Supporting Information

Table of contents

S-1. Synthetic procedure

S1.1. Synthesis of (*R*)-**1**

5-Octyl-5′′-[3-fluoro-4-{(*R*)-2-octyloxy}phenyl]-2,2′:5′,2′′-terthiophene: (*R*)-**1**

To a stirred solution of (*R*)-**5** (1.12 g, 2.40 mmol, 1.00 eq.), **4** (968 mg, 3.00 mmol, 1.25 eq.) and $Pd(PPh_3)_4$ (112 mg, 0.097 mmol, 0.04 eq.) in dry THF (55 mL) was added K_2CO_3 aqueous solution (2.0 M, 36.0 mL, 72 mmol, 30 eq.) under argon atmosphere. The reaction mixture was refluxed for 8 hours. After cooling to room temperature, H_2O (50 mL) was added. The product was extracted with *n*-hexane (100 mL). The organic layer was washed with brine (50 mL) and water (50 mL). The aqueous layer was extracted with *n*-hexane (50 mL ×3) and all organic layers were combined. The extract was dried over Na_2SO_4. After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: *n*-hexane/toluene = 10/1→5/1; v/v). The product was recrystallized from *n*-hexane and dried *in vacuo* to afford (*R*)-**1** as a yellow solid (1.03 g, 2.01 mmol, 74% yield).

S1.2. Synthesis of (*R*)-**2**

5-Octyl-5′′-({3-fluoro-4-[(*R*)-2-octyloxy]phenyl}ethynyl)-2,2′:5′,2′′-terthiophene: (*R*)-**2**

To a stirred solution of **6** (700 mg, 1.59 mmol, 1.00 eq.), (*R*)-**7** (514 mg, 2.07 mmol, 1.30 eq.), CuI (30 mg, 0.08 mmol, 0.05 eq.),and $Pd(PPh_3)_4$ (184 mg, 0.16 mmol, 0.10 eq.) in dry THF (50 mL) was added triethylamine (50 mL) under argon atmosphere. The reaction mixture was refluxed for 43 hours. After cooling to room temperature, the reaction mixture was filtrated to remove the insoluble residue. The solvents were removed from the filtrate by vacuum evaporation. Then, the resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane/toluene = 10/1→5/1; v/v). The product was recrystallized from *n*-hexane with small amount of methanol, and dried *in vacuo* to afford (*R*)-**2** as a yellow solid (490 mg, 0.81 mmol, 51 % yield).

S1.3. Synthesis of (*R*)-**3**

5,5′-Bis({3-fluoro-4-[(*R*)-2-octyloxy]phenyl}ethynyl)-2,2′-bithiophene: (*R*)-**3**

To a stirred solution of **8** (650 mg, 2.00 mmol, 1.00 eq.), (*R*)-**7** (1.24 g, 5.00 mmol, 2.50 eq.), CuI (76 mg, 0.40 mmol, 0.20 eq.) and $Pd(PPh_3)_4$ (280 mg, 0.40 mmol, 0.20 eq.) in dry THF (50 mL) was added triethylamine (50mL) under argon atmosphere. The reaction mixture was refluxed for 69 hours. After cooling to room temperature, the reaction mixture was filtrated to remove the insoluble residue. The solvents were removed from the filtrate by vacuum evaporation. Then, the resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane/toluene = 10/1→5/1; v/v). The product was recrystallized from *n*-hexane with small amount of methanol. After drying *in vacuo*, the desired compound (*R*)-**3** was obtained as a yellow solid (560 mg, 0.85 mmol, 42 % yield).

S-2. ^{1}H and ^{13}C NMR spectra

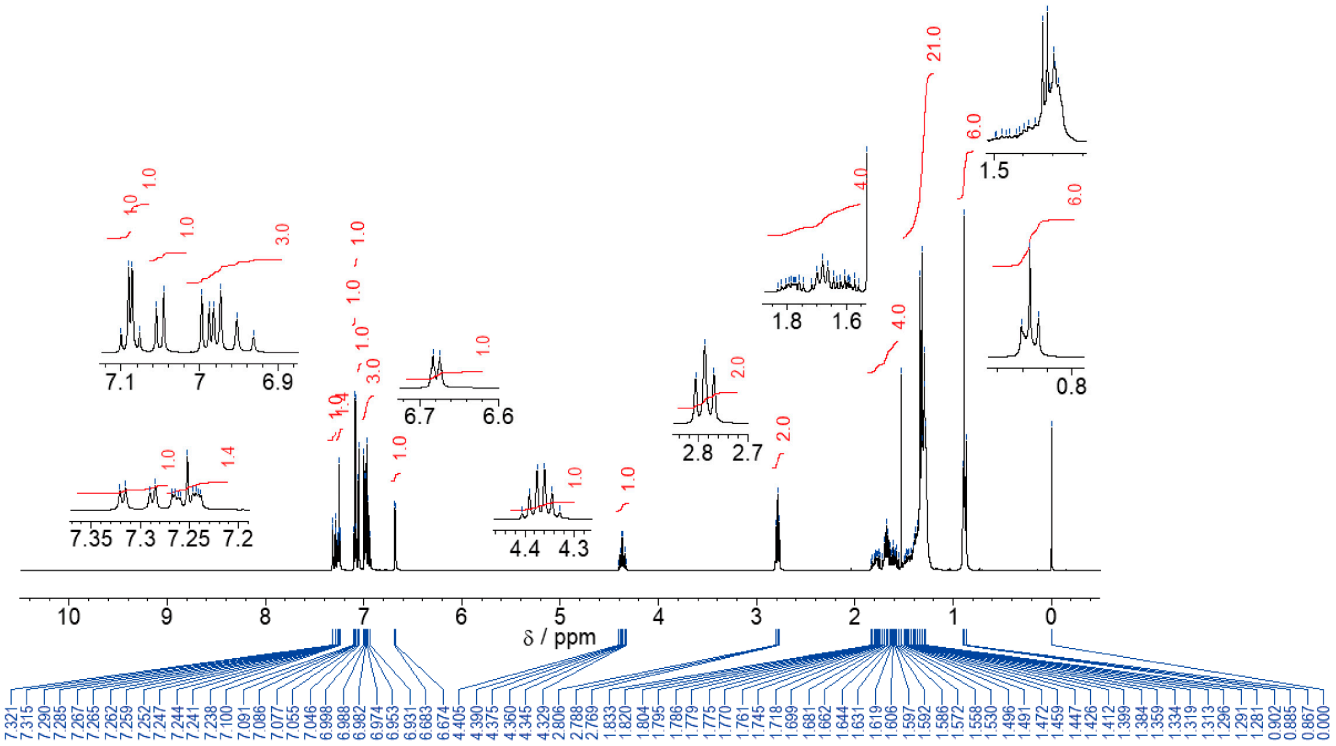

Figure S1. ^{1}H NMR spectrum of (*R*)-**1**.

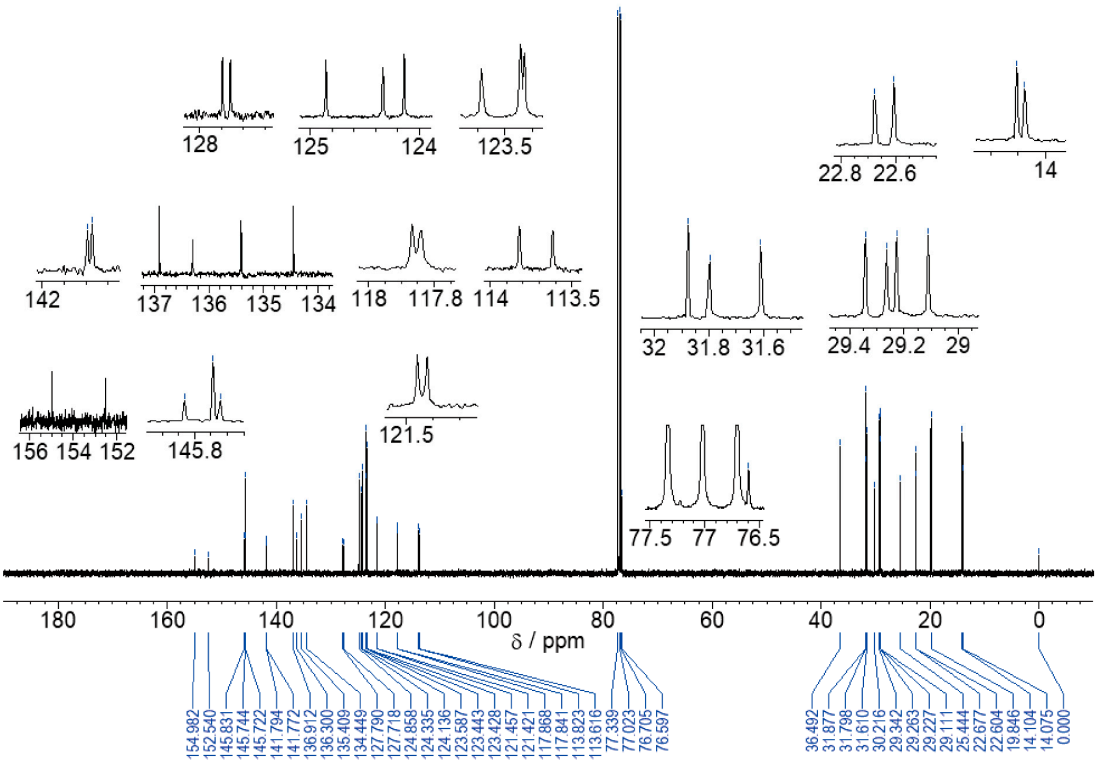

Figure S2. ^{13}C NMR spectrum of (*R*)-**1**.

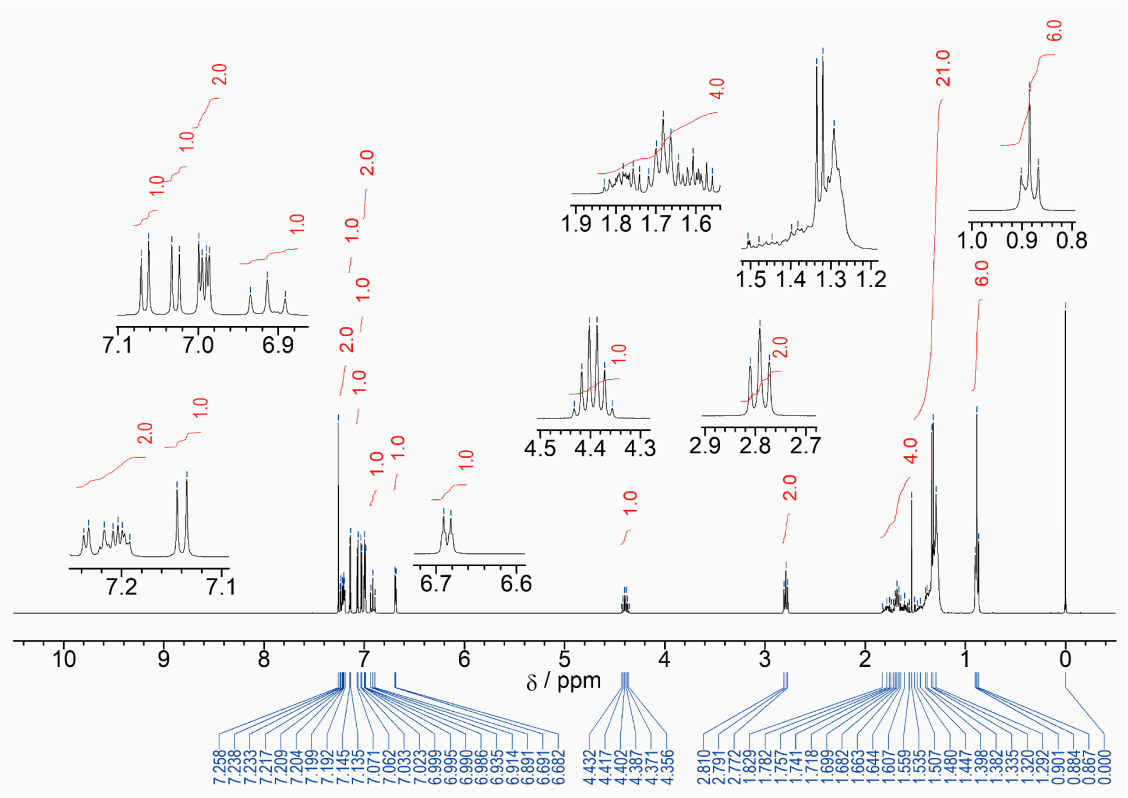

Figure S3. ^{1}H NMR spectrum of (*R*)-**2**.

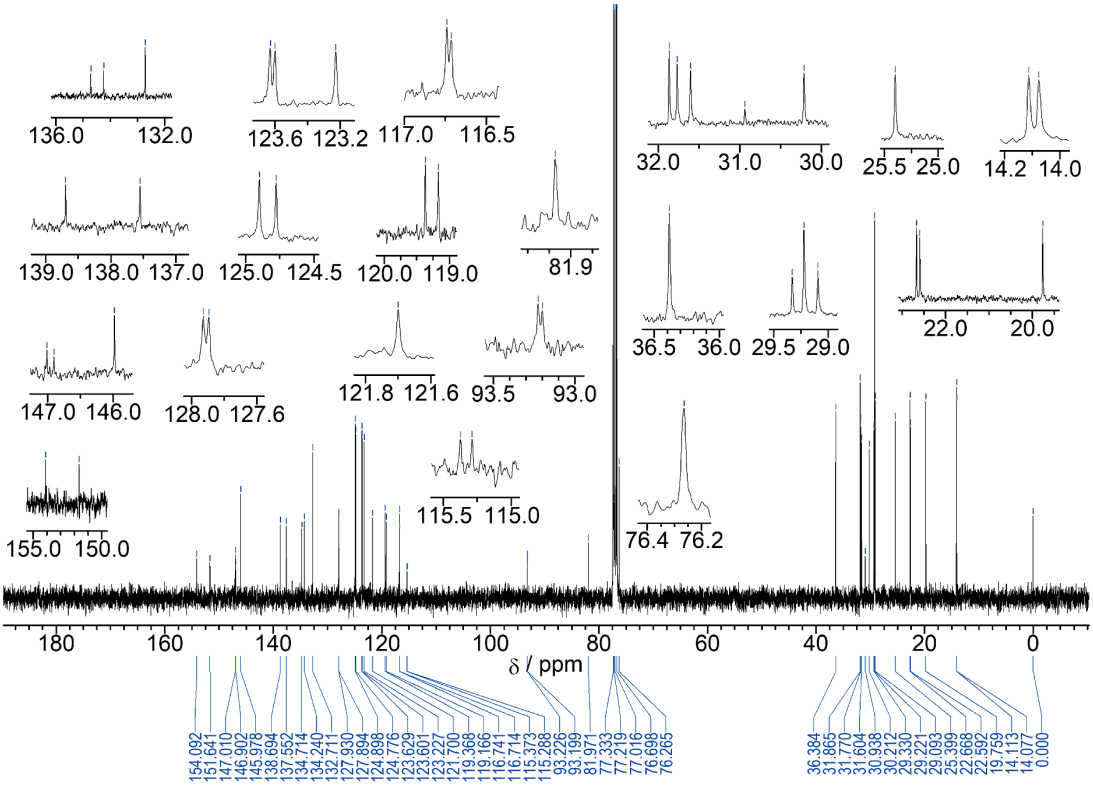

Figure S4. ^{13}C NMR spectrum of (*R*)-**2**.

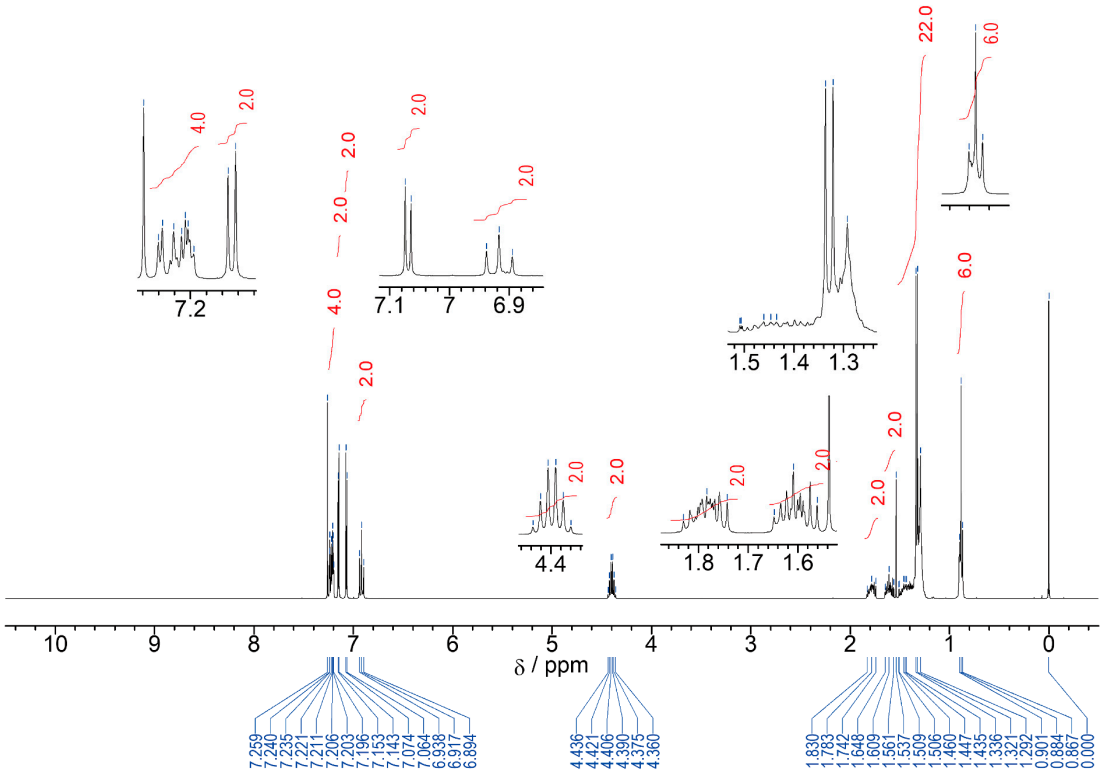

Figure S5. ^{1}H NMR spectrum of (*R*)-**3**.

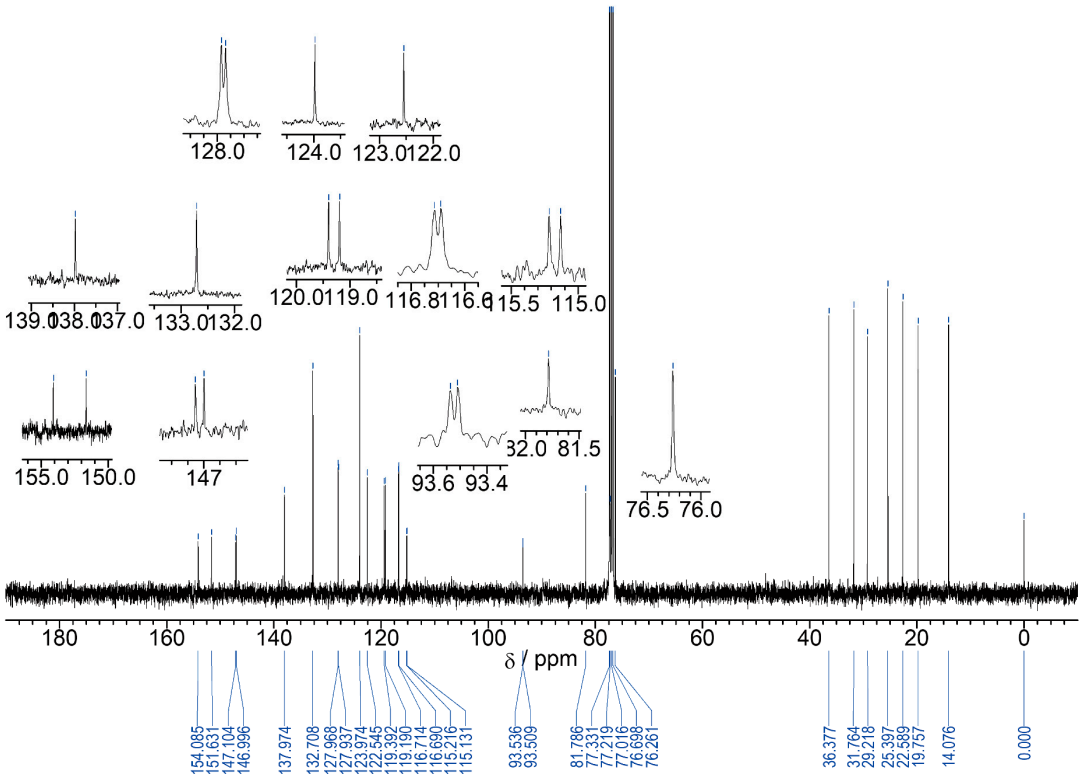

Figure S6. ^{13}C NMR spectrum of (*R*)-**3**.

S-3. High resolution ESI mass spectra

Formula $[M]^+$	Theoretical *m/z*	Found *m/z*	RDB	Delta *m/z* (ppm)	Resolution
$C_{34}H_{43}FOS_3$	582.2455	582.2456	13.5	0.2	30933

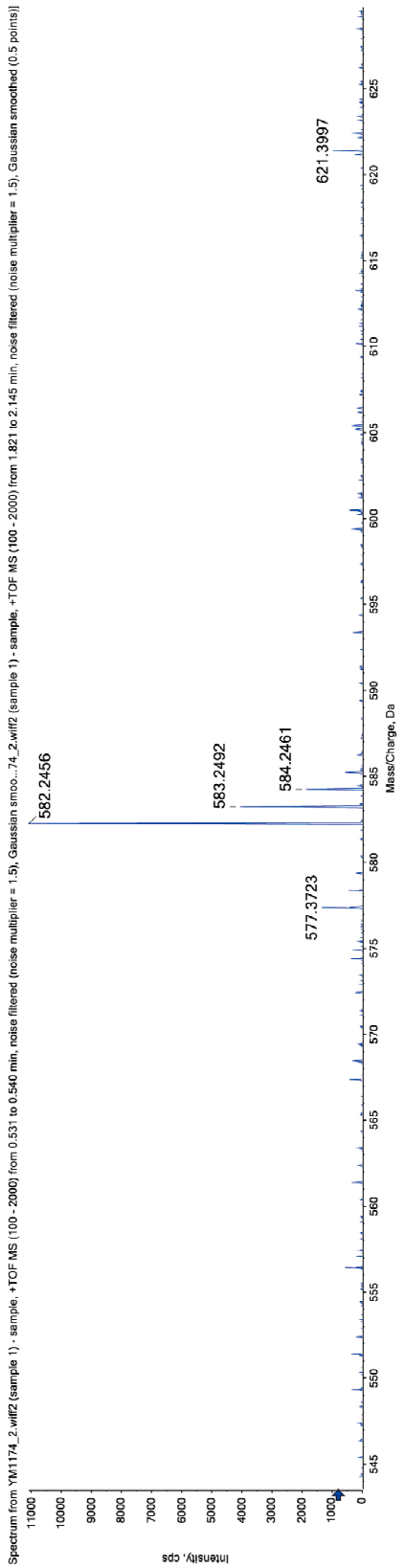

Figure S7. High resolution ESI mass spectrum of (*R*)-**1**.

Formula $[M]^+$	Theoretical *m/z*	Found *m/z*	RDB	Delta *m/z* (ppm)	Resolution
$C_{36}H_{43}FOS_3$	606.2455	606.2453	15.5	-0.3	27123

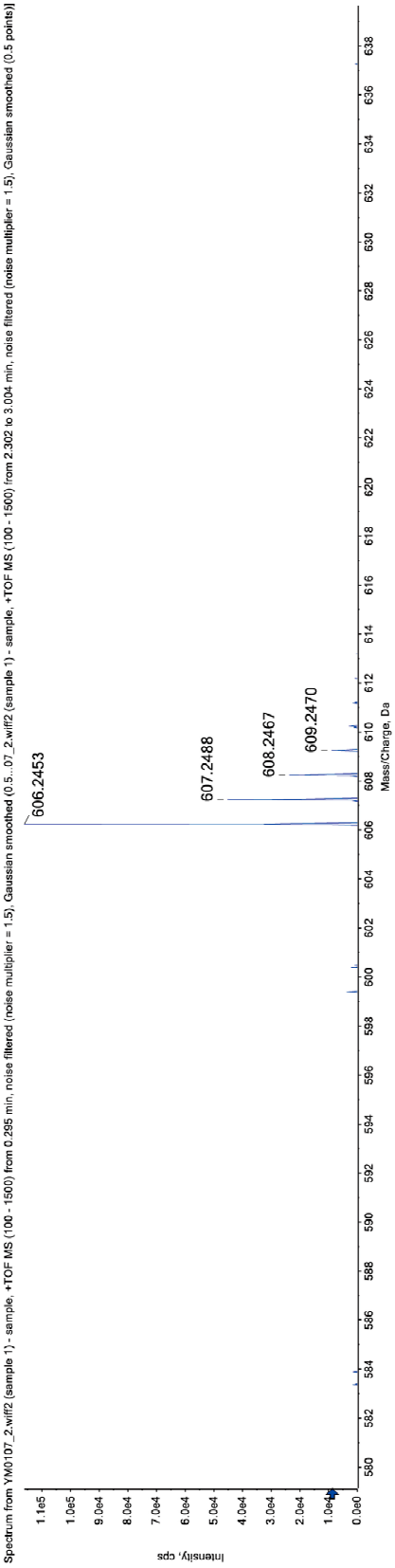

Figure S8. High resolution ESI mass spectrum of (*R*)-**2**.

Formula $[M+H]^+$	Theoretical *m/z*	Found *m/z*	RDB	Delta *m/z* (ppm)	Resolution
$C_{40}H_{45}F_2O_2S_2$	659.2824	659.2828	18.0	0.7	26337

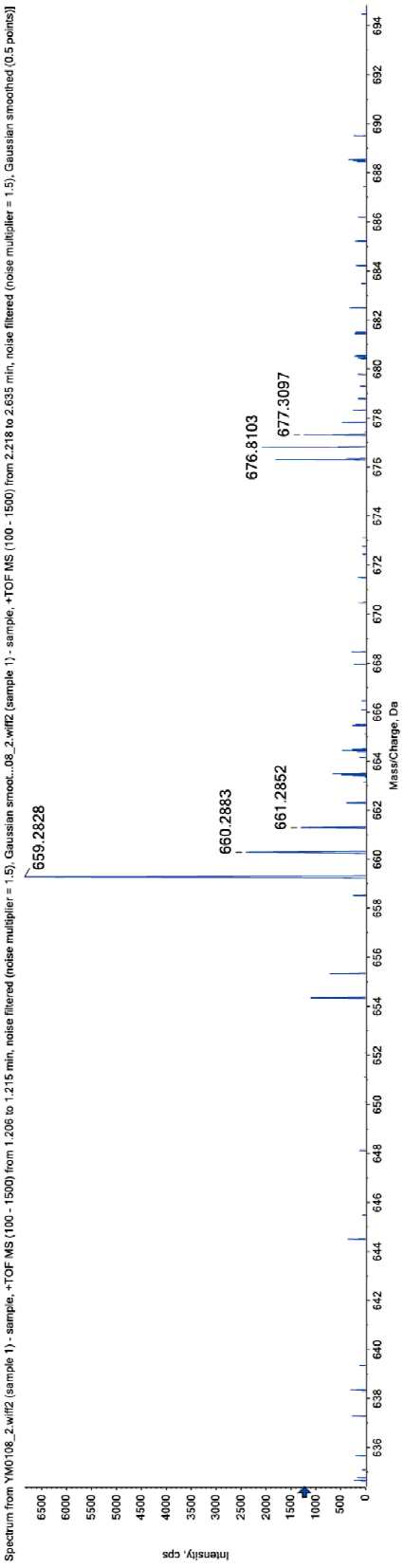

Figure S9. High resolution ESI mass spectrum of (*R*)-**3**.