Electronic Supporting Information

Fullerene-Based Liquid Crystals Acting as Acid-Sensitive Fluorescent Probes

Laura Pérez,[a] Julie Lenoble,[b] Joaquín Barberá,*[c] Pilar de la Cruz,[a] Robert Deschenaux*[b] and Fernando Langa*[a]

[a]*Instituto de Nanociencia, Nanotecnología y Materiales Moleculares (INAMOL), Universidad de Castilla-La Mancha, Campus de la Fábrica de Armas, 45071 Toledo, Spain*

[b]*Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, Case postale 158, 2009 Neuchâtel, Switzerland*

[c]*Química Orgánica, Facultad de Ciencias-Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*

Techniques. See the following reference: S. Campidelli, L. Pérez, J. Rodríguez-López, J. Barberá, F. Langa and R. Deschenaux, *Tetrahedron*, 2006, **62**, 2115.

Synthesis of 2. A mixture of C_{60} (130 mg, 0.18 mmol), **3** (67.8 mg, 0.12 mmol) and glycine (45 mg, 0.6 mmol) was heated under reflux for 6 h in degassed anhydrous chlorobenzene (30 mL) under inert atmosphere. After removal of the solvents, the residue was purified by column chromatography (silica gel, toluene/hexane 8:2). The product was centrifuged with CH_3OH and *n*-pentane to give **2** (28%) as a dark brown solid. ^{1}H NMR (200 MHz, $CDCl_3$) δ/ppm: 0.95 (t, 12H, *J* = 7.0 Hz), 1.23-1.44 (m, 8H), 1.49-1.67 (m, 8H), 3.28 (t, 8H, *J* = 7.4 Hz), 4.90 (d, 1H, , *J* = 10.4 Hz), 5.13 (d, 1H, *J* = 10.4 Hz), 5.80 (s, 1H), 6.61 (d, 4H, *J* = 8.5 Hz), 6.90 (d, 2H, *J* = 16.4 Hz), 7.07 (d, 2H, *J* = 16.4 Hz), 7.38 (d, 4H, *J* = 8.5 Hz), 7.53 (s, 1H), 7.70 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ/ppm: 156.3, 154.2, 153.9, 153.3, 151.4, 148.1, 147.4, 146.7, 146.5, 146.4, 146.1, 145.6, 145.5, 145.2, 144.8, 144.6, 144.5, 144.3, 143.3, 143.1, 142.7, 142.4, 141.9, 141.3, 140.3, 140.1, 139.9, 139.1, 138.3, 138.1, 136.6, 136.3, 136.1, 129.7, 129.1, 128.0, 124.5, 124.2, 123.6, 111.8, 73.1, 62.0, 51.0, 29.9, 20.5, 14.2. IR (KBr) ν/cm^{-1}: 525 (C_{60}). MALDI-TOF MS *m*/*z* calculated for $C_{100}H_{55}N_3$: 1297.44 (M^+), found: 1297.97 (M^+). UV–vis (CH_2Cl_2) λ_{max}/nm (log ε): 257 (4.8), 325 (4.5), 374 (4.5), 431 (3.7).

Synthesis of 1a. A mixture of **4a** (100 mg, 0.036 mmol) and thionyl chloride (0.1 mL, 1.3 mmol) was heated under reflux for 7 h in anhydrous CH_2Cl_2. The solvent was evaporated under reduced pressure and a solution of **2** (35 mg, 0.025 mmol) in CH_2Cl_2 (30 mL) and anhydrous pyridine (3.7 mg, 0.05 mmol) was added. The mixture was stirred at room temperature for 30 minutes. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, toluene/ethyl acetate 3:2). A further purification by centrifugation with CH_3OH afforded **1a** in quantitative yield as a green solid. ^{1}H NMR (200 MHz, $CDCl_3$) δ/ppm 0.98 (t, 12H, *J* = 7.0 Hz), 1.23-1.44 (m, 68H), 1.82 (broad m, 28H), 3.31 (t, 8H, *J* = 7.4 Hz), 4.04 (t, 10H, *J* = 6.4 Hz), 4.39 (t, 10H, *J*= 6.6 Hz), 5.75 (d, 1H, *J* = 10.4 Hz), 5.82 (d, 1H, *J* = 10.4 Hz), 6.00 (s, 1H), 6.65 (d, 4H, *J* = 8.6 Hz), 6.99 (m, 10H), 7.11 (d, 2H, *J* = 16.2 Hz), 7.15-7.35 (m, 10H), 7.43 (d, 4H, *J* = 8.6 Hz), 7.62-7.77 (m, 24H), 7.88 (s, 1H), 7.92 (s, 2H), 8.12-8.24 (m, 18H), 8.38 (t, 2H, *J* = 1.6 Hz), 8.67 (t, 2H, *J* = 1.6 Hz), 8.98 (t, 1H, *J* = 1.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 164.8, 164.72, 164.7, 164.6, 164.4, 164.1, 163.6, 163.0, 155.5, 152.8, 151.8, 151.6, 151.5, 150.5, 148.0, 147.9, 147.4, 146.3, 146.2, 146.0, 145.6, 145.4, 145.3, 144.8, 144.5, 144.3, 143.0,

142.6, 142.0, 141.9, 141.7, 141.5, 140.3, 140.2, 139.7, 139.5, 139.4, 136.9, 136.6, 132.9, 132.6, 132.5, 132.4, 132.3, 131.1, 130.8, 130.0, 129.0, 128.7, 128.2, 127.6, 126.9, 126.8, 122.5, 121.2, 120.3, 118.8, 117.1, 114.5, 114.3, 111.3, 111.0, 70.0, 68.4, 68.3, 68.1, 65.8, 65.5, 50.8, 50.7, 38.7, 37.3, 37.1, 33.7, 33.4, 33.1, 32.7, 31.9, 31.7, 31.4, 30.0, 29.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.6, 27.0, 26.7, 25.9, 23.7, 22.6, 20.3, 19.7, 14.1, 13.9, 10.9. FT-IR (KBr) ν/cm^{-1}: 528 (C_{60}). MALDI-TOF MS *m*/*z* calculated for $C_{269}H_{219}N_7O_{30}$: 4026.583 (M^+), found: 4026.93 (M^+).

Synthesis of 1b. A mixture of **4b** (75 mg, 0.014 mmol) and thionyl chloride (0.04 mL, 0.5 mmol) was heated under reflux for 40 h in anhydrous CH_2Cl_2. The solvent was evaporated under reduced pressure and a solution of **2** (18 mg, 0.014 mmol) in CH_2Cl_2 (30 mL) and anhydrous pyridine (2.3 mg, 0.03 mmol) was added. The mixture was stirred at room temperature for 30 minutes. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, toluene/ethyl acetate 7:3). A further purification by centrifugation with CH_3OH afforded **1b** in quantitative yield as a green solid. ^{1}H NMR (200 MHz, $CDCl_3$) δ/ppm 0.95 (m, 12H, *J* = 13.5 Hz), 1.25-1.57 (m, 116H), 1.57-1.76 (broad m, 44H), 3.28 (t, 8H, *J* = 7.4 Hz), 4.03 (t, 18H, *J* = 6.3 Hz), 4.36 (t, 18H, *J* = 6.6 Hz), 5.71 (d, 1H, *J* = 10.4 Hz), 5.77 (d, 1H, *J* = 10.4 Hz), 6.21 (s, 1H), 6.62 (d, 4H, *J* = 8.8 Hz), 6.88-7.17 (m, 20H), 7.27-7.42 (m, 22H), 7.60-7.81 (m, 49H), 7.86 (d, 2H, *J* = 8.8 Hz), 8.12 (m, 30H), 8.35 (t, 6H, *J* = 1.4 Hz), 8.63 (t, 4H, *J* = 1.4 Hz), 8.92 (t, 3H, *J* = 1.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 166.0, 165.0, 164.9, 163.8, 163.0, 151.7, 151.2, 150.7, 148.2, 146.3, 145.5, 145.0, 142.8, 142.3, 139.9, 139.7, 136.8, 132.8, 132.5, 131.6, 131.0, 130.4, 130.2, 128.5, 128.2, 127.8, 127.1, 124.3, 122.7, 121.4, 119.0, 114.7, 114.5, 111.8, 111.5, 111.2, 68.5, 66.0, 50.9, 41.5, 34.8, 31.7, 29.6, 29.4, 29.2, 28.8, 26.1, 25.5, 22.8, 20.8, 20.5, 18.9, 14.5, 14.3, 14.2, 11.6. IR (KBr) ν/cm^{-1}: 527 (C_{60}). MALDI-TOF MS *m*/*z* calculated for $C_{421}H_{359}N_{11}O_{58}$: 6495.55 ($M^+$), found: 6495.56 ($M^+$).

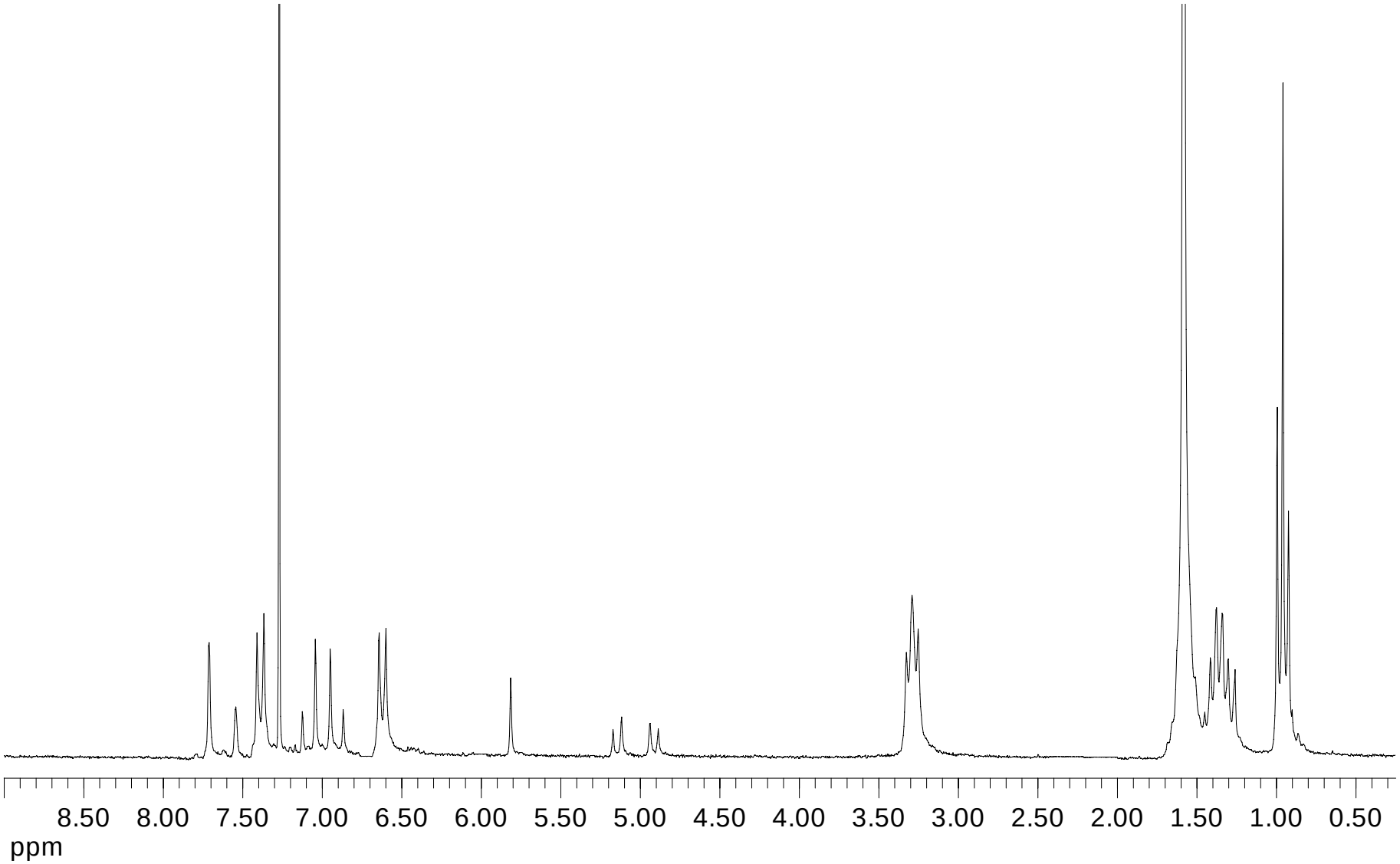

Figure S1. ^{1}H NMR spectrum of compound **2**

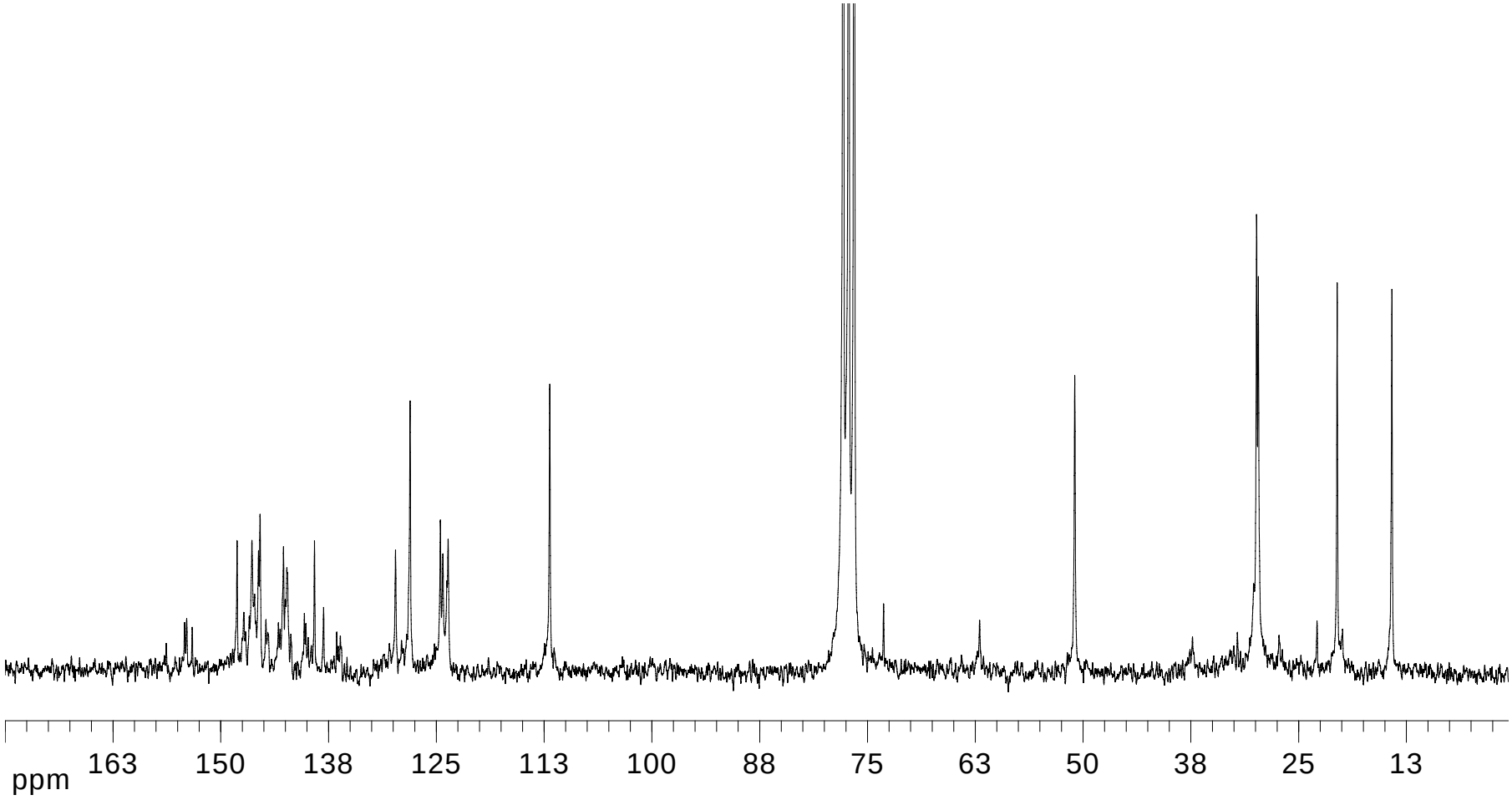

Figure S2. ^{13}C NMR spectrum of compound **2**

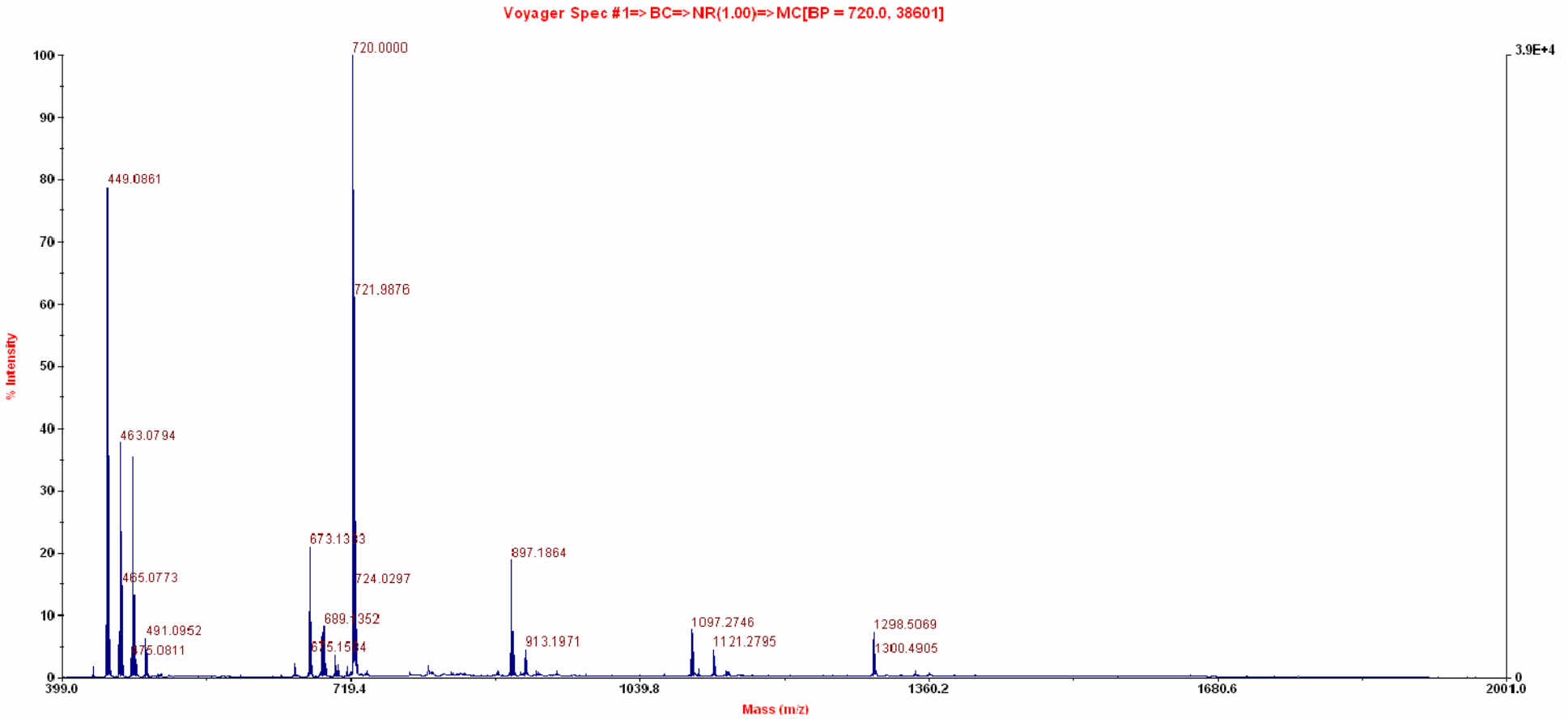

Figure S3. MALDI-TOF MS spectrum of compound **2**

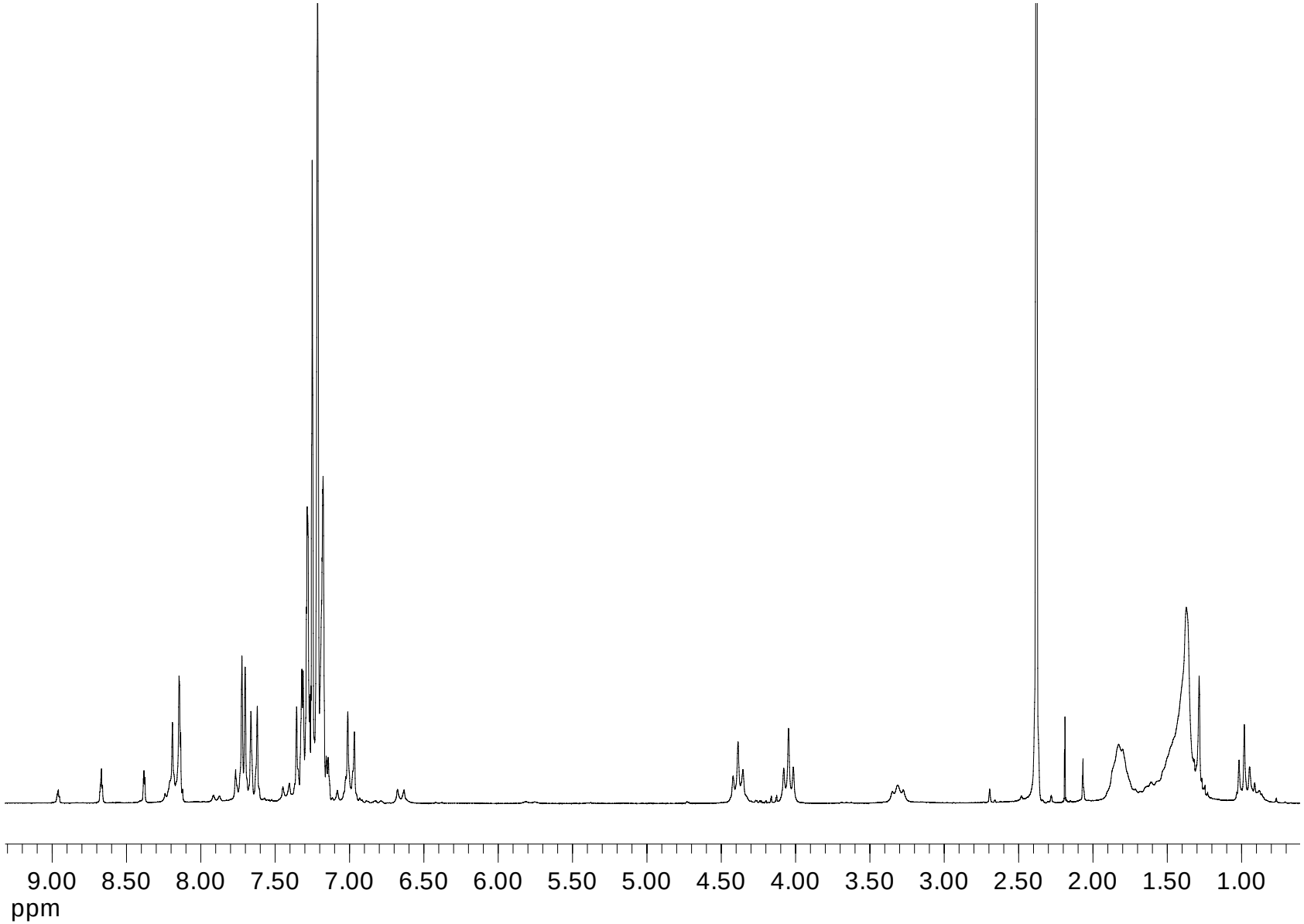

Figure S4. ^{1}H NMR spectrum of compound **1a**

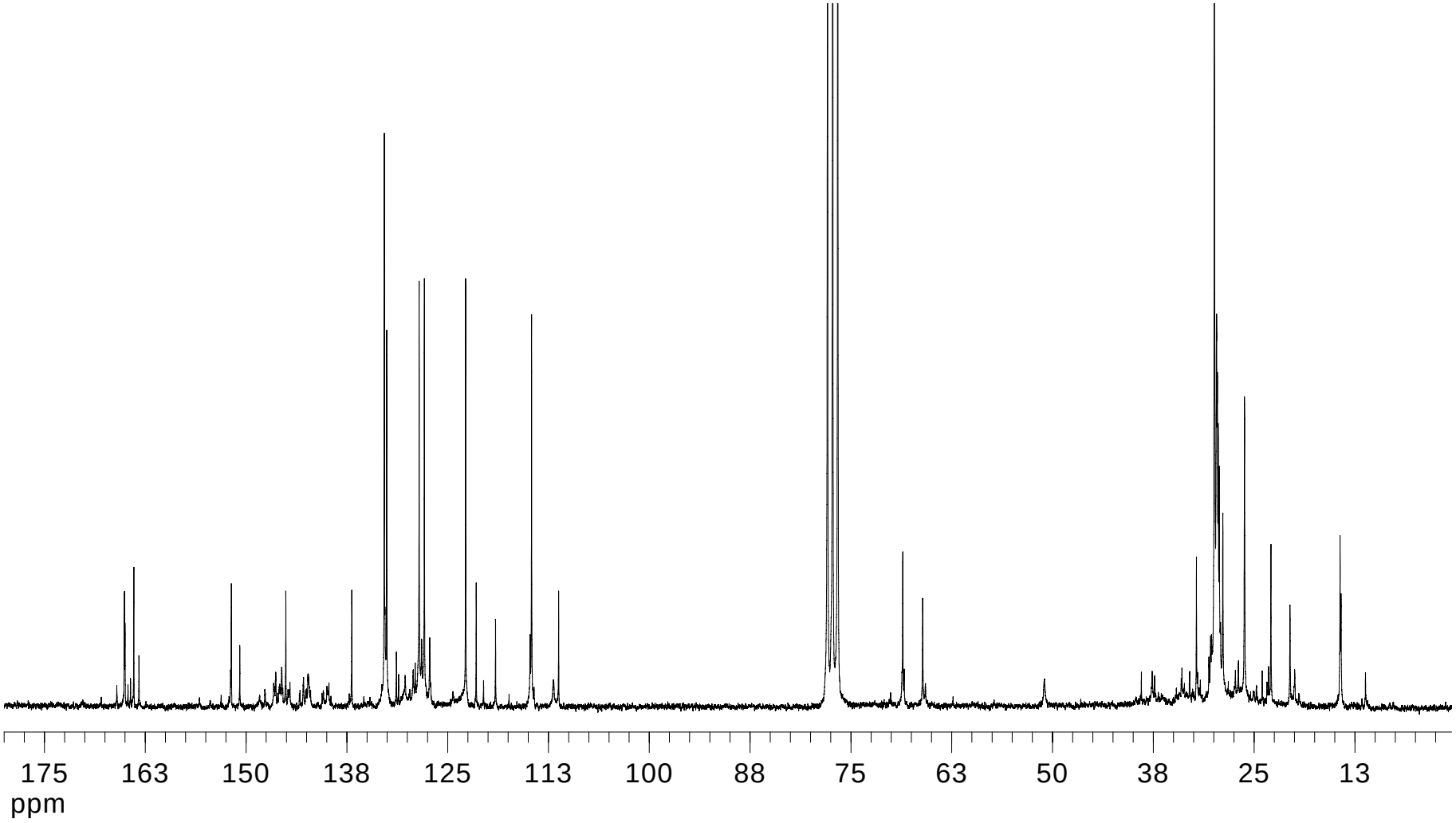

Figure S5. ^{13}C NMR spectrum of compound **1a**

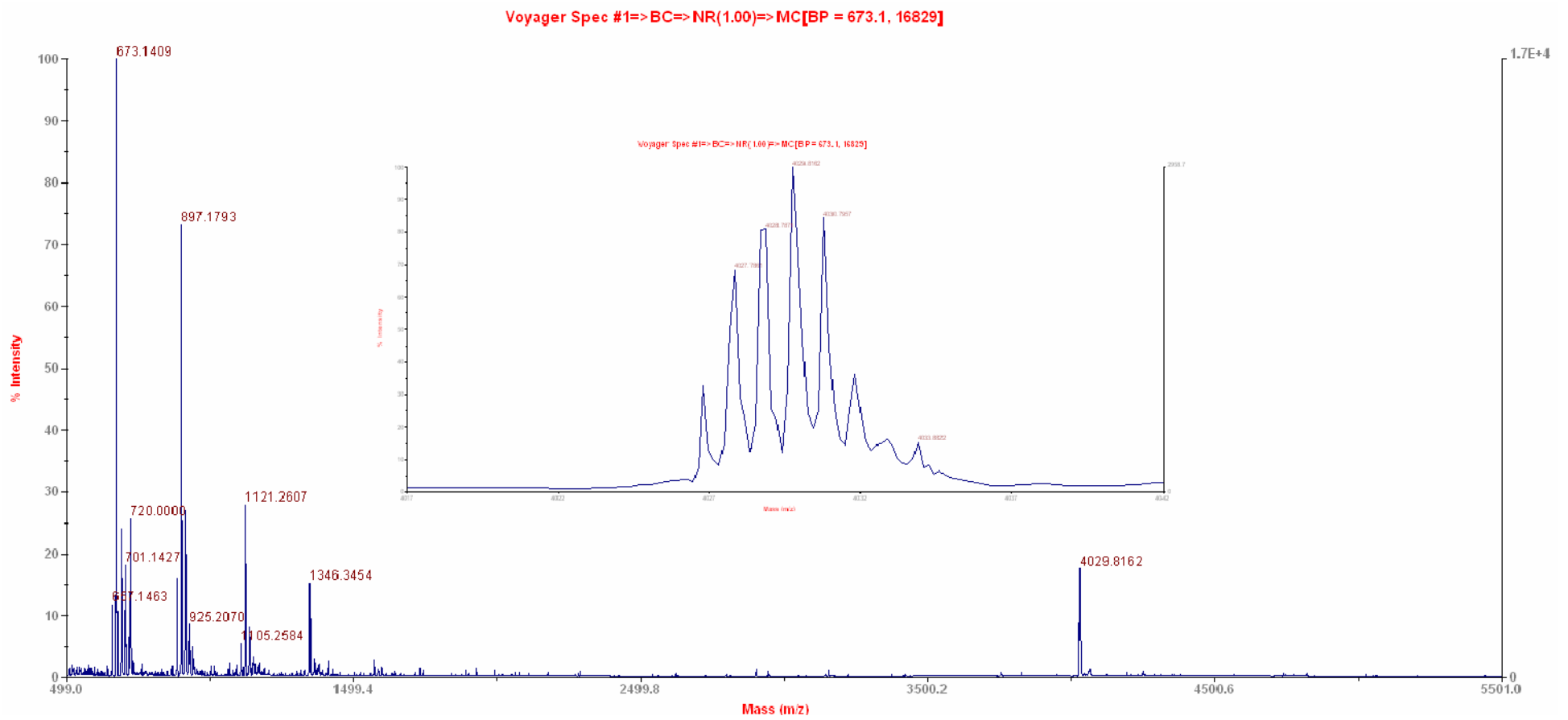

Figure S6. MALDI-TOF MS spectrum of compound **1a**

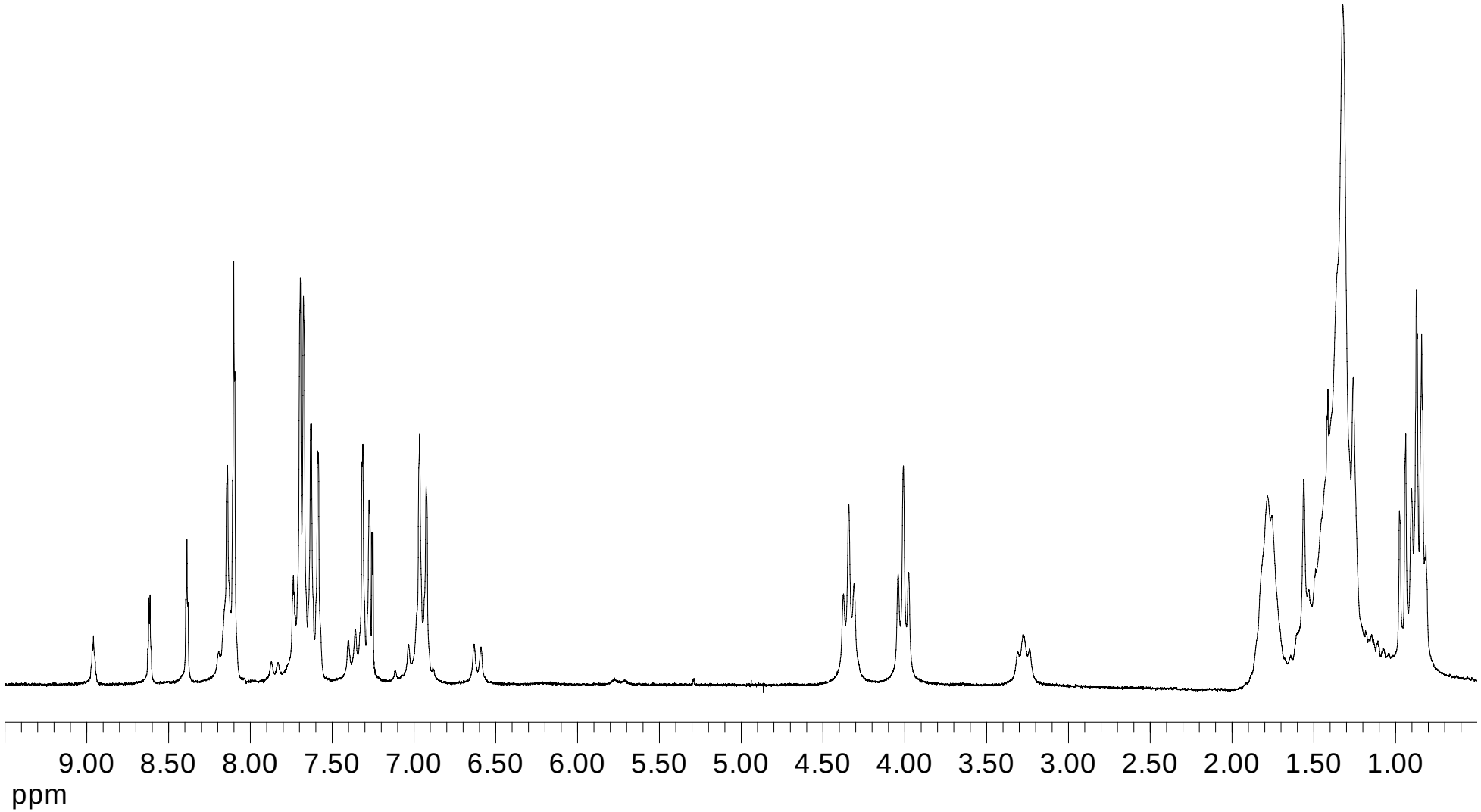

Figure S7. ^{1}H NMR spectrum of compound **1b**

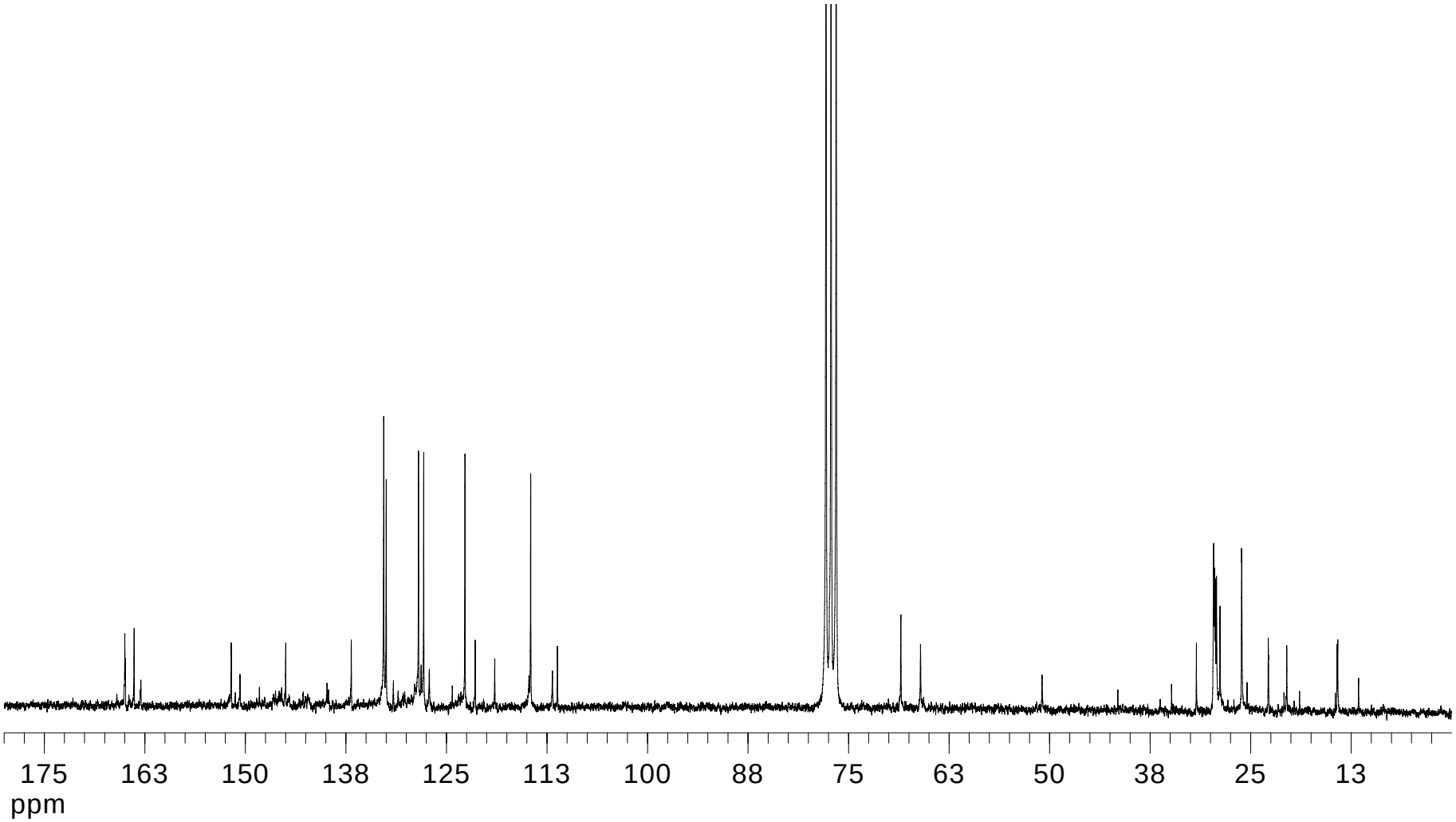

Figure S8. ^{13}C NMR spectrum of compound **1b**

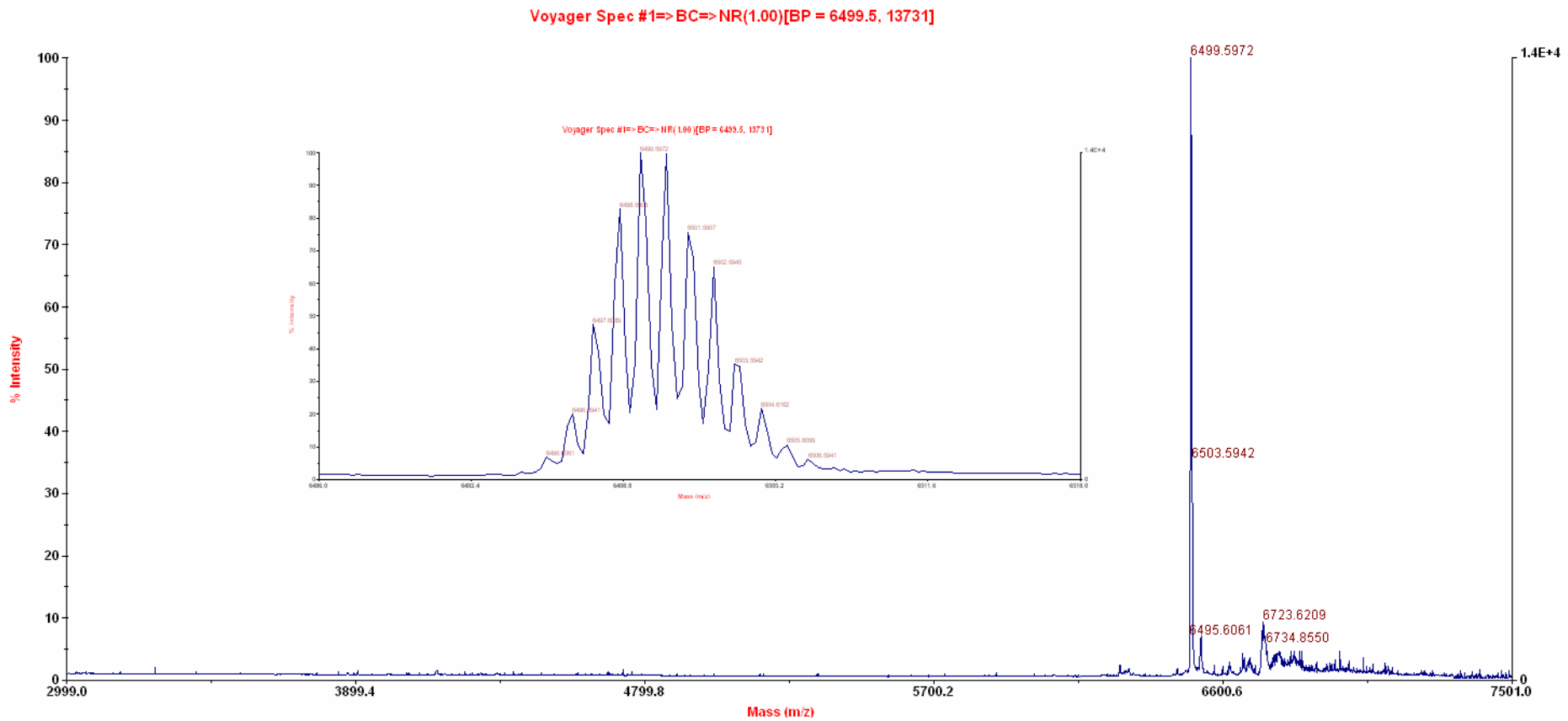

Figure S9. MALDI-TOF MS spectrum of compound **1b**

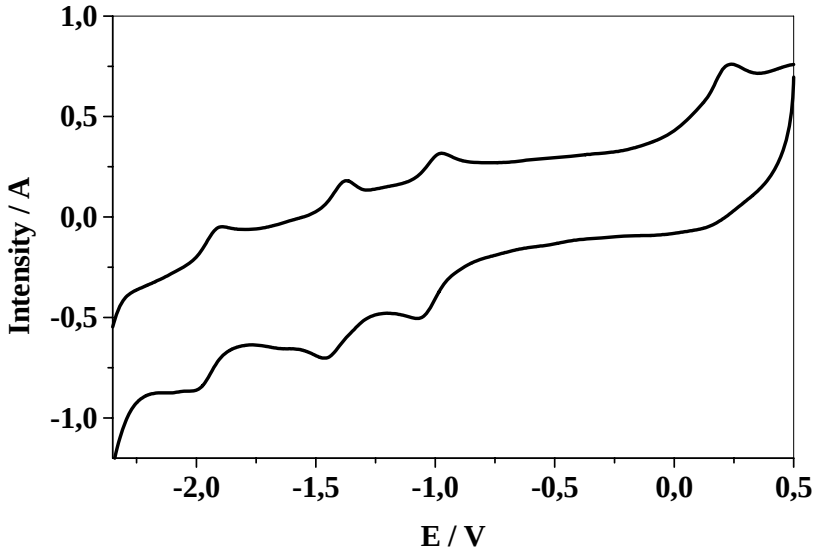

Figure S10. CV plot of compound **1a** in ODCB/CH_3CN 4:1 at room temperature

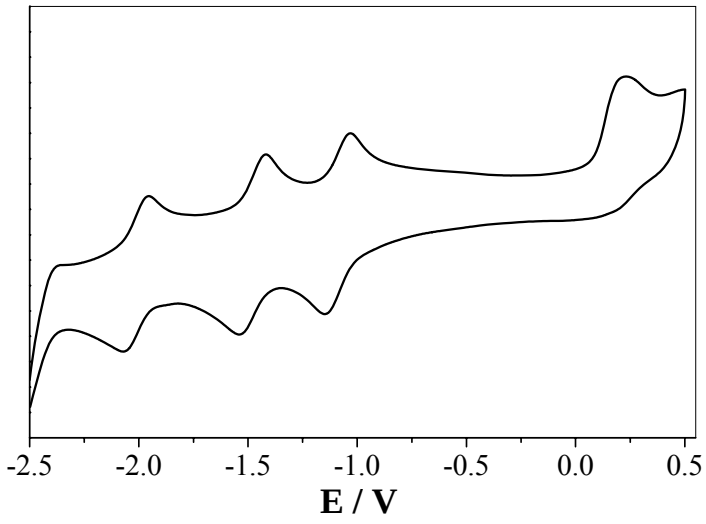

Figure S11. CV plot of compound **2** in ODCB/CH_3CN 4:1 at room temperature

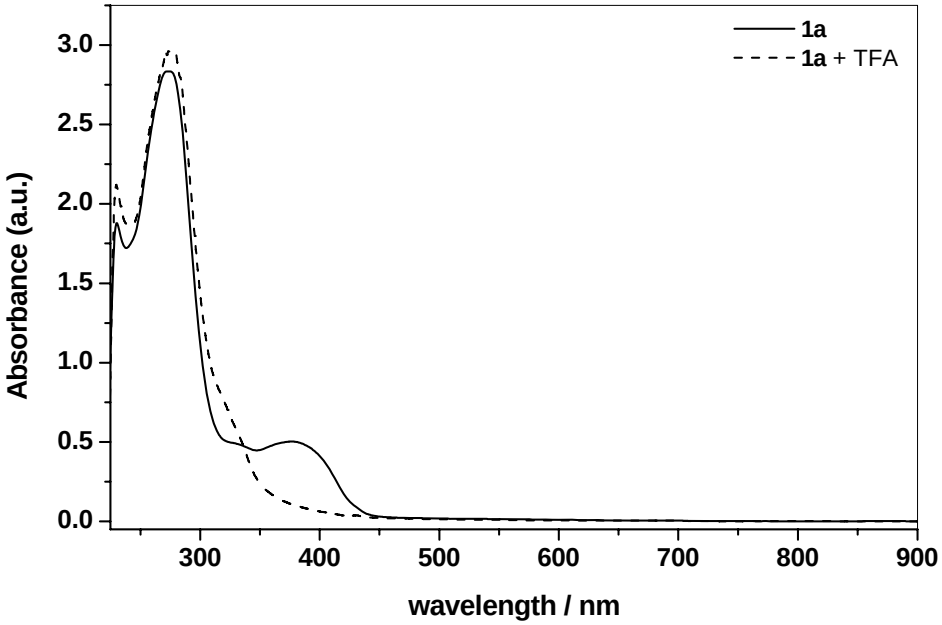

Figure S12. Absorption spectra of non-protonated (—) and protonated (---) **1a**

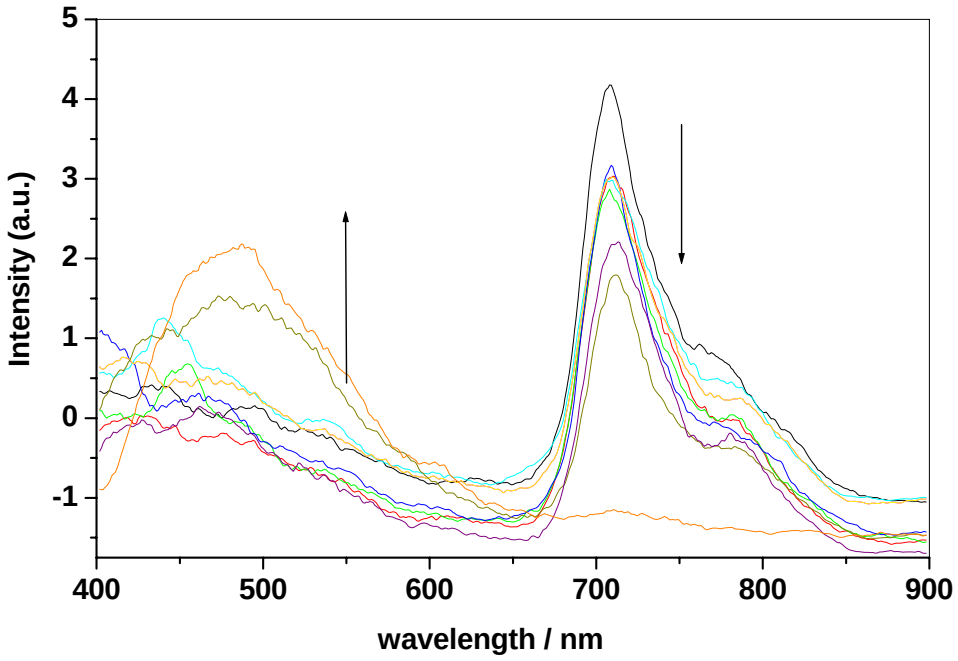

Figure S13. Emission spectra of fulleropyrrolidine **1a** in dichloromethane upon addition of Et_3N (λ_{exc} = 336 nm)

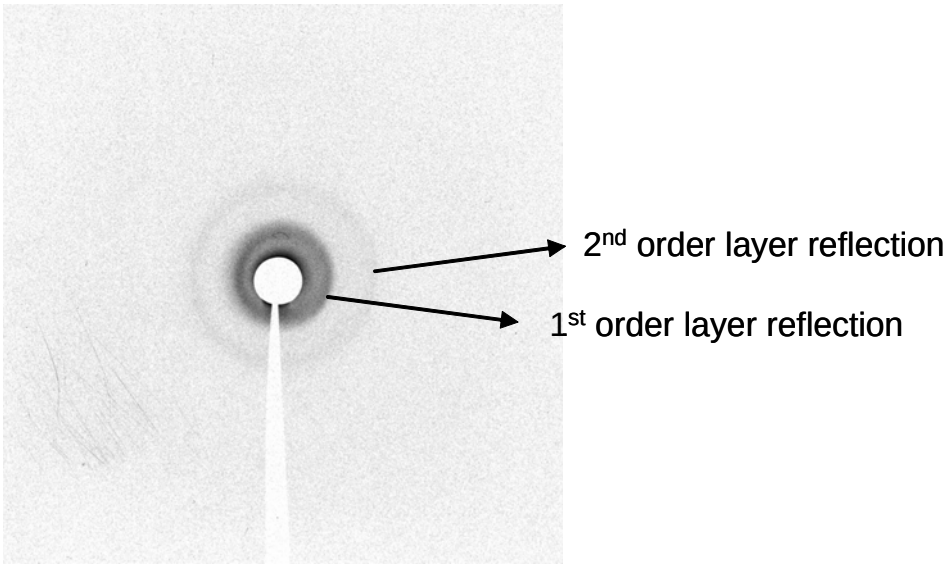

Figure S14. Small-angle diffraction pattern of compound **1a** in the smectic A phase

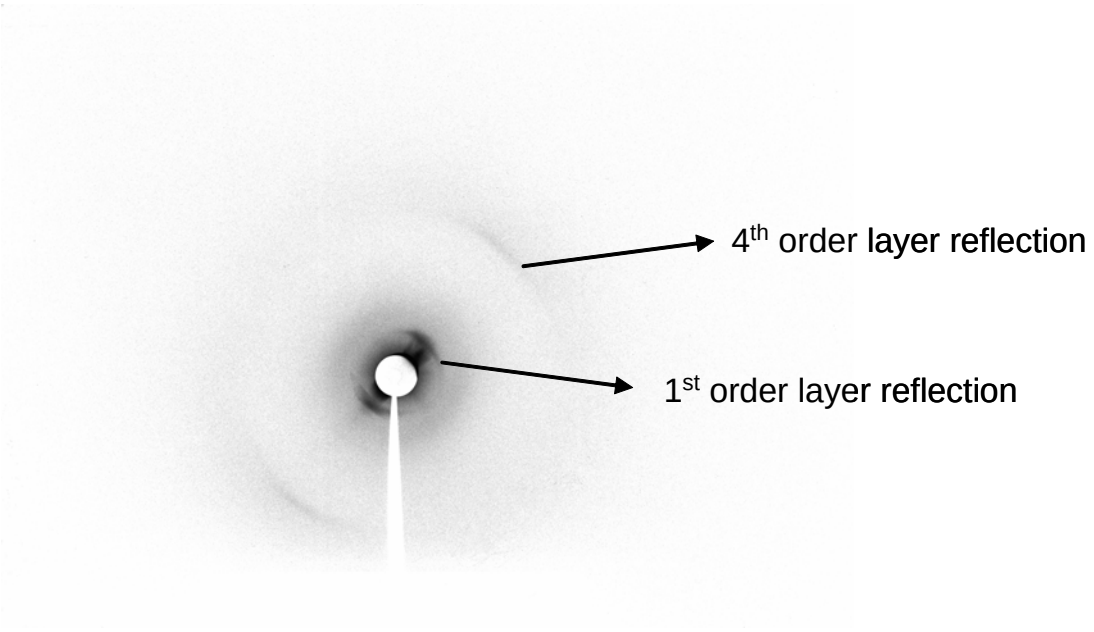

Figure S15. Small-angle diffraction pattern of compound **1b** in the smectic A phase. The sample adopts some preferential orientation