Chiral Ionic Liquid Crystals based on Thiourea - Supporting Information

S. Kirchhecker and Duncan W. Bruce

S1

Methods

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (^1H), 100.5 MHz (^{13}C) or 376.4 MHz (^{19}F)). Please note that for thiourea and thiouronium compounds the parts of the molecule close to the thiourea/uronium moiety displayed very broad and/or overlapping proton NMR signals due to aggregation. This happened in all commonly available deuterated solvents and attempts to break the aggregate with TFA or MeOD present in the mixture also led to no improvement. We therefore report the signals as good as we can but refer the reader to the MS and CHN for proof of structure.

Mass spectra were recorded on a Bruker micrOTOF MS-Agilent series 1200LC spectrometer in ESI or APCI mode. FTIR spectroscopy was performed using a Shimadzu IR Prestige-21 with Specac Golden Gate diamond ATR-IR insert.

CHN analysis was performed using a CE-440 elemental analyser from Exeter Analytical, in conjunction with a Sartorius S2 analytical balance. Samples were combusted at 975 °C in an oxygen atmosphere, and the combustion products analysed by a series of thermal conductivity detectors. S-benzyl thiouronium chloride was used as a standard. The reported data are the averages of two measurements.

Polarimetry was performed using a Jasco DIP-370 digital polarimeter in $CHCl_3$ at a concentration of 1.0 where possible, or lower (as indicated). The values reported are an average of ten measurements. Polarised optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hot stage controlled by a Mettler FP90 central processor. Photomicrographs were captured *via* an InfinityX-21 MP digital camera mounted atop the microscope in planar alignment cells with 5 μm spacing.

Differential scanning calorimetry was performed on a Mettler DSC822e calibrated before use against indium and zinc standards under an atmosphere of dry nitrogen. Three heating and cooling cycles were performed per sample. The data were analysed using Mettler Stare software and replotted using Origin.

Small-angle X-ray diffraction was performed using a Bruker D8 Discover equipped with a temperature-controlled, bored-graphite rod furnace, custom built at the University of York. The radiation used was copper Kα (λ = 0.154056 nm) from a 1 µS microfocus source. Diffraction patterns were recorded on a 2048 x 2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample, allowing simultaneous collection of small angle and wide angle scattering data. Samples were filled into 1mm capillary tubes and aligned with a pair of 1 T magnets. Diffraction patterns were collected as a function of temperature and the data were processed using Diffract Evaluation software.

Materials

All chemicals were purchased from commercial suppliers (Sigma, Fluorochem, Fisher) and used as received. (*R*)-(+)-1-(4-Methoxyphenyl)ethylamine was purchased from Sigma.

S2 Characterisation of ILC mesophases

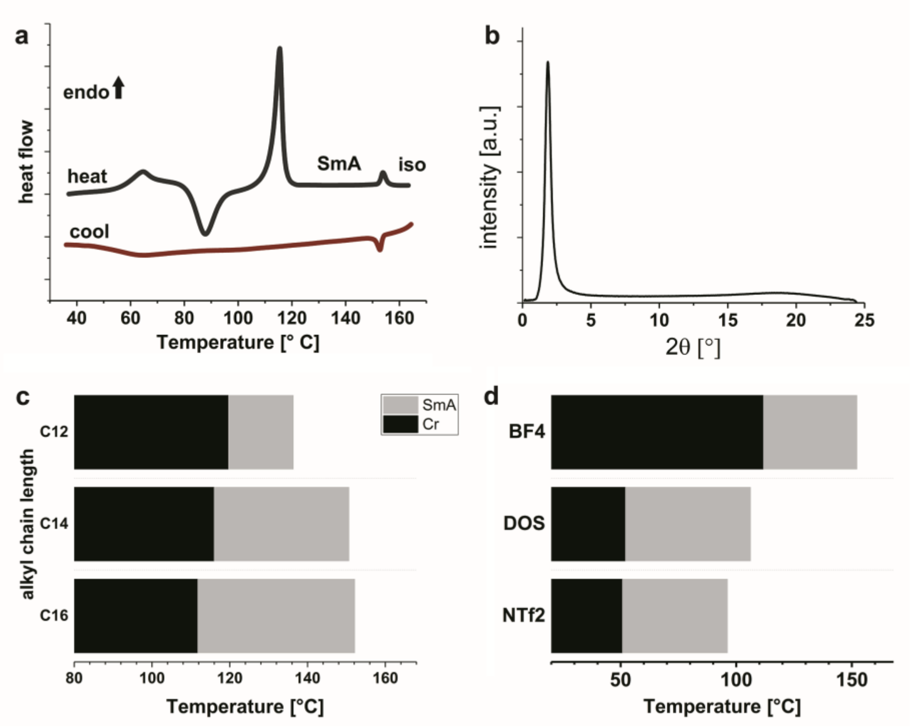
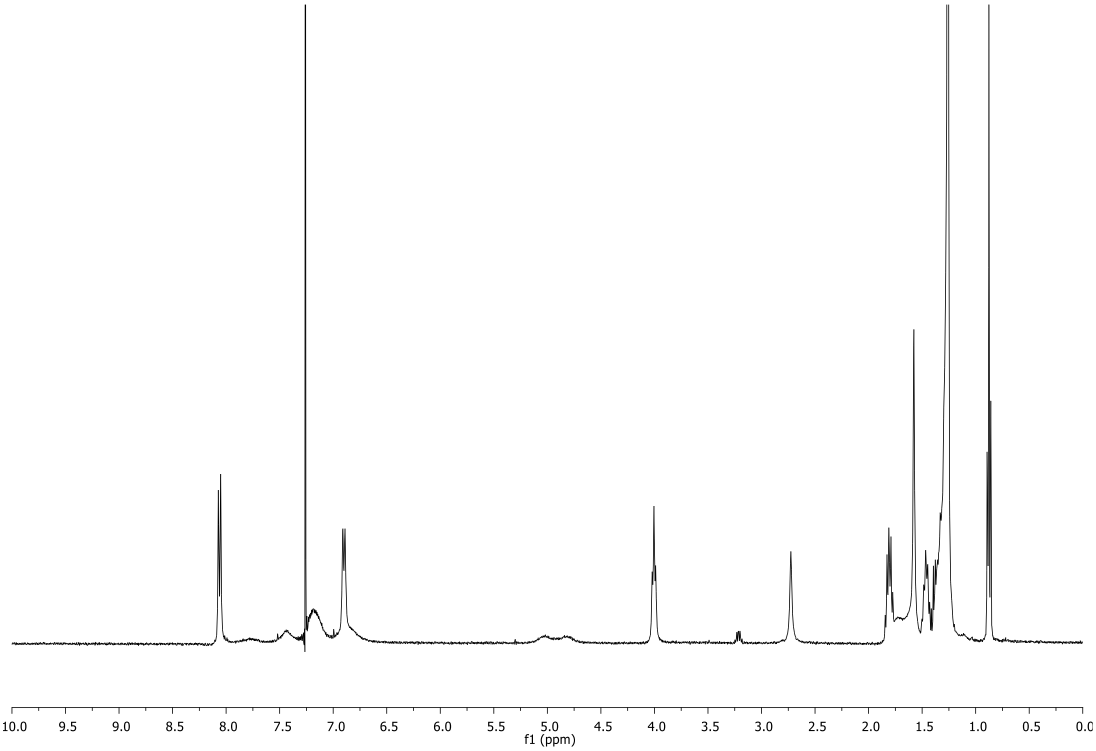


Figure S1 a) DSC trace of **5c BF$_4$**, b) X-ray diffractogram of **5c BF$_4$** in the SmA* phase at 132 °C, c) graphical representation of the dependence of phase transition temperatures and phase ranges on alkyl chain length for compounds **5 BF$_4$**, d) effect of anion metathesis on the phase transitions of compounds **5c**.

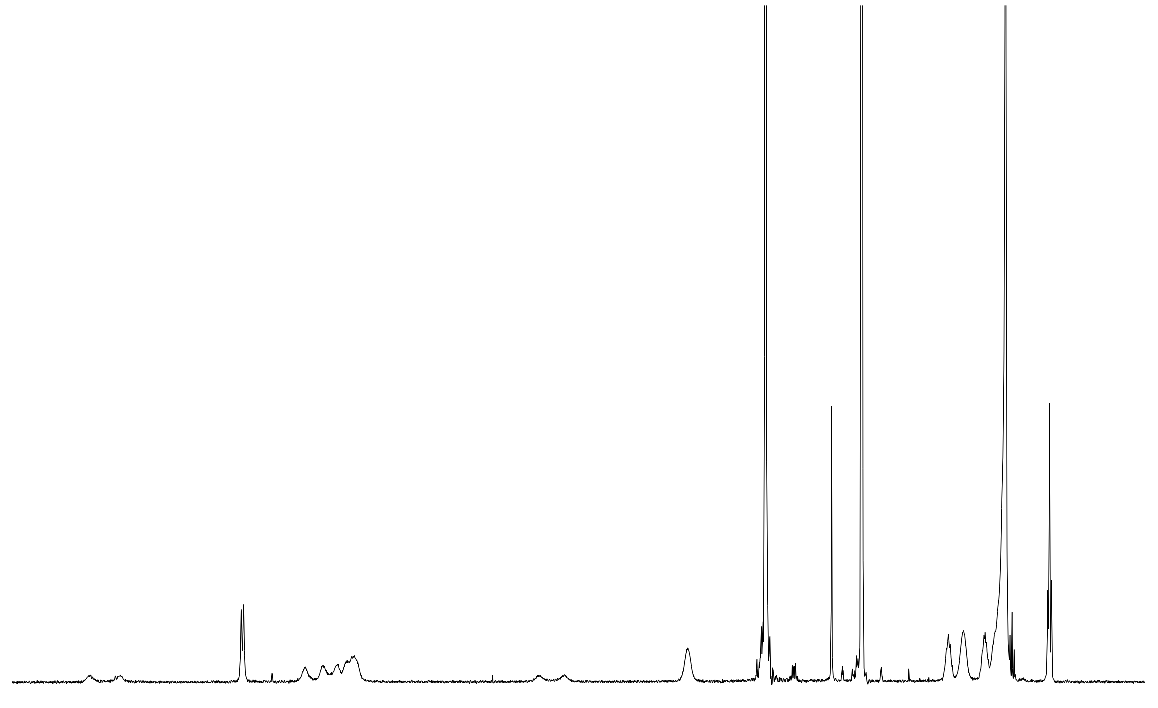
S3.1 Representative NMR spectra of compound 5c BF$_4$

The NMR spectra of all thiourea and thiouronium compounds display broadened peaks in the aromatic region due to reduced rotation. Depending on the solvent the shape and integration of these peaks can change due to their different hydrogen bonding strength. In the experimental the data are reported as they appear (often broad multiplets). Example NMR spectra of compound **5c**

BF₄ in different solvents are given below. Addition of a carboxylate such as acetate locks the conformation in place and leads to resolved peaks (S3.2)

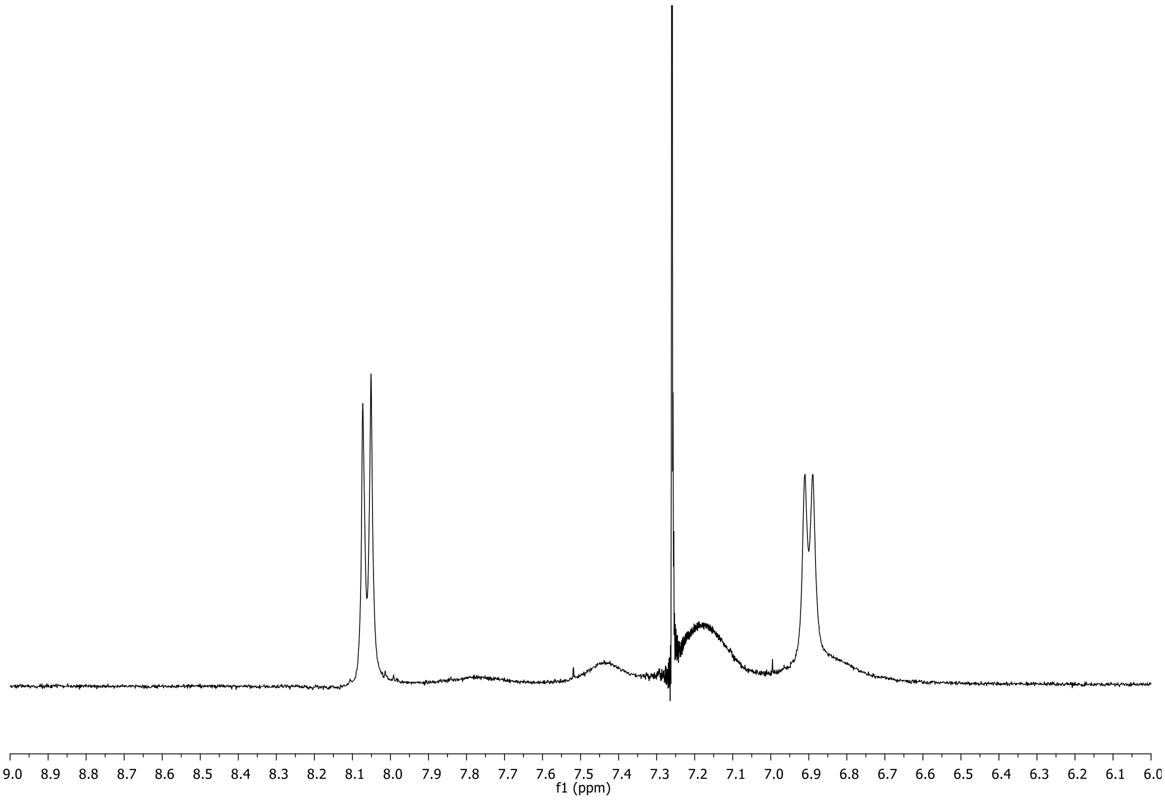


^{1}H-NMR spectrum of **5c BF₄** in $CDCl_3$

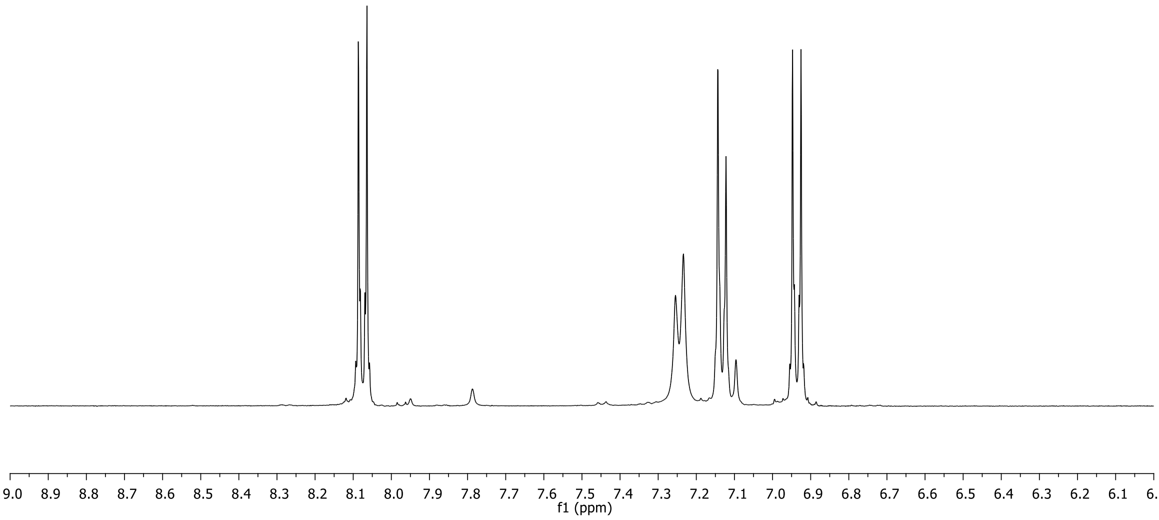


^{1}H-NMR spectrum of **5c BF₄** in DMSO-d_6

S3.2 Effect of the addition of acetate on the NMR spectrum



a



b

Aromatic region of the ^{1}H-NMR spectrum of **5c BF4** in DCM-d_2 in the presence of 1 equivalent of [NBu_4] OAc (b), compared to the aromatic section of the spectrum above in $CDCl_3$ (a).

S4 Experimental

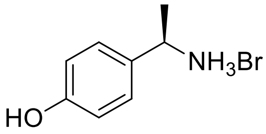
NB: for intermediates representative spectral data are reported for C16 chain length compounds. Spectra of other alkyl chain length compounds only differ in the integration of the alkyl chain and are available on request.

S4.1 Synthesis of alkoxy type compounds

Demethylation of (*R*)-4-Methoxy-α-methylbenzylamine

(*R*)-4-Methoxy-α-methylbenzylamine (4 mL, 25.88 mmol) was added slowly to a solution of 45% HBr in AcOH (20 mL) under N_2 and stirred at 100 °C for 2 h, followed by 2 h at 110 °C. After this time, the solvent was removed under vacuum and EtOAc was added to the remaining residue under stirring, which led to the precipitation of the product as white solid. Yield: 80.0%.

(R)-4-hydroxy-α-methylbenzylamine hydrobromide



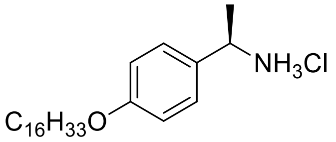
^{1}H NMR (400 MHz, D_2O): δ 7.37 – 7.31 (m, 2H), 6.95 – 6.90 (m, 2H), 4.45 (q, *J* = 6.9 Hz, 1H), 1.59 (d, *J* = 6.9 Hz, 3H) ppm; ESI-MS (m/z): calculated for $[M+H]^+$: 138.0913; found: 138.0912, 121.0669 ($[M-NH_2]^+$)

Synthesis of alkoxy-thiouronium ionic liquid crystals

General method for O-Alkylation

(*R*)-4-Hydroxy-α-methylbenzylamine hydrobromide (2.18 g, 10 mmol) was dissolved in dry DMF together with 1-bromo-alkane (13 mmol), $CsCO_3$ (9.77 g, 30 mmol) and di-benzo-18-crown-6 (0.40 g, 1.1 mmol) and stirred under N_2 for 24 h. After this time DMF was removed under reduced pressure and the residue redissolved in $CHCl_3$. The salt precipitate was removed by filtration and conc HCl (9.44 µl, 11 mmol) was added under stirring, leading to some precipitation of the amine salt. Et_2O was added to precipitate fully and the precipitate was collected by vacuum filtration and washed again with Et_2O. Yield (HCl salt): **2b**: 79.9%, **2c**: 59.6%

(*R*)-4-Hexadecyloxy-α-methylbenzylamine hydrochloride (2c)



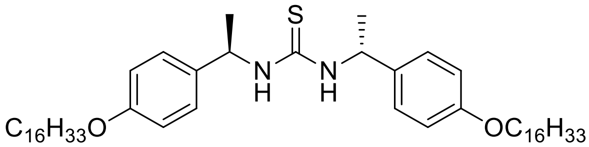
^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 4.26 (b, s, 1H), 3.89 (t, *J* = 6.2 Hz, 2H), 1.73 – 1.57 (m, 2H), 1.43 (d, *J* = 6.7 Hz, 3H), 1.39 – 1.30 (m, 2H), 1.18 (m, 26H), 0.80 (t, *J* = 6.2 Hz, 3H); ESI-MS (m/z): calculated for $[M+H]^+$: 362.3417, found 345.3234 ($[M-NH_2]$)

General method for thiourea formation

Compound **2** (2c: 3.98 g, 10 mmol) was dissolved in dry DMF together with thio-carbonyldiimidazole (thio-CDI, 0.89 g, 5 mmol). Triethylamine (NEt_3, 1.81 mL, 13 mmol) was added and the reaction was stirred at rt overnight under N_2. The solvent was removed under reduced pressure and the product was crystallised from ethyl acetate.

Yield: **4b**: 89.0%, **4c**: 97.0%

N,N'-Bis-(*(R)*-1-(4-hexadecyloxy)-phenylethyl)thiourea (4c)



^1H NMR (400 MHz, $CDCl_3$): δ 7.06-6.83(m, br, 4H), 6.73-6.89 (m, 4H), 5.91 (s, br, 1H), 4.92 (s, b, 1H), 3.89 (t, *J* = 6.5 Hz, 4H), 1.82 – 1.70 (m, 4H), 1.44 (d, *J* = 6.8 Hz, 6H), 1.28 (m, 52H), 0.88 (t, *J* = 6.7 Hz, 6H) ppm; ESI-MS (m/z): calculated for $[M+H]^+$: 733.6606, found 733.6600

Thiouronium iodide

Compound **4** (4c: 3.82 g, 5 mmol) was dissolved in dry DCM and methyl iodide (MeI, 0.47 mL, 7.5 mmol) were added. The reaction was stirred at rt under N_2 overnight. The solvent and excess MeI were evaporated and the product crystallised from EtOAc and used in the anion-exchange step. Yield: **6b**: 82.0%, **6c:** 78.1%

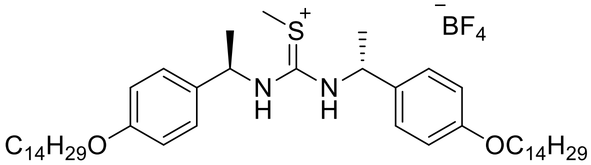
***S*-Methyl-*N*,*N*'-bis-((*R*)-1-(4-hexadecyloxy)-phenylethyl)thiouronium iodide (6c)**

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.97 – 6.79 (m, 6H), 6.74 (d, *J* = 7.6 Hz, 2H), 5.30 – 4.65 (b, m, 2H), 4.11 – 3.77 (m, 4H), 2.88 (bs, 3H), 1.84 – 1.73 (m, 4H), 1.53 – 1.41 (m, 10H), 1.42 – 1.22 (m, 52H), 0.89 (t, *J* = 6.8 Hz, 6H) ppm; ESI-MS (m/z): calculated for [M$^+$]: 779.6483, found 779.6508; [A$^-$]: 126.9050, found 126.9049.

General method for anion metathesis

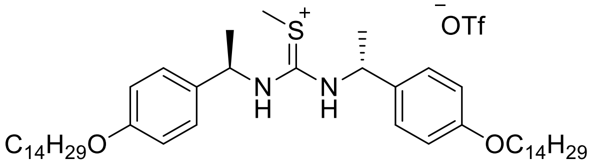
Compound **6 I** (**6c I**: 2.72 g, 3 mmol) was dissolved in DCM and stirred at rt overnight with an excess of Amberlyst A26 OH resin. The next morning the resin was filtered off. 1.1 eq of acid corresponding to the desired anion (HBF$_4$, HOTf) was added under stirring. The organic layer was washed with H$_2$O until the pH of the wash was neutral. The yields of exchange were between 95-98%.

***S*-Methyl-*N*, *N*'-bis-((*R*)-1-(4-tetradecyloxy)-phenylethyl)thiouronium tetrafluoroborate (6b BF$_4$)**



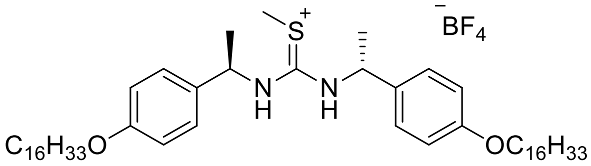
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.28 (b, 2H), 7.02 – 6.45 (m, 6H), 4.89 (s, 1H), 4.69 (b, s, 1H), 3.90 (br, m, 4H), 2.70 (s, 3H), 1.77 (s, 4H), 1.44 (d, *J* = 6.8 Hz, 6H), 1.40 – 1.21 (m, 44H), 0.88 (t, *J* = 6.9 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 180.07, 168.02, 159.31, 133.95, 131.60, 126.95, 115.00, 68.28, 55.73, 54.03, 32.07, 29.84, 29.81, 29.80, 29.77, 29.61, 29.51, 29.42, 26.23, 22.84, 14.27 ppm; ^{19}F NMR (376 MHz, CDCl$_3$) δ -148.33, -148.39 ppm; ESI-MS (m/z): calculated for [M$^+$]: 723.5857, found 723.5865; [A$^-$]: 87.0035, found 87.0034; elemental analysis calcd (%) for $C_{46}H_{79}BF_4N_2O_2S$: C: 68.12, H: 9.82, N: 3.45; found: C: 68.18; H: 9.77 N: 3.46

***S*-Methyl-*N*, *N*'-bis-((*R*)-1-(4-tetradecyloxy)-phenylethyl)thiouronium triflate (6b OTf)**



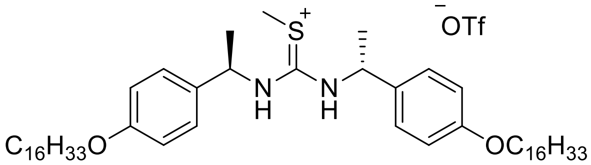
^{1}H NMR (400 MHz, CDCl$_3$) δ 6.81 (b, 4H), 6.73 (b, d, *J* = 7.6 Hz, 2H), 4.83 (b, 2H), 3.92 (dt, *J* = 13.3, 6.5 Hz, 4H), 2.66 (bs, 3H), 1.84 – 1.73 (m, 4H), 1.52 – 1.40 (m, 10H), 1.40 – 1.20 (m, 40H), 0.89 (t, *J* = 6.9 Hz, 6H) ppm; ^{19}F NMR (376 MHz,CDCl$_3$) δ -78.19 ppm; ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 206.94, 168.42, 159.35, 132.09, 127.15, 121.53, 119.26, 115.18, 68.33, 56.22, 32.08, 31.08, 29.86, 29.82, 29.79, 29.76, 29.60, 29.52, 29.40, 26.22, 22.84, 14.27; ESI-MS (m/z): calculated for [M+]: 723.5857, found 723.5846; [A-]: 148.9526, found 148.9527; elemental analysis calcd (%) for $C_{46}H_{79}F_3N_2O_5S$: C: 64.64, H: 9.12, N: 3.21; found: C: 64.44; H: 9.18, N: 3.18

S-Methyl-N, N'-bis-((R)-1-(4-hexadecyloxy)-phenylethyl)thiouronium tetrafluoroborate (6c BF_4)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (bd, *J* = 10.3 Hz, 2H), 6.82 (bdd, *J* = 38.5, 8.6 Hz, 6H), 4.80 (bs, 2H), 3.92 (br, m, 4H), 2.70 (bs, 3H), 1.90 – 1.73 (m, 4H), 1.50 – 1.40 (m, 4H), 1.40 – 1.20 (m, 54H), 0.88 (t, *J* = 6.9 Hz, 6H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -148.55 – -148.57, -148.62 ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.17, 127.48, 115.17, 87.20, 70.37, 68.10, 32.11, 29.86, 29.81, 29.80, 29.77, 29.61, 29.52, 29.41, 26.22, 22.86, 14.34 ppm; ESI-MS (m/z): calculated for [M+]: 779.6483, found 779.6515; elemental analysis calcd (%) for $C_{50}H_{87}BF_4N_2O_2S$: C: 69.26, H: 10.11, N: 3.23; found: C: 68.78; H: 10.85, N: 3.15

S-Methyl-N, N'-bis-((R)-1-(4-hexadecyloxy)-phenylethyl)thiouronium triflate (6c OTf)



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (s, b, 8H), 4.81 (s, 2H), 3.92 (t, *J* = 6.5 Hz, 4H), 2.67 (bs, 3H), 1.83 – 1.72 (m, 4H), 1.44 (dd, *J* = 14.9, 7.3 Hz, 4H), 1.41 – 1.20 (m, 54H), 0.88 (t, *J* = 7.0 Hz, 6H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.22; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 207.19, 168.18, 159.58, 131.87, 127.15, 115.42, 68.33, 32.08, 31.08, 29.86, 29.82, 29.79, 29.76, 29.60, 29.52, 29.40, 26.22, 22.84, 14.27 ppm; ESI-MS (m/z): calculated for [M+]: 779.6483, found 779.6505; [A$^-$]: 148.9526, found 148.9521

S 4.2 Synthesis of ester-thiouronium compounds

Synthesis of ester salt (1)

4-Alkoxybenzoic acid (12.5 mmol) was refluxed with an excess of thionyl chloride at 80 °C for 2 h. After this time, the excess $SOCl_2$ was removed by evaporation, the acid chloride product was dissolved in $CHCl_3$ and transferred under N_2 to a solution of (R)-4-hydroxy-α-methylbenzylamine hydrobromide (10 mmol) in TFA at 0 °C. The reaction was stirred overnight and allowed to warm to room temperature. The product was precipitated with Et_2O, filtered and crystallised from $CHCl_3/Et_2O$. Yield: **1a**: 88.5%, **1b**: 89.8%, **1c**: 76.1%.

(R)-4-(1-aminoethyl)phenyl 4-(hexadecyloxy)benzoate (1c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.95 – 6.92 (m, 2H), 4.57 (q, *J* = 7.1 Hz, 1H), 4.02 (t, *J* = 6.5 Hz, 2H), 1.88 – 1.75 (m, 5H), 1.46 (dd, *J* = 14.9, 7.2 Hz, 2H), 1.40 – 1.17 (m, 24H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm; ESI-MS (m/z): calculated for $[M+H]^+$: 482.3629, found 482.3615, 465.3357 $[M-NH_2+H]^+$

Thiourea (3)

Compound **1c** (5.63 g, 10 mmol) was dissolved in dry DMF together with thio-CDI (0.89 g, 5 mmol) under N_2. Triethylamine (1.81 mL, 13 mmol, 1.3 mol. eq.) was added and the reaction was stirred at rt overnight. The solvent was removed and the product crystallised from EtOAc. Yield: **3a**: 67.1%, **3b**: 81.7%, **3c**: 95.0%.

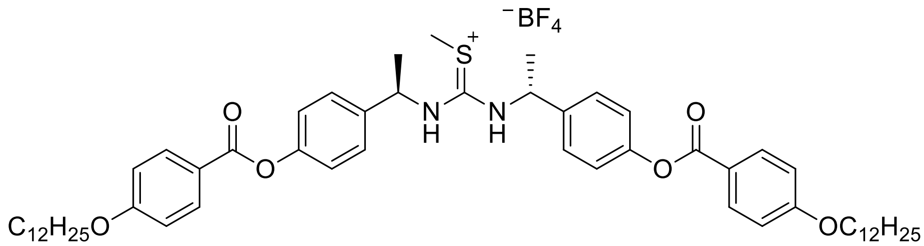
***N,N'*-Bis-((*R)*- 1-(phenylethyl-4-(4-hexadecyloxy)-benzoate)thiourea (3c)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 4H), 7.24 – 7.14 (m, 4H), 7.10 (d, *J* = 8.2 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 4H), 6.47 (br s, 1H), 5.22 (br,s, 1H), 4.00 (t, *J* = 6.5 Hz, 4H), 1.86 – 1.76 (m, 6H), 1.51 (d, *J* = 6.6 Hz, 6H), 1.48 – 1.40 (m, 4H), 1.40 – 1.23 (m, 48H), 0.87 (t, *J* = 6.6 Hz, 6H) ppm; APCI-MS (m/z): calculated for $[M+H]^+$: 1005.6749, found 1005.6713

Thiouronium tetrafluoroborate

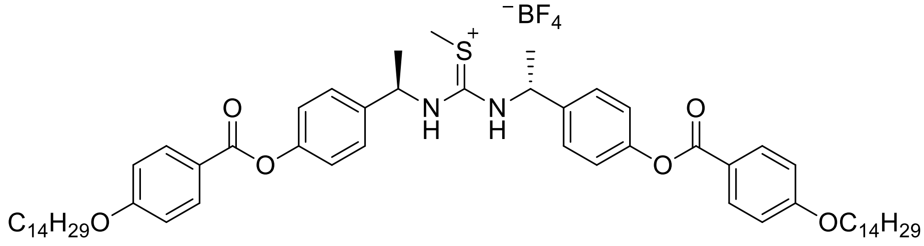
Compound **3c** (5.03 g, 5 mmol) was stirred with Me_3OBF_4 (2.22 g, 15 mmol) in dry DCM overnight at rt. The solvent was removed *in vacuo* and the product crystallised twice from EtOAc. Yield: **5a**: 70.2%, **5b**: 75.1%, **5c**: 74.7%

***S*-Methyl-*N,N'*-bis-((*R)*- 1-(phenylethyl-4-(4-dodecyloxy)-benzoate)thiouronium tetrafluoroborate (5a BF$_4$)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 4H), 7.46 (br, 3H), 7.25 – 7.03 (br, m, 5H), 6.89 (d, *J* = 7.7 Hz, 4H), 5.11 (br, s, 1H), 4.82 (br, s, 1H), 4.00 (t, *J* = 5.7 Hz, 4H), 2.72 (s, 3H), 1.86 – 1.76 (m, 4H), 1.61 (br, s, 6H), 1.52 – 1.40 (m, 4H), 1.41 – 1.20 (m, 32H), 0.88 (t, *J* = 6.9 Hz, 6H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -147.73, -147.79 ppm; $^{13}C\{^1H\}$ NMR (101 MHz, CDCl3) δ 192.13, 164.89, 163.73, 132.60, 114.18, 87.23, 68.48, 32.06, 29.81, 29.79, 29.75, 29.72, 29.54, 29.50, 29.26, 26.14, 22.84, 22.55, 14.27; ESI-MS (m/z): calculated for $[M^+]$: 907.5653, found 907.5680; elemental analysis calcd (%) for $C_{56}H_{79}BFN_2O_6S$: C: 67.59, H: 8.00, N: 2.82; found: C: 67.41; H: 7.89, N: 2.77

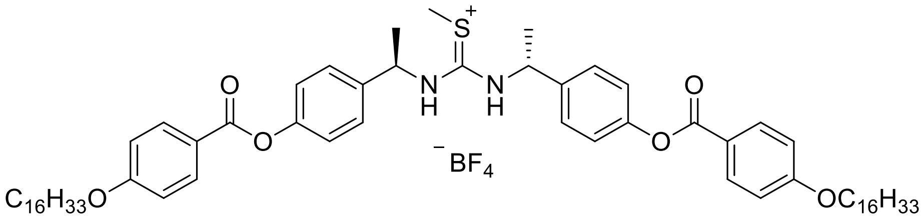
***S*-Methyl-*N,N'*-bis-((*R)*- 1-(phenylethyl-4-(4-tetradecyloxy)-benzoate)thiouronium tetrafluoroborate (5b BF$_4$)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 4H), 7.83 – 7.53 (br, 1H), 7.61 – 7.30 (br, m, 3H), 7.19 (br, s 4H), 6.89 (d, *J* = 6.3 Hz, 4H), 5.12 (br, s, 1H), 4.82 (br, s, 1H), 4.00 (s, 4H), 2.71 (s, 3H), 1.87 – 1.76 (m, 4H), 1.52 – 1.41 (m, 4H), 1.41 – 1.18 (m, 42H), 0.88 (t, *J* = 6.8 Hz, 6H) ppm; ^{19}F NMR (376

MHz, $CDCl_3$) δ -147.94 – -148.17 (m) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.91, 163.84, 137.38, 132.45, 114.41, 87.28, 68.48, 47.54, 32.12, 29.85, 29.83, 29.82, 29.81, 29.76, 29.73, 29.55, 29.51, 29.27, 26.11, 22.84, 22.48, 14.27, 8.94 ppm; ESI-MS (m/z): calculated for [M^+]: 963.6280, found 963.6240; elemental analysis calcd (%) for $C_{60}H_{87}BFN_2O_6S$: C: 68.55, H: 8.34, N: 2.66; found: C: 67.79; H: 8.25, N: 2.67

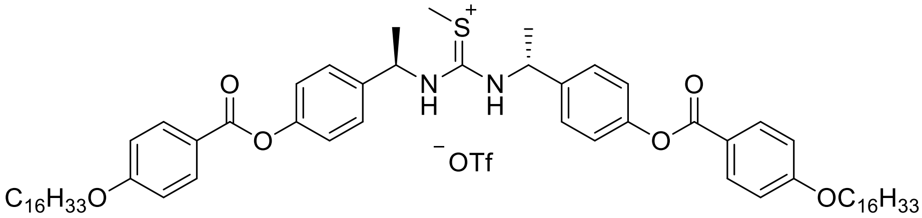
***S*-Methyl-*N,N'*-bis-((*R)*-1-(phenylethyl-4-(4-hexadecyloxy)-benzoate)thiouronium tetrafluoroborate (5c BF_4)**



$[\alpha]_D^{20}$ = -65.24 (*c* = 0.5, in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 4H), 7.76 (b,s, 1H), 7.52 – 7.31 (b, 2H), 7.24 – 7.04 (b, 6H), 6.89 (d, *J* = 8.0 Hz, 4H), 4.97 (bs, 1H), 4.84 (bs, 1H), 4.00 (t, *J* = 6.4 Hz, 4H), 2.72 (s, 3H), 1.88 – 1.76 (m, 4H), 1.58 (bs, 8H), 1.45 (td, *J* = 13.9, 6.6 Hz, 4H), 1.40 – 1.19 (m, 46H), 0.87 (t, *J* = 6.9 Hz, 6H) ppm; ^{19}F NMR (376 MHz,$CDCl_3$) δ -148.27, -148.32 ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.15, 164.96, 163.85, 137.51, 132.43, 127.03 (br), 122.87 (br), 121.28, 114.41, 68.47, 47.50, 32.06, 29.84, 29.83, 29.82, 29.80, 29.76, 29.72, 29.56, 29.51, 29.26, 22.90, 22.47, 14.28, 8.95 ppm; ESI-MS (m/z): calculated for [M^+]: 1019.6905, found 1019.6910; elemental analysis calcd (%) for $C_{64}H_{95}BF_4N_2O_6S$: C: 69.42, H: 8.65, N: 2.53; found: C: 69.22; H: 8.66, N: 2.53

Thiouronium triflate

Compound **3c** (1.0 g, 1 mmol) was stirred with methyl triflate (0.16 mL, 1.5 mmol) in dry DCM overnight at rt under N_2. The solvent was removed *in vacuo* and the product was crystallised twice from EtOAc. Yield: 72.3%



***S*-Methyl-*N,N'*-bis-((*R)*-1-(phenylethyl-4-(4-hexadecyloxy)-benzoate)thiouronium triflate (5c OTf)**

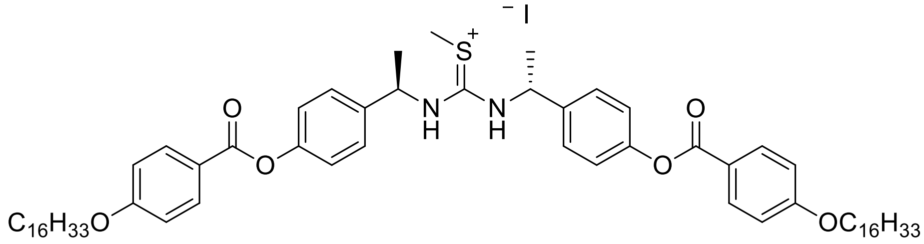
$[\alpha]_D^{20}$ = -49.24 (*c* = 0.5 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.7 Hz, 4H), 7.50 – 7.29 (br, 2H), 7.17 (br, s, 4H), 6.90 (d, *J* = 8.5 Hz, 4H), 5.11 (br, s, 1H), 4.88 (br, s,1H), 4.01 (t, *J* = 6.5 Hz, 4H), 2.67 (br, s, 3H), 1.86 – 1.76 (m, 4H), 1.65 (d, *J* = 18.7 Hz, 6H), 1.52 – 1.42 (m, 4H), 1.42 – 1.20 (m, 48H), 0.88 (t, *J* = 6.7 Hz, 6H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.21 ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.18, 164.89, 163.77, 132.45, 127.22, 122.93, 121.24, 114.43, 68.49, 32.08, 29.85, 29.84, 29.81, 29.76, 29.73, 29.55, 29.52, 29.26, 26.14, 22.84, 14.32 ppm; ESI-MS (m/z): calculated for $[M^+]$: 1019.6905, $[A^-]$: 148.9526; found: 1019.6912, 148.9527; elemental analysis calcd (%) for $C_{65}H_{95}F_3N_2O_9S_2$: C: 66.75, H: 8.19, N: 2.40; found: C: 66.35; H: 8.12, N: 2.30

Thiouronium Iodide

Compound **3** (3c: 2.01 g, 2 mmol) was stirred with MeI (0.37 mL, 6 mmol) in dry DMF (40 mL) overnight at rt. The solvent was removed *in vacuo* and the product crystallised twice from EtOAc.

Yield: **5a**: 43.2% **5b**: 60.1% **5c**: 87.8%

S-Methyl-*N,N'*-bis-((*R)*- 1-(phenylethyl-4-(4-hexadecyloxy)-benzoate)thiouronium iodide (5c I)



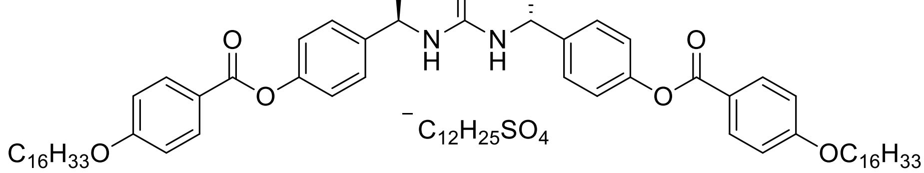
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 4H), 7.22 (s, 8H), 6.93 (d, *J* = 8.8 Hz, 4H), 4.02 (t, *J* = 6.6 Hz, 4H), 2.81 (bs, 3H), 1.89 – 1.64 (m, 10H), 1.51 – 1.41 (m, 4H), 1.41 – 1.18 (m, 48H), 0.88 (t, *J* = 6.9 Hz, 6H) ppm; ESI-MS (m/z): calculated for $[M]^+$: 1019.6905, found 1019.6864

Anion metathesis

Compound **5 I** (5c: 1.15g, 1mmol) was dissolved in hot MeOH (50 mL), after which a salt of the desired anion (NH_4PF_6, $LiNTf_2$, or sodium dodecylsulfate – 2.5 to 3 mol. equiv.) was added. The solution was stirred at 60 °C for 2 h. After this time the product was precipitated by the slow addition of H_2O. The product was filtered and washed again with H_2O, followed by crystallisation from EtOAc.

Yields: **5c DOS**: 72.0%, **5c Tf_2N**: 86.0%, **5c PF_6:** 82.6%

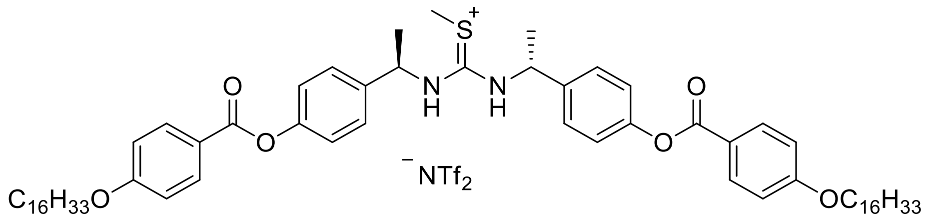
S-Methyl-*N,N'*-bis-((*R)*- 1-(phenylethyl-4-(4-hexadecyloxy)-benzoate)thiouronium dodecylsulfate (5c DOS)



$[\alpha]_D^{20}$= -33.98 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 4H), 7.50 – 7.28 (b, 4H), 7.17 (d, *J* = 7.7 Hz, 4H), 6.92 (d, *J* = 8.7 Hz, 4H), 5.06 (s, 2H), 4.10 (t, *J* = 6.8 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 4H), 2.6 (br, s, 3H), 1.85 – 1.78 (m, 4H), 1.70 (p, *J* = 7.0 Hz, 6H), 1.54 – 1.41 (m, 4H), 1.42 – 1.24

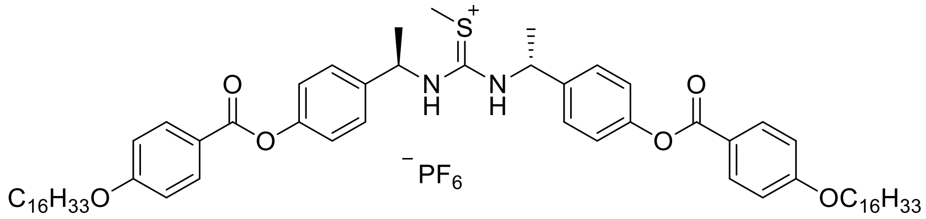
(m, 48H), 1.22 (s, 10H), 0.87 (q, *J* = 6.8 Hz, 8H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 164.91, 163.73, 132.43, 127.40, 122.68, 121.40, 114.42, 87.30, 68.44, 32.05, 29.85, 29.83, 29.81, 29.79, 29.76, 29.72, 29.60, 29.54, 29.54, 29.52, 29.50, 29.26, 26.14, 26.04, 22.84, 14.31; ESI-MS (m/z): calculated for [M$^+$]:1019.6905, found 1019.6933; [A$^-$]: 265.1479, found 265.1468; elemental analysis calcd (%) for $C_{76}H_{120}N_2O_{10}S_2$: C: 70.99, H: 9.41, N: 2.18; found: C: 70.86; H: 9.33, N: 2.22

S-Methyl-*N,N'*-bis-((*R)*-1-(phenylethyl-4-(4-hexadecyloxy)-benzoate)thiouronium bistrifluoromethanesulfonate (5c Tf$_2$N)



$[\alpha]_D^{20}$ = -65.86 (*c* = 1.0 in CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, *J* = 8.7 Hz, 4H), 7.57 – 7.27 (br, m, 2H), 7.10 (br, 4H), 6.90 (d, *J* = 8.3 Hz, 4H), 6.81 (br, 2H), 5.06 (br, s, 1H), 4.70 (br, s, H), 4.01 (t, *J* = 6.3 Hz, 2H), 2.69 (s, 3H), 1.87 – 1.75 (m, 4H), 1.60 (br, s, 6H), 1.51 – 1.41 (m, 4H), 1.41 – 1.19 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 6H) ppm; ^{19}F NMR (376 MHz, CDCl$_3$) δ -78.57 ppm; ^{13}C{^{1}H} NMR (101 MHz, DCM-d$_2$) δ 168.87, 165.19, 164.27, 132.69, 127.57, 121.98, 121.54, 118.75, 114.84, 68.96, 51.00, 32.50, 30.24, 30.23, 30.19, 30.16, 29.96, 29.94, 29.68, 26.60, 23.31, 14.43 ppm; ESI-MS (m/z): calculated for [M$^+$]: 1019.6905, found 1019.6890, [A$^-$]: 279.9178, 279.9190; elemental analysis calcd (%) for $C_{66}H_{95}F_6N_3O_{10}S_3$: C: 60.95, H: 7.36, N: 3.23; found: C: 61.44; H: 7.44, N: 3.17

S-Methyl-*N,N'*-bis-((*R)*-1-(phenylethyl-4-(4-hexadecyloxy)-benzoate)thiouronium hexafluorophosphate (5c PF$_6$)



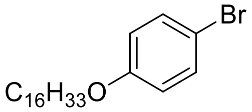
$[\alpha]^{20}_D$ = -86.88 (*c* = 0.5 in CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, *J* = 8.3 Hz, 4H), 7.42 (br, 2H), 7.35 – 6.97 (br, m, 4H), 6.91 (d, *J* = 7.2 Hz, 4H), 6.71 (br, 2H), 5.05 (br, s, 1H), 4.80 (br, s, 1H), 4.01 (t, 4H), 2.71 (s, 3H), 1.81 (m, 4H), 1.59 (br, 6H), 1.53 – 1.41 (m, 4H), 1.42 – 1.20 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 6H) ppm; ^{19}F NMR (376 MHz, CDCl$_3$) δ -69.79, -71.68 ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 164.87, 163.80, 132.46, 127.14, 121.11, 114.45, 68.50, 32.07, 29.85, 29.84, 29.82, 29.81, 29.76, 29.73, 29.56, 29.51, 29.26, 26.14, 22.84, 22.59, 14.28 ppm; ESI-MS (m/z): calculated for [M$^+$]: 1019.6905, found 1019.6934, [A$^-$]: 144.9647, 144.9650; elemental analysis calcd (%) for $C_{64}H_{95}F_6N_2O_6PS$: C: 65.95, H: 8.22, N: 2.40; found: C: 66.13; H: 8.25, N: 2.37

S4.3 Synthesis of biphenyl ILCs

Alkylation of 4-bromophenol

4-Bromophenol (2.0 g, 11.56 mmol), 1-bromohexadecane (4.6 mL, 15.03 mmol) and potassium hydroxide (1.30 g, 23.12 mmol) were stirred at 80 °C in acetonitrile overnight. On cooling, the salt precipitate was filtered off, the solvent was removed *in vacuo* and the product crystallised from EtOAc yielding 96.6% of the target compound as a colourless solid.

4-Hexadecyloxybromobenzene

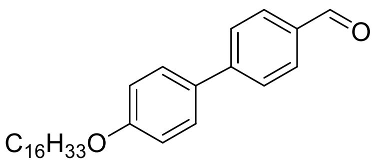


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 9.0 Hz, AA'XX', 2H), 6.77 (d, *J* = 9.0 Hz, AA'XX', 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 1.82 – 1.70 (m, 2H), 1.49 – 1.38 (m, 2H), 1.38 – 1.17 (m, 24H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; APCI-MS (m/z): calculated for [M+H]: 397.2101/399.2100, found 397.2095/399.2082

Suzuki coupling

4-Hexadecyloxybromobenzene (4.31 g, 10.84 mmol) and sodium carbonate (32.52 mmol, 3.45 g) were dissolved in a 1:1 mixture of THF and water (120 mL). The mixture was outgassed under an argon flow for 1 hr and 4-formylbenzeneboronic acid (1.79 g, 11.92 mmol) and tetrakistriphenylphosphine palladium (0.376 g, 2 mol%) were added. The reaction was stirred at 65 °C under N_2 overnight. The reaction mixture was then partitioned between DCM and H_2O and the aqueous layer was extracted three times with DCM. The combined organic fractions were concentrated and the product was purified by column chromatography in DCM followed by recrystallisation from acetone. Yield: 3.78 g (82.5%) as a colourless solid.

4-Hexadecyloxy-4'-formylbiphenyl (7)

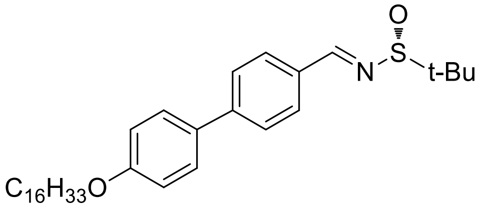


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), δ 7.92 (d, J = 8.3 Hz, AA'XX', 2H), 7.72 (d, J = 8.3 Hz, AA'XX', 2H), 7.58 (d, J = 8.8 Hz, AA'XX', 2H), 7.00 (d, J = 8.8 Hz, AA'XX', 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.48 (dt, *J* = 15.0, 6.8 Hz, 2H), 1.43 – 1.18 (m, 24H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; APCI-MS (m/z): calculated for [M+H]: 423.3258, found 423.3271

Sulfinylimide

Compound **7** (2.27 g, 5.13 mmol), *(R)-tert*-butanesulfinamide (0.622 g, 5.13 mmol) and $Ti(OEt)_4$ (10.26 mmol, 2.64 mL) were dissolved in dry THF (50 mL) and stirred at rt under N_2 overnight. The reaction mixture was poured into brine, filtered, and the filter cake was washed three times with EtOAc. The filtrate was also extracted three times with EtOAc. The combined organic fractions were concentrated and purified by column chromatography in 2:1 Hex:EtOAc yielding 1.94 g (72.0%) as an off-white waxy solid.

4-Hexadecyloxy-4'-*(R)-tert*-butanesulfinylimide-biphenyl (8)

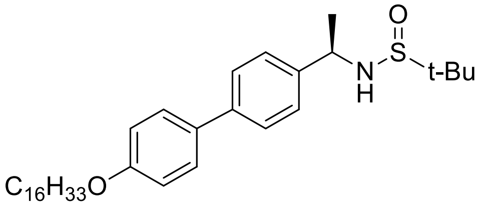


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 7.90 (d, J = 8.4 Hz, AA'XX', 2H), 7.66 (d, J = 8.4 Hz, AA'XX', 2H), 7.57 (d, J = 8.8 Hz, AA'XX', 2H), 6.99 (d, J = 8.8 Hz, AA'XX', 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.52 – 1.40 (m, 2H), 1.41 – 1.19 (m, 34H), 0.88 (t, J = 6.8 Hz, 3H) ppm; ESI-MS (m/z): calculated for [M+H]: 526.3713, found 526.3688

Methylation

Compound **8** (2.5 g, 4.75 mmol) was dissolved in anhydrous THF (125 mL) under N_2 and cooled to -15 °C. A solution of MeMgBr in diethyl ether (3 M, 1.58 mL) was added slowly under stirring and the reaction was allowed to warm to rt overnight. After this time the reaction was quenched with saturated NH_4Cl solution (75 mL) and the aqueous layer was extracted three times with EtOAc. The product was purified by column chromatography in 1:1 Hex/EtOAc. Yield: 64.9%

N-(*(R)*-1-(4'-(hexadecyloxy)-[1,1'-biphenyl]-4-yl)ethyl)-2-methylpropane-2-sulfinamide (9)



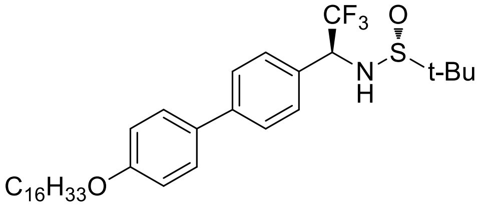
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, AA'XX', 2H), 7.52 (d, *J* = 1.3 Hz, AA'XX', 2H), 7.42 (d, *J* = 8.3 Hz, AA'XX', 2H), 6.96 (d, *J* = 8.8 Hz, AA'XX', 2H), 4.99 – 4.91 (m, 1H), 3.99 (t, *J* = 6.3 Hz, 2H), 3.68 – 3.60 (m, 1H), 1.85 – 1.76 (m, 2H), 1.54 (d, *J* = 6.5 Hz, 3H), 1.51 – 1.40 (m, 2H), 1.41 – 1.22 (m, 32H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm; ESI-MS (m/z): calculated for $[M+H]^+$, $[M+Na]^+$: 542.4026, 564.3846, found 542.4025, 564.3845

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 1.3 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H).

Trifluoromethylation

Compound **8** (2.5 g, 4.75 mmol) was dissolved together with TBAT (1.28 g, 2.38 mmol) in anhydrous THF (125 mL) under N_2 and cooled to -15 °C. TMS-CF3 (0.77 mL, 5.23 mmol) was added dropwise over the course of 30 – 60 min and the reaction was allowed to stir for 24 h at temperatures below 0 °C. After this time the reaction was quenched by pouring into saturated NH_4Cl solution and the aqueous layer was extracted three times with EtOAc. The product was purified by column chromatography in 2:1 Hex/EtOAc. Yield: 1.17 g (41.5%) of desired diastereomer.

***(R)*-N-[(S)-(1-(4'-hexadecyloxy-)biphenyl-2,2,2-trifluoroethyl]-*tert*-butanesulfinamide (10)**

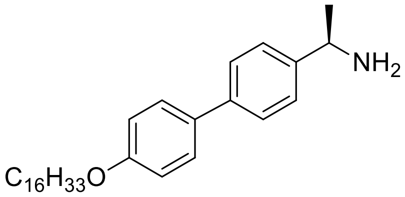


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.3 Hz, AA'XX', 2H), 7.50 (d, J = 8.8 Hz, , AA'XX', 2H), 7.47 (d, J = 8.3 Hz, AA'XX', 2H), 6.97 (d, J = 8.7 Hz, AA'XX', 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 3.71 (d, J = 6.1 Hz, 1H), 1.87 – 1.75 (m, 2H), 1.53 – 1.41 (m, 2H), 1.41 – 1.20 (m, 32H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.78 (d, *J* = 7.5 Hz, 3F) ppm; APCI-MS (m/z): calculated for $[M+H]^+$: 596.3744 , found 596.3754

Amine

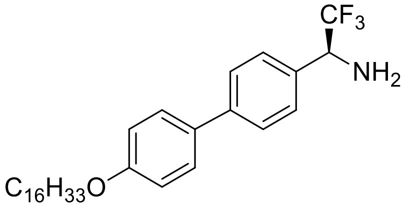
9 (0.80 g, 1.34 mmol) or **10** were dissolved in 1:1 dioxane/MeOH (20 mL) and 4 eq of concentrated HCl (0.46 mL) were added. The reaction was stirred at rt for 2 h. The solvent was removed and the residue dissolved in DCM and washed with 10% aq NaOH, backextracted twice with DCM, followed by the removal of the solvent. Respective yields of amines: 89.0% and 90.0%

***(R)*-1-(4'-hexadecyloxy)biphenylethylamine**



^{1}H NMR (400 MHz, acetone-*d$_6$*) δ 7.78 – 7.60 (m, 2H), 7.62 – 7.45 (m, 4H), 7.11 – 6.87 (m, 2H), 4.64 – 4.53 (m, 1H), 3.98 (t, *J* = 6.5 Hz, 1H), 1.81 – 1.70 (m, 2H), 1.67 (d, *J* = 6.9 Hz, 3H), 1.51 – 1.40 (m, 2H), 1.28 (d, *J* = 39.5 Hz, 23H), 0.83 (t, *J* = 6.7 Hz, 3H); ESI-MS (m/z): calculated for $[M+H]^+$: 438.3730, found 438.3732, 421.3475 ($M-NH_2$)

***(S)*-1-(4'-hexadecyloxy-)biphenyl-2,2,2-trifluoroethylamine**



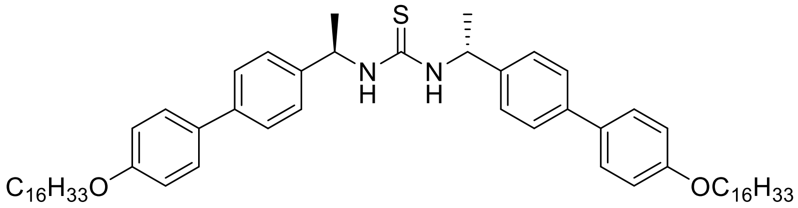
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.54 (m, 2H), 7.54 – 7.43 (m, 4H), 7.01 – 6.93 (m, 2H), 4.51 – 4.37 (m, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 1.87 – 1.74 (m, 2H), 1.52 – 1.41 (m, 2H), 1.43 – 1.20 (m, 23H), 0.88 (t, *J* = 6.5 Hz, 3H) ppm; ^{19}F-NMR (376 MHz, $CDCl_3$): δ -73.80 (d, *J* = 7.4 Hz, 3F) ppm; APCI-MS (m/z): calculated for $[M+H]^+$: 492.3448 , found 491.3361, 475.3171 $[M-NH_2]$

Thiourea

1 equivalent of the above amine (0.51 mmol) was dissolved in dry DCM (40 mL) under N_2 together with thio-CDI (0.054 g, 0.25 mmol) and stirred overnight. Afterwards the DCM was removed in vacuo

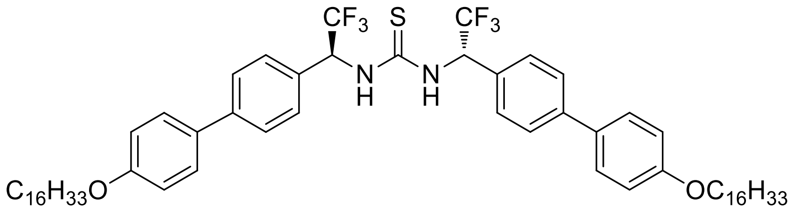
and the product crystallised from EtOAc (**11**) or purified by column chromatography in 2:1 Hex/EtOAc (**12**). Yield: **11**: 60.2 %, **12**: 62.5%

N, N'-bis-((*S)*-1-(4'-hexadecyloxy)-biphenylethyl)thiourea (11)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (b,m, 6H), 6.87 (d, *J* = 8.7 Hz, AA'XX', 2H), 3.97 (t, *J* = 6.6 Hz, 1H), 1.87 – 1.73 (m, 1H), 1.51 (d, *J* = 6.8 Hz, 1H), 1.45 (dd, *J* = 14.9, 8.0 Hz, 1H), 1.41 – 1.18 (m, 7H), 0.88 (t, *J* = 6.8 Hz, 1H), APCI-MS: calculated for $[M+H]^+$: 917.6953, found 917.6966

N, N'-bis-((*S)*-1-(4'-hexadecyloxy)-biphenyl-2,2,2-trifluoroethyl)thiourea (12)

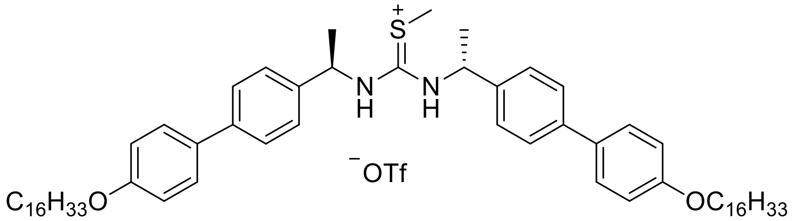


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.47 (m, 2H), 7.50 – 7.39 (m, 2H), 7.39 – 7.27 (m,br, 2H), 7.00 – 6.88 (m, 2H), 6.53 – 6.44 (m, 1H), 6.17 (d, *J* = 14.7 Hz, 1H), 3.99 (t, *J* = 6.6 Hz, 2H), 1.91 – 1.73 (m, 2H), 1.48 (dt, *J* = 15.1, 7.0 Hz, 2H), 1.42 – 1.16 (m, 24H), 0.88 (dd, *J* = 8.1, 5.6 Hz, 3H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.04 (d, *J* = 5.2 Hz, broad, 6F); APCI-MS (m/z): calculated for $[M+H]^+$: 1025.6387, found 1025.6347

Methylation using MeOTf

11 (0.05 g, 0.055 mmol) was dissolved in a mixture of DCM and DMF (30 mL) with MeOTf (18.05 uL, 0.165 mmol) and stirred under N_2 overnight. The solvent was removed under vacuum and the product was crystallised from EtOAc. Yield: 78.8%

S-Methyl-N, N'-bis-((*R)*-1-(4'-hexadecyloxy)-biphenylethyl)thiouronium triflate (13 OTf)

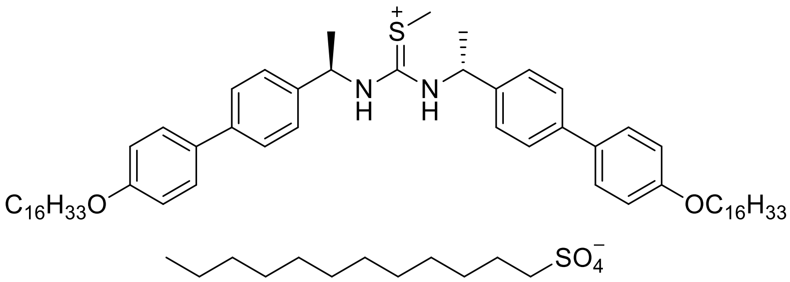


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.31 (m, 12H), 6.91 (d, *J* = 8.6 Hz, 4H), 5.17 (bs, 1H), 4.87 (bs, 1H), 3.98 (t, *J* = 6.6 Hz, 4H), 2.72 (b, s, 3H), 1.87 – 1.76 (m, 4H), 1.76 – 1.60 (m, 4H), 1.54 – 1.40 (m, 4H), 1.41 – 1.15 (m, 48H), 0.87 (t, *J* = 6.9 Hz, 6H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.24; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.17, 159.14, 141.09, 138.42, 132.35, 128.09, 127.53, 126.20, 124.40, 121.90, 119.24, 114.98, 68.26, 56.12, 32.08, 29.86, 29.82, 29.81, 29.78, 29.63, 29.52, 29.51, 26.26, 22.85, 22.67, 14.27; ESI-MS (m/z): calculated for [M$^+$]: 931.7109, found 931.7143, [A$^-$]: 148.9526, 148.9525; CHN: expct., found for $C_{63}H_{95}F_3N_2O_5S_2$: C: 69.96, 69.077; H: 8.85, 8.732; N: 2.59, 2.568

Methylation MeI/Anion metathesis

11 (0.2 g, 0.22 mmol) was stirred in DCM (30 mL) with 4 eq MeI (54.8 uL, 0.88 mmol) overnight. The solvent was removed in vacuo and the product crystallised from EtOAc. This was then used directly in the anion metathesis. The iodide salt was dissolved in hot MeOH and sodium dodecyl sulfate (0.66 mmol, 0.19 g) was added. The product was precipitated with H_2O and crystallised from EtOAc. Yield: 74.5%

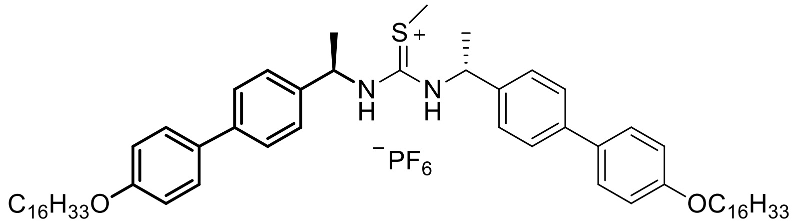
***S*-Methyl-*N, N*'-bis-(*(R)*-1-(4'-hexadecyloxy)-biphenylethyl)thiouronium dodecylsulfate (13 DOS)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, br, 12H), 6.92 (d, *J* = 8.5 Hz, 4H), 5.03 (s, b, 2H), 4.12 (t, *J* = 6.8 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 4H), 2.59 (s, br, 3H), 1.88 – 1.76 (m, 4H), 1.76 – 1.63 (m, 6H), 1.53 – 1.43 (m, 4H), 1.42 – 1.18 (m, 66H), 0.87 (m, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.95, 132.66, 128.03, 127.29, 126.56, 114.97, 68.34, 68.26, 32.08, 29.86, 29.81, 29.79, 29.77, 29.65, 29.61, 29.56, 29.52, 29.49, 26.25, 26.08, 22.84, 14.27; ESI-MS (m/z): calculated for [M$^+$]: 931.7109, found 931.7148, [A$^-$]: 265.1479, 265.1487; CHN: expct., found for $C_{74}H_{120}N_2O_6S_2$: C: 74.20, 74.087; H: 10.10, 10.007; N: 2.34, 2.452

***S*-Methyl-*N, N'*-bis-(*(R)*-1-(4'-hexadecyloxy)-biphenylethyl)thiouronium hexafluorophosphate (13 PF_6)**

13 I was dissolved in hot MeOH and 3 eq of NH_4PF_6 were added under stirring. The product precipitated with H2O and was crystallised from EtOAc. Yield: 72.9%



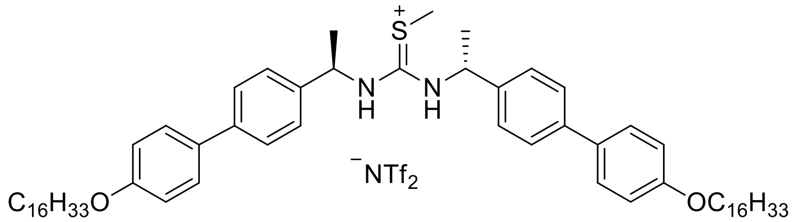
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.31 (b,m, 10H), 6.91 (d, *J* = 7.6 Hz, 4H), 6.65 (bs, 2H), 4.92 (b,s, 1H), 4.78 (b, s, 1H), 3.98 (t, *J* = 6.6 Hz, 4H), 2.77 (s, 3H), 1.94 – 1.70 (m, 5H), 1.52 – 1.42 (m, 4H), 1.41 – 1.17 (m, 53H), 0.87 (t, *J* = 6.8 Hz, 6H); ^{19}F NMR (376 MHz,$CDCl_3$) δ -70.18, -72.07; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.38, 159.28, 137.54, 132.57, 132.08, 130.22, 128.43, 128.13, 127.24, 126.53, 125.82, 115.05, 68.29, 55.67, 32.08, 29.86, 29.82, 29.80, 29.78, 29.62, 29.52, 29.49, 26.25, 22.85, 22.64, 14.27; ESI-MS (m/z): calculated for [M^+]: 931.7109, found 931.7124, [A^-]: 144.9647, 144.9642; CHN: expct., found for $C_{62}H_{95}N_2O_2PS$: C: 69.11, 68.81; H: 8.89, 8.77; N: 2.60, 2.57

Anion exchange via ion exchange resin

As the direct methylation using MeO_3BF_4 gave impure product in this case, the following compounds were prepared via anion exchange resin.

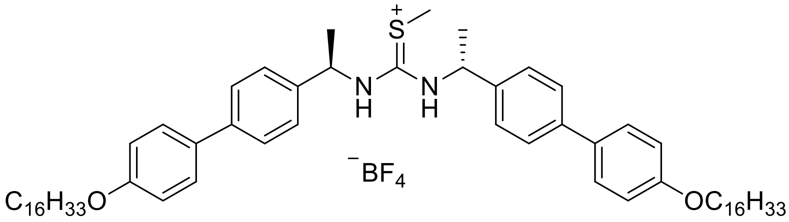
13 DOS was stirred with Amberlyst A26 resin overnight in DCM. The resin was filtered off and a slight excess of acid (1.05 eq) of the desired anion was added under stirring. ($HNTf_2$/HBF_4). The DCM was washed with H_2O until the pH of the wash was neutral. Yields: **13 Tf_2N:** 86.7%, **13 BF_4:** 72.3%

***S*-Methyl-*N, N'*-bis-(*(R)*-1-(4'-hexadecyloxy)-biphenylethyl)thiouronium bistrifluoromethanesulfonate (13 Tf_2N)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, b, 12H), 6.91 (d, *J* = 7.4 Hz, 4H), 4.91 (bs, 2H), 3.98 (t, *J* = 6.2 Hz, 4H), 2.48 (s, 3H), 1.86 – 1.75 (m, 4H), 1.52 – 1.42 (m, 6H), 1.41 – 1.16 (m, 48H), 0.88 (t, *J* = 6.5 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.87, 133.08, 128.09, 127.01, 126.62, 126.18, 114.90, 68.25, 32.08, 29.86, 29.84, 29.82, 29.79, 29.77, 29.61, 29.52, 29.50, 26.25, 22.84, 14.27; ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.54; ESI-MS (m/z): calculated for [M^+]: 931.7109, found 931.7137, [A^-]: 279.9178, 279.9180; CHN: expct., found for $C_{64}H_{95}F_6N_3O_6S_3$: C: 63.39, 67.80; H: 7.90, 8.67; N: 3.47, 2.80

_S_-Methyl-_N, N'_-bis-(_(R)_-1-(4'-hexadecyloxy)-biphenylethyl)thiouronium tetrafluoroborate (13 BF_4)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.30 (b, m, 12H), 6.91 (d, *J* = 8.7 Hz, 4H), 4.85 (s, 2H), 3.98 (t, *J* = 6.6 Hz, 4H), 2.55 (b, s, 3H), 1.86 – 1.76 (m, 4H), 1.52 – 1.40 (m, 7H), 1.40 – 1.19 (m, 51H), 0.88 (t, *J* = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.96, 132.57, 128.04, 127.56, 126.46, 114.96, 68.27, 32.09, 29.87, 29.83, 29.80, 29.78, 29.62, 29.53, 29.51, 26.26, 22.85, 14.28, 1.18; ^{19}F NMR (376 MHz, $CDCl_3$) δ -151.70, -151.76; ESI-MS (m/z): calculated for [M+]: 931.7109, found 931.7155; CHN expct., found for $C_{62}H_{95}BF_4N_2O_2S$: C: 69.77, 69.53; H: 8.97, 8.92; N: 2.62, 2.56

S4.4 Anion binding

Preparation of tetrabutylammonium salts of chiral carboxylic acids

Equimolar amounts of tetrabutylammonium hydroxide and desired carboxylic acid were added together in water under stirring followed by removal of the solvent.

Binding assays with thiouroniums

Equimolar amounts (0.03 mmol) of the tetrabutylammonium carboxylate and the thiouronium salt were dissolved together in $CDCl_3$ and added to an NMR tube.