Synthesis and Characterization of Modified Polyisobutylene Succinimide Dispersants

Yulin Wang

May 11, 2010

Outline

- Introduction
  - Dispersants
- Objectives
  - Synthesis of modified PIBSI
  - Characterization of modified PIBSI
- Experimental Results
  - Model reactions
  - ^{1}H NMR spectra of PIBSI and modified PIBSI
- Future Work
- Acknowledgements

Two Major Problems

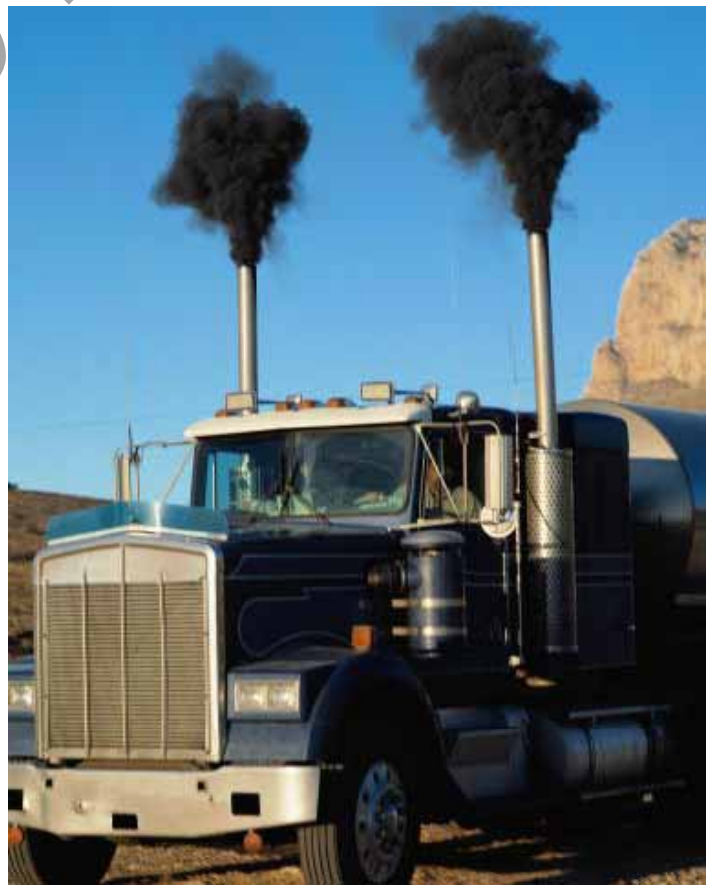
Sludge Formation

→ Engine Failure

OIL SLUDGE coats the inside of a BMW engine. Photo by M. Kline

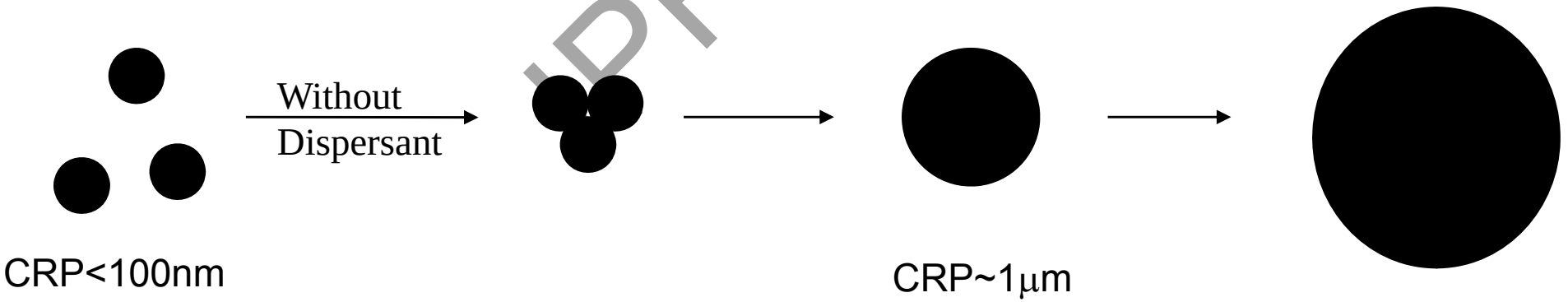
Particle Emission

→ Health Problem



Carbon Deposits

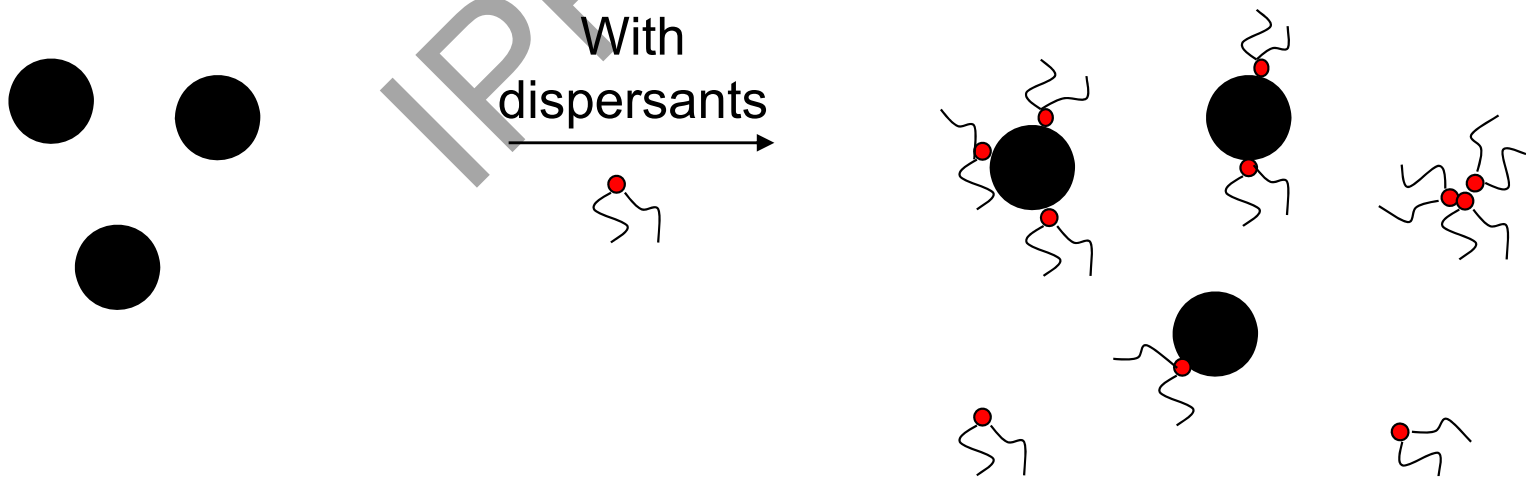
- During normal operation, the engine generates a lot of Ultrafine Particles (UFPs) which have a diameter smaller than 100 nm.
- UFPs are mostly carbon-rich.



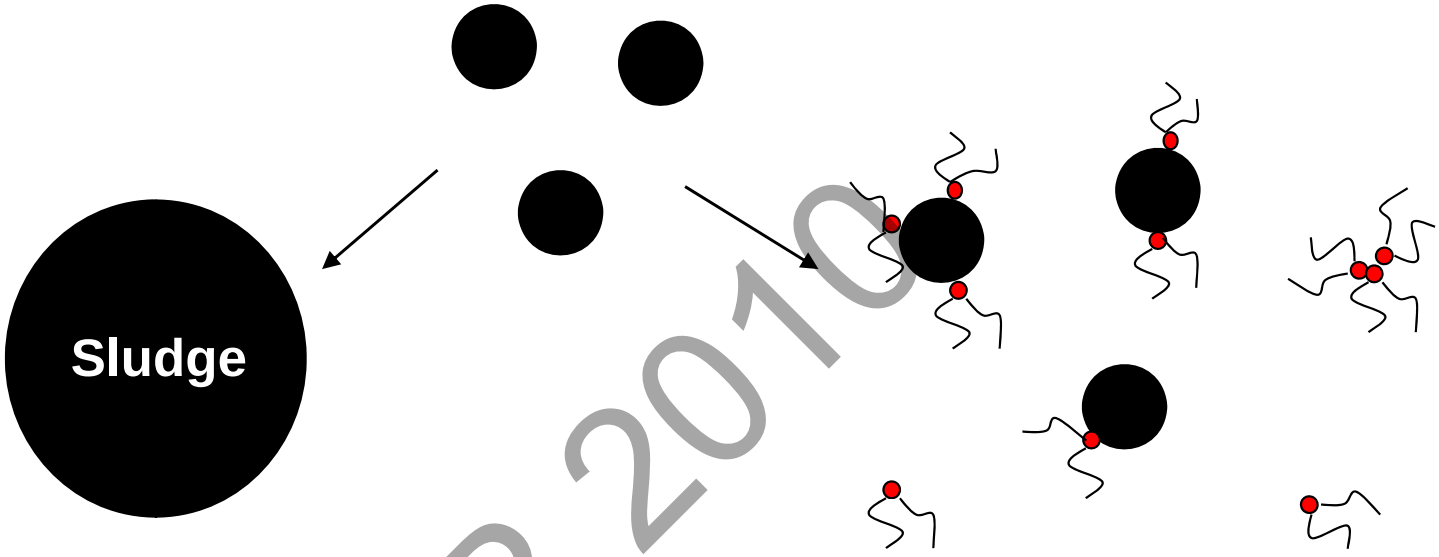
High degree of aggregation

Dispersants

- Dispersants are amphiphilic. They are composed of two long non-polar chains and a polar head.
- Dispersants are used in engine oils to prevent the coagulation of carbon deposits which might block oil flow. They help to stabilize small colloidal particles.



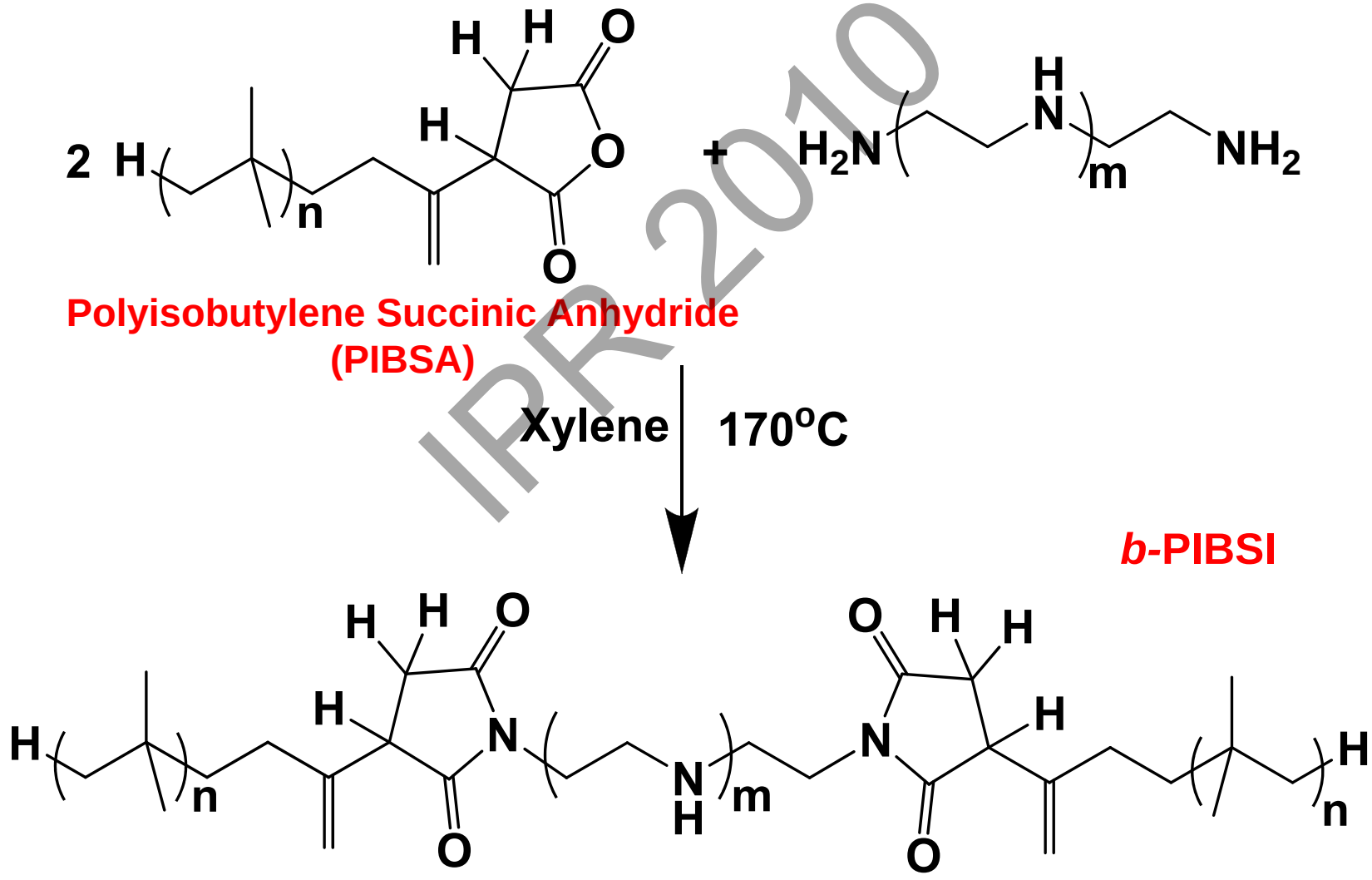
Dispersants



Without Dispersants

With Dispersants

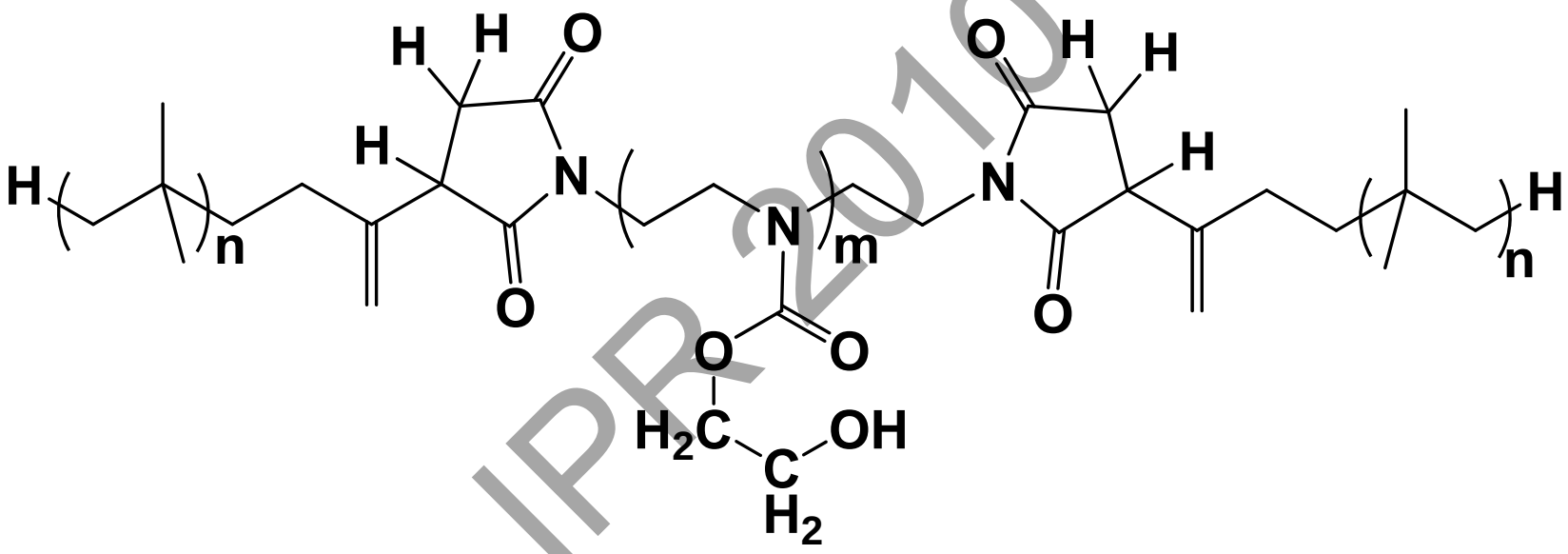
bis Polyisobutylene Succinimide (*b*-PIBSI)



Polyamines used to Synthesize PIBSI

DETA	**H_2N-CH_2CH_2-NH-CH_2CH_2-NH_2** **Diethylenetriamine** **~99%**
TEPA	**H_2N-$(CH_2CH_2$-NH$)_3$-CH_2CH_2-NH_2** **Tetraethylenepentamine** **~89%**
PEHA	**H_2N-$(CH_2CH_2$-NH$)_4$-CH_2CH_2-NH_2** **Pentaethyelenehexamine** **~86%**

Modified PIBSI Dispersant

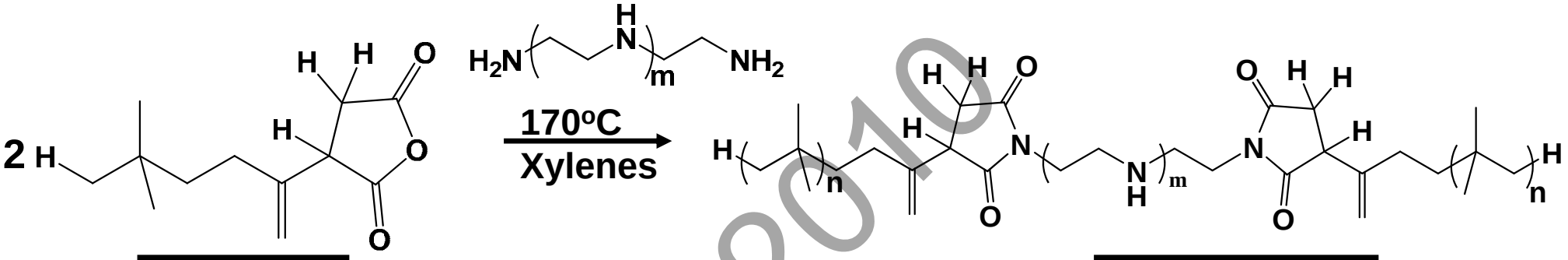


The modified succinimide possesses improved dispersancy properties when used in lubricating oil.

Objectives

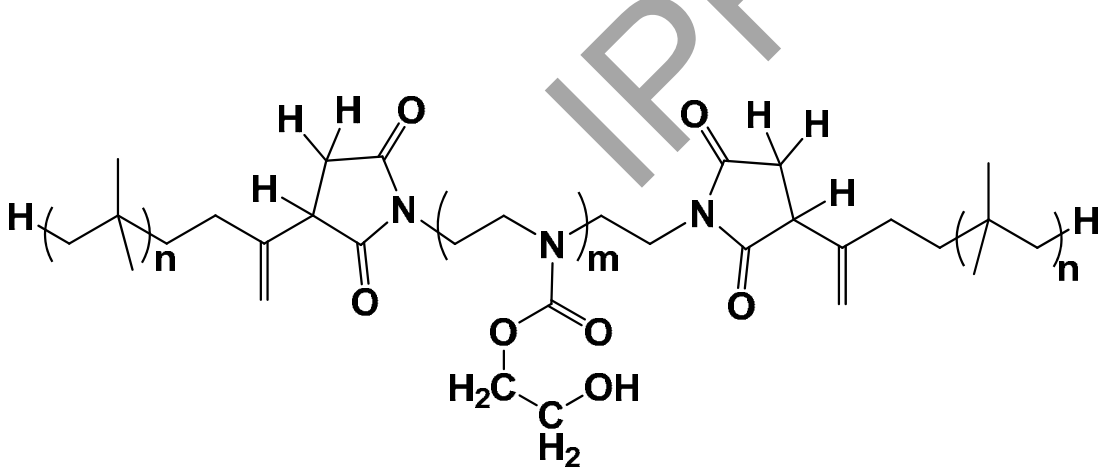
- Synthesize a series of modified *bis*-polyisobutylene succinimide (M-*b*-PIBSI) dispersants
- Characterize the modified dispersants
- Obtain the critical micelle concentration (CMC) of the modified dispersants.
- Model the adsorption of the modified dispersants onto carbon black particles (CBPs).

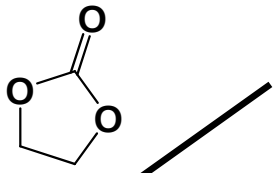
Synthesis Protocols

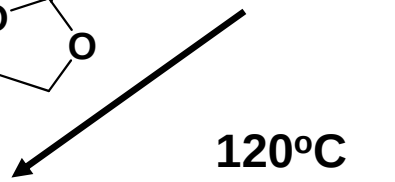


PIBSA

b-PIBSI

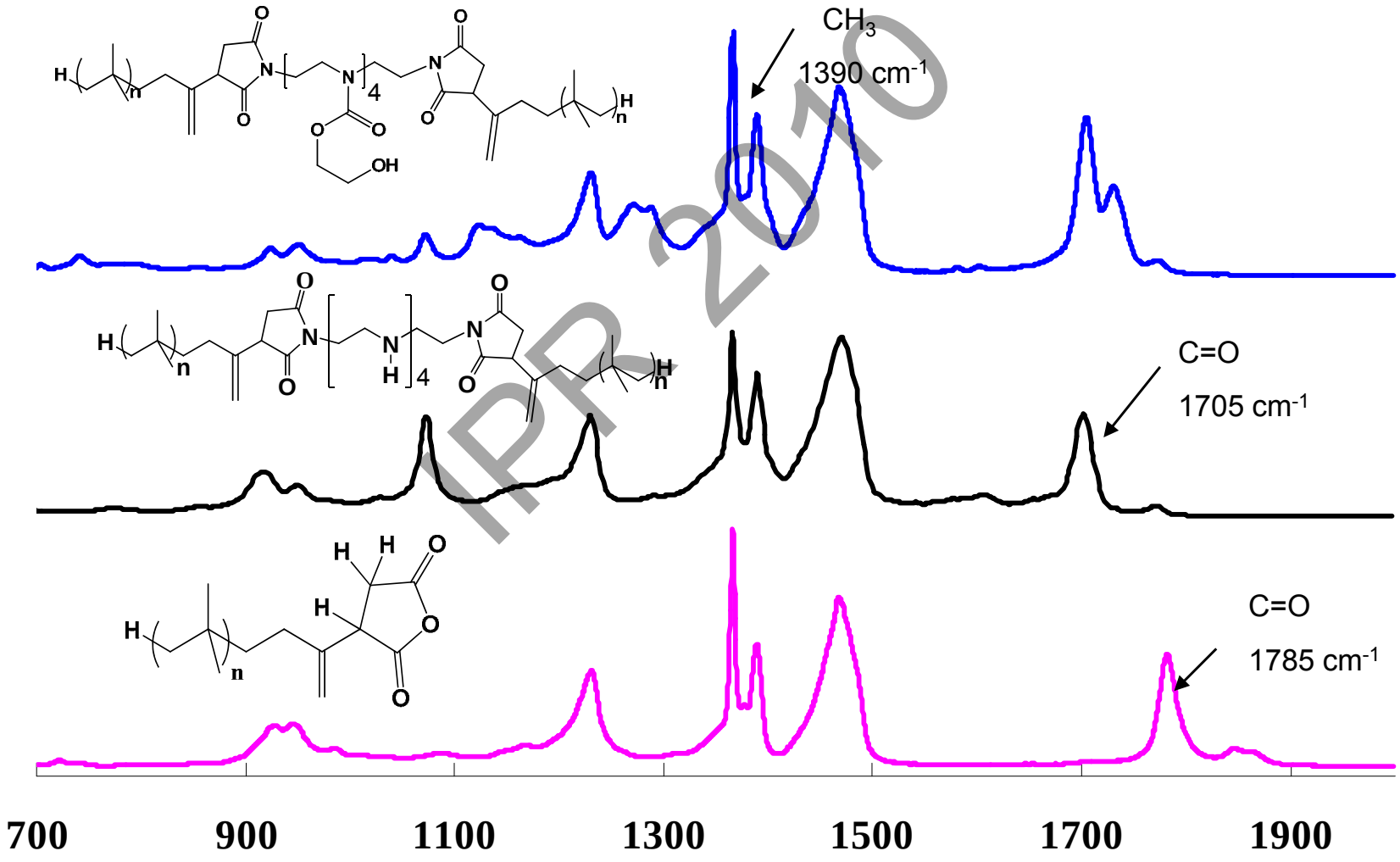






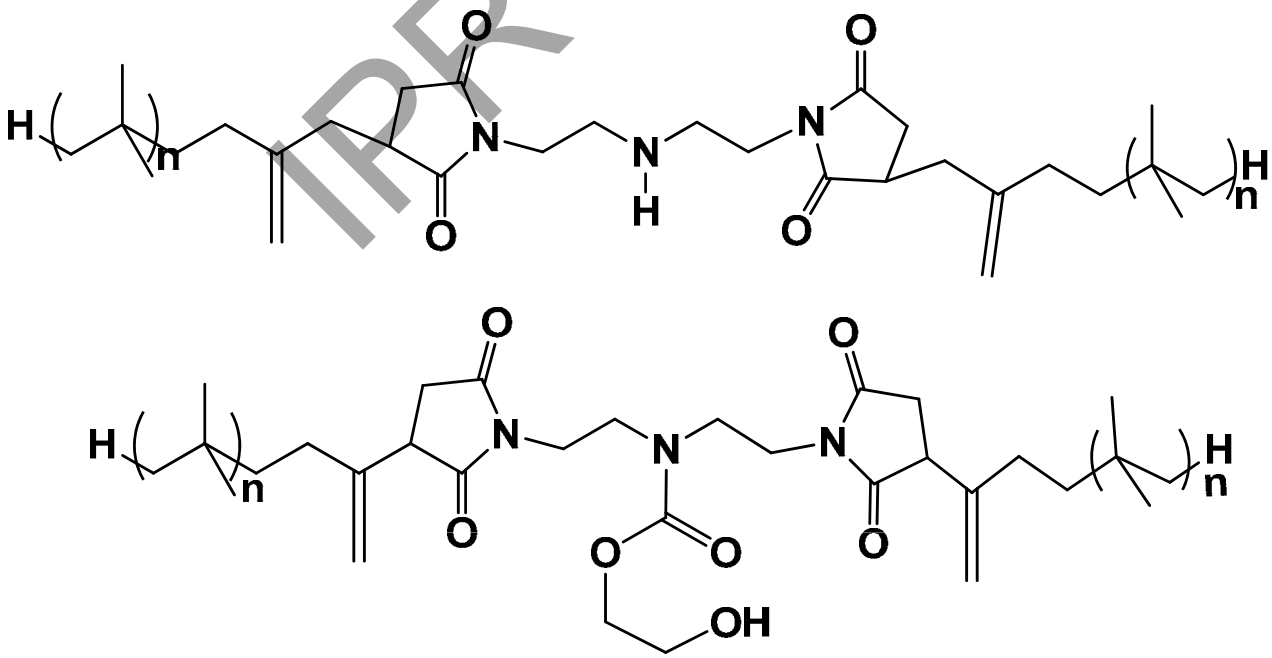
Modified *b*-PIBSI

Fourier Transform Infrared Spectrometry (FTIR)

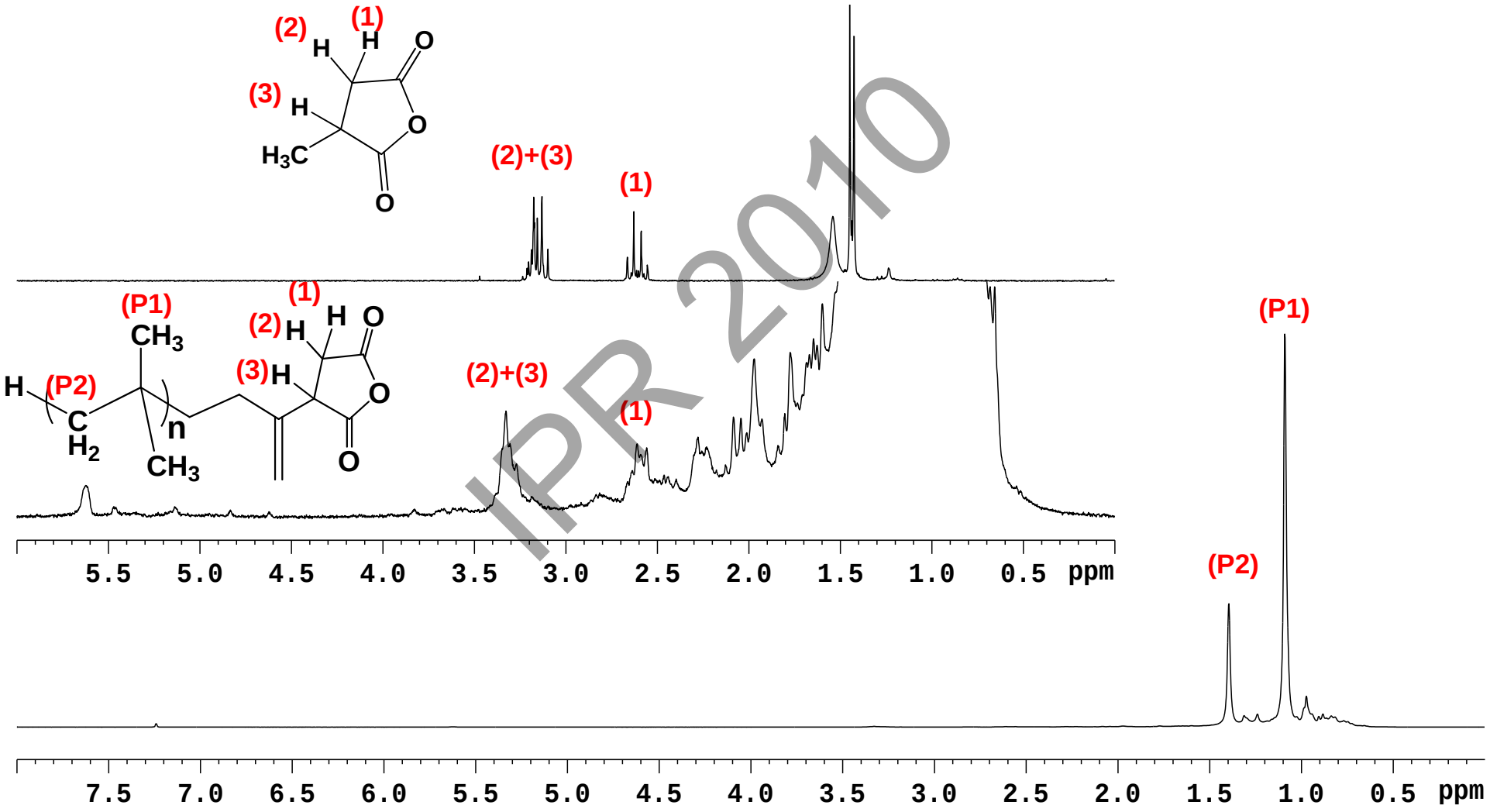


^{1}H NMR for Polymers

- *b*-PIBSI-DETA has only one secondary amine in the polymer.
- Clean and clear spectrum.

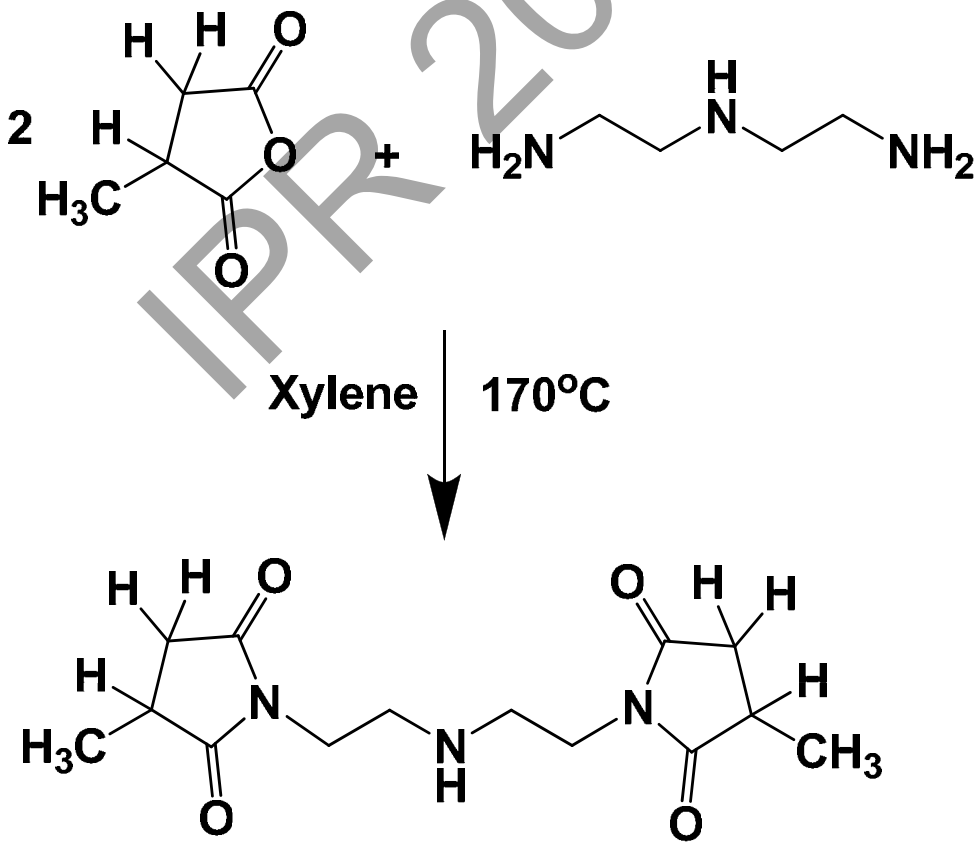


PIBSA ^{1}H NMR Spectrum



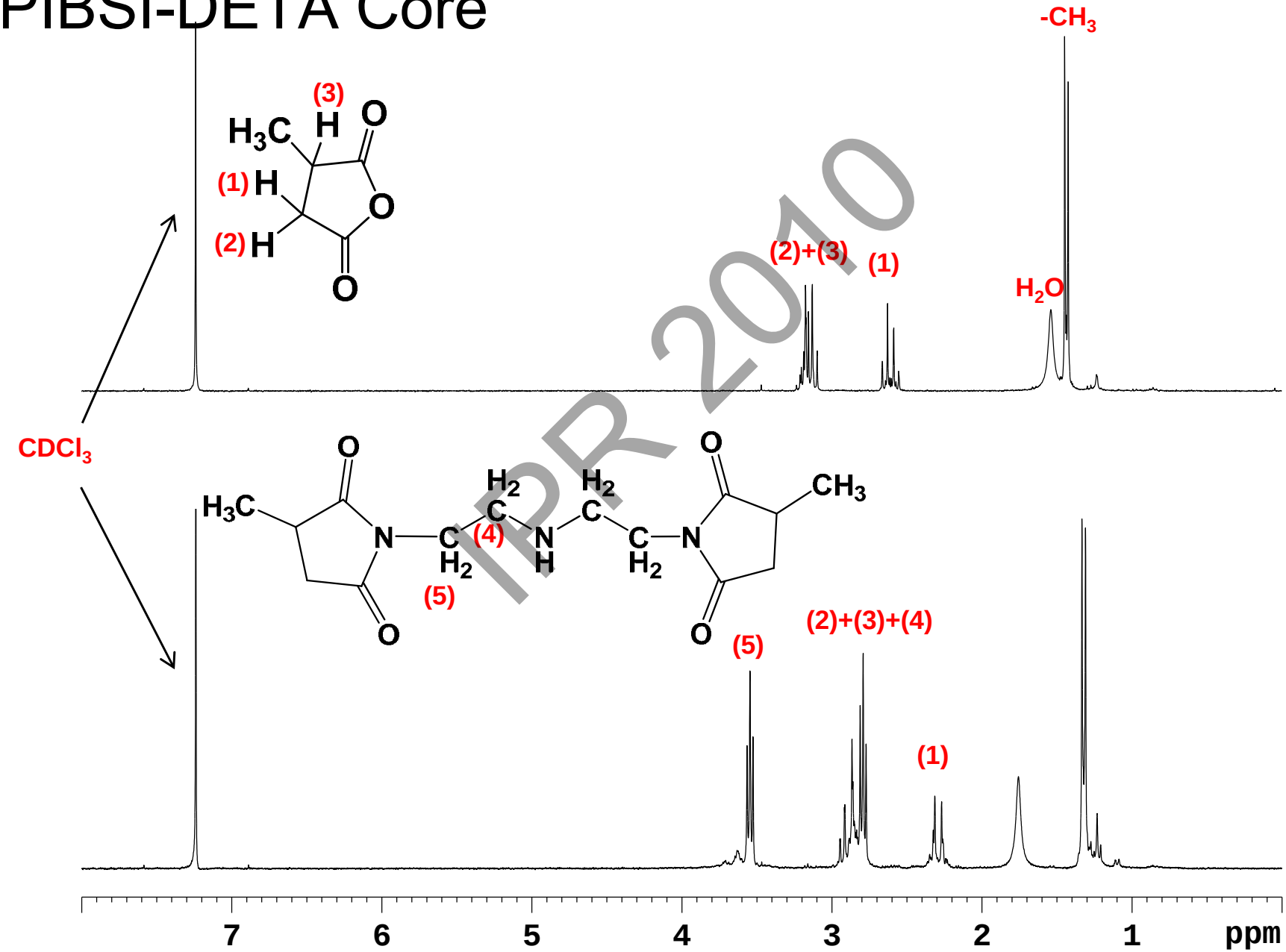
Model Reaction 1

- 2 units of MSA were reacted with 1 unit of DETA in xylene at 170°C for 20 hours.
- Methyl succinimide possess a similar structure as the polar core of the *b*-PIBSI-DETA dispersant.

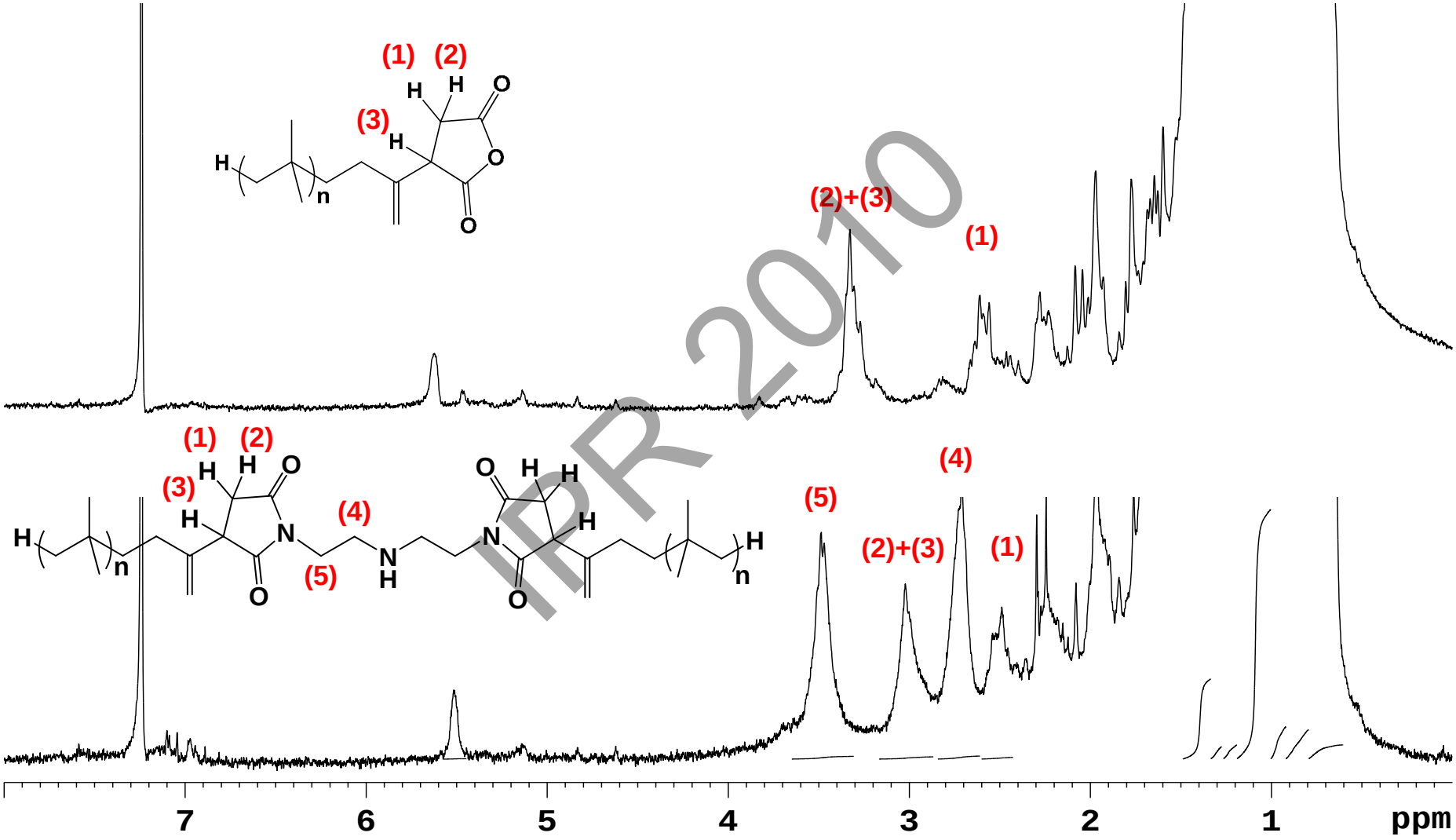


Model Reaction 1

PIBSI-DETA Core



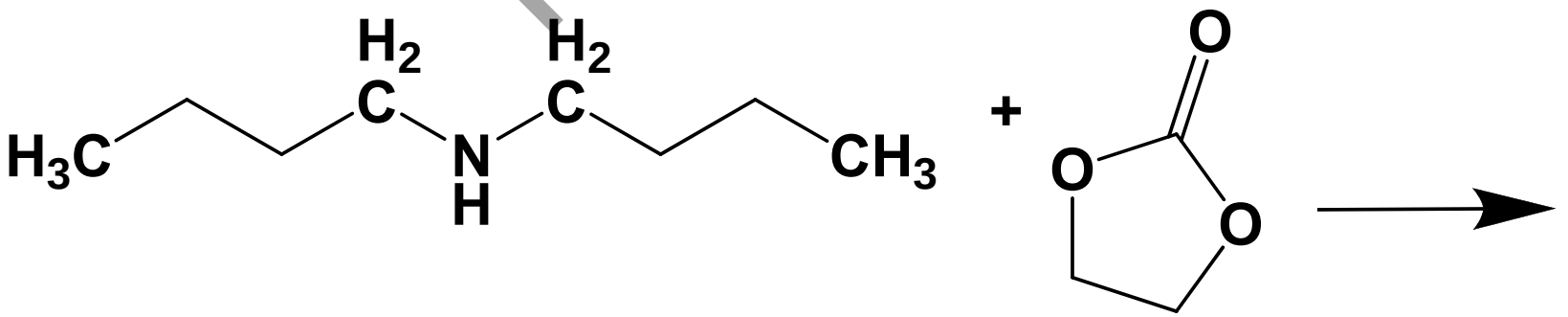
PIBSA and PIBSI



Model Reaction 2:

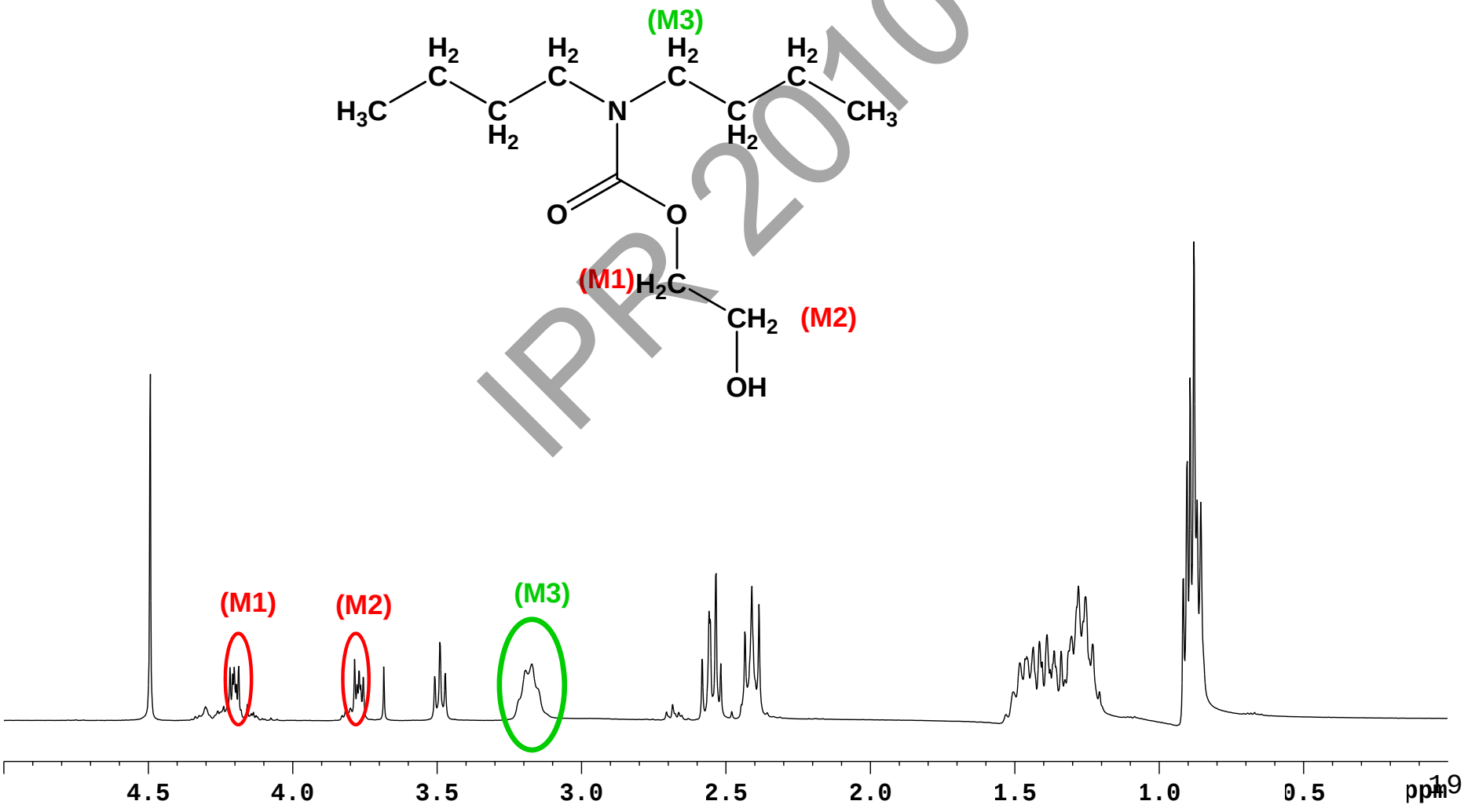
Dibutylamine Reacting with Ethylene Carbonate (1:1 Ratio)

- Dibutylamine is reacted with equal amount of ethylene carbonate.
- The reaction is run without any solvent.
- The reaction is run at 120°C.



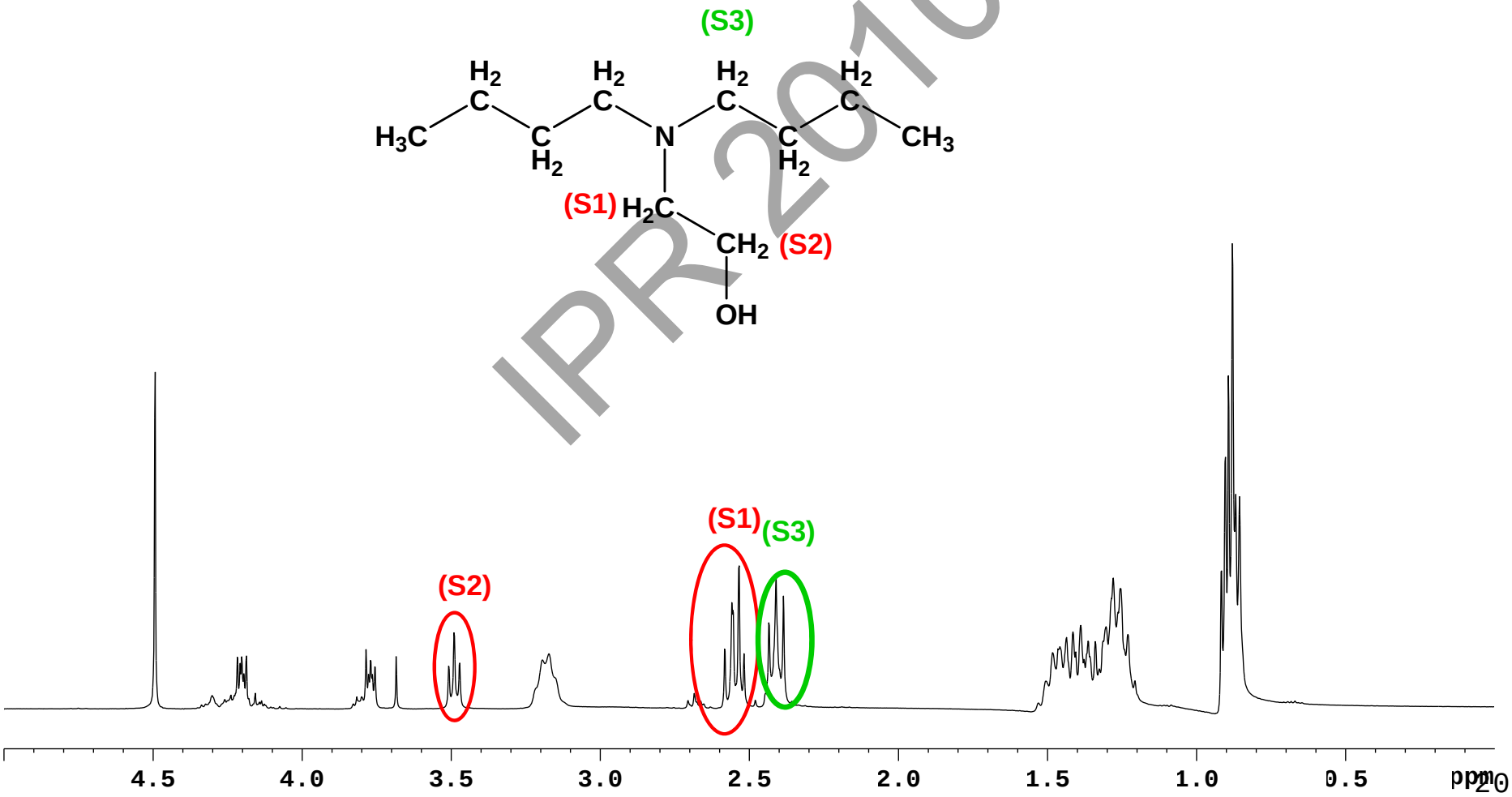
Model Reaction 2:

Dibutylamine Reacting with Ethylene Carbonate



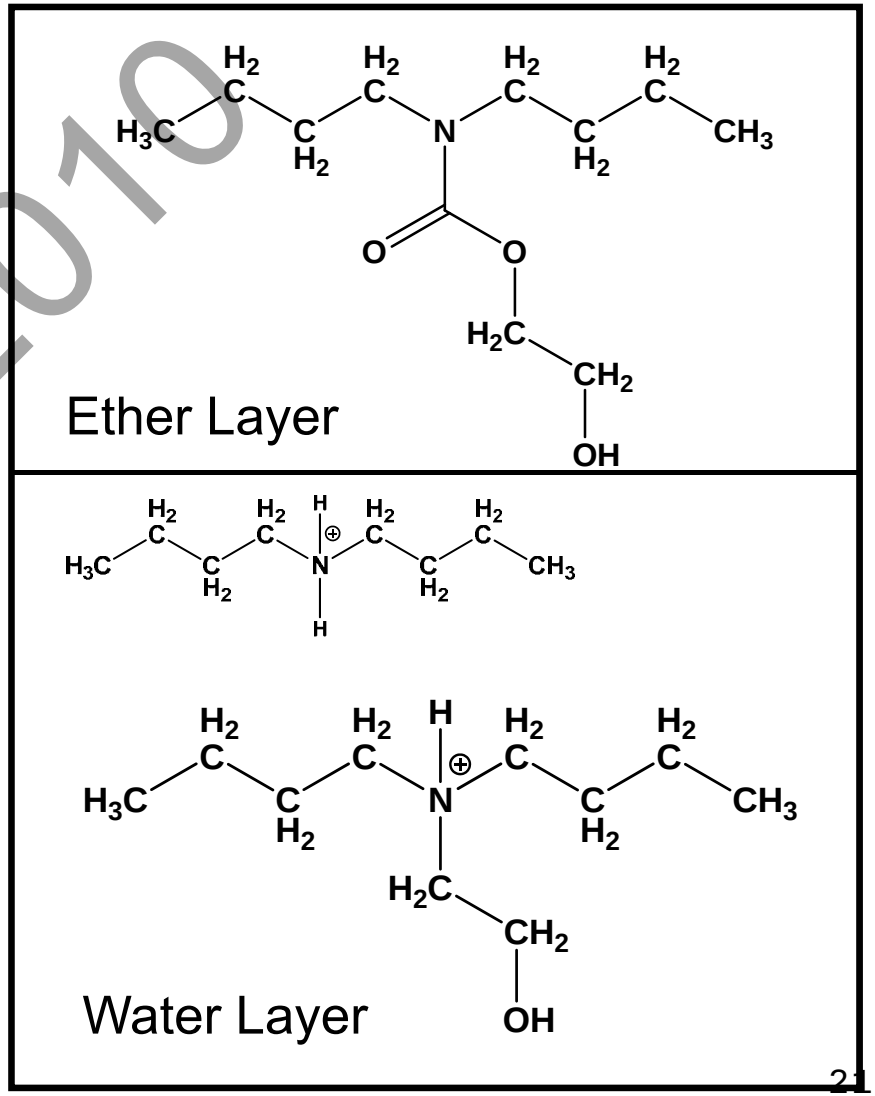
Model Reaction 2:

Dibutylamine Reacting with Ethylene Carbonate (1:1 Ratio)

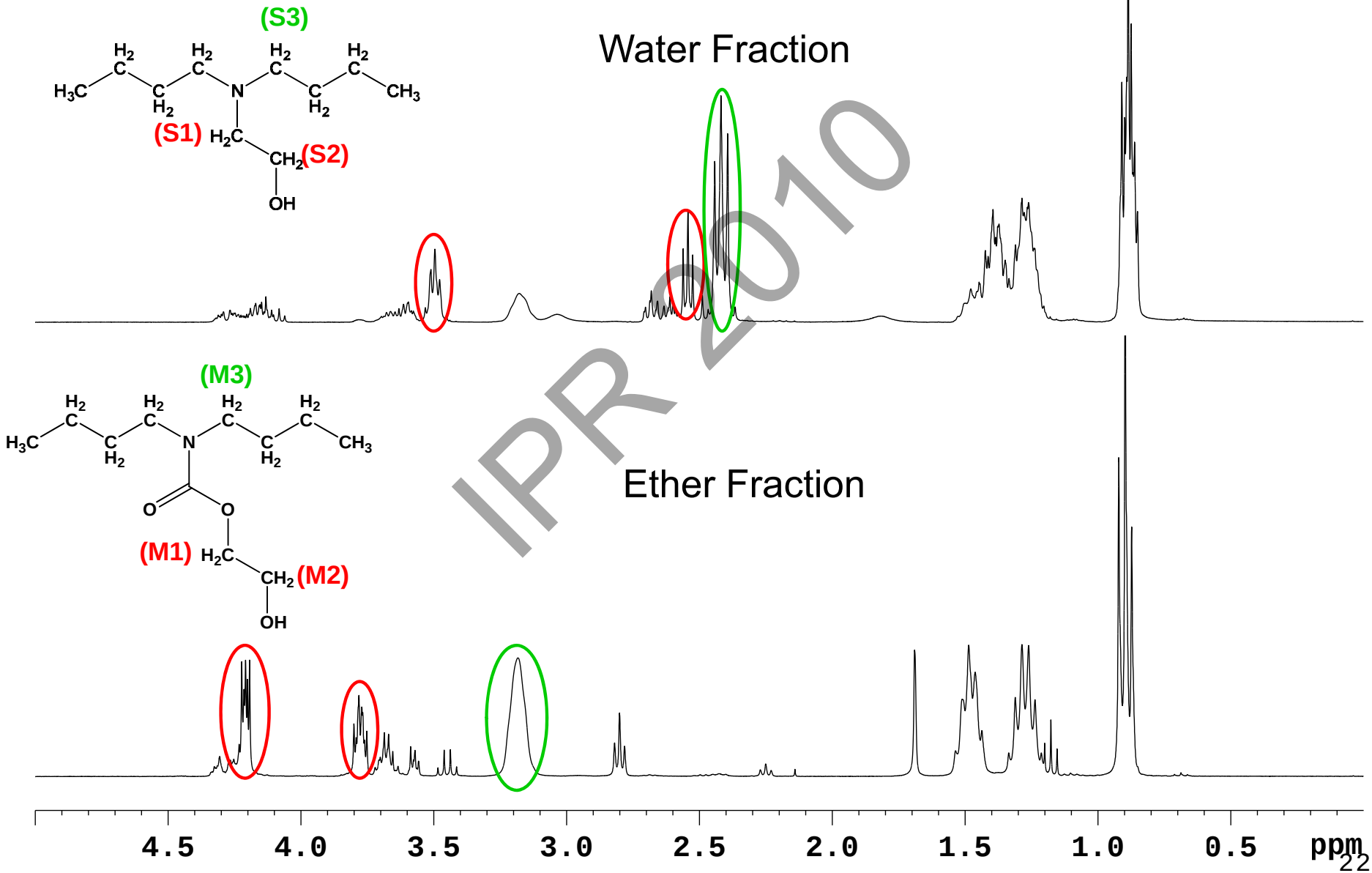


Extraction

- The product mixture was dissolved in ethyl ether and mixed with 1M HCl solution.
- Both of the ether layer and the water layer were deprotonated and then dried using $MgSO_4$.
- At the end, the solvents were removed to obtain NMR spectra of each fraction.



Two Fractions



Ether Layer Separation

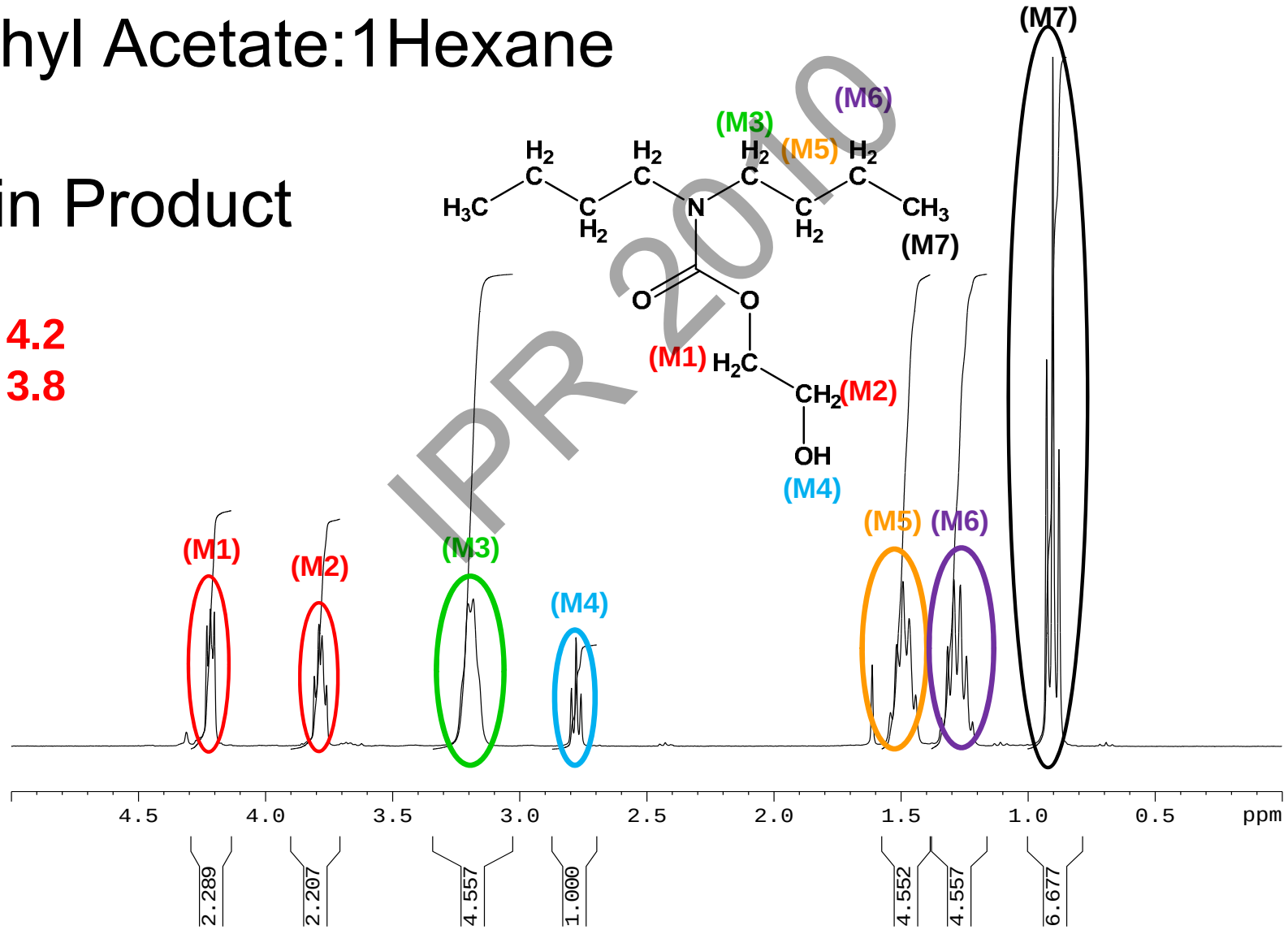
- Column Chromatography was used to separate the products in the ether layer.
- 1:1 Ratio of hexane and ethyl acetate was used as the eluent.
- Three different compounds were found.

Column Chromatography to Separate the Ether Layer

1Ethyl Acetate:1Hexane

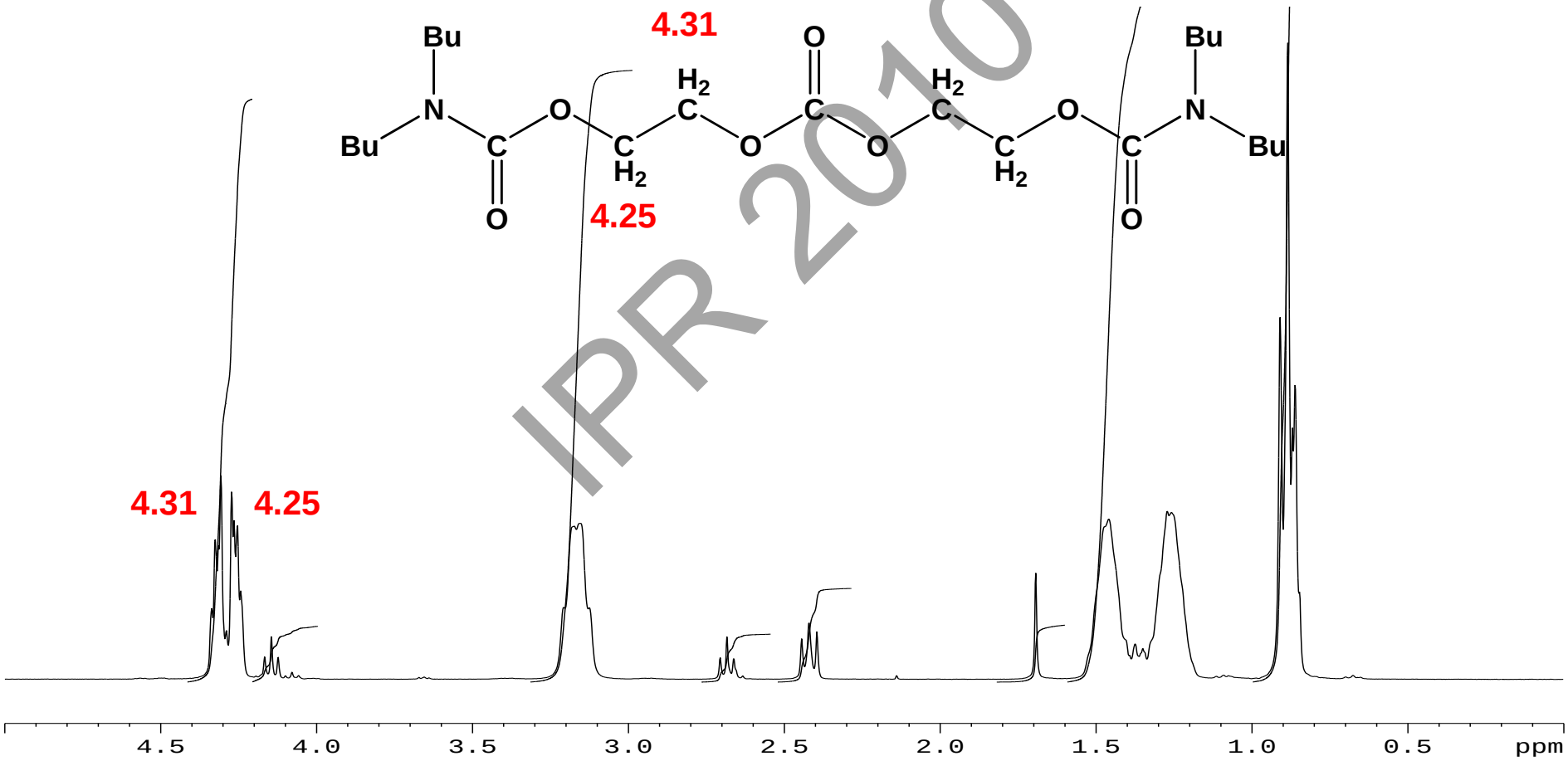
Main Product

M1: 4.2
M2: 3.8



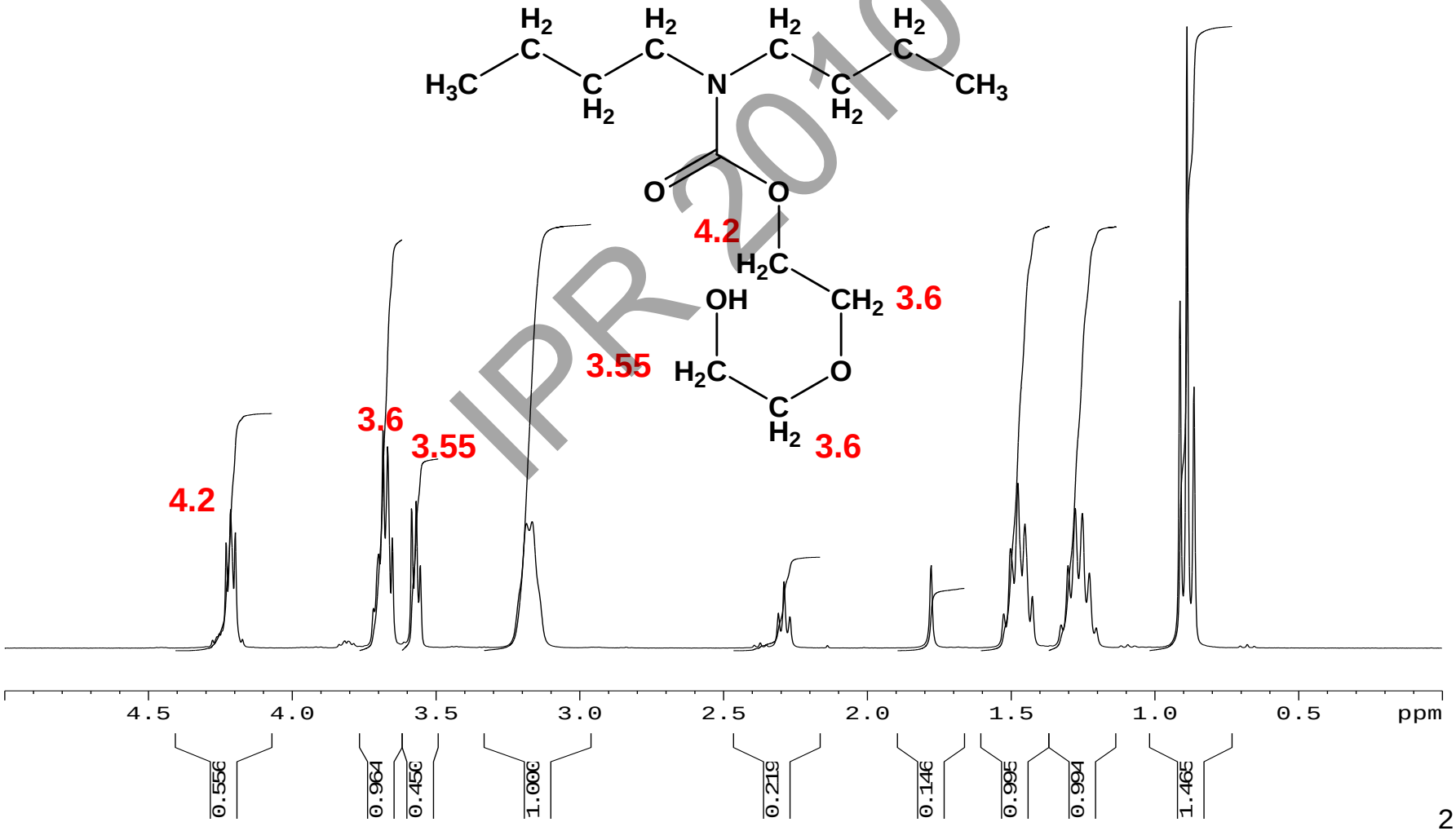
Ether Layer Separation

Side Product 1



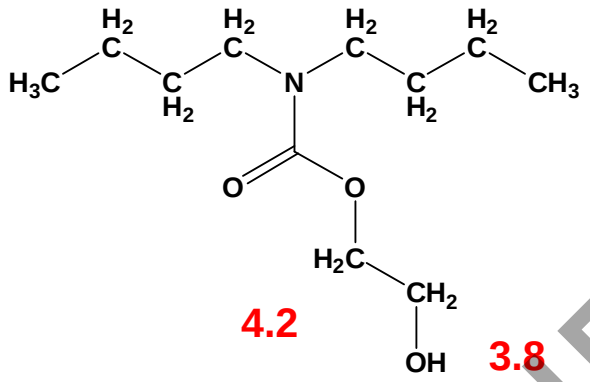
Ether Layer Separation

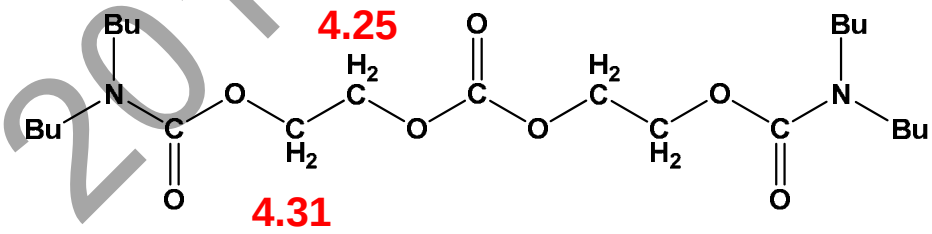
Side Product 2

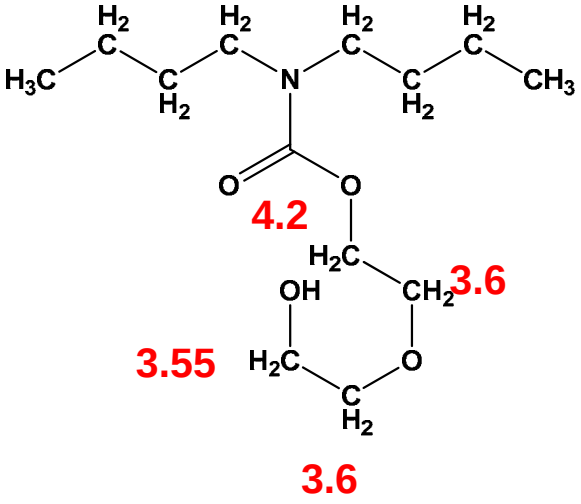


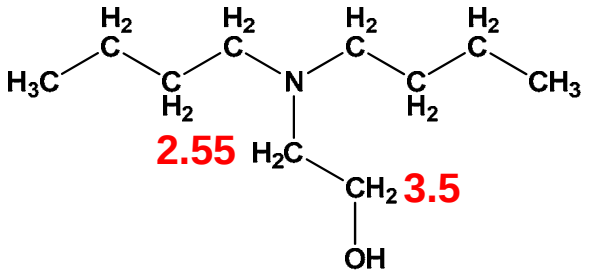
Products in the Model Reaction

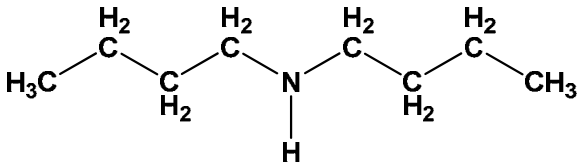
- There are 5 different compounds found in the reaction mixture.







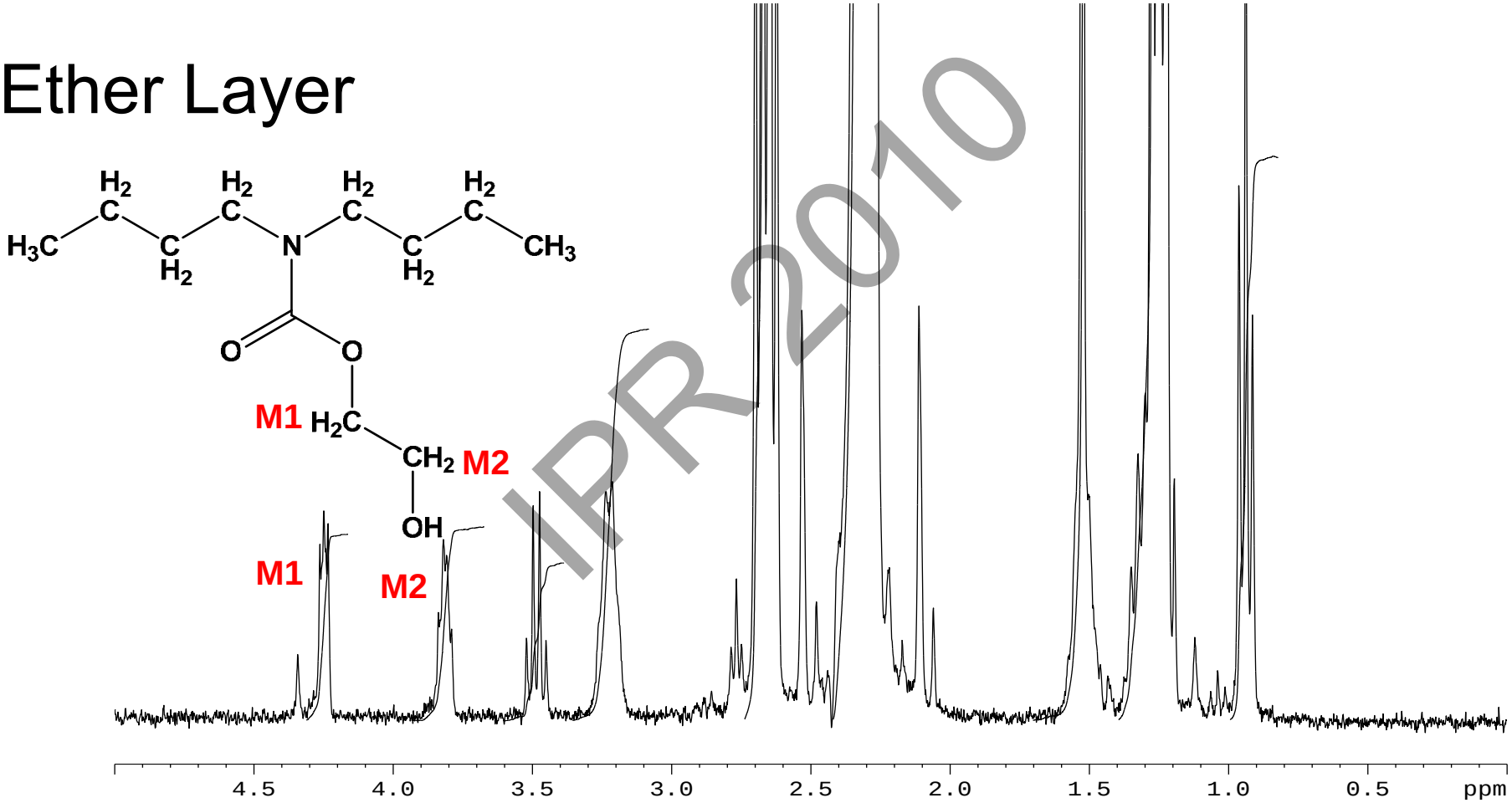




Dilute Model Reaction 2

1g Reaction Mixture dissolved in 10 mL Xylenes

Ether Layer

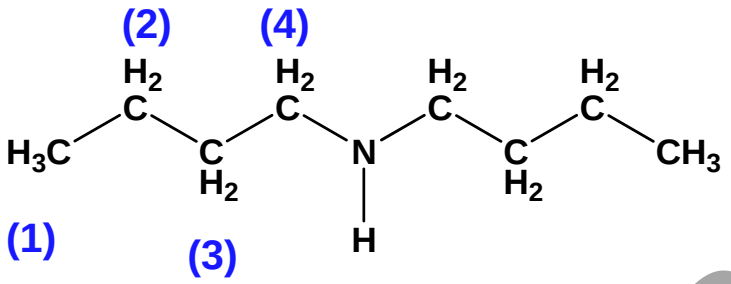


At the region 3.5 to 4.5, there are only peaks at 3.8 and 4.2, which means there is only the main product found in the ether layer of the dilute reaction.

Dilute Model Reaction

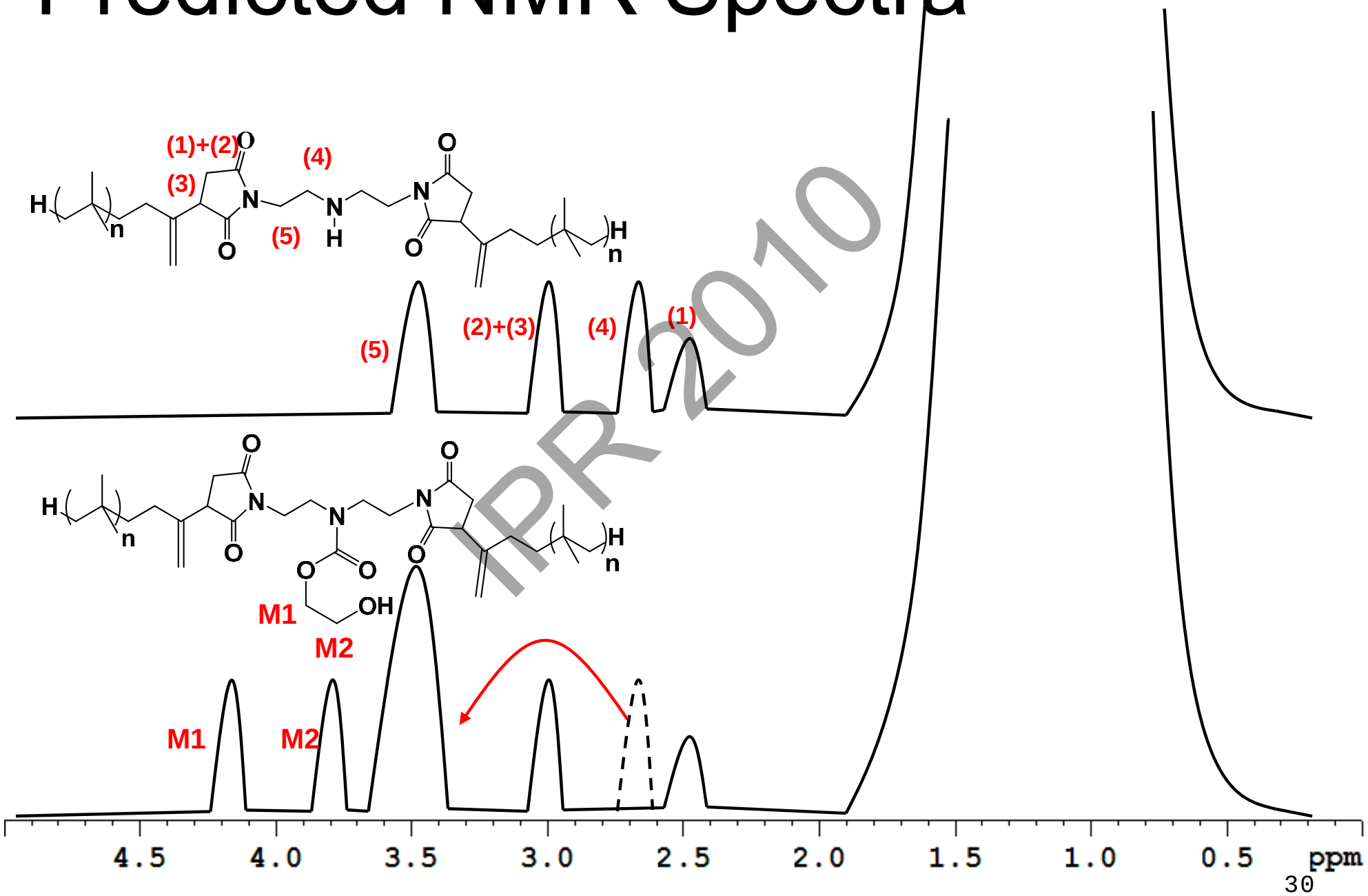
1g Reaction Mixture dissolved in 10 mL Xylenes

Water Layer

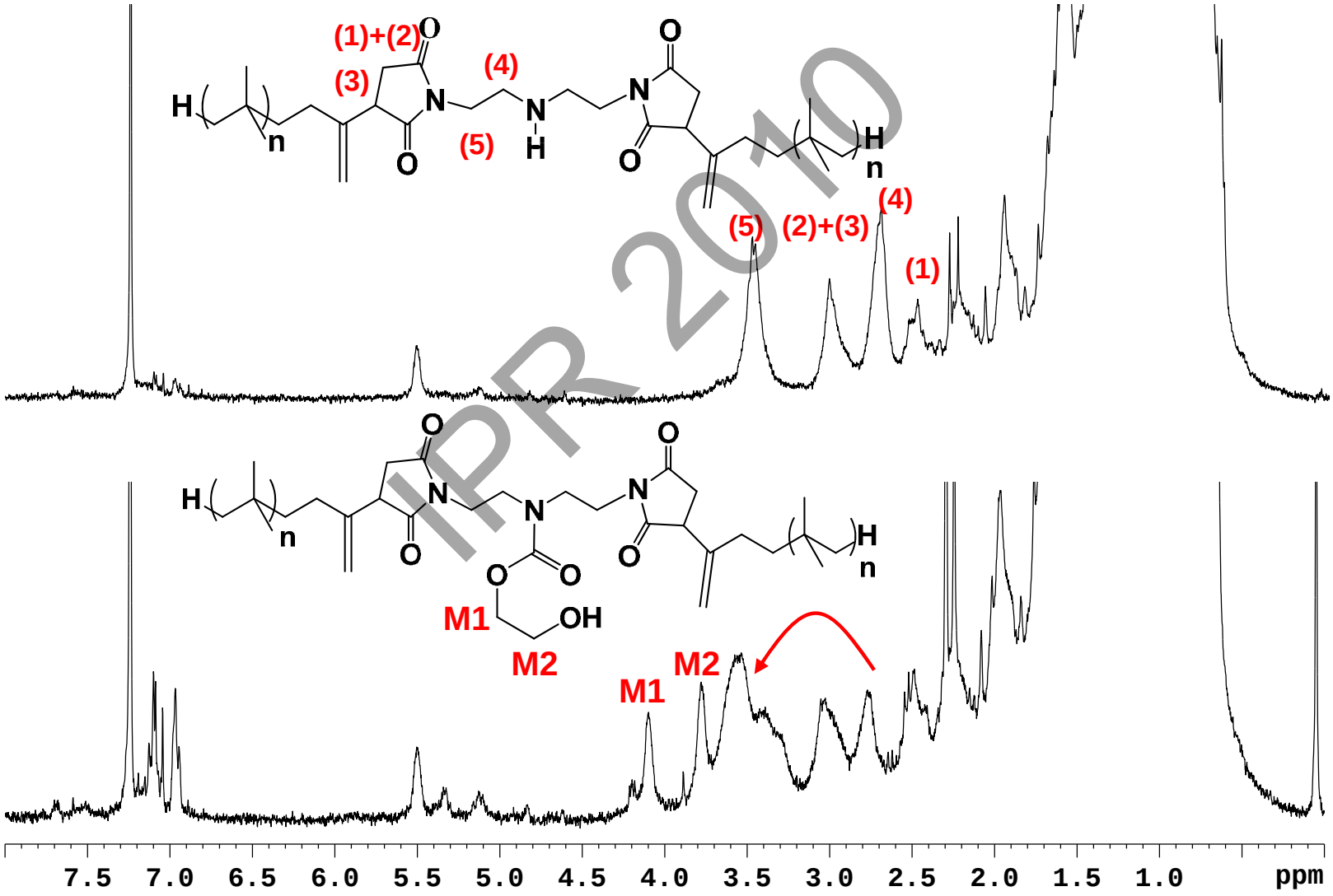


There is only DBA found in the spectrum of the water layer product, which means no side product is produced in the dilute reaction.

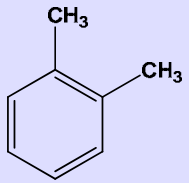
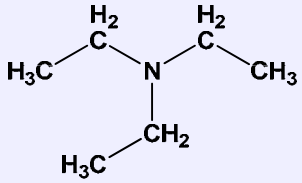
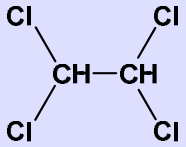
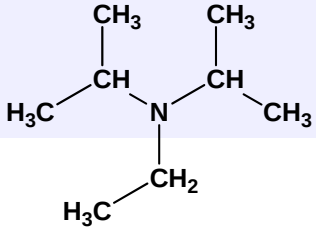
Predicted NMR Spectra



Spectra of the Modification Reaction



Solvents Comparison

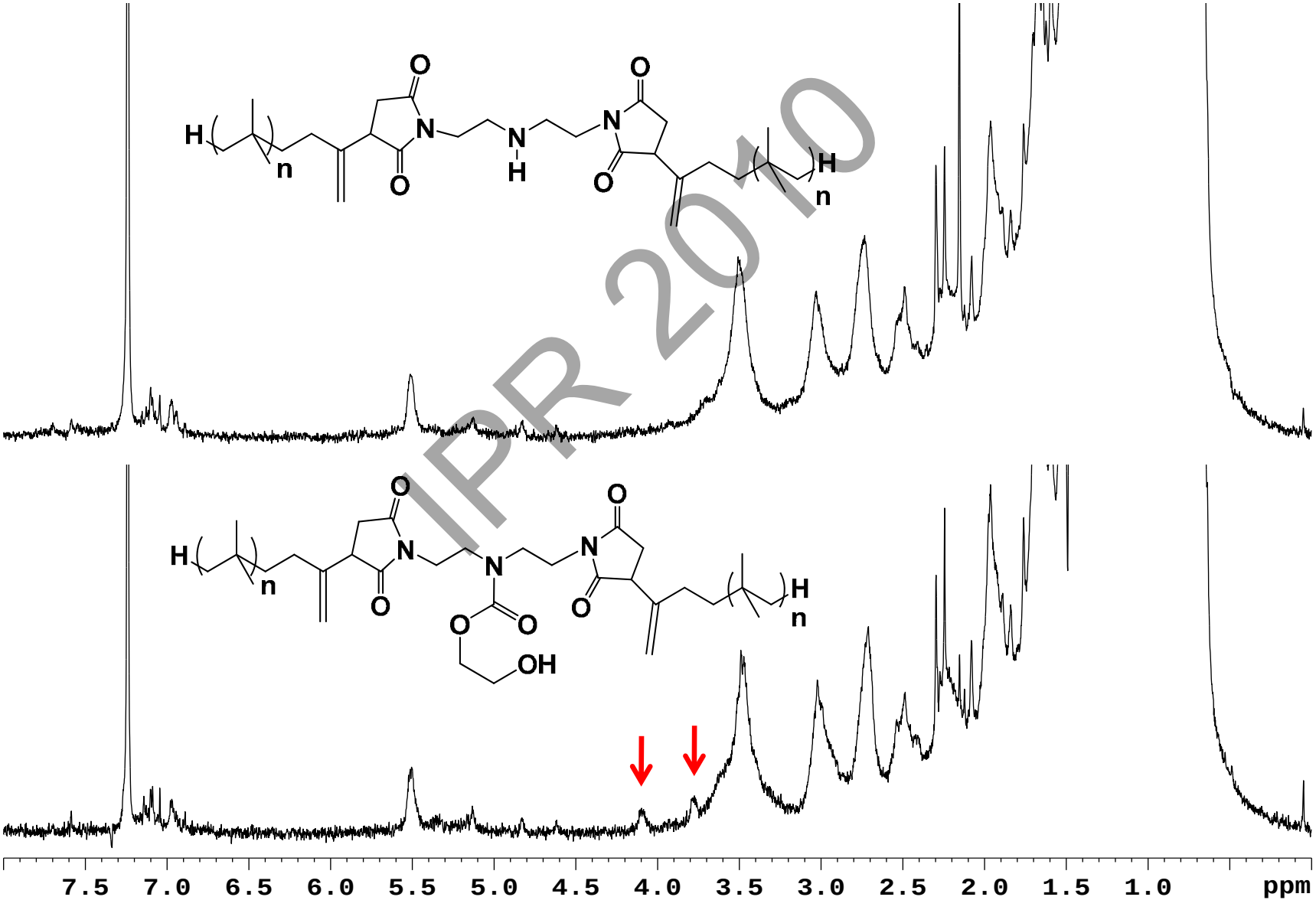
Solvents	Boiling Point (°C)	Vapour Pressure (mmHg)	Reaction Efficiency
Xylenes 	147	18 (37.7 °C)	Low yield <10%
Triethylamine 	88.8	51.75 (20 °C)	Low yield High yield obtained occasionally
1,1,2,2-Tetrachloroethane 	147	8 (20 °C)	React with PIBSIs
N,N-Diisopropylethylamine 	127	31 (37.7 °C)	Low yield

Yield of Modification Reaction of *b*-PIBSI-DETA

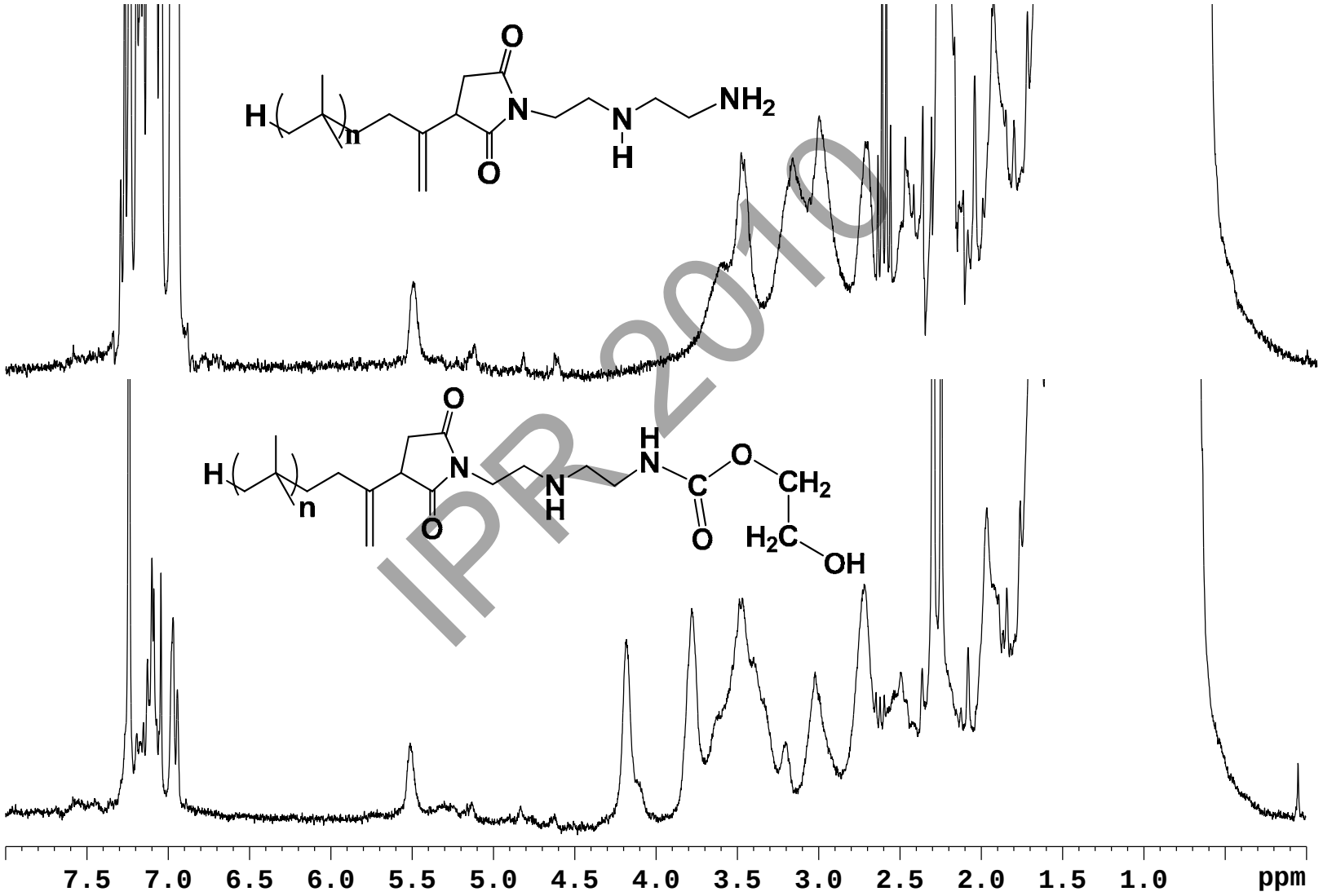
Temperature (°C)	Triethylamine (w%)	Xylenes (w%)	Reactant (w%)	Time (hours)	*b*-PIBSI-DETA:EC Ratio	Carbamate Side Chain Yield
130	0%	50%	50%	4	1:2	5%
125	60%	30%	10%	20	1:2	3%
120	40%	20%	40%	40	1:2	9%
120	50%	25%	25%	40	1:2	8%
120	80%	10%	10%	20	1:2	3%
120	80%	10%	10%	20	1:10	5%
125	15%	70%	15%	20	1:2	1%
120	0%	0%	100%	20	1:2	5%

The yield of the modification of *b*-PIBSI-DETA is always lower than 10%. The reactions were run in the sealed reaction vessel.

Modification of *b*-PIBSI-DETA



Modification of *m*-PIBSI-DETA

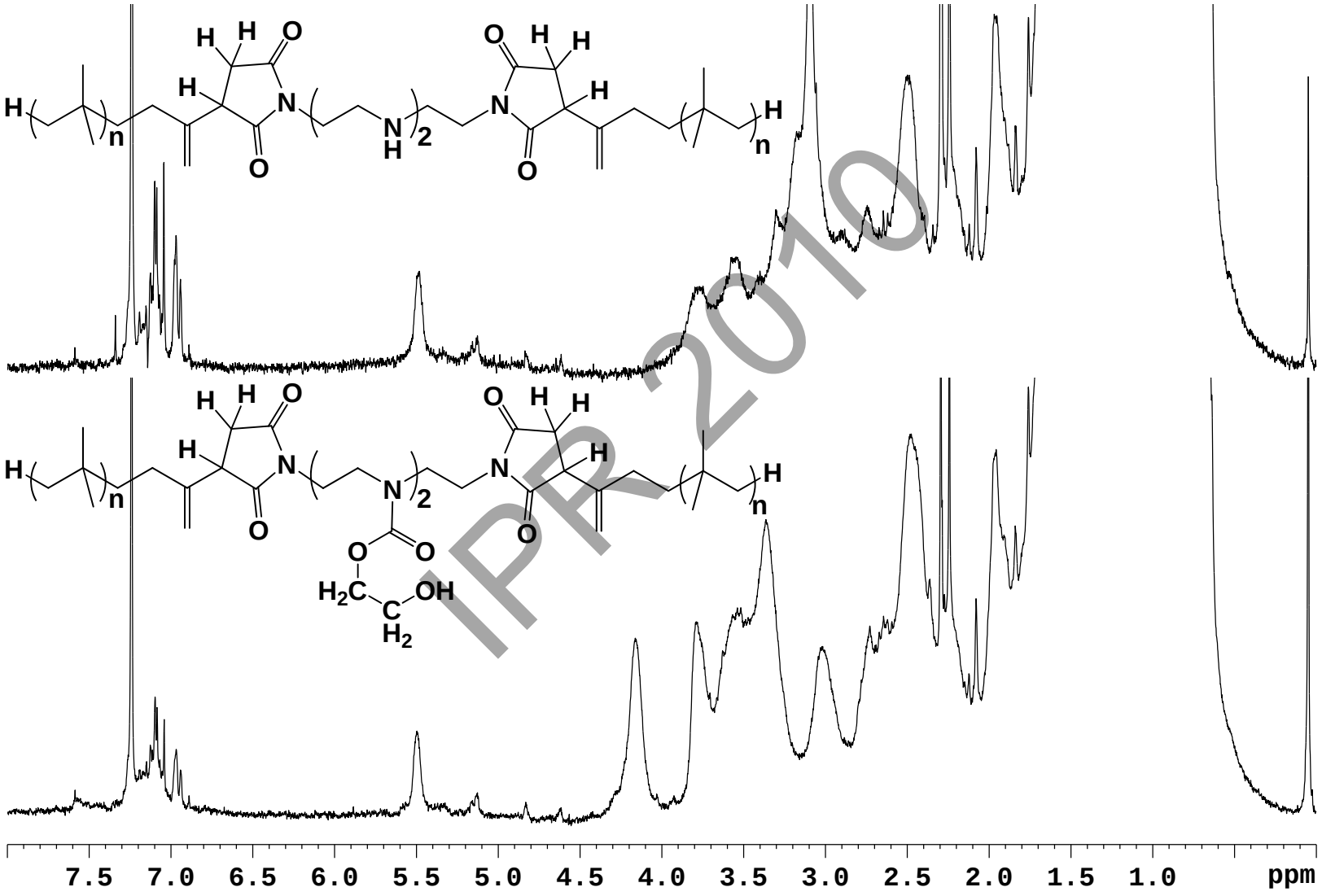


The yield obtained is 13%. It is a big improvement comparing to the yield obtained with *b*-PIBSI-DETA. The reaction was run with set up 1.

Polyamines used to Synthesize PIBSI

DETA	**H_2N-CH_2CH_2-NH-CH_2CH_2-NH_2** **Diethylenetriamine** **~99%**
TEPA	**H_2N-$(CH_2CH_2$-NH$)_3$-CH_2CH_2-NH_2** **Tetraethylenepentamine** **~89%**
PEHA	**H_2N-$(CH_2CH_2$-NH$)_4$-CH_2CH_2-NH_2** **Pentaethyelenehexamine** **~86%**

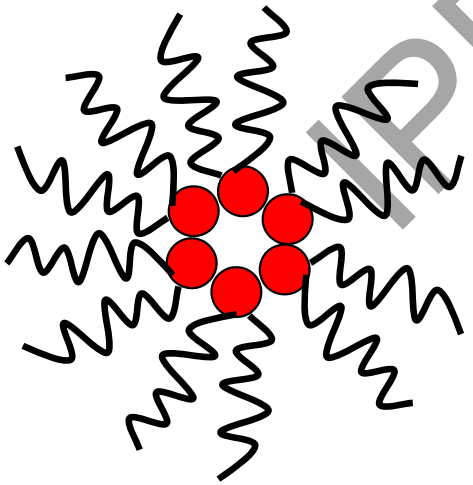
Modification of *b*-PIBISI-TEPA



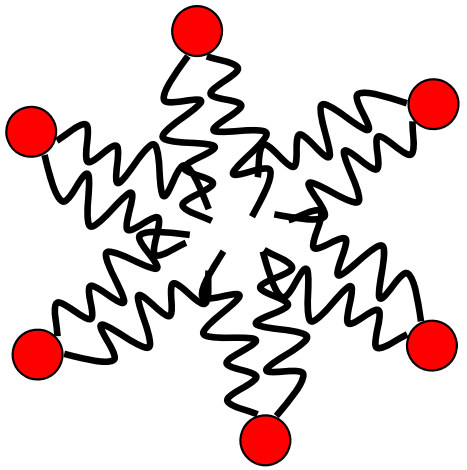
The yield obtained is17%.

Micelles

- Micelles are aggregates of dispersants in the solvent.
- Depending on the different solvents used, the dispersants form micelles or reverse micelles.
- Two Important parameters: Critical Micelle Concentration (CMC) and Aggregation Number (N_{agg}).



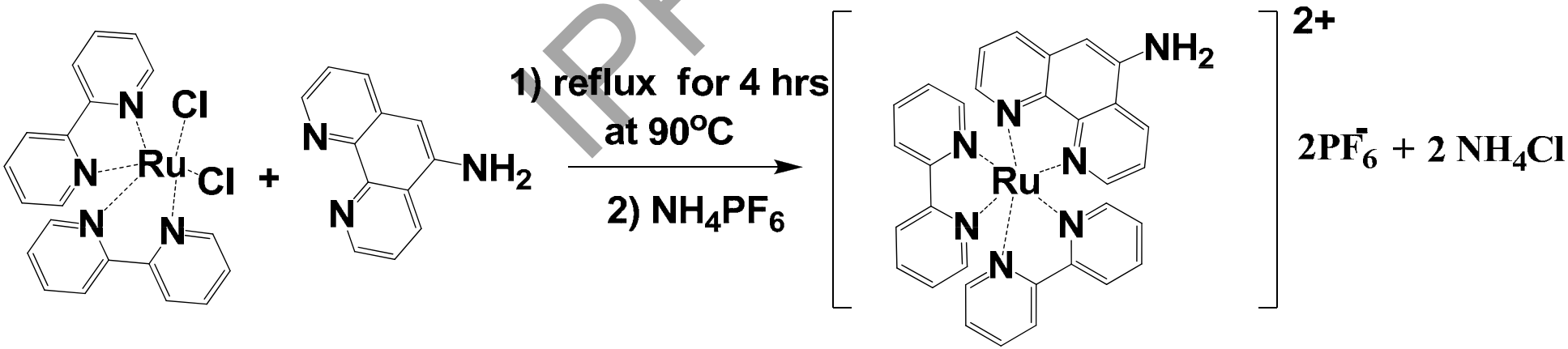
Reverse Micelles



Micelles

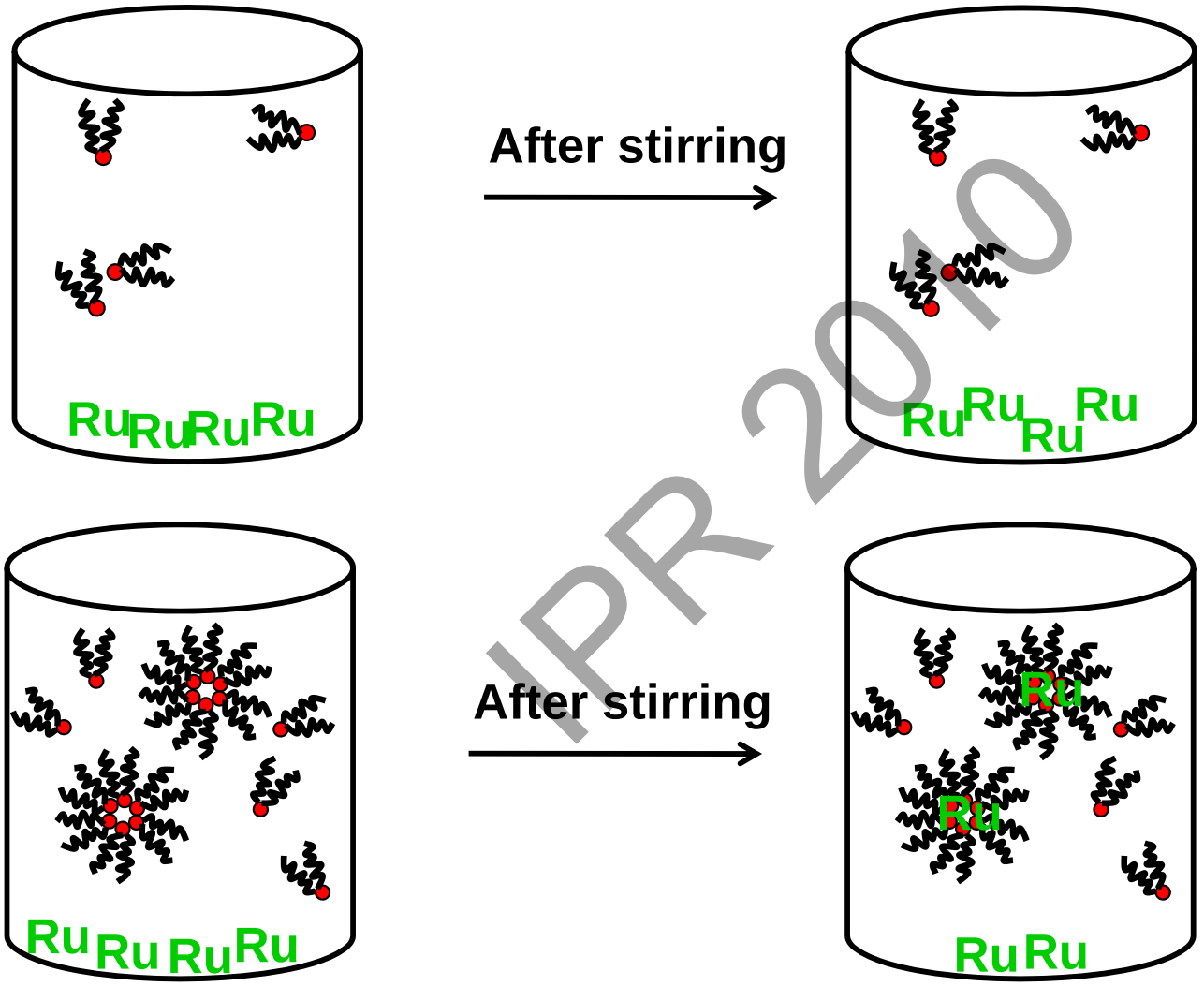
Critical Micelle Concentration

- The CMC is measured with the ruthenium complex ($RuNH_2$) which probes the dispersant micelles at the molecular level by fluorescence.
- $RuNH_2$ is soluble in polar solvents (e.g. Acetone), but not soluble in apolar solvents (e.g. Hexane).



ruthenium bisbipyridine
5-aminophenanthroline
hexafluorophosphate

CMC Measurement

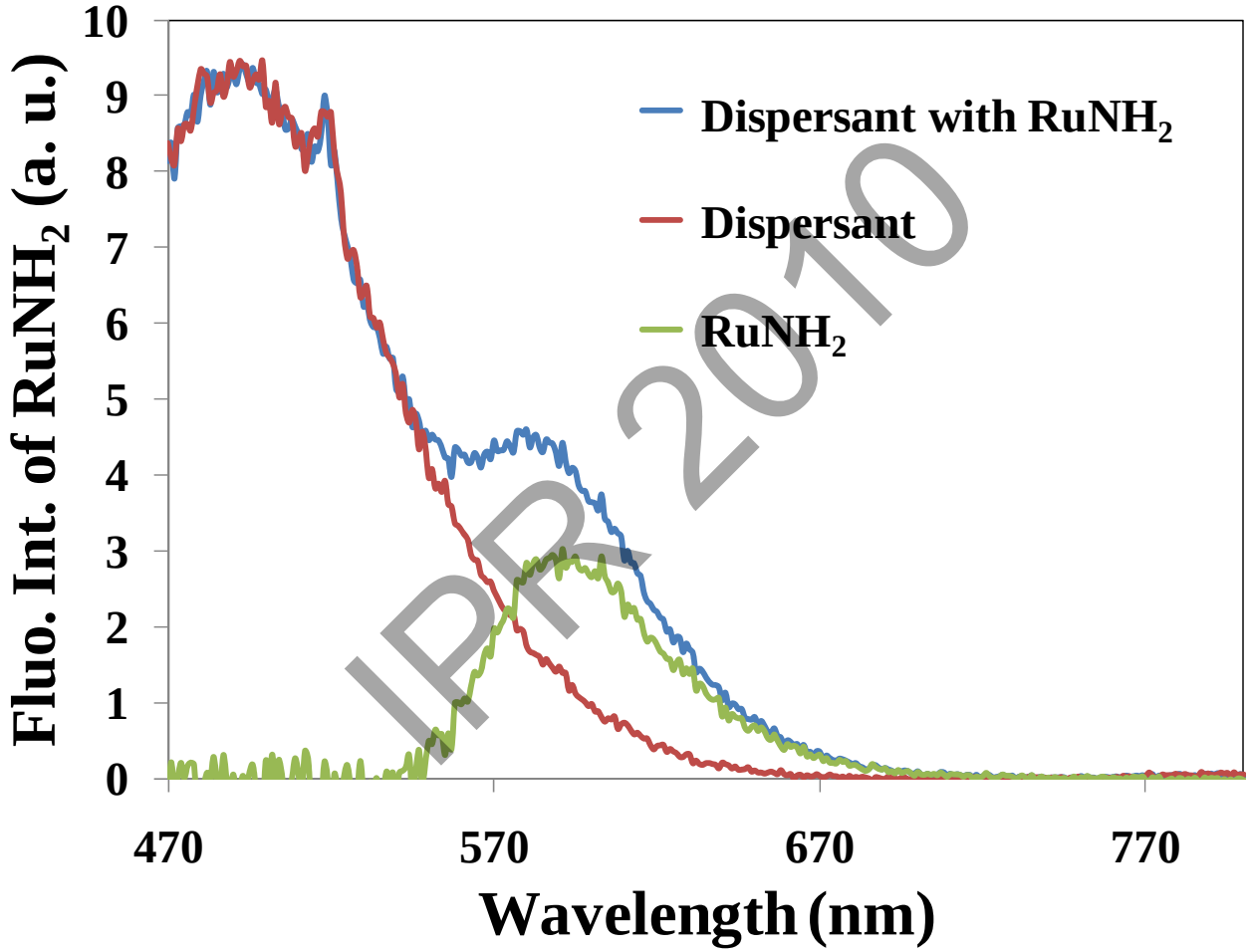


$RuNH_2$ is not solubilised.

$RuNH_2$ is solubilised..

Equal amount of $RuNH_2$ is added into each solution. $RuNH_2$ content of the solution increases when the dispersants form micelles.

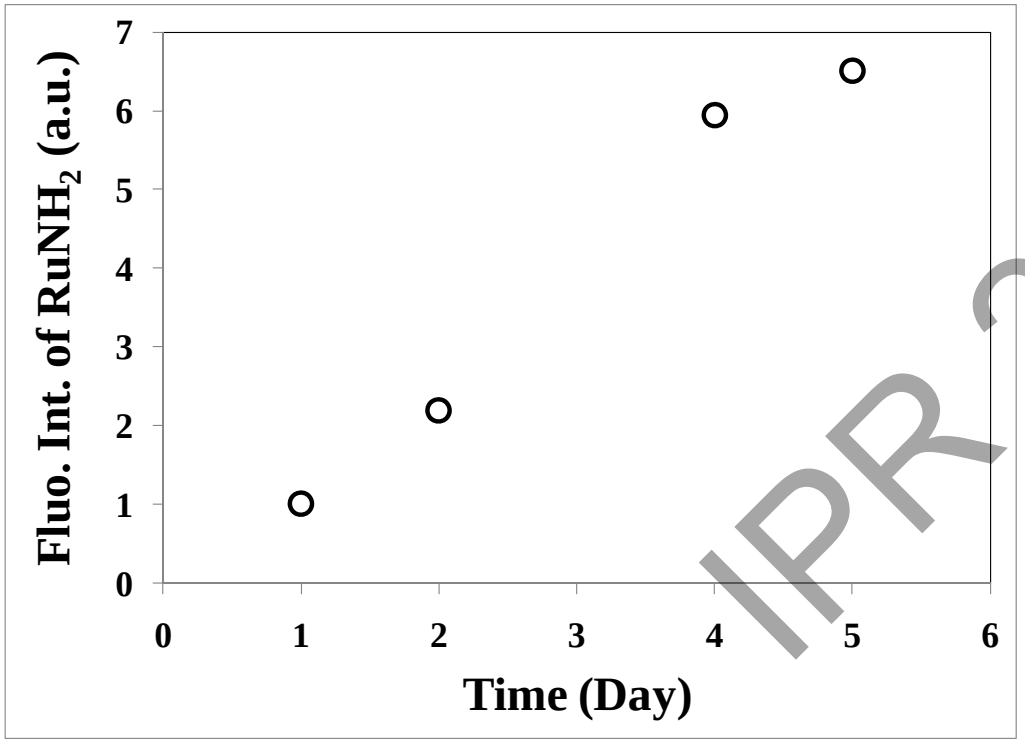
Fluorescence Spectrum of $RuNH_2$

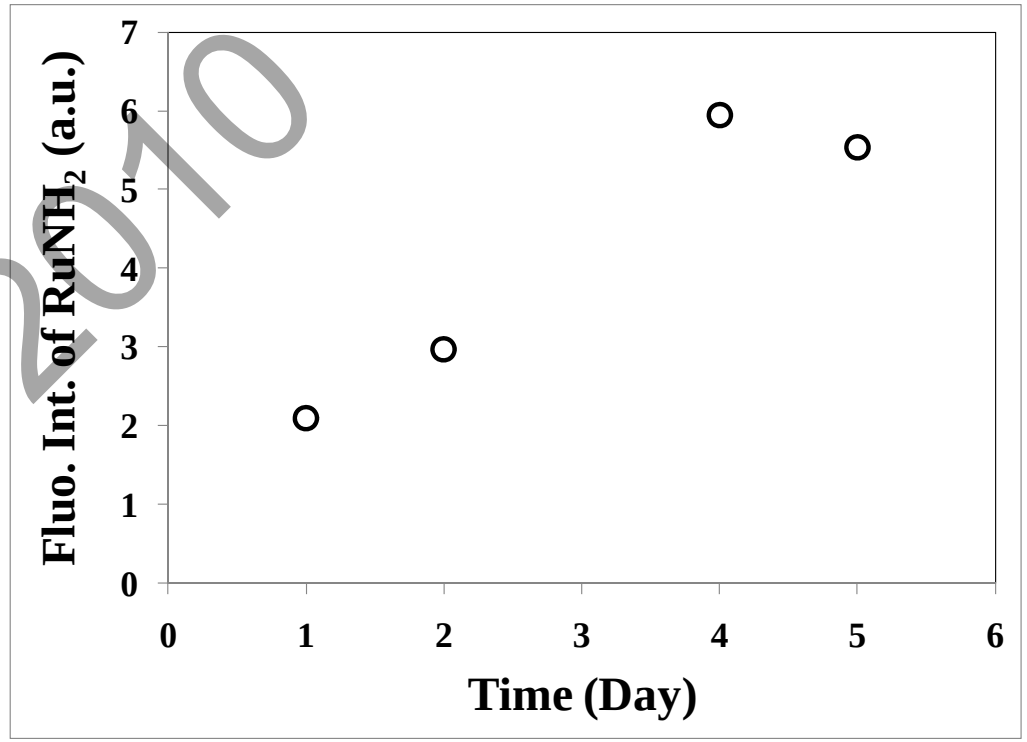


[PIBSI]=0.13 g/L, [RuNH2]= 4 μM

The fluorescence spectrum of PIBSI with $RuNH_2$ was subtracted by the PIBSI spectrum to obtain the fluorescence spectrum of $RuNH_2$.

Time Study of $RuNH_2$ Fluorescence Intensity



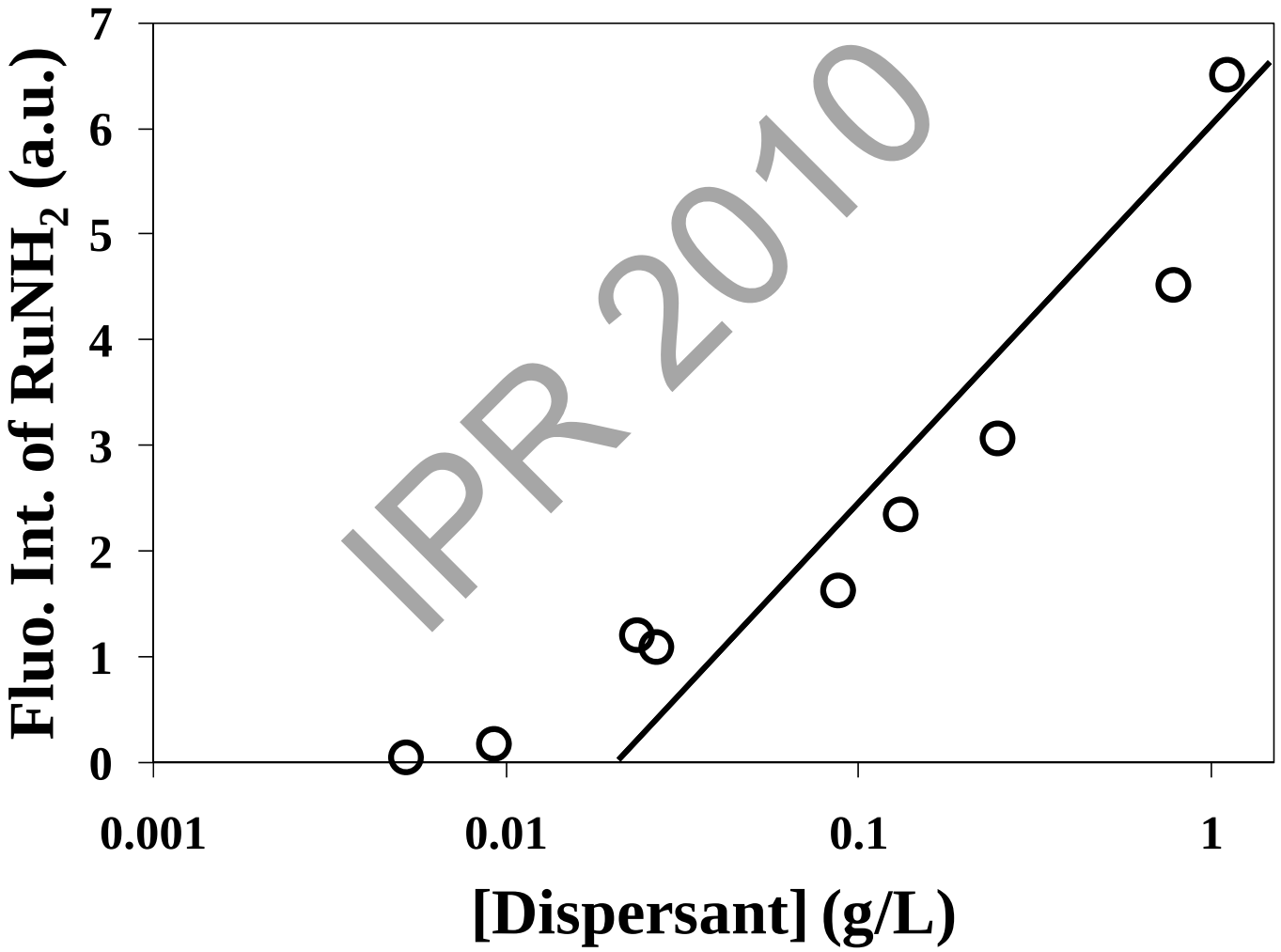


[PIBSI]=1.1 g/L, [$RuNH_2$]=4 μM

[M-PIBSI]=0.8 g/L, [$RuNH_2$]=4 μM

The fluorescence intensity of $RuNH_2$ increases as time increases.

Preliminary Result of PIBSI CMC



Conclusions

- Model reactions enable the assignment of ^{1}H NMR spectra of the polymers.
- Low yields are obtained in the modification of *b*-PIBSI-DETA.
- Higher degrees of modification are obtained with *m*-PIBSI-DETA, *b*-PIBSI-TEPA, and *m*-PIBSI-TEPA.

Future Work

- Determine the CMC of the modified PIBSI.
- Model the adsorption of the modified PIBSI onto the surface of carbon black particles.

Acknowledgements

- Dr. Jean Duhamel
- Dr. Chong
- Dr. Gauthier and Dr. Tzoganakis
- Imperial Oil and NSERC
- Everybody in the Duhamel and Gauthier Lab.

Questions?