SUPPORTING INFORMATION

A mechanistic study of the Lewis acid-Brønsted base-Brønsted acid catalysed asymmetric Michael addition of diethyl malonate to cyclohexenone.

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General experimental procedures

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on 300, 400 and 600 MHz spectrometers. Chemical shifts (δ, ppm) in ^{1}H NMR spectra were measured with respect to the residual protons signal of the deuterated solvent, to the signal of deuterated solvent in ^{13}C NMR spectra and with respect to external $CFCl_3$ in ^{19}F NMR spectra. DOSY experiments were performed on a 600 MHz spectrometer at 25°C using the DOSY-ONESHOT pulse sequence.[S1] The following parameters were used within the pulse sequence: diffusion time 0.2 s, gradient pulse duration 1 ms, unbalancing factor alpha 2.0, relaxation delay 5.0 s. Signal attenuation was achieved by increasing the gradient strength from 5% to 80% as defined by the pulse sequence in 16 steps, each with maximum gradient strength of 0.27 T/m. The rows of quasi-2D diffusion dataset were phased and baseline corrected. Pseudo-2D DOSY spectra were obtained using a standard fitting procedure within the software. The actual diffusion coefficients were determined using a T_1/T_2 analysis module within the software.

Optical rotations were measured in a thermostated cuvette (l = 5 cm) at 25 °C. IR spectra were recorded on a FTIR spectrometer with a resolution of 2 cm^{-1} using a 0.062 mm CaF_2 cell. Curve fitting analysis was carried out using a mixed Gaussian-Lorentzian function. Elemental analysis was performed in the laboratory of elemental analysis of INEOS RAS. Silica gel 60 was used for chromatographic separations. All solvents were purified by standard methods.[S2] Enantiomerically pure BINOL was purchased from commercial suppliers with *ee* = 99.9%.

Methodology for X-ray structure analysis

The crystal of (*S*)-BIFOL×H_2O ($C_{46}H_{32}O_5$, M = 664.71) is orthorhombic, space group $P2_12_12_1$, at T = 120 K: a = 9.6965(4) Å, b = 17.3653(7) Å, c = 19.2464(8) Å, V = 3240.8(2) Å^3, Z = 4, d_{calc} = 1.362 g/cm^3, $F(000)$ = 1392, μ = 0.088 mm^{-1}. 44815 total reflections (9922 unique reflections, R_{int} = 0.067) were measured on a three-circle CCD diffractometer ($\lambda(MoK_\alpha)$-radiation, graphite monochromator, φ and ω scan mode, $2\theta_{max}$ = 61.0°) and corrected for absorption (T_{min} = 0.969; T_{max} = 0.979).[S3] The crystal structure was determined by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms of the OH-groups and the solvate water molecule were localized in the difference-Fourier map and included into the refinement with fixed isotropic displacement parameters [$U_{iso}(H) = 1.5U_{eq}(O)$]. The other hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters ($U_{iso}(H) = 1.2U_{eq}(C)$). The final divergence factors were R_1 = 0.054 for 7141 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.146 for all independent reflections, S = 1.018. All calculations were carried out using the *SHELXTL* program.[S4] Crystallographic data for (*S*)-BIFOL • H_2O have been deposited with the Cambridge Crystallographic Data Center. CCDC 1409564 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: **deposit@ccdc.cam.ac.uk** or **www.ccdc.cam.ac.uk**).

Table S1. Crystal data and structure refinement for **(*S*)-BIFOL×H_2O**.

Identification code	**(*S*)-BIFOL×H_2O**	
Empirical formula	$C_{46}H_{32}O_5$	
Formula weight	664.71	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.6965(4) Å	α = 90°.
	b = 17.3653(7) Å	β = 90°.
	c = 19.2464(8) Å	γ = 90°.
Volume	3240.8(2) $Å^3$	
Z	4	
Density (calculated)	1.362 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	1392	
Crystal size	0.200 x 0.180 x 0.150 mm^3	
Theta range for data collection	2.116 to 30.575°.	
Index ranges	-13<=h<=13, -24<=k<=24, -27<=l<=27	
Reflections collected	44815	
Independent reflections	9922 [R(int) = 0.0669]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.979 and 0.969	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9922 / 0 / 460	
Goodness-of-fit on F^2	1.018	
Final R indices [for 7141 rflns with I>2σ(I)]	R1 = 0.0539, wR2 = 0.1281	
R indices (all data)	R1 = 0.0891, wR2 = 0.1457	
Absolute structure parameter	0.0(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.404 and -0.360 $e.Å^{-3}$	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for ***Sam2***. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	11396(2)	2888(1)	6752(1)	24(1)
O(2)	9182(2)	3087(1)	7531(1)	24(1)
O(3)	6226(2)	2456(1)	7558(1)	26(1)
O(4)	3664(2)	2840(1)	7583(1)	30(1)
C(1)	8508(3)	2079(1)	8320(1)	21(1)
C(2)	9273(3)	2340(2)	7766(1)	21(1)
C(3)	10185(3)	1849(2)	7380(1)	21(1)
C(4)	10359(3)	1108(2)	7609(1)	23(1)
C(4A)	9646(3)	819(2)	8199(1)	22(1)
C(5)	9825(3)	37(2)	8419(1)	28(1)
C(6)	9082(3)	-243(2)	8966(2)	31(1)
C(7)	8143(3)	232(2)	9329(2)	29(1)
C(8)	7941(3)	984(2)	9121(1)	25(1)
C(8A)	8693(3)	1299(2)	8552(1)	22(1)
C(9)	7419(3)	2594(1)	8616(1)	20(1)
C(10)	6292(3)	2779(2)	8203(1)	21(1)
C(11)	5241(3)	3296(1)	8438(1)	22(1)
C(12)	5350(3)	3607(2)	9091(2)	24(1)
C(12A)	6463(3)	3422(2)	9535(1)	21(1)
C(13)	6539(3)	3724(2)	10225(1)	25(1)
C(14)	7582(3)	3533(2)	10650(2)	30(1)
C(15)	8657(3)	3051(2)	10413(2)	30(1)
C(16)	8623(3)	2745(2)	9756(1)	26(1)
C(16A)	7515(3)	2914(2)	9299(1)	21(1)
C(17)	10782(3)	2124(2)	6689(1)	23(1)
C(17A)	9672(3)	2106(2)	6112(1)	26(1)
C(18)	8347(3)	2410(2)	6109(2)	34(1)
C(19)	7510(4)	2289(2)	5529(2)	43(1)
C(20)	7989(4)	1884(2)	4964(2)	45(1)
C(21)	9294(4)	1567(2)	4962(2)	39(1)
C(21A)	10141(3)	1670(2)	5547(2)	30(1)
C(21B)	11510(3)	1371(2)	5705(2)	29(1)

C(22)	12390(4)	911(2)	5303(2)	40(1)
C(23)	13663(4)	719(2)	5575(2)	43(1)
C(24)	14054(4)	957(2)	6236(2)	38(1)
C(25)	13154(3)	1401(2)	6645(2)	30(1)
C(25A)	11900(3)	1608(2)	6372(1)	25(1)
C(26)	4054(3)	3528(2)	7951(2)	25(1)
C(26A)	2846(3)	3895(2)	8340(2)	27(1)
C(27)	1970(3)	3562(2)	8816(2)	34(1)
C(28)	999(3)	4032(2)	9144(2)	41(1)
C(29)	940(4)	4812(2)	9001(2)	43(1)
C(30)	1803(3)	5144(2)	8518(2)	38(1)
C(30A)	2752(3)	4677(2)	8170(2)	30(1)
C(30B)	3756(3)	4856(2)	7633(2)	31(1)
C(31)	4030(4)	5542(2)	7289(2)	39(1)
C(32)	5037(4)	5556(2)	6795(2)	45(1)
C(33)	5801(4)	4895(2)	6632(2)	40(1)
C(34)	5545(3)	4204(2)	6972(2)	33(1)
C(34A)	4517(3)	4186(2)	7475(2)	27(1)
O(5)	8141(3)	4398(1)	8114(1)	47(1)

Table S3. Bond lengths [Å] and angles [°] for **(*S*)-BIFOL×H_2O**.

O(1)-C(17)	1.458(3)	C(13)-C(14)	1.342(4)
O(1)-H(1O)	0.9001	C(13)-H(13)	0.9500
O(2)-C(2)	1.377(3)	C(14)-C(15)	1.412(4)
O(2)-H(2O)	0.8988	C(14)-H(14)	0.9500
O(3)-C(10)	1.364(3)	C(15)-C(16)	1.371(4)
O(3)-H(3O)	0.8992	C(15)-H(15)	0.9500
O(4)-C(26)	1.439(3)	C(16)-C(16A)	1.421(4)
O(4)-H(4O)	0.9007	C(16)-H(16)	0.9500
C(1)-C(2)	1.376(4)	C(17)-C(25A)	1.535(4)
C(1)-C(8A)	1.438(4)	C(17)-C(17A)	1.546(4)
C(1)-C(9)	1.496(4)	C(17A)-C(18)	1.389(4)
C(2)-C(3)	1.435(4)	C(17A)-C(21A)	1.401(4)
C(3)-C(4)	1.372(4)	C(18)-C(19)	1.395(5)
C(3)-C(17)	1.528(4)	C(18)-H(18)	0.9500
C(4)-C(4A)	1.420(4)	C(19)-C(20)	1.378(5)
C(4)-H(4)	0.9500	C(19)-H(19)	0.9500
C(4A)-C(8A)	1.418(4)	C(20)-C(21)	1.380(6)
C(4A)-C(5)	1.432(4)	C(20)-H(20)	0.9500
C(5)-C(6)	1.366(4)	C(21)-C(21A)	1.405(4)
C(5)-H(5)	0.9500	C(21)-H(21)	0.9500
C(6)-C(7)	1.413(4)	C(21A)-C(21B)	1.457(5)
C(6)-H(6)	0.9500	C(21B)-C(25A)	1.400(4)
C(7)-C(8)	1.379(4)	C(21B)-C(22)	1.401(5)
C(7)-H(7)	0.9500	C(22)-C(23)	1.382(6)
C(8)-C(8A)	1.426(4)	C(22)-H(22)	0.9500
C(8)-H(8)	0.9500	C(23)-C(24)	1.391(5)
C(9)-C(10)	1.389(4)	C(23)-H(23)	0.9500
C(9)-C(16A)	1.430(4)	C(24)-C(25)	1.405(4)
C(10)-C(11)	1.431(4)	C(24)-H(24)	0.9500
C(11)-C(12)	1.372(4)	C(25)-C(25A)	1.373(4)
C(11)-C(26)	1.538(4)	C(25)-H(25)	0.9500
C(12)-C(12A)	1.413(4)	C(26)-C(26A)	1.530(4)
C(12)-H(12)	0.9500	C(26)-C(34A)	1.532(4)
C(12A)-C(16A)	1.422(4)	C(26A)-C(27)	1.376(5)
C(12A)-C(13)	1.430(4)	C(26A)-C(30A)	1.400(4)

C(27)-C(28)	1.396(5)	C(31)-C(32)	1.363(5)
C(27)-H(27)	0.9500	C(31)-H(31)	0.9500
C(28)-C(29)	1.384(5)	C(32)-C(33)	1.402(5)
C(28)-H(28)	0.9500	C(32)-H(32)	0.9500
C(29)-C(30)	1.378(5)	C(33)-C(34)	1.389(5)
C(29)-H(29)	0.9500	C(33)-H(33)	0.9500
C(30)-C(30A)	1.399(4)	C(34)-C(34A)	1.389(5)
C(30)-H(30)	0.9500	C(34)-H(34)	0.9500
C(30A)-C(30B)	1.453(5)	O(5)-H(5A)	0.9001
C(30B)-C(31)	1.389(4)	O(5)-H(5B)	0.9001
C(30B)-C(34A)	1.411(4)		

C(17)-O(1)-H(1O)	102.8	C(8)-C(7)-C(6)	120.1(3)
C(2)-O(2)-H(2O)	116.7	C(8)-C(7)-H(7)	120.0
C(10)-O(3)-H(3O)	109.0	C(6)-C(7)-H(7)	120.0
C(26)-O(4)-H(4O)	107.7	C(7)-C(8)-C(8A)	120.9(3)
C(2)-C(1)-C(8A)	118.9(2)	C(7)-C(8)-H(8)	119.6
C(2)-C(1)-C(9)	118.6(2)	C(8A)-C(8)-H(8)	119.6
C(8A)-C(1)-C(9)	122.3(2)	C(4A)-C(8A)-C(8)	118.5(2)
C(1)-C(2)-O(2)	122.0(2)	C(4A)-C(8A)-C(1)	119.1(2)
C(1)-C(2)-C(3)	122.6(2)	C(8)-C(8A)-C(1)	122.4(2)
O(2)-C(2)-C(3)	115.4(2)	C(10)-C(9)-C(16A)	119.1(2)
C(4)-C(3)-C(2)	117.8(2)	C(10)-C(9)-C(1)	118.5(2)
C(4)-C(3)-C(17)	121.8(2)	C(16A)-C(9)-C(1)	122.4(2)
C(2)-C(3)-C(17)	119.9(2)	O(3)-C(10)-C(9)	117.5(2)
C(3)-C(4)-C(4A)	121.9(2)	O(3)-C(10)-C(11)	120.8(2)
C(3)-C(4)-H(4)	119.0	C(9)-C(10)-C(11)	121.6(2)
C(4A)-C(4)-H(4)	119.0	C(12)-C(11)-C(10)	118.8(2)
C(8A)-C(4A)-C(4)	119.5(2)	C(12)-C(11)-C(26)	120.9(2)
C(8A)-C(4A)-C(5)	119.6(2)	C(10)-C(11)-C(26)	120.3(2)
C(4)-C(4A)-C(5)	120.8(2)	C(11)-C(12)-C(12A)	121.5(2)
C(6)-C(5)-C(4A)	120.1(3)	C(11)-C(12)-H(12)	119.2
C(6)-C(5)-H(5)	119.9	C(12A)-C(12)-H(12)	119.2
C(4A)-C(5)-H(5)	119.9	C(12)-C(12A)-C(16A)	119.7(2)
C(5)-C(6)-C(7)	120.9(3)	C(12)-C(12A)-C(13)	121.1(2)
C(5)-C(6)-H(6)	119.6	C(16A)-C(12A)-C(13)	119.2(2)
C(7)-C(6)-H(6)	119.6	C(14)-C(13)-C(12A)	120.9(3)

C(14)-C(13)-H(13)	119.5	C(21)-C(21A)-C(21B)	130.9(3)
C(12A)-C(13)-H(13)	119.5	C(25A)-C(21B)-C(22)	120.6(3)
C(13)-C(14)-C(15)	120.4(3)	C(25A)-C(21B)-C(21A)	109.4(3)
C(13)-C(14)-H(14)	119.8	C(22)-C(21B)-C(21A)	130.0(3)
C(15)-C(14)-H(14)	119.8	C(23)-C(22)-C(21B)	118.2(3)
C(16)-C(15)-C(14)	120.6(3)	C(23)-C(22)-H(22)	120.9
C(16)-C(15)-H(15)	119.7	C(21B)-C(22)-H(22)	120.9
C(14)-C(15)-H(15)	119.7	C(22)-C(23)-C(24)	121.2(3)
C(15)-C(16)-C(16A)	120.6(3)	C(22)-C(23)-H(23)	119.4
C(15)-C(16)-H(16)	119.7	C(24)-C(23)-H(23)	119.4
C(16A)-C(16)-H(16)	119.7	C(23)-C(24)-C(25)	120.4(3)
C(16)-C(16A)-C(12A)	118.2(2)	C(23)-C(24)-H(24)	119.8
C(16)-C(16A)-C(9)	122.6(2)	C(25)-C(24)-H(24)	119.8
C(12A)-C(16A)-C(9)	119.2(2)	C(25A)-C(25)-C(24)	118.6(3)
O(1)-C(17)-C(3)	111.5(2)	C(25A)-C(25)-H(25)	120.7
O(1)-C(17)-C(25A)	106.0(2)	C(24)-C(25)-H(25)	120.7
C(3)-C(17)-C(25A)	115.5(2)	C(25)-C(25A)-C(21B)	121.0(3)
O(1)-C(17)-C(17A)	111.3(2)	C(25)-C(25A)-C(17)	128.8(2)
C(3)-C(17)-C(17A)	110.8(2)	C(21B)-C(25A)-C(17)	110.2(3)
C(25A)-C(17)-C(17A)	101.2(2)	O(4)-C(26)-C(26A)	112.6(2)
C(18)-C(17A)-C(21A)	120.2(3)	O(4)-C(26)-C(34A)	113.7(2)
C(18)-C(17A)-C(17)	129.7(3)	C(26A)-C(26)-C(34A)	101.9(2)
C(21A)-C(17A)-C(17)	110.0(3)	O(4)-C(26)-C(11)	106.2(2)
C(17A)-C(18)-C(19)	119.0(3)	C(26A)-C(26)-C(11)	112.6(2)
C(17A)-C(18)-H(18)	120.5	C(34A)-C(26)-C(11)	109.9(2)
C(19)-C(18)-H(18)	120.5	C(27)-C(26A)-C(30A)	121.5(3)
C(20)-C(19)-C(18)	120.8(3)	C(27)-C(26A)-C(26)	128.6(3)
C(20)-C(19)-H(19)	119.6	C(30A)-C(26A)-C(26)	109.8(3)
C(18)-C(19)-H(19)	119.6	C(26A)-C(27)-C(28)	118.2(3)
C(19)-C(20)-C(21)	121.0(3)	C(26A)-C(27)-H(27)	120.9
C(19)-C(20)-H(20)	119.5	C(28)-C(27)-H(27)	120.9
C(21)-C(20)-H(20)	119.5	C(29)-C(28)-C(27)	120.6(3)
C(20)-C(21)-C(21A)	118.9(3)	C(29)-C(28)-H(28)	119.7
C(20)-C(21)-H(21)	120.6	C(27)-C(28)-H(28)	119.7
C(21A)-C(21)-H(21)	120.6	C(30)-C(29)-C(28)	121.3(3)
C(17A)-C(21A)-C(21)	120.1(3)	C(30)-C(29)-H(29)	119.4
C(17A)-C(21A)-C(21B)	109.1(2)	C(28)-C(29)-H(29)	119.4

C(29)-C(30)-C(30A)	118.7(3)	C(31)-C(32)-H(32)	119.4
C(29)-C(30)-H(30)	120.7	C(33)-C(32)-H(32)	119.4
C(30A)-C(30)-H(30)	120.7	C(34)-C(33)-C(32)	120.5(3)
C(30)-C(30A)-C(26A)	119.6(3)	C(34)-C(33)-H(33)	119.8
C(30)-C(30A)-C(30B)	131.1(3)	C(32)-C(33)-H(33)	119.8
C(26A)-C(30A)-C(30B)	109.3(3)	C(34A)-C(34)-C(33)	118.5(3)
C(31)-C(30B)-C(34A)	120.3(3)	C(34A)-C(34)-H(34)	120.8
C(31)-C(30B)-C(30A)	130.6(3)	C(33)-C(34)-H(34)	120.8
C(34A)-C(30B)-C(30A)	109.1(3)	C(34)-C(34A)-C(30B)	120.4(3)
C(32)-C(31)-C(30B)	119.1(3)	C(34)-C(34A)-C(26)	130.1(3)
C(32)-C(31)-H(31)	120.5	C(30B)-C(34A)-C(26)	109.4(3)
C(30B)-C(31)-H(31)	120.5	H(5A)-O(5)-H(5B)	108.9
C(31)-C(32)-C(33)	121.3(3)		

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **(*S*)-BIFOL×H_2O**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	26(1)	22(1)	25(1)	-1(1)	1(1)	1(1)
O(2)	29(1)	20(1)	24(1)	2(1)	4(1)	4(1)
O(3)	26(1)	27(1)	23(1)	-5(1)	-5(1)	4(1)
O(4)	27(1)	24(1)	40(1)	-8(1)	-11(1)	1(1)
C(1)	22(1)	20(1)	20(1)	-1(1)	-3(1)	1(1)
C(2)	22(1)	21(1)	19(1)	-2(1)	-2(1)	0(1)
C(3)	22(1)	22(1)	19(1)	-1(1)	-2(1)	1(1)
C(4)	27(1)	22(1)	20(1)	-2(1)	-2(1)	3(1)
C(4A)	28(1)	20(1)	19(1)	-1(1)	-3(1)	-1(1)
C(5)	37(2)	21(1)	25(1)	-3(1)	1(1)	0(1)
C(6)	45(2)	19(1)	29(2)	4(1)	-3(1)	0(1)
C(7)	33(2)	26(1)	29(1)	2(1)	0(1)	-5(1)
C(8)	28(1)	26(1)	21(1)	-2(1)	0(1)	-2(1)
C(8A)	26(1)	21(1)	20(1)	-1(1)	-5(1)	0(1)
C(9)	22(1)	19(1)	21(1)	1(1)	2(1)	-1(1)
C(10)	23(1)	19(1)	20(1)	-1(1)	1(1)	-1(1)
C(11)	22(1)	18(1)	24(1)	0(1)	-1(1)	-1(1)
C(12)	24(1)	20(1)	27(1)	-3(1)	2(1)	1(1)
C(12A)	24(1)	19(1)	21(1)	-1(1)	1(1)	-2(1)
C(13)	31(1)	22(1)	22(1)	-4(1)	6(1)	1(1)
C(14)	39(2)	29(1)	22(1)	-6(1)	-1(1)	-2(1)
C(15)	34(2)	32(2)	24(1)	-1(1)	-8(1)	2(1)
C(16)	25(1)	25(1)	26(1)	-2(1)	-1(1)	3(1)
C(16A)	22(1)	23(1)	19(1)	1(1)	1(1)	-1(1)
C(17)	28(1)	22(1)	18(1)	0(1)	0(1)	0(1)
C(17A)	30(1)	27(1)	22(1)	2(1)	-5(1)	-5(1)
C(18)	34(2)	38(2)	29(2)	4(1)	-4(1)	3(1)
C(19)	39(2)	47(2)	45(2)	7(2)	-15(2)	2(2)
C(20)	55(2)	44(2)	35(2)	4(2)	-24(2)	-7(2)
C(21)	55(2)	37(2)	24(2)	0(1)	-5(2)	-11(2)
C(21A)	40(2)	28(1)	22(1)	2(1)	-2(1)	-6(1)
C(21B)	39(2)	26(1)	23(1)	-2(1)	4(1)	-3(1)

C(22)	54(2)	42(2)	25(2)	-7(1)	6(2)	1(2)
C(23)	54(2)	37(2)	37(2)	-4(1)	16(2)	15(2)
C(24)	40(2)	35(2)	40(2)	-1(1)	4(2)	11(1)
C(25)	33(2)	28(1)	30(1)	-3(1)	1(1)	2(1)
C(25A)	31(1)	22(1)	22(1)	0(1)	5(1)	-2(1)
C(26)	26(1)	20(1)	31(1)	-3(1)	-4(1)	2(1)
C(26A)	24(1)	26(1)	32(1)	-5(1)	-7(1)	4(1)
C(27)	25(2)	33(2)	45(2)	-2(1)	-4(1)	2(1)
C(28)	27(2)	51(2)	46(2)	-5(2)	2(1)	-1(1)
C(29)	30(2)	46(2)	53(2)	-16(2)	-3(2)	10(2)
C(30)	35(2)	28(2)	51(2)	-8(1)	-7(2)	10(1)
C(30A)	25(1)	28(1)	35(2)	-6(1)	-10(1)	3(1)
C(30B)	34(2)	25(1)	34(2)	-1(1)	-12(1)	1(1)
C(31)	43(2)	26(2)	47(2)	4(1)	-14(2)	3(1)
C(32)	53(2)	37(2)	44(2)	15(2)	-10(2)	-3(2)
C(33)	46(2)	41(2)	32(2)	7(1)	-2(2)	-2(2)
C(34)	40(2)	31(2)	29(2)	-1(1)	-4(1)	2(1)
C(34A)	30(1)	25(1)	27(1)	-1(1)	-10(1)	1(1)
O(5)	48(2)	42(1)	50(2)	-2(1)	4(1)	-6(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **(*S*)-BIFOL×H_2O**.

Atom	x	y	z	U(iso)
H(1O)	10784	3141	7020	37
H(2O)	8809	3433	7823	36
H(3O)	5367	2514	7390	38
H(4O)	2942	2958	7309	45
H(4)	10973	778	7366	28
H(5)	10462	-286	8184	33
H(6)	9198	-764	9104	37
H(7)	7651	33	9716	35
H(8)	7291	1295	9361	30
H(12)	4662	3955	9249	28
H(13)	5842	4065	10385	30
H(14)	7597	3723	11112	36
H(15)	9411	2938	10711	36
H(16)	9348	2416	9606	31
H(18)	8016	2696	6496	41
H(19)	6598	2489	5525	52
H(20)	7413	1822	4569	54
H(21)	9615	1284	4572	47
H(22)	12119	737	4856	49
H(23)	14282	418	5306	51
H(24)	14935	820	6413	46
H(25)	13408	1555	7101	36
H(27)	2024	3028	8919	41
H(28)	372	3813	9468	50
H(29)	292	5125	9241	52
H(30)	1755	5681	8424	46
H(31)	3523	5994	7397	47
H(32)	5225	6024	6557	53
H(33)	6498	4919	6286	48
H(34)	6061	3755	6864	40
H(5A)	7227	4378	8196	70
H(5B)	8574	4538	8508	70

Table S6. Torsion angles [°] for **(*S*)-BIFOL×H_2O**.

C(8A)-C(1)-C(2)-O(2)	-177.8(2)	O(3)-C(10)-C(11)-C(26)	-3.1(4)
C(9)-C(1)-C(2)-O(2)	7.9(4)	C(9)-C(10)-C(11)-C(26)	176.2(2)
C(8A)-C(1)-C(2)-C(3)	4.2(4)	C(10)-C(11)-C(12)-C(12A)	-0.7(4)
C(9)-C(1)-C(2)-C(3)	-170.0(2)	C(26)-C(11)-C(12)-C(12A)	-177.6(2)
C(1)-C(2)-C(3)-C(4)	-4.5(4)	C(11)-C(12)-C(12A)-C(16A)	1.3(4)
O(2)-C(2)-C(3)-C(4)	177.4(2)	C(11)-C(12)-C(12A)-C(13)	-177.4(3)
C(1)-C(2)-C(3)-C(17)	167.8(2)	C(12)-C(12A)-C(13)-C(14)	178.5(3)
O(2)-C(2)-C(3)-C(17)	-10.3(3)	C(16A)-C(12A)-C(13)-C(14)	-0.2(4)
C(2)-C(3)-C(4)-C(4A)	1.3(4)	C(12A)-C(13)-C(14)-C(15)	2.5(4)
C(17)-C(3)-C(4)-C(4A)	-170.8(2)	C(13)-C(14)-C(15)-C(16)	-2.8(5)
C(3)-C(4)-C(4A)-C(8A)	2.0(4)	C(14)-C(15)-C(16)-C(16A)	0.8(4)
C(3)-C(4)-C(4A)-C(5)	178.8(3)	C(15)-C(16)-C(16A)-C(12A)	1.4(4)
C(8A)-C(4A)-C(5)-C(6)	0.0(4)	C(15)-C(16)-C(16A)-C(9)	-178.5(3)
C(4)-C(4A)-C(5)-C(6)	-176.8(3)	C(12)-C(12A)-C(16A)-C(16)	179.5(2)
C(4A)-C(5)-C(6)-C(7)	-0.9(4)	C(13)-C(12A)-C(16A)-C(16)	-1.7(4)
C(5)-C(6)-C(7)-C(8)	1.6(5)	C(12)-C(12A)-C(16A)-C(9)	-0.6(4)
C(6)-C(7)-C(8)-C(8A)	-1.5(4)	C(13)-C(12A)-C(16A)-C(9)	178.2(2)
C(4)-C(4A)-C(8A)-C(8)	176.9(3)	C(10)-C(9)-C(16A)-C(16)	179.1(2)
C(5)-C(4A)-C(8A)-C(8)	0.1(4)	C(1)-C(9)-C(16A)-C(16)	-2.4(4)
C(4)-C(4A)-C(8A)-C(1)	-2.3(4)	C(10)-C(9)-C(16A)-C(12A)	-0.8(4)
C(5)-C(4A)-C(8A)-C(1)	-179.1(2)	C(1)-C(9)-C(16A)-C(12A)	177.7(2)
C(7)-C(8)-C(8A)-C(4A)	0.7(4)	C(4)-C(3)-C(17)-O(1)	-137.6(3)
C(7)-C(8)-C(8A)-C(1)	179.9(3)	C(2)-C(3)-C(17)-O(1)	50.4(3)
C(2)-C(1)-C(8A)-C(4A)	-0.7(4)	C(4)-C(3)-C(17)-C(25A)	-16.4(4)
C(9)-C(1)-C(8A)-C(4A)	173.3(2)	C(2)-C(3)-C(17)-C(25A)	171.6(2)
C(2)-C(1)-C(8A)-C(8)	-179.9(3)	C(4)-C(3)-C(17)-C(17A)	97.9(3)
C(9)-C(1)-C(8A)-C(8)	-5.9(4)	C(2)-C(3)-C(17)-C(17A)	-74.1(3)
C(2)-C(1)-C(9)-C(10)	65.2(3)	O(1)-C(17)-C(17A)-C(18)	-73.9(4)
C(8A)-C(1)-C(9)-C(10)	-108.8(3)	C(3)-C(17)-C(17A)-C(18)	50.8(4)
C(2)-C(1)-C(9)-C(16A)	-113.3(3)	C(25A)-C(17)-C(17A)-C(18)	173.8(3)
C(8A)-C(1)-C(9)-C(16A)	72.7(3)	O(1)-C(17)-C(17A)-C(21A)	110.0(3)
C(16A)-C(9)-C(10)-O(3)	-179.2(2)	C(3)-C(17)-C(17A)-C(21A)	-125.4(3)
C(1)-C(9)-C(10)-O(3)	2.2(3)	C(25A)-C(17)-C(17A)-C(21A)	-2.3(3)
C(16A)-C(9)-C(10)-C(11)	1.5(4)	C(21A)-C(17A)-C(18)-C(19)	-1.5(5)
C(1)-C(9)-C(10)-C(11)	-177.1(2)	C(17)-C(17A)-C(18)-C(19)	-177.3(3)
O(3)-C(10)-C(11)-C(12)	180.0(2)	C(17A)-C(18)-C(19)-C(20)	-0.8(5)
C(9)-C(10)-C(11)-C(12)	-0.8(4)	C(18)-C(19)-C(20)-C(21)	1.9(6)

C(19)-C(20)-C(21)-C(21A)	-0.6(5)
C(18)-C(17A)-C(21A)-C(21)	2.8(4)
C(17)-C(17A)-C(21A)-C(21)	179.4(3)
C(18)-C(17A)-C(21A)-C(21B)	-175.5(3)
C(17)-C(17A)-C(21A)-C(21B)	1.1(3)
C(20)-C(21)-C(21A)-C(17A)	-1.7(5)
C(20)-C(21)-C(21A)-C(21B)	176.1(3)
C(17A)-C(21A)-C(21B)-C(25A)	0.8(3)
C(21)-C(21A)-C(21B)-C(25A)	-177.2(3)
C(17A)-C(21A)-C(21B)-C(22)	-179.7(3)
C(21)-C(21A)-C(21B)-C(22)	2.2(6)
C(25A)-C(21B)-C(22)-C(23)	-1.9(5)
C(21A)-C(21B)-C(22)-C(23)	178.7(3)
C(21B)-C(22)-C(23)-C(24)	1.5(5)
C(22)-C(23)-C(24)-C(25)	0.2(5)
C(23)-C(24)-C(25)-C(25A)	-1.6(5)
C(24)-C(25)-C(25A)-C(21B)	1.2(4)
C(24)-C(25)-C(25A)-C(17)	-175.9(3)
C(22)-C(21B)-C(25A)-C(25)	0.5(5)
C(21A)-C(21B)-C(25A)-C(25)	-180.0(3)
C(22)-C(21B)-C(25A)-C(17)	178.1(3)
C(21A)-C(21B)-C(25A)-C(17)	-2.4(3)
O(1)-C(17)-C(25A)-C(25)	64.0(4)
C(3)-C(17)-C(25A)-C(25)	-60.1(4)
C(17A)-C(17)-C(25A)-C(25)	-179.8(3)
O(1)-C(17)-C(25A)-C(21B)	-113.4(2)
C(3)-C(17)-C(25A)-C(21B)	122.6(3)
C(17A)-C(17)-C(25A)-C(21B)	2.8(3)
C(12)-C(11)-C(26)-O(4)	-142.5(3)
C(10)-C(11)-C(26)-O(4)	40.6(3)
C(12)-C(11)-C(26)-C(26A)	-18.8(4)
C(10)-C(11)-C(26)-C(26A)	164.3(2)
C(12)-C(11)-C(26)-C(34A)	94.1(3)
C(10)-C(11)-C(26)-C(34A)	-82.8(3)
O(4)-C(26)-C(26A)-C(27)	54.1(4)
C(34A)-C(26)-C(26A)-C(27)	176.2(3)
C(11)-C(26)-C(26A)-C(27)	-66.1(4)
O(4)-C(26)-C(26A)-C(30A)	-128.6(2)
C(34A)-C(26)-C(26A)-C(30A)	-6.5(3)
C(11)-C(26)-C(26A)-C(30A)	111.3(3)
C(30A)-C(26A)-C(27)-C(28)	-1.8(5)
C(26)-C(26A)-C(27)-C(28)	175.2(3)
C(26A)-C(27)-C(28)-C(29)	-1.1(5)
C(27)-C(28)-C(29)-C(30)	2.0(5)
C(28)-C(29)-C(30)-C(30A)	0.0(5)
C(29)-C(30)-C(30A)-C(26A)	-2.9(5)
C(29)-C(30)-C(30A)-C(30B)	178.5(3)
C(27)-C(26A)-C(30A)-C(30)	3.8(4)
C(26)-C(26A)-C(30A)-C(30)	-173.7(3)
C(27)-C(26A)-C(30A)-C(30B)	-177.3(3)
C(26)-C(26A)-C(30A)-C(30B)	5.2(3)
C(30)-C(30A)-C(30B)-C(31)	-2.8(6)
C(26A)-C(30A)-C(30B)-C(31)	178.4(3)
C(30)-C(30A)-C(30B)-C(34A)	177.2(3)
C(26A)-C(30A)-C(30B)-C(34A)	-1.5(3)
C(34A)-C(30B)-C(31)-C(32)	0.4(5)
C(30A)-C(30B)-C(31)-C(32)	-179.6(3)
C(30B)-C(31)-C(32)-C(33)	-0.3(5)
C(31)-C(32)-C(33)-C(34)	0.0(5)
C(32)-C(33)-C(34)-C(34A)	0.2(5)
C(33)-C(34)-C(34A)-C(30B)	-0.1(4)
C(33)-C(34)-C(34A)-C(26)	-176.9(3)
C(31)-C(30B)-C(34A)-C(34)	-0.2(4)
C(30A)-C(30B)-C(34A)-C(34)	179.8(3)
C(31)-C(30B)-C(34A)-C(26)	177.3(3)
C(30A)-C(30B)-C(34A)-C(26)	-2.8(3)
O(4)-C(26)-C(34A)-C(34)	-55.9(4)
C(26A)-C(26)-C(34A)-C(34)	-177.4(3)
C(11)-C(26)-C(34A)-C(34)	63.0(4)
O(4)-C(26)-C(34A)-C(30B)	127.0(3)
C(26A)-C(26)-C(34A)-C(30B)	5.5(3)
C(11)-C(26)-C(34A)-C(30B)	-114.1(3)

Table S7. Hydrogen bonds for **(*S*)-BIFOL×H_2O** [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1)-H(1O)...O(2)	0.90	1.84	2.641(2)	147
O(2)-H(2O)...O(5)	0.90	1.88	2.732(2)	157
O(3)-H(3O)...O(4)	0.90	1.78	2.572(2)	145
O(4)-H(4O)...O(1)#1	0.90	1.85	2.722(2)	163

Symmetry transformations used to generate equivalent atoms:

#1 *x*-1, *y*, *z*

DFT analysis of alternative conformation of MA with L1

We also analyzed the possibility of the coordination of cyclohexenone by the lithium cation (**Li1MA-2**, Figure S1) instead of formation of an O-H···O=C bond (**Li1MA**, Figure 8 of manuscript). The energy of cyclohexenone complexation in **Li1MA-2** is 20.3 kcal/mol and this is mainly attained due to the Li-O=C interaction. The optimization of this intermediate leads to the structure **Li1MA-2** which was more stable than **Li1MA**, but still less stable (by 4.3 kcal/mol) than **Li2MA**. Although **Li1MA-2** is more stable, the mutual disposition of cyclohexenone, diethyl malonate and OH groups of the second BIMBOL moiety are not appropriate for the intracomplex addition reaction.

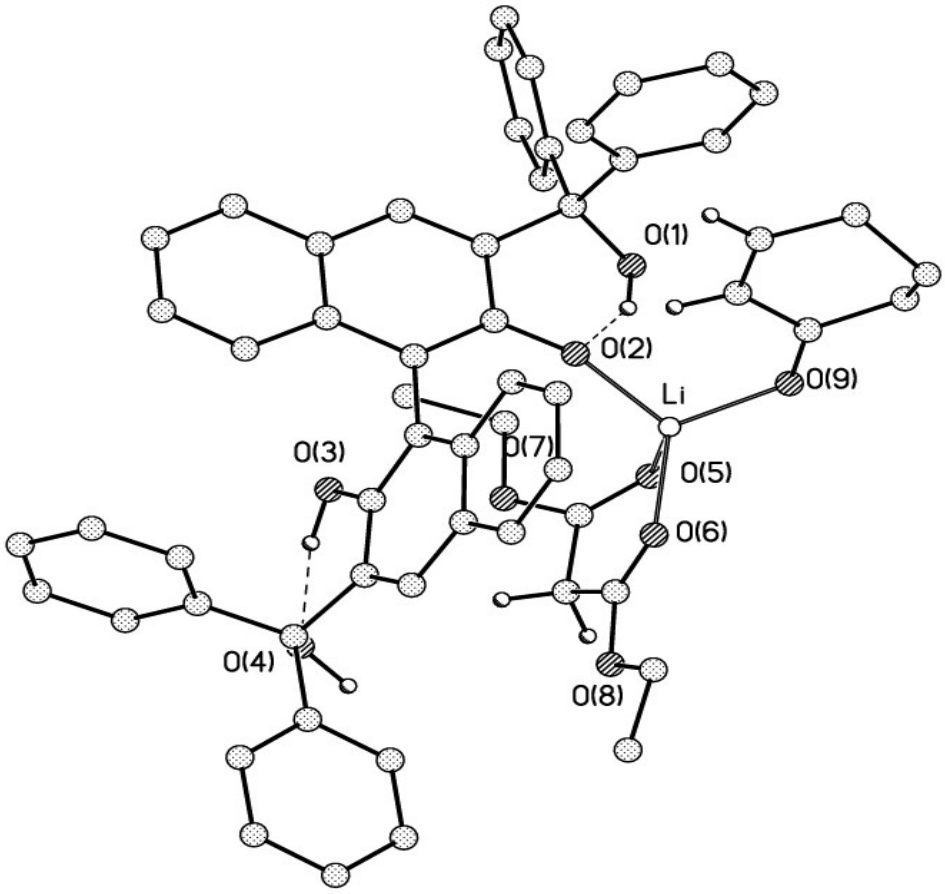


Figure S1. View of complex **Li1MA-2** formed by of coordination of MA and L1. Some hydrogen atoms are omitted for clarity. The intramolecular interactions are shown only for contacts for which critical points (3,-1) of electron density function were located.

Atomic coordinates according to DFT calculations

Li1

E= -2962.62480696 H

O1	-0.07992	0.14794	-0.04718
H2	-0.16798	0.19243	-0.04754
O3	0.19565	0.30430	-0.12003
O4	-0.29377	0.27242	-0.15962
H5	-0.22976	0.32574	-0.21145
O6	0.36672	0.41532	0.08150
H7	0.42231	0.49282	0.10943
C8	0.07273	0.06742	-0.20862
C9	-0.05628	0.10672	-0.17527
C10	-0.16344	0.10186	-0.27063
C11	-0.13609	0.06185	-0.39986
H12	-0.21645	0.05813	-0.47353
C13	-0.00557	0.02511	-0.44007
C14	0.02289	-0.01298	-0.57378
H15	-0.05890	-0.01400	-0.64627
C16	0.15070	-0.04808	-0.61159
H17	0.17156	-0.07751	-0.71456
C18	0.25508	-0.04628	-0.51608
H19	0.35613	-0.07449	-0.54621
C20	0.23048	-0.00993	-0.38535
H21	0.31098	-0.00954	-0.31181
C22	0.09992	0.02710	-0.34293
C23	0.18232	0.06780	-0.10826
C24	0.24375	0.19148	-0.07642
C25	0.36688	0.18703	0.00248
C26	0.41016	0.06762	0.05588
H27	0.50179	0.06450	0.11504
C28	0.34154	-0.05453	0.03449
C29	0.38590	-0.17598	0.09220
H30	0.47373	-0.17341	0.15726
C31	0.32076	-0.29515	0.06701
H32	0.35587	-0.38805	0.11211
C33	0.20806	-0.29590	-0.01846
H34	0.15650	-0.38998	-0.03884
C35	0.16249	-0.17927	-0.07650
H36	0.07541	-0.18135	-0.14226
C37	0.22685	-0.05456	-0.05192
C38	-0.30401	0.14186	-0.22571
C39	-0.36062	0.04764	-0.11884
C40	-0.46945	0.09040	-0.04160
H41	-0.51014	0.19030	-0.05742

C42	-0.52472	0.00647	0.05496
H43	-0.60925	0.04103	0.11472
C44	-0.47223	-0.12148	0.07530
H45	-0.51532	-0.18703	0.15115
C46	-0.36424	-0.16469	-0.00171
H47	-0.32191	-0.26401	0.01387
C48	-0.30887	-0.08056	-0.09849
H49	-0.22338	-0.11411	-0.15736
C50	-0.40211	0.15075	-0.34293
C51	-0.46429	0.03520	-0.39211
H52	-0.44560	-0.06060	-0.34337
C53	-0.54959	0.04164	-0.50227
H54	-0.59698	-0.04940	-0.53925
C55	-0.57478	0.16410	-0.56455
H56	-0.64172	0.16933	-0.65056
C57	-0.51417	0.27978	-0.51547
H58	-0.53365	0.37612	-0.56286
C59	-0.42824	0.27299	-0.40559
H60	-0.38236	0.36431	-0.36768
C61	0.45086	0.31445	0.01563
C62	0.49477	0.36841	-0.12180
C63	0.48132	0.29444	-0.23967
H64	0.43564	0.19563	-0.23593
C65	0.52412	0.34645	-0.36199
H66	0.51125	0.28726	-0.45282
C67	0.58219	0.47319	-0.36838
H68	0.61558	0.51380	-0.46400
C69	0.59839	0.54700	-0.25084
H70	0.64557	0.64540	-0.25389
C71	0.55568	0.49452	-0.12887
H72	0.57188	0.55186	-0.03744
C73	0.57401	0.29110	0.10375
C74	0.69710	0.25355	0.04850
H75	0.70686	0.24469	-0.05979
C76	0.80695	0.22737	0.13055
H77	0.90200	0.19796	0.08569
C78	0.79547	0.23895	0.26920
H79	0.88148	0.21902	0.33335
C80	0.67310	0.27647	0.32505
H81	0.66292	0.28575	0.43336
C82	0.56310	0.30171	0.24299
H83	0.46725	0.32982	0.28655
O84	0.07190	0.57726	-0.09608
O85	-0.07981	0.46597	-0.22286
O86	0.04574	0.41078	0.14282
O87	-0.16446	0.32995	0.16358
C88	-0.03609	0.52094	-0.10884
C89	-0.13343	0.50353	0.00618

C90	-0.07222	0.41028	0.11079
C91	0.02009	0.45921	-0.33256
C92	-0.05246	0.41753	-0.45805
C93	-0.11390	0.22796	0.25718
C94	-0.22320	0.12530	0.27492
H95	-0.23101	0.46558	-0.02557
H96	0.09579	0.38677	-0.29863
H97	0.06596	0.55854	-0.34095
H98	0.02037	0.41162	-0.54019
H99	-0.13019	0.49002	-0.48625
H100	-0.09762	0.31805	-0.44729
H101	-0.08766	0.27932	0.35077
H102	-0.02304	0.18501	0.21323
H103	-0.18938	0.04940	0.34688
H104	-0.24534	0.07458	0.18012
H105	-0.31557	0.17068	0.31328
Li16	0.19315	0.43664	0.00863
C107	0.42724	0.75347	0.13390
O108	0.47824	0.64886	0.17618
C109	0.45107	0.88551	0.20427
H110	0.54019	0.93085	0.15704
H111	0.47750	0.86475	0.30879
C112	0.33131	0.97997	0.19136
H113	0.35330	1.07653	0.23913
H114	0.24544	0.93652	0.24510
C115	0.29257	0.99999	0.04468
H116	0.36596	1.06562	-0.00616
H117	0.19615	1.05262	0.03616
C118	0.34545	0.75697	0.01221
H119	0.33702	0.66482	-0.04547
C120	0.28605	0.87048	-0.02997
H121	0.23000	0.86858	-0.12389
H122	-0.14604	0.60175	0.05421

Li2

E= -2654.18485025 H

O1	-0.07992	0.14794	-0.04718
H2	-0.16798	0.19243	-0.04754
O3	0.19565	0.30430	-0.12003
O4	-0.29377	0.27242	-0.15962
H5	-0.22976	0.32574	-0.21145
O6	0.36672	0.41532	0.08150
H7	0.42231	0.49282	0.10943
C8	0.07273	0.06742	-0.20862
C9	-0.05628	0.10672	-0.17527
C10	-0.16344	0.10186	-0.27063

C11	-0.13609	0.06185	-0.39986
H12	-0.21645	0.05813	-0.47353
C13	-0.00557	0.02511	-0.44007
C14	0.02289	-0.01298	-0.57378
H15	-0.05890	-0.01400	-0.64627
C16	0.15070	-0.04808	-0.61159
H17	0.17156	-0.07751	-0.71456
C18	0.25508	-0.04628	-0.51608
H19	0.35613	-0.07449	-0.54621
C20	0.23048	-0.00993	-0.38535
H21	0.31098	-0.00954	-0.31181
C22	0.09992	0.02710	-0.34293
C23	0.18232	0.06780	-0.10826
C24	0.24375	0.19148	-0.07642
C25	0.36688	0.18703	0.00248
C26	0.41016	0.06762	0.05588
H27	0.50179	0.06450	0.11504
C28	0.34154	-0.05453	0.03449
C29	0.38590	-0.17598	0.09220
H30	0.47373	-0.17341	0.15726
C31	0.32076	-0.29515	0.06701
H32	0.35587	-0.38805	0.11211
C33	0.20806	-0.29590	-0.01846
H34	0.15650	-0.38998	-0.03884
C35	0.16249	-0.17927	-0.07650
H36	0.07541	-0.18135	-0.14226
C37	0.22685	-0.05456	-0.05192
C38	-0.30401	0.14186	-0.22571
C39	-0.36062	0.04764	-0.11884
C40	-0.46945	0.09040	-0.04160
H41	-0.51014	0.19030	-0.05742
C42	-0.52472	0.00647	0.05496
H43	-0.60925	0.04103	0.11472
C44	-0.47223	-0.12148	0.07530
H45	-0.51532	-0.18703	0.15115
C46	-0.36424	-0.16469	-0.00171
H47	-0.32191	-0.26401	0.01387
C48	-0.30887	-0.08056	-0.09849
H49	-0.22338	-0.11411	-0.15736
C50	-0.40211	0.15075	-0.34293
C51	-0.46429	0.03520	-0.39211
H52	-0.44560	-0.06060	-0.34337
C53	-0.54959	0.04164	-0.50227
H54	-0.59698	-0.04940	-0.53925
C55	-0.57478	0.16410	-0.56455
H56	-0.64172	0.16933	-0.65056
C57	-0.51417	0.27978	-0.51547
H58	-0.53365	0.37612	-0.56286

C59	-0.42824	0.27299	-0.40559
H60	-0.38236	0.36431	-0.36768
C61	0.45086	0.31445	0.01563
C62	0.49477	0.36841	-0.12180
C63	0.48132	0.29444	-0.23967
H64	0.43564	0.19563	-0.23593
C65	0.52412	0.34645	-0.36199
H66	0.51125	0.28726	-0.45282
C67	0.58219	0.47319	-0.36838
H68	0.61558	0.51380	-0.46400
C69	0.59839	0.54700	-0.25084
H70	0.64557	0.64540	-0.25389
C71	0.55568	0.49452	-0.12887
H72	0.57188	0.55186	-0.03744
C73	0.57401	0.29110	0.10375
C74	0.69710	0.25355	0.04850
H75	0.70686	0.24469	-0.05979
C76	0.80695	0.22737	0.13055
H77	0.90200	0.19796	0.08569
C78	0.79547	0.23895	0.26920
H79	0.88148	0.21902	0.33335
C80	0.67310	0.27647	0.32505
H81	0.66292	0.28575	0.43336
C82	0.56310	0.30171	0.24299
H83	0.46725	0.32982	0.28655
O84	0.07190	0.57726	-0.09608
O85	-0.07981	0.46597	-0.22286
O86	0.04574	0.41078	0.14282
O87	-0.16446	0.32995	0.16358
C88	-0.03609	0.52094	-0.10884
C89	-0.13343	0.50353	0.00618
C90	-0.07222	0.41028	0.11079
C91	0.02009	0.45921	-0.33256
C92	-0.05246	0.41753	-0.45805
C93	-0.11390	0.22796	0.25718
C94	-0.22320	0.12530	0.27492
H95	-0.23101	0.46558	-0.02557
H96	0.09579	0.38677	-0.29863
H97	0.06596	0.55854	-0.34095
H98	0.02037	0.41162	-0.54019
H99	-0.13019	0.49002	-0.48625
H100	-0.09762	0.31805	-0.44729
H101	-0.08766	0.27932	0.35077
H102	-0.02304	0.18501	0.21323
H103	-0.18938	0.04940	0.34688
H104	-0.24534	0.07458	0.18012
H105	-0.31557	0.17068	0.31328
Li16	0.19315	0.43664	0.00863

C107	0.42724	0.75347	0.13390
O108	0.47824	0.64886	0.17618
C109	0.45107	0.88551	0.20427
H110	0.54019	0.93085	0.15704
H111	0.47750	0.86475	0.30879
C112	0.33131	0.97997	0.19136
H113	0.35330	1.07653	0.23913
H114	0.24544	0.93652	0.24510
C115	0.29257	0.99999	0.04468
H116	0.36596	1.06562	-0.00616
H117	0.19615	1.05262	0.03616
C118	0.34545	0.75697	0.01221
H119	0.33702	0.66482	-0.04547
C120	0.28605	0.87048	-0.02997
H121	0.23000	0.86858	-0.12389
H122	-0.14604	0.60175	0.05421

Li1MA-2

-2962.63970537 H

O1	-0.08011	0.07491	0.01927
H2	-0.17557	0.07201	0.04443
O3	0.22760	0.36807	-0.04783
O4	-0.34418	0.09273	0.00007
H5	-0.39378	0.17647	0.00476
O6	0.37247	0.43294	0.15635
H7	0.30879	0.43696	0.07874
C8	0.05307	0.16608	-0.15344
C9	-0.07280	0.12849	-0.10545
C10	-0.19072	0.14007	-0.18643
C11	-0.18085	0.19958	-0.31064
H12	-0.26933	0.20756	-0.37404
C13	-0.05672	0.24482	-0.36149
C14	-0.04664	0.30480	-0.48980
H15	-0.13793	0.31852	-0.54838
C16	0.07565	0.34300	-0.54074
H17	0.08234	0.38892	-0.63946
C18	0.19315	0.31997	-0.46531
H19	0.29003	0.34853	-0.50664
C20	0.18653	0.26152	-0.34059
H21	0.27693	0.24242	-0.28277
C22	0.06193	0.22435	-0.28344
C23	0.17383	0.13660	-0.07203
C24	0.25372	0.24190	-0.02145
C25	0.36628	0.20806	0.06435
C26	0.39309	0.07652	0.09396
H27	0.47654	0.05206	0.16006

C28	0.31707	-0.03048	0.04057
C29	0.34884	-0.16548	0.06960
H30	0.43371	-0.18567	0.13545
C31	0.27515	-0.26920	0.01608
H32	0.30039	-0.37278	0.03930
C33	0.16671	-0.23994	-0.06972
H34	0.10780	-0.32123	-0.11266
C35	0.13356	-0.10936	-0.09960
H36	0.04958	-0.08943	-0.16613
C37	0.20624	0.00002	-0.04496
C38	-0.31782	0.06665	-0.14281
C39	-0.29403	-0.08439	-0.15335
C40	-0.35286	-0.17244	-0.06184
H41	-0.41384	-0.13241	0.01907
C42	-0.33235	-0.31009	-0.07297
H43	-0.37790	-0.37734	-0.00011
C44	-0.25337	-0.36149	-0.17594
H45	-0.23656	-0.46903	-0.18394
C46	-0.19537	-0.27421	-0.26815
H47	-0.13282	-0.31305	-0.34871
C48	-0.21536	-0.13658	-0.25675
H49	-0.16826	-0.06894	-0.32816
C50	-0.44219	0.11124	-0.21992
C51	-0.51991	0.02256	-0.29497
H52	-0.48919	-0.08164	-0.30354
C53	-0.63646	0.06638	-0.35840
H54	-0.69586	-0.00432	-0.41653
C55	-0.67739	0.19923	-0.34693
H56	-0.76895	0.23307	-0.39559
C57	-0.59998	0.28887	-0.27282
H58	-0.63037	0.39330	-0.26394
C59	-0.48288	0.24539	-0.21090
H60	-0.42051	0.31818	-0.15823
C61	0.45483	0.32180	0.11832
C62	0.55667	0.36745	0.01213
C63	0.59793	0.28501	-0.09298
H64	0.55192	0.18679	-0.10488
C65	0.69825	0.32688	-0.18101
H66	0.73015	0.26082	-0.26192
C67	0.75862	0.45164	-0.16461
H68	0.83830	0.48338	-0.23221
C69	0.71638	0.53538	-0.06084
H70	0.76328	0.63306	-0.04698
C71	0.61579	0.49382	0.02619
H72	0.58187	0.55815	0.10750
C73	0.52973	0.27770	0.24470
C74	0.65674	0.21901	0.23986
H75	0.70747	0.20814	0.14390

C76	0.71937	0.17470	0.35661
H77	0.81834	0.12911	0.35078
C78	0.65613	0.18941	0.48015
H79	0.70510	0.15528	0.57149
C80	0.53000	0.24924	0.48592
H81	0.48004	0.26207	0.58215
C82	0.46735	0.29275	0.36915
H83	0.36965	0.34069	0.37273
O84	-0.03329	0.53923	-0.16234
O85	-0.25700	0.52460	-0.18605
O86	0.03784	0.53563	0.11159
O87	-0.05282	0.34347	0.19214
C88	-0.14277	0.51009	-0.11702
C89	-0.17048	0.45229	0.02046
C90	-0.04913	0.44958	0.11192
C91	-0.24034	0.57549	-0.32277
C92	-0.37366	0.56384	-0.39275
C93	0.06338	0.32359	0.28092
C94	0.07276	0.17614	0.31187
H95	-0.21049	0.35072	0.00816
H96	-0.16190	0.51625	-0.37168
H97	-0.20555	0.67951	-0.31538
H98	-0.36461	0.60462	-0.49438
H99	-0.45173	0.62044	-0.34010
H100	-0.40535	0.45900	-0.40045
H101	0.04580	0.38521	0.37036
H102	0.15285	0.36095	0.22969
H103	0.16070	0.15903	0.37562
H104	0.08577	0.11809	0.21964
H105	-0.01643	0.13967	0.36479
Li16	0.14066	0.52816	-0.07158
C107	0.35459	0.67720	-0.19200
O108	0.25458	0.67796	-0.11834
C109	0.43858	0.80163	-0.20991
H110	0.51986	0.79493	-0.13521
H111	0.37767	0.88926	-0.18398
C112	0.49769	0.81045	-0.35093
H113	0.56238	0.89897	-0.35976
H114	0.41554	0.82344	-0.42327
C115	0.57535	0.68337	-0.38616
H116	0.67218	0.68135	-0.33275
H117	0.60078	0.68116	-0.49332
C118	0.39837	0.55653	-0.26152
H119	0.34642	0.46413	-0.23566
C120	0.50097	0.55910	-0.34904
H121	0.53395	0.46525	-0.39438
H122	-0.24941	0.51239	0.06828

(*R*)-Li2MA

E= -2654.18803025 H

O1	0.05357	0.15768	-0.10715
H2	-0.01776	0.22836	-0.11803
O3	0.30504	0.22457	-0.24831
H4	0.22681	0.19957	-0.30200
O5	-0.14175	0.29182	-0.20163
H6	-0.18111	0.34086	-0.12515
O7	0.37121	0.36472	-0.02393
H8	0.34287	0.39869	-0.11133
C9	0.14043	-0.00409	-0.25762
C10	0.03495	0.07706	-0.21529
C11	-0.09287	0.07533	-0.28064
C12	-0.10882	-0.00631	-0.39036
H13	-0.20500	-0.00885	-0.44182
C14	-0.00357	-0.08776	-0.43971
C15	-0.02076	-0.16938	-0.55439
H16	-0.11787	-0.16914	-0.60437
C17	0.08293	-0.24665	-0.60251
H18	0.06875	-0.30861	-0.69114
C19	0.20832	-0.24474	-0.53722
H20	0.29038	-0.30521	-0.57616
C21	0.22810	-0.16695	-0.42490
H22	0.32499	-0.16574	-0.37480
C23	0.12322	-0.08685	-0.37274
C24	0.26483	-0.00136	-0.17637
C25	0.33593	0.11789	-0.16823
C26	0.43876	0.13831	-0.07138
C27	0.47782	0.03041	0.00509
H28	0.55627	0.04320	0.07980
C29	0.41566	-0.09646	-0.00631
C30	0.45701	-0.20638	0.07323
H31	0.54268	-0.19313	0.13967
C32	0.39018	-0.32691	0.06770
H33	0.42298	-0.41090	0.12910
C34	0.27771	-0.34101	-0.01678
H35	0.22392	-0.43593	-0.01957
C36	0.23511	-0.23609	-0.09571
H37	0.14836	-0.24816	-0.16061
C38	0.30387	-0.11182	-0.09485
C39	-0.20601	0.16212	-0.22357
C40	-0.25872	0.10913	-0.08961
C41	-0.35293	0.18650	-0.02006
H42	-0.38943	0.27985	-0.06346
C43	-0.40165	0.14499	0.10364

H44	-0.47409	0.20701	0.15661
C45	-0.35767	0.02466	0.15943
H46	-0.39541	-0.00769	0.25652
C47	-0.26517	-0.05354	0.09029
H48	-0.23014	-0.14763	0.13291
C49	-0.21601	-0.01151	-0.03356
H50	-0.14314	-0.07302	-0.08641
C51	-0.31968	0.17920	-0.32427
C52	-0.42644	0.08870	-0.32859
H53	-0.43132	0.00753	-0.25576
C54	-0.52684	0.10217	-0.42466
H55	-0.60965	0.03108	-0.42666
C56	-0.52198	0.20682	-0.51694
H57	-0.60093	0.21794	-0.59149
C58	-0.41597	0.29762	-0.51271
H59	-0.41177	0.38010	-0.58409
C60	-0.31510	0.28361	-0.41729
H61	-0.23235	0.35446	-0.41325
C62	0.48925	0.28099	-0.04723
C63	0.56870	0.33762	-0.16481
C64	0.62457	0.25498	-0.26268
H65	0.60814	0.14720	-0.25784
C66	0.70032	0.30957	-0.36658
H67	0.74316	0.24395	-0.44252
C68	0.72054	0.44744	-0.37377
H69	0.77929	0.49015	-0.45522
C70	0.66511	0.53056	-0.27606
H71	0.68099	0.63846	-0.28052
C72	0.59021	0.47598	-0.17190
H73	0.54820	0.54064	-0.09468
C74	0.57288	0.28848	0.08063
C75	0.70985	0.25952	0.07733
H76	0.75764	0.23652	-0.01800
C77	0.78552	0.26034	0.19457
H78	0.89217	0.23765	0.19018
C79	0.72518	0.29102	0.31671
H80	0.78428	0.29245	0.40843
C81	0.58883	0.32068	0.32050
H82	0.54083	0.34546	0.41532
C83	0.51291	0.31906	0.20335
H84	0.40675	0.34297	0.20715
O85	0.11495	0.45592	-0.10040
O86	-0.03846	0.61226	-0.16214
O87	0.04339	0.31800	0.14054
O88	-0.15580	0.38690	0.22502
C89	0.00476	0.51246	-0.07836
C90	-0.08828	0.48259	0.02432
C91	-0.05784	0.39147	0.12891

C92	0.04550	0.63789	-0.27663
C93	-0.02605	0.73941	-0.36335
C94	-0.13614	0.28819	0.32859
C95	-0.25089	0.30183	0.42642
H96	-0.17746	0.54415	0.03335
H97	0.06315	0.54339	-0.33031
H98	0.14331	0.67537	-0.24266
H99	0.03478	0.76229	-0.45200
H100	-0.04350	0.83288	-0.30831
H101	-0.12318	0.70069	-0.39709
H102	-0.03888	0.30504	0.37723
H103	-0.13354	0.18810	0.28268
H104	-0.23971	0.22843	0.50751
H105	-0.34729	0.28395	0.37678
H106	-0.25313	0.40229	0.47085
Li10	0.17400	0.30717	0.00403

Li1MA

-2962.62480696

O1	-0.07992	0.14794	-0.04718
H2	-0.16798	0.19243	-0.04754
O3	0.19565	0.30430	-0.12003
O4	-0.29377	0.27242	-0.15962
H5	-0.22976	0.32574	-0.21145
O6	0.36672	0.41532	0.08150
H7	0.42231	0.49282	0.10943
C8	0.07273	0.06742	-0.20862
C9	-0.05628	0.10672	-0.17527
C10	-0.16344	0.10186	-0.27063
C11	-0.13609	0.06185	-0.39986
H12	-0.21645	0.05813	-0.47353
C13	-0.00557	0.02511	-0.44007
C14	0.02289	-0.01298	-0.57378
H15	-0.05890	-0.01400	-0.64627
C16	0.15070	-0.04808	-0.61159
H17	0.17156	-0.07751	-0.71456
C18	0.25508	-0.04628	-0.51608
H19	0.35613	-0.07449	-0.54621
C20	0.23048	-0.00993	-0.38535
H21	0.31098	-0.00954	-0.31181
C22	0.09992	0.02710	-0.34293
C23	0.18232	0.06780	-0.10826
C24	0.24375	0.19148	-0.07642
C25	0.36688	0.18703	0.00248
C26	0.41016	0.06762	0.05588
H27	0.50179	0.06450	0.11504

C28	0.34154	-0.05453	0.03449
C29	0.38590	-0.17598	0.09220
H30	0.47373	-0.17341	0.15726
C31	0.32076	-0.29515	0.06701
H32	0.35587	-0.38805	0.11211
C33	0.20806	-0.29590	-0.01846
H34	0.15650	-0.38998	-0.03884
C35	0.16249	-0.17927	-0.07650
H36	0.07541	-0.18135	-0.14226
C37	0.22685	-0.05456	-0.05192
C38	-0.30401	0.14186	-0.22571
C39	-0.36062	0.04764	-0.11884
C40	-0.46945	0.09040	-0.04160
H41	-0.51014	0.19030	-0.05742
C42	-0.52472	0.00647	0.05496
H43	-0.60925	0.04103	0.11472
C44	-0.47223	-0.12148	0.07530
H45	-0.51532	-0.18703	0.15115
C46	-0.36424	-0.16469	-0.00171
H47	-0.32191	-0.26401	0.01387
C48	-0.30887	-0.08056	-0.09849
H49	-0.22338	-0.11411	-0.15736
C50	-0.40211	0.15075	-0.34293
C51	-0.46429	0.03520	-0.39211
H52	-0.44560	-0.06060	-0.34337
C53	-0.54959	0.04164	-0.50227
H54	-0.59698	-0.04940	-0.53925
C55	-0.57478	0.16410	-0.56455
H56	-0.64172	0.16933	-0.65056
C57	-0.51417	0.27978	-0.51547
H58	-0.53365	0.37612	-0.56286
C59	-0.42824	0.27299	-0.40559
H60	-0.38236	0.36431	-0.36768
C61	0.45086	0.31445	0.01563
C62	0.49477	0.36841	-0.12180
C63	0.48132	0.29444	-0.23967
H64	0.43564	0.19563	-0.23593
C65	0.52412	0.34645	-0.36199
H66	0.51125	0.28726	-0.45282
C67	0.58219	0.47319	-0.36838
H68	0.61558	0.51380	-0.46400
C69	0.59839	0.54700	-0.25084
H70	0.64557	0.64540	-0.25389
C71	0.55568	0.49452	-0.12887
H72	0.57188	0.55186	-0.03744
C73	0.57401	0.29110	0.10375
C74	0.69710	0.25355	0.04850
H75	0.70686	0.24469	-0.05979

C76	0.80695	0.22737	0.13055
H77	0.90200	0.19796	0.08569
C78	0.79547	0.23895	0.26920
H79	0.88148	0.21902	0.33335
C80	0.67310	0.27647	0.32505
H81	0.66292	0.28575	0.43336
C82	0.56310	0.30171	0.24299
H83	0.46725	0.32982	0.28655
O84	0.07190	0.57726	-0.09608
O85	-0.07981	0.46597	-0.22286
O86	0.04574	0.41078	0.14282
O87	-0.16446	0.32995	0.16358
C88	-0.03609	0.52094	-0.10884
C89	-0.13343	0.50353	0.00618
C90	-0.07222	0.41028	0.11079
C91	0.02009	0.45921	-0.33256
C92	-0.05246	0.41753	-0.45805
C93	-0.11390	0.22796	0.25718
C94	-0.22320	0.12530	0.27492
H95	-0.23101	0.46558	-0.02557
H96	0.09579	0.38677	-0.29863
H97	0.06596	0.55854	-0.34095
H98	0.02037	0.41162	-0.54019
H99	-0.13019	0.49002	-0.48625
H100	-0.09762	0.31805	-0.44729
H101	-0.08766	0.27932	0.35077
H102	-0.02304	0.18501	0.21323
H103	-0.18938	0.04940	0.34688
H104	-0.24534	0.07458	0.18012
H105	-0.31557	0.17068	0.31328
Li16	0.19315	0.43664	0.00863
C107	0.42724	0.75347	0.13390
O108	0.47824	0.64886	0.17618
C109	0.45107	0.88551	0.20427
H110	0.54019	0.93085	0.15704
H111	0.47750	0.86475	0.30879
C112	0.33131	0.97997	0.19136
H113	0.35330	1.07653	0.23913
H114	0.24544	0.93652	0.24510
C115	0.29257	0.99999	0.04468
H116	0.36596	1.06562	-0.00616
H117	0.19615	1.05262	0.03616
C118	0.34545	0.75697	0.01221
H119	0.33702	0.66482	-0.04547
C120	0.28605	0.87048	-0.02997
H121	0.23000	0.86858	-0.12389
H122	-0.14604	0.60175	0.05421

(*R*)-Li3MA

E= -2962.64621257

O1	0.03976	0.13992	-0.05079
H2	-0.04747	0.17985	-0.01999
O3	0.29389	0.26999	-0.19172
H4	0.21910	0.26048	-0.25496
O5	-0.20288	0.23120	-0.04671
H6	-0.19205	0.32085	-0.08851
O7	0.34950	0.34775	0.05744
H8	0.36869	0.43723	0.09687
C9	0.12909	0.05270	-0.25215
C10	0.01987	0.10151	-0.17989
C11	-0.11065	0.10897	-0.23870
C12	-0.12388	0.08081	-0.37294
H13	-0.22250	0.08698	-0.41941
C14	-0.01388	0.04013	-0.45279
C15	-0.02787	0.01340	-0.59131
H16	-0.12582	0.02746	-0.63761
C17	0.07961	-0.02997	-0.66623
H18	0.06757	-0.05048	-0.77270
C19	0.20562	-0.04831	-0.60472
H20	0.29022	-0.08287	-0.66435
C21	0.22261	-0.02295	-0.47015
H22	0.31989	-0.03691	-0.42274
C23	0.11414	0.02236	-0.39059
C24	0.25653	0.03423	-0.17742
C25	0.32652	0.14779	-0.13976
C26	0.42658	0.14609	-0.03835
C27	0.46704	0.02311	0.00898
H28	0.54367	0.01796	0.08647
C29	0.40875	-0.09800	-0.03654
C30	0.45198	-0.22399	0.01199
H31	0.53656	-0.22704	0.08107
C32	0.38826	-0.34031	-0.02596
H33	0.42251	-0.43659	0.01214
C34	0.27741	-0.33463	-0.11350
H35	0.22652	-0.42680	-0.14216
C36	0.23274	-0.21366	-0.16265
H37	0.14707	-0.20956	-0.23007
C38	0.29786	-0.09261	-0.12745
C39	-0.23202	0.12935	-0.14729
C40	-0.25523	0.00114	-0.06576
C41	-0.31912	0.00965	0.05867
H42	-0.34798	0.10750	0.09681
C43	-0.34465	-0.10552	0.13305
H44	-0.39395	-0.09722	0.23003
C45	-0.30717	-0.23083	0.08402

H46	-0.32664	-0.32082	0.14254
C47	-0.24400	-0.23997	-0.04002
H48	-0.21370	-0.33722	-0.07910
C49	-0.21819	-0.12465	-0.11445
H50	-0.16841	-0.13282	-0.21105
C51	-0.35748	0.16890	-0.22600
C52	-0.46701	0.08286	-0.23927
H53	-0.46466	-0.01526	-0.19199
C54	-0.57956	0.12155	-0.31264
H55	-0.66404	0.05303	-0.32171
C56	-0.58409	0.24679	-0.37372
H57	-0.67207	0.27709	-0.43072
C58	-0.47488	0.33315	-0.36141
H59	-0.47674	0.43135	-0.40898
C60	-0.36249	0.29439	-0.28860
H61	-0.27785	0.36297	-0.28259
C62	0.47311	0.27940	0.02178
C63	0.55482	0.36393	-0.07692
C64	0.60257	0.31238	-0.19769
H65	0.57931	0.20943	-0.22504
C66	0.67952	0.39134	-0.28355
H67	0.71534	0.34947	-0.37772
C68	0.71011	0.52304	-0.24936
H69	0.76996	0.58485	-0.31651
C70	0.66403	0.57498	-0.12805
H71	0.68839	0.67746	-0.09952
C72	0.58770	0.49580	-0.04239
H73	0.55360	0.53715	0.05271
C74	0.55545	0.25492	0.14886
C75	0.69422	0.23698	0.14251
H76	0.74521	0.24517	0.04640
C77	0.76758	0.20919	0.25795
H78	0.87566	0.19548	0.25127
C79	0.70317	0.19985	0.38149
H80	0.76052	0.17885	0.47191
C81	0.56494	0.21804	0.38850
H82	0.51364	0.21110	0.48459
C83	0.49141	0.24479	0.27288
H84	0.38342	0.25854	0.27790
O85	0.08071	0.41512	-0.20854
O86	-0.09140	0.49297	-0.33535
O87	0.03882	0.44060	0.07027
O88	-0.14542	0.56373	0.12014
C89	-0.03136	0.47098	-0.21350
C90	-0.10945	0.51486	-0.10394
C91	-0.06291	0.50157	0.03003
C92	-0.02181	0.43788	-0.44995
C93	-0.11486	0.44786	-0.56892

C94	-0.10972	0.54658	0.25927
C95	-0.19772	0.63932	0.34018
H96	-0.20092	0.57072	-0.12245
H97	0.00481	0.33337	-0.42896
H98	0.07154	0.49408	-0.46568
H99	-0.06500	0.40717	-0.65804
H100	-0.14275	0.55215	-0.58927
H101	-0.20654	0.38982	-0.55161
H102	-0.00291	0.56906	0.27241
H103	-0.12489	0.44103	0.28701
H104	-0.17509	0.62819	0.44724
H105	-0.30419	0.61667	0.32484
H106	-0.18037	0.74422	0.31202
Li17	0.16754	0.34921	-0.03891
C108	0.26589	0.67523	0.09140
O109	0.33624	0.59944	0.16013
C110	0.26391	0.66856	-0.05965
H111	0.19702	0.58515	-0.08711
H112	0.36390	0.64073	-0.09563
C113	0.21226	0.79686	-0.12503
H114	0.20203	0.78181	-0.23348
H115	0.28534	0.87808	-0.11021
C116	0.07835	0.83891	-0.06398
H117	-0.00086	0.76715	-0.09344
H118	0.04602	0.93708	-0.10191
C119	0.17541	0.77051	0.15612
H120	0.17833	0.77354	0.26525
C121	0.08513	0.84158	0.08521
H122	0.01157	0.90258	0.13855

MA

E= -308.61971639 H

C1	0.29439	-0.46731	0.06426
O2	0.35231	-0.37546	0.11889
C3	0.22990	-0.58009	0.14287
H4	0.12674	-0.54902	0.16364
H5	0.28078	-0.58820	0.23891
C6	0.22982	-0.71199	0.06561
H7	0.17835	-0.78955	0.12264
H8	0.33306	-0.74567	0.05218
C9	0.16521	-0.69508	-0.07191
H10	0.05628	-0.68520	-0.06175
H11	0.18097	-0.78414	-0.13332
C12	0.27865	-0.47266	-0.08235
H13	0.31722	-0.38768	-0.13735
C14	0.21767	-0.57454	-0.14385
H15	0.20432	-0.57126	-0.25155

The barrier to rotation in (*S*)-BIFOL according to DFT calculation

To estimate the barrier to rotation in (*S*)-BIFOL, we have performed potential energy surface (PES) scan along the coordinate corresponding to the torsion angle O(1)(C17)C(3)O(2) (θ) 10° steps and full optimization of other geometric parameters at each step (Fig. S4). The global minimum on PES is observed for the structure with the torsion angle equal to -40.0° (Fig. S5), which correspond to the conformation having both intramolecular hydrogen bonds with O···O separation equal to 2.59Å. This minimum is rather shallow, and variation of the relative energy for conformations with torsional angle θ in the range from -50 to 50° is 2 kcal/mol. For comparison, the same torsional angles in crystal of (*S*)-BIFOL are equal to 40.6 and 50.4(3)°. The highest energy was observed for two conformers with θ equal to -91.5 and 86.4 those are destabilized relative to the minimum on PES by 14.4 and 16.6 kcal/mol. For both of these confirmations, the corresponding H-bond breaks with the elongation of O…O separation up to 3.17Å.

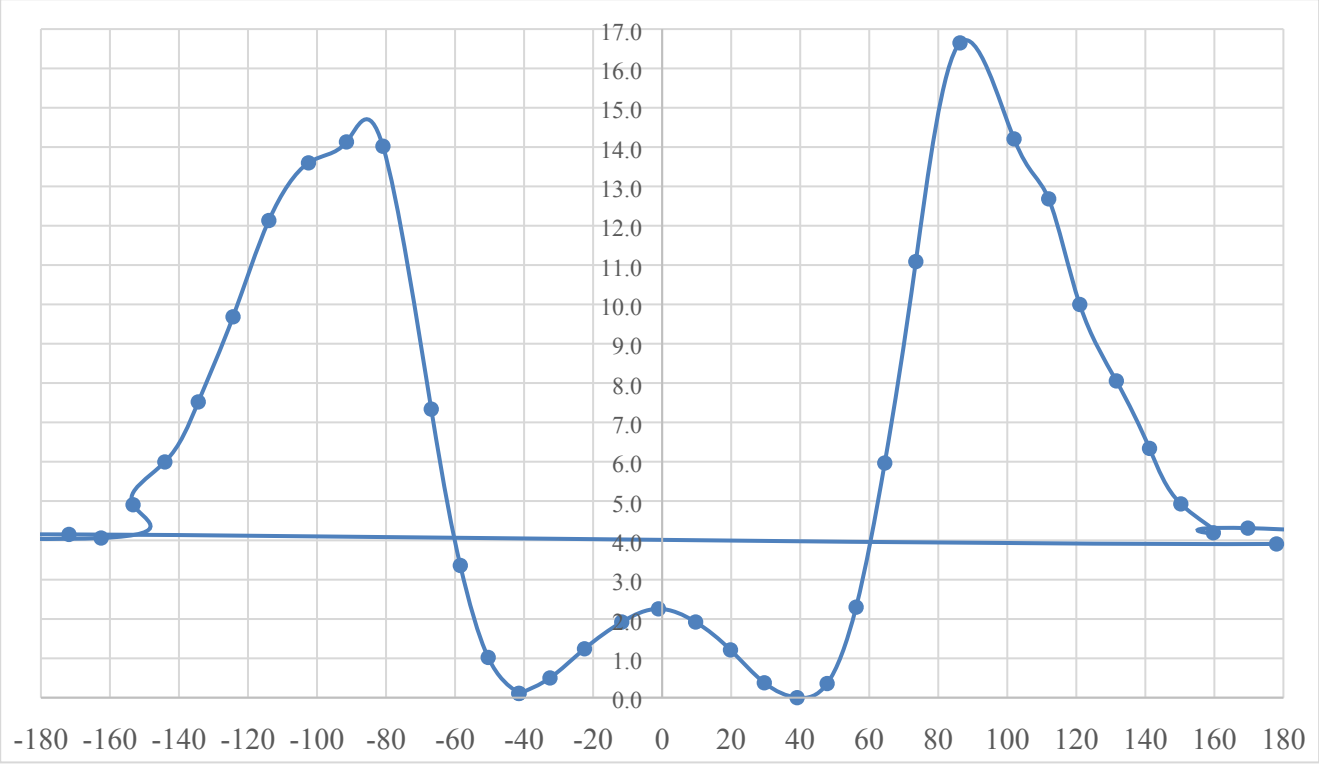


Figure S2. PES scan along the coordinate corresponding to the O(1)(C17)C(3)C(2) torsion angle in (*S*)-BIFOL.

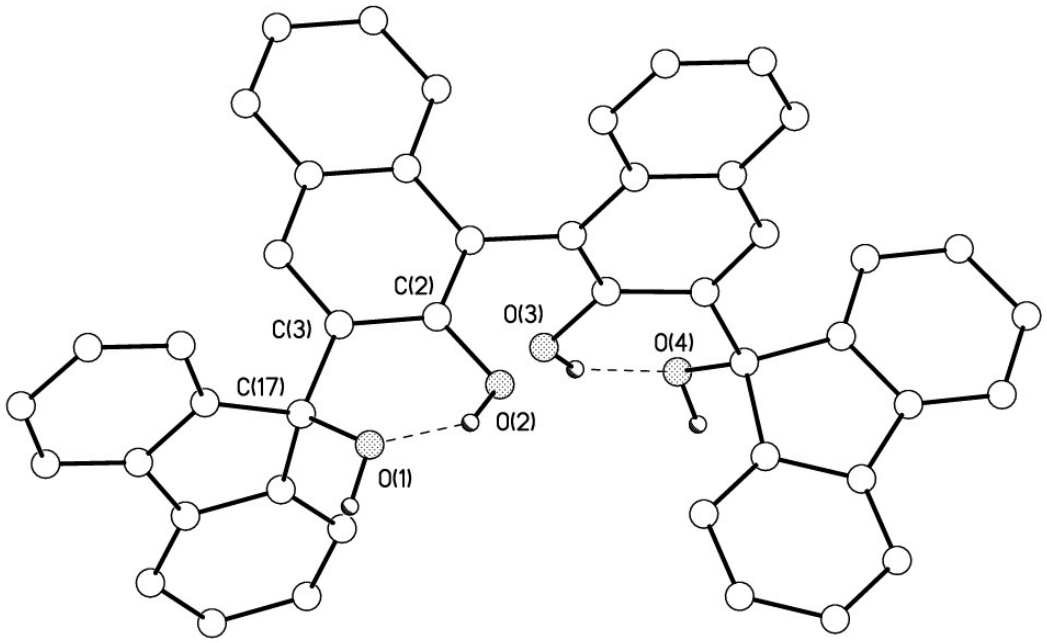


Figure S3. The general view of the global minimuma of (*S*)-BIFOL with θ equal to -40.0°.

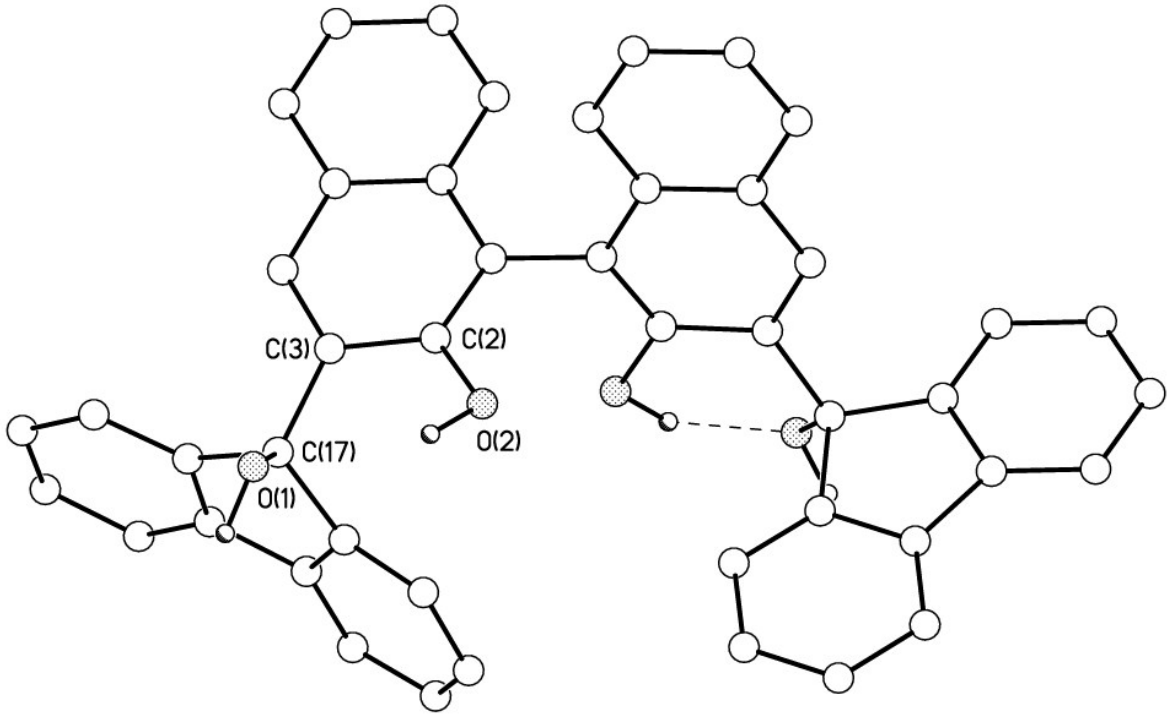


Figure S4. The general view of the global minimuma of (*S*)-BIFOL with θ equal to 86.4°.

^{1}H NMR spectra of BIMBOL-Li and different substrates.

Diethyl malonate and Cyclohexenone.

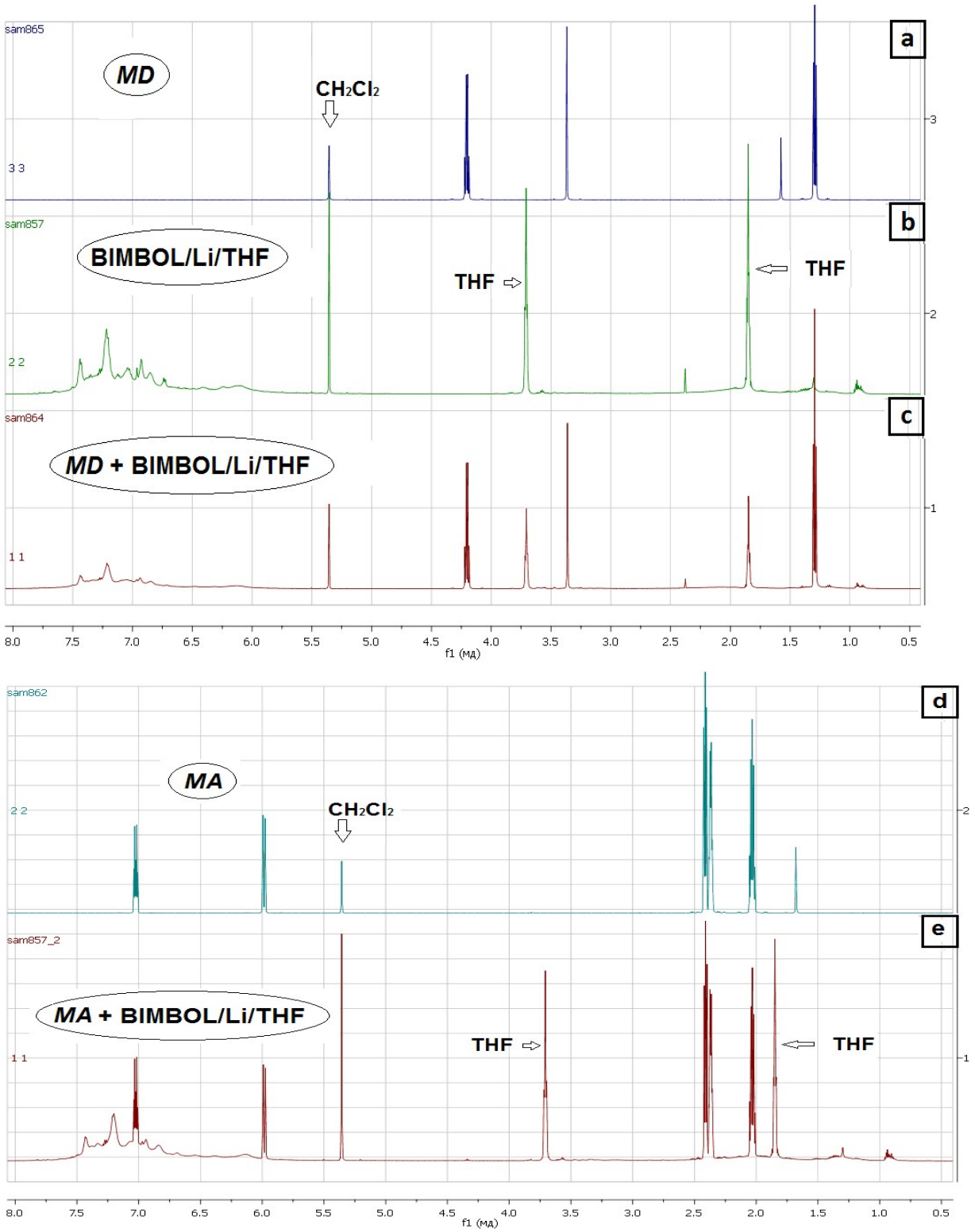


Figure S5. ^{1}H NMR spectra in CD_2Cl_2: (a) Diethyl malonate MD, (b) BIMBOL/Li/THF, (c) a mixture of BIMBOL/Li/THF and MD, (d) ***MA*** (cyclohexanone), (e) a mixture of BIMBOL/Li/THF and ***MA***.

As can be seen from Figure S5, there were no changes in the chemical shifts of ***MA*** or ***MD*** in the presence of BIMBOL-Li. However, ethyl α-nitropropanoate, ***MD2***, (pK_a 9 in DMSO[S5]) was completely converted under the same conditions into the corresponding carbanion (Figure S6d). The resonance of α–proton at 5.27 ppm disappeared and the doublet of the β-methyl group became a broad singlet at 1.99 ppm. The resonances of the ethyl ester group also became very broad at 4.08 ppm and 1.25 ppm. The ^{1}H NMR spectrum of the carbanion was different when the ionization was affected by PhOLi with the lines being almost as narrow as those of the initial CH-acid (Figure S6c). The difference may be an indication of a complex formation involving the nitropropionate and BIMBOL.

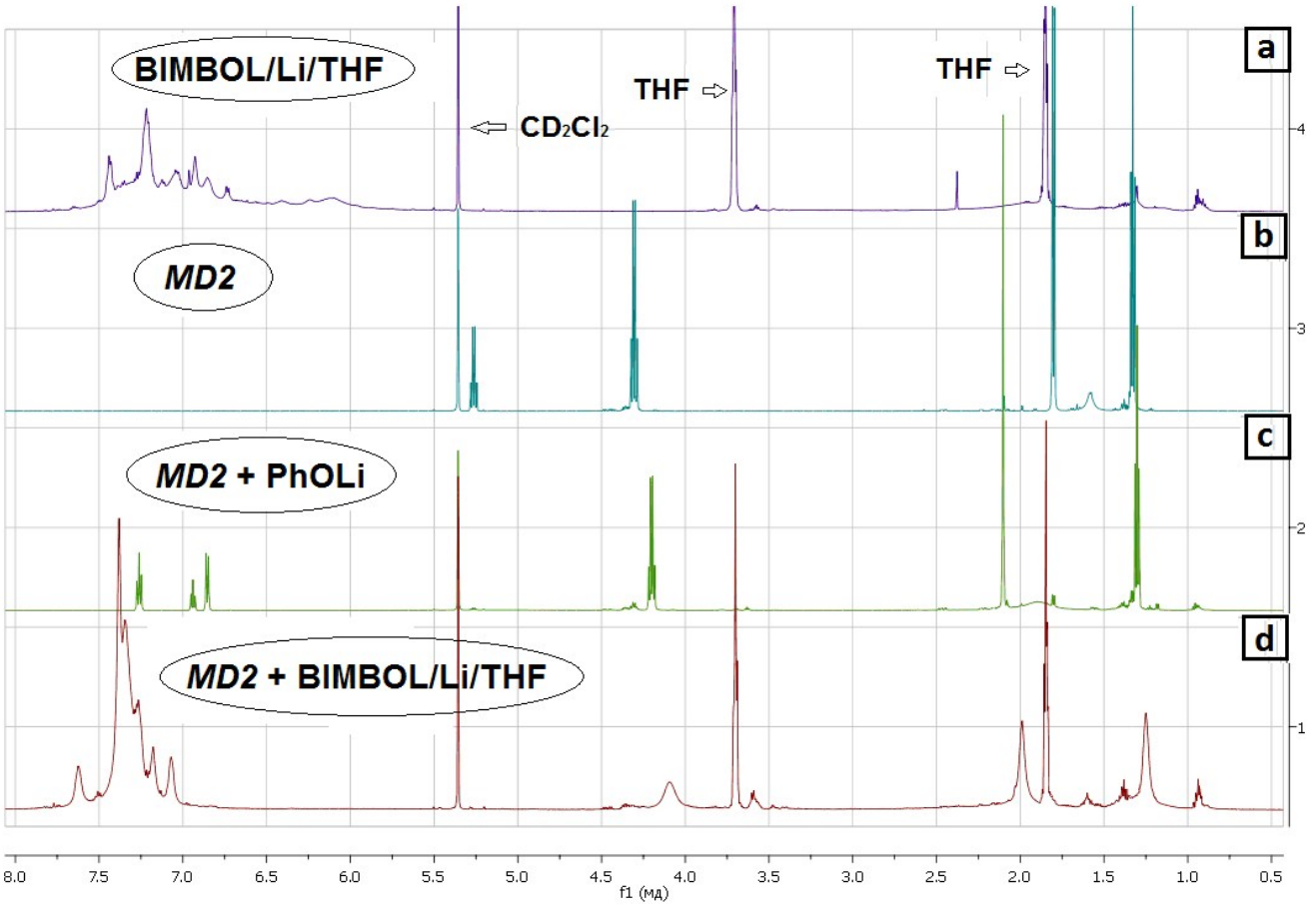
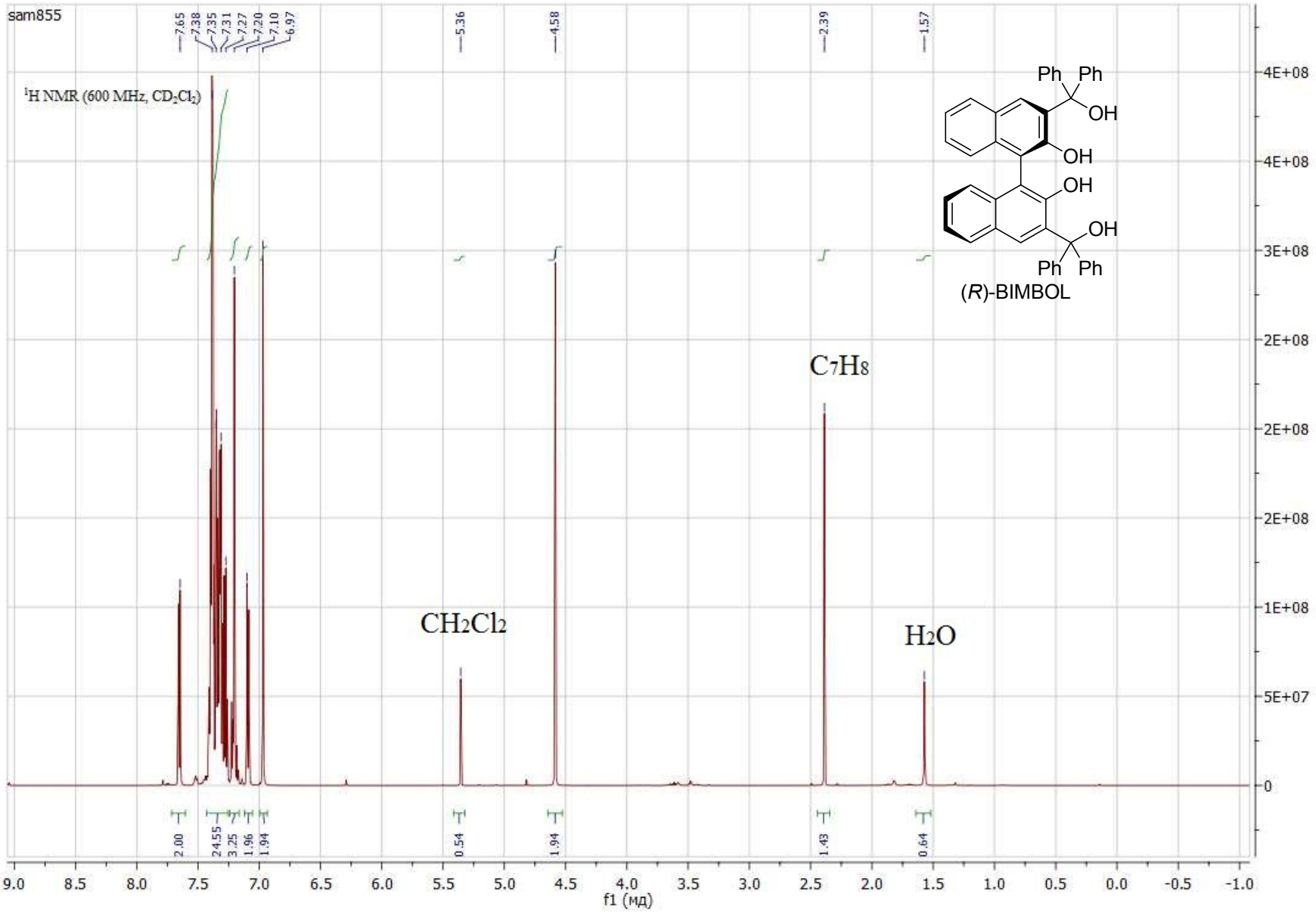
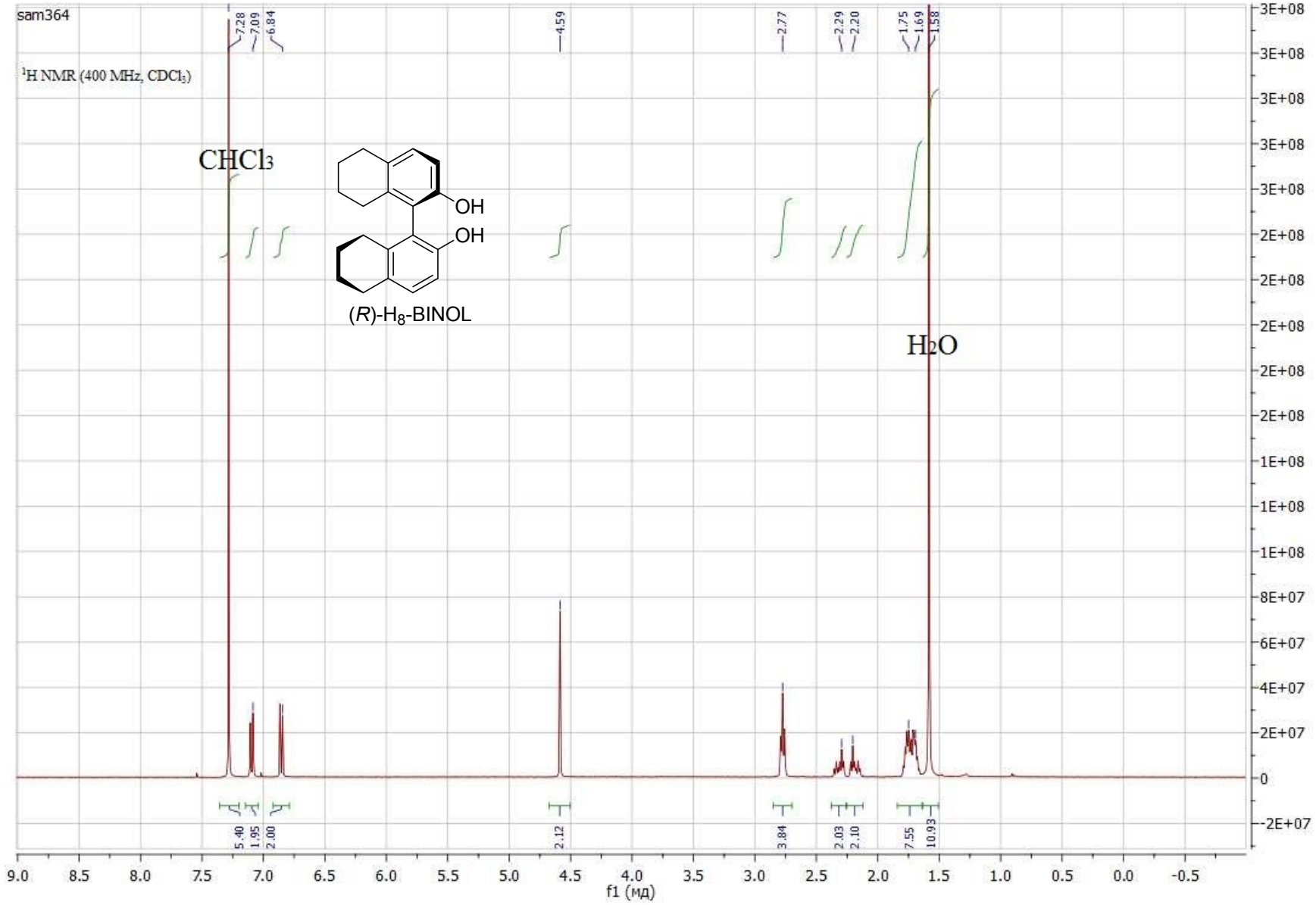


Figure S6. ^{1}H NMR spectra in CD_2Cl_2 of: (a) BIMBOL/Li/THF, (b) ethyl nitropropanoate, ***MD2***, (c) an equimolar mixture of PhOLi and MD2, (d) an equimolar mixture of BIMBOL/Li/THF and ***MD2***.

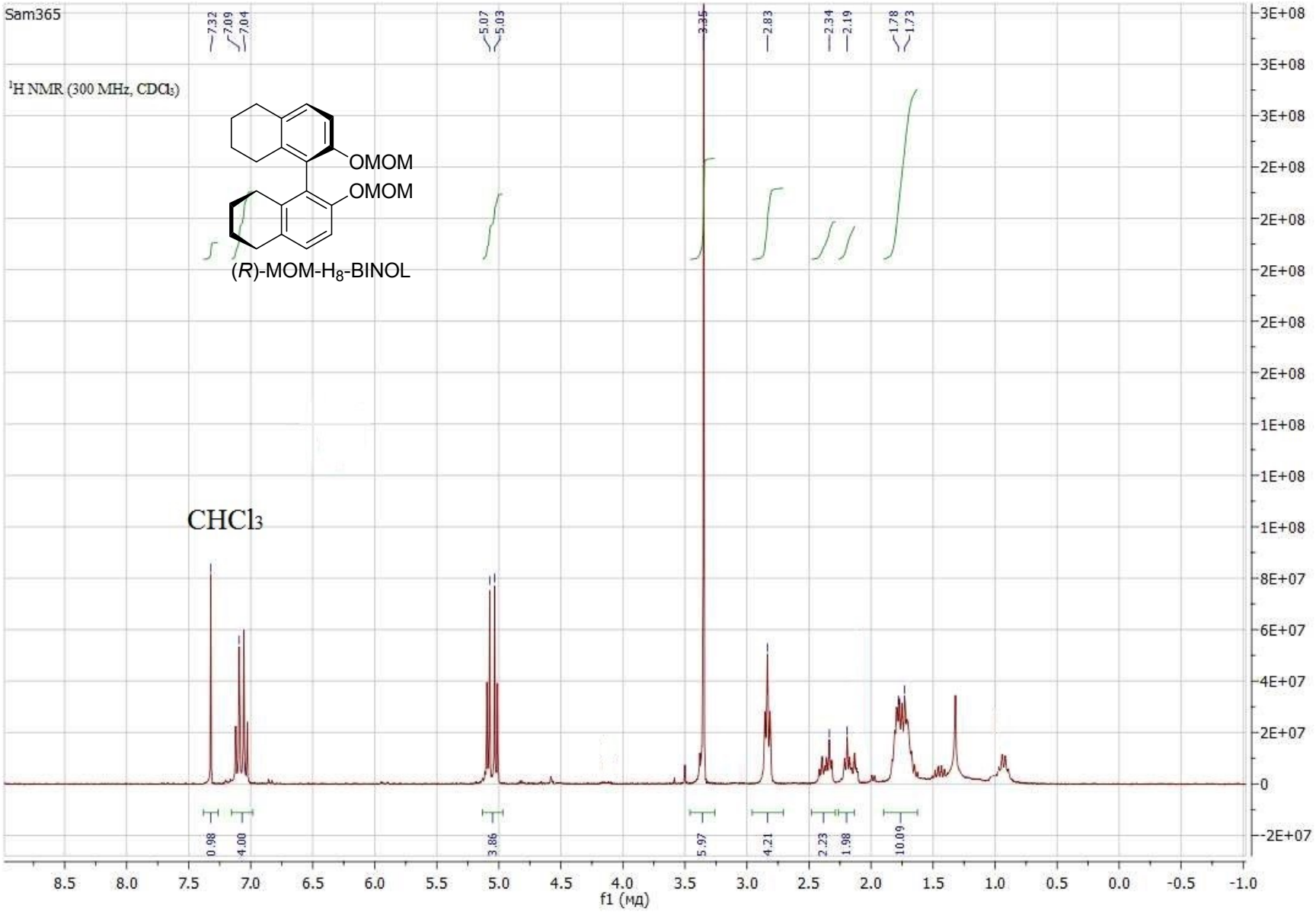
^{1}H NMR spectrum of (*R*)-BIMBOL



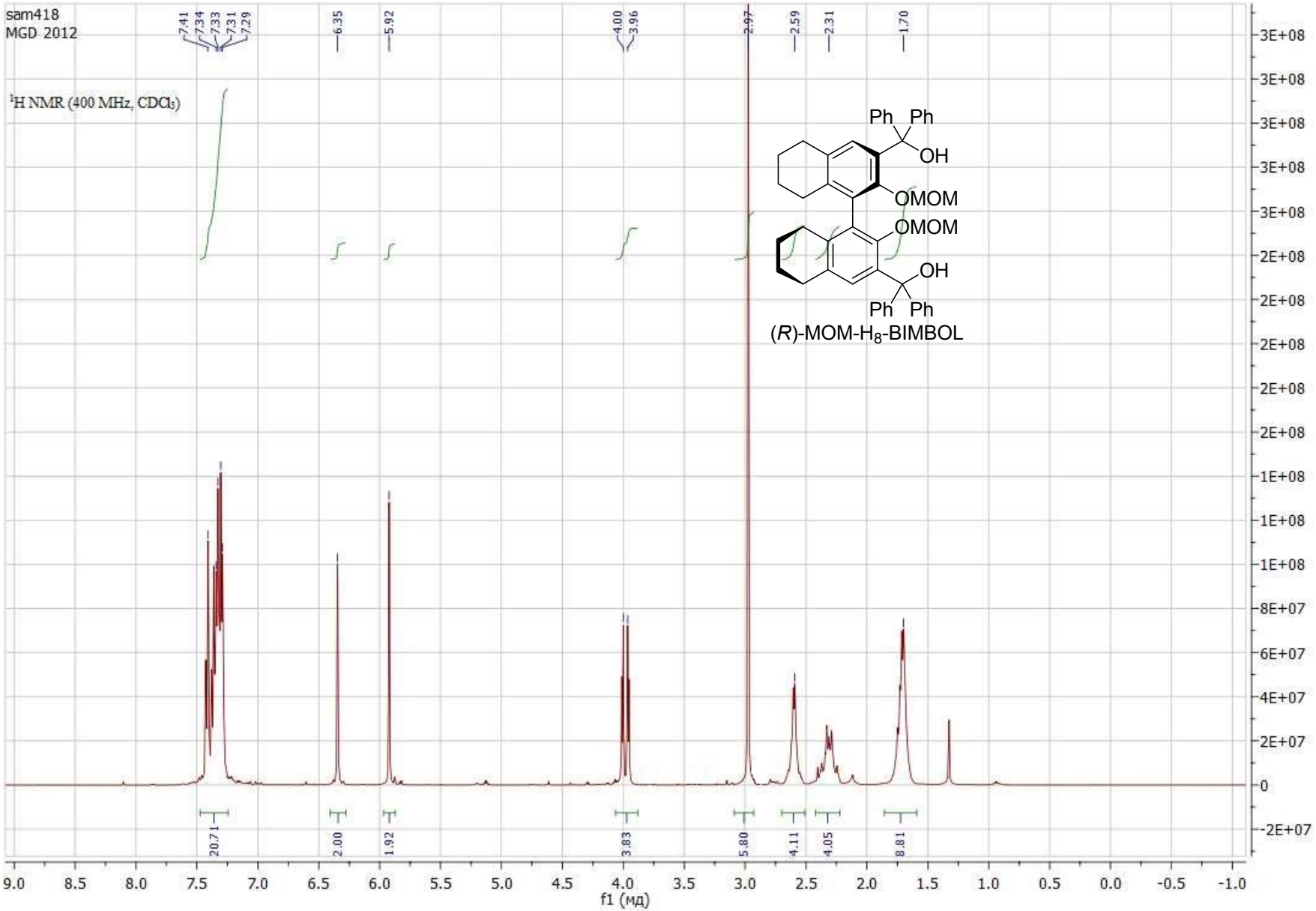
^{1}H NMR spectrum of (*R*)-H_8-BINOL



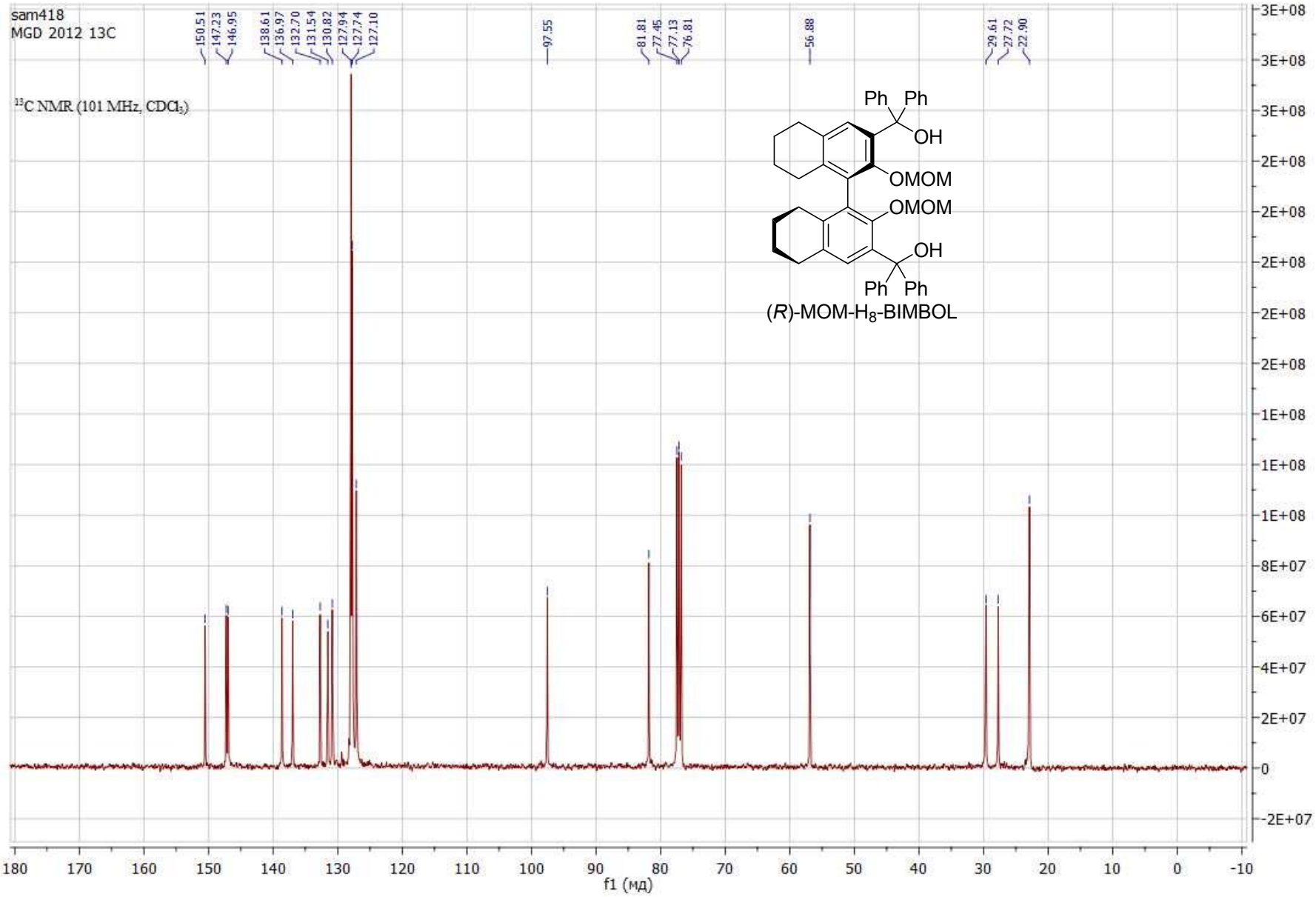
^{1}H NMR spectrum of *(R)*-MOM-H_8-BINOL



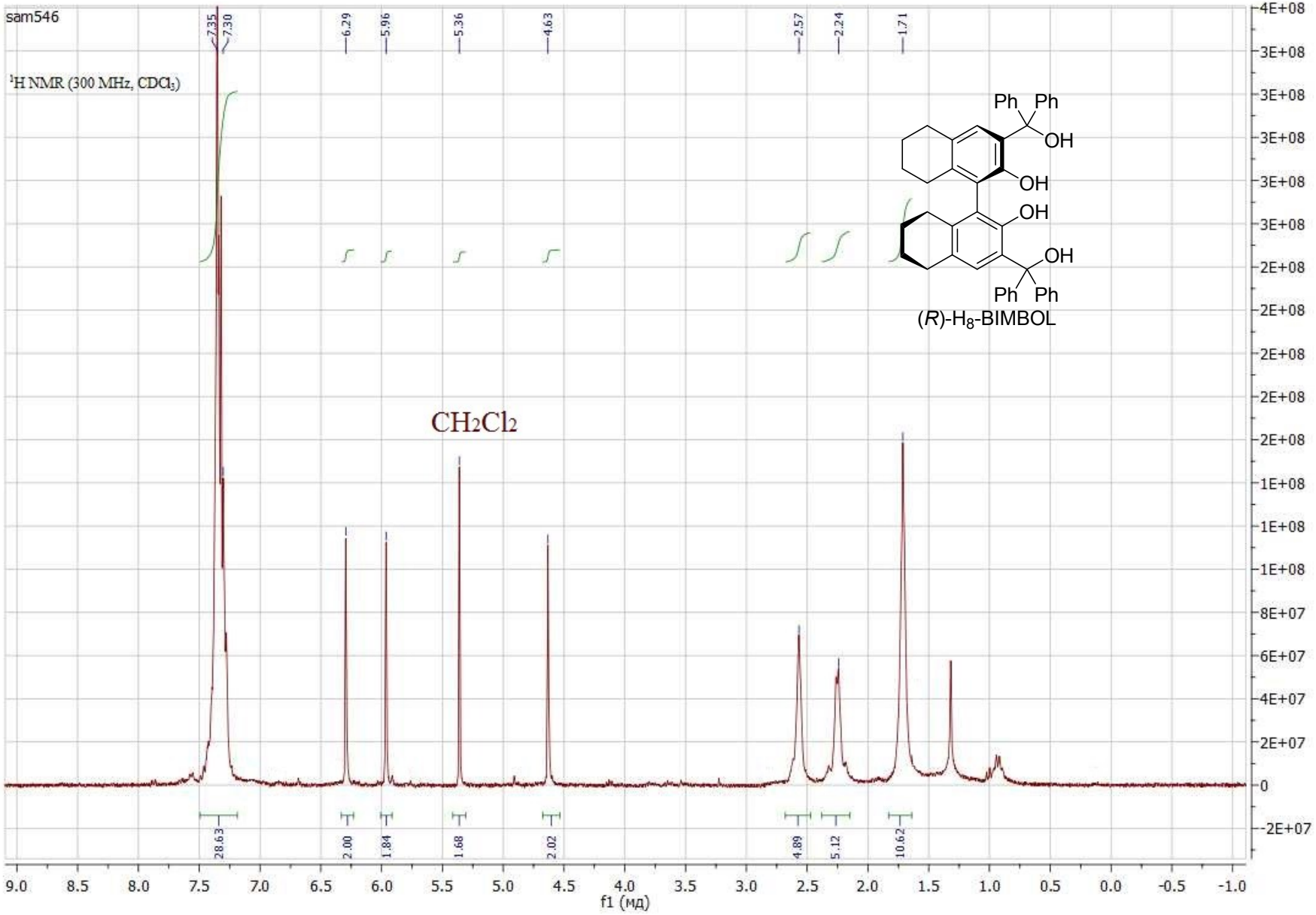
^{1}H NMR spectrum of *(R)*-MOM-H_8-BIMBOL



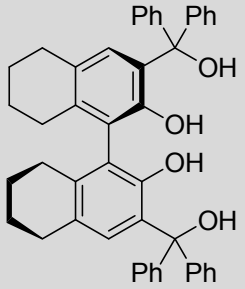
^{13}C NMR spectrum of (*R*)-MOM-H_8-BIMBOL



^{1}H NMR spectrum of (*R*)-H_8-BIMBOL

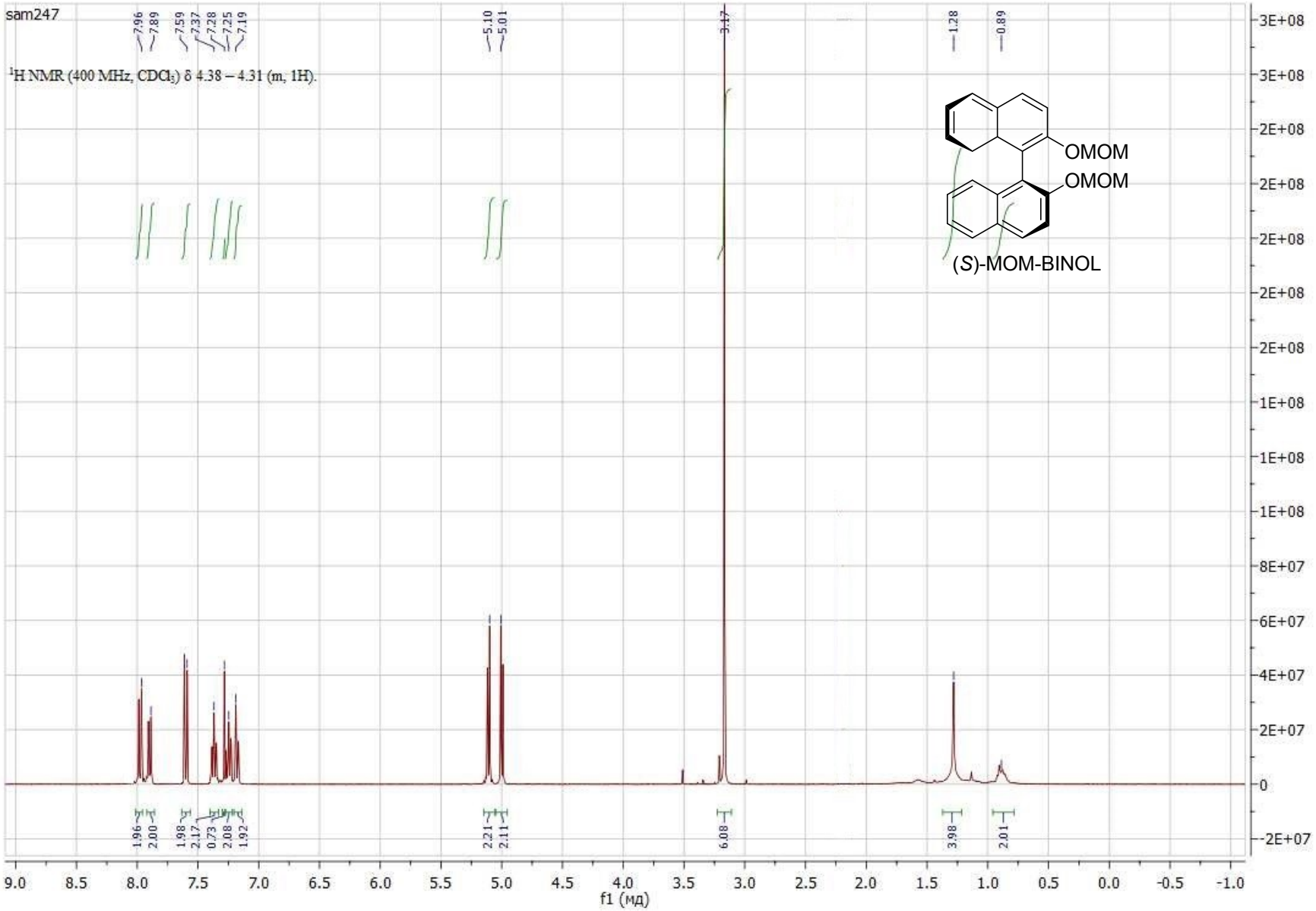


^{13}C NMR spectrum of (*R*)-H_8-BIMBOL

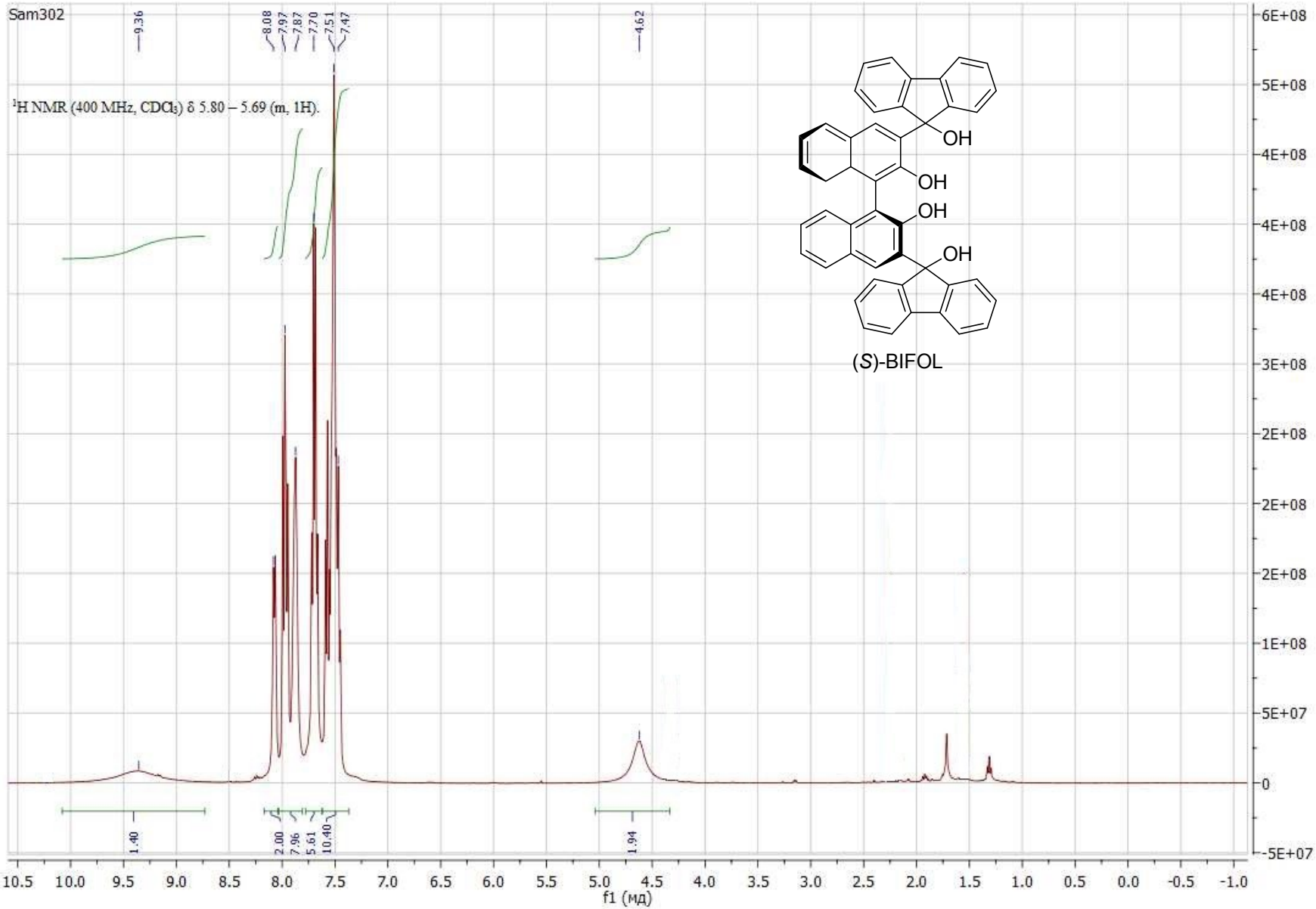


(*R*)-H_8-BIMBOL

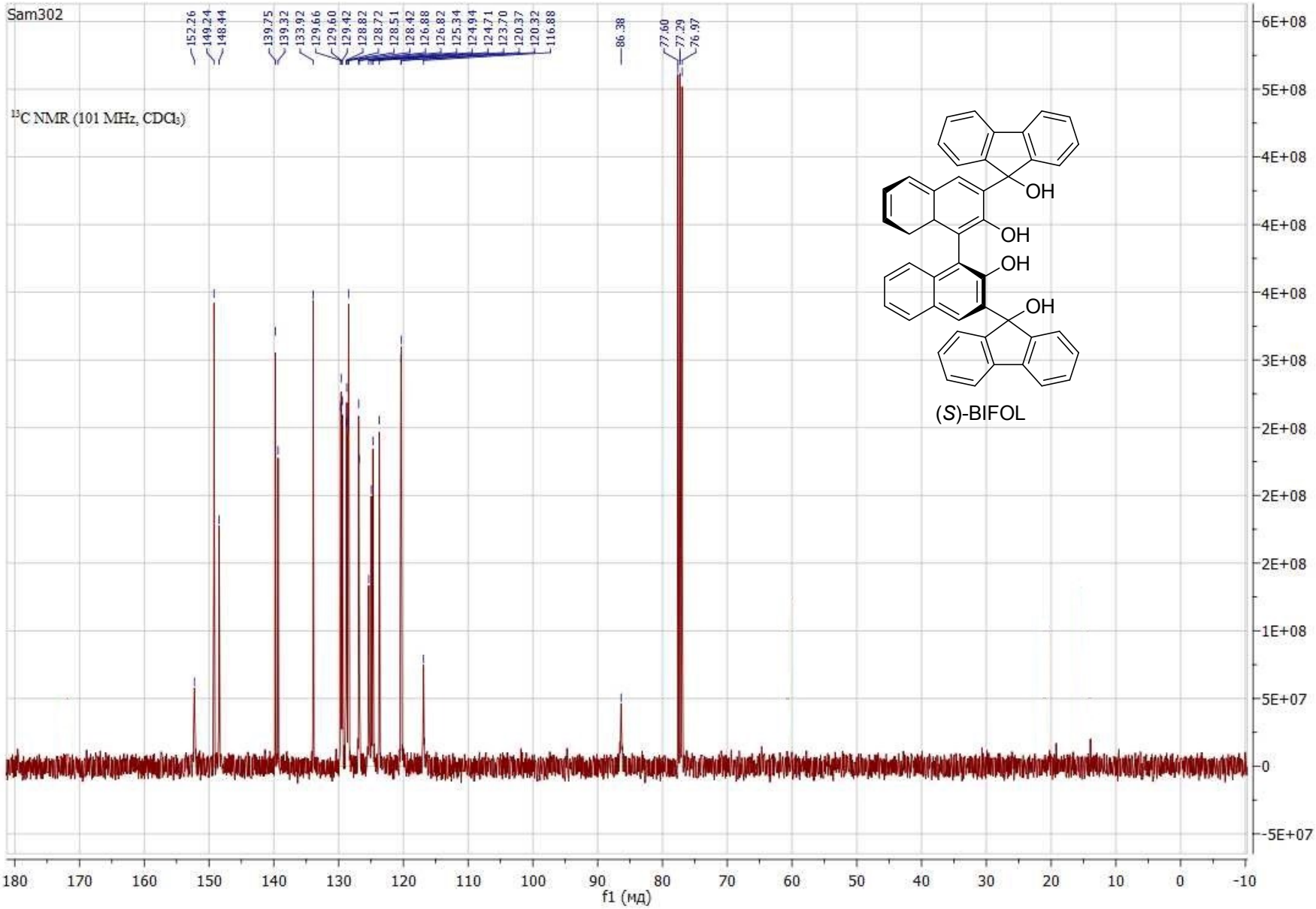
^{1}H NMR spectrum of (*S*)-MOM-BINOL



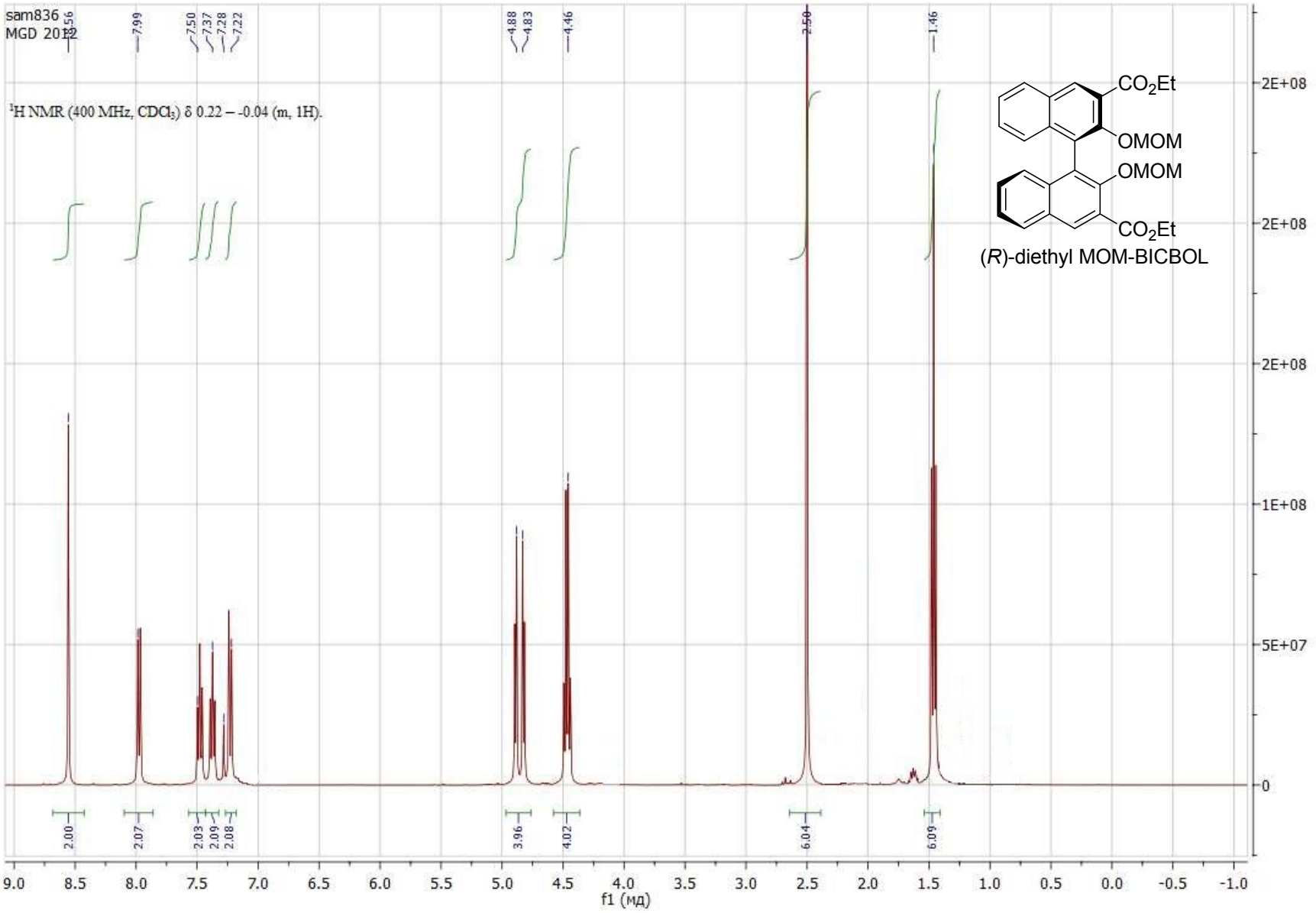
^{1}H NMR spectrum of (*S*)-BIFOL



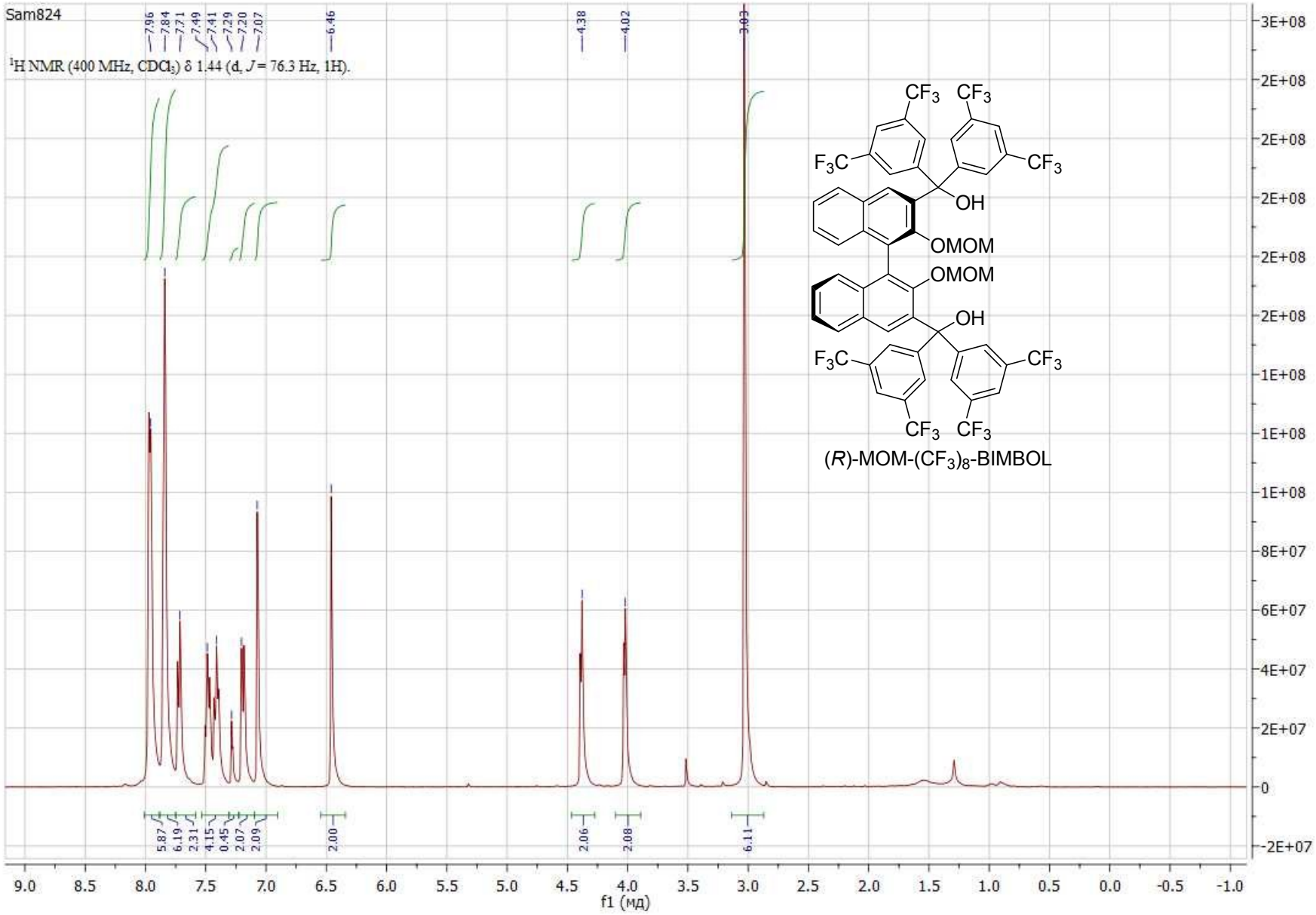
^{13}C NMR spectrum of (*S*)-BIFOL



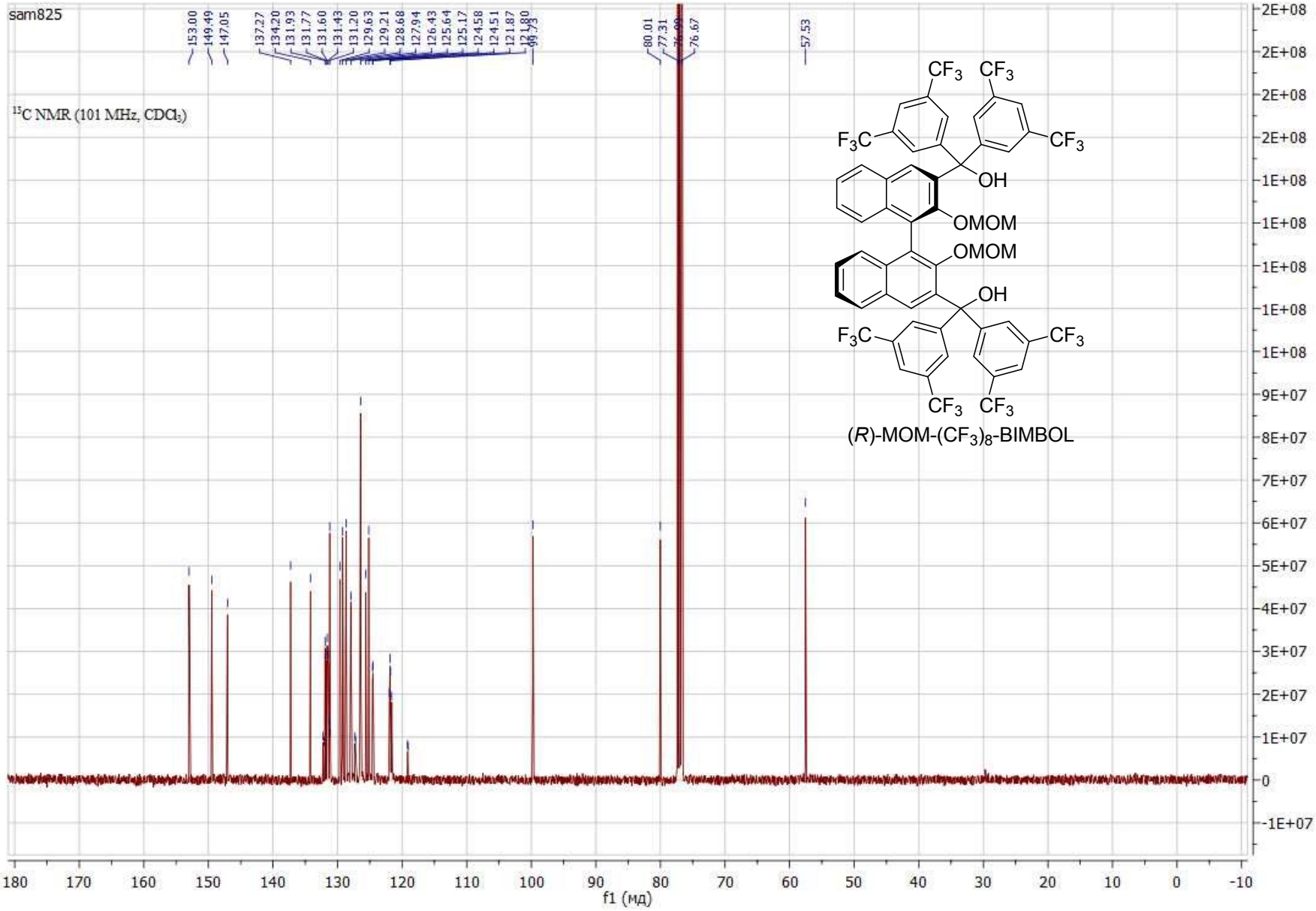
^{1}H NMR spectrum of (*R*)-Diethyl-MOM-BICBOL



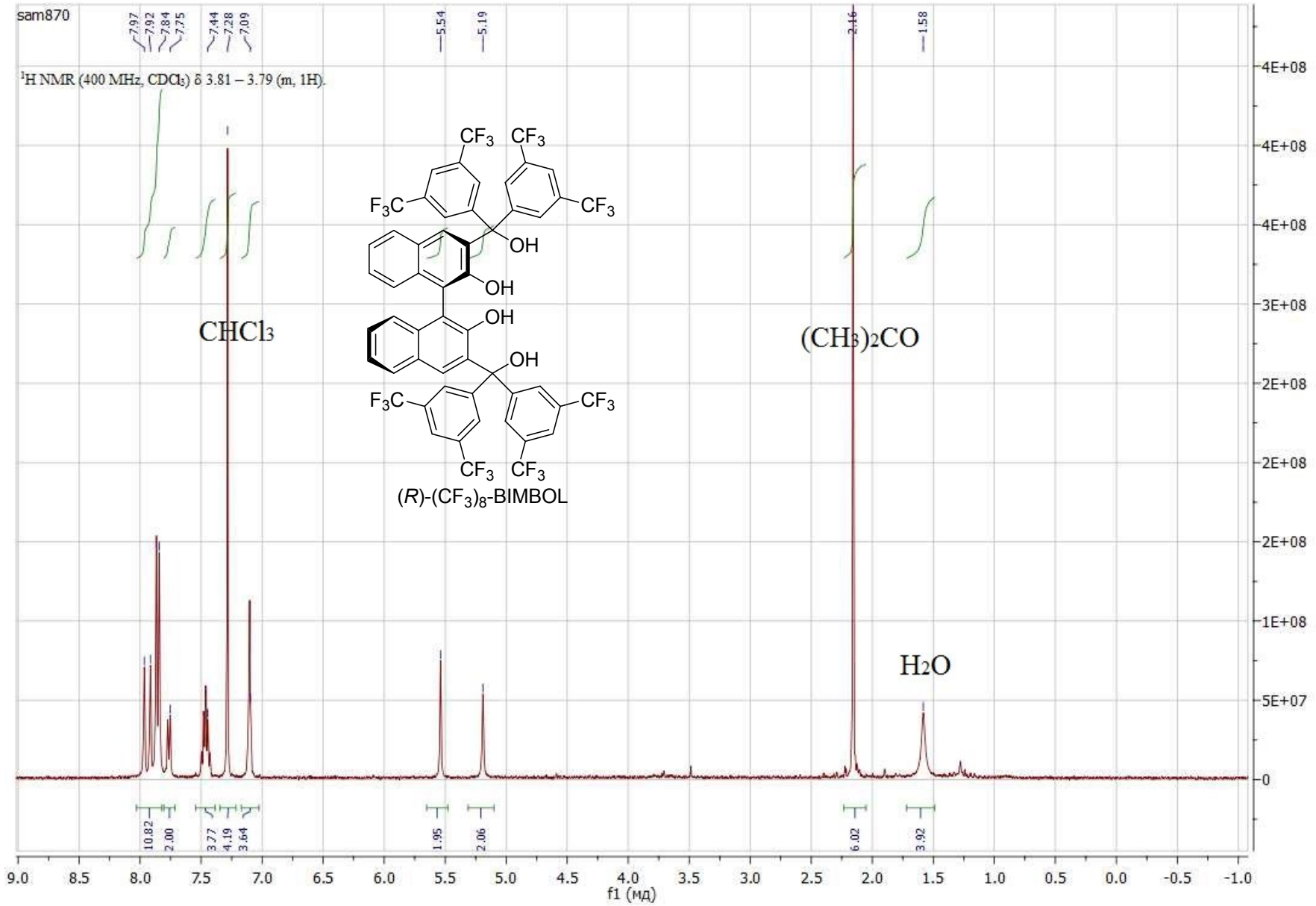
^{1}H NMR spectrum of (*R*)-MOM-$(CF_3)_8$-BIMBOL



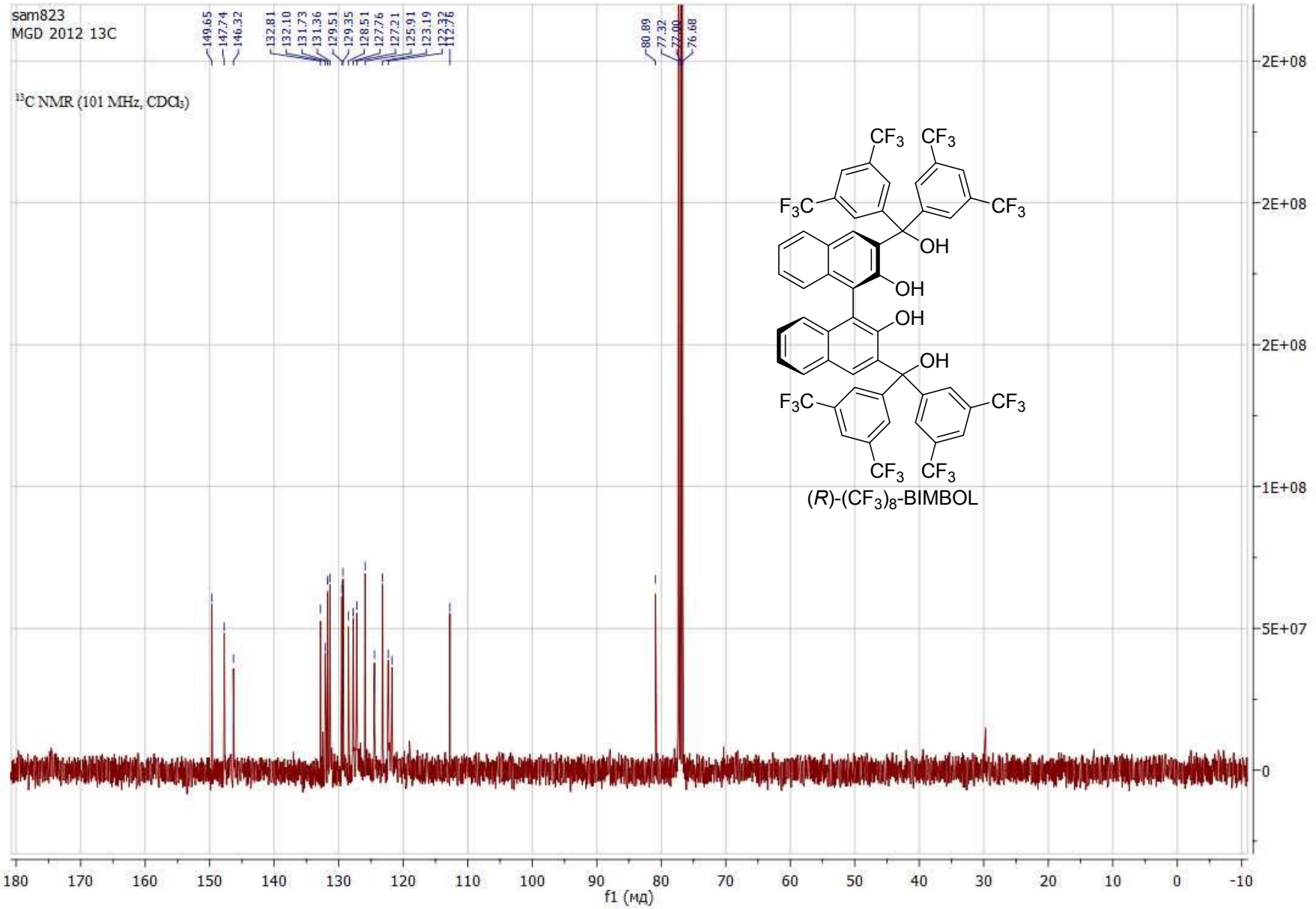
^{13}C NMR spectrum of (*R*)-MOM-$(CF_3)_8$-BIMBOL



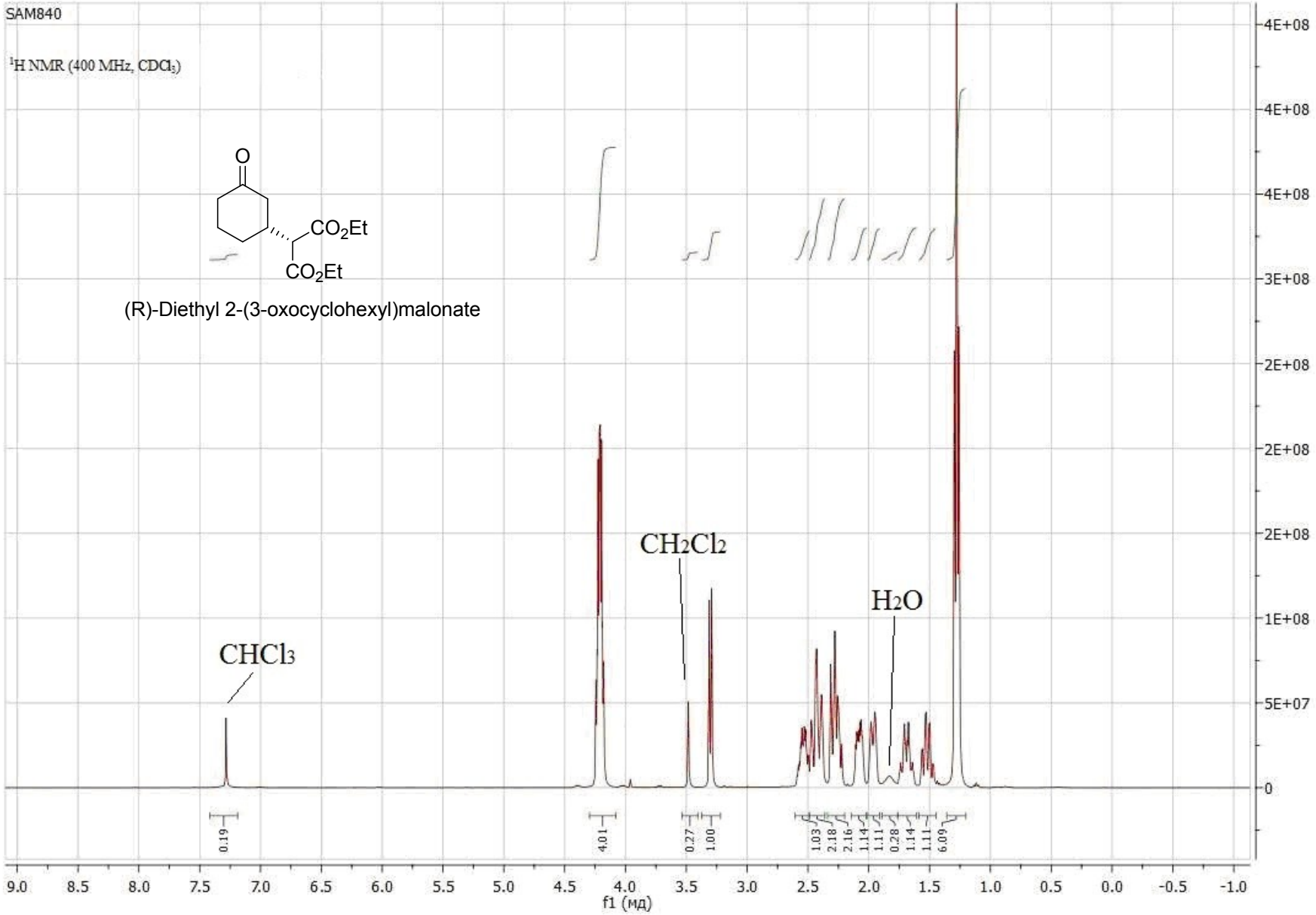
^{1}H NMR spectrum of (*R*)-$(CF_3)_8$-BIMBOL



^{13}C NMR spectrum of (*R*)-$(CF_3)_8$-BIMBOL



^{1}H NMR spectrum of (*R*)-Diethyl 2-(3-oxocyclohexyl)malonate



HPLC traces of racemic, (*S*)- and (*R*)-Diethyl 2-(3-oxocyclohexyl)malonate

The conditions: the column CHIRALPAK AS-H, 250 x 4,6 mm. Solvent system: heptane/isopropanol = 9/1. UV detector operated at a wavelength of 210 нм.

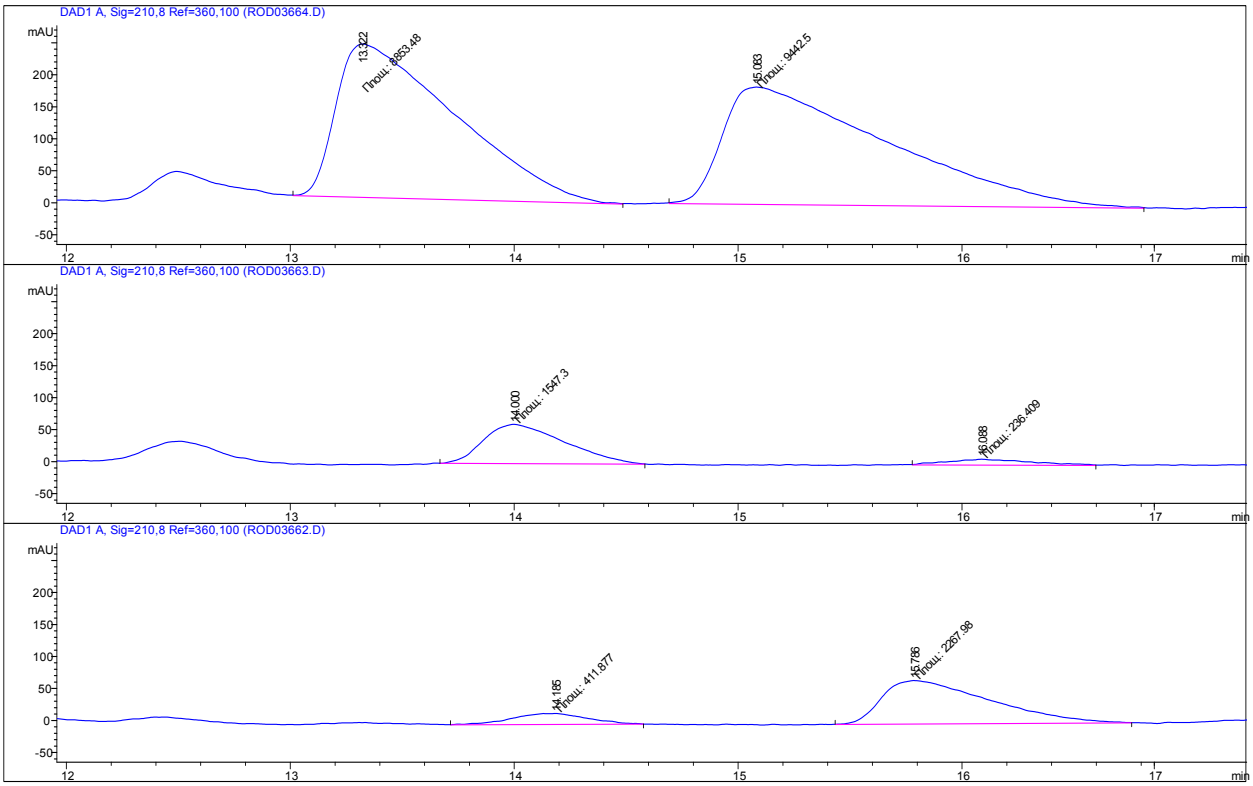


Figure S7 HPLC traces of racemic (top), (*R*)- and (*S*)-diethyl 2-(3-oxocyclohexyl)malonate obtained under the corresponding *(R)*- or (*S*)-BIMBOL/Li catalysis conditions.

Variable temperature ^{1}H NMR spectra of BIFOL

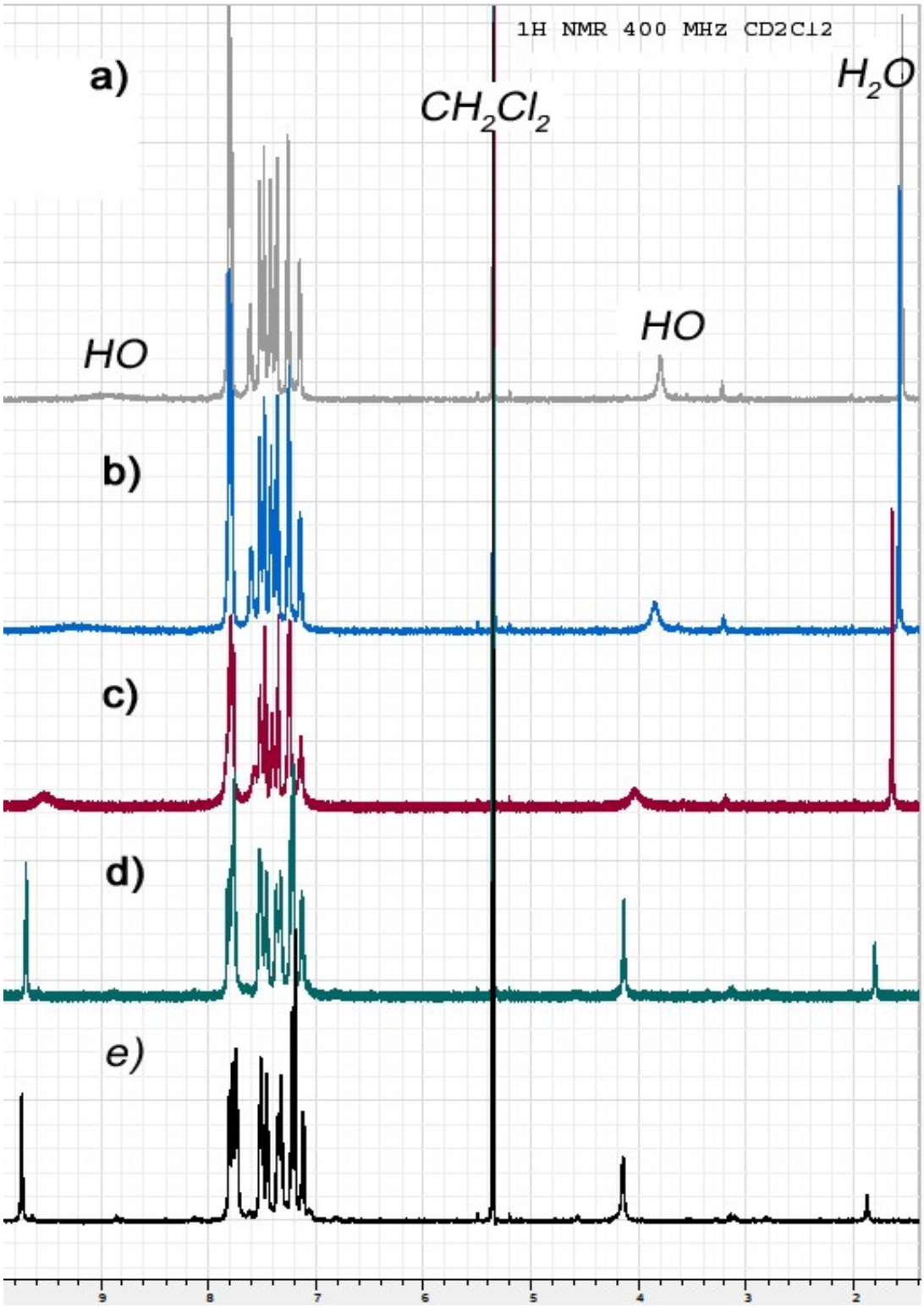


Figure S9 ^{1}H NMR spectra of BIFOL: a) a solution of BIFOL in CD_2Cl_2 at 30 °C. b) at 20 °C. c) at 0 °C. d) at −40 °C. e) at −50 °C

Variable temperature ^{1}H NMR spectra of BIMBOL

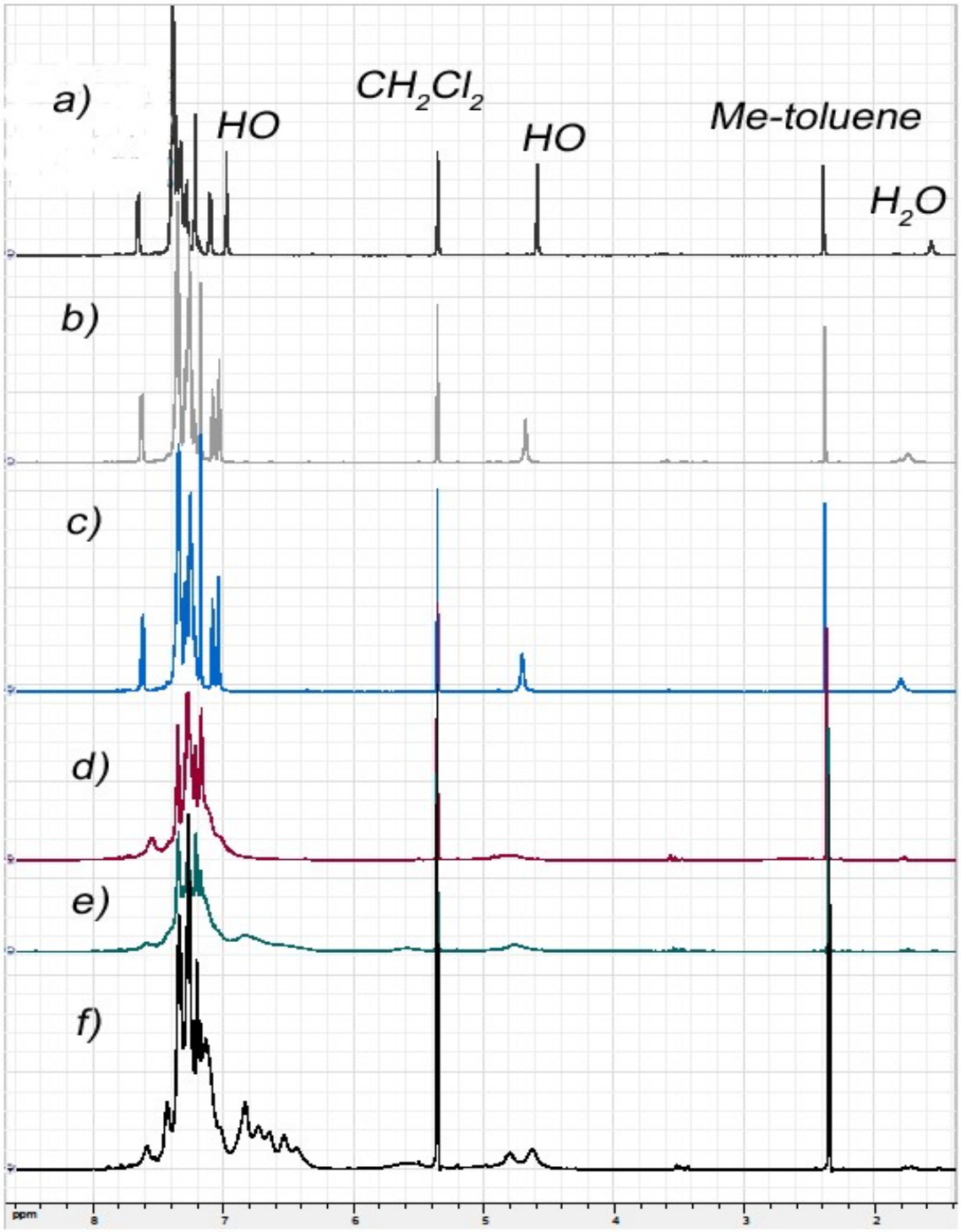


Figure S10. ^{1}H spectra of BIMBOL: a) a solution of BIMBOL in CD_2Cl_2 at 30 °C. b) at 20 °C. c) at 0°C. d) at −40 °C. e) at −50 °C.

Variable temperature ^{13}C NMR spectra of BIFOL

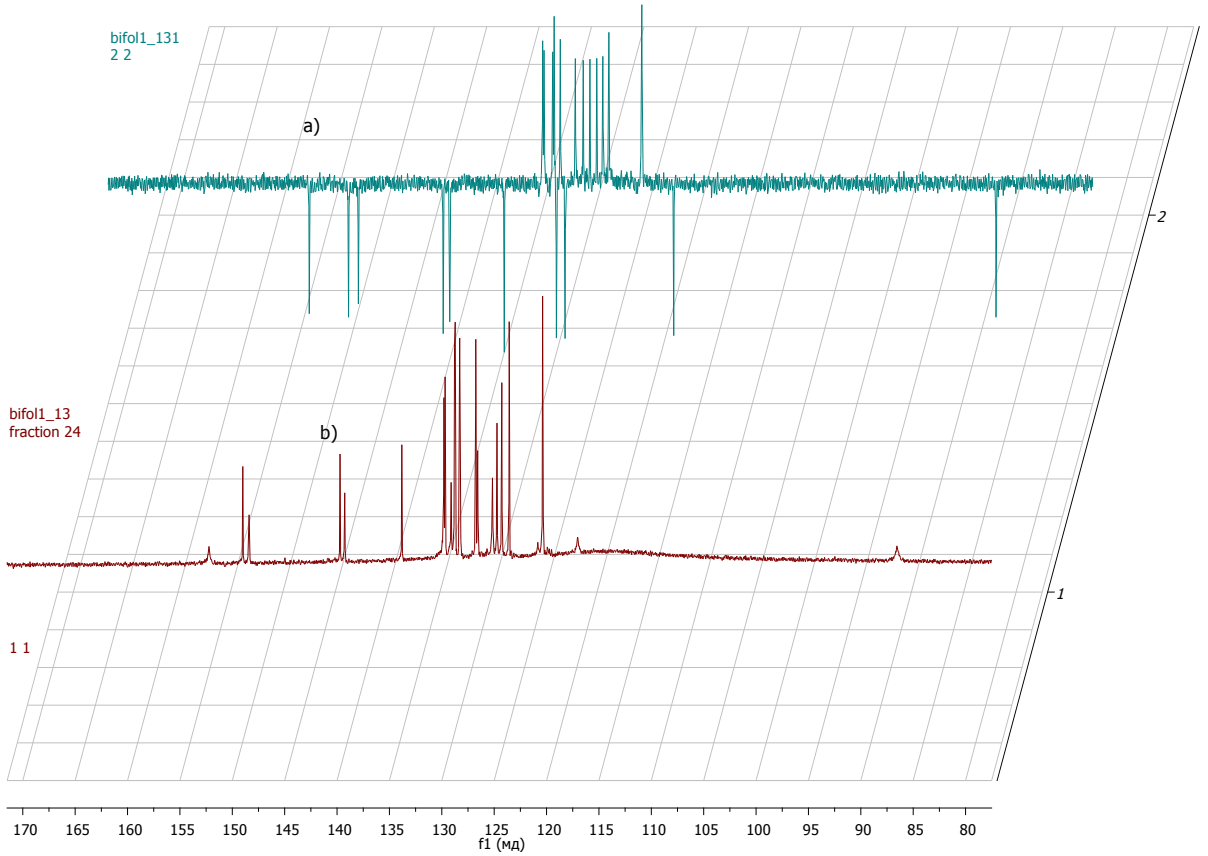


Figure S11 ^{13}C spectra of BIFOL: a) a solution of BIFOL in CD_2Cl_2 at −40 °C (JMODECHO mode). b) the same solution at 25 °C ($^{13}C\{^1H\}$ mode)

Variable temperature ^{13}C NMR spectra of BIMBOL

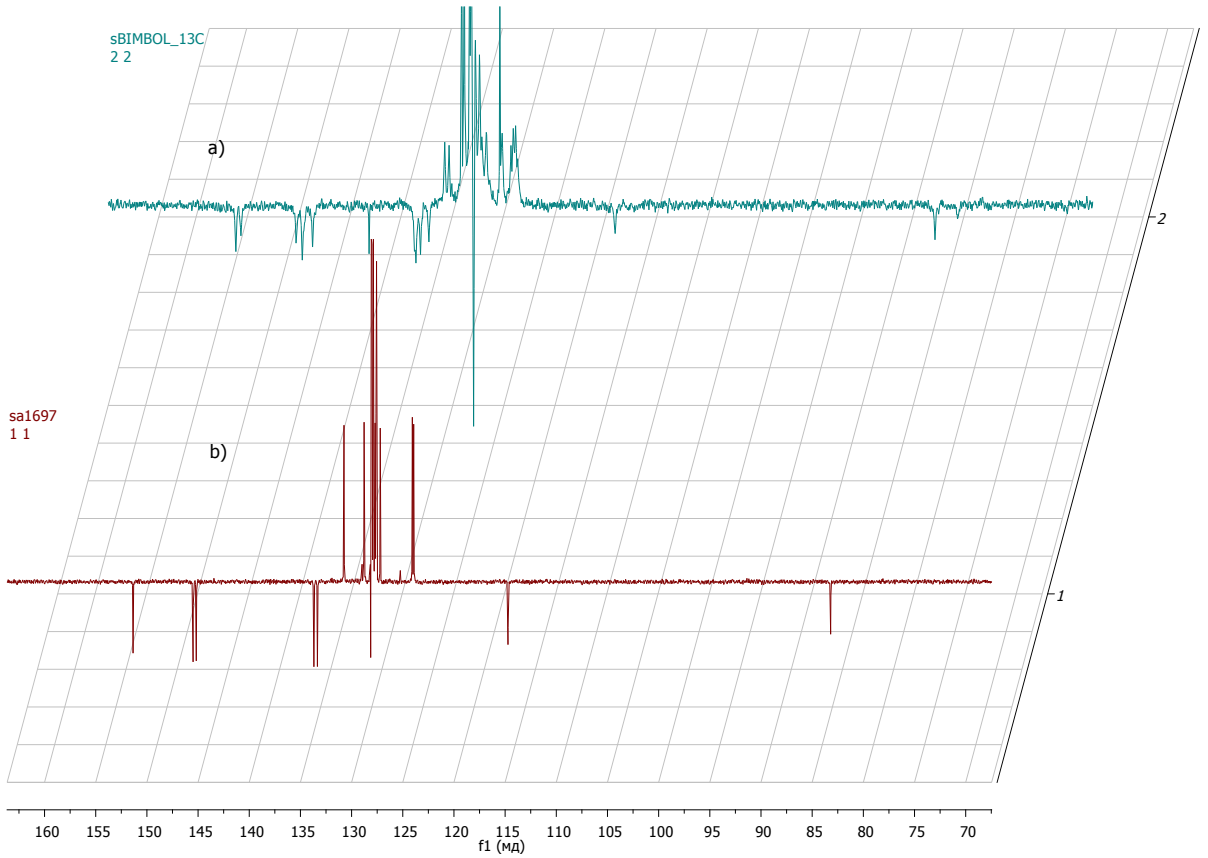
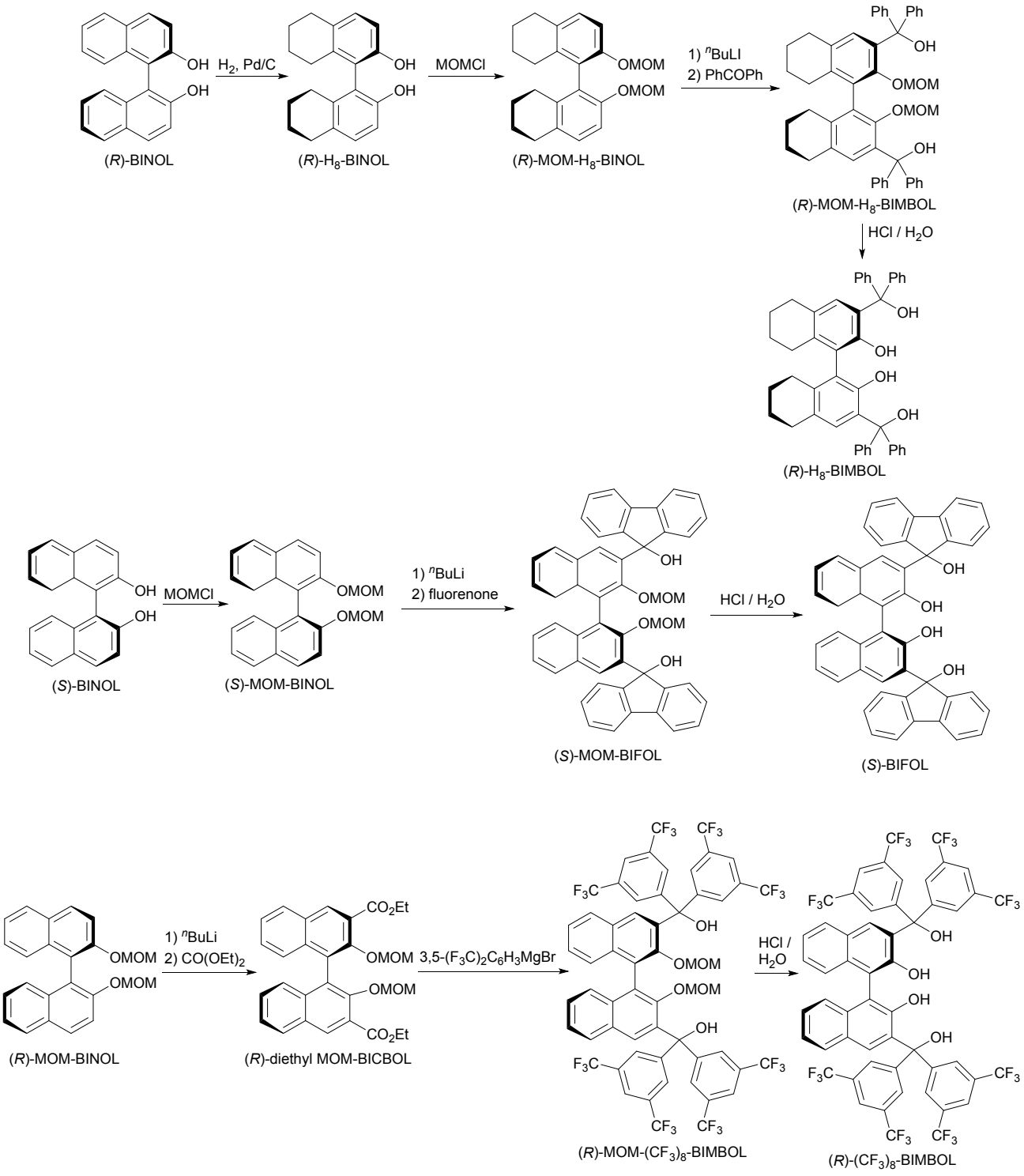


Figure S12. ^{13}C spectra of BIMBOL: a) a solution of BIMBOL in CD_2Cl_2 at −40 °C (JMODECHO mode). b) the same solution at 30 °C (JMODECHO mode).

Synthetic routes for the synthesis of (*R*)-H_8-BIMBOL, (*S*)-BIFOL and (*R*)-$(CF_3)_8$-BIMBOL



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S3 G. M. Sheldrick, 'SADABS, v. 2.03, Bruker/Siemens Area Detector Absorption Correction Program', Bruker AXS, Madison, Wisconsin, 2003.

S4 G. M. Sheldrick, *Acta. Crystallogr.,* 2008, **A64**, 112–122.

S5 X. Li, Q. Ding, J. Ge, J. Xie and D. Xu, *J. Org. Chem.*, 2009, **74**, 1785–1787.