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

Veejendra K. Yadav,*a Naganaboina Vijaya Kumar a and Masood Parvezb

*a Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India
b Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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 arylacetylenes. A solution of cyclopropylcarbinol (0.5 mmol) and an arylacetylene (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 SnCl$_4$-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 CH$_2$Cl$_2$ (8 mL) was cooled to −50 °C in a round bottom flask and mixed with 1.0 M solution of SnCl$_4$ in CH$_2$Cl$_2$ (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 NaHCO$_3$ (10 mL) and further vigorous stirring for 10 min. The layers were separated and the aqueous solution was extracted with CH$_2$Cl$_2$ (2 × 10 mL). The combined organic solution was washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated. The crude material was purified by chromatography.

Procedure (III): General Procedure for the oxidative cleavage of carbon-SiPh$_2$Bu$^1$ 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-Bu$_4$NF (2.04 mmol, 2.1 mL of 1M solution in THF). After stirring the reaction mixture for 60 h at 40 °C, saturated aqueous Na$_2$SO$_3$ (20 mL) was added and the mixture was stirred vigorously for 30 min. The solution was extracted with Et$_2$O (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.

$^1$H NMR (400 MHz, CDCl$_3$): 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). $^{13}$C NMR (100 MHz, CDCl$_3$): 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): $\nu_{\text{max}}/\text{cm}^{-1}$ 3377, 3070, 2932, 2860, 1494, 1468, 1446, 1266, 1106, 1017, 822, 737, 703. Anal Calcd for C$_{27}$H$_{32}$OSi: C, 80.95; H, 8.05. Found: C, 80.80; H, 7.90.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\text{max}}/\text{cm}^{-1}$ 3350, 3068, 2958, 2928, 2856, 1488, 1470, 1444, 1105, 1010, 820, 732, 700. Anal Calcd for C$_{27}$H$_{31}$BrOSi: C, 67.63; H, 6.52. Found: C, 67.50; H, 6.55.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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$_2$Cl$_2$): $\nu_{\text{max}}/\text{cm}^{-1}$ 3360 (broad), 3069, 2930, 2858, 1492, 1467, 1426, 1265, 1104, 1015, 823, 738, 703. Anal Calcd for C$_{27}$H$_{31}$ClOSi: C, 74.54; H, 7.18. Found: C, 74.30; H, 7.20.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\text{max/cm}}^{-1} 3360, 3069, 2930, 2858, 1492, 1426, 1265, 1015, 823, 738, 703$. Anal Calcd for C$_{28}$H$_{34}$OSi: C, 81.10; H, 8.26. Found: C, 81.20; H, 8.30.

![Diagram 1e](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\text{max/cm}}^{-1} 3374, 3069, 2995, 2959, 2856, 1427, 1105, 731, 701$. C$_{27}$H$_{30}$D$_2$OSi: C, 80.54; H, 8.51. Found: C, 80.40; H, 8.50.

![Diagram 6a](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\text{max}}/\text{cm}^{-1}$ 3054, 3026, 2929, 2856, 1598, 1493, 1427, 1266, 1105, 1028, 738, 700.

Anal Calcd for C$_{43}$H$_{42}$Si: C, 88.00; H, 7.21. Found: C, 88.20; H, 7.25.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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 C$_{43}$H$_{40}$D$_2$Si: C, 87.70; H, 7.53. Found: C, 87.60; H, 7.50.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\text{max}}$/cm$^{-1}$ 2926, 2856, 1598, 1423, 1104, 1020, 814, 698.

Anal Calcd for C$_{45}$H$_{46}$Si: C, 87.89; H, 7.54. Found: C, 87.90; H, 7.60.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\text{max}}$/cm$^{-1}$ 3068, 2928, 2856, 1592, 1491, 1427, 1263, 1098, 1014, 820, 738, 701. Anal Calcd for C$_{43}$H$_{40}$Cl$_2$Si: C, 78.76; H, 6.15. Found: C, 78.60; H, 6.10.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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 C$_{43}$H$_{40}$Br$_2$Si: C, 69.35; H, 5.41. Found: C, 69.40, H, 5.40.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 143.2, 140.8, 139.7, 138.0, 136.1, 136.0, 134.5, 134.5, 134.5, 134.4, 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 C$_{43}$H$_{41}$BrSi: C, 77.57; H, 6.21. Found: C, 77.50; H, 6.14.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\max}$/cm$^{-1}$ 3069, 2957, 2926, 2855, 1585, 1487, 1470, 1427, 1393, 1103, 1073, 1008, 818, 736, 723, 701. Anal Calcd for C$_{43}$H$_{39}$Br$_3$Si: C, 62.71; H, 4.77. Found: C, 62.55; H, 4.66.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\max}$/cm$^{-1}$ 3068, 2928, 2855, 1714, 1595, 1102, 1491, 1427, 1102, 1013, 822, 737, 700. Anal Calcd for C$_{43}$H$_{41}$ClSi: C, 83.12; H, 6.65. Found: C, 83.20; H, 6.60.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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 C\(_{43}\)H\(_{39}\)Cl\(_3\)Si: C, 74.83; H, 5.70. Found: C, 74.67; H, 5.72.

\[
\text{H}_3\text{C}
\]

\[
\text{TBDPS}
\]

\[
\text{6j}
\]

\(^1\text{H NMR (400 MHz, CDCl}_3\): } \delta \text{ 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 \text{ Hz), 2.43-2.38 (1H,dt, } J = 17.3, 2.7 \text{ Hz), 2.19 (3H,s), 1.95-1.91 (1H,dd, } J = 12.2, 4.6 \text{ Hz), 1.73 (1H,m), 1.46-1.40 (1H,m), 1.27-1.22 (1H,dd, } J = 14.9, 6.1 \text{ Hz), 1.18-1.13 (1H,dd, } J = 14.9, 8.1 \text{ Hz), 0.94 (9H,s).} \]

\(^1\text{C NMR (100 MHz, CDCl}_3\): } \delta \text{ 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} \text{ 3056, 2928, 2857, 1596, 1492, 1448, 1265, 1104, 1022, 819, 737, 700. Anal Calcd for C\(_{44}\)H\(_{44}\)Si: C, 87.95; H, 7.38. Found: C, 87.70; H, 7.40.}

\[
\text{TMS}
\]

\[
\text{TBDPS}
\]

\[
\text{7a}
\]

Crystalline solid, melting point = 198–200 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\text{max}}$/cm$^{-1}$ 3057, 3026, 2955, 2927, 2857, 1596, 1488, 1255, 1020, 860, 755, 699. Anal Calcd for C$_{49}$H$_{58}$Si$_3$: C, 80.48; H, 7.99. Found: C, 80.40; H, 7.95.

![Image](7b)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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): $\nu_{\text{max}}$/cm$^{-1}$ 3057, 3026, 2954, 2853, 1598, 1551, 1489, 1443, 1248, 1020, 860, 755, 695. Anal Calcd for C$_{49}$H$_{57}$DSi$_3$: C, 80.37; H, 8.12. Found: C, 80.25; H, 8.05.

![Image](12)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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 C$_{27}$H$_{23}$ClO: C, 81.29; H, 5.81. Found: C, 81.40; H, 5.74.

![Diagram of molecule 13]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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 C$_{28}$H$_{26}$O: C, 88.85; H, 6.92. Found: C, 88.72; H, 6.88.