

## Supplementary Information

### Liquid crystalline conjugated oligomers: synthesis and mesomorphic properties of laterally and terminally alkyl-substituted oligo(1,4-phenyleneethynylene)s

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## Synthesis

**Compound 7c.** Synthesized by the procedure described for **1**. Quantities: **18c** (166 mg, 0.379 mmol), **10f** (310 mg, 0.981 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (14 mg, 0.020 mmol), CuI (14 mg, 0.074 mmol), and piperidine–THF (1:1, 20 mL). Yield: 231 mg (75%) of a white solid; phase transitions (°C): Cr 150 N 183 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.8 Hz, 6H), 0.97 (t, *J* = 7.6 Hz, 6H), 1.23–1.36 (m, 20H), 1.43 (tq, *J* = 7.6 Hz, 4H), 1.57–1.74 (m, 8H), 2.62 (t, *J* = 7.6 Hz, 4H), 2.82 (t, *J* = 7.6 Hz, 4H), 7.17 (d, *J* = 8.2 Hz, 4H), 7.37 (s, 2H), 7.45 (d, *J* = 8.2 Hz, 4H), 7.47–7.52 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.04, 14.10, 22.59, 22.66, 29.24, 29.26, 29.44, 31.23, 31.87, 32.78, 33.78, 35.93, 88.51, 90.22, 91.60, 93.82, 120.11, 122.52, 123.03, 123.37, 128.51, 131.34, 131.51, 131.53, 132.39, 142.24, 143.73. Elemental analysis: calc. for C<sub>62</sub>H<sub>70</sub>: C, 91.35; H, 8.65; found: C, 91.23; H, 8.63%. APCI-MS: *m/z* = 816.2 ([M+H]<sup>+</sup>, calc. 815.6).

**Compound 7d.** Synthesized by the procedure described for **1**. Quantities: **18d** (179 mg, 0.384 mmol), **10f** (320 mg, 1.01 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (17 mg, 0.024 mmol), CuI (14 mg, 0.074 mmol), and piperidine–THF (1:1, 20 mL). Yield: 259 mg (80%) of a white solid; phase transitions (°C): Cr 156 N 167 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.8 Hz, 6H), 0.91 (t, *J* = 6.8 Hz, 6H), 1.02 (t, *J* = 7.2 Hz, 6H), 1.23–1.43 (m, 28H), 1.57–1.75 (m, 8H), 2.62 (t, *J* = 7.6 Hz, 4H), 2.81 (t, *J* = 7.6 Hz, 4H), 7.17 (d, *J* = 8.4 Hz, 4H), 7.37 (s, 2H), 7.45 (d, *J* = 8.4 Hz, 4H), 7.47–7.53 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.07, 14.10, 22.59, 22.66, 29.24, 29.26, 29.44, 30.31, 31.23, 31.74, 31.87, 34.10, 35.93, 88.50, 90.22, 91.60, 93.82, 120.11, 122.51, 123.03, 123.36, 128.51, 131.34, 131.50, 131.53, 132.36, 142.30, 143.73. Elemental analysis: calc. for C<sub>64</sub>H<sub>74</sub>: C, 91.15; H, 8.85; found: C, 90.88; H, 8.89%. APCI-MS: *m/z* = 844.3 ([M+H]<sup>+</sup>, calc. 843.6).

**Compound 7e.** Synthesized by the procedure described for **1**. Quantities: **18e** (190 mg, 0.385 mmol), **10f** (319 mg, 1.01 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (16 mg, 0.022 mmol), CuI (18 mg, 0.095 mmol), and piperidine–THF (1:1, 20 mL). Yield: 239 mg (71%) of a white solid; phase transitions (°C): Cr 122 N 155 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.8 Hz, 12H), 1.23–1.46 (m, 32H), 1.57–1.75 (m, 8H), 2.62 (t, *J* = 7.6 Hz, 4H), 2.81 (t, *J* = 7.6 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 4H), 7.37 (s, 2H), 7.45 (d, *J* = 8.0 Hz, 4H), 7.47–7.53 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.10, 14.11, 22.62, 22.66, 29.23, 29.26, 29.44, 30.63, 31.23, 31.75, 31.87, 34.13, 35.93, 88.51, 90.22, 91.60, 93.81, 120.10, 122.51, 123.03, 123.36, 128.51, 131.35, 131.50, 131.53, 132.35, 142.32, 143.73. Elemental analysis: calc. for C<sub>66</sub>H<sub>78</sub>: C, 90.98; H, 9.02; found: C, 90.83; H, 9.09%. APCI-MS: *m/z* = 872.4 ([M+H]<sup>+</sup>, calc. 871.6).

**Compound 7f.** Synthesized by the procedure described for **1**. Quantities: **18f** (171 mg, 0.310 mmol), **10f** (272 mg, 0.860 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (18 mg, 0.026 mmol), CuI (21 mg, 0.11 mmol), and piperidine–THF (1:1, 20 mL). Yield: 204 mg (71%) of a white solid; phase transitions (°C): Cr 96 N 135 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.87 (t, *J* = 7.0 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 6H), 1.21–1.45 (m, 40H), 1.57–1.75 (m, 8H), 2.62 (t, *J* = 7.6 Hz, 4H), 2.81 (t, *J* = 7.6 Hz, 4H), 7.17 (d, *J* = 8.2 Hz, 4H), 7.37 (s, 2H), 7.45 (d, *J* = 8.2 Hz, 4H), 7.47–7.52 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.10,

14.11, 29.25, 29.28, 29.44, 29.50, 29.56, 30.66, 31.23, 31.86, 31.90, 34.13, 35.93, 88.51, 90.22, 91.59, 93.81, 120.11, 122.51, 123.03, 123.36, 128.51, 131.35, 131.50, 131.53, 132.34, 142.32, 143.72. Elemental analysis: calc. for C<sub>70</sub>H<sub>86</sub>: C, 90.65; H, 9.35; found: C, 90.64; H, 9.36%. APCI-MS: *m/z* = 928.4 ([M+H]<sup>+</sup>, calc. 927.7).

**Compound 8b.** Synthesized by the procedure described for **1**. Quantities: **13** (255 mg, 0.516 mmol), **10b** (316 mg, 1.45 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (19 mg, 0.027 mmol), CuI (18 mg, 0.095 mmol), and piperidine (15 mL). Yield: 262 mg (75%) of a pale yellow solid; phase transitions (°C): Cr 179 N 243 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.31 (t, *J* = 7.6 Hz, 6H), 1.32 (t, *J* = 7.6 Hz, 6H) 1.33 (t, *J* = 7.6 Hz, 6H), 2.38 (s, 6H), 2.86 (q, *J* = 7.6 Hz, 4H), 2.87 (q, *J* = 7.6 Hz, 4H), 2.88 (q, *J* = 7.6 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 4H), 7.39 (s, 4H), 7.41 (s, 2H), 7.44 (d, *J* = 8.0 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.71, 14.97, 15.00, 21.52, 27.22, 27.27, 27.29, 87.57, 92.77, 92.97, 94.34, 120.36, 122.42, 122.68, 123.72, 129.15, 131.38, 131.52, 131.66, 131.73, 138.45, 143.23, 143.29, 143.38. Elemental analysis: calc. for C<sub>52</sub>H<sub>50</sub>: C, 92.53; H, 7.47; found: C, 92.55; H, 7.15%. APCI-MS: *m/z* = 675.7 ([M+H]<sup>+</sup>, calc. 675.4).

**Compound 8c.** Synthesized by the procedure described for **1**. Quantities: **13** (256 mg, 0.518 mmol), **10c** (295 mg, 1.27 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (22 mg, 0.031 mmol), CuI (20 mg, 0.11 mmol), and piperidine (10 mL). Yield: 277 mg (76%) of a pale yellow solid; phase transitions (°C): Cr 180 N 234 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.25 (t, *J* = 7.6 Hz, 6H), 1.315 (t, *J* = 7.6 Hz, 12H) 1.324 (t, *J* = 7.6 Hz, 6H), 2.67 (q, *J* = 7.6 Hz, 4H), 2.86 (q, *J* = 7.6 Hz, 4H), 2.87 (q, *J* = 7.6 Hz, 4H), 2.88 (q, *J* = 7.6 Hz, 4H), 7.20 (d, *J* = 8.2 Hz, 4H), 7.39 (s, 4H), 7.41 (s, 2H), 7.46 (d, *J* = 8.2 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.72, 14.98, 15.00, 15.38, 27.21, 27.27, 27.29, 28.85, 87.55, 92.77, 92.97, 94.37, 120.60, 122.42, 122.68, 123.74, 127.96, 131.48, 131.53, 131.66, 131.73, 143.23, 143.29, 143.41, 144.77. Elemental analysis: calc. for C<sub>54</sub>H<sub>54</sub>: C, 92.26; H, 7.74; found: C, 92.12; H, 7.49%. APCI-MS: *m/z* = 703.8 ([M+H]<sup>+</sup>, calc. 703.4).

**Compound 8d.** Synthesized by the procedure described for **1**. Quantities: **13** (257 mg, 0.520 mmol), **10d** (313 mg, 1.27 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (20 mg, 0.028 mmol), CuI (20 mg, 0.11 mmol), and piperidine (10 mL). Yield: 289 mg (76%) of a pale yellow solid; phase transitions (°C): Cr 149 N 240 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.95 (t, *J* = 7.2 Hz, 6H), 1.315 (t, *J* = 7.6 Hz, 6H) 1.317 (t, *J* = 7.6 Hz, 6H), 1.33 (t, *J* = 7.6 Hz, 6H), 1.66 (tq, *J* = 7.6 Hz, 4H), 2.61 (t, *J* = 7.6 Hz, 4H), 2.86 (q, *J* = 7.6 Hz, 4H), 2.87 (q, *J* = 7.6 Hz, 4H), 2.88 (q, *J* = 7.6 Hz, 4H), 7.18 (d, *J* = 8.2 Hz, 4H), 7.39 (s, 4H), 7.41 (s, 2H), 7.46 (d, *J* = 8.2 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 13.75, 14.73, 14.98, 15.00, 24.37, 27.21, 27.27, 27.30, 37.98, 87.58, 92.77, 92.98, 94.39, 120.61, 122.42, 122.68, 123.74, 128.57, 131.40, 131.53, 131.66, 131.73, 143.24, 143.29, 143.40. Elemental analysis: calc. for C<sub>56</sub>H<sub>58</sub>: C, 92.00; H, 8.00; found: C, 92.04; H, 7.69%. APCI-MS: *m/z* = 731.9 ([M+H]<sup>+</sup>, calc. 731.5).

**Compound 8e.** Synthesized by the procedure described for **1**. Quantities: **13** (252 mg, 0.510 mmol), **10e** (335 mg, 1.29 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (22 mg, 0.031 mmol), CuI (22 mg, 0.12 mmol), and piperidine (10 mL). Yield: 312 mg (81%) of a pale yellow solid; phase transitions (°C): Cr 142 N 211 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.94 (t, *J* = 7.2 Hz, 6H), 1.29–1.41 (m, 22H), 1.57–1.65 (m, 4H), 2.63 (t, *J* = 7.6 Hz, 4H), 2.86 (q, *J* = 7.6 Hz, 4H), 2.87 (q, *J* = 7.6 Hz, 4H), 2.88 (q, *J* = 7.6 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 4H), 7.39 (s, 4H), 7.41 (s, 2H), 7.45 (d, *J* = 8.0 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 13.92, 14.72, 14.98, 15.00, 22.30, 27.21, 27.27, 27.29, 33.42, 35.61, 87.56, 92.76, 92.97, 94.40, 120.55, 122.40, 122.68, 123.74, 128.51, 131.40, 131.52, 131.66, 131.73, 143.22, 143.29, 143.39, 143.47. Elemental analysis: calc. for C<sub>58</sub>H<sub>62</sub>: C, 91.77; H, 8.23; found: C, 91.58; H, 7.88%. APCI-MS: *m/z* = 760.0 ([M+H]<sup>+</sup>, calc. 759.5).

**Compound 9b.** Synthesized by the procedure described for **1**. Quantities: **18f** (170 mg, 0.309 mmol), **10b** (171 mg, 0.784 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (17 mg, 0.024 mmol), CuI (19 mg, 0.10 mmol), and piperidine–THF (1:2, 15 mL). Yield: 161 mg (71%) of a white solid; phase transition (°C): Cr 156 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.87 (t, *J* = 7.0 Hz, 6H), 1.21–1.45 (m, 20H), 1.66–1.75 (m, 4H), 2.38 (s, 6H), 2.81 (t, *J* = 7.6 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 4H), 7.37 (s, 2H), 7.43 (d, *J* = 8.0 Hz, 4H), 7.47–7.52 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.11, 21.54, 22.66, 29.28, 29.50, 29.56, 30.66, 31.89,

34.13, 88.51, 90.23, 91.53, 93.80, 119.94, 122.50, 123.04, 123.33, 129.16, 131.36, 131.50, 131.52, 132.35, 138.66, 142.32. Elemental analysis: calc. for C<sub>56</sub>H<sub>58</sub>: C, 92.00; H, 8.00; found: C, 91.78; H, 7.67%. APCI-MS: *m/z* = 731.9 ([M+H]<sup>+</sup>, calc. 731.5).

**Compound 9c.** Synthesized by the procedure described for **1**. Quantities: **18f** (168 mg, 0.305 mmol), **10e** (204 mg, 0.879 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (17 mg, 0.024 mmol), CuI (16 mg, 0.084 mmol), and piperidine–THF (1:2, 15 mL). Yield: 159 mg (69%) of a white solid; phase transitions (°C): Cr 123 N 158 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.87 (t, *J* = 7.0 Hz, 6H), 1.21–1.45 (m, 26H), 1.66–1.75 (m, 4H), 2.67 (q, *J* = 7.6 Hz, 4H), 2.81 (t, *J* = 7.6 Hz, 4H), 7.19 (d, *J* = 8.0 Hz, 4H), 7.37 (s, 2H), 7.44–7.53 (m, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.11, 15.32, 22.66, 28.85, 29.28, 29.50, 29.56, 30.65, 31.90, 34.13, 88.49, 90.22, 91.56, 93.80, 120.16, 122.50, 123.03, 123.34, 127.96, 131.35, 131.50, 131.61, 132.34, 142.31, 144.95. Elemental analysis: calc. for C<sub>58</sub>H<sub>62</sub>: C, 91.77; H, 8.23; found: C, 91.60; H, 8.07%. APCI-MS: *m/z* = 760.0 ([M+H]<sup>+</sup>, calc. 759.5).

**Compound 9d.** Synthesized by the procedure described for **1**. Quantities: **18f** (170 mg, 0.309 mmol), **10d** (221 mg, 0.898 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (18 mg, 0.026 mmol), CuI (24 mg, 0.13 mmol), and piperidine–THF (1:2, 15 mL). Yield: 160 mg (67%) of a white solid; phase transitions (°C): Cr 109 N 171 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.87 (t, *J* = 7.0 Hz, 6H), 0.95 (t, *J* = 7.6 Hz, 6H), 1.21–1.45 (m, 20H), 1.60–1.75 (m, 8H), 2.60 (t, *J* = 7.6 Hz, 4H), 2.81 (t, *J* = 7.6 Hz, 4H), 7.17 (d, *J* = 8.2 Hz, 4H), 7.37 (s, 2H), 7.45 (d, *J* = 8.2 Hz, 4H), 7.47–7.53 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 13.75, 14.11, 22.67, 24.32, 29.29, 29.50, 29.57, 30.66, 31.90, 34.13, 37.98, 88.52, 90.23, 91.58, 93.81, 120.18, 122.51, 123.03, 123.36, 128.57, 131.36, 131.50, 131.53, 132.35, 142.32, 143.44. Elemental analysis: calc. for C<sub>60</sub>H<sub>66</sub>: C, 91.55; H, 8.45; found: C, 91.54; H, 8.30%. APCI-MS: *m/z* = 788.1 ([M+H]<sup>+</sup>, calc. 787.5).

**Compound 9e.** Synthesized by the procedure described for **1**. Quantities: **18f** (151 mg, 0.274 mmol), **10e** (188 mg, 1.20 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (18 mg, 0.026 mmol), CuI (14 mg, 0.074 mmol), and piperidine–THF (1:1, 20 mL). Yield: 160 mg (72%) of a white solid; phase transitions (°C): Cr 101 N 158 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.87 (t, *J* = 7.0 Hz, 6H), 0.93 (t, *J* = 7.2 Hz, 6H), 1.21–1.45 (m, 24H), 1.54–1.75 (m, 8H), 2.62 (t, *J* = 7.6 Hz, 4H), 2.80 (t, *J* = 7.6 Hz, 4H), 7.17 (d, *J* = 8.2 Hz, 4H), 7.37 (s, 2H), 7.45 (d, *J* = 8.2 Hz, 4H), 7.47–7.53 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 13.92, 14.11, 22.30, 22.67, 29.29, 29.50, 29.56, 30.66, 31.90, 33.37, 34.13, 35.61, 88.51, 90.23, 91.58, 93.81, 120.12, 122.51, 123.03, 123.36, 128.51, 131.35, 131.50, 131.53, 132.34, 142.32, 143.67. Elemental analysis: calc. for C<sub>62</sub>H<sub>70</sub>: C, 91.35; H, 8.65; found: C, 91.35; H, 8.53%. APCI-MS: *m/z* = 816.2 ([M+H]<sup>+</sup>, calc. 815.6).

**Compound 14a.** To a solution of **12** (1.03 g, 3.05 mmol) and **11** (2.37 g, 6.66 mmol) in piperidine (50 mL) were added Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (97 mg, 0.14 mmol) and CuI (95 mg, 0.50 mmol). The mixture was stirred for 18 h at room temperature. Cyclohexane (100 mL) was added to the reaction mixture and the resulting salt was filtered off. The filtrate was washed with an NH<sub>4</sub>Cl aqueous solution. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was chromatographed on silica gel with CH<sub>2</sub>Cl<sub>2</sub>–hexane (1:8). The crude product was purified by recrystallization from ethanol–hexane. Yield: 1.92 g (79%) of white crystals; mp 165–166 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.27 (s, 18H), 1.26 (t, *J* = 7.6 Hz, 6H), 1.28 (t, *J* = 7.6 Hz, 6H), 1.315 (t, *J* = 7.6 Hz, 6H), 1.320 (t, *J* = 7.6 Hz, 6H), 2.78 (q, *J* = 7.6 Hz, 4H), 2.84 (q, *J* = 7.6 Hz, 4H), 2.87 (q, *J* = 7.6 Hz, 4H), 2.88 (q, *J* = 7.6 Hz, 4H), 7.33 (s, 2H), 7.35 (s, 2H), 7.39 (s, 2H), 7.40 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = -0.03, 14.52, 14.94, 15.00, 27.14, 27.22, 27.29, 92.86, 92.87, 92.93, 99.22, 103.80, 122.35, 122.67, 122.80, 131.61, 131.75, 131.88, 143.14, 143.31, 143.99. Elemental analysis: calc. for C<sub>56</sub>H<sub>66</sub>Si<sub>2</sub>: C, 84.57; H, 8.36; found: C, 84.64; H, 8.18%. APCI-MS: *m/z* = 796.0 ([M+H]<sup>+</sup>, calc. 795.5).

**Compound 14b.** To a solution of **14a** (818 mg, 1.03 mmol) in MeOH–THF (1:4, 25 mL) and water (0.1 mL) was added K<sub>2</sub>CO<sub>3</sub> (562 mg, 4.07 mmol). The mixture was stirred at 40 °C for 2 h. Cyclohexane (100 mL) was added to

the reaction mixture. The inorganic salt was filtered off. The filtrate was washed with water. The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The residue was chromatographed on silica gel with  $\text{CH}_2\text{Cl}_2$ -hexane (1:3). The crude product was purified by recrystallization from ethanol. Yield: 649 mg (97%) of a white solid; mp 156–157 °C (decomp.).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.27 (t,  $J$  = 7.6 Hz, 6H), 1.29 (t,  $J$  = 7.6 Hz, 6H), 1.318 (t,  $J$  = 7.6 Hz, 6H) 1.323 (t,  $J$  = 7.6 Hz, 6H), 2.80 (q,  $J$  = 7.6 Hz, 4H), 2.85 (q,  $J$  = 7.6 Hz, 4H), 2.87 (q,  $J$  = 7.6 Hz, 4H), 2.88 (q,  $J$  = 7.6 Hz, 4H), 3.32 (s, 2H), 7.36 (s, 2H), 7.37 (s, 2H), 7.40 (s, 2H), 7.41 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 14.72, 14.91, 15.00, 26.97, 27.20, 27.29, 81.60, 82.30, 92.67, 92.93, 121.33, 122.61, 122.74, 123.19, 131.66, 131.77, 132.34, 143.19, 143.33, 144.08. Elemental analysis: calc. for  $\text{C}_{50}\text{H}_{50}$ : C, 92.26; H, 7.74; found: C, 91.83; H, 7.51%. APCI-MS:  $m/z$  = 651.8 ([M+H] $^+$ , calc. 651.4).

**Compound 15a.** Synthesized by the procedure described for **14a**. Quantities: **13** (2.01 g, 4.07 mmol), **11** (3.24 g, 9.10 mmol), piperidine (80 mL),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (144 mg, 0.205 mmol), and  $\text{CuI}$  (154 mg, 0.811 mmol). The mixture was stirred for 14 h at room temperature and then at 40 °C for 2 h. Silica gel chromatography:  $\text{CH}_2\text{Cl}_2$ -cyclohexane (1:9). Recrystallization: ethanol-cyclohexane. Yield: 2.80 g (72%) of a pale yellow solid; mp 202–203 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.27 (s, 18H), 1.26 (t,  $J$  = 7.6 Hz, 6H), 1.29 (t,  $J$  = 7.6 Hz, 6H), 1.318 (t,  $J$  = 7.6 Hz, 6H), 1.324 (t,  $J$  = 7.6 Hz, 6H), 1.33 (t,  $J$  = 7.6 Hz, 6H), 2.78 (q,  $J$  = 7.6 Hz, 4H), 2.84 (q,  $J$  = 7.6 Hz, 4H), 2.87 (q,  $J$  = 7.6 Hz, 4H), 2.881 (q,  $J$  = 7.6 Hz, 4H), 2.884 (q,  $J$  = 7.6 Hz, 4H), 7.33 (s, 2H), 7.35 (s, 2H), 7.43 (s, 2H), 7.407 (s, 2H), 7.412 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = -0.04, 14.52, 14.94, 15.00, 27.14, 27.22, 27.30, 92.85, 92.87, 92.94, 99.22, 103.80, 122.35, 122.68, 122.79, 131.60, 131.76, 131.88, 143.14, 143.31, 143.99. Elemental analysis: calc. for  $\text{C}_{68}\text{H}_{78}\text{Si}_2$ : C, 85.83; H, 8.26; found: C, 85.83; H, 8.04%. APCI-MS:  $m/z$  = 952.3 ([M+H] $^+$ , calc. 951.6).

**Compound 15b.** Synthesized by the procedure described for **14b**. Quantities: **16a** (556 mg, 0.585 mmol),  $\text{MeOH}$ -THF (1:5, 30 mL), and  $\text{K}_2\text{CO}_3$  (478 mg, 3.46 mmol). The mixture was stirred at 40 °C for 16 h. Silica gel chromatography:  $\text{CH}_2\text{Cl}_2$ -cyclohexane (1:5). Recrystallization:  $\text{CH}_2\text{Cl}_2$ -hexane. Yield: 455 mg (96%) of a pale yellow solid; decomp. 185–186 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.27 (t,  $J$  = 7.6 Hz, 6H), 1.29 (t,  $J$  = 7.6 Hz, 6H), 1.32 (t,  $J$  = 7.6 Hz, 6H), 1.327 (t,  $J$  = 7.6 Hz, 6H), 1.330 (t,  $J$  = 7.6 Hz, 6H), 2.80 (q,  $J$  = 7.6 Hz, 4H), 2.85 (q,  $J$  = 7.6 Hz, 4H), 2.87 (q,  $J$  = 7.6 Hz, 4H), 2.89 (q,  $J$  = 7.6 Hz, 8H), 3.32 (s, 2H), 7.36 (s, 2H), 7.38 (s, 2H), 7.40 (s, 2H), 7.412 (s, 2H), 7.414 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 14.72, 14.91, 15.00, 26.98, 27.20, 27.30, 81.61, 82.30, 92.67, 92.93, 92.96, 121.33, 122.60, 122.69, 122.75, 123.19, 131.66, 131.77, 132.34, 143.19, 143.33, 144.08. Elemental analysis: calc. for  $\text{C}_{62}\text{H}_{62}$ : C, 92.26; H, 7.74; found: C, 90.27; H, 7.37%. APCI-MS:  $m/z$  = 808.1 ([M+H] $^+$ , calc. 807.5).