Electronic Supporting Information

Twist grain boundary (TGB) states of chiral liquid crystalline bent-core mesogens

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Content

1. Additional Data

1.1 Textures

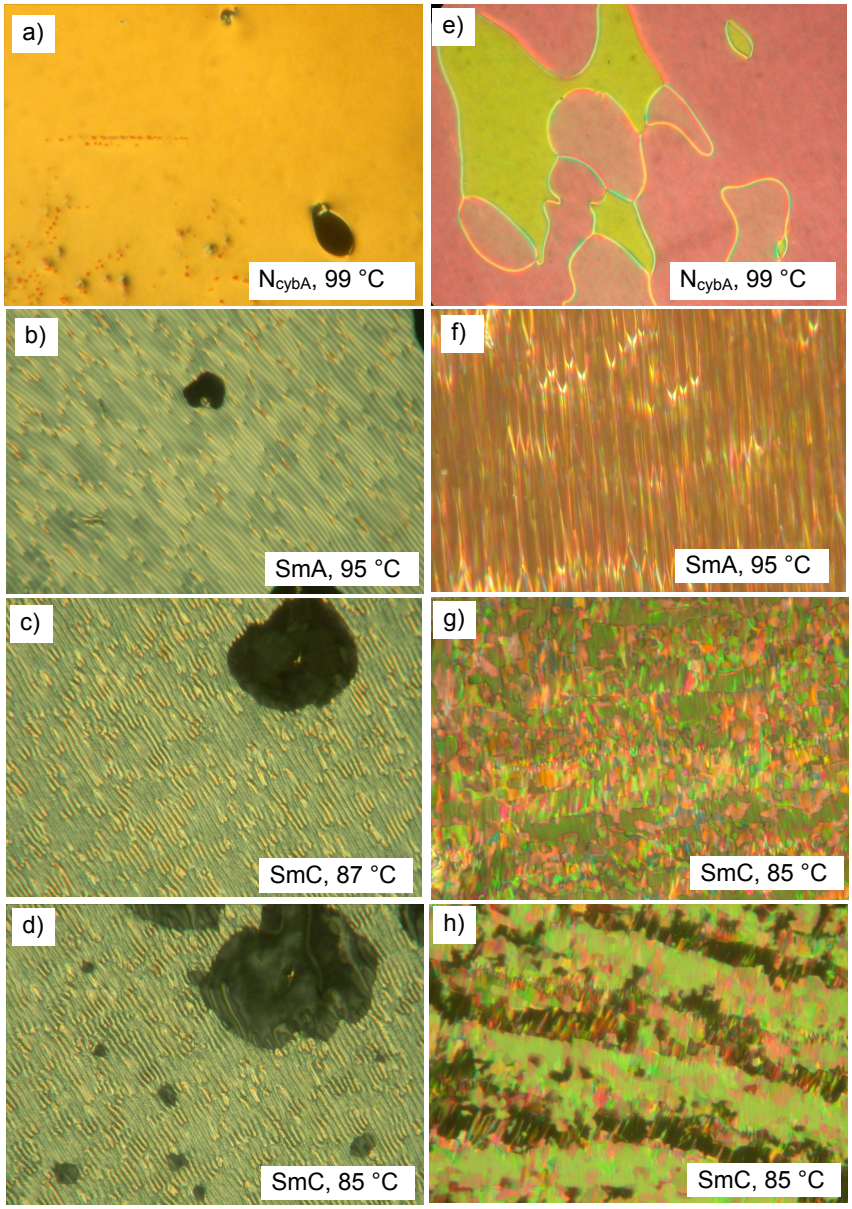

Figure S1. Textures of *rac*-**1/12** a-d) between non-treated glass plates and e-h) in polyimide coated ITO cell (10 µm) as observed between crossed polarizers (horizontal and vertical) on slow cooling; rubbing direction is horizontal in e-g); in h) the sample is rotated by ca. 12°, indicating the tilt. These textures are typical for N-SmA-SmC phase sequences. Note, that the textures of the SmA and SmC phases represent typical paramorphotic textures developing from the N and SmA phases, respectively. These textures are influenced by the texture of the preceding phase; therefore the typical fan texture of the SmA phase, as developing from the isotropic liquid state, cannot be observed in this case, see ref S1.

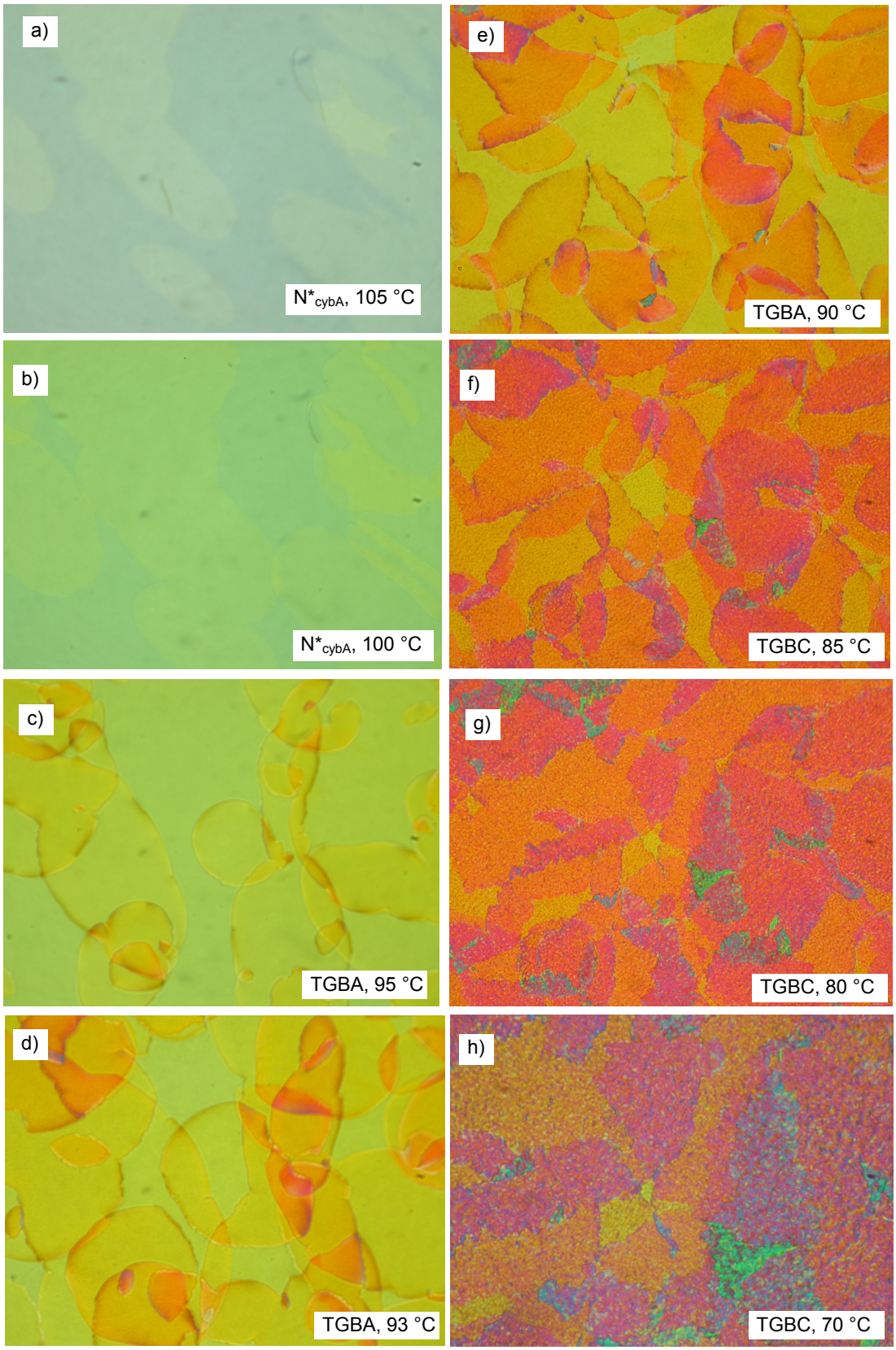

Figure S2. Textures of *(S)*-**1/12** in polyimide coated ITO cell (10 μm) as observed between crossed polarizers (horizontal and vertical) on slow cooling.

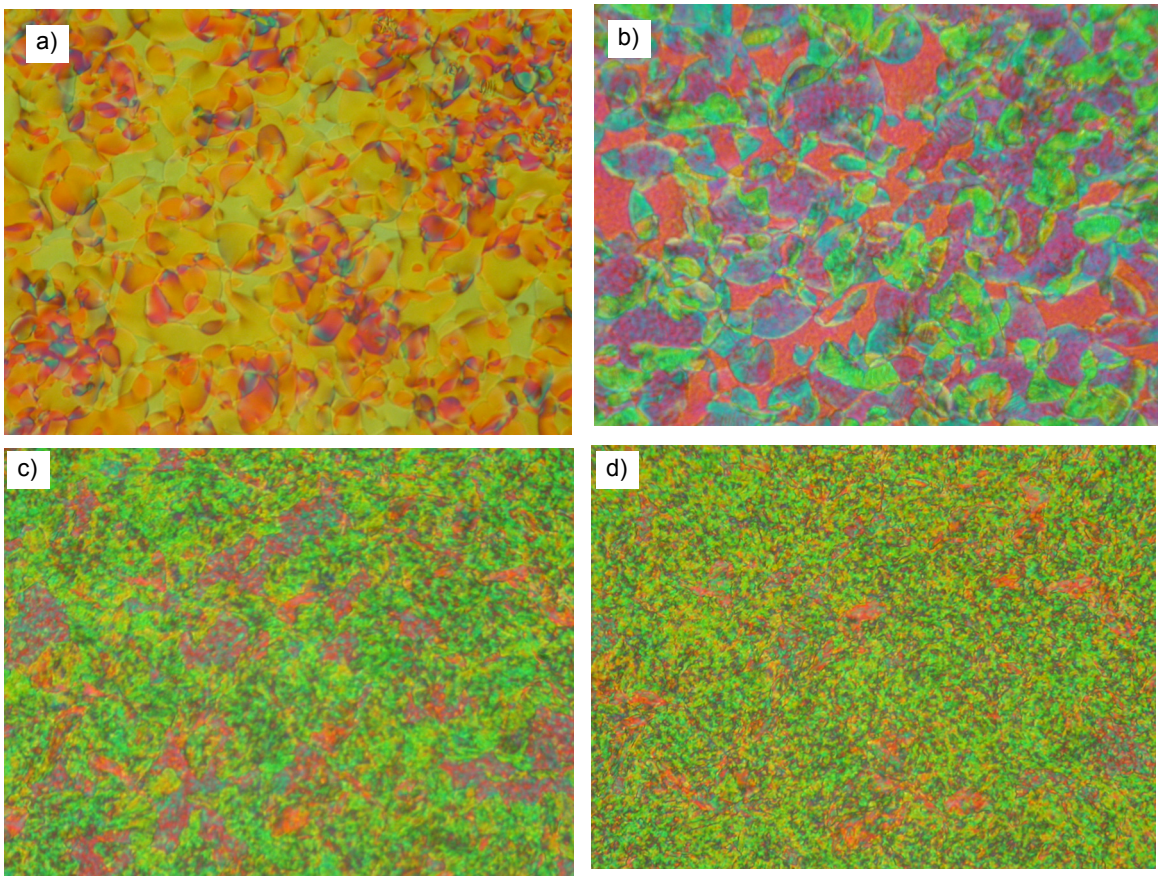

Figure S3. Textures of the LC phases of compound *(S)*-**1**/**14** as observed between crossed polarizers (horizontal and vertical) on cooling: in 10 μm coated- ITO cell; (a) TGBA texture at $T = 97$ °C, (b) TGBC-like texture at $T = 94$ °C and c) textures at $T = 91$ °C and d) 80 °C.

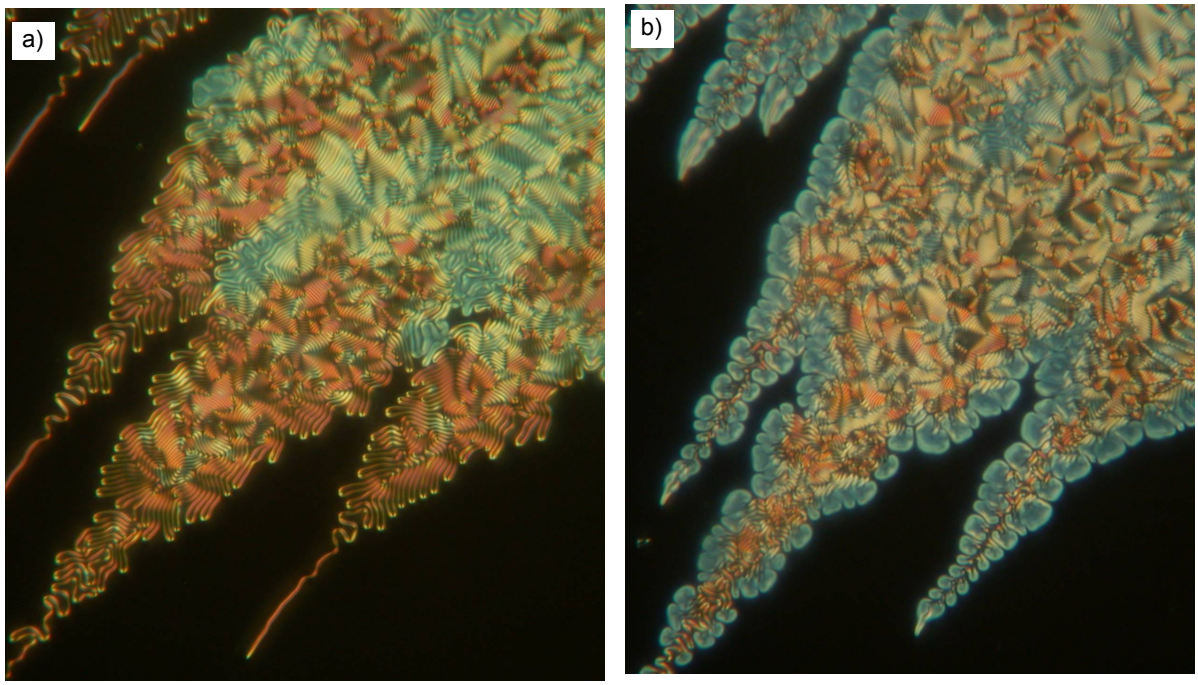

Figure S4. Textures showing the transition from TGBA to N^*_{cybA} on heating for compound (*S*)-**1**/**14** as observed between crossed polarizers (horizontal and vertical) (a) TGBA at $T = 95$ °C and b) transition to N^*_{cybA} at $T = 94$ °C; dark areas are homeotropic SmA regions.

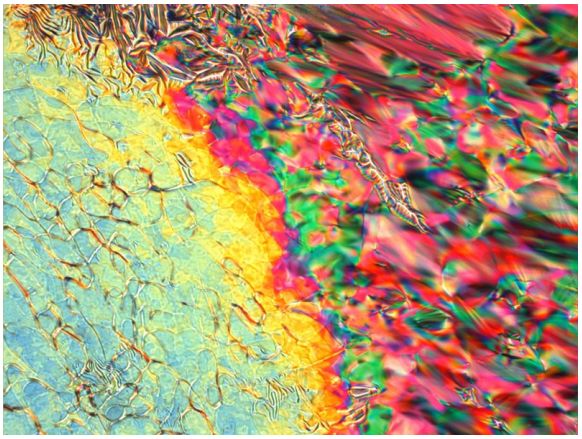

Figure S5. Texture as observed between non-trated glass plates (crossed polarizers, horizontal and vertical) of *(S)*-**1**/**14** at T = 102 °C with temperature gradient showing the transition from the blurred fan-like TGBA texture to N*.

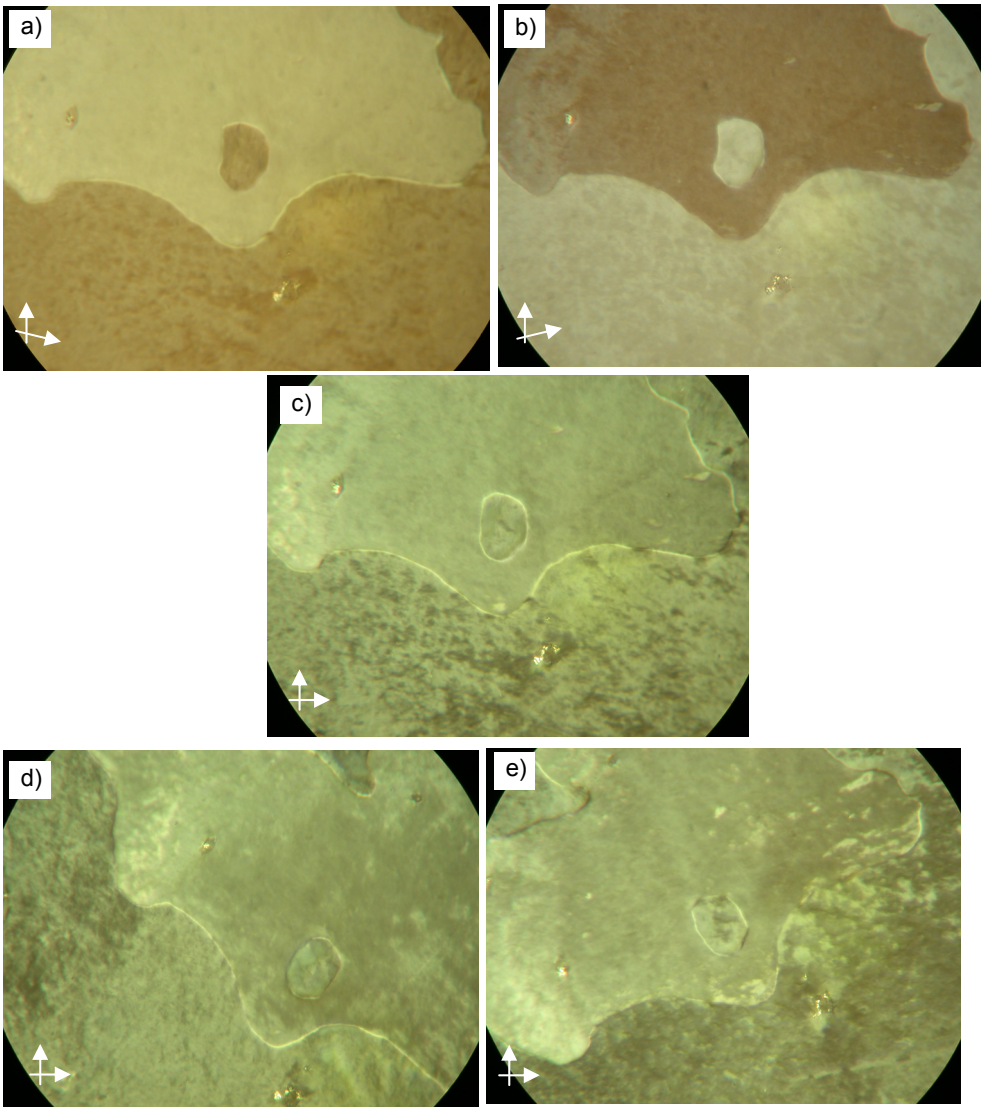

Figure S6. Textures of the homeotropic SmC phase of *rac*-**1**/**12** between non-treated glass plates at T = 77 °C: a,b) between weakly uncrossed polarizers (± 5°), c) between crossed polarizers and d,e) between crossed polarizers after rotating the sample by ± 30°, respectively; the positions of the polarizers is indicated by arrows.

1.2 DSC-traces

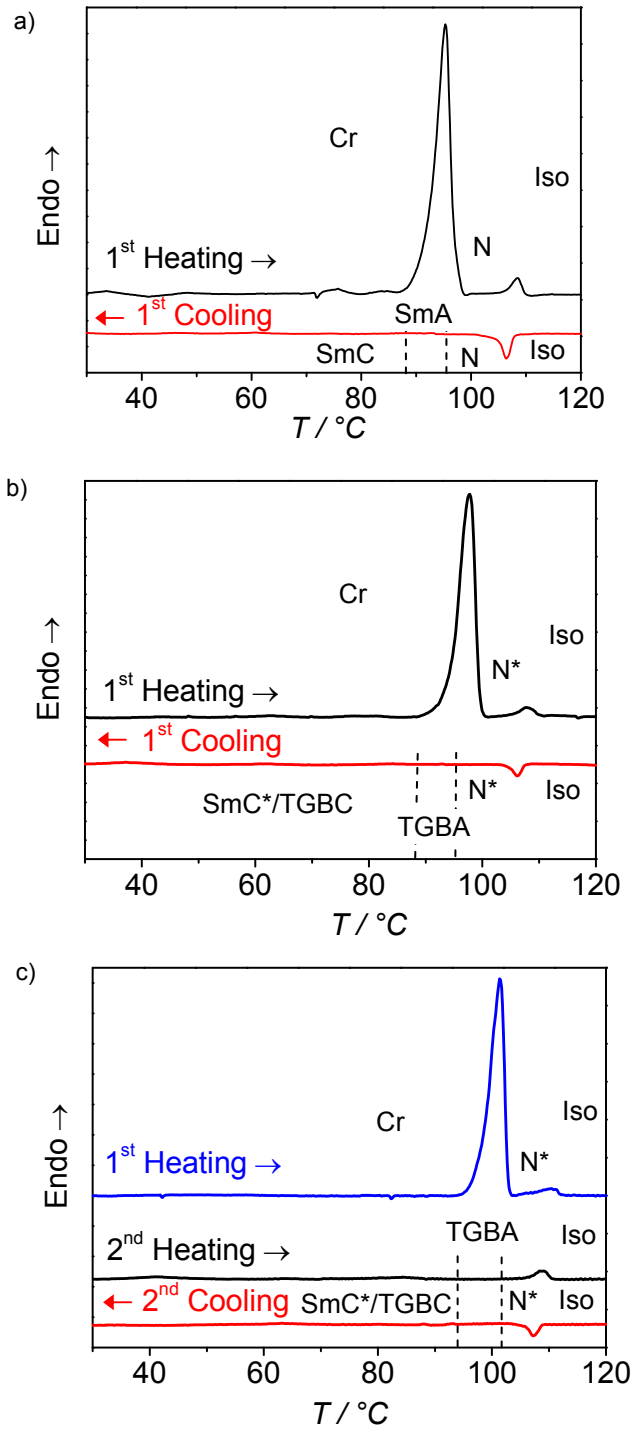

Figure S7. DSC-traces of a) *rac*-**12**, b) *(S)*-**1/12** and c) (*S*)-**1/14**; N/N* = N_{cybA}/N^*_{cybA}.

1.3 XRD-data

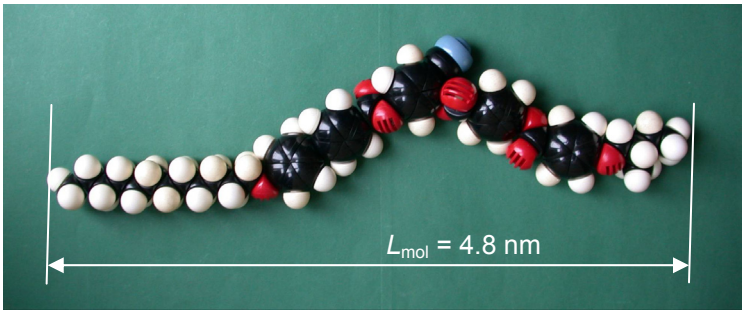

Figure S8. CPK model of **1/12**.

Table S1. XRD data, calculated *d*-values, line width at half maximum (FWHM) and estimated correlation lengths (L_ξ, as calculated using the Scherrer equation with Scherrer constant = 1) of the mesophase of compound *rac*-**1/12**.

T/°C	Phase	2*θ*/°	*θ*/°	*d*/nm	FWHM (2*θ*) /°	L_ξ/nm
110	Iso_{cyb}	2.304	1.152	3.834		
		19.630	9.815	0.452		
105	N_{cybA}	2.223	1.112	3.974	0.265	67
		19.700	9.850	0.451		
100	N_{cybA}	2.176	1.088	4.060	0.177	100
		19.790	9.895	0.449		
95	SmA	2.167	1.084	4.077		
		19.840	9.920	0.447		
90	SmA	2.163	1.082	4.084	0.169	111
		19.900	9.950	0.446		
85	SmC	2.172	1.086	4.067		
		19.950	9.975	0.445		
80	SmC	2.174	1.087	4.064		
		20.000	10.000	0.444		
75	SmC	2.172	1.086	4.067		
		20.030	10.015	0.443		
70	SmC	2.166	1.083	4.079	0.152	117
		20.120	10.060	0.441		
60	SmC	2.160	1.080	4.090		
		20.180	10.090	0.440		

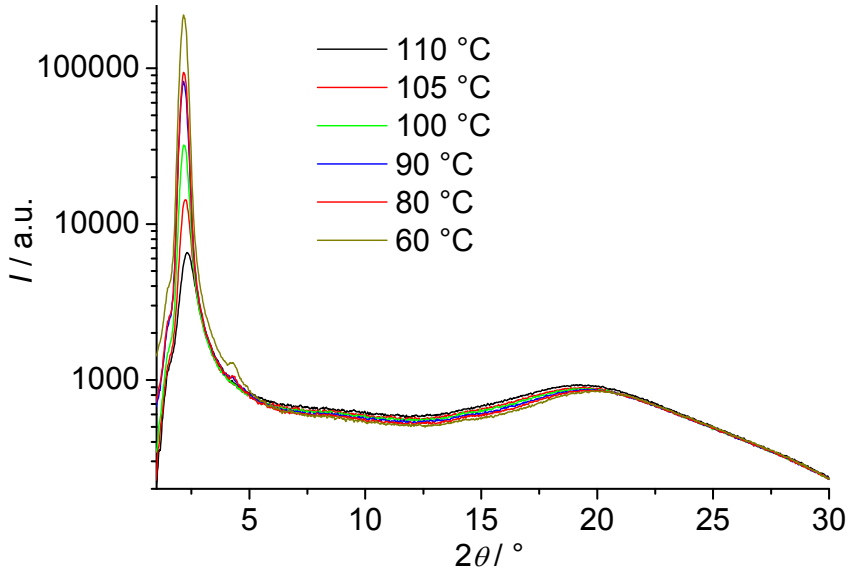

Figure S9. 2θ-scans in the XRD patterns of the mesophases of compound *rac*-**1/12**.

Table S2. XRD data and calculated *d*-values of the mesophases of compound *(S)*-**1/12.**

T/°C	Phase	2θ/°	θ/°	*d*/nm
110	Iso_{cyb}	2.321	1.161	3.806
		19.680	9.840	0.451
105	N^*_{cybA}	2.243	1.122	3.939
		19.730	9.865	0.450
100	N^*_{cybA}	2.189	1.095	4.036
		19.800	9.900	0.448
95	SmA/TGBA	2.168	1.084	4.075
		19.870	9.935	0.447
90	SmA/TGBA	2.175	1.088	4.062
		19.940	9.970	0.445
85	SmC*/TGBC	2.180	1.090	4.052
		19.970	9.985	0.445
80	SmC*/TGBC	2.180	1.090	4.052
		20.000	10.000	0.444
75	SmC*/TGBC	2.178	1.089	4.056
		20.070	10.035	0.442
70	SmC*/TGBC	2.169	1.085	4.073
		20.160	10.080	0.440

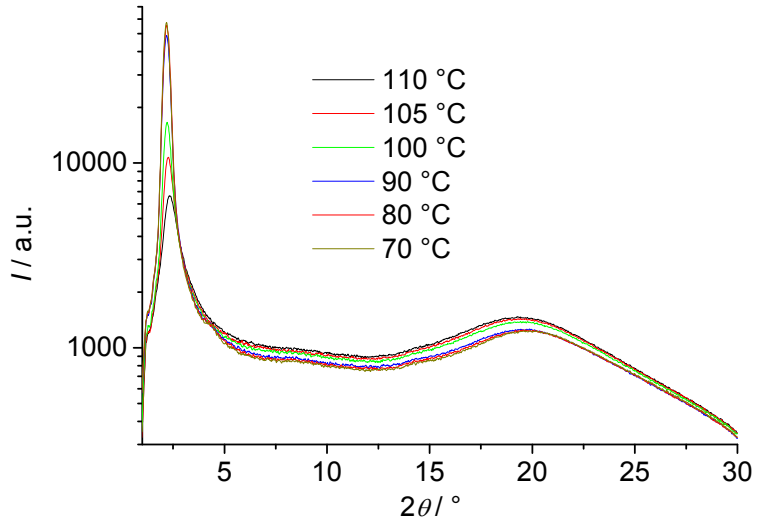

Figure S10. 2θ-scans in the mesophases of compound *(S)*-**1/12**.

2. Experimental methods

The characterization of the synthesized compounds is based on 1H-, ^{13}C-NMR (Bruker Avance III 500 spectrometer or Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$, CD_3OD and DMSO-d_6 solutions, with tetramethylsilane as internal standard), MS [AMD 402 (electron impact, 70 eV)]. Microanalyses were performed using a Leco CHNS-932 elemental analyzer.

Transition temperatures were measured using a Mettler FP-82 HT hot stage and control unit in conjunction with a Leica polarizing microscope. The associated enthalpies were obtained from DSC-thermograms which were recorded on a Perkin-Elmer DSC-7 (heating and cooling rate: 10 K min^{-1}. Electro-optical investigation of compounds were carried out under a triangular wave field (f = 10 Hz) using commercially available 10 µm polyimide coated indium tin oxide (ITO) cells (E.H.C. Japan) with a measuring area of 1 cm^2.

X-ray diffraction patterns of aligned samples were recorded with a 2D detector (HI-STAR, Siemens or Vantec 500, Bruker). Ni filtered and pin hole collimated Cu-K_α radiation was used. Alignment was achieved by slow cooling (0.1 K min^{-1}) of the compound sealed in a thin glass capillary in the presence of a magnetic field (B ~ 1T). The sample to detector distance was 9.3 cm and 27.05 cm for the wide angle and small angle measurements, respectively, and the exposure time was 15 min.

3. Synthesis and analytical data of compounds

(S)-(-)-2-Methyl-1-butanol (Fluka, 95.0%, $[\alpha]_D^{20}$ -6.3 ± 0.5°, c = 10 in EtOH), (+/-)-2-methyl-1-butanol (Fluka, ≥98.0%), 4-benzyloxy-2-hydroxybenzaldehyde (ABCR, 99.0%), ethyl 4'-hydroxy-4-biphenylcarboxylate (Aldrich, 98.0%), oxalyl chloride (Merck), pyridine (Acros Organic 99,5%, extra dry over molecular sieve), palladium 10 % on carbon (Alfa Aesar) *N,N'*-dicyclohexylcarbodiimide (Merck) and 4-(dimethylamino)pyridine (Merck) were purchased commercially. Dry 2-butanone (Merck) and THF (Merck 99%) were purchased commercially and were used without further purification. Methylene chloride was dried over P_4O_{10} (Merck) and distilled under a N_2 atmosphere. Hexane, ethyl acetate, chloroform, dichloromethane and ethanol were distilled for use in crystallization and column

chromatography. Analytical thin-layer chromatography (TLC) was carried out on aluminium plates coated with silica gel 60 F254 (Merck). Column chromatography was performed using silica gel 60 (Merck, pore size 60 Å, 230-400 mesh particle size).

3.1 Alkoxybenzoyloxybenzoic acids (*S*)-A and *rac*-A

4-[4-(*S*)-2-Methylbutoxybenzoyloxy]benzoic acid (*S*)-**A**[S2,S3] and 4-[4-(2-methylbutoxy)benzoyloxy]benzoic acid *rac*-**A**[S2,S4] were synthesized according to procedures reported in the literature[S5,S6]. Firstly, ethyl 4-hydroxybenzoate was alkylated with (*S*)-2-methylbutyl-1-tosylate or racemic 2-methylbutyl-1-tosylate which were prepared[S7] from the commercially available corresponding alcohols, followed by hydrolysis of the ester group (10 N sodium hydroxide solution in ethanol). Esterification of the obtained 4-(2-methylbutoxy)benzoic acids[S8,S9] with 4-hydroxybenzaldehyde using *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP)[S10], followed by $NaClO_2$ oxidation[S11] leads to final compounds (*S*)-**A** and *rac*-**A**. Spectroscopic data for both compounds were given in ref.[S2].

3.2 4-Benzyloxy-2-hydroxybenzonitrile B

4-Benzyloxy-2-hydroxybenzonitrile[S12] was prepared from commercially available 4-benzyloxy-2-hydroxybenzaldehyde by the formation of the oxime, followed by dehydration as described ref.[S12].
Yield: 79%, colorless crystals, m.p. 142 °C, **^{1}H-NMR** (400 MHz, CD_3OD): δ (ppm) = 7.41-7.29 (m, 6 Ar-H), 6.56 (dd, $J \approx 8.6$ Hz and $J \approx 2.3$ Hz; 1 Ar-H), 6.51 (d, $J \approx 2.3$ Hz; 1 Ar-H), 5.09 (s, 2H, $OC\underline{H_2}Ph$).

3.3 4'-Alkyloxy-4-biphenylcarbonyl chlorides D*n*

4'-Dodecyloxy-4-biphenylcarbonyl chloride[S13] and 4'-tetradecyloxy-4-biphenylcarbonyl chloride[S13] were prepared from 4'-alkoxy-4-biphenylcarboxylic acids[S14] by reacting with oxalyl chloride as described previously[S15]. For the synthesis of 4'-alkyloxy-4-biphenylcarbonyl chlorides, firstly the mixture of ethyl 4'-hydroxy-4-biphenylcarboxylate (2.42 g, 10 mmol), the appropriate alkyl bromides (15 mmol), and K_2CO_3 (2.07 g, 15 mmol) as base in dry 2-butanone (60 ml) was refluxed under argon atmosphere for 9h, and the end of reaction was monitored by TLC (hexane:ethyl acetate / 5:1). The resulting mixture was filtered on silica gel and washed with $CHCl_3$. After removing the volatile components in vacuo, the crude product was purified by column chromatography on silica gel eluting with hexane:ethylacetate / 20:1.
In the following step, the corresponding ethyl 4'-alkoxy-4-biphenylcarboxylate (8 mmol) was dissolved in ethanol (50 ml) and then sodium hydroxide solution (0.64 g NaOH in 2 ml H_2O) was added to this solution. The reaction mixture was refluxed for 12h. The end of the reaction was monitored by TLC (hexane: ethyl acetate / 2:1). The mixture was poured into 100 ml water and then the aqueous solution was acidified to pH 1 by adding 1 N HCl. The obtained precipitate was filtered, washed with water and purified by crystallization from ethanol.
Finally, the corresponding 4'-alkoxy-4-biphenylcarboxylic acid (4 mmol) was reacted with oxalyl chloride (4 ml) and this mixture was refluxed for 4h. The target 4'-alkyloxy-4-biphenylcarbonyl chloride was obtained after removing the excess of oxalyl chloride by distillation.

***Ethyl 4'-dodecyloxy-4-biphenylcarboxylate*:** Yield: 90 %, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.10 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 7.64 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 7.58 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.01 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 4.42 (q, *J* ≈ 7.1 Hz; 2H, $COOC\underline{H}_2$), 4.03 (t; *J* ≈ 6.5 Hz; 2H, OCH_2), 1.89-1.80, 1.51-1.46 (m; 4H, 2 CH_2), 1.43 (t; *J* ≈ 7.1 Hz; 3H, $COOCH_2C\underline{H}_3$), 1.40-1.28 (m, 16H, 8 CH_2), 0.91 (t, *J* ≈ 6.7 Hz; 3H, CH_3).

***Ethyl 4'-tetradecyloxy-4-biphenylcarboxylate*:** Yield: 84 %, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.08 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.62 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.56 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 6.98 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 4.39 (q, *J* ≈ 7.1 Hz; 2H, $COOC\underline{H}_2$), 4.00 (t; *J* ≈ 6.5 Hz; 2H, OCH_2), 1.88-1.78, 1.56-1.44 (m; 4H, 2 CH_2), 1.41 (t; *J* ≈ 7.1 Hz; 3H, $COOCH_2C\underline{H}_3$), 1.40-1.26 (m, 20H, 10 CH_2), 0.88 (t, *J* ≈ 6.7 Hz; 3H, CH_3).

***4'-Dodecyloxy-4-biphenylcarboxylic acid*:** Yield: 92%, colorless crystals. **^{1}H-NMR** (500 MHz, DMSO-d_6): δ (ppm) = 7.97 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 7.74 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 7.67 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 7.04 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 4.01 (t; *J* ≈ 6.5 Hz; 2H, OCH_2), 1.74-1.70, 1.42-1.39 (m; 4H, 2 CH_2), 1.31-1.24 (m, 16H, 8 CH_2), 0.85 (t, *J* ≈ 6.7 Hz; 3H, CH_3).

***4'-Tetradecyloxy-4-biphenylcarboxylic acid*:** Yield: 70%, colorless crystals. **^{1}H-NMR** (500 MHz, DMSO-d_6): δ (ppm) = 7.98 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 7.75 (d, *J* ≈ 8.4 Hz; 2 Ar-H), 7.68 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 7.04 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 4.02 (t; *J* ≈ 6.5 Hz; 2H, OCH_2), 1.77-1.70, 1.47-1.39 (m; 4H, 2 CH_2), 1.35-1.24 (m, 20H, 10 CH_2), 0.85 (t, *J* ≈ 6.7 Hz; 3H, CH_3).

***4'-Dodecyloxy-4-biphenylcarbonyl chloride*:** Yield: 80%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.16 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.69 (d, *J* ≈ 8.6 Hz; 2 Ar-H), 7.59 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 7.00 (d, *J* ≈ 8.8 Hz; 2 Ar-H), 4.01 (t; *J* ≈ 6.5 Hz; 2H, OCH_2), 1.84-1.79, 1.51-1.44 (m; 4H, 2 CH_2), 1.39-1.25 (m, 16H, 8 CH_2), 0.88 (t, *J* ≈ 6.6 Hz; 3H, CH_3).

***4'-Tetradecyloxy-4-biphenylcarbonyl chloride*:** Yield: 85%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.16 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.69 (d, *J* ≈ 8.5 Hz; 2 Ar-H), 7.59 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 7.00 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 4.01 (t; *J* ≈ 6.5 Hz; 2H, OCH_2), 1.84-1.78, 1.50-1.44 (m; 4H, 2 CH_2), 1.36-1.26 (m, 20H, 10 CH_2), 0.88 (t, *J* ≈ 6.7 Hz; 3H, CH_3).

3.4 2-Cyano-5-hydroxyphenyl 4-[4-(2-methylbutoxy)benzoyloxy]benzoates (*(S)*-C, rac-C)

The syntheses of the ***(S)*-Bz-C** and ***rac*-Bz-C** and were carried out by esterification of 4-benzyloxy-2-hydroxybenzonitrile **B** with alkoxybenzoyloxybenzoic acids **(*S*)-A** and ***rac*-A**, respectively, using *N,N'*-dicyclohexylcarbodiimide (DCC)/DMAP. In the following step, the benzyl group of ***rac*-Bz-C** and ***(S)*-Bz-C** was removed by the catalytic hydrogenation according to procedures described in ref[S12].

For the synthesis of the ***(S)*-Bz-C** and ***rac*-Bz-C**, the mixture 4-benzyloxy-2-hydroxybenzonitrile **B** (1.12 g, 5 mmol), **(*S*)-A** or ***rac*-A** (1.64 g, 5.0 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC) (1.18 g, 5.8 mmol) and 4-(dimethylamino)pyridine (DMAP) as catalyst in dry dichloromethane (60 ml) was stirred at room temperature under an argon atmosphere for 24 h. The end of reaction was monitored by TLC (chloroform). The reaction mixture was filtered on silica gel with CH_2Cl_2 and the solvent was evaporated. The crude products were purified by column chromatography on silica gel using CH_2Cl_2 as eluent.

(*S*)-Bz-C or ***rac*-Bz-C** (1.33 g, 2.5 mmol) was dissolved in THF (40 ml) and a catalytic amount of Pd/C-10% was added to this solution. The mixture was stirred in argon-flushed

vessel of autoclave at 40 °C under 5 bar pressure of H_2 gas for 8h. The end of reaction was monitored by TLC (chloroform). The resulting mixture was filtered on silica gel to remove the residue of catalyst and washed with THF. After removing the solvent in vacuo, the crude product was purified by column chromatography on silica gel, eluting with CH_2Cl_2.

***2-Cyano-5-benzyloxyphenyl 4-[4-((S)-2-methylbutoxy)benzoyloxy]benzoate (S)*-Bz-C:** Yield: 86%, colorless crystals; m.p.: 112 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) =8.34 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.18 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.65 (d, $J \approx 8.7$ Hz; 1 Ar-H), 7.45-7.38 (m, 7 Ar-H), 7.13 (d, $J \approx 2.3$ Hz; 1 Ar-H), 7.02 (d, $J \approx 8.9$ Hz, 2 Ar-H), 6.97 (dd, $J \approx 8.7$ Hz and $J \approx 2.3$ Hz; 1 Ar-H), 5.16 (s, 2H, OC$\underline{H_2}$Ph), 3.94, 3.86 (2dd, $J \approx 8.9$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.96-1.92 (m, 1H, CH), 1.65-1.59, 1.36-1.30 (m, 2H, CH_2), 1.07 (d, $J \approx 6.7$ Hz; 3H, CH_3), 1.00 (t, $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) =164.22, 163.18 (CO), 164.02, 163.02, 155.92, 154.12, 125.61, 120.84, 115.53, 98.83 (Ar-C), 135.30, 134.19, 132.43, 132.18, 128.79, 128.53, 127.58, 122.33, 114.45, 109.84 (Ar-CH), 113.34 (CN), 73.16, 70.74 (OCH_2), 34.63 (CH), 26.07 (CH_2), 16.47, 11.28 (CH_3). **MS (EI)**: m/z (%) = 535 (8) [M^+], 311 (85) [M^+-$C_{14}H_{10}O_2N$], 191 (100) [M^+-$C_{14}H_{10}O_2N$-$C_7H_4O_2$], 121 (100) [M^+-$C_{14}H_{10}O_2N$-$C_7H_4O_2$-C_5H_{11}].

***2-Cyano-5-benzyloxyphenyl 4-[4-(2-methylbutoxy)benzoyloxy]benzoate rac*-Bz-C:** Yield: 80%, colorless crystals; m.p.: 112 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) =8.34 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.18 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.65 (d, $J \approx 8.7$ Hz; 1 Ar-H), 7.45-7.38 (m, 7 Ar-H), 7.13 (d, $J \approx 2.3$ Hz; 1 Ar-H), 7.02 (d, $J \approx 8.9$ Hz, 2 Ar-H), 6.97 (dd, $J \approx 8.7$ Hz and $J \approx 2.3$ Hz; 1 Ar-H), 5.16 (s, 2H, OC$\underline{H_2}$Ph), 3.95, 3.87 (2dd, $J \approx 8.9$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.97-1.91 (m, 1H, CH), 1.65-1.58, 1.36-1.28 (m, 2H, CH_2), 1.07 (d, $J \approx 6.7$ Hz; 3H, CH_3), 1.00 (t, $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) =164.20, 163.16 (CO), 164.00, 163.00, 155.91, 154.11, 125.61, 120.84, 115.52, 98.83 (Ar-C), 135.30, 134.18, 132.42, 132.16, 128.78, 128.52, 127.56, 122.32, 114.44, 109.83 (Ar-CH), 113.33 (CN), 73.16, 70.74 (OCH_2), 34.63 (CH), 26.07 (CH_2), 16.47, 11.28 (CH_3).

***2-Cyano-5-hydroxyphenyl 4-[4-((S)-2-methylbutoxy)benzoyloxy]benzoate (S)*-C:** Yield: 73%, colorless crystals; m.p.: 177 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) =8.30 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.18 (d, $J \approx 8.8$ Hz; 2 Ar-H), 7.56 (d, $J \approx 8.6$ Hz; 1 Ar-H), 7.39 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.02 (d, $J \approx 8.8$ Hz; 2 Ar-H), 6.94 (d, $J \approx 2.2$ Hz; 1 Ar-H), 6.78 (dd, $J \approx 8.6$ Hz and $J \approx 2.2$ Hz; 1 Ar-H), 3.92, 3.86 (2dd, $J \approx 8.9$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.94-1.92 (m, 1H, CH), 1.63-1.59, 1.35-1.29 (m, 2H, CH_2), 1.07 (d, $J \approx 6.7$ Hz; 3H, CH_3), 0.99 (t, $J \approx 7.5$ Hz; 3H, CH_3). **APT-^{13}C-NMR:** δ (ppm) =164.69, 163.36 (CO), 164.16, 155.88, 154.00, 125.62, 120.61, 115.70, 98.03 (Ar-C), 134.45, 132.51, 132.22, 122.38, 114.51, 110.68 (Ar-CH), 114.07 (CN), 73.19 (OCH_2), 34.61 (CH), 26.07 (CH_2), 16.46, 11.28 (CH_3). **MS (EI)**: m/z (%) = 445 (4) [M^+], 311 (57) [M^+-$C_7H_4O_2N$], 191 (100) [M^+-$C_7H_4O_2N$-$C_7H_4O_2$], 121 (100) [M^+-$C_7H_4O_2N$-$C_7H_4O_2$-C_5H_{11}].

***2-Cyano-5-hydroxyphenyl 4-[4-(2-methylbutoxy)benzoyloxy]benzoate rac*-C:** Yield: 70%, colorless crystals; m.p.: 176 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) =8.30 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.17 (d, $J \approx 8.8$ Hz; 2 Ar-H), 7.56 (d, $J \approx 8.6$ Hz; 1 Ar-H), 7.39 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.02 (d, $J \approx 8.8$ Hz; 2 Ar-H), 6.96 (d, $J \approx 2.2$ Hz; 1 Ar-H), 6.80 (dd, $J \approx 8.6$ Hz and $J \approx 2.2$ Hz; 1 Ar-H), 3.94, 3.86 (2dd, $J \approx 8.9$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.97-1.90 (m, 1H, CH), 1.66-1.57, 1.37-1.27 (m, 2H, CH_2), 1.07 (d, $J \approx 6.7$ Hz; 3H, CH_3), 0.99 (t, $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ (ppm) =164.68, 163.33 (CO), 164.15, 155.86, 154.00, 125.61, 120.60, 115.68, 98.08 (Ar-C), 134.45, 132.50, 132.21, 122.37, 114.50, 110.70 (Ar-CH), 114.07 (CN), 73.18 (OCH_2), 34.61 (CH), 26.06 (CH_2), 16.46, 11.27 (CH_3).

3.4 *rac*-1/12, *(S)*-1/12 and *(S)*-1/14

A mixture of ***(S)*-C** or ***rac*-C** (0.67 g, 1.5 mmol) with the appropriate 4'-alkylloxy-4-biphenylcarbonyl chloride (1.5 mmol), dry pyridine (9 mmol) in dry dichloromethane (50 ml) was stirred at room temperature under an argon atmosphere for 4 h. The end of the reaction was monitored by TLC (hexane: ethyl acetate / 5:1). The mixture was poured into 10 ml water and then the aqueous solution was neutralized by adding 1 N HCl. The mixture was extracted into CH_2C1_2 (x 3) and the combined organic phases were washed with saturated aqueous $NaHCO_3$ solution, and dried over anhydrous $NaSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel eluting with chloroform : hexane / 2:1.

***rac*-1/12:** Yield: 20%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.26 (d; $J \approx$ 8.8 Hz; 2 Ar-H), 8.15 (d, $J \approx$ 8.5 Hz; 2 Ar-H), 8.08 (d, $J \approx$ 8.9 Hz; 2 Ar-H), 7.73 (d, $J \approx$ 8.6 Hz; 1 Ar-H), 7.64 (d, $J \approx$ 8.5 Hz; 2 Ar-H), 7.53 (d, $J \approx$ 8.8 Hz; 2 Ar-H), 7.47 (d; $J \approx$ 2.1 Hz; 1 Ar-H), 7.34 (d; $J \approx$ 8.8 Hz; 2 Ar-H), 7.26 (dd, $J \approx$ 8.5 Hz and $J \approx$ 2.1 Hz; 1 Ar-H), 6.95-6.91 (m; 4 Ar-H), 3.95 (t; $J \approx$ 6.5 Hz, 2H, OCH_2), 3.85, 3.77 (2dd, $J \approx$ 9.0 Hz and $J \approx$ 6.0 Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.88-1.82 (m, 1H, CH), 1.77-1.72, 1.55-1.50, 1.43-1.37, 1.30-1.19 (4m, 22H, $11CH_2$), 0.98 (d, $J \approx$ 6.7 Hz; 3H, CH_3), 0.91 (t, $J \approx$ 7.5 Hz; 3H, CH_3), 0.81 (t, $J \approx$ 6.7 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.22, 164.05, 163.97 (CO), 162.96, 159.78, 156.07, 154.99, 153.47, 146.71, 131.67, 125.36, 120.84, 120.10, 104.12 (Ar-C), 133.95, 132.47, 132.28, 130.93, 128.44, 126.76, 126.28, 122.43, 117.45, 115.06, 114.48 (Ar-CH), 114.85 (CN), 73.18, 68.20 (OCH_2), 34.65 (CH), 31.94, 29.68, 29.65, 29.62, 29.60, 29.41, 29.37, 29.26, 26.09, 26.06, 22.71 (CH_2), 16.50, 14.14, 11.32 (CH_3). **$C_{51}H_{55}NO_8$** (809.99); Anal. Calc.: C, 75.62; H, 6.84; N, 1.73. Found: C, 75.78; H, 6.65; N, 1.66%.

***(S)*-1/12:** Yield: 30%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.26 (d; $J \approx$ 8.8 Hz; 2 Ar-H), 8.15 (d, $J \approx$ 8.5 Hz; 2 Ar-H), 8.08 (d, $J \approx$ 8.9 Hz; 2 Ar-H), 7.73 (d, $J \approx$ 8.6 Hz; 1 Ar-H), 7.64 (d, $J \approx$ 8.5 Hz; 2 Ar-H), 7.53 (d, $J \approx$ 8.8 Hz; 2 Ar-H), 7.47 (d; $J \approx$ 2.1 Hz; 1 Ar-H), 7.34 (d; $J \approx$ 8.8 Hz; 2 Ar-H), 7.26 (dd, $J \approx$ 8.5 Hz and $J \approx$ 2.1 Hz; 1 Ar-H), 6.95-6.91 (m; 4 Ar-H), 3.94 (t; $J \approx$ 6.5 Hz, 2H, OCH_2), 3.85, 3.77 (2dd, $J \approx$ 9.0 Hz and $J \approx$ 6.0 Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.88-1.82 (m, 1H, CH), 1.77-1.72, 1.55-1.50, 1.43-1.37, 1.30-1.19 (4m, 22H, $11CH_2$), 0.98 (d, $J \approx$ 6.7 Hz; 3H, CH_3), 0.91 (t, $J \approx$ 7.5 Hz; 3H, CH_3), 0.81 (t, $J \approx$ 6.7 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.22, 164.05, 163.97 (CO), 162.96, 159.78, 156.07, 154.99, 153.48, 146.71, 131.67, 125.36, 120.84, 120.10, 104.12 (Ar-C), 133.95, 132.47, 132.27, 130.93, 128.44, 126.76, 126.29, 122.42, 117.45, 115.06, 114.48 (Ar-CH), 114.85 (CN), 73.18, 68.20 (OCH_2), 34.65 (CH), 31.94, 29.68, 29.65, 29.62, 29.60, 29.41, 29.37, 29.26, 26.09, 26.06, 22.71 (CH_2), 16.50, 14.14, 11.32 (CH_3). **$C_{51}H_{55}NO_8$** (809.99); Anal. Calc.: C, 75.62; H, 6.84; N, 1.73. Found: C, 75.60; H, 6.75; N, 1.63%.

***(S)*-1/14:** 35%, colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.26 (d, $J \approx$ 8.7 Hz; 2 Ar-H), 8.15 (d, $J \approx$ 8.4 Hz; 2 Ar-H), 8.09 (d, $J \approx$ 8.8 Hz; 2 Ar-H), 7.73 (d, $J \approx$ 8.5 Hz; 1 Ar-H), 7.64 (d, $J \approx$ 8.4 Hz; 2 Ar-H), 7.53 (d, $J \approx$ 8.7 Hz; 2 Ar-H), 7.47 (d; $J \approx$ 2.1 Hz; 1 Ar-H), 7.34 (d; $J \approx$ 8.7 Hz 2 Ar-H), 7.27 (dd, $J \approx$ 8.5 Hz and $J \approx$ 2.1 Hz ; 1 Ar-H), 6.95-6.92 (m; 4 Ar-H), 3.95 (t; $J \approx$ 6.5 Hz, 2H, OCH_2), 3.85, 3.77 (2dd, $J \approx$ 9.0 Hz and $J \approx$ 6.0 Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.88-1.83 (m, 1H, CH), 1.77-1.72, 1.55-1.50, 1.44-1.37, 1.30-1.19 (4m, 26H, $13CH_2$), 0.98 (d, $J \approx$ 6.7 Hz; 3H, CH_3), 0.91 (t, $J \approx$ 7.5 Hz; 3H, CH_3), 0.81 (t, $J \approx$ 6.7 Hz; 3H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 164.22, 164.05, 163.97 (CO),

162.96, 159.78, 156.07, 154.99, 153.48, 146.71, 131.67, 125.36, 120.84, 120.10, 104.12 (Ar-C), 133.95, 132.47, 132.27, 130.93, 128.44, 126.76, 126.29, 122.42, 117.45, 115.06, 114.48 (Ar-CH), 114.85 (CN), 73.18, 68.20 (OCH_2), 34.65 (CH), 31.94, 29.71, 29.69, 29.67, 29.61, 29.59, 29.41, 29.37, 29.25, 26.09, 26.06, 22.70 (CH_2), 16.49, 14.13, 11.31 (CH_3). **$C_{53}H_{59}NO_8$** (838.05); Anal. Calc.: C, 75.96; H, 7.09; N, 1.67. Found: C, 76.08; H, 6.91; N, 1.58%

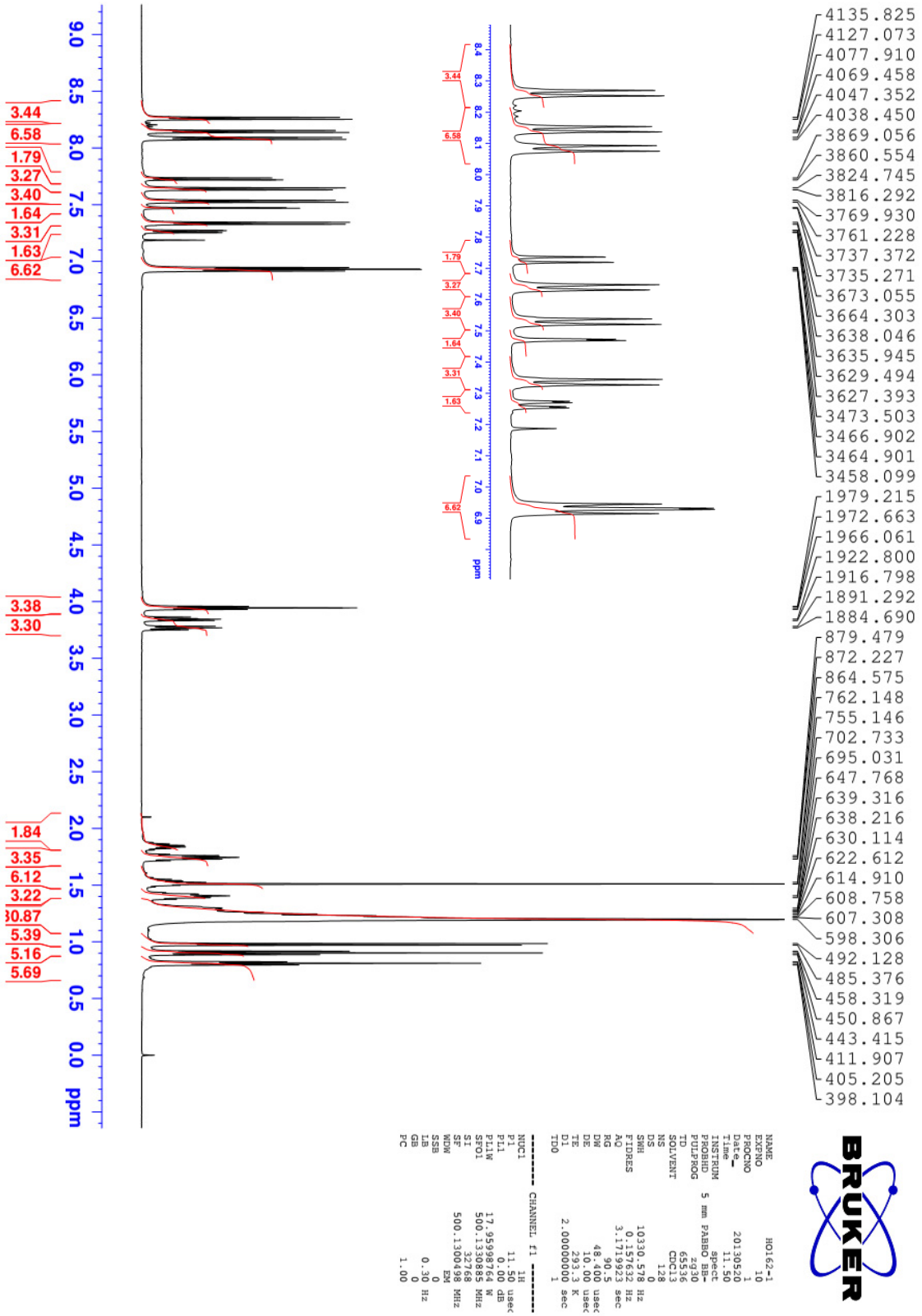

Figure S11. ^{1}H-NMR spectrum of compound ***rac*-1/12** ($CDCl_3$, 500 MHz).

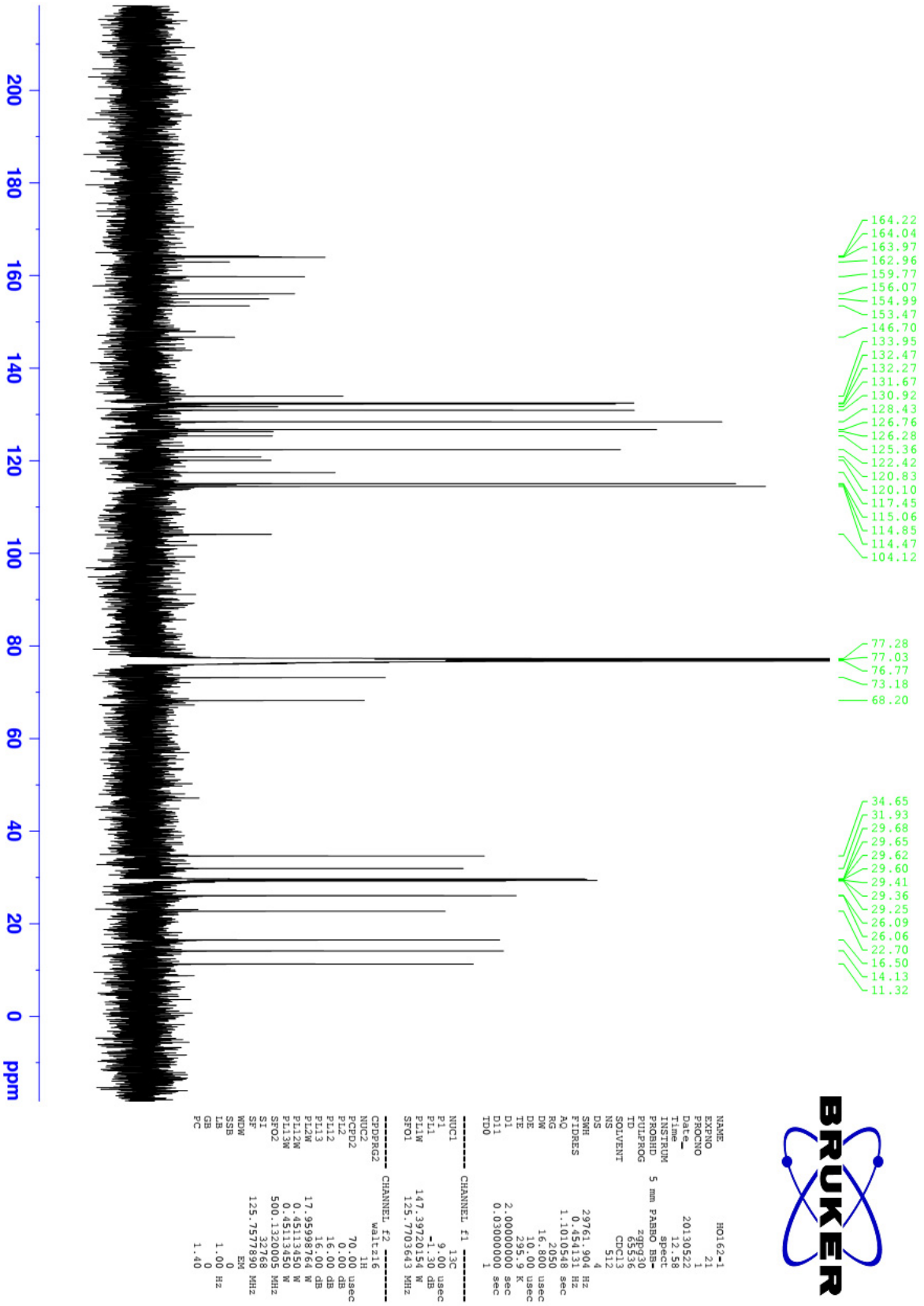

Figure S12. ^{13}C-NMR spectrum of compound ***rac*-1/12** ($CDCl_3$, 125 MHz).

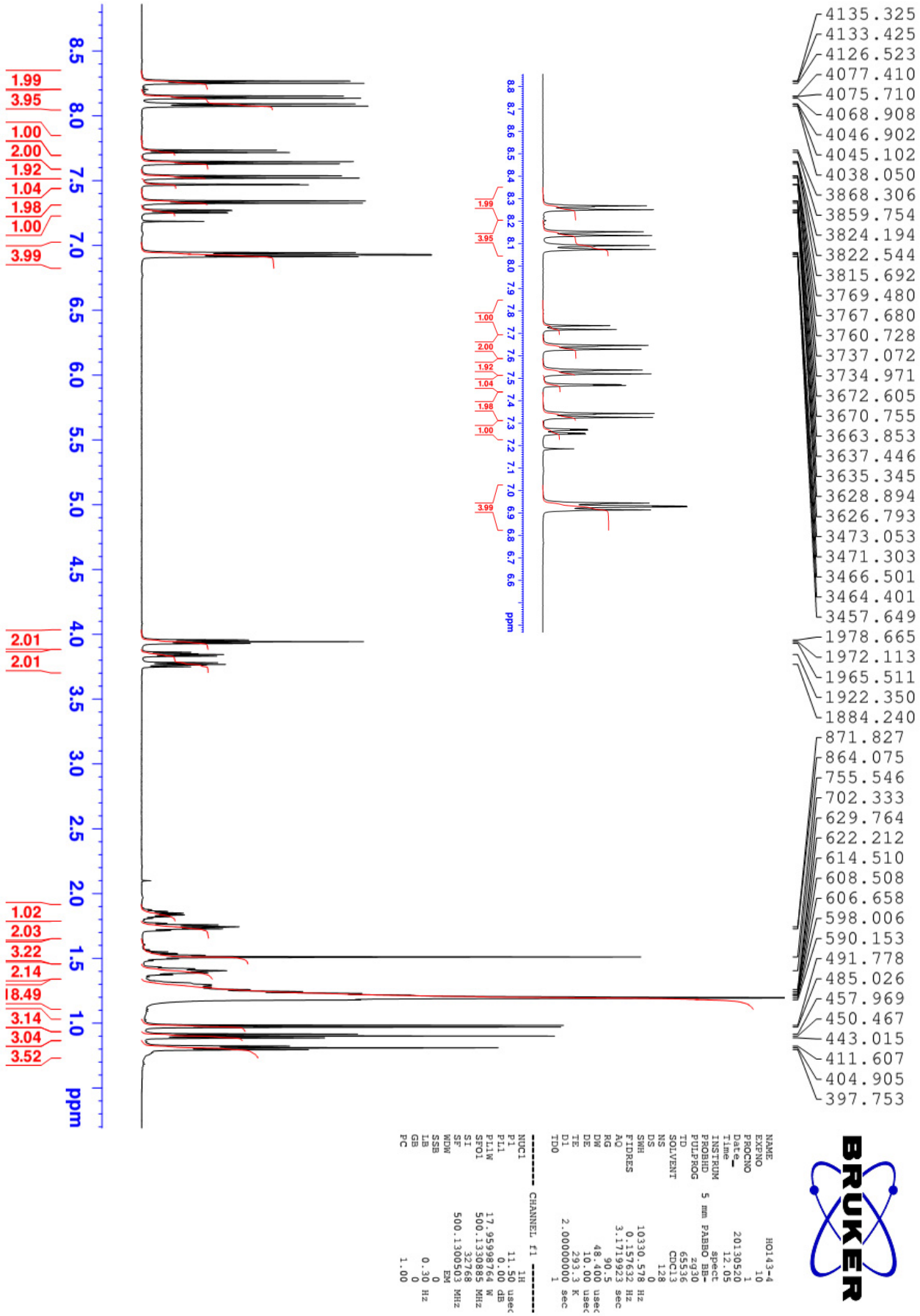

Figure S13. ^{1}H-NMR spectrum of compound ***(S)*-1/12** ($CDCl_3$, 500 MHz).

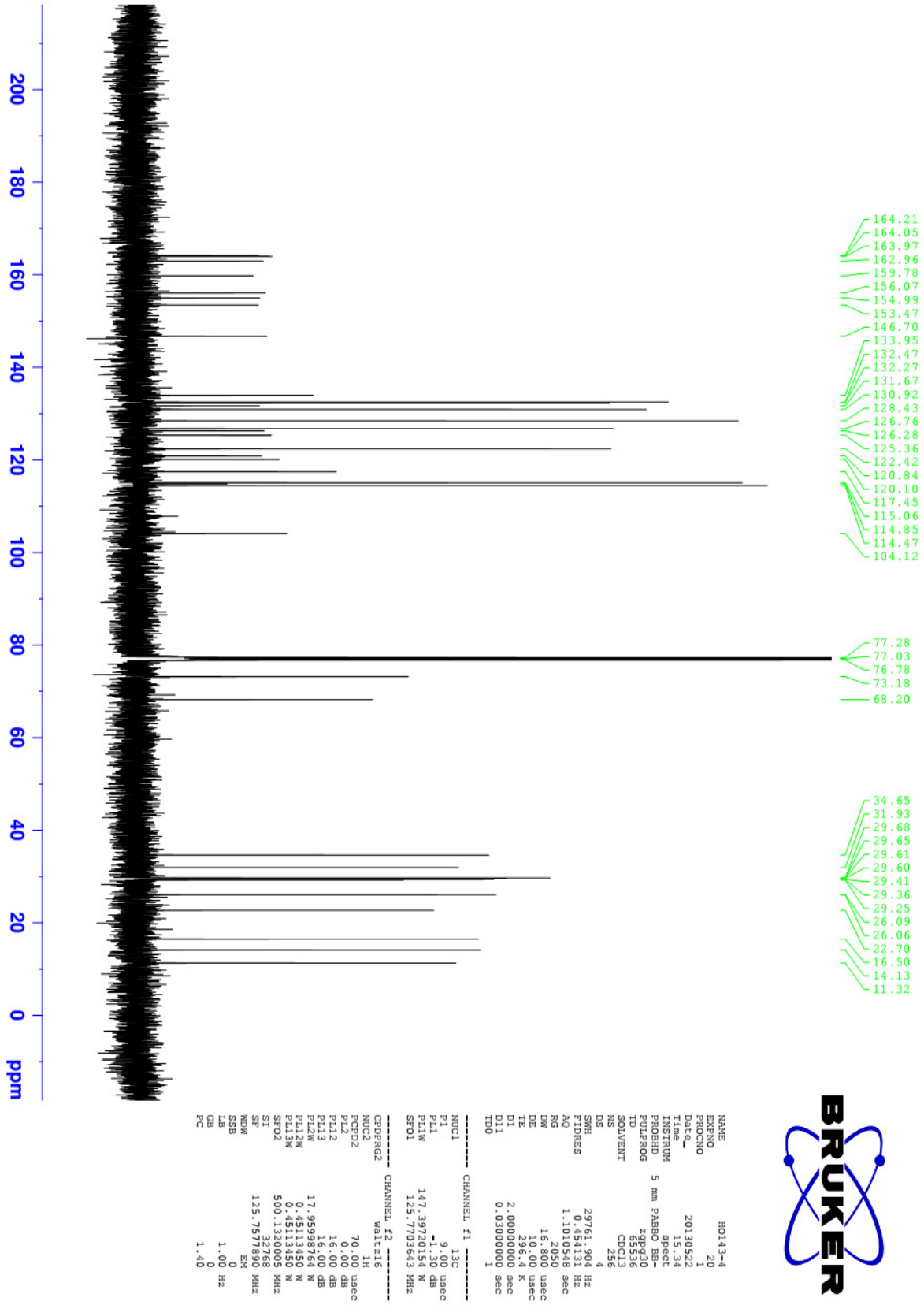

Figure S14. ^{13}C-NMR spectrum of compound ***(S)*-1/12** ($CDCl_3$, 125 MHz).

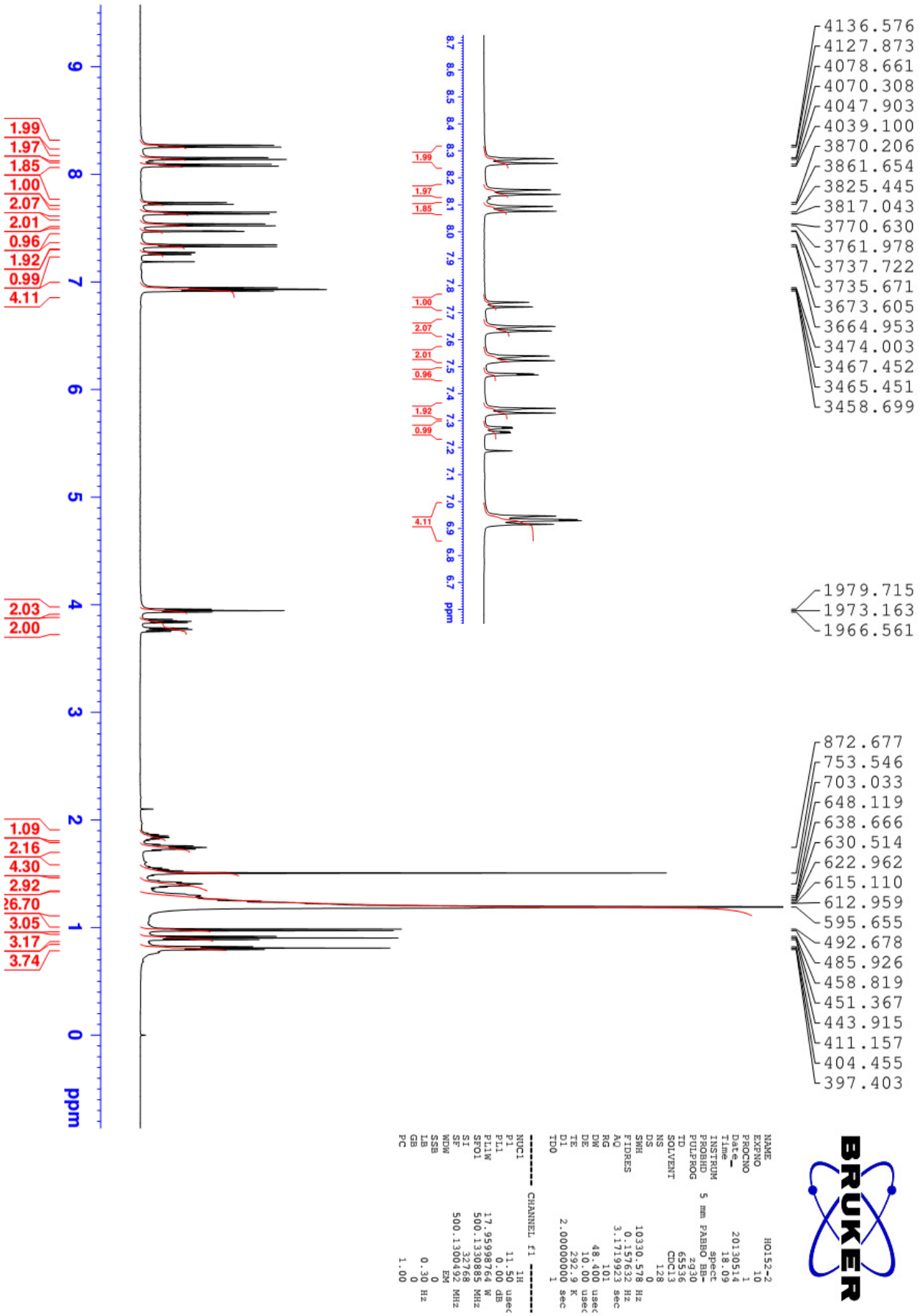

Figure S15. ^{1}H-NMR spectrum of compound ***(S)*-1/14** ($CDCl_3$, 500 MHz).

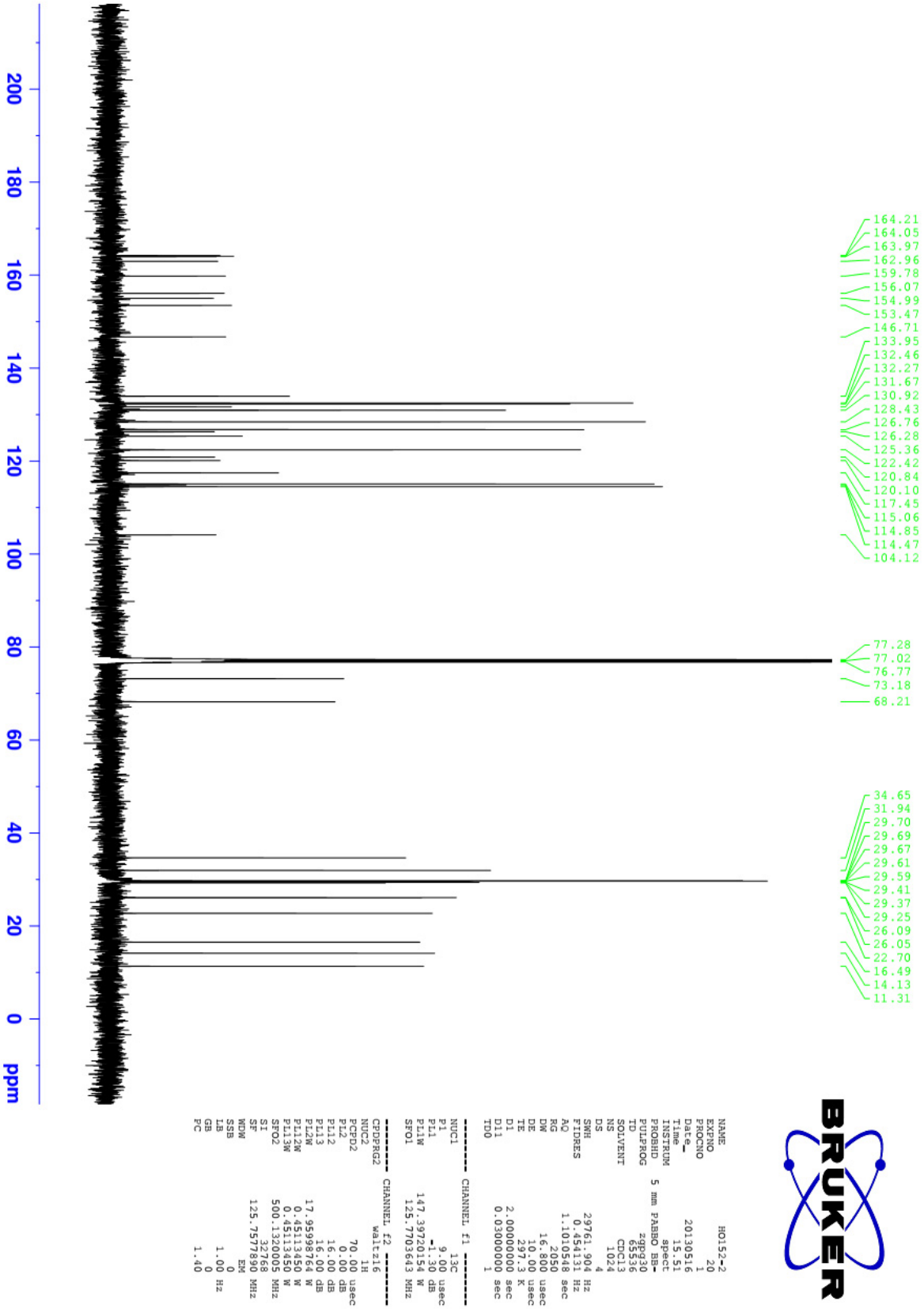

Figure S16. ^{13}C-NMR spectrum of compound ***(S)*-1/14** ($CDCl_3$, 125 MHz).

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