Three-Chain Truxene Discotic Liquid Crystal Showing Fast Charged Carrier Mobility

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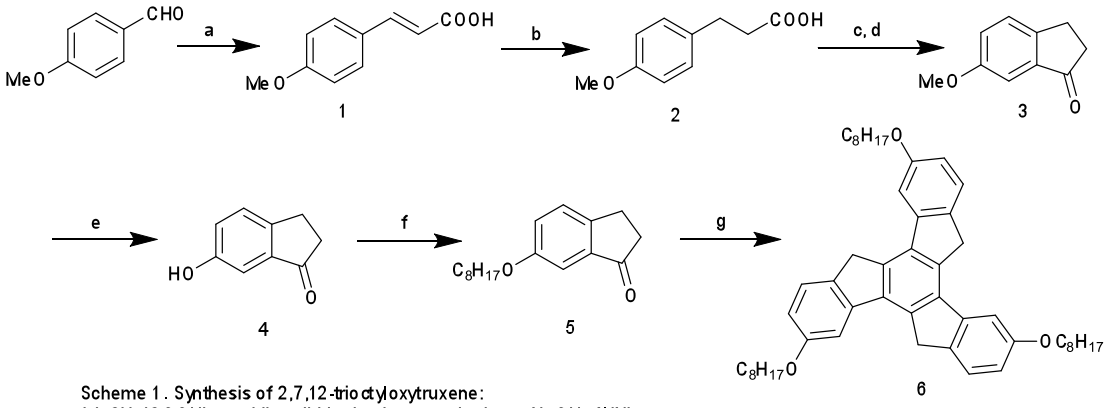
Synthetic Scheme of the compound, 3C8OTrx (6)



Scheme 1. Synthesis of 2,7,12-trioctyloxytruxene:
(a) $CH_2(COOH)_2$, pyridine, (b) hydrazine monohydrate, NaOH, Al/Ni,
(c) $SOCl_2$, (d) $AlCl_3$, (e) $AlCl_3$, toluene, (f) $C_8H_{17}Br$, K_2CO_3, (g) TsOH-H_2O, $(CH_2OH)_2$, toluene

Instruments and Reagents

^{1}H NMR was measured on a Bruker-Advance-600 NMR spectrometer in $CDCl_3$ at using TMS as the internal standard. The molecular mass was measured on a Q-TOF Premier mass spectroscopy. The optical textures of compound were observed using a XP-201 and Olympus BH2 Polarised Optical Microscopes equipped with a XP-201 and Mettler FP82HT hot-stages of which temperatures were controlled by a XPR-201 and Mettler FP90. The optical texture of the cell for mobility measurements was observed by Olympus BH2 polarised microscope combined to the Time-Of-Flight (TOF) system. The phase transition temperatures and enthalpies were investigated using a TA-DSC Q100 and TA2920 differential scanning calorimeters under N_2 atmosphere. The X-ray diffraction was carried out for the non-aligned sample by a Rigaku RINT2000 X-ray

diffractometer equipped with a hand made temperature controller. The charged carrier mobility was obtained by a TOF technique under controlled temperatures. All chemicals used for the compound syntheses were commercially available and all solvents used were distilled and dehydrated before uses. In particular, it should be noticed that further purification of **6** was carried out for obtaining the clear results in the TOF measurements by repetitive column chromatography and recrystalisation from solution using high grade solvents such as EL-grade solvents.

Synthesis and Characterization Data

Synthesis of (*E*)-3-(4-Methoxyphenyl)acrylic acid, 1. A mixture of 4-methoxybenzaldehyde (50.0 g, 0.368 mol), pyridine (69 mL, 0.858 mol) and malonic acid (60.0 g, 0.577 mol) in a 250 mL round-bottom flask was heated to 80 °C with stirring. The reaction was monitored by thin-layer chromatography. After 14 hours, the reaction was completed and the mixture was poured into ice-cold hydrochloric acid aqueous solution with vigorous stirring. The resulting white solid was filtered, and was washed with water. The crude product was then recrystallised in ethanol to give the titled compound **1** as a needle-like white crystal (60.0g, yield 92.0%). ^{1}H NMR ($CDCl_3$): δ 3.85(s, 3H), 6.32(d, J = 15.6 Hz, 1H), 6.92(d, J = 9.0 Hz, 2H), 7.51(d, J = 9.0 Hz, 2H), 7.75(d, J = 16.2 Hz, 1H).

Synthesis of 3-(4-methoxyphenyl)propanoic acid, 2. To a mixture of NaOH (16.0 g, 0.40 mol), Raney-Ni (2g) and distilled water (300 mL) in a 500 mL round-bottom flask added with (*E*)-3-(4-Methoxyphenyl)acrylic acid (**1**, 60.0g, 0.337 mol). The suspension was stirred under 90 °C to give a clear solution, followed by the slow addition of hydrazine hydrate (80%, 60.0 mL) (Note: massive gas evolution!) The reaction was allowed to stir under 90 °C for another 3 hours when no obvious gas emission was observed. Then the reaction was cooled to ambient temperature and filtered. The mother-liquor was poured into ice-cold hydrochloric acid aqueous solution with vigorous stirring. The resulting white solid was filtered, and was washed with water. The crude product was then recrystallised in ethanol to give the titled compound **2** as a needle-like white crystal (55.1 g, yield 92.0 %). ^{1}H NMR($CDCl_3$): δ 2.65(t, J = 7.8 Hz, 2H), 2.90(t, J = 7.8 Hz, 2H), 3.79(s, 3H), 6.84(d, J = 8.4 Hz, 2H), 7.14(d, J = 8.4 Hz, 2H).

Synthesis of 6-methoxy-2,3-dihydro-1*H*-inden-1-one, 3. A mixture of **2** (3.0 g, 0.017 mol), $SOCl_2$ (5.0 ml) and DMF (1mL) in a 25 mL round-bottom flask was stirred at room temperature. After 12 hours, the excessive $SOCl_2$ was removed by distillation under reduced pressure. The resulting brown yellow liquid was diluted in dichloromethane (10 mL), and was then added to a suspension of $AlCl_3$ (4.43 g, 0.333 mol) in CH_2Cl_2 (100 mL) on an ice-water bath. The mixture was then stirred further for another 3 hours and the reaction temperature was strictly controlled between 0 and 5 °C. Upon the completion of reaction, the mixture was poured into ice-cold hydrochloric acid. The organic layer was separated and to be washed with distilled water, followed by drying through $MgSO_4$. The solvent was removed under reduced pressure and the residue was then purified by column chromatography (Silica-gel, CH_2Cl_2 as the eluent). The resulting white solid was recrystallised in ethyl acetate and petroleum ether to give **3** as a white crystal (1.56 g, 58% yield). ^{1}H NMR($CDCl_3$): δ 2.72(t, J = 5.7 Hz, 2H), 3.07(t, J = 5.7 Hz, 2H), 3.83(s, 3H), 7.18(d, J = 9.0 Hz), 7.20(s, 1H), 7.37(d, J = 9.0 Hz, 1H).

Synthesis of 6-hydroxy-2,3-dihydro-1H-inden-1-one, 4. A mixture of **3** (2.0 g, 0.013 mol) and $AlCl_3$ (5.0 g, 0.038 mol) in toluene (50.0 mL) was heated to reflux (Note: massive gas evolution). When no obvious gas emission was observed, the reaction mixture was cooled to room temperature, and was poured into hydrochloric acid with vigorous stirring. The organic layer was separated and washed with distilled water. After dried through $MgSO_4$, the solvent was removed under reduced pressure to give the crude product as a red solid. The crude product was then washed with CH_2Cl_2 to give the titled compound **4** as a light-brown solid (1.50 g, 82%). ^{1}H NMR ($CDCl_3$): δ 2.73(t, J = 5.7 Hz, 2H), 3.07(d, J = 5.7 Hz, 2H), 6.20(b, 1H), 7.17(dd, J = 8.0 Hz and 2.4 Hz, 1H), 7.25(d, J = 1.8 Hz, 2H), 7.35(d, J = 8.1 Hz, 1H).

Synthesis of 6-octoxy-2,3-dihydro-1H-inden-1-ones, 5. A mixture of **4** (1.0 equiv.), K_2CO_3 (2.0 equiv.) and 1-bromooctane (1.7 equiv.) in ethanol (0.135 mol/L of **4**) was heated to reflux. The reaction was monitored by thin-layer chromatography. Upon the completion of reaction, the mixture was cooled to room temperature, and then filtered. The mother-liquor was concentrated under reduced pressure to give the crude product as a light-yellow solid. The crude product was

then purified by column chromatography. Resulting product was recrystallised in ethanol to give **5** as white crystals (yield 90 %). ^{1}H NMR ($CDCl_3$): δ 7.35(d, J = 9.0 Hz, 1H), 7.16-7.20(m, 2H), 3.97(t, J = 6.3 Hz, 2H), 3,06(t, J = 5.7 Hz, 2H), 2.72(d, J = 5.7 Hz, 2H), 1.74-1.82(m, 2H), 1.42-1.49(m, 2H), 1.22-1.39(m, 8H), 0.89(t, J = 6.6 Hz, 3H).

Synthesis of 2,7,12-trioctoxytruxene, 6. A mixture of **5** (1.0 equiv.), *p*-toluenesulfonic acid (0.34 equiv.) and ethylene glycol (0.17 equiv.) in toluene (0.07 mol/L of **5**) was heated to reflux. The reaction was monitored by thin-layer chromatography. Upon the completion of reaction, the mixture solution was concentrated under reduced pressure to remove toluene. The resulting red solid was purified by column chromatography to give the crude product as a white solid. The crude product was then recrystallised in ethyl acetate and ethanol to give **6** as white crystal, yield 24 %. ^{1}H NMR ($CDCl_3$): δ 7.49 (d, J = 8.4 Hz, 3H), 7.35 (d, J = 1.8 Hz, 3H), 6.91 (dd, J = 7.8 Hz, and J = 2.4 Hz, 3H), 4.08 (t, J = 6.6 Hz, 6H), 4.02(s, 6H), 1.91-1.86 (m, 6H), 1.58-1.53 (m, 6H), 1.45-1.36 (m, 24H), 0.92 (t, J = 6.6 Hz, 9H). HRMS: calcd. for $C_{51}H_{66}O_3$, 726.5012; found $(M)^+$: 726.5013. Elemental Analysis, calcd. for $C_{51}H_{66}O_3$ C 84.25, H 9.15: found C 84.68, H 8.98 %.

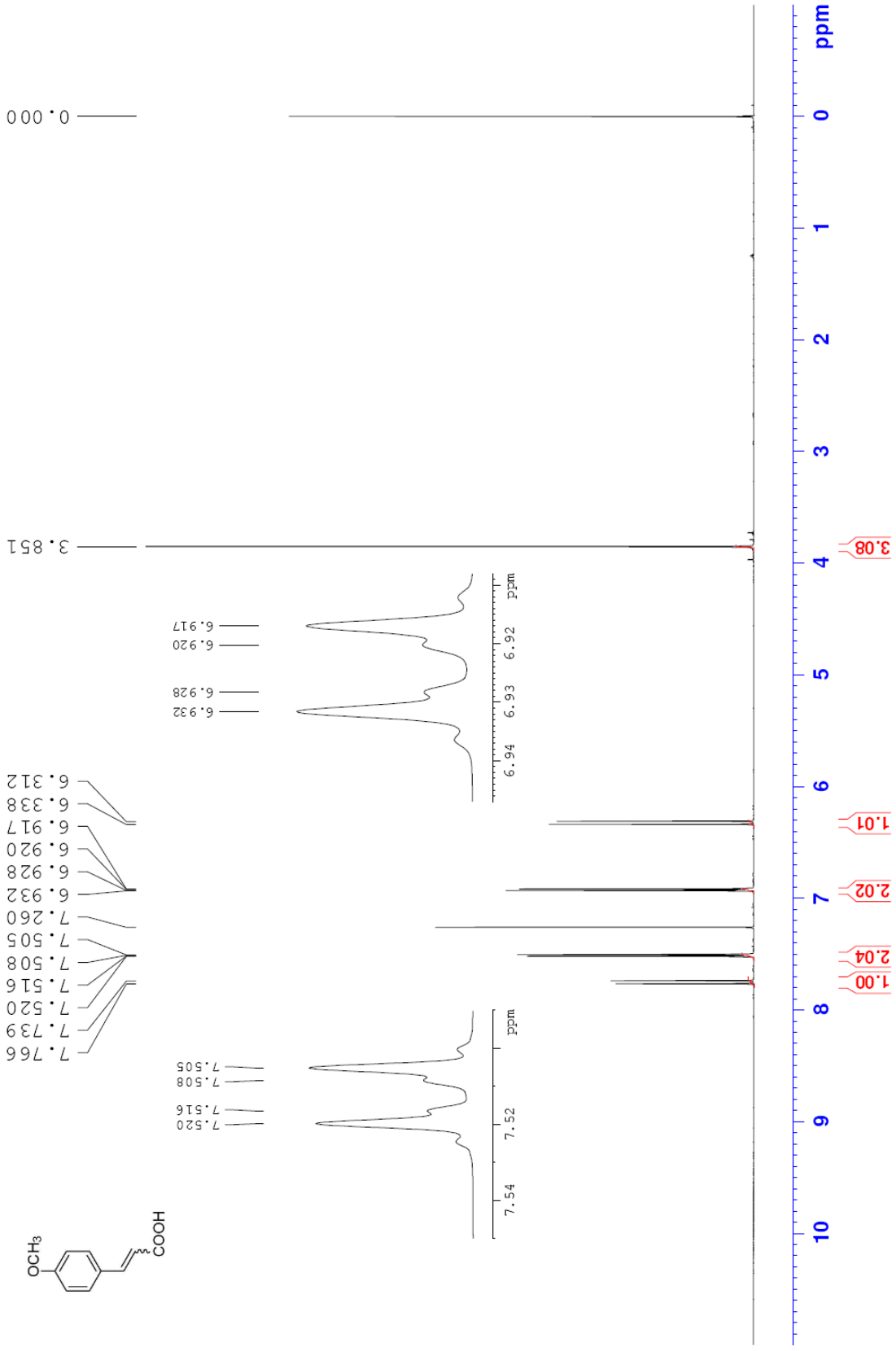


Fig. S1 ^{1}H NMR spectrum of **1**.

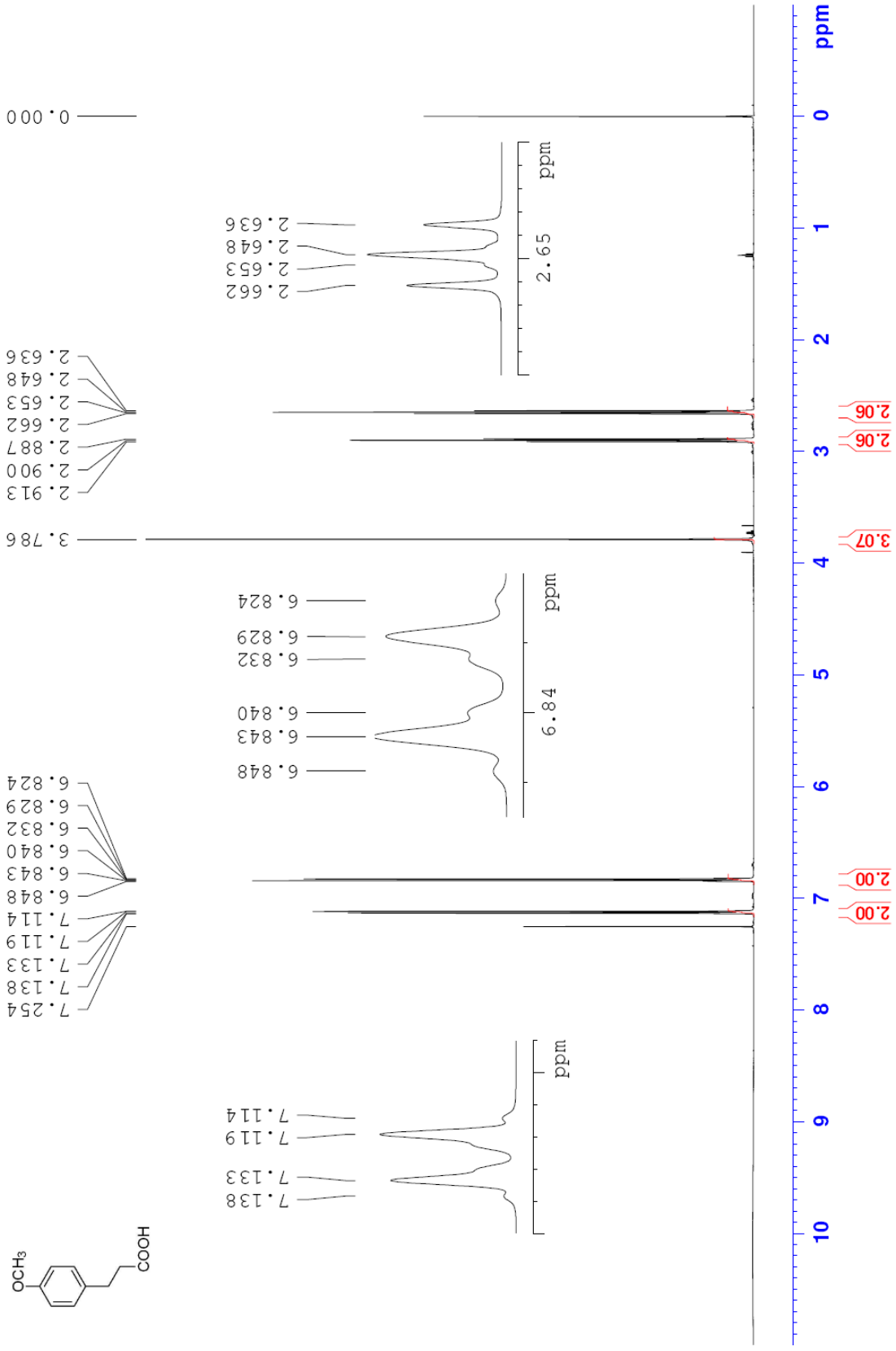


Fig. S2 ^{1}H NMR spectrum of **2**.

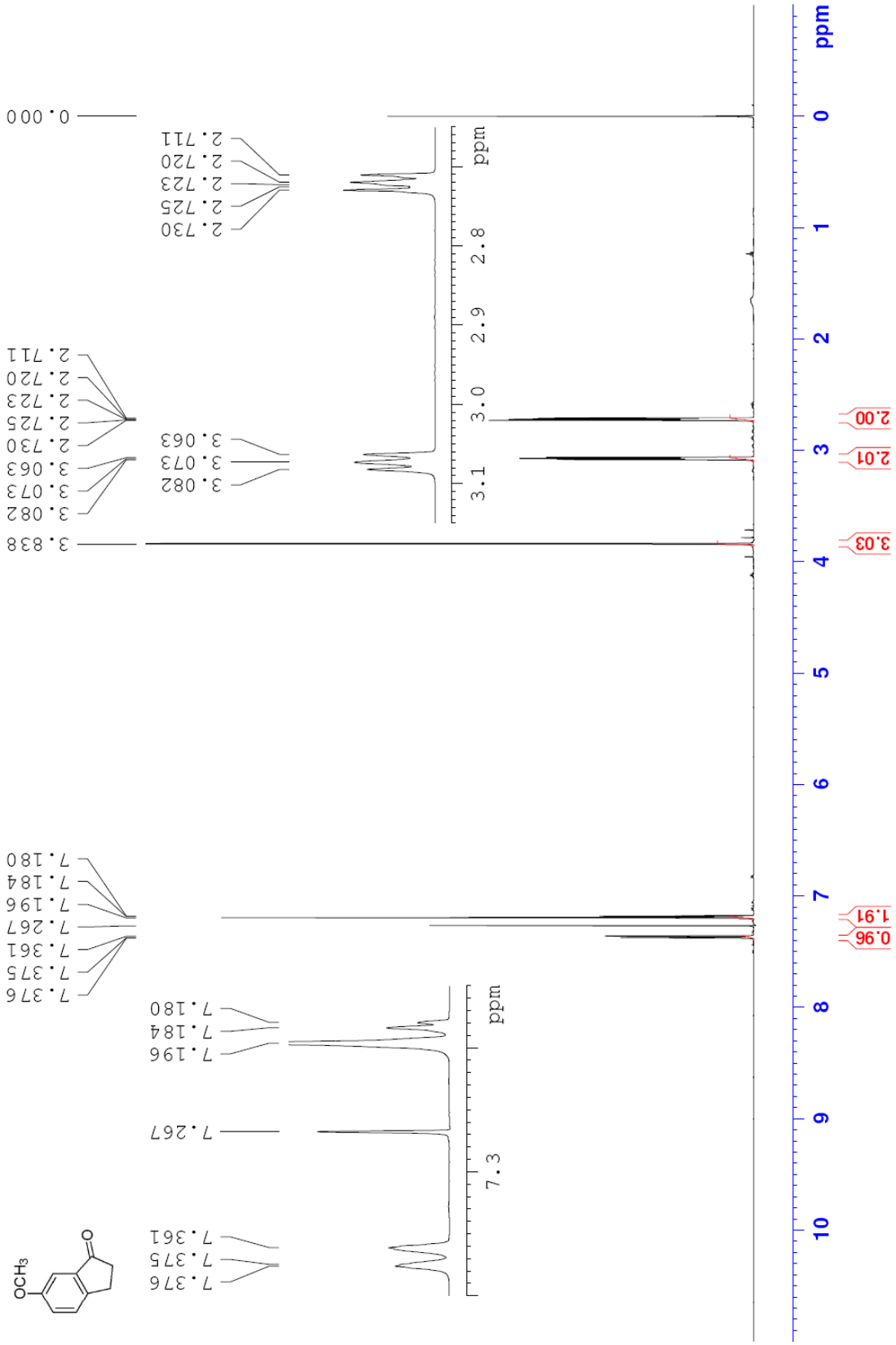


Fig. S3 ^{1}H NMR spectrum of **3**.

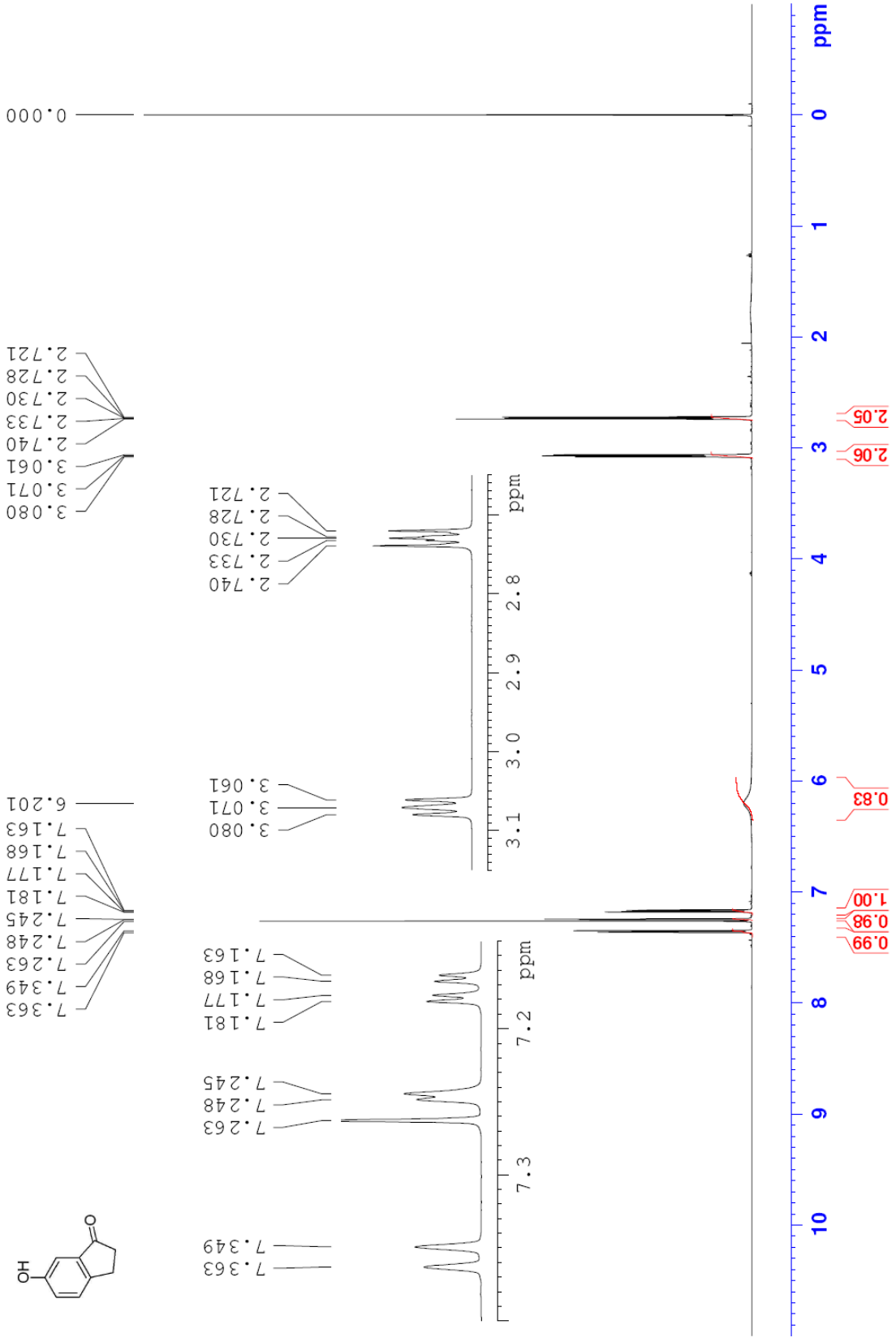


Fig. S4 ^{1}H NMR spectrum of **4**.

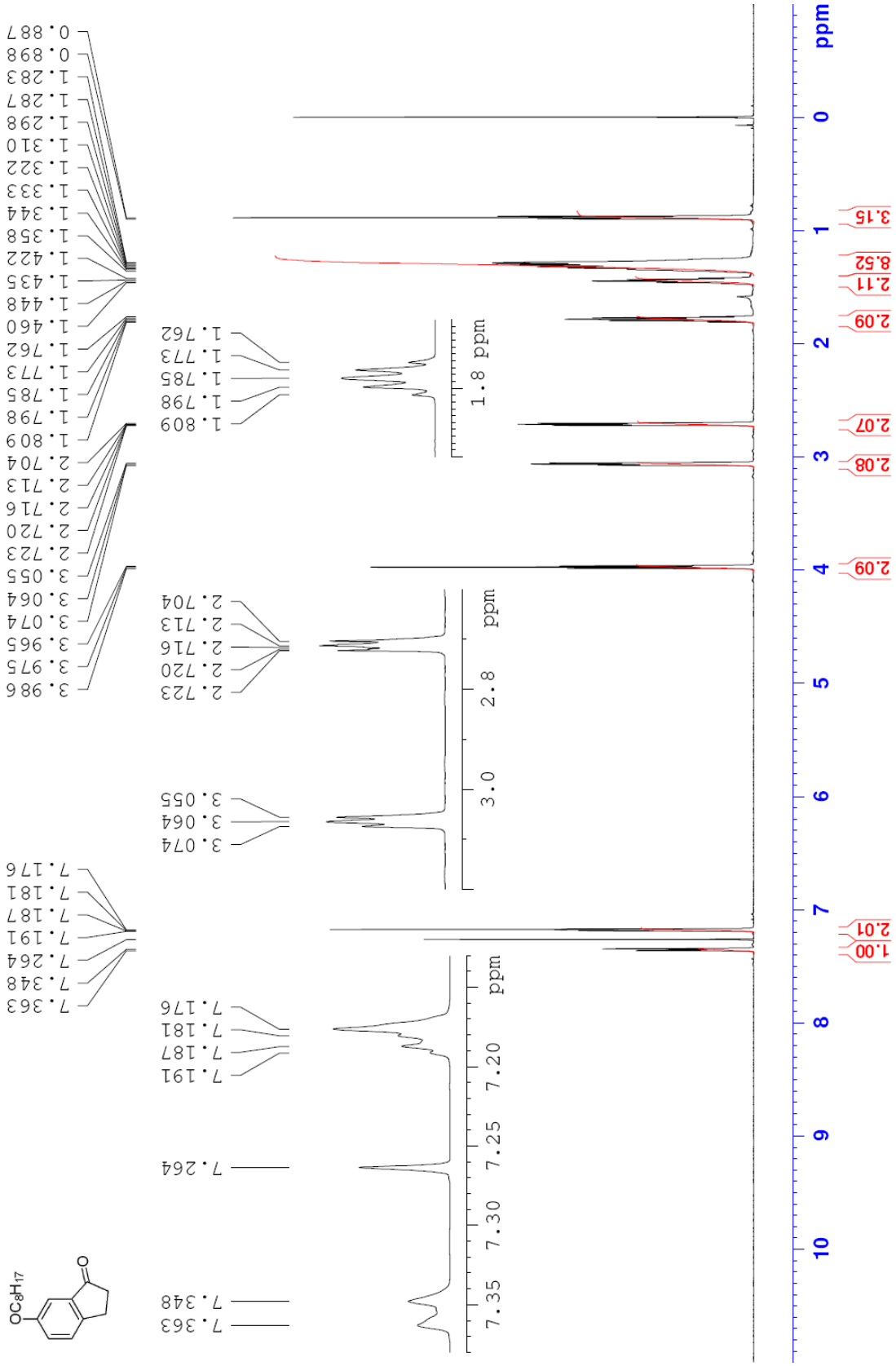


Fig. S5 ^{1}H NMR spectrum of **5**.

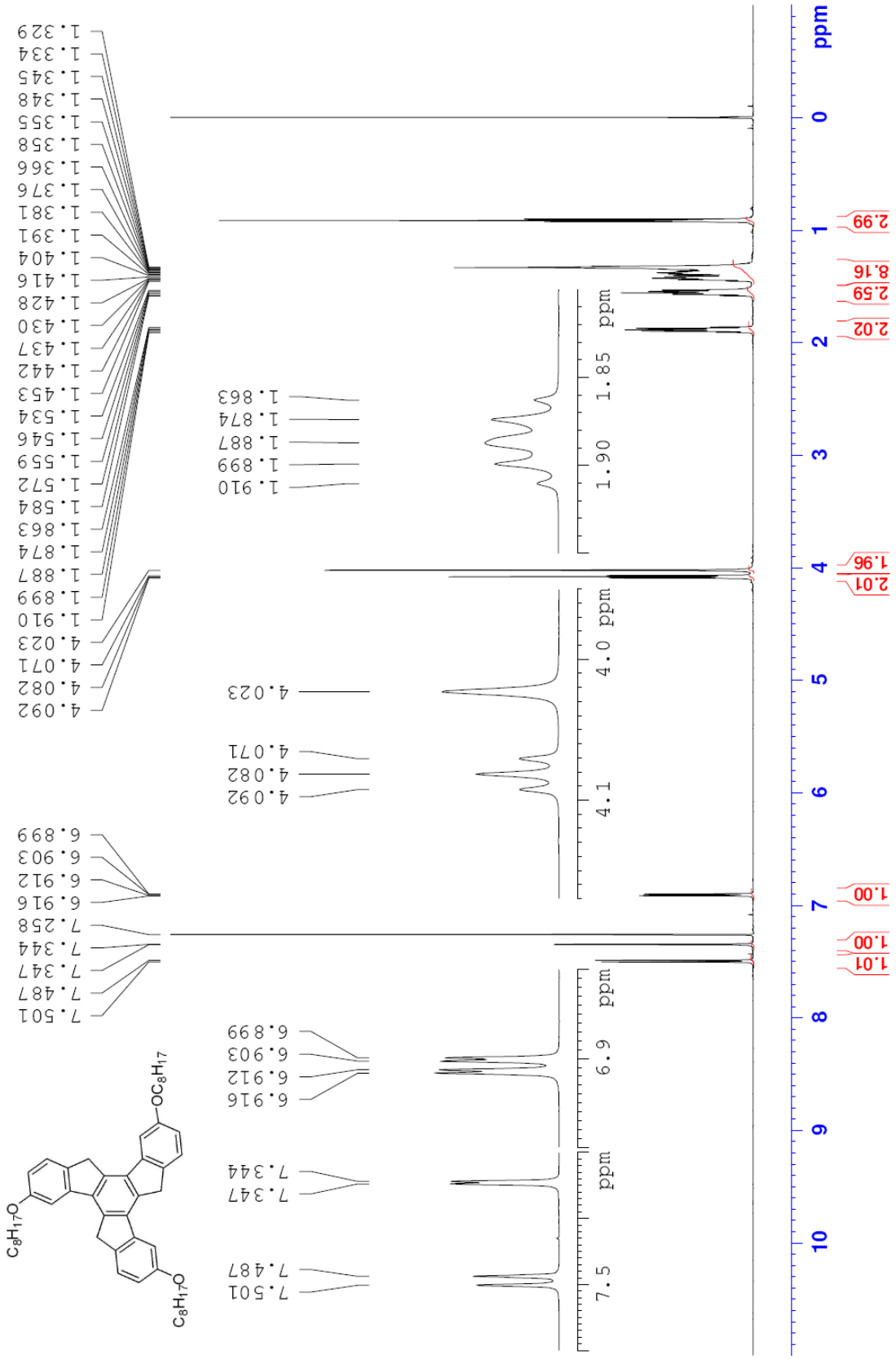


Fig. S6 ^{1}H NMR spectrum of **6**.