89 (1H, dd, $J = 12.4, 4.6$ Hz), 1.61 (1H, m), 1.54-1.46 (1H, m), 1.28-1.23 (1H, dd, $J = 14.9, 6.6$ Hz), 1.19-1.13 (1H, dd, $J = 14.9, 8.0$ Hz), 0.94 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 142.7, 140.2, 139.5, 136.8, 136.1, 136.0, 132.3, 134.4, 134.2, 132.3, 131.3, 131.2, 130.9, 130.7, 130.1, 129.2, 129.1, 128.3, 127.7, 127.6, 126.4, 126.3, 122.5, 120.8, 119.6, 45.8, 43.7, 36.4, 29.7, 27.7, 18.2, 16.3. FTIR

(neat): $\nu_{\max}/\text{cm}^{-1}$ 3069, 2957, 2926, 2855, 1585, 1487, 1470, 1427, 1393, 1103, 1073, 1008, 818, 736, 723, 701. Anal Calcd for $\text{C}_{43}\text{H}_{39}\text{Br}_3\text{Si}$: C, 62.71; H, 4.77. Found: C, 62.55; H, 4.66.

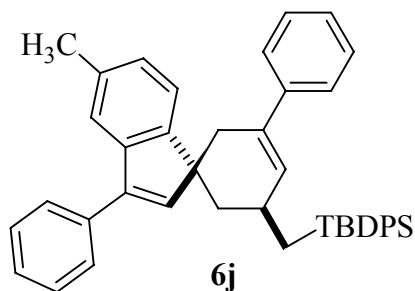


^1H NMR (400 MHz, CDCl_3): δ 7.56-7.51 (3H, m), 7.43-7.29 (6H, m), 7.26-7.02 (8H, m), 6.78-6.76 (4H, m), 6.48-6.45 (2H, m), 6.13 (1H, s), 5.61 (1H, broad s), 2.56-2.46 (2H, m), 1.92-1.88 (1H, dd, $J = 12.2, 4.4$ Hz), 1.60 (1H, m), 1.49-1.43 (1H, t, $J = 12.2$ Hz), 1.28-1.23 (1H, dd, $J = 15.1, 6.4$ Hz), 1.17-1.11 (1H, dd, $J = 15.1, 8.0$ Hz), 0.94 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 142.3, 140.1, 139.8, 138.0, 136.1, 136.0, 134.5, 134.47, 132.4, 132.2, 131.7, 131.0, 129.1, 129.0, 128.4, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 126.9, 124.7, 46.2, 43.7, 36.4, 29.6, 27.7, 18.2, 16.5. FTIR (neat): $\nu_{\max}/\text{cm}^{-1}$ 3068, 2928, 2855, 1714, 1595, 1102, 1491, 1427, 1102, 1013, 822, 737, 700. Anal Calcd for $\text{C}_{43}\text{H}_{41}\text{ClSi}$: C, 83.12; H, 6.65. Found: C, 83.20; H, 6.60.

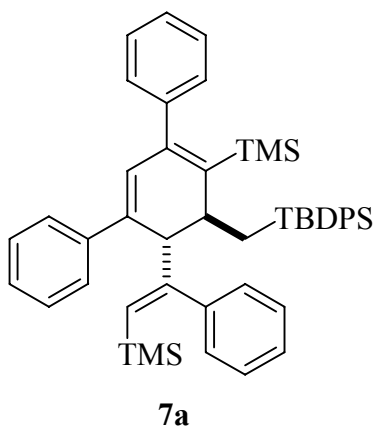


^1H NMR (400 MHz, CDCl_3): δ 7.56-7.51 (4H, m), 7.43-7.29 (5H, m), 7.21-7.19 (2H, m), 7.02-6.99 (2H, m), 6.94-6.92 (2H, m), 6.84-6.81 (2H, m), 6.68-6.65 (2H, m), 6.45-6.43 (2H, m), 6.15 (1H, s), 5.68 (1H, broad s), 2.46 (2H, broad s), 1.94-1.90 (1H, dd, $J = 12.4, 4.4$ Hz), 1.63 (1H, m), 1.50-1.44 (1H, t, $J = 12.4$ Hz), 1.28-1.23 (1H, dd, $J = 15.1, 6.6$ Hz), 1.19-1.13 (1H, dd, $J = 15.1, 8.0$ Hz), 0.94 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 142.3, 140.3, 139.1, 136.3, 136.0, 134.5, 134.3, 132.7, 132.2, 131.4, 131.3, 131.0, 129.8, 129.2, 129.1, 128.4,

127.9, 127.70, 127.65, 127.6, 125.9, 46.0, 43.7, 36.5, 29.7, 27.7, 18.2, 16.4. FTIR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3070, 3048, 2929, 2856, 1490, 1641, 1590, 1490, 1428, 1398, 1264, 1097, 1013, 820, 737, 704. Anal Calcd for $\text{C}_{43}\text{H}_{39}\text{Cl}_3\text{Si}$: C, 74.83; H, 5.70. Found: C, 74.67; H, 5.72.

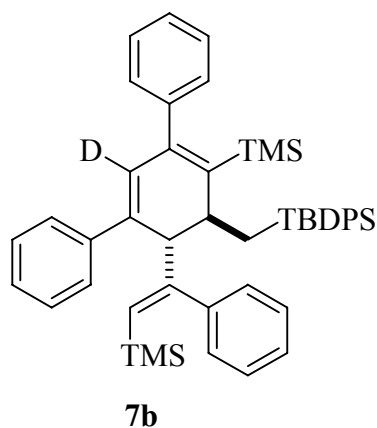


^1H NMR (400 MHz, CDCl_3): δ 7.55-7.52 (3H, m), 7.41-7.00 (15H, m), 6.86-6.84 (2H, m), 6.72-6.50 (3H, m), 6.15 (1H, s), 5.58 (1H, broad s), 2.56-2.52 (1H, d, $J = 17.3$ Hz), 2.43-2.38 (1H, dt, $J = 17.3, 2.7$ Hz), 2.19 (3H, s), 1.95-1.91 (1H, dd, $J = 12.2, 4.6$ Hz), 1.73 (1H, m), 1.46-1.40 (1H, m), 1.27-1.22 (1H, dd, $J = 14.9, 6.1$ Hz), 1.18-1.13 (1H, dd, $J = 14.9, 8.1$ Hz), 0.94 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 141.3, 141.1, 140.3, 138.4, 136.2, 136.1, 134.8, 134.7, 132.6, 131.6, 131.1, 129.0, 128.9, 128.7, 128.3, 128.1, 128.0, 127.6, 127.55, 126.7, 126.3, 124.7, 46.2, 43.7, 36.4, 29.7, 27.8, 20.8, 18.2, 16.8. FTIR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3056, 2928, 2857, 1596, 1492, 1448, 1265, 1104, 1022, 819, 737, 700. Anal Calcd for $\text{C}_{44}\text{H}_{44}\text{Si}$: C, 87.95; H, 7.38. Found: C, 87.70; H, 7.40.

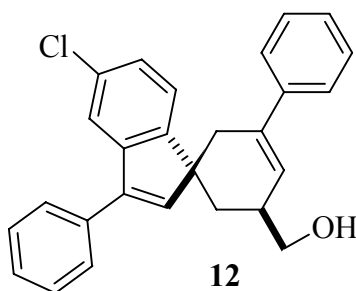


Crystalline solid, melting point = 198–200 °C.

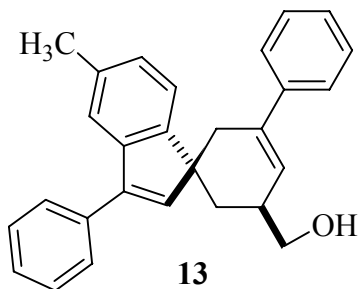
^1H NMR (400 MHz, CDCl_3): δ 7.71-7.58 (16H, m), 7.47-7.42 (3H, m), 7.38-7.37 (2H, m), 7.30-7.27 (2H, m), 7.09-7.07 (2H, m), 6.85 (1H, s), 5.85 (1H, s), 3.94 (1H, broad s), 3.08-3.05 (1H, d, $J = 11.5$ Hz), 2.27-2.20 (1H, m), 1.36-1.33 (1H, d, $J = 13.9$ Hz), 1.26 (9H, s), 0.0 (9H, s), -0.04 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 155.9, 145.2, 144.6, 143.1, 141.2, 138.4, 136.9, 136.5, 136.0, 133.8, 128.9, 128.87, 128.8, 128.4, 128.2, 127.9, 127.7, 127.6, 127.3, 127.1, 127.0, 126.9, 125.8, 50.8, 38.1, 27.9, 18.2, 13.8, 0.58, 0.0. FTIR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3057, 3026, 2955, 2927, 2857, 1596, 1488, 1255, 842, 742, 699. Anal Calcd for $\text{C}_{49}\text{H}_{58}\text{Si}_3$: C, 80.48; H, 7.99. Found: C, 80.40; H, 7.95.



^1H NMR (400 MHz, CDCl_3): δ 7.71-7.68 (2H, m), 7.65-7.55 (13H, m), 7.47-7.42 (4H, m), 7.38-7.36 (2H, d, $J = 6.4$), 7.30-7.26 (2H, t, $J = 7.6$ Hz), 7.09-7.07 (2H, d, $J = 7.3$ Hz), 5.84 (1H, s), 3.94 (1H, s), 3.06-3.05 (1H, d, $J = 12.1$ Hz), 2.27-2.20 (1H, dd, $J = 15.4, 12.1$ Hz), 1.40-1.36 (1H, dd, $J = 1.7, 15.4$ Hz), 1.25 (9H, s), 0.00 (9H, s), -0.04 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 155.3, 144.6, 144.0, 142.6, 140.7, 137.8, 136.3, 135.9, 135.3, 134.4, 133.2, 128.4, 128.3, 128.2, 127.9, 127.6, 127.4, 127.2, 127.0, 126.6, 126.5, 126.3, 125.2, 50.2, 37.5, 27.3, 17.6, 13.2, 0.0, -0.5. FTIR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3057, 3026, 2954, 2853, 1598, 1551, 1489, 1443, 1248, 1020, 860, 755, 695. Anal Calcd for $\text{C}_{49}\text{H}_{57}\text{DSi}_3$: C, 80.37; H, 8.12. Found: C, 80.25; H, 8.05.



^1H NMR (400 MHz, CDCl_3): δ 7.34-7.25 (5H, m), 7.19-7.08 (3H, m), 7.02-7.00 (2H, d, $J = 8.5$ Hz), 6.90-6.88 (3H, d, $J = 8.1$ Hz), 6.41 (1H, s), 5.87 (1H, s), 3.58-3.49 (2H, m), 2.73 (2H, broad s), 2.20-2.18 (1H, d, $J = 8.0$ Hz), 1.75 (1H, broad s), 1.60 (1H, broad s). ^{13}C NMR (100 MHz, CDCl_3): δ 142.9, 140.7, 138.0, 136.2, 132.6, 131.6, 128.4, 128.2, 127.9, 127.8, 127.4, 125.0, 66.5, 43.4, 40.0, 36.8, 29.7. Anal Calcd for $\text{C}_{27}\text{H}_{23}\text{ClO}$: C, 81.29; H, 5.81. Found: C, 81.40; H, 5.74.



^1H NMR (400 MHz, CDCl_3): δ 7.33-7.25 (5H, m), 7.12-7.10 (3H, m), 6.96-6.94 (2H, m), 6.90 (3H, broad s), 6.42 (1H, s), 5.87 (1H, broad s), 3.56-3.46 (2H, m), 2.75-2.70 (1H, d, $J = 17.4$ Hz), 2.65-2.59 (1H, m), 2.25 (3H, s), 2.15 (1H, broad s), 1.78 (1H, broad s), 1.70-1.67 (1H, d, $J = 12$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 141.5, 141.0, 140.1, 138.4, 136.5, 135.4, 131.6, 128.6, 128.3, 128.2, 127.7, 127.2, 126.7, 125.0, 66.7, 43.5, 39.7, 37.1, 29.3, 20.9. Anal Calcd for $\text{C}_{28}\text{H}_{26}\text{O}$: C, 88.85; H, 6.92. Found: C, 88.72; H, 6.88.