Supporting Information For

Electroactivated Alkylation of Amines with Alcohols via Both Direct and Indirect Borrowing Hydrogen Mechanisms

Benjamin Appiagyei, Souful Bhatia, Gabriela L. Keeney, Troy Dolmetsch, James E. Jackson*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States

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General Experimental Details

All organic reagents were purchased and used without further purification unless needed. Platinum wire was purchased form Alfa Aesar and Nafion™ membrane was purchased from Sigma-Aldrich. Hexammineruthenium (III) chloride ($Ru(NH_3)_6Cl_3$), 99% was purchased from Sigma-Aldrich, Zorflex® ACC FM110 was obtained from the Calgon Carbon Co. and with glass electrochemical cells obtained from the MSU-Chemistry glass shop, the catalyst was electrochemically prepared. Deuterium oxide (99.9%) was purchased from Cambridge Isotope Laboratories, Inc. and used as NMR solvent. Phosphate buffers (0.01 M) at pH 7.5 and 8.5 were prepared using potassium phosphate (monobasic) and potassium phosphate (dibasic) purchased from Sigma-Aldrich for running the reactions. Constant currents were provided by a Lambda (Model: LPD 422A FM) galvanostatic power supply and monitored with an Omegaette Model HHM33 multimeter.

Catalyst preparation

Following the earlier works of Li *et al.*,[1] and Bhatia *et al.,* [2] electrochemically deposited Ru/Acc catalyst was prepared. The Zorflex® activated carbon cloth (ACC) was cut into 3 cm x 1.5 cm and thoroughly washed with de-ionized water to remove any debris. The washed ACC was dried on the bench top for 12 hours and then in an oven at 105 °C overnight. The dried ACC was soaked in a solution of $Ru(NH_3)_6Cl_3$ prepared by dissolving 1.0089 g of $Ru(NH_3)_6Cl_3$ in 1.98 mL of NH_4OH and 13.03 mL of de-ionized water. The soaked ACC was air dried on the lab bench for 24 h, and then under vacuum at room temperature to the complete the removal of water. The Ru-impregnated ACC cathode was then electrochemically reduced in an H-cell at a constant current of 150 mA for 30 mins (about 3 times the quantity of charge required) using 0.2 M HCl as catholyte. Pt was the anode in 0.2 M carbonate buffer solution of pH 8.2. The Ph.D. thesis of Dr. Mahlet Garedew describes the optimum catalyst loading of 4% Ru on ACC (unpublished work).[3]

SEM image and EDS image analysis of activated carbon cloth (Unused)

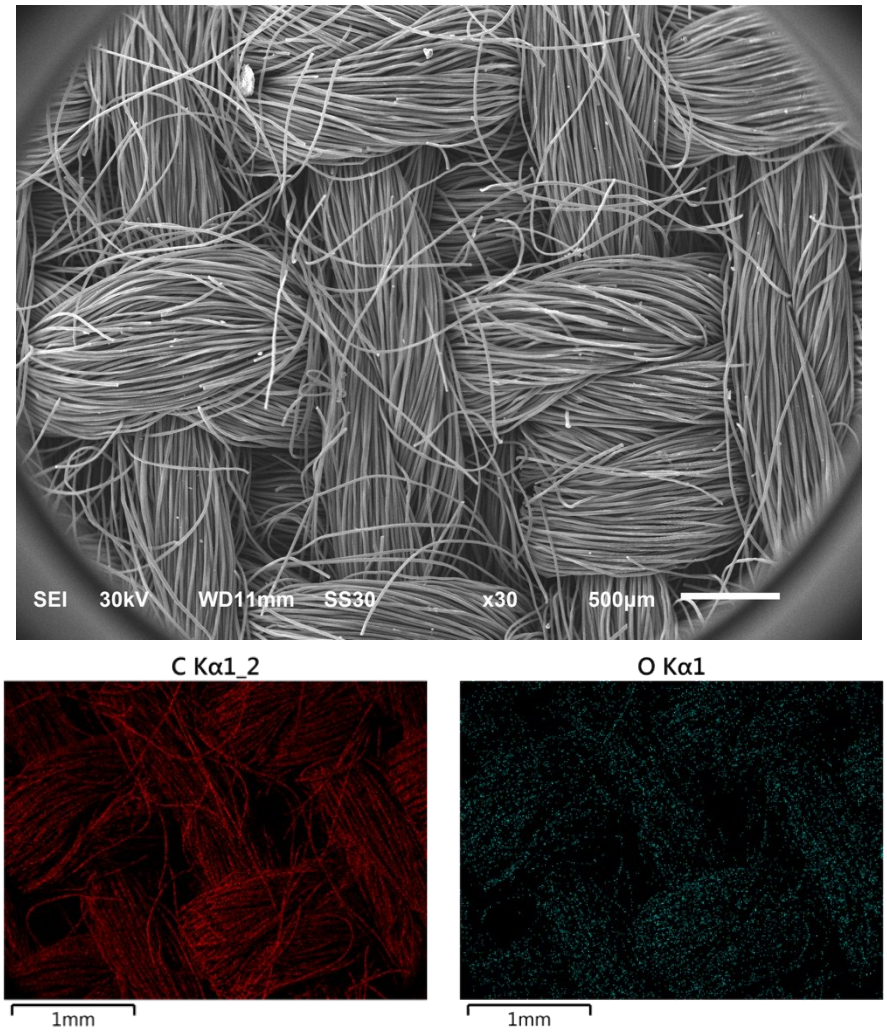


Figure 1. SEM images and EDS qualitative analysis of cleaned activated carbon cloth (ACC), washed in de-ionized water and dried in an oven at 105 °C for 24 h. The main elements observed with EDS are carbon and oxygen.

SEM and EDS of ACC after use as anode in an open (undivided) cell

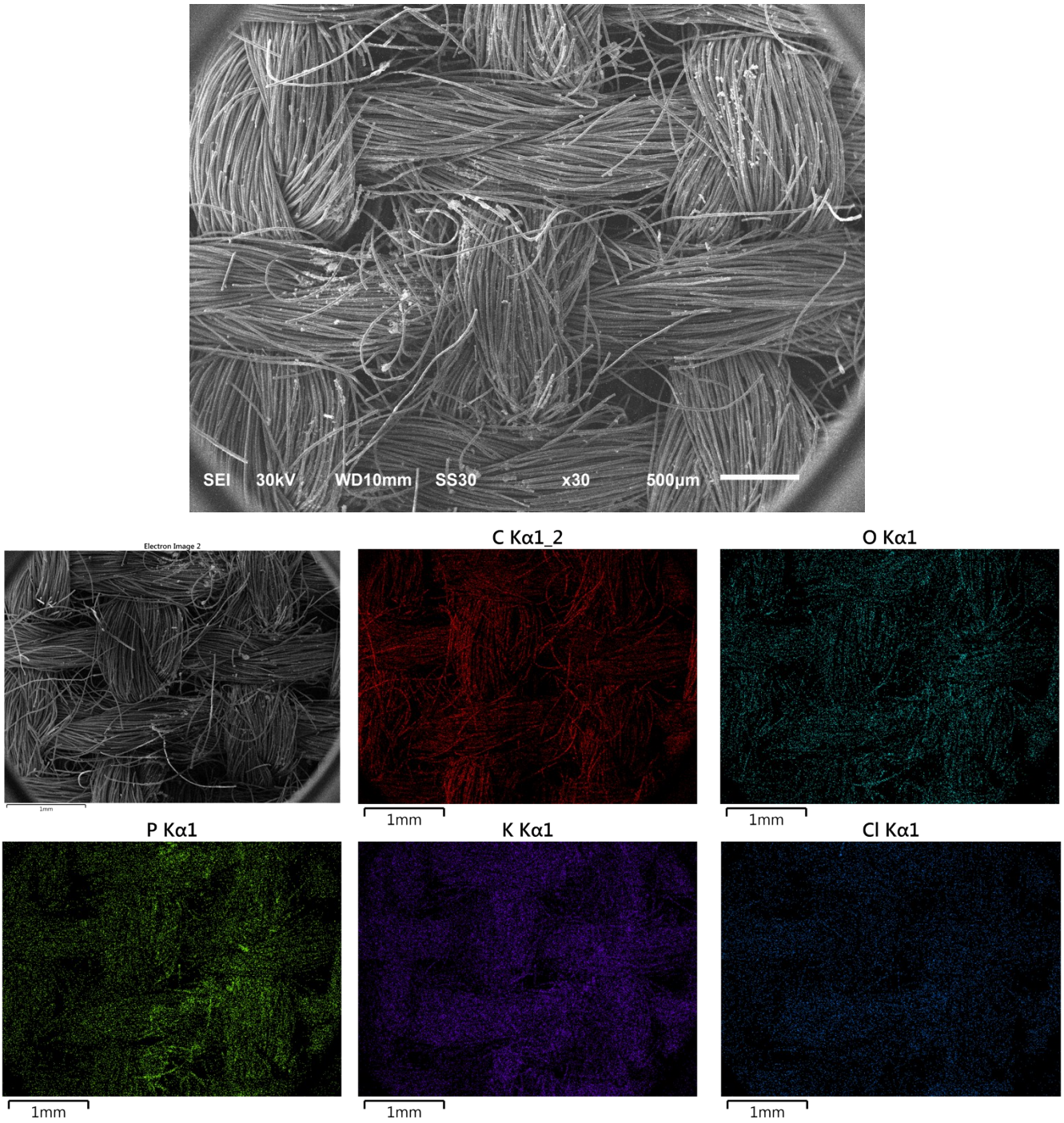
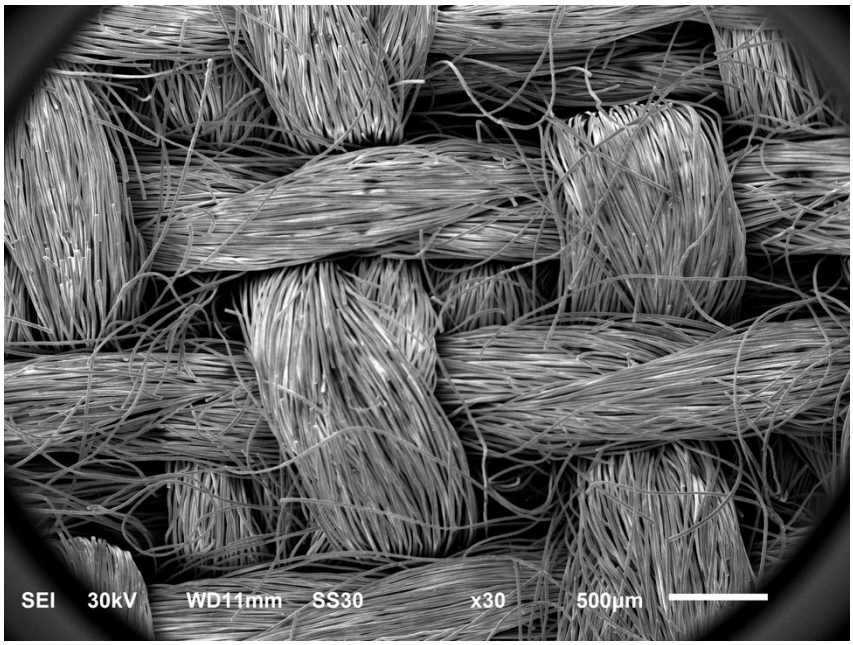


Figure 2. SEM images and EDS qualitative analysis of activated carbon cloth (ACC) after its use as an anode in an open cell (single-electrode mechanism). Though coupled with Ru/ACC (cathode) during the reaction process, there was no Ru observable on this ACC anode after use. Potassium and phosphorus are suspected to have come from the potassium phosphate buffer electrolyte. Chlorine presumably comes from the $Ru(NH_3)_6Cl_3$ salts used in the catalyst preparation.

SEM image and EDS quantitative analysis Ru on activated carbon cloth (unused)



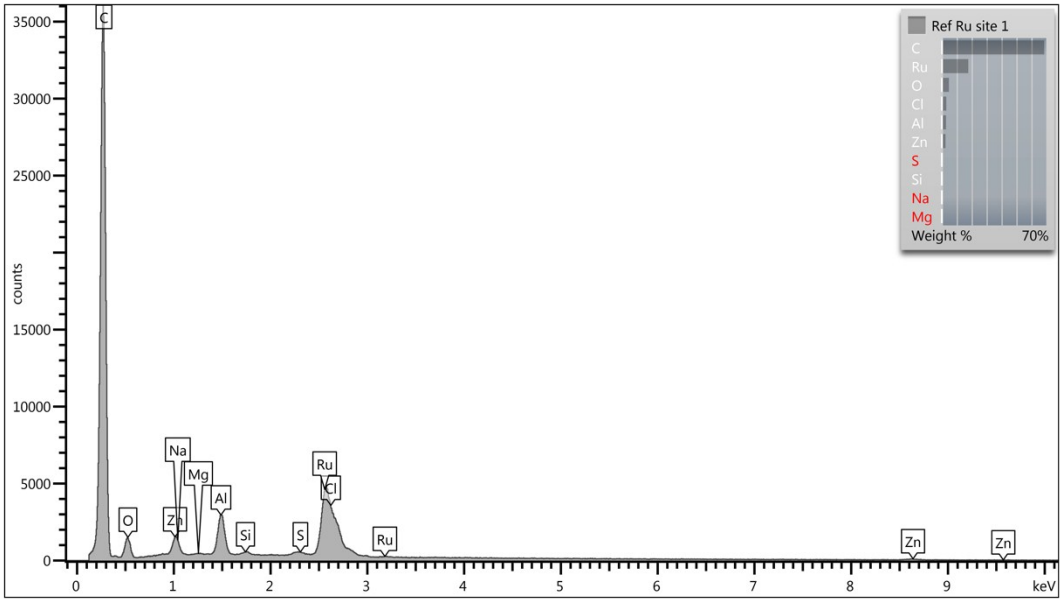


Figure 3. SEM image of freshly prepared Ru on activated carbon cloth (Ru/ACC); the shining surface was assigned to the metallic ruthenium from electrochemical reduction of the Ruthenium salt. The EDS quantitative analysis shows about 18% weight of Ru.

SEM image and EDS quantitative analysis of Ru on activated carbon cloth after use as anode in an open cell

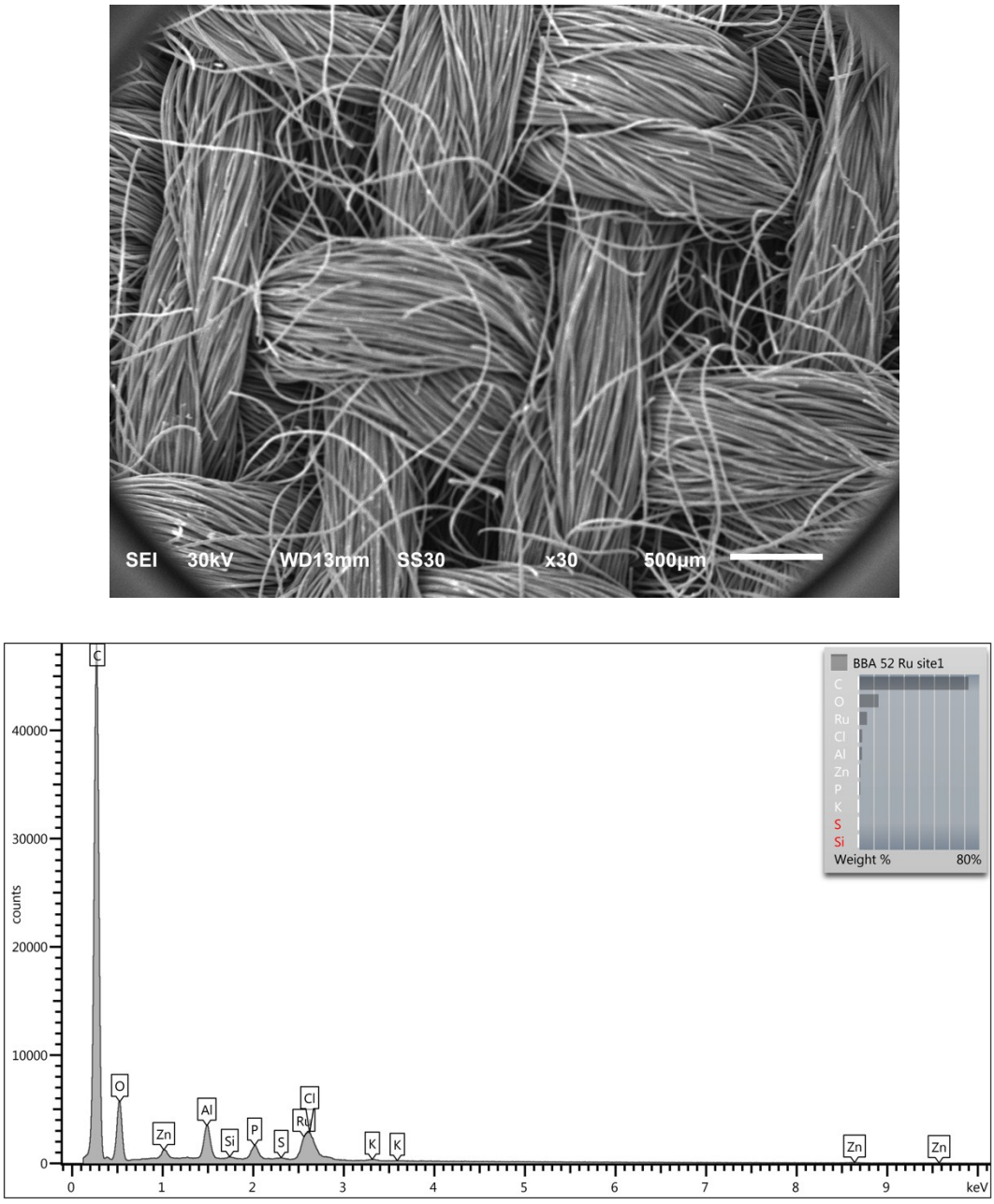


Figure 4. SEM image of Ru on activated carbon cloth (Ru/ACC) after use as an anode in an open cell reaction. Less shiny surface is visible after use. The EDS quantitative analysis shows about 10% weight of Ru on the surface. This decreased Ru loading may account for the loss of reactivity in the 2nd run shown in figure 6.

General Reaction Procedure

Experiments were carried out in an undivided 1-chamber (1-C) or divided 2-chamber (2-C) simple electrochemical H-cell. In the case of the 2-C a Dupont® Nafion-117 membrane was used to separate the two half cells. One half contained 20 mL of 0.01 M phosphate buffer (pH 7.5 or pH 8.5) was placed in one half and the other half had varied concentrations of added alcohol with the phosphate buffer. The cells were placed in an oil bath to operate at the desired temperature. The experiments were operated under galvanostatic control and at ambient pressure.

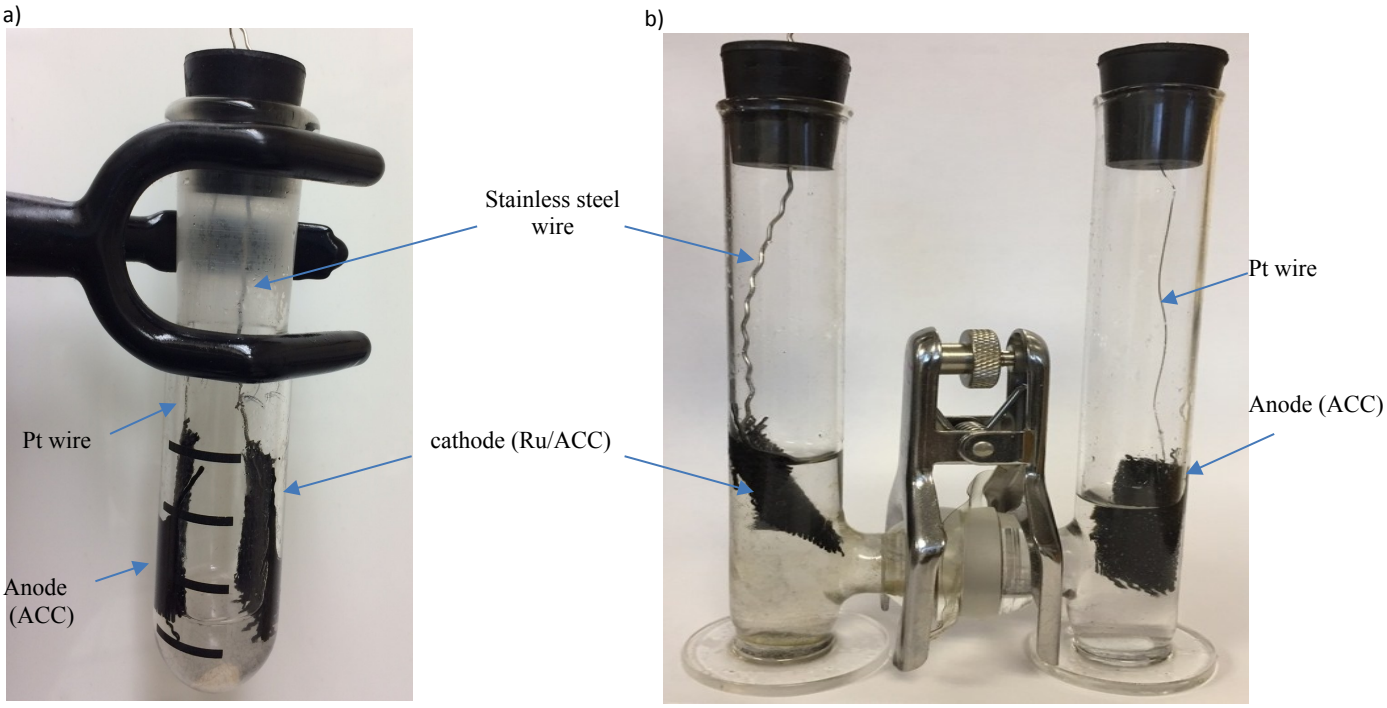


Figure 5. a) Undivided/open electrochemical cell, b) Divided/close electrochemical cell separated by a Nafion™ membrane.

Analysis

An aliquot of 1 mL was taken every 2 h and acidified with concentrated HCl (44 uL) to capture the amine as a quaternary salt solution. The salt solution was then evaporated under a stream of N_2 for 4 h to remove H_2O. The solid salt was then dissolved in 0.5 mL D_2O with internal standard of 20 mM *p*-dioxane. An Agilent 500 MHz superconducting NMR spectrometer at 298 K was used for both qualitative and quantitative analysis. The used electrodes were sonicated in 5 mL *t*-butyl alcohol for 2 h then acidified with 202 uL of conc. HCl and dried on a stream of N_2. The solid salt was then dissolved in 1 mL D_2O with internal standard of 20 mM *p*-dioxane and the concentration of the amine was similarly determined by NMR. The products were further characterized with GC-MS.

Catalyst reusability

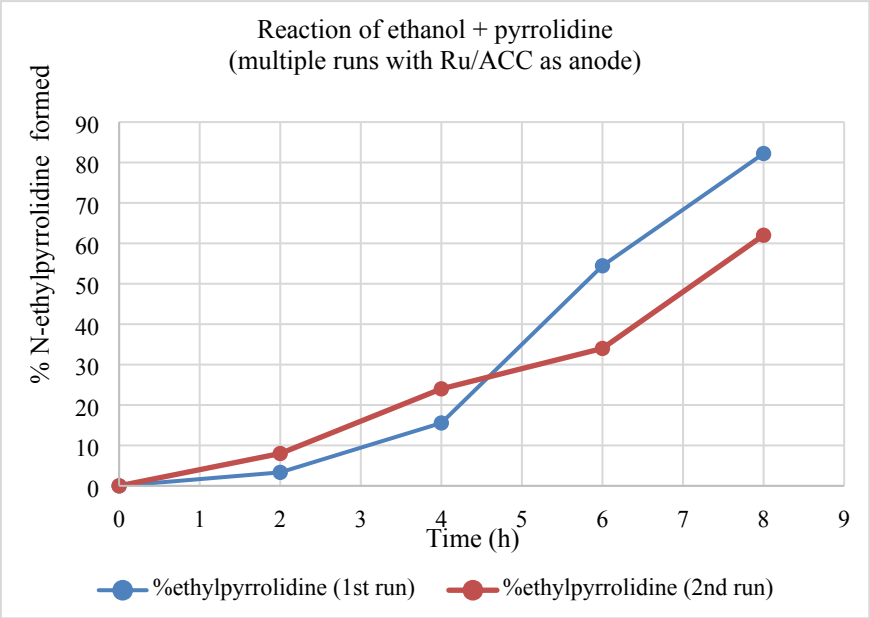


Figure 6. Reaction of ethanol with pyrrolidine in an open cell using Ru/ACC as anode and ACC as cathode; Blue line — 1st use of the catalyst and Red line— 2nd use. This revealed the loss of reactivity due to the slight loss of Ru from the electrode as seen in the EDS analysis in figure 4.

Crystal Structure of picrate salt of *trans*-4-methylcyclohexylpyrrolidine

To definitively identify the *cis* and *trans*-4-methylcyclohexylpyrrolidines, a crystal structure of the *trans* diastereomer was obtained from a reductive amination of 4-methylcyclohexanone and pyrrolidine using $NaBH_4$ in TFE.[4] The *trans* diastereomer was separated by column chromatography with ethyl acetate:hexane (1:4). A crystal of the picrate salt was obtained from 0.22 g (1.0 mmol) of picric acid and 0.17 g (1.0 mmol) of *trans*-4-methylcyclohexylpyrrolidine in 10 mL of a 1:4 v/v methanol:water mixture.[5] The structure was determined by X-ray diffraction, confirming the trans stereochemistry of the substituents on the cyclohexane ring (figure 6c). The melting point of 189-191 °C matched literature value for this picrate.[5]

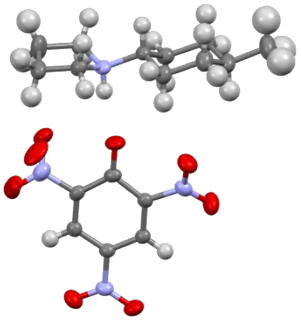


Figure 7. Crystal structure of picrate salt of 4-methylcyclohexylpyrrolidine obtained from methanol:water (1:4 v/v).

CCDC 1911565 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

References

1 Z. Li, M. Garedew, C. H. Lam, J. E. Jackson, D. J. Miller and C. M. Saffron, *Green Chem.*, 2012, **14**, 2540.
2 S. Bhatia, G. Spahlinger, N. Boukhumseen, Q. Boll, Z. Li and J. E. Jackson, *European J. Org. Chem.*, 2016, **2016**, 4230–4235.
3 M. Garedew, in *Ph.D. Dissertation, Michigan State University*, 2018, p. 69,94.
4 M. Tajbakhsh, R. Hosseinzadeh, H. Alinezhad, S. Ghahari, A. Heydari and S. Khaksar, *Synthesis (Stuttg).*, 2011, 490–496.
5 N. Goel, U. P. Singh, G. Singh and P. Srivastava, *J. Mol. Struct.*, 2013, **1036**, 427–438.
6 R. O. Hutchins, W. Y. Su, R. Sivakumar, F. Cistone and Y. P. Stercho, *J. Org. Chem.*, 1983, **48**, 3412–3422.

Characterization of Compounds

^{1}H NMR: Reaction of pyrrolidine with methanol

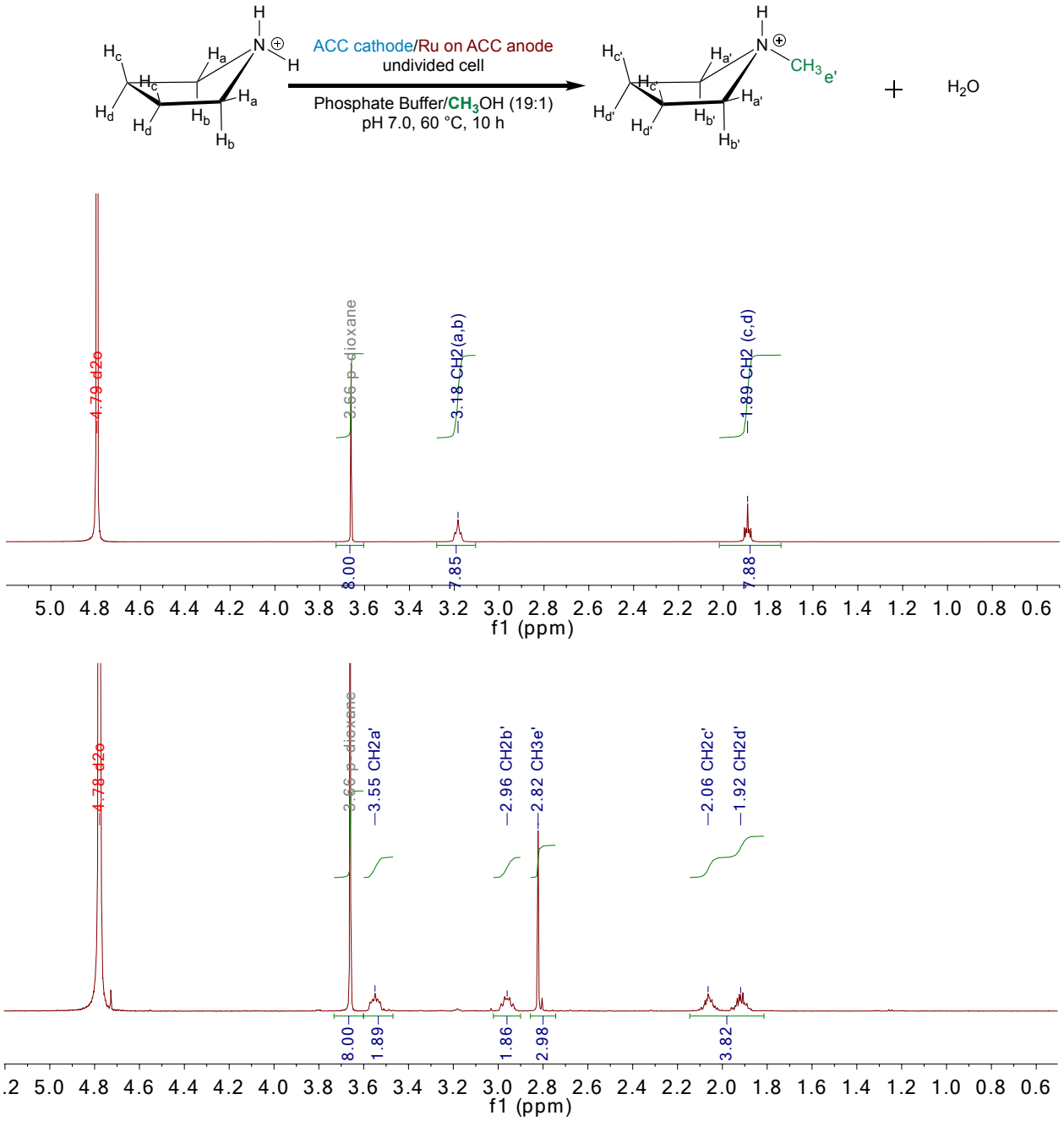


Figure 8. The reaction of pyrrolidine (top) with methanol at constant current of 2.2 mA/cm^2 yielded 85% *N*-methylpyrrolidine with 96% conversion (bottom).

^{1}H NMR: Reaction of pyrrolidine with ethanol

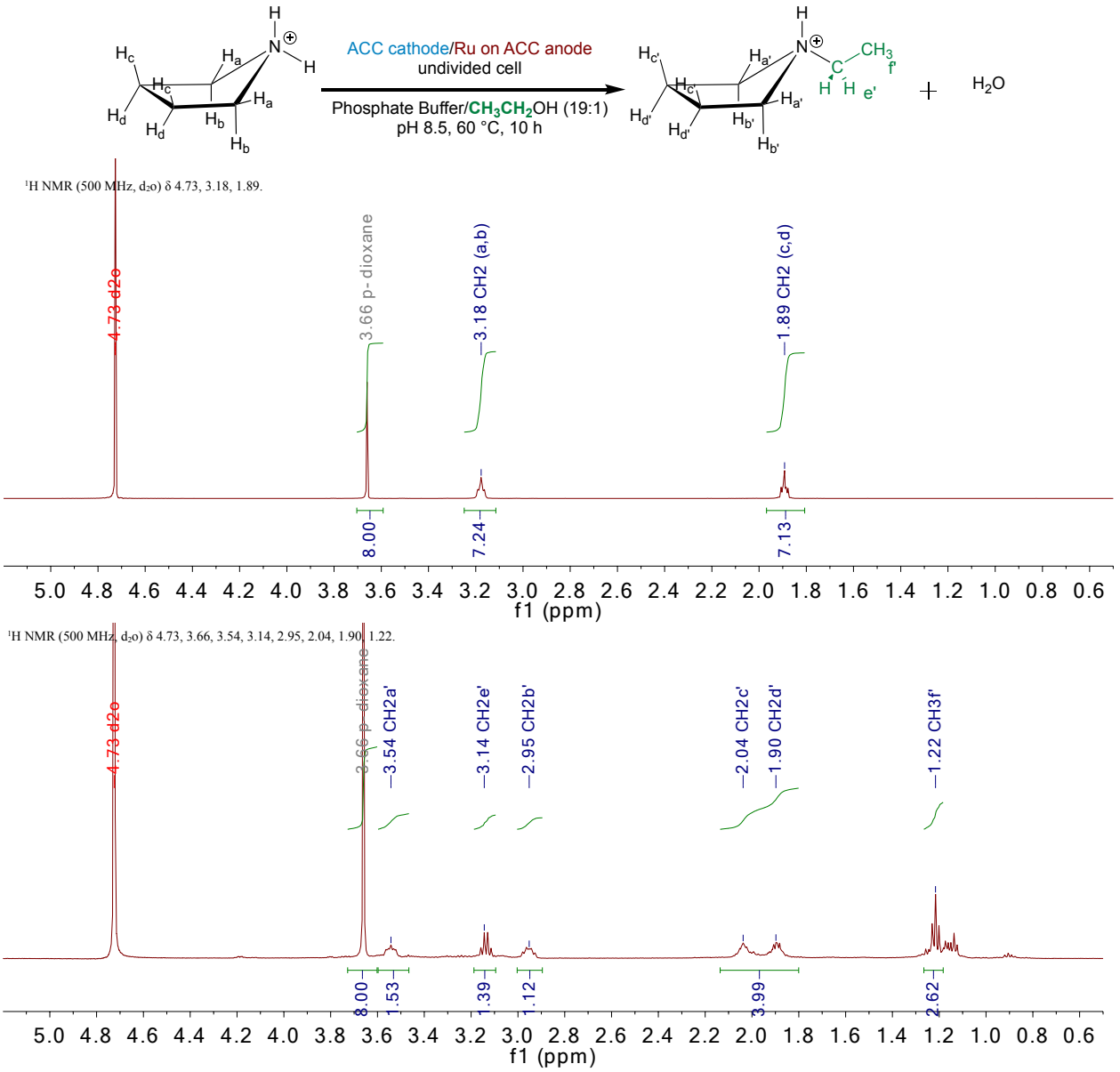


Figure 9. The end reaction of pyrrolidine (top) with ethanol at constant current of 2.2 mA/cm^2 yielded 89% *N*-ethylpyrrolidine with 93% conversion (bottom).

^{1}H NMR: Reaction of pyrrolidine with isopropyl alcohol

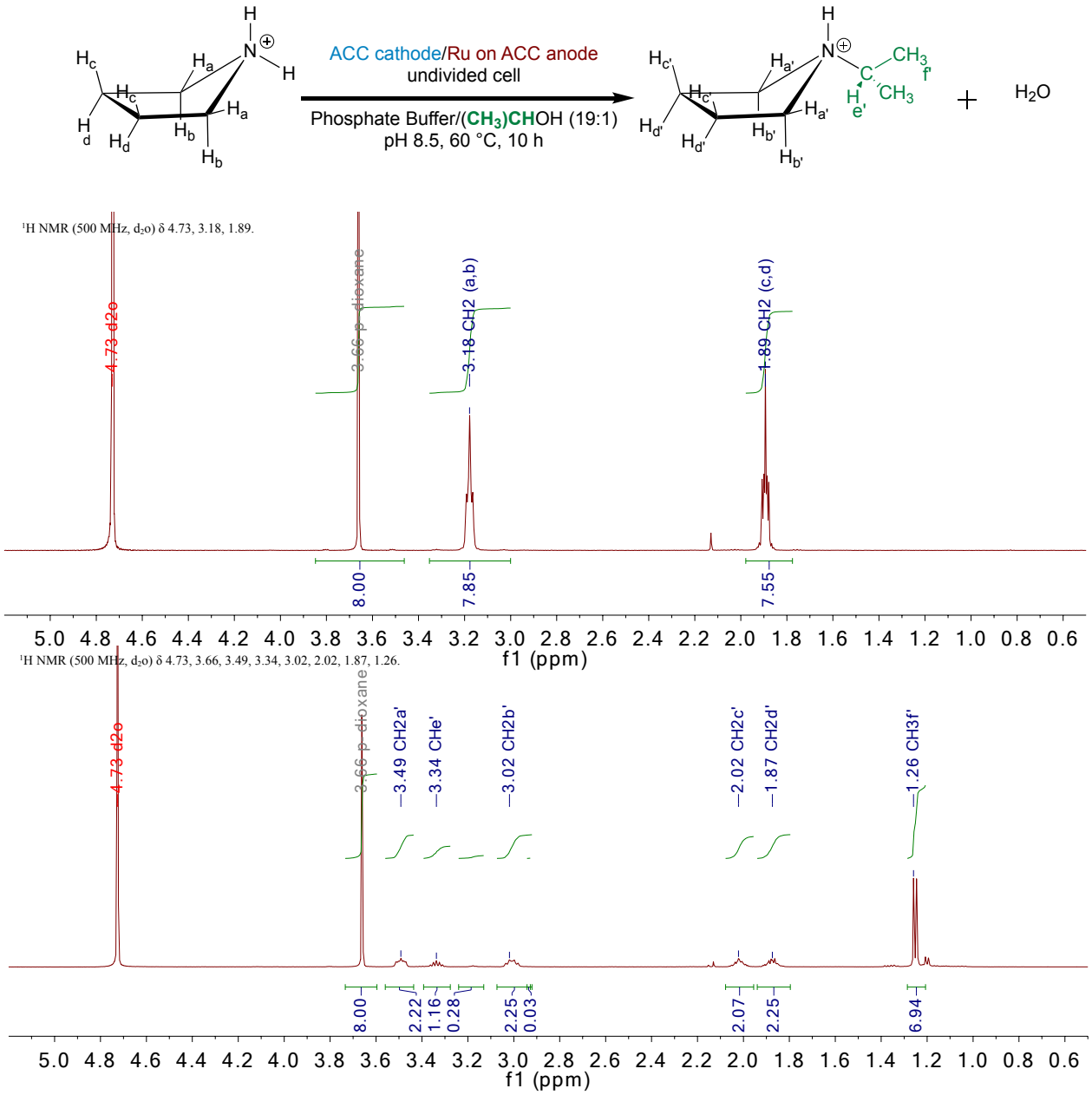


Figure 10. The end reaction of pyrrolidine (top) with isopropyl alcohol at constant current of 2.2 mA/cm^2 yielded 60% *N*-ethylpyrrolidine with 95% conversion (bottom).

^{1}H NMR: Reaction of morpholine with methanol

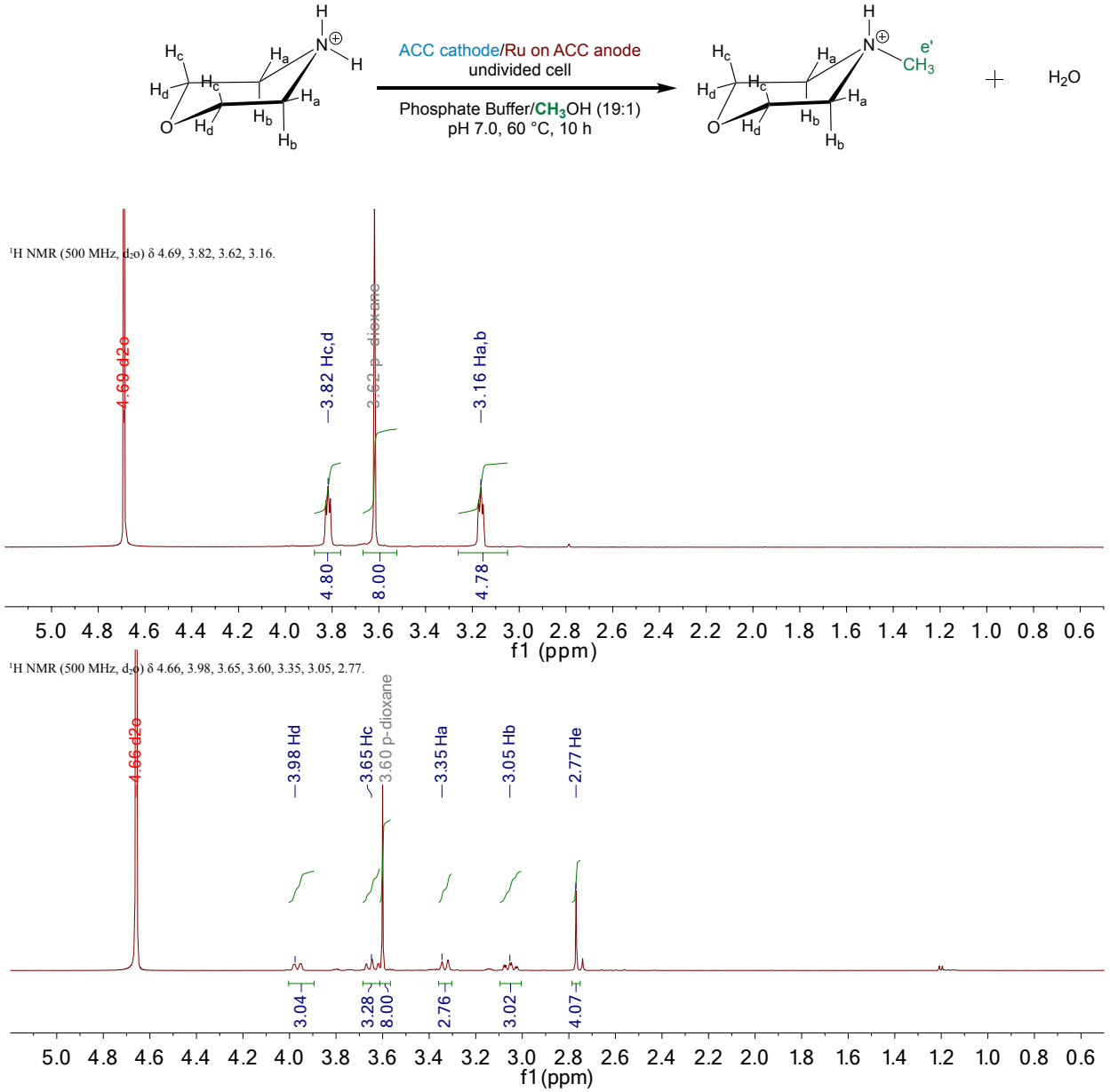


Figure 11. The reaction of morpholine (top) with methanol at constant current of 2.2 mA/cm^2 yielded 68% *N*-methylmorpholine with 87% conversion (bottom).

[1]HNMR: Reaction of morpholine with ethanol

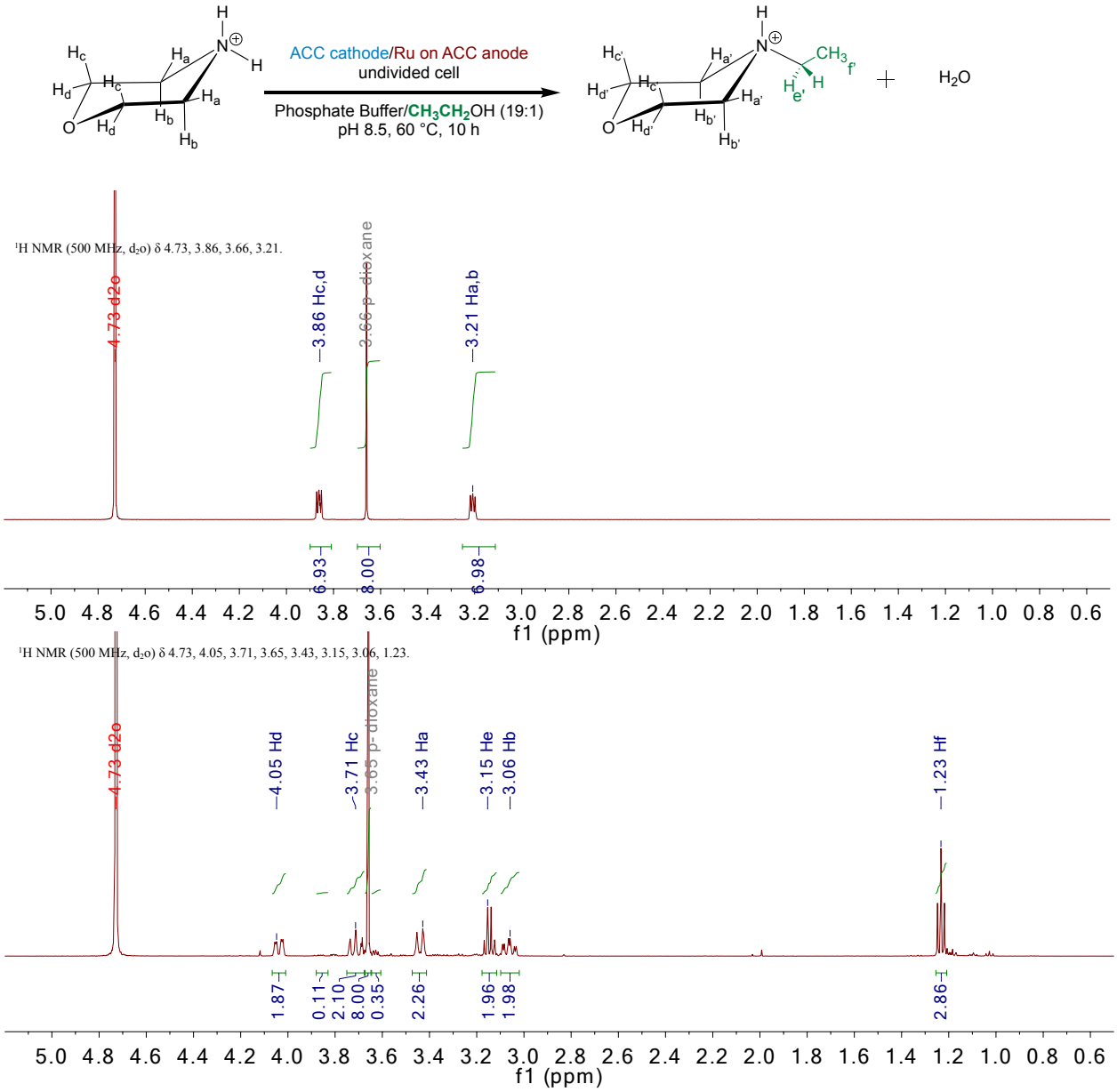


Figure 12. The reaction of morpholine (top) with ethanol at constant current of 2.2 mA/cm^2 yielded 69% *N*-ethylmorpholine with 98% conversion (bottom).

^{1}H NMR: Reaction of sarcosine with methanol

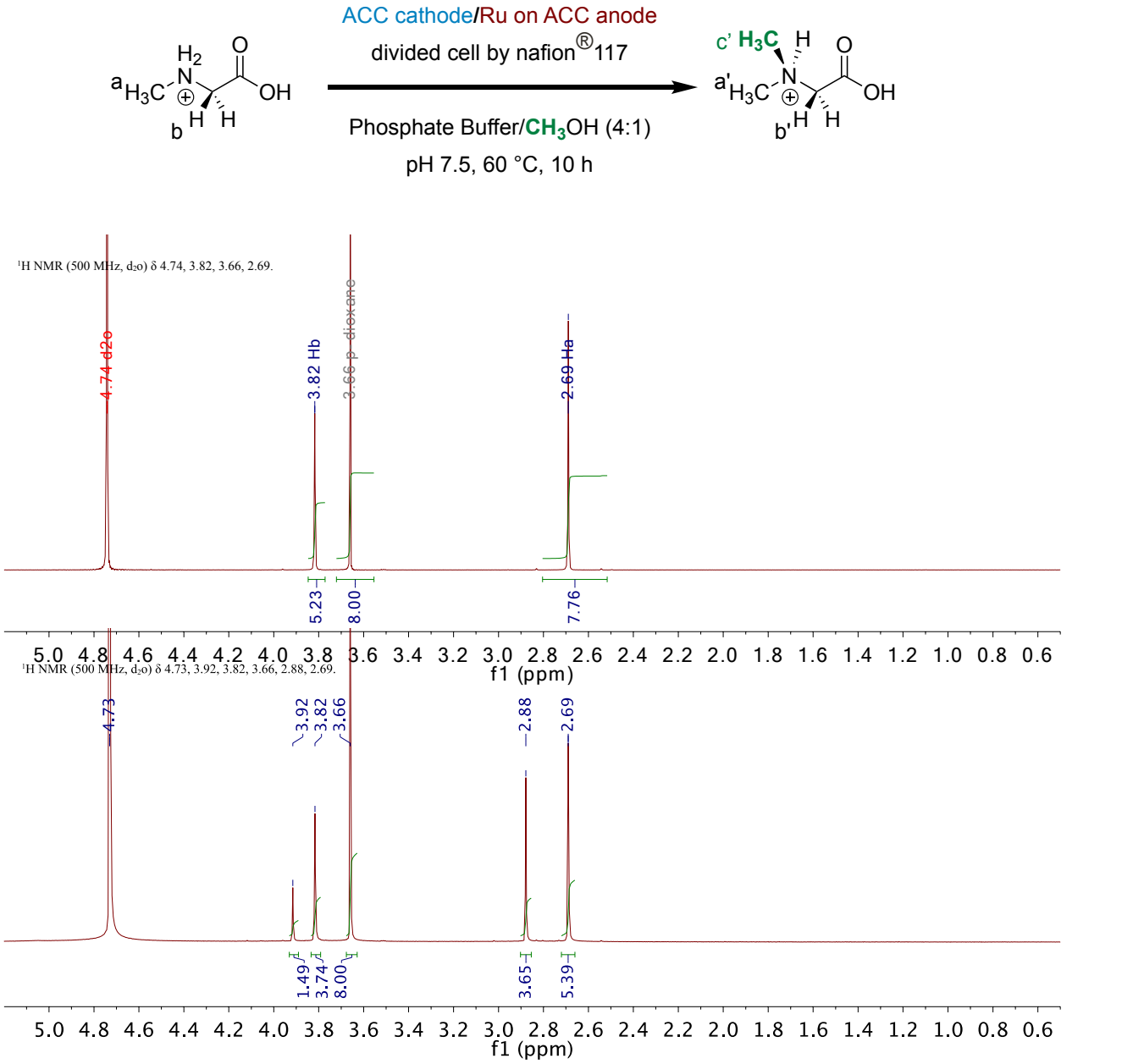
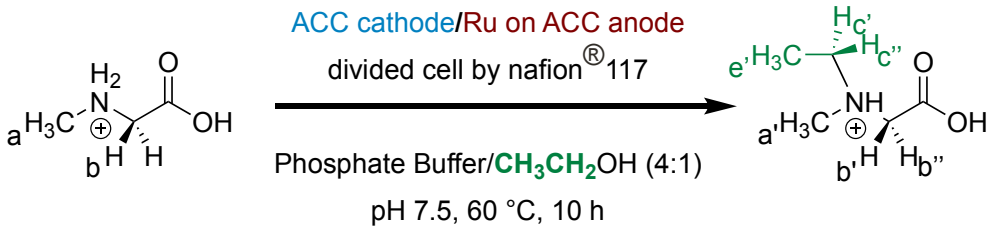


Figure 13. The reaction of sarcosine (top) with methanol at constant current of 2.2 mA/cm^2 yielded 62% *N*-methylsarcosine with 67% conversion (bottom).

^{1}H NMR: Reaction of sarcosine with ethanol



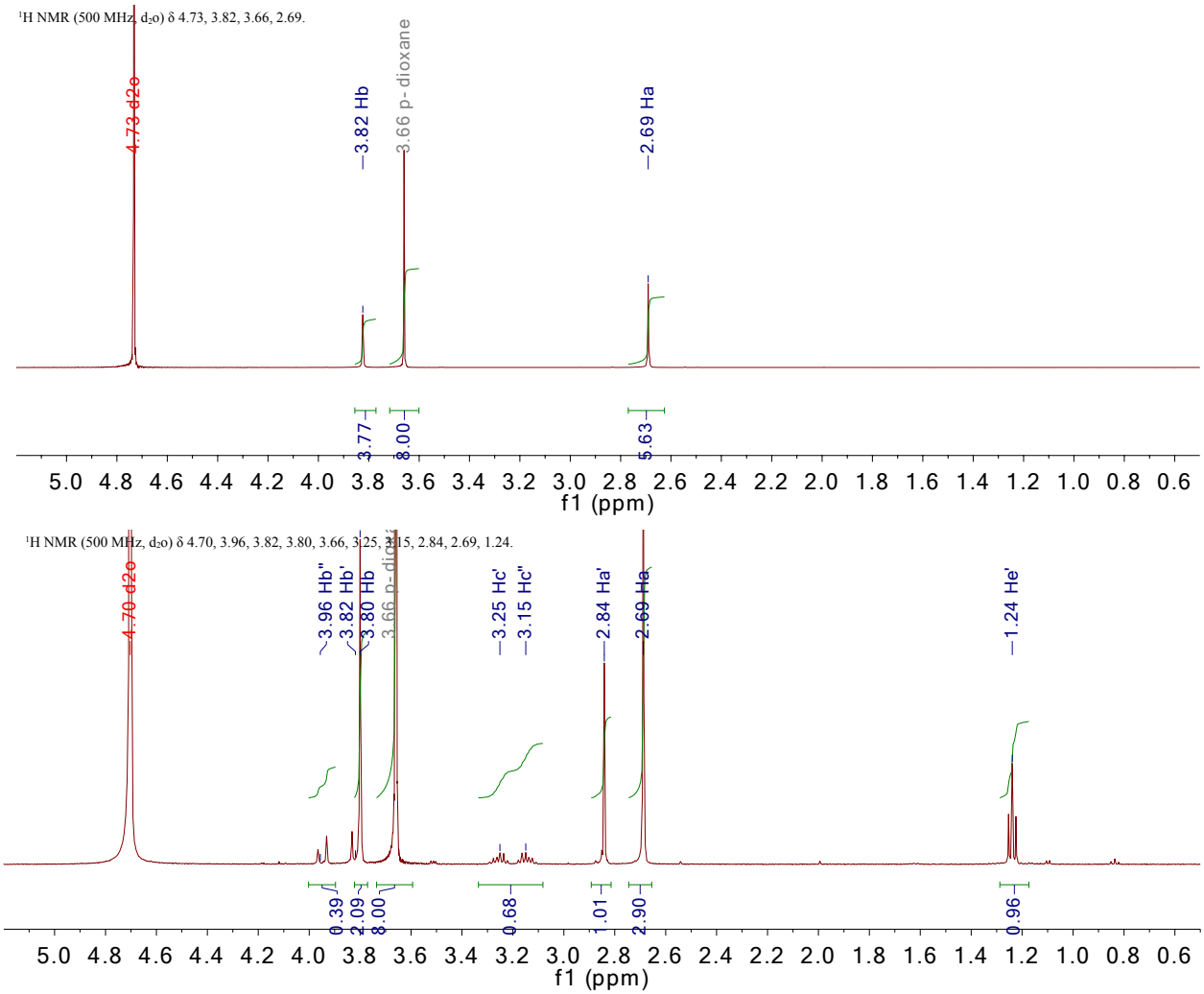


Figure 14. The reaction of sarcosine (top) with ethanol at constant current of 2.2 mA/cm^2 yielded 66% *N*-ethylsarcosine with 75% conversion (bottom).

^{1}H NMR: Reaction of ammonium acetate (generates ammonia in situ) with ethanol

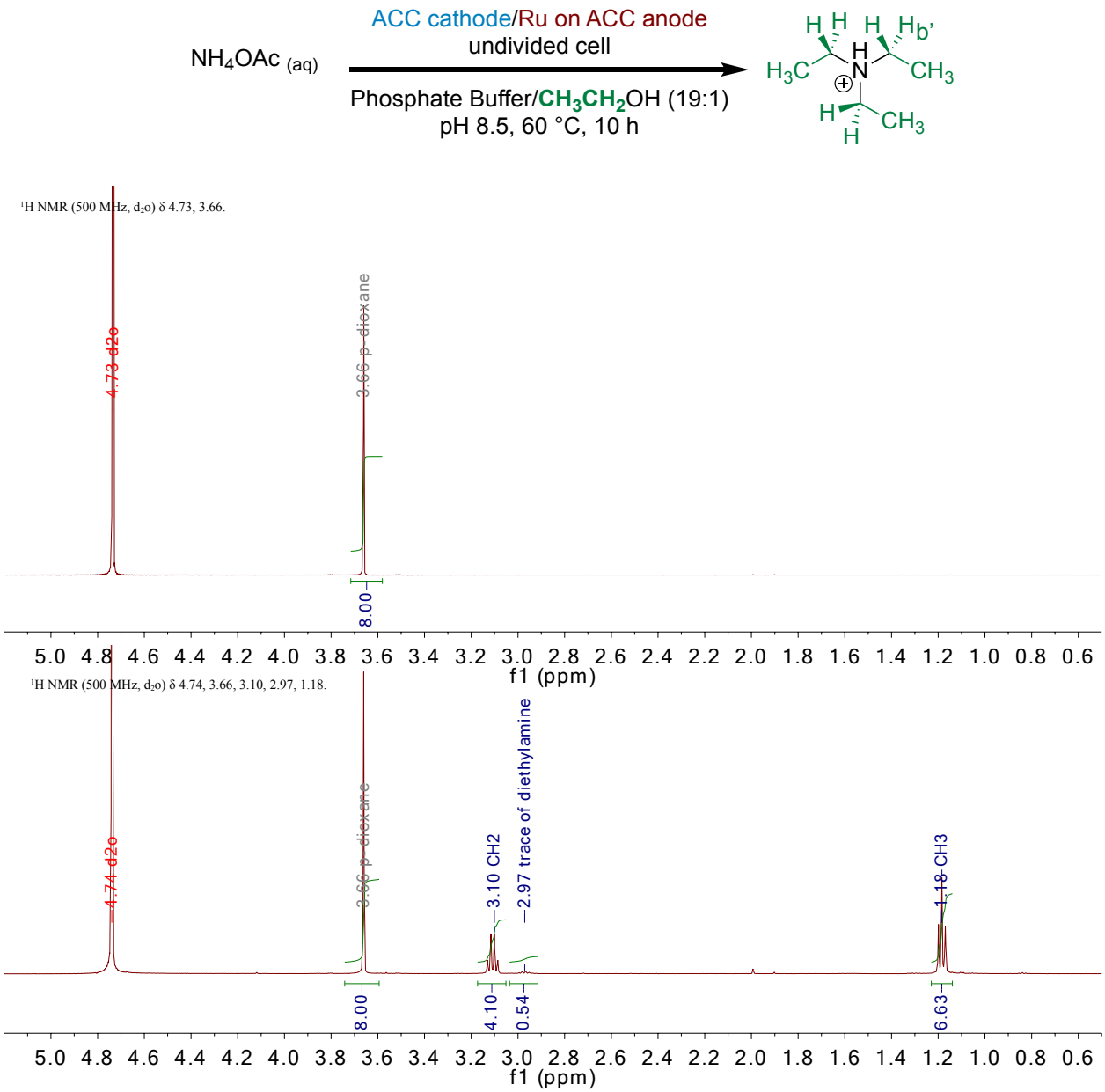


Figure 15. The reaction of ammonia acetate (ammonia) (top) with ethanol at constant current of 2.2 mA/cm^2 yielded 90% N-triethylamine with 92% conversion (bottom).

^{1}H NMR: Reaction of ethylamine with ethanol

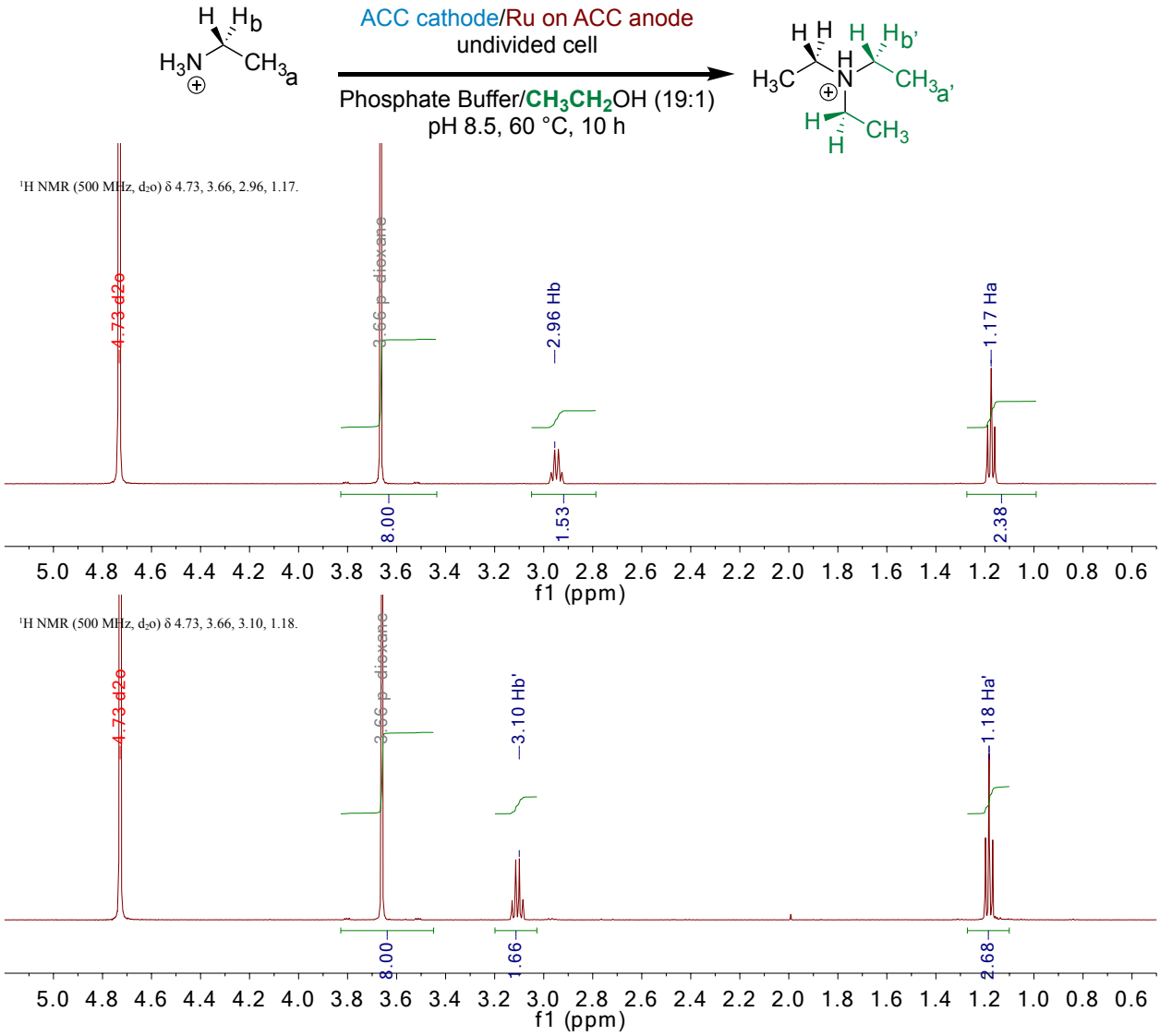


Figure 16. The reaction of ethylamine (top) with ethanol at constant current of 2.2 mA/cm^2 yielded 92% triethylamine and 97% conversion (bottom).

^{1}H NMR: Reaction of diethylamine with ethanol

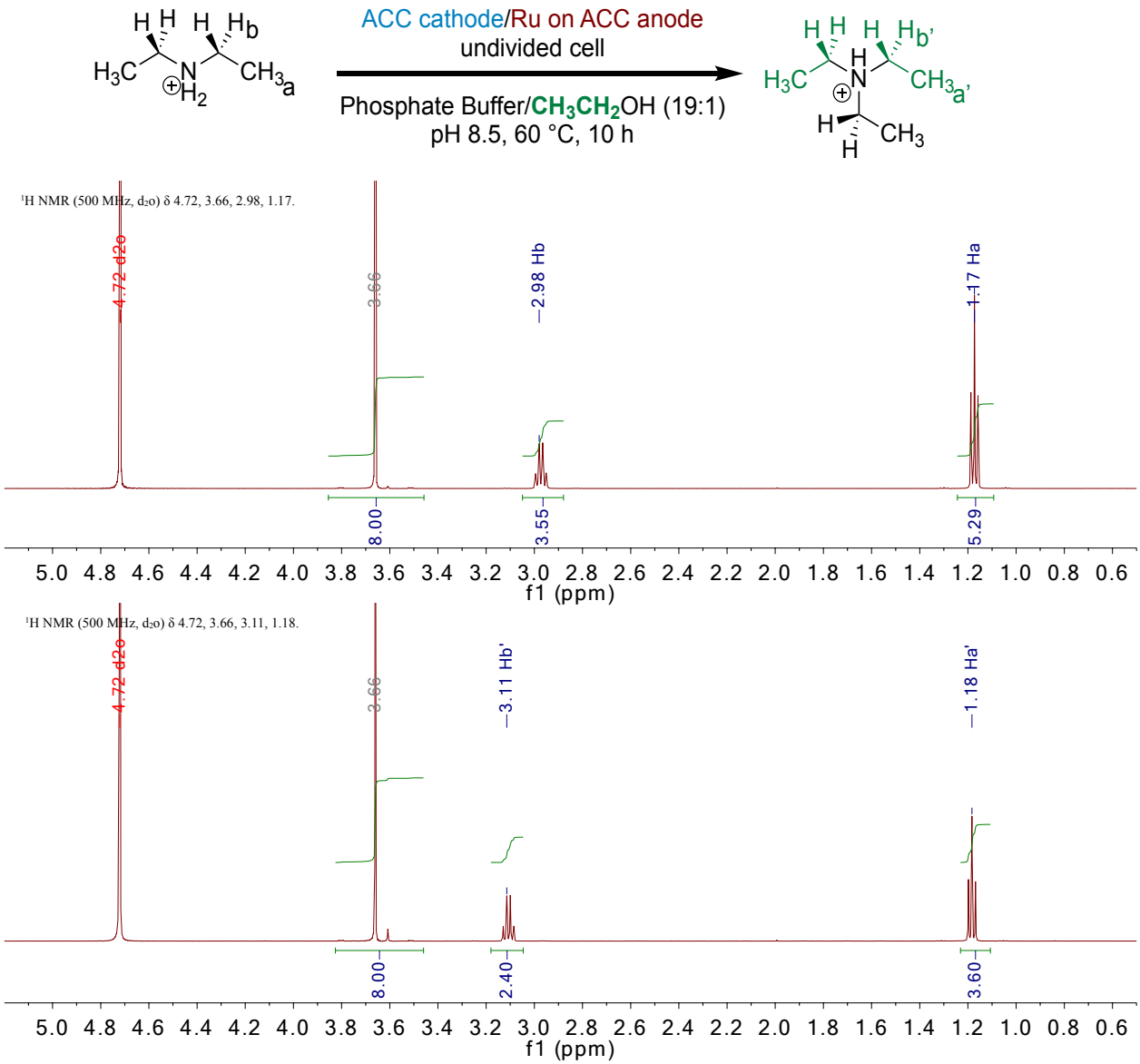


Figure 17. The reaction of diethylamine (top) with ethanol at constant current of 2.2 mA/cm^2 yielded 92% triethylamine and 100% conversion (bottom).

^{1}H NMR: Reaction of ammonium hydroxide with isopropyl alcohol

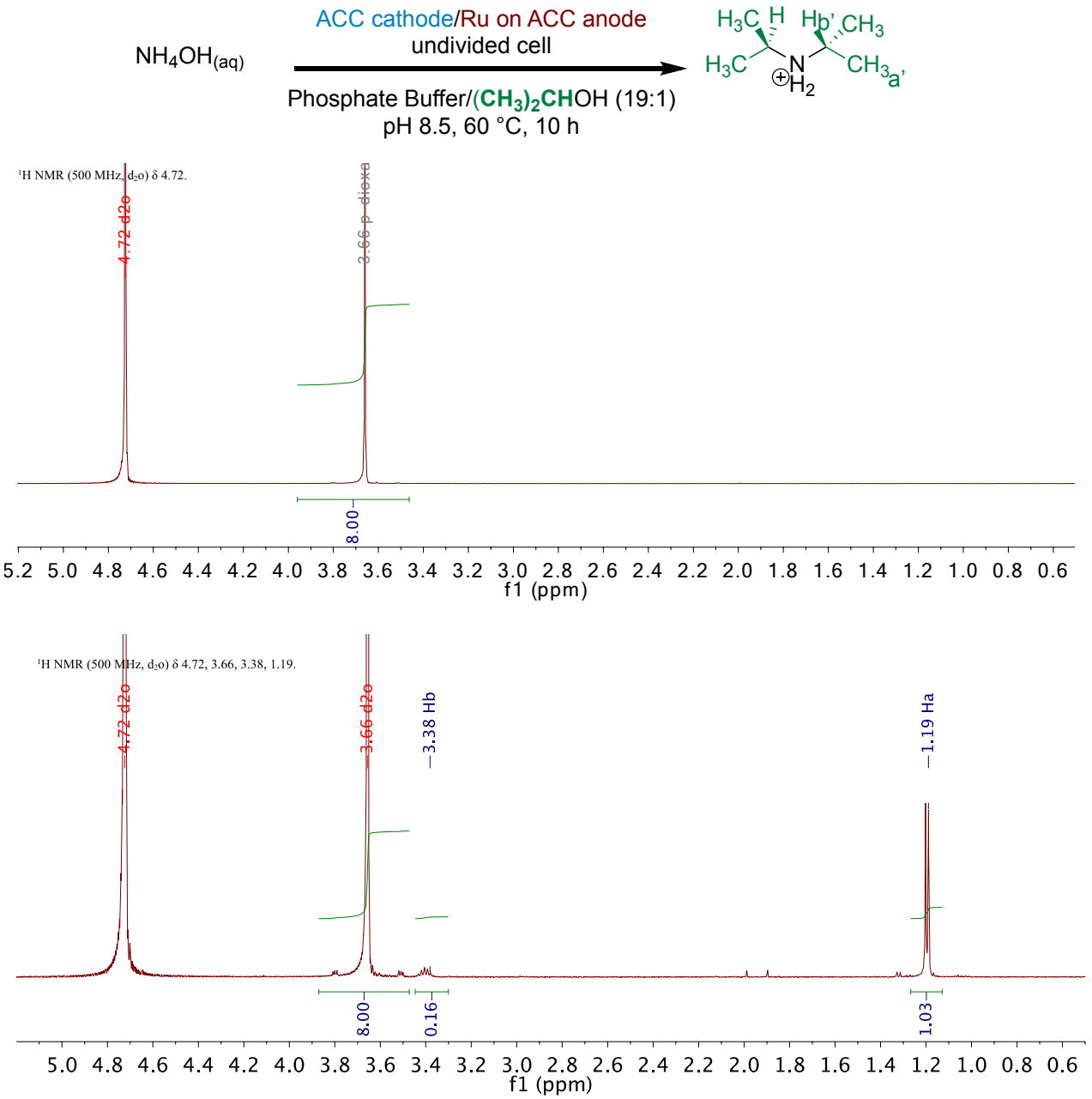


Figure 18. The end reaction of ammonium hydroxide (top) with isopropyl alcohol yielded 15% diisopropylamine at 60 °C (bottom).

^{1}H NMR: Reaction of ammonium acetate with isopropyl alcohol

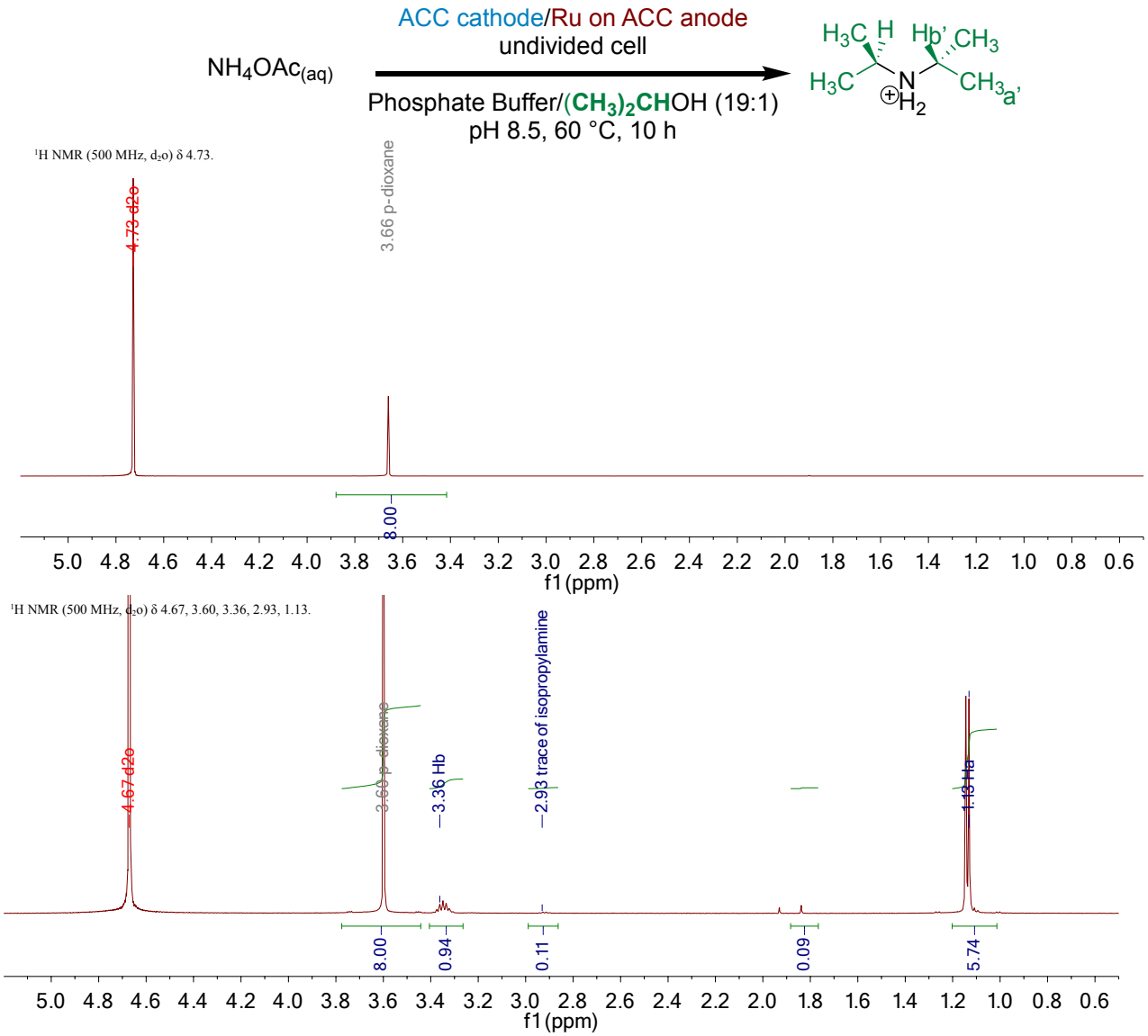


Figure 19. The end reaction of ammonium hydroxide (top) with isopropyl alcohol yielded 60 % diisopropylamine at 60 °C with trace of isopropylamine. (bottom)

[1]HNMR: Reaction of diisopropylamine with methanol

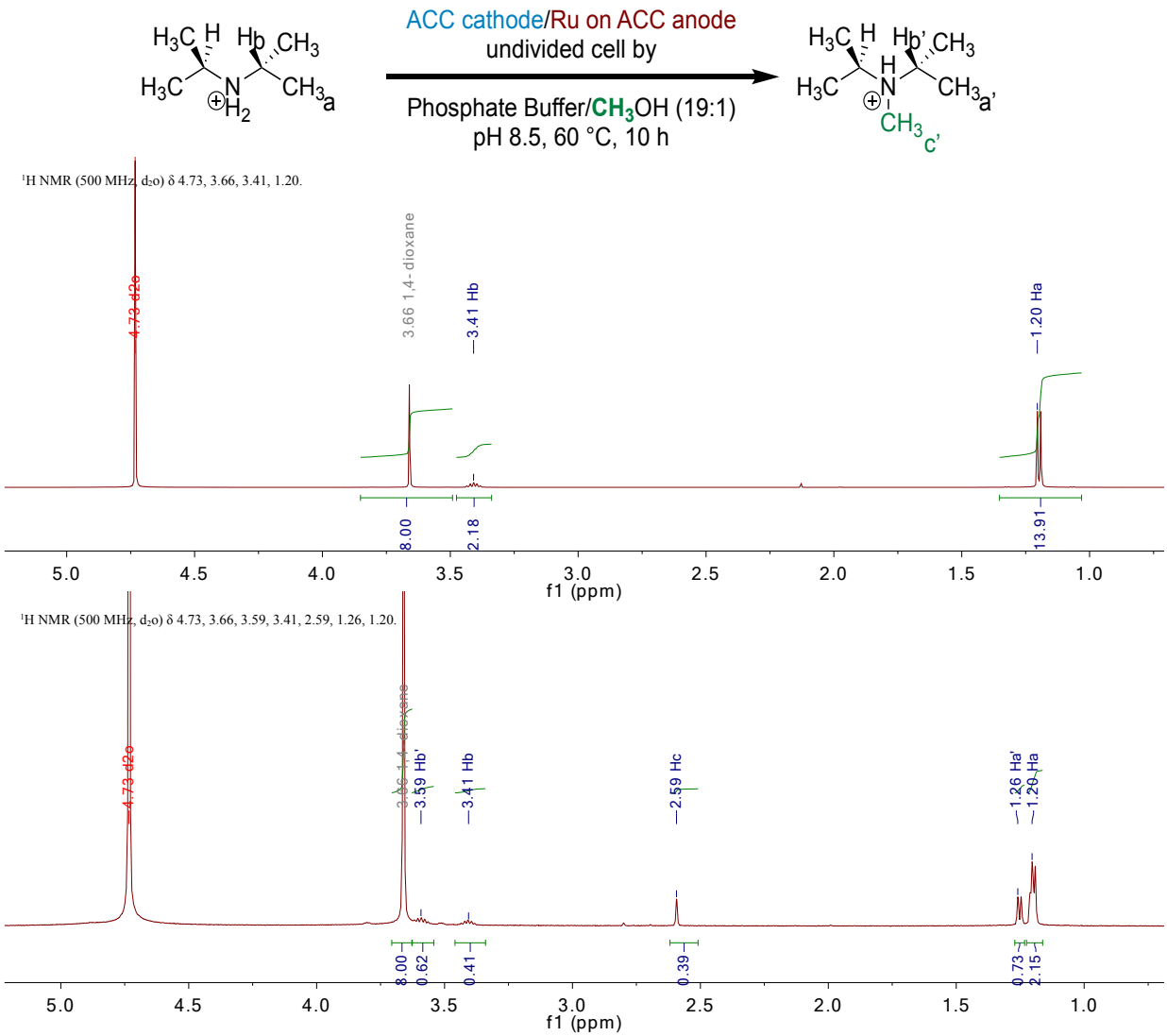


Figure 20. The reaction of diisopropylamine (top) with methanol at constant current of 2.2 mA/cm^2 yielded 30% *N*-methyldiisopropylamine and 34% conversion (bottom).

^{1}H NMR: Reaction of diisopropylamine with ethanol

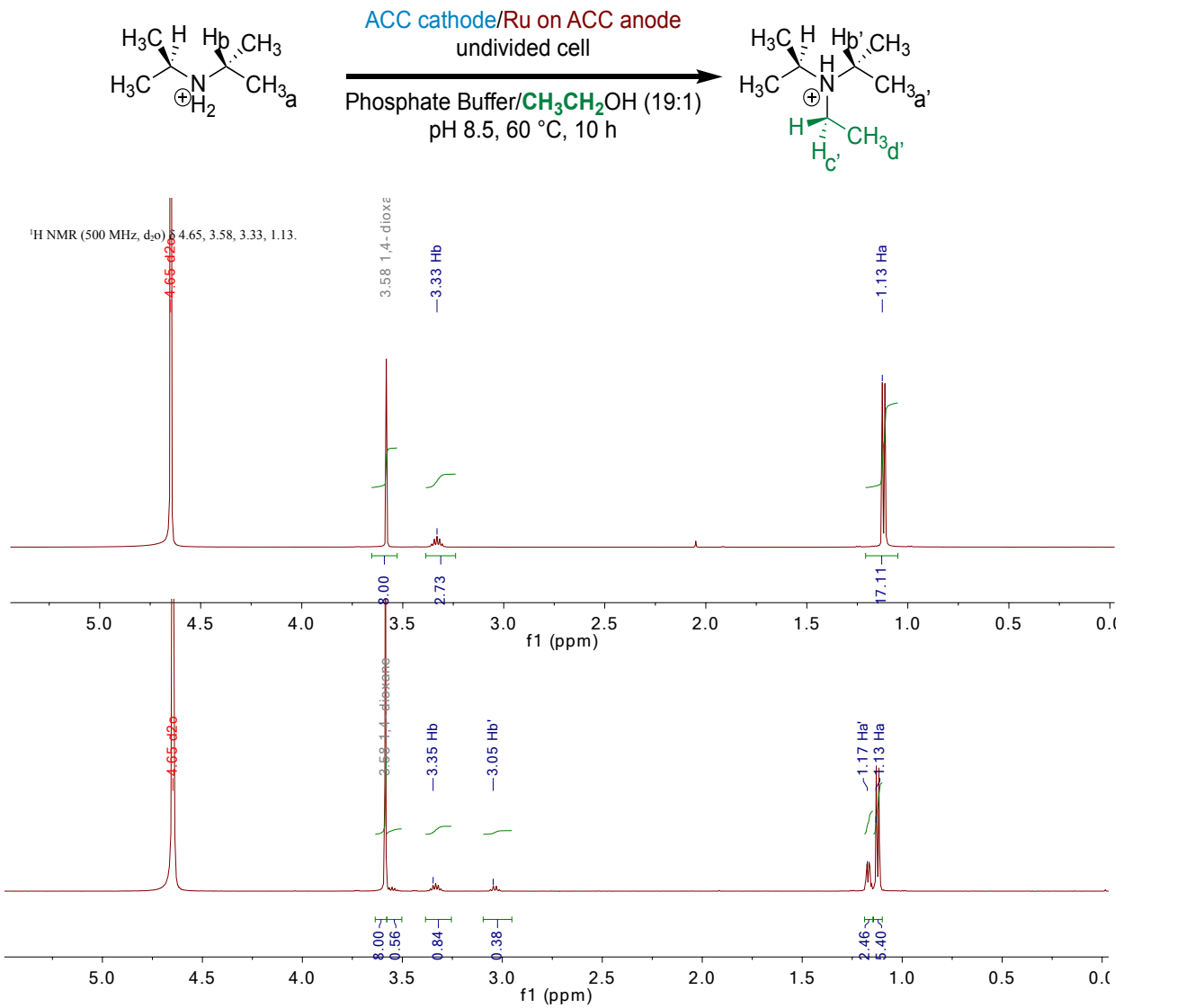


Figure 21. The reaction of diisopropylamine (top) with ethanol at constant current of 2.2 mA/cm^2 yielded 34% *N*-ethyldiisopropylamine, a.k.a. Hünig's base and 24% conversion (bottom).

^{1}H NMR: Reaction of butylamine with ethanol

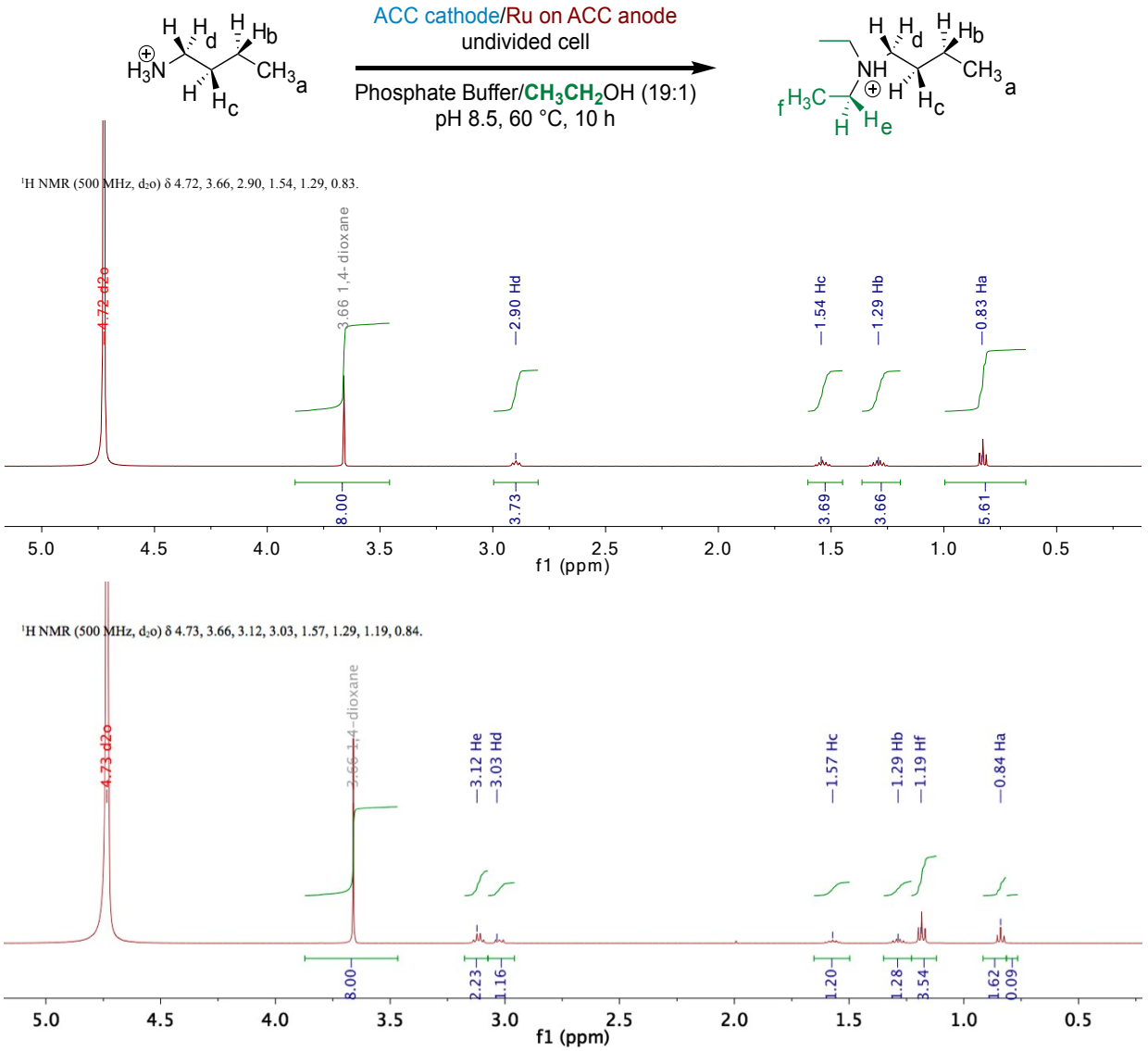


Figure 22. The reaction of *n*-butylamine (top)with ethanol at constant current of 2.2 mA/cm^2 yielded 90% *N,N*-diethylbutylamine and 100% conversion (bottom).

^{1}H NMR: Reaction of diethylamine with butanol

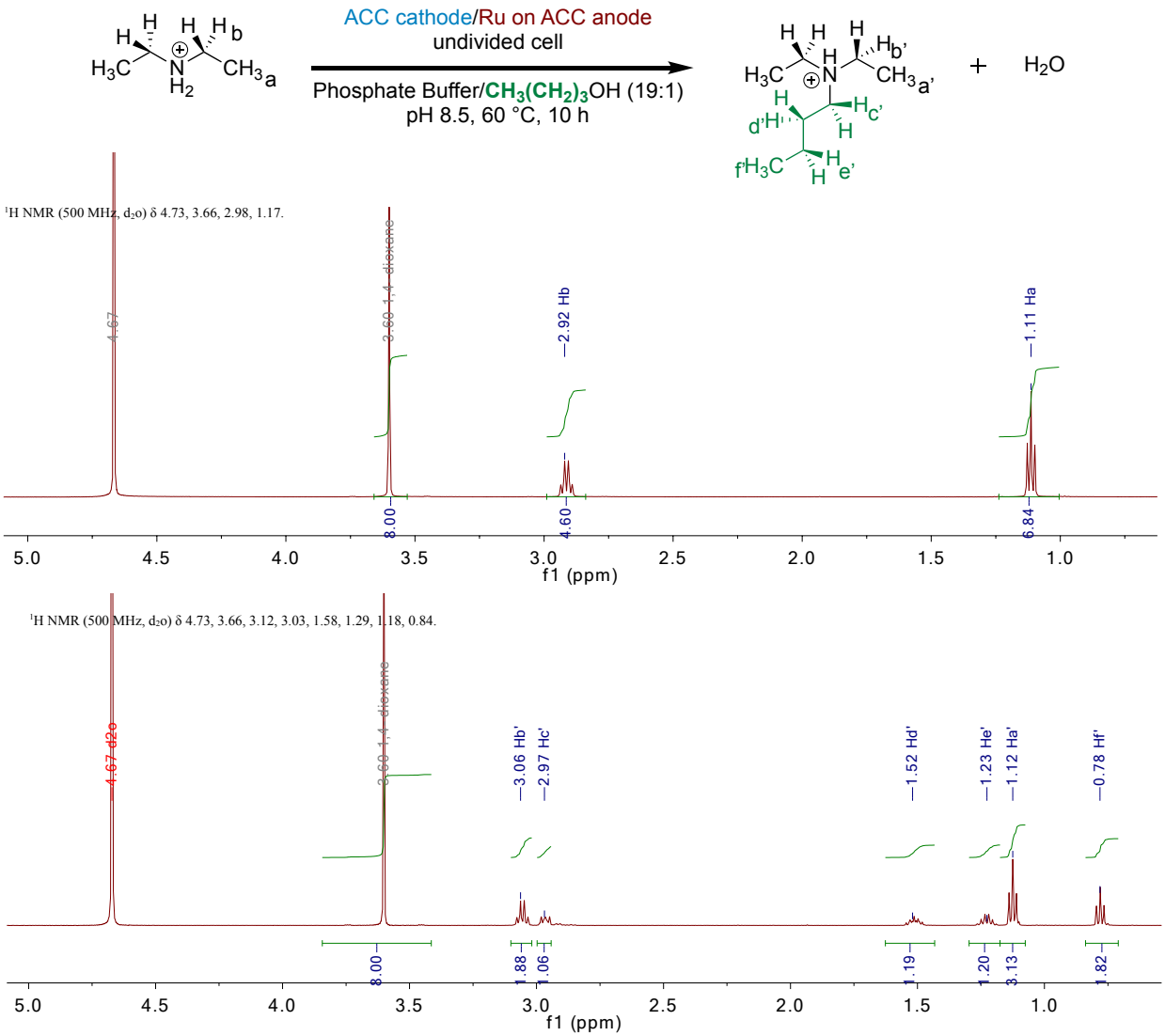


Figure 23. The reaction of diethylamine (top) with butanol at constant current of 2.2 mA/cm^2 yielded 90% *N,N*-diethylbutalamine and 100% conversion (bottom).

[1]HNMR: Reaction of pyrrolidine with 4-methylcyclohexanone (divided cell)

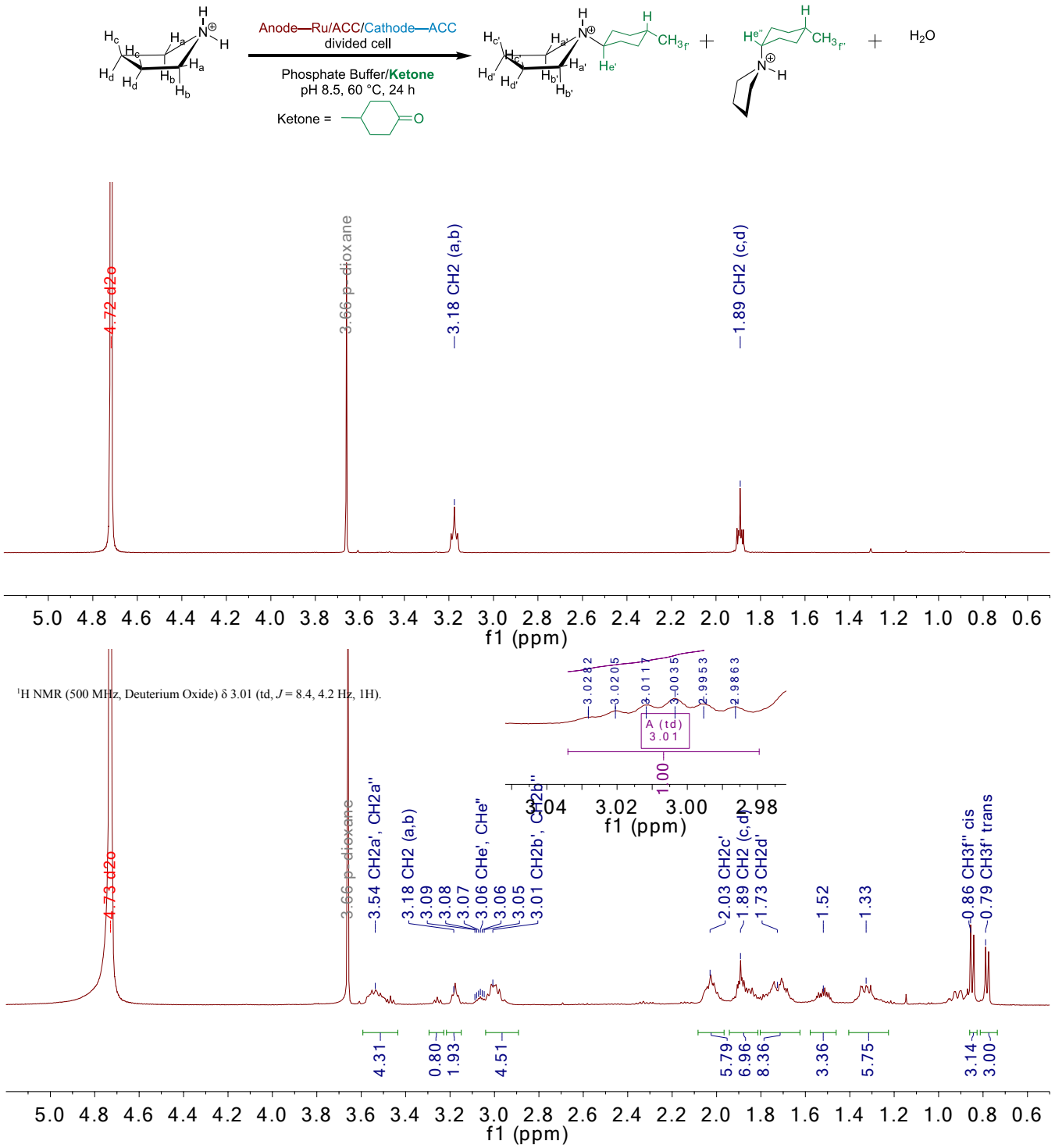


Figure 24. The reaction of pyrrolidine (top) with 4-methylcyclohexanone at constant current of 2.2 mA/cm^2 forming 1:1 ratio of cis/trans-4-methylcyclohexylpyrrolidine (bottom).

^{1}H NMR: Reaction of pyrrolidine with *cis*-4-methylcyclohexanol (divided cell)

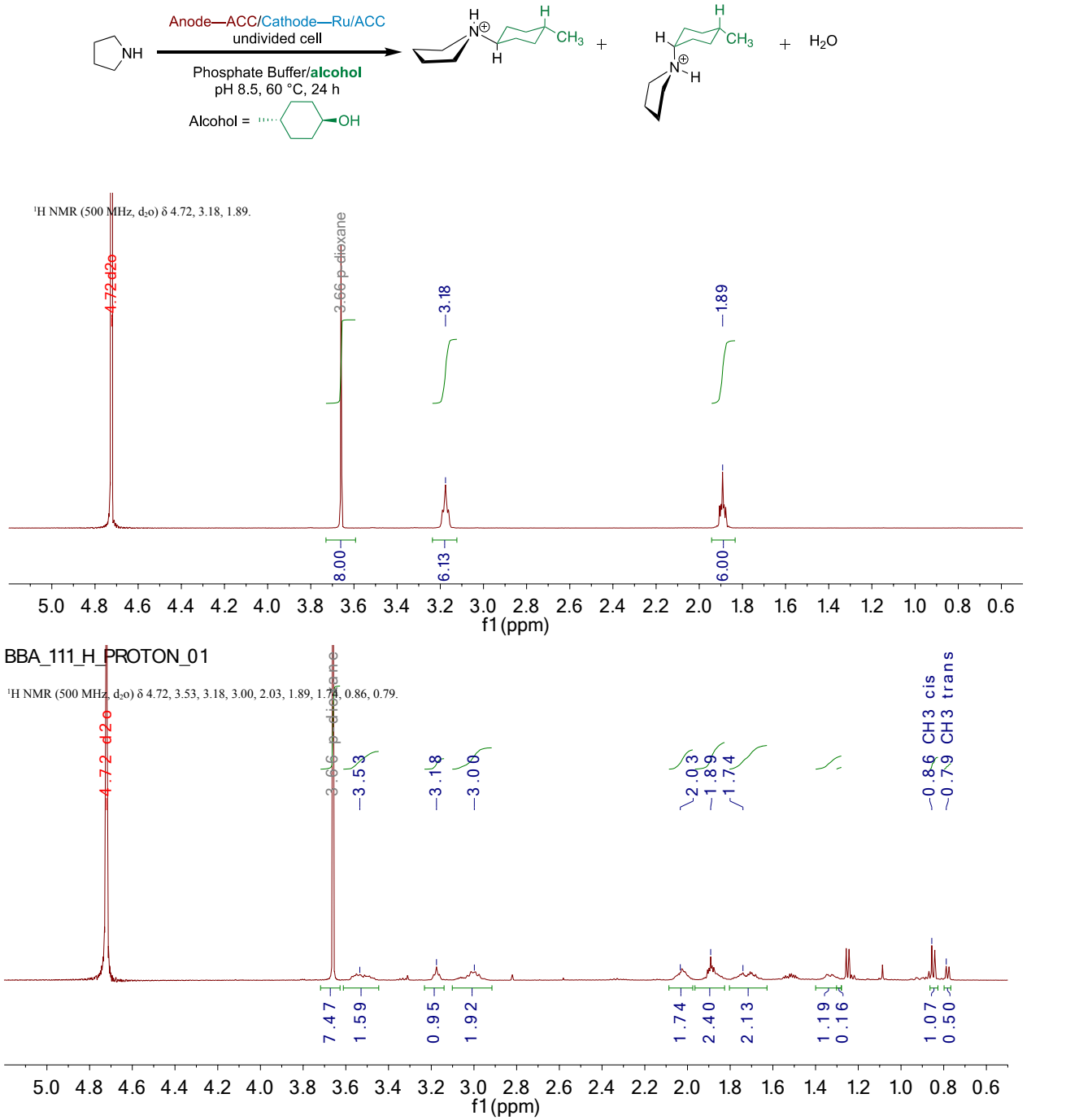
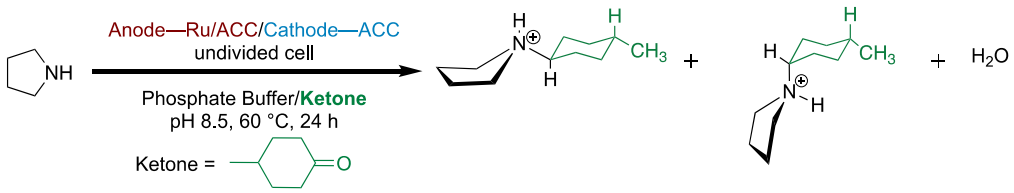


Figure 25. The reaction of pyrrolidine (top) with *cis*-4-methylcyclohexanol at constant current of 2.2 mA/cm^2 forming 2:1 ratio of cis/trans-4-methylcyclohexylpyrrolidine (bottom).

^{1}H NMR: Reaction of pyrrolidine with 4-methylcyclohexanone (undivided cell)



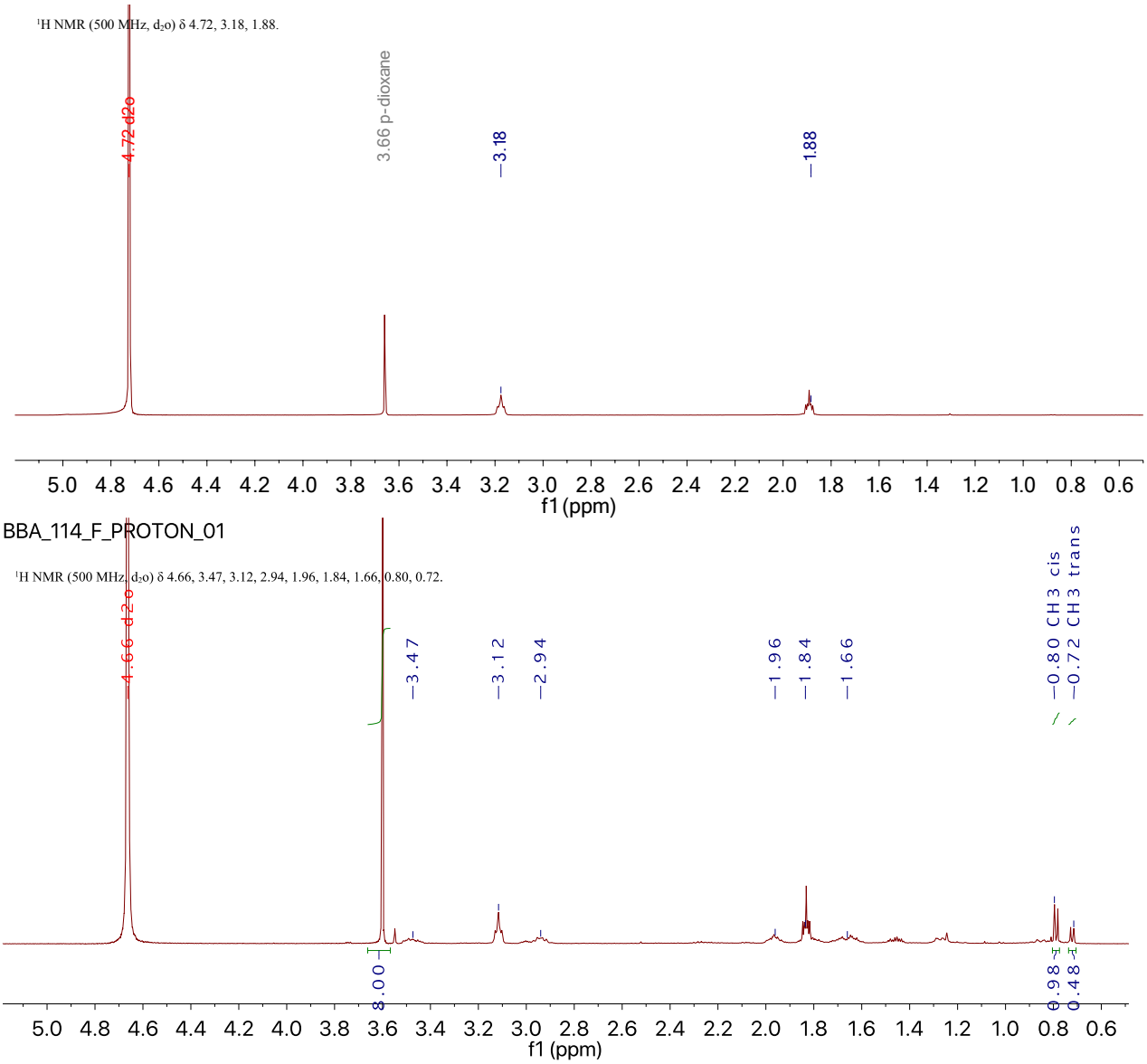
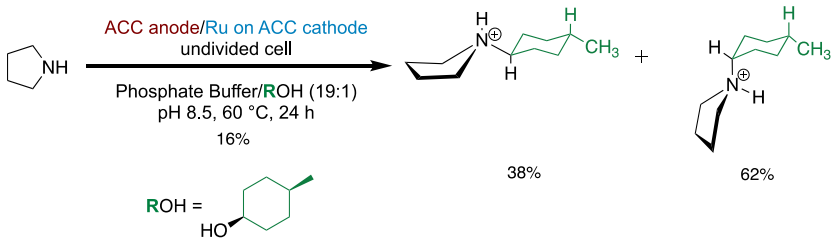


Figure 26. The reaction of pyrrolidine (top) with 4-methylcyclohexanone at constant current of 2.2 mA/cm^2 forming 2:1 ratio of cis/trans-4-methylcyclohexylpyrrolidine (bottom).

GC-MS of the Reaction of pyrrolidine with *cis*-4-methylcyclohexanol



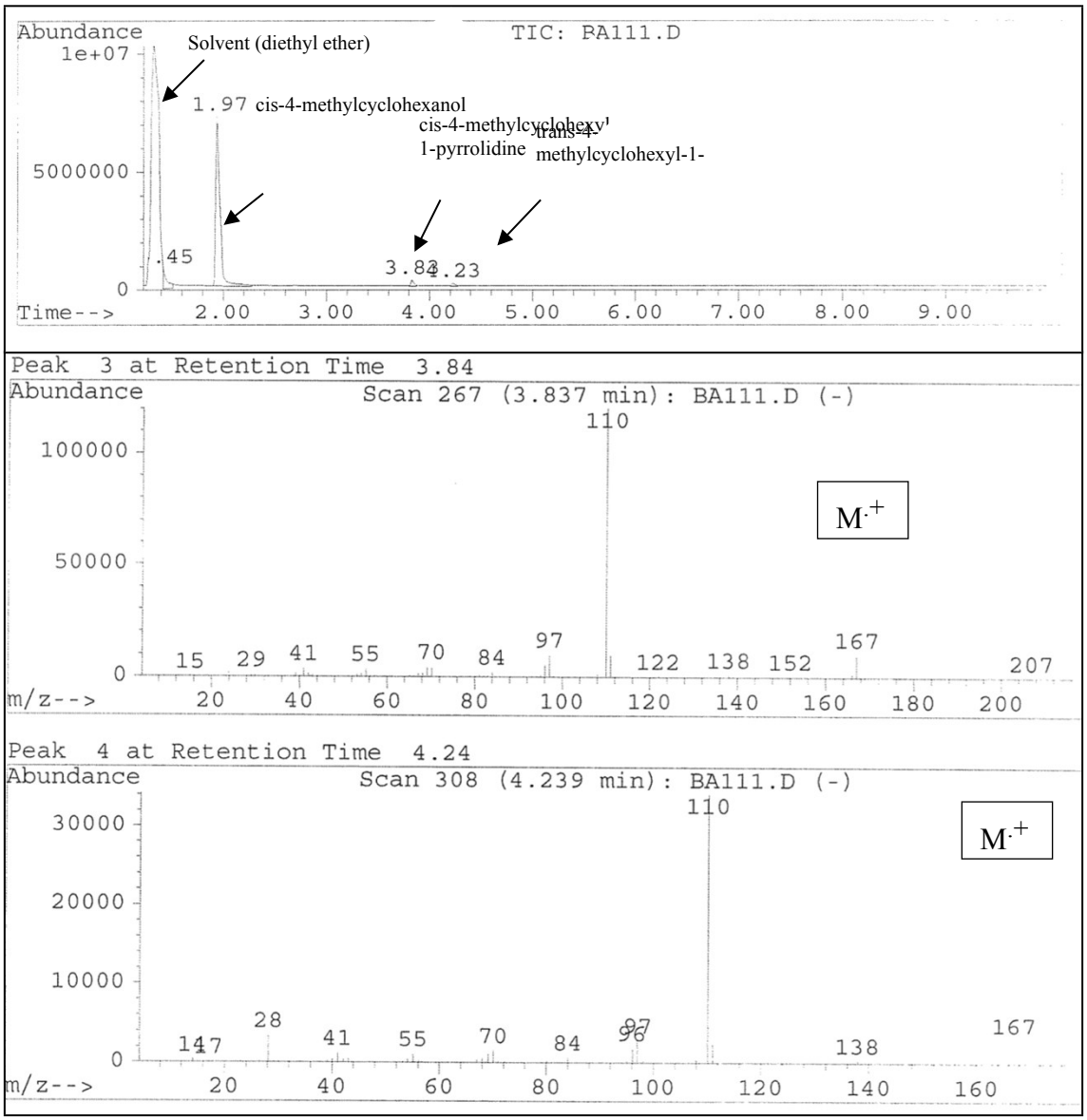


Figure 27. GC-MS of *cis* (mp = 137-137.5 ℃) and *trans*-4-methylcyclohexylpyrrolidine (190-192 ℃). [6]

Fragmentations of 4-methylcyclohexylpyrrolidine (deduced from spectra)

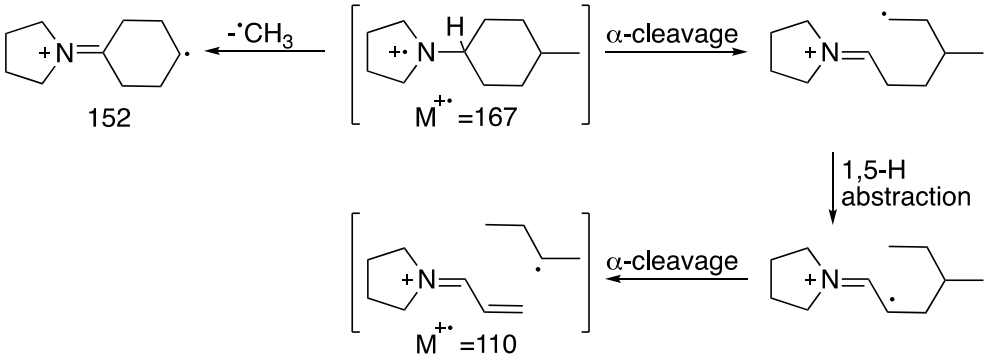
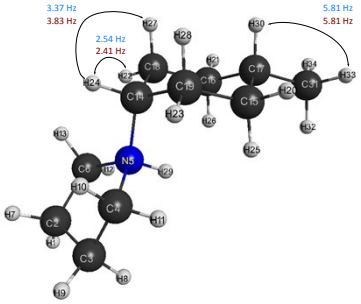


Figure 28. Proposed mass spectrometry fragmentation of 4-methylcyclohexylpyrrolidine

***Coupling constants of conformer 1 of Cis-N-*(4-methylcyclohexyl)-pyrrolidinium, gas phase**



Total nuclear spin-spin coupling J (Hz):

	1	2	3	4	5
1	0.000000D+00				
2	0.135457D+03	0.000000D+00			
3	-0.298171D+01	0.293479D+02	0.000000D+00		
4	0.665547D+01	-0.951630D+00	0.320686D+02	0.000000D+00	
5	0.206507D+01	0.803076D+00	0.130210D+01	0.173989D+01	0.000000D+00
6	0.375744D-01	0.325155D+02	-0.156671D+01	0.316004D+01	0.178717D+01
7	-0.135877D+02	0.132406D+03	-0.362571D+01	0.110791D+00	0.244515D+00
8	0.814348D+01	-0.279825D+01	0.128998D+03	-0.443851D+01	0.899706D-01
9	0.316814D+00	-0.225273D+01	0.136415D+03	0.112264D+01	0.454443D+01
10	-0.623041D+00	0.963152D+00	-0.285549D+01	0.140712D+03	-0.155820D+00
11	0.730685D+00	0.774877D+01	-0.762119D+00	0.143304D+03	0.636763D+00
12	0.905941D+01	-0.132412D+01	0.834206D+00	0.324699D+01	0.347133D+00
13	0.309744D+01	-0.234194D+01	0.240004D+01	-0.674866D-01	0.183944D+00
14	-0.145098D-01	0.938793D+00	0.135524D+01	-0.363752D+00	0.103312D+00
15	-0.292920D-01	0.408656D-02	0.460939D-02	-0.168205D-01	0.197361D+00
16	0.671761D-02	-0.460076D-02	-0.131402D-01	-0.851057D-01	0.226917D+00
17	-0.197137D-01	0.437822D-03	-0.466844D-02	0.159351D-01	-0.460480D-01
18	-0.390351D-01	-0.280148D-03	0.895575D-01	0.115032D+01	0.119360D-01
19	0.417232D+00	0.123377D+00	-0.683096D-02	0.111025D+01	-0.386446D-02
20	-0.113771D+00	-0.306472D-01	-0.335844D-01	-0.127192D-01	-0.150615D-01
21	-0.466533D-01	-0.286856D-01	-0.325851D-01	0.269007D-01	0.124087D-01
22	-0.304598D-01	0.137349D+00	0.716559D-01	-0.278982D+00	0.658983D+00
23	-0.776338D-01	0.622769D-01	0.108579D+00	0.570129D+00	0.600631D+00
24	-0.616131D-01	-0.131564D+00	-0.208280D+00	0.152090D+01	0.527853D+00
25	-0.445184D-01	-0.151532D-01	-0.115268D-01	0.667744D-01	0.129960D+00
26	0.366953D-01	-0.117256D-01	-0.154156D-01	-0.254998D-01	0.192628D+00
27	-0.127868D+00	-0.494326D-01	0.369418D+00	0.541693D+00	0.402316D+01
28	0.240482D-01	0.344191D+00	-0.314430D-01	0.303645D+00	0.407431D+01
29	-0.396880D+00	-0.114678D+00	0.296120D-01	-0.274158D+01	0.503240D+02
30	-0.702727D-01	-0.279324D-01	-0.264405D-01	0.219109D-02	0.192572D+00
31	-0.139042D-01	-0.244006D-02	-0.209056D-02	-0.798267D-02	-0.151431D-02
32	-0.155364D-01	-0.954627D-02	-0.498729D-02	-0.393106D-02	0.226950D-01
33	-0.619798D-01	-0.151083D-01	-0.150601D-01	-0.152733D-01	-0.184012D-02
34	-0.490034D-01	-0.168417D-01	-0.113569D-01	-0.191593D-01	-0.146841D-02

	6	7	8	9	10
6	0.000000D+00				
7	-0.270218D+01	0.000000D+00			
8	0.248744D+00	0.109173D+02	0.000000D+00		
9	0.695554D+01	0.780730D+01	-0.140845D+02	0.000000D+00	
10	0.407333D+00	-0.157497D+00	0.120719D+02	0.548071D+01	0.000000D+00
11	0.656268D+01	-0.840513D+00	0.615452D+01	0.319197D+00	-0.110828D+02
12	0.142087D+03	0.684619D+01	-0.293079D+00	-0.893041D+00	-0.638558D+00
13	0.141990D+03	0.116936D+02	-0.744597D+00	0.573782D-02	-0.105160D+00
14	-0.496500D-01	-0.129924D+00	-0.180196D+00	0.129334D+00	0.267612D+01
15	-0.915871D-01	-0.105773D-01	0.103294D-01	-0.176130D-01	0.312775D-01
16	-0.480543D-01	-0.107356D-01	0.181875D-01	-0.468746D-02	0.127157D+00
17	0.331321D-01	-0.212246D-01	-0.624365D-02	-0.199534D-01	-0.833407D-02
18	0.882102D+00	-0.425362D-01	-0.314562D-01	0.405316D+00	-0.152373D+00
19	0.114026D+01	-0.236835D-01	-0.501602D-01	-0.672534D-01	0.947672D-01

```
20  0.352161D-01 -0.101545D+00 -0.498849D-01 -0.690376D-01 -0.897438D-01
21 -0.235024D-01 -0.911748D-01 -0.659060D-01 -0.127435D+00 -0.120359D-01
22  0.491501D+00 -0.262351D-01 -0.815444D-01 -0.216786D-01 -0.471997D-01
23 -0.301023D+00 -0.616546D-01 -0.348165D-01 -0.213525D-02  0.232837D+00
24  0.205012D+01  0.184118D-01  0.527859D-01 -0.138221D+00  0.106570D+00
25 -0.169843D-01 -0.799141D-01  0.108755D+00 -0.452071D-01 -0.800057D-01
26  0.174279D-01 -0.571533D-01  0.571808D-01 -0.894807D-01  0.514860D-01
27  0.141545D+00 -0.963219D-01 -0.135362D+00  0.364997D+00 -0.756774D-01
28  0.409760D+00 -0.386737D-01 -0.130933D+00 -0.838300D-01 -0.548314D-01
29 -0.266033D+01 -0.680034D+00 -0.314604D-02 -0.779116D+00  0.978080D+01
30 -0.176789D-01 -0.821090D-01 -0.850770D-01 -0.908003D-01 -0.893446D-01
31 -0.938041D-02 -0.190224D-01 -0.501109D-02 -0.185950D-01 -0.180731D-01
32 -0.487440D-02 -0.576951D-01  0.426871D-01 -0.433062D-01 -0.696931D-01
33 -0.136801D-01 -0.730062D-01 -0.285776D-01 -0.633573D-01 -0.726984D-01
34 -0.162207D-01 -0.695142D-01 -0.390496D-01 -0.759000D-01 -0.829518D-01
      11            12            13            14            15
11  0.000000D+00
12  0.328332D+00  0.000000D+00
13 -0.767602D+00 -0.122688D+02  0.000000D+00
14  0.679211D-02  0.343458D+00  0.367406D+01  0.000000D+00
15  0.786378D-01  0.318970D-01  0.570585D-01 -0.202427D+01  0.000000D+00
16  0.313887D-01  0.294173D-01  0.120367D-01 -0.201227D+01 -0.134514D+01
17  0.340264D-02 -0.467814D-02 -0.554859D-02  0.148678D+01  0.322423D+02
18 -0.174139D+00  0.221435D+00  0.513798D+00  0.322086D+02  0.191765D+01
19  0.537170D+00  0.620307D-02 -0.585475D-01  0.321222D+02  0.315375D+02
20 -0.404216D-02 -0.380566D-01 -0.221884D-01  0.790543D+01  0.130695D+03
21 -0.925521D-01 -0.181389D-01 -0.624724D-01  0.796667D+01  0.736953D+01
22 -0.990237D-01  0.599649D+00  0.180680D+00 -0.429764D+01 -0.516836D+00
23  0.480570D+00 -0.774545D-01 -0.433762D-01 -0.429016D+01 -0.219575D+01
24 -0.224910D+00 -0.297811D+00  0.902350D-01  0.141494D+03  0.510929D+01
25  0.244171D+00  0.679662D-01  0.334297D-01  0.183955D+01  0.115504D+03
26  0.316760D-01  0.234709D+00 -0.500952D-01  0.179578D+01  0.216290D+01
27 -0.200868D+00  0.892472D-01 -0.741100D-01  0.524630D+00 -0.287074D+00
28  0.677997D-01 -0.158493D+00  0.393048D-01  0.561323D+00 -0.390123D+01
29  0.486360D+01  0.759651D+01  0.663011D+01 -0.182034D+01  0.414288D-01
30 -0.837611D-01 -0.898058D-01 -0.673594D-01 -0.342574D+00 -0.230271D+01
31 -0.693062D-03 -0.358761D-02 -0.129704D-01 -0.413065D+00 -0.298847D-02
32  0.329364D-01  0.316543D-01 -0.639222D-01  0.934339D-01  0.282128D+01
33 -0.120378D-01 -0.650274D-01 -0.819293D-01 -0.142592D-01  0.248404D+01
34 -0.663515D-01 -0.175771D-01 -0.655933D-01 -0.858472D-02  0.115089D+02
      16            17            18            19            20
16  0.000000D+00
17  0.322436D+02  0.000000D+00
18  0.315131D+02 -0.137247D+01  0.000000D+00
19  0.198604D+01 -0.136756D+01 -0.318672D+00  0.000000D+00
20  0.734526D+01 -0.345162D+01 -0.296044D+00 -0.285150D+01  0.000000D+00
21  0.130779D+03 -0.344484D+01 -0.281946D+01 -0.276394D+00  0.165392D+01
22 -0.227527D+01  0.650697D+01  0.125617D+03  0.592685D+01  0.254820D+00
23 -0.520341D+00  0.653792D+01  0.598465D+01  0.125872D+03  0.280544D+01
24  0.502567D+01 -0.481305D+00 -0.210365D+01 -0.207549D+01  0.658577D-01
25  0.215633D+01 -0.280457D+01 -0.203403D+00 -0.245551D+01 -0.146297D+02
26  0.115147D+03 -0.276257D+01 -0.240539D+01 -0.205666D+00 -0.515924D+00
27 -0.382614D+01  0.173842D+01  0.127217D+03  0.117960D+01 -0.158503D-01
28 -0.295298D+00  0.180226D+01  0.125777D+01  0.126703D+03  0.411138D+01
29 -0.200391D-01  0.578256D-01  0.132911D+01  0.838142D+00 -0.166804D+00
30 -0.225711D+01  0.123298D+03  0.176521D+01  0.180067D+01  0.355417D+01
31 -0.108417D-01  0.346335D+02  0.398508D+01  0.399252D+01  0.163320D+01
32  0.290832D+01 -0.397083D+01 -0.229289D+00 -0.231689D+00 -0.328832D+00
33  0.115337D+02 -0.300877D+01  0.164117D+01  0.680455D-02  0.306268D-01
34  0.243238D+01 -0.301356D+01  0.178492D-02  0.162376D+01 -0.387652D+00
      21            22            23            24            25
21  0.000000D+00
22  0.276613D+01  0.000000D+00
23  0.256561D+00  0.238796D+01  0.000000D+00
24  0.243910D-01  0.253789D+01  0.267363D+01  0.000000D+00
25 -0.515496D+00 -0.102396D+00  0.319429D+01 -0.698745D+00  0.000000D+00
26 -0.147980D+02  0.329847D+01 -0.101792D+00 -0.699321D+00 -0.431322D-01
27  0.416550D+01 -0.155051D+02 -0.562920D-01  0.336635D+01 -0.223415D+00
28 -0.243732D-02 -0.298966D-01 -0.156307D+02  0.321825D+01  0.127207D+02
29 -0.143383D+00 -0.214183D+00 -0.257100D+00  0.874576D+01 -0.209910D-01
```

```
30  0.353771D+01 -0.567497D+00 -0.559879D+00  0.632934D-01  0.978410D+01
31  0.163172D+01  0.418229D+00  0.442555D+00  0.664328D+00  0.256087D+01
32 -0.328446D+00 -0.146185D+00 -0.149038D+00 -0.160675D+00  0.112241D-01
33 -0.385341D+00  0.188847D+00 -0.693811D-01 -0.147977D+00 -0.242571D+00
34  0.295708D-01 -0.684370D-01  0.195442D+00 -0.148135D+00 -0.388697D+00
      26            27            28            29            30
26  0.000000D+00
27  0.126649D+02  0.000000D+00
28 -0.225355D+00  0.521356D+00  0.000000D+00
29 -0.907656D-01 -0.757340D+00 -0.845595D+00  0.000000D+00
30  0.977286D+01 -0.118876D-01 -0.718600D-02 -0.274255D+00  0.000000D+00
31  0.257958D+01 -0.286236D+00 -0.281900D+00 -0.302105D-02 -0.320699D+01
32  0.124225D-01  0.306635D-02  0.354498D-02  0.172732D+00  0.109459D+02
33 -0.386300D+00 -0.212052D+00 -0.131863D-01 -0.223031D-01  0.320452D+01
34 -0.243293D+00 -0.122855D-01 -0.209514D+00 -0.181927D-01  0.326780D+01
      31            32            33            34
31  0.000000D+00
32  0.120187D+03  0.000000D+00
33  0.124289D+03 -0.126041D+02  0.000000D+00
34  0.124259D+03 -0.126102D+02 -0.134589D+02  0.000000D+00
```

***Coupling constants of conformer 1 of Cis-N-*(4-methylcyclohexyl)-pyrrolidinium, SMD:water**

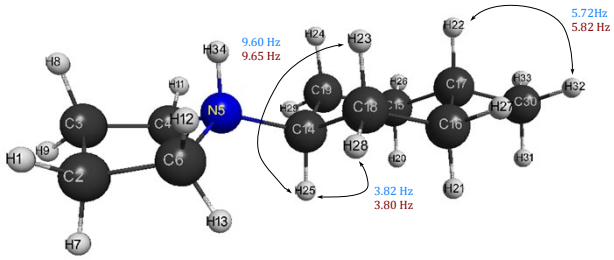
Total nuclear spin-spin coupling J (Hz):

```
     1             2             3             4             5
1   0.000000D+00
2   0.124256D+03  0.000000D+00
3  -0.361254D+01  0.267195D+02  0.000000D+00
4   0.600236D+01 -0.127347D+01  0.295423D+02  0.000000D+00
5   0.174087D+01  0.714405D+00  0.126988D+01  0.161291D+01  0.000000D+00
6  -0.126586D+01  0.302391D+02 -0.180740D+01  0.258630D+01  0.168958D+01
7  -0.130823D+02  0.122115D+03 -0.440601D+01  0.108912D+00  0.320600D+00
8   0.816745D+01 -0.364673D+01  0.120938D+03 -0.565614D+01  0.100111D+00
9   0.399674D+00 -0.278775D+01  0.124565D+03  0.479101D-01  0.424757D+01
10 -0.685130D+00  0.947203D+00 -0.356569D+01  0.132748D+03 -0.668452D+00
11  0.644438D+00  0.771275D+01 -0.144880D+01  0.135388D+03  0.271965D+00
12  0.897943D+01 -0.196241D+01  0.109608D+01  0.334245D+01 -0.301415D-01
13  0.323515D+01 -0.310697D+01  0.209337D+01 -0.123352D+00 -0.341177D+00
14 -0.606185D-01  0.116697D+01  0.161735D+01 -0.287469D+00  0.594783D+00
15 -0.338870D-01 -0.664363D-02  0.874862D-02 -0.467372D-01  0.201209D+00
16  0.523567D-02 -0.429615D-02 -0.142506D-01 -0.938431D-01  0.211467D+00
17 -0.187489D-01  0.303382D-03 -0.488763D-02  0.291361D-01 -0.389046D-01
18 -0.452403D-01 -0.495960D-02  0.910815D-01  0.123636D+01 -0.100518D+00
19  0.417033D+00  0.136587D+00 -0.292056D-01  0.110244D+01 -0.105462D+00
20 -0.105981D+00 -0.301110D-01 -0.311150D-01 -0.139978D-01 -0.871094D-01
21 -0.525396D-01 -0.242755D-01 -0.306017D-01  0.401967D-01 -0.867747D-01
22 -0.222971D-01  0.782910D-01  0.760545D-01 -0.284604D+00  0.714061D+00
23 -0.813050D-01  0.693423D-01  0.448549D-01  0.361539D+00  0.678574D+00
24 -0.519835D-01 -0.138184D+00 -0.247323D+00  0.152551D+01 -0.253971D+00
25 -0.469033D-01 -0.162106D-01 -0.995167D-02  0.123057D-01  0.154995D-01
26  0.268693D-01 -0.851669D-02 -0.135587D-01 -0.129773D-01  0.250055D-01
27 -0.122718D+00 -0.519423D-01  0.339933D+00  0.393654D+00  0.373973D+01
28 -0.118712D-01  0.345499D+00 -0.278037D-01  0.219821D+00  0.377502D+01
29 -0.403469D+00 -0.104707D+00  0.687581D-01 -0.342754D+01  0.497700D+02
30 -0.775223D-01 -0.260788D-01 -0.254423D-01 -0.210992D-01  0.862357D-01
31 -0.133368D-01 -0.291068D-02 -0.257192D-02 -0.993174D-02 -0.152687D-03
32 -0.145443D-01 -0.875544D-02 -0.529978D-02 -0.534663D-02  0.144562D-01
33 -0.594713D-01 -0.141484D-01 -0.143306D-01 -0.154218D-01 -0.279554D-02
34 -0.466304D-01 -0.156411D-01 -0.118232D-01 -0.177583D-01 -0.264759D-02
      6             7             8             9            10
6   0.000000D+00
7  -0.371832D+01  0.000000D+00
8   0.247542D+00  0.102943D+02  0.000000D+00
9   0.626083D+01  0.773223D+01 -0.136555D+02  0.000000D+00
10  0.407612D+00 -0.210679D+00  0.115375D+02  0.533180D+01  0.000000D+00
11  0.631203D+01 -0.891703D+00  0.608297D+01  0.410286D+00 -0.114667D+02
12  0.135161D+03  0.608292D+01 -0.316799D+00 -0.935119D+00 -0.676012D+00
13  0.133643D+03  0.114534D+02 -0.762111D+00 -0.443419D-01 -0.115413D+00
14  0.377967D-01 -0.144228D+00 -0.211738D+00  0.980228D-01  0.263054D+01
15 -0.946496D-01 -0.101272D-01  0.595562D-02 -0.166052D-01  0.235410D-01
```

```
16 -0.590181D-01 -0.117080D-01  0.175883D-01 -0.172110D-01  0.885691D-01
17  0.457204D-01 -0.210353D-01 -0.770873D-02 -0.200799D-01 -0.134185D-01
18  0.994365D+00 -0.497799D-01 -0.367736D-01  0.407749D+00 -0.167265D+00
19  0.123007D+01 -0.237545D-01 -0.525711D-01 -0.719350D-01  0.288330D-01
20  0.480096D-01 -0.995374D-01 -0.470700D-01 -0.730175D-01 -0.923399D-01
21 -0.204554D-01 -0.876991D-01 -0.688323D-01 -0.119315D+00 -0.401501D-01
22  0.323640D+00 -0.238775D-01 -0.796059D-01 -0.289201D-01 -0.445033D-01
23 -0.312274D+00 -0.631776D-01 -0.304227D-01  0.159496D-02  0.189525D+00
24  0.183440D+01  0.699942D-02  0.196944D-01 -0.161238D+00  0.902109D-01
25 -0.759342D-02 -0.781337D-01  0.103651D+00 -0.445018D-01 -0.827144D-01
26  0.102098D-01 -0.613112D-01  0.561677D-01 -0.823325D-01 -0.114269D-01
27  0.104566D+00 -0.945184D-01 -0.128876D+00  0.311558D+00 -0.979186D-01
28  0.297650D+00 -0.345935D-01 -0.130107D+00 -0.866935D-01 -0.401836D-01
29 -0.321772D+01 -0.677291D+00 -0.100400D-01 -0.768895D+00  0.913218D+01
30 -0.283225D-01 -0.820094D-01 -0.817787D-01 -0.913271D-01 -0.873025D-01
31 -0.111593D-01 -0.182622D-01 -0.523100D-02 -0.180454D-01 -0.180914D-01
32 -0.572712D-02 -0.558980D-01  0.382561D-01 -0.431139D-01 -0.681514D-01
33 -0.135047D-01 -0.710198D-01 -0.283587D-01 -0.616462D-01 -0.703802D-01
34 -0.160531D-01 -0.668500D-01 -0.385474D-01 -0.732973D-01 -0.818532D-01
     11       12       13       14       15
11  0.000000D+00
12  0.252976D+00  0.000000D+00
13 -0.833630D+00 -0.126914D+02  0.000000D+00
14  0.449528D-01  0.284052D+00  0.361281D+01  0.000000D+00
15  0.290771D-01  0.293760D-01  0.385752D-01 -0.235952D+01  0.000000D+00
16  0.224045D-01  0.108500D-01  0.237473D-01 -0.233939D+01 -0.141048D+01
17  0.398201D-02 -0.318523D-02 -0.286246D-02  0.153994D+01  0.302805D+02
18 -0.207671D+00  0.188049D+00  0.474451D+00  0.305998D+02  0.211996D+01
19  0.460504D+00 -0.377162D-01 -0.687825D-01  0.305085D+02  0.292797D+02
20 -0.267725D-02 -0.497896D-01 -0.375214D-01  0.724509D+01  0.117681D+03
21 -0.100993D+00 -0.167011D-01 -0.680308D-01  0.730830D+01  0.669884D+01
22 -0.980647D-01  0.466606D+00  0.145770D+00 -0.522608D+01 -0.530170D+00
23  0.348942D+00 -0.771856D-01 -0.435477D-01 -0.521082D+01 -0.282899D+01
24 -0.258160D+00 -0.332547D+00  0.713735D-01  0.135550D+03  0.546650D+01
25  0.231360D+00  0.538184D-01 -0.995446D-02  0.186418D+01  0.112767D+03
26  0.197522D-01  0.220508D+00 -0.566138D-01  0.178827D+01  0.202917D+01
27 -0.192412D+00  0.573434D-01 -0.674803D-01 -0.952068D+00 -0.306559D+00
28  0.816708D-02 -0.183672D+00 -0.114297D-01 -0.935630D+00 -0.462468D+01
29  0.472140D+01  0.739828D+01  0.659258D+01 -0.229559D+01  0.287039D-01
30 -0.767138D-01 -0.859320D-01 -0.682696D-01 -0.339946D+00 -0.350749D+01
31  0.919280D-03 -0.213176D-02 -0.124992D-01 -0.464523D+00 -0.345671D+00
32  0.275308D-01  0.304939D-01 -0.624135D-01  0.662449D-01  0.254655D+01
33 -0.142777D-01 -0.630808D-01 -0.799498D-01 -0.363185D-01  0.222177D+01
34 -0.645731D-01 -0.170702D-01 -0.628942D-01 -0.356056D-01  0.102355D+02
     16       17       18       19       20
16  0.000000D+00
17  0.302465D+02  0.000000D+00
18  0.292199D+02 -0.169522D+01  0.000000D+00
19  0.214481D+01 -0.167552D+01 -0.699671D+00  0.000000D+00
20  0.669742D+01 -0.412687D+01 -0.338565D+00 -0.354200D+01  0.000000D+00
21  0.117684D+03 -0.413403D+01 -0.350364D+01 -0.328798D+00  0.140623D+01
22 -0.290061D+01  0.677824D+01  0.118556D+03  0.573462D+01  0.231433D+00
23 -0.539161D+00  0.678634D+01  0.579862D+01  0.118745D+03  0.287575D+01
24  0.541050D+01 -0.525636D+00 -0.289093D+01 -0.283056D+01  0.460040D-01
25  0.204675D+01 -0.378488D+01 -0.247120D+00 -0.388183D+01 -0.143964D+02
26  0.112682D+03 -0.376856D+01 -0.383715D+01 -0.248023D+00 -0.565584D+00
27 -0.456958D+01  0.178234D+01  0.116318D+03  0.993618D+00 -0.243062D-01
28 -0.311374D+00  0.188962D+01  0.105323D+01  0.116130D+03  0.401461D+01
29  0.187207D-01  0.517686D-01  0.121274D+01  0.854637D+00 -0.116134D+00
30 -0.348941D+01  0.114848D+03  0.165084D+01  0.171280D+01  0.356036D+01
31 -0.353116D+00  0.323093D+02  0.396602D+01  0.397753D+01  0.175134D+01
32  0.255011D+01 -0.486479D+01 -0.239695D+00 -0.240966D+00 -0.350484D+00
33  0.102424D+02 -0.373607D+01  0.138230D+01 -0.802934D-02 -0.559463D-01
34  0.223730D+01 -0.374323D+01 -0.535474D-02  0.137539D+01 -0.439883D+00
     21       22       23       24       25
21  0.000000D+00
22  0.278001D+01  0.000000D+00
23  0.241251D+00  0.213717D+01  0.000000D+00
24  0.772571D-02  0.240522D+01  0.252152D+01  0.000000D+00
25 -0.562491D+00 -0.797964D-01  0.321806D+01 -0.760610D+00  0.000000D+00
```

```
26 -0.145081D+02  0.337075D+01 -0.815634D-01 -0.762149D+00 -0.822597D-01
27  0.416062D+01 -0.155024D+02 -0.114923D+00  0.383227D+01 -0.225168D+00
28 -0.147174D-01 -0.864147D-01 -0.155558D+02  0.368306D+01  0.122491D+02
29 -0.974044D-01 -0.246839D+00 -0.272523D+00  0.870861D+01  0.193259D+00
30  0.359963D+01 -0.601272D+00 -0.588604D+00  0.370905D-01  0.972954D+01
31  0.172319D+01  0.430522D+00  0.450708D+00  0.757163D+00  0.257732D+01
32 -0.352131D+00 -0.152562D+00 -0.154697D+00 -0.155791D+00 -0.681825D-01
33 -0.443926D+00  0.152175D+00 -0.621032D-01 -0.147899D+00 -0.282951D+00
34 -0.562868D-01 -0.600300D-01  0.160058D+00 -0.147716D+00 -0.455952D+00
               26            27            28            29            30
26  0.000000D+00
27  0.122221D+02  0.000000D+00
28 -0.226540D+00  0.345208D+00  0.000000D+00
29  0.184221D+00 -0.787640D+00 -0.826092D+00  0.000000D+00
30  0.974143D+01 -0.716693D-01 -0.692205D-01 -0.201550D+00  0.000000D+00
31  0.263062D+01 -0.350262D+00 -0.344309D+00 -0.139146D-02 -0.357320D+01
32 -0.678382D-01 -0.314241D-01 -0.349745D-01  0.159048D+00  0.109605D+02
33 -0.447039D+00 -0.219997D+00 -0.149108D-01 -0.246699D-01  0.324138D+01
34 -0.281425D+00 -0.157941D-01 -0.217172D+00 -0.223172D-01  0.323472D+01
               31            32            33            34
31  0.000000D+00
32  0.111468D+03  0.000000D+00
33  0.112325D+03 -0.131850D+02  0.000000D+00
34  0.112302D+03 -0.131993D+02 -0.135754D+02  0.000000D+00
```

***Coupling constants of conformer 1 of trans-N-*(4-methylcyclohexyl)-pyrrolidinium, gas phase**




```
Total nuclear spin-spin coupling J (Hz):
      1             2             3             4             5
1   0.000000D+00
2   0.137744D+03  0.000000D+00
3  -0.179872D+01  0.409379D+02  0.000000D+00
4   0.580445D+01 -0.240222D+01  0.384535D+02  0.000000D+00
5   0.186040D+01  0.150045D+01  0.406150D+00  0.384852D+01  0.000000D+00
6   0.156203D+01  0.440065D+02  0.348213D+00  0.309343D+01  0.425609D+01
7  -0.154535D+02  0.138259D+03 -0.182913D+01  0.176059D+00  0.252979D+00
8   0.834272D+01 -0.119344D+01  0.136536D+03 -0.237651D+01  0.101619D+00
9   0.102129D+00 -0.112489D+01  0.136212D+03  0.283072D+01  0.413846D+01
10 -0.868600D+00  0.830185D+00 -0.132990D+01  0.149629D+03  0.546971D+00
11  0.546990D+00  0.707627D+01  0.895187D-01  0.149872D+03  0.124389D+01
12  0.931095D+01 -0.246532D+00  0.105712D+01  0.285526D+01  0.985008D+00
13  0.283871D+01 -0.144706D+01  0.207217D+01  0.143799D+00  0.812371D+00
14 -0.122433D+00  0.677400D+00  0.193971D+01  0.210351D+00  0.235214D+01
15  0.420968D-01  0.673634D-01 -0.172231D-01  0.382153D-01  0.123418D+01
16 -0.385669D-01 -0.210891D-01  0.113026D+00  0.148967D+00  0.126662D+01
17 -0.460139D-01  0.180951D-01  0.196724D-02  0.564041D-01 -0.155353D+00
18 -0.704448D-01  0.624087D-02  0.676224D-01  0.125987D+01 -0.511804D-01
19  0.367161D+00  0.104513D+00  0.236751D-01  0.135916D+01 -0.344909D-01
20 -0.185613D+00 -0.415132D-01 -0.210332D-01 -0.285136D-01 -0.141431D+00
21 -0.136890D+00 -0.177859D-01 -0.413169D-01 -0.635164D-01 -0.134338D+00
22 -0.129247D+00 -0.312730D-01 -0.276864D-01 -0.371054D-01  0.242235D-01
23 -0.854232D-01 -0.185201D-01 -0.559507D-01 -0.164413D+00  0.102163D+01
24 -0.207631D+00 -0.243569D-01  0.251814D-01 -0.144433D-01  0.916068D+00
```

```
25 -0.218555D+00 -0.112044D+00 -0.188200D+00  0.993958D+00  0.157116D+01
26 -0.184225D+00 -0.106409D-01  0.203676D-01 -0.717498D-01  0.452234D+00
27 -0.140861D+00  0.109714D-01 -0.160241D-02  0.224750D+00  0.406797D+00
28 -0.730161D-01  0.181653D+00  0.134298D-02 -0.333912D+00  0.276780D+00
29 -0.214799D+00  0.198556D-01  0.153322D+00  0.590650D+00  0.225479D+00
30 -0.203968D-01 -0.911114D-02 -0.975065D-02 -0.891146D-02  0.261481D+00
31 -0.118330D+00 -0.213869D-01 -0.240601D-01 -0.266671D-01 -0.159485D-01
32 -0.111169D+00 -0.210627D-01 -0.185963D-01  0.155953D-01 -0.903971D-02
33 -0.134869D+00 -0.180755D-01 -0.223691D-01 -0.177275D-01 -0.980958D-02
34 -0.500972D+00 -0.769696D-01  0.726872D-01 -0.985418D+00  0.502517D+02
      6            7            8            9            10
6  0.000000D+00
7 -0.477313D+00  0.000000D+00
8  0.706846D-01  0.106007D+02  0.000000D+00
9  0.628515D+01  0.784934D+01 -0.159610D+02  0.000000D+00
10  0.267242D+00  0.860070D-01  0.118849D+02  0.536274D+01  0.000000D+00
11  0.618664D+01 -0.110139D+01  0.608994D+01  0.144216D+00 -0.128694D+02
12  0.151053D+03  0.643873D+01 -0.302925D+00 -0.116856D+01 -0.927983D+00
13  0.150186D+03  0.118218D+02 -0.104224D+01 -0.237443D+00  0.502823D-01
14 -0.172029D+00 -0.133090D+00 -0.238045D+00  0.972420D-01  0.217396D+01
15  0.109679D+00 -0.899046D-02 -0.331298D-01 -0.371744D-01  0.963020D-03
16 -0.286944D-03 -0.287298D-01 -0.411970D-01  0.164028D+00 -0.640083D-01
17  0.799911D-01 -0.367945D-01 -0.324864D-01 -0.525633D-01 -0.123595D-01
18  0.123712D+01 -0.590121D-01 -0.418967D-01  0.339050D+00 -0.153194D+00
19  0.119759D+01 -0.450187D-01 -0.574473D-01 -0.873205D-01  0.334140D-01
20 -0.518354D-01 -0.645997D-01 -0.160033D+00 -0.116672D+00  0.123410D+00
21 -0.409588D-03 -0.455671D-01 -0.173638D+00 -0.173662D+00  0.352022D-01
22 -0.404320D-01 -0.156119D+00 -0.641041D-01 -0.147820D+00 -0.160675D+00
23 -0.804462D-01 -0.213181D+00  0.213460D-01 -0.194092D+00 -0.155174D+00
24 -0.172454D+00 -0.215490D+00  0.226431D-01 -0.175377D+00 -0.124348D+00
25  0.143383D+01  0.726752D-01 -0.103612D+00 -0.230437D+00  0.523919D+00
26  0.251737D+00 -0.158012D+00 -0.126170D+00 -0.143928D+00 -0.704601D-01
27 -0.689255D-01 -0.147294D+00 -0.156648D+00 -0.131056D+00 -0.197543D+00
28  0.478777D+00 -0.626193D-01 -0.162314D+00 -0.186024D+00 -0.136336D+00
29 -0.329937D+00 -0.123487D+00 -0.880310D-01 -0.432926D-01  0.558606D+00
30 -0.935988D-02 -0.235477D-01 -0.245676D-01 -0.919454D-02 -0.208306D-01
31 -0.246345D-01 -0.685927D-01 -0.119933D+00 -0.108491D+00 -0.400880D-01
32 -0.243856D-01 -0.110430D+00 -0.113351D+00 -0.136963D+00 -0.138096D+00
33  0.661942D-02 -0.118066D+00 -0.103184D+00 -0.110088D+00 -0.949097D-01
34 -0.129936D+01 -0.101718D+01  0.285748D+00 -0.102931D+01  0.910930D+01
      11           12           13           14           15
11  0.000000D+00
12  0.700096D-01  0.000000D+00
13 -0.106054D+01 -0.141851D+02  0.000000D+00
14 -0.660912D-01  0.456078D+00  0.313036D+01  0.000000D+00
15  0.174267D+00 -0.579790D-01 -0.373509D-01 -0.958092D+00  0.000000D+00
16 -0.738500D-01  0.141278D+00  0.155139D-01 -0.945309D+00 -0.292772D+01
17  0.271647D-01  0.582295D-02  0.362807D-04  0.183287D+01  0.432793D+02
18 -0.234325D+00  0.151055D+00  0.247222D+00  0.433708D+02  0.257392D+01
19  0.484284D+00 -0.129623D+00 -0.101102D+00  0.434217D+02  0.404204D+02
20 -0.618120D-01 -0.174769D+00  0.527495D-01  0.194757D+01  0.132227D+03
21 -0.174479D+00 -0.864626D-01  0.176405D+00  0.196121D+01  0.196974D+01
22 -0.293715D-01 -0.563451D-01 -0.148184D+00 -0.204213D+00 -0.945946D+00
23 -0.404044D-01  0.351340D+00 -0.147236D+00 -0.235586D+01 -0.249069D+00
24  0.489551D+00 -0.792727D-01 -0.234371D+00 -0.250110D+01 -0.271295D+01
25 -0.323034D+00 -0.425602D+00  0.497931D+00  0.148742D+03  0.779486D+00
26  0.407537D-02 -0.219520D+00 -0.164454D+00  0.984603D+01  0.134802D+03
27 -0.252734D+00 -0.324203D-01 -0.432705D-01  0.980993D+01  0.728065D+01
28 -0.249368D+00  0.929013D+00  0.563915D+00 -0.258335D+01 -0.456801D+00
29  0.744210D+00 -0.238791D+00 -0.126151D+00 -0.253942D+01 -0.264583D+01
30 -0.422183D-03  0.186013D-02 -0.176785D-01 -0.179247D+00  0.456152D+00
31 -0.104015D+00 -0.112024D+00 -0.223840D-01  0.499100D-01  0.225646D+01
32 -0.130620D+00 -0.846873D-01 -0.835835D-01 -0.628941D-01  0.108052D+02
33 -0.700812D-01 -0.138203D+00 -0.129009D+00 -0.633239D-01  0.205086D+01
34  0.446161D+01  0.725158D+01  0.601624D+01 -0.280894D+00 -0.170344D+00
      16           17           18           19           20
16  0.000000D+00
17  0.433532D+02  0.000000D+00
18  0.400500D+02 -0.216798D+01  0.000000D+00
19  0.249932D+01 -0.214927D+01 -0.254946D+01  0.000000D+00
```

```
20  0.199745D+01 -0.132659D+01 -0.136228D+00 -0.100351D+01  0.000000D+00
21  0.132097D+03 -0.129585D+01 -0.101223D+01 -0.132163D+00  0.326811D+00
22 -0.918833D+00  0.133319D+03  0.177544D+01  0.177420D+01  0.983400D+01
23 -0.276764D+01  0.147671D+01  0.132759D+03  0.190125D+01 -0.436781D+00
24 -0.243552D+00  0.141201D+01  0.178357D+01  0.132598D+03  0.110073D+02
25  0.799142D+00 -0.118890D+00 -0.755430D+00 -0.661814D+00  0.412346D+00
26  0.726680D+01 -0.190802D+01 -0.430341D+00 -0.106650D+01 -0.156606D+02
27  0.134696D+03 -0.191906D+01 -0.116789D+01 -0.440948D+00 -0.649038D+00
28 -0.264043D+01  0.579505D+01  0.132073D+03  0.586648D+01 -0.235231D+00
29 -0.466745D+00  0.577089D+01  0.587902D+01  0.131873D+03  0.350181D+01
30  0.517282D+00  0.425033D+02  0.487063D+01  0.485570D+01  0.208604D+01
31  0.249158D+01 -0.205634D+01 -0.216724D+00 -0.227003D+00  0.333077D+00
32  0.182462D+01 -0.116428D+01 -0.483946D-01  0.156233D+01 -0.581569D+00
33  0.107839D+02 -0.118254D+01  0.159114D+01 -0.284451D-01 -0.227044D+00
34 -0.157103D+00 -0.265236D-02  0.109930D+01  0.582483D+00 -0.252817D+00
      21            22            23            24            25
21  0.000000D+00
22  0.976382D+01  0.000000D+00
23  0.109982D+02  0.385278D+00  0.000000D+00
24 -0.434410D+00  0.379788D+00  0.375606D+00  0.000000D+00
25  0.401941D+00 -0.379788D+00  0.959802D+01  0.965958D+01  0.000000D+00
26 -0.651463D+00  0.338219D+01 -0.141011D+00  0.391874D+01 -0.739414D+00
27 -0.156967D+02  0.340116D+01  0.383865D+01 -0.148023D+00 -0.740988D+00
28  0.344033D+01 -0.689447D+00 -0.133924D+02 -0.696592D+00  0.381032D+01
29 -0.234114D+00 -0.689338D+00 -0.691455D+00 -0.133585D+02  0.396660D+01
30  0.209987D+01 -0.207260D+01 -0.261987D+00 -0.266961D+00  0.633365D-02
31  0.340934D+00  0.107551D+02 -0.156536D+00 -0.146306D+00  0.417888D-01
32 -0.244268D+00  0.334049D+01 -0.753592D-01 -0.335389D+00 -0.206651D+00
33 -0.575350D+00  0.306453D+01 -0.335079D+00 -0.778630D-01 -0.202397D+00
34 -0.280288D+00  0.111956D+00  0.726954D+00  0.669067D+00  0.820639D+01
      26            27            28            29            30
26  0.000000D+00
27  0.173324D+01  0.000000D+00
28 -0.264346D+00  0.326101D+01  0.000000D+00
29  0.323619D+01 -0.258075D+00  0.210456D+01  0.000000D+00
30  0.143789D+01  0.140143D+01  0.156206D+00  0.145919D+00  0.000000D+00
31 -0.330770D+00 -0.315354D+00 -0.240153D+00 -0.235466D+00  0.125275D+03
32 -0.501895D+00  0.338879D+00 -0.156626D+00 -0.736355D-01  0.126196D+03
33  0.345414D+00 -0.507009D+00 -0.608046D-01 -0.146449D+00  0.126231D+03
34 -0.264014D+00 -0.220011D+00 -0.158208D+00 -0.275396D+00 -0.531657D-01
      31            32            33            34
31  0.000000D+00
32 -0.146257D+02  0.000000D+00
33 -0.146278D+02 -0.151601D+02  0.000000D+00
34 -0.178868D+00 -0.128702D+00 -0.135714D+00  0.000000D+00
```

***Coupling constants of conformer 1 of Trans-N-*(4-methylcyclohexyl)-pyrrolidinium, SMD:water**

Total nuclear spin-spin coupling J (Hz):

```
        1             2             3             4             5
1   0.000000D+00
2   0.124308D+03  0.000000D+00
3  -0.359166D+01  0.267488D+02  0.000000D+00
4   0.605036D+01 -0.124301D+01  0.295737D+02  0.000000D+00
5   0.174796D+01  0.710622D+00  0.126895D+01  0.155266D+01  0.000000D+00
6  -0.120591D+01  0.302755D+02 -0.179533D+01  0.258547D+01  0.161851D+01
7  -0.130834D+02  0.122114D+03 -0.439972D+01  0.115243D+00  0.303906D+00
8   0.811038D+01 -0.364186D+01  0.121009D+03 -0.566132D+01  0.112188D+00
9   0.397161D+00 -0.278464D+01  0.124678D+03  0.603172D-01  0.424796D+01
10 -0.676683D+00  0.972201D+00 -0.359071D+01  0.132644D+03 -0.660891D+00
11  0.660872D+00  0.771066D+01 -0.140433D+01  0.135989D+03  0.292386D+00
12  0.898108D+01 -0.195862D+01  0.104565D+01  0.331700D+01 -0.182704D-01
13  0.319585D+01 -0.310403D+01  0.213650D+01 -0.106392D+00 -0.299357D+00
14 -0.542959D-01  0.116878D+01  0.162962D+01 -0.457148D+00  0.895826D+00
15  0.704513D-01  0.137109D+00 -0.184100D-01  0.149559D+00  0.126337D+01
16 -0.185765D-01 -0.262633D-01  0.139530D+00  0.120565D+00  0.127943D+01
17 -0.274704D-01  0.154537D-01  0.115353D-01  0.860323D-01 -0.181885D+00
18 -0.488698D-01  0.195036D-02  0.713686D-01  0.128721D+01 -0.216871D+00
19  0.422284D+00  0.129604D+00 -0.639313D-02  0.119090D+01 -0.243839D+00
20 -0.863607D-01 -0.319725D-01 -0.102530D-01 -0.278558D-01 -0.148254D+00
```

```
21 -0.589363D-01 -0.847583D-02 -0.269642D-01 -0.414108D-01 -0.147248D+00
22 -0.550750D-01 -0.164017D-01 -0.140907D-01 -0.219951D-01  0.277370D-01
23 -0.265535D-01 -0.244355D-02 -0.365285D-01 -0.170333D+00  0.115706D+01
24 -0.102013D+00 -0.123331D-01  0.380485D-01 -0.663029D-01  0.108133D+01
25 -0.599030D-01 -0.133309D+00 -0.240605D+00  0.139525D+01 -0.129796D+00
26 -0.795408D-01  0.502196D-03  0.374490D-01 -0.468449D-01  0.354550D+00
27 -0.624745D-01  0.251943D-01  0.171776D-01  0.223015D+00  0.323615D+00
28 -0.278118D-01  0.117879D+00  0.441381D-01 -0.306767D+00  0.402848D+00
29 -0.813135D-01  0.375742D-01  0.982830D-01  0.375472D+00  0.366024D+00
30 -0.550064D-02 -0.584405D-02 -0.534573D-02 -0.738772D-02  0.263336D+00
31 -0.517111D-01 -0.108763D-01 -0.112400D-01 -0.126598D-01 -0.976383D-02
32 -0.467445D-01 -0.836768D-02 -0.761898D-02  0.219983D-01 -0.689872D-02
33 -0.587732D-01 -0.688672D-02 -0.917650D-02 -0.789253D-02 -0.704608D-02
34 -0.417309D+00 -0.111022D+00  0.573165D-01 -0.329513D+01  0.499677D+02
         6             7             8             9            10
6   0.000000D+00
7  -0.374853D+01  0.000000D+00
8   0.258675D+00  0.103311D+02  0.000000D+00
9   0.631757D+01  0.768313D+01 -0.136268D+02  0.000000D+00
10  0.409645D+00 -0.207510D+00  0.115231D+02  0.530739D+01  0.000000D+00
11  0.634312D+01 -0.889443D+00  0.601852D+01  0.404912D+00 -0.114594D+02
12  0.135396D+03  0.615225D+01 -0.321713D+00 -0.940188D+00 -0.678449D+00
13  0.133757D+03  0.114563D+02 -0.761161D+00 -0.414682D-01 -0.118623D+00
14 -0.154247D+00 -0.145570D+00 -0.215027D+00  0.115126D+00  0.269416D+01
15  0.710693D-01  0.346353D-02 -0.163932D-01 -0.148730D-01 -0.818927D-02
16  0.691841D-01 -0.162641D-01 -0.239791D-01  0.198500D+00 -0.565585D-01
17  0.103521D+00 -0.216323D-01 -0.190224D-01 -0.337045D-01 -0.103615D-01
18  0.955538D+00 -0.468914D-01 -0.373159D-01  0.418669D+00 -0.193693D+00
19  0.124974D+01 -0.170522D-01 -0.516311D-01 -0.684534D-01  0.285464D-01
20 -0.343166D-01 -0.338702D-01 -0.670979D-01 -0.531753D-01  0.459177D-01
21 -0.321581D-02 -0.211720D-01 -0.756846D-01 -0.846852D-01  0.292867D-01
22 -0.241025D-01 -0.678206D-01 -0.279202D-01 -0.634778D-01 -0.740174D-01
23 -0.135238D+00 -0.895344D-01  0.202075D-01 -0.685146D-01 -0.714545D-01
24 -0.174286D+00 -0.850714D-01  0.906568D-02 -0.734301D-01 -0.547810D-01
25  0.180642D+01  0.915443D-02  0.957551D-02 -0.156201D+00  0.891581D-01
26  0.242660D+00 -0.691108D-01 -0.549835D-01 -0.670098D-01 -0.323932D-01
27 -0.415463D-01 -0.650324D-01 -0.714228D-01 -0.397331D-01 -0.817673D-01
28  0.311181D+00 -0.263510D-01 -0.765850D-01 -0.616636D-01 -0.326430D-01
29 -0.311246D+00 -0.646126D-01 -0.399643D-01 -0.583851D-02  0.176575D+00
30 -0.100371D-01 -0.110780D-01 -0.113817D-01  0.598731D-02 -0.136700D-01
31 -0.115101D-01 -0.308598D-01 -0.513597D-01 -0.476847D-01 -0.172844D-01
32 -0.106645D-01 -0.477098D-01 -0.492955D-01 -0.602219D-01 -0.597890D-01
33  0.164985D-01 -0.523238D-01 -0.440653D-01 -0.468988D-01 -0.416375D-01
34 -0.313192D+01 -0.692474D+00 -0.401341D-01 -0.787723D+00  0.940259D+01
              11            12            13            14            15
11  0.000000D+00
12  0.241551D+00  0.000000D+00
13 -0.839900D+00 -0.127320D+02  0.000000D+00
14  0.366259D-01  0.367188D+00  0.369636D+01  0.000000D+00
15  0.144787D+00 -0.491518D-01 -0.262588D-01 -0.585195D+00  0.000000D+00
16 -0.618206D-01  0.112470D+00 -0.101822D-01 -0.594981D+00 -0.104254D+01
17  0.335935D-01  0.139592D-01  0.843525D-02  0.154753D+01  0.303617D+02
18 -0.253045D+00  0.162741D+00  0.474700D+00  0.313512D+02  0.140164D+01
19  0.495673D+00 -0.121784D+00 -0.122658D+00  0.312168D+02  0.290358D+02
20 -0.349201D-01 -0.688496D-01  0.345852D-01  0.209006D+01  0.114499D+03
21 -0.733686D-01 -0.505015D-01  0.683133D-01  0.213130D+01  0.220478D+01
22 -0.149951D-01 -0.242285D-01 -0.672754D-01 -0.283262D+00 -0.363559D+01
23 -0.198743D-02  0.116467D+00 -0.876972D-01 -0.558418D+01 -0.291205D+00
24  0.161683D+00 -0.165502D-01 -0.133240D+00 -0.562959D+01 -0.445210D+01
25 -0.242071D+00 -0.320790D+00  0.771745D-01  0.132070D+03  0.106513D+01
26  0.359948D-03 -0.996991D-01 -0.575059D-01  0.948956D+01  0.118043D+03
27 -0.127449D+00 -0.173332D-01 -0.180749D-01  0.948323D+01  0.738130D+01
28 -0.760162D-01  0.505832D+00  0.152941D+00 -0.523128D+01 -0.407335D+00
29  0.382380D+00 -0.630478D-01 -0.363833D-01 -0.524420D+01 -0.418288D+01
30  0.624847D-02  0.860926D-02 -0.122170D-01 -0.394322D+00 -0.128255D+00
31 -0.432625D-01 -0.489634D-01 -0.101525D-01  0.523124D-01  0.253163D+01
32 -0.531128D-01 -0.355042D-01 -0.342455D-01 -0.488742D-01  0.102007D+02
33 -0.283979D-01 -0.574059D-01 -0.539809D-01 -0.486205D-01  0.217147D+01
34  0.468128D+01  0.742588D+01  0.665764D+01 -0.278802D+01 -0.216229D+00
        16            17            18            19            20
```

```
16  0.000000D+00
17  0.303330D+02  0.000000D+00
18  0.291647D+02 -0.177482D+01  0.000000D+00
19  0.133707D+01 -0.178201D+01 -0.857181D+00  0.000000D+00
20  0.222513D+01 -0.391274D+01 -0.200800D+00 -0.405874D+01  0.000000D+00
21  0.114555D+03 -0.388226D+01 -0.406642D+01 -0.195937D+00 -0.844743D-01
22 -0.361984D+01  0.114995D+03  0.183672D+01  0.182797D+01  0.982441D+01
23 -0.446164D+01  0.185752D+01  0.115715D+03  0.209035D+01 -0.232628D+00
24 -0.283726D+00  0.177942D+01  0.200152D+01  0.115948D+03  0.111618D+02
25  0.111098D+01 -0.172329D+00 -0.257829D+01 -0.250150D+01 -0.477630D-01
26  0.740539D+01 -0.395268D+01 -0.418229D+00 -0.343875D+01 -0.138489D+02
27  0.117948D+03 -0.397012D+01 -0.347484D+01 -0.427329D+00 -0.523895D+00
28 -0.413465D+01  0.696426D+01  0.118775D+03  0.606126D+01 -0.701920D-01
29 -0.416493D+00  0.692064D+01  0.607603D+01  0.118828D+03  0.360399D+01
30 -0.127153D+00  0.322629D+02  0.421389D+01  0.421112D+01  0.251375D+01
31  0.254338D+01 -0.482120D+01 -0.250387D+00 -0.250194D+00 -0.835734D-01
32  0.215447D+01 -0.374170D+01 -0.608479D-01  0.133197D+01 -0.475674D+00
33  0.101830D+02 -0.374249D+01  0.133251D+01 -0.611043D-01 -0.305847D+00
34 -0.213116D+00  0.676081D-02  0.144578D+01  0.975696D+00 -0.967025D-01
        21            22            23            24            25
21  0.000000D+00
22  0.978462D+01  0.000000D+00
23  0.112039D+02 -0.769598D-01  0.000000D+00
24 -0.230983D+00 -0.803124D-01 -0.752678D-01  0.000000D+00
25 -0.517947D-01 -0.211128D+00  0.964968D+01  0.968737D+01  0.000000D+00
26 -0.526201D+00  0.338658D+01  0.585788D-02  0.390319D+01 -0.663046D+00
27 -0.138289D+02  0.340270D+01  0.383364D+01  0.135142D-02 -0.665153D+00
28  0.354184D+01 -0.597436D+00 -0.127945D+02 -0.558855D+00  0.375931D+01
29 -0.701356D-01 -0.599635D+00 -0.559008D+00 -0.126953D+02  0.389056D+01
30  0.251159D+01 -0.356060D+01 -0.341432D+00 -0.346725D+00  0.212979D-01
31 -0.829021D-01  0.109813D+02 -0.227349D-01 -0.203645D-01  0.165176D-01
32 -0.304972D+00  0.324732D+01 -0.170632D-01 -0.220079D+00 -0.904535D-01
33 -0.474659D+00  0.322639D+01 -0.219403D+00 -0.157362D-01 -0.893523D-01
34 -0.116847D+00  0.429625D-01  0.223619D+00  0.203731D+00  0.853865D+01
        26            27            28            29            30
26  0.000000D+00
27  0.170547D+01  0.000000D+00
28  0.504088D-01  0.323613D+01  0.000000D+00
29  0.321267D+01  0.575898D-01  0.181101D+01  0.000000D+00
30  0.177476D+01  0.176090D+01  0.253722D+00  0.237587D+00  0.000000D+00
31 -0.344088D+00 -0.344550D+00 -0.140116D+00 -0.137939D+00  0.111390D+03
32 -0.414425D+00 -0.504226D-01 -0.450836D-01  0.890587D-01  0.112334D+03
33 -0.497043D-01 -0.417136D+00  0.937446D-01 -0.424154D-01  0.112356D+03
34 -0.151113D+00 -0.132438D+00 -0.246344D+00 -0.273304D+00 -0.412427D-01
        31            32            33            34
31  0.000000D+00
32 -0.131917D+02  0.000000D+00
33 -0.132009D+02 -0.135635D+02  0.000000D+00
34 -0.809192D-01 -0.583564D-01 -0.609614D-01  0.000000D+00
```

Determination of chemical shift using (Gauge Including Atomic Orbitals (GIAO)

Theoretical NMR chemical shift (CS) of the 4-methyl of the two isomers was determined by the difference between average GIAO (gauge including atomic orbitals) 1H IMS (isotopic magnetic shielding) of the 4-methyl and the average GIAO 1H of TMS:

$$CS_x = IMS_{TMS} - IMS_x$$

Gas phase Determination of chemical shifts

TMS	Isotopic IMS	
0 Si	412.1809	
1 C	191.7893	
2 C	191.7963	Average C = 191.7838
3 C	191.7739	
4 C	191.7757	
5 H	31.7544	
6 H	31.7563	
7 H	31.7551	
8 H	31.7552	
9 H	31.7543	
10 H	31.7562	
11 H	31.7558	Average H = 31.7555417
12 H	31.7554	
13 H	31.7566	
14 H	31.7549	
15 H	31.7565	
16 H	31.7558	

Trans-4-methyl

Trans CH_3—	IMS	δ ppm = IMS_{TMS}- IMS_x	
30 C	170.5686	21.2152	
31 H	30.9031	0.85244167	Average δH = 1.2157 ppm
32 H	30.3505	1.40504167	
33 H	30.3657	1.38984167	

Cis-4-methyl

Cis CH_3—	IMS	δ ppm = IMS_{TMS}- IMS_x	
31 C	169.4167	22.3671	
32 H	31.0123	0.74324167	Average δH = 1.18480 ppm
33 H	30.3515	1.40404167	
34 H	30.3484	1.40714167	

Difference in the 4-methyl-chemical shift = 0.03 ppm

SMD:water Determination of chemical shifts

TMS	Isotopic IMS	
0 Si	342.6735	
1 C	187.8949	
2 C	187.8993	Average C = 187.899
3 C	187.9006	
4 C	187.9012	
5 H	31.6273	
6 H	31.6263	
7 H	31.6262	
8 H	31.6269	
9 H	31.6249	Average H = 31.62613
10 H	31.6267	
11 H	31.6259	
12 H	31.6258	
13 H	31.6261	
14 H	31.6256	
15 H	31.6256	
16 H	31.6265	

Trans-methyl

Trans CH_3—	IMS	δ ppm = IMS_{TMS}—IMS_x	
30 C	165.4835	22.4155	
31 H	31.1244	0.50173	Average δH = 0.8031ppm
32 H	30.6704	0.95573	
33 H	30.6741	0.95203	

Cis-methyl

Cis CH_3—	IMS	δ ppm = IMS_{TMS}—IMS_x	
31 C	164.8508	23.0482	Average δH = 0.83763 ppm
32 H	31.062	0.56413	
33 H	30.6515	0.97463	
34 H	30.652	0.97413	

Difference in the 4-methyl-chemical shift = 0.03 ppm
Experimental value in D_2O = 0.04 ppm