Supporting information

Bulky Metallocavitands with Chiral Cavity Constructed by Aluminium and Magnesium Atrane-likes and Enantioselective Recognition and Separation of Racemic Alcohol

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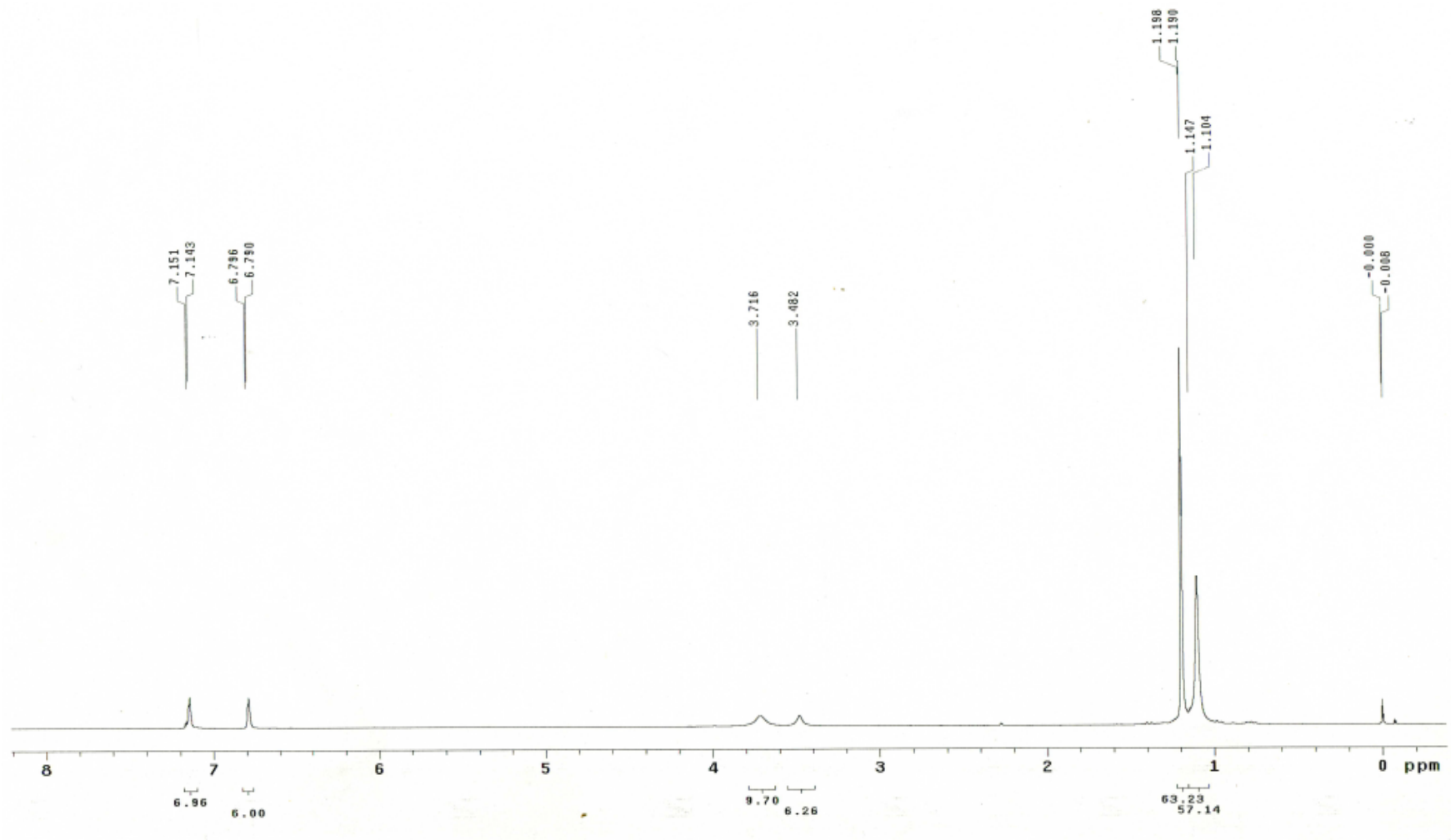


Figure S1. ^{1}H NMR of complex **1** in $CDCl_3$.

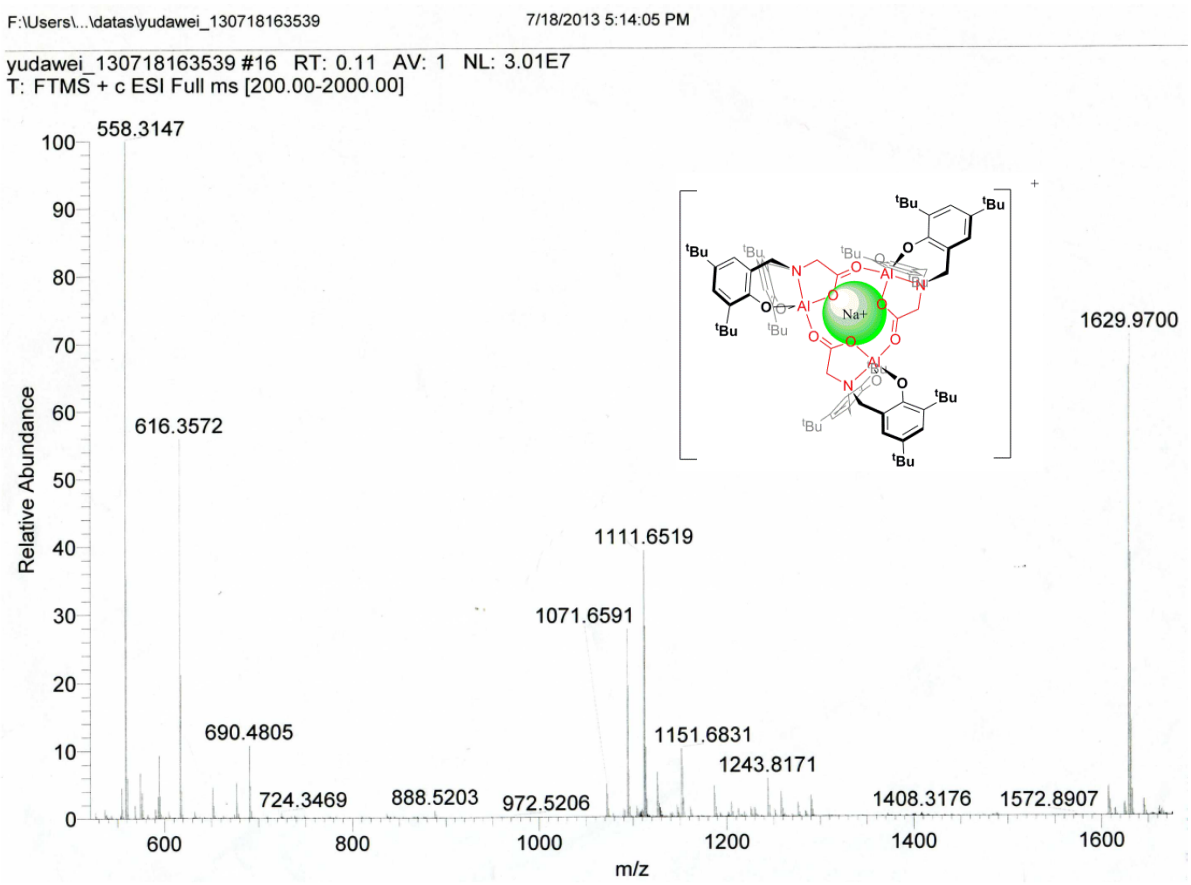


Figure S2. ESI-MS spectrum of complex **1**

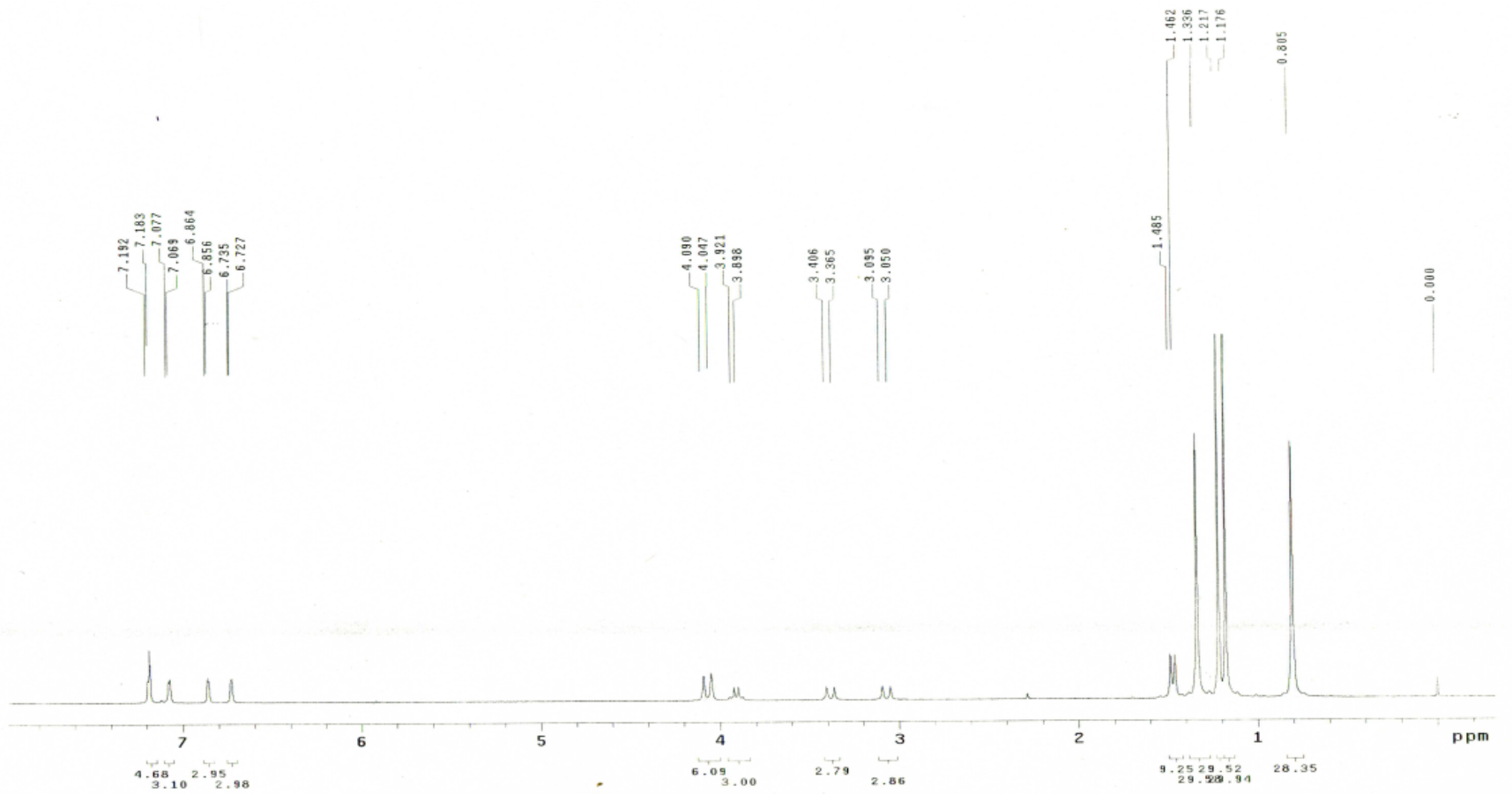


Figure S3. ^{1}H NMR of complex **2** in $CDCl_3$.

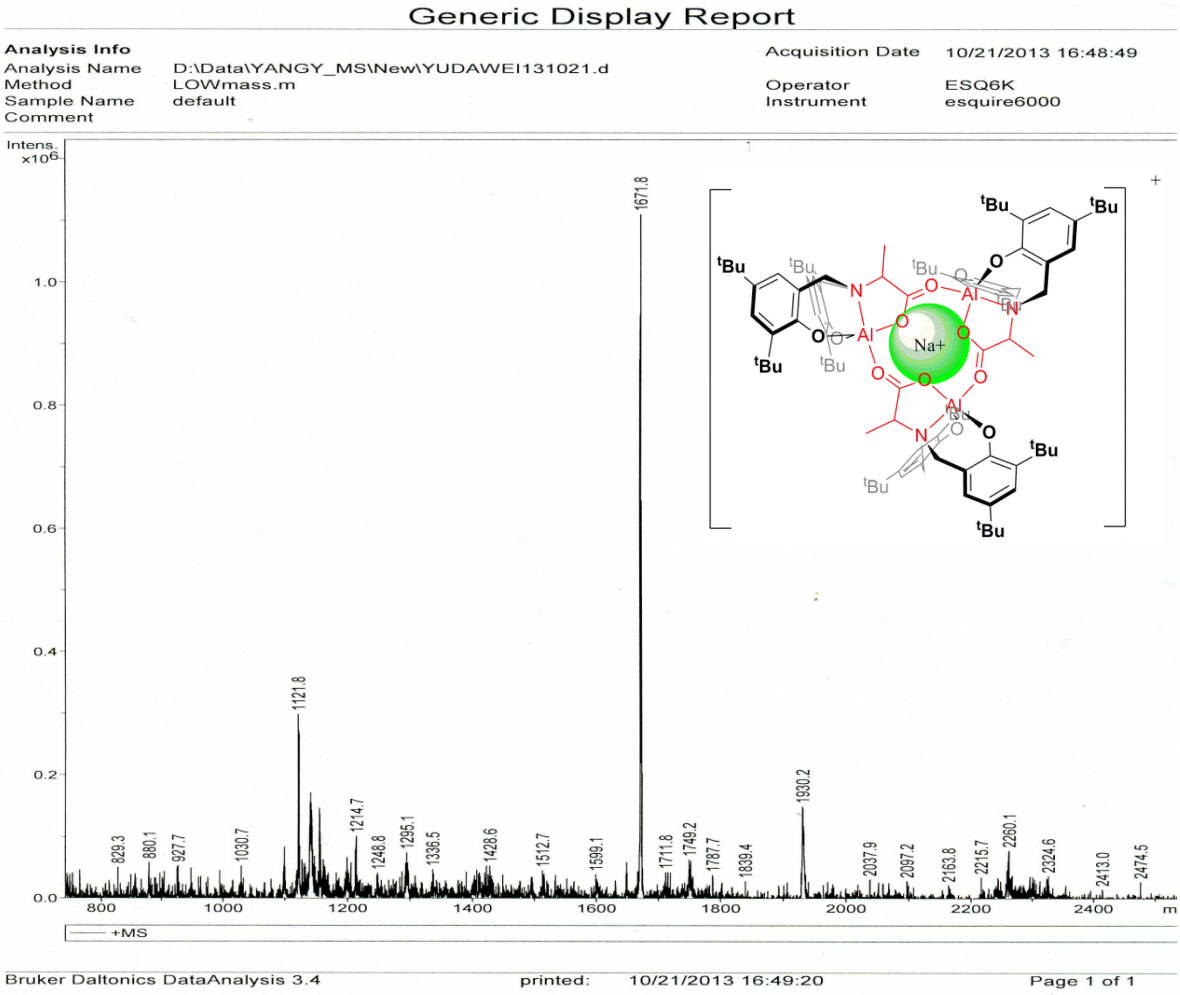
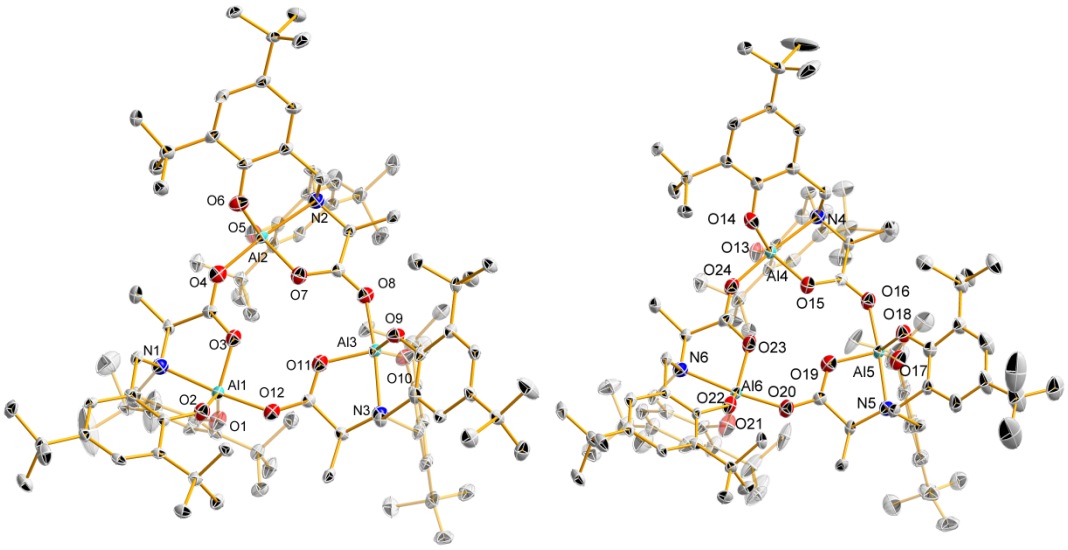


Figure S4. ESI-MS spectrum of complex **2**



a b

(S, S, S, M, M, M)

Figure S5 Molecular structure of **2** with absolute configuration of (S, S, S, M, M, M) as 30% ellipsoids. Selected bond lengths (Å): Al1 N1 2.115(7), Al1 O1 1.728(5), Al1 O2 1.729(5), Al1 O3 1.827(5), Al1 O12 1.879(5), Al2 N2 2.115(6), Al2 O4 1.868(5), Al2 O5 1.725(5), Al2 O6 1.723(5), Al2 O7 1.832(6), Al3 N3 2.125(7), Al3 O8 1.882(6), Al3 O9 1.727(5), Al3 O10 1.734(5), Al3 O11 1.822(5), Al4 N4 2.119(6), Al4 O13 1.733(5), Al4 O14 1.722(5), Al4 O15 1.821(6), Al4 O24 1.880(5), Al5 N5 2.095(7), Al5 O16 1.896(6), Al5 O17 1.740(5), Al5 O18 1.734(5), Al5 O19 1.826(5), Al6 N6 2.135(7), Al6 O20 1.862(6), Al6 O21 1.735(6), Al6 O22 1.732(5), Al6 O23 1.836(6), O12 Al1 N1 175.3(2), O4 Al2 N2 174.4(3), O8 Al3 N3 174.9(2), O24 Al4 N4 175.7(3), O16 Al5 N5 176.3(3), O20 Al6 N6 173.0(2).

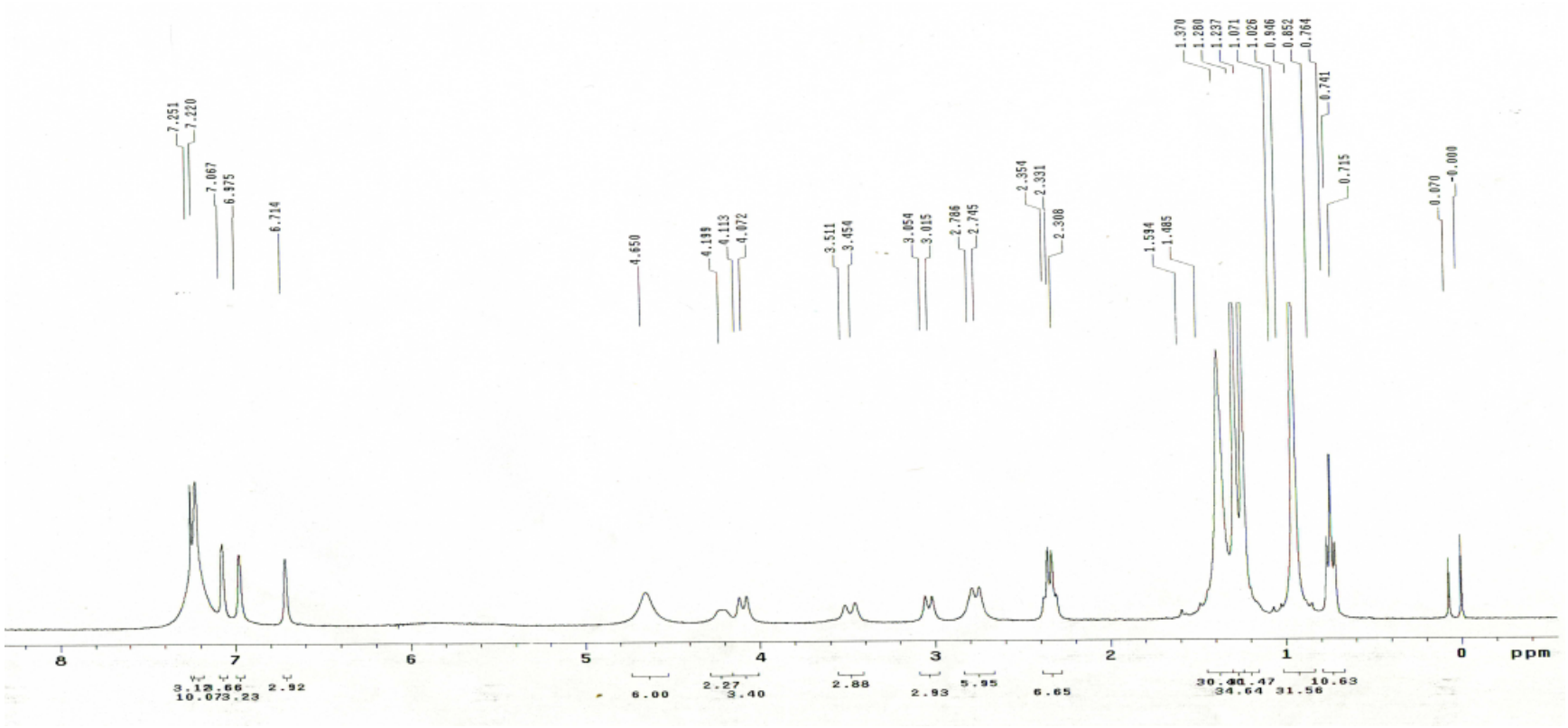


Figure S6. ^{1}H NMR of complex **3** in $CDCl_3$.

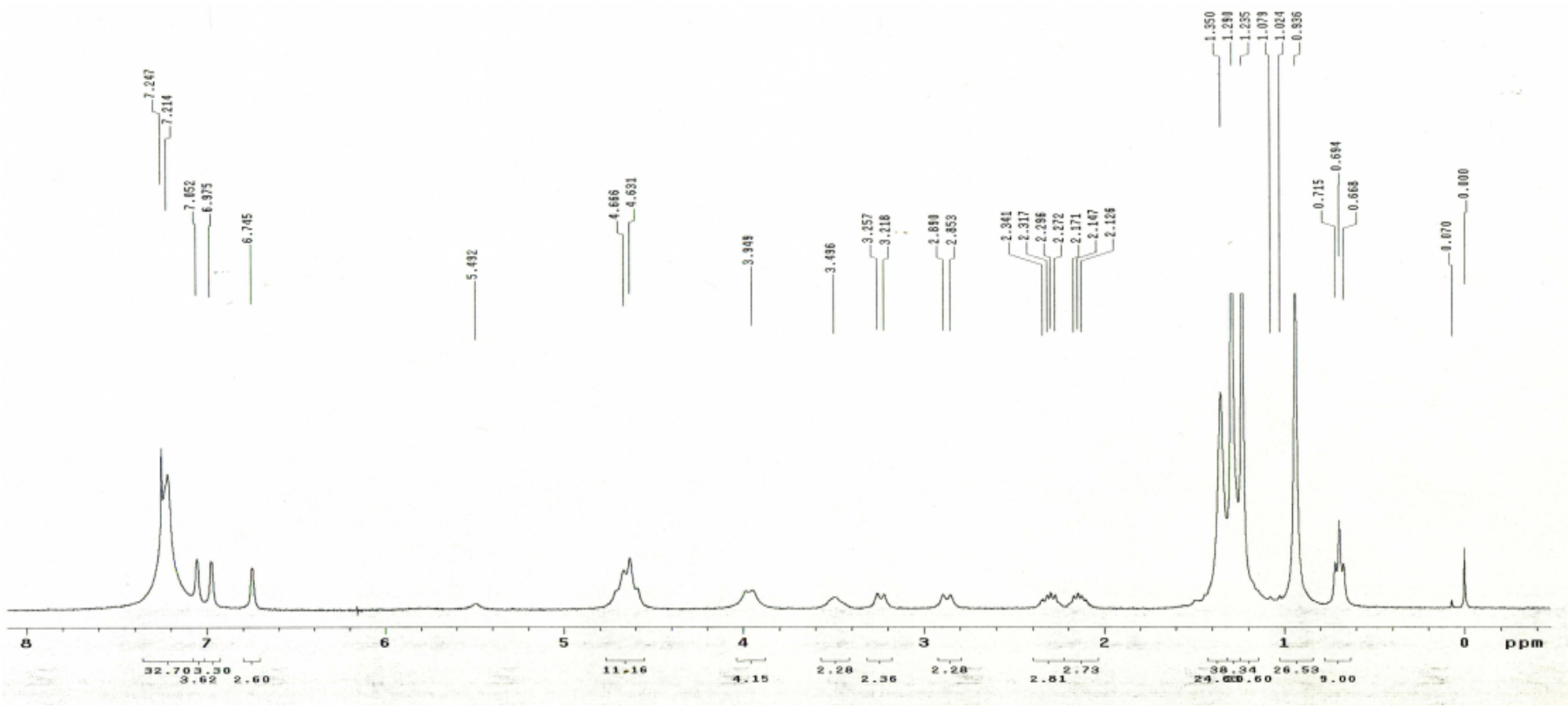


Figure S7. ^{1}H NMR of complex **4** in $CDCl_3$.

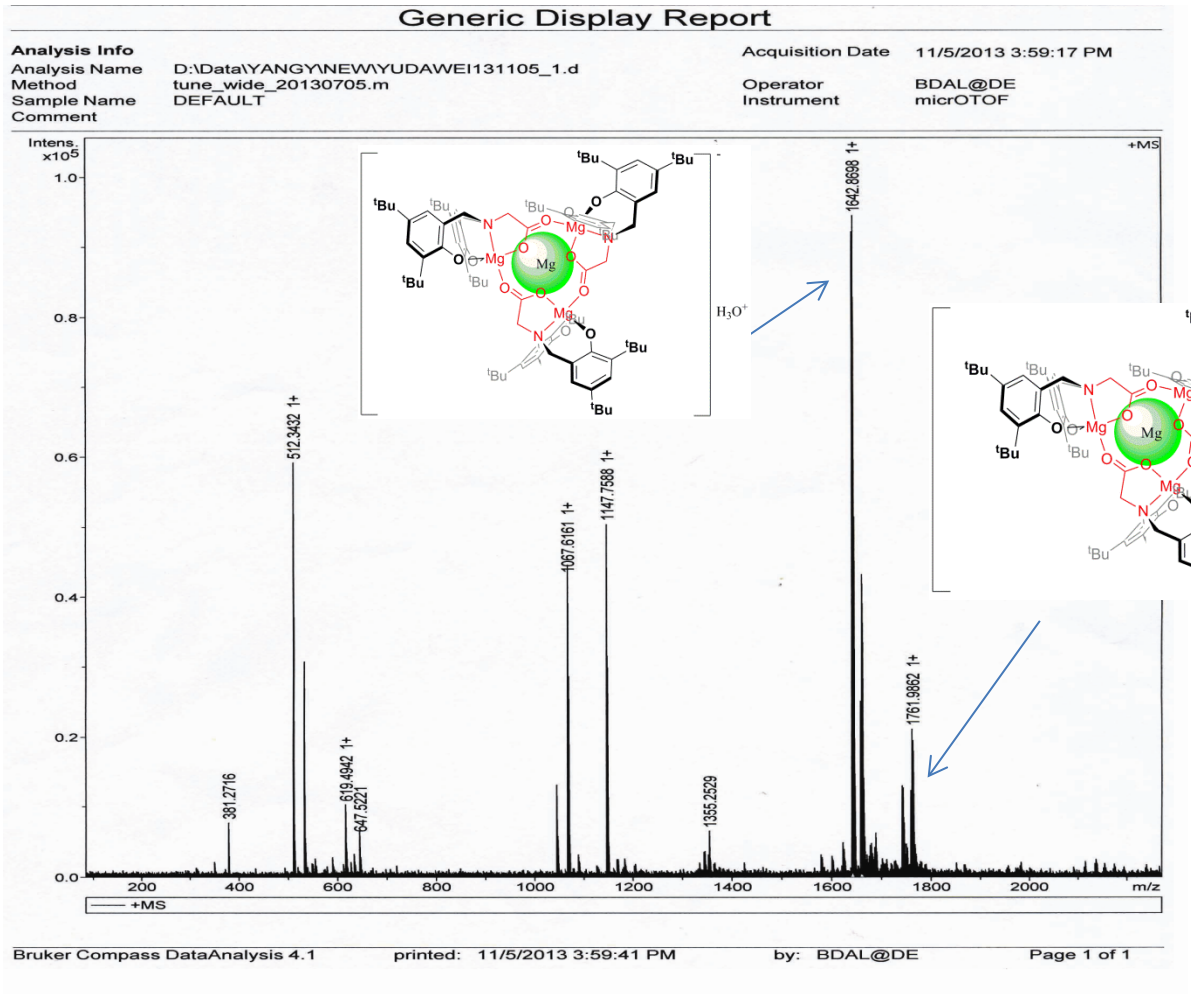


Figure S8. ESI-MS spectrum of complex **3.**

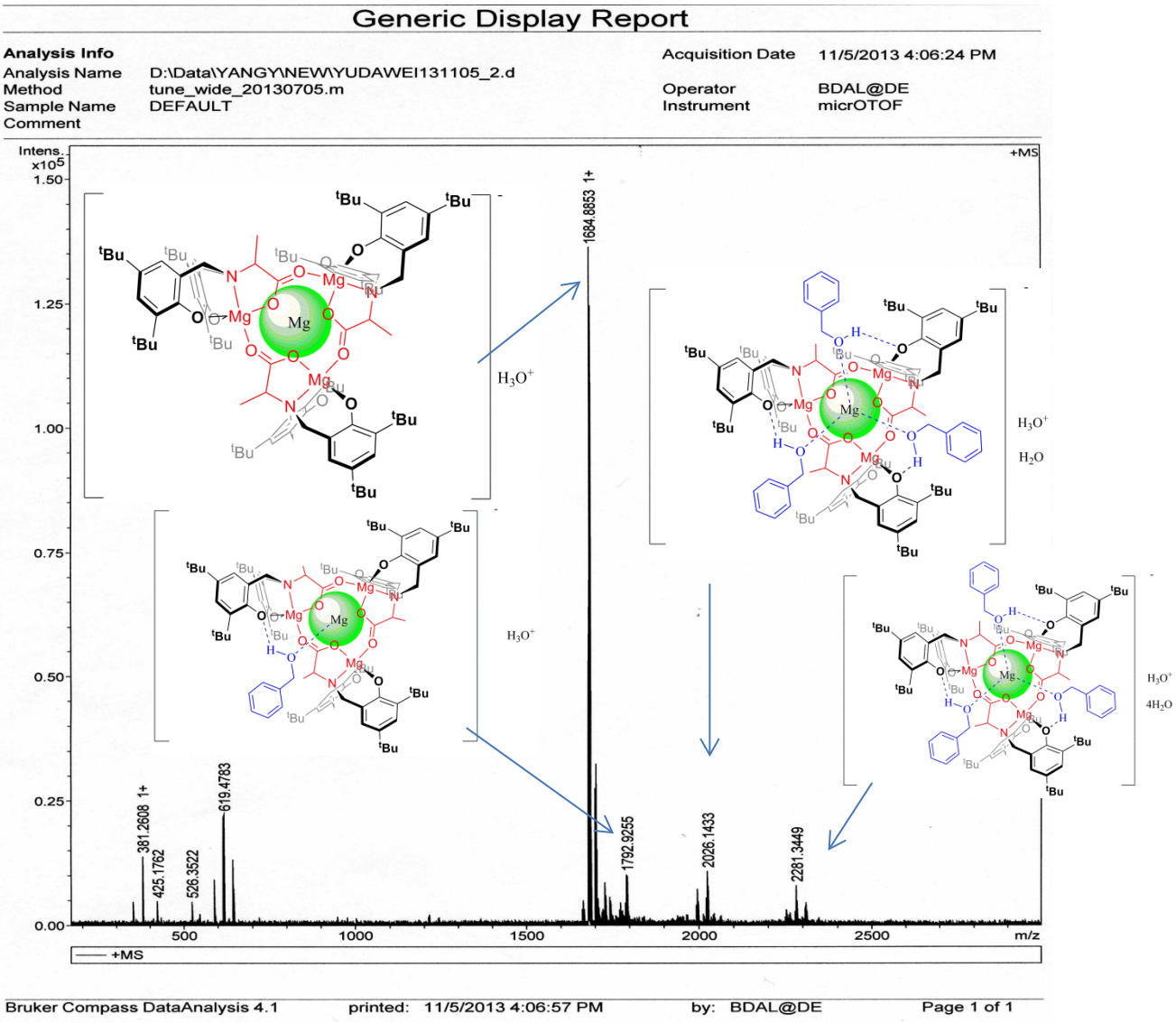
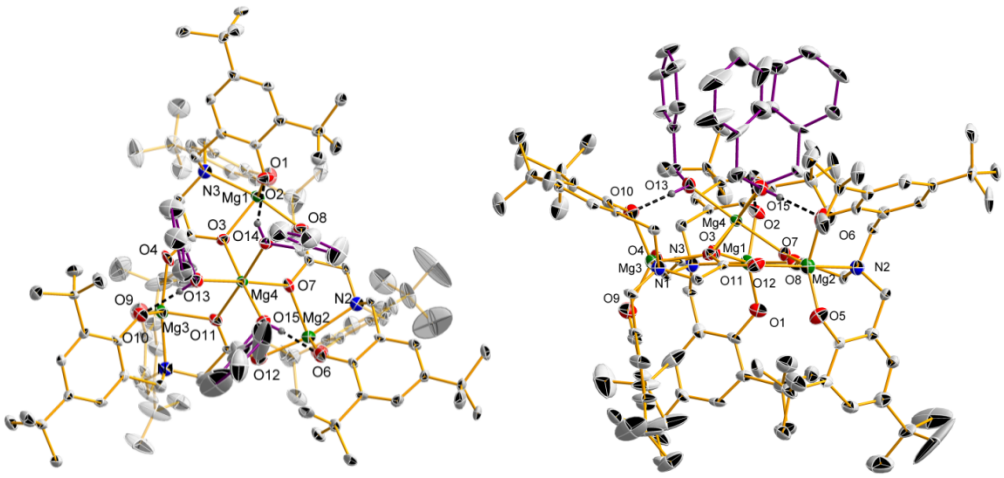


Figure S9. ESI-MS spectrum of complex **4**.



Top View Side View

Figure S10. Molecular structure of the anion portion of **3** as 30% ellipsoids (The hydrogen atoms were omitted for clarity, and the bonds in the benzyl alcohols are labeled with violet color). Selected bond lengths (Å) and angles (°): Mg1 O1 1.930(6), Mg1 O2 1.961(6), Mg1 O3 2.107(5), Mg1 O8 2.031(5), Mg1 N3 2.212(6), Mg2 O5 1.890(6), Mg2 O6 1.954(6), Mg2 O7 2.106(5), Mg2 O12 2.046(6), Mg2 N2 2.202(6), Mg3 O4 2.021(6), Mg3 O9 1.934(6), Mg3 O10 1.954(6), Mg3 O11 2.089(5), Mg3 N1 2.200(6), Mg4 O3 2.106(5), Mg4 O7 2.118(5), Mg4 O11 2.105(5), Mg4 O13 2.092(5), Mg4 O14 2.120(5), Mg4 O15 2.112(5).

For complex 3, the disordered solvents of this crystal are very difficult to resolve. The R factor cannot decrease to an acceptable level even using a squeeze program. Anyway, the main structure of complex 3 is similar to complex 4, and the R factor of complex 4 is acceptable after using SQUEEZE program to suppress the disordered triethyl amine cation. The information of this structure can also be obtained from CCDC with a number of 988261.

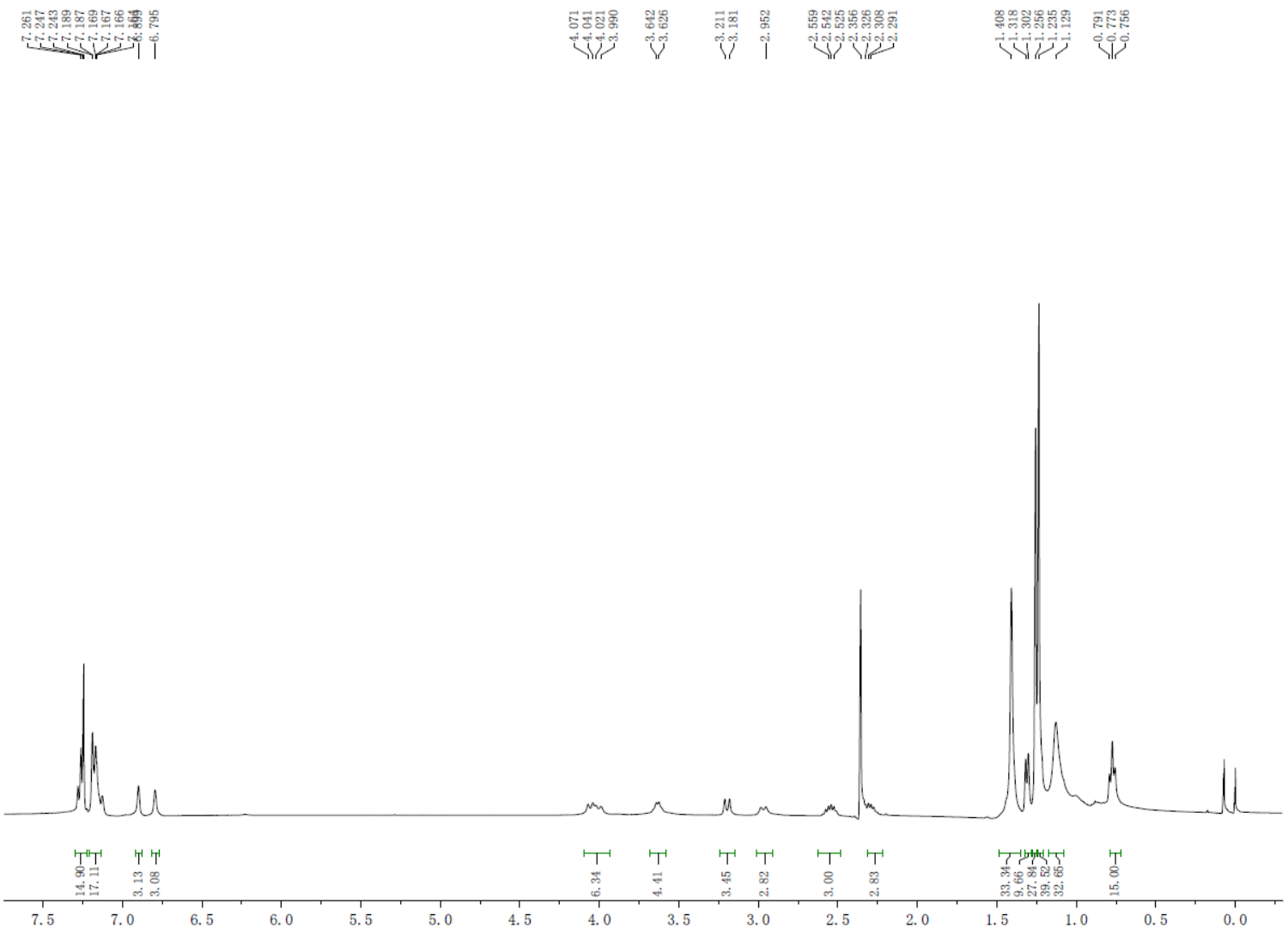
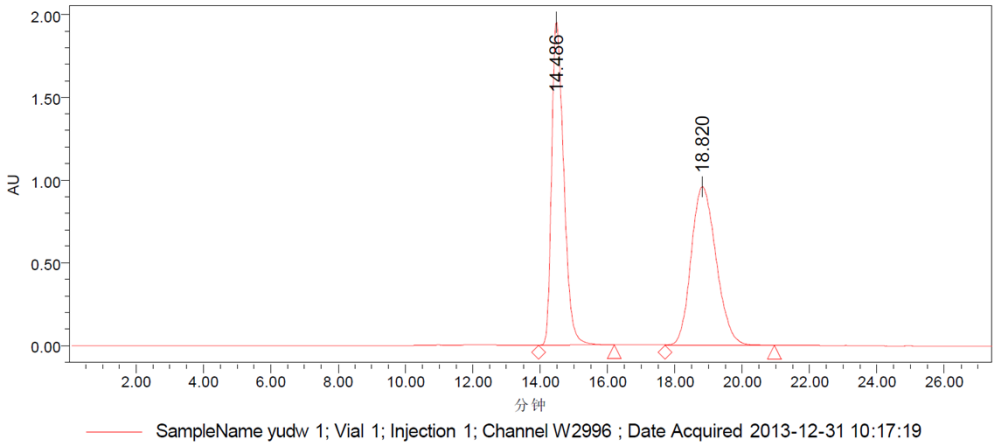


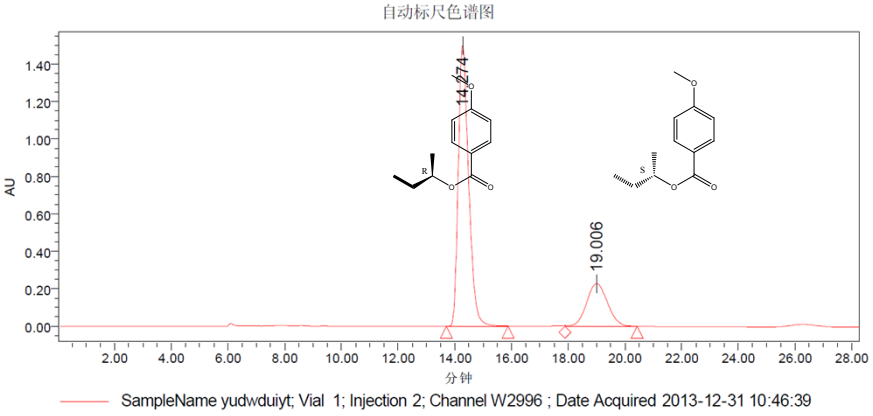
Figure S11. ^{1}H NMR of complex **6** in $CDCl_3$.



处理通道: **PDA 254.0** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 254.0 纳米	14.486	48591888	49.58	1954634
2	PDA 254.0 纳米	18.820	49406207	50.42	957994

(a) racemic 2-butanol derivatization.



处理通道: **PDA 254.0** 纳米

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1	PDA 254.0 纳米	14.274	38192215	76.53	1500139
2	PDA 254.0 纳米	19.006	11711600	23.47	228412

(b) separated 2-butanol derivatization with e.e. % of 53(±1)%.

Figure S12. HPLC graph of 2-butanol derivatization: sec-butyl 4-methoxybenzoate: a) racemic 2-butanol derivatization; b) separated 2-butanol derivatization with ee of 53(±1)%.

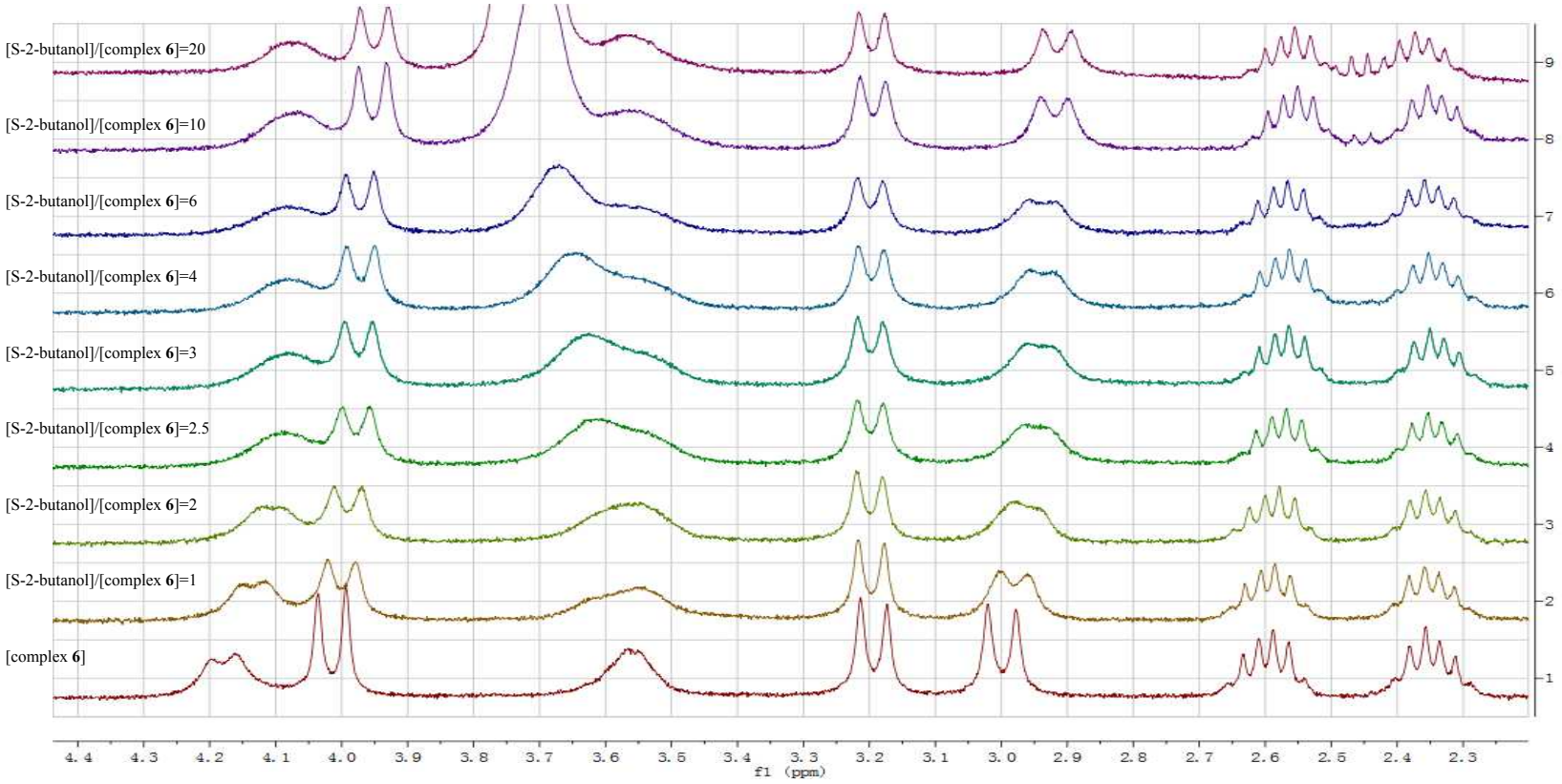


Figure S13. [1] H NMR spectrums of complex **6** + (S)-2-butanol.

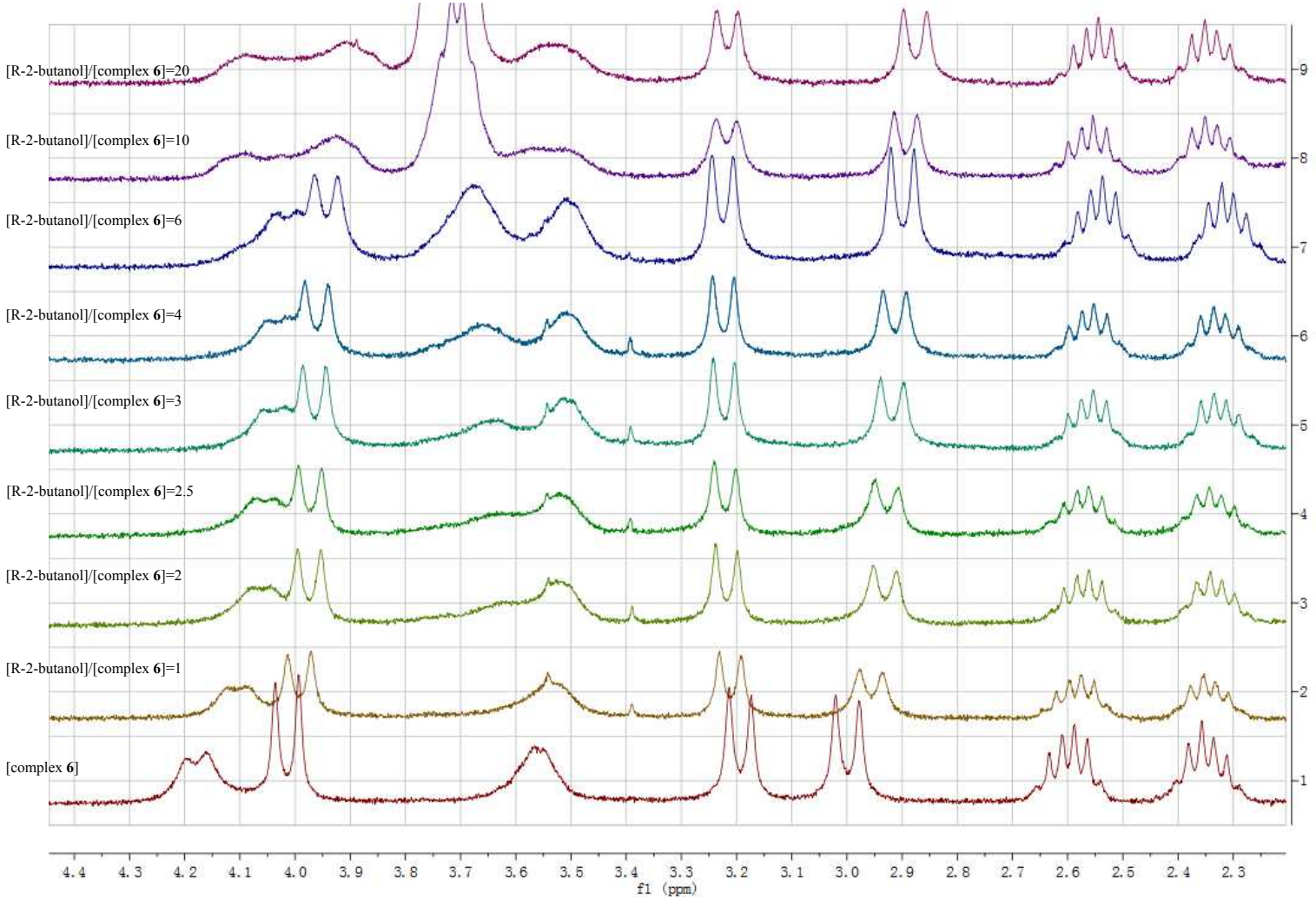
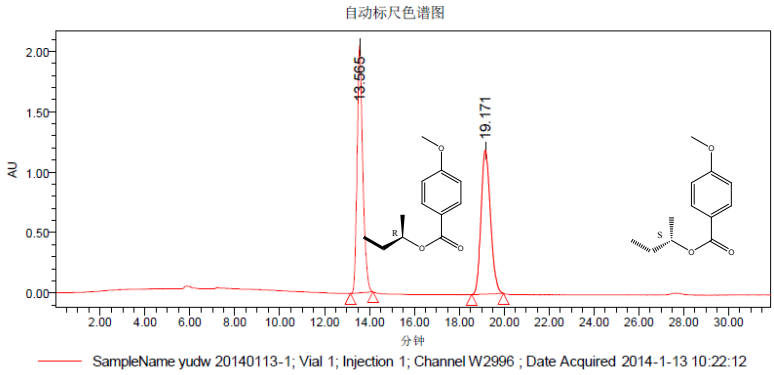


Figure S14. ^{1}H NMR spectrums of complex **6** + (R)-2-butanol.



处理通道: **PDA 210.4** 纳米

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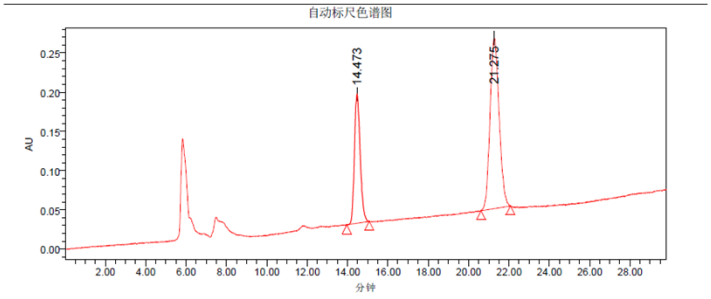
1	PDA 210.4 纳米	13.565	36355929	50.98	2060479
2	PDA 210.4 纳米	19.171	34957164	49.02	1190299

(a) HPLC graph of racemic 1-phenylethanol.



处理通道: **PDA 210.4** 纳米

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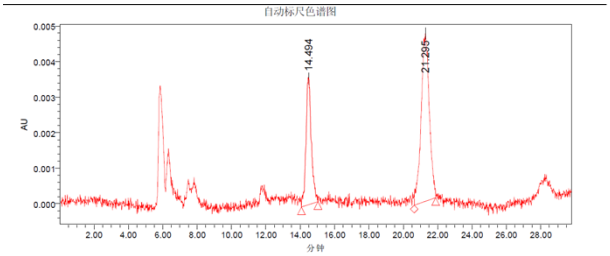
1	PDA 210.4 纳米	14.473	3251746	32.50	164427
2	PDA 210.4 纳米	21.275	6753923	67.50	216981

(b) HPLC graph of separated 1-phenylethanol analyzed at 210.4nm.



处理通道: **PDA 259.6** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 259.6 纳米	14.494	77645	33.13	3554
2	PDA 259.6 纳米	21.295	156711	66.87	4713

(c) HPLC graph of separated 1-phenylethanol analyzed at 259.6nm.

Figure S15. HPLC graph of separated 1-phenylethanol with ee of 33 (±1)%.

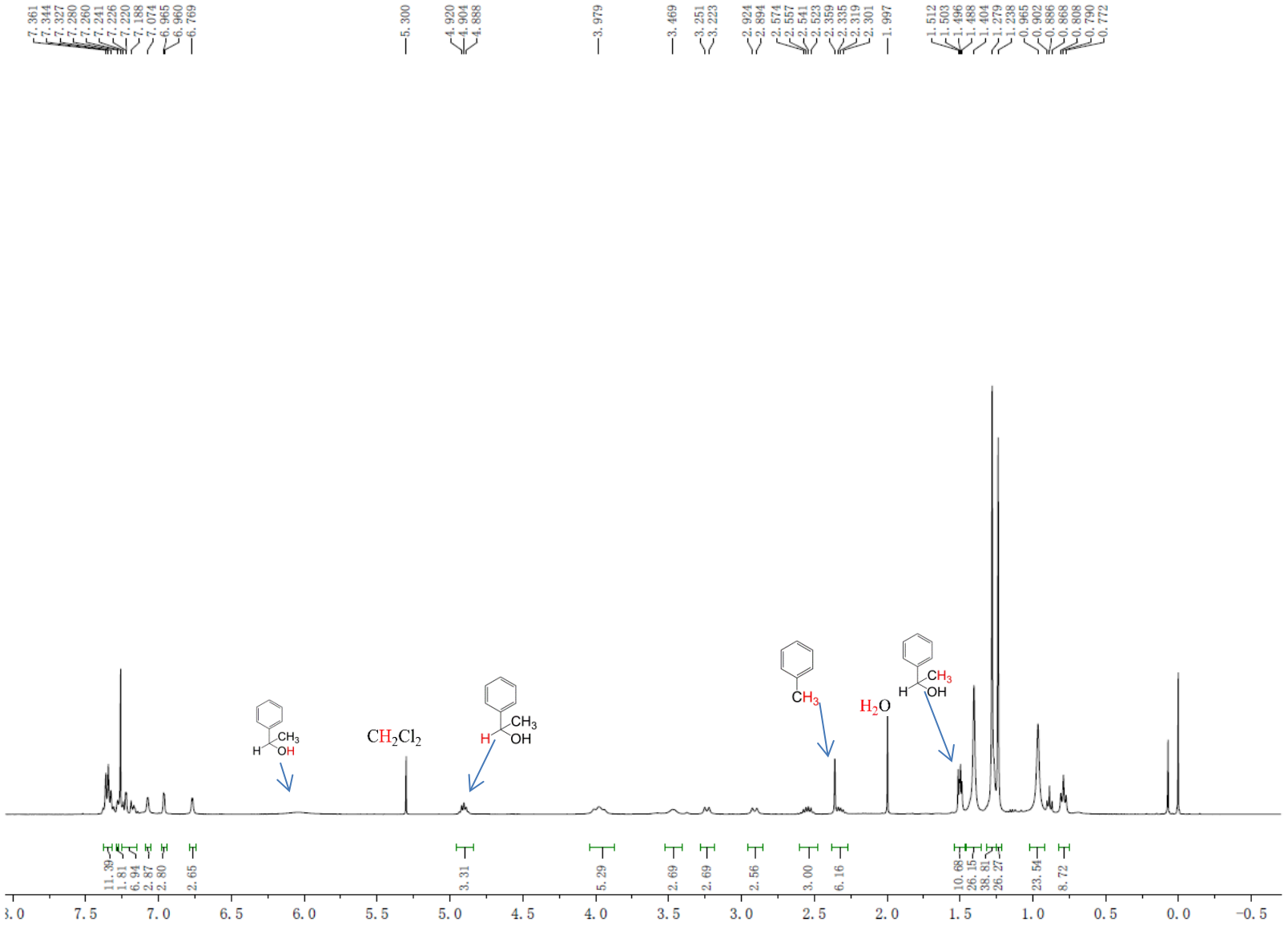


Figure S16. ^{1}H NMR of complex **7** in $CDCl_3$.