Controlling chiral organization of molecular rods on Au(111) by molecular design

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Contents:

A) Descriptions and UHV-STM images of the cross, complex and pillar minority adsorption structures

Cross structure

STM images and model of the cross structure are presented in Figure S 1(a,c,e). Here molecules form extended networks quite similar to the windmill structure described in the main text, but with a higher packing packing density achieved by shifting the molecular backbones such that all (*S*)-*sec*-butyl groups are positioned close to the central benzene rings of the neighboring orthogonal molecules (see Fig. S 1 b, white circle). As a result, the backbones of the molecules form two rhombic-shaped openings of large and small size, (depicted in Fig. S 1 a). The sense of rotation for the cross windmill motif and the molecular conformation correlates in the same way as for the windmill structures as shown in Figure S1c. The cross structure is observed with both clockwise and counterclockwise sense of rotation.

Complex structure

STM images and model of the complex structure are presented in Figure S 1(b,d,f). Here, a complex pattern is observed combining the motifs of the windmill and cross structures. As seen from the *sec*-butyl imaging mode in Fig. S 2b, the molecules self-assemble in such a way that the ends from one side of the molecules interact with neighboring molecules sharing the same node, while the ends from the opposite side are shifted towards the central benzene ring of the neighboring nearly orthogonal molecules. Thus, each molecule connects adjacent windmill and cross motifs constructing an extended highly ordered network with two types of openings. Despite the complexity of the pattern, conformationally enantiopure domains consisting of either RR or LL conformers are found.

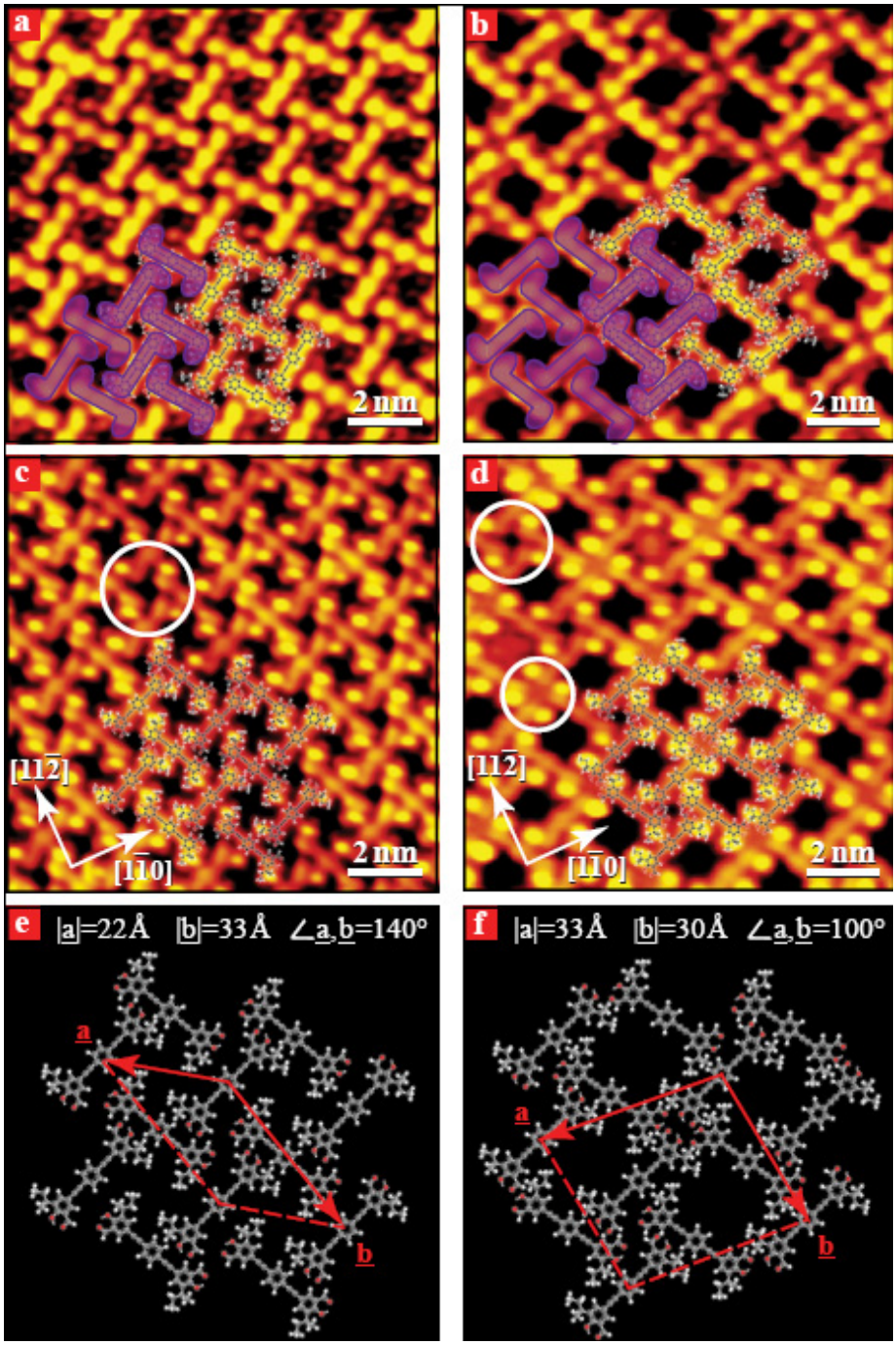


Figure S1: π-system imaging mode STM images of the complex and cross-like patterns formed by the (*S*)-*sec*-butyl molecules. (a) Cross-like pattern (120x120 Å^2, It = -0,4 nA, Vt = -1,54 V). (b) Complex-pattern mode (120x120 Å^2, It = -0.45 nA, Vt = -1.2 V). (*S*)-*sec*-butyl imaging mode STM images of the complex and cross-like patterns formed by the (*S*)-*sec*-butyl molecules (c) Cross-like pattern (120x120 Å^2, It = -0,45 nA, Vt = -1,54 V). (d) Complex pattern (120x120 Å^2, It = -0,56 nA, Vt = -1,32 V). (e)

Proposed schematic model of the cross-like adsorption structure deduced from the STM image. (f) Proposed schematic model of the complex-like adsorption structure as deduced from the STM image.

Pillar structures

Pillar structures, such as those presented in Figure S2 a,b (blue and violet molecules, respectively) are occasionally imaged, embedded in RR or LL Windmill structures. Here molecules arranged in parallel pillar structures are joining two windmills nodes, which are shifted by a molecular length with respect to each other. Each pillar structure has opposite conformation compared to the surrounding windmill phase, thus for the RR windmill phase the conformation of the pillar molecules will be LL and vice versa.

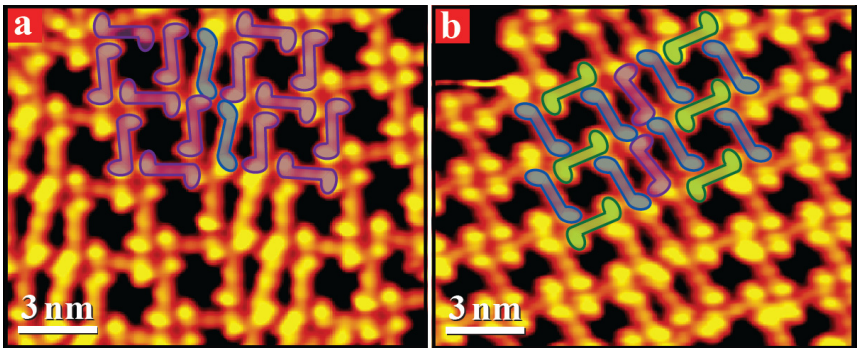


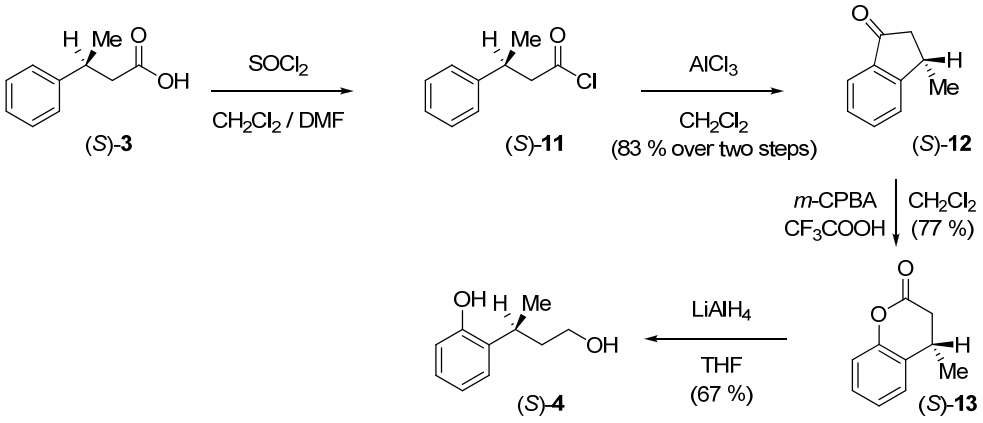
Figure S2: Pillar patterns embedded in Windmill structures. (a) LL pillars (blue molecules) in RR Windmill structure (violet molecules). (b) RR pillars (violet molecules) in LL Windmill structure (green and blue molecules).

B) General Synthetic Methods

Unless otherwise stated all reactions were performed under an atmosphere of nitrogen or argon. Standard Schlenk and vacuum line techniques were employed using argon or nitrogen as the inert atmosphere for all manipulations of air- or moisture-sensitive compounds. Yields refer to isolated chromatographically and spectroscopically homogeneous materials. Commercially available starting materials were used without further purification. (*S*)-Phenylbutyric acid ((*S*)-**3)** (99 % *ee*) was purchased from Sigma-Aldrich. Solvents were dried according to standard procedures. Purification of the products was carried out by flash chromatography using Merck silica gel 60 (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, using $CDCl_3$ as the solvent unless otherwise stated and were reported in ppm downfield from TMS (δ = 0.0 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR. Melting points are uncorrected.

C) Synthesis of (*S*)-4

(Spectral data are in agreement literature procedures)[1]



Phenylbutyric acid ((*S*)-3)

This compound is commercial available from Sigma-Aldrich in 99 % *ee*.

Methyl-indan-1-one ((*S*)-12)

A mixture of (*S*)-3-Phenylbutyryl acid ((*S*)-**3**) (5.35 g, 32.6 mmol), thionyl chloride (20 ml) and DMF (0.5 ml) in CH_2Cl_2 (100 ml) was heated to reflux and stirred for 1.5 hours until no starting material was observed by tlc analysis. The solvents and unreacted thionyl chloride was removed *in vacuo* and the remaining yellow oil was redissolved in 60 ml CH_2Cl_2. The solution of (*S*)-**11** was cooled to 0 °C and $AlCl_3$ (8.4 g, 64 mmol) was slowly added. The solution was stirred for 60 minutes, quenched by carefully addition of 100 ml of saturated aqueous $NaHCO_3$ and extracted twice with CH_2Cl_2 (100 ml). The combined organic layer was dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by column chromatography (CH_2Cl_2, $r_f = 0.3$) to yield 3.95 g (83 %) of the desired product as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 3.18 (m, 1H), 2.85 (dd, $J = 16.0$, 5.6 Hz, 1H), 2.59 (dd, $J = 16.0$, 7.2 Hz, 1H), 1.34 (d, $J = 6.8$ Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 160.2, 136.6, 135.0, 127.6, 125.5, 123.6, 45.5, 33.0, 21.5, HRMS (ES) m/z: [M + Na] calc. for $C_{10}H_{10}NaO$, 169,0629, found 169.0621

(*S*)-4-Methyl-chroman-2-one ((*S*)-13)

To a solution of (*S*)-**12** (3.80 g, 26.0 mmol) and *m*-chloroperoxybenzoic acid (17 g, 102 mmol) in CH_2Cl_2 (100 ml) was added TFA (1.5 ml) and the mixture was heated to 60 ºC for 14 h. The mixture was cooled

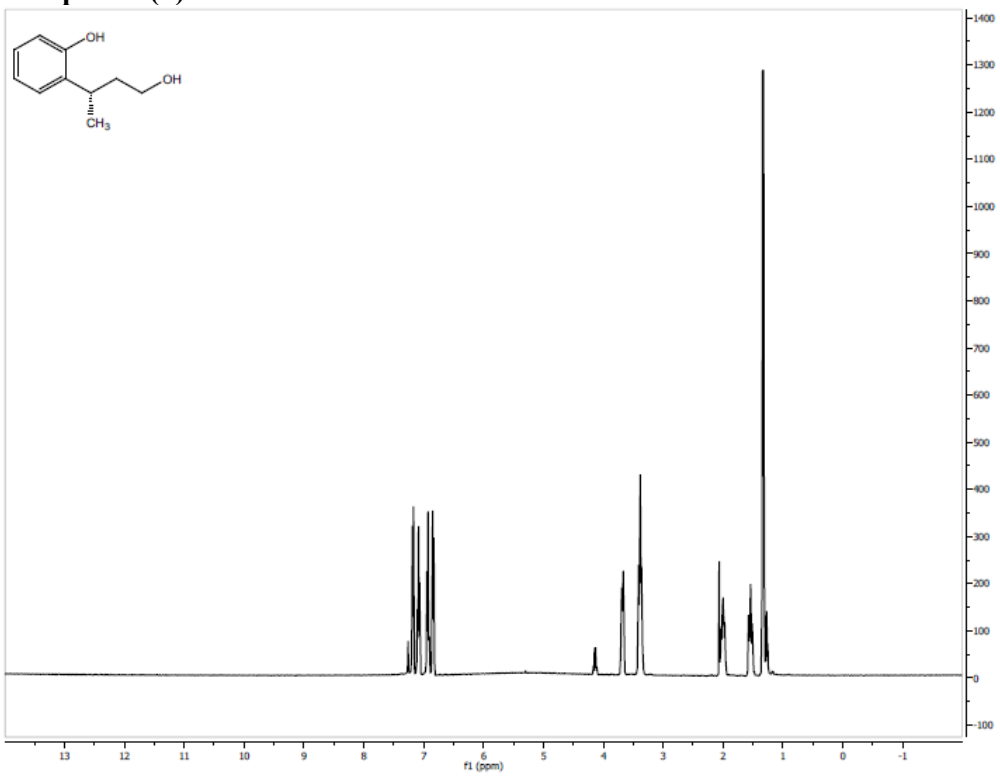
and extracted with aqueous NaOH (0.1 M), sat. aqueous $NaHCO_3$ and brine, dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was subjected to flash chromatography (CH_2Cl_2) to yield 3.25 g (77 %) of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 3.18 (m, 1H), 2.84 (dd, *J* = 15.6, 5.6 Hz, 1H), 2.58 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.33 (d, *J* = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 154,0; 132,1; 127,3; 126,9; 121,3; 116,1; 60,9; 41,0; 27,1; 21,0; HRMS (ES) m/z: [M + Na] calc. for $C_{10}H_{10}NaO_2$, 185,0578, found 185.0578

(*S*)-2-(3-Hydroxy-1-methyl-propyl)-phenol ((*S*)-4)

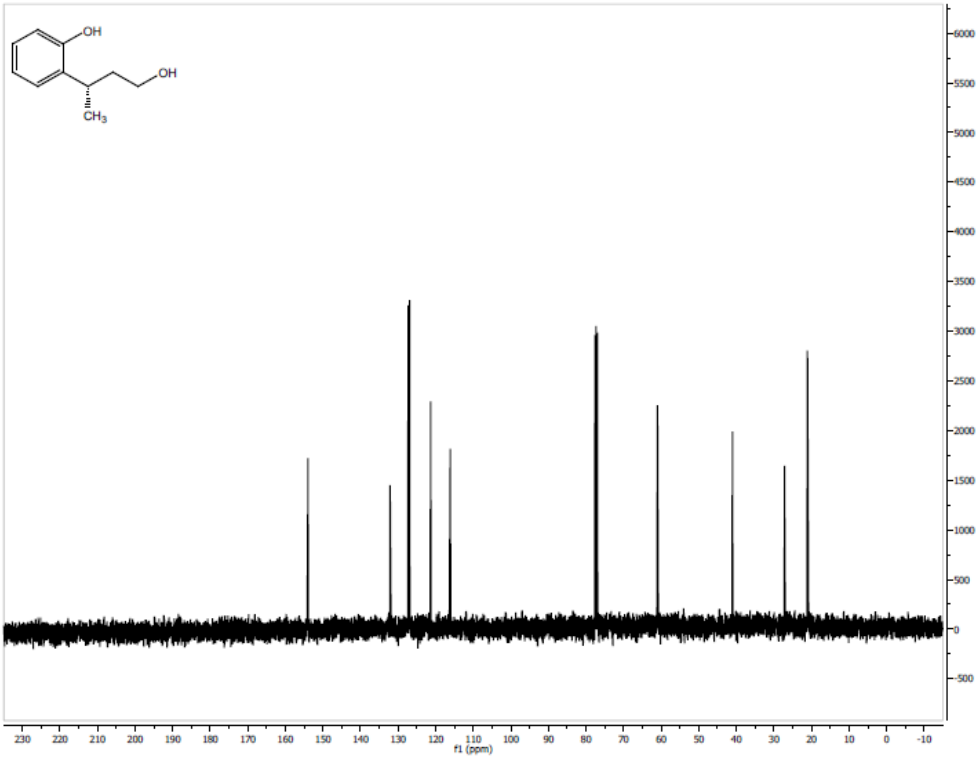
A stirred solution of (*S*)-**7** (3.0 g, 18.5 mmol) in THF under an atmosphere of nitrogen was cooled to 0 ºC and $LiAlH_4$ (500 mg, 13.2 mmol) was added. The mixture was stirred for 45 min and quenched by carefully addition of first MeOH and then water. The reaction mixture was filtered to remove inorganic salts and the aqueous phase was made neutral by addition of 0.1 M HCl. The mixture was extracted three times with CH_2Cl_2, dried ($MgSO_4$) and the solvent was removed *in vacuo*. The residue was purified by flash chromatography (CH_2Cl_2 : EtOAc 17:3) to yield 2.06 g (67 %) of the desired product as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.2 Hz; 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 3.67 (m, 1H), 3.39 (m, 2H), 2.00 (m, 1H), 1.55 (t, *J* = 10.8 Hz, 1H), 1.33 (d, *J* = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 154,0; 132,1; 127,3; 126,9; 121,3; 116,1; 60,9; 41,0; 27,1; 21,0; HRMS (ES) m/z: [M + Na] calc. for $C_{10}H_{14}NaO_2$, 189.0891, found 189.0895

D) Copies of ^{1}H and ^{13}C NMR spectra of compounds 2 and 4-10

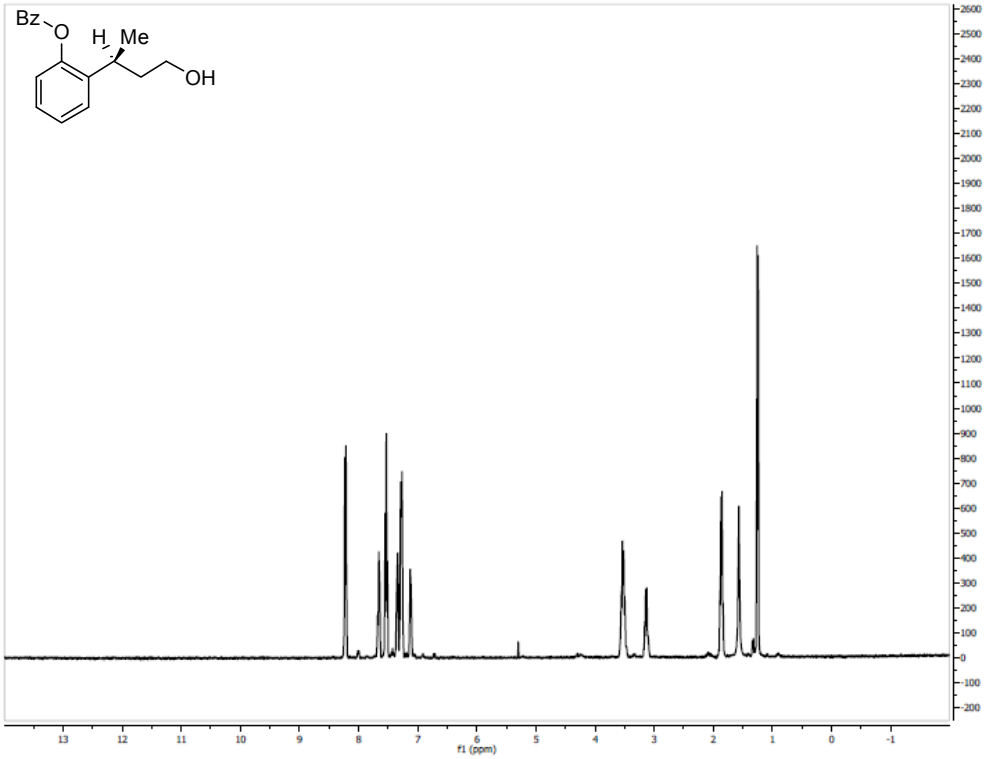
Compound (*S*)-4 ^{1}H NMR



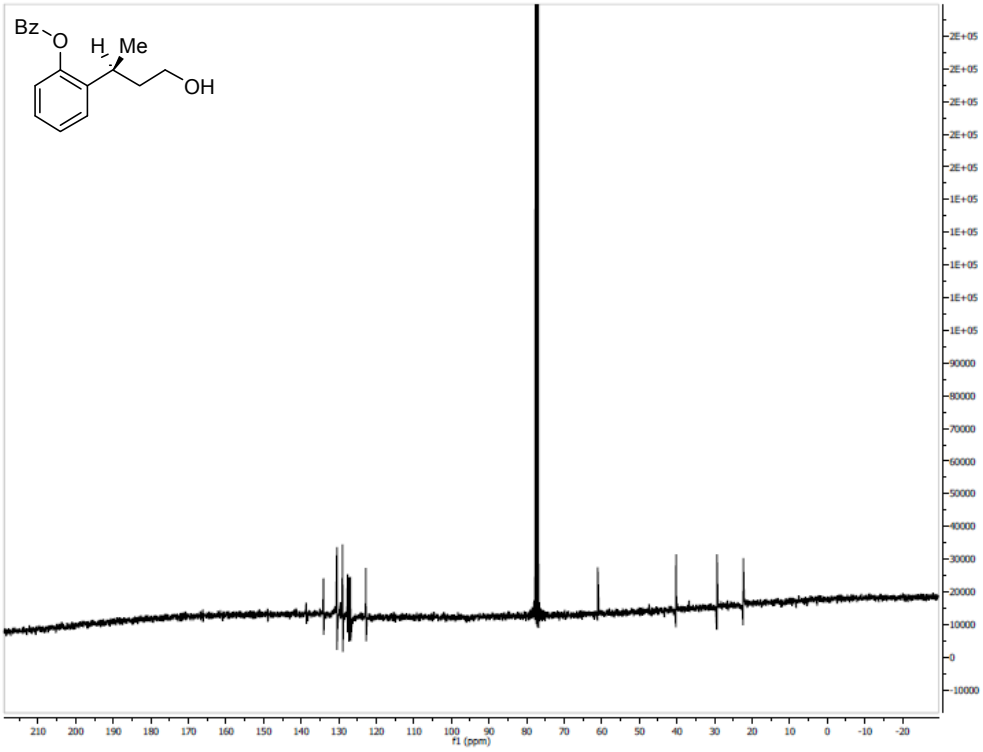
Compound (*S*)-4 ^{13}C NMR



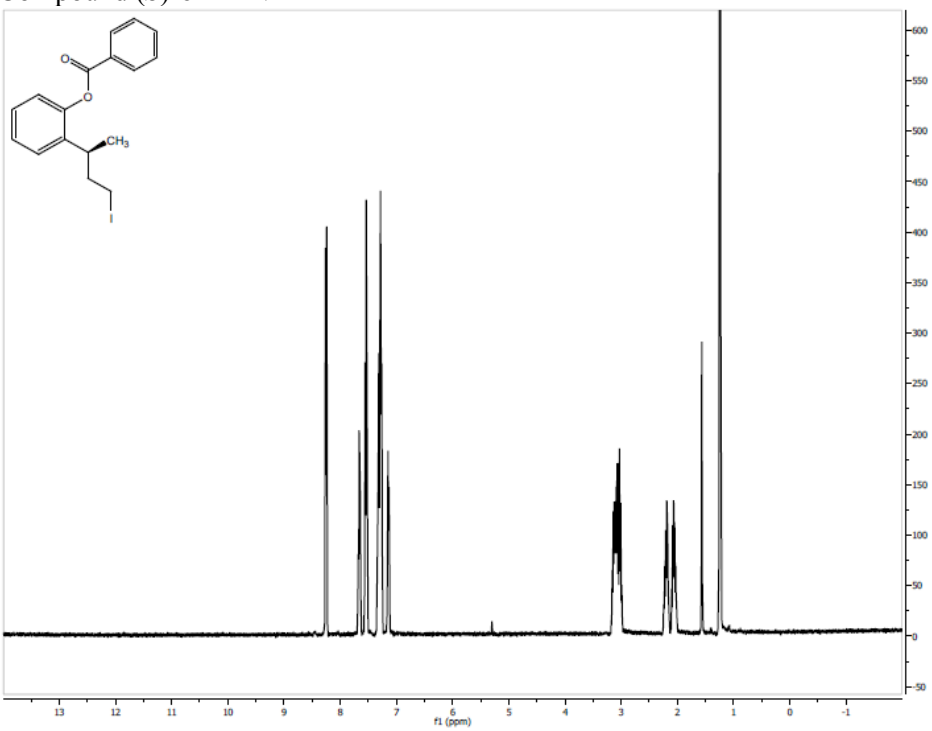
Compound (*S*)-5 ^{1}H NMR



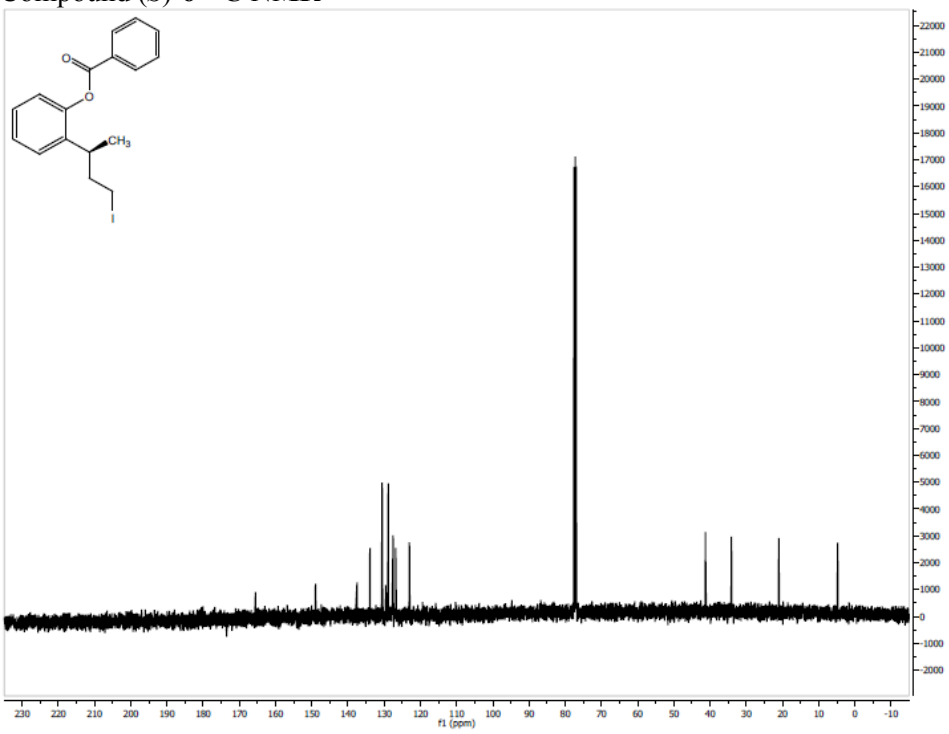
Compound (*S*)-5 ^{13}C NMR



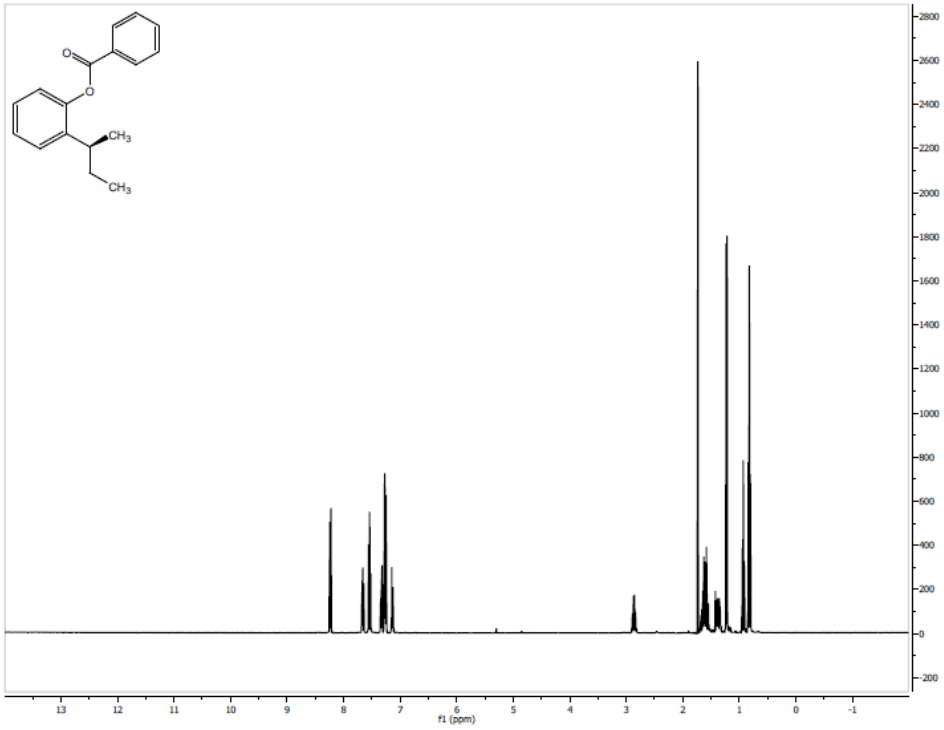
Compound (*S*)-**6** **^{1}H NMR**



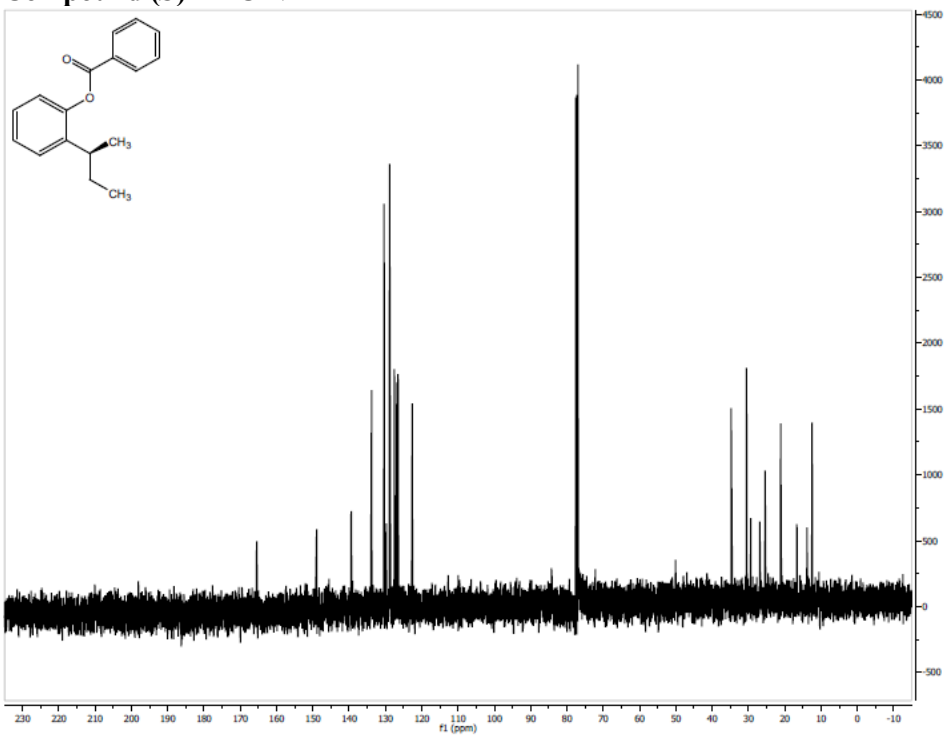
Compound (*S*)-**6** **^{13}C NMR**



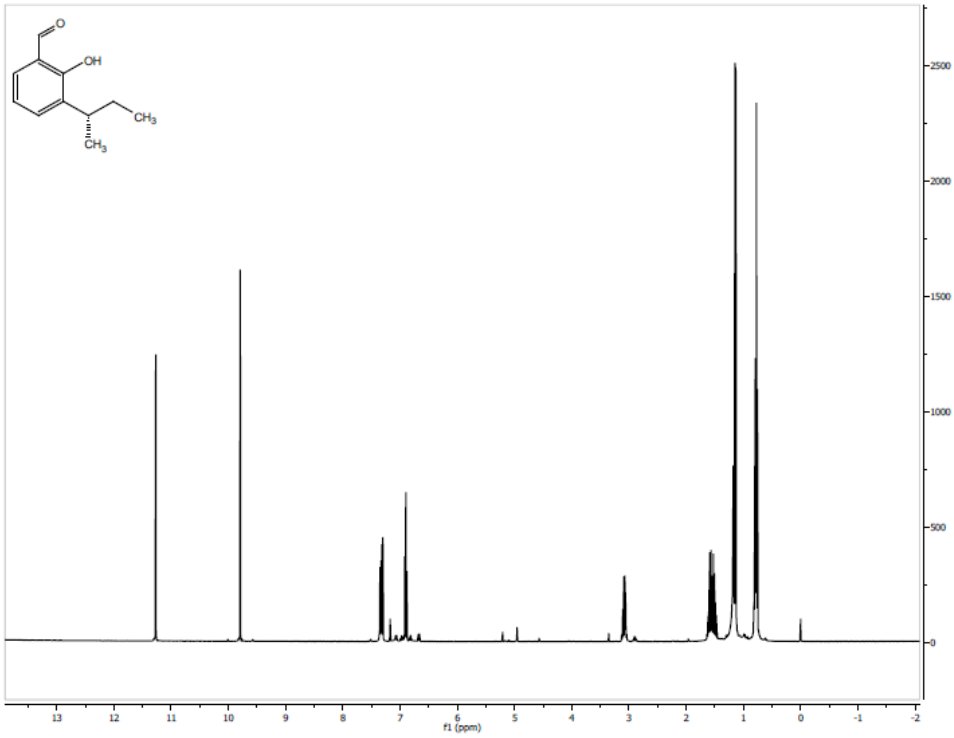
Compound (*S*)-7 **^{1}H NMR**



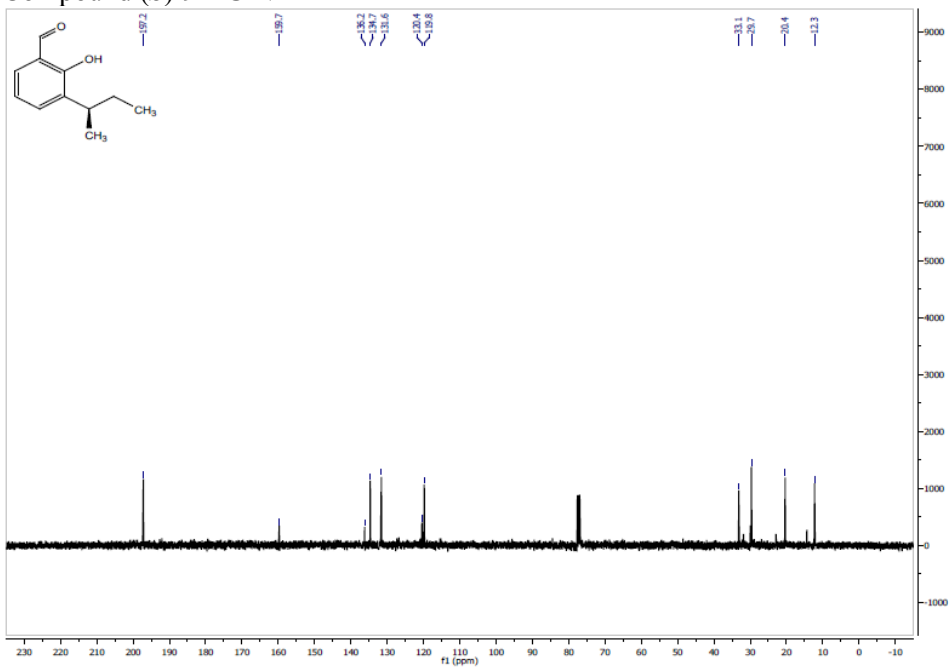
Compound (*S*)-7 ^{13}C NMR



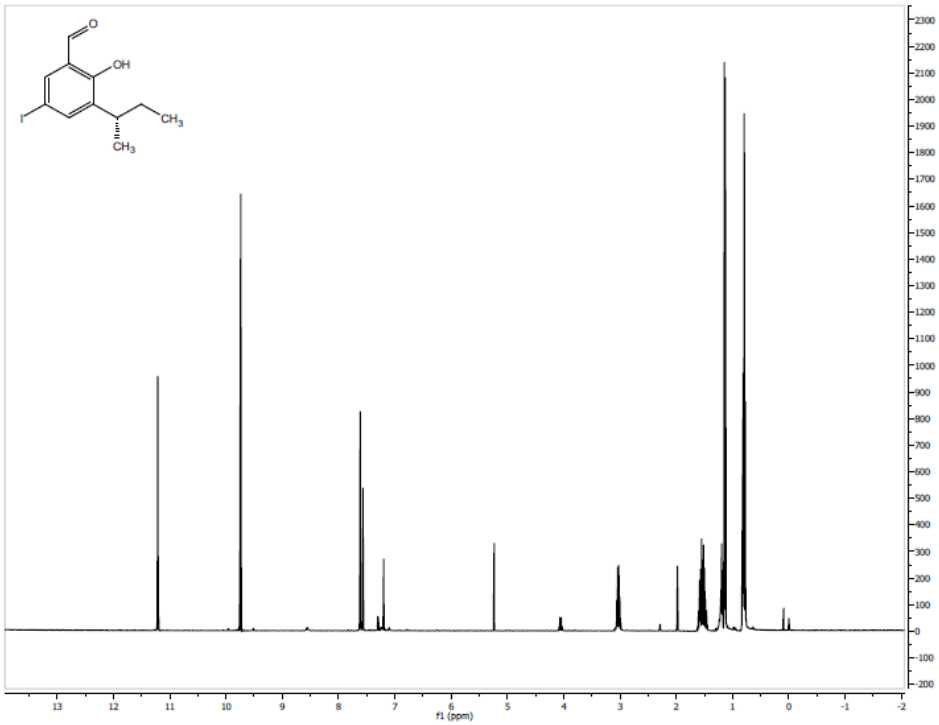
Compound (*S*)-**9** ^{1}**H NMR**



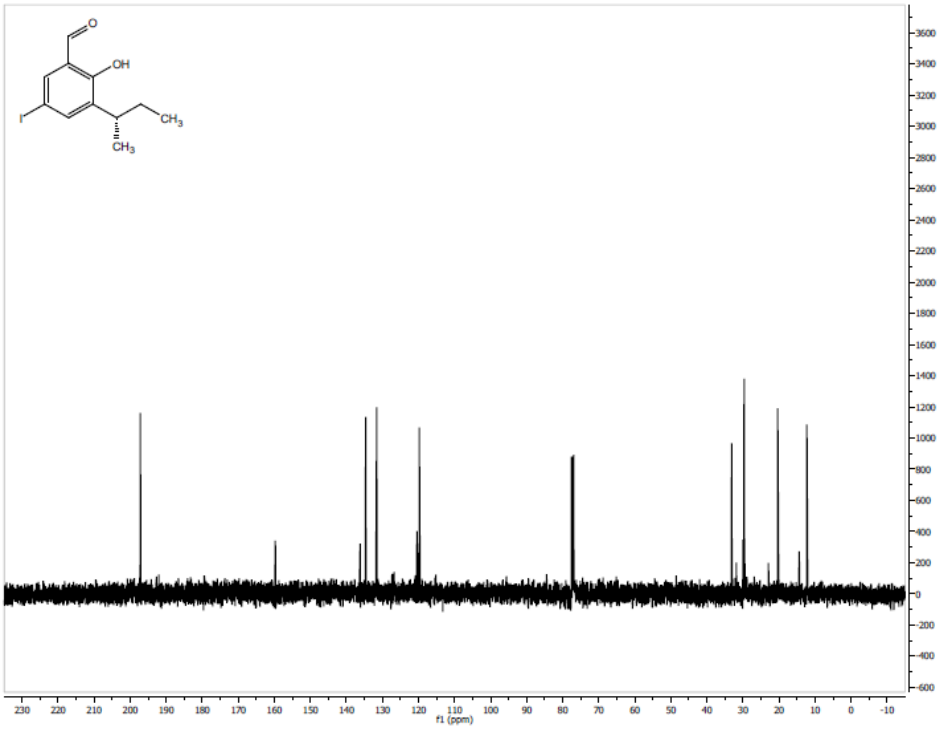
Compound (*S*)-**9** ^{13}**C NMR**



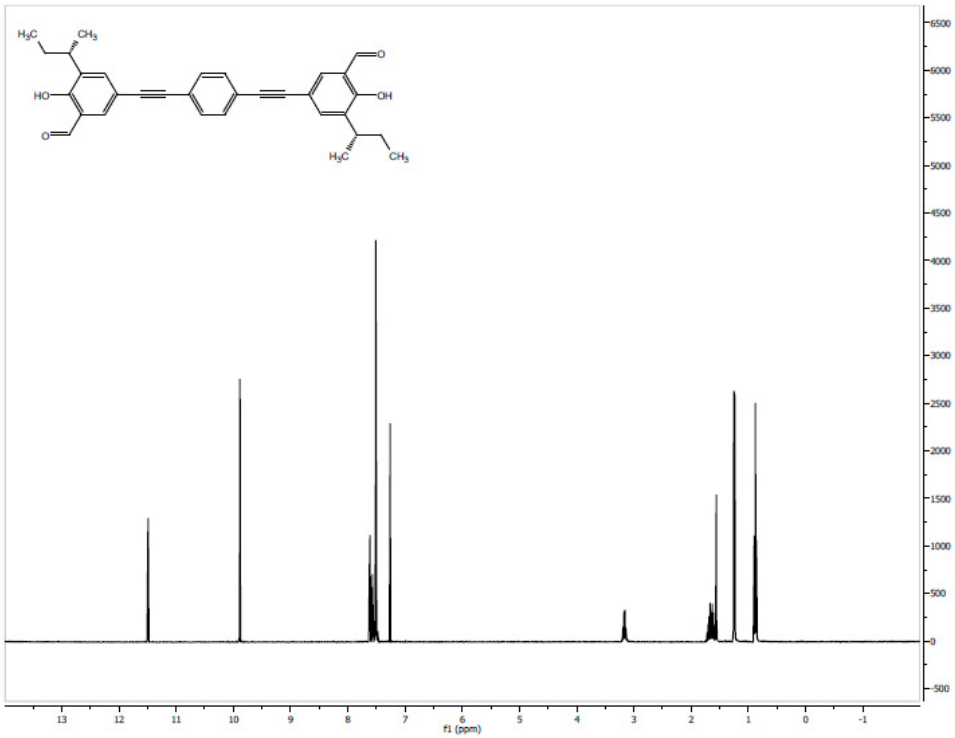
Compound (*S*)-10 ^{1}H NMR



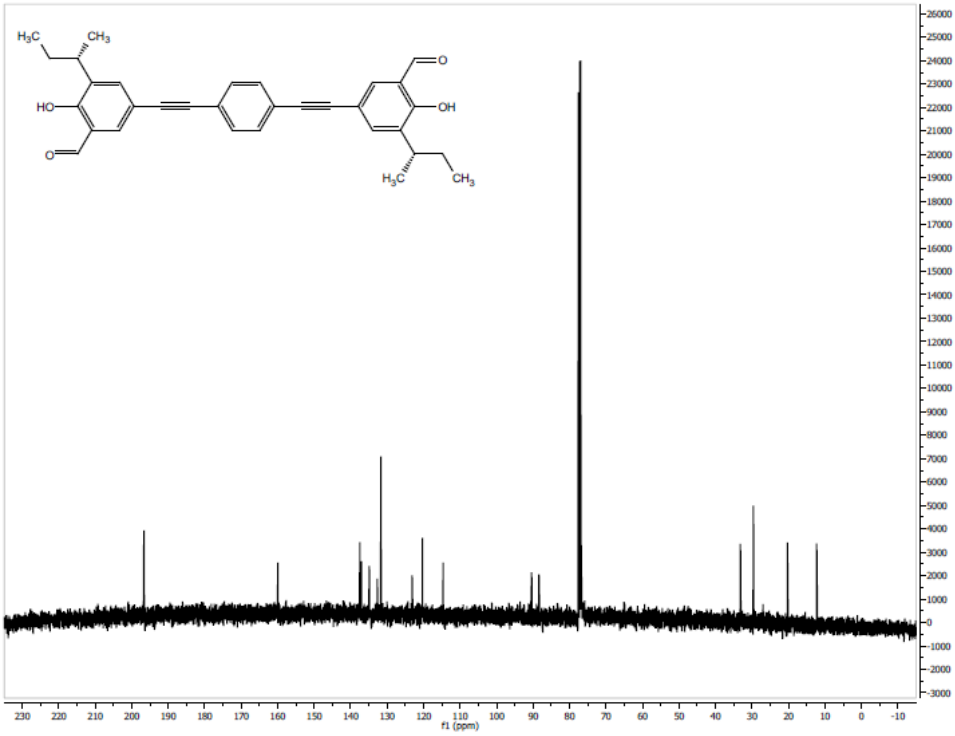
Compound (*S*)-10 ^{13}C NMR



Compound (*S*)-**2** ^{1}**H NMR**



Compound (*S*)-**2** ^{13}**C NMR**



[1] Loiodice, F.; Longo, A.; Bianco, P.; Tortorella, V. *Tetrahedron: Asymmetry* **1995***, 6*, 1001-1011.