Rotaxanes with Fluorocarbon Blocking Groups

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SUPPORTING INFORMATION

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3(4-pyridine)-1-propanol trimethyl silyl ether (2): 3(4-pyridine)-1-propanol (24.6 g, 0.179 mol) was dissolved in THF (400 mL, dried over MgSO_4). After the addition of triethylamine (23.8 g, 0.235 mol), chlorotrimethylsilane (21.4 g, 0.197 mol) was added, producing a copious amount of white precipitate. This mixture was stirred for 22 hours, after which time the precipitate was removed by vacuum filtration. The filtrate was concentrated by rotary evaporation, taken up in ether (500 mL), and extracted with water (2 x 75 mL). The organic layer was dried (MgSO_4) and evaporated to yield a golden yellow oil (29.3 g, 78%). ^1H NMR (200 MHz, CD_3COCD_3): δ = 1.74 (m, 2H), 2.61 (t, J = 6 Hz, 2H), 3.54 (t, J = 6 Hz, 2H), 7.12 (d, J = 6 Hz, 2H), 8.37 (d, J = 6 Hz, 2H); ^{13}C NMR (200 MHz, CD_3COCD_3): δ = 0.0, 32.4, 34.4, 62.5, 125.1, 150.9, 152.2; Calcd. For $\text{C}_{11}\text{H}_{19}\text{NOSi}$: C, 63.10; H, 9.15; N, 6.69. Found: C, 62.94; H, 9.24; N, 6.81.

3-2PF₆: The TMS protected compound **2** (29.3 g, 140 mmol) was dissolved in CH_3CN (125 mL, dried over MgSO_4). 1,2-dibromoethane (4.80 g, 25.5 mmol) was added and the reaction mixture was heated at 40 °C for 5 days. The brown solid that had formed was filtered by gravity and washed with small portions of CH_3CN . This material was then dissolved in H_2O (10 mL) and precipitated from an aqueous solution of NH_4PF_6 (25 mL). The precipitate was filtered by gravity, washed with H_2O , and then dissolved in a minimal amount of CH_3CN . This solution was dried (MgSO_4) and evaporated to yield the product as a brown solid (4.35 g, 29%). ^1H NMR (200 MHz, CD_3CN): δ = 1.88 (m, 4H), 2.79 (br s, 2H, OH), 2.99 (t, J = 8 Hz, 4 H), 3.54 (t, J = 8 Hz, 4H), 4.95 (s, 4H), 7.89 (d, J = 6 Hz, 4H), 8.39 (d, J = 6 Hz, 4H); ^{13}C NMR (200 MHz, CD_3CN): δ = 33.19, 33.23, 60.6, 61.1, 129.8, 145.3, 166.6; Calcd. For $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_2\text{P}_2\text{F}_{12}$: C, 36.50; H, 4.42; N, 4.73; F 38.49. Found: C, 36.41; H, 4.23; N, 4.74; F, 38.72.

4-2PF₆: A solution of **3-2PF₆** (0.349 g, 0.589 mmol) in CH_3CN (20 mL, dried over MgSO_4) was dried (MgSO_4) and filtered by gravity. The filtrate was placed in a flask that was purged with nitrogen. Triethylamine (0.151 g, 1.49 mmol) was added via syringe followed by heptafluorobutyryl chloride (0.622 g, 2.68 mmol). The resulting solution was stirred at room temperature overnight. The solvent was removed in vacuo to yield a yellow solid that was treated with CH_2Cl_2 . The undissolved product was removed by gravity filtration and washed with small portions of additional CH_2Cl_2 . This material was then dissolved in CH_3CN (5 mL) and precipitated from an aqueous solution of NH_4PF_6 (25 mL). The precipitate was filtered by gravity, washed with H_2O , and then dissolved in a minimal amount of CH_3CN . This solution was dried (MgSO_4) and evaporated to yield the product (0.33 g, 57%). ^1H NMR (200 MHz, CD_3CN): δ = 2.17 (m, 4H), 3.03 (t, J = 8 Hz, 4 H), 4.47 (t, J = 6 Hz, 4H), 4.97 (s, 4H), 7.91 (d, J = 8 Hz, 4H), 8.45 (d, J = 8 Hz, 4H); Calcd. For $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_4\text{P}_2\text{F}_{26}$: C, 31.72; H, 2.46; N, 2.85; F 50.18. Found: C, 31.37; H, 2.39; N, 2.76; F, 49.88.

5-2PF₆: A solution of **3-2PF₆** (0.350 g, 0.591 mmol) and DB24C8 (0.265 g, 0.591 mmol) in CH_3CN (50 mL, dried over MgSO_4) was dried (MgSO_4) and filtered by gravity. The filtrate was placed in a flask that was purged with nitrogen and cooled in an ice bath. Triethylamine (0.151 g, 1.49 mmol) was added via syringe followed by heptafluorobutyryl chloride (0.622 g, 2.68 mmol). The resulting solution was stirred at

room temperature overnight. The solvent was removed in vacuo to yield a yellow solid that was treated with CH_2Cl_2 . After the undissolved side product (**4-2PF₆**) was removed by gravity filtration, the filtrate was evaporated to yield a viscous orange oil, which was triturated with ether (50 mL). The resulting solid was isolated by gravity filtration and then dissolved in hot DMSO (10 mL, dried over MgSO_4). The rotaxane product was then precipitated from a hot aqueous solution of NH_4PF_6 (40 mL) and isolated by gravity filtration. After trituration with toluene, the undissolved product was taken up in CH_3CN and dried over MgSO_4 . Evaporation of the solvent in vacuo yielded the solid rotaxane product (272 mg, 16%). ^1H NMR (200 MHz, CD_3CN): δ = 1.86 (m, 4H), 2.59 (t, J = 8 Hz, 4 H), 3.90 (m, 8H), 3.93 (m, 8H), 3.98 (m, 8H), 4.37 (t, J = 6 Hz, 4H), 5.37 (s, 4H), 6.72 (m, 8H), 7.50 (d, J = 6 Hz, 4H), 8.91 (d, J = 6 Hz, 4H); Calcd. For $\text{C}_{50}\text{H}_{56}\text{N}_2\text{O}_{12}\text{P}_2\text{F}_{26}$: C, 41.91; H, 3.94; N, 1.96; F 34.47. Found: C, 41.97; H, 3.65; N, 1.94; F, 34.17.

^1H NMR (CD_3CN)

2: $\text{X} = (\text{CH}_2)_3\text{OTMS}$

^1H NMR (CD_3CN)

3: $\text{X} = (\text{CH}_2)_3\text{OH}$

^1H NMR (CD_3CN)

4: $\text{X} = (\text{CH}_2)_3\text{O}_2\text{C}(\text{CF}_2)_2\text{CF}_3$

^{13}C NMR (CD_3CN)

^1H NMR (CD_3CN)

Mahan, U. Hartford EJM-4-25E in 3NBA 14 Jun 78 3:52 pm LRP +FAB
 1848460001 scans 1-4 100% = 29594mV

^1H NMR (CD_3CN)

4: $\text{X} = (\text{CH}_2)_3\text{O}_2\text{C}(\text{CF}_2)_2\text{CF}_3$

DB24C8

Mahan, U. Hartford EJM-4-201 in 3NBA 14 Jun 78 3:35 pm LRP +FAB
 1848450001 scans 1-5 100% = 50000mV

^1H NMR (CD_3CN)

DB24C8

Mahan, U. Hartford EJM-4-19B in 3NBA 14 Jun 78 2:13 pm LRP +FAB
 184830004 scans 1-4 100%= 5544mV