Electronic Supporting Information

Effect of fluorocarbon chains on the mesomorphic properties of chiral imines and their complexes with copper(II)

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1. Experimental conditions for X-ray scattering and additional X-ray data

For X-ray scattering, powder-like samples were kept in glass capillaries (diameter 1 mm) and mounted in a temperature-controlled heating stage. Film patterns were recorded using a Guinier camera (Huber, Germany) and quartz-monochromatized CuKα radiation and calibrated by the powder pattern of $Pb(NO_3)_2$. Two-dimensional patterns were obtained from surface-alignment samples on a glass plate. The X-ray beam (Ni-filtered CuKα radiation) was parallel to the substrate and the diffraction patterns were recorded with an area detector HIStar (Siemens/Bruker, Germany).

Table S1. Small-angle X-ray data for **6c** from 2D patterns on heating (see Fig. S4 for θ-scans), for **7c** and **8b** from Guinier powder patterns on cooling (θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: calculated d value; n: order of the reflection, Layer spacing: used to calculate d_{calc} with an error in the order of 0.1 nm)**.**

Compound	T (°C)	Phase	θ_{obs} (°)	d_{obs} (nm)	n	d_{calc} (nm)	$d_{\mathrm{obs}}-d_{\mathrm{calc}}$ (nm)	Layer spacing d (nm)
6c	25	cr	3.396	2.60	1	2.72	-0.12	2.72
			6.498	1.36	2	1.36	0.00	
			9.756	0.91	3	0.91	0.00	
	82	SmC*	1.492	2.96	1	2.97	-0.01	2.97
			2.974	1.49	2	1.48	0.01	
	85	SmC*	1.488	2.97	1	2.97	0.00	2.97
			2.977	1.48	2	1.48	0.00	
	90	SmC*	1.481	2.98	1	2.98	0.00	2.98
			2.963	1.49	2	1.49	0.00	
	100	SmC*	1.463	3.02	1	3.02	0.00	3.02
			2.920	1.51	2	1.51	0.00	
	110	SmC*	1.442	3.06	1	3.07	-0.01	3.07
			2.880	1.53	2	1.53	0.00	
	120	SmC*	1.407	3.14	1	3.14	0.00	3.14
			2.816	1.57	2	1.57	0.00	
	122	SmC*	1.398	3.16	1	3.16	0.00	3.16
			2.797	1.58	2	1.58	0.00	
	124	SmC*	1.387	3.18	1	3.18	0.00	3.18
			2.777	1.59	2	1.59	0.00	
	126	SmC*	1.375	3.21	1	3.21	0.00	3.21
			2.750	1.61	2	1.61	0.00	
	128	SmC*	1.359	3.25	1	3.26	-0.01	3.26
			2.707	1.63	2	1.63	0.00	
	130	SmA	1.348	3.28	1	3.28	-0.01	3.28
			2.688	1.64	2	1.64	0.00	
	140	SmA	1.344	3.29	1	3.29	0.00	3.29
			2.679	1.65	2	1.65	0.00	
	150	SmA	1.347	3.28	1	3.28	0.00	3.28
			2.686	1.65	2	1.64	0.01	
	160	SmA	1.351	3.27	1	3.28	-0.01	3.28
			2.688	1.64	2	1.64	0.00	
	170	SmA	1.357	3.25	1	3.26	-0.01	3.26
			2.704	1.63	2	1.63	0.00	

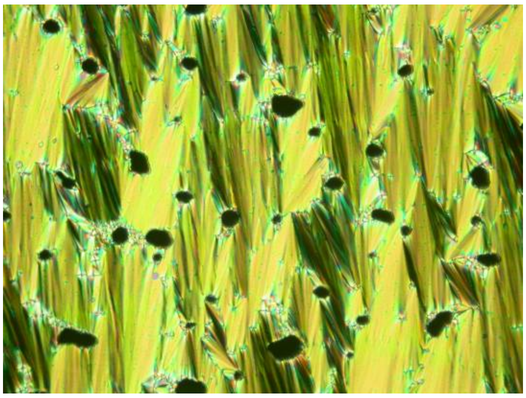
Table S1. Small-angle X-ray data (cont.)

Compound	T (°C)	Phase	θ_{obs} (°)	d_{obs} (nm)	n	d_{calc} (nm)	d_{obs}–d_{calc} (nm)	Layer spacing d (nm)
7c	130	SmA	1.361	3.24	1			3.24
	120	SmA	1.380	3.20	1			3.20
	110	SmC*	1.419	3.11	1			3.11
	100	SmC*	1.453	3.04	1			3.04
	90	SmC*	1.490	2.96	1			2.96
8b	185	SmA	1.447	3.05	1			3.05
	175	SmA	1.439	3.07	1			3.07
	165	SmA	1.434	3.08	1			3.08
	155	SmA	1.424	3.10	1	3.10	0.00	3.10
			2.842	1.55	2	1.55	0.00	

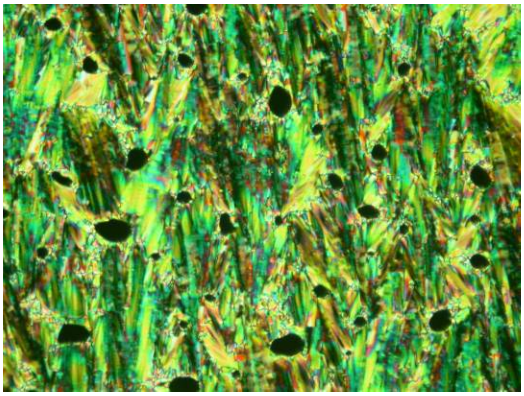
Table S2. Tilt angle for the molecules of **6c** in the SmC* phase derived from the χ positions for the maxima of the outer diffuse scattering (τ_{obs}) and from the ratio of the layer spacings in the SmA (at 130 °C near the phase transition to SmC*) and the SmC* phase calculated by $\cos(\tau_{calc}) = d(T)/d(\text{SmA})$. τ_{obs} has a relatively large experimental error, first because the alignment of the sample was only partial and second because the lower part of the 2D patterns was shadowed by the heating stage and only the χ range above the equator between 90 and 270° could be used (see Fig. S4).

T (°C)	χ_1 (°)	χ_2 (°)	τ_{obs} (°)	Layer spacing (nm)	τ_{calc} (°)
82	109	255	17	2.97	25
85	110	255	18	2.97	25
90	109	254	18	2.98	25
100	107	256	16	3.02	23
110	106	258	14	3.07	21
120	102	262	10	3.14	17
122	101	259	11	3.16	16
124	92	264	4	3.18	14
126	91	266	2	3.21	12
128	94	264	5	3.26	6
130	95	267	4	3.28	0

2. Electrooptical investigations of compound 6c



+ 25 V



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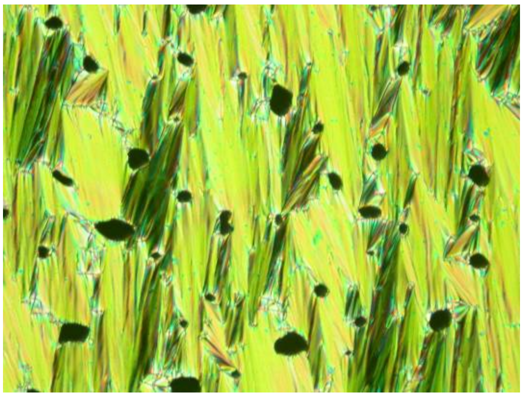
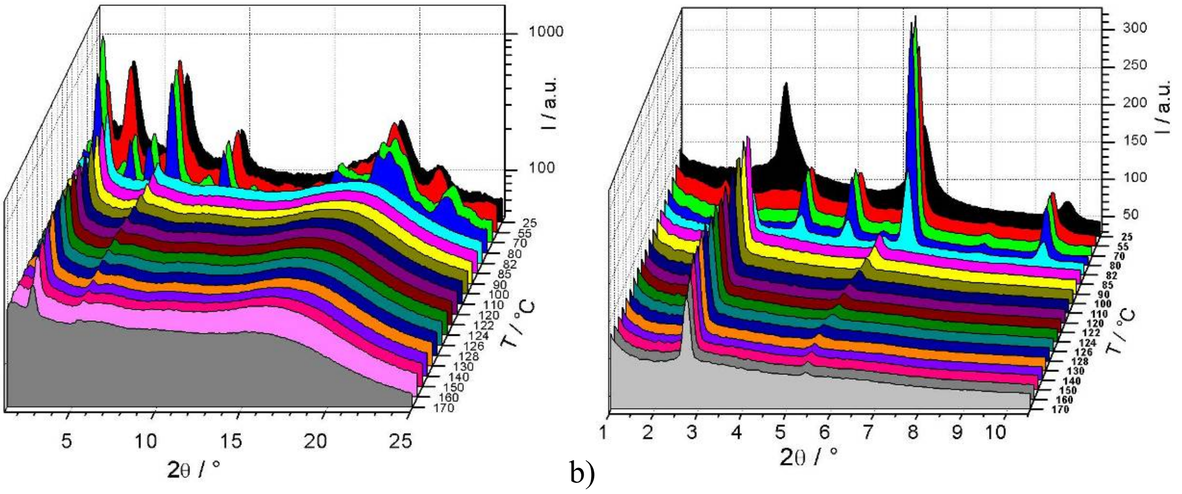


-25V

Figure S1. Polar (bistable, ferroelectric) switching of the SmC* phase of compound **6c** at 110 °C as seen between crossed polarizers (6 µm ITO cell, EHC, Japan).

Figure S2. Polarised light optical photomicrograph of the SmA phase of **8b** at 179 °C (magnification x 200).



a) b)

Figure S3. θ-scans for the 2D X-ray patterns of **6c** on heating, a) wide angle region, b) small angle region.

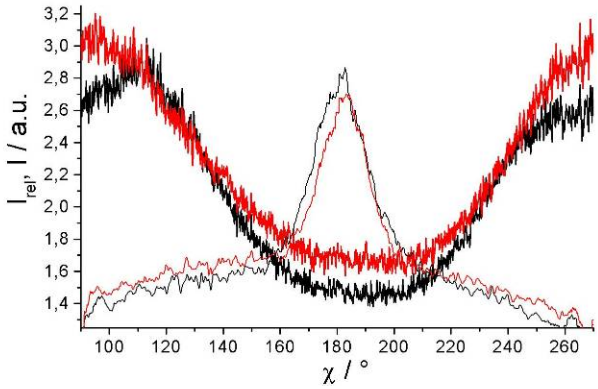


Figure S4. χ scans for the outer diffuse scattering in the 2D X-ray patterns of **6c** on heating in the SmC* phase at 85 °C (black line) and in the SmA phase at 150 °C (red line), $I_{\mathrm{rel}} = I(\mathrm{T})/I(180\ °\mathrm{C}$, isotropic liquid), scans with maxima around 180 ° for the layer reflections for comparison.

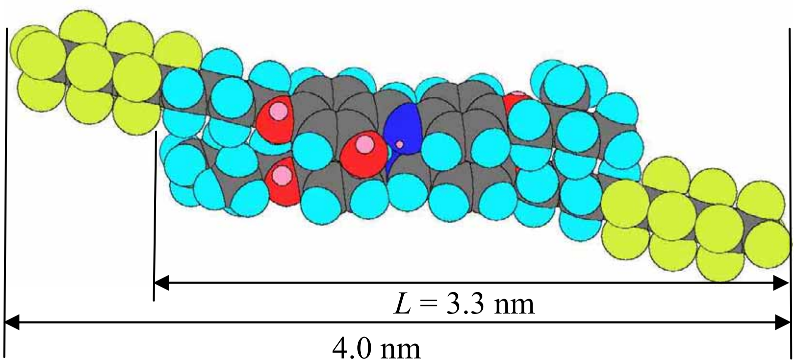


Figure S5. Model for a pair of antiparallel molecules of compound **6c** with completely overlapping aliphatic and aromatic moieties.

3. Synthesis and analytical data of compounds

The characterization of the synthesized compounds is based on ^{1}H-, ^{13}C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions, with tetramethylsilane as internal standard), UV-VIS (Agilent 8453, $CHCl_3$ solutions). Signals of the aliphatic chains are not given, full ^{1}H-NMR amd ^{13}C-NMR spectra are shown in Figures S6/S7 for compound **6c** as an example. FT-IR (Perkin Elmer, $CHCl_3$ solutions), MS [AMD 402 (electron impact, 70 eV)]. Microanalyses were performed using a Leco CHNS-932 elemental analyzer. Only structurally relevant resonances are given in the NMR data.

Transition temperatures were measured using a Leitz Laborlux 12 Pol polarizing microscope, equipped with a Linkam THMS 600 hot stage and a Linkam TMS93 temperature controller or a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope. DSC-thermograms were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 K min^{-1}.

The procedures for the preparation of compounds **2** and **3** are given in ref. 17b. 4-decyloxybenzaldehyde (**4a**) and 4-decyloxy-2-hydroxybenzaldehyde (**5a**) were synthesized according to the procedured described in ref. S1a and S1b respectively. (*S*)-(-)-2-Methyl-1-butanol (Fluka, 95.0%, $[\alpha]_{D}^{20}$ -6.3 ± 0.5°, *c* = 10 in EtOH), p-nitrophenol, 2,4-dihydroxybenzaldehyde, 4-hydroxybenzaldehyde and 1-bromodecan was purchased commercially.

*3.1. Synthesis of the semifluorinated aldehydes **4b**, **c** and **5b**, **c**:*

Following earlier descriptions,[S2] the synthesis was carried out by etherification of 2,4- or 4-hydroxy substituted benzaldehydes (10 mmol) with the corresponding semifluorinated alkyl bromides (11 mmol). The crude products were purified by column chromatography on silica gel, elution with petroleum ether (b.p. 30-70 °C) / ethyl acetate (20:1).

4b: Yield: 4.13 g (94 %) of cream crystals, m.p.: 64.9 ºC (35.6 kJ mol^{-1}). **^{1}H-NMR:** δ(ppm) = 11.45 (s; OH), 9.69 (s; CHO), 7.40 (d, $J \approx 8.7$ Hz; arom. H), 6.50 (dd, $J \approx 8.7$ Hz and $J \approx 2.3$ Hz; arom. H), 6.39 (d, $J \approx 2.3$ Hz; arom. H), 3.99 (t, $J \approx 6.3$ Hz; OCH$_2$). **^{13}C-NMR:** δ(ppm) = 194.12 (d; CHO), 166.19, 164.44, 115.10 (3s; 3 arom. C), 135.12, 108.63, 101.08 (3d; 3 arom. CH), 68.25 (t; OCH$_2$). **UV-VIS:** λ(nm) = 283.0, 316.0. **IR:** γ(cm^{-1}) = 1630 (C=O).

4c: Yield: 4.86 g (95 %) of white crystals, m.p.: 65.2 ºC (21.1 kJ mol^{-1}). **^{1}H-NMR:** δ(ppm) = 11.45 (s; OH), 9.70 (s; CHO), 7.41 (d, $J \approx 8.7$ Hz; arom. H), 6.51 (dd, $J \approx 8.7$ Hz and $J \approx 2.3$ Hz; arom. H), 6.40 (d, $J \approx 2.3$ Hz; arom. H), 4.04 (t, $J \approx 5.9$ Hz; OCH$_2$). **^{13}C-NMR:** δ(ppm) = 194.18 (d; CHO), 165.87, 164.42, 115.24 (3s; 3 arom. C), 135.18, 108.56, 101.09 (3d; 3 arom. CH), 67.72 (t; OCH$_2$). **UV-VIS:** λ(nm) = 279.0, 315.0. **IR:** γ(cm^{-1}) = 1629 (C=O).

5b: Yield: 4.17 g (98 %) of light yellow oil. **^{1}H-NMR:** δ(ppm) = 9.86 (s; CHO), 7.81, 6.97 (2d, $J \approx 8.7$ Hz each; 4 arom. H), 4.03 (t, $J \approx 6.4$ Hz; OCH$_2$). **^{13}C-NMR:** δ(ppm) = 190.53 (d; CHO), 163.96, 129.82 (2s; 2 arom. C), 131.88, 114.66 (2d; 4 arom. CH), 68.11 (t; OCH$_2$). **UV-VIS:** λ(nm) = 275.0. **IR:** γ(cm^{-1}) = 1692 (C=O).

5c: Yield: 4.72 g (95 %) of white crystals, m.p.: 40 ºC (10.6 kJ mol^{-1}). **^{1}H-NMR:** δ(ppm) = 9.87 (s; CHO); 7.82, 6.97 (2d, $J \approx 8.7$ Hz each; 4 arom. H), 4.07 (t, $J \approx 5.9$ Hz; OCH$_2$). **^{13}C-NMR:** δ(ppm) = 190.50 (d; CHO), 163.66, 130.03 (2s; 2 arom. C), 131.89, 114.64 (2d; 4 arom. CH), 67.60 (t; OCH$_2$). **UV-VIS:** λ(nm) = 276.0. **IR:** γ(cm^{-1}) = 1688 (C=O).

*3.2. Synthesis of the imines **6** and 7:*

Compounds **6a-c** and **7a-c** were prepared as described previously[2] by p-toluenesulfonic acid (40 mg) catalyzed condensation of the semifluorinated alkyloxybenzaldehydes **4** or **5** (2.5 mmol) with (*S*)-4-(2-methylbutoxy)aniline (3 mmol) in 25 ml toluene. The compounds were purified by crystallization from acetone/methanol.

6a: Yield: 0.80 g (73%) of yellow crystals. **^{1}H-NMR**: δ =13.90 (s; OH), 8.48 (s; HC=N), 7.22-7.19 (m; 3 arom. H), 6.91 (d, $J \approx 8.7$ Hz; 2 arom. H), 6.47-6.43 (m; 2 arom. H), 3.97 (t, J

≈ 6.6 Hz; OCH_2), 3.82, 3.74 (2dd, *J* ≈ 8.9 Hz and *J* ≈ 6.0 Hz each; OCH_2 (chiral alkyl chain)). **^{13}C-NMR**: δ = 163.68, 163.17, 158.13, 141.18, 113.09 (5s; 5 arom. C), 159.37 (d, H$\underline{C}$=N), 133.04, 121.89, 115.18, 107.34, 101.60 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 73.24, 68.22 (2t; 2 OCH_2). **UV-VIS**: λ (nm) = 285.0, 349.0. **IR**: γ = 1615 cm^{-1} (C=N). **MS** (EI): m/z (%) = 439 (100) [M$^+$], 368 (16) [M$^+$ - C_5H_{11}], 229 (41) [M$^+$ - C_5H_{11} - $C_{10}H_{21}$]. **$C_{28}H_{41}NO_3$** (439.6); Anal. Calc.: C, 76.49; H, 9.40; N, 3.18. Found: C, 76.54; H, 9.49, N 3.21%.

6b: Yield: 1.47 g (98%) of yellow crystals. **^{1}H-NMR**: δ =13.92 (s; OH), 8.48 (s; $\underline{H}$C=N), 7.23-7.19 (m; 3 arom. H), 6.91 (d, *J* ≈ 8.9 Hz; 2 arom. H), 6.46-6.43 (m; 2 arom. H), 3.99 (t, *J* ≈ 6.4 Hz; OCH_2), 3.82, 3.74 (2dd, *J* ≈ 8.9 Hz and *J* ≈ 6.0 Hz each; OCH_2 (chiral alkyl chain)). **^{13}C-NMR**: δ = 163.71, 162.99, 158.18, 141.13, 113.20 (5s; 5 arom. C), 159.33 (d, H$\underline{C}$=N), 133.08 121.91, 115.19, 107.28, 101.58 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 73.26, 67.86 (2t; 2 OCH_2). **UV-VIS**: λ (nm) = 285.0, 349.0. **IR**: γ = 1618 cm^{-1} (C=N). **MS** (EI): m/z (%) = 601 (100) [M$^+$], 531 (41) [M$^+$ - C_5H_{11}], 229 (43) [M$^+$ - C_5H_{11} - $C_{10}H_{12}F_9$]. **$C_{28}H_{32}F_9NO_3$** (601.6); Anal. Calc.: C, 55.90; H, 5.36; N, 2.32. Found: C, 56.05; H, 5.58, N 2.04%.

6c:Yield: 0.97 g (58%) of yellow crystals. $[\alpha]^{20}_{589}$ +11.8° , *c* = 0.4 in $CHCl_3$; **^{1}H-NMR**: δ =13.93 (s; OH), 8.49 (s; $\underline{H}$C=N), 7.22-7.19 (m; 3 arom. H), 6.91 (d, *J* ≈ 8.9 Hz; 2 arom. H), 6.46-6.43 (m; 2 arom. H), 4.02 (t, *J* ≈ 5.9 Hz; OCH_2), 3.82, 3.74 (2dd, *J* ≈ 8.9 Hz and *J* ≈ 6.0 Hz each; OCH_2 (chiral alkyl chain)). **^{13}C-NMR**: δ = 163.61, 162.62, 158.13, 141.01, 113.34 (5s; 5 arom. C), 159.20 (d, H$\underline{C}$=N), 133.06 121.87, 115.16, 107.18, 101.56 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 73.27, 67.36 (2t; 2 OCH_2). **UV-VIS**: λ (nm) = 285.0, 350.0. **IR**: γ = 1618 cm^{-1} (C=N). **MS** (EI): m/z (%) = 673 (100) [M$^+$], 603 (53) [M$^+$ - C_5H_{11}], 229 (35) [M$^+$ - C_5H_{11} - $C_{10}H_8F_{13}$]. **$C_{28}H_{28}F_{13}NO_3$** (673.5); Anal. Calc.: C, 49.93; H, 4.19; N, 2.08. Found: C, 50.17; H, 4.41, N 1.85%.

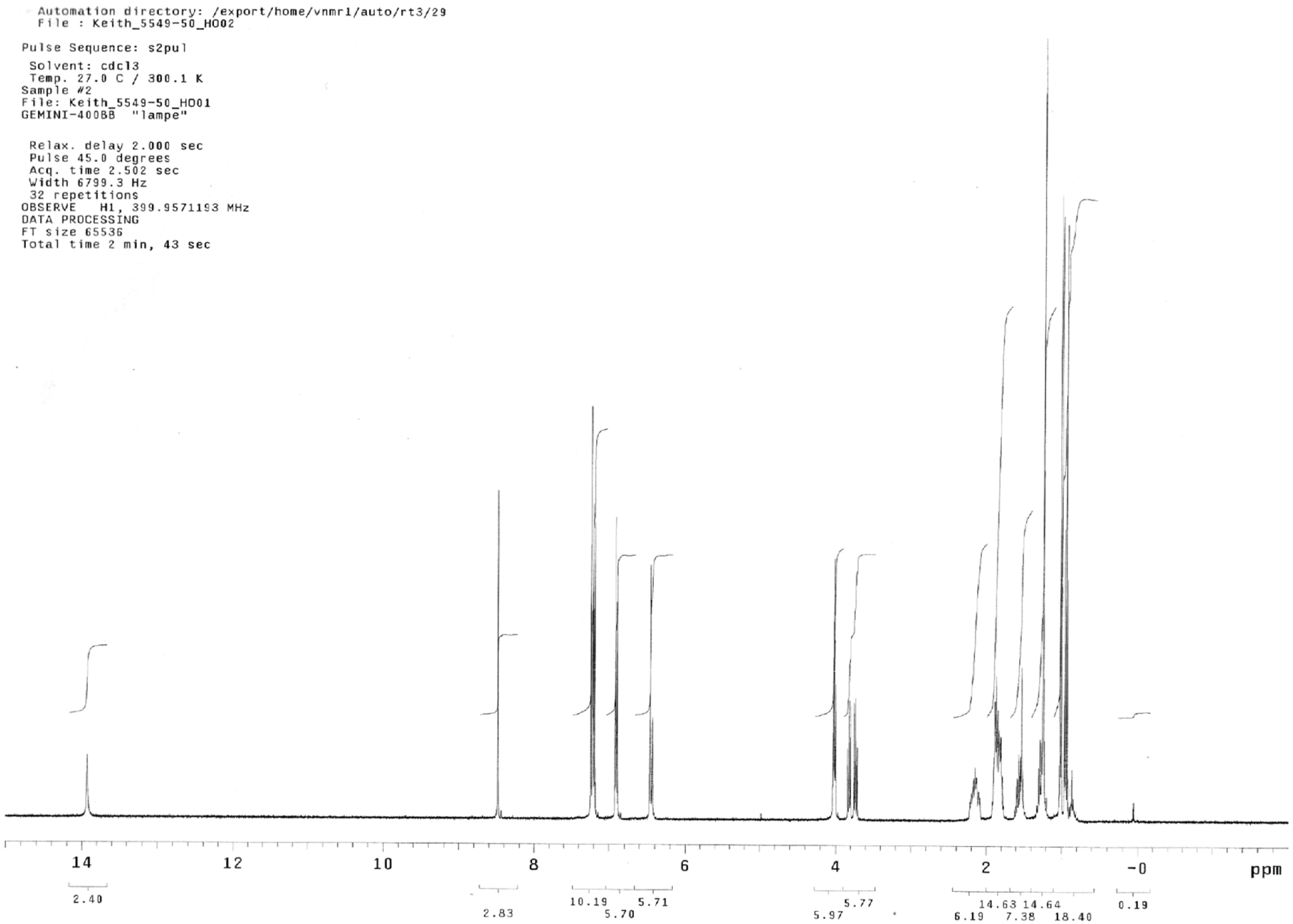


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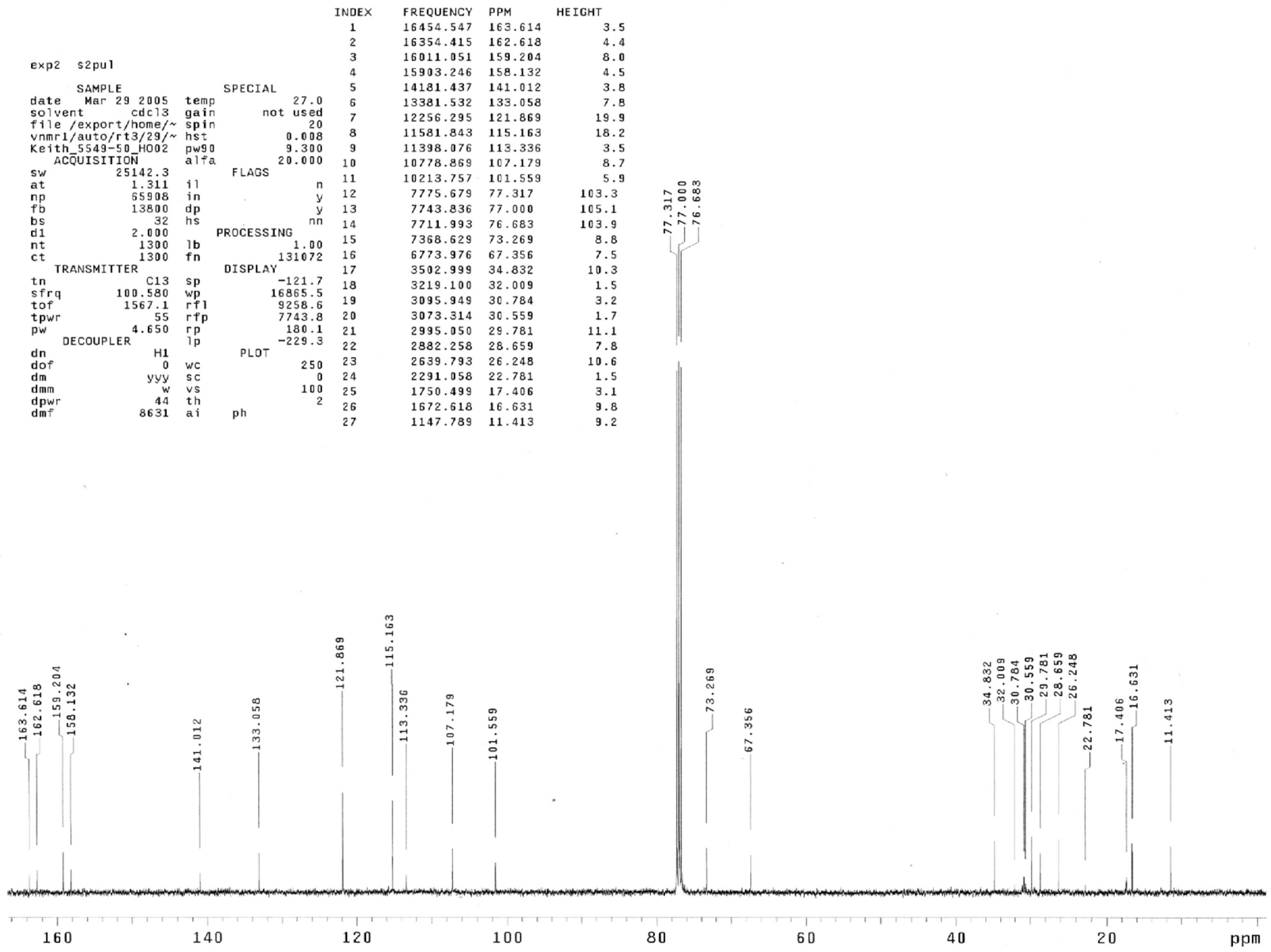
Figure S6. ^{1}-H-NMR spectrum of compound **6c**.



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7	12256.295	121.869	19.9
8	11581.843	115.163	18.2
9	11398.076	113.336	3.5
10	10778.869	107.179	8.7
11	10213.757	101.559	5.9
12	7775.679	77.317	103.3
13	7743.836	77.000	105.1
14	7711.993	76.683	103.9
15	7368.629	73.269	8.8
16	6773.976	67.356	7.5
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19	3095.949	30.784	3.2
20	3073.314	30.559	1.7
21	2995.050	29.781	11.1
22	2882.258	28.659	7.8
23	2639.793	26.248	10.6
24	2291.058	22.781	1.5
25	1750.499	17.406	3.1
26	1672.618	16.631	9.8
27	1147.789	11.413	9.2

Figure S7. ^{13}-C-NMR spectrum of compound **6c**.

7a: Yield: 0.47 g (44%) of white crystals. ^{1}H-NMR: δ = 8.37 (s; H̲C=N), 7.79, 7.17, 6.94, 6.90 (4d, $J \approx$ 8.9 Hz each; 8 arom. H), 4.00 (t, $J \approx$ 6.5 Hz; OCH_2), 3.82, 3.73 (2dd, $J \approx$ 8.9 Hz and $J \approx$ 6.0 Hz each; OCH_2 (chiral alkyl chain)). **^{13}C-NMR**: δ = 157.60 (d, HC̲=N), 161.45, 157.62, 145.02, 129.26 (4s; 4 arom. C), 130.08 121.91, 114.94, 114.60 (4d; 8 arom. CH), 73.23, 68.22 (2t; 2 OCH_2). **UV-VIS**: λ (nm) = 284.0, 335.0. **IR**: γ = 1606 cm^{-1} (C=N). **MS** (EI): m/z (%) = 423 (100) [M$^+$], 353 (41) [M$^+$ - C_5H_{11}], 213 (39) [M$^+$ - C_5H_{11} - $C_{10}H_{21}$]. **$C_{28}H_{41}NO_2$** (423.6); Anal. Calc.: C, 79.38; H, 9.75; N, 3.30. Found: C, 79.46; H, 10.03, N 3.35%.

7b: Yield: 0.82 g (56%) of white crystals. **^{1}H-NMR**: δ = 8.38 (s; H̲C=N), 7.79, 7.17, 6.94, 6.89 (4d, $J \approx$ 8.9 Hz each; 4 arom. H), 4.0 (t, $J \approx$ 6.4 Hz; OCH_2), 3.82, 3.73 (2dd, $J \approx$ 8.9 Hz and $J \approx$ 6.0 Hz each; OCH_2 (chiral alkyl chain)). **^{13}C-NMR**: δ = 157.58 (d, HC̲=N), 161.30, 157.64, 144.95, 129.38 (4s; 4 arom. C), 130.12, 121.92, 114.96, 114.58 (4d; 8 arom. CH), 73.24, 67.87 (2t; 2 OCH_2). **UV-VIS**: λ (nm) = 284.0, 335.0. **IR**: γ = 1604 cm^{-1} (C=N). **MS** (EI): m/z (%) = 585 (100) [M$^+$], 515 (90) [M$^+$ - C_5H_{11}], 213 (43) [M$^+$ - C_5H_{11} - $C_{10}H_{12}F_9$]. **$C_{28}H_{32}F_9NO_2$** (585.5); Anal. Calc.: C, 57.43; H, 5.50; N, 2.39. Found: C, 57.69; H, 5.71, N 2.11 %.

7c: Yield: 0.61 g (37%) of white crystals. **^{1}H-NMR**: δ = 8.39 (s; H̲C=N), 7.81, 7.18, 6.94, 6.90 (4d, $J \approx$ 8.9 Hz each; 8 arom. H), 4.05 (t, $J \approx$ 5.8 Hz; OCH_2), 3.82, 3.73 (2dd, $J \approx$ 8.9 Hz and $J \approx$ 6.0 Hz each; OCH_2 (chiral alkyl chain)). **^{13}C-NMR**: δ = 157.41 (d, HC̲=N), 161.01, 157.66, 144.90, 129.61 (4s; 4 arom. C), 130.13, 121.98, 114.90, 114.59 (4d; 8 arom. CH), 73.22, 67.35 (2t; 2 OCH_2). **UV-VIS**: λ (nm) = 283.0, 335.0. **IR**: γ = 1607 cm^{-1} (C=N). **MS** (EI): m/z (%) = 657 (100) [M$^+$], 587 (96) [M$^+$ - C_5H_{11}], 212 (27) [M$^+$ - C_5H_{11} - $C_{10}H_8F_{13}$]. **$C_{28}H_{28}F_{13}NO_2$** (657.5); Anal. Calc.: C, 51.14; H, 4.29; N, 2.13. Found: C, 51.36; H, 4.47, N 1.89%.

3.3. *Synthesis of the copper(II) complexes **8**:*

A suspension of 0.5 mmol of the appropriate ligand in dry ethanol (5 ml) was added 0.5 mmol of KOH dissolved in 10 ml of dry ethanol and 0.25 mmol of copper(II)acetate dihydrate. The mixture was stirred at room temperature under an argon atmosphere for 24 h; the greenish or greenish brown solid formed was filtered and recrystallized from chloroform/ethanol.

8a: Yield: 0.21 g (45%) of brown crystals. **UV-VIS**: λ(nm) = 309.0, 381.0. **IR**: γ = 1610 cm^{-1} (C=N). **MS** (EI): m/z (%) = 940 (24) [M$^+$], 439 (100) [M$^+$-$C_{28}H_{40}NO_3$], 299 (26) [M$^+$-$C_{28}H_{40}$ NO_3 - $C_{10}H_{21}$], 229 (60) [M$^+$-$C_{28}H_{40}$ NO_3 - $C_{10}H_{21}$-C_5H_{11}]. $\mathbf{C_{56}H_{80}CuN_2O_6}$ (940.8); Anal. Calc.: C, 71.49; H, 8.57; N, 2.98. Found: C, 71.56; H, 8.37, N 3.09%.

8b: Yield: 0.46 g (73%) of yellow-brown crystals. **UV-VIS**: λ(nm) = 307.0, 380.0. **IR**: γ = 1612 cm^{-1} (C=N). $\mathbf{C_{56}H_{62}CuF_{18}N_2O_6}$ (1264.6); Anal. Calc.: C, 53.18; H, 4.94; N, 2.21. Found: C, 52.97; H, 4.69, N 2.11%.

8c: Yield: 0.52 g (74%) of yellow-brown crystals. **UV-VIS**: λ(nm) = 302.0, 381.0. **IR**: γ = 1611 cm^{-1} (C=N). $\mathbf{C_{56}H_{54}CuF_{26}N_2O_6}$ (1408.5); Anal. Calc.: C, 47.75; H, 3.86; N, 1.98. Found: C, 47.94; H, 4.09, N 1.78%.

References

S1 (a) O.N. Bubel, V.S. Bezborodov, Y.L. Ptashnikov, *Zh. Org. Khim.*, 1979, **15**, 803; (b) R. M. Claramunt, I. Forfar, P. Cabildo, J. Lafuente, J. Barbare, R. Gimenez, J. Elguero, *Heterocycles*, 1999, **51**, 751.
S2 K. Praefcke, D. Singer, B. Gündogan, *Mol. Cryst. Liq. Cryst.* 1992, **223**, 181.