Supporting Information

Synthesis of Perfluoroalkylated Benzenes and Pyridines through Cationic Rh(I)/Modified-BINAP-Catalyzed Chemo- and Regioselective [2 + 2 + 2] Cycloaddition

Ken Tanaka*, Hiromi Hara, Goushi Nishida, and Masao Hirano

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

I. General

Anhydrous CH_2Cl_2 (No. 27,099-7) was obtained from Aldrich and used as received. H_8 -BINAP, Segphos, and tol-BINAP were obtained from Takasago International Corporation. 1,6-Diynes **1a**,¹ **1b**,¹ **1c**,² **1d**,³ **1e**,⁴ **1f**,⁴ **1g**,³ **1h**,¹ **1i**,⁵ and **1j**,⁵ were prepared according to the literatures. Perfluoroalkylacetylene **2** was prepared according to the literature.⁶ All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

II. Synthesis of 1,6-diyne

4-[But-2-ynyl(toluene-4-sulfonyl)amino]but-2-ynoic acid methyl ester (**1k**).

n-BuLi (1.60 M in hexane, 1.9 mL, 3.0 mmol) was added to a stirred solution of *N*-but-2-ynyl-4-methyl-*N*-prop-2-ynylbenzenesulfonamide (0.72 g, 2.8 mmol) in THF (10 mL) at -78°C , and the resulting mixture was stirred at -78°C for 2 h. Methyl chloroformate (0.42 g, 2.2 mmol) was added, and the resulting mixture was refluxed for 3 h. The reaction was quenched with water and extracted with Et_2O . The organic layer was washed with water and Et_2O , dried over Na_2SO_4 , and concentrated. The residue was purified on a silica gel column chromatography (hexane:EtOAc = 5:1), which furnished **1k** (0.21 g, 0.67 mmol, 24% yield) as a pale yellow solid.

Mp $45.7\text{--}46.9^\circ\text{C}$; IR (neat) 2955, 2242, 4718, 1352, 1260, 1163 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.71 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 4.28 (s, 2H), 4.08 (q, $J = 2.4$ Hz, 2H), 3.73 (s, 3H), 2.43 (s, 3H), 1.66 (t, $J = 2.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.1, 144.1, 134.9, 129.6, 127.9, 82.7, 80.6, 76.8, 70.9, 52.7, 37.3, 36.2, 21.5, 3.4; HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{NS}$ $[\text{M}+\text{H}]^+$ 320.0957, found 320.0984.

III. Synthesis of Perfluoroalkylated Benzenes

General procedure for [2 + 2 + 2] cycloaddition of 1,6-diynes with perfluoroalkylacetylene **2.** Under an Ar atmosphere, (*R*)-H₈-BINAP (3.2 mg, 0.0050 mmol) and [Rh(cod)₂]BF₄ (2.0 mg, 0.0050 mmol) were dissolved in CH₂Cl₂ (1.0 mL) and the mixture was stirred at rt for 5 min. H₂ was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 1 h, the resulting solution was concentrated to dryness and dissolved in (CH₂Cl)₂ (0.4 mL). To this solution was added **2** (37.9 mg, 0.110 mmol). To this solution was added dropwise over 15 min a (CH₂Cl)₂ (0.4 mL) solution of **1a** (23.6 mg, 0.100 mmol) at rt and washed remaining substrates away by using (CH₂Cl)₂ (0.2 mL). The mixture was stirred at rt for 3 h. The resulting solution was concentrated and purified by preparative TLC (hexane:EtOAc = 9:1), which furnished **3a** (49.6 mg, 0.0854 mmol, 85% yield) as a colorless solid.

4,7-Dimethyl-5-tridecafluorohexylindan-2,2-dicarboxylic acid dimethyl ester (3a**, Table 1, entry 1, 85% yield).**

Mp 74.5–76.0 °C; IR (neat) 2957, 1739, 1437, 1363, 1243, 811 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.17 (s, 1H), 3.78 (s, 6H), 3.60 (s, 2H), 3.59 (s, 2H), 2.31 (s, 3H), 2.26 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 172.0, 142.6 (t, *J*_{C-F} = 5.9 Hz), 141.0, 131.2 (t, *J*_{C-F} = 2.5 Hz), 131.1, 128.5 (t, *J*_{C-F} = 8.6 Hz), 125.7 (t, *J*_{C-F} = 21.5 Hz), 59.0, 53.2, 40.3, 39.7, 18.6, 16.4; ¹⁹F NMR (CDCl₃, 283 MHz) δ -127.4 (t, *J* = 6.8 Hz, 2F), -124.1 (s, 2F), -123.0 (s, 2F), -121.9 (s, 2F), -105.9 (t, *J* = 15.8 Hz, 2F), -82.0 (t, *J* = 9.0 Hz, 3F); HRMS (FAB) calcd for C₂₁H₁₈F₁₃O₄ [M+H]⁺ 581.0997, found 581.0964.

4,7-Dimethyl-2-(toluene-4-sulfonyl)-5-tridecafluorohexyl-2,3-dihydro-1*H*-isoindole (3b**, Table 1, entry 2, 94% yield).**

Colorless solid; Mp 127.1–128.9 °C; IR (neat) 2927, 1599, 1346, 1163, 813 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.20 (s, 1H), 4.61 (s, 4H), 2.42 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 143.9, 138.9 (t, *J*_{C-F} = 1.9 Hz), 137.5, 133.6, 130.22 (t, *J*_{C-F} = 2.5 Hz), 130.16, 129.9, 129.2 (t, *J*_{C-F} = 8.7 Hz), 127.5, 126.6 (t, *J*_{C-F} = 22.2 Hz), 53.7, 53.4, 21.5, 18.2, 16.2; ¹⁹F NMR (CDCl₃, 283 MHz) δ -127.6 to -127.2 (m, 2F), -124.0 (s, 2F), -123.0 (s, 2F), -122.0 (s, 2F), -106.4 (t, *J* = 16.1 Hz, 2F), -82.0 (t, *J* = 9.1 Hz, 3F); HRMS (FAB) calcd for C₂₃H₁₉F₁₃NO₂S [M+H]⁺ 620.0929, found 620.0888.

2-(Toluene-4-sulfonyl)-5-tridecafluorohexyl-2,3-dihydro-1H-isoindole (3c, Table 1, entry 3, 21% yield).

Colorless solid; Mp 128.5–129.3 °C; IR (neat) 2360, 1598, 1346, 1169 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.78 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 7.8 Hz, 1H), 7.39 (s, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 1H), 4.67 (s, 4H), 2.41 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 144.0, 140.6–140.5 (m), 137.1, 133.4, 130.0, 128.7 (t, $J_{\text{C-F}}$ = 24.0 Hz), 127.6, 126.6 (t, $J_{\text{C-F}}$ = 7.4 Hz), 123.1, 121.4 (t, $J_{\text{C-F}}$ = 8.0 Hz), 53.5, 53.4, 21.5; ^{19}F NMR (CDCl_3 , 283 MHz) δ -127.5 (t, J = 6.8 Hz, 2F), -124.2 (s, 2F), -123.1 (s, 2F), -122.8 (s, 2F), -111.6 (t, J = 11.3 Hz, 2F), -82.1 (t, J = 9.3 Hz, 3F); HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{15}\text{F}_{13}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 592.0616, found 592.0656.

5-Tridecafluorohexylindan-2,2,4,7-tetracarboxylic acid-4,7-diethylester-2,2-dimethyl ester (3d, Table 1, entry 4, 89% yield).

Colorless oil; IR (neat) 2987, 2362, 1437, 1147, 745 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.10 (s, 1H), 4.43 (q, J = 7.2 Hz, 2H), 4.42 (q, J = 7.2 Hz, 2H), 4.04 (s, 2H), 3.77 (s, 6H), 3.64 (s, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 171.3, 166.2, 164.6, 147.3 (t, $J_{\text{C-F}}$ = 1.2 Hz), 141.1, 133.2 (t, $J_{\text{C-F}}$ = 3.7 Hz), 129.4, 127.8, 125.1, 124.8 (t, $J_{\text{C-F}}$ = 23.4 Hz), 62.3, 61.2, 59.2, 53.2, 41.8, 38.8, 14.2, 13.8; ^{19}F NMR (CDCl_3 , 283 MHz) δ -127.4 to -127.2 (m, 2F), -123.9 (s, 2F), -122.9 (s, 2F), -120.8 (t, J = 16.1 Hz, 2F), -106.8 (t, J = 15.8 Hz, 2F), -82.0 (t, J = 9.3 Hz, 3F); HRMS (FAB) calcd for $\text{C}_{25}\text{H}_{22}\text{F}_{13}\text{O}_8$ $[\text{M}+\text{H}]^+$ 697.1107, found 697.1115.

2-Benzyl-5-tridecafluorohexyl-2,3-dihydro-1H-isoindole-4,7-dicarboxylic acid dimethyl ester (3e, Table 1, entry 5, 72% yield).

Yellow solid; Mp 88.5–90.3 °C; IR (neat) 2956, 2360, 1732, 1241, 1147 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.10 (s, 1H), 7.40–7.27 (m, 5H), 4.37 (s, 2H), 3.96 (s, 2H), 3.93 (s, 2H), 3.92 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 166.6, 164.9, 147.9, 142.0, 138.2, 131.1 (t, $J_{\text{C-F}}$ = 3.7 Hz), 129.1–128.8 (m), 128.6, 128.5, 127.3, 126.1, 124.8 (t, $J_{\text{C-F}}$ = 22.8 Hz), 59.7, 59.6, 57.0, 52.9, 52.5; ^{19}F NMR (CDCl_3 , 283 MHz) δ -127.4 (t, J = 9.1 Hz, 2F), -124.1 (s, 2F), -123.1 (s, 2F), -120.8 (s, 2F), -106.6 (t, J = 18.1 Hz, 2F), -82.1 (t, J =

9.0 Hz, 3F); HRMS (FAB) calcd for C₂₅H₁₉F₁₃NO₄ [M+H]⁺ 644.1106, found 644.1096.

5-Tridecafluorohexyl-1,3-dihydroisobenzofuran-4,7-dicarboxylic acid diethyl ester (3f, Table 1, entry 6, 75% yield).

Pale yellow solid; Mp 52.7–53.5 °C; IR (neat) 2987, 1729, 1242, 1147 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.18 (s, 1H), 5.46 (s, 2H), 5.15 (s, 2H), 4.47–4.36 (m, 4H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.7, 164.1, 146.6, 141.1, 130.6 (t, *J*_{C-F} = 3.8 Hz), 129.7 (t, *J*_{C-F} = 8.6 Hz), 126.1, 125.8 (t, *J*_{C-F} = 24.0 Hz), 74.9, 72.2, 62.6, 62.0, 14.2, 13.7; ¹⁹F NMR (CDCl₃, 283 MHz) δ -127.5 to -127.3 (m, 2F), -124.1 (s, 2F), -122.8 (s, 2F), -120.6 (s, 2F), -106.0 (t, *J* = 16.1 Hz, 2F), -82.0 (t, *J* = 9.1 Hz, 3F); HRMS (FAB) calcd for C₂₀H₁₆F₁₃O₅ [M+H]⁺ 583.0790, found 583.0840.

5-Tridecafluorohexylindan-4,7-dicarboxylic acid dimethyl ester (3g, Table 1, entry 7, 99% yield).

Colorless solid; Mp 72.5–73.9 °C; IR (neat) 2958, 1732, 1242, 1147, 1065, 984 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.06 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.37 (t, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.16 (quint, *J* = 7.5 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.5, 165.7, 152.0, 145.2, 132.7 (t, *J*_{C-F} = 3.7 Hz), 128.6 (t, *J*_{C-F} = 7.4 Hz), 127.4, 123.7 (t, *J*_{C-F} = 24.1 Hz), 52.7, 52.3, 34.1, 31.2, 24.5; ¹⁹F NMR (CDCl₃, 283 MHz) δ -127.4 to -127.2 (s, 2F), -123.9 (s, 2F), -122.9 (s, 2F), -121.0 (s, 2F), -107.1 (t, *J* = 13.9 Hz, 2F), -82.0 (t, *J* = 9.1 Hz, 3F); HRMS (FAB) calcd for C₁₈H₁₄F₁₃O₄ [M+H]⁺ 553.0684, found 553.0671.

5-Tridecafluorohexylbenzene-1,2,3,4-tetracarboxylic acid tetramethyl ester (5, eq 1). Under an Ar atmosphere, (*R*)-H₈-BINAP (3.2 mg, 0.0050 mmol) and [Rh(cod)₂][BF₄] (2.0 mg, 0.0050 mmol) were dissolved in CH₂Cl₂ (1.0 mL) and the mixture was stirred at rt for 5 min. H₂ was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 1 h, the resulting solution was concentrated to dryness and dissolved in (CH₂Cl)₂ (0.4 mL). To this solution was added **2** (34.4 mg, 0.100 mmol). To this solution was added a (CH₂Cl)₂ (0.4 mL) solution of **4** (42.6 mg, 0.300 mmol) at rt and washed remaining substrates away by using (CH₂Cl)₂ (0.2 mL). The mixture was stirred at rt for 3 h. The resulting solution was concentrated and purified by preparative TLC (hexane:EtOAc = 4:1),

which furnished **5** (50.2 mg, 0.0800 mmol, 80% yield) as a colorless solid.

Mp 89.3–90.8 °C; IR (neat) 2360, 1742, 1442, 1242 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.32 (s, 1H), 3.974 (s, 3H), 3.965 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 166.4, 165.4, 164.4, 163.6, 139.0, 137.3, 132.9–132.6 (m), 131.0, 130.3, 127.8 (t, $J_{\text{C-F}} = 24.7$ Hz), 53.6, 53.4, 53.3; ^{19}F NMR (CDCl_3 , 283 MHz) δ –127.3 (s, 2F), –123.9 (s, 2F), –122.8 (s, 2F), –120.2 (s, 2F), –107.5 (t, $J = 13.9$ Hz, 2F), –82.1 to –81.8 (m, 3F); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{10}\text{F}_{13}\text{O}_7$ [$\text{M}-\text{OMe}$] $^+$ 597.0219, found 597.0206.

4'-Tridecafluorohexyl-[1,1';2',1'']terphenyl-3',6'-dicarboxylic acid diethyl ester (7, eq 2). Under an Ar atmosphere, (*R*)- H_8 -BINAP (3.2 mg, 0.0050 mmol) and $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (2.0 mg, 0.0050 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and the mixture was stirred at rt for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 1 h, the resulting solution was concentrated to dryness and dissolved in $(\text{CH}_2\text{Cl}_2)_2$ (0.4 mL). To this solution was added **2** (34.4 mg, 0.100 mmol). To this solution was added over 20 min a $(\text{CH}_2\text{Cl}_2)_2$ (0.4 mL) solution of **6** (87.1 mg, 0.500 mmol) at rt and washed remaining substrates away by using $(\text{CH}_2\text{Cl}_2)_2$ (0.2 mL). The mixture was stirred at rt for 3 h. The resulting solution was concentrated and purified by preparative TLC (hexane:EtOAc = 15:1), which furnished **7** (34.3 mg, 0.0495 mmol, 50% yield) as a colorless oil.

IR (neat) 2985, 2360, 1739, 1444, 1240, 1151 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.02 (s, 1H), 7.20–7.06 (m, 6H), 7.06–6.92 (m, 4H), 4.02 (q, $J = 7.2$ Hz, 2H), 3.91 (q, $J = 7.2$ Hz, 2H), 0.93 (t, $J = 7.2$ Hz, 3H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 167.0, 166.1, 145.2 (t, $J_{\text{C-F}} = 1.3$ Hz), 141.5, 137.8 (t, $J_{\text{C-F}} = 3.7$ Hz), 136.5, 136.1, 133.8, 130.3, 129.2, 128.4–128.3 (m), 127.5, 127.4, 127.3, 127.2, 124.3 (t, $J_{\text{C-F}} = 22.7$ Hz), 61.7, 61.6, 13.5, 13.3; ^{19}F NMR (CDCl_3 , 283 MHz) δ –127.5 to –127.3 (m, 2F), –124.1 (s, 2F), –123.0 (s, 2F), –120.8 (s, 2F), –107.8 (t, $J = 13.6$ Hz, 2F), –82.0 (t, $J = 9.1$ Hz, 3F); HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{21}\text{F}_{13}\text{NaO}_4$ [$\text{M}+\text{Na}$] $^+$ 715.1130, found 715.1155.

2-Methyl-4,5-bis-tridecafluorohexylbenzoic acid ethyl ester (9, eq 3). Under an Ar atmosphere, (*R*)- H_8 -BINAP (3.2 mg, 0.0050 mmol) and $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (2.0 mg, 0.0050 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and the mixture was stirred at rt for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 1 h, the resulting solution was concentrated to dryness and dissolved in $(\text{CH}_2\text{Cl}_2)_2$ (0.4 mL). To this solution was added **2** (103.2 mg, 0.300 mmol). To this solution was added over 20 min a

(CH₂Cl)₂ (0.4 mL) solution of **8** (11.2 mg, 0.100 mmol) at rt and washed remaining substrates away by using (CH₂Cl)₂ (0.2 mL). The mixture was stirred at rt for 3 h. The resulting solution was concentrated and purified by preparative TLC (hexane:EtOAc = 10:1), which furnished **9** (67.1 mg, 0.0838 mmol, 84% yield) as a colorless oil.

IR (neat) 2928, 2360, 1720, 1466, 1263, 1197, 1136, 1082, 1052 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.08 (s, 1H), 7.85 (s, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.69 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 166.4, 143.3, 135.5, 131.2 (t, *J*_{C-F} = 5.6 Hz), 129.9–129.3 (m), 127.0 (t, *J*_{C-F} = 24.6 Hz), 62.2, 17.4, 14.1; ¹⁹F NMR (CDCl₃, 283 MHz) δ -127.5 (s, 4F), -124.1 (s, 4F), -123.1 (s, 2F), -122.9 (s, 2F), -122.7 (s, 2F), -121.7 (s, 2F), -112.7 (t, *J* = 15.8 Hz, 2F), -106.0 (s, 2F), -82.1 (t, *J* = 11.6 Hz, 6F); HRMS (FAB) calcd for C₂₂H₁₁F₂₆O₂ [M+H]⁺ 801.0344, found 801.0330.

4,5-Dihexyl-2-methylbenzoic acid ethyl ester (11), 2,4-dihexyl-6-methylbenzoic acid ethyl ester (12), 3,5-dihexyl-2-methylbenzoic acid ethyl ester (13), and 3,6-dihexyl-2-methylbenzoic acid ethyl ester (14) [eq 4, 56% yield (11:12:13:14 = 48:18:27:7)].

The reaction was conducted by the procedure used for **9**. Colorless oil; IR (neat) 2928, 2360, 1720, 1610, 1466, 1263, 1196, 1136, 1081 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.70 (s, 1H), 7.00 (s, 1H), 4.44–4.28 (m, 2H), 2.67–2.46 (m, 4H), 2.53 (s, 3H), 1.65–1.45 (m, 3H), 1.45–1.16 (m, 16H), 0.98–0.80 (m, 6H); aryl and methyl protons of regio isomer **12**: 6.85 (s, 2H), 2.29 (s, 3H); aryl and methyl protons of regio isomer **13**: 7.40 (s, 1H), 7.1 (s, 1H), 2.42 (s, 3H); aryl and methyl protons of regio isomer **14**: 7.09 (d, *J* = 6.0 Hz, 1H), 6.96 (d, *J* = 6.0 Hz, 1H), 2.22 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.3, 169.2, 167.9, 145.1, 144.1, 142.2, 139.7, 138.0, 137.6, 137.2, 136.6, 134.6, 133.5, 132.6, 131.7, 131.1, 129.9, 127.7, 127.2, 127.1, 126.9, 126.5, 60.8, 60.7, 60.4, 35.7, 35.3, 33.9, 33.8, 33.3, 32.6, 32.2, 31.70, 31.66, 31.6, 31.4, 31.3, 31.1, 30.4, 29.42, 29.39, 29.3, 29.0, 22.62, 22.60, 22.57, 21.4, 19.7, 15.8, 14.4, 14.33, 14.27, 14.1; HRMS (EI) calcd for C₂₂H₃₆O₂ [M]⁺ 332.2715, found 332.2756.

IV. Synthesis of Perfluoroalkylated Pyridines

General procedure for [2 + 2 + 2] cycloaddition of 1,6-diynes with perfluoroalkynitrile **15.** Under an Ar atmosphere, (*R*)-tol-BINAP (6.8 mg, 0.010 mmol) and [Rh(cod)₂]₂BF₄ (4.1 mg, 0.010 mmol) were dissolved in CH₂Cl₂ (1.0 mL) and the mixture was stirred at rt for 5 min. H₂ was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 1 h, the resulting solution was concentrated to dryness and dissolved in (CH₂Cl)₂ (1.0 mL). To this solution was added a (CH₂Cl)₂ (0.6 mL) solution of **15** (86.9 mg, 0.220 mmol) and **1a** (47.3 mg, 0.200 mmol) at rt and washed remaining substrates away by using (CH₂Cl)₂ (0.4 mL). The mixture was stirred at rt for 3 h. The resulting solution was concentrated and purified by preparative TLC (hexane:EtOAc = 4:1), which furnished **16a** (107.6 mg, 0.0170 mmol, 85% yield) as a colorless solid.

1,4-Dimethyl-3-pentadecafluoroheptyl-5,7-dihydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (16a**, Table 2, entry 1, 85% yield).**

Colorless solid; Mp 61.0–61.9 °C; IR (neat) 2960, 1739, 1438, 1203, 1101, 1066, 967 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.84–3.67 (m, 6H), 3.62 (s, 4H), 2.46 (s, 3H), 2.35 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 171.4, 151.0, 150.9, 143.3 (t, *J*_{C-F} = 24.1 Hz), 136.7, 128.0, 58.9, 53.3, 40.1, 39.1, 21.5; ¹⁹F NMR (CDCl₃, 283 MHz) δ -127.4 to -127.3 (m, 2F), -123.9 (s, 2F), -123.2 (s, 2F), -122.0 (s, 2F), -121.8 (s, 2F), -108.3 (t, *J* = 13.9 Hz, 2F), -82.0 (t, *J* = 11.6 Hz, 3F); HRMS (FAB) calcd for C₂₁H₁₇F₁₅NO₄ [M+H]⁺ 632.0918, found 632.0894.

3-Pentadecafluoroheptyl-5,7-dihydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (16h**, Table 2, entry 2, 62% yield).**

Colorless solid; Mp 79.3–80.5 °C; IR (neat) 2960, 2360, 1739, 1437, 1203, 1073 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.58 (s, 1H), 7.54 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.70 (s, 2H), 3.69 (s, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 171.0, 151.1, 146.5 (t, *J*_{C-F} = 25.9 Hz), 145.7, 139.5, 118.5, 59.9, 53.3, 40.3, 38.2; ¹⁹F NMR (CDCl₃, 283 MHz) δ -127.4 to -127.3 (m, 2F), -123.9 (s, 2F), -123.2 (s, 2F), -122.9 (s, 2F), -122.8 (s, 2F), -114.5 (t, *J* = 13.9 Hz, 2F), -82.0 (t, *J* = 9.3 Hz, 3F); HRMS (FAB) calcd for C₁₉H₁₃F₁₅NO₄ [M+H]⁺ 604.0605, found 604.0659.

3-Pentadecafluoroheptyl-5,7-dihydro-[2]pyrindine-1,4,6,6-tetracarboxylic acid 1,4-diethyl ester-6,6-dimethyl ester (16d**, Table 2, entry 3, 55% yield).**

Colorless solid; Mp 48.0–49.7 °C; IR (neat) 2960, 2360, 1740, 1438, 1222, 1150, 1021 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.45 (q, $J = 7.2$ Hz, 2H), 4.44 (q, $J = 7.2$ Hz, 2H), 4.07 (s, 2H), 3.78 (s, 6H), 3.70 (s, 2H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.38 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 170.8, 164.8, 163.7, 152.6, 143.7, 142.7 (t, $J_{\text{C-F}} = 26.6$ Hz), 142.0, 128.7, 62.8, 62.2, 59.0, 53.4, 40.5, 39.1, 14.0, 13.8; ^{19}F NMR (CDCl_3 , 283 MHz) δ –127.4 to –127.3 (m, 2F), –123.9 (s, 2F), –123.2 (s, 2F), –122.2 (s, 2F), –120.8 (s, 2F), –109.1 (t, $J = 13.6$ Hz, 2F), –82.0 (t, $J = 9.3$ Hz, 3F); HRMS (FAB) calcd for $\text{C}_{25}\text{H}_{21}\text{F}_{15}\text{NO}_8$ $[\text{M}+\text{H}]^+$ 748.1028, found 748.1014.

4,7-Dimethyl-6-pentadecafluoroheptyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1H-pyrrolo[3,4-c]pyridine (16b, Table 2, entry 4, 92% yield).

Colorless solid; Mp 169.9–171.5 °C; IR (neat) 2922, 2360, 1598, 1140, 1098 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.79 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 4.63 (s, 4H), 2.42 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 149.9, 147.6, 144.2, 144.1 (t, $J_{\text{C-F}} = 19.7$ Hz), 133.4, 133.3, 130.1, 127.4, 126.8, 53.4, 52.6, 29.7, 21.5, 14.5; ^{19}F NMR (CDCl_3 , 283 MHz) δ –127.5 (s, 2F), –124.0 (s, 2F), –123.3 (s, 2F), –122.2 (s, 2F), –122.0 (s, 2F), –108.8 (s, 2F), –82.1 (s, 3F); HRMS (FAB) calcd for $\text{C}_{23}\text{H}_{18}\text{F}_{15}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 671.0849, found 671.0851.

4,7-Diethyl-6-pentadecafluoroheptyl-1,3-dihydrofuro[3,4-c]pyridine (16i, Table 2, entry 5, 86% yield).

Colorless oil; IR (neat) 2978, 1600, 1464, 1207, 991, 911, 788 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 5.18 (s, 4H), 2.74–2.64 (m, 4H), 1.27 (t, $J = 7.5$ Hz, 3H), 1.19 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 153.6, 150.4, 143.5 (t, $J_{\text{C-F}} = 21.6$ Hz), 135.6, 131.8, 72.7, 72.3, 28.7, 22.9, 14.7, 12.0; ^{19}F NMR (CDCl_3 , 283 MHz) δ –127.3 (s, 2F), –123.8 (s, 2F), –123.1 (s, 2F), –121.7 (s, 2F), –121.4 (s, 2F), –107.2 (t, $J = 13.6$ Hz, 2F), –82.0 (t, $J = 9.1$ Hz, 3F); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{15}\text{F}_{15}\text{NO}$ $[\text{M}+\text{H}]^+$ 546.0914, found 546.0891.

1,4-Diethyl-3-pentadecafluoroheptyl-6,7-dihydro-5H-[2]pyrindine (16j, Table 2, entry 6, 85% yield).

Colorless oil; IR (neat) 2973, 1587, 1464, 1205, 1148 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 2.99–2.92 (m, 4H), 2.78–2.70 (m, 4H), 2.16 (quint, $J = 7.5$ Hz, 2H), 1.24 (t, $J = 7.5$ Hz, 3H), 1.17 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 155.7 (t, $J_{\text{C-F}} = 1.3$ Hz), 154.9, 142.0 (t, $J_{\text{C-F}} = 24.0$ Hz), 140.3, 134.1, 31.4, 30.6, 28.4, 24.1, 22.6, 14.7, 12.3; ^{19}F NMR (CDCl_3 , 283 MHz) δ –127.4 to –127.3 (s, 2F), –123.9 (s, 2F), –123.2 (s, 2F), –121.6 (s, 2F), –121.4 to –121.3 (m, 2F), –106.9 (t, $J = 13.6$ Hz, 2F), –82.0 (t, $J = 9.1$ Hz, 3F); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{17}\text{F}_{15}\text{N}$ $[\text{M}+\text{H}]^+$ 544.1121, found 544.1140.

7-Methyl-6-pentadecafluoroheptyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1H-pyrrolo[3,4-c]pyridine-4-carboxylic acid methyl ester (16k, eq 5, 85% yield).

Colorless solid; Mp 179.9–181.3 $^{\circ}\text{C}$; IR (neat) 2359, 1733, 1560, 1346, 1152 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.77 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 4.67 (s, 4H), 3.93 (s, 3H), 2.51 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.3, 154.5, 146.4, 144.4, 143.6 (t, $J_{\text{C-F}} = 26.5$ Hz), 134.1, 133.1, 130.1, 127.5, 122.5, 53.2, 53.1, 52.1, 21.9, 21.5; ^{19}F NMR (CDCl_3 , 283 MHz) δ –127.4 (s, 2F), –124.0 (s, 2F), –123.2 (s, 2F), –122.5 (s, 2F), –120.4 (s, 2F), –109.0 (t, $J = 13.6$ Hz, 2F), –82.0 (t, $J = 9.1$ Hz, 3F); HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{18}\text{O}_4\text{N}_2\text{F}_{15}\text{S}$ $[\text{M}+\text{H}]^+$ 715.0748, found 715.0807.

V. References

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4-[But-2-ynyl(toluene-4-sulfonyl)amino]but-2-ynoic acid methyl ester (1k)

4,7-Dimethyl-5-tridecafluorohexylindan-2,2-dicarboxylic acid dimethyl ester (3a)

**4,7-Dimethyl-2-(toluene-4-sulfonyl)-5-tridecafluorohexyl-2,3-dihydro-1*H*-isoindole
(3b)**

2-(Toluene-4-sulfonyl)-5-tridecafluorohexyl-2,3-dihydro-1*H*-isoindole (3c)

5-Tridecafluorohexylindan-2,2,4,7-tetracarboxylicacid-4,7-diethylester-2,2-dimethyl ester (3d)

acid

**5-Tridecafluorohexyl-1,3-dihydroisobenzofuran-4,7-dicarboxylic acid diethyl ester
(3f)**

5-Tridecafluorohexylindan-4,7-dicarboxylic acid dimethyl ester (3g)

5-Tridecafluorohexylbenzene-1,2,3,4-tetracarboxylic acid tetramethyl ester (5)

4'-Tridecafluorohexyl-[1,1';2',1'']terphenyl-3',6'-dicarboxylic acid diethyl ester (7)

2-Methyl-4,5-bis-tridecafluorohexylbenzoic acid ethyl ester (9)

4,5-Dihexyl-2-methylbenzoic acid ethyl ester (11), 2,4-dihexyl-6-methylbenzoic acid ethyl ester (12), 3,5-dihexyl-2-methylbenzoic acid ethyl ester (13), and 3,6-dihexyl-2-methylbenzoic acid ethyl ester (14) (11:12:13:14 = 48:18:27:7)

1,4-Dimethyl-3-pentadecafluoroheptyl-5,7-dihydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (16a)

3-Pentadecafluoroheptyl-5,7-dihydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (16h)

3-Pentadecafluoroheptyl-5,7-dihydro-[2]pyrindine-1,4,6,6-tetracarboxylic acid 1,4-diethyl ester-6,6-dimethyl ester (16d)

4,7-Dimethyl-6-pentadecafluoroheptyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine (16b)

1

1,4-Diethyl-3-pentadecafluoroheptyl-6,7-dihydro-5H-[2]pyrindine (16j)

7-Methyl-6-pentadecafluoroheptyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-4-carboxylic acid methyl ester (16k)