Supporting Information for

Comparison of chiral counterion, solvent, and ligand in inducing chiroptical response from Au_{25}^{-} nanoclusters

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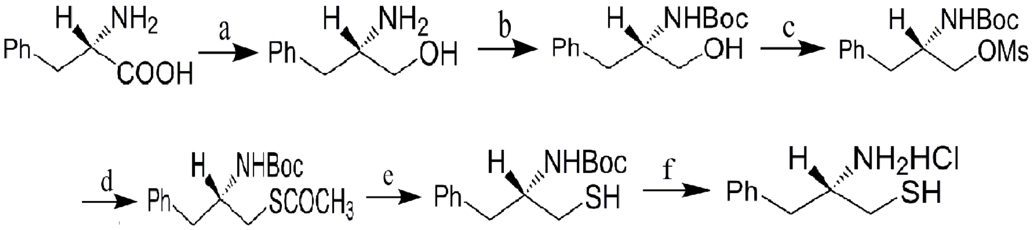
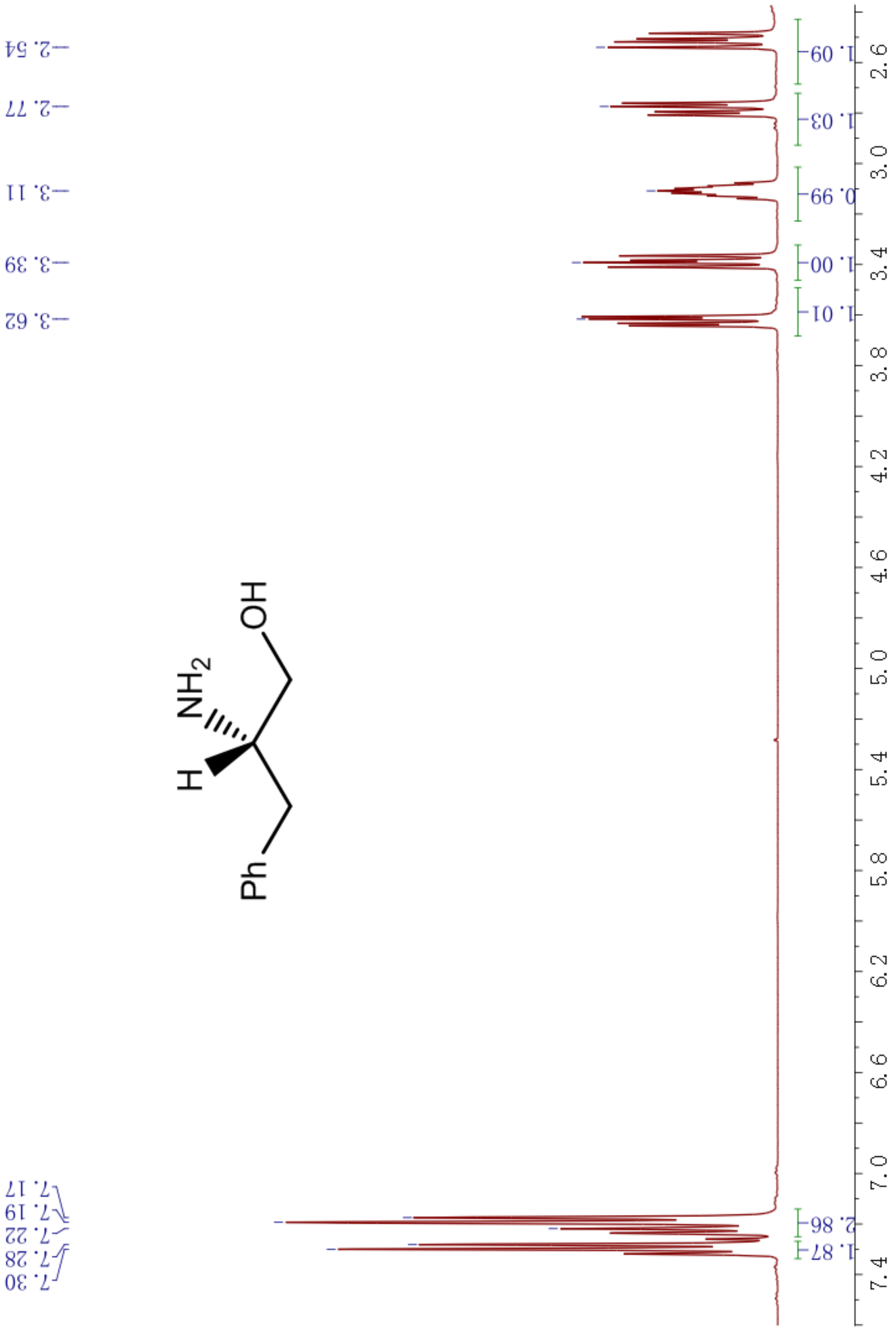
Experimental Details

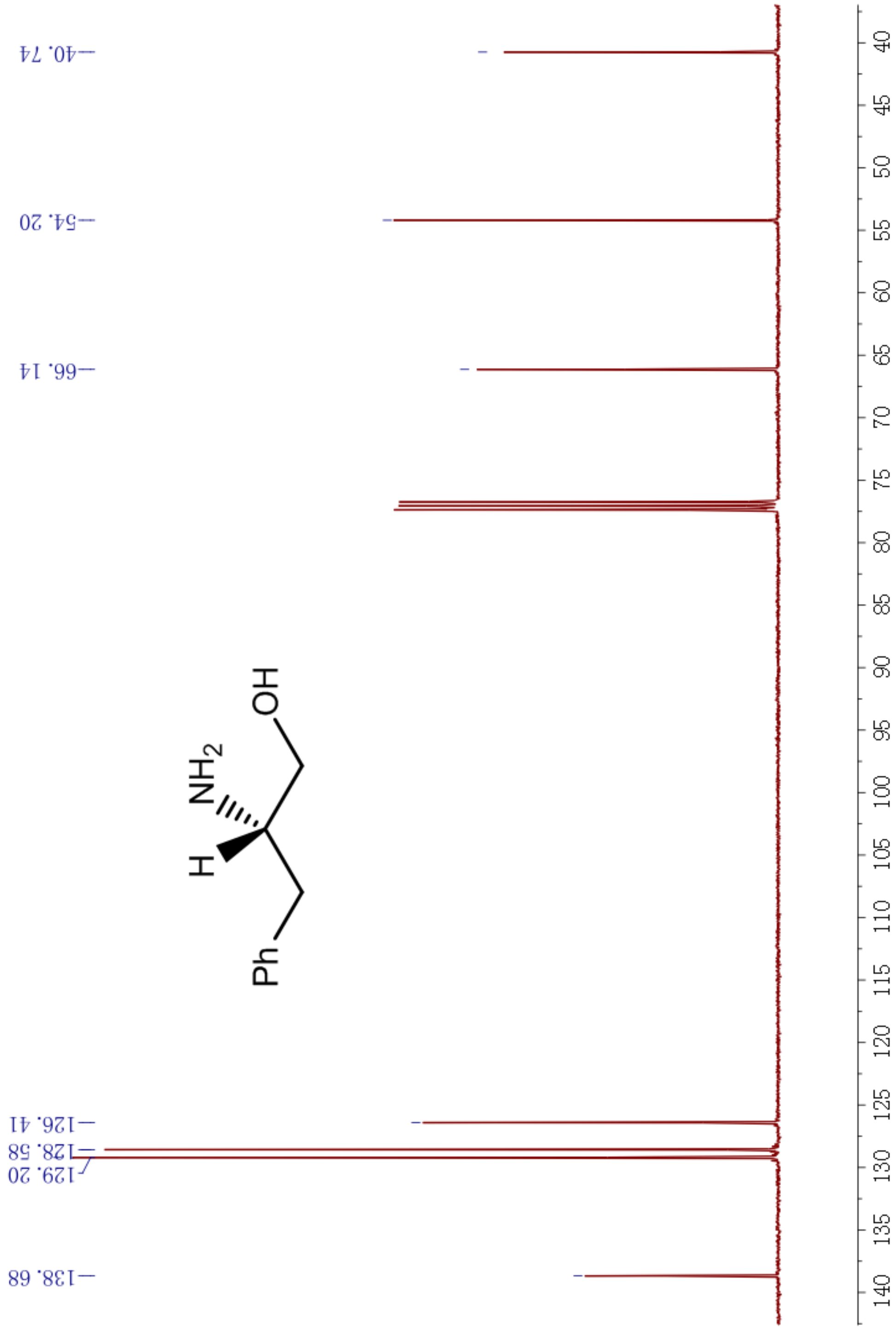
1. Synthesis of (R)- and (S)-2-phenylpropane-1-thiol.

The synthetic routine is illustrated below:

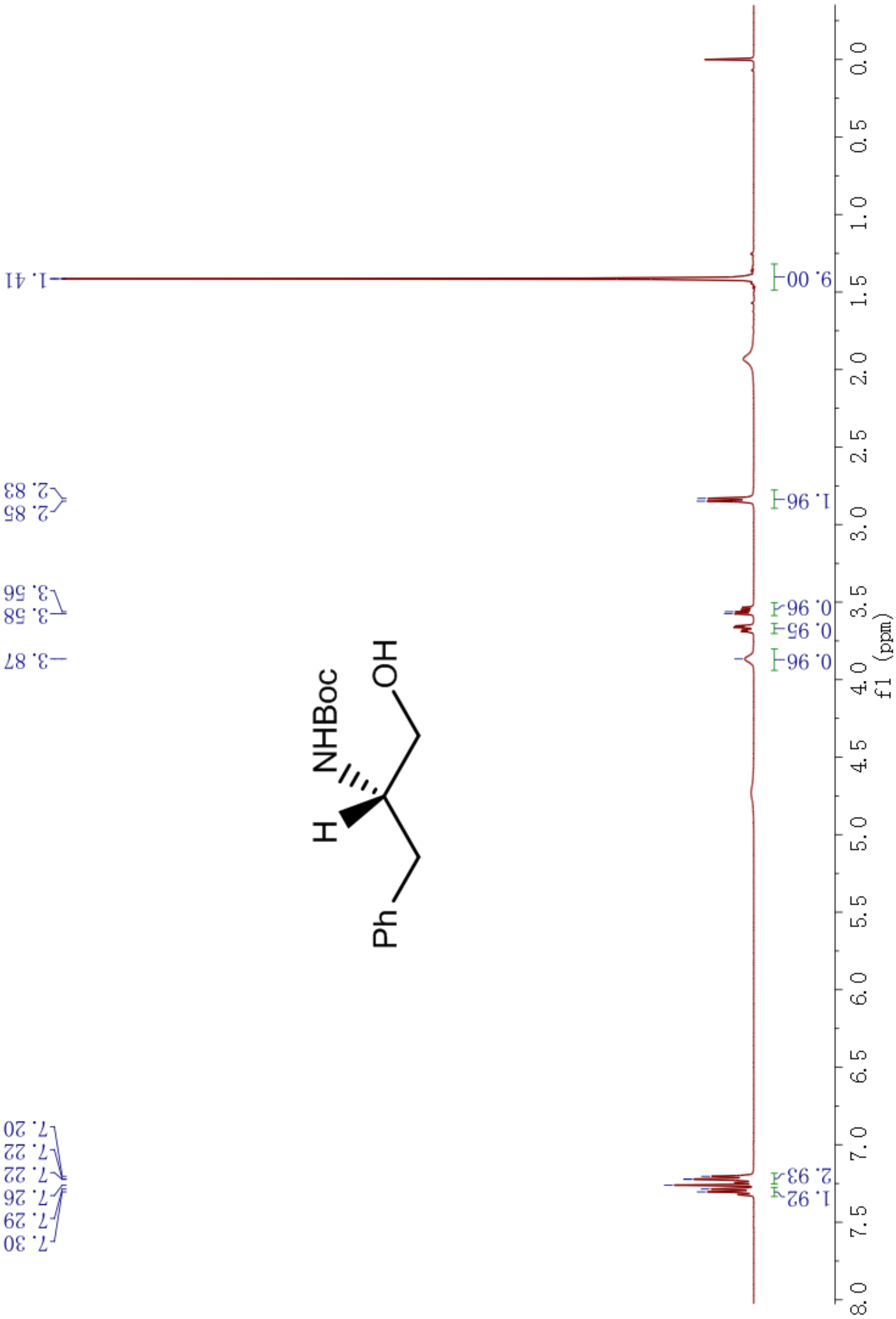


a: (D/L)- phenylalanine (40g, 0.297mol) was dissolved in THF in N_2 atmosphere. The solution was cooled to 0℃, and then lithium aluminium hydride powder(14g, 0.371mol) was added in portion. This solution was stirred for 2h at 0 ℃, before the reaction was quenched by water adding dropwise. After drying under vacuum, the residue was extracted with dichloromethane and washed by water. The dichloromethane layer was evaporated to obtain (R/S)-2-amino-3-phenylpropan-1-ol as yellow oil. At last the product as purified by recrystallization. ^{1}H NMR ($CDCl_3$/TMS): δ1.42 (s, H), 2.4~2.8 (2H, mm), 3.3-3.7 (2H, mm) , 3.11 (1H, m), 7.1～7.3(5H, m).^{13}C NMR(400MHz, $CDCl_3$, ppm): δ 138.68, 129.20, 128.58, 126.41, 66.14, 54.20, 40.74.

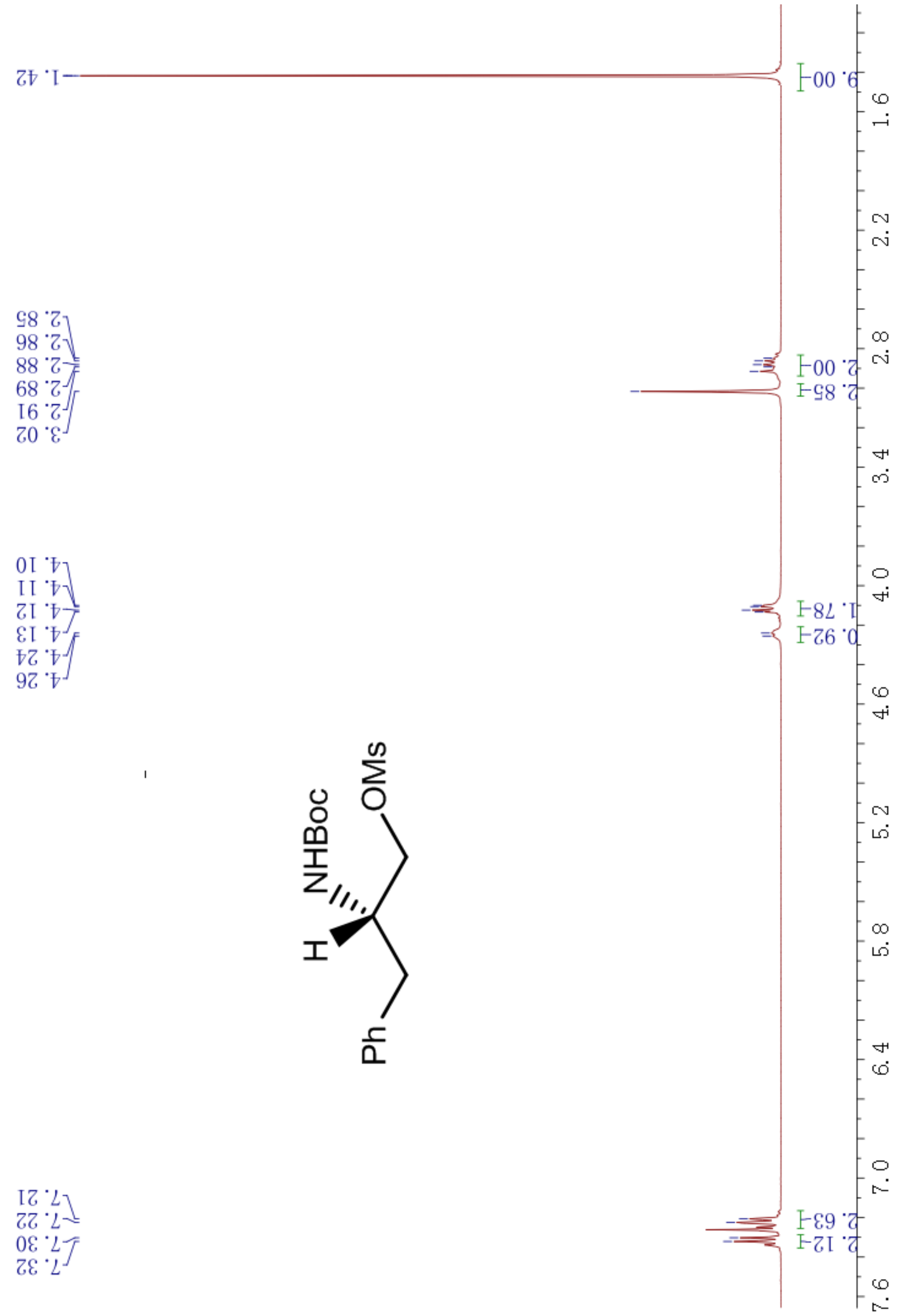

2.54
2.77
3.11
3.39
3.62
7.17
7.19
7.22
7.28
7.30
1.09
1.03
0.99
1.00
1.01
2.86
1.87
2.6
3.0
3.4
3.8
4.2
4.6
5.0
5.4
5.8
6.2
6.6
7.0
7.4
Ph
H
NH_2
OH



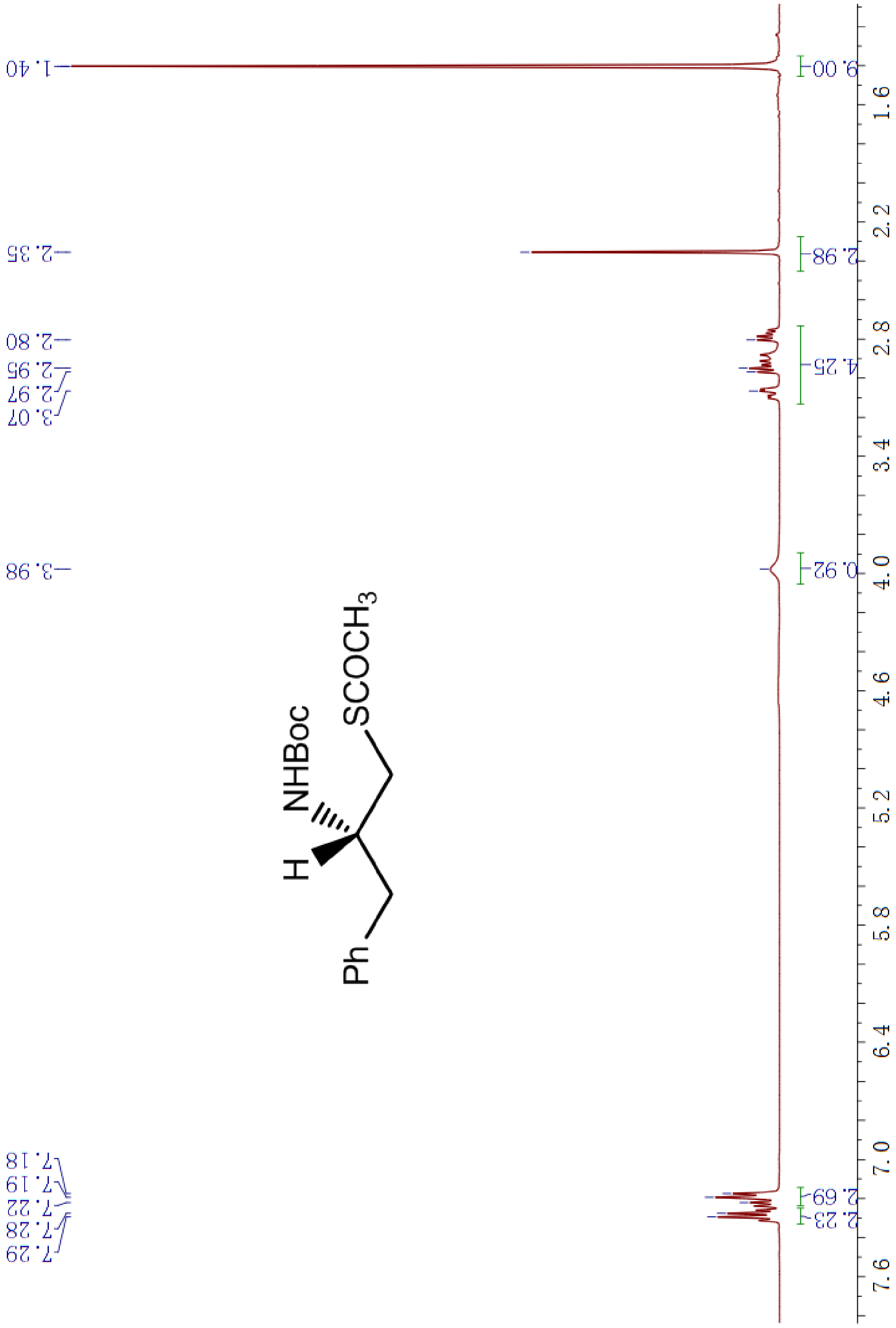
b. (R/S)-2-amino-3-phenylpropan-1-ol (15.2g, 0.1mol) was dissolved in 1, 4-dioxane and water (v/v=1:1), then $(Boc)_2O$ (24.0g,0.110mol) and NaOH (5.0g,0.125mol) were added slowly at the same time under 0℃. 2 h later, the mixture was kept stirring at room temperature over night. The product was extracted with dichloromethane and washed by water. The dichloromethane solution was dried by evaporation, and the crude material was purified by recrystallization in dichloromethane and petroleum ether. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 1.41(9H, s), 1.96(2H, d), 3.5-3.6(2H, dd), 3.87(H, d), 7.2-7.3(5H, d).



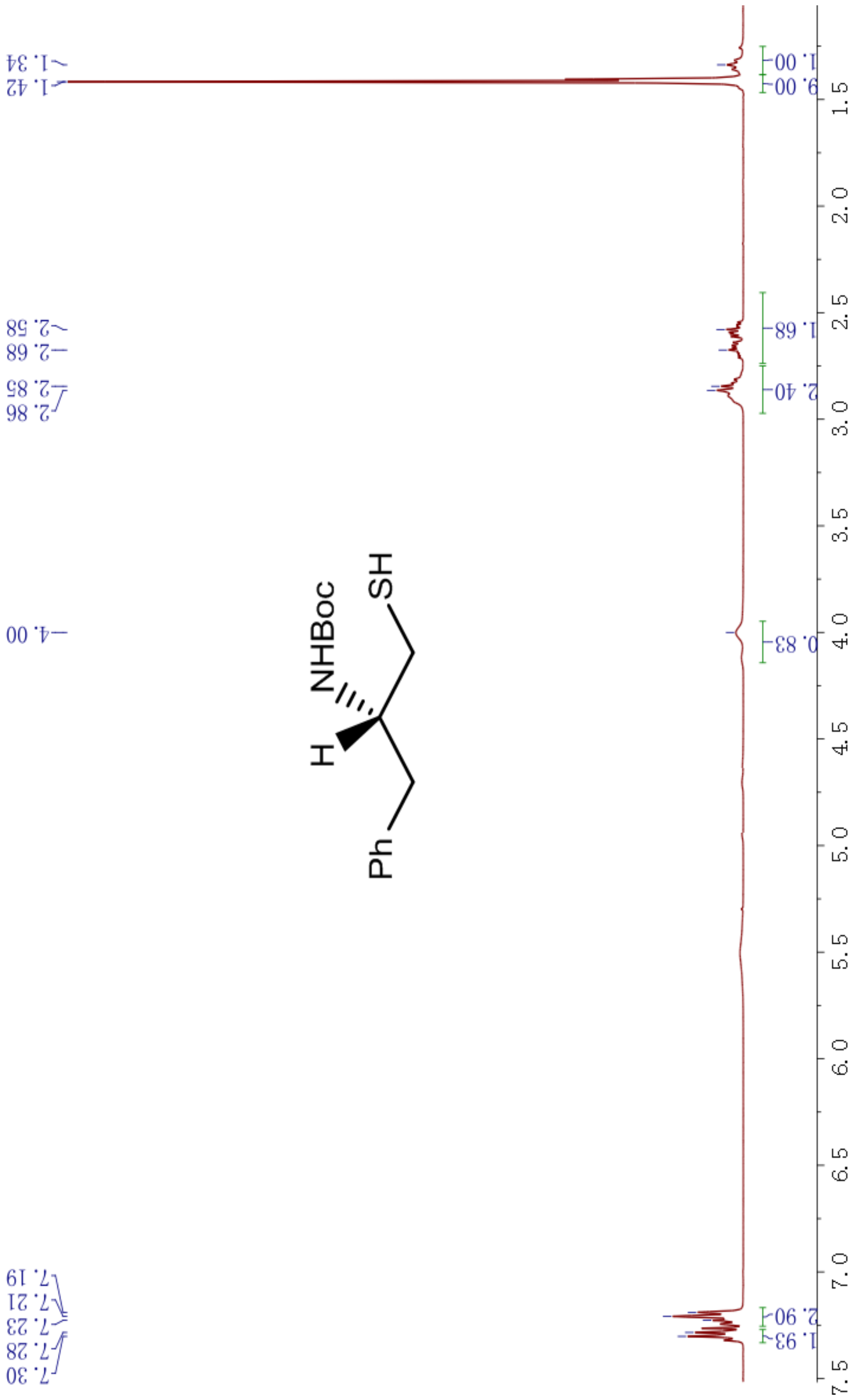
c. A mixture of (S/R)-tert-butyl-1-hydroxy-3-phenylpropan-2-ylcarbamate (5.0 g, 20 mmol), triethylamine (6mL, 40 mmol) and tetrahydrofuran (100 mL) was stirred together at 0℃, then methylsufonyl chloride (2.0 mL, 25mmol) was added dropwise. After stirring for 2 h, the solution was extracted by DCM (50ml×3) and washed by water. The organic phase was combined and dried by Na_2SO_4 then evaporated to give crude product. Then the crude material was purified by recrystallization in dichloromethane and petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.42 (9H, s), 2.8-2.9(2H, m), 2.91(3H, s), 4-4.13(2H, m), 4.2-4.3(2H, m), 7.2-7.4(5H, m).



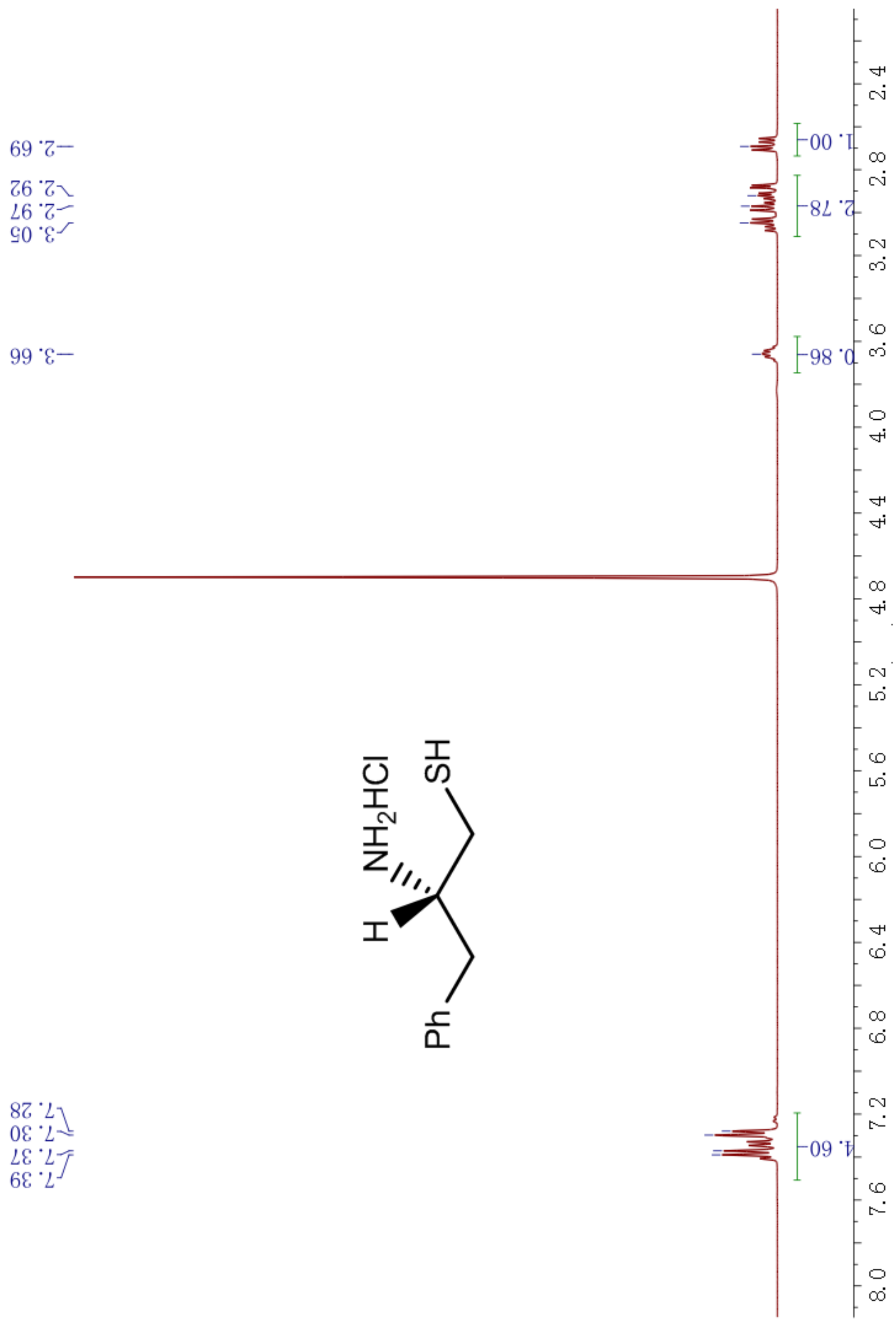
d. A solution of (S)-2-(tert-butoxycarbonylamino)-3-phenylpropyl methanesulfonate (4.4 g, 13.4 mmol) and potassium thioacetate (1.8 g, 15.8 mmol) dissloved in 30 mL DMF was stirred at room temperature over 3 d. Then 50 mL cool water was added and the mixture was extracted by DCM. The organic phase was combined and dried by Na2SO4 then evaporated to give crude product. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 1.40 (9H, s), 2.35 (3H, s), 2.8-3.1 (4H, m), 3.98 (H, m), 7.16-7.3 (5H, m).



e. Ammonia (2.0 g) was dissolved in anhydrous ethanol under 0℃. And then (S)-S-2-(tert-butoxycarbonylamino)-3-phenylpropyl ethanethioate (2.0 g, 6.5 mmol) was added into the solution. Then the mixture was stirred at room temperature before TLC shows no raw material exists. Target product was attained by evaporating the solution to dryness. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 1.34(H, t), 1.42(9H, s), 2.58-2.68(2H, m), 2.8-2.9(2H, m), 4.0(H, m), 7.1-7.3(5H, m).



f. A mixture of (S)-tert-butyl 1-mercapto-3-phenylpropan-2-ylcarbamate (1.5 g, 5.6 mmol) dissolved in dichloromethane and concentrated hydrochloric acid (3 mL) was stirred at room temperature for 5h. The mixture was evaporated to give crude residue. The impurity was dissolved in dichloromethane and the solid was the target product. ^{1}H NMR (400MHz, D_2O, ppm): δ 2.6-3.0(4H, m), 3.66(H, m), 7.2-7.4(5H, m).


2.69
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2.97
3.05
3.66
7.28
7.30
7.37
7.39
1.00
2.78
0.86
4.60
2.4
2.8
3.2
3.6
4.0
4.4
4.8
5.2
5.6
6.0
6.4
6.8
7.2
7.6
8.0
H
NH2HCl
SH
Ph

2. Spectroscopic characterization of products

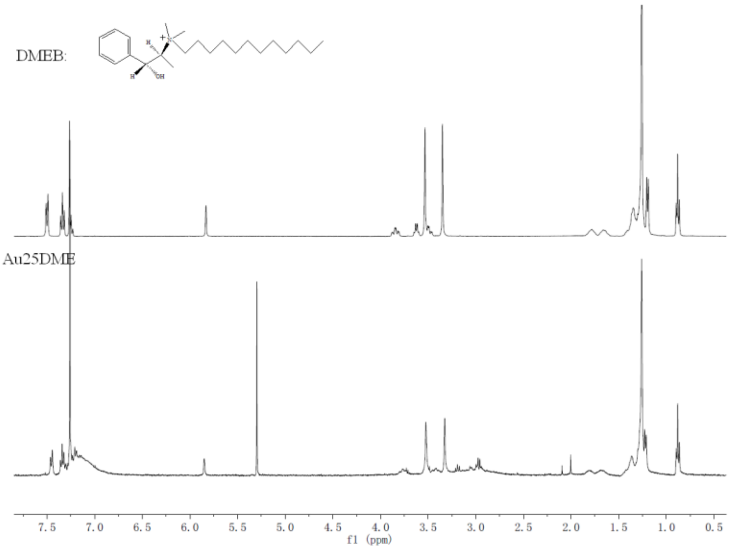

Fig. S1 ^{1}H NMR spectrum of DMEB and $[Au_{25}(SC_2H_4Ph)_{18}]^-DME^+$ in $CDCl_3$.

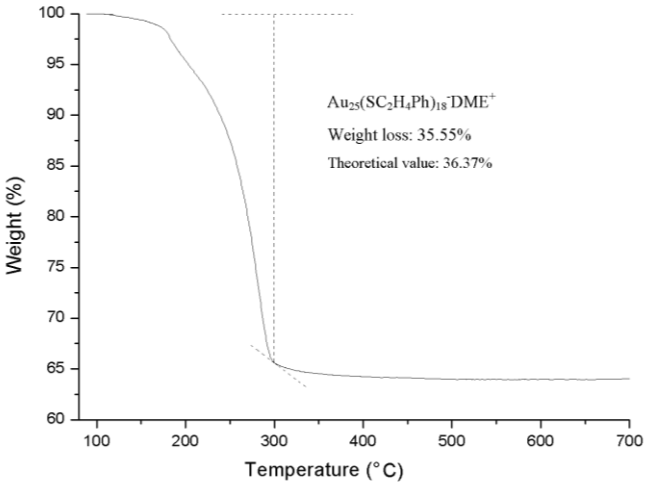

Fig. S2 Thermogravimetric analysis of $[Au_{25}(SC_2H_4Ph)_{18}]^-DME^+$ cluster

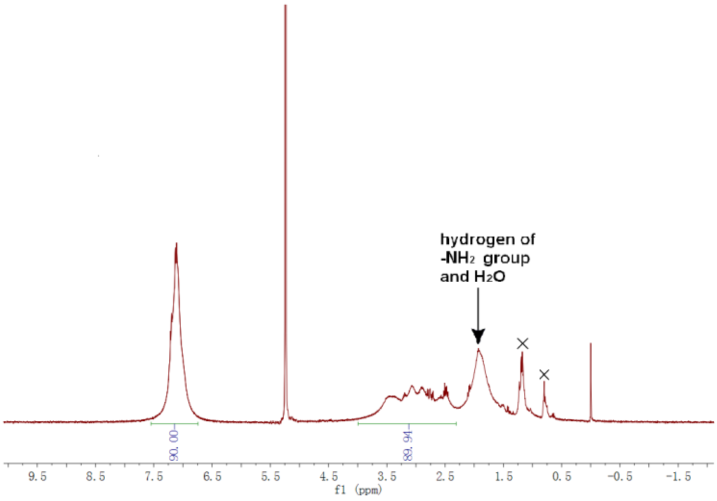

Fig. S3 ^{1}H NMR spectra of $Au_{25}(appt^*)_{18}$

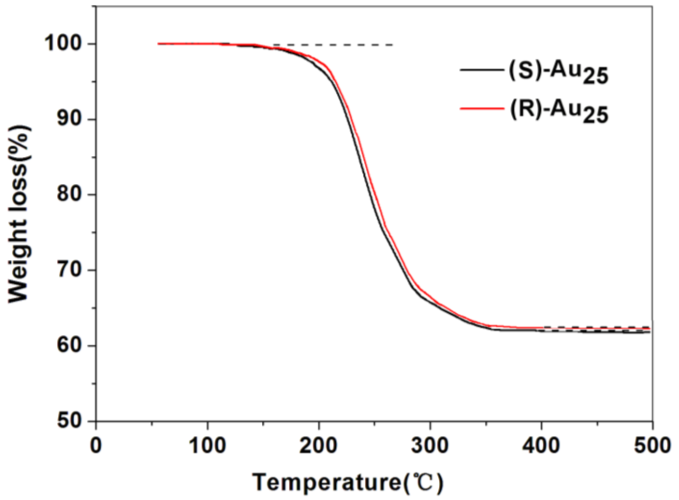

Fig. S4 Thermogravimetric analysis of $Au_{25}(appt^*)_{18}$ nanoclusters.

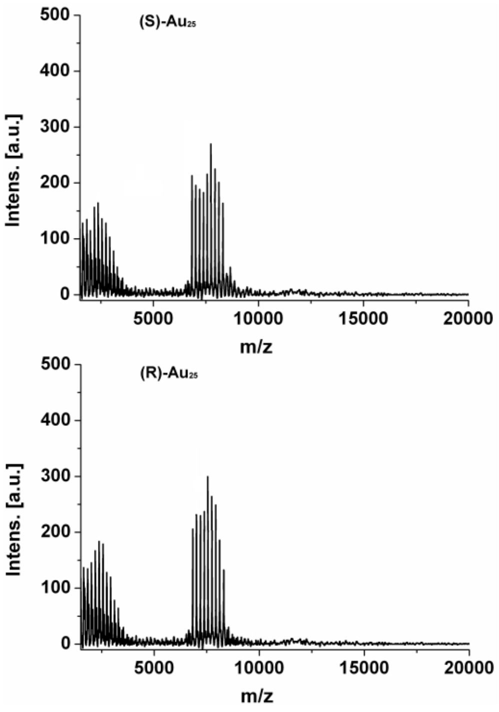

Fig. S5 The Negative-ion MALDI-TOF spectra of (R)-Au_{25} and (S)-Au_{25} clusters.