Supporting information

Versatile synthesis of α-fused BODIPY displaying intense absorption in the NIR and high electron affinity

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Instrumentation

NMR spectroscopy

^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on a Brucker Avance 300 and 400 MHz spectrometers at room temperature if not specified. ^{1}H and ^{13}C chemical shifts are reported to the relative difference in ppm with respect to the residual deuterated solvent peak: **chloroform-d** ($\delta(^{1}H)$=7.26 ppm, $\delta(^{13}C)$=77.16 ppm), **MeOD-d_4** ($\delta(^{1}H)$=3.31 ppm, $\delta(^{13}C)$= 49.00 ppm), **benzene-d_6** ($\delta(^{1}H)$=7.16 ppm, $\delta(^{13}C)$=128.00 ppm), **DMSO-d_6** ($\delta(^{1}H)$= 2.50 ppm, $\delta(^{13}C)$= 39.70 ppm), **acetone-d_6** ($\delta(^{1}H)$= 2.05 ppm, $\delta(^{13}C)$= 29.8 ppm).

Absorption and emission spectroscopies

UV-Visible absorption spectra were recorded with a Schimadzu UV-3600 dual-beam grating spectrophotometer using a 1.0 cm quartz cell.

The steady-state fluorescence emission and excitation spectra were recorded with a Horiba Jobin Yvon Fluoromax 4P spectrofluorimeter. All fluorescence spectra were corrected. The fluorescence quantum yield was determined using the following equation:

$$\Phi_F = \Phi_{Réf} \frac{I \ OD_{Réf} \ \eta^2}{I_{Réf} \ OD \ \eta_{Réf}^2}$$

In the previous equation, Φ_F denotes the fluorescence quantum yield of the analyzed compound, I denotes the integral of the corrected fluorescence spectra, OD the optical density at the excitation wavelength and η the refractive index of the measurement solvent. Depending on the emission wavelength of the compound, different references are used: Rhodamine 6G ($\Phi_{Réf}$=0.88 in EtOH, λ_{ex}=488 nm)[1] , cresyl violet ($\Phi_{Réf}$=0.50 in EtOH, λ_{ex}=546 nm) or a published BODIPY dye ($\Phi_{Réf}$=0.49 in DCM, λ_{ex}=650 nm)[2].

Low temperature measurements emission were recorded on a FL920 Edinburgh instrument equipped with Hamamastu R928 photomultiplier. The studied compounds were solubilized in 2-methyl-THF in closed vials equipped with a septum, and the solution was degassed for at least 30 min with Argon.

Fluorescence lifetimes were measured on the same instrument as above, equipped this time with a R928 photomultiplier and a PicoQuant PDL 800-D pulsed diode connected to a G^{w}Instect GFG-8015G delay generator. Emission wavelengths were selected by a monochromator. Lifetimes were deconvoluted with FS-900 software using a light-scattering solution for instrument response.

General methods and reagents

Anhydrous solvents

Anhydrous solvents were obtained by distillation over drying agent: DCM was distilled over CaH_2, DCE over P_2O_5, THF and Et_2O over sodium and benzophenone, toluene over sodium and DMF over KOH under reduced pressure.

Reagents

The commonly used catalysts were synthetized according to the reported literature: $Pd(PPh_3)_4$, $Pd(dppf)Cl_2$. Some of the reagents were purified before use according to the literature[3]: Et_3N, *i*PrNH, N-bromosuccinimide. All the other reagents were purchased from commercial suppliers and used without further purification.

Materials

Chromatographic purifications were performed on standardized silica gel (0.063-0.200mm) or on aluminium oxide+6% H_2O in weight. Thin Layer Chromatography were performed on silica or alumina gel plate precoated with a fluorescent indicator. The mixture of solvents are always given in volume ratio.

Synthetic procedures

Synthetic procedures

Synthesis of the organostannane derivatives

The synthesis of the organostannane derivatives was carried out following procedures described in Reference 4.

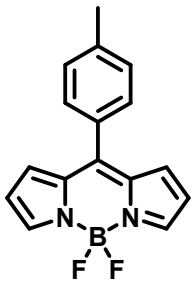
General procedure 1: Stille cross-coupling reactions.

In a dried Schlenk tube were added the appropriate halogenated (1.0 eq) and the appropriate stannane derivative (2.0 eq per reactive position). Distilled toluene was added (0.1 M) and the mixture was degased for 30min with Ar. $Pd(PPh_3)_4$ (5% per reactive position) was added and the mixture heated at 110°C for the indicated time.

General procedure 2: oxidative ring closure reactions.

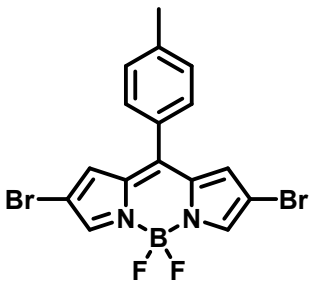
To a stirred solution of tetrasubstituted BODIPY derivative in dry DCM (BODIPY concentration 1 $mmol.L^{-1}$) was added at 0°C anhydrous $FeCl_3$ (2.5 eq per covalent bond formation). The mixture was stirred for the indicated temperature at the indicated time. The reaction was quenched by addition of water. The aqueous layer was extracted with DCM. The combined organic layer was washed with water, brine, and was then dried over $MgSO_4$. Column chromatography on silica followed by a recrystallization using the appropriate solvents combination afforded the analytically pure product.

Compound 1[5]



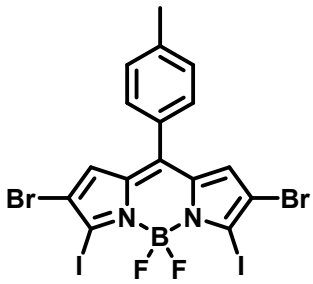
To a degased 0.018M HCl solution (1.5mL of 37% HCl in 100 mL H_2O) was added p-toluylaldehyde (2.0mL, 16.9mmol, 1.0eq). Pyrrole (3.5mL, 50.7mmol, 3.0eq) was slowly added and the mixture was stirred, protected from light, for 16h. The solid was collected by filtration, washed with water and petroleum ether and finally dissolved in DCM. The organic layer was washed with water and brine. The obtained crude product was dissolved in anhydrous DCM. DDQ (4.03g, 17.7mmol, 1.05eq) was added in one portion in the reaction mixture. After stirring 1h at room temperature, NEt_3 (101mmol, 6.0eq) and $BF_3.OEt_2$ (135mmol, 8.40eq) were added. The reaction mixture was stirred at R.T. for 16h. The mixture was diluted with DCM and poured on a saturated $NaHCO_3$ solution. The aqueous layer was extracted twice with DCM. The combined organic layer was washed with water, brine, and was then dried over $MgSO_4$. Column chromatography (PE/DCM 1:1), followed by recrystallization from DCM/EtOH afforded the expected compound 1 as blue crystals (1.12g, 3.97mmol, 23%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ =7.28 (d, 2H, ^{3}J=7.9Hz), 7.14 (d, 2H, ^{3}J=7.9Hz), 2.55 (s, 6H), 2.43 (s, 3H), 1.40 (s, 6H). **^{13}C NMR** (100 MHz $CDCl_3$): δ =155.4, 143.3, 142.3, 139.0, 132.1, 131.7, 130.0, 128.0, 121.2, 21.6, 14.7, 14.6.

Compound 2 [5]



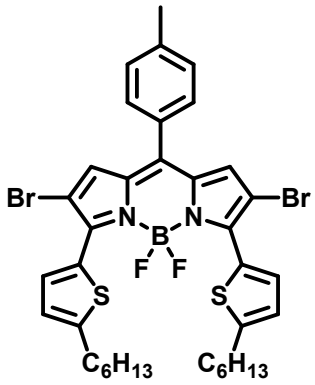
To a solution of compound **1** (198 mg, 0.700mmol, 1.0eq) in DCM/DMF (1:1 mixture, 32 mL) was added in one portion NBS (299mg, 1.68mmol, 2.4eq). The mixture was stirred at R.T. protected from light for 3h30. The reaction was quenched with a saturated $Na_2S_2O_3$ solution and diluted with DCM. The aqueous layer was extracted twice with DCM. The combined organic layer was washed with water, brine, and was then dried over $MgSO_4$. Column chromatography (PE/PhMe 7:3 to 1:1) followed by recrystallization from DCM/EtOH afforded the analytically pure compound 2 as a metallic green solid (280mg, 0.636mmol, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.83 (s, 2H), 7.44 (d, 2H, ^{3}J=8.0 Hz), 7.36 (d, 2H, ^{3}J=8.0 Hz), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 147.6, 144.0, 142.6, 134.3, 131.8, 130.7, 130.3, 129.7, 107.2, 21.7.

Compound 3



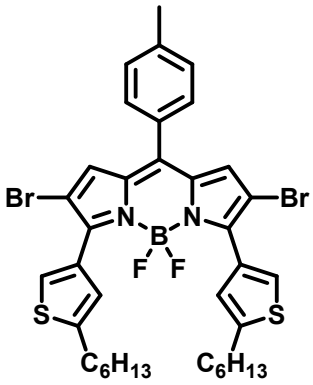
To a solution of compound **2** (281 mg, 0.64 mmol, 1.0 eq) in EtOH (50 mL) were added I_2 (405 mg, 1.6 mmol, 2.5 eq) and HIO_3 (281 mg; 1.6 mmol, 2.5 eq). The resulting mixture was stirred for 3h30 min at 80°C. At R.T., a saturated solution of $Na_2S_2O_3$ was added and the reaction mixture was diluted with DCM. The organic layer was washed with water, dried over $MgSO_4$ and the solvent was removed under vacuum. The residue was purified by column chromatography (PE/DCM 4:1 to 7:3) to afford the pure expected product as a purple solid (328 mg, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 (d, 2H, ^{3}J=8.3 Hz,), 7.34 (d, 2H, ^{3}J=8.3 Hz), 6.86 (s, 2 H), 2.47 (s, 3 H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 142.4, 141.7, 137.9, 130.9, 130.5, 129.7, 129.2, 119.1, 110.1, 21.7. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.26 (t, $J_{B\text{-}F}$=29.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -146.40 (q, $J_{F\text{-}B}$=28.9 Hz). **HRMS** (ESI-TOF): calcd $C_{16}H_9BBr_2F_2I_2N_2$ $[M+K]^+$: 730.6898; found: 730.6868.

Compound 4α



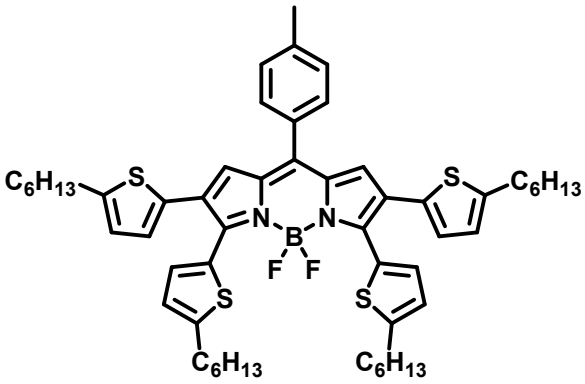
Compound **4α** was synthetized according to *General Procedure 1* in presence of 2.2 eq of compound **Tα**. The reaction mixture was heated at 110°C for 16h. Using compound **3** (210 mg, 0.304 mmol, 1.0 eq) as starting material, column chromatography (PE/PhMe/DCM 8:1:1) afforded the pure compound **4α** as a blue solid (233 mg, 0.303 mmol, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.76 (d, 2H, ^{3}J=3.6Hz), 7.42 (d, 2H, ^{3}J=7.7Hz), 7.34 (d, 2H, ^{3}J=7.7Hz), 6.96 (s, 2H), 6.87 (d, 2H, ^{3}J=3.6Hz), 2.87 (t, 4H, ^{3}J=7.8Hz), 2.48 (s, 3H), 1.70-1.80 (m, 4H), 1.37-1.46 (m, 4H); 1.30-1.37 (m, 8H), 0.91 (t, 6H, ^{3}J=7.1Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ =151.9, 148.7, 141.1, 134.6, 133.6 (t, *J*=5.9 Hz), 131.8, 130.7, 130.5, 129.3, 127.4, 124.9, 109.4, 31.5, 31.3, 30.3, 29.0, 22.6, 21.5, 14.1. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.96 (t, $J_{B\text{-}F}$ = 31.2Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -134.4 (q, $J_{F\text{-}B}$= 31.1Hz). **HRMS** (ESI-TOF): calcd for $C_{36}H_{39}BBr_2F_2N_2S_2$ $[M]^+$: 772.0962; found: 772.0958.

Compound 4β



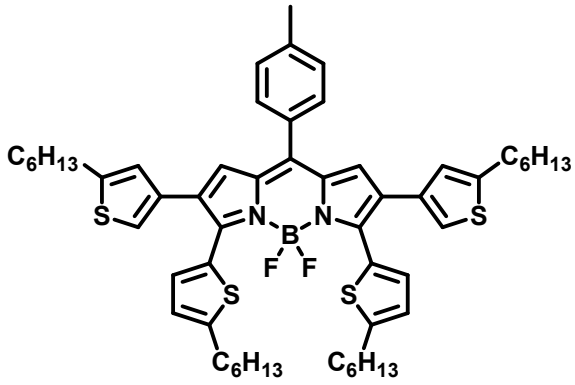
Compound **4β** was synthetized according to *General Procedure 1* in presence of 2.2 eq of compound **Tβ**. The reaction mixture was heated at 110°C for 16h. Starting from compound **3** (219 mg, 0.320 mmol, 1.0 eq), column chromatography (PE/Toluene 9:1) afforded the pure product as a purple solid (146mg, 0.189 mmol, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = = 7.80 (s, 2 H), 7.44 (d, ^{3}J=7.9 Hz, 2 H), 7.35 (d, ^{3}J=7.7 Hz, 2 H), 7.26 (s, 2 H), 6.97 (s, 2 H), 2.84 (t, ^{3}J=7.6 Hz, 4 H), 2.49 (s, 3 H), 1.71 (quint., ^{3}J=7.4 Hz, 4 H), 1.37 - 1.46 (m, 4 H), 1.28 - 1.36 (m, 8 H), 0.82 - 0.97 (m, 6 H). **^{13}C NMR** (100 MHz, CDCl3): δ = 150.86, 144.88, 142.59, 141.17, 134.12, 131.71, 130.71, 130.46, 129.37, 129.29, 128.03 (t, J=5.4 Hz), 126.14, 108.96, 31.54, 31.39, 29.92, 28.73, 22.57, 21.46, 14.08. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.76 (t, J_{B-F}=30.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -134.47 (q, J_{F-B}=30.4 Hz). **HRMS** (ESI-TOF): calcd for $C_{36}H_{39}BBr_2F_2N_2S_2$ $[M]^+$: 772.0965; found: 772.1019.

Compound 5αα



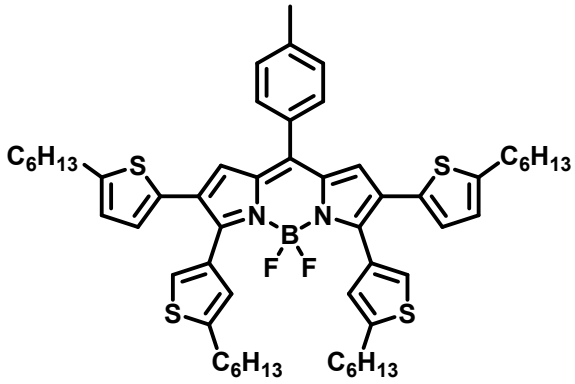
Compound **5αα** was synthetized according to *General Procedure 1*. The reaction mixture was heated at 110°C for 16h. Starting from Compound **3** (193mg, 0.246mmol, 1.0eq), column chromatography (PE/toluene 75:25) afforded the pure compound **5αα** as a green solid (189mg, 0.200mmol, 81%). **^{1}H NMR** (400 MHz, C_6D_6): δ =7.89 (d, 2H, ^{3}J=3.6Hz), 7.12 (d, 2H, ^{3}J=8.0Hz), 6.96 (s, 2H), 6.84 (d, 2H, ^{3}J=7.8Hz), 6.73 (d, 2H, ^{3}J=3.5Hz), 6.58 (d, 2H, ^{3}J=3.7Hz), 6.52 (d, 2H, ^{3}J=3.6Hz), 6.15 (s, 2H), 2.54 (t, 4H, ^{3}J=7.8Hz), 2.45 (t, 4H, ^{3}J=7.8Hz), 2.08 (s, 3H), 1.45-1.53 (m, 4H), 1.37-1.44 (m, 4H), 1.08-1.23 (m, 24H), 0.87 (t, 6H, ^{3}J=7.2Hz), 0.84 (t, 6H, ^{3}J=7.2Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.8, 149.0, 146.3, 142.2, 140.7, 135.0, 133.1, 132.5, 131.6, 130.7, 129.3, 129.2, 128.8, 126.1, 124.6, 124.3, 31.7, 31.7, 31.5, 30.3, 30.2, 28.90, 28.87, 22.73, 22.71, 14.22, 14.21. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 2.82 (t, J_{B-F}=34.9Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -134.3 (d, J_{B-F}=30.9Hz). **HRMS** (ESI-TOF): calcd for $C_{56}H_{69}BF_2N_2S_4$ $[M]^+$: 946.4405; found: 946.4443.

Compound 5αβ



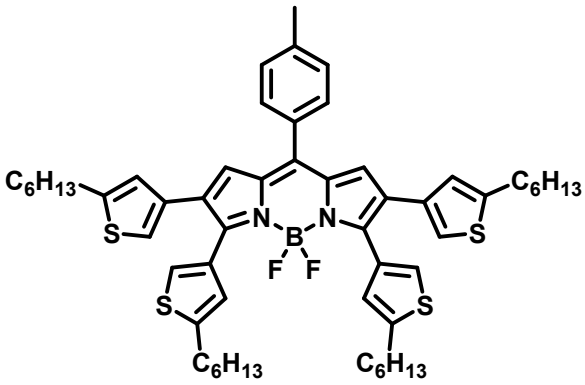
Compound **5αβ** was synthetized according to *General Procedure 1*. The reaction mixture was heated at 110°C for 16h. Starting from compound **4α** (97 mg, 0.130 mmol, 1.0 eq), column chromatography (PE/PhMe 4:1 to 7:3) afforded the pure compound **5αβ** as a green solid (100 mg, 0.109 mmol, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51 (d, ^{3}J=7.9 Hz, 2H), 7.41 (d, ^{3}J=3.5 Hz, 2H), 7.34 (d, ^{3}J=7.9 Hz, 2H), 6.86 (s, 2H), 6.77 (d, ^{3}J=3.7 Hz, 2H), 6.75 (d, ^{3}J=1.1 Hz, 2H), 6.52 (s, 2H), 2.81 (t, ^{3}J=7.6 Hz, 4H), 2.71 (t, ^{3}J=7.6 Hz, 4H), 2.49 (s, 3H), 1.51 - 1.73 (m, 8H), 1.22 - 1.43 (m, 24H), 0.83 - 0.97 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.5, 148.8, 145.3, 141.6, 140.35, 134.9, 133.9, 132.1 (t, J_{C-F}=4.0 Hz), 131.6, 130.8, 130.7, 130.6, 129.3, 129.1, 127.5, 125.1, 124.5, 120.1, 31.5, 31.3, 30.2, 29.9, 28.8, 28.7, 22.6, 22.5, 21.4, 14.1, 14.05. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 1.13 (t, J_{B-F}=31.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ =-135.28 (q, J_{F-B}=31.4 Hz). **HRMS** (ESI-TOF): calcd for $C_{56}H_{69}BF_2N_2S_4$ [M+K]: 985.4046, found: 985.4077.

Compound 5βα



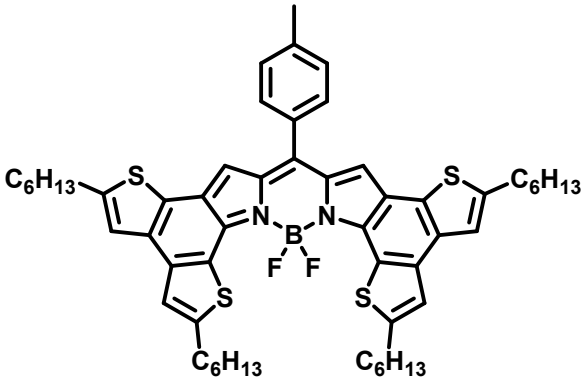
Compound **5βα** was synthetized according to *General Procedure 1*. The reaction mixture was heated at 110°C for 16h. Starting from compound 4**β** (146 mg, 0.190 mmol, 1.0 eq), column chromatography (PE/DCM 9:1 to 4:1) afforded the pure compound **5βα** as a blue solid (142 mg, 0.150 mmol, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.59 (s, 2H), 7.54 (d, ^{3}J=7.9 Hz, 2H), 7.38 (d, ^{3}J=7.9 Hz, 2H), 6.91 (s, 2H), 6.90 (s, 2H), 6.57 (d, ^{3}J=3.3 Hz, 2H), 6.51 (d, ^{3}J=3.5 Hz, 2H), 2.81 (t, ^{3}J=7.5 Hz, 4H), 2.74 (t, ^{3}J=7.6 Hz, 4H), 2.52 (s, 3H), 1.58 - 1.73 (m, 8H), 1.25 - 1.45 (m, 24H), 0.85 - 0.99 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 150.9, 145.5, 144.6, 142.5, 140.5, 134.5, 133.3, 131.5, 130.6, 130.5, 129.1, 128.2, 126.7 (t, J_{C-F}=4.5 Hz), 126.6, 126.5, 125.1, 124.2, 31.6, 31.5, 31.4, 30.0, 29.8, 28.7, 28.6, 22.54, 22.53, 21.4, 14.1, 14.0. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 0.93 (t, J_{B-F}=30.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ =-135.24 (q, J_{F-B}=30.4 Hz). **HRMS** (ESI-TOF): calcd $C_{56}H_{69}BF_2N_2S_4$, $[M]^+$: 946.4409 ; found: 946.4411.

Compound 5ββ



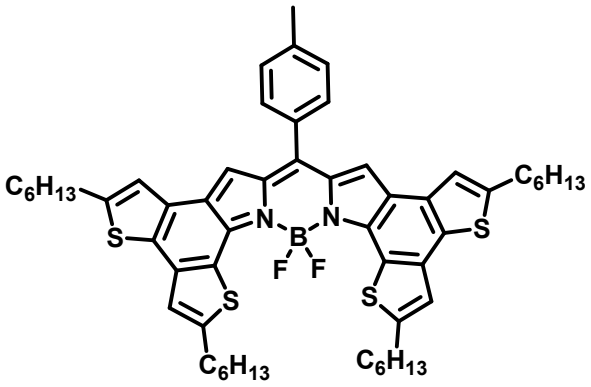
Compound **5ββ** was synthetized according to *General Procedure 1 i*n presence of lithium chloride (2.0 eq). The reaction mixture was heated at 110°C for 16h. Starting from compound **3** (74.2 mg, 0.0944 mmol, 1.0eq), column chromatography (PE/DCM 4:1) afforded the pure product as a blue solid (61 mg, 0.0644 mmol, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.55 (s, 2H), 7.52 (d, 2H, ^{3}J=8.1Hz), 7.35 (d, 2H, ^{3}J=8.1Hz), 6.88 (s, 2H), 6.82 (s, 2H), 6.66 (s, 2H), 6.49 (s, 2H), 2.76 (t, 4H, ^{3}J=7.9Hz), 2.69 (t, 4H, ^{3}J=7.2Hz), 2.50 (s, 3H), 1.57-1.66 (m, 8H), 1.26-1.41 (m, 24H), 0.93 (t, 6H, ^{3}J=7.7Hz), 0.88 (t, 6H, ^{3}J=7.7Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.3, 145.5, 144.8, 142.4, 140.5, 134.6, 134.2, 131.8, 131.3, 130.7, 130.1, 130.0, 129.2, 127.2, 126.7, 124.8, 119.4, 31.7, 31.6, 30.1, 30.0, 29.2, 28.9, 28.8, 26.8, 22.7, 22.7, 14.3, 14.2. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 1.0 (t, $J_{B\text{-}F}$ = 31.1Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -135.0 (q, $J_{F\text{-}B}$=30.7Hz). **HRMS** (ESI-TOF): calcd for $C_{56}H_{69}BF_2N_2S_4$ $[M + K]^+$:,985.4042; found 985:.4047.

Compound 6αα



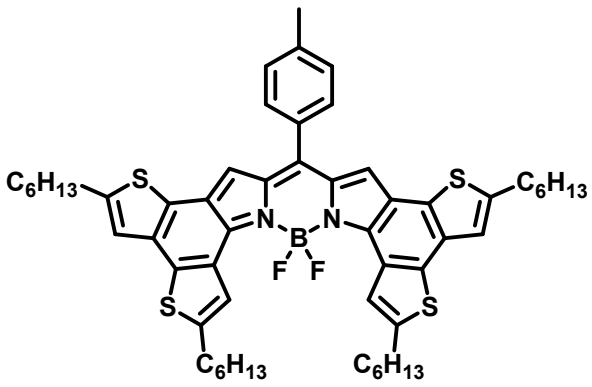
Compound **6αα** was synthetized according to *General Procedure 2* starting from compound **5αα** (202 mg, 0.213 mmol, 1.0 eq). The reaction mixture was stirred 1h at 0°C. Column chromatography (EP/DCM 7:3) followed by recrystallization by diffusion of acetone in a DCM solution afforded the pure compound **6αα** (126mg, 0.134 mmol, 63%) as a dark green solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.52 (d, 2H, ^{3}J=7.8Hz), 7.34 (d, 2H, ^{3}J=7.8Hz), 7.27 (s, 2H), 7.18 (s, 2H), 7.10 (s, 2H), 3.03 (t, ^{3}J=7.5Hz), 2.91 (t, ^{3}J=7.5Hz), 2.54 (s, 3H), 1.85-1.93 (m, 4H), 1.71-1.79 (m, 4H), 1.28-1.44 (m, 24H), 0.94 (t, 6H, ^{3}J=7.1Hz), 0.90 (t, 6H, ^{3}J=7.1Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 154.5, 145.51, 145.49, 143.4, 140.6, 140.3, 138.9, 132.2, 132.1, 131.6, 129.22, 129.21, 126.6, 122.2, 120.8, 120.5, 120.1, 31.8, 31.7, 31.6, 31.4, 31.1, 30.7, 29.2, 28.9, 22.8, 22.7, 14.3, 14.2. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 1.86 (t, $J_{B\text{-}F}$ = 32.6Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -141.3 (q, $J_{F\text{-}B}$=32.8Hz). **HRMS** (ESI-TOF): calcd for $C_{56}H_{65}BF_2N_2S_4$ $[M]^+$: 942.4092; found: 942.4120.

Compound 6αβ



Compound **6αβ** was synthetized according to *General Procedure 2* starting from compound **5αβ** (98 mg, 0.100 mmol). The reaction mixture was stirred 30min at 0°C. Column chromatography (EP/DCM 9:1 to 4:1) followed by recrystallization by diffusion of acetone in q DCM solution afforded the pure compound **6αβ** (95mg, 0.970 mmol, 97%) as a black solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.60 (d, ^{3}J=7.9 Hz, 2H), 7.41 (d, ^{3}J=7.9 Hz, 2H), 7.23 (s, 2H), 7.17 (s, 2H), 7.14 (s, 2H), 3.03 (t, ^{3}J=7.7 Hz, 4H), 2.90 (t, ^{3}J=7.5 Hz, 4H), 2.54 (s, 3H), 1.89 (quint., ^{3}J=7.6 Hz, 4H), 1.75 (quint., ^{3}J=7.4 Hz, 4H), 1.45 - 1.52 (m, 4H), 1.36 - 1.44 (m, 12H), 1.26 - 1.35 (m, 8H), 0.93 (t, ^{3}J=7.1 Hz, 6H), 0.89 (t, ^{3}J= 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 154.85, 146.48, 145.47, 143.44, 140.33, 138.98, 138.59, 132.19, 131.37, 131.19, 129.66, 129.02, 127.26, 121.89, 121.09, 120.18, 119.67, 31.58, 31.36, 31.13, 30.92, 30.59, 29.05, 28.74, 22.61, 22.54, 21.50, 14.11, 14.07. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 1.91 (t, $J_{B\text{-}F}$=33.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ =-140.91 (q, $J_{F\text{-}B}$=33.4 Hz). **HRMS** (ESI-TOF): calcd for $C_{56}H_{65}BF_2N_2S_4$ $[M]^+$: 942.4096; found: 942.4127.

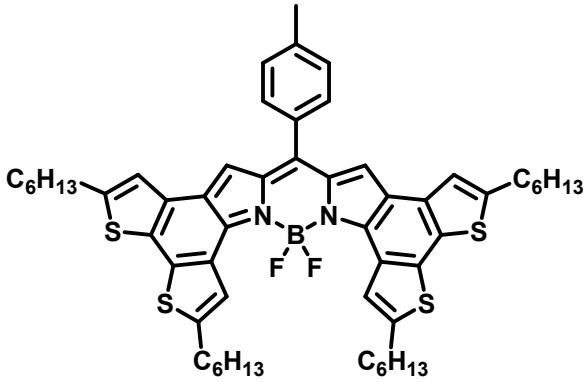
Compound 6βα



Compound **6βα** was synthetized according to *General Procedure 2* starting from compound **5βα** (100 mg, 0.11 mmol). The reaction mixture was stirred 1h at 0°C. Column chromatography (EP/DCM 9:1 to 4:1) followed by recrystallization by diffusion of acetone in a DCM solution afforded the pure compound **6βα** (95mg, 0.104 mmol, 95%) as a dark green solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.29 (s, 2H), 7.62 (d, *J*=7.9 Hz, 2H), 7.44 (d, *J*=7.9 Hz, 2H), 7.18 (s, 2H), 7.09 (s, 2H), 3.04 (t, ^{3}J=7.5 Hz, 4H), 2.91 (t, ^{3}J=7.5 Hz, 4H), 2.56 (s, 3H), 1.90 (quin, ^{3}J=7.5 Hz, 4H), 1.75 (quin, ^{3}J=7.5 Hz, 4H), 1.48-1.56 (m, 4H), 1.27-1.46 (m, 20H), 0.93(t, ^{3}J=7.0 Hz, 6H), 0.90 (t, ^{3}J=6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 146.3, 145.8, 143.3, 140.8, 140.1, 138.2, 132.1, 131.5, 130.8, 129.1, 127.89, 126.9, 125.5, 123.5, 121.2, 119.4, 31.7, 31.6, 31.4, 31.1, 30.8, 30.6, 28.9, 28.74, 22.7, 22.6, 21.5, 14.10, 14.08. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 2.07 (t, $J_{B\text{-}}$

$_F$=33.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ =-141.83 (q, J_{F-B}=32.8 Hz). **HRMS** (ESI-TOF): calcd for $C_{56}H_{65}BF_2N_2S_4$ $[M]^+$: 942.4096; found: 942.4133.

Compound 6ββ



Compound **6ββ** was synthetized according to *General Procedure 2* starting from compound **5ββ** (50.0 mg, 0.0528 mmol, 1.0 eq). The reaction mixture was stirred 2h at 0°C. Column chromatography (EP/DCM 4:1) followed by recrystallization by diffusion of acetone in a DCM solution afforded the pure compound **6ββ** (33.1mg, 0.0351 mmol, 66%) as a dark blue solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.28 (s, 2H), 7.62 (d, 2H, ^{3}J=8.0Hz), 7.42 (d, 2H, ^{3}J=8.0Hz), 7.28 (s, 2H), 7.17 (s, 2H), 3.03 (t, 4H, ^{3}J=7.5Hz), 2.89 (t, 4H, ^{3}J=7.5Hz), 2.56 (s, 3H), 1.85-1.93 (m, 4H), 1.71-1.78 (m, 4H), 1.35-1.44 (m, 12H), 1.27-1.35 (m, 12H), 0.86-0.94 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 146.5, 146.1, 145.9, 143.2, 140.7, 139.2, 138.3, 132.3, 131.6, 130.8, 129.2, 128.7, 125.9, 125.2, 123.6, 122.6, 120.3, 31.9, 31.7, 31.4, 31.2, 31.0, 30.8, 29.1, 28.9, 22.8, 22.7, 14.3, 14.2. **^{11}B NMR** (128 MHz, $CDCl_3$): δ = 2.12 (t, J_{B-F} = 33.0Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -141.6 (q, J_{F-B}=32.9Hz). **HRMS** (ESI-TOF): calcd for $C_{56}H_{65}BF_2N_2S_4$ $[M]^+$: 942.4092; found: 942.4158.

NMR traces

Figure S1: ^{1}H-NMR trace of compound **1** (400 MHz, $CDCl_3$, 298K)

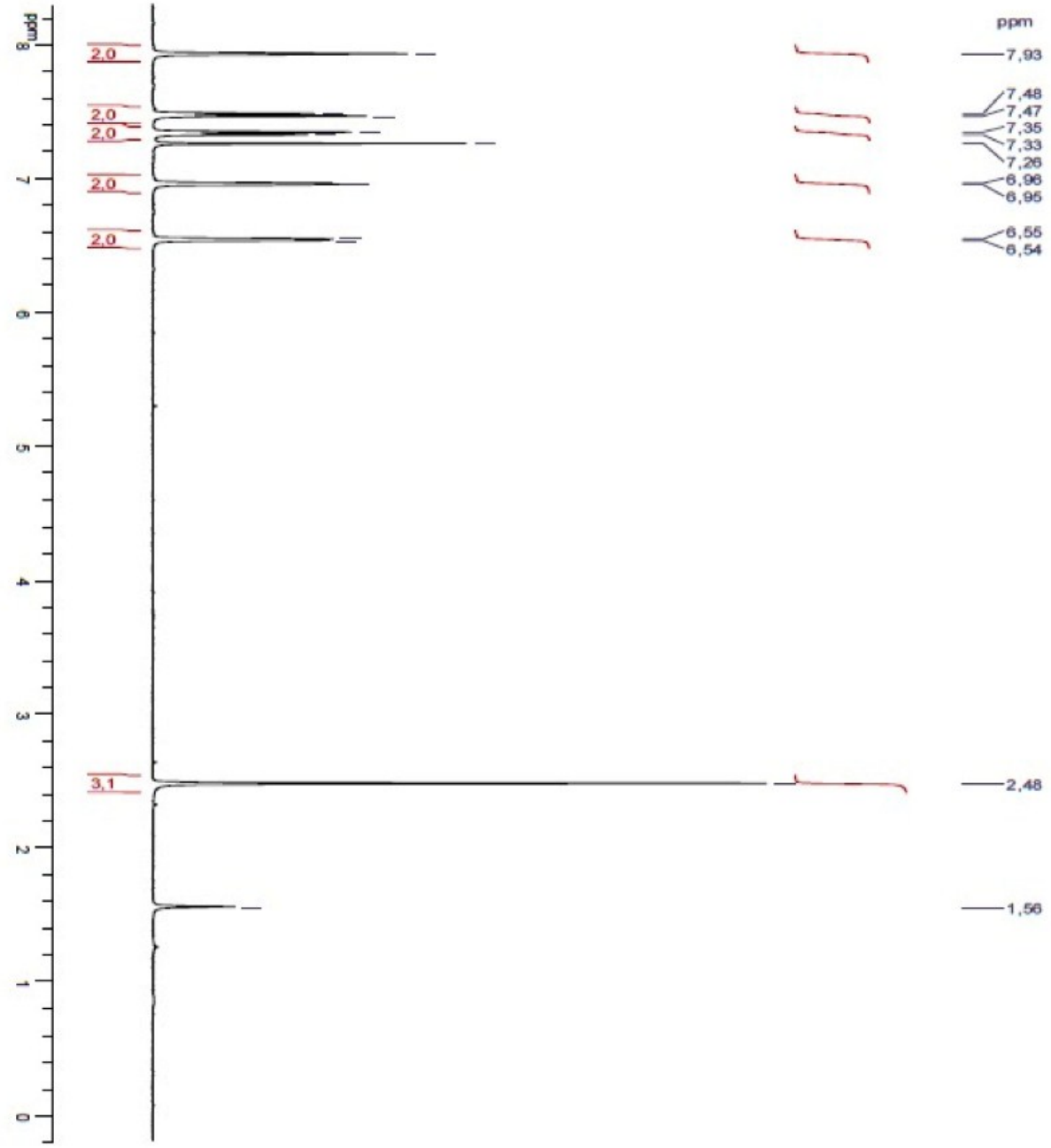


Figure S2: ^{13}C-NMR trace of compound **1** (100 MHz, $CDCl_3$, 298K)

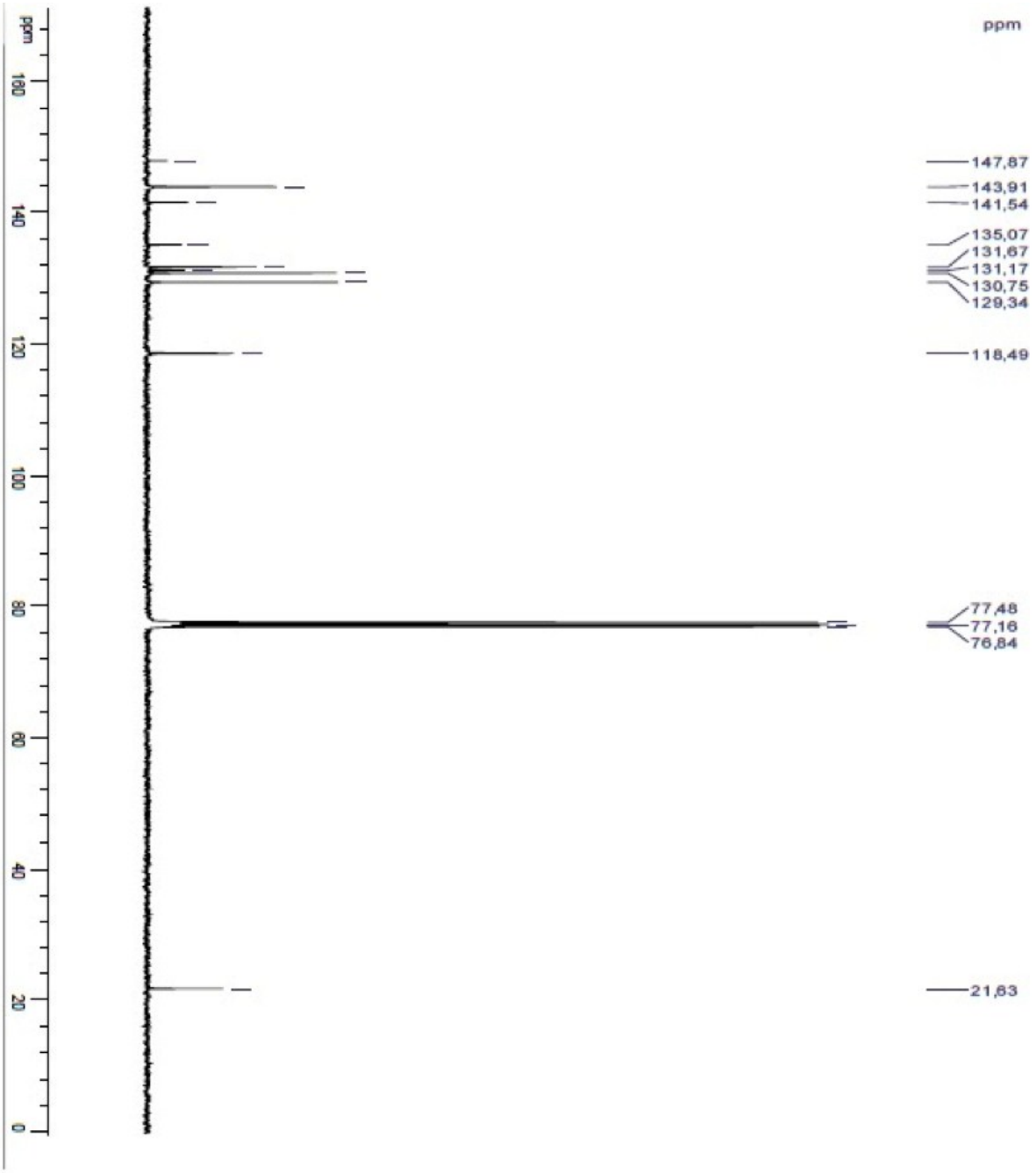


Figure S3: ^{1}H-NMR trace of compound **2** (400 MHz, $CDCl_3$, 298K)

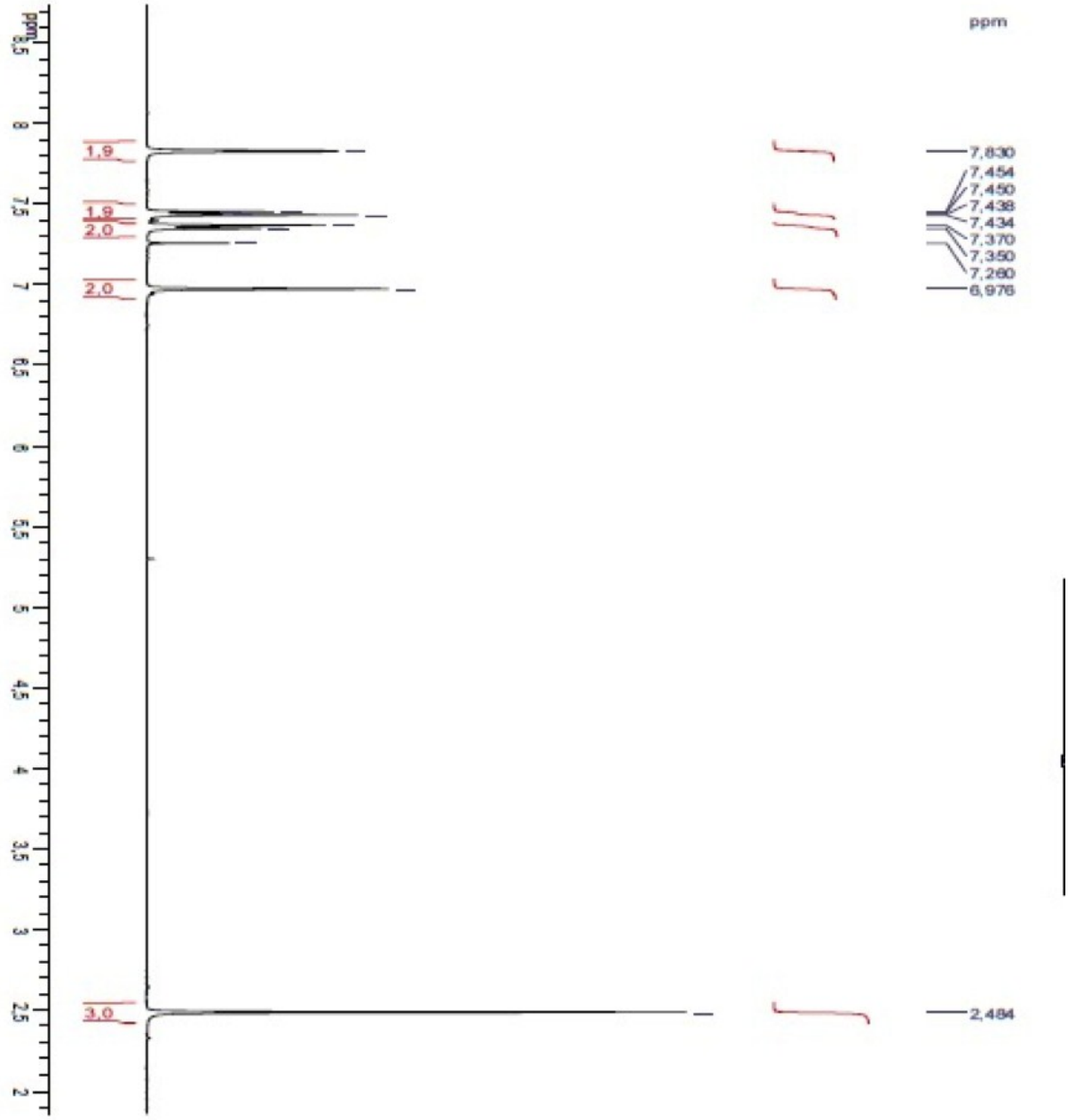


Figure S4: ^{13}C-NMR trace of compound **2** (100 MHz, $CDCl_3$, 298K)

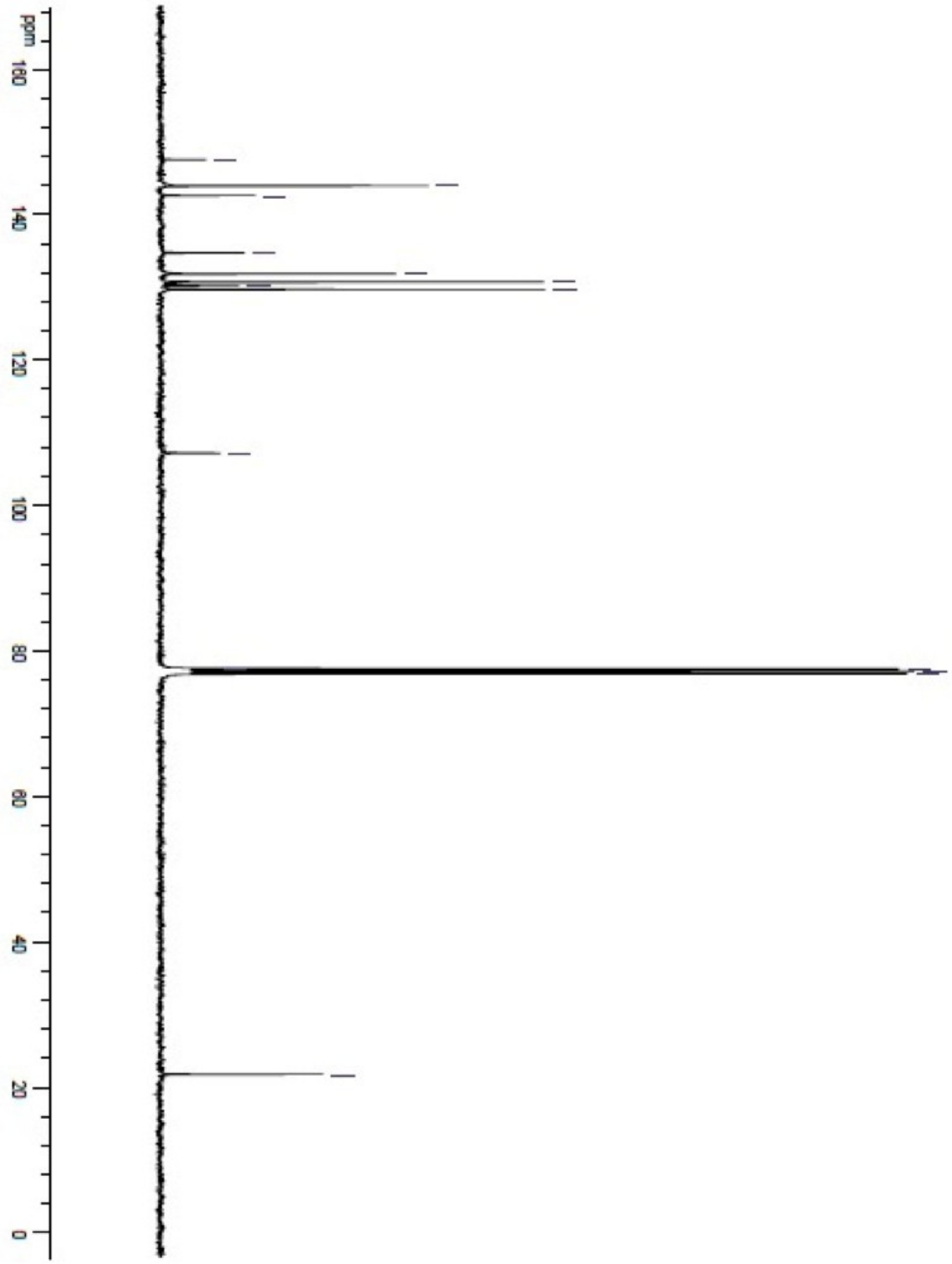


Figure S5: ^{1}H-NMR trace of compound **3** (400 MHz, $CDCl_3$, 298K)

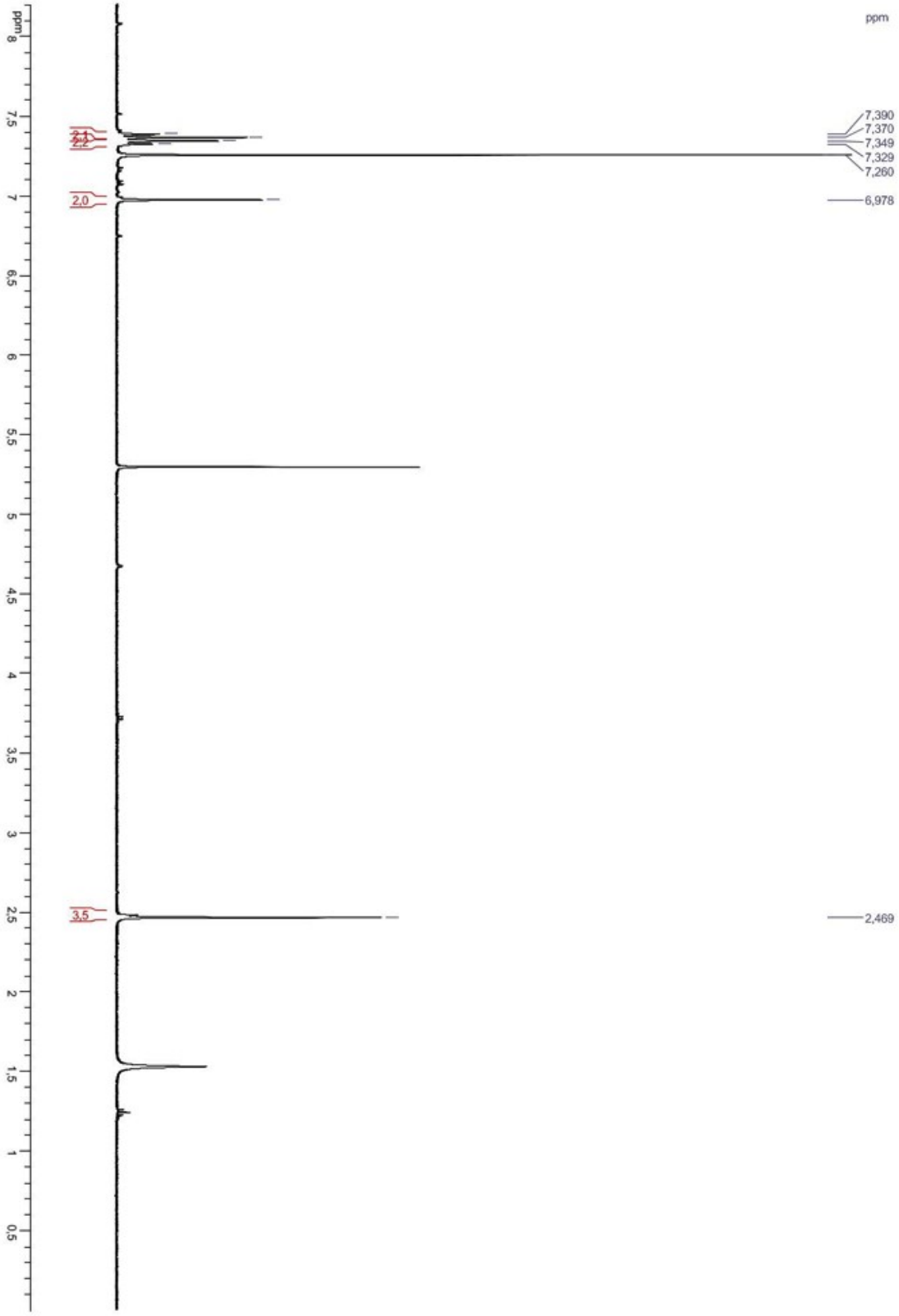


Figure S6: ^{11}B-NMR trace of compound **3** (128 MHz, $CDCl_3$, 298K)

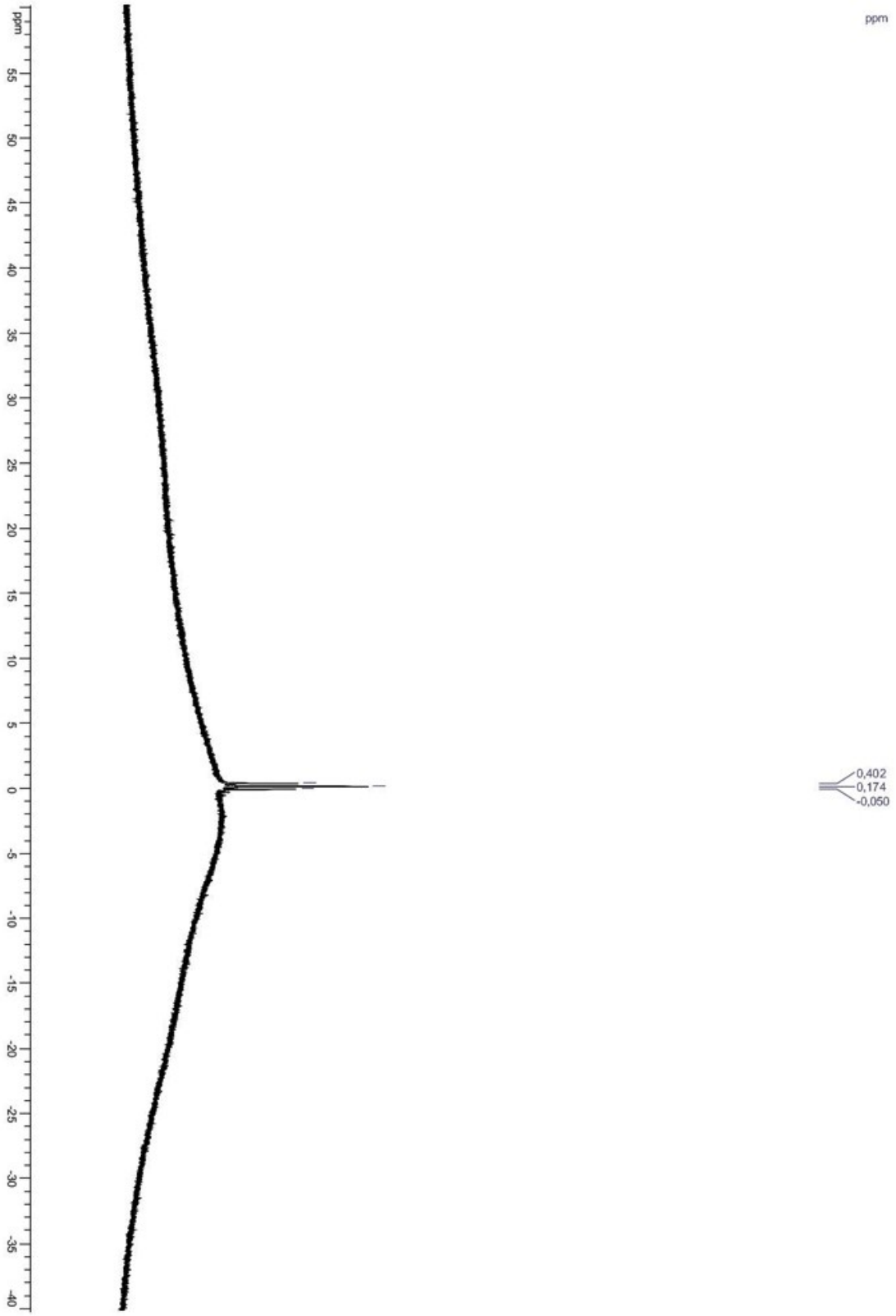


Figure S7: ^{13}C-NMR trace of compound **3** (100 MHz, $CDCl_3$, 298K)

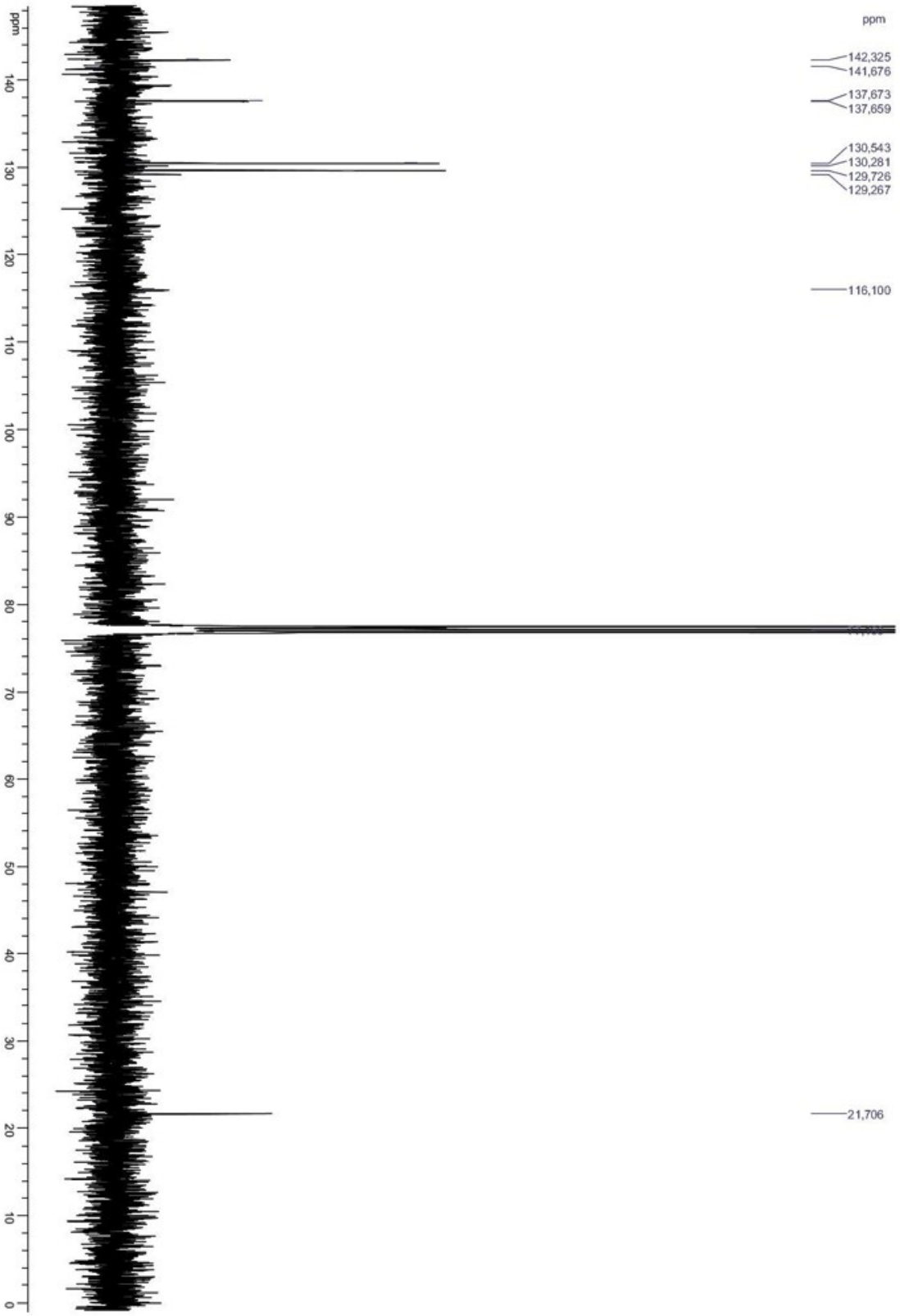


Figure S8: ^{19}F-NMR trace of compound **3** (376 MHz, $CDCl_3$, 298K)

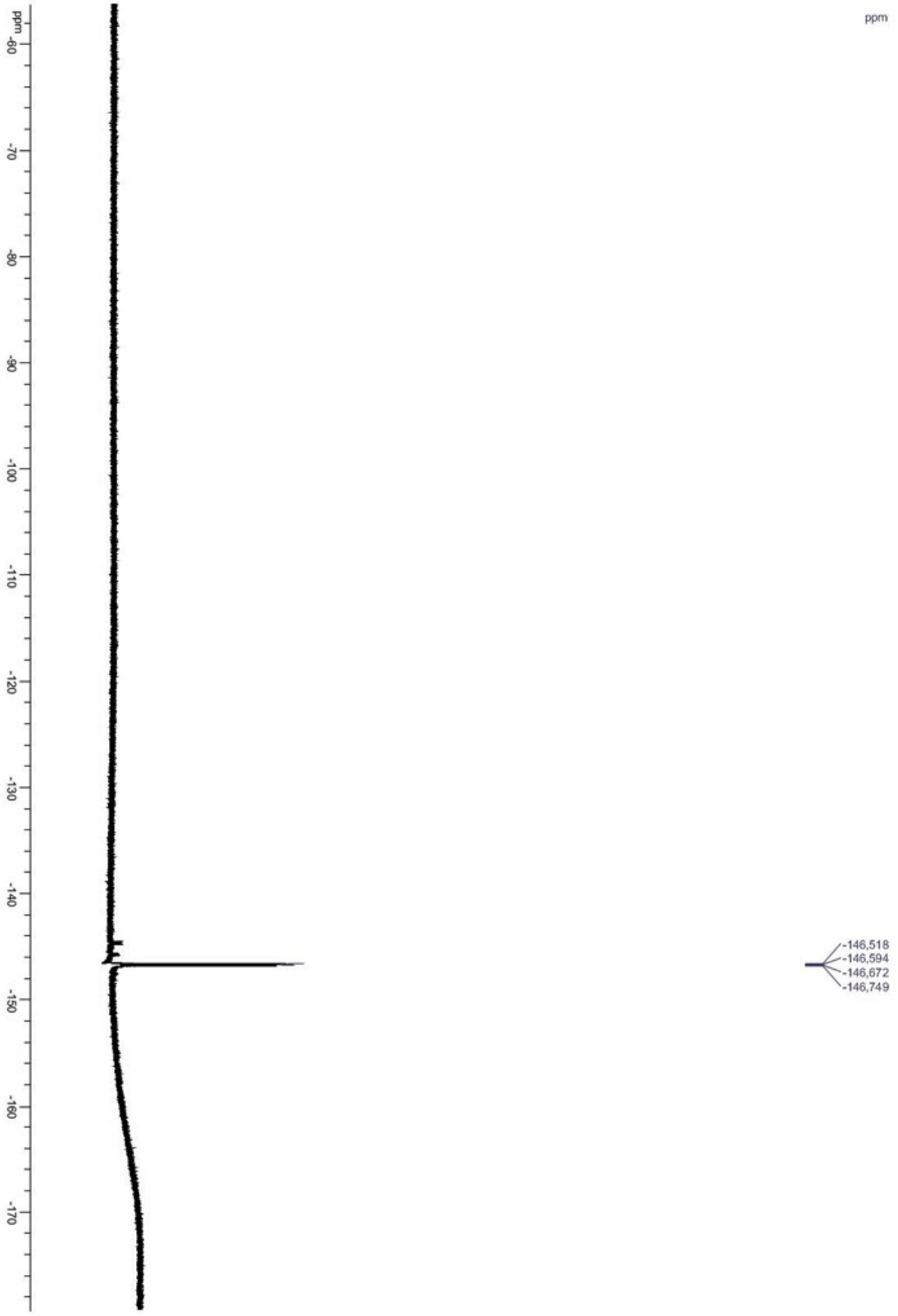


Figure S9: ^{1}H-NMR trace of compound **4α** (400 MHz, $CDCl_3$, 298K)

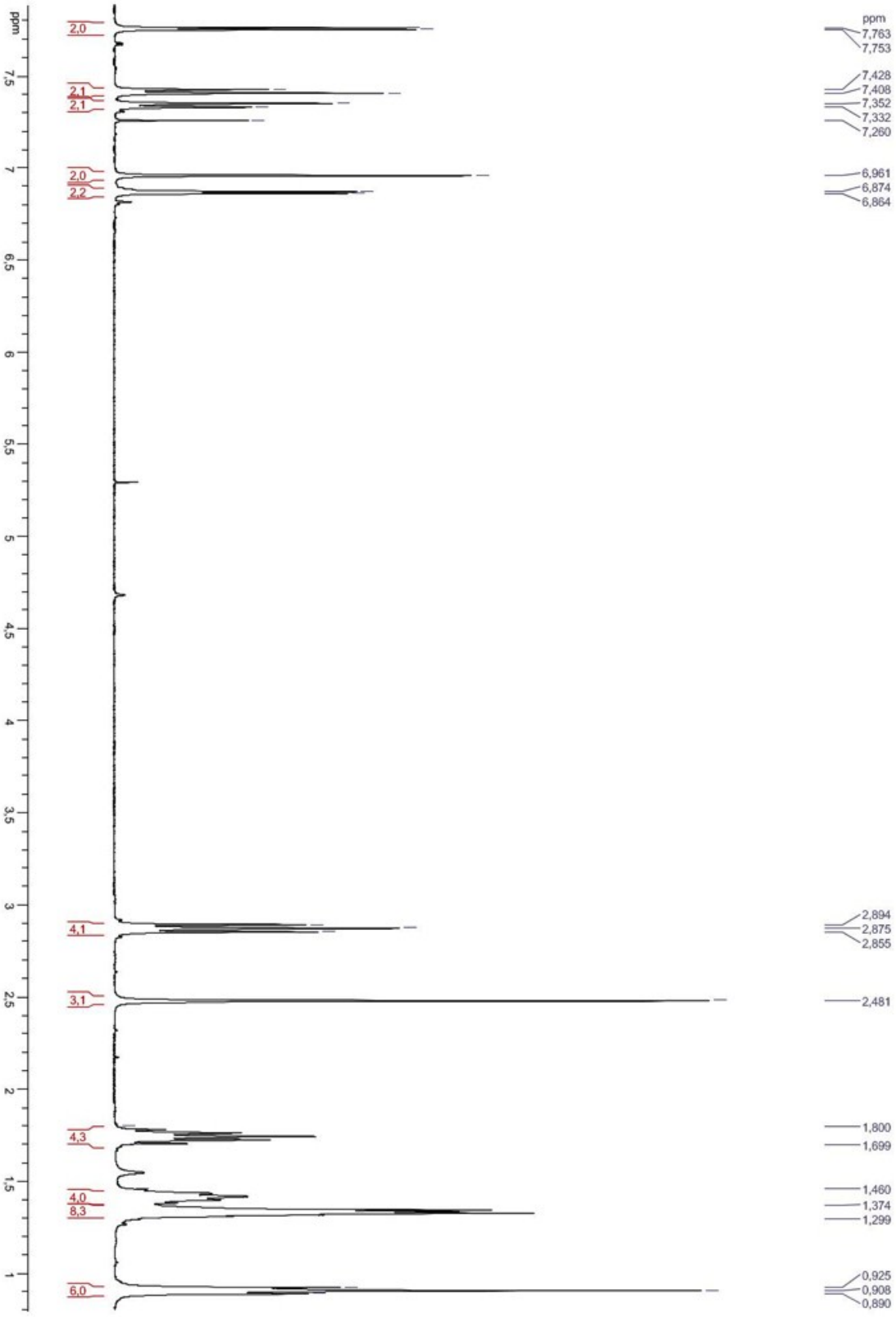


Figure S10: ^{11}B-NMR trace of compound **4α** (128 MHz, $CDCl_3$, 298K)

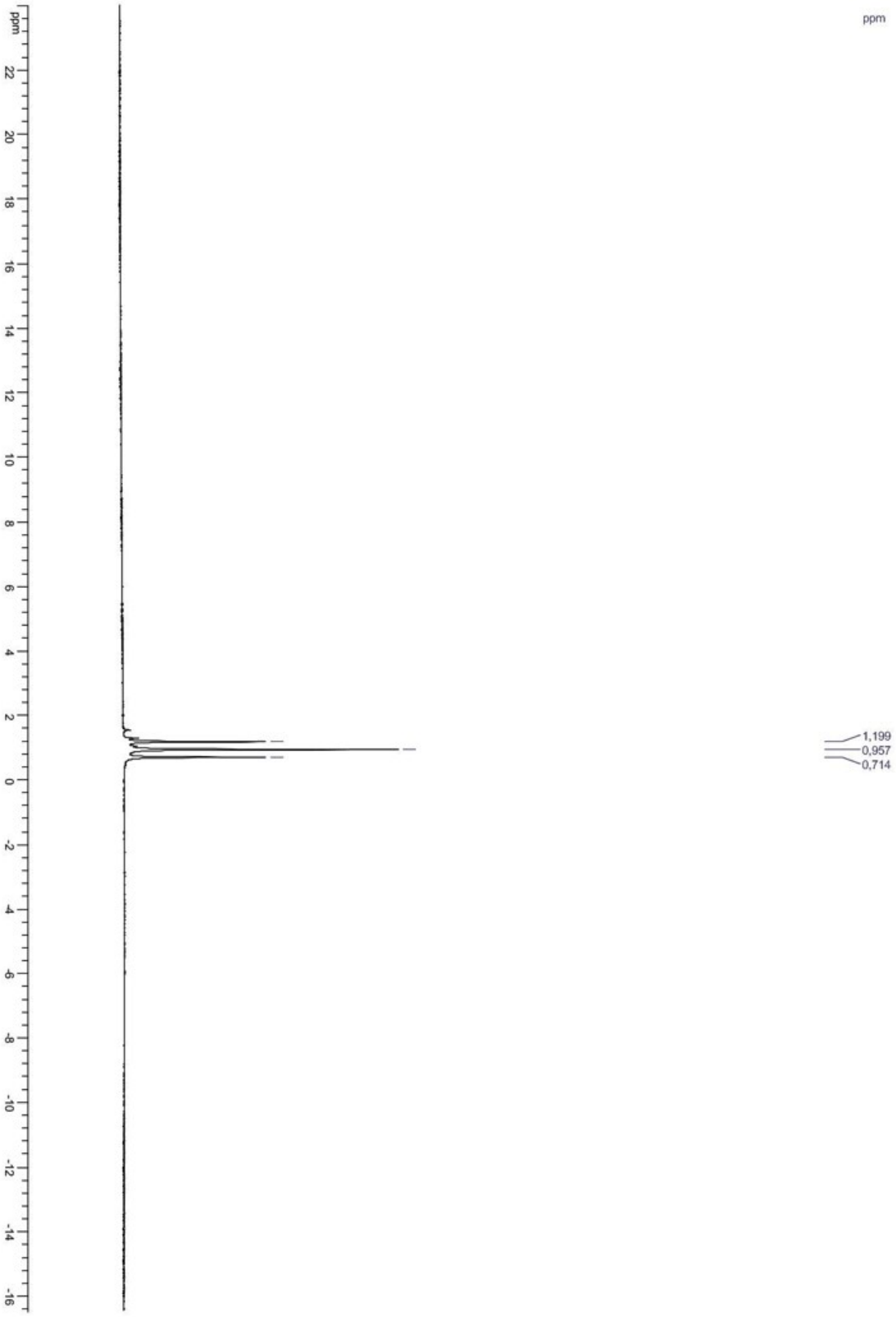


Figure S11: ^{13}C-NMR trace of compound **4α** (100 MHz, $CDCl_3$, 298K)

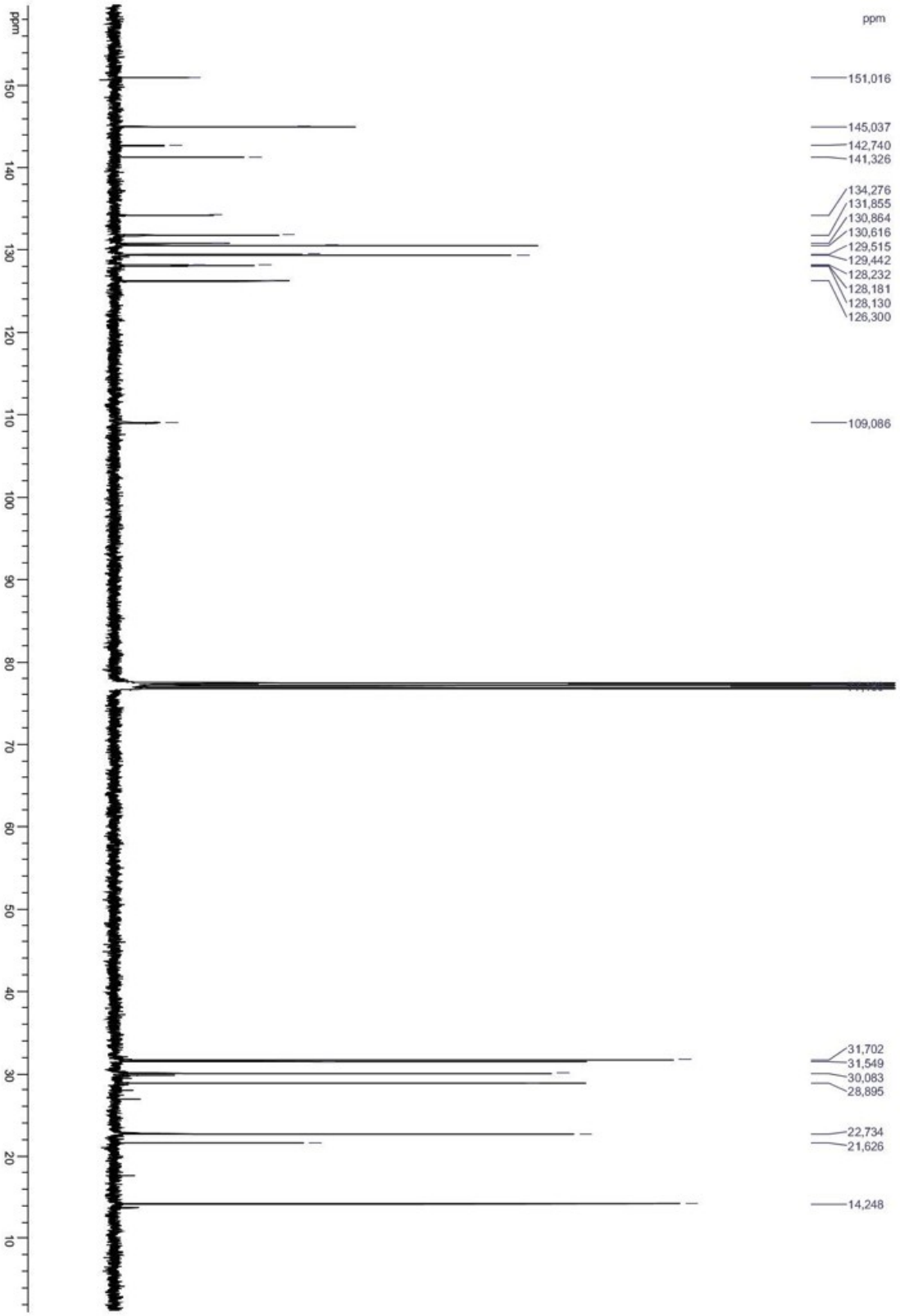


Figure S12: ^{19}F-NMR trace of compound **4α** (376 MHz, $CDCl_3$, 298K)

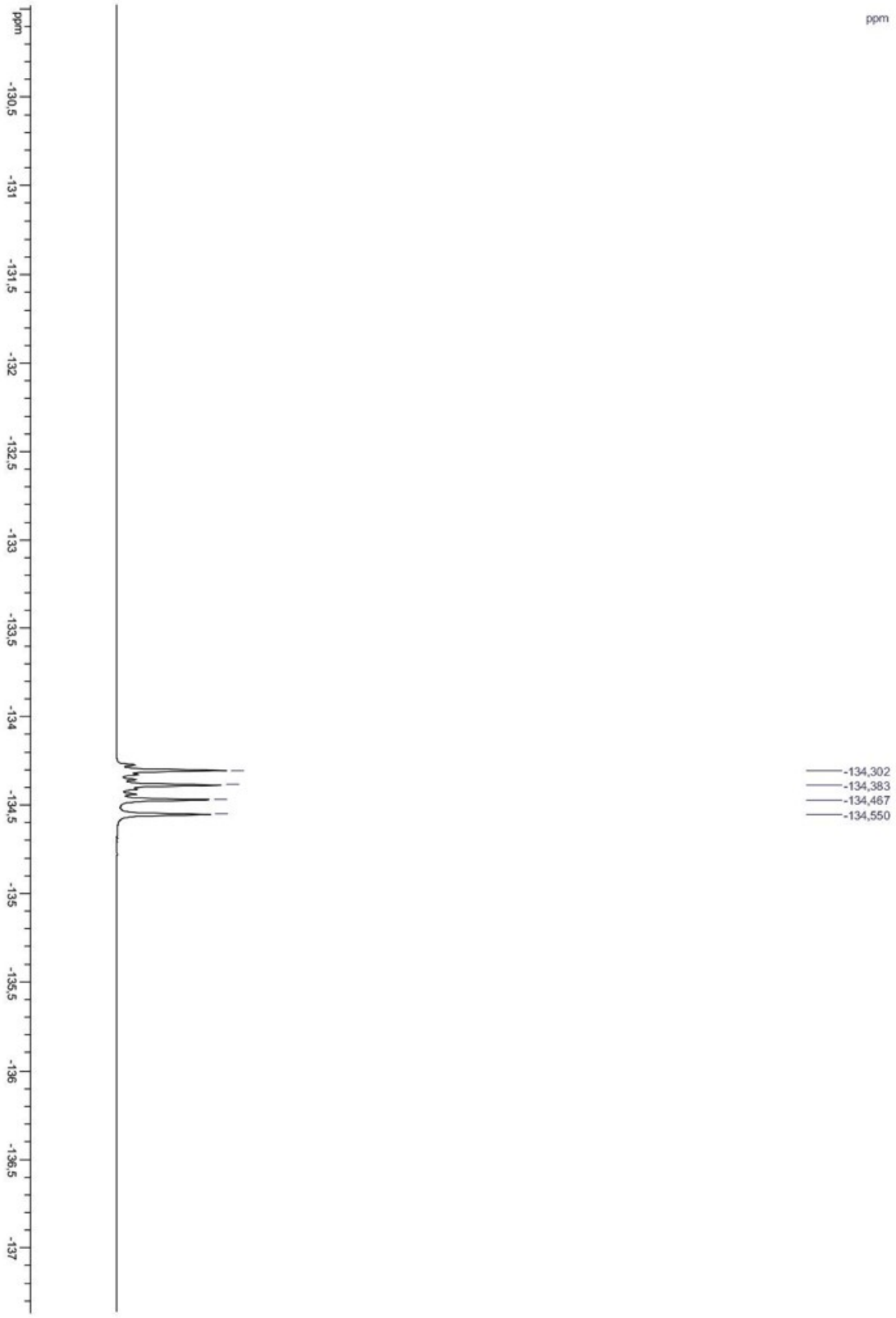


Figure S13: ^{1}H-NMR trace of compound **4β** (400 MHz, $CDCl_3$, 298K)

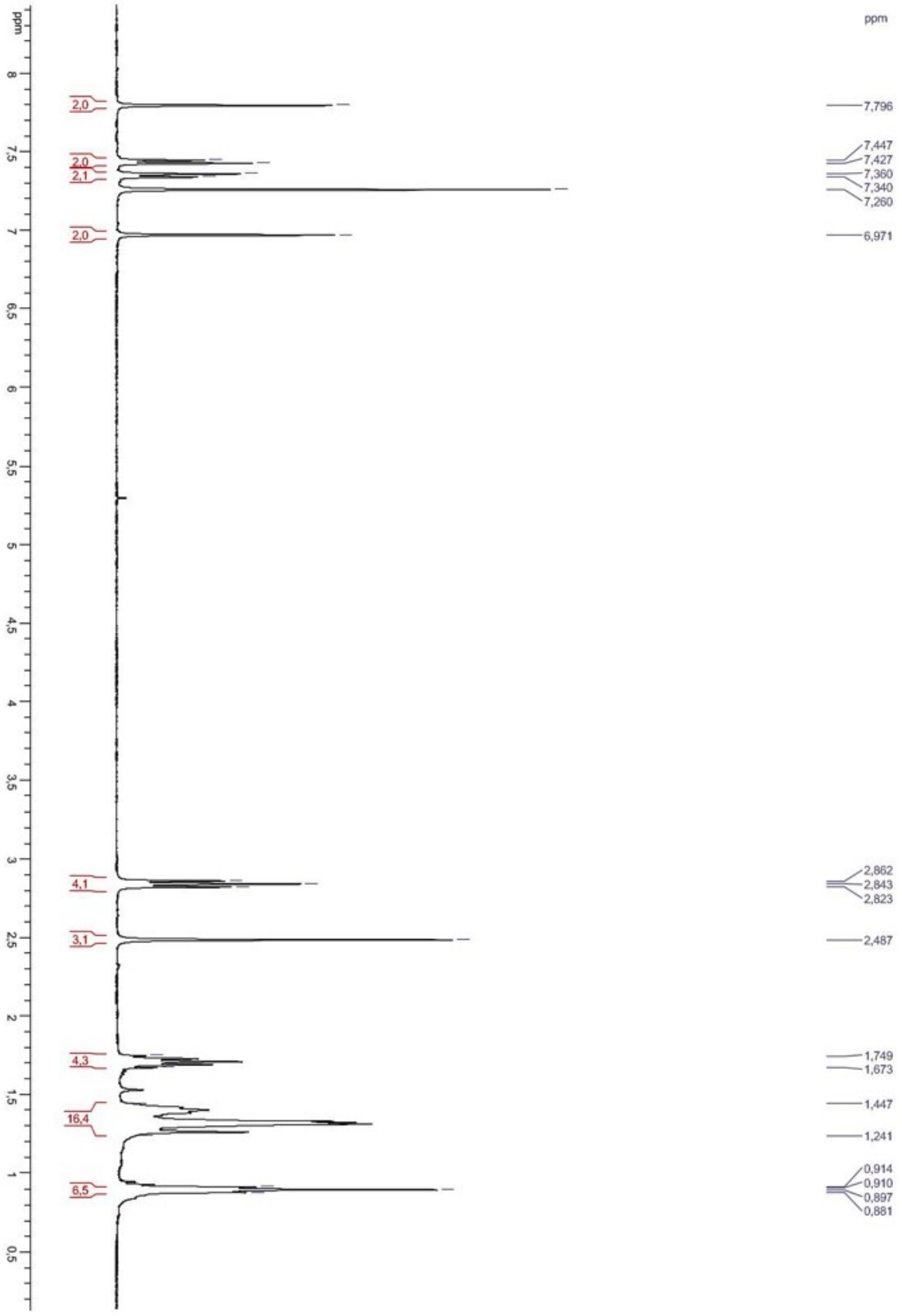


Figure S14: ^{11}B-NMR trace of compound **4β** (128 MHz, $CDCl_3$, 298K)

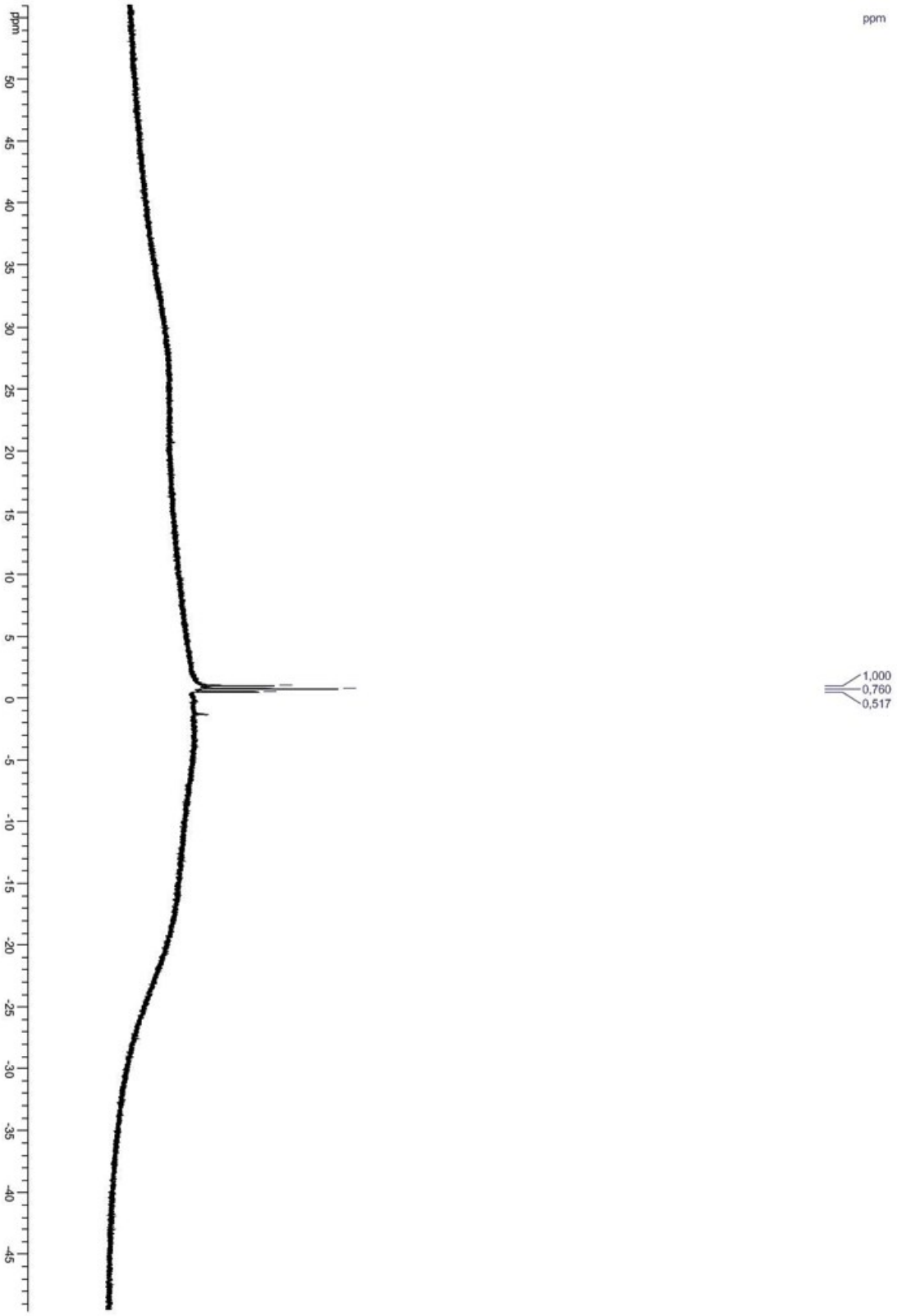


Figure S15: ^{13}C-NMR trace of compound **4β** (100 MHz, $CDCl_3$, 298K)

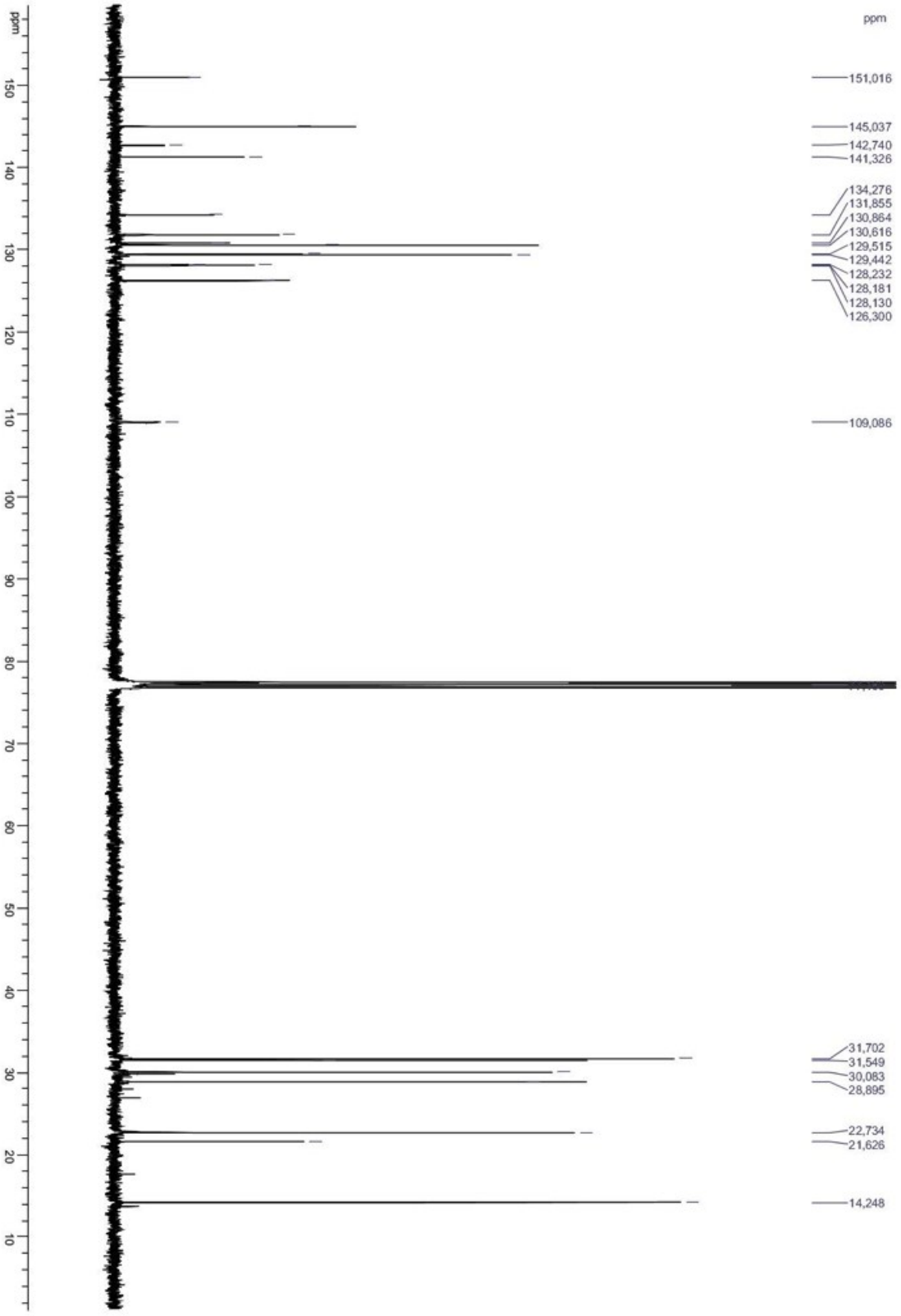


Figure S16: ^{19}F-NMR trace of compound **4β** (376 MHz, $CDCl_3$, 298K)

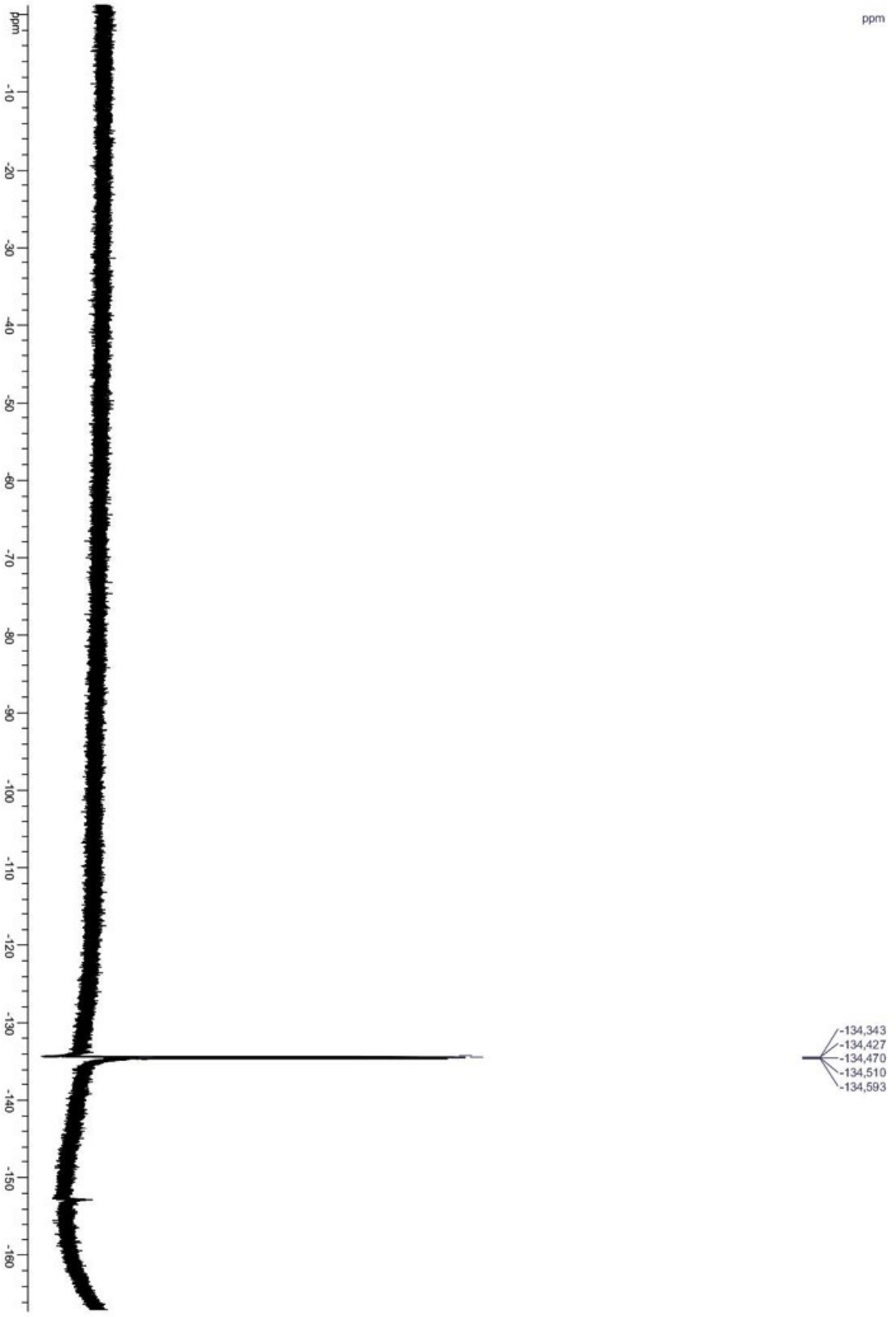


Figure S17: ^{1}H-NMR trace of compound **5αα** (400 MHz, $CDCl_3$, 298K)

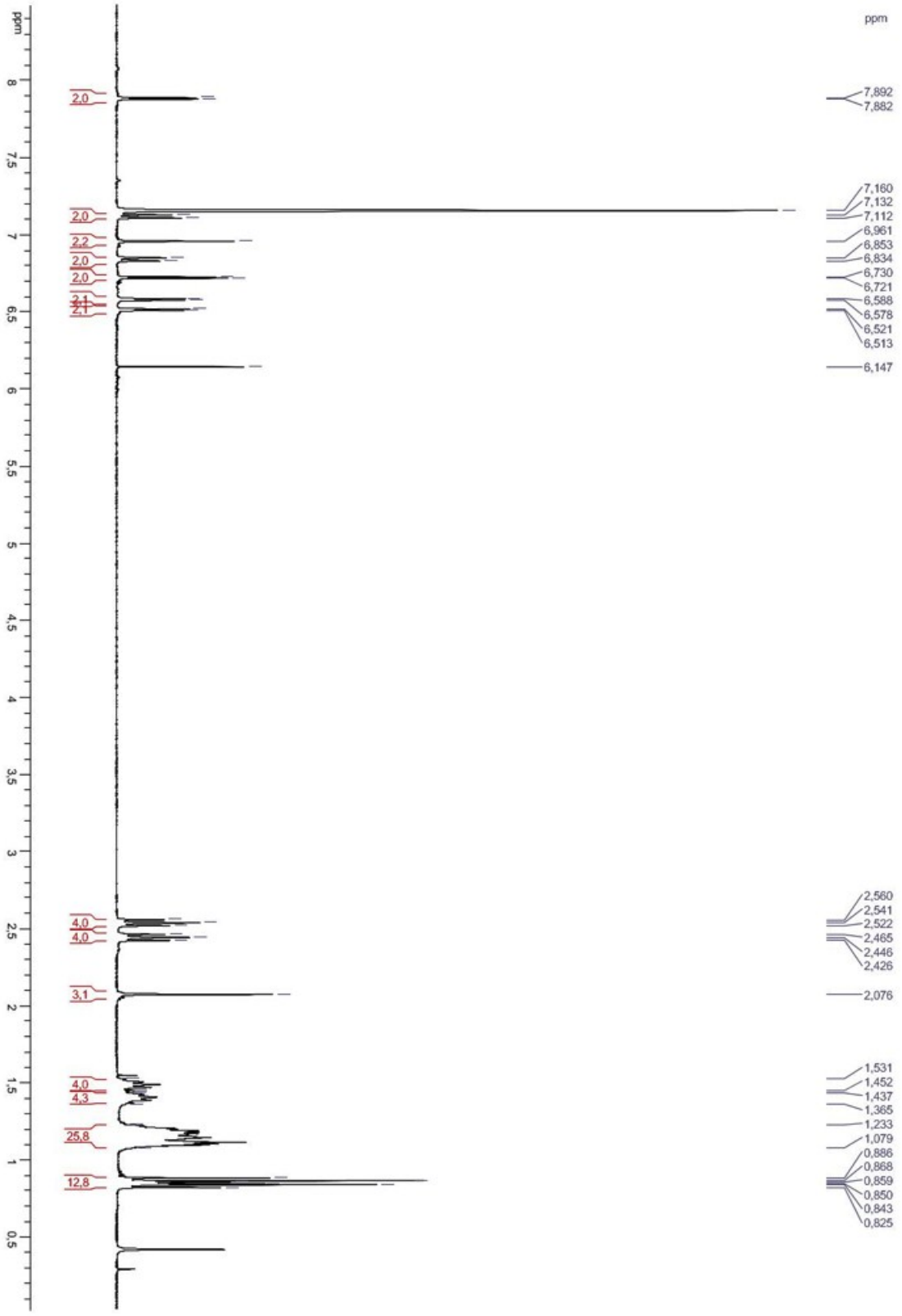


Figure S18: ^{11}B-NMR trace of compound **5αα** (128 MHz, $CDCl_3$, 298K)

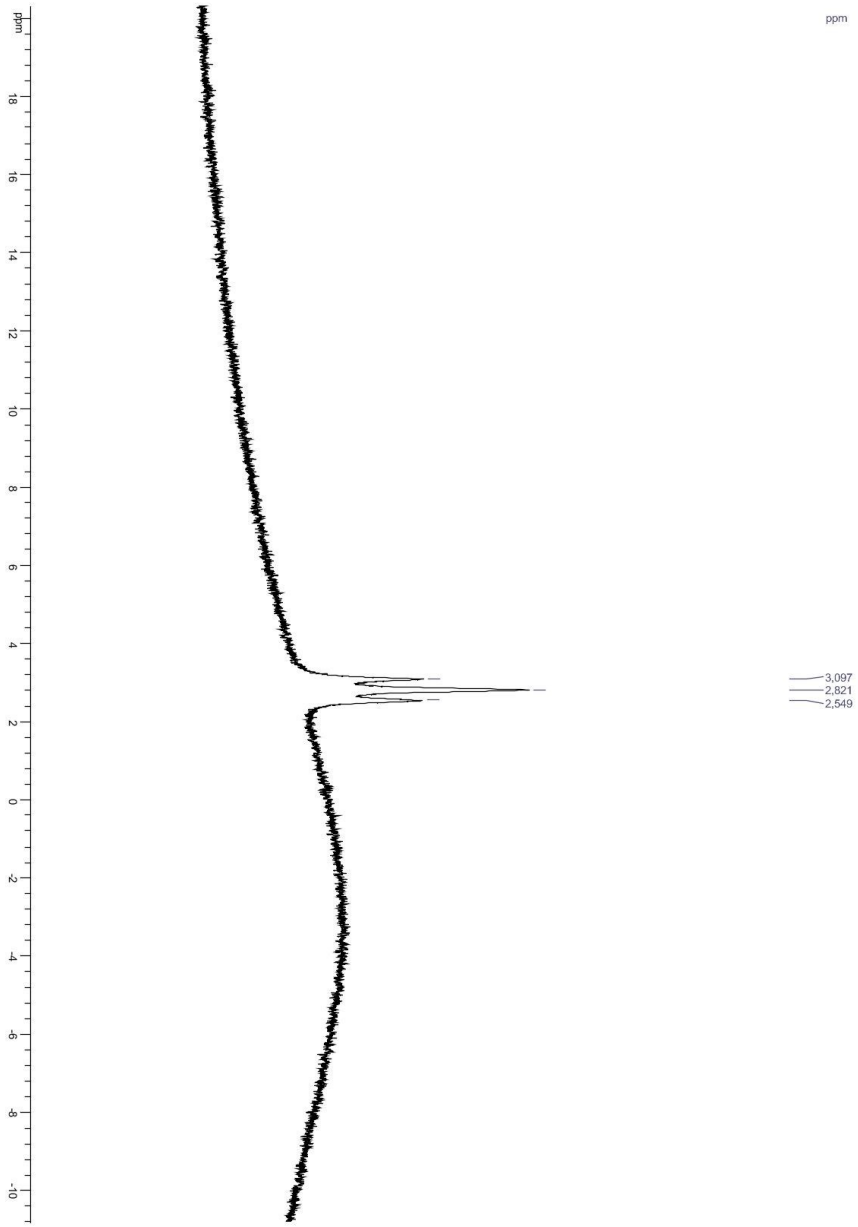


Figure S19: ^{13}C-NMR trace of compound **5αα** (100 MHz, $CDCl_3$, 298K)

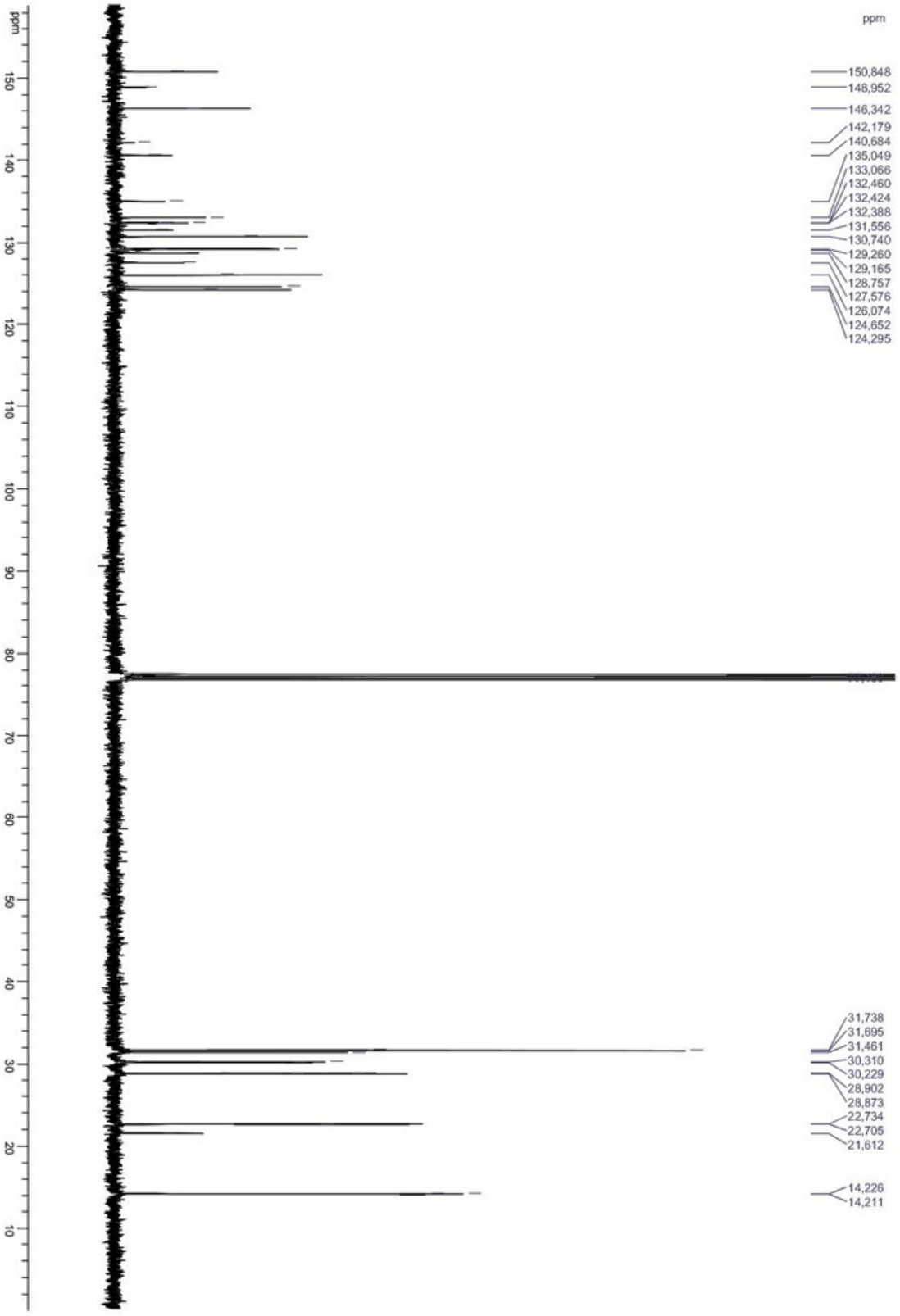


Figure S20: ^{19}F-NMR trace of compound **5αα** (376 MHz, $CDCl_3$, 298K)

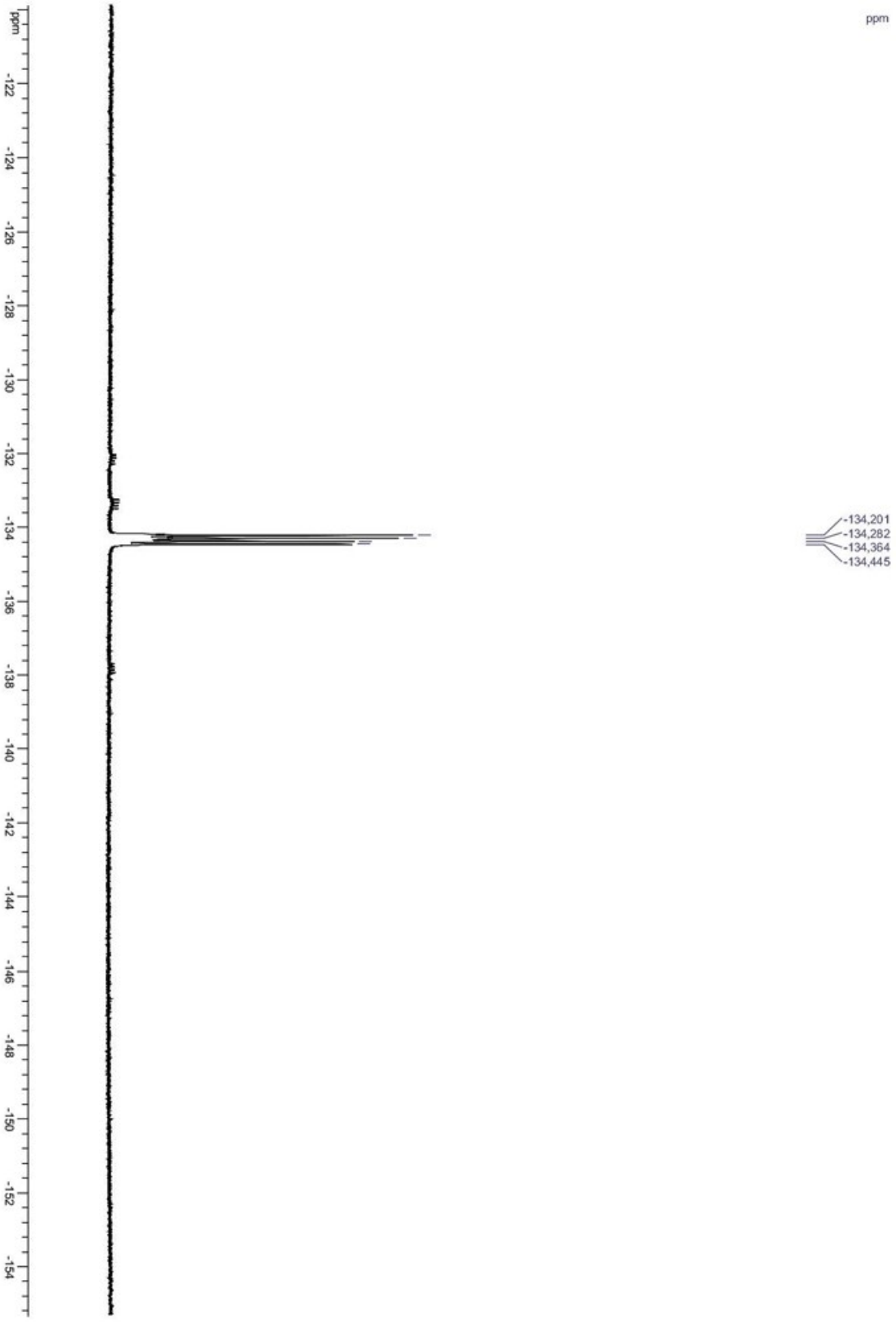


Figure S21: ^{1}H-NMR trace of compound **5αβ** (400 MHz, $CDCl_3$, 298K)

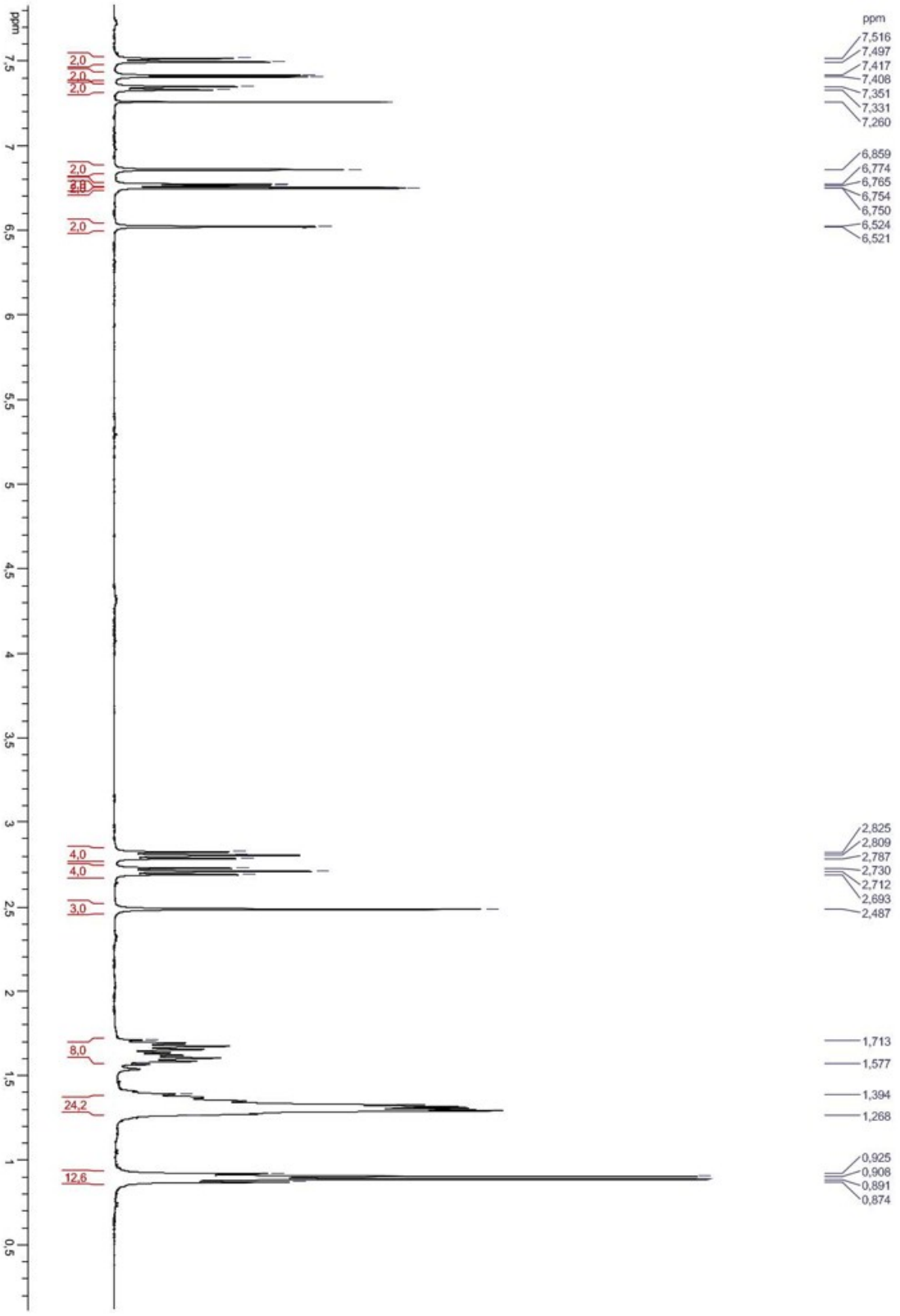


Figure S22: ^{11}B-NMR trace of compound **5αβ** (128 MHz, $CDCl_3$, 298K)

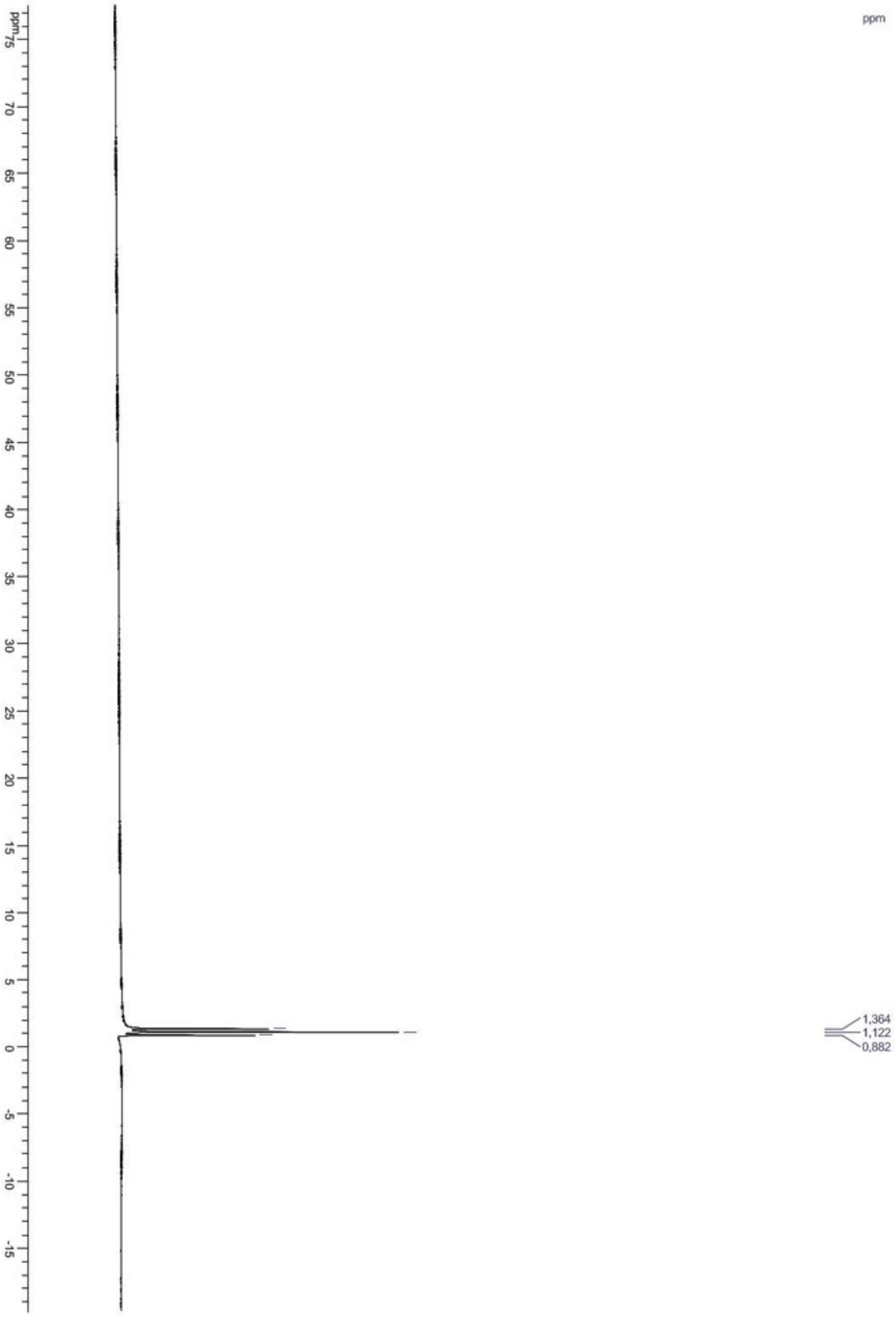


Figure S23: ^{13}C-NMR trace of compound **5αβ** (100 MHz, $CDCl_3$, 298K)

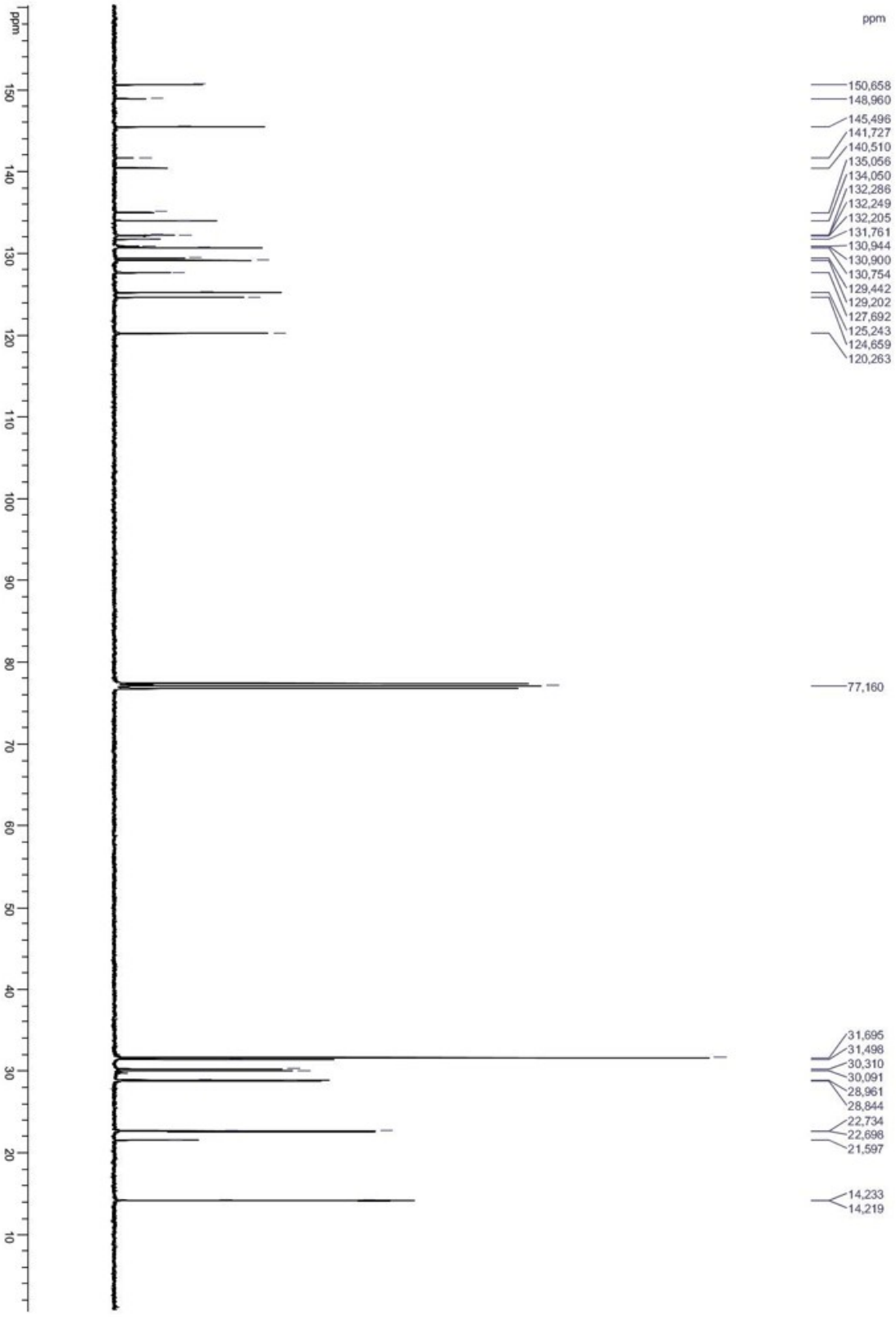


Figure S24: ^{19}F-NMR trace of compound **5αβ** (376 MHz, $CDCl_3$, 298K)

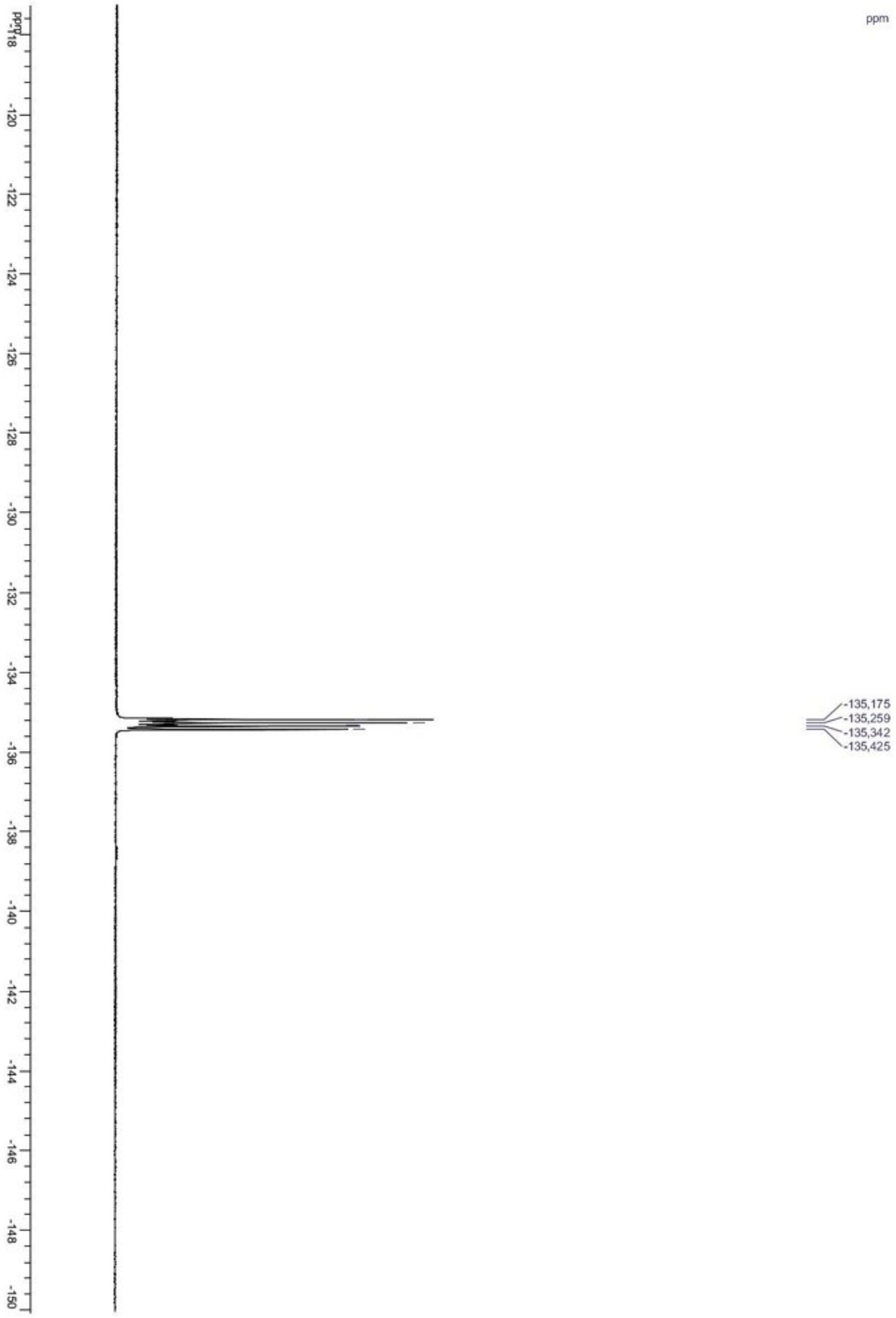


Figure S25: ^{1}H-NMR trace of compound **5βα** (400 MHz, $CDCl_3$, 298K)

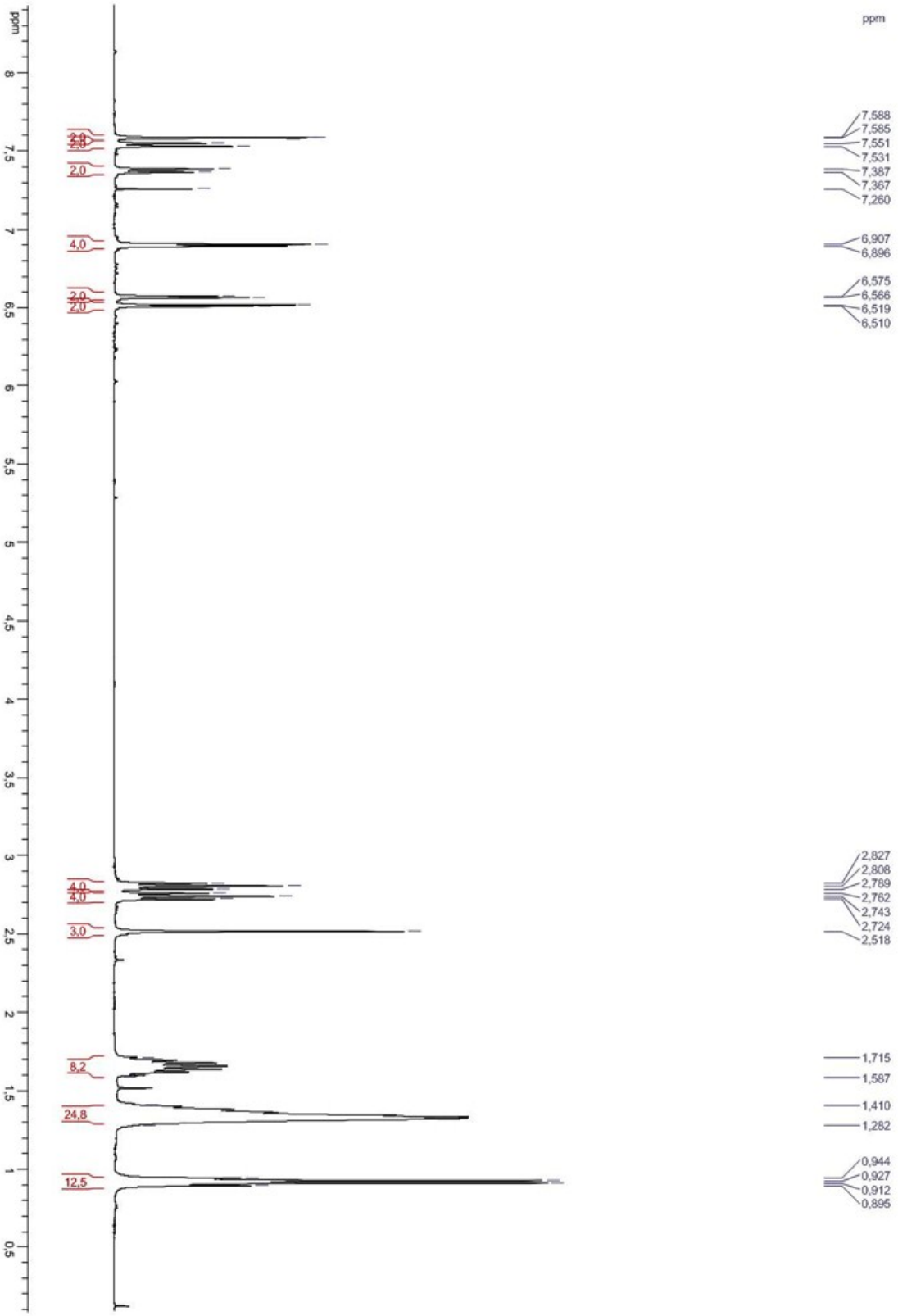


Figure S26: ^{11}B-NMR trace of compound **5βα** (128 MHz, $CDCl_3$, 298K)

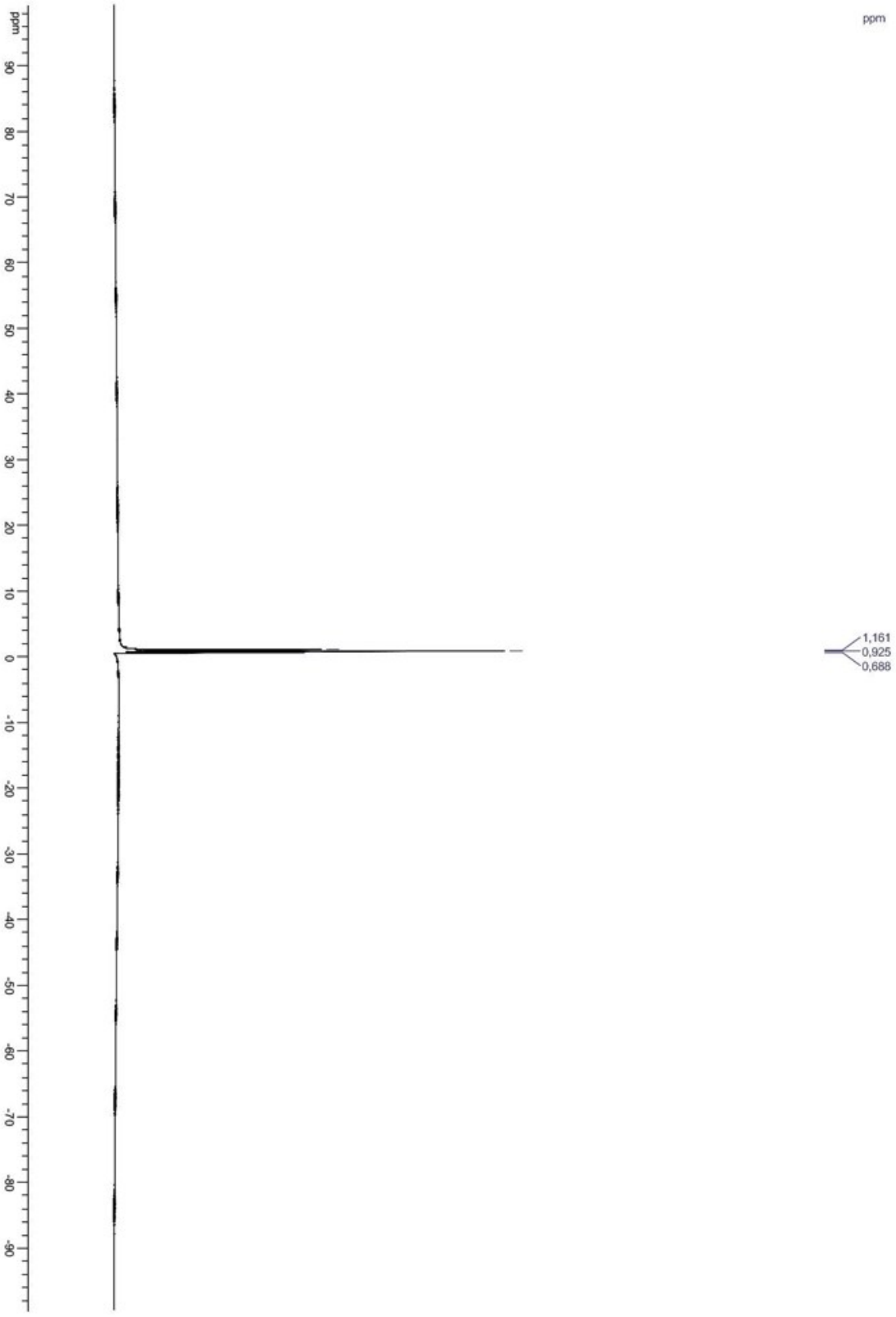


Figure S27: ^{13}C-NMR trace of compound **5βα** (100 MHz, $CDCl_3$, 298K)

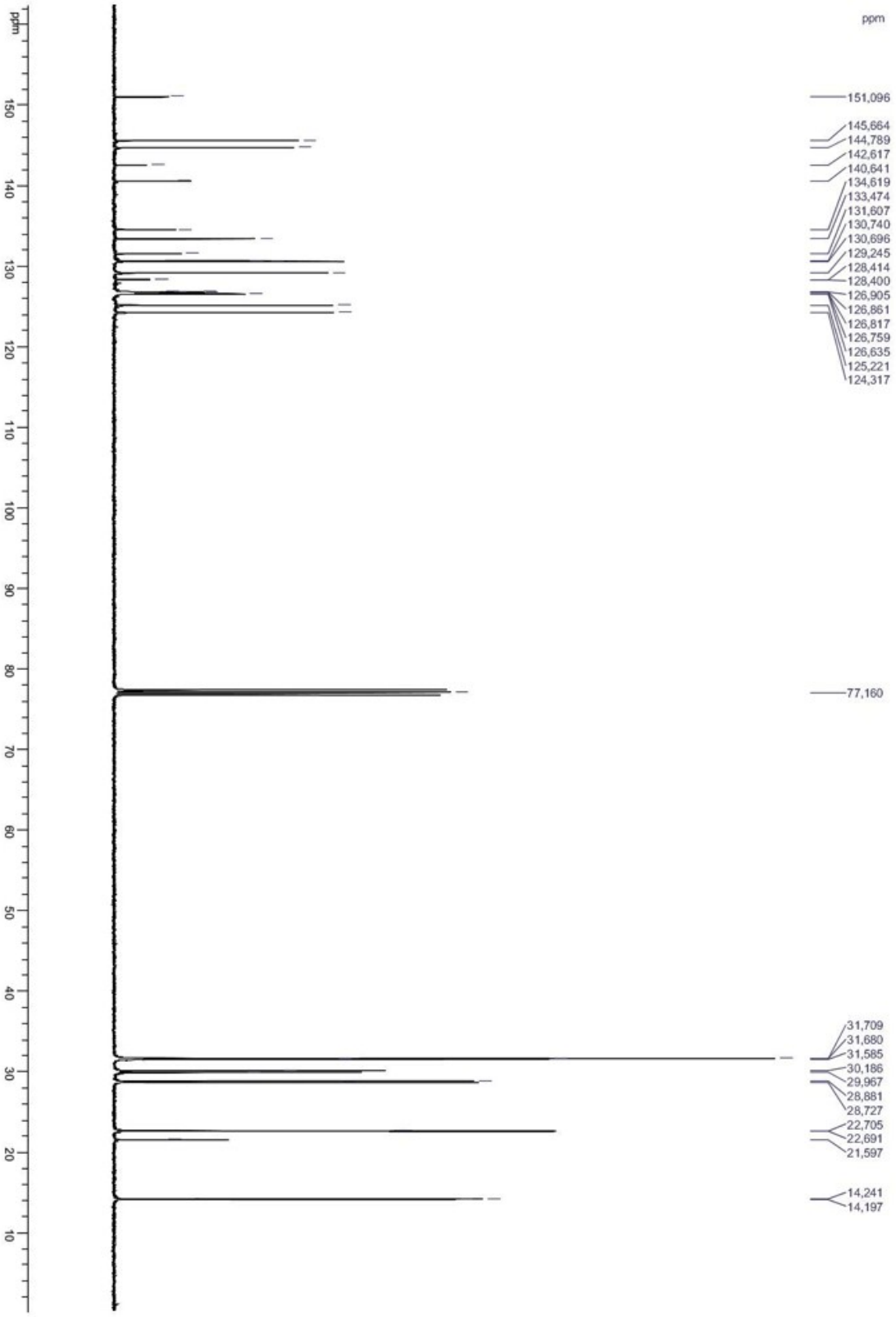


Figure S28: ^{19}F-NMR trace of compound **5βα** (376 MHz, $CDCl_3$, 298K)

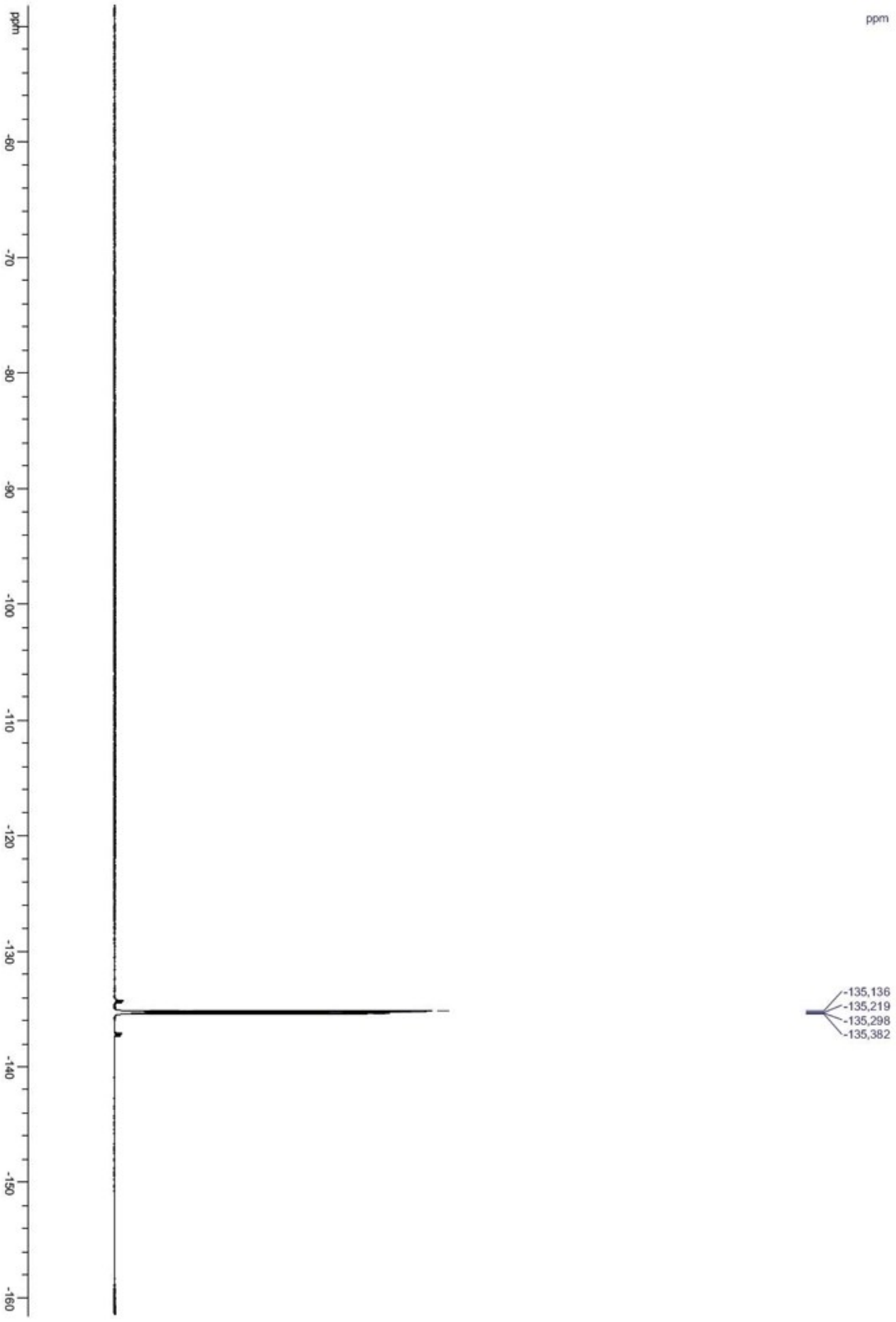


Figure S29: ^{1}H-NMR trace of compound **5ββ** (400 MHz, $CDCl_3$, 298K)

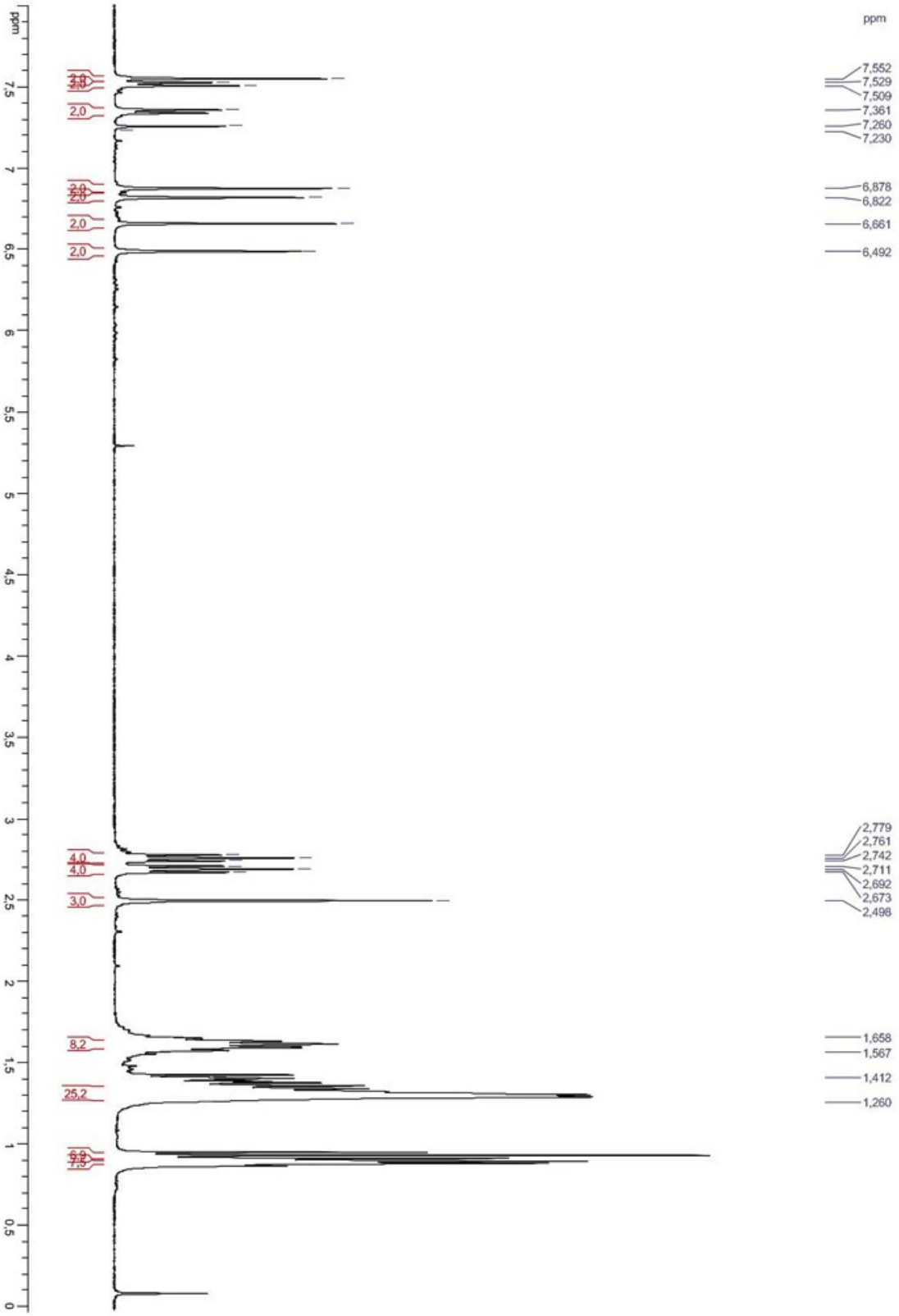


Figure S30: ^{11}B-NMR trace of compound **5ββ** (128 MHz, $CDCl_3$, 298K)

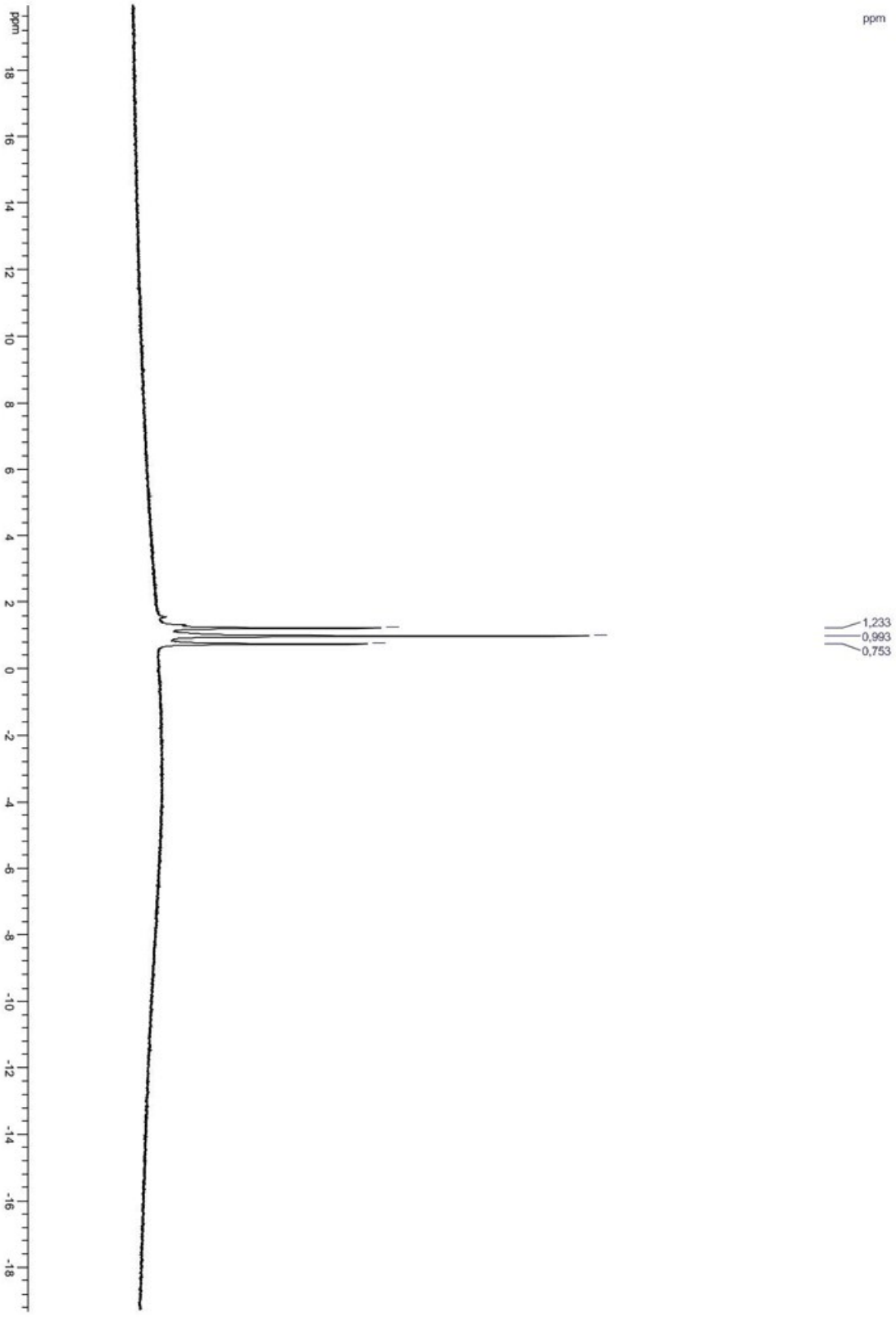


Figure S31: ^{13}C-NMR trace of compound **5ββ** (100 MHz, $CDCl_3$, 298K)

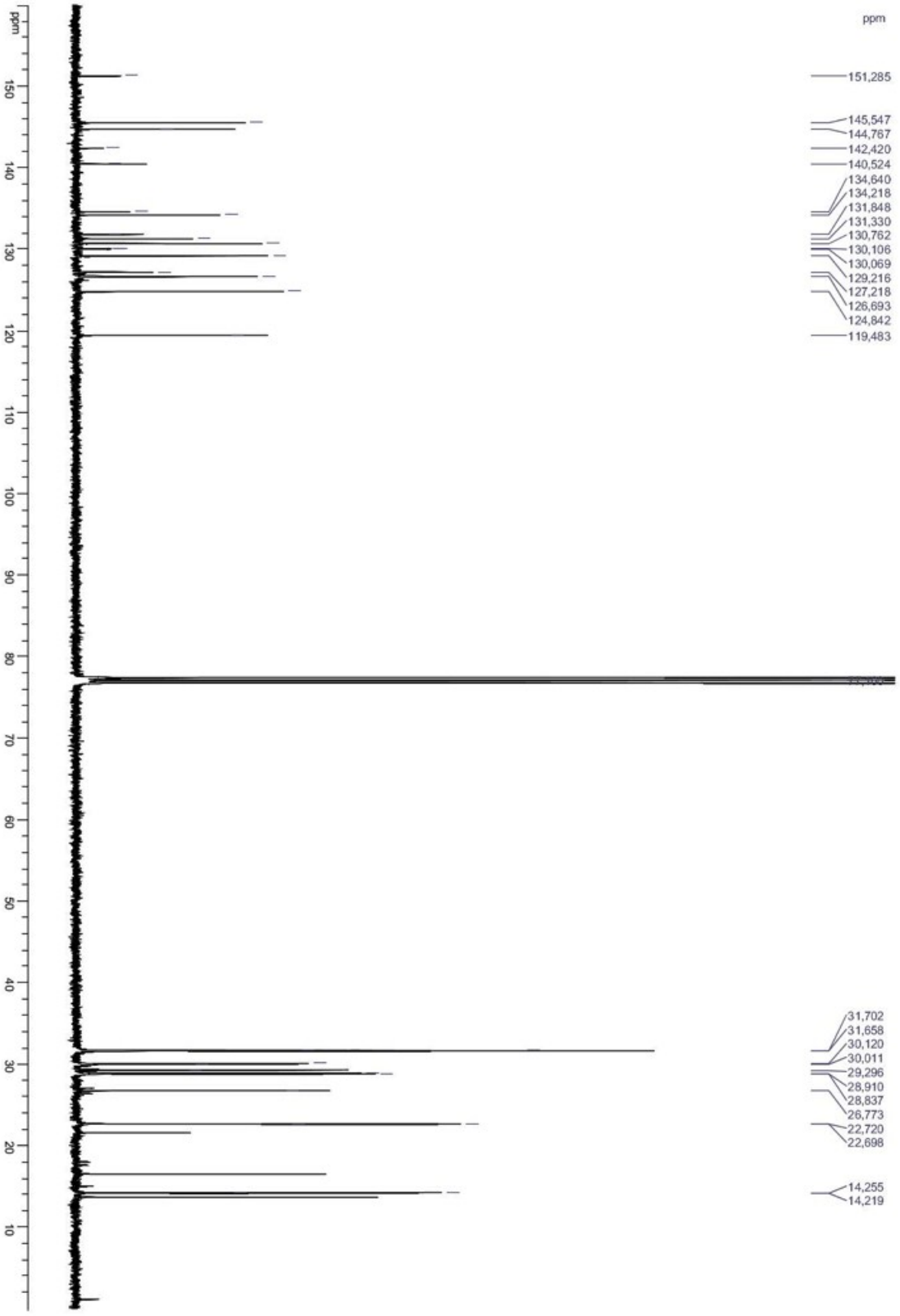


Figure S32: ^{19}F-NMR trace of compound **5ββ** (376 MHz, $CDCl_3$, 298K)

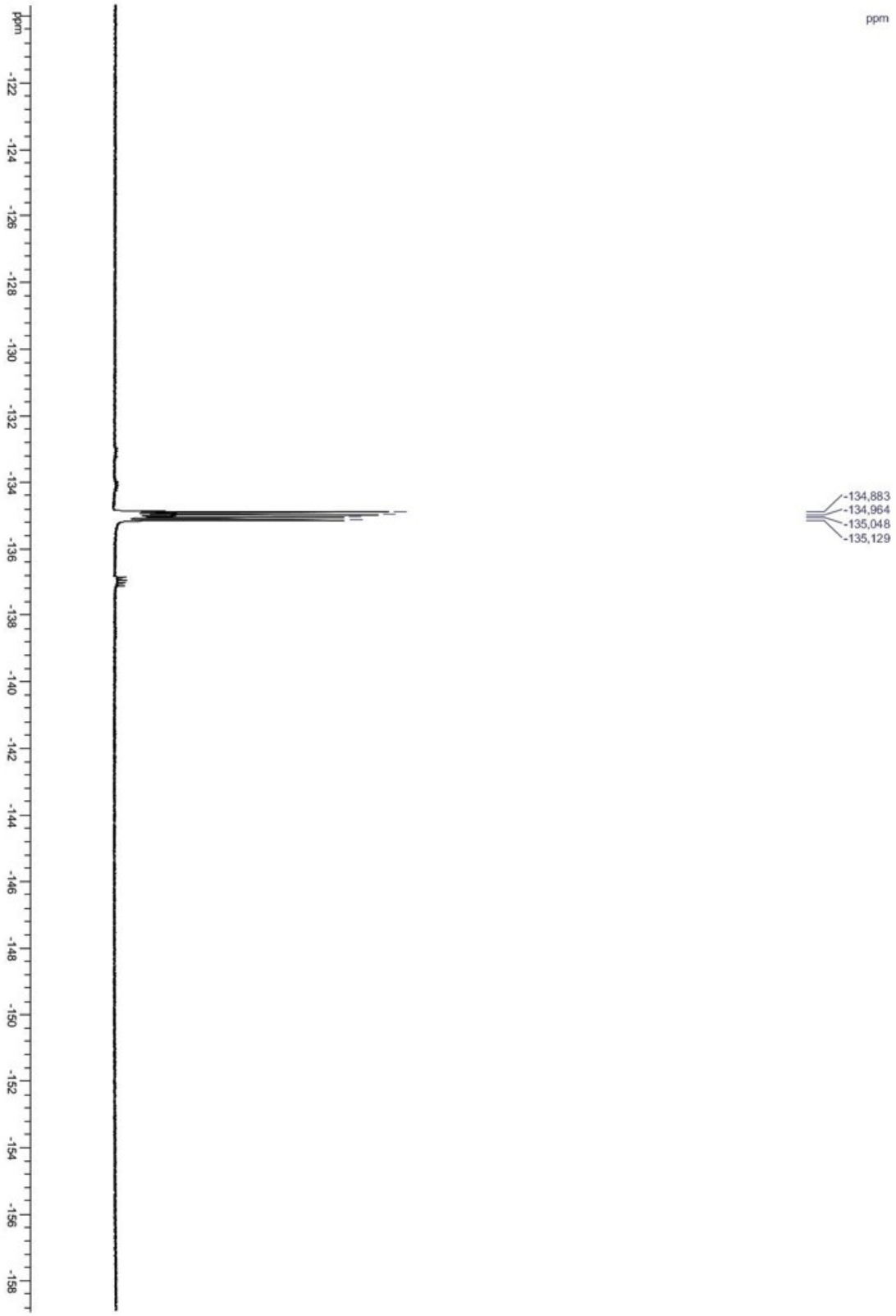
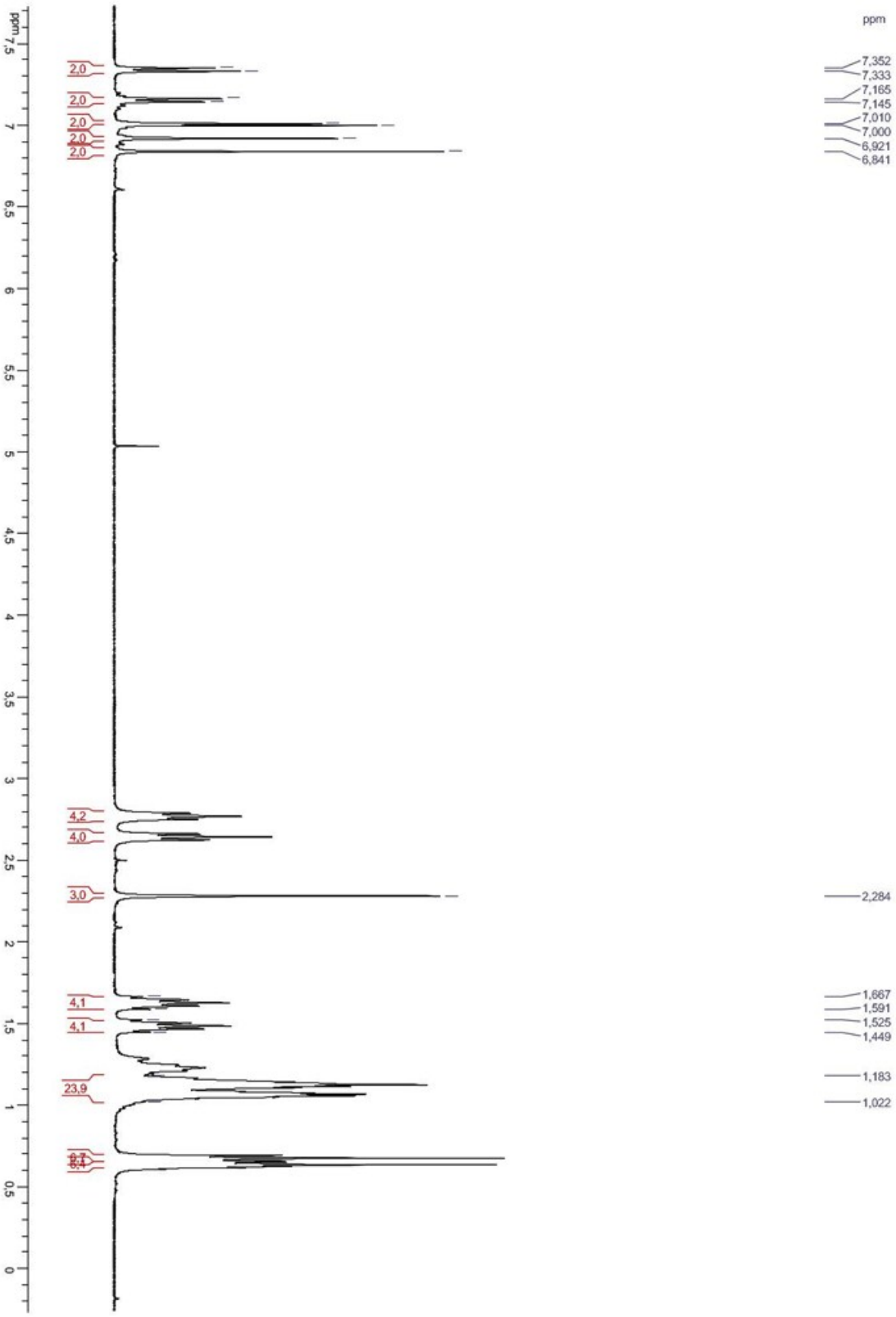


Figure S33: ^{1}H-NMR trace of compound **6αα** (400 MHz, $CDCl_3$, 298K)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6
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1,591
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1,449
1,183
1,022

Figure S34: ^{11}B-NMR trace of compound **6αα** (128 MHz, $CDCl_3$, 298K)

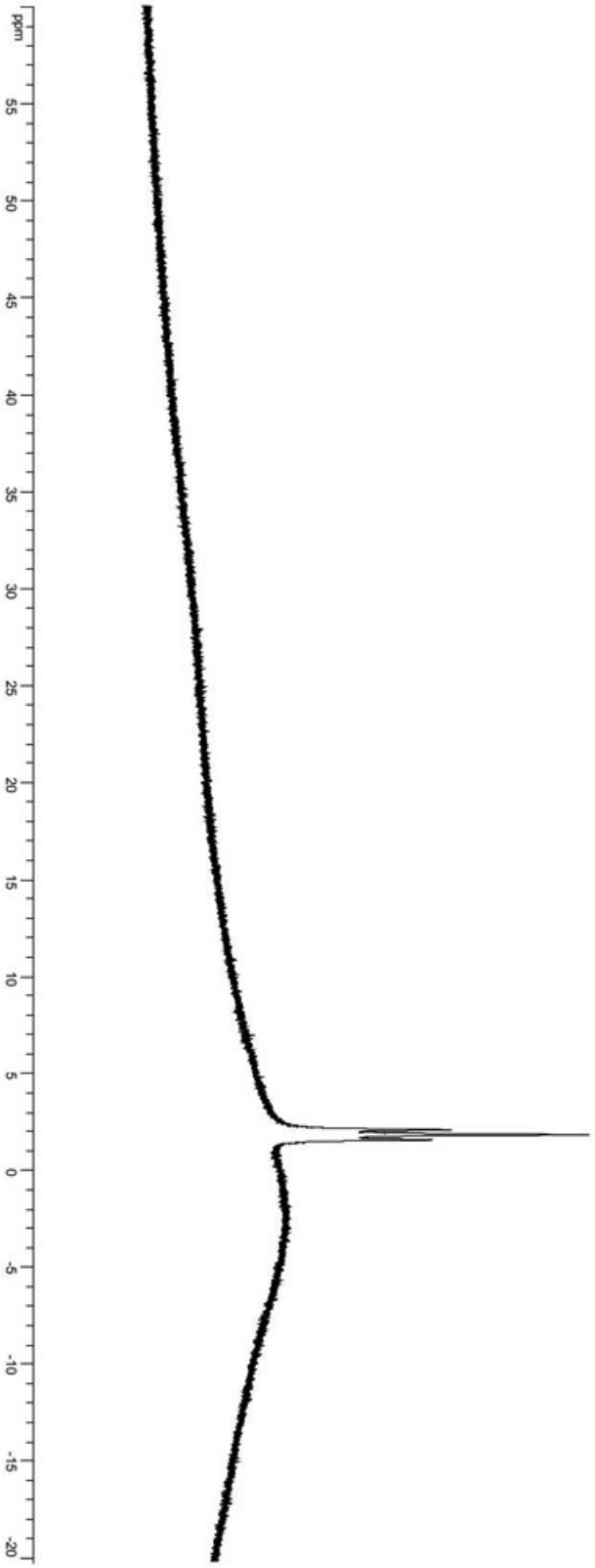


Figure S35: ^{13}C-NMR trace of compound **6αα** (100 MHz, $CDCl_3$, 298K)

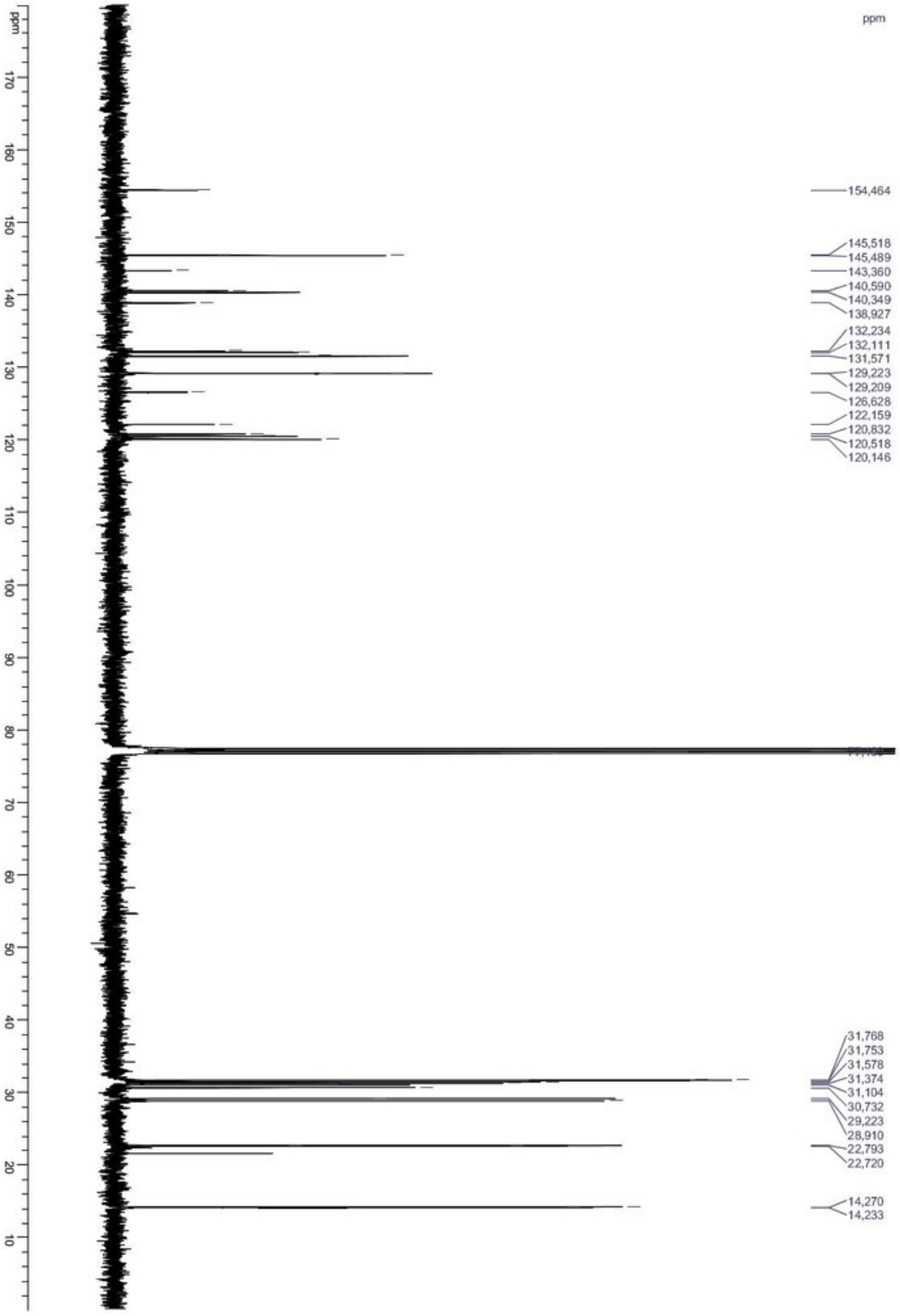


Figure S36: ^{19}F-NMR trace of compound **6αα** (376 MHz, $CDCl_3$, 298K)

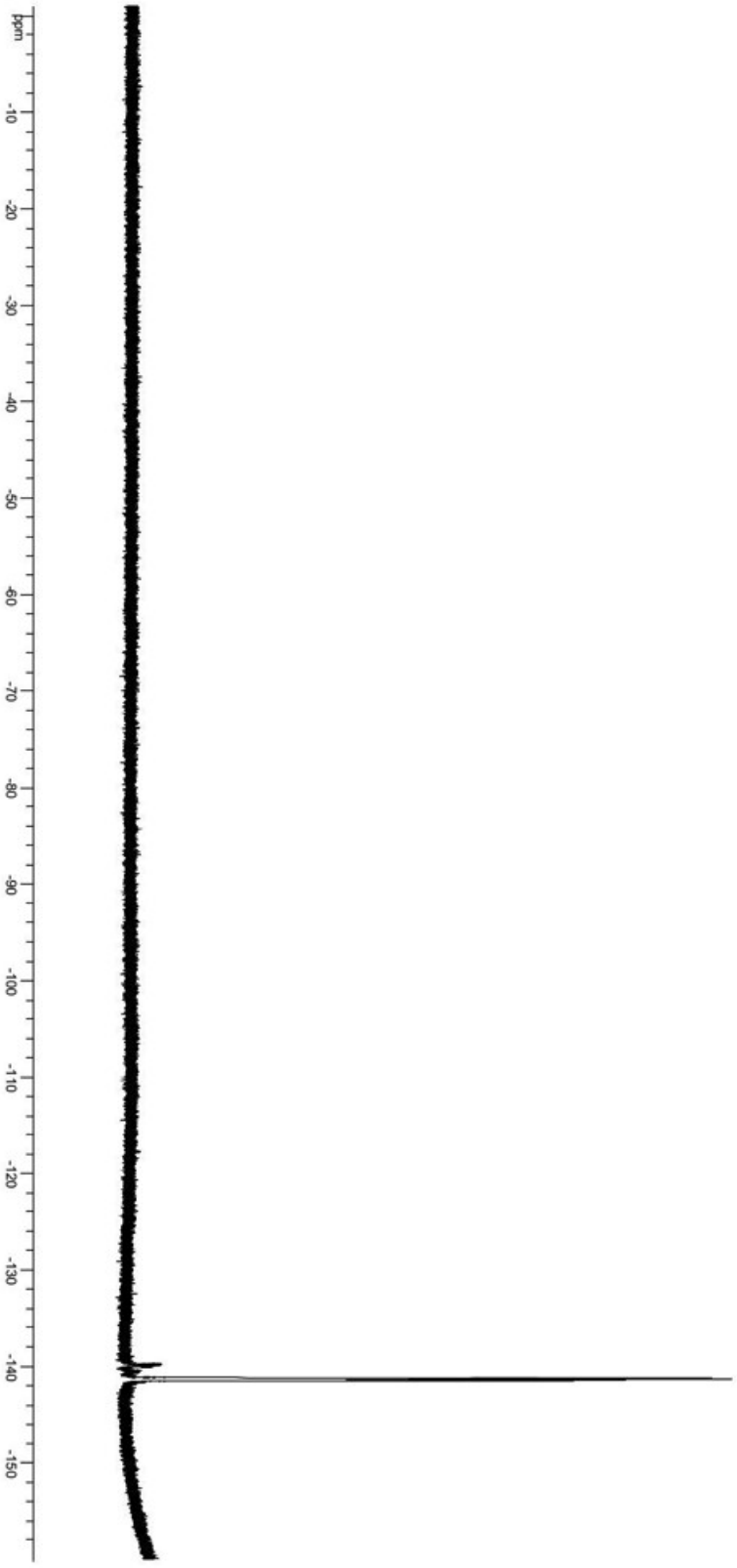


Figure S37: ^{1}H-NMR trace of compound **6αβ** (400 MHz, $CDCl_3$, 298K)

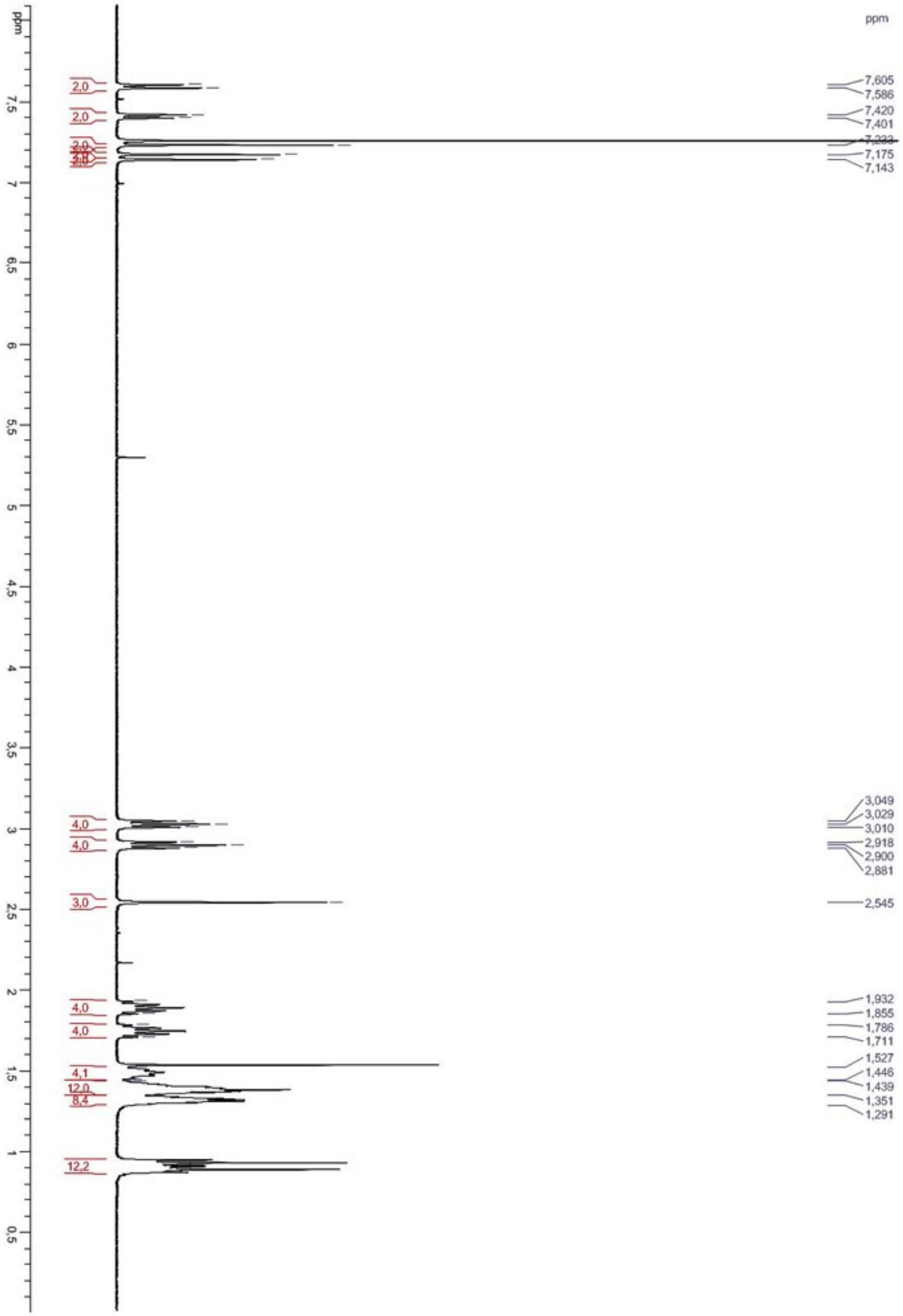


Figure S38: ^{11}B-NMR trace of compound **6αβ** (128 MHz, $CDCl_3$, 298K)

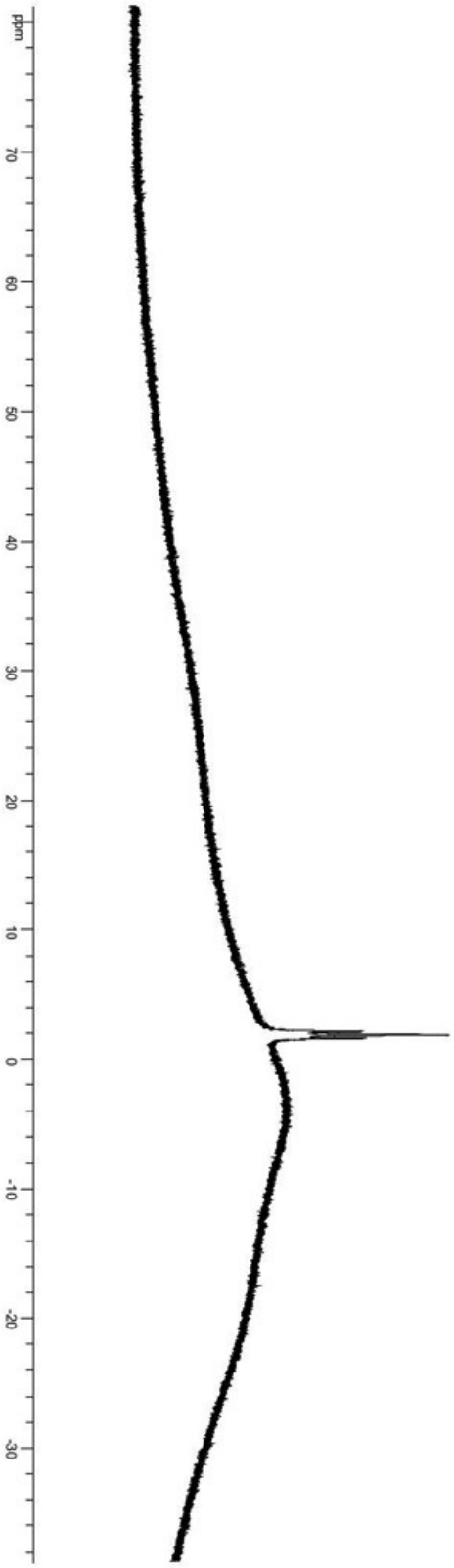


Figure S39: ^{13}C-NMR trace of compound **6αβ** (100 MHz, $CDCl_3$, 298K)

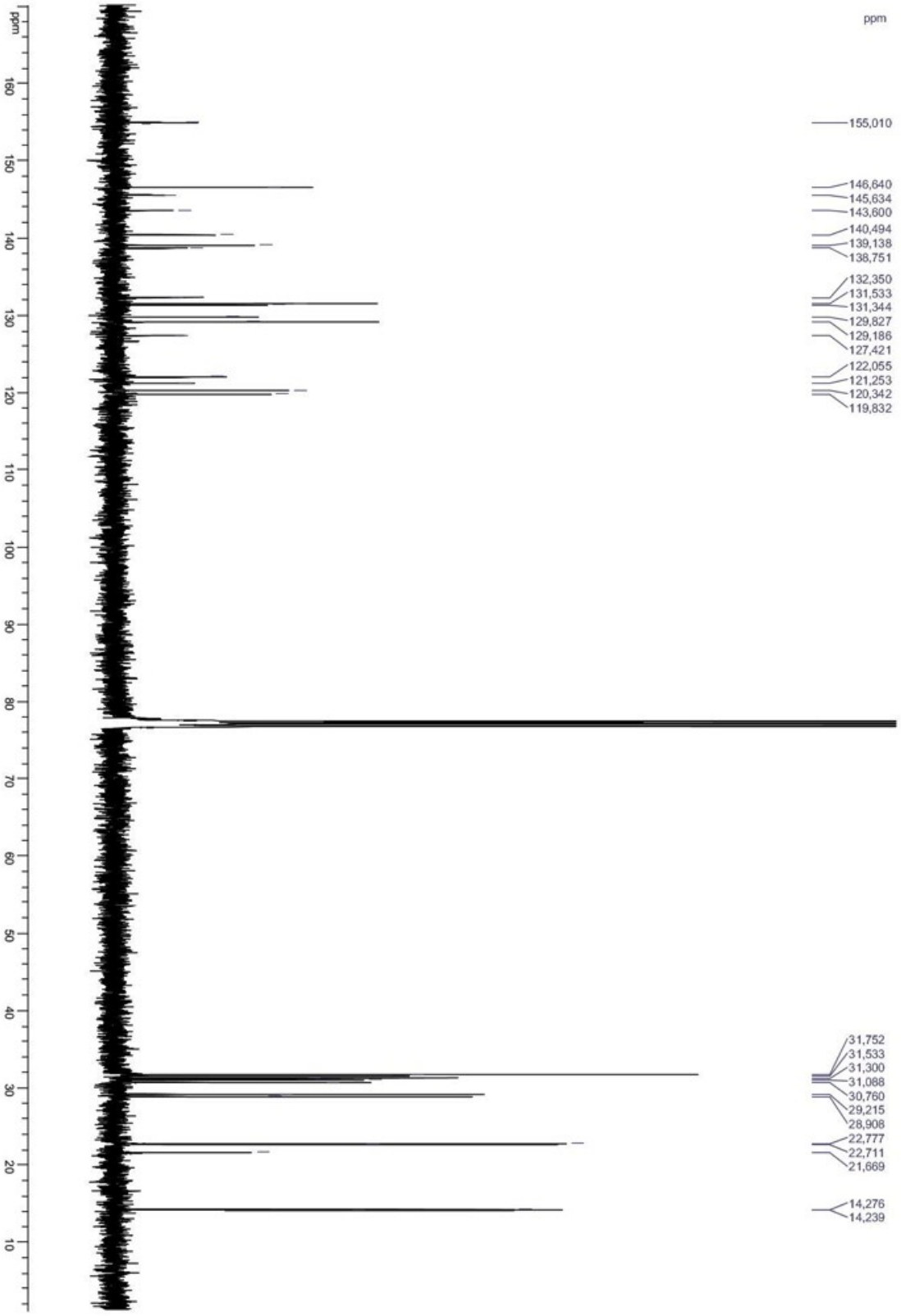


Figure S40: ^{19}F-NMR trace of compound **6αβ** (376 MHz, $CDCl_3$, 298K)

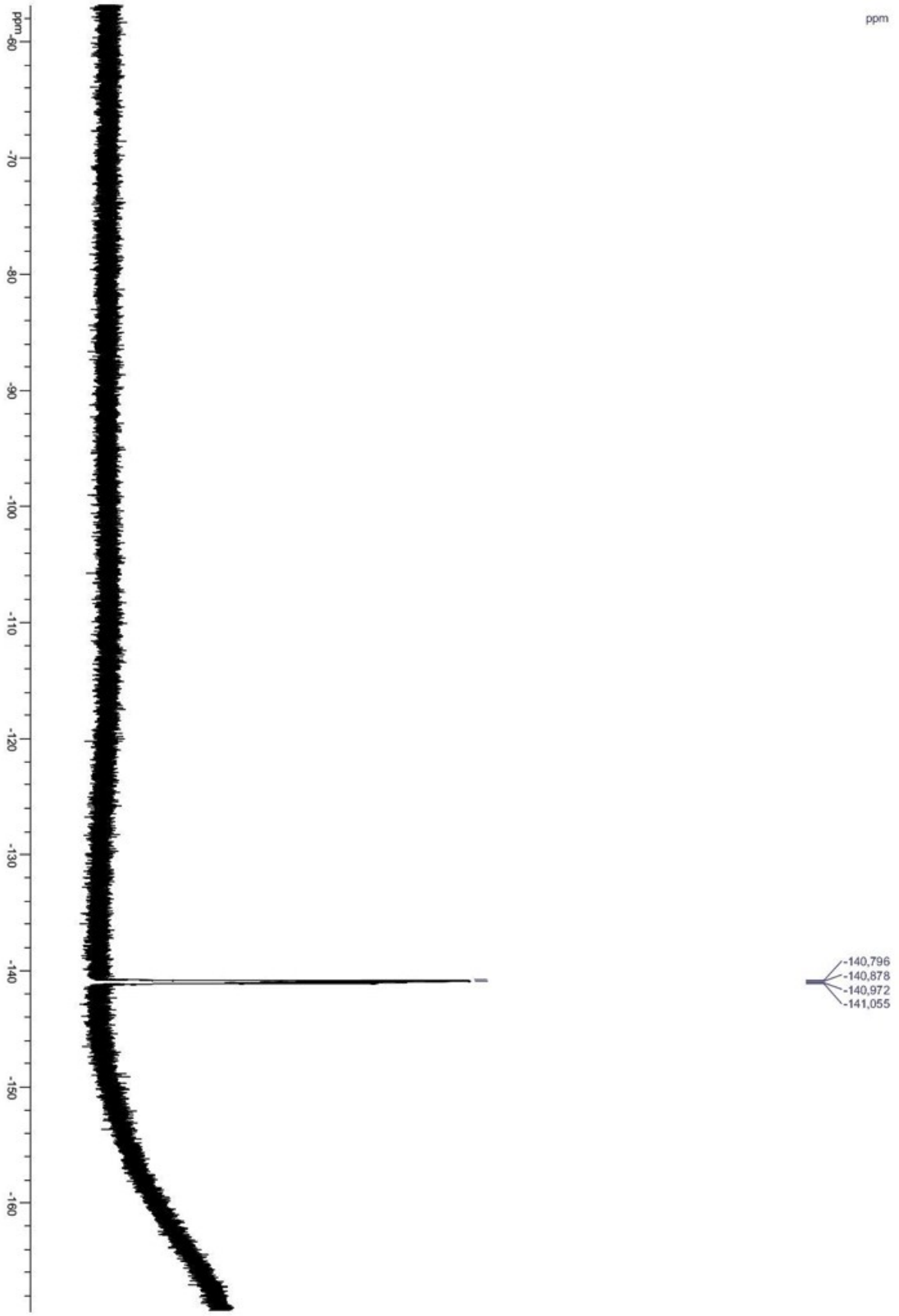


Figure S41: ^{1}H-NMR trace of compound **6βα** (400 MHz, $CDCl_3$, 298K)

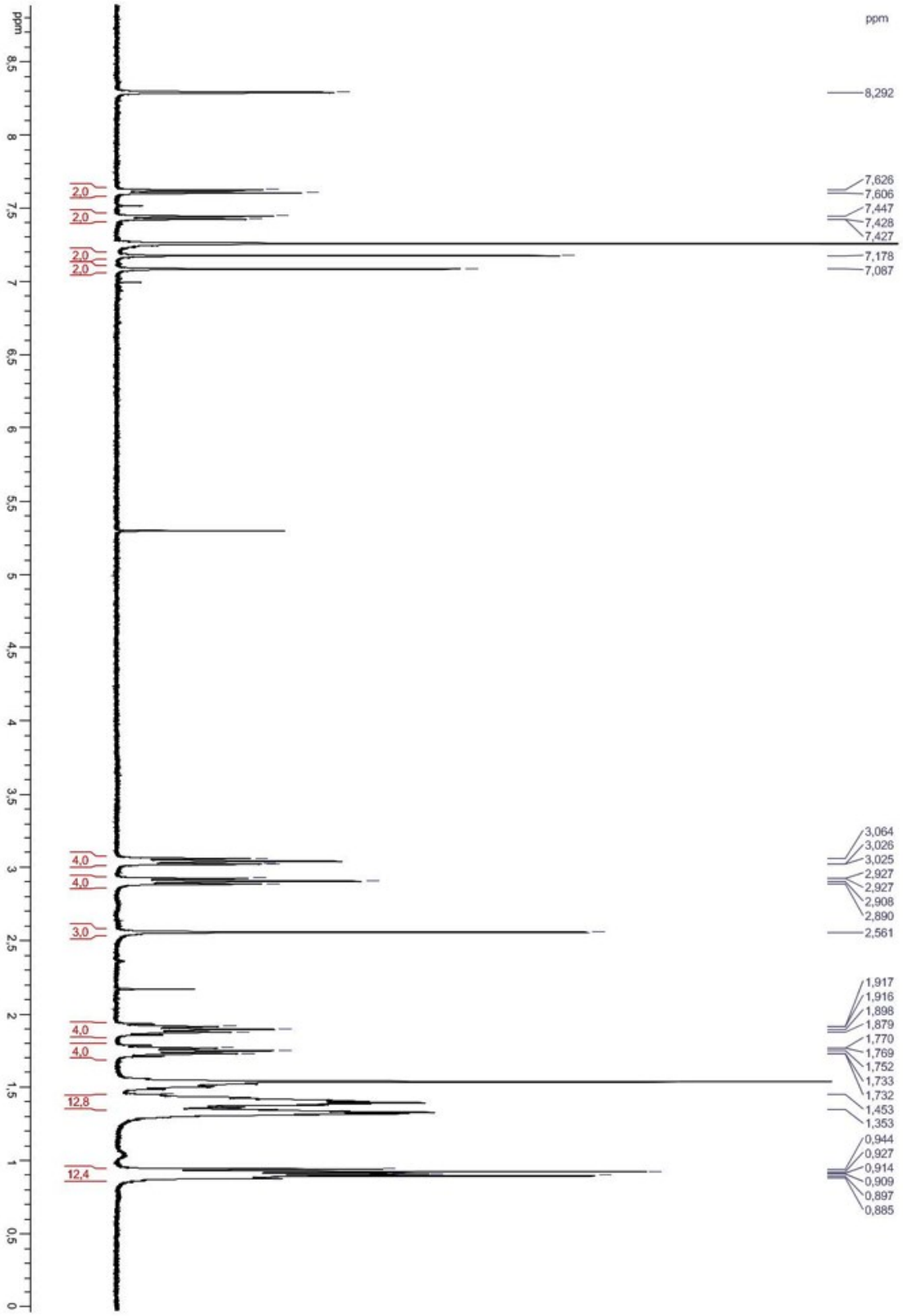


Figure S42: ^{11}B-NMR trace of compound **6βα** (128 MHz, $CDCl_3$, 298K)

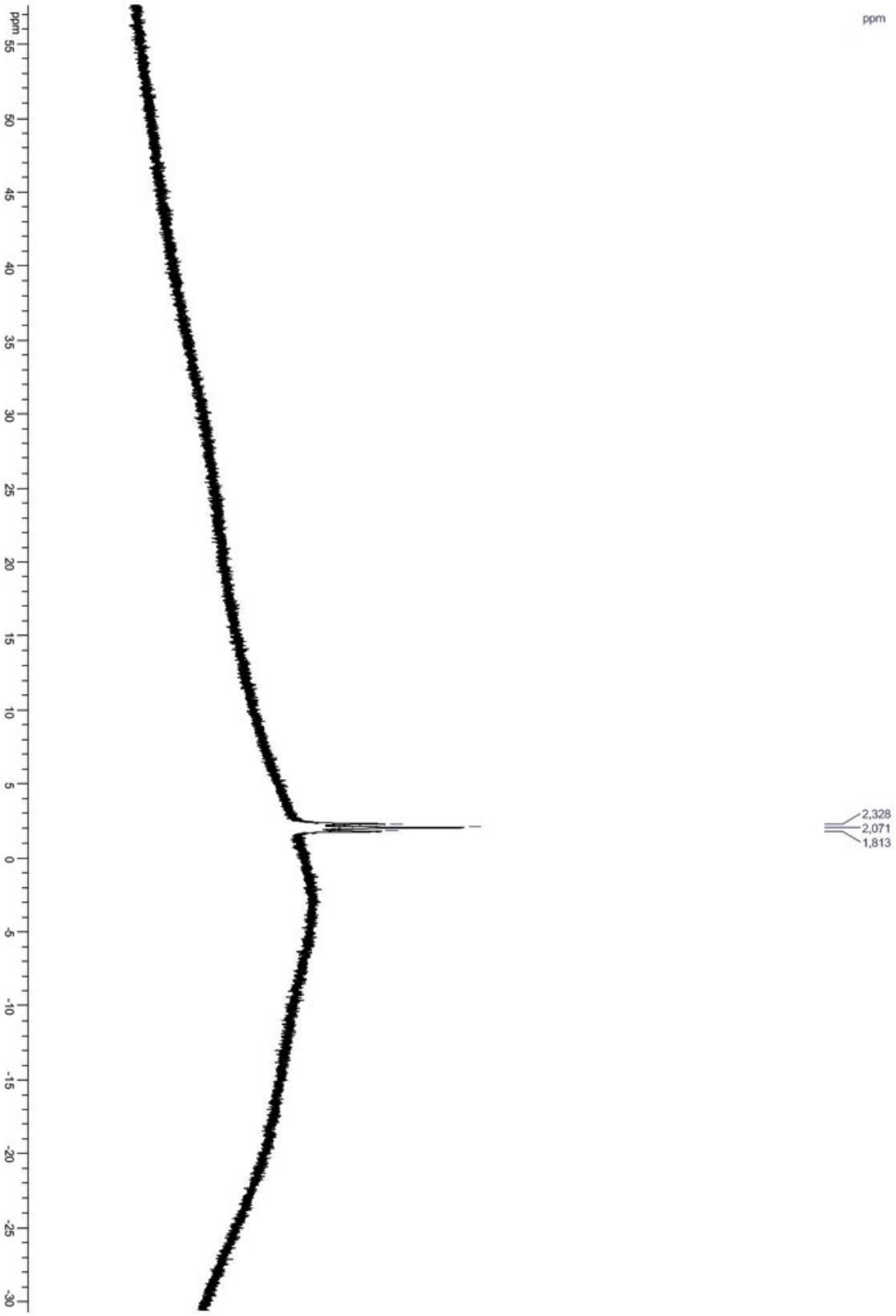


Figure S43: ^{13}C-NMR trace of compound **6βα** (100 MHz, $CDCl_3$, 298K)

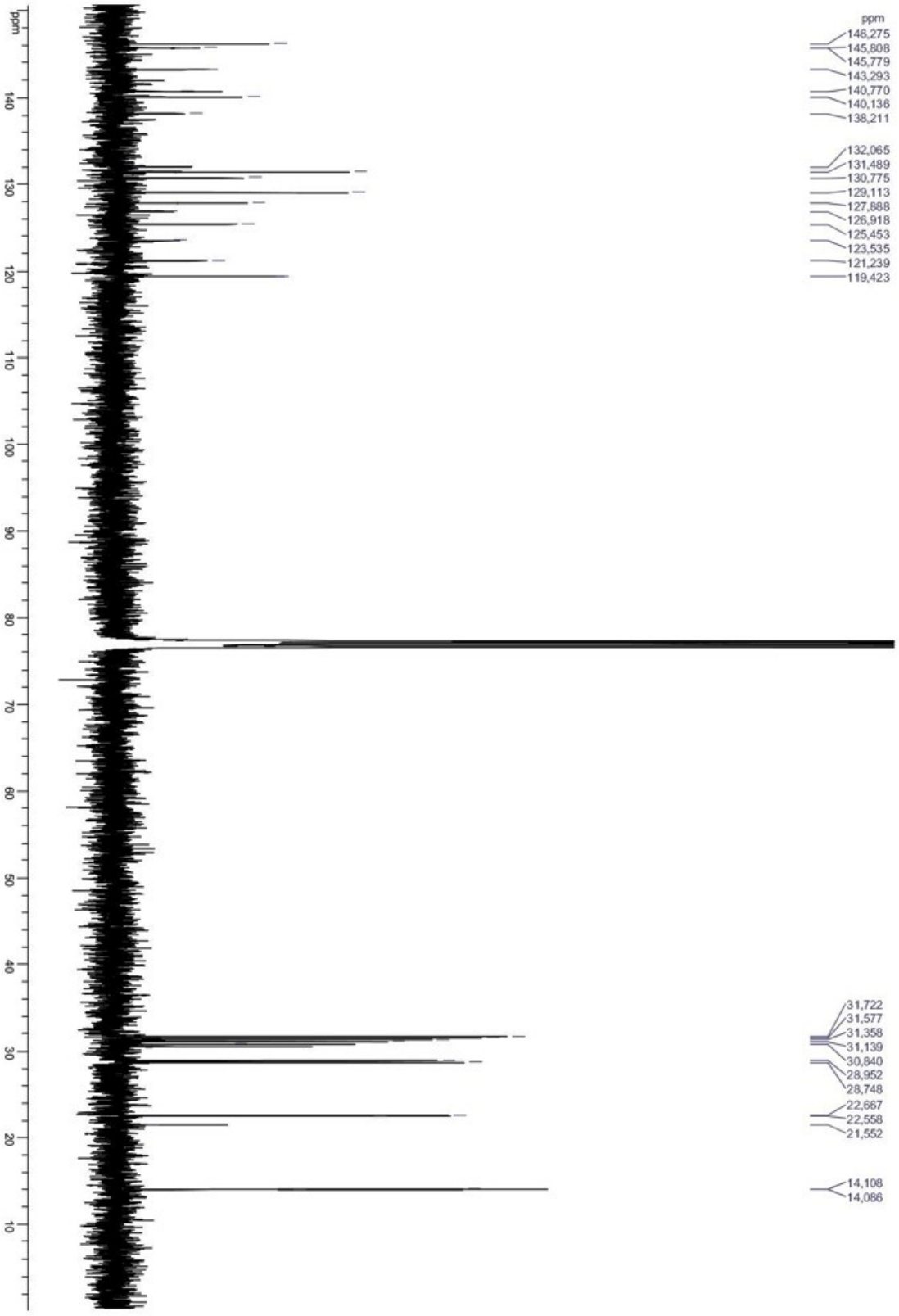


Figure S44: ^{19}F-NMR trace of compound **6βα** (376 MHz, $CDCl_3$, 298K)

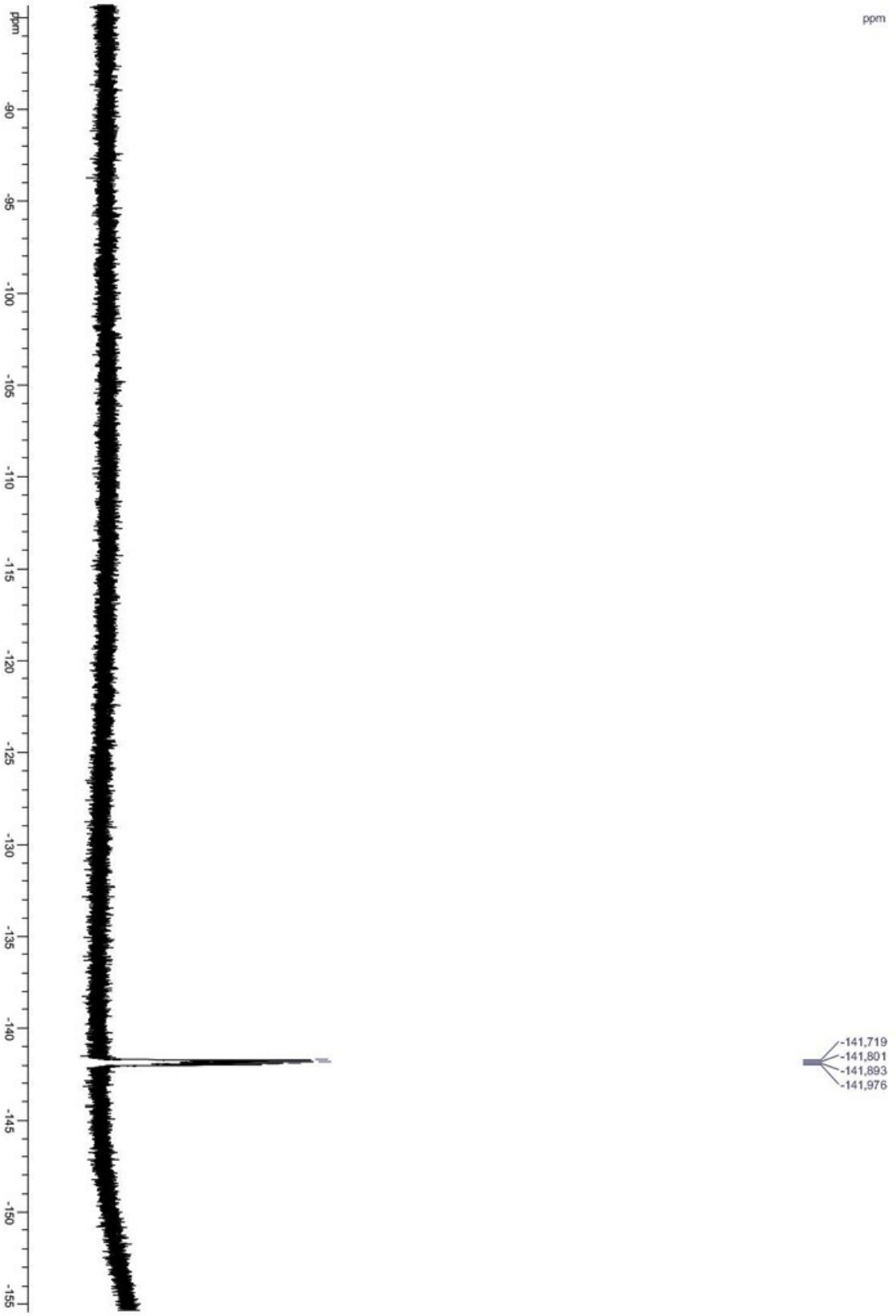


Figure S45: ^{1}H-NMR trace of compound **6ββ** (400 MHz, $CDCl_3$, 298K)

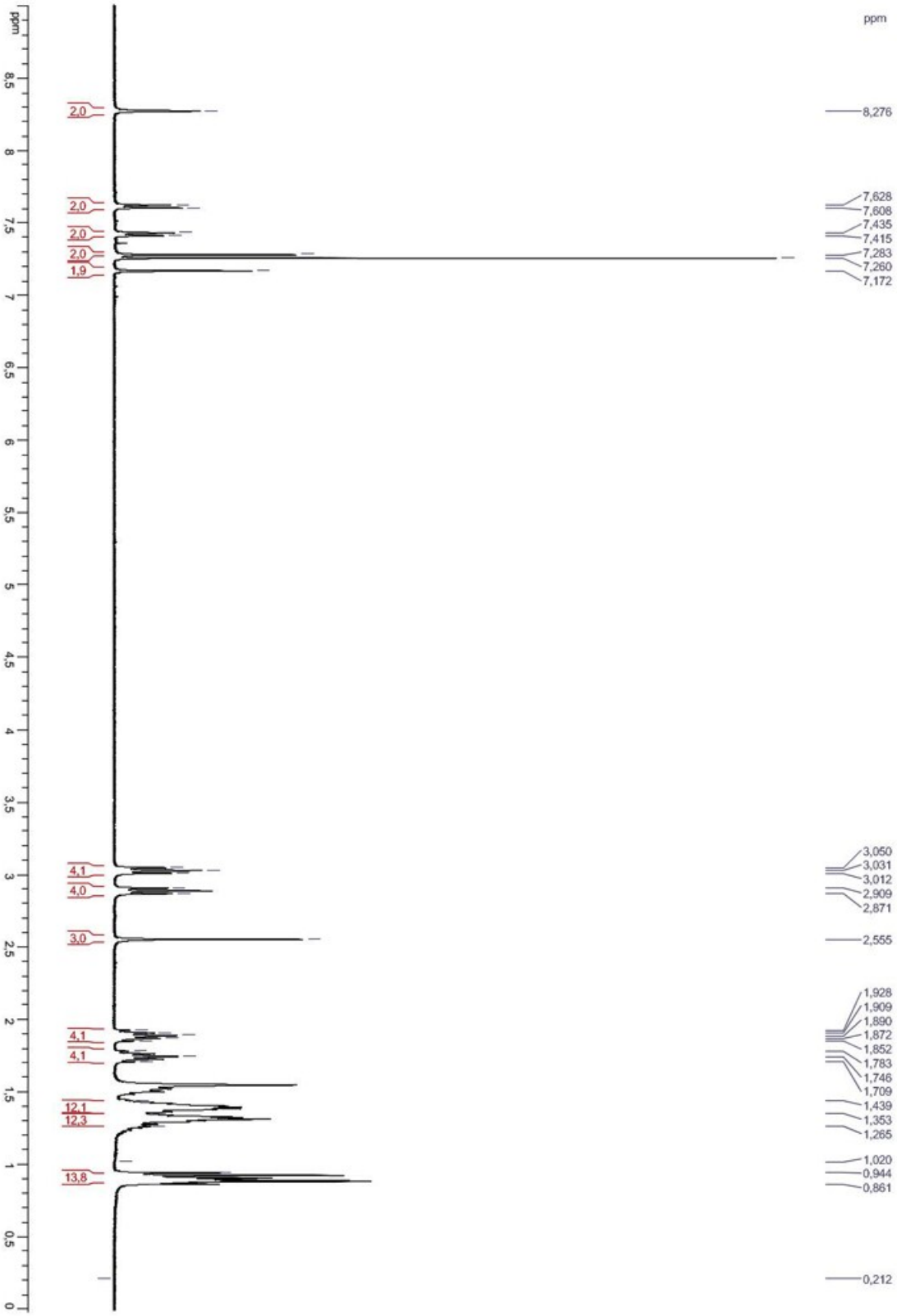


Figure S46: ^{11}B-NMR trace of compound **6ββ** (128 MHz, $CDCl_3$, 298K)

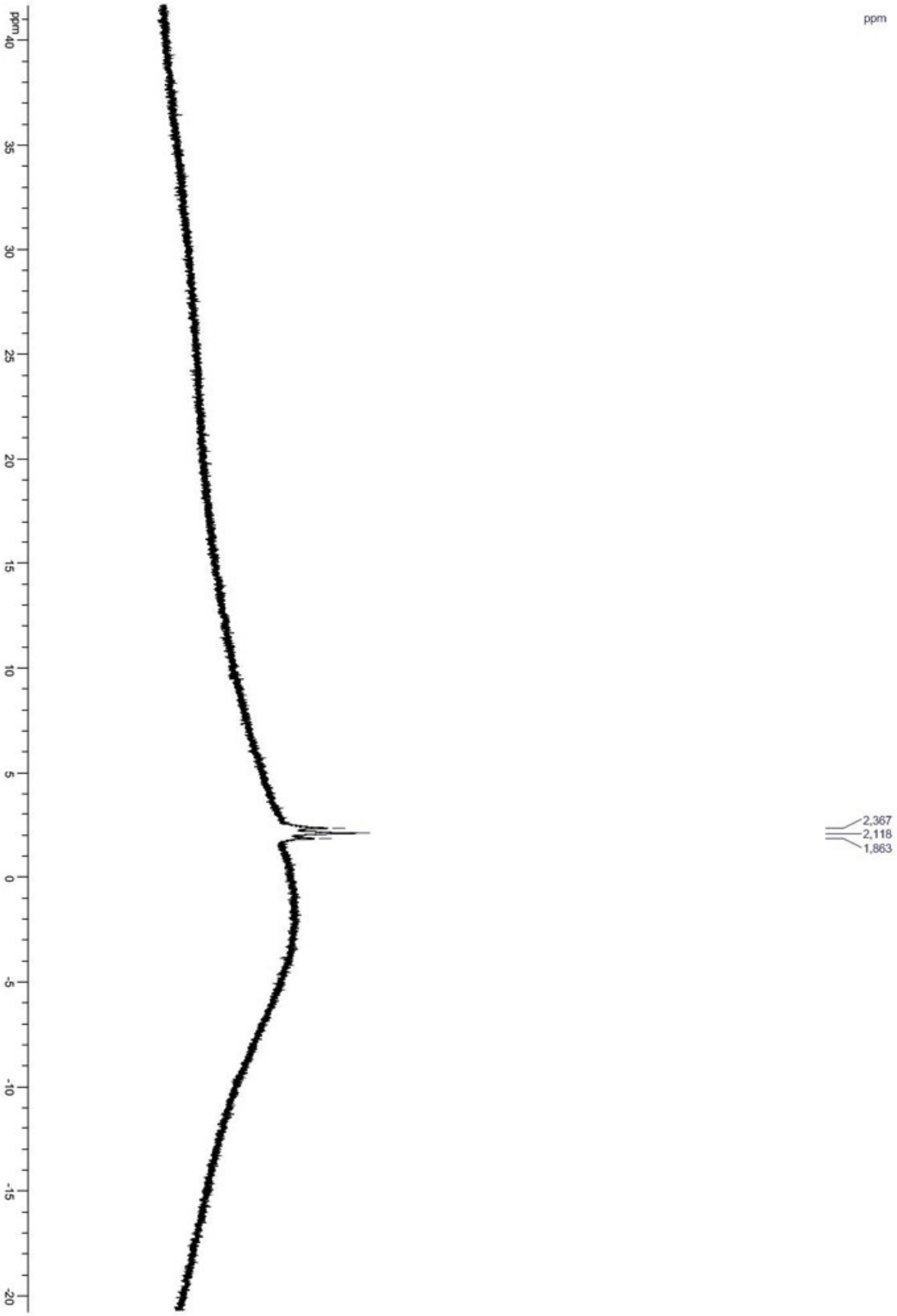


Figure S47: ^{13}C-NMR trace of compound **6ββ** (100 MHz, $CDCl_3$, 298K)

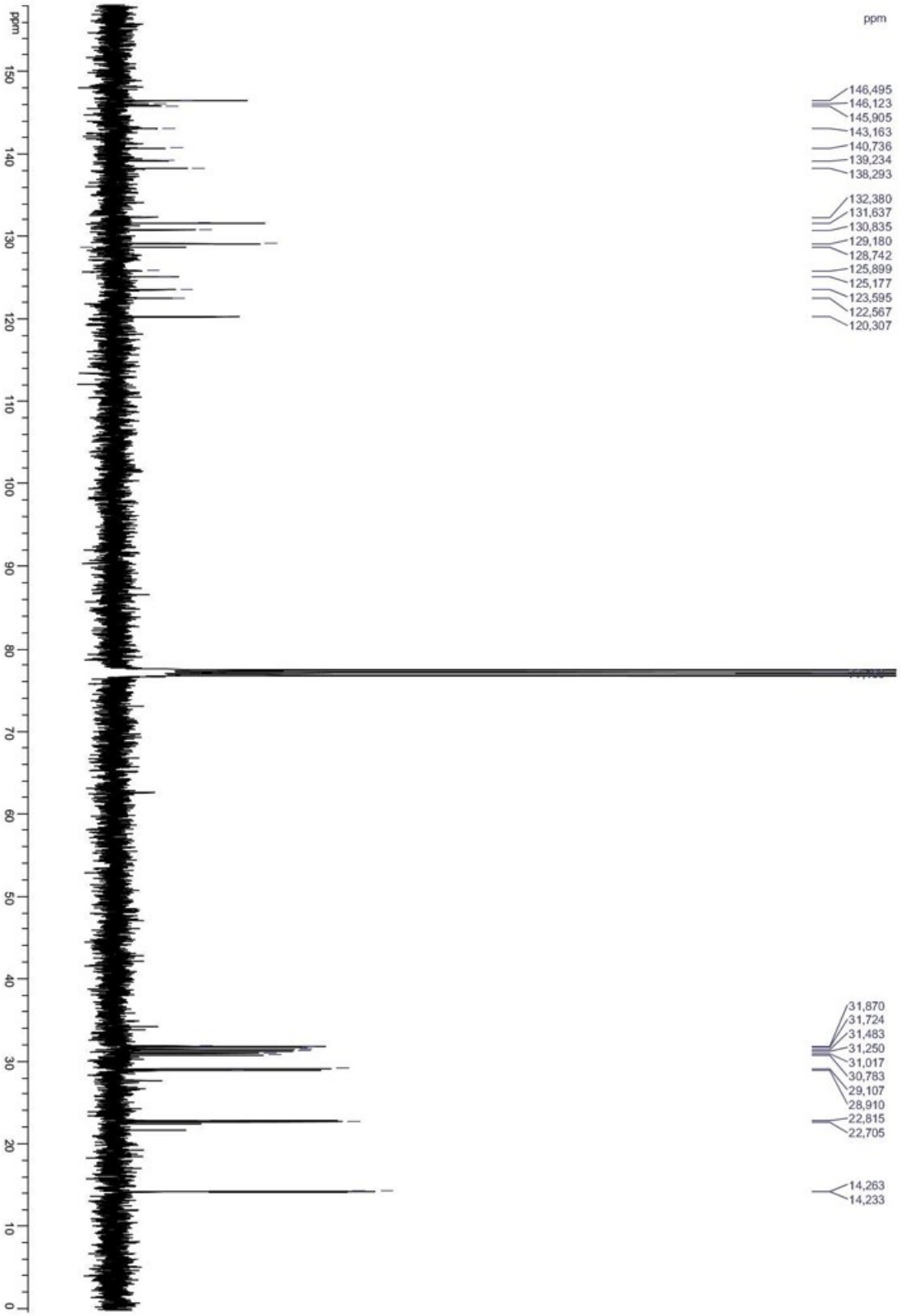
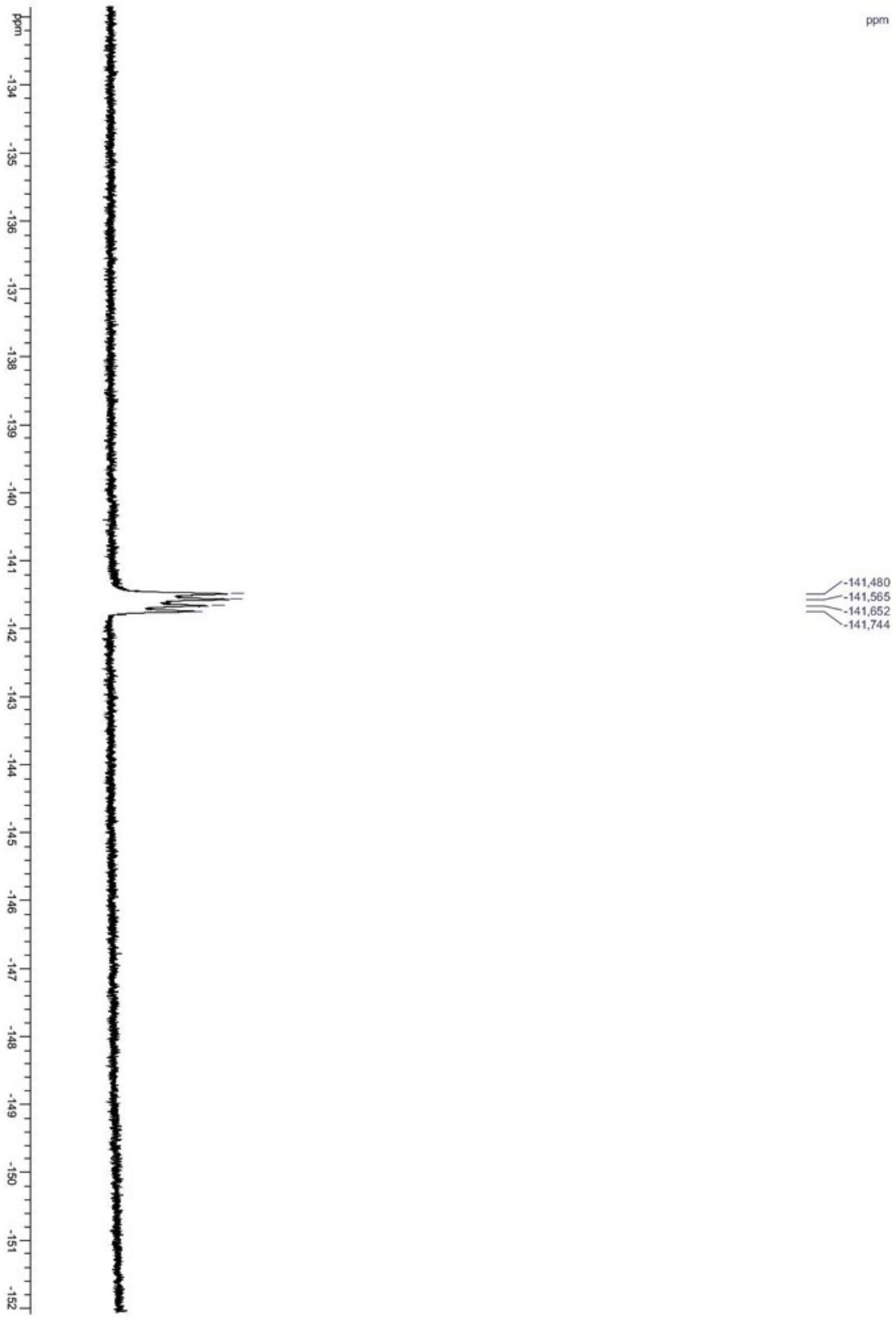


Figure S48: ^{19}F-NMR trace of compound **6ββ** (376 MHz, $CDCl_3$, 298K)



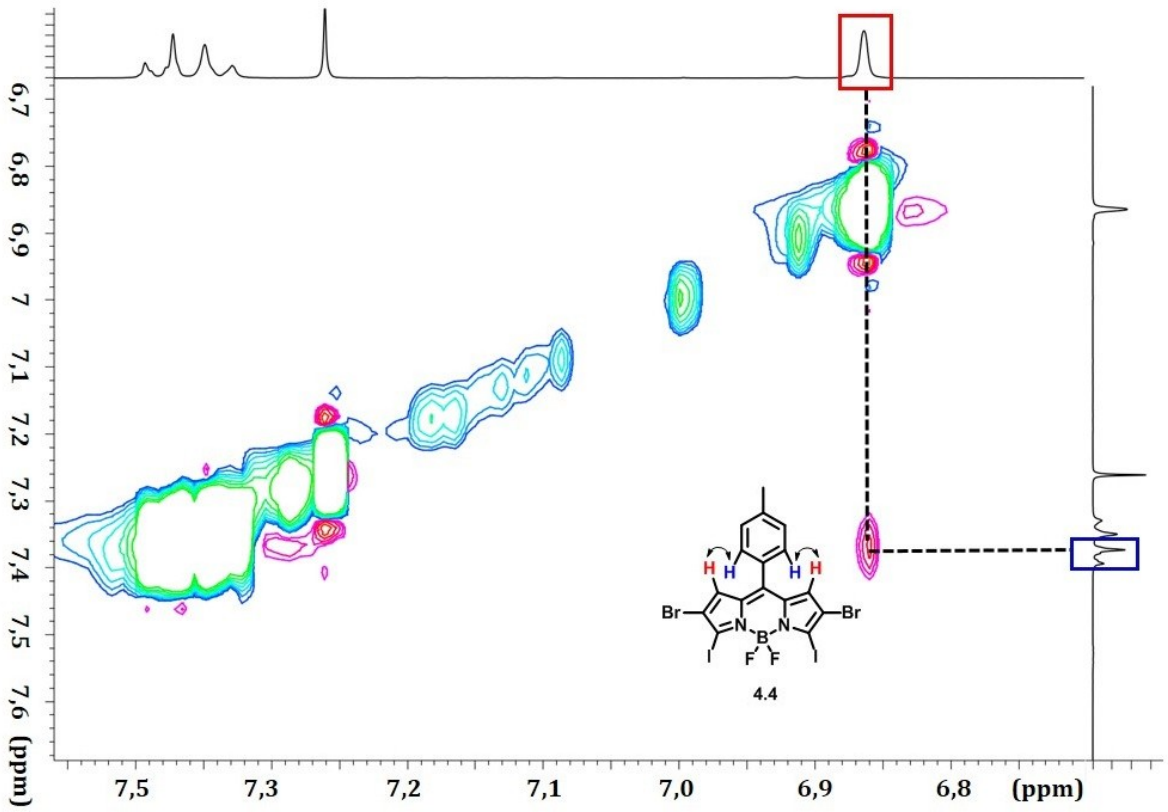


Figure S49: ^{1}H-^{1}H NOESY spectrum of compound **3** ($CDCl_3$, 298K).

Spectroscopic characterization

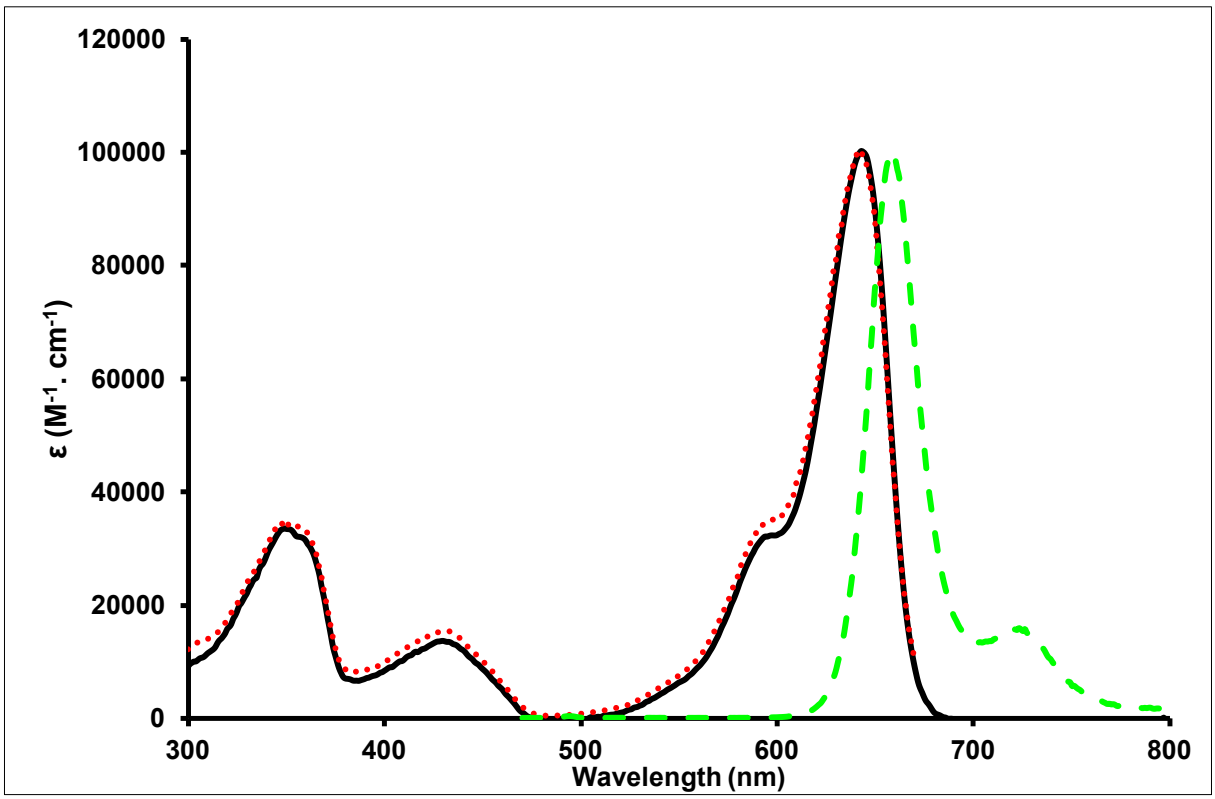


Figure S50: Absorption (solid line), emission (dashed line) and excitation (dot line) spectra of compound **4α** (PhMe, 298K, 10^{-6}M)

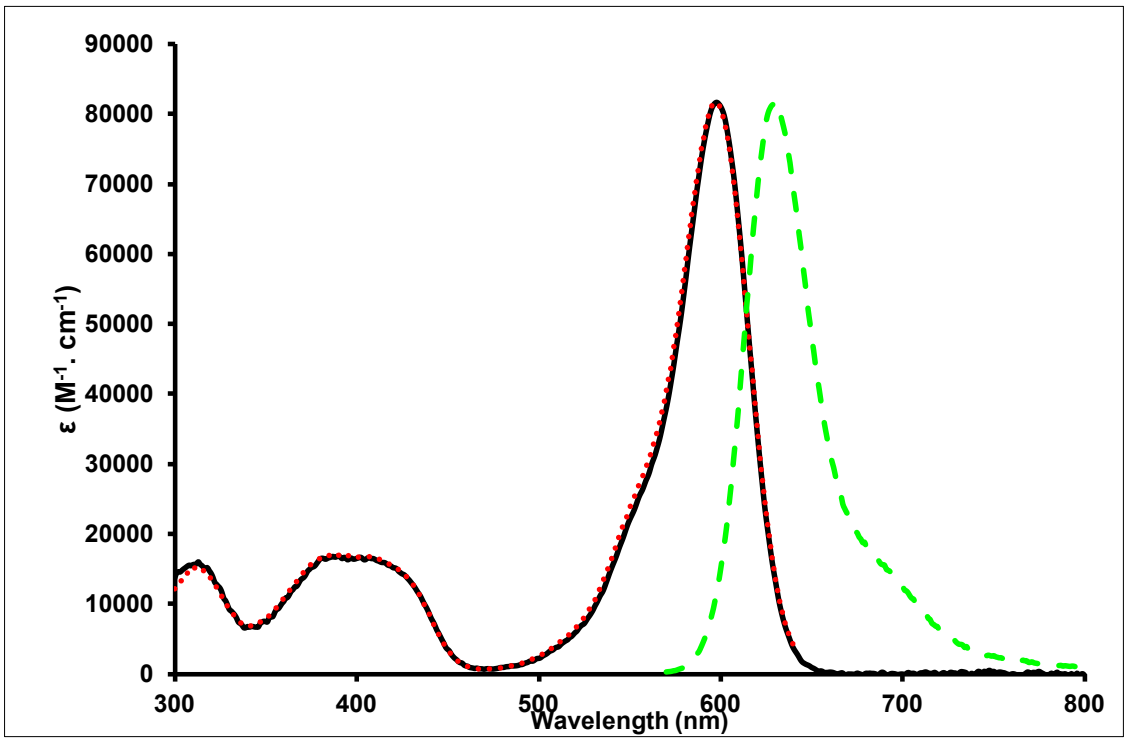


Figure S51: Absorption (solid line), emission (dashed line) and excitation (dot line) spectra of compound **4β** (PhMe, 298K, 10^{-6}M)

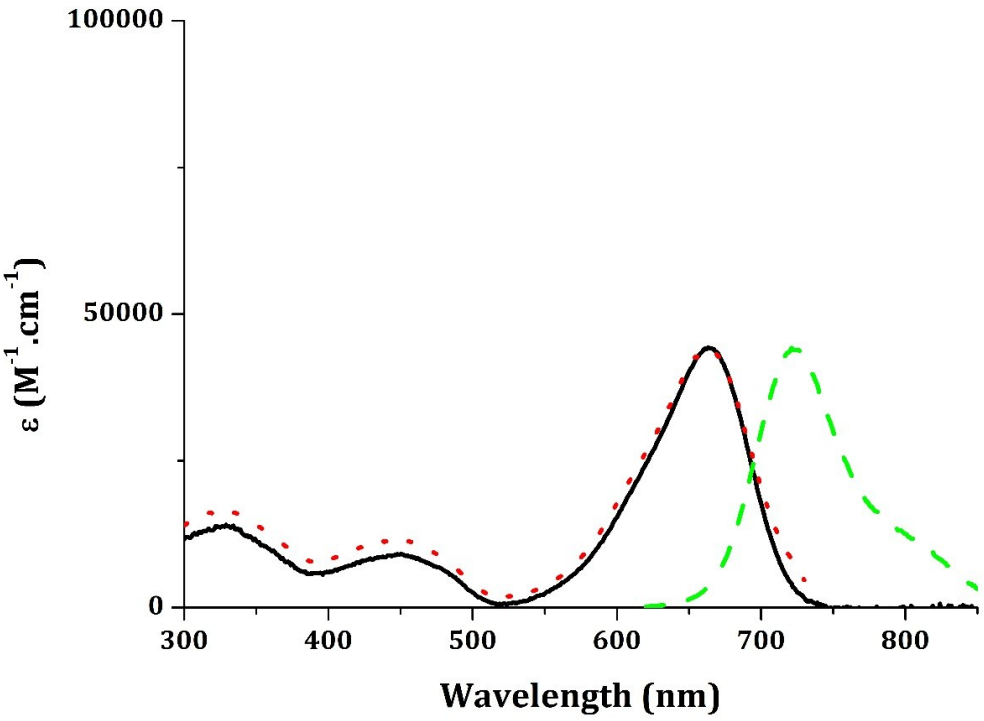


Figure S52: Absorption (solid line), emission (dashed line) and excitation (dot line) spectra of compound **5αα** (PhMe, 298K, 10^{-6}M)

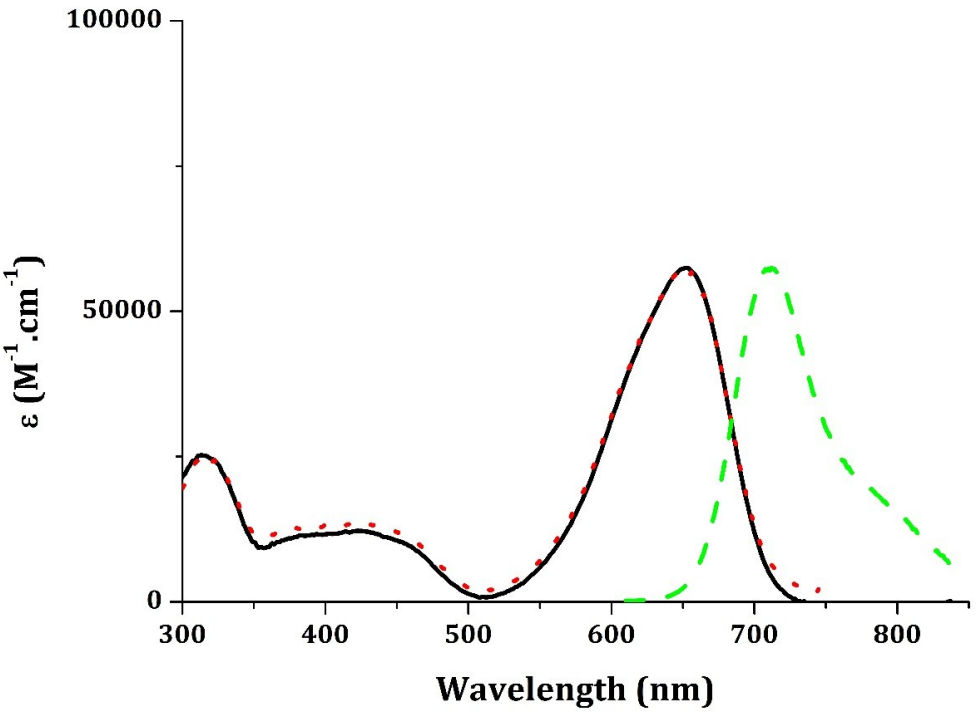


Figure S53: Absorption (solid line), emission (dashed line) and excitation (dot line) spectra of compound **5αβ** (PhMe, 298K, 10^{-6}M)

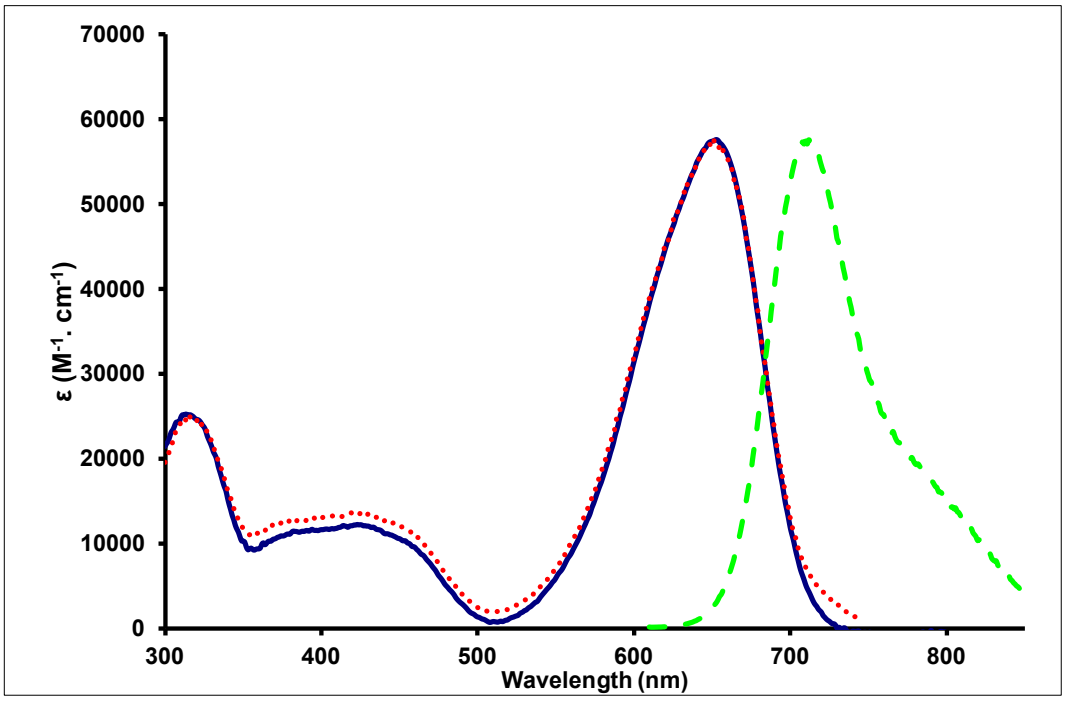


Figure S54: Absorption (solid line), emission (dashed line) and excitation (dot line) spectra of compound **5βα** (PhMe, 298K, 10^{-6}M)

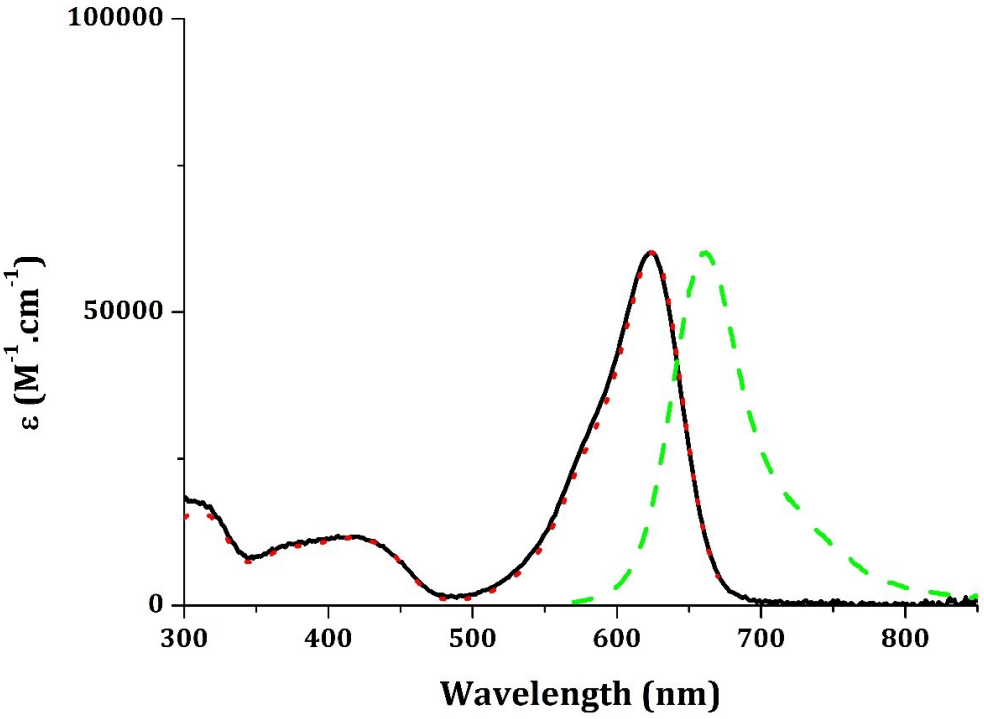


Figure S55: Absorption (solid line), emission (dashed line) and excitation (dot line) spectra of compound **5ββ** (PhMe, 298K, 10^{-6}M)

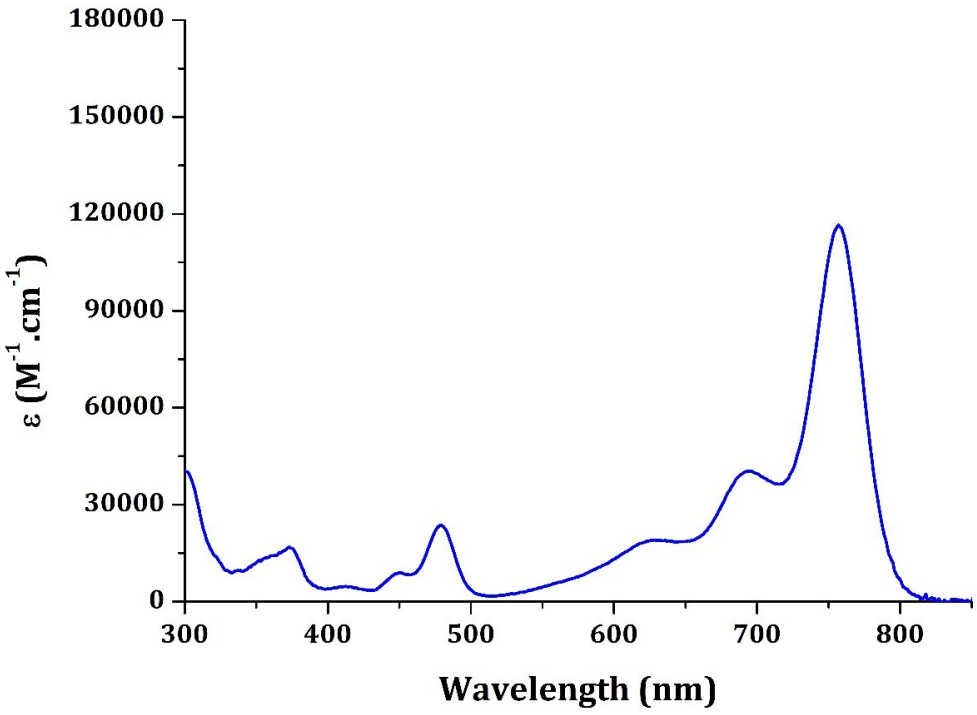


Figure S56: Absorption spectrum of compound **6αα** (PhMe, 298K, 10^{-6}M)

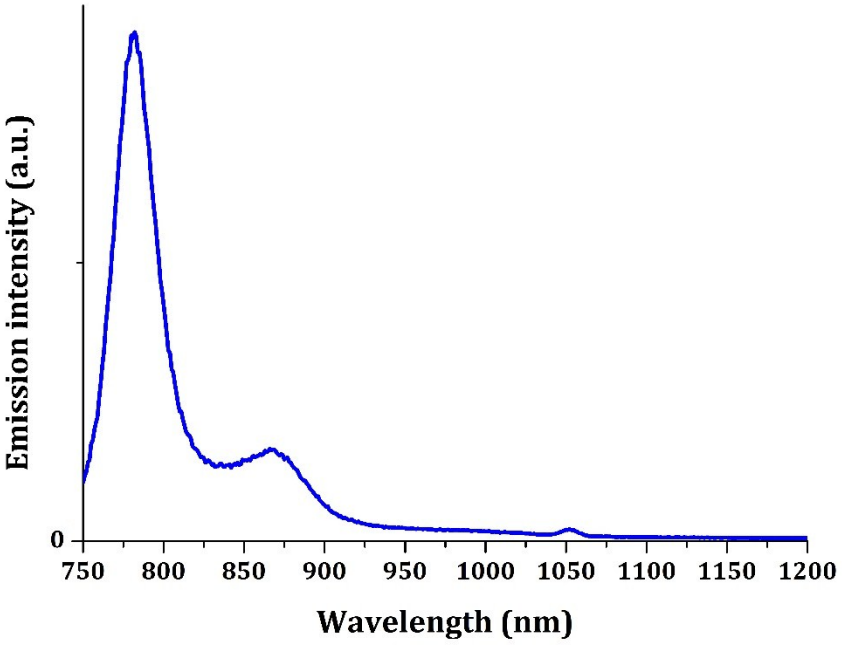


Figure S57: Emission spectrum of compound **6αα** (Me-THF, 77K, 10^{-6}M)

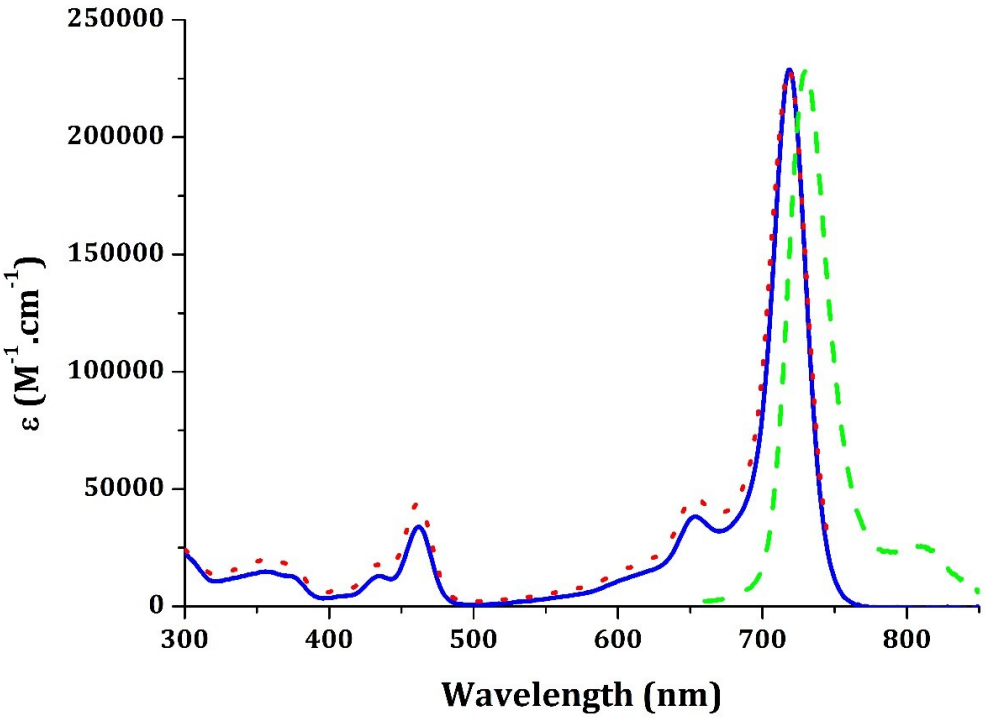


Figure S58: Absorption, emission (dashed line) and excitation (dot line) spectra of compound **6αβ** (PhMe, 298K, 10^{-6}M)

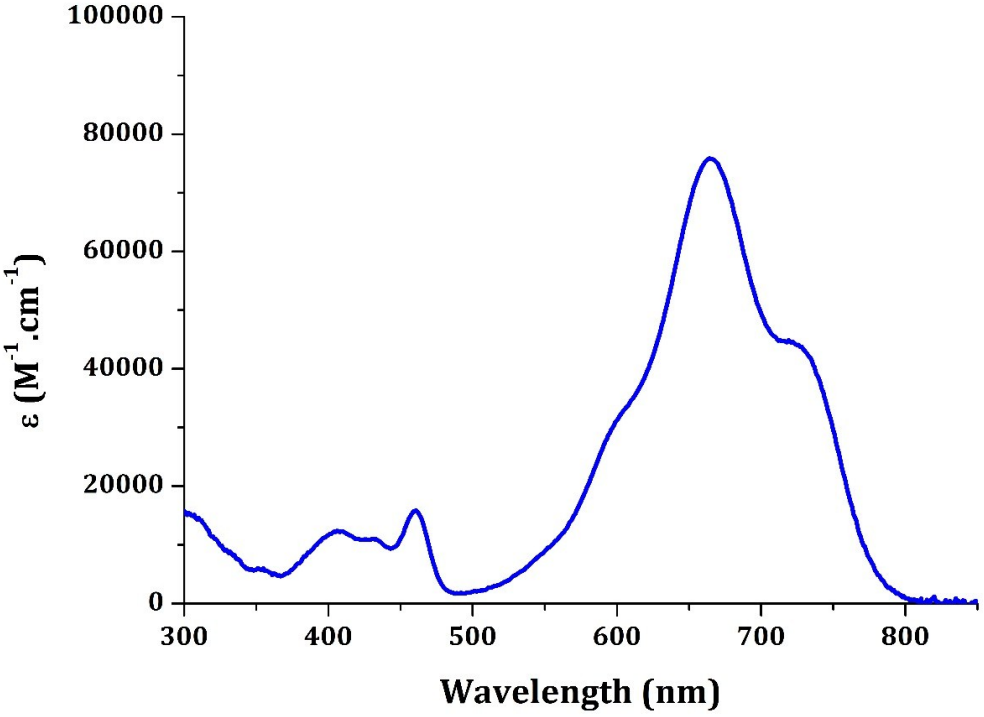


Figure S59: Absorption spectrum of compound **6βα** (PhMe, 298K, 10^{-6}M)

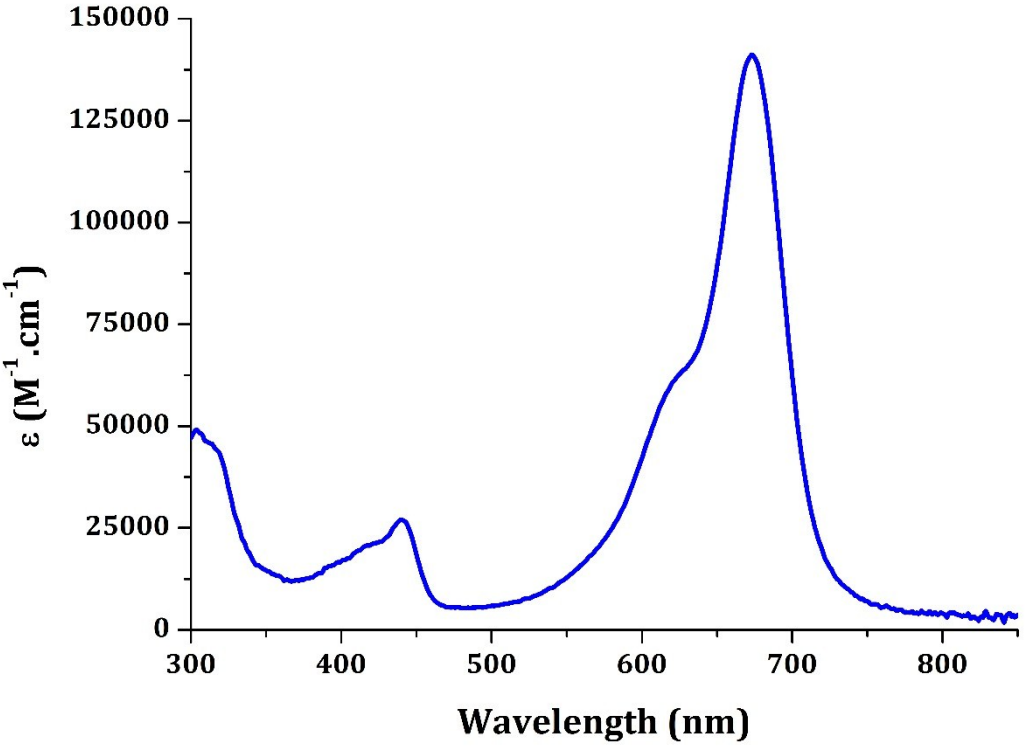


Figure S60: Absorption spectrum of compound **6ββ** (PhMe, 298K, 10^{-6}M)

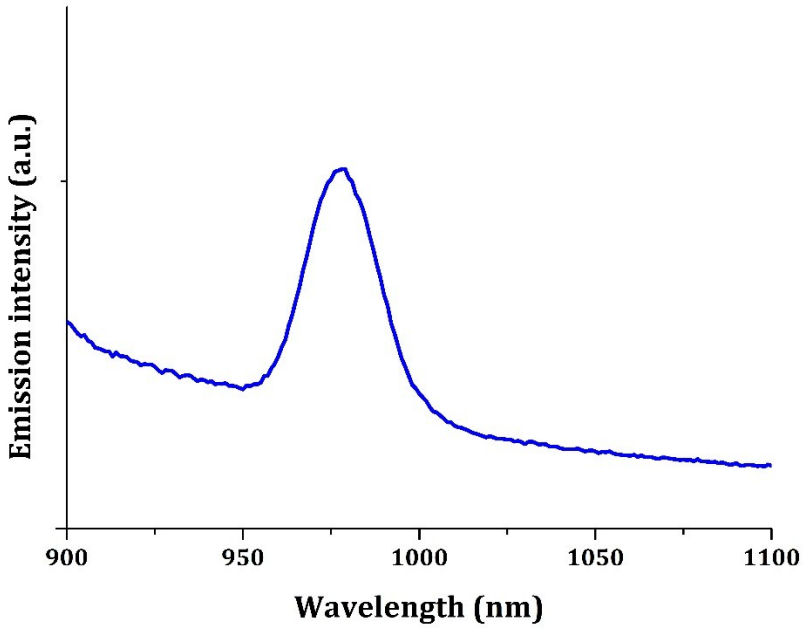


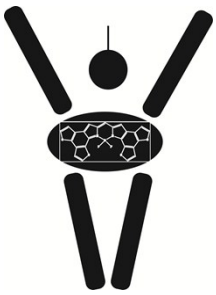
Figure S61: Emission spectrum of compound **6ββ** (Me-THF, 77K, 10^{-6}M)

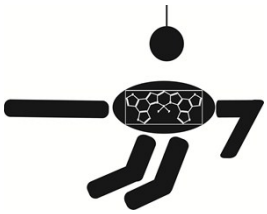
X-ray structures

Crystallographic data for both compounds **6αβ** and **6βα** were recorded on a RIGAKU XtaLabPro diffractometer delivering Mo radiation from a microfocus sealed tube generator coupled to a double-bounce confocal Max-Flux® multilayer optic equipped with HPAD PILATUS3 R 200K detector. Samples coated by Paratone oil were frozen under a stream of liquid nitrogen at 100K. Crystal data collection and reduction performed using *CrystalClear-SM Expert 2.1 b45*. Both structures were solved by intrinsic phasing methods (SHELXT program)[7] and structure refinement carried out by full-matrix least-squares methods (SHELXL-2018/1 program).[8] All details (*vide infra*) are summarized in Table 1. A riding model was used for H atoms bonded to C atoms, with C—H = 0.95 (aromatic), 0.99 (CH_2), and 0.98 Å (CH_3) and with *U*iso(H) = 1.2*U*eq(C) or 1.5*U*eq(Cmethyl). For **6αβ**, slight disorder of hexyl legs was treated as static over two atomic sites with refined occupancy fators of 0.511(4)/ 0.489(4), breaking the strict internal C2h symmetry.

CCDC 1824219 (compound **6αβ**) and CCDC 1824220 (compound **6βα**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1: Experimental details





Identification code		**6αβ**	**6βα**
Empirical formula		C_{56} H_{65} B F_2 N_2 S_4	C_{56} H_{65} B F_2 N_2 S_4
Formula weight		943.15	943.15
Temperature (K)		100(2)	100(2)
Wavelength (Å)		0.71075	0.71075
Crystal system,		Monoclinic,	Triclinic,
space group		C2/c	P-1
Unit cell dimensions	a (Å)	8.8300(7)	12.4977(9)
	b	22.2396(16)	13.2100(9)
	c	24.8071(19)	17.2490(12)
	α (°)	90	86.049(5)
	β	96.111(7)	71.684(5)
	γ	90	65.153(5)
Volume ($Å^3$)		4843.8(6)	2446.6(3)
Z,		4,	2,
Calculated density (Mg/m3)		1.293	1.280
Absorption coefficient (mm^{-1})		0.245	0.242
F(000)		2008	1004
Crystal size (mm)		0.30 x 0.16 x 0.12	0.24 x 0.17 x 0.13
θ range for data collection (°)		3.597 to 27.367	3.515 to 27.548.
Limiting indices		-11 ≤ h ≤ 11,	-16 ≤ h ≤ 16,
		-28 ≤ k ≤ 27,	-17 ≤ k ≤ 14,
		-28 ≤ l ≤ 32	-22 ≤ l ≤ 22

Reflections collected / unique		19572 / 5435	43530 / 11101
R(int)		0.0384	0.0356
Completeness to θ full (%)		99.1	99.0
Absorption correction		Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission		1.000 and 0.818	0.96 and 0.84
Refinement method		Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters		5427 / 6 / 328	11090 / 0 / 591
Goodness-of-fit on F^2		1.038	1.040
Final R indices [$I>2\sigma(I)$]	R1	0.0363,	0.0346,
	wR2	0.0950	0.0825
R indices (all data)	R1	0.0458,	0.0414,
	wR2	0.0999	0.0872
Largest diff. peak and hole (e.Å^{-3})		0.343 and -0.566	0.401 and -0.288
CSD deposit number		1824219	1824220

Theoretical methods

We have started our calculations by performing DFT and TD-DFT calculations with the Gaussian 16 code,[9] on all dyes of $\mathbf{6T_1T_2}$ type, for which the large alkyl chains have been substituted by methyl groups during the calculations for obvious computational reasons. Default Gaussian16 thresholds and algorithms were used but for an improved optimization threshold (10^{-5} au on average residual forces), a stricter self-consistent field convergence criterion (10^{-10} a.u.) and the use of the *ultrafine* DFT integration grid. First, the GS geometries have been optimized with DFT and the vibrational frequencies have been analytically determined, using the M06-2X *meta*-GGA hybrid exchange-correlation functional.[10] These calculations were performed with the 6-31G(d) atomic basis set and account for solvent effects through the linear-response PCM approach considering toluene as solvent.[11] All optimized structures correspond to true minima of the potential energy surface. Second, the vertical transition energies with TD-DFT were determined with the same functional, but a larger basis set, namely 6-311+G(2d,p), in gas-phase as well as in solution using the linear-response variant of the PCM,[10] in its *non-equilibrium* limit. The obtained transition energies were next corrected using CC2 transition energies calculated the Turbomole code.[12] More in details, the CC2 energies were calculated in gas phase applying the resolution of identity scheme, and using the diffuse containing *aug*-cc-pVDZ atomic basis set. The RI approximation was applied with the corresponding auxicllary basis set. Importantly, as most of the studied dyes are not fluorescent, one cannot straightfowardly compare experimental and theoretical 0-0 energies, and we have therefore decided to turn towards the vertical approximation. This approximation neglects vibronic couplings, but we were here interested in the results in an hologous series of compounds.

Table S2: Main theoretical results. Transition energies (in eV) and oscillator strengths obtained for the two lowest excited-states of all structures. The first line corresponds to the H-L dominated state, the second to the H-1-L dominated state. The best estimates are obtained assuming additive solvent effects.

Dye	TD-DFT (gas)	TD-DFT (tol)	CC2 (gas)	Best estimate
6αα	2.10 (*f=0.81)* 2.38 (*f=0.17)*	1.97 (*f=1.05*) 2.39 *(f=0.10)*	1.86 2.10	1.73 2.11
6αβ	2.15 (*f=0.96)* 2.36 (*f=0.05)*	2.02 (*f=1.05*) 2.38 *(f=0.03)*	1.96 2.05	1.83 2.07
6βα	2.20 (*f=0.61)* 2.37 (*f=0.50)*	2.11 (*f=1.12*) 2.34 *(f=0.20)*	2.15 1.89	2.06 1.86
6ββ	2.29 (*f=1.06)* 2.30 (*f=0.09)*	2.16 (*f=1.37*) 2.32 *(f=0.00)*	2.13 1.94	2.00 1.96

Field-Effect Transistors elaboration and characterization

Organic field-effect transistors (OFETs) were elaborated on commercially available pre-patterned test structures whose source and drain contacts were composed of a 30 nm thick gold layer on top of a 10 nm thick Indium Tin Oxide (ITO) layer. A 230 nm thick silicon oxide was used as the gate dielectric and an n-doped ($3x10^{17}/cm^3$) silicon crystal as the gate electrode. The channel length and channel width were 20 µm and 10 mm, respectively. The test structures were cleaned in acetone and isopropyl alcohol and subsequently in an ultra-violet ozone system for 30 minutes. Then, hexamethyldisilazane (HMDS) was spincoated (500 rpm for 5 s and then 4000 rpm for 50 s) under nitrogen ambient followed by an annealing step at 130°C for 10 minutes. Then, 7 mg/mL anhydrous chloroform of the different isomers solutions were spin coated (1250 rpm for 120 s) on the devices. For bottom-gate/bottom-contact (BGBC) OFETs, the samples were then simply left overnight under vacuum (<10^{-6} mbar) to remove residual solvent traces. For top-gate/bottom-contact (TGBC) OFETs, a layer of 770nm of Cytop (from Asahi glass) was further spincoated (1200 rpm for 10 s and then 2500 rpm for 40 s) and annealed at 100°C for 2h. Then, the device elaboration was completed by the evaporated through an appropriate shadow mask of a 120nm thick layer of silver as gate electrode. Both the FET elaboration and characterizations were performed in nitrogen ambient. The transistor output and transfer characteristics were recorded using a Keithley 4200 semiconductor characterization system. The charge carrier mobility was extracted in the saturation regime using the usual formalism on FET devices.

The output characteristics of the OFETs for every isomer in the optimized annealing conditions on BCBG OFETs are presented in Figure S62-65.

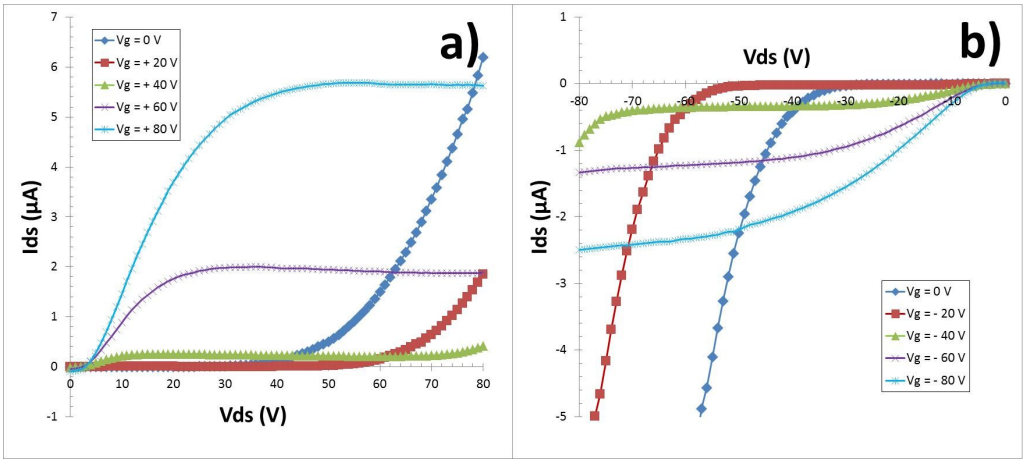


Figure S62: Output characteristics measured on a **6αα** OFET annealed at 130°C for 15 minutes. Figure a) corresponds to the output characteristics where the electrons are the main charge-

carriers and figure b) to the output characteristics where the holes are the main charge-carriers. *Ids*, *Vds* and *Vg* stands for drain-source current, drain-source voltage and gate voltage, respectively.

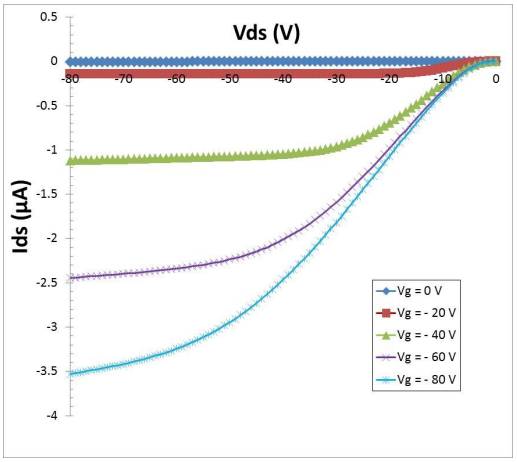


Figure S63: Holes output characteristics measured on a **6αβ** OFET annealed at 80°C for 15 minutes. *Ids*, *Vds* and *Vg* stands for drain-source current, drain-source voltage and gate voltage, respectively.

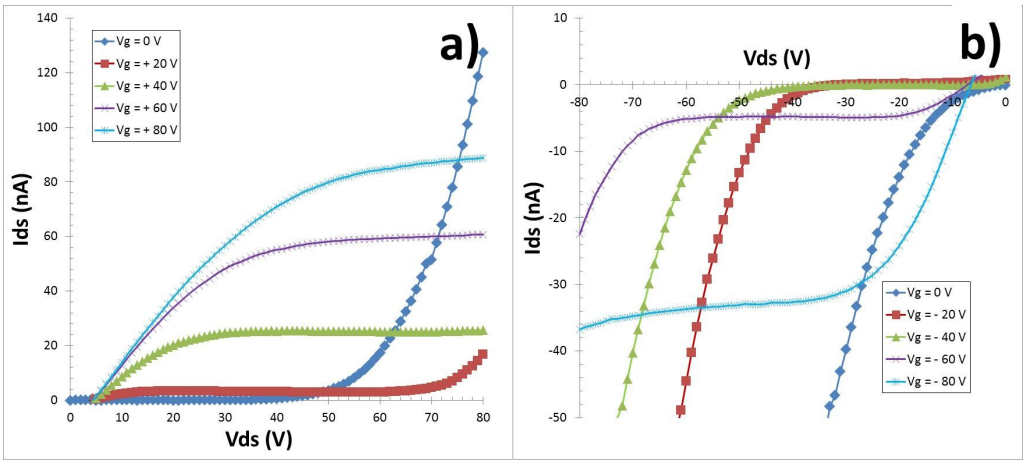


Figure S64: Output characteristics measured on a **6βα** OFET. Figure a) corresponds to the output characteristics where the electrons are the main charge-carriers and figure b) to the output characteristics where the holes are the main charge-carriers. *Ids*, *Vds* and *Vg* stands for drain-source current, drain-source voltage and gate voltage, respectively.

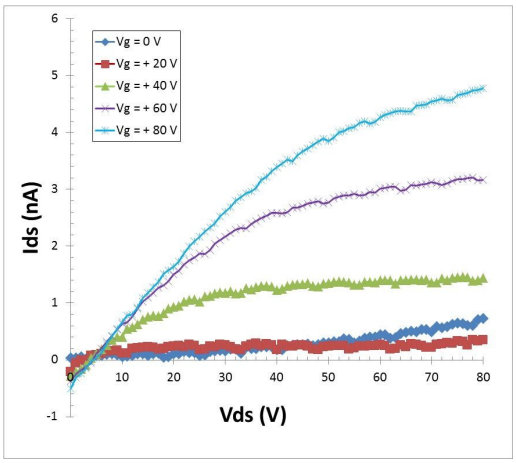


Figure S65: Electron output characteristics measured on a **6ββ** OFET annealed at 80°C for 15 minutes. *Ids*, *Vds* and *Vg* stands for drain-source current, drain-source voltage and gate voltage, respectively.

The transfer characteristics of the OFETs for every isomer in the optimized annealing conditions on BCBG OFETs are presented in Figure S66-69.

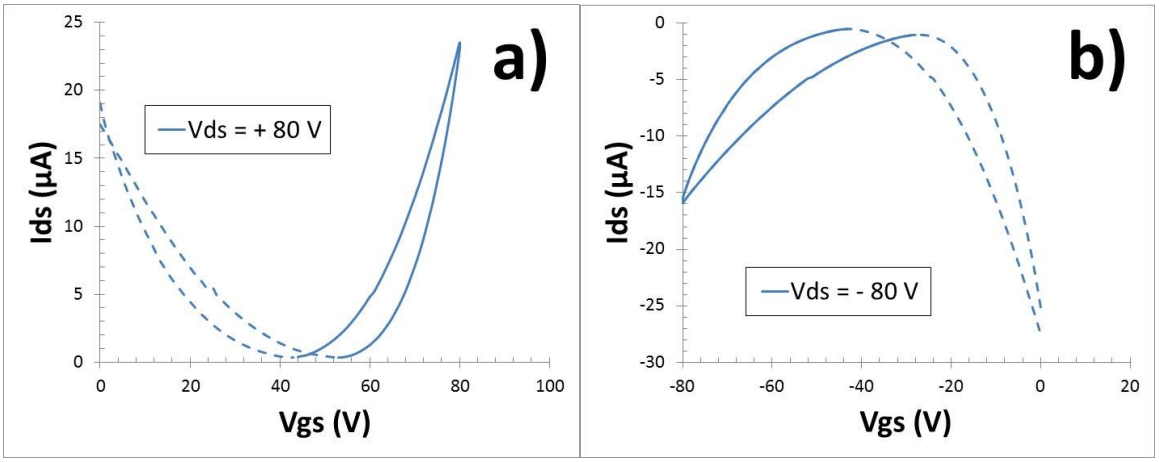


Figure S66: Transfer characteristics measured on a **6αα** OFET annealed at 130°C for 15 minutes. Figure a) corresponds to the transfer characteristics where the electrons are the main charge-carriers and figure b) to the transfer characteristics where the holes are the main charge-carriers. *Ids*, *Vds* and *Vgs* stands for drain-source current, drain-source voltage and gate-source voltage, respectively.

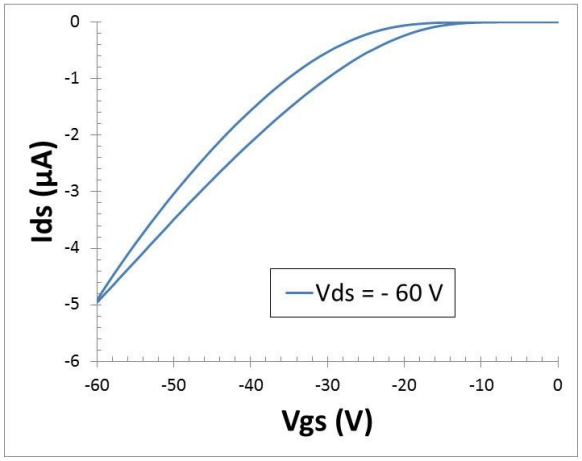


Figure S67: Transfer characteristics measured on a **6αβ** OFET annealed at 80°C for 15 minutes. *Ids*, *Vds* and *Vgs* stands for drain-source current, drain-source voltage and gate-source voltage, respectively.

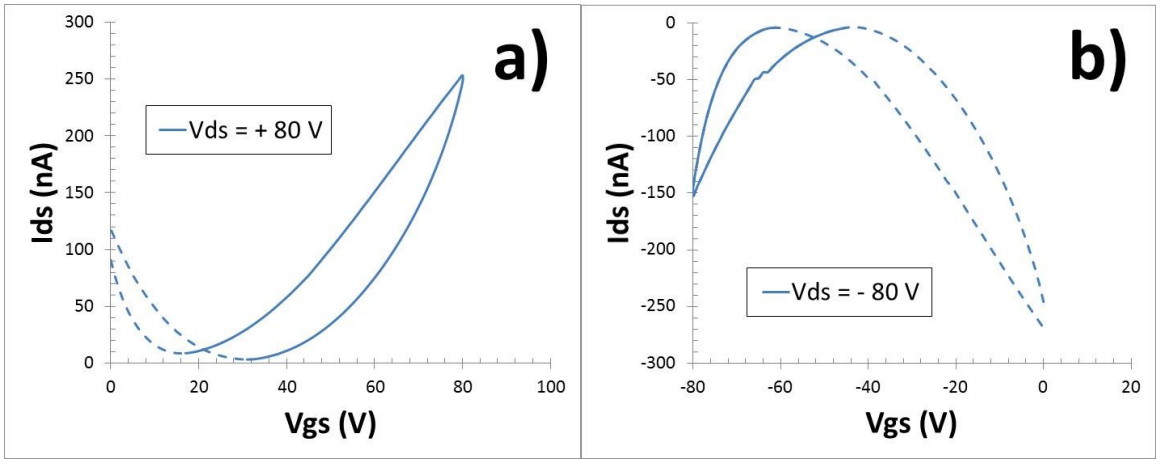


Figure S68: Transfer characteristics measured on a **6βα** OFET. Figure a) corresponds to the transfer characteristics where the electrons are the main charge-carriers and figure b) to the transfer characteristics where the holes are the main charge-carriers. *Ids*, *Vds* and *Vgs* stands for drain-source current, drain-source voltage and gate-source voltage, respectively.

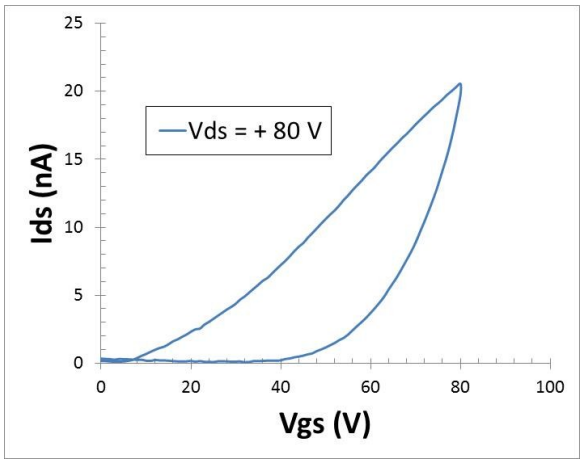


Figure S69: Transfer characteristics measured on a **6ββ** OFET annealed at 80°C for 15 minutes. *Ids*, *Vds* and *Vgs* stands for drain-source current, drain-source voltage and gate-source voltage, respectively.

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