Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Highly efficient synthesis of C_3-symmetry *O*-alkyl substituted triphenylene and related Mannich derivatives for supramolecular applications

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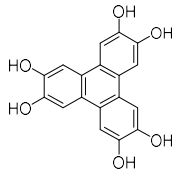
S1 Experimental Section

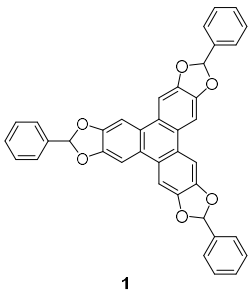
S1.1 General Methods

The reactions were followed with TLC Polygram® Sil G/UV$_{254}$, 0.25 mm thickness. ^{1}H NMR, ^{13}C NMR, and 2D spectra were recorded with a Bruker Avance 300 and Ascend 400 spectrometers, working at 300-400 and 75-100 MHz respectively. Resonance frequencies are referred to tetramethylsilane. IR spectra were recorded with a Perkin Elmer Spectrum One spectrophotometer. Mass spectrometric measurements were performed using a Thermo Scientific LTQ Orbitrap XL equipped with HESI source. The compounds studied were dissolved in methanol or acetonitrile with a concentration of 5×10^{-3} M. They were injected into the HESI source by direct infusion with the syringe pump integrated in the mass spectrometer at a 5 mL·min^{-1} flow rate. Mass spectra were acquired in positive-polarity mode with the following tuning conditions: Temperature 40 °C, Sheath gas 8 (arbitrary units, arb), Aux gas and Sweep gas 0 arb, Spray Voltage 4.5 kV, Capillary temperature 275 °C, Capillary Voltage -9 V, Tube lence 150 V. In negative polarity the following tuning parameters were employed: Temperature 40 °C, Sheath gas 19 (arbitrary units, arb), Aux gas and Sweep gas 0 arb, Spray Voltage 3.0 kV, Capillary temperature 275 °C, Capillary Voltage 10 V, Tube lence 120 V. Mass spectra were collected in full scan with a resolution of 100000 at m/z 400. The Orbitrap MS was calibrated just before analysis and during the acquisition in order to improve mass accuracy lock masses were employed. Reagents and solvents with high purity degree purchased by the providers were used as given. Otherwise, they were purified following the procedures reported in literature.[1] Anhydrous solvents were prepared by adding activated 3 Å molecular sieves to the solvent under inert atmosphere. Molecular sieves were activated shortly before the use by continuous heating under vacuum. Flash chromatography were performed with silica gel Merk 60, 230-400 mesh, following procedures reported in literature.[2]

S1.2 Experimental procedures / Syntheses



HHTP



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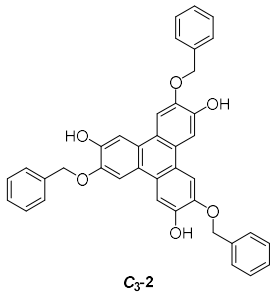
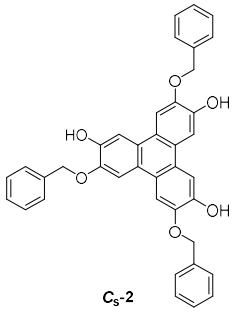


C_3-2



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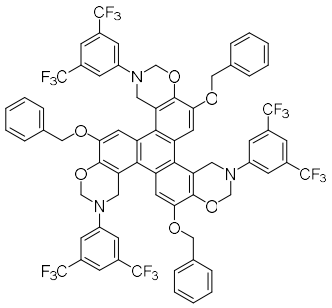

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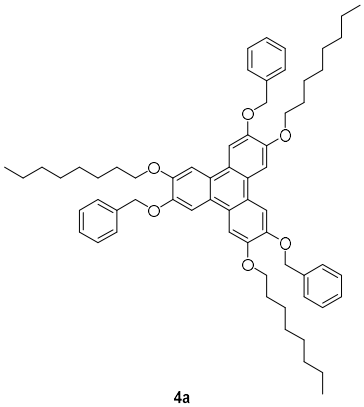
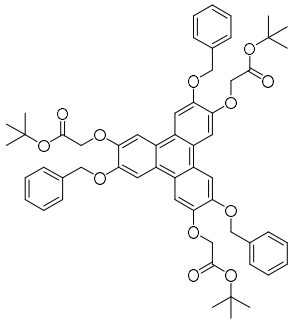
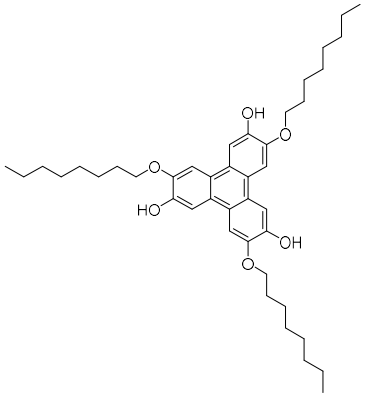


4a



4b



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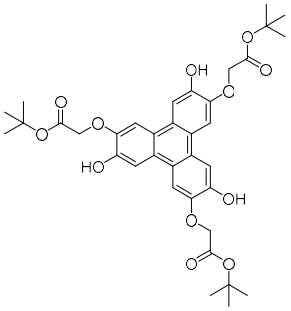

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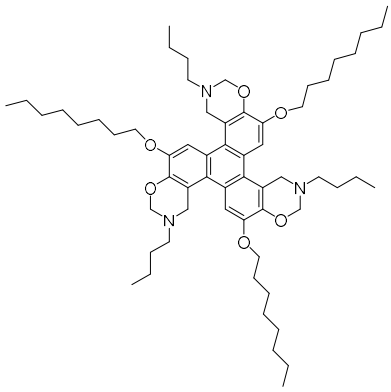

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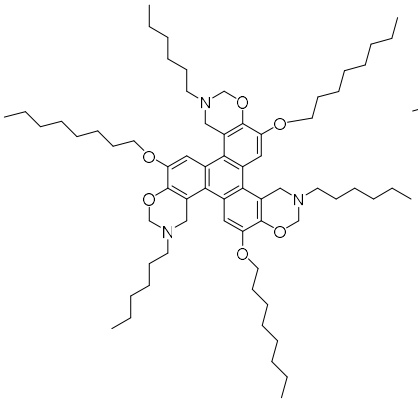

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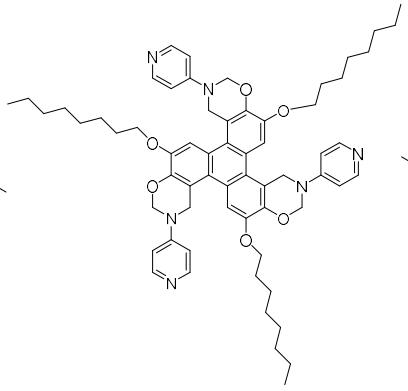

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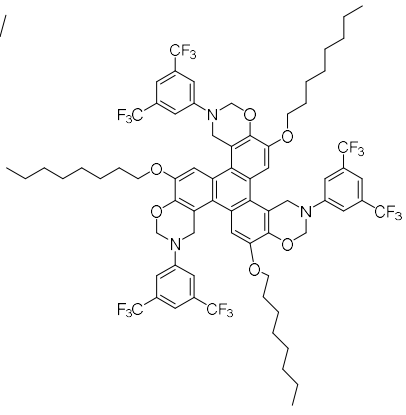

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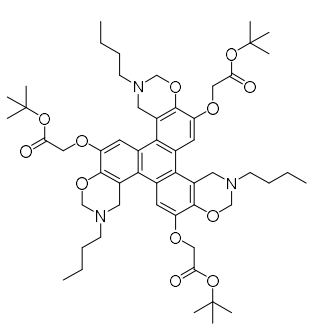

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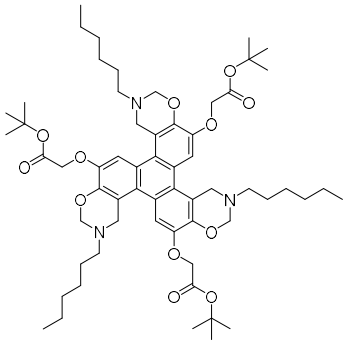

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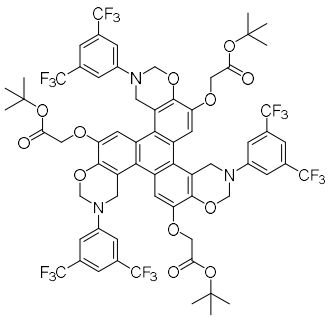
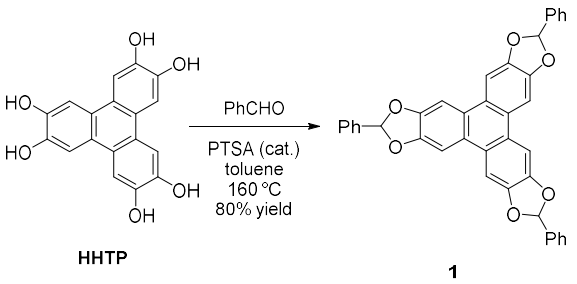


7c

HHTP was synthetized according to literature procedure.[3]

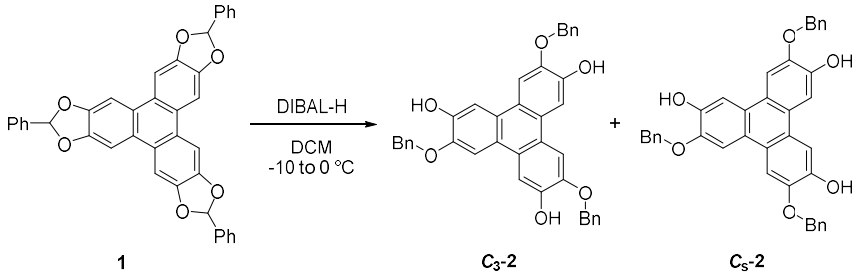
2,7,12-Triphenyltriphenyleno[2,3-d:6,7-d':10,11-d"]tris([1,3]dioxole) (**1**)



HHTP **1**

In a 500 mL round bottomed flask, hexahydroxytriphenylene (4.56 g, 14 mmol) was dispersed in 130 mL of toluene, then benzaldehyde (100 mL) and PTSA monohydrate (0.106 g, 0.6 mmol) were added to the suspension. A pressure-equalizing dropping funnel filled with activated 3 Å molecular sieves was placed over the flask and topped with a reflux condenser. The apparatus was purged with argon and the suspension refluxed for 96 hours. The resulting solution was cooled to room temperature and washed with saturated $NaHCO_3$ (3 × 100 mL). The organic phase was diluted with Et_2O (300 mL) and the precipitate was filtered and recovered. Ether was removed from the mother liquors with rotavapor, and benzaldehyde was recovered by vacuum distillation. The residue of the distillation was diluted in Et_2O (100 mL) and the precipitate was filtered and washed with Et_2O. The product was obtained as a light brown solid (6.6 g, 11.2 mmol, 80% yield). M.P. 244 °C. ^1H NMR (400 MHz): ($CDCl_3$) δ 7.83 (6H, s), 7.67-7.62 (6H, set of m), 7.49-7.46 (9H, set of m), 7.12 (3H, s). ^{13}C NMR (100 MHz): δ 147.9, 136.2, 136.2, 130.6, 128.9, 126.5, 125.1, 110.8, 101.5. IR (KBr): v 1638, 1494, 1453, 1396, 1383, 1292, 1240, 1163, 1106, 1033, 1017, 907, 848, 829, 762, 732, 697, 642 cm^{-1}. HRMS (ESI): calcd. for $C_{39}H_{24}O_6$ [M^+] 588.1567; found: 588.1571.

DIBAL-H procedure for the benzilidene reductive ring opening



1 C_3-2 C_s-2

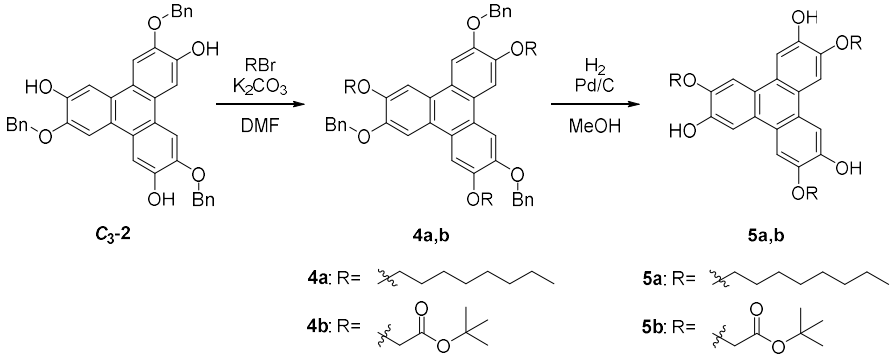
In a 500 mL two necked flask, equipped with argon inlet and septum, **1** (3.44 g, 5.85 mmol) was suspended in anhydrous DCM (210 mL). The mixture was cooled to -10 °C and DIBAL-H solution (1.5 M in toluene, 23.4 mL, 35.1 mmol) was added dropwise with a syringe during 20-25 minutes. The resulting solution was stirred at -10 °C for 2 hours, and finally at 0 °C for 3 hours. The exceeding DIBAL-H was quenched with methanol (10 mL) at 0 °C, aqueous 1M HCl (135 mL) and the resulting mixture was vigorously stirred at room temperature for 30 minutes. The mixture was decanted and the organic phase collected. The aqueous layer was extracted with DCM (2 × 30 mL) and the combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuum. The crude mixture of isomers (C_3 and C_s, 1:1) was purified by flash chromatography, eluting with DCM until complete recovery of the first isomer, ***C*$_3$-2**, then with AcOEt to recover the ***C*$_s$-2**.

3,7,11-tris(benzyloxy)triphenylene-2,6,10-triol (***C*$_3$-2**): 1.68 g, 2.8 mmol, 48% yield. M.P. 222 °C (lit. 221 °C). ^{1}H NMR (400 MHz, DMSO d_6): δ 9.32 (3H, s), 7.89 (3H, s), 7.88 (3H, s), 7.62 (6H, d, J = 7.0 Hz), 7.43 (6H, t, J = 7.0 Hz), 7.35 (3H, t, J = 7.0 Hz), 5.38 (6H, s). Further spectroscopic data (^{13}C, MS, IR) are in accordance with the literature.[4]

3,7,10-tris(benzyloxy)triphenylene-2,6,11-triol (***C*$_s$-2**): 1.70 g, 2.8 mmol, 49% yield. M.P. 208 °C; ^{1}H NMR (400 MHz): (DMSO d_6) δ 9.49 (1H, s), 9.47 (1H, s), 9.29 (1H, s), 7.92 (1H, s), 7.91 (1H, s), 7.88 (1H, s), 7.87 (1H, s), 7.73 (1H, s), 7.72 (1H, s), 7.66-7.58 (6H, set of m), 7.43 (6H t, J = 7 Hz), 7.38-7.35 (3H, set of m), 5.39 (2H, s), 5.39 (2H, s), 5.36 (2H, s). ^{13}C NMR (100 MHz): δ 147.3, 147.2, 147.0, 146.9, 137.9, 137.9, 137.8, 128.9, 128.9, 128.4, 128.4, 128.3, 128.2, 123.7, 123.4, 123.2, 122.4, 122.1, 122.0, 109.0, 108.6, 108.6, 107.6, 107.4, 107.2, 70.6, 70.6, 70.3. IR (KBr): v 1629, 1619, 1596, 1515, 1451, 1434, 1402, 1382, 1312, 1267, 1176, 1151, 1037, 1023, 852, 787, 738, 696 cm^{-1}. HRMS (ESI): calcd. for $C_{39}H_{31}O_6$ [M$^+$] 593.1970; found: 593.1968.

General Procedure 1 (GP1)

General procedure for the alkylation and debenzylation of ***C*$_3$-2**.



In a pear-shaped two necked 25 mL flask, equipped with argon inlet ad septum, a solution of ***C*$_3$-2** (0.30 g, 0.5 mmol)**,** K_2CO_3 (0.63 g, 4.5 mmol) and alkylbromide (2.3 mmol) in anhydrous DMF (6 mL) was stirred at room temperature for 72 hours. The flask content was poured in aqueous 1M HCl (30 mL) and extracted with DCM (3 × 10 mL). The organic solution was washed with water (2 × 10 mL), dried over $MgSO_4$, filtered and concentrated in vacuum. The crude product was crystallized from absolute EtOH, to afford the product as white crystals. A suspended mixture of alkylated compound and Pd/C 5% (0.088 g) in MeOH (20 mL) was stirred under H_2 atmosphere (1 atm, baloon) at room temperature for 18 h. The resulting mixtyre was filtered on a celite plug and washed with DCM. The resulting solution was concentrated in vacuum, to afford the product as a waxy solid.

2,6,10-tris(benzyloxy)-3,7,11-tris(octyloxy)triphenylene (**4a**): **GP1** was applied to ***C*$_3$-2** and octylbromide. 84% yield. M.P.: 125 °C. ^{1}H NMR (400 MHz): ($CDCl_3$) δ 7.82 (3H, s), 7.64 (3H, s), 7.59-7.52 (6H, set of m), 7.40 (6H, set of m), 7.36-7.29 (3H, set of m), 5.34 (6H, s), 4.19 (6H, t, *J* = 6.4 Hz), 2.01-1.91 (6H, set of m), 1.64-1.27 (30H, set of m) 0.90 (9H, t, *J* = 6.9 Hz). ^{13}C NMR (100 MHz): δ 149.4, 148.3, 137.8, 128.7, 128.0, 127.5, 124.3, 123.2, 109.3, 106.6, 72.3, 69.4, 32.0, 29.6, 29.6, 29.5, 26.4, 22.9, 14.3. IR (KBr): v 1618, 1574, 1519, 1437, 1386, 1261, 1198, 1165, 1038, 858, 822, 798, 749, 701 cm^{-1}. HRMS (ESI): calcd. for $C_{63}H_{79}O_6$ [M^+] 931.5871; found: 931.5845.

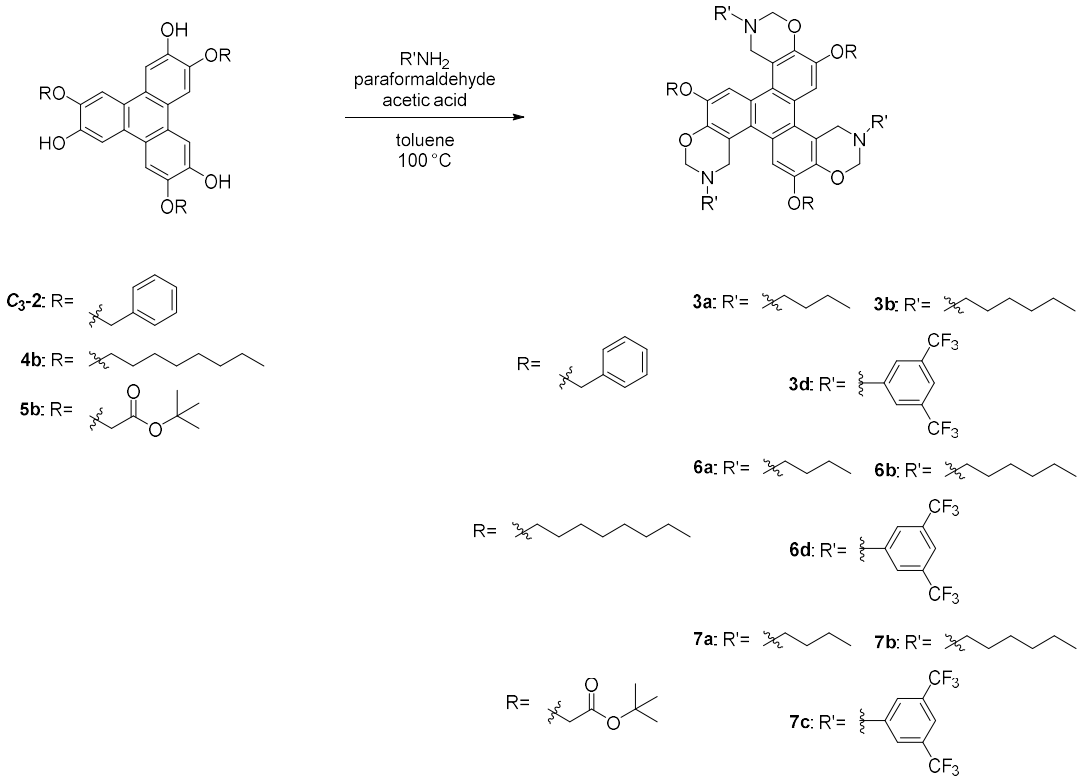
tri-*tert*-butyl 2,2',2''-((3,7,11-tris(benzyloxy)triphenylene-2,6,10-triyl)tris(oxy))triacetate (**4b**): **GP1** was applied to ***C*$_3$-2** and *tert*-butyl bromoacetate. 79% yield. M.P. 104 °C (lit. 104-103 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (3H, s), 7.66 (3H, s), 7.60 (6H, d, *J* = 7.5 Hz), 7.43 (6H, t, *J* = 7.5 Hz), 7.34 (3H, t, *J* = 7.4 Hz), 5.36 (6H, s), 4.74 (6H, s), 1.51 (27H, s). Further spectroscopic data (^{13}C, MS, IR) are in accordance with the literature.[4]

3,7,11-tris(octyloxy)triphenylene-2,6,10-triol (**5a**): **GP1** was continued on **4a**. 95% yield. Waxy solid. ^{1}H NMR (400 MHz): (DMSO d_6) δ 9.09 (3H, s), 7.88 (3H, s), 7.75 (3H, s), 4.19 (6H, t, J = 5.6 Hz), 1.89-1.78 (6H, set of m), 1.57-1.21 (30H set of m), 0.87 (9H, t, J = 6.7 Hz). ^{13}C NMR (100 MHz): δ 146.9, 146.4, 123.2, 121.3, 108.1, 105.6, 68.2, 28.9, 28.9, 28.7, 25.6, 22.10, 13.9. IR (KBr): v 1632, 1596, 1516, 1454, 1390, 1360, 1303, 1270, 1223, 1179, 1164, 1028, 1006, 853, 801, 576 cm^{-1}. HRMS (ESI): calcd. for $C_{42}H_{59}O_6$ [M$^-$] 659.4317; found: 659.4305.

tri-*tert*-butyl 2,2',2''-((3,7,11-trihydroxytriphenylene-2,6,10-triyl)tris(oxy))triacetate (**5b**): **GP1** was continued on **4b**. 91% yield. Waxy solid. ^{1}H NMR (300 MHz, DMSO d_6) δ 7.84 (3H, s), 7.72 (3H, s), 4.89 (6H, s), 1.46 (27H, s). Further spectroscopic data (^{13}C, MS, IR) are in accordance with the literature.[4]

General Procedure 2 (GP2)

General procedure for the Mannich reaction of 3,7,11-tris(alkyloxy)triphenylene-2,6,10-triol with butylamine, hexylamine or 3,5-bis(trifluoromethyl)aniline.



In a 10 mL screw-caped Pyrex test tube, a mixture of 3,7,11-tris(alkyloxy)triphenylene-2,6,10-triol (0.08 mmol), paraformaldehyde (0.087 g, 2.88 mmol), acetic acid (0.021 g, 0.35 mmol), and amine (1.44 mmol) in anhydrous toluene (2 mL) was purged with argon and stirred overnight at 100 °C. The resulting red solution was then cooled to room temperature and dried in vacuum. The product was obtained after precipitation with absolute EtOH (in the case of **3a**,**b**,**d**) or after flash chromatography (in the case of **6a**,**b**,**d**, **7a**-**c**).

6,12,18-tris(benzyloxy)-3,9,15-tributyl-3,4,9,10,15,16-hexahydro-2H,8H,14H-triphenyleno[1,2-*e*:5,6-*e′*:9,10-*e″*]tris([1,3]oxazine) (**3a**): **GP2** was applied on ***C*$_3$-2** and butylamine. 83% yield. M.P. 112 °C. ^{1}H NMR (400 MHz): δ ($CDCl_3$) 7.53-7.43 (6H, set of m), 7.37 (6H, t, *J* = 7.4 Hz), 7.33-7.28 (3H, set of m), 7.25 (3H, s), 5.31 (6H, s), 5.10(6H, s), 4.30(6H, s), 2.43 (6H, t, *J* = 7.2 Hz), 1.44-1.30 (6H, set of m), 1.30-1.15 (6H, set of m), 0.84 (6H, t, *J* = 6.8 Hz). ^{13}C NMR (100 MHz): δ 144.2, 143.7, 137.2, 128.8, 128.1, 127.0, 126.3, 123.2, 115.9, 111.1, 81.9, 71.4, 53.5, 50.2, 30.4, 20.4, 14.1. IR (KBr): v 1668, 1592, 1484, 1420, 1374, 1313, 1274, 1240, 1148, 1088, 1028, 955, 912, 857, 785, 732, 696 cm^{-1}. HRMS (ESI): calcd. for $C_{57}H_{64}N_3O_6$ [M^+] 886.4790; found: 886.4791.

6,12,18-tris(benzyloxy)-3,9,15-trihexyl-3,4,9,10,15,16-hexahydro-2H,8H,14H-triphenyleno[1,2-*e*:5,6-*e′*:9,10-*e″*]tris([1,3]oxazine) (**3b**): **GP2** was applied on ***C*$_3$-2** and hexylamine. 69% yield. M.P.

98 °C. ^{1}H NMR (400 MHz): ($CDCl_3$) δ 7.50-7.45 (6H, m), 7.37 (6H, t, *J* = 7.7 Hz), 7.32-7.28 (3H, m), 7.24 (3H, s), 5.31 (6H, s), 5.10 (6H, s), 4.31 (6H, s), 2.42 (6H, t, *J* = 7.3 Hz), 1.45-1.11 (24H, m), 0.84 (9H, t, *J* = 7.1 Hz). ^{13}C NMR (100 MHz): δ 144.3, 143.7, 137.2, 128.8, 128.1, 127.0, 126.2, 123.2, 115.9, 111.1, 81.9, 71.4, 53.5, 50.5, 31.8, 28.3, 26.9, 22.7, 14.2. IR (KBr): v 1592, 1483, 1420, 1374, 1313, 1274, 1242, 1163, 1147, 1089, 1028, 1012, 953, 919, 857, 785, 731, 696 cm^{-1}. HRMS (ESI): calcd. for $C_{63}H_{76}N_3O_6$ [M^+] 970.5729; found: 970.5734.

6,12,18-tris(benzyloxy)-3,9,15-tris(3,5-bis(trifluoromethyl)phenyl)-3,4,9,10,15,16-hexahydro-2H,8H,14H-triphenyleno[1,2-*e*:5,6-*e′*:9,10-*e″*]tris([1,3]oxazine) (**3d**): **GP2** was applied on ***C*$_3$-2** and 3,5-bis(trifluoromethyl)aniline. 52% yield. M.P. 202 °C. ^{1}H NMR (400 MHz): ($CDCl_3$) δ 7.47-7.43 (6H, set of m), 7.37 (6H, t, *J* = 7.6 Hz), 7.27 (3H, s), 7.25-7.20 (3H, set of m), 7.12 (6H, s), 7.02 (3H, s), 5.59 (6H, s), 5.35 (6H, s), 4.50 (6H, s). ^{13}C NMR (100 MHz): δ 148.4, 144.5, 143.3, 136.9, 132.5 (q, *J* = 34.0 Hz), 129.1, 128.3, 126.4, 125.3, 123.2 (q, *J* = 272.9 Hz) 123.2, 118.2, 116.1, 115.1, 111.1, 78.0, 70.9, 53.4; IR (KBr): v 1539, 1476, 1423, 1404, 1346, 1278, 1186, 1131, 1073, 1001, 963, 872, 735, 698, 682 cm^{-1}. HRMS (ESI): calcd. for $C_{69}H_{45}F_{18}N_3O_6$ [M^+] 1353.3015; found: 1353.3064.

3,9,15-tributyl-6,12,18-tris(octyloxy)-3,4,9,10,15,16-hexahydro-2H,8H,14H-triphenyleno[1,2-*e*:5,6-*e′*:9,10-*e″*]tris([1,3]oxazine) (**6a**): **GP2** was applied on **4b** and butylamine. Eluent cyclohexane/AcOEt, 9:1, 98% yield. Oil. ^{1}H NMR (400 MHz): ($CDCl_3$) δ 7.27 (3H, s), 5.08 (6H, s), 4.59 (6H, s), 4.08 (6H, t, *J* = 6.9 Hz), 2.44 (6H, t, *J* = 7.3 Hz), 1.90-1.77 (6H, set of m), 1.46-1.10 (42H, set of m), 0.83 (9H, t, *J* = 7.4 Hz), 0.75 (9H, t, *J* = 7.4 Hz). ^{13}C NMR (100 MHz): δ 144.7, 143.4, 125.7, 123.4, 115.4, 109.7, 81.7, 69.4, 53.7, 50.1, 48.7, 31.8, 30.3, 29.4, 29.2, 26.1, 22.7, 20.2, 14.1, 13.9. IR (KBr): v 1724, 1593, 1488, 1469, 1423, 1376, 1314, 1274, 1242, 1192, 1148, 1101, 1089, 951, 924, 785, 723 cm^{-1}. HRMS (ESI): calcd. for $C_{60}H_{94}N_3O_6$ [M^+] 952.7137; found: 952.7154.

3,9,15-trihexyl-6,12,18-tris(octyloxy)-3,4,9,10,15,16-hexahydro-2H,8H,14H-triphenyleno[1,2-*e*:5,6-*e′*:9,10-*e″*]tris([1,3]oxazine) (**6b**): **GP2** was applied on **4b** and hexylamine. Eluent cyclohexane/AcOEt, 9:1, 98% yield. Waxy solid. ^{1}H NMR (400 MHz): ($CDCl_3$) δ 7.34 (3H, s), 5.14 (6H, s), 4.65 (6H, s), 4.15 (6H, t, *J* = Hz), 2.50 (6H, t, *J* = Hz), 1.96-1.86 (6H, set of m) 1.62-1.10 (54H, set of m), 0.88 (9H, t, *J* = Hz), 0.81 (9H, t, *J* = Hz). ^{13}C NMR (100 MHz): 144.9, 143.5, 125.9, 123.5, 115.6, 109.9, 81.8, 77.5, 77.4, 77.2, 76.8, 69.5, 53.9, 50.6, 32.0, 31.8, 29.6, 29.4, 28.3, 26.9, 26.2, 22.8, 22.7, 14.2, 14.1, 14.1. IR (KBr): v 1720, 1593, 1488, 1468, 1422, 1377, 1314, 1273, 1237, 1148, 1091, 950, 728 cm^{-1}. HRMS (ESI): calcd. for $C_{66}H_{106}N_3O_6$ [M^+] 1036.8092; found: 1036.8092.

3,9,15-tris(3,5-bis(trifluoromethyl)phenyl)-6,12,18-tris(octyloxy)-3,4,9,10,15,16-hexahydro-2H,8H,14H-triphenyleno[1,2-*e*:5,6-*e′*:9,10-*e″*]tris([1,3]oxazine) (**6d**): **GP2** was applied on **4b** and 3,5-bis(trifluoromethyl)aniline. Eluent cyclohexane/AcOEt, 9:1, 52% yield. M.P. 162 °C. ^{1}H NMR

(400 MHz): ($CDCl_3$) δ 7.32 (3H, s), 7.30 (6H, s), 7.29 (3H, s), 5.68 (6H, s), 5.26 (6H, s), 4.16 (6H, t, *J* = 6.7 Hz), 1.98-1.87 (6H, set of m), 1.62-1.23 (30H, set of m), 0.87 (9H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz): δ 148.6, 145.8, 143.6, 132.7 (q, *J* = 33.1 Hz), 125.3, 123.8, 123.2 (q, *J* = 273.0 Hz), 118.1, 115.9, 115.2, 110.3, 78.4, 69.9, 53.8, 31.9, 29.5, 29.4, 29.3, 26.2, 22.8, 14.2. IR (KBr): v 1618, 1591, 1475, 1423, 1404, 1347, 1275, 1183, 1133, 1080, 1001, 965, 875, 682 cm^{-1}. HRMS (ESI): calcd. for $C_{72}H_{75}F_{18}N_3O_6$ [M^+]1419.5363; found: 1419.5430.

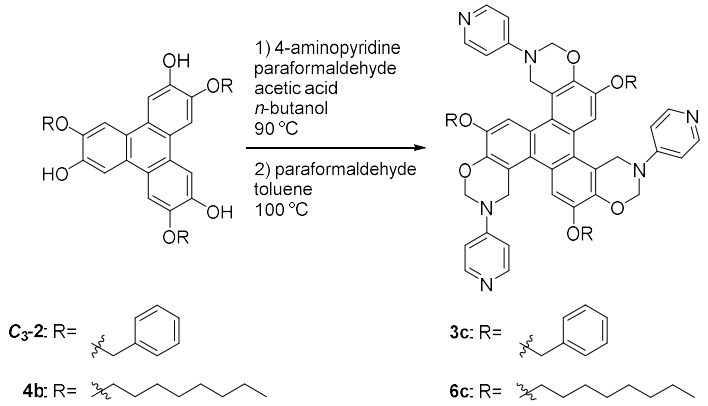
tri-*tert*-butyl 2,2',2''-((3,9,15-tributyl-3,4,9,10,15,16-hexahydro-2*H*,8*H*,14*H*-triphenyleno[1,2-*e*:5,6-*e'*:9,10-*e''*]tris([1,3]oxazine)-6,12,18-triyl)tris(oxy))triacetate (**7a**): **GP2** was applied on **5b** and butylamine. Eluent cyclohexane/AcOEt, 7:3, 35% yield. Waxy solid. ^1H NMR (400 MHz): δ ($CDCl_3$) δ 7.28 (3H, s), 5.14 (6H, s), 4.68 (6H, s), 4.60 (6H, s), 2.49 (6H, t, *J* = 7.6 Hz), 1.50 (27H, s), 1.45-1.32 (6H, set of m), 1.29-1.17 (6H, set of m), 0.82 (9H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz): δ 168.0, 143.8, 143.6, 127.0, 123.2, 116.1, 110.5, 82.7, 81.8, 66.8, 53.8, 50.2, 30.4, 28.3, 20.3, 14.0. IR (KBr): v 1753, 1728, 1594, 1487, 1451, 1419, 1368, 1316, 1278, 1245, 1225, 1151, 1111, 1017, 959, 916, 848, 785, 719 cm^{-1}. HRMS (ESI): calcd. for $C_{54}H_{76}N_3O_{12}$ [M^+] 958.5424; found: 958.5420.

tri-*tert*-butyl 2,2',2''-((3,9,15-trihexyl-3,4,9,10,15,16-hexahydro-2*H*,8*H*,14*H*-triphenyleno[1,2-*e*:5,6-*e'*:9,10-*e''*]tris([1,3]oxazine)-6,12,18-triyl)tris(oxy))triacetate (**7b**): **GP2** was applied on **5b** and hexylamine. Eluent cyclohexane/AcOEt, 7:3, 50% yield. Oil. ^1H NMR (400 MHz): ($CDCl_3$) δ 7.28 (3H, s), 5.14 (6H, s), 4.68 (6H, s), 4.60 (6H, s), 2.39 (6H, t, *J* = 7.4 Hz), 1.50 (27H, s), 1.47-1.38 (6H, set of m), 1.36- 1.24 (18H, set of m), 0.88 (9H, t, *J* = 6.9 Hz). ^{13}C NMR (100 MHz): δ 168.0, 143.8, 143.6, 127.0, 123.2, 116.1, 110.5, 81.8, 74.9, 66.8, 53.8, 53.1, 31.9, 28.3, 28.2, 27.4, 22.8, 14.2. IR (KBr): v 1753, 1728, 1626, 1593, 1574, 1486, 1465, 1415, 1371, 1314, 1229, 1151, 1108, 957, 924, 875, 716 cm^{-1}. HRMS (ESI): calcd. for $C_{60}H_{88}N_3O_{12}$ [M^+] 1042.6363; found: 1042.6389.

tri-*tert*-butyl 2,2',2''-((3,9,15-tris(3,5-bis(trifluoromethyl)phenyl)-3,4,9,10,15,16-hexahydro-2H,8H,14H-triphenyleno[1,2-*e*:5,6-*e'*:9,10-*e''*]tris([1,3]oxazine)-6,12,18-triyl)tris(oxy))triacetate (**7c**): **GP2** was applied on **5b** and 3,5-bis(trifluoromethyl)aniline. Eluent cyclohexane/AcOEt, gradient from 85:15 to 80:20, 52% yield. M.P. 213 °C. ^1H NMR (400 MHz): ($CDCl_3$) δ 7.36 (3H, s), 7.33 (6H, s), 7.28 (3H, s), 5.69 (6H, s), 5.23 (6H, s), 4.68 (6H, s), 1.45 (27H, s); ^{13}C NMR (100 MHz): 168.2, 148.5, 144.7, 143.8, 132.7 (q, *J* = 33 Hz), 126.5, 123.3, 123.1 (q, *J* = 273 Hz) ,118.1, 116.6, 115.2, 112.1, 82.9, 78.3, 67.5, 53.6, 28.1. IR (KBr): v 1747, 1621, 1577, 1541, 1477, 1415, 1347, 1275, 1231, 1176, 1130, 1091, 1001, 954, 875, 842, 682 cm^{-1}. HRMS (ESI): calcd. for $C_{66}H_{57}F_{18}N_3O_{12}$ [M^+] 1425.3649; found: 1425.3636.

General Procedure 3 (GP3)

General procedure for the Mannich reaction of 3,7,11-tris(alkyloxy)triphenylene-2,6,10-triol with 4-aminopyridine.



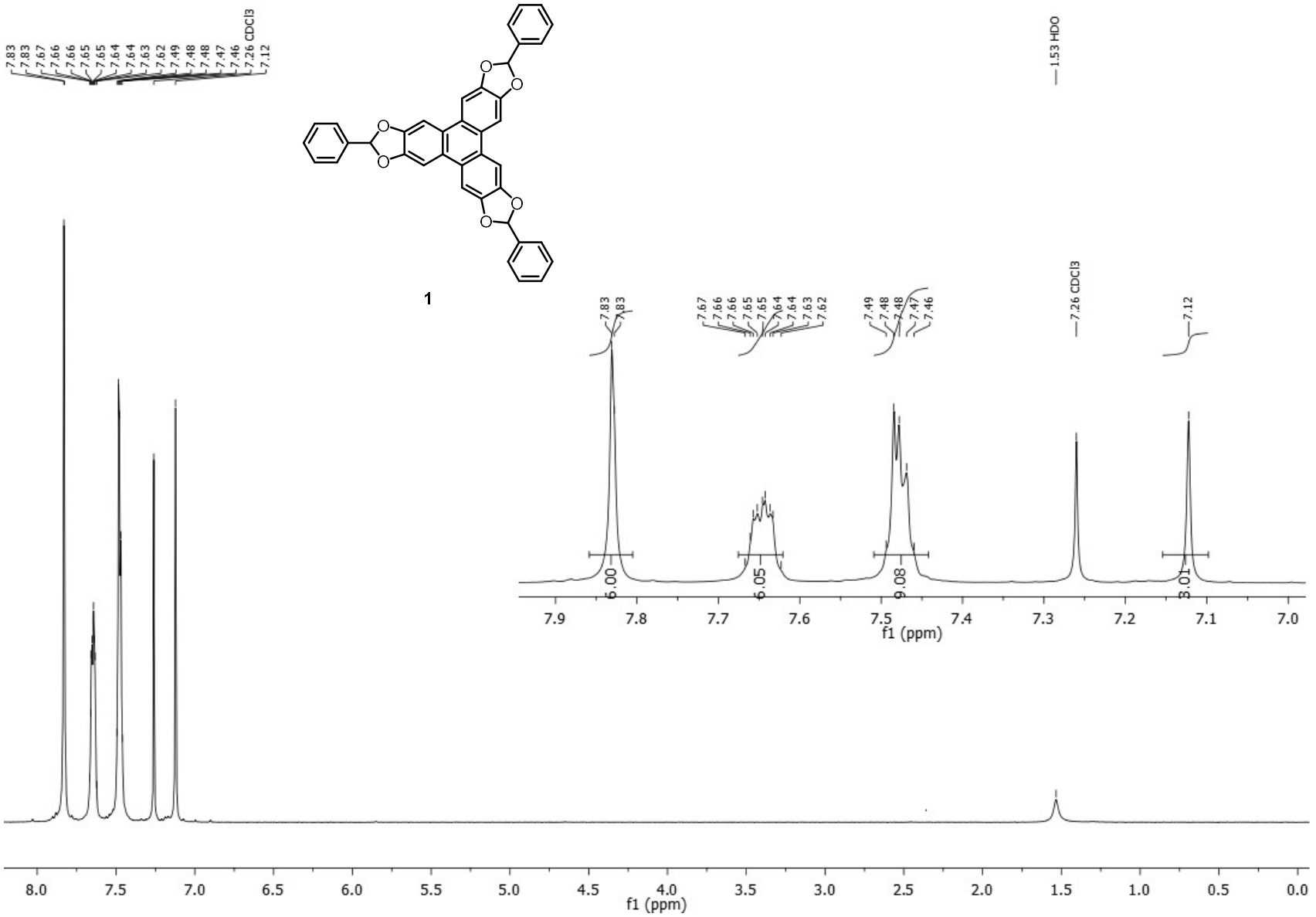
In a pear-shaped 25 mL round bottomed flask, a mixture of 4-aminopyridine (0.112 g, 1.2 mmol), paraformaldehyde (0.04 g, 1.33 mmol), and acetic acid (0.08 g, 1.2 mmol) in *n*-butanol (2 mL) was stirred at 90 °C overnight under argon atmosphere. The resulting solution was cooled to room temperature and concentrated in vacuum. The residue was transferred in a 10 mL screw-capped Pyrex test tube and 3,7,11-tris(alkyloxy)triphenylene-2,6,10-triol (0.08 mmol), paraformaldehyde (0.04 g, 1.33 mmol), and anhydrous toluene (2 mL) were added. The mixture was purged with argon and stirred overnight at 100 °C. The resulting mixture was cooled to room temperature and concentrated in vacuum. The resulting crude oil was suspended with EtOH (in the case of **3c**) or Et_2O (in the case of **6c**) and the resulting precipitate was filtered, washed with EtOH or Et_2O and dried in vacuum, to afford the product as a pale yellow solid.

6,12,18-tris(benzyloxy)-3,9,15-tri(pyridin-4-yl)-3,4,9,10,15,16-hexahydro-2*H*,8*H*,14*H*-triphenyleno[1,2-*e*:5,6-*e′*:9,10-*e″*]tris([1,3]oxazine) (**3c**): **GP3** was applied on ***C*$_3$-2**. 75% yield. M.P. 170-171 °C. ^{1}H NMR (400 MHz): δ ($CDCl_3$) 8.21 (6H, dd, *J* = 5.0, 1.6 Hz), 7.46-7.41 (6H, set of m), 7.34 (6H, t, *J* = 7.8 Hz), 7.24-7.19 (3H, set of m), 7.12 (3H, s), 6.56 (6H, dd, *J* = 5.0, 1.6 Hz), 5.64 (6H, s), 5.31 (6H, s), 4.61 (6H, s). ^{13}C NMR (100 MHz): δ 152.8, 149.7, 144.8, 143.5, 136.8, 128.9, 128.2, 126.5, 125.4, 123.1, 116.5, 111.2, 111.0, 76.6, 71.2, 50.3. IR (KBr): v 1643, 1593, 1552, 1511, 1483, 1459, 1421, 1383, 1319, 1278, 1245, 1159, 1111, 1072, 1034, 997, 960, 874, 799, 782, 740, 697 cm^{-1}; HRMS (ESI): calcd. for $C_{60}H_{49}N_6O_6$ [M^+] 949.3708; found: 949.3744.

6,12,18-tris(octyloxy)-3,9,15-tri(pyridin-4-yl)-3,4,9,10,15,16-hexahydro-2H,8H,14H-triphenyleno[1,2-*e*:5,6-*e′*:9,10-*e″*]tris([1,3]oxazine) (**6c**): **GP3** was applied on **4b**. 83% yield. M.P. 191-192 °C. ^{1}H NMR (400 MHz): ($CDCl_3$) δ 8.22 (6H, d, *J* = 5.2 Hz), 7.34 (3H, s), 6.70 (6H, d, *J* = 5.2 Hz), 5.73 (6H, s), 5.26 (6H, s), 4.14 (6H, t, *J* = 6.5 Hz), 1.99 - 1.85 (6H, set of m), 1.61 - 1.18 (36H, set of m), 0.87 (9H, t, *J* = 6.6 Hz). ^{13}C NMR (100 MHz): δ 152.9, 150.7, 145.9, 143.7, 125.4, 123.7, 116.4, 111.3, 110.1, 69.7, 51.1, 31.9, 29.5, 29.4, 26.2, 22.8, 14.2. IR (KBr): v 1594, 1553,

1484, 1422, 1380, 1318, 1246, 1163, 1112, 1080, 995, 965, 818, 725 cm^{-1}. HRMS (ESI): calcd. for $C_{63}H_{79}N_6O_6$ [M^+] 1015.6056; found: 1015.6050.

S2. NMR and MS Spectroscopy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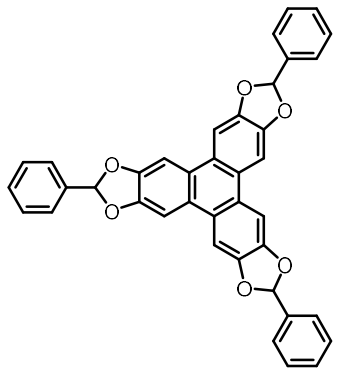
f1 (ppm)



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76.84 CDCl3
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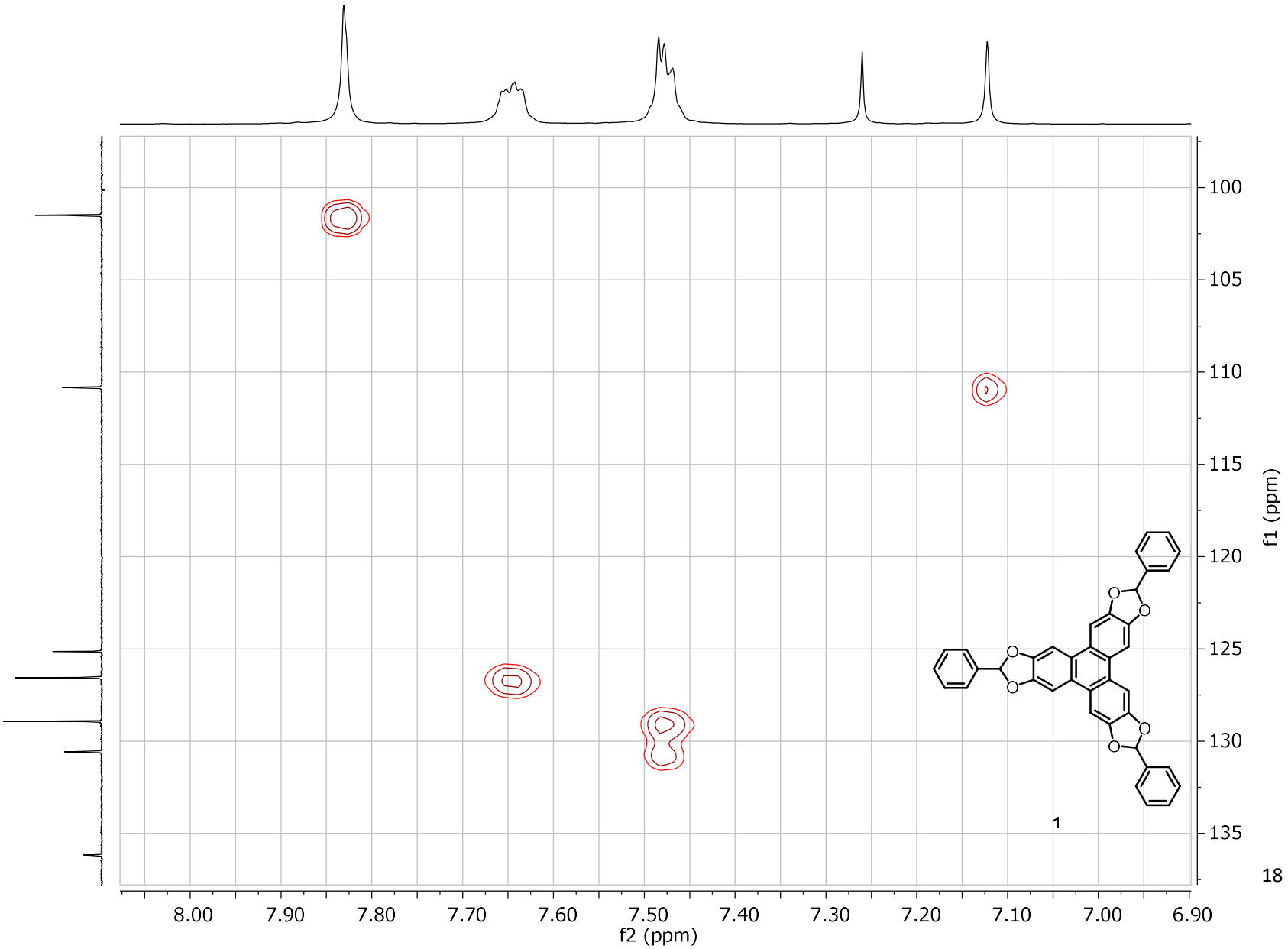
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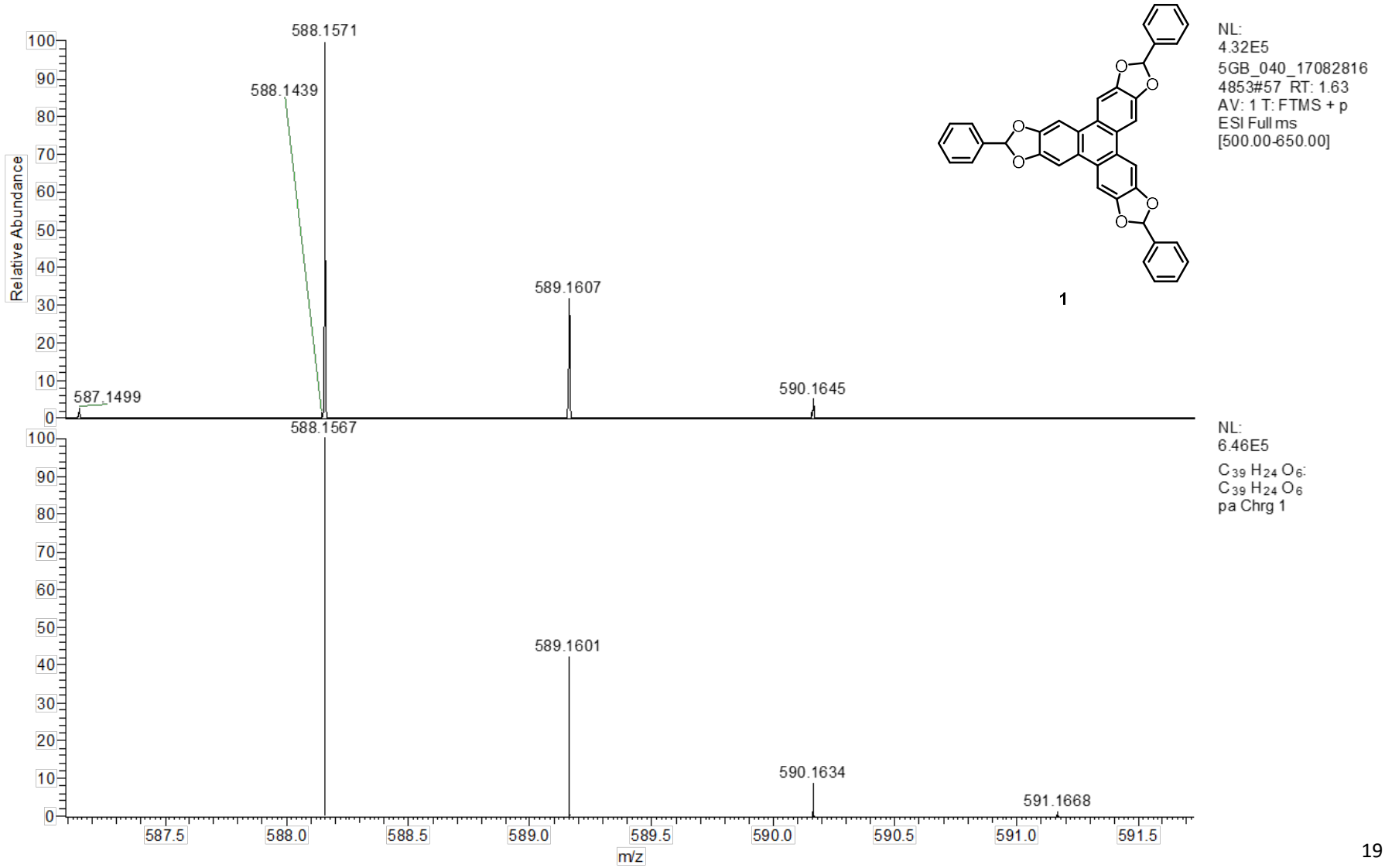

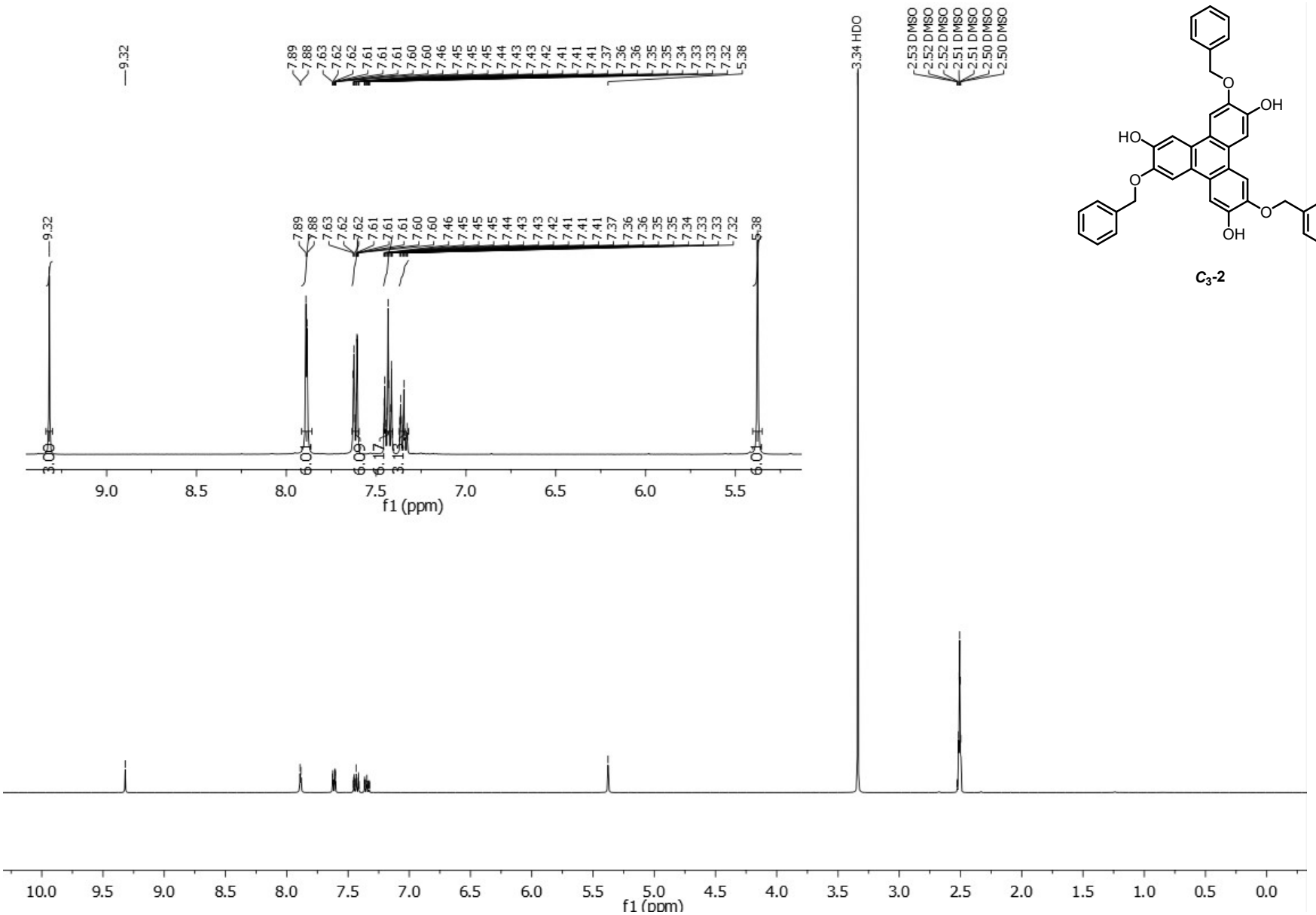
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f1 (ppm)

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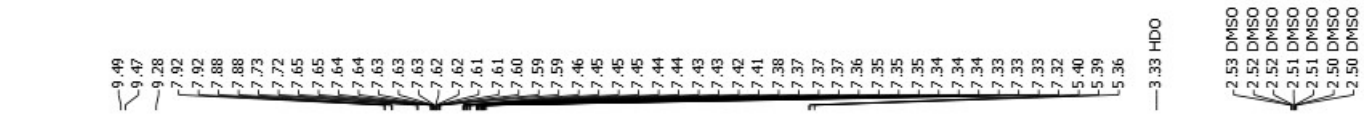
OH

C_3-2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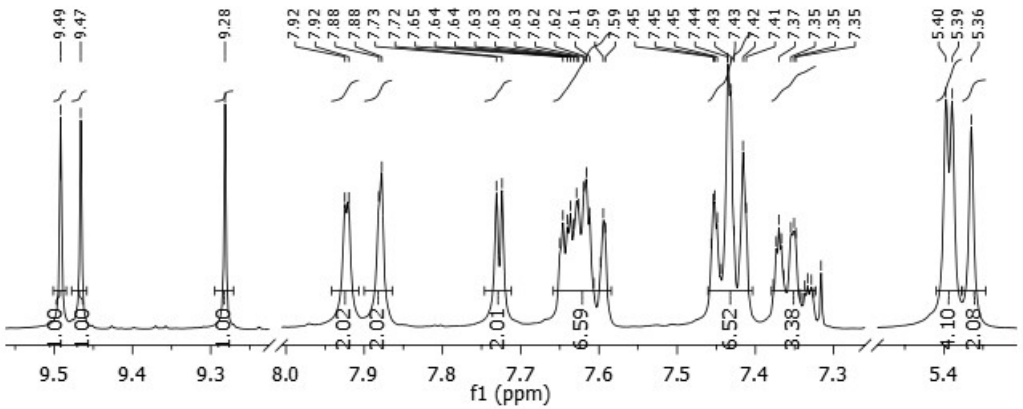
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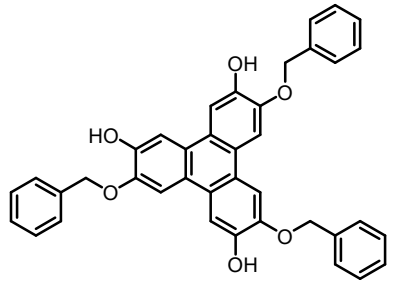
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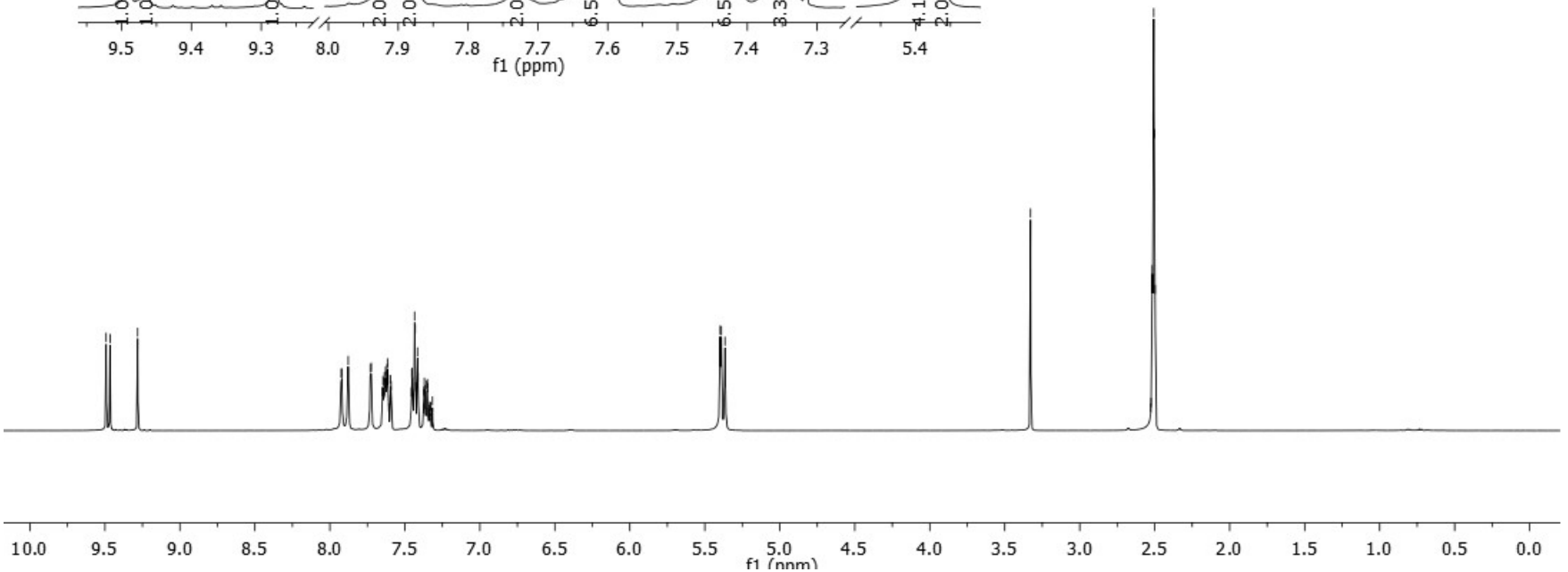
***C*$_s$-2**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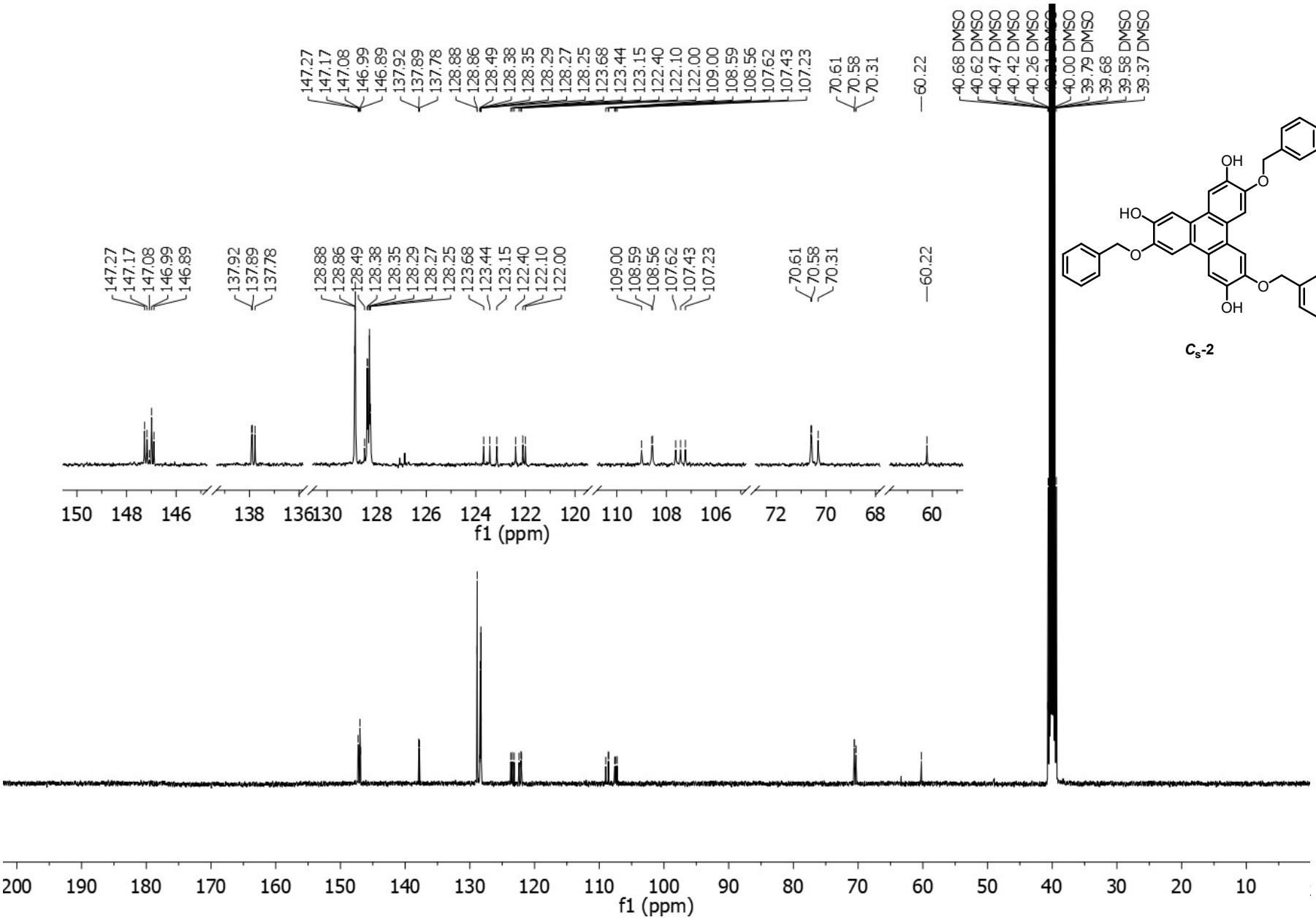
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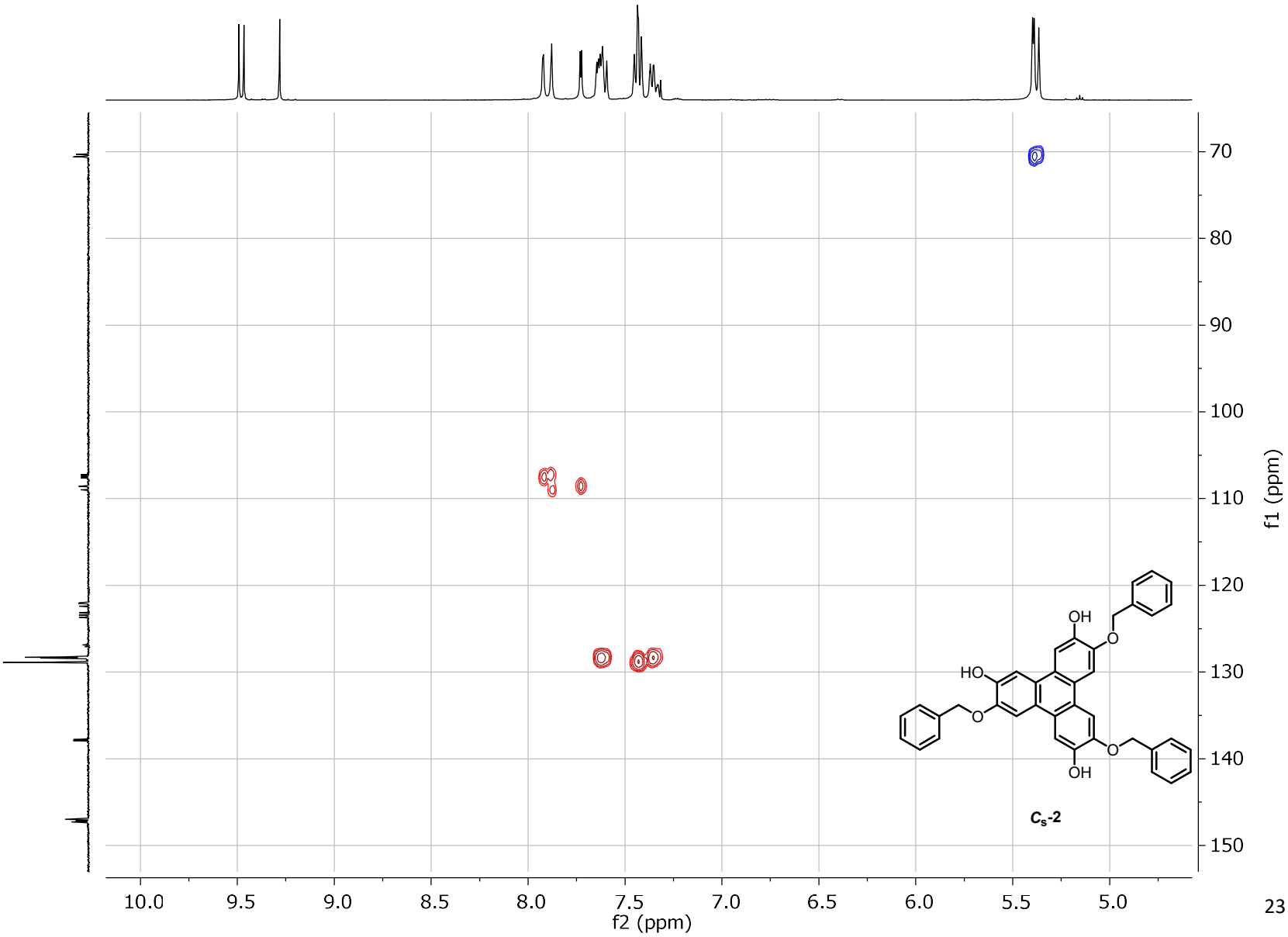
f1 (ppm)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f1 (ppm)
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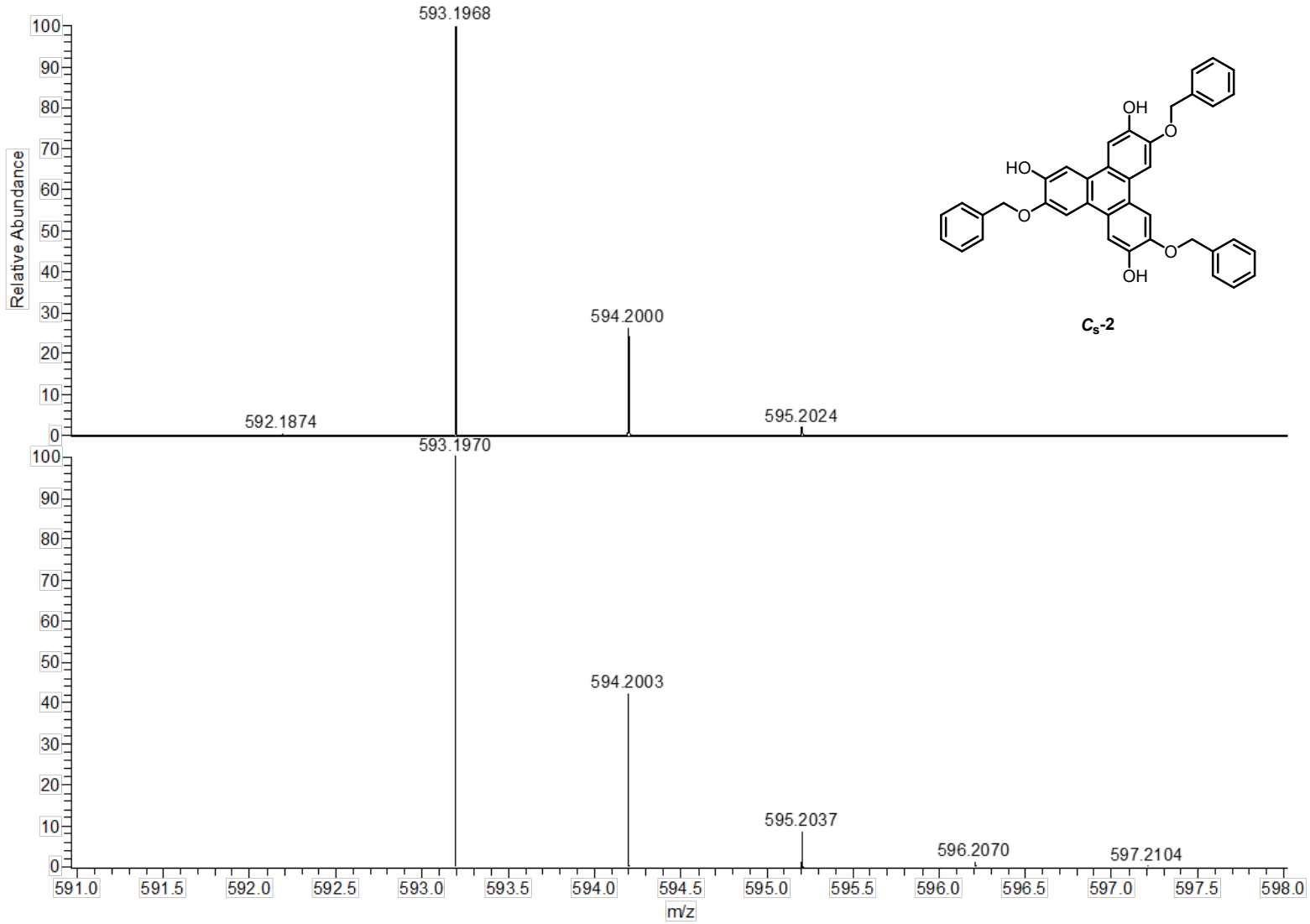
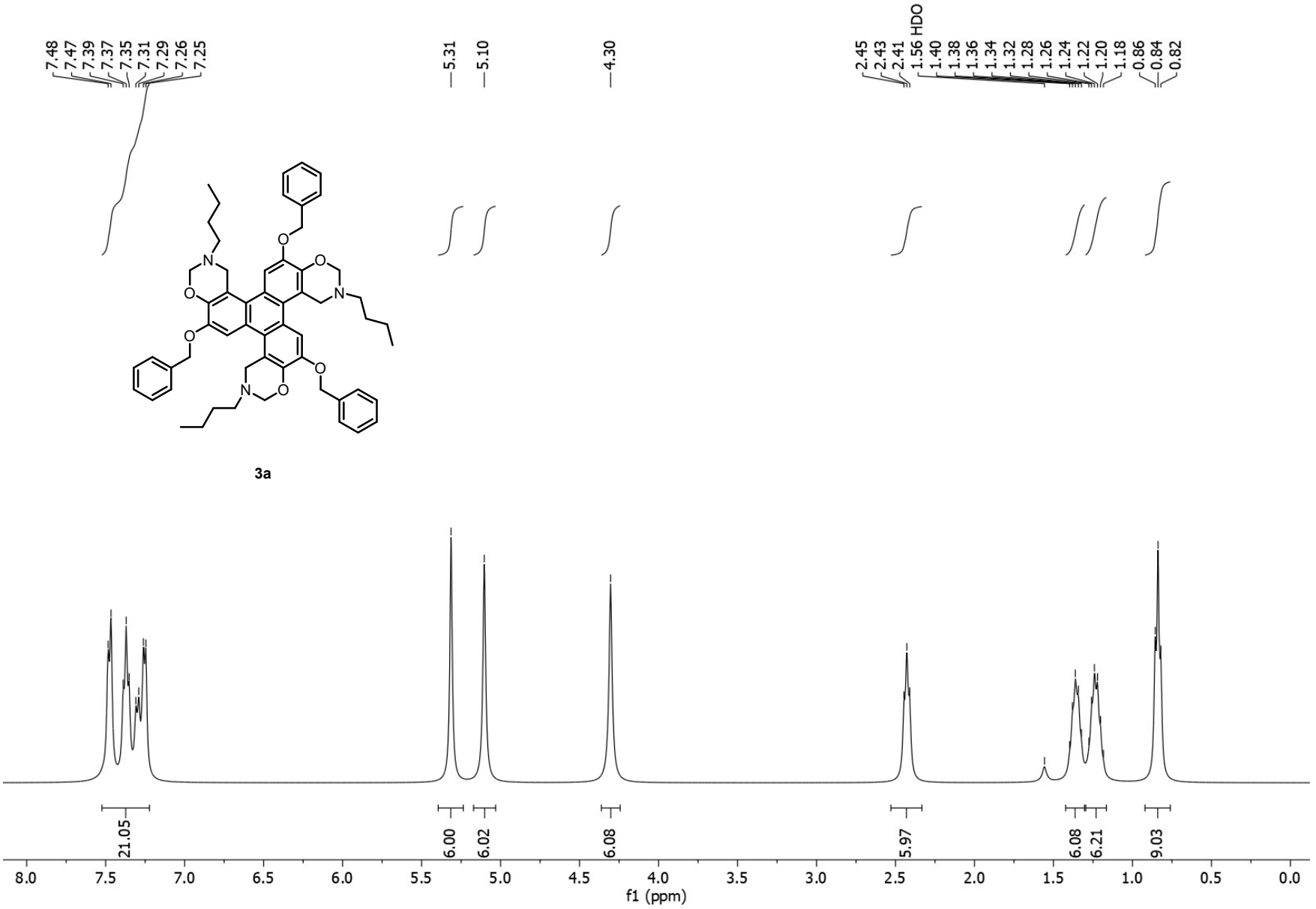
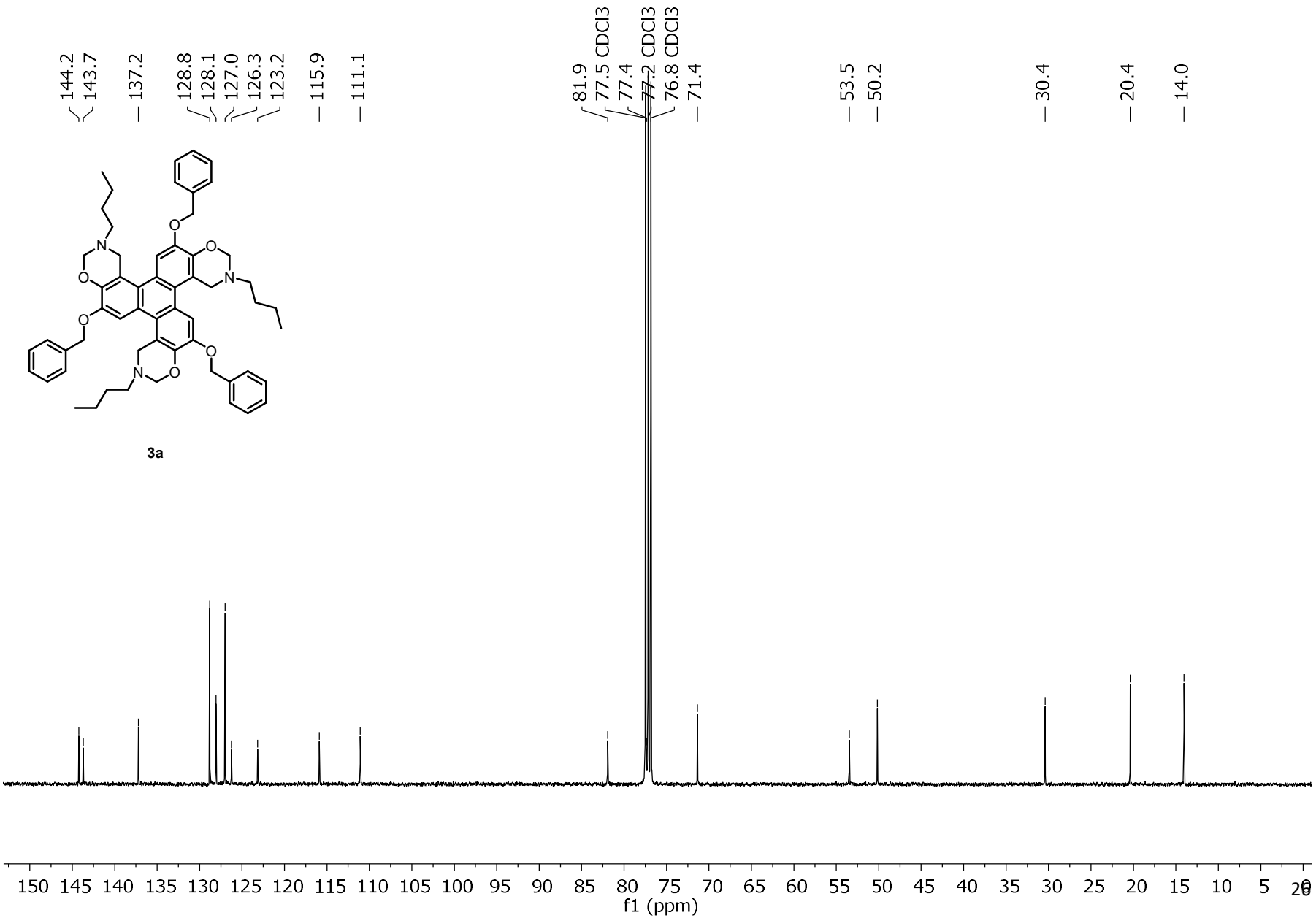
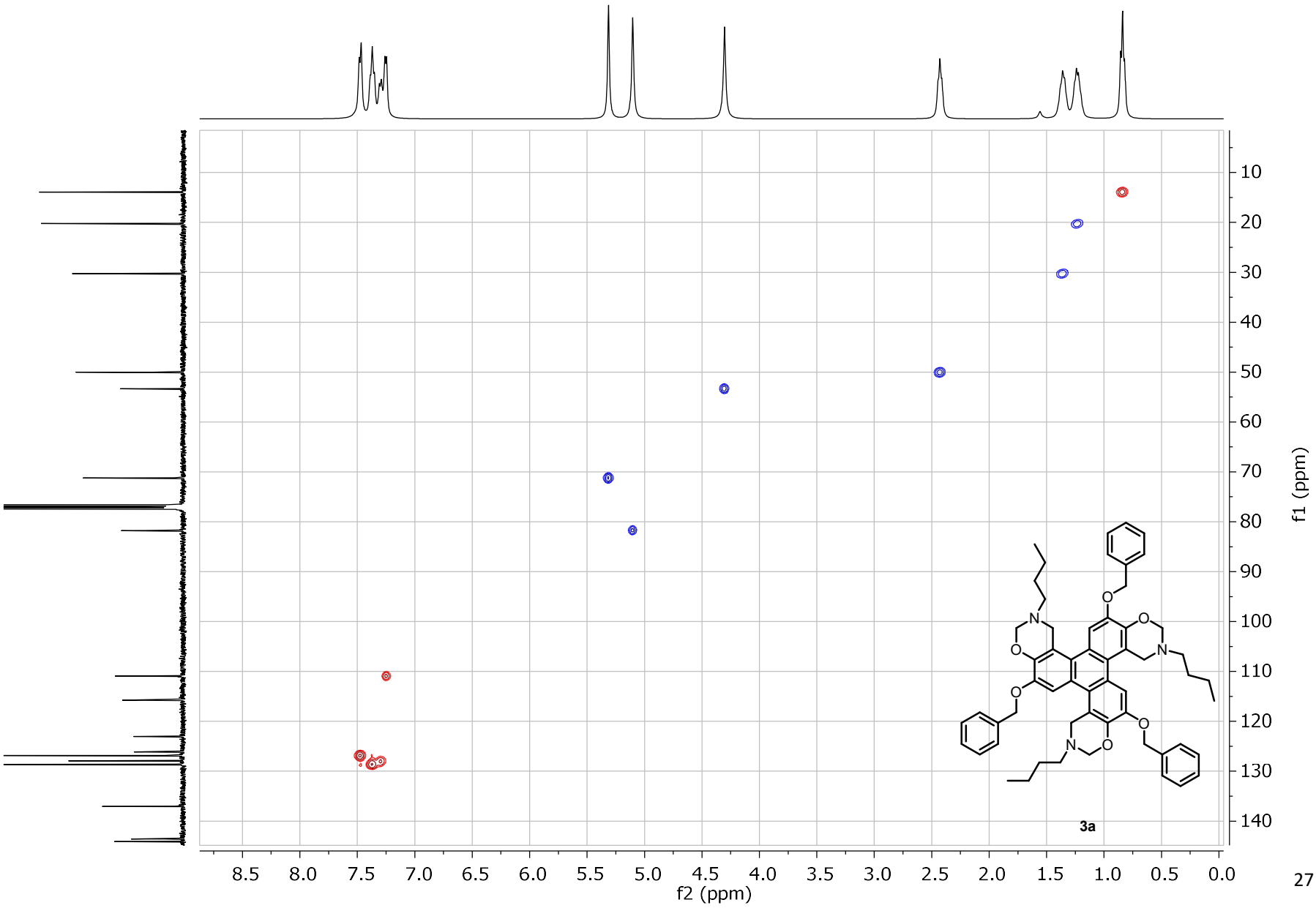
C_s-2

C:\Progetti\...\5GB_071 neg_170828164853 12/4/2017 2:48:25 PM

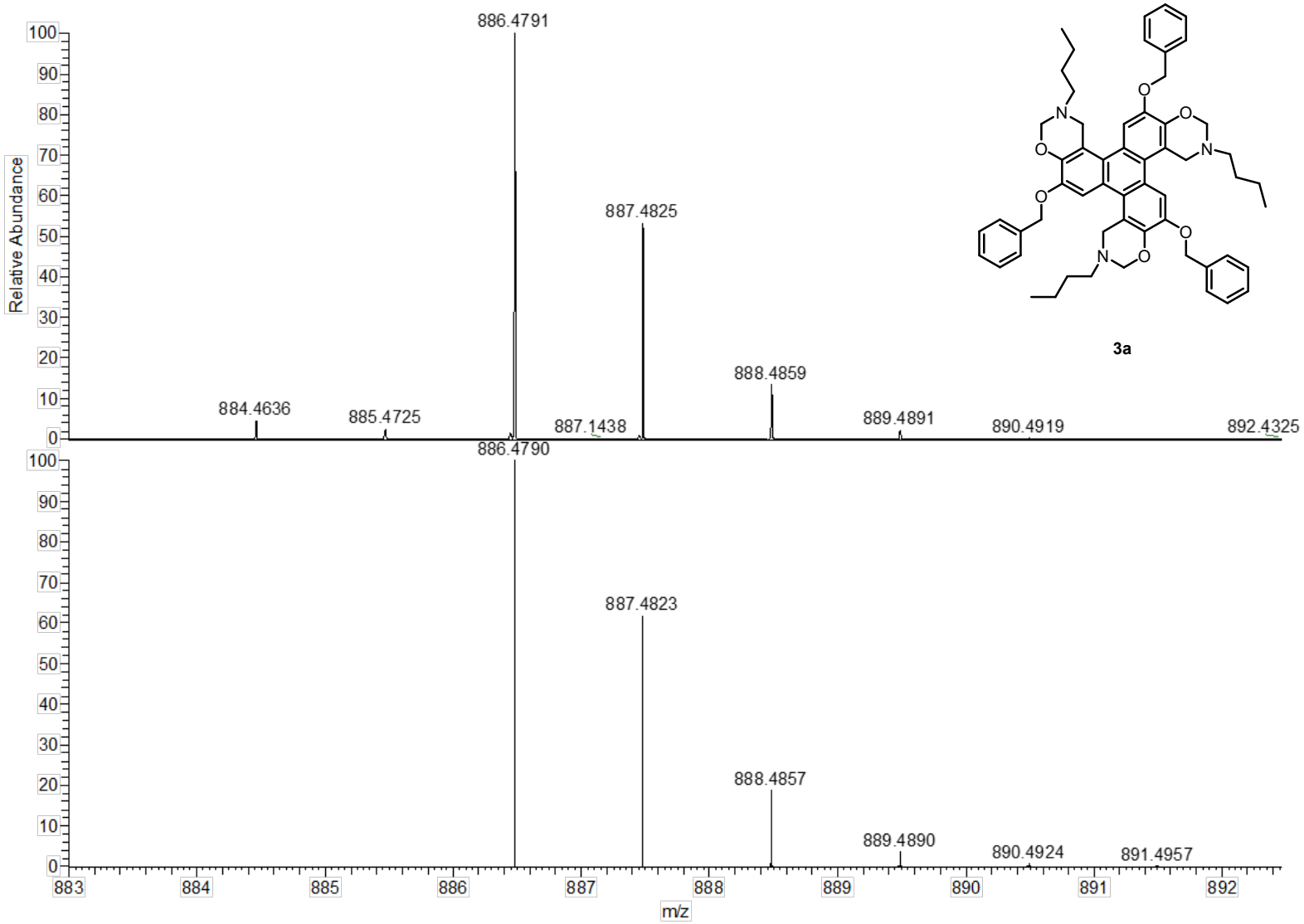


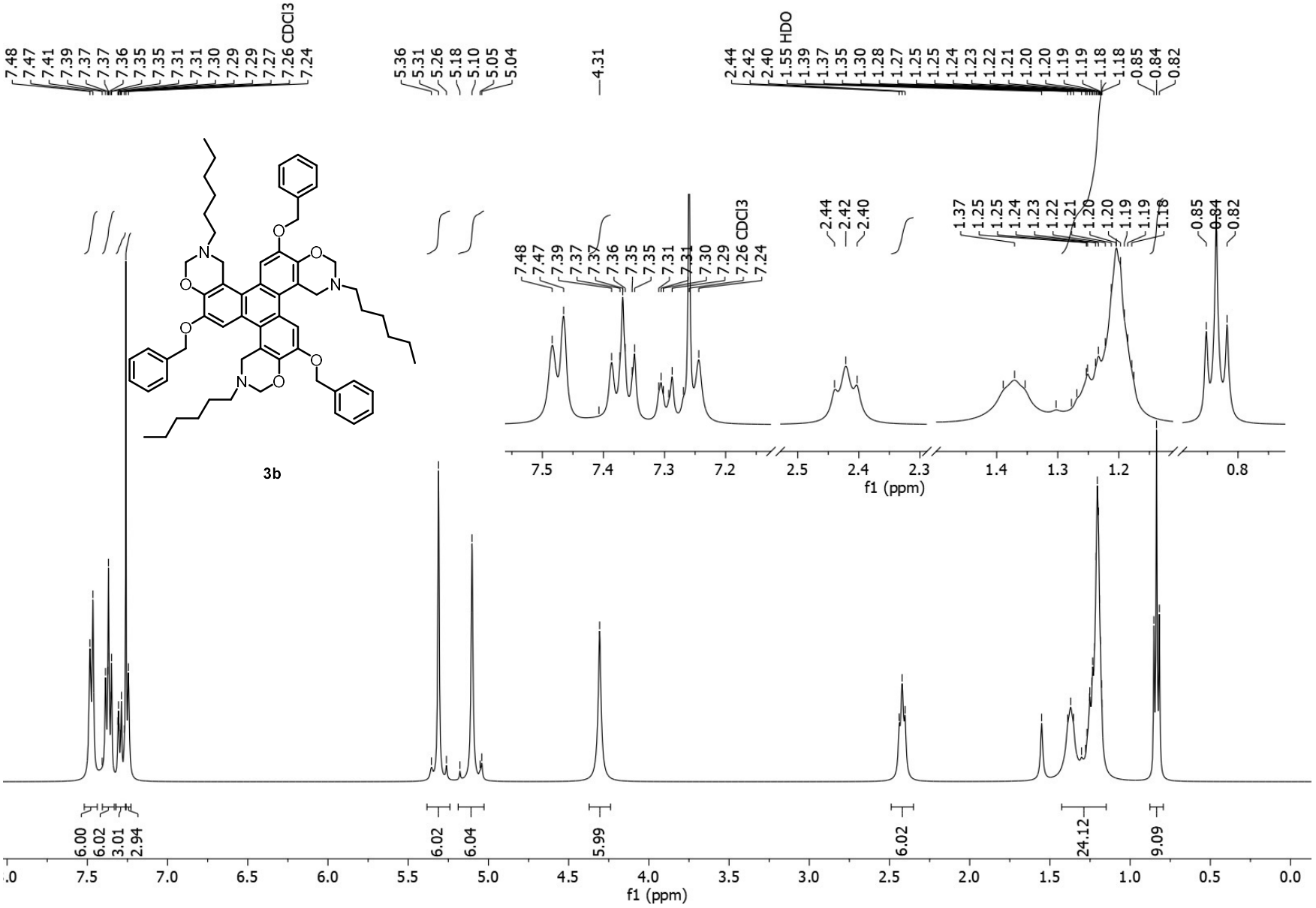

7.48
7.47
7.39
7.37
7.35
7.31
7.29
7.26
7.25
5.31
5.10
4.30
2.45
2.43
2.41
1.56 HDO
1.40
1.38
1.36
1.34
1.32
1.28
1.26
1.24
1.22
1.20
1.18
0.86
0.84
0.82
3a
21.05
6.00
6.02
6.08
5.97
6.08
6.21
9.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

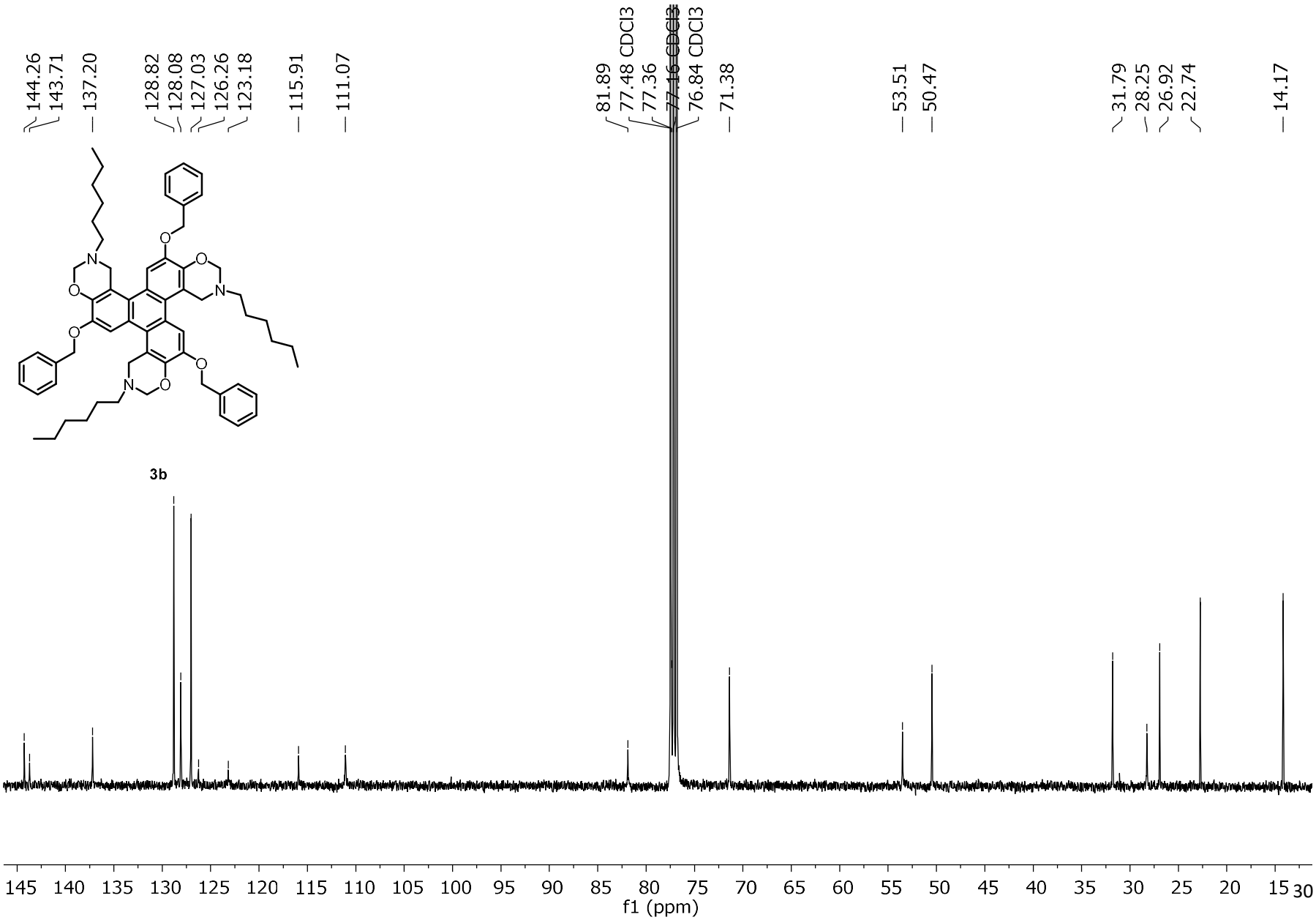

144.2
143.7
137.2
128.8
128.1
127.0
126.3
123.2
115.9
111.1
81.9
77.5 CDCl3
77.4
77.2 CDCl3
76.8 CDCl3
71.4
53.5
50.2
30.4
20.4
14.0
3a
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

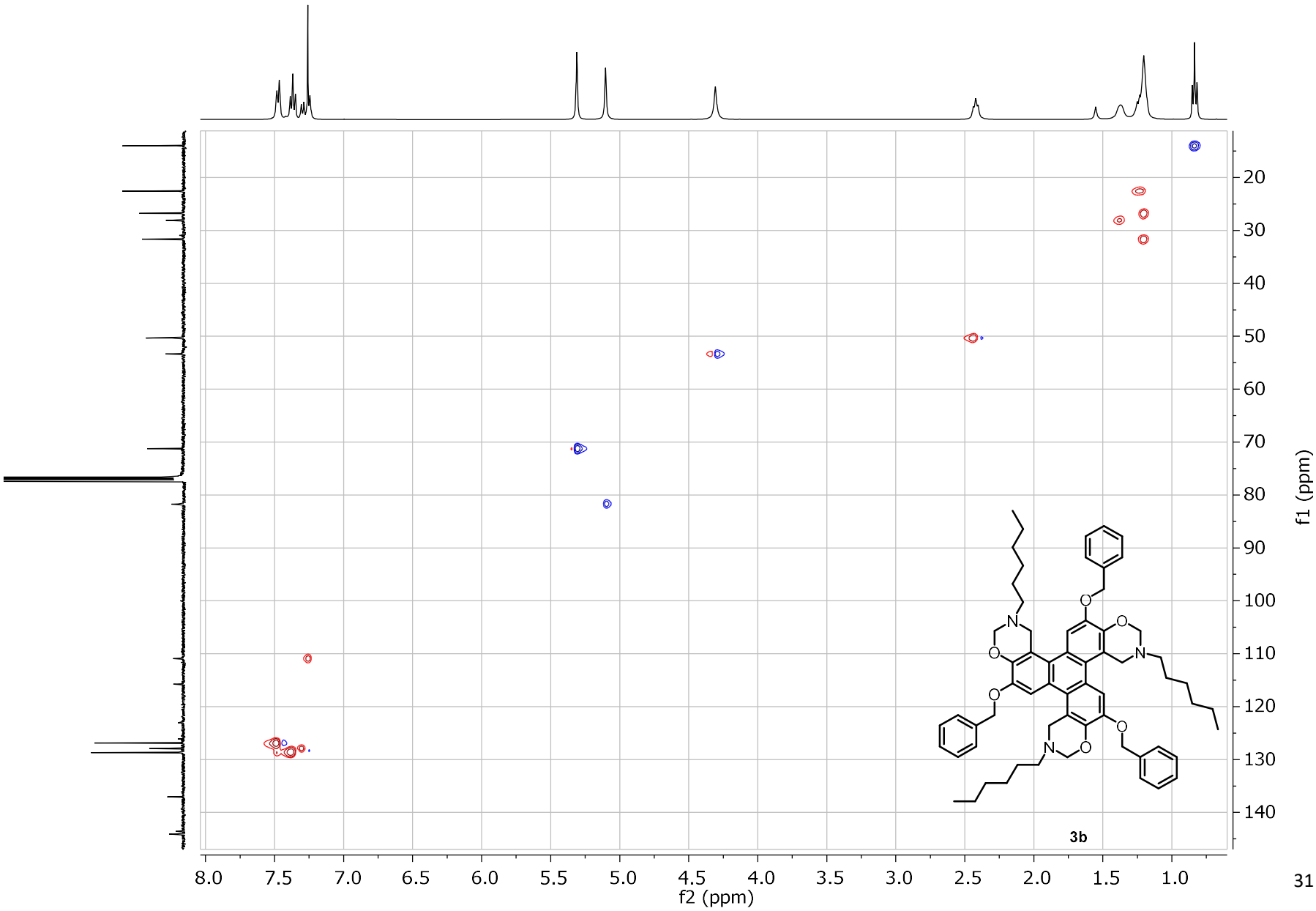

f2 (ppm)
f1 (ppm)
3a

C:\Progetti\...\6GB_052_171204150225 12/4/2017 3:06:25 PM

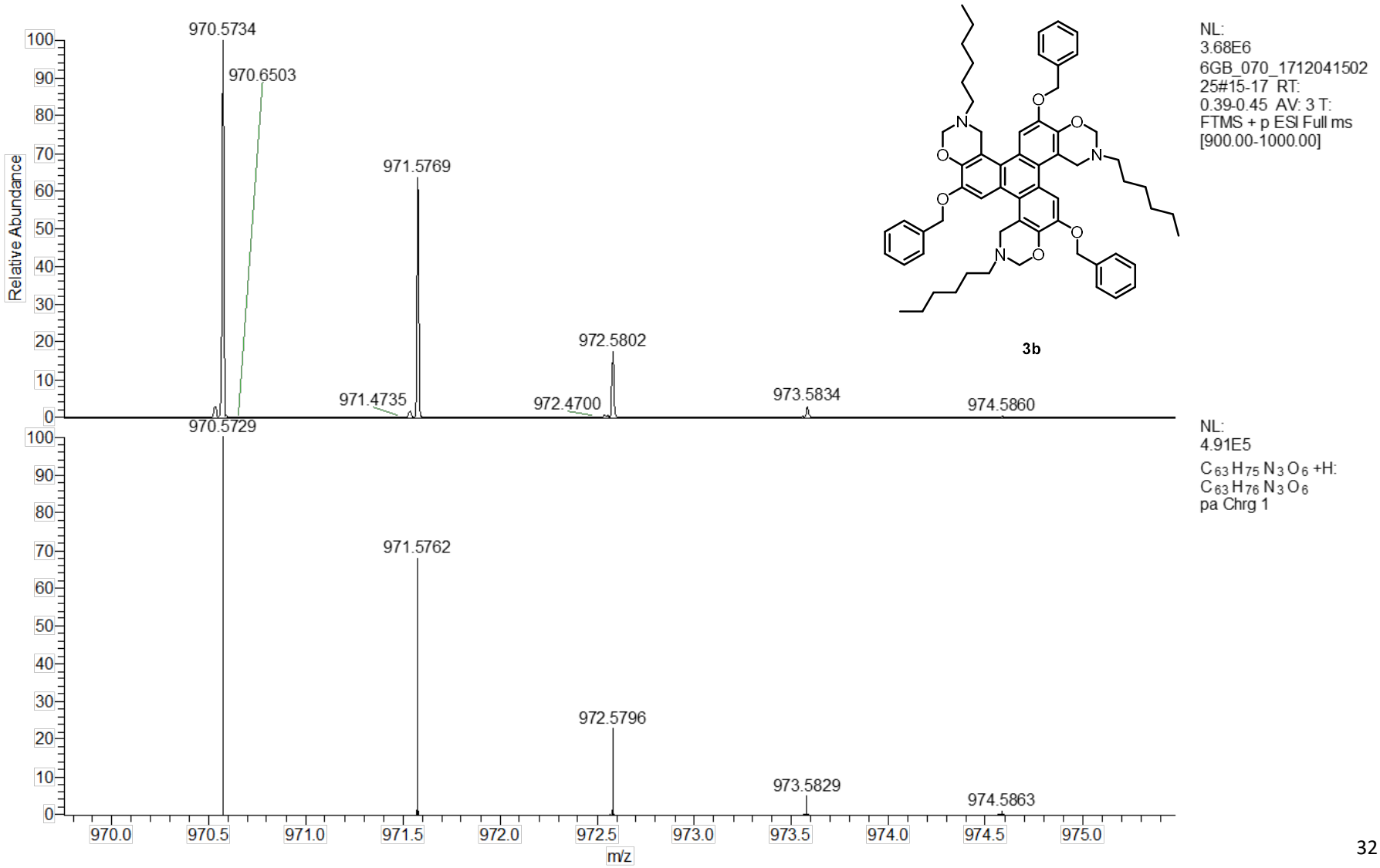


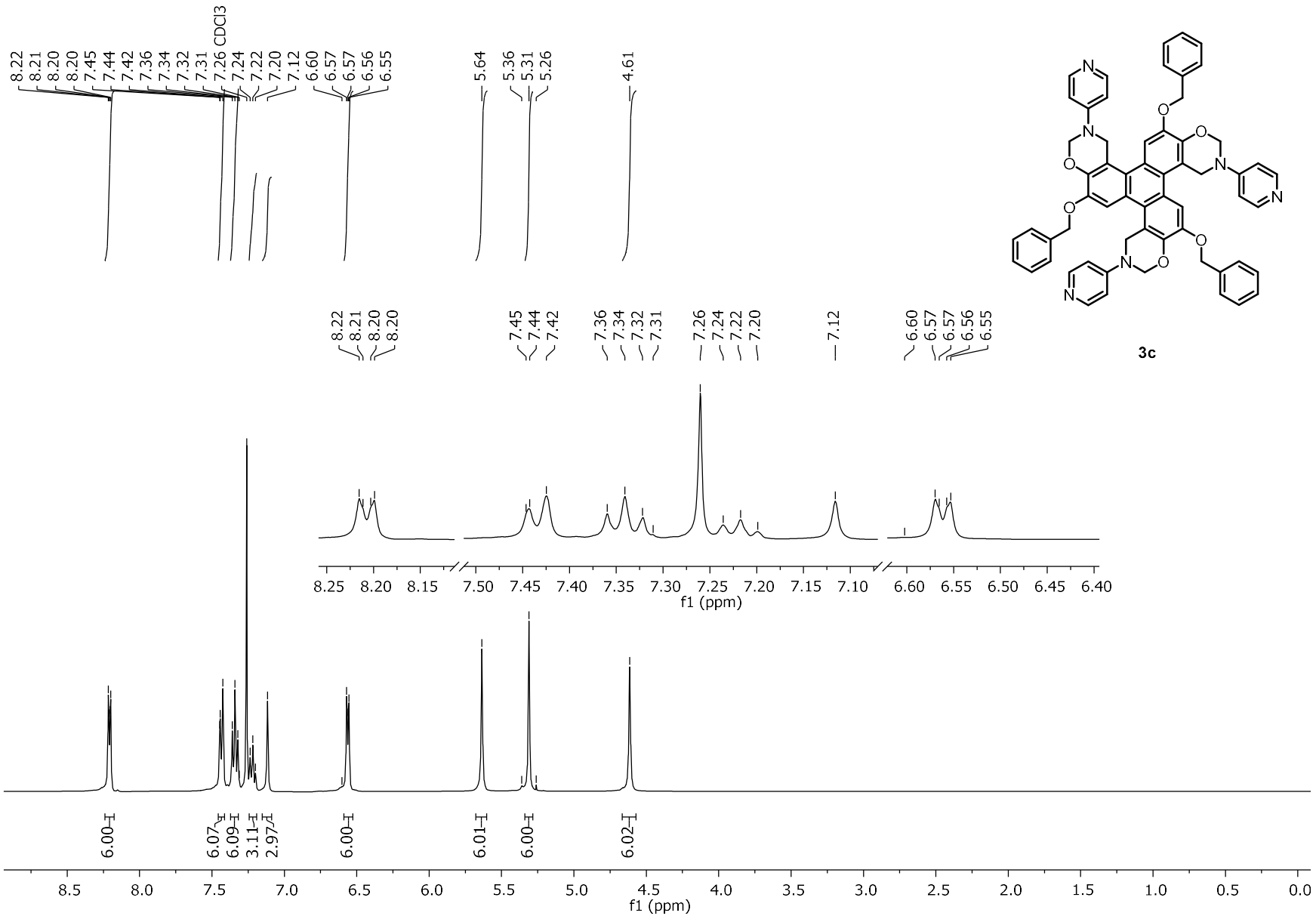

7.48
7.47
7.41
7.39
7.37
7.37
7.36
7.35
7.35
7.31
7.31
7.30
7.29
7.29
7.27
7.26 CDCl3
7.24
5.36
5.31
5.26
5.18
5.10
5.05
5.04
4.31
2.44
2.42
2.40
1.55 HDO
1.39
1.37
1.35
1.30
1.28
1.27
1.25
1.25
1.24
1.23
1.22
1.21
1.20
1.20
1.19
1.19
1.18
1.18
0.85
0.84
0.82
3b
f1 (ppm)
6.00
6.02
3.01
2.94
6.02
6.04
5.99
6.02
24.12
9.09

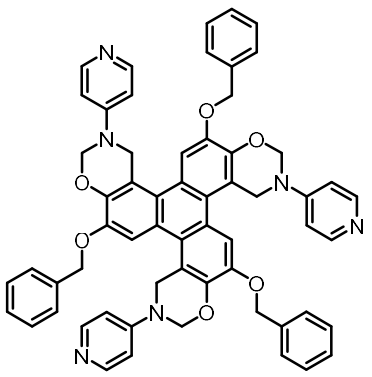

144.26
143.71
137.20
128.82
128.08
127.03
126.26
123.18
115.91
111.07
81.89
77.48 CDCl3
77.36
77.16 CDCl3
76.84 CDCl3
71.38
53.51
50.47
31.79
28.25
26.92
22.74
14.17
3b
f1 (ppm)


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)
3b

C:\Progetti\...\6GB_070_171204150225 12/4/2017 3:12:34 PM

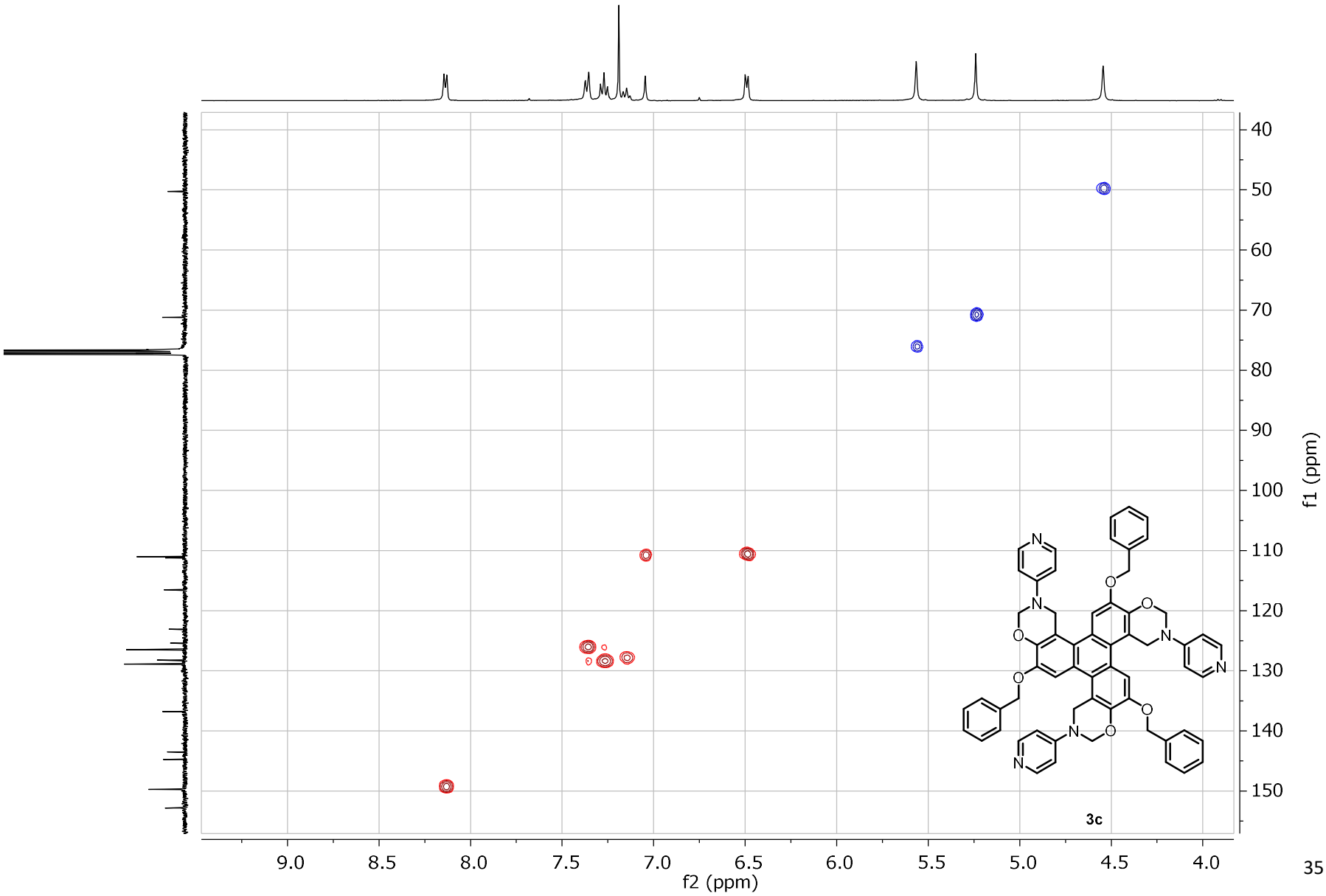



8.22
8.21
8.20
8.20
7.45
7.44
7.42
7.36
7.34
7.32
7.31
7.26 CDCl3
7.24
7.22
7.20
7.12
6.60
6.57
6.57
6.56
6.55
5.64
5.36
5.31
5.26
4.61
3c
f1 (ppm)
6.00
6.07
6.09
3.11
2.97
6.00
6.01
6.00
6.02

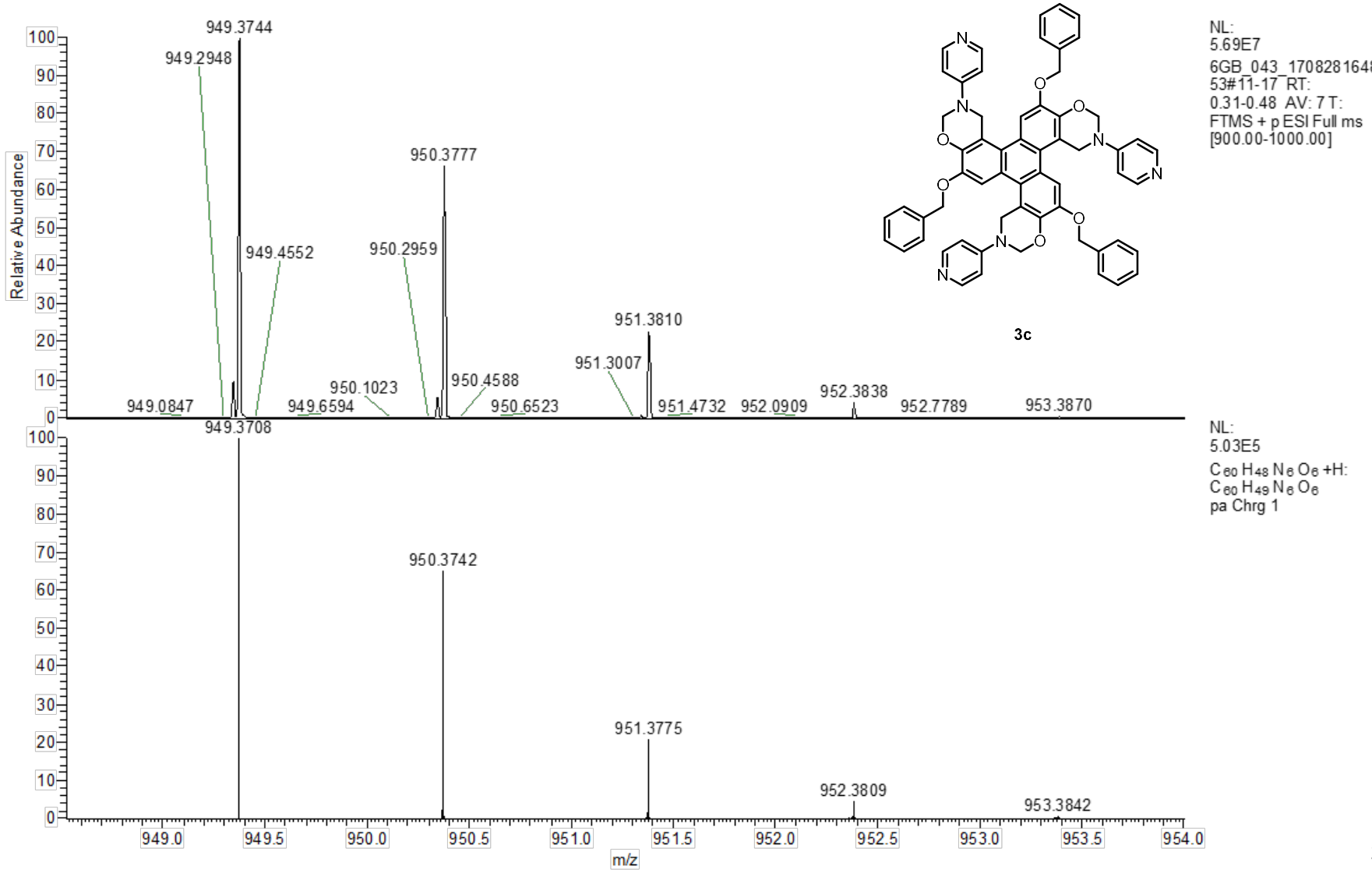


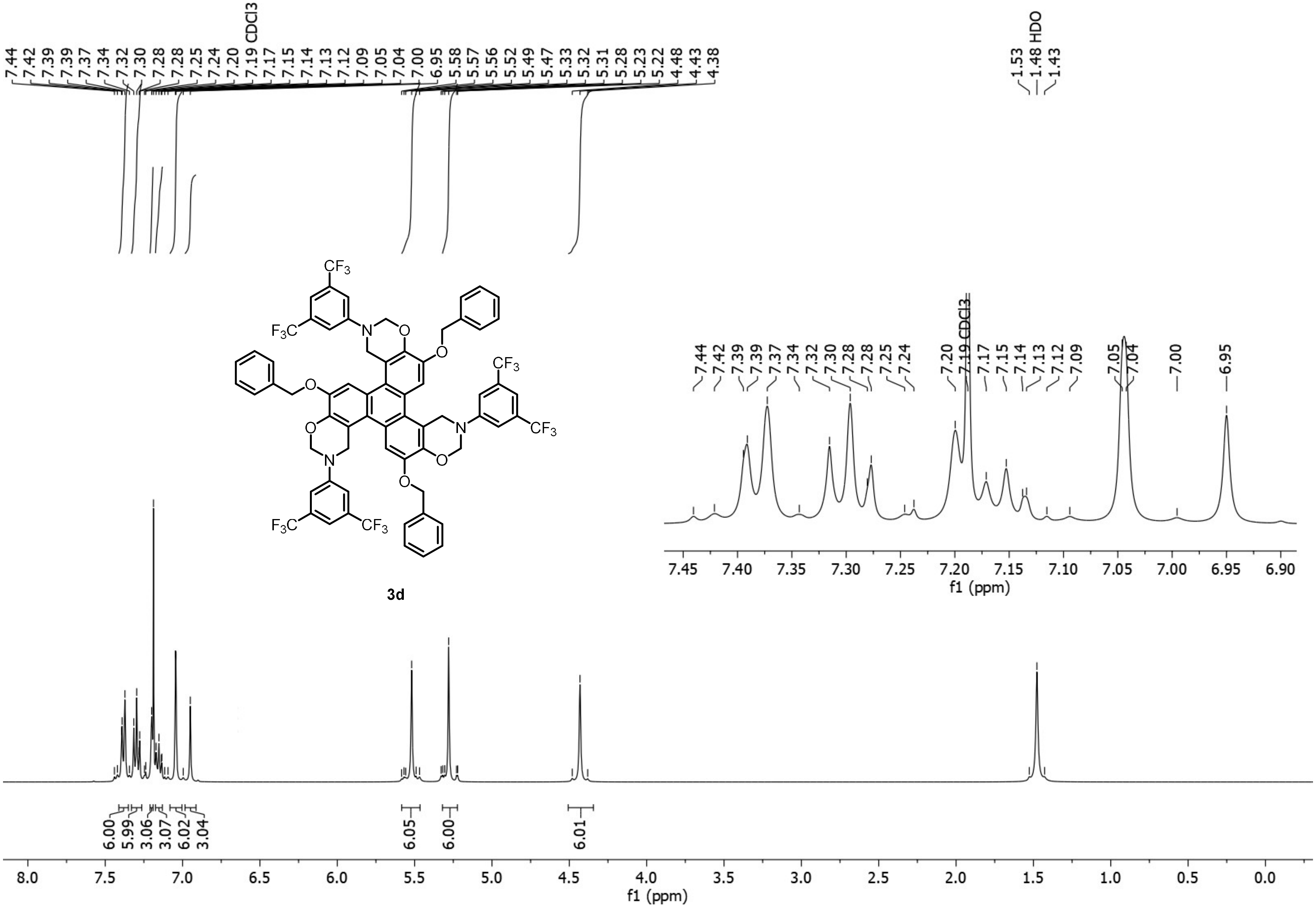
3c

152.8
149.7
144.8
143.5
136.8
128.9
128.2
126.5
125.4
123.1
116.5
111.2
111.0
77.3 CDCl3
77.2
77.0 CDCl3
76.7 CDCl3
71.2
50.3
20.9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

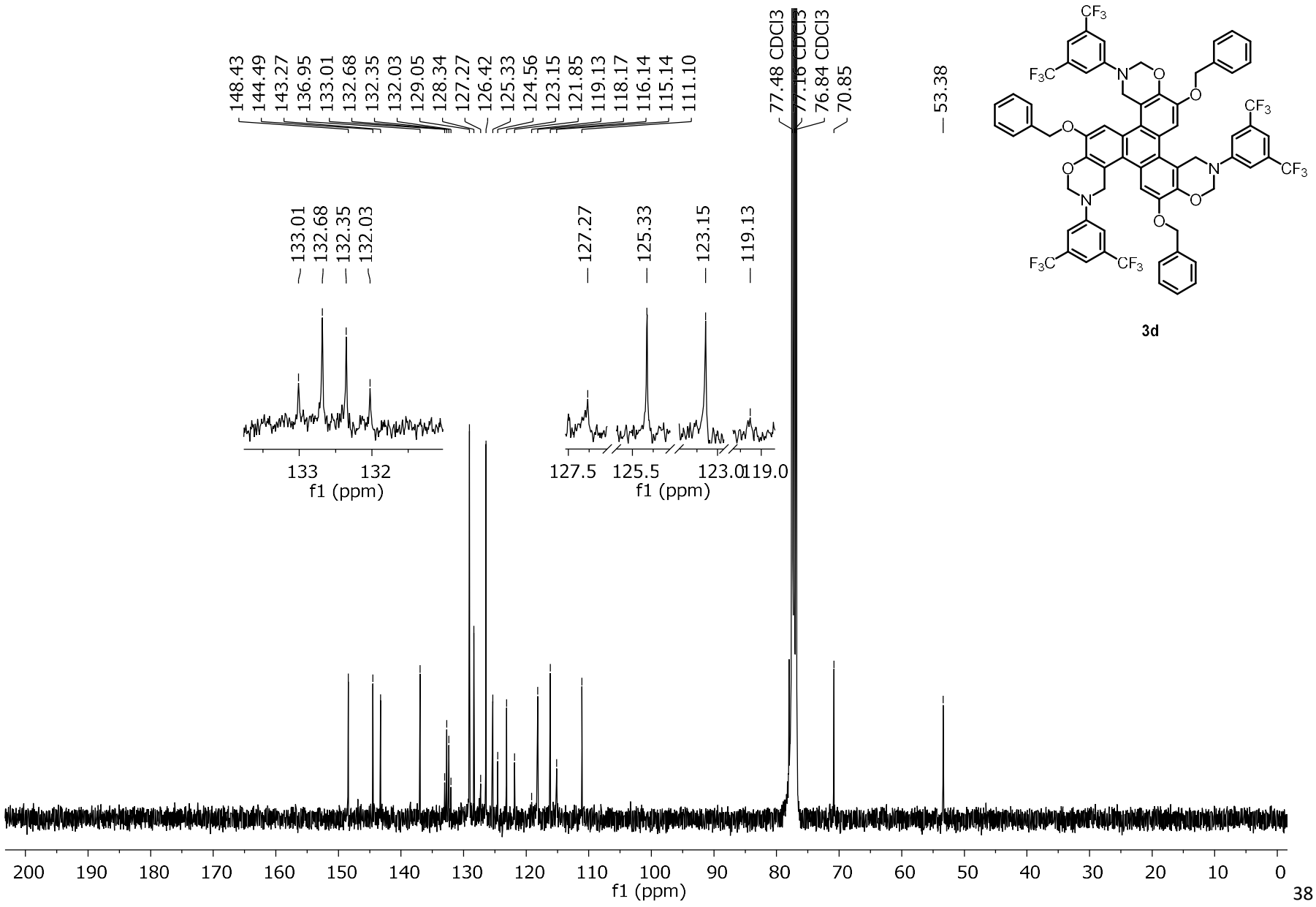

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f2 (ppm)
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
3c

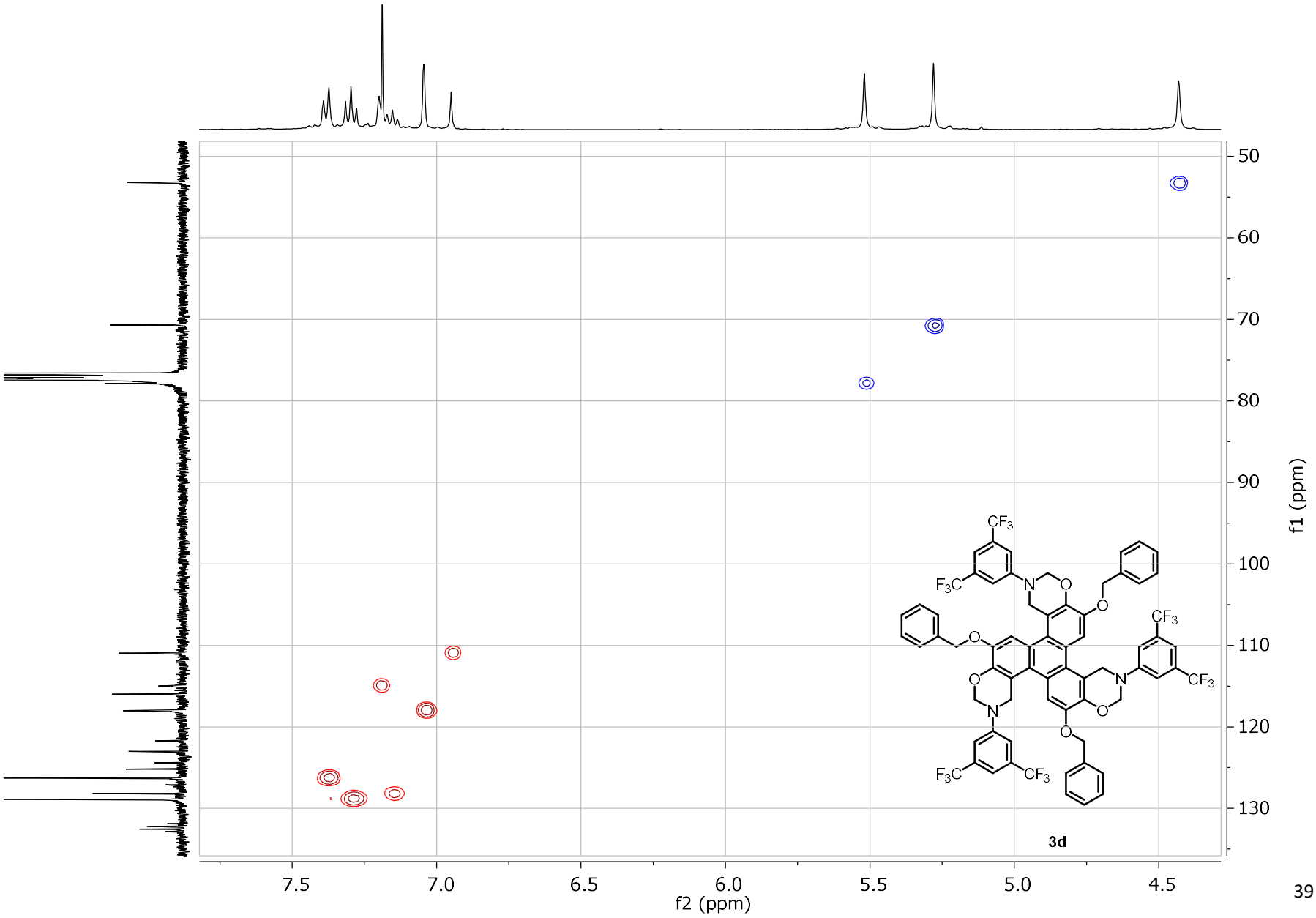
C:\Progetti\...\6GB_043_170828164853 12/4/2017 2:55:03 PM

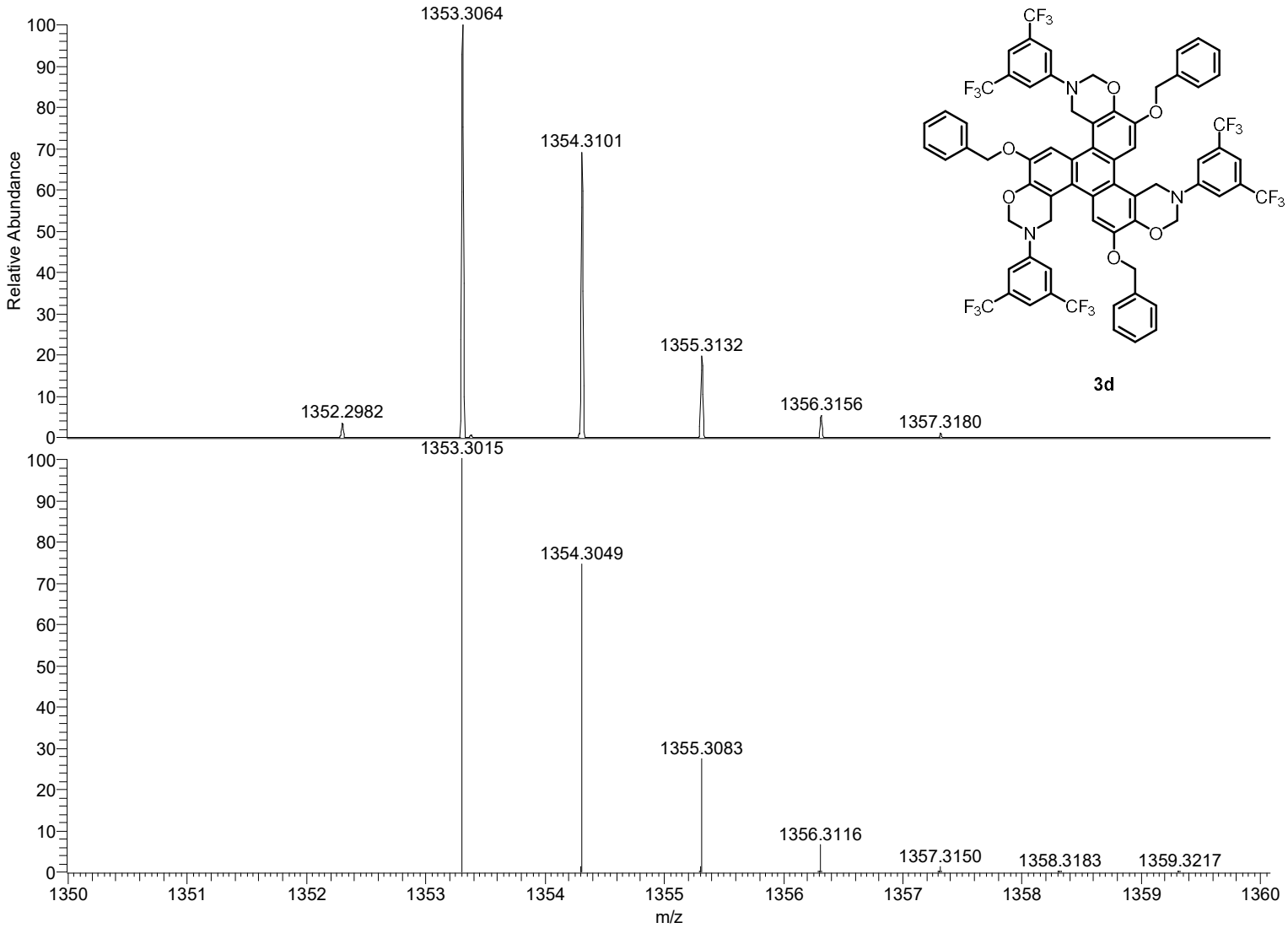


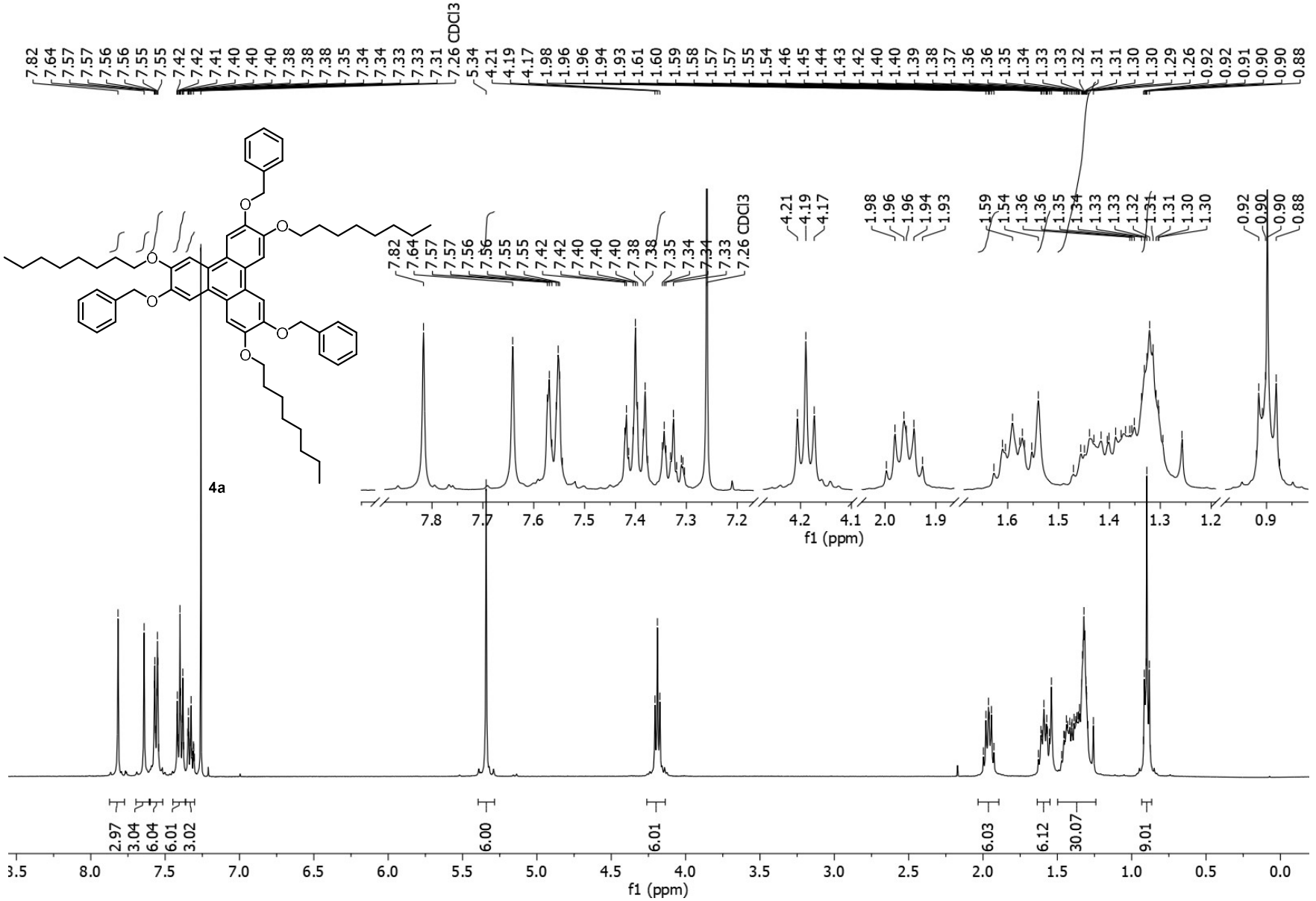

7.44 7.42 7.39 7.39 7.37 7.34 7.32 7.30 7.28 7.28 7.25 7.24 7.20 7.19 CDCl3 7.17 7.15 7.14 7.13 7.12 7.09 7.05 7.04 7.00 6.95 5.58 5.57 5.56 5.52 5.49 5.47 5.33 5.32 5.31 5.28 5.23 5.22 4.48 4.43 4.38
1.53 1.48 HDO 1.43
CF3
F3C
N
O
O
CF3
CF3
N
O
O
N
O
O
F3C
CF3
6.00 5.99 3.06 3.07 6.02 3.04
6.05
6.00
6.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
f1 (ppm)

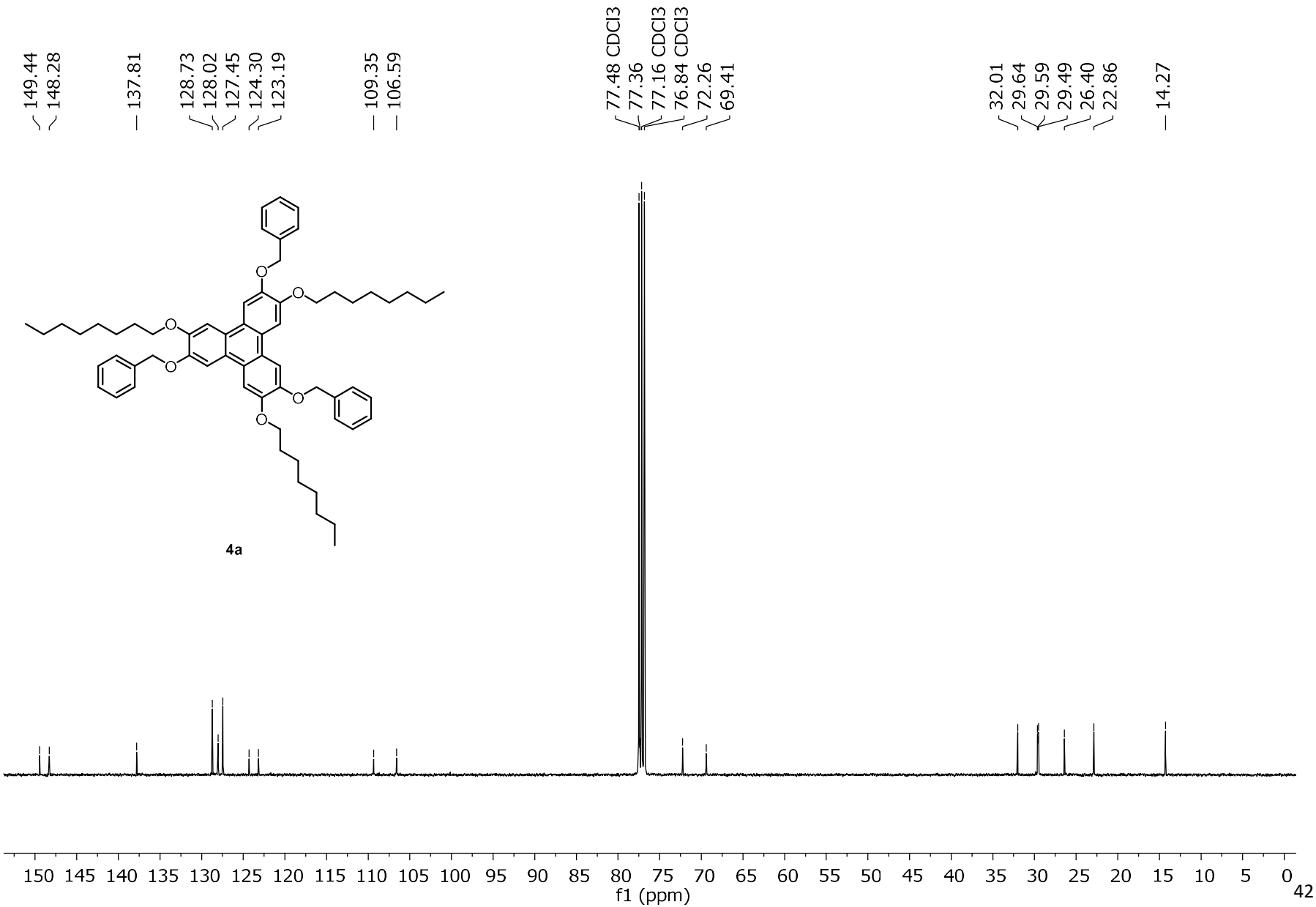
3d

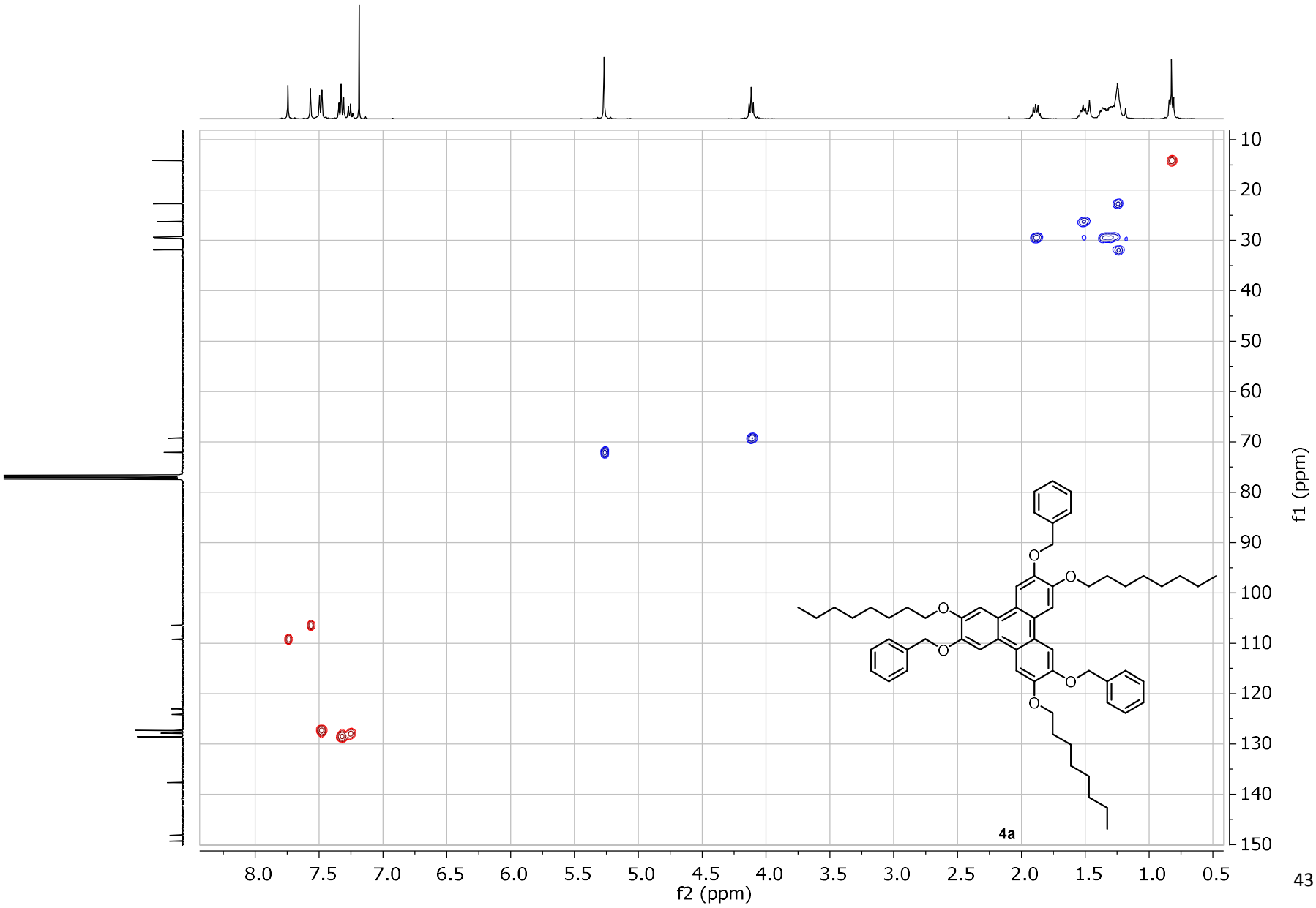

148.43
144.49
143.27
136.95
133.01
132.68
132.35
132.03
129.05
128.34
127.27
126.42
125.33
124.56
123.15
121.85
119.13
118.17
116.14
115.14
111.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.85
53.38
133.01
132.68
132.35
132.03
133
132
f1 (ppm)
127.27
125.33
123.15
119.13
127.5
125.5
123.0
119.0
f1 (ppm)
CF3
F3C
N
O
CF3
CF3
F3C
CF3
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

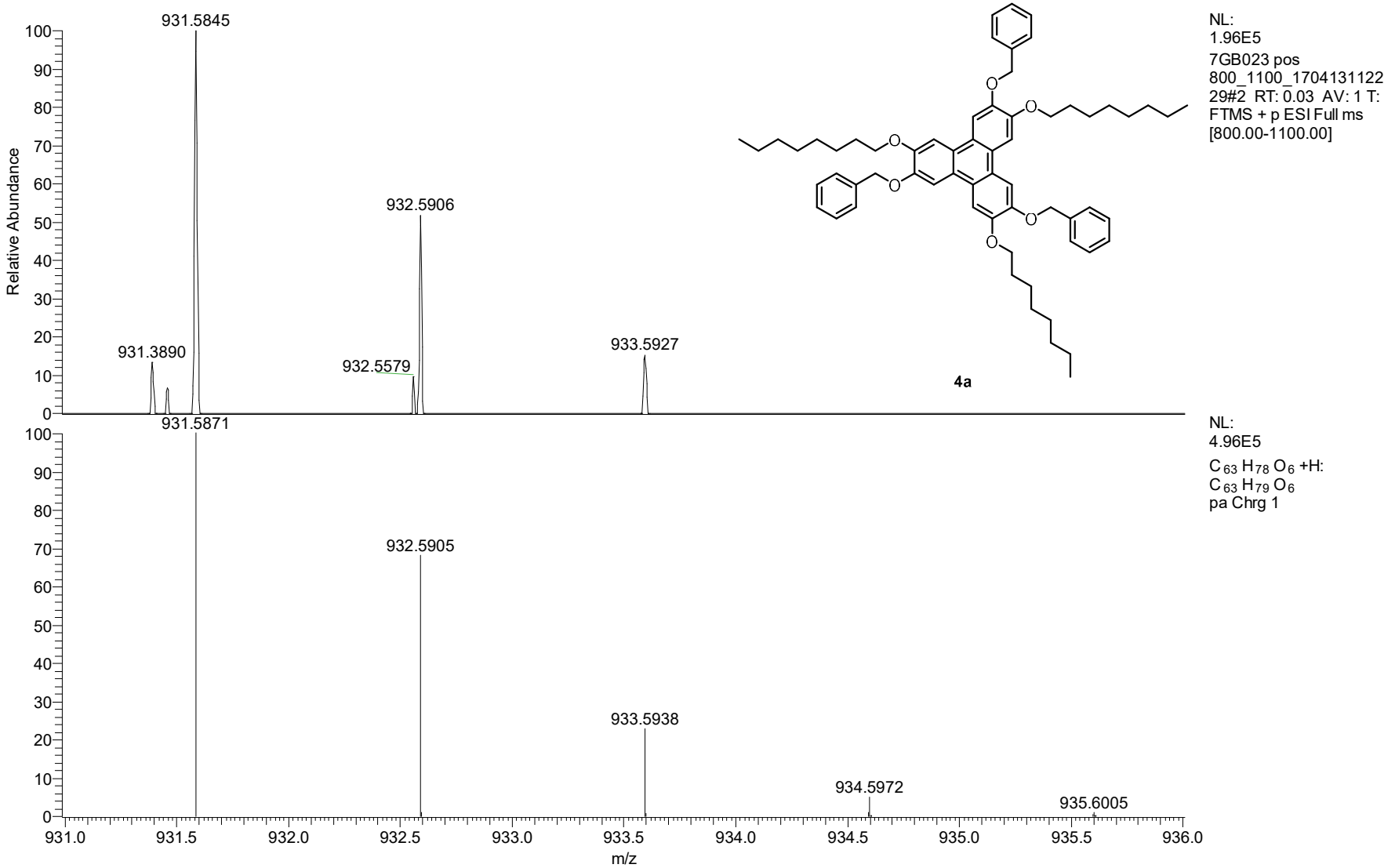

7.5
7.0
6.5
6.0
5.5
5.0
4.5
f2 (ppm)
50
60
70
80
90
100
110
120
130
f1 (ppm)
CF3
F3C
N
O
CF3
CF3
F3C
CF3
3d

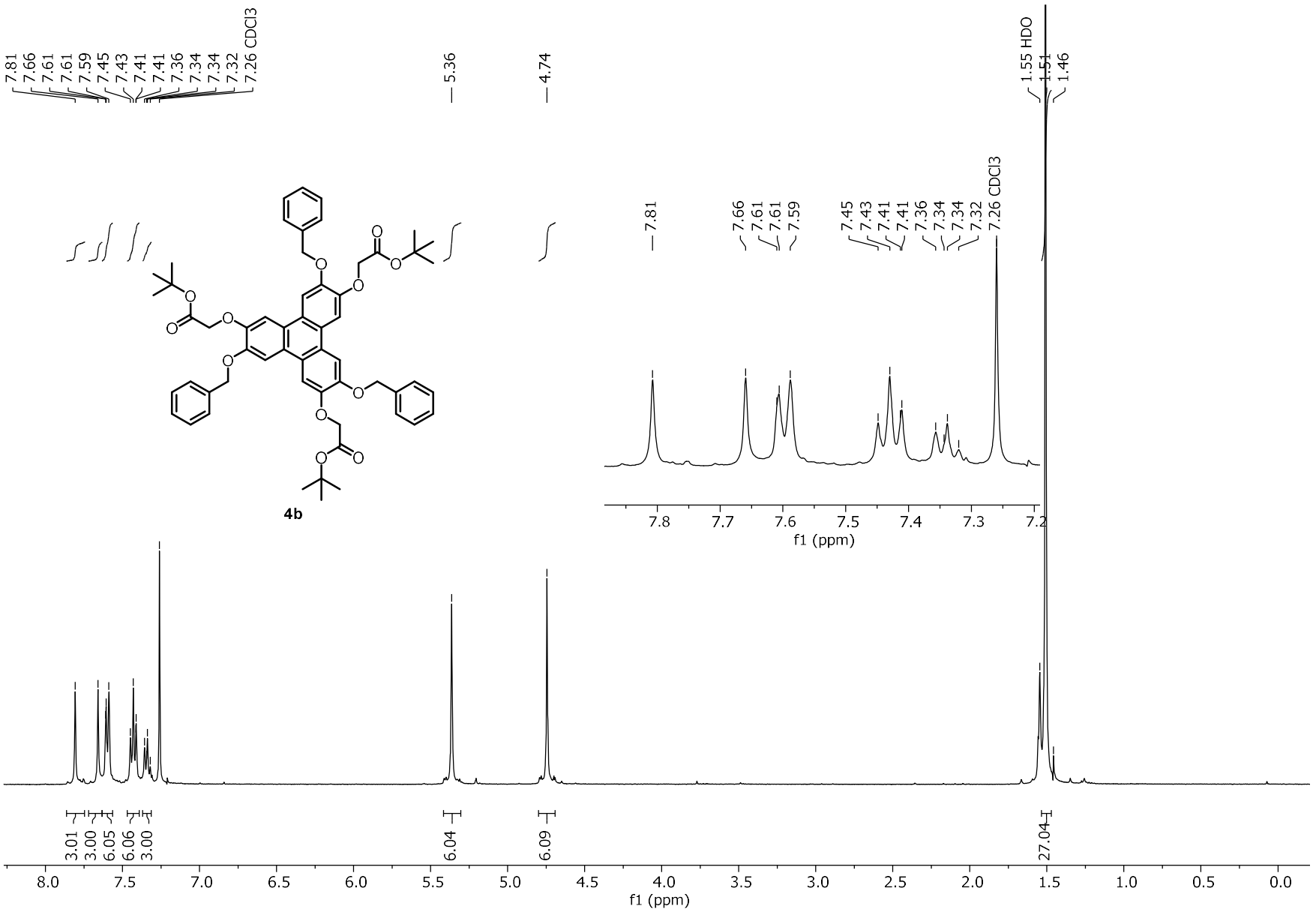

1353.3064
1354.3101
1355.3132
1352.2982
1356.3156
1357.3180
Relative Abundance
NL:
1.81E6
Campione 7GB055
pos_170705152746#20
RT: 0.57 AV: 1 T: FTMS
+ p ESI Full ms
[1100.00-1500.00]
3d
1353.3015
1354.3049
1355.3083
1356.3116
1357.3150
1358.3183
1359.3217
NL:
4.62E5
C69 H45 F18 N3 O6:
C69 H45 F18 N3 O6
pa Chrg 1
m/z

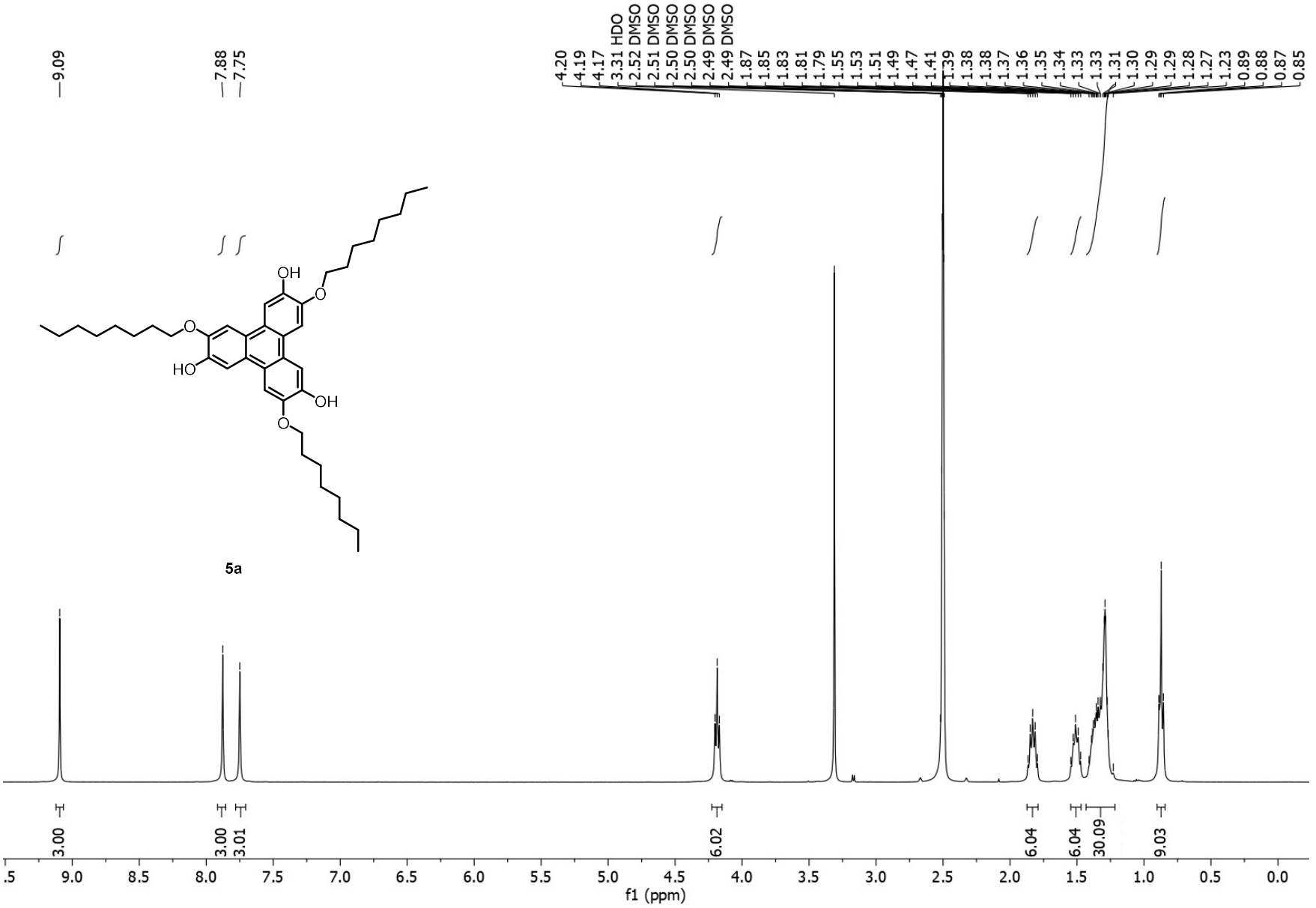

7.82 7.64 7.57 7.57 7.56 7.56 7.55 7.55 7.42 7.42 7.41 7.40 7.40 7.40 7.38 7.38 7.38 7.35 7.34 7.34 7.33 7.33 7.31 7.26 CDCl3 5.34 4.21 4.19 4.17 1.98 1.96 1.96 1.94 1.93 1.61 1.60 1.59 1.58 1.57 1.57 1.55 1.54 1.46 1.45 1.44 1.43 1.42 1.40 1.40 1.39 1.38 1.37 1.36 1.36 1.35 1.34 1.33 1.33 1.32 1.31 1.31 1.30 1.30 1.29 1.26 0.92 0.92 0.91 0.90 0.90 0.88
4a
f1 (ppm)
2.97 3.04 6.04 6.01 3.02 6.00 6.01 6.03 6.12 30.07 9.01

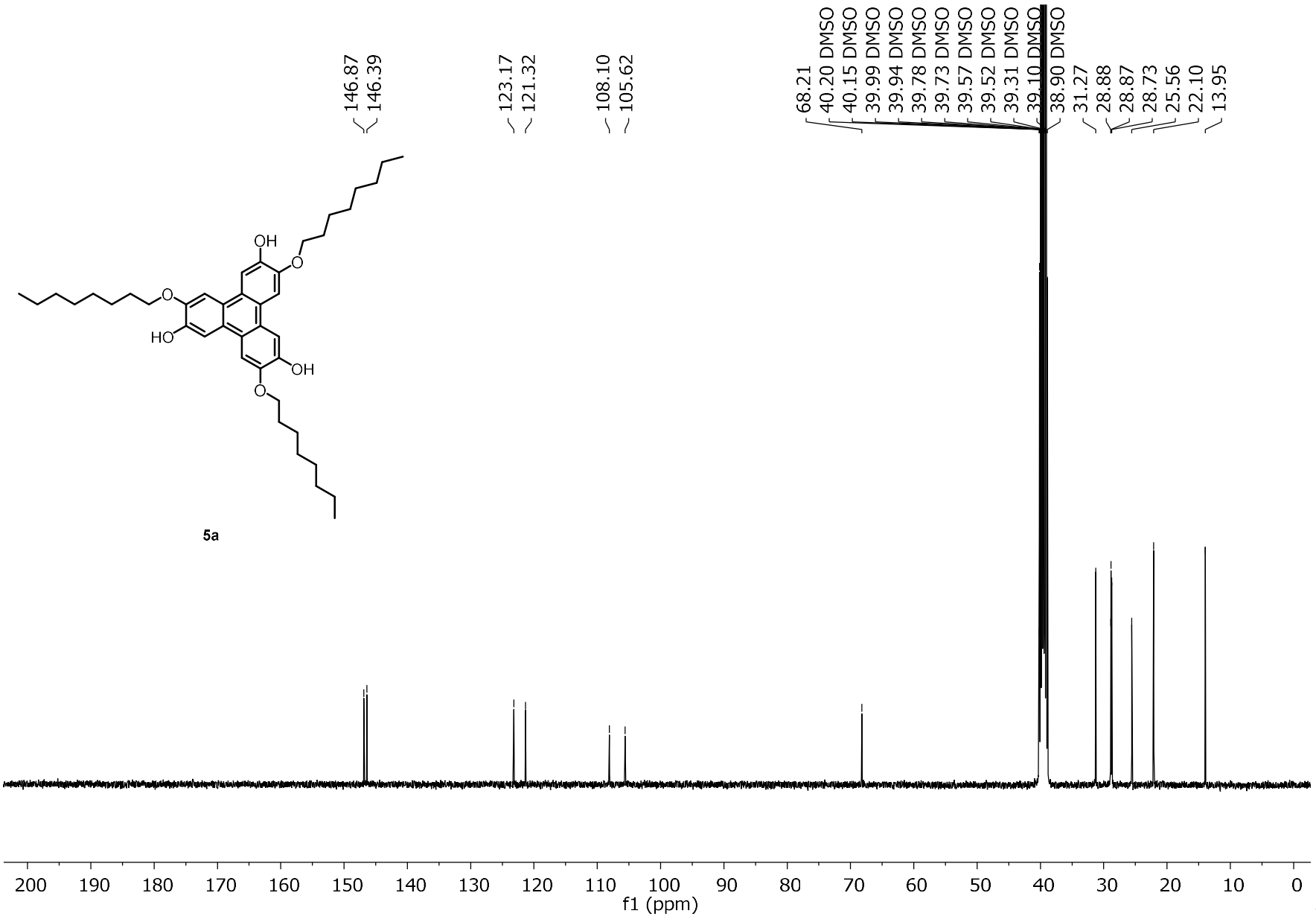

149.44
148.28
137.81
128.73
128.02
127.45
124.30
123.19
109.35
106.59
77.48 CDCl3
77.36
77.16 CDCl3
76.84 CDCl3
72.26
69.41
32.01
29.64
29.59
29.49
26.40
22.86
14.27
4a
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

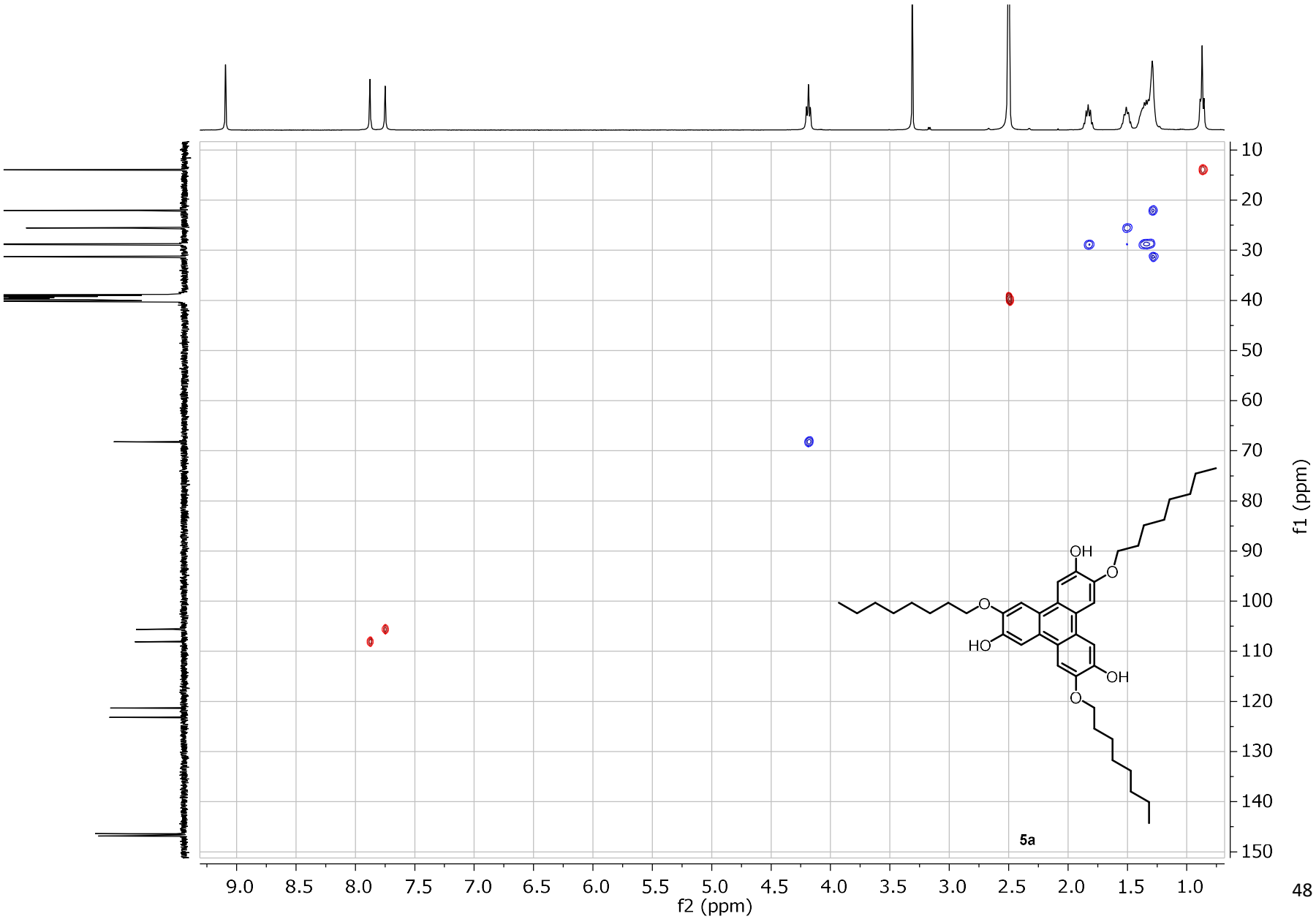

f2 (ppm)
f1 (ppm)
4a

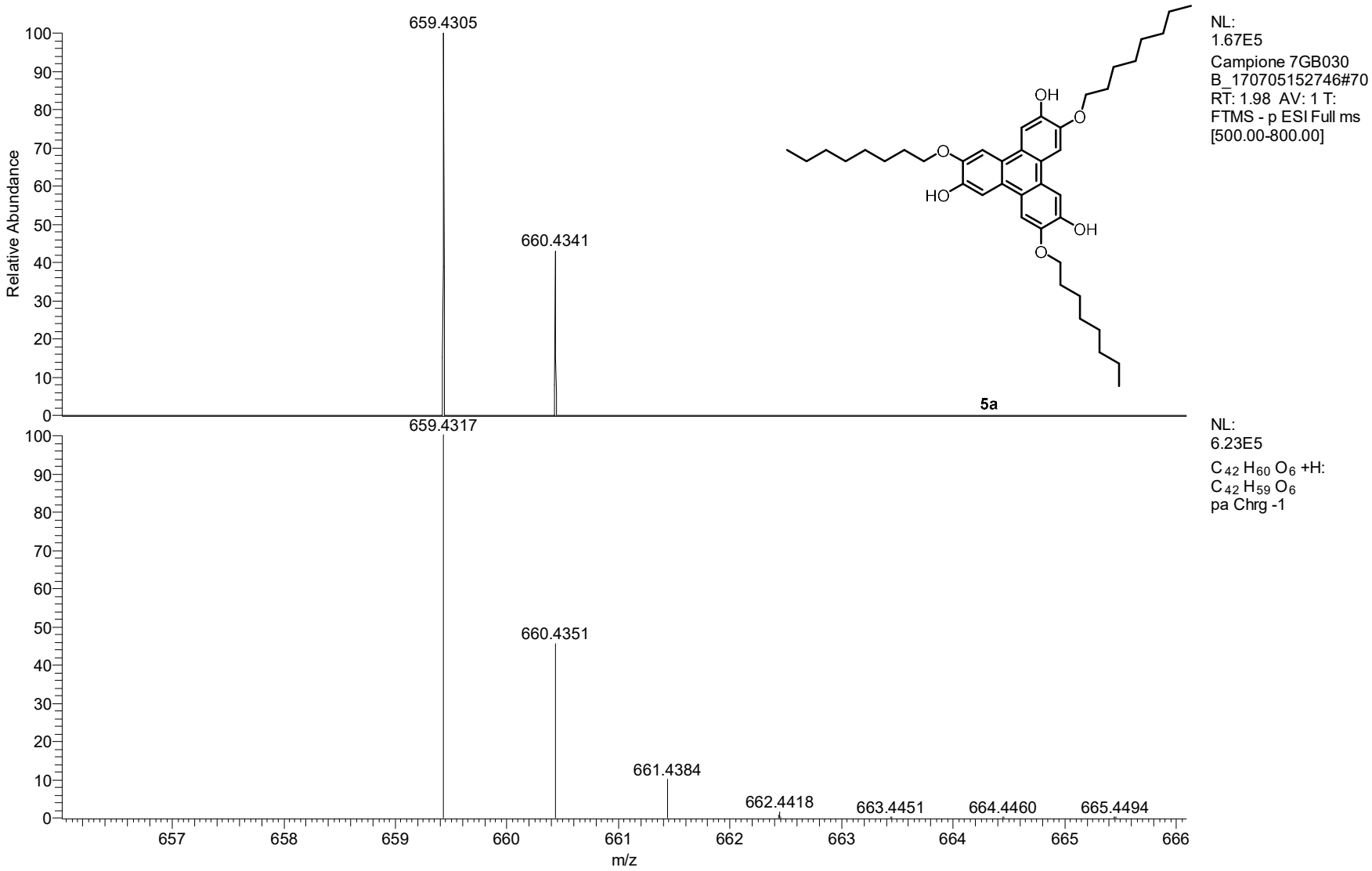

931.5845
932.5906
931.3890
932.5579
933.5927
4a
NL:
1.96E5
7GB023 pos
800_1100_1704131122
29#2 RT: 0.03 AV: 1 T:
FTMS + p ESI Full ms
[800.00-1100.00]
Relative Abundance
931.5871
932.5905
933.5938
934.5972
935.6005
NL:
4.96E5
C 63 H 78 O 6 +H:
C 63 H 79 O 6
pa Chrg 1
m/z

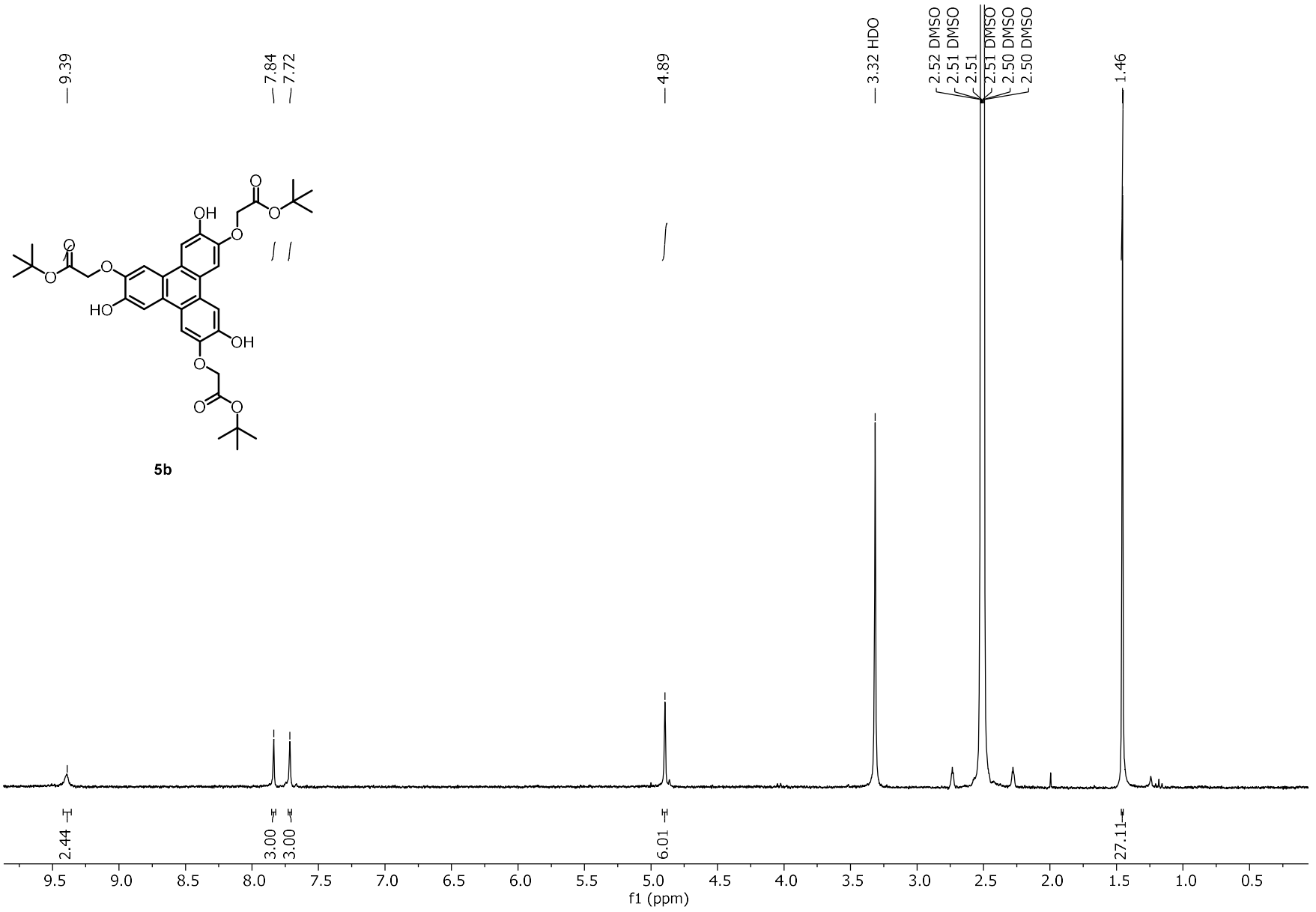

7.81
7.66
7.61
7.61
7.59
7.45
7.43
7.41
7.41
7.36
7.34
7.34
7.32
7.26 CDCl3
5.36
4.74
1.55 HDO
1.51
1.46
4b
3.01
3.00
6.05
6.06
3.00
6.04
6.09
27.04
f1 (ppm)


9.09
7.88
7.75
4.20
4.19
4.17
3.31 HDO
2.52 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
1.87
1.85
1.83
1.81
1.79
1.55
1.53
1.51
1.49
1.47
1.41
1.39
1.38
1.38
1.37
1.36
1.35
1.34
1.33
1.33
1.31
1.30
1.29
1.29
1.28
1.27
1.23
0.89
0.88
0.87
0.85
OH
O
O
HO
OH
O
5a
3.00
3.00
3.01
6.02
6.04
6.04
30.09
9.03
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

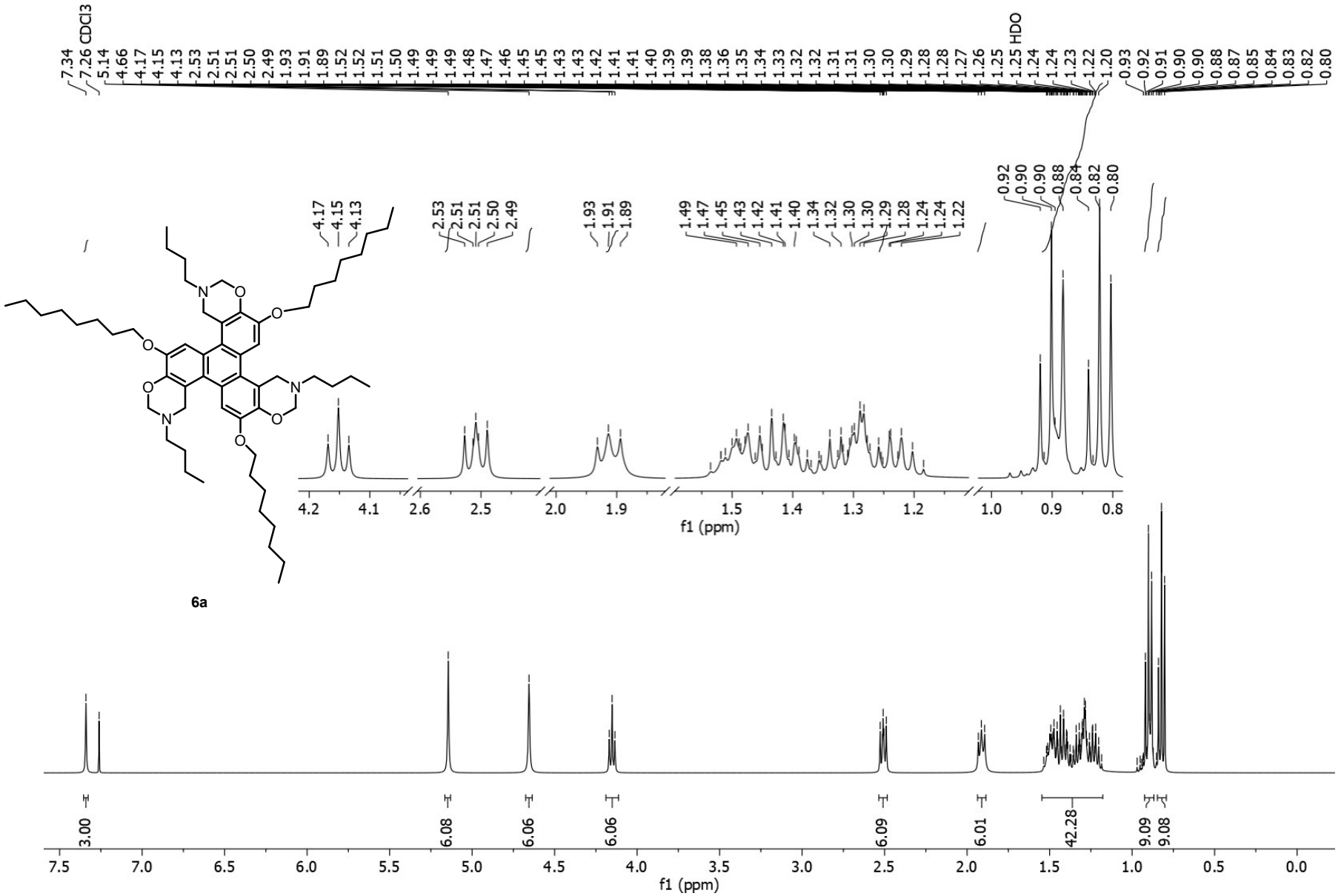

146.87
146.39
123.17
121.32
108.10
105.62
68.21
40.20 DMSO
40.15 DMSO
39.99 DMSO
39.94 DMSO
39.78 DMSO
39.73 DMSO
39.57 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.90 DMSO
31.27
28.88
28.87
28.73
25.56
22.10
13.95
OH
O
O
HO
OH
O
5a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

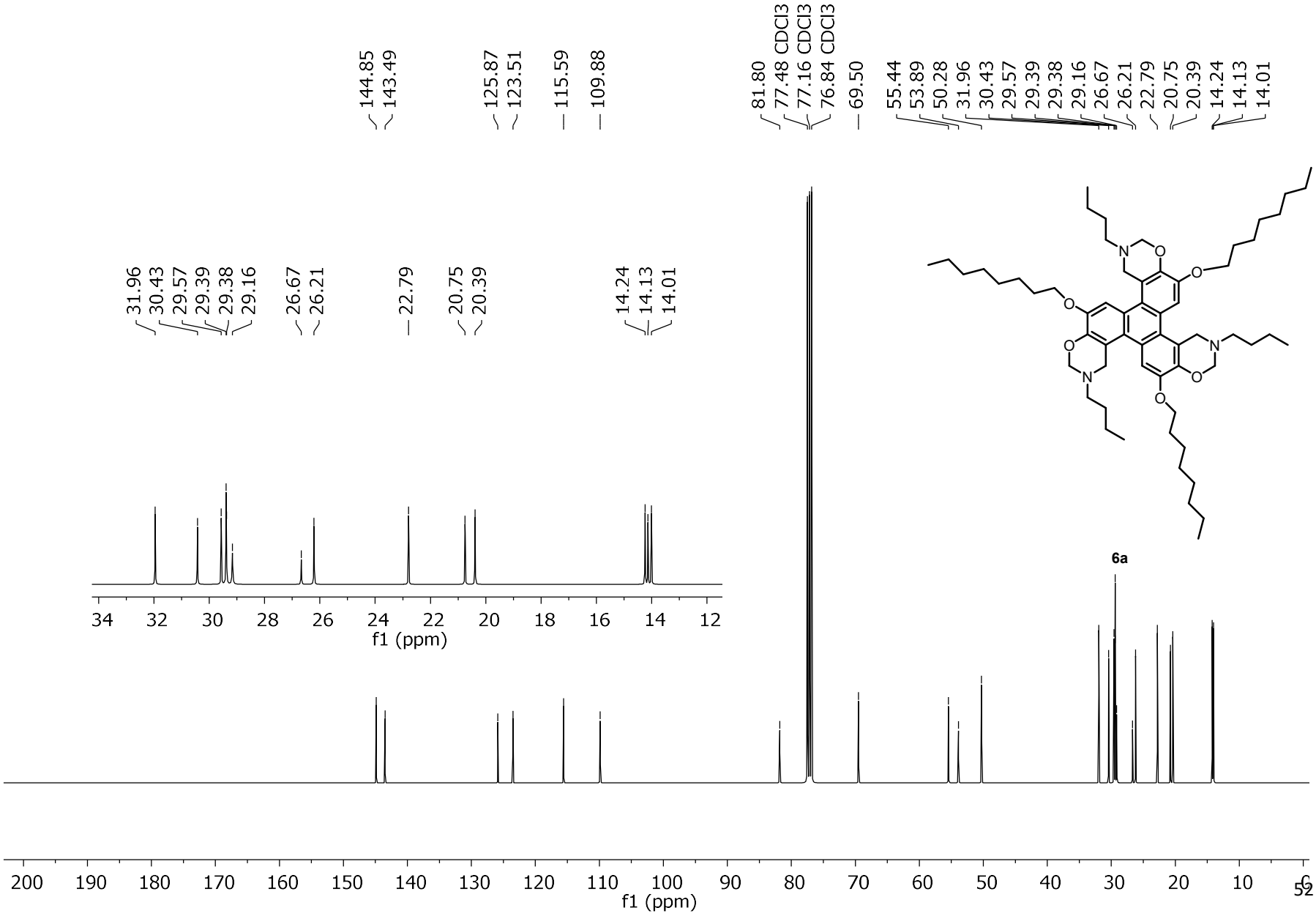

f2 (ppm)
f1 (ppm)
OH
O
HO
OH
O
5a

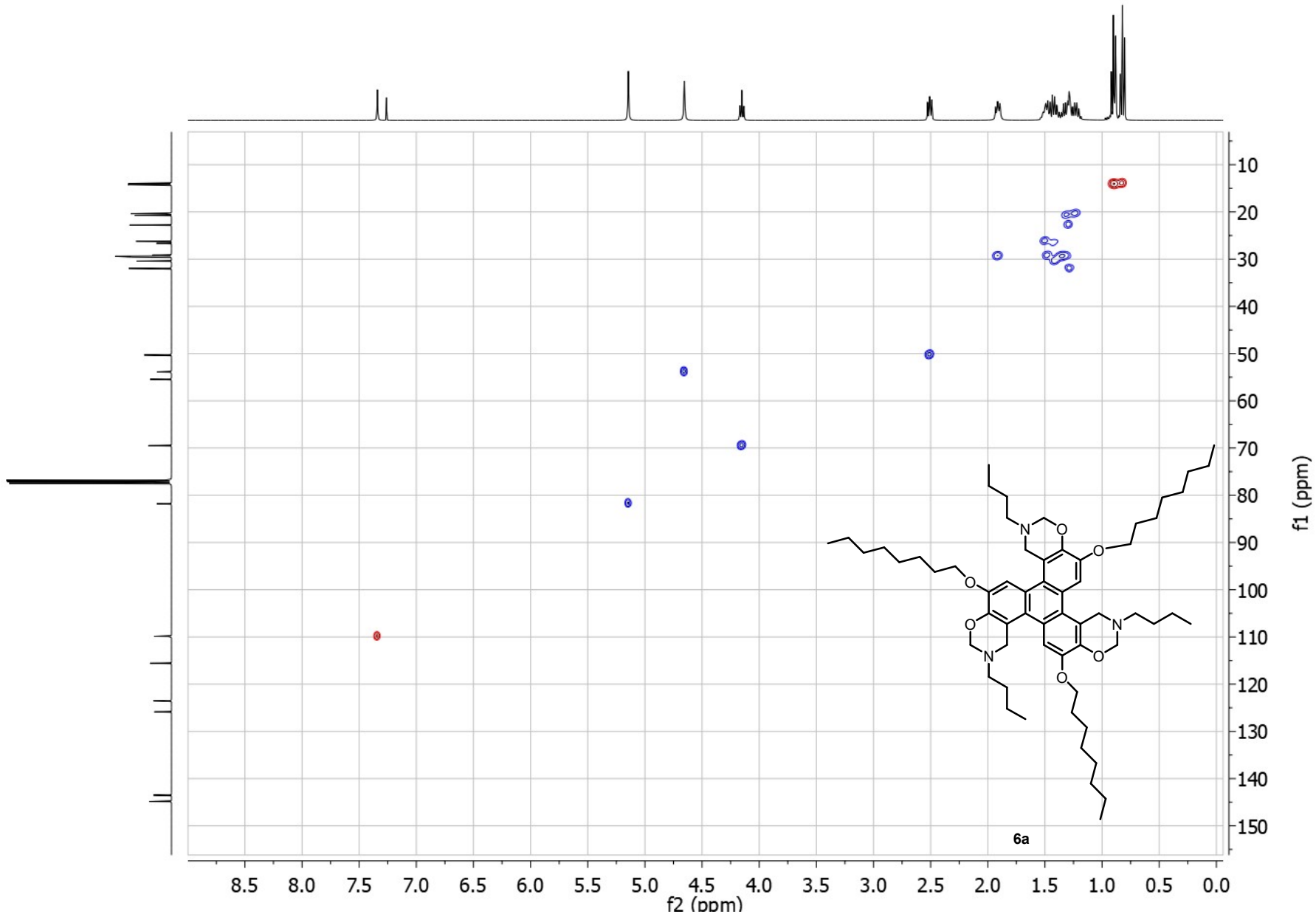

659.4305
660.4341
Relative Abundance
100
90
80
70
60
50
40
30
20
10
0
OH
O
HO
OH
O
5a
NL:
1.67E5
Campione 7GB030
B_170705152746#70
RT: 1.98 AV: 1 T:
FTMS - p ESI Full ms
[500.00-800.00]
659.4317
660.4351
661.4384
662.4418
663.4451
664.4460
665.4494
657
658
659
660
661
662
663
664
665
666
m/z
NL:
6.23E5
C42 H60 O6 +H:
C42 H59 O6
pa Chrg -1

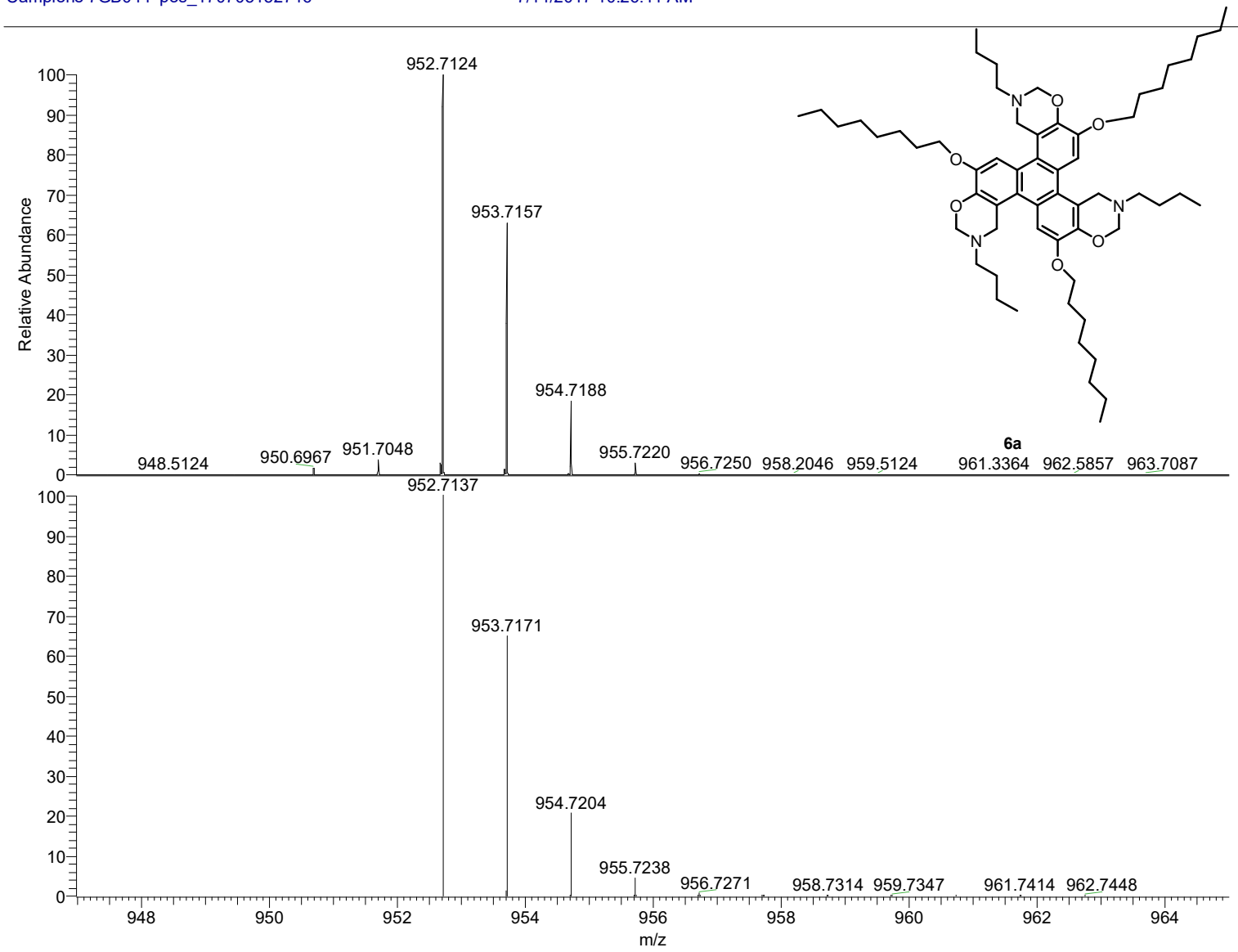

9.39
7.84
7.72
4.89
3.32 HDO
2.52 DMSO
2.51 DMSO
2.51
2.51 DMSO
2.50 DMSO
2.50 DMSO
1.46
OH
HO
OH
O
O
O
O
O
O
O
O
O
O
2.44
3.00
3.00
6.01
27.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

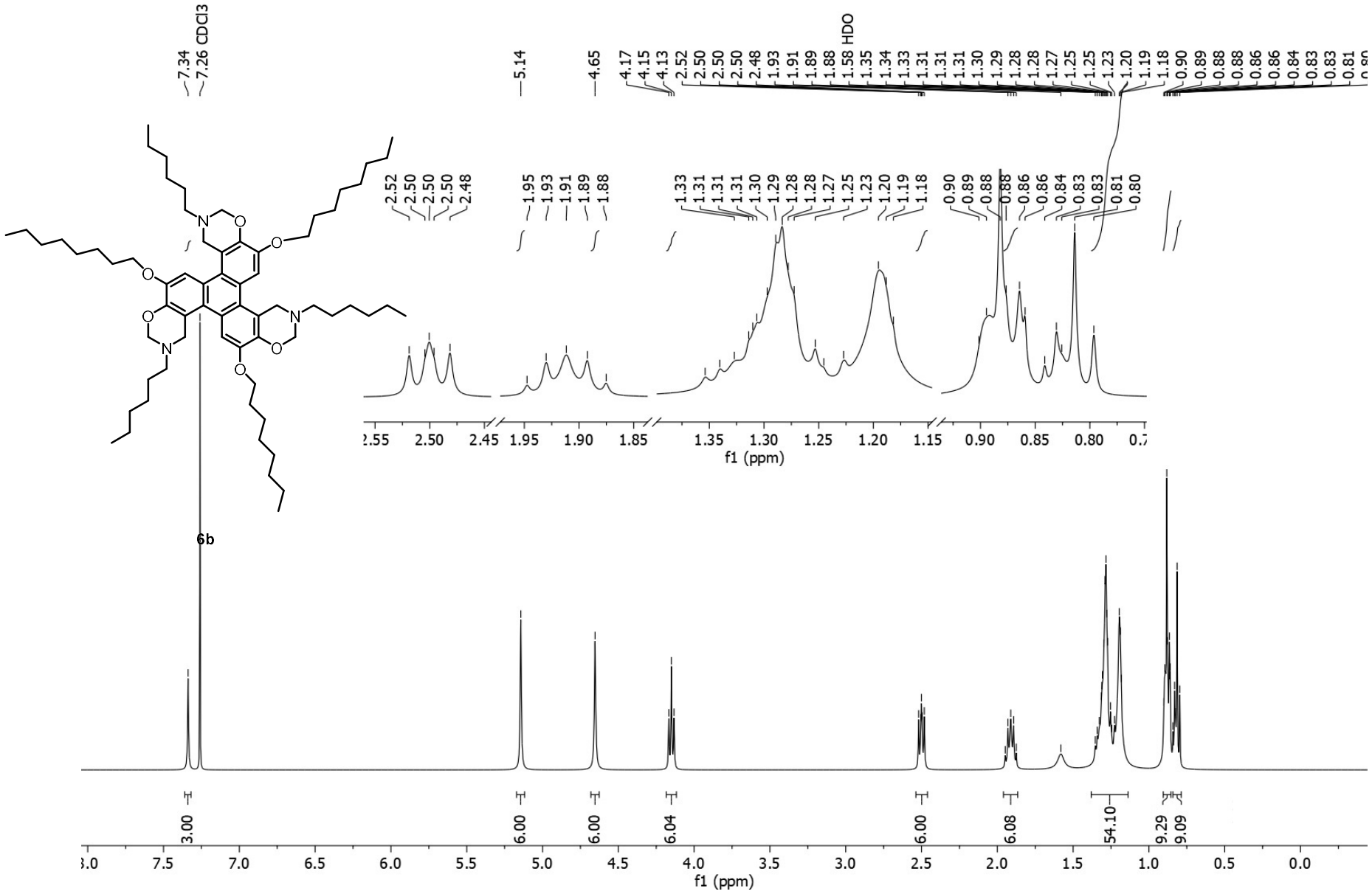
5b

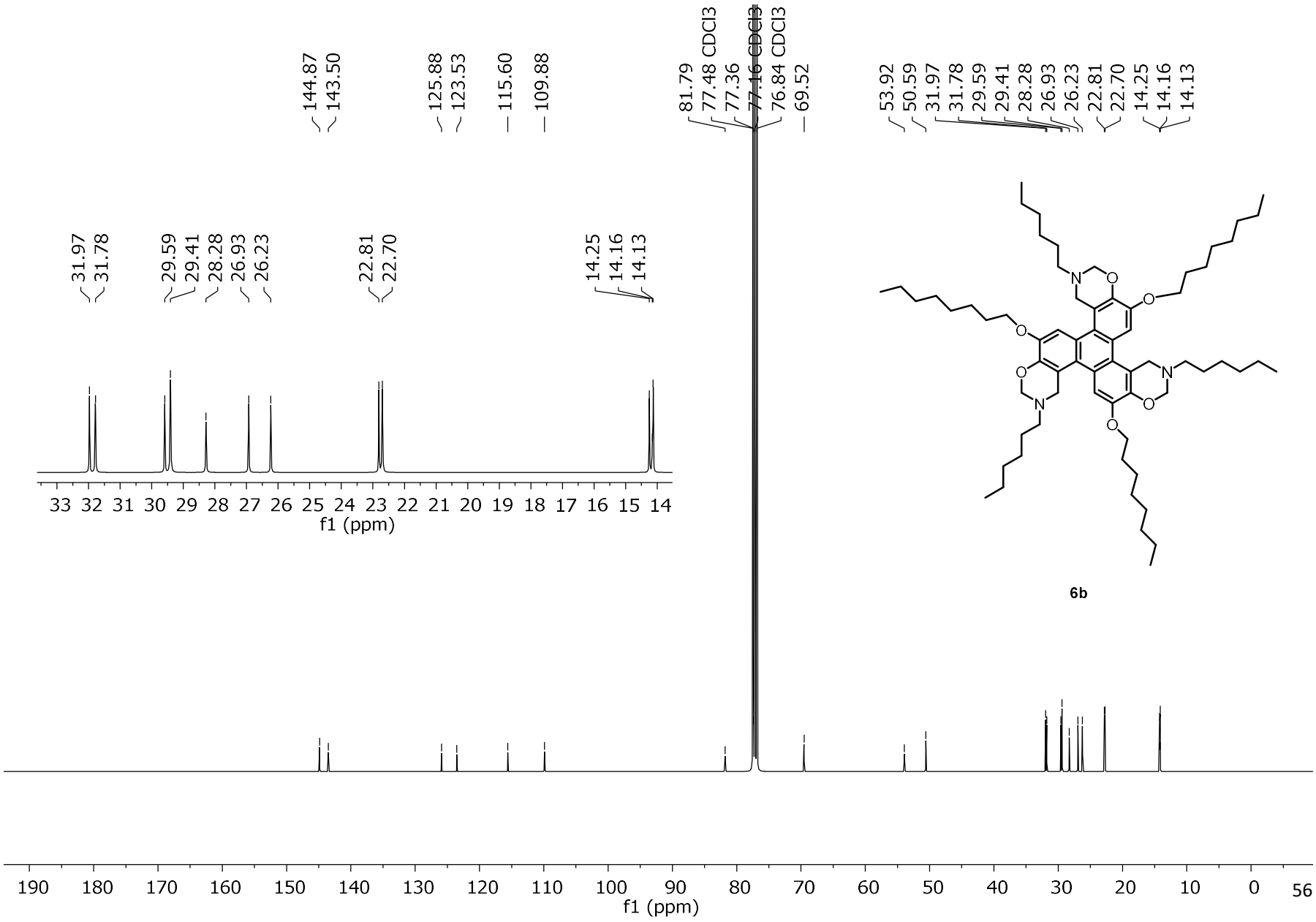

7.34
7.26 CDCl3
5.14
4.66
4.17
4.15
4.13
2.53
2.51
2.51
2.50
2.49
1.93
1.91
1.89
1.52
1.52
1.51
1.50
1.49
1.49
1.49
1.48
1.47
1.46
1.45
1.45
1.43
1.43
1.42
1.41
1.41
1.40
1.39
1.39
1.38
1.36
1.35
1.34
1.33
1.32
1.32
1.31
1.31
1.30
1.30
1.29
1.28
1.28
1.27
1.26
1.25
1.25 HDO
1.24
1.24
1.23
1.22
1.20
0.93
0.92
0.91
0.90
0.90
0.88
0.87
0.85
0.84
0.83
0.82
0.80
4.17
4.15
4.13
2.53
2.51
2.51
2.50
2.49
1.93
1.91
1.89
1.49
1.47
1.45
1.43
1.42
1.41
1.40
1.34
1.32
1.30
1.30
1.29
1.28
1.24
1.24
1.22
0.92
0.90
0.90
0.88
0.84
0.82
0.80
4.2
4.1
2.6
2.5
2.0
1.9
1.5
1.4
1.3
1.2
1.0
0.9
0.8
f1 (ppm)
6a
3.00
6.08
6.06
6.06
6.09
6.01
42.28
9.09
9.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

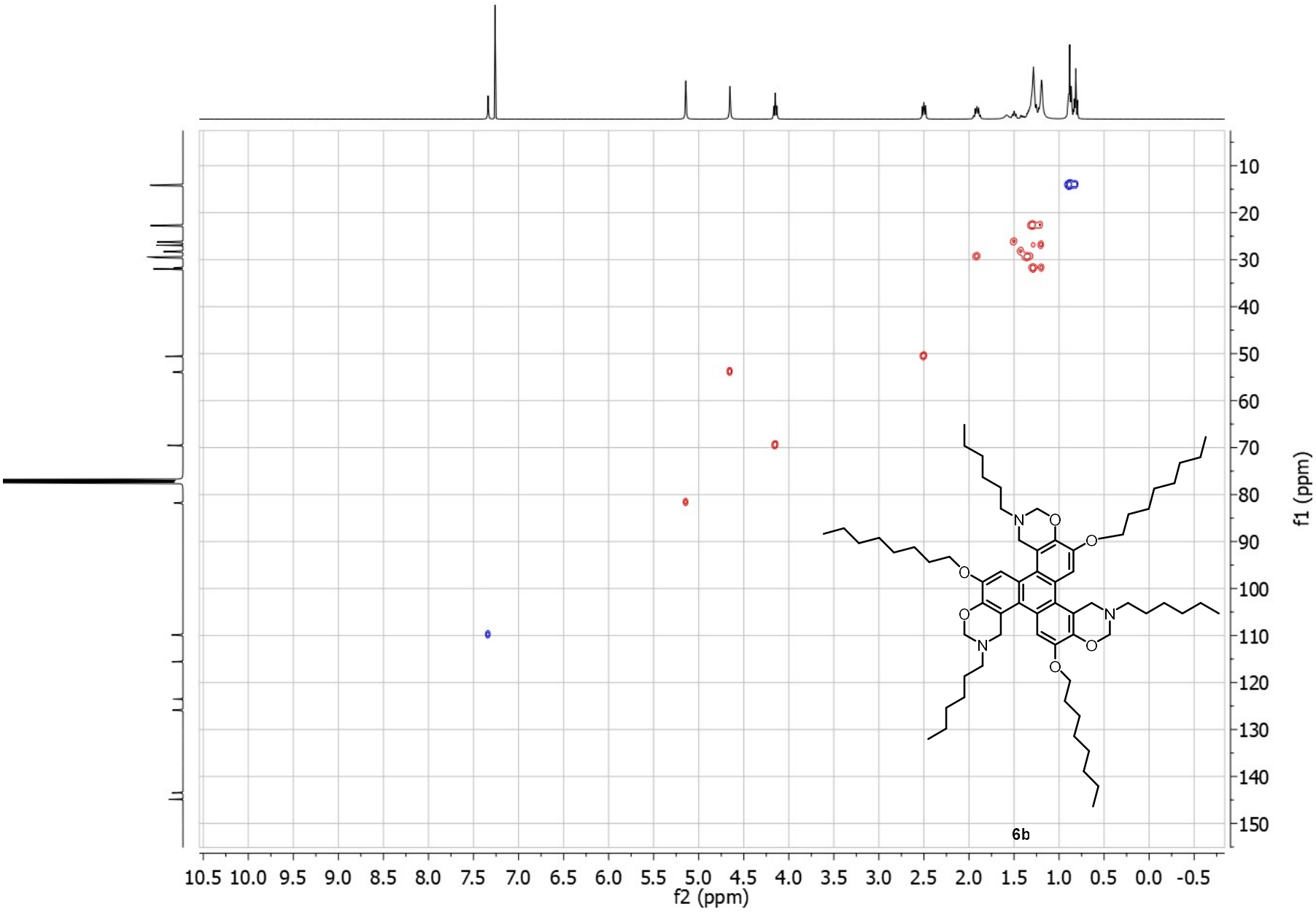

144.85
143.49
125.87
123.51
115.59
109.88
81.80
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.50
55.44
53.89
50.28
31.96
30.43
29.57
29.39
29.38
29.16
26.67
26.21
22.79
20.75
20.39
14.24
14.13
14.01
6a
f1 (ppm)
f1 (ppm)


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
N
O
6a

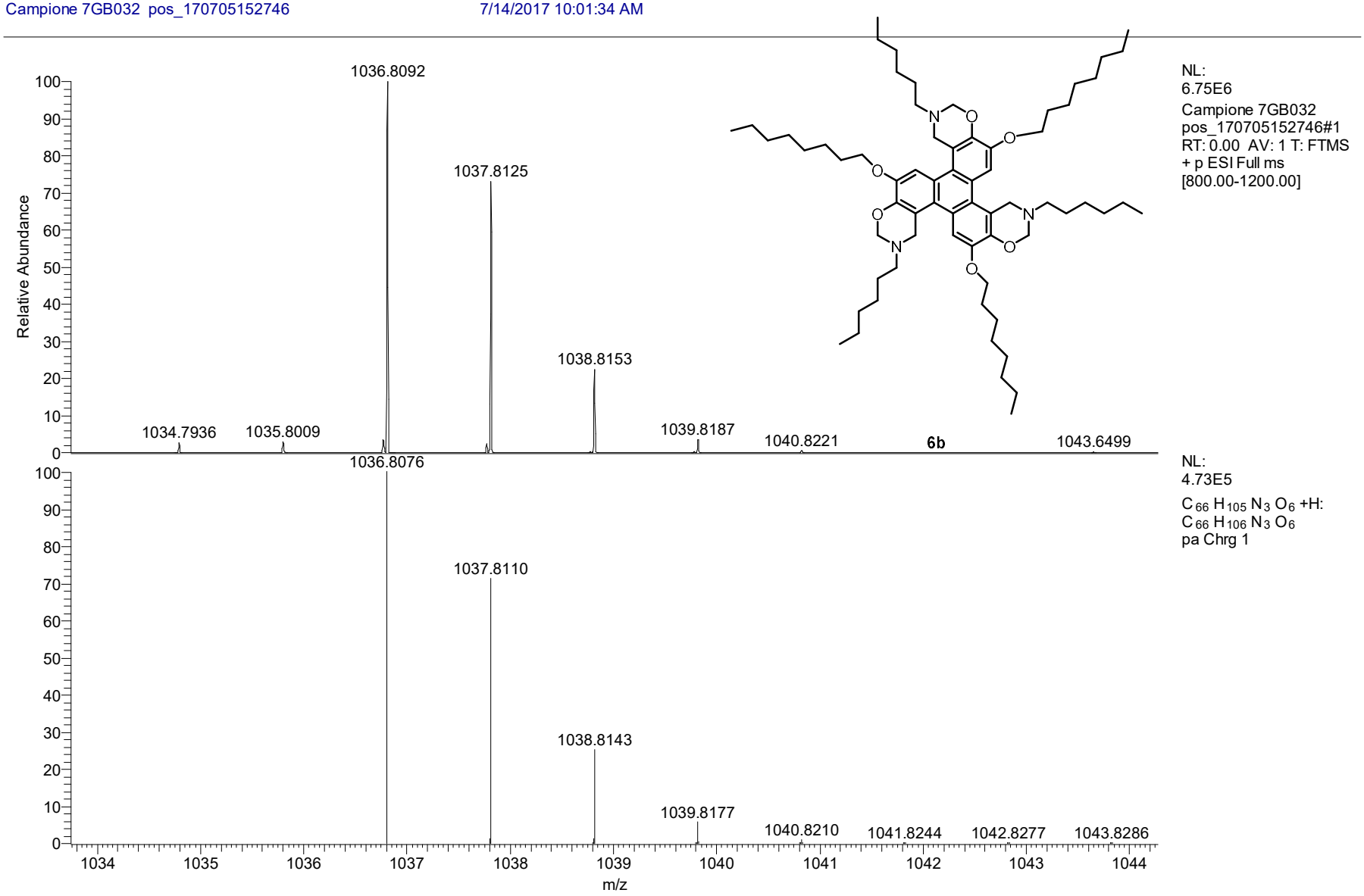

952.7124
953.7157
954.7188
948.5124
950.6967
951.7048
955.7220
956.7250
958.2046
959.5124
961.3364
962.5857
963.7087
Relative Abundance
6a
NL:
1.16E7
Campione 7GB044
pos_170705152746#4-20
RT: 0.09-0.55 AV: 17 T:
FTMS + p ESI Full ms
[700.00-1100.00]
952.7137
953.7171
954.7204
955.7238
956.7271
958.7314
959.7347
961.7414
962.7448
NL:
5.06E5
C60 H93 N3 O6 +H:
C60 H94 N3 O6
pa Chrg 1
m/z

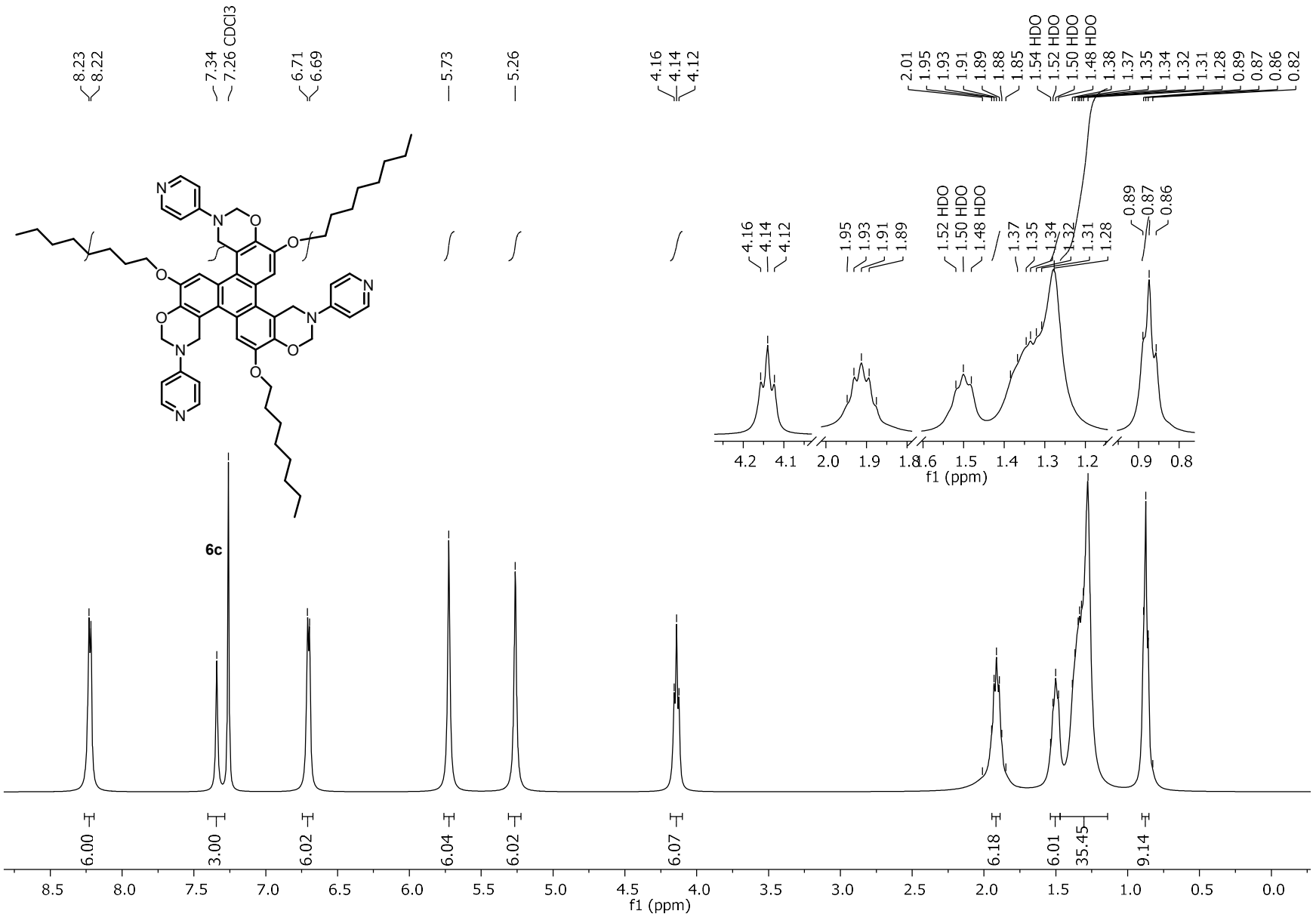

7.34
7.26 CDCl3
5.14
4.65
HDO
6b
f1 (ppm)
3.00
6.00
6.00
6.04
6.00
6.08
54.10
9.29
9.09

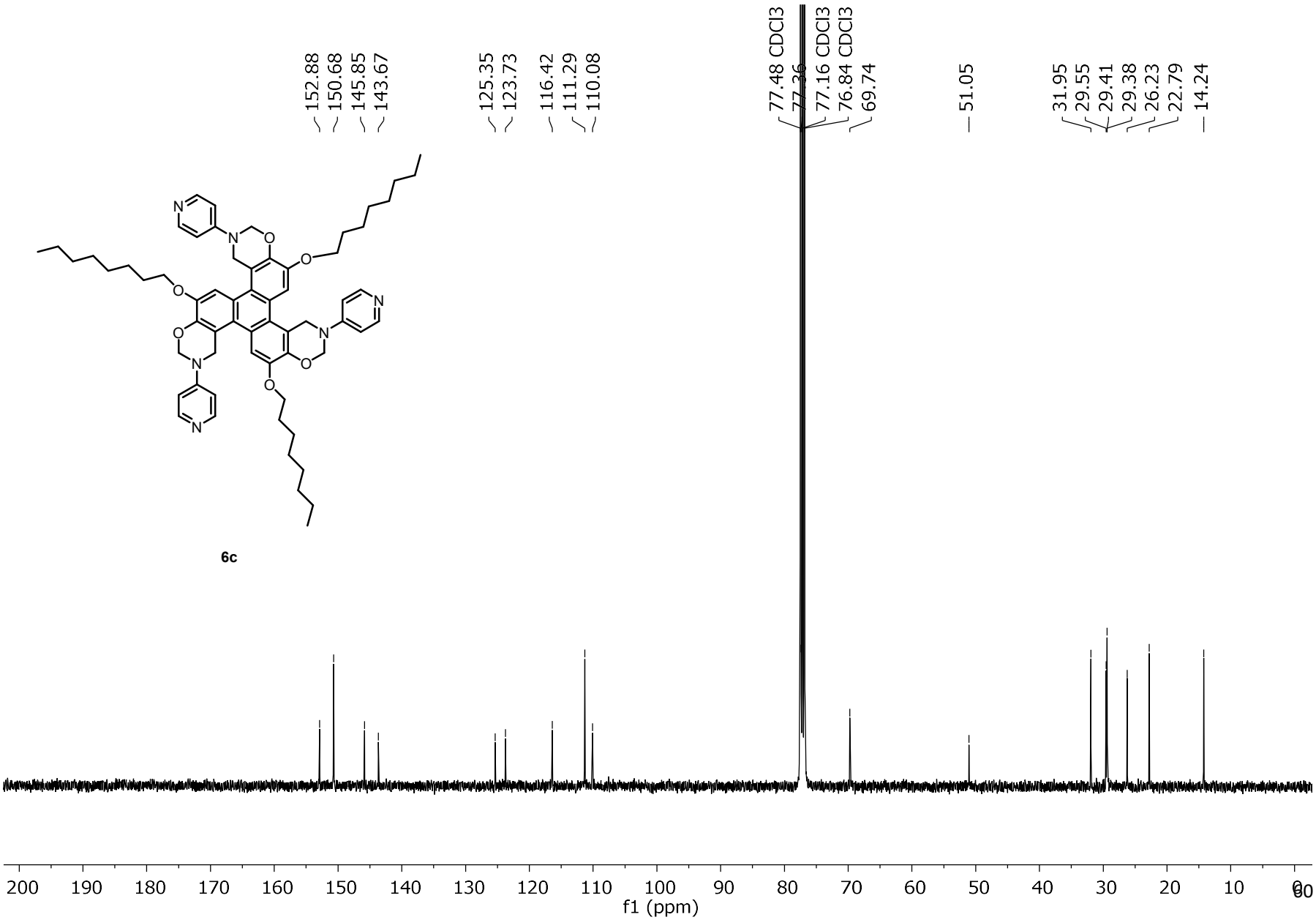

144.87
143.50
125.88
123.53
115.60
109.88
81.79
77.48 CDCl3
77.36
77.16 CDCl3
76.84 CDCl3
69.52
53.92
50.59
31.97
31.78
29.59
29.41
28.28
26.93
26.23
22.81
22.70
14.25
14.16
14.13
f1 (ppm)
6b

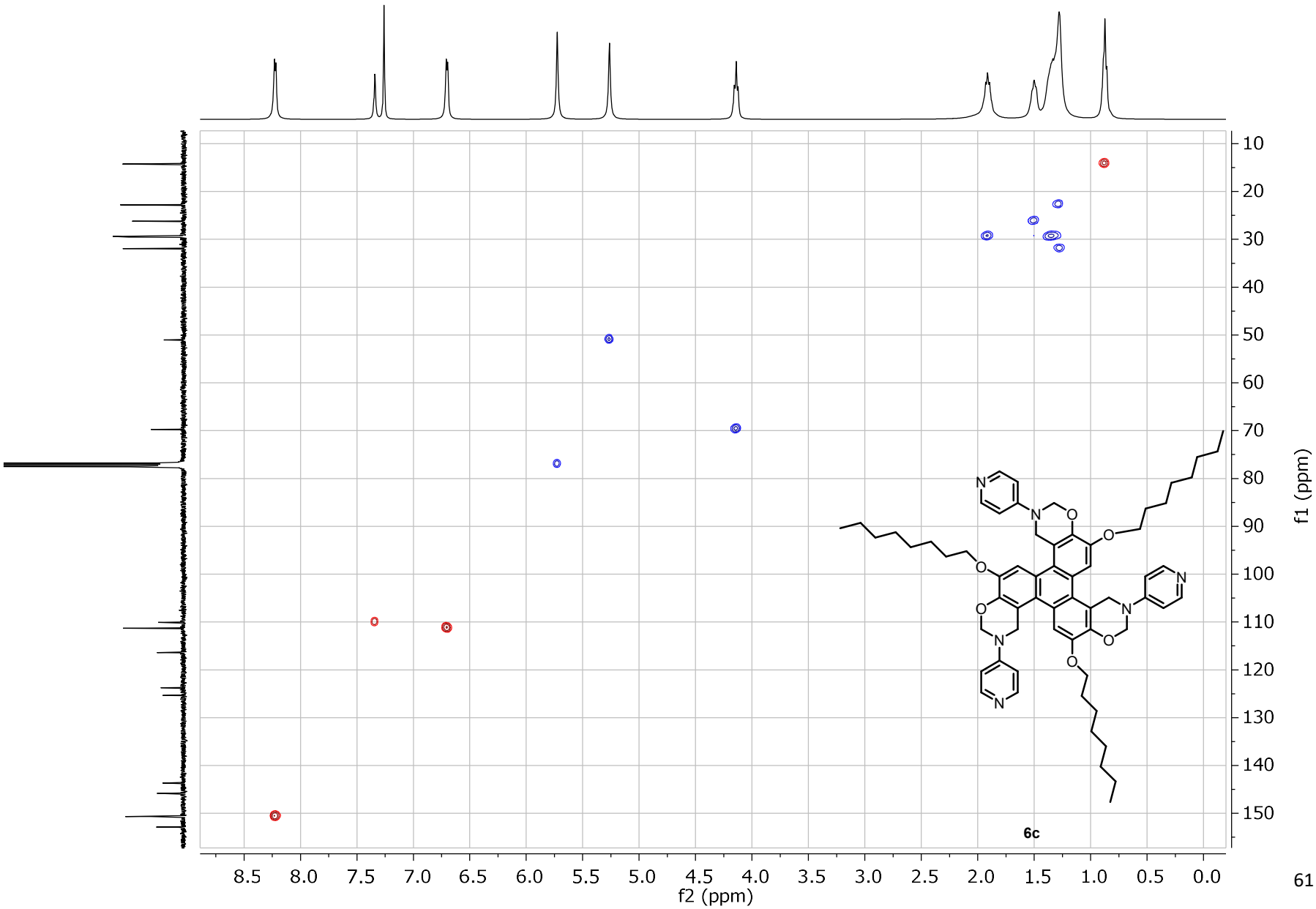

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)
6b

Campione 7GB032 pos_170705152746 7/14/2017 10:01:34 AM

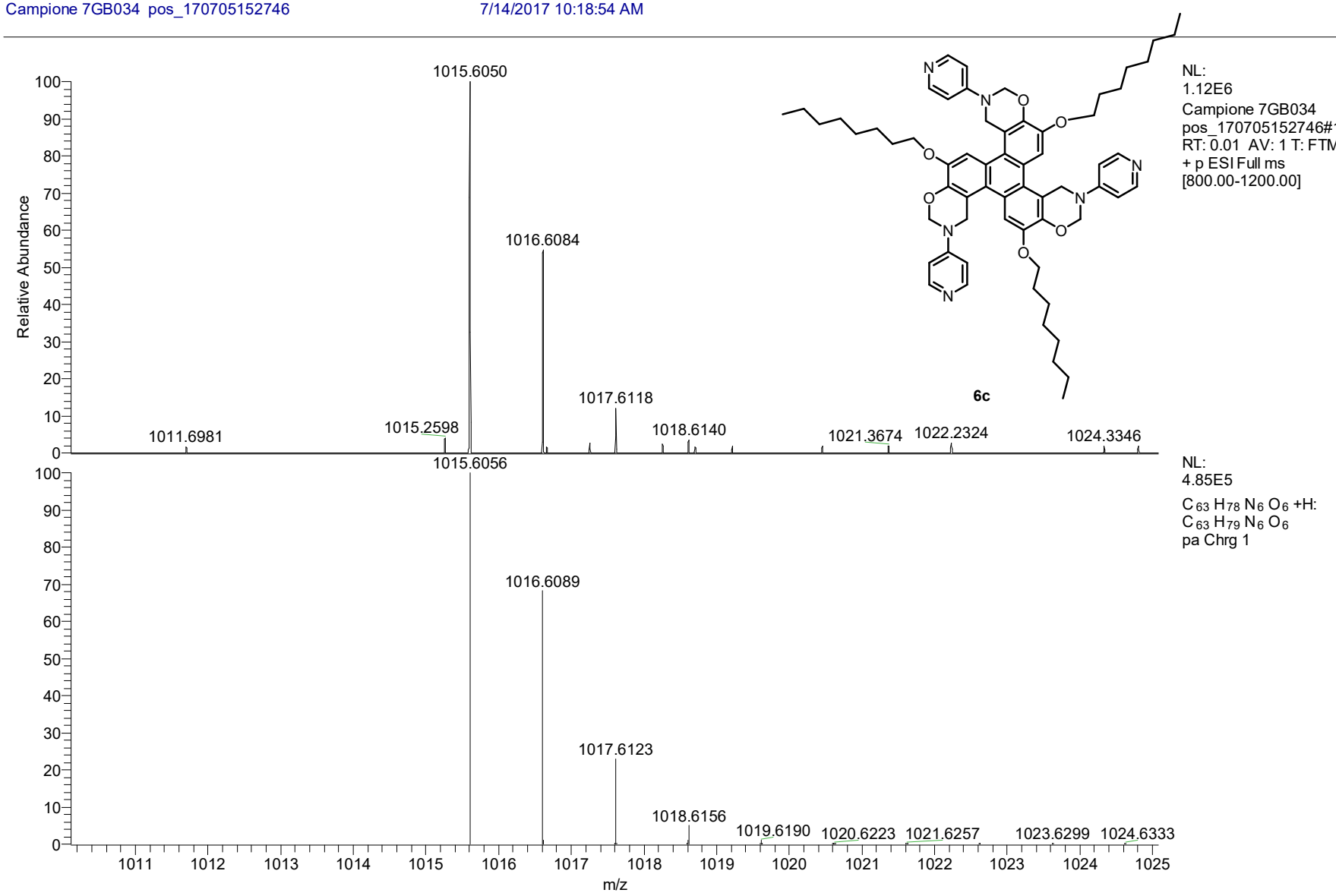


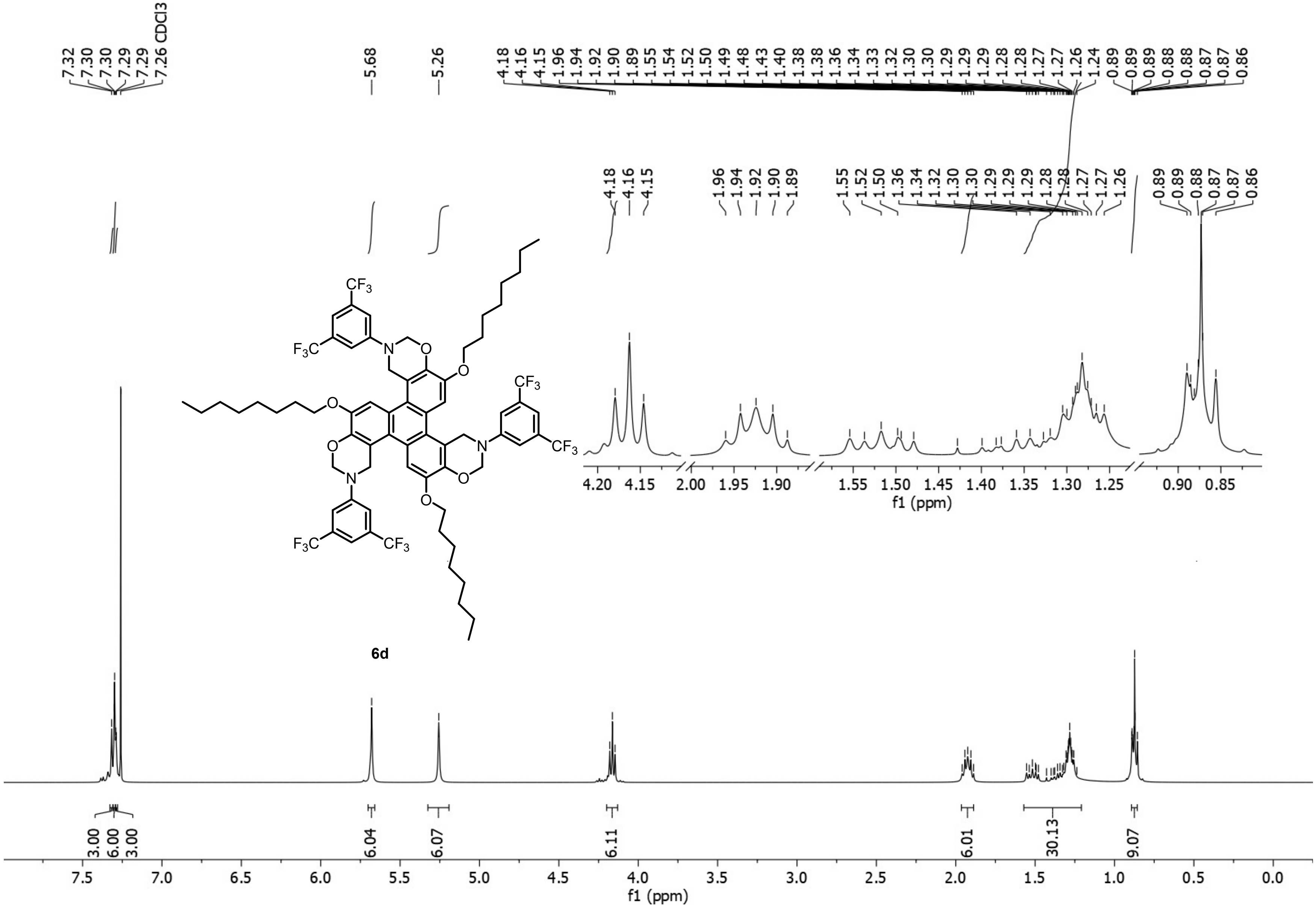

8.23
8.22
7.34
7.26 CDCl3
6.71
6.69
5.73
5.26
4.16
4.14
4.12
2.01
1.95
1.93
1.91
1.89
1.88
1.85
1.54 HDO
1.52 HDO
1.50 HDO
1.48 HDO
1.38
1.37
1.35
1.34
1.32
1.31
1.28
0.89
0.87
0.86
0.82
6c
6.00
3.00
6.02
6.04
6.02
6.07
6.18
6.01
35.45
9.14
f1 (ppm)

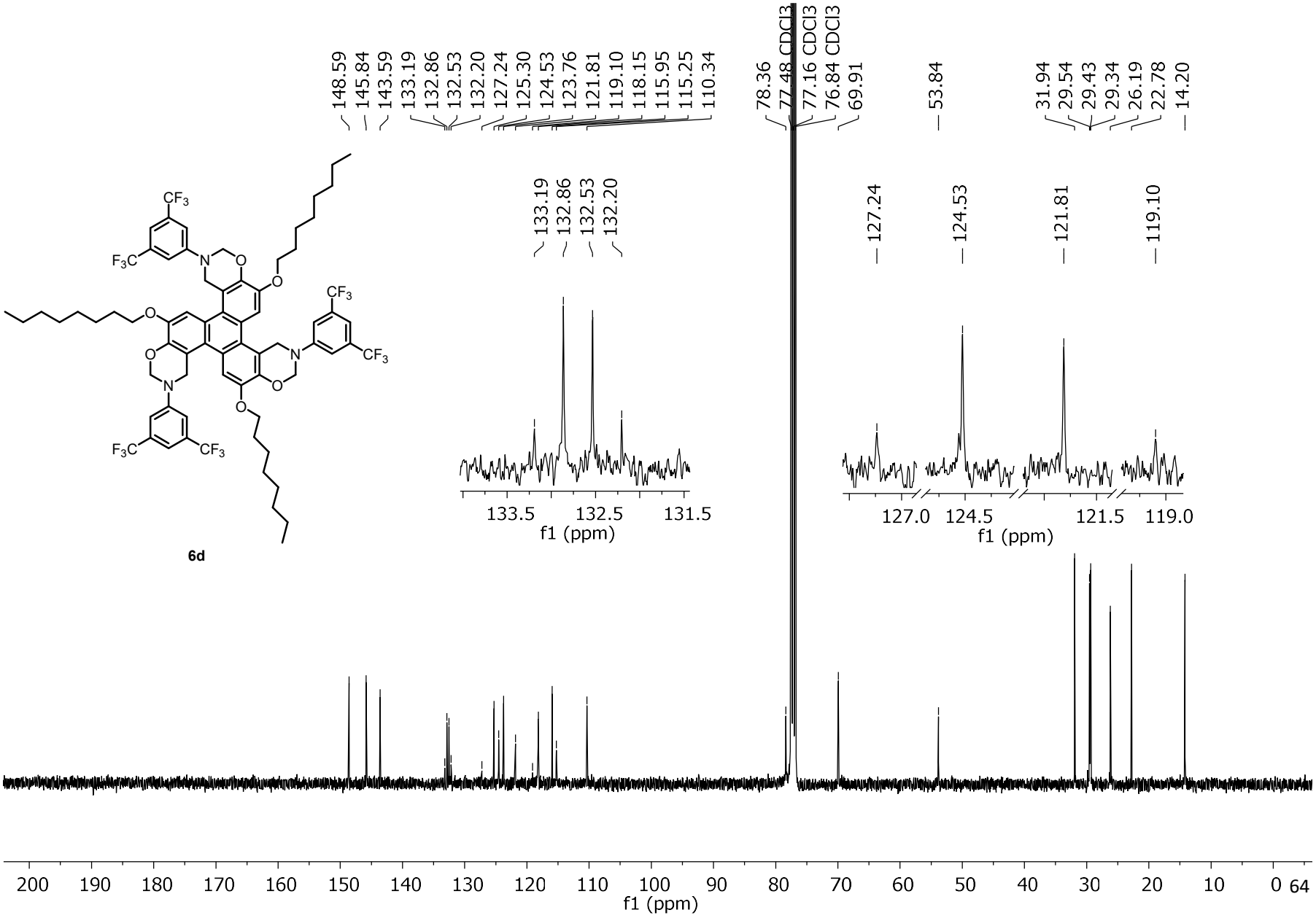

152.88
150.68
145.85
143.67
125.35
123.73
116.42
111.29
110.08
77.48 CDCl3
77.36
77.16 CDCl3
76.84 CDCl3
69.74
51.05
31.95
29.55
29.41
29.38
26.23
22.79
14.24
6c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

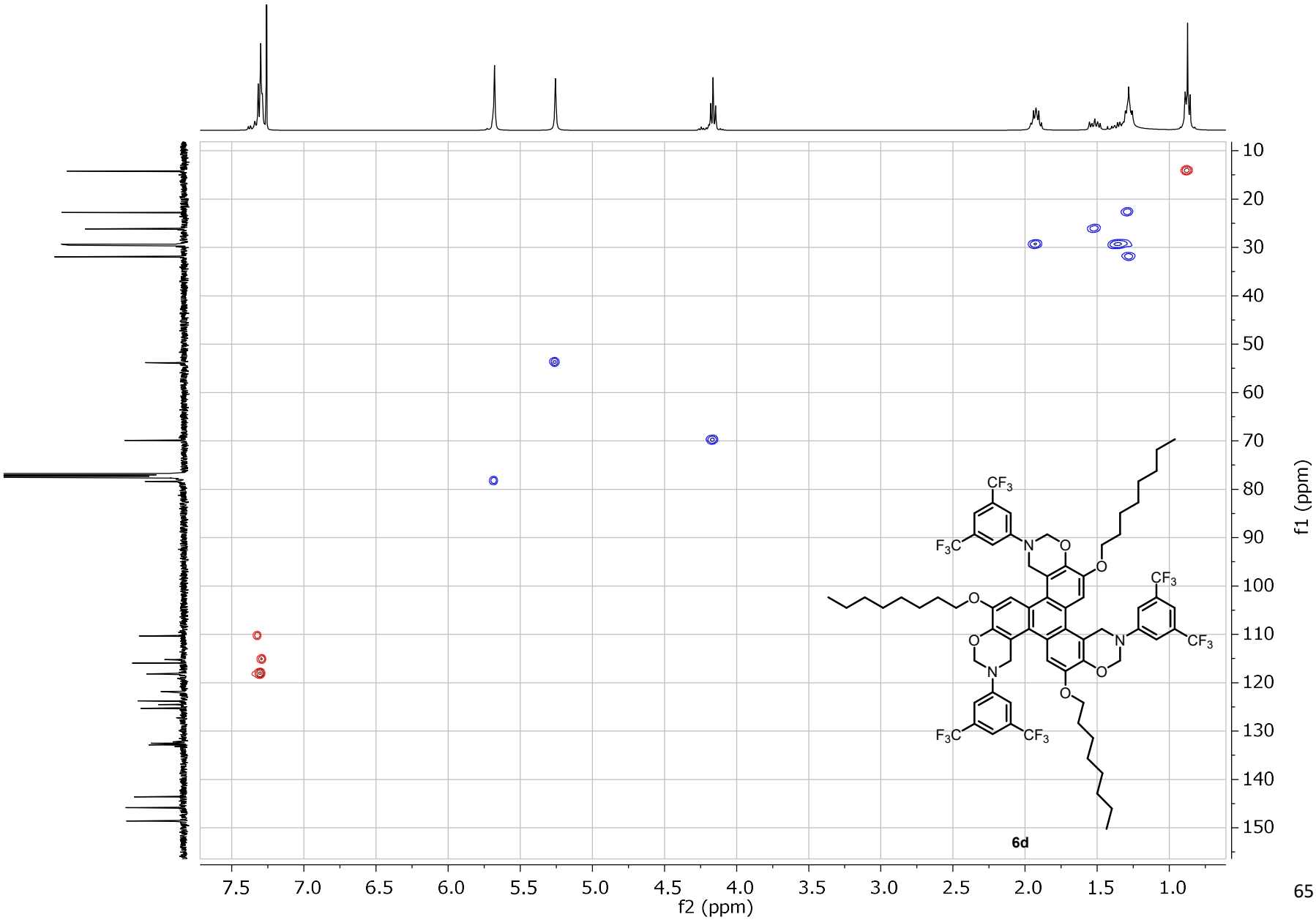

f2 (ppm)
f1 (ppm)
6c

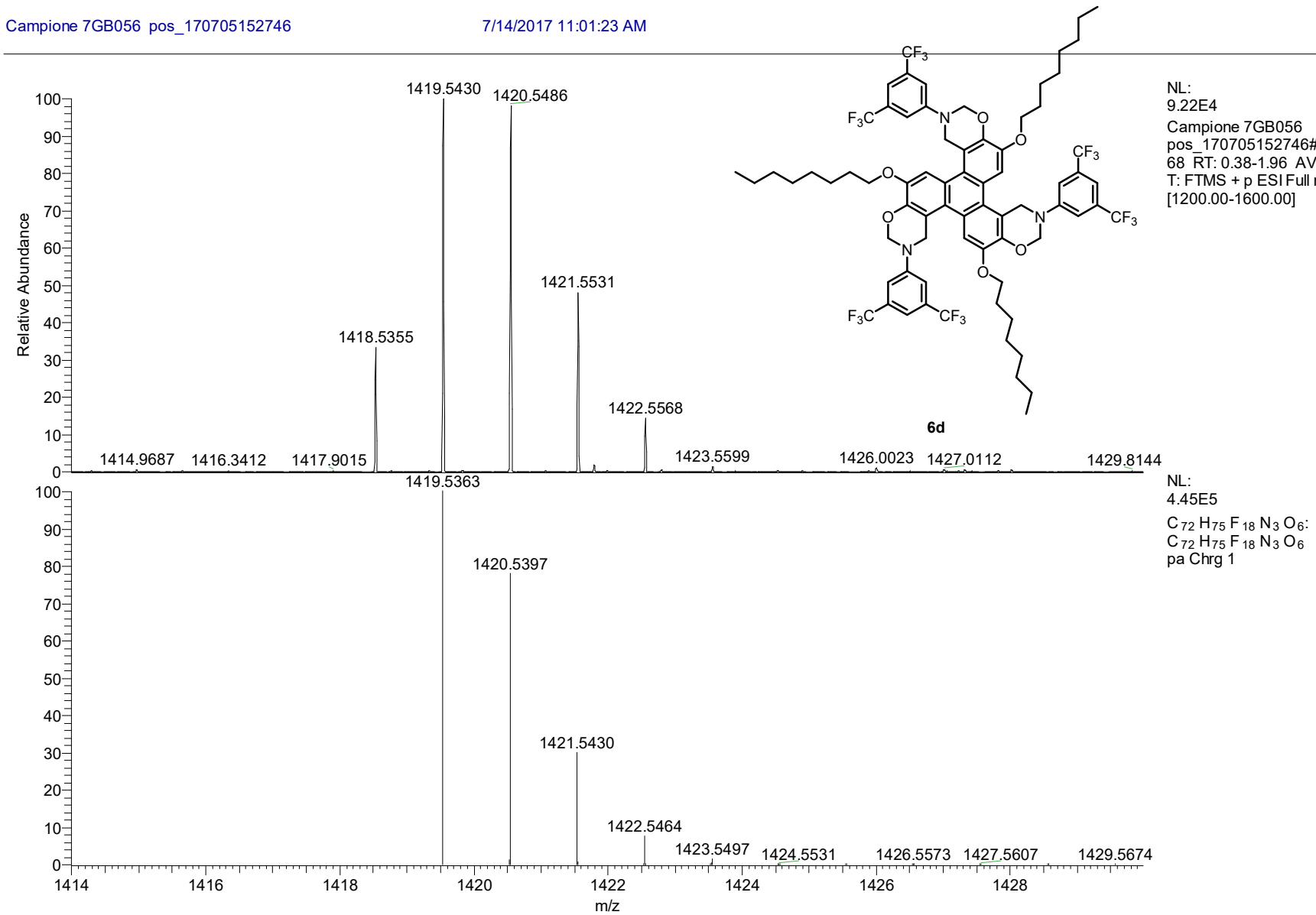
Campione 7GB034 pos_170705152746 7/14/2017 10:18:54 AM

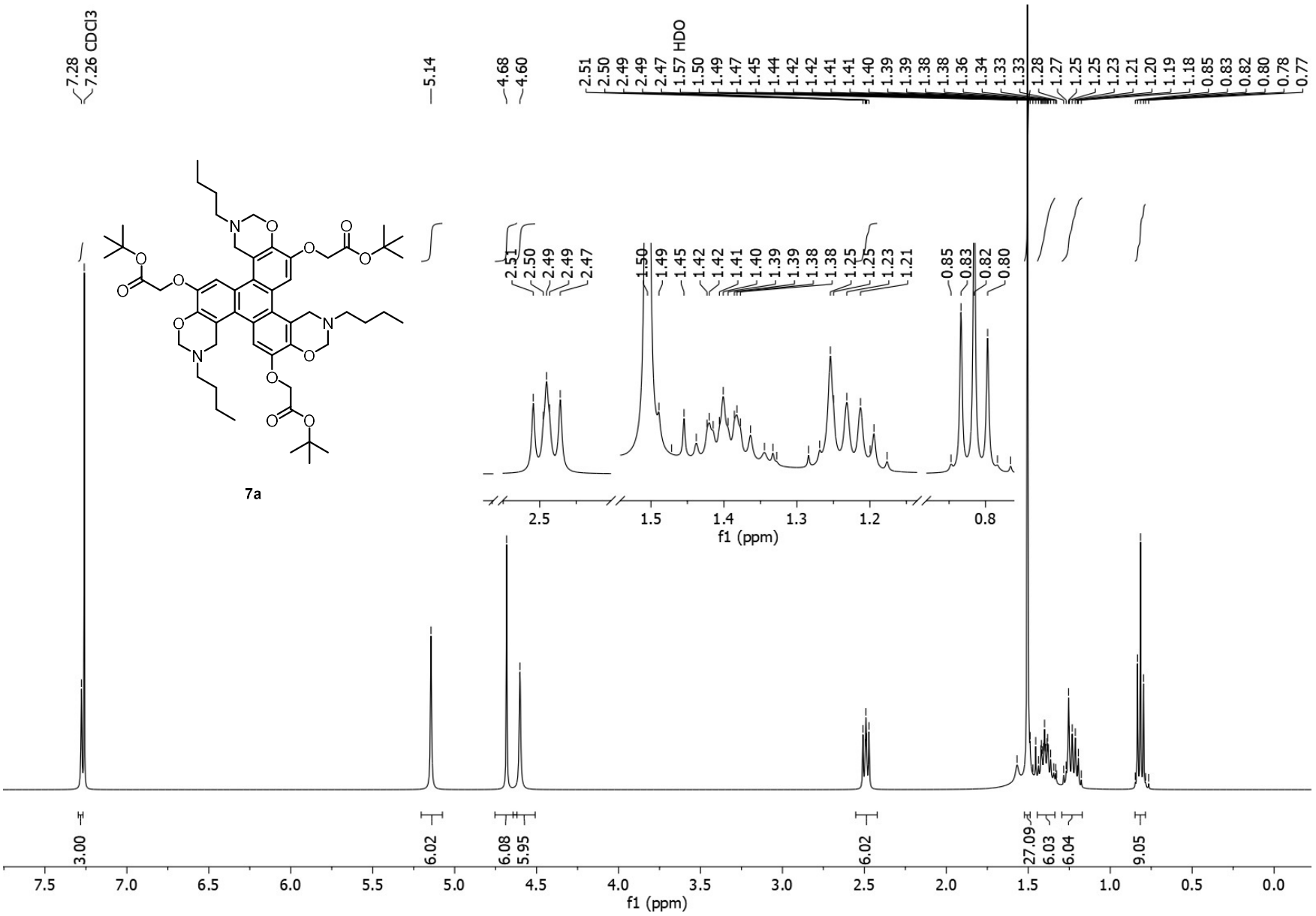


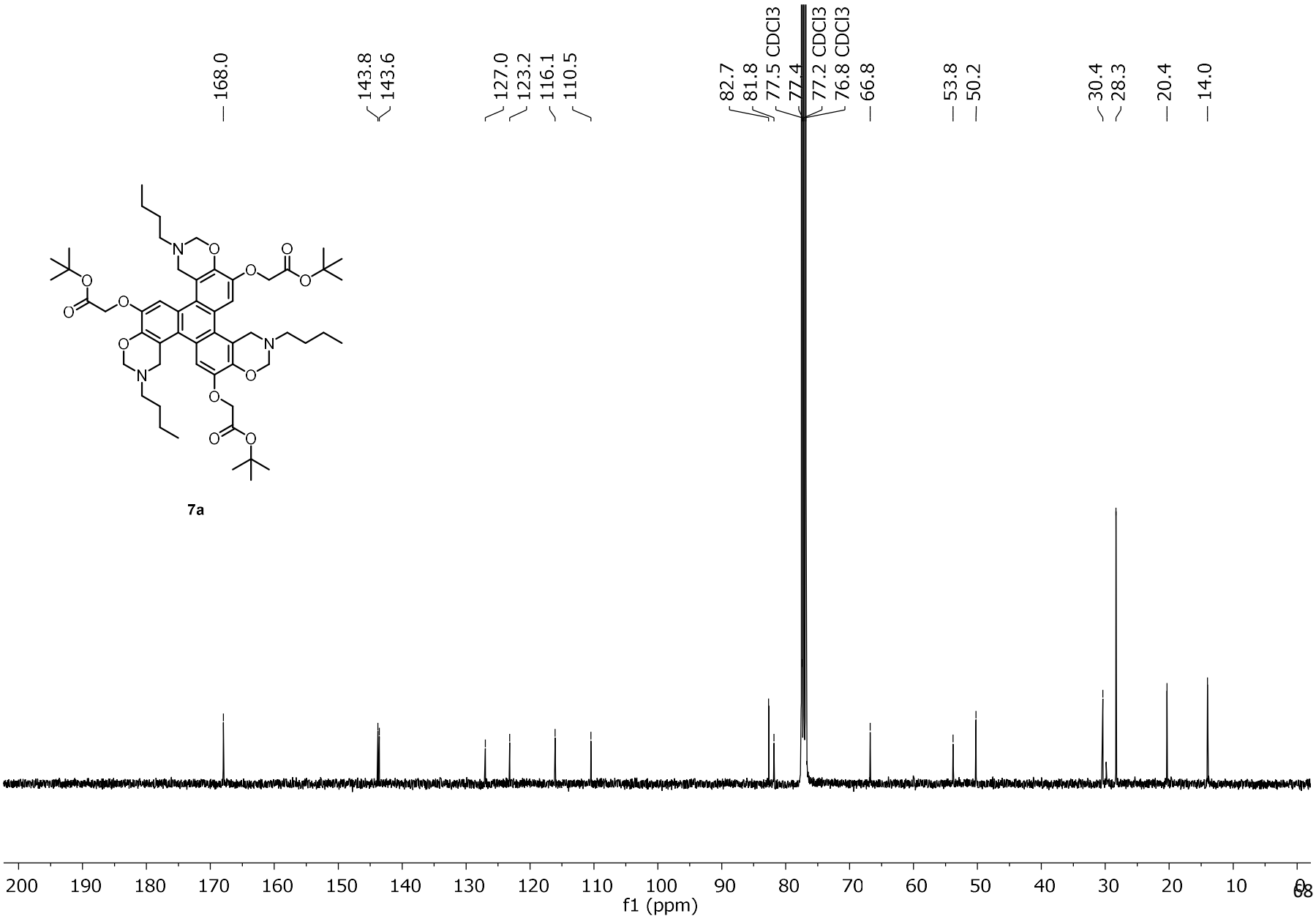

7.32
7.30
7.30
7.29
7.29
7.26 CDCl3
5.68
5.26
4.18
4.16
4.15
1.96
1.94
1.92
1.90
1.89
1.55
1.54
1.52
1.50
1.49
1.48
1.43
1.40
1.38
1.38
1.36
1.34
1.33
1.32
1.30
1.30
1.29
1.29
1.29
1.28
1.28
1.27
1.27
1.26
1.24
0.89
0.89
0.88
0.88
0.87
0.87
0.86
CF3
F3C
CF3
CF3
F3C
CF3
6d
f1 (ppm)
3.00
6.00
3.00
6.04
6.07
6.11
6.01
30.13
9.07

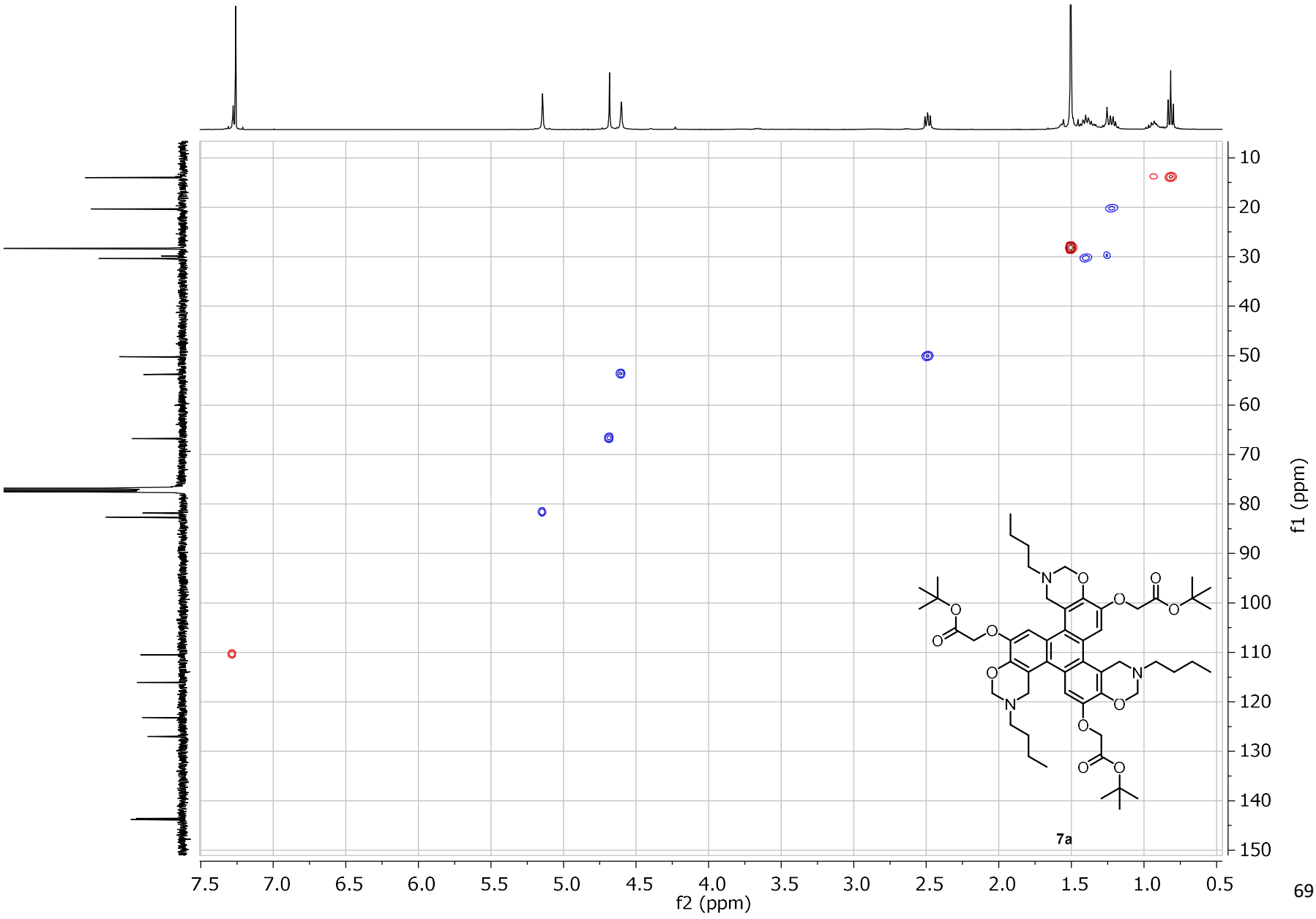

148.59
145.84
143.59
133.19
132.86
132.53
132.20
127.24
125.30
124.53
123.76
121.81
119.10
118.15
115.95
115.25
110.34
78.36
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.91
53.84
31.94
29.54
29.43
29.34
26.19
22.78
14.20
6d
133.5
132.5
131.5
f1 (ppm)
127.0
124.5
121.5
119.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

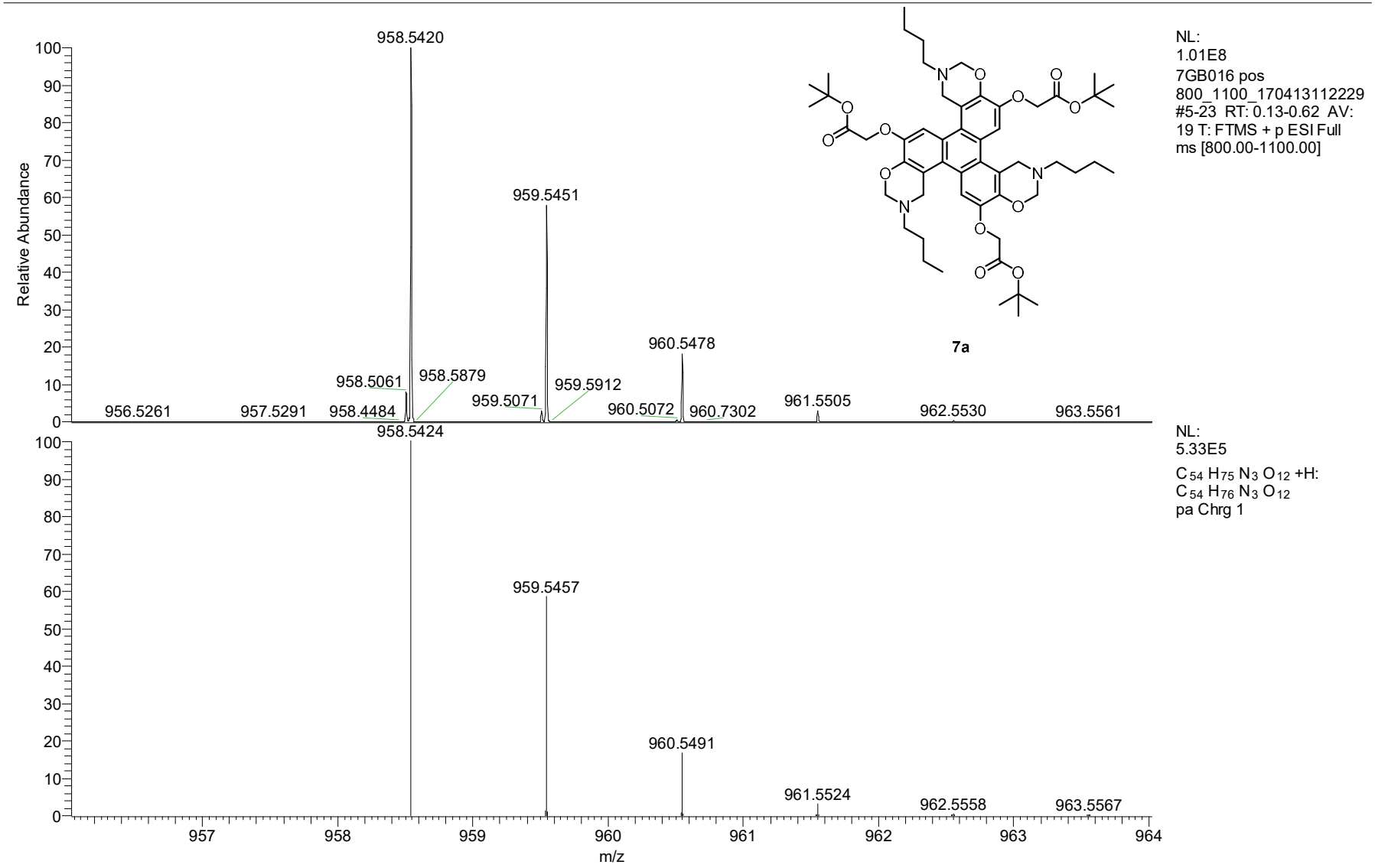

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
CF3
F3C
N
O
CF3
CF3
F3C
CF3
6d


Campione 7GB056 pos_170705152746
7/14/2017 11:01:23 AM
Relative Abundance
m/z
1419.5430
1420.5486
1421.5531
1418.5355
1422.5568
1414.9687
1416.3412
1417.9015
1423.5599
1426.0023
1427.0112
1429.8144
6d
NL:
9.22E4
Campione 7GB056
pos_170705152746#14-
68 RT: 0.38-1.96 AV: 55
T: FTMS + p ESI Full ms
[1200.00-1600.00]
1419.5363
1420.5397
1421.5430
1422.5464
1423.5497
1424.5531
1426.5573
1427.5607
1429.5674
NL:
4.45E5
C72 H75 F18 N3 O6:
C72 H75 F18 N3 O6
pa Chrg 1

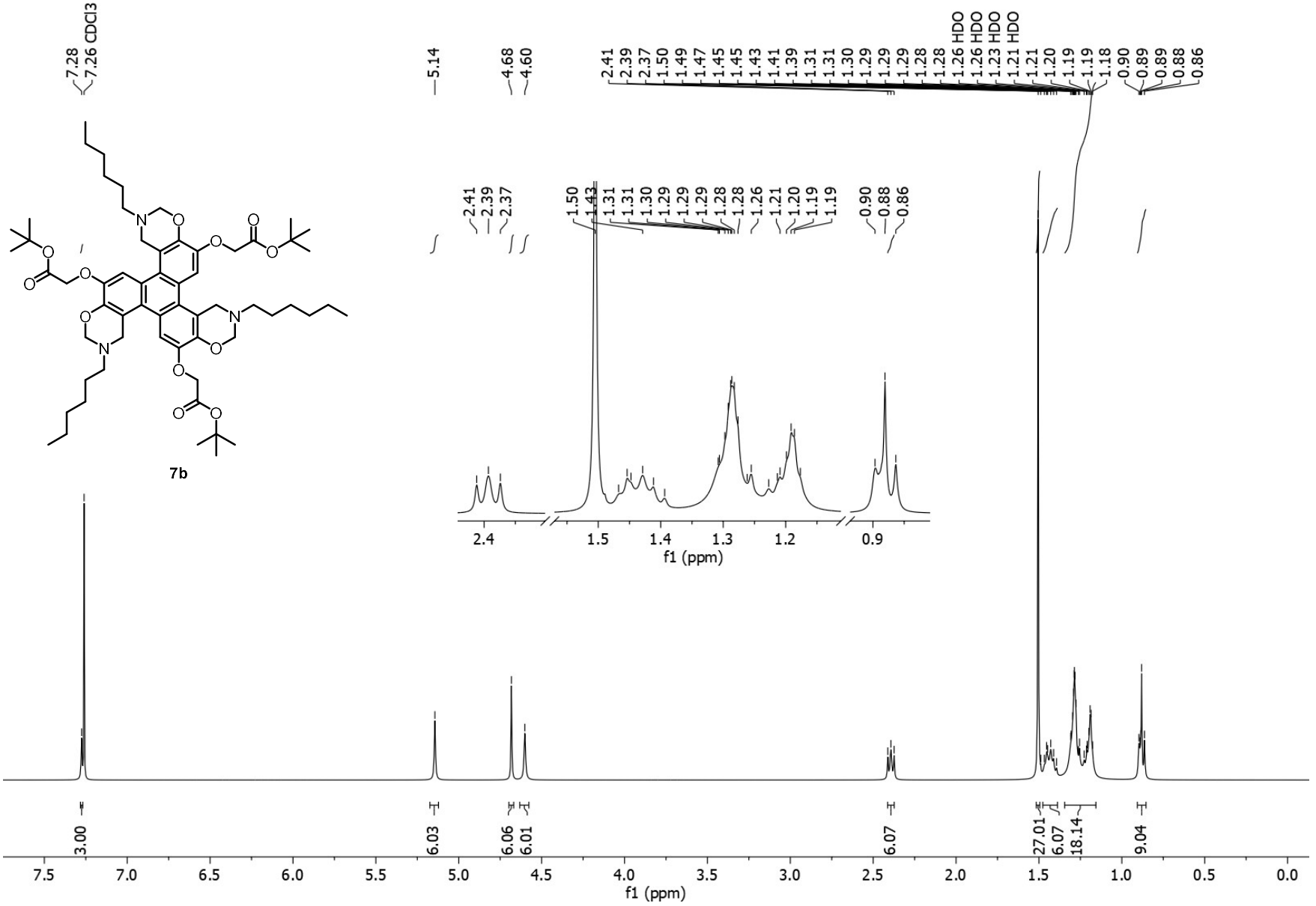

7.28
7.26 CDCl3
5.14
4.68
4.60
2.51
2.50
2.49
2.49
2.47
HDO
1.57
1.50
1.49
1.47
1.45
1.44
1.42
1.42
1.41
1.41
1.40
1.39
1.39
1.38
1.38
1.36
1.34
1.33
1.33
1.28
1.27
1.25
1.25
1.23
1.21
1.20
1.19
1.18
0.85
0.83
0.82
0.80
0.78
0.77
7a
f1 (ppm)
3.00
6.02
6.08
5.95
6.02
27.09
6.03
6.04
9.05
f1 (ppm)

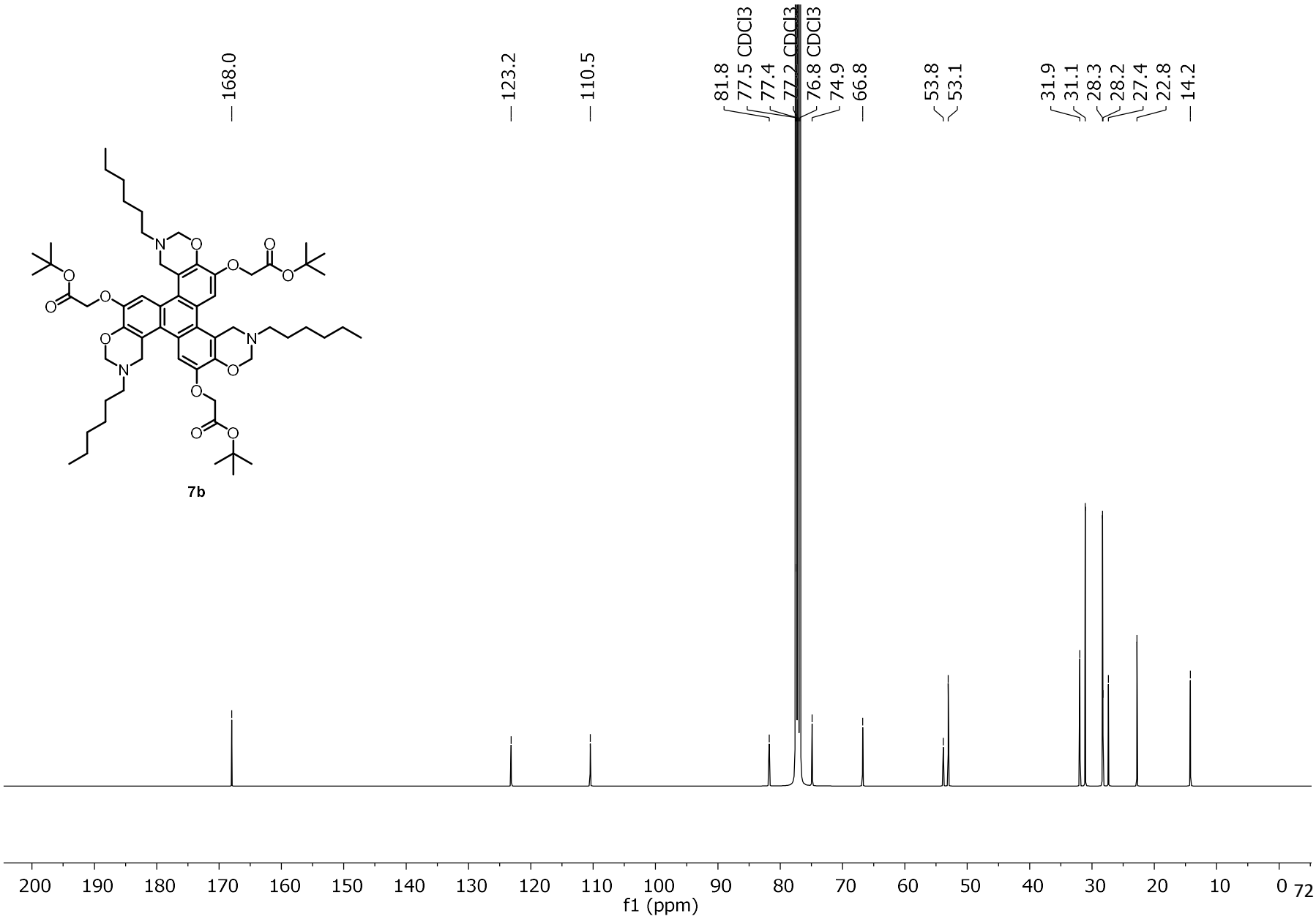

168.0
143.8
143.6
127.0
123.2
116.1
110.5
82.7
81.8
77.5 CDCl3
77.4
77.2 CDCl3
76.8 CDCl3
66.8
53.8
50.2
30.4
28.3
20.4
14.0
7a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

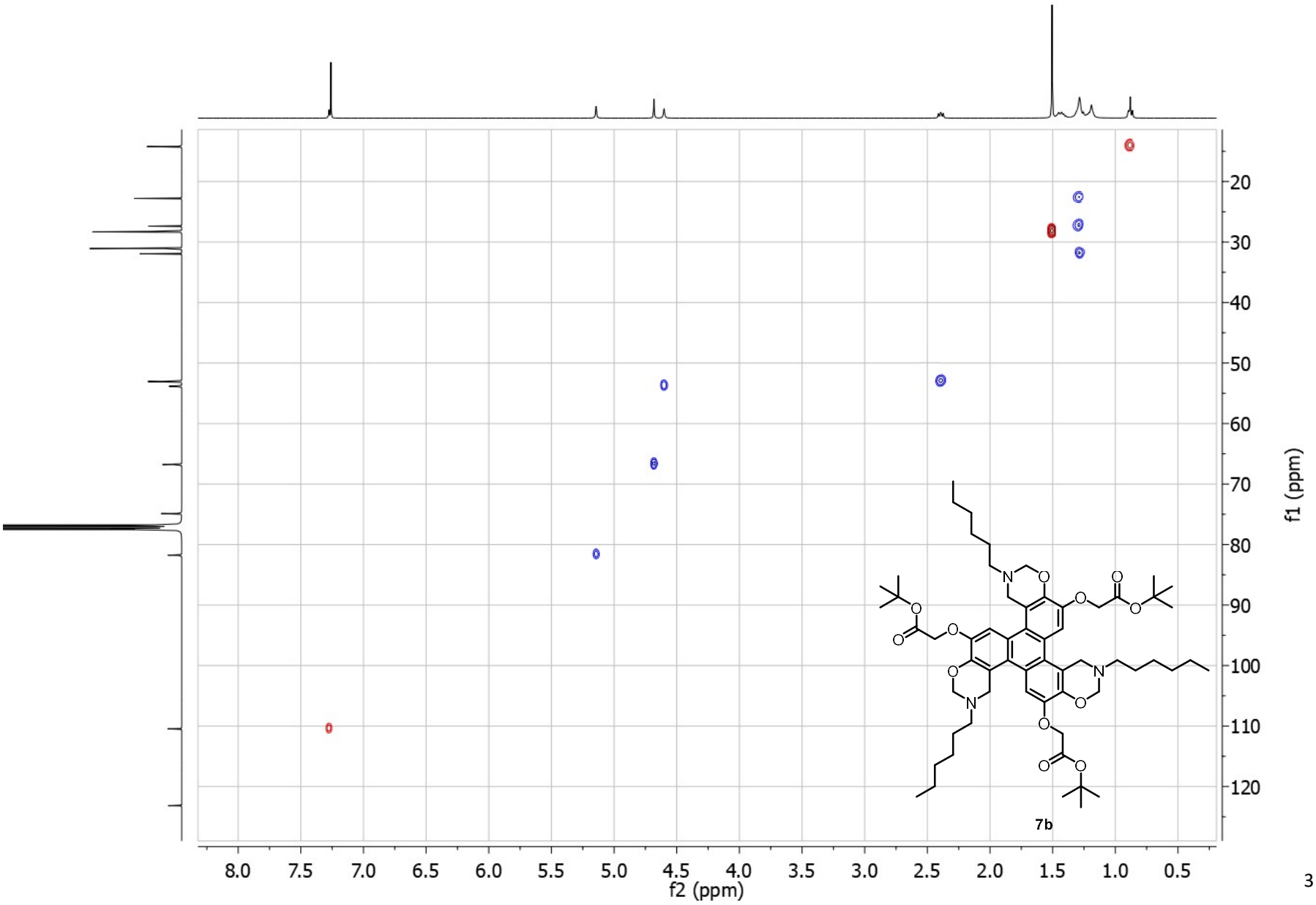

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
7a

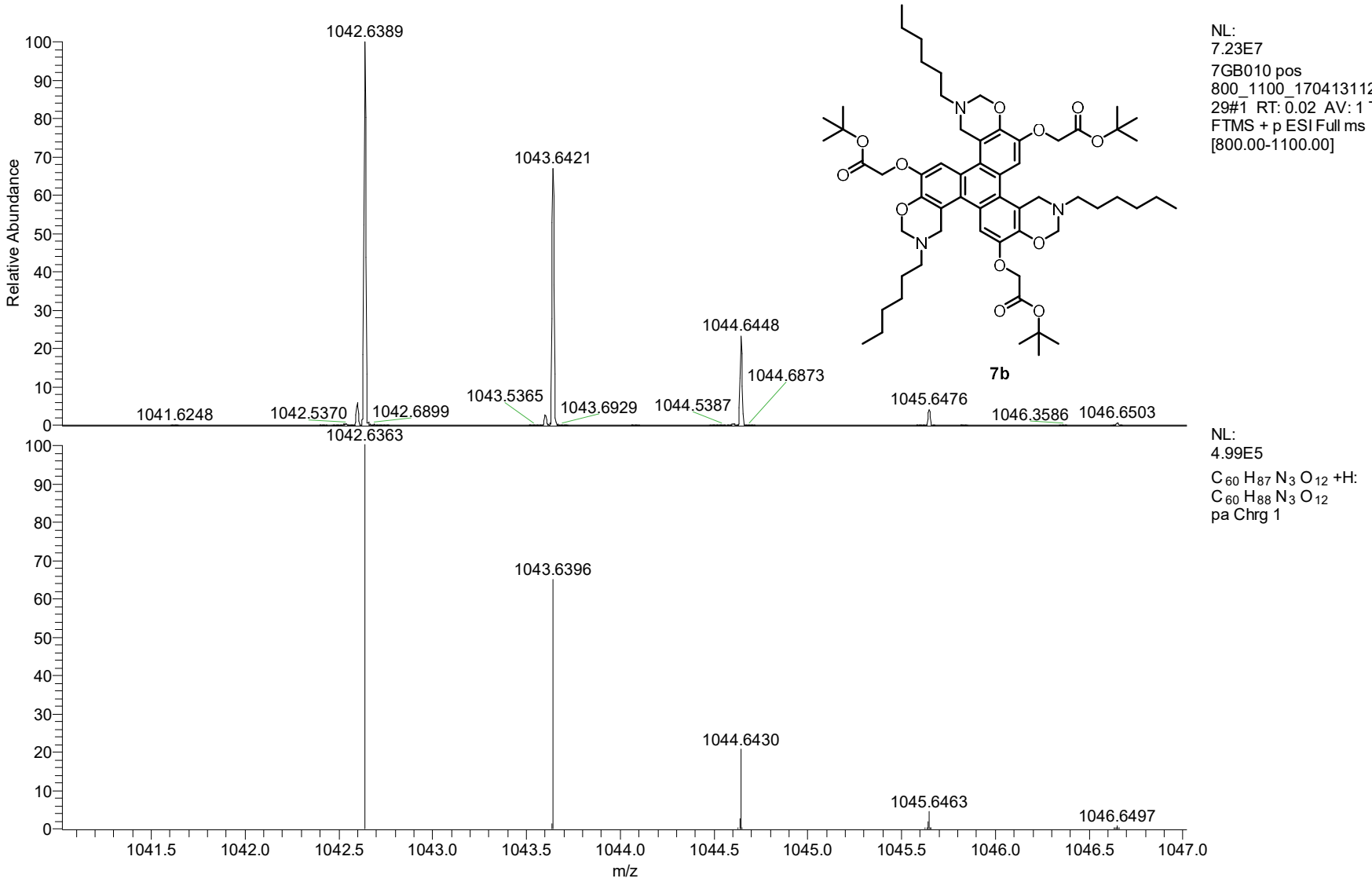

Relative Abundance
m/z
958.5420
959.5451
960.5478
958.5061
958.5879
959.5912
959.5071
956.5261
957.5291
958.4484
960.5072
960.7302
961.5505
962.5530
963.5561
958.5424
959.5457
960.5491
961.5524
962.5558
963.5567
NL:
1.01E8
7GB016 pos
800_1100_170413112229
#5-23 RT: 0.13-0.62 AV:
19 T: FTMS + p ESI Full
ms [800.00-1100.00]
NL:
5.33E5
C54 H75 N3 O12 +H:
C54 H76 N3 O12
pa Chrg 1

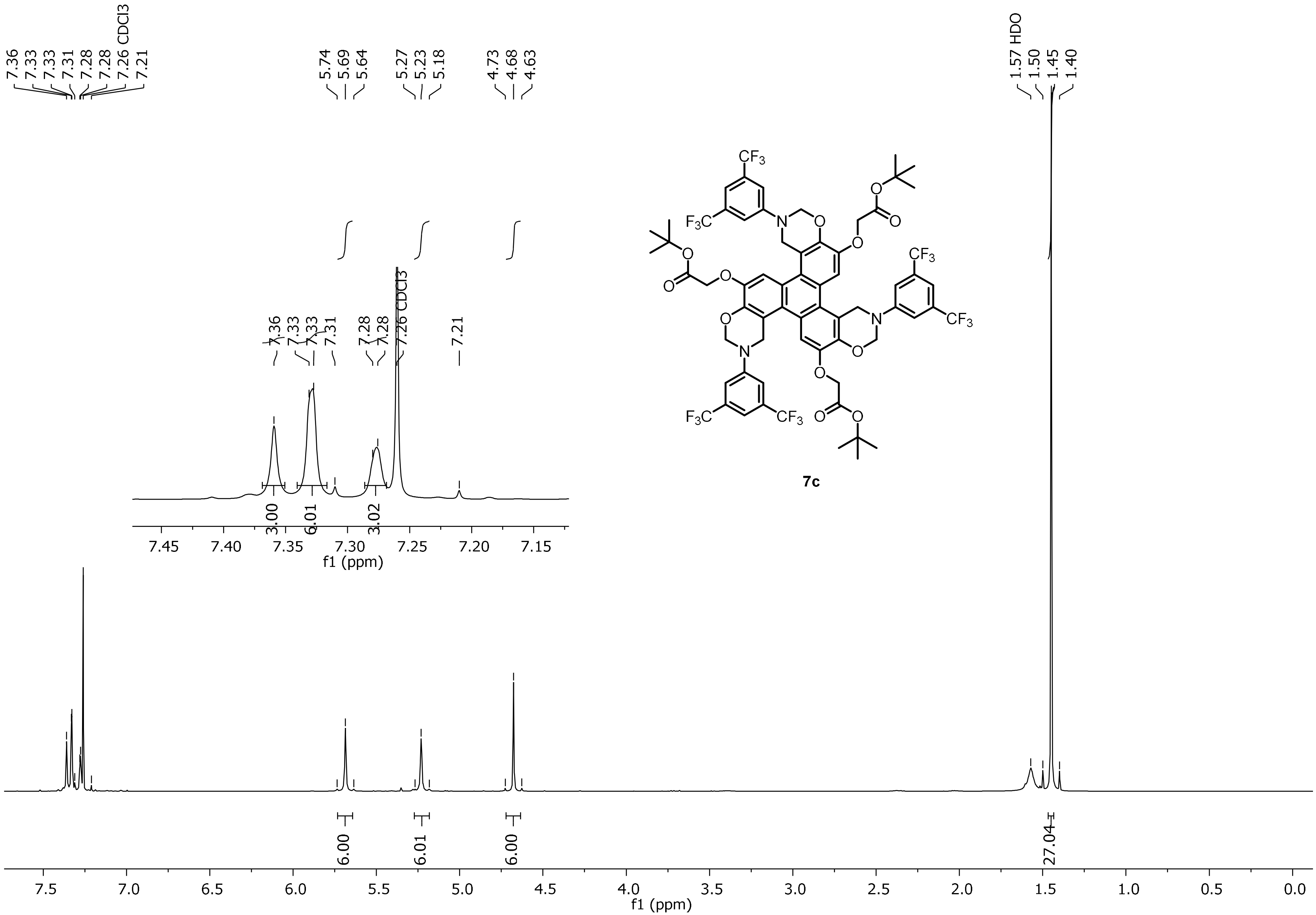
7a

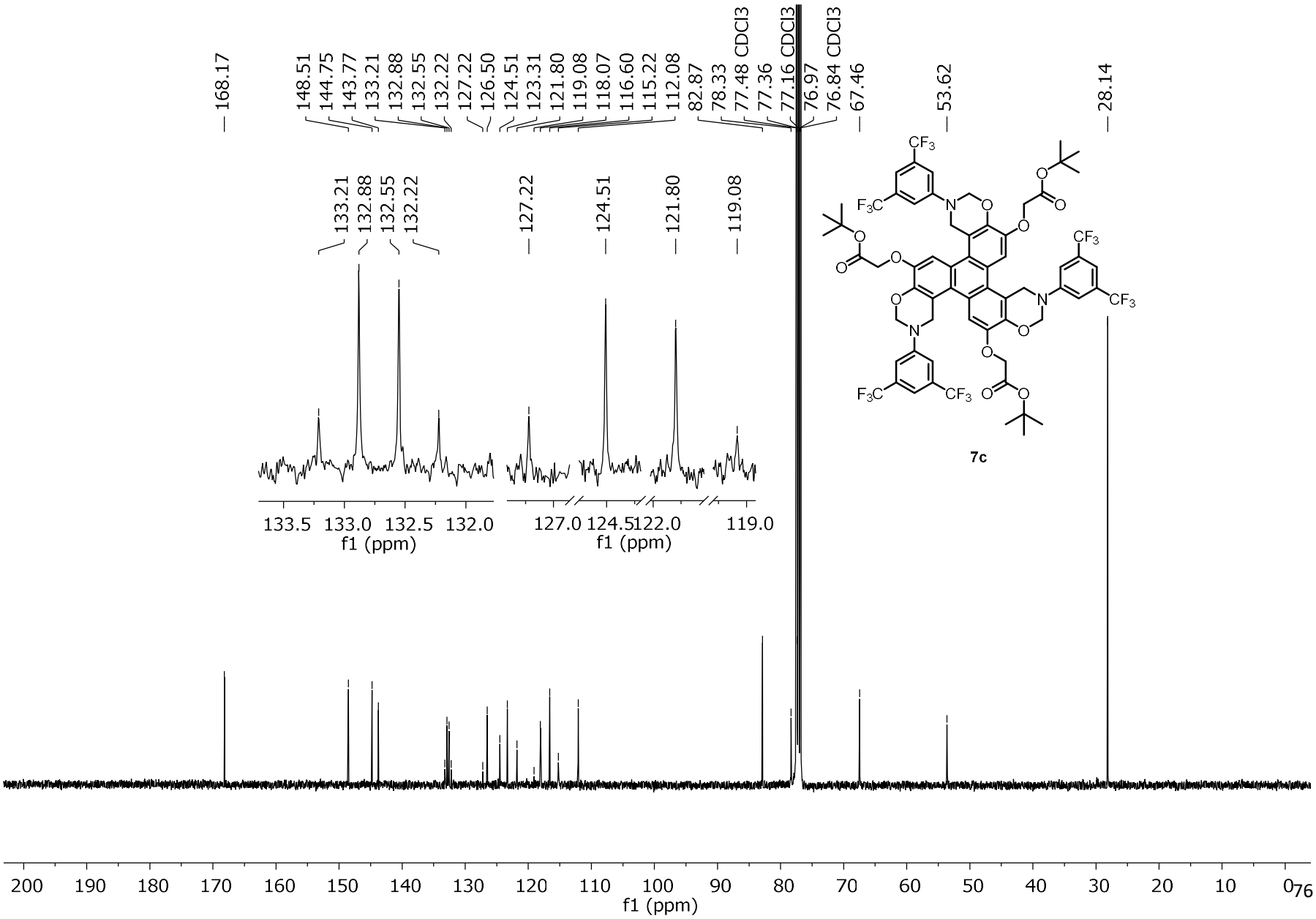

7.28
7.26 CDCl3
5.14
4.68
4.60
2.41
2.39
2.37
1.50
1.49
1.47
1.45
1.45
1.43
1.41
1.39
1.31
1.31
1.30
1.29
1.29
1.29
1.28
1.28
1.26 HDO
1.26 HDO
1.23 HDO
1.21 HDO
1.21
1.20
1.19
1.19
1.18
0.90
0.89
0.89
0.88
0.86
7b
f1 (ppm)
3.00
6.03
6.06
6.01
6.07
27.01
6.07
18.14
9.04
f1 (ppm)

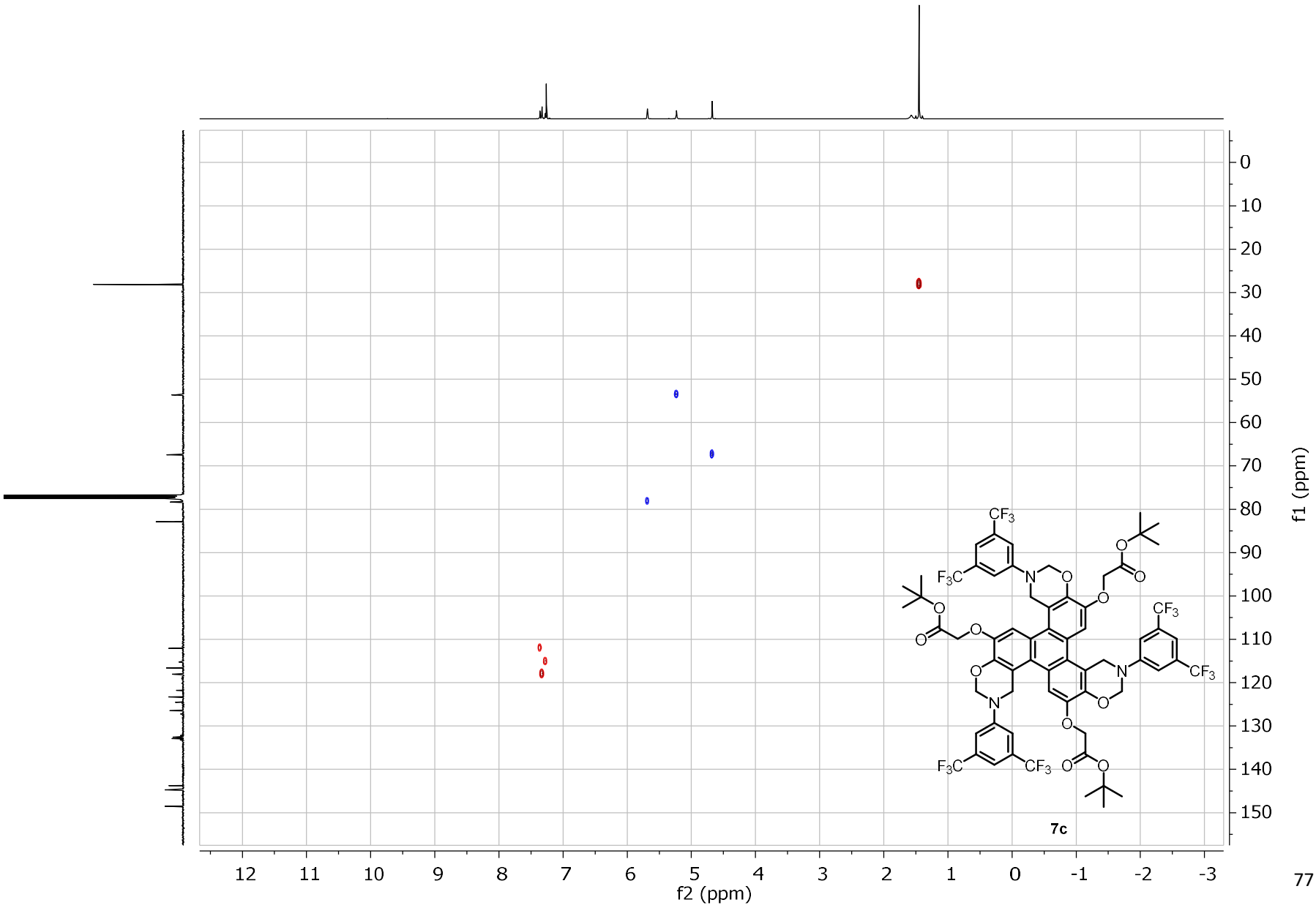

168.0
123.2
110.5
81.8
77.5 CDCl3
77.4
77.2 CDCl3
76.8 CDCl3
74.9
66.8
53.8
53.1
31.9
31.1
28.3
28.2
27.4
22.8
14.2
7b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

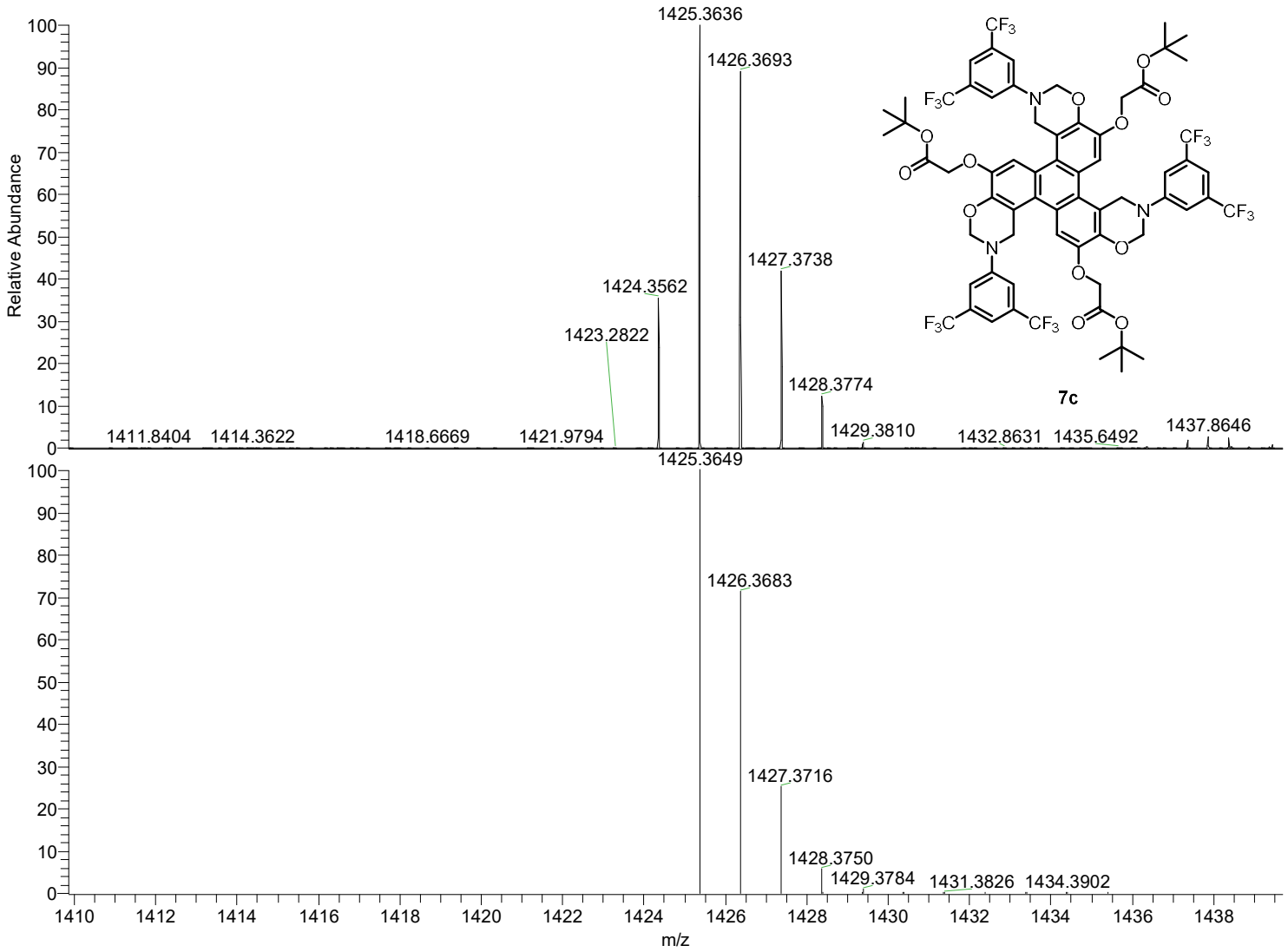

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
f1 (ppm)
7b


1042.6389
1043.6421
1044.6448
1044.6873
1043.5365
1043.6929
1044.5387
1045.6476
1041.6248
1042.5370
1042.6899
1046.3586
1046.6503
1042.6363
1043.6396
1044.6430
1045.6463
1046.6497
Relative Abundance
m/z
NL:
7.23E7
7GB010 pos
800_1100_1704131122
29#1 RT: 0.02 AV: 1 T:
FTMS + p ESI Full ms
[800.00-1100.00]
NL:
4.99E5
C60 H87 N3 O12 +H:
C60 H88 N3 O12
pa Chrg 1
7b


7.36
7.33
7.33
7.31
7.28
7.28
7.26 CDCl3
7.21
5.74
5.69
5.64
5.27
5.23
5.18
4.73
4.68
4.63
1.57 HDO
1.50
1.45
1.40
3.00
6.01
3.02
f1 (ppm)
6.00
6.01
6.00
27.04
f1 (ppm)
7c

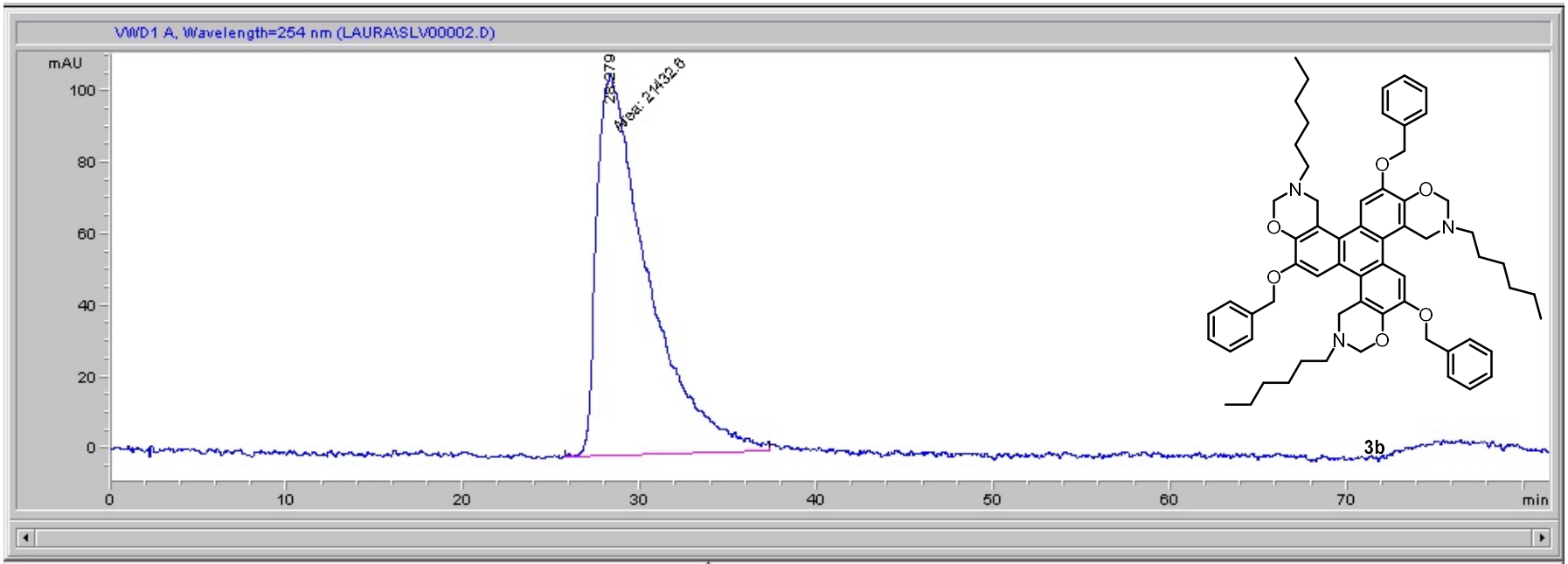

168.17
148.51
144.75
143.77
133.21
132.88
132.55
132.22
127.22
126.50
124.51
123.31
121.80
119.08
118.07
116.60
115.22
112.08
82.87
78.33
77.48 CDCl3
77.36
77.16 CDCl3
76.97
76.84 CDCl3
67.46
53.62
28.14
133.21
132.88
132.55
132.22
127.22
124.51
121.80
119.08
133.5 133.0 132.5 132.0
f1 (ppm)
127.0 124.5 122.0 119.0
f1 (ppm)
7c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
76


f2 (ppm)
f1 (ppm)
7c


1425.3636
1426.3693
1427.3738
1424.3562
1423.2822
1428.3774
1429.3810
1411.8404
1414.3622
1418.6669
1421.9794
1432.8631
1435.6492
1437.8646
Relative Abundance
7c
NL:
5.24E5
Campione 7GB049
pos_170705152746#10-
50 RT: 0.26-1.41 AV: 41
T: FTMS + p ESI Full ms
[1300.00-1600.00]
1425.3649
1426.3683
1427.3716
1428.3750
1429.3784
1431.3826
1434.3902
NL:
4.69E5
C66 H57 F18 N3 O12:
C66 H57 F18 N3 O12
pa Chrg 1
m/z

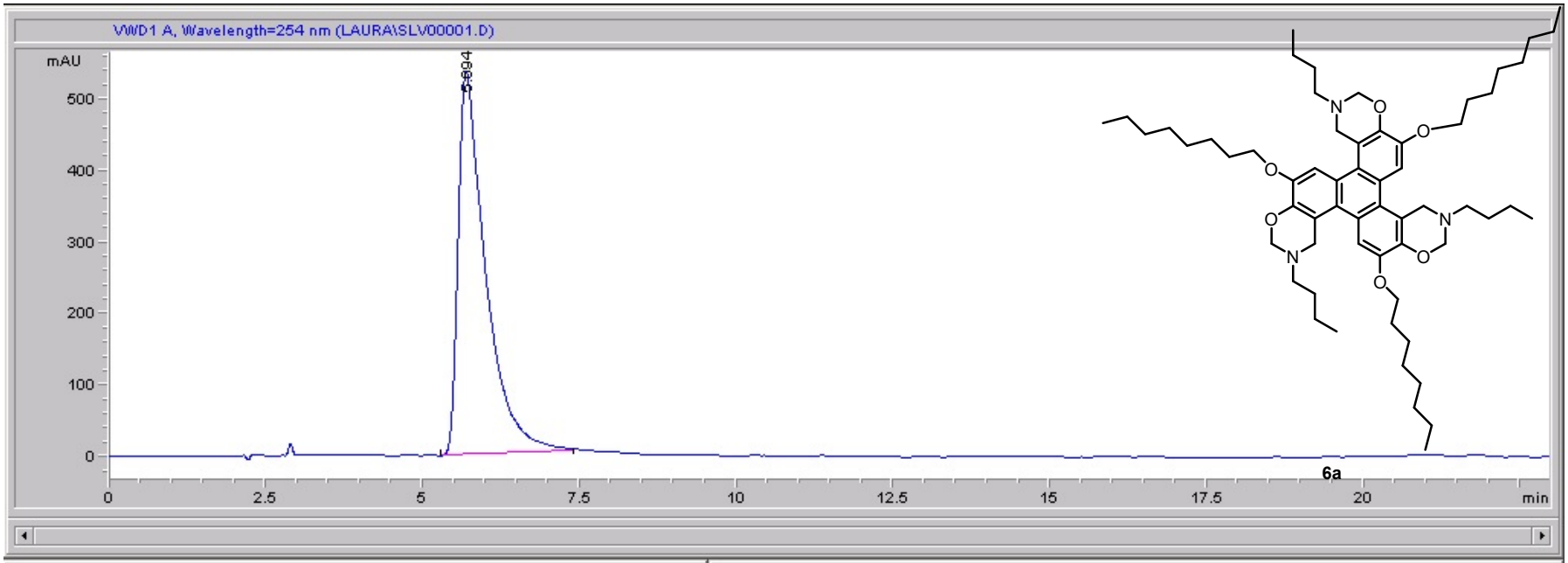
S3. Chiral HPLC

The attempts to separate the enantiomers of **3b** and **6a** were carried out by HPLC analyses on a Hewlett Packard Series 1100 G1311A Quat-Pump with a 20 μL injection loop using 1 ml/min flow of eluent with a composition hexane/iPrOH from 97:3 to 90:10 on a Amylose-2 chiral 25 cm column.



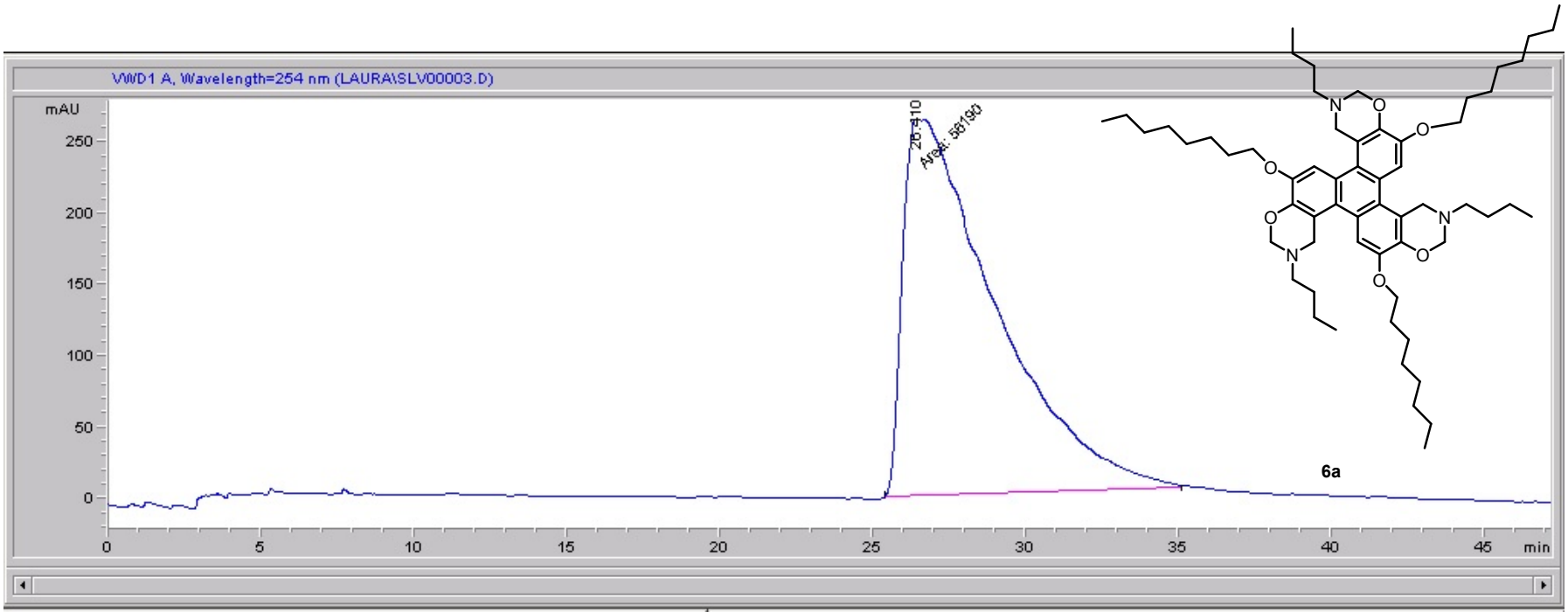
File Information	
LC-File	SLV00002.D
File Path	C:\HPCHEM\1\DATA\LAURA\
Date	13-Apr-18, 11:44:55
Sample	Gia70
Sample Info	Amylose 2 campione giacomo 70
	1.5 mL/min - isocratica 10% iPrOH 254 nm
Barcode	
Operator	Laura
Method	STYLBENE.M
Analysis Time	81.458 min

#	Time	Area	Height	Width	Symmetry
1	28.279	21432.6	107	3.3388	0.35



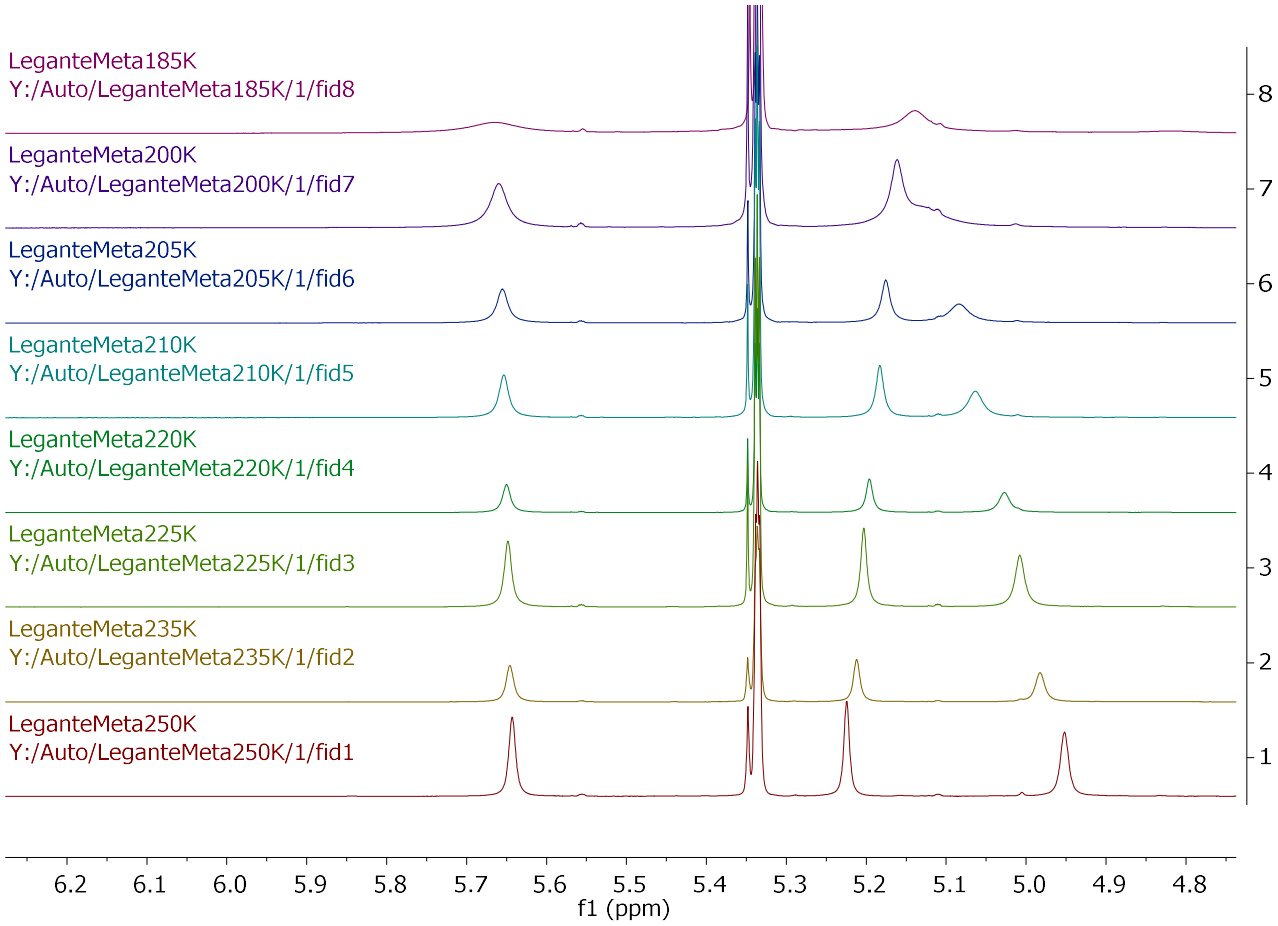
File Information	
LC-File	SLV00001.D
File Path	C:\HPCHEM\1\DATA\LAURA\
Date	13-Apr-18, 11:19:49
Sample	Gia44
Sample Info	Amylose 2 campione giacomo 44
	1.5 mL/min - isocratica 10% iPrOH 254 nm
Barcode	
Operator	Laura
Method	STYLBENE.M
Analysis Time	22.966 min
Sampling Rate	0.0049 min (0.294 sec), 4733 datapoints

#	Time	Area	Height	Width	Symmetry
1	5.694	16316.9	536.2	0.4235	0.382



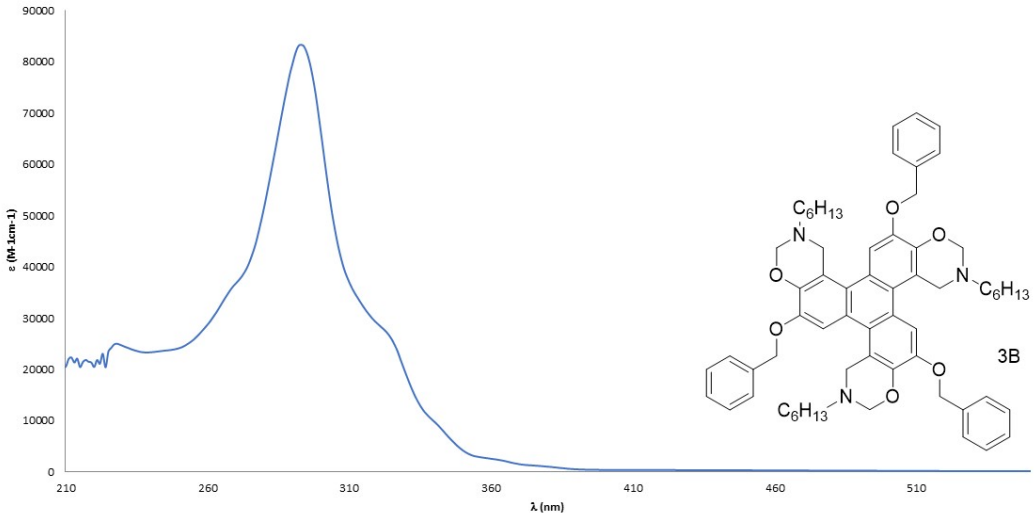
File Information	
LC-File	SLV00003.D
File Path	C:\HPCHEM\1\DATA\LAURA\
Date	16-Apr-18, 10:42:22
Sample	Gia44
Sample Info	Amylose 2 campione giacomo 44
	1.0 mL/min - isocratica 3% iPrOH 254 nm
Barcode	
Operator	Laura
Method	STYLBENE.M
Analysis Time	47.165 min

#	Time	Area	Height	Width	Symmetry
1	26.41	56190	264.4	3.5423	0.176

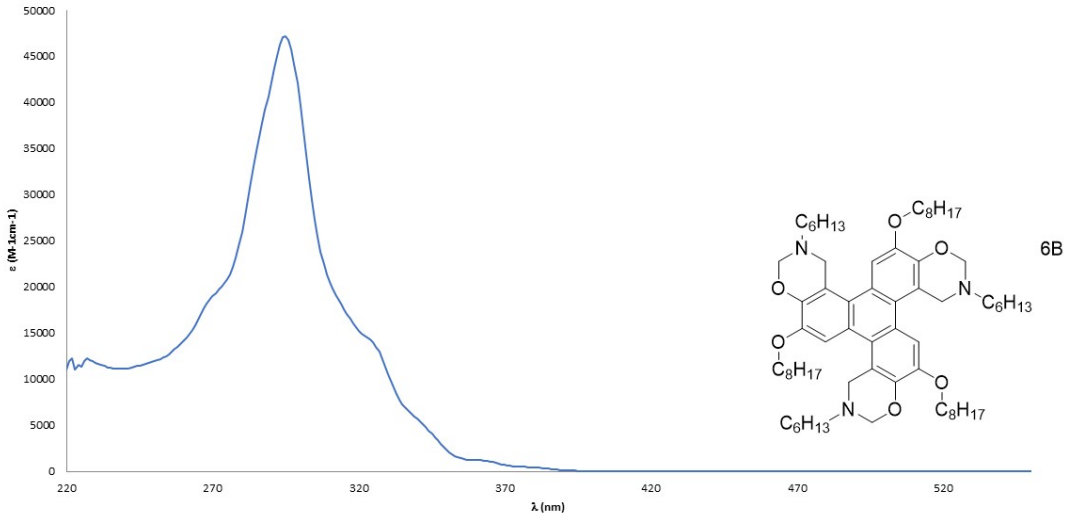


Low temperature NMR spectra for **3c** in the range 250-185 K in CD_2Cl_2 showing only broadening and not splitting of the methylene units of the benzoxazine rings.

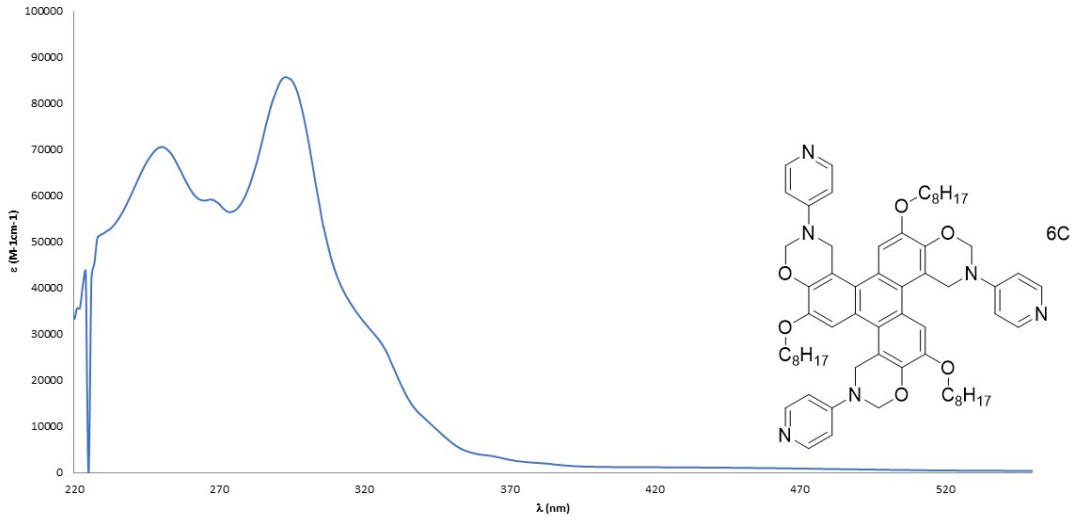
S4. UV-VIS spectra



UV-VIS spectrum of **3b** ($2.5 \cdot 10^{-5}$ M) in dichloromethane.



UV-VIS spectrum of **6b** ($2.9 \cdot 10^{-5}$ M) in dichloromethane.



UV-VIS spectrum of **6c** ($2.4 \cdot 10^{-5}$ M) in dichloromethane.

S5. Literature

[1] W. L. F. Armarego, C. Chai in *Purification of Laboratory Chemicals (Seventh Edition)*, Butterworth-Heinemann, Boston, **2013.**

[2] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.*, **1978**, *14*, 2923-2925.

[3] M. Piattelli, E. Fattorusso, R. A. Nicolaus, S. Magno, *Tetrahedron*, **1965**, *21*, 3229-3236. R. Zniber, R. Achour, M. Z. Cherkaoui, B. Donnio, L. Gehringerb, D. Guillon, *J. Mater. Chem.*, **2002**, *12*, 2208–2213. V. Percec, R.M. Imam, M. Peterca, D. A. Wilson, R. Graf, H. W. Spiess, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.* **2009**, *131*, 7662-7677.

[4] P. T. Wright, I. Gillies, J. D. Kilburn, *Synthesis*, **1997**, *9*, 1007-1009.