# Supplemental Information:

The Synthesis of 1-Biphenyl-[1,2,3]-Triazoles and their Mesomorphic Behavior

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## SI.1.1 Synthesis of 1-(3-fluoro-4'-alkylbiphenyl-4-yl)-4-alkyl-1H-[1,2,3]triazole liquid crystals 1-14

**1-(4-Bromo-2-fluorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole**

To a test tube fitted with a magnetic stirbar was added 1-azido-4-bromo-2-fluorobenzene (2.0 mmol, 432 mg, 1.0 equiv.), 1-heptyne (2.0 mmol, 196 mg), CuSO4·5H2O (18 mg), sodium ascorbate (42 mg), ethanol (3 mL), toluene (1 mL) and H2O (1 mL). The test tube was then capped and placed in the microwave reactor. The reaction was run under the following parameters (starting with 250 pressure, 150W power, 65 °C, 180 min). The reaction was monitored occasionally by TLC analysis until completion. The mixture was poured into H2O (100 mL) and the mixture was extracted with dichloromethane. The organic layers were combined, dried with MgSO4 and concentrated by rotary evaporation to give the product as a brown oil (590 mg, 95%), which was then recrystallized from hexanes to give light yellow crystals.

1HNMR (400 MHz, CDCl3) δ (ppm): 7.84 (m, 1H), 7.47 (m, 1H), 7.25 (m, 1H), 7.16 (m, 1H), 2.80 (t, *J* = 7.2 Hz, 2H), 1.74 (m, 2H), 1.37-1.32 (m, 4H), 0.91 (m, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 152.7 (d, *J* = 253.1 Hz), 149.2, 137.9, 129.1, 128.7 (d, *J* = 3.5 Hz), 128.2, 125.3 (d, *J* = 32.5 Hz), 122.2 (d, *J* = 8.8 Hz), 121.7 (d, *J* = 8.1 Hz), 120.7 (d, *J* = 23.2 Hz), 31.4, 29.0, 25.6, 22.4, 14.0; 19FNMR (376 MHz, CDCl3) δ (ppm): -120.9 (m, 1F); IR(cm-1): 3135, 2967, 2953, 2921, 2872, 2855, 1592, 1558, 1502, 1440, 1398, 1224, 1211, 1128, 1047, 988, 872, 846, 819, 725, 581. HPLC/MS (H+): 314.20 found 312.18 calc.

## Palladium tetrakistriphenylphosphine

In a 250 ml round bottom flask was added palladium dichloride (0.448 g, 2.5 mmol), triphenylphosphine (3.287 g, 5.0 equiv.) and DMSO (30 mL) and the mixture was heated up to 150 °C until all the solids were dissolved. Hydrazine monohydrate (0.508 g, 4.0 equiv.) was added all at once to the solution and it was cooled down to room temperature. The precipitate was vacuum filtered and washed with diethyl ether (3x10 mL) and ethanol (3x10 mL) to give golden crystals (3.0 g, quantitatively)

**1-(3-Fluoro-4'-*n*-pentylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (1)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-pentylphenylboronic acid (120 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (166 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified with column chromatography (eluted with DCM: ethyl acetate = 50:1) as light yellow crystals after evaporation (70 mg, 61%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.01 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.54-7.47 (m, 4H), 7.29 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 1.76 (m, 2H), 1.64 (m, 2H), 1.39 (m, 8H), 0.97-0.90 (m, 6H); 13CNMR (100 MHz, CDCl3) δ (ppm): 152.3 (d, *J* = 248.3 Hz), 148.9, 143.6, 143.3, 135.8, 129.4 (d, *J* = 18.8 Hz), 126.9, 124.9, 124.0 (d, *J* = 10.5 Hz), 123.4 (d, *J* = 2.8 Hz), 121.9 (d, *J* = 8.1 Hz), 115.0 (d, *J* = 13.5 Hz), 35.6, 35.0, 31.5, 31.4, 31.1, 29.0, 25.6, 22.6, 22.4, 14.3; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.60 (m, 1F); IR (cm-1): 3150, 2958, 2929, 2856, 1471, 1456, 1048, 1029, 817, 758. HPLC/MS (H+): 380.70 found 379.51 calc.

POM: Cr 94 SmA 134.5 Iso

**1-(3-Fluoro-4'-*n*-butylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (2)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-butylphenylboronic acid (120 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (166 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and driedwith MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as light yellow crystals after evaporation (78 mg, 69%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.01 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.54-7.47 (m, 4H), 7.29 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 1.77 (m, 2H), 1.64 (m, 2H), 1.40 (m, 6H), 0.97-0.90 (m, 6H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.3 (d, *J* = 244.5 Hz), 148.9, 143.6, 143.3, 135.8, 129.4 (d, *J* = 17.9 Hz), 126.9, 124.9, 124.0 (d, *J* = 11.1 Hz), 123.4, 121.9, 115.0 (d, *J* = 12.8 Hz), 35.6, 35.0, 31.5, 31.4, 31.1, 29.0, 25.6, 22.6, 14.3; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.60 (m, 1F); IR (cm-1): 3150, 2958, 2929, 2856, 1471, 1456, 1048, 1029, 817, 758. HPLC/MS (H+): 366.70 found 365.49 calc.

POM: Cr 89 SmA 129 Iso

**1-(3-Fluoro-4'-*n*-propylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (3)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-propylphenylboronic acid (110 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (166 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as light yellow crystals after evaporation (82 mg, 73%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.02 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.54-7.47 (m, 4H), 7.29 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.74 (m, 2H), 1.68 (m, 2H), 1.39 (m, 4H), 1.00-0.90 (m, 6H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.3 (d, *J* = 244.6 Hz), 148.9, 143.5, 129.2, 126.8, 124.8, 124.0, 123.3, 121.9 (d, *J* = 8.0 Hz), 115.2 (d, *J* = 13.5 Hz), 37.7, 31.5, 29.1, 25.6, 24.5, 22.4, 13.8; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.61 (m, 1F); IR (cm-1): 3150, 2958, 2929, 2856, 1471, 1456, 1048, 1029, 817, 758. HPLC/MS (H+): 352.50 found 351.46 calc.

POM: Cr 91.4 SmA 128.5 Iso

**1-(3-Fluoro-4'-*n*-ethylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (4)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-ethylphenylboronic acid (110 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (166 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as light yellow crystals after evaporation (75 mg, 68%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.01 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.54-7.47 (m, 4H), 7.29 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 1.77 (m, 2H), 1.39 (m, 4H), 1.28 (t, *J* = 7.6 Hz, 3H), 0.92 (t, *J* = 7.6 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.3 (d, *J* = 239.5 Hz), 148.9, 143.2, 135.9, 130.9, 128.8, 126.9, 124.8, 124.1, 123.4, 121.8 (d, *J* = 8.4 Hz), 115.1 (d, *J* = 19.7 Hz), 31.5, 29.1, 28.6, 25.6, 22.4, 15.4, 14.0; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.65 (m, 1F); IR (cm-1): 3150, 2958, 2929, 2856, 1471, 1456, 1048, 1029, 817, 758. HPLC/MS (H+): 338.50 found 337.43 calc.

POM: Cr 70 SmX 91 SmA 109 Iso

**1-(3-Fluoro-4'-*n*-methylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (5)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-tolylboronic acid (105 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (166 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as light yellow crystals after evaporation (75 mg, 61%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.02 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.54-7.47 (m, 4H), 7.29 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.76 (m, 2H), 1.39-1.29 (m, 4H), 0.92 (t, *J* = 7.6 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.2 (d, *J* = 240.5 Hz), 148.9, 143.2, 138.5, 135.7, 129.8(d, *J* = 22.0 Hz), 126.8, 124.8, 123.4 (d, *J* = 3.0 Hz), 121.8 (d, *J* = 8.3 Hz), 115.0 (d, *J* = 20.7 Hz), 31.5, 29.1, 25.6, 22.4, 21.2, 14.0; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.64 (m, 1F); IR (cm-1): 3150, 2958, 2929, 2856, 1471, 1456, 1048, 1029, 817, 758. HPLC/MS (H+): 324.40 found 323.41 calc.

POM: Cr 85.8 SmA 102.2 Iso

**1-(3-Fluorobiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (6)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and phenylboronic acid (90 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (166 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as light yellow crystals (75 mg, 61%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.05 (t, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 2.8 Hz, 1H), 7.61 (m, 2H), 7.56-7.47 (m, 4H), 7.44 (m, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 1.77 (m, 2H), 1.39 (m, 4H), 0.92 (t, *J* = 7.6 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.4 (d, *J* = 243.3 Hz), 148.9, 143.2, 128.8, 127.1, 124.8, 123.7, 115.0 (d, *J* = 20.3 Hz), 31.5, 29.1, 25.6, 22.4, 14.0; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.67 (m, 1F); IR (cm-1): 3139, 3098, 2951, 2924, 2855, 1531, 1496, 1231, 1048, 844, 757. HPLC/MS (H+): 310.50 found 309.38 calc.

POM: Cr 64 Iso

**1-(3-Fluoro-4'-cyanobiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (7)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (130 mg, 0.4 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (46 mg, 1.0 mol%) and 4-cyanophenylboronic acid (200 mg, 1.5 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (110 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as yellow crystals after evaporation (80 mg, 60%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.14 (dd, *5JF-H*= 8.0 Hz, *4J* H-H = 0.8 Hz, 1H), 7.89 (d, *J* = 2.8 Hz, 1H), 7.78 (m, 2H), 7.71 (m, 2H), 7.56-7.51 (m, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.77 (m, 2H), 1.38 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 154.4, 149.2, 142.8, 140.8 (d, *J* = 7.4 Hz), 134.1, 132.9, 132.0 (d, *J* = 9.9 Hz), 128.6 (d, *J* = 12.6 Hz), 127.7, 125.5, 123.9, 121.7, 118.5, 116.5, 115.6 (d, *J* = 21.4 Hz), 112.3, 31.4, 29.0, 25.6, 22.1, 14.0; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.65 (m, 1F); IR (cm-1): 3160, 2960, 2880, 2227, 1606, 1498, 815. HPLC/MS (H+): 335.5 found 334.39 calc.

POM: Cr 82 (N 74) Iso

**1-(4-Bromo-2-fluorophenyl)-4-*n*-octyl-1*H*-[1,2,3]triazole**

To a test tube fitted with a magnetic stirbar was added 1-azido-4-bromo-2-fluorobenzene (2.0 mmol, 432 mg, 1.0 equiv.), 1-decyne (2.0 mmol, 196 mg), CuSO4·5H2O (18 mg), sodium ascorbate (42 mg), ethanol (3 mL), toluene (1 mL) and H2O (1 mL). The test tube was then capped and placed in the microwave reactor. The reaction was run under the following parameters (starting with 250 pressure, 150W power, 65 °C, 180 min). TLC analysis indicated the disappearance of the starting material azide and the formation of one new compound. The mixture was poured into H2O (100 mL) and the mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4 and condensed by rotary evaporation to give the product as a brown oil (610 mg, 95%), which was then recrystallized from hexanes to give light yellow crystals. HPLC/MS (H+): 356.20 found 354.26 calc.

1HNMR (400 MHz, CDCl3) δ (ppm): 7.85 (m, 1H), 7.47 (m, 1H), 7.25 (m, 1H), 7.16 (m, 1H), 2.80 (t, *J* = 7.2 Hz, 2H), 1.74 (m, 2H), 1.37 (m, 10H), 0.91 (m, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 152.8 (d, *J* = 250.3 Hz), 149.2, 137.9, 129.1, 128.7, 128.2, 125.3 (d, *J* = 33.3 Hz), 122.2 (d, *J* = 8.7 Hz), 121.7 (d, *J* = 8.3 Hz), 120.7 (d, *J* = 23.1 Hz), 31.4, 29.4, 29.3, 29.2, 29.0, 25.6, 22.4, 14.0; 19FNMR (376 MHz, CDCl3) δ (ppm): -120.9 (1F); IR(cm-1): 3135, 2967, 2953, 2921, 2872, 2855, 1592, 1558, 1502, 1440, 1398, 1224, 1211, 1128, 1047, 988, 872, 846, 819, 725, 581.

**1-(3-Fluoro-4'-*n*-pentylbiphenyl-4-yl)-4-*n*-octyl-1*H*-[1,2,3]triazole (8)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-octyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-pentylphenylboronic acid (115 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give white crystals (78 mg, 60%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.01 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.50 (m, 4H), 7.29 (m, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.74 (m, 2H), 1.66 (m, 2H), 1.37 (m, 14H), 0.93-0.87 (m, 6H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.3 (d, *J* = 248.3 Hz), 148.9, 143.6, 143.2, 135.9, 129.3 (d, *J* = 8.3 Hz), 126.8, 124.8, 123.4 (d, *J* = 2.8 Hz), 121.7(d, *J* = 8.2 Hz), 115.1 (d, *J* = 20.8 Hz), 35.6, 31.9, 31.5, 31.1, 29.4, 29.3, 29.2, 25.7, 22.7, 14.1; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.64 (m, 1F); HPLC/MS (H+): 422.90 found 421.59 calc.

POM: Cr 65 SmA 136 Iso

**1-(3-Fluoro-4'-*n*-butylbiphenyl-4-yl)-4-*n*-octyl-1*H*-[1,2,3]triazole (9)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-octyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-butylphenylboronic acid (107 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give white crystals (80 mg, 71%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.00 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.51 (m, 4H), 7.30 (m, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.74 (m, 2H), 1.65 (m, 2H), 1.37 (m, 12H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.2 (d, *J* = 248.2 Hz), 148.7, 143.3, 143.0 (d, *J* = 7.5 Hz), 135.7, 129.0, 126.7, 124.7, 124.0 (d, *J* = 10.4 Hz), 123.2 (d, *J* = 2.8 Hz), 121.7 (d, *J* = 8.2 Hz), 115.1 (d, *J* = 20.8 Hz), 35.6, 31.9, 31.5, 31.1, 29.4, 29.3, 29.2, 25.7, 22.7, 14.1; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.64 (m, 1F); HPLC/MS (H+): 408.70 found 407.57 calc.

POM: Cr 70 SmA 126 Iso

**1-(3-Fluoro-4'-*n*-propylbiphenyl-4-yl)-4-*n*-octyl-1*H*-[1,2,3]triazole (10)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-octyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-propylphenylboronic acid (98 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give white crystals (81 mg, 74%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.01 (t, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 2.8 Hz, 1H), 7.51 (m, 4H), 7.30 (m, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.74 (m, 2H), 1.65 (m, 2H), 1.37 (m, 10H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 154.1 (d, *J* = 248.3 Hz), 149.2, 143.3, 129.2, 126.8, 124.8, 123.4, 121.7 (d, *J* = 8.3 Hz), 115.1 (d, *J* = 21.1 Hz), 37.7, 31.9, 29.4, 29.3, 29.2, 25.7, 24.5, 22.7, 14.1, 13.8; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.64 (m, 1F); HPLC/MS (H+): 394.40 found 393.54 calc.

POM: Cr 58 SmA 129 Iso

**1-(3-Fluoro-4'-*n*-ethylbiphenyl-4-yl)-4-*n*-octyl-1*H*-[1,2,3]triazole (11)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-octyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 2-ethylphenylboronic acid (90 mg, 2.0 equiv., 0.6 mmol) were and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give white crystals (70 mg, 70%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.00 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.50 (m, 4H), 7.29 (m, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.74 (m, 2H), 1.66 (m, 2H), 1.37 (m, 8H), 0.93-0.87 (m, 6H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.3 (d, *J* = 248.4 Hz), 148.9, 143.6 (d, *J* = 7.4 Hz), 135.9, 128.6 (d, *J* = 8.3 Hz), 126.8, 124.8 (d, *J* = 12.1 Hz), 124.0 (d, *J* = 10.5 Hz), 123.4 (d, *J* = 2.9 Hz), 121.7 (d, *J* = 8.3 Hz), 115.1 (d, *J* = 8.3 Hz), 35.6, 31.9, 31.5, 31.1, 29.4, 29.3, 29.2, 25.7, 22.7, 14.1; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.64 (m, 1F); HPLC/MS (H+): 380.60 found 379.51 calc.

POM: Cr 46 Colr 68 SmA 118 Iso

**1-(3-Fluoro-4'-*n*-methylbiphenyl-4-yl)-4-*n*-octyl-1*H*-[1,2,3]triazole (12)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-*n*-octyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-methylphenylboronic acid (82 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give white crystals (76 mg, 75%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.01 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.51 (m, 4H), 7.30 (m, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.74 (m, 2H), 1.65 (m, 2H), 1.37 (m, 8H), 0.93 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.4 (d, *J* = 251.2 Hz), 148.9, 143.6, 143.2, 135.9, 129.3 (d, *J* = 8.8 Hz), 126.8, 124.8, 123.4, 121.7, 115.0 (d, *J* = 8.7 Hz), 35.6, 31.9, 31.5, 31.1, 29.4, 29.3, 29.2, 25.7, 22.7, 14.1; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.64 (m, 1F); HPLC/MS (H+): 366.90 found 365.49 calc.

POM: Cr 81 SmA 119 Iso

**1-(3-Fluoro-4'-biphenyl-4-yl)-4-*n*-octyl-1*H*-[1,2,3]triazole (13)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluorophenyl)-4-octyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and phenylboronic acid (73 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give white crystals (80 mg, 78%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.05 (t, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 2.8 Hz, 1H), 7.61 (m, 2H), 7.56-7.47 (m, 4H), 7.44 (m, 1H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.76 (m, 2H), 1.67 (m, 2H), 1.35 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 149.1 (d, *J* = 247.3 Hz), 143.1, 138.4, 129.1, 128.5 (d, *J* = 8.3 Hz), 127.0, 124.9, 123.7, 121.9 (d, *J* = 8.3 Hz), 115.3 (d, *J* = 20.3 Hz), 31.9, 29.4, 29.3, 29.2, 29.1, 25.7, 22.7, 14.1; 19FNMR (376 MHz, CDCl3) δ (ppm): -123.49 (m, 1F); HPLC/MS (H+): 352.50 found 351.46 calc.

POM: Cr 68 Iso

**1-(3-Fluoro-4'-cyanobiphenyl-4-yl)-4-*n*-octyl-1*H*-[1,2,3]triazole (14)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-fluoro-phenyl)-4-*n*-octyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-cyanophenylboronic acid (88 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slight more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give a white solid (73 mg, 67%).

1HNMR (400 MHz, CDCl3) δ (ppm): 8.14 (t, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 3.2 Hz, 1H), 7.78 (m, 2H), 7.71 (m, 2H), 7.53 (m, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 1.76 (m, 2H), 1.66 (m, 2H), 1.35 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 153.2 (d, *J* = 249.2 Hz), 149.2, 142.9, 140.8, 132.9, 127.7, 125.5, 125.1, 123.9 (d, *J* = 3.1 Hz, 1C), 121.7 (d, *J* = 9.0 Hz), 118.5, 115.8 (d, *J* = 21.4 Hz), 112.3, 31.9, 29.4, 29.3, 29.2, 25.6, 22.7, 14.1;19FNMR (376 MHz, CDCl3) δ (ppm): -122.39 (m, 1F); HPLC/MS (H+): 377.60 found 376.47 calc.

POM: Cr 79 Cr1 80 SmA 83 N 117 Iso

## SI.1.2 Synthesis of 1-(3-chloro-4'-alkylbiphenyl-4-yl)-4-alkyl-1H-[1,2,3]triazole compounds 15-19

**1-(4-Bromo-2-chlorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole**

To a test tube fitted with a magnetic stirbar was added 1-azido-4-bromo-2-chlorobenzene (1.0 mmol, 232 mg, 1.0 equiv.), 1-heptyne (1.0 mmol, 98 mg), CuSO4·5H2O (18 mg), sodium ascorbate (42 mg), ethanol (3 mL), toluene (1 mL) and H2O (1 mL). The test tube was then capped and placed in the microwave reactor. The reaction was run under the following parameters (starting with 250 pressure, 150W power, 65 °C, 180 min). The reaction was monitored occasionally by TLC analysis until completion. The mixture was poured into H2O (100 mL) and the mixture was extracted with dichloromethane (100 mL). The organic layers were combined, dried with MgSO4 and concentrated by rotary evaporation to give the product as a brown oil after evaporation, which was recrystallized from hexanes as light yellow crystals (280 mg, 85%). Melting point 37-38 °C.

1HNMR (400 MHz, CDCl3) δ (ppm): 7.71 (m, 2H), 7.57 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 2.81 (t, *J* = 7.6 Hz, 2H), 1.76 (m, 2H), 1.37 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 148.5, 133.4, 131.2, 129.3, 128.7, 123.5, 122.5, 31.4, 29.0, 25.6, 22.4, 14.0. HPLC/MS (H+): 329.60 found 328.64 calc.

**1-(3-Chloro-4'-*n*-pentylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (15)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-chlorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-pentylphenylboronic acid (115 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a yellow oil after evaporation (80 mg, 78%).

1HNMR (400 MHz, CDCl3) δ (ppm): 7.75 (m, 2H), 7.67 (dd, *3J* = 8.4 Hz, *4J* = 0.4 Hz, 1H), 7.62 (dd, *3J* = 8.0 Hz, *4J* = 1.6 Hz, 1H), 7.52 (dd, *3J* = 6.4 Hz, *4J* = 2.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.77 (m, 2H), 1.67 (m, 2H), 1.37 (m, 8H), 0.94-0.88 (m, 6H); 13CNMR (100 MHz, CDCl3) δ (ppm): 148.2, 143.8, 143.7, 135.7, 133.7, 129.4, 129.2, 129.0, 128.9, 128.7, 128.6, 128.4, 127.9, 127.0, 126.2, 122.7, 115.1, 35.6, 35.0, 31.5, 31.4, 31.1, 29.1, 25.6, 22.6, 22.4, 14.0. HPLC/MS (H+): 396.90 found 395.97 calc.

Note: the product is isotropic at room temperature.

**1-(3-Chloro-4'-*n*-butylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (16)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-chlorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-butylphenylboronic acid (107 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a yellow oil after evaporation (80 mg, 71%).

1HNMR (400 MHz, CDCl3) δ (ppm): 7.76 (m, 2H), 7.66 (dd, *3J* = 8.4 Hz, *4J* = 0.4 Hz, 1H), 7.62 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 1H), 7.52 (m, 2H), 7.30 (m, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 1.77 (m, 2H), 1.67 (m, 2H), 1.37 (m, 6H), 0.97-0.90 (m, 6H); 13CNMR (100 MHz, CDCl3) δ (ppm): 148.2, 143.8, 143.7, 135.7, 133.7, 129.4, 129.2, 128.9, 128.6, 127.9, 127.0, 126.2, 122.7, 115.1, 35.3, 34.7, 33.9, 33.6, 31.4, 29.1, 25.6, 22.5, 22.4, 22.3, 14.0. HPLC/MS (H+): 382.90 found 381.94 calc.

Note: the product is isotropic at room temperature.

**1-(3-Chloro-4'-*n*-propylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (17)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-chlorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-propylphenylboronic acid (98 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give white crystals (70 mg, 63%).

1HNMR (400 MHz, CDCl3) δ (ppm): 7.76 (m, 1H), 7.74 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.62 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 1H), 7.53 (m, 2H), 7.30 (m, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.65 (m, 2H), 1.77 (m, 2H), 1.68 (m, 2H), 1.38 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 148.4, 143.3, 143.6, 135.9, 129.4, 129.3, 129.0, 128.2, 128.0, 127.2, 127.0, 126.4, 122.9, 120.8, 118.9, 37.9, 31.6, 29.3, 25.9, 25.8, 24.7, 24.6, 22.6, 14.2,14.0. HPLC/MS (H+): 368.60 found 367.91 calc.

POM: Cr 76 Iso

**1-(3-Chloro-4'-*n*-ethylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (18)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-chloro-phenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 2-ethylphenylboronic acid (90 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted by hexane: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give white crystals (75 mg, 71%).

1HNMR (400 MHz, CDCl3) δ (ppm): 7.76 (dd, *4J* = 2.0 Hz, *5J* = 0.4 Hz, 1H), 7.75 (t, *J* = 0.8 Hz, 1H), 7.67 (dd, *3J* = 8.0 Hz, *4J* = 0.4 Hz, 1H), 7.62 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 1H), 7.53 (m, 2H), 7.32 (m, 2H), 2.83 (m, 2H), 2.73 (m, 2H), 1.76 (m, 2H), 1.37 (m, 4H), 1.29 (t, *J* = 7.6 Hz, 3H), 0.92 (t, *J* = 6.8 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 148.1, 145.3, 143.7, 135.7, 133.9, 128.9, 128.7, 127.9, 127.0, 126.2, 122.7, 31.5, 29.1, 28.6, 25.6, 22.4, 15.5, 14.0. HPLC/MS (H+): 354.80 found 353.89 calc.

POM: Cr 60 Iso

**1-(3-Chloro-4'-*n*-methylbiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (19)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-chlorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-methylphenylboronic acid (82 mg, 2.0 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (83 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 50:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified with column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation, which was then recrystallized from hexanes to give white crystals (70 mg, 75%).

1HNMR (400 MHz, CDCl3) δ (ppm): 7.76 (m, 1H), 7.74 (d, *J* = 1.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.61 (dd, *3J* = 8.4 Hz, *4J* = 2.0 Hz, 1H), 7.51 (dd, *3J* = 6.8 Hz, *4J* = 2.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.78 (m, 2H), 1.39 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 148.0, 143.5, 138.8, 135.4, 134.1, 129.8, 128.8, 127.9, 127.0, 126.2, 122.7, 120.0, 31.5, 29.1, 25.6, 22.4, 21.2, 14.0. HPLC/MS (H+): 340.60 found 339.86 calc.

POM: Cr 63 Iso

**1-(3-Chloro-4'-cyanobiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (20)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo-2-chlorophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (130 mg, 0.4 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (46 mg, 1.0 mol%) and 4-cyanophenylboronic acid (200 mg, 1.5 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (110 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as a white solid after evaporation (86 mg, 61%).

1HNMR (400 MHz, CDCl3) δ (ppm): 7.82-7.80 (m, 5H (including one triazoyl-H), 7.73-7.70 (m, 2H), 7.64 (dd, *3J* = 8.0 Hz, *4J* = 1.6 Hz, 1H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.78 (m, 2H), 1.42 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 143.0, 141.6, 132.9, 132.0, 129.4, 128.2, 127.9, 126.6, 122.6, 118.4, 31.5, 29.1, 25.6, 22.4, 14.0. IR (cm-1): 2221 found for –CN group. HPLC/MS (H+): 351.70 found 350.84 calc.

POM: Cr 119 Iso

## SI.1.3 Synthesis of 1-(4'-subtituted biphenyl-4-yl)-4-alkyl-1H-[1,2,3]triazole compounds 21-22

**1-(4'-*n*-Pentyloxybiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (21)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromophenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (120 mg, 0.3 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (35 mg, 1.0 mol%) and 4-*n*-pentyloxyphenylboronic acid (120 mg, 1.5 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (110 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with hexanes: ethyl acetate = 5: 1) as a light yellow solid after evaporation (90 mg, 77%). The product was recrystallized from hexanes to give white crystals.

1HNMR (400 MHz, CDCl3) δ (ppm): 7.75 (dd, *3J* = 6.8 Hz, *4J* = 2.0 Hz, 2H), 7.33 (s, 1H), 7.67 (dd, *3J* = 6.8 Hz, *4J* = 2.0 Hz, 2H), 7.54 (dd, *3J* = 6.8 Hz, *4J* =2.0 Hz, 2H), 6.99 (dd, *3J* = 6.8 Hz, *4J* = 2.0 Hz, 2H), 4.01 (t, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 1.84-1.73 (m, 4H), 1.47-1.38 (m, 8H), 0.97-0.90 (m, 6H); 13CNMR (100 MHz, CDCl3) δ (ppm): 159.3, 141.1, 132.1, 128.1, 127.7, 120.7, 118.7, 115.0, 68.2, 29.1, 28.9, 28.2, 25.7, 22.5, 14.0. HPLC/MS (H+): 378.90 found 377.52 calc.

POM: Cr 164 SmA 214 Iso

**1-(4'-Cyanobiphenyl-4-yl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (22)**

A 100 ml round bottom flask fitted with a magnetic stirbar was charged with 1-(4-bromo phenyl)-4-*n*-pentyl-1*H*-[1,2,3]triazole (100 mg, 0.4 mmol) and a mixture of H2O (4.0 mL) and 1,4-dioxane (10 mL) to give a colorless solution. Next, Pd(PPh3)4 (46 mg, 1.0 mol%) and 4-cyanophenylboronic acid (200 mg, 1.5 equiv., 0.6 mmol) were added and the mixture was stirred at room temperature for 10 minutes followed by the addition of potassium carbonate (110 mg, 2.0 equiv.). This mixture was stirred and refluxed for 24 hours. TLC analysis (eluted with hexanes: ethyl acetate = 10:1) indicated the formation of one new compound that was slightly more polar and a trace amount of starting bromide. After cooling to the room temperature, H2O (200 mL) was added to the mixture and the resulting mixture was extracted with dichloromethane (100 mL). The organic layers were combined and dried with MgSO4. The desired product was purified by column chromatography on silica gel (eluted with DCM: ethyl acetate = 50:1) as white crystals after evaporation (75 mg, 63%).

1HNMR (400 MHz, CDCl3) δ (ppm): 7.88-7.83 (m, 3H (including one triazoyl H)), 7.78-7.50 (m, 6H), 2.81 (t, *J* = 7.6 Hz, 2H), 1.75 (m, 2H), 1.37 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ (ppm): 144.0, 139.5, 137.2, 134.2, 132.8, 128.6, 127.7, 120.9, 118.7, 116.7, 111.6, 31.4, 29.0, 25.5, 22.4, 14.0. IR (cm-1): 2230 found for -CN group. HPLC/MS (H+): 317.60 found 316.40 calc.

POM: Cr 129.8 Iso

## SI.2 Nuclear Magnetic Resonance (NMR) spectra of representative compounds.

Figure SI2.1.tif

Figure SI.2.1 The 1H NMR spectrum of compound **2**.

Figure SI2.2.tif

Figure SI.2.2 The 19F NMR spectrum of compound **2**.

Figure SI2.3.tif

Figure SI.2.3 The 1H NMR spectrum of compound **3**.

Figure SI2.4.tif

Figure SI.2.4 The 19F NMR spectrum of compound **3**.

Figure SI2.5.tif

Figure SI.2.5 The 1H NMR spectrum of compound **4**.

Figure SI2.6.tif

Figure SI.2.6 The 19F NMR spectrum of compound **4**.

Figure SI2.7.tif

Figure SI.2.7 The 1H NMR spectrum of compound **9**.

Figure SI2.8.tif

Figure SI.2.8 The 19F NMR spectrum of compound **9**.

Figure SI2.9.tif

Figure SI.2.9 The 1H NMR spectrum of compound **14**.

Figure SI2.10.tif

Figure SI.2.10 The 19F NMR spectrum of compound **14**.

## SI.3. DSC of the liquid crystals that are not shown in main text

SI.3.1.tif

Figure SI.3.1 The DSC of compound **1**.

SI.3.2.tif

Figure SI.3.2 The DSC of compound **2**.

SI.3.3.tif

Figure SI.3.3 The DSC of compound **4**.

SI.3.4.tif

Figure SI.3.4 The DSC of compound **5**.

SI.3.5.tif

Figure SI.3.5 The DSC of compound **7**.

SI.3.6.tif

Figure SI.3.6 The DSC of compound **8**.

SI.3.7.tif

Figure SI.3.7 The DSC of compound **9**.

SI.3.8.tif

Figure SI.3.8 The DSC of compound **10**.

SI.3.9.tif

Figure SI.3.9 The DSC of compound **12**.

SI.3.10.tif

Figure SI.3.10 The DSC of compound **14**.